Electronic Supplementary Material (ESI) for Chemical Communications.

Domino Ring-Opening Cyclization (DROC) of Activated Aziridines and Epoxides with Nitrones via Dual-Catalysis "On Water"

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Supporting Information

Table of Contents

1. General experimental

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. Silica gel 230-400 mesh size were used for column chromatography using the combination of ethyl acetate and petroleum ether as an eluent. Unless noted, all reactions were carried out in oven-dried glassware under an atmosphere of nitrogen using anhydrous solvents. Where appropriate, solvents and all reagents were purified prior to use following the guidelines of Perrin and Armarego[1] and Vogel.[2] 2-aryl-1-tosylaziridines were prepared from different styrene derivatives following a reported procedure.[3] Chiral 2-phenyl-1-tosylaziridine[4] were prepared from corresponding amino alcohol following a reported procedure. All the nitrones (**2a**-**l**) were prepared following the reported procedure.[5a,b,c] All commercial reagents were used as received without prior purification unless mentioned. IR spectra were recorded in potassium bromide (KBr) pellet. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz at the temperature of 55 ºC. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethyl silane (δ 0.00). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C {1H} NMR) spectra were recorded at 125 MHz. Mass spectra (MS) were obtained using FAB and ESI mass spectrometer (TOF). Melting point was determined using a hot stage apparatus and are reported as uncorrected. Enantiomeric ratios (er) were determined by HPLC using Chiralcel OD-H, and Lux 5u Cellulose 2 analytical column (detection at 254 nm). Optical rotations were measured using a 6 mL cell with a 1.0 dm path length and are reported as $[\alpha]^{25}_D$ (*c* in gm per 100 mL solvent) at 25 ºC.

General Experimental Procedure for the Synthesis of Oxadiazinane/ Dioxazinane. A clean seal tube was charged with aziridine (0.100 mmol, 1.0 equiv.)/ epoxide (0.200 mmol, 1.0 equiv.), nitrone (0.150 mmol, 1.5 equiv.), anhydrous $LiClO_4$ (10 mol%) and quaternary ammonium salt Bu_4NBF_4 (10 mol%) in water (2.0 mL). The reaction mixture was then stirred at 80 °C for appropriate time. After complete consumption of starting compound (monitored by TLC), the aqueous layer was extracted with ethyl acetate (3 × 10.0 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography on silica gel (230−400 mesh) using ethyl acetate in petroleum ether as the eluent to give the pure products.

2. X-ray crystal structures:

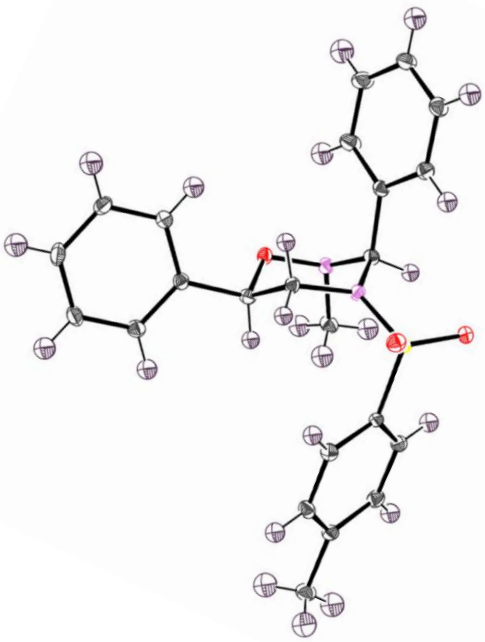

Figure 1. ORTEP diagram of compound **3a** (30% thermal ellipsoids)

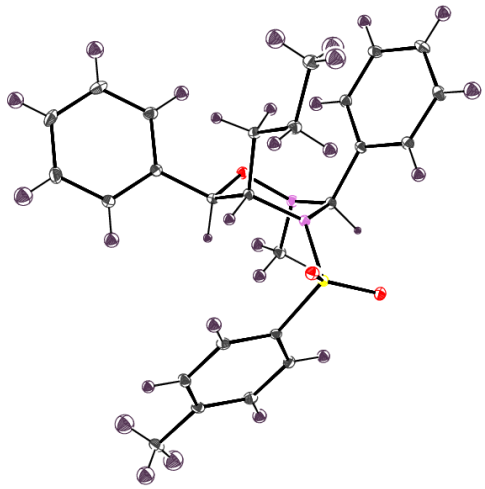

Figure 2. ORTEP diagram of compound **6a** (30% thermal ellipsoids)

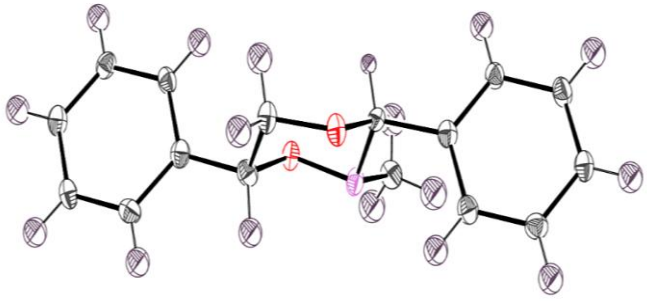

Figure 3. ORTEP diagram of compound **9a** (30% thermal ellipsoids)

3. X-ray crystallographic analysis of 3a, 6a and 9a:

The crystals used in the analyses were glued to a glass fiber and mounted on SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71069 Å) at low temperature (100K). Cell constants were obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all-reciprocal space in the stated θ range. All data were collected with SMART 5.628 and were integrated with the SAINT[6] program. An empirical absorption correction was applied to collect reflections with SADABS[7] using XPREP[8]. The structure was solved using SIR-97[9] and refined using SHELXL-97[10]. The space group of the compounds was determined based on the lack of systematic absence and intensity statistics. Full matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms are fixed by using geometrical constrains using idealized geometries and have been defined isotropically.

Table 1. Data collection and structure refinement parameters for **3a, 6a** and **9a.**

Compound	**3a**	**6a**	**9a**
Formula	$C_{23}H_{24}N_2O_3S$	$C_{26}H_{30}N_2O_3S$	$C_{16}H_{17}NO_2$
Formula weight	408.50	450.58	255.31
CCDC No.	1489202	1518181	1489201
Crystal color, habit	White, block	White, Prism	White, block
T / K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	*P-1*	$P2_1$ (no. 4)
a/Å	9.9562(6)	8.774(5)	5.4942(17)
b/Å	12.5624(7)	10.058(5)	18.284(6)
c/Å	16.3026(10)	14.512(5)	6.781(2)
α/°	90.00	96.541(5)	90.00
β/°	92.165(2)	105.912(5)	103.824(5)
γ/°	90.00	108.607(5)	90.00
V/Å^3	2037.6(2)	1138.4(9)	661.5(4)
Z	4	2	2
D_c/g cm^{-3}	1.332	1.315	1.282
μ/mm^{-1}	0.186	0.173	0.084

Reflections measured	20220	17573	4022
Unique reflections	3753	4399	2272
Reflections used $I > 2\sigma(I)$]	5051	5693	2817
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	R_1 = 0.0467^a wR_2 = 0.1073^b	R_1 = 0.0454^a wR_2 = 0.1040^b	R_1 = 0.0555^a wR_2 = 0.1348^b
$R_1{}^a$, $wR_2{}^b$(all data)	R_1= 0.0721^a wR_2= 0.1216^b	R_1= 0.0669^a wR_2= 0.1133^b	R_1= 0.0765^a wR_2 = 0.1826^b
GOF on F^2	1.015	1.014	0.998
$^aR_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$. $^bwR_2 = \{\Sigma[w(\|F_o\|^2 - \|F_c\|^2)^2]/\Sigma[w(\|F_o\|^2)^2]\}^{1/2}$			

4. References.

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5. Spectral Data:

2-Methyl-3,6-diphenyl-4-tosyl-1,2,4-oxadiazinane (3a). The general method described above was followed when aziridine **1a** (27.3 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3a** (35.9 mg, 0.088 mmol) as a white solid in 88% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether), mp 124–126 °C; IR ν_{max} (KBr, cm^{-1}) 2924, 1597, 1493, 1449, 1341, 1159, 1106, 1089, 952, 814, 736, 698, 672, 615, 545; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.87 (s, 3H), 3.18 (t, *J* = 12.0 Hz, 1H), 3.69 (dd, *J* = 13.7, 3.4 Hz, 1H), 5.02 (dd, *J* = 11.2, 3.0 Hz, 1H), 5.81 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.25−7.34 (m, 8H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 41.1, 45.5, 72.4, 75.0, 126.5, 127.3, 128.2, 128.4, 128.5, 128.6, 128.7, 129.0, 129.7, 136.7, 137.7, 143.5; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_3S$ $(M+H)^+$ 409.1586, found 409.1581.

4-Methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (4a). white solid, mp 122–124 °C; IR ν_{max} (KBr, cm^{-1}) 3280, 2923, 2852, 1687, 1596, 1580, 1493, 1449, 1412, 1345, 1325, 1234, 1185, 1160, 1092, 1021, 987, 930, 817, 758, 672, 651, 547; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 4.45 (d, *J* = 4.5 Hz, 2H), 5.64 (t, *J* = 4.5 Hz, 1H), 7.25 (s, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 48.7, 127.2, 127.9, 129.0, 129.9, 133.8, 134.4, 136.2, 143.8, 192.6; HRMS (ESI) calcd for $C_{15}H_{15}NO_3S$ $(M+H)^+$ 290.0851, found 290.0859.

6-(2-Bromophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3b). The general method described above was followed when aziridine **1b** (35.2 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for

45 minutes to afford **3b** (38.96 mg, 0.080 mmol) as a gummy liquid in 80% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 2956, 2924, 2853, 1742, 1641, 1597, 1493, 1464, 1377, 1345, 1304, 1261, 1186, 1162, 1099, 1020, 989, 961, 910, 861, 861, 751, 698, 671, 613, 589, 558, 542: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.84 (s, 3H), 3.08 (t, *J* = 12.6 Hz, 1H), 3.95 (dd, *J* = 13.7, 4.2 Hz, 1H), 5.32 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.77 (s, 1H), 7.10 (t, *J* = 8.5 Hz, 1H), 7.19−7.37 (m, 7H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 41.1, 44.1, 71.4, 76.3, 122.1, 127.5, 127.8, 128.2, 128.4, 128.5, 129.7, 129.8, 132.3, 132.8, 136.8, 137.4, 137.8, 143.6; HRMS (ESI) calcd for $C_{23}H_{24}BrN_2O_3S$ $(M+H)^+$ 487.0691, found 487.0694.

6-(4-Fluorophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3c). The general method described above was followed, when aziridine **1c** (29.1 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3c** (35.86 mg, 0.084 mmol) as a viscuss liquid in 84% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3708, 3526, 3017, 2849, 2881, 1635, 1488, 1124, 1103, 1029, 830, 568: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.89 (s, 3H), 3.15 (t, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 13.7, 4.2 Hz, 1H), 5.0 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.8 (s, 1H), 6.96 (t, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 1H), 7.14 (t, *J* = 5.7 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.30−7.37 (m, 3H), 7.53 (d, *J* = 6.3 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 40.0, 45.4, 71.2, 73.3, 115.5, 115.6, 115.7, 115.8, 127.2, 127.3, 127.7, 127.8, 128.2, 128.4, 128.6, 129.0, 129.8, 134.5, 136.2, 136.5, 137.4, 143.6, 143.7, 161.7, 161.8, 163.4, 163.8; HRMS (ESI) calcd for $C_{23}H_{24}FN_2O_3S$ $(M+H)^+$ 427.1492, found 427.1493.

6-(4-Chlorophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3d). The general method described above was followed when aziridine **1d** (30.7 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3d** (39.8 mg, 0.090 mmol) as a gummy liquid in 90% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3061, 2924, 2853, 1598, 1492, 1449, 1405, 1342, 1305, 1161, 1111, 1090, 1065, 1015, 988, 958, 913, 868, 814, 741, 700, 671, 621, 589, 557, 542: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.86 (s, 3H), 3.15 (t, J = 11.8 Hz, 1H), 3.69 (dd, J = 14.0, 4.2 Hz, 1H), 5.0 (dd, J = 10.8, 3.4 Hz, 1H), 5.78 (s, 1H), 7.12 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 4H), 7.30−7.35 (m, 3H), 7.52 (d, J = 6.7 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.1, 40.0, 44.3, 70.7, 75.0, 126.2, 126.8, 127.2, 127.4, 127.5, 127.8, 128.7, 133.5, 135.4, 135.5, 136.6, 142.6; HRMS (ESI) calcd for $C_{23}H_{23}ClN_2O_3S$ $(M+H)^+$ 443.1196, found 443.1195.

6-(4-Bromophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3e). The general method described above was followed when aziridine **1e** (35.2 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3e** (40.90 mg, 0.083 mmol) as a thick liquid in 83% yield: R_f 0.8 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3442, 3062, 2956, 2924, 2854, 1739, 1597, 1490, 1454, 1403, 1341, 1304, 1262, 1161, 1110, 1088, 1070, 989, 959, 912, 866, 740, 699, 675, 616, 589, 577, 521: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.86 (s, 3H), 3.15 (t, J = 12.0 Hz, 1H), 3.98 (dd, 10.8, 3.4 Hz, 1H), 4.98 (dd, J = 10.3, 4.6 Hz, 1H), 5.77 (s, 1H), 7.06 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.29−7.33 (m, 3H), 7.42 (d, J = 8.6 Hz, 2H), 7.52 (dd, J = 10.8, 4.6 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 36.3, 40.51, 67.0, 71.4, 117.8,

122.5, 123.4, 123.5, 123.7, 124.9, 127.0, 131.8, 132.1, 132.9, 137.8, 138.8; HRMS (ESI) calcd for $C_{23}H_{24}BrN_2O_3S$ $(M+H)^+$ 487.0691, found 487.0692.

6-(3-bromophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3f). The general method described above was followed when aziridine **1f** (35.2 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3f** (41.8 mg, 0.086 mmol) as a gummy liquid in 86% yield: R_f 0.8 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3442, 3062, 2923, 2853, 1597, 1570, 1493, 1449, 1428, 1342, 1305, 1261, 1198, 1190, 1160, 1071, 1018, 997, 918, 881, 862, 741, 695, 615, 592, 545: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.86 (s, 3H), 3.21 (t, J = 12.0 Hz, 1H), 3.76 (dd, J = 14.0, 3.4 Hz, 1H), 5.02 (dd, J = 10.8, 2.8 Hz, 1H), 5.80 (s, 1H), 7.13−7.20 (m, 2H), 7.25−7.38 (m, 7H), 7.43 (d, J = 5.0 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 41.2, 45.3, 71.8, 76.3, 122.7, 124.7, 127.3, 128.2, 128.4, 128.5, 129.6, 129.7, 130.2, 131.6, 136.5, 137.6, 140.2, 143.6; HRMS (ESI) calcd for $C_{23}H_{24}BrN_2O_3S$ $(M+H)^+$ 487.0691, found 487.0683.

6-(2-Fluorophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3g). The general method described above was followed when aziridine **1g** (29.1 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3g** (36.3 mg, 0.085 mmol) as a gummy liquid in 85% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3848, 3416, 2917, 2849, 1634, 1491, 1456, 1161, 1089, 670: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.81 (s, 3H), 3.24 (t, J = 11.9 Hz, 1H), 3.82 (dd, J = 13.8, 3.6 Hz, 1H), 5.27 (dd, J = 11.0, 3.0 Hz, 1H), 5.77 (s, 1H), 6.99 (t, J = 8.7 Hz, 1H), 7.06 (t, J = 7.0, 1H), 7.23−7.35 (m, 7H), 7.61 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 8.0 Hz,

2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 41.1, 44.5, 66.9, 76.4, 115.3, 115.5, 124.5, 127.4, 127.8, 128.2, 128.5, 129.7, 129.8, 136.7, 137.9, 143.6; HRMS (ESI) calcd for $C_{23}H_{24}FN_2O_3S$ $(M+H)^+$ 427.1492, found 427.1490.

6-(3-Chlorophenyl)-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3h). The general method described above was followed when aziridine **1h** (30.7 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3h** (33.6 mg, 0.076 mmol) as a gummy liquid in 76% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3063, 2924, 2854, 1738, 1599, 1575, 1494, 1449, 1432, 1342, 1305, 1203, 1161, 1107, 1090, 1064, 1018, 988, 958, 865, 862, 814, 784, 743, 695, 616, 593, 546; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.86 (s, 3H), 3.17 (t, J = 11.5 Hz, 1H), 3.72 (dd, J = 13.2, 3.5 Hz, 1H), 4.99 (d, J = 9.2 Hz, 1H), 5.77 (s, 1H), 7.07 (d, J = 6.8 Hz, 1H), 7.19 (s, 1H), 7.22−7.27 (m, 4H), 7.31−7.36 (m, 3H), 7.53 (d, J = 4.6 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 41.2, 45.3, 72.0, 76.3, 124.5, 126.6, 127.3, 128.3, 128.4, 128.5, 128.6, 129.7, 130.0, 134.7, 136.5, 137.7, 140.0, 143.7; HRMS (ESI) calcd for $C_{23}H_{23}ClN_2O_3S$ $(M+H)^+$ 443.1196, found 443.1190.

2-Methyl-3-phenyl-6-(m-tolyl)-4-tosyl-1,2,4-oxadiazinane (3i). The general method described above was followed when aziridine **1i** (29.7 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3i** (36.8 mg, 0.087 mmol) as a gummy liquid in 87% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 2924, 1597, 1493, 1449, 1341, 1159, 1106, 1089, 952, 814, 736, 698, 672, 615, 545; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.42 (s, 3H), 2.89 (s, 3H), 3.19 (t, J = 12.6 Hz, 1H), 3.70 (dd, J = 13.2, 3.5 Hz, 1H), 5.0 (dd, J = 10.9, 2.9 Hz, 1H),

5.82 (s, 1H), 6.98 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.34 (m, 3H), 7.58 (d, J = 6.9 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 21.6, 41.1, 45.4, 72.1, 75.7, 123.6, 127.3, 127.6, 127.9, 128.2, 128.5, 128.55, 128.6, 129.2, 129.4, 129.8, 136.4, 137.5, 138.3, 143.6; HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3S$ $(M+H)^+$ 423.1742, found 423.1741.

2-Methyl-3-phenyl-4-tosyl-6-(3-(trifluoromethyl)phenyl)-1,2,4-oxadiazinane (3j). The general method described above was followed when aziridine **1j** (34.1 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3j** (36.6 mg, 0.082 mmol) as a gummy liquid in 82% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 2956, 2854, 1733, 1598, 1493, 1450, 1405, 1327, 1197, 1163, 1127, 1092, 1073, 1019, 989, 957, 907, 837, 812, 762, 739, 701, 673, 613, 587, 554: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.88 (s, 3H), 3.20 (t, J = 12.6 Hz, 1H), 3.76 (dd, J = 14.9, 4.6 Hz, 1H), 5.08 (dd, J = 11.5, 4.6 Hz, 1H), 5.79 (s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.32−7.34 (m, 3H), 7.37−7.43 (m, 2H), 7.46 (s, 1H), 7.51−7.54 (m, 3H), 7.69 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 41.1, 45.2, 71.6, 75.4, 114.0, 123.5, 125.3, 127.3, 128.2, 128.3, 128.4, 128.5, 129.1, 129.7, 129.8, 131.0, 136.5, 137.6, 143.7; HRMS (ESI) calcd for $C_{24}H_{23}F_3N_2O_3S$ $(M+H)^+$ 477.1460, found 477.1468.

2-Methyl-3-phenyl-4-tosyl-6-(2-(trifluoromethyl)phenyl)-1,2,4-oxadiazinane (3k). The general method described above was followed when aziridine **1k** (34.1 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 45 minutes to afford **3k** (31.7 mg, 0.071 mmol) as a gummy liquid in 71% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3064, 2956, 2924, 2854, 1919, 1744,

1641, 1598, 1492, 1454, 1402, 1350, 1314, 1289, 1261, 1164, 1121, 1096, 1056, 1034, 1019, 987, 933, 913, 864, 815, 770, 739, 715, 698, 644, 616, 588, 558, 542, 525: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.81 (s, 3H), 3.19 (t, J = 11.4 Hz, 1H), 3.77 (dd, J = 13.8, 2.9 Hz, 1H), 5.35 (dd, J = 12.6, 3.8 Hz, 1H), 5.78 (s, 1H), 7.31−7.40 (m, 7H), 7.44 (t, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 40.8, 45.7, 67.3, 75.4, 123.0, 125.2, 125.7, 127.4, 128.2, 128.3, 128.5, 128.6, 129.8, 132.3, 136.5, 136.9, 137.7, 143.7; HRMS (ESI) calcd for $C_{24}H_{23}F_3N_2O_3S$ $(M+H)^+$ 477.1460, found 477.1450.

2-Methyl-6-(4-nitrophenyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (3l). The general method described above was followed when aziridine **1l** (31.8 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 45 minutes to afford **3l** (32.6 mg, 0.072 mmol) as a gummy liquid in 72% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 2957, 2924, 2853, 1736, 1600, 1522, 1493, 1449, 1401, 1347, 1305, 1261, 1161, 1088, 1066, 1016, 989, 960, 913, 852, 814, 744, 698, 671, 615, 558, 542: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.87 (s, 3H), 3.18 (t, J = 12.6 Hz, 1H), 3.80 (dd, 17.2, 4.0 Hz, 1H), 5.13 (dd, J = 11.2, 4.0 Hz, 1H), 5.78 (s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.29−7.33 (m, 3H), 7.38 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 4.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 14.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 41.2, 45.7, 72.0, 76.5, 123.8, 127.2, 127.3, 128.3, 128.4, 128.5, 129.8, 136.4, 137.5, 143.8, 145.2, 148.0; HRMS (ESI) calcd for $C_{23}H_{23}N_3O_5S$ $(M+H)^+$ 454.1437, found 454.1430.

(3S,6S)-2-Methyl-3,6-diphenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3m). The general method described above was followed when (*R*)-**1m** (25.9 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30

minutes to afford **3m** (35.1 mg, 0.089 mmol) as a gummy liquid in 89% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3449, 3062, 3031, 2923, 1602, 1494, 1447, 1345, 1311, 1165, 1103, 1088, 1029, 988, 957, 910, 866, 806, 741, 719, 697, 652, 638, 578, 548, 519, : ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 (s, 3H), 3.23 (t, J = 12.6 Hz, 1H), 3.75 (dd, J = 13.7, 2.8 Hz, 1H), 5.02 (dd, J = 12.6, 3.4 Hz, 1H), 5.79 (s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.28−7.31 (m, 5H), 7.46 (t, J = 7.4 Hz, 2H), 7.53−7.56 (m, 3H), 7.80 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.0, 45.5, 72.5, 76.1, 126.5, 127.2, 127.9, 128.2, 128.4, 128.5, 128.6, 129.0, 132.7, 136.5, 137.8, 140.7; HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3S$ $(M+H)^+$ 395.1429, found 395.1415. $[\alpha]_D^{25}$ = 79.26 (c 0.16, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 10.22 min (minor), tR (2) = 14.49 min (major).

4-(Mesitylsulfonyl)-2-methyl-3,6-diphenyl-1,2,4-oxadiazinane (3n). The general method described above was followed when aziridine **1n** (30.1 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3n** (37.1 mg, 0.085 mmol) as a gummy liquid in 85% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3051, 2824, 2822, 1588, 1492, 1455, 1407, 1332, 1305, 1261, 1141, 1070, 1075, 1025, 978, 958, 913, 868, 814, 741, 710, 671, 621, 589, 542: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.57 (s, 6H), 2.87 (s, 3H), 3.37−3.40 (m, 1H), 3.71 (dd, J = 14.9, 3.4 Hz, 1H), 5.25 (dd, J = 10.8, 4.1 Hz, 1H), 5.61 (s, 1H), 6.91 (d, J = 8.2 Hz, 2H), 7.26−7.35 (m, 8H), 7.45 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ20.8, 22.2, 23.1, 41.4, 45.0, 74.5, 76.2, 126.5, 127.4, 128.3, 128.4, 128.7, 129.8, 131.4, 132.1, 133.6, 136.4, 140.1, 142.6; HRMS (ESI) calcd for $C_{25}H_{28}N_2O_3S$ $(M+H)^+$ 437.1899, found 437.1895.

4-((4-Methoxyphenyl)sulfonyl)-2-methyl-3,6-diphenyl-1,2,4-oxadiazinane (3o). The general method described above was followed when aziridine **1o** (28.9 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3o** (33.1 mg, 0.078 mmol) as a gummy liquid in 78% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3062, 2925, 1700, 1596, 1578, 1496, 1454, 1413, 1308, 1260, 1179, 1155, 1102, 1090, 1060, 1026, 987, 956, 865, 743, 698, 675, 612, 562: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.89 (s, 3H), 3.12 (t, J = 12.3 Hz, 1H), 3.67 (dd, J = 12.6, 3.4 Hz, 1H), 3.86 (s, 3H), 5.02 (dd, J = 10.8, 3.4 Hz, 1H), 5.80 (s, 1H), 6.93 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.27−7.36 (m, 6H), 7.59 (d, J = 6.9 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.1, 45.4, 55.6, 72.6, 76.0, 114.3, 126.5, 128.1, 128.4, 128.5, 128.6, 129.4, 132.3, 134.4, 136.7, 137.8, 163.0; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_4S$ $(M+H)^+$ 425.1535, found 425.1537.

4-((4-(Tert-butyl)phenyl)sulfonyl)-2-methyl-3,6-diphenyl-1,2,4-oxadiazinane (3p). The general method described above was followed when aziridine **1p** (31.5 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 35 minutes to afford **3p** (32.4 mg, 0.072 mmol) as a gummy liquid in 72% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3452, 3062, 3032, 2963, 2928, 2869, 1595, 1494, 1450, 1397, 1293, 1267, 1199, 1164, 1112, 1100, 1085, 1061, 1030, 1014, 1002, 957, 865, 840, 749, 740, 698, 658, 593, 531: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.40 (s, 3H), 3.22 (t, J = 12.3 Hz, 1H), 3.75 (dd, 14.3, 3.4 Hz, 1H), 5.08 (dd, J = 10.8, 3.4 Hz, 1H), 5.80 (s, 1H), 7.21 (d, J = 5.7 Hz, 2H), 7.27−7.31 (m, 6H), 7.46 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 5.8 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.0, 35.0, 41.0, 45.5, 72.4, 75.9,

126.0, 126.6, 127.2, 128.1, 128.4, 128.5, 128.6, 129.9, 136.5, 137.5, 139.9, 156.6; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_3S$ $(M+H)^+$ 451.2055, found 451.2050.

2,3,6-triphenyl-4-tosyl-1,2,4-oxadiazinane (3pa). The general method described above was followed when aziridine **1a** (27.3 mg, 0.100 mmol) was reacted with nitrone **2l** (29.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3pa** (41.36 mg, 0.088 mmol) as a white solid in 88% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether), mp 162–164 °C; IR ν_{max} (KBr, cm^{-1}) 3445, 3062, 3031, 2957, 2922, 2852, 1954, 1732, 1597, 1493, 1453, 1419, 1342, 1242, 1216, 1162, 1125, 1095, 1056, 1045, 957, 865, 840, 749, 738, 695, 658, 594, 538: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.33 (dd, 14.2, 11.4 Hz, 1H), 3.64 (dd, J = 14.8, 2.7 Hz, 1H), 4.62 (dd, J = 11.4, 3.2 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 7.04−7.11 (m, 5H), 7.15 (d, J = 7.7 Hz, 2H), 7.27−7.39 (m, 8H), 7.62−7.67 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 45.6, 70.8, 74.9, 114.0, 121.3, 126.5, 127.5, 128.2, 128.3, 128.6, 128.7, 129.0, 129.5, 129.7, 136.0, 136.3, 136.9, 143.8, 146; HRMS (ESI) calcd for $C_{28}H_{26}N_2O_3S$ $(M+H)^+$ 471.1742, found 471.1745.

(3S,6S)-3-(4-Bromo-2-fluorophenyl)-2-methyl-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3q). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2b** (34.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 45 minutes to afford **3q** (32.8 mg, 0.067 mmol) as a thick liquid in 67% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3064, 2924, 2853, 1601, 1572, 1481, 1447, 1406, 1352, 1310, 1289, 1260, 1217, 1162, 1088, 1070, 990, 910, 870, 817, 753, 720, 689, 637, 546: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.32 (t, J = 14.8 Hz, 1H), 3.79 (dd, J = 13.7, 3.4 Hz, 1H), 5.08 (dd, J = 10.8, 4.0 Hz, 1H), 6.05 (s, 1H), 7.24 (d, J = 8.5 Hz,

2H), 7.31−7.38 (m, 6H), 7.42 (t, *J* = 8.0 Hz, *2H*), 7.52 (t, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.2, 45.5, 69.7, 75.6, 119.4, 119.6, 122.9, 123.2, 126.3, 127.3, 127.5, 128.3, 128.9, 131.7, 132.6, 137.8, 139.9, 159.5, 161.5; HRMS (ESI) calcd for $C_{22}H_{21}BrFN_2O_3S$ $(M+H)^+$ 491.0440, found 491.0442. $[\alpha]_D^{25}$ = +66.0 (c 0.15, $CHCl_3$) for a >99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (chiralpak Cellulose 2 column), n-hexane/i-propanol = 80:20, flow rate = 1 mL/min, tR (1) = 9.30 min (minor), tR (2) = 11.20 min (major).

(3S,6S)-3-(4-Methoxyphenyl)-2-methyl-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3r). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2c** (24.7 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3r** (41.2 mg, 0.097 mmol) as a colourless solid in 97% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); m.p 130–132 °C; IR ν_{max} (KBr, cm^{-1}) 3064, 2961, 2925, 1610, 1585, 1511, 1446, 1344, 1252, 1163, 1103, 1088, 1031, 958, 914, 875, 782, 715, 690, 548: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.82 (s, 3H), 3.24 (t, *J* = 12.4 Hz, 1H), 3.74 (dd, *J* = 14.9, 4.3 Hz, 1H), 3.80 (s, 3H), 4.99 (dd, *J* = 10.2, 3.7 Hz, 1H), 5.70 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.20 (bd, *J* = 9.0 Hz, 2H), 7.27−7.30 (m, 3H), 7.44−7.46 (m, 4H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.1, 45.4, 55.3, 73.0, 75.8, 113.4, 113.9, 126.5, 127.2, 128.5, 128.6, 129.0, 129.8, 132.6, 137.8, 140.7, 159.6; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_4S$ $(M+H)^+$ 425.1535, found 425.1539. $[\alpha]_D^{25}$ = +115.2 (c 0.15, $CHCl_3$) for a >99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 14.70 min (minor), tR (2) = 25.41 min (major).

(3S,6S)-3-(4-(Tert-butyl)phenyl)-2-methyl-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3s). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2d** (34.0 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3s** (32.9 mg, 0.073 mmol) as a gummy liquid in 73% yield: R_f 0.8 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 2960, 1446, 1346, 1164, 1087, 957, 879, 754, 719, 689, 638, 602, 577, 547: ^{1}H MR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H), 2.81 (s, 3H), 3.26 (t, *J* = 12.0 Hz, 1H), 3.76 (dd, *J* = 13.7, 2.8 Hz, 1H), 5.02 (dd, *J* = 10.8, 3.4 Hz, 1H), 5.75 (s, 1H), 7.22−7.32 (m, 8H), 7.40−7.45 (m, 3H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ31.3, 41.2, 45.5, 73.4, 76.2, 125.3, 126.5, 126.6, 127.2, 127.9, 128.3, 128.5, 128.6, 128.9, 129.1, 132.5, 133.2, 140.6, 151.3 ; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_3S$ $(M+H)^+$ 451.2055, found 451.2063. $[\alpha]_D^{25}$ = +54.0 (c 0.16, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (chiral pak Cellulose 2 column), n-hexane/i-propanol = 80:20, flow rate = 1 mL/min, tR (1) = 8.56 min (minor), tR (2) = 10.73 min (major).

(3S,6S)-2-Methyl-6-phenyl-4-(phenylsulfonyl)-3-(4-(trifluoromethyl)phenyl)-1,2,4-oxadiazinane (3t). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2e** (30.4 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3t** (40.7 mg, 0.088 mmol) as a gummy liquid in 88% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3065, 2925, 2854, 1619, 1586, 1496, 1447, 1412, 1326, 1263, 1166, 1125, 1110, 1088, 1018, 990, 962, 925, 832, 804, 755, 719, 690, 673, 639, 580, 550, 539, : ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (s, 3H), 3.15 (t, *J* = 13.7 Hz, 1H), 3.78 (dd, *J* = 14.3, 3.4 Hz, 1H), 5.04 (dd, *J* = 10.8, 3.4 Hz, 1H), 5.84 (s, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.28−7.30 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.0

Hz, 3H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.8, 45.5, 71.5, 75.2, 123.0, 125.4, 125.5, 126.5, 127.1, 128.1, 128.7, 128.8, 129.3, 132.9, 137.0, 140.5, 140.7; HRMS (ESI) calcd for $C_{23}H_{22}F_3N_2O_3S$ $(M+H)^+$ 463.1303, found 463.1302. . $[\alpha]_D^{25}$ = +79.2 (c 0.30, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (chiralpak Cellulose 2 column), n-hexane/i-propanol = 80:20, flow rate = 1 mL/min, tR (1) = 7.43 min (minor), tR (2) = 8.67 min (major).

(3S,6S)-3-(furan-2-yl)-2-methyl-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3u). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3u** (39.5 mg, 0.099 mmol) as a white solid in 99% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); m.p 132–134 °C; IR ν_{max} (KBr, cm^{-1}) 3063, 2962, 2927, 2889, 1585, 1496, 1479, 1447, 1349, 1310, 1260, 1226, 1201, 1165, 1119, 1087, 1058, 1003, 995, 955, 930, 913, 883, 816, 754, 719, 698, 689, 601, 578, 545; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.66 (s, 3H), 3.25 (t, *J* = 11.5 Hz, 1H), 3.75 (dd, *J* = 13.2, 3.4 Hz, 1H), 5.01 (dd, *J* = 11.5, 3.4 Hz, 1H), 5.84 (s, 1H), 6.30 (d, *J* = 1.7 Hz, 1H), 6.44 (d, *J* = 2.9 Hz, 1H), 7.25-7.33 (m, 6H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 14.9 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.2, 46.0, 70.6, 76.6, 110.1, 110.9, 126.3, 127.2, 128.6, 129.0, 132.4, 137.4, 139.6, 142.3, 148.1; HRMS (ESI) calcd for $C_{20}H_{20}N_2O_4S$ $(M+H)^+$ 385.1222, found 385.1229. $[\alpha]_D^{25}$ = +136.00 (c 0.10, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (chiralpak Cellulose 2 column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 34.51 min (minor), tR (2) = 57.70 min (major).

