[Supporting Information for:]

$Sc(OTf)_3$-Catalyzed Condensation of 2-Alkyl-*N*-tosylaziridine with Aldehydes or Ketones: An Efficient Synthesis of 5-Alkyl-1,3-oxazolidines

Byungman Kang, Aaron W. Miller, Sandra Goyal, and SonBinh T. Nguyen*

Department of Chemistry and the Institute for Catalysis in Energy Processes, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

General Information. ^1H and ^{13}C NMR spectra were recorded on either a Varian INOVA 500 FTNMR (499.6 MHz for ^1H, 125.6 MHz for ^{13}C) or a Varian Mercury 400 FT-NMR spectrometer (400.6 MHz for ^1H, 100.7 MHz for ^{13}C). ^1H NMR data are reported as follows: chemical shift (multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant and integration). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards. ^{45}Sc NMR spectra were recorded on a Varian INOVA 400 FTNMR spectrometer (97.3 MHz for ^{45}Sc) and externally referenced to 0.1M $ScCl_3$ solution in D_2O.

GC analyses of reaction mixtures were carried out on a Hewlett-Packard 5890A instrument equipped with an FID detector interfaced to an HP 3396A integrator. The column used was a 30-m HP-5 capillary column with a 0.32-mm inner diameter and a 0.25-μm film thickness (flow rate = 1.8 mL/min for He carrier gas). GC conversions and yields were determined through integration of the product and starting material peaks against undecane (internal standard) using pre-established response factors.

HPLC analyses were carried out on a Varian ProStar HPLC system (Varian Inc., USA) equipped with a Varian ProStar 335 UV–vis photodiode array detector and a Varian ProStar 230 ternary LC pump. The column used was a 25-cm (*S,S*)-Whekl-O1 column (Regis Technologies Inc., USA) with a 0.46-cm inner diameter. Retention times of enantiomerically enriched products were referenced to racemic samples.

The infrared (IR) spectra of 1,3-oxazolidine compounds were recorded on a Thermo-Nicolet Nexus 670 FTIR spectrophotometer; samples were analyzed neat as thin films deposited on a sodium chloride plate. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High-Resolution Electrospray Mass Spectrometric (HRESIMS) data were obtained by staff members in the Integrated Molecular Structure Education and Research Center (IMSERC), Northwestern University (Evanston, IL).

Materials. All air- or water-sensitive reactions were carried out under nitrogen either in a drybox or using oven-dried glassware. All flash-chromatography was carried out using silica gel (MP silitech 60-200 mesh) or basic aluminum oxide (EMD 80-200 mesh) under a positive pressure of nitrogen, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using glass-backed silica gel 60 F_{254} plates (Merck EMD-571507) or basic aluminum oxide 60 F_{254} plates (Merck-HX763817). Visualization of the TLC results was achieved either by observation under UV light (254 nm), or via treatment with 10 % phosphomolybdic acid in ethanol followed by heating. Dichloromethane (Fisher Scientific) was dried over neutral alumina in a Dow-Grubbs solvent system.[1] All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise noted. Deuterated solvents were purchased from Cambridge

Isotope Laboratories and used without further purification.

Synthesis of racemic 2-methyl-*N*-tosylaziridine (1). 2-Methyl-*N*-tosylaziridine was synthesized following a modified literature procedure.[2] To a 250-mL round-bottom flask equipped with a magnetic stir bar was added aqueous KOH (10% w/w, 50 mL) and 2-methylaziridine (5.2 g, 91 mmol). This mixture was cooled down in an ice bath while stirring before *p*-toluenesulfonyl chloride (17.6 g, 92 mmol) was added as a solid. The resulting mixture was stirred inside the ice bath for 30 minutes before being warmed on the bench top to ambient temperature and allowed to stir overnight, during which time a white precipitate formed. Precipitate was filtered and washed with cold water (3 x 20 mL). The crude white product was recrystallized in hexanes at 0 ^{o}C. Isolated crystals were then filtered and dried under reduced pressure to yield a white solid (10.8 g, 51 mmol, 56%). Spectroscopic data for **1** was in good agreement with literature data.[2] ^{1}H NMR (400.6 MHz, $CDCl_3$): δ 1.22 (d, J = 6.0 Hz, 3H, aziridine CH_3), 1.99 (d, J = 4.4 Hz, 1H, aziridine CH_2), 2.42 (s, 3H, Ts-CH_3), 2.58 (d, J = 7.2 Hz, 1H, aziridine CH_2), 2.80 (m, 1H, aziridine CH), 7.31 (d, J = 8.0 Hz, 2H, Ar-H), 7.79 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ 16.9 (aziridine CH$_3$), 21.8 (Ts-CH$_3$), 34.9 (aziridine CH), 36.0 (aziridine CH$_2$), 127.9 (C_o), 129.8 (C_m), 135.5 (C_p), 144.6 (C_i). HPLC conditions: 10% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. (*S*)-2-Methyl-*N*-tosylaziridine retention time = 24.4 min, (*R*)-2-methyl-*N*-tosylaziridine retention time = 26.3 min.

General procedure for the synthesis of 2-alkyl-*N*-tosylaziridine 8, 9, and 13. 2-Alkyl-*N*-tosylaziridine **8, 9,** and **13** were synthesized following reported literature procedure.[3] Triethylamine (4.18 mL, 30.0 mmol, 3.0 equiv) was added to a solution containing 1,2-amino alcohol (2-amino-1-hexanol, 2-amino-3-methyl-1-butanol, or (*R*)-2-amino-1-propanol 10.0 mmol), *p*-TsCl (4.76 g, 25.0 mmol, 2.5 equiv), and DMAP (12.2 mg, 1 mol %) in dry CH_2Cl_2 (40 mL) at 0 ^{o}C. The reaction mixture was allowed to rt and stirred for 24 h at this temperature. A solution of saturated NH_4Cl (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification via silica gel chromatography (Et_2O/*n*-pentane = 1:3) afforded 2-alkyl-*N*-tosylaziridine **8** and **9**.

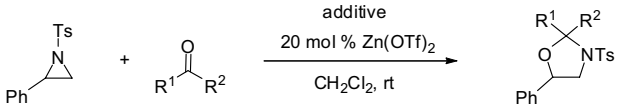
2-butyl-*N*-tosylaziridine (8). ^{1}H NMR (400.6 MHz, $CDCl_3$): δ 0.82 (t, J = 7.5 Hz, 3H, ^{n}Hex CH_3), 1.24 (m, 4H, ^{n}Hex CH_2), 1.35 (m, 1H, ^{n}Hex CH_2), 1.56 (m, 1H, ^{n}Hex CH_2), 2.06 (d, J = 4.5 Hz, 1H, aziridine CH_2), 2.45 (s, 3H, Ts-CH_3), 2.64 (d, J = 7.0 Hz, 1H, aziridine CH_2), 2.73 (m, 1H, aziridine CH), 7.34 (d, J = 8.0 Hz, 2H, Ar-H), 7.83 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ 14.0 (^{n}Hex CH$_3$), 21.8 (Ts-CH$_3$), 22.3 (^{n}Hex CH$_2$), 29.0 (^{n}Hex CH$_2$), 31.1 (^{n}Hex CH$_2$), 34.0 (aziridine CH), 40.6 (aziridine CH$_2$), 128.2 (C_o), 129.8 (C_m), 135.4 (C_p), 144.6 (C_i).

2-isopropyl-*N*-tosylaziridine (9). ^{1}H NMR (400.6 MHz, $CDCl_3$): δ 0.79 (d, J = 6.5 Hz, 3H, ^{i}Pr CH_3), 0.90 (d, J = 7.0 Hz, 3H, ^{i}Pr CH_3), 1.41 (m, 1H, ^{i}Pr CH), 2.10 (d, J = 4.5 Hz, 1H, aziridine CH_2), 2.45 (s, 3H, Ts-CH_3), 2.51 (m, 1H, aziridine CH), 2.62 (d, J = 7.5 Hz, 1H, aziridine CH_2), 7.34 (d, J = 7.5 Hz, 2H, Ar-H), 7.83 (d, J = 8.5 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$): δ 19.2 (^{i}Pr CH$_3$), 19.7 (^{i}Pr CH$_3$), 21.8 (Ts-CH$_3$), 30.3 (^{i}Pr CH), 32.9 (aziridine CH), 46.5 (aziridine CH$_2$), 128.3 (C_o), 129.8 (C_m), 135.3 (C_p), 144.6 (C_i).

(*R*)-2-methyl-*N*-tosylaziridine (13). See characterization data as described above for **1**.

Synthesis of 2-methyl-*N*-mesylaziridine (11). 2-Methyl-*N*-mesylaziridine was synthesized following a modified literature procedure.[4] Methanesulfonyl chloride (0.64 mL, 8.3 mmol, 1.1 equiv) was added dropwise to a solution containing 2-methylaziridine (0.53 mL, 7.5 mmol) and Et_3N (1.6 mL, 11.3 mmol, 1.5 equiv) in dry CH_2Cl_2 (20 mL) at -30 ^oC. The reaction mixture was stirred for 30 min and then allowed to 0 ^oC. Ice-water (10 mL) was added, followed by cold HCl (10 mL of a 10 wt% solution), and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed with saturated $NaHCO_3$ (20 mL) and NaCl (20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification via basic alumina (EtOAc/hexanes = 1:1) afforded 2-alkyl-*N*-mesylaziridine **11** as a white solid. Spectroscopic data for **11** was in good agreement with literature data.[4] ^1H NMR (499.6 MHz, $CDCl_3$): δ 1.33 (d, J = 5.5 Hz, 3H, aziridine CH_3), 2.07 (d, J = 4.5 Hz, 1H, aziridine CH_2), 2.59 (d, J = 7.0 Hz, 1H, aziridine CH_2), 2.79 (m, 1H, aziridine C*H*), 3.04 (s, 3H, Ms-CH_3). $^{13}C\{^1H\}$ NMR (125.6 MHz, $CDCl_3$): δ 17.0 (aziridine *C*H_3), 34.5 (aziridine *C*H), 35.4 (Ms-*C*H_3), 39.8 (aziridine *C*H_2).

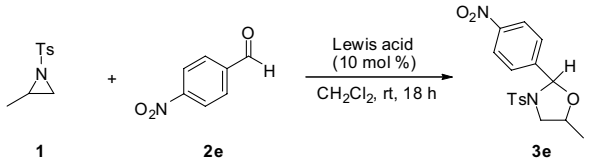
Table S1. Reproducibility for the $Zn(OTf)_2$-catalyzed condensation of 2-phenyl-*N*-tosylaziridine with organic carbonyls



Entry	R^1	R^2	Additive	Time (h)	Conv. (%)[b]	GC yield (%)[c]
1	CH_3	CH_3	none	2	82	75
2	CH_3	CH_3	4Å MS	2	27	***0***
3[d]	CH_3	CH_3	4Å MS	2	-	***80***[e]
4	CH_3	CH_3	$MgSO_4$	2	100	29
5	-$(CH_2)_5$-		none	0.5	26	25
6	-$(CH_2)_5$-		4Å MS	0.5	17	***13***
7[d]	-$(CH_2)_5$-		4Å MS	0.5	-	***96***[e]
8	Ph	H	none	3.5	91	88
9	Ph	H	4Å MS	3.5	90	***88***
10[d]	Ph	H	4Å MS	3.5	-	***52***[e]

[a]Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.5 mmol), carbonyl compound (1.5 mmol), $Zn(OTf)_2$ (20 mol %), additive (150 mg), undecane (20 mg), CH_2Cl_2, rt, N_2 atmosphere. [b]Conversion determined by GC analysis based on aziridine. [c]GC yield was determined with internal standard. [d] Reported results by Singh et al. in ref. 15. [e]Isolated yield.

Table S2. Effects of various Lewis acids in the condensation of **1** with **2e**

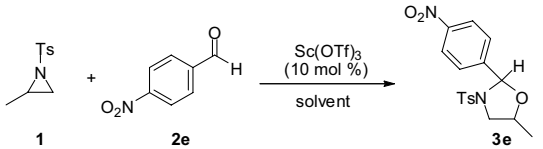


1 2e 3e

Entry	Lewis acid	GC yield (%)[b]
1	(salcen)Zn	0
2	(salcen)CrCl	0
3	$SnCl_4$	7
4	$AlCl_3$	0
5	$TiCl_4$	<5
6	$Sc(OTf)_3$	32
7	$Cu(OTf)_2$	<5
8	$Zn(OTf)_2$	0
9	$Sn(OTf)_2$	9

[a] Reaction conditions: **1** (0.5 mmol), **2e** (1.0 mmol, 2.0 equiv), Lewis acid (0.05 mmol, 10 mol %), undecane (15 mg), CH_2Cl_2 (0.5 mL), rt, 18 h. [b] GC yield was determined with internal standard. Salcen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine.

Table S3. The $Sc(OTf)_3$-catalyzed condensation of **1** with **2e** in various solvents and at various temperatures



1 2e 3e

Entry	Solvent	Temp (°C)	Time (h)	Conv. (%)[b]	Yield (%)[c]
1	THF	20	18	<5	0
2	CH_3CN	20	18	11	<5
3	CH_2Cl_2	20	18	37	25
4	CH_2Cl_2	40	12	74	33
5[d]	CH_2Cl_2	40	12	0	0
6	1,2-dichloroethane	80	1	100	46
7	chlorobenzene	80	1	100	33
8	nitromethane	80	1	100	35

[a] Reaction conditions: **1** (0.5 mmol), **2e** (0.6 mmol, 1.2 equiv), $Sc(OTf)_3$ (0.05 mmol, 10 mol %), undecane (15 mg), solvent (1.0 mL). [b] Conversion determined by GC analysis based on aziridine **1**. [c] Determined using GC analysis against an internal standard. [d] Reaction was performed without $Sc(OTf)_3$ catalyst.

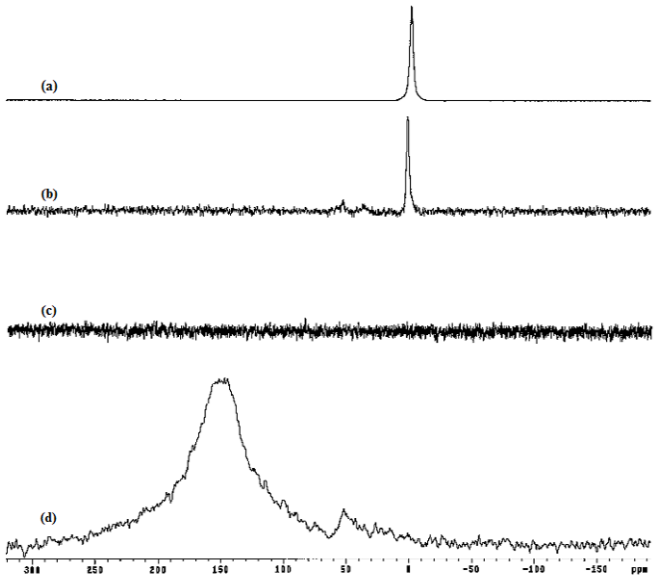


Figure S1. The ^{45}Sc NMR spectra of various complexes of Sc^{3+} measured against 0.1 M external standard of $ScCl_3$ in D_2O: (a) scandium triflate in CD_3CN; (b) mixture of scandium triflate and aziridine **1** in CD_3CN; (c) scandium triflate (insoluble) in CD_2Cl_2; (d) mixture of scandium triflate and aziridine **1** after stirring for 1 h in CD_2Cl_2.

Table S4. Optimization of reaction conditions in the condensation of **1** with aldehydes

Entry	$[Sc(OTf)_3]$ (mol %)	**2a** or **2e** (equiv)	Time (h)	**[1]** (M)	Conv. (%)[b]	Yield (%)[c]
1	10	**2e** (2)	2	0.2	9	<5[c]
2	20	**2e** (2)	2	0.2	28	17[c]
3	20	**2e** (5)	2	0.2	39	26[c]
4	20	**2e** (5)	2	0.5	100	91[c]
5	20	**2e** (5)	6	0.5	100	74[c]
6	20	**2e** (5)	2	1.0	100	92[c]
7[d]	10	**2a** (5)	3	1.0	100	83[e]
8	5	**2a** (5)	6	1.0	100	83[e]
9	1	**2a** (5)	12	1.0	90	80[e]
10[f]	1	**2a** (1.1)	6	8.5	100	81[e]

[a] Reaction conditions: **1** (0.5 mmol), **2e**, $Sc(OTf)_3$, undecane (15 mg), CH_2Cl_2, 40 °C, ambient atmosphere. [b] Conversion determined by GC analysis based on aziridine **1** [c] Determined using GC analysis against an internal standard. [d] Reaction was carried out in CH_2Cl_2. [e] Isolated yield. [f] Reaction was carried out in neat **2a** (valeraldehyde).

Experimental procedure for the observation of the diastereomeric ratio for the 1,3-oxazolidine product 3e as a function of reaction time. To a solution of 2-methyl-*N*-tosylaziridine (1.5 mmol, 1 equiv) and undecane (45 mg) in anhydrous dichloromethane (1.5 mL) was added 4-nitrobenzaldehyde (2.5 mmol, 5 equiv) followed by scandium triflate (0.3 mmol, 20 mol%). The reaction mixture was stirred at 40 °C under ambient atmosphere, aliquots were taken and filtered through a pad of silica gel washing with dichloromethane at the indicated interval (15, 30, 45, 60, 75, 90, 105, and 120 min). The conversion of aziridine was then monitored by GC

using an internal standard and diastereomeric ratio was determined by comparing the area of cis/trans isomers (Figure S2 and Table S5).

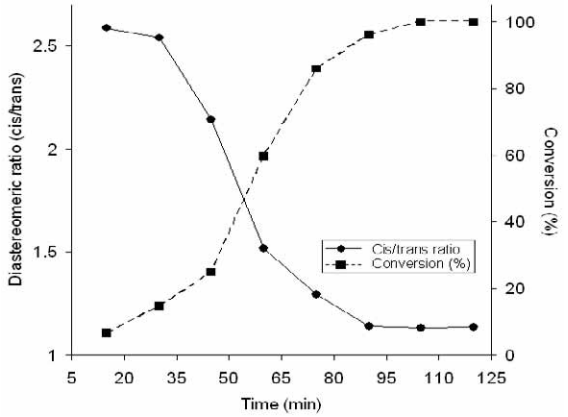


Figure S2. Plots of reaction conversion and the evolution of product cis/trans ratio in the condensation of **1** with **2e**.

Table S5. The evolution of product cis/trans ratio in the condensation of **1** with **2e**

Time (min)	Cis/trans ratio	Conv. (%)
15	2.587	6.6
30	2.542	14.5
45	2.143	24.8
60	1.517	59.8
75	1.294	85.9
90	1.139	96.2
105	1.128	100
120	1.133	100

Experiment to observe the change in diastereomeric ratio of a *cis*-enriched sample of 1,3-oxazolidine 3e in the presence of $Sc(OTf)_3$. A sample of *cis*-enriched 1,3-oxazolidine **3e** was obtained by the following procedure: a 1.1:1 cis/trans sample of **3e** (2 g) was dissolved in hexanes (500 mL) at rt and then cooled down to –20°C in a freezer overnight. The resulting mixture was warmed to rt and filtered over a Buchner funnel. The resulting white crystals was washed with cold hexanes (100 mL), vacuum-dried, and subjected to this cold recrystallization procedure two more times to afford *cis*-enriched **3e** (450 mg cis/trans = 8.5:1).

