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Supporting Information

Thioamination of Alkenes with Hypervalent Iodine Reagents

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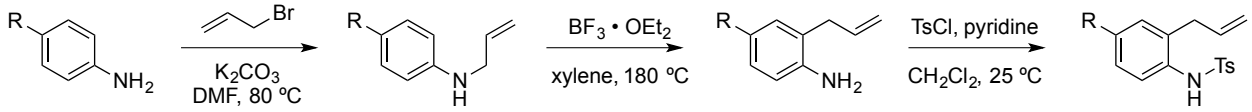
Supporting Information:

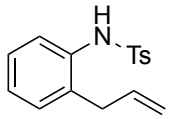
Materials and Methods: All reactions were carried out under a nitrogen atmosphere in oven dried glassware with magnetic stirring using usual Schlenk technique. THF, toluene, diethyl ether and CH_2Cl_2 were purified and dried using standard methods. Triethylamine and diethylamine were distilled from sodium hydroxide. Reagents were purified prior to use unless otherwise stated. Purification of reaction products was carried out by flash chromatography using Fisher silica gel (35-70 mesh). NMR spectra were recorded on Bruker DPX 250, Bruker DPX 400, Bruker DPX 500, Bruker DPX 600, or Oxford 300. ^{1}H NMR spectra were measured at 250, 300, 400 and 500 MHz. ^{13}C NMR spectra were measured at 63, 100, 126 and 150 MHz using $CDCl_3$, or DMSO-d_6 as a solvent and internal reference. Coupling constants J are given in Hz. Multiplicity as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Mass spectrometric data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Typical procedure for the synthesis of 2-allylanilines [1]



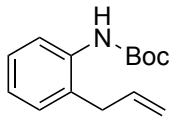
Allylbromide (1.40 mL, 16.24 mmol) was added dropwise to a solution of commercially available aniline (16.24 mmol) [aniline: 1.51 g, 4-methoxyaniline: 2.00 g, 4-chloroaniline: 2.06 g] and K_2CO_3 (5.39 g, 38.97 mmol) in DMF (37 mL). The solution was heated to 80 ºC and stirred at this temperature overnight. The reaction mixture was then filtered, washed with water (3 x 20 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (CH_2Cl_2) to afford the *N*-allyl aniline as yellowish oil. Next, BF_3•OEt_2 (0.93 mL, 7.36 mmol) was added to a solution of the *N*-allyl aniline (7.36 mmol) in xylene (4 mL). The mixture was heated to 180 ºC in a sealed tube and stirred at this temperature for 2 h. After cooling, the reaction mixture was poured into 10% aq NaOH (10 mL), and extracted with EtOAc (3 x 15 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc, 4:1) to yield the 2-allyl aniline as colourless oil. The ^{1}H and ^{13}C NMR were in agreement with the reported data.[6] The anilines were protected with the tosyl group using the procedure described above.

***N*-(2-Allylphenyl)-4-methylbenzenesulfonamide (1a)**



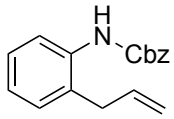
Tosylation yield: 0.45 g (1.56 mmol, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.51 (d, J = 8 Hz, 2H), 7.35 (dd, J = 1, 8 Hz, 1H), 7.13-7.18 (m, 3H), 6.96-7.08 (m, 2H), 6.43 (br, 1H), 5.67-5.74 (m, 1H), 5.03 (dd, J = 1.5, 10 Hz, 1H), 4.85 (dd, J = 2, 11 Hz, 1H), 2.92 (d, J = 4Hz, 2H), 2.33 (s, 3H) ppm; Spectral data are in agreement with reported data.[6]

***tert*-Butyl (2-allylphenyl)carbamate (1b)**



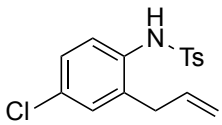
Boc-protection yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.7 Hz, 1H), 7.25-7.23 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.44 (br, 1H), 6.03-5.90 (m, 1H), 5.16 (dd, *J* = 1.5, 9.0 Hz, 1H), 5.07 (dd, *J* = 1.5, 16.8 Hz, 1H), 3.37 (d, *J* = 5.7 Hz, 1H), 1.53 (s, 9H) ppm; Spectral data are in agreement with reported data.[2]

Benzyl (2-allylphenyl)carbamate (1c)



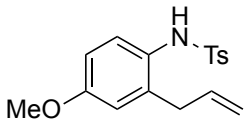
Carboxybenzylation yield: 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.42-7.23 (m, 6H), 7.19 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.09 (td, *J* = 1.2, 7.6 Hz, 1H), 6.61 (br s, 1H), 5.96 (m, 1H), 5.22 (s, 2H), 5.15 (m, 1H), 5.07 (m, 1H), 3.37 (m, 2H) ppm; Spectral data are in agreement with reported data.[3]

***N*-(2-Allyl-4-chlorophenyl)-4-methylbenzenesulfonamide (3)**



Tosylation Yield: 1.4 g (4.3 mmol, 87%). (Overall yield: 60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.61 (d, J = 8Hz, 2H), 7.38 (d, 8 Hz, 1H), 7.25 (d, J = 8Hz, 2H), 7.21 (dd, J = 2, 8 Hz, 1H), 7.10 (d, J = 2Hz, 1H), 6.47 (br, 1H), 5.73-5.81 (m, 1H), 5.17 (dd, J = 1.6, 12 Hz, 1H), 4.96 (dd, J = 1.5, 17 Hz, 1H), 2.98 (d, 6Hz, 2H), 2.45 (s, 3H); Spectral data are in agreement with reported data.[6]

***N*-(2-Allyl-4-methoxyphenyl)-4-methylbenzenesulfonamide (5)**

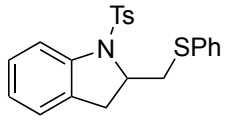


Tosylation Yield: 1.2 g (3.8 mmol, 89%) (Overall yield: 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, J = 8Hz, 2H), 7.26 (d, J = 8Hz, 2H), 6.77 (m, 2H), 6.65(s, 1H), 6.25 (br, 1H), 5.74-5.81 (m, 1H), 5.14 (dd, J = 2, 12 Hz, 1H), 4.98 (dd, J = 2, 13 Hz, 1H), 3.81 (s, 3H), 2.94 (d, J = 5 Hz, 2H), 2.45 (s, 3H) ppm; Spectral data are in agreement with reported data.[6]

Procedure for Cyclisation:

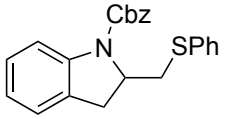
Into an oven-dried round-bottom flask under nitrogen a solution of *N*-(2-allylphenyl)-4-methylbenzenesulfamide **1a** (100 mg, 0.35 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a suspension of [(bistrifluoroacetoxy)iodo]benzene (208 mg, 0.52 mmol) in dry CH_2Cl_2 (2 mL) at –20 °C. The reaction mixture was stirred for 15 min and treated carefully with suspension of sodium benzenethiolate (46 mg, 0.35 mmol) in dry CH_2Cl_2 (3 mL). The reaction was stirred for further 15 min and quenched with saturated sodium thiosulfate solution (5 mL), diluted with water (5 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined, washed with brine (10 mL) and dried over $MgSO_4$, filtered and the solvent was carefully removed under reduced pressure. The crude material was purified by column chromatography on silica gel using ethyl acetate/hexane (20%).

2-((Phenylthio)methyl)-1-tosylindoline (2a)



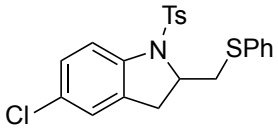
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8 Hz, 1H), 7.59 (d, *J* = 8 Hz, 2H), 7.25 – 7.15 (m, 6H), 7.09 – 7.00 (m, 4H), 4.40 – 4.31 (m, 1H), 3.70 (dd, *J* = 10, 3 Hz, 1H), 3.30 (t, *J* = 10 Hz, 1H), 2.98 (dd, *J* = 17, 9 Hz, 1H) 2.34 (dd, *J* = 17, 3 Hz, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 141.3, 136.1, 134.7, 130.5, 129.9, 129.5, 128.9, 128.1, 127.2, 125.4, 125.2, 125.0, 116.9, 62.7, 34.9, 129.4, 21.7 ppm; HRMS (ESI): calc. for $C_{22}H_{22}NO_2S_2$ $[M+H]^+$: 396.1014, found: 396.1022.

Benzyl 2-((phenylthio)methyl)indoline-1-carboxylate (2c)



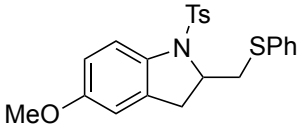
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (br s, 1H), 7.47–7.31 (m, 10H), 7.21 (br s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.32 (s, 2H), 4.93 (br s, 1H), 3.41 (dd, *J* = 16.5, 4.5 Hz, 1H), 3.27 (br s, 1H), 2.93 (m, 2H) ppm.

5-Chloro-2-((phenylthio)methyl)-1-tosylindoline (4)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 4.8, 8.4 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39-7.34 (m, 4H), 7.27-7.23 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.91 (td, *J* = 2.4, 9.2 Hz, 1H), 6.74 (dd, *J* = 2.8, 8.0 Hz, 1H), 4.30-4.22 (m, 1H), 3.67 (dd, *J* = 3.6, 13.6 Hz, 1H), 2.92-2.73 (m, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 144.1, 137.2, 134.7, 134.2, 133.3, 129.6, 129.1, 126.9, 126.3, 118.2, 114.5, 112.4, 61.2, 38.5, 33.2, 21.5 ppm; IR (neat): 3058, 2923, 1599, 1482, 1356, 1166, 1090, 1026, 935, 814 cm^{-1}; HRMS (ESI): calc. for $C_{22}H_{21}ClNO_2S_2$ $[M+H]^+$: 430.0624, found: 430.0618.

5-Methoxy-2-((phenylthio)methyl)-1-tosylindoline (6)



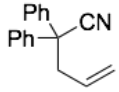
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 17, 9 Hz, 3H), 7.21-7.27 (m, 5H), 7.17 (d, *J* = 8 Hz, 2H), 6.77 (dd, *J* = 9, 3 Hz, 1H), 6.60 (d, *J* = 3 Hz, 1H), 4.36 – 4.28 (m, 1H), 3.78 (s, 3H), 3.64 (dd, *J* = 10, 4 Hz, 1H), 3.26 (t, *J* = 10 Hz, 1H), 2.84 – 2.70 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 144.3, 135.7, 134.7, 134.4, 132.5, 129.8, 129.6, 128.3, 127.3, 125.7, 118.3, 113.3, 111.0, 63.0, 55.7, 39.2, 35.0, 21.8 ppm; HRMS (ESI): calc. for $C_{23}H_{24}NO_3S_2$ $[M+H]^+$: 426.1119, found: 426.1126.

