Supporting Information

TMSOTf mediated '*5/6-endo-dig*' Reductive Hydroamination for the Stereoselective Synthesis of Pyrrolidine and Piperidine derivatives

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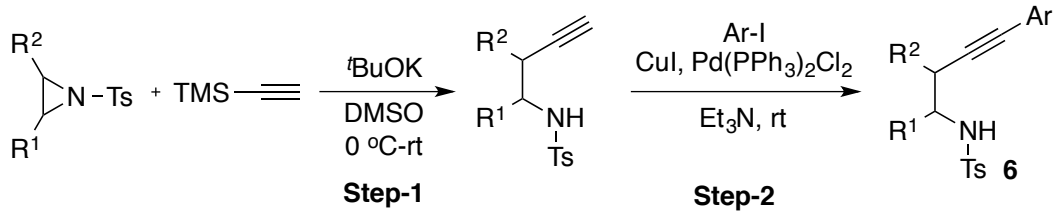
General experimental:

Melting points are recorded using sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.

High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{254} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane was prepared by refluxing over anhydrous P_2O_5 and distillation on to calcium hydride. $BF_3{\cdot}OEt_2$, $Cu(OTf)_2$, TMSOTf, TfOH, AgOTf were obtained from Aldrich. All other Lewis/Bronsted acids, phenyl acetylene are commercial reagents and were used as such without further purification. All other alkyne and alkynylamines were prepared using literature established protocol.

Experimental Procedure:

Genaral procedure for synthesis of alkynylamines 6:



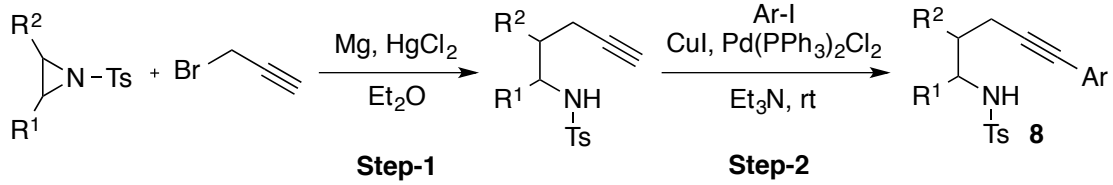
Step-1: aziridine ring opening

To a stirred solution of ^{t}BuOK (1.5 equiv) in DMSO (5 ml), TMS-acetylene (1.5 equiv) and aziridine (1 equiv) was added successively under nitrogen. Reaction was monitored by TLC, quenched with distill water (5 mL) at 0 ^{o}C upon completion and stirred extra for 5 minute. The resulting mixture was extracted with EtOAc (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (3:97) as eluent furnished corresponding terminal alkynylamine.

Step-2: Sonogashira

To stirred solution of terminal alkynylamine (1 equiv) and aryl iodie (1 equiv) in trimethyl amine (6 mL), $Pd(PPh_3)_2Cl_2$ (0.015 equiv) and CuI (0.02 equiv) was added under N_2 atmosphere. The reaction mixture was allowed to stir overnight, the reaction mixture was quenched with aqueous sat. NH_4Cl (5 mL) and prouduct was extracted with EtOAC (3 x 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished corresponding alkynylamine.

Genaral procedure for synthesis of alkynylamines 8:



Step-1: aziridine ring opening

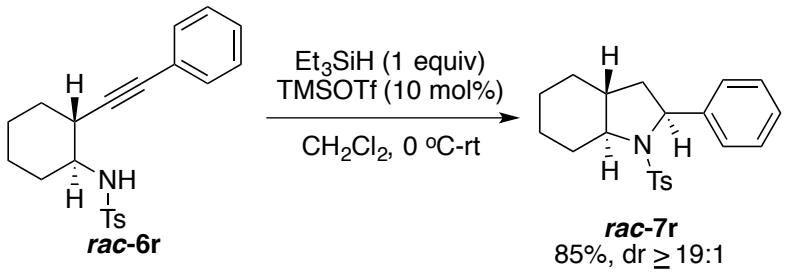
The stirred suspension of magnesium turnings (3 equiv) in dry Et_2O (20 mL) with mercury(II) chloride (0.01 equiv) and a pinch of I_2 was cooled to 0 °C. To the reaction mixture propargyl bromide (80 wt% in toluene) (2 equiv) was added drop wise. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred

for 1 h. Then to a solution of aziridine (1 equiv) in ether (10 mL), propargyl magnesium bromide in ether (prepared as above) was slowly added at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched at 0 °C with saturated aqueous NH_4Cl solution (30 mL) carefully as it is exothermic, extracted with Et_2O (3 × 30 mL). The combined extracts were washed with brine (30 mL), dried over anh. Na_2SO4 and concentrated, followed by purification on a silica gel column using ethyl acetate-petroleum ether (15:85) as eluent furnished the corresponding terminal alkynylamine.

Step-2: Sonogashira

To stirred solution of terminal alkynylamine (1 equiv) and aryl iodie (1 equiv) in trimethyl amine (6 ml), $Pd(PPh_3)_2Cl_2$ (0.015 equiv) and CuI (0.02 equiv) was added under N_2 atmosphere. The reaction mixture was allowed to stir overnight, the reaction mixture was quenched with aqueous sat. NH_4Cl (5 mL) and prouduct was extracted with EtOAC (3 x 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished corresponding alkynylamine.

Representative reductive hydroamination cascade on 1.6 mmol:



***rac*-6r** ***rac*-7r**

85%, dr ≥ 19:1

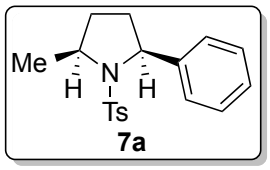
To a magnetically stirred solution of alkynylamine ***rac*-6r** (535 mg, 1.6 mmol) and Et_3SiH (255 μL, 1.6 mmol) in dry CH_2Cl_2 (15 ml), TMSOTf (30 μL mg, 0.16 mmol) was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion (14 hrs), extracted with CH_2Cl_2 (3 × 10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished pyrrolidine derivative ***rac*-7r** (461 mg, 85%).

General procedure of reductive hydroamination cascade for the streoeselective synthesis of pyrrolidines and piperidines:

(Note: In the cases where diastereomeric mixture of products was obtained, the isomers could not be separated and data for the major isomer is mentioned. In the cases where *ca.* 1:1 mixture of diastereomers was formed, all the peaks are mentioned. Wherever the diastereomers were separated by coloumn chromatography data of each diastereomer is given).

(*2S,5S*)-2-methyl-5-phenyl-1-tosylpyrrolidine (7a):[1]

To a magnetically stirred solution of alkynylamine **6a** (63 mg, 0.2 mmol) and Et_3SiH (35 μL, 0.2 mmol) in dry CH_2Cl_2 (3 mL), TMSOTf (4 μL mg, 0.02 mmol) was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion (24 hrs), extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished pyrrolidine derivative **7a** (52.6 mg, 83%).



7a

Physical appearance: white solid.

M.P: 112-114 ^oC.

R*f*: 0.2 (2:8 ethyl acetate-petroleum ether).

$[\alpha]_D^{25}$: -115.177 (c 0.31, $CHCl_3$).

IR (neat): 3020, 2970, 1599, 1493, 1337, 1156, 1092, 757, cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 4.74 (t, *J* = 6.5 Hz, 1H), 3.94 (sext, *J* = 6.0 Hz, 1H), 2.42 (s, 3H), 1.92-1.82 (m, 2H), 1.74-1.67 (m, 1H), 1.52-1.46 (m, 4H).

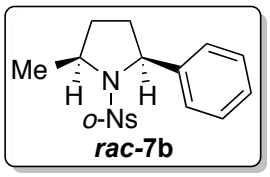
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 143.4 (C), 143.0 (C), 135. 3 (C), 129.7 (2 × CH), 128.4 (2 × CH), 127.7 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 65.0 (CH), 57.8 (CH), 34.5 (CH_2), 33.2 (CH_2), 22.8 (CH_3), 21.4 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{18}H_{21}NNaO_2S$ 338.1185, found 338.1182.

(2*S,5*S**)-2-methyl-1-((2-nitrophenyl)sulfonyl)-5-phenylpyrrolidine (*rac*-7b) and (2*S**,5*R**)-2-methyl-1-((2-nitrophenyl)sulfonyl)-5-phenylpyrrolidine (*rac*-7b'):**

Reaction of alkynylamine **6b** (86.1 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 14 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7b** (77 mg, 89%) as mixture of diastereomer (dr-2.3:1).

***Cis*-Major isomer**



Physical appearance: Pale yellow solid.

M.P: 124-126 ^oC.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

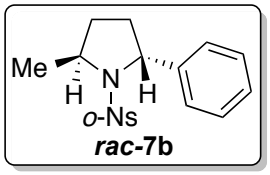
IR (neat): 3016, 2960, 1559, 1366, 1162, 754 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.63 (td, *J* = 7.6, 1.2 Hz, 1H), 7.57-7.50 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.96 (t, *J* = 6.4 Hz, 1H), 4.19 (sext, *J* = 6.4 Hz, 1H), 2.23-2.16 (m, 1H), 2.02-1.93 (m, 2H), 1.67-1.60 (m, 1H), 1.51 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 148.6 (C), 142.2 (2 × C), 133.7 (CH), 131.5 (CH), 131.2 (CH), 128.5 (2 × CH), 127.3 (CH), 126.4 (2 × CH), 123.8 (CH), 65.5 (CH), 58.1 (CH), 34.9 (CH_2), 32.5 (CH_2), 22.5 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{18}N_2NaO_4S$ 369.0879, found 369.0872.

***Trans*-Minor isomer**



Physical appearance: Sticky solid.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2922, 1547, 1374, 1164, 757 cm^{-1}.

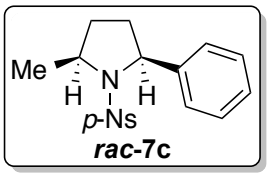
^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.08-7.02 (m, 3H), 6.98-6.93 (m, 3H), 5.00 (dd, *J* = 9.2, 2.0 Hz, 1H), 4.58 (quint, *J* = 6.2 Hz, 1H), 2.72-2.61 (m, 1H), 2.46-2.36 (m, 1H), 1.82 (dd, *J* = 12.8, 7.6 Hz, 1H), 1.69 (dd, *J* = 12.4, 7.0 Hz, 1H), 1.44 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 141.5 (C), 135.0 (C), 132.4 (CH), 131.2 (CH), 130.8 (CH), 128.2 (2 × CH), 127.4 (CH), 127.0 (2 × CH), 123.4 (CH), 63.0 (CH), 59.6 (CH), 34.9 (CH_2), 31.4 (CH_2), 20.0 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{18}N_2NaO_4S$ 369.0879, found 369.0875.

(2*S,5*S**)-2-methyl-1-((4-nitrophenyl)sulfonyl)-5-phenylpyrrolidine (*rac*-7c):**[2]

Reaction of alkynylamine **6c** (103 mg, 0.30 mmol), with Et_3SiH (48 μL, 0.30 mmol) and TMSOTf (5.5 μL, 0.03 mmol) in dry CH_2Cl_2 (3 mL) 23 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7c** (89.2 mg, 87%) as mixture of diastereomer (dr-4:1)



Physical appearance: Pale yellow solid.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

M.P: 158-160 ^oC.

IR (neat): 2984, 2969, 1523, 1351, 1164, 749 cm^{-1}.

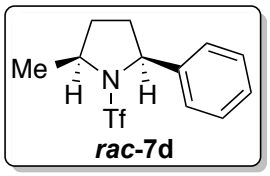
^1H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.26-7.22 (m, 5H), 4.78 (t, *J* = 6.8 Hz, 1H), 4.11 (sext, *J* = 6.0 Hz, 1H), 2.05 (sext, *J* = 6.5 Hz, 1H), 1.97-1.91 (m, 1H), 1.89-1.83 (m, 1H), 1.64-1.58 (m, 1H), 1.49 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 149.9 (C), 144.9 (C), 141.6 (C), 128.7 (2 × CH), 128.5 (2 × CH), 127.5 (2 × CH), 126.6 (2 × CH), 124.1 (2 × CH), 65.5 (CH), 58.2 (CH), 34.8 (CH_2), 32.3 (CH_2), 22.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{18}N_2NaO_4S$ 369.0879, found 369.0876.

(2*S,5*S**)-2-methyl-5-phenyl-1((trifluoromethyl)sulfonyl)pyrrolidine (*rac*-7d):**

Reaction of alkynylamine **6d** (81 mg, 0.26 mmol), with Et_3SiH (41 μL, 0.26 mmol) and TMSOTf (5 μL, 0.026 mmol) in dry CH_2Cl_2 (3 mL) 36 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl EtOAc-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7d** (67.2 mg, 81%) as mixture of diastereomer (dr-2.1:1).



Physical appearance: Pale yellow liquid.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3017, 2984, 1523, 1494, 1329, 1150, 755 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.38-7.33 (m, 3H), 7.23-7.21 (m, 2H), 5.11-5.07 (m, 1H), 4.49-4.43 (m, 1H), 2.57-2.49 (m, 1H), 2.42-2.34 (m, 1H), 1.89 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.71-1.66 (m, 1H), 1.45 (d, *J* = 6.5 Hz, 3H).

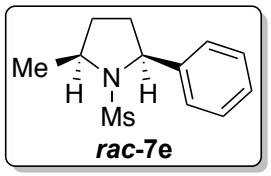
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 141.9 (C), 128.7 (2 × CH), 128.6 (2 × CH), 126.2 (CH), 119.9 (q, *J* = 322.5 Hz, C), 65.5 (CH), 59.2 (CH), 32.5 (2 × CH_2), 21.3 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{12}H_{14}F_3NNaO_2S$ 316.0595, found 316.0598.

(2*S,5*S**)-2-methyl-5-phenyl-1-(methylsulfonyl)-5-phenylpyrrolidine (*rac*-7e)**

Reaction of alkynylamine **6e** (60 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 26 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7e** (55.8 mg, 90%) as single diasteromer.

Physical appearance: Pale yellow solid.



rac-7e

M.P: 87-89 ^oC.

R$_f$: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3017, 2984, 1523, 1494, 1329, 1150, 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 7.28-7.24 (m, 1H), 4.86 (t, *J* = 6.8 Hz, 1H), 4.16 (sext, *J* = 6.4 Hz, 1H), 2.68 (s, 3H), 2.36-2.28 (m, 1H), 2.14-2.07 (m, 1H), 2.05-1.96 (m, 1H), 1.72-1.64 (m, 1H), 1.47 (d, *J* = 6.4 Hz, 3H).

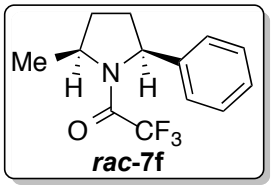
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 142.5 (C), 128.7 (2 × CH), 127.5 (CH), 126.6 (2 × CH), 64.9 (CH), 57.5 (CH), 39.2 (CH_3), 35.1 (CH_2), 32.6 (CH_2), 22.5 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{12}H_{17}NNaO_2S$ 262.0872, found 262.0877.

2,2,2-trifluoro-1-((2*S,5*S**)-2-methyl-5-phenylpyrrolidin-1-yl)ethan-1-one (*rac*-7f)**

Reaction of alkynylamine **6f** (73 mg, 0.286 mmol), with Et_3SiH (45 μL, 0.286 mmol) and TMSOTf (5 μL, 0.028 mmol) in dry CH_2Cl_2 (3 mL) 36 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7f** (26.6 mg, 36%) as mixture of diastereomer (dr-1.8:1).

Physical appearance: Pale yellow liquid.



rac-7f

R$_f$: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3017, 2984, 1523, 1494, 1329, 1150, 755 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.28 (m, 3H), 7.05 (d, *J*

= 7.5 Hz, 2H), 5.33 (d, *J* = 8.0 Hz, 1H), 4.61-4.45 (m, 1H), 2.58-2.50 (m, 1H), 2.13-2.05 (m, 1H), 1.87 (dd, *J* = 12.5, 6.5 Hz, 1H), 1.57-1.53 (m, 1H), 1.35 (d, *J* = 6.5 Hz, 3H).

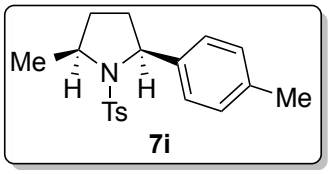
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 156.4 (C), 143.3 (C), 128.8 (2 × CH), 127.3 (CH), 124.9 (2 × CH), 116.1 (q, *J* = 286.2 Hz, C), 62.5 (CH), 56.7 (CH), 33.9 (CH_2), 27.3 (CH_2), 18.55 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{13}H_{14}F_3NNaO$ 280.0925, found 280.0929.

(*2S,5S*)-2-methyl-5-(*p*-tolyl)-1-tosylpyrrolidine (7i):

Reaction of alkynylamine **6i** (82 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 16 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7i** (73.2 mg, 89%) as single diasteromer.

Physical appearance: white solid.



7i

M.P: 68-70 ^oC.

R_f: 0.2 (2:8 ethyl acetate-petroleum ether).

IR (neat): 2926, 1711, 1682, 1611, 1576, 1510, 1207, 1018 cm^{-1}.

[α]$_D$ ^{25}: -112.421 (c 0.26, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.67 (t, *J* = 6.4 Hz, 1H), 3.92 (sext, *J* = 6.4 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.88-1.82 (m, 2H), 1.70 (dq, *J* = 12.4, 7.2 Hz, 1H), 1.51-1.43 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 143.3 (C), 140.0 (C), 136.6 (C), 135.3 (C), 129.6 (2 × CH), 129.1 (2 × CH), 127.7 (2 × CH), 126.3 (2 × CH), 64.9 (CH), 57.9 (CH), 34.5 (CH_2), 33.2 (CH_2), 22.9 (CH_3), 21.6 (CH_3), 21.1 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{19}H_{23}NNaO_2S$ 352.1342, found 352.1348.

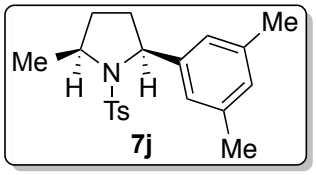
(*2S,5S*)-2-(3,5-dimethylphenyl)-5-methyl-1-tosylpyrrolidine (7j):

Reaction of alkynylamine **6j** (85.5 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 15 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7j** (70 mg, 83%) as single diasteromer.

Physical appearance: Pale yellow solid.

M.P: 108-110 ^{o}C.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).



7j

IR (neat): 3018, 2969, 2876, 1601, 1459, 1160, 756 cm^{-1}.

$[\alpha]_D$ ^{25}: -107.537 (c 0.315, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 6.85 (s, 1H), 4.66 (t, *J* = 6.4 Hz, 1H), 3.93 (sext, *J* = 6.4 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 6H), 1.89-1.80 (m, 2H), 1.70 (dq, *J* = 12.4, 7.2 Hz, 1H), 1.53-147 (m, 4H).

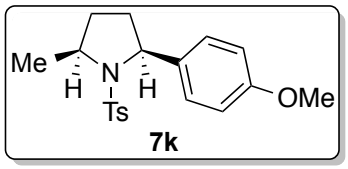
^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 143.2 (C), 142.8 (C), 137.8 (2 × C), 135.5 (C), 129.5 (2 × CH), 128.8 (CH), 127.7 (2 × CH), 124.2 (2 × CH), 65.1 (CH), 57.9 (CH), 34.7 (CH_2), 32.2 (CH_2), 22.8 (CH_3), 21.6 (CH_3), 21.5 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{20}H_{25}NNaO_2S$ 366.1498, found 366.1492.

(*2S,5S*)-2-(4-methoxyphenyl)-5-methyl-1-tosylpyrrolidine (7k):[3]

Reaction of alkynylamine **6k** (85 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 14 hrs as described for the THF-derivative **8a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7k** (41.5 mg, 48%) as single diasteromer.

Physical appearance: Pale yellow solid.



7k

M.P: 72-74 ^{o}C.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2962, 1613, 1587, 1515, 1352, 1083, 997 cm^{-1}.

$[\alpha]_D$ ^{25}: -110.196 (c 0.115, $CHCl_3$).

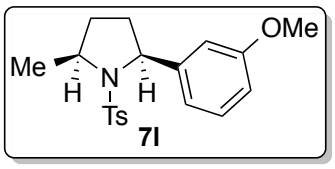
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.66 (t, *J* = 6.0 Hz, 1H), 3.92 (sext, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 1.84 (q, *J* = 7.0 Hz, 2H), 1.73-1.66 (m, 1H), 1.52-1.46 (m, 1H), 1.45 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 158.7 (C), 143.3 (C), 135.4 (C), 135.0 (C), 129.6 (2 × CH), 127.7 (2 × CH), 127.5 (2 × CH), 113.8 (2 × CH), 64.6 (CH), 57.9 (CH), 55.4 (CH_3), 34.4 (CH_2), 32.2 (CH_2), 23.0 (CH_3), 21.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{19}H_{23}NNaO_3S$ 368.1296, found 368.1291.

(2*S*,5*S*)-2-(3-methoxyphenyl)-5-methyl-1-tosylpyrrolidine (7l):

Reaction of alkynylamine **6l** (57.8 mg, 0.18 mmol), with Et_3SiH (30 μL, 0.18 mmol) and TMSOTf (3 μL, 0.018 mmol) in dry CH_2Cl_2 (3 mL) 24 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7l** (48 mg, 83%) as single diasteromer.



7l

Physical appearance: Pale yellow solid.

M.P: 70-72 ^oC.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2905, 1618, 1603, 1587, 1354, 1078, 995 cm^{-1}.

$[\alpha]_D$ ^{25}: -116.211 (c 0.150, $CHCl_3$).

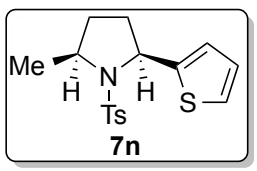
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.96-6.91 (m, 2H), 6.76 (dd, *J* = 2.4, 8.0 Hz, 1H), 4.71 (t, *J* = 6.4 Hz, 1H), 3.92 (sext, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 1.88-1.83 (m, 2H), 1.74-1.66 (m, 1H), 1.52-1.46 (m, 1H), 1.46 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 159.7 (C), 144.7 (C), 143.4 (C), 135.4 (C), 129.6 (2 × CH), 129.4 (CH), 127.4 (2 × CH), 118.7 (CH), 112.3 (CH), 112.2 (CH), 64.9 (CH), 57.9 (CH), 55.2 (CH_3), 34.5 (CH_2), 32.3 (CH_2), 22.8 (CH_3), 21.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{19}H_{23}NNaO_3S$ 368.1296, found 368.1299.

(*2S,5S*)-2-methyl-5-(thiophen-2-yl)-1-tosylpyrrolidine (7n):

Reaction of alkynylamine **6n** (89 mg, 0.28 mmol), with Et_3SiH (45 μL, 0.28 mmol) and TMSOTf (5 μL, 0.028 mmol) in dry CH_2Cl_2 (3 mL) 14 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7n** (67 mg, 75%) as single diasteromer.



7n

Physical appearance: Pale yellow solid.

M.P: 108-110 ^oC.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

$[\alpha]_D$ ^{25}: -100.565 (c 0.34, $CHCl_3$).

IR (neat): 2971, 1598, 1445, 1345, 1161, 1094, 1038, 818 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 1H), 6.97 (d, *J* = 3.0 Hz, 1H), 6.92 (d, *J* = 4.5 Hz, 1H), 5.07 (dd, *J*

= 7.5, 3.5 Hz, 1H), 3.80 (sext, *J* = 6.5 Hz, 1H), 1.97-1.91 (m, 1H), 1.87-1.81 (m, 1H), 1.79-1.72 (m, 1H), 1.66-1.59 (m, 1H), 1.43 (d, *J* = 6.5 Hz, 3H).

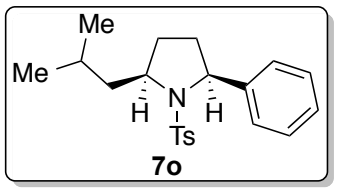
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.9 (C), 143.5 (C), 135.4 (C), 129.7 (2 × CH), 127.7 (2 × CH), 126.9 (CH), 124.4 (CH), 124.3 (CH), 60.9 (CH), 57.9 (CH), 34.4 (CH_2), 32.8 (CH_2), 22.9 (CH_3), 21.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{19}NNaO_2S_2$ 344.0755, found 344.0751.

(*2R,5S*)-2-isobutyl-5-phenyl-1-tosylpyrrolidine (7o):

Reaction of alkynylamine **6o** (88.3 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 24 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7o** (72 mg, 81%) as single diasteromer.

Physical appearance: Pale yellow solid.



7o

M.P: 102-104 ^oC.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

$[\alpha]_D$ ^{25}: -90.042 (c 0.195, $CHCl_3$).

IR (neat): 3028, 2958, 2870, 1600, 1451, 1161, 1093, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.33-7.28 (m, 4H), 7.23 (t, *J* = 7.2 Hz, 1H), 4.73 (t, *J* = 6.8 Hz, 1H), 3.88-3.82 (m, 1H), 1.94-1.82 (m, 3H), 1.71-1.57 (m, 2H), 1.52-1.43 (m, 2H), 0.97 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.4 (C), 143.1 (C), 135.3 (C), 129.7 (2 × CH), 128.4 (2 × CH), 127.8 (2 × CH), 127.0 (CH), 126.3 (2 × CH), 64.6 (CH), 60.7 (CH), 45.9 (CH_2), 34.5 (CH_2), 30.25 (CH_2), 25.7 (CH_2), 23.7 (CH_3), 22.0 (CH_3), 21.6 (CH_3).

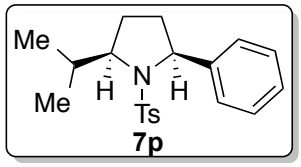
HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{21}H_{27}NNaO_2S$ 380.1655, found 380.1655.

(*2R,5S*)-2-isopropyl-5-phenyl-1-tosylpyrrolidine (7p):

Reaction of alkynylamine **6p** (85 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 36 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7p** (66.2 mg, 76%) as single diasteromer.

Physical appearance: Pale yellow solid.

M.P: 76-78 ^{o}C.



7p

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2960, 1600, 1495, 1346, 1161, 815 cm^{-1}.

[α]$_D$ ^{25}: -116.374 (c 0.20, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (d, *J* = 8.0 Hz, 2H), 7.4 (d, *J* = 6.8 Hz, 2H), 7.33-7.28 (m, 4H), 7.23 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.63 (t, *J* = 7.6 Hz, 1H), 3.63 (td, *J* = 7.6, 3.6 Hz, 1H), 2.43 (s, 3H), 2.04-1.82 (m, 3H), 1.74-1.60 (m, 1H) 1.42-1.34 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).

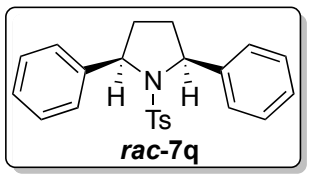
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.5 (C), 142.8 (C), 134.9 (C), 129.7 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 127.0 (CH), 126.4 (2 × CH), 68.3 (CH), 64.9 (CH), 33.9 (CH_2), 32.0 (CH), 26.7 (CH_2), 21.6 (CH_3), 20.7 (CH_3), 18.5 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{20}H_{25}NNaO_2S$ 366.1498, found 366.1494.

(2*R,5*S**)-2,5-diphenyl-1-tosylpyrrolidine (*rac*-7q):**

Reaction of alkynylamine 6**q** (92 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 24 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7q** (73.2 mg, 80%) as single diasteromer.

Physical appearance: Pale yellow solid.



***rac*-7q**

M.P: 102-104 ^{o}C.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3018, 2923, 1624, 1600, 1451, 1349, 1161, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.92 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.07-2.01 (m, 4H).

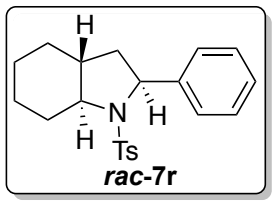
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.5 (C), 142.2 (2 × C), 135.1 (C), 129.5 (2 × CH), 128.4 (2 × CH), 127.9 (4 × CH), 127.3 (2 × CH), 127.1 (4 × CH), 65.4 (2 × CH), 34.1 (2 × CH_2), 21.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{23}H_{23}NNaO_2S$ 400.1342, found 400.1343.

(2*R,3a*S**,7a*R**)-2-phenyl-1-tosyloctahydro-1*H*-indole (*rac*-7r):**

Reaction of alkynylamine **6r** (89.2 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 12 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7r** (70 mg, 78%) as single diasteromer.

Physical appearance: Pale yellow solid.



rac-7r

R*f*: 0.2 (1:9 ethyl acetate-petroleum ether).

M.P: 141-143 ^oC.

IR (neat): 3017, 2929, 2878, 1600, 1451, 1346, 1160, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.34-7.30 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 8.8 Hz, 1H), 2.69-2.58 (m, 2H), 2.44 (s, 3H), 1.88-1.83 (m, 1H), 1.74-1.64 (m, 4H), 1.59-1.47 (m, 2H), 1.35-1.21 (m, 1H), 1.16 (tt, *J* = 13.2, 3.6 Hz, 1H), 0.99 (qd, *J* = 12.0, 3.6 Hz, 1H).

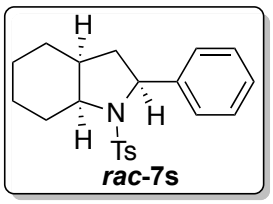
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 144.1 (C), 143.5 (C), 134.5 (C), 129.6 (2 × CH), 128.2 (2 × CH), 127.9 (2 × CH), 126.9 (CH), 126.4 (2 × CH), 67.1 (CH), 63.5 (CH), 42.5 (CH), 39.5 (CH_2), 32.6 (CH_2), 29.6 (CH_2), 25.4 (CH_2), 24.8 (CH_2), 21.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{21}H_{25}NNaO_2S$ 378.1498, found 378.1496.

(2*R,3a*R**,7a*R**)-2-phenyl-1-tosyloctahydro-1*H*-indole (*rac*-7s):**[3]

Reaction of alkynylamine **6s** (98.2 mg, 0.275 mmol), with Et_3SiH (44 μL, 0.275 mmol) and TMSOTf (5 μL, 0.027 mmol) in dry CH_2Cl_2 (3 mL) 12 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7s** (87.1 mg, 87%) as single diasteromer.

Physical appearance: Pale yellow solid.



rac-7s

M.P: 97-99 ^oC.

R*f*: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2935, 1601, 1455, 1344, 1161, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33-7.24 (m, 4H), 7.23 (t, *J* = 7.2 Hz, 1H), 4.60 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.86 (dt, *J* = 12.0, 6.4 Hz, 2H), 2.42 (s, 3H), 2.11-2.04 (m, 2H), 1.93 (td, *J* = 13.2, 10.0 Hz, 1H),

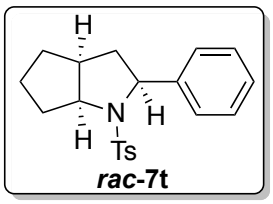
1.84-1.77 (m, 1H), 1.74-1.68 (m, 1H), 1.62-1.46 (m, 3H), 1.43-1.39 (m, 1H), 1.29-1.15 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.4 (C), 143.2 (C), 135.7 (C), 129.6 (2 × CH), 128.4 (2 × CH), 127.6 (2 × CH), 127.0 (CH), 126.2 (2 × CH), 64.4 (CH), 61.1 (CH), 39.1 (CH_2), 37.1 (CH), 31.0 (CH_2), 26.0 (CH_2), 24.4 (CH_2), 21.6 (CH_3), 20.5 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{21}H_{25}NNaO_2S$ 378.1498, found 378.1497.

(2*R,3a*R**,6a*R**)-2-phenyl-1-tosyloctahydrocyclopenta[*b*]pyrrole (*rac*-7t):**[3]

Reaction of alkynylamine **6t** (47.4 mg, 0.14 mmol), with Et_3SiH (22 μL, 0.14 mmol) and TMSOTf (3 μL, 0.014 mmol) in dry CH_2Cl_2 (3 mL) 12 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7t** (40.1 mg, 82%) as single diasteromer.



rac-7t

Physical appearance: Pale yellow solid.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

M.P: 116-118 ^oC.

IR (neat): 3017, 2959, 1600, 1495, 1350, 1164, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.28-7.21 (m, 5H), 4.38 (dd, *J* = 9.2, 7.2 Hz, 1H), 4.19 (dt, *J* = 8.0, 3.6 Hz, 2H), 2.52-2.43 (m, 1H), 2.41 (s, 3H), 2.27-2.20 (m, 1H), 2.16-2.10 (m, 1H), 2.00-1.90 (m, 1H), 1.83-1.74 (m, 1H), 1.69-1.52 (m, 2H), 1.40-1.35 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.3 (C), 142.0 (C), 134.7 (C), 129.5 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 127.2 (CH), 126.7 (2 × CH), 67.2 (CH), 66.6 (CH), 43.0 (CH_2), 41.6 (CH), 35.1 (CH_2), 31.4 (CH_2), 24.1 (CH_2), 21.6 (CH_3),

HRMS (ESI, M+Na^+): m/z calcd. for $C_{20}H_{23}NNaO_2S$ 364.1342, found 364.1347.

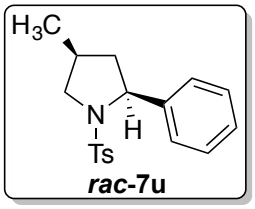
(*2S,*4S**)-4-methyl-2-phenyl-1-tosylpyrrolidine (7u):**[4]

Reaction of alkynylamine **6u** (78.3 mg, 0.25 mmol), with Et_3SiH (40 μL, 0.25 mmol) and TMSOTf (5 μL, 0.025 mmol) in dry CH_2Cl_2 (3 mL) 12 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7u** (71 mg, 91%, dr-9:1).

Physical appearance: Pale yellow solid.

M.P: 99-101 ^oC.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).



rac-7u

IR (neat): 3016, 2960, 1599, 1346, 1162, 754 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.31-7.22 (m, 7H), 4.64 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.83 (dd, *J* = 11.0, 7.5 Hz, 1H), 3.09 (t, *J* = 10.5 Hz, 1H), 2.41-2.31 (m, 4H), 1.87-1.78 (m, 1H), 1.51-1.44 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 3H).

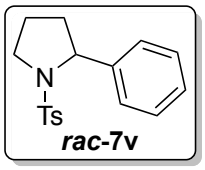
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 143.3 (C), 143.1 (C), 135.6 (C), 129.6 (2 × CH), 128.4 (2 × CH), 127.5 (2 × CH), 127.2 (CH), 126.4 (2 × CH), 64.7 (CH), 56.8 (CH_2), 45.7 (CH_2), 33.5 (CH), 21.6 (CH_3), 16.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{18}H_{21}NNaO_2S$ 338.1185, found 338.1183.

2-phenyl-1-tosylpyrrolidine (*rac*-7v):[4]

Reaction of alkynylamine **6v** (58 mg, 0.194 mmol), with Et_3SiH (31 μL, 0.194 mmol) and TMSOTf (3.5 μL, 0.0194 mmol) in dry CH_2Cl_2 (3 mL) 18 hrs as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7v** (54 mg, 90%).

Physical appearance: White solid.



rac-7v

M.P: 103-105 °C.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2961, 1600, 1344, 1160, 1098, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 6H), 7.24-7.21 (m, 1H), 4.78 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.65-3.59 (m, 2H), 3.44-3.38 (m, 1H), 2.42 (s, 3H), 2.00-1.93 (m, 1H), 1.90-1.77 (m, 1H), 1.69-1.61 (m, 1H).

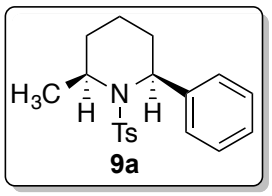
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.4 (C), 143.16 (C), 135.2 (C), 129.7 (2 × CH), 128.4 (2 × CH), 127.6 (2 × CH), 127.1 (CH), 126.2 (2 × CH), 63.4 (CH), 49.5 (CH_2), 35.9 (CH_2), 24.1 (CH_2), 21.6 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{29}NNaO_2S$ 324.1029, found 324.1017.

(*2S,6S*)-2-methyl-6-phenyl-1-tosylpiperidine (9a):

To a magnetically stirred solution of alkynylamine **8a** (70 mg, 0.214 mmol) and Et_3SiH (68 μL, 0.428 mmol) in dry CH_2Cl_2 (3 ml), TMSOTf (38 μL, 0.214 mmol) was added at 0 °C. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion (18 hrs), extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of

the residue over a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9a** (56 mg, 80 %, dr-7:1).



9a

Physical appearance: yellow solid.

M.P.: 121-125 ^{o}C.

R_f: 0.7 (0.5:9.5, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -45.15 (c 0.26, $CHCl_3$)

IR (neat): 2942, 2716, 1464, 1329, 1139, 986, 970, 790, 766, 568 cm^{-1}.

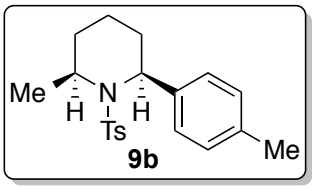
^{1}H NMR (500, MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.36-7.31 (m, 4H), 7.24 (t, *J* = 8.0 Hz, 1H), 5.28 (d, *J* = 5.0 Hz, 1H), 4.27-4.20 (m, 1H), 2.44 (s, 3H), 2.35-2.32 (m, 1H), 1.80-1.70 (m, 1H), 1.44-1.36 (m, 2H), 1.28-1.25 (m, 2H), 0.82 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 143.0 (C), 141.4 (C), 138.8 (C), 129.9 (2 × CH), 128.2 (2 × CH), 127.4 (2 × CH), 127.0 (2 × CH), 126.8 (CH), 52.9 (CH), 49.2 (CH), 29.0 (CH_2), 25.0 (CH_2), 21.7 (CH_3), 21.4 (CH_3), 14.4 (CH_2).

HRMS (ESI, M+K^+): m/z calc for $C_{19}H_{23}NKO_2S$ 368.1084, found 368.1081.

(*2S,6S*)-2-methyl-6-(p-tolyl)-1-tosylpiperidine (9b):

Reaction of alkynylamine **8b** (65 mg, 0.205 mmol) with Et_3SiH (65 μL, 0.410 mmol) and TMSOTf (37 μL, 0.205 mmol) in dry CH_2Cl_2 (3 ml) 6 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9b** (40 mg, 62 %, dr-9:1).



9b

Physical appearance: yellow solid.

R_f: 0.6 (0.5:9.5, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -4.8 (c 0.11, $CHCl_3$)

IR (neat): 2943, 1598, 1461, 1329, 1164, 1107, 992, 925, 822, 752, 661, 547 cm^{-1}.

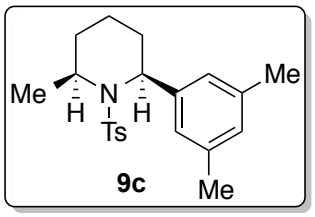
^{1}H NMR (400, MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 5.2 Hz, 1H), 4.26-4.20 (m, 1H), 2.44 (s, 3H), 2.34-2.29 (m, 4H), 1.80-1.70 (m, 1H), 1.44-1.33 (m, 2H), 1.28-1.24 (m, 2H), 0.84 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100, MHz, $CDCl_3$, DEPT): δ 143.0 (C), 139.0 (C),138.4 (C), 136.4 (C), 129.9 (2 × CH), 129.0 (2 × CH), 127.3 (2 × CH), 127.0 (2 × CH), 52.8 (CH), 49.2 (CH), 29.1 (CH_2), 25.1 (CH_2), 21.7 (CH_3), 21.5 (CH_3), 21.1 (CH_3), 14.4 (CH_2).

HRMS (ESI, M+Na^+): m/z calc for $C_{20}H_{25}NNaO_2S$ 366.1498, found 366.1498.

(*2S,6S*)-2-(3,5-dimethylphenyl)-6-methyl-1-tosylpiperidine (9c):

Reaction of alkynylamine **8c** (65 mg, 0.182 mmol) with Et_3SiH (58 μL, 0.356 mmol) and TMSOTf (33 μL, 0.182 mmol) in dry CH_2Cl_2 (3 ml) 6 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9c** (45 mg, 70 %, dr-7:1).



Physical appearance: yellow solid.

M.P.: 177-179 ^oC

R_f: 0.4 (1:9, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -38.04 (c 0.255, $CHCl_3$)

IR (neat): 2936, 1465, 1327, 1161, 1141, 990, 971, 865, 679, 577 cm^{-1}.

