Supporting Information

Efficient Copper-Mediated Reactions of Nitrenes Derived from Sulfonimidamides

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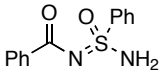
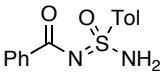
General Remarks: Reactions were carried out under an inert gas, with magnetic stirring and redistilled, degassed solvents when necessary. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35-70 μm) was used for column chromatography. PE and EA are petroleum ether, and ethyl acetate. The melting points reported were measured with a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded with a Bruker Tensor 27 ATR diamant PIKE spectrometer. ^{1}H NMR (resp. ^{13}C NMR) spectra were recorded at rt with 200 MHz (resp. 50 MHz) Bruker AC 200 and ARX 200 spectrometers, 250 MHz (resp. 62.5 MHz) Bruker ARX 250 and 400 MHz (resp. 100 MHz) Bruker ARX 400 and AVANCE 400 spectrometers. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (δ = 7.26 -resp. 77.0- for $CDCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t, q, quint. mean multiplet, singlet, doublet, triplet, quadruplet, quintuplet, respectively. The term br means that the signal is broad. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie and Exact Mass were recorded at ICSN (CNRS, Gif) on a LCT micromass apparatus (Electrospray source). When liquid, the commercial starting chemicals were redistilled prior to use. THF was distilled from Na/benzophenone. Dry acetone was purchased from various retailers and used without further purification. Benzene and toluene were distilled from CaH_2. MeCN was dried and distilled from CaH_2. Optical rotatory powers were recorded on a Perkin Elmer 343 device. The diastereomeric excess (d.s.) values were measured by chiral HPLC (Waters 1525 binary with a Waters 2487 detector) using a CHIRALPAK AD-H stationary phase.

The sulfonimidamides were prepared following reported procedures.[1]



Sulfonimidamide **1** (5.1 g, 81%) was isolated as a white solid. M.p. = 176 °C. IR (neat): nu(tilde) = 3311, 3058, 1595, 1565 cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.42-7.46 (m, 2 H arom.), 7.50-7.53 (m, 1 H arom.), 7.59-7.67 (m, 3 H arom.), 7.81-7.84 6.31 (m, 2 H, NH_2), 7.94-7.99 (m, 4 H arom.). ^{13}C NMR (100 MHz, d_6-DMSO): δ = 127.2 (CH arom.), 128.5 (CH arom.), 129.1 (CH arom.), 129.3 (CH arom.), 132.2 (CH arom.), 132.8 (CH arom.), 136.6 (C arom.), 143.3 (C arom.), 171.7 (C=O).

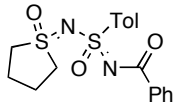


The sulfonimidamide **1'** was isolated as a white solid, M.p. = 139-141 °C. IR (neat): nu(tilde) = 3307, 3126, 3052, 1597 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, Tol), 6.26 (s, 2 H, NH_2), 7.32-7.34 (d, *J* = 8.3 Hz, 2 H arom.), 7.39-7.43 (m, 2 H arom.), 7.49-7.53 (m, 1 H arom.), 7.92-7.94 (d, *J* = 8.3 Hz, 2 H arom.), 8.14-8.16 (d, *J* = 7.3 Hz, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (Tol), 126.8 (CH arom.), 128.2 (CH arom.), 129.6 (CH arom.), 130.0 (CH arom.), 132.5 (CH arom.), 135.4 (C arom.), 138.3 (C arom.), 144.7 (C arom.), 173.7 (C=O).

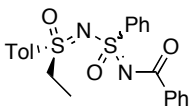
General procedure 1 (GP1): Preparation of aziridines (resp. sulfoximines, sulfimides). To a solution of $Cu(OTf)_2$ (0.05 mmol; 0.1 equiv.; 18 mg) and alkene (resp. sulfoxide, sulfide) (0.5 mmol; 1 equiv.) in acetonitrile (1.5 mL) in the presence of 0.5 g of activated 3 Å molecular sieves were added, at rt under argon, sulfonimidamide (0.5 mmol; 1 equiv.; 130 mg) and iodosylbenzene (0.65 mmol; 1.1 equiv.; 121 mg) *in 5 lots (one portion every 15 minutes).* The reaction was stirred at rt for 1 hour. The molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the aziridines (resp. sulfoximines, sulfimides).

[1] (a) Harpp, D., N.; Friendlander, B., T.; Smith, R. A. *Synthesis*, **1979**, *39*, 181-182. (b) Miura, Y.; Shibata, Y.; Kinoshita M. *Bull. Chem. Soc. Jpn.*, **1986**, *59*, 3291-3292. (c) Harpp, D., N.; Mullins, D., F.; Steliou, K.; Triassy, I. *J. Org. Chem.*, **1979**, *44*, 23, 4196-4197. (d) Reggelin, M.; Junker, B. *Chem. Eur. J.*, **2001**, *7*, 1232-1239.

General procedure 2 (GP2): Preparation of aziridines (resp. sulfoximines, sulfimides). To a solution of $Cu(OTf)_2$ (0.05 mmol; 0.1 equiv.; 18 mg) and alkene (resp. sulfoxide, sulfide) (0.5 mmol; 1 equiv.) in acetonitrile (1.5 mL) in the presence of 0.5 g of activated 3 Å molecular sieves were added, at rt under argon, sulfonimidamide (0.5 mmol; 1 equiv.; 130 mg) and iodosylbenzene (0.65 mmol; 1.1 equiv.; 121 mg) *in one batch*. The reaction was stirred at rt for 1 hour. The molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the aziridines (resp. sulfoximines, sulfimides).



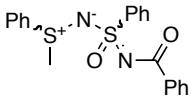
Following **GP1** from tetrahydrothiophene 1-oxide (45 μL), the corresponding sulfoximine (**2a**) was isolated (PE/EA 50:50, 150 mg, 80%) as a white solid. M.p. = 50-51 °C. IR (neat): nu(tilde) = 3063, 3023, 2950, 1626 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33-2.46 (m, 7 H, Tol+$CH_2(CH_2)_2CH_2$), 3.36-3.45 (m, 2 H, C*H*HS), 3.76-3.83 (m, 1 H, CH*H*S), 4.28-4.35 (m, 1 H, CH*H*S), 7.31 (d, *J* = 8.1 Hz, 2 H arom.), 7.36-7.40 (m, 2 H arom.), 7.45-7.47 (m, 1 H arom.), 8.03 (d, *J* = 8.1 Hz, 2 H arom.), 8.11-8.13 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Tol), 23.4 (CH_2), 24.0 (CH_2), 55.2 (CH_2), 55.8 (CH_2), 126.9 (CH arom.), 128.0 (CH arom.), 129.3 (CH arom.), 129.6 (CH arom.), 131.8 (CH arom.), 136.6 (C arom.), 139.7 (C arom.), 143.5 (C arom.), 173.1 (C=O). HRMS calcd. for $C_{18}H_{20}N_2O_3S_2$: $[M+Na]^+$ 399.0813; found 399.0818.



Following **GP1** from ethyl *p*-tolyl-sulfoxide (84 mg), two diastereomers of the corresponding sulfoximine (**2b**) were isolated (PE/EA 75:25).

Diastereomer 1 (56 mg, 26%, $R_f = 0.2$, $[\alpha]_D^{20}$ – 0.16, c1.00 ($CHCl_3$)). Orange solid, M.p. = 129°C. IR (neat): nu(tilde) = 2961, 1630, 1576 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.3 Hz, 3 H, SCH_2CH_3), 2.46 (s, 3 H, Tol), 3.75 (B of ABX_3, *J* = 7.3, 7.3 Hz, 1 H, SC*H*HMe), 3.86 (A of ABX_3, *J* = 7.3, 7.3 Hz, 1 H ,SCH*H*Me), 7.28-7.32 (m, 2 H arom.), 7.41-7.43 (m, 3 H arom.), 7.50-7.56 (m, 3 H arom.), 7.88 (d, *J* = 8.1 Hz, 2 H arom.), 7.96 (d, *J* = 8.1 Hz, 2 H arom.), 8.17-8.19 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.5 (SCH_2Me), 21.7 (Tol), 53.6 (SCH_2Me), 126.8 (CH arom.), 127.7 (CH arom.), 128.6 (CH arom.), 128.8 (CH arom.), 129.3 (CH arom.), 130.3 (CH arom.), 131.5 (CH arom.), 132.4 (CH arom.), 132.8 (C arom.), 136.4 (C arom.), 143.2 (C arom.), 145.8 (C arom.), 172.6 (C=O). Elemental Analyses for $C_{21}H_{20}N_2O_3S_2$ (412,53): calcd C 61.14, H 4.89, N 6.79; found C 60.97, H 5.07, N 6.41.

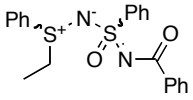
Diastereomer 2 (59 mg, 28%, $R_f = 0.1$, $[\alpha]_D^{20}$ – 0.72, c1.00 ($CHCl_3$)). Orange solid. M.p. = 139°C. IR (neat): nu(tilde) = 2926, 1628, 1577 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.3 Hz, 3 H, SCH_2CH_3), 2.48 (s, 3 H, Tol), 3.69 (q, *J* = 7.3 Hz, 2 H, SCH_2CH_3), 7.35-7.39 (m, 2 H arom.), 7.44-7.56 (m, 6 H arom.), 8.03 (d, *J* = 8.2 Hz, 2 H arom.), 8.07-8.09 (m, 2 H arom.), 8.12 (d, *J* = 8.2 Hz, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.4 (SCH_2Me), 21.7 (Tol), 53.8 (SCH_2Me), 127.0 (CH arom.), 127.8 (CH arom.), 128.7 (CH arom.), 128.8 (CH arom.), 129.3 (CH arom.), 130.3 (CH arom.), 131.5 (CH arom.), 132.4 (CH arom.), 132.7 (C arom.), 136.6 (C arom.), 143.0 (C arom.), 145.9 (C arom.), 172.6 (C=O). Elemental Analyses for $C_{21}H_{20}N_2O_3S_2$ (412,53): calcd C 61.14, H 4.89, N 6.79; found C 60.97, H 5.07, N 6.41.



Following **GP1** from phenylmethyl sulfide (62 µL), two diastereomers of the corresponding sulfimide (**3a**) were isolated (PE/EA 70:30). Both diastereomers were contaminated (<5%) by traces of phenylmethyl sulfoxide. The yields correspond to the actual amount of products.

Diastereomer 1 (58 mg, 30%, R_f = 0.2). Orange oil. IR (neat): nu(tilde) = 3061, 1607, 1572 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, SMe), 7.35-7.39 (m, 2 H arom.), 7.45-7.57 (m, 7 H arom.), 7.79-7.81 (m, 2 H arom.), 8.11-8.13 (m, 2 H arom.), 8.13-8.18 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.3 (SMe), 125.9 (CH arom.), 127.0 (CH arom.), 127.8 (CH arom.), 128.6 (CH arom.), 129.3 (CH arom.), 130.1 (CH arom.), 131.4 (CH arom.), 132.1 (CH arom.), 132.4 (CH arom.), 136.7 (C arom.), 136.8 (C arom.), 142.8 (C arom.), 173.1 (C=O). HRMS calcd. for $C_{20}H_{18}N_2O_2S_2$: $[M+Na]^+$ 405.0707; found 411.0698.

