Electronic Supplementary Information (ESI)

Synthesis in Mesoreactors:

Ru(porphyrin)CO-Catalyzed Aziridination of Olefins Under Continuous Flow Conditions

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General:

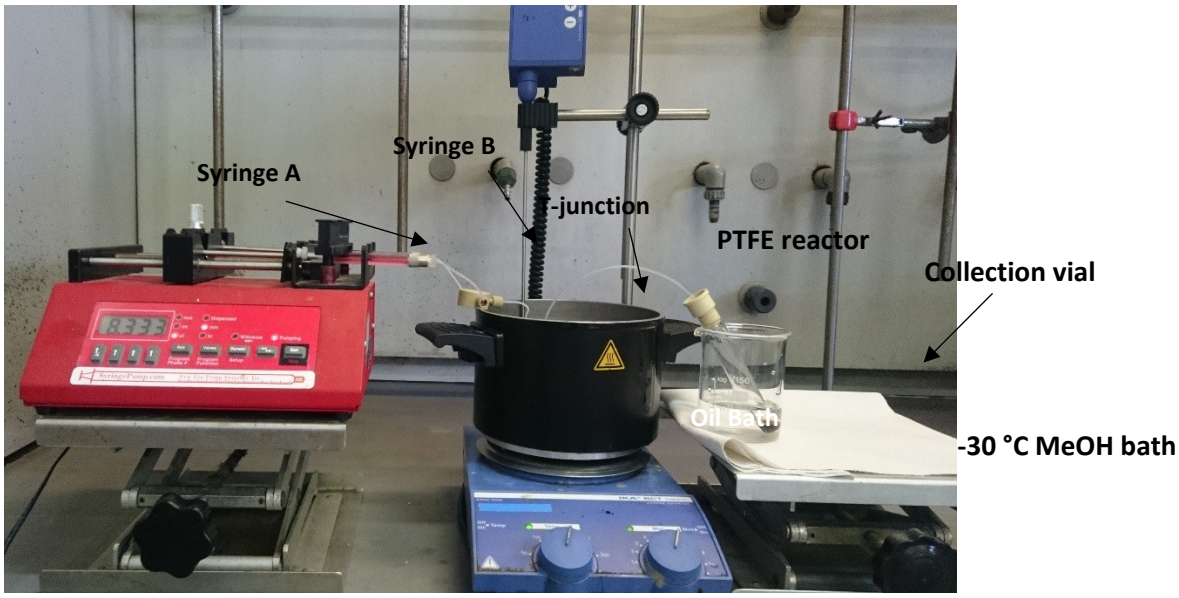
Proton NMR spectra were recorded on spectrometers operating at 300 MHz (Bruker Fourier 300 or AMX 300) or at 500 MHz (Bruker Avance 500). Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$ δ = 7.26 ppm). ^{13}C NMR spectra were recorded operating at 75 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ = 77.0 ppm). ^{19}F NMR spectra were recorded operating at 282 MHz. Fluorine chemical shifts are reported in ppm (δ) relative to CF_3Cl. GC analysis were performed using Agilent 6850 single channel GC system. Mesoreactor was prepared using PTFE tubing for HPLC connections purchased from Supelco inner diameter 0.58 mm, length 1.89 m, total volume 500 µL.

Materials:

Solvents were freshly distilled under CaH_2 prior to use by standard procedures and stored under nitrogen. All starting materials were commercial products and were used as received unless otherwise reported. Aryl azides[1-3] and [Ru(β-Ph_4TPP)(CO)][4] were synthesized according to literature procedure or by using minor modifications of them. The purity of the azides and olefins employed was checked by GC or ^1H NMR analyses.

500 µL Fluidic module:

This module was constructed using a PTFE tubing (1.58 mm outer diameter, 0.58 mm inner diameter, 1.89 m length, 500 µl effective volume) coiled in a bundle and immersed in an oil bath. A New Era NE 300 syringe pumps, equipped with one or two Hamilton gastight syringes, fed the reactant solutions through a T-junction into the above-mentioned PTFE tubing.



General Procedure A for continuous flow synthesis using one feeding syringe (Table 1)

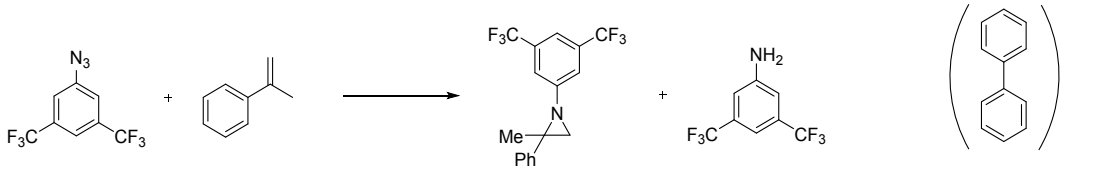
In a typical experiment, a syringe was filled with a mixture obtained dissolving 0.02 eq (0.004 mmol, 3.03 mg) of [Ru(β-Ph_4TPP)(CO)] in 10 ml of the appropriate solvent. The mixture was sonicated for 10 min prior the addition of 1 eq of 3,5-bis(trifluoromethyl)phenyl azide (0.2 mmol, 51.02 mg), 5 eq of α-methylstyrene (1 mmol, 118.1 mg) and 0.075 eq of byphenyl (0.015 mmol, 2.3 mg) as internal standard, in order to have 0.02 M concentration of azide. The syringe was then connected to a syringe pump and the reagents were fed into the PTFE mesoreactor at the desired flow rate (mL/min) and temperature. One reactor volume was discarded before starting sample collection in order to achieve steady-state conditions. Reaction outcome was collected into a vial cooled at - 30 °C and directly analyzed through GC.

The analysis of the residual mixture in the feeding syringe showed 11.4% of product after 24h at RT. The feeding procedure was then modified according to the following procedure.