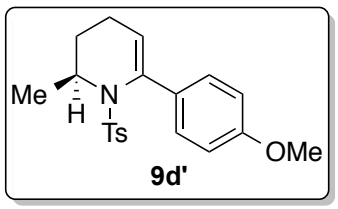
^{1}H NMR (500, MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 2H), 6.87 (s, 1H), 5.20 (d, *J* = 4 Hz, 1H), 4.27-4.24 (m, 1H), 2.44 (s, 3H), 2.31-2.28 (m, 7H), 1.80-1.71 (m, 1H), 1.43-1.34 (m, 2H), 1.29-1.24 (m, 2H), 0.86 (d, *J* = 8 Hz, 3H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 142.9 (C), 141.4 (C), 139.0 (C), 137.6 (2 × C), 129.8 (2 × CH), 128.4 (CH), 127.0 (2 × CH), 125.2 (2 × CH), 53.0 (CH), 49.3 (CH), 29.1 (CH_2), 25.2 (CH_2), 21.6 (2 × CH_3), 21.5 (2 × CH_3), 14.6 (CH_2).

HRMS (ESI, M+Na^+): m/z calc for $C_{21}H_{27}NNaO_2S$ 380.1657, found 380.1655.

(*S*)-6-(4-methoxyphenyl)-2-methyl-1-tosyl-1,2,3,4-tetrahydropyridine (9d'):

Reaction of alkynylamine **8d** (116 mg, 0.324 mmol) with Et_3SiH (105 μL, 0.648 mmol) and TMSOTf (60 μL, 0.324 mmol) in dry CH_2Cl_2 (3 ml) at 0 ^oC 0.5 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the cyclic enamine derivative **9d'** (75 mg, 62 %).



Physical appearance: yellow solid.

M.P.: 120-123 ^oC

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: 46.66 (c 0.27, $CHCl_3$)

IR (neat): 2926, 1610, 1512, 1461, 1337, 1251, 1161, 925, 759, 663, 552 cm^{-1}.

^{1}H NMR (400, MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.0 Hz, 2H), 5.41 (t, *J* = 4.0 Hz, 1H), 4.49-

4.42 (m, 1H), 3.81 (s, 3H), 2.41 (s, 3H), 2.13-2.02 (m, 1H), 1.89-1.81 (m, 1H), 1.34-1.27 (m, 2H), 1.24 (d, J = 6.8 Hz, 3H).

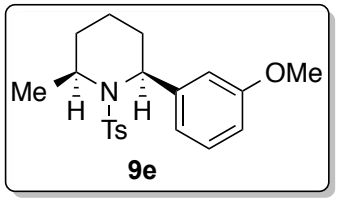
^{13}C NMR (100, MHz, $CDCl_3$, DEPT): δ 159.2 (C), 143.3 (C), 136.5 (C), 136.0 (C), 133.5 (C), 129.5 (2 × CH), 127.9 (2 × CH), 127.7 (2 × CH), 118.3 (CH), 113.3 (2 × CH), 55.4 (CH_3), 50.2 (CH) 24.9 (CH_2), 21.7 (CH_3), 19.5 (CH_2), 17.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calc for $C_{20}H_{23}NNaO_3S$ 380.1292 found 380.1291.

(*2S,6S*)-2-(3,5-dimethylphenyl)-6-methyl-1-tosylpiperidine (9e):

Reaction of alkynylamine **8e** (65 mg, 0.182 mmol) with Et_3SiH (58 μL, 0.356 mmol) and TMSOTf (33 μL, 0.182 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate- petroleum ether (4:96) as eluent furnished the piperidine derivative **9e** (32 mg, 59 %, dr-1.3:1).

Physical appearance: sticky solid.



9e

R$_f$: 0.4 (1:9, EtOAc: Petroleum ether).

IR (neat): 2936, 1465, 1327, 1161, 1141, 990, 971, 865, 679, 577 cm^{-1}.

[α]$_D$ ^{25}: 0.860 (c 0.300, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 7.16-7.10 (m, 2H), 6.70 (dd, J = 2.4, 8.0 Hz, 1H), 5.24 (d, J = 4.8 Hz, 1H), 4.25-4.21 (m, 1H), 3.85 (s, 3H), 2.44 (s, 3H), 2.31-2.27 (m, 1H), 2.18-2.21 (m, 1H), 1.99-1.92 (m, 1H), 1.76-1.62 (m, 3H), 1.38 (d, J = 7.0 Hz, 3H), 1.28-1.25 (m, 1H).

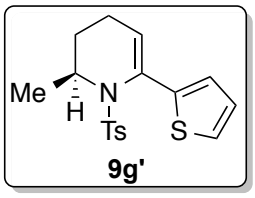
^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 159.7 (C), 143.3 (C), 143.0 (C), 141.3 (C), 129.9 (2 × CH), 129.2 (CH), 126.9 (2 × CH), 119.6 (CH), 113.4 (CH), 112.3 (CH), 58.0 (CH), 55.3 (CH_3), 49.3 (CH), 29.1 (CH_2), 25.2 (CH_2), 21.4 (CH_3), 19.2 (CH_3), 14.4 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calc for $C_{20}H_{25}NNaO_3S$ 382.1453, found 382.1458.

(*S*)-2-methyl-6-(thiophen-2-yl)-1-tosyl-1,2,3,4-tetrahydropyridine (9g'):

Reaction of alkynylamine **8g** (80 mg, 0.240 mmol) with Et_3SiH (76 μL, 0.480 mmol) and TMSOTf (43 μL, 0.240 mmol) in dry CH_2Cl_2 (3 ml) at 0 ^{o}C 0.5 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9g'** (37 mg, 46 %).

Physical appearance: White solid.



9g'

M.P.: 116-119 ^{o}C

R_f: 0.7 (1:9, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: 93.233 (c 0.23, $CHCl_3$)

IR (neat): 3077, 2943, 1638, 1458, 1346, 1166, 982, 759, 569 cm^{-1}.

^{1}H NMR (400, MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.05 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.93 (dd *J* = 5.2, 3.6 Hz, 1H), 5.67 (t, *J* = 4.0 Hz, 1H), 4.42-4.37 (m, 1H), 2.42 (s, 3H), 2.15-2.04 (m, 1H), 1.90-1.82 (m, 1H), 1.47-1.38 (m, 1H), 1.36-1.30 (m, 1H), 1.21 (d, *J* = 4.0 Hz, 3H).

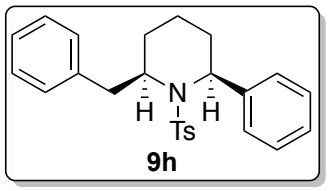
^{13}C NMR (100, MHz, $CDCl_3$, DEPT): δ 144.1 (C), 143.6 (C), 136.4 (C), 130.5 (C), 129.6 (2 × CH), 127.8 (2 × CH), 126.7 (CH), 124.5 (CH), 124.3 (CH), 120.1 (CH), 50.4 (CH), 24.9 (CH_2), 21.7 (CH_3), 19.5 (CH_2), 17.8 (CH_3).

HRMS (ESI, M+K^+): m/z calc for $C_{17}H_{19}NKO_2S_2$ 372.0490, found 372.0489.

(*2R,6S*)-2-benzyl-6-phenyl-1-tosylpiperidine (9h)

Reaction of alkynylamine **8h** (65 mg, 0.161 mmol) with Et_3SiH (51 μL, 0.322 mmol) and TMSOTf (29 μL, 0.161 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9h** (40 mg, 62 %, dr-3:1).

Physical appearance: white solid.



9h

M.P.: 163-165 ^{o}C

R_f: 0.7 (1:9, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: 66.05 (c 0.285, $CHCl_3$)

IR (neat): 3026, 2944, 1453, 1328, 1162, 934, 762, 548 cm^{-1}.

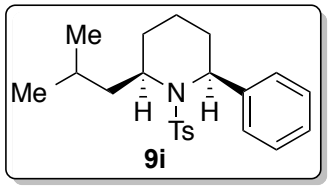
^{1}H NMR (500, MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31-7.27 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 2H) 7.14 (t, *J* = 7.5 Hz, 1H), 7.0 (d, *J* = 7 Hz, 2H), 5.35 (d, *J* = 5.0 Hz, 1H), 4.22-4.19 (m, 1H), 2.67 (dd *J* = 13.5, 3.0 Hz, 1H), 2.43-2.38 (m, 4H), 2.18 (t, *J* = 12.5 Hz, 1H), 1.87 (q, *J* = 13.0 Hz, 1H), 1.48-1.40 (m, 2H), 1.33-1.27 (m, 1H), 1.01-0.95 (m, 1H)

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 143.1 (C), 141.1 (C), 139.5 (C), 138.8 (C), 129.9 (2 × CH), 129.3 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.6 (2 × CH), 127.1 (CH), 127.0 (2 × CH), 126.3 (CH), 55.4 (CH), 53.0 (CH), 40.8 (CH_2), 24.9 (CH_2), 24.2 (CH_2), 21.6 (CH_3), 14.4 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calc for $C_{25}H_{27}NNaO_2S$ 428.1655, found 428.1651.

(*2R,6S*)-2-isobutyl-6-phenyl-1-tosylpiperidine (9i):

Reaction of alkynylamine **8i** (80 mg, 0.216 mmol) with Et_3SiH (69 μL, 0.433 mmol) and TMSOTf (39 μL 0.216 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9i** (50 mg, 63 %, dr-11.5:1).



9i

Physical appearance: Pale yellow solid.

M.P.: 71-73 ^oC

R$_f$: 0.7 (1:9, EtOAc: Petroleum ether).

[α]$_D$ ^{25}: -32.039 (c 0.340, $CHCl_3$)

IR (neat): 3011, 2946, 2872, 1463, 1336, 1164, 932, 815, 758, 552 cm^{-1}.

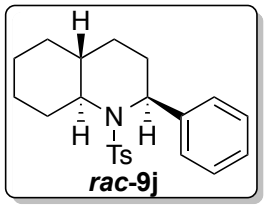
^{1}H NMR (500, MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.34-7.31 (m, 4H), 7.23 (t, *J* = 7.0 Hz, 1H), 5.24 (d, *J* = 5.5 Hz, 1H), 4.13-4.10 (m, 1H), 2.44 (s, 3H), 2.45 (dd, *J* = 12.5, 3.0 Hz, 1H), 1.82-1.74 (m, 1H), 1.54-1.46 (m, 1H), 1.40-1.35 (m, 1H), 1.33-1.25 (m, 3H), 1.15 (ddd, *J* = 12.5, 8.5, 4.5 Hz, 1H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.56 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 0.39 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 143.0 (C), 141.4 (C), 138.9 (C), 129.9 (2 × CH), 128.3 (2 × CH), 127.3 (2 × CH), 127.1 (2 × CH), 126.8 (CH), 52.6 (CH), 51.6 (CH), 42.4 (CH_2), 28.2 (CH_2), 24.3 (CH_2), 24.1 (CH), 22.6 (CH_3), 21.9 (CH_3), 21.6 (CH_3), 14.9 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calc for $C_{22}H_{29}NNaO_2S$ 394.1811, found 394.1814.

(*2R*,4aS*,8aR)-2-phenyl-1-tosyldecahydroquinoline (*rac*-9j):**

Reaction of alkynylamine **8j** (80 mg, 0.217 mmol) with Et_3SiH (69 μL, 0.435 mmol) and TMSOTf (39 μL 0.217 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate- petroleum ether (4:96) as eluent furnished the piperidine derivative **9j** (45 mg, 56 %, dr-1.5:1).



***rac*-9j**

Physical appearance: Sticky solid.

R$_f$: 0.7 (1:9, EtOAc: Petroleum ether).

IR (neat): 3011, 2924, 2857, 1451, 1336, 1162, 809, 758, 559 cm^{-1}.

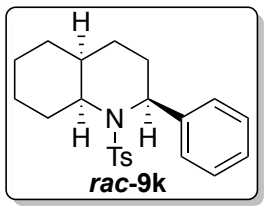
^{1}H NMR (400, MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.40-7.37 (m, 3H), 7.30-7.28 (m, 3H), 7.24-7.21 (m, 1H), 5.72 (d, *J* = 3.6 Hz, 1H), 2.84 (td, *J* = 12.0, 4.0 Hz, 1H), 2.44 (s, 3H), 2.37 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.13 (tt, *J* = 13.6, 4.0 Hz, 1H), 1.91-1.86 (m, 1H), 1.63-1.46 (m, 5H), 1.29-1.28 (m, 1H), 1.11 (tt, *J* = 13.2, 3.6 Hz, 1H), 1.02-0.832 (m, 2H), 0.81-0.67 (m, 1H).

^{13}C NMR (100, MHz, $CDCl_3$, DEPT): δ 143.3 (C), 142.8 (C), 139.6 (C), 129.6 (2 × CH), 128.9 (2 × CH), 127.5 (CH), 127.3 (2 × CH), 126.9 (2 × CH), 61.1 (CH), 58.1 (CH), 39.4 (CH), 33.5 (CH_2), 30.1 (CH_2), 28.4 (CH_2), 27.4 (CH_2), 26.7 (CH_2), 25.3 (CH_2), 21.63 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calc for $C_{22}H_{27}NNaO_2S$ 392.1655, found 392.1656.

(*2R*,4aR*,8aR)-2-phenyl-1-tosyldecahydroquinoline (*rac*-9k):**

Reaction of alkynylamine **8k** (75 mg, 0.20 mmol) with Et_3SiH (65 μL, 0.41 mmol) and TMSOTf (37 μL 0.210 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** followed by purification on silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9k** (55 mg, 71 %, dr-2.3:1).



***rac*-9k**

Physical appearance: sticky white solid.

R$_f$: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2942, 2716, 1464, 1329, 1139, 986, 970, 790, 766, 568 cm^{-1}.

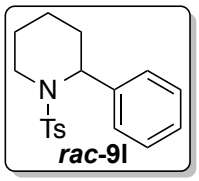
^{1}H NMR (400, MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.36-7.30 (m, 3H), 7.26-7.22, (m, 1H), 6.94-6.88 (m, 1H), 5.24 (d, *J* = 5.6 Hz, 1H), 3.97 (td, *J* = 12.4, 4.4 Hz, 1H), 2.42-2.39 (m, 4H), 2.03-1.97 (m, 1H), 1.92-1.79 (m, 1H), 1.71-1.65 (m, 1H), 1.49-1.34 (m, 5H), 1.29-1.05 (m, 2H), 1.10-0.87 (m, 2H).

^{13}C NMR (100, MHz, $CDCl_3$, DEPT): δ 143.0 (C), 141.6 (C), 139.1 (C), 129.9 (2 × CH), 128.3 (2 × CH), 127.3 (2 × CH), 126.9 (2 × CH), 126.8 (CH), 56.6 (CH), 52.6 (CH), 34.7 (CH), 31.8 (CH_2), 29.4 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 21.6 (CH_3), 20.1 (CH_2), 19.9 (CH_2).

2-phenyl-1-tosylpiperidine (*rac*-9l):[5]

Reaction of alkynylamine **8l** (80 mg, 0.255 mmol) with Et_3SiH (80 μL, 0.51 mmol) and TMSOTf (45 μL 0.255 mmol) in dry CH_2Cl_2 (3 ml) 12 hrs as described for the piperidine derivative **8a** fallowed by purification on silica gel column using ethyl

acetate-petroleum ether (4:96) as eluent furnished the piperidine derivative **9l** (65 mg, 80 %).



***rac*-9l**

Physical appearance: yellow solid.

M.P: 135-137 ^{o}C.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

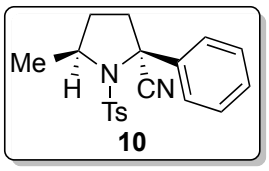
IR (neat): 2942, 2716, 1464, 1329, 1139, 986, 970, 790, 766, 568 cm^{-1}.

^{1}H NMR (500, MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 6H), 7.24-7.21 (m, 1H), 5.27 (d, *J* = 4.5 Hz, 1H), 3.84 (dd, *J* = 14.5, 3.6 Hz, 1H), 3.01(td, *J* = 12.5, 3.0 Hz, 1H), 2.43 (s, 3H), 2.21 (dd, *J* = 13.5, 2.0 Hz, 1H), 1.66 (tt, *J* = 14.0, 5.0 Hz, 1H), 1.52-1.48 (m, 1H), 1.44-1.37 (m, 2H), 1.33-1.26 (m, 1H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 143.1 (C), 139.1 (C), 138.8 (C), 129.8 (2 × CH), 128.7 (2 × CH), 127.1 (2 × CH), 127.0 (2 × CH), 126.9 (CH), 55.4 (CH), 42.0 (CH_2), 27.4 (CH_2), 24.4 (CH_2), 21.63 (CH_3), 19.1(CH_2).

(2*S*,5*S*)-5-methyl-2-phenyl-1-tosylpyrrolidine-2-carbonitrile (10):

To a magnetically stirred solution of alkynylamine **6a** (65 mg, 0.2 mmol) and TMSCN (51 μL, 0.4 mmol) in dry CH_2Cl_2 (3 mL), TMSOTf (40 μL, 0.2 mmol) was added dropwise at 0 ^{o}C. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion (18 hrs), extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether (4:96) as eluent furnished pyrrolidine derivative **10** (57 mg, 83%, dr-9:1).



10

Physical appearance: white solid.

M.P: 142-144 ^{o}C.

R_f: 0.2 (2:8 ethyl acetate-petroleum ether).

$[\alpha]_D$ ^{25}: -27.31 (c 0.185, $CHCl_3$).

IR (neat): 3020, 2970, 2220, 1599, 1493, 1337, 1156, 1092, 757, cm^{-1}.

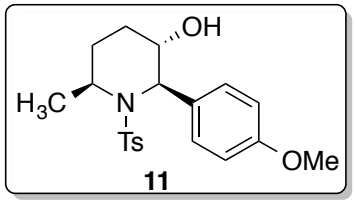
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.40-7.32 (m, 3H), 7.25 (d, *J* = 7.0 Hz, 2H), 4.11 (quint, *J* = 13.0 Hz, 1H), 2.58 (dd, *J* = 12.0, 5.0 Hz, 1H), 2.41 (s, 3H), 2.41-2.32 (m, 1H), 2.31-2.22 (m, 1H), 1.72 (dd, *J* = 12.0, 5.0 Hz, 1H), 1.47 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 144.1 (C), 138.5 (C), 135. 7 (C), 129.5 (2 × CH), 128.9 (2 × CH), 128.7 (CH), 128.4 (2 × CH), 125.4 (2 × CH), 119.2 (C), 67.9 (C), 57.2 (CH), 44.4 (CH_2), 31.7 (CH_2), 22.2 (CH_3), 21.7 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{19}H_{20}N_2NaO_2S$ 363.1143, found 363.1145.

(2*R*,3*S*,6*R*)-2-(4-methoxyphenyl)-6-phenyl-1-tosylpiperidin-3-ol (11):

To a magnetically stirred solution of cyclicenamine **9d'** (87.5 mg, 0.245 mmol) in dry THF (2 ml), $BH_3{\cdot}SMe_2$ (2M, 485 µL) was added at 0 ^oC. Reaction mixture was stirred at room temperature till starting material get consumed (TLC control). After that reaction was cooled to 0 ^oC and EtOH (1.5 ml), NaOH (3N, 440 µL) and H_2O_2 (30%, 220 µL) were added. The resulting mixture was heated to reflux for 2 hrs. The reaction was brought to room temperature quenched with cold water and product was extracted with EtOAc (3 x 5 ml). combined organic layer was dried over Na_2SO_4, and evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (8:92) as eluent furnished **11** (71.6 mg, 67%) as a single diastereoisomer.



11

Physical appearance: white solid.

M.P: 125-127 ^oC.

R_f: 0.3 (1:9, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -37.860 (c 0.065, $CHCl_3$).

IR (neat): 3524, 2952, 1611, 1514, 1317, 1159, 1033, 821, cm^{-1}.

^{1}H NMR (500, MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.18 (s, 1H), 4.60 (bs, 1H), 4.08-4.06 (m, 1H), 3.79 (s, 3H), 2.42(s, 3H), 2.04-1.95 (m, 1H), 1.84-1.77 (m, 2H), 1.60-1.56 (m, 1H), 1.14-1.11 (m, 1H), 0.86 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 158.7 (C), 143.3 (C), 138.1 (C), 132.2 (C), 129.7 (2 × CH), 128.5 (2 × CH), 127.6 (2 × CH), 113.7 (2 × CH), 65.3 (CH), 59.9 (CH), 55.3 (CH_3), 48.7 (CH), 22.7 (CH_2), 21.9 (CH_2), 21.67 (CH_3), 21.1 (CH_3).

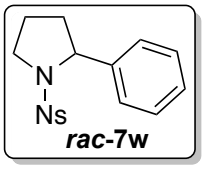
HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{20}H_{27}NNaO_4S$ 400.1553, found 400.1610.

1-((2-nitrophenyl)sulfonyl)-2-phenylpyrrolidine (*rac*-7w):[1]

Reaction of alkynylamine **6w** (346 mg, 1.04 mmol), with Et_3SiH (170 µL, 1.04 mmol) and TMSOTf (20 µL, 0.104 mmol) in dry CH_2Cl_2 (7 ml) at 0 °C as described for the pyrrolidine derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished the pyrrolidine derivative **7w** (312 mg, 90%).

Physical appearance: White solid.

M.P: 103-105 ^{o}C.



R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2961, 1600, 1344, 1160, 1098, 753 cm^{-1}.

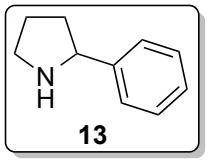
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.477 (m, 2H), 7.42 (d, *J* = 9.5 Hz, 1H), 7.29-7.25 (m, 1H), 7.18-7.14 (m, 2H), 7.13-7.10 (m, 3H), 5.00 (dd, *J* = 9.5, 7.0 Hz 1H), 3.87-3.76 (m, 2H), 2.44-2.35 (m, 1H), 2.09-1.99 (m, 1H), 1.97-1.91 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.7 (C), 141.6 (C), 133.3 (C), 132.9 (CH), 131.1 (CH), 130.9 (CH), 128.3 (2 × CH), 127.4 (CH), 126.7 (2 × CH), 123.6 (CH), 64.1 (CH), 50.1 (CH_2), 37.0 (CH_2), 24.7 (CH_2).

HRMS (ESI, M+Na^{+}): m/z calcd. for $C_{16}H_{16}N_2NaO_4S$ 355.0728, found 355.0731.

2-phenylpyrrolidine (*rac*-13):[6]

To meganetically sittered solution of pyrrolidine **7w** (346 mg, 1.04 mmol), in dry acetonitrile (6 ml) Cs_2CO_3 (1.1 mmol, 370 mg) and thiophenol (0.97 mmol, 80 μL) was added at room temperature. After completion of reaction (TLC control, 3h) reaction mixture was pass through celite. The combine organic layer was concentrate and residue was purified by colum chromatography using ethyl acetate-petroleum ether (60:40) as eluent furnished the 2-phenylpyrrolidine **13** (104 mg, 66%).



Physical appearance: Pale yellow oily.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2961, 1600, 1344, 1160, 1098, 753 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 4.12 (d, *J* = 7.5 Hz, 1H), 3.23-3.18 (m, 1H), 3.04-2.93 (m, 1H), 2.22-2.16 (m, 1H), 1.95-1.91 (m, 1H), 1.89-1.83 (m, 1H), 1.74-1.66 (m, 1H).

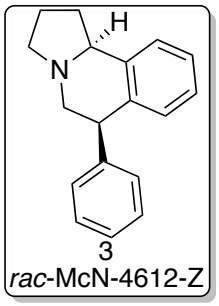
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 144.5 (C), 128.5 (2 × CH), 127.1 (CH), 126.7 (2 × CH), 62.7 (CH), 46.9 (CH_2), 34.2 (CH_2), 25.6 (CH_2).

***6-phenyl-1,2,3,5,6,10b-hexahydropyrrolo[2,1-a]isoquinoline* (*rac*-3):**[6]

13 (100 mg, 0.68 mmol) and styrene oxide (84 mg, 0.68 mmol) were combined in 2 ml of ethanol and refluxed. After 19 hrs, no starting material **13** was detected by TLC. Then the solution was evaporated, which was combined with PPA (2.0 g) and 2 ml toluene and heated at 100 ^{o}C for 4 hrs. The reaction was cooled, diluted

with cold water basified with 40% of aqueous KOH under cooling, and extracted with CH_2Cl_2 (3 x 15 ml). The mixture was evaporated and and the residue was purified by silica gel column using ethyl acetate-petroleum ether (4:96) as eluent furnished quinoline derivative **3** (88 mg, 52%) as a single diastereoisomer.

Physical appearance: Brown oil.



R_f: 0.6 (2:8, EtOAc: Petroleum ether).

^{1}H NMR (500, MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.27-7.22 (m, 2H), 7.19-7.12 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.40 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.60 (t, *J* = 8.0 Hz, 1H), 3.46 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.15 (td, *J* = 8.5, 4.0 Hz, 1H), 2.69 (t, *J* = 11.5 Hz, 1H), 2.54-2.42 (m, 2H), 1.99-1.81 (m, 3H).

^{13}C NMR (125, MHz, $CDCl_3$, DEPT): δ 144.4 (C), 139.3 (C), 137.8 (C), 129.3 (2 × CH), 129.3 (CH), 128.6 (2 × CH), 126.6 (CH), 126.4 (CH), 126.3 (CH), 125 (CH), 64.02 (CH), 58.2 (CH_2), 53.2 (CH_2), 45.3 (CH), 30.7 (CH_2), 22.2 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{18}H_{19}NNa$ 272.1410, found 272.1419.

The analytical data are consistent with the literature.[6]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7.379
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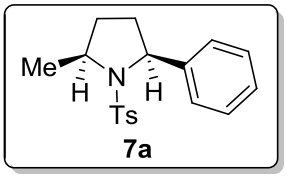
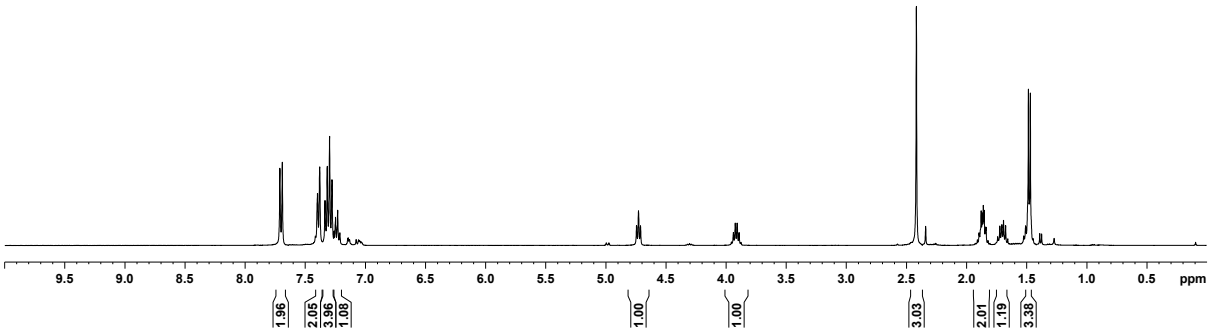

Me
H
N
H
Ts

7a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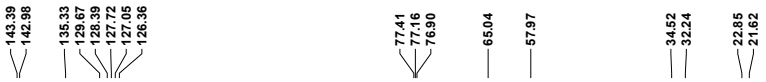
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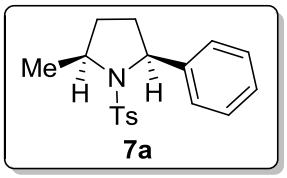
21.62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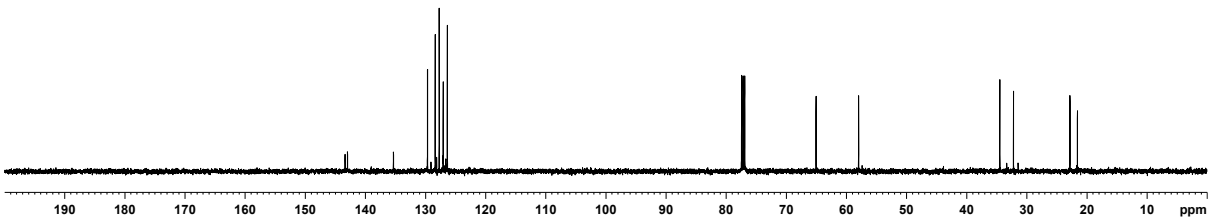
Ts

7a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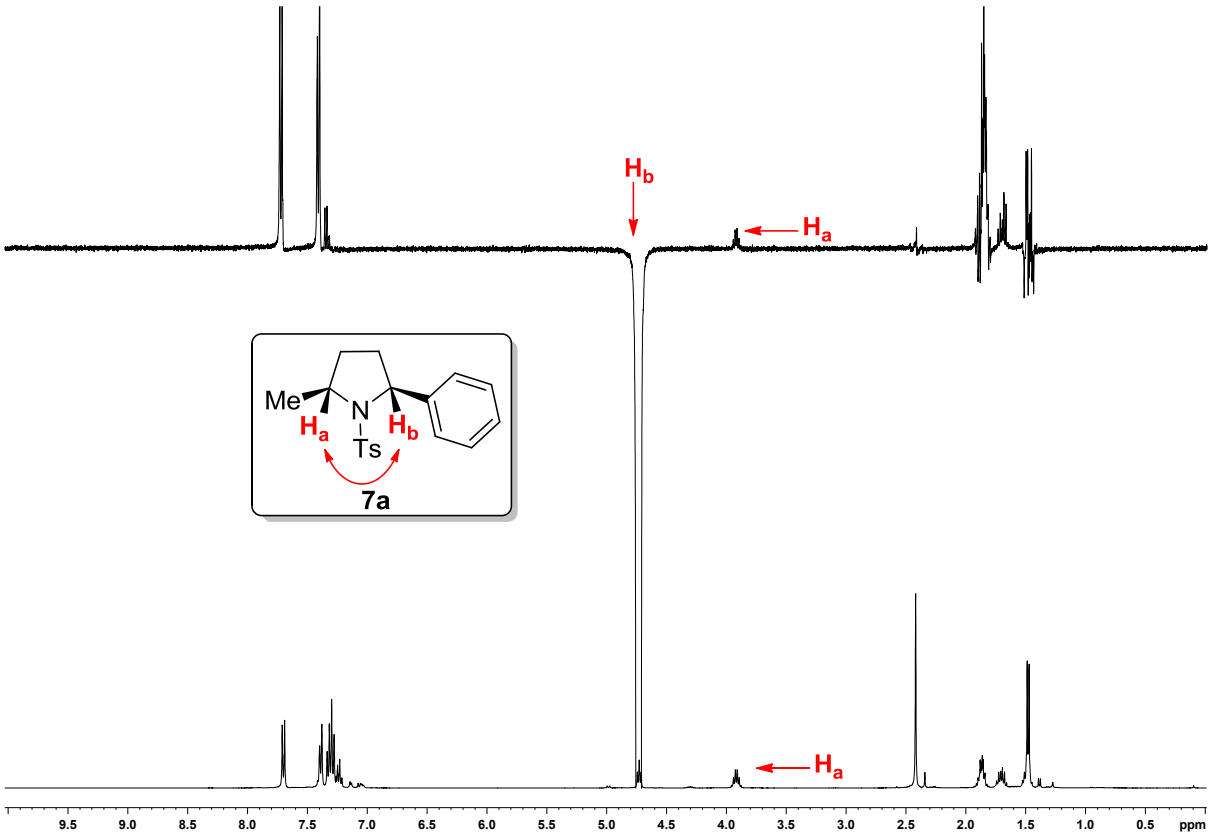
ppm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Ha
Me
N
Ha
Hb
Ts
7a
Ha
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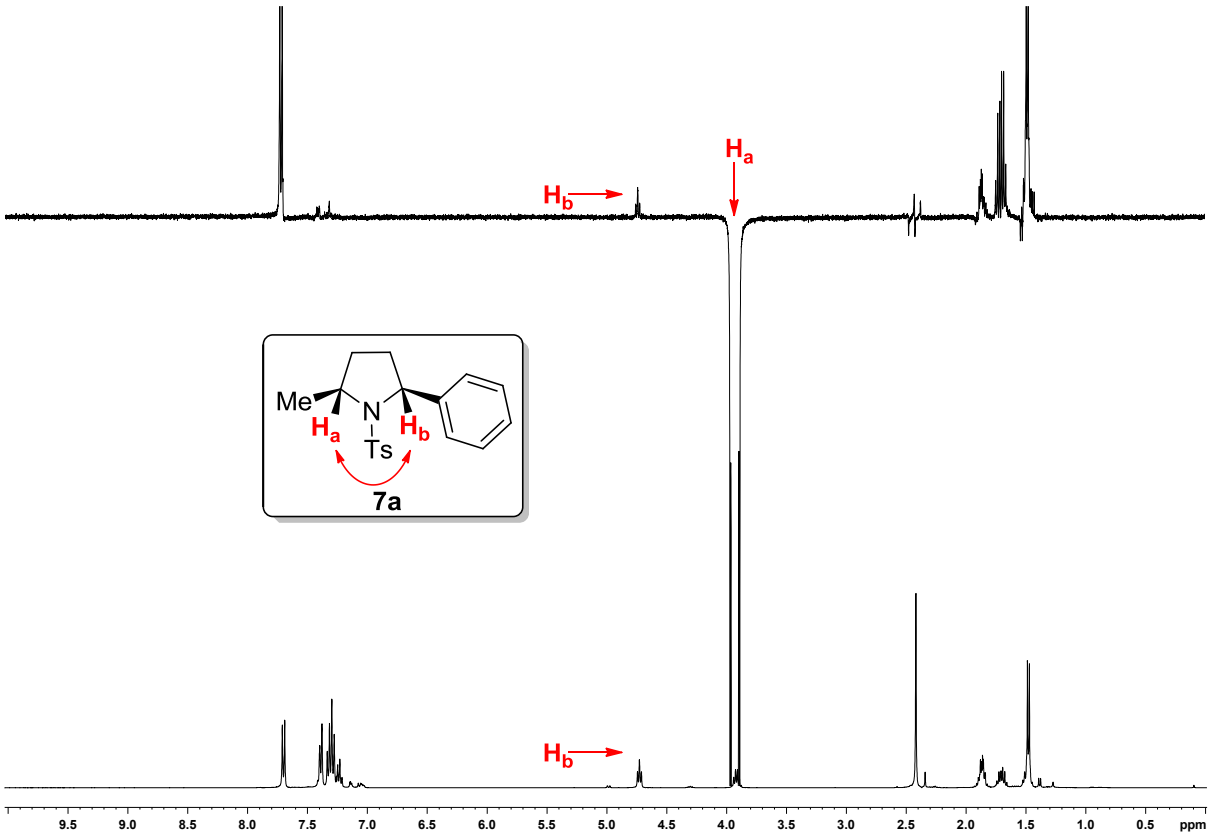
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Hb
Me
N
Ha
Hb
Ts
7a
Hb
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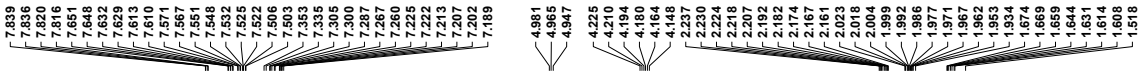
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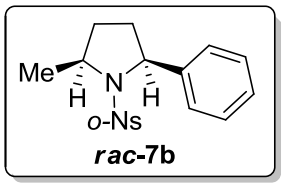
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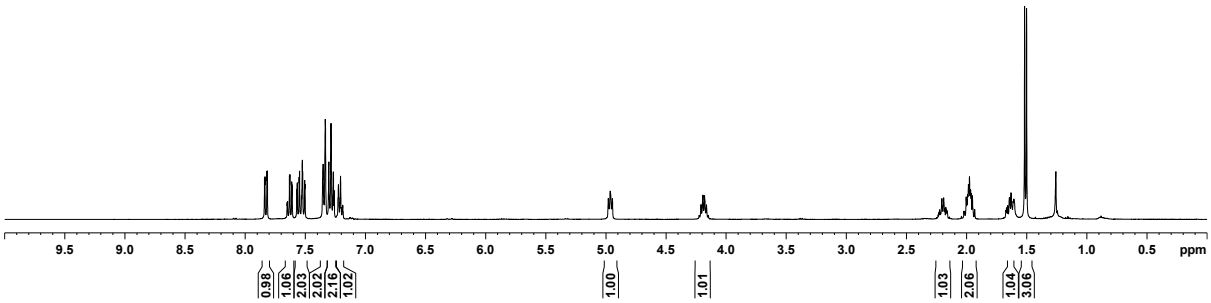
H
N
H
o-Ns

***rac*-7b**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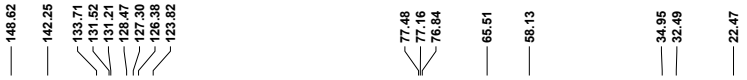
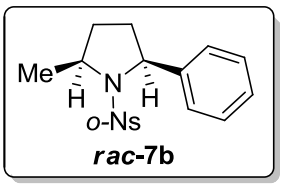
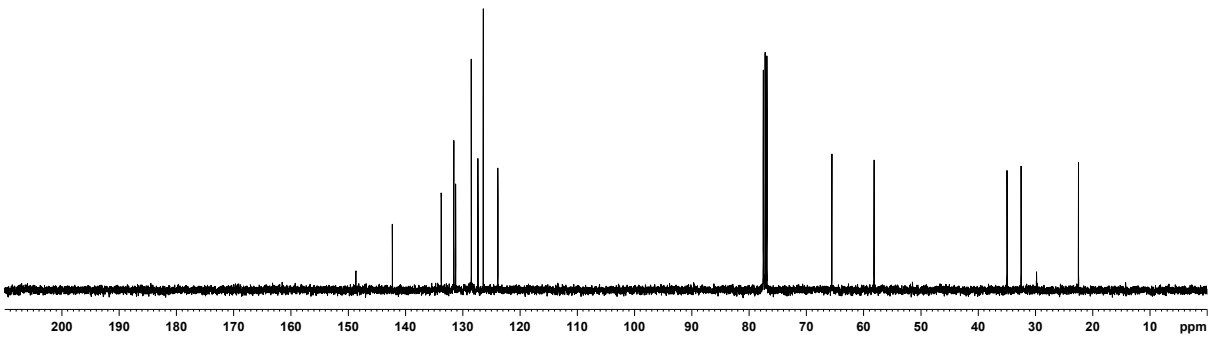
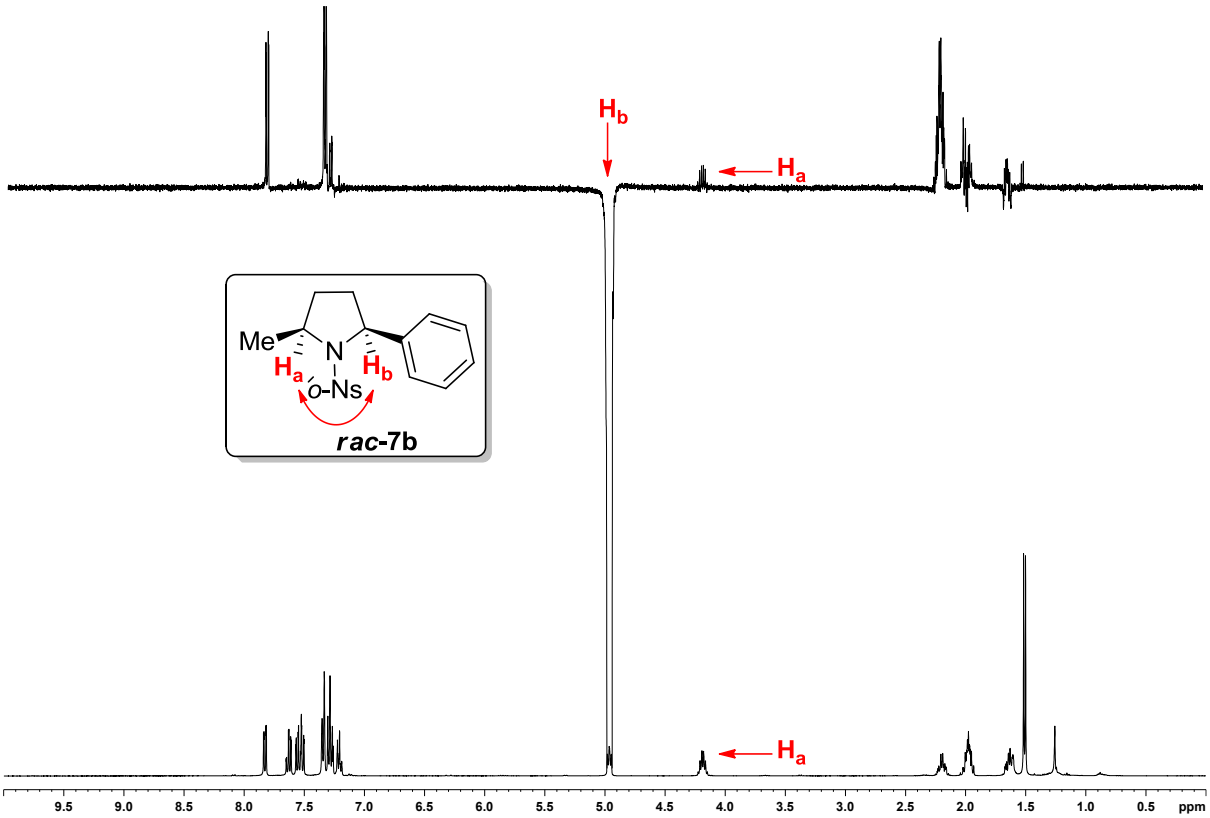
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.98
1.06
2.03
2.02
2.16
1.02
1.00
1.01
1.03
2.06
1.04
3.06

