# Catalytic Enantioselective Access to N(III)-Stereogenic Aziridines via Chiral Brønsted Acid-Catalyzed N–Cl Bond Formation

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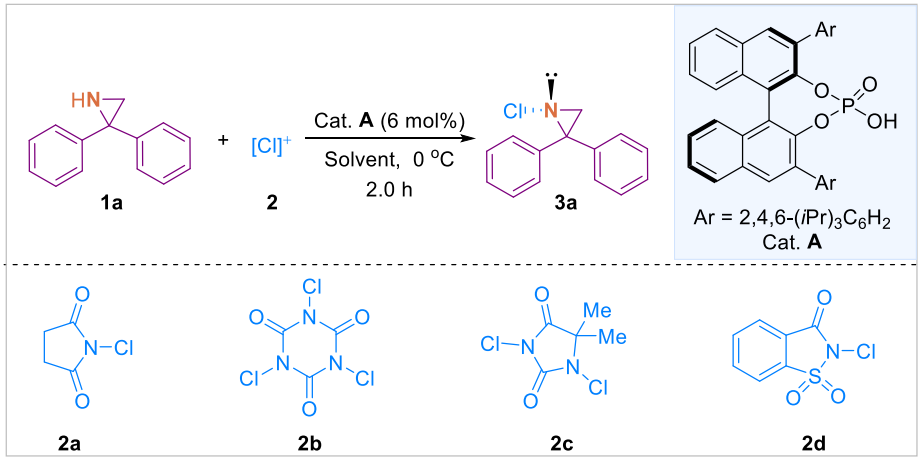
## 1. General information

Commercially available materials purchased from J&K or Energy Chemical were used as received. Unless otherwise specified, all reactions were carried out under nitrogen atmosphere in 10.0 mL dry screw cap vial. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, $\delta$) relative to tetramethylsilane ($\delta$ = 0.00) or chloroform ($\delta$ = 7.26, singlet). $^1$H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first–order splitting patterns were assigned based on the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Fluorine nuclear magnetic resonance ($^{19}$F NMR) spectra were recorded on a Bruker (AVANCE III HD 376 MHz) spectrometer. The melting points (m.p.) of the title compounds were determined when left untouched on a XT-4-MP apparatus from Beijing Tech. Instrument Co. (Beijing, China). High resolution mass spectral analysis (HRMS) was performed on a quadrupole/electrostatic field orbitrap mass spectrometer. The absolute configuration of the products was determined by X-ray crystallography. HPLC analyses were measured on Waters systems with Empower 3 system controller, Alliance 2695, and 2998 Diode Array Waters 2489 UV/Vis detector. Chiralcel brand chiral columns from Daicel Chemical Industries were used with models OD-H, AS-H, OJ-H, AD-H, IA, IB, IC, IE, IF in 4.6 × 250 mm size. The racemic products used to determine the e.r. values were synthesized using racemic catalyst. Optical rotations were measured on an Insmark IP-digi Polarimeter in a 1 dm cuvette at 40 °C. The concentration (c) is given in g/100 mL. Analytical thin–layer chromatography (TLC) was carried out pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

# 2. Experimental section

## 2.1 Supplemental results on condition optimization

**Table S1**. Additional screening of oxidant and solvents[a]

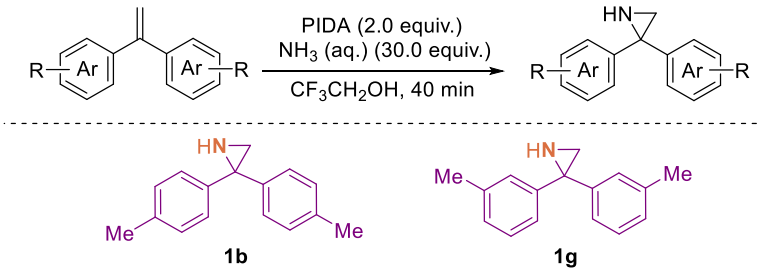



| Entry | **2** | Solvent | T (°C) | Yield of **3a** (%) [b] | E.r. [c] |
|---|---|---|---|---|---|
| 1 | **2a** | $CH_2Cl_2$ | r.t. | >95 | 30:70 |
| 2 | **2a** | $CH_2Cl_2$ | 0 | >95 | 28:72 |
| 3 | **2a** | $CH_2Cl_2$ | -10 | >95 | 31:69 |
| 4 | **2a** | $CH_2Cl_2$ | -20 | >95 | 36:64 |
| 5 | **2a** | $CH_2Cl_2$ | -30 | >95 | 42:58 |
| 7 | **2b** | $CH_2Cl_2$ | 0 | >95 | 43:57 |
| 8 | **2c** | $CH_2Cl_2$ | 0 | >95 | 22:78 |
| 9 | **2d** | $CH_2Cl_2$ | 0 | >95 | 34:66 |
| 10 | **2c** | Tetrahydrofuran | 0 | >95 | 21:79 |
| 11 | **2c** | Dibutyl ether | 0 | >95 | 15:85 |
| 12 | **2c** | *n*-Propyl ether | 0 | >95 | 38:62 |
| 13 | **2c** | *n*-octyl ether | 0 | >95 | 18:82 |
| 14 | **2c** | Isopropyl ether | 0 | >95 | 22:78 |
| 15 | **2c** | CPME | 0 | >95 | 12:88 |

[a] The reactions were performed with **1a** (0.1 mmol, 19.6 mg, 1.0 equiv.), **2a**–**2d** (0.6–1.2 mmol, 0.6–1.2 equiv.), Cat. **A** (6 mol%, 4.5 mg), in solvent (2.0 mL) for 2.0 h; [b] Yield of **3a** was determined by $^1$H NMR spectroscopy, based on **1a**, by using 1,3,5-trimethoxybenzene as an internal standard; [c] *E.r.* was determined by chiral HPLC analysis; CPME = Cyclopentyl methyl ether.

## 2.2 Typical procedure for the preparation of aziridines

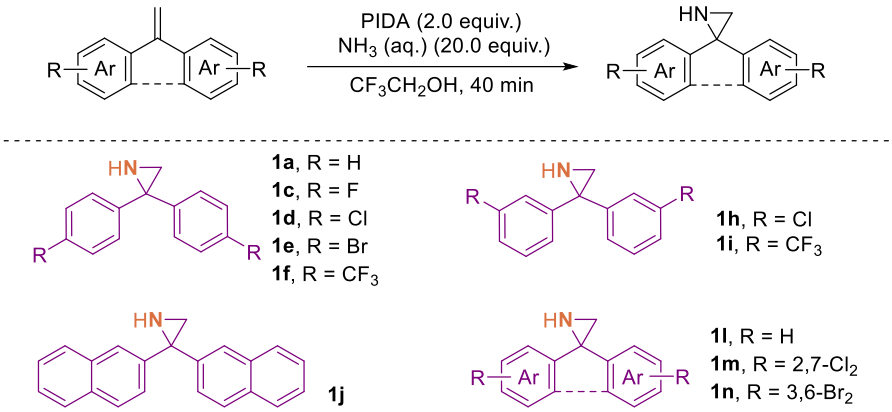
**Scheme S1.** General procedure A for the synthesis of aziridines **1b** and **1g**.[1]




To a round bottom flask charged with a stir bar, were added the alkene (1.0 equiv., 0.35 mmol), and trifluoroethanol (0.7 mL). The solution was cooled down to 0 °C using an ice bath. Aqueous ammonia (15 M in $H_2O$, 30.0 equiv., 10.5 mmol) was added in one portion and immediately followed by (Diacetoxyiodo)benzene (PIDA, 2.0 equiv., 0.7 mmol). The flask was capped with a stopper. The reaction was stirred in the ice bath for 40 minutes and then stopped. The reaction mixture was diluted with diethyl ether (10.0 mL) and water (10.0 mL) and transferred to a separatory funnel where it was extracted three times with 30.0 mL of diethyl ether. The organic extracts were combined, dried over $Na_2SO_4$, filtered and concentrated in vacuo using a rotatory evaporator. The crude reaction mixture was purified by flash column chromatography on silica gel.[1]

**Note**: It is important to titrate ammonia before use to make sure that the title is not below 14.5 M. In order to make sure that PIDA is added quickly enough, it is best to already have it weighed out in a vial, before ammonia is added.

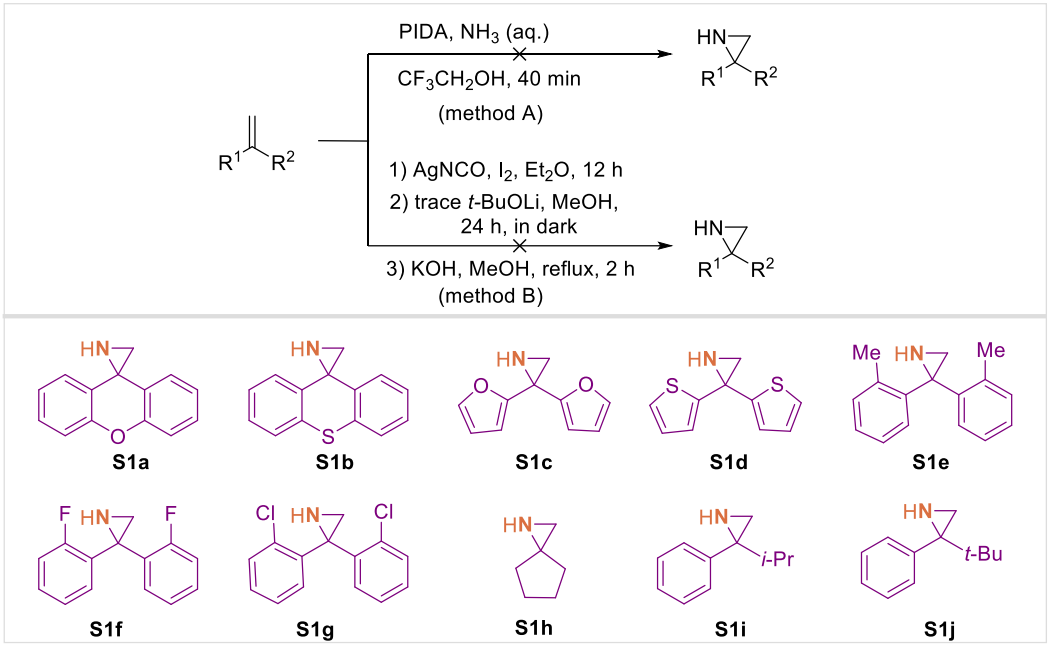
**Scheme S2.** General procedure B for the synthesis of aziridine*s* **1a**, **1c**−**1f**, **1h**−**1j** and **1l**−**1n**




To a round bottom flask charged with a stir bar, were added the alkene (1.0 equiv., 0.35 mmol), and trifluoroethanol (0.7 mL). The solution was cooled down to 0 °C using an ice bath. Aqueous ammonia (6 M in $H_2O$, 20 equiv., 7 mmol) was added in one portion and immediately followed by PIDA (3 equiv., 1.05 mmol). The flask was capped with a stopper. The reaction was stirred in the ice bath for 40 minutes and then stopped. The reaction mixture was diluted with diethyl ether (10.0 mL) and water (10.0 mL) and transferred to a separatory funnel where it was extracted three times with 30 mL of diethyl ether. The organic extracts were combined, dried over $Na_2SO_4$, filtered and concentrated in vacuo using a rotatory evaporator. The crude reaction mixture was purified by flash column chromatography on silica gel.

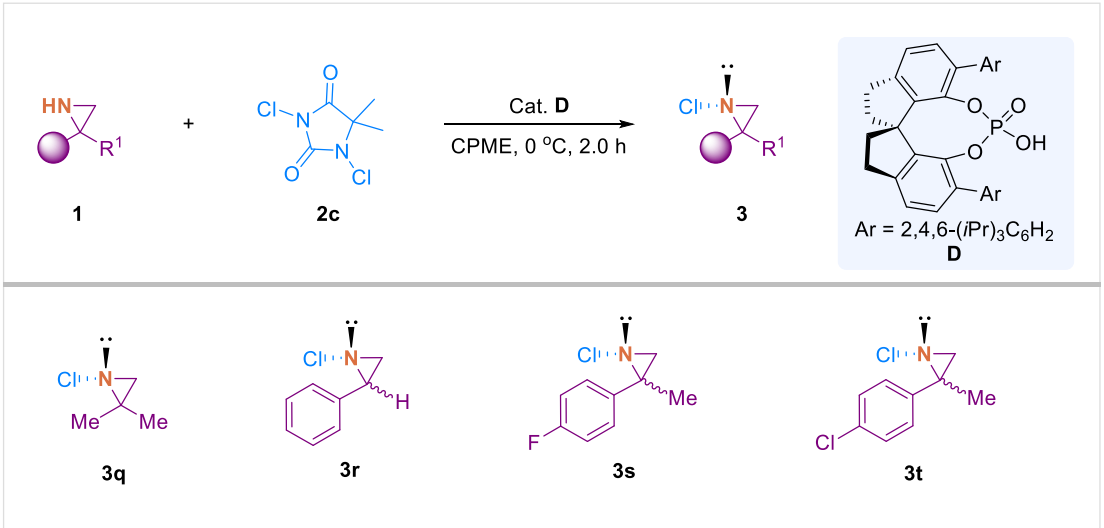
**Note**: 6 M ammonia should be freshly prepared by dilution of 15 M ammonia with the appropriate amount of distilled water. It is possible to add distilled water after the addition of trifluoroethanol and then proceed with the addition of 15 M ammonia and PIDA. In order to make sure that PIDA is added quickly enough, it is best to already have it weighed out in a vial, before ammonia is added.

**Scheme S3.** Unsuccessful aziridine substrates




Meanwhile, extensive efforts were directed toward synthesizing a diverse library of aziridines utilizing reported protocols (Method A and B)[1] (Scheme S3). This expanded scope encompassed substrates featuring heterocyclic (**S1a**, **S1b**) and bis(heteroaryl) (**S1c**, **S1d**) motifs, *ortho*-substituted aryl rings with electronically distinct groups (**S1e**, **S1f**, **S1g**), as well as various cyclic alkenyl (**S1h**), and unsymmetrical 2,2-disubstituted variants (**S1i**, **S1j**). Regrettably, these established methods consistently delivered either complex mixtures or unacceptably diminished yields, underscoring the synthetic challenge of these motifs.

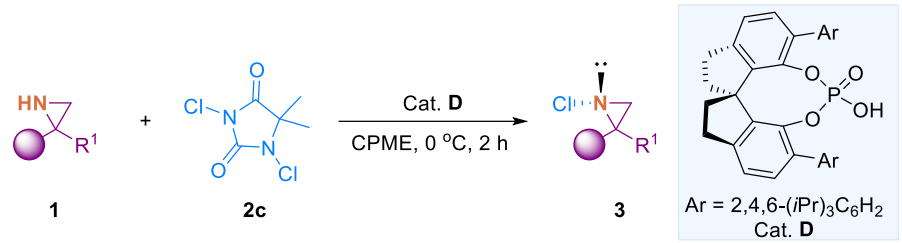
**Scheme S4.** Unsuccessful examples of chiral chlorinated aziridines **3**



We subsequently evaluated the substrate scope regarding various 2,2-dialkyl, monoaryl, and unsymmetrical 2,2-disubstituted aziridines (Scheme S4). Under the optimized conditions, the commercially available 2,2-dimethylaziridine proved completely inert, with no desired product **3q** detectable by TLC or HRMS analysis. Conversely, while monoaryl-substituted substrates underwent smooth conversion to form the corresponding products (**3r**–**3t**), their enantiomeric components proved intractable to resolution via chiral HPLC analysis.

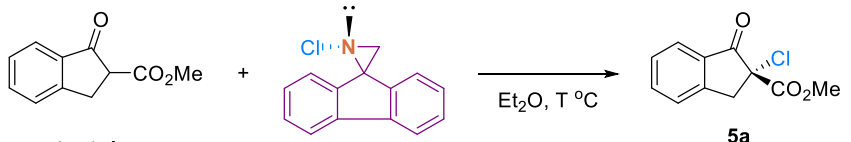
## 2.3 Preparation of chiral chlorinated aziridines product (*R*)-3

**Scheme S5**. General method for the synthesis of chiral chloroaziridines **3** (General procedure C)



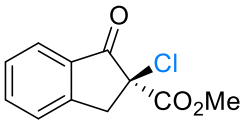

To a flask charged with compound **2c** (11.8 mg, 0.6 mmol, 0.6 equiv.) and Cat. **D** (6 mol%) was added the solvent CPME (2.0 mL). The reaction mixture was stirred at 0 °C for 30 min. Subsequently, compound **1** (19.6 mg, 0.1 mmol, 1 equiv.) was added, and stirring was continued at the same temperature for another 2 h. The reaction progress was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure to remove the solvent. The residue was purified by flash column chromatography (Petroleum ether/Ethyl acetate) to afford compound (*R*)-**3**.

**Scheme S6.** Synthetic application[2]




To evaluate the synthetic utility of the newly developed chiral chloroaziridines, we envisioned utilizing the obtained chloroaziridine **3l** as a novel chiral chlorine source for asymmetric chlorination by selecting **4a** as the model substrate (Scheme S6). Initially, the reaction proceeded smoothly at room temperature to afford the racemic product **5a** in good yield. Upon lowering the temperature to 0 °C, a promising, albeit modest, enantioselectivity (53:47 *er*) was detected. Nevertheless, these preliminary results offer a proof-of-concept that chloroaziridines can serve as viable chiral chlorinating agents for asymmetric transformations.

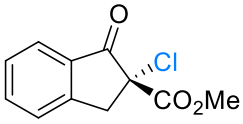
Determination of configuration of the chiral product **5a**



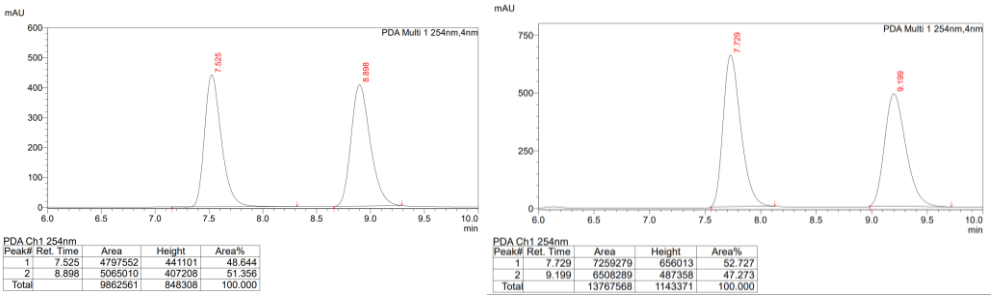

(*S*)-**5a** characterized by previous literature[2]:

HPLC analysis: 14:86 *e.r.* (Chiralcel OD-H 10:90 *i*-PrOH/n-Hexane, 1.0 mL/min), Rt (major) = 9.6 min, Rt (minor) = 8.1 min.

HPLC trace of product **5a** prepared by our method:




(*R*)-**5a**




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.525 | 4797552 | 441101 | 48.644 |
| 2 | 8.898 | 5065010 | 407208 | 51.356 |
| Total | | 9862561 | 848308 | 100.000 |

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.729 | 7259279 | 656013 | 52.727 |
| 2 | 9.199 | 6508289 | 487358 | 47.273 |
| Total | | 13767568 | 1143371 | 100.000 |

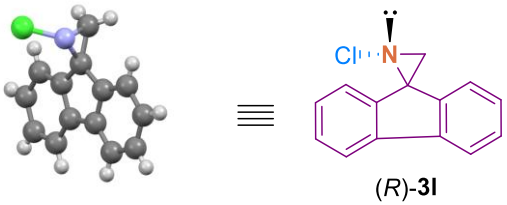
HPLC analysis: 53:47 *e.r.* (Chiralcel OD-H, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 7.7 min, Rt (minor) = 9.2 min. By comparing the HPLC trace of **5a** with the literature reported title compound, it can be inferred that the absolute configuration of **5a** was (*R*).

## 2.4 Determination of configuration

### Determination of configuration of the obtained chiral product 3l

Stereochemistry determination of **3l** via X-ray crystallographic analysis

**Experimental**. Single white plate-shaped crystals of the compound **3l** were recrystallized from slow diffusion of Hex/THF solution. A suitable crystal with dimensions 0.23 × 0.22 × 0.19 $mm^3$ was selected and the crystal was mounted on a mylar loop in perfluoroether oil on a STOE STADIVARI Cu diffractometer. The crystal was kept at a steady $T$ = 298 K during data collection. **CCDC 2525820** for (*R*)-**3l** contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data request/cif](www.ccdc.cam.ac.uk/data request/cif).




(*R*)-**3l**

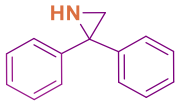
| Compound | (*R*)-**3l** |
|---|---|
| Empirical formula | $C_{14}H_{10}ClN$ |
| Formula weight | 227.68 |
| Temperature/K | 298.00 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 4.67020(10) |
| b/Å | 12.4822(2) |
| c/Å | 37.9133(7) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/$Å^3$ | 37.9133(7) |
| Z | 8 |
| $\rho_{calc}g/cm^3$ | 1.369 |
| $\mu/mm^{-1}$ | 2.779 |

| | |
|---|---|
| F(000) | 944.0 |
| Crystal size/$mm^3$ | 0.23 × 0.22 × 0.19 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.662 to 136.468 |
| Index ranges | $-5 \leq h \leq 5$, $-15 \leq k \leq 14$, $-45 \leq l \leq 45$ |
| Reflections collected | 21161 |
| Independent reflections | 4021 [$R_{int}$ = 0.0383, $R_{sigma}$ = 0.0361] |
| Data/restraints/parameters | 4021/0/289 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0303, $wR_2$ = 0.0797 |
| Final R indexes [all data] | $R_1$ = 0.0312, $wR_2$ = 0.0803 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.11/-0.23 |
| Flack parameter | 0.055(4) |

## 3. Characterizations of substrates and products

### 3.1 Characterization of substrates products

**2,2-Diphenylaziridine (1a):**



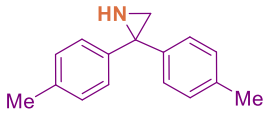

Prepared according to general procedure A, Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1a**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28 – 7.12 (m, 10H), 2.26 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 142.7, 128.4, 127.8, 127.2, 44.0, 35.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{14}N^+$ $[M + H]^+$: 196.1126, found: 196.1113.

**2,2-Di-*p*-tolylaziridine (1b):**



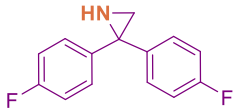

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1b**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 8.4 Hz, 4H), 7.09 (d, $J$ = 8.0 Hz, 4H), 2.30 (s, 8H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 140.0, 136.8, 130.3, 129.1, 127.7, 126.2, 43.6, 35.5, 21.2 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{18}N^+$ $[M + H]^+$: 224.1439, found: 224.1437.

**2,2-Bis(4-fluorophenyl)aziridine (1c):**



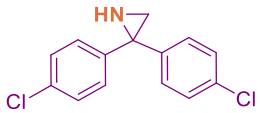

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1c**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.19 (m, 4H), 6.88 (m, 4H), 2.22 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, $J$ = 246.1 Hz), 138.4 (d, $J$ = 3.3 Hz), 129.4 (d, $J$ = 8.0 Hz), 115.3 (d, $J$ = 21.4 Hz), 42.9, 35.5.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}F_2N^+$ $[M + H]^+$: 232.0938, found: 232.0933.

**2,2-Bis(4-chlorophenyl)aziridine (1d):**



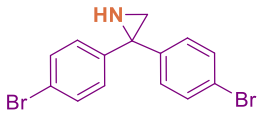

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 40:1) to afford **1d**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35 – 7.21 (m, 8H), 2.34 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 140.8, 133.4, 129.2, 128.8, 43.1, 35.6. ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{12}Cl_2N^+$ $[M + H]^+$: 264.0347, found: 264.0338.

**2,2-Bis(4-bromophenyl)aziridine (1e):**



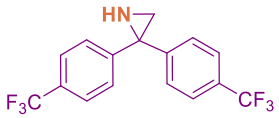

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1e**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.43 (d, $J$ = 8.8 Hz, 4H), 7.19 (d, $J$ = 8.4 Hz, 4H), 2.34 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 141.3, 131.7, 129.6, 121.5, 43.2, 35.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{12}Br_2N^+$ $[M + H]^+$: 351.9316, found: 351.9312.

**2,2-Bis(4-(trifluoromethyl)phenyl)aziridine (1f):**




Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1f**, colorless oil;

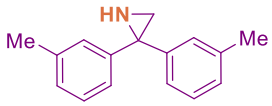
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.60 (d, $J$ = 8.0 Hz, 4H), 7.46 (d, $J$ = 8.0 Hz, 4H), 2.44 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.9, 130.0 (q, $J$ = 32.3 Hz), 128.3, 125.7 (d, $J$ = 3.9 Hz), 124.2 (q, $J$ = 272.0 Hz), 43.5, 35.7.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.6 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{12}F_6N^+$ $[M + H]^+$: 332.0874, found: 332.0863.

**2,2-Di-*m*-tolylaziridine (1g):**



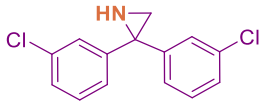

Prepared according to general procedure A. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1g**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.22 – 7.15 (m, 4H), 7.13 (dt, $J$ = 7.6, 1.6 Hz, 2H), 7.08 – 7.03 (m, 2H), 2.34 (s, 8H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 142.8, 138.1, 128.4, 128.3, 128.0, 125.0, 44.0, 35.4, 21.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{18}N^+$ $[M + H]^+$: 224.1439, found: 224.1435.

**2,2-Bis(3-chlorophenyl)aziridine (1h):**



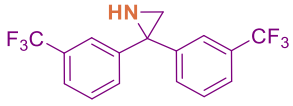

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1h**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34 (m, 2H), 7.25 (m, 4H), 7.23 – 7.20 (m, 2H), 2.36 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 144.1, 134.6, 129.9, 128.0, 127.8, 126.2, 43.4, 35.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{12}Cl_2N^+$ $[M + H]^+$: 264.0347, found: 264.0339.

**2,2-Bis(3-(trifluoromethyl)phenyl)aziridine (1i):**




Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1i**, colorless oil;

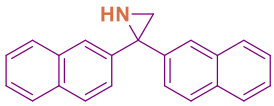
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.65 (s, 2H), 7.54 (m, 4H), 7.45 (m, 2H), 2.60 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 143.0, 131.9 – 130.7 (m,1C), 129.3, 124.5, 124.1 (q, $J$ = 272.4 Hz), 43.6, 35.6.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.6 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{12}F_6N^+$ $[M + H]^+$: 332.0874, found: 332.0868.

**2,2-Di(naphthalen-2-yl)aziridine (1j):**



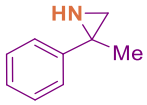
Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1j**, yellow oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.9 (d, $J$ = 1.81 Hz, 2H), 7.9 – 7.8 (m, 6H), 7.6 – 7.5 (m, 6H), 2.6 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 140.0, 133.3, 132.7, 128.4, 128.1, 127.8, 126.7, 126.4, 126.1, 126.0, 44.5, 35.6 ppm.

**HRMS** (ESI, m/z): calculated for $C_{22}H_{18}N^+$ $[M + H]^+$: 296.1439, found: 296.1442.

**2-Methyl-2-phenylaziridine (1k):**

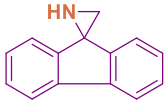


Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1k**, colorless oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.29 (m, 4H), 7.26 – 7.20 (m, 1H), 1.95 (s, 2H), 1.61 (s, 3H).

**HRMS** (ESI, m/z): calculated for $C_9H_{12}N^+$ $[M + H]^+$: 134.0970, found: 134.0968.

**Spiro[aziridine-2,9'-fluorene] (1l):**



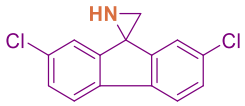
Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1l**, pale yellow oil;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.83 – 7.76 (m, 2H), 7.40 (m, 2H), 7.31 (m, 2H), 7.22 – 7.03 (m, 2H), 2.78 (d, $J$ = 61.2 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 144.5, 128.0, 127.5, 120.4, 44.0, 36.0 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{12}N^+$ $[M + H]^+$: 194.0970, found: 194.0962.

**2',7'-Dichlorospiro[aziridine-2,9'-fluorene] (1m):**



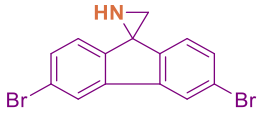

Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1m**, yellow solid;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 8.1 Hz, 2H), 7.33 (dd, $J$ = 8.1, 1.9 Hz, 2H), 7.09 (s, 2H), 2.74 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 146.2, 138.1, 133.6, 128.4, 121.4, 43.7, 36.3 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{10}Cl_2N^+$ $[M + H]^+$: 262.0190, found: 262.0184.

**3',6'-Dibromospiro[aziridine-2,9'-fluorene] (1n):**




Prepared according to general procedure B. Flash column chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford **1n**, yellow solid. m.p. 153.1 – 155.2 °C;

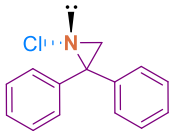
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 1.8 Hz, 2H), 7.44 (dd, $J$ = 8.1, 1.8 Hz, 2H), 7.01 (s, 2H), 2.76 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 143.5, 130.9, 124.0, 122.1, 43.7, 36.0 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{10}Br_2N^+$ $[M + H]^+$: 349.9180, found: 349.9186.

### 3.2 Characterization of N(III)-chiral products

**(*R*)-1-Chloro-2,2-diphenylaziridine (3a)**:



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3a**, colorless oil (18.6 mg, 81% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 (m, 5H), 7.24 (m, 5H), 3.06 (d, $J$ = 3.2 Hz, 1H), 2.81 (d, $J$ = 3.2 Hz, 1H).

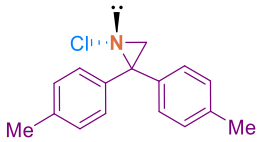
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 141.7, 137.1, 131.3, 128.8, 128.4, 127.5, 127.3, 55.4, 50.2 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{13}ClN^+$ $[M + H]^+$: 230.0737, found: 230.0731.

$[\alpha]^{25}_D$ = -159.9 (c = 0.13 in $CHCl_3$).

**HPLC** analysis: 96:4 *e.r.* (Chiralcel OJ-H 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), 40 °C (major) = 14.2 min, (minor) = 13.1 min.

**(*R*)-1-Chloro-2,2-di-*p*-tolylaziridine (3b):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3b**, colorless oil (22.1 mg, 86% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$. 7.30 (m, 2H), 7.23 (m, 2H), 7.14 (d, $J$ = 8.4 Hz, 2H), 7.08 (d, $J$ = 8.0 Hz, 2H), 3.03 (d, $J$ = 3.2 Hz, 1H), 2.78 (d, $J$ = 3.2 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H).

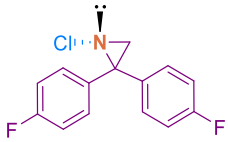
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 138.9, 138.5, 137.1, 134.2, 131.0, 129.0, 128.9, 127.1, 55.0, 50.1, 21.3, 21.1.ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{17}ClN^+$ $[M + H]^+$: 258.1050, found: 258.1034.

$[\alpha]^{25}_D$ = -26.8 (c = 0.3 in $CHCl_3$).

**HPLC** analysis: 97:3 *e.r.* (Chiralcel OD-H 5:95 *i*-PrOH/*n*-Hexane, 0.5 mL/min), Rt (major) = 7.8 min, Rt (minor) = 8.7 min.

**(*R*)-1-Chloro-2,2-bis(4-fluorophenyl)aziridine (3c):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3c**, colorless oil (26.6 mg, 80% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 – 7.33 (m, 2H), 7.26 – 7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 7.03 – 6.91 (m, 2H), 3.02 (d, $J$ = 3.2 Hz, 1H), 2.78 (d, $J$ = 3.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.9 (d, $J$ = 248.7 Hz), 162.2 (d, $J$ = 247.0 Hz), 137.3 (d, $J$ = 3.1 Hz), 133.0 (d, $J$ = 8.4 Hz), 132.9 (d, $J$ = 3.2 Hz), 128.9 (d, $J$ = 8.1 Hz), 115.6 (d, $J$ = 18.9 Hz), 115.4 (d, $J$ = 18.6 Hz), 54.2, 50.4 ppm.

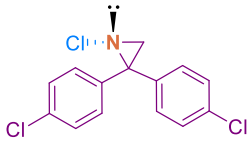
**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -112.2, -114.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}ClF_2N^+$ $[M + H]^+$: 266.0548, found: 266.0542.

$[\alpha]^{25}_D$ = -115.3 (c = 0.13 in $CHCl_3$).

**HPLC** analysis: 95:5 *e.r.* (Chiralcel OJ-H 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 8.5min, Rt (minor) = 6.3 min.

**(*R*)-1-Chloro-2,2-bis(4-chlorophenyl)aziridine (3d):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3d**, colorless oil (24.1 mg, 81% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.43 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.22 – 7.12 (m, 2H), 3.02 (d, $J$ = 3.2 Hz, 1H), 2.77 (d, $J$ = 3.2 Hz, 1H).

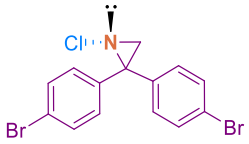
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 139.7, 135.2, 135.1, 133.7, 132.5, 128.8, 128.7, 128.6, 54.3, 50.3 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}Cl_3N^+$ $[M + H]^+$: 297.9957, found: 297.9951.

$[\alpha]^{25}_D$ = -74.4 (c = 0.2 in $CHCl_3$).

**HPLC** analysis: 95:5 *e.r.* (Chiralcel OJ-H 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 6.3 min, Rt (minor) = 6.9 min.

**(*R*)-2,2-Bis(4-bromophenyl)-1-chloroaziridine (3e):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 40:1) to afford **3e**, colorless oil (27.1 mg, 70% yield); $R_f$ = 0.32 (Petroleum ether/Ethyl acetate = 40:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.67 – 7.49 (m, 2H), 7.44 – 7.33 (m, 2H), 7.30 – 7.20 (m, 2H), 7.15 – 7.05 (m, 2H), 3.02 (d, $J$ = 3.2 Hz, 1H), 2.76 (d, $J$ = 3.2 Hz, 1H).

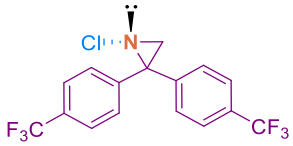
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 140.2, 135.6, 132.8, 131.8, 131.6, 128.9, 123.4, 121.9, 54.4, 50.2 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}Br_2ClN^+$ $[M+H]^+$: 385.8947, found: 385.8936

$[\alpha]^{25}_D$ = -38.8 (c = 0.3 in $CHCl_3$).

**HPLC** analysis: 98:2 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 8.2 min, Rt (minor) = 9.9 min.

**(*R*)-1-Chloro-2,2-bis(4-(trifluoromethyl)phenyl)aziridine (3f):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3f**, colorless oil (29.6 mg, 81% yield); $R_f$ = 0.30 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.72 (d, $J$ = 8.4 Hz, 2H), 7.54 (t, $J$ = 8.6 Hz, 4H), 7.37 (d, $J$ = 8.4 Hz, 2H), 3.13 (d, $J$ = 3.2 Hz, 1H), 2.85 (d, $J$ = 3.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 144.7, 140.1, 131.7, 131.3 (d, $J$ = 32.7 Hz), 130.7, 130.2 (d, $J$ = 32.5 Hz), 127.7, 125.7 (dq, $J$ = 3.7 Hz), 124.0 (q, $J$ = 272.2 Hz), 124.0 (q, $J$ = 272.3 Hz), 54.6, 50.2.

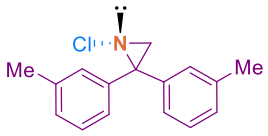
**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.68, -62.75 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{10}ClF_6N^+$ $[M+H]^+$: 366.0484, found: 366.0478.

$[\alpha]^{25}_D$ = -89.8 (c = 0.4 in $CHCl_3$).

**HPLC** analysis: 97:3 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 4.9 min, Rt (minor) = 6.0 min.

**(*R*)-1-Chloro-2,2-di-*m*-tolylaziridine (3g):**




Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3g**, colorless oil (19.4 mg, 75% yield); $R_f$ = 0.40 (Petroleum ether/Ethyl acetate = 50:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.31 (m, 2H), 7.25 – 7.12 (m, 4H), 7.11 – 7.01 (m, 2H), 3.07 (d, $J$ = 2.8 Hz, 1H), 2.83 (d, $J$ = 2.8 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H).

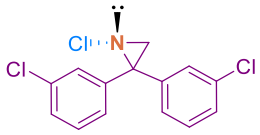
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 141.8, 138.1, 138.0, 137.2, 131.8, 129.5, 128.3, 128.3, 128.2, 127.7, 124.6, 55.5, 50.0, 21.57, 21.65 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{17}ClN^+$ $[M + H]^+$: 258.1050, found: 258.1040.

$[\alpha]^{25}_D$ = -98.0 (c = 0.1 in $CHCl_3$).

**HPLC** analysis: 96:4 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 9.3 min, Rt (minor) = 7.5 min.

**(*R*)-1-Chloro-2,2-bis(3-chlorophenyl)aziridine (3h):**




Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3h**, colorless oil (24.1 mg, 81% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$. 7.45 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.15 – 7.07 (m, 1H), 3.02 (d, $J$ = 3.2 Hz, 1H), 2.76 (d, $J$ = 3.2 Hz, 1H).

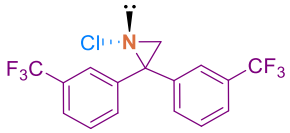
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 143.0, 138.4, 134.5, 134.4, 131.1, 129.8, 129.8, 129.5, 129.3, 128.0, 127.3, 54.4, 50.0 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}Cl_3N^+$ $[M + H]^+$: 297.9957, found: 297.9943.

$[\alpha]^{25}_D$ = -45.1 (c = 0.13 in $CHCl_3$).

**HPLC** analysis: 96:4 *e.r.* (Chiralcel OJ-H 1:99 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 6.9 min, Rt (minor) = 6.3 min.