To a solution of *cis*-enriched **3e** (200 mg, 0.55 mmol, prepared as described above) in anhydrous CH_2Cl_2 (0.55 mL) was added scandium triflate (54 mg, 0.11 mmol, 20 mol%). The reaction mixture was stirred at 40 °C under ambient atmosphere, aliquots were taken and filtered through a pad of silica gel washing with CH_2Cl_2 at the indicated interval (5, 10, 15, 20, 40, and 60 min). The diastereomeric ratio was then monitored by GC and determined by comparing the area of cis/trans isomers (Figure S3).

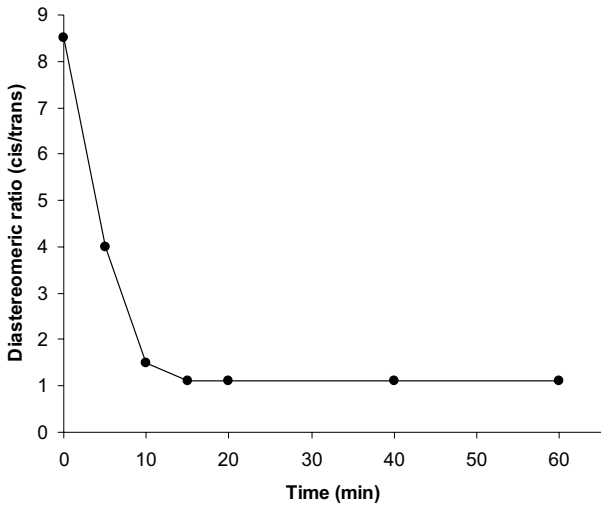
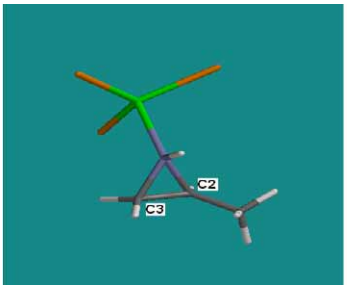


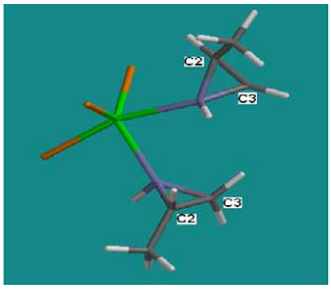
Figure S3. The change of the diastereomeric ratio starting from *cis* major isomer **3e** (8.5:1) in the presence of 20 mol% $Sc(OTf)_3$

DFT calculations. Density functional theory (DFT) calculations were carried out using Spartan'02 for Windows on an Intel Core2 Duo CPU E4500 desktop running Windows XP operating system.[5] To facilitate geometry optimization, the OTf group of Sc^{3+} and the tosyl group of 2-methyl-*N*-tosylaziridine were replaced by Cl and H atoms, respectively. Cl_3Sc(2-methylaziridine) was modeled as a tetrahedral center using the initial geometry obtained from the crystal structure of $Cl_2Sc[(2,6\text{-}^{i}Pr\text{-}C_6H_3)N{=}C(^{t}Bu)CH{=}C(^{t}Bu)N(2,6\text{-}^{i}Pr\text{-}C_6H_3)]$.[6] Cl_3Sc(2-methylaziridine)$_2$ and Cl_3Sc(aldehyde)(2-methylaziridine) complexes were modeled as trigonal bipyramids with two equatorial and one axial Cl following the initial geometry obtained from the crystal structure of $Cl_3Sc(DME)(CH_3CN)$.[7] The energy-minimized structures were used as the initial geometries for DFT calculations. The geometry optimizations (equilibrium geometries) for each complex at the ground state were performed with the 6-31G* basis set, using the Becke three-parameter hybrid method (B3LYP).[8] The total charge was kept neutral and the multiplicity was set at singlet. Because Mulliken population analysis was sensitive to basis set and gave the results which are not in agreement with chemical expectations for ionic and non-covalent complexes,[9, 10] the partial charge distributions shown in Table S8 were derived from the electrostatic potential.

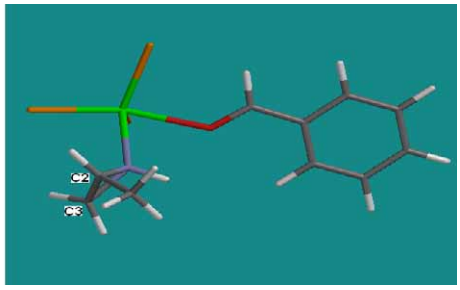
Figure S4 showed the optimized geometry of the calculated intermediates; the corresponding calculated energies were listed in Tables S6 and S7. In all cases, the product complexes were found to be lower in energy than the corresponding sums of the energies of the starting fragments, suggesting that Cl_3Sc can readily combine with aziridine and aldehydes. Among all calculated intermediates, Cl_3Sc(aldehyde)(2-methylaziridine) complexes are energetically favored over Cl_3Sc(2-methylaziridine)$_2$, which in turn is lower in energy than Cl_3Sc(2-methylaziridine). Thus, they were selected as likely intermediates in the mechanism shown in Scheme 2.



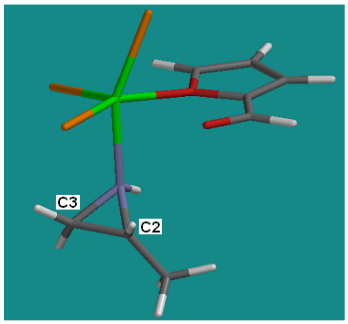
Cl_3Sc(2-methylaziridine)



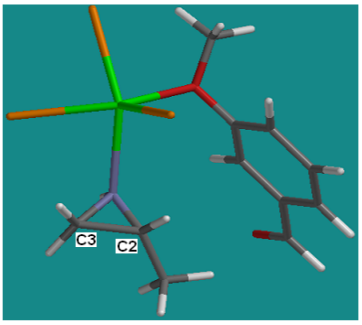
Cl_3Sc(2-methylaziridine)$_2$



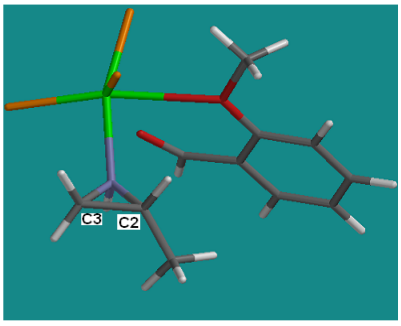
Cl_3Sc(benzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$



Cl_3Sc(2-furaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$



Cl_3Sc(*m*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$



Cl_3Sc(*o*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$

Figure S4. Optimized B3LYP geometries for the Cl_3Sc(2-methylaziridine), Cl_3Sc(2-methylaziridine)$_2$, and Cl_3Sc(aldehyde)$_{eq}$(2-methylaziridine)$_{ax}$ structures.

Table S6. Relative energies of Cl_3Sc(2-methylaziridine), Cl_3Sc(2-methylaziridine)$_2$, and Cl_3Sc(aldehyde)$_{eq}$(2-methylaziridine)$_{ax}$ complexes compared to the corresponding sums of the energies of the starting fragments.

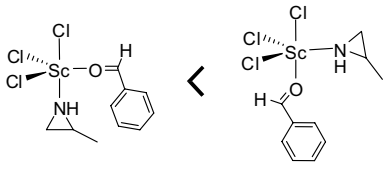
Complex	Total energy (Hartree)	Relative energy ($\Delta E = E_{product} - E_{reactant}$) (kcal/mol)
Cl_3Sc(2-methylaziridine) + benzaldehyde →	-2660.39433	-16.07
Cl_3Sc(benzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	-2660.41994	
Cl_3Sc(2-methylaziridine) + 2-furaldehyde →	-2658.16720	-15.95
Cl_3Sc(2-furaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	-2658.19262	
Cl_3Sc(2-methylaziridine) + *m*-methoxybenzaldehyde →	-2774.91810	-6.04
Cl_3Sc(*m*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	-2774.92773	
Cl_3Sc(2-methylaziridine) + *o*-methoxybenzaldehyde →	-2774.90860	-19.97
Cl_3Sc(*o*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	-2774.94043	
Cl_3Sc + 2-methylaziridine →	-2314.74985	-44.56
Cl_3Sc(2-methylaziridine)	-2314.82086	
Cl_3Sc(2-methylaziridine) + 2-methylaziridine →	-2488.05975	-17.97
Cl_3Sc(2-methylaziridine)$_2$	-2488.08838	

Between the two possible isomers of Cl_3Sc(aldehyde)(2-methylaziridine) complexes, Cl_3Sc(aldehyde)$_{eq}$(2-methylaziridine)$_{ax}$ are uniformly lower in energy than the Cl_3Sc(aldehyde)$_{ax}$(2-methylaziridine)$_{eq}$ isomers (Table S7 and Figure S5). As such, the former complexes were used in the evaluation of the atomic charges on the C^2 and C^3

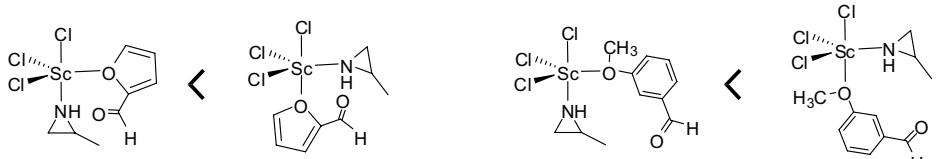
atoms of the coordinated 2-methylaziridine (Table S8), leading to the proposed intramolecular condensation shown in Scheme S1.

Table S7. Total energies and relative energies (ΔE in kcal/mol) for the Cl_3Sc(aldehyde)(2-methylaziridine) structures

Complex	Total energy (Hartree)		Relative energy ($\Delta E = E_{eq} - E_{ax}$) (kcal/mol)
Cl_3Sc(2-methylaziridine)	-2314.82086		n/a
Cl_3Sc(2-methylaziridine)$_2$	-2488.08838		n/a
	Axial-aziridine	**Equatorial-aziridine**	
Cl_3Sc(benzaldehyde)(2-methylaziridine)	-2660.41994	-2660.41797	1.24
Cl_3Sc(2-furaldehyde)(2-methylaziridine)	-2658.19262	-2658.19243	0.12
Cl_3Sc(*m*-methoxybenzaldehyde)(2-methylaziridine)	-2774.92773	-2774.92394	2.38
Cl_3Sc(*o*-methoxybenzaldehyde)(2-methylaziridine)	-2774.94043	-2774.92999	6.55



Axial-aziridine Equatorial-aziridine

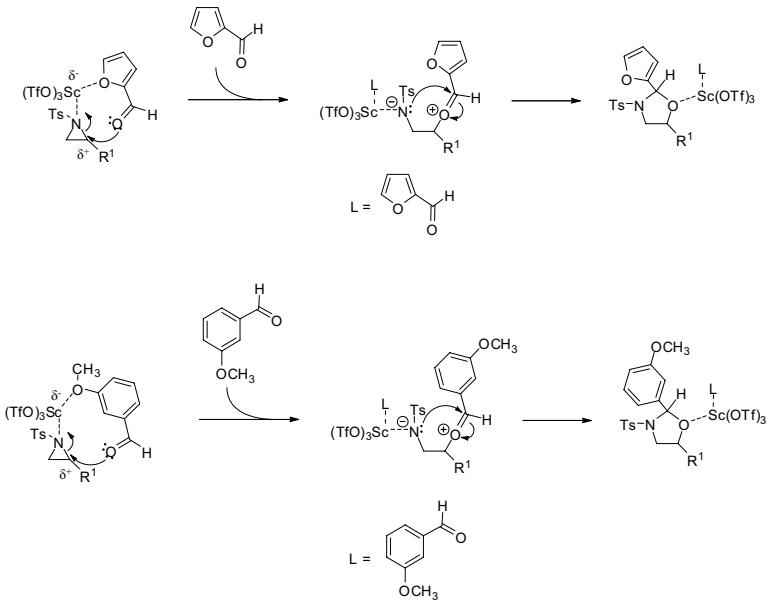


Axial-aziridine Equatorial-aziridine Axial-aziridine Equatorial-aziridine

Figure S5. Comparison of energies for the Sc(aldehyde)$_{eq}$(aziridine)$_{ax}$ and Sc(aldehyde)$_{ax}$(aziridine)$_{eq}$ structures.

Table S8. Atomic charges for C^2 and C^3 atoms of 2-methylaziridine in Cl_3Sc(aldehyde)$_{eq}$(2-methylaziridine)$_{ax}$ complex

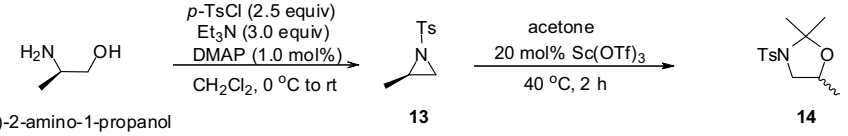
	Complex	Q(C^2)	Q(C^3)	ΔQ	Selectivity
	2-methylaziridine	+0.162	-0.124	0.286	n/a
	Cl_3Sc(2-methylaziridine)$_2$	+0.168	-0.258	0.426	n/a
	Cl_3Sc(benzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	+0.171	-0.241	0.412	11:1
Intramolecular reaction between coordinated aldehydes and aziridine	Cl_3Sc(2-furaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	+0.201	-0.300	0.501	>50:1
	Cl_3Sc(*m*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	+0.172	-0.239	0.411	>50:1
	Cl_3Sc(*o*-methoxybenzaldehyde)$_{eq}$(2-methylaziridine)$_{ax}$	+0.127	-0.233	0.360	9.4:1



Scheme S1. A proposed mechanism for the $Sc(OTf)_3$-catalyzed intramolecular condensation of *N*-tosyl-2-alkylaziridine with 2-furaldehyde and *m*-methoxybenzaldehyde.

Monitoring the $Sc(OTf)_3$-catalyzed racemization of optically pure 2-methyl-*N*-tosylaziridine. Combining enantiomerically pure (*R*)-2-methyl-*N*-tosylaziridine **13** (58.8 mg, 0.25 mmol) with acetone (0.25 mL) in the presence of 20 mol% $Sc(OTf)_3$ at 40 ^oC (Scheme S2) afforded product **14** as a racemic mixture, suggesting that the starting chiral aziridine **13** can be readily racemized in the presence of $Sc(OTf)_3$ before the ring-opening step. (The enantiomeric excess of 1,3-oxazolidine product **14** was determined by HPLC analysis of crude reaction mixture using (*S,S*)-Whelk-O1 column (Figure S6)).

To confirm the aforementioned hypothesis, we monitored the change in *ee* of **13** without the carbonyl compound in the presence of 20 mol% $Sc(OTf)_3$ in CH_2Cl_2 (1.0 M) at 40 ^oC. HPLC and GC-MS analyses of crude reaction mixture after 5 and 15 min clearly showed a mixture of racemized 2-methyl-*N*-tosylaziridine as well as the ring-opened product *N*-allyl-4-methylbenzenesulfonamide (Figure S7).



Scheme S2. The reaction of enantiomerically pure (*R*)-2-methyl-*N*-tosylaziridinec **13** with acetone in the presence of $Sc(OTf)_3$.

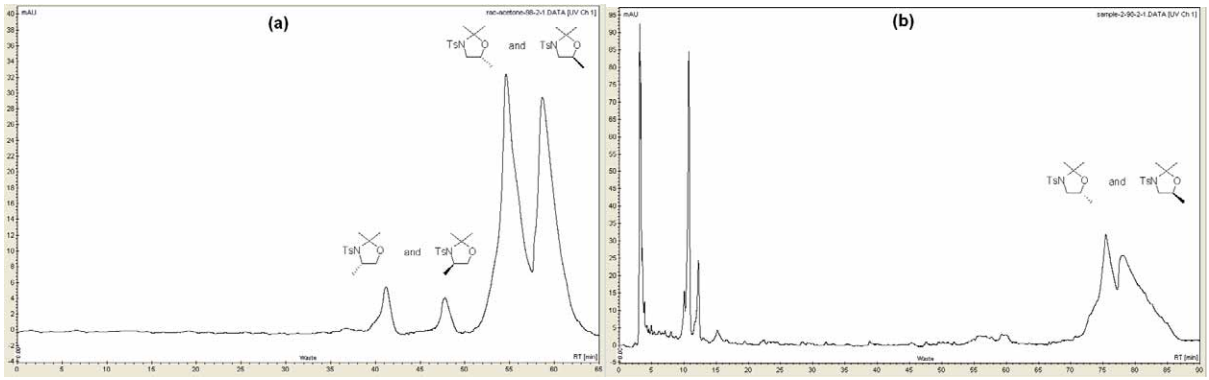
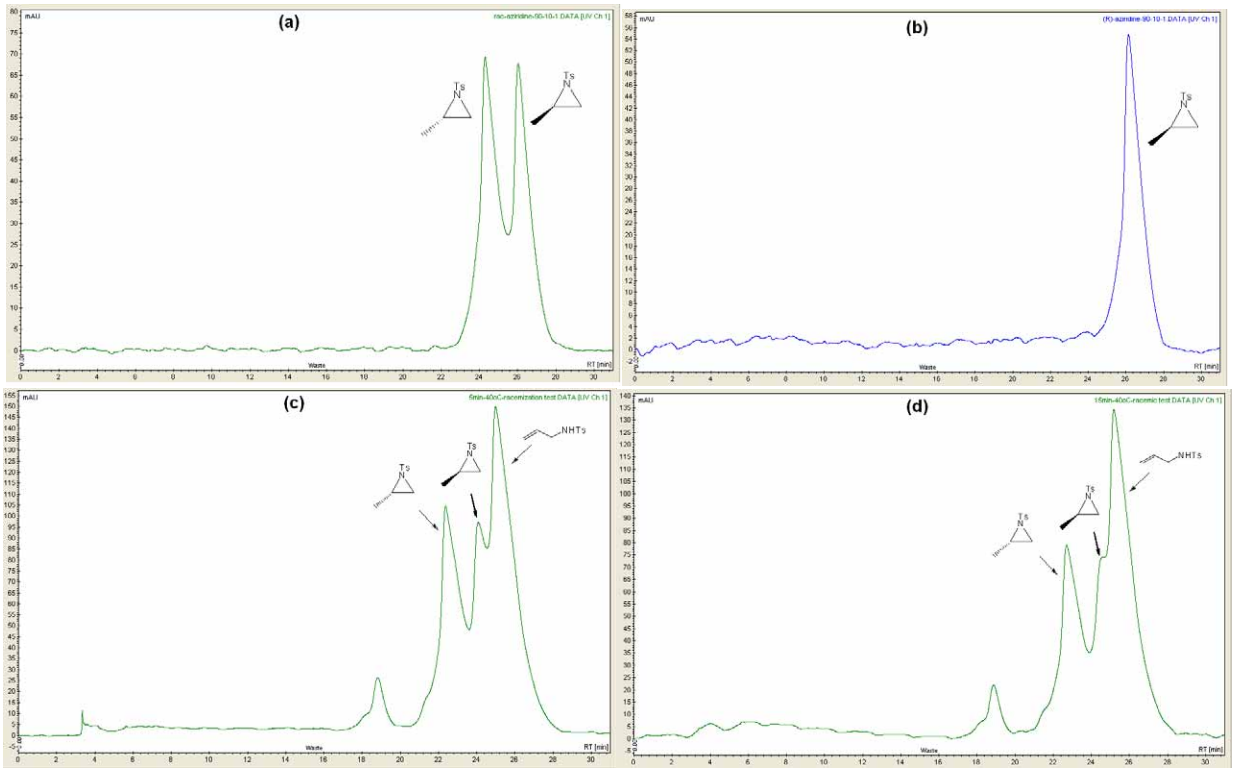


Figure S6. Chiral HPLC traces for: (a) racemic **7a**; (b) the crude reaction product from the condensation of **13** with acetone. HPLC conditions are listed together with the other analytical data for **7a** in a later section.



