Supplementary Information

The asymmetric synthesis of terminal aziridines by methylene transfer from sulfonium ylides to imines

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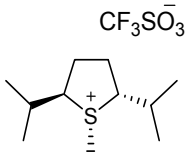
1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 or 600 MHz spectrometer in $CDCl_3$ referenced relative to residual $CHCl_3$ (δ = 7.26 ppm) or DMSO-d_6 referenced relative to residual DMSO-d_6 (δ = 2.50 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instruments (100 or 150 MHz) with total proton decoupling. All melting points are uncorrected. Infrared spectra were obtained on a Perkin Elmer Spectrum One spectrophotometer. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised by UV irradiation, $KMnO_4$, phosphomolybdic acid, or anisaldehyde staining. Specific rotation measurements were made on a Rudolph research analytical Autopol IV instrument, and are quoted in units of 10^{-1}degcm^{2}g^{-1}. Anhydrous THF was distilled over sodium-benzophenone ketyl radical before use. Methylene chloride, toluene and triethylamine were distilled from calcium hydride. All reactions were carried out under a protective argon atmosphere. Analytical CSP-HPLC was performed on Daicel CHIRALCEL OJ-H (4.6 mm x 25 cm) and CHIRALPAK AD-H (4.6 mm x 25 cm). Solid reagents for all catalysed reactions were weighed using a Precisa balance, series 320XR, model XR125SM-FR (readability 0.01 mg/0.1 mg). For all known compounds the spectral characteristics were in agreement with those reported in the literature. (2*R*,5*R*)-2,5-Diisopropyl-thiolane was prepared according to a literature procedure.[1] Imines *N*-benzylidene-4-methoxybenzenamine **(1b)**[2], *N*-(benzylidene)-4-methylbenzenesulfonamide **(1a)**[3], *P*,*P*-diphenyl-*N*-(phenylmethylene)phosphinic amide **(1e)**[4] and *N*-Phenyl benzaldehyde imine **(1d)**[5] were prepared according to literature procedures. The spectroscopic data of the aforementioned compounds were consistent with those previously reported.

2.0 Synthesis of chiral salt (*R*,*R*)-13



A 5 cm^3 oven dried round bottomed flask was charged with (2*R*,5*R*)-2,5-diisopropyl-thiolane[1] (17 mg, 0.09 mmol). The flask was fitted with a septum and placed under an atmosphere of argon (balloon) when CH_2Cl_2 (0.5 cm^3, 0.2 M) and methyl triflate (10.8 µL, 0.099 mmol) were added sequentially *via* syringe. The resulting solution was allowed to stir at room temperature for 1.5 h. The solvent was removed *in vacuo* and the resulting sulfonium salt **(*R*,*R*)-13** was obtained as a yellow tacky solid in quantitative yield. $[\alpha]_D^{20}$ = -168.3 (c 0.3, CH_2Cl_2).

δ_H (600 MHz, $CDCl_3$): 1.12 (d, J 6.4, 3H), 1.16-1.18 (m, 9H), 1.87 (ddd, J 5.5, 12.3, 27.3, 1H), 2.10 (m, 1H), 2.21 (qd, J 6.8, 7.1, 1H), 2.45 (ddd, J 5.5, 13.2, 27.6, 1H), 2.56 (m, 1H), 2.73 (m, 1H), 2.91 (s, 3H), 3.42 (m, 1H), 4.26 (m, 1H).

δ_C (150 MHz, $CDCl_3$): 19.8, 20.3, 20.9, 21.1, 22.9, 28.2, 31.7, 32.8, 32.9, 68.5, 75.1.

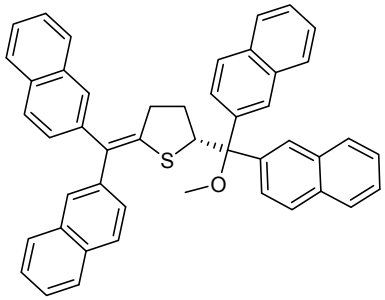
δ_F (376 MHz, $CDCl_3$): -78.9 (s, 3F).

υ (cm^{-1}): 755, 841, 952, 968, 1027, 1158, 1224, 1260, 1371, 1389, 1425, 1449, 1471, 2877, 2961.

HRMS (ESI): $[M]^+$ Calcd. for $C_{11}H_{23}S$ 187.1520; found 187.1517.

3.0 Decomposition products derived from (*R*,*R*)-8

Decomposition product 9



Was obtained as a yellow solid. M.p. 109-110 ˚C.

δ_H (600 MHz, $CDCl_3$): 2.04-2.13 (m, 2H), 2.32-2.37 (m, 1H), 2.55-2.59 (m, 1H), 3.15 (s, 3H), 4.98-5.06 (m, 1H), 6.90 (d, J 7.7, 1H), 7.14 (s, 1H), 7.29 (d, J 9.7, 1H), 7.35 (d, J 8.8, 1H), 7.37-7.60 (m, 11H), 7.69-7.85 (m, 9H), 7.91 (d, J 7.9, 1H), 7.95 (d, J 7.9, 1H), 8.03 (s, 1H), 8.12 (s, 1H).

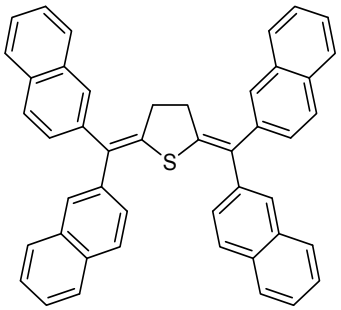
δ_C (150 MHz, $CDCl_3$): 31.4, 35.7, 51.7, 55.1, 85.6 (q), 125.6, 125.7, 125.80, 125.82, 126.0, 126.1, 126.37, 126.39, 126.8, 127.2, 127.3, 127.4 (2xC), 127.45, 127.51, 127.56,

127.64 (2xC), 127.7, 127.79, 127.84, 128.0, 128.1, 128.2, 128.3, 128.4, 128.62, 128.63 (C+C(q)), 131.9 (q), 132.3 (q), 132.49 (q), 132.54 (q), 132.77 (q), 132.80 (q), 133.1 (q), 133.3 (q), 138.4 (q), 139.1 (q), 139.9 (q), 140.5 (q), 143.0 (q).

υ (cm^{-1}): 745, 799, 819, 856, 1073, 1124, 1504, 1597, 2854, 2925, 3053.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{47}H_{36}OSNa$ 671.2385; found 671.2370.

Decomposition product 10



Was obtained as an orange solid. M.p. 253-255 ˚C.

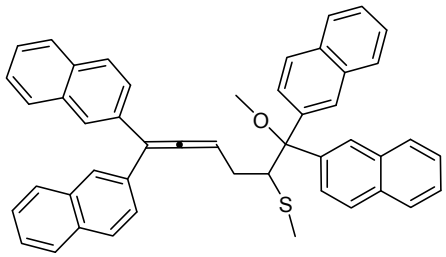
δ_H (600 MHz, $CDCl_3$): 3.07 (s, 4H), 7.29-7.31 (m, 2H), 7.39-7.47 (m, 10H), 7.71-7.82 (m, 16H).

δ_C (100 MHz, $CDCl_3$): 36.4, 126.18, 126.22 (2xC), 126.5, 127.87, 127.93 (2xC), 128.0, 128.1, 128.2 (2xC), 128.4, 128.6, 128.8, 131.2 (q), 132.5 (q), 132.7 (q), 133.5 (q), 133.6 (q), 139.9 (q), 140.2 (q), 141.7 (q).

υ (cm^{-1}): 745, 799, 819, 856, 1073, 1124, 1504, 1597, 2854, 2925, 3053.

HRMS (MALDI): $[M]^+$ Calcd. for $C_{46}H_{32}S$ 616.2225; found 616.2199.

Decomposition product 11



Was obtained as a yellow solid. M.p. 133-134 ˚C.

δ_H (600 MHz, $CDCl_3$): 1.87 (s, 3H), 2.09-2.14 (m, 1H), 3.08 (s, 3H), 3.15-3.19 (m, 1H), 4.02 (dd, J 1.7, 11.0, 1H), 6.04 (t, J 6.9, 1H), 7.287.33 (m, 1H), 7.46-7.92 (m, 25H, H-Ar), 8.05 (s, 2H).

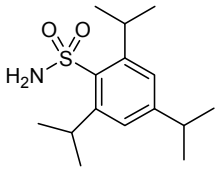
δ_C (150 MHz, $CDCl_3$): 14.09, 31.7, 51.8, 53.6, 87.2 (q), 92.9, 110.6 (q), 125.88, 125.93 (2xCH), 125.99, 126.1, 126.17, 126.25, 126.27, 126.89, 126.92, 127.1(2xCH), 127.23, 127.24, 127.27 (2xCH), 127.34, 127.4, 127.60, 127.64, 127.92, 127.98, 127.99, 128.02, 128.3, 128.49, 128.53, 128.7, 132.49 (q), 132.53 (q), 132.6 (q), 132.67 (q), 132.71 (2xq), 133.48 (q), 133.52 (q), 134.3 (q), 134.4 (q), 137.7 (q), 137.9 (q), 206.9 ((q) allene),

υ (cm^{-1}): 744, 818, 951, 1125, 1504, 1596, 2854, 2923, 3054, 3338.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{48}H_{38}OSNa$ 685.2541; found 685.2542.

4.0 Synthesis of imines 1c and 14-20

2,4,6-Triisopropylbenzenesulfonamide



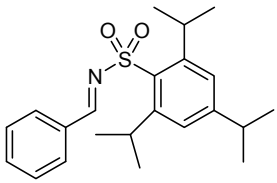
A 100 cm^3 round bottomed flask containing a stirring bar was charged with 2,4,6-triisopropylbenzenesulfonyl chloride (6.057 g, 20.00 mmol) followed by $CHCl_3$ (30 cm^3, 0.66 M). The solution was then treated with NH_3(aq) (5.5 cm^3, 100 mmol, 28% solution) and allowed to stir at room temperature for 2 h. The reaction mixture was transferred to a separating funnel and extracted with $CHCl_3$ (3 x 30 cm^3). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was placed on a frit, washed with hexane and dried by suction filtration to afford 2,4,6-triisopropylbenzenesulfonamide (5.385 g, 95%) as a white solid. M.p. 130-131 °C (lit[6] 118.5-119.5 °C). The NMR spectrum was consistent with those previously reported.[7]

δ_H (400 MHz, $CDCl_3$): 1.25 (d, J 6.8, 6H), 1.29 (d, J 6.8, 12H), 2.90 (septet, J 6.9, 1H), 4.11 (septet, J 6.7, 2H), 4.80 (br s, 2H, NH), 7.17 (s, 2H).

General procedure A: synthesis of imines (1c and 14-20)

An oven dried round bottomed flask was charged with 2,4,6-triisopropylbenzenesulfonamide (1 equiv.), fitted with a septum and placed under an atmosphere of argon (balloon). CH_2Cl_2 was then added *via* syringe followed by triethylamine (3 equiv.) and the appropriate aldehyde (1 equiv.). The resulting solution was cooled to 0 °C. Titanium(IV) chloride (0.5 equiv.) in CH_2Cl_2 was then added dropwise to the cooled solution and the resulting solution was allowed to stir for 1 h at this temperature. The reaction mixture was filtered through Celite and washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the resulting solid was suspended in toluene and then filtered. The filtrate was then concentrated under reduced pressure to afford the desired imine which was purified as required.

***N*-Phenylmethylidene-2,4,6-triisopropylbenzenesulfonamide (1c)**

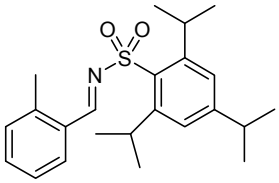


Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (1 g, 3.528 mmol), triethylamine (1.50 cm^3, 10.6 mmol), benzaldehyde (357 µL, 3.53 mmol), CH_2Cl_2 (7.0 cm^3) and titanium(IV) chloride (195 µL, 1.76 mmol) in CH_2Cl_2 (2 cm^3). The product **1c** was obtained as an off white solid (976 mg,

74%). M.p. 128-129 °C (lit.[8] 128-130 °C). The NMR spectrum of **1c** was consistent with those previously reported.[8]

δ_H (400 MHz, $CDCl_3$): 1.26 (d, J 7.0, 6H), 1.29 (d, J 6.8, 12H), 2.91 (septet, J 7.0, 1H), 4.36 (septet, J 6.7, 2H), 7.20 (s, 2H), 7.44-7.52 (m, 2H), 7.61 (t, J 7.5, 1H), 7.92 (d, J 7.1, 2H), 9.02 (s, 1H).

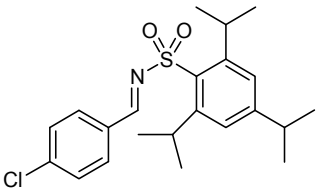
***N*-(2-Methylphenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (16)**



Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (500 mg, 1.764 mmol), triethylamine (738 µL, 5.29 mmol), *o*-tolualdehyde (204 µL, 1.76 mmol), CH_2Cl_2 (6.0 cm^3) and titanium(IV) chloride (97 µL, 0.88 mmol) in CH_2Cl_2 (1 cm^3). After purification of the crude material by flash chromatography (1:1 hexane/$CHCl_2$), **16** was obtained as a yellow solid (551 mg, 81%). M.p. 79-81 °C. The NMR spectrum of **16** was consistent with those previously reported.[7]

δ_H (400 MHz, $CDCl_3$): 1.25 (d, J 6.4, 6H), 1.29 (d, J 7.0, 12H), 2.60 (s, 3H), 2.91 (septet, J 6.4, 1H), 4.37 (septet, J 6.7, 2H), 7.19 (s, 2H), 7.26-7.31 (m, 2H), 7.42-7.51 (m, 1H), 8.01 (d, J 7.6, 1H), 9.35 (s, 1H).

