Supporting Information For

Gold Catalyzed Enantioselective Intermolecular [2+3] Dipolar Cycloaddition of *N*-Allenyl amides with Nitrones

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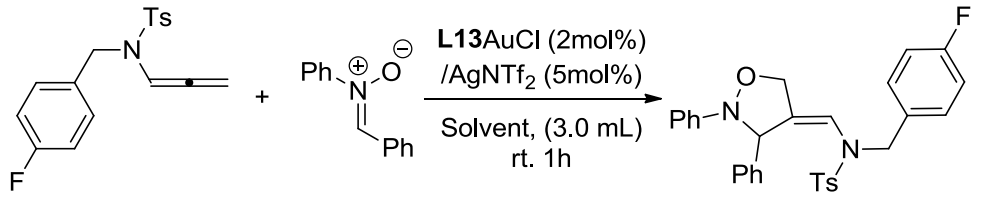
General Conditions

All reactions were run under an inert atmosphere (Ar gas) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. THF and CH_2Cl_2 were obtained by fresh distilled over sodium/benzophenone or Calciumhydride respectively. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis using $KMnO_4$ stain and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and bs = broad singlet), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.0 ppm) as the internal standard. IR spectra were recorded on an FTIR spectrometer (KBr) and reported in reciprocal centimeters (cm^{-1}). Low-resolution MS and HRMS data were obtained using ESI ionization. Mp data were measured with micro melting point apparatus.

N-allenyl amides **1a-1e** were prepared according to the published methods.[1-4] Nitrones **2a-2k** were prepared according to the published methods.[5-11] The chiral catalysts **L7-L14** was prepared according to the published methods.[15]

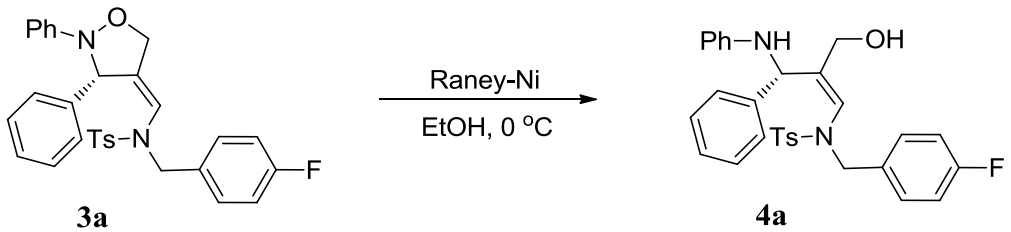
General Procedure for [2+3] cycloaddition reaction of *N*-allenyl amides with nitrones.



1a **2a** **3a**

A solution of **L13**AuCl (2 mol%)/AgNTf $_2$(5 mol%) in dry CH_2Cl_2 (3 mL) with 100mg activated 4Å MS was stirred at room temperature for three minutes. Then, *N*-allenyl amide **1a** (32 mg, 0.1 mmol) and diphenyl nitrone 2**a** (39 mg, 0.2 mmol) were added to the solution at -20 ^oC. The reaction mixture was stirred at -20 ^oC until the complete consumption of the starting material **1a** (TLC monitoring). Concentration of the reaction mixture in vacuo followed by purification through flash chromatography on silica gel column (hexane/EtOAc=10/1 as the eluent) afforded **3a** (51 mg, 99% yield) as a white solid**.**

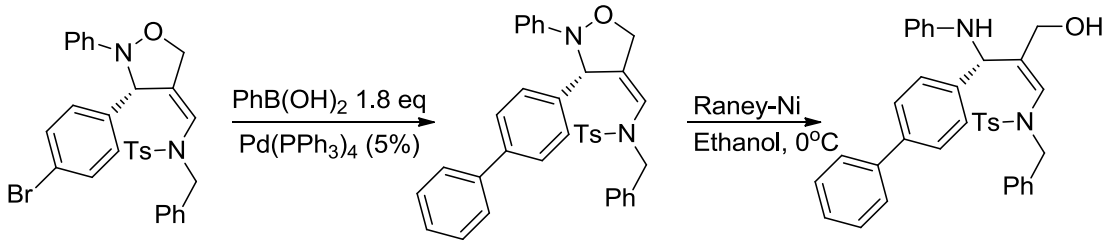
Ring Opening Reaction of 3a via Raney-Ni Reduction.[12, 13]



3a **4a**

To a solution of isoxazolidine **3a** (51 mg, 0.1 mmol) in EtOH (2 mL), was added Raney Ni (50% activated catalyst in H_2O, 5 x 200µL) in 5 portions at 0 ^oC. Upon completion, as indicated by TLC, the crude reaction mixture was filtered through SiO_2 and washed with EtOAc (5 mL). The combined filtrate was dried with anhydrous Na_2SO_4, and was then concentrated in vacuo. The resultant residue was purified by flash chromatography over SiO_2 (20% EtOAc/hexanes) to afford compound **4a** (51 mg, 99% yield) as a white solid. *Caution!: Raney Ni should never be left without solvent in order to prevent a spontaneous and highly exothermic reaction from occurring.*

Transformation of compound 3f to 6



3f, 97% ee **5**, 92%, 98% ee **6**, 81%, 98% ee[d]

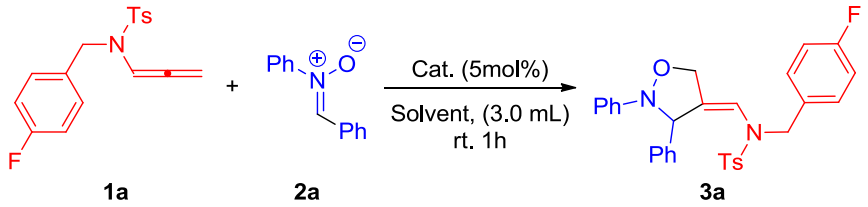
Preparation of compound 5 from 3f:[14]

To a solution of **3f** (50mg, 0.087mmol) in THF (1.5 mL), was added $Pd(PPh_3)_4$ (1.7 mg, 5% equiv), $PhB(OH)_2$ (18.6 mg, 1.8 equiv) and 3M aqueous K_2CO_3 (1 mL). The reaction mixture was then heated at reflux for 8h. Upon completion, as indicated by TLC, the reaction mixture was cooled down to room temperature, and was then diluted with 10 mL EtOAc. The organic layer was washed with brine (5 mL) and distilled water (10 mL), and dried with anhydrous Na_2SO_4. After concentrated in vacuo, the resultant residue was purified by flash chromatography over SiO_2 (EtOAc/hexanes = 1/10) to afford compound **5** (41 mg, 92% yield) as a white solid.

Preparation of compound 6 from 6:

Following the same procedure for the reaction of **3a**, the desired compound **6** can be obtained from **5** (30 mg, 0.052 mmol) as a white solid (24 mg, 81% yield).

Table S1. Optimization of the Reaction Conditions for the Racemic [2 + 3] Dipolar Cycloaddition[a]

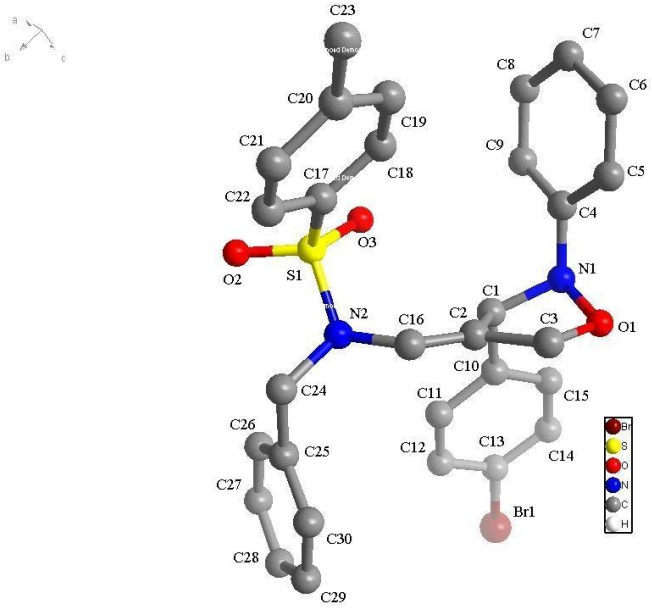


1a **2a** **3a**

	Catalyst (5 mol %)	Solvent/Time(h)	Yield 3a (%)[b]
1	$Ph_3PAuCl/AgSbF_6$ (5)	DCM/1.5	37 [c]
2	$Ph_3PAuCl/AgSbF_6$ (5)	DCM/9	80
3	$Ph_3PAuCl/AgNTf_2$ (5)	DCM/0.5	92
4	$Ph_3PAuCl/AgPF_6$ (5)	DCM/0.5	63
5	$Ph_3PAuCl/AgOTf$ (5)	DCM/0.5	77
6	$Ph_3PAuCl/AgBF_4$ (5)	DCM/0.5	87
7	JohnphosAuCl/$AgNTf_2$(5)	DCM/6	< 5%
8	$dppmAu_2Cl_2/AgNTf_2$ (5)	DCM/1	31
9	(IPR)$AuNTf_2$, (5)	DCM/16	21
10	(SIPR)$AuNTf_2$, (5)	DCM/16	<5
11	$Au(OPh)_3Cl/AgNTf_2$ (5)	DCM/1	53
12	$Ph_3PAuCl/AgNTf_2$ (5)	Toluene/18	84
13	$Ph_3PAuCl/AgNTf_2$ (5)	THF/18	75
14	$Ph_3PAuCl/AgNTf_2$ (5)	$CHCl_3$/18	82
15	$Ph_3PAuCl/AgNTf_2$ (5)	DCE/0.5	>99
16	$Ph_3PAuNTf_2$ (5)	DCE/1	71
17	$AgNTf_2$ (5)	DCE/24	NR
18	Ph_3PAuCl	DCE/24	Mixture

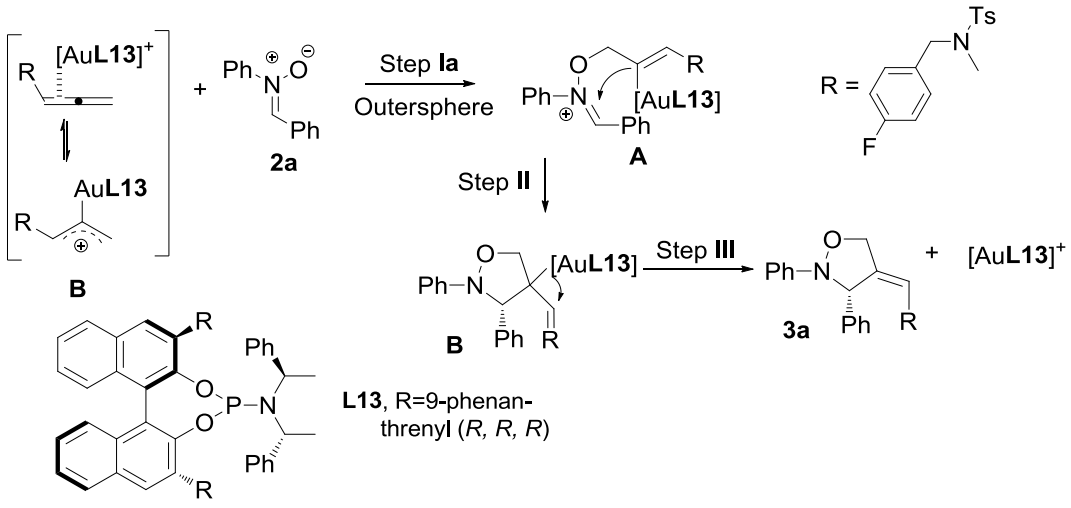
[a] Unless noted, all reactions were carried out at 0.1 mmol scale in 2 mL solvent with the addition of 5 mol % catalyst at rt. [b]Isolated yields. [c] 100 mg 4 Å MS was added.

The absolute configuration of compound (*s*)-3f was determined by its X-ray structure.



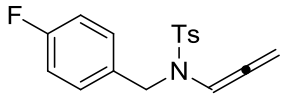
X-ray structure of compound **3f**.

A plausible reaction mechanism for asymmetric [2+3] cycloaddition reaction of substrate 1a with 2a in the condition of chiral catalyst L13.



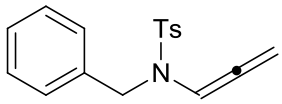
Characterization Data

N-(4-fluorobenzyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 1a[4]



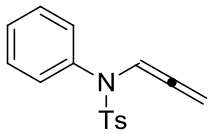
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J =8.2 Hz, 2H), 7.32 (d, J =8.1 Hz, 2H), 7.27 (dd, J =8.2, 5.4 Hz, 2H), 6.96 (t, J = 5.3 Hz, 2H), 6.81 (t, J = 6.2 Hz, 1H), 5.15 (d, J = 6.2 Hz, 2H), 4.3 (s, 2H), 2.4 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 162.1 (d, J = 244.3 Hz), 143.9, 135.2, 131.8, 129.7, 129.5 (d, J = 8.1 Hz), 127.1, 115.1 (d, J = 21.3 Hz), 99.9, 88.0, 49.3, 21.5.

N-benzyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 1b[4]



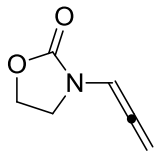
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3Hz, 2H), 7.32 (d, J = 7.9Hz, 2H), 7.30 - 7.24 (m, 5H), 6.83 (t, J = 6.2 Hz, 1H), 5.15 (d, J = 6.2 Hz, 2H), 4.30 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 143.8, 136.2, 135.4, 129.7, 128.3, 127.8, 127.4, 127.2, 100.1, 87.9, 50.0, 21.5.

4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 1c[4]



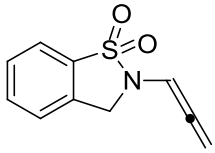
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.31 - 7.26 (m, 5H), 7.10 (t, J = 6.3 Hz, 1H), 7.01 - 6.98 (m, 2H), 5.02 (d, J = 6.3 Hz, 2H), 2.43 (S, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 143.8, 137.1, 135.2, 129.5, 129.4, 128.6, 128.5, 127.6, 102.3, 87.4, 21.5.

3-(propa-1,2-dien-1-yl)oxazolidin-2-one 1d[4]



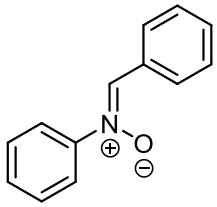
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (t, J = 6.4 Hz, 1H), 5.39 (d, J = 6.3 Hz, 2H), 4.37 (t, J = 7.9 Hz, 2H), 3.56 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 155.2, 96.9, 87.8, 62.3, 43.1.

2-(propa-1,2-dien-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 1e[4]



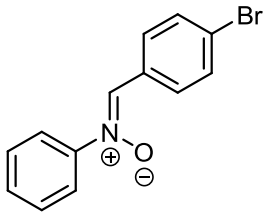
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.63 (td, J = 7.5, 0.9 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 6.76 (t, J = 6.2 Hz, 1H), 5.51 (d, J = 6.2 Hz, 2H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 134.8, 133.1, 132.8, 129.2, 124.6, 121.4, 95.3, 88.6, 48.6.

(*Z*)-N-benzylideneaniline oxide 2a [5]



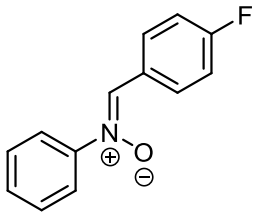
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 - 8.38 (m, 2H), 7.92 (s, 1H), 7.78 - 7.76 (m, 2H), 7.48 - 7.47 (m, 2H); ^{3}C NMR (100 MHz, $CDCl_3$) δ 149.1, 134.6, 130.9, 129.9, 129.1, 128.6, 121.7.

(*Z*)-N-(4-bromobenzylidene) aniline oxide 2b[8]



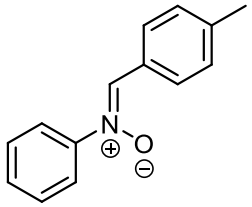
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.6Hz, 2H), 7.88 (s, 1H), 7.76 - 7.73 (m, 2H), 7.59 - 7.57 (m, 2H), 7.47 - 7.46 (m, 3H), 3.80 (s, 3H), 2.70 (t, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 133.4, 131.8, 130.2, 130.1, 129.5, 129.2, 124.7, 121.6.

(*Z*)-N-(4-fluorobenzylidene) aniline oxide 2c[9]



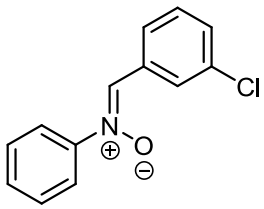
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 - 8.41 (m, 2H), 7.89 (s, 1H), 7.74 - 7.72 (m, 2H), 7.45 - 7.43 (m, 3H), 7.14 - 7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, J = 251.9 Hz), 148.7, 133.2, 131.2 (d, J = 8.2 Hz), 129.8, 129.0, 127.0, 121.5, 115.6(d, J = 21.6Hz).

(*Z*)-N-(4-methylbenzylidene) aniline oxide 2d[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.2 Hz, 2H), 7.87 (s, 1H), 7.76 - 7.74 (m, 2H), 7.45 - 7.43 (m, 3H), 7.27 - 7.25 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.4, 134.4, 129.6, 129.2, 129.0, 127.9, 121.5, 21.6.

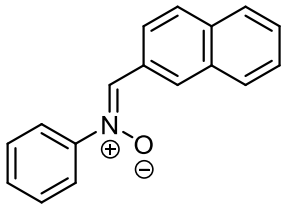
(*Z*)-N-(3-chlorobenzylidene) aniline oxide 2e[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.17 - 8.14 (m, 1H), 7.90 (s, 1H), 7.77 -

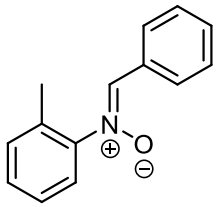
7.75 (m, 2H), 7.51 - 7.417 (m, 3H), 7.45-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7, 133.1, 132.2, 130.7, 130.2, 129.8, 129.2, 128.4, 127.0, 121.7.

(*Z*)-N-(naphthalen-2-ylmethylene) aniline oxide 2f[9]



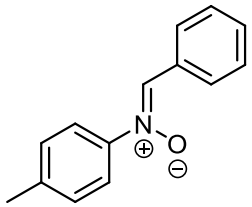
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.06 (s, 1H)， 8.02 - 7.96 (m, 2H), 7.88 (d, J = 8.6 Hz, 1H), 7.83 - 7.81 (m, 3H), 7.56 - 7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 134.4, 134.3, 133.1, 129.8, 129.3, 129.1, 129.0, 128.0, 127.8, 127.6, 127.5, 126.5, 126.1, 121.6.

(*Z*)-N-benzylidene-2-methylaniline oxide 2g[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 - 8.34 (m, 2H), 7.57 (s, 1H), 7.49 - 7.47 (m, 3H), 7.39 (d, J = 7.6 Hz, 1H), 7.36 - 7.25 (m, 3H), 2.4 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.5, 131.7, 131.4, 130.8, 130.4, 129.3, 128.7, 128.6, 126.7, 123.3, 17.0.

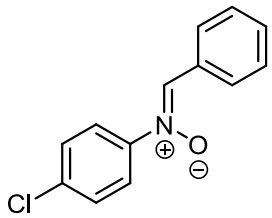
(*Z*)-N-benzylidene-4-methylaniline oxide 2h[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 - 8.37 (m, 2H), 7.89 (s, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.47 - 7.45(m, 3H), 7.26 - 7.24 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz,

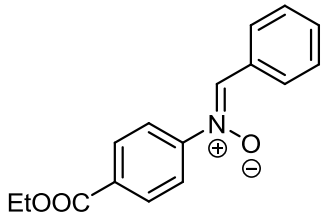
$CDCl_3$) δ 146.7, 140.1, 134.0, 130.7, 129.5, 128.9, 128.5, 121.4, 21.2.

(*Z*)-N-benzylidene-4-chloroaniline oxide 2i [10]



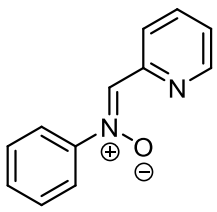
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 - 8.36 (m, 2H), 7.89 (s, 1H), 7.72 (d, *J* = 8.8Hz, 2H), 7.47 - 7.46 (m, 3H), 7.44 - 7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 135.7, 134.4, 131.1, 130.3, 129.2, 129.0, 128.6, 122.9.

(*Z*)-N-benzylidene-4-(ethoxycarbonyl) aniline oxide 2j[9]



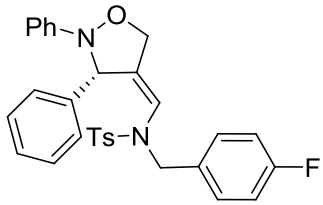
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 - 8.40 (m, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.97 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.50 - 7.49 (m, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 151.7, 135.2, 131.7, 131.3, 130.5, 130.2, 129.2, 128.6, 121.6, 61.4, 14.2.

(*Z*)-N-(pyridin-2-ylmethylene) aniline oxide 2k[11]



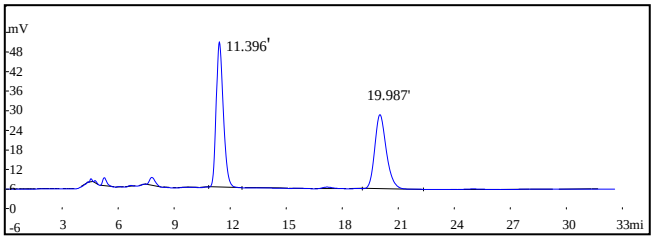
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 4.4 Hz, 1H), 8.26 (s, 1H), 7.84 - 7.78 (m, 3H), 7.47 - 7.46 (m, 3H), 7.32 - 7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.7, 148.7, 136.7, 135.5, 130.4, 129.2, 124.5, 123.9, 121.6.

(*S, E*)-N-((2,3-diphenylisoxazolidin-4-ylidene)methyl)-N-(4-fluorobenzyl)-4-meth ylbenzenesulfonamide 3a



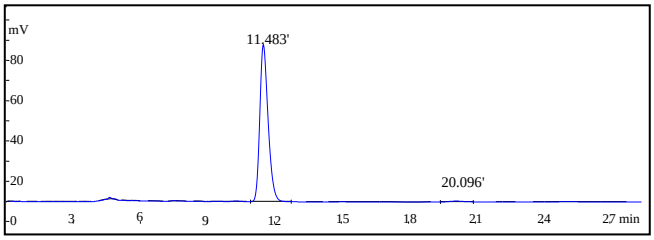
Obtained as a white solid in 99% yield and 98.3% ee. $[\alpha]_D^{20}$ = - 6.0 (*c* = 0.25); M.p. 170 – 172 ^{o}C; IR (neat) 3030, 2922, 1597, 1508, 1348, 1220, 1165, 750, 696, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.33 - 7.25 (m, 7H), 7.21 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.82 - 6.73 (m, 4H), 5.69 (s, 1H), 5.53 (s, 1H), 4.63 (s, 2H), 4.30 (d, *J* = 14.9 Hz, 1H), 3.76 (d, *J* = 14.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 244.5 Hz), 149.5, 144.0, 141.6, 139.3, 134.9, 130.7, 129.7, 129.4 (d, *J* = 8.1 Hz), 128.7, 127.9, 127.6, 127.3, 122.4, 117.9, 115.4 (d, *J* = 17.4 Hz), 70.2, 69.5, 52.7, 21.5. HRMS (ESI) calcd for $C_{30}H_{28}FN_2O_3S$ $[M+H]^+$ 515.1799; found, 515.1793. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S, E*)-**3a**, t_R = 11.3 min, (*R, E*)-**3a**, t_R = 19.9min.

Racemic sample



	R. T.	Area (%)	Area
1	11. 396	54. 04	1170073
2	19. 987	45. 96	995016

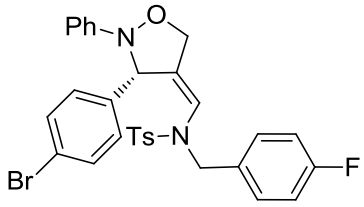
3a, 98.3% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



	R. T.	Area (%)	Area
1	11. 483	99. 18	2008666
2	20. 096	0. 8138	16482

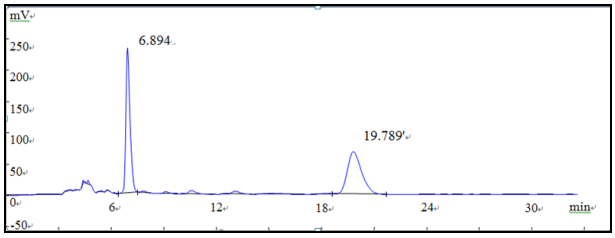
(*S, E*)-N-((3- (4-bromophenyl)-2-phenylisoxazolidin-4ylidene)methyl)-N-(4-fluoro

benzyl) -4-methylbenzenesulfonamide 3b



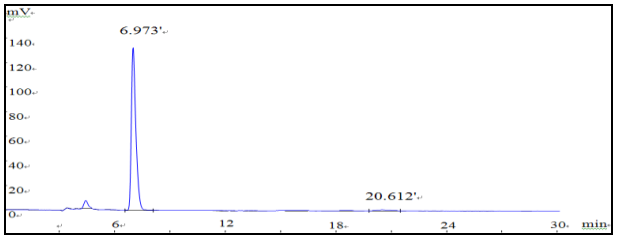
Obtained as a white solid in 94% yield and 96.7% ee. $[\alpha]_D^{20}$ = - 11.6 (*c* = 0.4); M.p. 166 – 168 ^oC; IR (neat) 3061, 2922, 1595, 1510, 1344, 1224, 1165, 1010, 748, 567; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.35 - 7.33 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 - 7.17 (m, 4H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.82 (t, *J* = 8.6 Hz, 2H), 6.75 – 6.71 (m, 2H), 5.61 (s, 1H), 5.53 (s, 1H), 4.64 – 4.56 (m, 2H), 4.44 (d, *J* = 14.3 Hz, 1H), 3.53 (d, *J* = 14.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.5 Hz), 149.3, 144.2, 143.5, 138.3, 134.5, 131.5, 130.3, 129.8, 129.7 (d, *J* = 8.3 Hz), 128.8, 127.4, 122.6, 121.7, 118.3, 115.6, 115.4 (d, *J* = 21.5 Hz), 69.8, 69.4, 53.6, 21.6. HRMS (ESI) calcd for $C_{30}H_{27}BrFN_2O_3S$ $[M+H]^+$ 593.0904; found, 593.0902. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3b**, t_R = 6.8 min, (*R*, *E*)-**3b**, t_R = 19.7min.