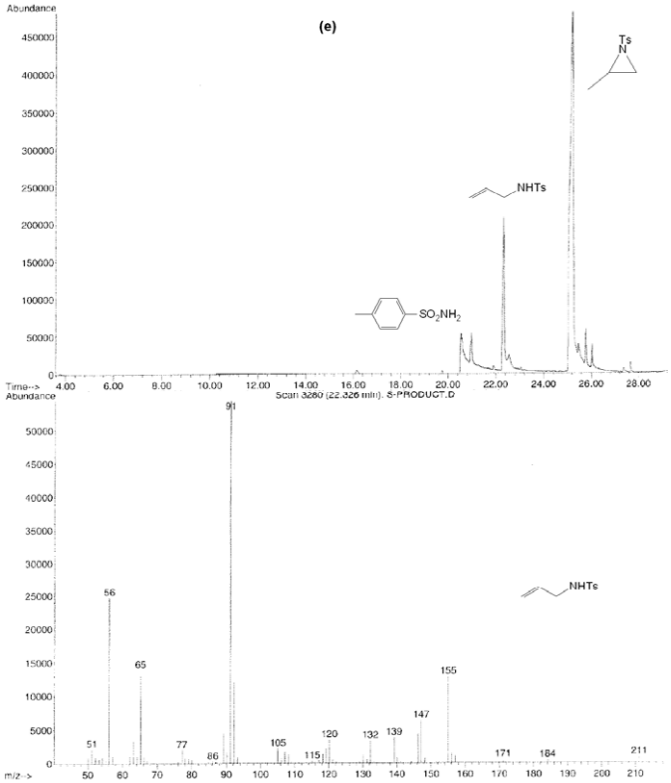


Figure S7. Chiral HPLC traces for: (a) racemic aziridine **1**; (b) chiral aziridine **13**; (c) crude reaction mixture after 5 min; (d) crude reaction mixture after 15 min. (e) GC-MS analysis of crude reaction mixture after 15 min. HPLC conditions are listed together with the other analytical data for **1** in a previous section.

General procedure for the Sc(OTf)$_3$-catalyzed condensation of 2-methyl-*N*-tosylaziridine with organic carbonyls. *With aldehyde substrates*. Under bench-top conditions, a 4-mL vial equipped with a magnetic stir bar was charged with scandium triflate (24.6 mg, 0.1 mmol, 20 mol %), 2-methyl-*N*-tosylaziridine (0.5 mmol, 1 equiv), and anhydrous dichloromethane (0.5 mL). An aldehyde (2.5 mmol, 5 equiv) was then added to the reaction mixture at room temperature. The reaction vial was capped and allowed to stir at 40 ^{o}C in an oil bath. After an allotted time (0.5-2 h, depending on the substrate), the reaction was removed from the oil bath and the cooled solution was passed through a plug of silica gel with ethyl acetate (10 mL) to remove the catalyst. The resulting yellow liquid was concentrated under reduced pressure and subsequent purification via column chromatography on silica gel with EtOAc/hexanes or Et$_2$O/*n*-pentane eluants to afford the pure oxazolidine product.

With ketone substrates. In the drybox, a 4-mL vial equipped with a magnetic stir bar was charged with dried scandium triflate (24.6 mg, 0.1 mmol, 20 mol %), 2-methyl-*N*-tosylaziridine (0.5 mmol, 1 equiv), and anhydrous dichloromethane (0.5 mL). A ketone (2.5 mmol, 5 equiv) was then added to the reaction mixture at room temperature. The reaction vial was capped, taken out of the drybox, and then allowed to stir at 40 ^{o}C in an oil bath. After an allotted time (1.5-4 h, depending on the substrate), the reaction was removed from the oil bath and the cooled solution was passed through a plug of basic alumina with ethyl acetate eluent (10 mL) to remove the catalyst. The resulting liquid was concentrated under reduced pressure and subsequent purification via column chromatography on basic alumina with Et$_2$O/*n*-pentane eluants to afford the pure oxazolidine product (Table 4,

entries 2 and 4: products were the mixture of two diastereomers). Note: *The main limiting factor in isolating these hydrolytically sensitive compounds lies in finding the appropriate purification method to avoid their decomposition.*

2-Butyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3a, Table 3, entry 1). A colorless oil. R_f = 0.42 (EtOAc/hexanes = 1:3 v/v). FTIR (neat, cm^{-1}): ν 2957, 2932, 2872, 1598, 1454, 1349, 1167, 1090. HRESIMS: Calcd for $C_{15}H_{23}NO_3S$: 297.1399, found: *m/z* 297.1398 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 10 min, final temperature = 190 °C (*cis*-5-methyl isomer = 57.2 min; *trans*-5-methyl isomer = 58.0 min; *cis*-4-methyl isomer = 57.5 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.5 Hz, 3H, ^{n}Bu CH_3), 1.14 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 1.33-1.46 (m, 4H, ^{n}Bu CH_2), 1.66-1.79 (m, 2H, ^{n}Bu CH_2), 2.44 (s, 3H, Ts-CH_3), 2.89 (t, *J* = 10.0 Hz, 1H, N-CH_2), 3.25 (m, 1H, O-C*H*CH_3), 3.65 (dd, J_1 = 11.5 Hz, J_2 = 5.0 Hz, 1H, N-CH_2), 5.05 (dd, J_1 = 6.5 Hz, J_2 = 4.0 Hz, 1H, N-C*H*-O), 7.34 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 7.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 14.3 (^{n}Bu *C*H_3), 17.9 (O-CH*C*H_3), 21.8 (Ts-*C*H_3), 22.7 (^{n}Bu *C*H_2), 26.1 (^{n}Bu *C*H_2), 36.3 (^{n}Bu *C*H_2), 53.5 (N-*C*H_2), 73.3 (O-*C*HCH_3), 91.9 (N-*C*H-O), 127.9 (C_o), 130.1 (C_m), 135.1 (C_p), 144.2 (C_i).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.5 Hz, 3H, ^{n}Bu CH_3), 0.95 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 1.33-1.46 (m, 4H, ^{n}Bu CH_2), 1.81-1.90 (m, 2H, ^{n}Bu CH_2), 2.44 (s, 3H, Ts-CH_3), 2.81 (t, *J* = 10.0 Hz, 1H, N-CH_2), 3.56 (dd, J_1 = 9.5 Hz, J_2 = 5.5 Hz, 1H, N-CH_2), 4.26 (m, 1H, O-C*H*CH_3), 5.13 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 1H, N-C*H*-O), 7.34 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 7.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 14.2 (^{n}Bu *C*H_3), 18.4 (O-CH*C*H_3), 21.8 (Ts-*C*H_3), 22.6 (^{n}Bu *C*H_2), 27.0 (^{n}Bu *C*H_2), 35.4 (^{n}Bu *C*H_2), 52.9 (N-*C*H_2), 72.4 (O-*C*HCH_3), 91.9 (N-*C*H-O), 128.1 (C_o), 130.0 (C_m), 133.9 (C_p), 144.2 (C_i).

2-Isopropyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3b, Table 3, entry 2). A colorless oil. R_f = 0.43 (EtOAc/hexanes = 1:3 v/v). FTIR (neat, cm^{-1}): ν 2972, 2933, 2876, 1599, 1460, 1350, 1166, 1090. HRESIMS: Calcd for $C_{14}H_{21}NO_3S$: 283.1242, found: *m/z* 283.1244 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C /min, final time = 10 min, final temperature = 190 °C (*cis*-5-methyl isomer = 50.9 min; *trans*-5-methyl isomer = 51.4 min; *trans*-4-methyl isomer = 51.8 min; *cis*-4-methyl isomer = 52.2 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.95 (d, *J* = 7.0 Hz, 3H, ^{i}Pr CH_3), 0.99 (d, *J* = 7.0 Hz, 3H, ^{i}Pr CH_3), 1.11 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 2.01 (m, 1H, ^{i}Pr C*H*), 2.44 (s, 3H, Ts-CH_3), 2.84 (dd, J_1 = 12.5 Hz, J_2 = 10.5 Hz, 1H, N-CH_2), 3.21 (m, 1H, O-C*H*CH_3), 3.68 (dd, J_1 = 12.5 Hz, J_2 = 5.5 Hz, 1H, N-CH_2), 4.93 (d, *J* = 4.5 Hz, 1H, N-C*H*-O), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.74 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 15.7 (^{i}Pr *C*H_3), 17.8 (^{i}Pr *C*H_3), 18.2 (O-CH*C*H_3), 21.7 (Ts-*C*H_3), 33.9 (^{i}Pr *C*H), 53.7 (N-*C*H_2), 73.0 (O-*C*HCH_3), 95.6 (N-*C*H-O), 127.8 (C_o), 130.1 (C_m), 135.2 (C_p), 144.2 (C_i).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.83 (d, *J* = 6.0 Hz, 3H, ^{i}Pr CH_3), 0.94 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H, ^{i}Pr CH_3), 2.01 (m, 1H, ^{i}Pr C*H*), 2.44 (s, 3H, Ts-CH_3), 2.94 (dd, J_1 = 10.5 Hz, J_2 = 6.5 Hz, 1H, N-CH_2), 3.55 (dd, J_1 = 10.5 Hz, J_2 = 6.0 Hz, 1H, N-CH_2), 4.23 (m, 1H, O-C*H*CH_3), 4.93 (d, *J* = 4.5 Hz, 1H, N-C*H*-O), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.74 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 16.9 (^{i}Pr *C*H_3), 18.6 (^{i}Pr *C*H_3), 19.1 (O-CH*C*H_3), 21.7 (Ts-*C*H_3), 32.5 (^{i}Pr *C*H), 52.7 (N-*C*H_2), 72.7 (O-*C*HCH_3), 96.4 (N-*C*H-O), 128.1 (C_o), 129.8 (C_m), 134.2 (C_p), 144.1 (C_i).

2-*tert*-Butyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3c, Table 3, entry 3). A white solid. R_f = 0.44 (EtOAc/hexanes = 1:3 v/v). FTIR (neat, cm^{-1}): ν 2956, 2927, 1599, 1460, 1355, 1168, 1119. HRESIMS: Calcd for $C_{15}H_{23}NO_3S$: 297.1399, found: *m/z* 297.1398 $[M+H]^+$. GC temperature program: initial time = 2 min., initial temperature = 80 °C, ramp rate = 2 °C /min, final time = 10 min., final temperature = 190 °C (*cis*-5-methyl isomer = 53.2 min; *trans*-5-methyl isomer = 53.6 min; *cis*-4-methyl isomer = 54.8 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.98 (s, 9H, ^{t}Bu CH_3), 1.09 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 2.45 (s, 3H, Ts-CH_3), 2.83 (t, *J* = 11.0 Hz, 1H, N-CH_2), 3.08 (m, 1H, O-C*H*CH_3), 3.68 (dd, J_1 = 12.0 Hz, J_2 = 5.0 Hz, 1H, N-CH_2), 4.98 (s, 1H, N-C*H*-O), 7.34 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.77 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 17.4 (O-CH*C*H_3), 21.7 (Ts-*C*H_3), 25.5 (^{t}Bu *C*H_3), 37.0 (^{t}Bu *C*), 54.4 (N-*C*H_2), 72.8 (O-*C*HCH_3), 98.4 (N-*C*H-O), 128.1 (C_o), 130.2 (C_m), 135.6 (C_p), 144.3 (C_i).

2-Phenyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3d, Table 3, entry 4). A white solid. R_f = 0.32 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 3064, 3033, 2978, 2933, 2892, 1723, 1692, 1598, 1451, 1350, 1166, 1091, 1023. HRESIMS: Calcd for $C_{17}H_{19}NO_3S$: 317.1086, found: *m/z* 317.1084 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C /min, final time = 5 min, final temperature = 260 °C (*cis*-5-methyl isomer = 68.4 min; *trans*-5-methyl isomer = 69.1 min; *cis*-4-methyl isomer = 67.3 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.23 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 2.45 (s, 3H, Ts-CH_3), 3.01 (t, *J* = 8.5 Hz, 1H, N-CH_2), 3.64 (m, 1H, O-C*H*CH_3), 3.88 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, N-CH_2), 6.12 (s, 1H, N-C*H*-O), 7.36 (m, 5H, Ar-*H*), 7.56 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.71 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.3 (O-CH*C*H_3), 21.8 (Ts-*C*H_3), 53.2 (N-*C*H_2), 72.7 (O-*C*HCH_3), 91.6 (N-*C*H-O), 127.0 (Ph-C_i), 127.8 (Ph-C_o), 128.4 (Ts-C_o), 128.8 (Ph-C_m), 130.4 (Ts-C_m), 134.2 (Ts-C_p), 139.1 (Ph-C_i), 144.2 (Ts-C_i).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.02 (d, *J* = 6.0 Hz, 3H, O-CHCH_3), 2.47 (s, 3H, Ts-CH_3), 3.01 (t, *J* = 8.5 Hz, 1H, N-CH_2), 3.58 (dd, J_1 = 10.0 Hz, J_2 = 6.5 Hz, 1H, N-CH_2), 4.14 (m, 1H, O-C*H*CH_3), 6.31 (s, 1H, N-C*H*-O), 7.36 (m, 5H, Ar-*H*), 7.51 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.80 (d, *J* = 8.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.4 (O-CH*C*H_3), 21.8 (Ts-*C*H_3), 52.9 (N-*C*H_2), 74.4 (O-*C*HCH_3), 91.1 (N-*C*H-O), 126.7 (Ph-C_p), 128.2 (Ph-C_o), 128.6 (Ts-C_o), 128.7 (Ph-C_m), 130.0 (Ts-C_m), 133.9 (Ts-C_p), 138.6 (Ph-C_i), 144.4 (Ts-C_i).

2-(4-Nitrophenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3e, Table 3, entry 5). A pale yellow oil. R_f = 0.30 (EtOAc/hexanes = 1:2 v/v). FTIR (neat, cm^{-1}): ν 3082, 2979, 2934, 2894, 1598, 1529, 1349, 1165, 1106, 1090. HRESIMS: Calcd for $C_{17}H_{18}N_2O_5S$: 362.0936, found: *m/z* 362.0938 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C /min to 230 °C and 5 °C /min from 230 to 260 °C, final time = 10 min, final temperature = 260 °C (*cis*-5-methyl isomer = 83.7 min; *trans*-5-methyl isomer = 84.3 min; *cis*-4-methyl isomer = 82.2 min; *trans*-4-methyl isomer = 82.9 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.22 (d, *J* = 6.5 Hz, 3H, O-CHCH_3), 2.46 (s, 3H, Ts-CH_3), 2.96 (t, *J* = 10.0 Hz, 1H, N-CH_2), 3.59 (m, 1H, O-C*H*CH_3), 3.86 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, N-CH_2),

6.15 (s, 1H, N-C*H*-O), 7.35 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.71 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 8.20 (d, *J* = 8.0 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125.6 MHz, $CDCl_3$): δ 18.2 (O-CH*C*H$_3$), 21.8 (Ts-*C*H$_3$), 53.2 (N-*C*H$_2$), 74.9 (O-*C*HCH$_3$), 90.3 (N-*C*H-O), 123.7 (nitrophenyl-C_o), 127.8 (nitrophenyl-C_m), 128.1 (Ts-C_o), 130.3 (Ts-C_m), 134.9 (Ts-C_p), 144.9 (Ts-C_i), 146.2 (nitrophenyl-C_i), 148.4 (nitrophenyl-C_p).

Trans-5-methyl isomer. ^1H NMR (499.6 MHz, $CDCl_3$): δ 1.03 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 2.47 (s, 3H, Ts-C*H*$_3$), 2.99 (t, *J* = 9.5 Hz, 1H, N-C*H*$_2$), 3.59 (m, 1H, N-C*H*$_2$), 4.10 (m, 1H, O-C*H*CH$_3$), 6.28 (s, 1H, N-C*H*-O), 7.39 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.77 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 8.22 (d, *J* = 7.5 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125.6 MHz, $CDCl_3$): δ 18.3 (O-CH*C*H$_3$), 21.8 (Ts-*C*H$_3$), 52.9 (N-*C*H$_2$), 73.4 (O-*C*HCH$_3$), 90.1 (N-*C*H-O), 123.8 (nitrophenyl-C_o), 127.9 (nitrophenyl-C_m), 128.2 (Ts-C_o), 130.2 (Ts-C_m), 133.5 (Ts-C_p), 144.9 (Ts-C_i), 145.9 (nitrophenyl-C_i), 148.2 (nitrophenyl-C_p).

2-(4-Methoxyphenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3f, Table 3, entry 6). A white solid. R_f = 0.20 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 3064, 2976, 2934, 2838, 1612, 1513, 1460, 1349, 1249, 1165, 1029. HRESIMS: Calcd for $C_{18}H_{21}NO_4S$: 347.1191, found: *m/z* 347.1194 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C /min to 230 °C and 5 °C /min from 230 to 260 °C, final time = 10 min, final temperature = 260 °C (*cis*-5-methyl isomer = 77.2 min; *trans*-5-methyl isomer = 77.8 min; *cis*-4-methyl isomer = 76.8 min).

Cis-5-methyl isomer. ^1H NMR (499.6 MHz, C_6D_6): δ 0.79 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 1.89 (s, 3H, Ts-C*H*$_3$), 2.85 (dd, J_1 = 10.5 Hz, J_2 = 8.5 Hz, 1H, N-C*H*$_2$), 3.25 (dd, J_1 = 10.0 Hz, J_2 = 6.0 Hz, 1H, N-C*H*$_2$), 3.29 (s, 3H, O-C*H*$_3$), 3.36 (m, 1H, O-C*H*CH$_3$), 6.28 (s, 1H, N-C*H*-O), 6.78 (m, 4H, Ar-*H*), 7.66 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 8.0 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125.6 MHz, C_6D_6): δ 18.7 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 53.7 (N-*C*H$_2$), 55.4 (O-*C*H$_3$), 74.7 (O-*C*HCH$_3$), 92.3 (N-*C*H-O), 114.7 (methoxyphenyl-C_m), 128.9 (Ts-C_o), 129.3 (methoxyphenyl-C_o), 130.4 (Ts-C_m), 132.1 (Ts-C_p), 137.4 (methoxyphenyl-C_i), 144.2 (Ts-C_i), 160.9 (methoxyphenyl-C_p).