***N*-(4-Chlorophenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (14)**

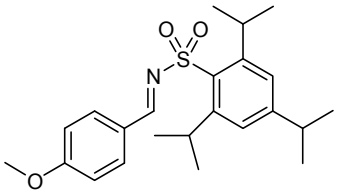


Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (500 mg, 1.764 mmol), triethylamine (738 µL, 5.29 mmol), *p*-chlorobenzaldehyde (248 mg, 1.76 mmol), CH_2Cl_2 (3.5 cm^3)

and titanium(IV) chloride (97 μL, 0.88 mmol) in CH_2Cl_2 (1.0 cm^3). The crude product was recrystallised from CH_2Cl_2/hexane to afford **14** as an amorphous white solid (130 mg, 18%). M.p. 198-199 °C. The NMR spectrum of **14** was consistent with those previously reported.[7]

δ_H (400 MHz, $CDCl_3$): 1.26 (d, J 7.0, 6H), 1.28 (d, J 6.5, 12H), 2.91 (septet, J 7.0, 1H), 4.32 (septet, J 6.5, 2H), 7.20 (s, 2H), 7.48 (d, J 8.5, 2H), 7.86 (d, J 8.5, 2H), 8.98 (s, 1H).

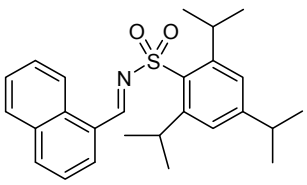
_N_-(4-Methoxyphenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (18)



Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (500 mg, 1.764 mmol), triethylamine (738 μL, 5.29 mmol), *p*-anisaldehyde (215 μL, 1.76 mmol), CH_2Cl_2 (6.0 cm^3) and titanium(IV) chloride (97 μL, 0.88 mmol) in CH_2Cl_2 (1 cm^3). The crude product was recrystallised from EtOAc/hexane to afford **18** as a yellow crystalline solid (403 mg, 57%). M.p. 189-190 °C. The NMR spectrum of **18** was consistent with those previously reported.[7]

δ_H (400 MHz, $CDCl_3$): 1.25 (d, J 7.0, 6H), 1.28 (d, J 6.8, 12H), 2.90 (septet, J 6.9, 1H), 3.88 (s, 3H), 4.36 (septet, J 6.8, 2H), 6.97 (d, J 8.8, 2H), 7.18 (s, 2H), 7.88 (d, J 8.8, 2H), 8.92 (s, 1H).

_N_-(1-Naphthyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (15)

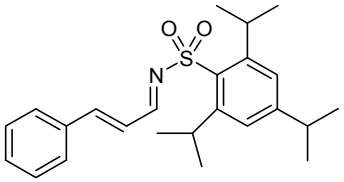


Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (400 mg, 1.411 mmol), triethylamine (590 μL, 4.23 mmol), 1-naphthaldehyde (193 μL, 1.41 mmol), CH_2Cl_2 (10.0 cm^3) and

titanium(IV) chloride (78 μL, 0.71 mmol). The crude product was recrystallised from CH_2Cl_2/hexane to afford **15** as a yellow solid (412 mg, 69%). M.p. 169-170 °C. The NMR spectrum of **15** was consistent with those previously reported.[7]

δ_H (600 MHz, $CDCl_3$): 1.26 (d, J 6.9, 6H), 1.32 (d, J 6.8, 12H), 2.91 (septet, J 6.9, 1H), 4.46 (septet, J 6.7, 2H), 7.21 (s, 2H), 7.53-7.60 (m, 2H), 7.60-7.70 (m, 1H), 7.92 (d, J 8.1, 1H), 8.10 (d, J 8.2, 1H), 8.12 (d, J 7.1, 1H), 9.09 (d, J 8.5, 1H), 9.59 (s, 1H).

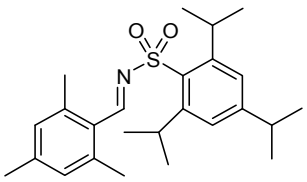
2,4,6-Triisopropyl-*N*-(3-phenylallylidene)benzenesulfonamide (19)



Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (400 mg, 1.41 mmol), triethylamine (590 μL, 4.234 mmol), *trans*-cinnamaldehyde (178 μL, 1.411 mmol), CH_2Cl_2 (10.0 cm^3) and titanium(IV) chloride (78 μL, 0.71 mmol). The crude product was recrystallised from EtOAc /hexane to afford **19** as a yellow solid (239 mg, 43%). M.p. 164-165 °C (lit[9] 166-167 °C). The NMR spectrum of **19** was consistent with those previously reported.[9]

δ_H (400 MHz, $CDCl_3$): 1.25 (d, J 7.0, 6H), 1.27 (d, J 6.8, 12H), 2.91 (septet, J 6.9, 1H), 4.24 (septet, J 6.8, 2H), 7.00 (dd, J 9.3, 15.8, 1H), 7.19 (s, 2H), 7.41-7.48 (m, 4H), 7.55-7.58 (m, 2H), 8.75 (d, J 9.3, 1H).

***N*-(Mesityl)methylidene-2,4,6-triisopropylbenzenesulfonamide (17)**



Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (400 mg, 1.411 mmol), triethylamine (590 μL, 4.23 mmol), mesitaldehyde (205 μL, 1.41 mmol), CH_2Cl_2 (10.0 cm^3) and

titanium(IV) chloride (78 µL, 0.71 mmol). The product was purified by column chromatography (7:3 hexane:CH_2Cl_2) to yield **17** as a white crystalline solid (378 mg, 65%). M.p. 64-66 °C.

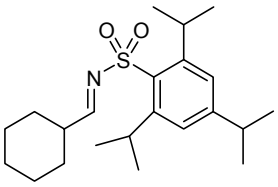
δ_H (400 MHz, $CDCl_3$): 1.25 (d, J 7.1, 6H), 1.28 (d, J 6.8, 12H), 2.32 (s, 3H), 2.55 (s, 6H), 2.91 (septet, J 6.9, 1H), 4.36 (septet, J 6.7, 2H), 6.93 (s, 2H), 7.18 (s, 2H), 9.49 (s, 1H).

δ_C (100 MHz, $CDCl_3$): 21.7, 21.9, 23.7, 24.9, 29.9, 34.4, 123.9, 126.4 (q), 130.8, 131.6 (q), 142.8 (q), 144.5 (q), 151.4 (q), 153.6 (q), 168.0.

υ (cm^{-1}): 667, 772, 829, 1041, 1148, 1294, 1314, 1560, 1594, 2871, 2926, 2960.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{25}H_{36}NO_2S$ 414.2467; found 414.2477.

***N*-(Cyclohexyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (20)**



Prepared according to general procedure **A** using 2,4,6-triisopropylbenzenesulfonamide (400 mg, 1.411 mmol), triethylamine (590 µL, 4.23 mmol), cyclohexanecarboxaldehyde (171 µL, 1.411 mmol), CH_2Cl_2 (10.0 cm^3) and titanium(IV) chloride (78 µL, 0.71 mmol). The crude product was recrystallised from CH_2Cl_2 /hexane to afford **20** as a white solid (214 mg, 40%). M.p. 93-95 °C.

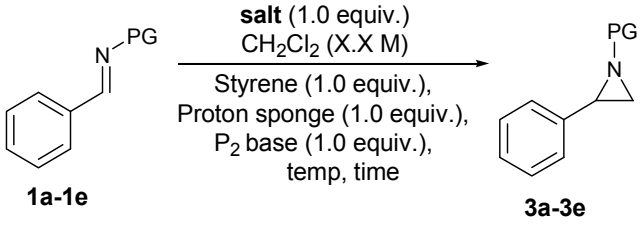
δ_H (400 MHz, $CDCl_3$): 1.24-1.36 (m, 23H), 1.66-1.69 (m, 1H, H-4b), 1.74-1.80 (m, 2H), 1.87-1.93 (m, 2H), 2.42-2.45 (m, 1H), 2.90 (septet, J 6.9, 1H), 4.16 (septet, J 6.8, 2H), 7.17 (s, 2H), 8.45 (d, J 4.2, 1H).

δ_C (100 MHz, $CDCl_3$): 23.7, 24.9, 25.3, 25.8, 28.5, 29.9, 34.4, 43.8, 123.9, 130.6 (q), 151.5 (q), 153.8 (q), 179.1.

υ (cm^{-1}): 671, 778, 799, 1152, 1295, 1312, 1621, 2852, 2926, 2953.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{22}H_{36}NO_2S$ 378.2467; found 378.2451.

5.0 Catalysis of the aziridination of imines 1a-1e (Table 2): General procedure B

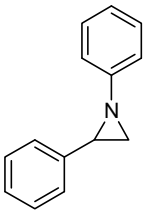


Note: These reactions must be carried out under rigorous anhydrous conditions.

An oven dried round bottomed flask containing a magnetic stirring bar and **(*R*,*R*)-13** (1 equiv.) was charged with proton sponge (1 equiv.) and the appropriate imine (1 equiv.). The flask was placed on a Schlenk line for 1 h. The flask was then immediately flushed with argon, fitted with a rubber septum and placed under an atmosphere of argon (balloon). Freshly distilled CH_2Cl_2 and styrene (1 equiv.) were then added sequentially *via* syringe. The resulting solution was allowed to stir at the appropriate temperature until such time as temperature equilibration was reached. P_2 base (2.0 M in THF, 1 equiv.) was then added dropwise. Upon completion (analysis by ^{1}H-NMR), the crude material was purified by column chromatography to furnish the corresponding aziridine.

5.1 Characterisation data for aziridines 3a-3e

(-)-1,2-Diphenylaziridine (3d)



Prepared according to general procedure **B** at ambient temperature using **(*R*,*R*)-13** (86.23 mg, 0.256 mmol), proton sponge (54.93, 0.256 mmol), *N*-benzylideneaniline (46.45 mg, 0.256 mmol), CH_2Cl_2 (0.64 cm^3), styrene (29.4 µL, 0.256 mmol) and P_2 base (128.2 µL, 0.256 mmol). Upon completion, *i.e.* 1.5 h, the yield was determined by ^{1}H-NMR spectroscopy using styrene as an internal standard (31%). To determine the enantiomeric excess, a small amount of the crude material was purified by column chromatography (6:4 hexane/CH_2Cl_2) to furnish the desired aziridine as a light yellow oil (13% *ee*). $[\alpha]_D^{20}$ = -59.3 (c 0.10, $CHCl_3$,

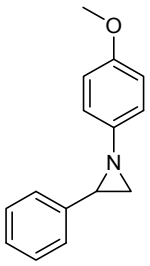
13% *ee*); lit.[10] $[\alpha]_D$ = -381.2 (*c* 0.25, $CHCl_3$, 90% *ee*). The NMR spectrum of **3d** was consistent with those previously reported.[11]

CSP-HPLC analysis: Chiralpak OJ-H (4.6 mm x 25 cm), hexane/IPA: 7/3, 1.0 mL min^{-1}, RT, UV detection at 254 nm, retention times: 11.7 min (minor enantiomer) and 13.9 min (major enantiomer).

δ_H (400 MHz, $CDCl_3$): 2.37-2.43 (m, 1H), 2.45-2.50 (m, 1H), 3.11 (dd, J 3.3, 6.6, 1H), 6.99 (t, J 7.4, 1H), 7.05 (d, J 7.7, 2H), 7.24-7.40 (m, 7H).

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{14}N$ 196.1126; found 196.1120.

1-(4'-Methoxyphenyl)-2-phenylaziridine (3b)

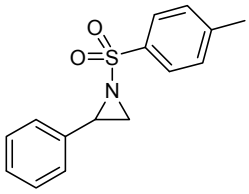


Prepared according to general procedure **B** at ambient temperature using **7** (60.00 mg, 0.238 mmol), proton sponge (50.97 mg, 0.238 mmol), ***N***-benzylidene-4-methoxybenzenamine (50.25 mg, 0.238 mmol), CH_2Cl_2 (0.6 cm^3), styrene (27.3 µL, 0.238 mmol) and P_2 base (119.0 µL, 0.238 mmol). Upon completion, *i.e.* 40 min, the yield was determined by ^{1}H-NMR spectroscopy using styrene as an internal standard (55%). To determine the enantiomeric excess, a small amount of the crude material was purified by column chromatography (95:5 hexane/Et_2O) to furnish the desired aziridine as a light yellow oil. The NMR spectrum of **3b** was consistent with those previously reported.[12]

δ_H (400 MHz, $CDCl_3$): 2.37-2.43 (m, 1H), 2.45-2.50 (m, 1H), 3.03 (dd, J 3.3, 6.6, 1H), 3.77 (s, 3H), 6.80 (d, J 8.8, 2H), 6.99 (d, J 8.7, 2H), 7.28-7.39 (m, 5H).

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{15}H_{16}NO$ 226.1232; found 226.1224.

(*R*)-2-Phenyl-1-(*p*-toluenesulfonyl)aziridine (3a)

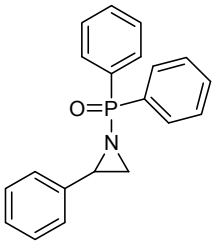


Prepared according to general procedure **B** at ambient temperature using **(*R*,*R*)-13** (80.04 mg, 0.238 mmol), proton sponge (50.99, 0.238 mmol), *N*-(benzylidene)-4-methylbenzenesulfonamide (61.64 mg, 0.238 mmol), CH_2Cl_2 (0.60 cm^3), styrene (27.3 µL, 0.238 mmol) and P_2 base (119.0 µL, 0.238 mmol). Upon completion, *i.e.* 40 min, the yield was determined by ^{1}H-NMR spectroscopy using styrene as an internal standard (87%). To determine the enantiomeric excess, a small amount of the crude material was purified by column chromatography (9:1 hexane/EtOAc) to furnish the desired aziridine as a white solid (6% *ee*). M.p. 93-95 ˚C (lit.[13] 92-93 ˚C). $[\alpha]_D^{20}$ = -15.30 (c 0.3, $CHCl_3$, 6% *ee*); lit.[13] $[\alpha]_D^{24}$ = -80.25 (*c* 0.8, $CHCl_3$). The NMR spectrum of **3a** was consistent with those previously reported. [13]

CSP-HPLC analysis: Chiralpak OJ-H (4.6 mm x 25 cm), hexane/IPA: 1/1, 0.7 mL min^{-1}, RT, UV detection at 220 nm, retention times: 17.5 min (minor enantiomer) and 21.1 min (major enantiomer).

δ_H (400 MHz, $CDCl_3$): 2.39 (d, J 4.4, 1H), 2.43 (s, 3H), 2.99 (d, J 7.2, 1H), 3.77 (dd, J 4.5, 7.0, 1H), 7.20-7.34 (m, 7H), 7.87 (d, J 8.3, 2H).