Racemic sample



	R. T.	Area (%)	Area
1	6. 894	50. 02	3853713
2	19. 789	49. 98	3851139

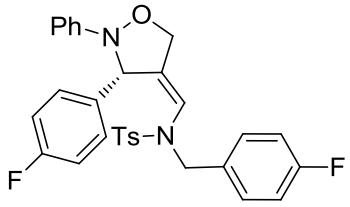
3b, 96.7% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



	R. T.	Area (%)	Area
1	6. 973	98. 47	2264014
2	20. 612	1. 525	35061

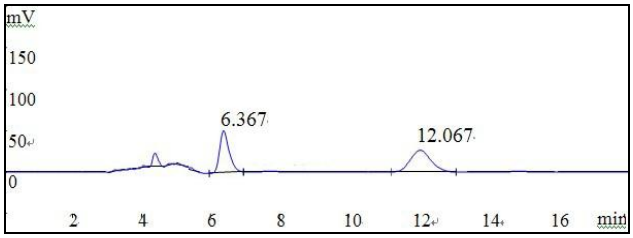
(*S*, *E*)-N-(4-fluorobenzyl)-N-((3-(4-fluorophenyl)-2-phenylisoxazolidin-4-ylidene)

methyl)-4-methylbenzenesulfonamide 3c



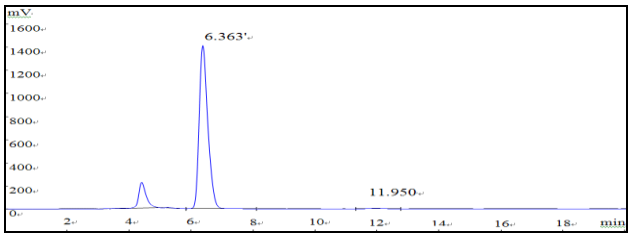
Obtained as a white solid in 91% yield and 98.1% ee. $[\alpha]_D^{20}$ = - 9.0 (*c* = 0.25); M.p. 165 – 167 °C; IR (neat) 2920, 1597, 1508, 1346, 1274, 1259, 1165, 1087, 750, 546; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53(d, *J* = 8.2 Hz, 2H), 7.28 – 7.25 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.93 – 6.90 (m, 4H), 6.83 – 6.74 (m, 4H), 5.59 (s, 1H), 5.57 (s, 1H), 4.65 – 4.58 (m, 2H), 4.38 (d, *J* = 14.5 Hz, 1H), 3.63 (d, *J* = 14.5 Hz, 1H), 2.43(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.0 Hz), 149.3, 144.2, 143.2, 135.1, 134.7, 130.54, 129.8 (d, *J* = 4.9 Hz), 129.7, 128.8, 127.4, 122.6, 118.2, 115.6, 115.4 (d, *J* = 12.0 Hz), 115.3, 115.2, 69.7, 69.4, 53.8, 21.5. HRMS (ESI) calcd for $C_{30}H_{27}F_2N_2O_3S$ $[M+H]^+$ 533.1705; found, 533.1708. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3c**, t_R = 6.3 min, (*R*, *E*)-**3c**, t_R = 12.0min.

Racemic sample



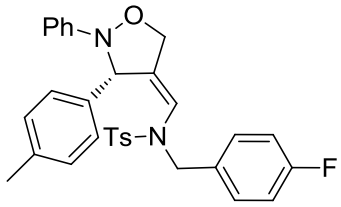
	R. T.	Area (%)	Area
1	6. 367	47. 34	970969
2	12. 067	52. 66	1080030

3c, 98.1% ee (Catalyst: (*R, R*)-L13AuCl /$AgNTf_2$)



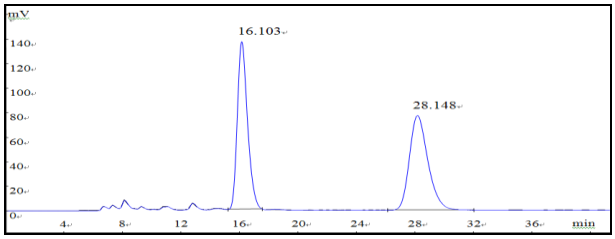
	R. T.	Area (%)	Area
1	6. 363	99. 13	27564634
2	11. 950	0. 8682	241414

(*S, E*)-N-(4-fluorobenzyl)-4-methyl-N-((2-phenyl-3-(p-tolyl)isoxazolidin-4-ylidene)methyl)benzenesulfonamide 3d



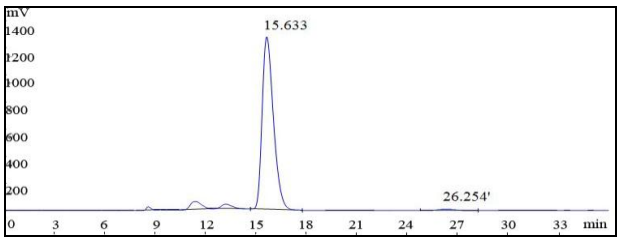
Obtained as a white solid in 99% yield and 97.4% ee. $[\alpha]_D^{20}$ = - 2.6 (*c* = 0.25); M.p. 142 – 144 ^oC; IR (neat) 2922, 1597, 1510, 1348, 1220, 1165, 1089, 815, 750, 545; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.22 - 7.17 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.79 – 6.77 (m, 4H), 5.70 (s, 1H), 5.46 (s, 1H), 4.62 (s, 2H), 4.32 (d, *J* = 15.0 Hz, 1H), 3.76 (d, *J* = 14.9 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.0 Hz), 149.6, 144.0, 141.5, 137.3, 136.4, 135.1, 130.9, 129.7, 129.5 (d, *J* = 8.0 Hz), 129.2, 128.7, 127.9, 127.3, 122.3, 117.8, 115.5, 115.3 (d, *J* = 21.5 Hz), 115.2, 70.1, 69.6, 52.7, 21.5, 21.1. HRMS (ESI) calcd for $C_{31}H_{30}FN_2O_3S$ $[M+H]^+$ 529.1955; found, 529.1960. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3d**, t_R = 16.1 min, (*R*, *E*)-**3d**, t_R = 28.1 min.

Racemic sample



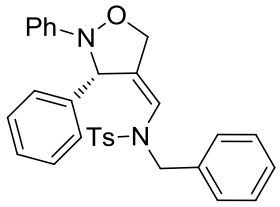
	R. T.	Area (%)	Area
1	16. 103	49. 35	6613062
2	28. 148	50. 65	6787278

3d, 97.4% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



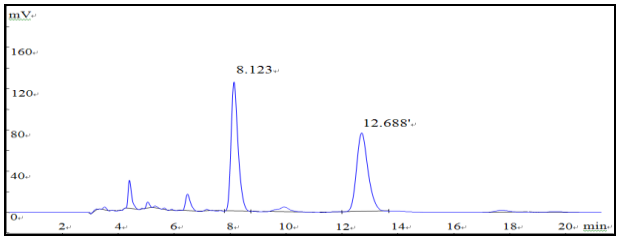
	R.T.	Area(%)	Area
1	15.633	98.74	59201050
2	26.254	1.267	759526

(*S*, *E*)-N-benzyl-N-((2,3-diphenylisoxazolidin-4-ylidene)methyl)-4-methylbenzenesulfonamide 3e



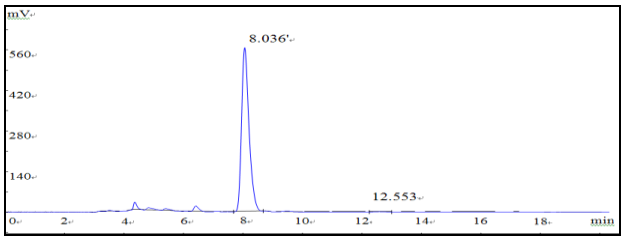
Obtained as a white solid in 99% yield and 99.1% ee. $[\alpha]_D^{20}$ = + 18.6 (*c* = 0.25); M.p. 132 – 134 ^{o}C; IR (neat) 3030, 2920, 1597, 1490, 1348, 1168, 1089, 750, 694, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.20 (m, 7H), 7.17 – 7.09 (m, 5H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 4H), 5.80 (s, 1H), 5.44 (s, 1H), 4.57 (s, 2H), 4.29 (d, *J* = 15.2 Hz, 1H), 3.84 (d, *J* = 15.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.9, 139.6, 139.3, 135.3, 135.2, 129.7, 128.8, 128.7, 128.6, 128.0, 127.6, 127.3, 122.4, 118.2, 115.5, 70.0, 69.7, 53.0, 21.5. HRMS (ESI) calcd for $C_{30}H_{29}N_2O_3S$ $[M+H]^+$ 497.1893; found, 497.1895. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3e**, t_R = 9.1 min, (*R*, *E*)-**3e**, t_R = 12.6 min.

Racemic sample



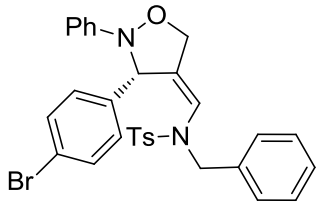
	R.T.	Area(%)	Area
1	8.123	49.95	2176856
2	12.688	50.05	2181308

3e, 99.1% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



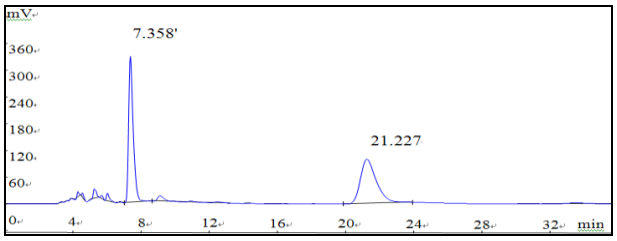
	R.T.	Area(%)	Area
1	8.036	99.57	9797066
2	12.553	0.4292	42231

(*S*, *E*)-N-benzyl-N-((3-(4-bromophenyl)-2-phenylisoxazolidin-4-ylidene)methyl) -4-methylbenzenesulfonamide 3f



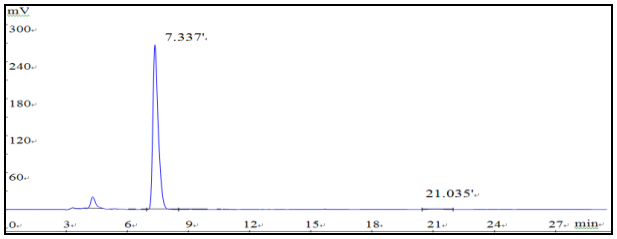
Obtained as a white solid in 98% yield and 98.3% ee. $[\alpha]_D^{20}$ = - 4.2 (*c* = 0.25); M.p. 188 – 190 ^{o}C; IR (neat) 2926, 1595, 1487, 1348, 1274, 1165, 1025, 750, 694, 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.24 – 7.14 (m, 7H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.3 Hz, 2H), 5.64 (s, 1H), 5.62 (s, 1H), 4.63 – 4.56 (m, 2H), 4.50 (d, *J* = 14.5 Hz, 1H), 3.62 (d, *J* = 14.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 144.1, 141.8, 138.4, 134.7, 131.5, 129.8, 128.8, 128.6, 127.9, 127.8, 127.4, 122.6, 118.6, 115.6, 69.5, 54.0, 21.6. HRMS (ESI) calcd for $C_{30}H_{28}BrN_2O_3S$ $[M+H]^+$ 575.0998; found, 575.1010. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3f**, t_R = 7.3 min, (*R*, *E*)-**3f**, t_R = 21.2 min.

Racemic sample



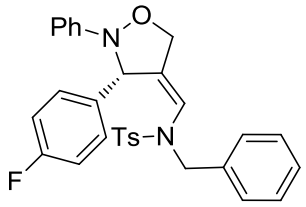
	R.T.	Area(%)	Area
1	7.358	49.07	6182725
2	21.227	50.93	6417183

3f, 98.3% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



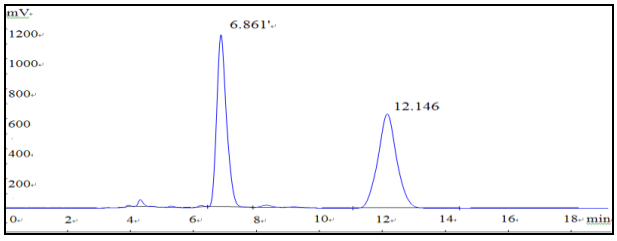
	R.T.	Area(%)	Area
1	7.337	99.19	4893578
2	21.035	0.8091	39916

(*S, E*)-N-benzyl-N-((3-(4-fluorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl) -4-methylbenzenesulfonamide 3g



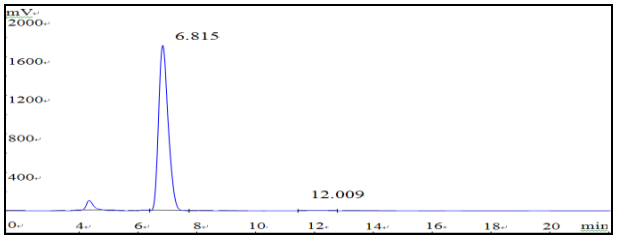
Obtained as a white solid in 88% yield and 98.8% ee. $[\alpha]_D^{20}$ = + 3.6 (*c* = 0.25); M.p. 174 – 176 ^{o}C; IR (neat) 2922, 1597, 1508, 1348, 1220, 1167, 1089, 754, 694, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.14 (m, 9H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.92 – 6.88 (m, 4H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.70 (s, 1H), 5.62 (s, 1H), 4.61 (s, 2H), 4.47 (d, *J* = 14.7 Hz, 1H), 3.71 (d, *J* = 14.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.3 Hz), 149.4, 144.1, 141.3, 135.3, 134.9, 129.8, 129.7 (d, *J* = 8.1 Hz), 128.8, 128.6, 127.9, 127.7, 127.4, 122.5, 118.4, 115.6, 115.3 (d, *J* = 21.3 Hz), 69.5, 69.4, 53.8, 21.5. HRMS (ESI) calcd for $C_{30}H_{28}FN_2O_3S$ $[M+H]^+$ 515.1799; found, 515.1800. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3g**, t_R = 6.8 min, (*R*, *E*)-**3g**, t_R = 12.1 min.

Racemic sample



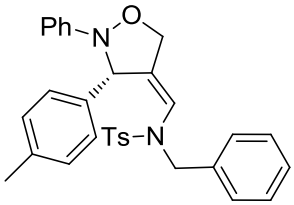
	R.T.	Area(%)	Area
1	6.861	48.59	24808362
2	12.146	51.41	26243290

3g, 98.8% ee (Catalyst: (*R, R*)-L13AuCl /$AgNTf_2$)



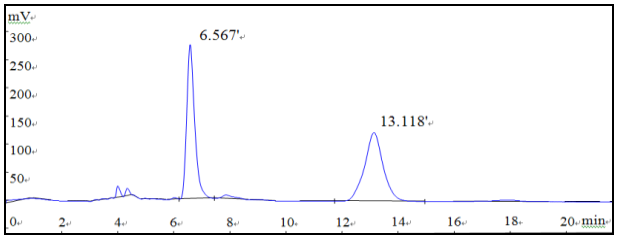
	R.T.	Area(%)	Area
1	6.815	99.43	38763357
2	12.009	0.5688	221756

(*S, E*)-N-benzyl-4-methyl-N-((2-phenyl-3-(p-tolyl)isoxazolidin-4-ylidene)methyl) benzenesulfonamide 3h



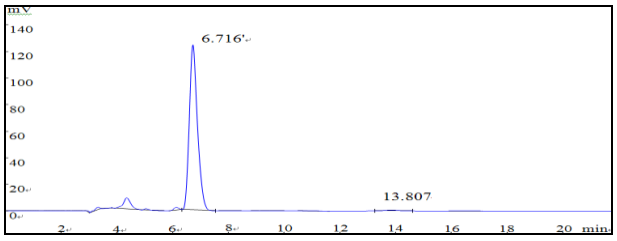
Obtained as a white solid in 99% yield and 97.7% ee. $[\alpha]_D^{20}$ = + 14.0 (*c* = 0.25); M.p. 158 – 159 ^{o}C; IR (neat) 3028, 2920, 1595, 1487, 1346, 1274, 1165, 1029, 750, 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55(d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.14 (m, 7H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 5.88(s, 1H), 5.41 (s, 1H), 4.60 (s, 2H), 4.35 (d, *J* = 15.3 Hz, 1H), 3.89 (d, *J* = 15.3 Hz, 1H), 3.89 (d, *J* = 15.3 Hz 1H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.8, 138.9, 137.2, 136.6, 135.4, 135.3, 129.7, 129.2, 128.7, 128.5, 127.8, 127.5, 127.3, 122.2, 117.9, 115.5, 69.7, 52.8, 21.5, 21.1. HRMS (ESI) calcd for $C_{31}H_{31}N_2O_3S$ $[M+H]^+$ 511.2049; found, 511.2060. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3h**, t_R = 6.5 min, (*R*, *E*)-**3h**, t_R = 13.1 min.

Racemic sample



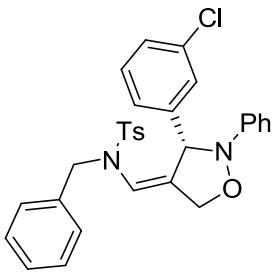
	R.T.	Area(%)	Area
1	6.567	49.04	5425518
2	13.118	50.96	5636826

3h, 97.7% ee (Catalyst: (*R, R*)-L13AuCl /AgNTf$_2$)



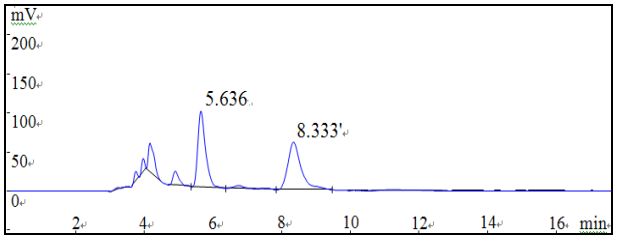
	R.T.	Area(%)	Area
1	6.716	98.76	2522700
2	13.807	1.239	31658

(*S, E*)-N-benzyl-N-((3-(3-chlorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)-4-methylbenzenesulfonamide 3i



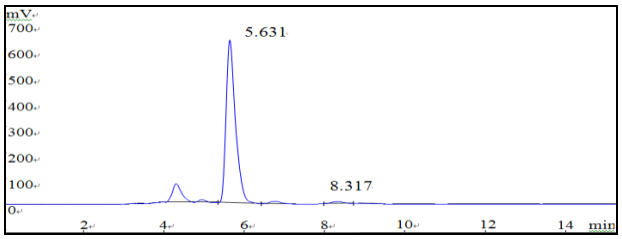
Obtained as a white solid in 99% yield and 96.7% ee. $[\alpha]_D^{20}$ = - 4.4 (*c* = 0.25); M.p. 160 – 162 ^{o}C; IR (neat) 3062, 2922, 1595, 1490, 1348, 1213, 1165, 1089, 763, 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.31 - 7.24 (m, 4H), 7.23 - 7.13 (m, 7H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 5.74 (s, 1H), 5.58 (s, 1H), 4.59 (s, 2H), 4.44 (d, *J* = 14.8 Hz, 1H), 3.74 (d, *J* = 14.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 144.1, 141.5, 140.1, 134.8, 134.7, 134.4, 129.8, 129.6, 128.8, 128.6, 128.0, 127.9, 127.8, 127.7, 127.3, 126.4, 122.5, 118.6, 115.5, 69.5, 69.4, 53.6, 21.5. HRMS (ESI) calcd for $C_{30}H_{28}ClN_2O_3S$ $[M+H]^+$ 531.1503; found, 513.1499. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3i**, t_R = 5.6 min, (*R*, *E*)-**3i**, t_R = 8.3 min.

Racemic sample



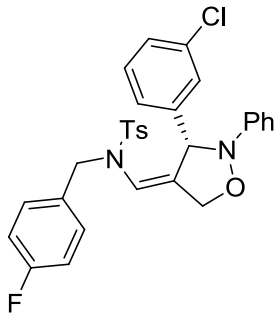
	R.T.	Area(%)	Area
1	5.636	48.31	1534894
2	8.333	51.69	1642602

3i, 96.7% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



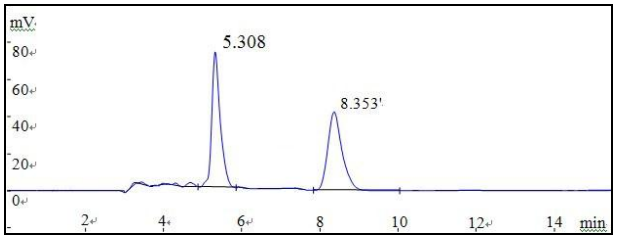
	R.T.	Area(%)	Area
1	5.631	98.38	10133623
2	8.317	1.622	167101

(*S*, *E*)-N-(4-fluorobenzyl)-N-((3-(3-chlorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)-4-methylbenzenesulfonamide 3j



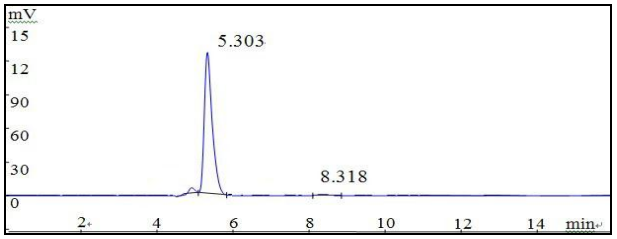
Obtained as a white solid in 95% yield and 97.7% ee. $[\alpha]_D^{20}$ = - 10.8 (*c* = 0.25); M.p. 183 – 185 ^oC; IR (neat) 3622, 3026, 1595, 1510, 1348, 1274, 1165, 750, 692, 545; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 - 7.28 (m, 2H), 7.26 – 7.16 (m, 6H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.80 - 6.74 (m, 4H), 5.63 (s, 1H), 5.59 (s, 1H), 4.61 (s, 2H), 4.41 (d, *J* = 14.5 Hz, 1H), 3.62 (d, *J* = 14.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.1 Hz), 149.2, 144.2, 142.5, 141.4, 134.5, 134.3, 130.4, 129.8, 129.5 (d, *J* = 7.9 Hz), 128.8, 128.0, 127.8, 127.3, 126.4, 122.6, 118.4, 115.5, 115.4 (d, *J* = 21.3 Hz), 69.6, 69.3, 53.3, 21.5. HRMS (ESI) calcd for $C_{30}H_{27}ClFN_2O_3S$ $[M+H]^+$ 549.1420; found, 549.1421. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3j**, t_R = 5.3 min, (*R*, *E*)-**3j**, t_R = 8.3 min.

Racemic sample



	R.T.	Area(%)	Area
1	5.308	50.35	1096149
2	8.353	49.65	1081011

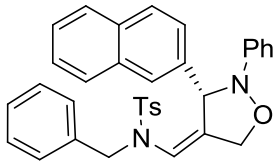
3j, 97.7% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



	R.T.	Area(%)	Area
1	5.303	98.87	1816656
2	8.318	1.132	20803

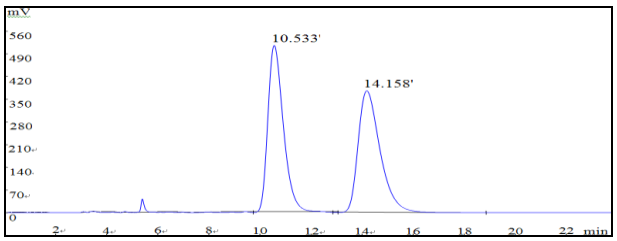
(*S*, *E*)-N-benzyl-4-methyl-N-((3-(naphthalen-2-yl)-2-phenylisoxazolidin-4-

ylidene)methyl)benzenesulfonamide 3k



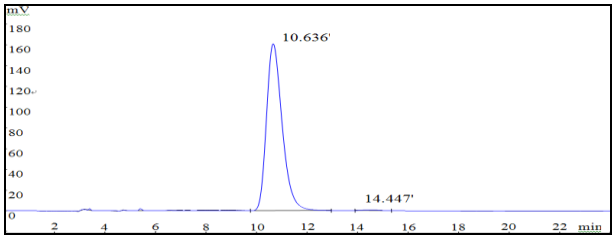
Obtained as a white solid in 92% yield and 98.9% ee. $[\alpha]_D^{20}$ = - 3.6 (*c* = 0.25); M.p. 158 – 160 ^oC; IR (neat) 3059, 2920, 1597, 1489, 1348, 1165, 1089, 1028, 734, 545; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.76 – 7.72 (m, 3H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51-7.48 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.08 (t, *J* = 7.4Hz, 1H), 6.97 – 6.87 (m, 5H), 6.71 (d, *J* = 7.4 Hz, 1H), 5.90 (s, 1H), 5.70 (s, 1H), 4.73 – 4.66 (m, 2H), 4.38 (d, *J* = 15.1 Hz, 1H), 3.77 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.9, 137.0, 135.1, 134.9, 132.9, 129.7, 128.7, 128.3, 128.1, 127.5, 127.4, 127.3, 127.2, 127.0, 126.0, 125.9, 122.3, 118.3, 115.5, 70.1, 69.8, 53.0, 21.5. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_3S$ $[M+H]^+$ 547.2049; found, 547.2054. Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3k**, t_R = 10.3 min, (*R*, *E*)-**3k**, t_R = 14.1 min.

Racemic sample



	R.T.	Area(%)	Area
1	10.533	49.45	21889803
2	14.158	50.55	22376795

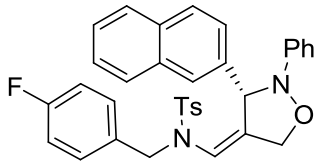
3k, 98.9% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



	R.T.	Area(%)	Area
1	10.636	99.46	6952249
2	14.447	0.5456	38136

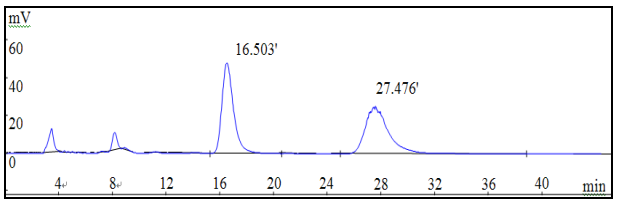
(*S*, *E*)-N-(4-fluorobenzyl)-4-methyl-N-((3-(naphthalen-2-yl)-2-phenylisoxazolidin

-4-ylidene)methyl)benzenesulfonamide 3m



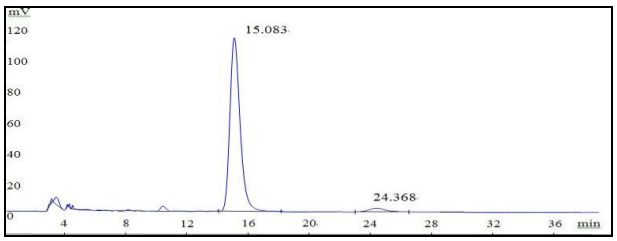
Obtained as a white solid in 92% yield and 92.1% ee. $[\alpha]_D^{20}$ = - 13.8 (*c* = 0.25); M.p. 169 – 171 ^oC; IR (neat) 3423, 3059, 2905, 1508, 1346, 1222, 1165, 1089, 742, 545; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.77 – 7.72 (m, 3H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.53 -7.47 (m, 3H), 7.24 – 7.20 (m, 3H), 6.97 - 6.95(m, 3H), 6.58 (d, *J* = 5.4 Hz, 1H), 6.57 (d, *J* = 5.3 Hz, 1H), 6.44 (t, *J* = 8.6 Hz, 2H), 5.77 (s, 1H), 5.68 (s, 1H), 4.71 (s, 2H), 4.34 (d, *J* = 14.7 Hz, 1H), 3.58 (t, *J* = 14.7 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.7 Hz), 149.7, 144.1, 142.3, 136.8, 134.8, 133.3, 133.0, 130.4, 129.4 (d, *J*= 8.1 Hz), 128.8, 128.4, 128.1, 127.6, 127.3, 127.2, 126.1, 125.9, 122.4, 118.2, 115.5, 115.1 (d, *J* = 21.4 Hz), 70.6, 69.7, 53.1, 21.5. HRMS (ESI) calcd for $C_{34}H_{30}FN_2O_3S$ $[M+H]^+$ 565.1955; found, 565.1964. Enantioselectivity determined by chiral HPLC analysis, Phenomenex-Lux, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3m**, t_R = 16.5 min, (*R*, *E*)-**3m**, t_R = 27.4 min.