Trans-5-methyl isomer. ^1H NMR (499.6 MHz, C_6D_6): δ 0.64 (d, *J* = 5.5 Hz, 3H, O-CHC*H*$_3$), 1.87 (s, 3H, Ts-C*H*$_3$), 2.69 (dd, J_1 = 11.5 Hz, J_2 = 9.5 Hz, 1H, N-C*H*$_2$), 3.31 (s, 3H, O-C*H*$_3$), 3.68 (dd, J_1 = 11.5 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 3.75 (m, 1H, O-C*H*CH$_3$), 6.46 (s, 1H, N-C*H*-O), 6.78 (m, 4H, Ar-*H*), 7.56 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.60 (d, *J* = 8.5 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125.6 MHz, C_6D_6): δ 18.6 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 53.7 (N-*C*H$_2$), 55.5 (O-*C*H$_3$), 73.1 (O-*C*HCH$_3$), 91.8 (N-*C*H-O), 114.5 (methoxyphenyl-C_m), 129.0 (Ts-C_o), 129.3 (methoxyphenyl-C_o), 130.3 (Ts-C_m), 132.7 (Ts-C_p), 135.8 (methoxyphenyl-C_i), 144.1 (Ts-C_i), 161.1 (methoxyphenyl-C_p).

2-(2-Furanyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3i, Table 3, entry 9). A white solid. R_f = 0.25 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 3540, 3297, 3123, 3032, 2979, 2932, 1598, 1351, 1167, 1092, 1012. HRESIMS: Calcd for $C_{15}H_{17}NO_4S$: 307.0878, found: *m/z* 307.0871 $[M+H]^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 5 min, final temperature = 230 °C (*cis*-5-methyl isomer = 60.7 min; *trans*-5-methyl isomer = 61.2 min).

Cis-5-methyl isomer. ^1H NMR (499.6 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.5 Hz, 3H, O-CHC*H*$_3$), 2.43 (s, 3H, Ts-C*H*$_3$), 3.13 (t, *J* = 10.0 Hz, 1H, N-C*H*$_2$), 3.68 (m, 1H, O-C*H*CH$_3$), 3.88 (dd, J_1 = 11.5 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 6.12 (s, 1H, N-C*H*-O), 6.33 (m, 1H, furyl-C*H*), 6.45 (d, *J* = 3 Hz, 1H, furyl-C*H*), 7.34 (m, 3H, Ar-*H* and furyl-C*H*), 7.67 (d, *J* = 8.5 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125.6 MHz, $CDCl_3$): δ 18.2 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 52.9 (N-

CH_2), 74.5 (O-*C*HCH$_3$), 85.2 (N-*C*H-O), 109.3 (furyl-*C*H), 110.4 (furyl-*C*H), 127.6 (Ts-C_o), 130.0 (Ts-C_m), 135.4 (Ts-C_p), 143.3 (furyl-*C*H), 144.2 (Ts-C_i), 151.3 (furyl-*C*H).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.11 (d, J = 5.5 Hz, 3H, O-CHCH_3), 2.44 (s, 3H, Ts-CH_3), 2.95 (t, J = 9.0 Hz, 1H, N-CH_2), 3.68 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 1H, N-CH_2), 4.35 (m, 1H, O-C*H*CH$_3$), 6.16 (s, 1H, N-C*H*-O), 6.34 (m, 1H, furyl-C*H*), 6.47 (d, J = 3 Hz, 1H, furyl-C*H*), 7.34 (m, 3H, Ar-*H* and furyl-C*H*), 7.72 (d, J = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.0 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 52.9 (N-*C*H$_2$), 73.5 (O-*C*HCH$_3$), 85.1 (N-*C*H-O), 109.6 (furyl-*C*H), 110.4 (furyl-*C*H), 127.9 (Ts-C_o), 129.9 (Ts-C_m), 134.0 (Ts-C_p), 143.3 (furyl-*C*H), 144.3 (Ts-C_i), 151.5 (furyl-*C*H).

2-(3-Hydroxyphenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (3k, Table 3, entry 11). An off-white solid. R_f = 0.23 (Et_2O/*n*-pentane = 1:1 v/v). FTIR (neat, cm^{-1}): ν 3435, 3057, 2979, 2933, 2895, 1598, 1453, 1344, 1162, 1090. HRESIMS: Calcd for $C_{17}H_{19}NO_4S$: 333.1035, found: *m/z* 333.1036 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min to 230 °C and 5 °C/min from 230 to 260 °C, final time = 10 min, final temperature = 260 °C (*cis*-5-methyl isomer = 78.4 min; *trans*-5-methyl isomer = 78.9 min; *cis*-4-methyl isomer = 79.5 min)

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, CD_2Cl_2): δ 1.21 (d, J = 6.0 Hz, 3H, O-CHCH_3), 2.47 (s, 3H, Ts-CH_3), 3.04 (t, J = 10.5 Hz, 1H, N-CH_2), 3.56 (m, 1H, O-C*H*CH$_3$), 3.86 (dd, J_1 = 11.5 Hz, J_2 = 5.0 Hz, 1H, N-CH_2), 6.01 (s, 1H, N-C*H*-O), 6.05 (s, 1H, O*H*), 6.84 (d, J = 7.5 Hz, 1H, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 7.25 (d, J = 8.5 Hz, 1H, Ar-*H*), 7.39 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.76 (d, J = 8.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2): δ 18.2 (O-CH*C*H$_3$), 21.9 (Ts-*C*H$_3$), 53.6 (N-*C*H$_2$), 74.8 (O-*C*HCH$_3$), 91.7 (N-*C*H-O), 114.2 (hydroxyphenyl-C_2), 116.4 (hydroxyphenyl-C_6), 119.5 (hydroxyphenyl-C_4), 128.1 (Ts-C_o), 130.0 (Ts-C_m), 130.6 (hydroxyphenyl-C_5), 135.3 (Ts-C_p), 141.3 (hydroxyphenyl-C_3), 145.1 (Ts-C_i), 156.5 (hydroxyphenyl-C_1).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, CD_2Cl_2): δ 1.00 (d, J = 6.0 Hz, 3H, O-CHCH_3), 2.48 (s, 3H, Ts-CH_3), 3.01 (t, J = 9.0 Hz, 1H, N-CH_2), 3.60 (dd, J_1 = 9.5 Hz, J_2 = 6.0 Hz, 1H, N-CH_2), 4.15 (m, 1H, O-C*H*CH$_3$), 6.09 (s, 1H, O*H*), 6.22 (s, 1H, N-C*H*-O), 6.84 (d, J = 7.5 Hz, 1H, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 7.25 (d, J = 8.5 Hz, 1H, Ar-*H*), 7.43 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.82 (d, J = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2): δ 18.4 (O-CH*C*H$_3$), 21.8 (Ts-*C*H$_3$), 53.3 (N-*C*H$_2$), 73.3 (O-*C*HCH$_3$), 91.1 (N-*C*H-O), 114.0 (hydroxyphenyl-C_2), 116.1 (hydroxyphenyl-C_6), 119.0 (hydroxyphenyl-C_4), 128.5 (Ts-C_o), 130.2 (Ts-C_m), 130.4 (hydroxyphenyl-C_5), 134.1 (Ts-C_p), 140.9 (hydroxyphenyl-C_3), 145.2 (Ts-C_i), 156.7 (hydroxyphenyl-C_1).

2,2,5-Trimethyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (7a, Table 4, entry 1). A white solid. R_f = 0.35 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 2983, 2937, 2878, 1599, 1460, 1343, 1158, 1120, 1031. HRESIMS: Calcd for $C_{13}H_{19}NO_3S$: 269.1086, found: *m/z* 269.1085 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 5 min, final temperature = 230 °C (5-methyl isomer = 49.3 min; 4-methyl isomer = 48.4 min). HPLC conditions: 2% ^{i}PrOH in hexanes, flow rate = 1.0 mL/min, detector set at 254 nm. Retention time = 54.6 and 58.7 min.

^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.25 (d, J = 5.5 Hz, 3H, O-CHCH_3), 1.58 (s, 3H, C(CH_3)$_2$), 1.60 (s, 3H, C(CH_3)$_2$), 2.43 (s, 3H, Ts-CH_3), 2.88 (t, J = 8.5 Hz, 1H, N-CH_2), 3.61 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 1H, N-CH_2), 4.22 (m, 1H, O-C*H*CH$_3$), 7.31 (d, J = 7.5 Hz, 2H, Ar-*H*), 7.74 (d, J = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6

MHz, $CDCl_3$): δ 18.2 (O-CH*C*H_3), 21.7 (Ts-*C*H_3), 27.5 (C(*C*H_3)$_2$), 53.5 (N-*C*H_2), 70.8 (O-*C*HCH$_3$), 97.1 (N-*C*-O), 127.5 (Ts-C_o), 129.7 (Ts-C_m), 137.6 (Ts-C_p), 143.4 (Ts-C_i).

2-Isopropyl-2,5-dimethyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (7b, Table 4, entry 2). A white solid. R_f = 0.45 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 2976, 2936, 2878, 1599, 1453, 1335, 1247, 1155, 1114. HRESIMS: Calcd for $C_{15}H_{23}NO_3S$: 297.1399, found: *m/z* 297.1403 [M+H]$^+$.

(2*R*,5*S* and 2*S*,5*R*)-**7b**. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.84 (d, *J* = 6.5 Hz, 3H, ^{i}Pr C*H*$_3$), 0.98 (d, *J* = 7.0 Hz, 3H, ^{i}Pr C*H*$_3$), 1.23 (d, *J* = 5.5 Hz, 3H, O-CHC*H*$_3$), 1.60 (s, 3H, C(C*H*$_3$)), 2.43 (s, 3H, Ts-C*H*$_3$), 2.47 (m, 1H, ^{i}Pr C*H*), 2.81 (t, *J* = 9.0 Hz, 1H, N-C*H*$_2$), 3.60 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 4.11 (m, 1H, O-C*H*CH$_3$), 7.29 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.75 (d, *J* = 8.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 16.9 (^{i}Pr *C*H$_3$), 17.6 (^{i}Pr *C*H$_3$), 17.9 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 23.7 (C(*C*H$_3$)), 36.8 (^{i}Pr *C*H), 54.2 (N-*C*H$_2$), 70.9 (O-*C*HCH$_3$), 102.4 (N-*C*-O), 127.3 (Ts-C_o), 129.7 (Ts-C_m), 138.3 (Ts-C_p), 143.3 (Ts-C_i).

(2*R*,5*R* and 2*S*,5*S*)-**7b**. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.0 Hz, 3H, ^{i}Pr C*H*$_3$), 1.01 (d, *J* = 6.5 Hz, 3H, ^{i}Pr C*H*$_3$), 1.19 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 1.49 (s, 3H, C(C*H*$_3$)), 2.44 (s, 3H, Ts-C*H*$_3$), 2.47 (m, 1H, ^{i}Pr C*H*), 2.94 (t, *J* = 8.5 Hz, 1H, N-C*H*$_2$), 3.56 (dd, J_1 = 8.5 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 4.23 (m, 1H, O-C*H*CH$_3$), 7.31 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.76 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 17.8 (O-CH*C*H$_3$), 19.6 (^{i}Pr *C*H$_3$), 21.7 (Ts-*C*H$_3$), 24.4 (C(*C*H$_3$)), 37.6 (^{i}Pr *C*H), 53.7 (N-*C*H$_2$), 72.5 (O-*C*HCH$_3$), 102.1 (N-*C*-O), 127.8 (Ts-C_o), 129.7 (Ts-C_m), 137.3 (Ts-C_p), 143.5 (Ts-C_i).

2-Methyl-4-[(4-methylbenzene)sulfonyl]-1-oxa-4-azaspiro[4.5]decane (7c, Table 4, entry 3). A white solid. R_f = 0.41 (Et_2O/*n*-pentane = 1:2 v/v). FTIR (neat, cm^{-1}): ν 2934, 2863, 1598, 1450, 1334, 1163, 1065. HRESIMS: Calcd for $C_{16}H_{23}NO_3S$: 309.1399, found: *m/z* 309.1399 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 5 min, final temperature = 230 °C (5-methyl isomer = 49.4 min; 4-methyl isomer = 48.4 min).

^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.23 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 1.25 (m, 1H, ^{c}Hex-C*H*$_2$), 1.47-1.65 (m, 6H, ^{c}Hex-C*H*$_2$), 1.83 (m, 1H, ^{c}Hex-C*H*$_2$), 2.06 (dt, J_1 = 13.5 Hz, J_2 = 4.5 Hz, 1H, ^{c}Hex-C*H*$_2$), 2.28 (dt, J_1 = 13.0 Hz, J_2 = 4.5 Hz, 1H, ^{c}Hex-C*H*$_2$), 2.41 (s, 3H, Ts-C*H*$_3$), 2.86 (t, *J* = 9.0 Hz, 1H, N-C*H*$_2$), 3.62 (dd, J_1 = 8.5 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 4.16 (m, 1H, O-C*H*CH$_3$), 7.28 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.2 (O-CH*C*H$_3$), 21.6 (Ts-*C*H$_3$), 23.6 (^{c}Hex-*C*H$_2$), 23.7 (^{c}Hex-*C*H$_2$), 24.8 (^{c}Hex-*C*H$_2$), 35.3 (^{c}Hex-*C*H$_2$), 36.5 (^{c}Hex-*C*H$_2$), 53.5 (N-*C*H$_2$), 70.5 (O-*C*HCH$_3$), 98.9 (N-*C*-O), 127.4 (Ts-C_o), 129.6 (Ts-C_m), 138.1 (Ts-C_p), 143.2 (Ts-C_i).

2,5-Dimethyl-2-(4-nitrophenyl)-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (7d, Table 4, entry 4). A white solid. R_f = 0.42 and 0.35 (Et_2O/*n*-pentane = 1:1 v/v, two diastereomers). FTIR (neat, cm^{-1}): ν 2978, 2927, 1692, 1599, 1525, 1347, 1159, 1090. HRESIMS: Calcd for $C_{18}H_{20}N_2O_5S$: 376.1093, found: *m/z* 376.1088 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min to 220 °C and 5 °C/min from 220 to 260 °C, final time = 10 min, final temperature = 260 °C ((2*R*,5*S* and 2*S*,5*R*)-**7d** isomer = 78.5 min; (2*R*,5*R* and 2*S*,5*S*)-**7d** isomer = 79.7 min; 4-methyl isomer = 80.3 min).

(2*R*,5*S* and 2*S*,5*R*)-**7d**. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.38 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 2.09 (s, 3H, C(C*H*$_3$)), 2.36 (s, 3H, Ts-C*H*$_3$), 3.02 (t, *J* = 9.0 Hz, 1H, N-C*H*$_2$), 3.96 (dd, J_1 = 8.5 Hz, J_2 = 6.0 Hz, 1H, N-C*H*$_2$), 4.46 (m, 1H, O-C*H*CH$_3$), 7.06 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.18 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.60 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 8.04 (d, *J* = 9.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.0 (O-CH*C*H$_3$), 21.6 (Ts-*C*H$_3$), 25.8 (C(*C*H$_3$)), 54.3 (N-*C*H$_2$), 72.4 (O-*C*HCH$_3$), 97.9 (N-*C*-O), 123.1 (nitrophenyl-*C*$_o$), 126.8 (nitrophenyl-*C*$_m$), 127.5 (Ts-*C*$_o$), 129.5 (Ts-*C*$_m$), 136.6 (Ts-*C*$_p$), 143.7 (Ts-*C*$_i$), 147.8 (nitrophenyl-*C*$_i$), 147.9 (nitrophenyl-*C*$_p$).

(2*R*,5*R* and 2*S*,5*S*)-**7d**. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.26 (d, *J* = 6.0 Hz, 3H, O-CHC*H*$_3$), 1.92 (s, 3H, C(C*H*$_3$)), 2.46 (s, 3H, Ts-C*H*$_3$), 3.13 (t, *J* = 9.0 Hz, 1H, N-C*H*$_2$), 3.62 (dd, J_1 = 8.0 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 3.96 (m, 1H, O-C*H*CH$_3$), 7.34 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.76 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.86 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 8.21 (d, *J* = 8.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 18.2 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 26.4 (C(*C*H$_3$)), 54.4 (N-*C*H$_2$), 71.1 (O-*C*HCH$_3$), 96.1 (N-*C*-O), 123.7 (nitrophenyl-*C*$_o$), 127.8 (nitrophenyl-*C*$_m$), 128.3 (Ts-*C*$_o$), 129.9 (Ts-*C*$_m$), 136.9 (Ts-*C*$_p$), 144.1 (Ts-*C*$_i$), 148.2 (nitrophenyl-*C*$_i$), 151.1 (nitrophenyl-*C*$_p$).

2,2-Diphenyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (7e, Table 4, entry 5). A colorless oil. R_f = 0.52 (Et_2O/*n*-pentane = 1:1 v/v). FTIR (neat, cm^{-1}): ν 3061, 3029, 2977, 2930, 2871, 1659, 1598, 1448, 1346, 1161, 1049. HRESIMS: Calcd for $C_{23}H_{23}NO_3S$: 393.1399, found: *m/z* 393.1399 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min to 220 °C and 5 °C/min from 220 to 260 °C, final time = 10 min, final temperature = 260 °C (5-methyl isomer = 80.9 min; 4-methyl isomer = 81.4 min).

^{1}H NMR (499.6 MHz, $CDCl_3$): δ 1.36 (d, *J* = 6.5 Hz, 3H, O-CHC*H*$_3$), 2.37 (s, 3H, Ts-C*H*$_3$), 3.19 (t, *J* = 9.0 Hz, 1H, N-C*H*$_2$), 3.98 (dd, J_1 = 8.0 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 4.10 (m, 1H, O-C*H*CH$_3$), 6.83 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.00 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.16 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.31 (m, 1H, Ar-*H*), 7.41 (m, 3H, Ar-*H*), 7.69 (d, *J* = 6.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 17.8 (O-CH*C*H$_3$), 21.7 (Ts-*C*H$_3$), 55.2 (N-*C*H$_2$), 70.7 (O-*C*HCH$_3$), 100.3 (N-*C*-O), 127.2 (Ph-*C*$_p$) 127.4 (Ph-*C*$_p$), 127.9 (Ts-*C*$_o$), 128.4 (Ph-*C*$_o$), 128.5 (Ph-*C*$_o$), 129.1 (Ts-*C*$_m$), 130.3 (Ph-*C*$_m$), 132.7 (Ph-*C*$_m$), 136.5 (Ts-*C*$_p$), 138.6 (Ph-*C*$_i$), 142.3 (Ph-*C*$_i$), 142.8 (Ts-*C*$_i$).

