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Electronic Supplementary Information

Catalytic aziridination with alcoholic substrates via a chromium tetracarbene catalyst

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Experimental Section

All reactions were performed under a dry nitrogen atmosphere in a glovebox. Solvents were dried on an Innovative Technologies (Newburgport, MA) Pure Solv MD-7 Solvent Purification System and degassed by three freeze-pump-thaw cycles on a Schlenk line to remove O_2 prior to use and dried over activated molecular sieves. Chloroform-d and acetonitrile-d_3 were purchased from Cambridge Isotope Lab and used without further purification. All azides were synthesized by the procedure developed by Smith and Brown.[1] The compounds *p*-tolyl azide,[1] 4-azidobenzaldehyde,[2] 1-azido-4-methoxybenzene,[3] 1-azido-4-chlorobenzene,[4] and 3-azidophenol[5] were prepared from literature procedures or as described previously. The compounds $[(^{Me,Et}TC^{Ph})Cr(Cl)_2](PF_6)$ (**1**) and $[(^{Me,Et}TC^{Ph})Fe(NCCH_3)_2](PF_6)_2$ (**2**) were prepared as previously described in the literature.[6] All other reagents were purchased from commercial vendors and degassed by three freeze-pump-thaw cycles and dried over activated molecular sieves. ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or a Varian VNMRS 500 MHz narrow-bore broadband system. ^1H and ^{13}C NMR chemical shifts were referenced to the residual solvent. DEPT, HSQC, and COSY were performed on a Varian VNMRS 500 MHz narrow-bore broadband system. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). Mass spectrometry sample solutions of organic compounds from catalysis reactions were prepared in chloroform or acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance.

General Catalytic Reaction: $[(^{Me,Et}TC^{Ph})Cr(Cl)_2](PF_6)$ (**1**) was added to a 20mL vial, along with 4 mL of acetonitrile as the solvent. The solution was stirred at room temperature until dissolution was achieved. Three equivalents of alkene and one equivalent of azide were added, and the reaction was heated at 85 °C for three days, unless otherwise noted. Then the reaction solution was filtered over Celite and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using gradient dilution unless otherwise noted. Excess alkene and any unreacted azide can be recovered in the pure hexanes fraction.

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decene (0.116 g, 0.824 mmol), *p*-tolyl azide (0.101 g, 0.825 mmol), and **1** (0.0202, 0.0165 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0532 g, 26.3%. The characterization (^1H and ^{13}C NMR) matched the literature data.[7] (Table 1, entry 1)

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decene (0.321 g, 2.29 mmol), *p*-tolyl azide (0.102 g, 0.762 mmol), and **1** (0.0186 g, 0.0152 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.114 g, 61.1%. The characterization (^1H and ^{13}C NMR) matched the literature data.[7] (Table 1, entry 2)

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decene (0.998 g, 7.11 mmol), *p*-tolyl azide (0.0947 g, 0.711 mmol), and **1** (0.0174 g, 0.0142 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.117 g, 67.2%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7] (Table 1, entry 3)

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *0% catalyst loading:* 1-decene (0.104 g, 0.722 mmol) and *p*-tolyl azide (0.103 g, 0.723 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica gravity column, resulting in a yield of 0.0086 g, 4.7%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7] (Table 1, entry 4)

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *0% catalyst loading:* 1-decene (0.294 g, 2.09 mmol) and *p*-tolyl azide (0.0954 g, 0.698 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica gravity column, resulting in a yield of 0.0217 g, 12.3%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7] (Table 1, entry 5)

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* **1** was isolated from a recrystallization of a reaction stored in a -30 °C freezer. 1-decene (0.2198 g, 1.567 mmol), *p*-tolyl azide (0.0696 g, 0.522 mmol), and **1** (0.0128 g, 0.0104 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0711g, 55.4%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decene (0.3078 g, 2.194 mmol), *p*-tolyl azide (0.0974 g, 0.731 mmol), and **1** (0.0179 g, 0.0146 mmol) were used in the General Catalytic Reaction, substituting DMF for acetonitrile, purification was achieved using 5% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0832g, 46.4%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decne (0.310 g, 2.209 mmol), *p*-tolyl azide (0.0991 g, 0.744 mmol), and **1** (0.0182 g, 0.0149 mmol) were used in the General Catalytic Reaction, substituting DMSO for acetonitrile, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0231g, 12.6%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% catalyst loading:* 1-decene (0.288 g, 2.05 mmol), *p*-tolyl azide (0.0911 g, 0.684 mmol), and **1** (0.0168g, 0.0137 mmol) were used in the General Catalytic Reaction, substituting pyridine for acetonitrile, purification was achieved using 5% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0525g, 31.3%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

Synthesis of 9-(*p*-tolyl)-9-azabicyclo[6.1.0]nonane, 4. *2% catalyst loading: cis*-cyclooctene (0.296 g, 2.68 mmol), *p*-tolyl azide (0.119 g, 0.895 mmol), and **1** (0.0219 g,

0.0179 mmol) were used in the General Catalytic Reaction, purification was achieved using 5% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.101 g, 52.4%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7] (Table S1, entry 1)

Synthesis of 1-(4-methoxyphenyl)-2-octylaziridine, 5. *2% catalyst loading:* 1-decene (0.349 g, 2.49 mmol), 1-azido-4-methoxybenzene (0.124 g, 0.829 mmol), and **1** (0.0203 g, 0.0166 mmol) were used in the General Catalytic Reaction, purification was achieved using 20% ethyl acetate in hexanes, resulting in a yield of 0.122 g, 56.2%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[8] (Table S1, entry 2)

Synthesis of 4-(2-octylaziridin-1-yl)benzaldehyde, 6. *2% catalyst loading:* 1-decene (0.313 g, 2.23 mmol), 4-azidobenzaldehyde (0.110 g, 0.745 mmol), and **1** (0.0196 g, 0.0160 mmol) were used in the General Catalytic Reaction, purification was achieved using 10% ethyl acetate in hexanes, resulting in a yield of 0.0769 g, 39.8% ^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 9.86 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3Hz, 2H), 2.18 (s, 2H), 2.15, (m, 1H), 1.58 (m, 4H), 1.31 (m, 10H), 0.89 (t, *J* = 7.1Hz, 3H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 191.05, 161.19, 131.34, 131.15, 121.05, 40.67, 34.34, 33.10, 31.99, 29.69, 29.64, 29.39, 27.70, 22.79, 14.24. IR: 2923, 2853, 1694, 1596, 1570, 1506, 1463, 1406, 1302, 1212, 1156, 836, 721 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 260.20059 (found); $C_{17}H_{26}NO$ 260.20144 (calcd). (Table S1, entry 3)

Synthesis of 1-(4-chlorophenyl)-2-octylaziridine, 7. *2% catalyst loading:* 1-decene (0.352 g, 2.51 mmol), 1-azido-4-chlorobenzene (0.128 g, 0.831 mmol), and **1** (0.0207 g, 0.0169 mmol) were used in the General Catalytic Reaction, purification was achieved using purification was achieved using 1 % ethyl acetate in hexanes, resulting in a yield of 0.0767 g, 34.7%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[8] (Table S1, entry 4)

Synthesis of ethyl 9-(1-(*p*-tolyl)aziridin-2-yl)nonanoate, 8. *2% catalyst loading:* ethyl 10-undecenoate (0.402 g, 1.89 mmol), *p*-tolyl azide (0.0840 g, 0.631 mmol), and **1** (0.0155 g, 0.0127 mmol) were used in the General Catalytic Reaction, purification was achieved using 10% ethyl acetate in hexanes, resulting in a yield of 0.0465 g, 23.2%. ^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.01 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 2.02 (m, 3H), 1.58 (m, 6H), 1.35 (m, 8H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 174.00, 152.74, 131.49, 129.52, 120.65, 60.28, 40.31, 34.51, 34.18, 33.37, 29.60, 29.56, 29.34, 29.25, 27.81, 25.10, 20.79, 14.39. IR: 2925, 2853, 1734, 1509, 1462, 1293, 1173, 1111, 1033, 820, 712, 677 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 318.24290(found); $C_{20}H_{32}NO_2$ 318.24276 (calcd). (Table S1, entry 5)

Synthesis of 8-(1-(*p*-tolyl)aziridin-2-yl)octanol, 9. *2% catalyst loading:* 9-decenol (0.312 g, 2.00 mmol), *p*-tolyl azide (0.0887 g, 0.666 mmol), and **1** (0.0163 g, 0.0133 mmol) were used in the General Catalytic Reaction, purification was achieved using 20% ethyl acetate in hexanes, resulting in a yield of 0.0555 g, 31.8%. ^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.01 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 3.60 (q, *J* = 6.5 Hz, 2H), 2.26 (s, 3H), 2.01 (m, 3H), 1.79 (t, *J* = 4.9 Hz, 1H), 1.55 (m, 6H), 1.34 (m, 8H). ^{13}C NMR

($CDCl_3$, 125.66 MHz): δ 152.55, 131.56, 129.50, 120.66, 63.00, 40.38, 34.18, 33.29, 32.88, 29.67, 29.56, 29.47, 27.78, 25.84, 20.77. IR: 3334, 2924, 2853, 1510, 1291, 1055, 820 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 262.21693 (found); $[C_{17}H_{28}NO]^+$ 262.21654 (calcd). (Table 2, entry 1)

Synthesis of 4-methyl-N-((tetrahydrofuran-2-yl)methyl)aniline, 10. *2% catalyst loading:* 4-pentenol (0.197 g, 2.29 mmol), *p*-tolyl azide (0.102 g, 0.762 mmol), and **1** (0.0180 g, 0.0147 mmol) were used in the General Catalytic Reaction, purification was achieved using 50% ethyl acetate in hexanes, resulting in a yield of 0.0602 g, 41.3%. The characterization (^1H and ^{13}C NMR) matched the literature data.[9] (Table 2, entry 2)

Synthesis of 4-((1-(*p*-tolyl)aziridin-2-yl)methyl)phenol, 11. *2% catalyst loading:* 4-allylphenol (0.308 g, 2.30 mmol), *p*-tolyl azide (0.102 g, 0.765 mmol), and **1** (0.0188 g, 0.0153 mmol) were used in the General Catalytic Reaction, purification was achieved using 20% ethyl acetate in hexanes, resulting in a yield of 0.0478 g, 26.1%. ^1H NMR ($CDCl_3$, 499.74 MHz): δ 7.15 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.2 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 2.84 (dd, J_1 = 14.2 Hz, J_2 = 4.5Hz, 1H), 2.80 (dd, J_1 = 14.2 Hz, J_2 = 7.5 Hz, 1H), 2.32 (m, 1H), 2.25 (m, 4H), 2.15 (d, J = 7.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 154.82, 151.28, 132.29, 130.83, 130.08, 129.64, 120.83, 115.73, 42.39, 38.48, 34.35, 20.79. IR: 3311, 2919, 1612, 1509, 1239, 1110, 908, 770, 729 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 240.13900 (found); $[C_{16}H_{18}NO]^+$ 240.13829 (calcd). (Table 2, entry 3)