(3S,6S)-2-Methyl-3-(naphthalen-2-yl)-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3v). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2g** (27.7 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 45 minutes to afford **3v** (31.1 mg, 0.070 mmol) as a gummy liquid in 70% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3060, 2956, 2924, 2854, 1738, 1601, 1507, 1496, 1446, 1345, 1311, 1265, 1203, 1119, 1103, 1087, 1062, 972, 948, 612, 861, 805, 784, 698, 636, 546, 522: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.97 (s, 3H), 2.29 (t, J = 12.5 Hz, 1H), 3.82 (dd, 13.9, 3.4 Hz, 1H), 5.10 (dd, J = 11.0, 3.6 Hz, 1H), 5.96 (s, 1H), 7.18−7.20 (m, 2H), 7.26−7.28 (m, 3H), 7.43−7.50 (m, 4H), 7.55 (t, J = 7.3 Hz, 1H), 7.66−7.72 (m, 2H), 7.78−7.86 (m, 4H), 7.94 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.0, 45.6, 72.2, 76.3, 125.9, 126.2, 126.4, 126.6, 127.2, 127.5, 127.9, 128.2, 128.3, 128.6, 129.1, 131.9, 132.7, 132.2, 134.0, 137.7; HRMS (ESI) calcd for $C_{26}H_{24}N_2O_3S$ $(M+H)^+$ 445.1586, found 445.1580. $[\alpha]_D^{25}$ = –35.00 (c 0.15, CHCl3) for a >98% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 13.63 min (minor), tR (2) = 20.36 min (major).

(3S,6S)-3-(2,6-Dichlorophenyl)-2-methyl-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3w). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2h** (30.3 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 45 minutes to afford **3w** (31.4 mg, 0.068 mmol) as a gummy liquid in 68% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3063, 2921, 2852, 1579, 1563, 1492, 1438, 1351, 1289, 1254, 1206, 1192, 1133, 1093, 1059, 1027, 990, 957, 954, 871, 781, 713, 690, 576, 555: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.53 (s, 3H), 4.10−4.72 (m, 2H), 4.78 (dd, J = 10.3, 7.1 Hz, 1H), 6.26 (s, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.25−7.35 (m, 7H), 7.43 (t, J = 7.6

Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.80 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.8, 46.1, 79.2, 79.6, 125.8, 127.3, 128.2, 128.6, 128.9, 129.6, 130.1, 132.4, 132.7, 136.5, 140.0, 141.3; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_3S$ $(M+H)^+$ 463.0650, found 463.0659. $[\alpha]_D^{25}$ = +82.5 (c 0.16, $CHCl_3$) for a >99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 11.41 min (minor), tR (2) = 13.90 min (major).

(3S,6S)-2-Benzyl-3-(furan-2-yl)-6-phenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3x). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2i** (31.6 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3x** (44.2 mg, 0.096 mmol) as a white solid in 96% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether), m.p 123–125 °C; IR ν_{max} (KBr, cm^{-1}) 3063, 3032, 2923, 1586, 1496, 1447, 1350, 1310, 1263, 1226, 1201, 1167, 1101, 1087, 1071, 1014, 990, 914, 884, 815, 792, 719, 698, 639, 599, 577: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (t, J = 11.7 Hz, 1H), 3.84−3.91 (m, 2H), 4.06 (d, J = 13.2 Hz, 1H), 4.96 (dd, J = 11.5, 3.4 Hz, 1H), 5.90 (s, 1H), 6.31 (s, 1H), 6.51 (d, J = 3.4 Hz, 2H), 7.23−7.32 (m, 11H), 7.42 (t, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.2, 57.8, 68.8, 76.7, 110.2, 110.9, 126.4, 127.5, 127.6, 128.4, 128.6, 128.8, 129.0, 132.5, 135.8, 137.4, 139.9, 142.5, 148.4; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_4S$ $(M+H)^+$ 461.1535, found 461.1534. $[\alpha]_D^{25}$ = +57.3 (c 0.10, $CHCl_3$) for a >99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 13.01 min (minor), tR (2) = 13.71 min (major).

(3S,6S)-2-benzyl-6-phenyl-4-(phenylsulfonyl)-3-(4-(trifluoromethyl)phenyl)-1,2,4-oxadiazinane (3y). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2j** (41.8 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3y** (49.5 mg, 0.092 mmol) as a gummy liquid in 92% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3065, 3033, 2924, 2854, 1619, 1496, 1447, 1411, 1325, 1263, 1165, 1124, 1068, 1018, 960, 881, 840, 802, 755, 720, 698, 601: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21 (dd, *J* = 14.3, 10.3 Hz, 1H), 3.86 (dd, *J* = 14.3, 3.4 Hz, 1H), 4.26 (d, *J* = 13.2 Hz, 1H), 4.38 (d, *J* = 13.7 Hz, 1H), 5.07 (dd, *J* = 11.5, 2.3 Hz, 1H), 5.90 (s, 1H), 7.11 (dd, *J* = 5.2, 1.7 Hz, 2H), 7.26−7.35 (m, 6H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.57−7.64 (m, 3H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.5, 57.1, 72.4, 72.5, 125.4, 125.5, 126.5, 127.2, 127.8, 128.5, 128.7, 128.8, 128.9, 129.2, 129.3, 130.2, 133.0, 135.7, 136.9, 140.5, 140.8; HRMS (ESI) calcd for $C_{29}H_{26}F_3N_2O_3S$ $(M+H)^+$ 539.1616, found 539.1610. $[\alpha]_D^{25}$ = +126.3 (c 0.15, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 10.08 min (minor), tR (2) = 11.26 min (major).

(3S,6S)-2-Benzyl-3,6-diphenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (3z). The general method described above was followed when (*R*)-**1m** (26.0 mg, 0.100 mmol) was reacted with nitrone **2k** (31.6 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **3z** (40.5 mg, 0.086 mmol) as a gummy liquid in 86% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3063, 3061, 2924, 2855, 1603, 1494, 1447, 1347, 1264, 1165, 1099, 1070, 1029, 957, 911, 867, 805, 755, 740, 721, 697, 642, 577: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.29 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.84 (dd, *J* = 14.3, 2.9 Hz, 1H), 4.21 (d, *J* = 13.2

Hz, 1H), 4.33 (d, *J* = 13.7 Hz, 1H), 5.04 (dd, *J* = 11.4, 3.4 Hz, 1H), 5.88 (s, 1H), 7.14 (t, *J* = 3.4 Hz, 2H), 7.25−7.33 (m, 9H), 7.37 (d, *J* = 6.9 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 3H), 7.83 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.8, 45.5, 71.5, 75.2, 123.0, 125.4, 125.5, 126.5, 127.1, 128.1, 128.7, 128.8, 129.3, 132.9, 137.0, 140.5, 140.7; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3S$ $(M+H)^+$ 471.1742, found 471.1746. $[\alpha]_D^{25}$ = +41.00 (c 0.10, $CHCl_3$) for a 99% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (chiralpak Cellulose 2 column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 14.47 min (minor), tR (2) = 18.84 min (major).

2-Methyl-3-phenyl-4-tosyl-6-vinyl-1,2,4-oxadiazinane (5a). The general method described above was followed when aziridine **1q** (22.3 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30 minutes to afford **5a** (29.4 mg, 0.082 mmol) as a colourless liquid in 82% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3063, 3030, 2958, 2956, 2924, 1917, 1728, 1645, 1598, 1493, 1449, 1406, 1343, 1306, 1288, 1261, 1161, 1103, 1088, 1066, 985, 890, 740, 699, 614, 585, 522: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.75 (s, 3H), 3.03 (dd, *J* = 13.7, 10.8 Hz, 1H), 3.59 (dd, *J* = 13.7, 3.4 Hz, 1H), 4.44−48 (m, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.26 (d, *J* = 17.4 Hz, 1H), 5.60−5.67 (m, 2H), 7.24−7.30 (m, 5H), 7.47−7.50 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 41.2, 43.7, 70.6, 76.1, 119.2, 126.6, 127.2, 128.2, 128.4, 129.7, 133.8, 136.4, 137.4, 143; HRMS (ESI) calcd for $C_{19}H_{23}N_2O_3S$ $(M+H)^+$ 359.1429, found 359.1423.

2-Methyl-3,6-diphenyl-5-propyl-4-tosyl-1,2,4-oxadiazinane (6a). The general method described above was followed when aziridine **1r** (31.5 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 30

minutes to afford **6a** (38.7 mg, 0.086 mmol) as a white solid in 86% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether), m.p 117–119 °C; IR ν_{max} (KBr, cm^{-1}) 3061, 3029, 2961, 2929, 2871, 1598, 1494, 1450, 1377, 1349, 1163, 1122, 1087, 1058, 1005, 962, 925, 885, 866, 848, 816, 762, 732, 684, 661, 630, 583, 564, 542, 496: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.22 (t, J = 6.8 Hz, 3H), 0.56−0.79 (m, 3H), 0.98−1.06 (m, 1H), 2.45 (s, 3H), 2.82 (s, 3H), 3.88−3.91 (m, 1H), 5.00 (d, J = 4.0 Hz, 1H), 5.88 (s, 1H), 7.14 (d, J = 7.4 Hz, 2H), 7.20−7.37 (m, 8H), 7.84 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.3, 18.9, 21.5, 29.6, 44.4, 57.1, 73.7, 74.4, 125.6, 127.5, 127.6, 127.8, 128.0, 128.3, 128.8, 129.7, 138.1, 138.2, 138.8, 143.7; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_3S$ $(M+H)^+$ 451.2055, found 451.2049.

6-(2,4-dichlorophenyl)-5-ethyl-2-methyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (6b). The general method described above was followed when aziridine **1s** (36.9 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 120 minutes to afford **6b** (36.2 mg, 0.072 mmol) as a viscus liquid in 72% yield: R_f 0.6 (10 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3484, 2955, 2925, 2854, 1727, 1640, 1590, 1561, 1493, 1465, 1378, 1350, 1305, 1284, 1164, 1123, 1049, 1020, 999, 971, 912, 864, 814, 771, 744, 724, 679, 667, 581: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (bt, J = 6.8 Hz, 3H), 0.59 (bs, 1H), 1.10 (bs, 1H), 2.44 (s, 3H), 2.74 (s, 3H), 4.09−4.14 (m, 1H), 5.15 (d, J = 3.6 Hz, 1H), 5.88 (s, 1H), 7.19 (dd, J = 8.7, 2.3 Hz, 1H), 7.26−7.38 (m, 7H), 7.82 (d, J = 7.3 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 21.5, 21.8, 41.6, 55.2, 72.4, 74.8, 127.2, 127.9, 128.0, 128.2, 128.5, 128.9, 129.0, 129.6, 131.9, 134.0, 134.8, 137.8, 138.8, 143.8; HRMS (ESI) calcd for $C_{25}H_{27}Cl_2N_2O_3S$ $(M+H)^+$ 505.1119, found 505.1119.

6-(2,5-dichlorophenyl)-2,5-dimethyl-3-phenyl-4-tosyl-1,2,4-oxadiazinane (6c). The general method described above was followed when aziridine **1t** (35.5 mg, 0.100 mmol) was reacted with nitrone **2a** (20.5 mg, 0.150 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 120 minutes to afford **6c** (33.3 mg, 0.068 mmol) as a white solid in 68% yield: R_f 0.7 (10 % ethyl acetate in petroleum ether), m.p 147–149 °C; IR ν_{max} (KBr, cm^{-1}) 3066, 2929, 2870, 1917, 1592, 1560, 1493, 1447, 1451, 1447, 1402, 1382, 1349, 1330, 1290, 1234, 1164, 1120, 1092, 1053, 995, 886, 814, 772, 742, 675, 600, 580, 546: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.47 (d, J = 6.8 Hz, 3H), 2.44 (s, 3H), 2.76 (s, 3H), 4.30−4.37 (m, 1H), 5.20 (d, J = 4.1 Hz, 1H), 5.76 (s, 1H), 7.16 (dd, J = 8.2, 2.2 Hz, 1H), 7.23−7.39 (m, 7H), 7.79 (d, J = 7.7 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 21.5, 41.2, 48.9, 69.6, 74.2, 127.2, 127.6, 127.8, 128.2, 128.3, 128.9, 129.0, 129.8, 132.0, 134.2, 134.3, 137.7, 139.5, 143.8; HRMS (ESI) calcd for $C_{24}H_{25}Cl_2N_2O_3S$ $(M+H)^+$ 491.0963, found 491.0963.

2-Methyl-3,6-diphenyl-1,2,4-oxadiazinane (7a). To a Solution of oxadiazinane **3a** (81.2 mg, 0.200 mmol) in anhydrous methanol was added Na_2HPO_4 (4 equiv) and Na-Hg (2 equiv). The reaction mixture was stirred for 60 min at rt. The reaction mixture was then quenched with water, extracted with diethyl ether (3 × 10.0 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography on silica gel (230−400 mesh) using ethyl acetate in petroleum ether as the eluent to afford NH-free **7a** (37.08, 0.146 mmol) as a clear liquid in 73% yield: R_f 0.4 (20 % ethyl acetate in petroleum ether); IR ν_{max} (KBr, cm^{-1}) 3064, 2961, 2925, 1610, 1585, 1511, 1446, 1344, 1252, 1163, 1103, 1088, 1031, 958, 914, 875, 782, 715, 690, 548: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.02 (dd, J = 13.7, 9.7 Hz, 1H), 3.21 (dd, J = 14.9, 2.3 Hz, 1H), 4.28 (s, 1H), 5.01 (dd, J = 12.6, 4.0 Hz, 1H), 7.29−7.40 (m, 8H), 7.44 (dd, J = 8.6, 2.7

Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.8, 51.2, 81.2, 83.9, 126.6, 127.4, 128.2, 128.6, 128.8, 128.9, 138.6, 139.5; HRMS (ESI) calcd. for $C_{16}H_{19}N_2O$ $(M+H)^+$ 255.1497, found 255.1498.

(3R,6S)-2-Methyl-3,6-diphenyl-1,4,2-dioxazinane (9a). The general method described above was followed when (*R*)-**4** (24.0 mg, 0.200 mmol) was reacted with nitrone **2a** (40.5 mg, 0.300 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 60 minutes to afford **9a** (48.5 mg, 0.176 mmol) as colourless solid in 85% yield: R_f 0.7 (5 % ethyl acetate in petroleum ether), m.p 90–92 °C; IR ν_{max} (KBr, cm^{-1}) 3031, 2956, 2911, 2853, 1956, 1494, 1451, 1364, 1310, 1251, 1196, 1143, 1091, 1051, 989, 898, 667: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.77 (dd, *J* = 10.9, 10.4 Hz, 1H), 4.11 (dd, *J* = 11.4, 2.7 Hz, 1H), 4.87 (s, 1H), 5.27 (dd, *J* = 10.5, 2.7 Hz, 1H), 7.31−7.42 (m, 8H), 7.49−7.52 (m, 2H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.9, 71.4, 78.6, 98.0, 126.9, 127.9, 128.6, 128.7, 128.8, 129.6, 136.6, 136.9; HRMS (ESI) calcd for $C_{16}H_{17}NO_2$ $(M+Na)^+$ 278.1157, found 278.1153. $[\alpha]_D^{25}$ = +46.7 (c 0.13, $CHCl_3$) for a >98% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), n-hexane/i-propanol = 95:5, flow rate = 1 mL/min, tR (1) = 5.88 min (minor), tR (2) = 6.82 min (major).

2-Methyl-6-phenyl-3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazinane (9b). The general method described above was followed when epoxide **4** (24.0 mg, 0.200 mmol) was reacted with nitrone **2e** (60.9 mg, 0.300 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 60 minutes to afford **9b** (46.6 mg, 0.144 mmol) as a colourless solid in 72% yield: R_f 0.6 (5 % ethyl acetate in petroleum ether); m.p 105–107 °C; IR ν_{max} (KBr, cm^{-1}) 3063, 3031, 2960, 2928, 1917, 1598, 1495, 1452, 1409, 1378, 1348, 1326, 1305, 1290, 1242, 1162, 1091, 1019, 998, 908, 838, 763, 730, 699, 674, 630, 552: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.78 (dd, *J* = 10.8, 10.3 Hz, 1H), 4.12 (dd, *J* = 11.4, 2.4 Hz, 1H), 4.96 (s, 1H), 5.28 (dd, *J* = 10.3, 2.8 Hz, 1H),

7.33−7.40 (m, 5H), 7.62−7.68 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.5, 71.3, 78.3, 96.9, 125.6, 125.7, 126.8, 128.4, 128.7, 128.8, 131.6, 131.8, 136.4, 140.7; HRMS (ESI) calcd for $C_{17}H_{17}F_3NO_2$ $(M+H)^+$ 324.1211, found 324.1208

3-(4-Methoxyphenyl)-2-methyl-6-phenyl-1,4,2-dioxazinane (9c). The general method described above was followed when epoxide **4** (24.0 mg, 0.200 mmol) was reacted with nitrone **2c** (49.5 mg, 0.300 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 60 minutes to afford **9c** (51.7 mg, 0.168 mmol) as yellow solid in 84% yield: R_f 0.5 (5 % ethyl acetate in petroleum ether); m.p 114–116 °C; IR ν_{max} (KBr, cm^{-1}) 2956, 2924, 2853, 1742, 1613, 1586, 1515, 1496, 1462, 1377, 1364, 1251, 1103, 1036, 994, 964, 898,M 823, 806, 754, 725, 698, 650, 599: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.76 (dd, J = 11.4, 10.5 Hz, 1H), 3.82 (s, 3H), 4.10 (dd, J = 11.4, 2.8 Hz, 1H), 4.81 (s, 1H), 5.25 (dd, J = 10.3, 2.8 Hz, 1H), 6.91 (d, J = 16.3 Hz, 2H), 7.33−7.40 (m, 5H), 7.43 (d, J = 11.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.9, 55.4, 71.4, 78.7, 97.7, 114.1, 126.8, 128.5, 128.6, 129.2, 129.4, 136.7, 160.5; HRMS (ESI) calcd for $C_{17}H_{19}NO_3$ $(M+Na)^+$ 308.1263, found 308.1265.

3-(2,6-Dichlorophenyl)-2-methyl-6-phenyl-1,4,2-dioxazinane (9d). The general method described above was followed when epoxide **4** (24.0 mg, 0.200 mmol) was reacted with nitrone **2h** (60.6 mg, 0.300 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 90 minutes to afford **9d** (40.8 mg, 0.126 mmol) as a white solid in 63% yield: R_f 0.6 (5 % ethyl acetate in petroleum ether); m.p 122–124 °C; IR ν_{max} (KBr, cm^{-1}) 3063, 3032, 2965, 2880, 2853, 1698, 1581, 1563, 1495, 1453, 1403, 1368, 1343, 1328, 1266, 1186, 1105, 1052, 996, 965, 899, 757, 698: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.79 (dd, J = 10.9, 10.5 Hz, 1H), 4.15 (dd, J = 12.8, 4.1 Hz, 1H), 5.33 (dd, J = 10.5, 2.7 Hz, 1H), 5.77 (s, 1H), 7.20 (t, J = 8.2 Hz, 1H), 7.28−7.43 (m, 7H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 40.5, 71.3, 79.3, 94.1, 126.8, 127.8, 128.5, 128.6, 130.6, 131.1, 131.5, 136.4; HRMS (ESI) calcd for $C_{16}H_{16}Cl_2NO_2$ $(M+H)^+$ 324.0558, found 324.0553

3-(Furan-2-yl)-2-methyl-6-phenyl-1,4,2-dioxazinane (9e). The general method described above was followed when epoxide **4** (24.0 mg, 0.200 mmol) was reacted with nitrone **2f** (37.5 mg, 0.300 mmol) in presence of $LiClO_4$ (10 mol%) and Bu_4NBF_4 (10 mol%) at 80 °C for 60 minutes to afford **9e** (44.4 mg, 0.166 mmol) as a colourless solid in 83% yield: R_f 0.7 (5 % ethyl acetate in petroleum ether); m.p 102–104 °C; IR ν_{max} (KBr, cm^{-1}) , 3034, 2954, 2920, 1910, 1698, 1595, 1552, 1456, 1401, 1388, 1344, 1321, 1301, 1278, 1224, 1182, 1085, 1011, 999, 930, 838, 762, 735, 699, 675, 630, 522: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.73 (dd, J = 11.4, 10.4 Hz, 1H), 4.10 (dd, J = 11.9, 2.7 Hz, 1H), 4.96 (s, 1H), 5.24 (dd, J = 10.5, 2.7 Hz, 1H), 6.40 (dd, J = 3.2, 1.8 Hz, 1H), 6.53 (t, J = 3.2 Hz, 1H), 7.29−7.38 (m, 5H), 7.45 (bd, J = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.0, 71.3, 78.8, 91.1, 110.1, 110.5, 126.8, 128.6, 136.3, 143.2, 149.4; HRMS (ESI) calcd for $C_{14}H_{16}NNaO_3$ $(M+H)^+$ 268.0950, found 268.0948

6. NMR Spectra

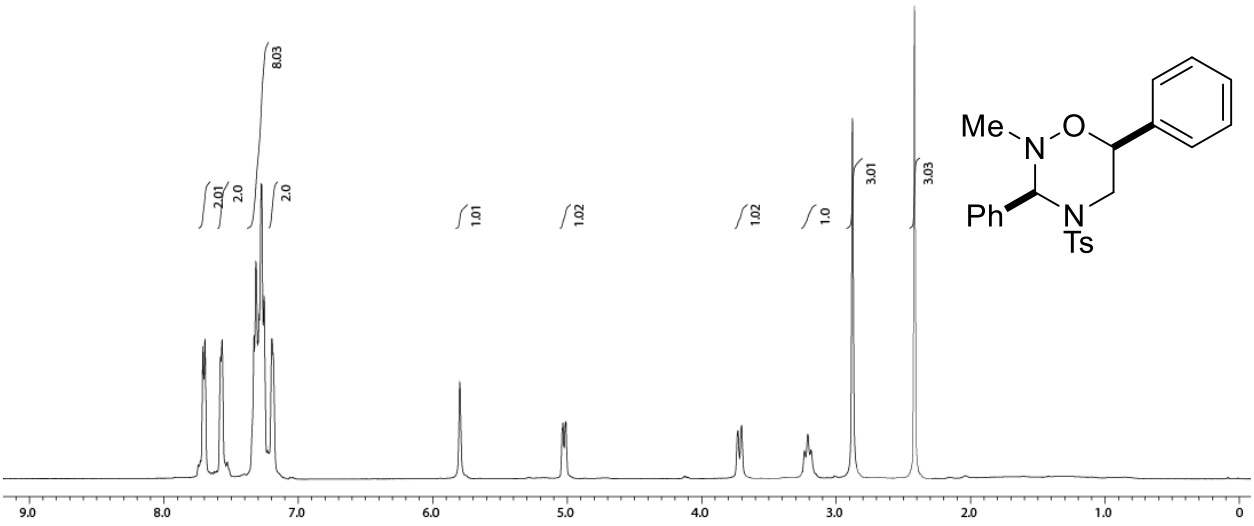

Figure 4: ^{1}H NMR spectrum **3a** at 55 ˚C ($CDCl_3$, 500 MHz)

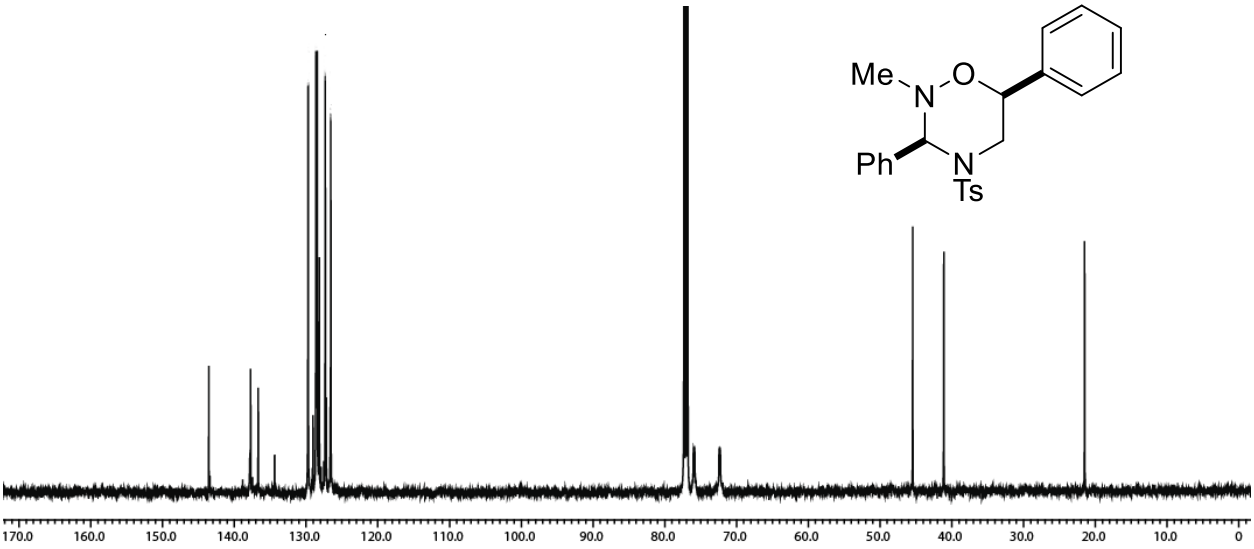

Figure 5: ^{13}C NMR spectrum of **3a** at 55 ˚C ($CDCl_3$, 125 MHz

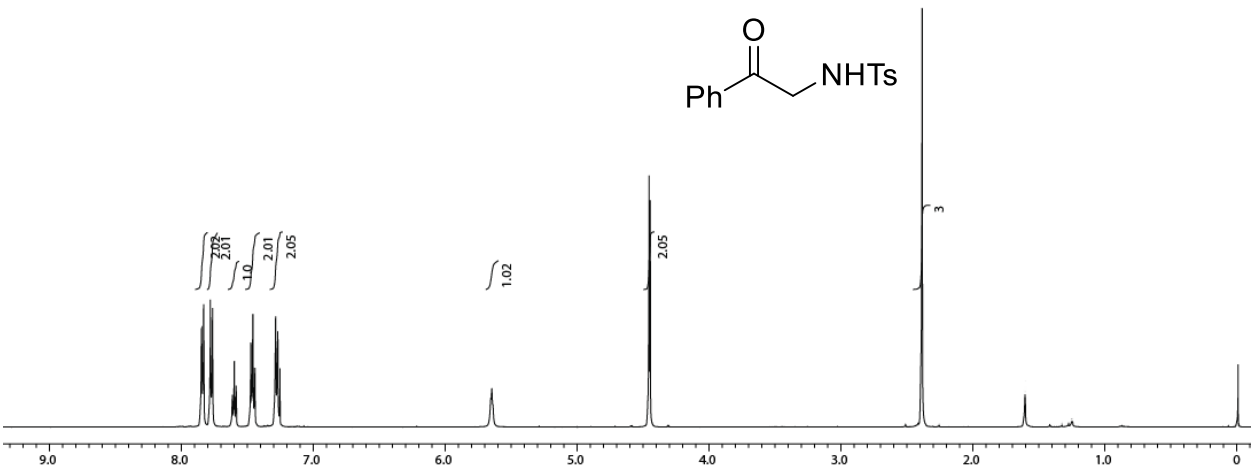

Figure 6: 1H NMR spectrum of **4a** at 55 ˚C (CDCl3, 500 MHz)

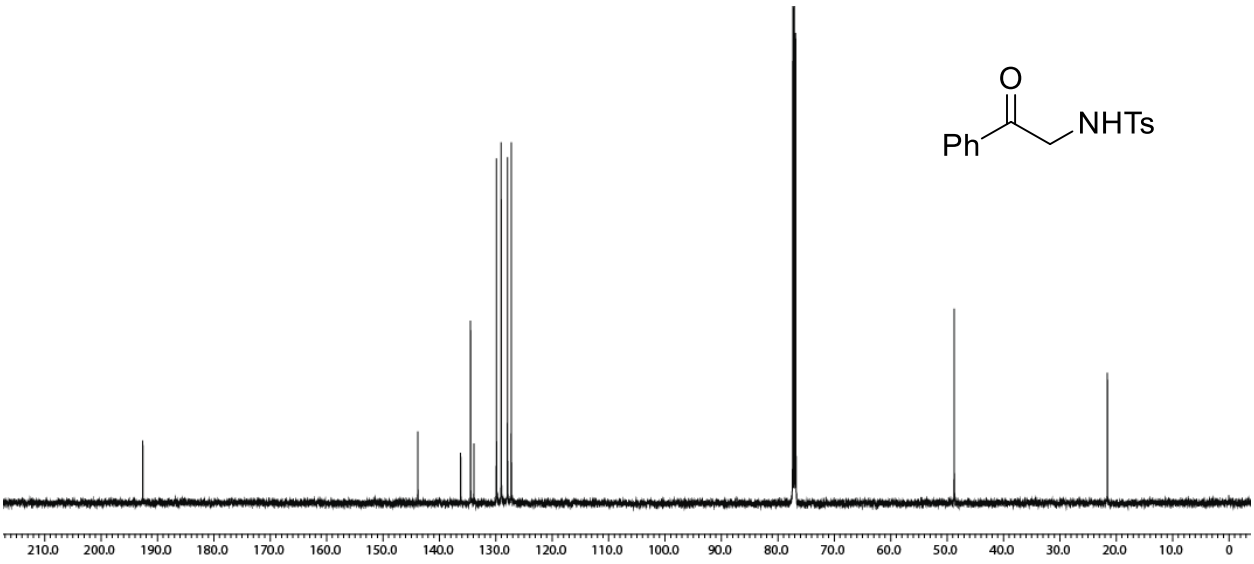

Figure 7: ^{13}C NMR spectrum of **4a** at 55 ˚C ($CDCl_3$, 125 MHz)

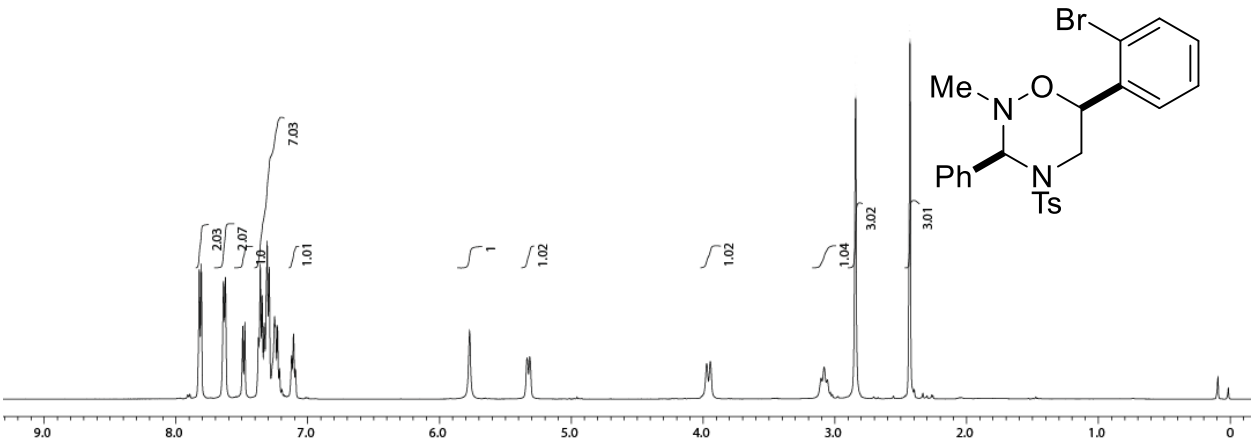

Figure 8: ^{1}H NMR spectrum of **3b** at 55 ˚C ($CDCl_3$, 500 MHz)

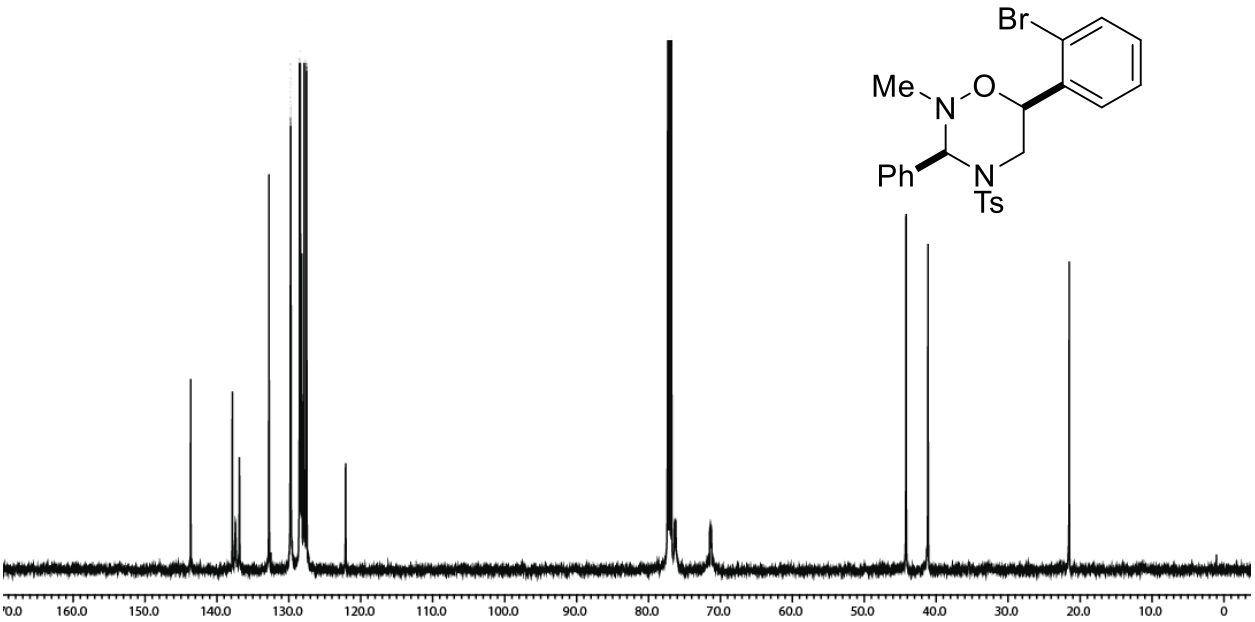

Figure 9: ^{13}C NMR spectrum of **3b** at 55 ˚C ($CDCl_3$, 125 MHz)