**(*R*)-1-Chloro-2,2-bis(3-(trifluoromethyl)phenyl)aziridine (3i):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3i**, colorless oil (28.7 mg, 79% yield); $R_f$ = 0.32 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.73 – 7.65 (m, 2H), 7.61 – 7.58 (m, 2H), 7.57 – 7.52 (m, 2H), 7.44 – 7.40 (m, 2H), 3.13 (d, $J$ = 3.6 Hz, 1H), 2.86 (d, $J$ = 3.2 Hz, 1H).

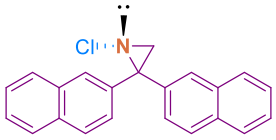
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 141.9, 137.4, 134.8, 131.22 (q, $J$ = 33.3 Hz), 131.20 (q, $J$ = 32.3 Hz),130.9, 129.3, 129.2, 127.7 (d, $J$ = 3.8 Hz), 126.1 (q, $J$ = 3.7 Hz), 124.9 (q, $J$ = 3.7 Hz), 124.0 (q, $J$ = 272.5 Hz), 123.9 (q, $J$ = 272.5 Hz), 123.8 (q, $J$ = 3.9 Hz), 54.6, 50.2.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.6, -62.7 ppm.

**HRMS** (ESI, m/z): calculated for $C_{16}H_{10}ClF_6N^+$ $[M + H]^+$: 366.0484, found: 366.0480. $[\alpha]^{25}_D$ = -68.5 (c = 0.2 in $CHCl_3$).

**HPLC** analysis: 97:3 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 0.4 mL/min), Rt (major) = 12.3 min, Rt (minor) = 14.2 min.

**(*R*)-1-Chloro-2,2-di(naphthalen-2-yl)aziridine (3j):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford **3j**, yellow oil (25.6 mg, 78% yield); $R_f$ = 0.32 (Petroleum ether/Ethyl acetate = 50:1);

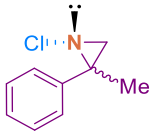
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.0 (d, $J$ = 1.7 Hz, 1H), 7.9 – 7.8 (m, 4H), 7.8 – 7.7 (m, 3H), 7.6 – 7.5 (m, 3H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 1H), 3.3 (d, $J$ = 3.1 Hz, 1H), 3.0 (d, $J$ = 3.14 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 138.9, 134.7, 133.4, 133.2, 133.0, 132.8, 130.4, 128.8, 128.4, 128.2, 128.2, 128.0, 127.7, 126.9, 126.6, 126.5, 126.4, 126.3, 125.2 , 55.9, 50.3 ppm.

**HRMS** (ESI, m/z): calculated for $C_{22}H_{18}ClN^+$ $[M + H]^+$: 330.1044, found: 330.1039. $[\alpha]^{25}_D$ = -44.9 (c = 0.3 in $CHCl_3$).

**HPLC** analysis: 96:4 *e.r.* (Chiralcel OD-H 1:99 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 5.7 min, Rt (minor) = 7.0 min.

**(*R*)-1-Chloro-2-methyl-2-phenylaziridine (3k):**




**Minor diastereoisomer:**

Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford the minor diastereoisomer of **3k**, colorless oil (29% yield); $R_f$ = 0.40 (Petroleum ether/Ethyl acetate = 50:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 2.71 (d, $J$ = 2.8 Hz, 1H), 2.37 (d, $J$ = 2.8 Hz, 1H), 1.91 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 141.4, 128.5, 127.6, 126.5, 49.7, 20.9 ppm.

**HRMS** (ESI, m/z): calculated for $C_9H_{11}ClN^+$ $[M + H]^+$: 168.0580, found: 168.0573 $[\alpha]^{25}_D$ = -106.0 (c = 0.1 in $CHCl_3$).

**HPLC** analysis: 95:5 e.r. (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 9.1 min, Rt (minor) = 10.3 min.

**Major diastereoisomer:**

Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 50:1) to afford the major diastereoisomer of **3k**, colorless oil (46% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 50:1);

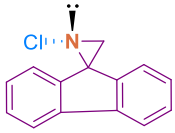
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.43 – 7.32 (m, 5H), 2.65 (d, $J$ = 3.2 Hz, 1H), 2.58 (d, $J$ = 3.2 Hz, 1H), 1.60 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 138.5, 129.6, 128.57, 128.63, 128.4, 126.6, 47.9, 25.9.ppm.

**HRMS** (ESI, m/z): calculated for $C_9H_{11}ClN^+$ $[M + H]^+$: 168.0580, found: 168.0568,. $[\alpha]^{25}_D$ = -19.6 (c = 0.4 in $CHCl_3$).

**HPLC** analysis: 73:27 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 14.6 min, Rt (minor) = 11.1 min.

**(*R*)-1-Chlorospiro[aziridine-2,9'-fluorene] (3l):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 40:1) to afford **3l**, white solid (20.1 mg, 88% yield); $R_f$ = 0.34 (Petroleum ether/Ethyl acetate = 5:1). m.p. 100.8 – 102.7 °C;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 7.2 Hz, 1H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.59 (d, $J$ = 7.6 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.34 (m, 1H), 7.33 – 7.28 (m, 1H), 7.12 (m, 1H), 3.43 (d, $J$ = 3.2 Hz, 1H), 3.27 (d, $J$ = 3.2 Hz, 1H).

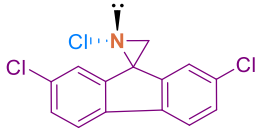
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 142.6, 140.9, 138.3, 129.2, 129.1, 127.9, 126.6, 125.1, 121.5, 120.6, 120.2, 53.6, 49.7 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{11}ClN^+$ $[M + H]^+$: 228.0580, found: 228.0570.

$[\alpha]^{25}_D$ = +16.7 (c = 0.13 in $CHCl_3$).

**HPLC** analysis: 98:2 *e.r.* (Chiralcel OJ-H 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 10.5 min, Rt (minor) = 9.5 min.

**(*R*)-1,2',7'-Trichlorospiro[aziridine-2,9'-fluorene] (3m):**



Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 40:1) to afford **3m**, yellow solid (26.4 mg, 89% yield); $R_f$ = 0.44 (Petroleum ether/Ethyl acetate = 40:1). m.p. 161.4 – 163.4 °C;

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.66 (m, 1H), 7.60 (m, 1H), 7.55 (m, 1H), 7.45 (m, 1.9 Hz, 1H), 7.38 (m, 1H), 7.07 (m, 1H), 3.42 (d, $J$ = 3.6 Hz, 1H), 3.25 (d, $J$ = 3.2 Hz, 1H).

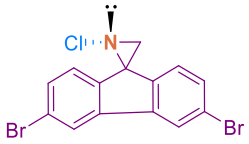
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 144.2, 139.9, 139.8, 138.2, 134.0, 132.7, 129.4, 129.4, 125.4, 122.1, 121.4, 121.2, 52.8, 49.9 ppm.

**HRMS** (ESI, m/z): calculated for $C_{14}H_9ClN^+$ $[M + H]^+$: 295.9801, found: 295.9788.

$[\alpha]^{25}_D$ = +6.0 (c = 0.1 in $CHCl_3$).

**HPLC** analysis: 97:3 *e.r.* (Chiralcel OJ-H 1:99 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 9.2 min, Rt (minor) = 8.5 min.

**(*R*)-3',6'-Dibromo-1-chlorospiro[aziridine-2,9'-fluorene] (3n):**




Prepared according to general procedure C. Flash column chromatography (Petroleum ether/Ethyl acetate = 40:1) to afford **3n**, yellow solid (25.1 mg, 65% yield); $R_f$ = 0.28 (Petroleum ether/Ethyl acetate = 40:1); m.p. 140.6 – 142.6 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.89 (d, $J$ = 1.8 Hz, 1H), 7.83 (d, $J$ = 1.8 Hz, 1H), 7.50 (dd, $J$ = 8.2, 1.8 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.97 (m, 1H), 3.42 (d, $J$ = 3.6 Hz, 1H), 3.26 (d, $J$ = 3.2 Hz, 1H).

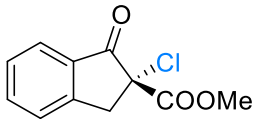
Note: Owing to the poor solubility of this compound in a range of deuterated solvents ($CDCl_3$, MeOD, DMSO-$d_6$, and acetone-$d_6$), a satisfactory **$^{13}$C NMR** spectrum could not be obtained.

**HRMS** (ESI, m/z): calculated for $C_{14}H_{10}Br_2ClN^+$ $[M+H]^+$: 387.8770, found: 387.8774.

$[\alpha]^{25}_D$ = -14.7 (c = 0.1 in $CHCl_3$).

**HPLC** analysis: 86:14 *e.r.* (Chiralcel OJ-H, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 11.3 min, Rt (minor) = 13.7 min.

**(*R*)-Methyl 2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5a)**




Prepared according to general procedure. Flash column chromatography (Petroleum ether/Ethyl acetate = 6:1) to afford **5a**, yellow solid (17.7 mg, 79% yield); $R_f$ = 0.4 (Petroleum ether/Ethyl acetate = 10:1);

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.9 (d, $J$ = 7.70 Hz, 1H), 7.8 – 7.7 (m, 1H), 7.5 (d, $J$ = 7.8 Hz, 2H), 4.1 (d, $J$ = 17.8 Hz, 1H), 3.8 (s, 3H), 3.6 (d, $J$ = 17.8 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 195.1, 167.8, 150.7, 136.6, 132.5, 128.8, 126.4, 126.1, 68.0, 54.2, 43.5 ppm.

**HRMS** (ESI, m/z): calculated for $C_{11}H_9Cl_2O_3^+$ $[M + H]^+$: 225.0318, found: 225.0317.

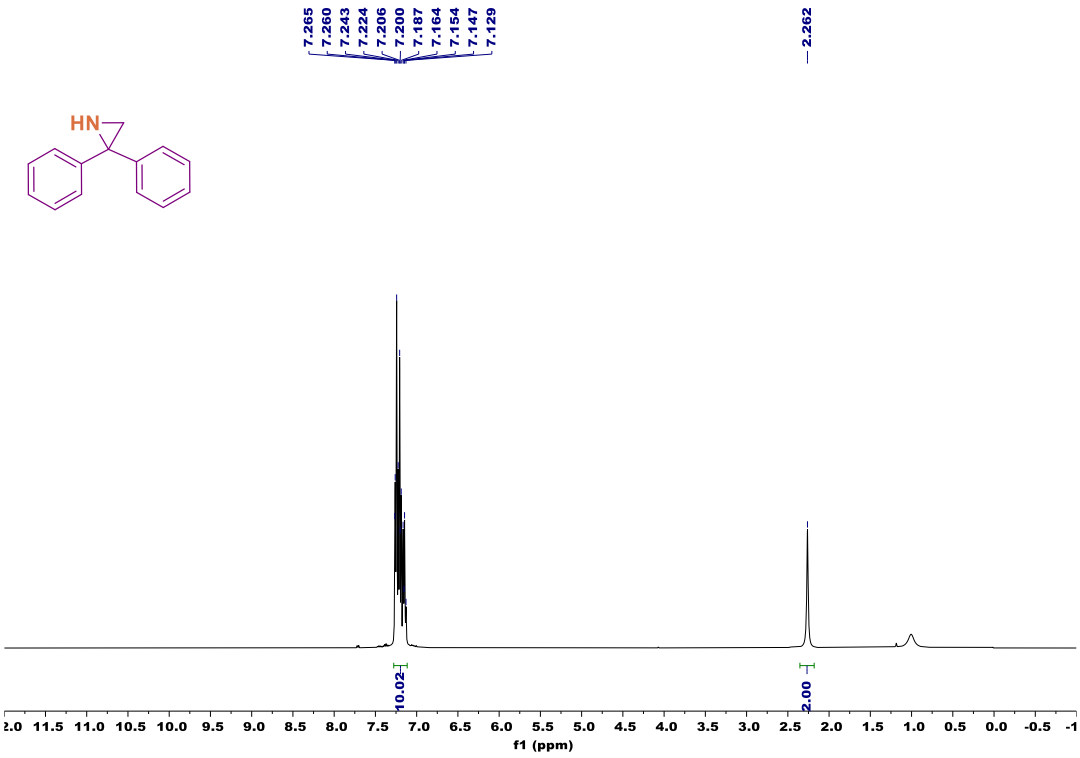
**HPLC** analysis: 53:47 *e.r.* (Chiralcel OD-H, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 7.7 min, Rt (minor) = 9.2 min.

### 3.3 References

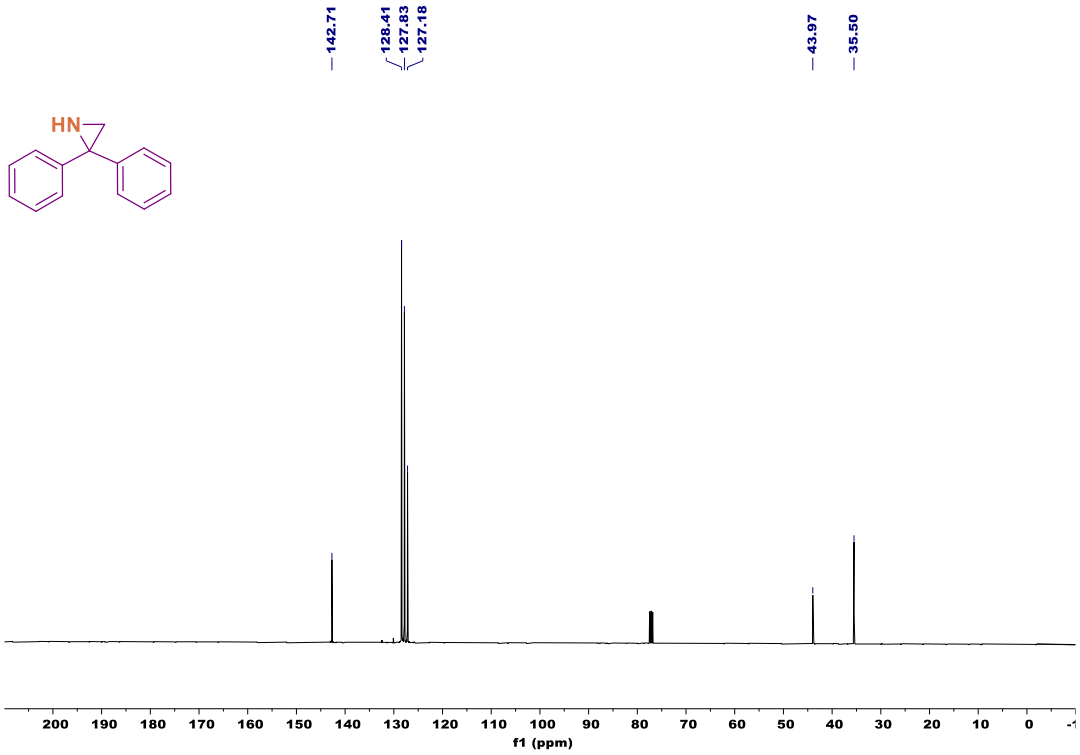

1. (a) Y. Gelato, L. Marraffa, F. Pasca, P. Natho, G. Romanazzi, A. Tota, M. Colella, R. Luisi. Iodonitrene-Mediated Nitrogen Transfer to Alkenes for the Direct Synthesis of NH-Aziridines. *J. Am. Chem. Soc.***2025**, *147*, 35567–35575; (b) Q. Wu, J. Xu. Regio- and stereoselective synthesis of thiazoline derivatives via the thioketene-induced ring expansion of aziridines. *Chem. Commun.* **2022**, *58*, 2714–2717.
2. S. Wu, P. Chen, M. Duan, P.-Y. Jiang, Q. Zhou, S.-H. Xiang, K. N. Houk and B. Tan. Controlling pyramidal nitrogen chirality by asymmetric organocatalysis. *Nature*. **2025**, *647*, 897-905.
3. C. Song, C. Pang, Y. Deng, H. Cai, X. Gan, Y. R. Chi, Catalytic N-Acylation for Access to N-N Atropisomeric N-Aminoindoles: Choice of Acylation Reagents and Mechanistic Insights. *ACS Catal*. **2024**, *14*, 6926–6935.

## 3.4 Copies of $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra

### 2,2-Diphenylaziridine (1a):

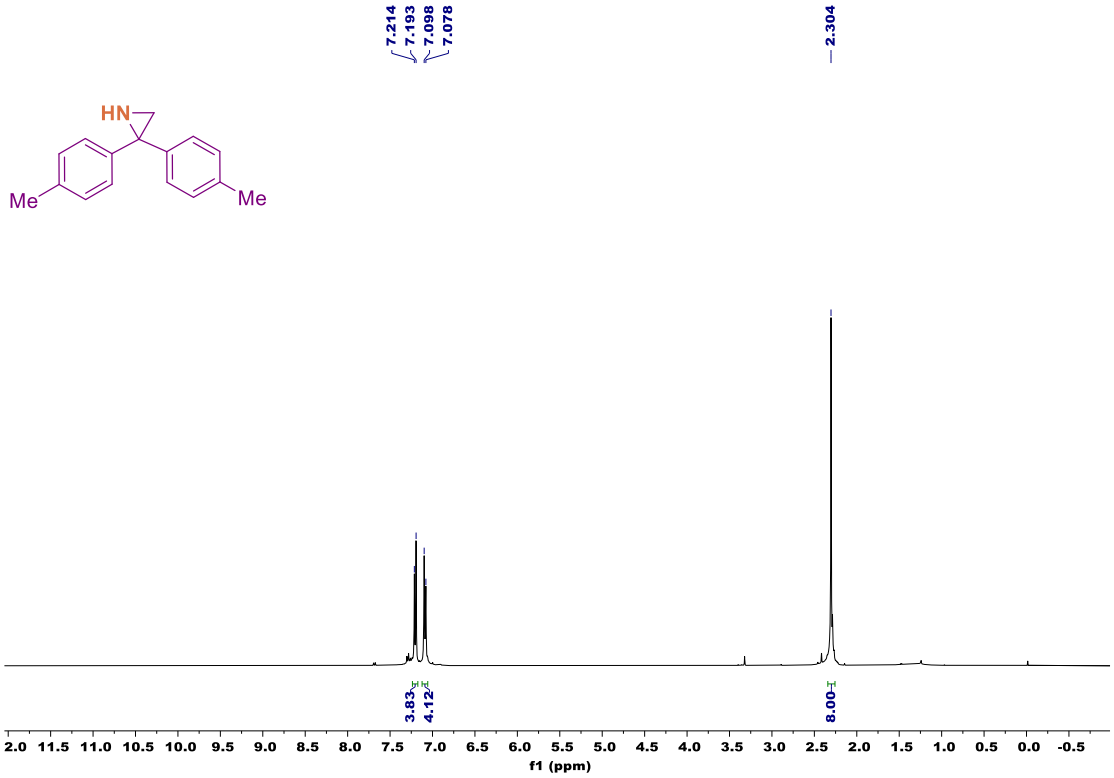



**$^{1}H$ NMR** spectrum of **1a** (400 MHz, $CDCl_3$)

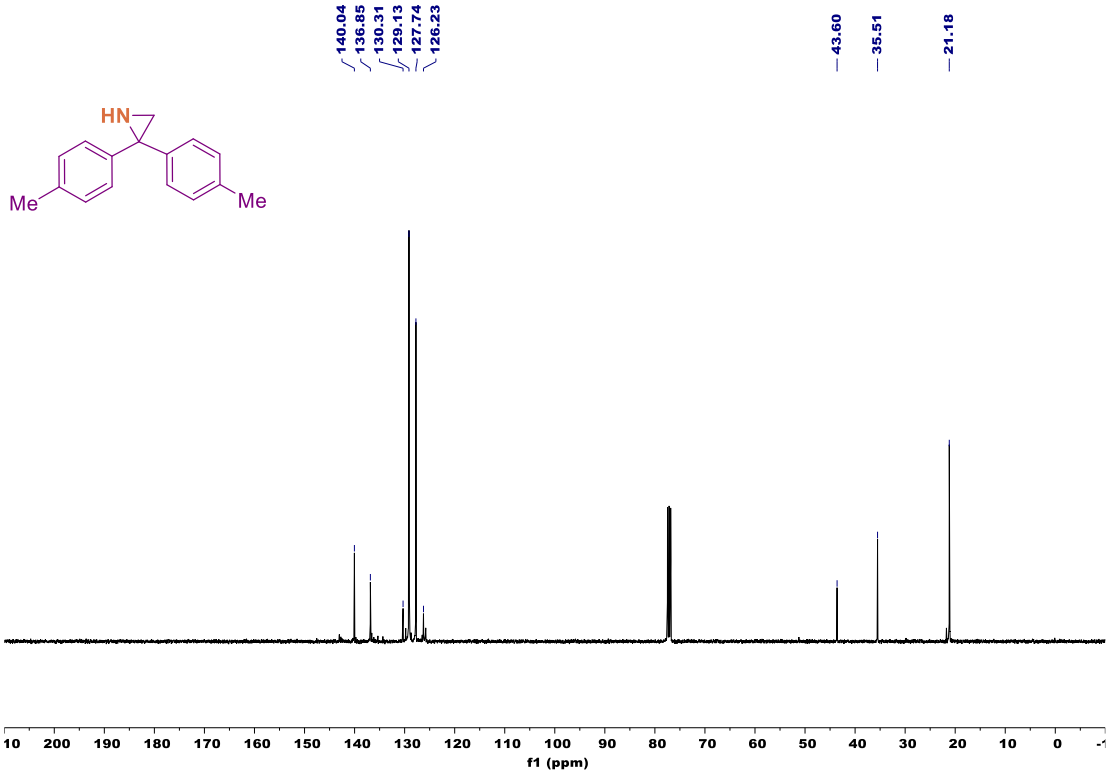



**$^{13}C$ NMR** spectrum of **1a** (101 MHz, $CDCl_3$)

**2,2-Di-*p*-tolylaziridine (1b):**

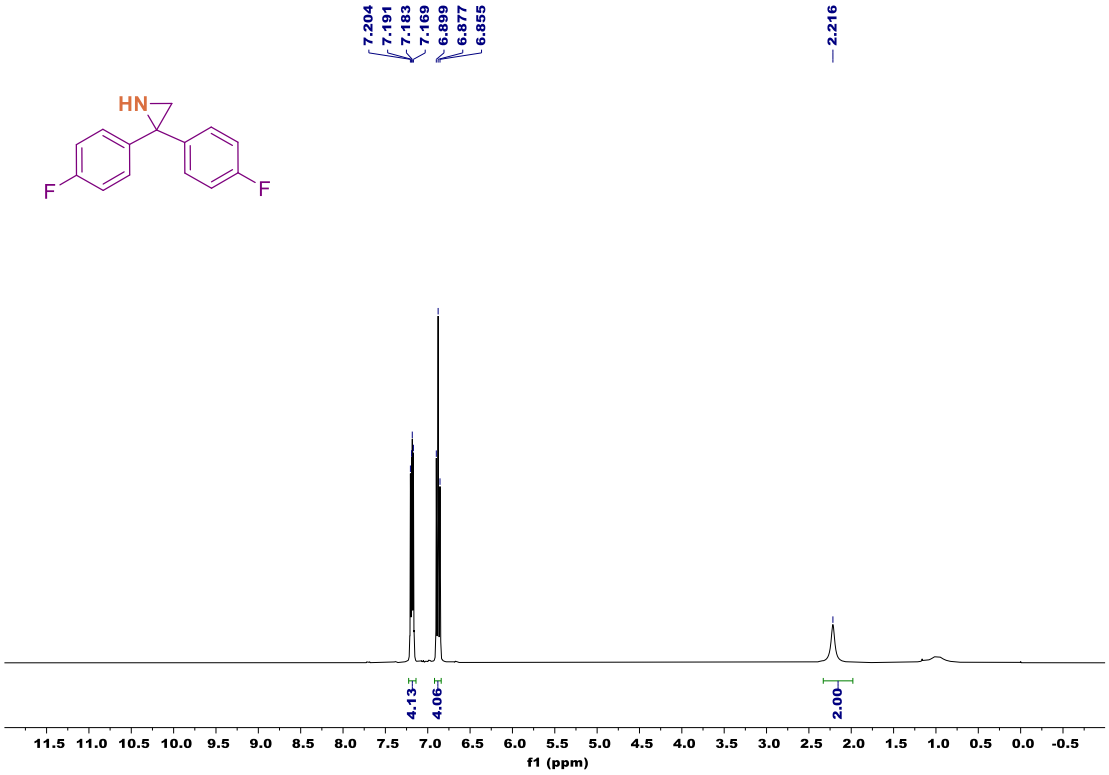



$^{1}$**H NMR** spectrum of **1b** (400 MHz, $CDCl_3$)

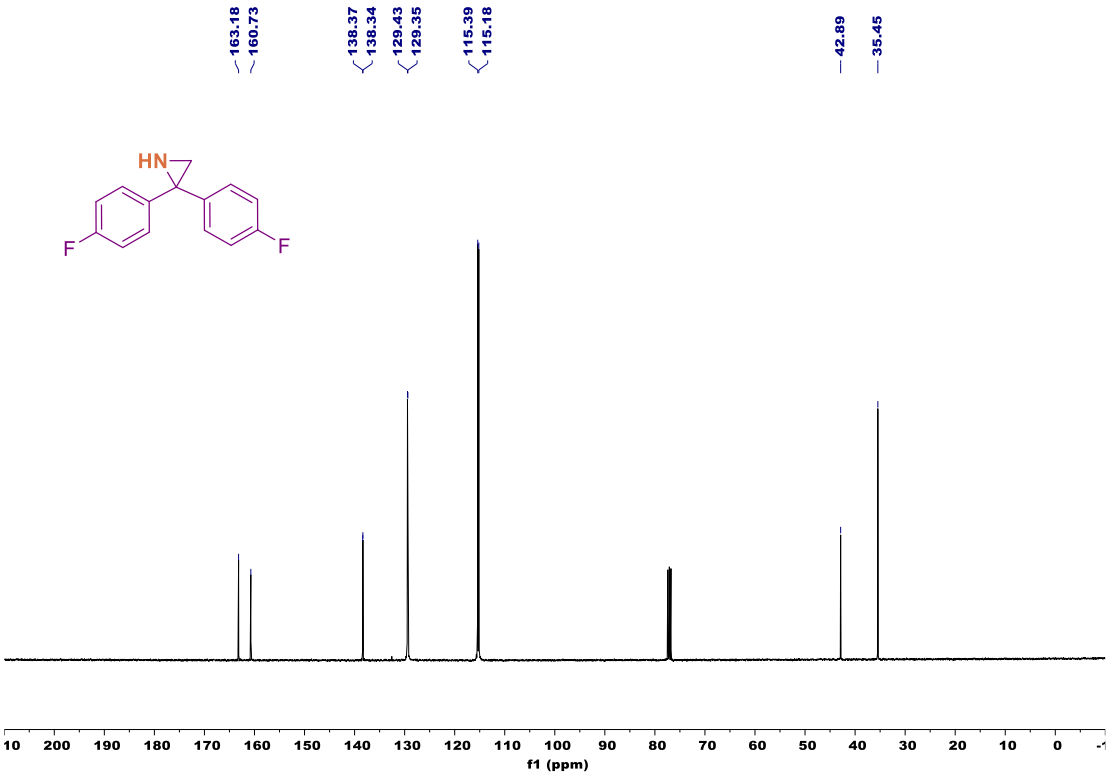



$^{13}$**C NMR** spectrum of **1b** (101 MHz, $CDCl_3$)

**2,2-Dis(4-fluorophenyl)aziridine (1c):**

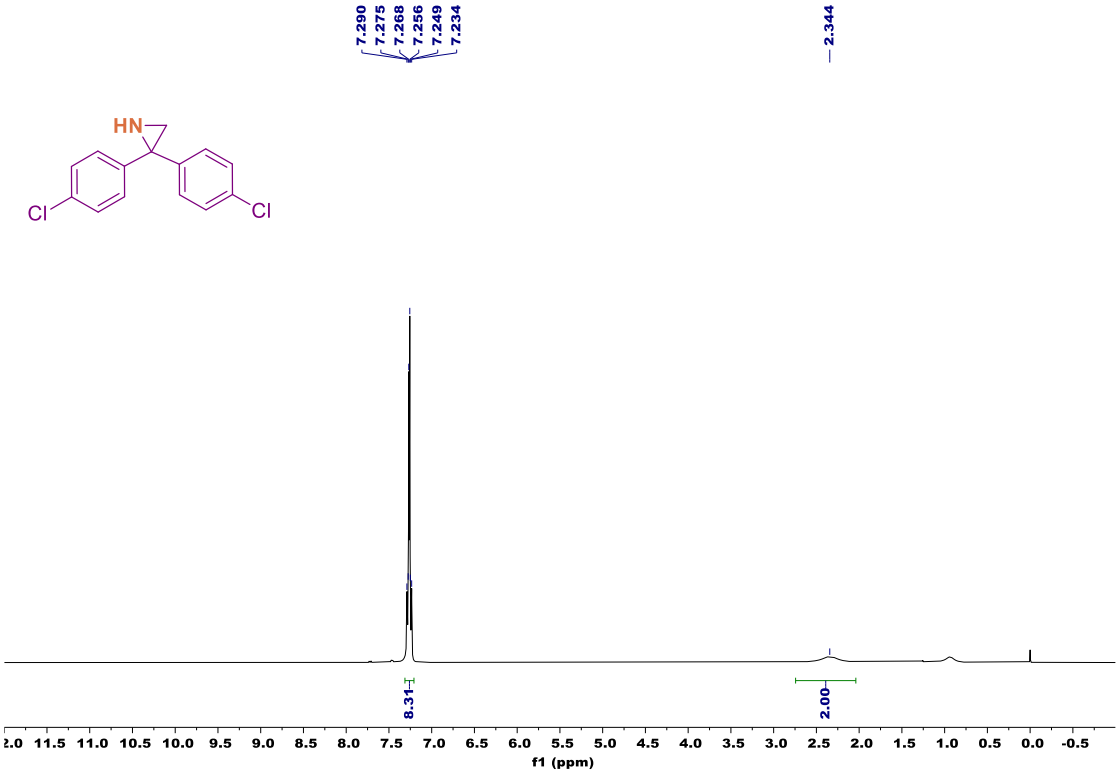



**$^{1}$H NMR** spectrum of **1c** (400 MHz, $CDCl_3$)

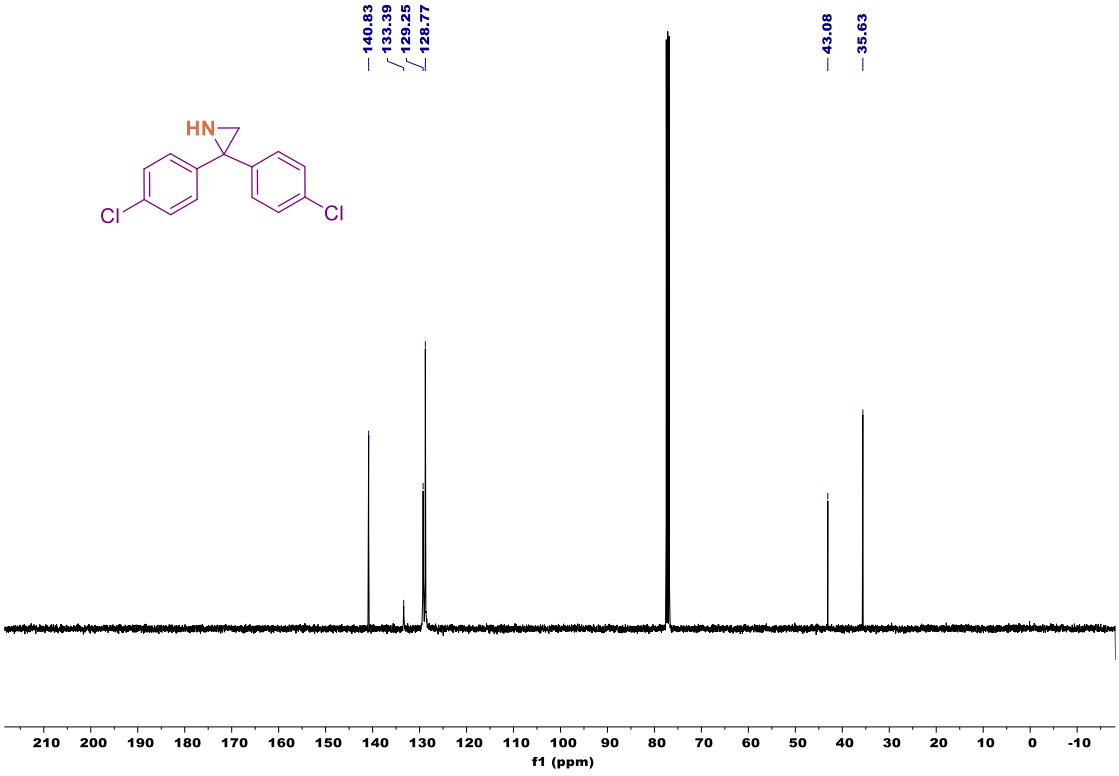



**$^{13}$C NMR** spectrum of **1c** (101 MHz, $CDCl_3$)

**2,2-Bis(4-chlorophenyl)aziridine (1d):**

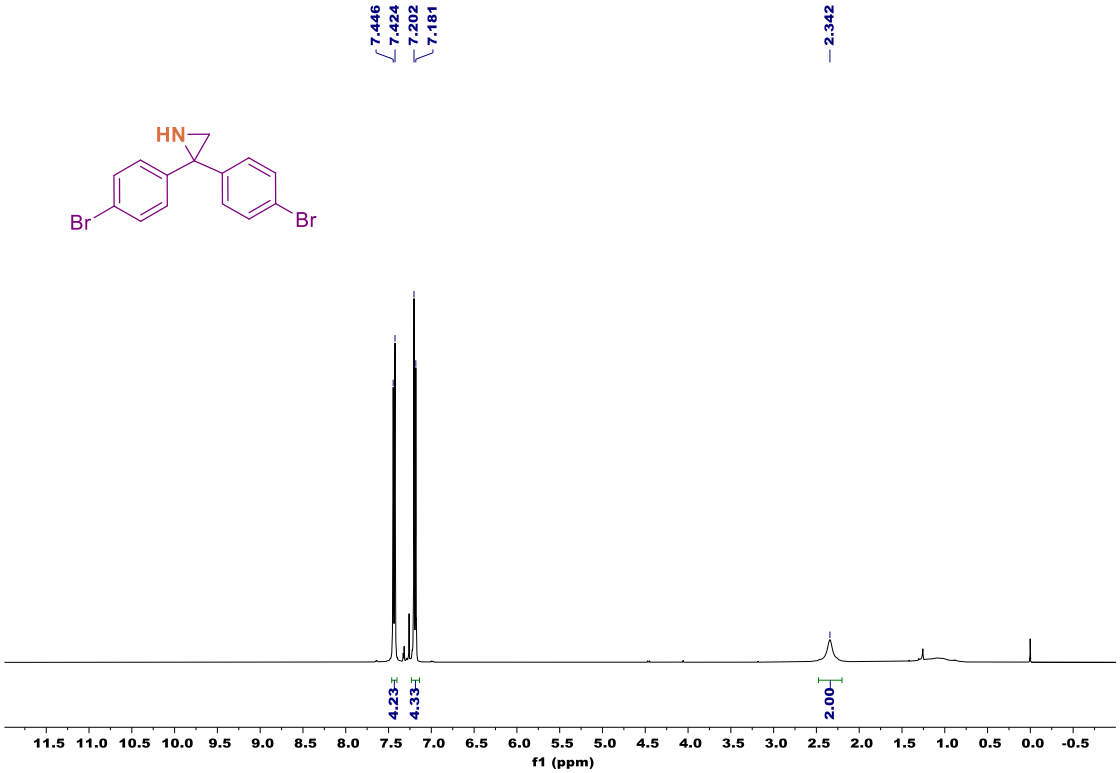



$^{1}$**H NMR** spectrum of **1d** (400 MHz, $CDCl_3$)

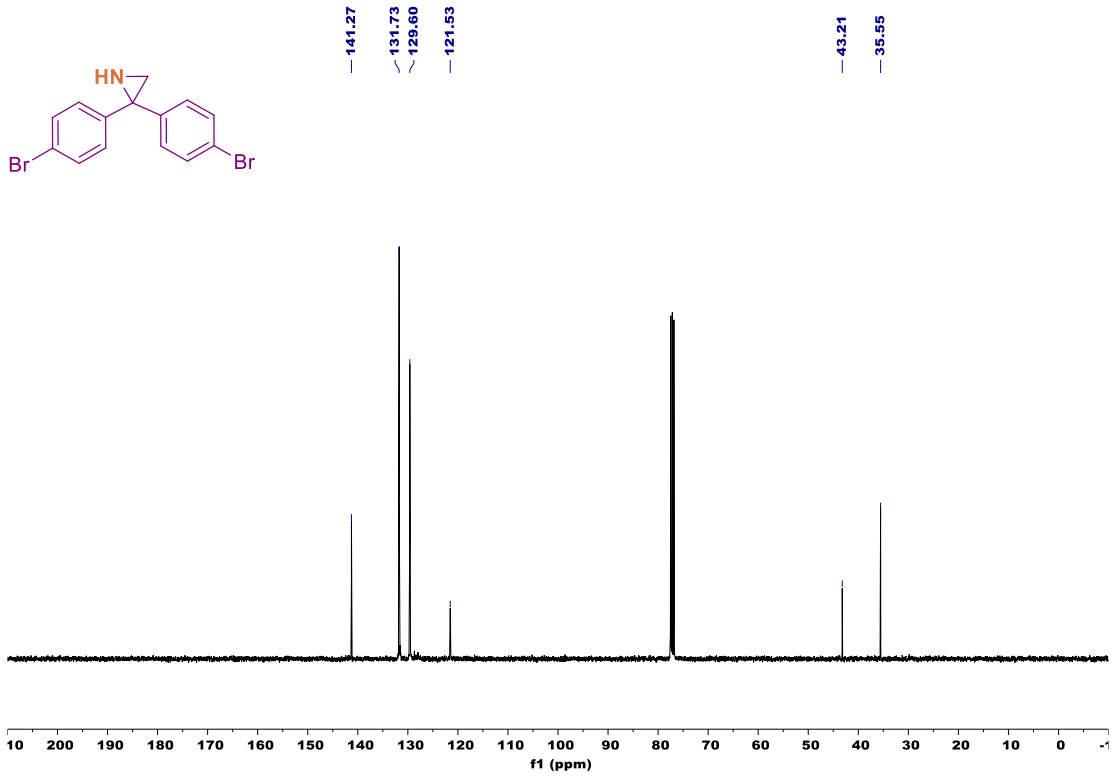



$^{13}$**C NMR** spectrum of **1d** (101 MHz, $CDCl_3$)