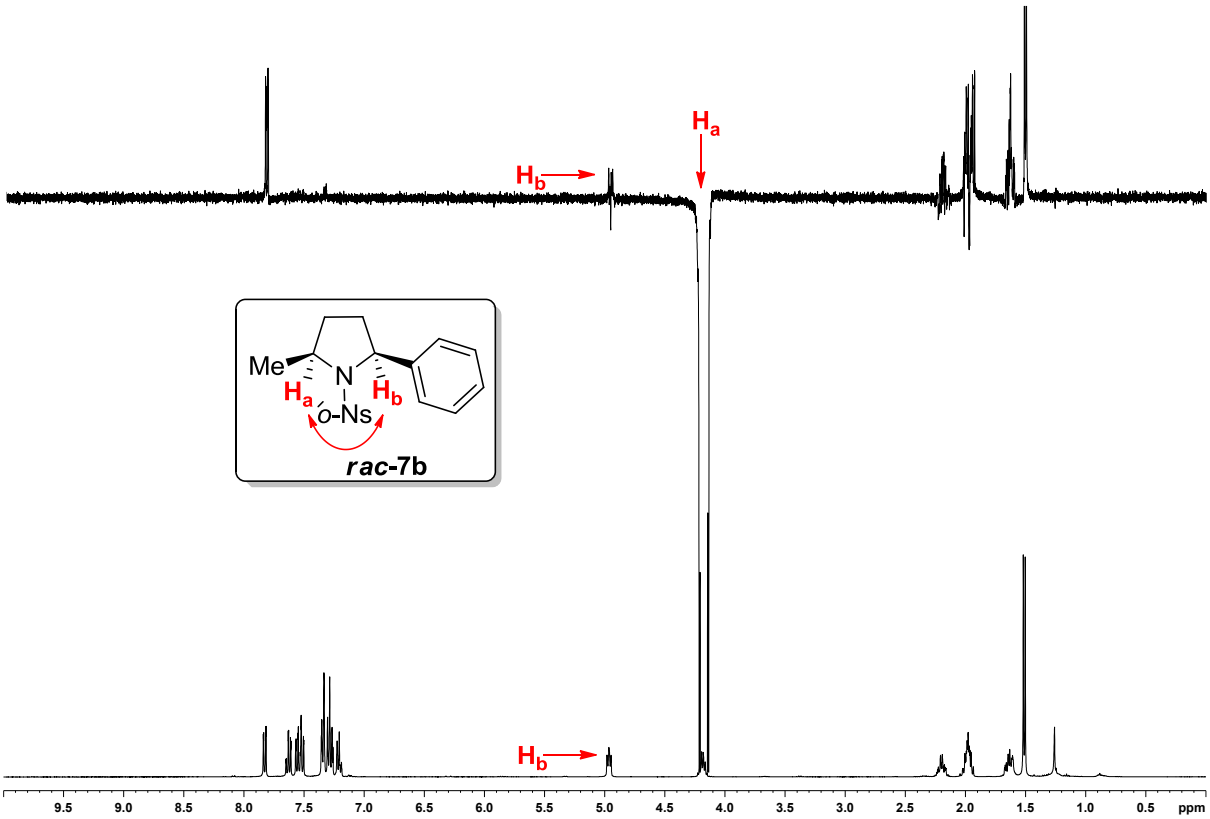

148.62
142.25
133.71
131.52
131.21
128.47
127.30
126.38
123.82
77.48
77.16
76.84
65.51
58.13
34.95
32.49
22.47

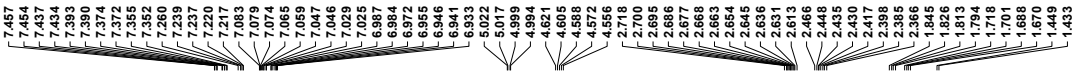

Me
H
N
H
o-Ns

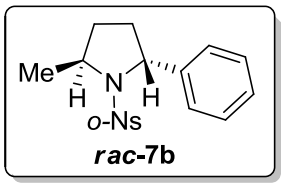
***rac*-7b**


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

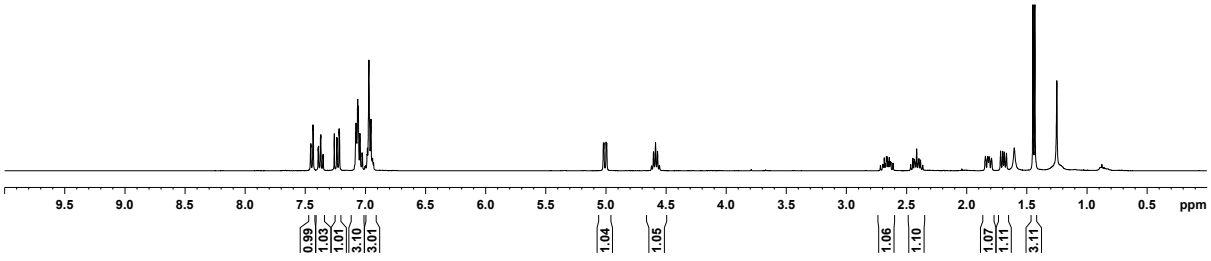

Hb
Ha
Me
N
Ha
Hb
o-Ns
rac-7b
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

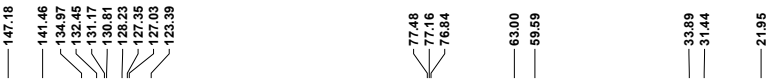

Ha
Hb
Me
N
Ha
Hb
o-Ns
rac-7b
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

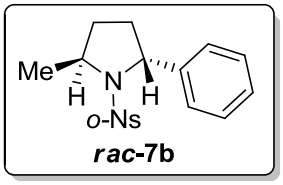

7.457
7.454
7.437
7.434
7.393
7.390
7.374
7.372
7.355
7.352
7.260
7.239
7.237
7.220
7.217
7.083
7.079
7.074
7.065
7.059
7.047
7.046
7.029
7.025
6.987
6.984
6.972
6.955
6.946
6.941
6.933
5.022
5.017
4.999
4.994
4.621
4.605
4.588
4.572
4.556
2.718
2.700
2.695
2.686
2.677
2.668
2.663
2.654
2.645
2.636
2.631
2.613
2.466
2.448
2.435
2.430
2.417
2.398
2.385
2.366
1.845
1.826
1.813
1.794
1.718
1.701
1.688
1.670
1.449
1.433


Me
H
N
H
o-Ns

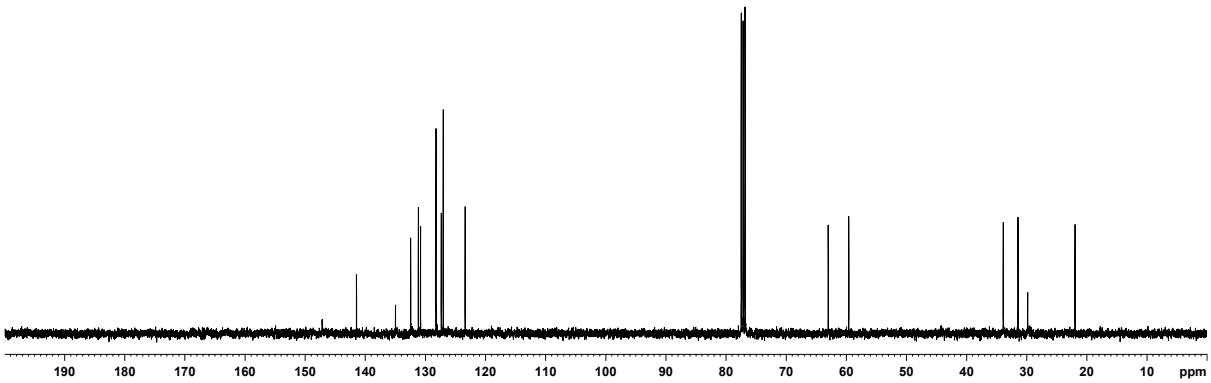
***rac*-7b**

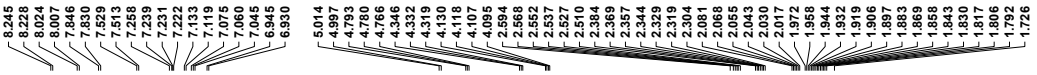

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.99
1.03
1.01
3.10
3.01
1.04
1.05
1.06
1.10
1.07
1.11
3.11

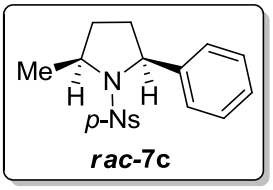

147.18
141.46
134.97
132.45
131.17
130.81
128.23
127.35
127.03
123.39
77.48
77.16
76.84
63.00
59.59
33.89
31.44
21.95


Me
H
N
H
o-Ns

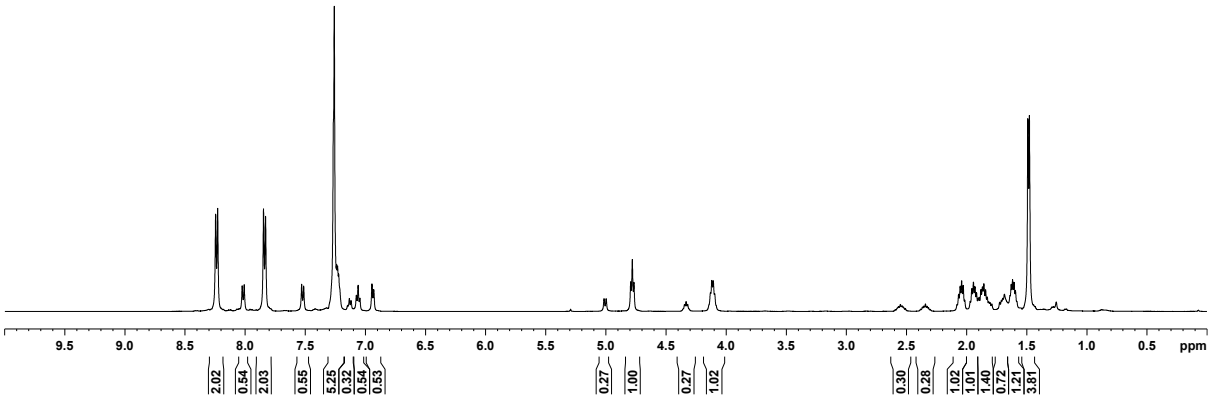
***rac*-7b**

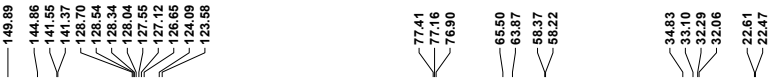

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

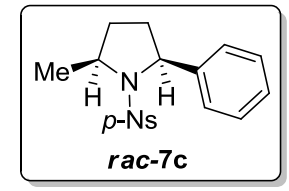

8.245
8.228
8.024
8.007
7.846
7.830
7.529
7.513
7.258
7.239
7.231
7.222
7.133
7.119
7.075
7.060
7.045
6.945
6.930
5.014
4.997
4.793
4.780
4.766
4.346
4.332
4.319
4.130
4.118
4.107
4.095
2.594
2.568
2.552
2.537
2.527
2.510
2.384
2.369
2.357
2.344
2.329
2.319
2.304
2.081
2.068
2.055
2.043
2.030
2.017
1.972
1.958
1.944
1.932
1.919
1.906
1.897
1.883
1.869
1.858
1.843
1.830
1.817
1.806
1.792
1.726


Me
H
N
H
p-Ns

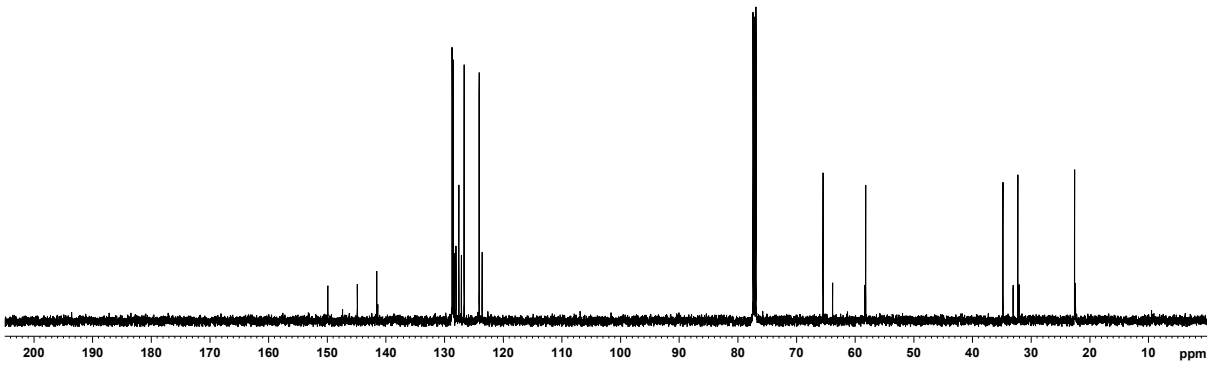
***rac*-7c**

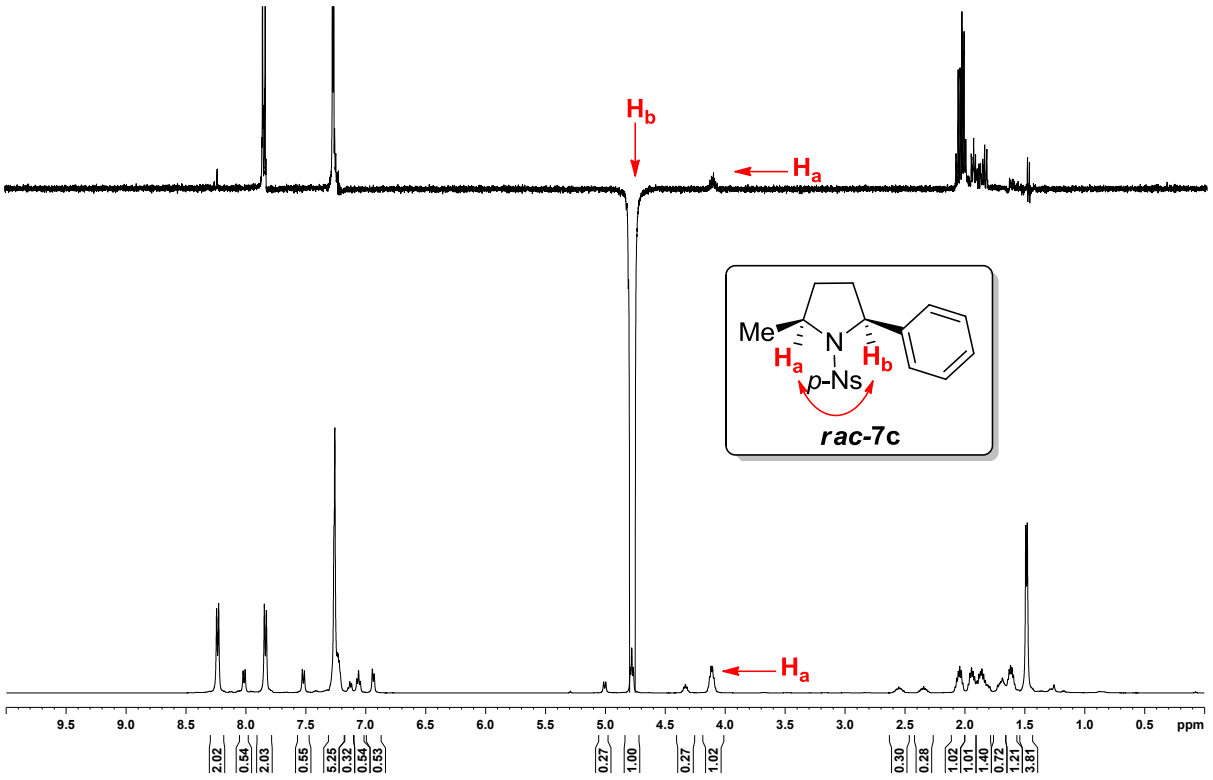

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
0.54
2.03
0.55
5.25
0.32
0.54
0.53
0.27
1.00
0.27
1.02
0.30
0.28
1.02
1.01
1.40
0.72
1.21
3.81

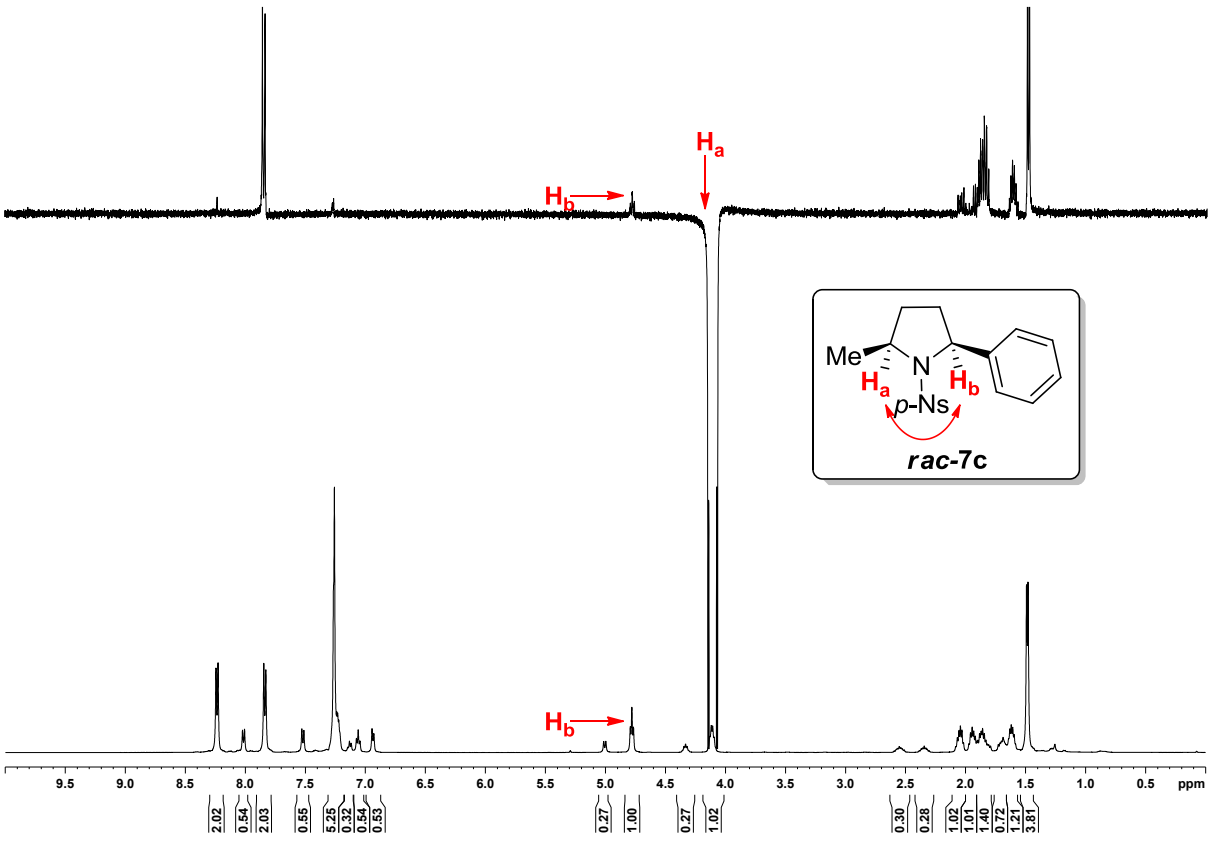

149.89
144.86
141.55
141.37
128.70
128.54
128.34
128.04
127.55
127.12
126.65
124.09
123.58
77.41
77.16
76.90
65.50
63.87
58.37
58.22
34.83
33.10
32.29
32.06
22.61
22.47

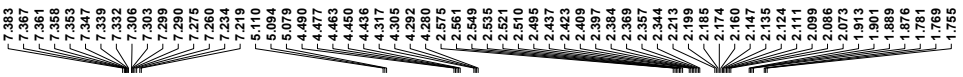

Me
H
N
H
p-Ns

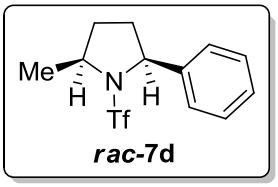
***rac*-7c**


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

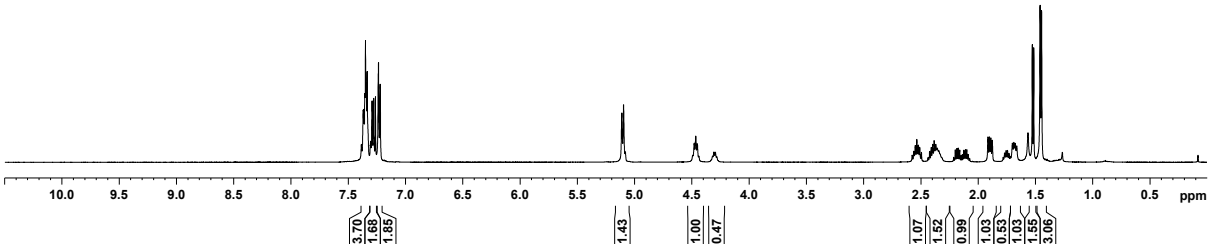

Hb
Ha
Me
N
Ha
Hb
p-Ns
rac-7c
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02 0.54 2.03 0.55 5.26 0.32 0.54 0.53 0.27 1.00 0.27 1.02 0.30 0.28 1.02 1.01 1.40 0.72 1.21 3.81

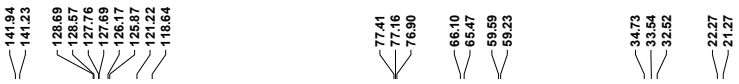

Ha
Hb
Me
N
Ha
Hb
p-Ns
rac-7c
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02 0.54 2.03 0.55 5.26 0.32 0.54 0.53 0.27 1.00 0.27 1.02 0.30 0.28 1.02 1.01 1.40 0.72 1.21 3.81

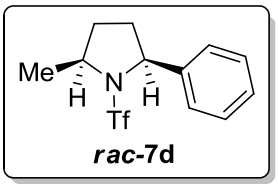

7.383
7.367
7.361
7.358
7.353
7.347
7.339
7.332
7.306
7.303
7.299
7.290
7.275
7.260
7.234
7.219
5.110
5.094
5.079
4.490
4.477
4.463
4.450
4.436
4.317
4.305
4.292
4.280
2.575
2.561
2.549
2.535
2.521
2.510
2.495
2.437
2.423
2.409
2.397
2.384
2.369
2.357
2.344
2.213
2.199
2.185
2.174
2.160
2.147
2.135
2.124
2.111
2.099
2.086
2.073
1.913
1.901
1.889
1.876
1.781
1.769
1.755


Me
H
N
H
Tf

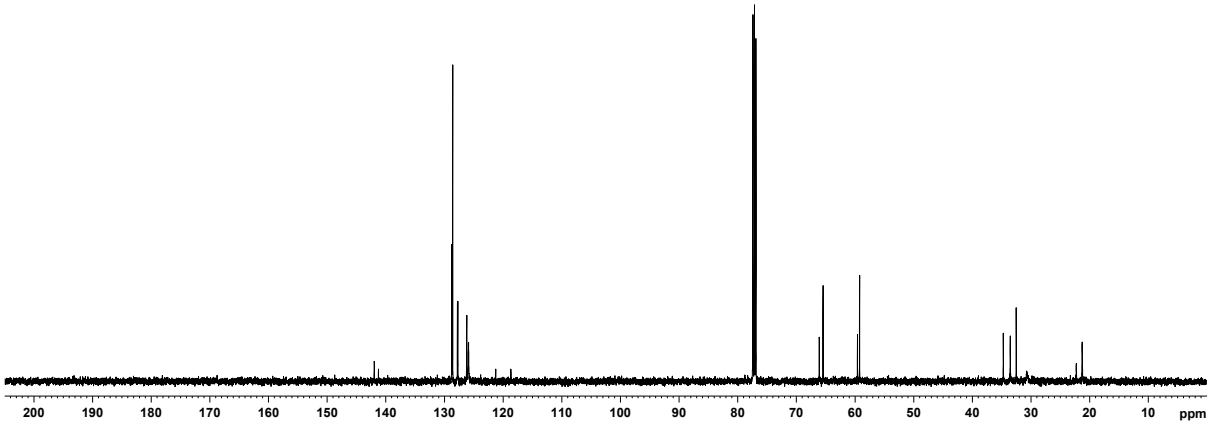
***rac*-7d**

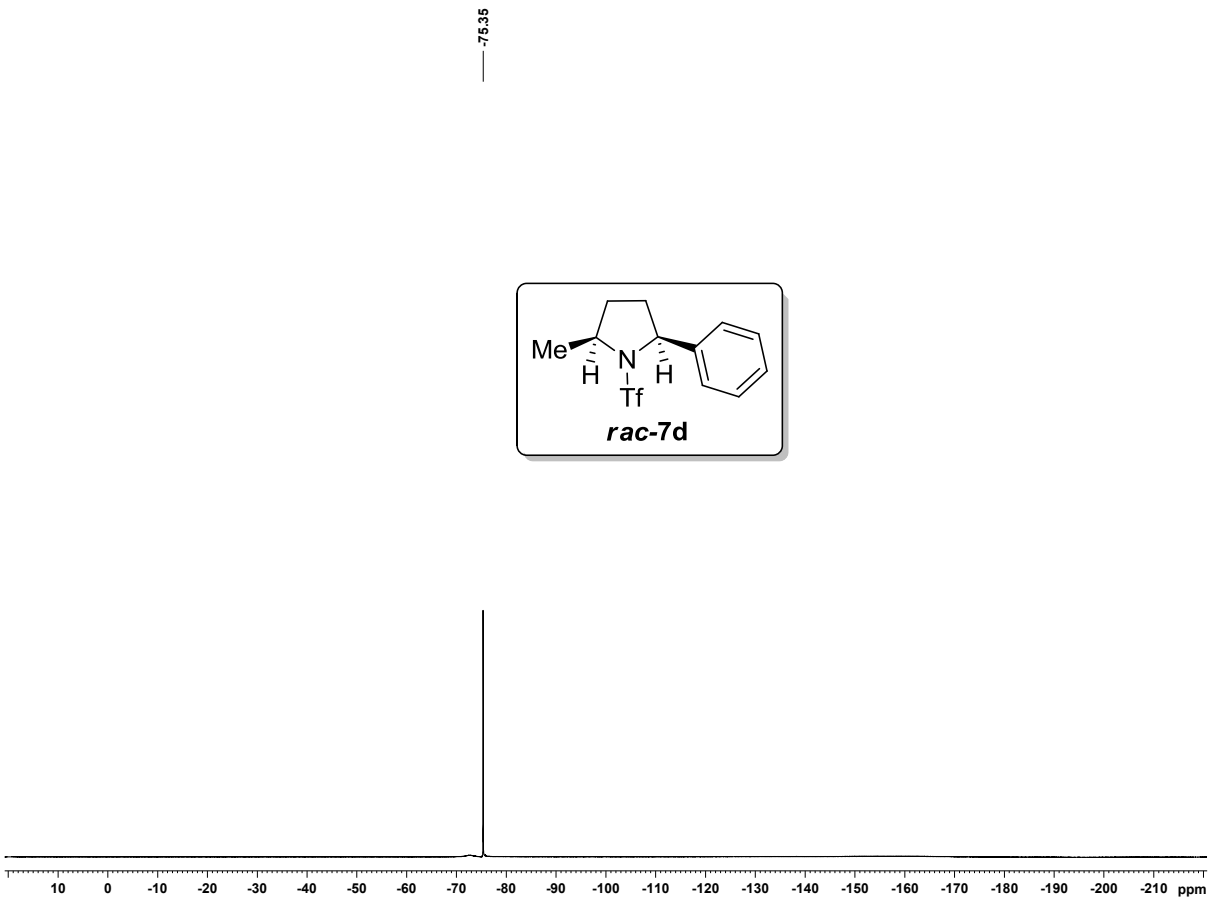

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.70
1.68
1.85
1.43
1.00
0.47
1.07
1.52
0.99
1.03
0.53
1.03
1.55
3.06

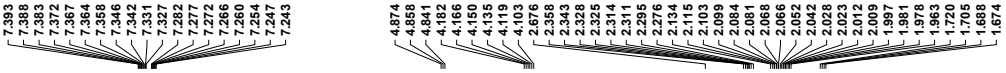

141.94
141.23
128.69
128.57
127.76
127.69
126.17
125.87
121.22
118.64
77.41
77.16
76.90
66.10
65.47
59.59
59.23
34.73
33.54
32.52
22.27
21.27

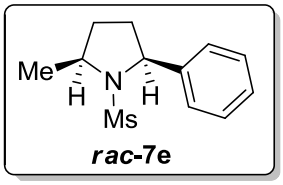

Me
H
N
H
Tf

***rac*-7d**


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

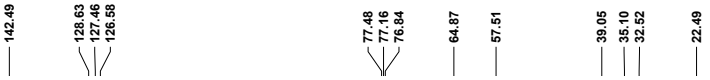

-75.35
Me
H
N
H
Tf
rac-7d
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

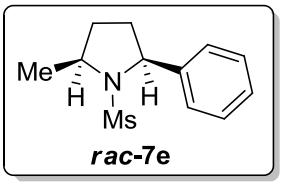

7.393
7.388
7.383
7.372
7.367
7.364
7.358
7.346
7.342
7.331
7.327
7.282
7.277
7.272
7.266
7.260
7.254
7.247
7.243
4.874
4.858
4.841
4.182
4.166
4.150
4.135
4.119
4.103
2.676
2.358
2.343
2.328
2.325
2.314
2.311
2.295
2.276
2.134
2.115
2.103
2.099
2.084
2.081
2.068
2.066
2.052
2.042
2.028
2.023
2.012
2.009
1.997
1.981
1.978
1.963
1.720
1.705
1.688
1.674


Me
H
N
H
Ms

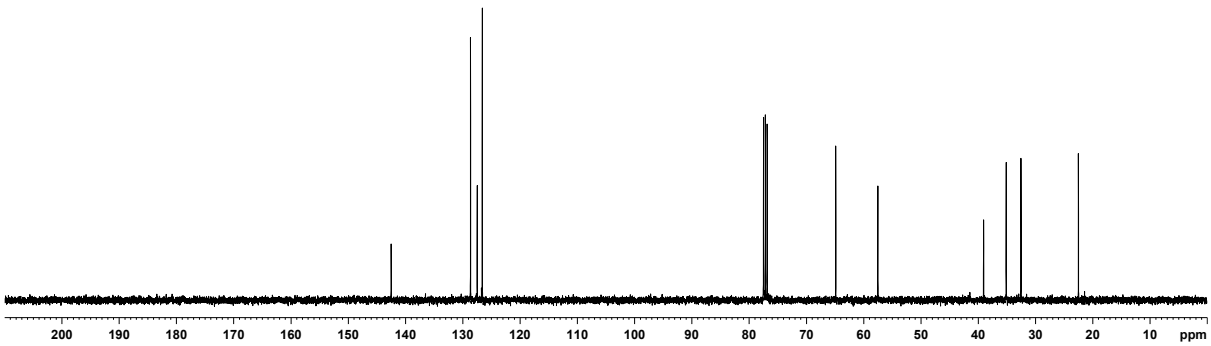
***rac*-7e**

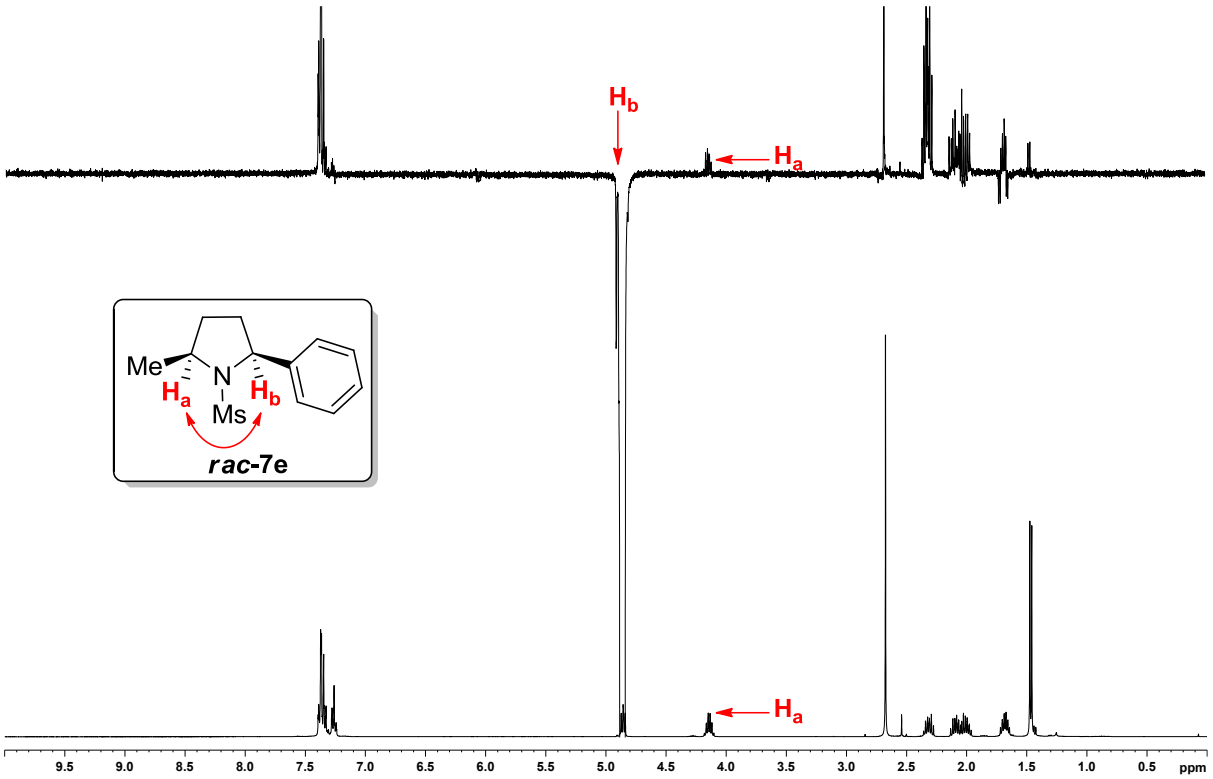
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.07
1.12
1.00
1.00
3.02
1.07
2.07
1.27
3.02

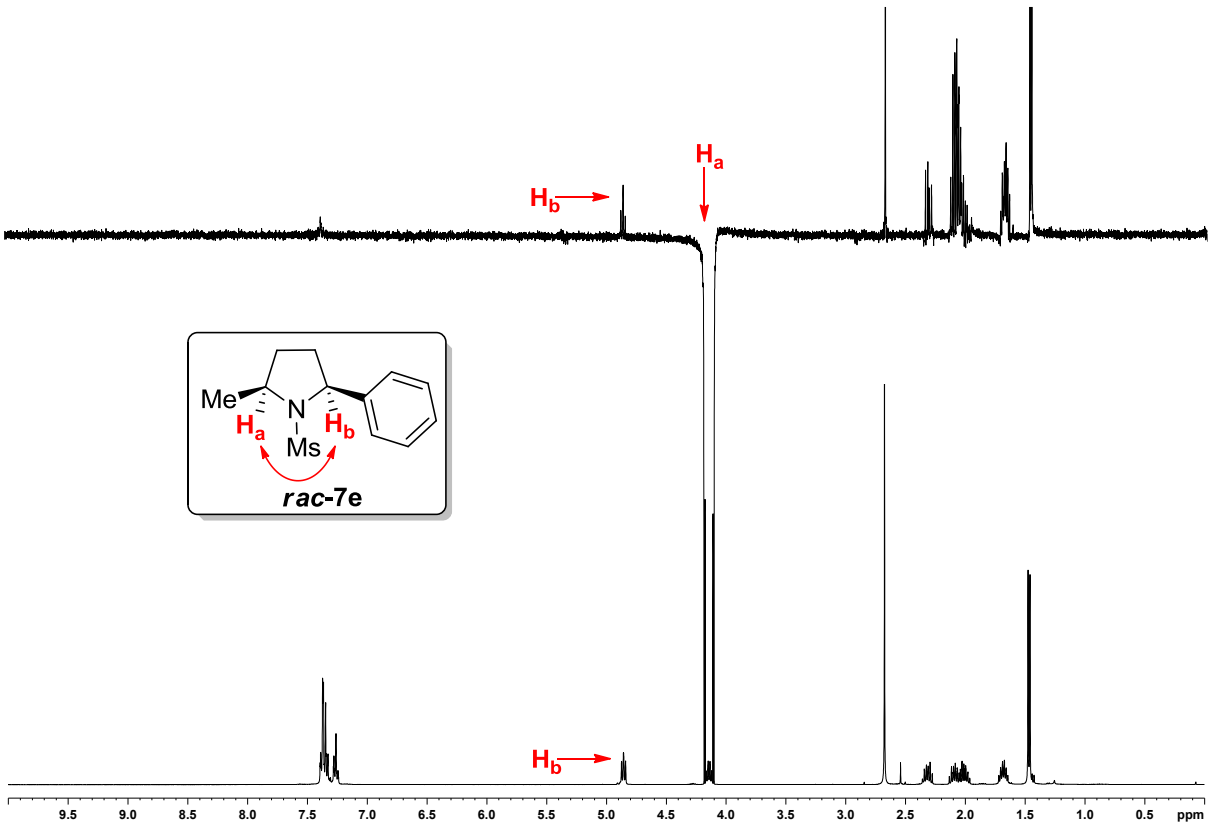

142.49
128.63
127.46
126.58
77.48
77.16
76.84
64.87
57.51
39.05
35.10
32.52
22.49

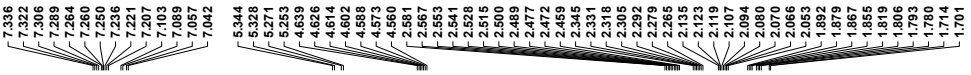

Me
H
N
H
Ms

***rac*-7e**


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Hb
Ha
Me
N
Ha
Hb
Ms
rac-7e
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Ha
Hb
Me
N
Ha
Hb
Ms
rac-7e
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


7.336
7.322
7.306
7.289
7.264
7.260
7.250
7.236
7.221
7.207
7.103
7.089
7.057
7.042
5.344
5.328
5.271
5.253
4.639
4.626
4.614
4.602
4.588
4.573
4.560
2.581
2.567
2.553
2.541
2.528
2.515
2.500
2.489
2.477
2.472
2.459
2.345
2.331
2.318
2.305
2.292
2.279
2.265
2.135
2.123
2.119
2.107
2.094
2.080
2.070
2.066
2.053
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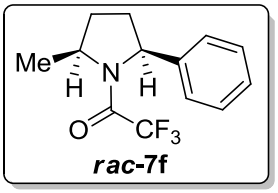
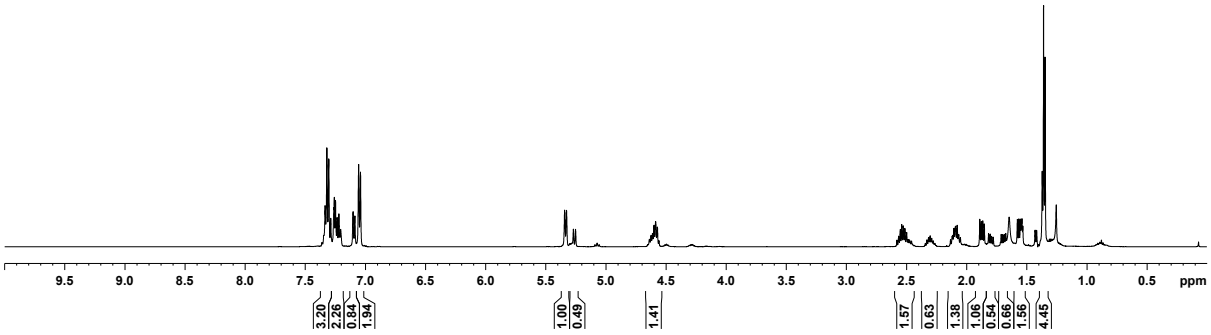
1.879
1.867
1.855
1.819
1.806
1.793
1.780
1.714
1.701