General Procedure B for continuous flow synthesis using two feeding syringes

In a typical experiment, syringe A was filled with a mixture obtained dissolving 0.02 eq (0.016 mmol, 12.1 mg) of [Ru(β-Ph_4TPP)(CO)] in 2 ml of the desired olefin in order to have 0.008 M concentration of catalyst. The mixture was sonicated for 10 min and heated until a complete dissolution of the catalyst. Syringe B was filled with a mixture obtained dissolving 1 eq of azide (0.8 mmol, 204 mg) and 0.075 eq of byphenyl (0.06 mmol, 9.2 mg) as internal standard in 2 ml of the desired olefin in order to have 0.4 M concentration of azide. (note: the concentrations of all reagents in the syringes were doubled with respect to the final concentration, to achieve the desired concentration after mixing). Syringes A and B were connected to a syringe pump and the reagents were pumped into PTFE mesoreactor through a T-junction at the desired flow rate (μL/min) at the desired temperature. One reactor volume was discarded before starting sample collection in order to achieve steady-state conditions. Reaction outcome was collected into a vial cooled at - 30 °C and directly analyzed through GC or ^{1}H NMR.

GC Calibration curve1



Three mixtures containing different amount of reactants dissolved in 2 ml of benzene were prepared as follows:

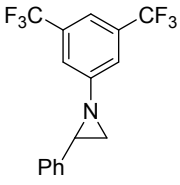
- **Mixture A**: 0.018 mmol of IS, 0.031 mmol of aziridine, 0.254 mmol of azide, 0.064 mmol amine.
- **Mixture B**: 0.039 mmol of IS, 0.137 mmol of aziridine, 0.141 mmol of azide, 0.128 mmol amine.
- **Mixture C**: 0.021 mmol of IS, 0.229 mmol of aziridine, 0.040 mmol of azide, 0.256 mmol amine.

The response factor was determined as the main value of 15 injections (3 mixture x 5 time each).

GC Conditions: Helium was used as GC carrier gas and maintained at a constant flow rate of 1.6 mL/min (9.51 psi). Column HP-1. The programmable temperature gradient was optimized as follows: the capillary column was ramped from the initial temperature to 100 °C, held for 5 min, increased at 15 °C/min up to 250 °C, where it was held for 1 min. The total duration of GC analysis was 16 min, t_1 = 2.873 min (3,5-bis(trifluoromethyl)phenyl azide), t_2 = 4.451 min (3,5-bis(trifluoromethyl)aniline) t_3 = 9.546 (byphenyl), t_4 = 12.350 min (*N*-(3,5-bis(trifluoromethyl)phenyl)-2-methyl-2-phenylaziridine).

R_f (aziridine) = 1.398 (std = 0.049), R_f (azide) = 0.525 (std = 0.017), R_f (amine) = 0.636 (std = 0.033)

GC Calibration curve2



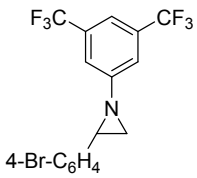
4-ba

Three mixtures containing different amount of aziridine dissolved in 2 ml of benzene were prepared according to GC calibration curve1. The response factor was determined as the main value of 15 injections (3 mixture x 5 time each).

GC Conditions: Helium was used as GC carrier gas and maintained at a constant flow rate of 1.6 mL/min (9.51 psi). Column HP-1. The programmable temperature gradient was optimized as follows: the capillary column was ramped from the initial temperature to 100 °C, held for 5 min, increased at 15 °C/min up to 250 °C, where it was held for 1 min. The total duration of GC analysis was 16 min, t_1 = 2.873 min (3,5-bis(trifluoromethyl)phenyl azide), t_2 = 4.451 min (3,5-bis(trifluoromethyl)aniline) t_3 = 9.546 (byphenyl), t_4 = 12.112 min (*N*-(3,5-bis(trifluoromethyl)phenyl)-2-phenylaziridine).

R_f (aziridine) = 1.089 (std = 0.037)

GC Calibration curve3



4-ca

Three mixtures containing different amount of reactants dissolved in 2 ml of benzene were prepared according to GC calibration curve1. The response factor was determined as the main value of 15 injections (3 mixture x 5 time each).

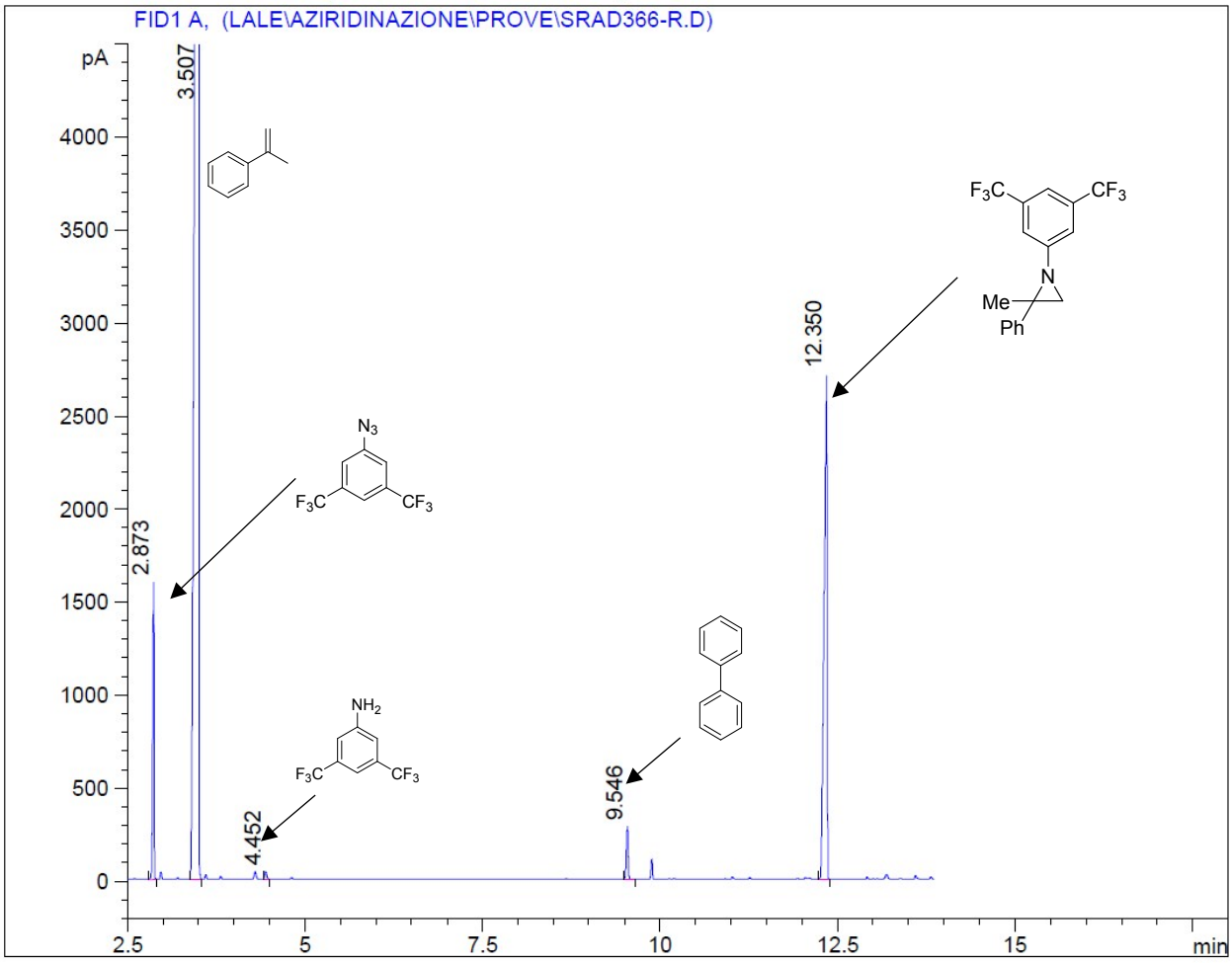
GC Conditions: Helium was used as GC carrier gas and maintained at a constant flow rate of 1.6 mL/min (9.51 psi). Column HP-1. The programmable temperature gradient was optimized as follows: the capillary column was ramped from the initial temperature to 100 °C, held for 5 min, increased at 15 °C/min up to 250 °C, where it was held for 1 min. The total duration of GC analysis was 16 min, t_1 = 2.873 min (3,5-bis(trifluoromethyl)phenyl azide), t_2 = 4.451 min (3,5-bis(trifluoromethyl)aniline) t_3 = 9.546 (byphenyl), t_4 = 14.593 min (*N*-(3,5-bis(trifluoromethyl)phenyl)-2-((4-bromo)-phenyl)aziridine).

