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1. General Conditions

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere employing standard Schlenk techniques and magnetic stirring. Anhydrous solvents (acetonitrile, benzene, chloroform, decaline, DMF, dichloromethane, *n*-hexane, methanol) were purified and dried by using standard procedures and stored under nitrogen.

2. Reagents

3,5-*Bis*(trifluoromethyl)phenyl azide,[1] Fe(F_{20}TPP)Cl,[2] Fe(F_{20}TPP)OMe,[3] Ru(TPP)CO),[4] Ru(TMP)CO,[5] Ru(OEP)CO,[6] Ru(TPP)$(py)_2$,[7] [Ru(TPP)$OCH_3)_2$]O,[8] Ru(TPP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$)[9] and Ru(TPP)$(NAr')_2$ (Ar' = 4(*t*Bu)C_6H_4)[10] were synthesized by methods reported in literature or by using minor modifications of them. Aziridines were synthesized by modifying the procedure reported by L.-N. He[11] and analytical data were in accordance with those reported in literature. All the other starting materials were commercial products and used as received. Analytical data of oxazolidinones **1A**-**10A** and **15A** were in accordance with reported data.

3. Instruments

NMR spectra were recorded at room temperature either on a Bruker Avance 300-DRX, operating at 300 MHz for ^{1}H, at 75 MHz for ^{13}C and at 282 MHz for ^{19}F or on a Bruker Avance 400-DRX spectrometers, operating at 400 MHz for ^{1}H, at 100 MHz for ^{13}C and 376 MHz for ^{19}F. Chemical shift (ppm) are reported relative to TMS. The ^{1}H NMR signals of the compounds described in the following were attributed by 2D NMR techniques. Assignments of the resonance in ^{13}C NMR were made by using the APT pulse sequence, HSQC and HMBC techniques. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV/Vis spectra were recorded on an Agilent 8453E instrument. Mass spectra were recorded in the analytical laboratories of Milan University.

4. Synthesis of porphyrin complexes

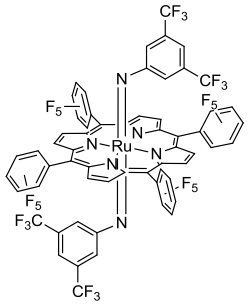
General procedure for the synthesis of ruthenium imido complexes[9]

3,5-*Bis*(trifluoromethyl)phenyl azide (2.54×10^{-4} mol) was added to a benzene (20.0 mL) suspension of Ru(porphyrin)(CO) (8.46×10^{-5} mol) and the resulting dark mixture was refluxed for

4 hours. After observing the complete Ru(porphyrin)(CO) consumption by TLC analysis (*n*-hexane/CH_2Cl_2 = 1:1), the solution was concentrated to about 5.0 mL and *n*-hexane (20.0 mL) was added. A crystalline violet solid was collected by filtration and dried *in vacuo.*

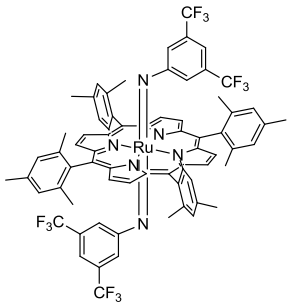
All the complexes, except Ru(TMP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$) which was purified by chromatography (alumina 0.063-0.200 µm, from *n*-hexane to *n*-hexane/CH_2Cl_2 = 7:3), were directly obtained in pure form.

Synthesis of Ru(F_{20}TPP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$).



The complex was obtained with 55% yield. The very low solubility of this compound in typical deuterated solvents prevented the NMR spectroscopic analysis and the structure was assigned by IR and mass spectrometry. IR (ATR): ν = 1980, 1520, 1493, 1365, 1278, 1171, 1130, 1080, 1064, 984, 946, 885, 763 cm^{-1}. Elemental analysis calcd (%) for $C_{60}H_{14}F_{32}N_6Ru$: C, 47.17; H, 0.92; N, 5.50. Found: C, 48.50; H, 1.05; N, 5.05. *m/z* (ESI) 1568.94 [$M+K^+$].

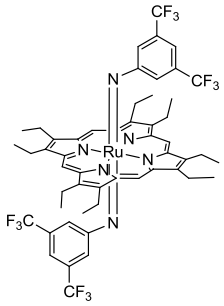
Synthesis of Ru(TMP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$).



The complex was obtained with 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 8H, H_β), 7.27 (s, 8H, Ar), 6.38 (s, 2H, $Ar_{CF3\text{-}para}$), 3.07 (s, 4H, $Ar_{CF3\text{-}ortho}$), 2.62 (s, 12H, CH_{3para}), 1.71 ppm (s, 24H, CH_{3ortho}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 138.2, 138.0, 137.98, 130.5, 127.8, 120.6, 119.9, 117.5, 116.2, 21.40, 21.39, 20.6 ppm; CF_3 signals and two quaternary carbons were not detected. ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -63.91 ppm. IR (ATR): ν = 1367, 1276, 1174, 1132, 1012, 996, 797

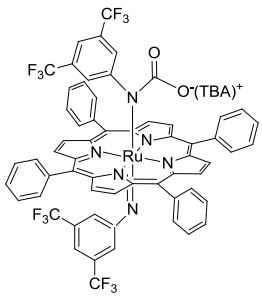
cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log_\varepsilon$) 423 (6.01), 527 (4.69), 628 (4.40), 657 nm (4.49). Elemental analysis calcd (%) for $C_{72}H_{58}F_{12}N_6Ru$: C, 64.71; H, 4.37; N, 6.29. Found: C, 65.02; H, 4.55; N, 5.93. *m/z* (ESI) 1337.56 [$M+H^+$].

Synthesis of Ru(OEP)(NAr)$_2$ (Ar = 3,5(CF$_3$)$_2$C$_6$H$_3$)



The complex was obtained with 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.23 (s, 4H, H_{meso}), 6.36 (s, 2H, $Ar_{CF3\text{-}para}$), 4.09 (q, 16H, *J*=7.6 Hz, CH_2), 2.22 (s, 4H, $Ar_{CF3\text{-}ortho}$), 1.93 ppm (t, 24H, *J*=7.6 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 151.9, 139.7, 128.9 (q, J_{CF}=33.8 Hz, C-CF_3), 128.7, 122.4 located by ZG-DC sequence (q, J_{CF}=278,6 Hz, CF_3), 117.4 (q, J_{CF}=3.6 Hz, C-Ar_{CF3}), 117.0, 99.6, 19.9, 18.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.0 ppm (s, 12F, CF_3). IR (ATR): ν= 2969, 2933, 2873, 1458, 1450, 1360, 1274, 1167, 1129, 1058, 1018, 992, 960, 886, 846 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log_\varepsilon$) 397 (5.27), 516 (4.06), 538 (4.08), 585 nm (3.67). Elemental analysis calcd (%) for $C_{52}H_{50}F_{12}N_6Ru$: C, 57.40; H, 4.63; N, 7.72. Found: C, 57.95; H, 4.85; N, 7.44. *m/z* (ESI) 1088.23 [M].

Synthesis of complex Ru(TPP)(NAr)(ArNCOO$^-$NBu$_4^+$) (Ar = 3,5(CF$_3$)$_2$C$_6$H$_3$) (16)



In a 100 mL glass liner equipped with a screw cap and a glass wool, tetrabutyl ammonium chloride (120.0 mg, 4.32×10^{-4} mol) were added to a benzene (15.0 mL) solution of Ru(TPP)(NAr)$_2$ (100.0 mg, 8.64×10^{-5} mol). The reaction mixture was cooled with liquid nitrogen and the flask was transferred into a stainless-steel autoclave, three vacuum-nitrogen cycles were performed and 0.6 MPa of CO_2 was charged at room temperature. The autoclave was placed in a preheated oil bath at 100°C and stirred for 6 h, then it was cooled at room temperature and slowly vented. The solvent

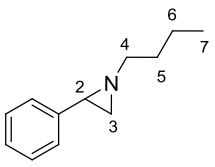
was evaporated to dryness and the crude was washed with H_2O (3 x 10.0 mL) in order to remove excess of TBACl. Toluene (20.0 mL) was added to the solid and the suspension was refluxed for removing water as an azeotropic mixture. The toluene suspension was evaporated to dryness and the solid resulted to be a mixture of different ruthenium species containing **16** as revealed by the ESI-MS analysis. The ^{1}H NMR spectroscopy in CD_3OD disclosed the presence of paramagnetic species and the IR (ATR) spectrum showed the C=O stretching at 1604 cm^{-1}. *m/z* (ESI) 242.48 [M^+]; 1212.29 [M^-]. Unfortunately, any attempt to isolate **16** in a pure form have failed up to now.

5. Synthesis of aziridines

General procedure[11]

A distilled methylene chloride (40.0 mL) solution of dimethyl sulphide (2.00×10^{-1} mol) was placed in an ice-bath and 10.2 mL of bromine (2.00×10^{-1} mol), dissolved in 40.0 mL of distilled methylene chloride, was added dropwise over 45 minutes during which, the formation of light orange crystals of bromodimethyl sulfonium bromide was observed. The obtained solid was collected by filtration, washed with 150.0 mL of cold diethyl ether, dried and dissolved in 160.0 mL of acetonitrile. Then, the desired styrene (2.00×10^{-1} mol) was added dropwise over 30 minutes to the solution placed in an ice-bath. The resulting mixture was stirred for 10 minutes and the so-formed white solid was collected by filtration, washed several times with cold acetonitrile and dried *in vacuo*. The white crystals of styrene sulphonium bromide (8.62×10^{-3} mol) were suspended in 40.0 mL of water and 20.00 mL of water solution of desired amine (4.30×10^{-2} mol) was added dropwise over 25 minutes. The resulting mixture was stirred overnight and then 40.0 mL of saturated brine was added. The solution was extracted with diethyl ether (3 x 20.0 mL), the combined organic phases were dried over Na_2SO_4 and the solvent was evaporated to dryness under a reduced pressure. The crude was purified by flash chromatography (silica gel, 60 µm, *n*-hexane/AcOEt = 8:2).

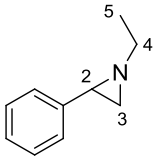
Synthesis of 1-butyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and butyl amine as reagents to obtain a yellowish oil (60% yield). The collected data are in accordance with those

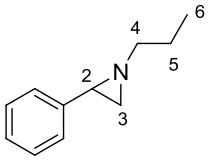
reported in literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.12 (m, 5H, Ar), 2.45 (dt, 1H, ^{2}J=11.5 Hz, J=7.3 Hz, H^4), 2.28 (dt, 1H, ^{2}J=11.5 Hz, J=7.3 Hz, $H^{4'}$), 2.23 (dd, 1H, J=6.4, 3.2 Hz, H^2), 1.83 (d, 1H, J=3.2 Hz, H^3), 1.59 (d, 1H, J=6.5 Hz, $H^{3'}$), 1.55 (m, 2H, H^5), 1.35 (m, 2H, H^6), 0.88 ppm (t, 3H, J=7.3 Hz, H^7).

Synthesis of 1-ethyl-2-phenylaziridine



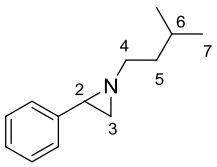
The general procedure for the synthesis of aziridines was followed using styrene and ethylamine as reagents to obtain a yellowish oil (20% yield). The collected data are in accordance with those reported in literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.12 (m, 5H, Ar), 2.42 (q, 2H, J=7.1 Hz, H^4), 2.27 (dd, 1H, J=6.4, 3.3 Hz, H^2), 1.87 (d, 1H, J=3.2 Hz, H^3), 1.62 (d, 1H, J=6.5 Hz, $H^{3'}$), 1.19 ppm (t, 3H, J=7.1 Hz, H^5).

Synthesis of 1-propyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and propylamine as reagents to obtain a yellowish oil (21% yield). The collected data are in accordance with those reported in literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.19 (m, 5H, Ar), 2.48 (dt, 1H, ^{2}J=11.5 Hz, J=7.5 Hz, H^4), 2.30 (m, 2H, $H^{4'}$ and H^2), 1.90 (d, 1H, J=3.2 Hz, H^3), 1.65 (m, 3H, $H^{3'}$ and H^5), 0.97 ppm (t, 3H, J=7.4 Hz, H^6).

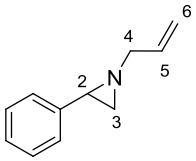
Synthesis of 1-isoamyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and isoamylamine as reagents to obtain a yellowish oil (68% yield). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 4H, Ar), 7.29-7.24 (m, 1H,

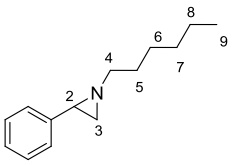
Ar), 2.61-2.50 (m, 1H, H^4), 2.48-2.37 (m, 1H, $H^{4'}$), 2.35 (dd, 1H, *J*=6.5, 3.3 Hz, H^2), 1.94 (d, 1H, *J*=3.1 Hz, H^3), 1.77 (heptet, 1H, *J*=6.6 Hz, H^6), 1.70 (d, 1H, *J*=6.5 Hz, $H^{3'}$), 1.65-1.55 (m, 2H, H^5), 0.99 ppm (dd, 6H, *J*=6.9 Hz, ^4J=1.6 Hz, H^7).

Synthesis of 1-allyl-2-phenylaziridine



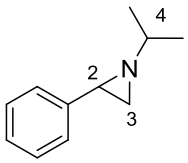
The general procedure for the synthesis of aziridines was followed using styrene and allylamine as reagents to obtain a yellowish oil (60% yield). The collected data are in accordance with those reported in literature.[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.18 (m, 4H, Ar), 5.96 (ddd, 1H, *J*=22.4, 10.7, 5.5 Hz, H^5), 5.22 (d, 1H, *J*=17.2 Hz, H^{6trans}), 5.10 (d, 1H, *J*=10.4 Hz, H^{6cis}), 3.14 (dd, 1H, ^2J=14.3 Hz, *J*=5.4 Hz, H^4), 2.98 (dd, 1H, ^2J=14.2 Hz, *J*=5.4 Hz, $H^{4'}$), 2.35 (dd, 1H, *J*=6.4, 3.4 Hz, H^2), 1.93 (d, 1H, *J*=3.3 Hz, H^3), 1.71 ppm (d, 1H, *J*=6.5 Hz, $H^{3'}$).

Synthesis of 1-hexyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and hexylamine as reagents to obtain a yellowish oil (72% yield). The collected data are in accordance with those reported in literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.05 (m, 5H, Ar), 2.46 (dt, 1H, ^2J=11.5 Hz, *J*=7.3 Hz, H^4), 2.28 (dt, 1H, ^2J=11.5 Hz, *J*=7.3 Hz, $H^{4'}$), 2.26 (dd, 1H, *J*=6.4, 3.2 Hz, H^2), 1.85 (d, 1H, *J*=3.2 Hz, H^3), 1.62 (d, 1H, *J*=6.3 Hz, $H^{3'}$), 1.60 (m, 2H, H^5), 1.35 (m, 2H, H^6), 1.31 (m, 4H, H^7 and H^8), 0.86 ppm (t, 3H, *J*=6.9 Hz, H^9).

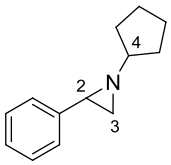
Synthesis of 1-isopropyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and isopropylamine as reagents to obtain a yellowish oil (21% yield). The collected data are in

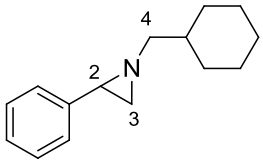
accordance with those reported in literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.18 (m, 5H, Ar), 2.34 (dd, 1H, *J*=6.4, 3.3 Hz, H^2), 1.89 (d, 1H, *J*=3.3 Hz, $H^{3'}$), 1.66 (d, 1H, *J*=6.6 Hz, H^3), 1.61 (m, 1H, H^4), 1.19 (d, 3H, *J*=1.4 Hz, CH_3), 1.17 ppm (d, 3H, *J*=1.3 Hz, CH_3).

Synthesis of 1-cyclopentyl-2-phenylaziridine



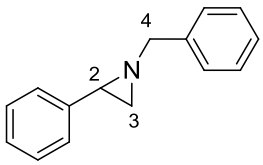
The general procedure for the synthesis of aziridines was followed using styrene and cyclopentylamine as reagents to obtain a yellowish oil (81% yield). The collected data are in accordance with those reported in literature.[15] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.24 (m, 4H, Ar), 7.18-7.15 (m, 1H, Ar), 2.34 (dd, 1H, *J*=6.5, 3.3 Hz, H^2), 2.09-2.00 (m, 1H, H^4), 1.81 (d, 1H, *J*=3.1 Hz, H^3), 1.79-1.74 (m, 1H, $H_{cyclopentyl}$), 1.72-1.66 (m, 1H, $H_{cyclopentyl}$), 1.64 (d, 1H, *J*=6.5 Hz, $H^{3'}$), 1.53-1.49 ppm (m, 2H, $H_{cyclopentyl}$).