Me
H
N
H
O
CF3

***rac*-7f**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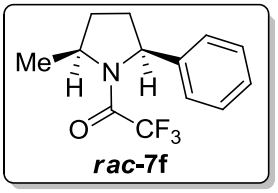
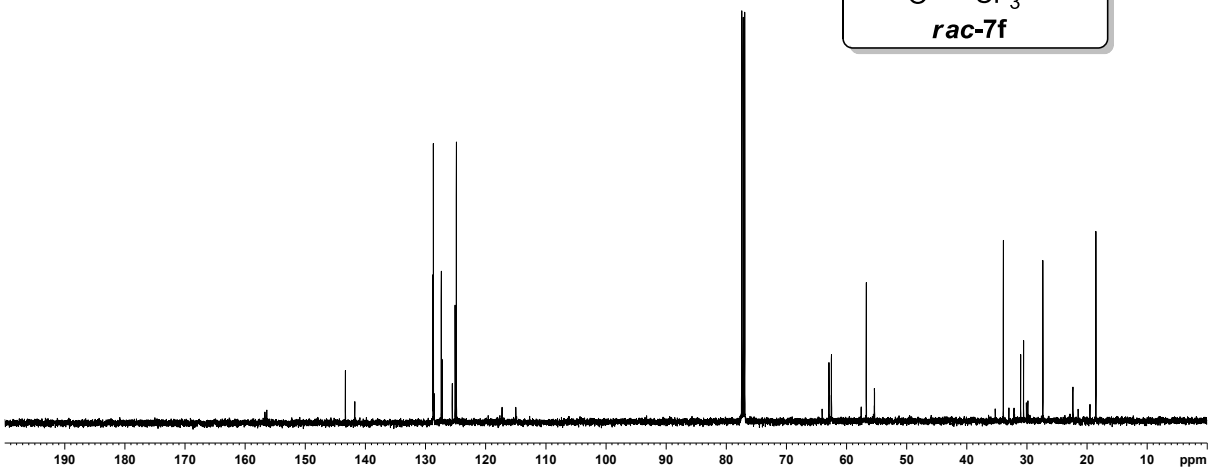
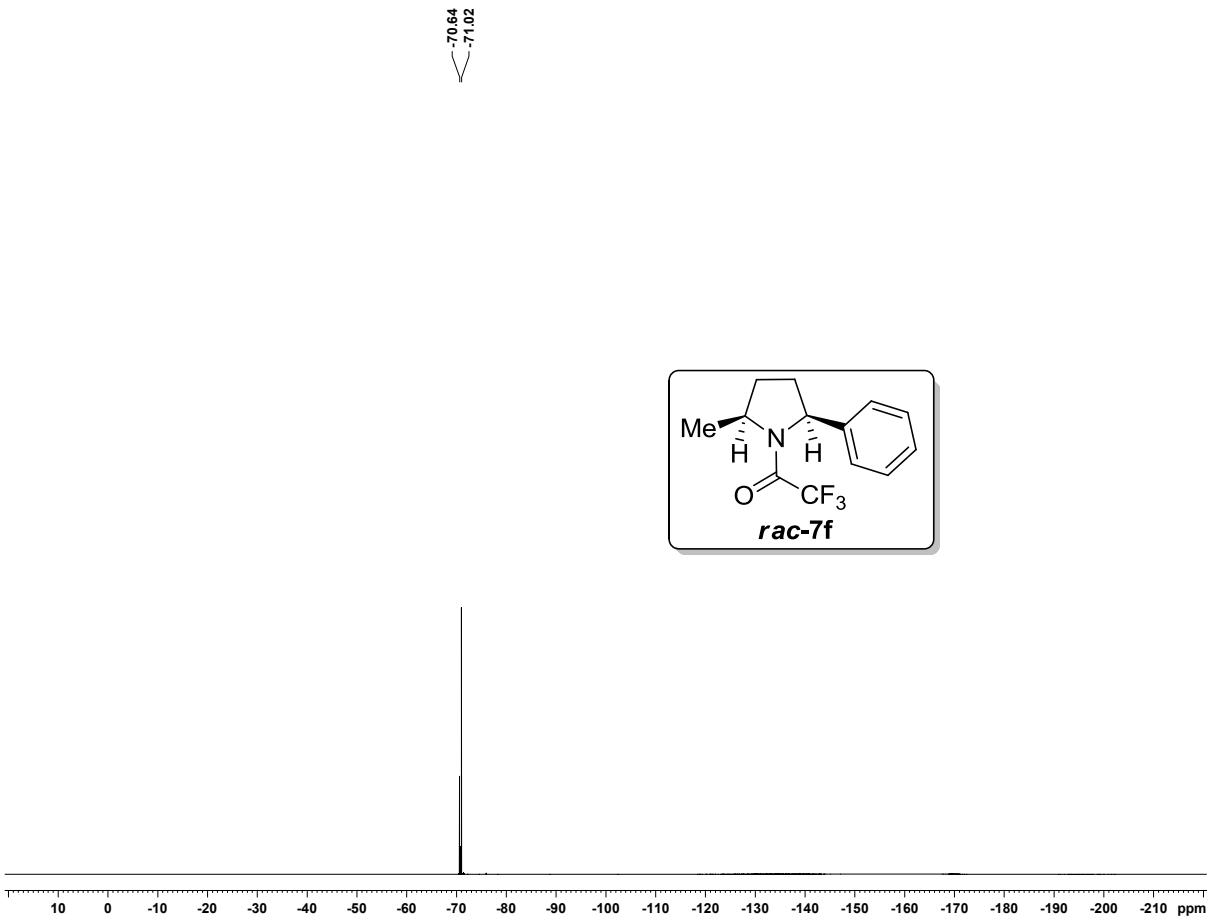
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.20
2.26
0.84
1.94
1.00
0.49
1.41
1.57
0.63
1.38
1.06
0.54
0.66
1.56
4.45


156.69
156.40
143.32
141.76
128.77
128.69
128.55
127.37
127.33
127.25
125.53
125.07
124.86
117.27
114.98
77.41
77.16
76.90
62.91
62.52
62.50
56.70
33.91
31.03
30.54
27.33
18.55

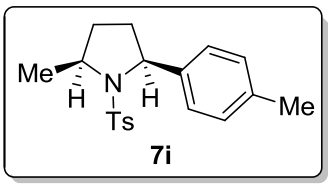

Me
H
N
H
O
CF3

***rac*-7f**

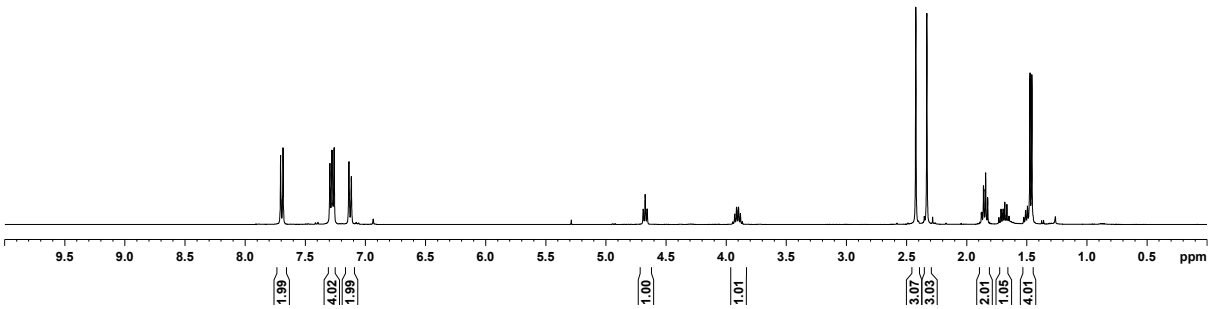

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

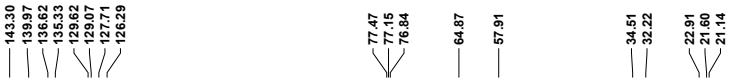

-70.64
-71.02
Me
H
N
H
O
CF3
rac-7f
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

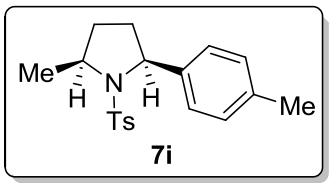

7.705
7.701
7.688
7.684
7.295
7.280
7.275
7.260
7.137
7.117
4.691
4.675
4.658
3.946
3.930
3.914
3.899
3.882
3.867
2.424
2.332
1.879
1.875
1.861
1.859
1.843
1.826
1.733
1.715
1.702
1.698
1.684
1.667
1.649
1.510
1.496
1.474
1.458


Me
H
N
H
Ts
Me

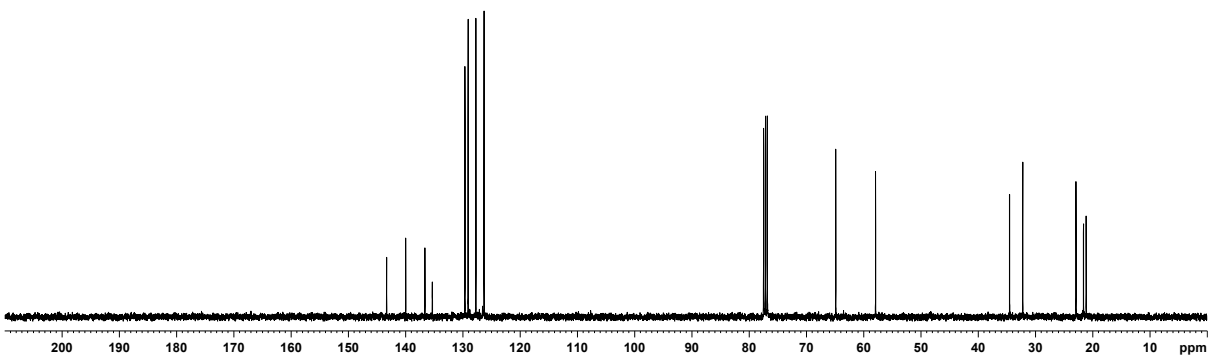
7i

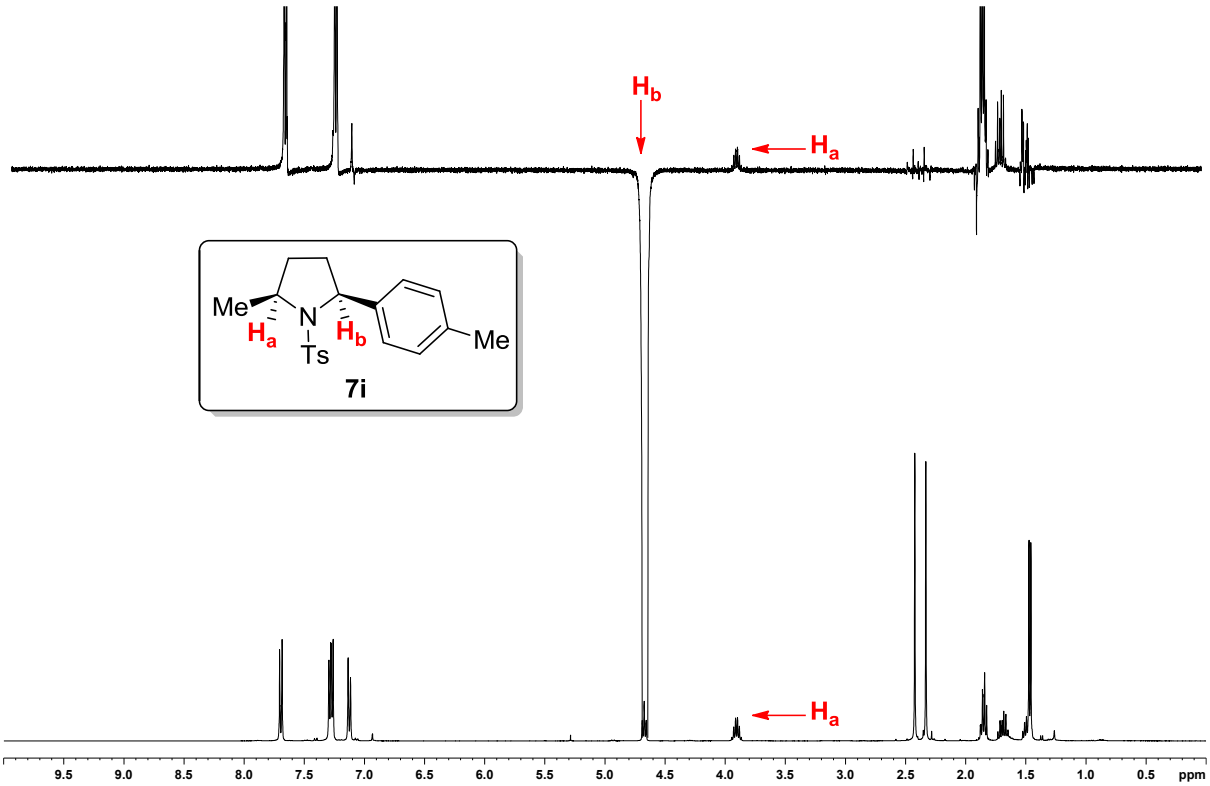

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
4.02
1.99
1.00
1.01
3.07
3.03
2.01
1.05
4.01

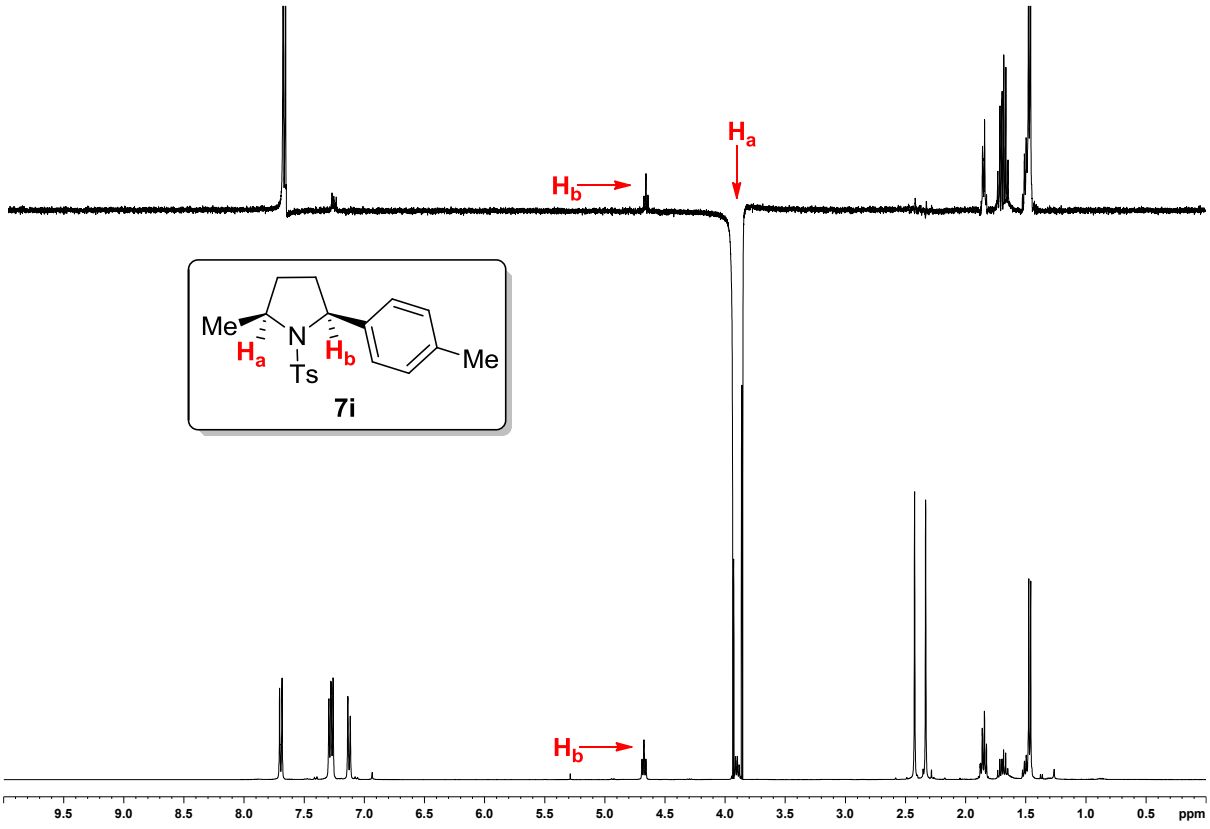

143.30
139.97
136.62
135.33
129.62
129.07
127.71
126.29
77.47
77.15
76.84
64.87
57.91
34.51
32.22
22.91
21.60
21.14

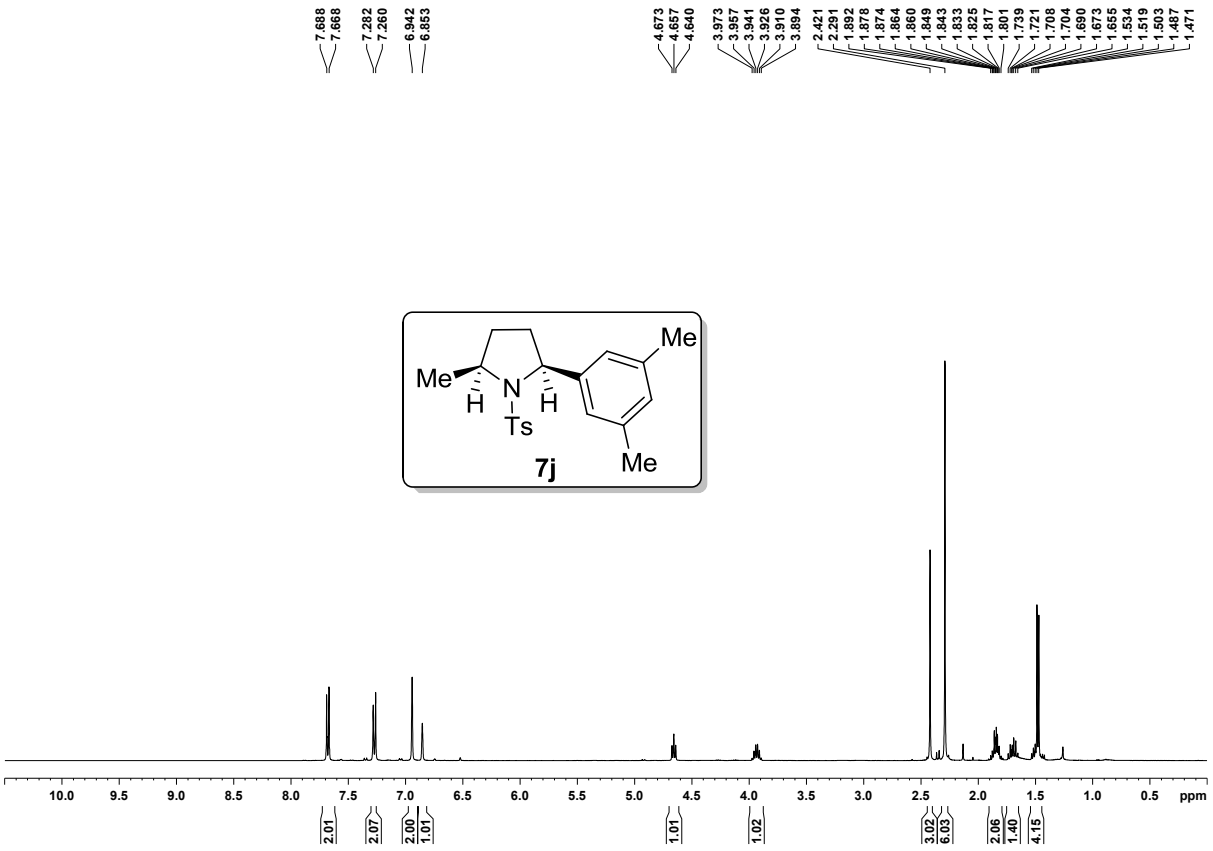

Me
H
N
H
Ts
Me

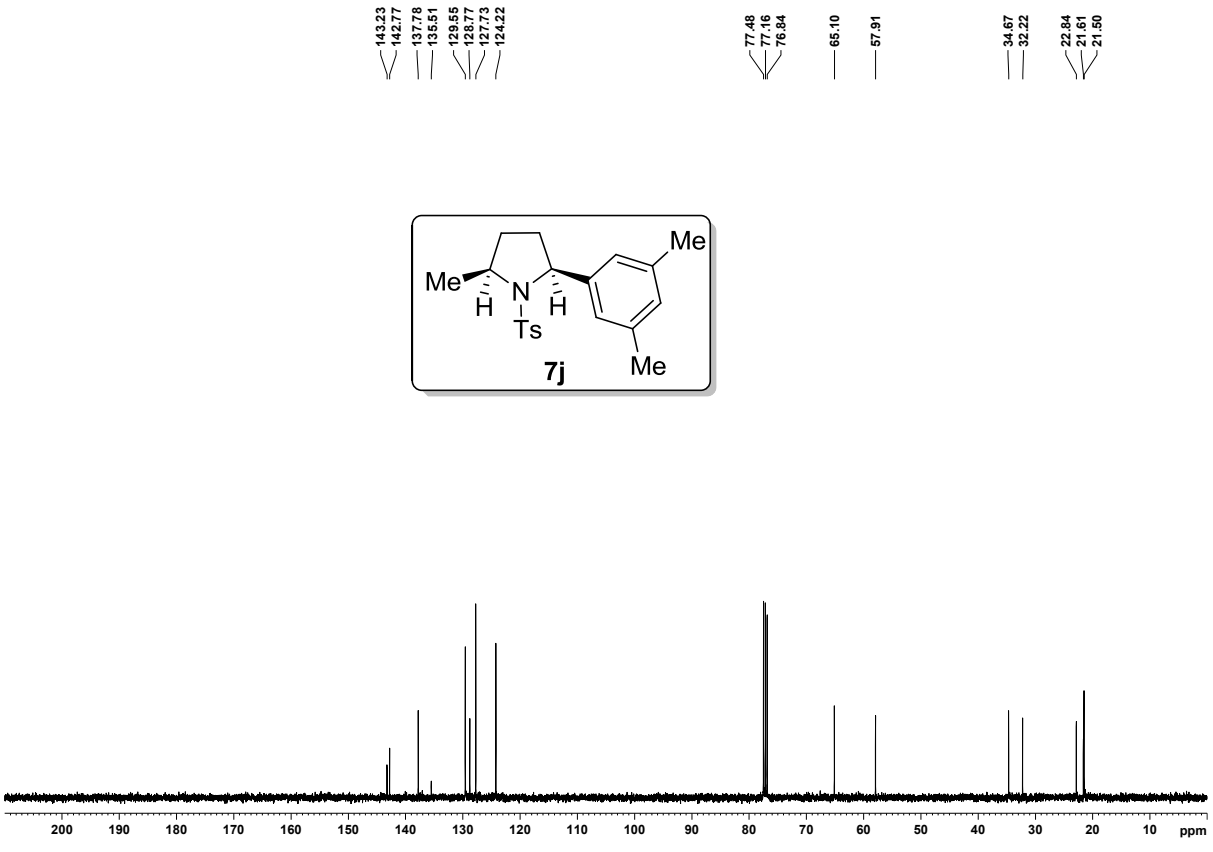
7i

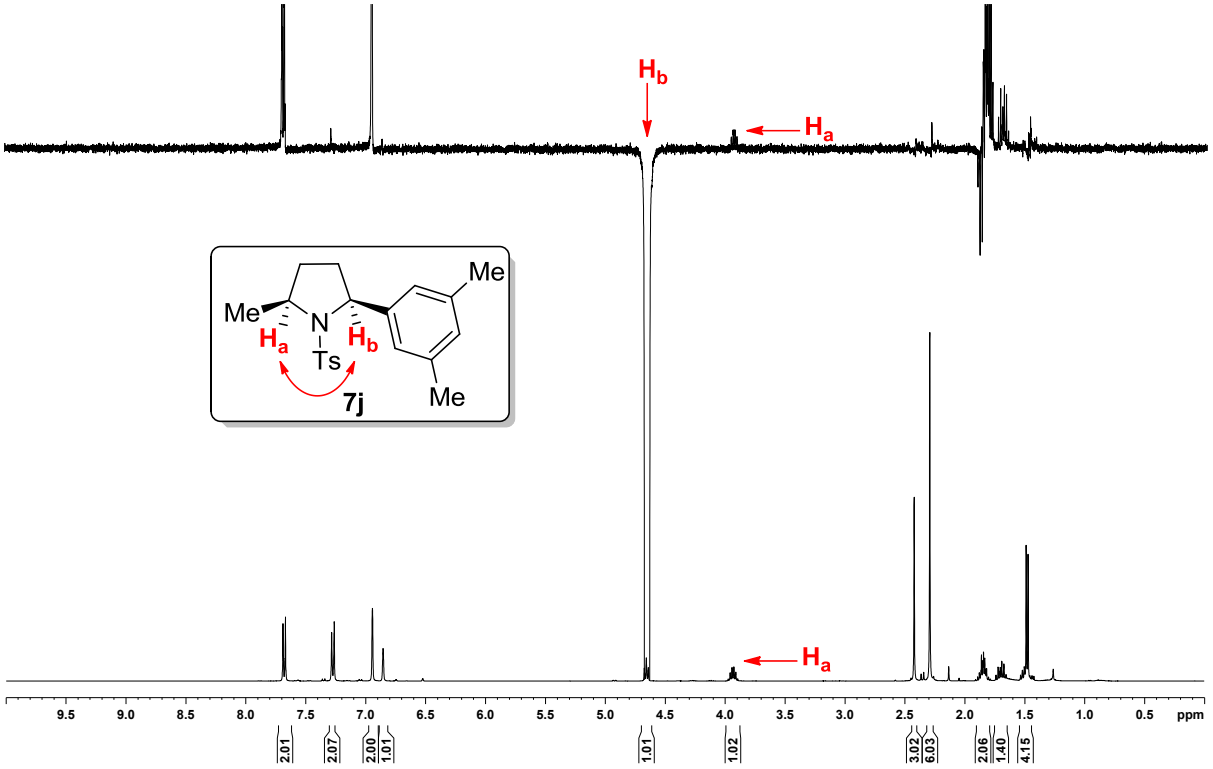

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

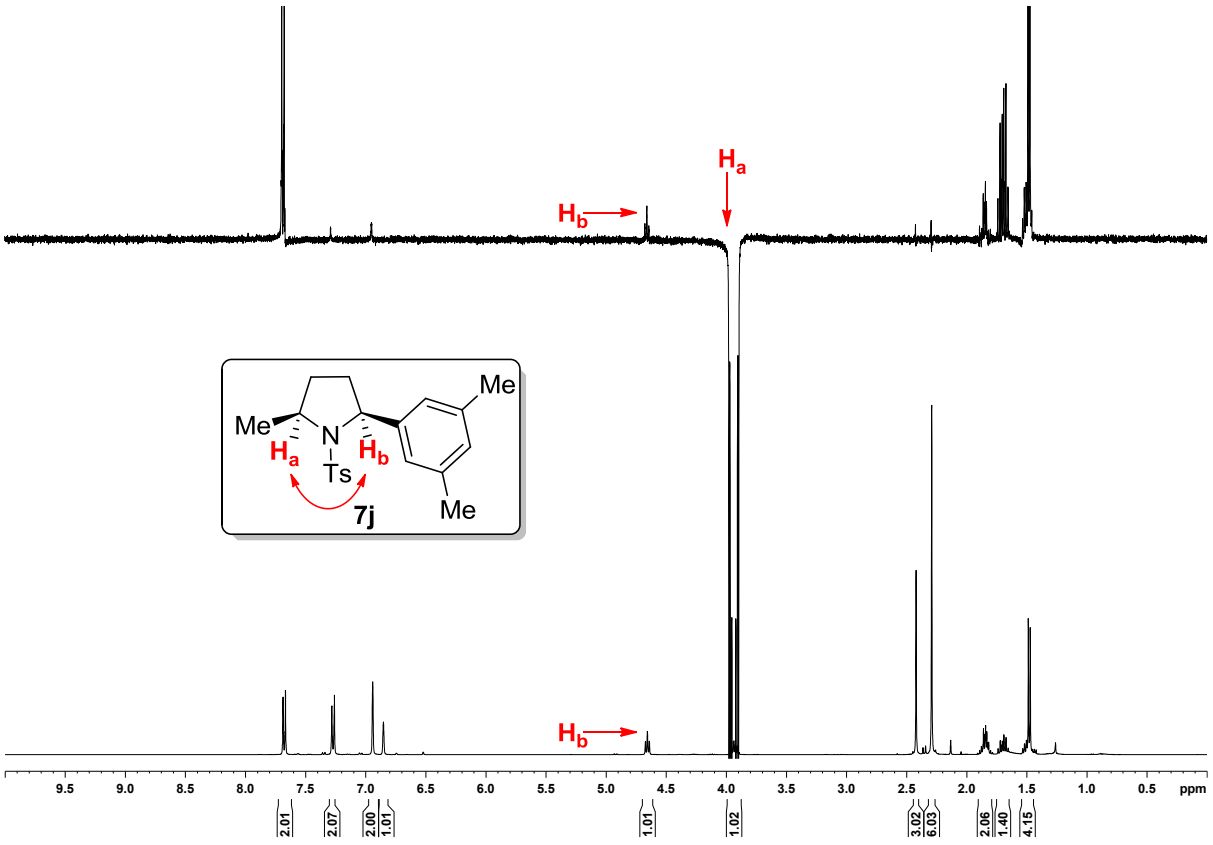

Hb
Ha
Me
Ha
N
Hb
Ts
Me
7i
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Ha
Hb
Me
Ha
N
Hb
Ts
Me
7i
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


7.688
7.668
7.282
7.260
6.942
6.853
4.673
4.657
4.640
3.973
3.957
3.941
3.926
3.910
3.894
2.421
2.291
1.892
1.878
1.874
1.864
1.860
1.849
1.843
1.833
1.825
1.817
1.801
1.739
1.721
1.708
1.704
1.690
1.673
1.655
1.534
1.519
1.503
1.487
1.471
Me
Me
H
N
H
Ts
Me
7j
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.07
2.00
1.01
1.01
1.02
3.02
6.03
2.06
1.40
4.15


143.23
142.77
137.78
135.51
129.55
128.77
127.73
124.22
77.48
77.16
76.84
65.10
57.91
34.67
32.22
22.84
21.61
21.50
Me
Me
H
N
H
Ts
Me
7j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Hb
Ha
Me
Me
N
Ha
Hb
Ts
7j
Me
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01 2.07 2.00 1.01 1.01 1.02 3.02 6.03 2.06 1.40 4.15


Ha
Hb
Me
Me
N
Ha
Hb
Ts
7j
Me
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01 2.07 2.00 1.01 1.01 1.02 3.02 6.03 2.06 1.40 4.15


7.685
7.669
7.293
7.284
7.276
7.268
7.260
6.856
6.838
4.676
4.664
4.650
3.938
3.933
3.925
3.912
3.900
3.887
3.792
2.418
1.858
1.844
1.831
1.817
1.734
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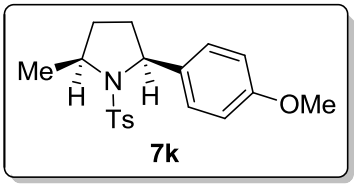
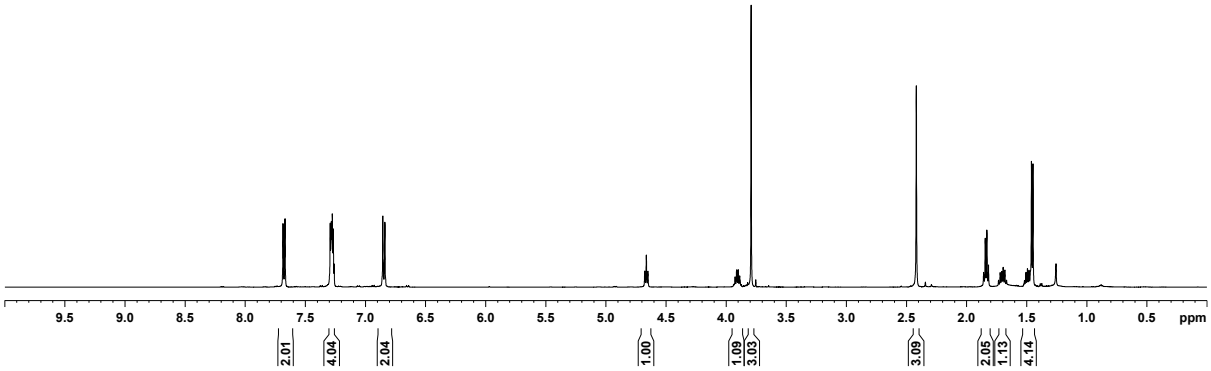
1.695
1.681
1.667
1.518
1.506
1.494
1.480
1.460
1.447


Me
H
N
H
Ts
OMe

7k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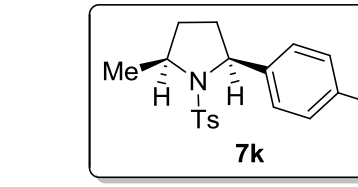
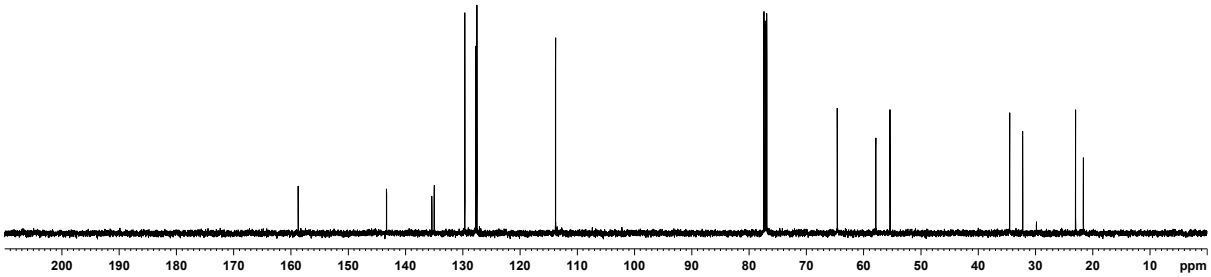
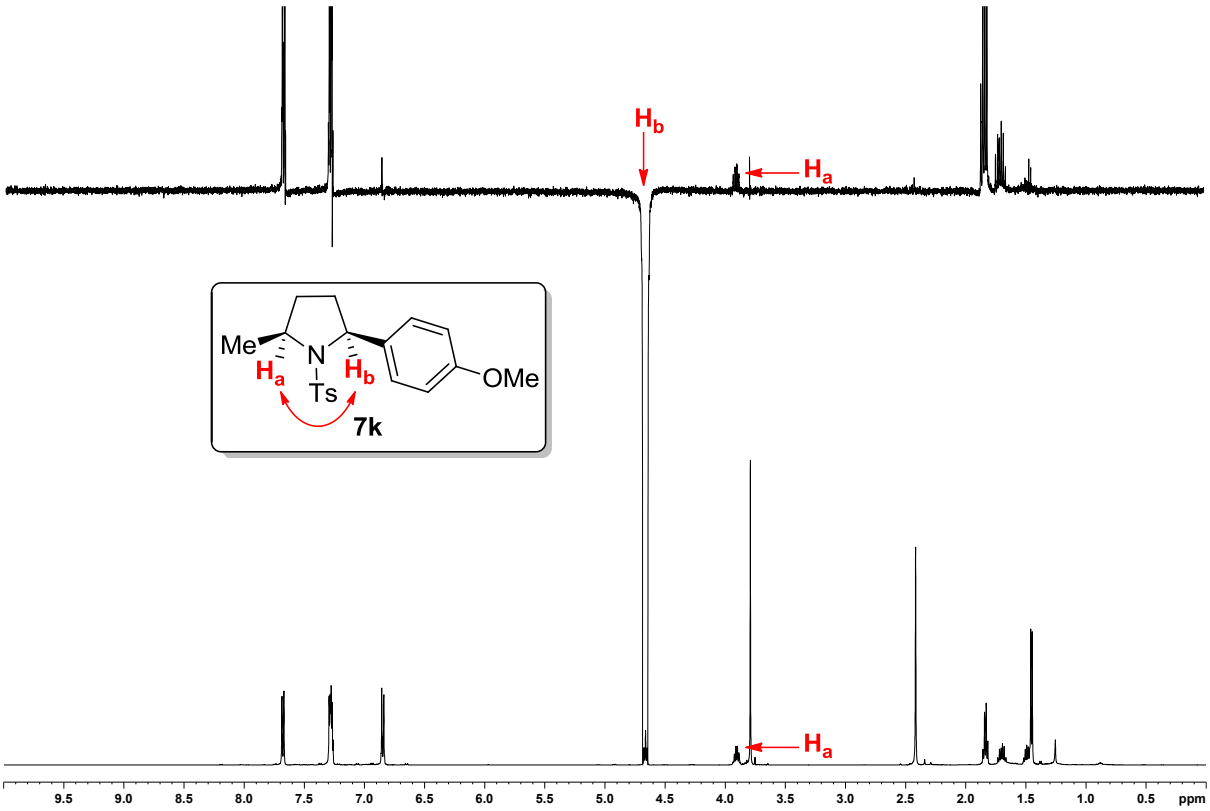
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
4.04
2.04
1.00
1.09
3.03
3.09
2.05
1.13
4.14

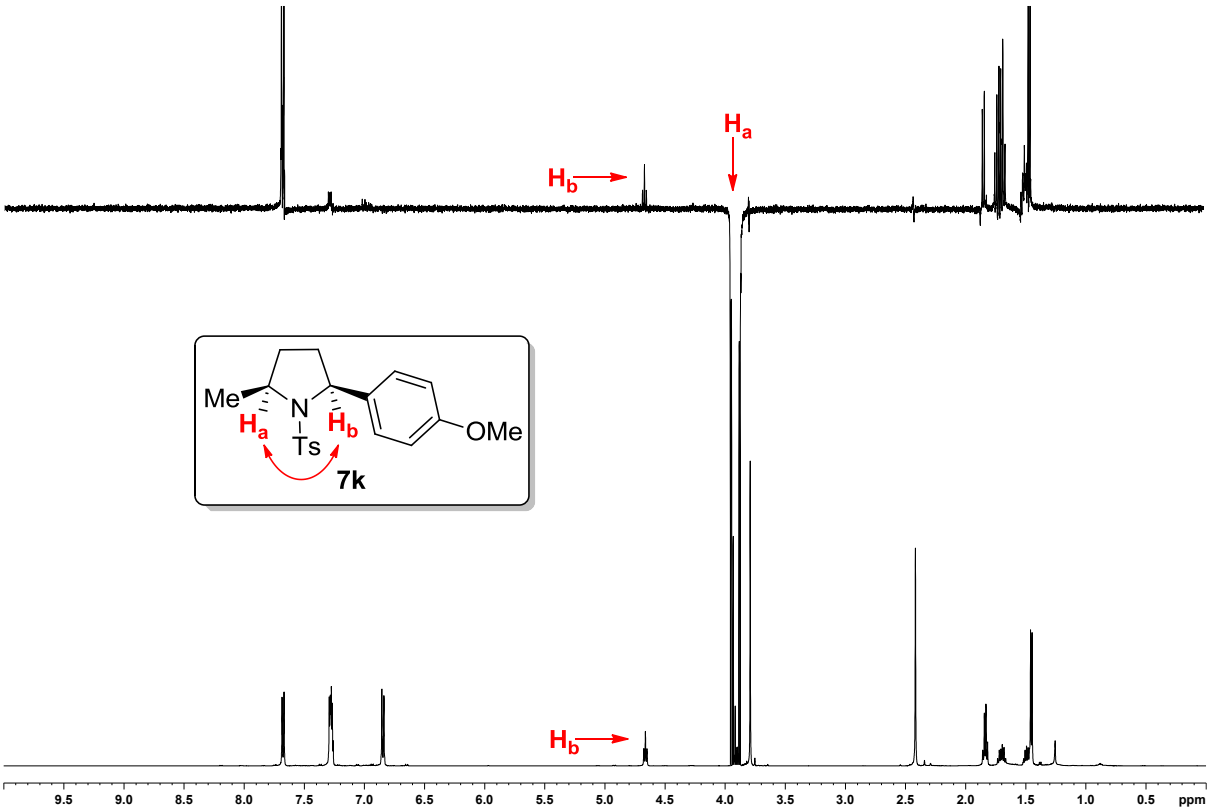

158.70
143.30
135.39
134.97
129.63
127.70
127.52
113.78
77.41
77.16
76.90
64.59
57.86
55.38
34.49
32.21
22.98
21.62