R_f (aziridine) = 1.401 (std = 0.087)

GC chromatogram of entry 4, table 1 **-** *N-(3,5-bis(trifluoromethyl)phenyl)-2-methyl-2-phenylaziridine* (4aa)

(0.2 M of **1a** in benzene at 90 °C for 30 min. **4aa** yield = 51.7%).

SRAD 366 S (0.2 M in substrate)
90°C, 500 uL, 30 min
HP-1 column, 100°C per 5 minuti, rampa 15°C/min fino a ->



Signal 1: FID1 A,

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	2.873	MM	0.024	2269.270	4.988	
2	3.507	MM	0.056	34826.848	76.552	
3	4.452	MM	0.034	82.090	0.180	
4	9.546	VV	0.029	517.403	1.137	
5	12.350	VV	0.040	7798.875	17.142	

GC chromatogram of entry 10, table 2 *- N-(3,5-bis(trifluoromethyl)phenyl)-2-methyl-2-phenylaziridine* (4aa)

(0.2 M of **1a** in α-Me-styrene at 120 °C for 30 min. **4aa** yield = 98.0%).

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SRAD 371 d2 (0.2 M in substrate, a-Me-styrene as solven
t) pre-heat
double syringe 500 uL, 120°C 30 min                    ->
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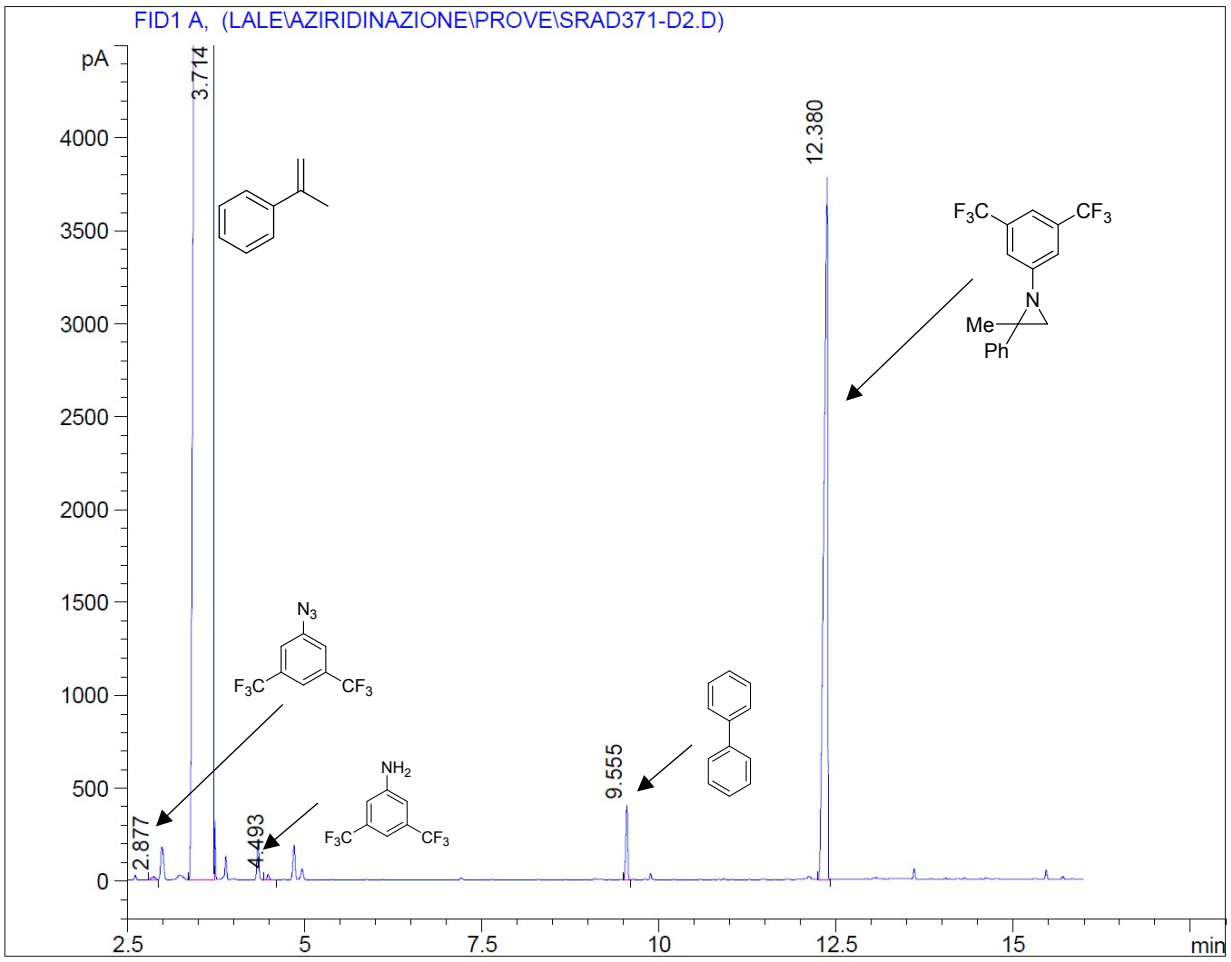