Diastereomer 2 (62 mg, 33%, R_f = 0.1). Orange oil. IR (neat): nu(tilde) = 3062, 1609, 1572 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.04 (s, SMe), 7.34-7.38 (m, 2 H arom.), 7.41-7.61 (m, 7 H arom.), 7.80-7.83 (m, 2 H arom.), 7.97-7.99 (m, 2 H arom.), 8.10-8.12 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.6 (SMe), 126.1 (CH arom.), 126.8 (CH arom.), 127.8 (CH arom.), 128.7 (CH arom.), 129.3 (CH arom.), 130.1 (CH arom.), 131.4 (CH arom.), 132.0 (CH arom.), 132.7 (CH arom.), 136.2 (C arom.), 136.7 (C arom.), 142.8 (C arom.), 173.0 (C=O). HRMS calcd. for $C_{20}H_{18}N_2O_2S_2$: $[M+Na]^+$ 405.0707; found 411.0698.

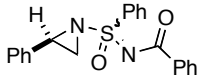


Following **GP1** from ethylphenyl sulfide (67 μL), two diastereomers of the corresponding sulfimide (**3b**) were isolated (PE/EA 70:30). Both diastereomers were contaminated (<5%) by traces of phenylmethyl sulfoxide. The yields correspond to the actual amount of products.

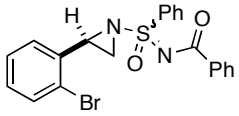
Diastereomer 1 (43 mg, 22%, R_f = 0.2). Orange oil. IR (neat): nu(tilde) = 2927, 1610, 1573 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.3 Hz, 3 H, SCH_2CH_3), 3.28 (B of ABX_3, *J* = 13.2, 7.3 Hz, 1 H, SC*H*HMe), 3.33 (A of ABX_3, *J* = 13.2, 7.4 Hz, 1 H, SCH*H*Me), 7.31-7.35 (m, 2 H arom.), 7.42-7.63 (m, 7 H arom.), 7.75-7.77 (m, 2 H arom.), 8.08-8.14 (m, 4 H arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.1 (SCH_2Me), 47.3 (SCH_2Me), 126.6 (CH arom.), 127.0 (CH arom.), 127.7 (CH arom.), 128.6 (CH arom.), 129.3 (CH arom.), 129.9 (CH arom.), 131.3 (CH arom.), 132.0 (CH arom.), 132.4 (CH arom.), 134.0 (C arom.), 136.9 (C arom.), 143.1 (C arom.), 172.8

(C=O).

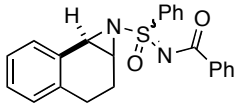
Diastereomer 2 (63 mg, 31%, R_f = 0.1). Orange oil. IR (neat): nu(tilde) = 2925, 1610, 1573 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.3 Hz, 3 H, SCH_2CH_3), 3.21 (m, 2 H, SCH_2CH_3), 7.32-7.36 (m, 2 H arom.), 7.40-7.48 (m, 4 H arom.), 7.54-7.60 (m, 3 H arom.), 7.78-7.80 (m, 2 H arom.), 7.99-8.01 (m, 2 H arom), 8.08-8.10 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.7 (SCH_2Me), 48.1 (SCH_2Me), 126.7 (CH arom.), 126.9 (CH arom.), 127.7 (CH arom.), 128.6 (CH arom.), 129.2 (CH arom.), 130.0 (CH arom.), 131.3 (CH arom.), 131.9 (CH arom.), 132.6 (CH arom.), 134.1 (C arom.), 136.9 (C arom.), 142.9 (C arom.), 172.6 (C=O). CI–MS (NH_3): 397 (100, $[M+1]^+$), 369 (15), 261 (16).



Following **GP2** from styrene (57 µL), the corresponding aziridine (**4a**) was isolated (PE/EA 90:10, 142 mg, 78%) as an unseparable mixture of two diastereomers. Colorless oil. IR (neat): nu(tilde) = 3065, 1720, 1633, 1278 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.50 (d, *J* = 4.8 Hz, 1 H, *trans*-NC*H*H, dia majo), 2.81 (d, *J* = 4.8 Hz, 1 H, *trans*-NC*H*H, dia mino), 3.17 (d, *J* = 7.2 Hz, 1 H, *cis*-NCH*H*, dia majo), 3.56 (d, *J* = 7.2 Hz, 1 H, *cis*-NCH*H*, dia mino), 3.94 (dd, *J* = 7.2, 4.8 Hz, 1 H, NCH, dia mino), 4.33 (dd, *J* = 7.2, 4.8 Hz, 1 H, NCH, dia majo), 7.05-7.06 (m, 1 H arom., dia majo+dia mino), 7.14-7.18 (m, 2 H arom., dia majo+dia mino), 7.26-7.51 (m, 8 H arom., dia majo+dia mino), 7.98-8.09 (m, 4 H arom., dia majo+dia mino). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.3 (CH_2N, dia majo), 37.4 (CH_2N, dia mino), 41.4 (CHN, dia majo), 42.5 (CHN, dia mino), 126.6 (CH arom., dia mino), 126.9 (CH arom., dia majo), 127.8 (CH arom.,), 127.9 (CH arom.), 128.0 (CH arom.), 128.0 (CH arom.), 128.5 (CH arom.), 128.6 (CH arom.), 128.6 (CH arom.), 128.7 (CH arom.), 129.3 (CH arom., dia mino), 129.5 (CH arom., dia majo), 132.1 (CH arom., dia majo), 132.2 (CH arom., dia mino), 133.7 (CH arom., dia majo+dia mino), 134.3 (C arom., dia majo), 134.6 (C arom., dia mino), 135.5 (C arom., dia majo+dia mino), 138.0 (C arom., dia majo+dia mino), 172.8 (C=O, dia majo), 173.0 (C=O, dia mino).

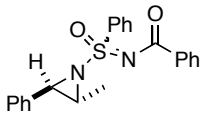


Following **GP2** from *o*-bromo-styrene (62 μL), the corresponding aziridine (**4b**) was isolated (PE/EA 90:10, 141 mg, 64%) as an unseparable mixture of two diastereomers. Colorless oil. IR (neat): nu(tilde) = 3060, 1720, 1633, 1275 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (d, *J* = 4.8 Hz, 1 H, *trans*-NC*H*H, dia majo), 2.66 (d, *J* = 4.8 Hz, 1 H, *trans*-NCHH, dia mino), 3.21 (d, *J* = 7.3 Hz, 1 H, *cis*-NCH*H*, dia majo), 3.59 (d, *J* = 7.3 Hz, 1 H, *cis*-NCH*H*, dia mino), 4.14 (dd, *J* = 7.3, 4.8 Hz, 1 H, NCH, dia mino), 4.46 (dd, *J* = 4.8, 7.3 Hz, 1 H, NCH, dia majo), 7.06-7.17 (m, 1 H arom., dia mino), 7.18-7.26 (m, 1 H arom., dia majo), 7.26-7.71 (m, 10 H arom., dia majo+dia mino), 8.12-8.23 (m, 4 H arom., dia majo+dia mino). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.6 (CH_2N, dia majo), 37.5 (CH_2N, dia mino), 41.4 (CHN, dia mino), 42.6 (CHN, dia majo), 123.2 (C arom., dia majo), 123.4 (C arom., dia mino), 127.6 (CH arom.), 127.7 (CH arom.), 127.9 (CH arom.), 128.0 (CH arom.), 128.5 (CH arom.), 129.3 (CH arom.), 129.5 (CH arom.), 129.7 (CH arom.), 129.8 (CH arom.), 132.1 (CH arom., dia majo), 132.2 (CH arom., dia mino), 132.4 (CH arom., dia majo), 132.5 (CH arom., dia mino), 133.9 (CH arom., dia majo), 134.0 (CH arom., dia mino), 134.1 (C arom., dia mino), 134.6 (C arom., dia majo), 135.4 (C arom., dia majo+dia mino), 137.7 (C arom., dia mino), 137.8 (C arom., dia majo), 172.7 (C=O, dia majo), 172.9 (C=O, dia mino).



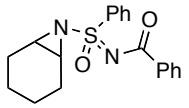
Following **GP1** from dihydronaphthalene (65 μL), the corresponding aziridine (**4c**) was isolated (PE/EA 90:10, 132 mg, 68%) as an unseparable mixture of two diastereomers. Orange solid. IR (neat): nu(tilde) = 3064, 2920, 1741, 1609, 1277 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58-1.67 (m, 1 H, $ArCH_2CHH$, dia mino), 1.68-1.77 (m, 1 H, $ArCH_2CHH$, dia majo), 2.02-2.09 (m, 1 H, $ArCH_2CHH$, dia mino), 2.37-2.45 (m, 1 H, $ArCH_2CHH$, dia majo), 2.46-2.55 (m, 1 H, ArC*H*H, dia majo+dia mino), 2.63-2.74 (m, 1 H, ArCH*H*, dia mino), 2.70-2.82 (m, 1 H, ArCH*H*, dia

majo), 3.76 (bd, *J* = 7.1 Hz, 1 H, ArCH(N)C*H*, dia mino), 3.97 (d, *J* = 7.1 Hz, 1 H, ArC*H*(N)CH, dia majo), 4.17 (bd, *J* = 7.1 Hz, 1 H, ArCH(N)C*H*, dia majo), 4.39 (d, *J* = 7.1 Hz, 1 H, ArC*H*(N)CH, dia mino), 7.09-7.19 (m, 2 H arom., dia majo+dia mino), 7.23-7.46 (m, 2 H arom., dia mino+dia majo), 7.49-7.66 (m, 6 H, dia majo+dia mino), 8.05-8.23 (m, 4 H arom., dia majo+dia mino). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9 ($ArCH_2CH_2$, dia mino), 20.1 ($ArCH_2CH_2$, dia majo), 24.7 ($ArCH_2$, dia mino+dia majo), 42.3 (ArCH(N)*CH*, dia mino), 42.9 (Ar*CH*N, dia majo), 43.8 (Ar*CH*N, dia mino), 44.4 (ArCH(N)*CH*, dia majo), 126.3 (CH arom., dia majo), 126.6 (CH arom., dia mino), 127.5 (CH arom., dia majo), 127.6 (CH arom., dia mino), 127.9 (CH arom., dia mino), 128.0 (CH arom., dia majo), 128.6 (CH arom.), 128.7 (CH arom.), 128.8 (CH arom.), 129.1 (CH arom., dia majo), 129.2 (CH arom., dia mino), 129.4 (CH arom., dia mino), 129.4 (C arom., dia majo), 129.5 (CH arom., dia majo), 129.5 (CH arom., dia majo), 129.6 (C arom., dia mino), 129.9 (CH arom., dia mino), 131.9 (CH arom., dia mino), 132.0 (CH arom., dia majo), 133.5 (CH arom., dia majo+dia mino), 135.7 (C arom., dia mino), 135.8 (C arom., dia majo), 136.6 (C arom., dia mino), 136.8 (C arom., dia majo), 138.5 (C arom., dia majo+dia mino), 172.7 (C=O, dia mino+dia majo). HRMS calcd. for $C_{23}H_{20}N_2O_2S$: $[M+Na]^+$ 411.1143; found 411.1113.