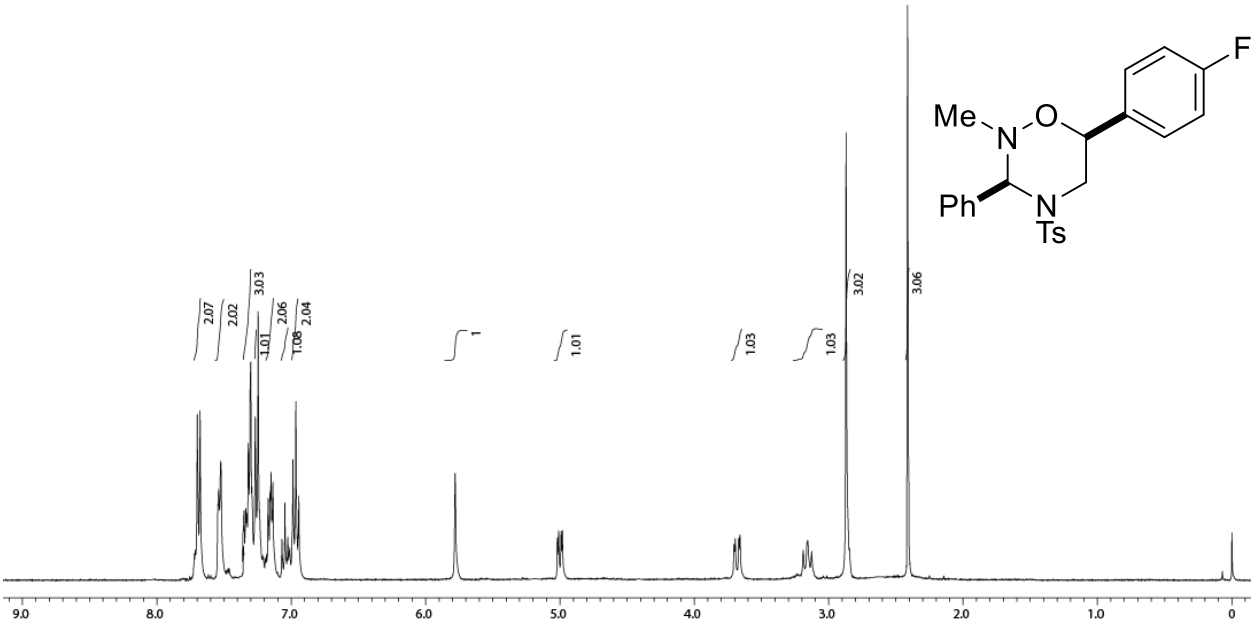

Figure 10: ^{1}H NMR spectrum of **3c** at 55 ˚C ($CDCl_3$, 500 MHz)

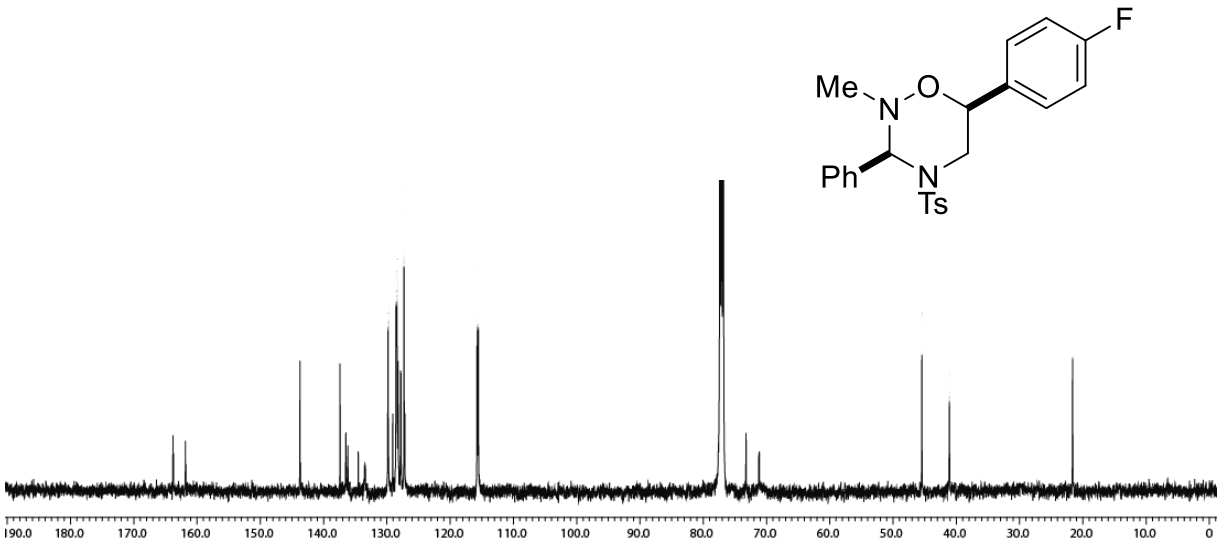

Figure 11: ^{13}C NMR spectrum of **3c** at 55 ˚C ($CDCl_3$, 125 MHz)

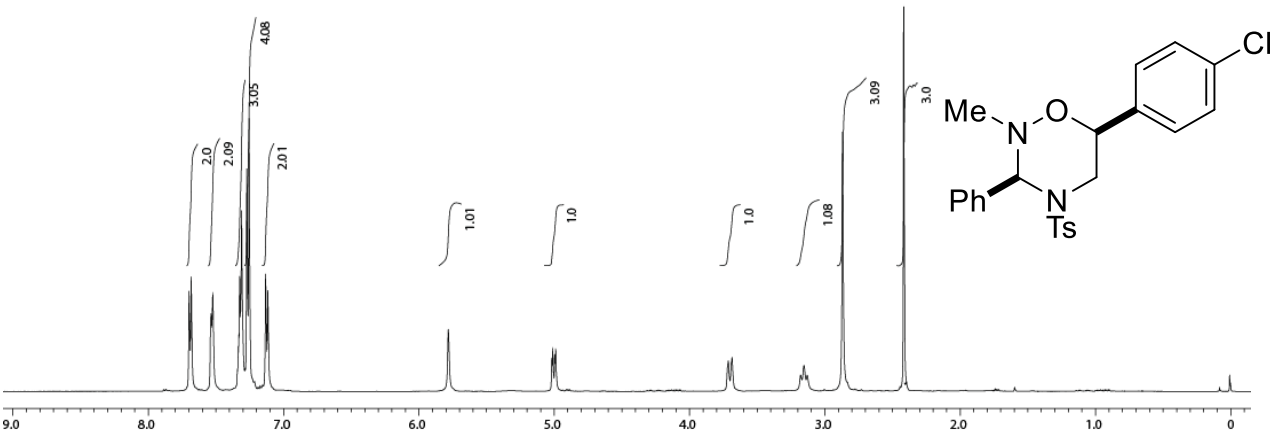

Figure 12: ^{1}H NMR spectrum of **3d** at 55 ˚C ($CDCl_3$, 500 MHz)

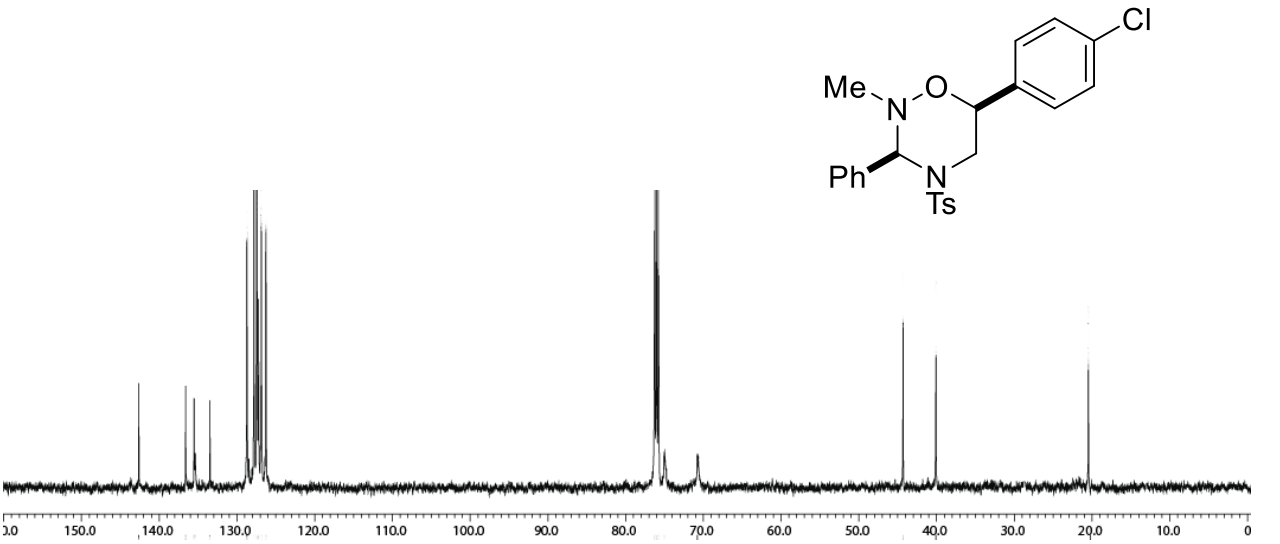

Figure 13: ^{13}C NMR spectrum of **3d** at 55 ˚C ($CDCl_3$, 125 MHz)

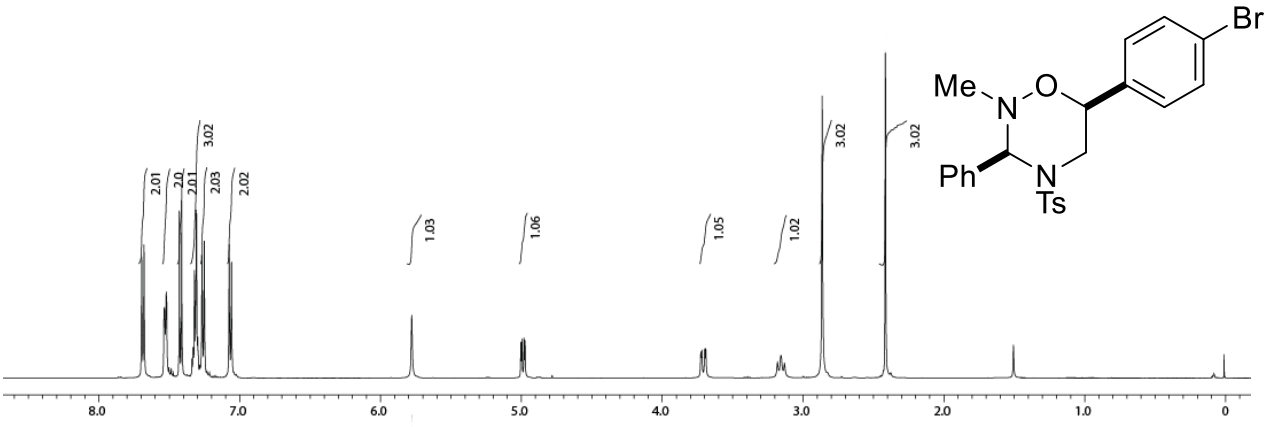

Figure 14: ^{1}H NMR spectrum of **3e** at 55 ˚C ($CDCl_3$, 500 MHz)

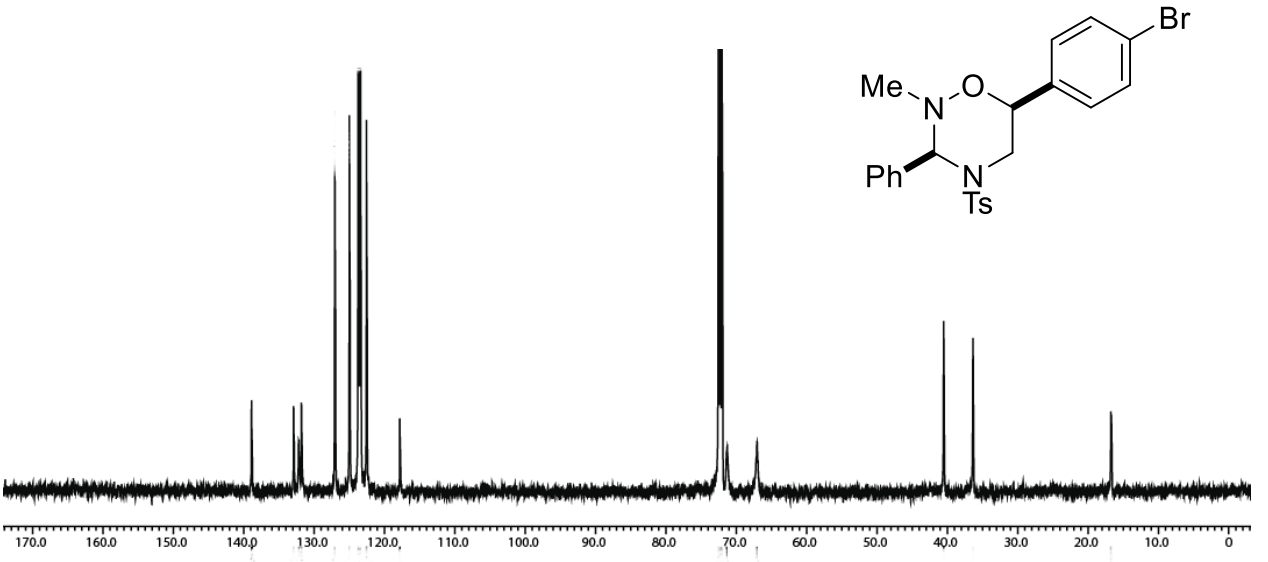

Figure 15: ^{13}C NMR spectrum of **3e** at 55 ˚C ($CDCl_3$, 125 MHz)

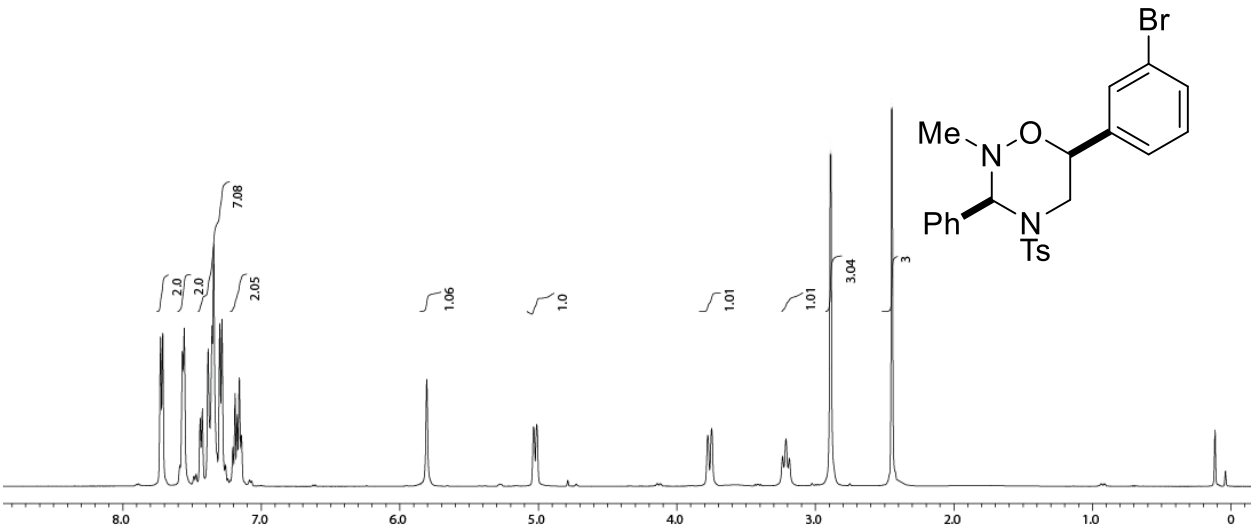

Figure 16: ^{1}H NMR spectrum of **3f** at 55 ˚C ($CDCl_3$, 500 MHz)

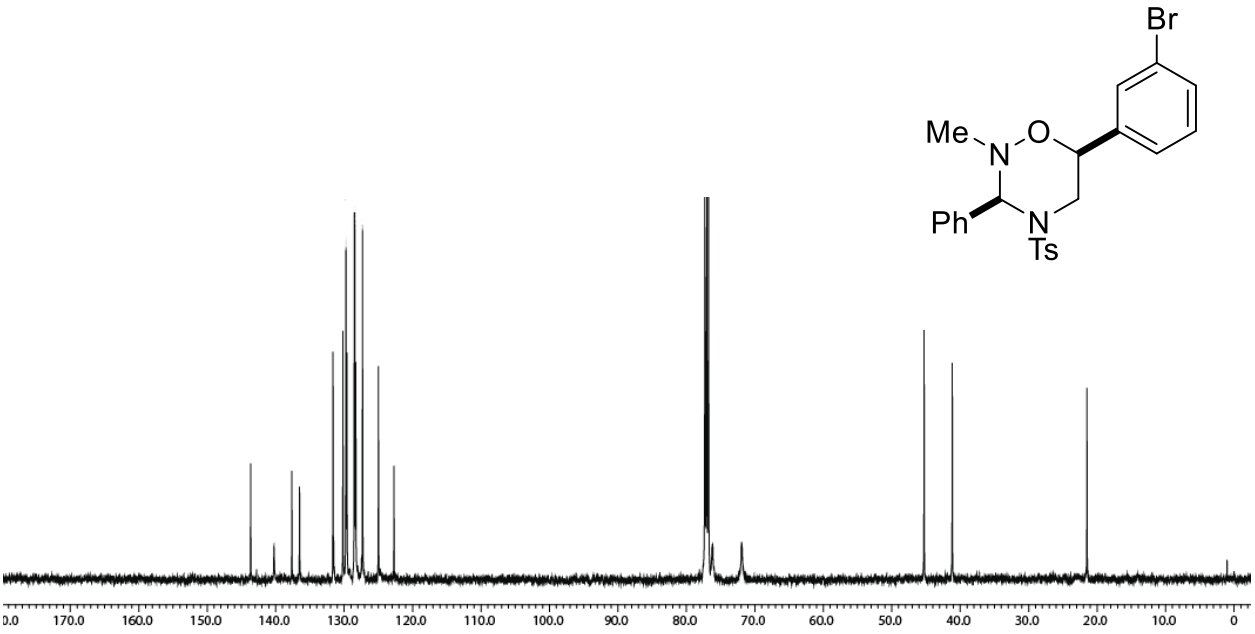

Figure 17: ^{13}C NMR spectrum of **3f** at 55 ˚C ($CDCl_3$, 125 MHz)

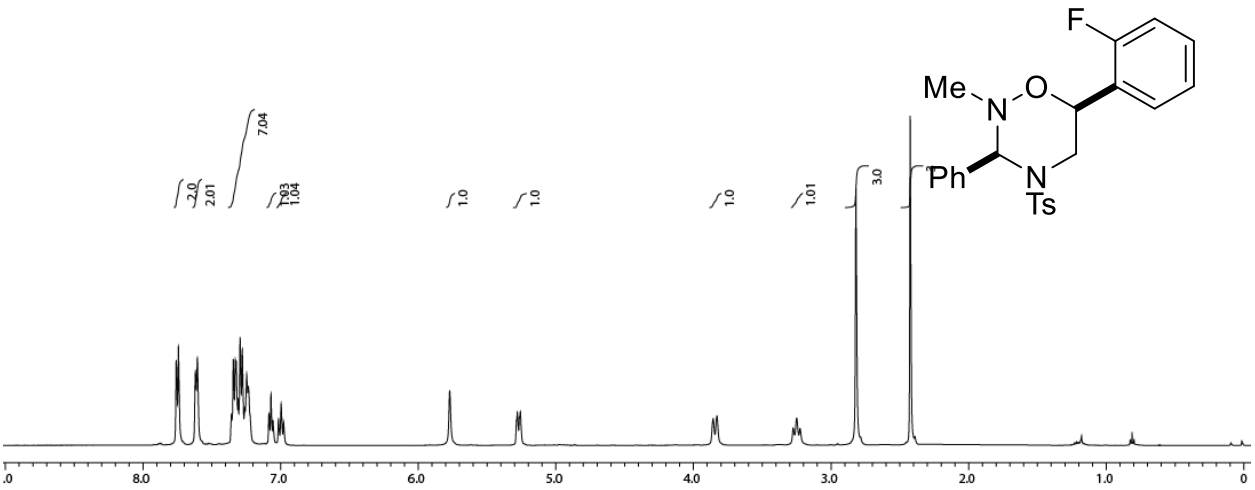

Figure 18: ^{1}H NMR spectrum of **3g** at 55 ˚C ($CDCl_3$, 500 MHz)

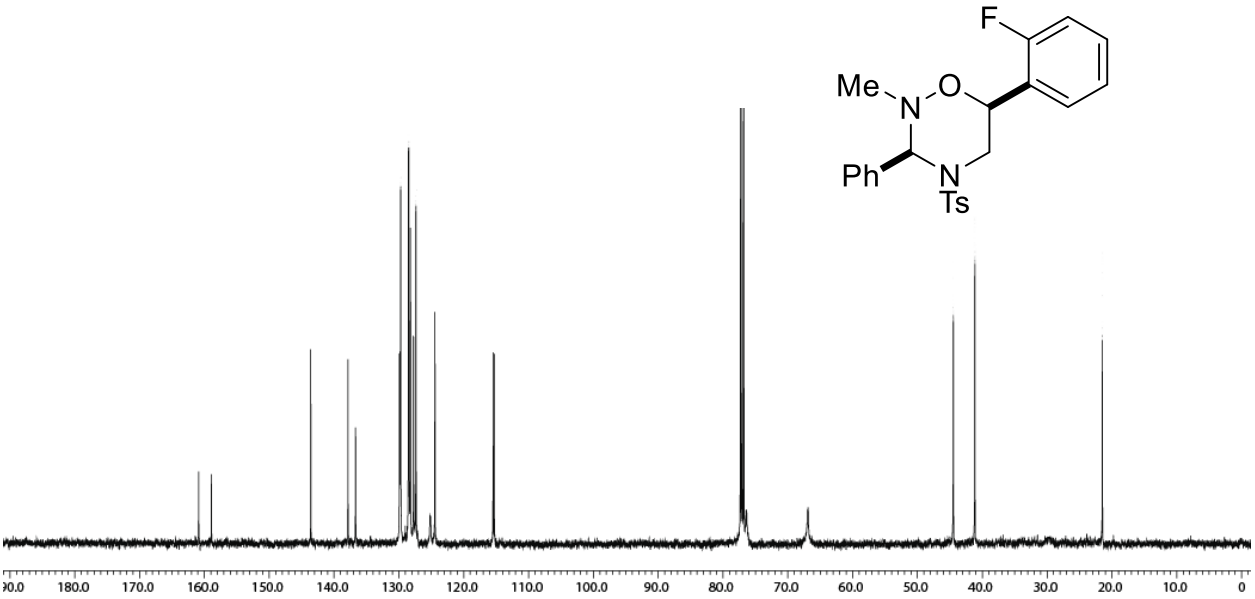

Figure 19: ^{13}C NMR spectrum of **3g** at 55 ˚C ($CDCl_3$, 125 MHz)

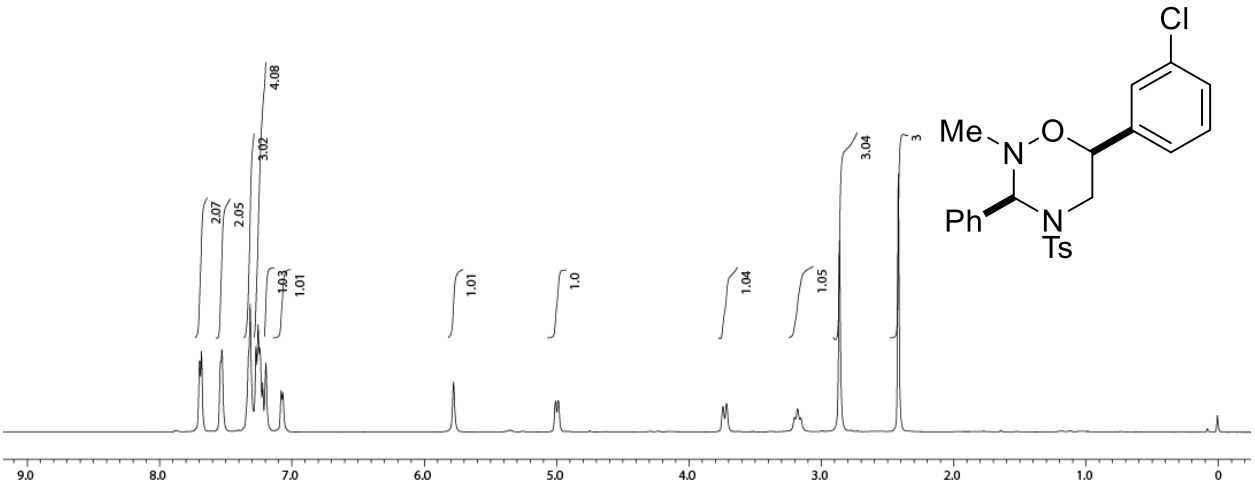

Figure 20: ^{1}H NMR spectrum of **3h** at 55 ˚C ($CDCl_3$, 500 MHz)

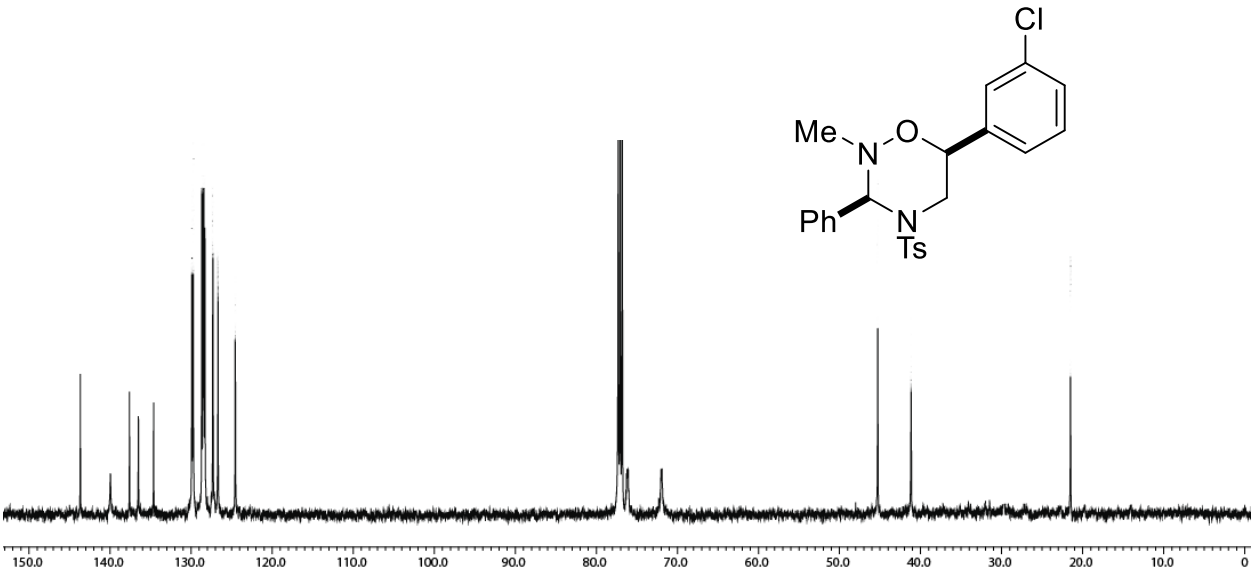

Figure 21: ^{13}C NMR spectrum of **3h** at 55 ˚C ($CDCl_3$, 125 MHz)

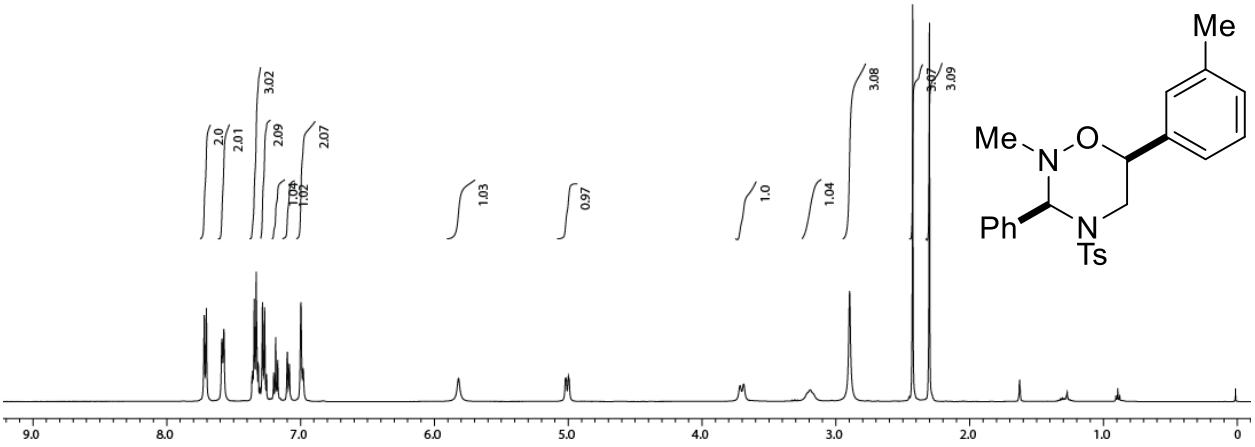

Figure 22: ^{1}H NMR spectrum of **3i** at 55 ˚C ($CDCl_3$, 500 MHz

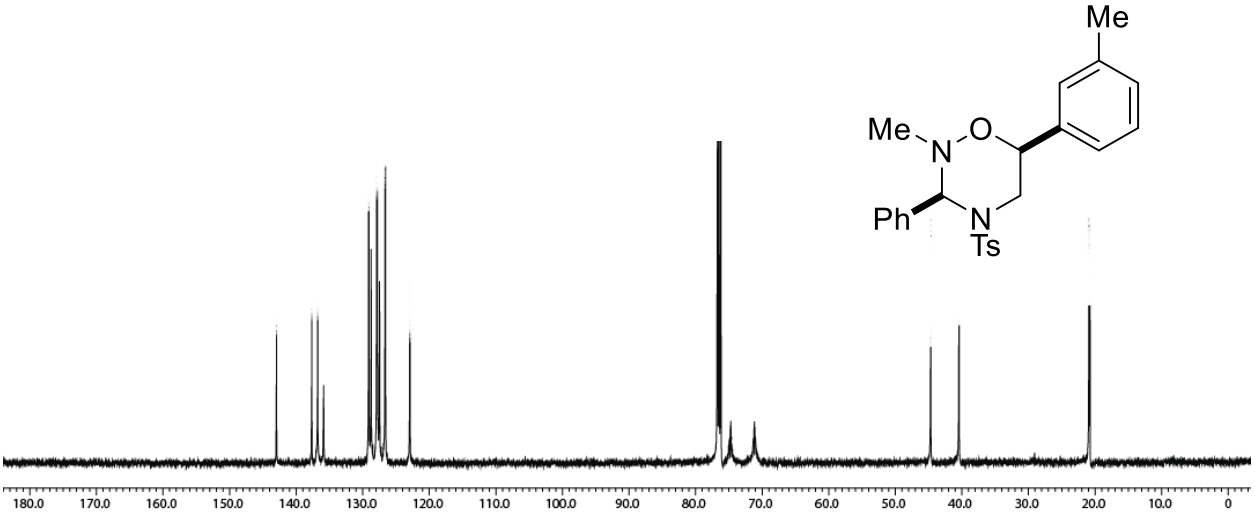

Figure 23: ^{13}C NMR spectrum of **3i** at 55 ˚C ($CDCl_3$, 125 MHz)

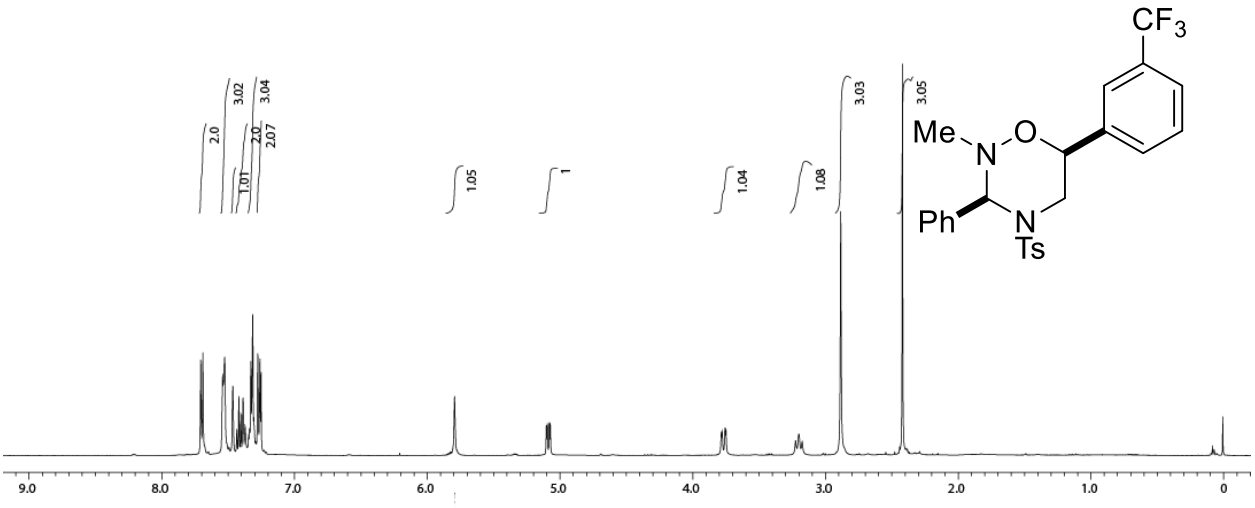

Figure 24: ^{1}H NMR spectrum of **3j** at 55 ˚C ($CDCl_3$, 500 MHz)

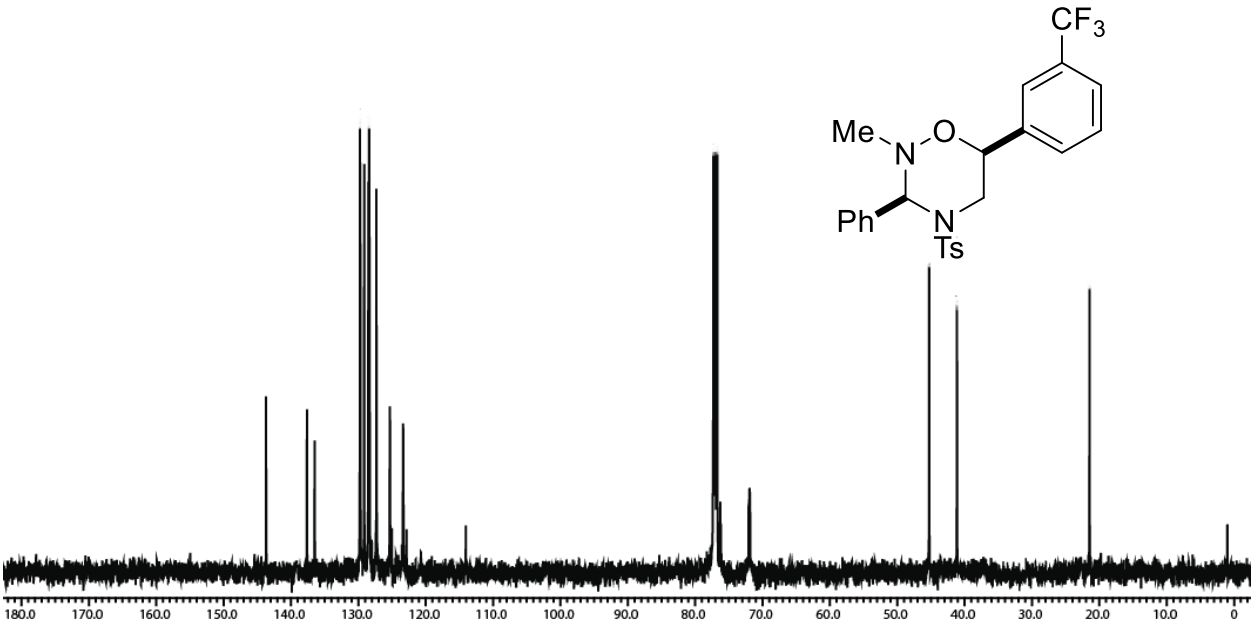

Figure 25: ^{13}C NMR spectrum of **3j** at 55 ˚C ($CDCl_3$, 125 MHz)