*Procedure for the synthesis of starting materials **S1** and **S2***

Into an oven-dried round-bottom flask under nitrogen, sodium hydride (60% in oil, 3.52 g, 91.6 mmol) and dimethylformamide (10.3 mL) was added at 0 °C. Diphenylacetonitrile (2.0 g, 10.35 mmol) [or isobutyronitrile (0.71 g, 10.35 mmol)] was added portionswise over 10 min and stirred

45 min at 0 °C. The resulting suspension was treated dropwise with allylbromide (1.57 mL, 18 mmol), warmed up to room temperature and stirred for 16 h. The resulting solution was cooled to 0 °C and quenched by adding water (20 mL). The mixture was diluted 1:1 with diethyl ether washed with water (3 x 10 mL) and brine (1 x 10 mL). The aqueous layers were extracted with CH_2Cl_2 (1 x 15 mL). The combined organic layers were dried with $MgSO_4$ and filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using ethyl acetate/hexane (1:5).

2,2-Diphenyl-pent-4-enenitrile (S1)



Yield: 3.3 g (14.1 mmol, 70 %); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15-7.30 (m, 10H), 5.56-5.65 (m, 1H), 5.04-5.14 (m, 2H), 3.02-3.04 (d, *J* = 7 Hz, 2H) ppm; Spectral data are in agreement with literature.[4]

2,2-Dimethyl-pent-4-enenitrile (S2)

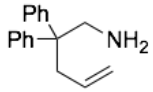
Yield: 1.8 g (16.4 mmol, 62%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.78-5.95 (m, 1H), 5.25-5.15 (m, 2H), 2.27-2.30 (d, *J* = 7 Hz, 2H), 1.34 (s, 6H) ppm; Spectral data are in agreement with literature.[4]

General method of reduction using lithium aluminium hydride

Into an oven-dried round-bottom flask under nitrogen a solution of compound **S1** (3.3 g, 15 mmol) [or compound **S2** (1.63 g, 15 mmol)] in Et_2O (100 mL) was added dropwise to a suspension of $LiAlH_4$ (1.2 g, 32 mmol) in Et_2O (250 mL) at 0 °C, warmed up to room temperature and stirred for 16 h. The reaction mixture was cooled to 0 °C and treated carefully with 20% aq. NaOH (5 mL), then diluted with Et_2O (50 mL) and the precipitation salts were filtered. The precipitation was washed with Et_2O. The organic layers were combined, washed with brine (3 x 10 mL) and dried over $MgSO_4$, filtered and the solvent was carefully removed under reduced pressure. The crude material was purified by column chromatography on silica gel using ethyl acetate/hexane (1:5).

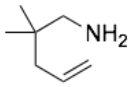
2,2-Diphenyl-pent-4-enylamine (S3)



Yield: 2.5 g (10.5 mmol, 75%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08-7.25 (m, 10H), 5.28-5.39 (m, 1H), 4.83-5.02 (m, 2H), 3.25 (m, 2H), 2.84-2.86 (d, *J* = 6 Hz, 2H), 1.03 (s, 2H) ppm; Spectral data are in agreement with literature.[4]

2,2-Dimethyl-pent-4-enylamine (S4)



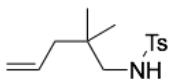
Yield: 0.9 g (7.9 mmol, 53%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71-5.82 (m, 1 H), 4.95-7.99 (m, 2H), 2.38 (s, 2H), 2.03 (m, 2H), 0.87 (s, 6H) ppm; Spectral data are in agreement with literature.[5]

Protection of amines

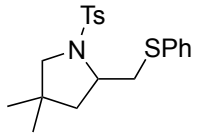
The amine (6.5 mmol) was dissolved in 20 mL of dry CH_2Cl_2, and treated with tosyl chloride or benzoyl chloride or di-*tert*-butyl dicarbonate (7.1 mmol) and pyridine (1.5 mL, 19.4 mmol). The mixture was stirred at room temperature for 24 h. The solution was diluted with H_2O (10 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified by column chromatography on silica gel using ethyl acetate/hexane (1:9).

***N*-(2,2-Dimethyl-pent-4-enyl)-4-methyl-benzenesulfonamide (7)**



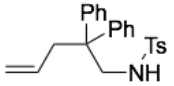
Yield: 0.266 g (0.99 mmol, 23%); colourless solid; m.p.: 73-74 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 6 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 5.70 (m, 1H), 5.02-4.90 (m, 2H), 4.98 (t, *J* = 8 Hz, 1H), 2.68 (d, *J* = 7 Hz, 2H), 2.40 (s, 3H), 1.99 (d, *J* = 7 Hz, 2H), 0.85 (s, 6H) ppm; Spectral data are in agreement with literature.[6,7]

4,4-Dimethyl-2-((phenylthio)methyl)-1-tosylpyrrolidine (8)



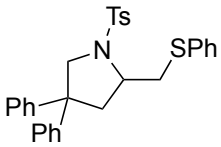
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.08-7.12 (m, 5H), 3.82 (dd, *J* = 13.3, 3.0 Hz, 1H), 3.55-3.48 (m, 1H), 3.12 (d, *J* = 10.5 Hz, 1H), 2.93 (d, *J* = 10.4 Hz, 1H), 2.78 (dd, *J* = 13.3, 10.4 Hz, 1H), 2.30 (s, 3H), 1.76 (dd, *J* = 12.8, 7.6 Hz, 1H), 1.53 (dd, *J* = 12.9, 7.8 Hz, 1H), 0.95 (s, 3H), 0.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 135.2, 132.9, 130.6, 129.1, 128.8, 128.5, 126.5, 60.9, 58.1, 44.9, 39.2, 36.2, 25.4, 24.8, 20.5 ppm.[8]

***N*-(2,2-Diphenyl-pent-4-enyl)-4-methyl-benzenesulfonamide (9)**



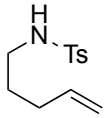
Yield: 2.0 g (5.1 mmol, 61%); colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 9 Hz, 2H), 7.29-7.29 (m, 8H), 7.07 (d, *J* = 8 Hz, 4H), 5.21-5.32 (m, 1H), 4.92-4.96 (m, 2H), 3.82 (t, *J* = 8 Hz, 1H), 3.52 (d, *J* = 6 Hz, 2H), 2.90 (d, *J* = 7 Hz, 2H), 2.43 (s, 3H) ppm; Spectral data are in agreement with literature.[5]

4,4-Diphenyl-2-((phenylthio)methyl)-1-tosylpyrrolidine (10)



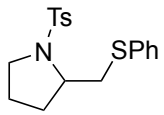
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-6.57 (m, 19H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.27-3.07 (m, 3 H), 3.02 (dd, *J* = 12.3, 8.2 Hz, 1H), 2.64 (s, 1H), 2.50 (d, *J* = 12.3 Hz, 1H), 2.31 (s, 1H), 2.16-2.06 (m, 1H), 1.67 (ddd, *J* = 21.7, 10.9, 7.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 146.9, 138.9, 136.1, 133.6, 130.05, 129.7, 129.6, 128.3, 128.2, 128.1, 127.9, 127.4, 127.2, 125.8, 125.7, 60.2, 59.4, 59.1, 46.4, 36.1, 33.3, 26.9 ppm; HRMS (ESI): calc. for $C_{30}H_{30}NO_2S_2$ $[M+H]^+$: 500.1640, found: 500.1648.

4-Methyl-N-(pent-4-en-1-yl)benzenesulfonamide (11)



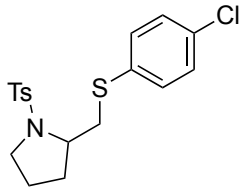
Prepared according to literature.[9]

2-((Phenylthio)methyl)-1-tosylpyrrolidine (12) [10]



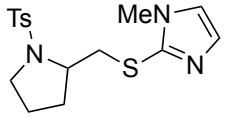
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.0 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.21 (m, 3H), 3.71 (dd, *J* = 13, 3 Hz, 1H), 3.65 (ddt, *J* = 11, 7.2, 3.1 Hz, 1H), 3.51 (ddd, *J* = 10, 6.2, 4.2 Hz, 1H), 3.12 (ddd, *J* = 10.0, 8.0, 7 Hz, 1H), 2.79 (dd, *J* = 13.5, 11.0 Hz, 1H), 2.42 (s, 3H), 1.94-1.86 (m, 1H), 1.86-1.77 (m, 1H), 1.70-1.60 (m, 1H), 1.58-1.50 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 135.3, 133.7, 129.6, 129.0, 128.9, 127.4, 126.0, 58.8, 49.7, 38.3, 30.2, 23.7, 21.5 ppm.

2-(((4-Chlorophenyl)thio)methyl)-1-tosylpyrrolidine (13) [11]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46-1.70 (m, 2H), 1.71-1.94 (m, 2H), 2.41 (s, 3H), 2.77 (dd, *J* = 13.4, 10.4 Hz, 1H), 3.03 (m, 1H), 3.57 (m, 2H), 3.64 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 133.9 , 133.7, 131.9, 130.2, 129.7, 129.1, 127.4, 58.7, 49.7, 38.5, 30.2, 23.7, 21.5 ppm.

1-Methyl-2-(((1-tosylpyrrolidin-2-yl)methyl)thio)-1*H*-imidazole (14) [12]

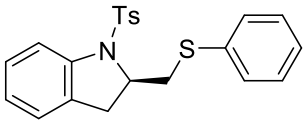


^{1}H NMR (400 MHz, [D_6]-DMSO): *δ* = 1.68-1.77 (m, 1H), 1.83-1.98 (m, 2H), 2.07-2.16 (m, 1H), 3.19-3.22 (m, 2H), 3.35–3.42 (m, 2 H), 3.61 (s, 3 H), 3.81–3.84 (m, 1 H), 7.01 (d, *J* = 1.6Hz, 1 H), 7.33 (d, *J* = 1.6 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ = 23.4, 29.2, 33.2, 34.4, 44.6, 59.1, 123.6, 127.9, 139.7 ppm.