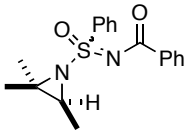


Following **GP1** from *trans*-β-methylstyrene (65 µL), the corresponding aziridine (**4d**) was isolated (PE/EA 90:10, 112 mg, 59%) as an unseparable mixture of two diastereomers. White solid. IR (neat): nu(tilde) = 2923, 1720, 1630, 1276 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (d, *J* = 6.1 Hz, 3 H, NCH*Me*, dia mino), 1.88 (d, *J* = 6.1 Hz, 3 H, NCH*Me*, dia majo), 3.06 (qd, *J* = 6.1, 4.8 Hz, 1 H, NC*H*Me, dia mino), 3.12 (qd, *J* = 6.1, 4.6 Hz, 1 H, NC*H*Me, dia majo), 3.81 (d, *J* = 4.6 Hz, 1 H, NC*H*CHMe, dia majo), 4.16 (d, *J* = 4.8 Hz, NC*H*CHMe, dia mino), 7.04-7.06 (m, 1 H arom., dia majo+dia mino), 7.14-7.17 (m, 2 H arom., dia majo+dia mino), 7.25-7.51 (m, 8 H, dia majo+dia mino), 7.93-7.95 (m, 2 H arom., dia mino), 7.99-8.01 (m, 2 H arom., dia majo+dia mino), 8.08-8.11 (m, 2 H arom., dia majo). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (NCH*Me*, dia mino), 14.4 (NCH*Me*, dia majo), 47.5 (N*CH*Ph, dia majo), 48.9 (N*CH*Me, dia

mino), 50.0 (N*CH*Ph, dia mino), 50.5 (N*CH*Me, dia majo), 126.3 (CH arom., dia majo), 127.1 (CH arom., dia mino), 127.4 (CH arom., dia mino), 127.8 (CH arom., dia majo), 127.9 (CH arom., dia mino), 128.0 (CH arom., dia majo), 128.3 (CH arom., dia majo), 128.5 (CH arom., dia mino), 128.6 (CH arom., dia majo+dia mino), 129.0 (CH arom., dia majo), 129.0 (CH arom., dia mino), 129.4 (CH arom., dia mino), 129.5 (CH arom., dia majo), 131.9 (CH arom., dia mino), 132.0 (CH arom., dia majo), 133.3 (CH arom., dia majo+dia mino), 134.5 (C arom., dia mino), 134.7 (C arom., dia majo), 135.8 (C arom., dia majo), 135.9 (C arom., dia mino), 139.7 (C arom., dia mino), 140.0 (C arom., dia majo), 172.1 (C=O, dia mino), 172.7 (C=O, dia majo). CI–MS (NH_3): 377 (100, $[M+1]^+$).

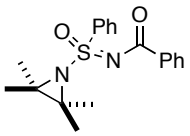


Following **GP1** from cyclohexene (5 equiv., 0.25 mL), the corresponding aziridine (**4e**) was isolated (PE/EA 90:10, 104 mg, 60%) as an unseparable mixture of two diastereomers, which could not be separated by any spectroscopical method. White solid. IR (neat): nu(tilde) = 2944, 1720, 1629, 1283 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22-1.37 (m, 2 H, $NCHCH_2CH_2$), 1.41-1.55 (m, 2 H, $NCHCH_2CH_2$), 1.61-1.84 (m, 2 H, $NCHCH_2$), 1.91-2.10 (m, 2 H, $NCHCH_2$), 3.14 (ddd, *J* = 6.6, 4.8, 1.3 Hz, 1 H, NCH), 3.53 (ddd, *J* = 6.6, 4.8, 1.3 Hz, 1 H, NCH), 7.39-7.42 (m, 2 H arom.), 7.48-7.52 (m, 1 H arom.), 7.57-7.60 (m, 2 H arom.), 7.64-7.68 (m, 1 H arom.), 8.09-8.11 (m, 2 H arom.), 8.14-8.16 (m, 2 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 ($NCHCH_2CH_2$), 19.4 ($NCHCH_2CH_2$), 22.6 ($NCHCH_2$), 22.7 ($NCHCH_2$), 40.4 (NCH), 42.1 (NCH), 127.6 (CH arom.), 127.9 (CH arom.), 129.1 (CH arom.), 129.5 (CH arom.), 131.9 (CH arom.), 133.3 (CH arom.), 135.9 (C arom.), 138.7 (C arom.), 172.7 (C=O).

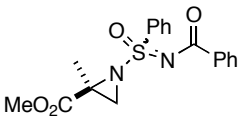


Following **GP1** from 2-methyl-but-2-ene (5 equiv., 0.17 mL), the corresponding aziridine (**4f**)

was isolated (PE/EA 90:10, 96 mg, 59%) as an unseparable mixture of two diastereomers. White solid. IR (neat): nu(tilde) = 2930, 1719, 1630, 1277 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (d, *J* = 5.8 Hz, 3 H, NCH*Me*, dia majo), 1.25 (s, 3 H, NC*Me*Me, dia mino), 1.45 (d, *J* = 6.0 Hz, 3 H, NCH*Me*, dia mino), 1.48 (s, 3 H, NC*Me*Me, dia majo), 1.56 (s, 3 H, NCMe*Me*, dia mino), 1.86 (s, 3 H, NCMe*Me*, dia majo), 3.04 (q, *J* = 5.8 Hz, 1 H, NC*H*Me, dia majo), 3.43 (q, *J* = 6.0 Hz, 1 H, NC*H*Me, dia mino), 7.37-7.64 (m, 6 H arom., dia majo+dia mino), 8.08-8.17 (m, 4 H arom., dia majo+dia mino). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6 (NCH*Me*, dia majo), 13.2 (NCH*Me*, dia mino), 20.3 (NCH*Me*Me, dia mino), 20.8 (NCHMe*Me*, dia mino), 20.9 (NCH*Me*Me, dia majo), 21.5 (NCHMe*Me*, dia majo), 46.1 (N*CH*Me, dia majo), 48.5 (N*CH*Me, dia mino), 53.4 (N*C*Me_2, dia mino), 53.6 (N*C*Me_2, dia majo), 127.3 (CH arom.), 127.7 (CH arom.), 127.9 (CH arom.), 128.8 (CH arom.), 128.9 (CH arom.), 129.4 (CH arom.), 131.7 (CH arom., dia majo+dia mino), 132.9 (CH arom., dia majo), 133.1 (CH arom., dia mino), 136.0 (C arom., dia majo+dia mino), 140.3 (C arom., dia mino), 140.6 (C arom., dia majo), 172.3 (C=O, dia majo), 172.5 (C=O, dia mino).