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Signal  1: FID1 A,
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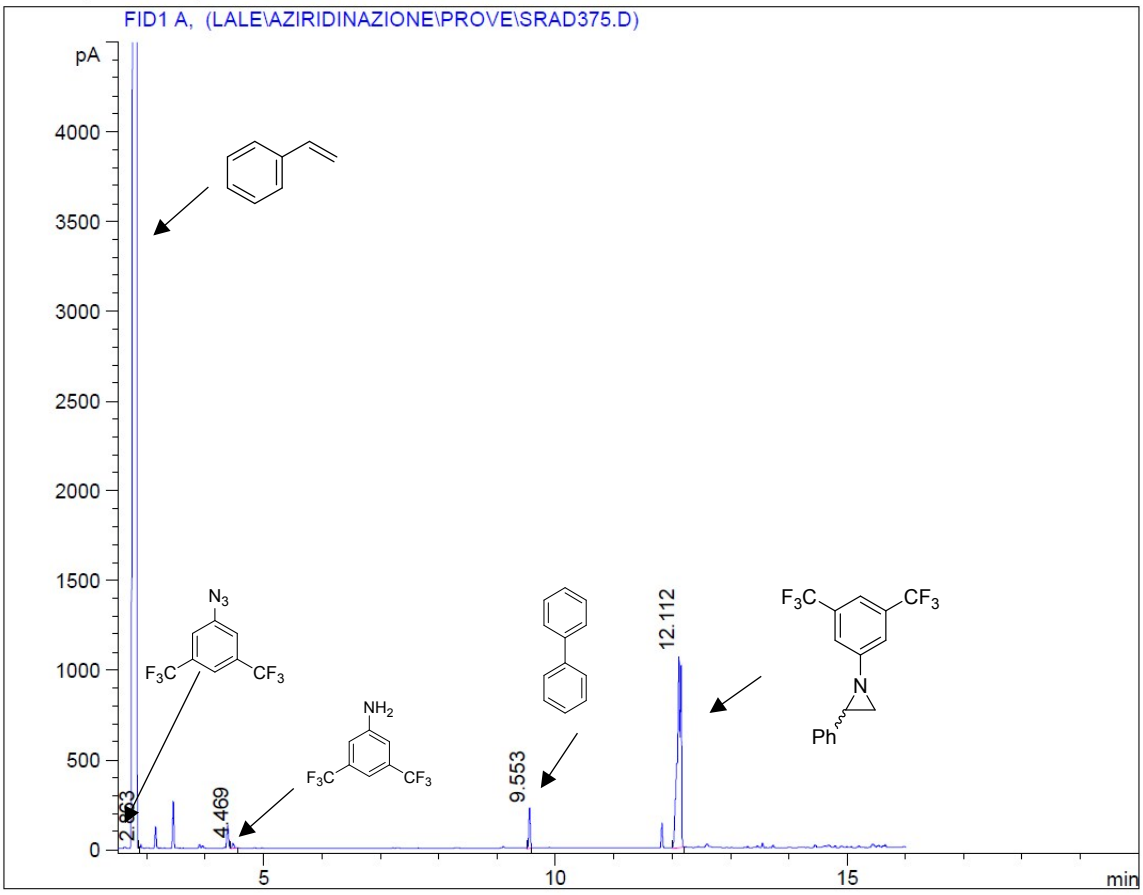
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	2.877	VV	0.051	60.274	0.018	
2	3.714	VV	0.121	315081.313	95.528	
3	4.493	VB	0.032	55.840	0.017	
4	9.555	VV	0.029	742.012	0.225	
5	12.380	VV	0.051	13893.545	4.212	

GC chromatogram of entry 2, table 4 **-** *N-(3,5-bis(trifluoromethyl)phenyl)-2-phenylaziridine* (4ba)

(0.2 M of **1a** in styrene at 120 °C for 30 min. **6a** yield = 90.1%).

SRAD 375
HP-1 column, 100°C per 5 minuti, rampa 15°C/min fino a
250°C, 9.51 psi ->