Procedure for asymmetric cyclization:

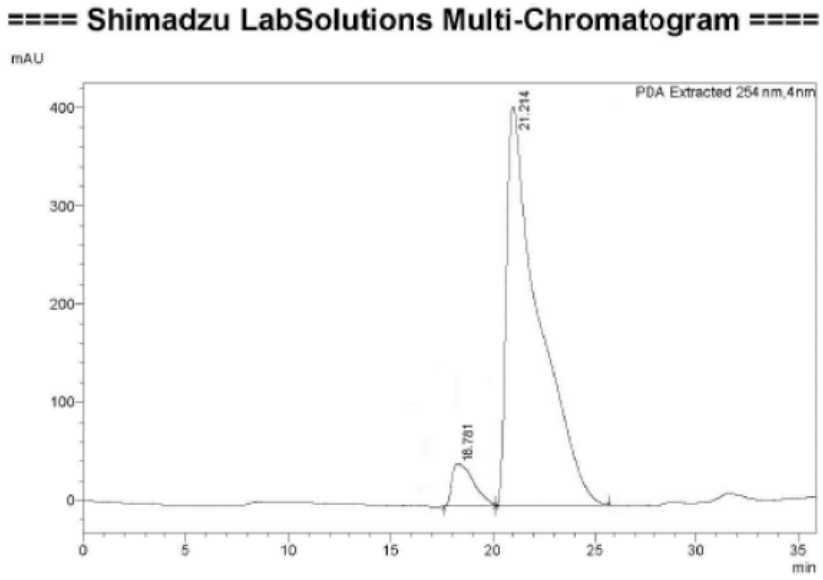
Into an oven-dried round-bottom flask under nitrogen a solution of *N*-(2-allylphenyl)-4-methylbenzenesulfamide **1a** (50 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to a suspension of **18a** (125 mg, 0.21 mmol) in dry CH_2Cl_2 (2 mL) at –20 °C. The reaction mixture was stirred for 15 min and then treated carefully with suspension of sodium benzenethiolate (25 mg, 0.19 mmol) in dry CH_2Cl_2 (2 mL). The reaction was stirred for further 15 min and quenched with saturated sodium thiosulfate solution (5 mL), diluted with water (5 mL) and extracted with CH_2Cl_2 (3 x 5 ml). The organic layers were combined, washed with brine (5 mL) and dried over $MgSO_4$, filtered and the solvent was carefully removed under reduced pressure. The crude material was purified by column chromatography on silica gel using ethyl acetate/hexane (20%).

(*R*)-2-((Phenylthio)methyl)-1-tosylindoline [(*R*)-2a]



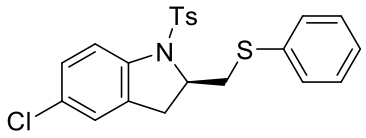
$[\alpha]^{20}_D$ = 11.5 (c = 0.5, $CHCl_3$)

HPLC analysis: Daicel Chiralcel AD-H column, hexane/*i*-PrOH = 94/6, 0.8 mL/min, 254 nm; t_R (*S*) = 18.78 min, t_R (*R*) = 21.21 min; 79% *ee*.



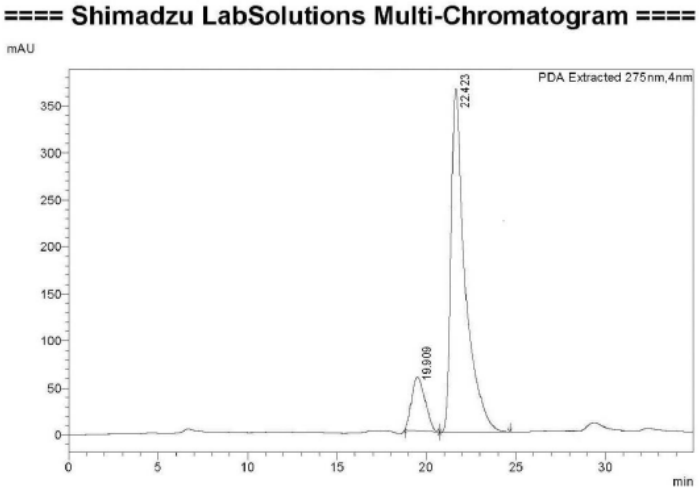
Peak #	Ret.Time	Area %
1	18.781	10.59
2	21.214	89.41
		78.82

(*R*)-5-Chloro-2-((phenylthio)methyl)-1-tosylindoline [(*R*)-4]



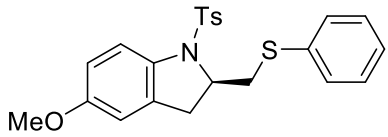
$[\alpha]^{20}_{D}$ = 12.2 (c = 0.5, $CHCl_3$)

HPLC analysis: Daicel Chiralcel AD-H column, hexane/*i*-PrOH = 95/5, 0.8 mL/min, 275nm; t_R (*S*) = 19.91 min), t_R (*R*) = 22.43 min; 74% *ee* [absolute stereochemistry assigned in comparison to the literature: (*S*)-5-fluoro-2-((phenylthio)methyl)-1-tosylindoline $[\alpha]^{25}_{D}$ = –15.5 (c = 0.57, $CHCl_3$)].[1]



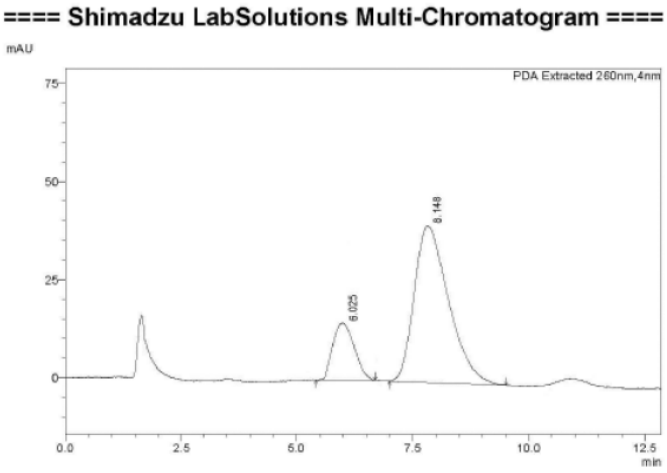
Peak #	Ret.Time	Area %
1	19.909	13.02
2	22.423	86.98
		73.96

(*R*)-5-Methoxy-2-((phenylthio)methyl)-1-tosylindoline [(*R*)-6]



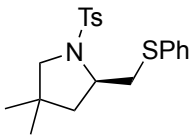
$[\alpha]^{20}_{D}$ = 9.3 (c = 0.5, $CHCl_3$)

HPLC analysis: Daicel Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 1.5 mL/min, 260 nm; t_R (*S*) = 6.02 min), t_R (*R*) = 8.14 min; 70% *ee* [absolute stereochemistry assigned in comparison to the literature: (*S*)-5-fluoro-2-((phenylthio)methyl)-1-tosylindoline $[\alpha]^{25}_{D}$ = –15.5 (c = 0.57, $CHCl_3$)].[1]



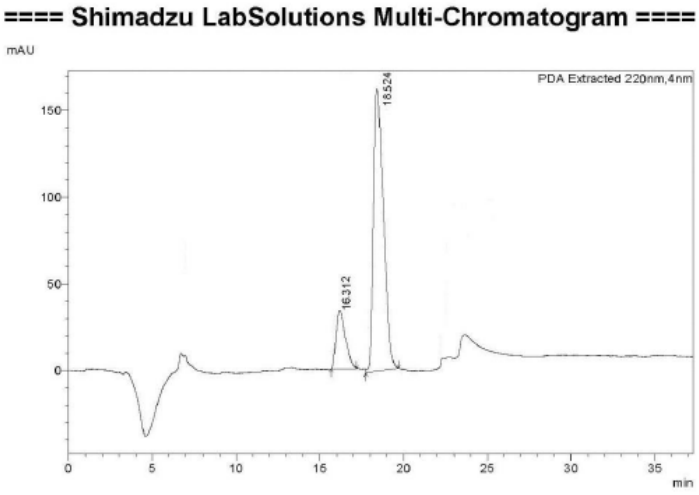
Peak #	Ret.Time	Area %
1	6.025	15.21
2	8.148	84.79
		69.58

(*R*)-4,4-Dimethyl-2-((phenylthio)methyl)-1-tosylpyrrolidine [(*R*)-8]



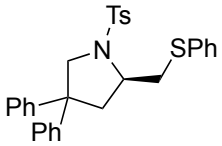
$[\alpha]^{20}_{D}$ = 98.7 (c = 0.5, $CHCl_3$)

HPLC analysis: Daicel Chiralcel OD column, hexane/*i*-PrOH = 90/10, 1 mL/min, 220 nm; t_R (*S*) = 16.32 min, t_R (*R*) = 18.52 min; 60% *ee* (absolute stereochemistry assigned in analogy to **(*R*)-12**).



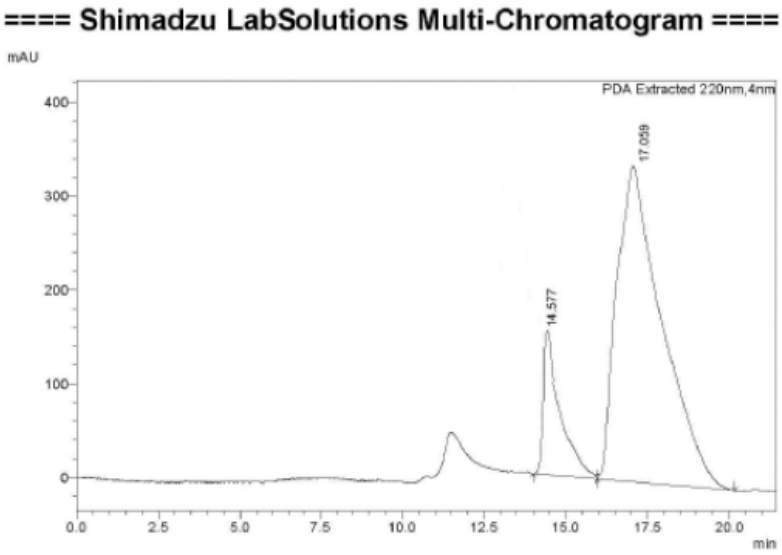
Peak #	Ret.Time	Area %
1	16.312	19.97
2	18.524	80.03
		60.06

(*R*)-4,4-Diphenyl-2-((phenylthio)methyl)-1-tosylpyrrolidine [(*R*)-10]



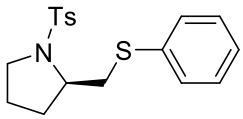
$[\alpha]^{20}_{D}$ = 69.8 (c = 0.5, $CHCl_3$)

HPLC analysis: Daicel Chiralcel OD column, hexane/*i*-PrOH = 92/8, 1 mL/min, 220 nm; t_R (*S*) = 14.58 min, t_R (*R*) = 17.05 min; 61% *ee* (absolute stereochemistry assigned in analogy to **(*R*)-12**).