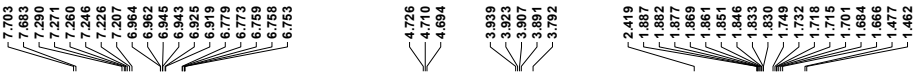

Me
H
N
H
Ts
OMe

7k


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Hb
Ha
Me
N
Ts
Ha
Hb
OMe
7k
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Ha
Hb
Me
N
Ts
Ha
Hb
OMe
7k
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


7.703
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7.290
7.271
7.260
7.246
7.226
7.207
6.964
6.962
6.945
6.943
6.925
6.919
6.779
6.773
6.759
6.758
6.753
4.726
4.710
4.694
3.939
3.923
3.907
3.891
3.792
2.419
1.887
1.882
1.877
1.869
1.861
1.851
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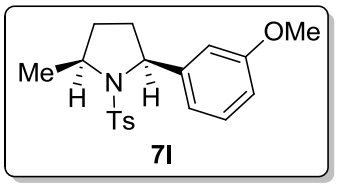
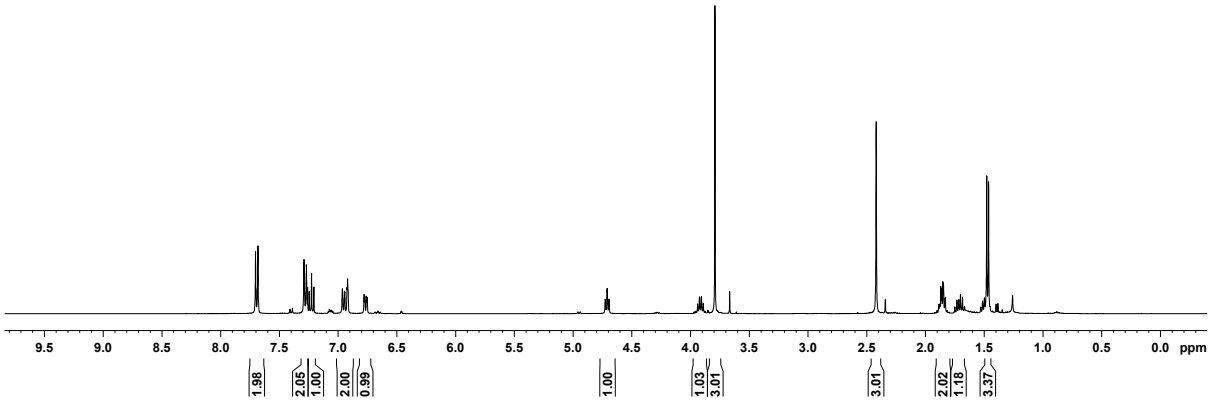
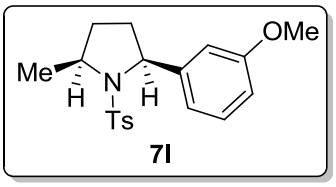
1.701
1.684
1.666
1.477
1.462


OMe
Me
H
N
H
Ts

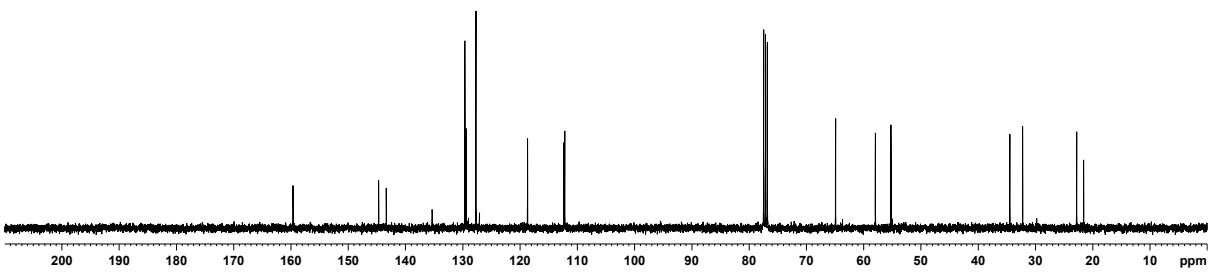
7l

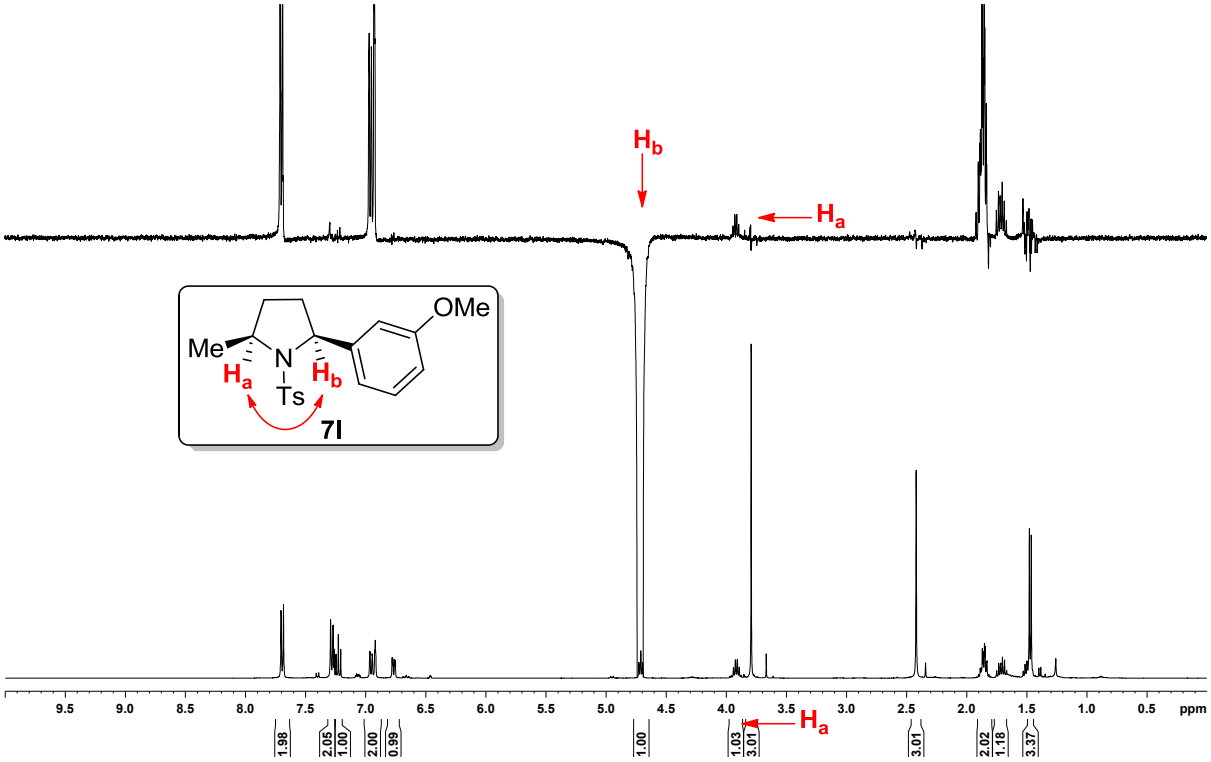

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.98
2.05
1.00
2.00
0.99
1.00
1.03
3.01
3.01
2.02
1.18
3.37

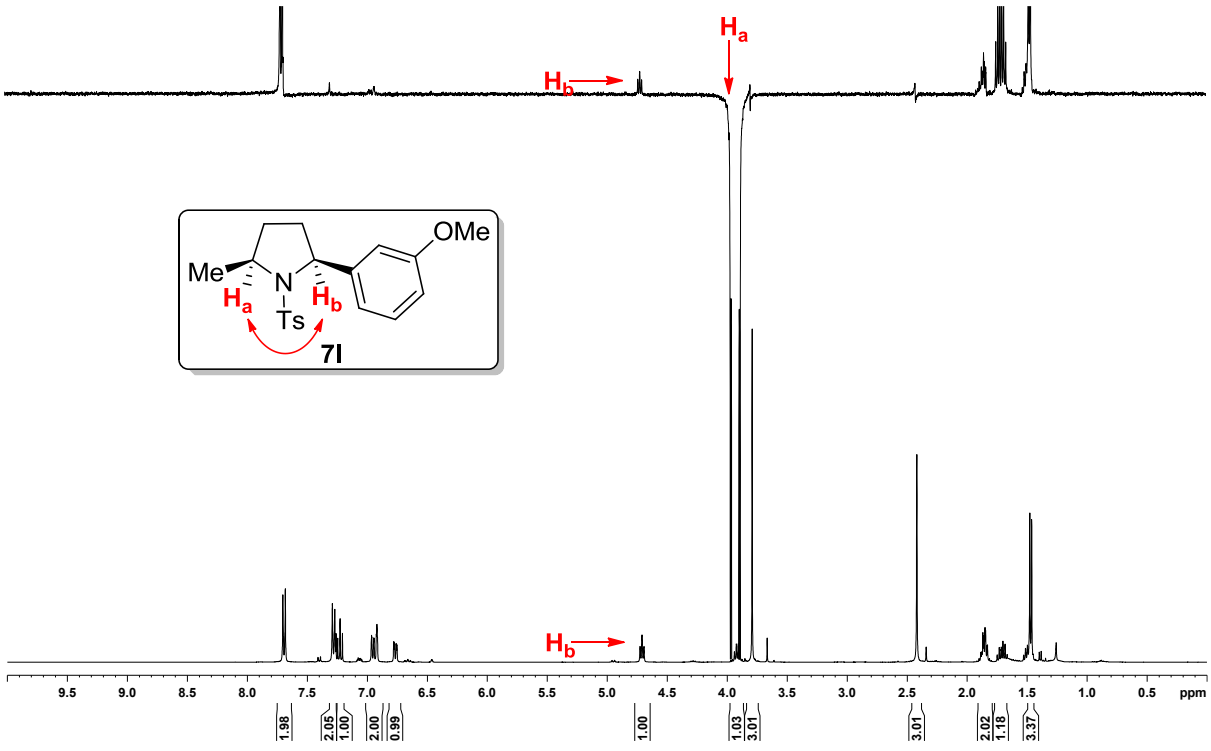

159.67
144.72
143.38
135.36
129.65
129.41
127.72
118.71
112.35
112.21
77.48
77.16
76.84
64.93
57.97
55.25
34.49
32.26
22.83
21.62

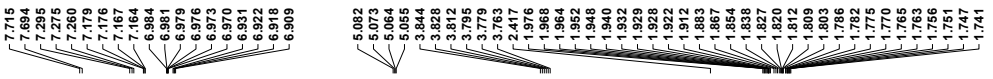

OMe
Me
H
N
H
Ts

7l


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Hb
Ha
OMe
Me
N
Ha
Hb
Ts
7l
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98 2.05 1.00 2.00 0.99 1.00 1.03 3.01 3.01 2.02 1.18 3.37


Ha
Hb
OMe
Me
N
Ha
Hb
Ts
7l
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98 2.05 1.00 2.00 0.99 1.00 1.03 3.01 3.01 2.02 1.18 3.37


7.715
7.694
7.295
7.275
7.260
7.179
7.176
7.167
7.164
6.984
6.981
6.979
6.976
6.973
6.970
6.931
6.922
6.918
6.909
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5.073
5.064
5.055
3.844
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3.779
3.763
2.417
1.976
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1.964
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1.948
1.940
1.932
1.929
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1.922
1.912
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1.867
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1.838
1.827
1.820
1.812
1.809
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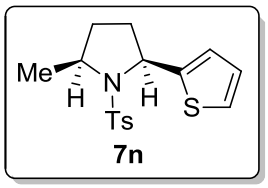
1.741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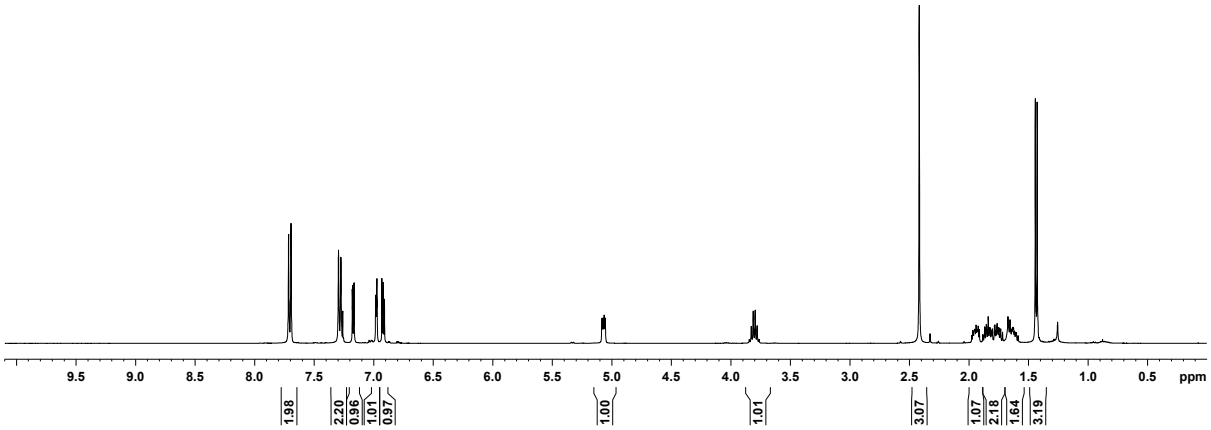
N
Ts
H
S
7n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6.0
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2.5
2.0
1.5
1.0
0.5
ppm
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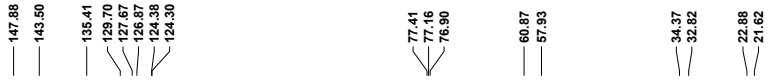
0.96
1.01
0.97
1.00
1.01
3.07
1.07
2.18
1.64
3.19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124.30
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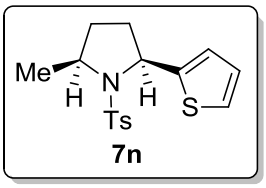
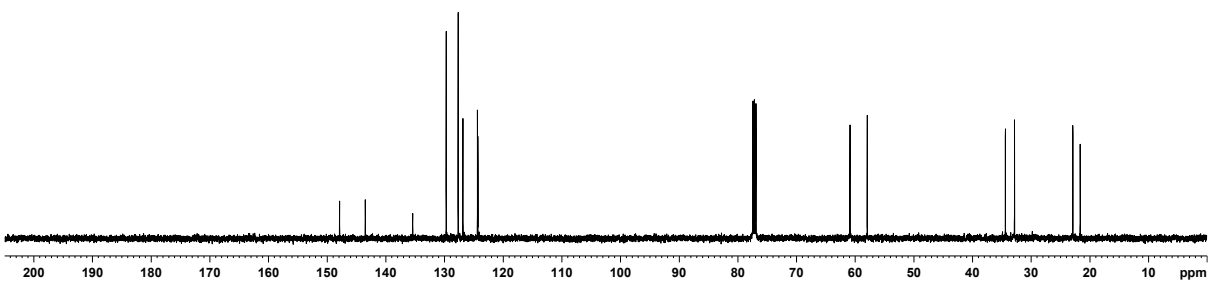
76.90
60.87
57.93
34.37
32.82
22.88
21.62


Me
H
N
Ts
H
S
7n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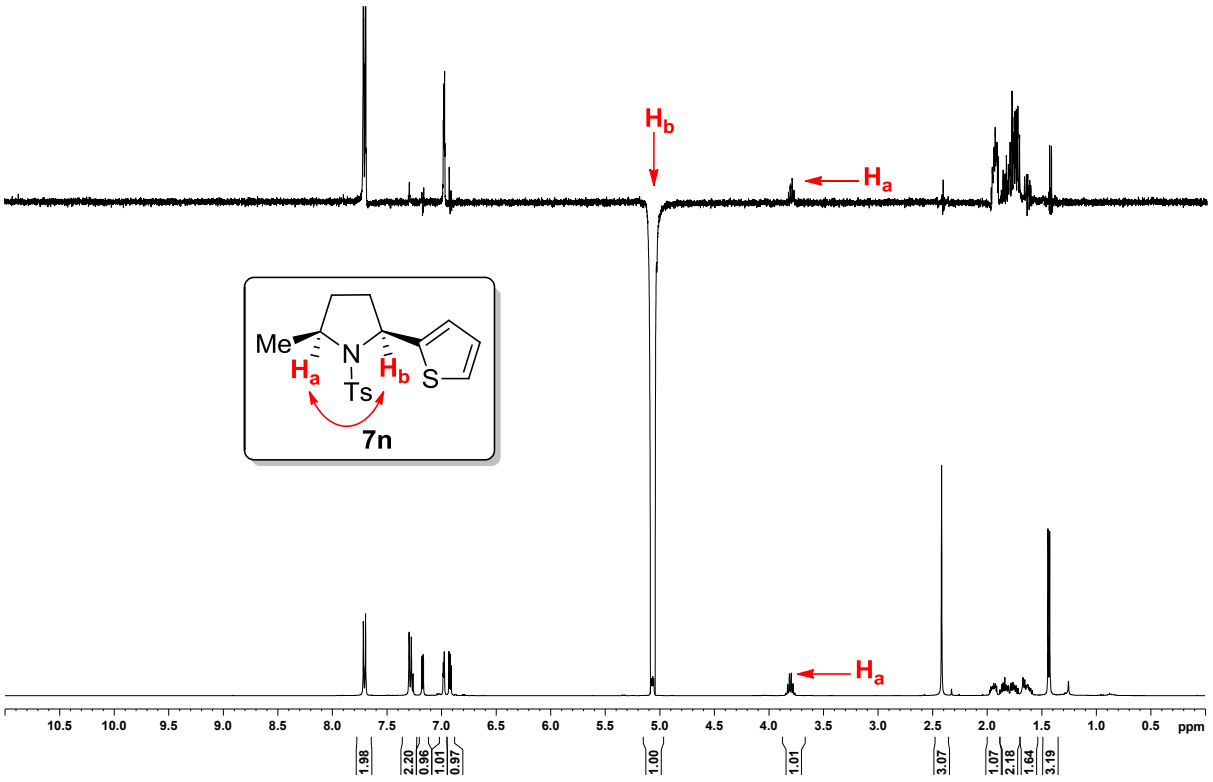
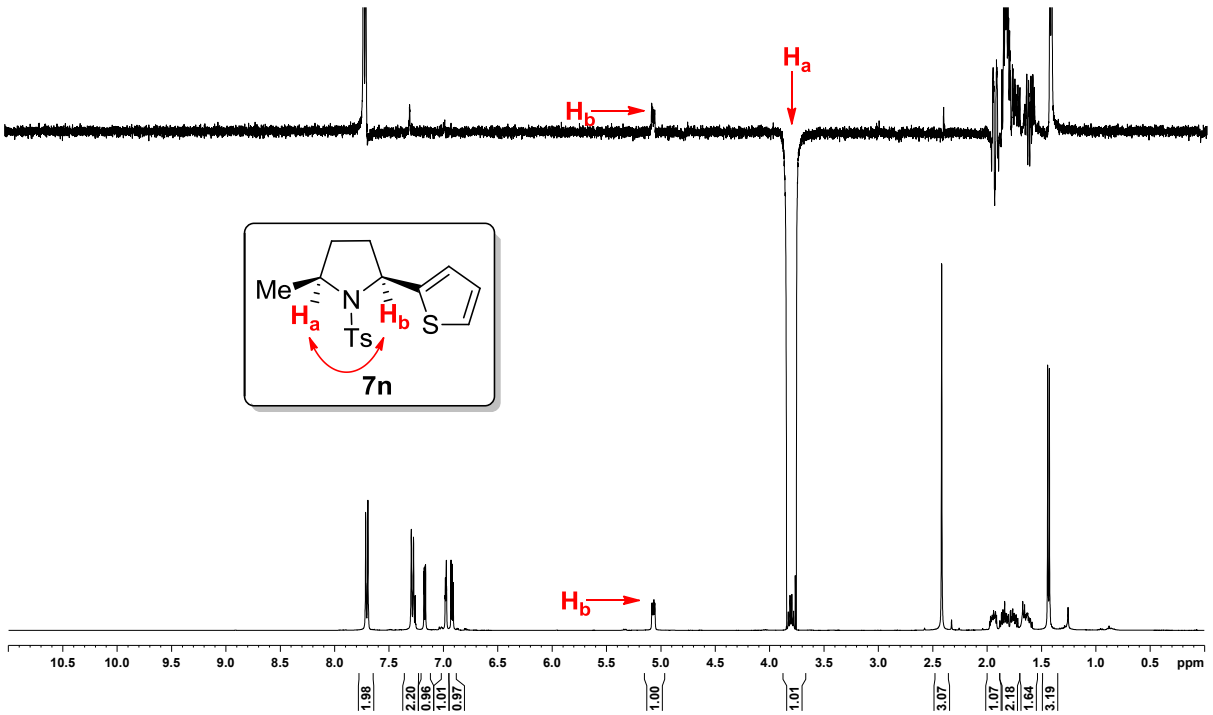
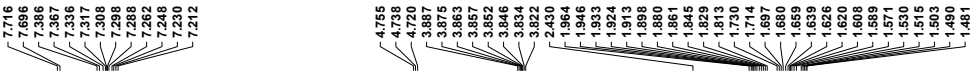
30
20
10
ppm


Hb
Ha
Me
N
Ha
Hb
S
Ts
7n
Ha
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98 2.20 0.96 1.01 0.97 1.00 1.01 3.07 1.07 2.18 1.64 3.19


Ha
Hb
Me
N
Ha
Hb
S
Ts
7n
Hb
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98 2.20 0.96 1.01 0.97 1.00 1.01 3.07 1.07 2.18 1.64 3.19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7.248
7.230
7.212
4.755
4.738
4.720
3.887
3.875
3.863
3.857
3.852
3.846
3.834
3.822
2.430
1.964
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1.933
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1.913
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1.861
1.845
1.829
1.813
1.730
1.714
1.697
1.680
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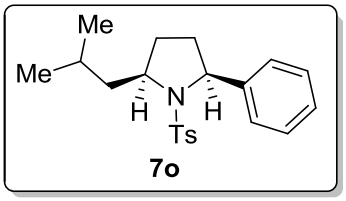
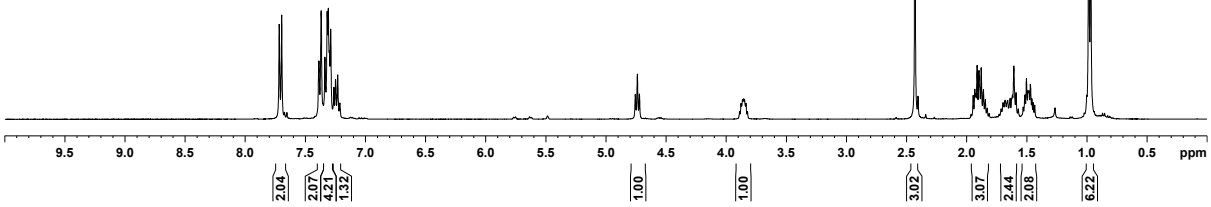
1.503
1.490
1.481


Me
Me
H
N
H
Ts

7o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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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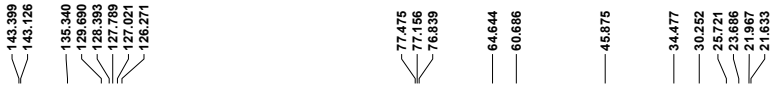
2.07
4.21
1.32
1.00
1.00
3.02
3.07
2.44
2.08
6.22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127.021
126.271
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76.839
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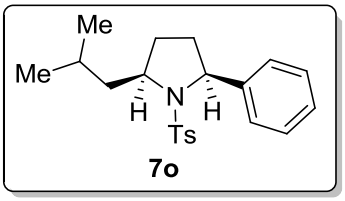
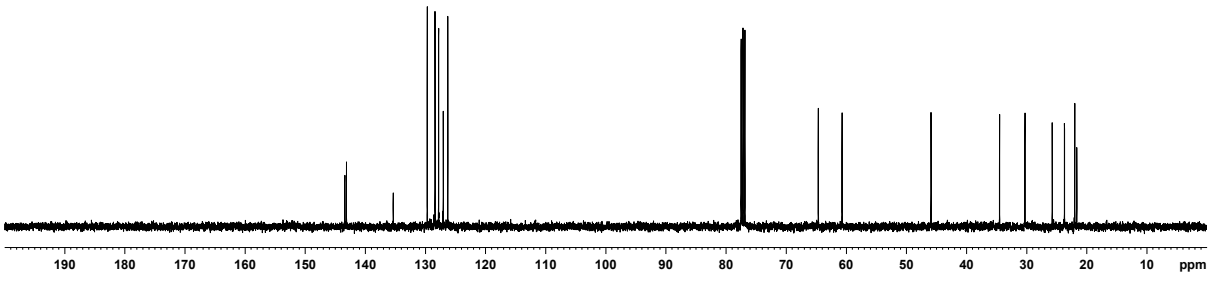
30.252
25.721
23.686
21.967
21.633


Me
Me
H
N
H
Ts

7o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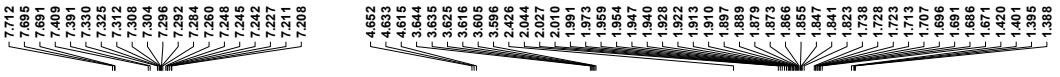
50
40
30
20
10
ppm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7.292
7.284
7.260
7.248
7.245
7.242
7.227
7.211
7.208
4.652
4.633
4.615
3.644
3.635
3.625
3.616
3.605
3.596
2.426
2.044
2.027
2.010
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1.973
1.959
1.954
1.947
1.940
1.928
1.922
1.913
1.910
1.897
1.889
1.879
1.873
1.866
1.855
1.847
1.841
1.823
1.738
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1.671
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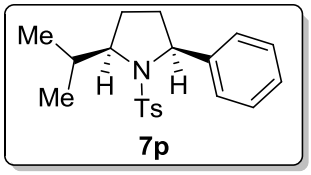
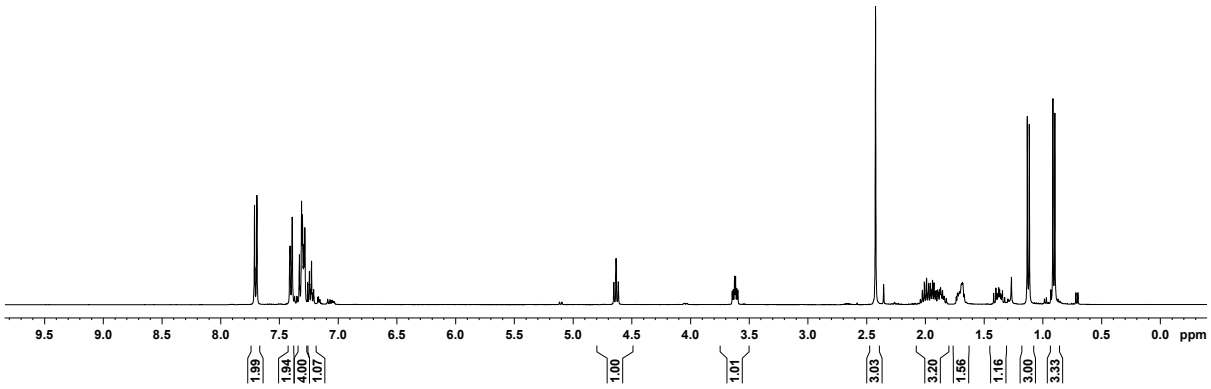
1.395
1.388


Me
H
N
H
Me
Ts

7p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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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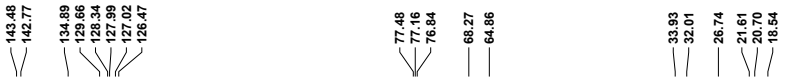
4.00
1.07
1.00
1.01
3.03
3.20
1.56
1.16
3.00
3.33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127.99
127.02
126.47
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77.16
76.84
68.27
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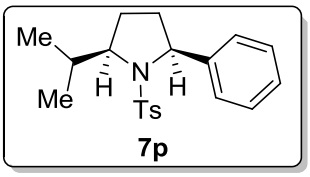
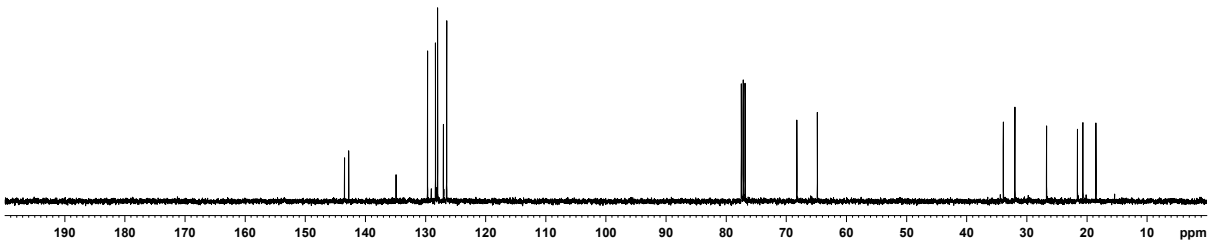
32.01
26.74
21.61
20.70
18.54


Me
H
N
H
Me
Ts

7p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110
100
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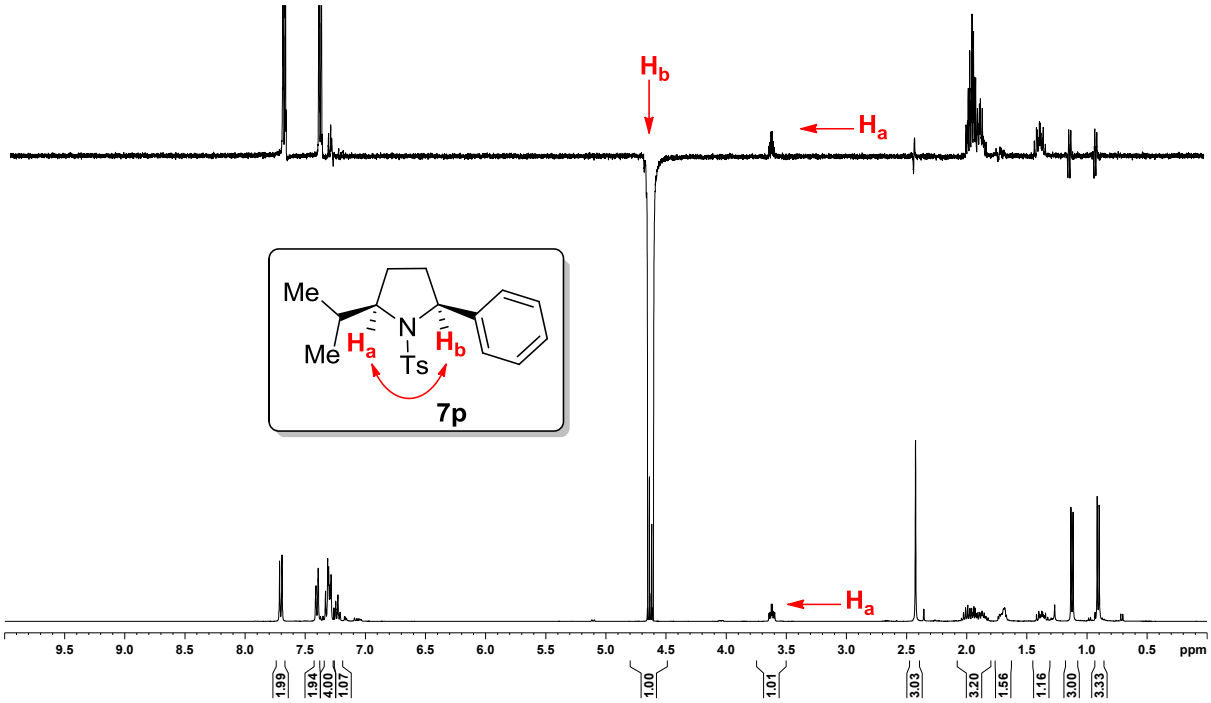
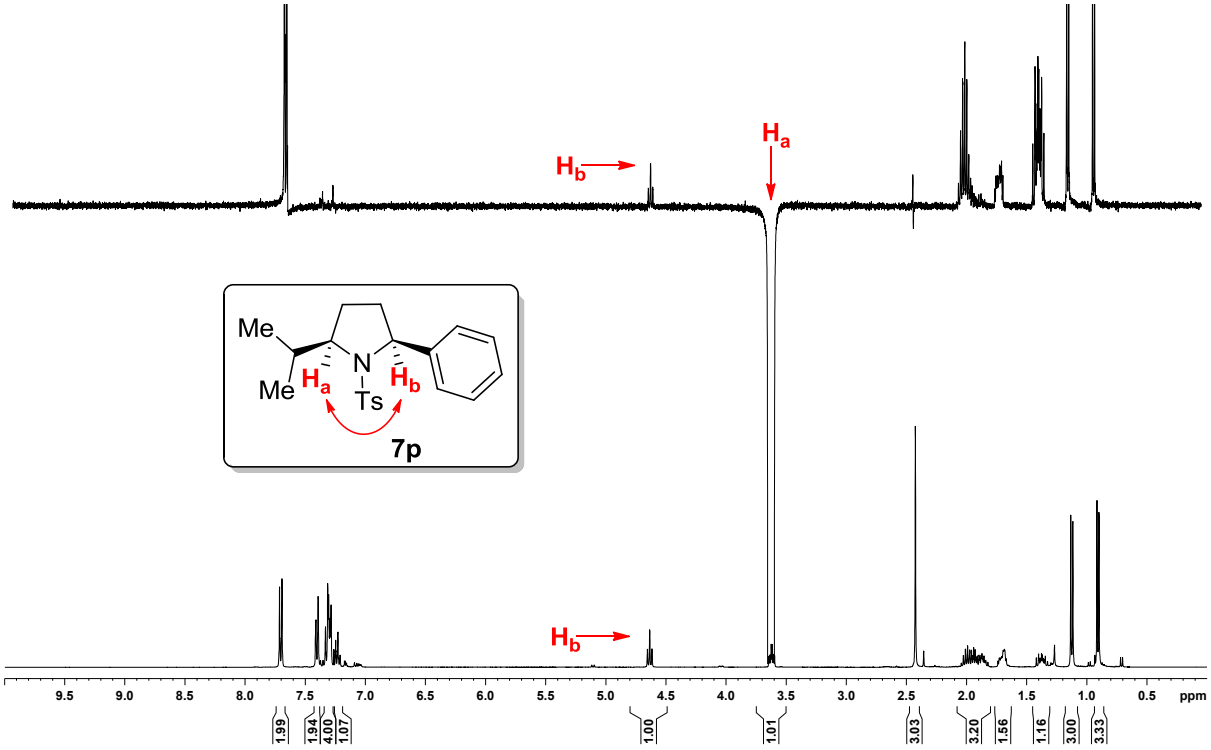
80
70
60
50
40
30
20
10
ppm


Hb
Ha
Me
Me
Ha
N
Hb
Ts
7p
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99 1.94 4.00 1.07 1.00 1.01 3.03 3.20 1.56 1.16 3.00 3.33


Ha
Hb
Me
Me
Ha
N
Hb
Ts
7p
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99 1.94 4.00 1.07 1.00 1.01 3.03 3.20 1.56 1.16 3.00 3.33


7.583
7.563
7.476
7.457
7.362
7.344
7.325
7.291
7.273
7.259
7.255
7.243
7.223
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4.925
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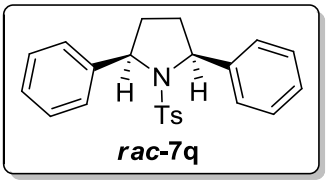
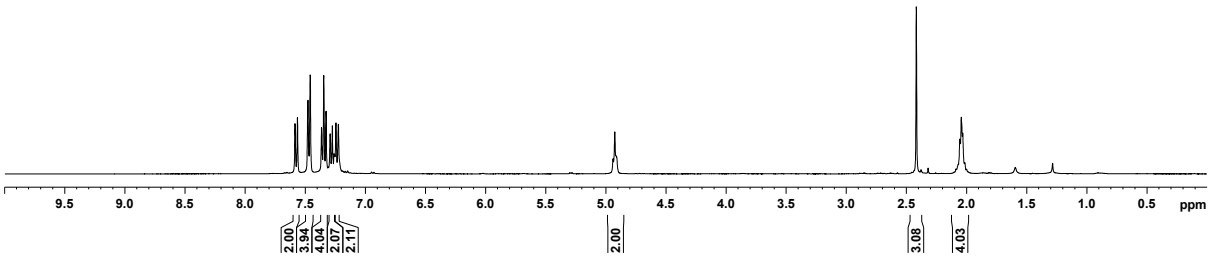
2.070
2.056
2.044
2.031
2.014


H
N
H
Ts

***rac*-7q**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6.0
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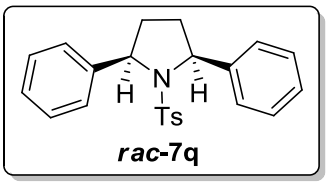
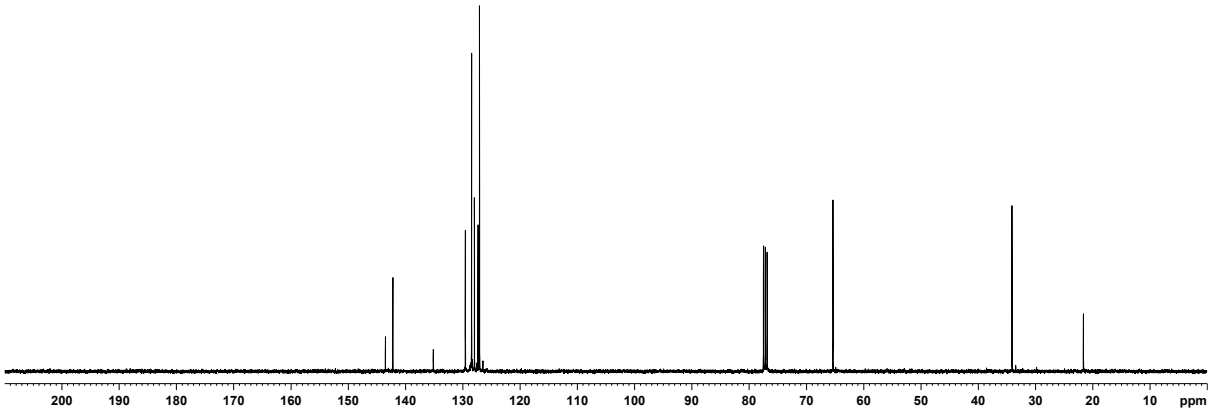
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
3.94
4.04
2.07
2.11
2.00
3.08
4.03


143.49
142.20
135.14
129.53
128.44
127.95
127.32
127.06
77.48
77.16
76.84
65.35
34.09
21.61