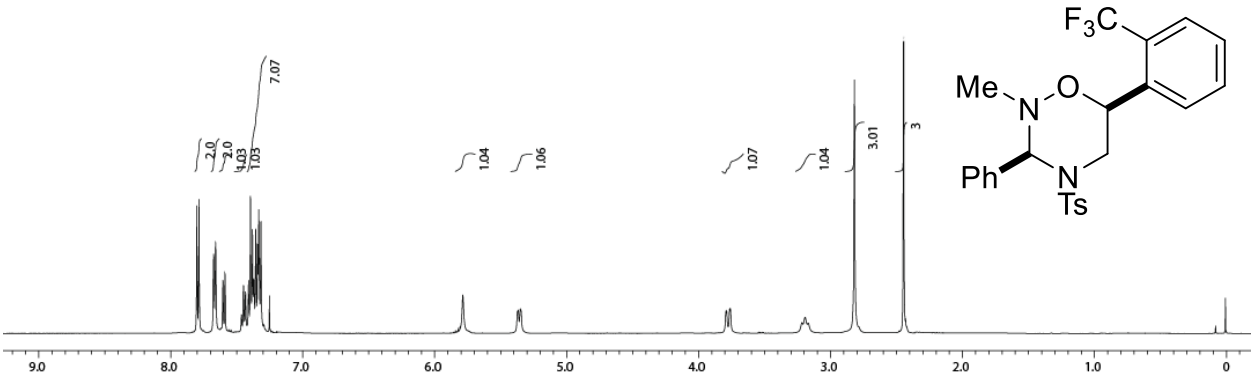

Figure 26: ^{1}H NMR spectrum of **3k** at 55 ˚C ($CDCl_3$, 500 MHz)

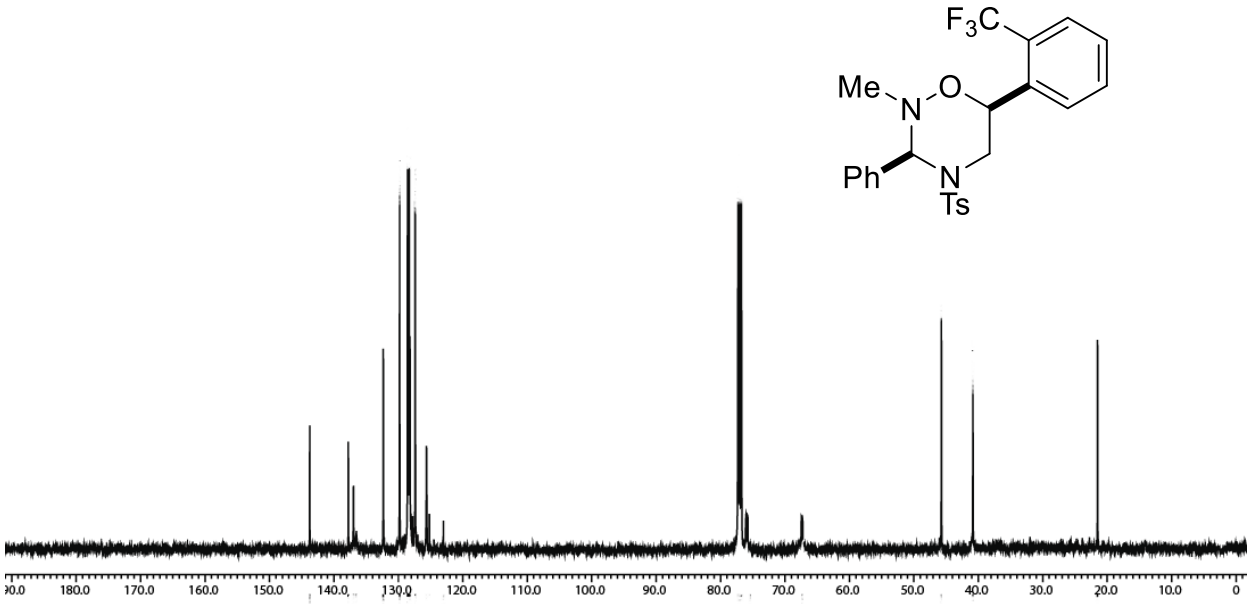

Figure 27: ^{13}C NMR spectrum of **3k** at 55 ˚C ($CDCl_3$, 125 MHz)

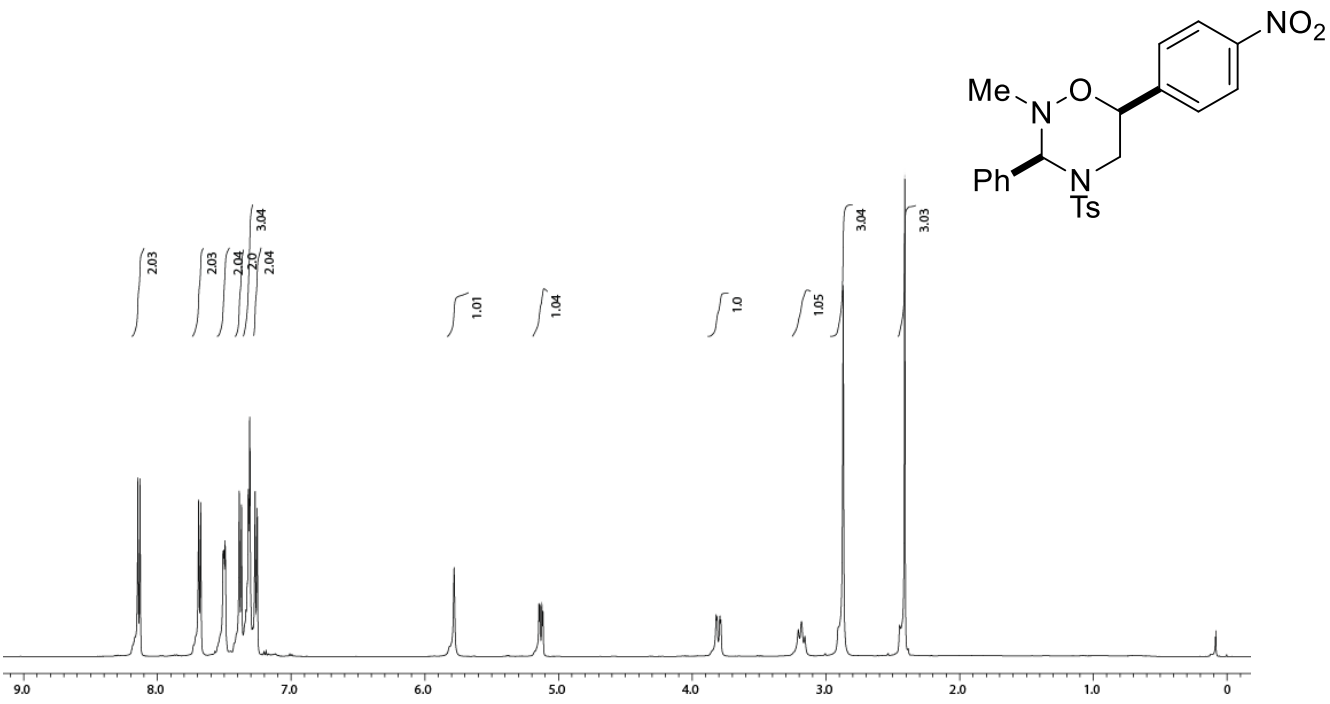

Figure 28: ^{1}H NMR spectrum of **3l** at 55 ˚C ($CDCl_3$, 500 MHz)

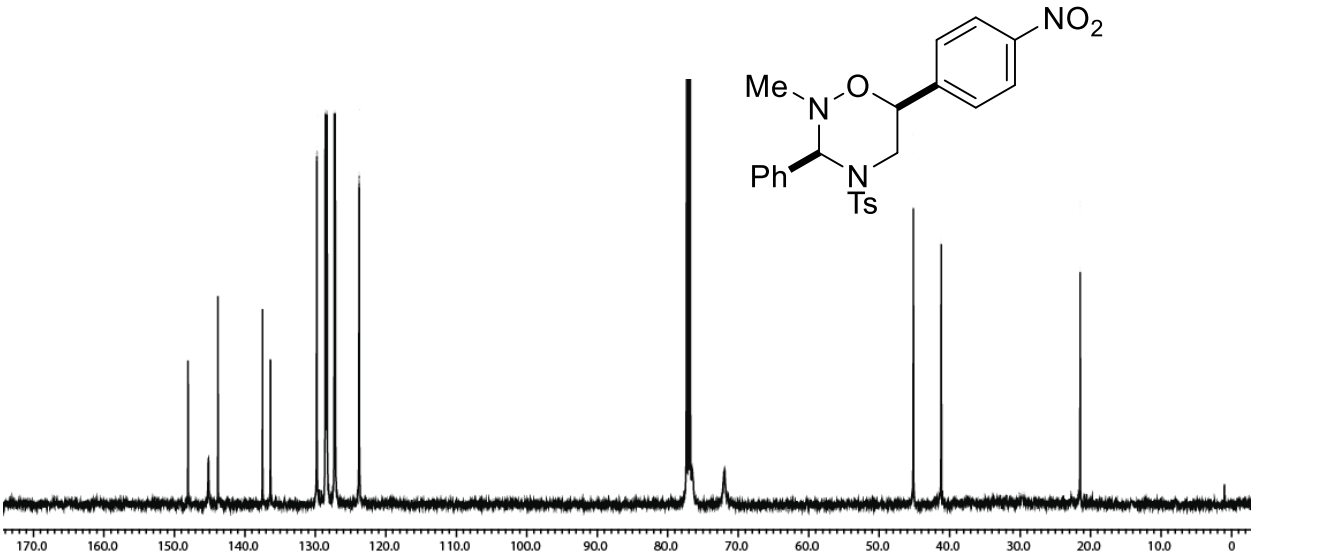

Figure 29: ^{13}C NMR spectrum of **3l** at 55 ˚C ($CDCl_3$, 125 MHz)

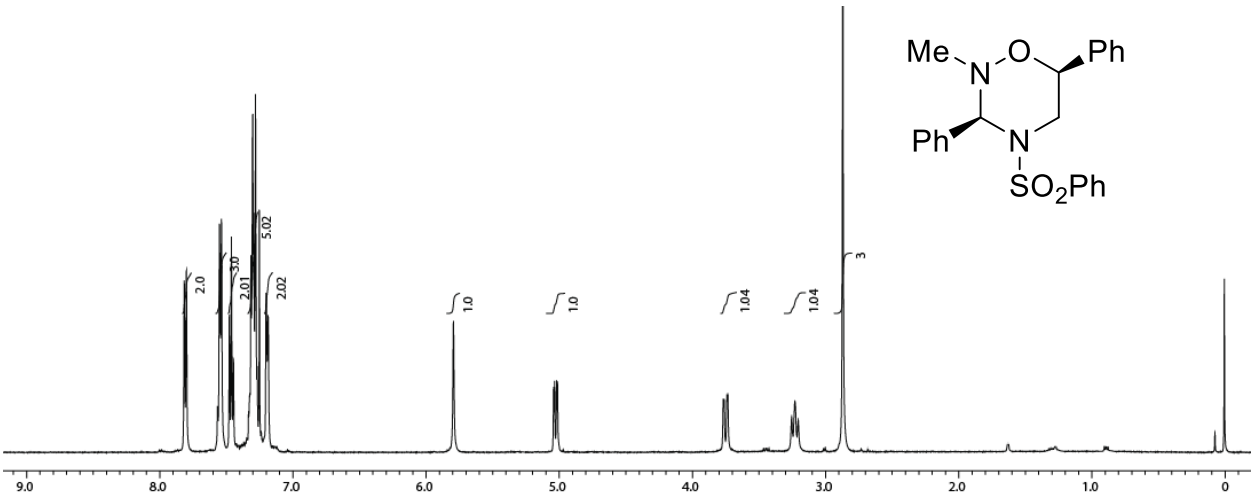

Figure 30. ^{1}H NMR spectrum of **3m** at 55 ˚C ($CDCl_3$, 500 MHz)

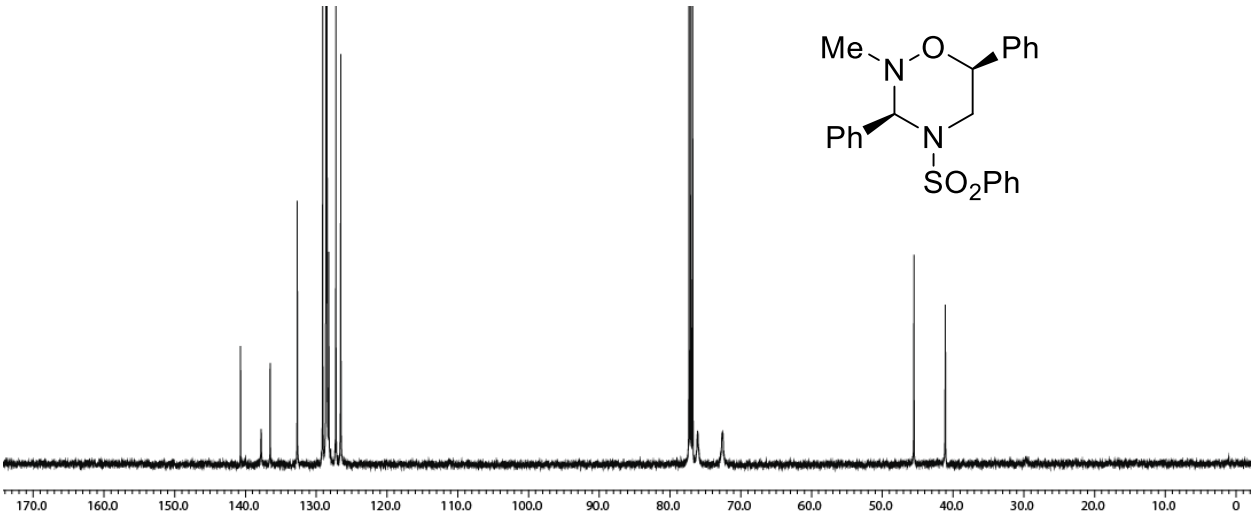

Figure 31: ^{13}C NMR spectrum of **3m** at 55 ˚C ($CDCl_3$, 125 MHz)

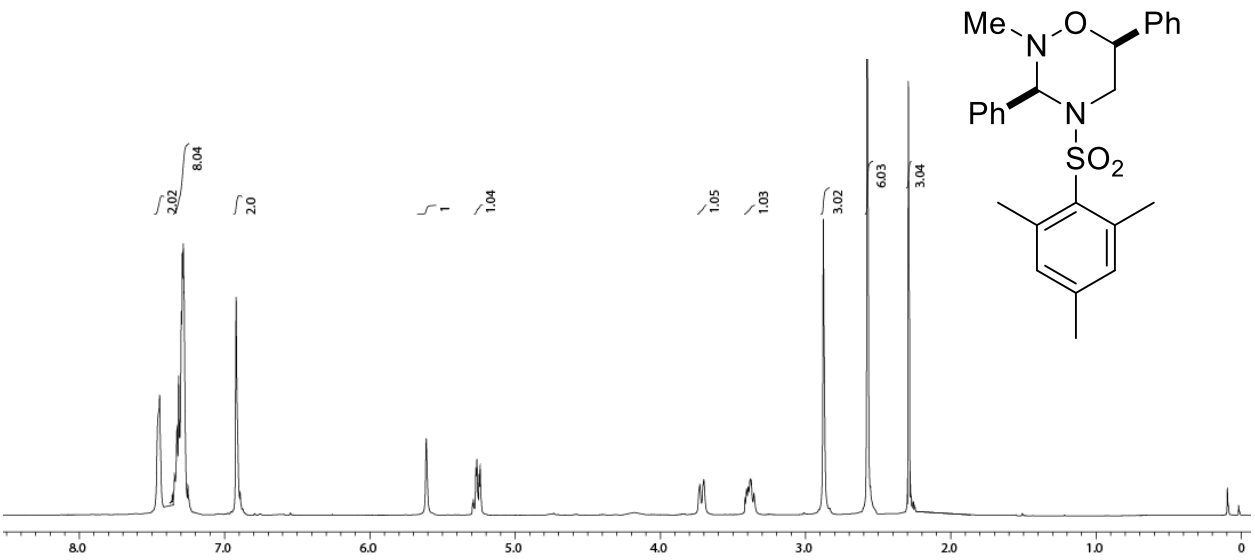

Figure 32. ^{1}H NMR spectrum of **3n** at 55 ˚C ($CDCl_3$, 500 MHz)

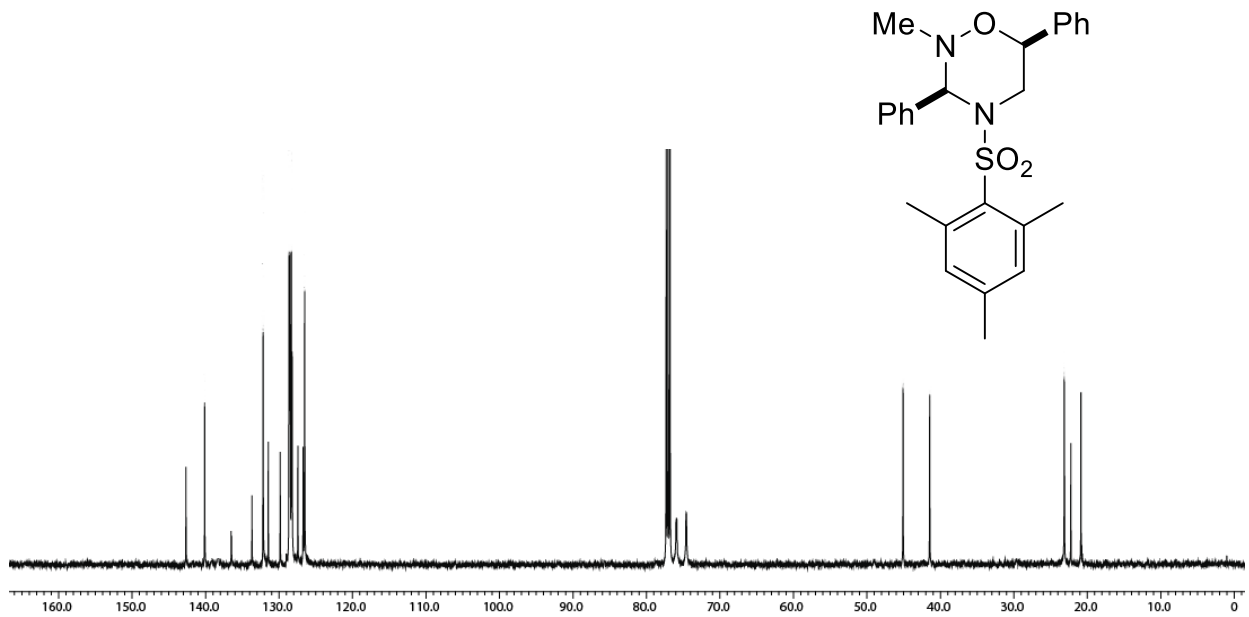

Figure 33: ^{13}C NMR spectrum of **3n** at 55 ˚C ($CDCl_3$, 125 MHz)

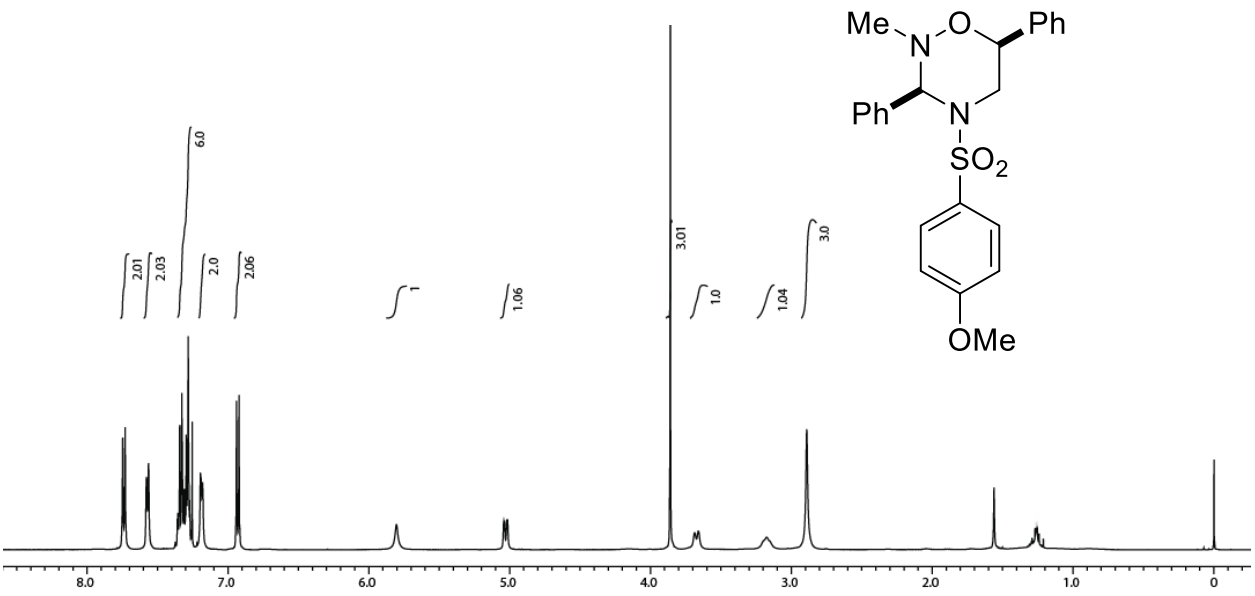

Figure 34. ^{1}H NMR spectrum of **3o** at 55 ˚C ($CDCl_3$, 500 MHz)

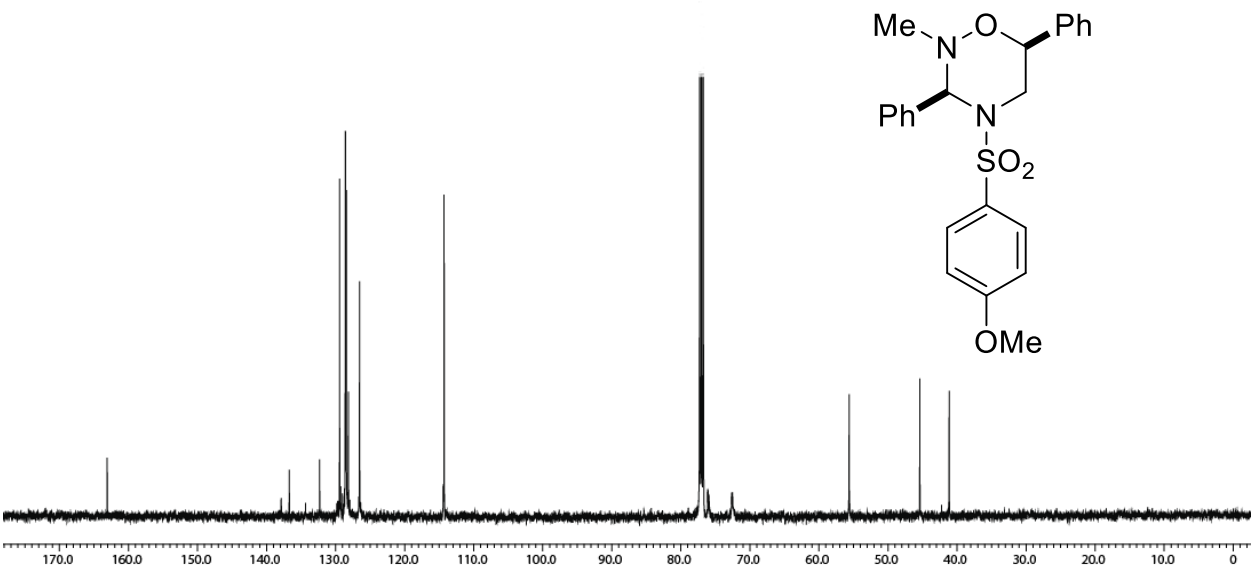

Figure 35: ^{13}C NMR spectrum of **3o** at 55 ˚C ($CDCl_3$, 125 MHz)

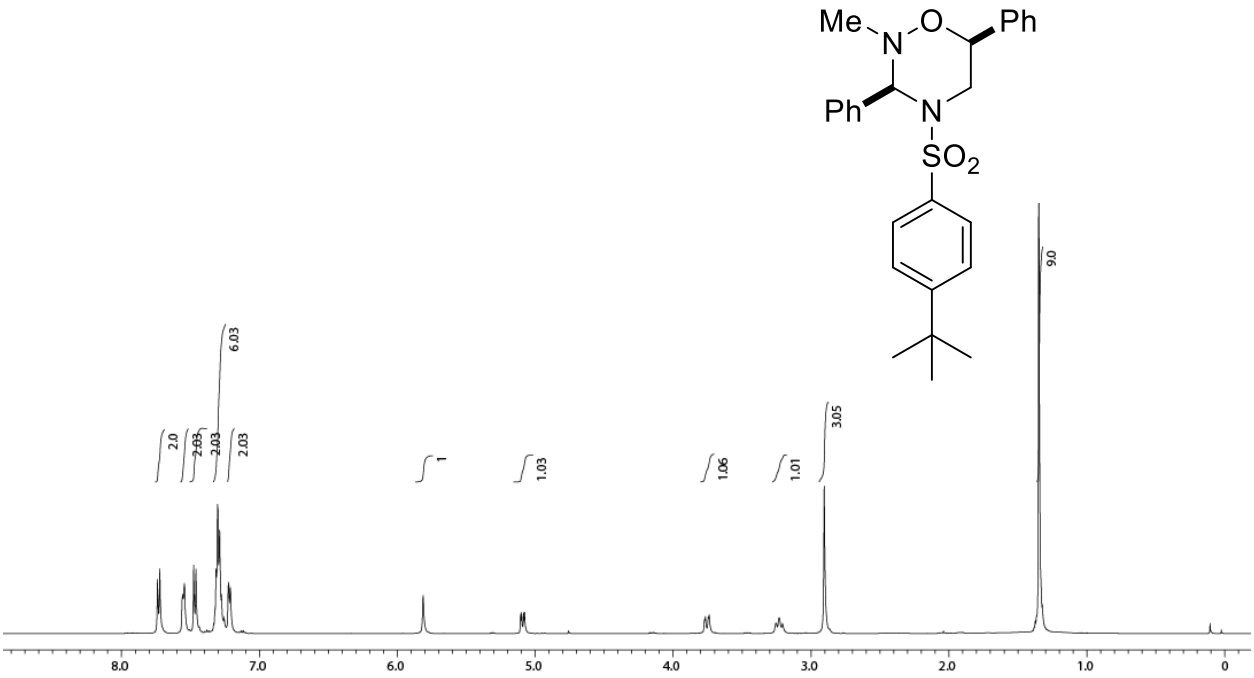

Figure 36. ^{1}H NMR spectrum of **3p** at 55 ˚C ($CDCl_3$, 500 MHz)

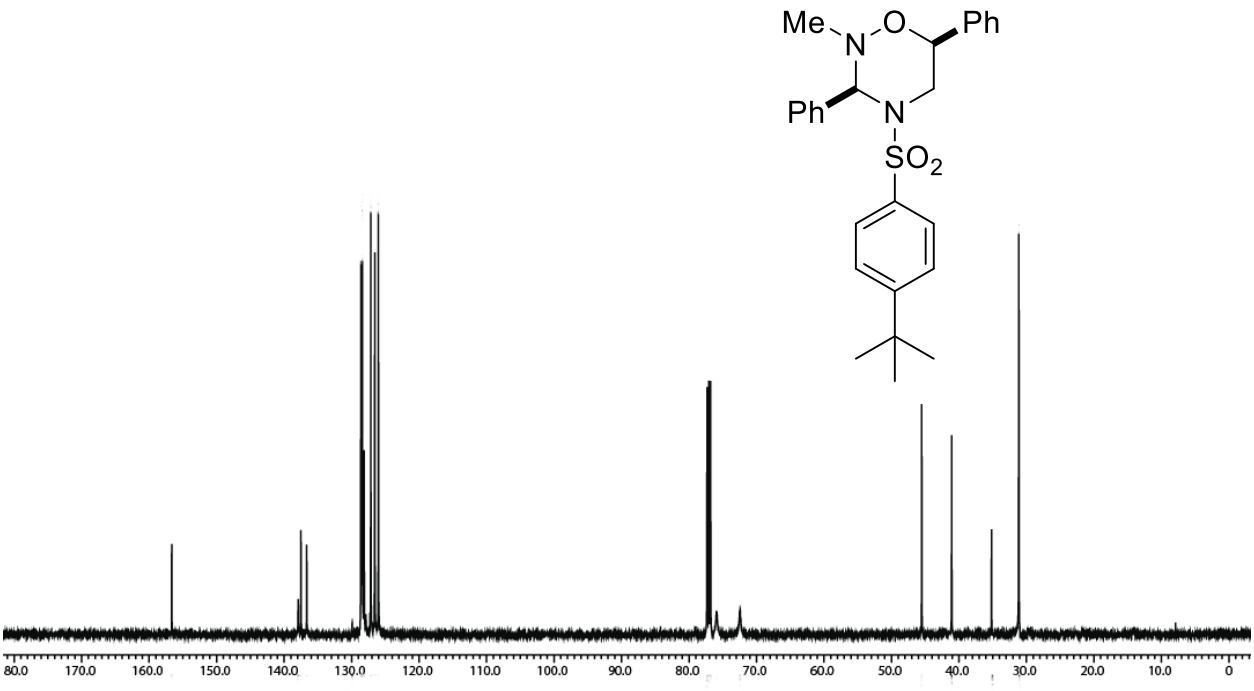

Figure 37: ^{13}C NMR spectrum of **3p** at 55 ˚C ($CDCl_3$, 125 MHz)

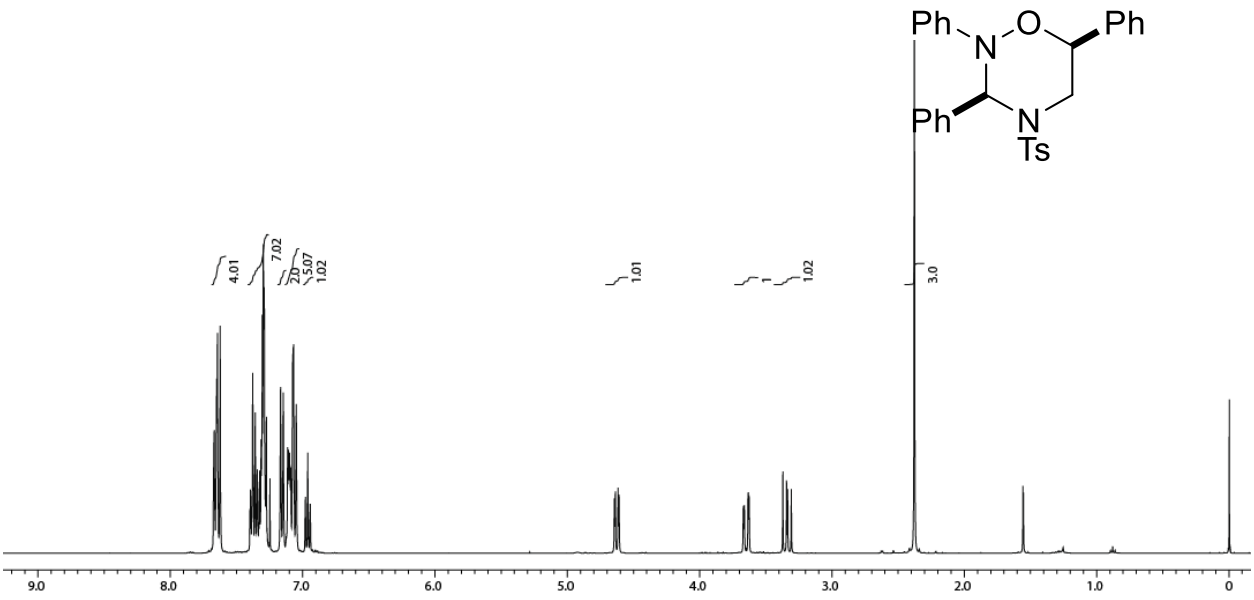

Figure 38. ^{1}H NMR spectrum of **3pa** at 55 ˚C ($CDCl_3$, 500 MHz)

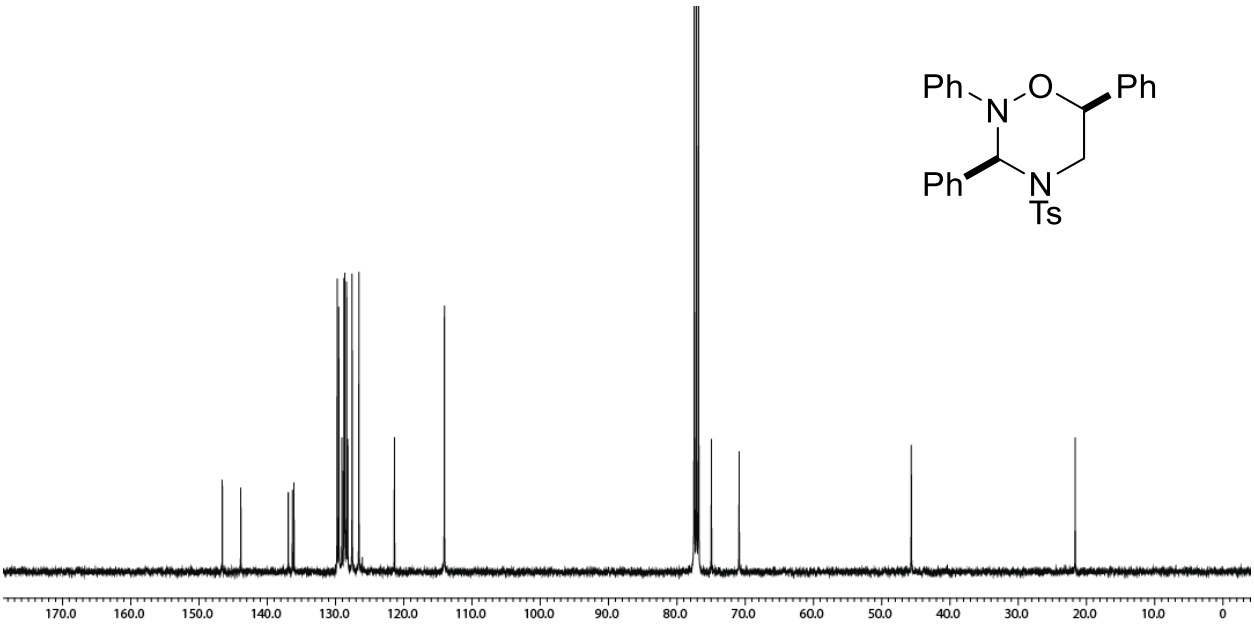

Figure 39: ^{13}C NMR spectrum of **3pa** at 55 ˚C ($CDCl_3$, 125 MHz)