Synthesis of N-((2,3-dihydrobenzofuran-2-yl)methyl)-4-methylaniline, 12. *2% catalyst loading:* 2-allylphenol (0.397 g, 2.96 mmol), *p*-tolyl azide (0.131 g, 0.987 mmol), and **1** (0.0242 g, 0.0198 mmol) were used in the General Catalytic Reaction, purification was achieved using a gravity column with chloroform as the eluent, resulting in a yield of 0.0922 g, 39.1%. ^1H NMR (CD_3CN, 499.74 MHz): δ 7.19 (d, J = 7.3 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 8.3 Hz, 2H), 6.83 (t, J = 7.9 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 6.59 (d, J = 8.2 Hz, 2H), 4.96 (dtd, J_1 = 9.2 Hz, J_2 = 7.0 Hz, J_3 = 4.7 Hz, 1H), 4.38 (s br, 1H), 3.33 (m, 3H), 3.02 (dd, J_1 = 15.8 Hz, J_2 = 7.2 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 160.36, 147.36, 130.53, 128.83, 128.05, 126.98, 126.15, 121.33, 113.82, 110.04, 82.53, 49.00, 33.67, 20.40. IR: 3397, 2917, 2103, 1614, 1519, 1478, 1226, 806, 747 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 240.13826 (found); $[C_{16}H_{18}NO]^+$ 240.13829 (calcd). (Table 2, entry 4)

Synthesis of 3-(2-octylaziridin-1-yl)phenol, 13. *2% catalyst loading:* 1-decene (0.316 g, 2.25 mmol), 3-azidophenol (0.101 g, 0.750 mmol), and **1** (0.0184 g, 0.0150 mmol) were used in the General Catalytic Reaction, the reaction ran for five days instead of three. Purification was achieved using 1% methanol in chloroform, resulting in a yield of 0.0649 g, 35.0%. ^1H NMR ($CDCl_3$, 499.74 MHz): δ 7.05 (t, J = 7.9 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.46 (m, 2H), 2.11 (m, 1H), 2.06 (d, J = 3.8 Hz, 1H), 2.03 (d, J = 6.4 Hz, 1H) 1.54 (m, 4H), 1.27 (m, 10H), 0.89 (t, J = 7.0, 3H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 156.91, 155.22, 130.07, 113.08, 110.61, 108.79, 41.11, 34.38, 32.83, 32.01, 29.69, 29.62, 29.41, 27.77, 22.81, 14.26. IR: 3339, 3059, 2923, 2853, 1590, 1458, 1178, 1153, 856, 755, 691 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 248.20005 (found); $[C_{16}H_{26}NO]^+$ 248.20089 (calcd). (Table 2, entry 5)

Synthesis of N-((1-(p-tolyl)aziridin-2-yl)methyl)aniline, 14. *2% catalyst loading:* N-allylaniline (0.301 g, 2.26 mmol), *p*-tolyl azide (0.100 g, 0.752 mmol), and **1** (0.0184 g, 0.0150 mmol) were used in the General Catalytic Reaction, purification was achieved using 10% ethyl acetate in hexanes, resulting in a yield of 0.0538 g, 30.1%. ^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.34 (m, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.4 Hz, 2H), 6.87 (m, 3H), 4.19 (br s, 1H), 3.67 (d, J = 12.9 Hz, 1H), 3.37 (dd, J_1 = 12.3 Hz, J_2 = 6.0 Hz, 1H), 2.53 (m, 1H), 2.41 (s, 3H), 2.38 (m, 1H), 2.21 (d, J = 6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 151.95, 148.18, 131.97, 129.63, 129.42, 120.55, 117.84, 113.32, 46.08, 39.01, 32.38, 20.78. IR: 3394, 3021, 2918, 1600, 1507, 1313, 1255, 809, 750, 612 cm^{-1}. DART HR MS (*m*/*z*): $[M+H]^+$ 239.15394 (found); $[C_{16}H_{19}N_2]^+$ 239.15428 (calcd). **14** was found to be thermodynamically unstable, decomposing within a week. (Table 2, entry 6)

Synthesis of 8-(1-(*p*-tolyl)aziridin-2-yl)octanoic acid. *2% catalyst loading:* 9-decenoic acid (0.361 g, 2.12 mmol), *p*-tolyl azide (0.0943 g, 0.707 mmol), and **1** (0.0174 g, 0.0142 mmol) were used in the General Catalytic Reaction, no aziridine product or byproduct was identified in the reaction.

Comparison aziridination reactions with $[(^{Me,Et}TC^{Ph})Fe(NCCH_3)_2](PF_6)_2$ (2) under general catalytic conditions:

Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, 3. *2% **2** loading*: 1-decene (0.310 g, 2.21 mmol), *p*-tolyl azide (0.0979 g, 0.735 mmol), and **2** (0.0204 g, 0.0147 mmol) were used in the General Catalytic Reaction (substituting **2** for **1**), purification was achieved using 5% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0176 g, 9.8%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[2] (Table 1, entry 6)

Synthesis of 8-(1-(*p*-tolyl)aziridin-2-yl)octanol, 9. *2% **2** loading*: 9-decenol (0.344 g, 2.20 mmol), *p*-tolyl azide (0.0977 g, 0.734 mmol), and **2** (0.0203 g, 0.0147 mmol) were used in the General Catalytic Reaction (substituting **2** for **1**), no aziridine product or byproduct was identified in the reaction. (Table 3, entry 1)

Synthesis of 3-(2-octylaziridin-1-yl)phenol, 13. *2% **2** loading*: 1-decene (0.313 g, 2.23 mmol), 3-azidophenol (0.101 g, 0.744 mmol), and **2** (0.0206 g, 0.0149 mmol) were used in the General Catalytic Reaction (substituting **2** for **1**), no aziridine product or byproduct was identified in the reaction. (Table 3, entry 2)

Comparison aziridination reactions with 1 with additional halide abstraction reagents:

1-decene (0.110 g, 0.787 mmol), *p*-tolyl azide (0.109 g, 0.816 mmol), silver(I) hexafluorophosphate (0.0083 g, 0.033 mmol) and **1** (0.0200 g, 0.0163 mmol) were used in the General Catalytic Reaction, purification was achieved using 5% ethyl acetate in

hexanes on a silica flash column, resulting in a yield of 0.0077 g, 4.0%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

1-decene (0.315 g, 2.24 mmol), *p*-tolyl azide (0.098 g, 0.748 mmol), thallium(I) hexafluorophosphate (0.0051 g, 0.0145 mmol) and **1** (0.0179 g, 0.0146 mmol) were used in the General Catalytic Reaction, purification was achieved using 5% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0423 g, 23.4%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

1-decene (0.271 g, 1.93 mmol), *p*-tolyl azide (0.087 g, 0.644 mmol), silver(I) hexafluorophosphate (0.0033 g, 0.013 mmol) and **1** (0.0163 g, 0.0133 mmol) were used in the General Catalytic Reaction, purification was achieved using 1% ethyl acetate in hexanes on a silica flash column, resulting in a yield of 0.0289 g, 18.0%. The characterization (^{1}H and ^{13}C NMR) matched the literature data.[7]

Aziridination reactions for quantitative ^{1}H NMR analysis:

9-decenol (0.266 g, 1.70 mmol), *p*-tolyl azide (0.0756 g, 0.568 mmol), and **1** (0.009 g, 0.0073 mmol) were used in the General Catalytic Reaction, with CD_3CN substituted for the solvent. CH_2Br_2 (0.040 mL, 0.568 mmol) was added as an internal standard for integration. ^{1}H NMR integration showed the following products to be present: **9**, 50% conversion; *p*-tolyl azide, 30%; *p*-toluidine, 18%. Additionally, 2.5 equivalents of 9-decenol were found to be present.

1-decene (0.227 g, 1.61 mmol), 3-azidophenol (0.073 g, 0.539 mmol), and **1** (0.0132 g, 0.0108 mmol) were used in the General Catalytic Reaction, with CD_3CN substituted for the solvent. CH_2Br_2 (0.038 mL, 0.539 mmol) was added as an internal standard for integration. ^{1}H NMR integration showed the following products to be present: **13**, 44%, 3-azidophenol 28%, 3-aminophenol 28%. Additionally, 2.3 equivalents of 1-decene were found to be present.

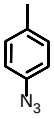
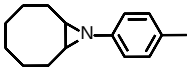
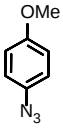
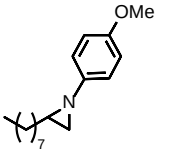
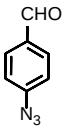
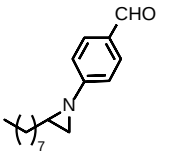
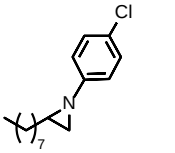
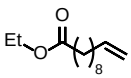
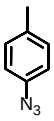
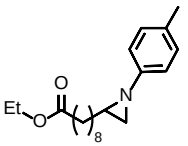
Entry	Alkene	Azide	Aziridine	Isolated Yield
1			 **4**	52.4
2			 **5**	56.2
3			 **6**	39.8
4			 **7**	34.7
5			 **8**	23.2

Table S1. Catalytic reaction with 1 and aprotic functionalized alkenes and organic azides. 4 mL of CH_3CN as solvent at 85 °C for 3 days. **1** employed as catalyst at 2% loading with a 3/1 alkene to azide ratio.