Synthesis of 1-cyclohexylmethyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and cyclohexylmethylamine as reagents to obtain a yellowish oil (82% yield). The collected data are in accordance with those reported in literature.[16] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.17 (m, 5H, Ar), 2.42 (dd, 1H, ^2J=11.7 Hz, *J*=7.0 Hz, H^4), 2.25 (dd, 1H, *J*=6.4, 3.2 Hz, H^2), 2.09 (dd, 1H, ^2J=11.7 Hz, *J*=6.4 Hz, $H^{4'}$), 1.85 (d, 1H, *J*=6.5 Hz, H^3), 1.79-1.58 (m, 5H, $H_{cyclohexyl}$), 1.62 (d, 1H, *J*=6.5 Hz, $H^{3'}$), 1.20-1.10 (m, 3H, $H_{cyclohexyl}$), 0.98-0.90 ppm (m, 2H, $H_{cyclohexyl}$).

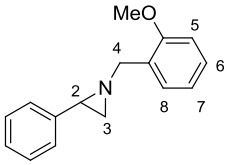
Synthesis of 1-benzyl-2-phenylaziridine



The general procedure for the synthesis of aziridines was followed using styrene and benzylamine as reagents to obtain a yellowish oil (80% yield). The collected data are in accordance with those

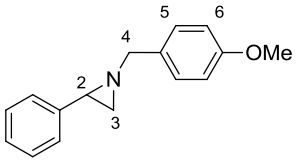
reported in literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.28 (m, 10H, Ar), 3.78 (d, 1H, *J*=13.7 Hz, H^4) 3.70 (d, 1H, *J*=13.7 Hz, $H^{4'}$), 2.59 (dd, 1H, *J*=6.4, 3.3 Hz, H^2), 2.07 (d, 1H, *J*=3.3 Hz, H^3), 1.93 ppm (d, 1H, *J*=6.5 Hz, $H^{3'}$).

Synthesis of 1-(2-methoxy)benzyl-2-phenylaziridine



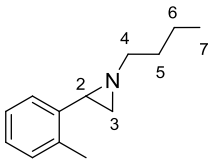
The general procedure for the synthesis of aziridines was followed using styrene and (2-methoxy)benzylamine as reagents to obtain a yellowish oil (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 1H, *J*=7.5 Hz, H^8), 7.28-7.25 (m, 4H, Ar), 7.22-7.18 (m, 1H, H^6), 6.89 (pst, 1H, *J*=7.8, 7.1 Hz, H^7), 6.83 (d, 1H, *J*=8.1 Hz, H^5), 3.80 (s, 3H, OCH_3) overlapping with 3.79 (m, 1H, H^4), 3.53 (d, 1H, *J*=14.9 Hz, $H^{4'}$) 2.48 (dd, 1H, *J*=6.5, 3.4 Hz, H^2), 2.00 (d, 1H, *J*=3.4 Hz, H^3), 1.86 ppm (d, 1H, *J*=6.5 Hz, $H^{3'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 140.6, 128.9, 128.4, 127.9, 127.8, 126.9, 126.4, 120.7, 109.9, 59.1, 55.3, 41.7, 38.2 ppm. *m/z* (ESI) 240.39 [M+H].

Synthesis of 1-(4-methoxy)benzyl-2-phenylaziridine



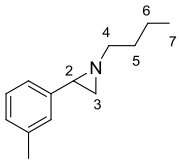
The general procedure for the synthesis of aziridines was followed using styrene and (4-methoxy)benzylamine as reagents to obtain a yellowish oil (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.18 (m, 7H, Ar), 6.85 (d, 2H, *J*=8.6 Hz, H^6), 3.77 (s, 3H, OCH_3), 3.61 (d, 1H, *J*=13.4 Hz, H^4), 3.53 (d, 1H, *J*=13.4 Hz, $H^{4'}$), 2.48 (dd, 1H, *J*=6.5, 3.3 Hz, H^2), 1.95 (d, 1H, *J*=3.3 Hz, H^3), 1.82 ppm (d, 1H, *J*=6.5 Hz, $H^{3'}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 140.3, 131.3, 129.2, 128.4, 126.9, 126.4, 113.4, 64.3, 55.3, 41.5, 37.9 ppm. *m/z* (ESI) 240.14 [M+H].

Synthesis of 1-butyl-2-(2-methyl)phenylaziridine



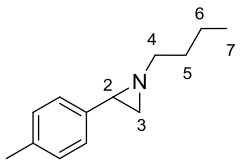
The general procedure for the synthesis of aziridines was followed using 2-methylstyrene and butylamine as reagents to obtain a yellowish oil (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 1H, Ar), 7.20-7.09 (m, 3H, Ar), 2.51 (dt, 1H, ^{2}J=11.0 Hz, J=7.5 Hz, H^4), 2.41 (s, 3H, CH_3) overlapping with 2.44-2.41 (m, 1H, $H^{4'}$), 2.38 (dd, J=6.5, 3.2 Hz, H^2), 1.80 (d, 1H, J=3.2 Hz, H^3), 1.66 (d, 1H, J=6.5 Hz, $H^{3'}$), 1.65-1.58 (m, 2H, H^5), 1.50-1.37 (m, 2H, H^6), 0.95 ppm (t, 3H, J=7.3 Hz, H^7). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.6, 129.6, 126.6, 126.2, 126.1, 61.7, 39.5, 36.7, 32.2, 20.7, 19.2, 14.2 ppm. *m/z* (ESI) 190.18 [M+H].

Synthesis of 1-butyl-2-(3-methyl)phenylaziridine



The general procedure for the synthesis of aziridines was followed using 3-methylstyrene and butylamine as reagents to obtain a yellowish oil (46% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.17 (t, 1H, J=7.7 Hz, Ar), 7.08-7.03 (m, 3H, Ar), 2.51 (dt, 1H, ^{2}J=11.6 Hz, J=7.3 Hz, H^4), 2.34 (s, 3H, CH_3) overlapping with 2.35-2.31 (m, 1H, $H^{4'}$), 2.27 (dd, 1H, J=6.4, 3.2 Hz, H^2), 1.89 (d, 1H, J=3.2 Hz, H^3), 1.65 (d, 1H, J=6.5 Hz, $H^{3'}$), 1.62 (m, 2H, H^5), 1.41 (m, 2H, H^6), 0.94 ppm (t, 3H, J=7.3 Hz, H^7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 138.0, 128.2, 127.6, 126.7, 123.5, 61.7, 41.3, 37.8, 32.1, 21.4, 20.7, 14.2 ppm. *m/z* (ESI) 190.24 [M+H].

Synthesis of 1-butyl-2-(4-methyl)phenylaziridine



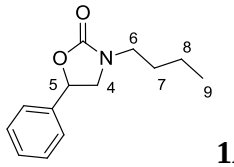
The general procedure for the synthesis of aziridines was followed using 4-methylstyrene and butylamine as reagents to obtain a yellowish oil (54% yield). The collected data are in accordance with those reported in literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (q, 4H, J=8.1 Hz, Ar), 2.52 (dt, 1H, ^{2}J=11.5 Hz, J=7.3 Hz, H^4), 2.32-2.25 (m, 2H, $H^{4'}$ and H^2), 2.33 (s, 3H, CH_3), 1.87 (d, 1H, J=3.2 Hz, H^3), 1.63 (d, 1H, J=6.3 Hz, $H^{3'}$), 1.65-1.68 (m, 2H, H^5), 1.49-1.33 (m, 2H, H^6), 0.93 ppm (t, 3H, J=7.3 Hz, H^7).

6. Synthesis of oxazolidin-2-ones

General catalytic procedure

In a 100 mL glass liner equipped with a screw cap and a glass wool, tetrabutyl ammonium chloride (14.2 mg, 5.13×10^{-5} mol) and aziridine (5.13×10^{-4} mol) were added to a benzene (2.50 mL) solution of catalyst (5.13×10^{-6} mol). The reaction mixture was cooled with liquid nitrogen and the glass liner was transferred into a stainless-steel autoclave, three vacuum-nitrogen cycles were performed and 0.6 MPa of CO_2 was charged at room temperature. The autoclave was placed in a preheated oil bath at 100°C and stirred for 6 h, then it was cooled at room temperature and slowly vented. The solvent was evaporated to dryness and the crude was analyzed by ^{1}H NMR and then purified by flash chromatography (silica gel, 60 μm, *n*-hexane/AcOEt = 8:2).

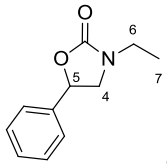
Synthesis of 3-butyl-5-phenyloxazolidin-2-one



1A

The general catalytic procedure was followed using *N*-butyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 71%, **1A**/**1B** = 90:10). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$) **1A**: δ 7.42-7.28 (m, 5H, Ar), 5.49 (t, 1H, *J*=8.0 Hz, H^5), 3.92 (t, 1H, *J*=8.8 Hz, H^4), 3.43 (t, 1H, *J*=8.0 Hz, $H^{4'}$), 3.38-3.23 (m, 2H, H^6), 1.58-1.51 (m, 2H, CH_2), 1.40-1.31 (m, 2H, CH_2), 0.94 ppm (t, 3H, *J*=6.8 Hz, CH_3).

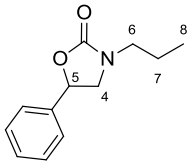
Synthesis of 3-ethyl-5-phenyloxazolidin-2-one



2A

The general catalytic procedure was followed using *N*-ethyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 65%, **2A**/**2B** = 95:5). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$) **2A**: δ 7.34-7.65 (m, 5H, Ar), 5.46 (m, 1H, H^5), 3.93 (t, 1H, *J*=8.8 Hz, H^4), 3.40-3.39 (m, 3H, $H^{4'}$ and H^6), 1.14 ppm (t, 3H, *J*=7.1 Hz, H^7).

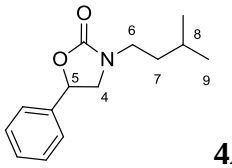
Synthesis of 3-propyl-5-phenyloxazolidin-2-one



3A

The general catalytic procedure was followed using *N*-propyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 60%, **3A**/**3B** = 90:10). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$) **3A**: δ 7.42-7.34 (m, 5H, Ar), 5.49 (t, 1H, *J*=8.1 Hz, H^5), 3.91 (t, 1H, *J*=8.7 Hz, $H^{4'}$), 3.43 (dd, 1H, *J*=8.5, *J*=7.5 Hz, H^4), 3.35-3.17 (m, 2H, H^6), 1.67-1.51 (m, 2H, H^7), 0.94 ppm (t, 3H, *J*=7.4 Hz, H^8).

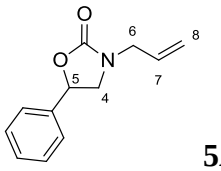
Synthesis of 3-isoamyl-5-phenyloxazolidin-2-one



4A

The general catalytic procedure was followed using *N*-isoamyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 81%, **4A**/**4B** = 92:8). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) **4A**: δ 7.43-7.32 (m, 5H, Ar), 5.47 (t, 1H, *J*=8.1 Hz, H^5), 3.90 (t, 1H, *J*=8.7 Hz, H^4), 3.41 (t, 1H, *J*=8.0, *J*=7.5 Hz, $H^{4'}$), 3.37-3.20 (m, 2H, H^6), 1.66-1.54 (m, 1H, H^8), 1.49-1.39 (m, 2H, H^7), 0.94 (d, 3H, *J*=3.3 Hz, CH_3), 0.92 (t, 3H, *J*=7.4 Hz, CH_3).

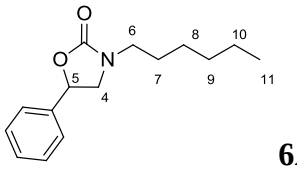
Synthesis of 3-allyl-5-phenyloxazolidin-2-one



5A

The general catalytic procedure was followed using *N*-allyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 70%, **5A**/**5B** = 94:6). The collected data are in accordance with those reported in literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) **5A**: δ 7.43-7.35 (m, 5H, Ar), 5.84-5.73 (m, 1H, H^7), 5.50 (t, 1H, *J*=8.0 Hz, H^8), 5.28-5.22 (m, 2H, $H^{8'}$ and H^5), 3.98-3.84 (m, 3H, H^4, $H^{4'}$ and H^6), 3.44-3.38 ppm (m, 1H, $H^{6'}$).

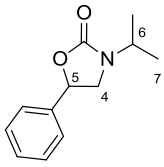
Synthesis of 3-hexyl-5-phenyloxazolidin-2-one



6A

The general catalytic procedure was followed using *N*-hexyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 55%, **6A**/**6B** = 94:6). The collected data are in accordance with those reported in literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) **6A**: δ 7.31-7.25 (m, 5H, Ar), 5.37 (t, 1H, *J*=8.0 Hz, H^5), 3.82 (t, 1H, *J*=8.8 Hz, H^4), 3.31 (t, 1H, *J*=8.0 Hz, $H^{4'}$), 3.23-3.13 (m, 2H, H^6), 1.47-1.43 (m, 2H, CH_2), 1.24-1.20 (m, 6H, CH_2), 0.79 ppm (t, 3H, *J*=6.6 Hz, H^{11}).

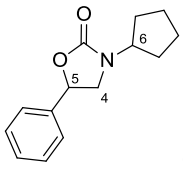
Synthesis of 3-isopropyl-5-phenyloxazolidin-2-one



7A

The general catalytic procedure was followed using *N*-Isopropyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 20%, **7A**/**7B** = 90:10). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) **7A**: δ 7.42-7.31 (m, 5H, Ar), 5.47 (t, 1H, *J*=8.1 Hz, H^5), 4.18 (dt, 1H, *J*=13.5, *J*=6.7 Hz, H^6), 3.86 (t, 1H, *J*=8.7 Hz, $H^{4'}$), 3.37 (t, 1H, *J*=8.0 Hz, H^4), 1.22 (d, 3H, *J*=6.8 Hz, H^7), 1.16 ppm (d, 3H, *J*=6.7 Hz, $H^{7'}$).

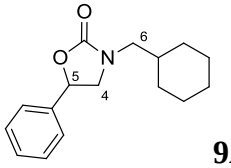
Synthesis of 3-cyclopentyl-5-phenyloxazolidin-2-one



8A

The general catalytic procedure was followed using *N*-cyclopentyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 10%, **8A**/**8B** = 99:1). The collected data are in accordance with those reported in literature.[19] ^{1}H NMR (400 MHz, $CDCl_3$) **8A**: δ 7.31-7.25 (m, 5H, Ar), 5.47 (t, 1H, *J*=8.0 Hz, H^5), 4.29 (t, 1H, *J*=8.8 Hz, H^4), 3.88 (t, 1H, *J*=8.0 Hz, $H^{4'}$), 3.23-3.13 (m, 1H, H^6), 1.90-1.87 (m, 2H, $H_{cyclopentyl}$), 1.67-1.49 ppm (m, 6H, $H_{cyclopentyl}$).

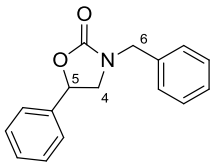
Synthesis of 3-cyclohexanemethyl-5-phenyloxazolidin-2-one



9A

The general catalytic procedure was followed using *N*-cyclohexanemethyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 55%, **9A**/**9B** = 94:6). The collected data are in accordance with those reported in literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) **9A**: δ 7.34-7.24 (m, 5H, Ar), 5.44 (t, 1H, *J*=8.0 Hz, H^5), 3.89 (t, 1H, *J*=8.7 Hz, H^4), 3.39 (t, 1H, *J*=8.0 Hz, $H^{4'}$), 3.13 (dd, 1H, ^2J=13.7 Hz, *J*=7.4 Hz, H^6), 3.03 (dd, 1H, ^2J=1.7 Hz, *J*=7.2 Hz, $H^{6'}$), 1.67-1.58 (m, 5H, $H_{cyclohexyl}$), 1.19-1.09 (m, 3H, $H_{cyclohexyl}$), 0.98-0.92 ppm (m, 2H, $H_{cyclohexyl}$).