2,5-Dibutyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (10a, Eq 4). A colorless oil. R_f = 0.55 (EtOAc/hexanes = 1:3 v/v). FTIR (neat, cm^{-1}): ν 2957, 2932, 2872, 1598, 1460, 1351, 1166, 1091. HRESIMS: Calcd for $C_{18}H_{29}NO_3S$: 339.1868, found: *m/z* 339.1871 [M+H]$^+$. GC temperature program: initial time = 2 min., initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 5 min, final temperature = 230 °C (*cis*-5-butyl isomer = 63.7 min; *trans*-5-butyl isomer = 65.4 min; *cis*-4-butyl isomer = 65.2 min).

Cis-5-butyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.79-0.95 (m, 6H, ^{n}Bu C*H*$_3$), 1.06-1.55 (m, 10H, ^{n}Bu C*H*$_2$), 1.65-1.88 (m, 2H, ^{n}Bu C*H*$_2$), 2.44 (s, 3H, Ts-C*H*$_3$), 2.93 (dd, J_1 = 11.5 Hz, J_2 = 10.0 Hz, 1H, N-C*H*$_2$), 3.12 (m, 1H, O-C*H*CH$_3$), 3.63 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, N-C*H*$_2$), 5.04 (dd, J_1 = 6.5 Hz, J_2 = 4.0 Hz, 1H, N-C*H*-O), 7.33 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.72 (d, *J* = 7.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): δ 14.1 (^{n}Bu *C*H$_3$), 21.6 (Ts-*C*H$_3$), 22.6 (^{n}Bu *C*H$_2$), 26.1 (^{n}Bu *C*H$_2$), 27.7 (^{n}Bu *C*H$_2$), 32.6 (^{n}Bu *C*H$_2$), 36.2 (^{n}Bu *C*H$_2$), 52.1 (N-*C*H$_2$), 77.3 (O-*C*HCH$_3$), 91.6 (N-*C*H-O), 127.8 (Ts-*C*$_o$), 130.0 (Ts-*C*$_m$), 135.0 (Ts-*C*$_p$), 144.1 (Ts-*C*$_i$).

Trans-5-butyl isomer. ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 0.79-0.95 (m, 6H, ^{n}Bu C*H*$_3$), 1.06-1.55 (m, 10H, ^{n}Bu C*H*$_2$), 1.65-1.88 (m, 2H, ^{n}Bu C*H*$_2$), 2.44 (s, 3H, Ts-C*H*$_3$), 2.85 (dd, J_1 = 9.5 Hz, J_2 = 7.5 Hz, 1H, N-C*H*$_2$), 3.52 (dd,

J_1 = 10.0 Hz, J_2 = 6.0 Hz, 1H, N-CH_2), 4.09 (m, 1H, O-CHCH$_3$), 5.12 (dd, J_1 = 7.5 Hz, J_2 = 4.0 Hz, 1H, N-CH-O), 7.33 (d, J = 7.5 Hz, 2H, Ar-H), 7.72 (d, J = 7.5 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (125.6 MHz, CDCl$_3$): δ 14.2 (^{n}Bu CH$_3$), 21.6 (Ts-CH$_3$), 22.6 (^{n}Bu CH$_2$), 26.9 (^{n}Bu CH$_2$), 28.3 (^{n}Bu CH$_2$), 32.6 (^{n}Bu CH$_2$), 35.2 (^{n}Bu CH$_2$), 51.3 (N-CH$_2$), 76.4 (O-CHCH$_3$), 91.6 (N-CH-O), 128.0 (Ts-C_o), 129.9 (Ts-C_m), 133.9 (Ts-C_p), 144.1 (Ts-C_i).

2-Butyl-5-isopropyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (10b, Eq 5). A colorless oil. R_f = 0.57 (EtOAc/hexanes = 1:3 v/v). FTIR (neat, cm^{-1}): ν 2958, 2932, 2872, 1599, 1469, 1350, 1166, 1091. HRESIMS: Calcd for $C_{17}H_{27}NO_3S$: 325.1712, found: *m/z* 325.1710 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 2 °C/min, final time = 5 min, final temperature = 230 °C (*cis*-5-isopropyl isomer = 65.3 min; *trans*-5-isopropyl isomer = 65.9 min; *cis*-4-isopropyl isomer = 66.3 min).

Cis-5-isopropyl isomer. ^{1}H NMR (499.6 MHz, CDCl$_3$): δ 0.76 (d, J = 6.0 Hz, 3H, ^{i}Pr CH_3), 0.87 (d, J = 7.0 Hz, 3H, ^{i}Pr CH_3), 0.92 (m, 3H, ^{n}Bu CH_3), 1.28-1.44 (m, 4H, ^{n}Bu CH_2), 1.58-1.73 (m, 2H, ^{n}Bu CH_2), 1.87 (m, 1H, ^{i}Pr CH), 2.44 (s, 3H, Ts-CH_3), 2.85 (m, 1H, O-CHCH$_3$), 3.01 (t, J = 10.0 Hz, 1H, N-CH_2), 3.60 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, N-CH_2), 5.05 (dd, J_1 = 6.0 Hz, J_2 = 4.0 Hz, 1H, N-CH-O), 7.34 (d, J = 7.5 Hz, 2H, Ar-H), 7.72 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (125.6 MHz, CDCl$_3$): δ 14.1 (^{n}Bu CH$_3$), 18.8 (^{i}Pr CH$_3$), 19.8 (^{i}Pr CH$_3$), 21.7 (Ts-CH$_3$), 22.6 (^{n}Bu CH$_2$), 26.1 (^{n}Bu CH$_2$), 31.5 (^{i}Pr CH), 36.1 (^{n}Bu CH$_2$), 50.4 (N-CH$_2$), 82.4 (O-CHCH$_3$), 91.7 (N-CH-O), 127.7 (Ts-C_o), 130.0 (Ts-C_m), 135.1 (Ts-C_p), 144.1 (Ts-C_i).

Trans-5-isopropyl isomer. ^{1}H NMR (499.6 MHz, CDCl$_3$): δ 0.69 (d, J = 7.0 Hz, 3H, ^{i}Pr CH_3), 0.80 (d, J = 6.0 Hz, 3H, ^{i}Pr CH_3), 0.92 (m, 3H, ^{n}Bu CH_3), 1.28-1.44 (m, 4H, ^{n}Bu CH_2), 1.58-1.73 (m, 2H, ^{n}Bu CH_2), 1.87 (m, 1H, ^{i}Pr CH), 2.44 (s, 3H, Ts-CH_3), 2.86 (t, J = 9.5 Hz, 1H, N-CH_2), 3.48 (dd, J_1 = 9.5 Hz, J_2 = 6.0 Hz, 1H, N-CH_2), 3.78 (m, 1H, O-CHCH$_3$), 5.12 (dd, J_1 = 7.5 Hz, J_2 = 4.0 Hz, 1H, N-CH-O), 7.34 (d, J = 7.5 Hz, 2H, Ar-H), 7.72 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (125.6 MHz, CDCl$_3$) δ 14.1 (^{n}Bu CH$_3$), 18.1 (^{i}Pr CH$_3$), 19.8 (^{i}Pr CH$_3$), 21.6 (Ts-CH$_3$), 22.4 (^{n}Bu CH$_2$), 26.9 (^{n}Bu CH$_2$), 31.2 (^{i}Pr CH), 35.3 (^{n}Bu CH$_2$), 49.8 (N-CH$_2$), 81.5 (O-CHCH$_3$), 91.9 (N-CH-O), 128.0 (Ts-C_o), 129.8 (Ts-C_m), 133.8 (Ts-C_p), 144.1 (Ts-C_i).

2-(4-Nitrophenyl)-5-methyl-3-methanelsulfonyl-1,3-oxazolidine (12, Eq 4). A pale yellow solid. R_f = 0.41 and 0.33 (EtOAc/pet ether = 1:1 v/v, two diastereomers). FTIR (neat, cm^{-1}): ν 2979, 2917, 2850, 1592, 1460, 1165, 1105, 1090. HRESIMS: Calcd for $C_{11}H_{14}N_2O_5S$: 286.0623, found: *m/z* 286.0592 [M+H]$^+$. GC temperature program: initial time = 2 min, initial temperature = 80 °C, ramp rate = 20 °C /min to 280 °C, final time = 10 min, final temperature = 280 °C (*cis*-5-methyl isomer = 12.1 min; *trans*-5-methyl isomer = 11.9 min; *cis*-4-methyl isomer = 10.8 min).

Cis-5-methyl isomer. ^{1}H NMR (499.6 MHz, CDCl$_3$): δ 1.44 (d, J = 6.0 Hz, 3H, O-CHCH_3), 2.99 (s, 3H, Ms-CH_3), 3.01 (t, J = 9.5 Hz, 1H, N-CH_2), 3.99 (dd, J_1 = 11.5 Hz, J_2 = 5.5 Hz, 1H, O-CHCH$_3$), 4.22 (m, 1H, N-CH_2), 6.21 (s, 1H, N-CH-O), 7.73 (d, J = 9.0 Hz, 2H, Ar-H), 8.25 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C{^{1}H} NMR (125.6 MHz, CDCl$_3$): δ 18.4 (O-CHCH$_3$), 39.2 (Ms-CH$_3$), 53.2 (N-CH$_2$), 73.6 (O-CHCH$_3$), 89.9 (N-CH-O), 123.9 (nitrophenyl-C_o), 128.1 (nitrophenyl-C_m), 145.9 (nitrophenyl-C_i), 148.5 (nitrophenyl-C_p).

Trans-5-methyl isomer. ^{1}H NMR (499.6 MHz, CDCl$_3$): δ 1.40 (d, J = 6.0 Hz, 3H, O-CHCH_3), 2.88 (s, 3H, Ts-CH_3), 3.18 (t, J = 9.0 Hz, 1H, N-CH_2), 3.62 (dd, J_1 = 10.5 Hz, J_2 = 6.5 Hz, 1H, N-CH_2), 4.35 (m, 1H, O-CHCH$_3$), 6.28 (s, 1H, N-CH-O), 7.75 (d, J = 8.5 Hz, 2H, Ar-H), 7.77 (d, J = 7.5 Hz, 2H, Ar-H), 8.25 (d, J = 8.0 Hz, 2H, Ar-H).

$^{13}C\{^{1}H\}$ NMR (125.6 MHz, $CDCl_3$): δ 18.8 (O-CH*C*H_3), 36.0 (Ms-*C*H_3), 53.2 (N-*C*H_2), 75.6 (O-*C*HCH$_3$), 89.9 (N-*C*H-O), 123.9 (nitrophenyl-C_o), 127.9 (nitrophenyl-C_m), 145.3 (nitrophenyl-C_i), 148.6 (nitrophenyl-C_p).

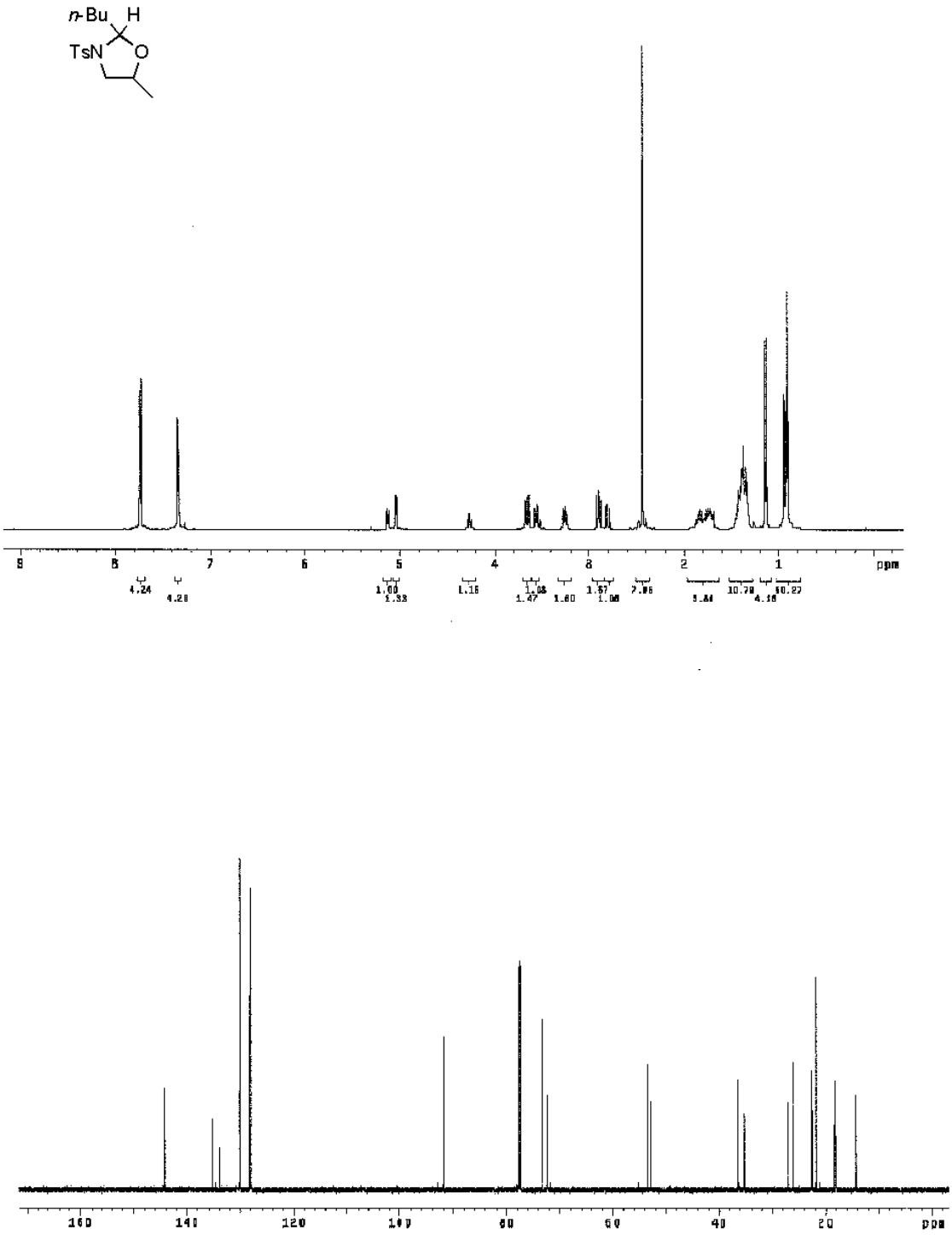


Figure S8. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-butyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3a**, Table 3, entry 1).

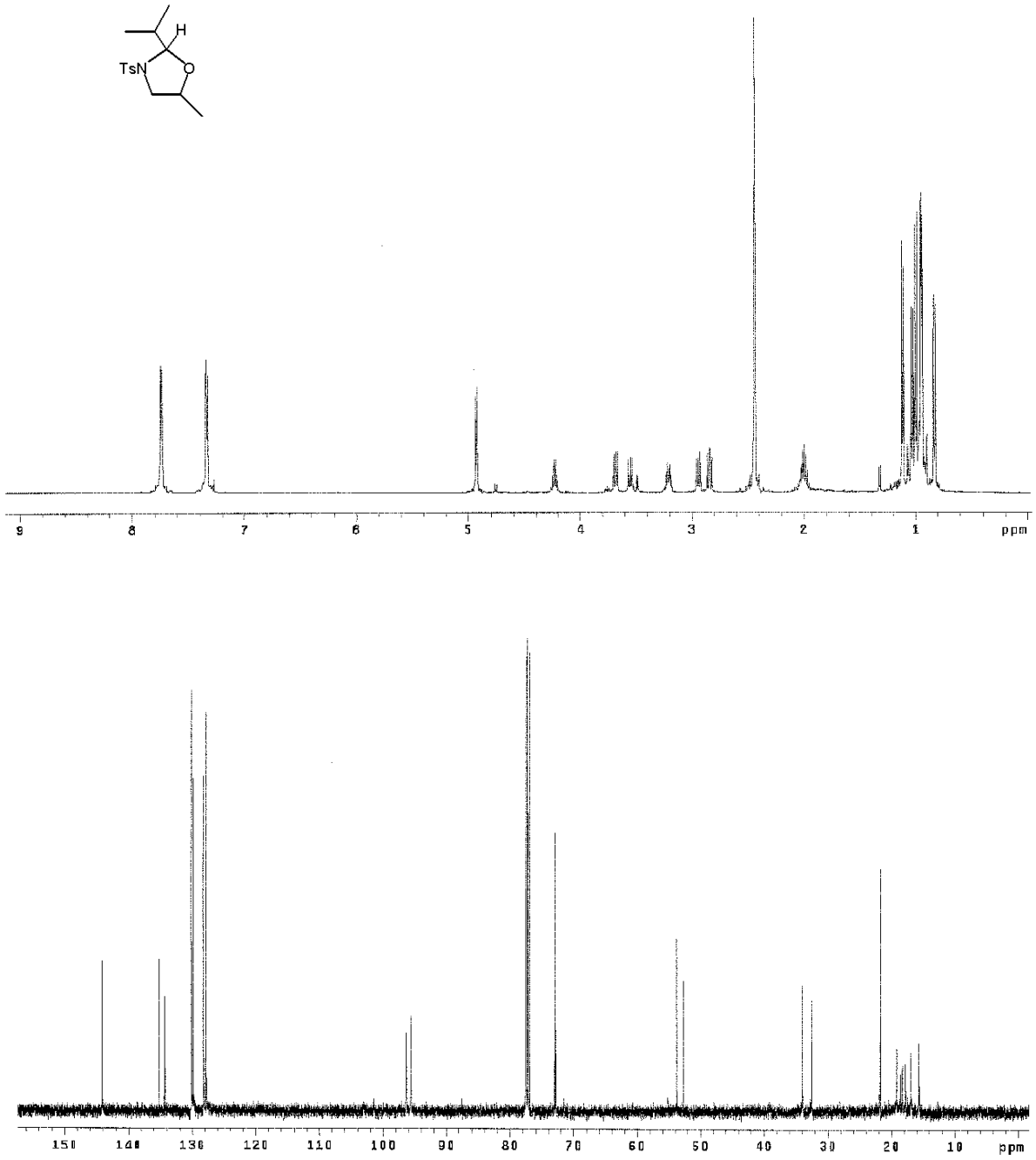


Figure S9. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-isopropyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3b**, Table 3, entry 2).