**2,2-Bis(4-bromophenyl)aziridine (1e):**

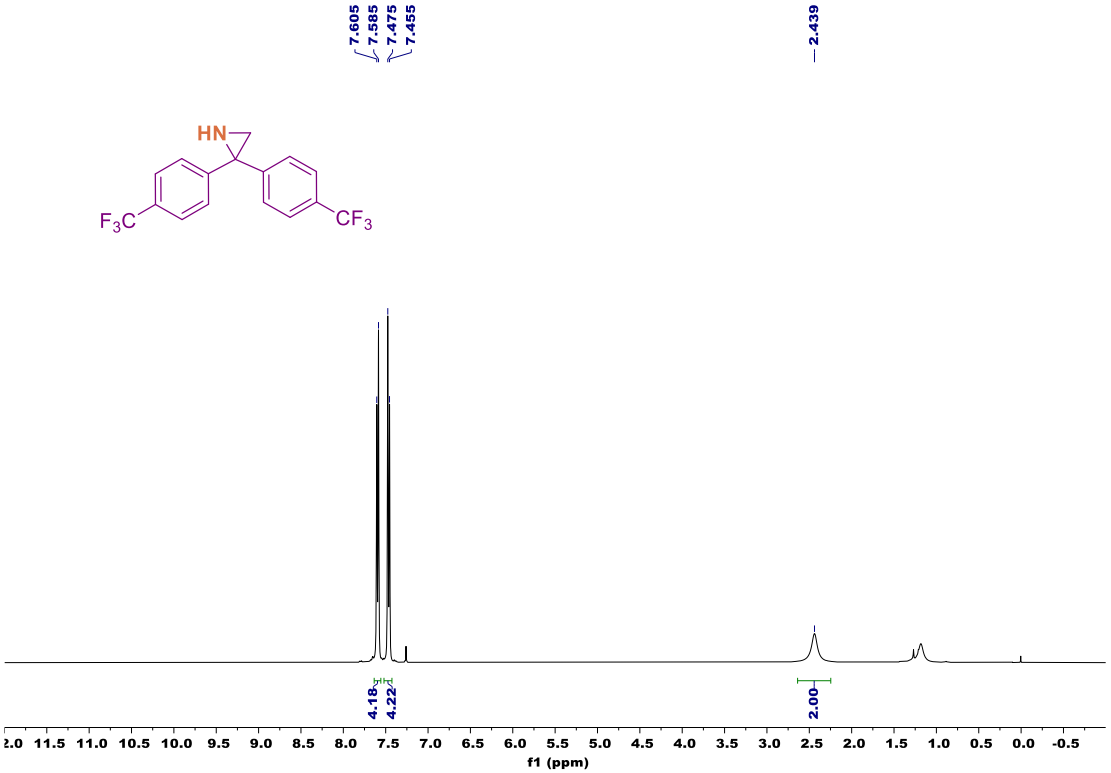



$^{1}$**H NMR** spectrum of **1e** (400 MHz, $CDCl_3$)

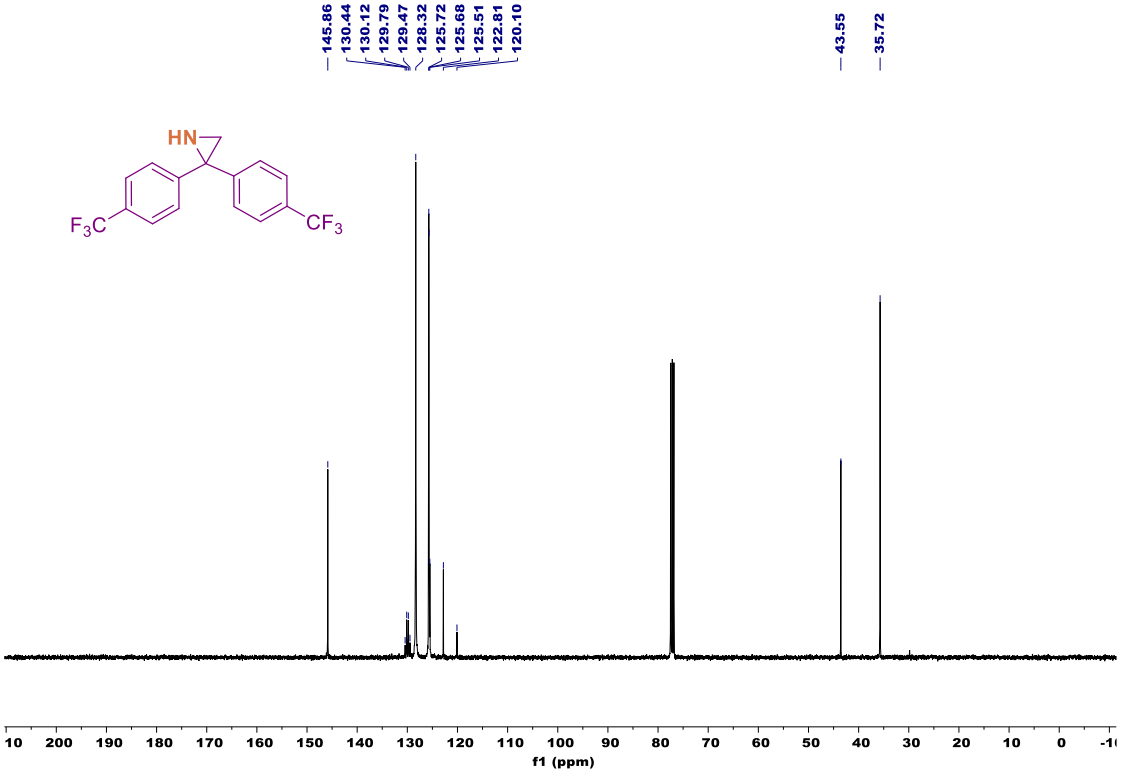



$^{13}$**C NMR** spectrum of **1e** (101 MHz, $CDCl_3$)

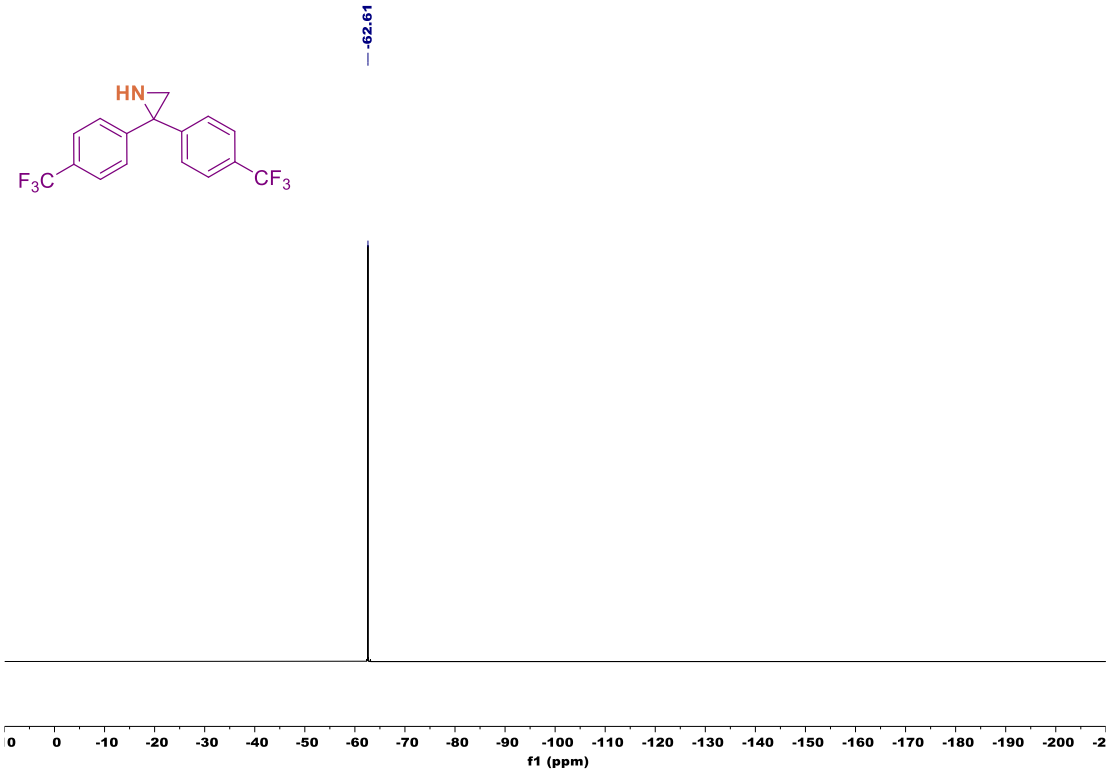
**2,2-Bis(4-(trifluoromethyl)phenyl)aziridine (1f):**




**$^{1}$H NMR** spectrum of **1f** (400 MHz, $CDCl_3$)

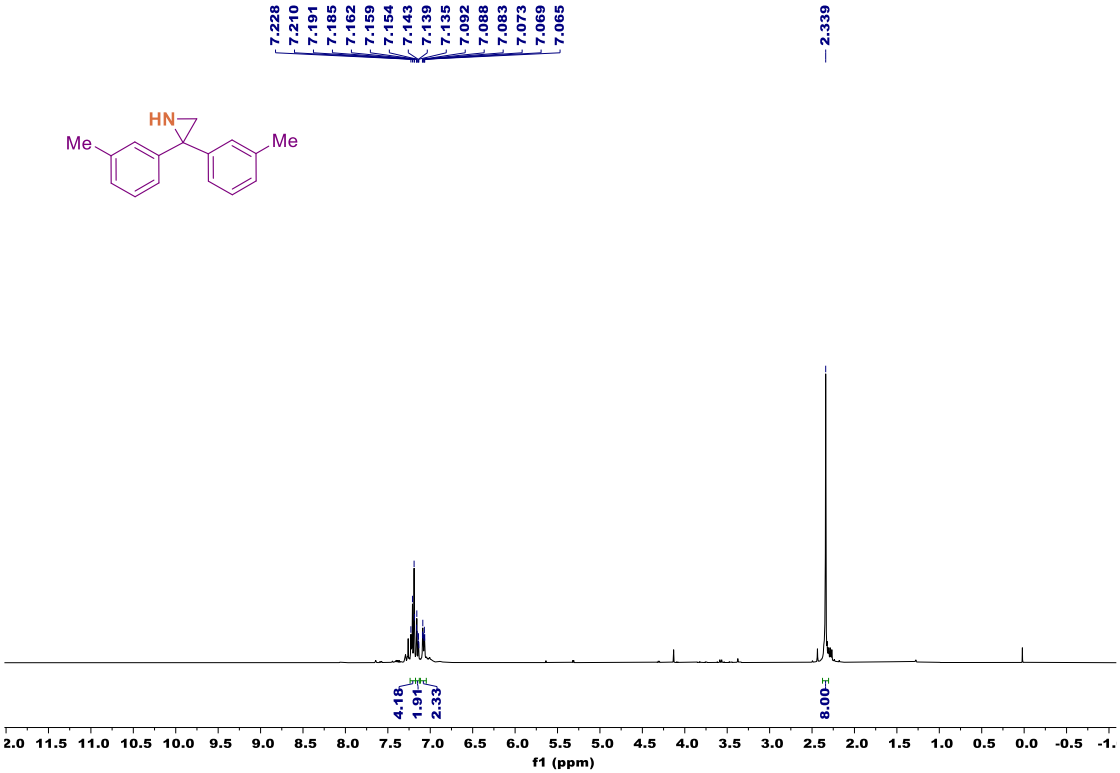



**$^{13}$C NMR** spectrum of **1f** (101 MHz, $CDCl_3$)

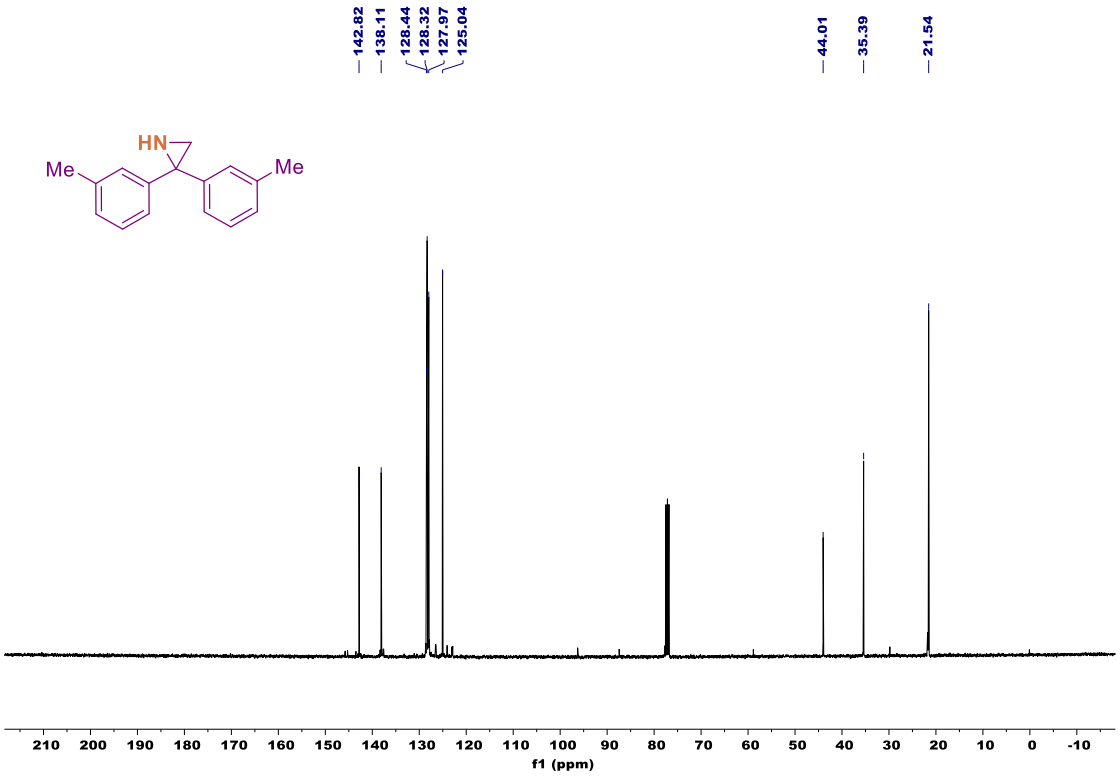



**$^{19}$F NMR** spectrum of **1f** (377 MHz, $CDCl_3$)

**2,2-Di-*m*-tolylaziridine (1g):**

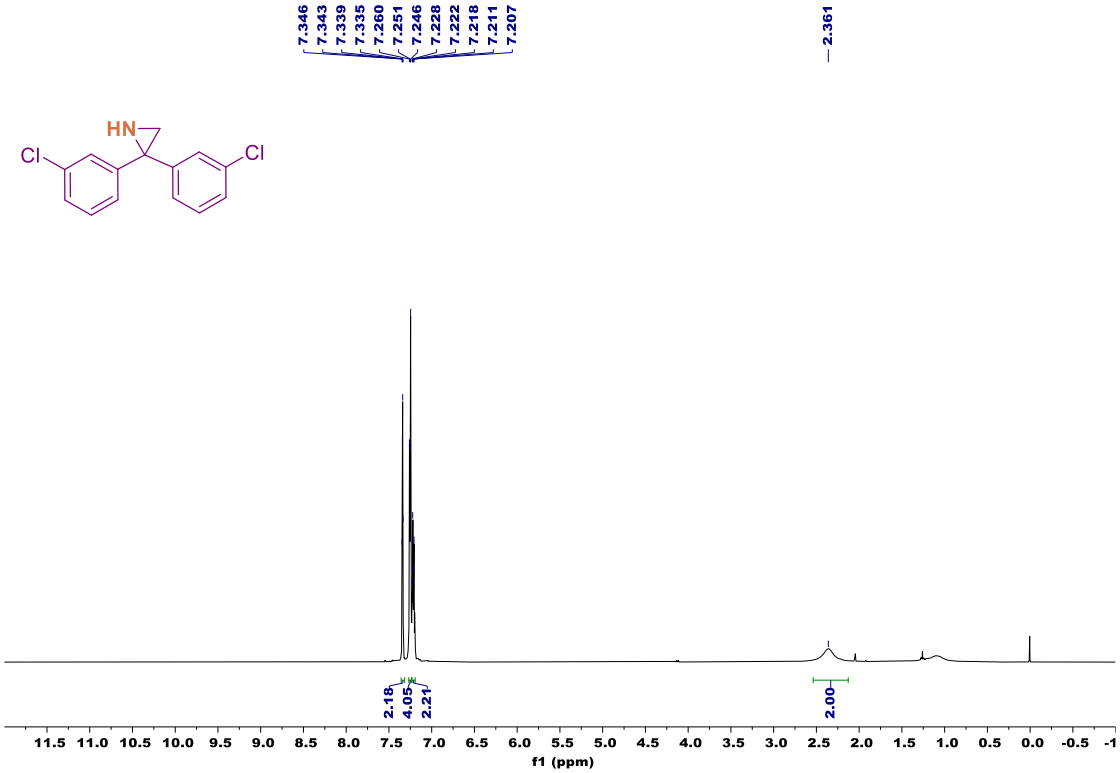



**$^{1}$H NMR** spectrum of **1g** (400 MHz, $CDCl_3$)

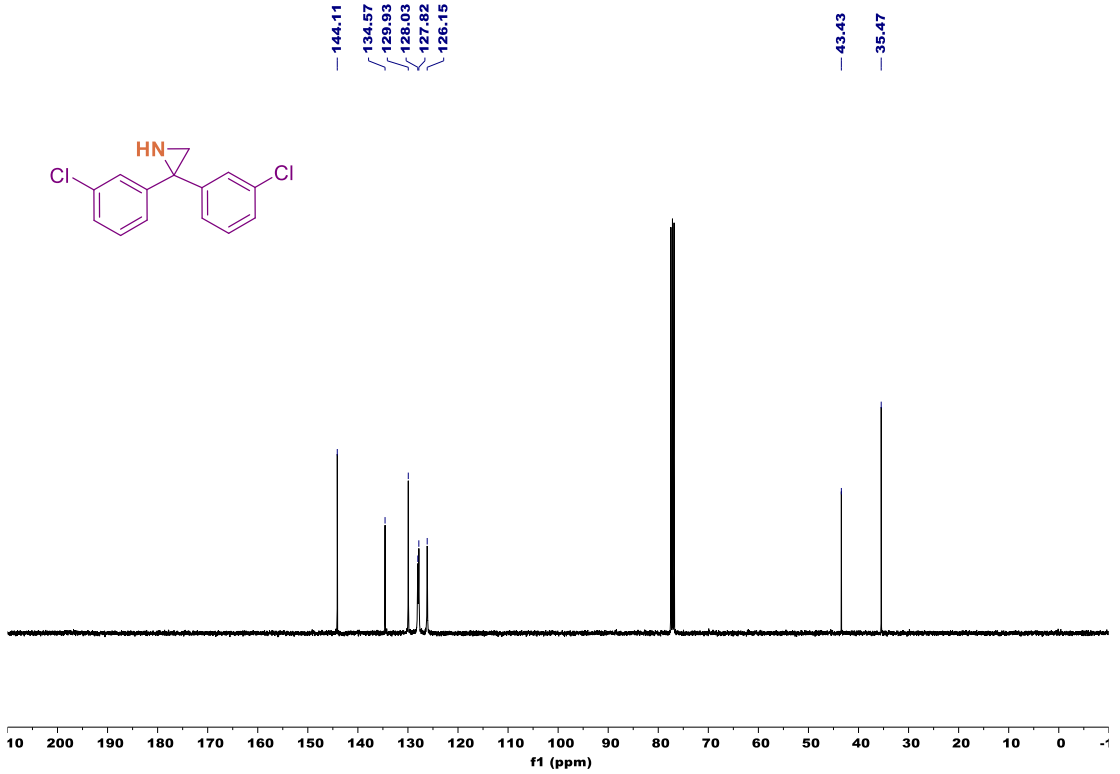



**$^{13}$C NMR** spectrum of **1g** (101 MHz, $CDCl_3$)

**2,2-Bis(3-chlorophenyl)aziridine (1h):**

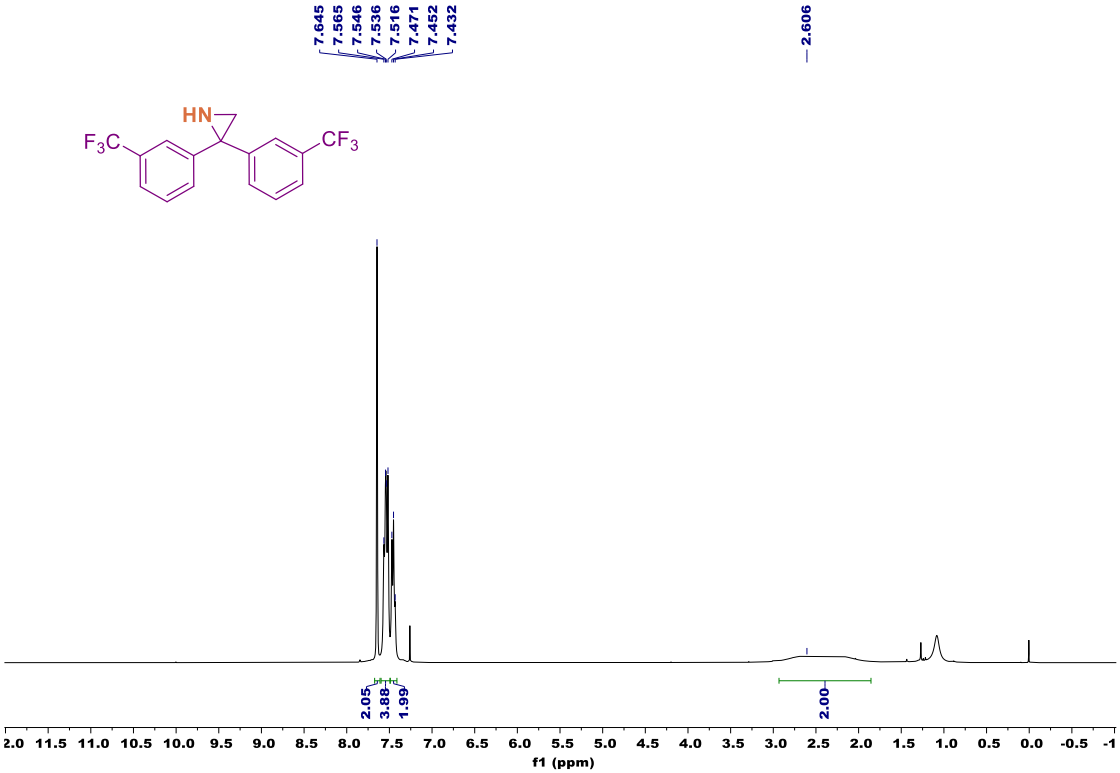



$^{1}$**H NMR** spectrum of **1h** (400 MHz, $CDCl_3$)

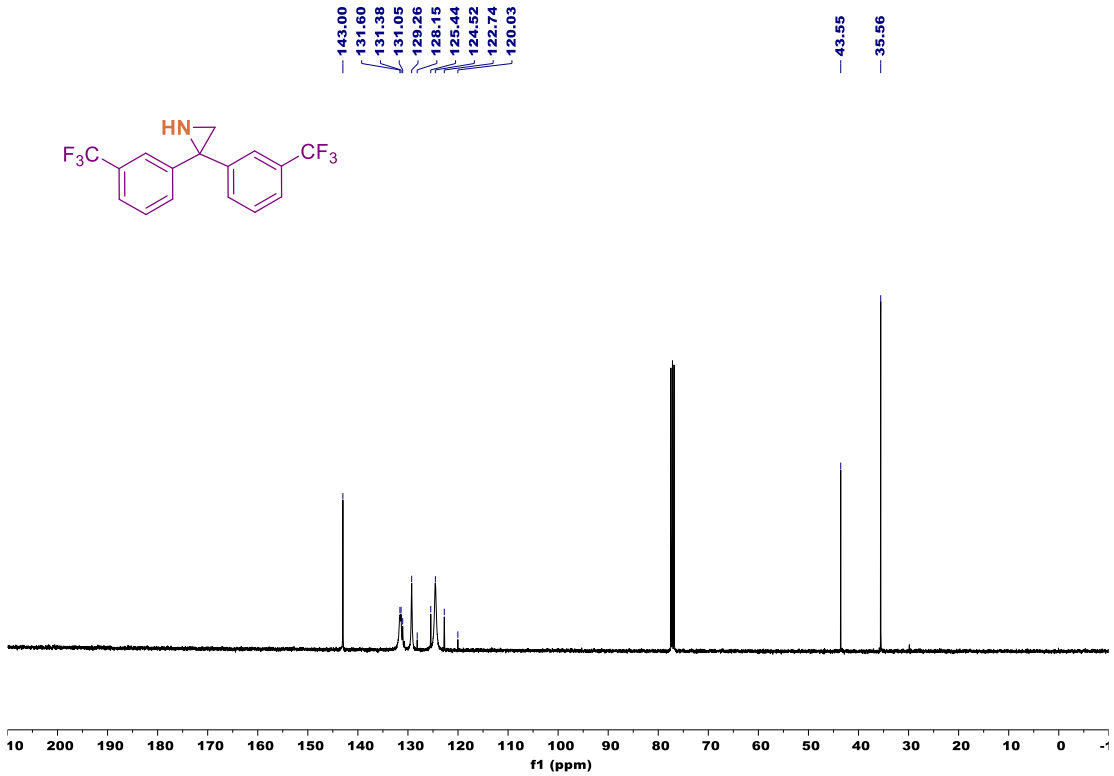



$^{13}$**C NMR** spectrum of **1h** (101 MHz, $CDCl_3$)

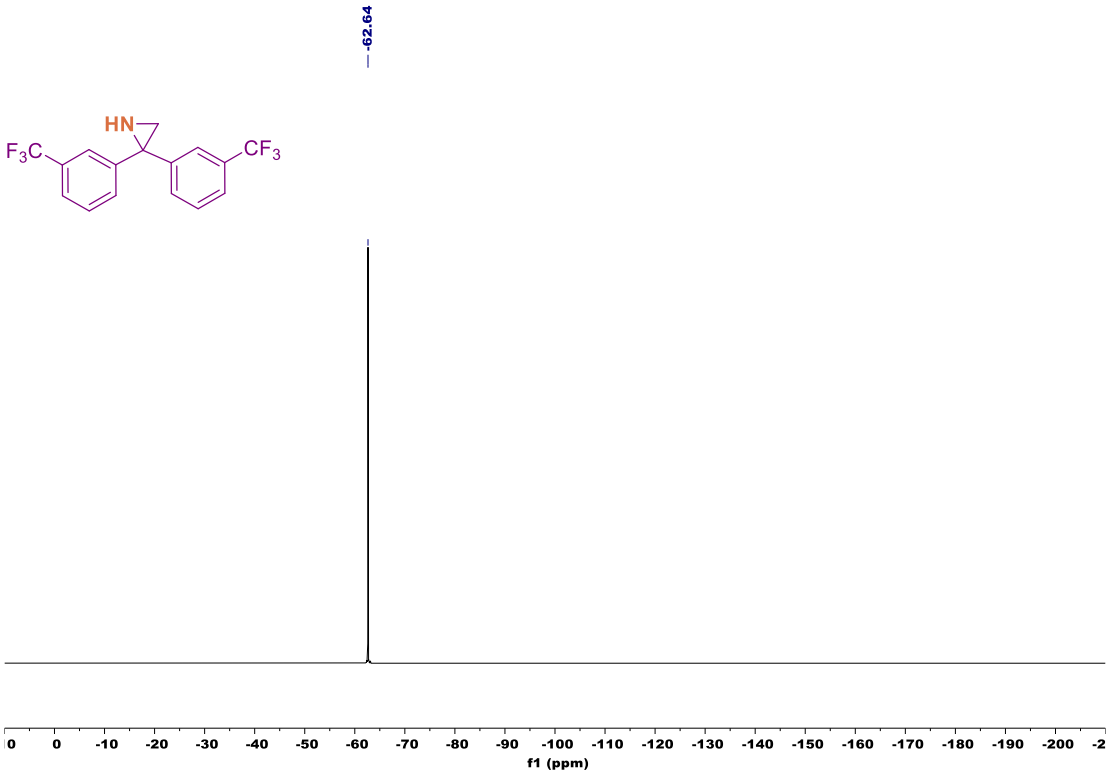
**2,2-Bis(3-(trifluoromethyl)phenyl)aziridine (1i):**




**$^{1}$H NMR** spectrum of **1i** (400 MHz, $CDCl_3$)

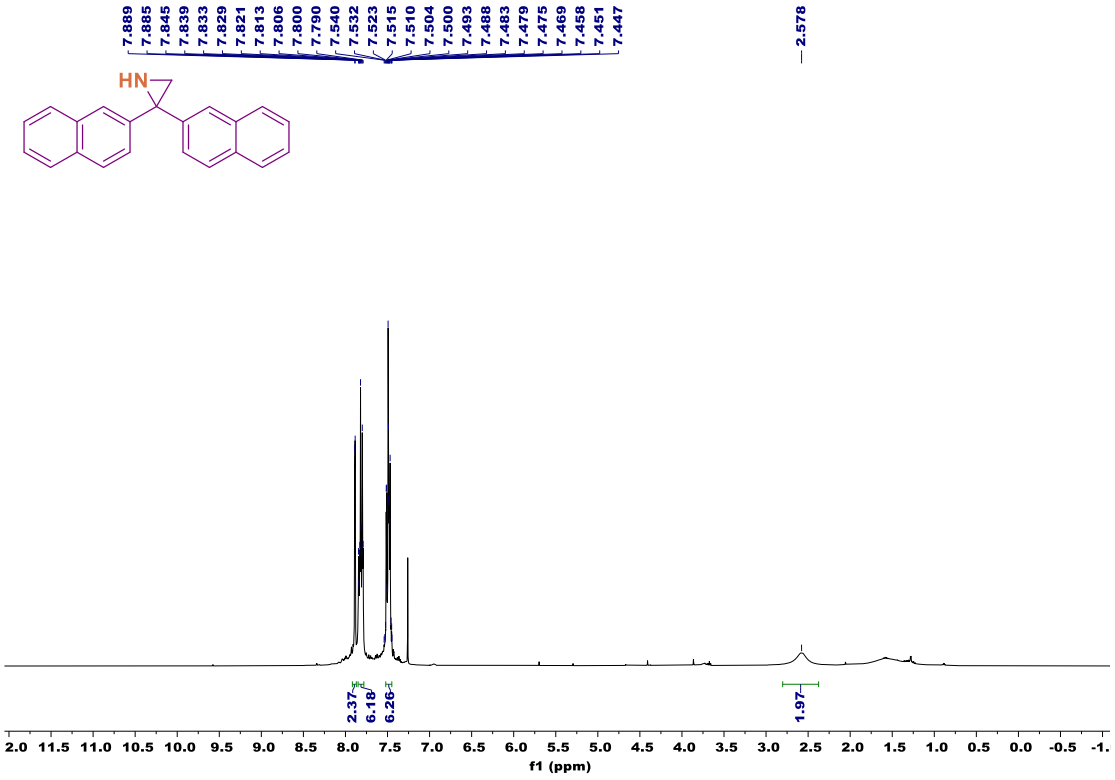



**$^{13}$C NMR** spectrum of **1i** (101 MHz, $CDCl_3$)

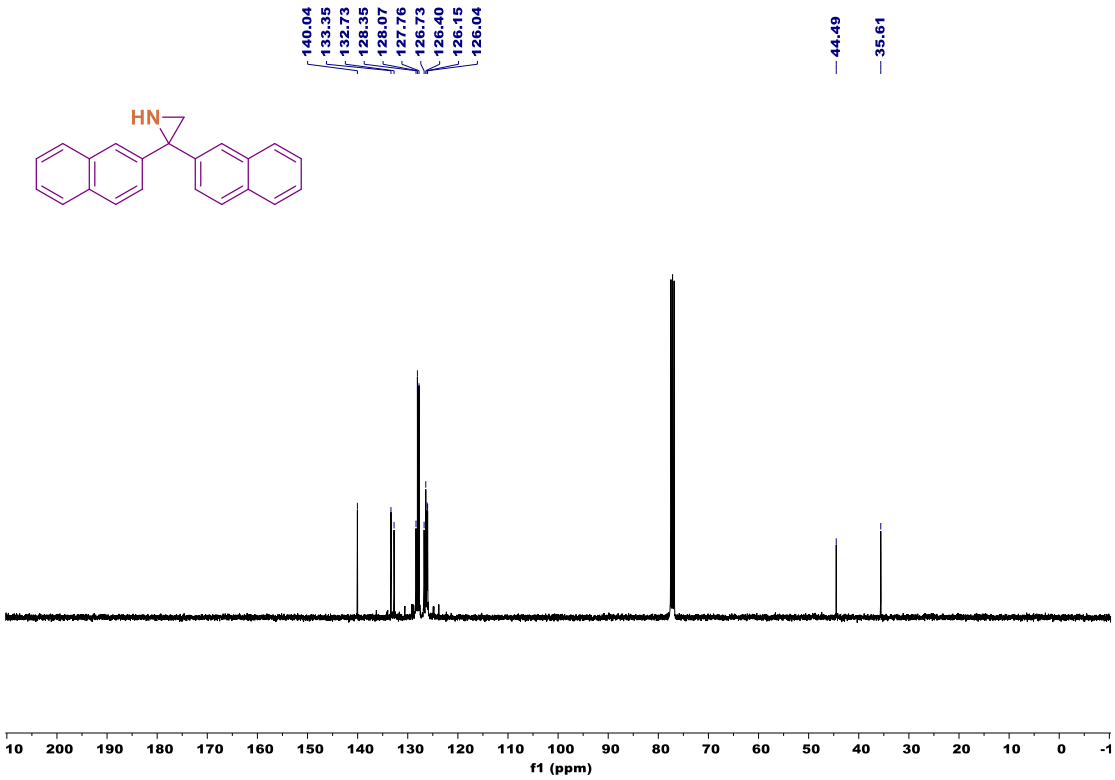



**$^{19}$F NMR** spectrum of **1i** (377 MHz, $CDCl_3$)

**2,2-Di(naphthalen-2-yl)aziridine (1j):**

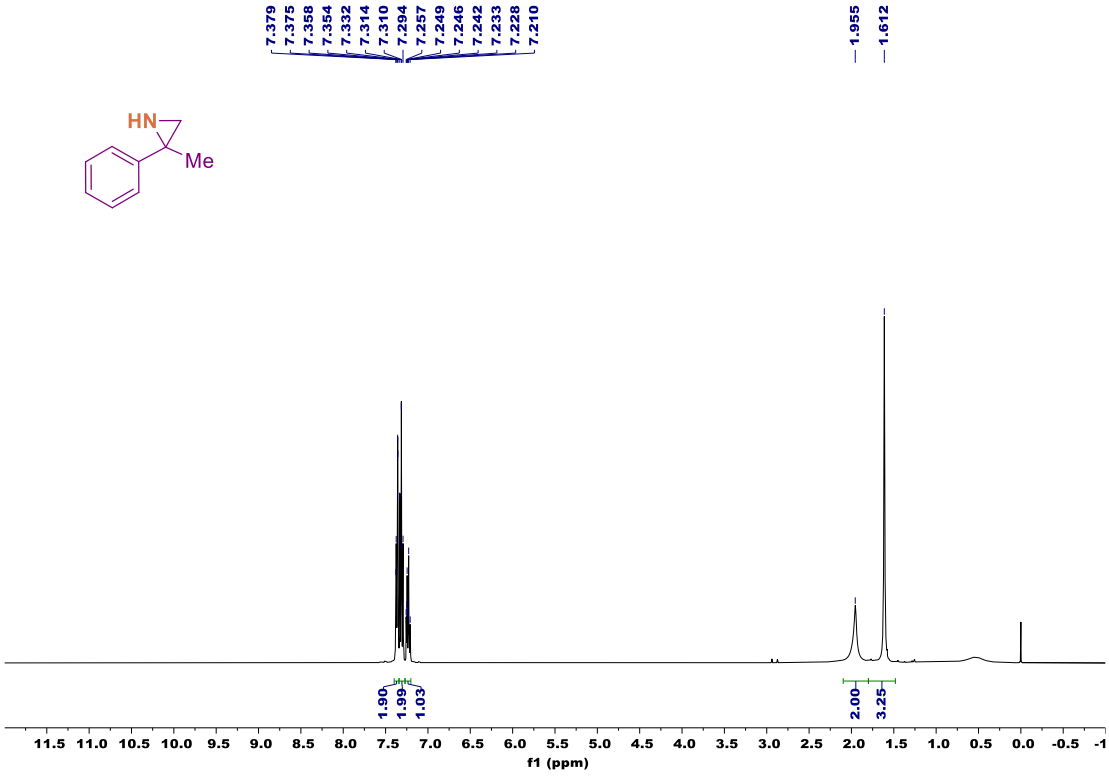



$^{1}$**H NMR** spectrum of **1j** (400 MHz, $CDCl_3$)