Peak #	Ret.Time	Area %
1	14.577	19.31
2	17.059	80.69
		61.38

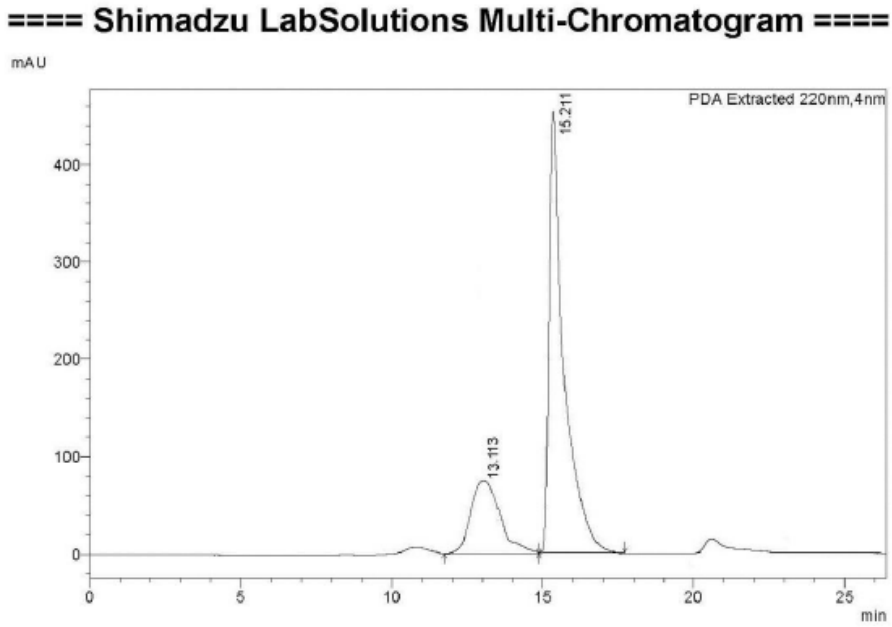
(*R*)-2-((Phenylthio)methyl)-1-tosylpyrrolidine [(*R*)-12]



$[\alpha]^{20}_{D}$ = 127.3 (c = 1, $CHCl_3$)

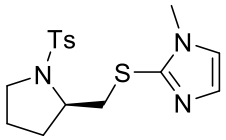
[Literature value: (*S*)-((phenylthio)methyl)-1-tosylpyrrolidine (85% *ee*): $[\alpha]^{24}_{D}$ = –228.7° (c = 1, $CHCl_3$)][10]

HPLC analysis: Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 0.8 mL/min, 220 nm; t_R (*S*) = 13.11 min, t_R (*R*) = 15.21 min; 55% *ee*.



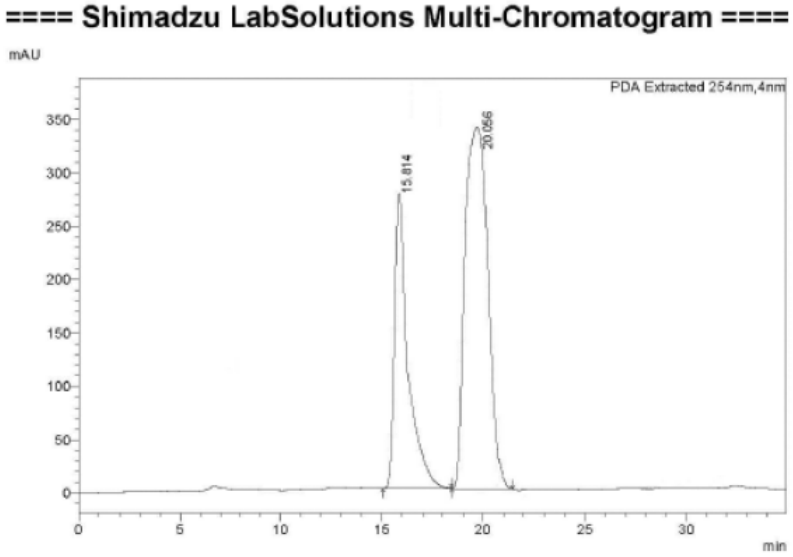
Peak #	Ret.Time	Area %
1	13.113	22.69
2	15.211	77.31
		54.62

(*R*)-1-Methyl-2-(((1-tosylpyrrolidin-2-yl)methyl)thio)-1*H*-imidazole [(*R*)-14]



$[\alpha]^{20}_{D}$ = 32.1 (c = 1, $CHCl_3$)

HPLC analysis: Daicel Chiralpak OD-H, hexane/*i*PrOH = 95:5, flow rate 1.0 mL/min, 254 nm: t_R (*S*) = 15.81, t_R (*R*) 20.05 min; 25% *ee* (absolute stereochemistry assigned in analogy to **(*R*)-12**).



Peak #	Ret.Time	Area %
1	15.814	37.57
2	20.056	62.43
		24.86

[1] M. T. Bovino, S. R. Chemler, *Angew. Chem. Int. Ed.* **2012**, *51*, 3923-3927.

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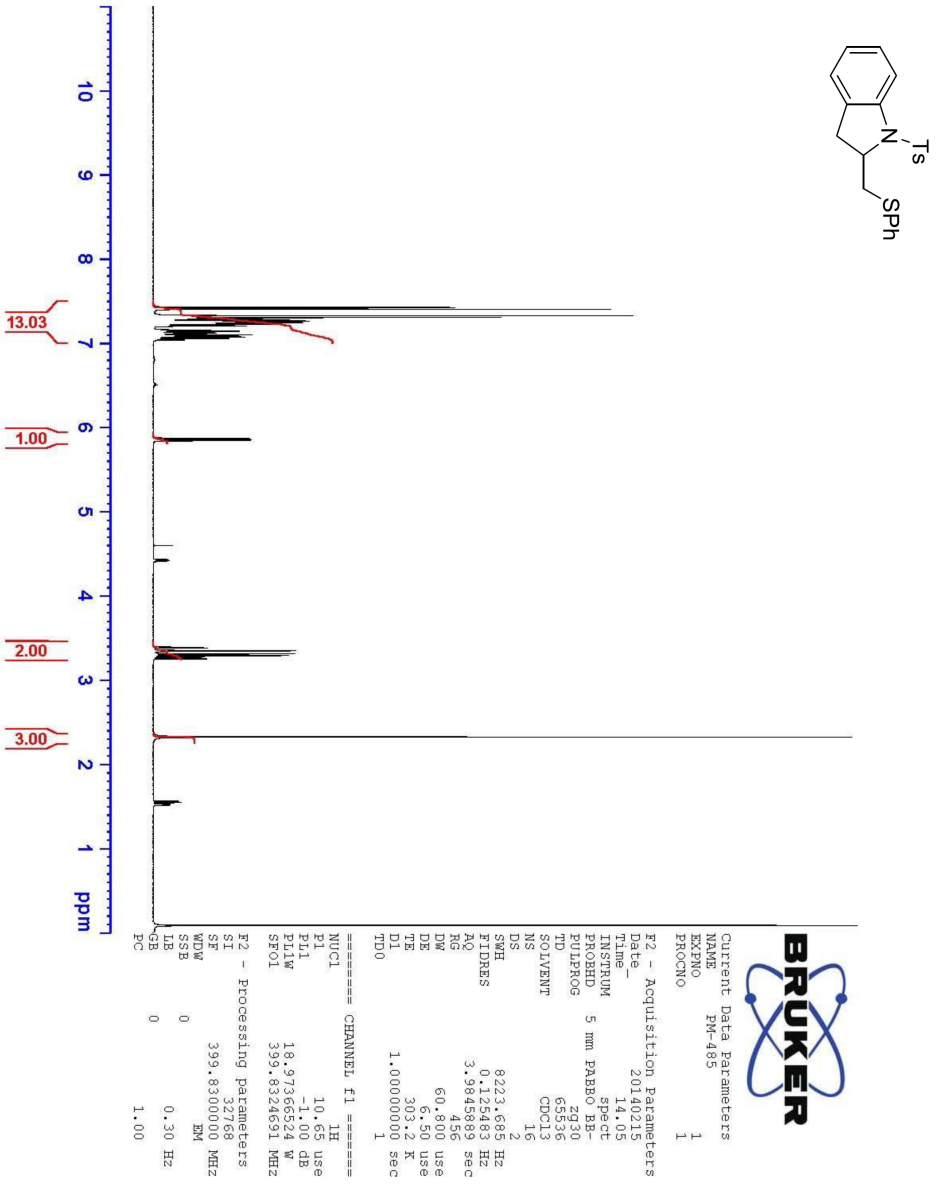
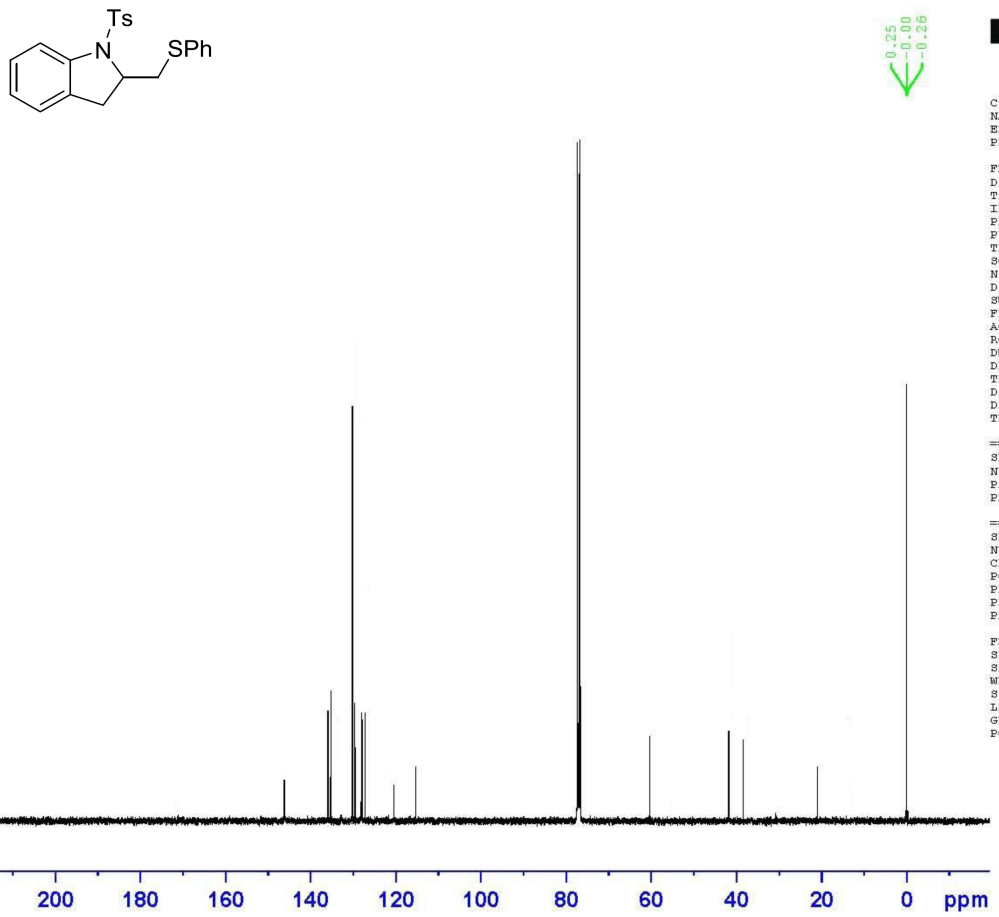
NMR spectra