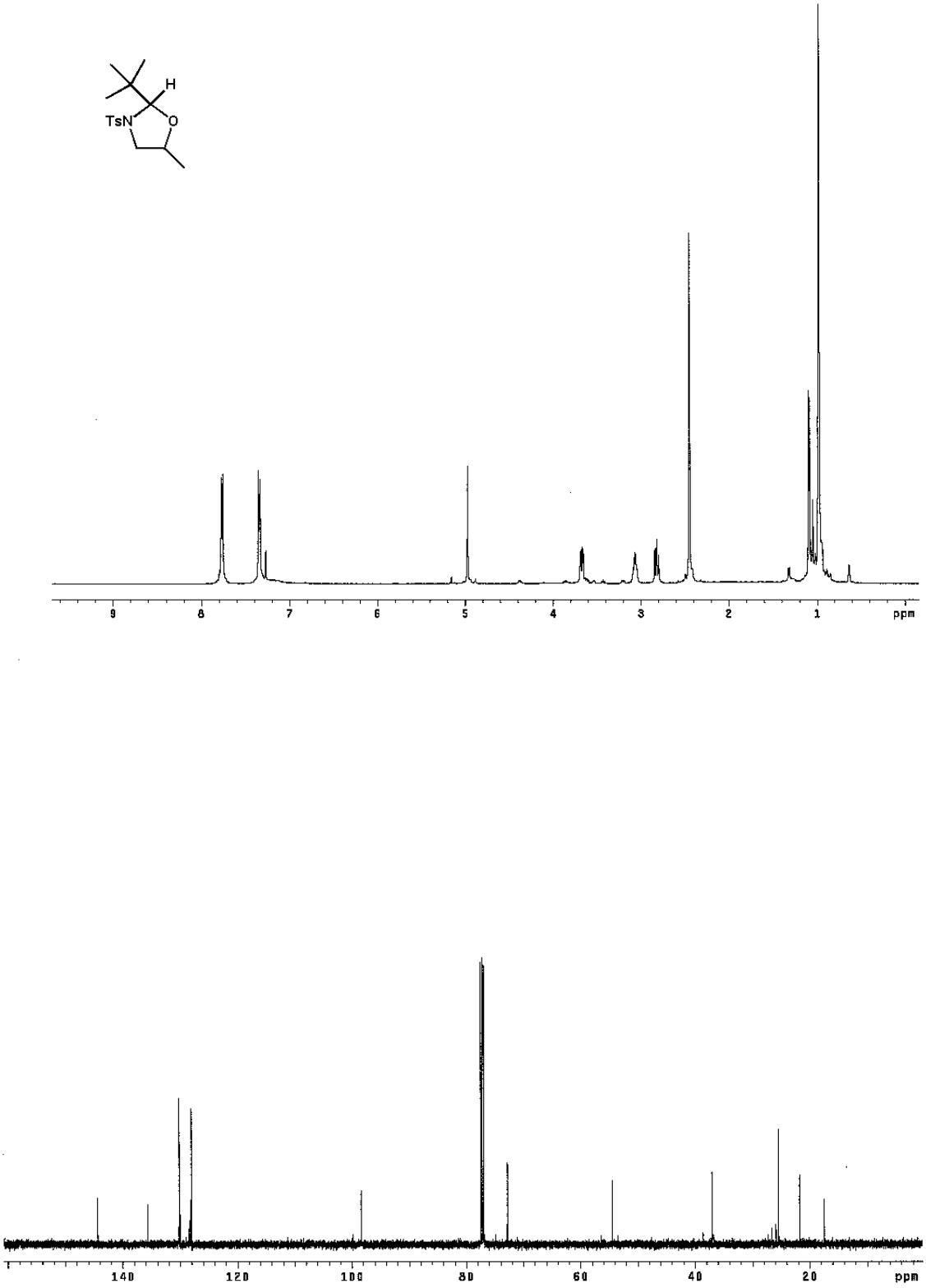


Figure S10. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-*tert*-butyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3c**, Table 3, entry 3).

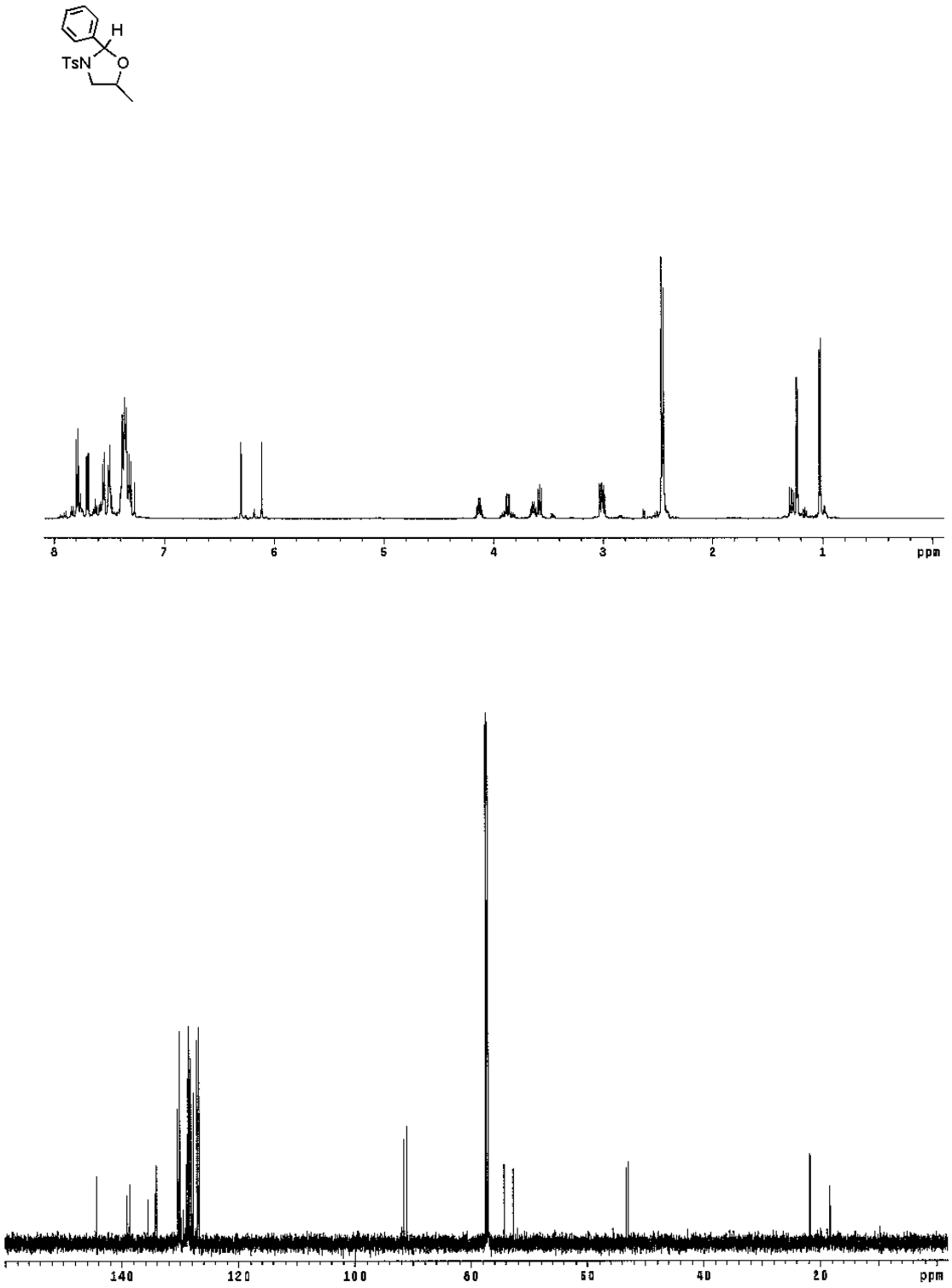


Figure S11. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-phenyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3d**, Table 3, entry 4).

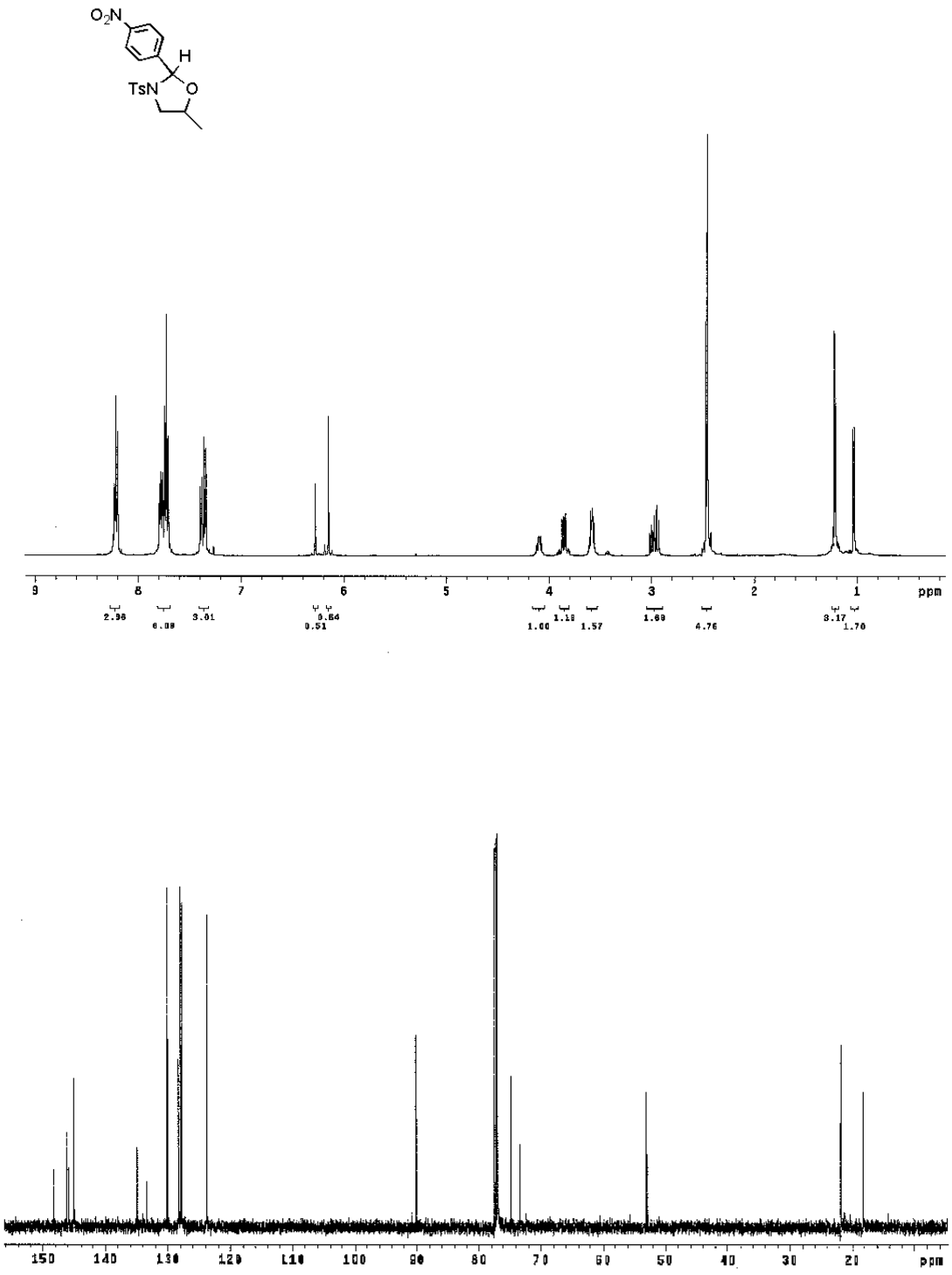


Figure S12. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-(4-nitrophenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3e**, Table 3, entry 5).

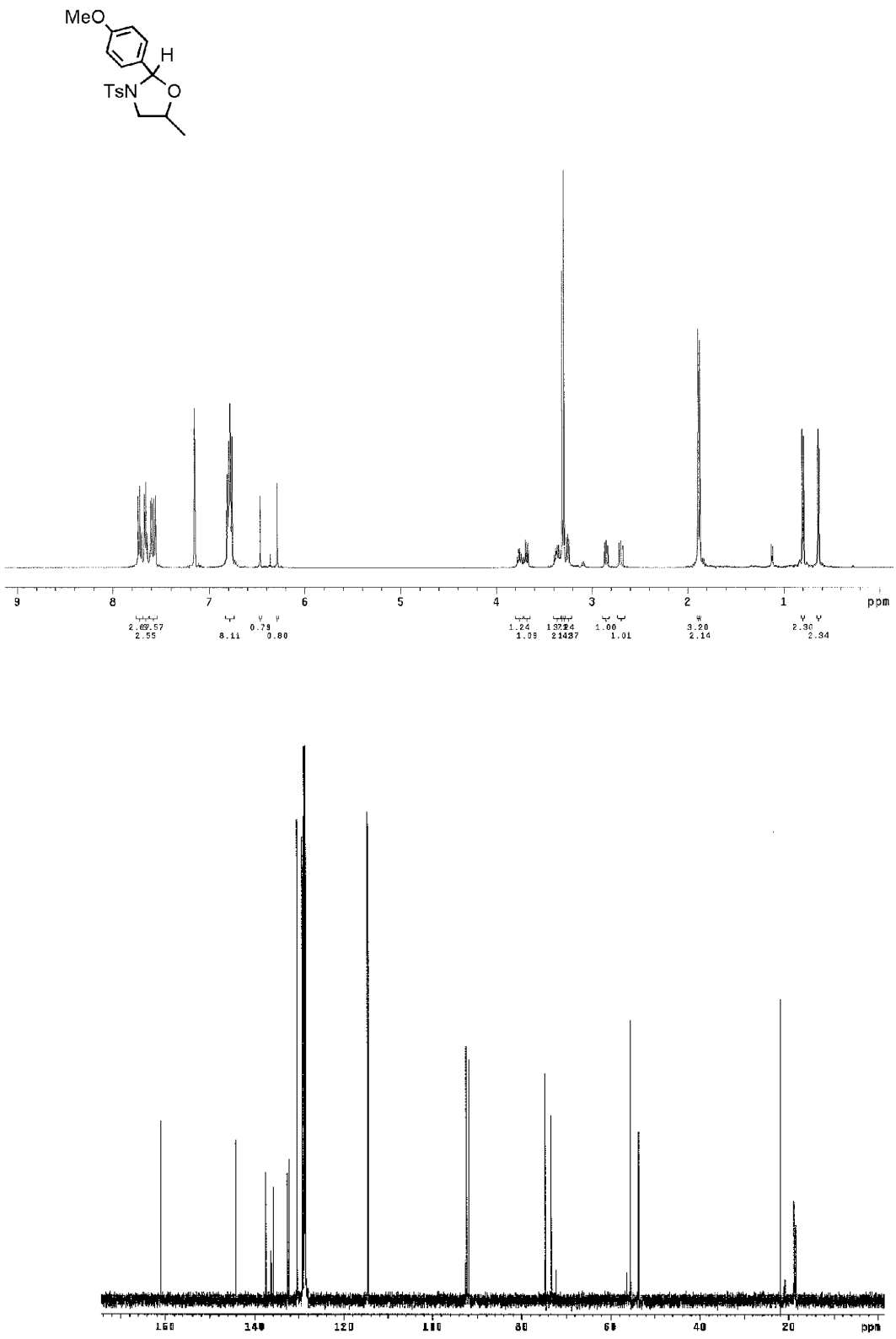


Figure S13. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-(4-methoxyphenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3f**, Table 3, entry 6).

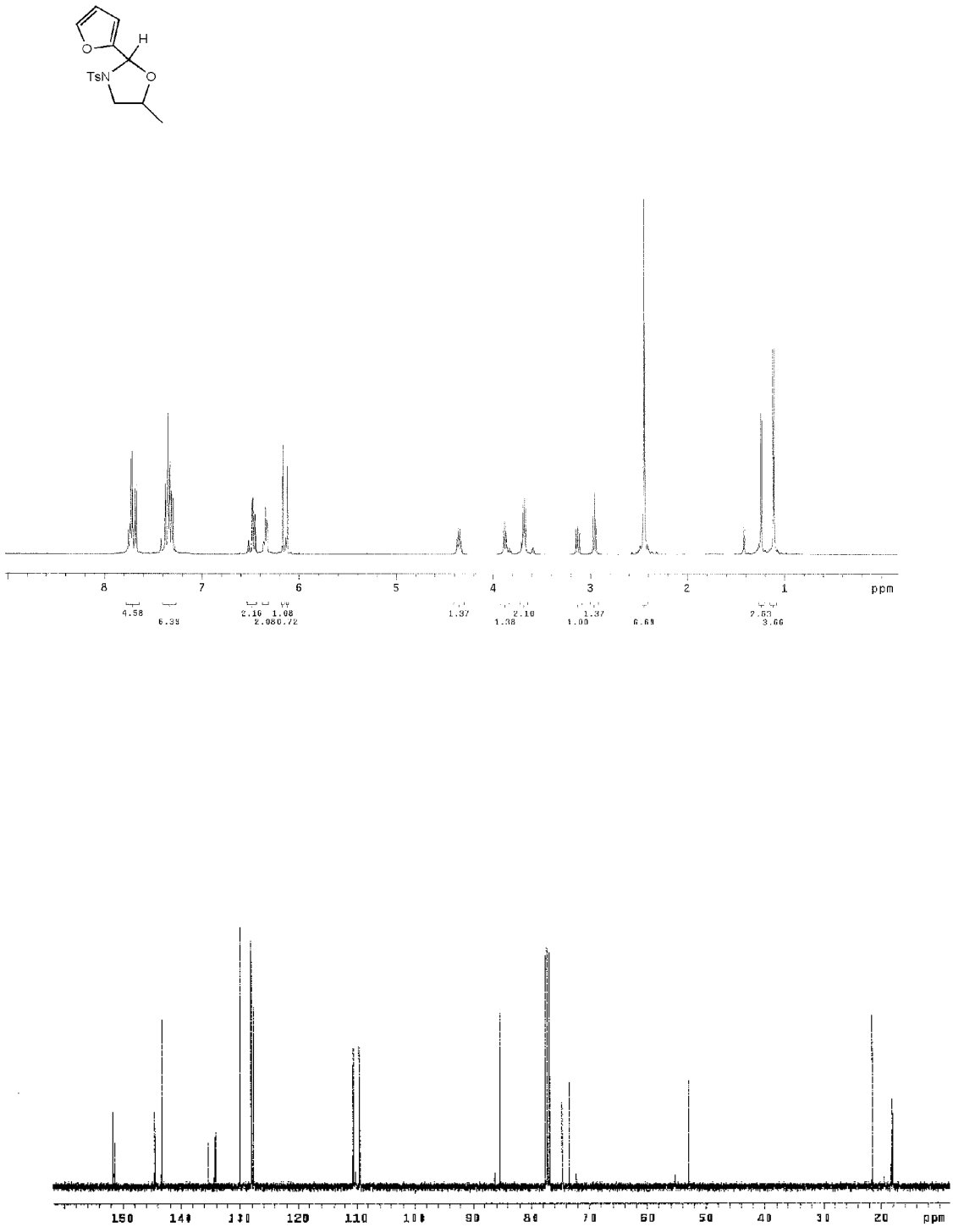


Figure S14. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-(2-furanyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3i**, Table 3, entry 9).