***N*-Diphenylphosphinyl-2-phenyl aziridine (3e)**



Prepared according to general procedure **B** at 60 ˚C using **(*R*,*R*)-13** (31.41 mg, 0.093 mmol), proton sponge (20.00 mg, 0.093 mmol), *P*,*P*-diphenyl-*N*-(phenylmethylene)phosphinic amide (28.50 mg, 0.093 mmol), CH_2Cl_2 (0.23 cm^3), styrene (10.7 µL, 0.09 mmol) and P_2 base (47.0 µL, 0.09 mmol). Upon completion, *i.e.* 30

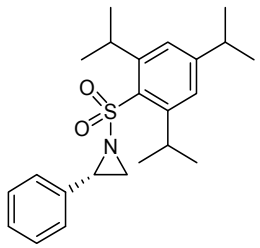
min, the yield was determined by ^{1}H-NMR spectroscopy using styrene as an internal standard (98%). To determine the enantiomeric excess, a small amount of the crude material was purified by column chromatography (7:3 hexane/EtOAc) to furnish the desired aziridine as a white solid (10% *ee*). M.p. 92-93 ˚C (lit.[14] 91 ˚C). $[\alpha]_D^{20}$ = +25.0 (c 0.1, CH_2Cl_2, 10% *ee*); lit.[14] $[\alpha]_D^{23}$ = -4.6 (*c* 5.0, CH_2Cl_2), opposite enantiomer. The NMR spectra of **3e** were consistent with those previously reported.[14]

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 18.8 min (major enantiomer) and 28.9 (minor enantiomer).

δ_H (600 MHz, $CDCl_3$): 2.22 (ddd, J 1.8, 3.6, 13.1, 1H), 2.94 (ddd, J 1.4, 6.2, 17.8, 1H), 3.77 (ddd, J 3.3, 6.3, 15.6, 1H), 7.29-7.40 (m, 7H), 7.44-7.56 (m, 4H), 7.87-7.92 (m, 2H), 7.97-8.03 (m, 2H).

δ_P (162 MHz, $CDCl_3$): 33.9 (s, 1P).

(*R*)-2-Phenyl-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (3c)



An oven dried round bottomed flask containing a magnetic stirring bar and (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (21.36 mg, 0.063 mmol) was charged with proton sponge (13.60 mg, 0.063 mmol), *N*-phenylmethylidene-2,4,6-triisopropylbenzenesulfonamide (23.58 mg, 0.063 mmol) and activated 3Å molecular sieves. The flask was placed on a Schlenk line for 1 h. The flask was then immediately flushed with argon, fitted with a rubber septum and placed under an atmosphere of argon (balloon). Freshly distilled CH_2Cl_2 (0.79 cm^3) stored over activated 3Å molecular sieves and styrene (7.3 µL, 0.063 mmol), were then added sequentially *via* syringe. The resulting solution was cooled to -78 ˚C. P_2 base (2.0 M in THF, 31.7 µL, 0.063 mmol) was then added dropwise. Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (8:2 hexane/CH_2Cl_2) to furnish the desired aziridine **3c** as a white solid (22.20 mg, 91%, 23% *ee*). M.p. 82-84 °C. $[\alpha]_D^{20}$ = - 7.9 (c 0.16, CH_2Cl_2, 23% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.5/0.5, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 10.0 min (minor enantiomer) and 12.2 (major enantiomer).

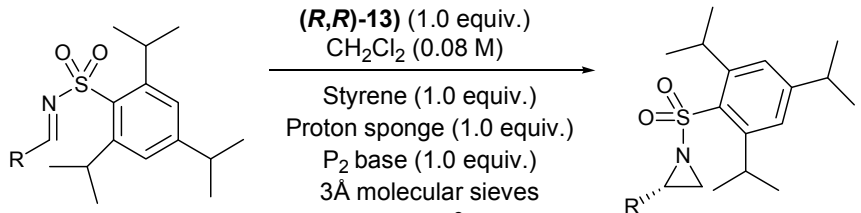
δ_H (400 MHz, $CDCl_3$): 1.23-1.28 (m, 18H), 2.37 (d, J 4.4, 1H), 2.90 (septet, J 6.9, 1H), 3.04 (d, J 7.2, 1H), 3.80 (dd, J 4.4, 7.2, 1H), 4.40 (septet, J 6.8, 2H), 7.17 (s, 2H), 7.18-7.21 (m, 2H), 7.26-7.32 (m, 3H).

δ_C (100 MHz, $CDCl_3$): 23.7, 24.9, 25.1, 29.9, 34.4, 36.3, 40.7, 124.0, 126.6, 128.3, 128.6, 131.4 (q), 135.8 (q), 151.4 (q), 153.7 (q).

υ (cm^{-1}): 694, 758, 1151, 1313, 1462, 1562, 1602, 2869, 2929, 2957.

HRMS (EI): $[M]^+$ Calcd. for $C_{23}H_{31}NO_2S$ 385.2076; found 385.2061.

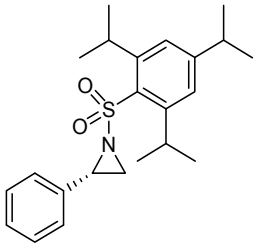
6.0 Catalysis of the aziridination of imines 1c and 14-20 using (*R*,*R*)-13 under optimised conditions (Table 3): General procedure C



An oven dried round bottomed flask containing a magnetic stirring bar and **(*R*,*R*)-13** (1 equiv.) was charged with proton sponge (1 equiv.), appropriate imine (1 equiv.) and activated 3Å molecular sieves. The flask was placed on a Schlenk line for 1 h. The flask was then immediately flushed with argon, fitted with a rubber septum and placed under an atmosphere of argon (balloon). Freshly distilled CH_2Cl_2 (0.08 M) stored over activated 3Å molecular sieves and styrene (1 equiv.), were then added sequentially *via* syringe. The resulting solution was cooled to -78 ˚C. P_2 base (2.0 M in THF, 1 equiv.) was then added dropwise. Upon completion (analysis by ^{1}H-NMR spectroscopy), the crude material was purified by column chromatography to furnish the corresponding aziridine.

6.1 Characterisation data and HPLC chromatograms for aziridines 3c and 21-27

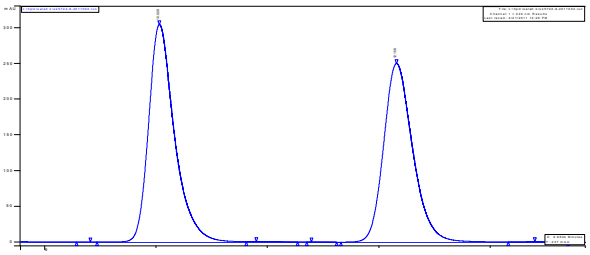
(*R*)-2-Phenyl-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (3c)



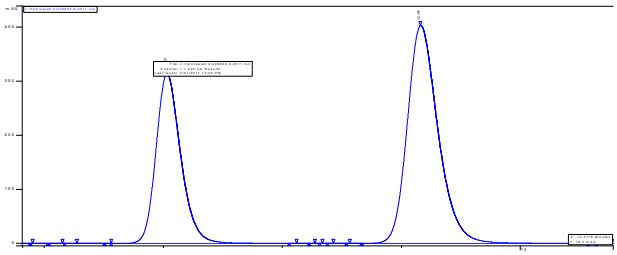
Prepared according to general procedure **C** in 91% yield, 23% *ee*. For characterisation data see section 5.1 (*vide supra*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.5/0.5, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 10.0 min (minor enantiomer) and 12.2 (major enantiomer).

(±)-(3c)

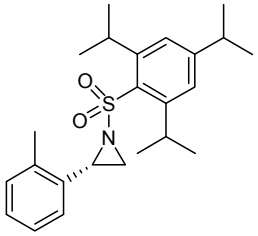


(*R*)-(3c)



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		10.029	38.5529	0.000	0.00	45500176	VV	13.1		0
2		12.161	61.4471	0.000	0.00	72519912	VB	16.6		0
	Totals		**100.0000**	**0.000**		**118020088**				

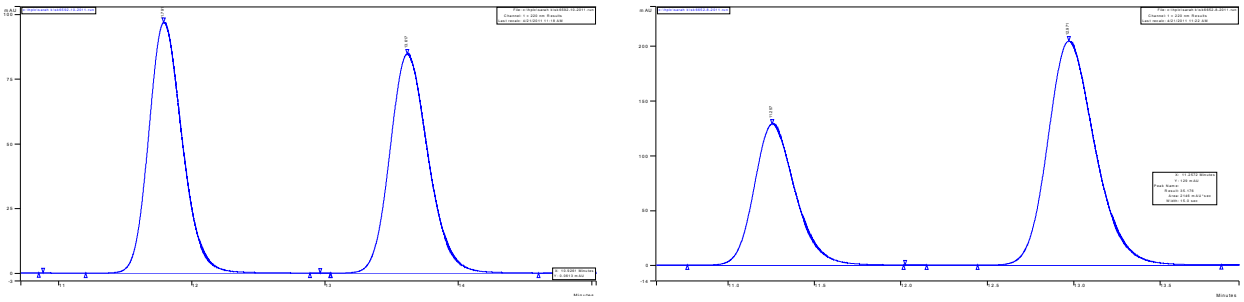
(*R*)-2-(2-Methylphenyl)-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (23)



Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (22.18 mg, 0.066 mmol), *N*-(2-methylphenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (25.42 mg, 0.066 mmol), proton sponge (14.13 mg, 0.066 mmol), CH_2Cl_2 (0.82 cm^3), styrene (7.6 µL, 0.07 mmol) and P_2 base (2.0 M in THF, 33.0 µL, 0.066 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (8:2 hexane/CH_2Cl_2) to furnish the desired aziridine **23** as a white solid (22.90 mg, 87%, 30% *ee*). M.p. 68-70 °C. $[\alpha]_D^{20}$ = - 16.0 (c 0.2, CH_2Cl_2, 30% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.8/0.2, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 11.3 min (minor enantiomer) and 13.0 (major enantiomer).

(±)-(23) **(*R*)-(23)**



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		11.257	35.1760	0.000	0.00	21460178	VV	15.0		0
2		12.971	64.8240	0.000	0.00	39547804	VP	17.4		0
	Totals		**100.0000**	**0.000**		**61007984**				

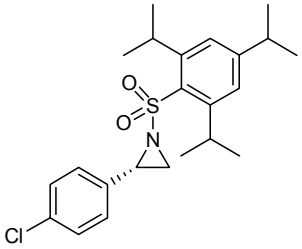
δ_H (600 MHz, $CDCl_3$): 1.25-1.28 (m, 18H), 2.29 (d, J 4.5, 1H), 2.34 (s, 3H), 2.91 (septet, J 6.9, 1H), 3.02 (d, J 7.2, 1H), 3.94 (dd, J 4.5, 7.3, 1H), 4.42 (septet, J 6.8, 2H), 7.12-7.19 (m, 6H).

δ_C (150 MHz, $CDCl_3$): 19.1, 23.7, 25.0, 25.1, 30.0, 34.4, 35.5, 38.8, 124.0, 125.9, 126.3, 128.0, 130.1, 131.5 (q), 134.0 (q), 136.8 (q), 151.4 (q), 153.7 (q).

υ (cm^{-1}): 661, 773, 894, 1105, 1319, 1460, 1601, 2865, 2925, 2959.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{24}H_{33}NO_2SNa$ 422.2130; found 422.2111.

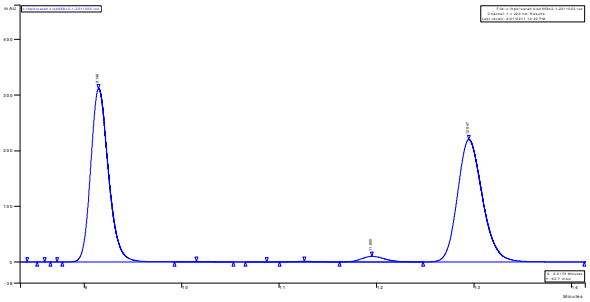
(*R*)-2-(4-Chlorophenyl)-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (21)



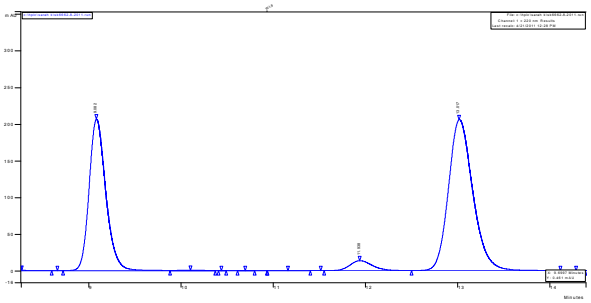
Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (22.47 mg, 0.067 mmol), *N*-(4-chlorophenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (27.11 mg, 0.067 mmol), proton sponge (14.31 mg, 0.067 mmol), CH_2Cl_2 (0.84 cm^3), styrene (7.7 µL, 0.07 mmol) and P_2 base (2.0 M in THF, 33.4 µL, 0.067 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (7:3 hexane/CH_2Cl_2) to furnish the desired aziridine **(21)** as a white solid (24.68 mg, 88%, 18% *ee*). M.p. 122-124 °C. $[\alpha]_D^{20} = -11.0$ (c 0.2, CH_2Cl_2, 18% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 9.1 min (minor enantiomer) and 13.0 (major enantiomer).

(±)-(21)



(*R*)-(21)



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		9.082	39.3725	0.000	0.00	26126124	VB	11.4		0
2		11.938	3.5308	0.000	0.00	2342939	VV	15.5		0
3		13.017	57.0966	0.000	0.00	37887196	VB	16.7		0
	Totals		**99.9999**	**0.000**		**66356260**				

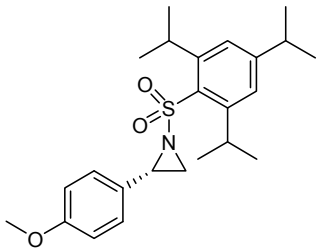
δ_H (600 MHz, $CDCl_3$): 1.24-1.27 (m, 18H), 2.33 (d, J 4.3, 1H), 2.90 (septet, J 6.9, 1H), 3.03 (d, J 7.1, 1H), 3.76 (dd, J 4.3, 7.3, 1H), 4.37 (septet, J 6.8, 2H), 7.13 (d, J 8.5, 2H), 7.18 (s, 2H), 7.27 (d, J 8.5, 2H).

δ_C (150 MHz, $CDCl_3$): 23.7, 25.0, 25.1, 29.9, 34.4, 36.4, 39.9, 124.1, 128.0, 128.9, 131.2 (q), 134.3 (q), 134.4 (q), 151.4 (q), 153.9 (q).