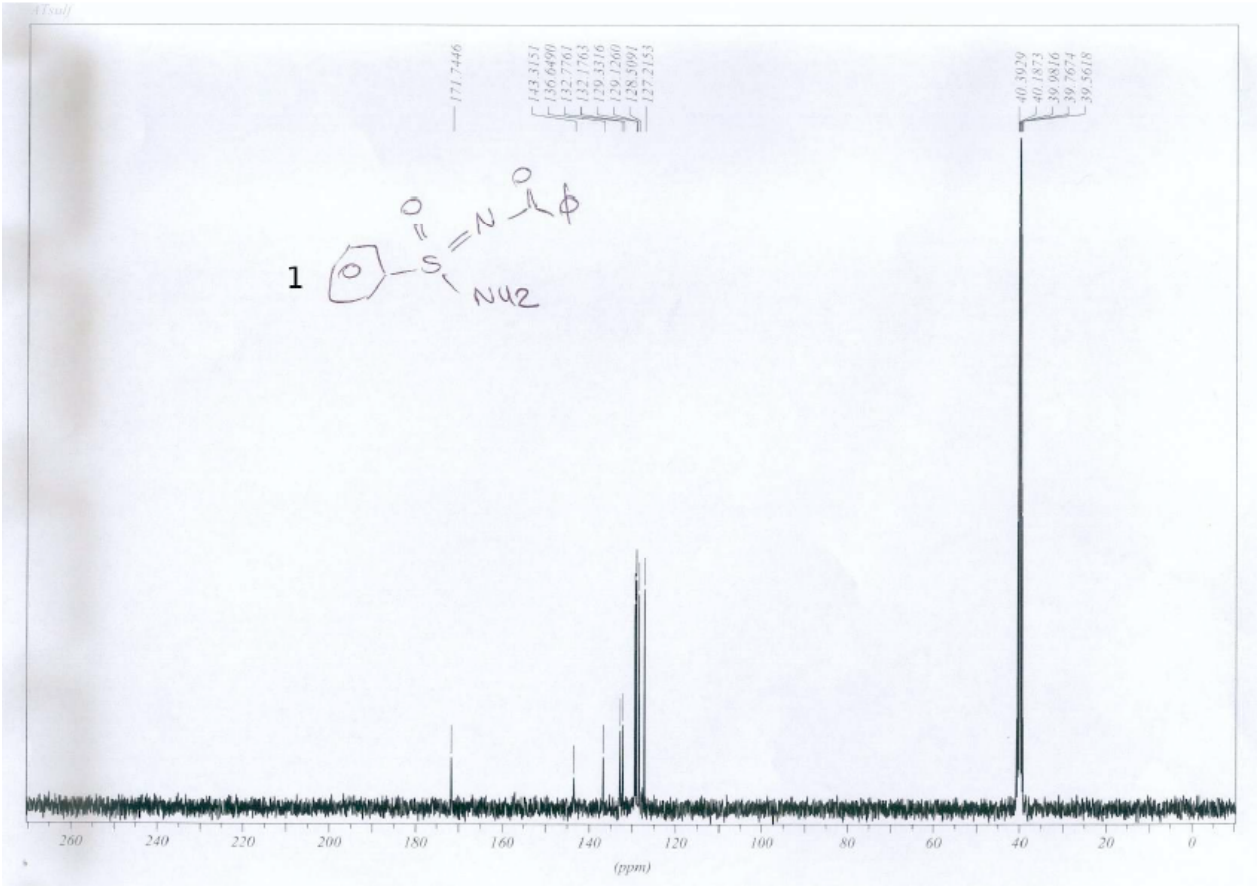


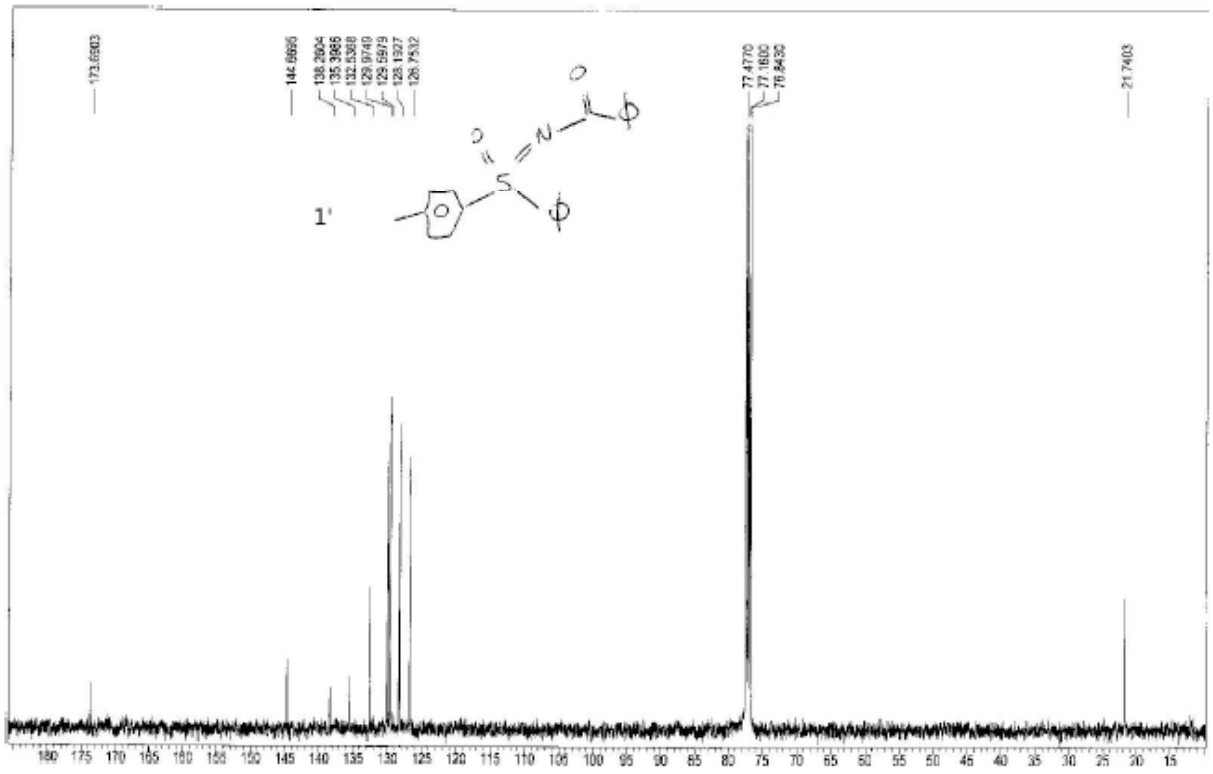
Following **GP1** from 2,3-dimethyl-but-2-ene (5 equiv., 0.21 mL), the corresponding aziridine (**4g**) was isolated (PE/EA 90:10, 101 mg, 59%). White solid, M. p. 154°C. IR (neat): nu(tilde) = 3070, 2970, 1720, 1633, 1282 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 6 H, C*Me*), 1.56 (s, 6 H, C*Me*), 7.37-7.40 (m, 2 H arom.), 7.45-7.49 (m, 1 H arom.), 7.52-7.56 (m, 2 H arom.), 7.58-7.62 (m, 1 H arom.), 8.10-8.16 (m, 4 H arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (s, C*Me*), 20.5 (C*Me*), 54.6 (CN), 127.8 (CH arom.), 128.8 (CH arom.), 129.3 (CH arom.), 131.5 (CH arom.), 132.9 (CH arom.), 136.4 (C arom.), 141.4 (C arom.), 171.8 (C=O). HRMS calcd. for $C_{19}H_{22}N_2O_2S$: $[M+Na]^+$ 365.1300; found 305.1301.



Following **GP1** from α-methyl methyl acrylate (5 equiv., 0.27 mL), the corresponding aziridine (**4h**) was isolated (PE/EA 90:10, 77 mg, 43%) as an unseparable mixture of two diastereomers. White solid. IR (neat): nu(tilde) = 2970, 1743, 1633, 1282 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, C*Me*, dia majo), 2.05 (s, 3 H, C*Me*, dia mino), 2.86 (s, 1 H, NC*H*H, dia mino), 2.87 (s, 1 H, NCH*H*, dia mino), 3.13 (s, 1 H, NC*H*H, dia majo), 3.31 (s, 1 H, NCH*H*, dia majo), 3.74 (s, 3 H, COOMe, dia majo), 3.87 (s, 3 H, COOMe, dia mino), 7.39-7.69 (m, 6 H, dia majo+dia mino), 8.09-8.11 (m, 4 H, dia majo+dia mino). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (C*Me*, dia majo), 15.5 (C*Me*, dia mino), 37.1 (NCH_2, dia mino), 39.4 (NCH_2, dia majo), 47.5 (N*C*Me), 47.8 (N*C*Me), 53.1 (OMe, dia majo), 53.3 (OMe, dia mino), 127.7 (CH arom.), 128.0 (CH arom.), 128.2 (CH arom.), 129.1 (CH arom.), 129.2 (CH arom.), 129.5 (CH arom.), 132.1 (CH arom., dia majo+dia mino), 133.6 (CH arom.), 133.7 (CH arom.), 135.4 (C arom., dia mino+dia majo), 139.1 (C arom., dia majo+dia mino), 168.3 ((MeO)C=O, dia majo), 168.6 ((MeO)C=O, dia mino), 172.5 (C=O, dia majo), 172.6 (C=O, dia majo).

Proof of purity for describedproducts

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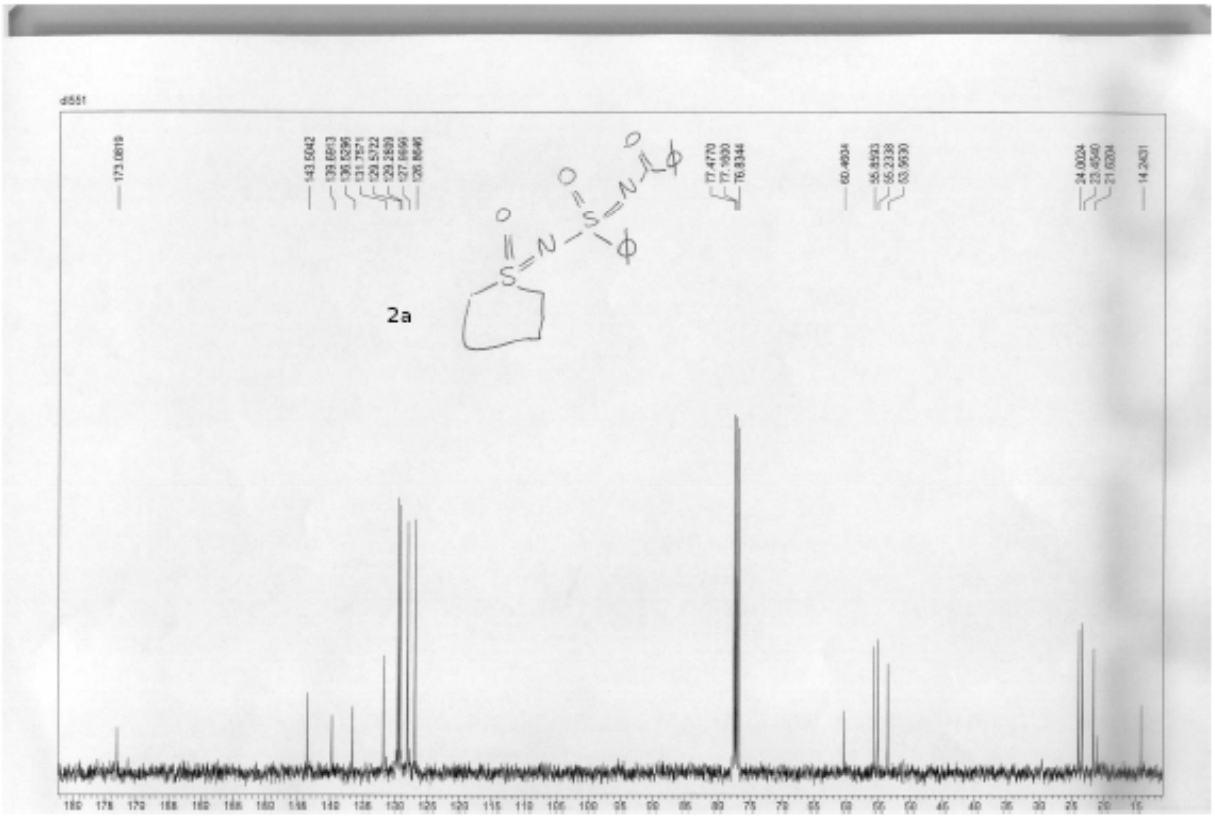
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77.1600
76.8344
60.4924
55.8923
55.2338
53.5930
24.0024
23.4540
21.6204
14.2431
2a

Service de Microanalyse

I.C.S.N. - C.N.R.S. 91198 Gif sur Yvette Cedex tél. 01 69 82 30 88

Analyse n° **48986** du **16/06/04** 2b dia2

A l'attention de **Melle Toussaint**

Téléphone Réf Produit AT132-2

Elément	Mesure 1	Mesure 2	Mesure 3
% *carbone*	**60,96**	**60,97**	
% *hydrogène*	**5,09**	**5,07**	
% *azote*	**6,28**	**6,24**	
%			
%			
%			
%			
%			

61.14
4.89
6.79

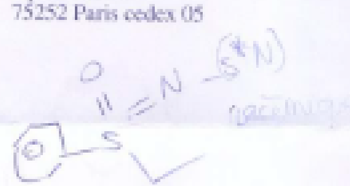
Ab ou Tr = absence ou trace

CNRS UMR 7611

Service **Malacria**

adresse

Université Pierre et Marie Curie
Laboratoire de Chimie Organique
B 229
4 place Jussieu
75252 Paris cedex 05



Le Responsable

Service de Microanalyse

I.C.S.N. - C.N.R.S. 91198 Gif sur Yvette Cedex tél. 01 69 82 30 88

Analyse n° **48987** du **16/06/04** 2b dia1

A l'attention de **Melle Toussaint**

Téléphone Réf Produit AN132-1

Elément	Mesure 1	Mesure 2	Mesure 3	
% *carbone*	61,59	61,65		61.14
% *hydrogène*	5,26	5,11		4.89
% *azote*	6,41	6,25		6.79
%				
%				
%				
%				
%				

Ab ou Tr = absence ou trace

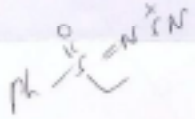
CNRS UMR 7611

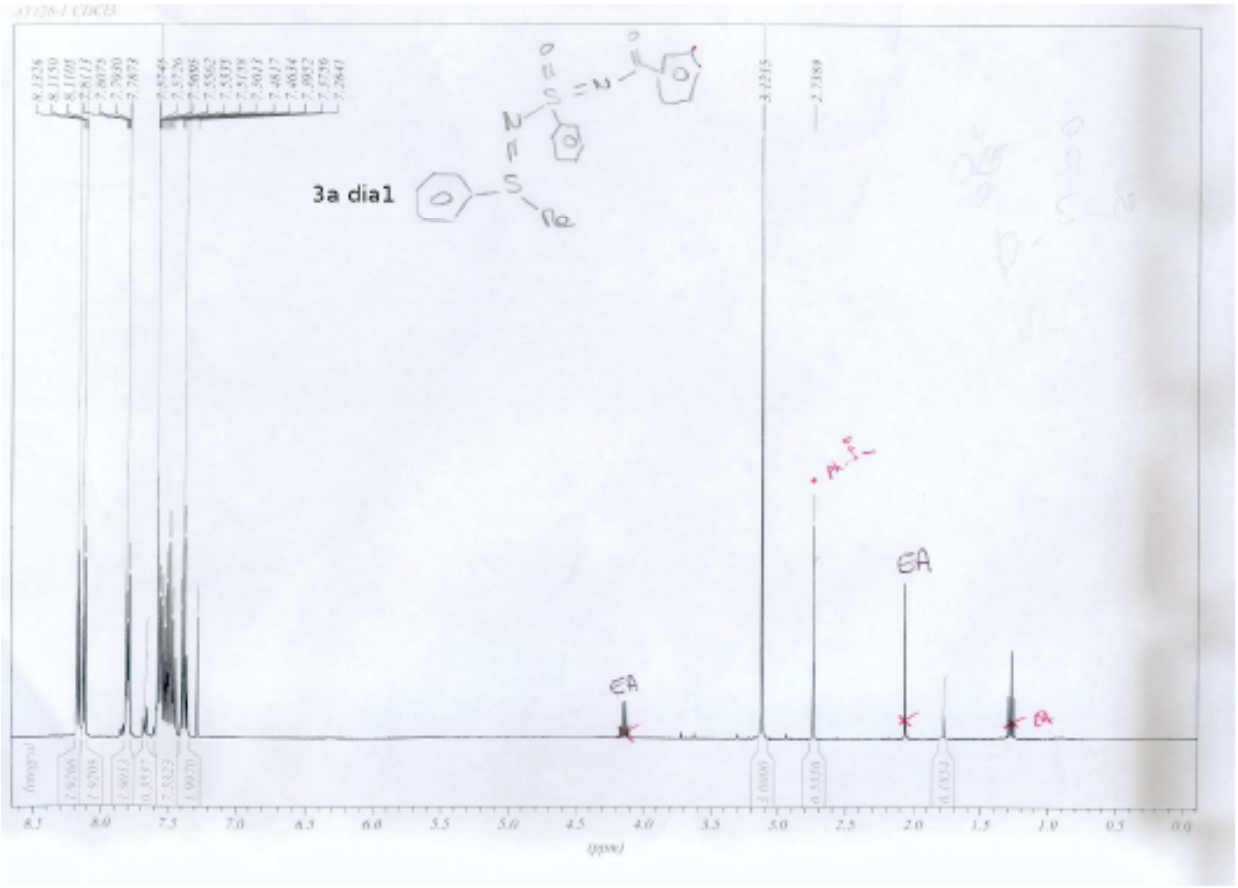
adresse

Service **Malacria**
Université Pierre et Marie Curie
Laboratoire de Chimie Organique
B 229
4 place Jussieu
75252 Paris cedex 05