2-((Phenylthio)methyl)-1-tosylindoline (2a)





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DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 199.98
DW 20.800 usec
DE 6.50 usec
TE 303.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

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NUC1 13C
P1 9.75 usec
PLW1 75.00000000 W

======== CHANNEL f2 ========
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NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 21.00000000 W
PLW12 0.22000000 W
PLW13 0.17010000 W

F2 - Processing parameters
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SSB 0
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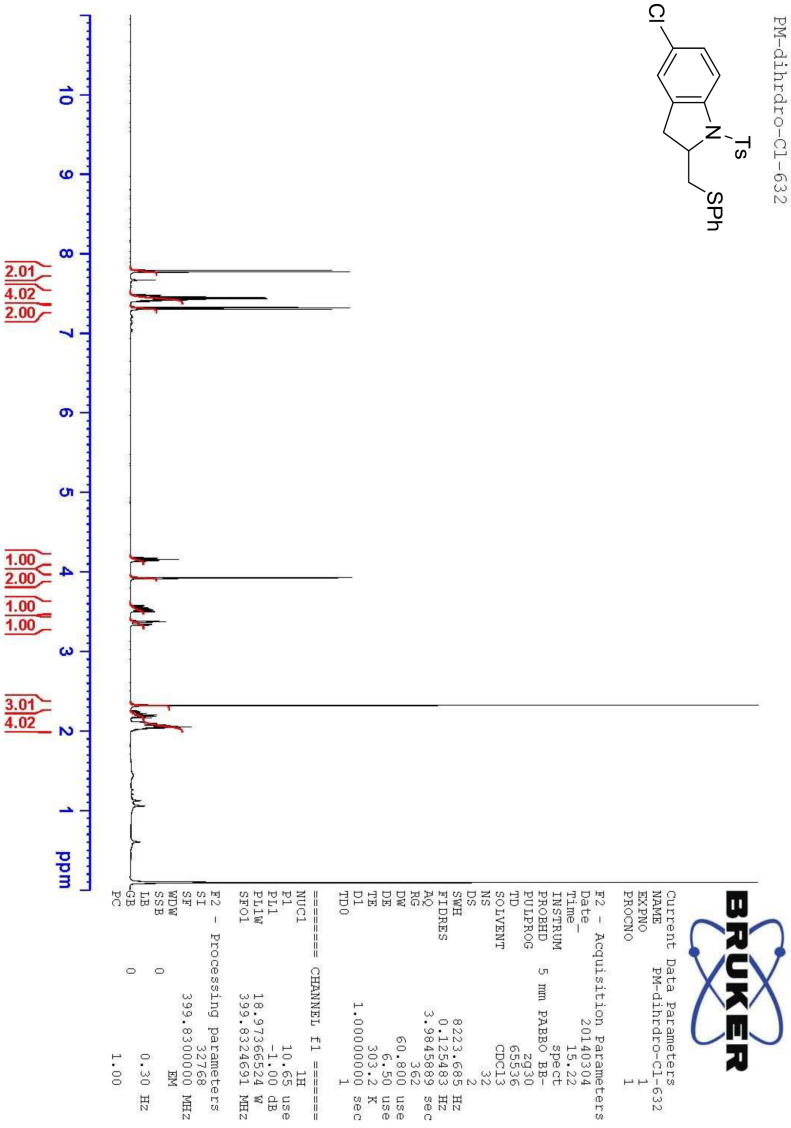
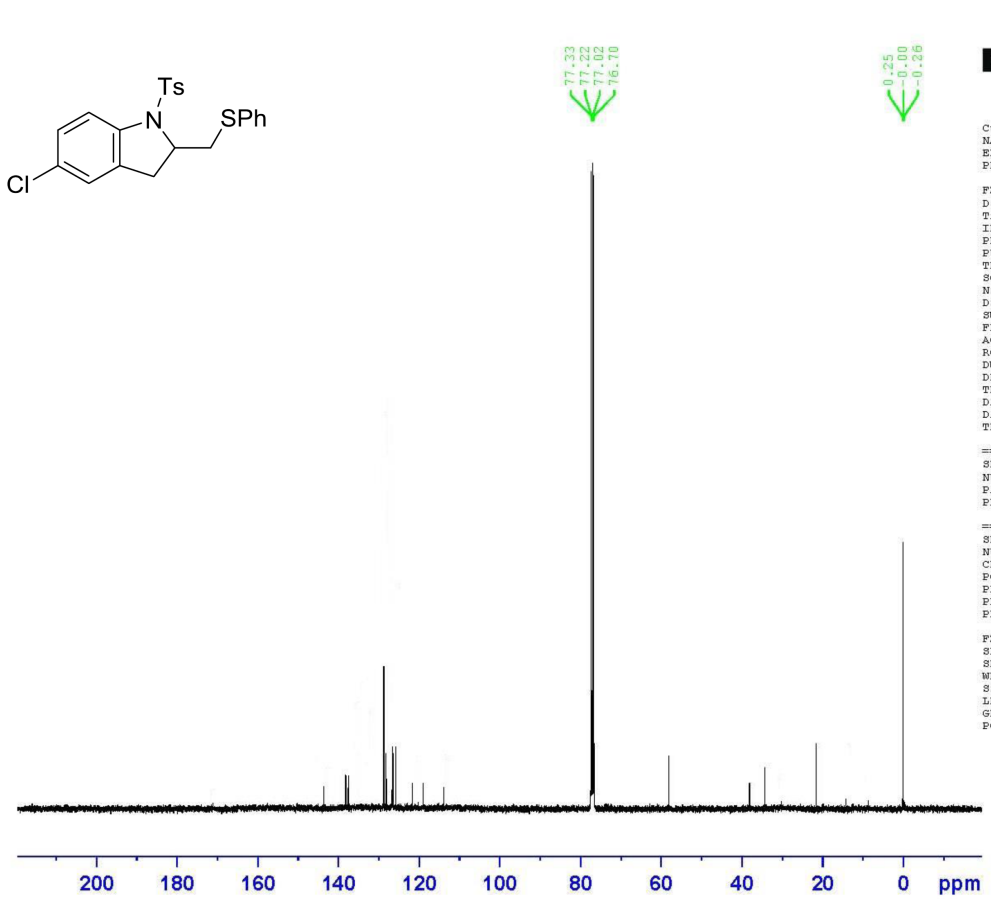
GB 0
PC 1.40

5-Chloro-2-((phenylthio)methyl)-1-tosylindoline (4)





BRUKER

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SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                199.98
DW                20.800 usec
DE                 6.50 usec
TE                303.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

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NUC1                 13C
P1                  9.75 usec
PLW1         75.00000000 W

======== CHANNEL f2 ========
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NUC2                 1H
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PCPD2              90.00 usec
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PLW13         0.17010000 W