Racemic sample



	R.T.	Area(%)	Area
1	16.503	48.38	2896902
2	27.476	51.62	3090540

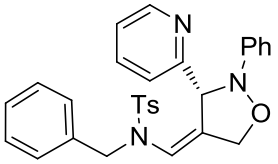
3m, 92.1% ee (Catalyst: (*R*, *R*)-L13AuCl/$AgNTf_2$)



	R.T.	Area(%)	Area
1	15.083	96.09	5192813
2	24.368	3.912	211415

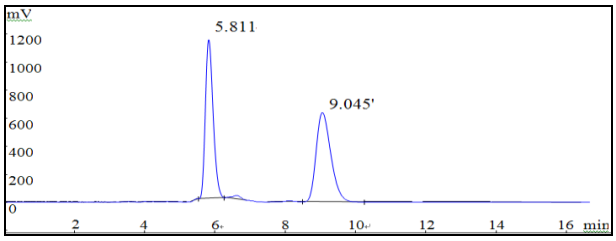
(*R*, *E*)-N-benzyl-4-methyl-N-((2-phenyl-3-(pyridin-2-yl)isoxazolidin-4-ylidene)me

thyl)benzenesulfonamide 3n



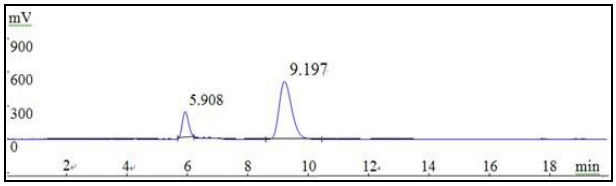
Obtained as a yellow oil in 30% yield and 63.0% ee. $[\alpha]_D^{20}$ = - 10.0 (*c* = 0.25); IR (neat) 2924, 1475, 1346, 1274, 1165, 1091, 1047, 750, 694, 543; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.6 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.63 (td, *J* = 7.7, 1.6 Hz, 1H), 7.37 (t, *J* = 8.1 Hz, 4H), 7.32 (s, 1H), 7.25-7.19 (m, 4H), 7.15-7.10 (m, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.74 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 2H), 5.14(s, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 4.45 (d, *J* = 16.1 Hz, 1H), 4.29 (d, *J* = 16.2 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.1, 147.9, 147.7, 143.7, 137.3, 137.1, 136.7, 129.4, 128.5, 128.1, 128.0, 127.9, 127.1, 122.9, 122.4, 122.0, 116.1, 113.6, 87.8, 72.2, 48.2, 21.5. HRMS (ESI) calcd for $C_{29}H_{28}N_3O_3S$ $[M+H]^+$ 498.1845; found, 498.1848. Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3n**, t_R = 5.8 min, (*R*, *E*)-**3n**, t_R = 9.0 min.

Racemic sample



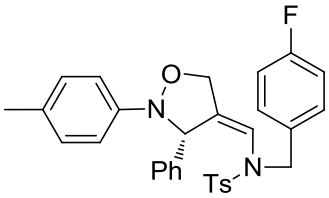
	R.T.	Area(%)	Area
1	5.811	48.33	17336698
2	9.045	51.67	18537333

3n, 63.0% ee (Catalyst: (*R*, *R*)-L13AuCl /$AgNTf_2$)



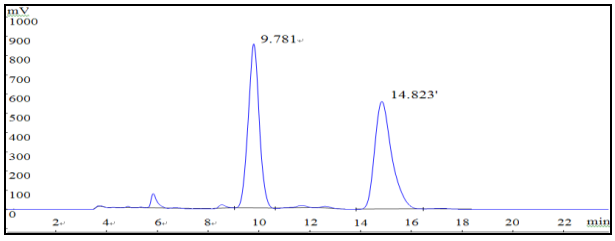
	R.T.	Area(%)	Area
1	5.908	18.5	3390725
2	9.197	81.5	14938024

(*S*, *E*)-N-(4-fluorobenzyl)-4-methyl-N-((3-phenyl-2-(p-tolyl)isoxazolidin-4-ylidene)methyl)benzenesulfonamide 3o



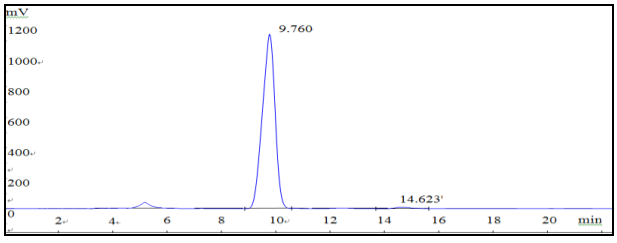
Obtained as a pale yellow solid in 96% yield and 97.2% ee. $[\alpha]_D^{20}$ = + 6.0 (*c* = 1); M.p. 163 – 165 ^{o}C; IR (neat) 3030, 2922, 1604, 1508, 1348, 1222, 1165, 1089, 750, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.29 -7.25 (m, 7H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.81 - 6.73 (m, 6H), 5.72 (s, 1H), 5.47 (s, 1H), 4.61 (s, 2H), 4.30 (d, *J* = 14.9 Hz, 1H), 3.75 (d, *J* = 14.9 Hz, 1H), 2.43 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 249.2 Hz), 147.1, 144.0, 141.6, 139.4, 135.0, 134.1, 134.0, 132.0, 129.7, 129.4 (d, *J*= 8.1 Hz), 129.2, 128.5, 128.0, 127.6, 127.3, 117.8, 115.9, 115.3 (d, *J* = 21.4 Hz), 70.4, 69.5, 52.6, 21.5, 20.5. HRMS (ESI) calcd for $C_{31}H_{30}FN_2O_3S$ $[M+H]^+$ 529.1955; found, 529.1958. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3o**, t_R = 9.7 min, (*R*, *E*)-**3o**, t_R = 14.8 min.

Racemic sample



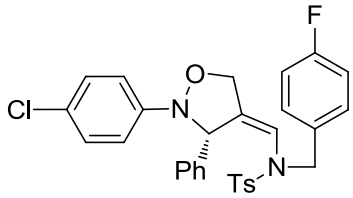
	R.T.	Area(%)	Area
1	9.781	49.8	25911437
2	14.823	50.2	26114744

3o, 97.2% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



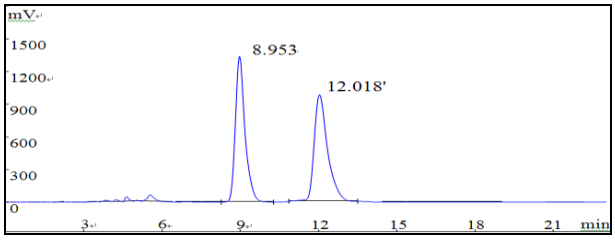
	R.T.	Area(%)	Area
1	9.760	98.63	36957296
2	14.623	1.37	513170

(*S, E*)-N-((2-(4-chlorophenyl)-3-phenylisoxazolidin-4-ylidene)methyl)-N-(4-fluorobenzyl)-4-methylbenzenesulfonamide 3p



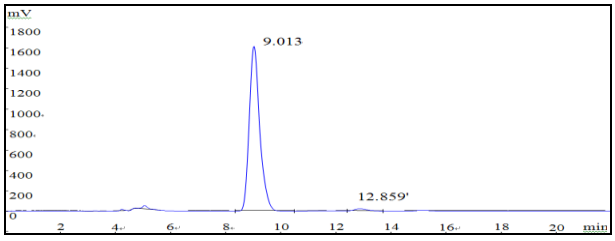
Obtained as a pale yellow solid in 83% yield and 96.8% ee. $[\alpha]_D^{20}$ = - 2.0 (*c* = 0.25); M.p. 153 – 155 ^oC; IR (neat) 2924, 1597, 1510, 1487, 1348, 1222, 1672, 1091, 746, 545; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.29 - 7.26 (m, 7H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.77 (t, *J* = 8.6 Hz, 2H), 6.73 – 6.69 (m, 2H), 5.61 (s, 1H), 5.52 (s, 1H), 4.61 (s, 2H), 4.29 (d, *J* = 14.5 Hz, 1H), 3.69 (d, *J* = 14.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.9 Hz), 148,2, 144.2, 142.4, 138.9, 134.7, 130.6, 129.8, 129.6 (d, *J* = 8.1 Hz), 128.7, 128.6, 128.0, 127.8, 127.5, 127.4, 118.2, 116.9, 115.4 (d, *J* = 21.4 Hz), 70.4, 69.5, 53.1, 21.6. HRMS (ESI) calcd for $C_{30}H_{27}ClFN_2O_3S$ $[M+H]^+$ 549.1405; found, 549.1411. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3p**, t_R = 8.9 min, (*R*, *E*)-**3p**, t_R = 12.0 min.

Racemic sample



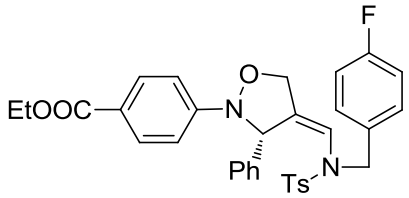
	R.T.	Area(%)	Area
1	8.953	49.66	34081171
2	12.018	50.34	34553274

3p, 96.8% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



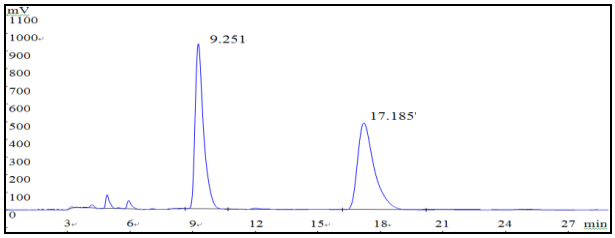
	R.T.	Area(%)	Area
1	9.013	98.43	42865494
2	12.859	1.575	686012

(*S, E*)-ethyl 4-(4-((N-(4-fluorobenzyl)-4-methylphenylsulfonamido)methylene)-3-phenylisoxazolidin-2-yl) benzoate 3q



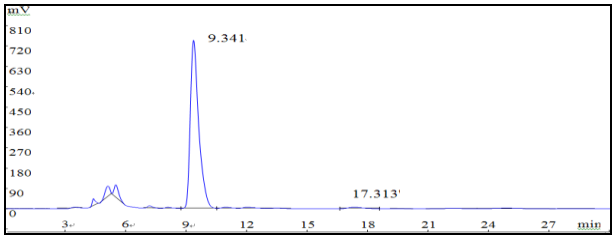
Obtained as a white solid in 45% yield and 96.7% ee. $[\alpha]_D^{20}$ = + 18.2 (*c* = 0.25); M.p. 138 – 140 ^{o}C; IR (neat) 2980, 1707, 1602, 1508, 1623, 1165, 1222, 1165, 1107, 742, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.26 (m, 7H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.75 (t, *J* = 8.6 Hz, 2H), 6.70 – 6.66 (m, 2H), 5.69 (s, 1H), 5.55 (s, 1H), 4.63 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.27 (d, *J* = 14.6 Hz, 1H), 3.68 (d, *J* = 14.4 Hz, 1H), 2.42 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.1 (d, *J* = 231.8 Hz), 153.1, 144.1, 143.0, 138.7, 134.6, 130.6, 130.4, 129.8, 129.6 (d, *J* = 8.1 Hz), 128.6, 127.9, 127.8, 127.3, 123.7, 118.2, 115.3 (d, *J* = 21.3 Hz), 114.1, 69.7, 69.6, 60.5, 53.2, 21.5, 14.3. HRMS (ESI) calcd for $C_{33}H_{32}FN_2O_5S$ $[M+H]^+$ 587.2010; found, 587.2014. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3q**, t_R = 9.2 min, (*R*, *E*)-**3q**, t_R = 17.1 min.

Racemic sample



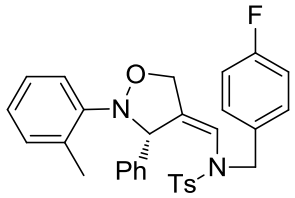
	R.T.	Area(%)	Area
1	9.251	49.18	26134594
2	17.185	50.82	27008637

3q, 96.7% ee (Catalyst: (*R*, *R*)-L13AuCl/AgNTf$_2$)



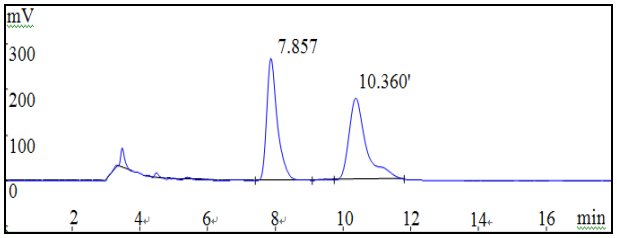
	R.T.	Area(%)	Area
1	9.341	98.36	21555614
2	17.313	1.64	359449

(*S*, *E*) -N-(4-fluorobenzyl)-4-methyl- N-((3-phenyl-2-(o-tolyl)isoxazolidin- 4-ylidene)methyl)benzenesulfonamide 3r



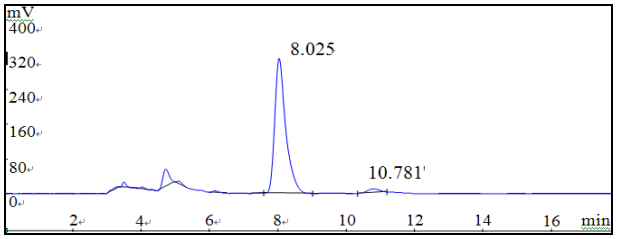
Obtained as a white solid in 72% yield and 93.9% ee. $[\alpha]_D^{20}$ = - 16.2 (*c* = 0.25); M.p. 140 – 142 ^oC; IR (neat) 3062, 2924, 1600, 1510, 1348, 1222, 1160, 815, 750, 547; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.20 (m, 5H), 7.09 – 6.98 (m, 4H), 6.84 – 6.77 (m, 4H), 5.71 (s, 1H), 5.28 (s, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.63 (q, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 14.8 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 2.44 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.5 Hz), 147.1, 143.9, 143.5, 138.5, 135.0, 131.2, 130.9, 130.8, 129.7, 129.6 (d, *J*= 8.1 Hz), 128.2, 128.0, 127.5, 127.3, 125.8, 124.8, 118.1, 117.7, 115.3 (d, *J* = 21.4 Hz), 69.9, 69.05, 52.9, 21.5, 18.6. HRMS (ESI) calcd for $C_{31}H_{30}FN_2O_3S$ $[M+H]^+$529.1955; found, 529.1961. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3r**, t_R = 7.8 min, (*R*, *E*)-**3r**, t_R = 10.3 min.

Racemic sample



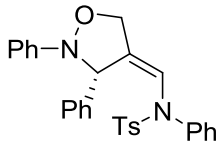
	R.T.	Area(%)	Area
1	7. 857	47. 76	5850377
2	10. 360	52. 24	6399024

3r, 93.9% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



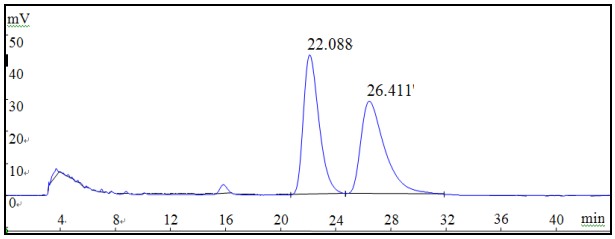
	R.T.	Area(%)	Area
1	8. 025	96. 95	6938352
2	10. 781	3. 049	218232

(*S, E*)-N-((2,3-diphenylisoxazolidin-4-ylidene)methyl)-4-methyl-N-phenyl benzenesulfonamide 3s



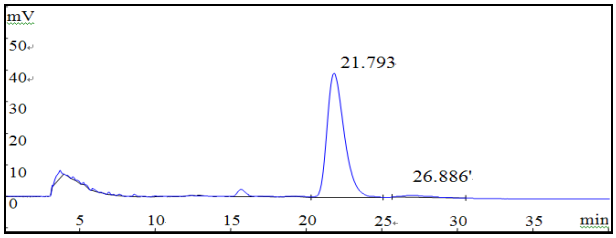
Obtained as a pale yellow solid in 88% yield and 94.4% ee. $[\alpha]_D^{20}$ = + 38.0 (*c* = 0.25); M.p. 179 – 181 ^{o}C; IR (neat) 2922, 2854, 1595, 1487, 1354, 1166, 1089, 763, 694, 569; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.13 (m, 6H), 7.11 – 7.01 (m, 7H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.65 (m, 3H), 6.61 (s, 1H), 6.59 (s, 1H), 4.60 (s, 2H), 4.53 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.1, 138.5, 138.1, 134.6, 131.7, 129.5, 128.9, 128.7, 128.2, 128.0, 127.6, 127.5, 122.3, 120.0, 115.2, 69.5, 69.2, 21.5. HRMS (ESI) calcd for $C_{29}H_{27}N_2O_3S$ $[M+H]^+$ 483.1736; found, 483.1746. Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 90: 10, 1.0 ml/min). (*S*, *E*)-**3s**, t_R = 22.08 min, (*R*, *E*)-**3s**, t_R = 26.4 min.

Racemic sample



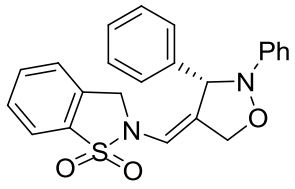
	R.T.	Area(%)	Area
1	22. 088	49. 7	3434378
2	26. 411	50. 3	3475826

3s, 94.4% ee (Catalyst: (*R, R*)-L13AuCl/AgNTf$_2$)



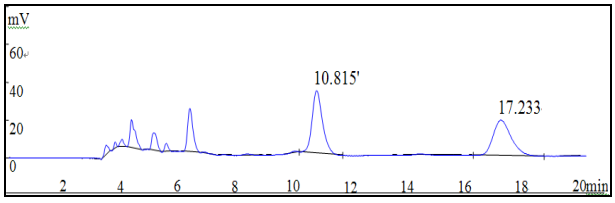
	R.T.	Area(%)	Area
1	21. 793	97. 22	3115950
2	26. 886	2. 786	89305

(*S, E*)-2-((2,3-diphenylisoxazolidin-4-ylidene)methyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 3t



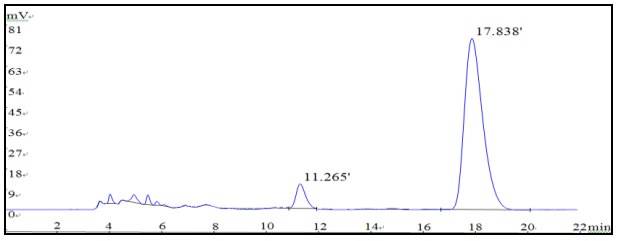
Obtained as a white solid in 97% yield and 86.1% ee. $[\alpha]_D^{20}$ = - 22.0 (*c* = 0.25); M.p. 187 – 189 ^oC; IR (neat) 3442, 2920, 1687, 1597, 1487, 1305, 1170, 1029, 750, 567; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.50 (m, 4H), 7.31 – 7.26 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 6.9 Hz, 1H), 6.12 (s, 1H), 5.77 (s, 1H), 4.81 (s, 2H), 4.16 (d, *J* = 13.6 Hz, 1H), 3.74 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 145.4, 140.0, 133.9, 132.9, 132.8, 129.2, 128.9, 128.5, 127.8, 127.7, 124.3, 122.7, 121.5, 115.5, 113.8, 70.8, 68.9, 50.8. HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$ 405.1267; found, 405.1271. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 30: 70, 1.0 ml/min). (*R*, *E*)-**3t**, t_R = 10.8 min, (*S*, *E*)-**3t**, t_R = 17.2 min.

Racemic sample



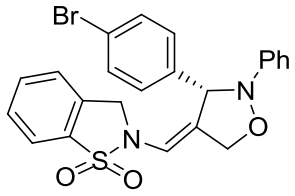
	R.T.	Area(%)	Area
1	10.815	50.58	842645
2	17.233	49.42	823473

3t, 86.1% ee (Catalyst: (*R*, *R*)-L9AuCl/AgNTf$_2$)



	R.T.	Area(%)	Area
1	11.265	6.944	274831
2	17.838	93.05	3682631

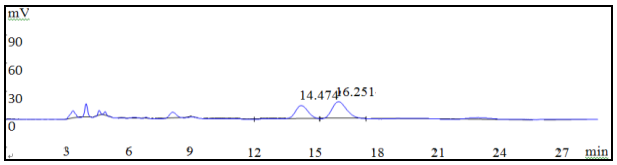
(*S*, *E*)-2-((3-(4-bromophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 3u



Obtained as a white solid in 85% yield and 97.7% ee. $[\alpha]_D^{20}$ = - 12.0 (*c* = 0.25); M.p. 225 – 227 ^oC; IR (neat) 2920, 1593, 1487, 1305, 1261, 1170, 1010, 750, 694, 552; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.45 – 7.38

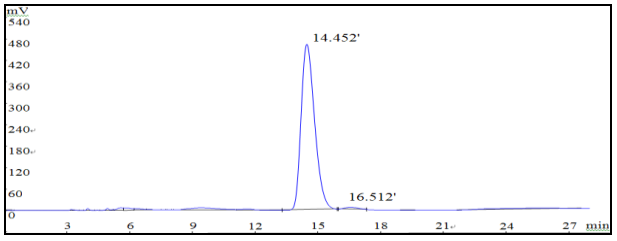
(m, 4H), 7.30 – 7.26 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.06 (s, 1H), 5.76 (s, 1H), 4.82 (s, 2H), 4.20 (d, *J* = 13.6 Hz, 1H), 3.81 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 146.2, 133.2, 132.7, 131.6, 129.7, 129.6, 129.4, 129.1, 127.9, 126.0, 124.5, 122.9, 121.6, 115.6, 114.4, 70.1, 68.8, 51.1. HRMS (ESI) calcd for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$ 483.0372; found, 483.0373. Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3u**, t_R = 14.7 min, (*R*, *E*)-**3u**, t_R = 16.2 min.

Racemic sample



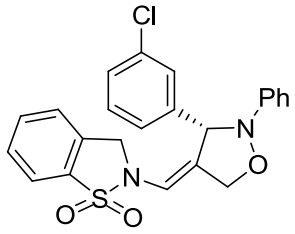
	R.T.	Area(%)	Area
1	14. 474	40. 94	628081
2	16. 251	59. 06	906137

3u, 97.7% ee (Catalyst: (*R*, *R*)- L9AuCl /$AgNTf_2$)



	R.T.	Area(%)	Area
1	14. 452	98. 87	20742637
2	16. 512	1. 13	237051

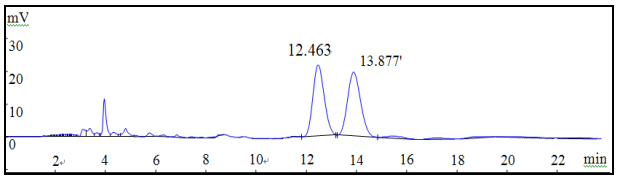
(*S*, *E*)-2-((3-(3-chlorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 3v



Obtained as a pale yellow solid in 68% yield and 93.5% ee. $[\alpha]_D^{20}$ = - 58.6 (*c* = 0.25); M.p. 98 – 100 °C; IR (neat) 3061, 2922, 1593, 1489, 1305, 1170, 1132, 758, 694, 567; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.07 (s, 1H), 5.80 (s, 1H), 4.79 (s, 2H), 4.22 (d, *J* = 13.6 Hz, 1H), 3.81 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 146.3, 133.1,

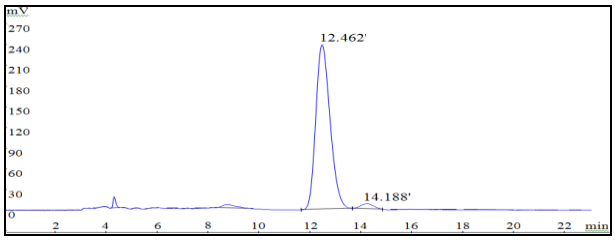
129.6, 129.4, 129.0, 128.0, 127.9, 126.0, 124.4, 122.9, 121.6, 115.5, 114.4, 70.1, 68.7, 51.1. HRMS (ESI) calcd for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$ 439.0877; found, 439.0878. Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3v**, t_R = 12.4 min, (*R*, *E*)-**3v**, t_R = 13.8 min.

Racemic sample



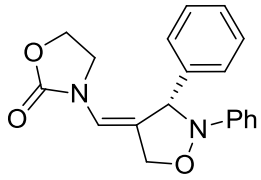
	R.T.	Area(%)	Area
1	12.463	48.94	679530
2	13.877	51.06	709034

3v, 93.5% ee (Catalyst: (*R*, *R*)-L9AuCl/AgNTf$_2$)



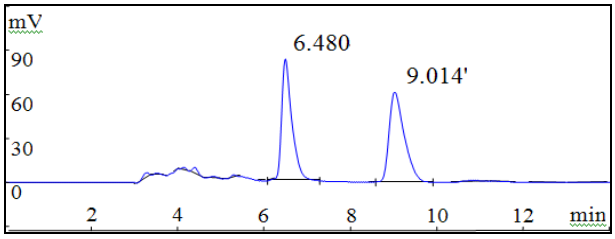
	R.T.	Area(%)	Area
1	12.462	97.26	9306261
2	14.188	2.734	261608

(*S*, *E*)-3-((2,3-diphenylisoxazolidin-4-ylidene)methyl)oxazolidin-2-one 3w



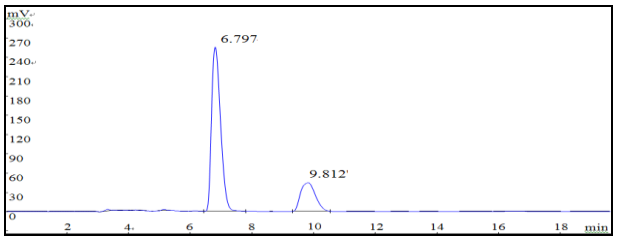
Obtained as a white solid in 91% yield and 55.4% ee. $[\alpha]_D^{20}$ = + 60.0 (*c* = 0.25); M.p. 164 – 166 ^oC; IR (neat) 2920, 1751, 1697, 1415, 1247, 1085, 1037, 738, 698, 540; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.40-7.36 (m, 2H), 7.34 - 7.27 (m, 3H), 7.11 (t, *J* = 7.6Hz, 2H), 7.00 (t, *J* = 7.2Hz, 1H), 6.53 (s, 1H), 5.50 (s, 1H), 4.80 – 4.72 (m, 2H), 4.14 (td, *J* = 8.8, 2.0 Hz, 2H), 3.58 (dd, *J* = 15.5, 8.4 Hz, 1H), 3.58 (dd, *J* = 16.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.1, 139.8, 129.1, 128.8, 128.2, 127.7, 126.3, 122.9, 116.3, 115.5, 70.8, 70.1, 62.0, 44.1. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1390; found, 323.1393. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 50: 50, 1.0 ml/min). (*S*, *E*)-**3w**, t_R = 6.4 min, (*R*, *E*)-**3w**, t_R = 9.0 min.