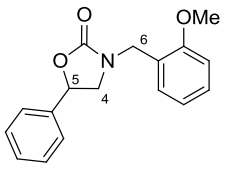
Synthesis of 3-benzyl-5-phenyloxazolidin-2-one



10A

The general catalytic procedure was followed using *N*-benzyl-phenyl aziridine as reagent to obtain a yellowish oil (yield 85%, **10A**/**10B** = 99:1). The collected data are in accordance with those reported in literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) **10A**: δ 7.35-7.27 (m, 10H, Ar), 5.43 (t, 1H, *J*=8.1 Hz, H^5), 4.49 (d, 1H, *J*=15.0 Hz, H^6),4.41 (d, 1H, *J*=15.0 Hz, $H^{6'}$), 3.75 (t, 1H, *J*=8.7 Hz, H^4), 3.28 ppm (t, 1H, ^2J=8.4 Hz, $H^{4'}$).

Synthesis of 3-(2-methoxy)benzyl -5-phenyloxazolidin-2-one

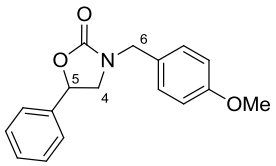


11A

The general catalytic procedure was followed using *N*-(2-methoxy)benzyl-phenyl aziridine as reagent to obtain a yellowish oil (64% yield, **11A**/**11B** = 99:1). ^{1}H NMR (300 MHz, $CDCl_3$) **11A**: δ 7.40-7.26 (m, 7H, Ar), 6.34 (t, 1H, *J*=7.5 Hz, Ar), 6.87 (d, 1H, *J*=8.0 Hz, Ar), 5.43 (pst, 1H, *J*=8.1 Hz, H^5), 4.54 (d, 1H, *J*=14.7 Hz, H^6), 4.47 (d, 1H, *J*=14.7 Hz, 1H, $H^{6'}$), 3.81 (s, 3H, OCH_3) overlapping with 3.78 (m, 1H, H^4), 3.32 ppm (m, 1H, $H^{4'}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.3,

129.5, 128.9, 125.7, 120.9, 110.5, 74.6, 55.5, 52.1, 43.2 ppm, quaternary carbons were not detected. *m/z* (ESI) 306.40 [M+Na].

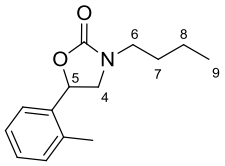
Synthesis of 3-(4-methoxy)benzyl -5-phenyloxazolidin-2-one



12A

The general catalytic procedure was followed using *N*-(4-methoxy)benzyl-phenyl aziridine as reagent to obtain a yellowish oil (60% yield, **12A**/**12B** = 99:1). ^{1}H NMR (400 MHz, $CDCl_3$) **12A**: δ 7.38-7.32 (m, 3H, Ar), 7.31-7.28 (m, 2H, Ar), 7.21 (d, 2H, *J*=8.6 Hz, $H_{benzyl\text{-}orto}$), 6.87 (d, 2H, *J*=8.6 Hz, $H_{benzyl\text{-}meta}$), 5.45 (pst, 1H, *J*=8.2 Hz, H^5), 4.47 (d, 1H, *J*=14.7 Hz, H^6), 4.35 (d, 1H, *J*=14.7 Hz, $H^{6'}$), 3.80 (s, 3H, OCH_3), 3.74 (pst, 1H, *J*=8.8 Hz, H^4), 3.28 ppm (dd, 1H, *J*=8.7, 7.6 Hz, $H^{4'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 129.7, 129.0, 128.9, 127.8, 125.7, 114.3, 74.6, 55.4, 51.6, 48.0 ppm, one quaternary carbon was not detected. *m/z* (ESI) 306.31 [M+Na].

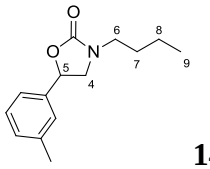
Synthesis of 3-butyl-5-(2-methyl)phenyloxazolidin-2-one



13A

The general catalytic procedure was followed using *N*-butyl-2-(2-methyl)phenyl aziridine as reagent to obtain a yellowish oil (92% yield, **13A**/**13B** = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) **13A**: δ 7.27 (pst, 1H, *J*=7.6 Hz, Ar), 7.16 (s, 1H, Ar), 7.16-7.08 (m, 2H, Ar), 5.43 (t, 1H, *J*=8.1 Hz, H^5), 3.89 (pst, 1H, *J*=8.7 Hz, $H^{4'}$), 3.40 (dd, 1H, *J*=8.6, 7.5 Hz, H^4), 3.37-3.20 (m, 2H, H^6), 2.35 (s, 3H, CH_3), 1.58-1.48 (m, 1H, CH_2), 1.38-1.30 (m, 1H, CH_2), 0.93 ppm (t, 3H, *J*=7.3 Hz, H^9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 138.9, 138.7, 129.5, 128.8, 126.1, 122.6, 74.39, 52.2, 43.9, 29.4, 21.4, 19.9, 13.7. *m/z* (ESI) 256.24 [M+Na].

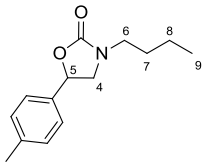
Synthesis of 3-butyl-5-(3-methyl)phenyloxazolidin-2-one



14A

The general catalytic procedure was followed using *N*-butyl-2-(3-methyl)phenyl aziridine as reagent to obtain a yellowish oil (96% yield, **14A**/**14B** = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) **14A**: δ 7.44 (m, 1H, Ar), 7.26-7.24 (m, 4H, Ar), 7.18 (m, 1H, Ar), 5.67 (pst, 1H, *J*=8.1 Hz, H^5), 3.95 (pst, 1H, *J*=8.7 Hz, H^4), 3.40-3.20 (m, 3H, $H^{4'}$ and H^6), 2.31 (s, 3H, CH_3), 1.53 (m, 2H, H^7), 1.34 (m, 1H, H^8), 0.93 ppm (t, 3H, *J*=7.3 Hz, H^9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 137.3, 134.2, 130.8, 128.5, 126.6, 124.7, 72.1, 51.4, 44.0, 29.5, 19.9, 19.0, 13.8 ppm. *m/z* (ESI) 256.27 [M+Na].

Synthesis of 3-butyl-5-(4-methyl)phenyloxazolidin-2-one



15A

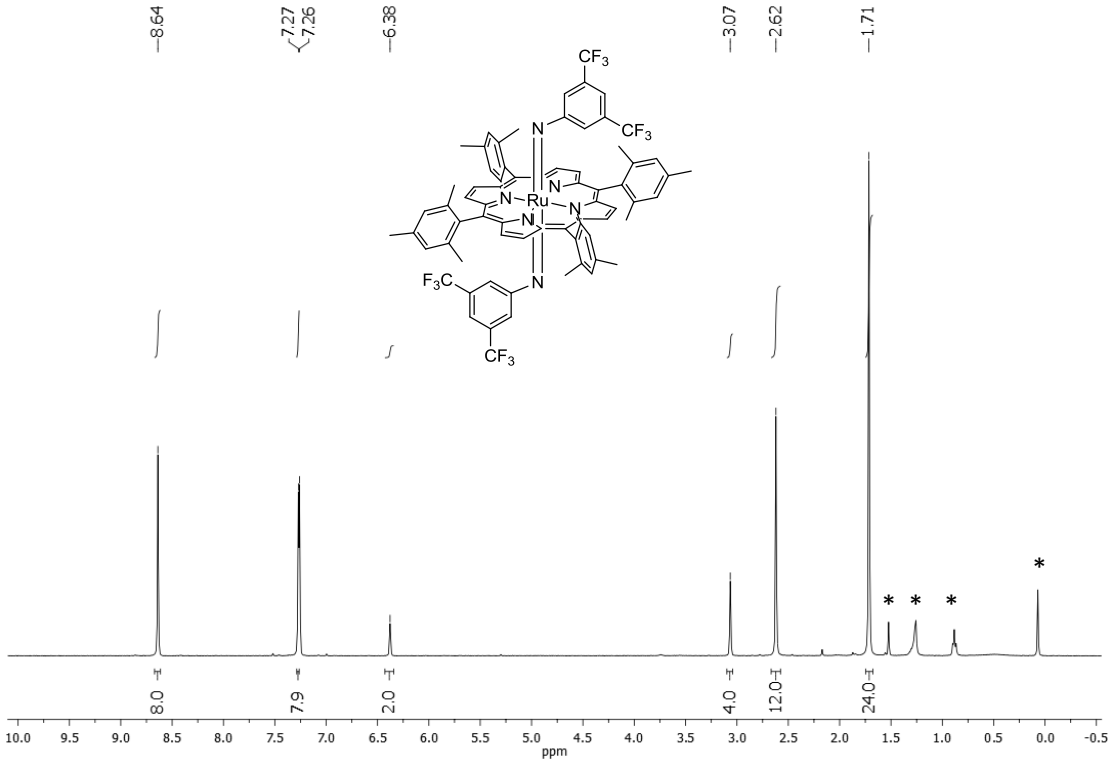
The general catalytic procedure was followed using *N*-butyl-2-(4-methyl)phenyl aziridine as reagent to obtain a yellowish oil (90% yield, **15A**/**15B** = 90:10). The collected data are in accordance with those reported in literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) **15A**: δ 7.23 (dd, 4H, J=17.4 Hz, Ar), 5.44 (t, 1H, J=8.0 Hz, H^5), 3.88 (t, 1H, J=8.7 Hz, $H^{4'}$), 3.41 (t, 1H, J=8.1 Hz, H^4), 3.38-3.22 (m, 2H, H^6), 2.36 (s, 3H, CH_3), 1.57-1.50 (m, 2H, CH_2), 1.39-1.33 (m, 2H, CH_2), 0.94 ppm (t, 3H, J=7.3 Hz, H^9).

7. Recycle of the catalyst Ru(TPP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$)

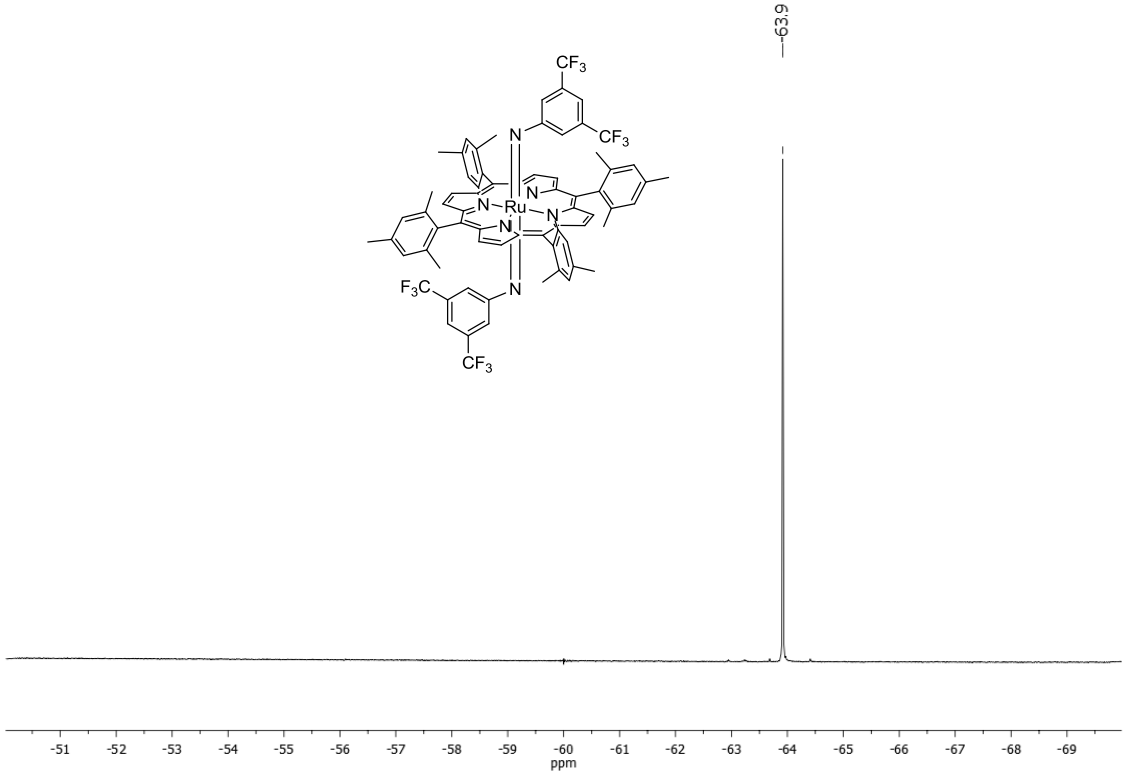
The general catalytic procedure was followed using *N*-butyl-phenyl aziridine as reagent. The consumption of the aziridine was monitored by TLC analysis (*n*-hexane/AcOEt = 8:2). After the consumption of the starting material, *N*-butyl-phenyl aziridine was added again to the catalytic mixture for two more consecutive times. The NMR analysis of the crude revealed 70% of global yield and **1A**/**1B** ratio of 90:10.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of reported compounds

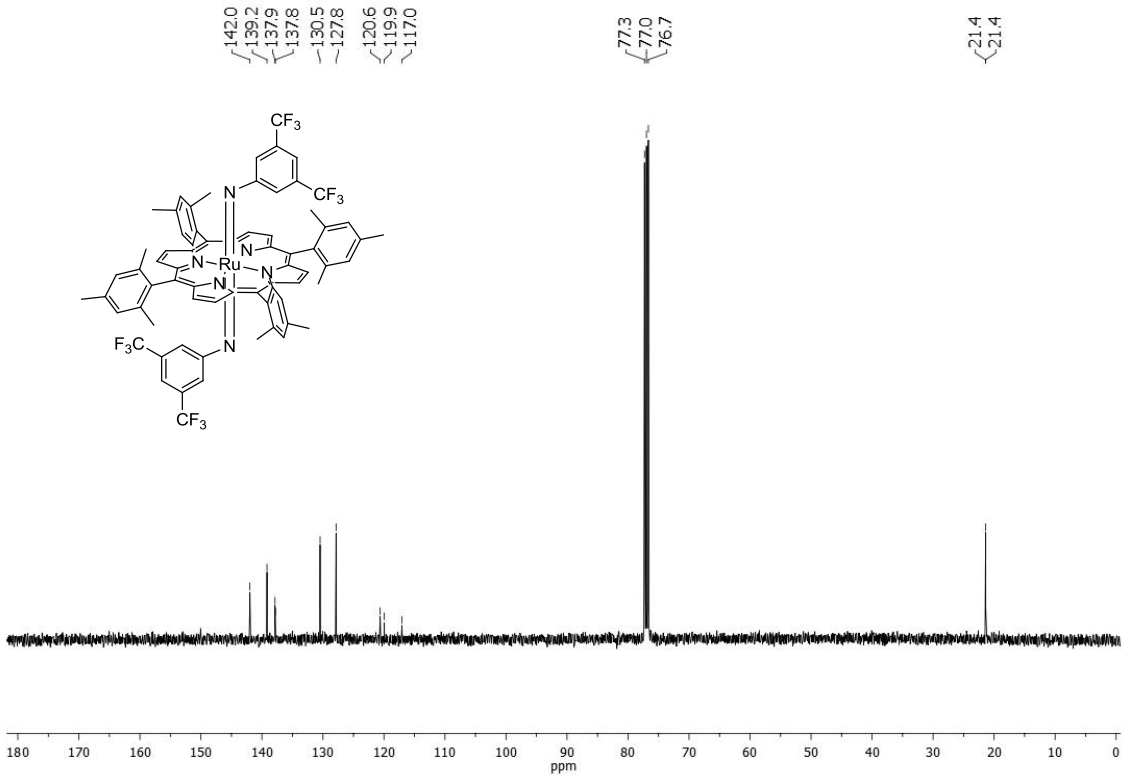
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of Ru(TMP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$)