H
N
H
Ts

***rac*-7q**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120
110
100
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80
70
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50
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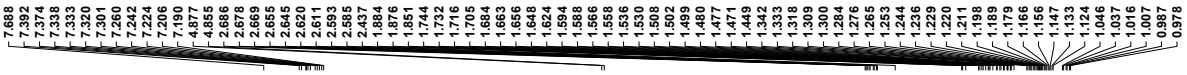
30
20
10
ppm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1.876
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1.732
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1.705
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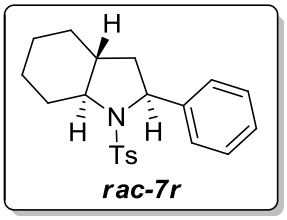
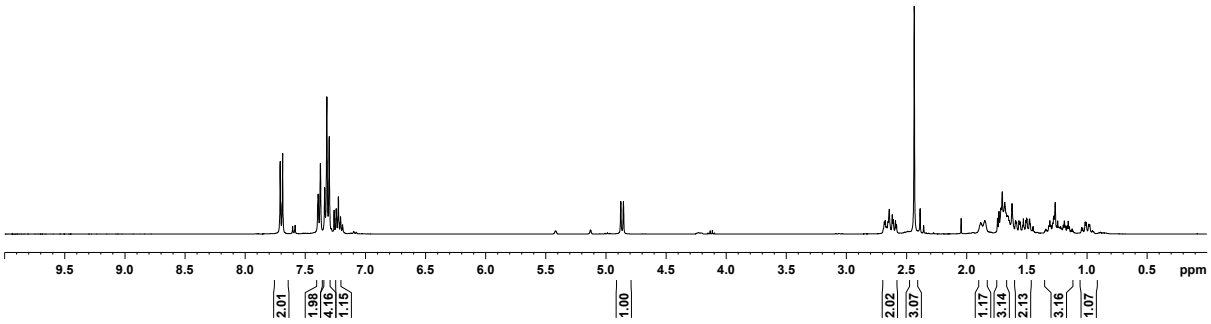

H
N
H
H
Ts

rac-7r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3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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2.02
3.07
1.17
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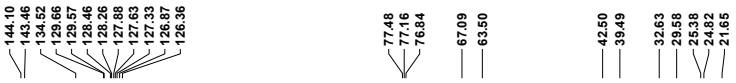
2.13
3.16
1.07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32.63
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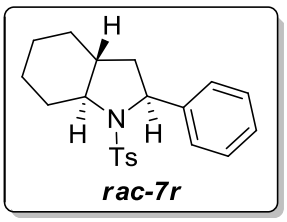
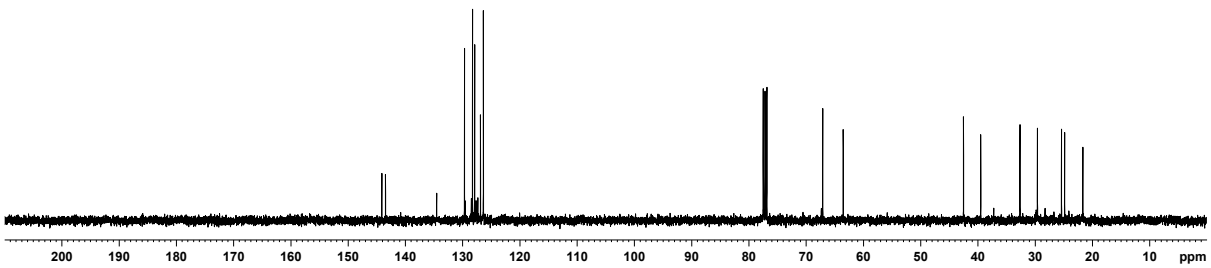
24.82
21.65


H
N
H
H
Ts

rac-7r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100
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70
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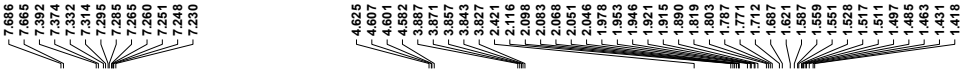
30
20
10
ppm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7.265
7.260
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7.230
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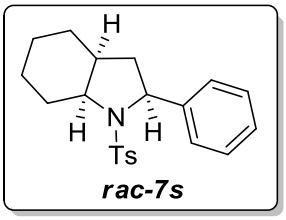
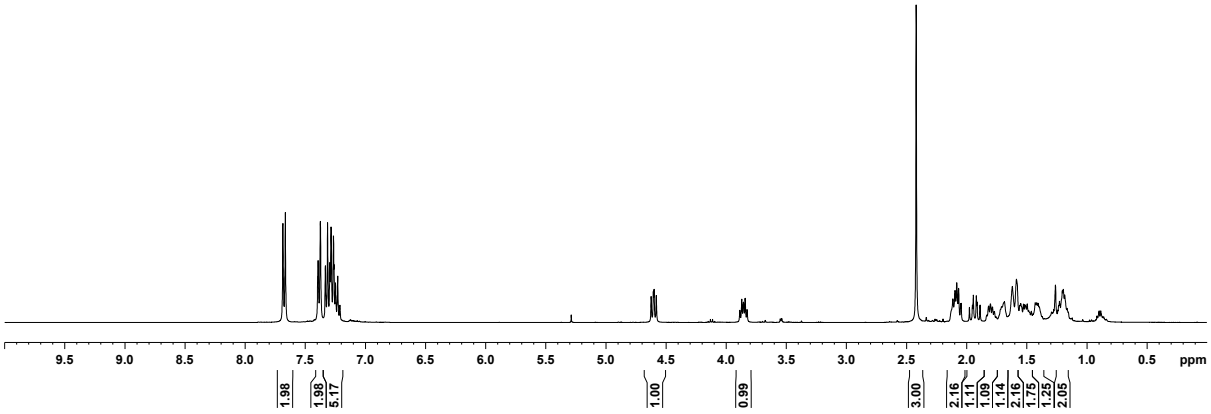
1.463
1.431
1.418


H
H
N
H
Ts

rac-7s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6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
1.98
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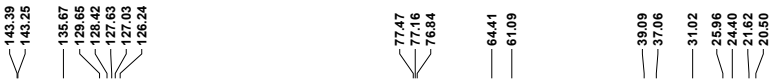
3.00
2.16
1.11
1.09
1.14
2.16
1.75
1.25
2.05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127.63
127.03
126.24
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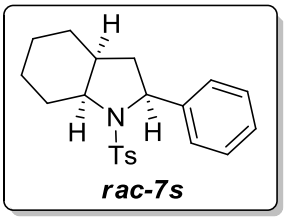
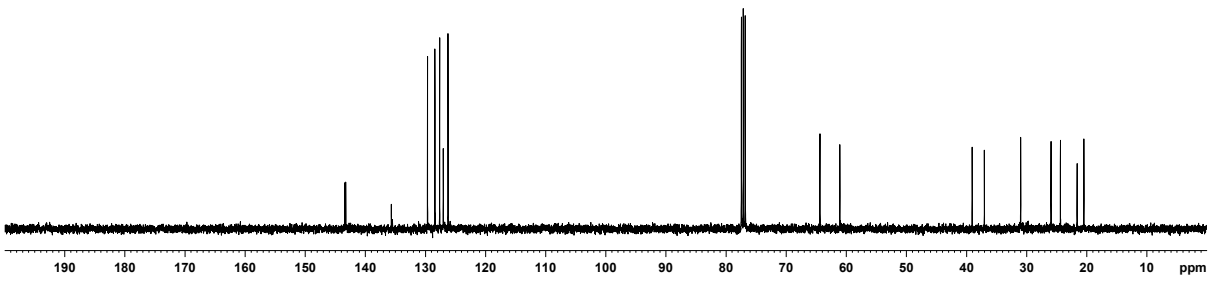
64.41
61.09
39.09
37.06
31.02
25.96
24.40
21.62
20.50


H
H
N
H
Ts

rac-7s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110
100
90
80
70
60
50
40
30
20
10
ppm


7.592
7.572
7.330
7.313
7.284
7.279
7.266
7.260
7.255
7.235
7.228
7.216
7.210
4.410
4.392
4.387
4.369
4.216
4.207
4.196
4.187
4.176
4.167
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2.487
2.473
2.452
2.447
2.414
2.274
2.256
2.241
2.235
2.223
2.203
2.164
2.156
2.144
2.130
2.121
2.112
2.102
2.000
1.982
1.979
1.960
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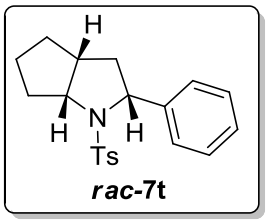
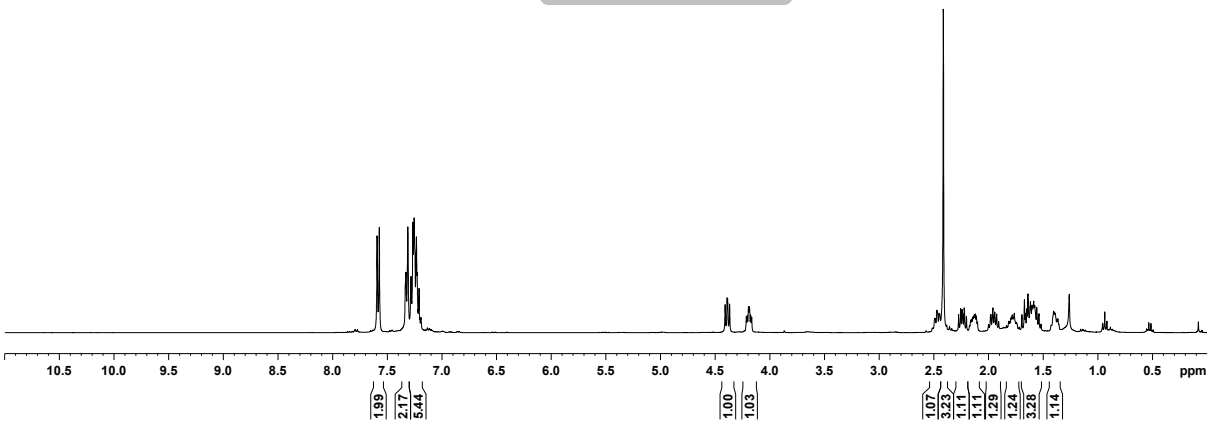
1.805
1.796
1.783
1.774
1.765
1.746
1.695


H
H
N
H
Ts

***rac*-7t**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7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
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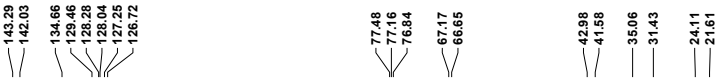
5.44
1.00
1.03
1.07
3.23
1.11
1.11
1.29
1.24
3.28
1.14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128.04
127.25
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77.16
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67.17
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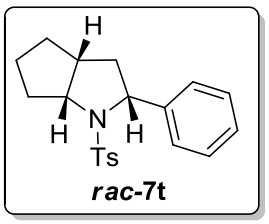
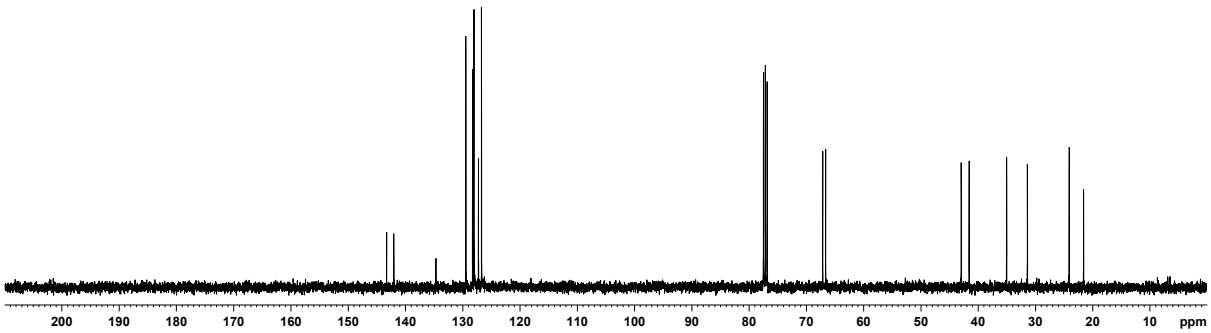
42.98
41.58
35.06
31.43
24.11
21.61


H
H
N
H
Ts

***rac*-7t**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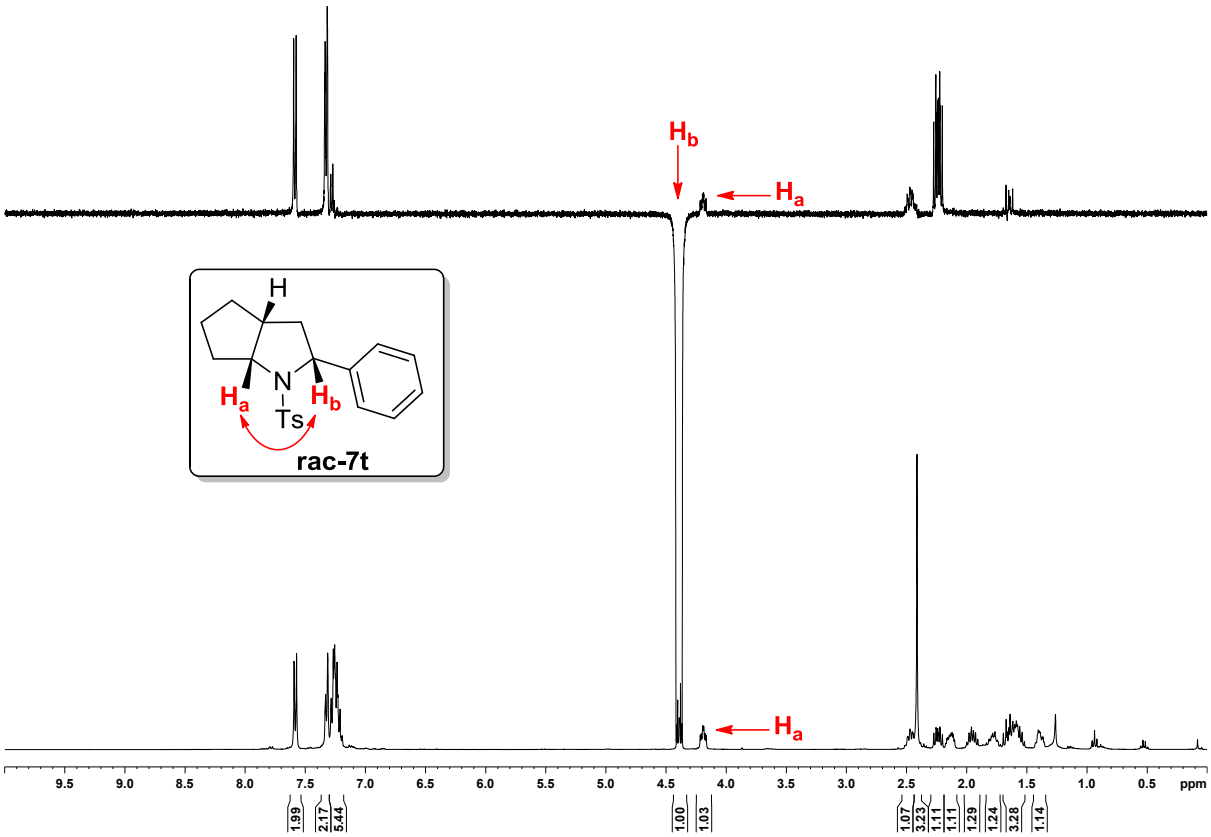
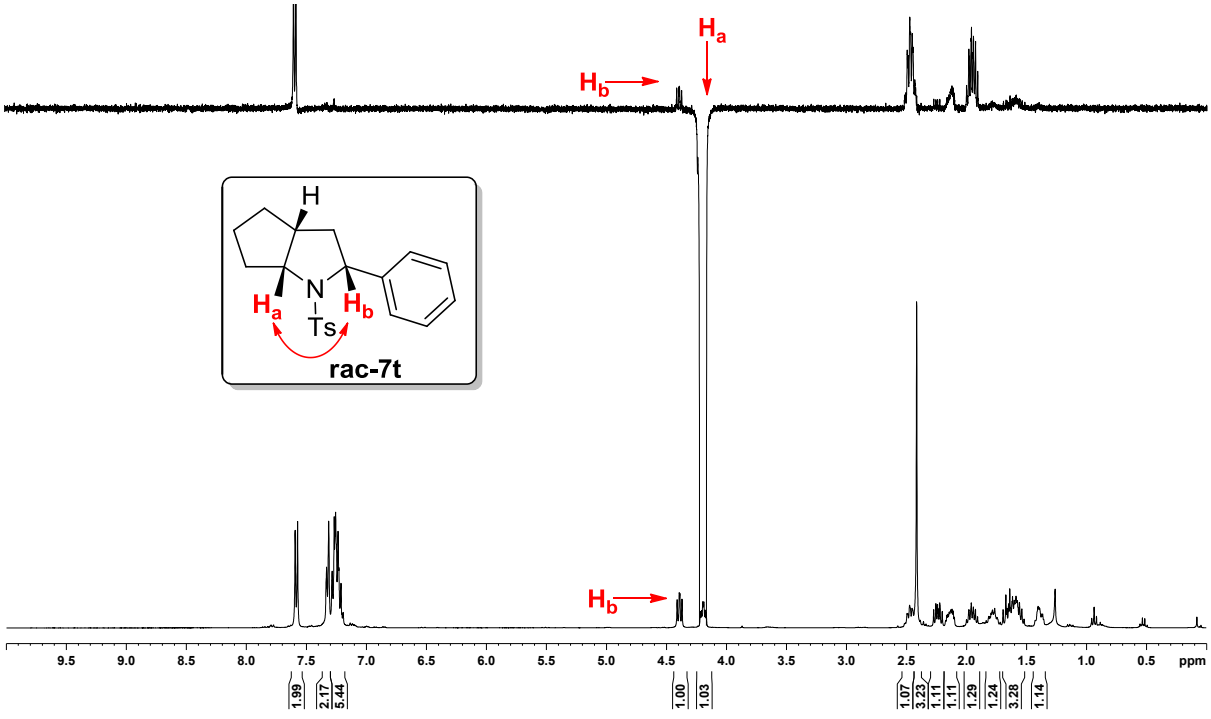
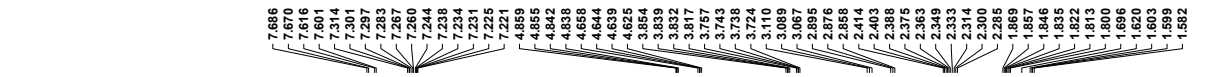
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Hb
Ha
H
N
Ts
Ha
Hb
rac-7t
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99 2.17 5.44 1.00 1.03 1.07 3.23 1.11 1.11 1.29 1.24 3.28 1.14


Ha
Hb
H
N
Ts
Ha
Hb
rac-7t
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99 2.17 5.44 1.00 1.03 1.07 3.23 1.11 1.11 1.29 1.24 3.28 1.14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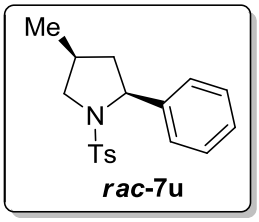
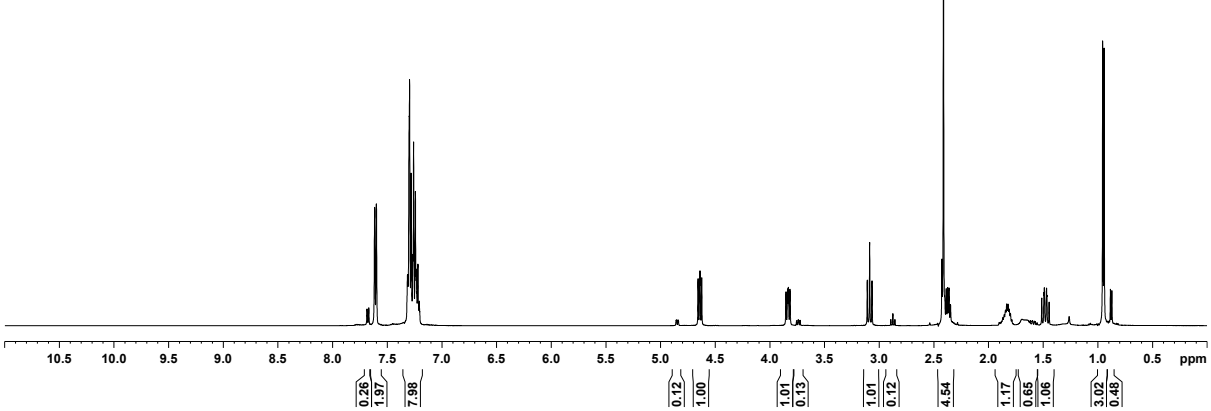
7.297
7.283
7.267
7.260
7.244
7.238
7.234
7.231
7.225
7.221
4.859
4.855
4.842
4.838
4.658
4.644
4.639
4.625
3.854
3.839
3.832
3.817
3.757
3.743
3.738
3.724
3.110
3.089
3.067
2.895
2.876
2.858
2.414
2.403
2.388
2.375
2.363
2.349
2.333
2.314
2.300
2.285
1.869
1.857
1.846
1.835
1.822
1.813
1.800
1.696
1.620
1.603
1.599
1.582


Me
N
Ts

***rac*-7u**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10.0
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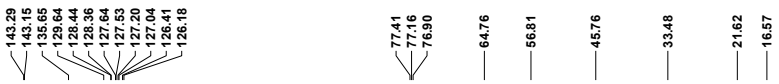
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.26
1.97
7.98
0.12
1.00
1.01
0.13
1.01
0.12
4.54
1.17
0.65
1.06
3.02
0.48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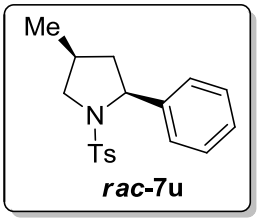
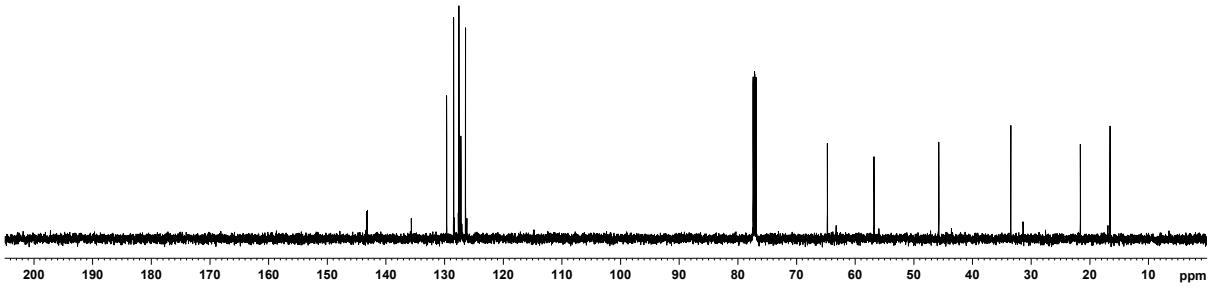
143.15
135.65
129.64
128.44
128.36
127.64
127.53
127.20
127.04
126.41
126.18
77.41
77.16
76.90
64.76
56.81
45.76
33.48
21.62
16.57


Me
N
Ts

***rac*-7u**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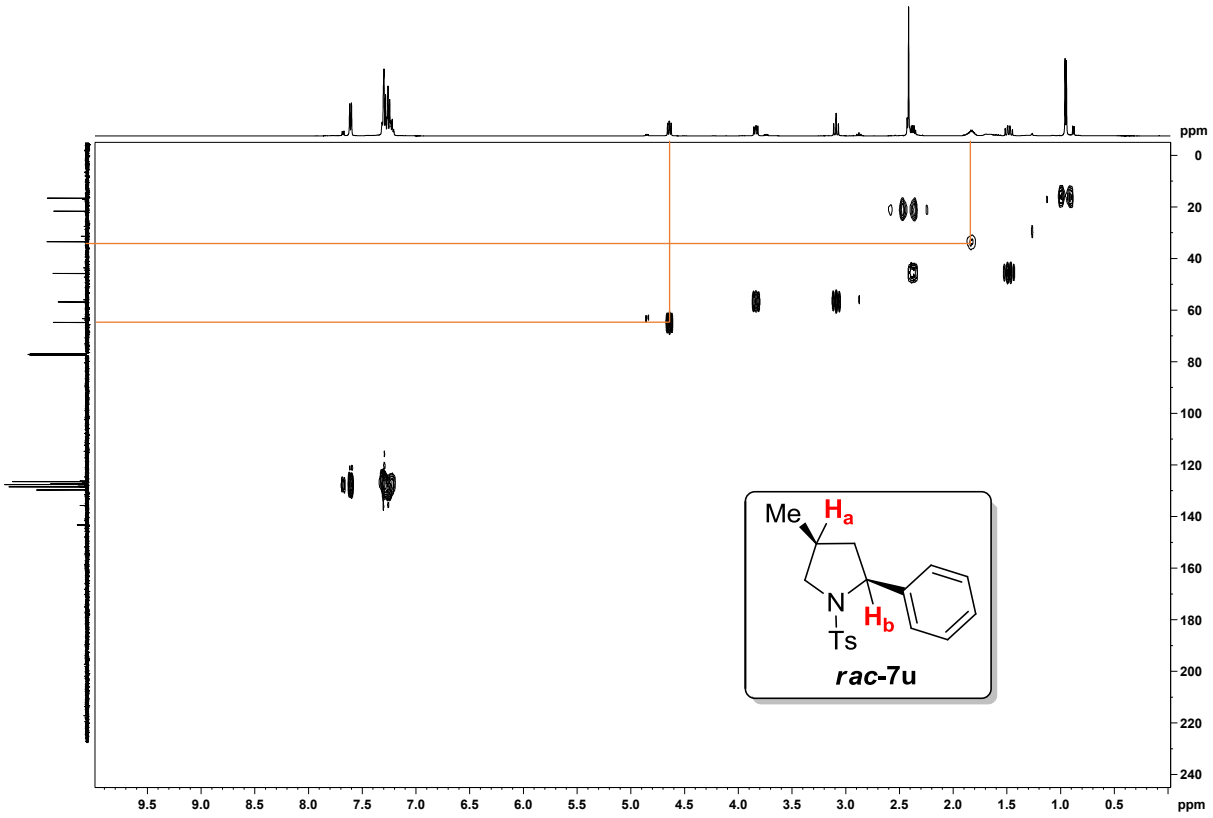
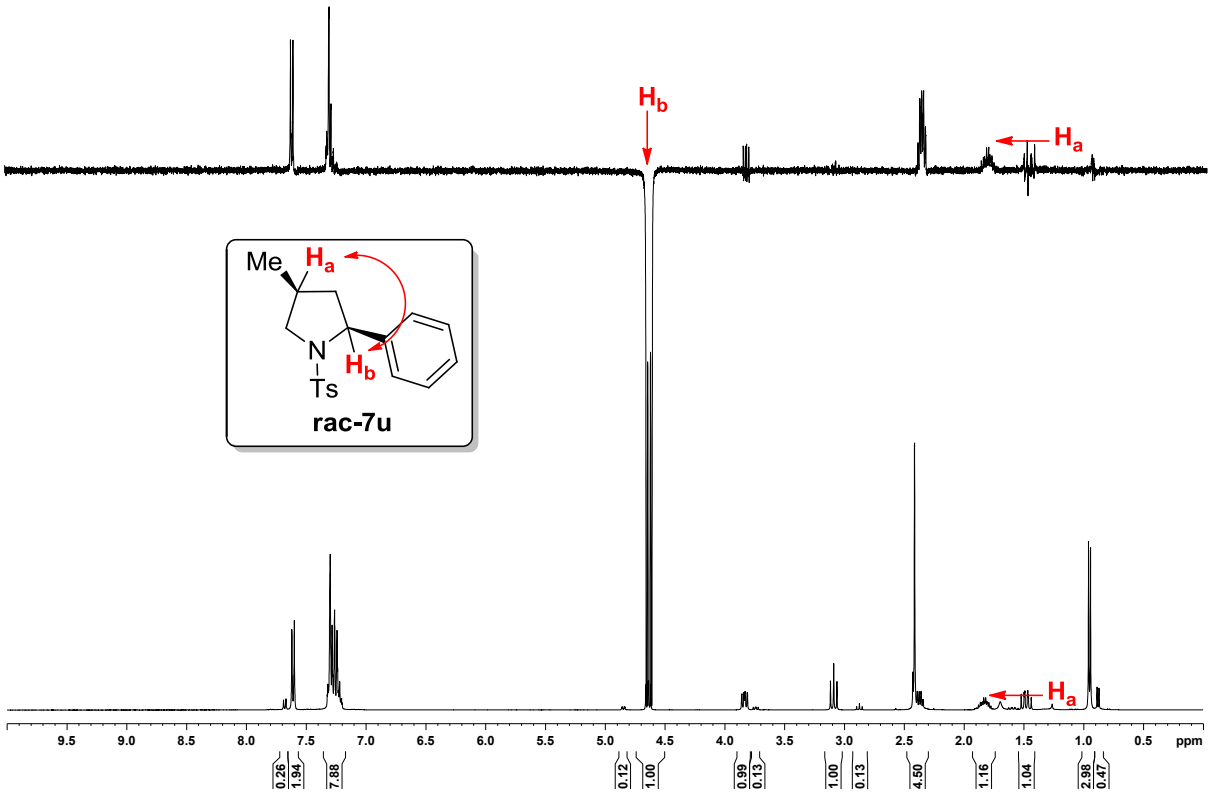
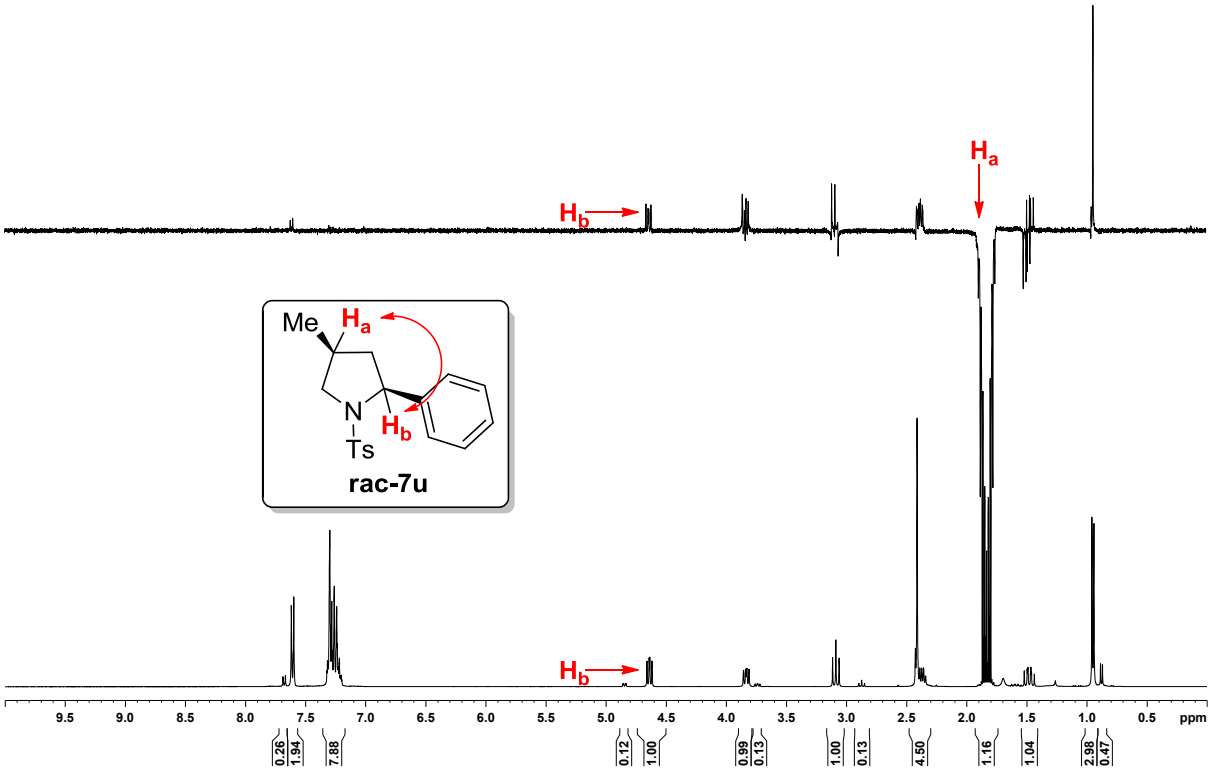
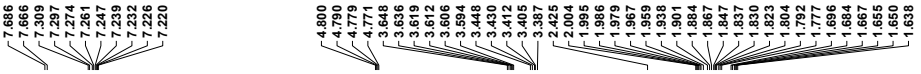
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
Me
Ha
N
Hb
Ts
rac-7u


Hb
Ha
Me
Ha
N
Hb
Ts
rac-7u
Ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.26 1.94 7.88 0.12 1.00 0.99 0.13 1.00 0.13 4.50 1.16 1.04 2.98 0.47


Ha
Hb
Me
Ha
N
Hb
Ts
rac-7u
Hb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.26 1.94 7.88 0.12 1.00 0.99 0.13 1.00 0.13 4.50 1.16 1.04 2.98 0.47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7.226
7.220
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4.779
4.771
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3.387
2.425
2.004
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1.986
1.979
1.967
1.959
1.938
1.901
1.884
1.867
1.847
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1.830
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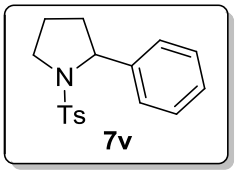
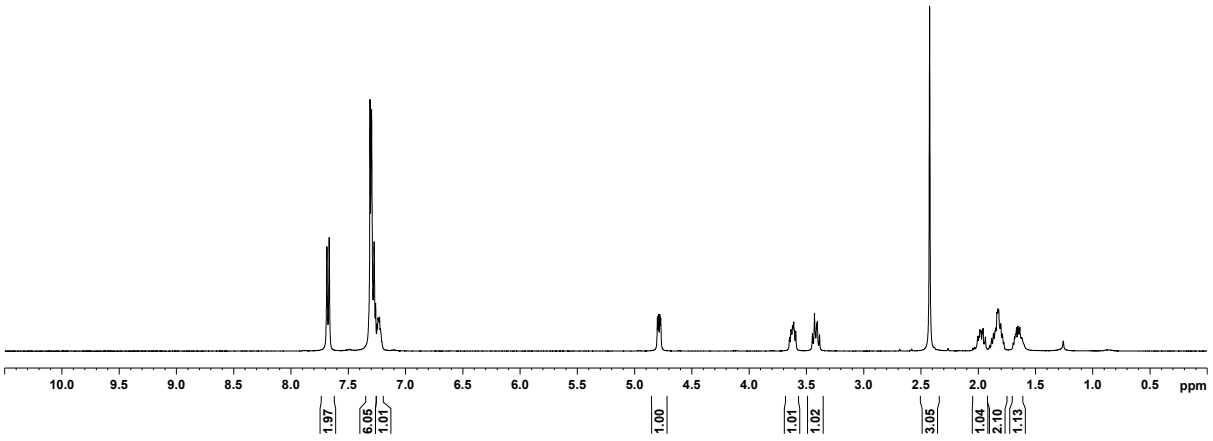
1.777
1.696
1.684
1.667
1.655
1.650
1.638


N
Ts

7v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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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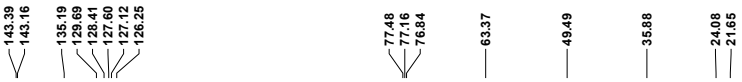
6.05
1.01
1.00
1.01
1.02
3.05
1.04
2.10
1.13


143.39
143.16
135.19
129.69
128.41
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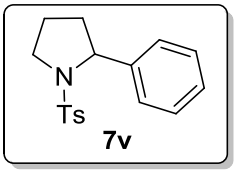
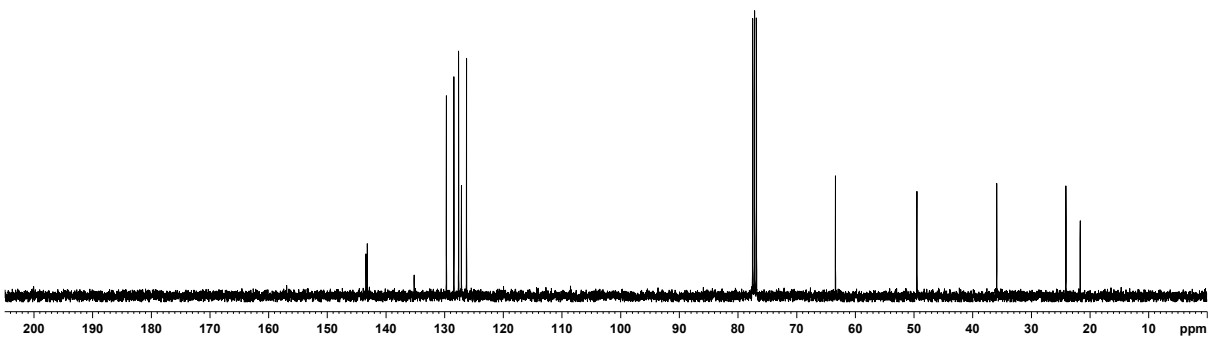
127.12
126.25
77.48
77.16
76.84
63.37
49.49
35.88
24.08
21.65


N
Ts

7v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150
140
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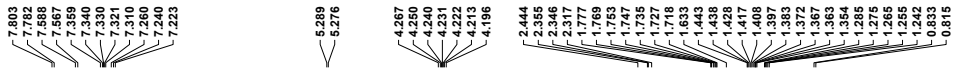
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.340
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7.260
7.240
7.223
5.289
5.276
4.267
4.250
4.240
4.231
4.222
4.213
4.196
2.444
2.355
2.346
2.317
1.777
1.769
1.753
1.747
1.735
1.727
1.718
1.633
1.443
1.438
1.428
1.417
1.408
1.397
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1.372
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1.285
1.275
1.265
1.255
1.242
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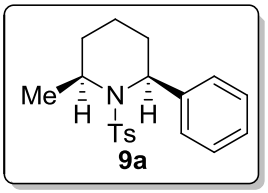
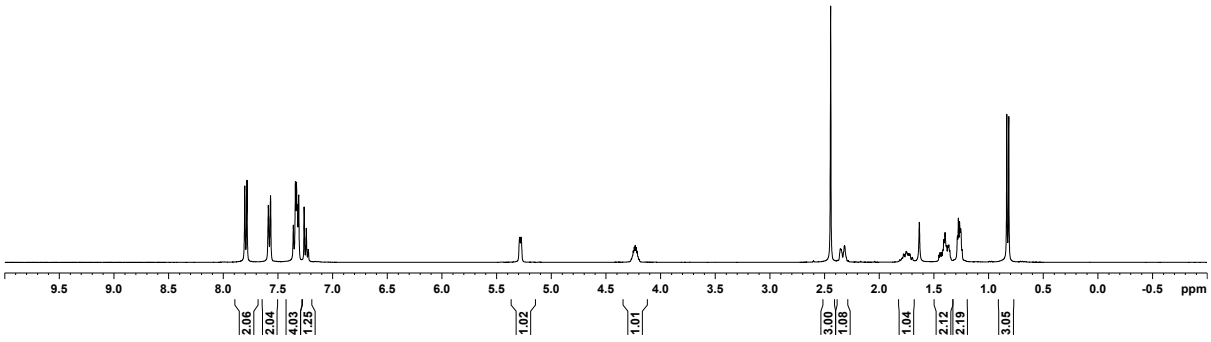
0.815


Me
H
N
H
Ts
9a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7.0
6.5
6.0
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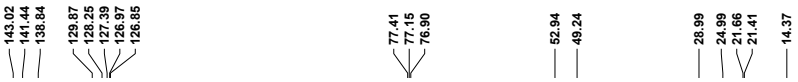
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.06
2.04
4.03
1.25
1.02
1.01
3.00
1.08
1.04
2.12
2.19
3.05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128.25
127.39
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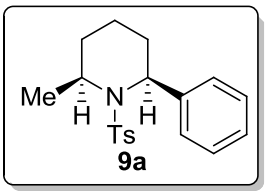
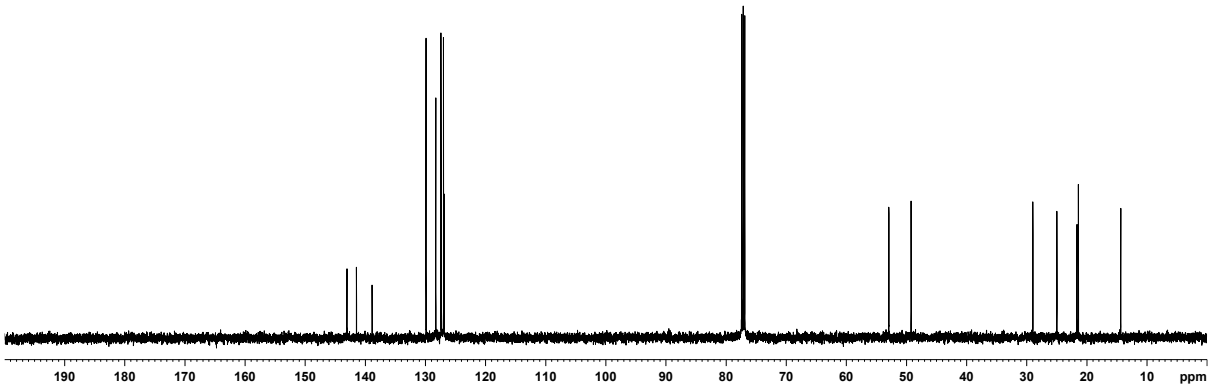
77.15
76.90
52.94
49.24
28.99
24.99
21.66
21.41
14.37