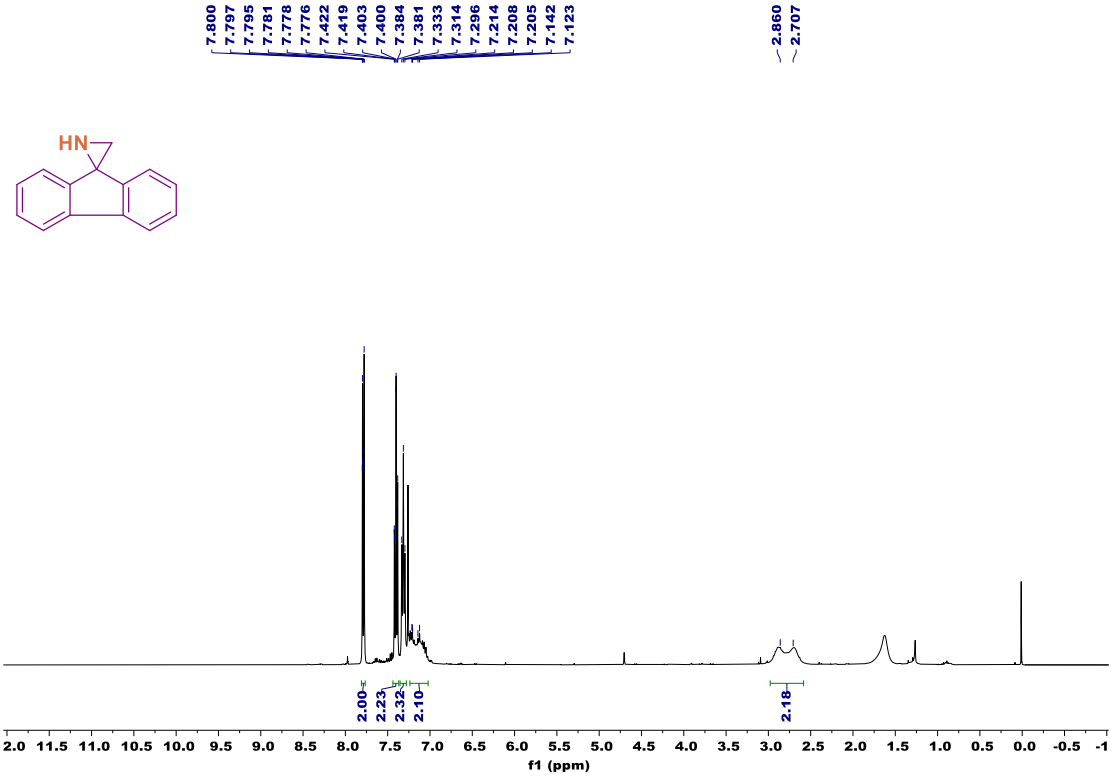

$^{13}$**C NMR** spectrum of **1j** (101 MHz, $CDCl_3$)

**2-Methyl-2-phenylaziridine (1k)**

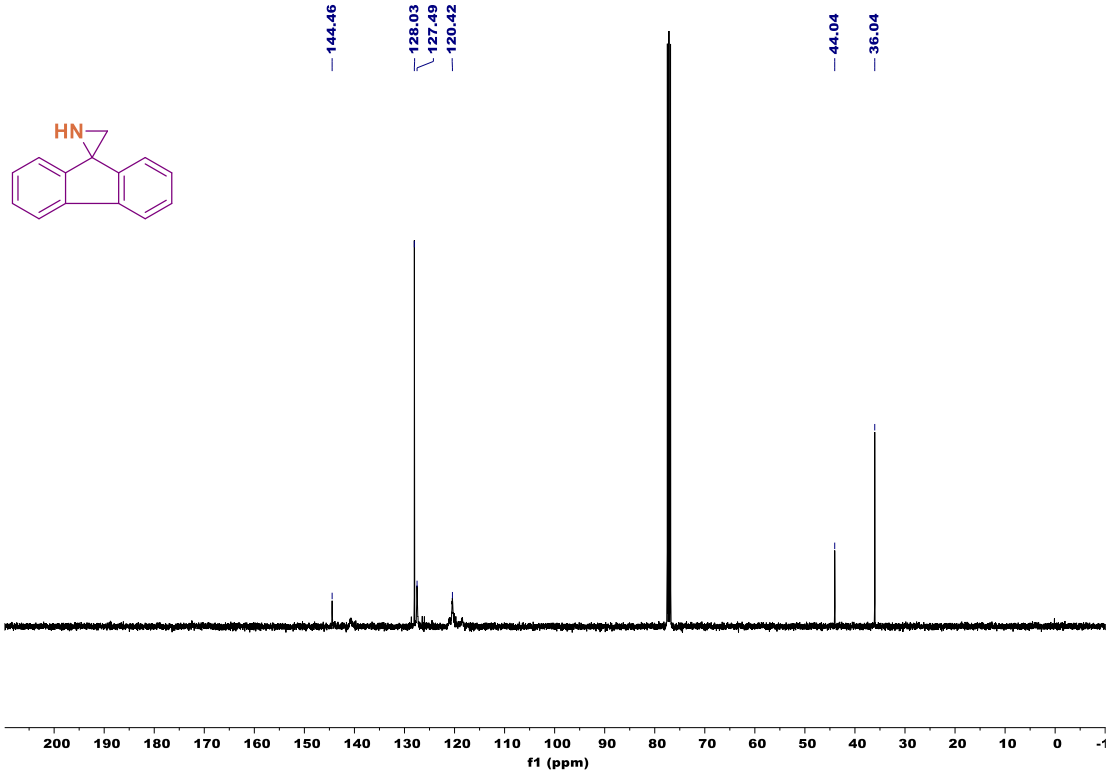



**$^1$H NMR** spectrum of **1k** (400 MHz, $CDCl_3$)

**Spiro[aziridine-2,9'-fluorene] (1l):**

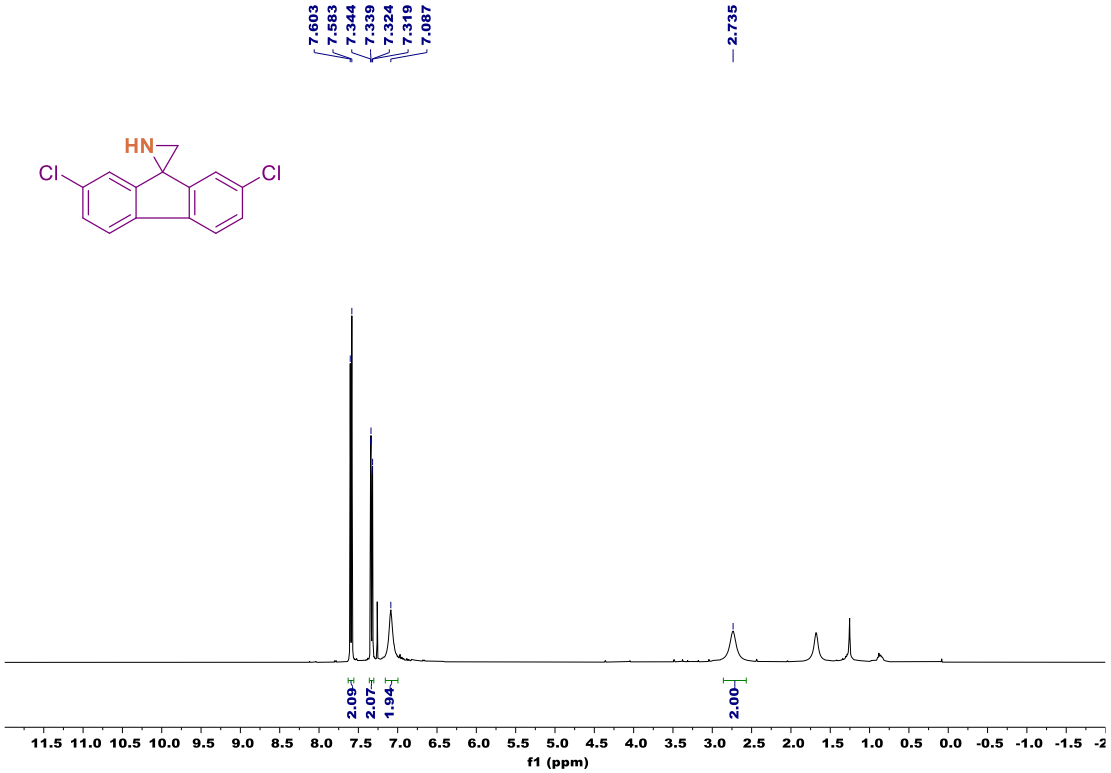



$^{1}$**H NMR** spectrum of **1l** (400 MHz, $CDCl_3$)

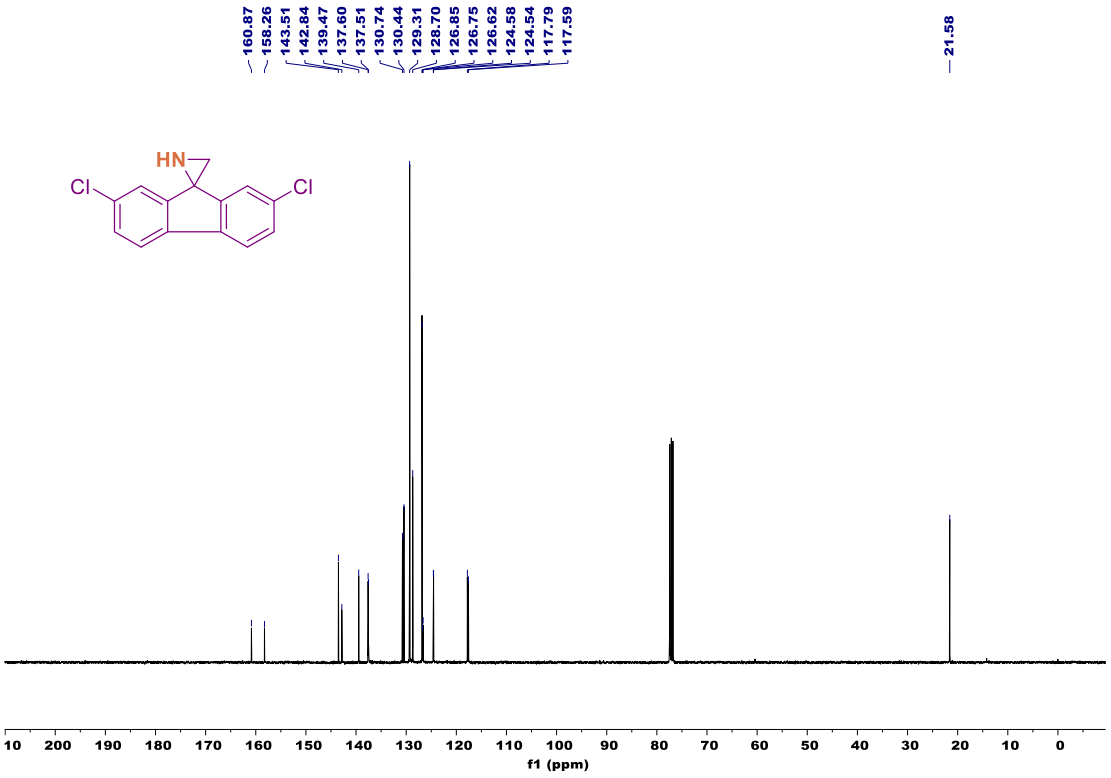



$^{13}$**C NMR** spectrum of **1l** (101 MHz, $CDCl_3$)

**3',6'-Dibromospiro[aziridine-2,9'-fluorene] (1m):**

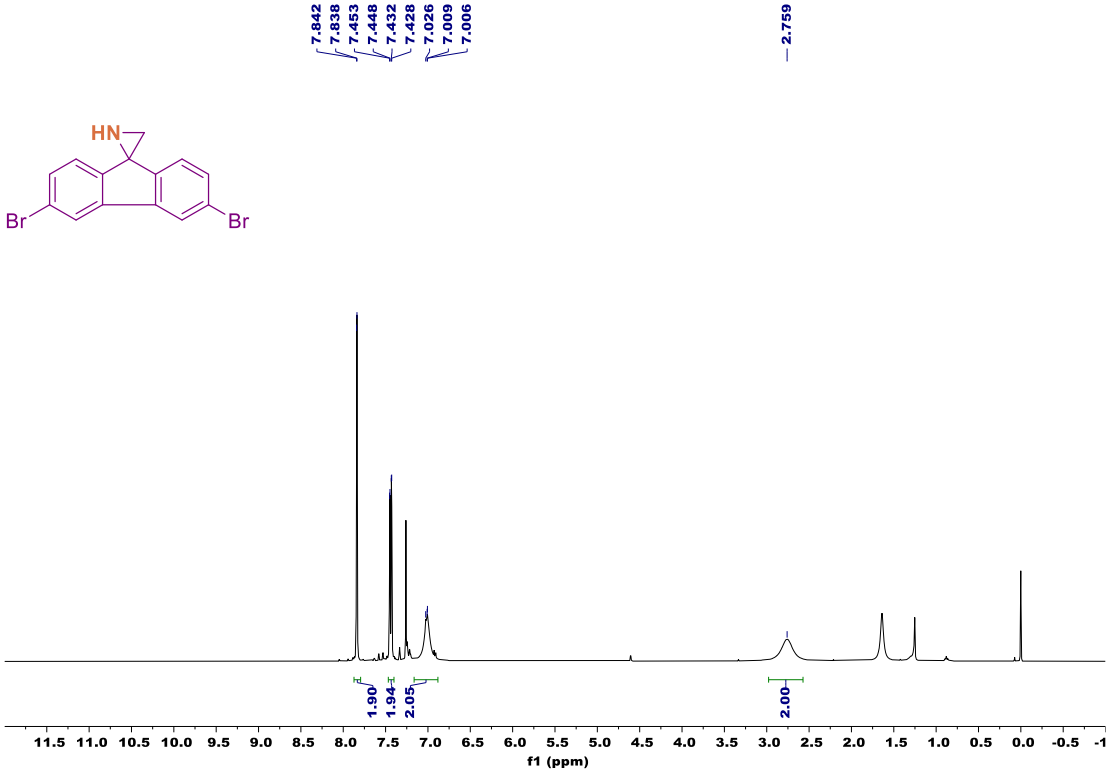



$^{1}$**H NMR** spectrum of **1m** (400 MHz, $CDCl_3$)

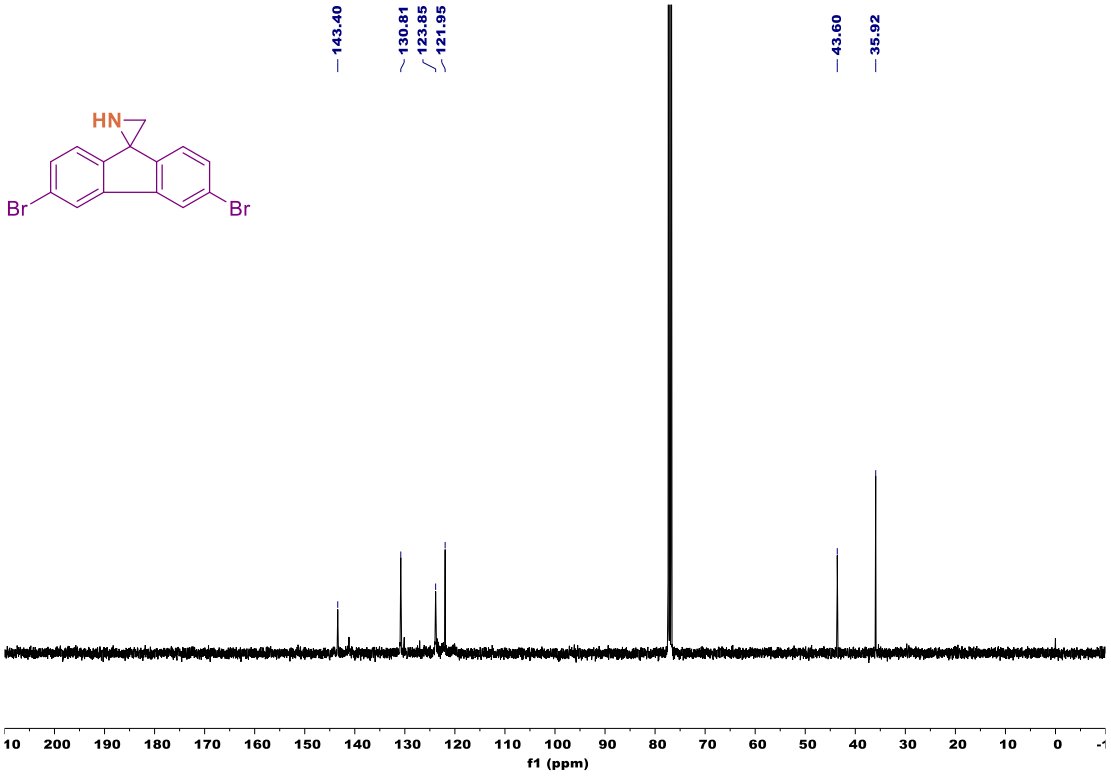



$^{13}$**C NMR** spectrum of **1m** (101 MHz, $CDCl_3$)

**2',7'-Dichlorospiro[aziridine-2,9'-fluorene] (1n):**

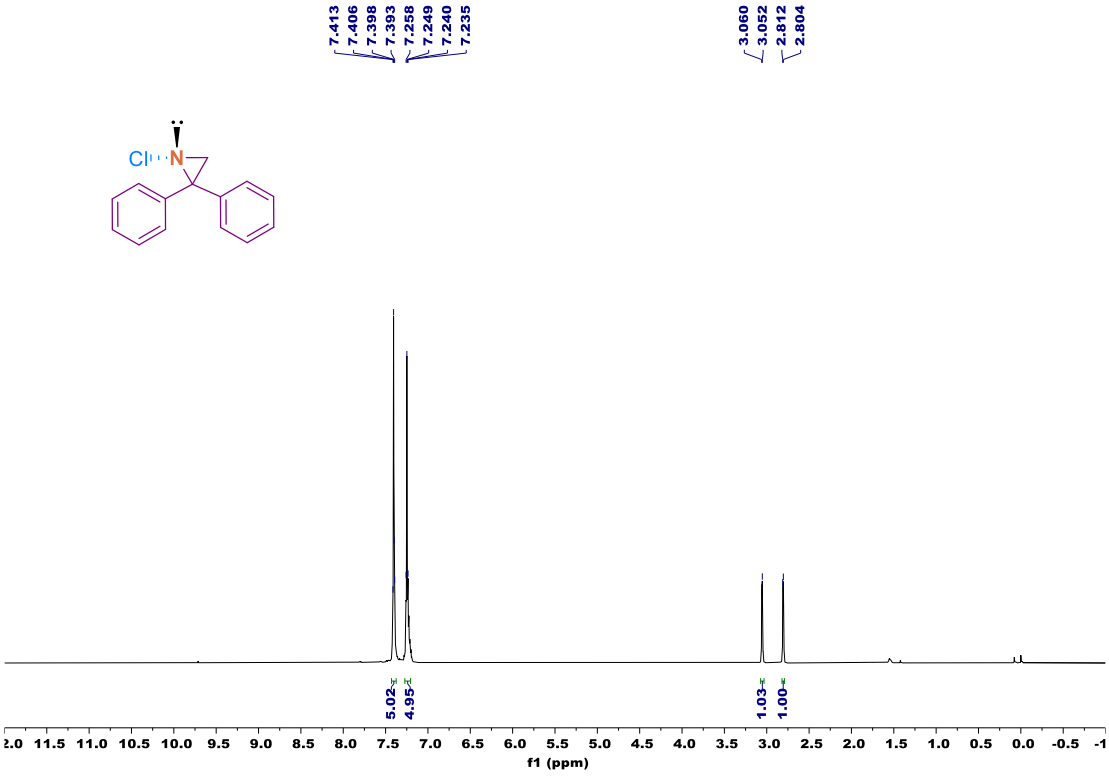



**$^{1}$H NMR** spectrum of **1n** (400 MHz, $CDCl_3$)

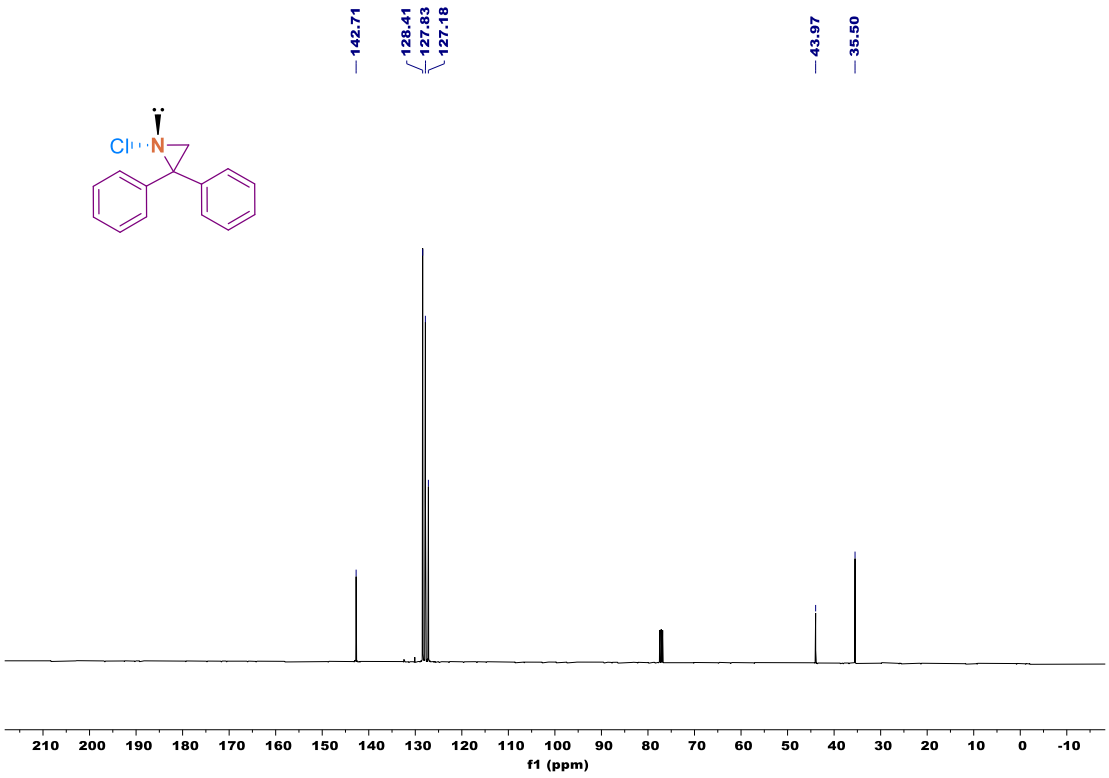



**$^{13}$C NMR** spectrum of **1n** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-diphenylaziridine (3a):**

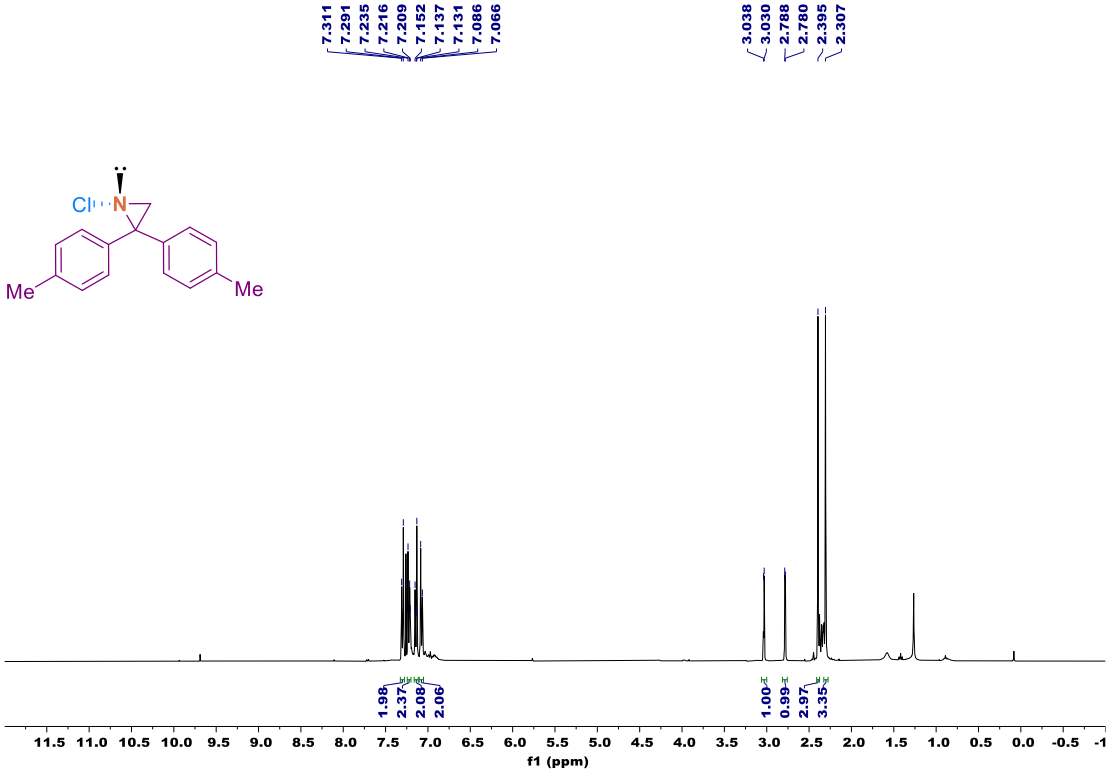



**$^{1}$H NMR** spectrum of **3a** (400 MHz, $CDCl_3$)

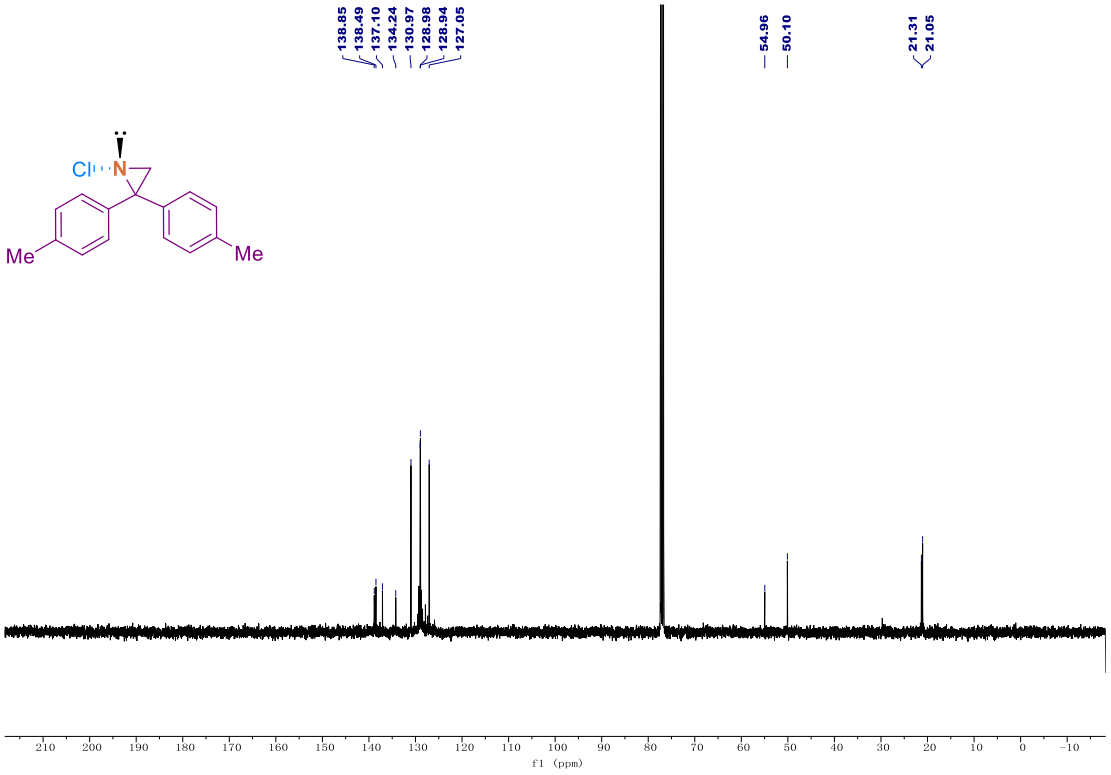



**$^{13}$C NMR** spectrum of **3a** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-di-*p*-tolylaziridine (3b):**

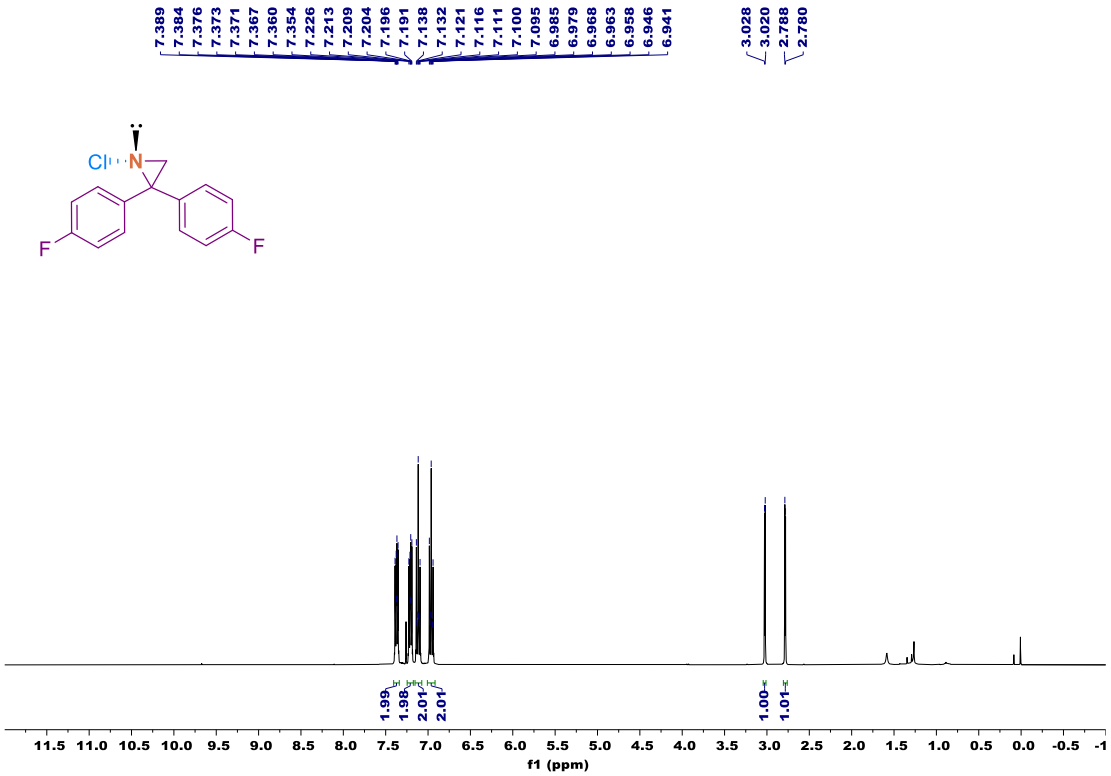



$^{1}$**H NMR** spectrum of **3b** (400 MHz, $CDCl_3$)

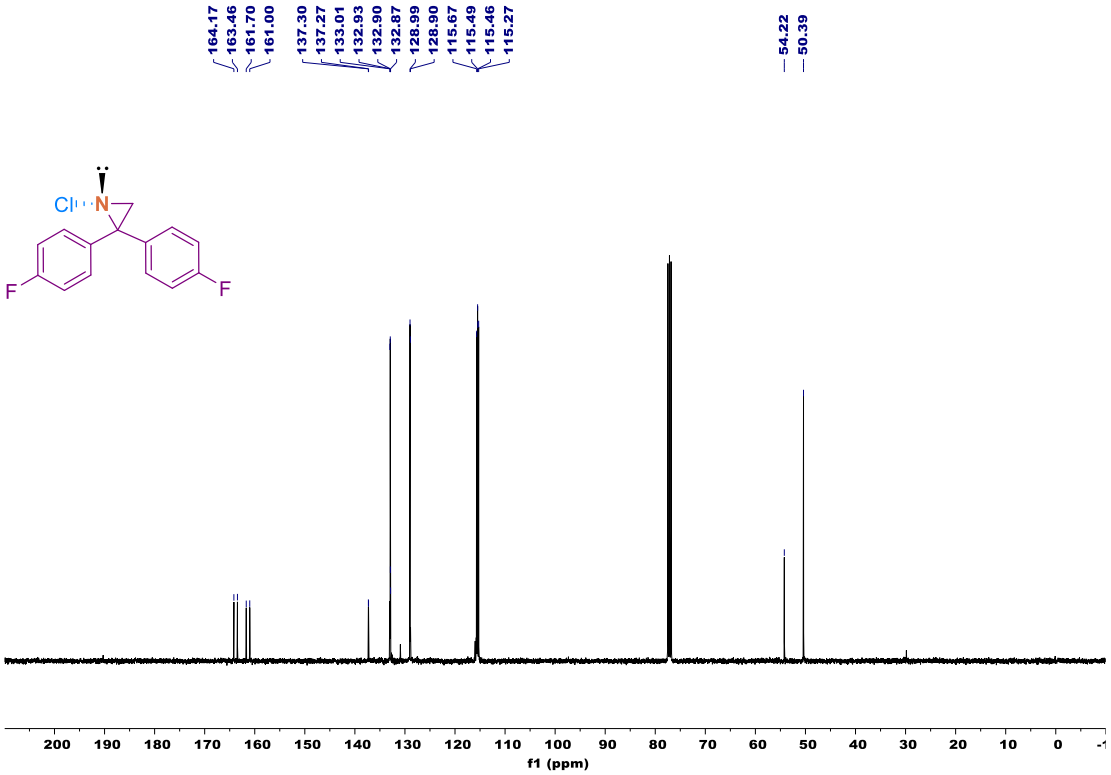



$^{13}$**C NMR** spectrum of **3b** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-bis(4-fluorophenyl)aziridine (3c):**



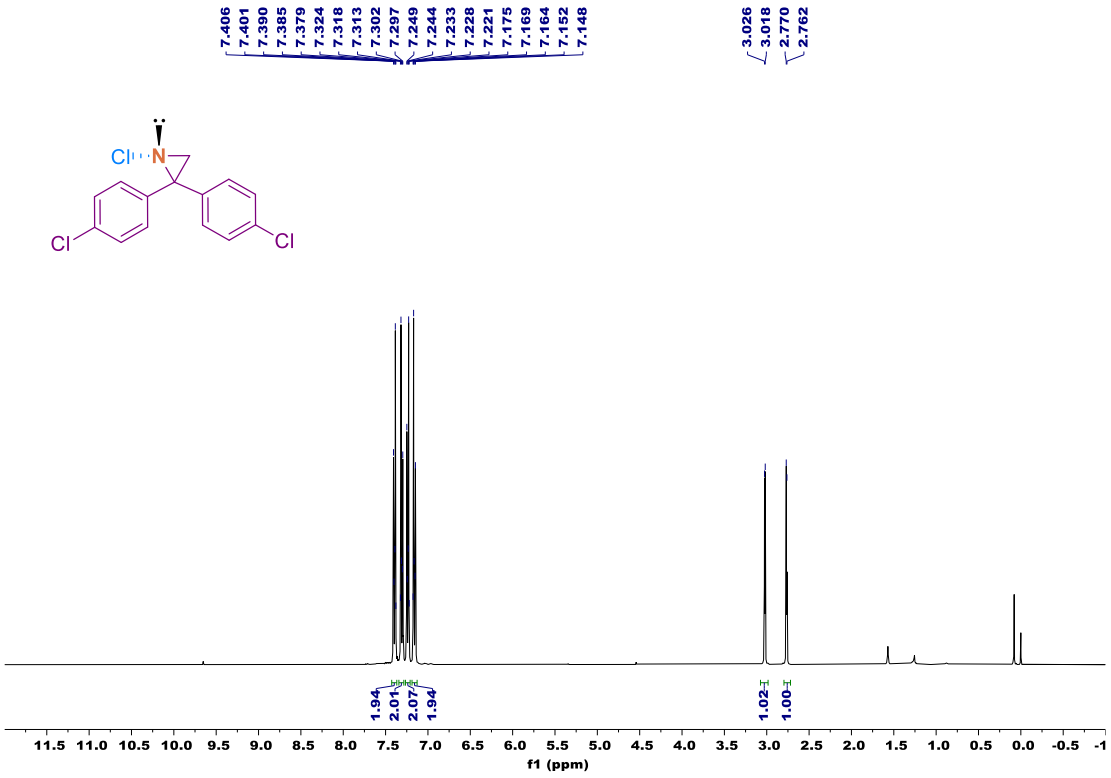

**$^{1}$H NMR** spectrum of **3c** (400 MHz, $CDCl_3$)



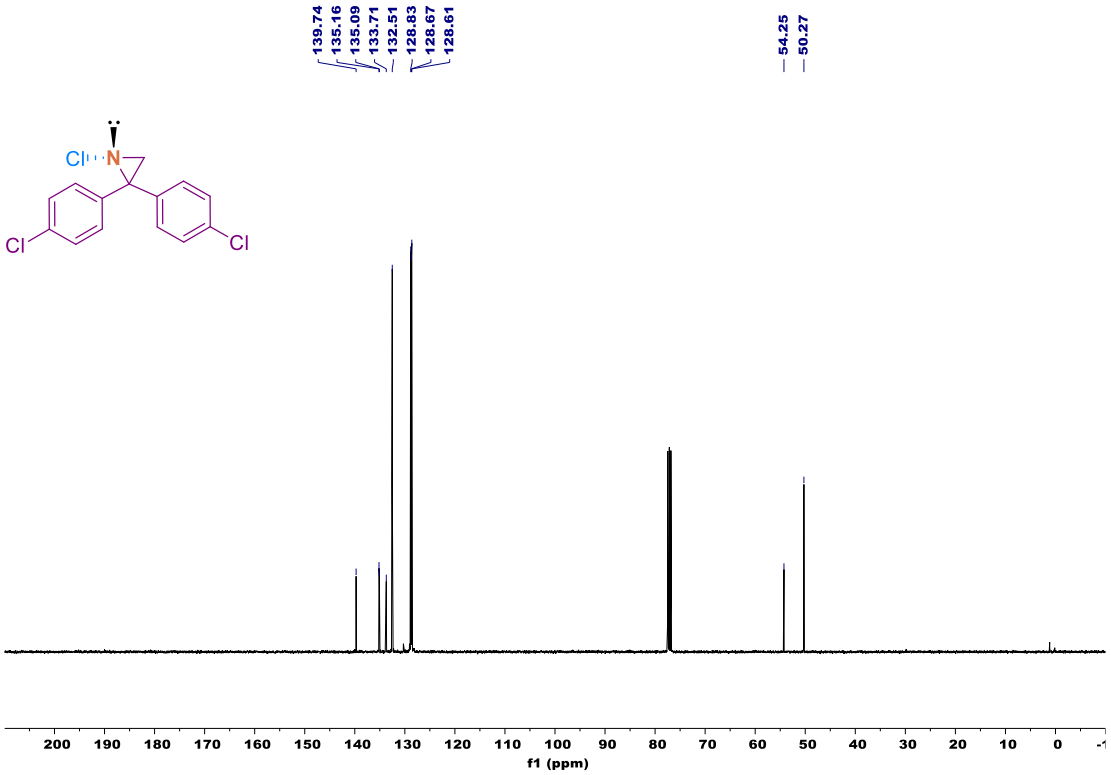

**$^{13}$C NMR** spectrum of **3c** (101 MHz, $CDCl_3$)


**$^{19}$F NMR** spectrum of **3c** (377 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-bis(3-chlorophenyl)aziridine (3d):**