C.N.R.S. I.C.S.N. * SERVICE MICROANALYSE

Le Responsable

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EA
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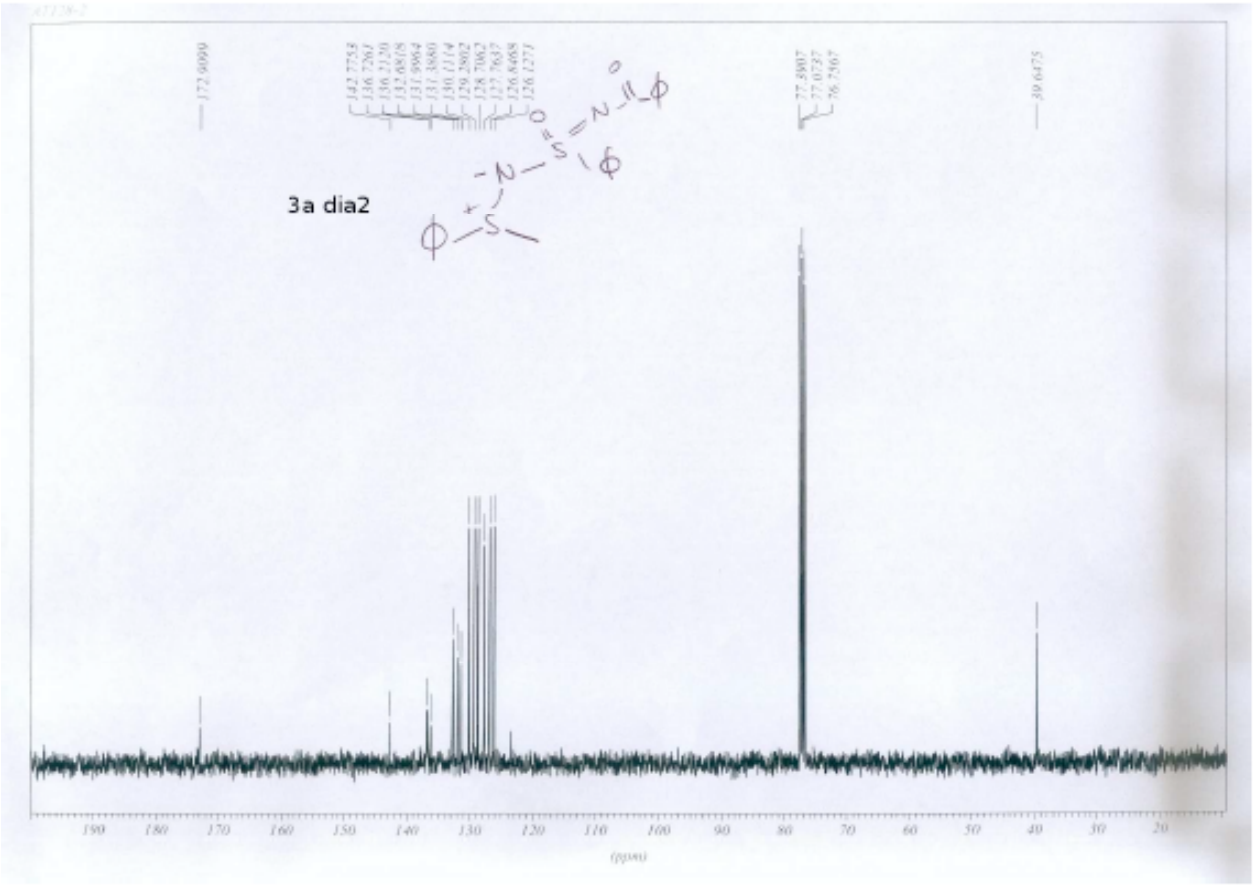
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77.5907
77.0737
76.7567
39.6475
3a dia2
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150
140
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90
80
70
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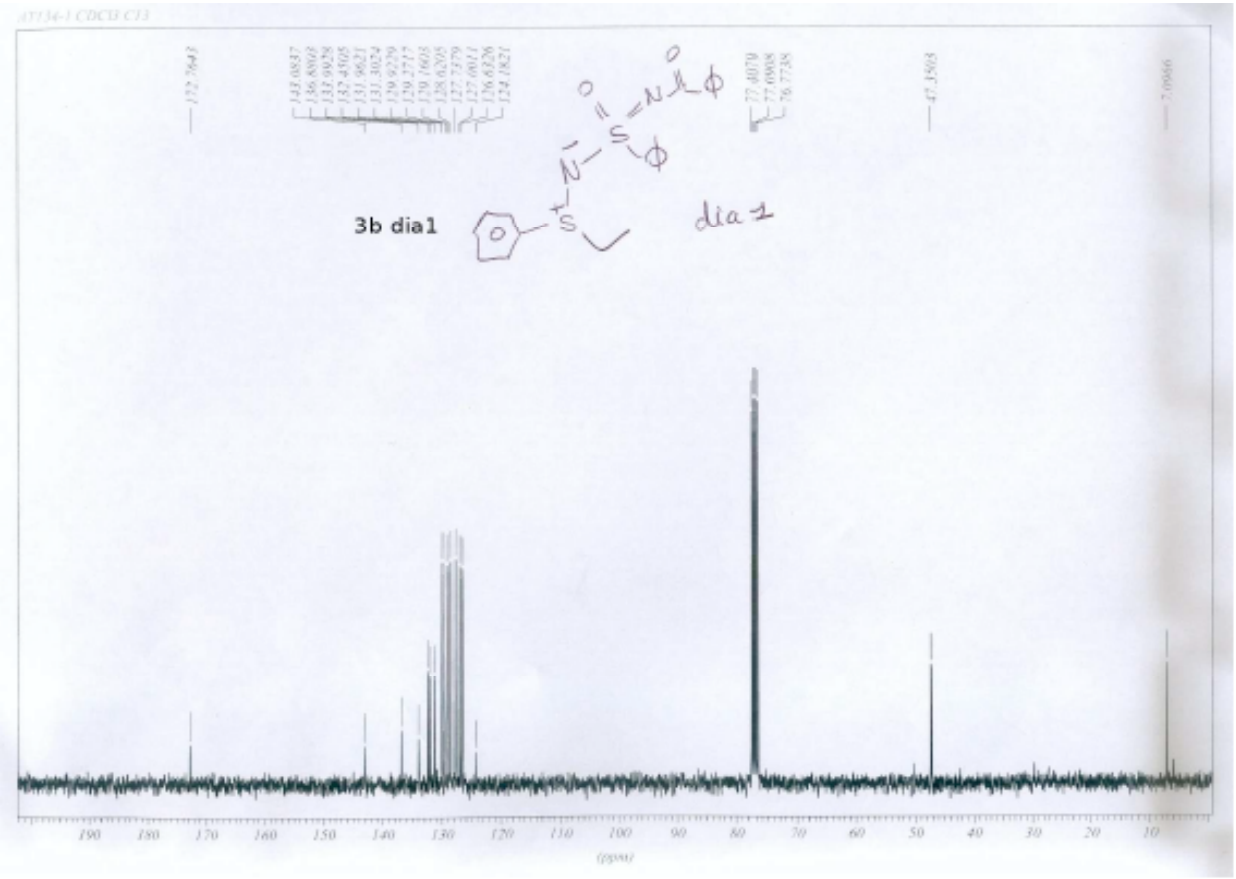
50
40
30
20
(ppm)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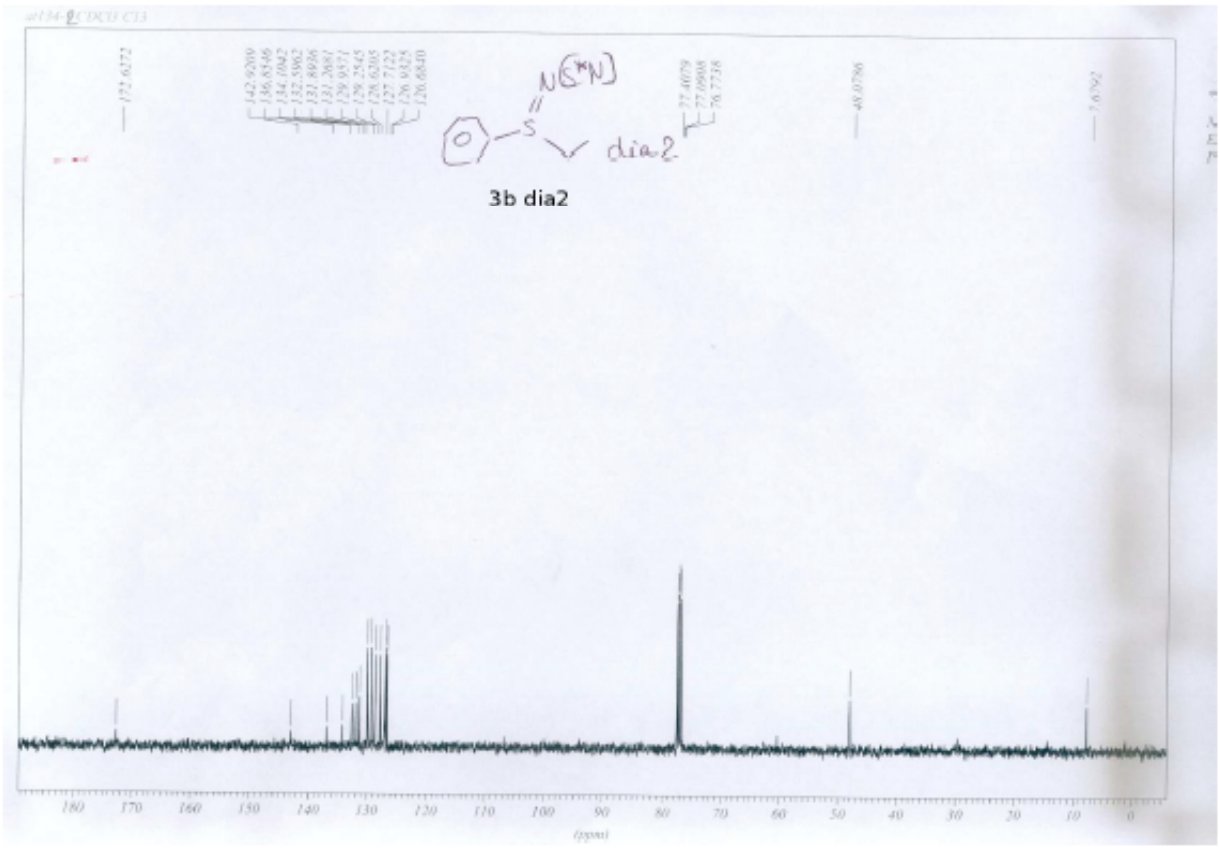
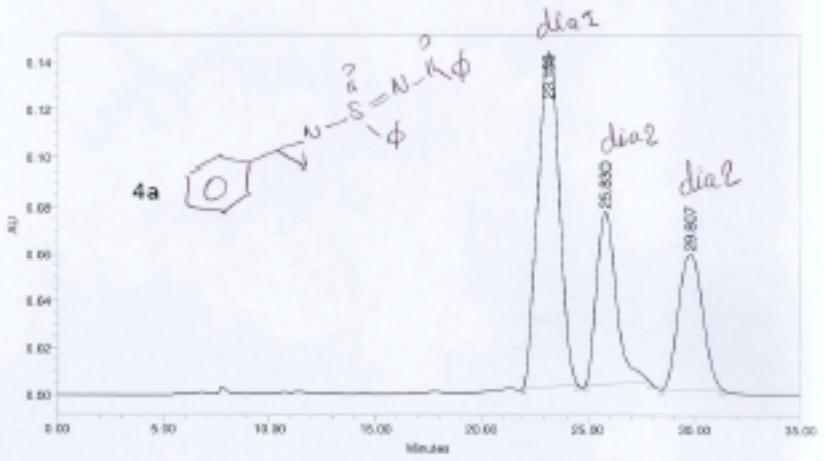