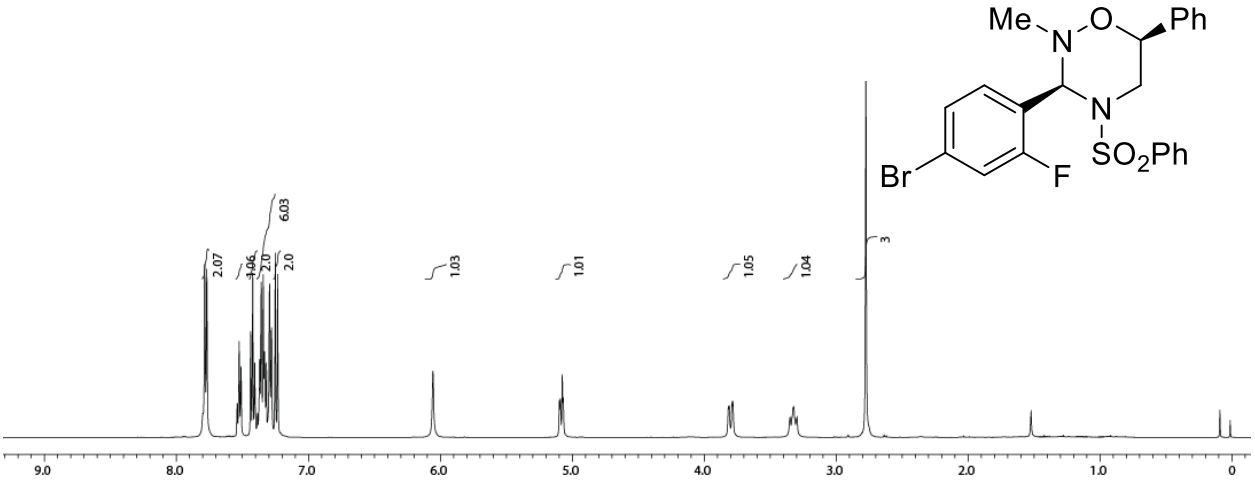

Figure 40. ^{1}H NMR spectrum of **3q** at 55 ˚C ($CDCl_3$, 500 MHz)

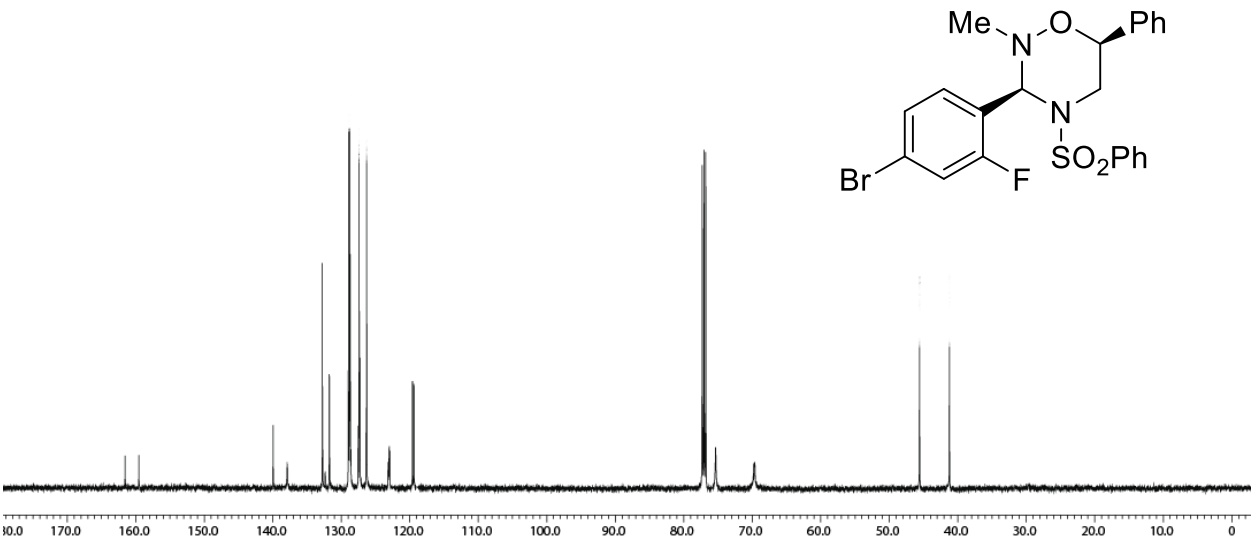

Figure 41. ^{13}C NMR spectrum of **3q** at 55 ˚C ($CDCl_3$, 125 MHz)

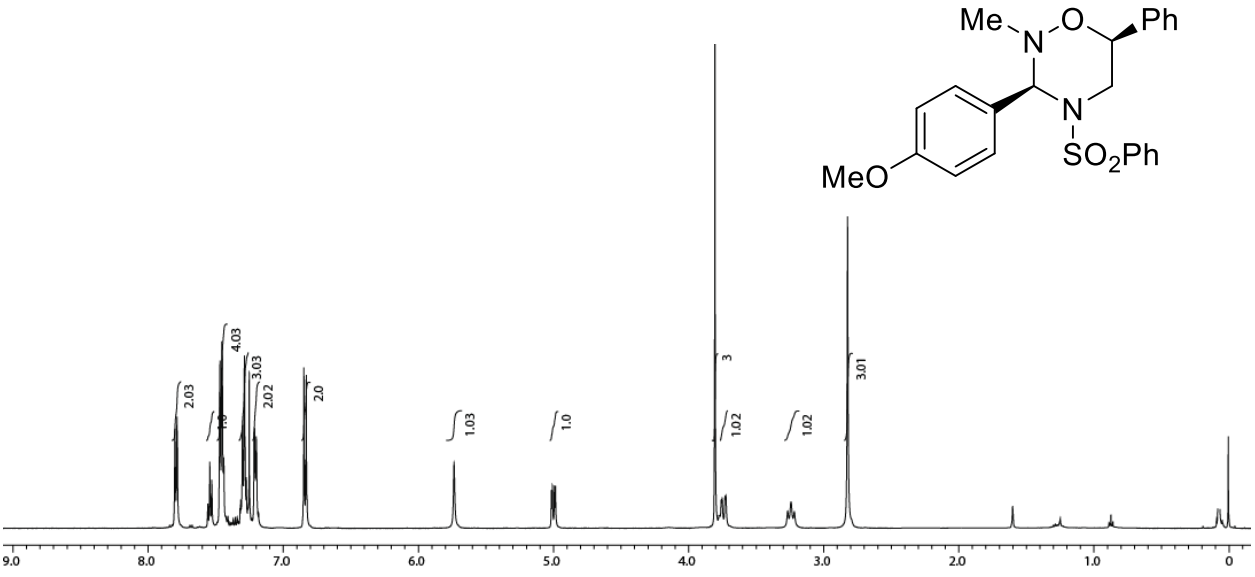

Figure 42. ^{1}H NMR spectrum of **3r** at 55 ˚C ($CDCl_3$, 500 MHz)

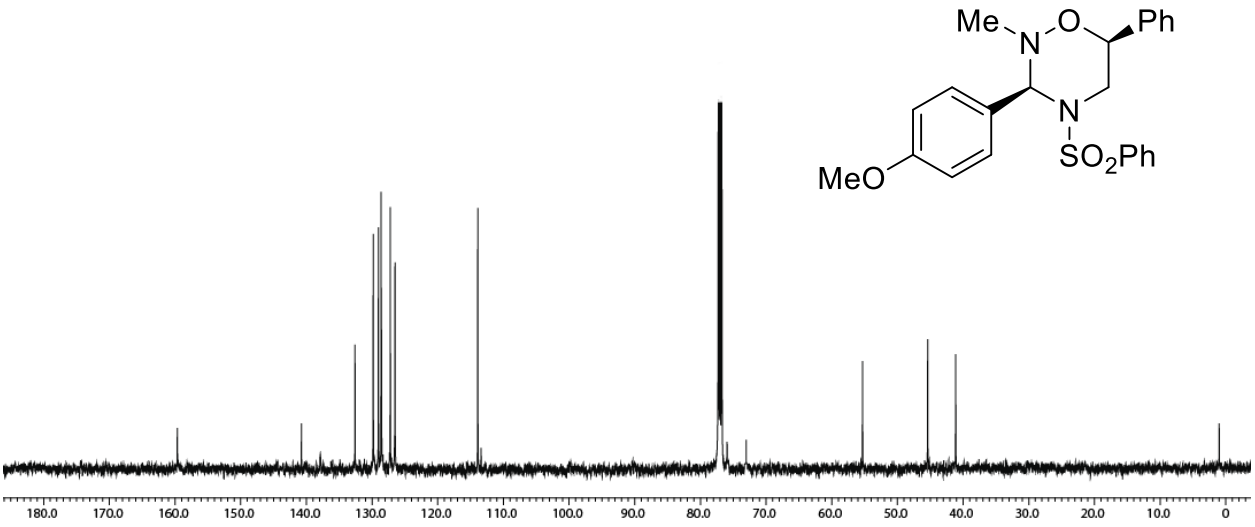

Figure 43. ^{13}C NMR spectrum of **3r** at 55 ˚C ($CDCl_3$, 125 MHz)

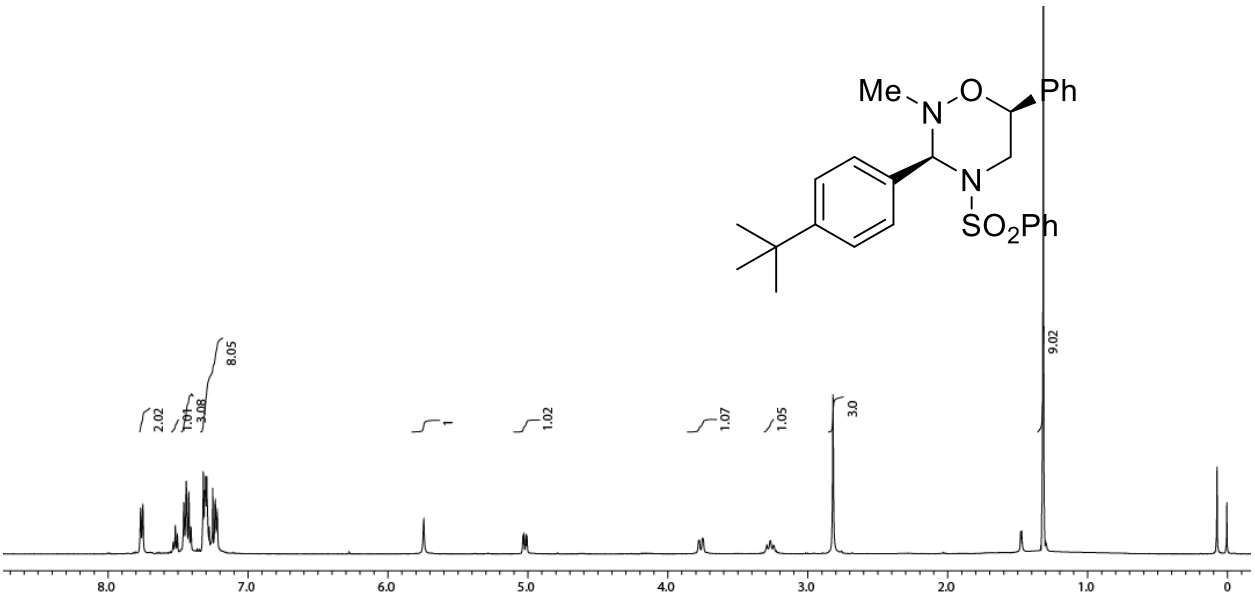

Figure 44. ^{1}H NMR spectrum of **3s** at 55 ˚C ($CDCl_3$, 500 MHz)

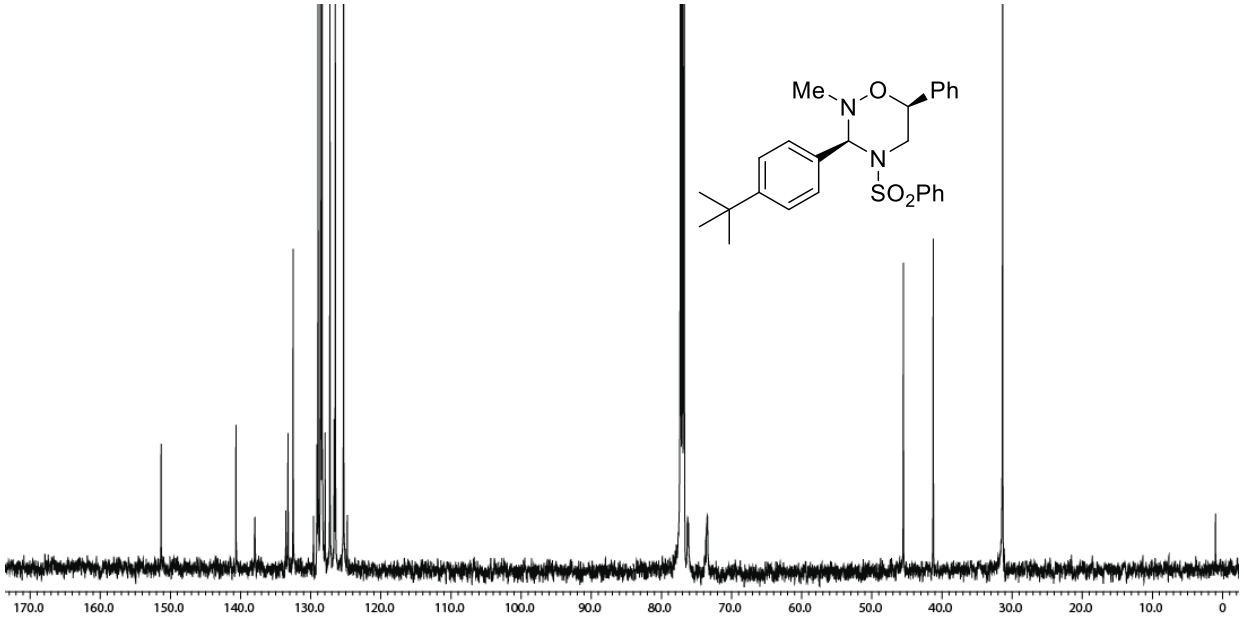

Figure 45. ^{13}C NMR spectrum of **3s** at 55 ˚C ($CDCl_3$, 125 MHz)

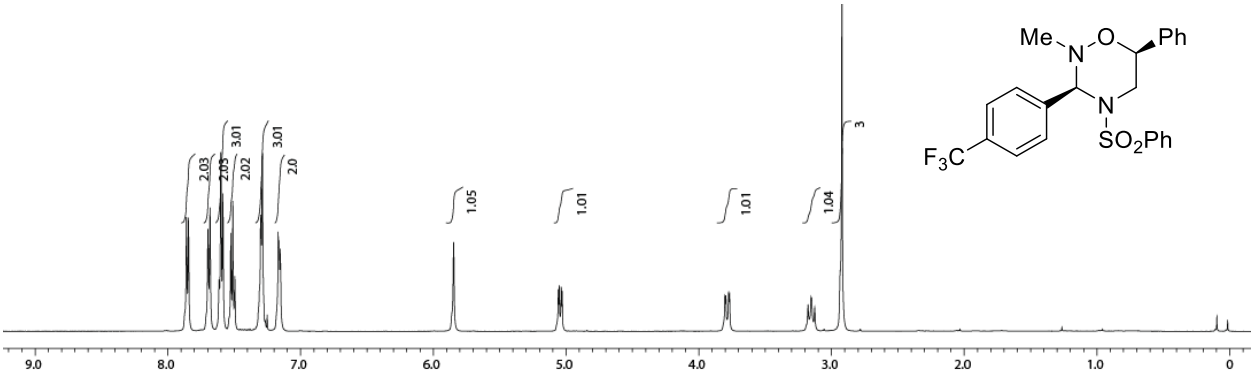

Figure 46. ^{1}H NMR spectrum of **3t** at 55 ˚C ($CDCl_3$, 500 MHz)

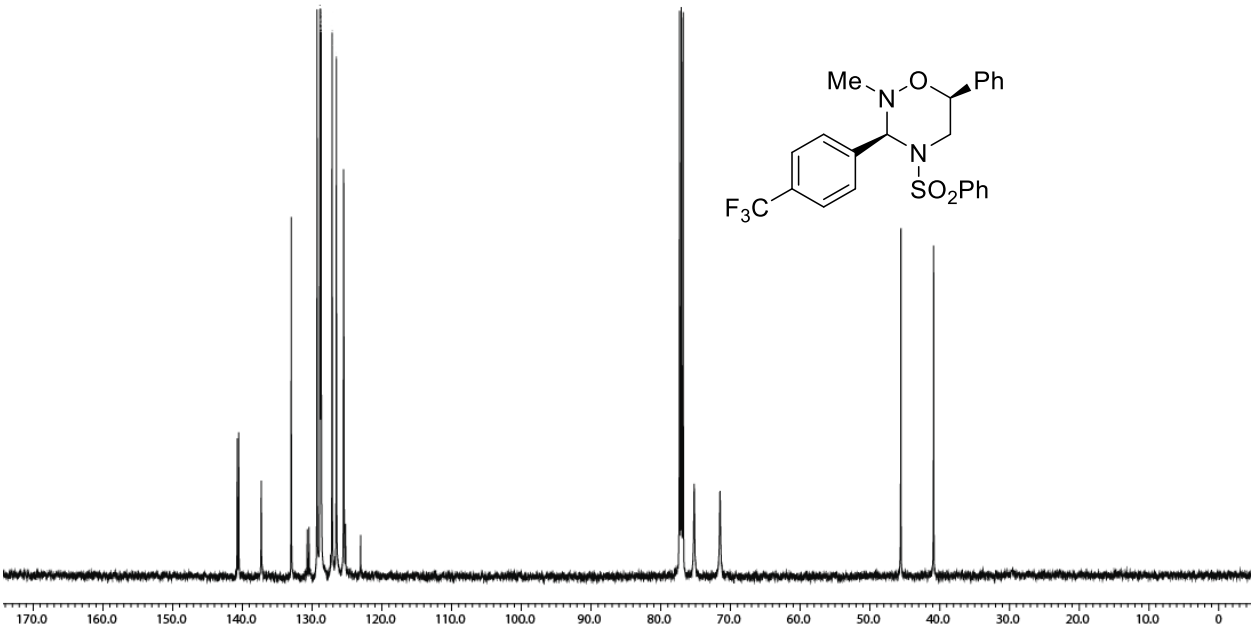

Figure 47. ^{13}C NMR spectrum of **3t** at 55 ˚C ($CDCl_3$, 125 MHz)

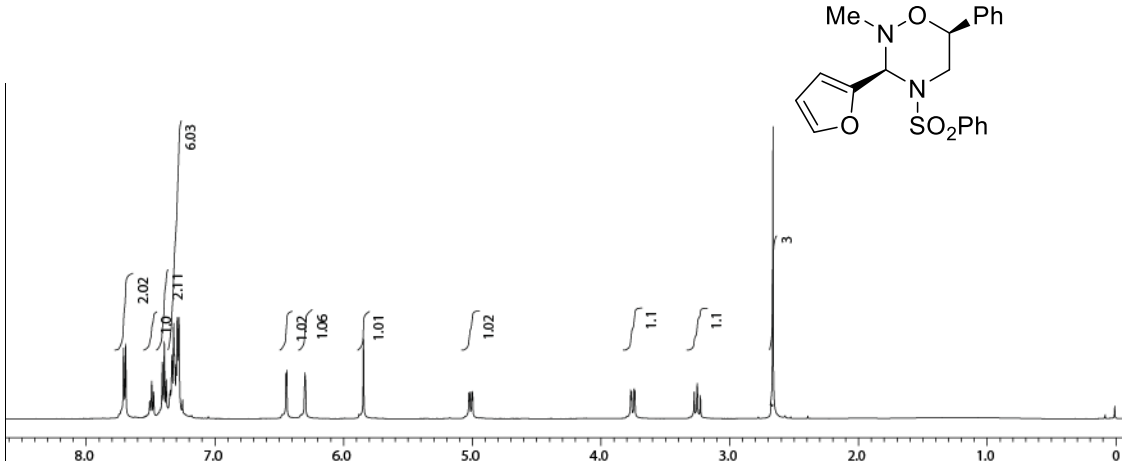

Figure 48. ^{1}H NMR spectrum of **3u** at 55 ˚C ($CDCl_3$, 500 MHz)

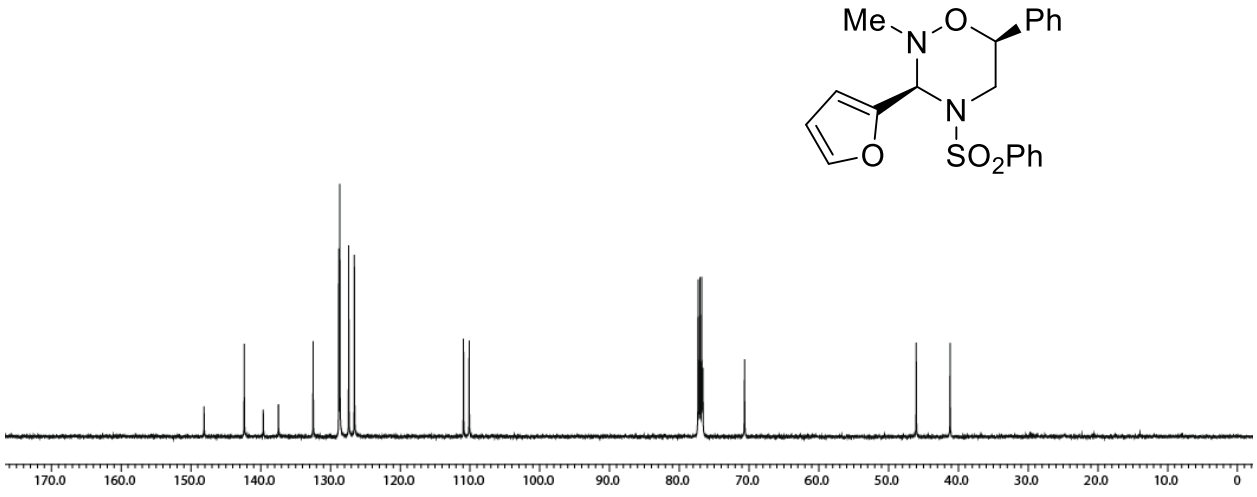

Figure 49. ^{13}C NMR spectrum of **3u** at 55 ˚C ($CDCl_3$, 125 MHz)

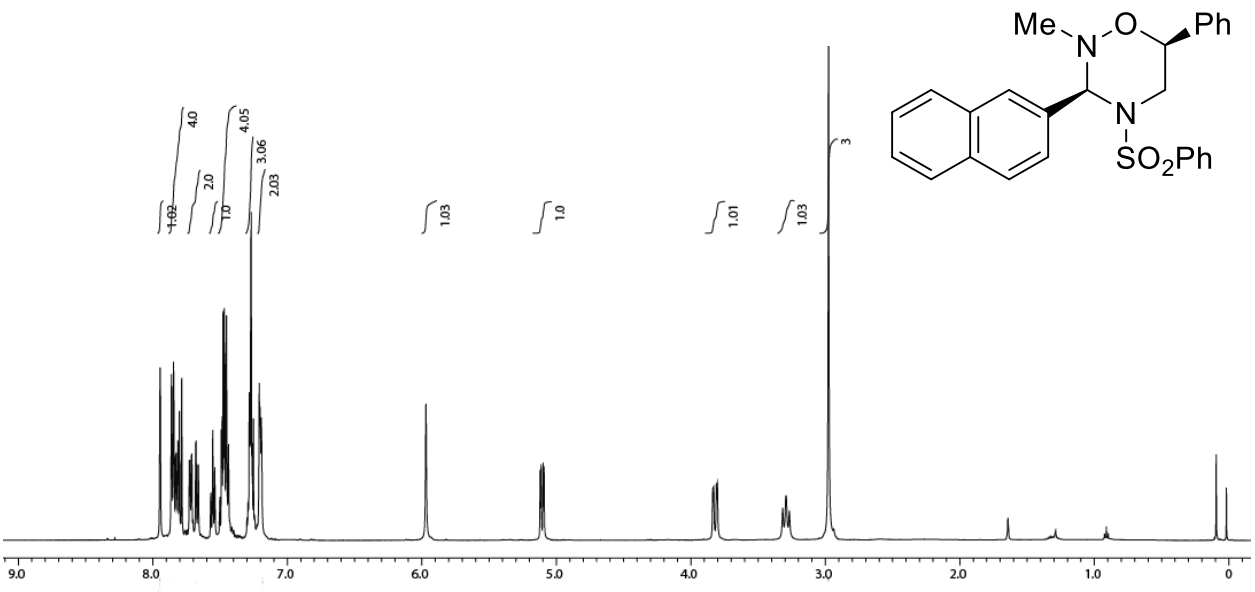

Figure 50. ^{1}H NMR spectrum of **3v** at 55 ˚C ($CDCl_3$, 500 MHz)

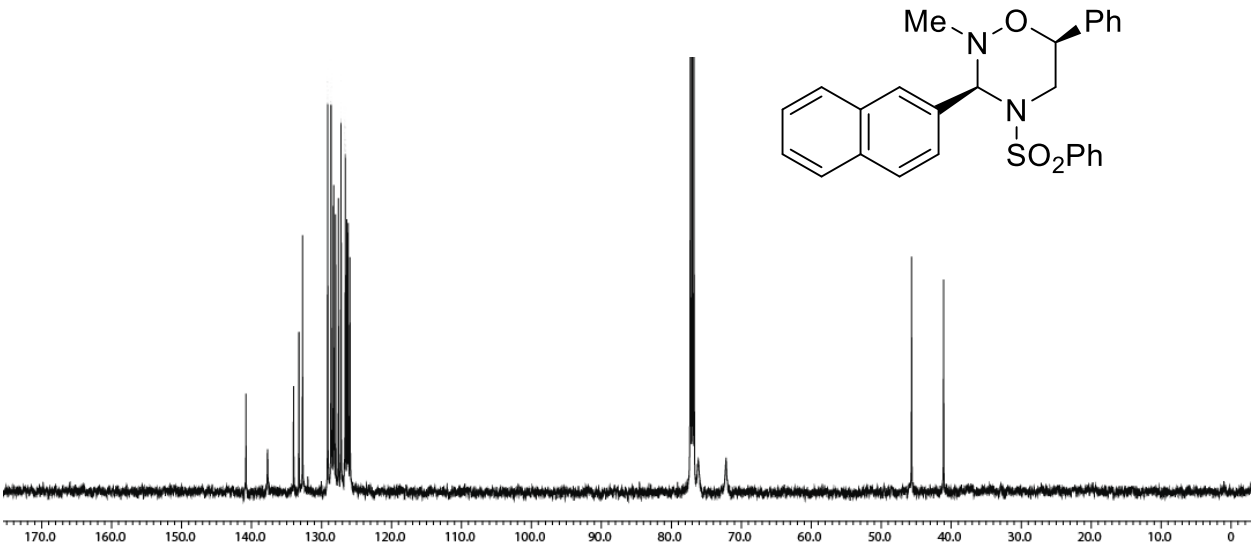

Figure 51. ^{13}C NMR spectrum of **3v** at 55 ˚C ($CDCl_3$, 125 MHz)

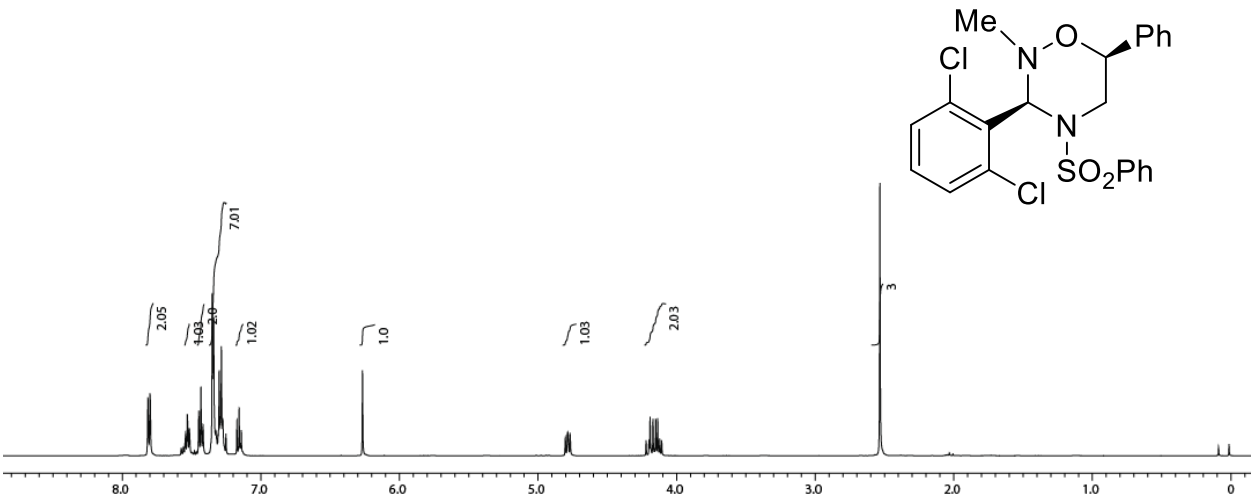

Figure 52. ^{1}H NMR spectrum of **3w** at 55 ˚C ($CDCl_3$, 500 MHz)

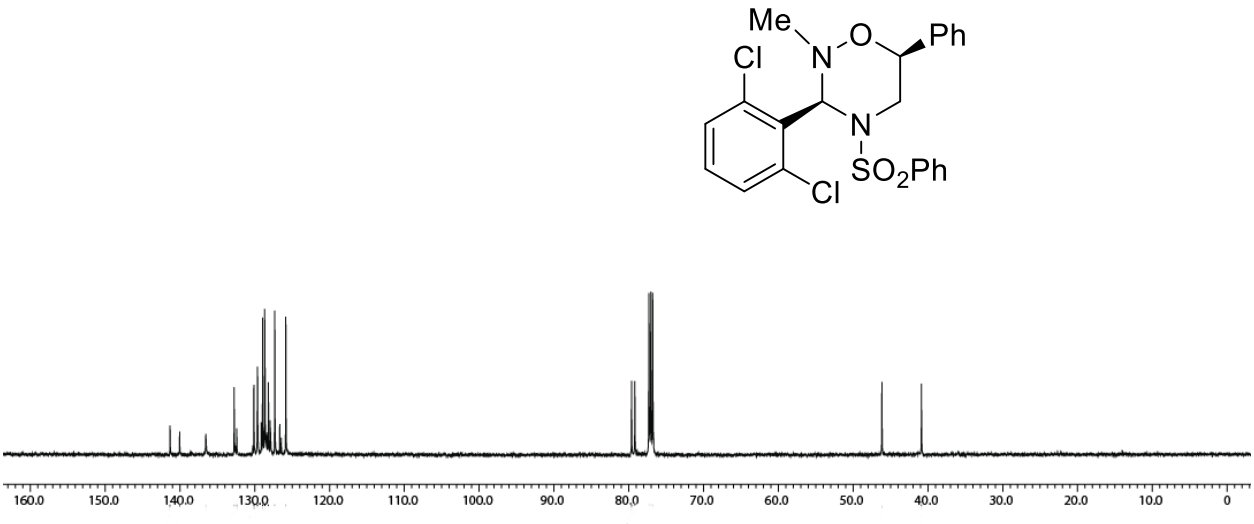

Figure 53. ^{13}C NMR spectrum of **3w** at 55 ˚C ($CDCl_3$, 125 MHz)

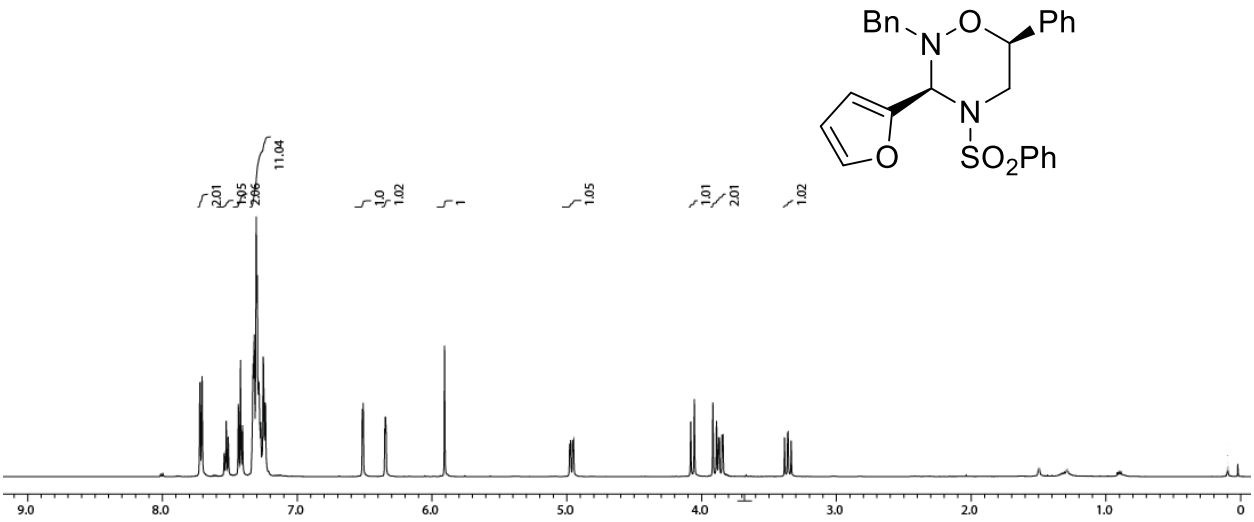

Figure 54. ^{1}H NMR spectrum of **3x** at 55 ˚C ($CDCl_3$, 500 MHz)