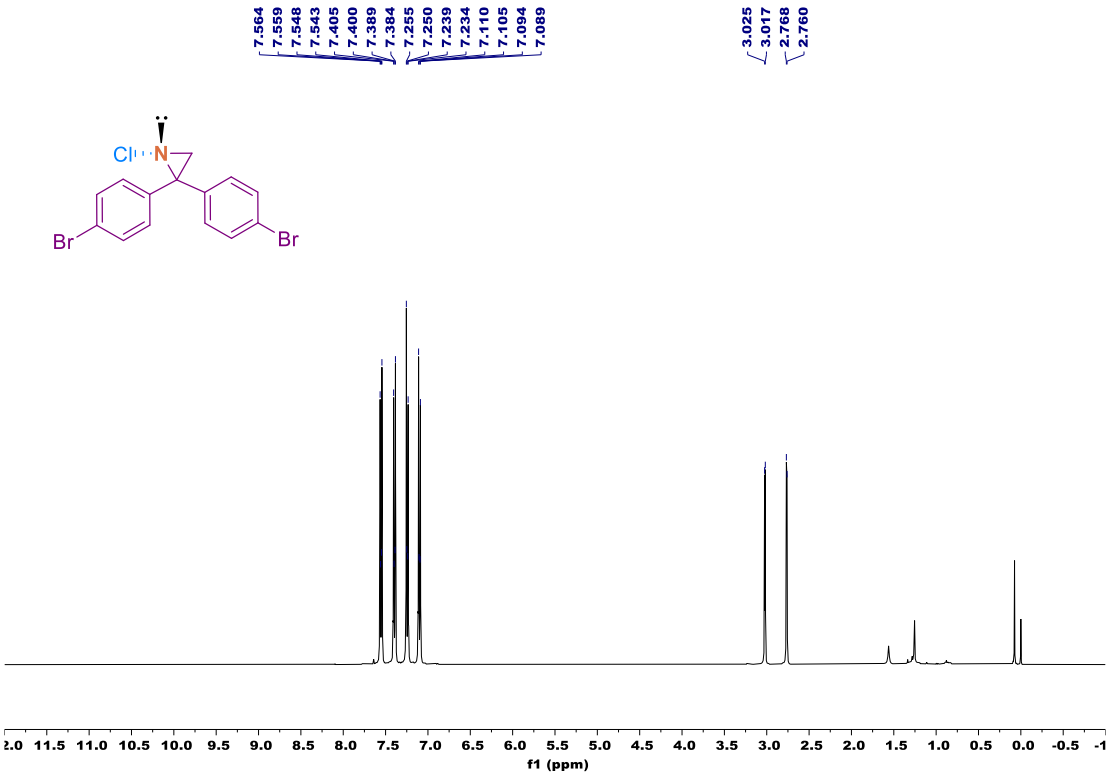



$^{1}$**H NMR** spectrum of **3d** (400 MHz, $CDCl_3$)

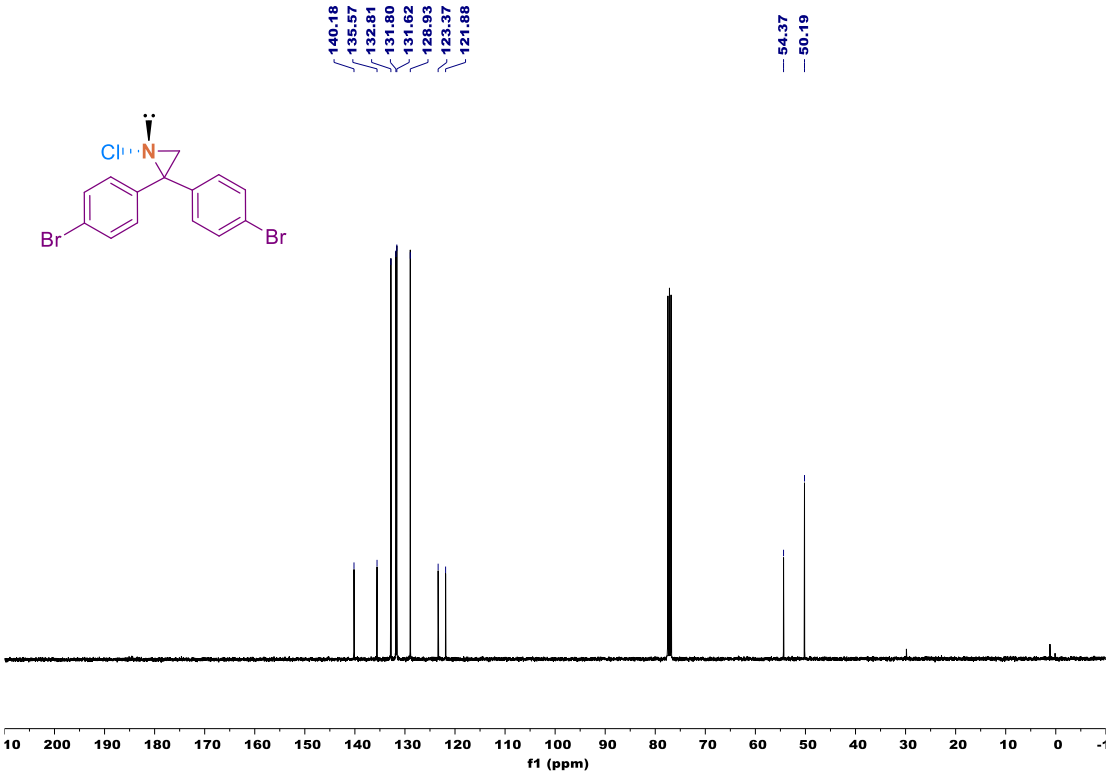



$^{13}$**C NMR** spectrum of **3d** (101 MHz, $CDCl_3$)

**(*R*)-2,2-Bis(4-bromophenyl)-1-chloroaziridine (3e):**

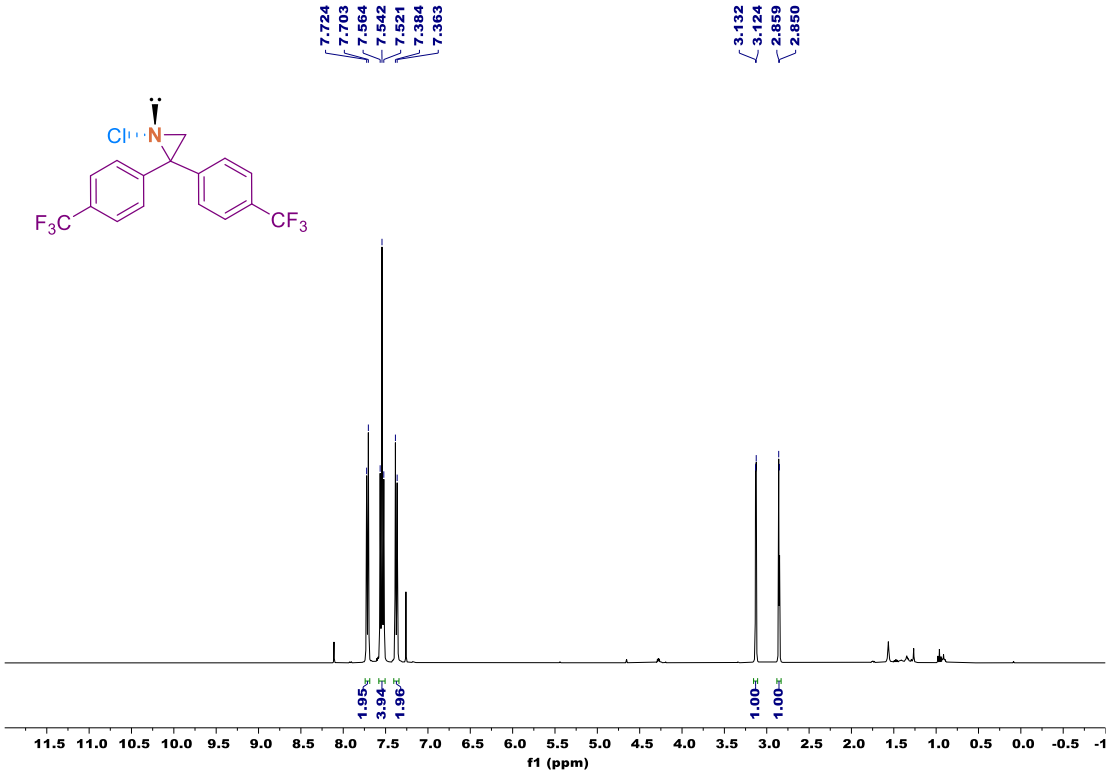



**$^{1}$H NMR** spectrum of **3e** (400 MHz, $CDCl_3$)

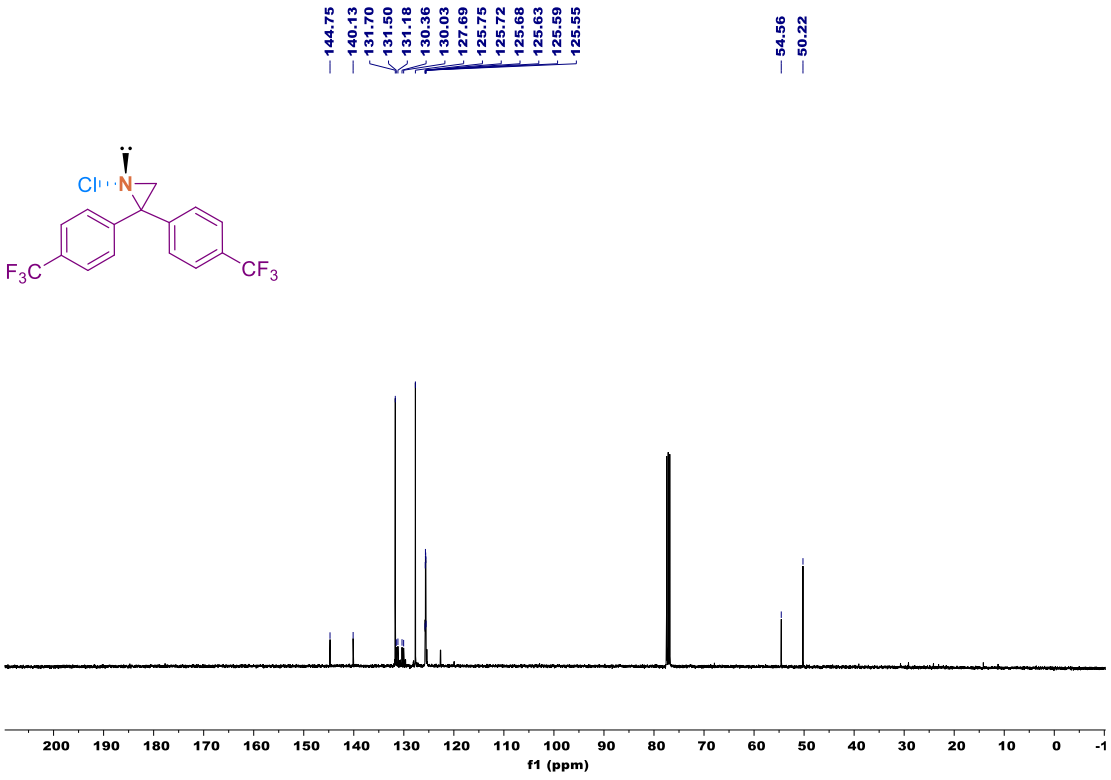



**$^{13}$C NMR** spectrum of **3e** (101 MHz, $CDCl_3$)

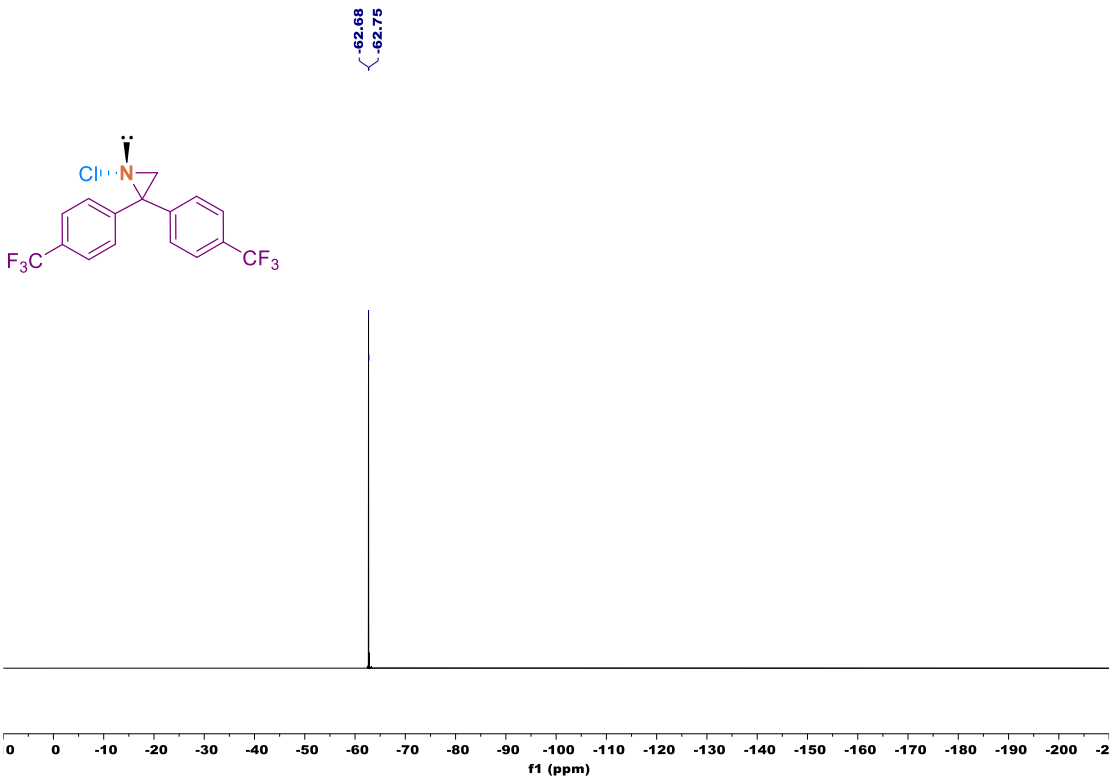
**(*R*)-1-Chloro-2,2-bis(4-(trifluoromethyl)phenyl)aziridine (3f):**




**$^{1}$H NMR** spectrum of **3f** (400 MHz, $CDCl_3$)

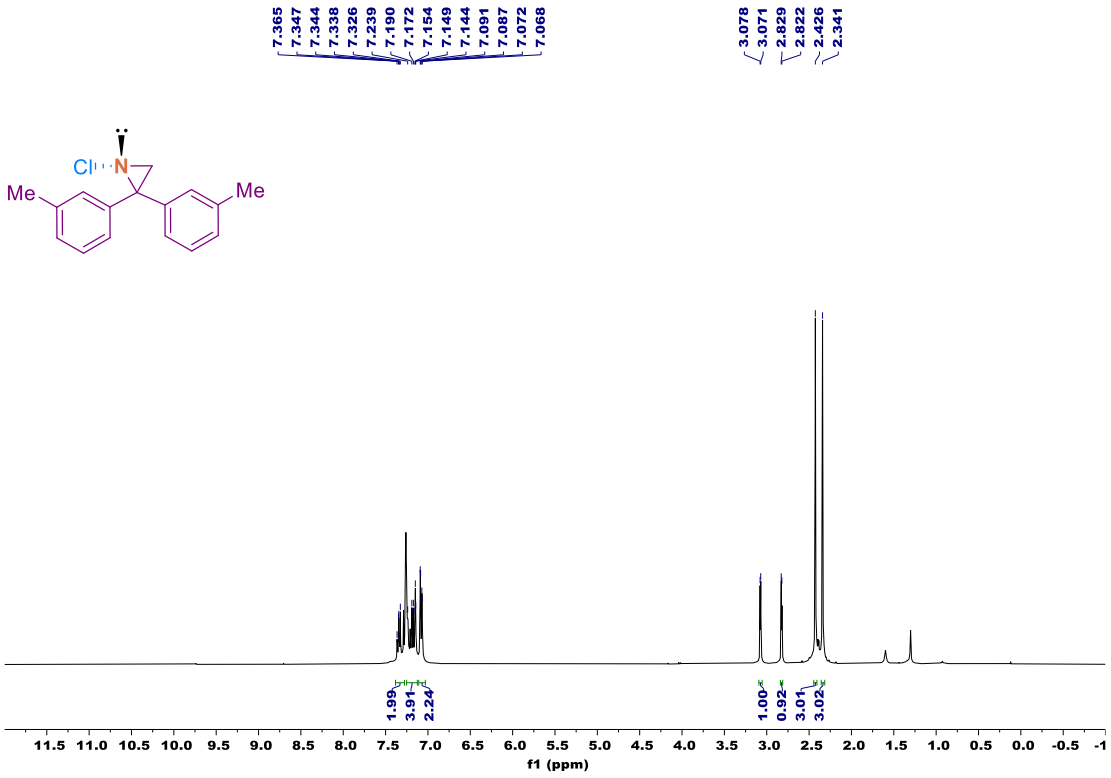



**$^{13}$C NMR** spectrum of **3f** (101 MHz, $CDCl_3$)

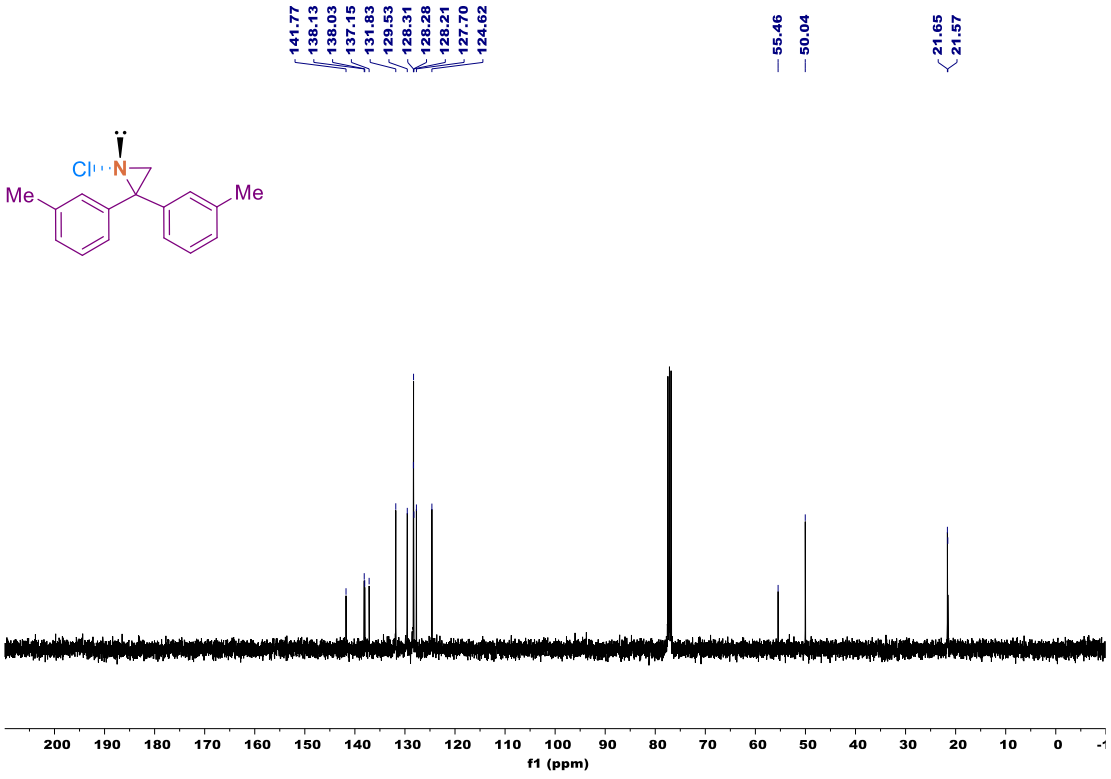



**$^{19}$F NMR** spectrum of **3f** (377 MHz, $CDCl_3$)

**(*R*)-2,6-Dichlorophenyl (3g):**

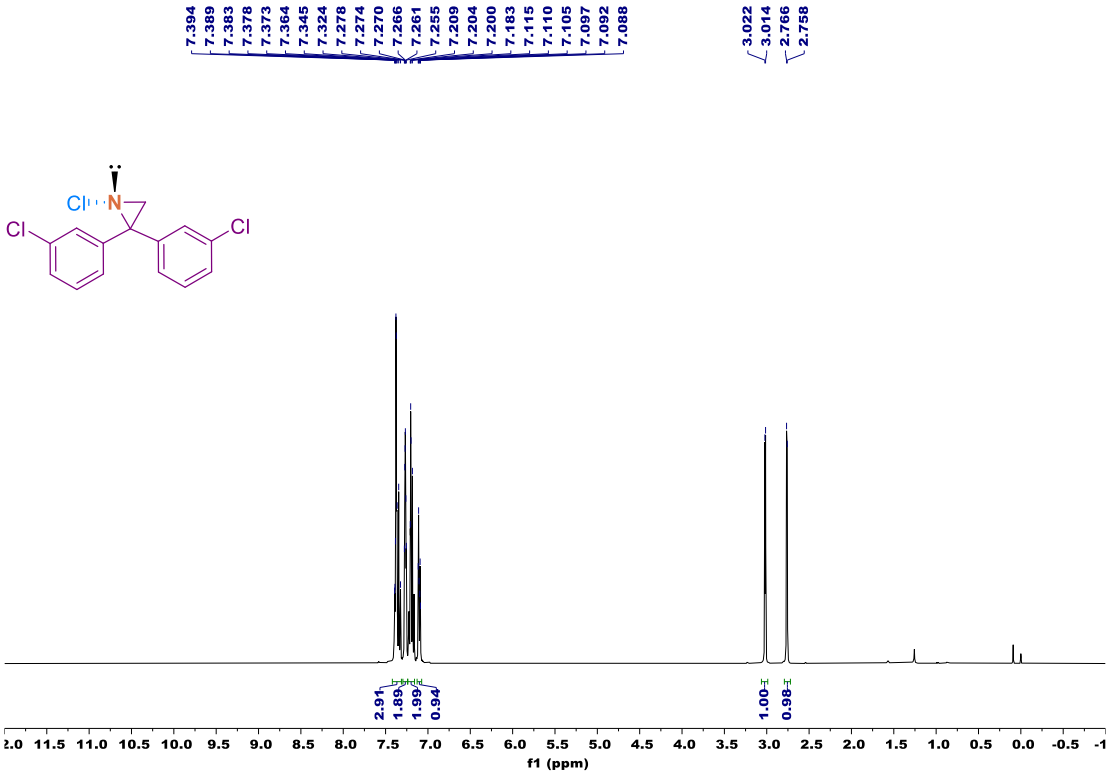



**$^{1}$H NMR** spectrum of **3g** (400 MHz, $CDCl_3$)

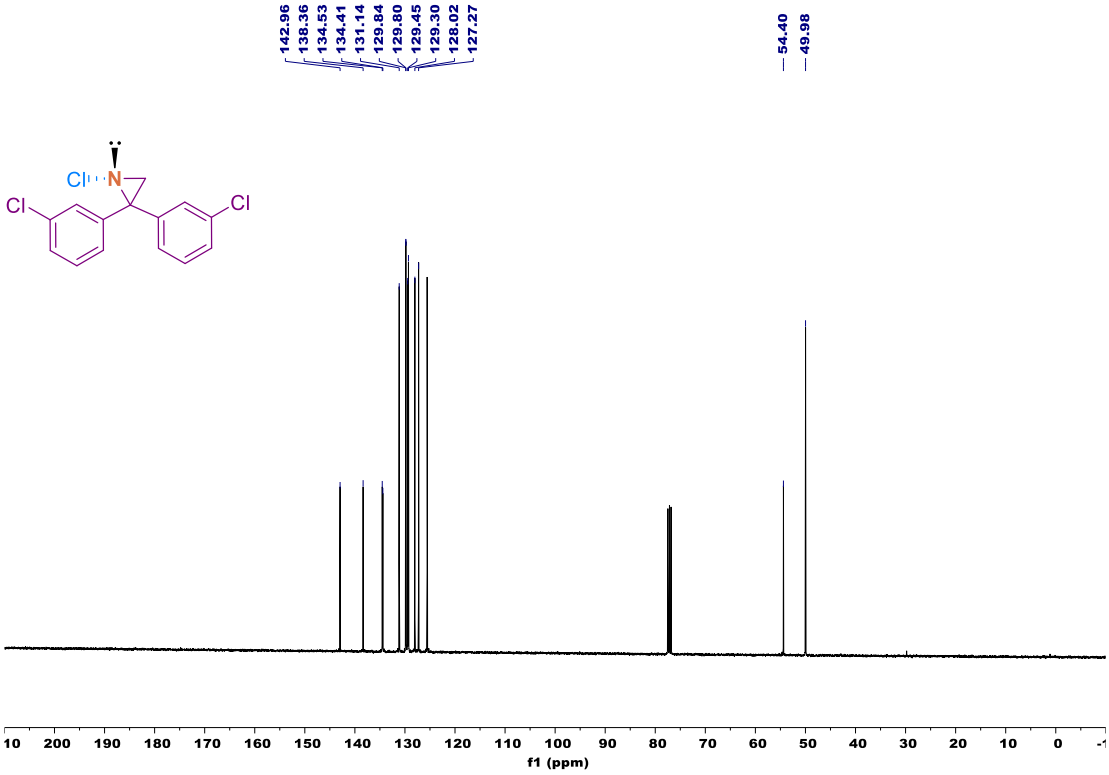



**$^{13}$C NMR** spectrum of **3g** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-bis(3-chlorophenyl)aziridine (3h):**

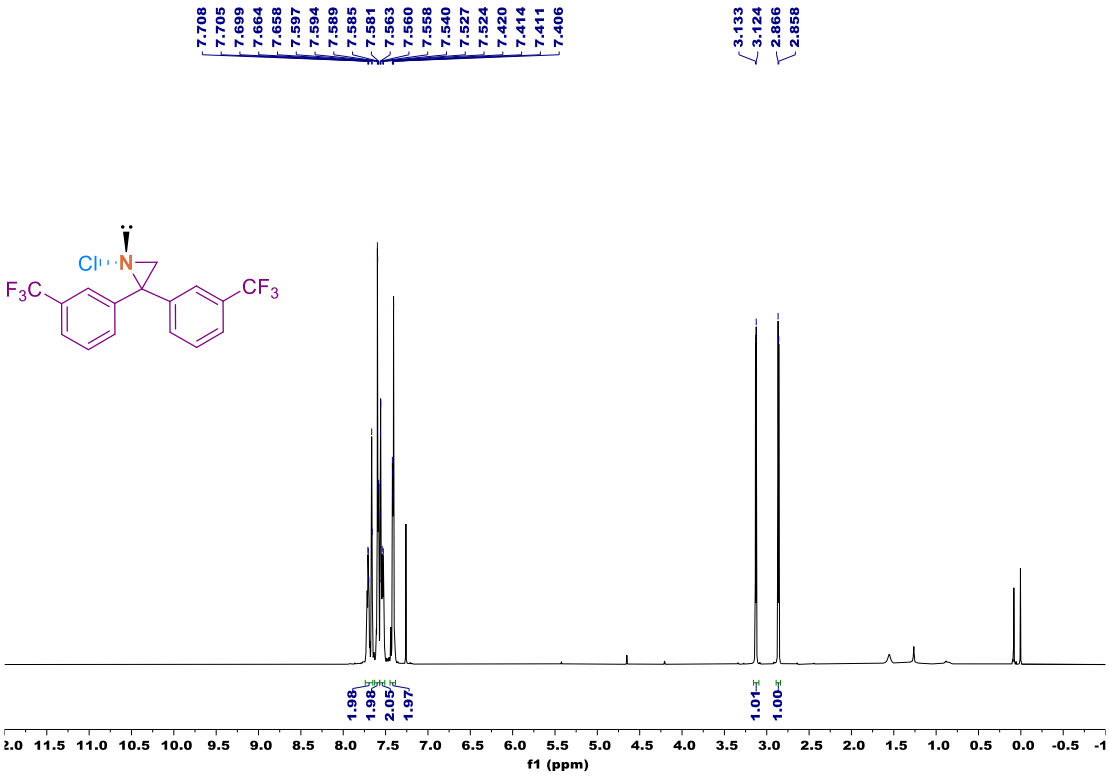



**$^{1}$H NMR** spectrum of **3h** (400 MHz, $CDCl_3$)

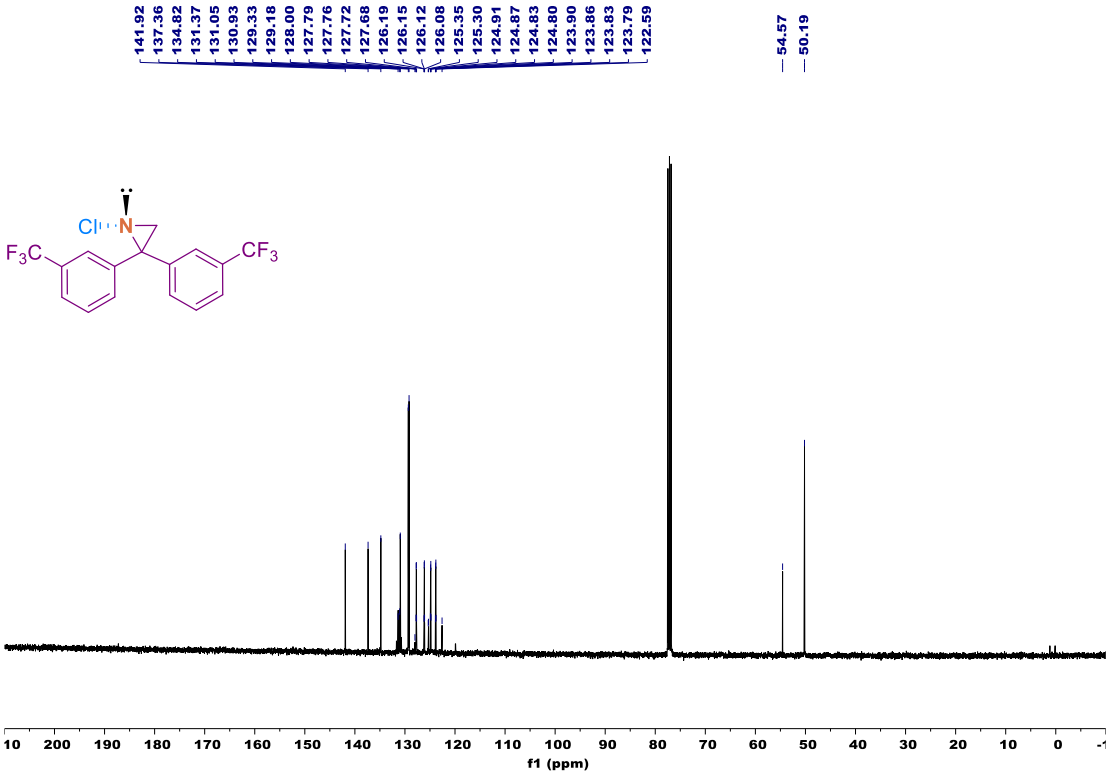



**$^{13}$C NMR** spectrum of **3h** (101 MHz, $CDCl_3$)

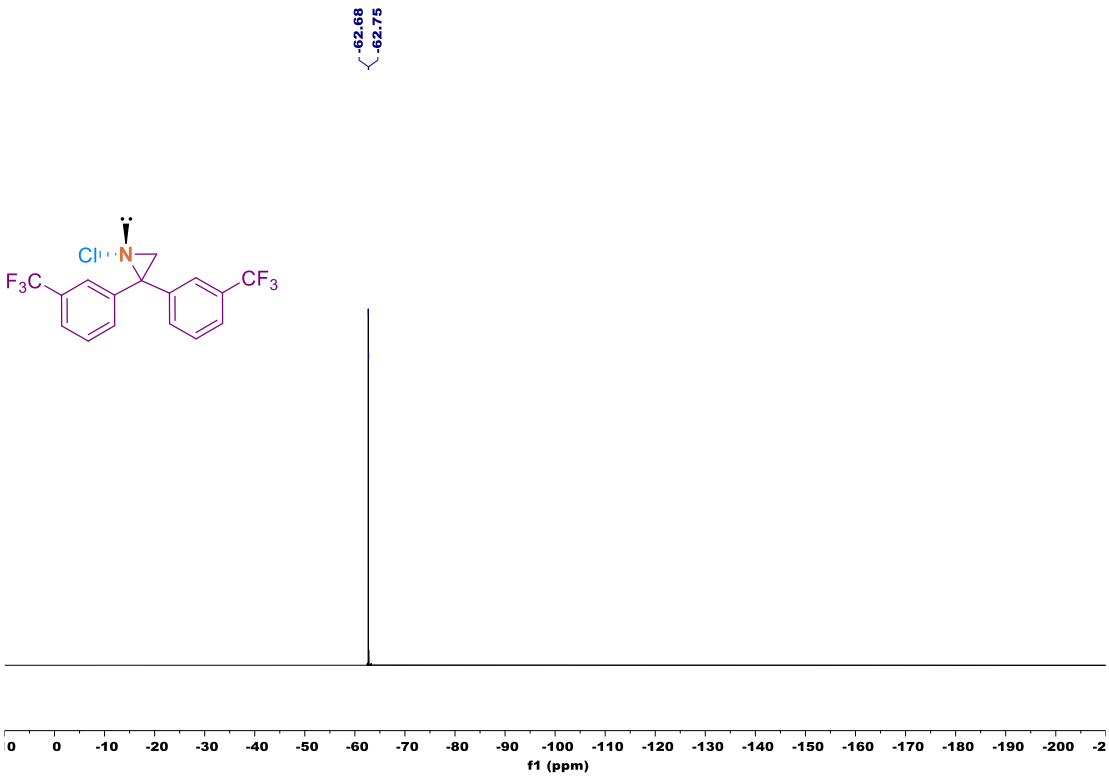
**(*R*)-1-Chloro-2,2-bis(3-(trifluoromethyl)phenyl)aziridine (3i):**




$^{1}$**H NMR** spectrum of **3i** (400 MHz, $CDCl_3$)

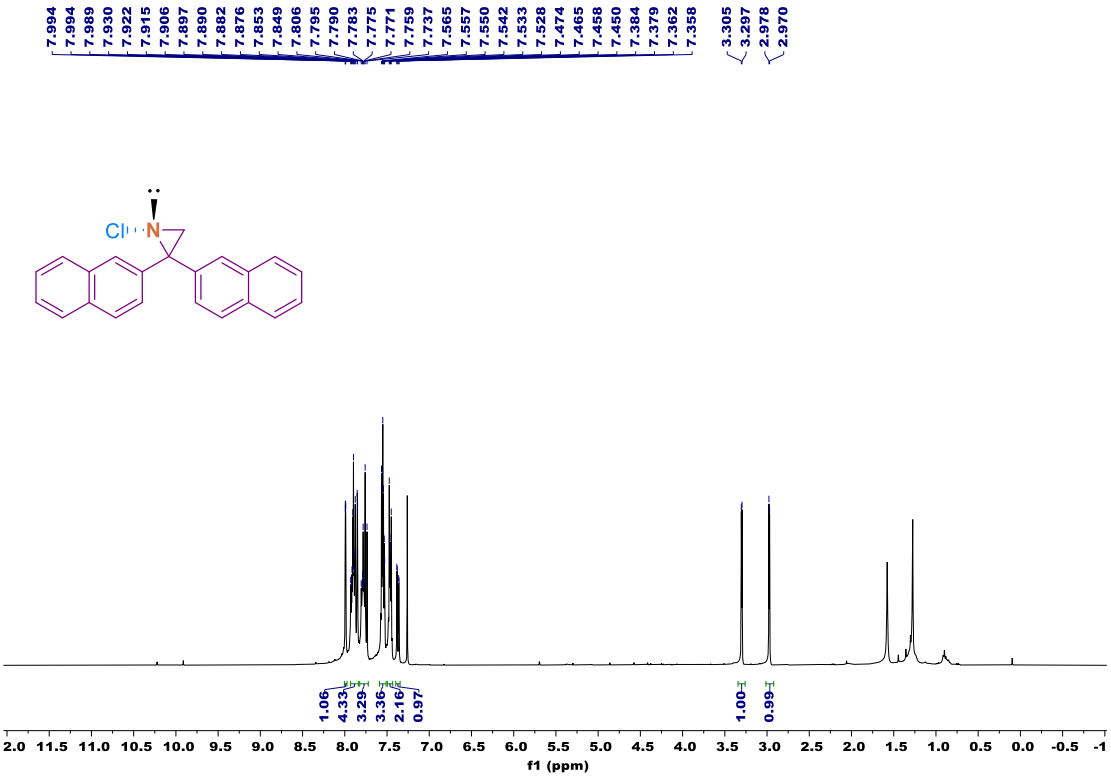



$^{13}$**C NMR** spectrum of **3i** (101 MHz, $CDCl_3$)