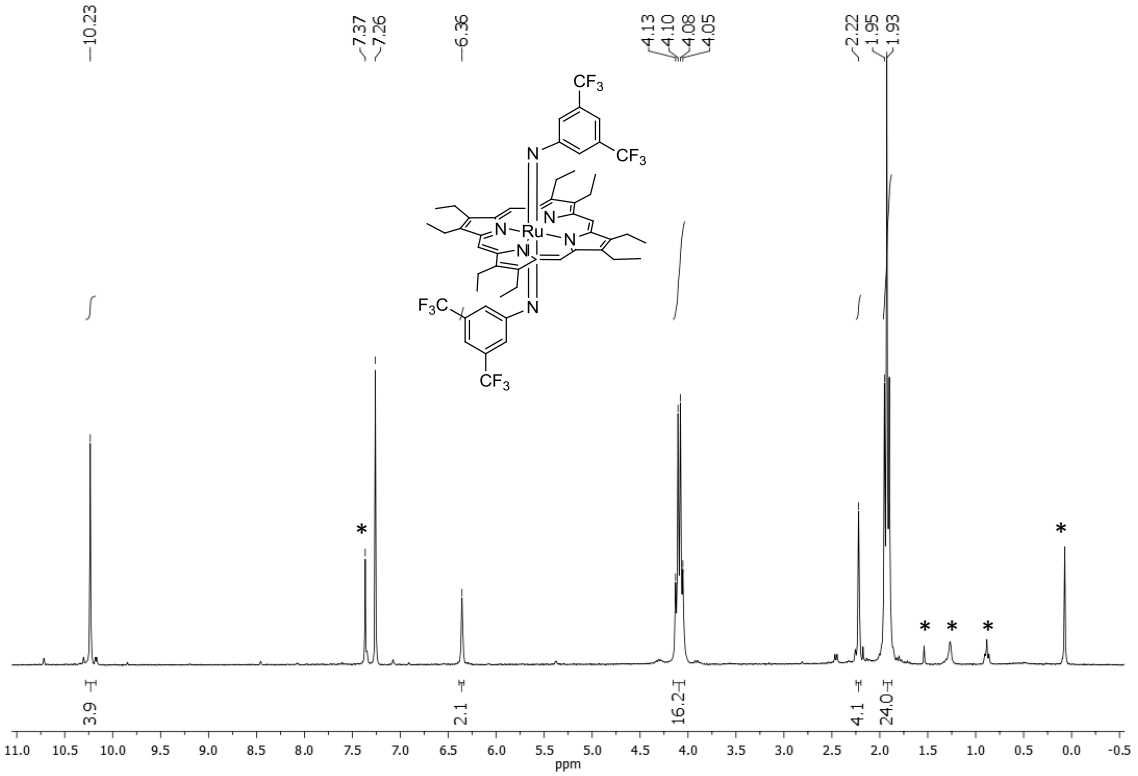
^{19}F NMR spectrum (376 MHz, $CDCl_3$, 298 K) of Ru(TMP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$)



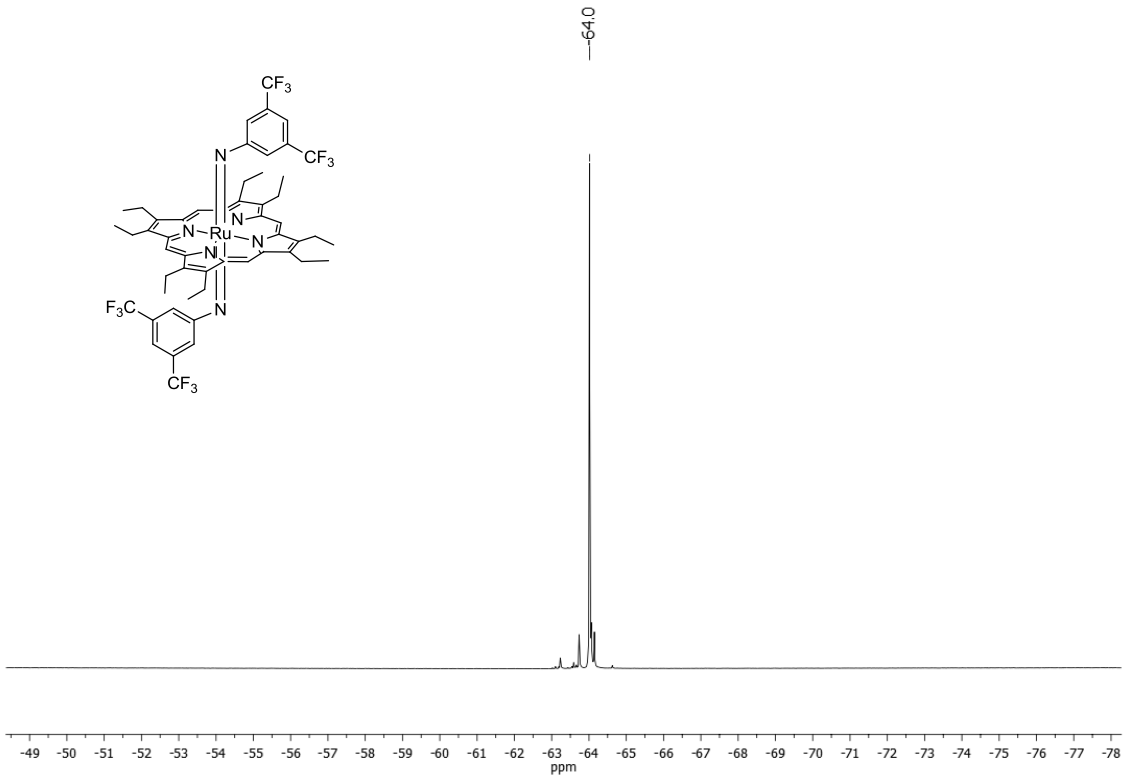
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of Ru(TMP)$(NAr)_2$ (Ar = 3,5-$(CF_3)_2C_6H_4$)



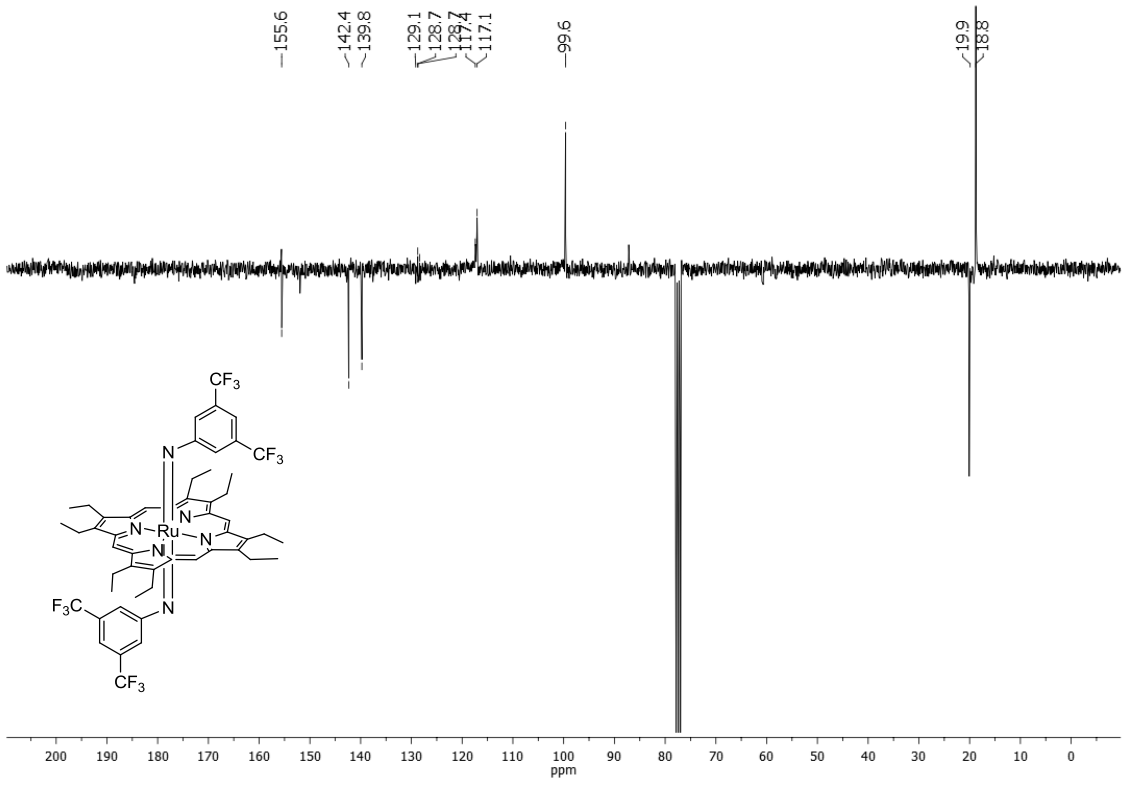
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of Ru(OEP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$)



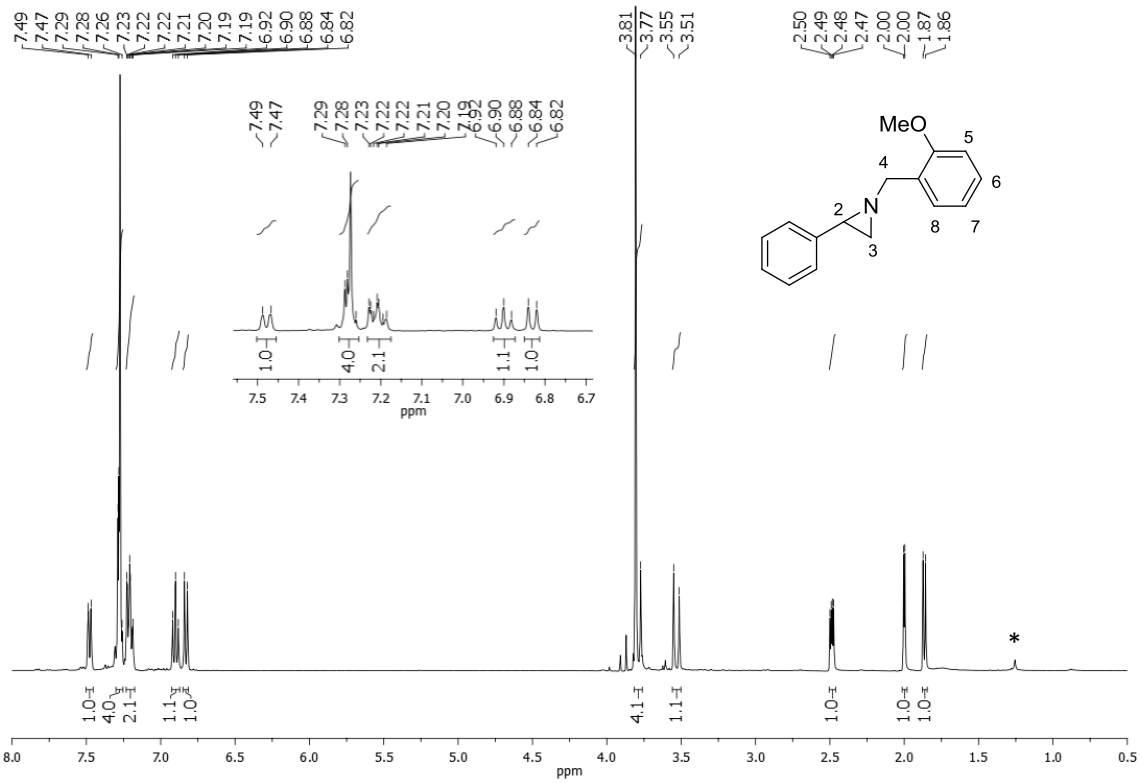
^{19}F NMR spectrum (376 MHz, $CDCl_3$, 298 K) of $Ru(OEP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)



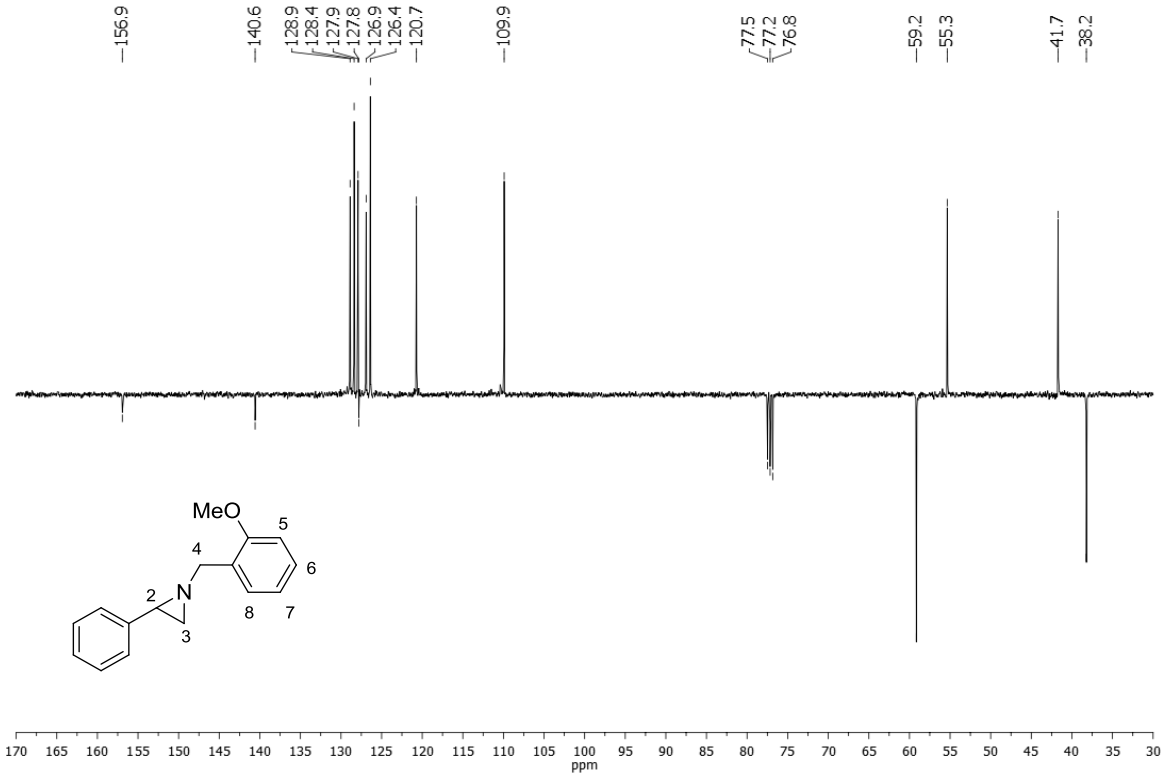
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of $Ru(OEP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)



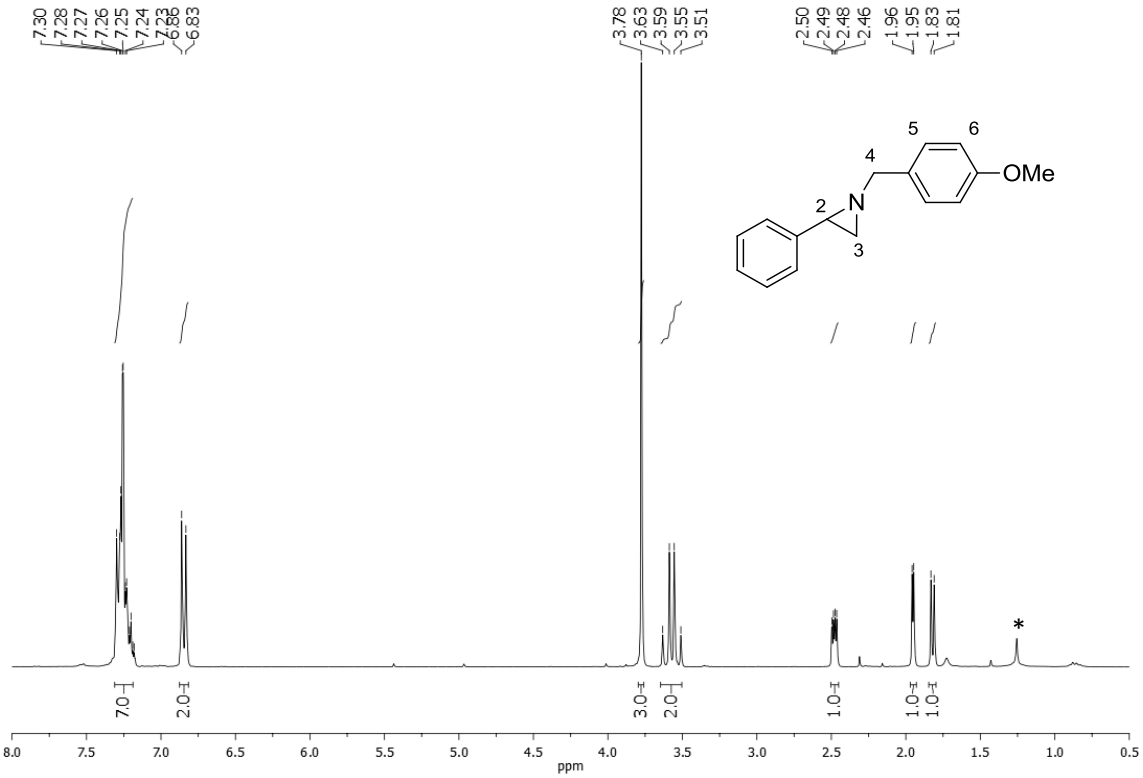
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1-(2-methoxy)benzyl-2-phenylaziridine