Me
H
N
H
Ts
9a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110
100
90
80
70
60
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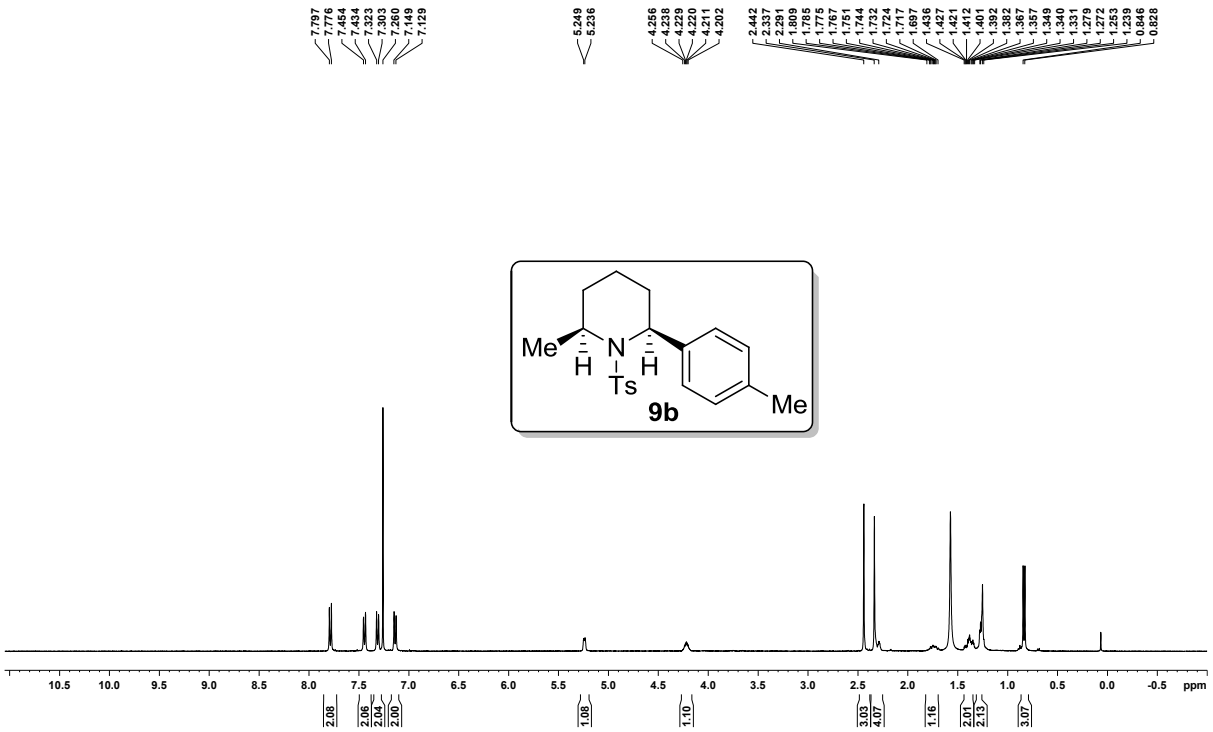
40
30
20
10
ppm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7.434
7.323
7.303
7.260
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H
N
H
Ts
9b
Me
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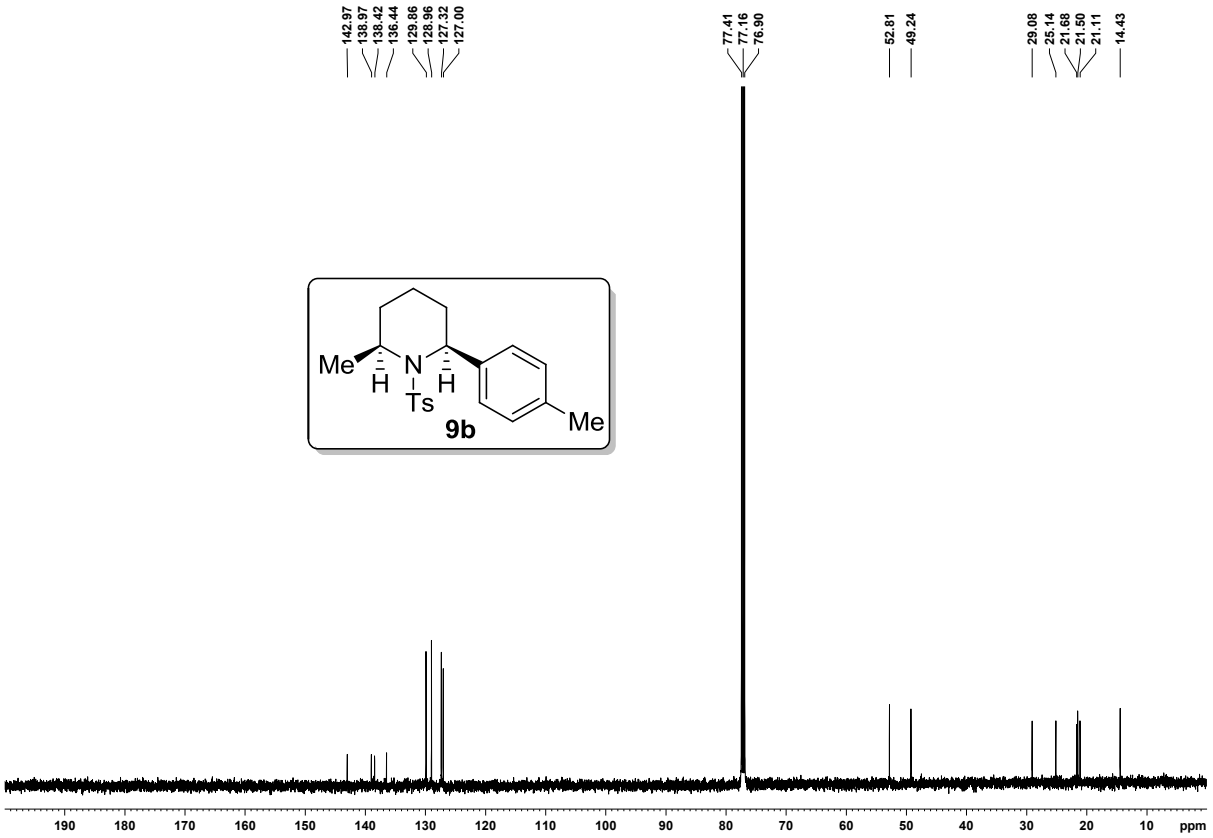
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N
H
Ts
9b
Me
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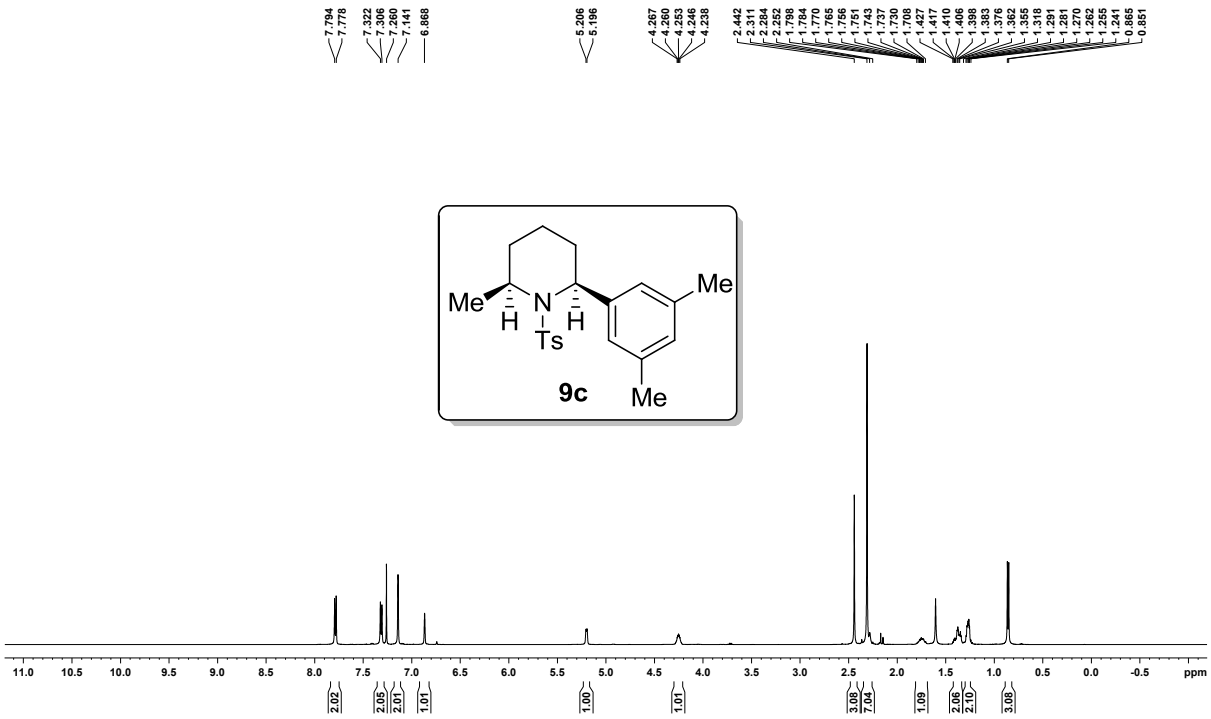
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H
Ts
Me
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Me
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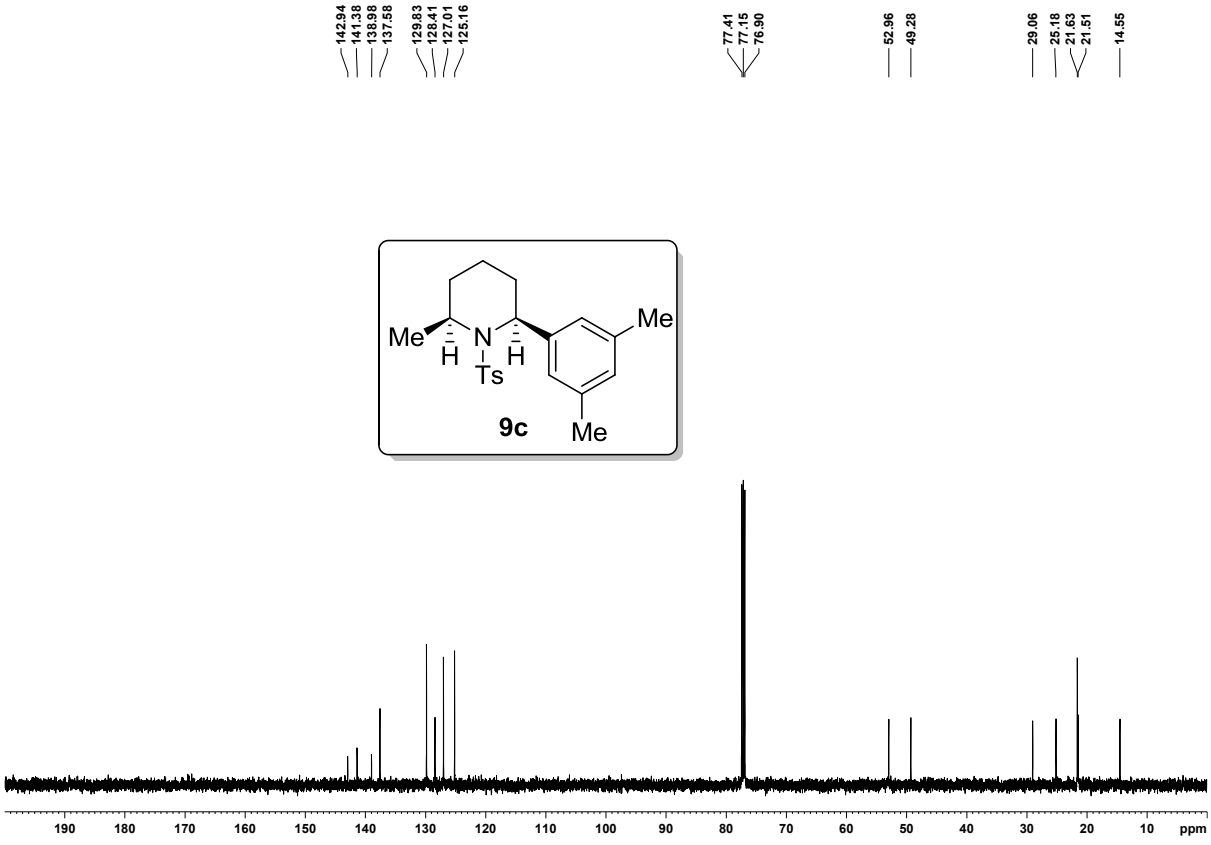
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H
Ts
Me
9c
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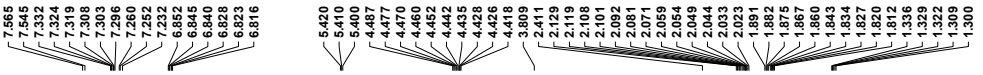
ppm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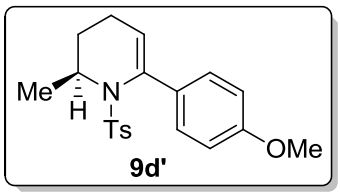
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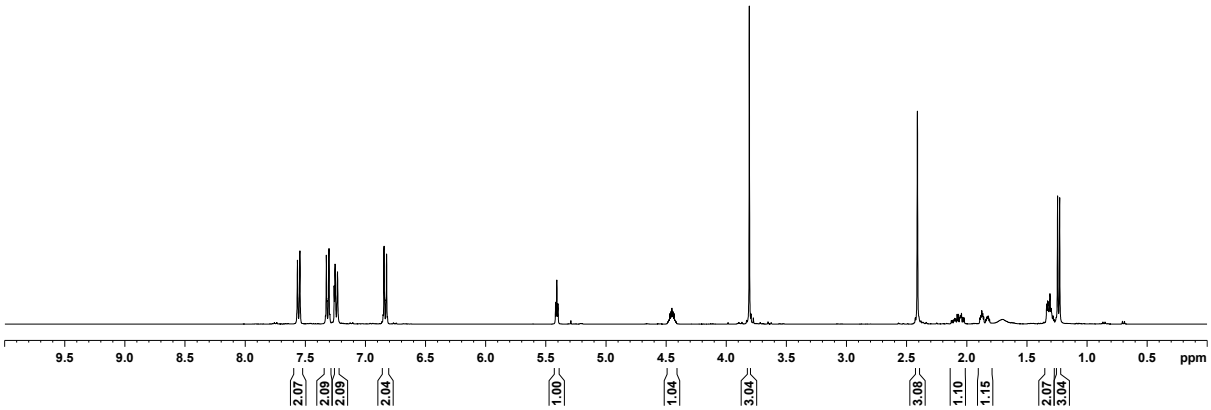
Ts
OMe
9d'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3.04
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1.10
1.15
2.07
3.04


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19.49
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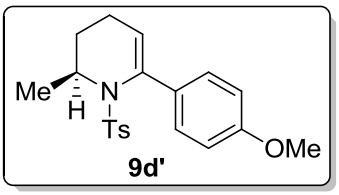
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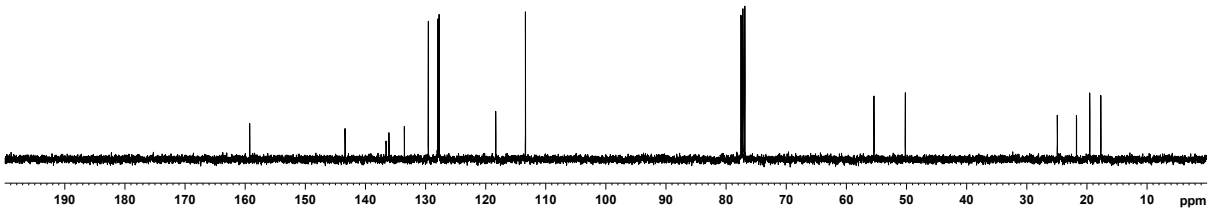
Ts
OMe
9d'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30
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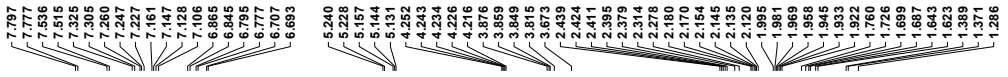
10
ppm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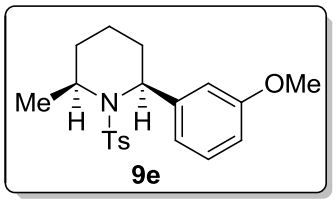
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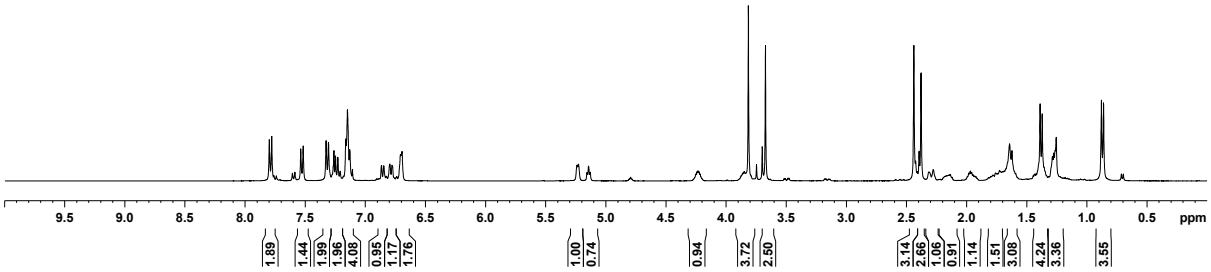
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3.08
4.24
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3.55


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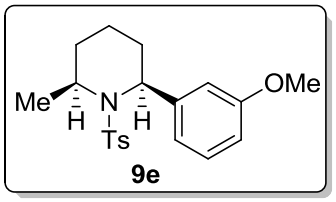
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OMe
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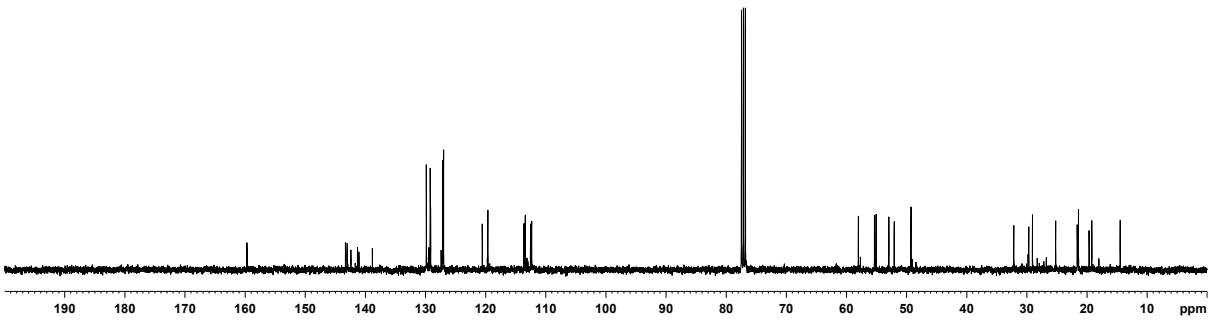
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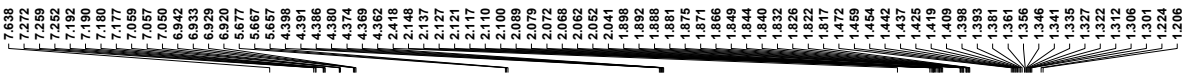
10
ppm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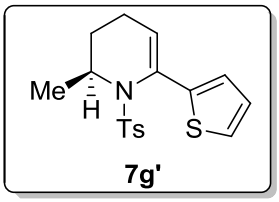
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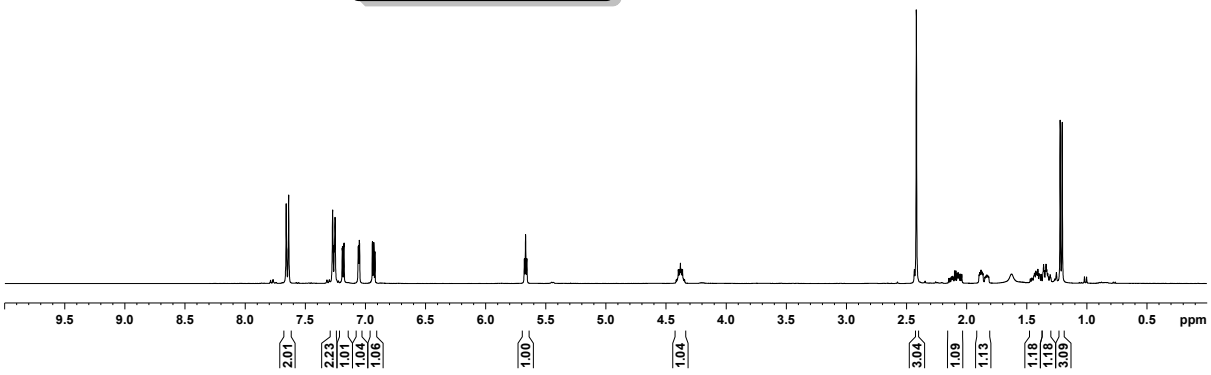
Ts
S

7g'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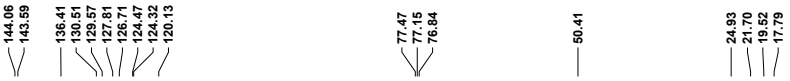
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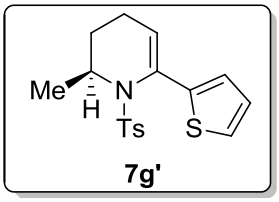
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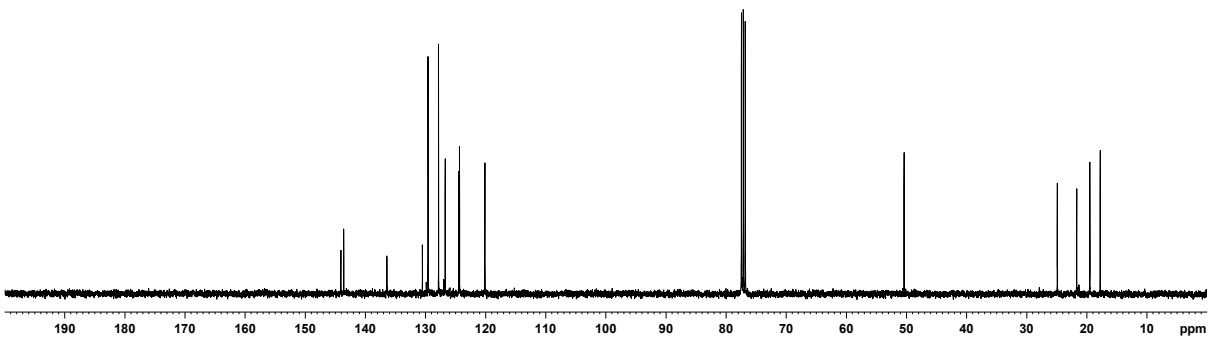
S

7g'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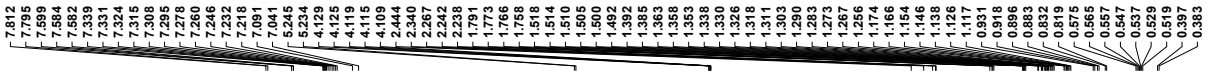

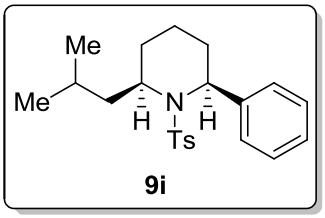

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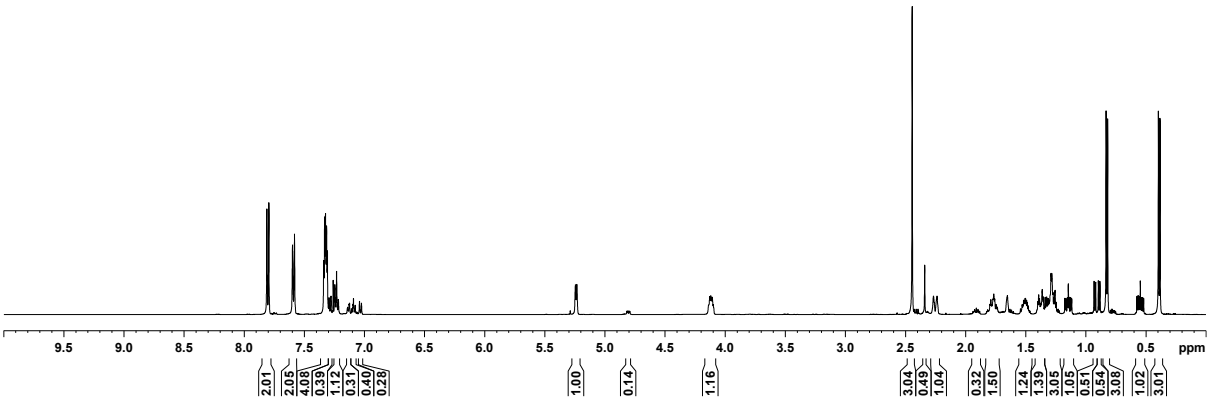

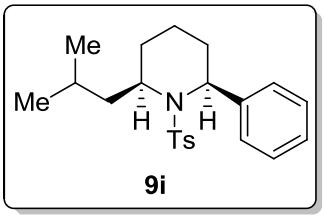

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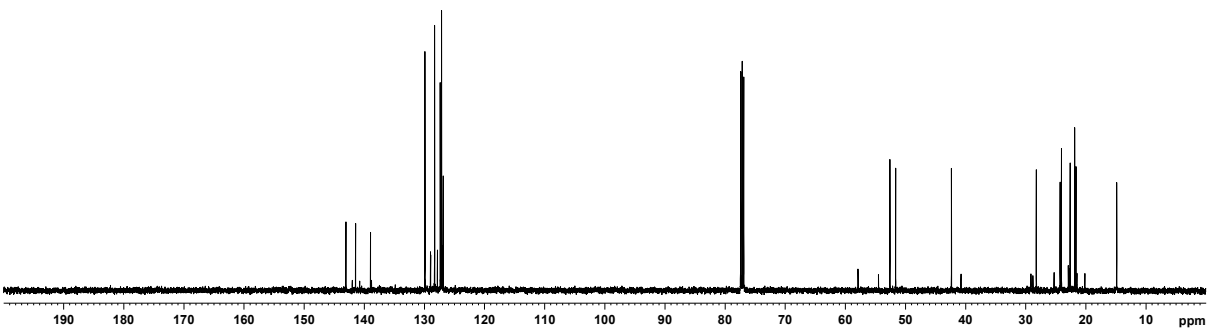

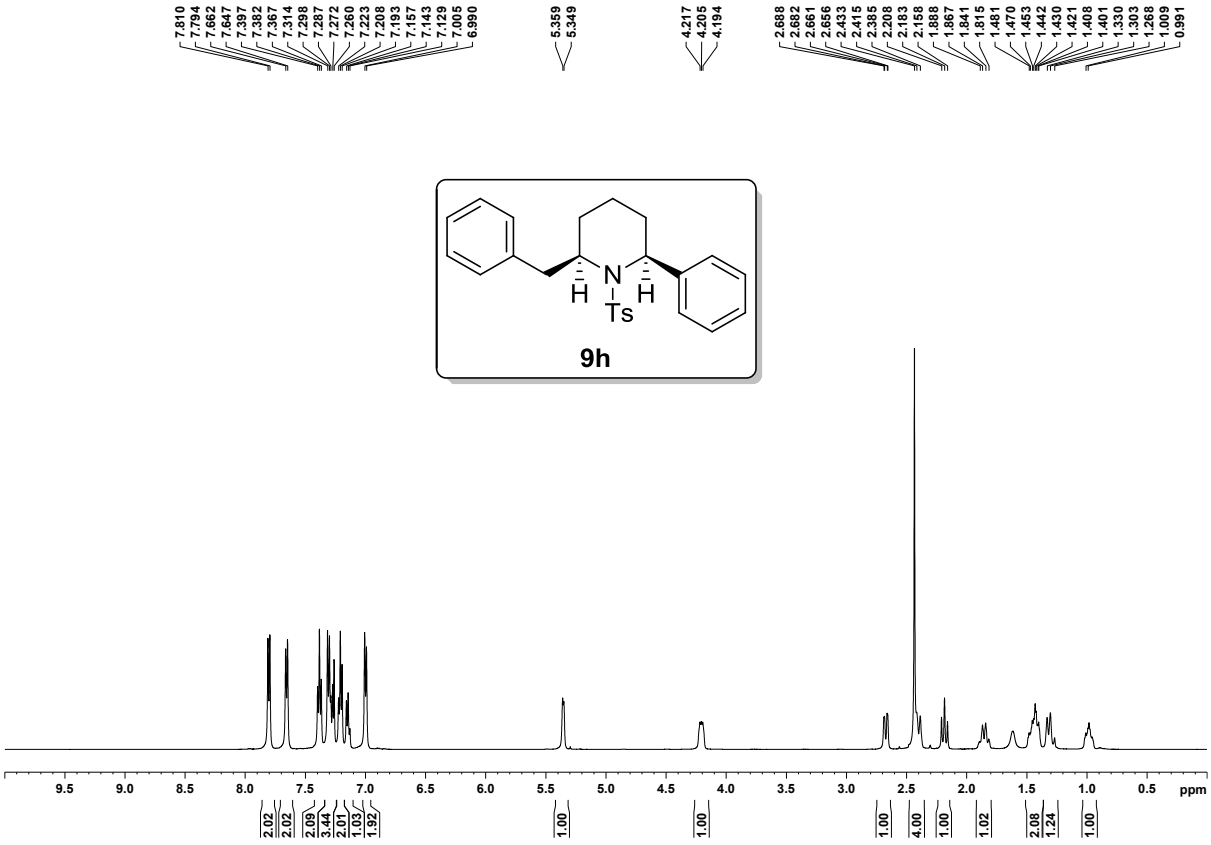
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Ts
9h
ppm
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2.02
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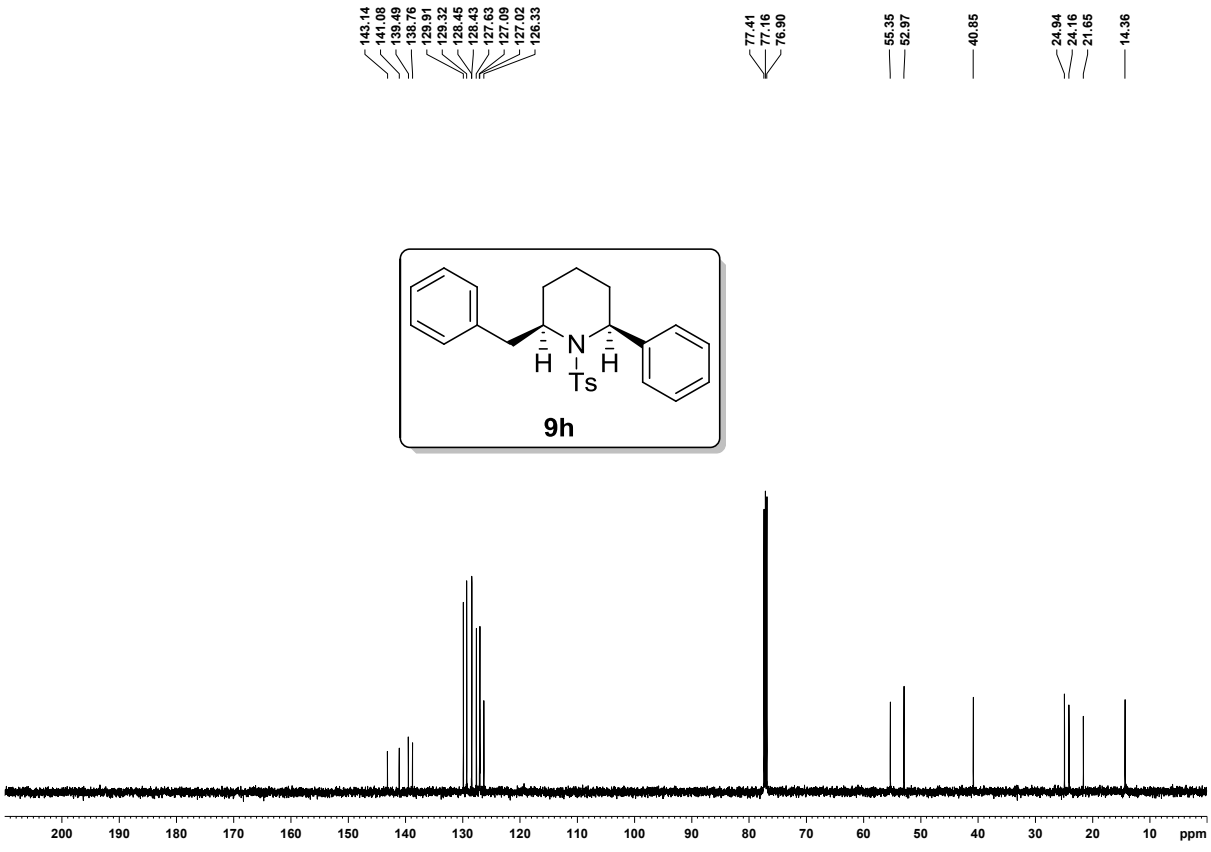
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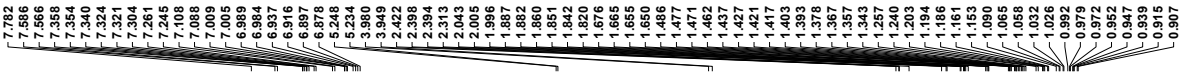
9h
ppm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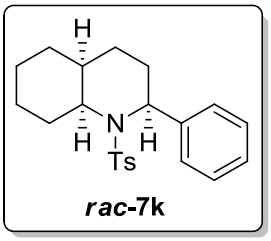
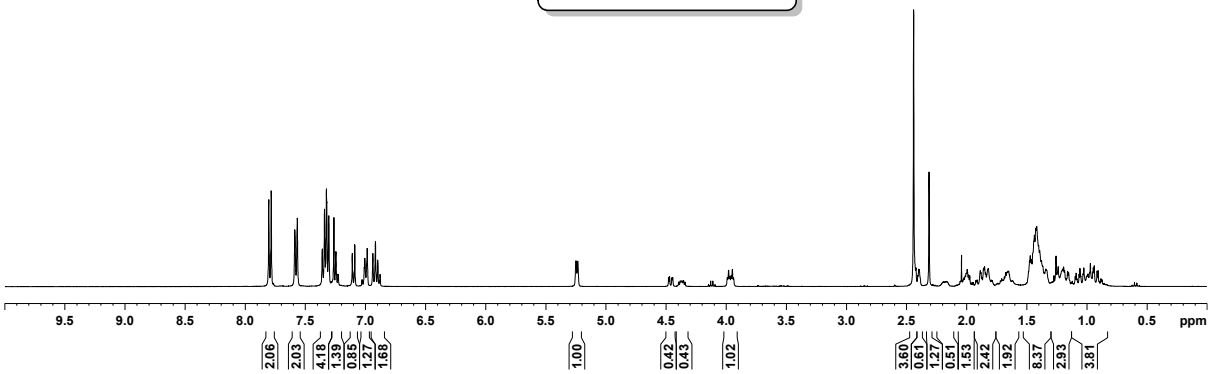

H
N
H
H
Ts

***rac*-7k**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3.5
3.0
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1.0
0.5
ppm
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2.03
4.18
1.39
0.85
1.27
1.68
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0.43
1.02
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0.61
1.27
0.51
1.53
2.42
1.92
8.37
2.93
3.81


142.966
141.686
141.601
140.721
139.235
139.131
129.871
129.752
128.755
128.277
127.301
127.226
127.088
126.868
126.811
77.473
77.155
76.837
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52.546
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33.398
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25.561
23.256
21.648
21.457
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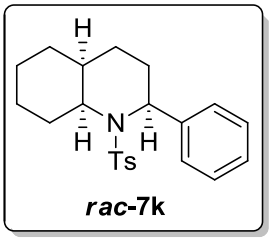
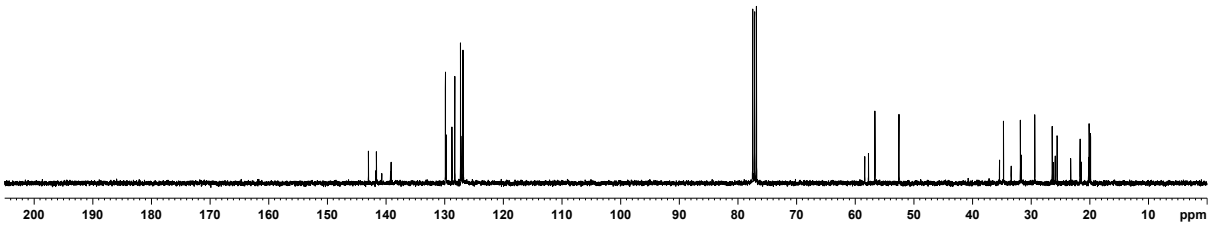
20.104
19.866


H
N
H
H
Ts

***rac*-7k**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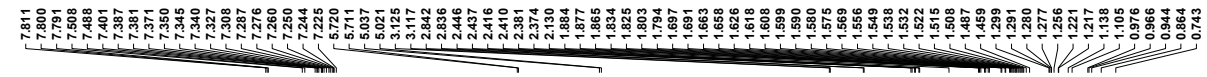
10
ppm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7.340
7.327
7.308
7.287
7.276
7.260
7.250
7.244
7.225
5.720
5.711
5.037
5.021
3.125
3.117
2.842
2.836
2.446
2.437
2.416
2.410
2.381
2.374
2.130
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1.877
1.865
1.834
1.825
1.803
1.794
1.697
1.691
1.663
1.658
1.626
1.618
1.608
1.599
1.590
1.580
1.575
1.569
1.556
1.549
1.538
1.532
1.522
1.515
1.508
1.487
1.459
1.299
1.291
1.280
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1.217
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0.966
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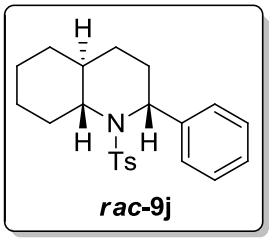
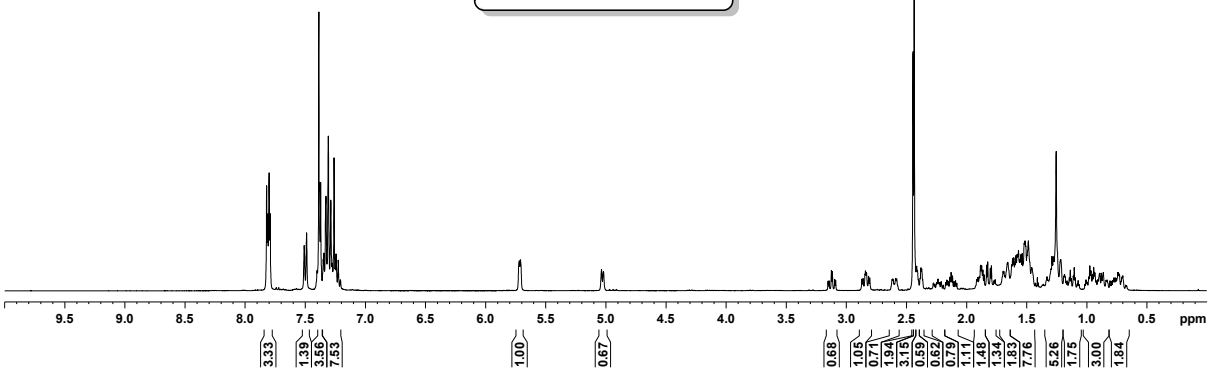
0.864
0.743