NMR Spectra

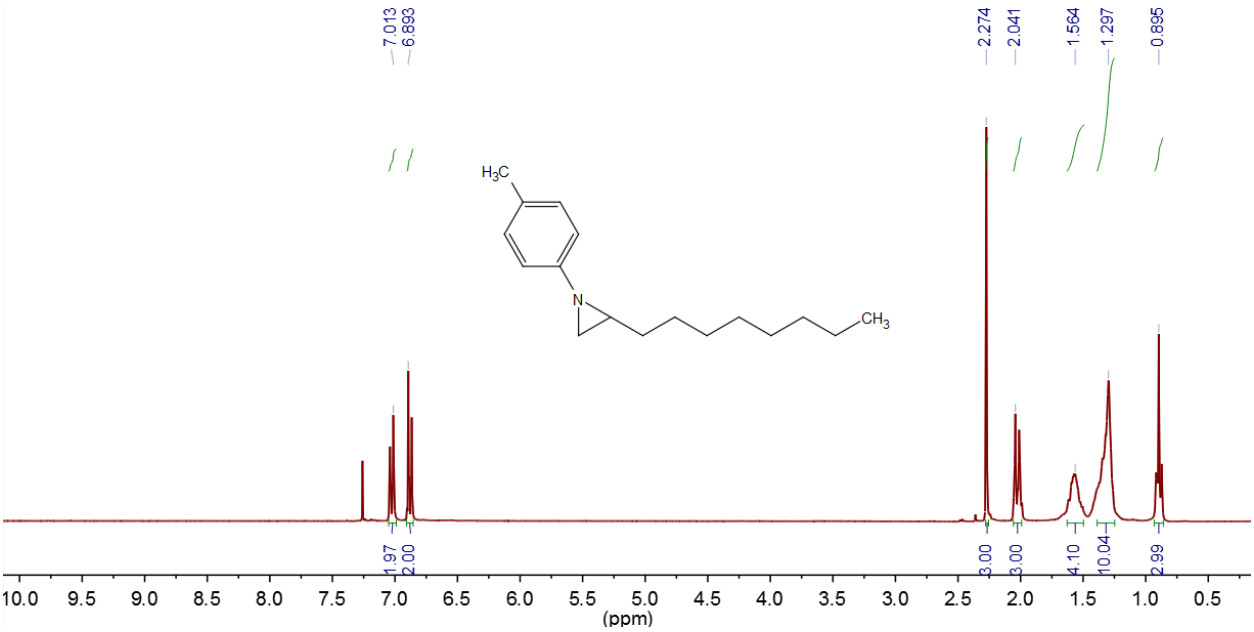


Fig. S1. ^{1}H NMR of 2-octyl-1-(*p*-tolyl)aziridine, **3**, in $CDCl_3$, reported previously.[7]

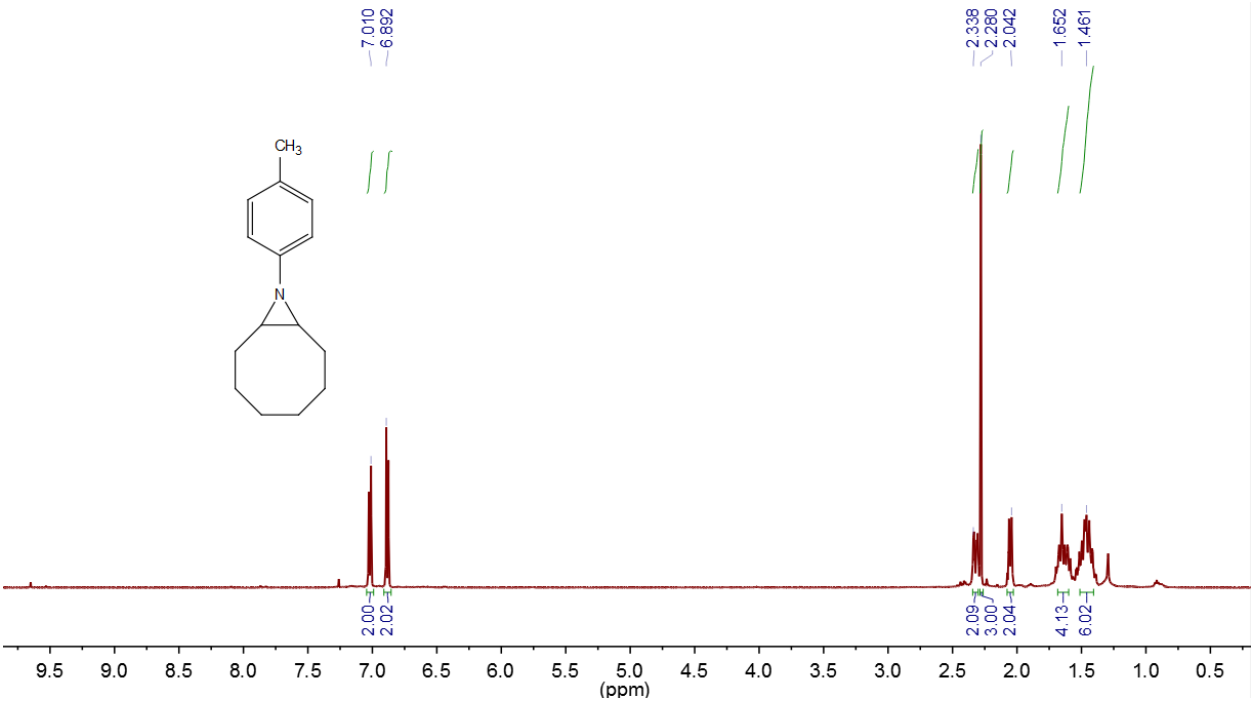


Fig. S2. ^{1}H NMR of 9-(*p*-tolyl)-9-azabicyclo[6.1.0]nonane, **4**, in $CDCl_3$, reported previously.[7]

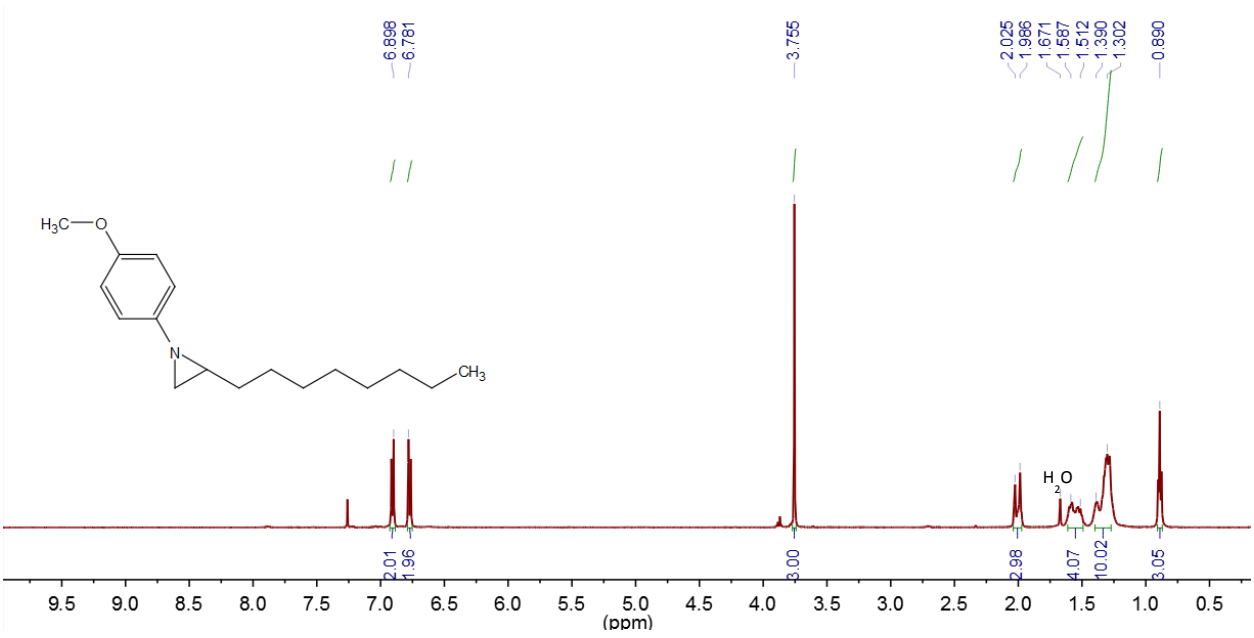


Fig. S3. ^{1}H NMR of 1-(4-methoxyphenyl)-2-octylaziridine, **5**, in $CDCl_3$, reported previously.[8]

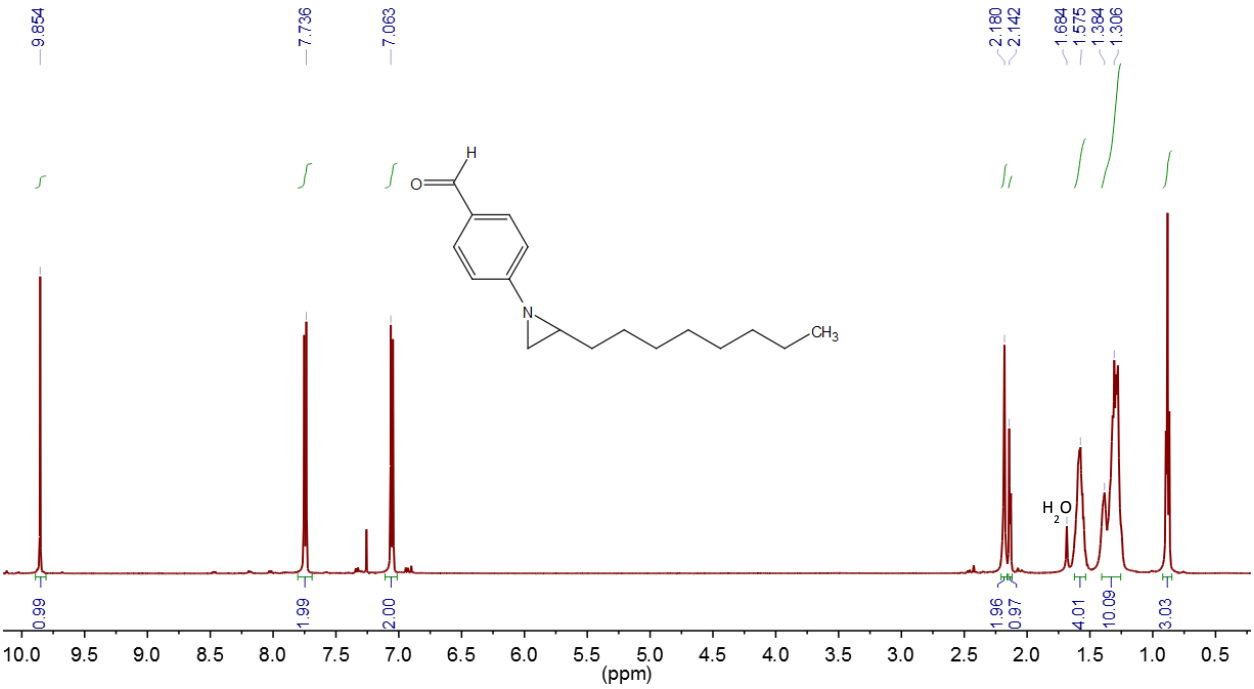


Fig. S4. ^{1}H NMR of 4-(2-octylaziridin-1-yl)benzaldehyde, **6**, in $CDCl_3$.