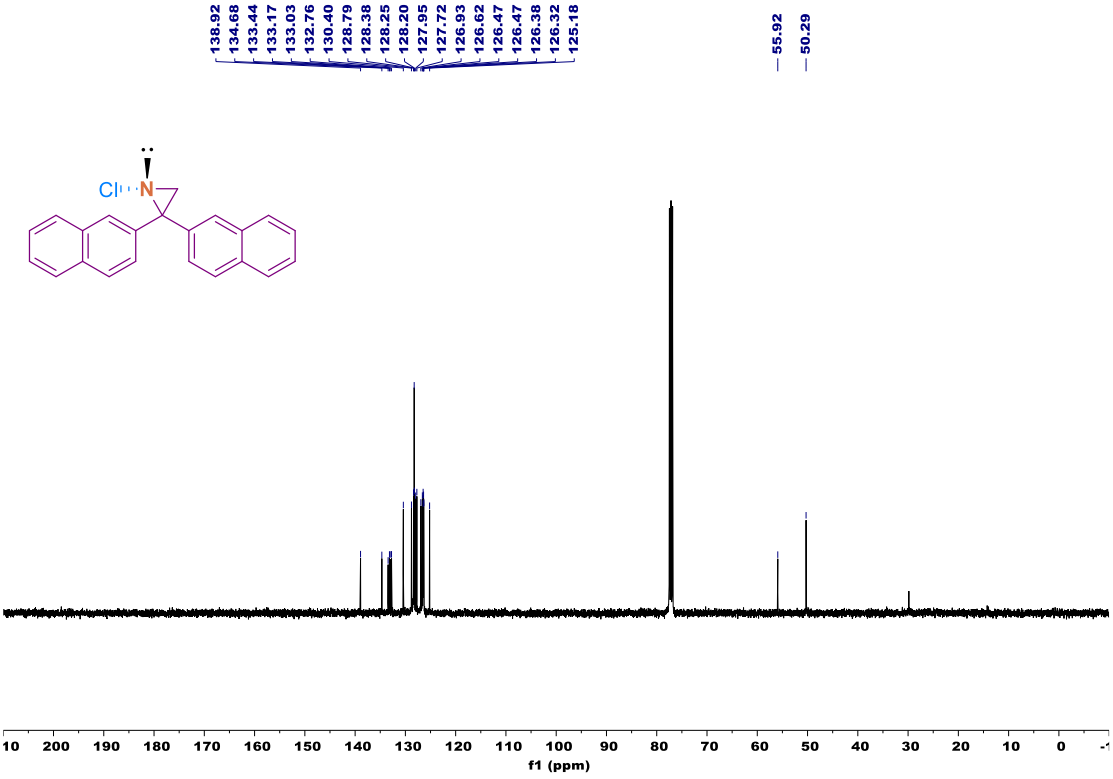



**$^{19}$F NMR** spectrum of **3i** (377 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2,2-di(naphthalen-2-yl)aziridine (3j):**

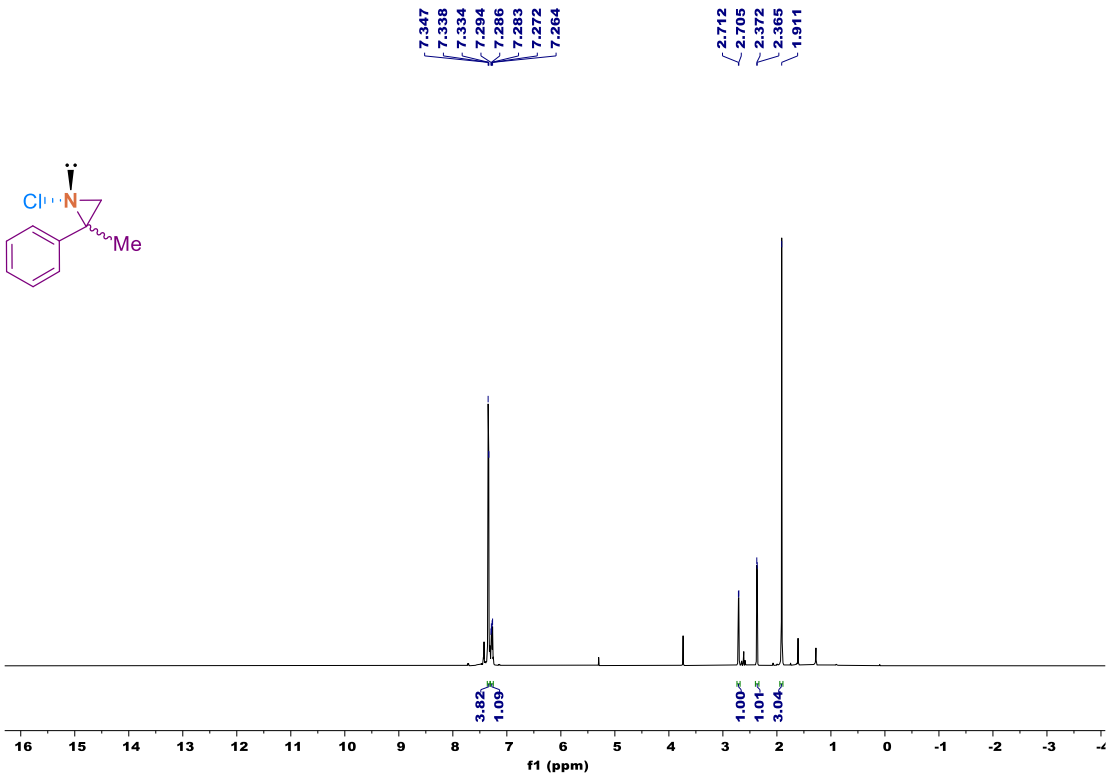



**$^{1}$H NMR spectrum of 3j (400 MHz, $CDCl_3$)**

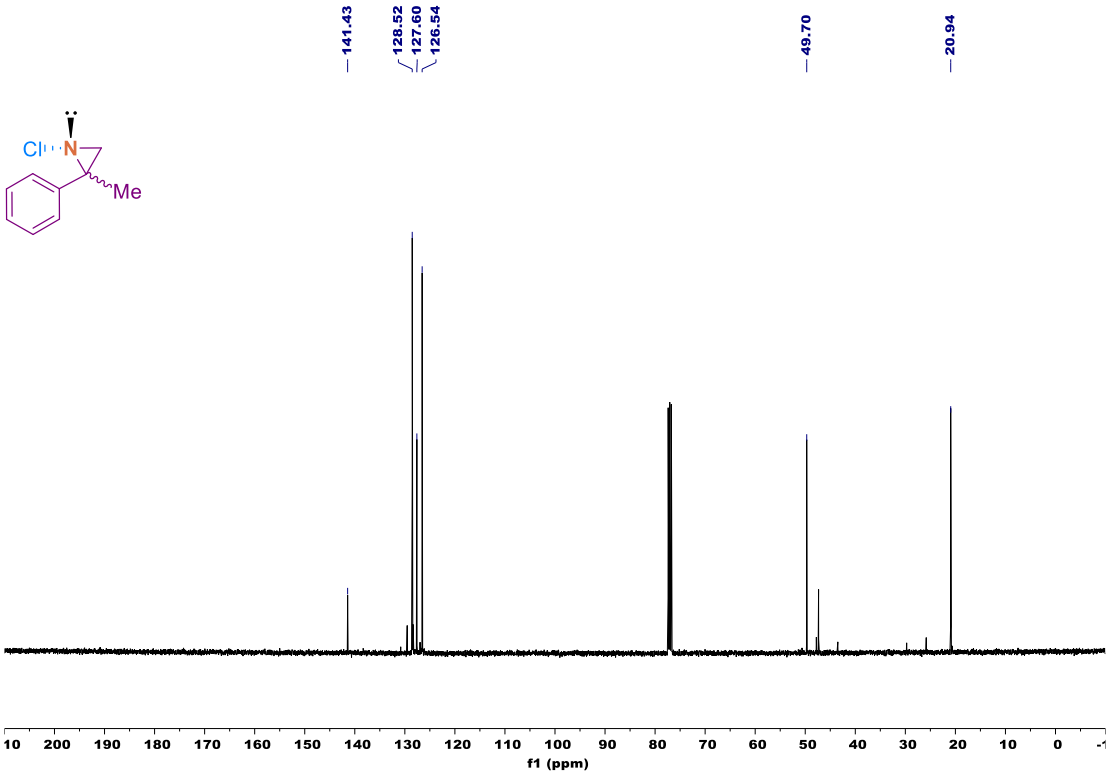



**$^{13}$C NMR** spectrum of **3j** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2-methyl-2-phenylaziridine- Minor diastereoisomer(3k):**

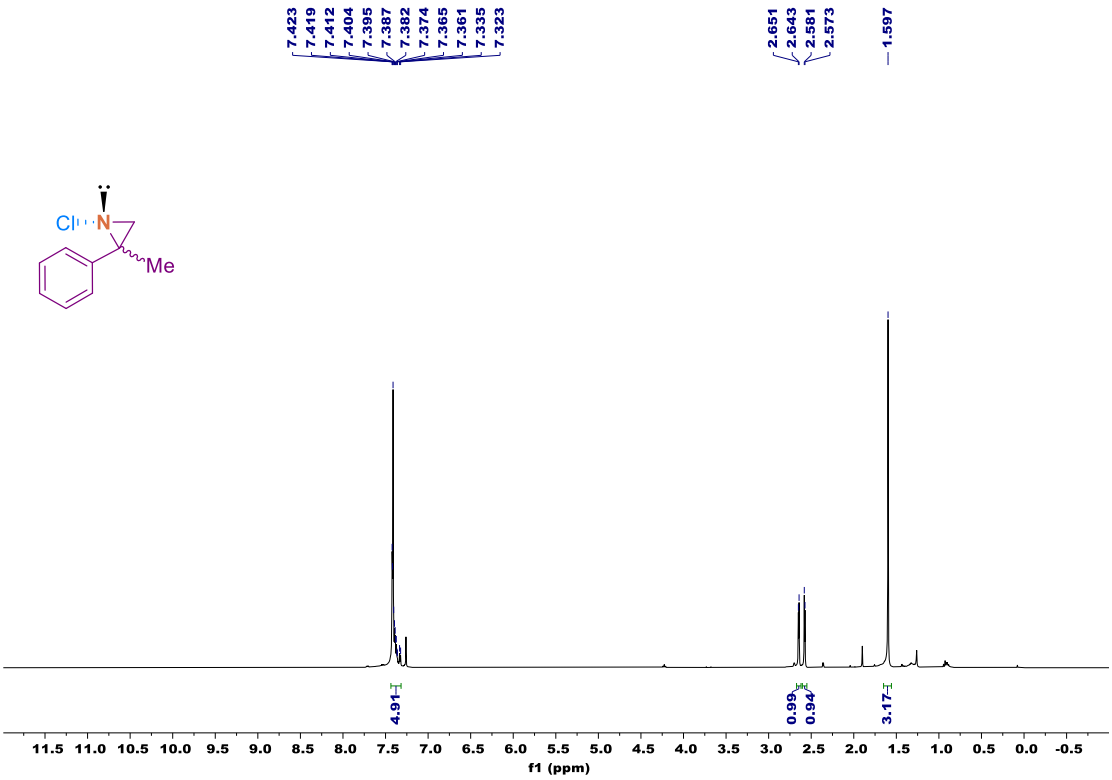



**$^{1}$H NMR** spectrum of **3k** (400 MHz, $CDCl_3$)

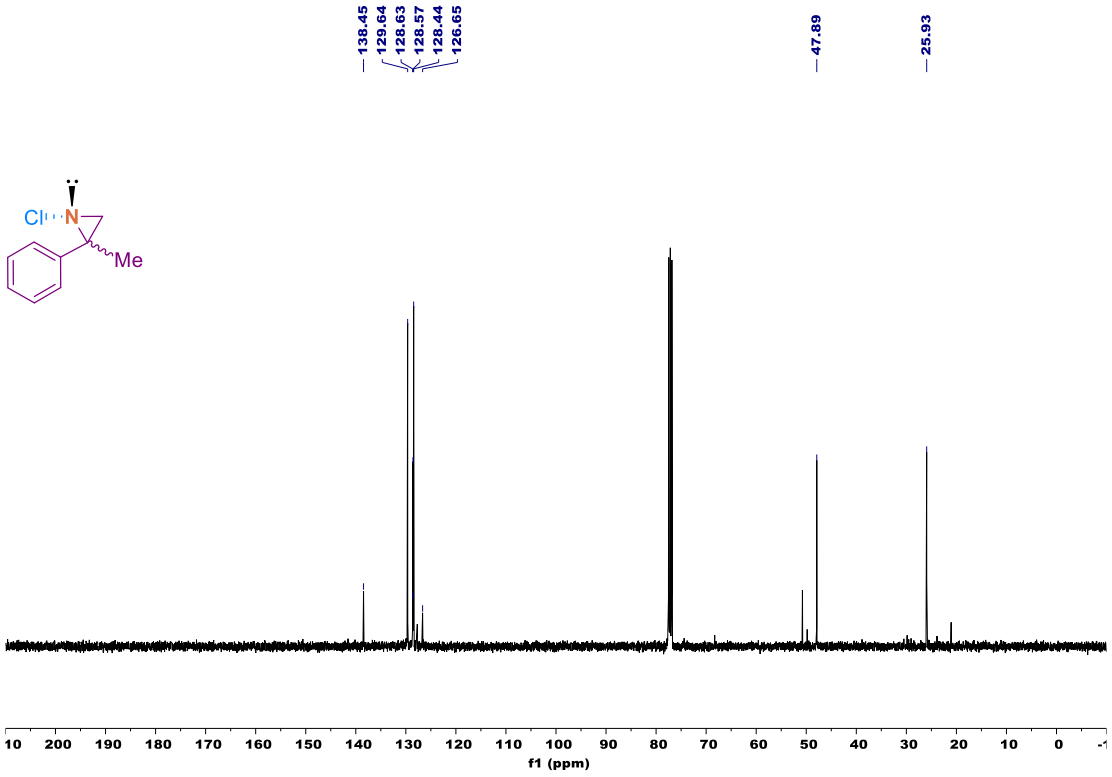



**$^{13}$C NMR** spectrum of **3k** (101 MHz, $CDCl_3$)

**(*R*)-1-Chloro-2-methyl-2-phenylaziridine- Major diastereoisomer (3k):**

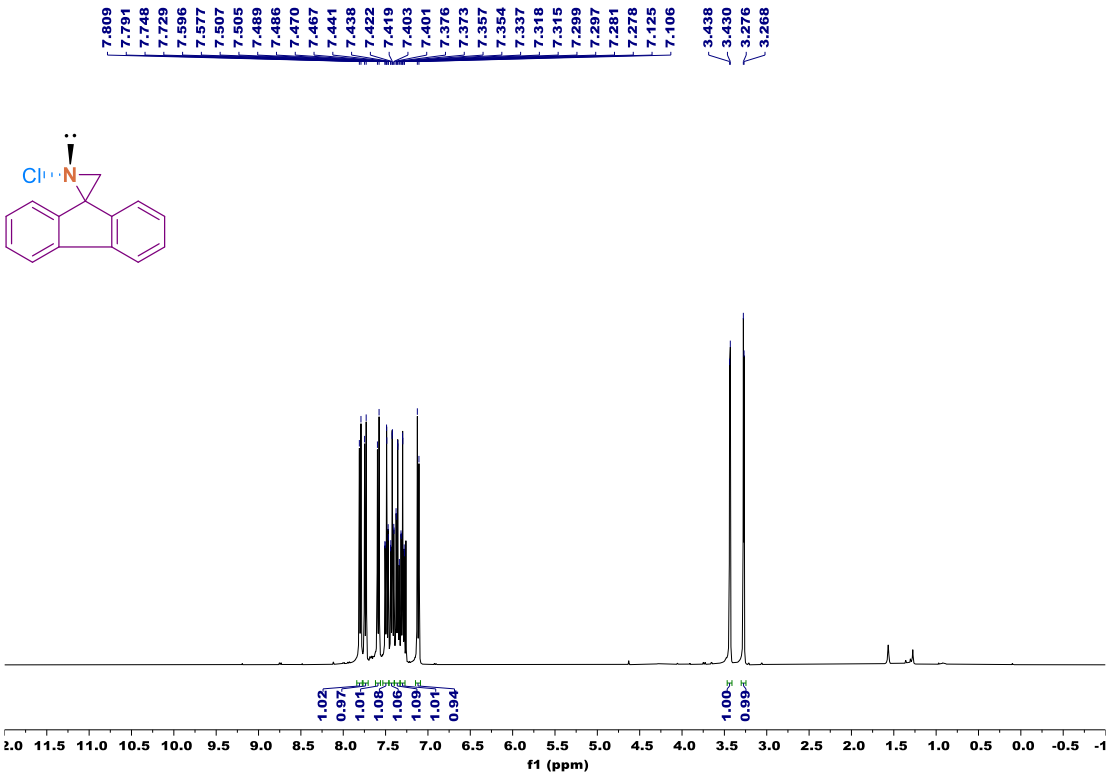



**$^{1}$H NMR** spectrum of **3k** (400 MHz, $CDCl_3$)

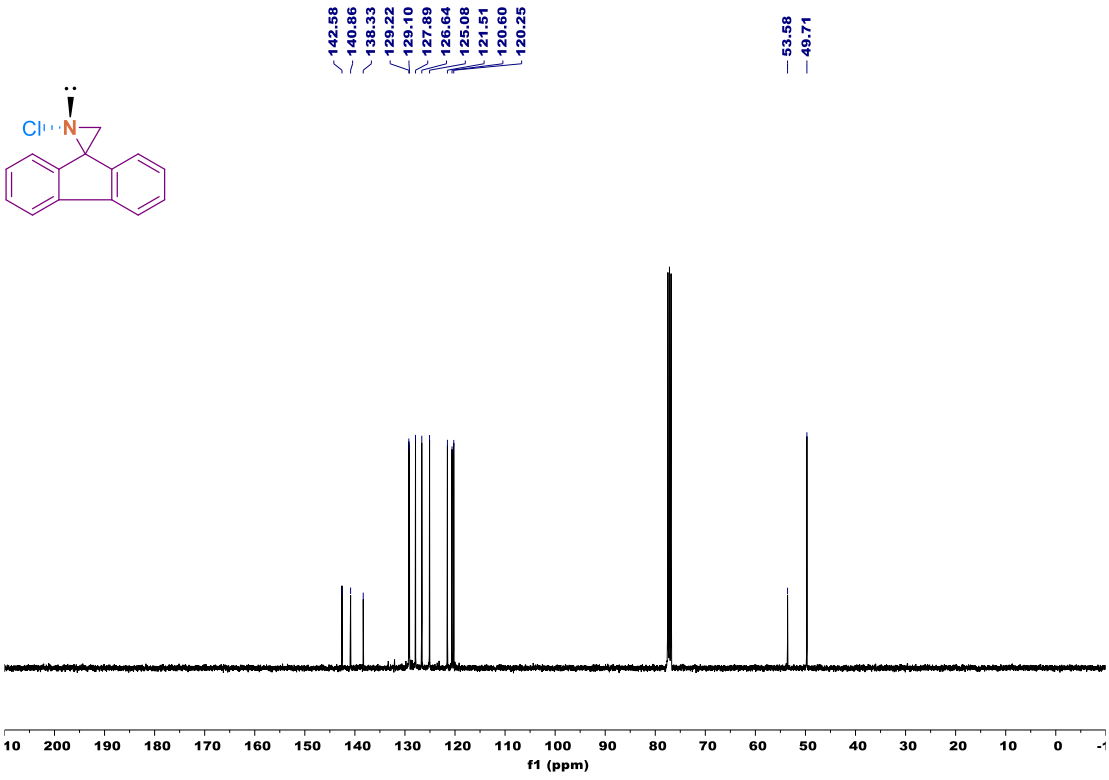



**$^{13}$C NMR** spectrum of **3k** (101 MHz, $CDCl_3$)

**(*R*)-1-Chlorospiro[aziridine-2,9'-fluorene] (3l):**

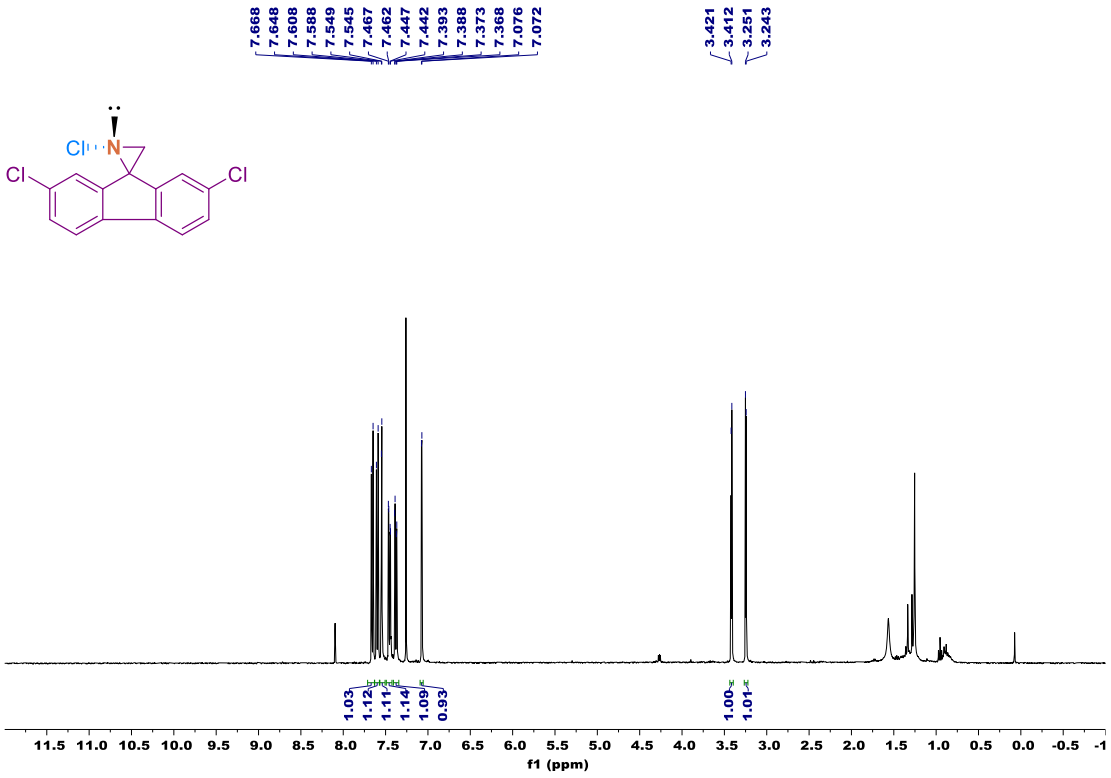



**$^{1}$H NMR** spectrum of **3l** (400 MHz, $CDCl_3$)

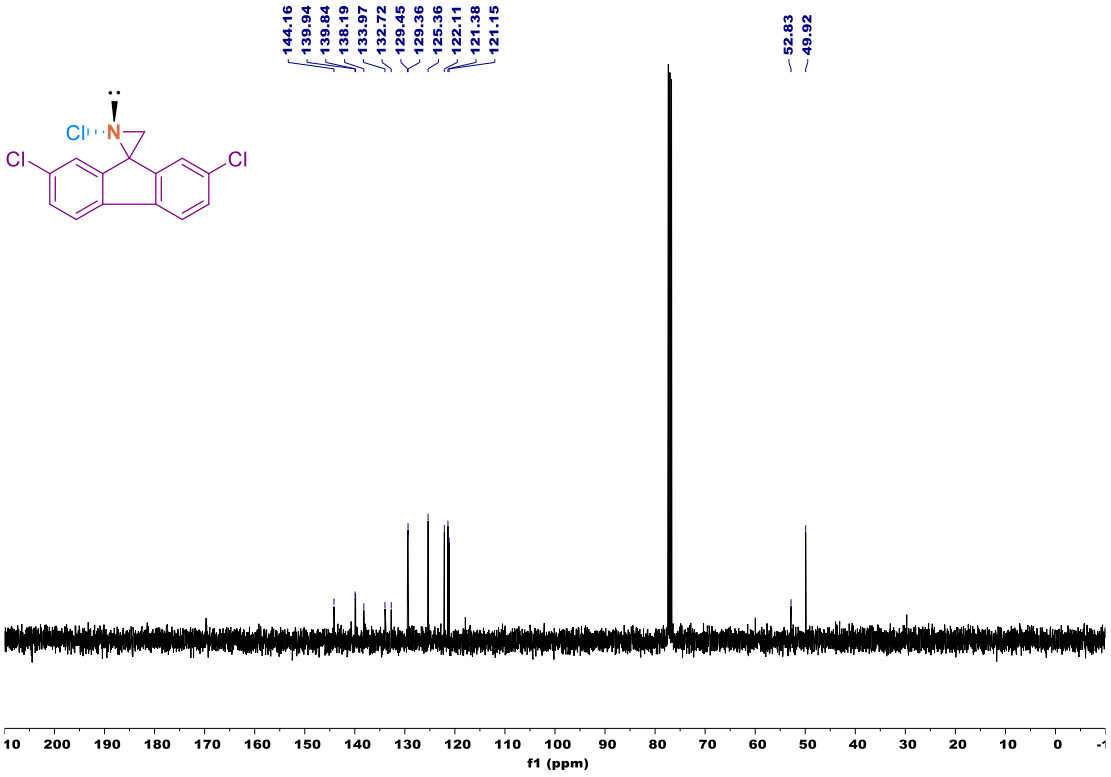



**$^{13}$C NMR** spectrum of **3l** (101 MHz, $CDCl_3$)

**(*R*)-1,2',7'-Trichlorospiro[aziridine-2,9'-fluorene] (3m):**

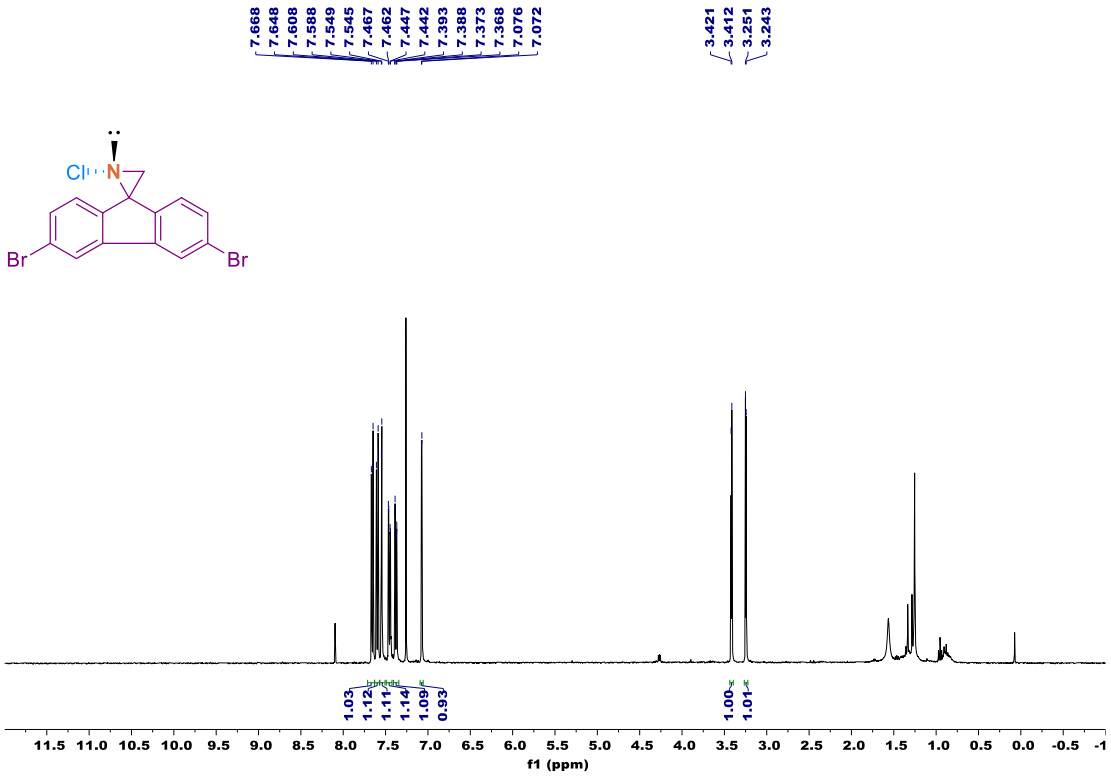



**$^{1}$H NMR** spectrum of **3m** (400 MHz, $CDCl_3$)



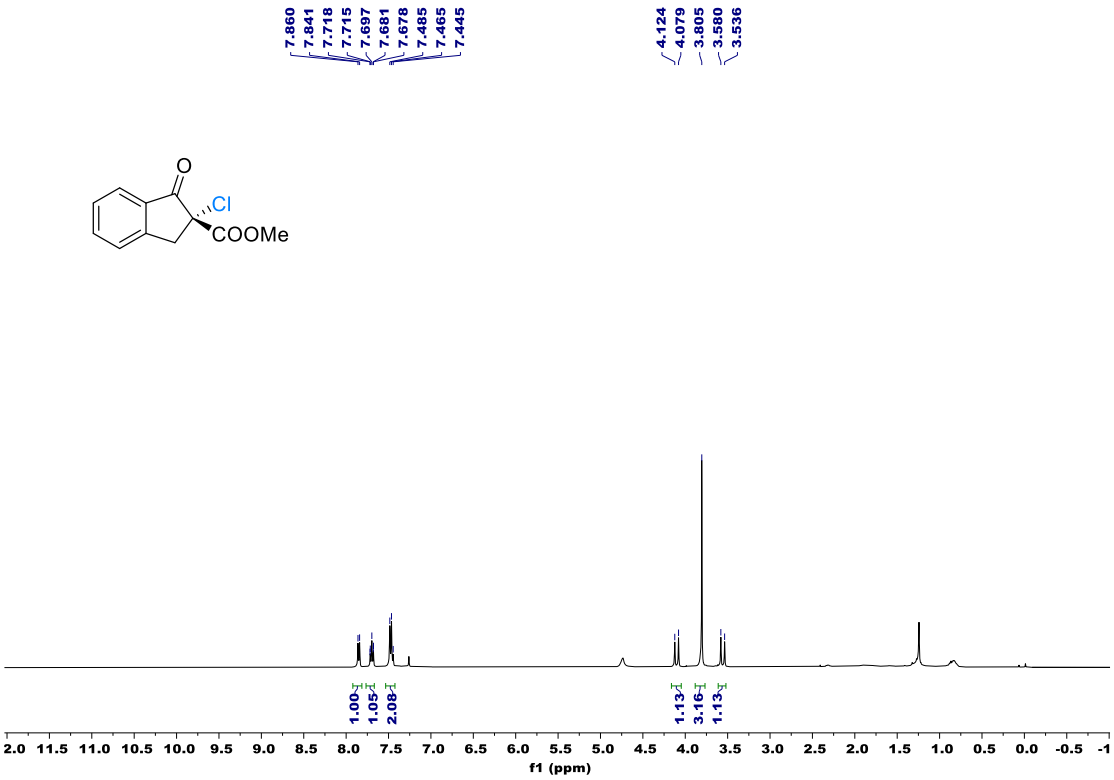

**$^{13}$C NMR** spectrum of **3m** (101 MHz, $CDCl_3$)

**(*R*)-3',6'-Dibromo-1-chlorospiro[aziridine-2,9'-fluorene] (3n):**

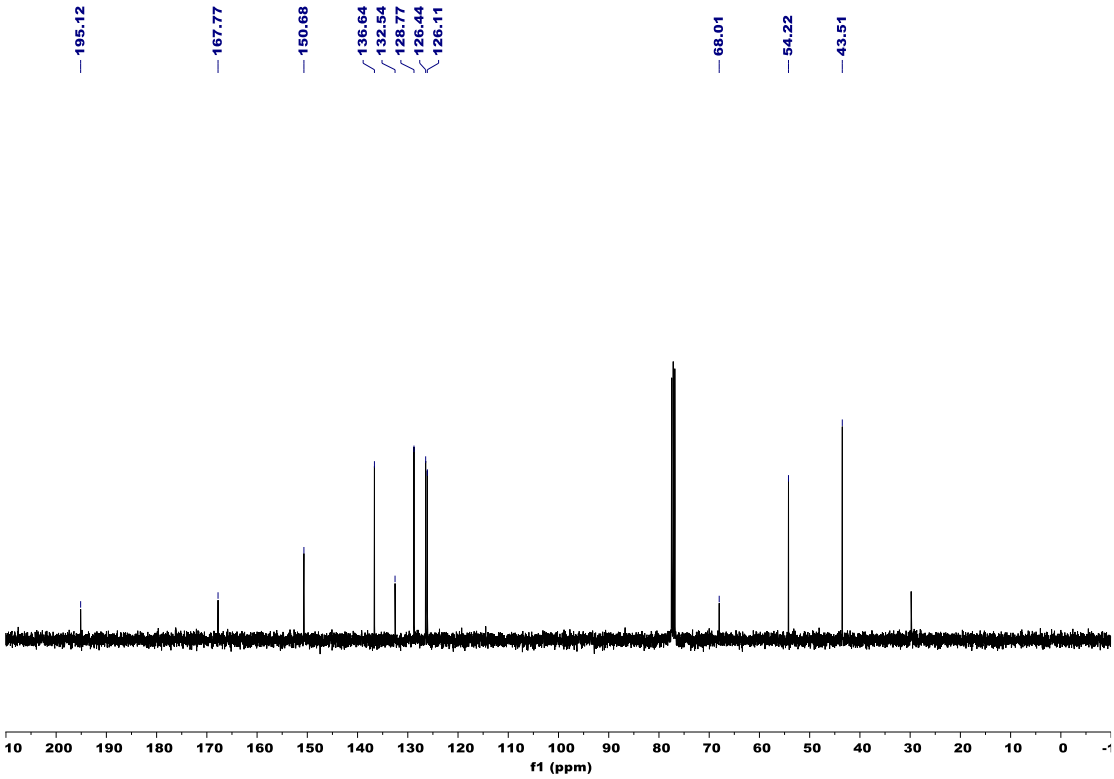



**$^1$H NMR** spectrum of **3n** (400 MHz, $CDCl_3$)

**(*R*)-Methyl 2-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5a)**



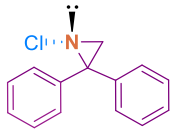

$^{1}$**H NMR** spectrum of **5a** (400 MHz, $CDCl_3$)



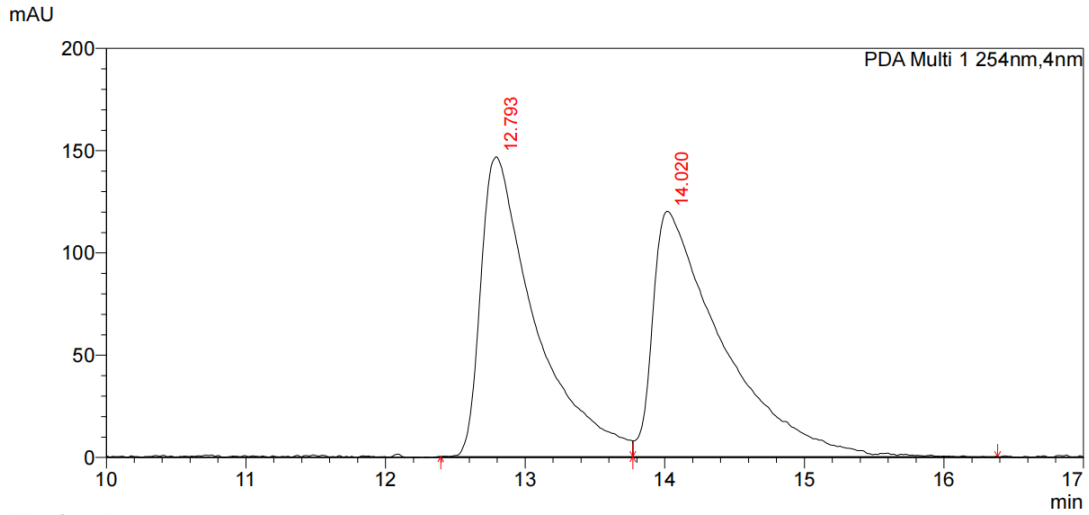

$^{13}$**C NMR** spectrum of **5a** (101 MHz, $CDCl_3$)

### 3.5 HPLC traces of the obtained chiral products

**(*R*)-1-Chloro-2,2-diphenylaziridine (3a):**

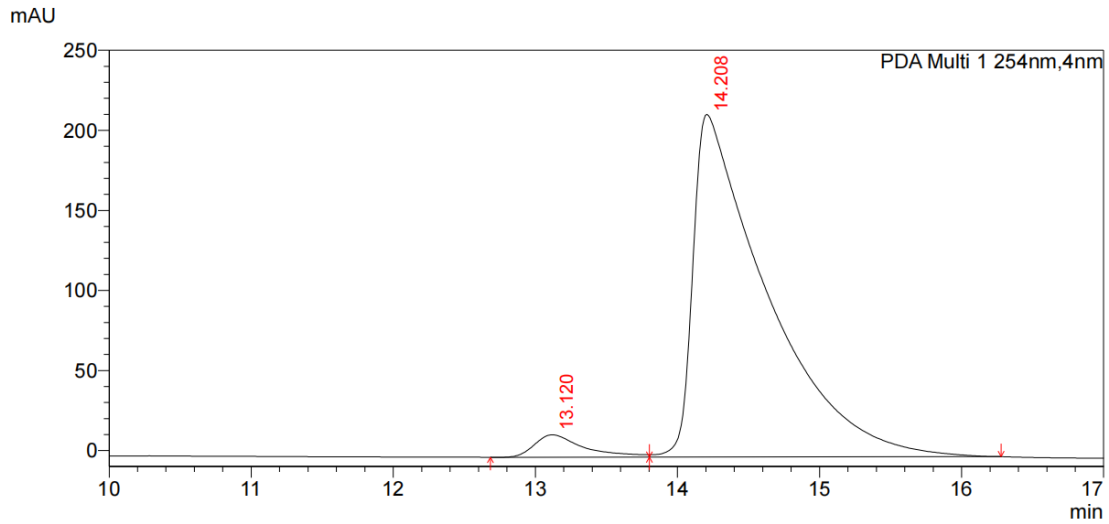



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 12.793 | 3973433 | 146616 | 49.042 |
| 2 | 14.020 | 4128640 | 119920 | 50.958 |
| Total | | 8102073 | 266536 | 100.000 |