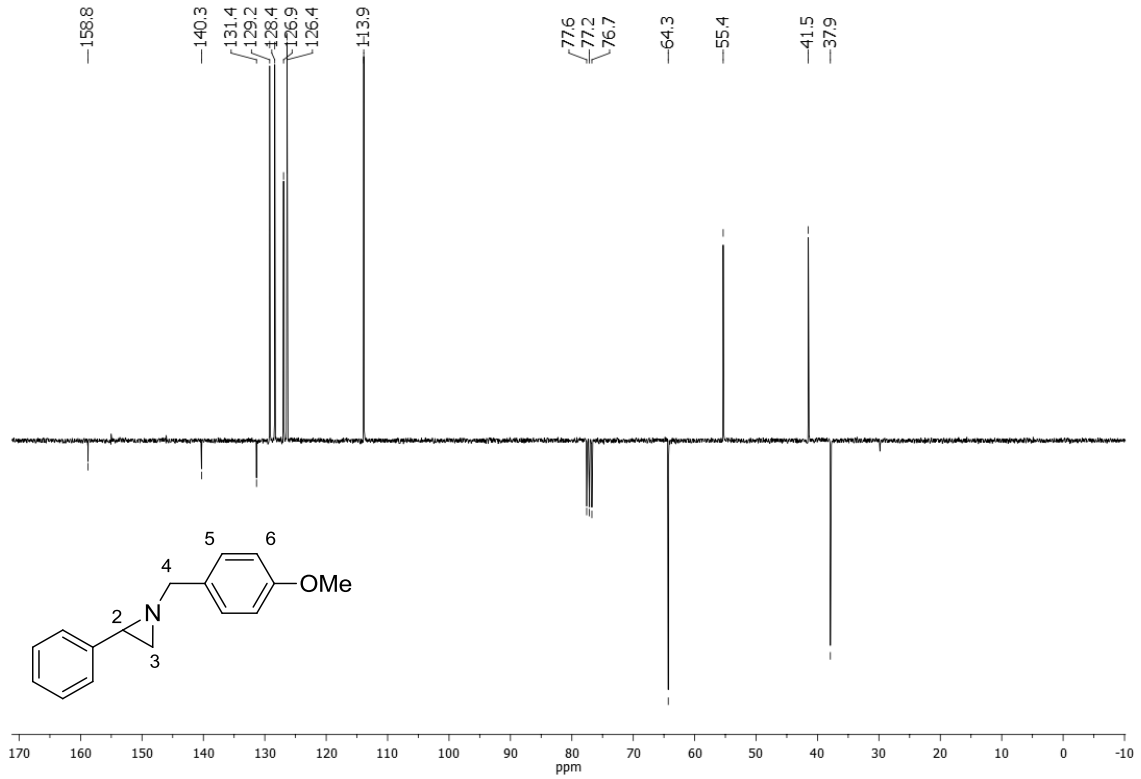
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 1-(2-methoxy)benzyl-2-phenylaziridine



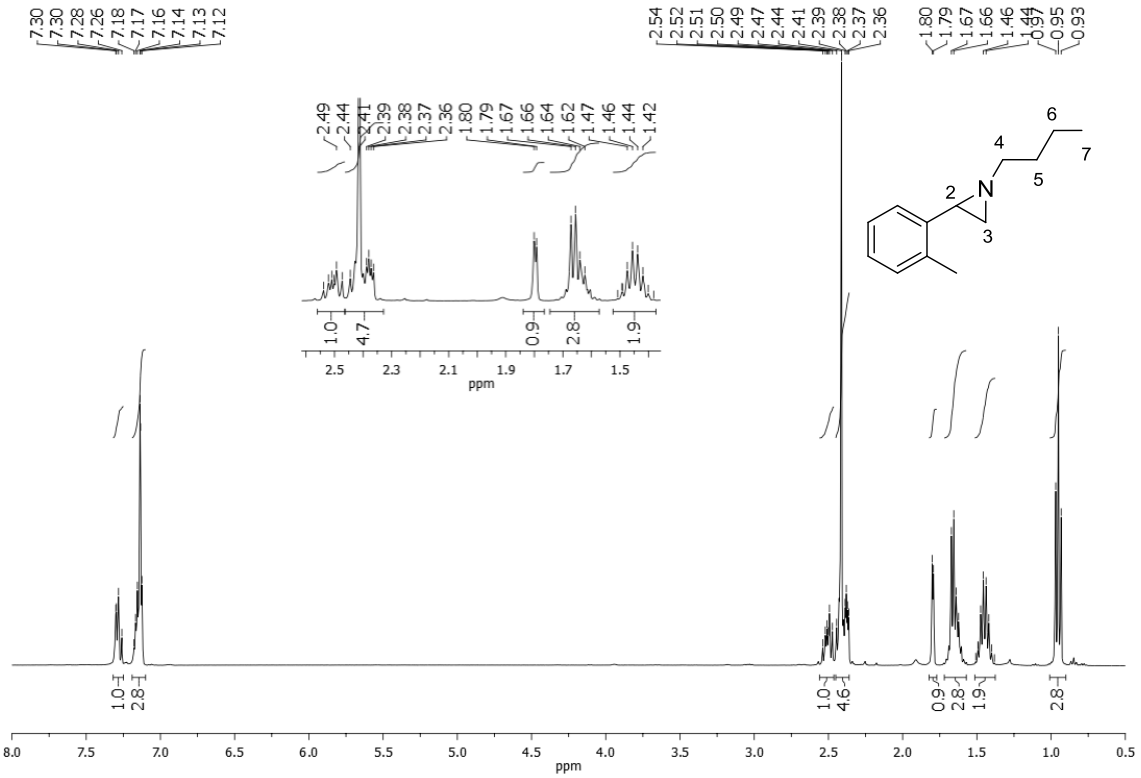
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of 1-(4-methoxy)benzyl-2-phenylaziridine



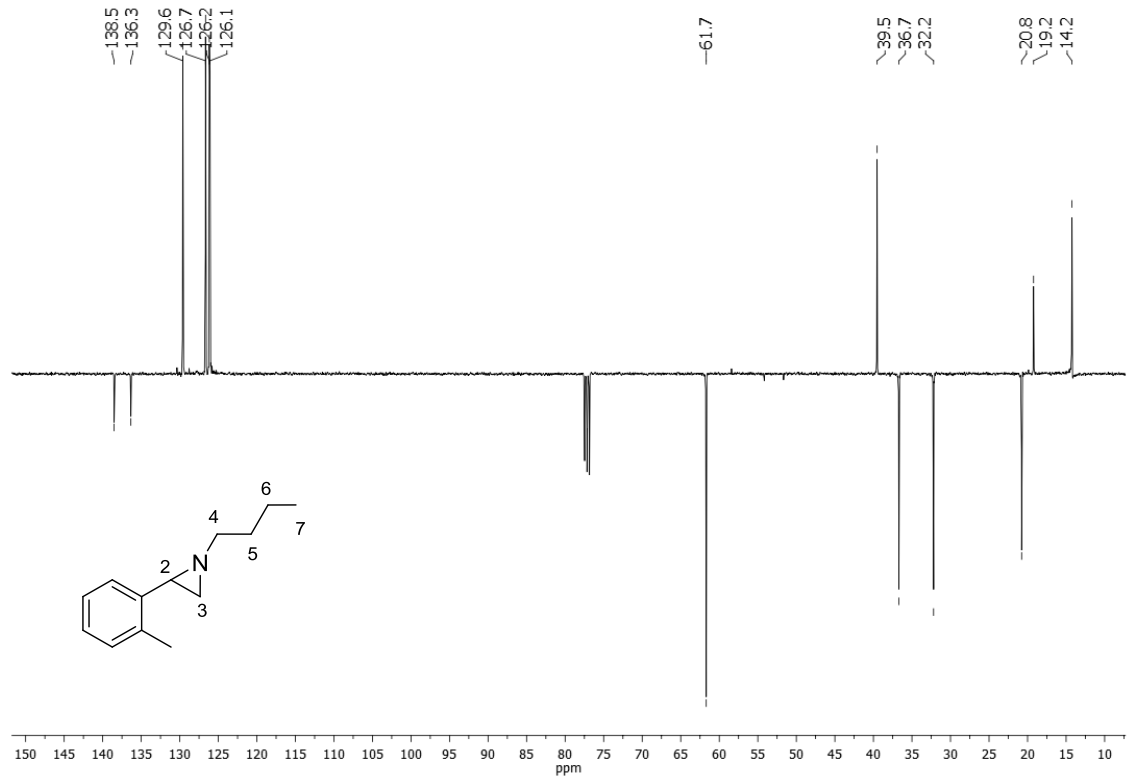
^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of 1-(4-methoxy)benzyl-2-phenylaziridine



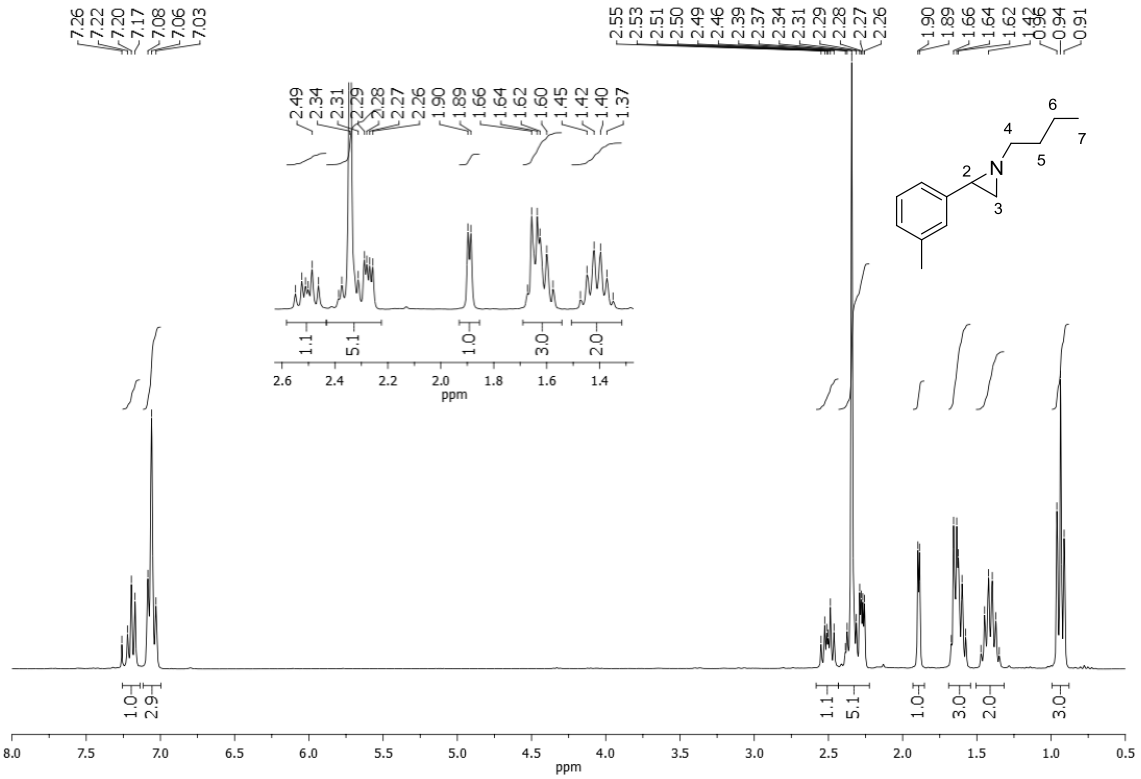
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1-butyl-2-(2-methyl)phenylaziridine



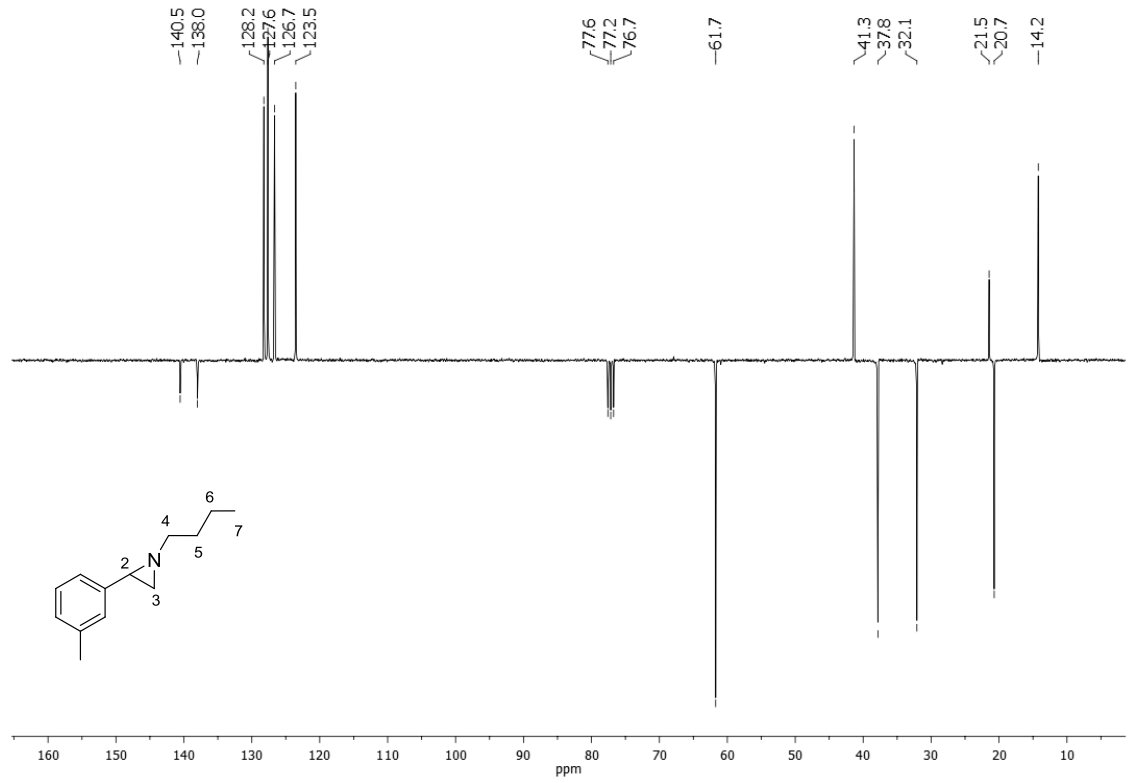
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 1-butyl-2-(2-methyl)phenylaziridine



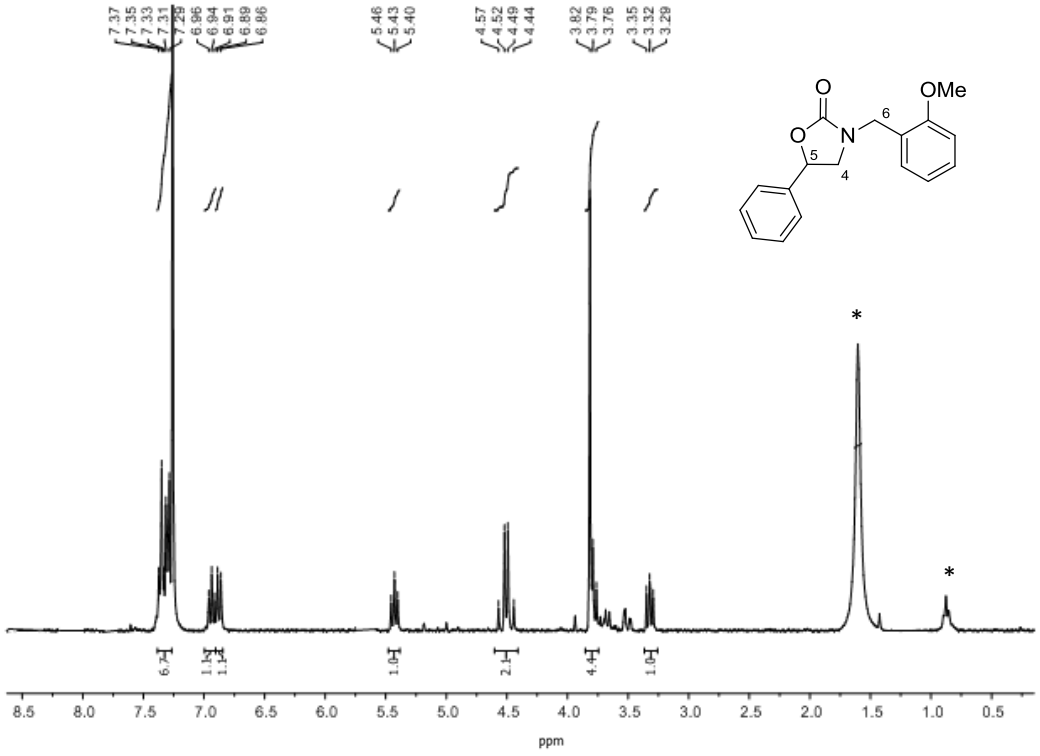
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of 1-butyl-2-(3-methyl)phenylaziridine