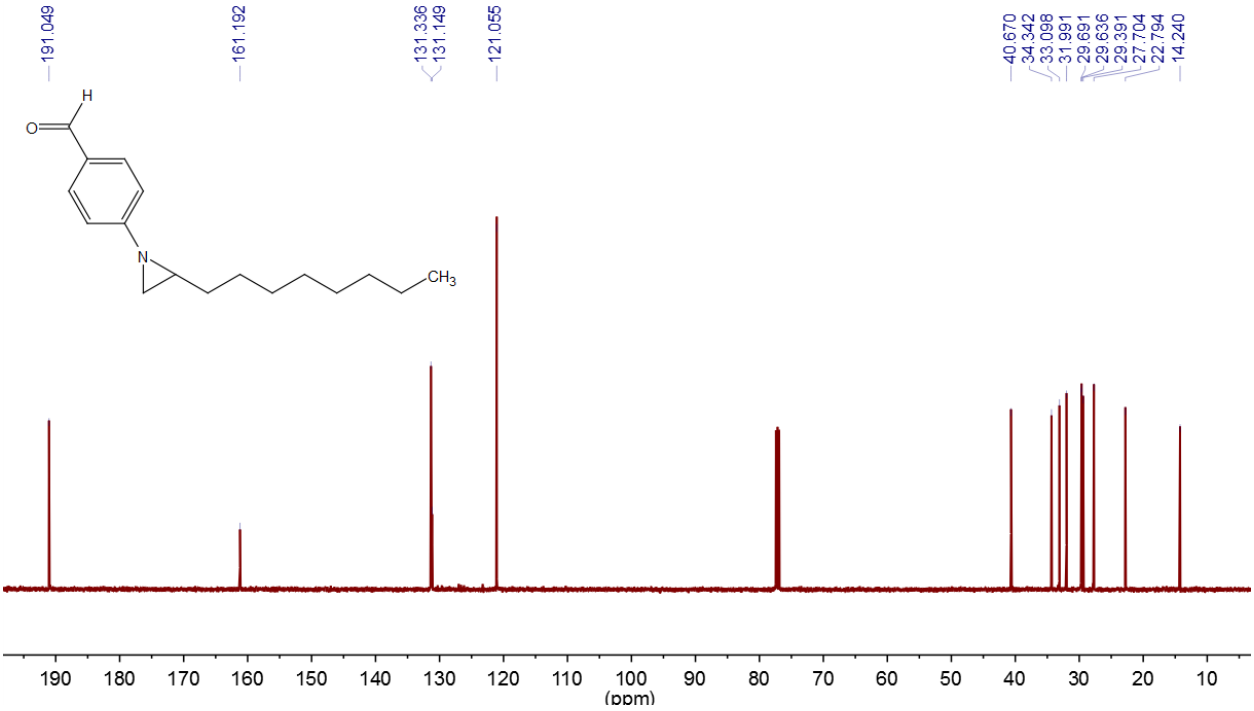


Fig. S5. ^{13}C NMR of 4-(2-octylaziridin-1-yl)benzaldehyde, **6**, in $CDCl_3$.

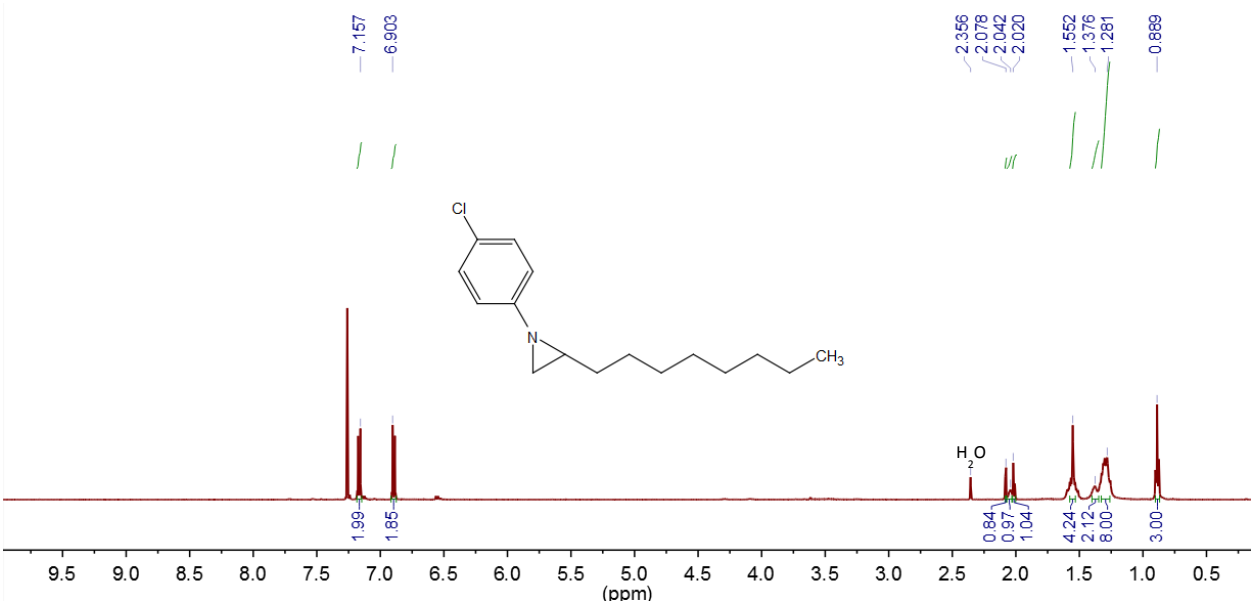


Fig. S6. ^{1}H NMR of 1-(4-chlorophenyl)-2-octylaziridine, **7**, in $CDCl_3$, reported previously.[8]

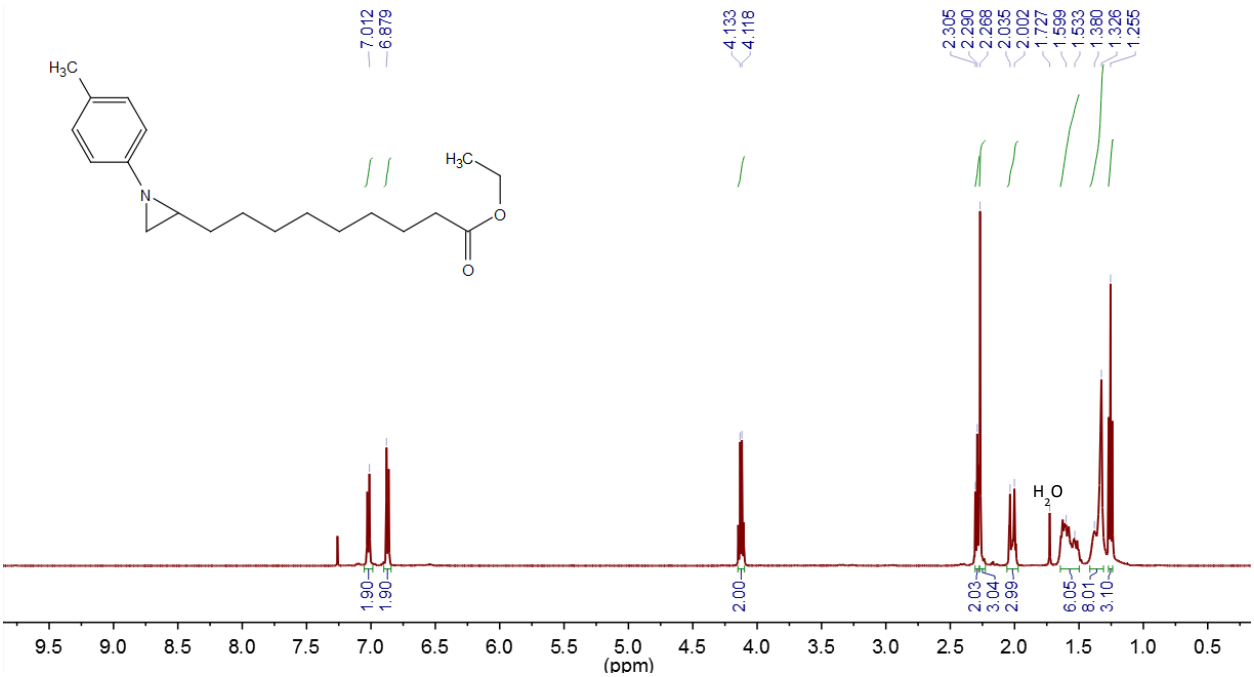


Fig. S7. ^{1}H NMR of ethyl 9-(1-(*p*-tolyl)aziridin-2-yl)nonanoate, **8**, in $CDCl_3$.

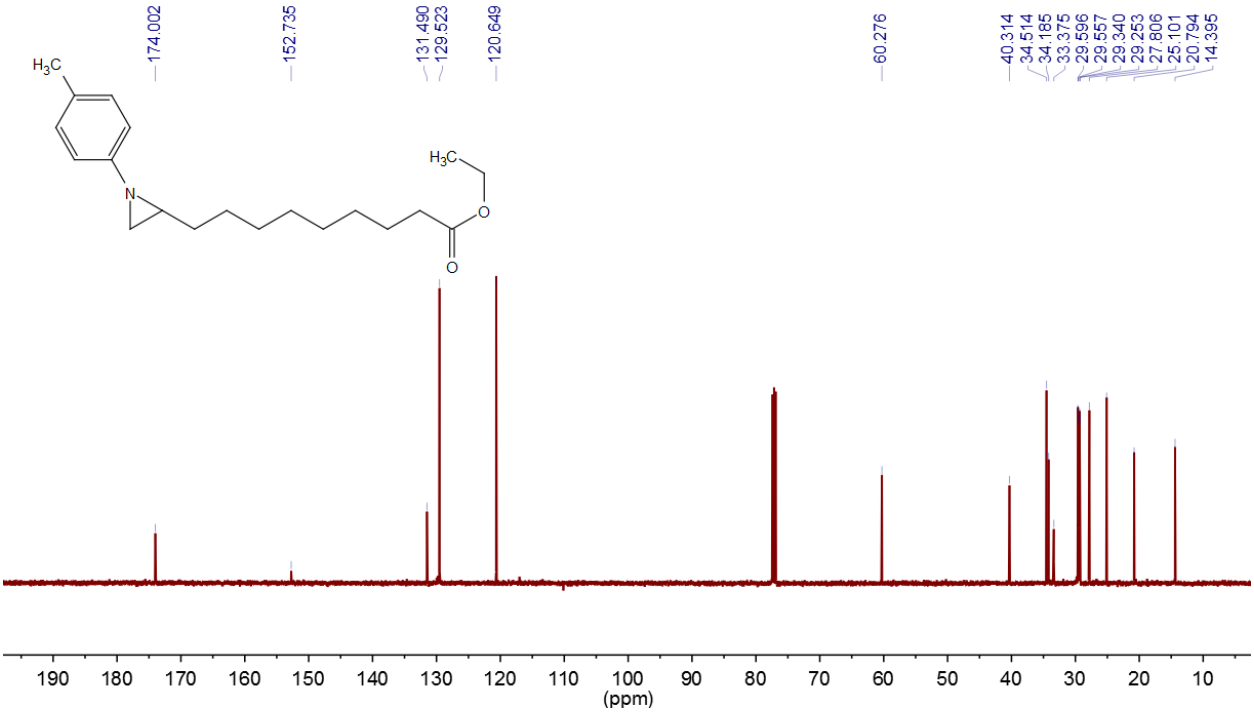


Fig. S8. ^{13}C NMR of ethyl 9-(1-(*p*-tolyl)aziridin-2-yl)nonanoate, **8**, in $CDCl_3$.