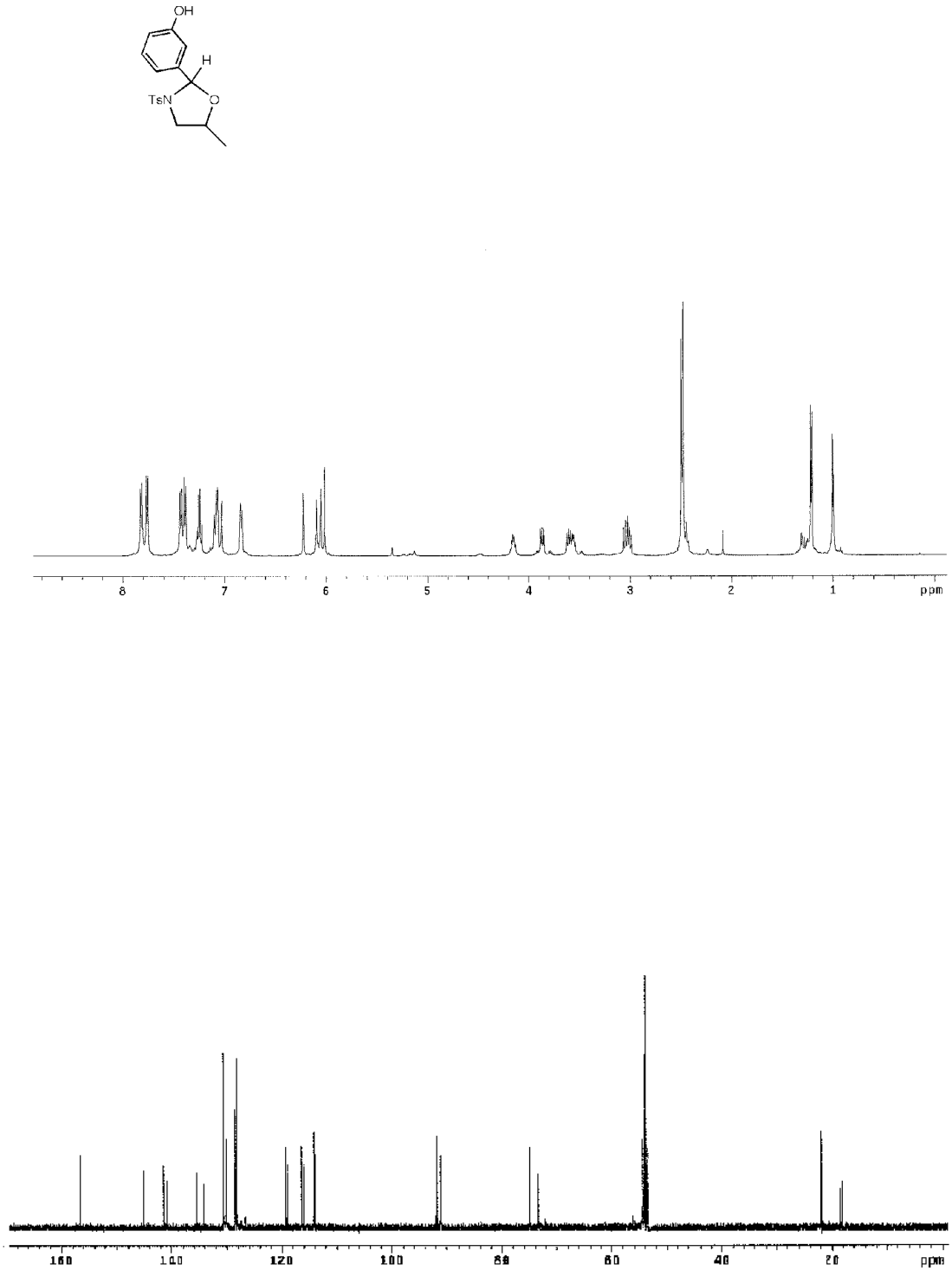


Figure S15. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-(3-hydroxyphenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3k**, Table 3, entry 11).

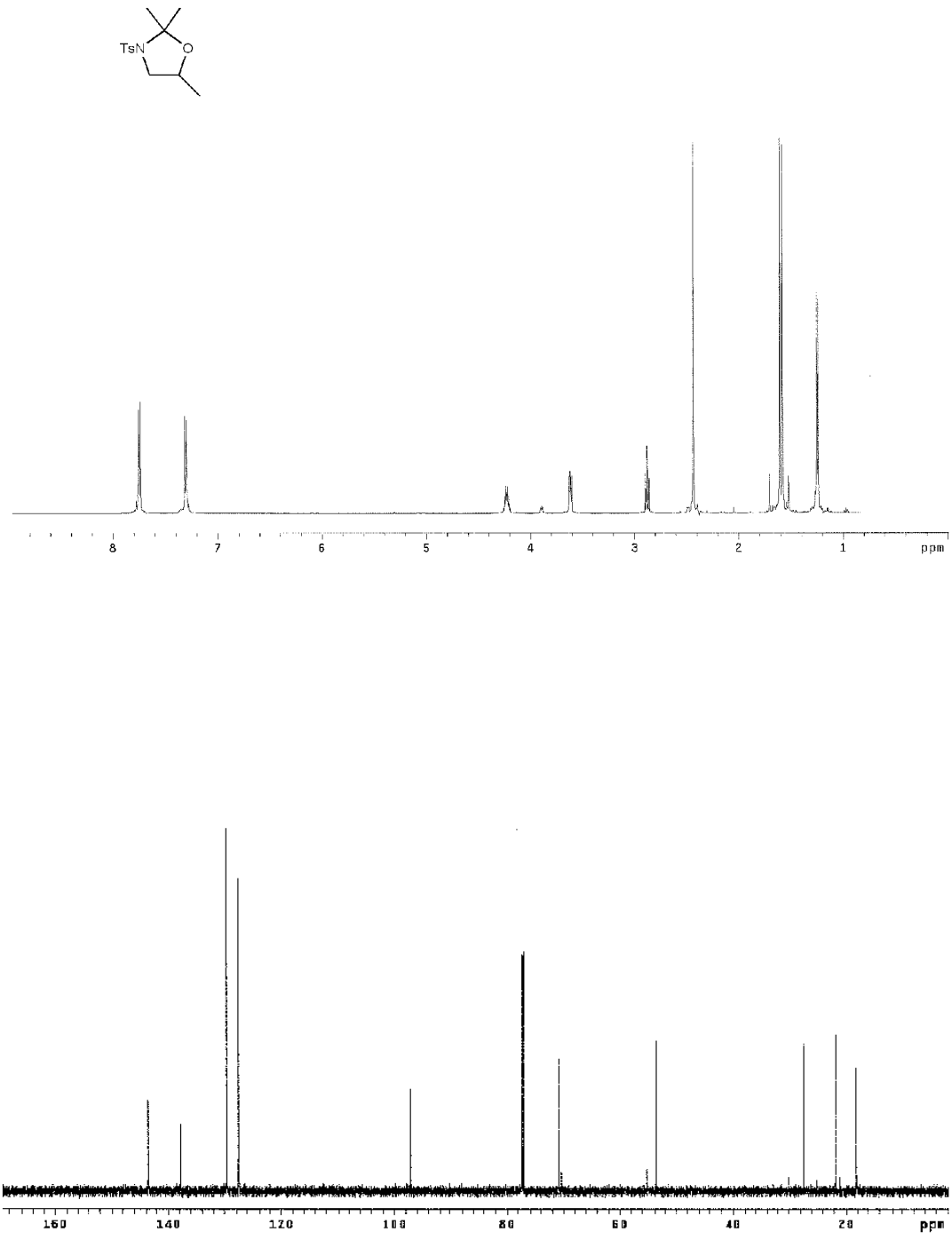


Figure S16. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2,2,5-trimethyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**7a**, Table 4, entry 1).

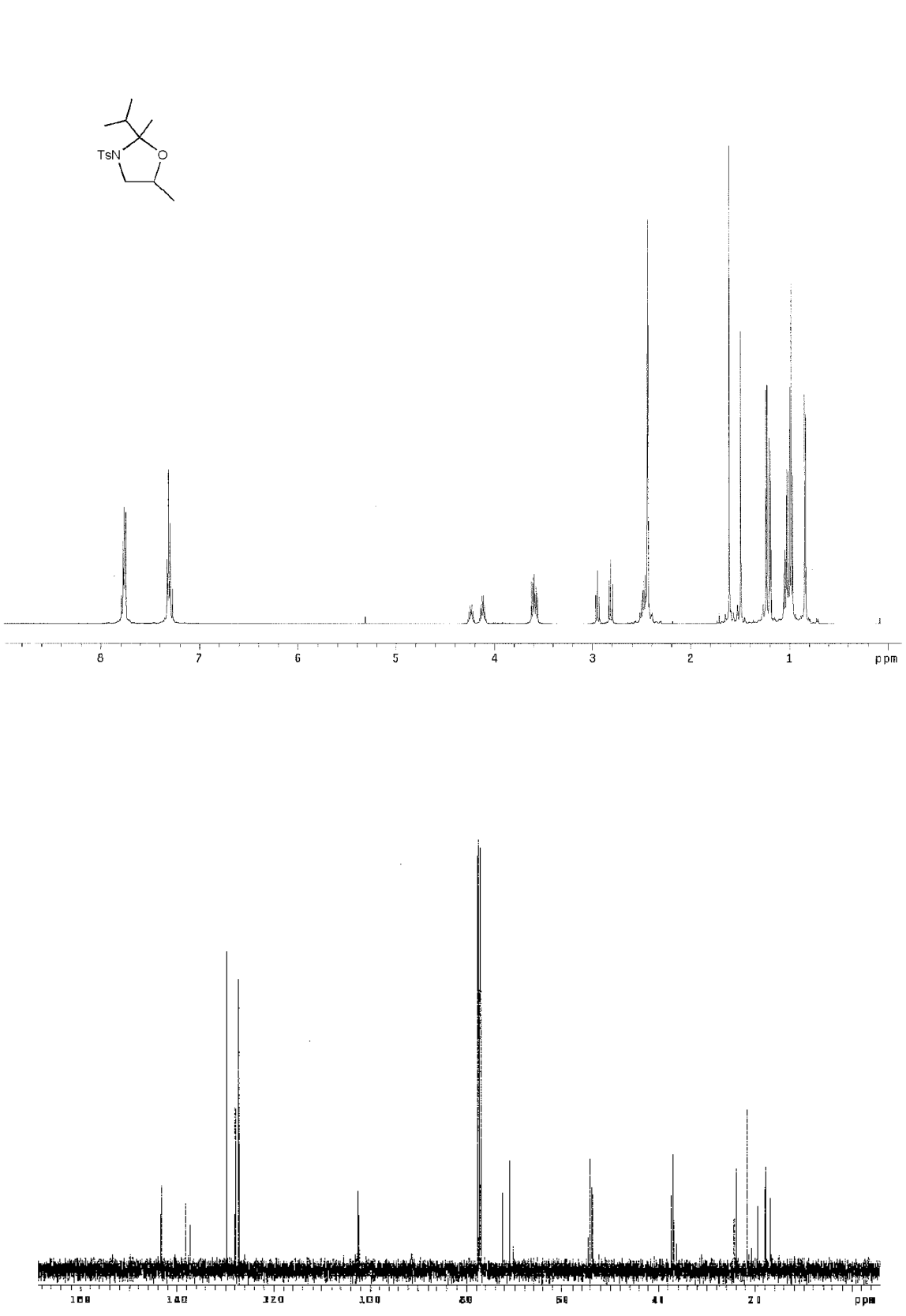


Figure S17. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-isopropyl-2,5-dimethyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**7b**, Table 4, entry 2).

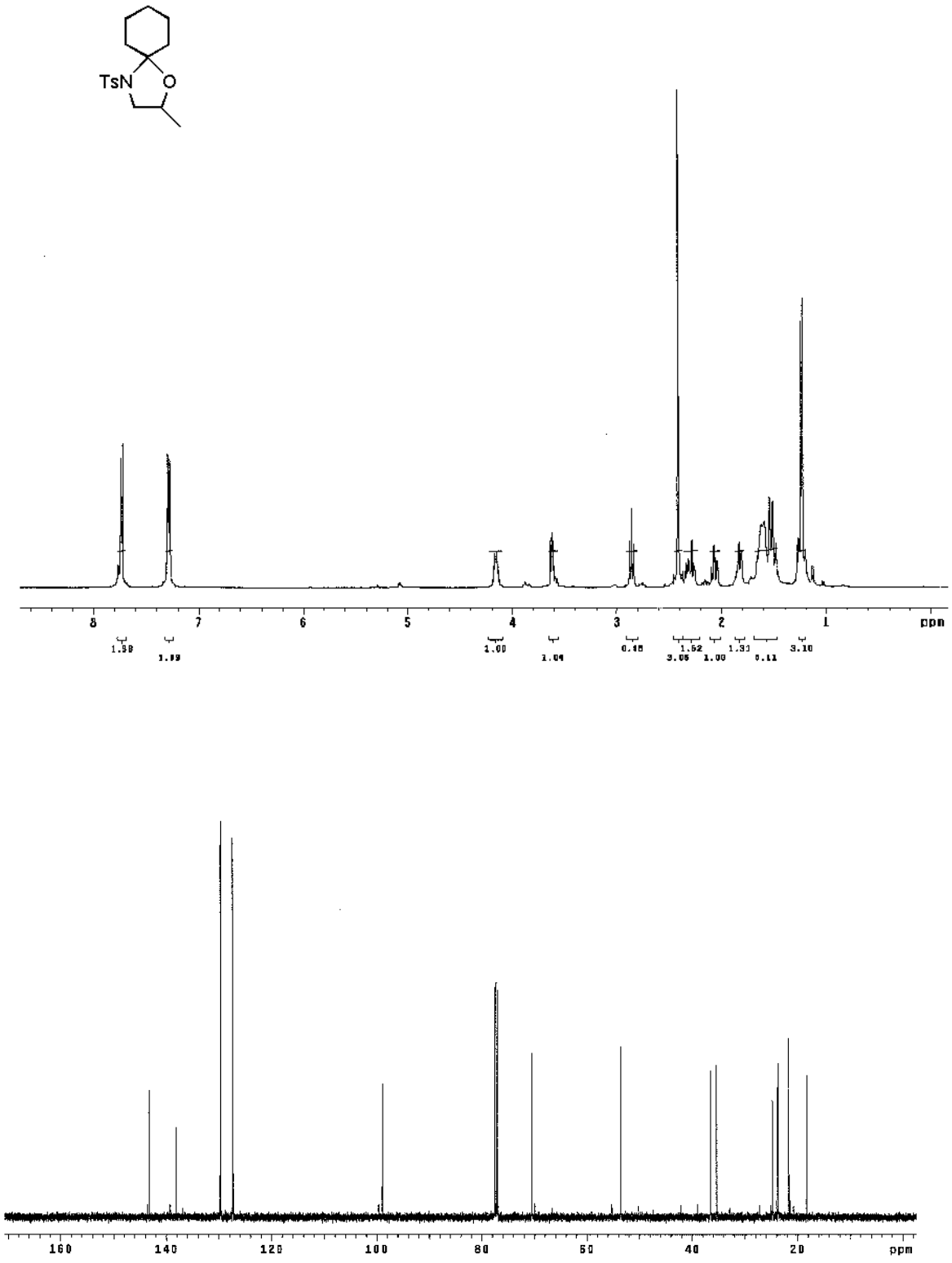


Figure S18. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-methyl-4-[(4-methylbenzene)sulfonyl]-1-oxa-4-azaspiro[4.5]decane (**7c**, Table 4, entry 3).

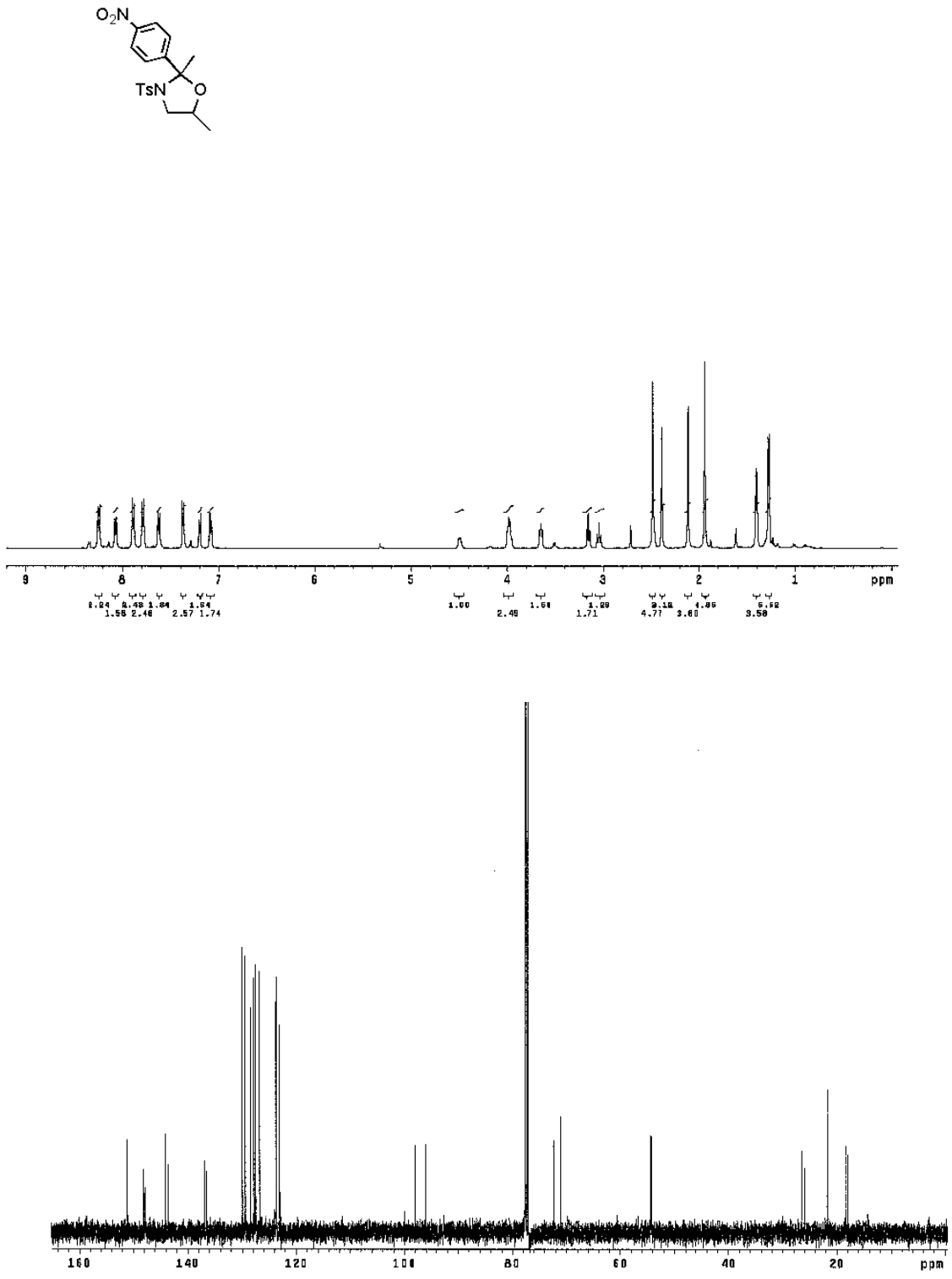


Figure S19. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2,5-dimethyl-2-(4-nitrophenyl)-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**7d**, Table 4, entry 4).