F2 - Processing parameters
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SF           100.6127665 MHz
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GB        0
PC                 1.40
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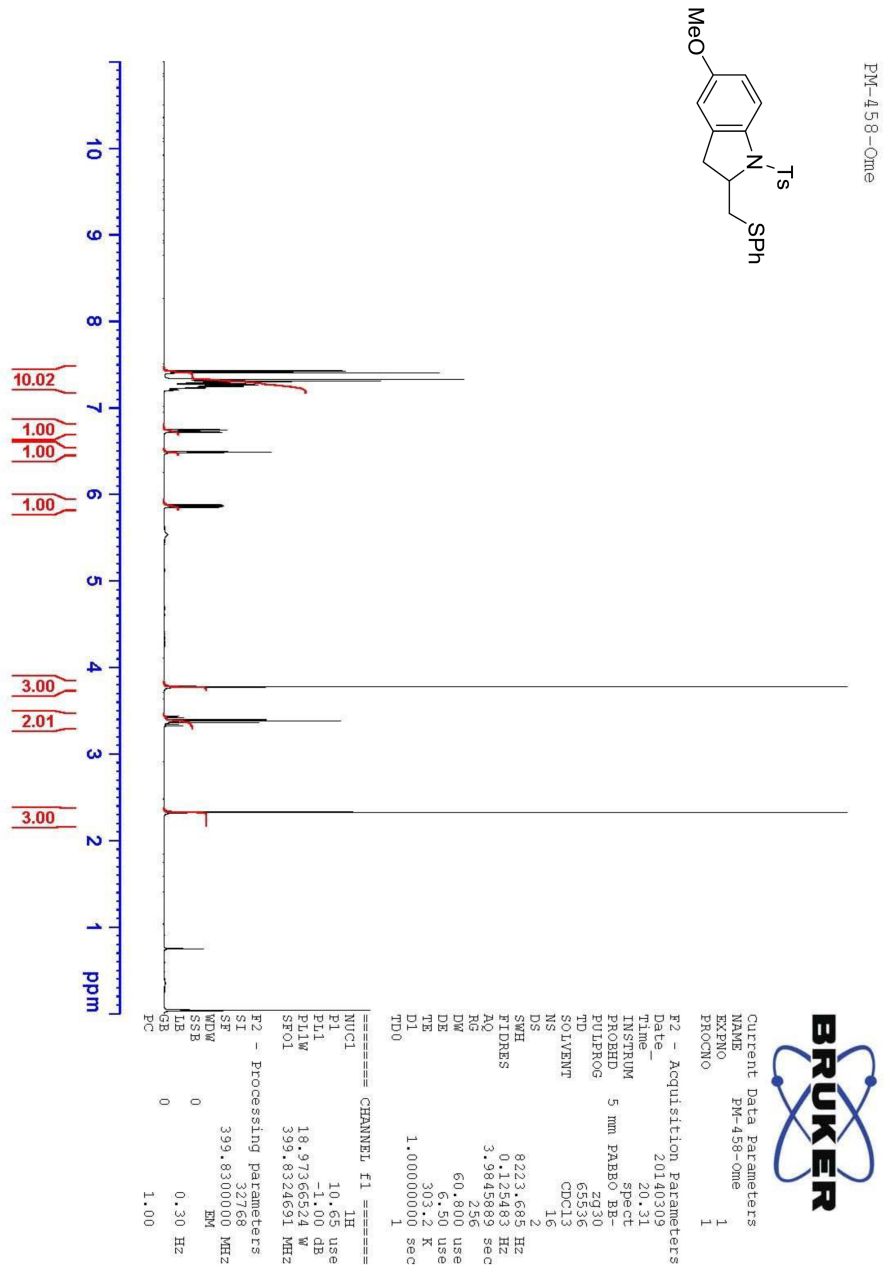
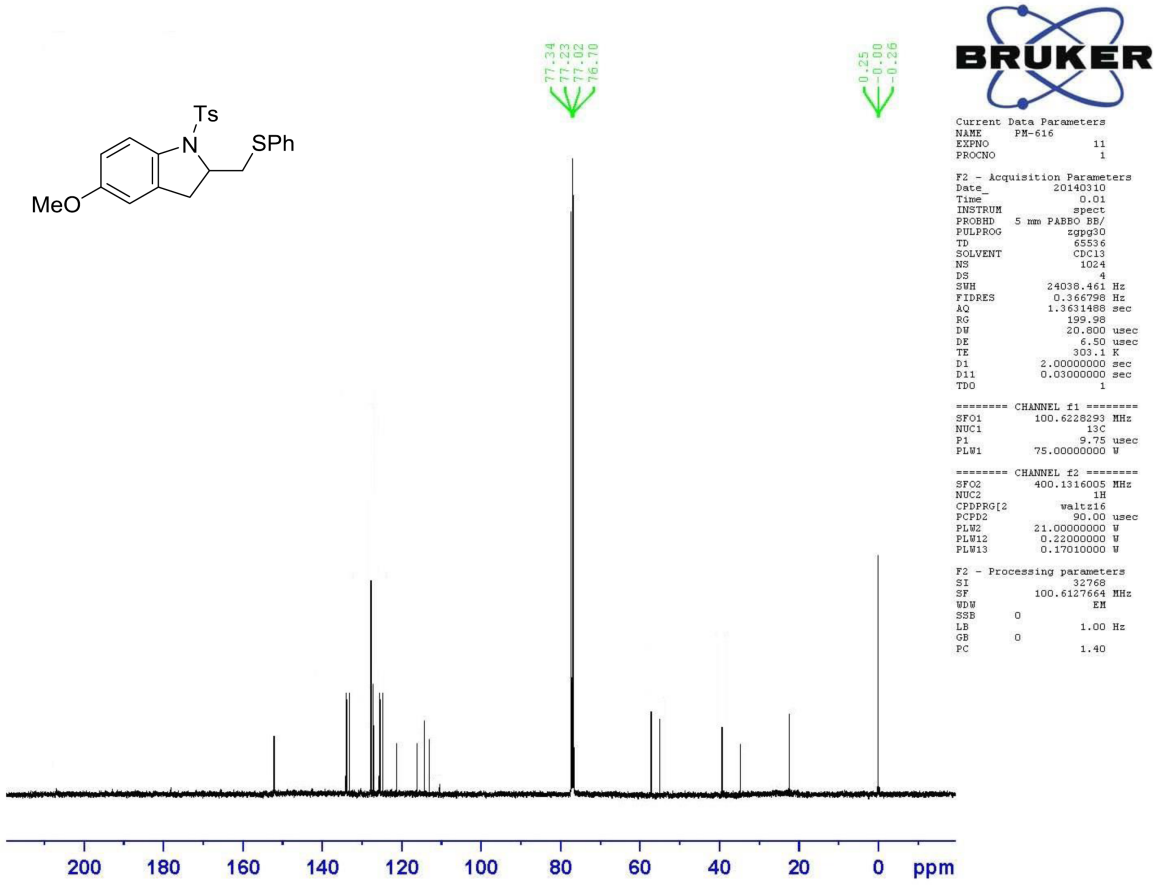
5-Methoxy-2-((phenylthio)methyl)-1-tosylindoline (6)





BRUKER

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FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG              199.98
DW             20.800 usec
DE              6.50 usec
TE              303.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                1

======== CHANNEL f1 ========
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NUC1              13C
P1               9.75 usec
PLW1       75.00000000 W

======== CHANNEL f2 ========
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NUC2              1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2       21.00000000 W
PLW12       0.22000000 W
PLW13       0.17010000 W

F2 - Processing parameters
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PC              1.40
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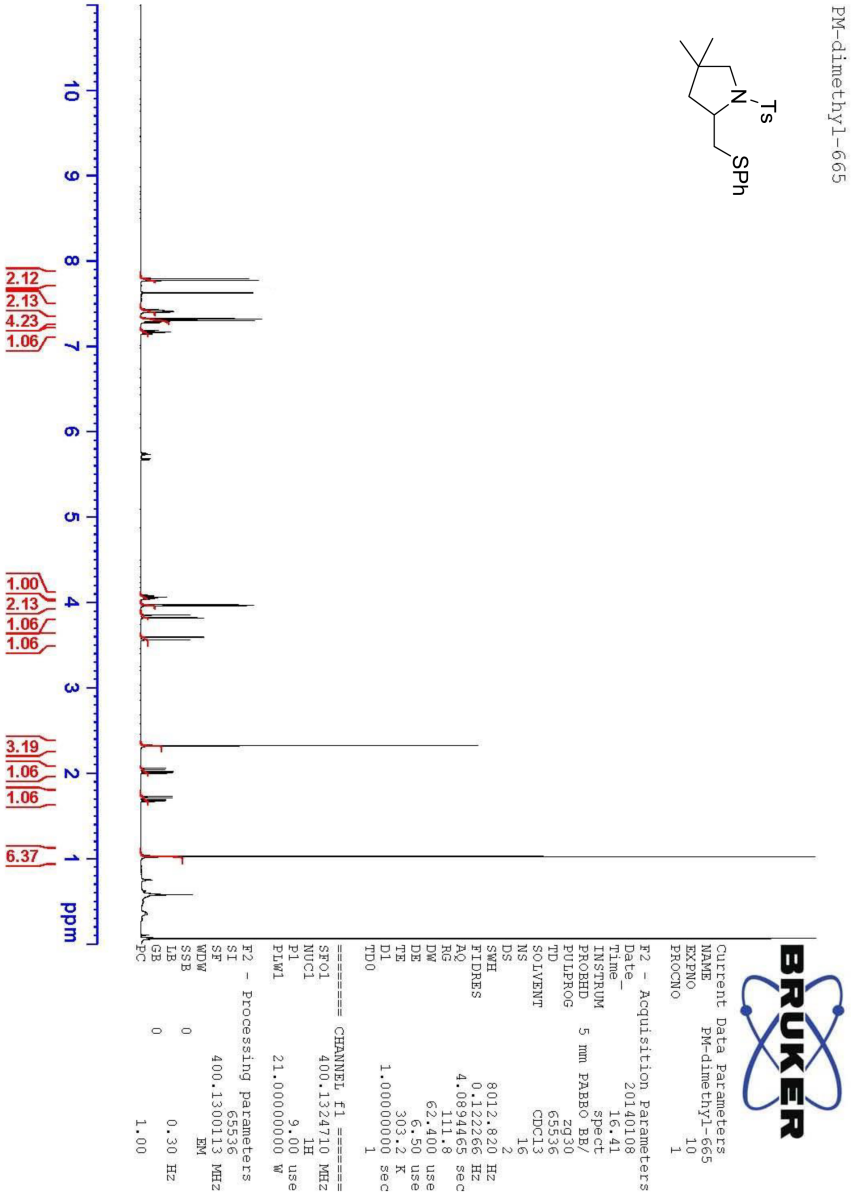
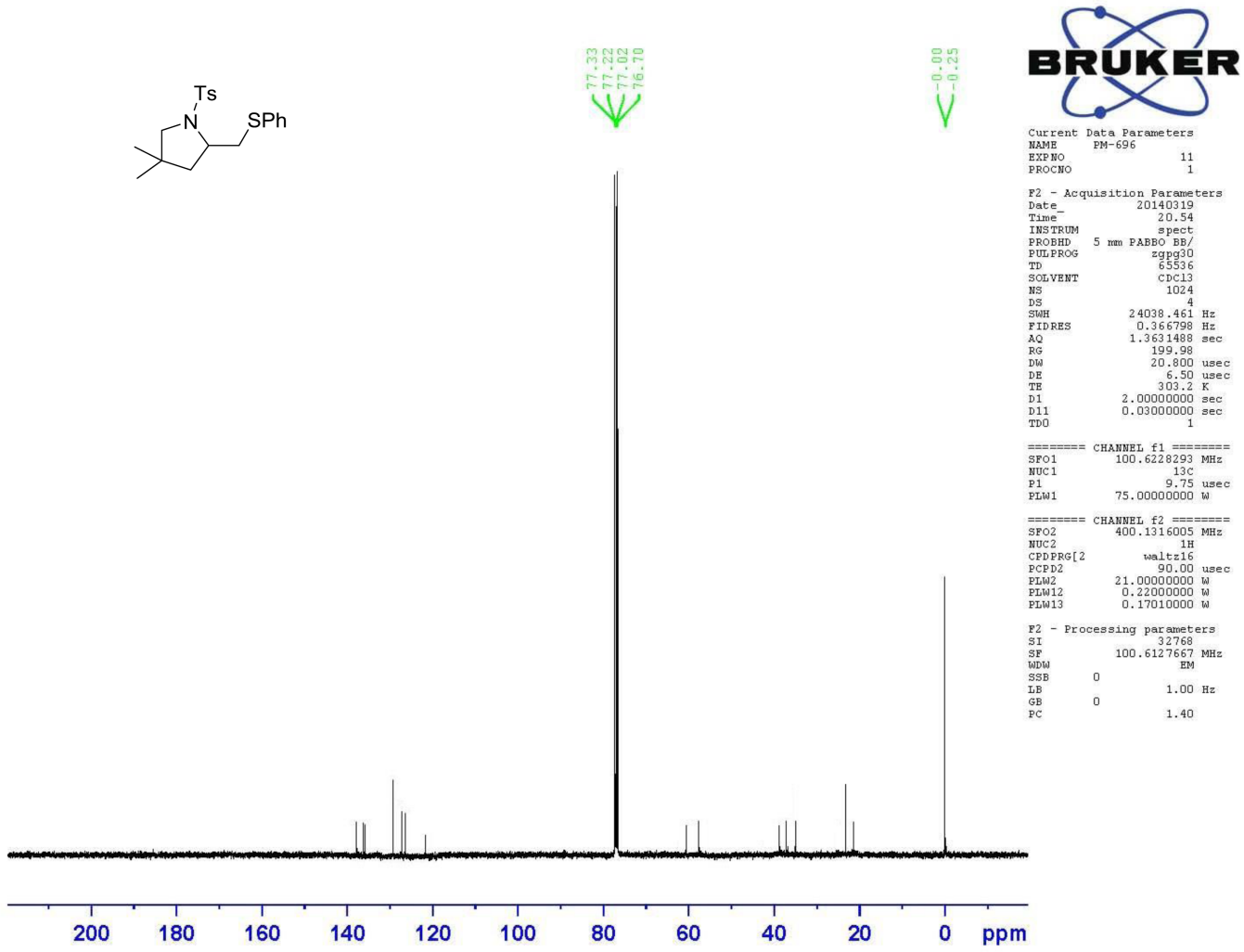
4,4-Dimethyl-2-((phenylthio)methyl)-1-tosylpyrrolidine (8)