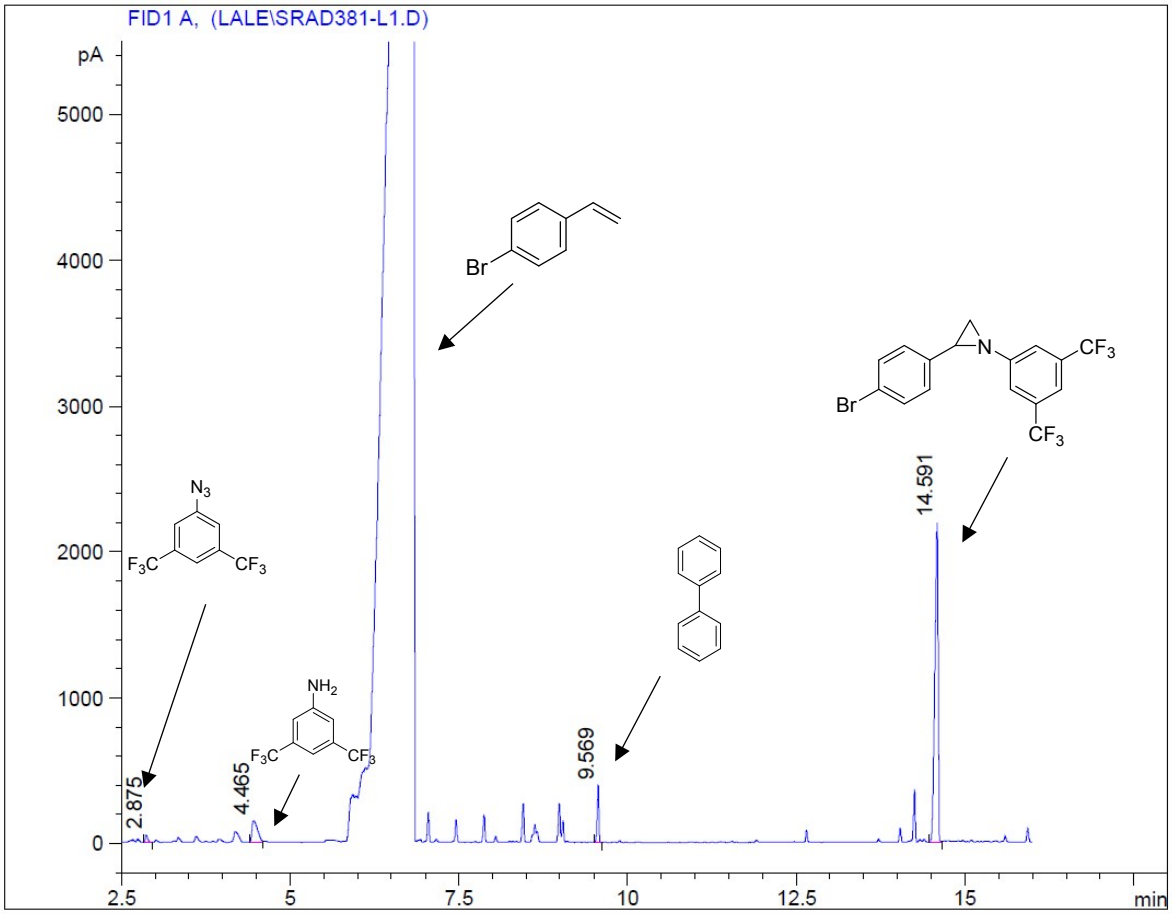
Signal 1: FID1 A,

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	2.863	MM	0.013	3.227	0.060	
2	4.469	MM	0.038	58.240	1.090	
3	9.553	MM	0.030	406.279	7.602	
4	12.112	MM	0.076	4876.715	91.248	

GC chromatogram of entry 3, table 4 **-** *N-(3,5-bis(trifluoromethyl)phenyl)-2-(4-bromophenyl)aziridine* (4-ca)

(0.2 M of **1a** in 4-Bromostyrene at 120 °C for 30 min. **6b** yield = 61.9%).

SRAD 381 L1
HP-1 column, 100°C per 5 minuti, rampa 15°C/min fino a
250°C, 9.51 psi ->



Signal 1: FID1 A,

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	2.875	VV	0.040	129.026	1.436	
2	4.465	MF	0.097	870.674	9.689	
3	9.569	VV	0.027	677.959	7.545	
4	14.591	VV	0.049	7308.327	81.330	

Productivity and space time yield calculations (Table 5)

Productivity is measured as:

$$Productivity = \left(\frac{mmol\ product}{mmol\ catalyst * time(h)}\right) * 1000$$

expressed as h^{-1}.

Space-time yield is measured as:

$$SpaceTimeYield = \left(\frac{mass\ product(Kg)}{reactor\ volume\ (m^3) *\ reaction\ time\ (s)}\right)$$

as Kg/m^3s^{-1}

Entry 1 - Flask conditions: according to the literature,[1] the reaction was performed using 0.012 mmol of catalyst **3**, 0.61 mmol of azide **1a** and 3.8 mmol of α-Me-styrene. After 30 min at 90 °C, the product was obtained in 97% yield.

$$Productivity = \left(\frac{0.61(mmol) * 0.97(yield)}{0.012(mmol) * 0.5\ (h)}\right) * 1000 = 98617$$

$$SpaceTimeYield = \left(\frac{[0.61(mmol) * 0.97(yield) * 345.29(PM)] * 10^{-6}(Kg)}{3 * 10^{-5}(m^3) * 1800(s)}\right) = 3.78 * 10^{-3}$$

Entry 2 - Flask conditions: the reaction was performed using 0.012 mmol of catalyst **3**, 0.61 mmol of azide **1a** and α-Me-styrene as solvent. After 5 min at 120 °C, the product was obtained in 99% yield.

$$Productivity = \left(\frac{0.61(mmol) * 0.99(yield)}{0.012(mmol) * 0.0833\ (h)}\right) * 1000 = 604142$$

$$SpaceTimeYield = \left(\frac{[0.61(mmol) * 0.99(yield) * 345.29(PM)] * 10^{-6}(Kg)}{3 * 10^{-5}(m^3) * 300(s)}\right) = 23.17 * 10^{-3}$$

Entry 3 – Flow conditions: the reaction was performed using a 0.2 M solution of azide **1a** (0.1 mmol) and a 0.004 M solution of catalyst **3** (0.002 mmol). After 5 min at 120 °C in a 500 μL PTFE mesoreactor, the product was obtained in 87.6% yield. In order to compare the productivity and the space time yield of the two processes, the calculation was normalized in terms of mmol of catalyst (0.012 mmol, see above).

$$Productivity = \left(\frac{6 * \ 0.1(mmol) * 0.876(yield)}{[6 * 0.002(mmol)] * [6 * 0.0833\ (h)]}\right) * 1000 = 87600$$

$$SpaceTimeYield = \left(\frac{[6 * 0.1(mmol) * 0.876(yield) * 345.29(PM)] * 10^{-6}(Kg)}{5 * 10^{-6}(m^3) * [6 * 300(s)]}\right) = 20.16 * 10^{-3}$$

Entry 4 – Flow conditions: the reaction was performed using a 0.2 M solution of azide **1a** (0.1 mmol) and a 0.004 M solution of catalyst **3** (0.002 mmol). After 10 min at 120 °C in a 500 μL PTFE mesoreactor, the product was obtained in 95.1% yield. In order to compare the productivity and the space time yield of the two processes, the calculation was normalized in terms of mmol of catalyst (0.012 mmol, see above).