H
N
H
H
Ts

***rac*-9j**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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.33
1.39
3.56
7.53
1.00
0.67
0.68
1.05
0.71
1.94
3.15
0.59
0.62
0.79
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1.34
1.83
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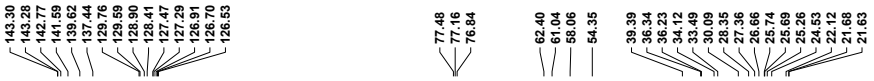
1.75
3.00
1.84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142.77
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137.44
129.76
129.59
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128.41
127.47
127.29
126.91
126.70
126.53
77.48
77.16
76.84
62.40
61.04
58.06
54.35
39.39
36.34
36.23
34.12
33.49
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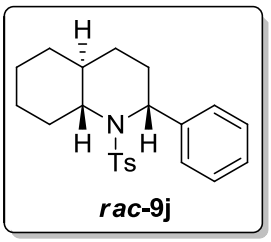
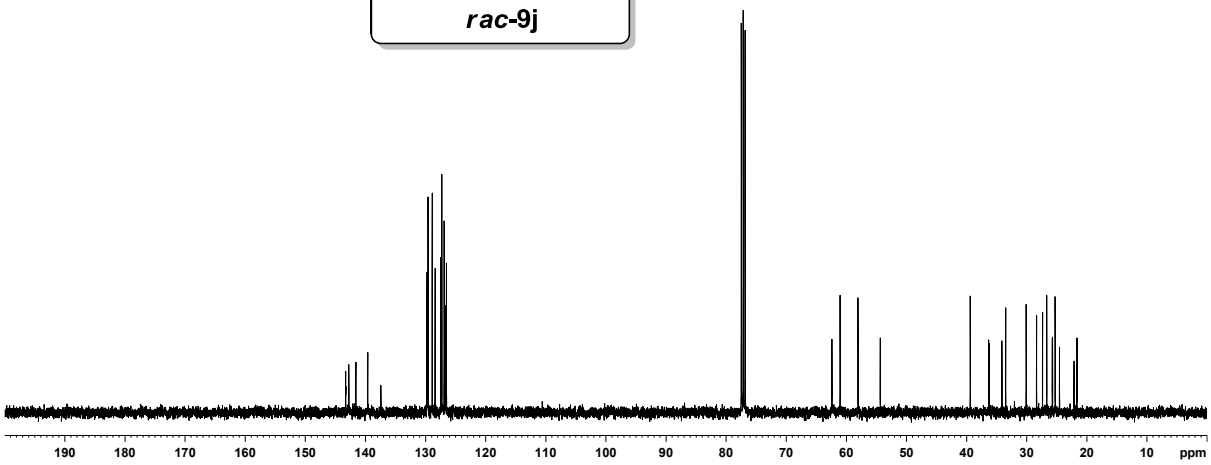
25.69
25.26
24.53
22.12
21.68
21.63


H
N
H
H
Ts

***rac*-9j**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130
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100
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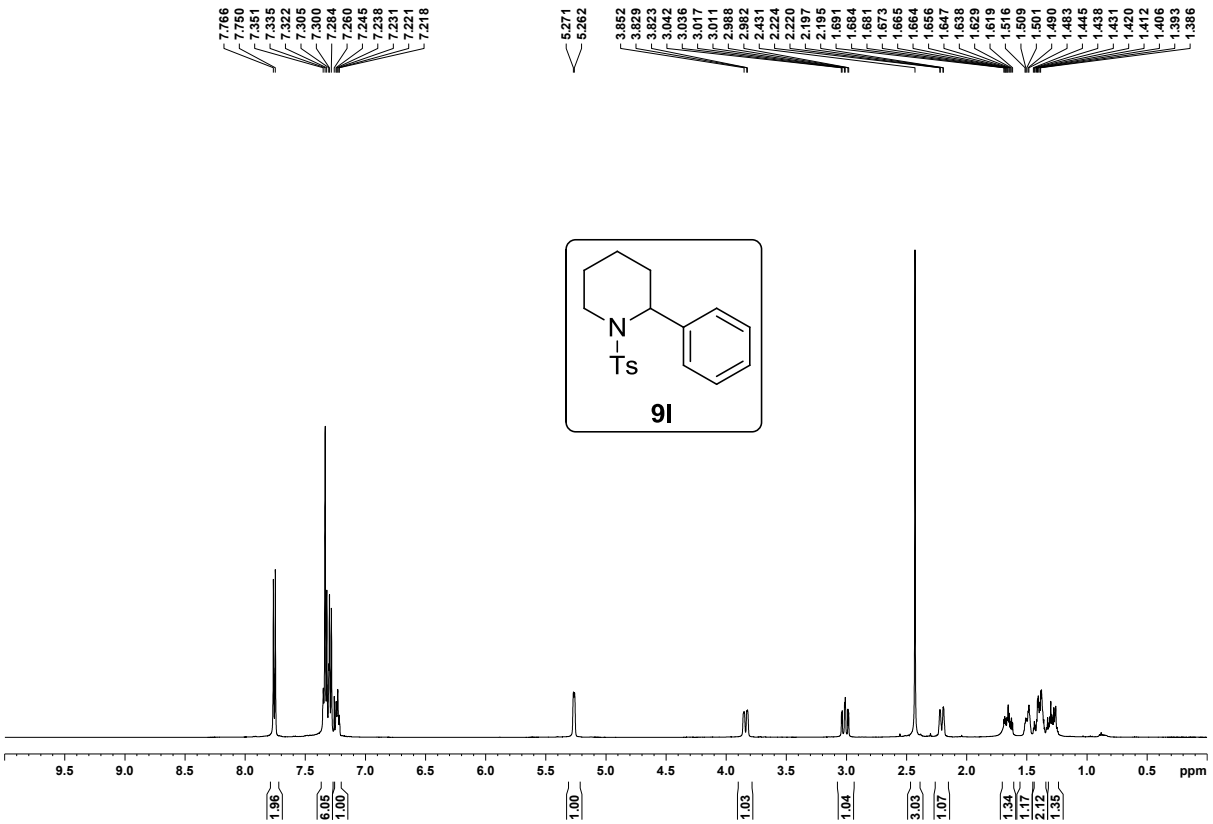
30
20
10
ppm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7.238
7.231
7.221
7.218
5.271
5.262
3.852
3.829
3.823
3.042
3.036
3.017
3.011
2.988
2.982
2.431
2.224
2.220
2.197
2.195
1.891
1.884
1.681
1.673
1.665
1.664
1.656
1.647
1.638
1.629
1.619
1.516
1.509
1.501
1.490
1.483
1.445
1.438
1.431
1.420
1.412
1.406
1.393
1.386
N
Ts
9l
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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1.00
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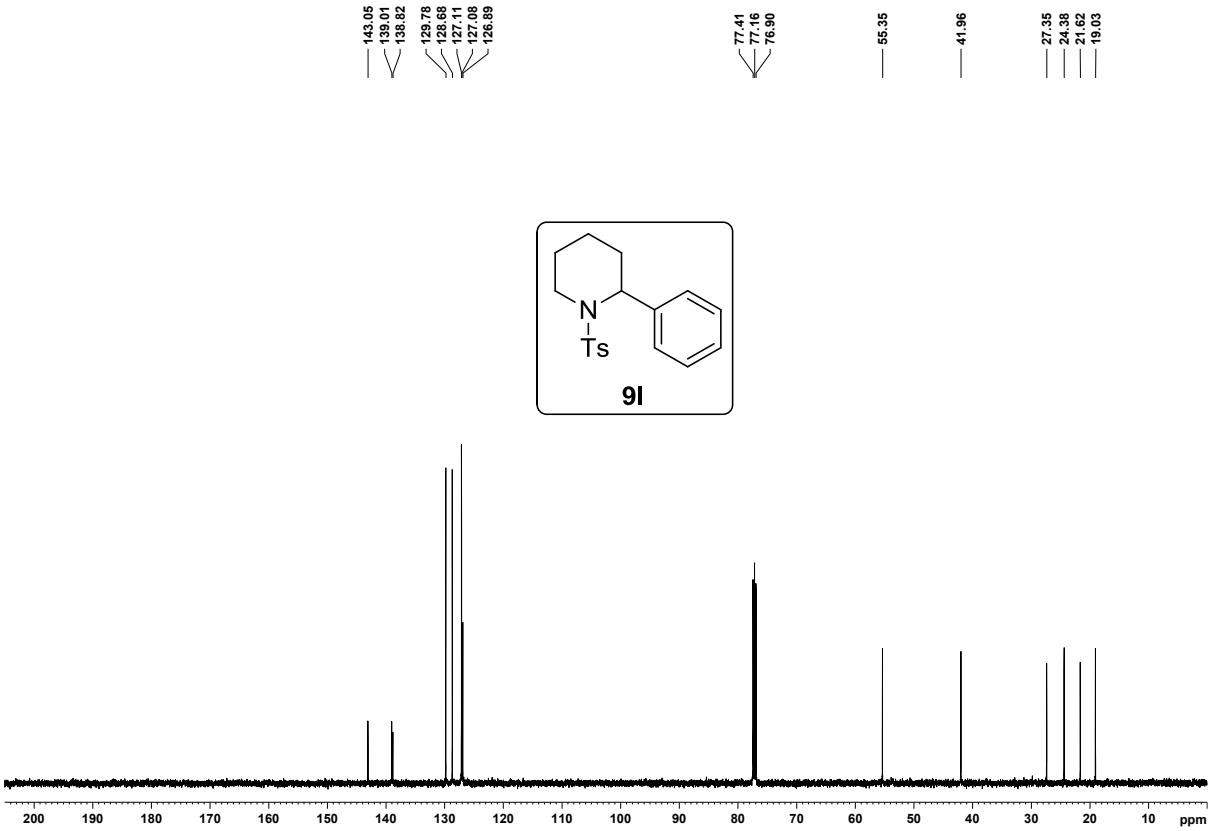
3.03
1.07
1.34
1.17
2.12
1.35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126.89
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77.16
76.90
55.35
41.96
27.35
24.38
21.62
19.03
N
Ts
9l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.704
7.688
7.611
7.608
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7.388
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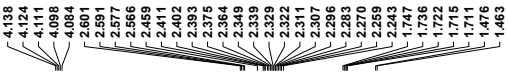
7.358
7.349
7.344
7.329
7.260
7.259
7.245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4.111
4.098
4.084
2.601
2.591
2.577
2.566
2.459
2.411
2.402
2.393
2.375
2.364
2.349
2.339
2.329
2.322
2.311
2.307
2.296
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2.243
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1.736
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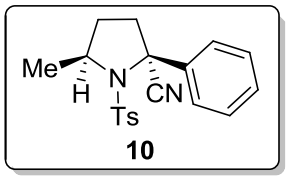
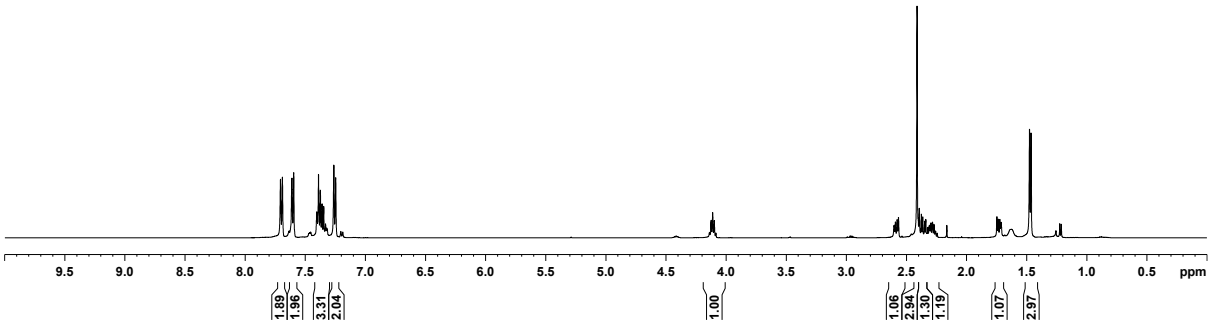
1.715
1.711
1.476
1.463


Me
H
N
Ts
CN
10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7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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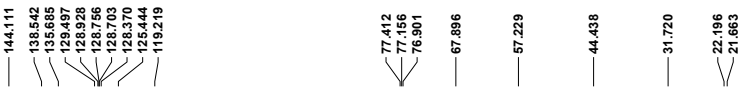
1.00
1.06
2.94
1.30
1.19
1.07
2.97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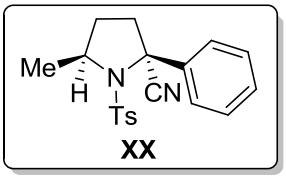
135.685
129.497
128.928
128.756
128.703
128.370
125.444
119.219
77.412
77.156
76.901
67.896
57.229
44.438
31.720
22.196
21.663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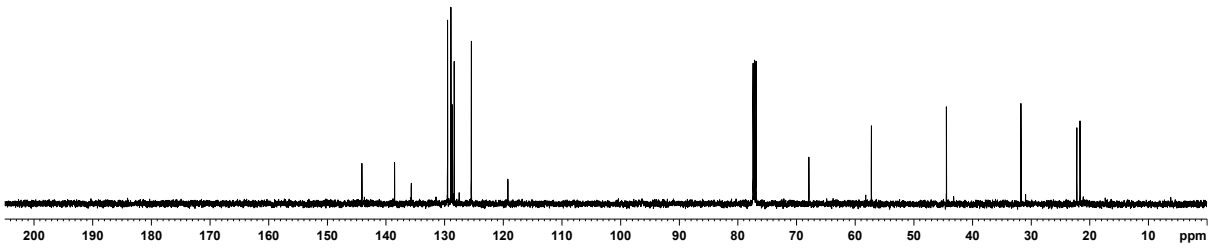
H
N
Ts
CN
XX


200
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140
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120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.900
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7.389
7.372
7.300
7.284
7.260
6.857
6.840
5.175
4.598
4.066
3.796
2.416
2.008
1.981
1.954
1.835
1.826
1.815
1.808
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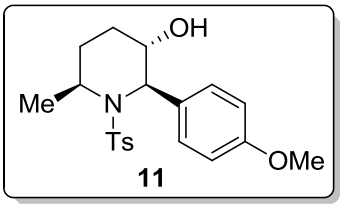
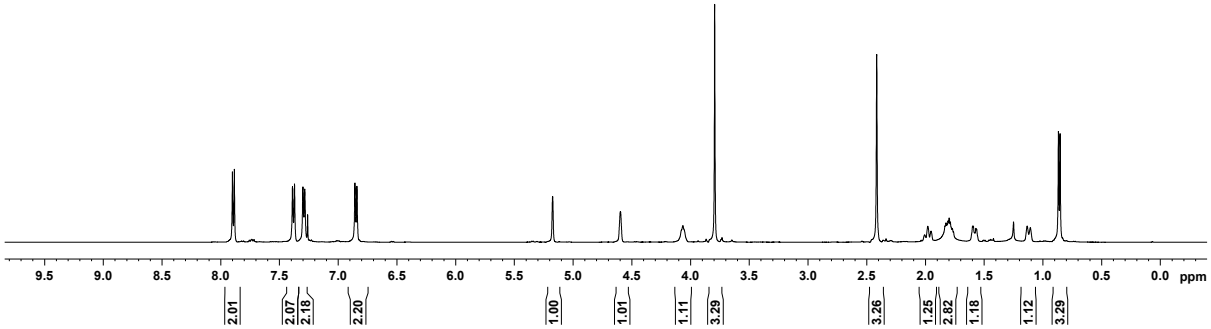
0.855


OH
Me
N
Ts
OMe
11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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
2.07
2.18
2.20
1.00
1.01
1.11
3.29
3.26
1.25
2.82
1.18
1.12
3.29


158.672
143.280
138.065
132.171
129.688
128.458
127.618
113.738
77.411
77.157
76.903
65.256
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48.726
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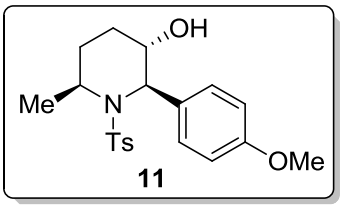
21.137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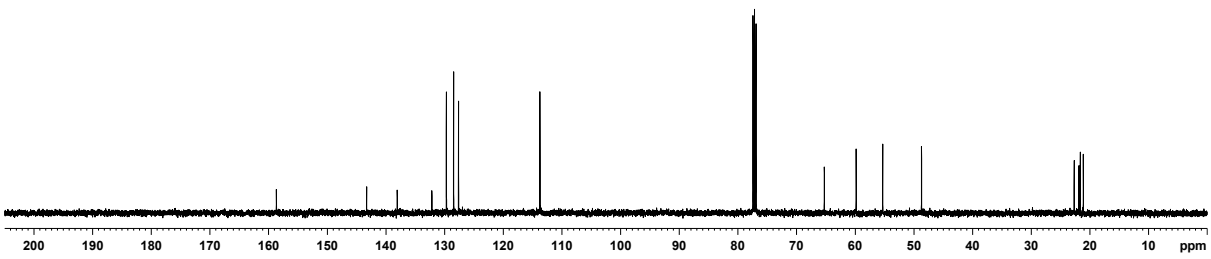
Me
N
Ts
OMe
11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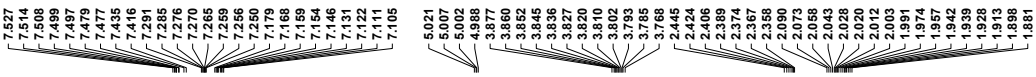
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.499
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7.479
7.477
7.435
7.416
7.291
7.285
7.276
7.270
7.265
7.259
7.256
7.250
7.179
7.168
7.159
7.154
7.146
7.131
7.122
7.111
7.105
5.021
5.007
5.002
4.988
3.877
3.860
3.852
3.845
3.836
3.827
3.820
3.810
3.802
3.793
3.785
3.768
2.445
2.424
2.406
2.389
2.374
2.367
2.358
2.090
2.073
2.058
2.043
2.028
2.020
2.012
2.003
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1.913
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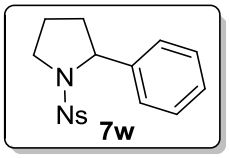
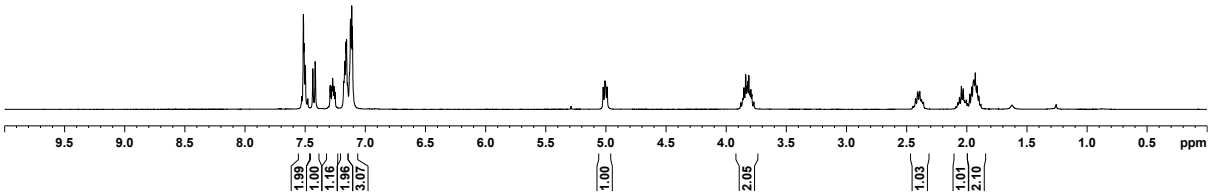
1.881


N
Ns
7w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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.00
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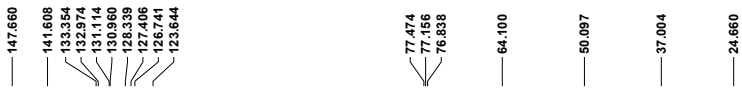
1.03
1.01
2.10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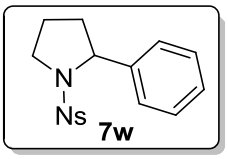
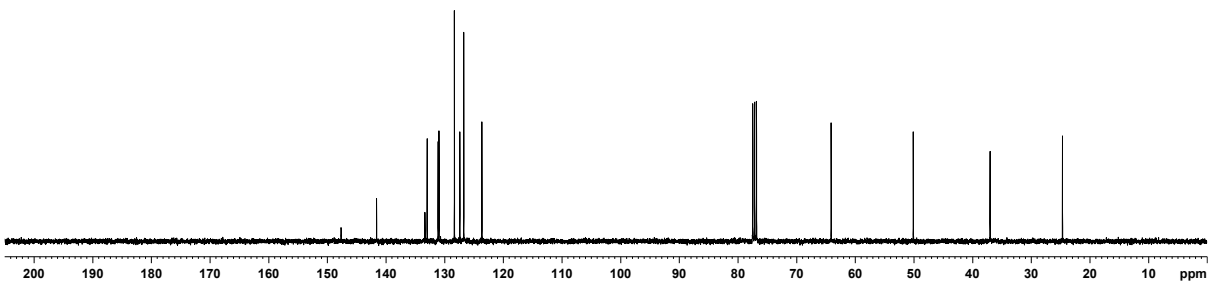
123.644
77.474
77.156
76.838
64.100
50.097
37.004
24.660


N
Ns
7w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140
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120
110
100
90
80
70
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50
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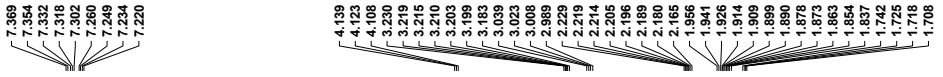
30
20
10
ppm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7.318
7.302
7.280
7.249
7.234
7.220
4.139
4.123
4.108
3.230
3.219
3.215
3.210
3.203
3.199
3.183
3.039
3.023
3.008
2.989
2.229
2.219
2.214
2.205
2.196
2.189
2.180
2.165
1.956
1.941
1.926
1.914
1.909
1.899
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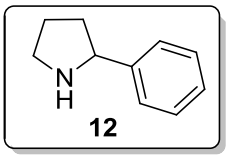
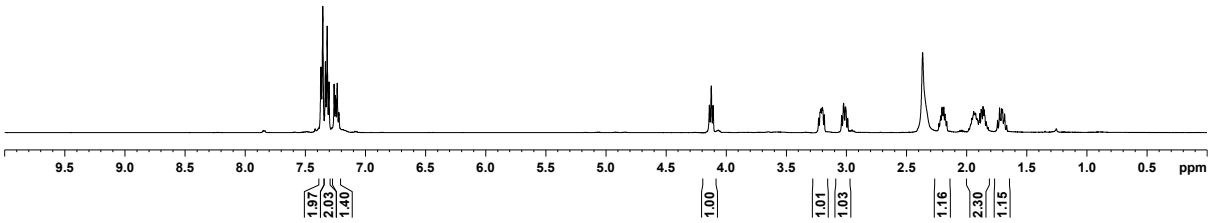
1.718
1.708


N
H
12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6.0
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2.5
2.0
1.5
1.0
0.5
ppm
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1.00
1.01
1.03
1.16
2.30
1.15


143.95
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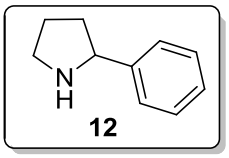
127.13
126.76
77.48
77.16
76.84
62.74
46.90
34.16
25.57


N
H
12

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.332
7.328
7.314
7.311
7.299
7.296
7.280
7.267
7.264
7.260
7.251
7.246
7.239
7.234
7.231
7.227
7.224
7.198
7.194
7.190
7.176
7.165
7.156
7.140
7.138
7.123
7.087
7.086
7.083
7.068
7.066
7.064
7.049
7.046
6.852
6.833
4.426
4.410
4.400
4.384
3.618
3.491
3.475
3.461
3.445
3.189
3.179
3.170
3.167
3.159
3.157
3.147
3.137
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2.706
2.679
2.546
2.525
2.472
2.462
2.451
2.445
2.440
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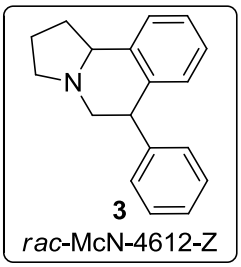
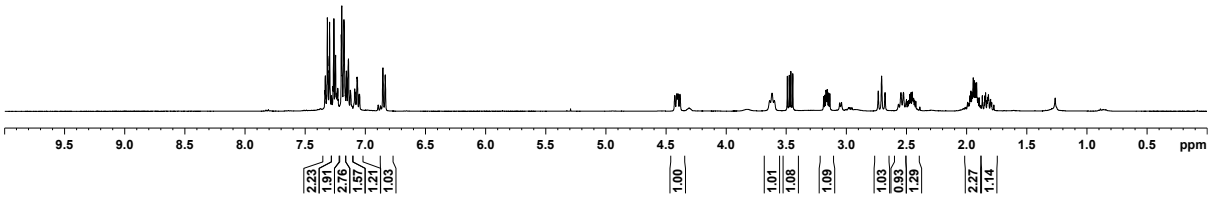
1.842
1.823
1.818


N
3
rac-McN-4612-Z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8.0
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7.0
6.5
6.0
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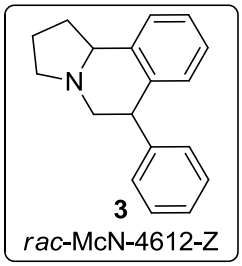
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.23
1.91
2.76
1.57
1.21
1.03
1.00
1.01
1.08
1.09
1.03
0.93
1.29
2.27
1.14


144.431
139.327
137.832
129.334
129.299
128.595
126.663
126.342
126.298
125.339
77.411
77.157
76.903
64.021
58.234
53.147
45.350
30.697
22.185


N
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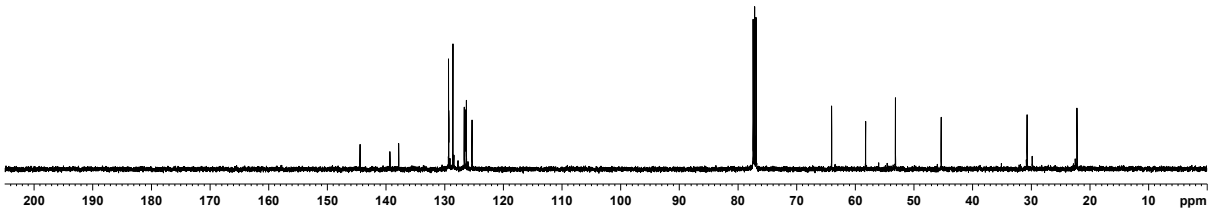
rac-McN-4612-Z


200
190
180
170
160
150
140
130
120
110
100
90
80
70
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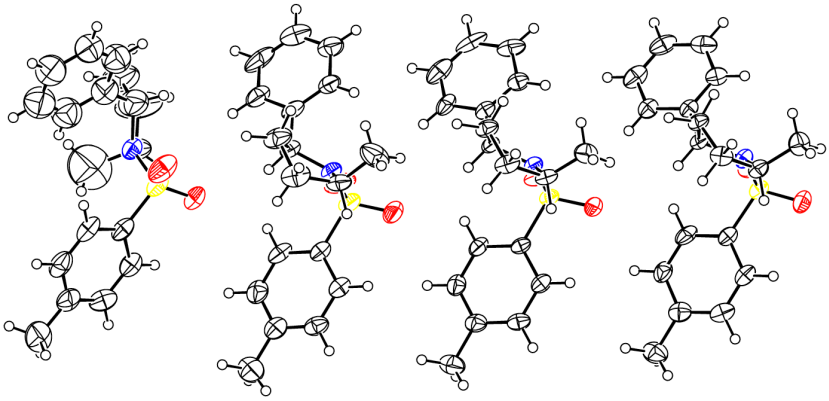
50
40
30
20
10
ppm

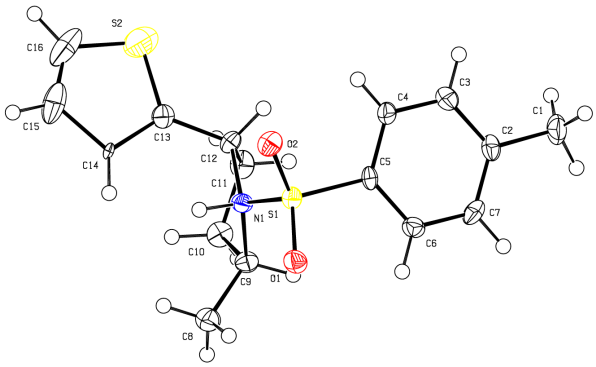
X-Ray crystallographic analysis:

Crystal data and structure refinement for 7a:



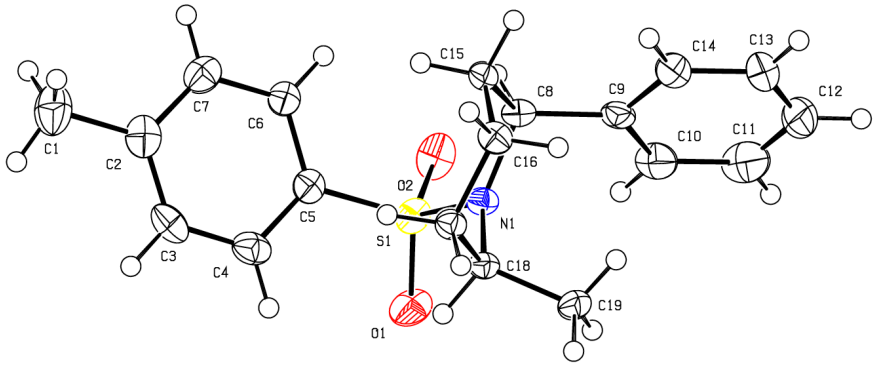
Identification code		**7a**	
Solvent		CH_2Cl_2	
CCDC	1907335		
Bond precision:	C-C = 0.0134 A	Wavelength=1.54184	
Cell:	a= 17.8848(4)	b= 7.37022(15)	c= 25.6676(6)
	alpha=90	beta= 107.315(3)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	3230.05(13)	3230.06(13)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C18 H21 N O2 S	4(C18 H21 N O2 S)	
Sum formula	C18 H21 N O2 S	C72 H84 N4 O8 S4	
Mr	315.42	1261.67	
Dx, g cm-3	1.297	1.297	
Z	8	2	
Mu (mm-1)	1.829	1.829	
F000	1344.0	1344.0	
F000’	1350.14		
h,k,l max	21,8,30	21,8,30	
Nref	11002[5977]	10110	
Tmin,Tmax	0.728,0.694	0.399,1.000	
Tmin’	0.661		
Correction method =	Numerical		
Data completeness =	1.69/0.92	Theta(max)= 64.995	
R(reflections) =	0.0818(8044)	wR2(reflections)= 0.2400(10110)	
S = 1.038			
	Npar = 789		

Crystal data and structure refinement for 7n:



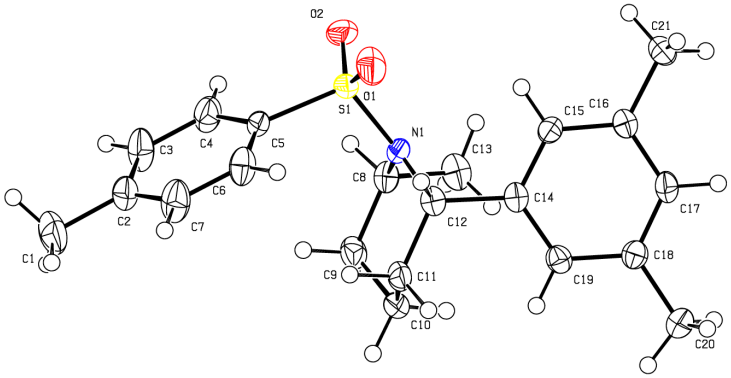
Identification code		**7n**	
Solvent		CH_2Cl_2	
CCDC	1907330		
Bond precision:	C-C = 0.0071 A	Wavelength=0.71073	
Cell:	a= 10.6010(5)	b= 11.7414(5)	c= 12.8810(6)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1603.31(13)	1603.31(13)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C16 H20 N O2 S2	C16 H20 N O2 S2	
Sum formula	C16 H20 N O2 S2	C16 H20 N O2 S2	
Mr	322.45	322.45	
Dx, g cm-3	1.336	1.336	
Z	4	4	
Mu (mm-1)	0.336	0.336	
F000	684.0	684.0	
F000’	685.24		
h,k,l max	12,13,15	12,13,15	
Nref	2829[1631]	2741	
Tmin,Tmax	0.932,0.941	0.734,1.000	
Tmin’	0.932		
Correction method =	Numerical		
Data completeness =	1.68/0.97	Theta(max)= 24.989	
R(reflections) =	0.0622(2511)	wR2(reflections)= 0.2092(2741)	
S = 1.212			
	Npar = 192		

Crystal data and structure refinement for 9a:



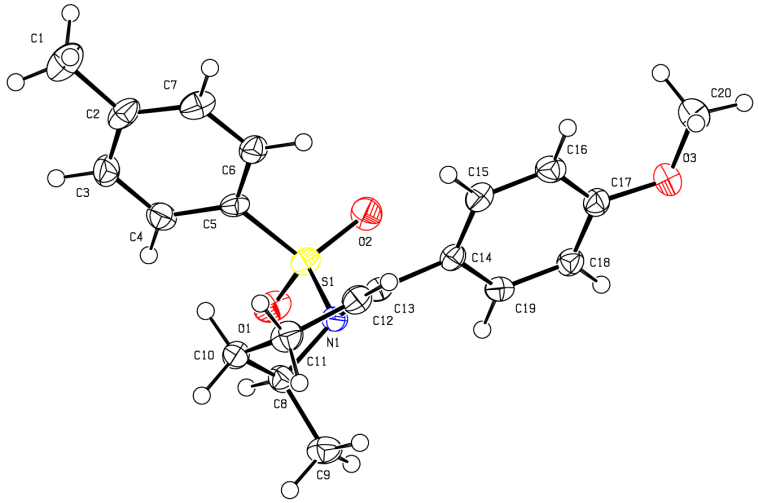
Identification code		**9a**	
Solvent		CH_2Cl_2	
CCDC	1907333		
Bond precision:	C-C =0.0059 A	Wavelength=0.71073	
Cell:	a=7.6838(3)	b= 11.6378(7)	c= 19.1666(13)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1713.93(17)	1713.92(16)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C19 H23 N O2 S	C19 H23 N O2 S	
Sum formula	C19 H23 N O2 S	C19 H23 N O2 S	
Mr	329.44	329.44	
Dx, g cm-3	1.277	1.277	
Z	4	4	
Mu (mm-1)	0.198	0.198	
F000	704.0	704.0	
F000’	704.77		
h,k,l max	9,13,22	9,13,22	
Nref	3016[1751]	2964	
Tmin,Tmax	0.964,0.990	0.886,1.000	
Tmin’	0.960		
Correction method =	Numerical		
Data completeness =	1.69/0.98	Theta(max)= 24.993	
R(reflections) =	0.0438(2709)	wR2(reflections)= 0.1412(2964)	
S = 1.210			
	Npar = 210		

Crystal data and structure refinement for 9c:



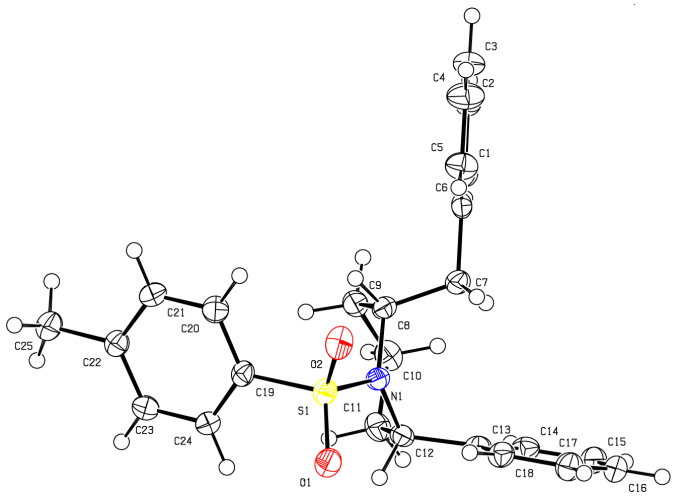
Identification code		**9c**	
Solvent		CH_2Cl_2	
CCDC	1907331		
Bond precision:	C-C = 0.0055 A	Wavelength=0.71073	
Cell:	a= 8.0063(3)	b= 12.0533(8)	c= 19.6151(7)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1892.90(16)	1892.90(16)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C21 H27 N O2 S	C21 H27 N O2 S	
Sum formula	C21 H27 N O2 S	C21 H27 N O2 S	
Mr	357.50	357.49	
Dx, g cm-3	1.255	1.255	
Z	4	4	
Mu (mm-1)	0.185	0.185	
F000	768.0	768.0	
F000’	768.79		
h,k,l max	9,14,23	9,14,23	
Nref	3331[1927]	3261	
Tmin,Tmax	0.967,0.981	0.672,1.000	
Tmin’	0.962		
Correction method =	Numerical		
Data completeness =	1.69/0.98	Theta(max)= 24.998	
R(reflections) =	0.0487(2885)	wR2(reflections)= 0.1204(3261)	
S = 1.036			
	Npar = 230		

Crystal data and structure refinement for 9d':



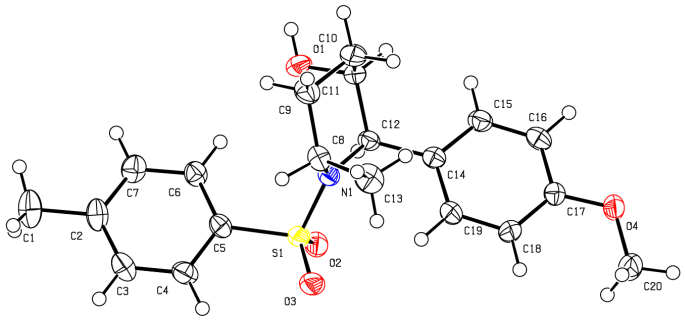
Identification code		**9d'**	
Solvent		CH_2Cl_2	
CCDC	1907332		
Bond precision:	C-C = 0.0047 A	Wavelength=0.71073	
Cell:	a= 6.4626(3)	b= 7.6863(3)	c= 36.6394(17)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1820.01(14)	1820.01(14)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C20 H23 N O3 S	C20 H23 N O3 S	
Sum formula	C20 H23 N O3 S	C20 H23 N O3 S	
Mr	357.45	357.45	
Dx, g cm-3	1.304	1.305	
Z	4	4	
Mu (mm-1)	0.196	0.196	
F000	760.0	760.0	
F000'	760.82		
h,k,l max	7,9,43	7,9,43	
Nref	3192[1897]	3129	
Tmin,Tmax	0.959,0.971	0.891,1.000	
Tmin'	0.959		
Correction method =	Numerical		
Data completeness =	1.65/0.98	Theta(max)= 24.993	
R(reflections) =	0.0398(2815)	wR2(reflections)= 0.0921(3129)	
S = 1.042			
	Npar = 229		

Crystal data and structure refinement for 9h:



Identification code		**9h**	
Solvent		CH_2Cl_2	
CCDC	1907334		
Bond precision:	C-C = 0.0038 A	Wavelength=0.71073	
Cell:	a= 9.2849(3)	b= 11.8237(3)	c= 19.1053(5)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	2097.42(10)	2097.41(10)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C25 H27 N O2 S	C25 H27 N O2 S	
Sum formula	C25 H27 N O2 S	C25 H27 N O2 S	
Mr	405.54	405.53	
Dx, g cm-3	1.284	1.284	
Z	4	4	
Mu (mm-1)	0.176	0.176	
F000	864.0	864.0	
F000’	864.83		
h,k,l max	11,14,22	11,14,22	
Nref	3680[2112]	3654	
Tmin,Tmax	0.952,0.954	0.408,1.000	
Tmin’	0.952		
Correction method =	Numerical		
Data completeness =	1.73/0.99	Theta(max)= 24.998	
R(reflections) =	0.0355(3451)	wR2(reflections)= 0.0847(3654)	
S = 1.043			
	Npar = 263		

Crystal data and structure refinement for 11:



Identification code		**11**	
Solvent		CH_2Cl_2	
CCDC	1907336		
Bond precision:	C-C = 0.0051 A	Wavelength=0.71073	
Cell:	a=9.7140(5)	b=11.6951(5)	c=16.9879(8)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1929.93(16)	1929.94(16)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C20 H25 N O4 S	C20 H25 N O4 S	
Sum formula	C20 H25 N O4 S	C20 H25 N O4 S	
Mr	375.47	375.47	
Dx, g cm-3	1.292	1.292	
Z	4	4	
Mu (mm-1)	0.192	0.192	
F000	800.0	800.0	
F000’	800.86		
h,k,l max	11,13,20	11,13,20	
Nref	3400[1954]	3354	
Tmin,Tmax	0.977,0.989	0.784,1.000	
Tmin’	0.965		
Correction method =	Numerical		
Data completeness =	1.72/0.99	Theta(max)= 24.999	
R(reflections) =	0.0438(2959)	wR2(reflections)= 0.1013(3354)	
S = 1.069			
	Npar = 239		

Reference:

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[4] O'Broin, C. Q.; Fernandez, P.; Martinez, C.; Muniz, K. *Org. Lett*. **2016**, *18*, 436.

[5] Yamada, K. I.; Yamamoto, Y.; Maekawa, M.; Akindele, T.; Umeki, H.; Tomioka, K. *Org. Lett*. **2006**, *8*, 87.

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