dia2
3b dia2

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	at125 40 10	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	01/juin/2004 18:02:04
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	14	Date Processed:	01/juin/2004 19:04:01
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



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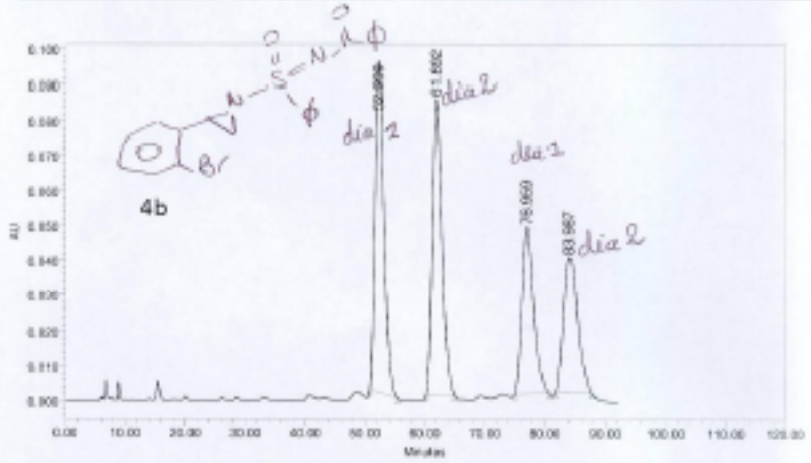
Report Method: Standard Report Printed 11:57:38 21/juil/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	at58 46 5	Acquired By:	malacria
Sample Type:	Unknown	Data Acquired:	28/mai/2004 16:27:02
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	11	Date Processed:	01/jun/2004 09:15:43
Injection Volume:	10.00 ul	Processing Method:	test avatars PM
Run Time:	301.0 Minutes	Channel Name:	2487/Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



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Report Method: Standard Report Printed 11:56:51 21/jul/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

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Sample Type:	Unknown	Date Acquired:	08/juin/2004 14:30:33
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Injection #:	16	Last Processed:	08/juin/2004 16:55:14
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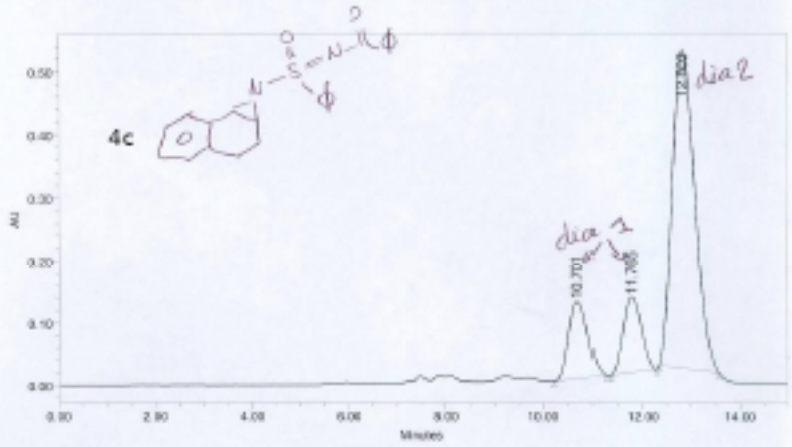
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



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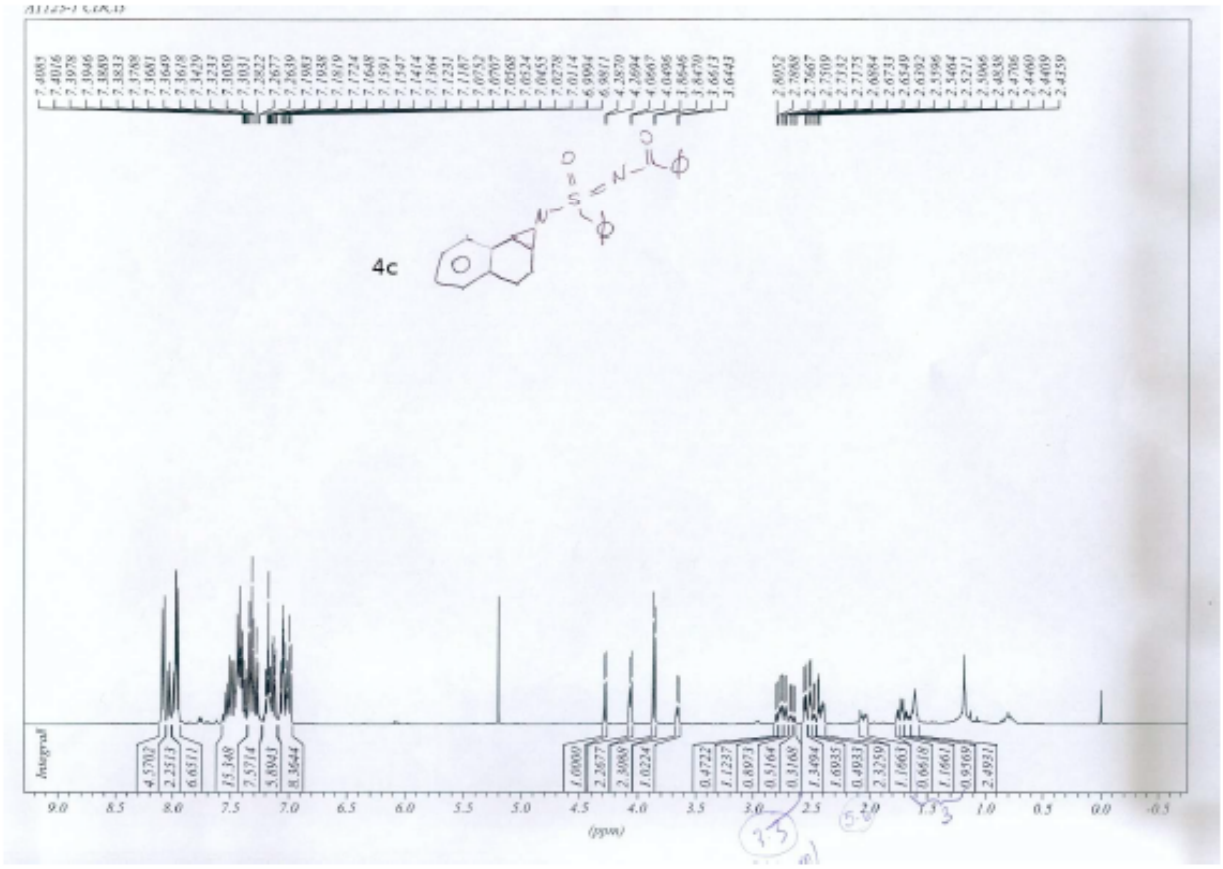
Report Method: Standard Report Printed 11:59:10 21/juil/2004 Page: 1 of 1


4c
Integral
(ppm)

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

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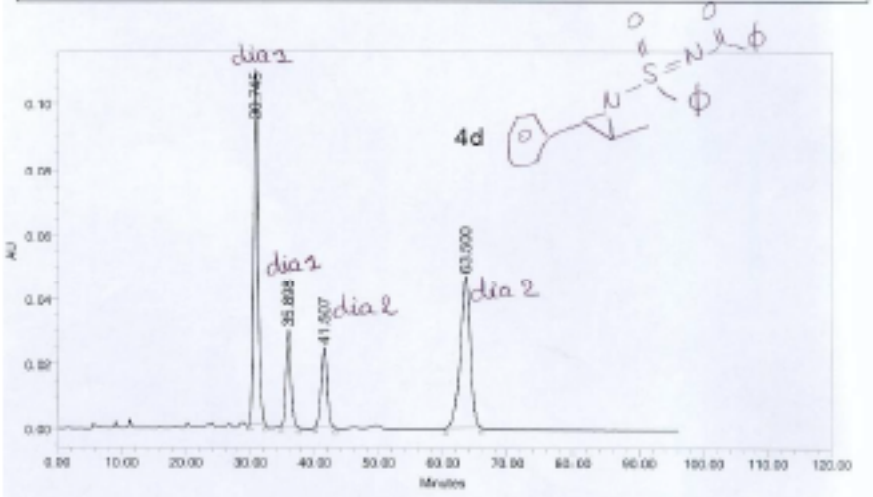
Sample Set Name:		Proc. Chnl. Descr.:	254