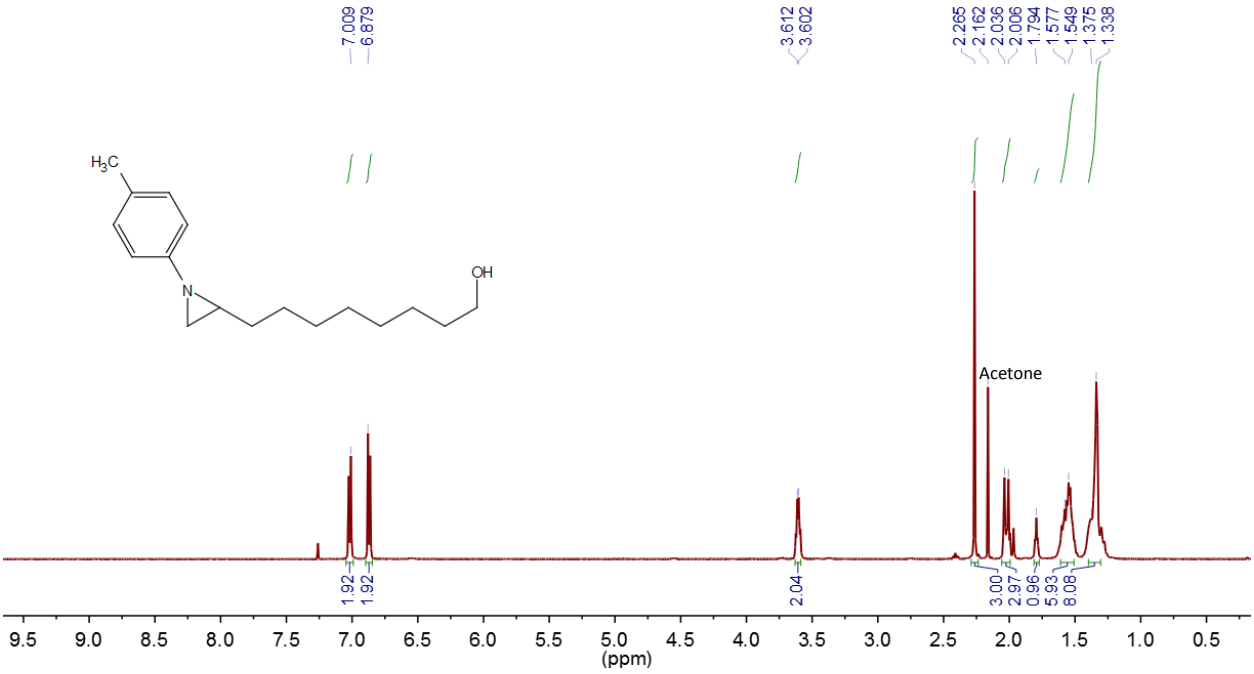


Fig. S9. ^{1}H NMR of 8-(1-(*p*-tolyl)aziridin-2-yl)octanol, **9**, in $CDCl_3$.

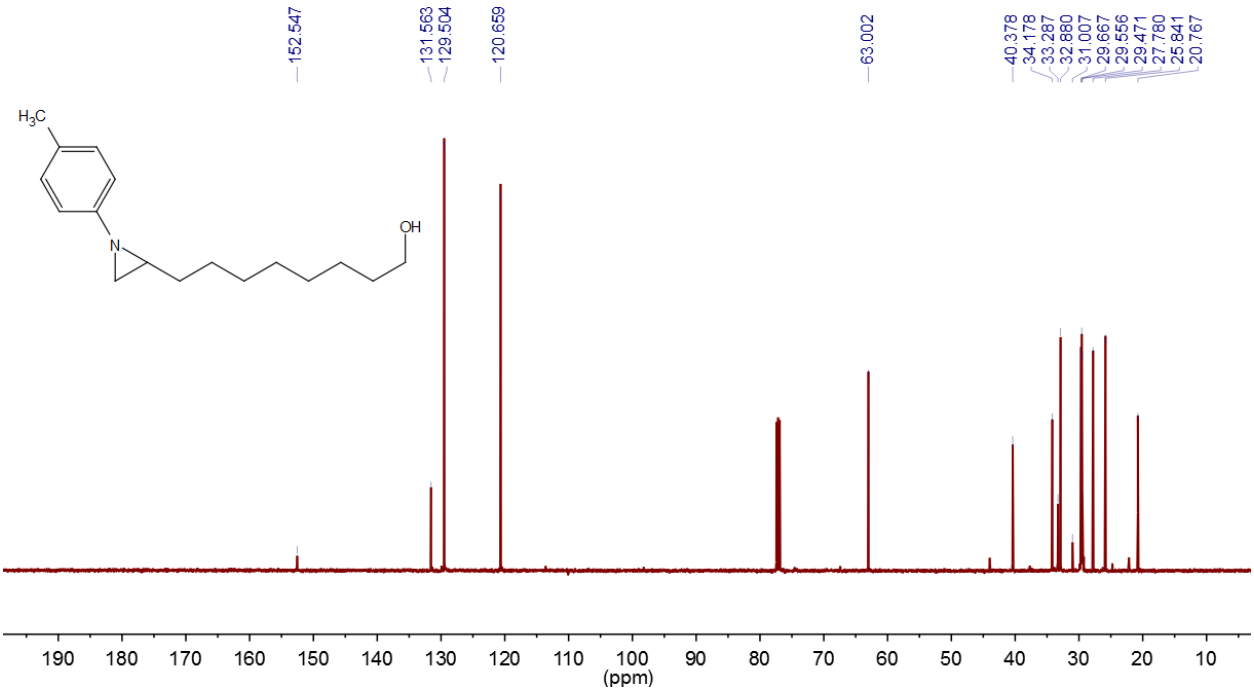


Fig. S10. ^{13}C NMR of 8-(1-(*p*-tolyl)aziridin-2-yl)octanol, **9**, in $CDCl_3$.

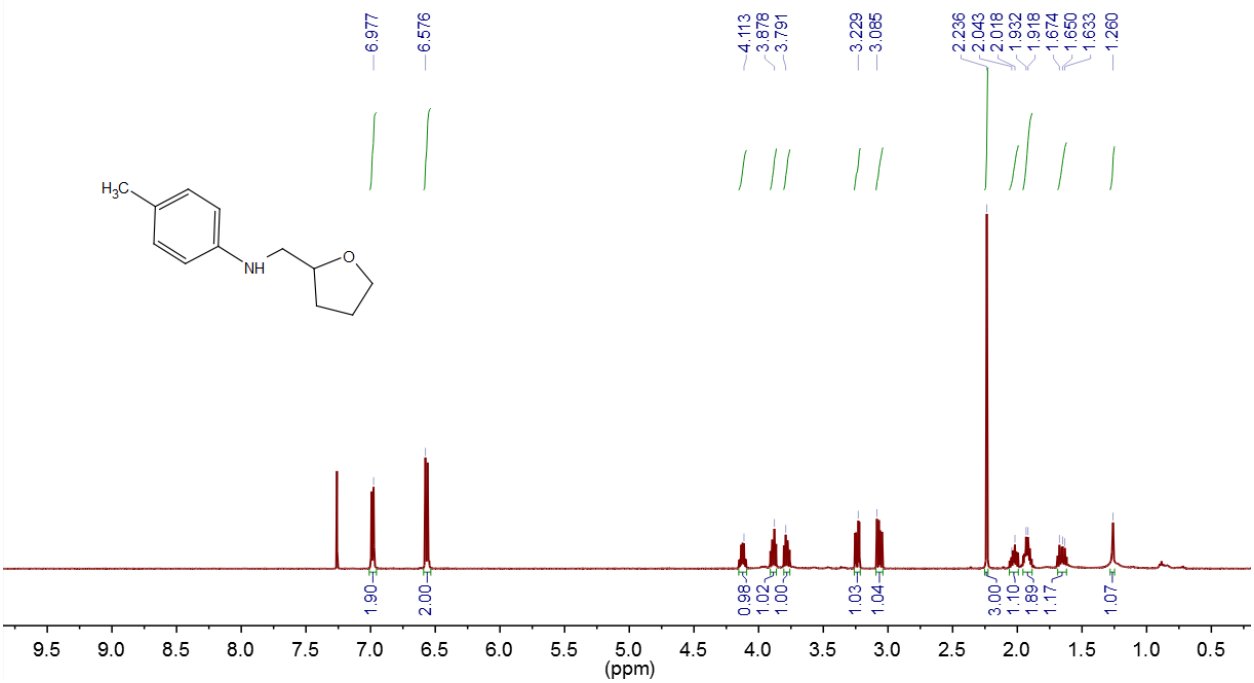


Fig. S11. ^{1}H NMR of 4-methyl-N-((tetrahydrofuran-2-yl)methyl)aniline, **10**, in $CDCl_3$, reported previously.[9]