υ (cm^{-1}): 694, 811, 914, 1151, 1310, 1494, 1602, 2869, 2928, 2960.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{23}H_{30}NO_2ClSNa$ 442.1583; found 442.1564.

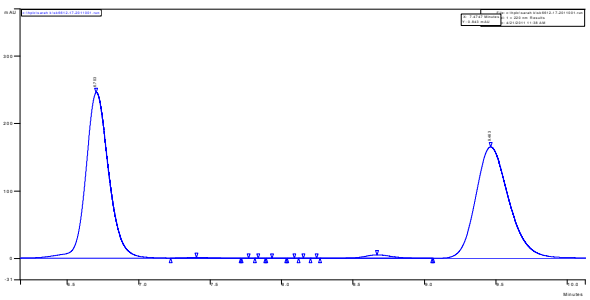
(*R*)-2-(4-Methoxyphenyl)-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (25)



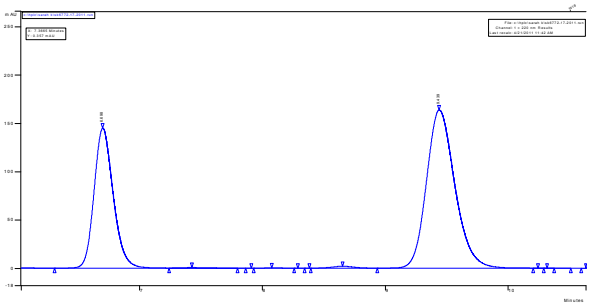
Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (29.24 mg, 0.087 mmol), *N*-(4-methoxyphenyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (34.90 mg, 0.087 mmol), CH_2Cl_2 (1.09 cm^3), styrene (10.0 µL, 0.087 mmol) and P_2 base (2.0 M in THF, 44.0 µL, 0.087 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography on silica that had been deactivated by packing column using 7:3:0.5 hexane/ CH_2Cl_2/triethylamine and using 8:2 hexane/CH_2Cl_2 as eluent. The desired aziridine **(25)** was obtained as a white solid (33.23 mg, 92%, 25% *ee*). M.p. 86-88 °C. $[\alpha]_D^{20}$ = - 29.0 (c 0.2, CH_2Cl_2, 25% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.5/0.5, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 6.7 min (minor enantiomer) and 9.4 (major enantiomer).

(±)-(25)



(*R*)-(25)



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		6.698	37.5295	0.000	0.00	15808877	VP	9.9		0
2		9.439	62.4705	0.000	0.00	26315040	VB	14.6		0
	Totals		**100.0000**	**0.000**		**42123916**				

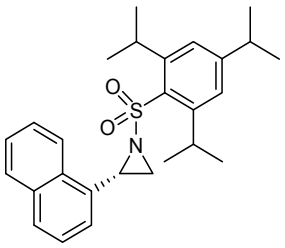
δ_H (600 MHz, $CDCl_3$): 1.21-1.27 (m, 18H), 2.35 (d, J 4.4, 1H), 2.90 (septet, J 6.9, 1H), 3.01 (d, J 7.1, 1H), 3.75 (dd, J 4.6, 7.3, 1H), 3.78 (s, 3H), 4.39 (septet, J 6.8, 2H), 6.82 (d, J 8.7, 2H), 7.11 (d, J 8.7, 2H), 7.17 (s, 2H).

δ_C (150 MHz, $CDCl_3$): 23.7, 25.0, 25.1, 29.9, 34.4, 36.1, 40.5, 55.4, 114.1, 124.0, 127.7 (q), 127.9, 131.5 (q), 151.3 (q), 153.6 (q), 159.8 (q).

υ (cm^{-1}): 668, 695, 818, 902, 1152, 1256, 1303, 1519, 1601, 2868, 2929, 2959.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{24}H_{33}NO_3SNa$ 438.2079; found 438.2077.

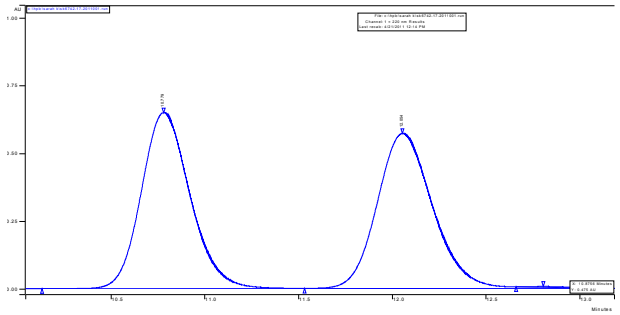
(*R*)-2-(1-Naphthyl)-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (22)

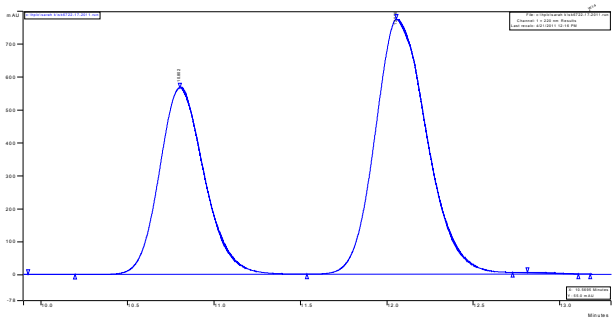


Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (27.37 mg, 0.081 mmol), *N*-(1-naphthyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (34.30 mg, 0.081 mmol), proton sponge (17.43 mg, 0.081 mmol), CH_2Cl_2 (1.00 cm^3), styrene (9.3 µL, 0.08 mmol) and P_2 base (2.0 M in THF, 40.7 µL, 0.08 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (7:3 hexane/CH_2Cl_2) to furnish the desired aziridine **(22)** as a white solid (32.60 mg, 92%, 23% *ee*). M.p. 66-68 °C. $[\alpha]_D^{20}$ = - 2.3 (c 0.2, CH_2Cl_2, 23% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.9/0.1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 10.8 min (minor enantiomer) and 12.1 (major enantiomer).

(±)-(22) **(*R*)-(22)**





Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.888	0.5488	0.000	0.00	1468506	VV	33.0		0
2		8.490	0.3863	0.000	0.00	1033701	VV	11.0		0
3		10.802	38.3555	0.000	0.00	102637968	PV	16.9		0
4		12.056	60.7095	0.000	0.00	162456512	VB	19.0		0
	Totals		**100.0001**	**0.000**		**267596688**				

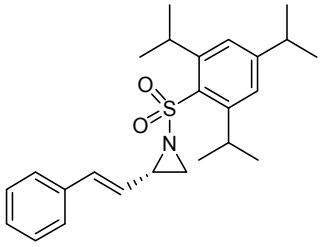
δ_H (600 MHz, $CDCl_3$): 1.21-1.34 (m, 18H), 2.44 (d, J 4.4, 1H), 2.92 (septet, J 6.9, 1H), 3.18 (d, J 7.1, 1H), 4.42 (dd, J 4.6, 7.1, 1H), 4.48 (septet, J 6.7, 2H), 7.20 (s, 2H), 7.37-7.43 (m, 2H), 7.46-7.51 (m, 2H), 7.79 (d, J 7.7, 1H), 7.86 (d, J 7.4, 1H), 8.09 (d, J 8.0, 1H).

δ_C (100 MHz, $CDCl_3$): 23.7, 25.0, 25.1, 30.0, 34.4, 35.2, 39.1, 123.1, 124.1, 124.4, 125.4, 126.1, 126.6, 128.7, 128.8, 131.4 (q), 131.6 (q), 131.7 (q), 133.4 (q), 151.4 (q), 153.8 (q).

υ (cm^{-1}): 670, 699, 779, 903, 1151, 1313, 1601, 2868, 2927, 2959.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{27}H_{33}NO_2SNa$ 458.2130; found 458.2130.

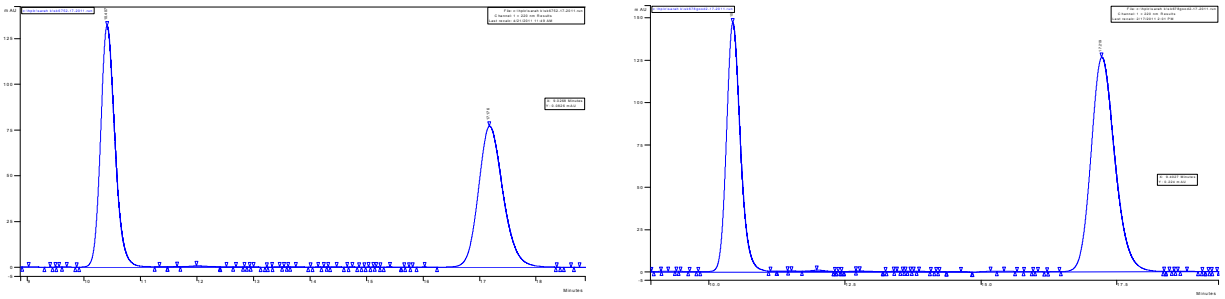
(*R*)-2-(Styryl)-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (26)



Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (28.25 mg, 0.084 mmol), 2,4,6-triisopropyl-*N*-(3-phenylallylidene)benzenesulfonamide (33.38 mg, 0.084 mmol), CH_2Cl_2 (1.05 cm^3), styrene (9.6 µL, 0.084 mmol) and P_2 base (2.0 M in THF, 42.0 µL, 0.084 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography on silica that had been deactivated by packing column using 7:3:0.5 hexane/ CH_2Cl_2/triethylamine and using 8:2 hexane/CH_2Cl_2 as eluent. The desired aziridine **(26)** was obtained as a white solid (31.79 mg, 92%, 18% *ee*). M.p. 134-136 °C.
$[\alpha]_D^{20}$ = - 20.0 (*c* 0.17, CH_2Cl_2, 18% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.9/0.1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 10.4 min (minor enantiomer) and 17.2 (major enantiomer).

(±)-(26) **(*R*)-(26)**



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		10.434	41.1931	0.000	0.00	27166134	VP	16.1		0
2		17.219	58.8069	0.000	0.00	38782088	VP	28.1		0
	Totals		**100.0000**	**0.000**		**65948224**				

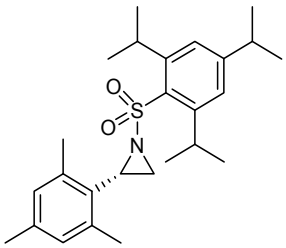
δ_H (400 MHz, $CDCl_3$): 1.24-1.29 (m, 18H), 2.30 (d, J 4.4, 1H), 2.85-2.91 (m, 2H), 3.45-3.50 (m, 1H), 4.36 (septet, J 6.8, 2H), 5.86 (dd, J 7.7, 16.2, 1H), 6.69 (d, J 15.9, 1H), 7.18 (s, 2H), 7.24-7.32 (m, 5H).

δ_C (100 MHz, $CDCl_3$): 23.7, 25.0, 25.1, 29.9, 34.4, 34.8, 40.8, 124.0, 124.8, 126.5, 128.3, 128.8, 131.6 (q), 134.7 , 136.0 (q), 151.2 (q), 153.6 (q).

υ (cm^{-1}): 663, 700, 755, 786, 939, 973, 1145, 1308, 1602, 2868, 2956.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{25}H_{33}NO_2SNa$ 434.2130; found 434.2135.

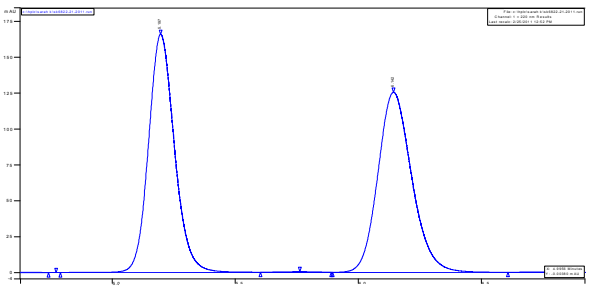
(*R*)-2-Mesityl-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (24)



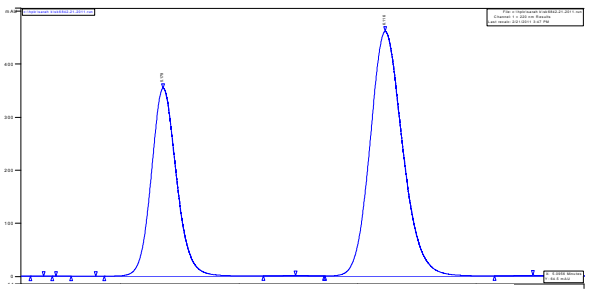
Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (27.27 mg, 0.081 mmol), *N*-(mesityl)methylidene-2,4,6-triisopropylbenzenesulfonamide (33.53 mg, 0.081 mmol), proton sponge (17.37 mg, 0.081 mmol), CH_2Cl_2 (1.01 cm^3), styrene (9.3 µL, 0.081 mmol) and P_2 base (2.0 M in THF, 40.5 µL, 0.081 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (7:3 hexane/CH_2Cl_2) to furnish the desired aziridine **(24)** as a white solid (30.16 mg, 87%, 25% *ee*). M.p. 87-89 °C. $[\alpha]_D^{20}$ = - 8.6 (c 0.3, CH_2Cl_2, 25% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9.9/0.1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 5.2 min (minor enantiomer) and 6.1 (major enantiomer).

(±)-(24)



(*R*)-(24)



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		5.179	37.2835	0.000	0.00	26231832	VV	6.7		0
2		6.116	62.7165	0.000	0.00	44125916	VB	8.7		0
	Totals		**100.0000**	**0.000**		**70357744**				

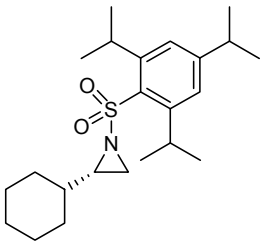
δ_H (600 MHz, $CDCl_3$): 1.24-1.29 (m 18H), 2.16 (d, J 4.7, 1H), 2.24 (s, 3H), 2.29 (s, 6H), 2.89 (d, J 7.2, 1H), 2.92 (septet, J 6.9, 1H), 3.96 (dd, J 5.1, 7.3, 1H), 4.40 (septet, J 6.8, 2H), 6.80 (s, 2H), 7.19 (s, 2H).

δ_C (100 MHz, $CDCl_3$): 20.2, 21.0, 23.7, 24.9, 25.3, 29.9, 34.37, 34.41, 39.9, 124.0, 128.8 (q), 129.3, 131.6 (q), 137.5 (q), 137.6 (q), 151.4 (q), 153.7 (q).