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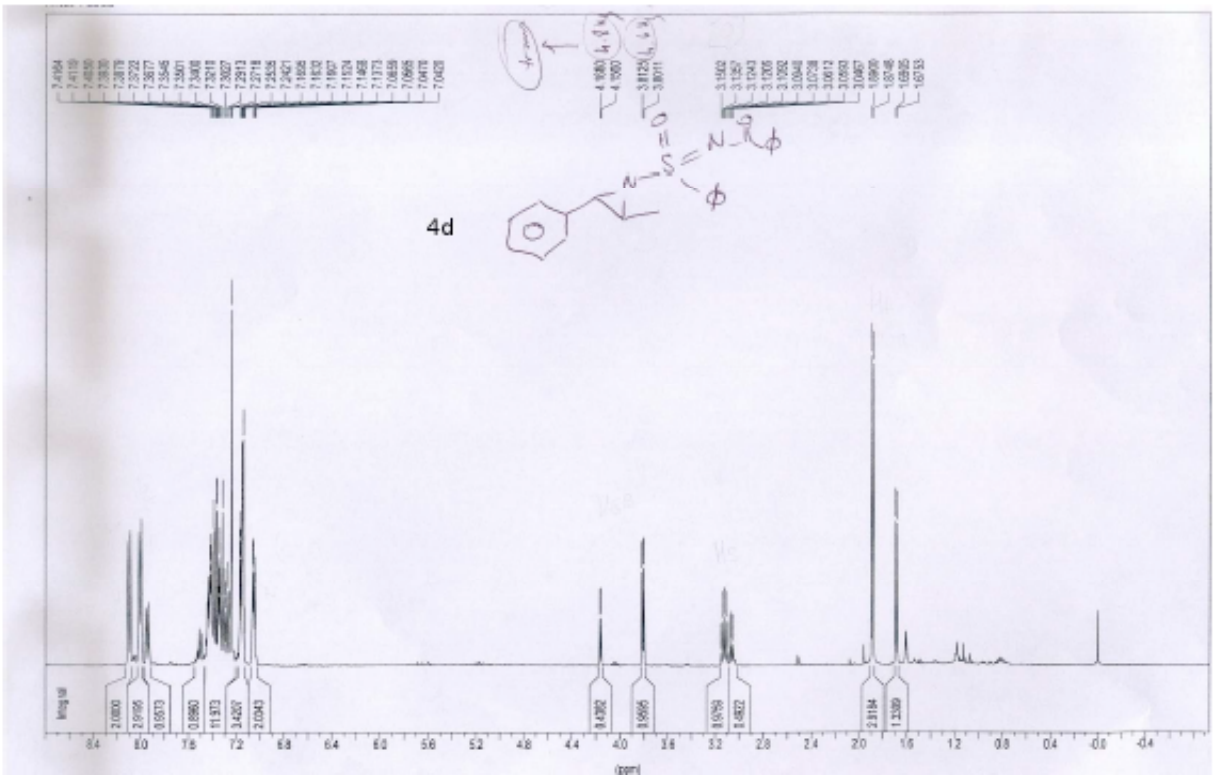
Report Method: Standard Report Printed: 12:01:23 21/jul/2004 Page: 1 of 1

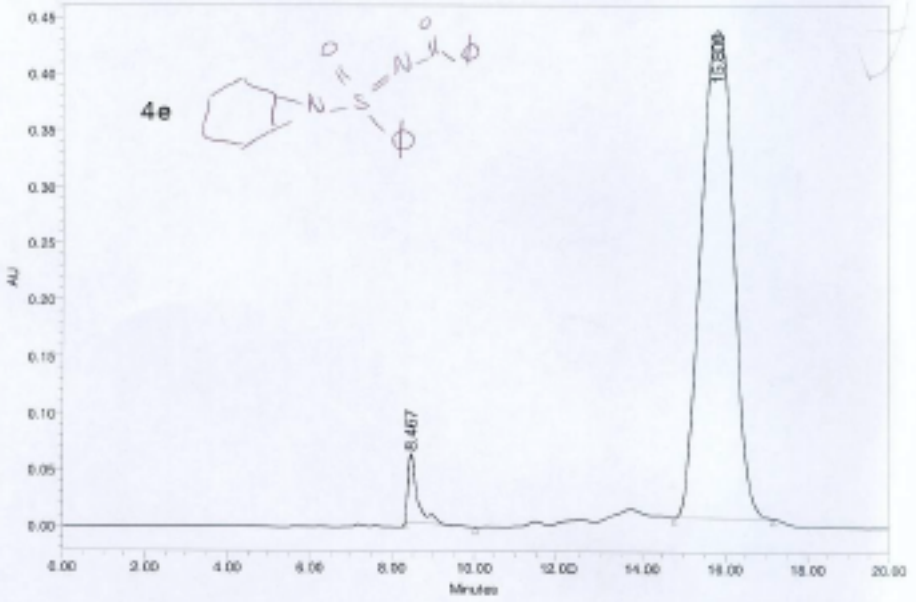

4d

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	at065 35 15	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	21/mai/2004 15:46:36
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	8	Date Processed:	21/juil/2004 15:39:22
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	122.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



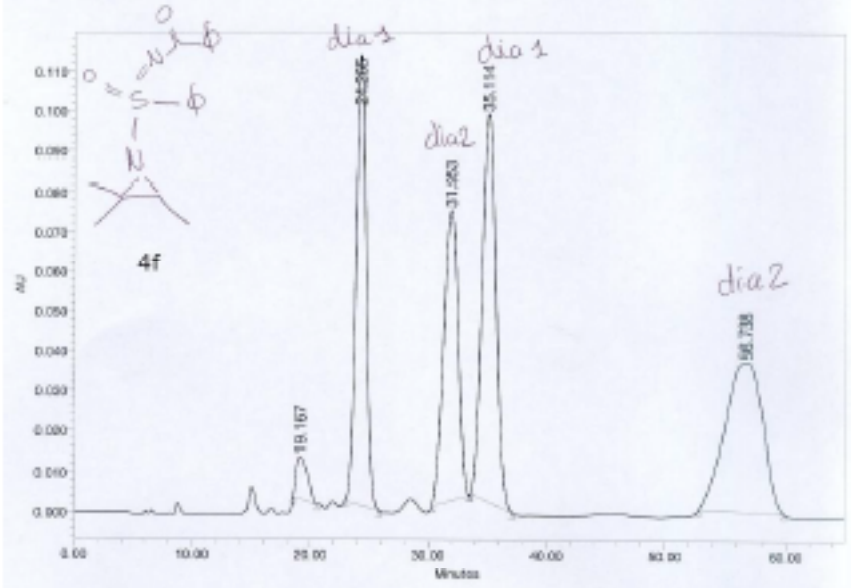
	RT	Area	% Area
1	8.467	939663	3.90
2	15.806	23166048	96.10

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

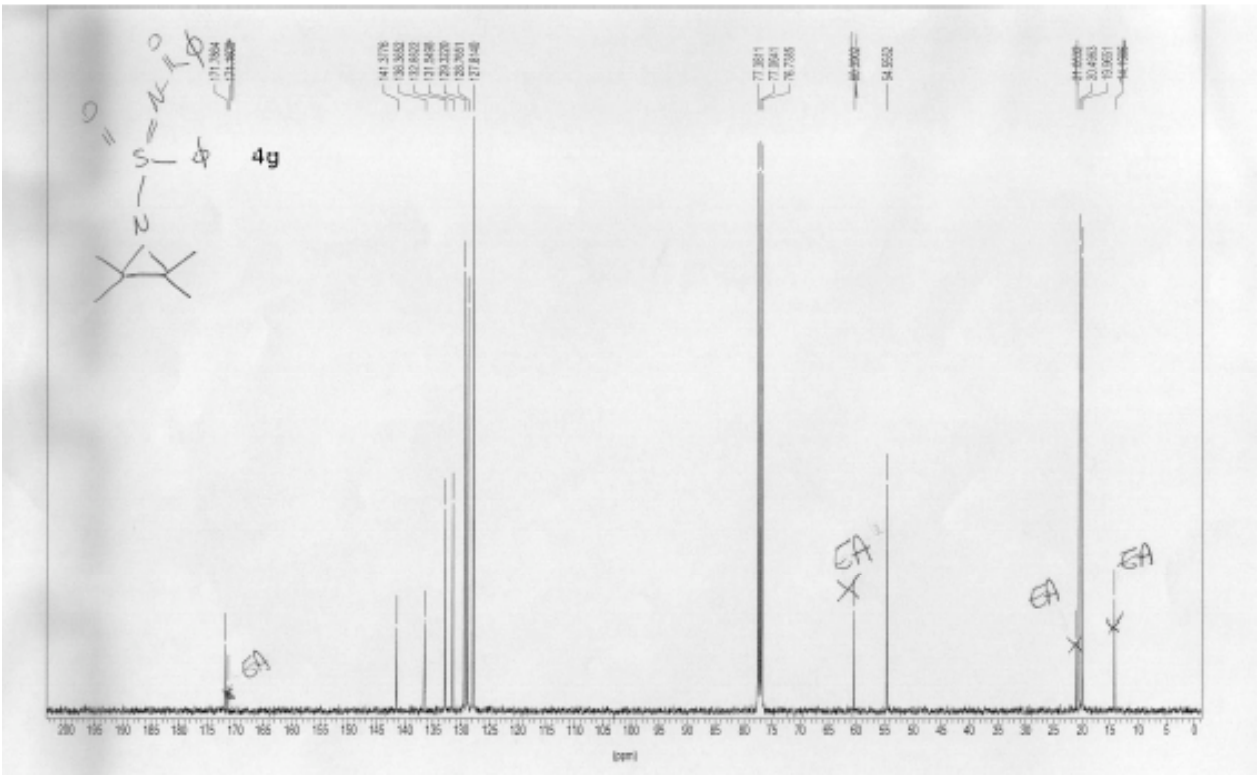
Sample Name:	st066-1 45 05	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	27/mai/2004 11:21:22
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	2	Date Processed:	21/juil/2004 15:30:59
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	19.167	691098	2.39
2	24.265	6539945	22.58
3	31.953	6179879	21.35
4	35.114	7859427	27.15

	RT	Area	% Area
5	56.738	7674528	26.52

Report Method: Standard Report Printed 15:31:45 21/juil/2004 Page: 1 of 1

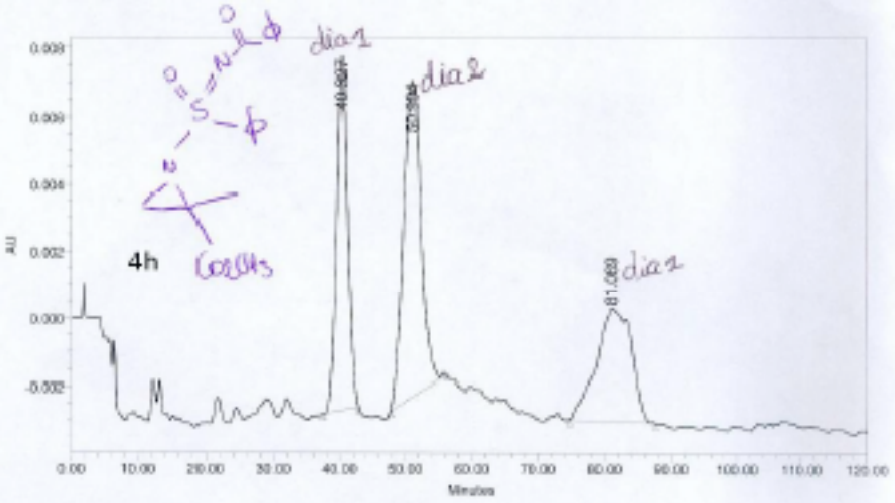

4g
EA
EA
EA
EA
(ppm)