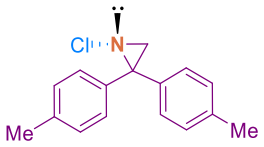



**<Peak Table>**

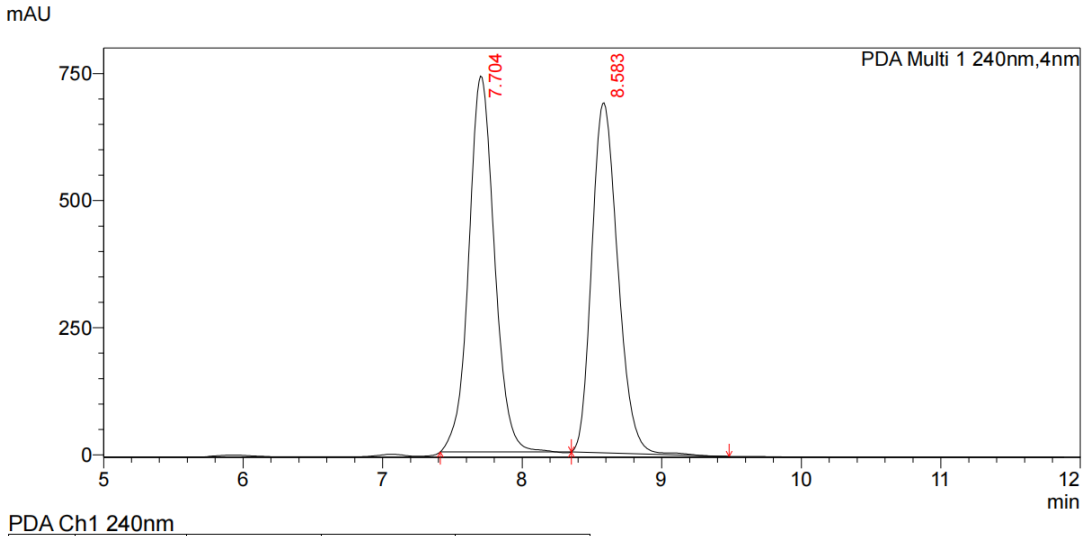
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 13.120 | 339893 | 14039 | 4.202 |
| 2 | 14.208 | 7749370 | 214075 | 95.798 |
| Total | | 8089263 | 228114 | 100.000 |

**(*R*)-1-Chloro-2,2-di-*p*-tolylaziridine (3b):**

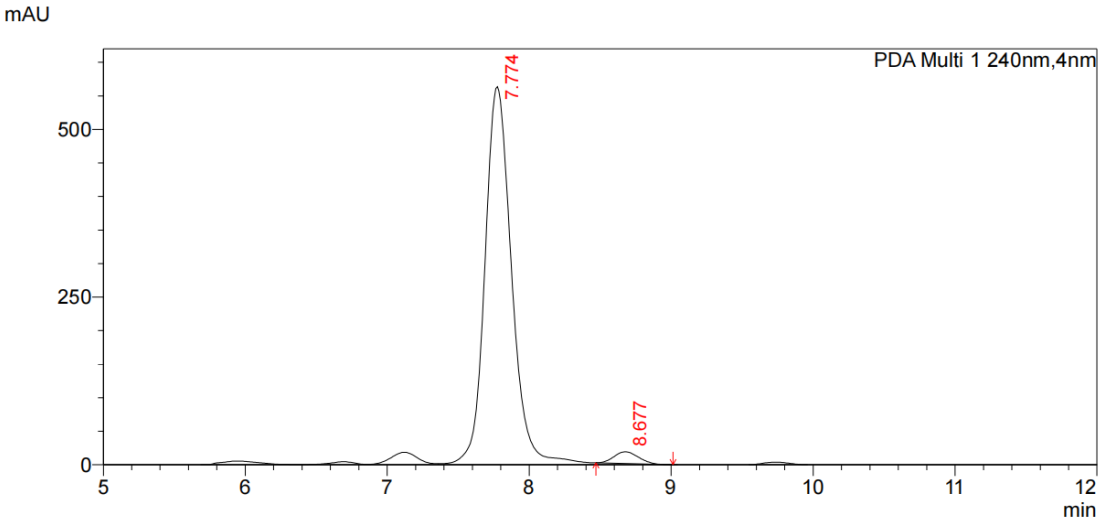



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 0.5 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 240nm

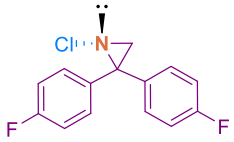
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.704 | 9435258 | 739142 | 51.396 |
| 2 | 8.583 | 8922654 | 688077 | 48.604 |
| Total | | 18357912 | 1427219 | 100.000 |



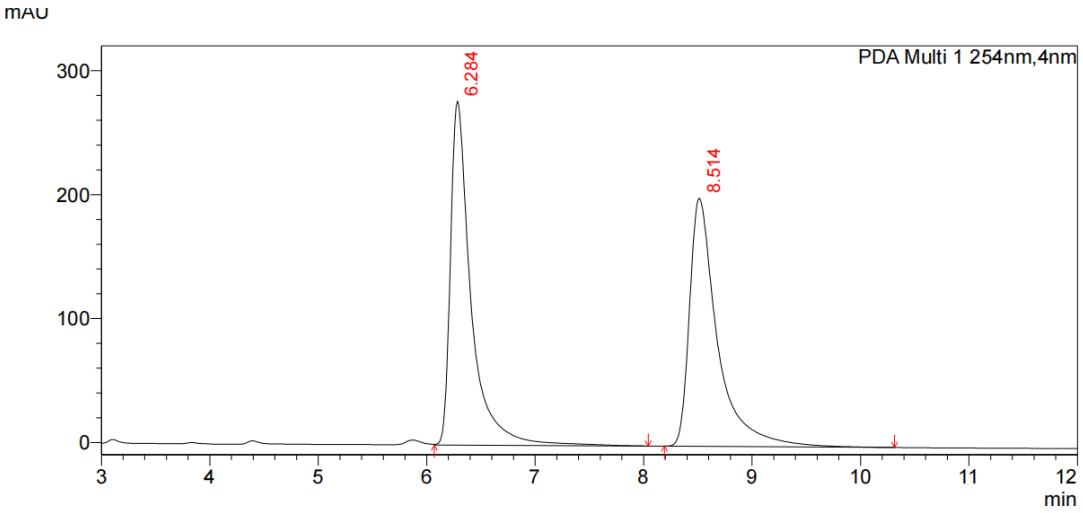

PDA Ch1 240nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.774 | 7679347 | 565227 | 97.296 |
| 2 | 8.677 | 213407 | 17591 | 2.704 |
| Total | | 7892755 | 582818 | 100.000 |

**(*R*)-1-Chloro-2,2-diphenylaziridine (3c):**

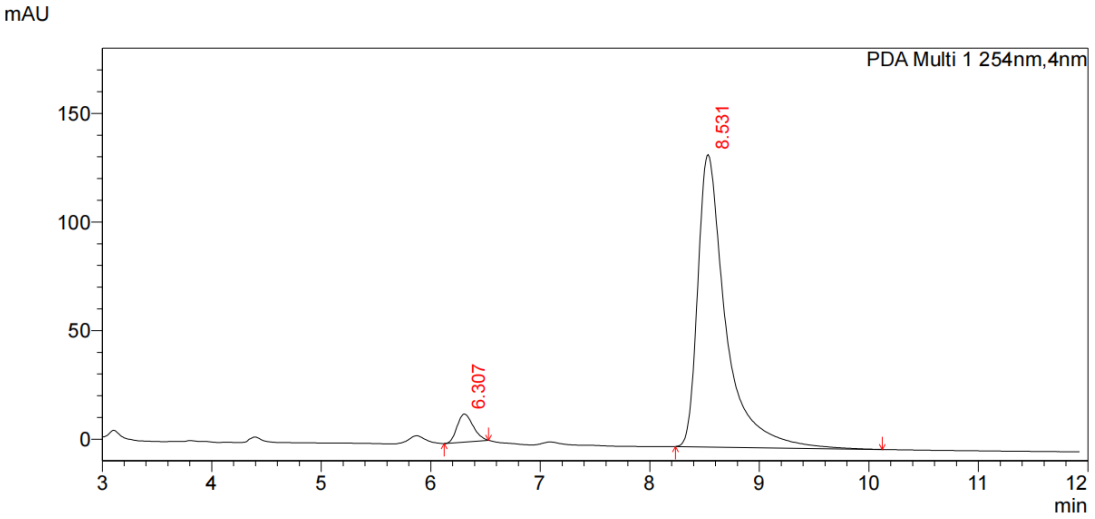



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane,20:80), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

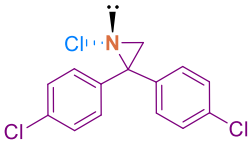
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.284 | 3663713 | 277445 | 50.496 |
| 2 | 8.514 | 3591678 | 200086 | 49.504 |
| Total | | 7255391 | 477531 | 100.000 |



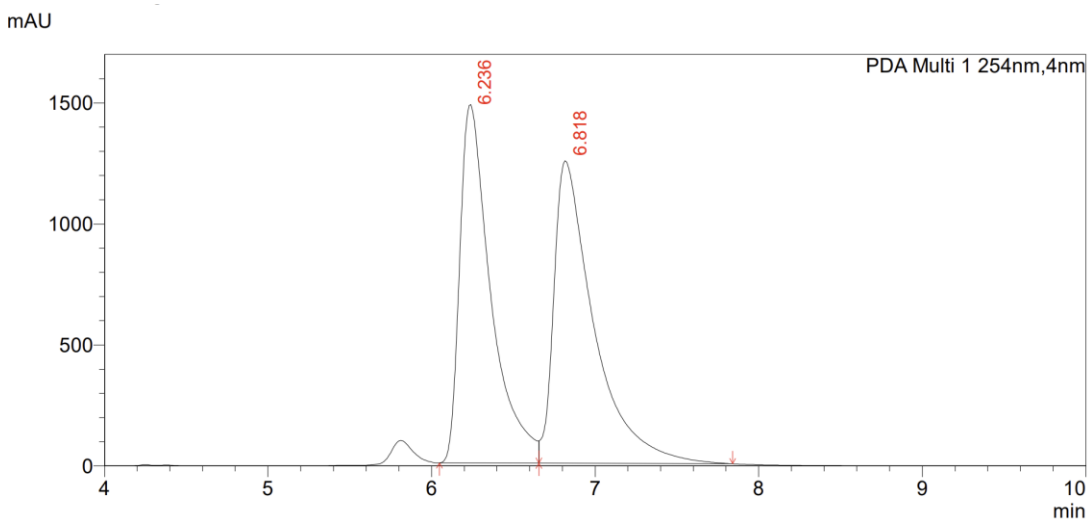

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.307 | 132070 | 12945 | 5.233 |
| 2 | 8.531 | 2391550 | 134581 | 94.767 |
| Total | | 2523620 | 147526 | 100.000 |

**(*R*)-1-Chloro-2,2-bis(4-chlorophenyl)aziridine (3d):**

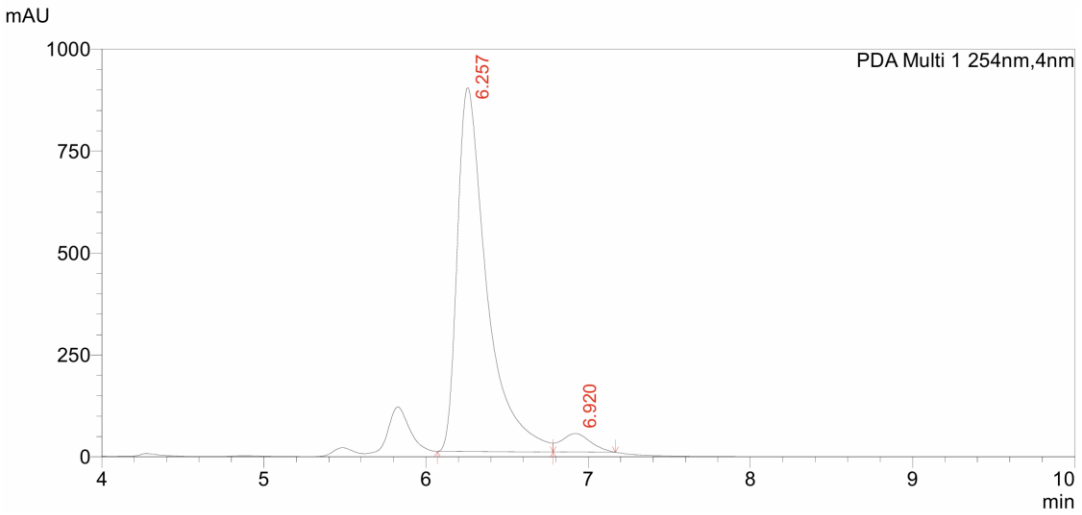



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

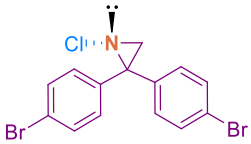
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.236 | 19597142 | 1480156 | 47.999 |
| 2 | 6.818 | 21231132 | 1249433 | 52.001 |
| Total | | 40828274 | 2729588 | 100.000 |



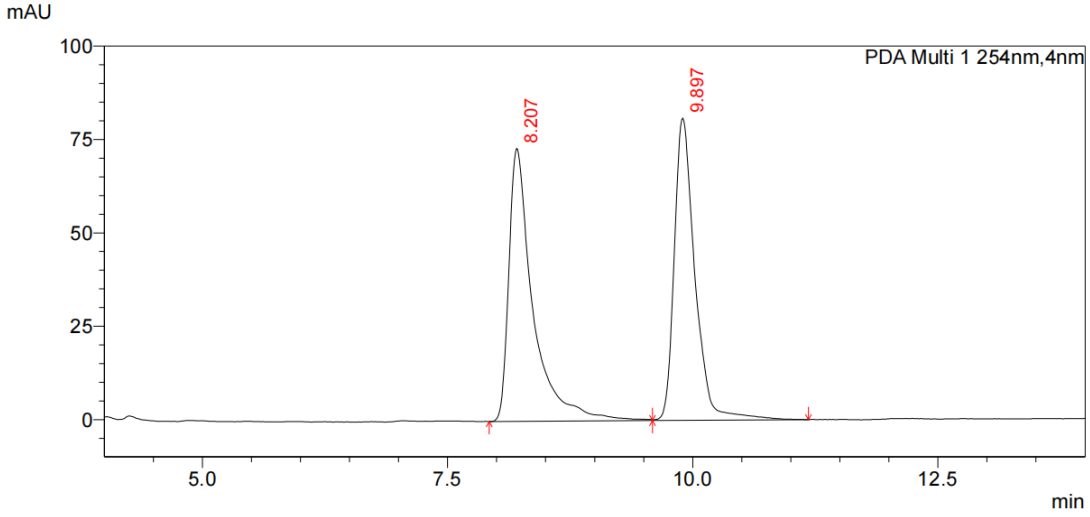

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.257 | 11297301 | 892369 | 95.202 |
| 2 | 6.920 | 569316 | 45664 | 4.798 |
| Total | | 11866618 | 938033 | 100.000 |

**(*R*)-2,2-Bis(4-bromophenyl)-1-chloroaziridine (3e):**

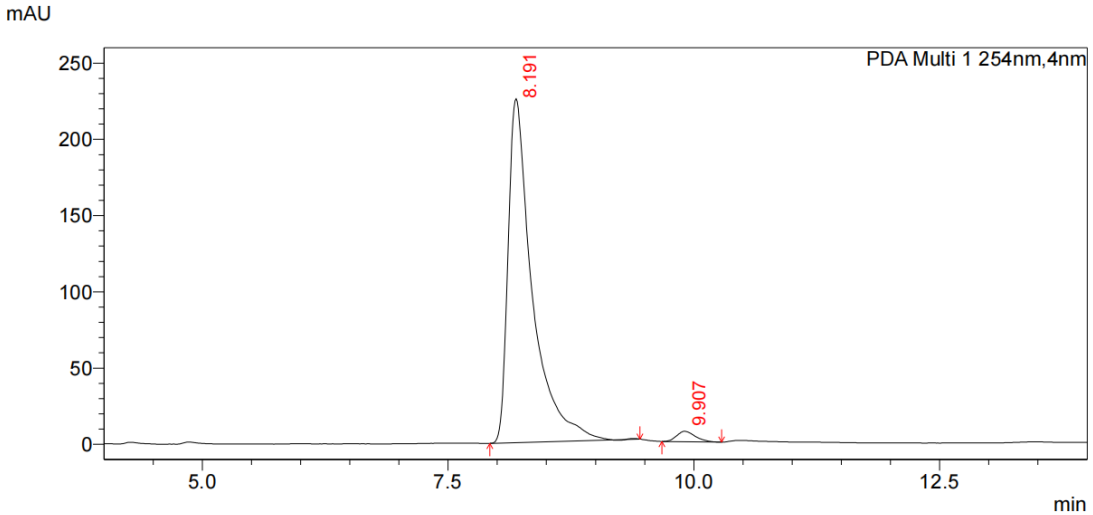



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

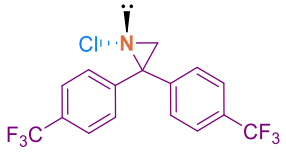
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 8.207 | 1253993 | 73057 | 51.311 |
| 2 | 9.897 | 1189916 | 80967 | 48.689 |
| Total | | 2443910 | 154024 | 100.000 |



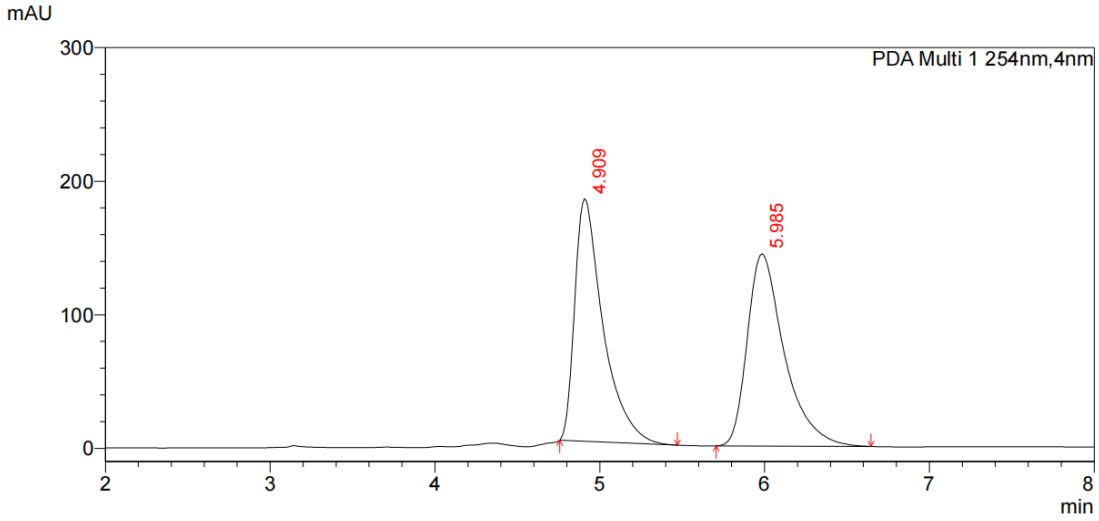

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 8.191 | 3861603 | 225553 | 97.722 |
| 2 | 9.907 | 90031 | 6867 | 2.278 |
| Total | | 3951633 | 232420 | 100.000 |

**(*R*)-1-Chloro-2,2-bis(4-(trifluoromethyl)phenyl)aziridine (3f):**

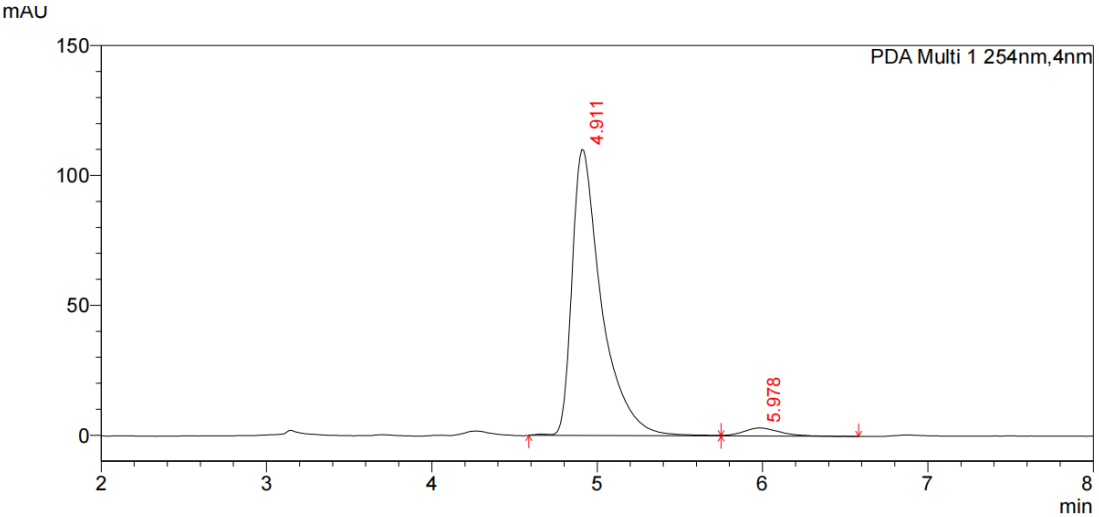



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

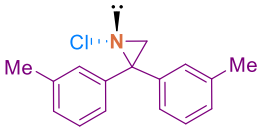
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 4.909 | 2167309 | 181569 | 49.106 |
| 2 | 5.985 | 2246235 | 144001 | 50.894 |
| Total | | 4413544 | 325569 | 100.000 |



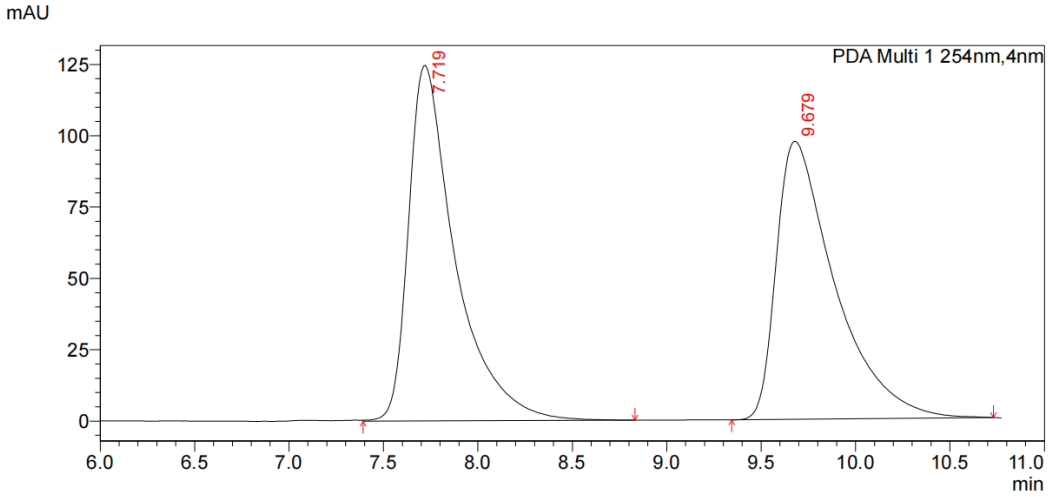

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 4.911 | 1368835 | 110048 | 96.629 |
| 2 | 5.978 | 47750 | 3125 | 3.371 |
| Total | | 1416586 | 113173 | 100.000 |

**(*R*)-1-Chloro-2,2-di-*m*-tolylaziridine (3g):**

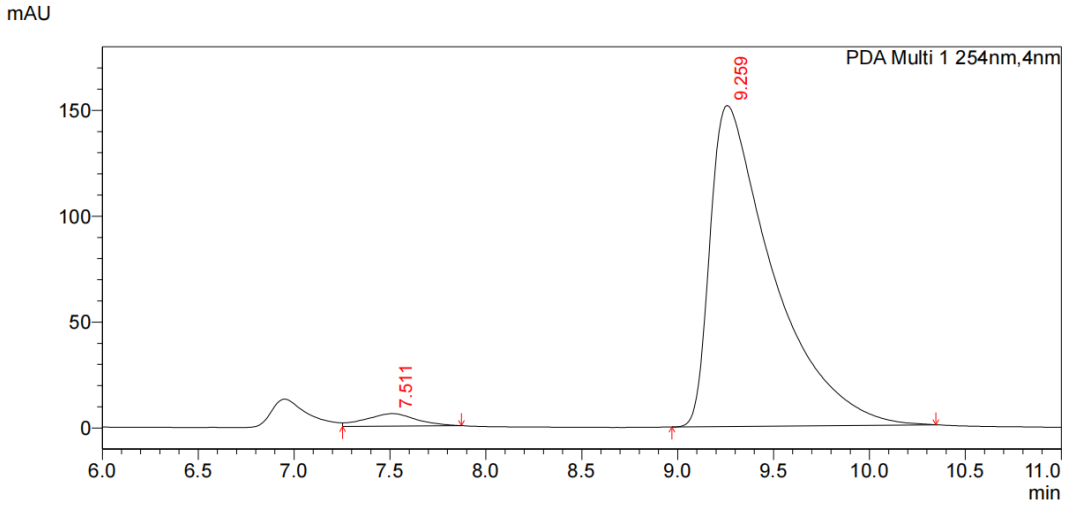



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

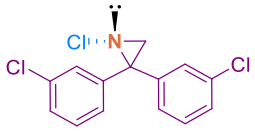
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.719 | 2144088 | 124598 | 50.510 |
| 2 | 9.679 | 2100823 | 97463 | 49.490 |
| Total | | 4244911 | 222061 | 100.000 |



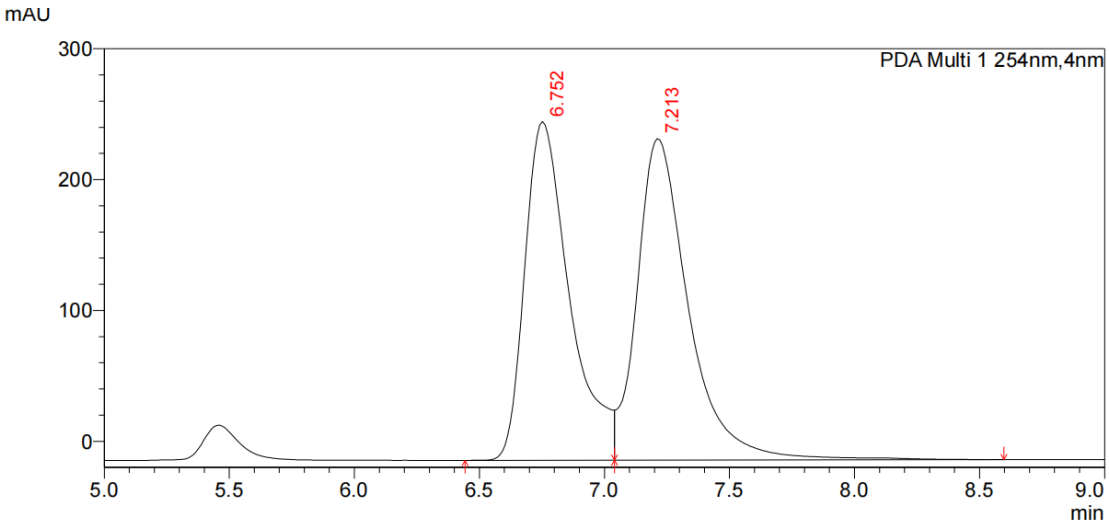

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.511 | 108574 | 5937 | 3.039 |
| 2 | 9.259 | 3464079 | 151691 | 96.961 |
| Total | | 3572653 | 157628 | 100.000 |

**(*R*)-1-Chloro-2,2-bis(3-chlorophenyl)aziridine (3h):**

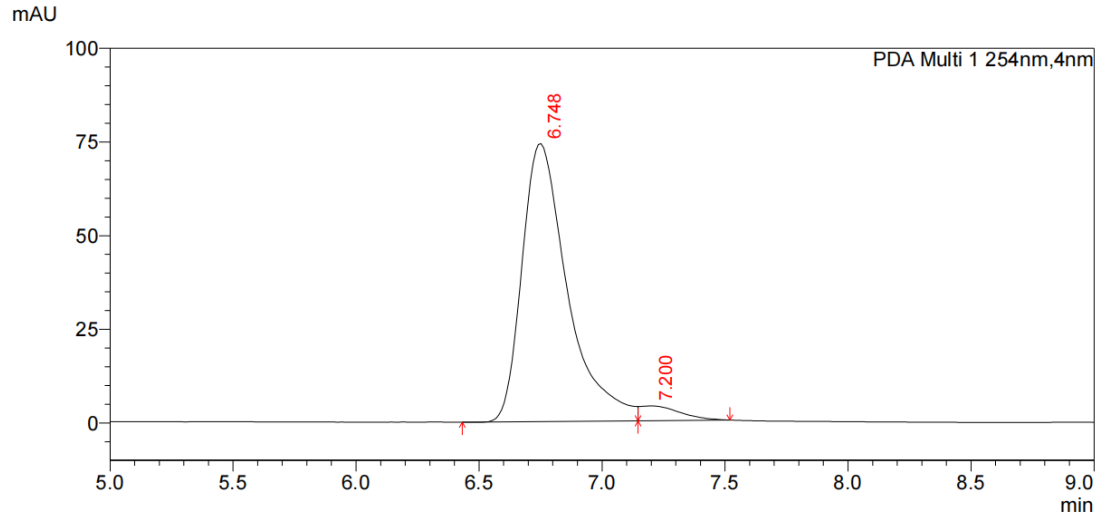



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 1:99), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

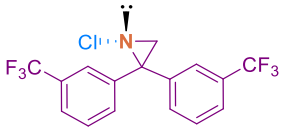
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.752 | 3232945 | 258839 | 47.991 |
| 2 | 7.213 | 3503631 | 245698 | 52.009 |
| Total | | 6736576 | 504537 | 100.000 |



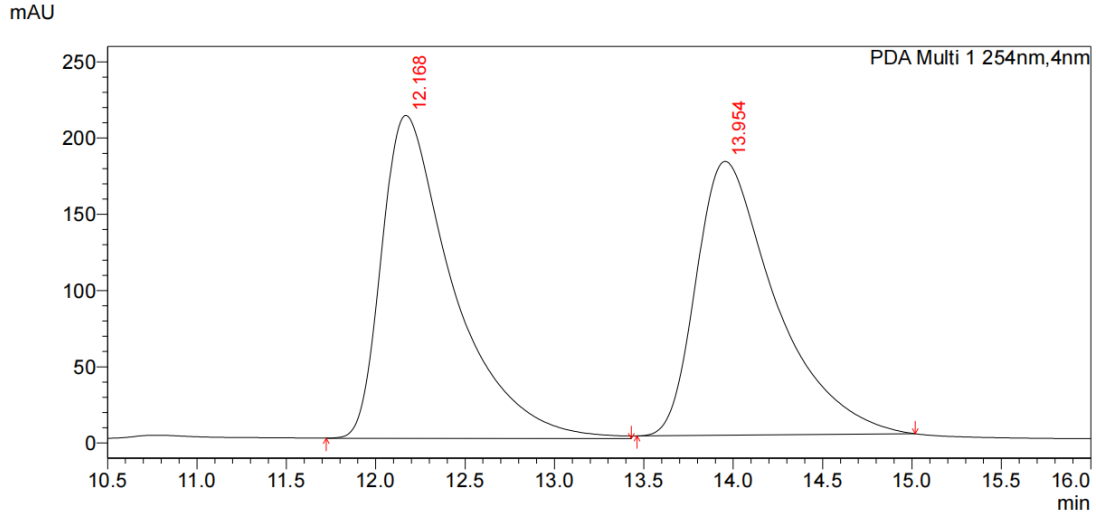

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 6.748 | 956479 | 74209 | 95.678 |
| 2 | 7.200 | 43202 | 3931 | 4.322 |
| Total | | 999681 | 78140 | 100.000 |

**(*R*)-1-Chloro-2,2-bis(3-(trifluoromethyl)phenyl)aziridine (3i):**

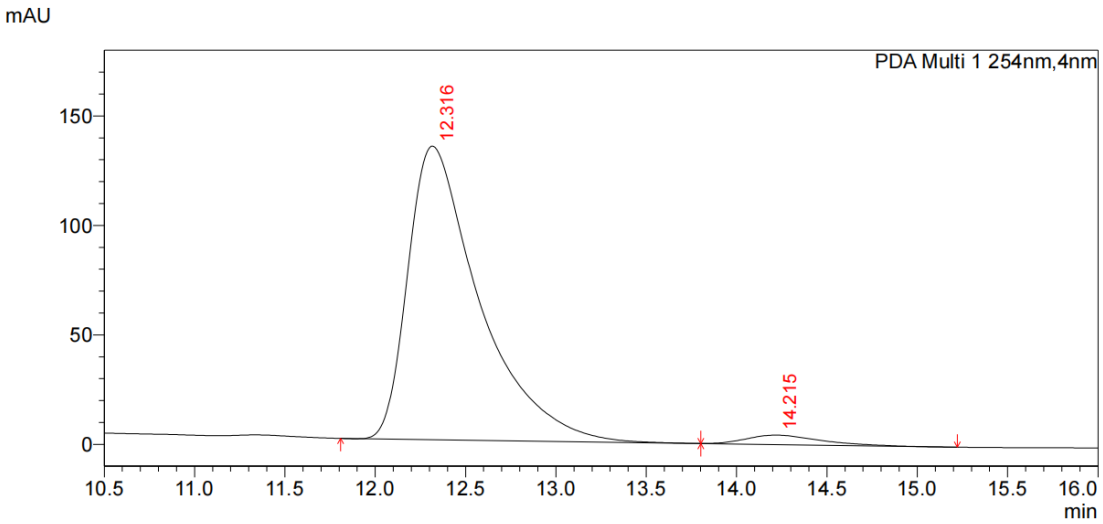



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 0.4 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

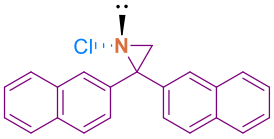
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 12.168 | 5928407 | 211907 | 51.591 |
| 2 | 13.954 | 5562709 | 179658 | 48.409 |
| Total | | 11491116 | 391566 | 100.000 |



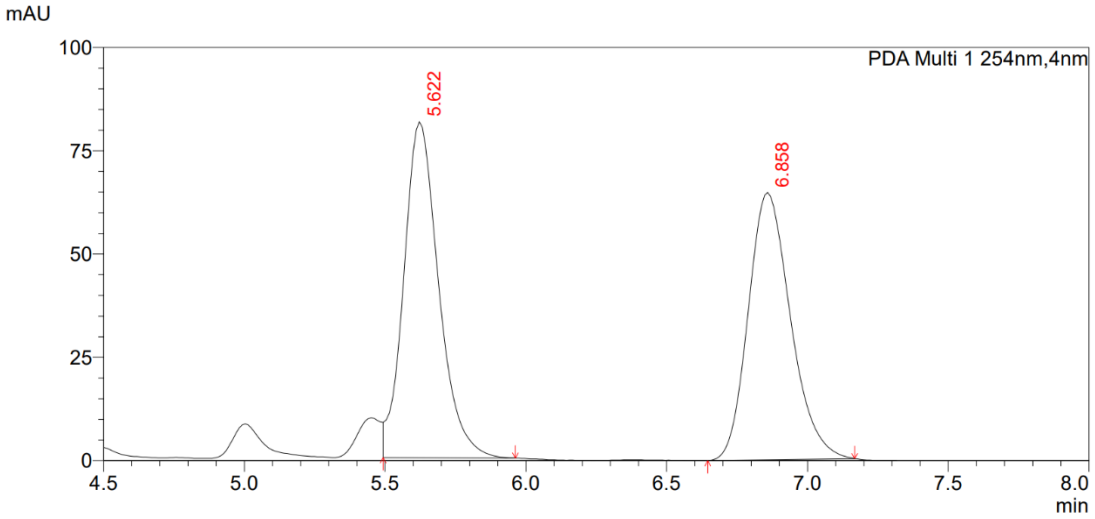

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 12.316 | 3696687 | 134169 | 96.763 |
| 2 | 14.215 | 123669 | 4341 | 3.237 |
| Total | | 3820355 | 138510 | 100.000 |

**(*R*)-1-Chloro-2,2-di(naphthalen-2-yl)aziridine (3j):**

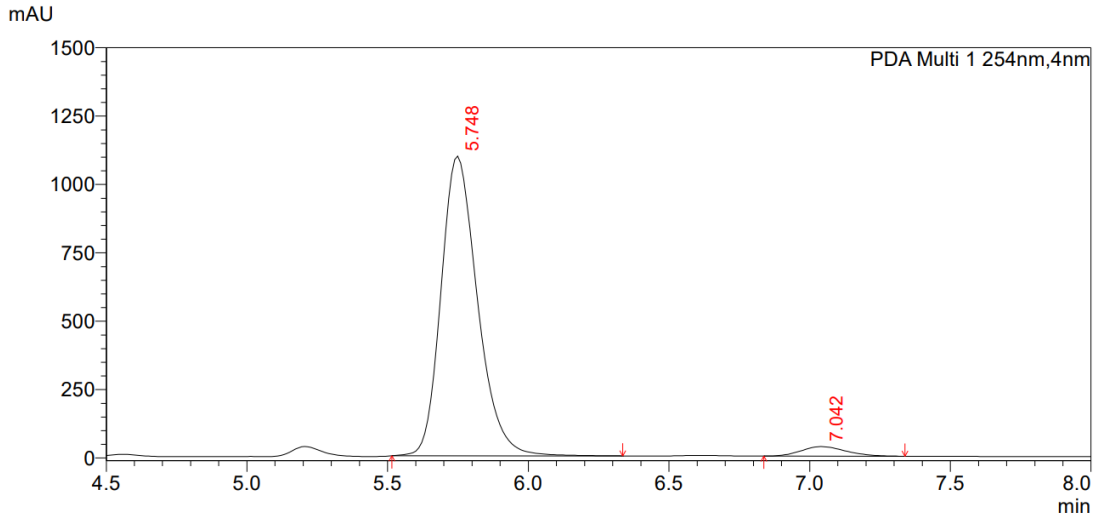



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

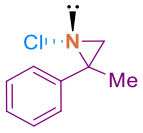
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 5.622 | 701209 | 81325 | 50.947 |
| 2 | 6.858 | 675135 | 64694 | 49.053 |
| Total | | 1376344 | 146019 | 100.000 |