υ (cm^{-1}): 660, 699, 716, 834, 911, 1152, 1313, 1460, 1599, 2869, 2927, 2960.

HRMS (ESI): $[M+Na]^+$ Calcd. for $C_{26}H_{37}NO_2SNa$ 450.2443; found 450.2453.

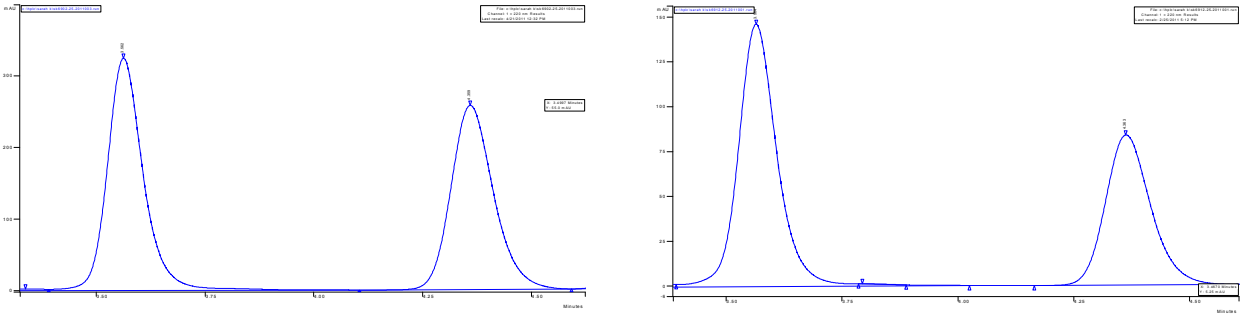
(*R*)-2-Cyclohexyl-1-(2,4,6-triisopropylbenzenesulfonyl)aziridine (27)



Prepared according to general procedure **C** using (2*R*,5*R*)-2,5-diisopropyl-thiolane triflate (30.05 mg, 0.089 mmol), *N*-(cyclohexyl)methylidene-2,4,6-triisopropylbenzenesulfonamide (33.72 mg, 0.089 mmol), proton sponge (19.14 mg, 0.089 mmol), CH_2Cl_2 (1.12 cm^3), styrene (10.2 µL, 0.089 mmol) and P_2 base (2.0 M in THF, 45.0 µL, 0.089 mmol). Upon completion, *i.e.* 16 h, the crude material was purified by column chromatography (7:3 hexane/CH_2Cl_2) to furnish the desired aziridine **(27)** as a white solid (31.82 mg, 91%, 20% *ee*). M.p. 111-113 °C. $[\alpha]_D^{20}$ = - 9.5 (c 0.2, CH_2Cl_2, 20% *ee*).

CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 3.6 min (major enantiomer) and 4.4 (minor enantiomer).

(±)-(27) **(*R*)-(27)**



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.564	60.0163	0.000	0.00	8545495	VB	5.1		0
2		4.363	39.9837	0.000	0.00	5693129	BP	6.2		0
	Totals		**100.0000**	**0.000**		**14238624**				

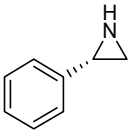
δ_H (600 MHz, $CDCl_3$): 0.85-0.91 (m, 1H), 0.95-1.02 (m, 1H), 1.08-1.21 (m, 4H), 1.25-1.27 (m, 18H), 1.40-1.43 (m, 1H), 1.60-1.70 (m, 4H), 2.09 (d, J 4.6, 1H), 2.55-2.58 (m, 1H), 2.62 (d, J 7.0, 1H), 2.91 (septet, J 6.9, 1H), 4.36 (septet, J 6.7, 2H), 7.17 (s, 2H).

δ_C (100 MHz, $CDCl_3$): 23.72 (2xC), 25.0, 25.1, 25.6, 25.8, 26.2, 29.8 (2xC), 30.0, 31.9, 34.4, 39.3, 44.6, 123.8, 131.6 (q), 151.2 (q), 153.4 (q).

υ (cm^{-1}): 666, 716, 884, 948, 1153, 1312, 1445, 1601, 2863, 2928, 2952, 2965.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{23}H_{38}NO_2S$ 392.2623; found 392.2630.

7.0 Deprotection of aziridine 3c: synthesis of (*R*)-2-diphenylaziridine for determination of configuration



An oven dried 25 cm^3 round bottomed flask containing a magnetic stirring bar was charged with naphthalene (912 mg, 7.112 mmol) and finely chopped sodium (149 mg, 6.465 mmol). The flask was fitted with a rubber

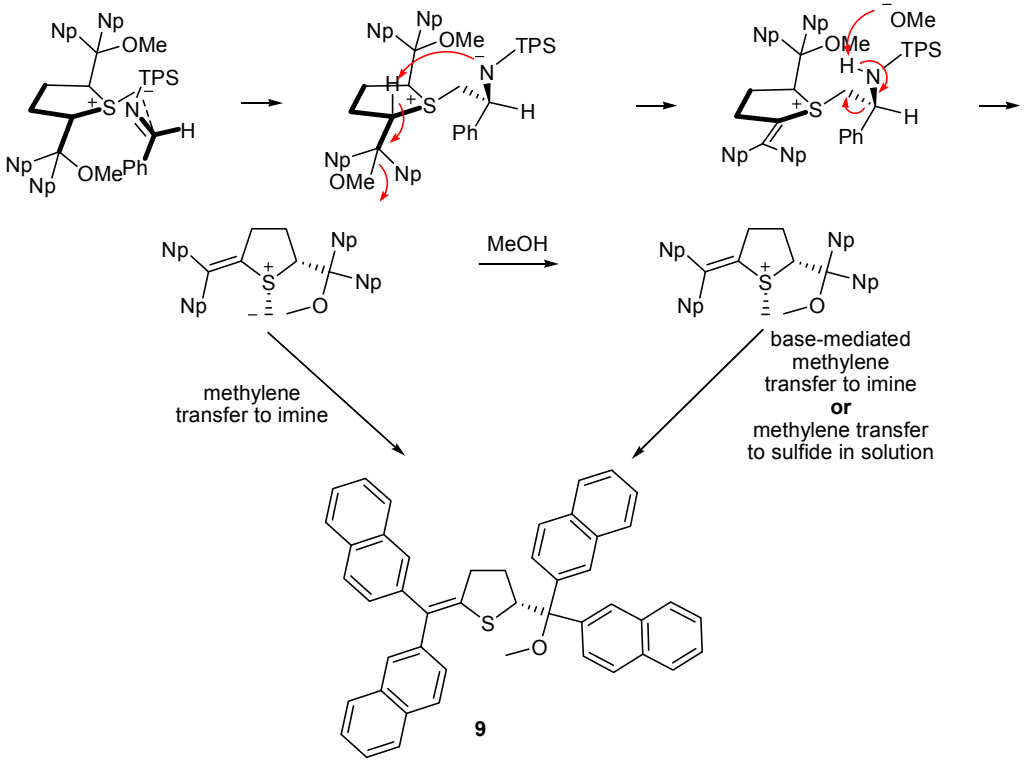
septum and placed under an atmosphere of argon (balloon). Anhydrous THF (6.4 cm^3) was added *via* syringe. The resulting solution was allowed to stir at ambient temperature for 2 h. An oven dried 25 cm^3 round bottomed flask containing a magnetic stirring bar was then charged with **3c** (124.64 mg, 0.323 mmol), fitted with a rubber septum and placed under an atmosphere of argon (balloon). Anhydrous THF (1.8 cm^3) was added *via* syringe and the resulting solution was cooled to - 78 ˚C. The sodium naphthalide solution was then added dropwise *via* syringe to the cooled solution and allowed to stir at this temperature for 10 min. The reaction mixture was then quenched by the addition of H_2O (1 cm^3). The resulting solution was diluted with Et_2O (10 cm^3), poured onto $MgSO_4$, filtered and reduced *in vacuo*. Note; due to the volatile nature of the product, the water bath of the rotary evaporator was set at 15 °C. Purification by flash chromatography using 100% hexane initially to remove excess naphthalene, followed by 100% Et_2O, afforded (*R*)-2-diphenylaziridine as a colourless oil (14.03 mg, 36%). $[\alpha]_D^{20}$ = -9.5 (c 0.1, Ethanol, 23% *ee*); lit.[15] $[\alpha]_D^{20}$ = -43.2 (*c* 1.0, EtOH). The NMR spectra of (*R*)-2-diphenylaziridine were consistent with those previously reported.[16a, 16b]

δ_H (400 MHz, $CDCl_3$): [16a] 1.04 (br s, 1H, NH), 1.84 (br s, 1H), 2.20-2.30 (m, 1H), 3.05 (br s, 1H), 7.25-7.36 (m, 5H, H-Ar).

δ_C (100 MHz, $CDCl_3$): [16b] 29.5, 32.2, 125.8, 127.2, 128.6, 140.6 (q).

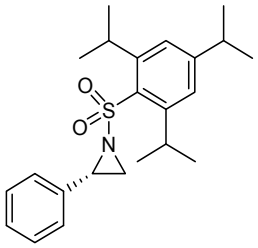
HRMS (ESI): $[M+H]^+$ Calcd. for $C_8H_{10}N$ 120.0813; found 120.0810.

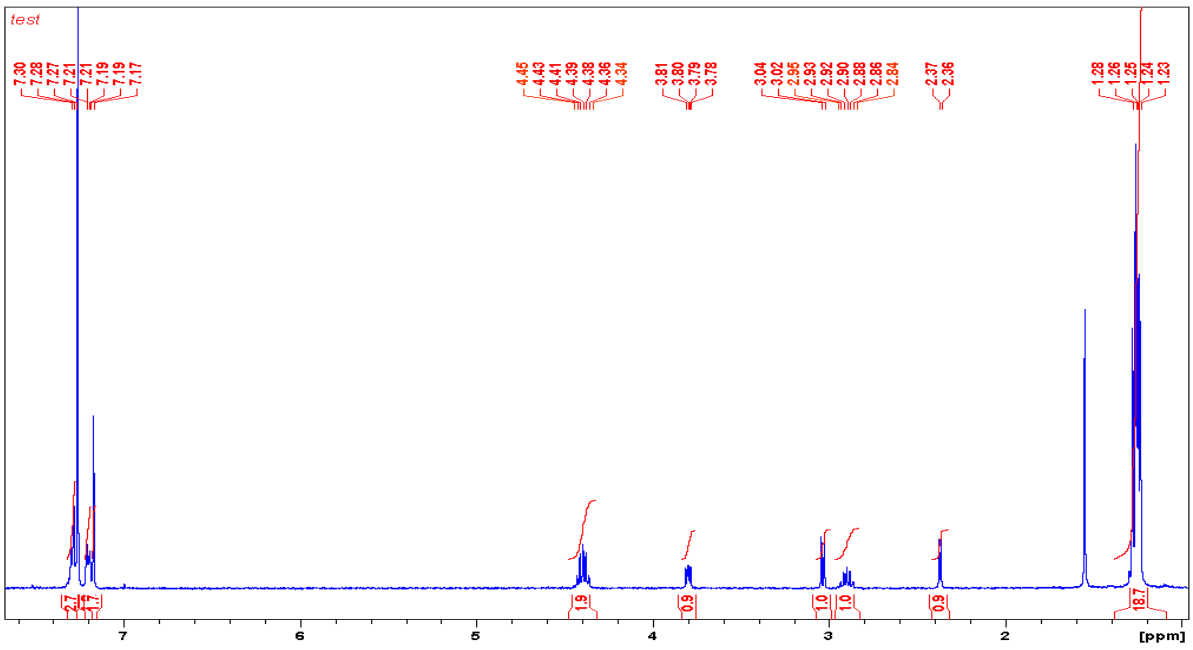
8.0 Proposed mechanism for the decomposition of salt (*R*,*R*)-8 to 9