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

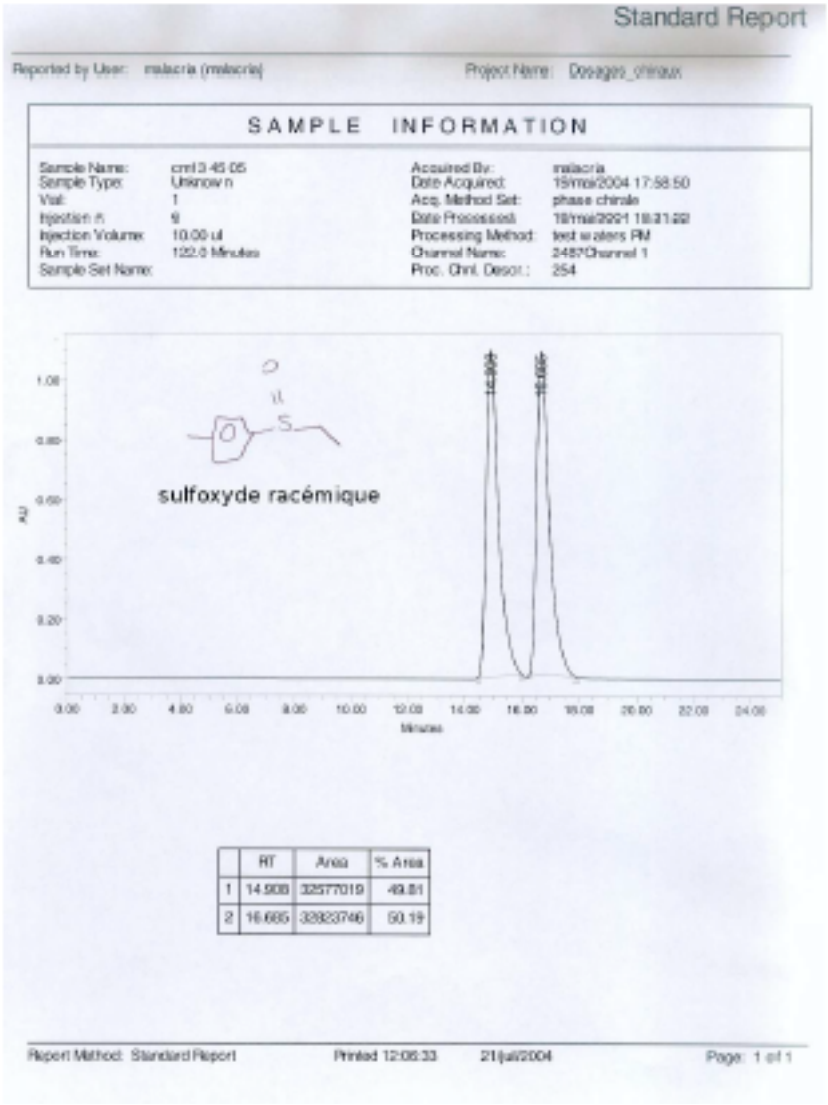
SAMPLE INFORMATION

Sample Name:	at263-1 45 05	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	27/mai/2004 15:29:00
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	5	Date Processed:	27/mai/2004 17:53:09
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	40.327	1198645	28.99
2	50.994	1735363	41.97
3	81.069	1200408	29.03

Determination of ee for sulfoximine 2b



Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	cmf3 45 05	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	19/mai/2004 17:58:50
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	9	Date Processed:	19/mai/2021 18:21:22
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	122.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254

	RT	Area	% Area
1	14.908	32577019	49.81
2	16.685	32823746	50.19

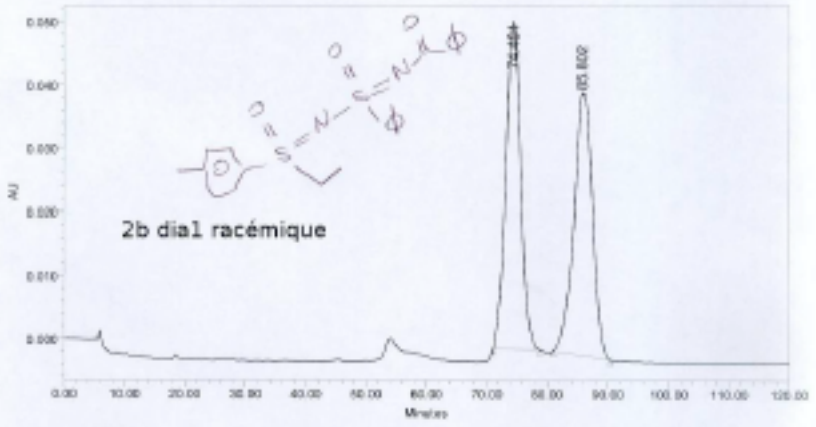
Report Method: Standard Report Printed 12:06:33 21/jul/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	cm251140 10 le 15/06 bis	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	15/jun/2004 11:18:25
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	9	Date Processed:	16/jun/2004 09:50:01
Injection Volume:	10.00 ul	Processing Method:	cm25 11 40 10
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



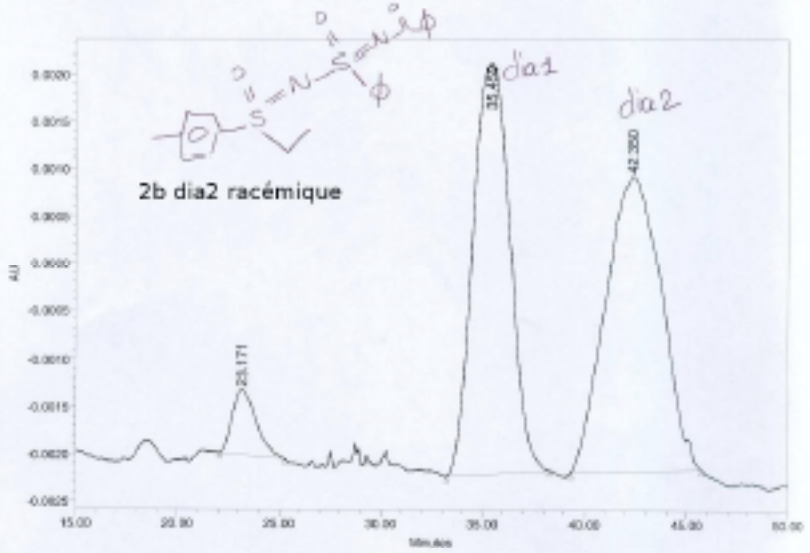
	RT	Area	% Area
1	74.464	8862742	50.16
2	85.802	8807220	49.84

Standard Report

Reported by User: malacria (malacria) Project Name: Dossiers_chiraux

SAMPLE INFORMATION

Sample Name:	cm 25 40 10	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	08/juin/2004 16:38:06
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	17	Date Processed:	21/juil/2004 15:28:54
Injection Volume:	10.00 ul	Processing Method:	test w.dors PM
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	23.171	55710	4.71
2	35.459	544541	46.01
3	42.350	583161	49.28

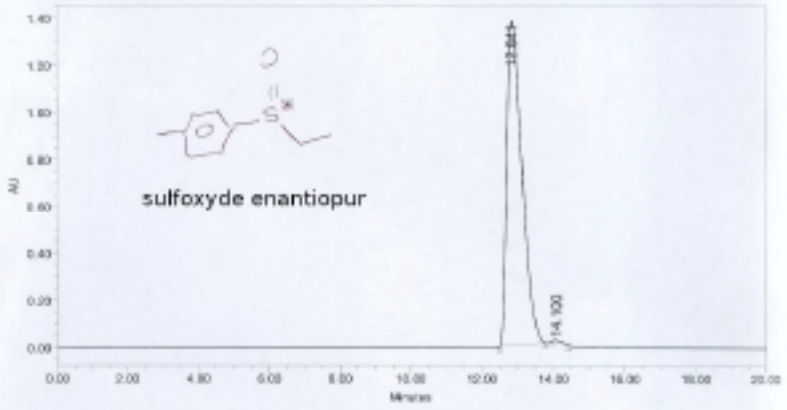
Report Method: Standard Report Printed 15:29:51 21/juil/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	cmt4 40 10	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	19/mai/2004 15:12:38
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	5	Date Processed:	19/mai/2004 18:51:27
Injection Volume:	10.00 ul	Processing Method:	test waters RM
Run Time:	122.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	12.841	40120149	99.65
2	14.100	141003	0.35

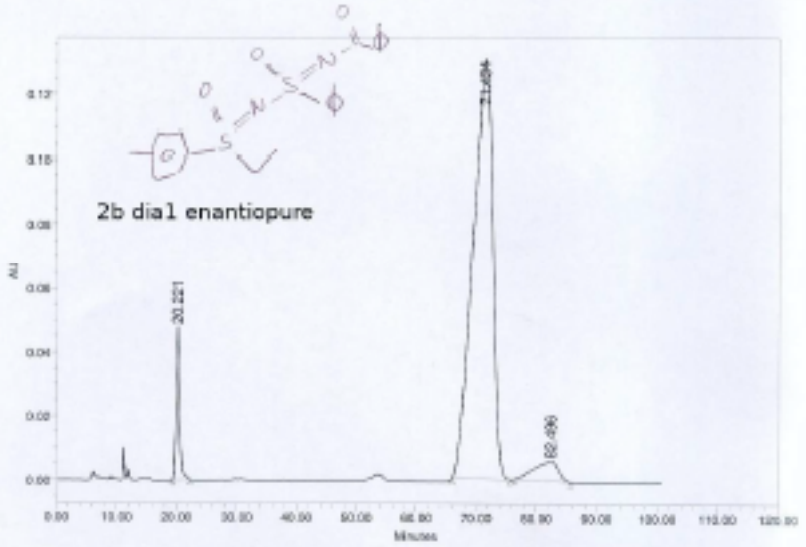
Report Method: Standard Report Printed 12:05:06 21/jul/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	gil 131 11 40 10 la 1608 bis	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	16/juin/2004 16:49:51
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	16	Date Processed:	21/juil/2004 15:37:15
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	301.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	20.221	1980069	5.95
2	71.434	29620688	88.97
3	82.496	1693039	5.09

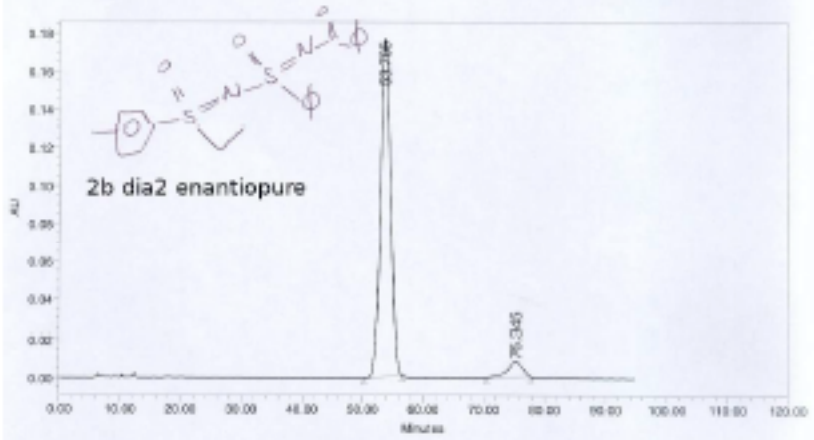
Report Method: Standard Report Printed 15:37:59 21/juil/2004 Page: 1 of 1

Standard Report

Reported by User: malacria (malacria) Project Name: Dosages_chiraux

SAMPLE INFORMATION

Sample Name:	at 131 12 40 10	Acquired By:	malacria
Sample Type:	Unknown	Date Acquired:	15/juin/2004 16:44:27
Vial:	1	Acq. Method Set:	phase chirale
Injection #:	11	Date Processed:	16/juin/2004 10:16:04
Injection Volume:	10.00 ul	Processing Method:	test waters PM
Run Time:	301.0 Minutes	Channel Name:	2487/Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254



	RT	Area	% Area
1	53.766	20382329	93.74
2	75.345	1360895	6.26

Report Method: Standard Report Printed 12:05:32 21/juil/2004 Page: 1 of 1