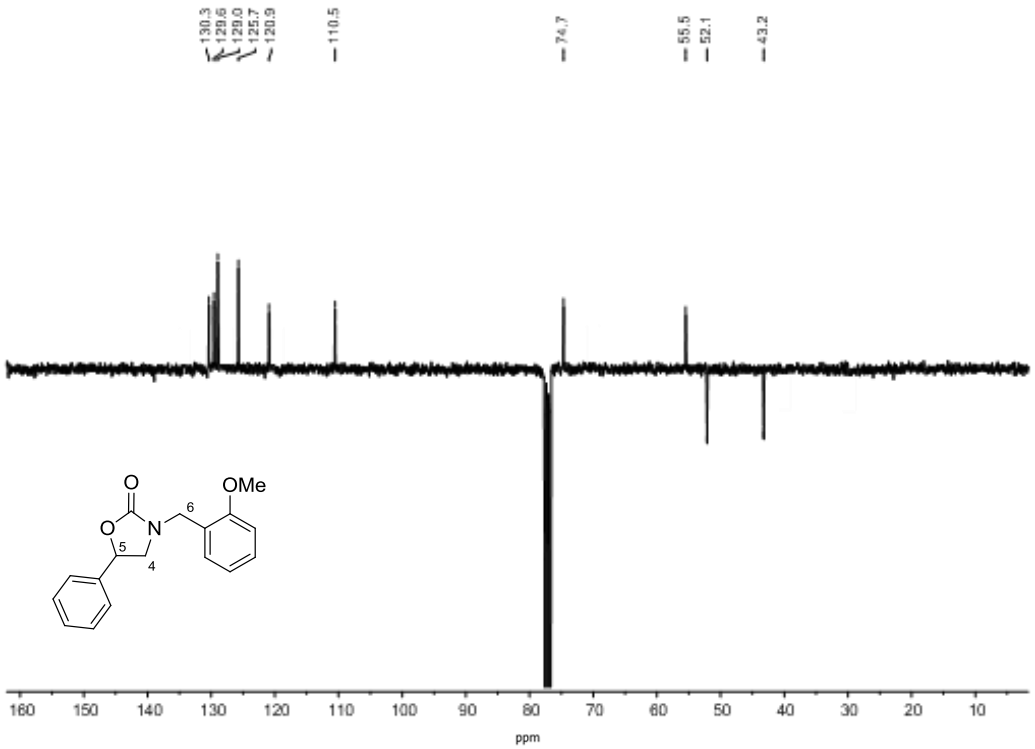
^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of 1-butyl-2-(3-methyl)phenylaziridine



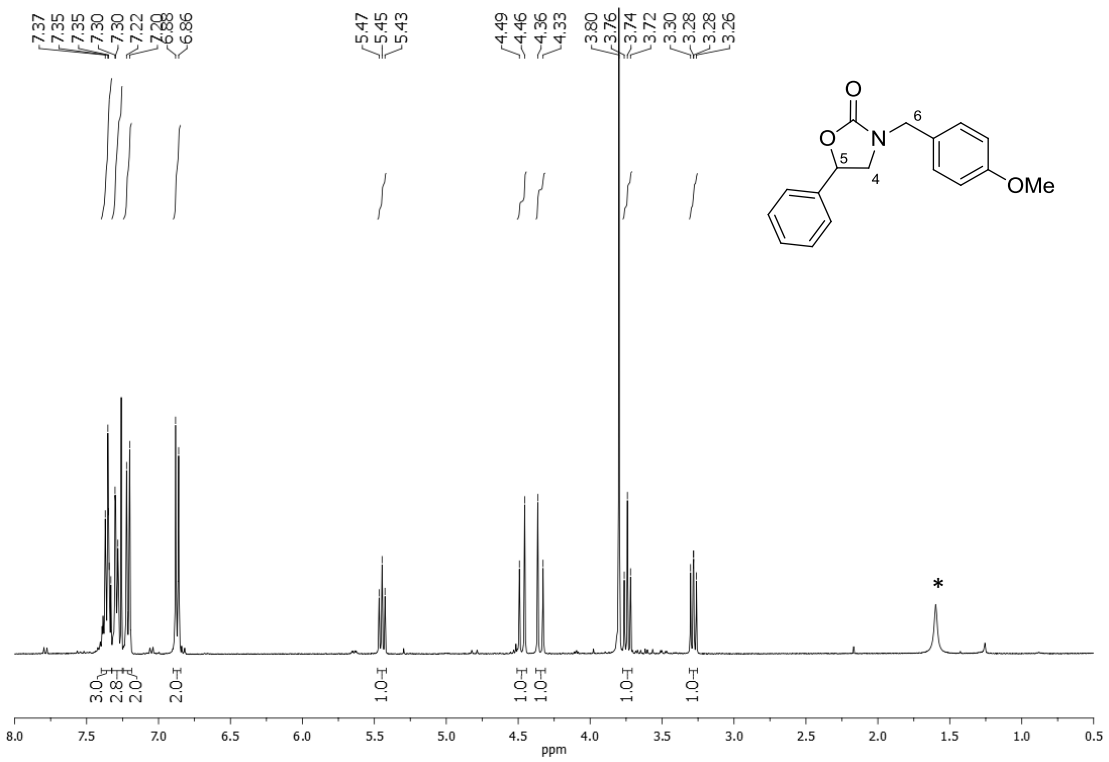
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of 3-(2-Methoxy)benzyl -5-phenyloxazolidin-2-one (11A)



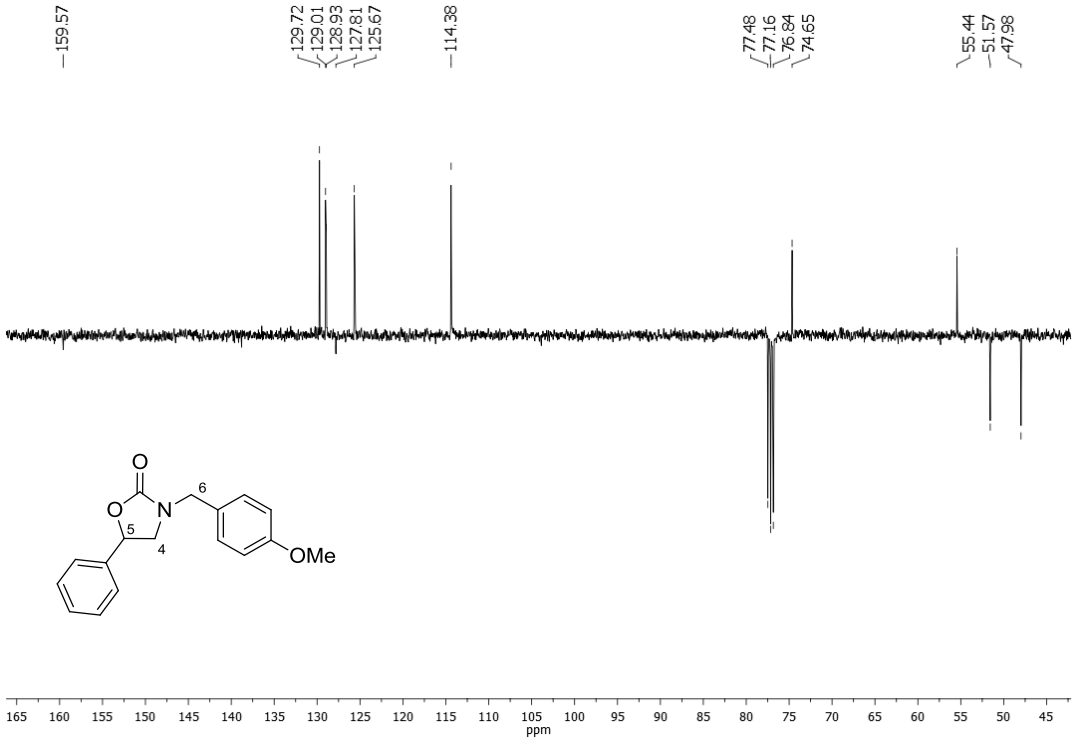
^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of 3-(2-Methoxy)benzyl-5-phenyloxazolidin-2-one (11A)



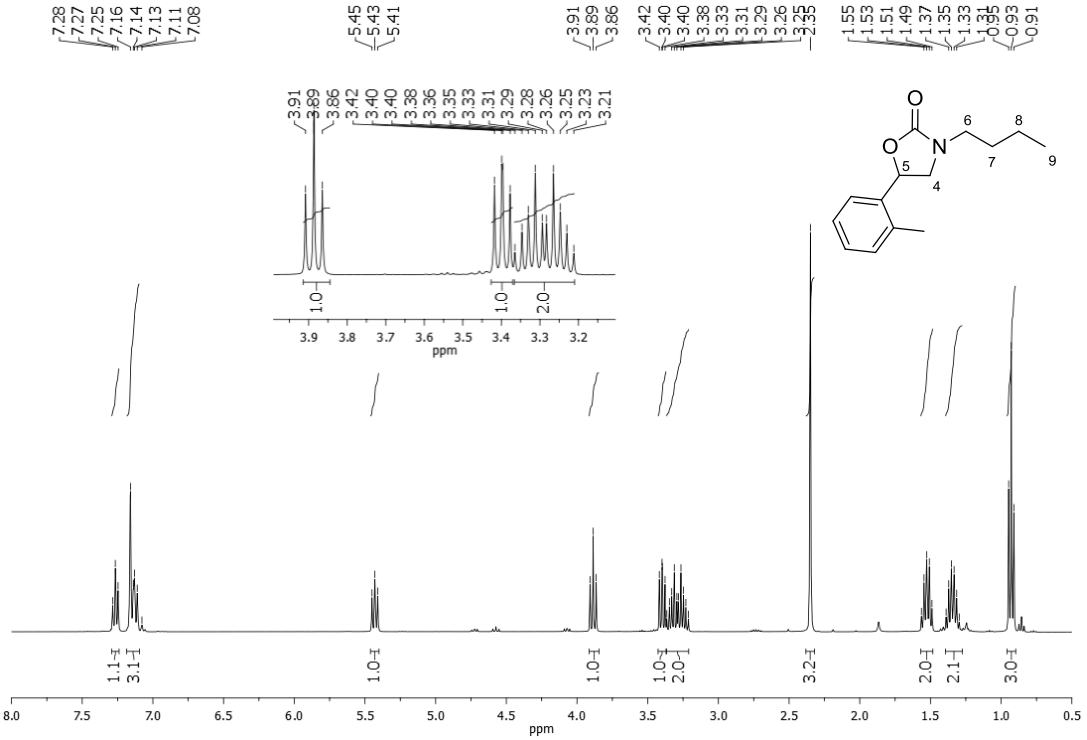
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-(4-methoxy)benzyl-5-phenyloxazolidin-2-one (12A)



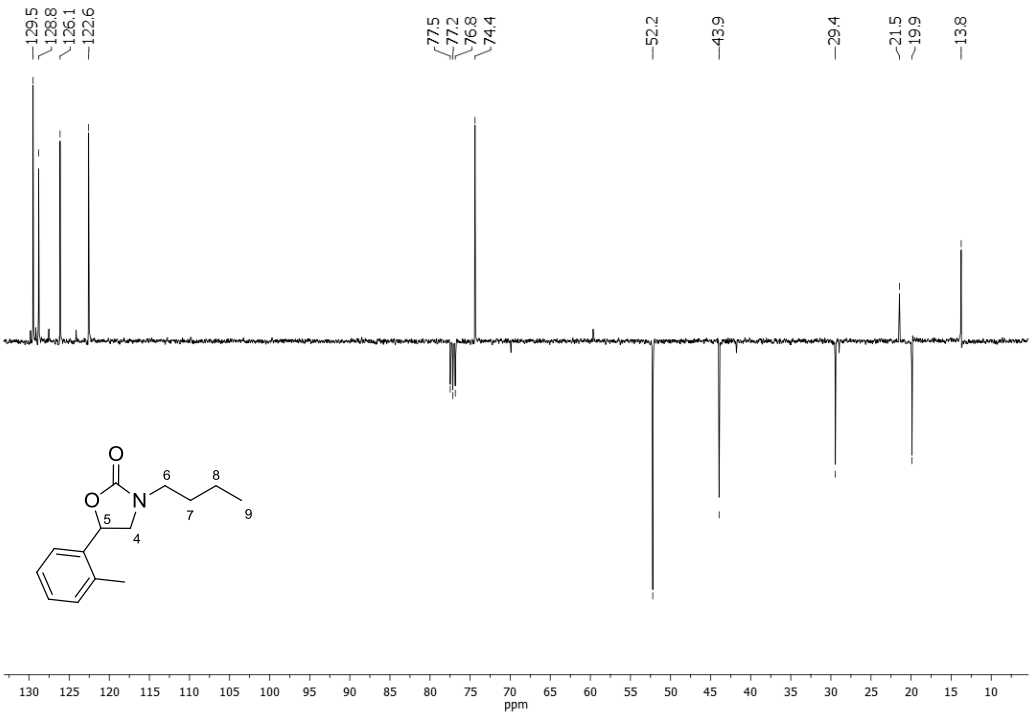
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 3-(4-Methoxy)benzyl-5-phenyloxazolidin-2-one (12A)



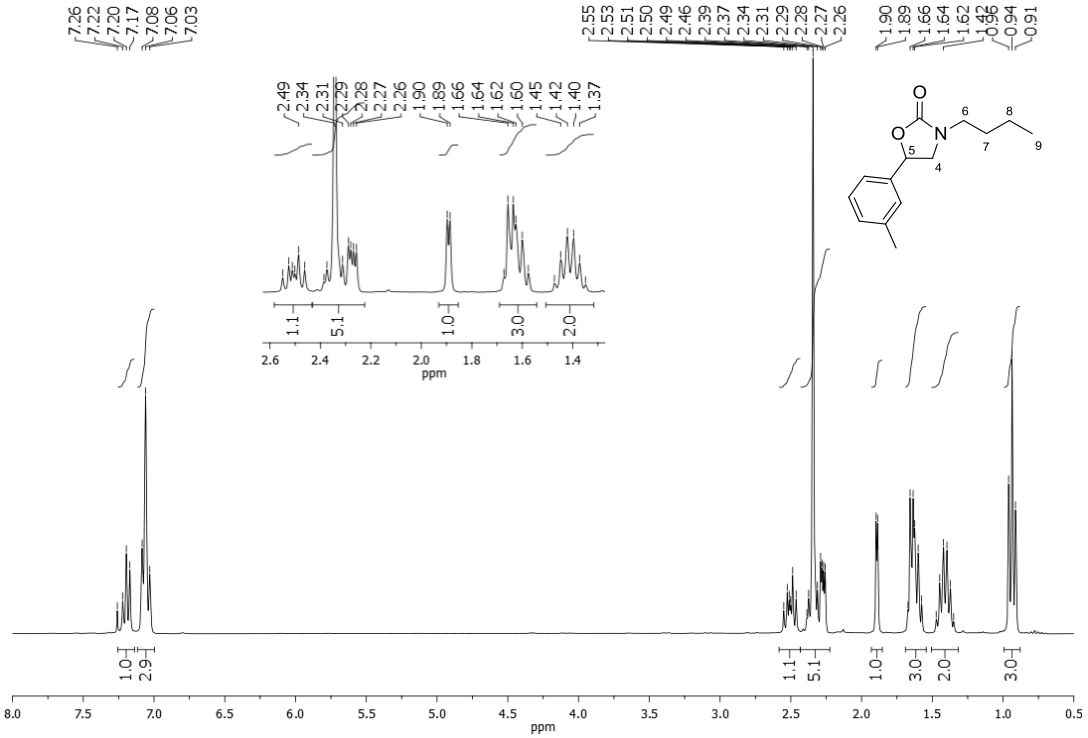
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-Butyl-5-(2-methyl)phenyloxazolidin-2-one (13A)