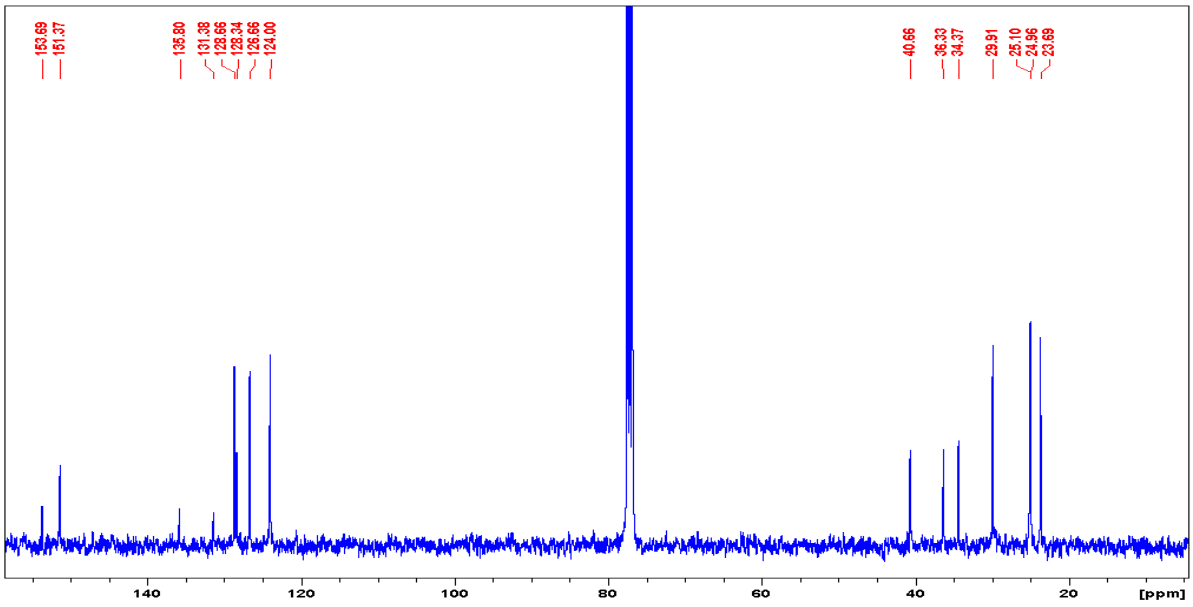
9.0 NMR spectra

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

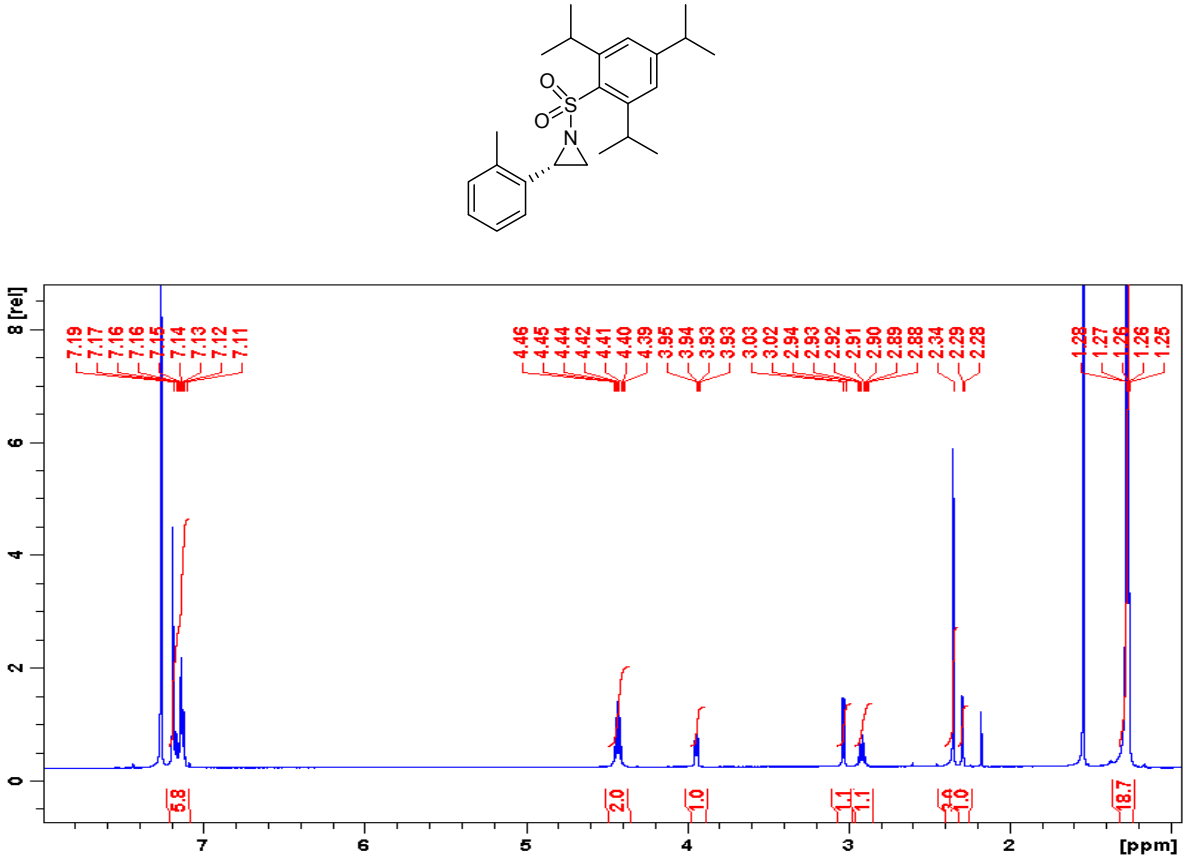




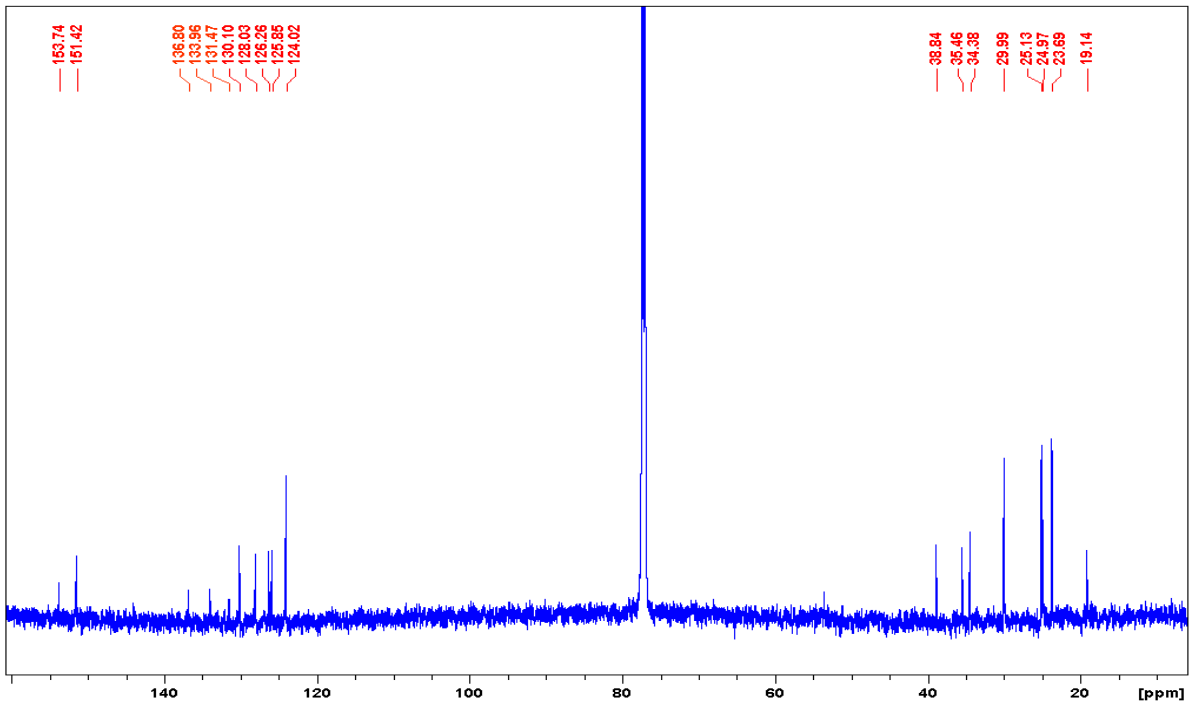
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3c**



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **23**

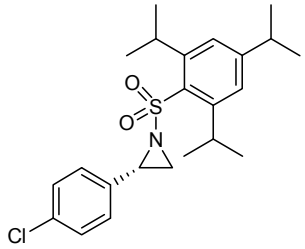


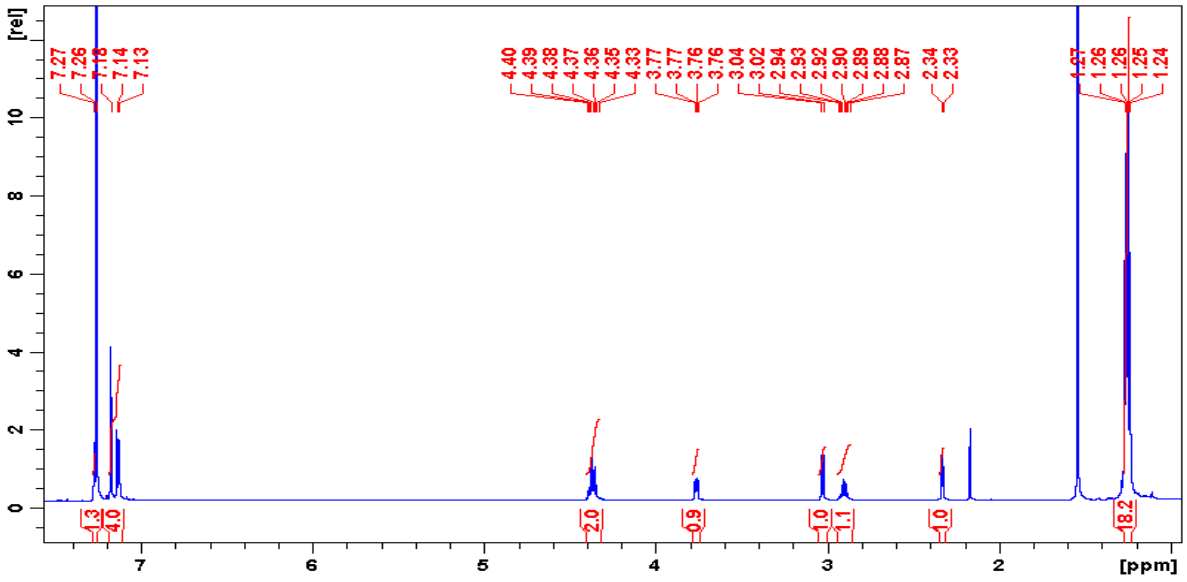
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of **23**