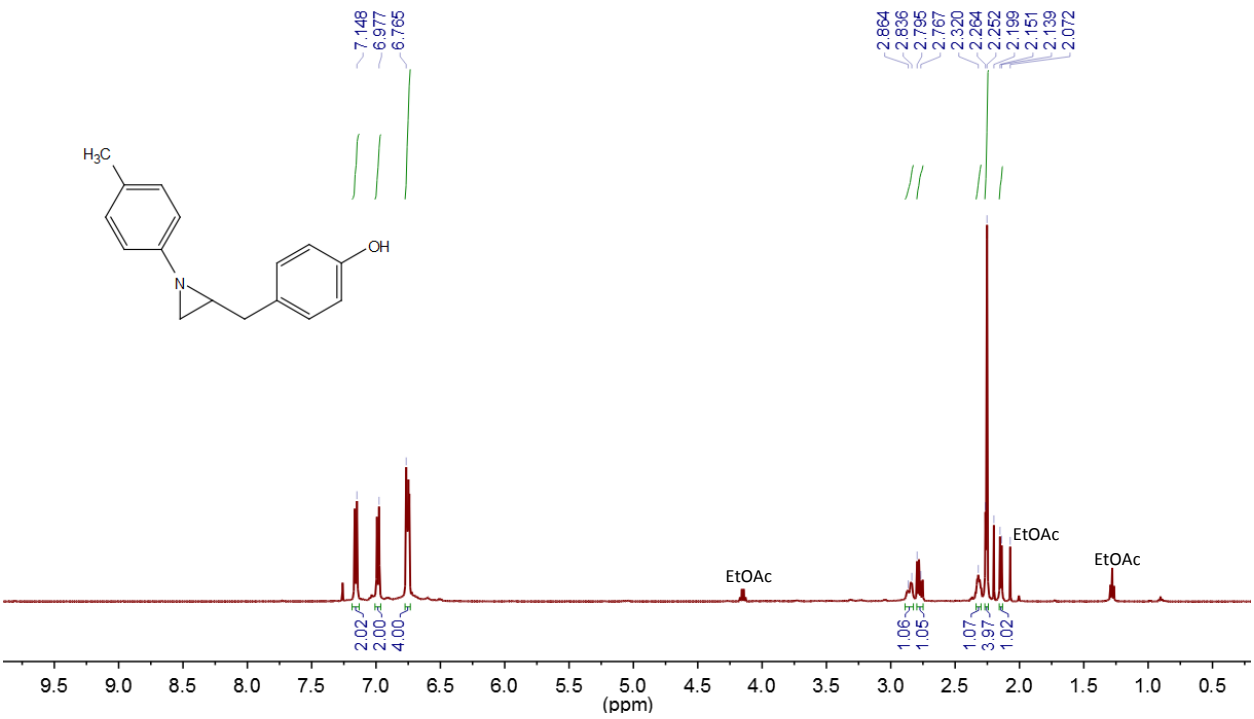


Fig. S12. ^{1}H NMR of 4-((1-(*p*-tolyl)aziridin-2-yl)methyl)phenol, **11**, in $CDCl_3$.

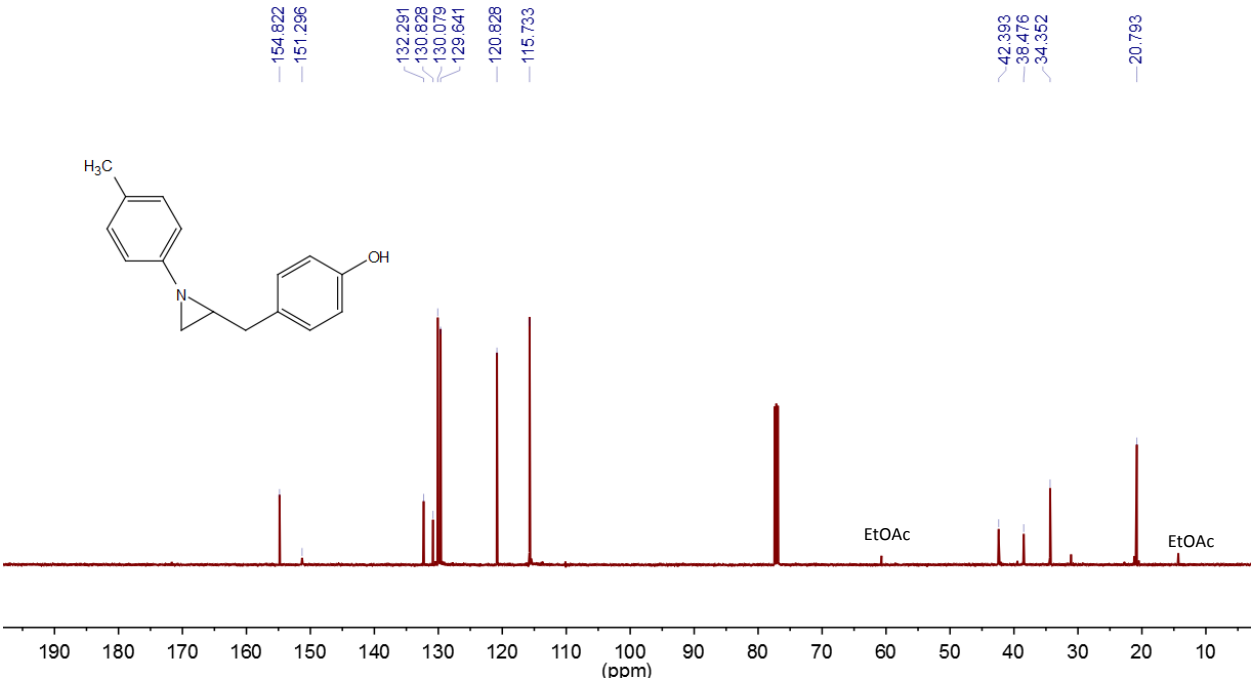


Fig. S13. ^{13}C NMR of 4-((1-(*p*-tolyl)aziridin-2-yl)methyl)phenol, **11**, in $CDCl_3$.

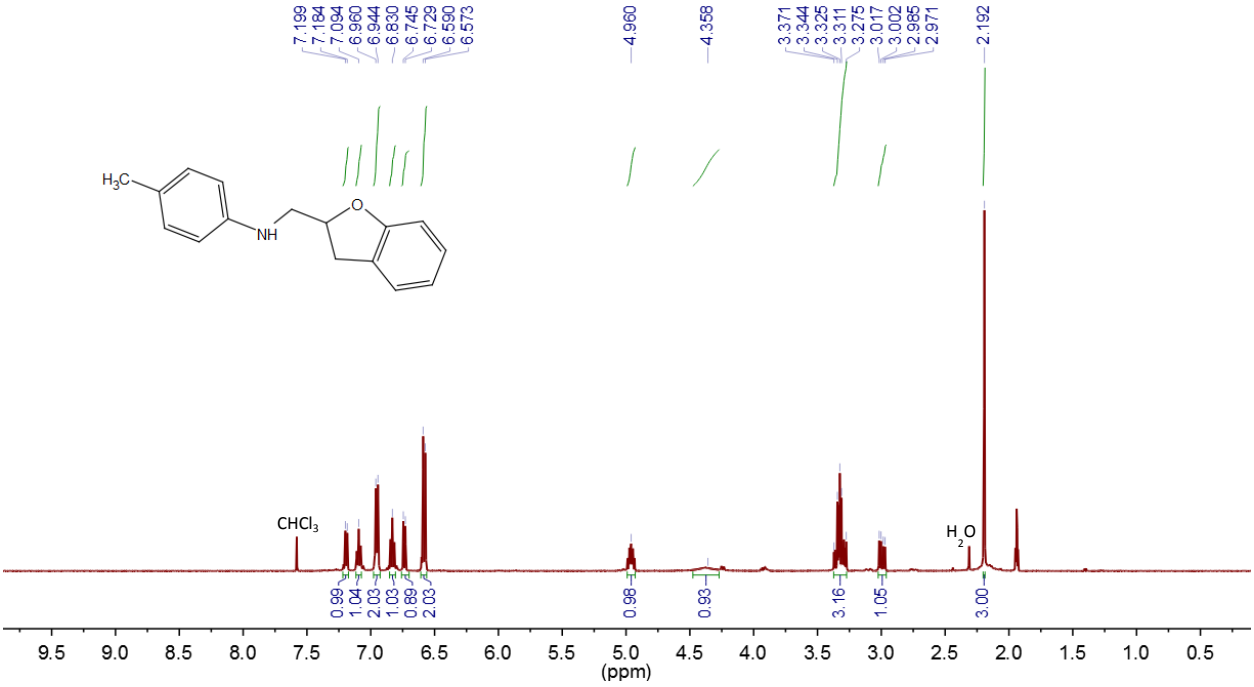


Fig. S14. ^{1}H NMR of N-((2,3-dihydrobenzofuran-2-yl)methyl)-4-methylaniline, **12**, in CD_3CN.

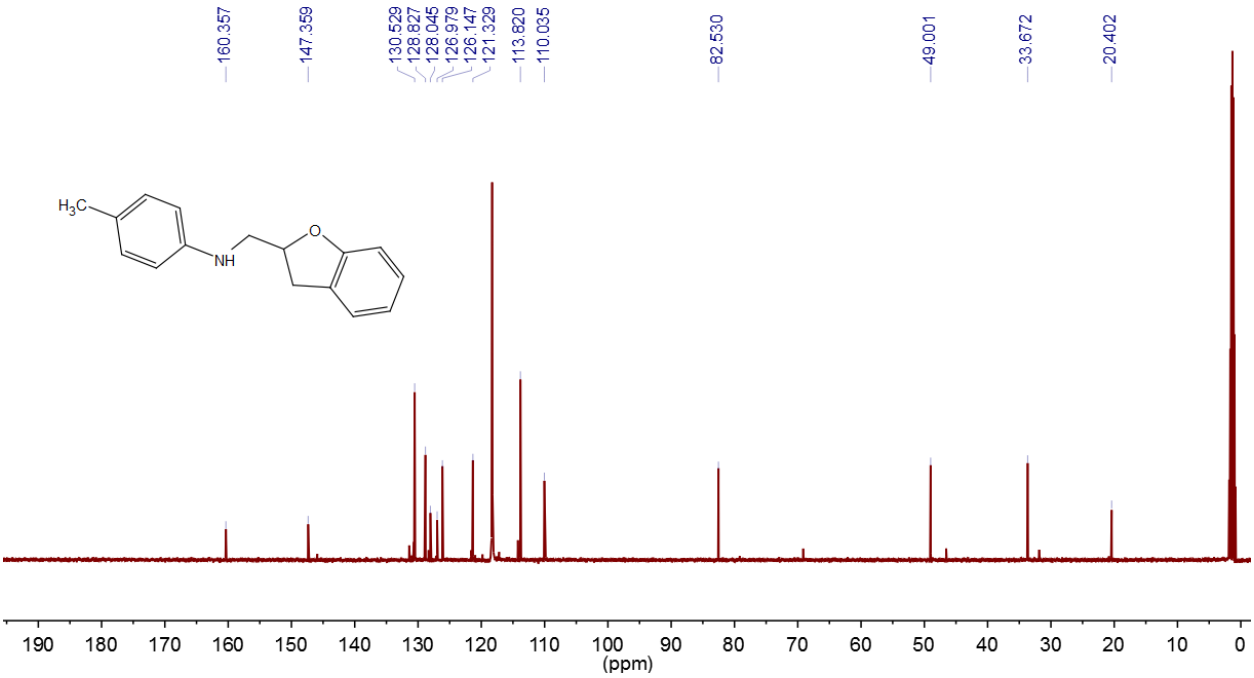


Fig. S15. ^{13}C NMR of N-((2,3-dihydrobenzofuran-2-yl)methyl)-4-methylaniline, **12**, in CD_3CN.