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PROCNO             1

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RG              199.98
DW              20.800 usec
DE               6.50 usec
TE              303.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                1

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NUC1              13C
P1               9.75 usec
PLW1       75.00000000 W

======== CHANNEL f2 ========
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NUC2              1H
CPDPRG[2       waltz16
PCPD2            90.00 usec
PLW2       21.00000000 W
PLW12       0.22000000 W
PLW13       0.17010000 W

F2 - Processing parameters
SI                32768
SF         100.6127667 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
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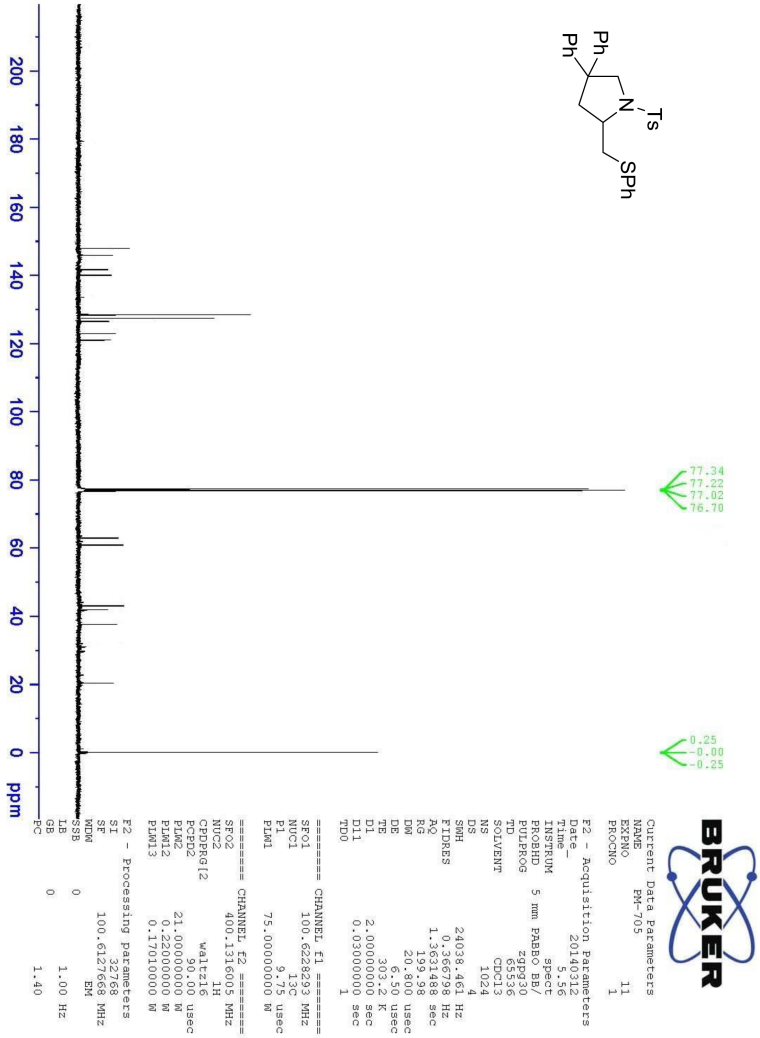
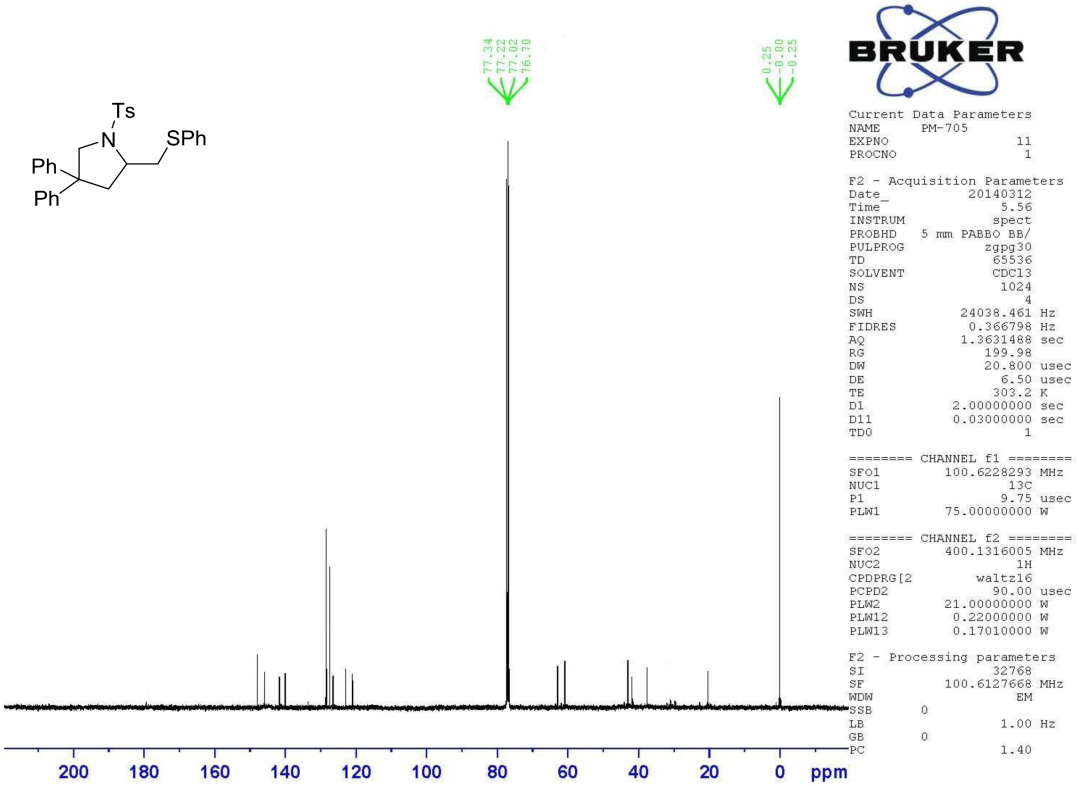
4,4-Diphenyl-2-((phenylthio)methyl)-1-tosylpyrrolidine (10)