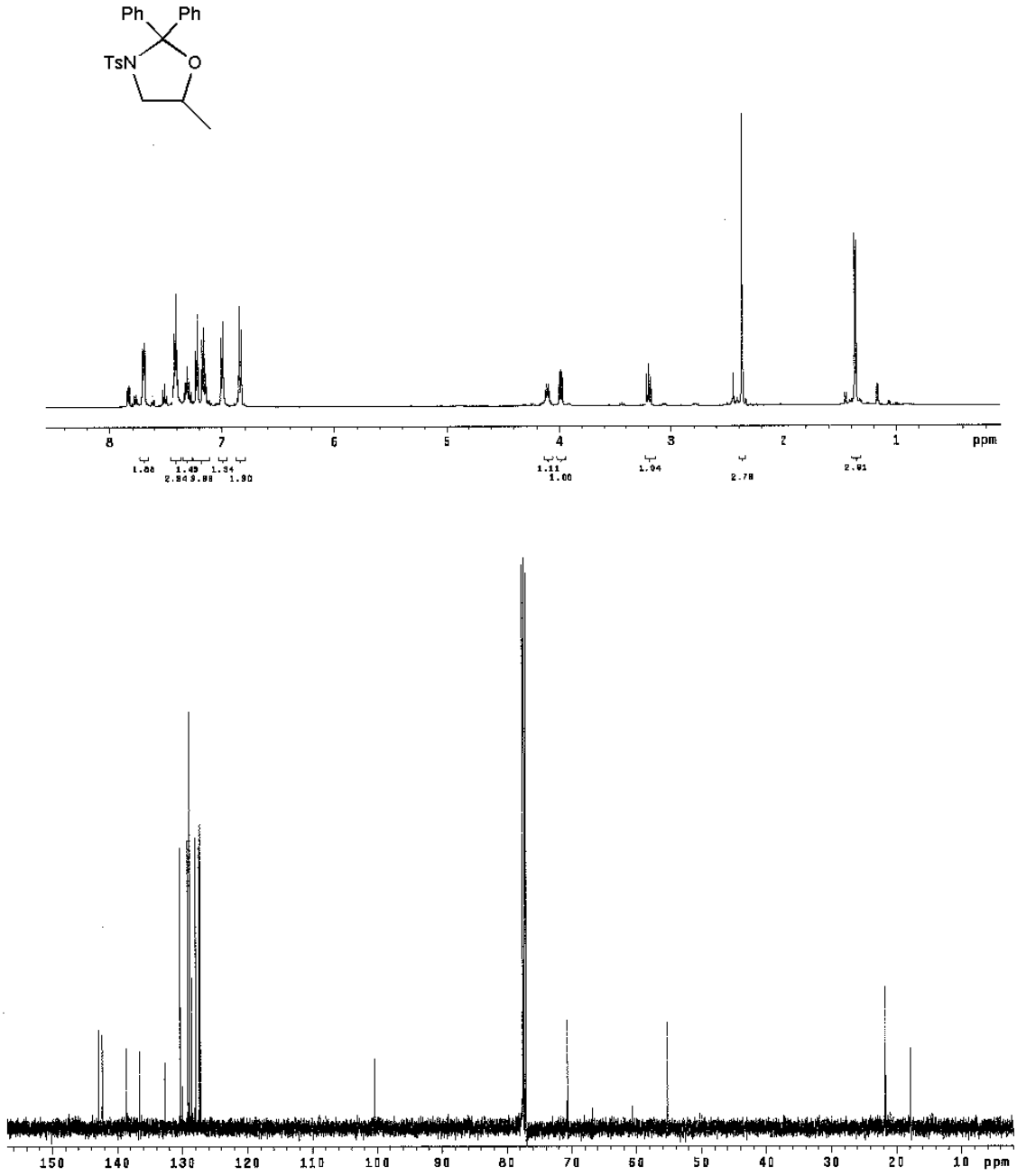


Figure S20. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2,2-diphenyl-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**7e**, Table 4, entry 5).

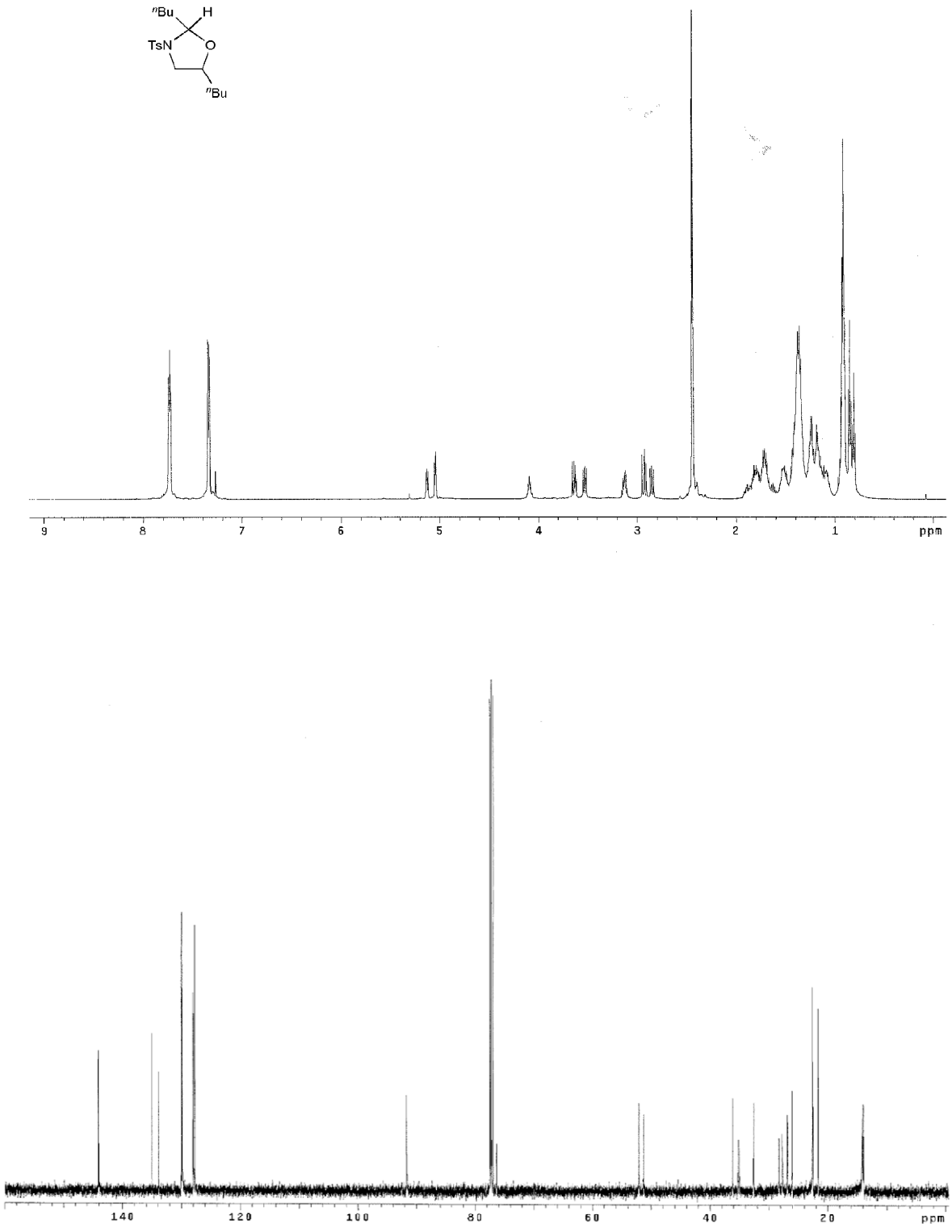


Figure S21. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2,5-dibutyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**10a**, Eq 3).

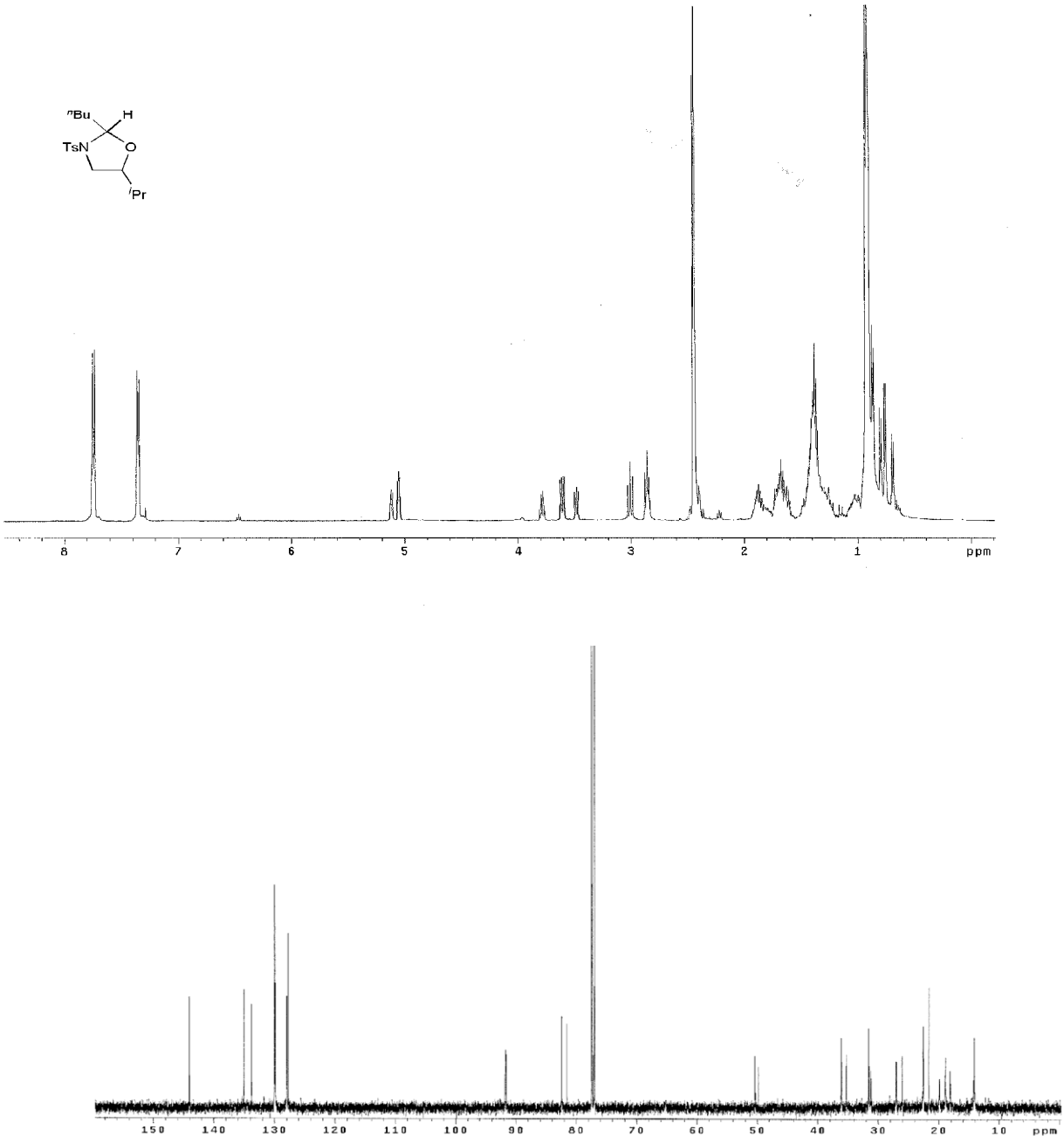


Figure S22. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-butyl-5-isopropyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**10b**, Eq 3).

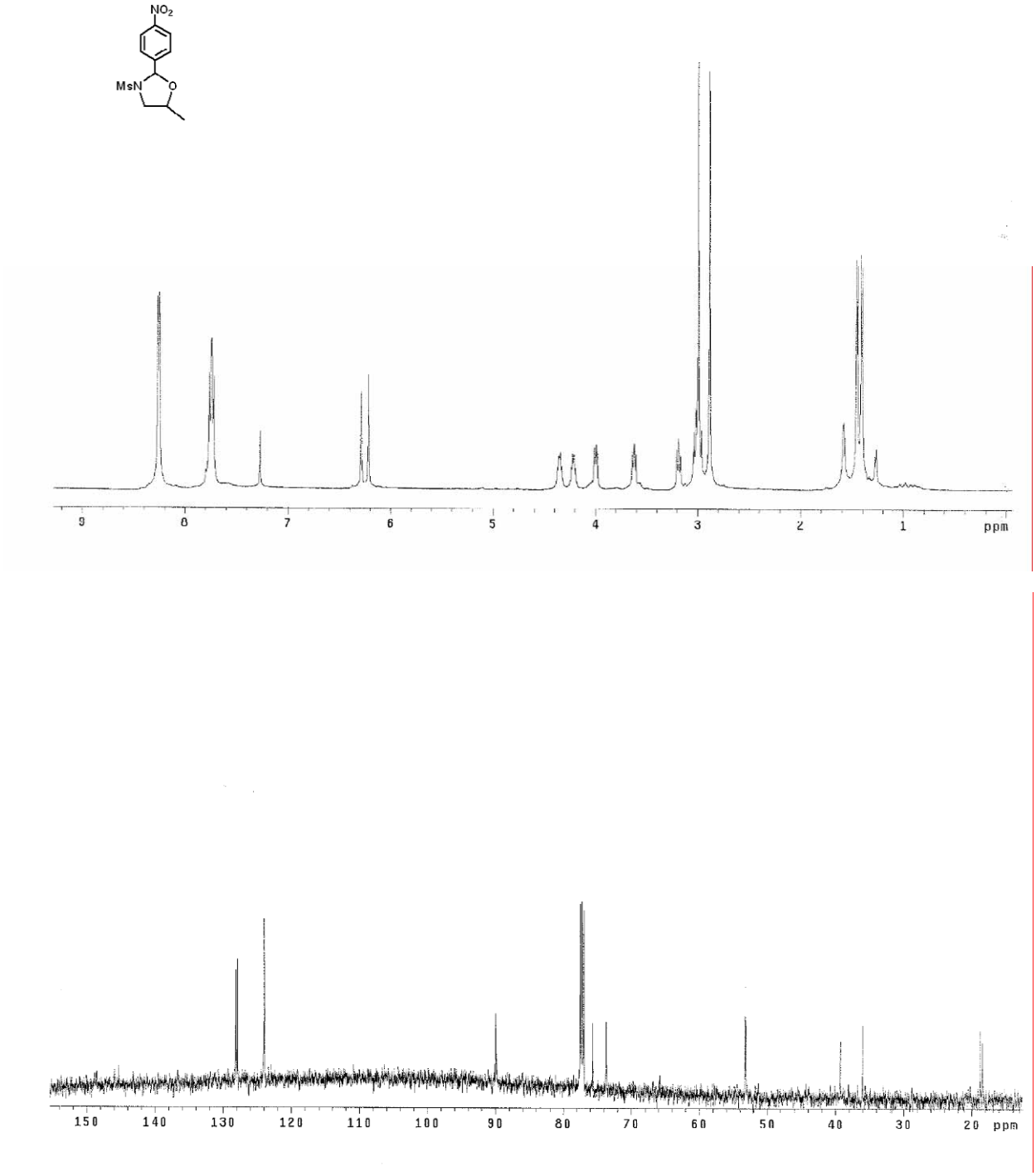
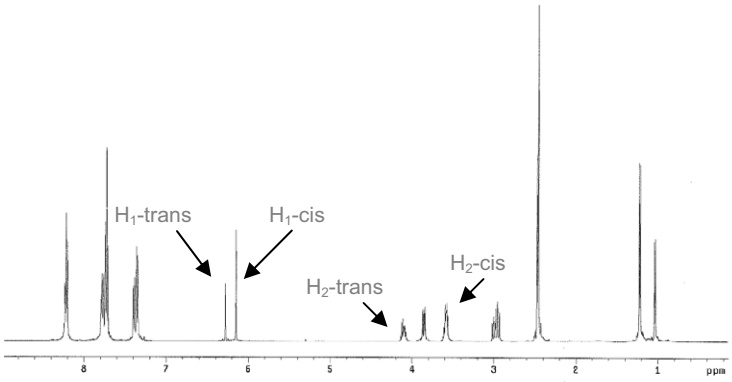
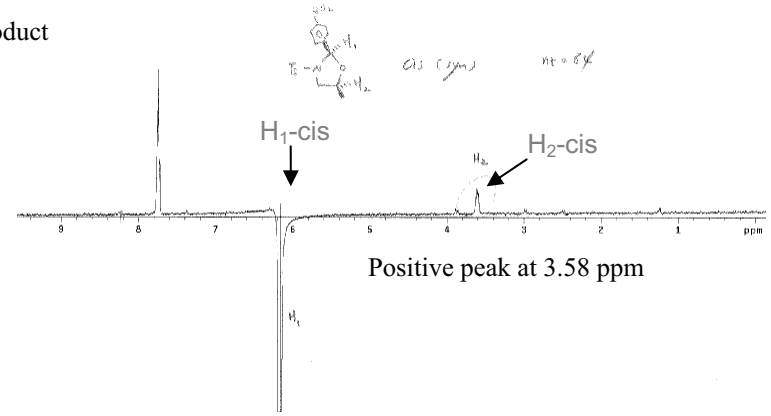


Figure S23. ^{1}H (top) and ^{13}C NMR (bottom) spectra for 2-(4-Nitrophenyl)-5-methyl-3-methanesulfonyl-1,3-oxazolidine (**12**, Eq 4).



(a) Cis product



Positive peak at 3.58 ppm

(b) Trans product

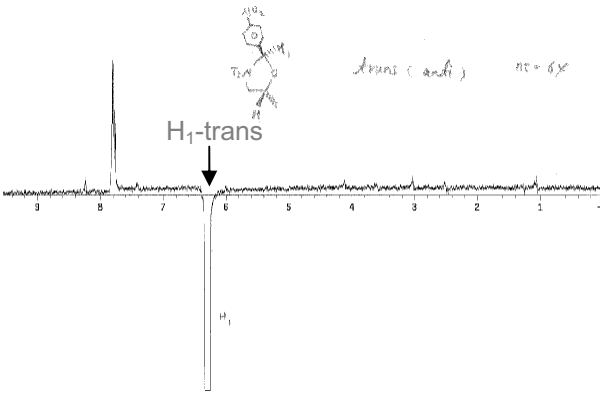


Figure S24. Data from the NOE experiments for the determination of *cis*/*trans* stereochemistry of 2-(4-nitrophenyl)-5-methyl-3-[(4-methylbenzene)sulfonyl]-1,3-oxazolidine (**3e**, Table 3, entry 5).

References.

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.
2. G. W. Coates, Y. D. Y. L. Getzler, P. Wolczanski, V. Mahadevan, Catalytic Carbonylation of Three and Four Membered Heterocycles. U. S. Patent 6,852,865, June 819, 2003.
3. J. L. Vicario, D. Badia and L. Carrillo, *ARKIVOC*, 2007, 304-311.
4. I. C. Stewart, C. C. Lee, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2005, **127**, 17616-17617.
5. *Spartan'02 for Windows*; Wavefunction, Inc. Irvine, CA, 2001.
6. P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533-2544.
7. V. Ripert, L. G. Hubert-Pfalzgraf and J. Vaissermann, *Polyhedron*, 1999, **18**, 1845-1851.
8. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
9. T. Brinck, J. S. Murray and P. Politzer, *Inorg. Chem.*, 1993, **32**, 2622-2625.
10. J. Y. Kempf, B. Maigret and D. C. Crans, *Inorg. Chem.*, 1996, **35**, 6485-6494.