$$Productivity = \left(\frac{6 * \ 0.1(mmol) * 0.951(yield)}{[6 * 0.002(mmol)] * [6 * 0.1666\ (h)]}\right) * 1000 = 47550$$

$$SpaceTimeYield = \left(\frac{[6 * 0.1(mmol) * 0.951(yield) * 345.29(PM)] * 10^{-6}(Kg)}{5 * 10^{-6}(m^3) * [6 * 600(s)]}\right) = 10.95 * 10^{-3}$$

Entry 5 – Flow conditions: the reaction was performed using a 0.2 M solution of azide **1a** (0.1 mmol) and a 0.004 M solution of catalyst **3** (0.002 mmol). After 30 min at 120 °C in a 500 μL PTFE mesoreactor, the product was obtained in 98.0% yield. In order to compare the productivity and the space time yield of the two processes, the calculation was normalized in terms of mmol of catalyst (0.012 mmol, see above).

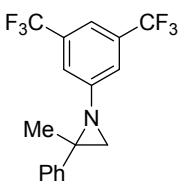
$$Productivity = \left(\frac{6 * \ 0.1(mmol) * 0.980(yield)}{[6 * 0.002(mmol)] * [6 * 0.5\ (h)]}\right) * 1000 = 16334$$

$$SpaceTimeYield = \left(\frac{[6 * 0.1(mmol) * 0.980(yield) * 345.29(PM)] * 10^{-6}(Kg)}{5 * 10^{-6}(m^3) * [6 * 1800(s)]}\right) = 3.75 * 10^{-3}$$

Products characterization

Pure aziridine samples were isolated by column chromatography on silica gel (hexane/AcOEt = 9/1 + 5% triethylamine) in order to perform spectroscopic characterization. The data obtained for aziridines **4-aa**, **4-ab**, **4-ac**, **4-ae**, **4-af**, **4-ag**, **4-ba** were in agreement with data reported in the literature.[4] Compounds **4-ad**, **4-ca**, **4-da** and **4-ea** were fully characterized.

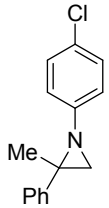
***N*-(3,5-*bis*(Trifluoromethyl)phenyl)-2-methyl-2-phenylaziridine (4-aa)[4].**



4-aa

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.55–7.51 (m, 3 H, Ar*H*), 7.44–7.38 (m, 5 H, Ar*H*), 2.70 (s, 1 H, CH_2), 2.42 (s, 1 H, CH_2), 1.50 (s, 3 H, CH_3). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 7.57 (s, 1 H, Ar*H*), 7.37–7.34 (m, 2 H, Ar*H*), 7.25–7.19 (m, 5 H, Ar*H*), 2.14 (s, 1 H, C*H*2), 1.65 (s, 1 H, C*H*2), 0.99 (s, 3 H, C*H*3).^{13}C NMR (75 MHz, $CDCl_3$, 300 K): *δ* = 152.4 (C), 142.2 (C), 132.5 (q, C, 2*JC–F* = 33.0 Hz), 128.9 (CH), 127.9 (CH), 126.6 (CH), 123.7 (q, C, J_{C-F} = 271.0 Hz), 120.9 (CH, Cc), 115.8 (hept, CH, $^3J_{C-F}$ = 3.9 Hz), 44.9 (C), 43.0 (CH_2), 20.3 (CH_3). ^{13}C NMR (75 MHz, C_6D_6, 300 K): *δ* = 152.9 (C), 142.3 (C), 132.7 (q, C, $^2J_{C-F}$ = 32.9 Hz), 128.8 (CH), 127.7 (CH), 126.5 (CH), 124.1 (q, C, J_{C-F} = 271.3 Hz), 120.9 (broad), 115.4 (hept, CH, $^3J_{C-F}$ = 3.8 Hz), 44.4 (C), 42.6 (CH2), 19.4 (CH3). ^{19}F NMR (282 MHz, $CDCl_3$, 300 K): δ = –63.31. ^{19}F NMR (282 MHz, C_6D_6, 300 K): δ –62.95. Anal. Calcd (%) for $C_{17}H_{13}F_6N$ (345.1): C 59.13, H 3.79, N 4.06, found: C 59.20, H 3.91, N 4.00. IR (Nujol): ν (cm^{-1}) = 1169 (s) (CF_3), 1123 (s) (CF_3). MS (EI): *m/z* 345 [M+], 329 [M+–CH_3], 240 [M+–C(CH_3)(Ph)], 227 [$NC_6H_3(CF_3)_2$].

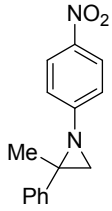
***N*-(4-Chlorophenyl)-2-methyl-2-phenylaziridine (4-ab)[4].**



4-ab

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.51 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.37 (dd, *J* = 7.6, 7.1 Hz, 2 H, Ar*H*), 7.30 (t, *J* = 7.1 Hz, 1 H, Ar*H*), 7.24 (d, *J* = 7.7 Hz, 2 H, Ar*H*), 6.90 (d, *J* = 7.7 Hz, 2 H, Ar*H*), 2.56 (s, 1 H, C*H*2), 2.29 (s, 1 H, CH_2), 1.42 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): *δ* = 149.3 (C), 143.4 (C), 129.3 (CH), 128.8 (CH), 127.5 (CH), 126.7 (CH), 122.4 (CH), 44.1 (C), 42.4 (CH_2), 20.2 (CH_3). Anal. Calcd (%) for $C_{15}H_{14}ClN$ (243.1): C 73.92, H 5.79, N 5.75; found: C 73.85, H 5.70, N 5.69. MS (EI): *m/z* 243 [M+].