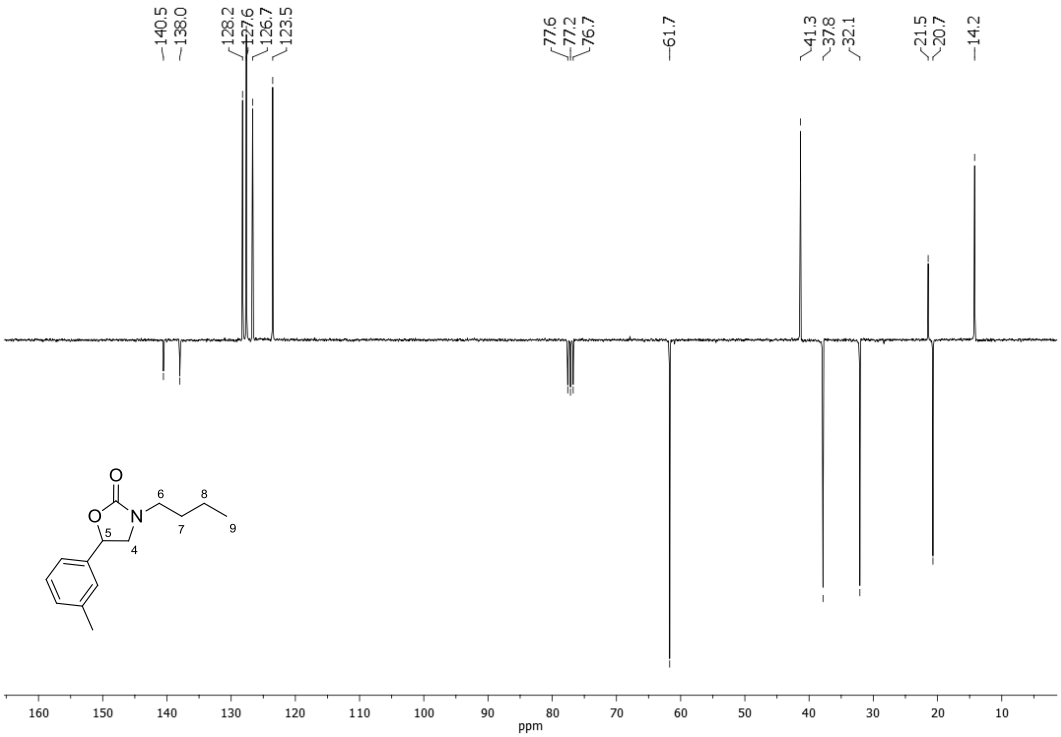
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 3-Butyl-5-(2-methyl)phenyloxazolidin-2-one (13A)



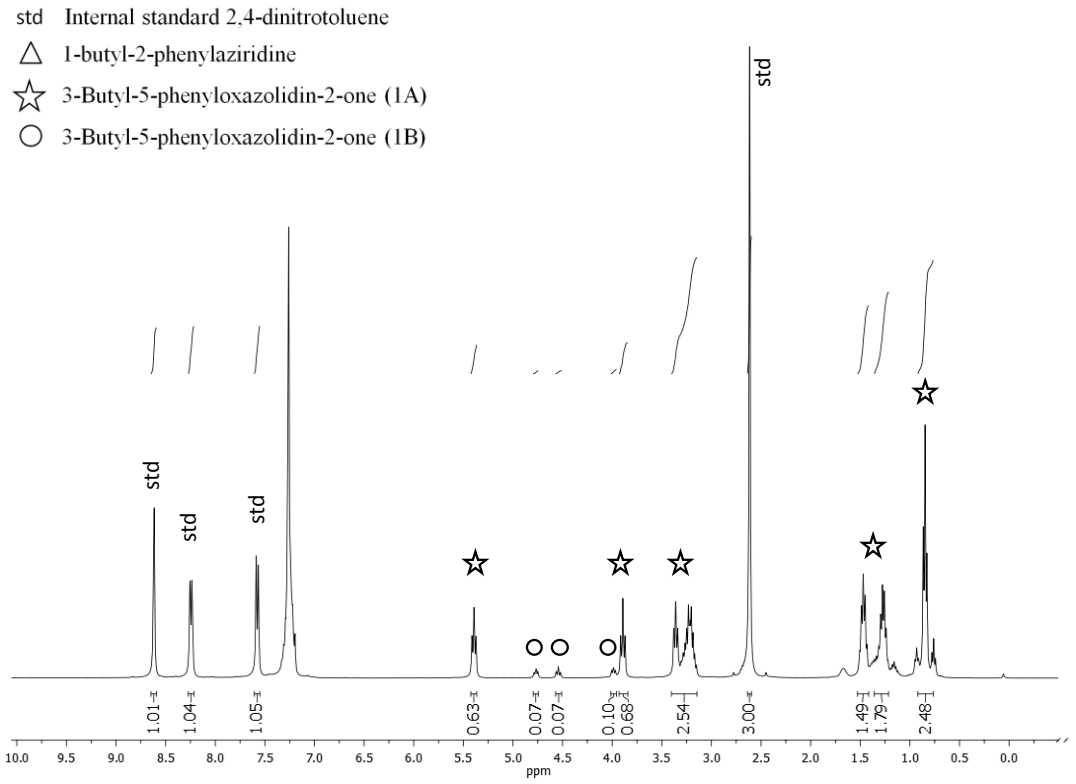
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 3-Butyl-5-(3-methyl)phenyloxazolidin-2-one (14A)



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of 3-Butyl-5-(3-methyl)phenyloxazolidin-2-one (14A)

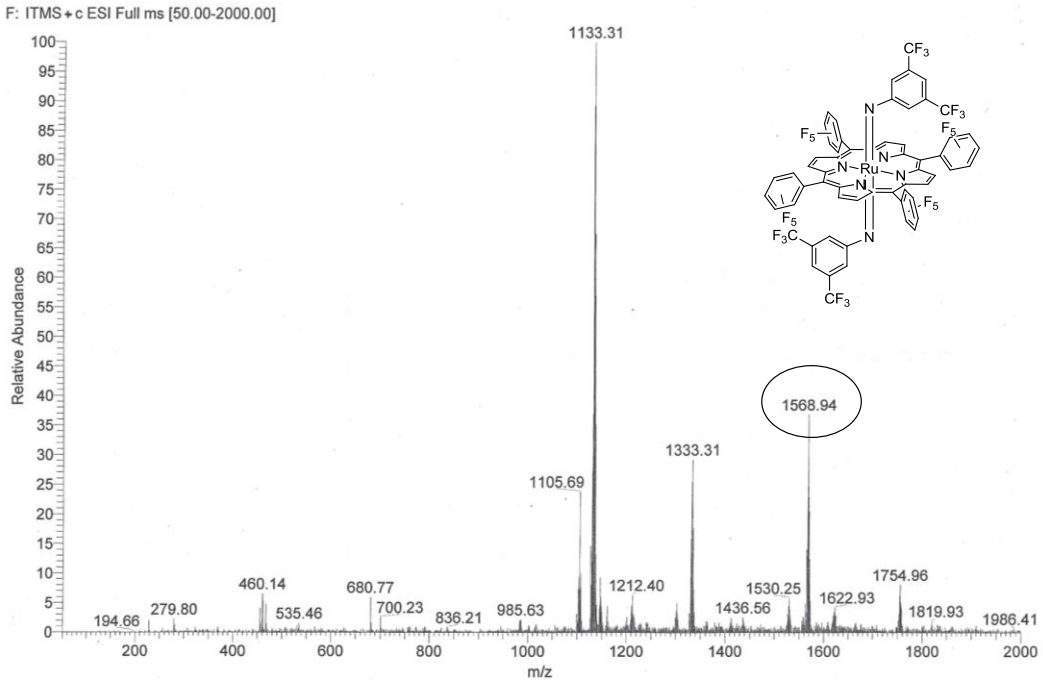


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the recycle of $Ru(TPP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)

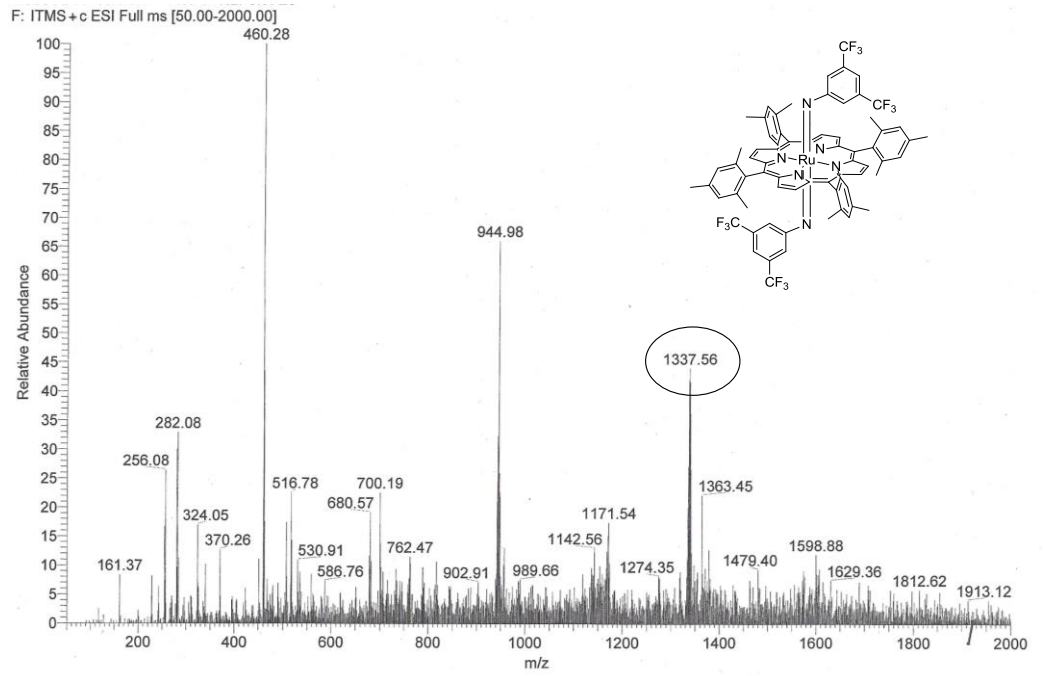


9. ESI-MS spectra of reported compounds

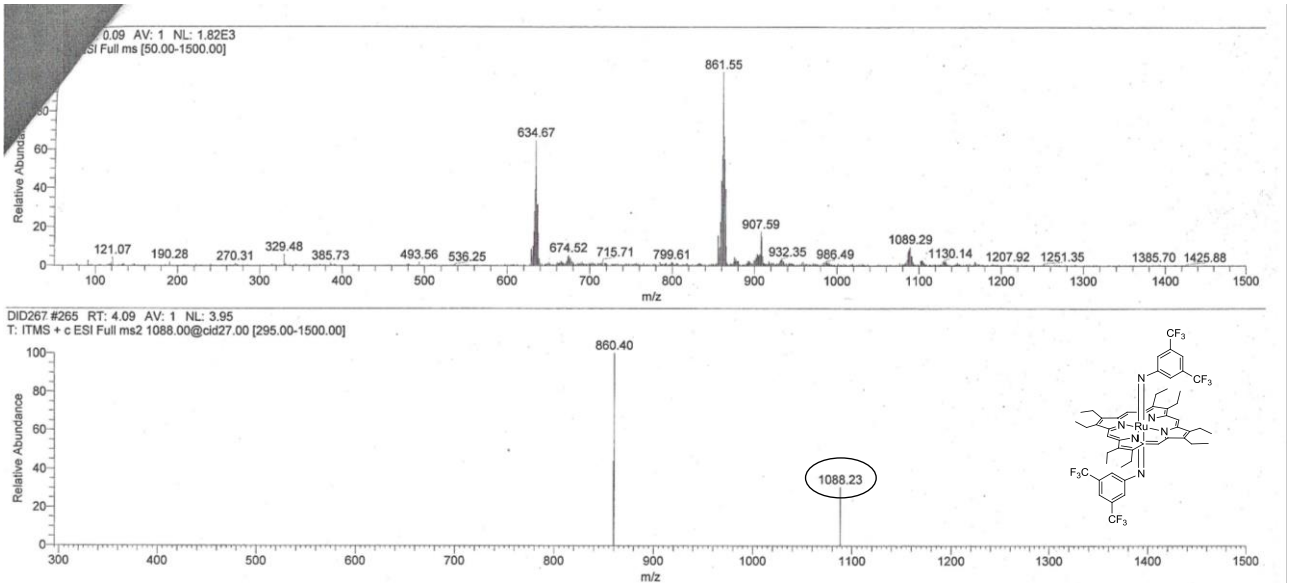
ESI-MS spectrum of $Ru(F_{20}TPP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)



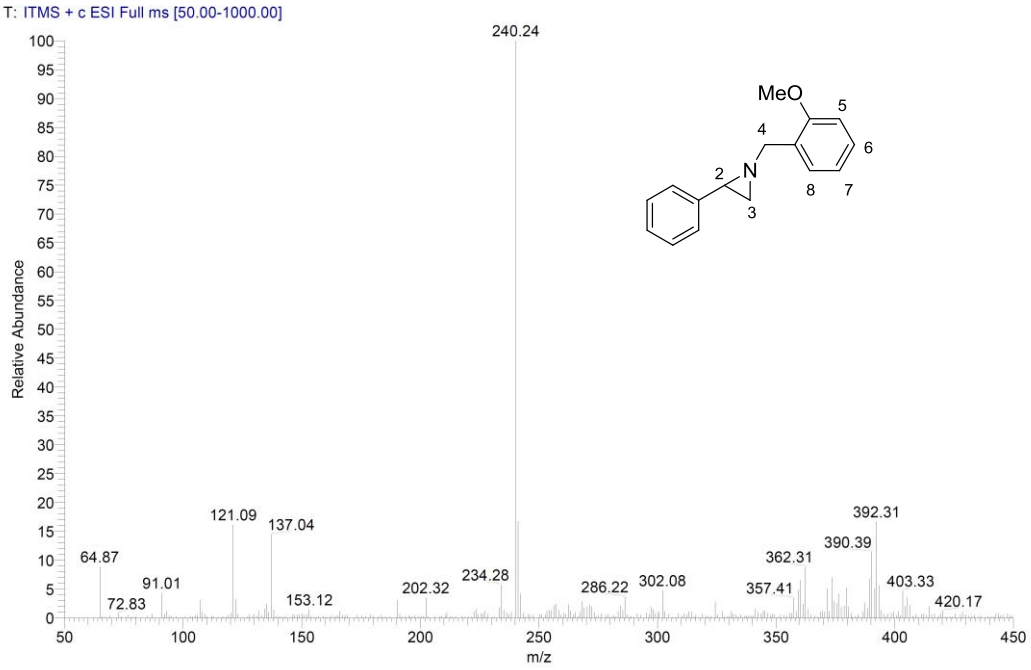
ESI-MS spectrum of $Ru(TMP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)



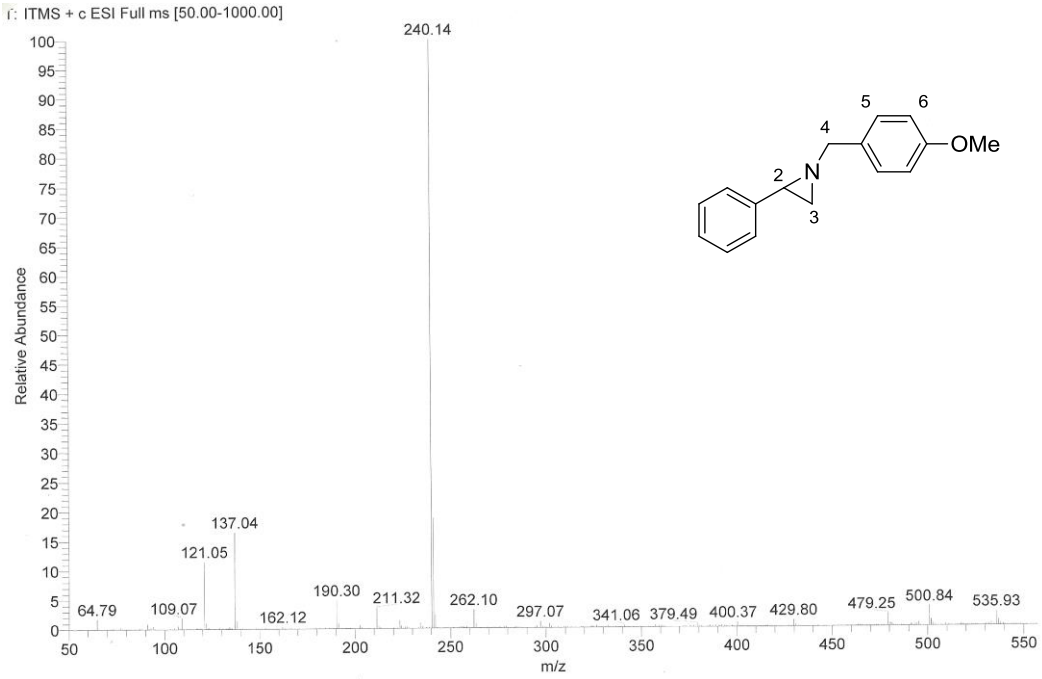
ESI-MS spectrum of $Ru(OEP)(NAr)_2$ (Ar = $3,5(CF_3)_2C_6H_3$)