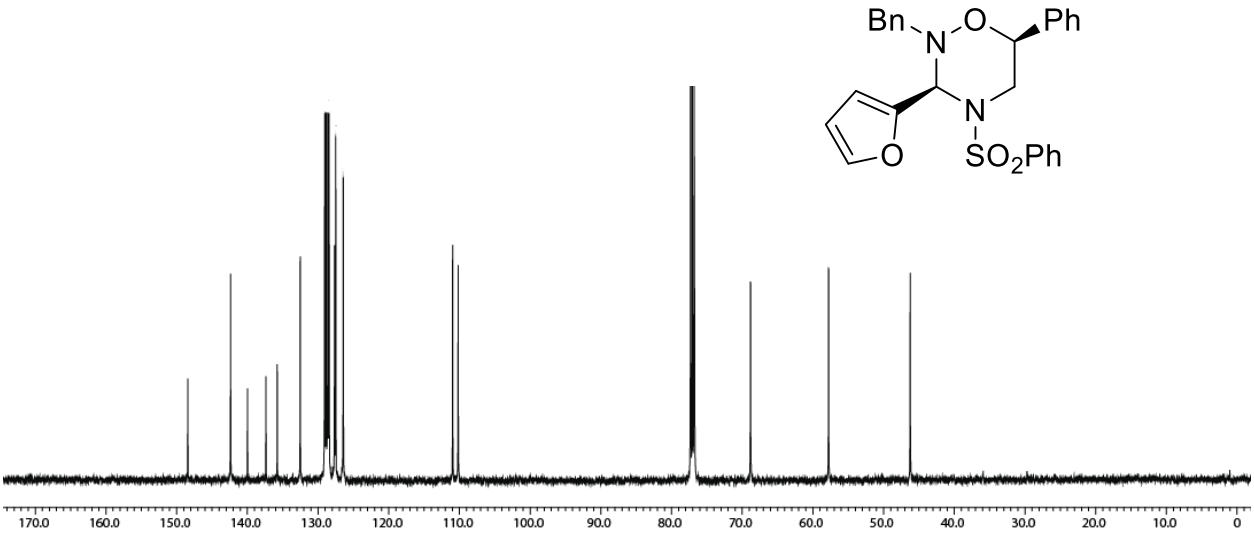

Figure 55. ^{13}C NMR spectrum of **3x** at 55 ˚C ($CDCl_3$, 125 MHz)

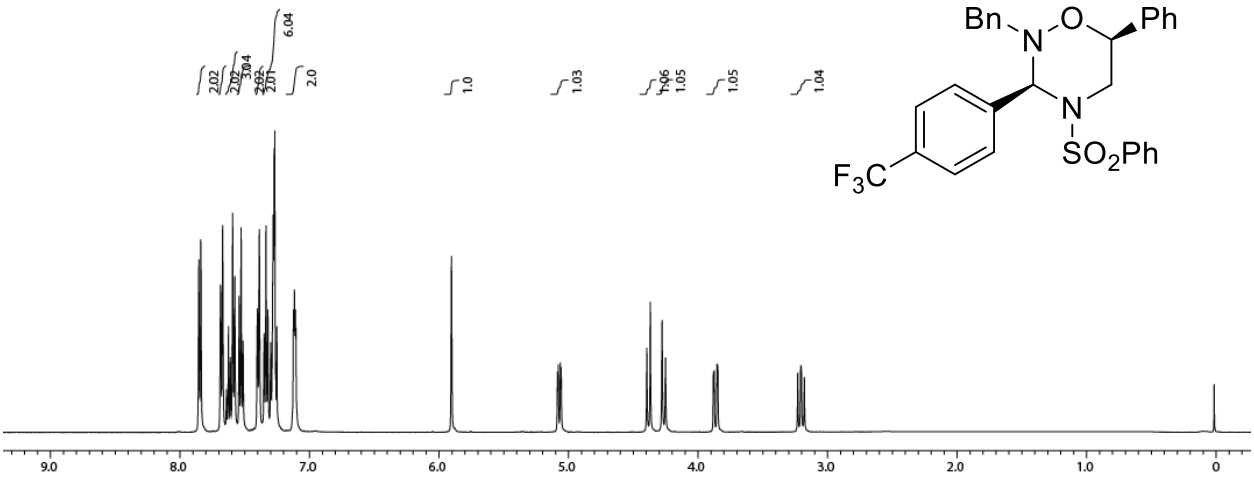

Figure 56. ^{1}H NMR spectrum of **3y** at 55 ˚C ($CDCl_3$, 500 MHz)

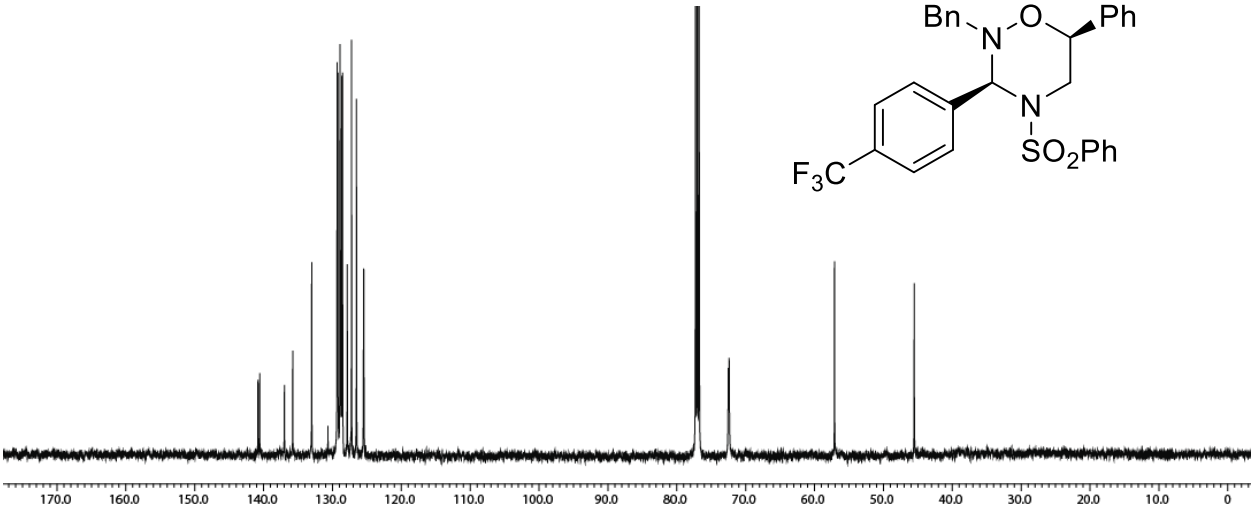

Figure 57. ^{13}C NMR spectrum of **3y** at 55 ˚C ($CDCl_3$, 125 MHz)

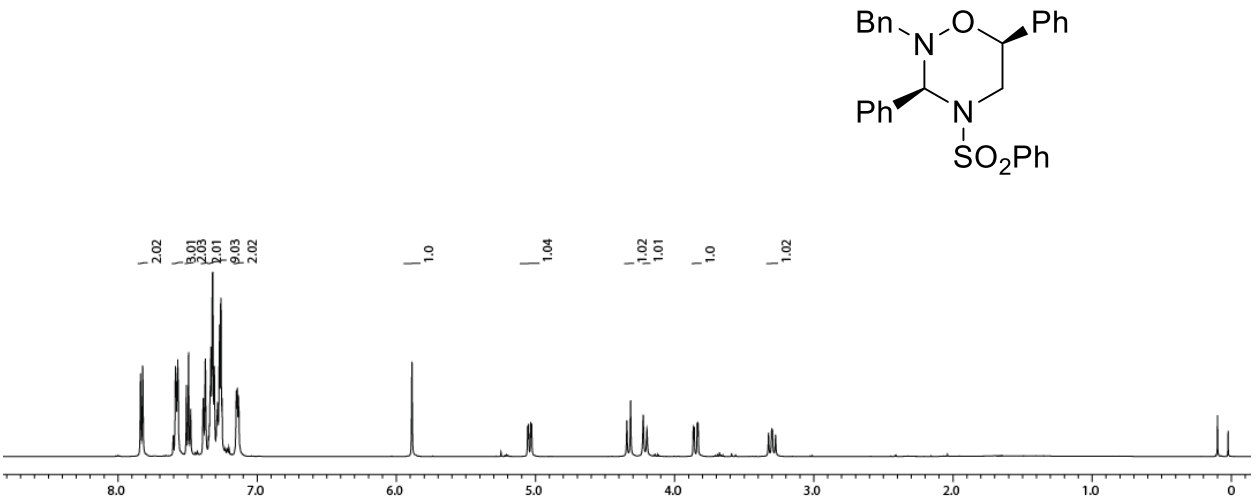

Figure 58. ^{1}H NMR spectrum of **3z** at 55 ˚C ($CDCl_3$, 500 MHz)

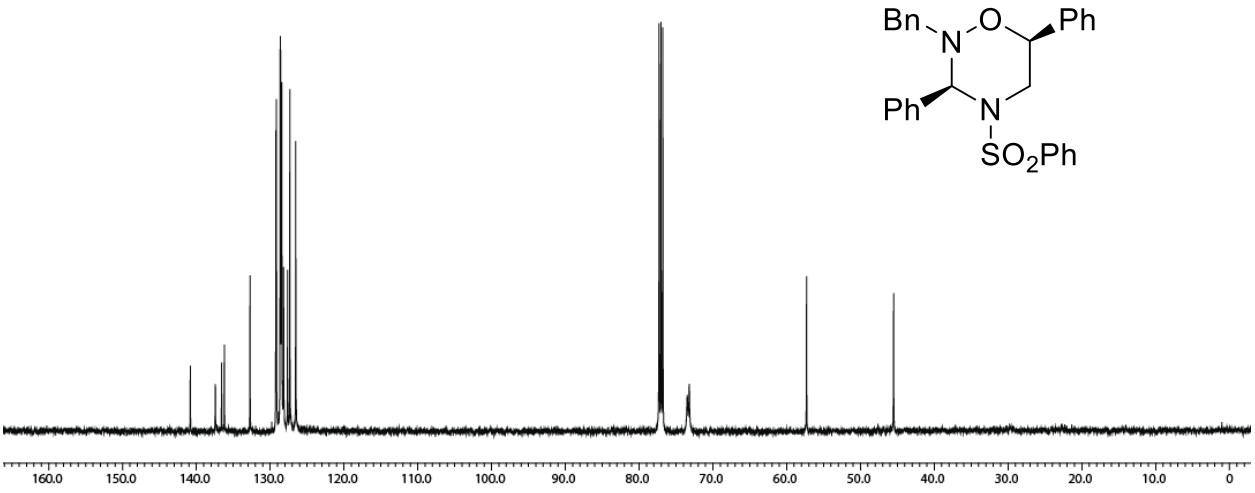

Figure 59. ^{13}C NMR spectrum of **3z** at 55 ˚C ($CDCl_3$, 125 MHz)

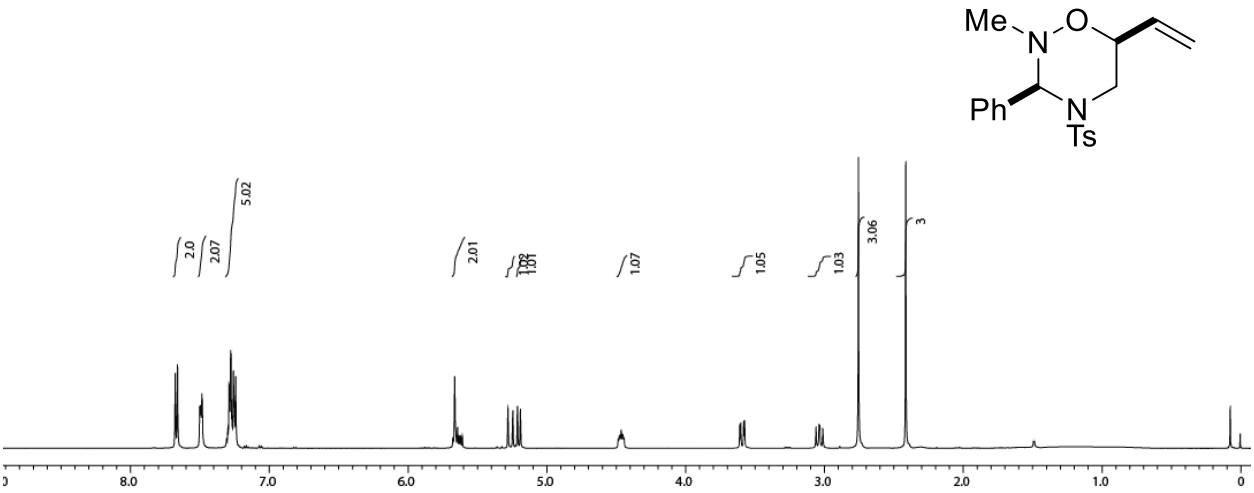

Figure 60. ^{1}H NMR spectrum of **5a** at 55 ˚C ($CDCl_3$, 500 MHz)

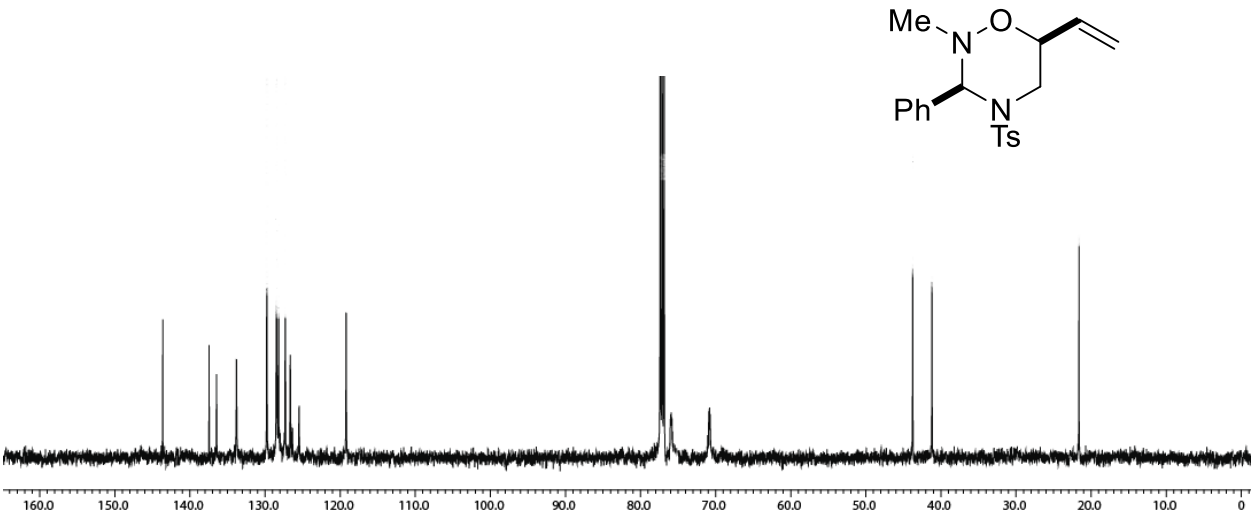

Figure 61. ^{13}C NMR spectrum of **5a** at 55 ˚C ($CDCl_3$, 125 MHz)

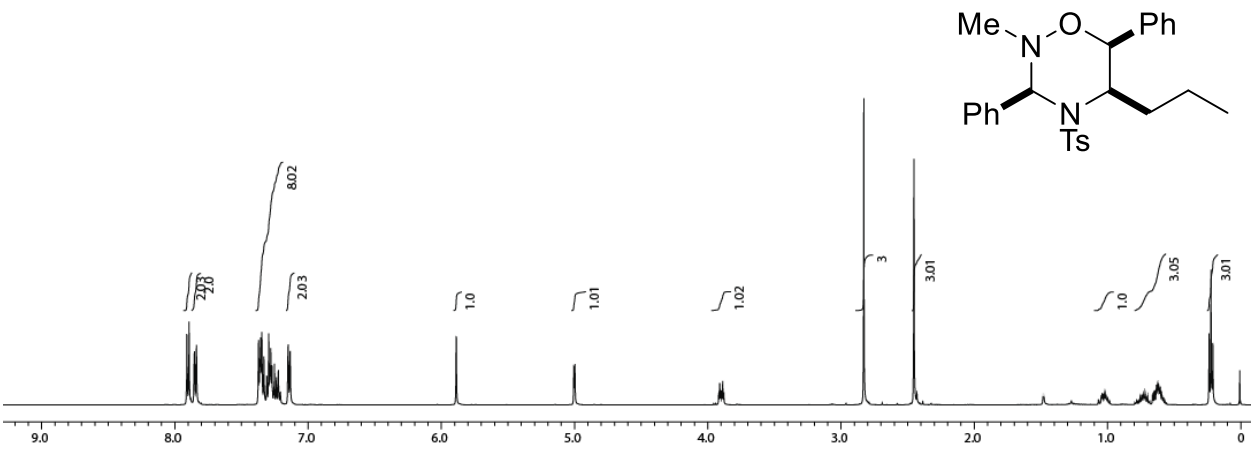

Figure 62. ^{1}H NMR spectrum of **6a** at 55 ˚C ($CDCl_3$, 500 MHz)

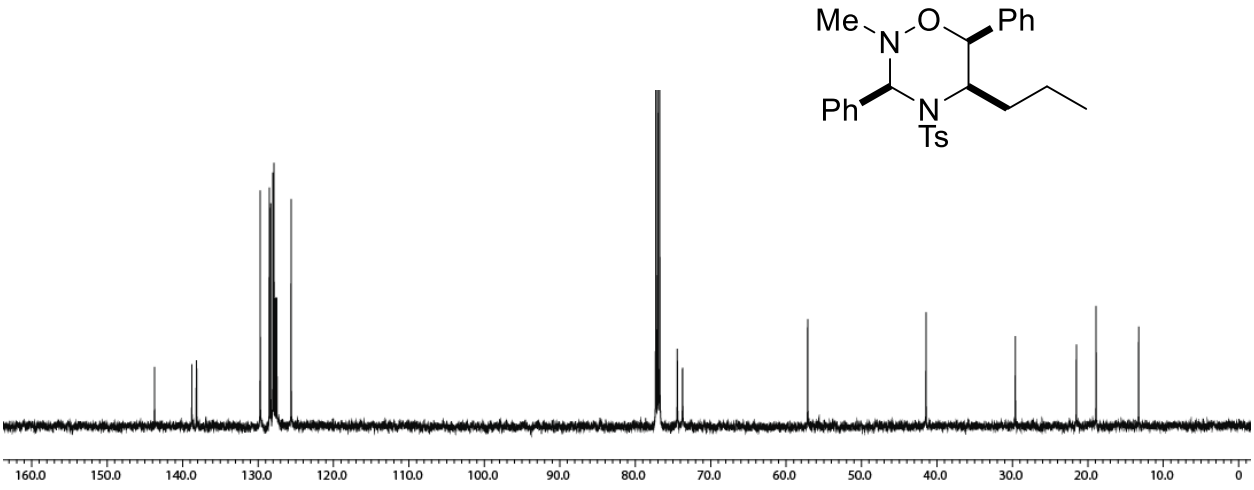

Figure 63. ^{13}C NMR spectrum of **6a** at 55 ˚C ($CDCl_3$, 125 MHz)

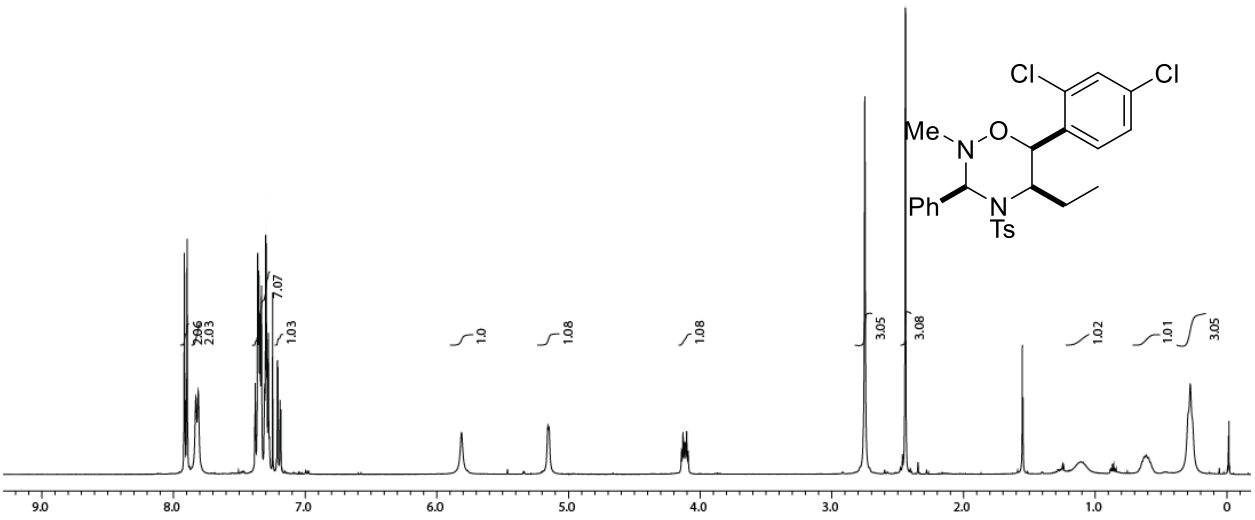

Figure 64. ^{1}H NMR spectrum of **6b** at 55 ˚C ($CDCl_3$, 500 MHz)

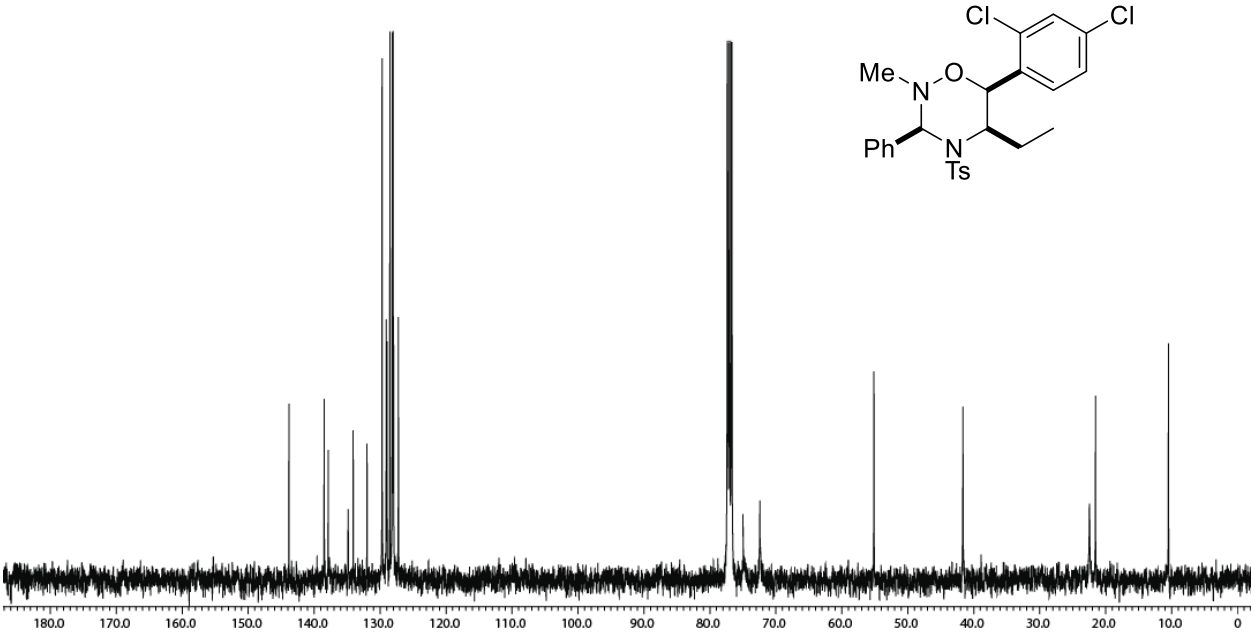

Figure 65. ^{13}C NMR spectrum of **6b** at 55 ˚C ($CDCl_3$, 125 MHz)

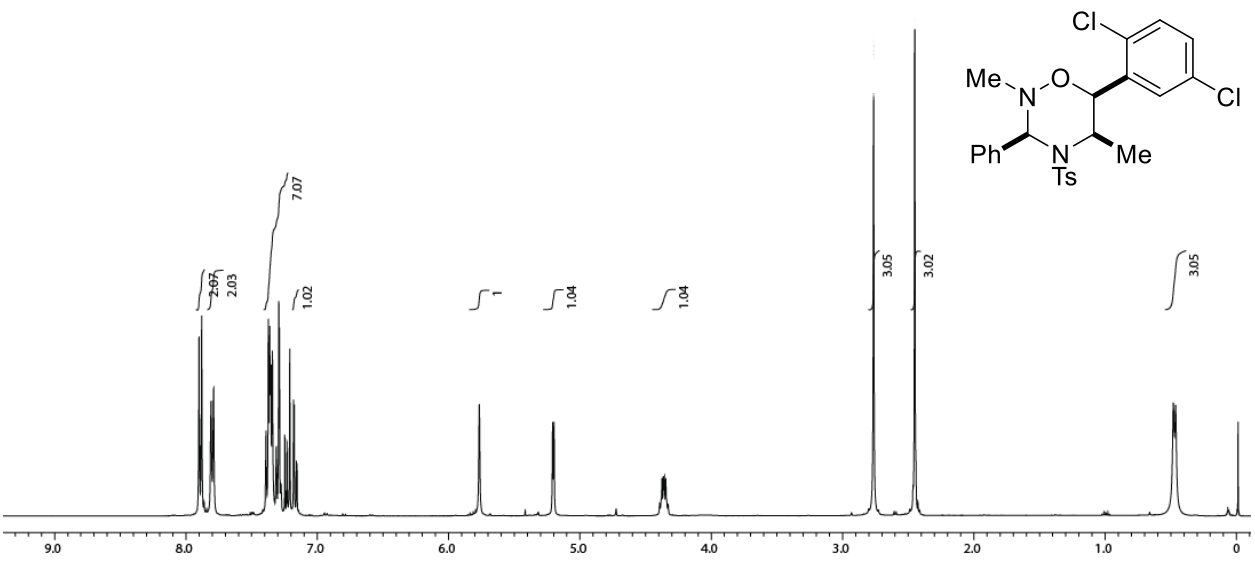

Figure 66. ^{1}H NMR spectrum of **6c** at 55 ˚C ($CDCl_3$, 500 MHz)

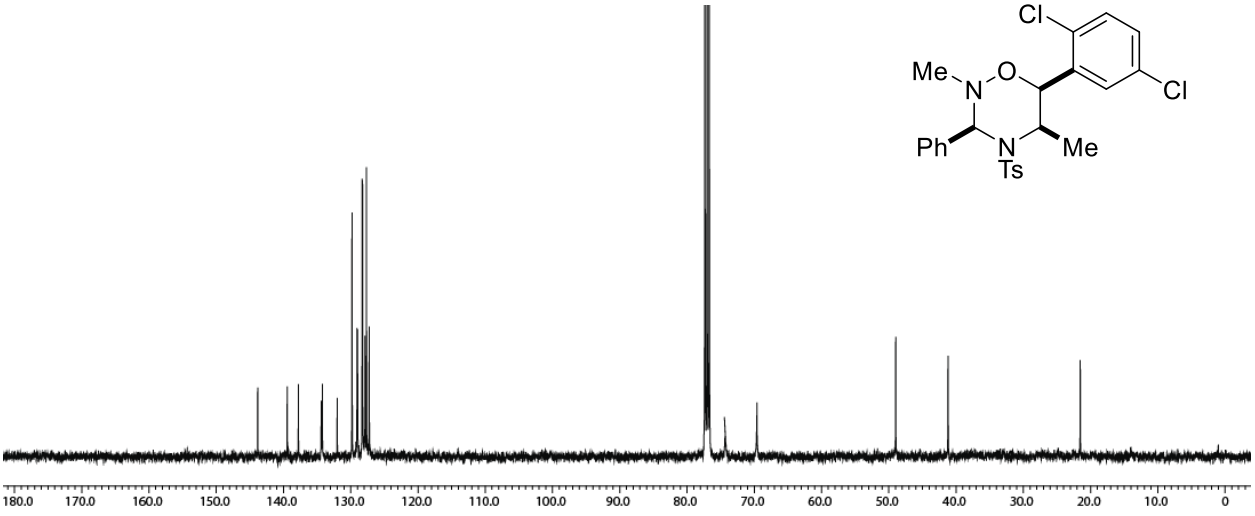

Figure 67. ^{13}C NMR spectrum of **6c** at 55 ˚C ($CDCl_3$, 125 MHz)

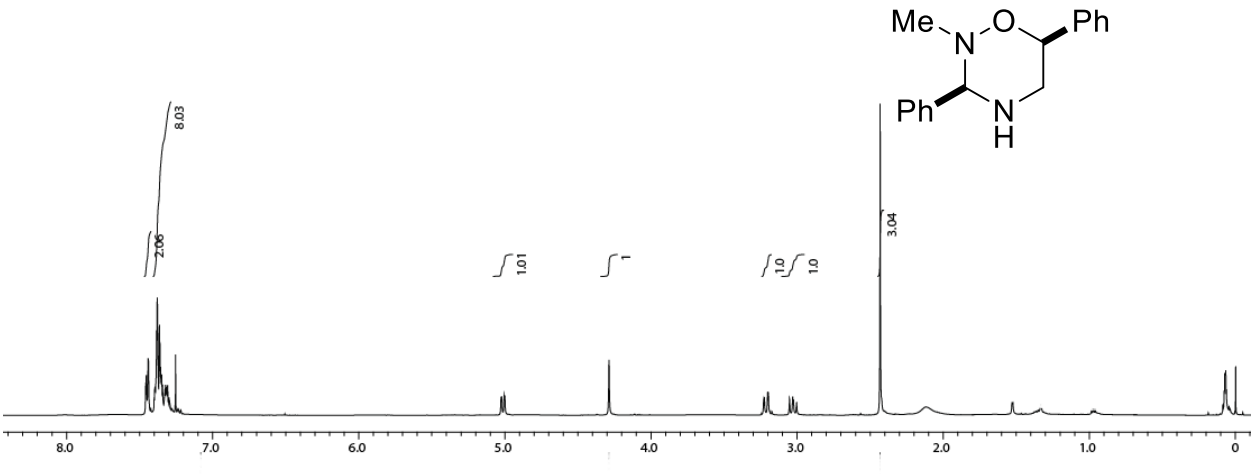

Figure 68. ^{1}H NMR spectrum of **7a** at 55 ˚C ($CDCl_3$, 500 MHz)

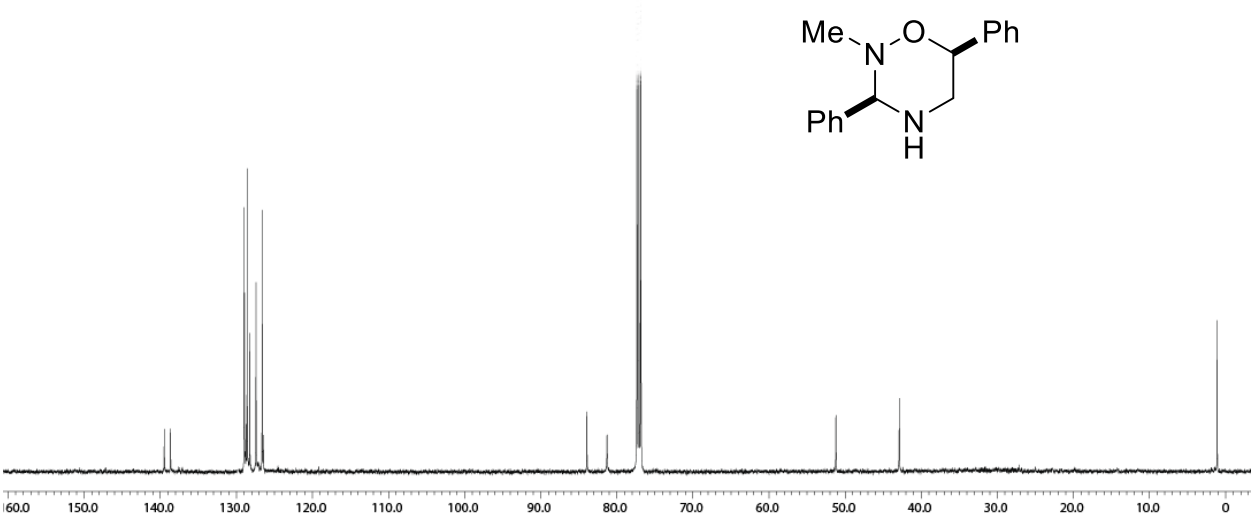

Figure 69. ^{13}C NMR spectrum of **7a** at 55 ˚C ($CDCl_3$, 125 MHz)

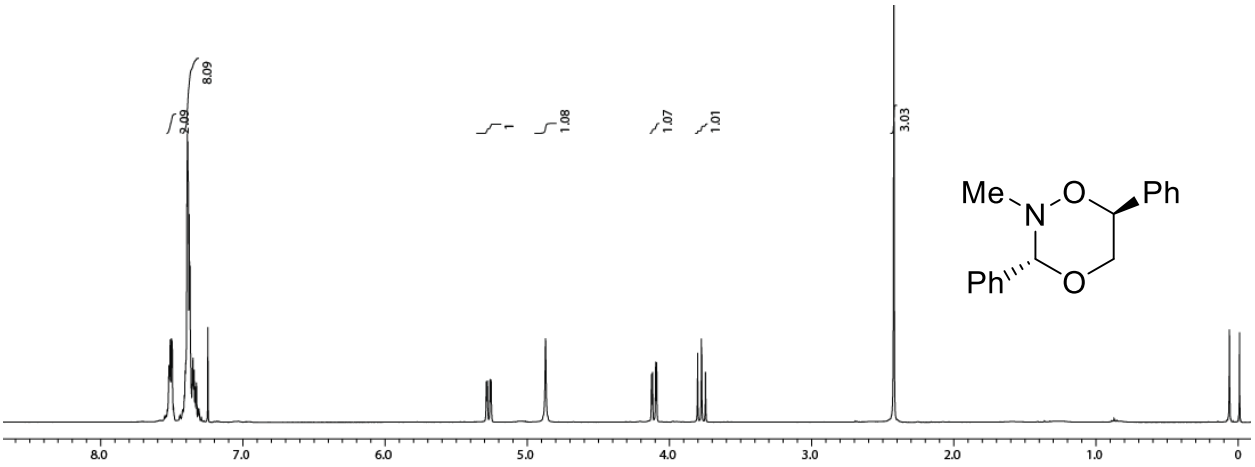

Figure 70. ^{1}H NMR spectrum of **9a** at 55 ˚C ($CDCl_3$, 500 MHz)