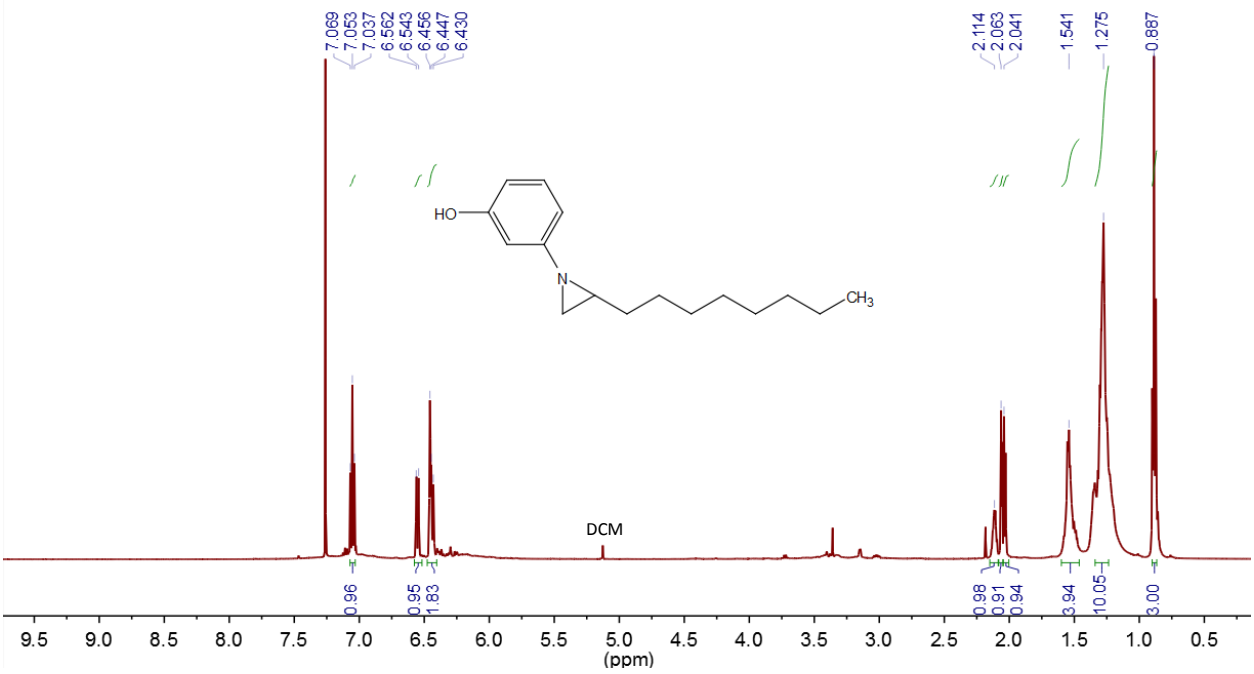


Fig. S16. ^{1}H NMR of 3-(2-octylaziridin-1-yl)phenol, **13**, in $CDCl_3$.

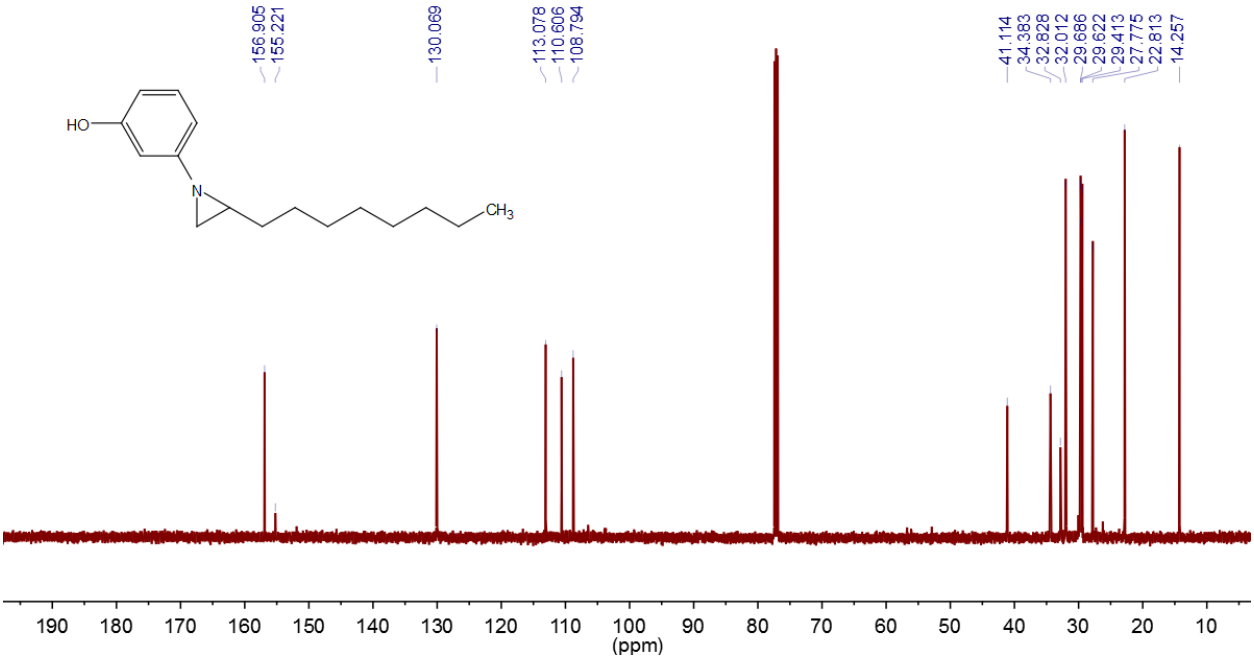


Fig. S17. ^{13}C NMR of 3-(2-octylaziridin-1-yl)phenol, **13**, in $CDCl_3$.

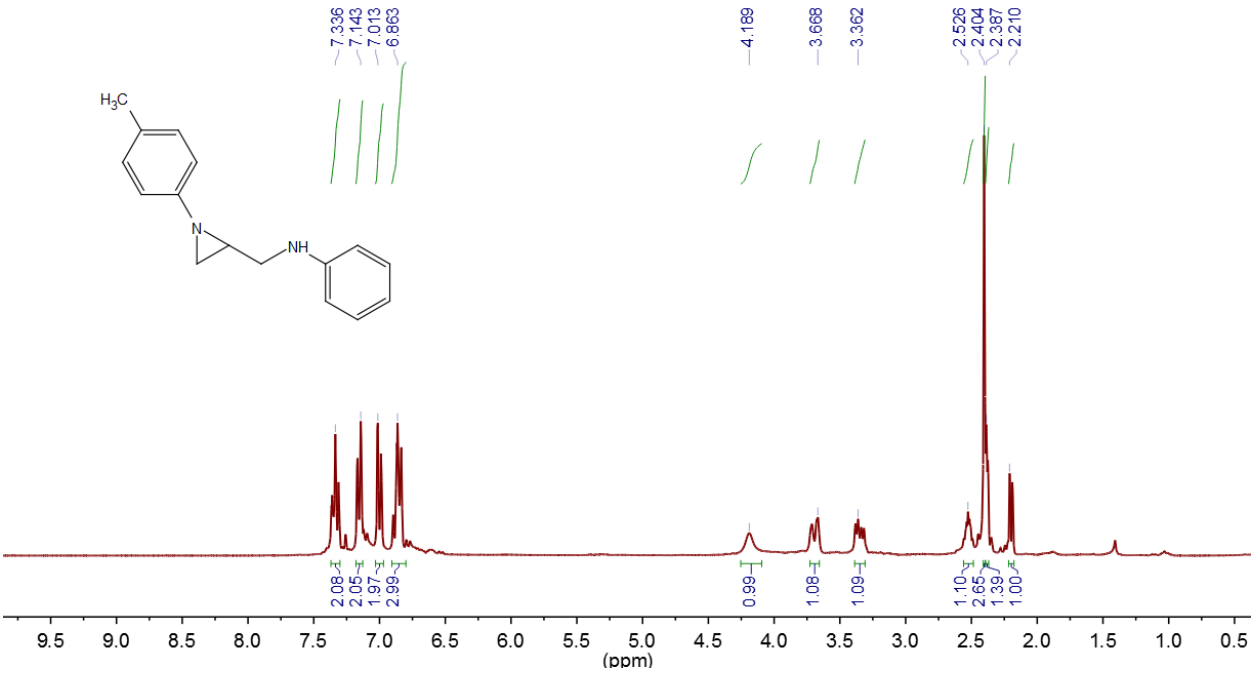


Fig. S18. ^{1}H NMR of N-((1-(p-tolyl)aziridin-2-yl)methyl)aniline, **14**, in $CDCl_3$.

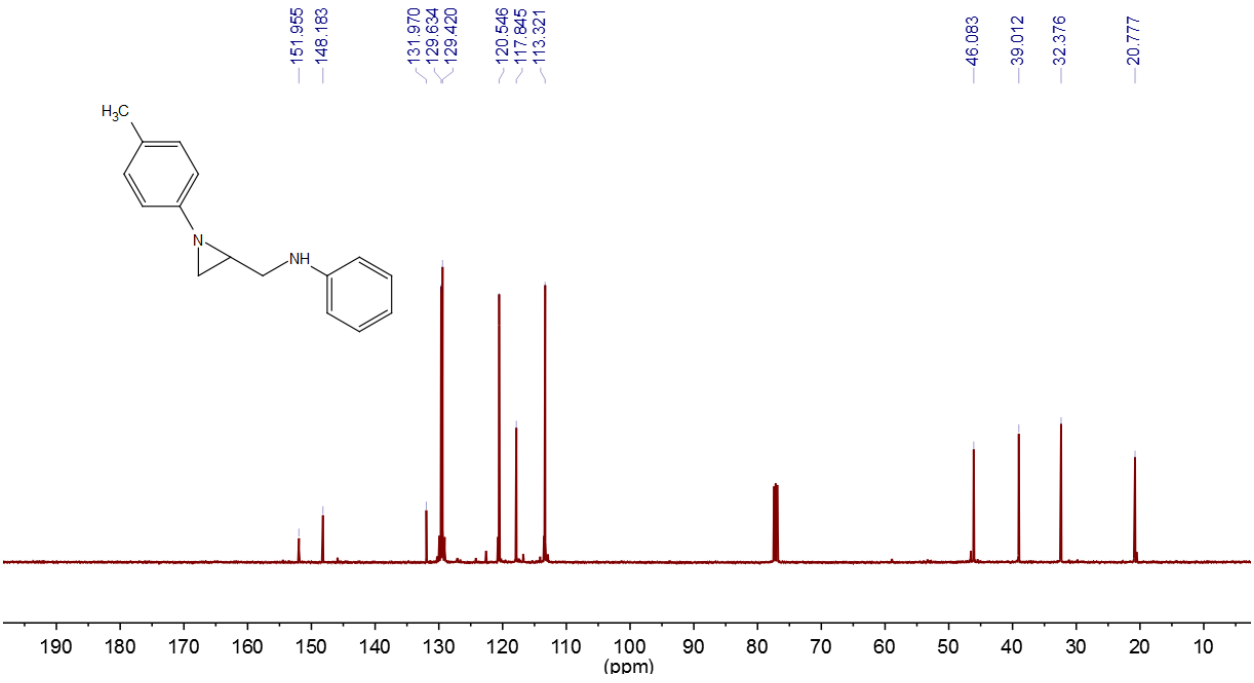


Fig. S19. ^{13}C NMR of N-((1-(p-tolyl)aziridin-2-yl)methyl)aniline, **14**, in $CDCl_3$.