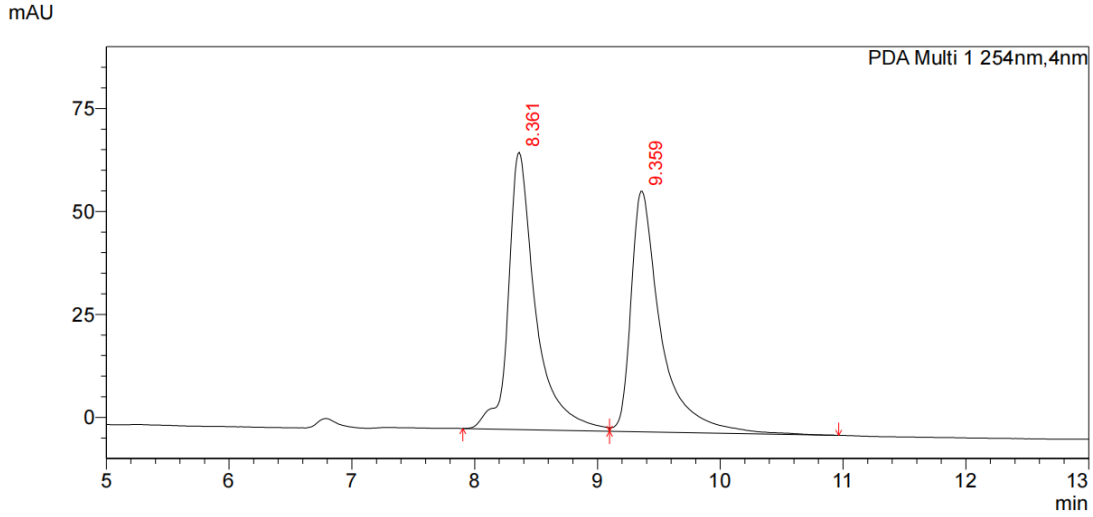

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 5.748 | 9873848 | 1095716 | 96.205 |
| 2 | 7.042 | 389495 | 35036 | 3.795 |
| Total | | 10263342 | 1130753 | 100.000 |

**(*R*)-1-Chloro-2-methyl-2-phenylaziridine- Minor diastereoisomer (3k):**

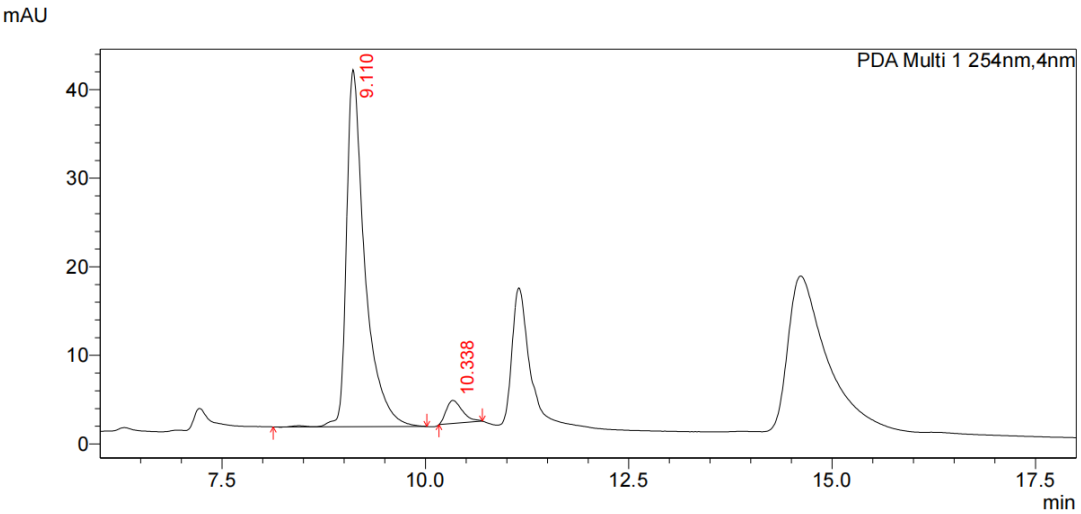



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 8.361 | 1041078 | 67305 | 51.254 |
| 2 | 9.359 | 990146 | 58418 | 48.746 |
| Total | | 2031224 | 125724 | 100.000 |

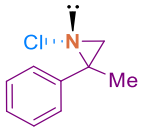



**<Peak Table>**

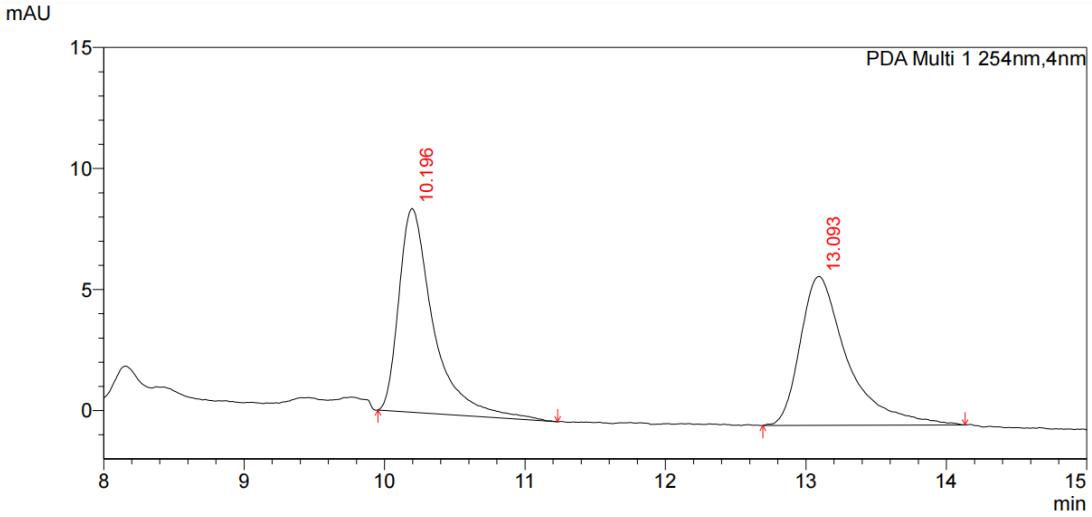
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.110 | 632184 | 40298 | 94.610 |
| 2 | 10.338 | 36015 | 2615 | 5.390 |
| Total | | 668199 | 42913 | 100.000 |

**(*R*)-1-Chloro-2-methyl-2-phenylaziridine- Major diastereoisomer (3k):**

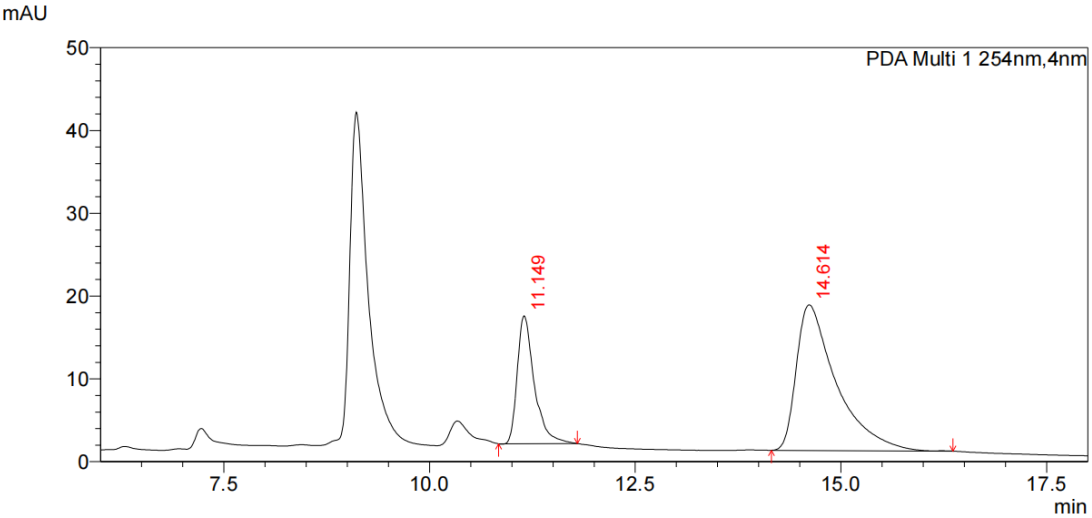



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 10.196 | 143461 | 8425 | 49.876 |
| 2 | 13.093 | 144175 | 6153 | 50.124 |
| Total | | 287636 | 14578 | 100.000 |

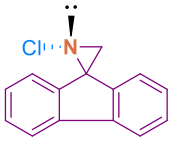



**<Peak Table>**

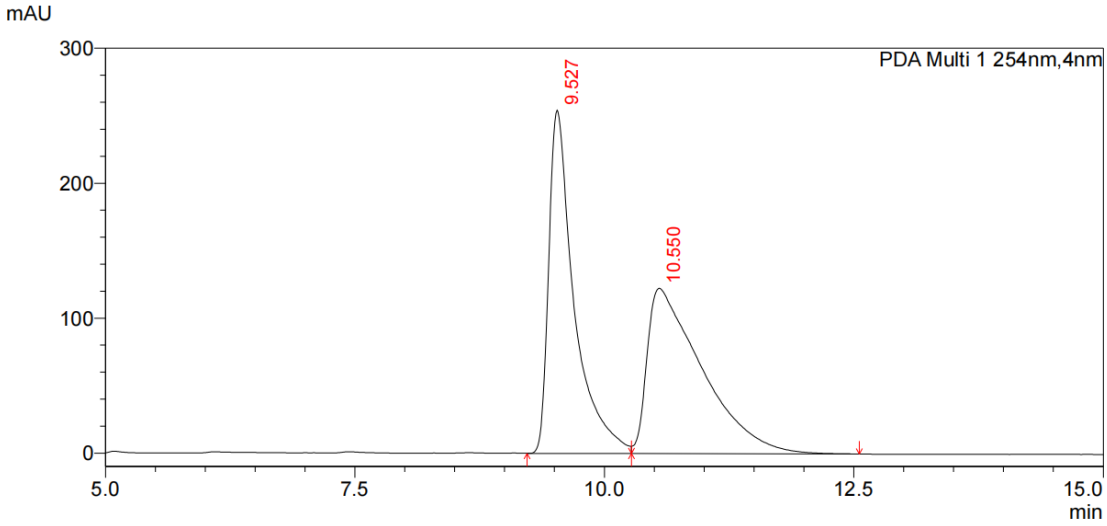
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 11.149 | 222857 | 15463 | 27.288 |
| 2 | 14.614 | 593829 | 17596 | 72.712 |
| Total | | 816686 | 33059 | 100.000 |

**(*R*)-1-Chlorospiro[aziridine-2,9'-fluorene] (3l):**

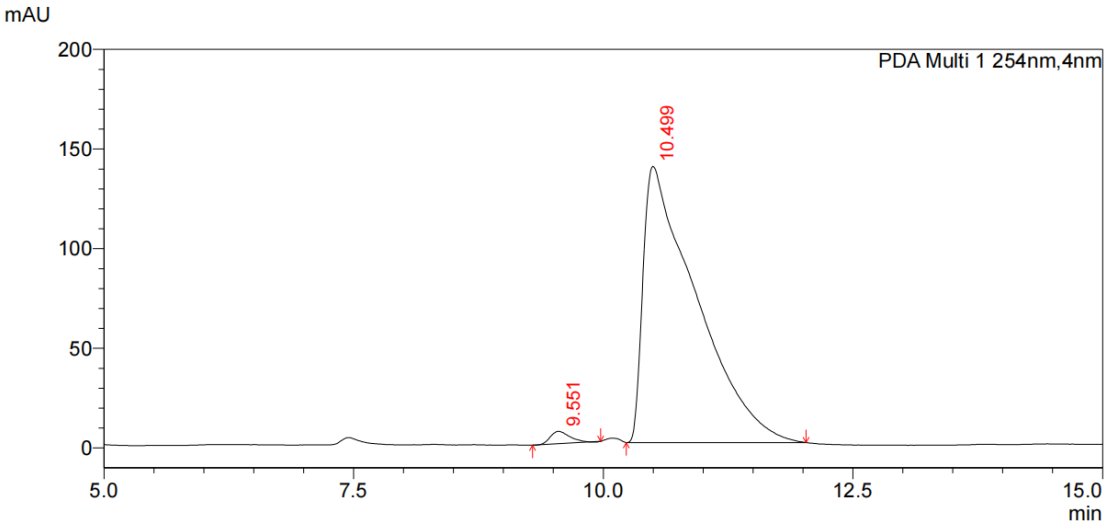


**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

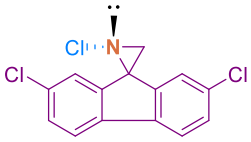
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.527 | 4493069 | 254397 | 48.920 |
| 2 | 10.550 | 4691538 | 122540 | 51.080 |
| Total | | 9184608 | 376937 | 100.000 |



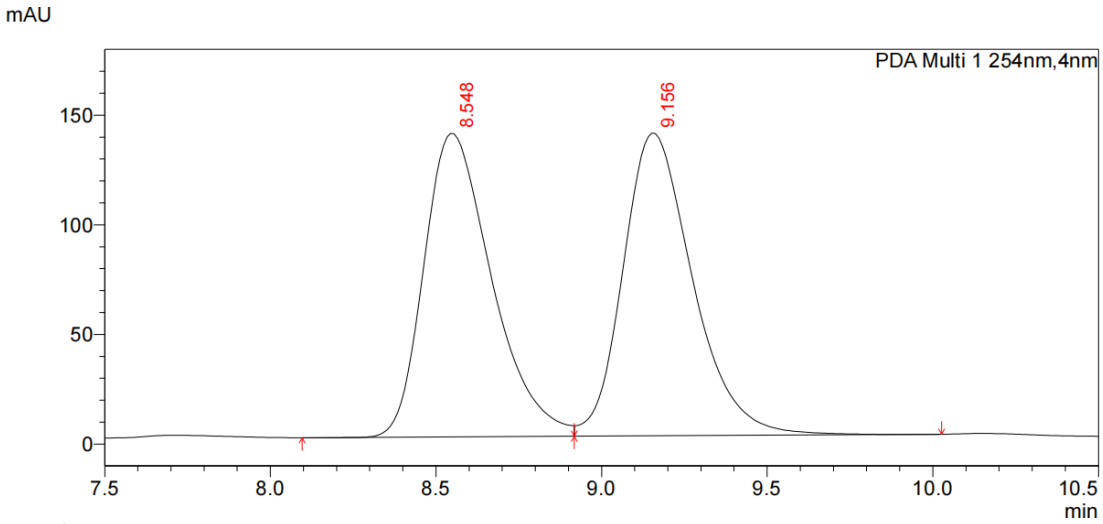

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.551 | 83542 | 6206 | 1.595 |
| 2 | 10.499 | 5152700 | 138642 | 98.405 |
| Total | | 5236242 | 144848 | 100.000 |

**(*R*)-1,2',7'-trichlorospiro[aziridine-2,9'-fluorene] (3m):**

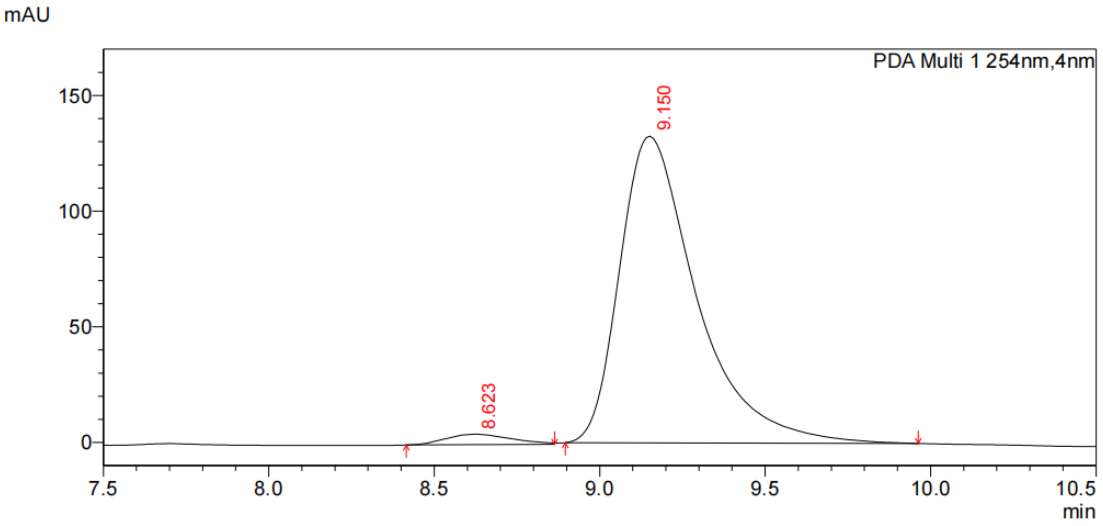



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 1:99), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

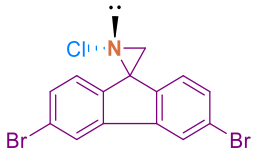
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 8.548 | 1971150 | 138432 | 49.411 |
| 2 | 9.156 | 2018113 | 138134 | 50.589 |
| Total | | 3989263 | 276566 | 100.000 |



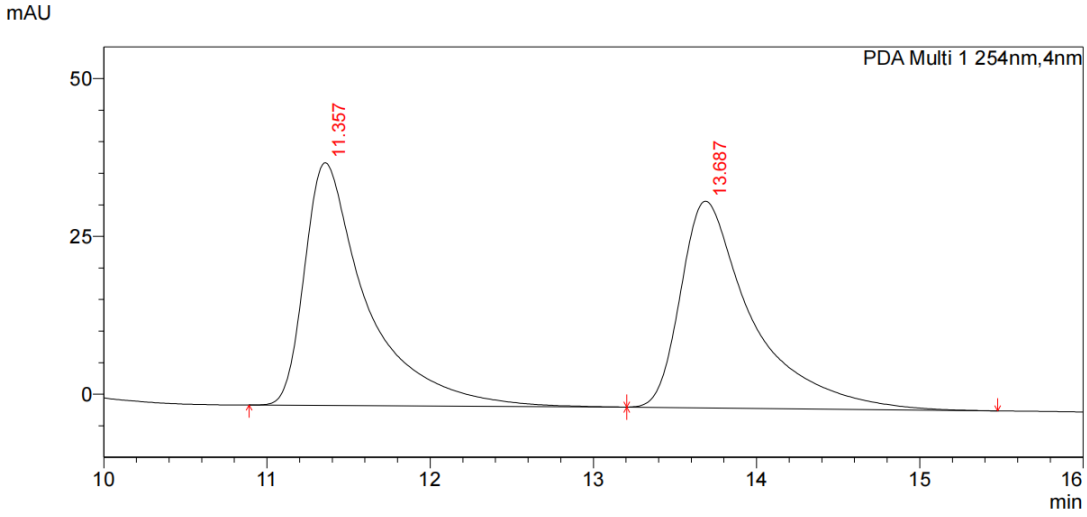

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 8.623 | 63035 | 4545 | 2.856 |
| 2 | 9.150 | 2144064 | 132509 | 97.144 |
| Total | | 2207099 | 137054 | 100.000 |

**(*R*)-3',6'-Dibromo-1-chlorospiro[aziridine-2,9'-fluorene] (3n):**

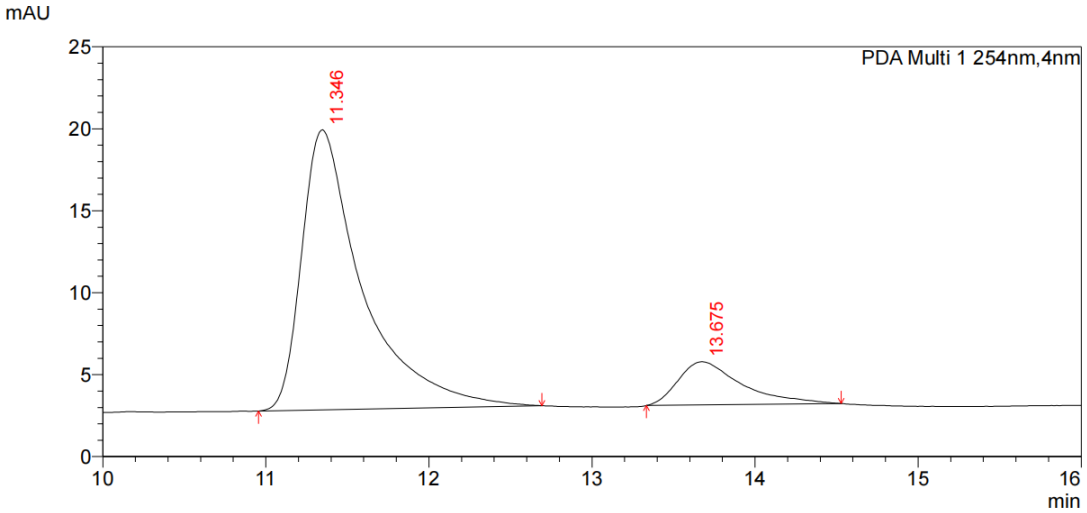



**HPLC conditions**: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 11.357 | 1022044 | 38453 | 50.581 |
| 2 | 13.687 | 998547 | 32750 | 49.419 |
| Total | | 2020591 | 71204 | 100.000 |

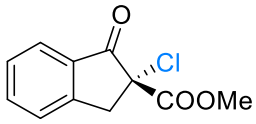



**<Peak Table>**

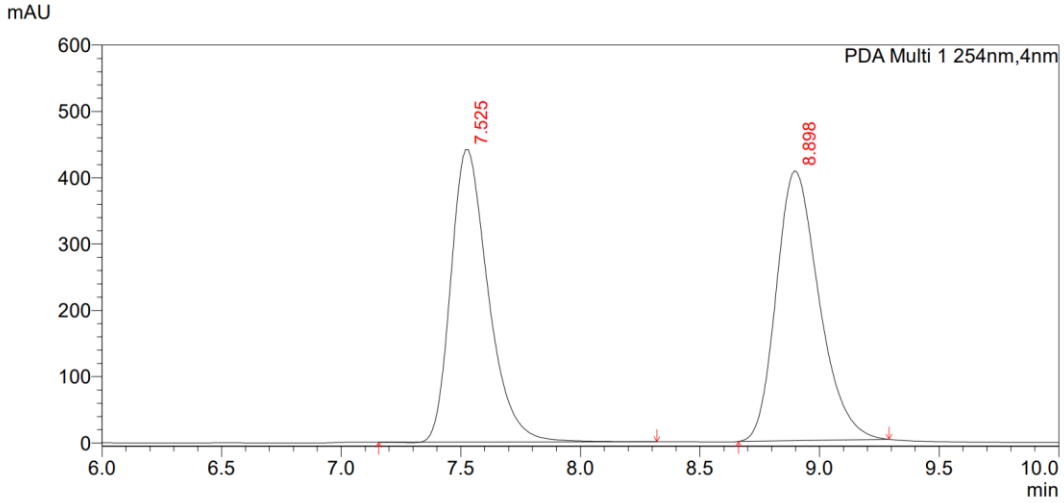
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 11.346 | 442473 | 17080 | 86.147 |
| 2 | 13.675 | 71151 | 2633 | 13.853 |
| Total | | 513624 | 19713 | 100.000 |

**(*R*)-Methyl 2-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (5a)**

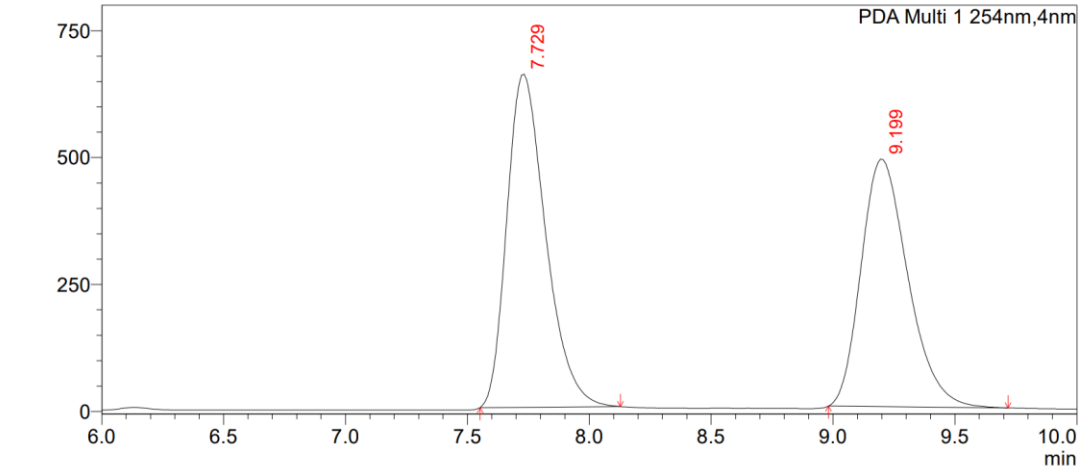



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min$^{-1}$, Temp: RT.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.525 | 4797552 | 441101 | 48.644 |
| 2 | 8.898 | 5065010 | 407208 | 51.356 |
| Total | | 9862561 | 848308 | 100.000 |

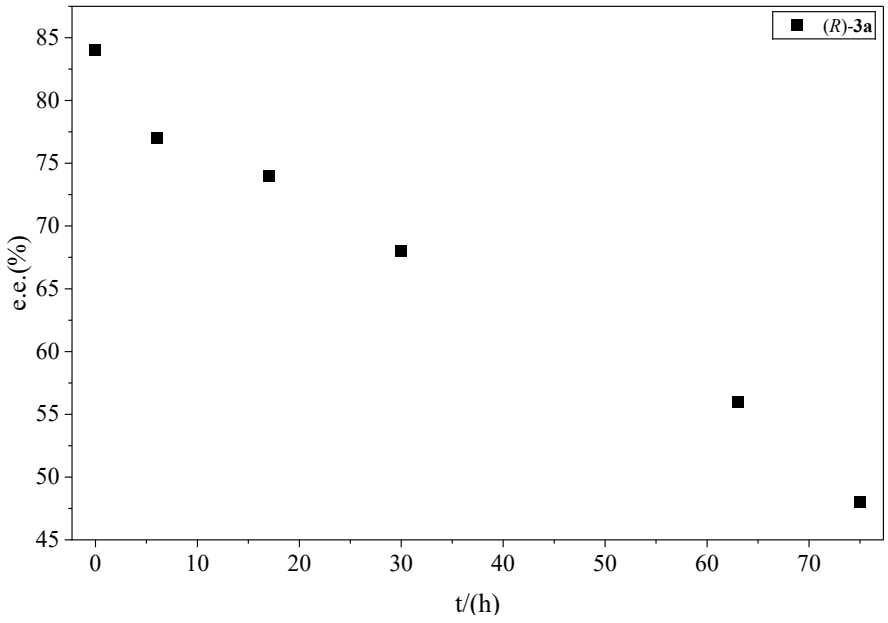


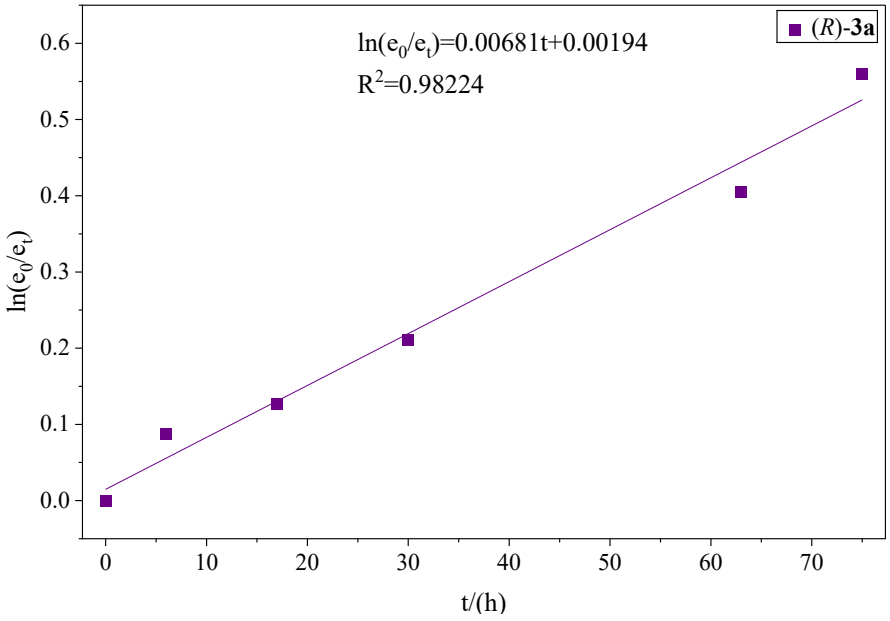

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 7.729 | 7259279 | 656013 | 52.727 |
| 2 | 9.199 | 6508289 | 487358 | 47.273 |
| Total | | 13767568 | 1143371 | 100.000 |

### 3.6 Inversion barrier of 3a, 3b and 3l

Determination of $t_{1/2rac}$ for **3a**: The barrier to rotation of **3a** was determined according to the literature method ($t_{1/2rac}$ = 101.9 h at r.t. (298 K), *i*PrOH; $\Delta G^{\neq}$ = 25.7 kcal/mol).[3]




$\ln ee_0/ee_t = 2k_{ent}t + C$

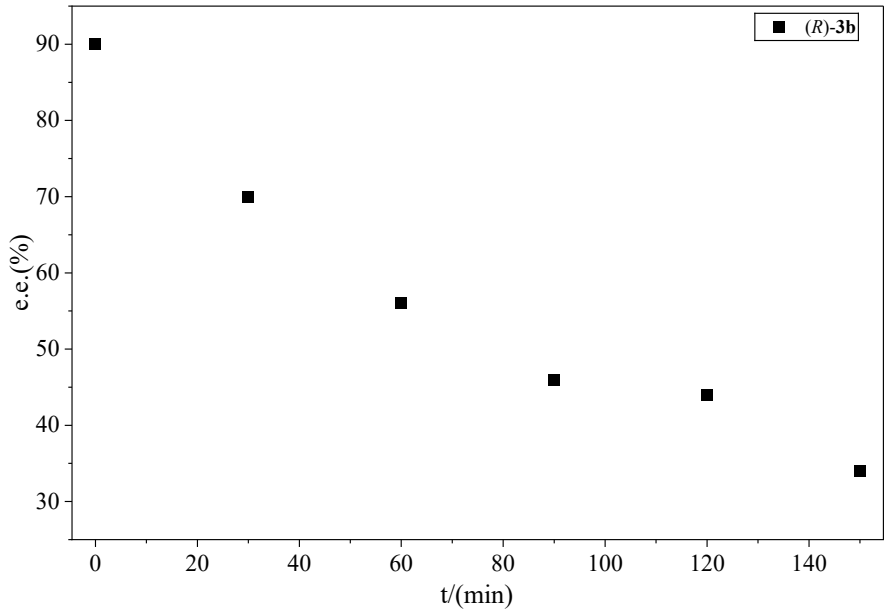
Therefore, $k_{ent}$= 1/2 slope = $3.4\times10^{-3}$

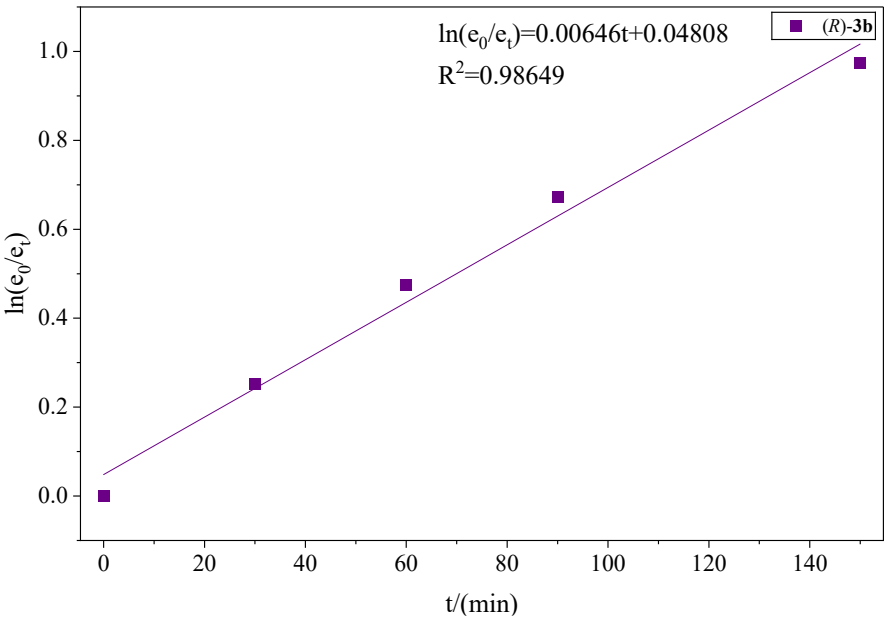
$K_{rac} = 2k_{ent} = 6.8\times10^{-3}$ $h^{-1}$

$t_{1/2rac} = \ln2/k_{rac}$ = 101.9 h

$\Delta G^{\neq} = -RT\ln(k_{ent}h/k_BT)$ = 25.7 kcal/mol

Determination of $t_{1/2rac}$ for **3b**: The barrier to rotation of **3b** was determined according to the literature method ($t_{1/2rac}$ = 1.8 h at 40 ºC. (313 K), *i*PrOH; $\Delta G^{\neq}$ = 24. 5 kcal/mol).




$lnee_0/ee_t = 2k_{ent}t + C$

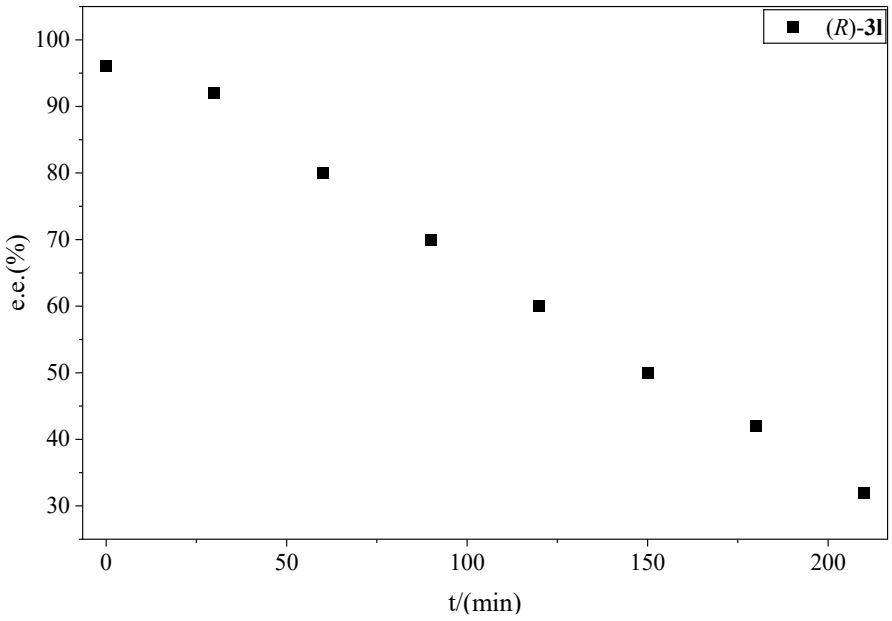
Therefore, $k_{ent}$ = 1/2 slope = $3.3\times10^{-3}$

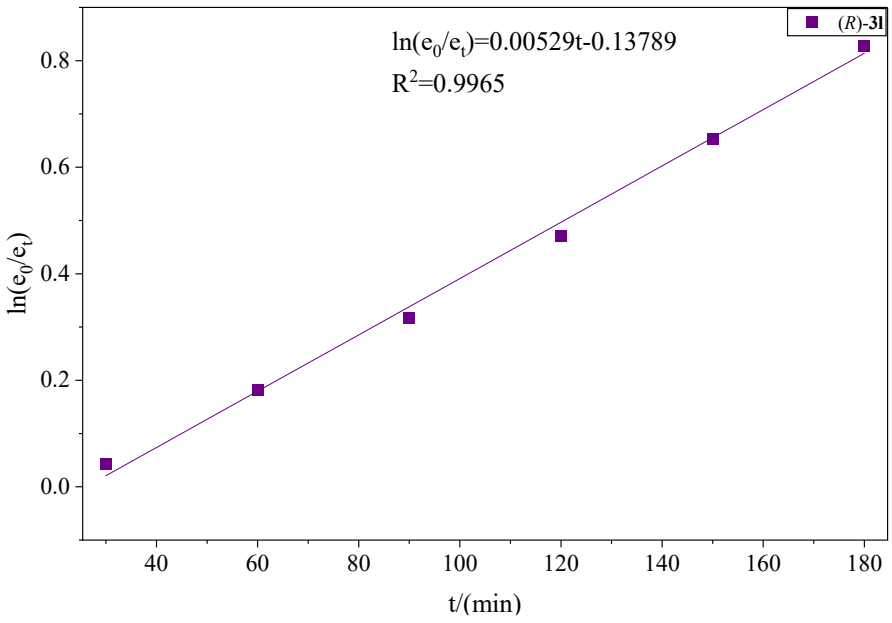
$K_{rac} = 2k_{ent} = 6.6\times10^{-3}$ $min^{-1}$

$t_{1/2rac} = ln2/k_{rac}$ = 1.8 h

$\Delta G^{\neq} = -RTln(k_{ent}h/k_BT)$ = 24. 5 kcal/mol

Determination of $t_{1/2rac}$ for **3l**: The barrier to rotation of **3l** was determined according to the literature method ($t_{1/2rac}$ = 2.2 h at 40 ºC. (313 K), *i*PrOH; $\Delta G^{\neq}$ = 24.6 kcal/mol).




$lnee_0/ee_t = 2k_{ent}t + C$

$K_{ent}$ = 1/2 slope = $2.6\times10^{-3}$

$K_{rac} = 2k_{ent} = 5.29\times10^{-3}$ $min^{-1}$

$t_{1/2rac} = ln2/k_{rac}$ = 2.2 h

$\Delta G^{\neq} = -RTln(k_{ent}h/k_BT)$ = 24.6 kcal/mol