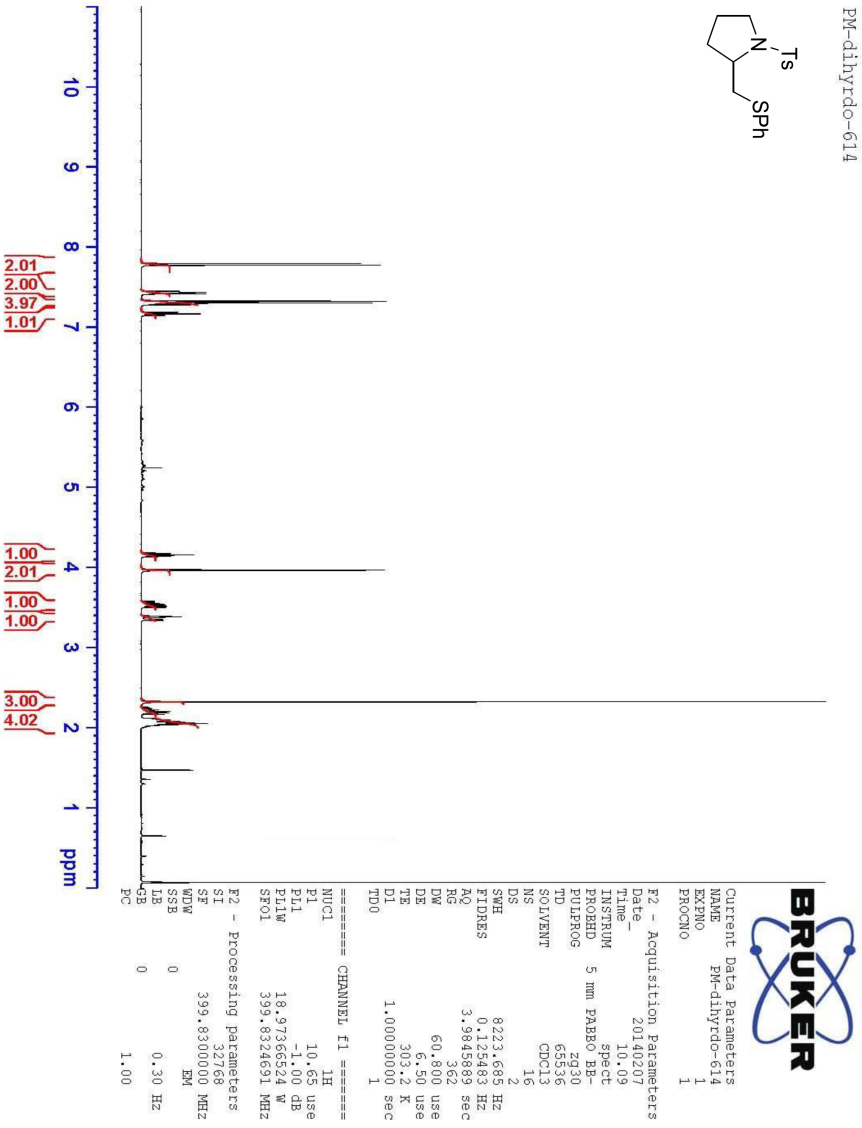


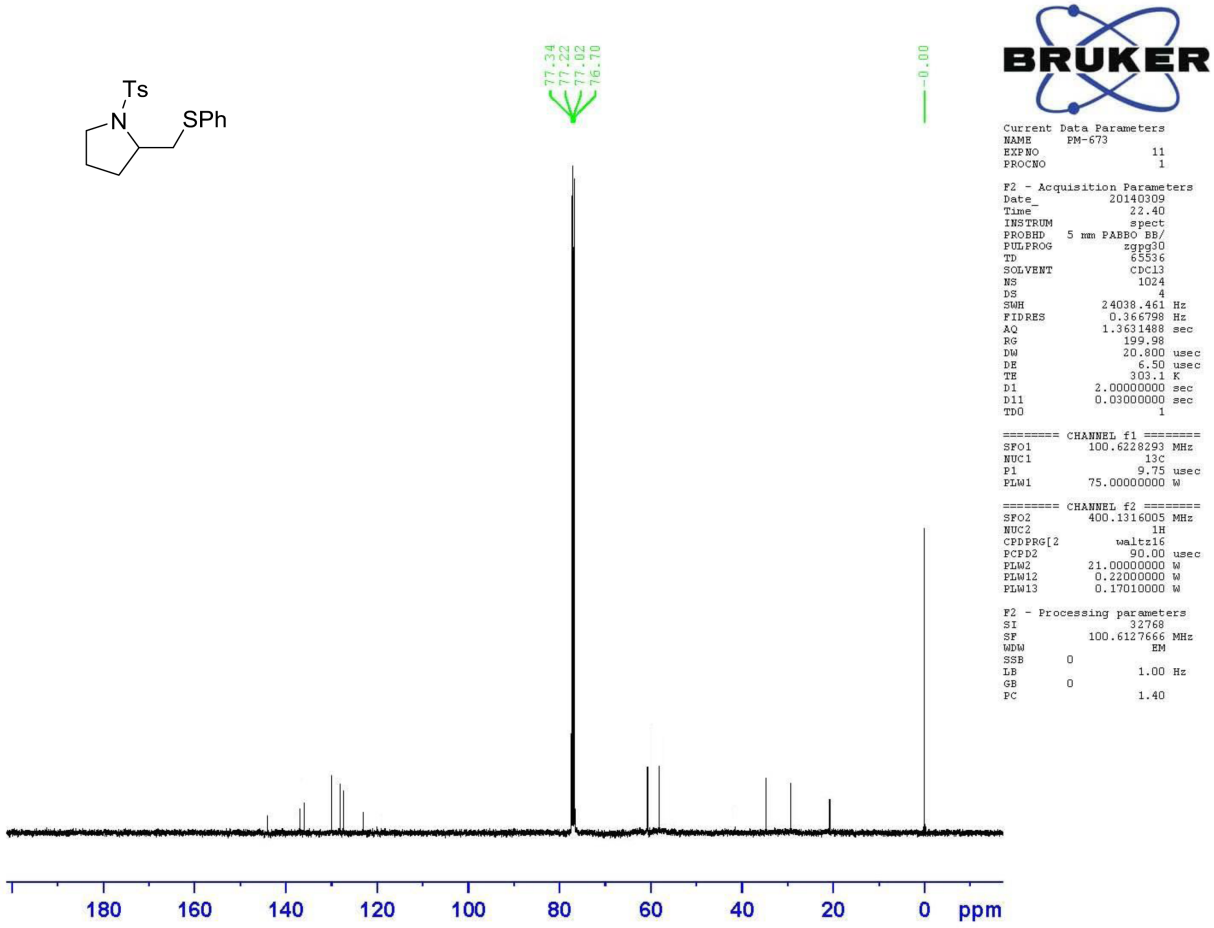


BRUKER

```
Current Data Parameters
NAME      PM-705
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140312
Time                5.56
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                199.98
DW                20.800 usec
DE                 6.50 usec
TE                303.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                 9.75 usec
PLW1         75.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         21.00000000 W
PLW12         0.22000000 W
PLW13         0.17010000 W

F2 - Processing parameters
SI                 32768
SF           100.6127668 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

2-((Phenylthio)methyl)-1-tosylpyrrolidine (12)

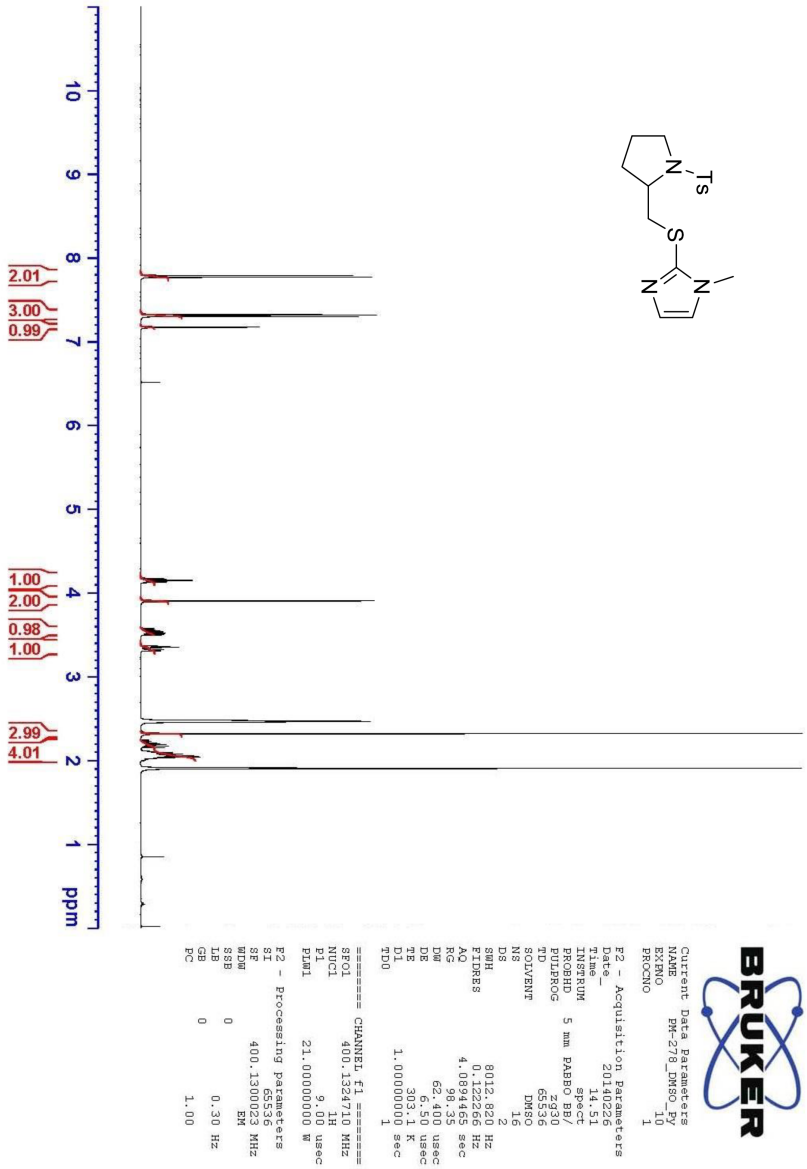


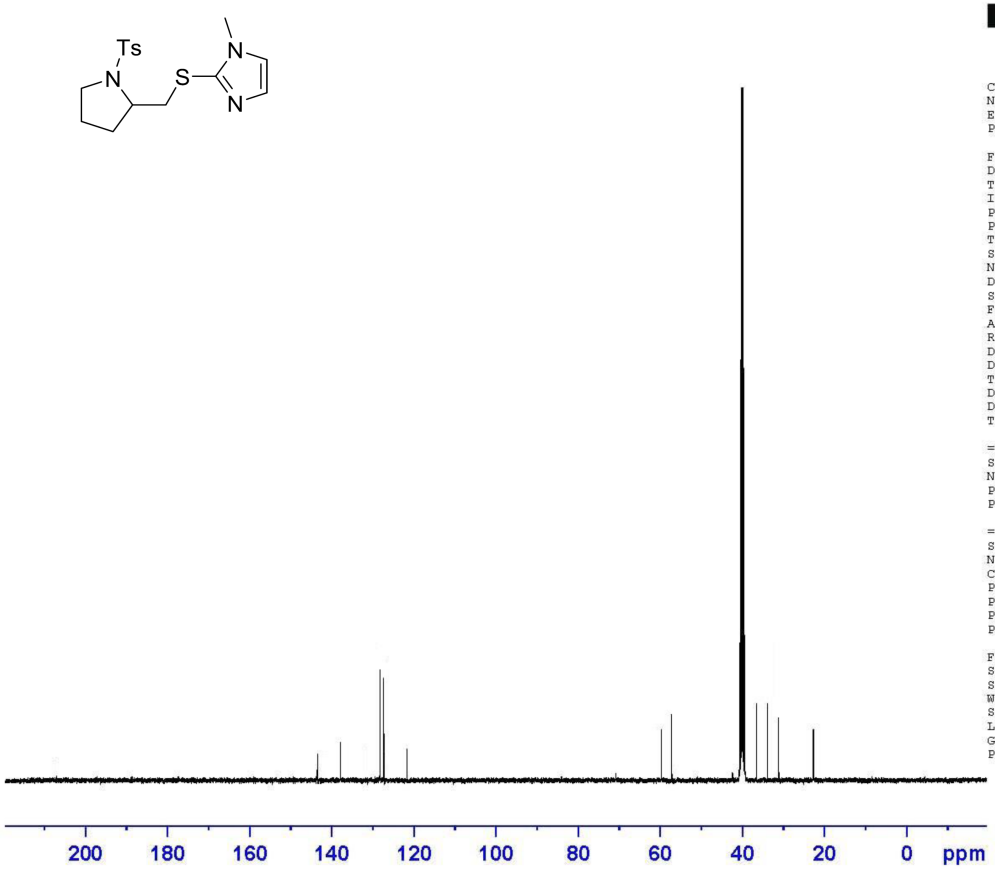


BRUKER

```
Current Data Parameters
NAME      PM-673
EXPNO              11
PROCNO              1

F2 - Acquisition Parameters
Date_        20140309
Time             22.40
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS               1024
DS                  4
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ           1.3631488 sec
RG              199.98
DW              20.800 usec
DE               6.50 usec
TE              303.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       100.6228293 MHz
NUC1              13c
P1               9.75 usec
PLW1       75.00000000 W

======== CHANNEL f2 ========
SFO2       400.1316005 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2       21.00000000 W
PLW12       0.22000000 W
PLW13       0.17010000 W

F2 - Processing parameters
SI               32768
SF         100.6127666 MHz
WDW                 EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

1-Methyl-2-(((1-tosylpyrrolidin-2-yl)methyl)thio)-1*H*-imidazole (14)





BRUKER

```
Current Data Parameters
NAME      PM-278_DMSO-
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20140306
Time              19.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                1024
DS                   4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               199.98
DW               20.800 usec
DE                6.50 usec
TE               303.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                9.75 usec
PLW1        75.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            90.00 usec
PLW2        21.00000000 W
PLW12        0.22000000 W
PLW13        0.17010000 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```