Computational Section

All calculations were performed using Gaussian09[10] on the Newton High-Performance Computing cluster at the University of Tennessee, Knoxville.

Functional validation. In order to choose a density functional theory (DFT) exchange-correlation functional that accurately describes the systems under investigation, we first validated the TPSSh functional[11] against the known spin states and geometries for the isolated catalysts. Functional validation was performed using the cc-pVTZ basis set.[12] For $[(^{Me,Et}TC^{Ph})CrCl_2]^+$, (**1**), the DFT method must show a quartet-spin (S = 3/2) ground state, in accordance with the magnetic characterization of the complex. TPSSh/cc-pVTZ correctly predicts the quartet spin state as the ground state. Results show that the complex is energetically more stable in the quartet spin state than in the doublet spin state by 38.1 kcal/mol. In addition, calculated bond lengths around the Cr center were compared to corresponding bond lengths in the crystal structure.[6] The mean absolute error (MAE) of the 6 bonds to Cr is 0.010 Å. Based on its performance, TPSSh was chosen for all further calculations.

Key bond lengths of $[(^{Me,Et}TC^{Ph})CrCl_2]^+$ predicted by TPSSh/cc-pVTZ.

$[(^{Me,Et}TC^{Ph})CrCl_2]^+$ (S=3/2)	d(DFT) (Å)	d(Crystal) (Å)
Cr-C1	2.105	2.094 ± 0.006
Cr-C2	2.105	2.101 ± 0.005
Cr-C3	2.154	2.135 ± 0.005
Cr-C4	2.154	2.142 ± 0.005
Cr-Cl1	2.354	2.340 ± 0.016
Cr-Cl2	2.356	2.356 ± 0.016
MAE	**0.010**	---

Free energy calculations. The general steps for obtaining free energies of the catalyst species are (1) construct an initial guess structure, (2) run a geometry optimization with the cc-pVDZ basis set,[13] (3) perform a frequency calculation on the cc-pVDZ-optimized structure, and (4) run a geometry optimization with the cc-pVTZ basis set using the cc-pVDZ-optimized structure as input. Initial guess structures are built using the Avogadro molecular visualization software.[14] The CIF file of the base catalyst is used as a starting point for builds of all structures, with the chloride ligands being replaced with imides, tetrazenes, or vacancies as necessary. Geometry optimizations are then performed using (a) the TPSSh functional, (b) the cc-pVDZ basis set, and (c) Grimme's D3 dispersion with Becke-Johnson parameters[15] (TPSSh/cc-pVDZ/GD3BJ). The final structure from this optimization is used for a frequency calculation, from which the free energy correction G_{corr} is obtained. This structure is then further optimized using the TPSSh/cc-pVTZ/GD3BJ method, from which energy E is obtained. For each species, free energy G is computed as $G = E + G_{corr}$.

Figure S20. Free-energy (ΔG) profile of the different intermediates formed on the methylene bridge face in the catalytic cycles. Very similar energies were obtained on the ethylene bridge face. Imid stands for Cr imide; Tetr stands for tetrazene; and Azir stands for aziridine plus initial Cr complex (minus one chloride). Zero energy is set at initial chromium complex minus a single chloride. The depictions of the complexes are shown in Scheme 2 in the main text.

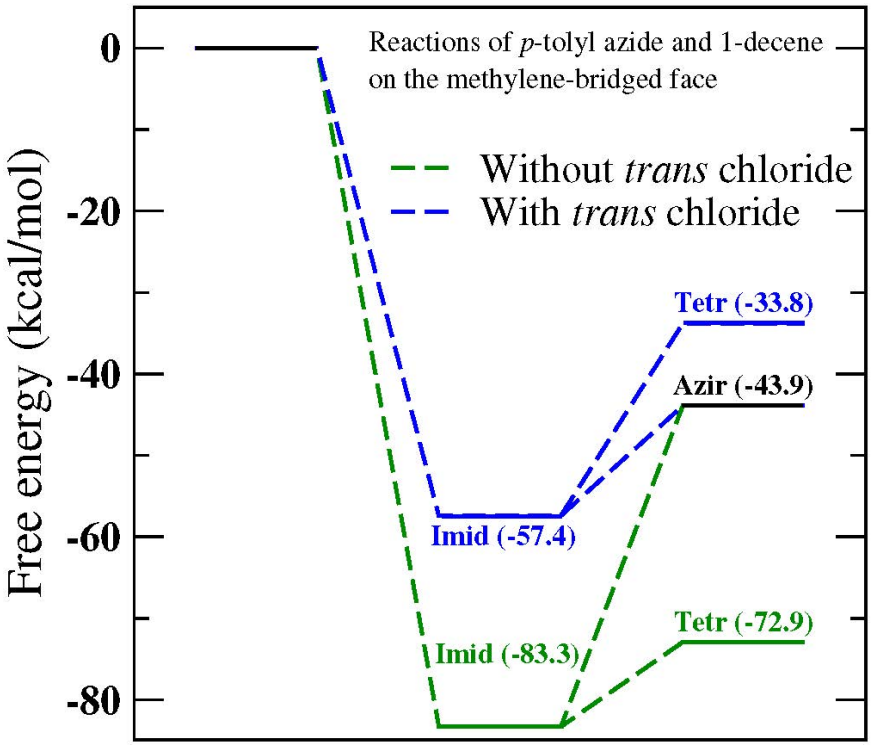


Figure S21. Representation of the calculated tetrazene complex with *trans* chloride (ΔG = -33.8 kcal/mol in Figure S20). This complex is a seven-coordinate species. The methylene C – Cr – methylene C angle is 113.3°.

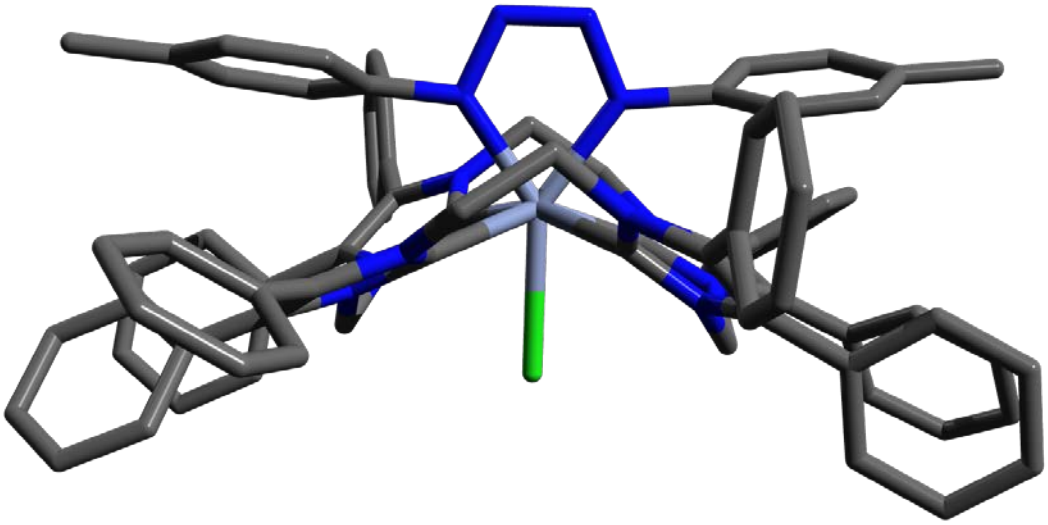
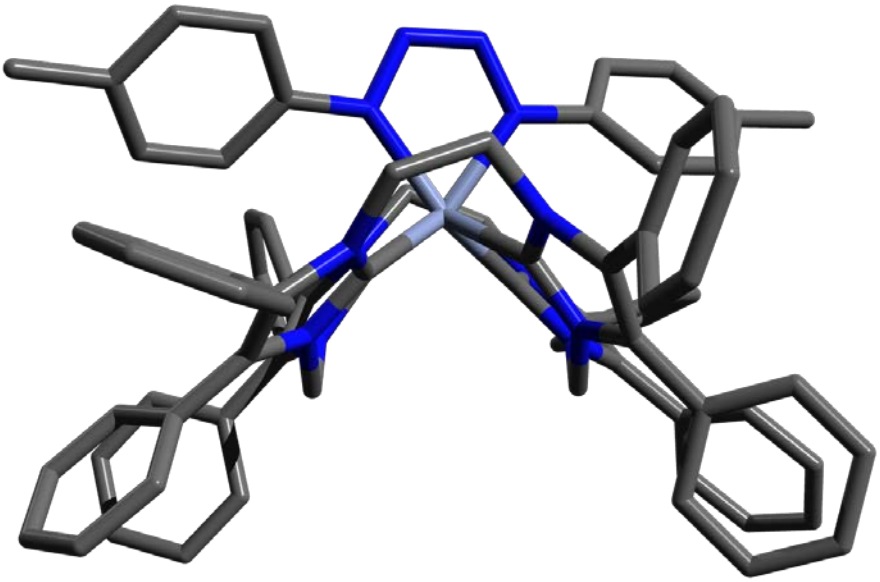


Figure S22. Representation of the calculated tetrazene complex without trans-chloride (ΔG = -72.9 kcal/mol in Figure S20). This complex is a six-coordinate species. The methylene C – Cr – methylene C angle is 74.9°. Comparison of this angle to the corresponding angle in Figure S21 shows that tetrazene formation is sterically more unfavorable in the presence of a *trans* chloride.



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