***N*-(4-Nitrophenyl)-2-methyl-2-phenylaziridine (4-ac)[4].**

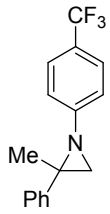


4-ac

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.19 (d, *J* = 9.0 Hz, 2 H, ArH), 7.51 (d, *J* = 7.2 Hz, 2 H, ArH), 7.40 (pst, *J* = 7.2 Hz, 2 H, ArH), 7.34 (t, *J* = 7.2 Hz, 1 H, ArH), 7.02 (d, *J* = 9.0 Hz, 2 H, ArH), 2.69 (s, 1 H, CH_2), 2.42 (s, 1 H, CH_2), 1.50 (s, 3 H, CH_3). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 7.90 (d, *J* = 8.9 Hz, 2 H, ArH), 7.29 (d, J = 7.7 Hz, 2 H, ArH), 7.19 (pst, *J* = 7.7 Hz, 2 H, ArH), 7.12 (t, *J* = 7.7 Hz,

1 H, ArH), 6.31 (d, *J* = 8.9 Hz, 2 H, ArH), 2.07 (s, 1 H, CH_2), 1.63 (s, 1 H, CH_2), 0.95 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, CDCl3, 300 K): δ = 157.3 (C), 142.9 (C), 142.2 (C), 128.9 (CH), 127.9 (CH), 126.6 (CH), 125.6 (CH), 120.8 (CH), 45.2 (C), 42.9 (CH_2), 20.7 (CH3). Anal. Calcd (%) for $C_{15}H_{14}N_2O_2$ (254.1): C 70.58, H 5.55, N 11.02; found: C 70.69, H 5.66, N 11.35. IR (Nujol): ν (cm^{-1}) = 1590 (s) (NO_2), 1504 (s) (NO_2), 1329 (s) (NO_2). MS (EI): *m/z* 254 [M+].

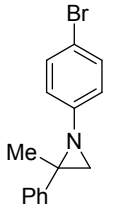
_N_-(4-Trifluoromethylphenyl)-2-methyl-2-phenylaziridine (4-ad).



4-ad

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.55 (d, *J* = 4.4 Hz, 2 H, ArH), 7.52 (d, *J* = 4.8 Hz, 2 H, ArH), 7.40 (t, *J* = 6.9 Hz, 2 H, ArH), 7.34-7.28 (m, 1H, ArH), 7.04 (d, *J* = 4.4 Hz, 2 H, ArH), 2.60 (s, 1 H, CH_2), 2.34 (s, 1 H, CH_2), 1.44 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 153.6 (C), 142.7 (C), 128.4 (CH), 127.2 (CH), 126.2 (CH), 126.1 (CH), 126.0 (C), 123.5 (q, C, J_{C-F} = 39 Hz, CF_3), 120.6 (CH), 43.9 (C), 42.1 (CH_2), 20.0 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$, 300 K): δ = –62.03. MS (ESI+): m/z = 278.1 [M+].

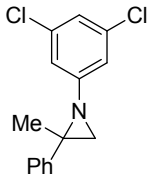
_N_-(4-Bromophenyl)-2-methyl-2-phenylaziridine (4-ae)[4].



4-ae

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.53–7.50 (m, 2 H, Ar*H*), 7.40 (d, *J* = 8.4 Hz, 2 H, Ar*H*), 7.39–7.36 (m, 2 H, Ar*H*), 7.33–7.31 (m, 1 H, Ar*H*), 6.86 (d, *J* = 8.4 Hz, 2 H, Ar*H*), 2.55 (s, 1 H, CH_2), 2.28 (s, 1 H, CH_2), 1.41 (s, 3 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): *δ* = 149.8 (C), 143.4 (C), 132.2 (CH), 128.8 (CH), 127.5 (CH), 126.7 (CH), 122.9 (CH), 115.0 (C), 44.1 (C), 42.4 (CH_2), 20.2 (CH_3). Anal. Calcd (%) for $C_{15}H_{14}BrN$ (287.0): C 62.52, H 4.90, N 4.86; found: C 62.80, H 5.05, N 4.62. MS (EI): *m/z* 287 [M+].

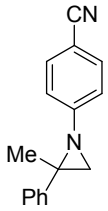
_N_-(3,5-Dichlorophenyl)-2-methyl-2-phenylaziridine (4-af)[4].



4-af

^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 7.27–7.23 (m, 2 H, Ar*H*), 7.17–7.10 (m, 3 H, Ar*H*), 6.89 (t, *J* = 1.5 Hz, 1 H, Ar*H*), 6.66 (d, *J* = 1.5 Hz, 2 H, Ar*H*), 1.96 (s, 1 H, CH_2), 1.50 (s, 1 H, CH_2), 0.90 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, C_6D_6, 300 K): *δ* = 153.4 (C), 142.9 (C), 135.6 (C), 128.7 (CH), 127.5 (CH), 126.6 (CH), 122.4 (CH), 119.7 (CH), 44.2 (C), 42.3 (CH_2), 19.3 (CH_3). Anal. Calcd (%) for $C_{15}H_{13}Cl_2N$ (278.2): C 64.76, H 4.71, N 5.04; found: C 65.00, H 4.78, N 5.10. MS (EI): *m/z* 278 [M+].

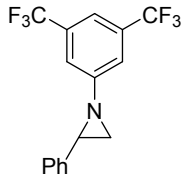
***N*-(4-Cyanophenyl)-2-methyl-2-phenylaziridine (4-ag)**[4]**.**



4-ag

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.56 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.50 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.40 (pst, *J* = 7.2 Hz, 2 H, Ar*H*), 7.33 (t, *J* = 7.2 Hz, 1 H, Ar*H*), 7.01 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 2.63 (s, 1 H, CH_2), 2.35 (s, 1 H, CH_2), 1.46 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): *δ* = 155.2 (C), 142.5 (C), 133.6 (CH), 128.9 (CH), 127.8 (CH), 126.6 (CH), 121.5 (CH), 119.9 (C, *C*N), 105.2 (C), 44.9 (C), 42.6 (CH_2), 20.6 (CH_3). Anal. Calcd (%) for $C_{16}H_{14}N_2$ (234.3): C 82.02, H 6.02, N 11.96; found: C 82.20, H 6.17, N 11.60. IR (Nujol): ν (cm^{-1}) = 2221 (s) (CN). IR (CH_2Cl_2): ν (cm^{-1}) = 2224 (CN). MS (EI): *m/z* 234 [M+].