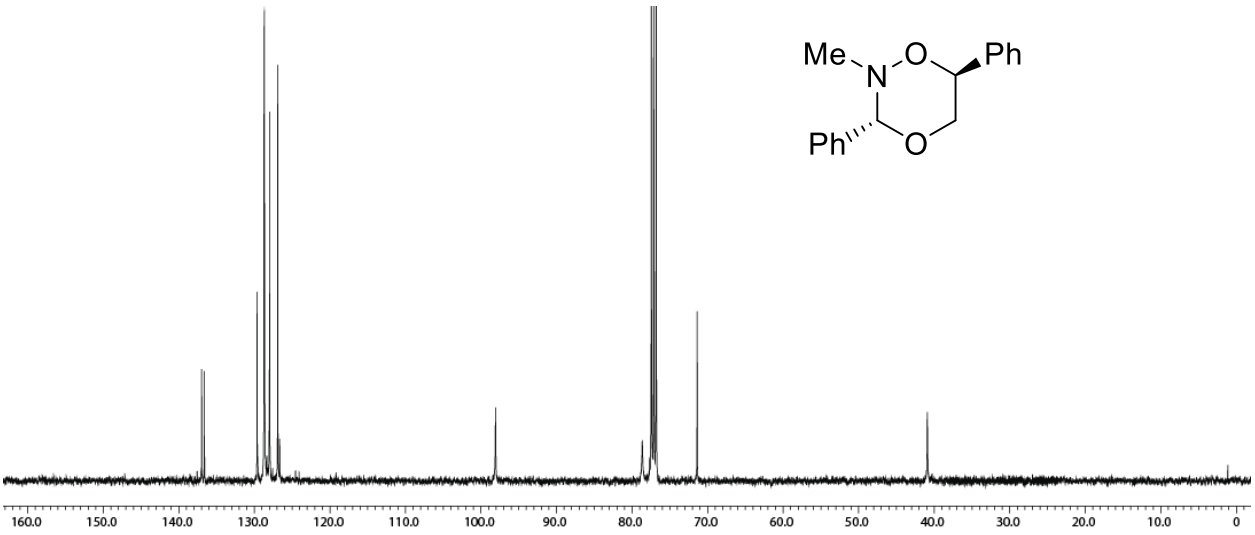

Figure 71. ^{13}C NMR spectrum of **9a** at 55 ˚C ($CDCl_3$, 125 MHz)

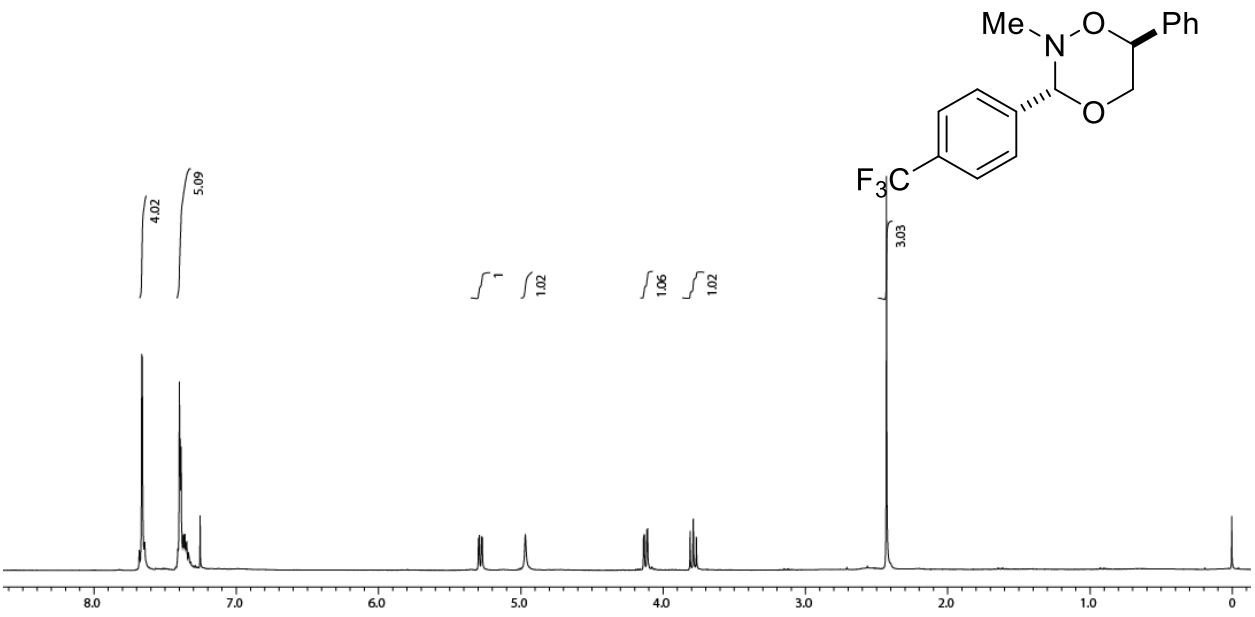

Figure 72. ^{1}H NMR spectrum of **9b** at 55 ˚C ($CDCl_3$, 500 MHz)

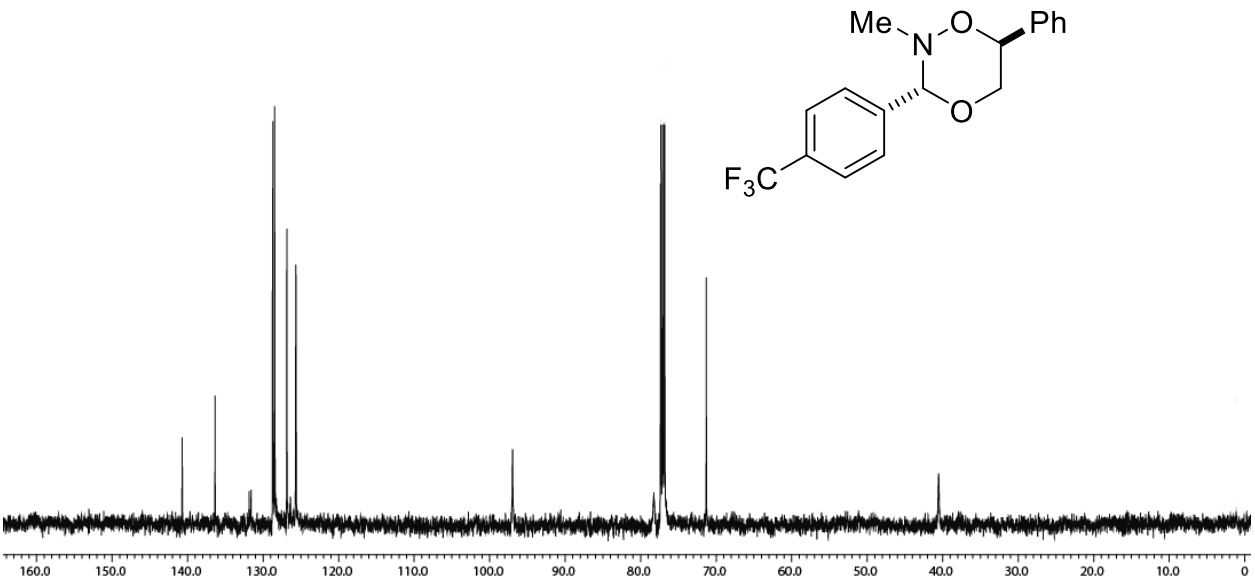

Figure 73. ^{13}C NMR spectrum of **9b** at 55 ˚C ($CDCl_3$, 125 MHz)

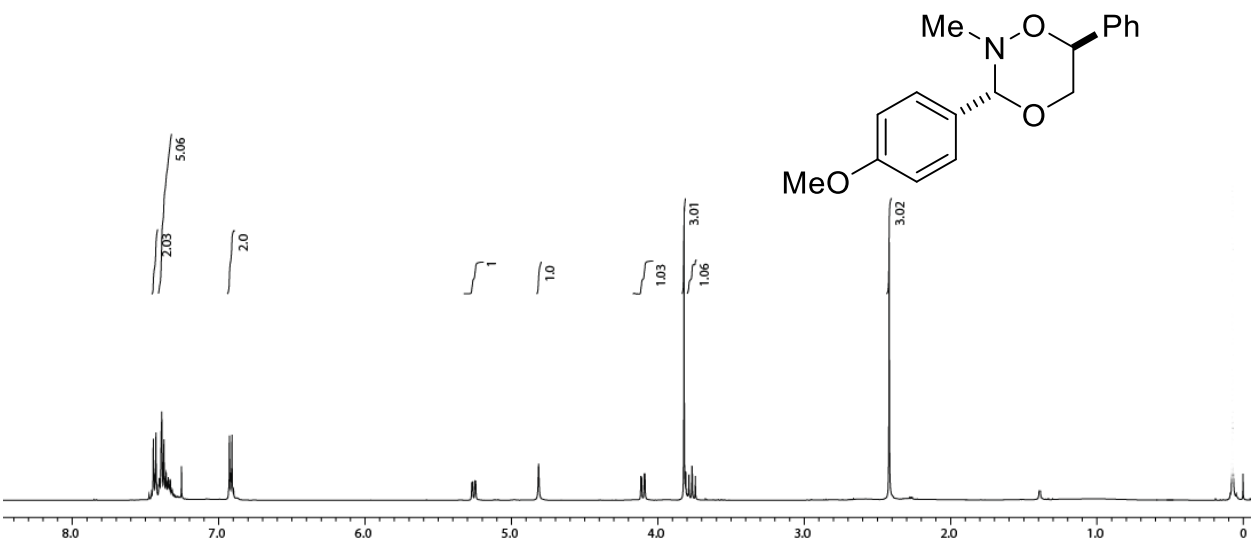

Figure 74. ^{1}H NMR spectrum of **9c** at 55 ˚C ($CDCl_3$, 500 MHz)

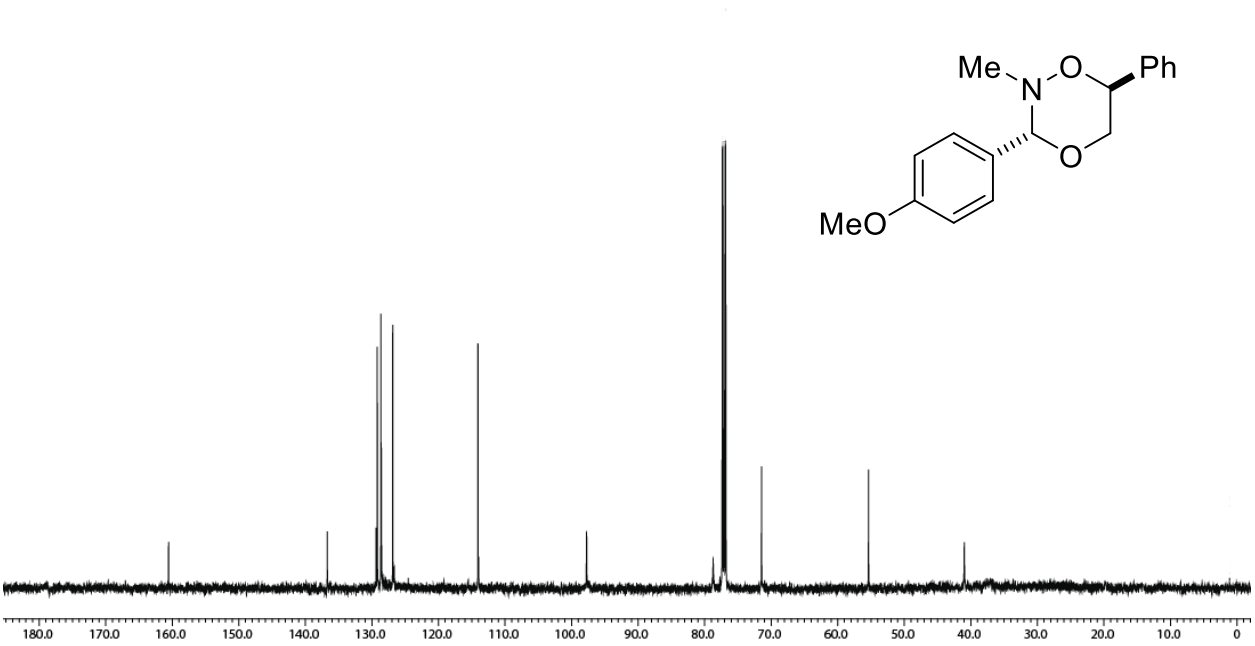

Figure 75. ^{13}C NMR spectrum of **9c** at 55 ˚C ($CDCl_3$, 125 MHz)

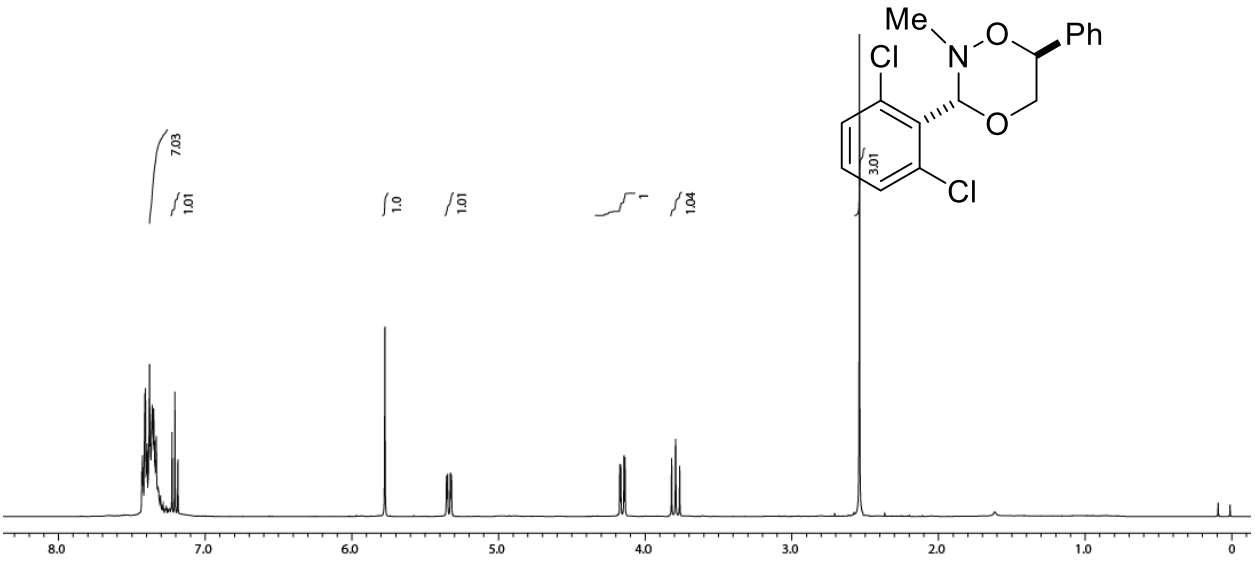

Figure 76. ^{1}H NMR spectrum of **9d** at 55 ˚C ($CDCl_3$, 500 MHz)

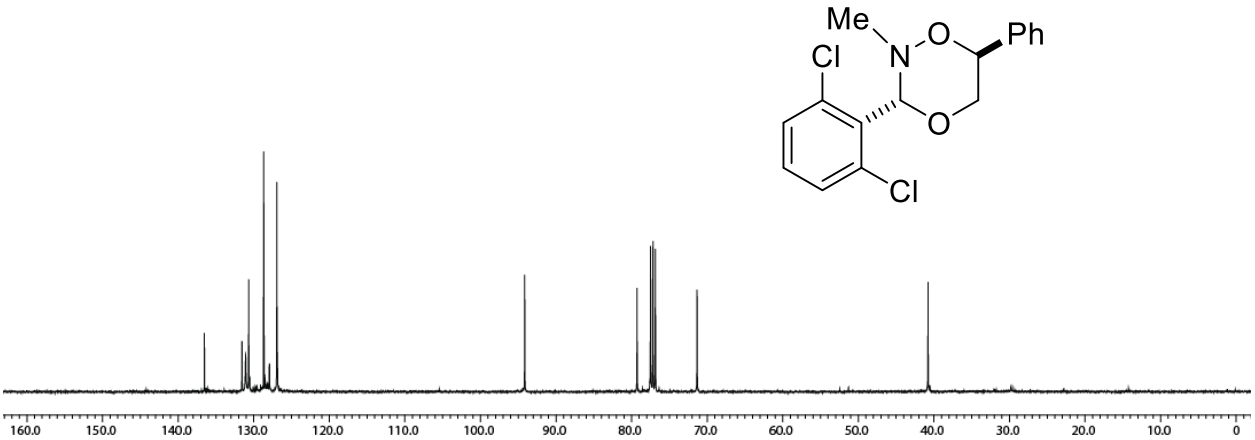

Figure 77. ^{13}C NMR spectrum of **9d** at 55 ˚C ($CDCl_3$, 125 MHz)

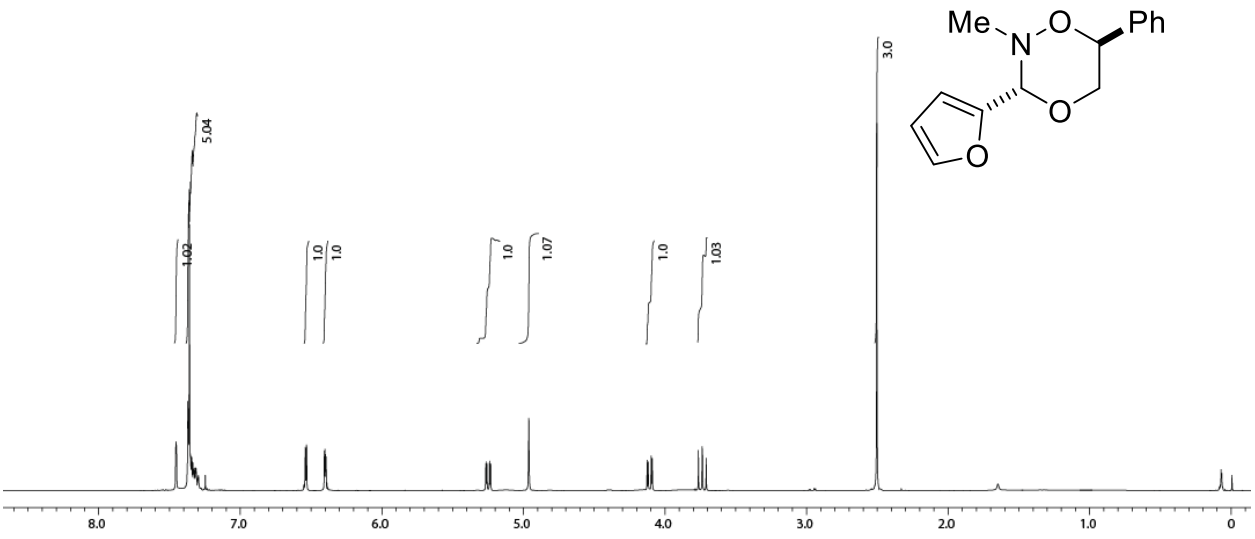

Figure 78. ^{1}H NMR spectrum of **9e** at 55 ˚C ($CDCl_3$, 500 MHz)

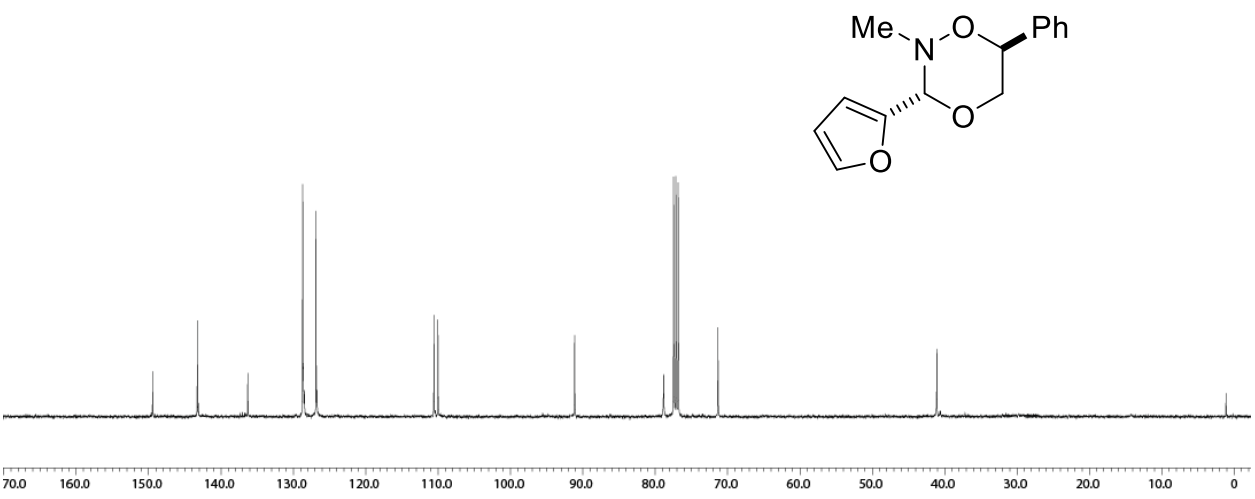

Figure 79. ^{13}C NMR spectrum of **9e** at 55 ˚C ($CDCl_3$, 125 MHz)

7. HPLC chromatograms:

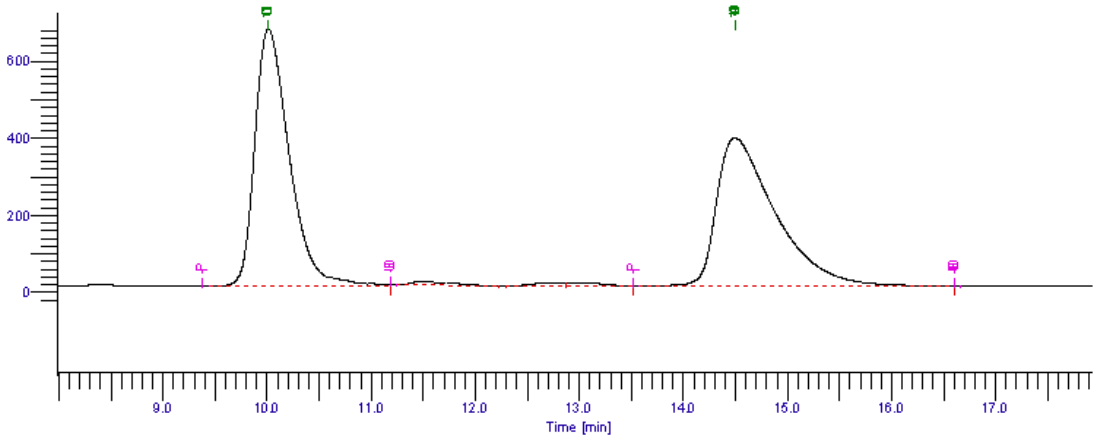

Figure 80. HPLC chromatogram of racemic compound **3m** (OD-H column; 95:5 Hexane–Isopropanol; 1 mL min^{-1})

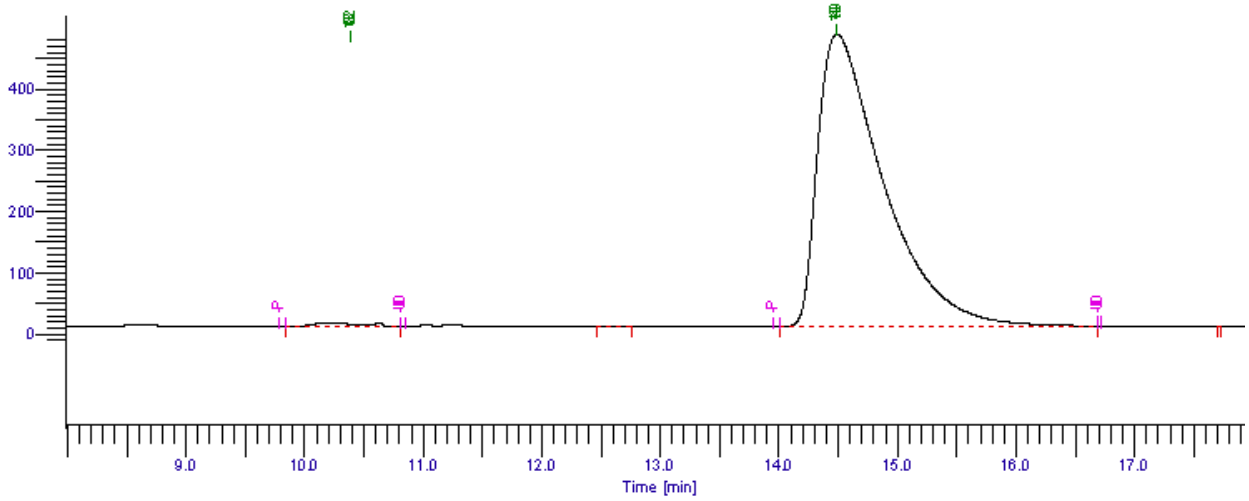

Figure 81. HPLC chromatogram of chiral compound **3m** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99%)

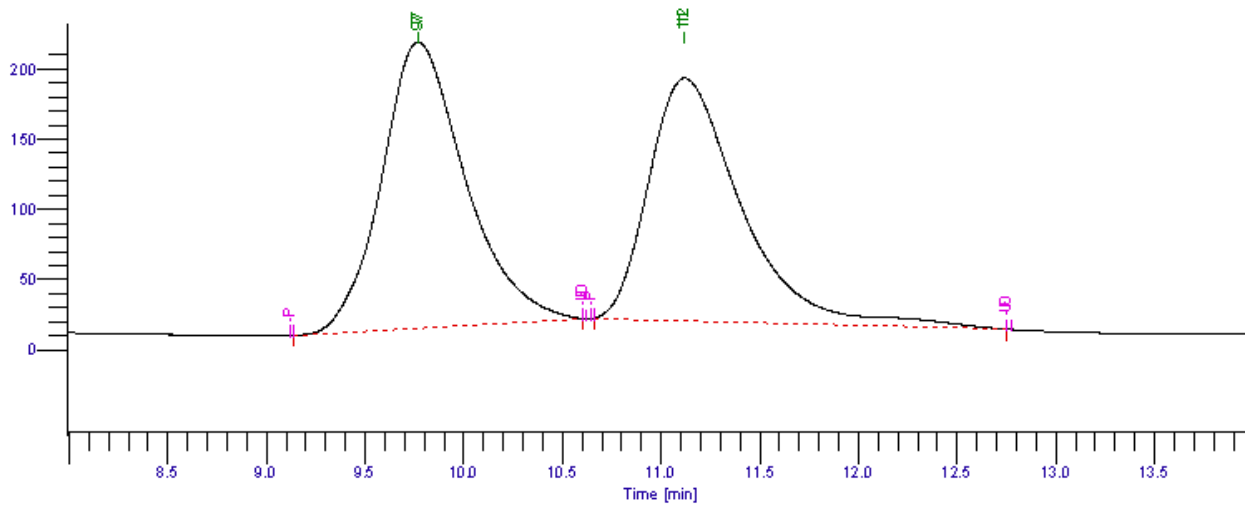

Figure 82. HPLC chromatogram of racemic compound **3q** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1})

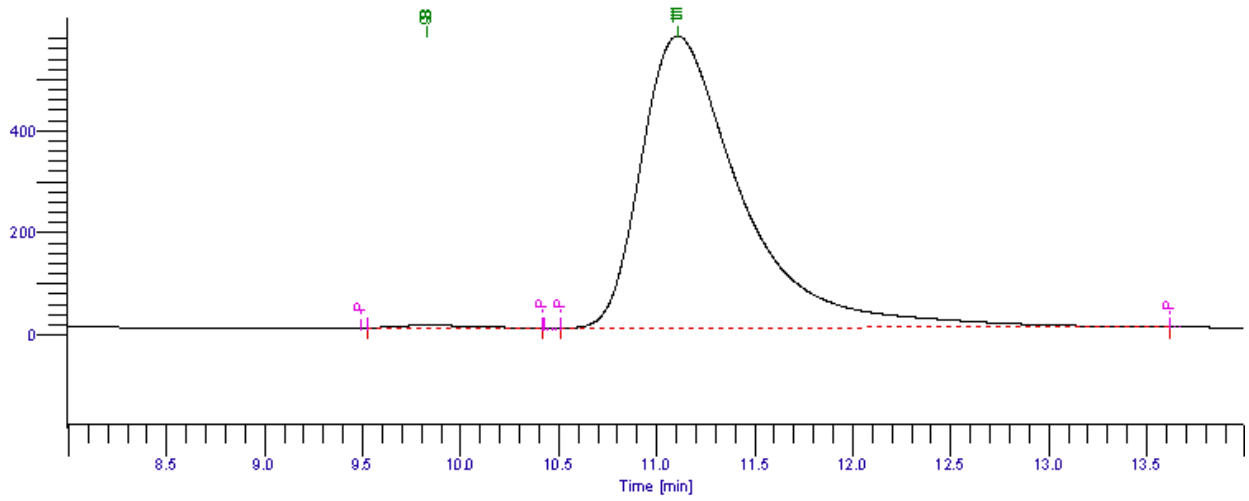

Figure 83. HPLC chromatogram of chiral compound **3q** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1}) (ee >99%)

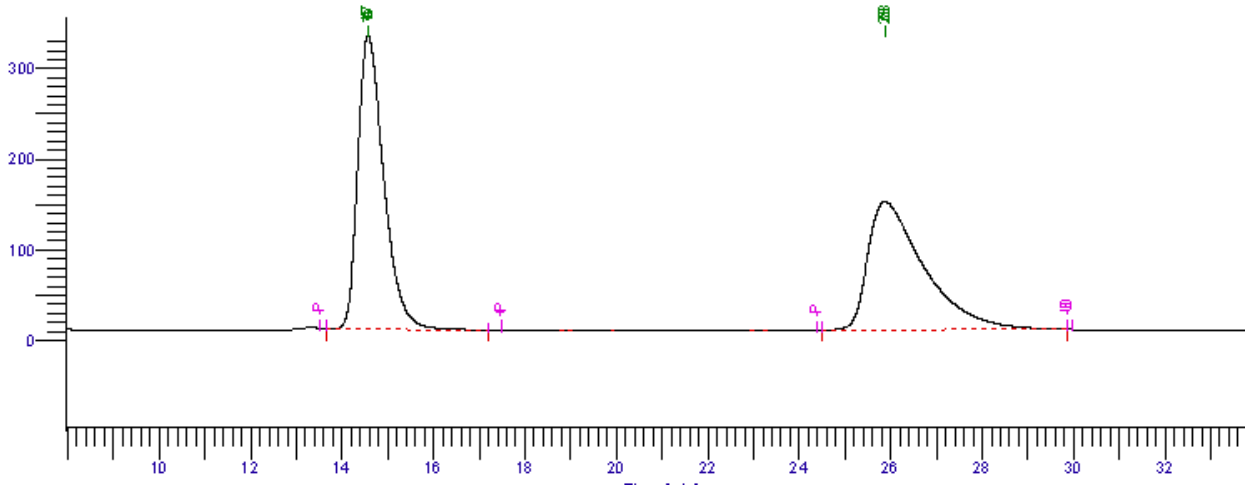

Figure 84. HPLC chromatogram of racemic compound **3r** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

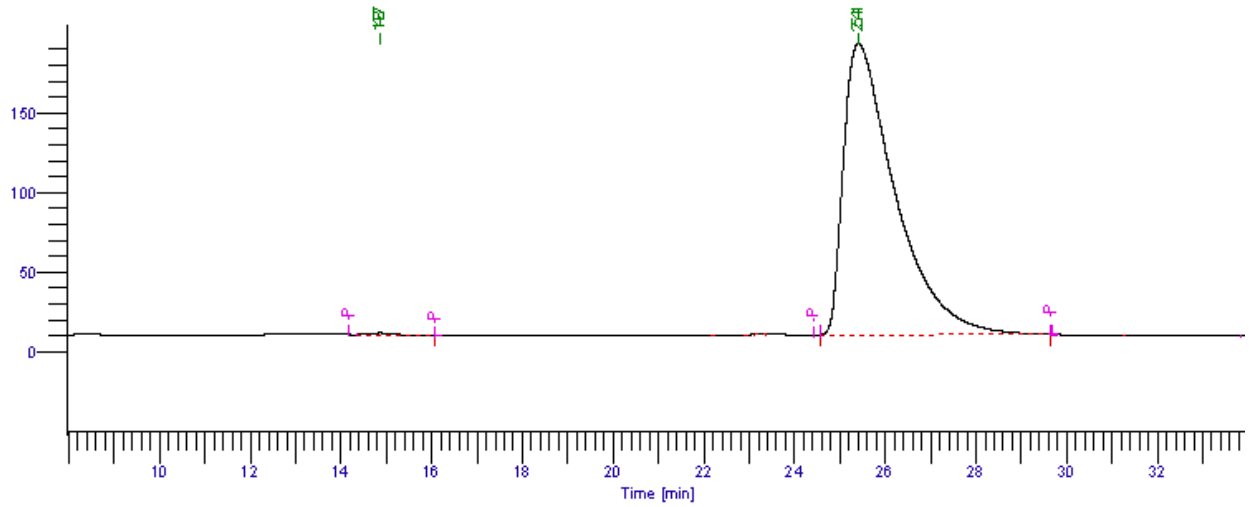

Figure 85. HPLC chromatogram of chiral compound **3r** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee >99%)

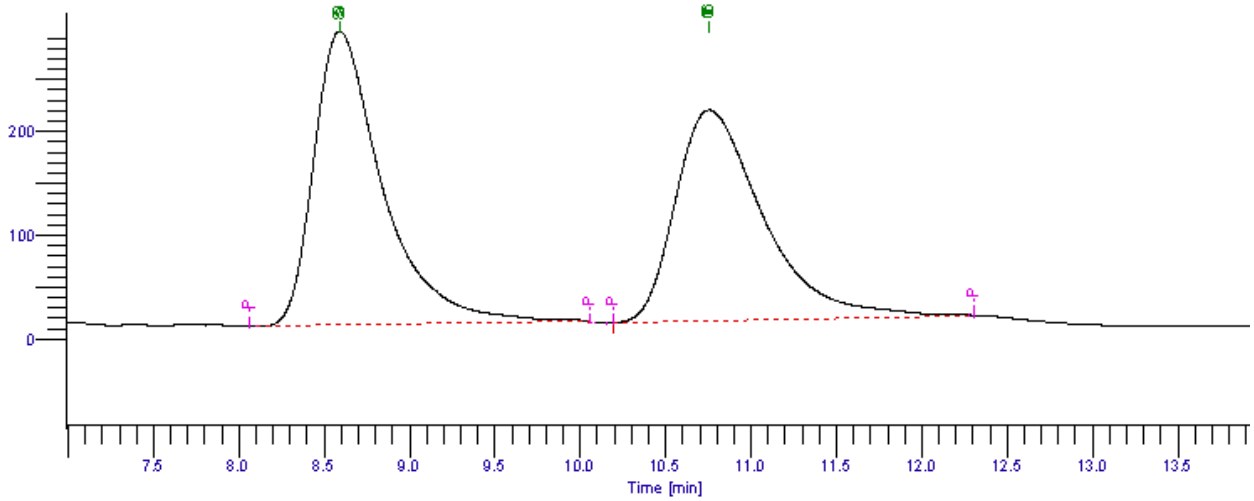

Figure 86. HPLC chromatogram of racemic compound **3s** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1})