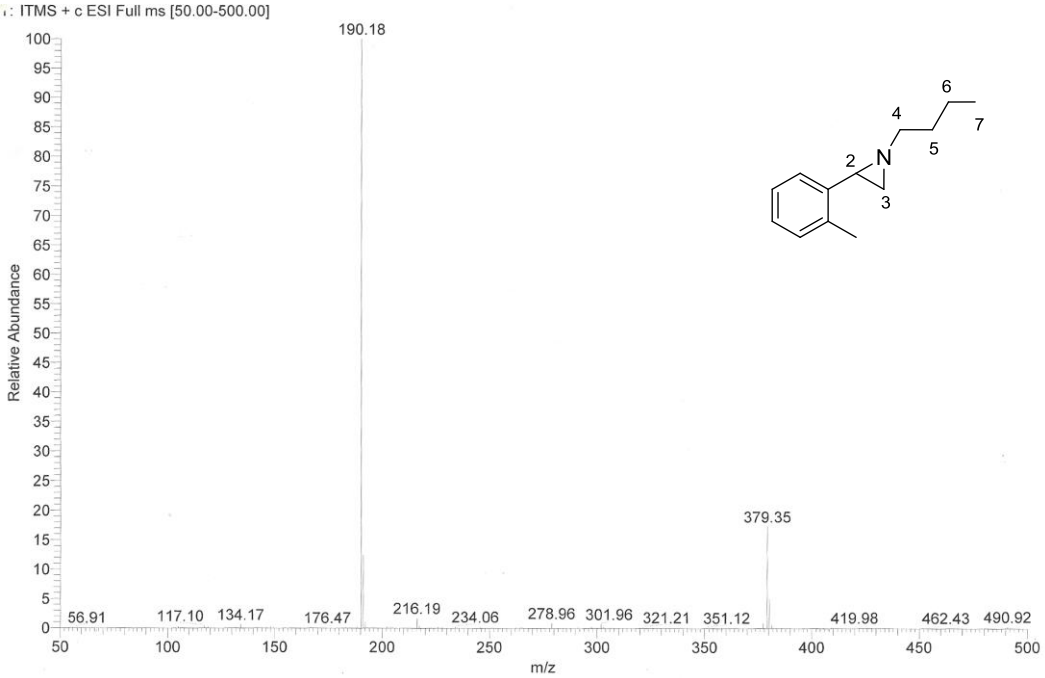
ESI-MS spectrum of 1-(2-methoxy)benzyl-2-phenylaziridine



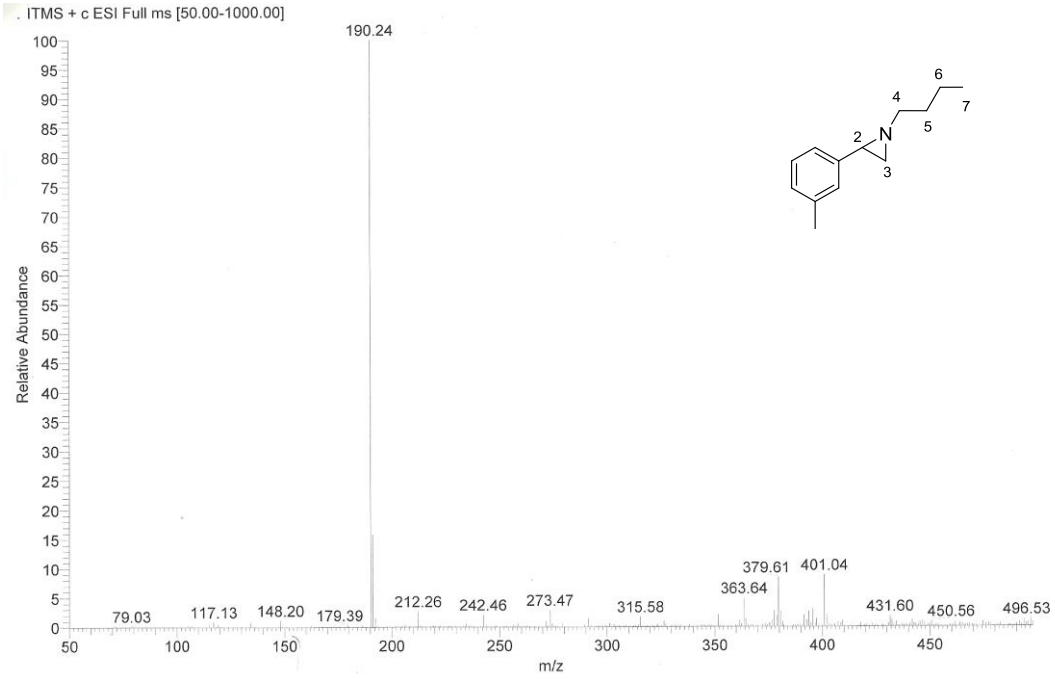
ESI-MS spectrum of 1-(4-methoxy)benzyl-2-phenylaziridine



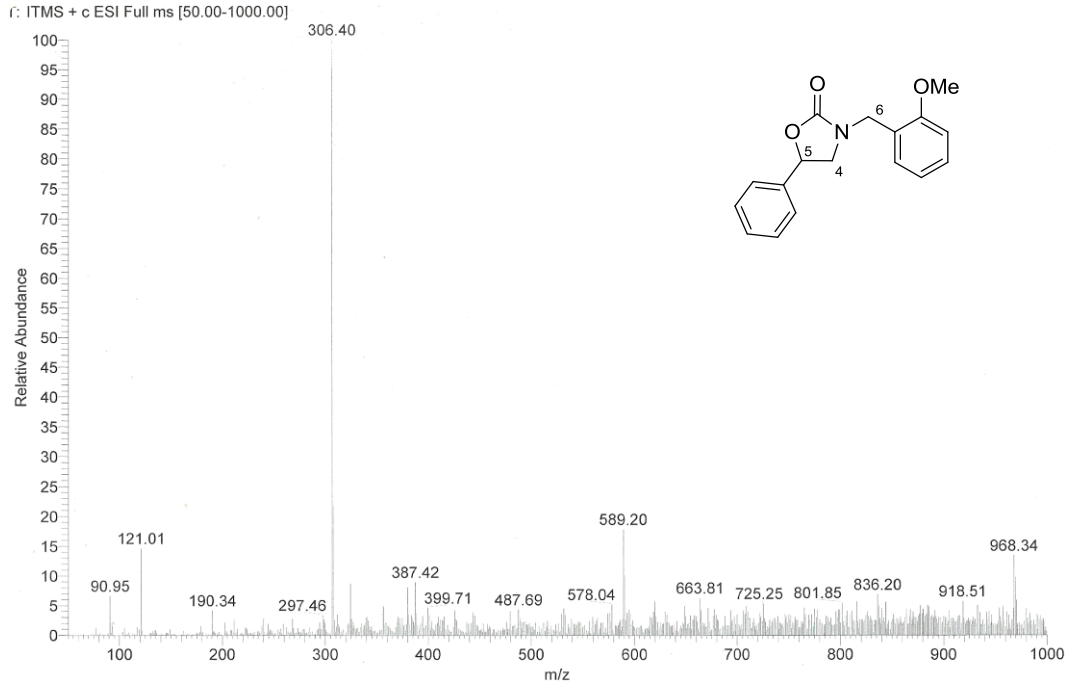
ESI-MS spectrum of 1-butyl-2-(2-methyl)phenylaziridine



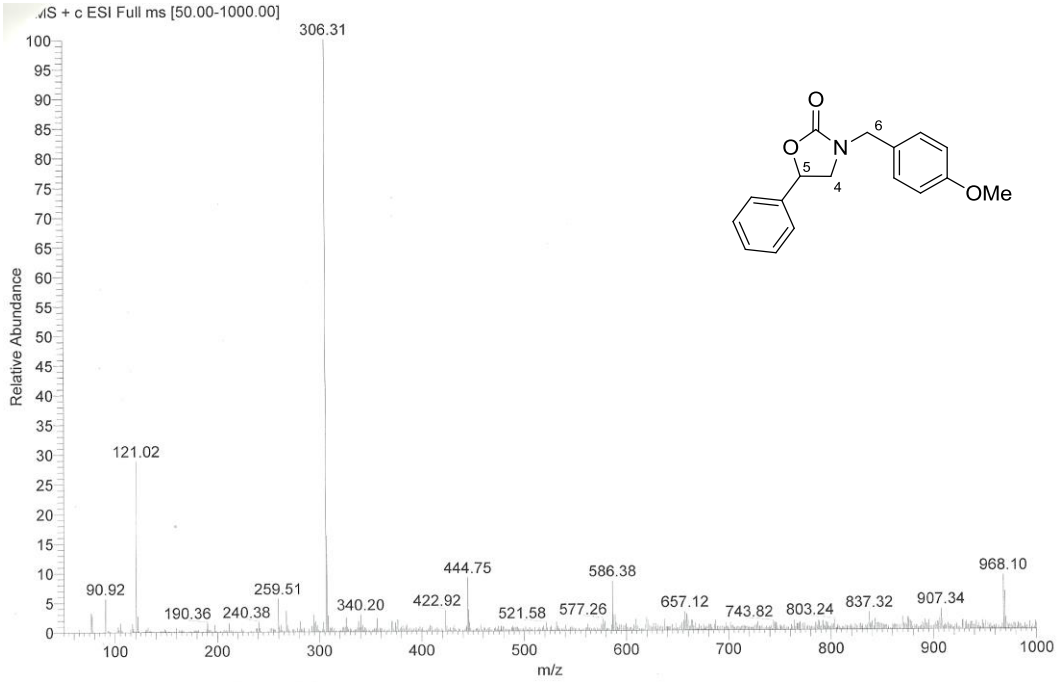
ESI-MS spectrum of 1-butyl-2-(3-methyl)phenylaziridine



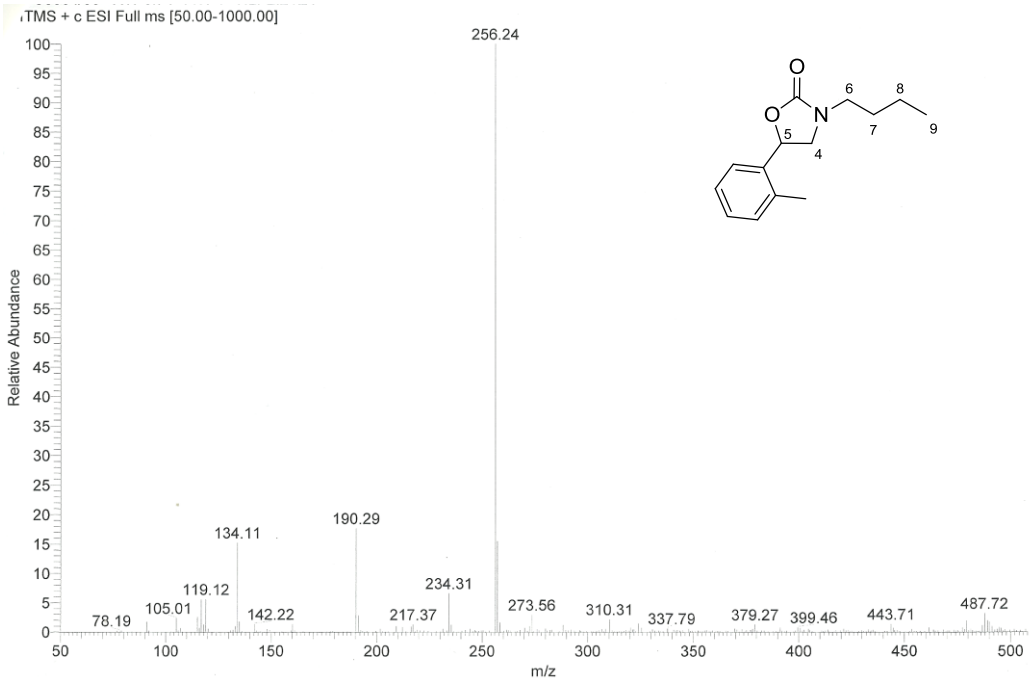
ESI-MS spectrum of 3-(2-Methoxy)benzyl-5-phenyloxazolidin-2-one (11A)



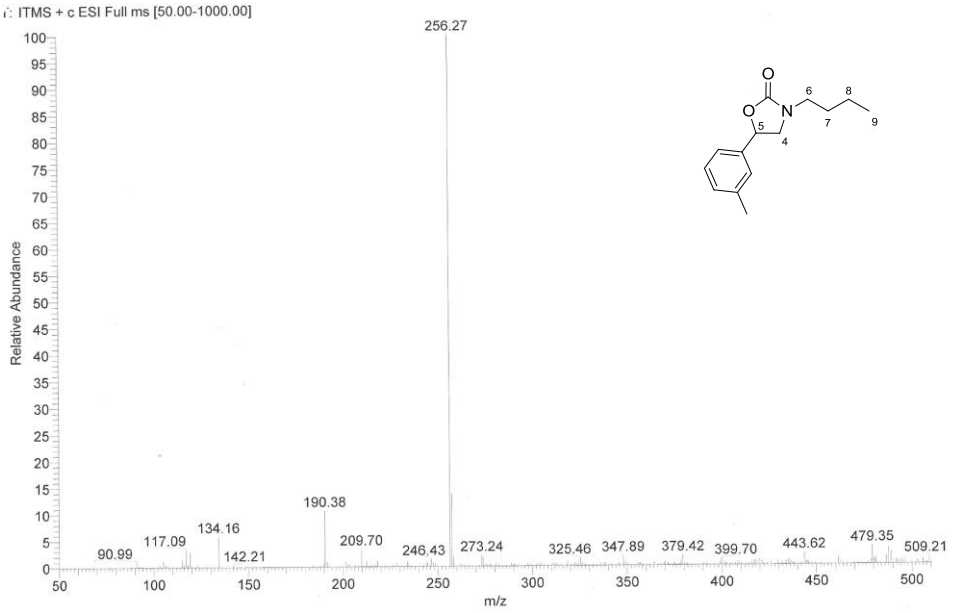
ESI-MS spectrum of 3-(4-Methoxy)benzyl-5-phenyloxazolidin-2-one (12A)



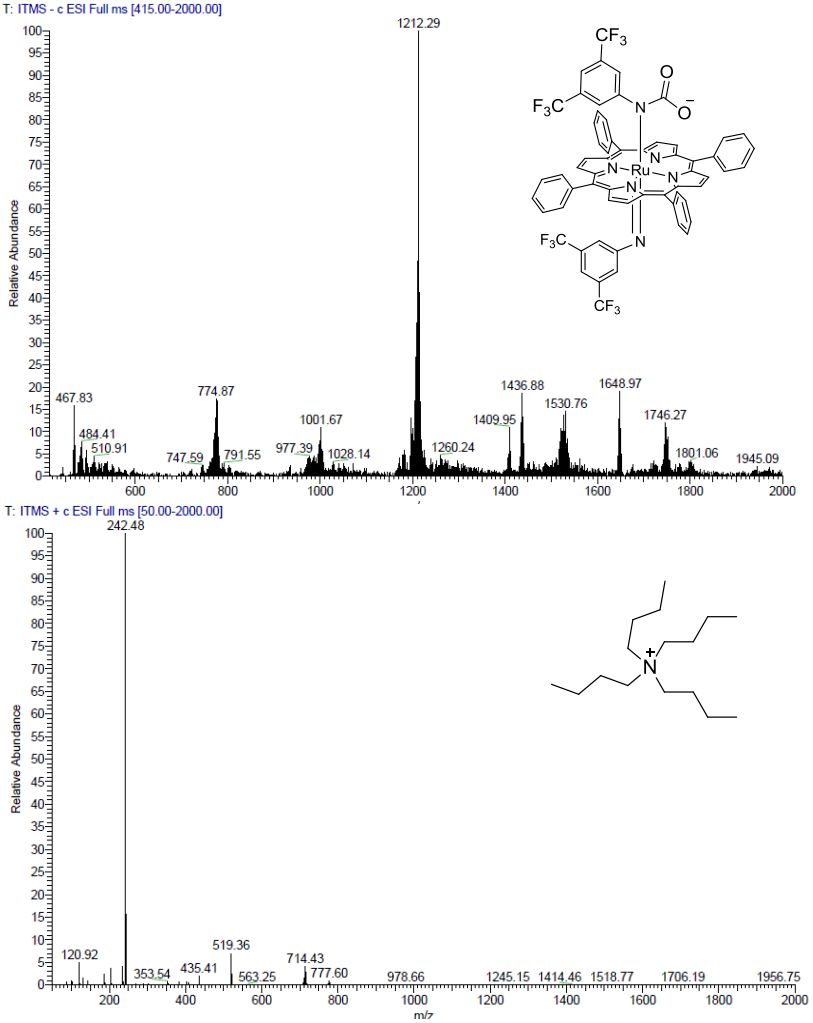
ESI-MS spectrum 3-Butyl-5-(2-methyl)phenyloxazolidin-2-one (13A)



ESI-MS spectrum 3-Butyl-5-(3-methyl)phenyloxazolidin-2-one (14A)



ESI-MS spectrum of the crude containing compound 16



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