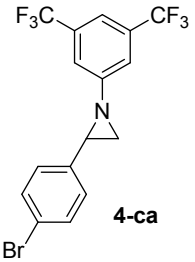
***N*-(3,5-*bis*(Trifluoromethyl)phenyl)-2-phenylaziridine (4-ba)**[4]**.**



4-ba

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.53–7.37 (m, 8 H, Ar*H*), 3.28 (dd, *J* = 6.4, 3.3 Hz, 1 H, C(Ph)*H*), 2.60 (d, *J* = 6.4, 1 H, CH_2), 2.58 (d, *J* = 3.3 Hz, 1 H, CH_2). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 7.54 (s, 1 H, Ar*H*), 7.27–7.20 (m, 7 H, Ar*H*), 2.60 (dd, *J* = 6.6, 3.0 Hz, 1 H, C(Ph)*H*), 1.95 (d, *J* = 3.0, 1 H, CH_2), 1.74 (d, *J* = 6.6 Hz, 1 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): *δ* = 156.2 (C), 138.3 (C), 132.9 (q, C, $^2J_{C–F}$ = 33.3 Hz), 129.1 (CH), 128.3 (CH), 126.5 (CH), 123.6 (q, C, $J_{C–F}$ = 271.1 Hz, CF_3), 121.0 (CH), 116.4 (hept, CH, $^3J_{C–F}$ = 3.8 Hz), 42.4 (CH), 38.4 (CH_2). ^{13}C NMR (75 MHz, C_6D_6, 300 K): *δ* = 156.5 (C), 138.6 (C), 132.8 (q, C, $^2J_{C–F}$ = 32.9 Hz), 129.0 (CH), 128.2 (CH), 126.4 (CH), 124.0 (q, C, $J_{C–F}$ = 271.0 Hz, CF_3), 121.0 (CH), 116.0 (hept, CH, $^3J_{C–F}$ = 3.8 Hz), 42.0 (CH), 38.0 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$, 300 K): δ = –63.31; ^{19}F NMR (282 MHz, C_6D_6, 300 K): δ – 62.91. Anal. Calcd (%) for $C_{16}H_{11}F_6N$ (331.3): C 58.01, H 3.35, N 4.23; found: C 58.36, H 3.60, N 4.50. IR (Nujol): ν (cm^{-1}) = 1140 (s) (CF_3), 1110 (s) (CF_3). MS (EI): *m/z* 330 [M+].

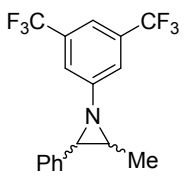
***N*-(3,5-*bis*(Trifluoromethyl)phenyl)-2-(4-bromophenyl)aziridine (4ca).**



4-ca

^{1}H NMR (300 MHz, C_6D_6, 300 K) δ = 7.54 (s, 1H, Ar*H*), 7.25 (d, *J* = 8.4 Hz, 2H, Ar*H*) , 6.83 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.10 (s, 2H, Ar*H*), 6.72 (d, *J* = 8.4 Hz, 2H, Ar*H*), 2.28 (dd, *J* = 6.4 Hz, *J* = 3.2 Hz, 1H, C(Ph)*H*), 1.66 (d, 1H, *J* = 3.2 Hz, CH_2), 1.54 (d, 1H, *J* = 6.5 Hz, CH_2). ^{13}C NMR (75 MHz, C_6D_6, 300 K) δ = 155.6 (C), 137.0 (C), 132.3 (q, C, J_{C-F} = 30.5), 131.5 (C), 131.2 (C), 130.0 (C), 129.36 (C), 120.5 (q, C, J_{C-F} = 279.0 Hz), 120.3, 115.7 (broad), 116.5 (broad), 40.7 (CH), 37.3 (CH_2). ^{19}F NMR (282 MHz, $CHCl_3$, 300 K) = δ -63.4**.** MS (ESI+): *m/z* 410.1 [M+].

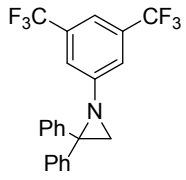
***N*-(3,5-*bis*(Trifluoromethyl)phenyl)-2-phenyl-3-methylaziridine (4da).**



4-da

The product was isolated as a 9:1 mixture of *cis*:*trans* isomers. ^{1}H NMR (300 MHz, $CHCl_3$, 300 K) δ = 7.48 (s, 1H, Ar*H*), 7.44-7.28 (m, 7H, Ar*H*) , 3.44 (d, *J* = 6.5 Hz, 1H, C*H*Ph *trans*), 3.08 (d, *J* = 2.6 Hz, 1H, C*H*Ph *cis*), 2.80 – 2.71 (m, 4H, C*H*Me *trans*), 2.70 – 2.62 (m, 4H, C*H*Me *cis*), 1.32 (d, 3H, *J* = 5.7 Hz, CH_3 *cis*), 1.21 (d, 3H, *J* = 5.7 Hz, CH_3 *trans*). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 151.3 (C), 137.2 (C), 132.2 (q, C, $^{2}J_{C-F}$ = 33.2 Hz), 128.6 (CH), 127.8 (CH), 126.4 (CH), 123.3 (q, C, J_{C-F} = 272.8 Hz, CF_3), 120.7 (CH), 116.4 (hept, CH, $^{3}J_{C-F}$ = 3.8 Hz), 48.5 (CH), 44.2 (CH), 15.0 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$, 300 K) = δ -63.5. MS (ESI+): *m/z* 346.1 [M+].

_N_-(3,5-_bis_(Trifluoromethyl)phenyl)-2,2-diphenylaziridine (4ea).



4-ea

^{1}H NMR (300 MHz, $CHCl_3$, 300 K) δ = 7.84 (d, 1H, *J* = 7.3 Hz, Ar*H*), 7.65-7.58 (m, 1H, Ar*H*) , 7.54-7.46 (m, 1H, Ar*H*), 7.30 (s, 8H, Ar*H*), 7.18 (s, 2H, Ar*H*), 3.09 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 151.2 (C), 138.3 (C), 137.6 (C), 132.4 (C), 131.5 (q, C, $^{2}J_{C-F}$ = 33.1 Hz), 130.1 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 115.14 (hept, CH, $^{3}J_{C-F}$ = 4.5 Hz), 53.0 (C), 40.5 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$, 300 K) = δ -63.6**.** MS (ESI+): *m/z* 408.1 [M+].

References

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