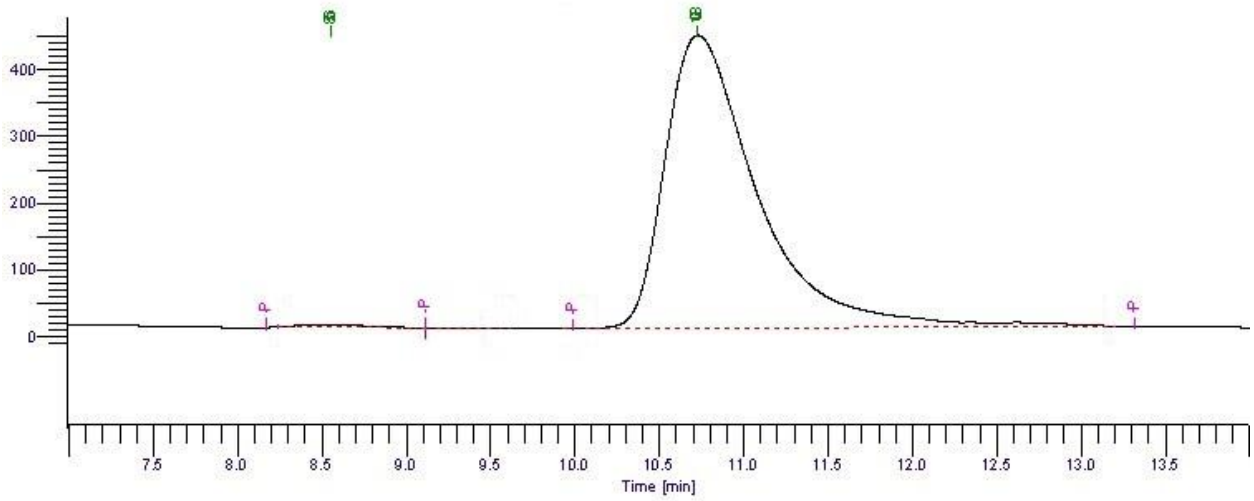

Figure 87. HPLC chromatogram of chiral compound **3s** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99%)

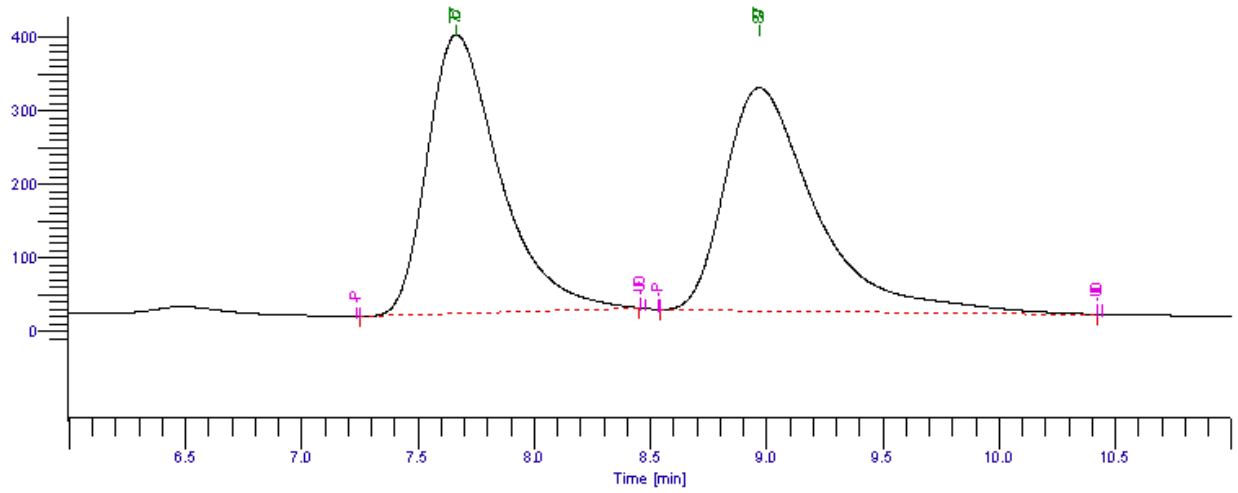

Figure 88. HPLC chromatogram of racemic compound **3t** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1})

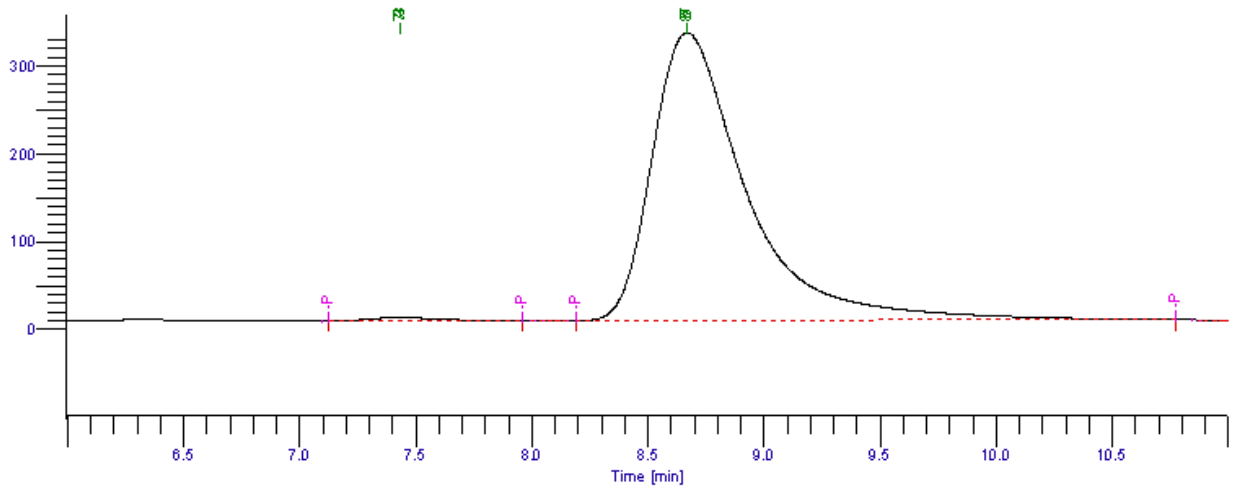

Figure 89. HPLC chromatogram of chiral compound **3t** (Cellulose 2 column; 80:20 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99%)

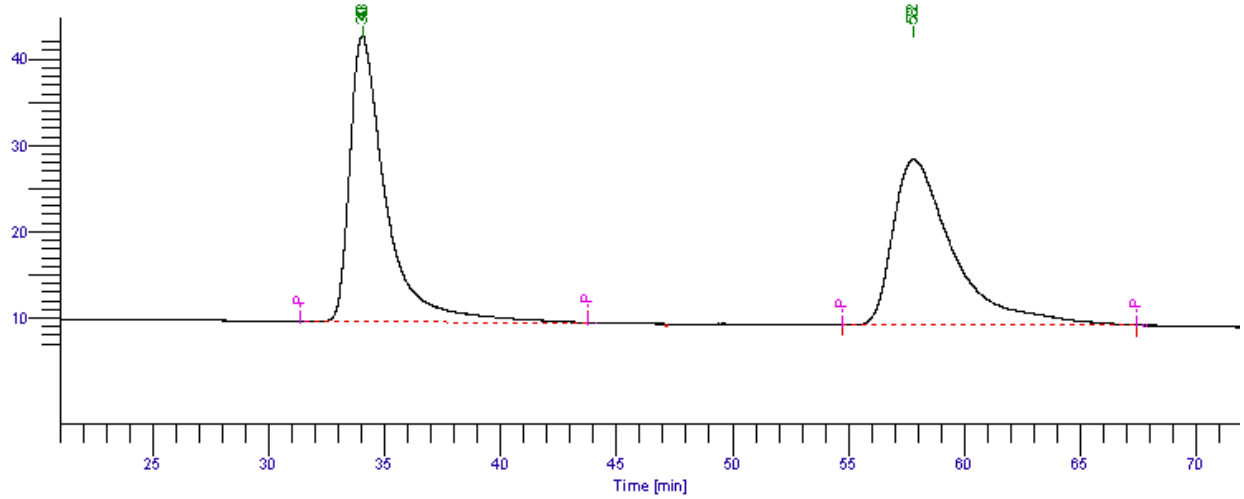

Figure 90. HPLC chromatogram of racemic compound **3u** (Cellulose 2 column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

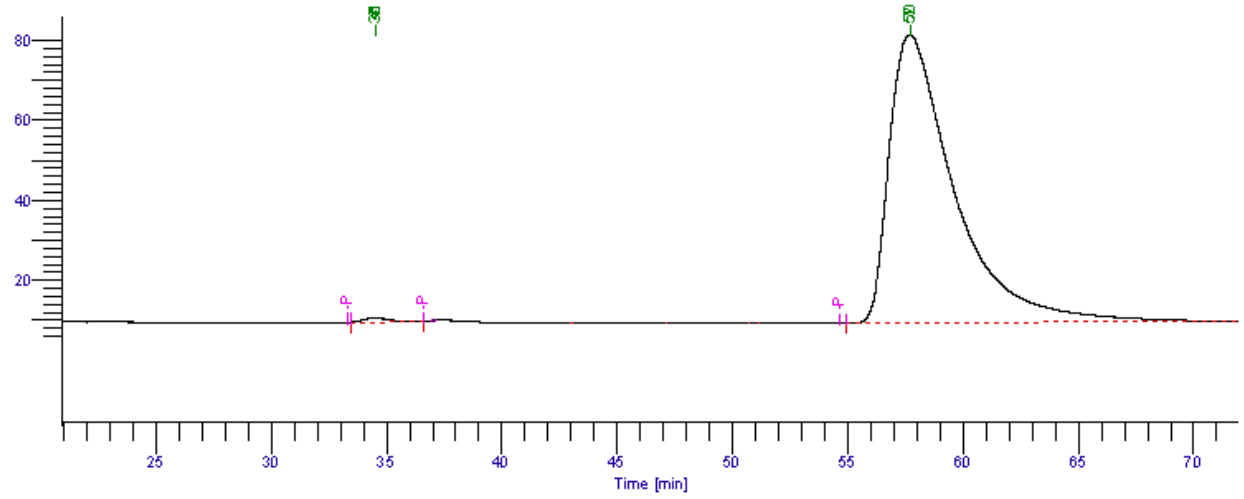

Figure 91. HPLC chromatogram of chiral compound **3u** (Cellulose 2 column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99%)

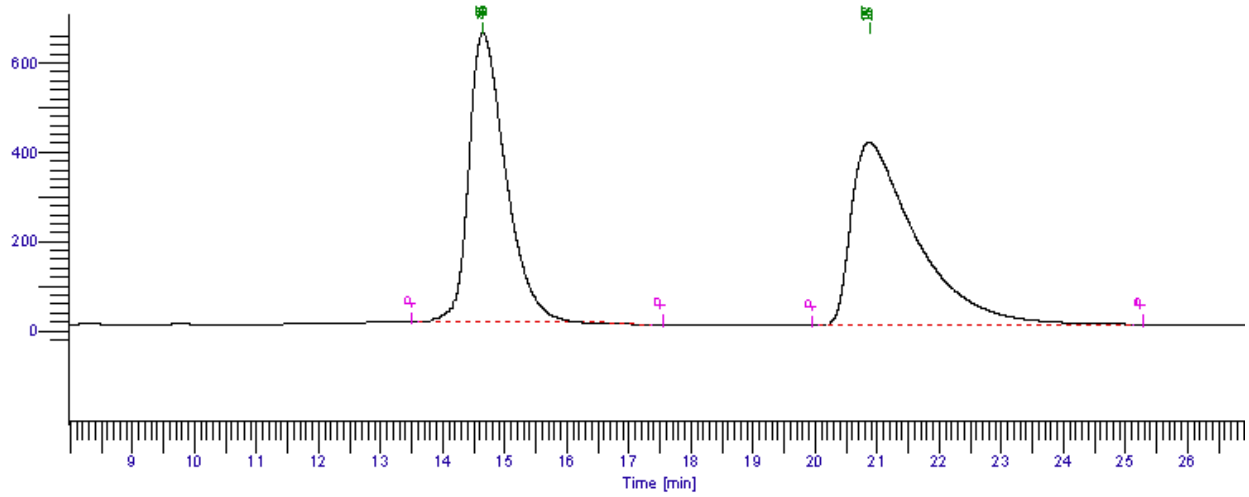

Figure 92. HPLC chromatogram of racemic compound **3v** (OD-H column; 95:5 Hexane–Isopropanol; 1 mL min^{-1})

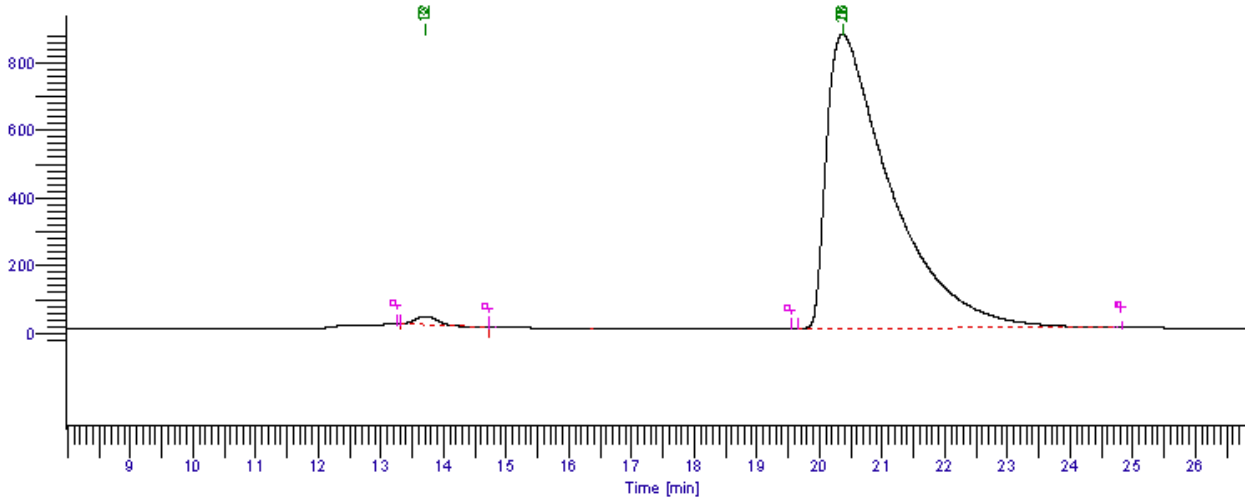

Figure 93. HPLC chromatogram of chiral compound **3v** (OD-H column; 95:5 Hexane–Isopropanol; 1 mL min^{-1}) (ee 98%)

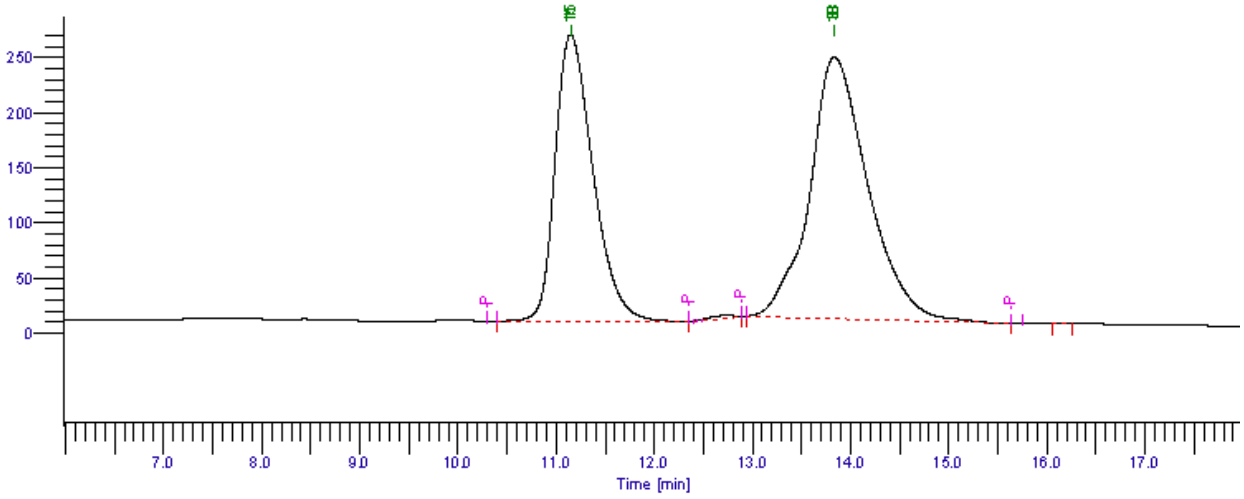

Figure 94. HPLC chromatogram of racemic compound **3w** (OD-H column; 95:5 Hexane–Isopropanol; 1 mL min^{-1})

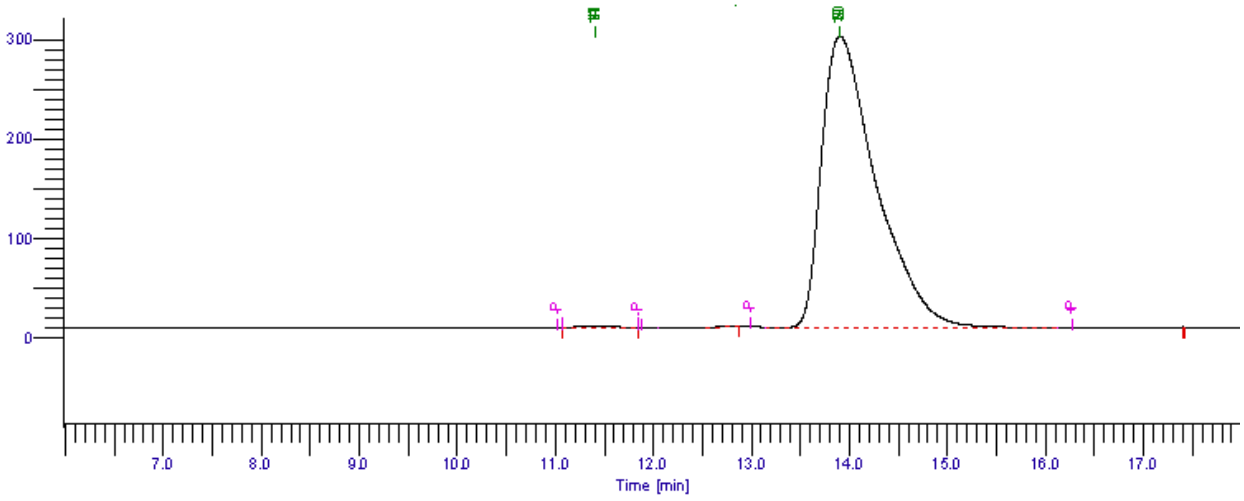

Figure 95. HPLC chromatogram of chiral compound **3w** (OD-H column; 95:5 Hexane–Isopropanol; 1 mL min^{-1}) (ee >99%)

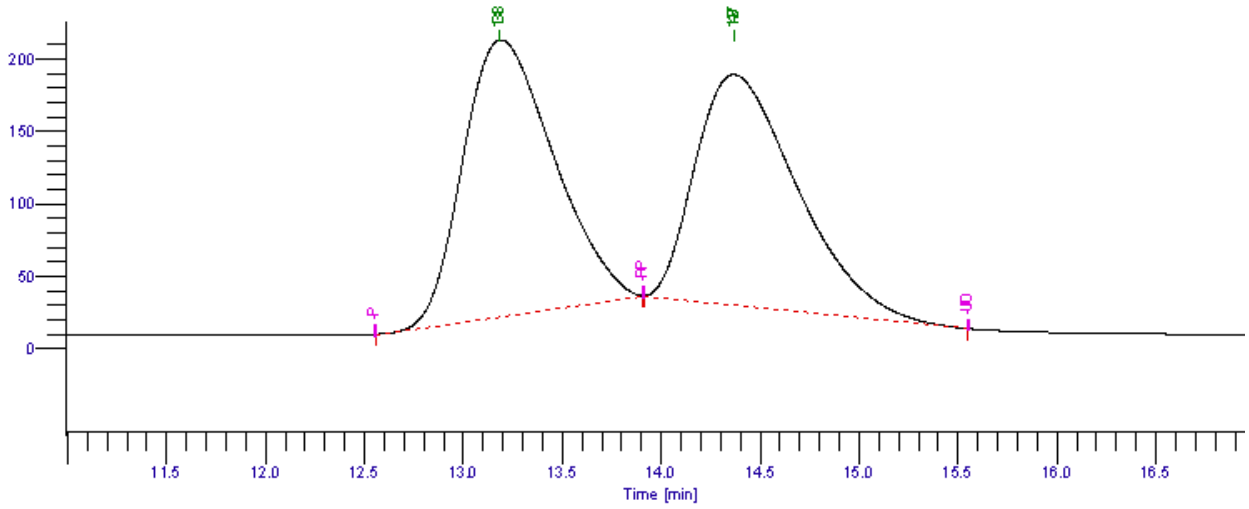

Figure 96. HPLC chromatogram of racemic compound **3x** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

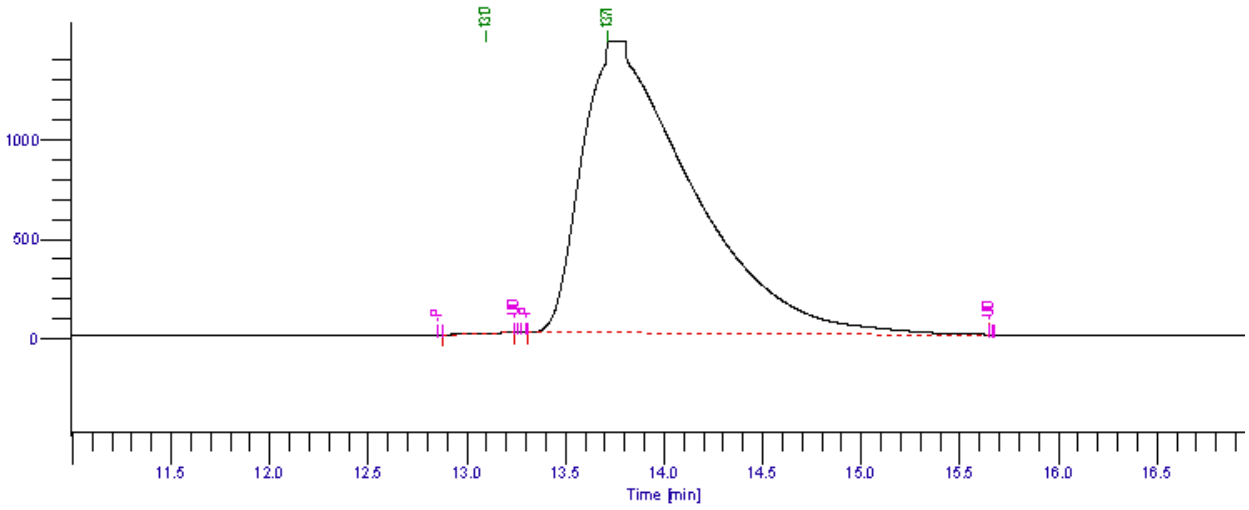

Figure 97. HPLC chromatogram of chiral compound **3x** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee >99%)

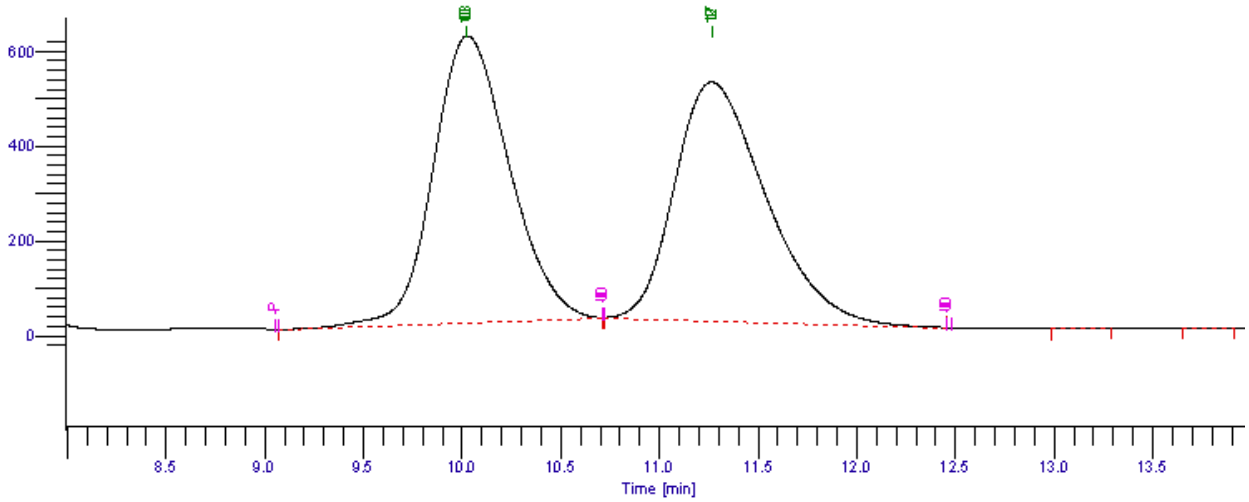

Figure 98. HPLC chromatogram of racemic compound **3y** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

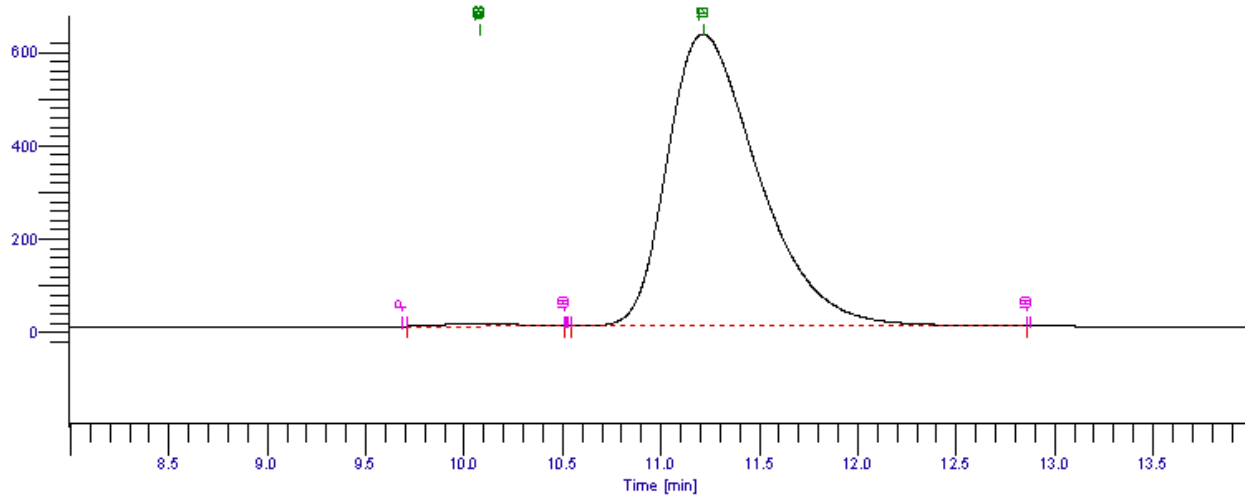

Figure 99. HPLC chromatogram of chiral compound **3y** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min) (ee 99%)

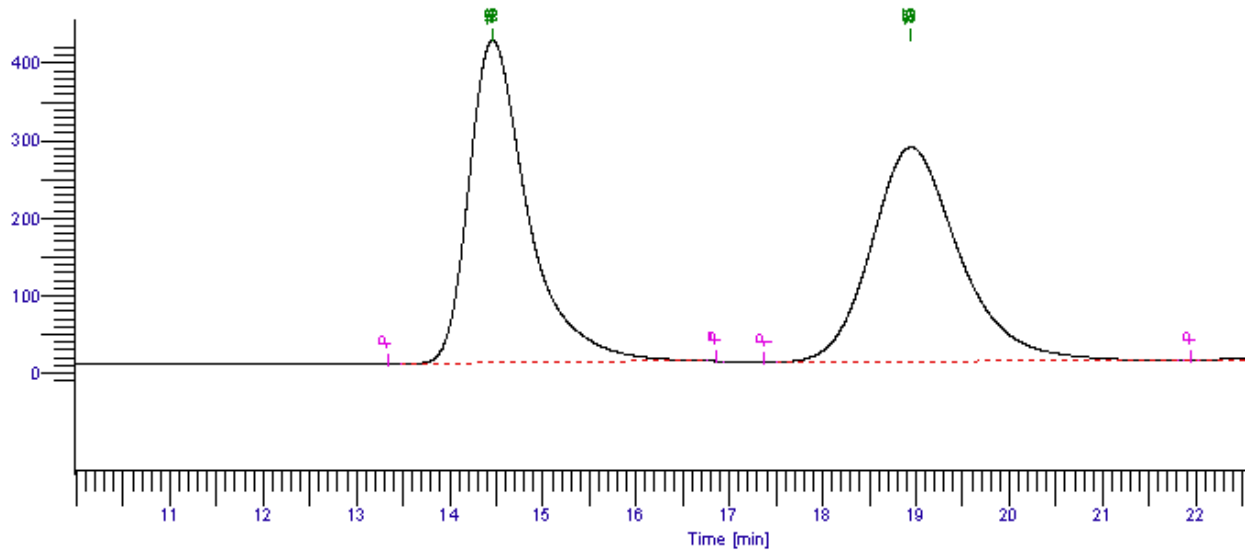

Figure 100. HPLC chromatogram of racemic compound **3z** (Cellulose 2 column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

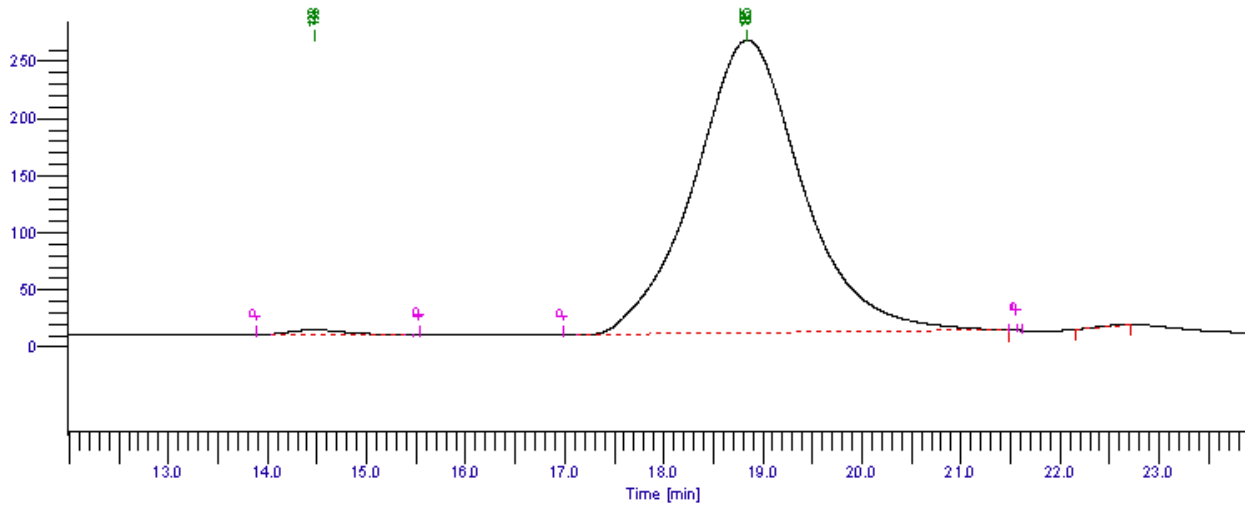

Figure 101. HPLC chromatogram of chiral compound **3z** (Cellulose 2 column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99%)

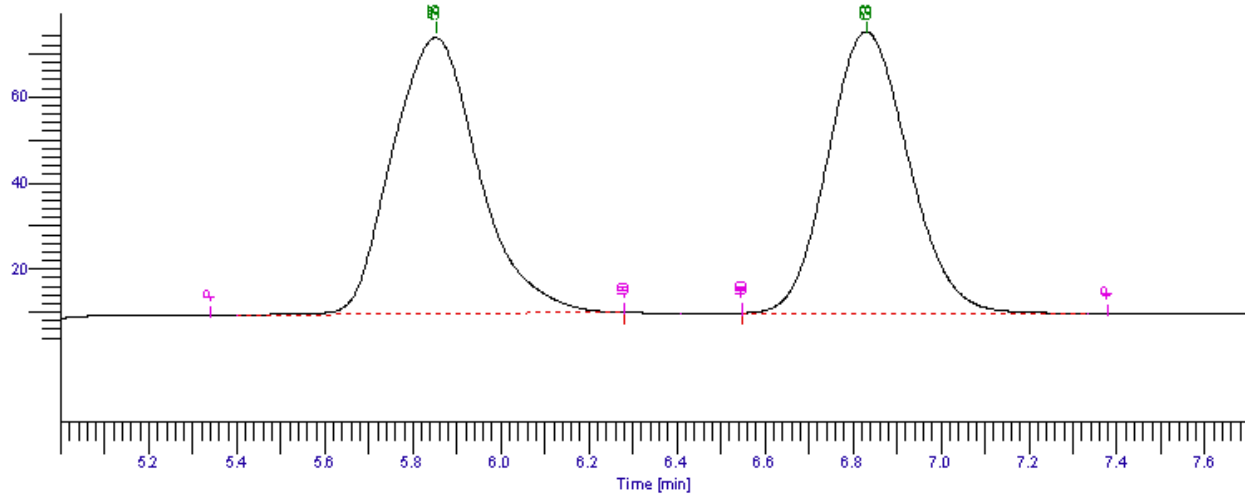

Figure 102. HPLC chromatogram of racemic compound **9a** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1})

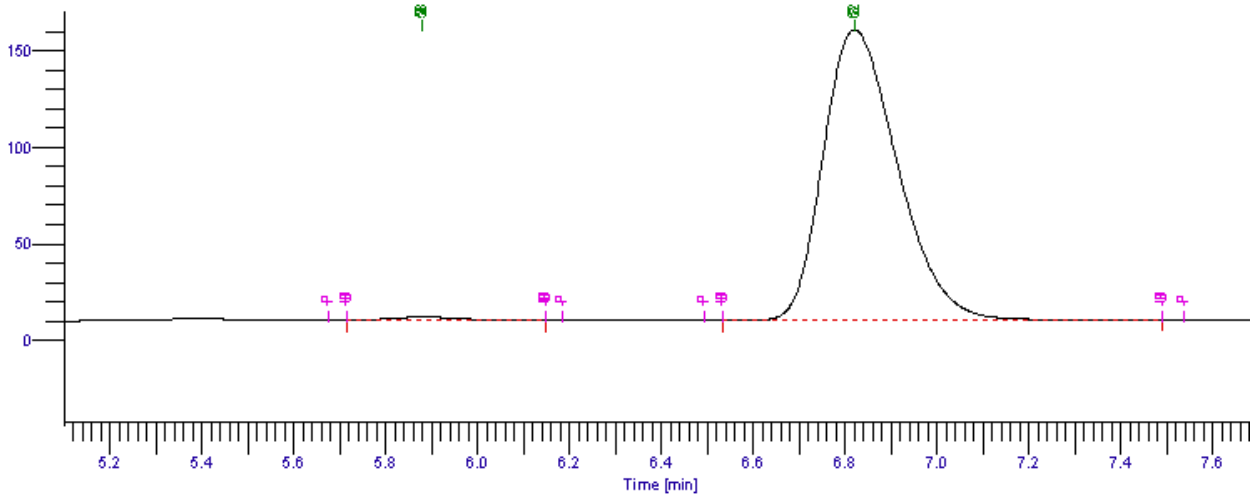

Figure 103. HPLC chromatogram of chiral compound **9a** (OD-H column; 95:5 Hexane−Isopropanol; 1 mL min^{-1}) (ee 99)