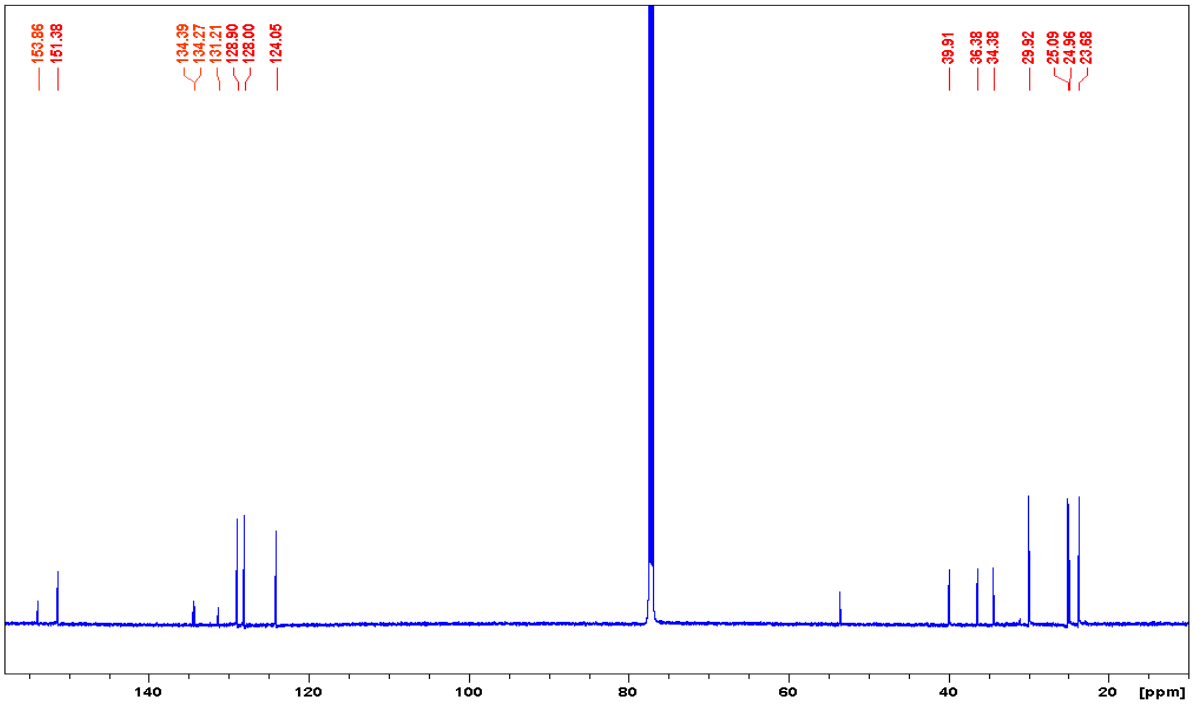
^{1}H

NMR spectrum (600 MHz, $CDCl_3$) of **21**

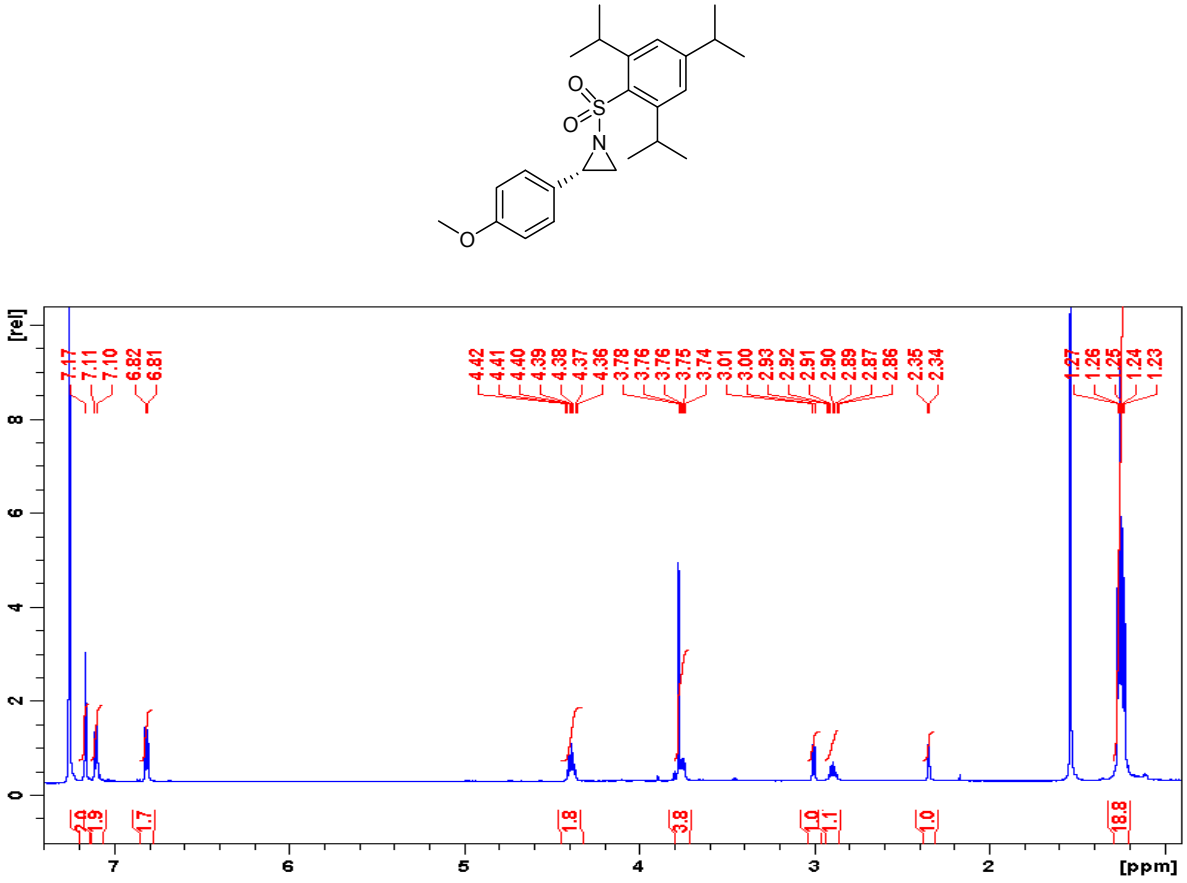




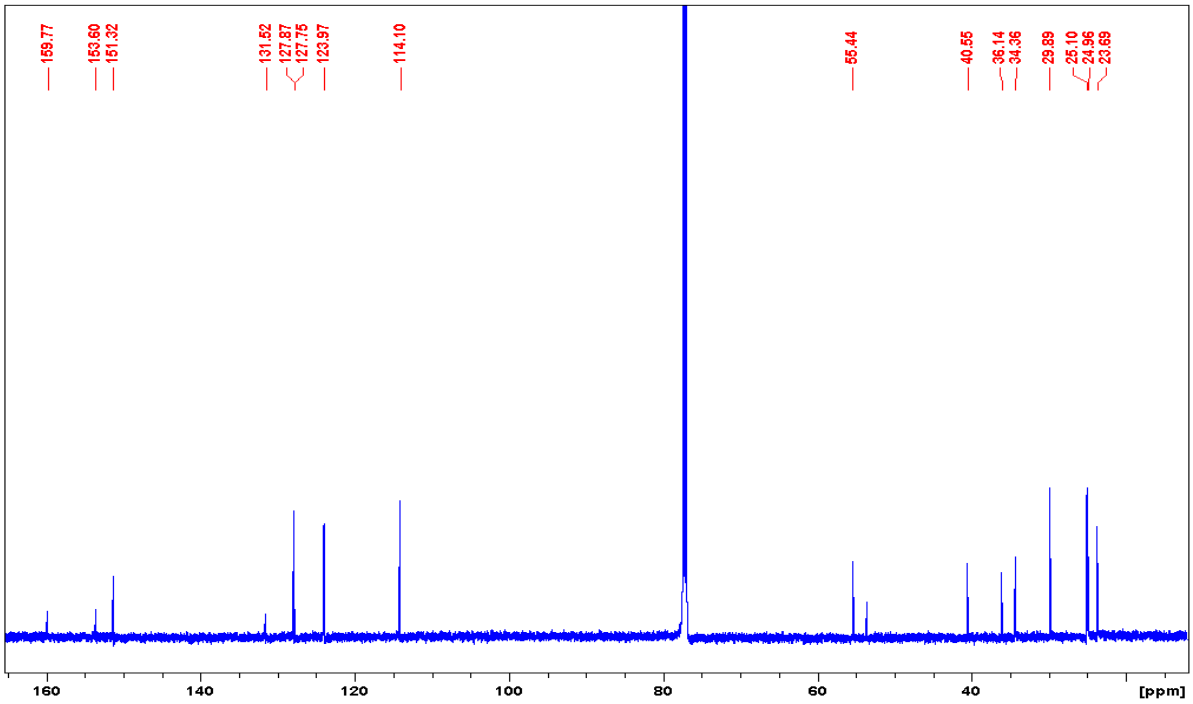
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of **21**



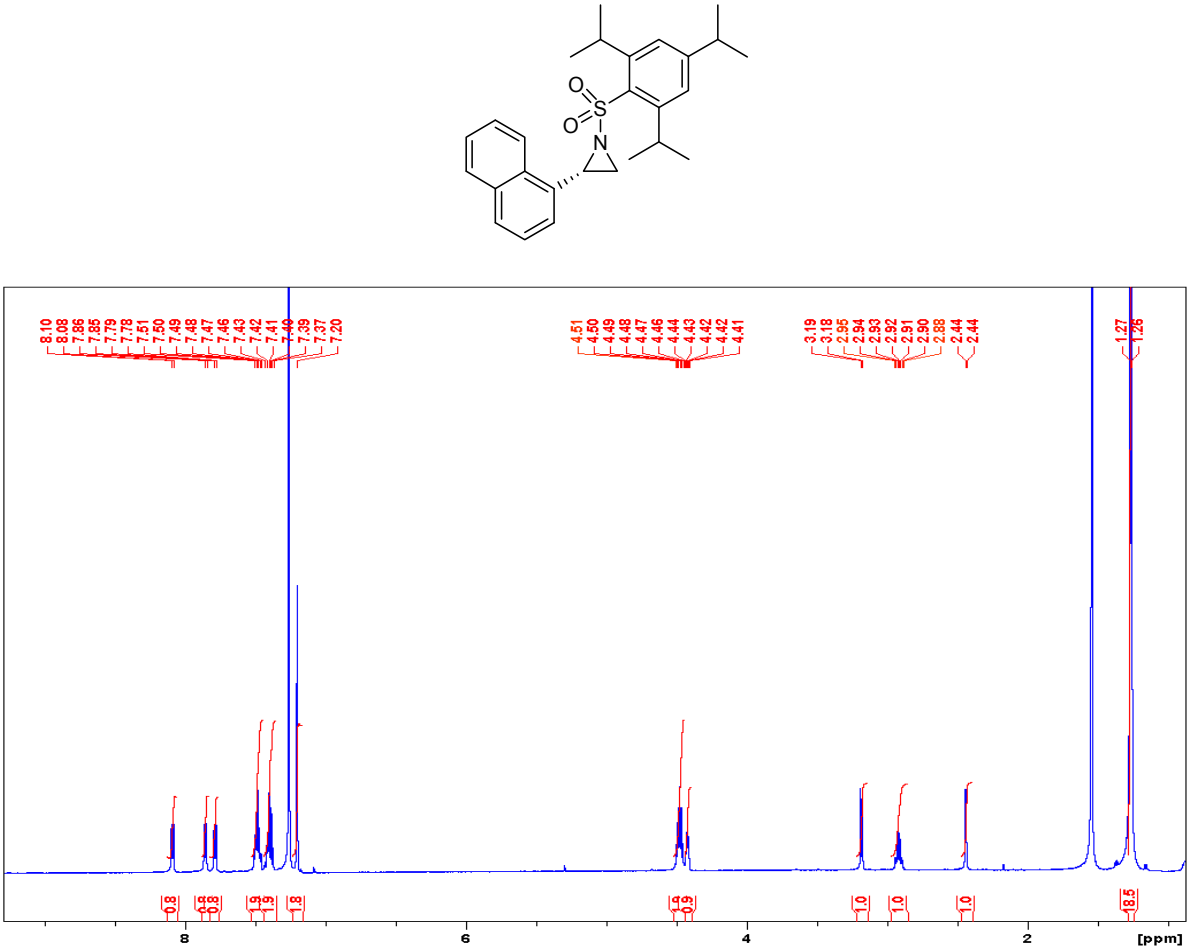
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **25**



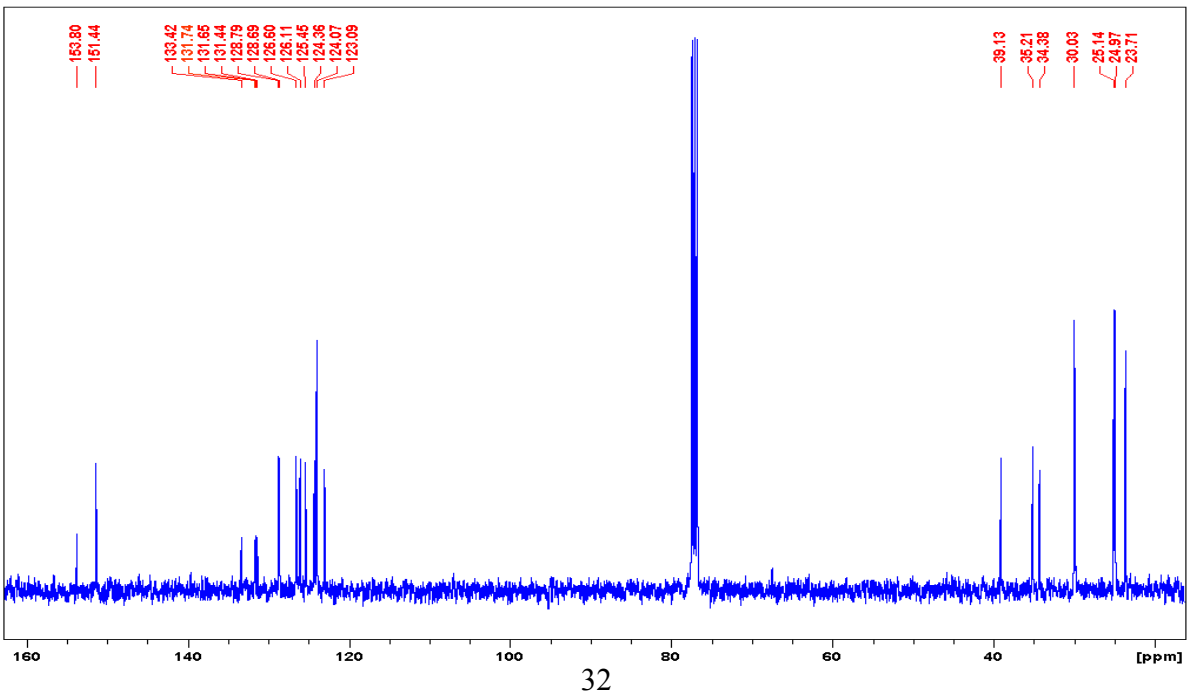
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of **25**



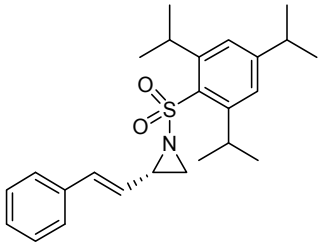
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **22**

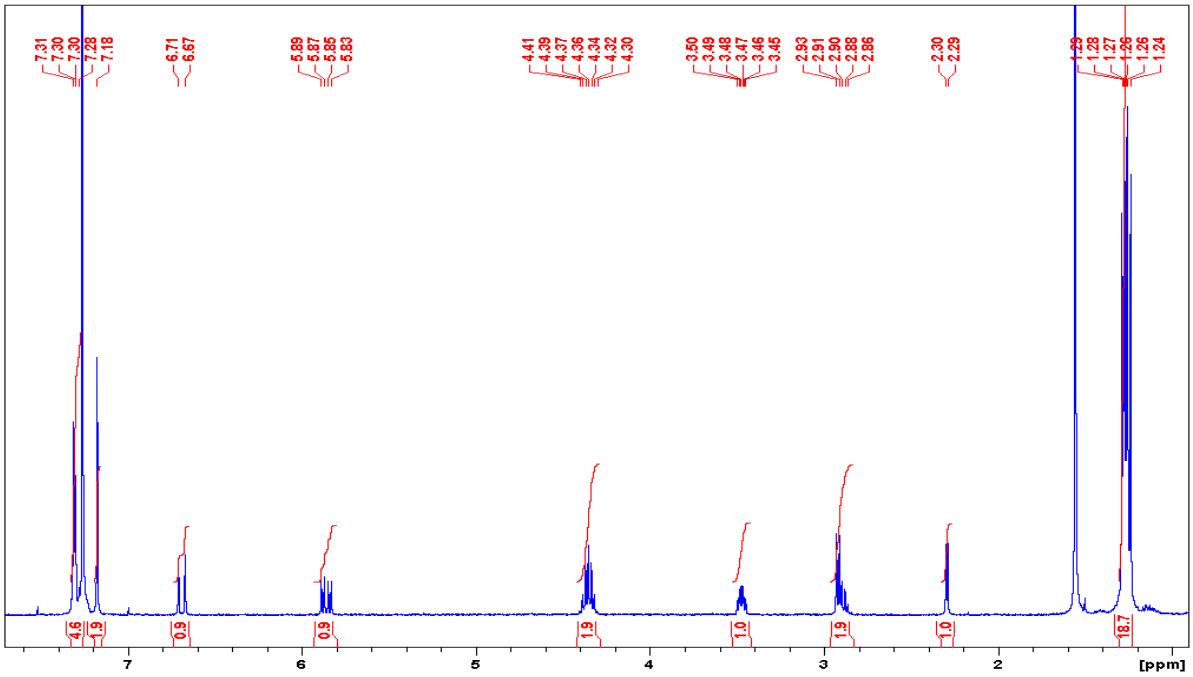


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **22**

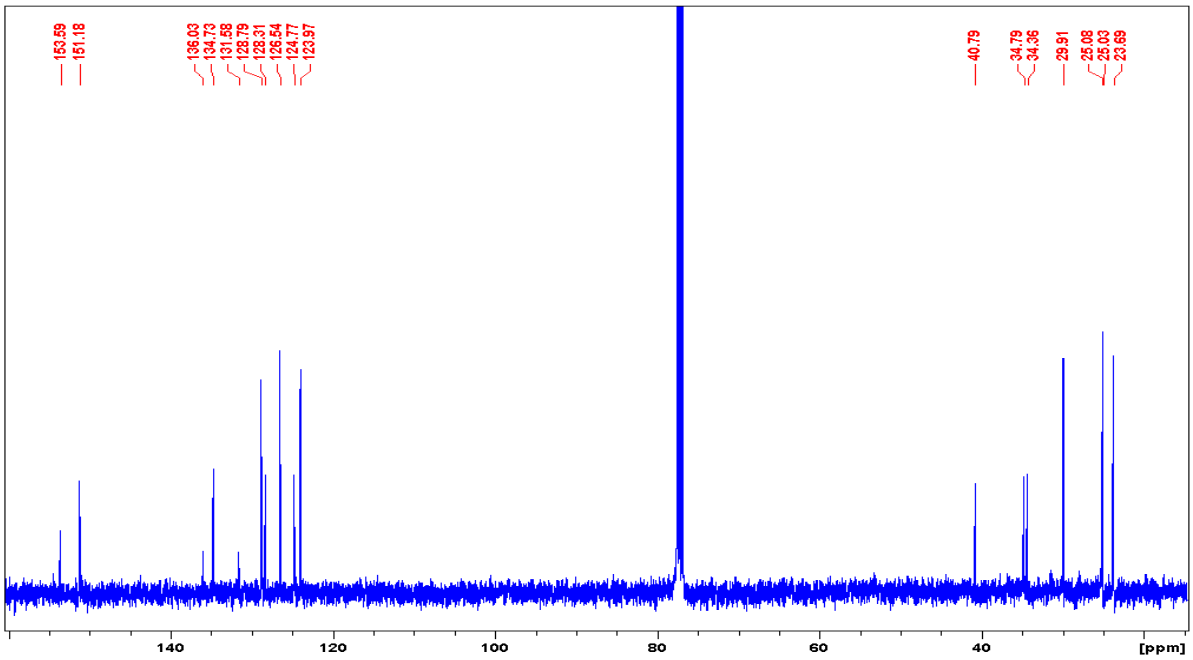


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **26**

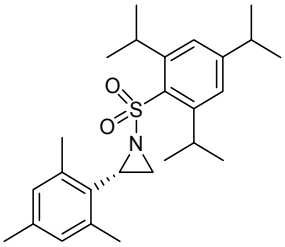


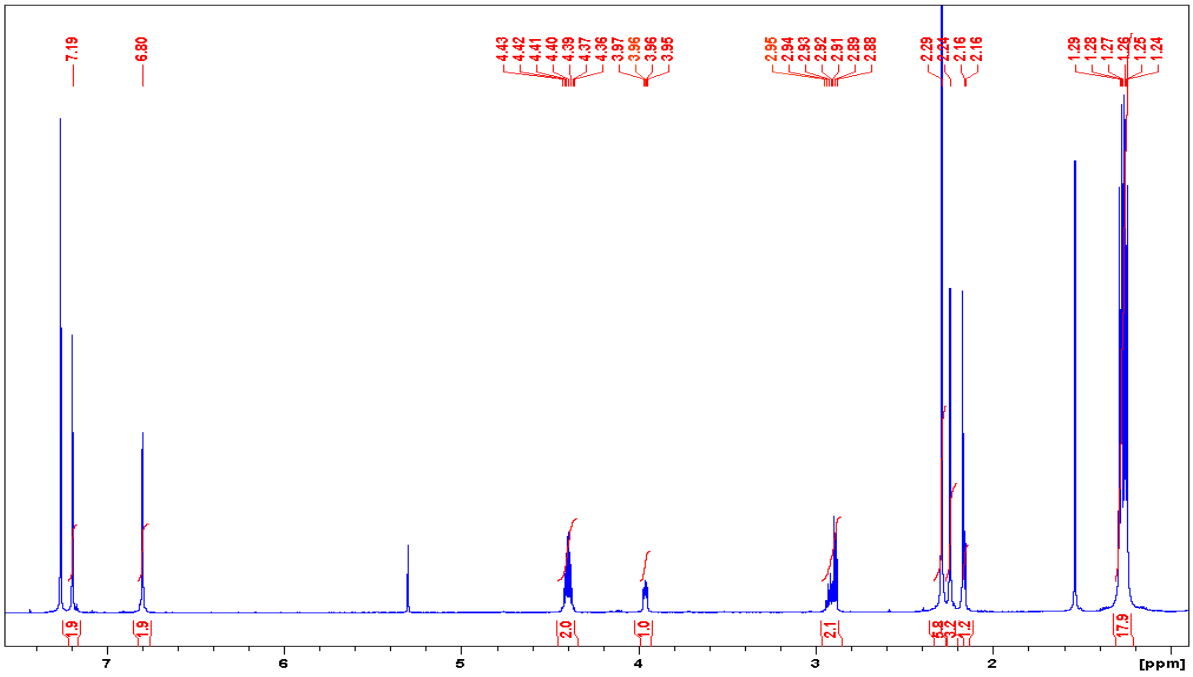


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **26**

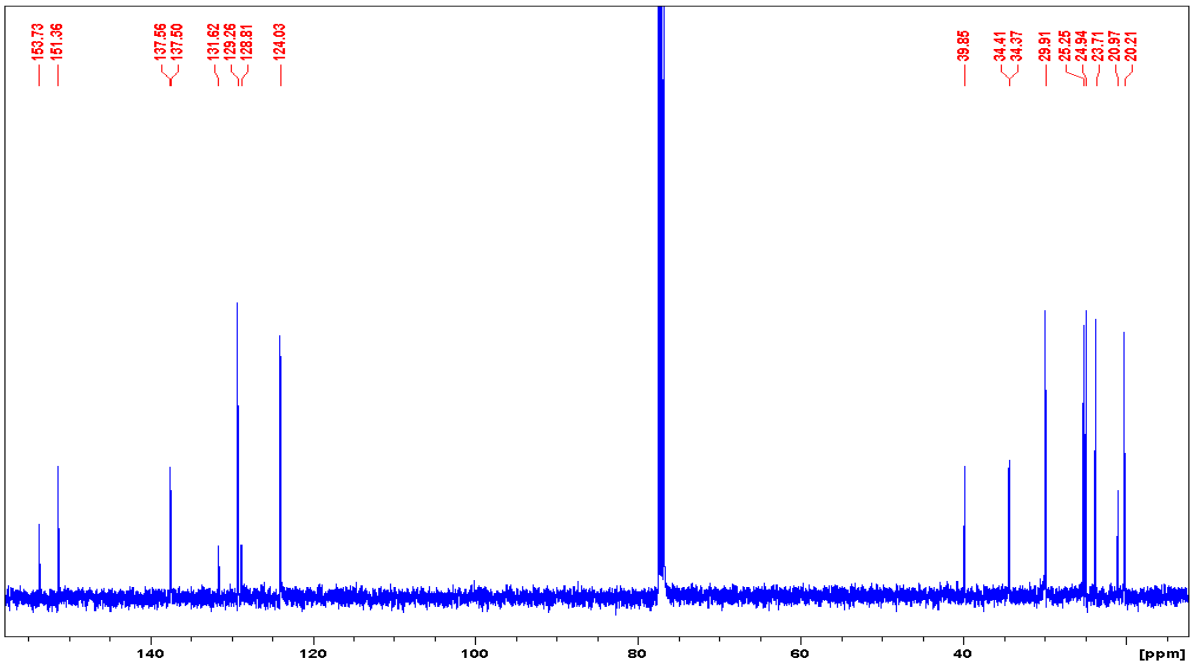


^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **24**

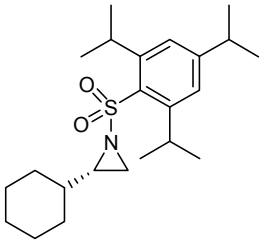


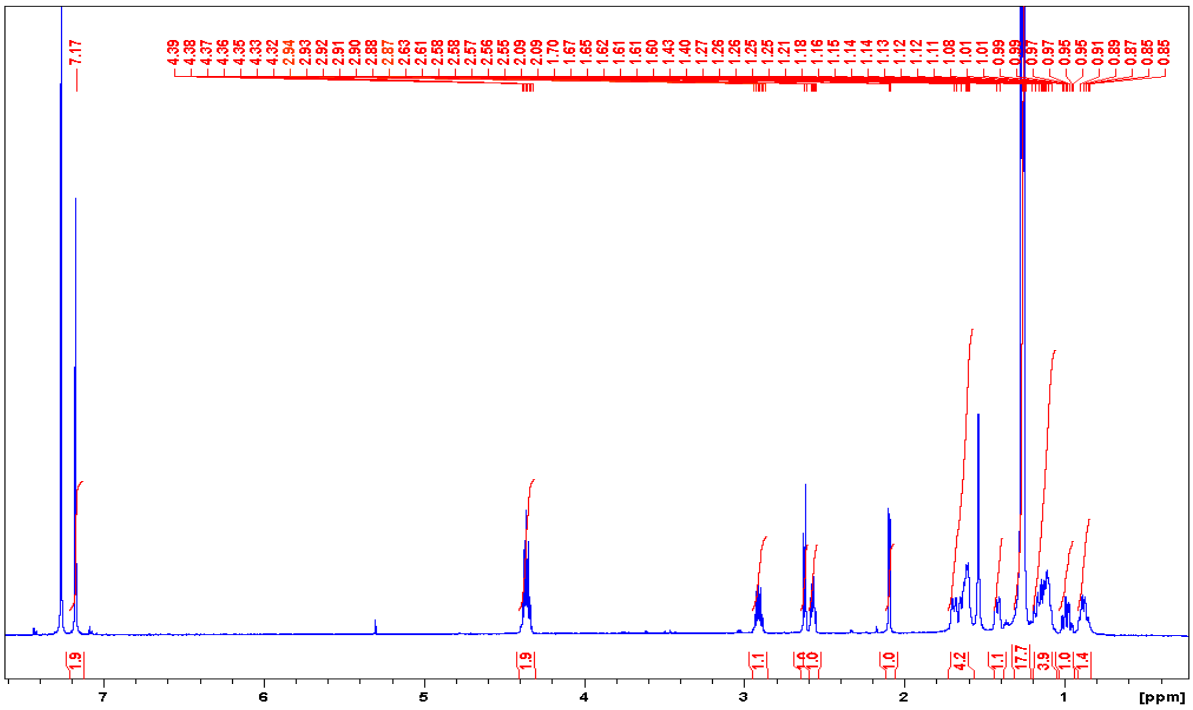


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **24**

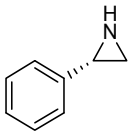


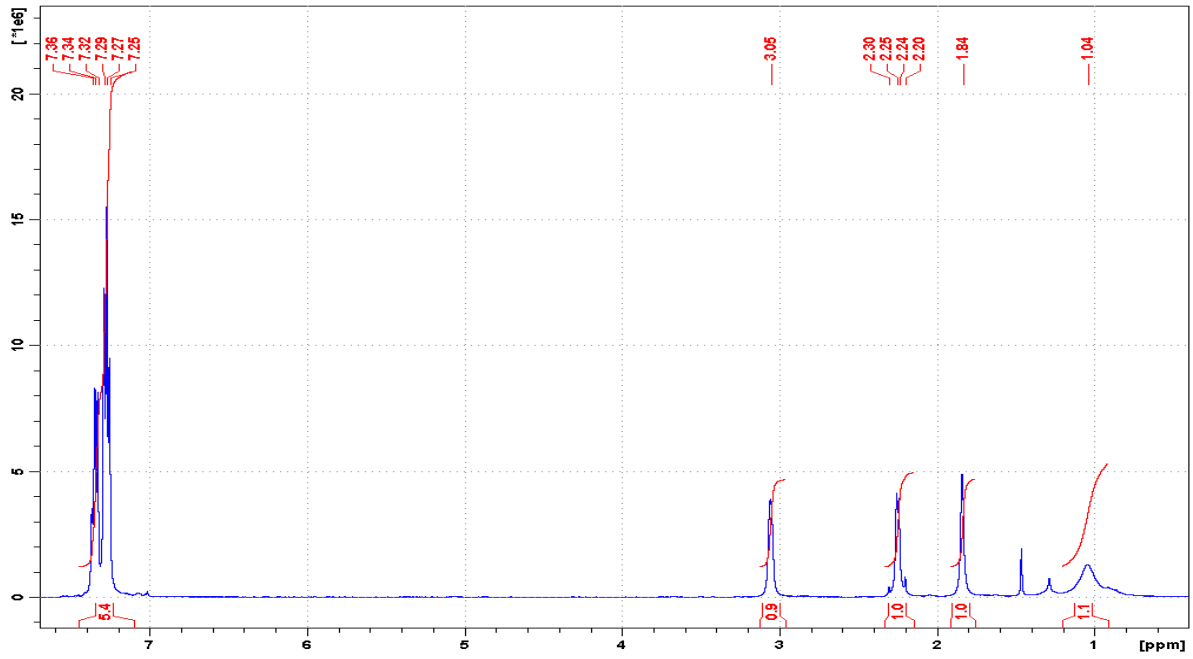
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **27**



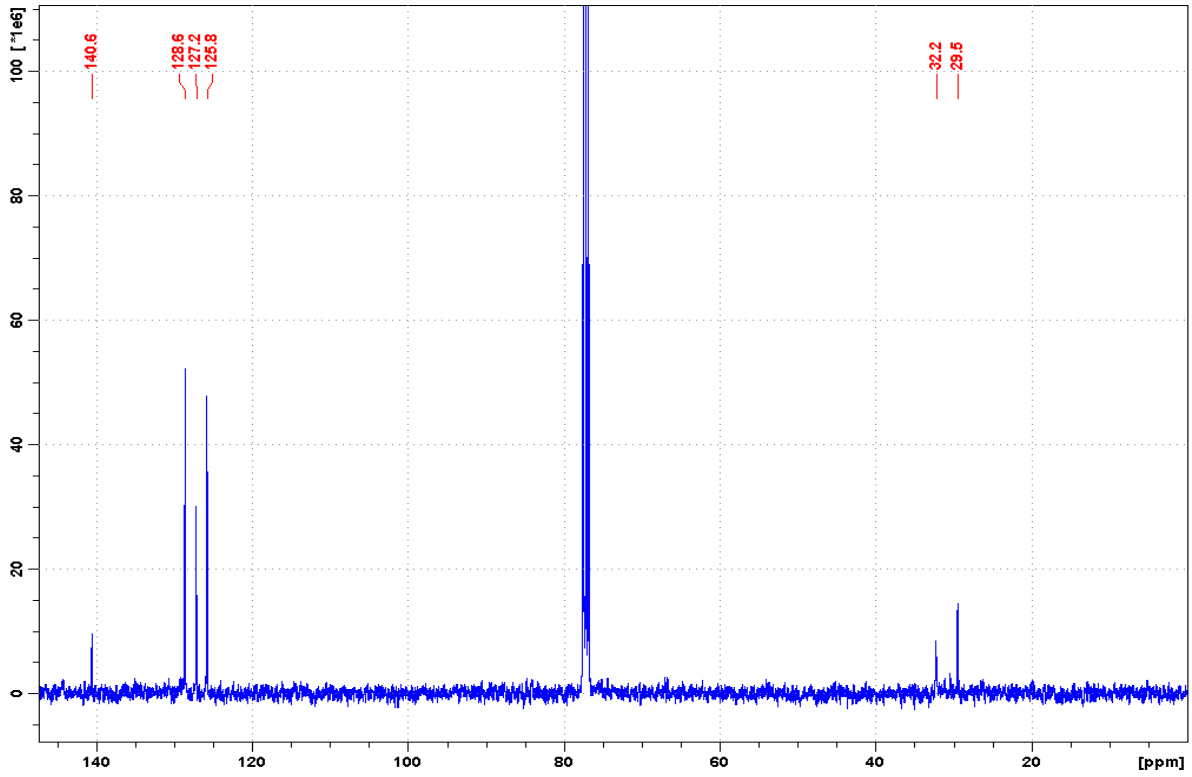


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R*)-2-diphenylaziridine





^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-2-diphenylaziridine



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