Racemic sample



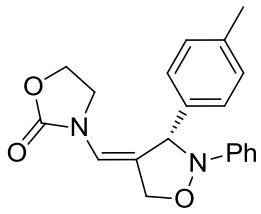
	R.T.	Area(%)	Area
1	6.480	47.79	1365590
2	9.014	52.21	1491726

3w, 55.4% ee (Catalyst: (*R*, *S*)-L12AuCl/AgNTf$_2$)



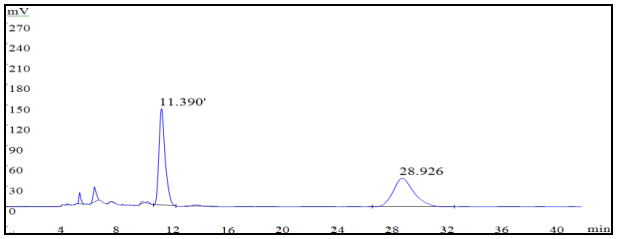
	R.T.	Area(%)	Area
1	6.797	77.7	5185944
2	9.812	22.3	1488553

(*S*, *E*)-3-((2-phenyl-3-(p-tolyl)isoxazolidin-4-ylidene)methyl)oxazolidin-2-one 3x



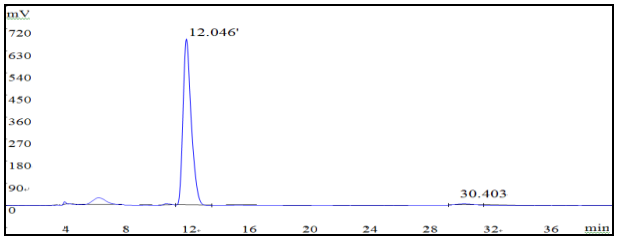
Obtained as a white solid in 99% yield and 96.8% ee. $[\alpha]_D^{20}$ = + 64.2 (*c* = 0.25); M.p. 194 – 196 ^{o}C; IR (neat) 3396, 2920, 1751, 1697, 1485, 1415, 1247, 1037, 754, 546; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.31 - 7.27 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.55 (s, 1H), 5.47 (s, 1H), 4.79 – 4.72 (m, 2H), 4.16 (t, *J* = 8.0 Hz, 2H), 3.64 – 3.54 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.2, 137.9, 136.7, 129.4, 129.0, 127.6, 125.9, 122.7, 116.0, 115.4, 70.5, 70.0, 61.9, 44.0, 21.09. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$ 337.1546; found, 337.1549. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**3x**, t_R = 11.3 min, (*R*, *E*)-**3x**, t_R = 28.9 min.

Racemic sample



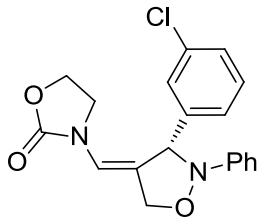
	R.T.	Area(%)	Area
1	11.390	50.05	4493761
2	28.926	49.95	4484179

3x, 96.8% ee (Catalyst: (*R, S*)-L12AuCl/AgNTf$_2$)



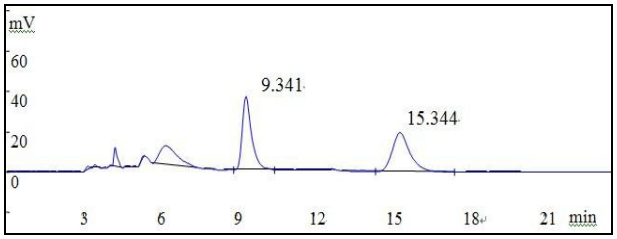
	R.T.	Area(%)	Area
1	12.046	98.43	25599912
2	30.403	1.578	410304

(*S, E*)-3-((3-(3-chlorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)oxazolidin-2-one 3y



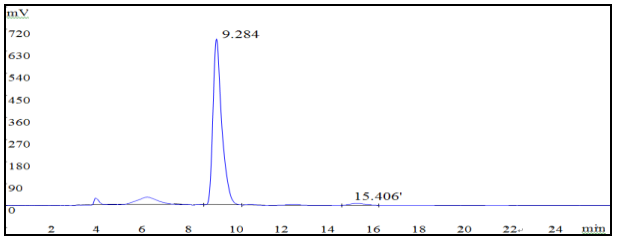
Obtained as a white solid in 99% yield and 95.7% ee. $[\alpha]_D^{20}$ = + 44.4 (*c* = 0.25); M.p. 200 – 202 ^{o}C; IR (neat) 3061, 2920, 1749, 1697, 1479, 1415, 1247, 1083, 756, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.36 - 7.28 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 5.51 (s, 1H), 4.78 – 4.71 (m, 2H), 4.25 – 4.15 (m, 2H), 3.64 – 3.58 (m, 1H), 3.57 – 3.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 149.8, 141.8, 134.7, 130.0, 129.1, 128.3, 127.8, 126.2, 125.8, 123.0, 116.6, 115.4, 70.0, 69.9, 61.9, 44.2. HRMS (ESI) calcd for $C_{19}H_{18}ClN_2O_3$ $[M+H]^+$ 357.1000; found, 357.1006. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S, E*)-**3y**, t_R = 9.3 min, (*R, E*)-**3y**, t_R = 15.3 min.

Racemic sample



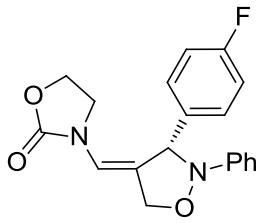
	R.T.	Area(%)	Area
1	9. 341	49. 56	930113
2	15. 344	50. 44	946511

3y, 95.7% ee (Catalyst: (*R, S*)-L12AuCl/AgNTf$_2$)



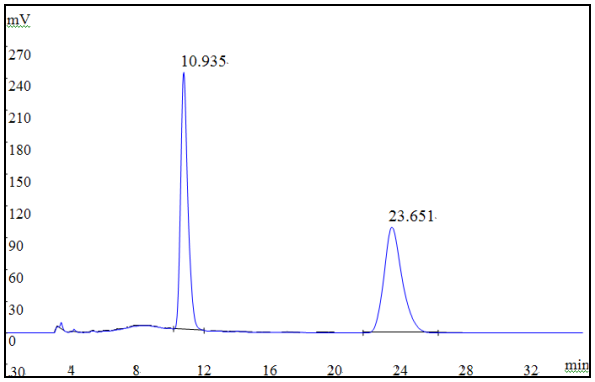
	R.T.	Area(%)	Area
1	9. 284	97. 88	18146150
2	15. 406	2. 12	392987

(*S,E*)-3-((3-(4-fluorophenyl)-2-phenylisoxazolidin-4-ylidene)methyl)oxazolidin-2-one 3z



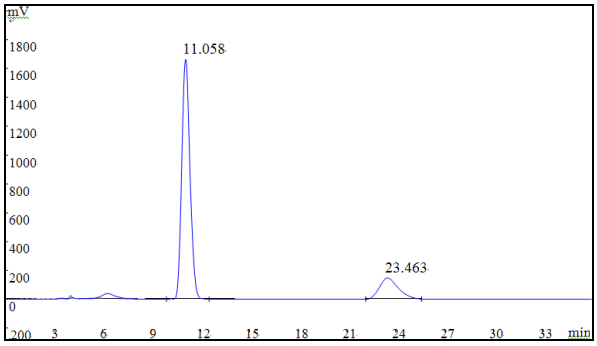
Obtained as a white solid in 99% yield and 66.1% ee. $[\alpha]_D^{20}$ = + 52.3 (*c* = 0.25); M.p. 198 – 200 ^oC; IR (neat) 3130, 2920, 1762, 1701, 1506, 1423, 1249, 1083, 758, 692; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.42 (m, 2H), 7.31 - 7.27 (m, 2H), 7.10 - 7.00 (m, 5H), 6.50 (s, 1H), 5.49 (s, 1H), 4.79 – 4.71 (m, 2H), 4.23 – 4.14 (m, 2H), 3.62 – 3.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.0 Hz), 155.7, 149.9, 135.5, 129.5 (d, *J* =8.1 Hz), 129.1, 126.9, 123.0, 116.3, 115.7 (d, *J* = 20.8 Hz), 70.1, 70.0, 61.9, 44.2. HRMS (ESI) calcd for $C_{19}H_{18}FN_2O_3$ $[M+H]^+$ 341.1301; found, 341.1306. Enantioselectivity determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S, E*)-**3z**, t_R = 10.9 min, (*R, E*)-**3z**, t_R = 23.6 min.

Racemic sample



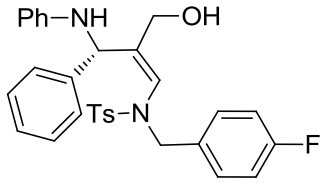
	R.T.	Area(%)	Area
1	10.935	49.12	7438567
2	23.651	50.88	7705533

3z, 66.1% ee (Catalyst: (*R, S*)-L12AuCl/AgNTf$_2$)



	R.T.	Area(%)	Area
1	11.058	83.05	58361517
2	23.463	16.95	11910199

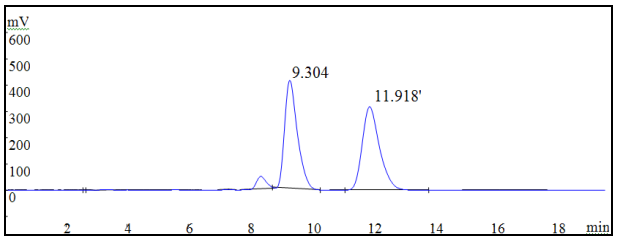
(*S, E*)-N-(4-fluorobenzyl)-N-(2-(hydroxymethyl)-3-phenyl-3-(phenylamino)prop-1-en-1-yl)-4-methylbenzenesulfonamide 4a



Obtained as a white solid in 99% yield and 98.2% ee. $[\alpha]_D^{20}$ = - 86.2 (*c* = 0.25); M.p. 86 – 87 ^{o}C; IR (neat) 3223, 2922, 1598, 1510, 1348, 1267, 1165, 750, 663, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.13 (m, 5H), 7.08 (t, *J* = 7.9 Hz, 2H), 7.03 – 7.01 (m, 2H), 6.84 (t, *J* = 8.6 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 5.59 (s, 1H), 5.54 (s, 1H), 4.22 (d, *J* = 13.8 Hz, 1H), 4.13 (d, *J* = 13.8 Hz, 1H), 3.95 (d, *J* = 13.1 Hz, 1H), 3.77 (d, *J* = 13.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.4 Hz), 146.9, 145.3, 144.2, 139.6, 134.3, 130.9 (d, *J* = 8.1 Hz), 129.8, 128.8, 128.4, 127.8, 127.1, 126.8, 125.3, 117.9, 115.4 (d, *J* = 21.3 Hz), 114.3, 62.5, 55.9, 54.4, 21.5. HRMS (ESI) calcd for $C_{30}H_{30}FN_2O_3S$ $[M+H]^+$ 517.1955; found, 517.1958. Enantioselectivity

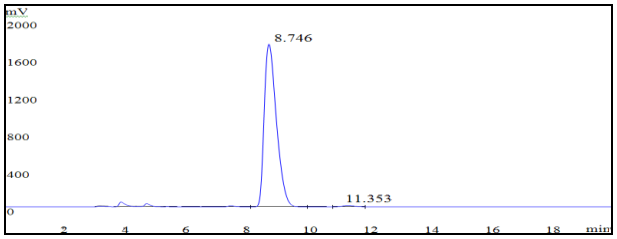
determined by chiral HPLC analysis, Chiralpak AD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**4a**, t_R = 9.3 min, (*R*, *E*)-**4a**, t_R = 11.9 min.

Racemic sample



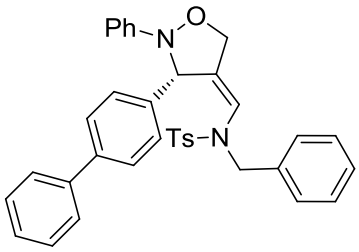
	R.T.	Area(%)	Area
1	9. 304	48. 82	11898504
2	11. 918	51. 18	12471801

4a, 98.2% ee



	R.T.	Area(%)	Area
1	8.746	99.11	48775827
2	11.353	0.89	438024

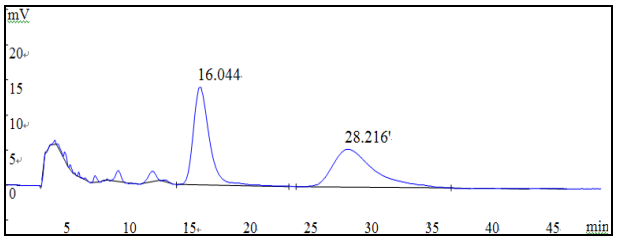
(*S*, *E*)-N-((3-([1,1'-biphenyl]-4-yl)-2-phenylisoxazolidin-4-ylidene)methyl)-N-benzyl-4-methylbenzenesulfonamide 5



Obtained as a white solid in 92% yield and 99.1% ee. $[\alpha]_D^{20}$ = + 5.6 (*c* = 0.25); M.p. 170 – 172 ^oC; IR (neat) 3028, 2920, 1595, 1487, 1348, 1165, 1089, 758, 696, 547; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.35 (m, 4H), 7.28 - 7.25 (m, 3H), 7.17 – 7.15 (m, 2H), 7.13 – 7.07 (m, 3H), 7.02 (dd, *J* = 7.5, 7.0 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.78 (dd, *J* = 8.7, 8.1 Hz, 4H), 5.76 (s, 1H), 5.53 (s, 1H), 4.54 (s, 2H), 4.39 (d, *J* = 15.1 Hz, 1H), 3.73 (d, *J* = 15.1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 143.9, 140.7, 140.4, 139.3, 138.5, 135.1, 129.7, 128.7, 128.5, 128.3, 127.5, 127.2, 126.9, 122.4, 118.2, 115.5, 69.7, 69.6, 53.1, 21.4. HRMS (ESI) calcd for $C_{36}H_{33}N_2O_3S$ $[M+H]^+$ 573.2206; found, 573.2205.

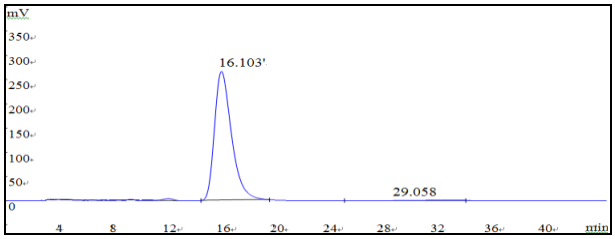
Enantioselectivity determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**5**, t_R = 16.0 min, (*R*, *E*)-**5**, t_R = 28.2 min.

Racemic sample



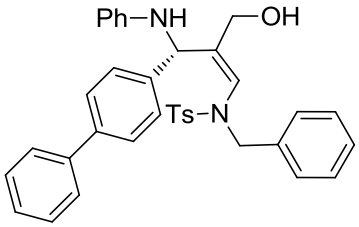
	R. T.	Area (%)	Area
1	16. 044	49. 47	1291963
2	28. 216	50. 53	1319530

5, 99.1% ee



	R. T.	Area (%)	Area
1	16. 103	99. 58	23374627
2	29. 058	0. 4205	98704

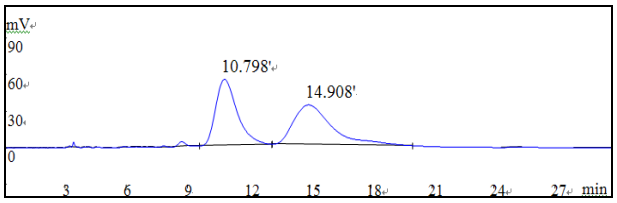
(*S*, *E*)-N-(3-([1,1'-biphenyl]-4-yl)-2-(hydroxymethyl)-3-(phenylamino)prop-1-en-1-yl)-N-benzyl-4-methylbenzenesulfonamide 6



Obtained as a white solid in 81% yield and 97.6% ee. $[\alpha]_D^{20}$ = - 37.2 (*c* = 3); M.p. 101 – 103 ^oC; IR (neat) 3404, 3028, 2924, 1600, 1498, 1344, 1163, 1089, 740, 549; ^1H NMR (400 MHz, MeOD-d_4) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.35 (dd, *J* = 9.4, 8.3 Hz, 4H), 7.29 – 7.17 (m, 6H), 7.01 (t, *J* = 10.1 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 2H), 5.70 (s, 1H), 5.53 (s, 1H), 4.43 (d, *J* = 13.9 Hz, 1H), 4.05 – 4.00 (m, 2H), 3.66 (d, *J* = 14.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, MeOD-d_4) δ 147.6, 145.3, 144.2, 140.7, 139.6, 139.5, 135.7, 134.6, 129.6, 129.0, 128.4, 128.3, 128.2, 127.7, 127.6, 127.3, 126.7, 126.4, 126.3, 124.1, 116.7, 113.6, 60.5, 55.4, 55.0, 20.1. HRMS (ESI) calcd for $C_{36}H_{35}N_2O_3S$ $[M+H]^+$ 575.2362; found, 575.2363. Enantioselectivity

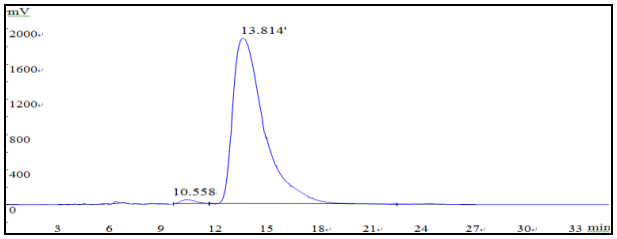
determined by chiral HPLC analysis, Chiralpak OD-H, rt, (Hexane - iPrOH = 70: 30, 1.0 ml/min). (*S*, *E*)-**6**, t_R = 10.7 min, (*R*, *E*)-**6**, t_R = 14.9 min.

Racemic sample



	R. T.	Area (%)	Area
1	10.798	47.98	3962450
2	14.908	52.02	4296823

6, 97.6% ee



	R. T.	Area (%)	Area
1	10.558	1.189	2857799
2	13.814	98.81	237547699

References

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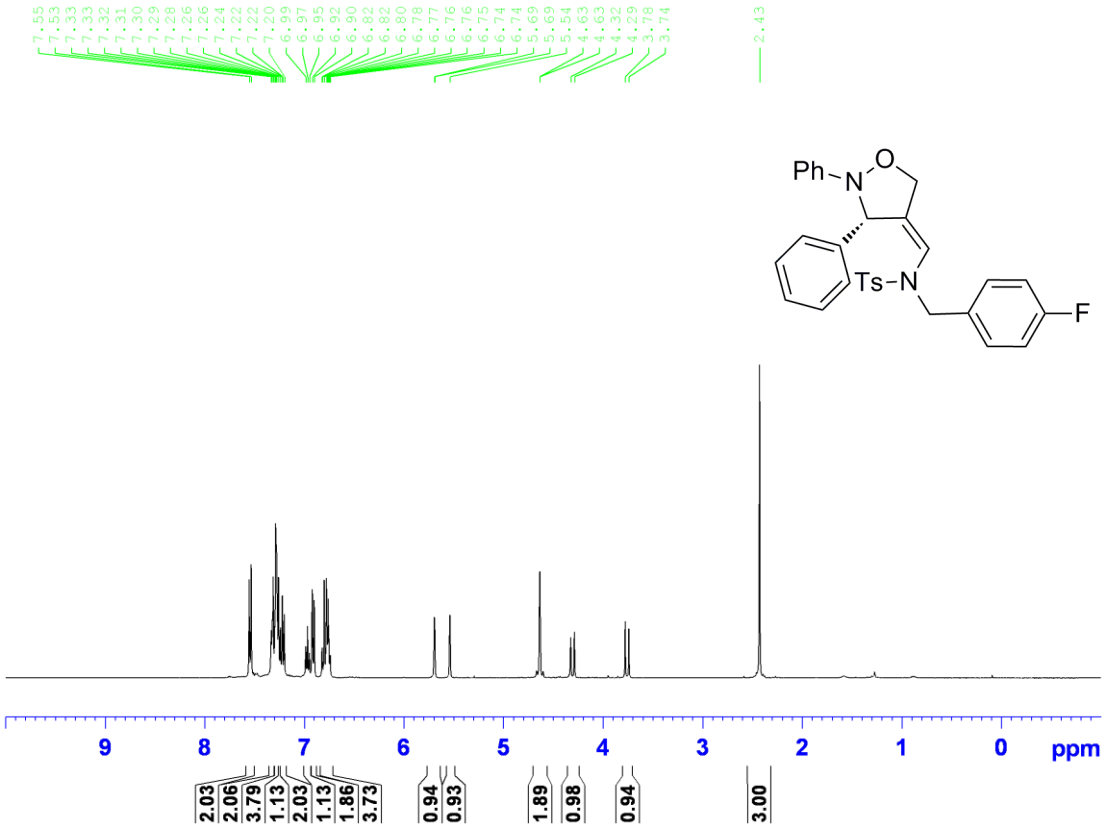
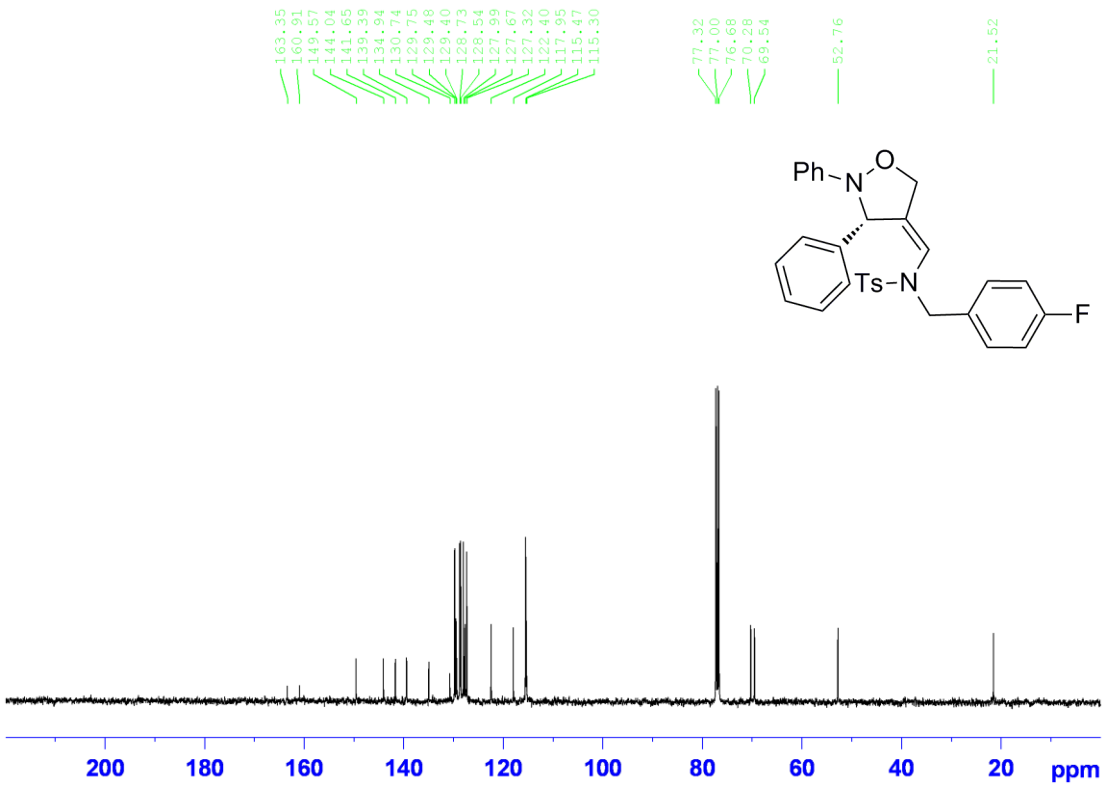
H[1]NMR and C[13]NMR spectra

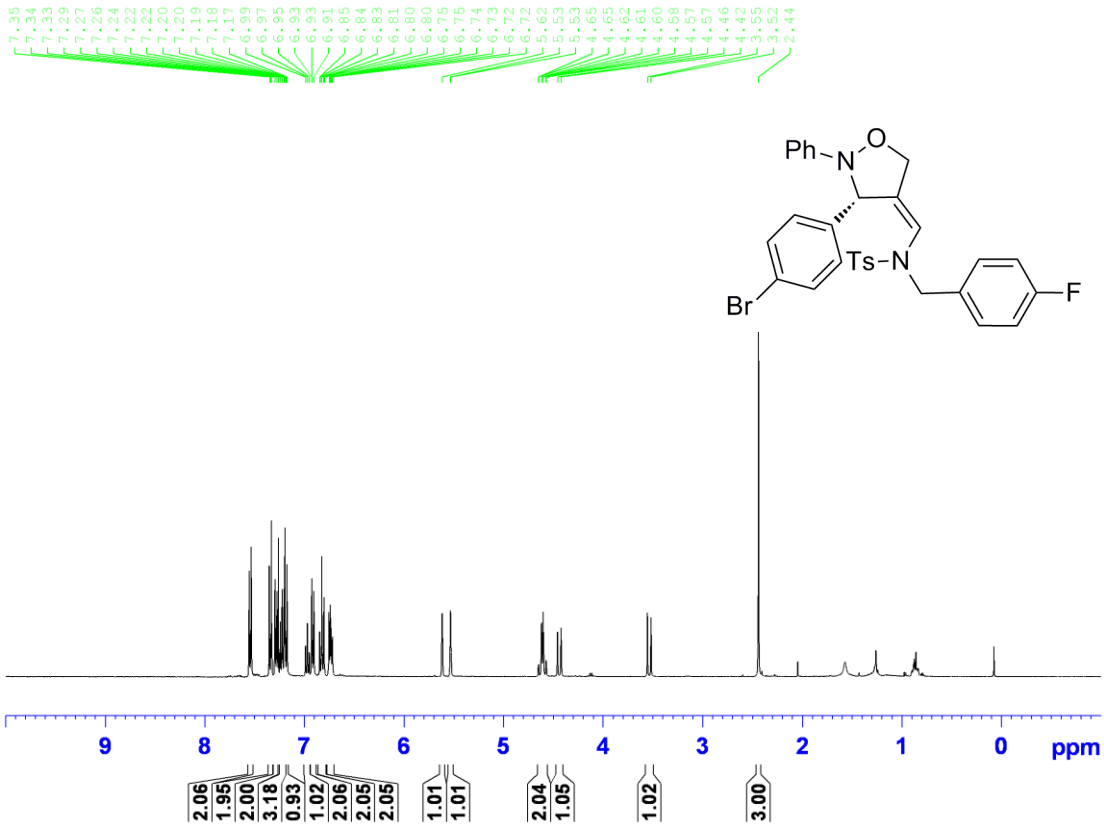
^{1}H NMR (400MHz, $CDCl_3$) of **3a**:



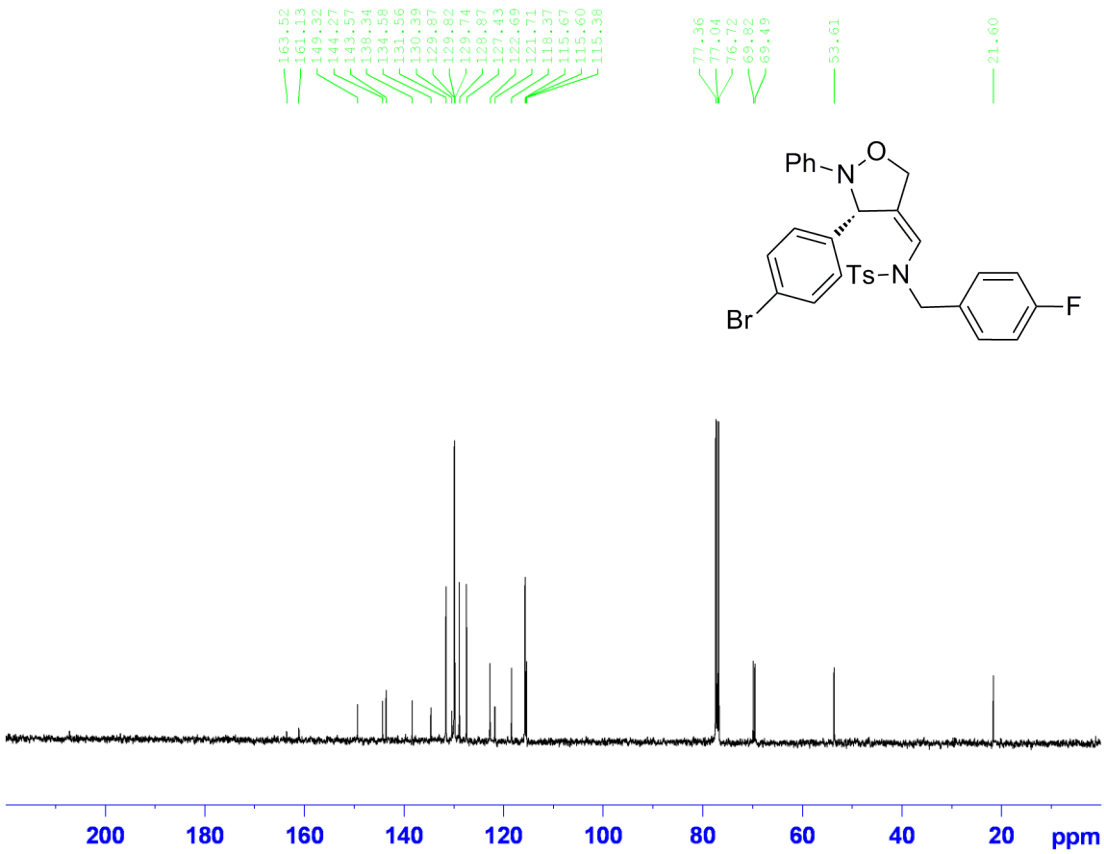
^{13}C NMR (100MHz, $CDCl_3$) of **3a**:



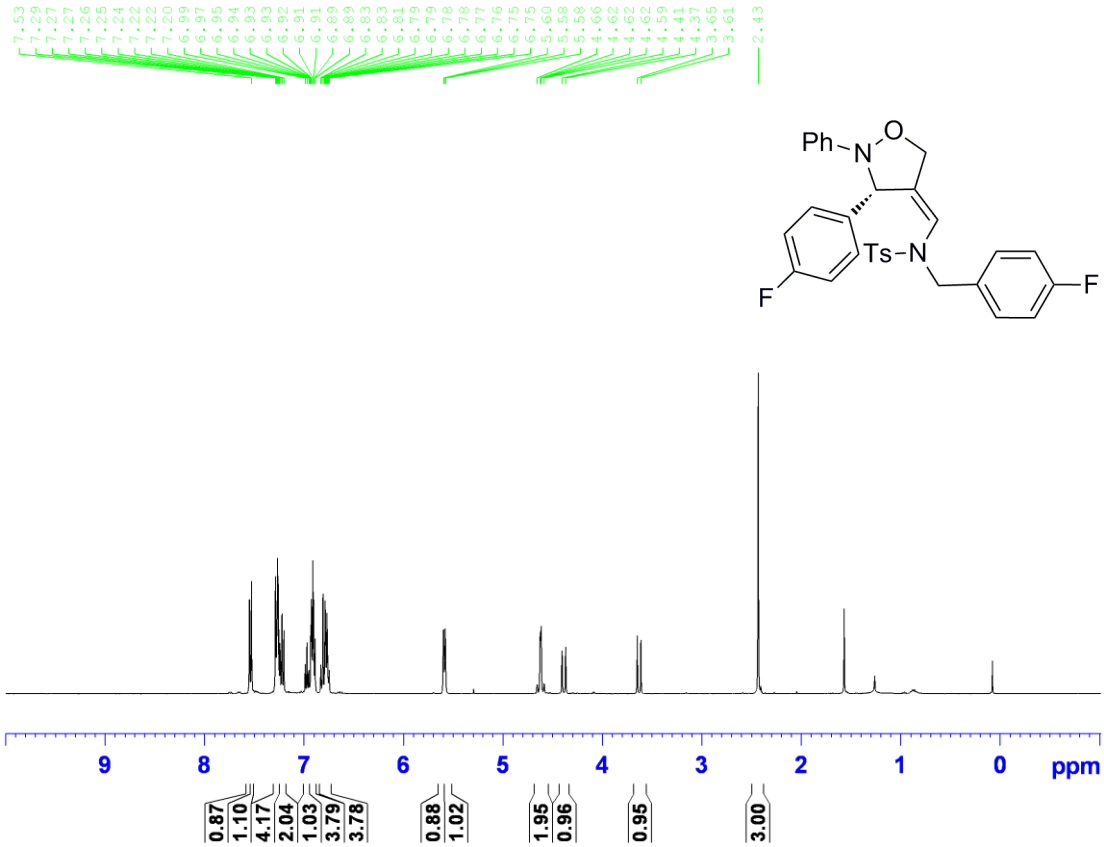
^{1}H NMR (400MHz, $CDCl_3$) of **3b**:



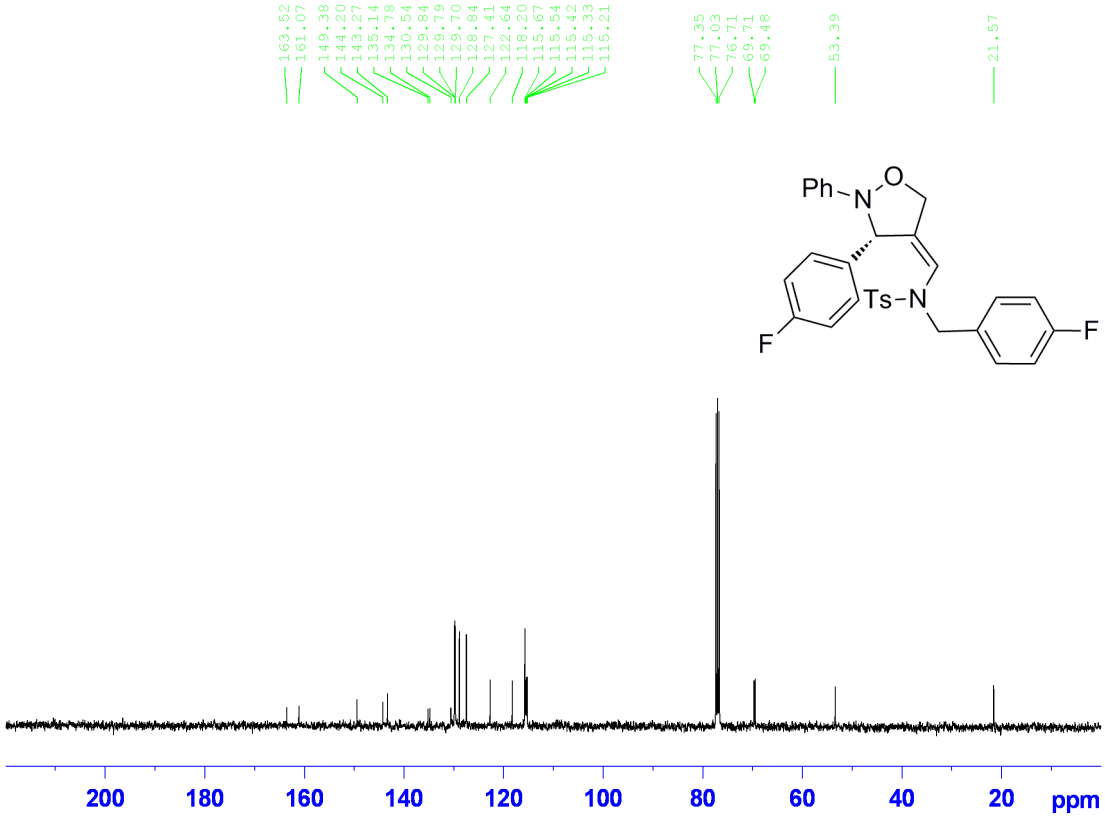
^{13}C NMR (100MHz, $CDCl_3$) of **3b**:



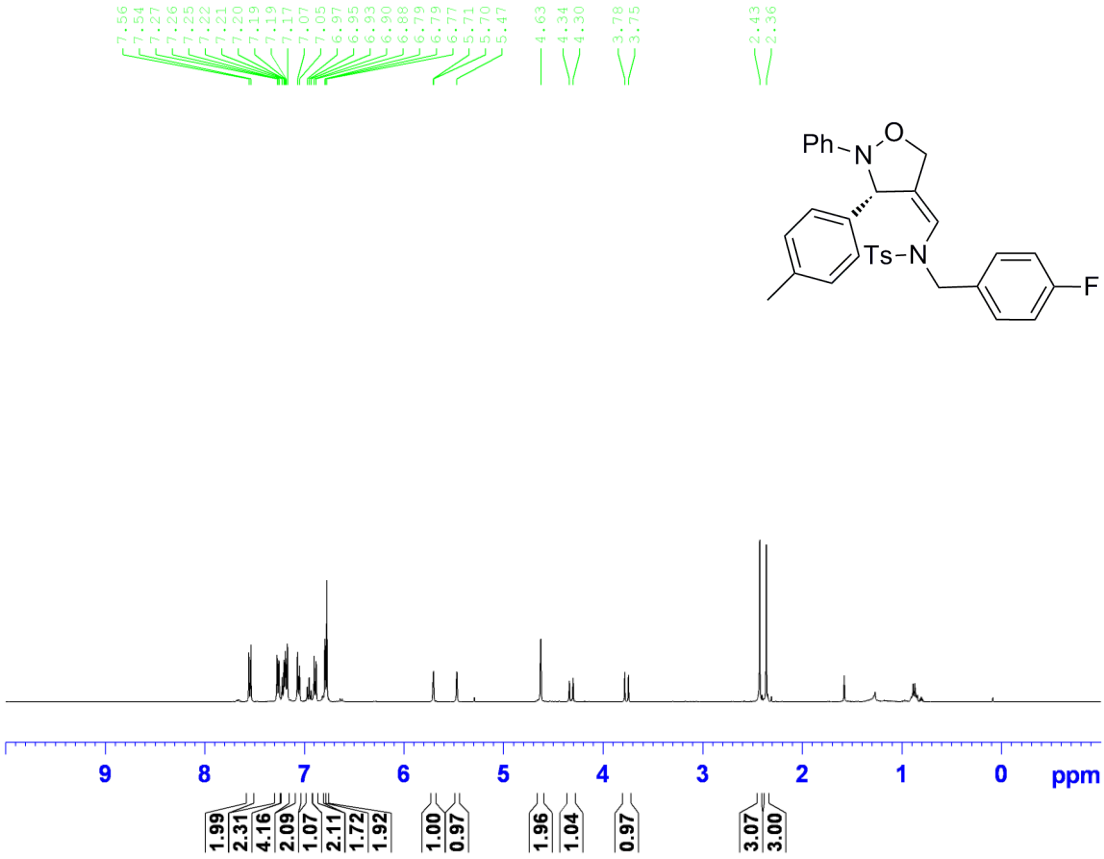
^{1}H NMR (400MHz, $CDCl_3$) of **3c**:



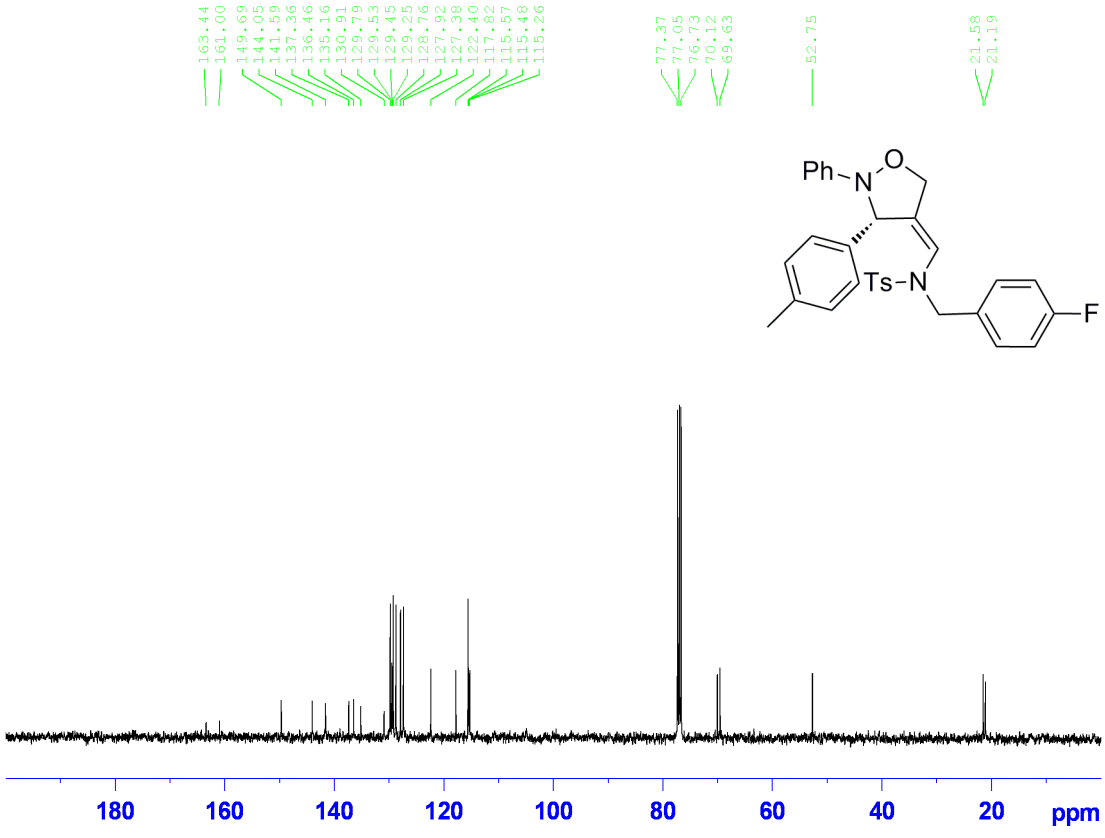
^{13}C NMR (100MHz, $CDCl_3$) of **3c**:



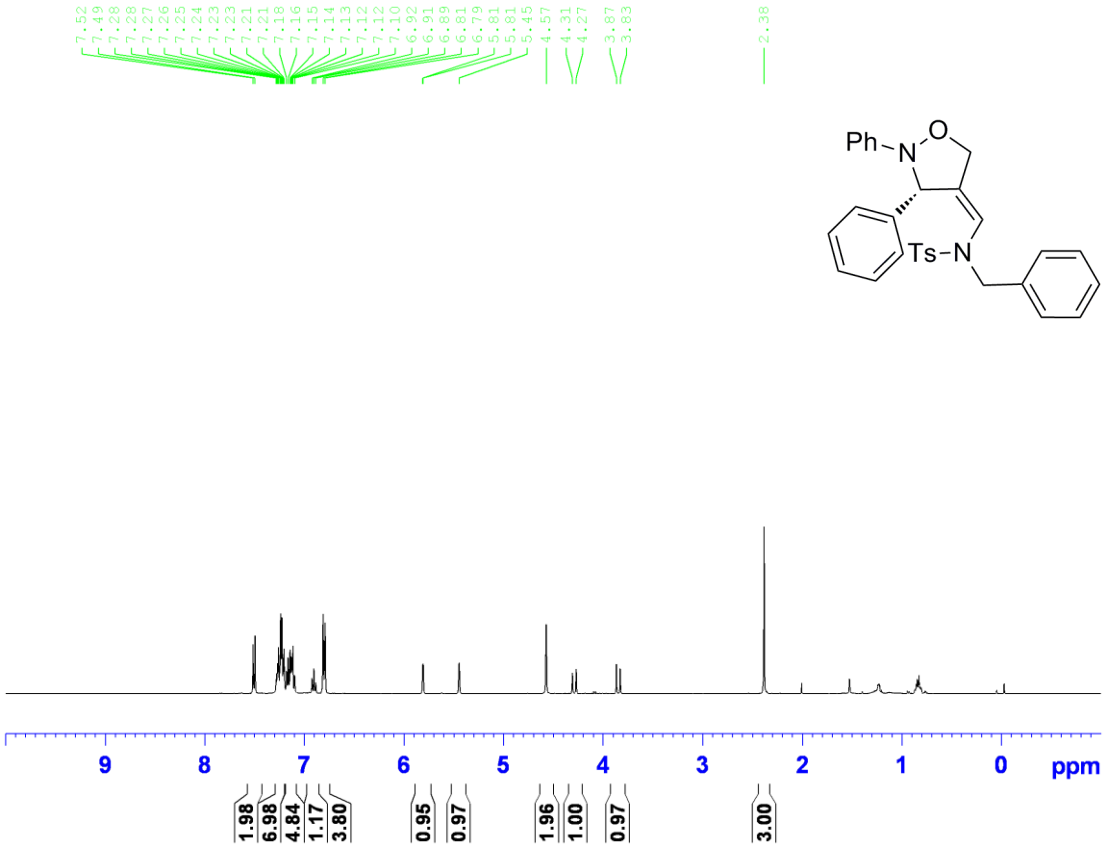
^{1}H NMR (400MHz, $CDCl_3$) of **3d**:



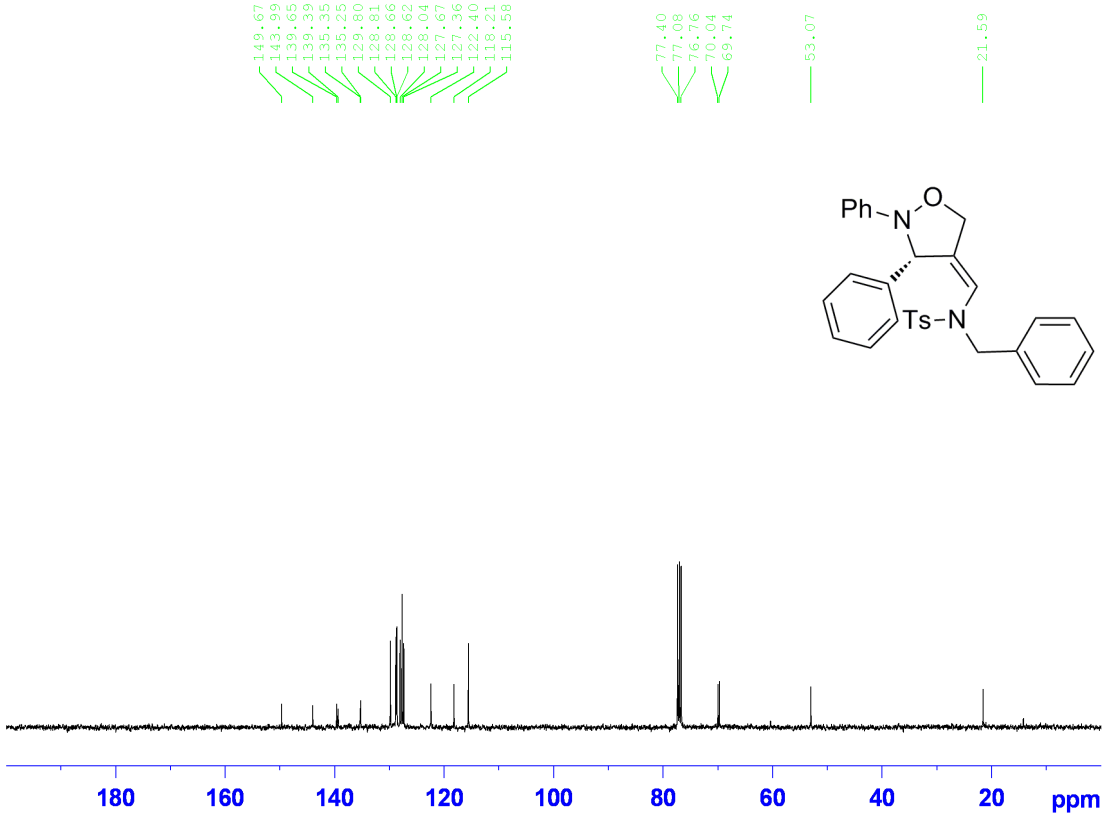
^{13}C NMR (100MHz, $CDCl_3$) of **3d**:



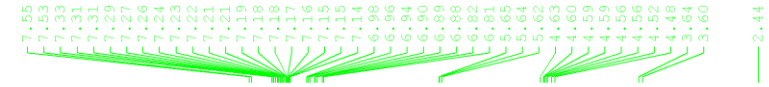
^{1}H NMR (400MHz, $CDCl_3$) of **3e**:

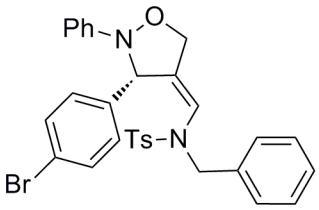


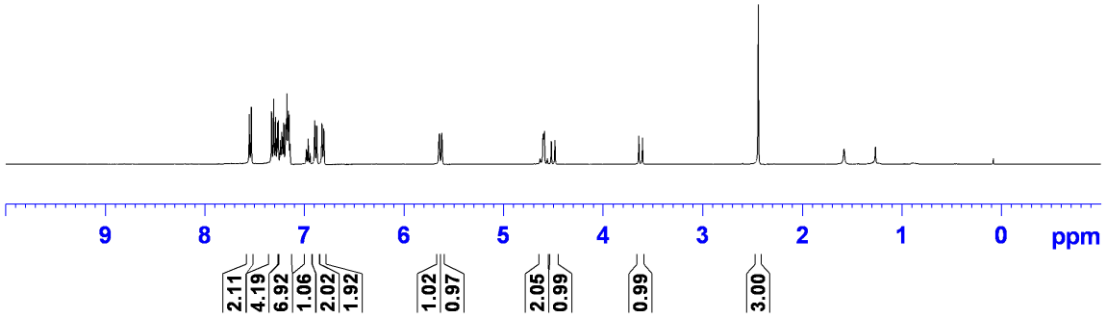
^{13}C NMR (100MHz, $CDCl_3$) of **3e**:



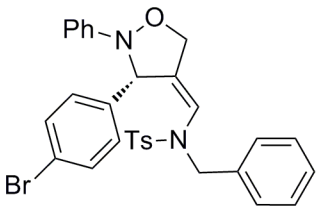
^{1}H NMR (400MHz, $CDCl_3$) of **3f**:

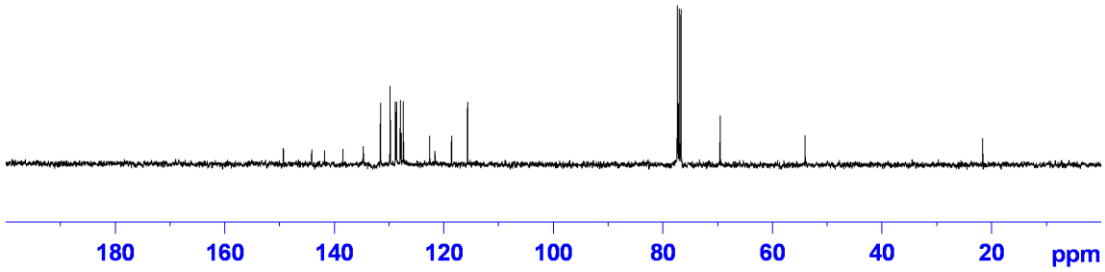




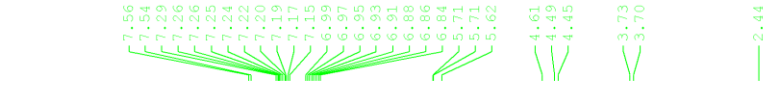


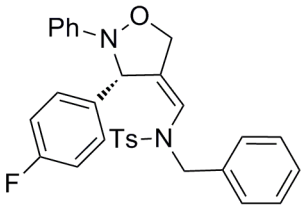
^{13}C NMR (100MHz, $CDCl_3$) of **3f**:

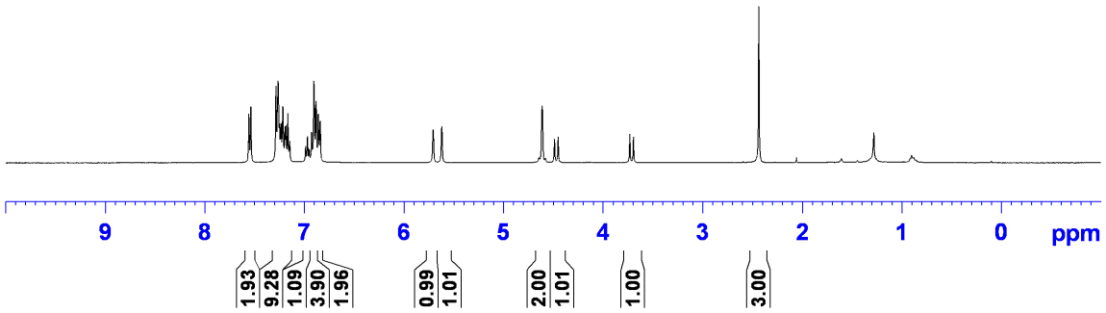




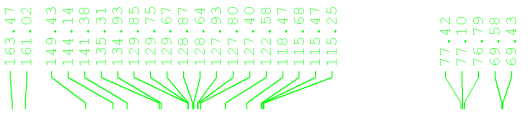
^{1}H NMR (400MHz, $CDCl_3$) of **3g**:

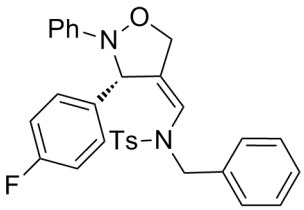


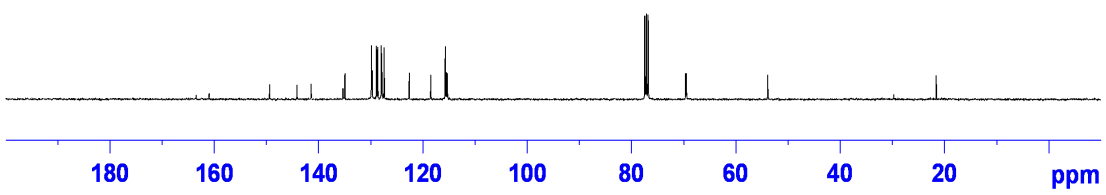




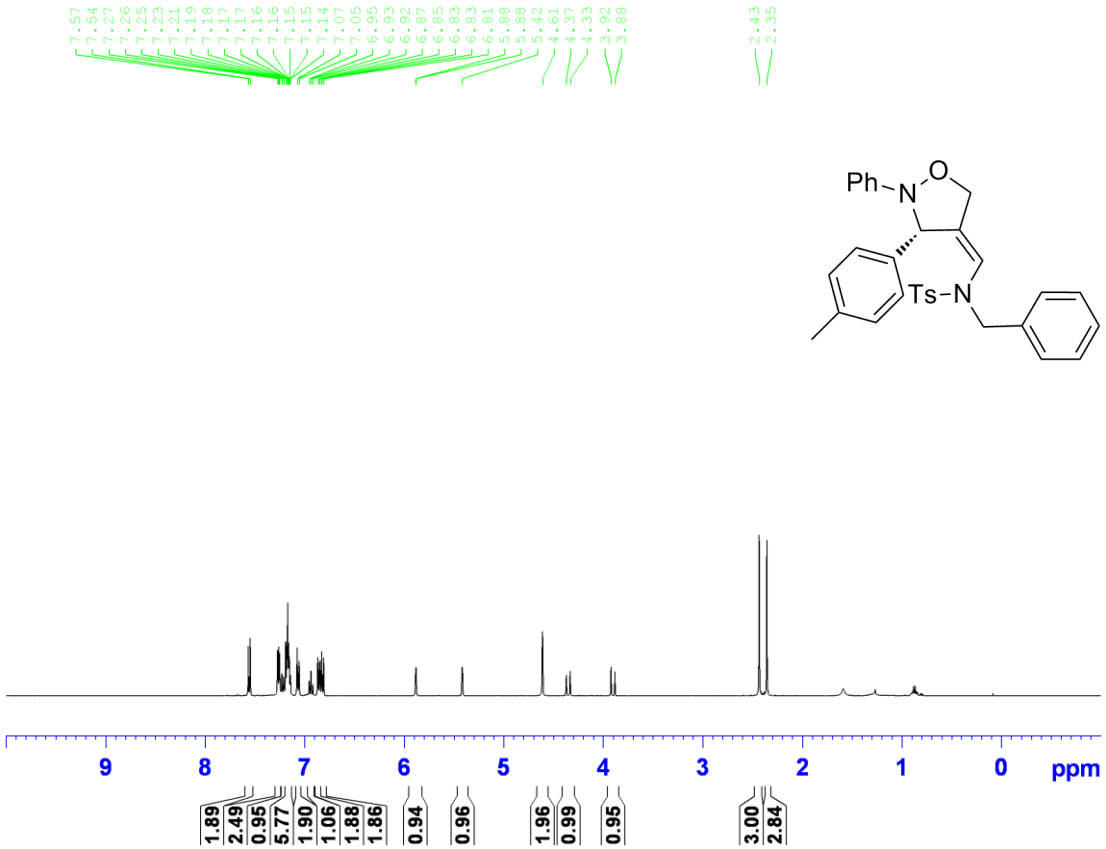
^{13}C NMR (100MHz, $CDCl_3$) of **3g**:



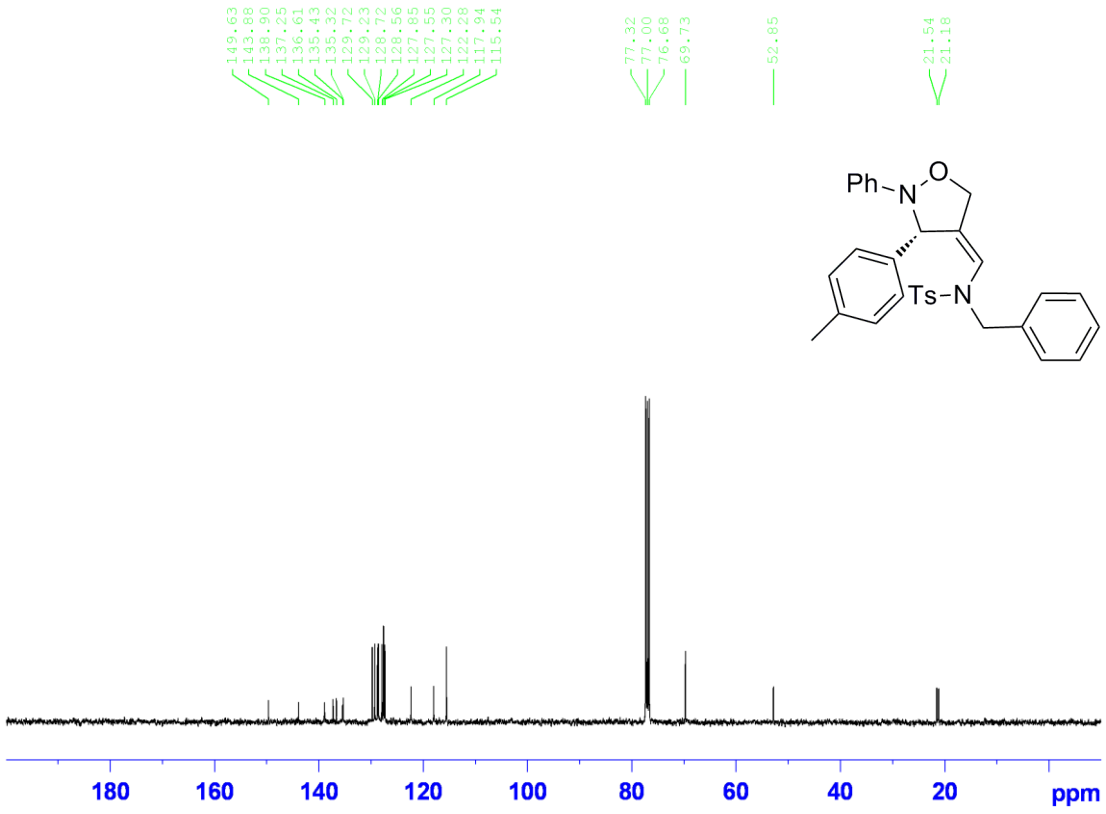




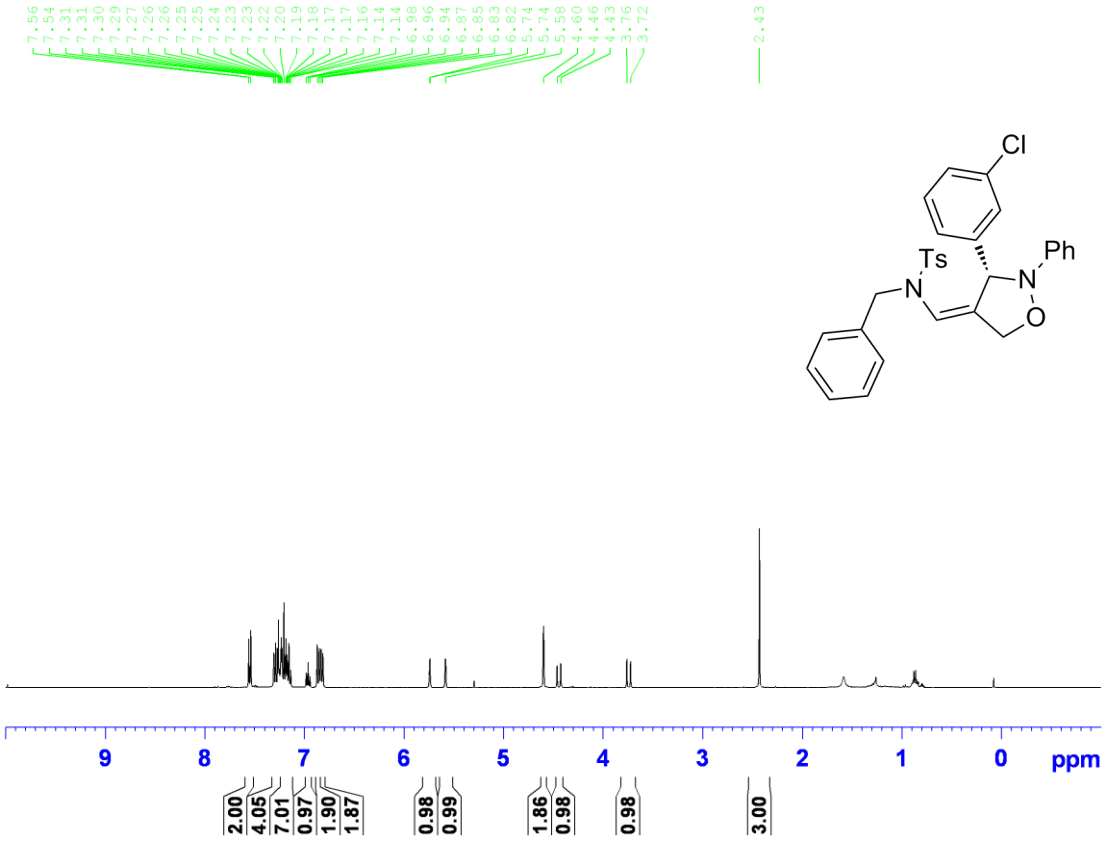
^{1}H NMR (400MHz, $CDCl_3$) of **3h**:



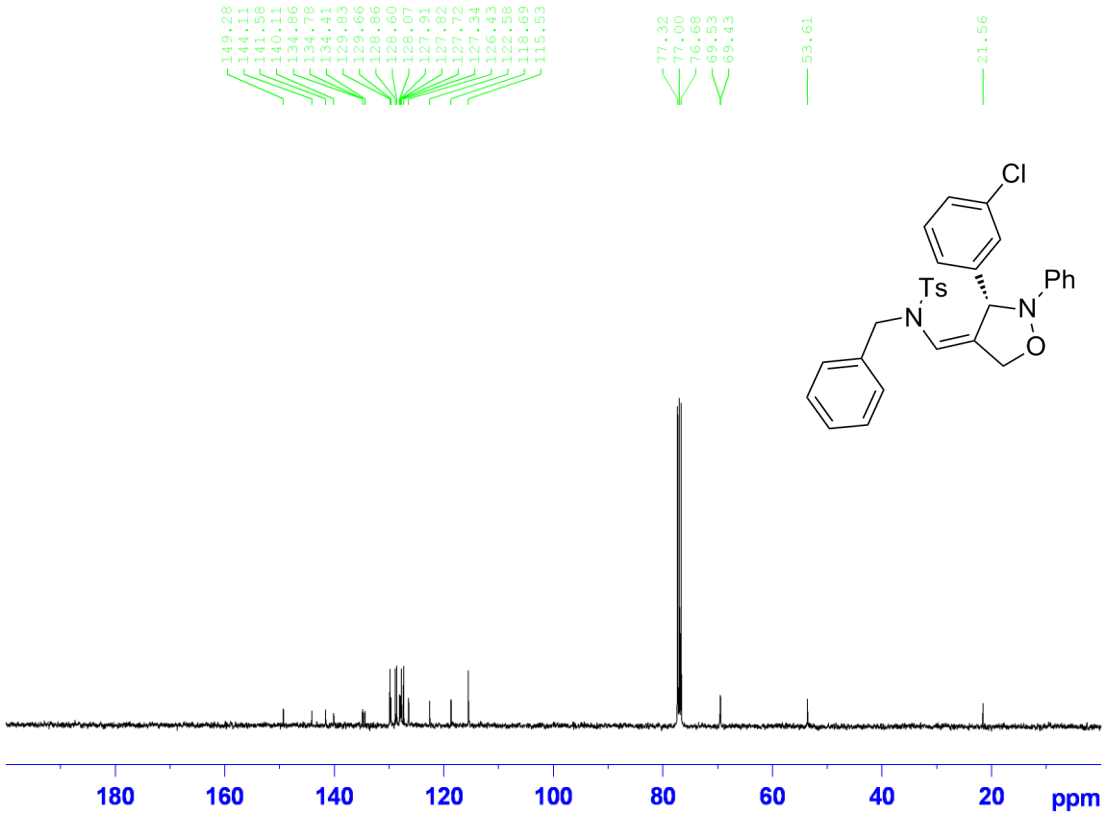
^{13}C NMR (100MHz, $CDCl_3$) of **3h**:



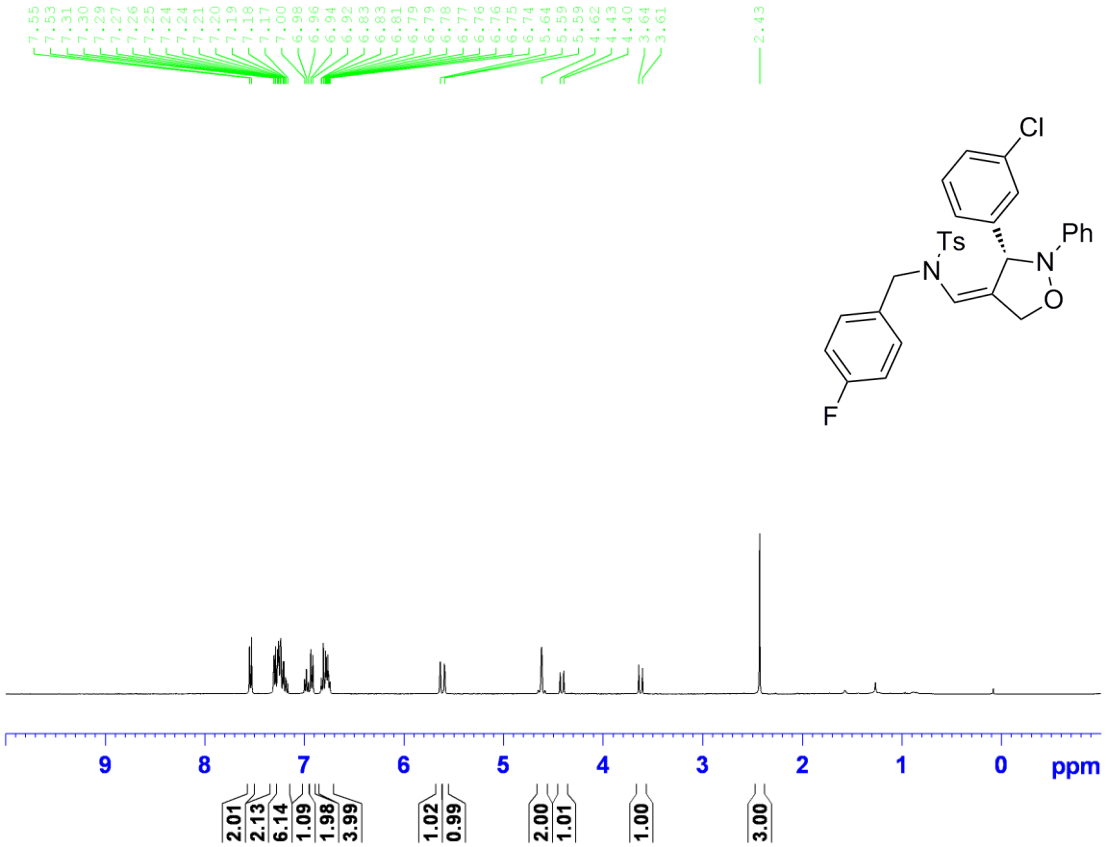
^{1}H NMR (400MHz, $CDCl_3$) of **3i**:



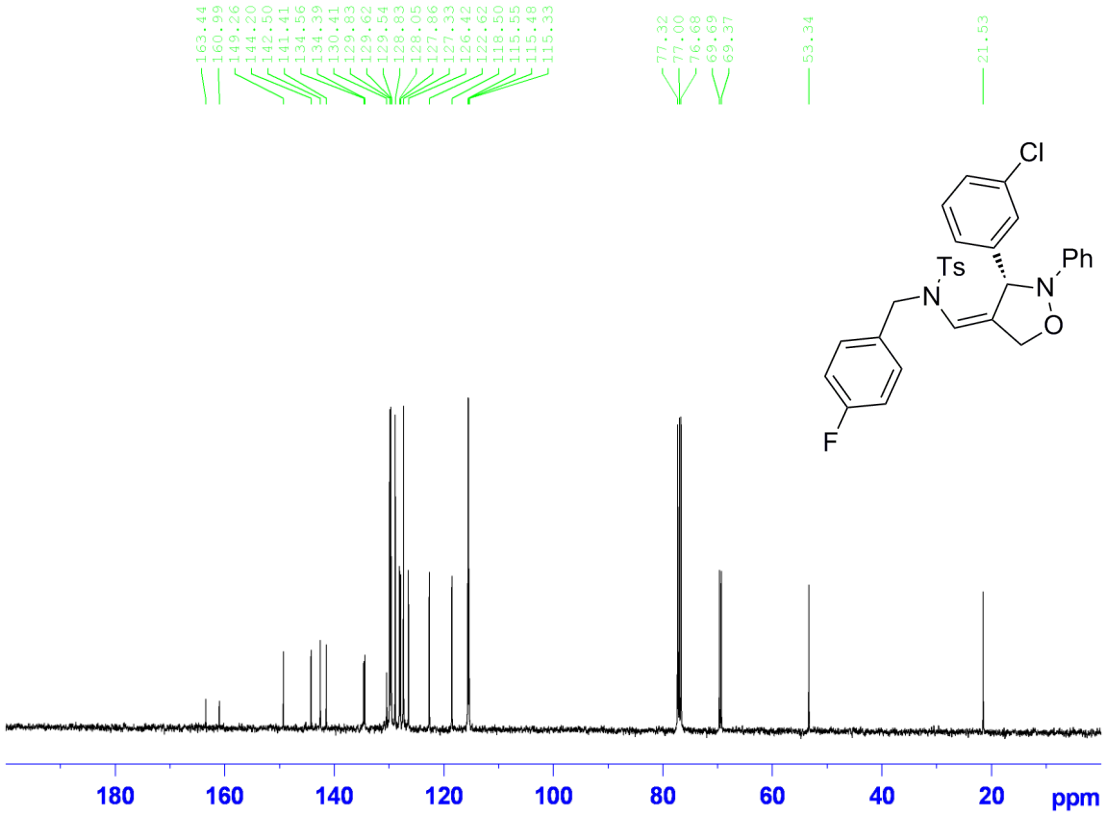
^{13}C NMR (100MHz, $CDCl_3$) of **3i**:



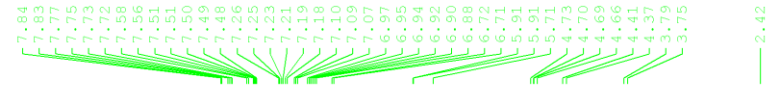
^{1}H NMR (400MHz, $CDCl_3$) of **3j**:

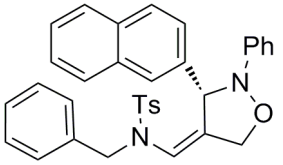


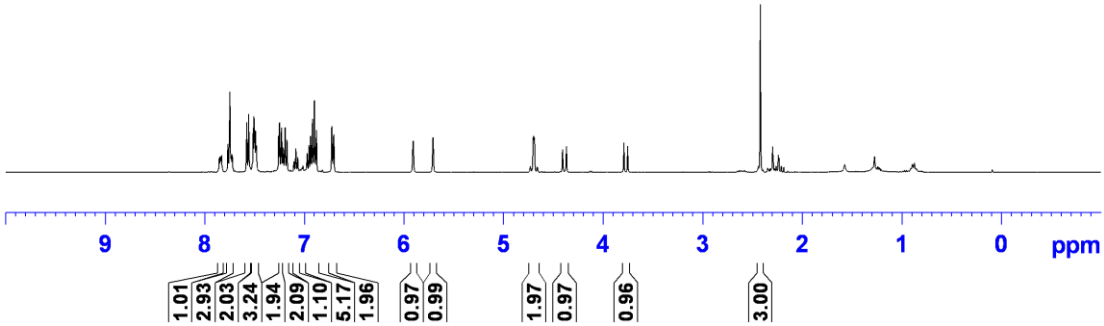
^{13}C NMR (100MHz, $CDCl_3$) of **3j**:



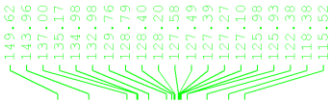
^{1}H NMR (400MHz, $CDCl_3$) of **3k**:

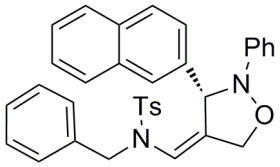


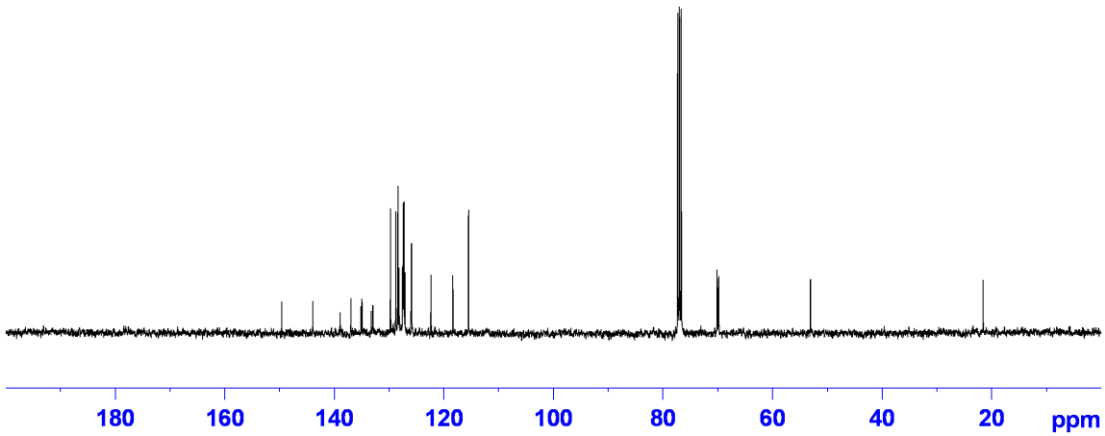




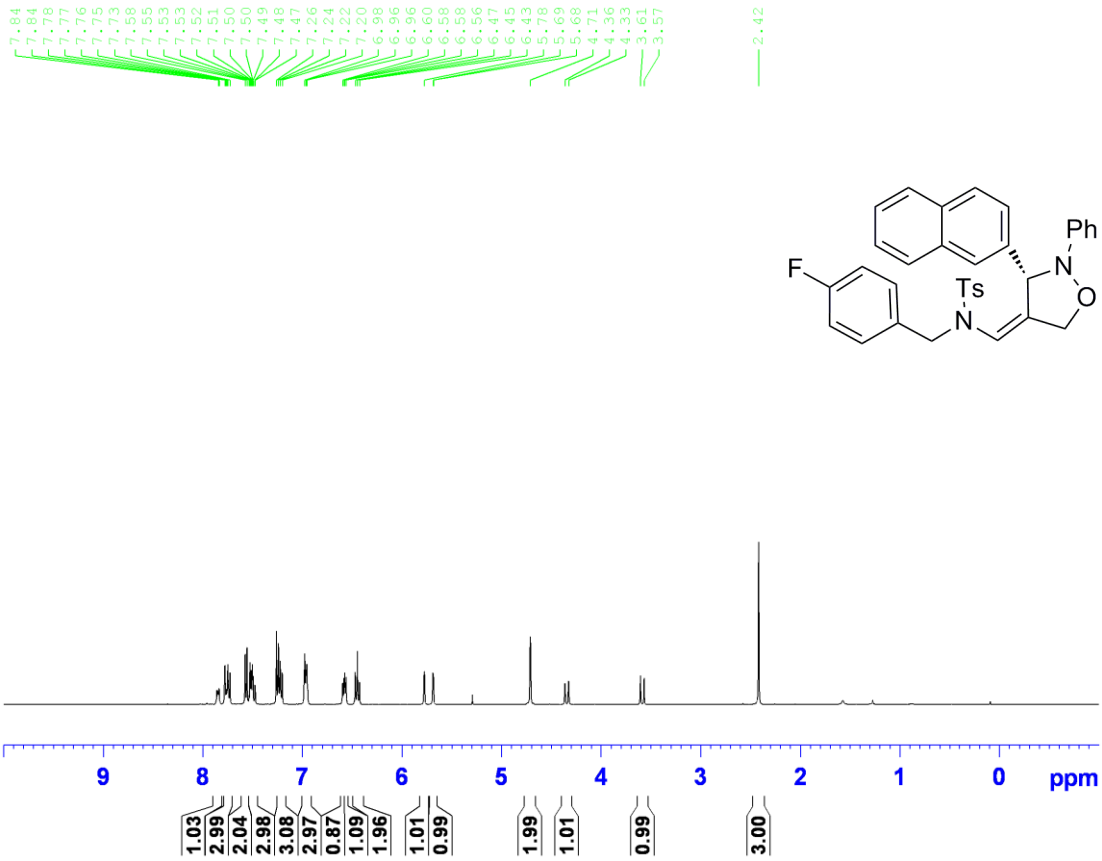
^{13}C NMR (100MHz, $CDCl_3$) of **3k**:



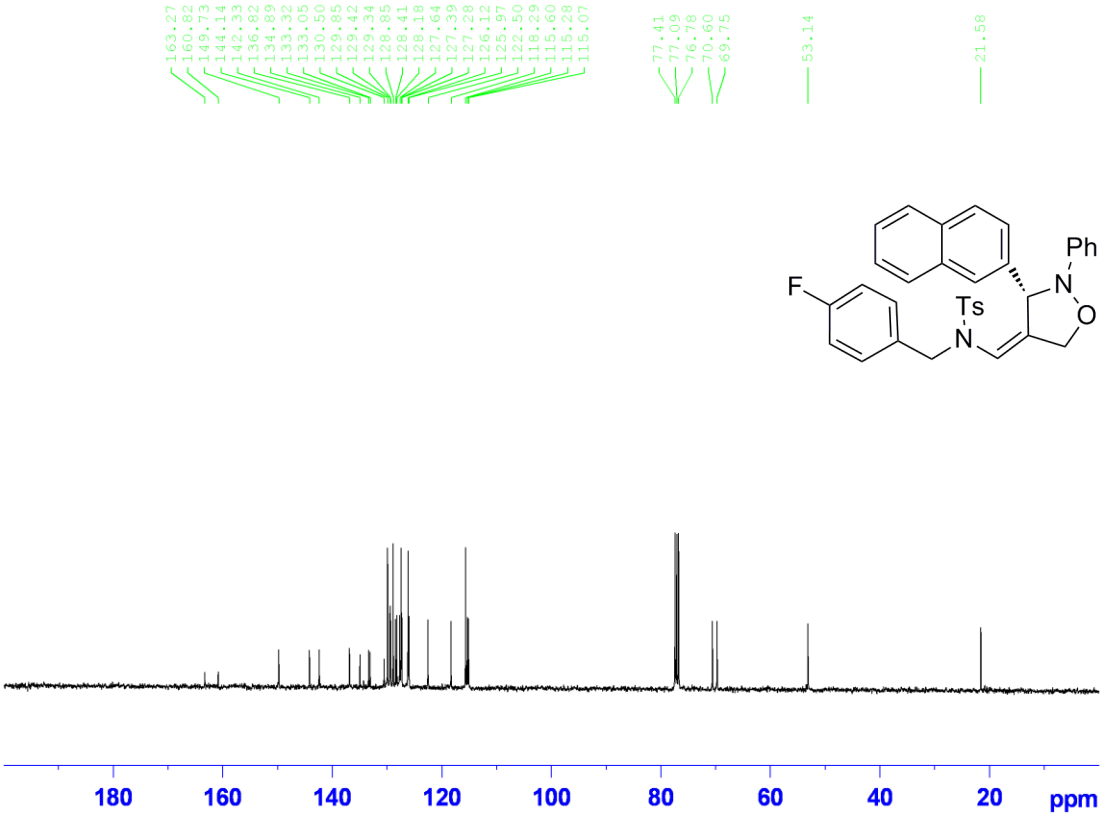




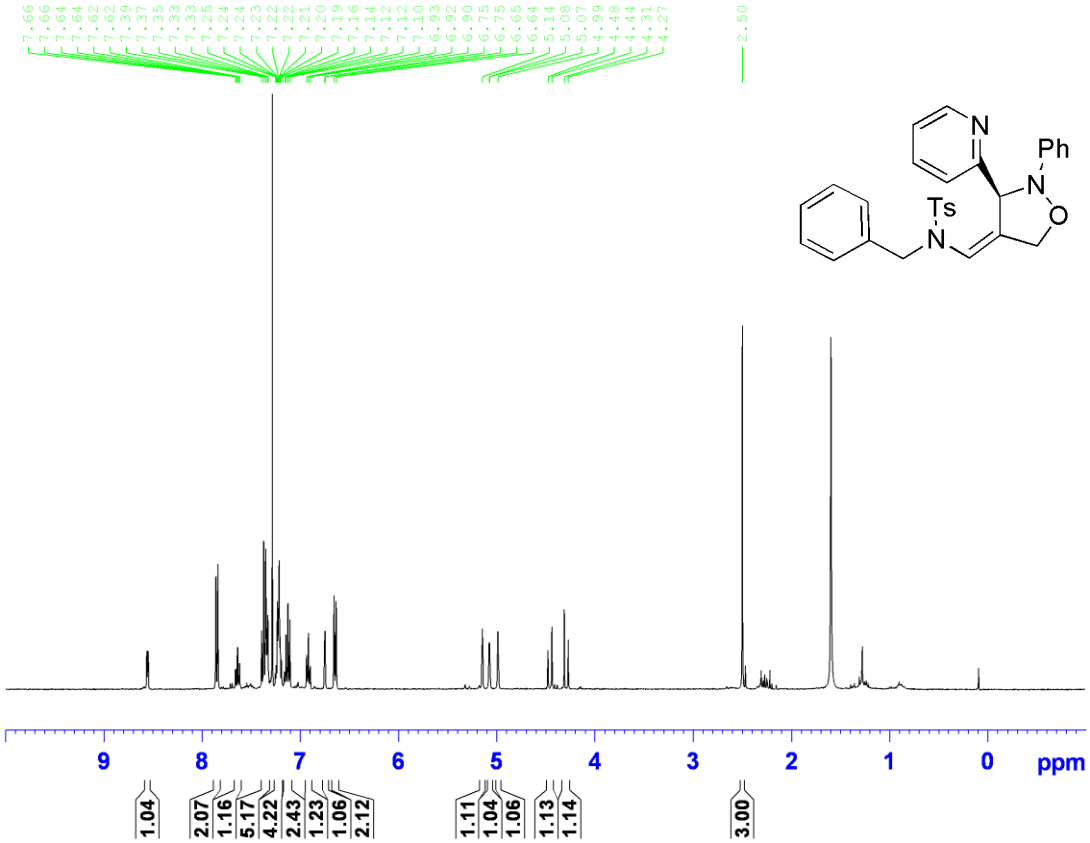
^{1}H NMR (400MHz, $CDCl_3$) of **3m**:



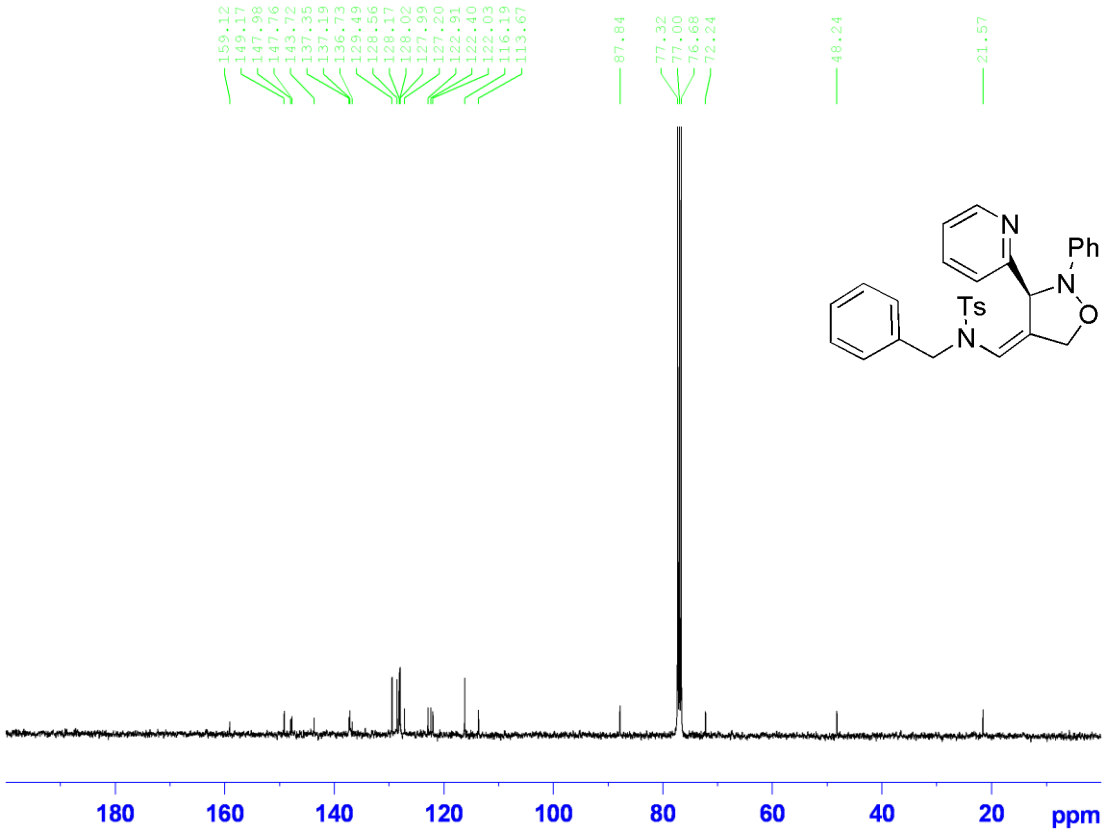
^{13}C NMR (100MHz, $CDCl_3$) of **3m**:



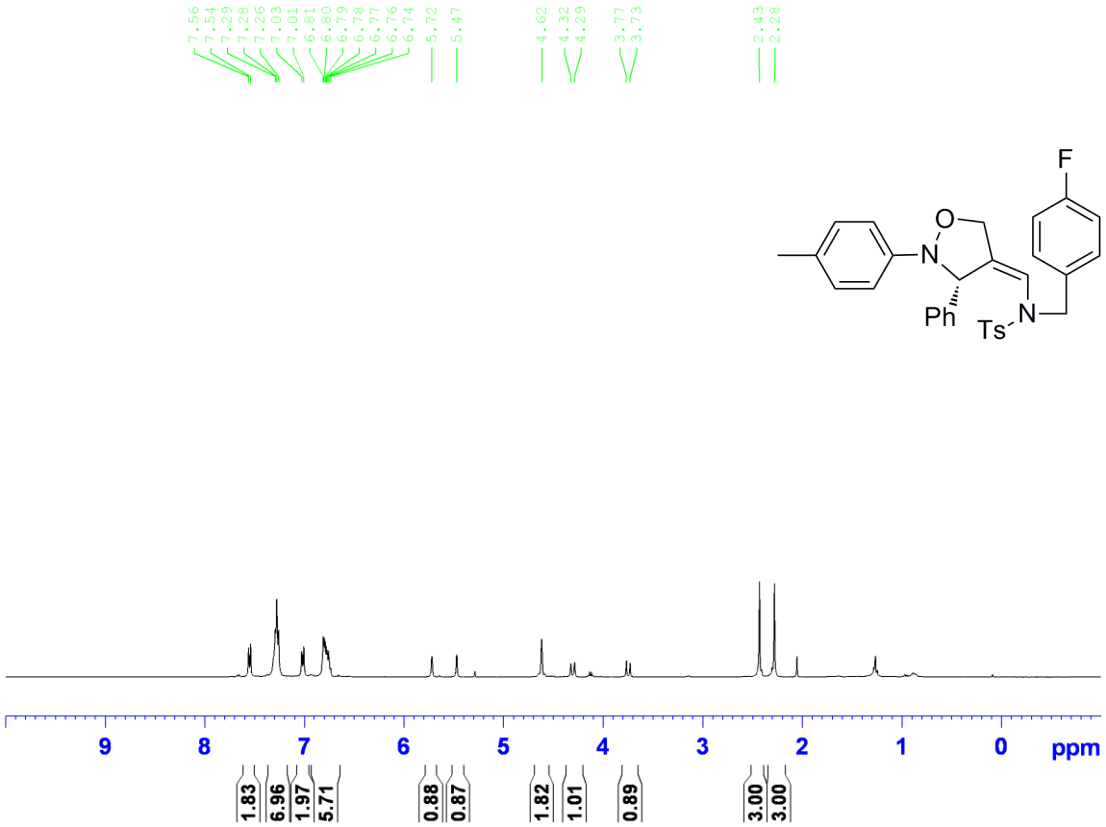
^{1}H NMR (400MHz, $CDCl_3$) of **3n**:



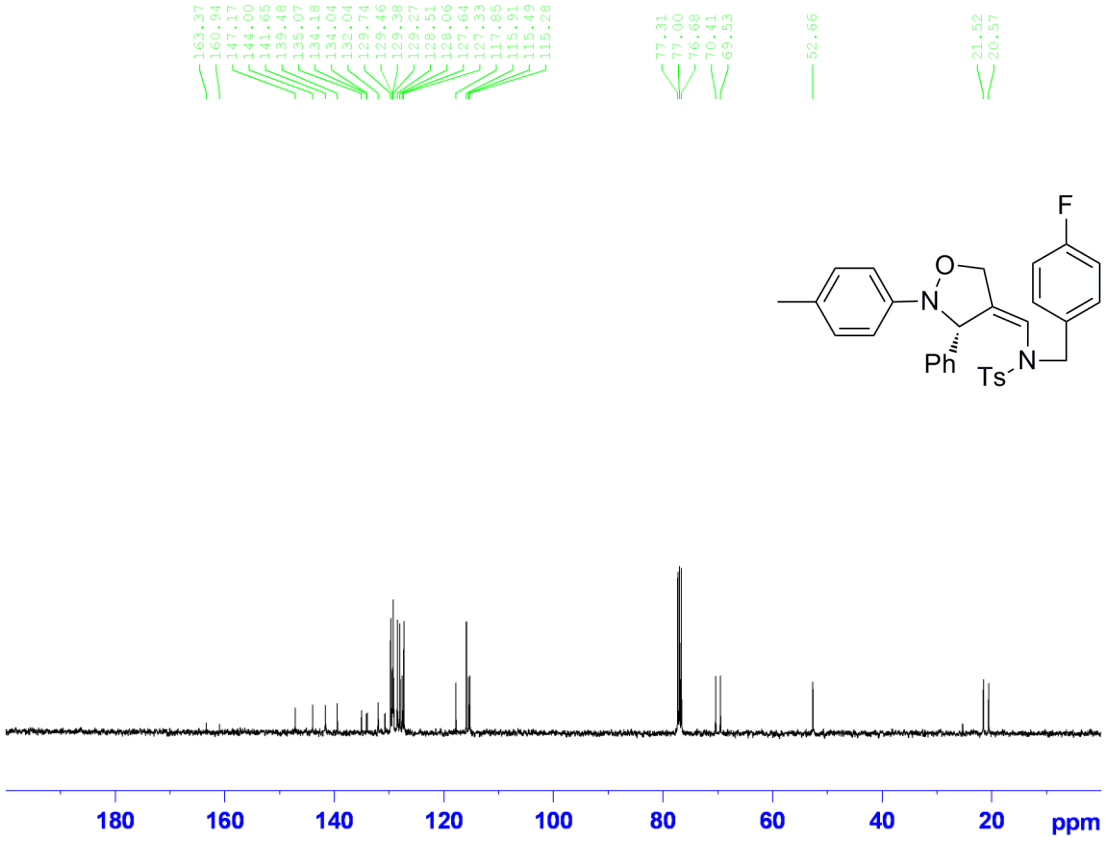
^{13}C NMR (100MHz, $CDCl_3$) of **3n**:



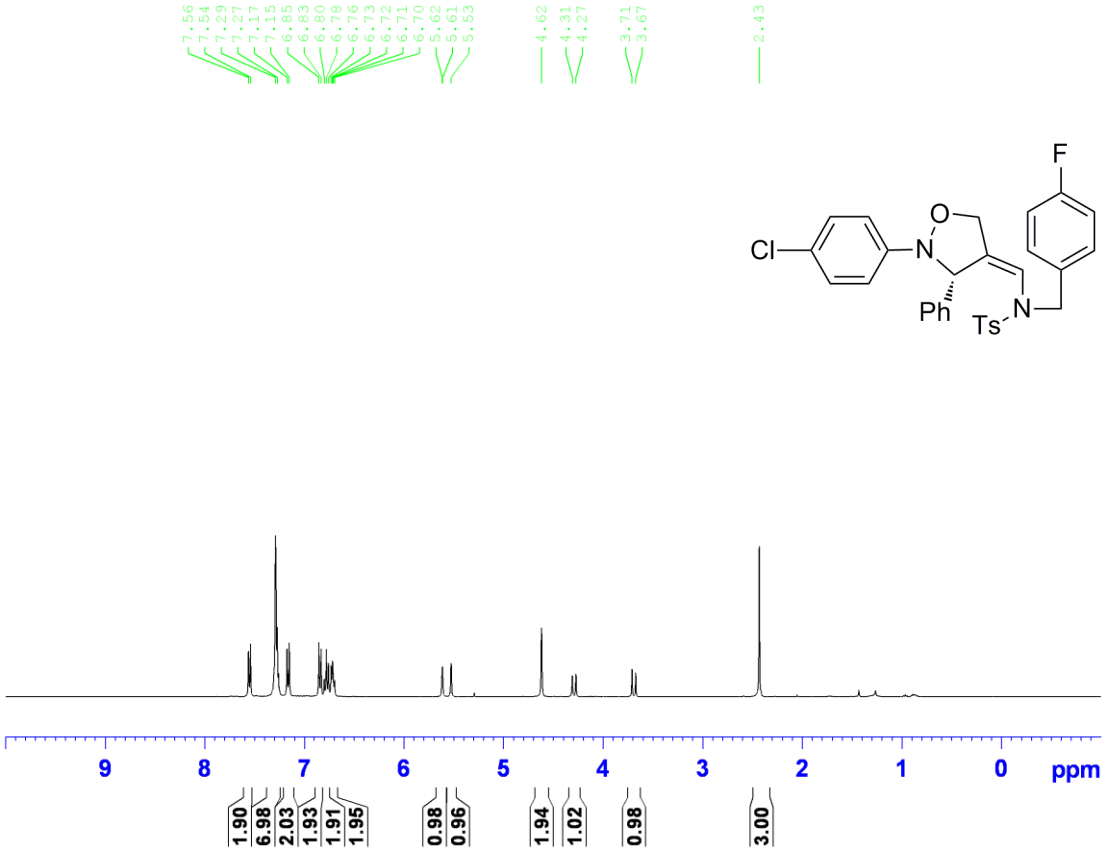
^{1}H NMR (400MHz, $CDCl_3$) of **3o**:



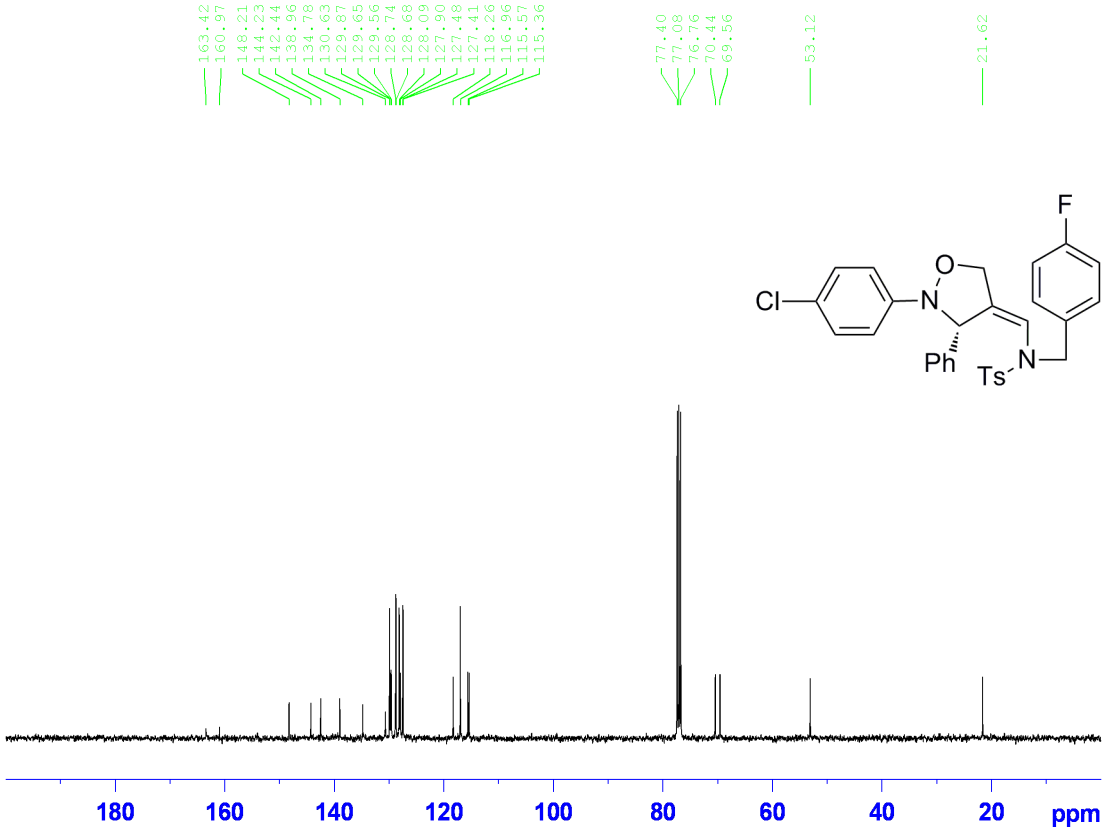
^{13}C NMR (100MHz, $CDCl_3$) of **3o**:



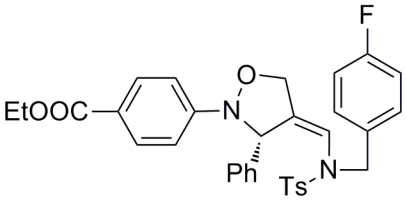
^{1}H NMR (400MHz, $CDCl_3$) of **3p**:

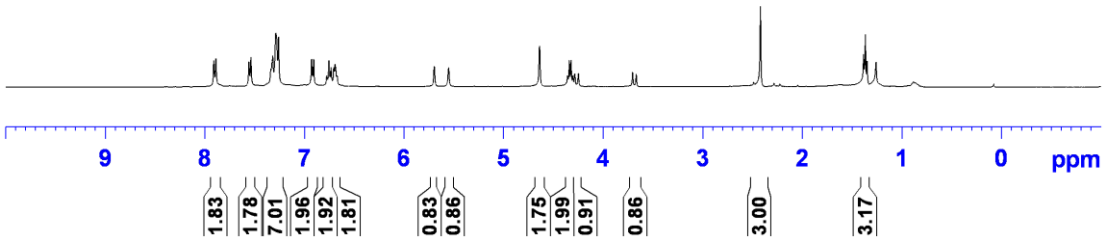


^{13}C NMR (100MHz, $CDCl_3$) of **3p**:

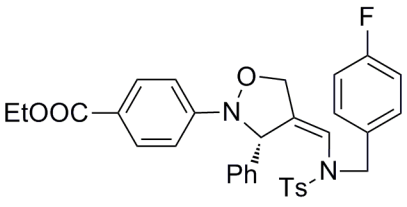


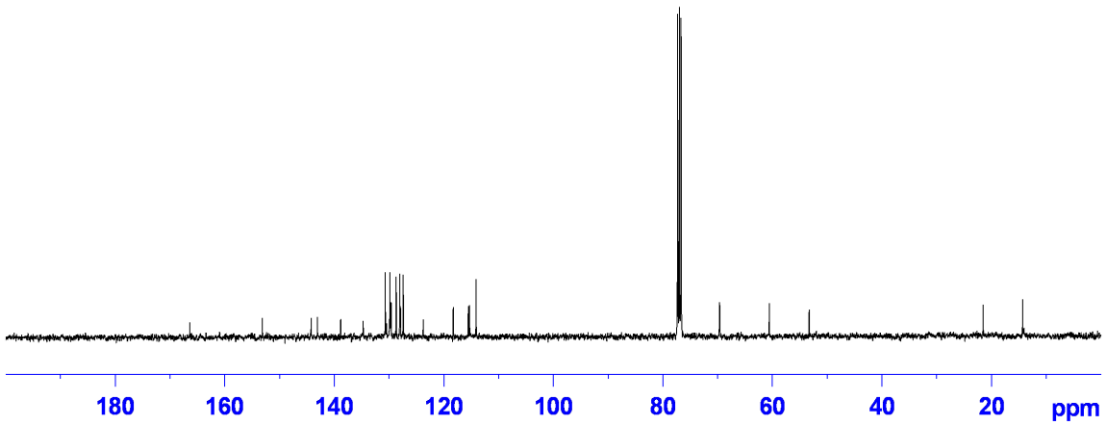
^{1}H NMR (400MHz, $CDCl_3$) of **3q**:



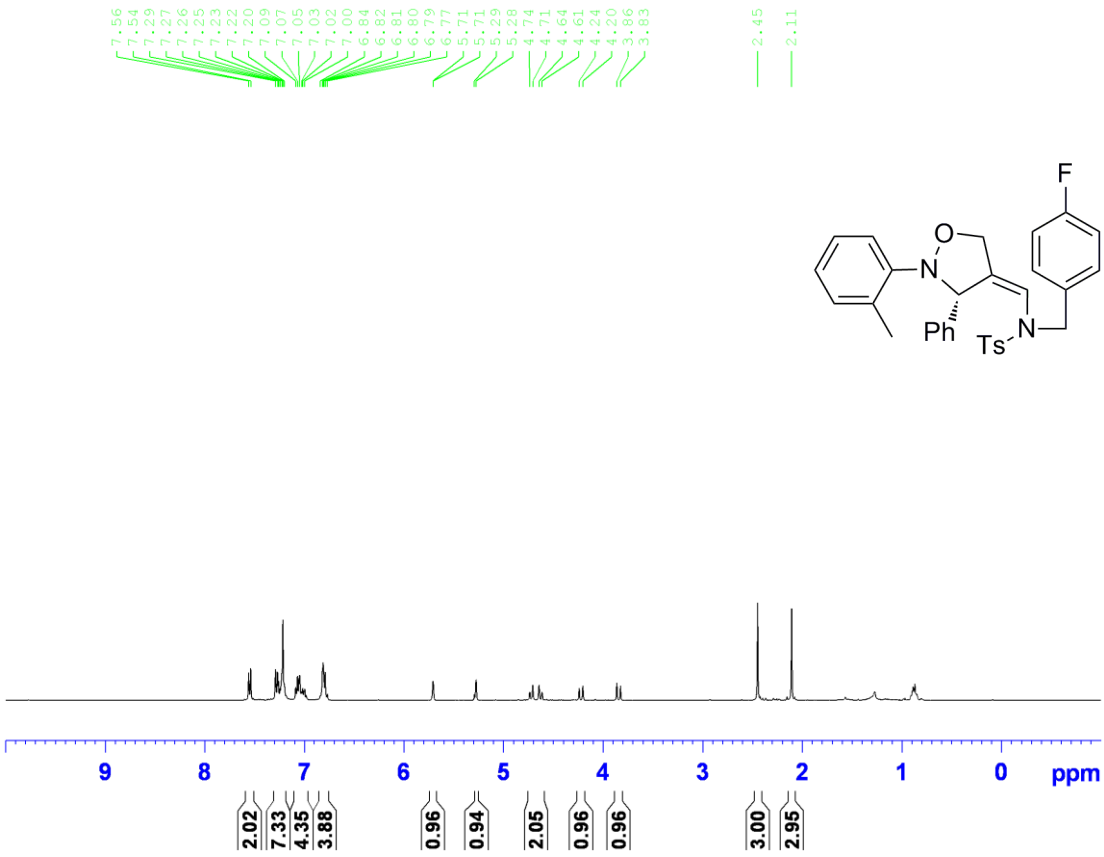


^{13}C NMR (100MHz, $CDCl_3$) of **3q**:

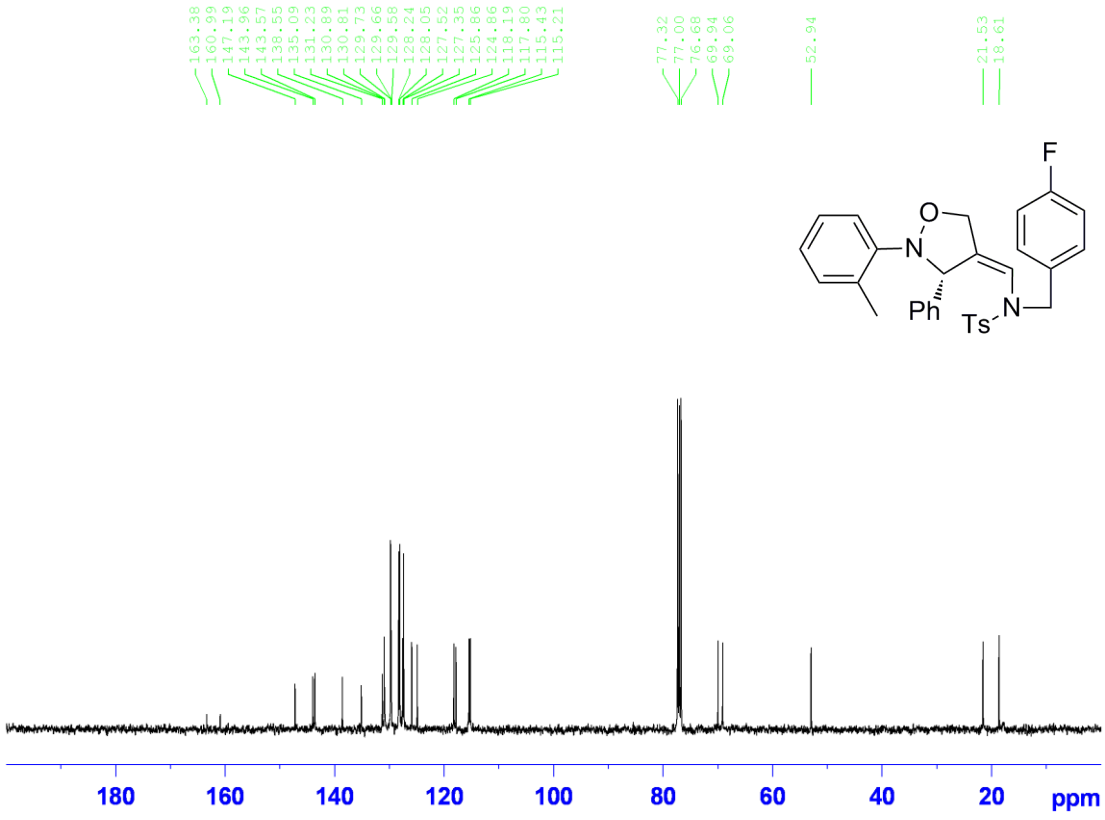




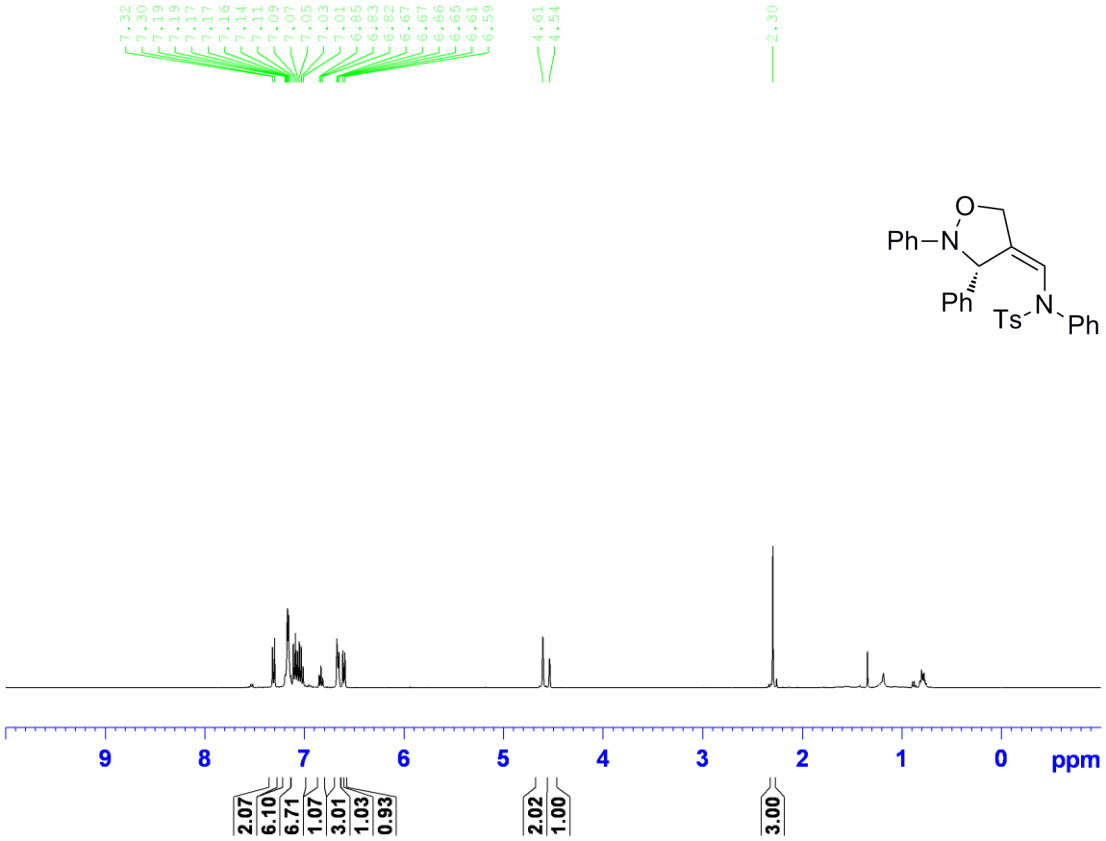
^{1}H NMR (400MHz, $CDCl_3$) of **3r**:



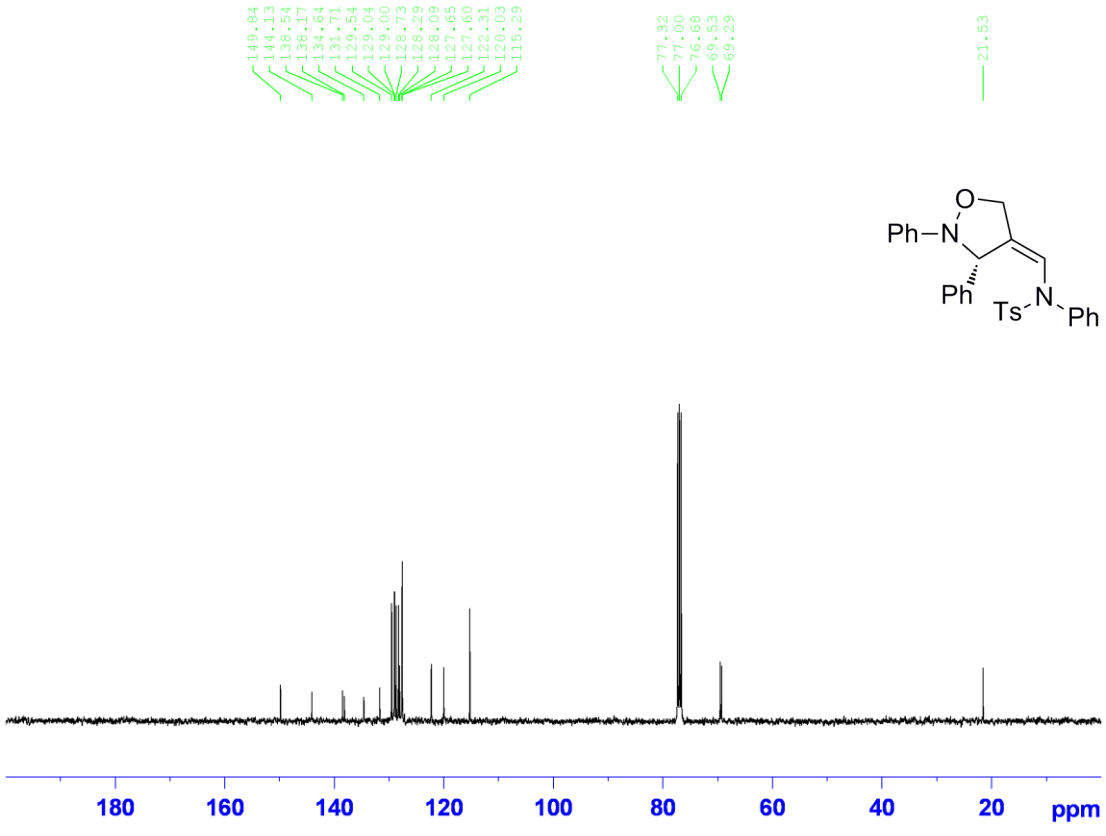
^{13}C NMR (100MHz, $CDCl_3$) of **3r**:



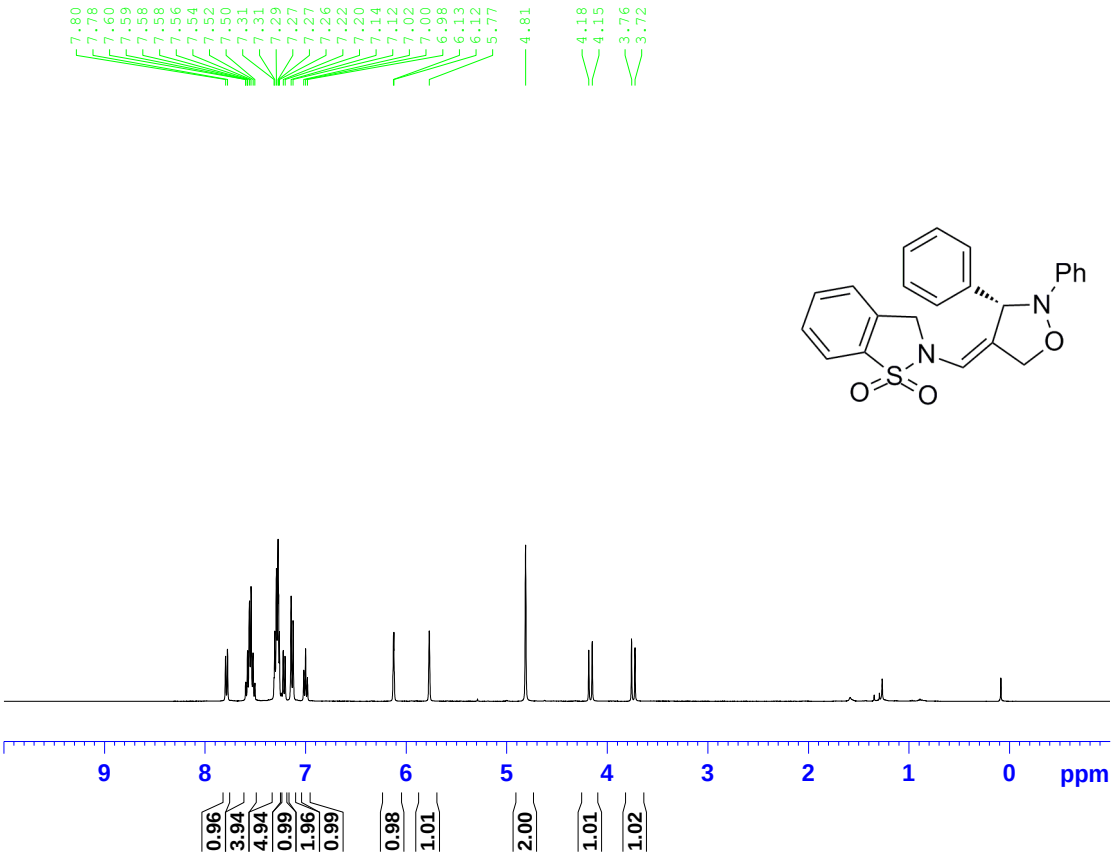
^{1}H NMR (400MHz, $CDCl_3$) of **3s**:



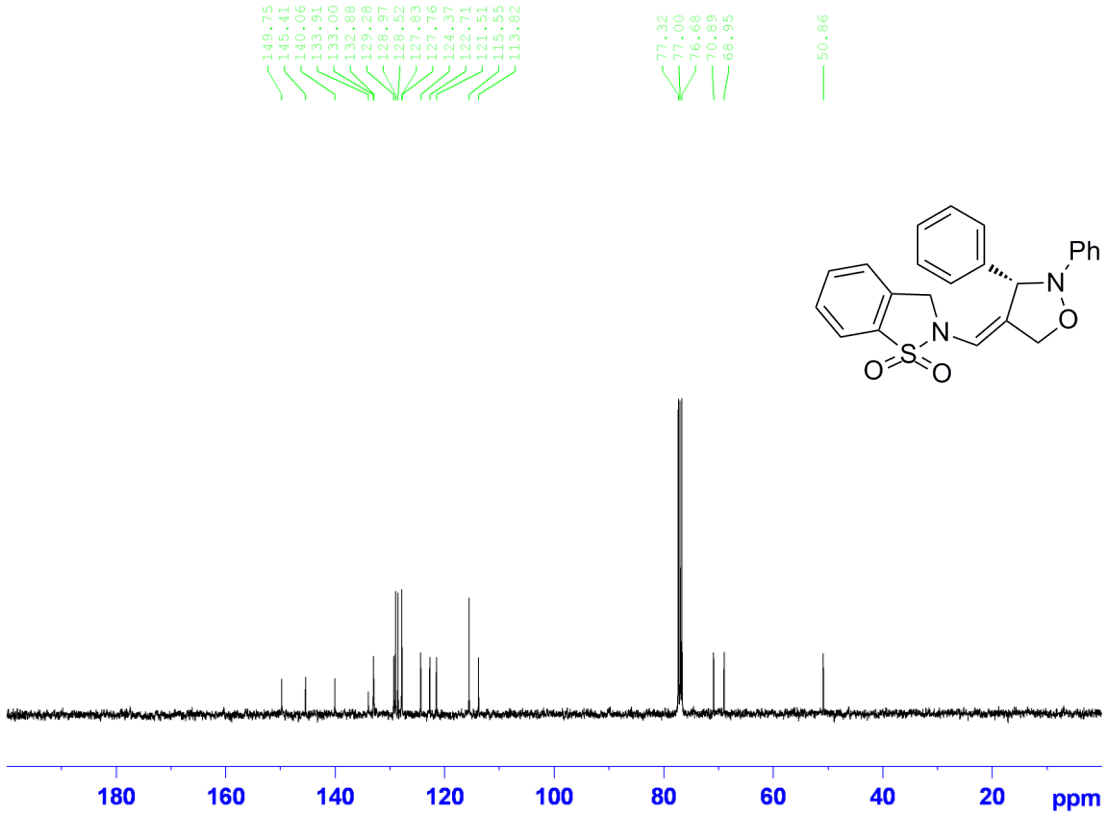
^{13}C NMR (100MHz, $CDCl_3$) of **3s**:



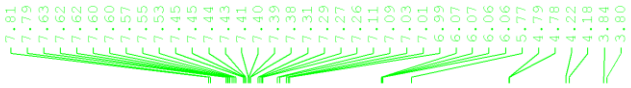
^{1}H NMR (400MHz, $CDCl_3$) of **3t**:

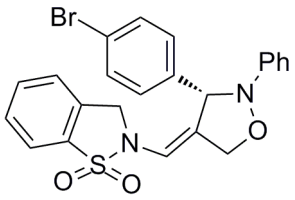


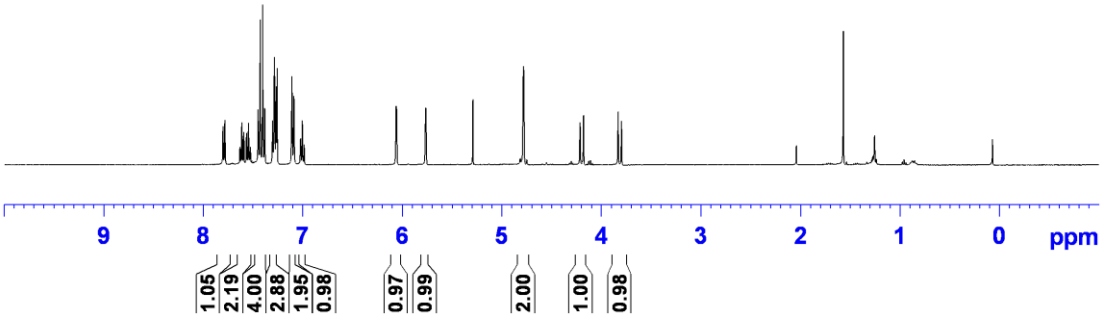
^{13}C NMR (100MHz, $CDCl_3$) of **3t**:



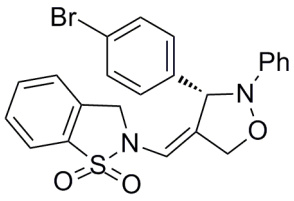
^{1}H NMR (400MHz, $CDCl_3$) of **3u**:

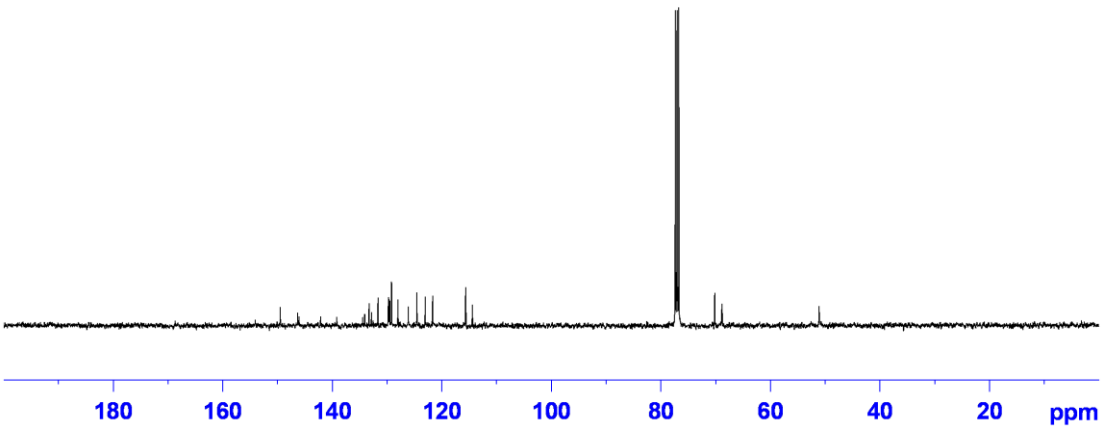




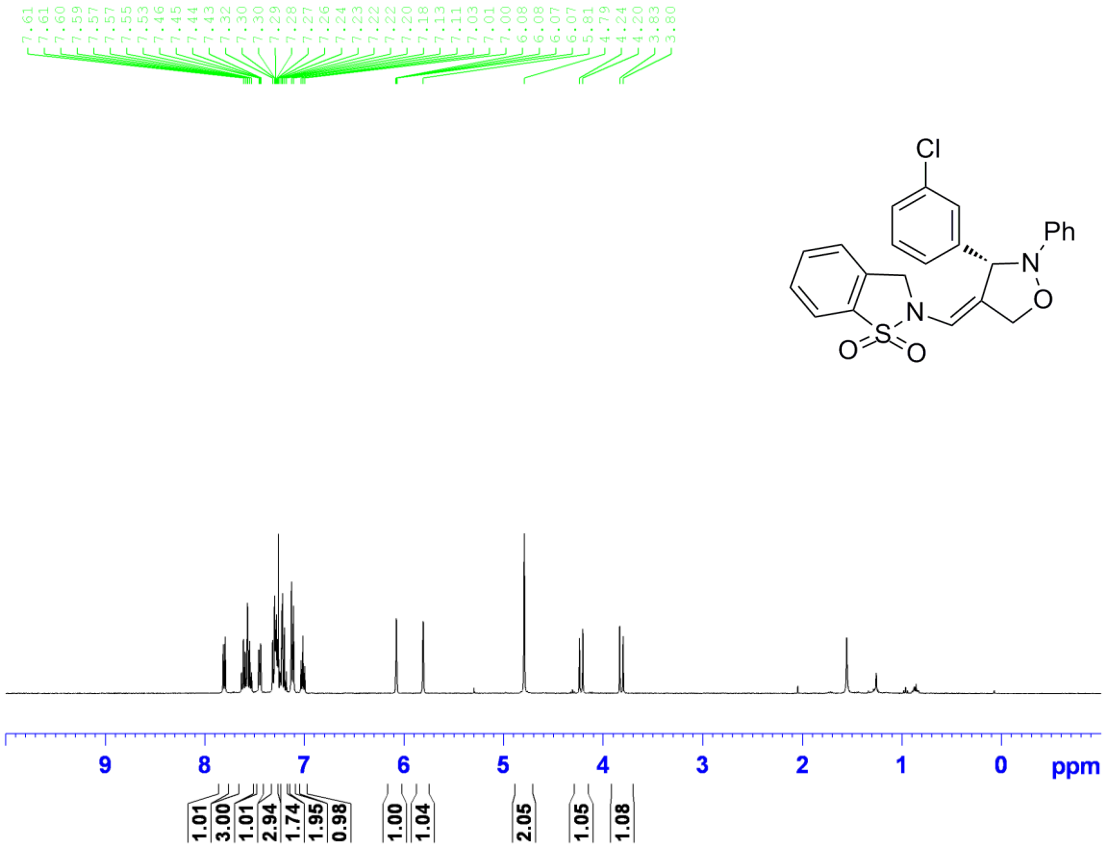


^{13}C NMR (100MHz, $CDCl_3$) of **3u**:

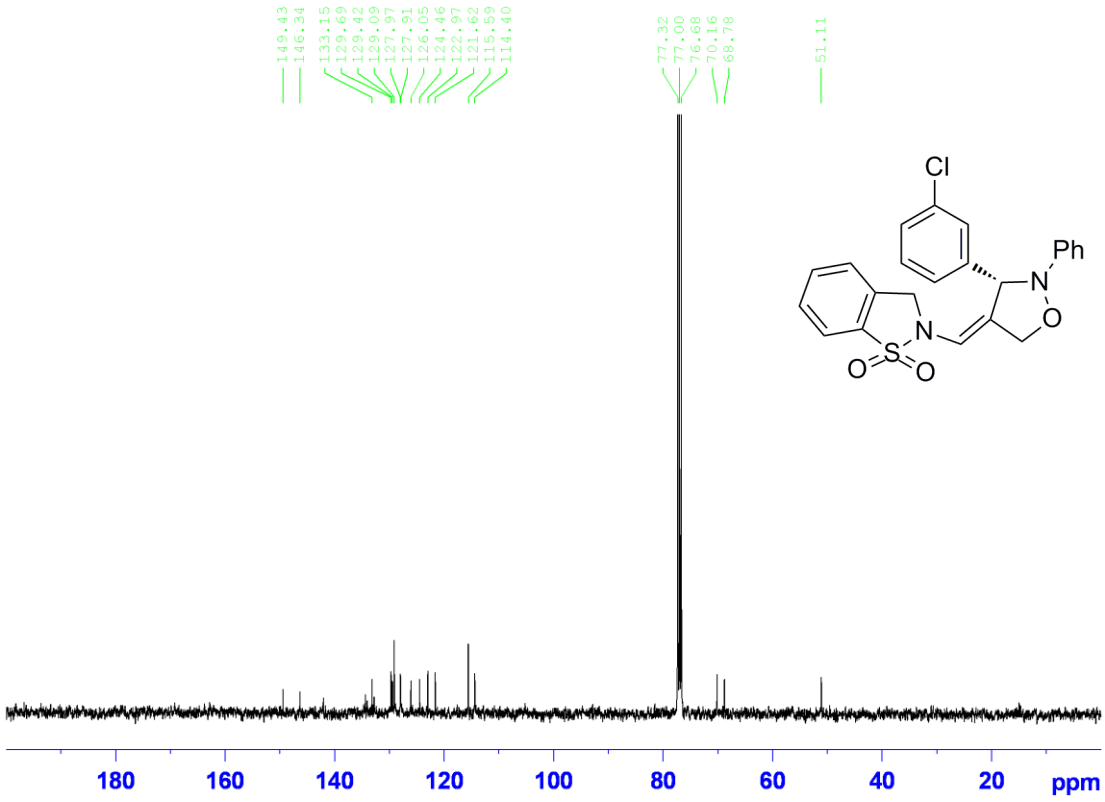




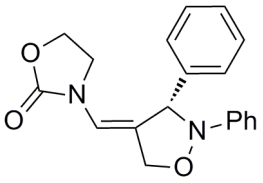
^{1}H NMR (400MHz, $CDCl_3$) of **3v**:

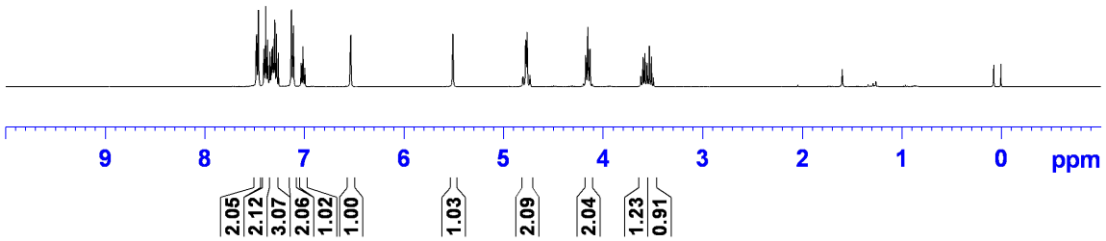


^{13}C NMR (100MHz, $CDCl_3$) of **3v**:

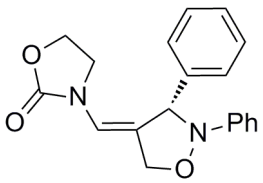


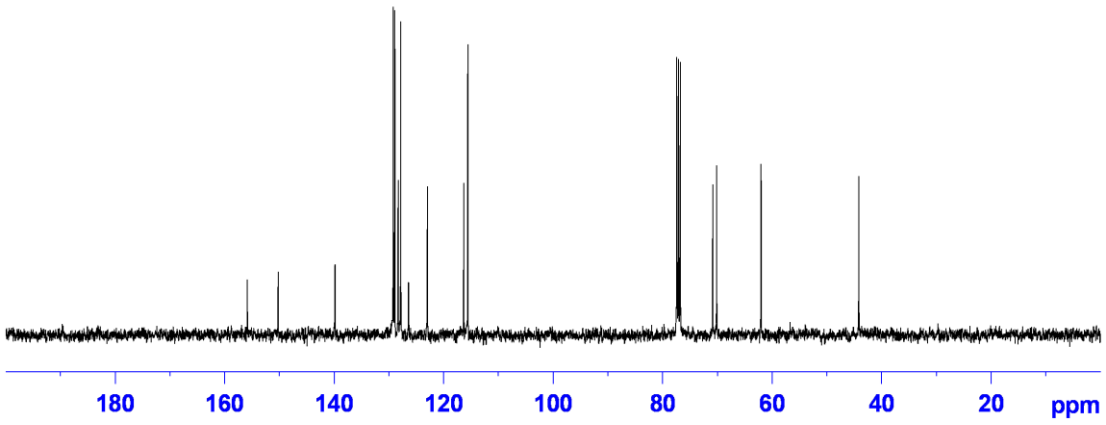
^{1}H NMR (400MHz, $CDCl_3$) of **3w**:



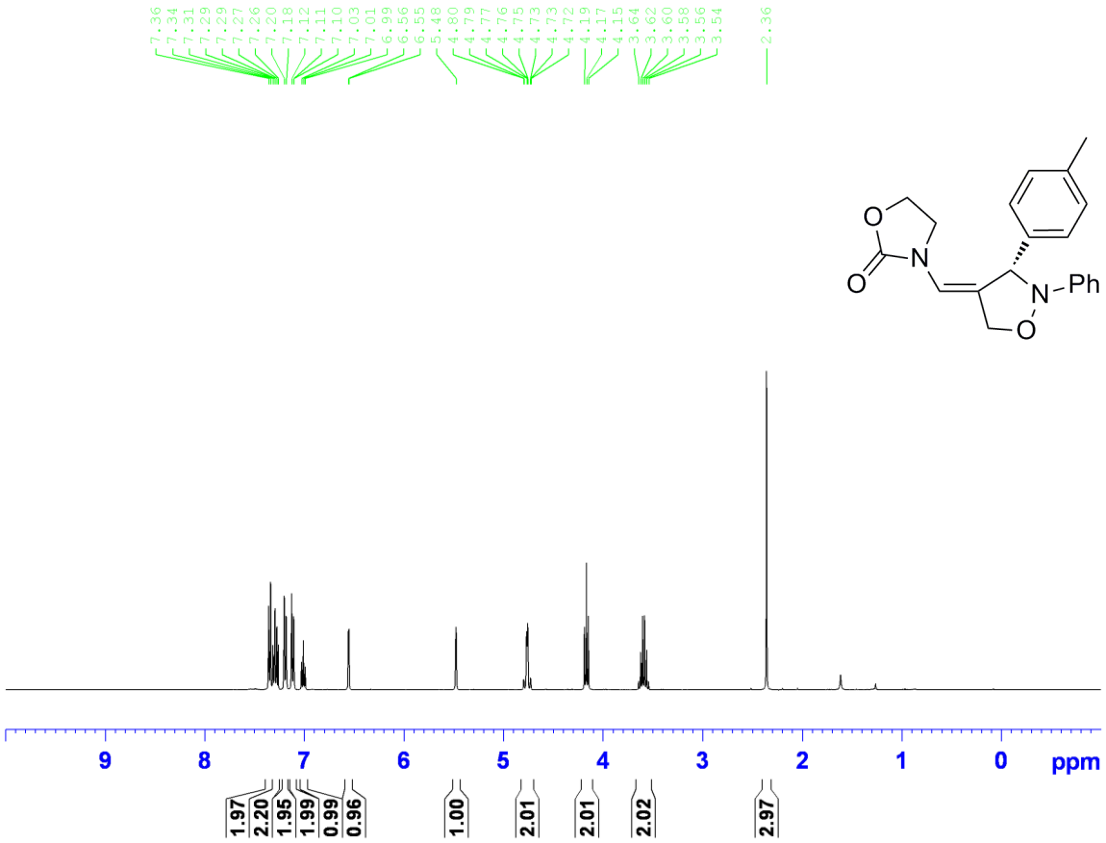


^{13}C NMR (100MHz, $CDCl_3$) of **3w**:

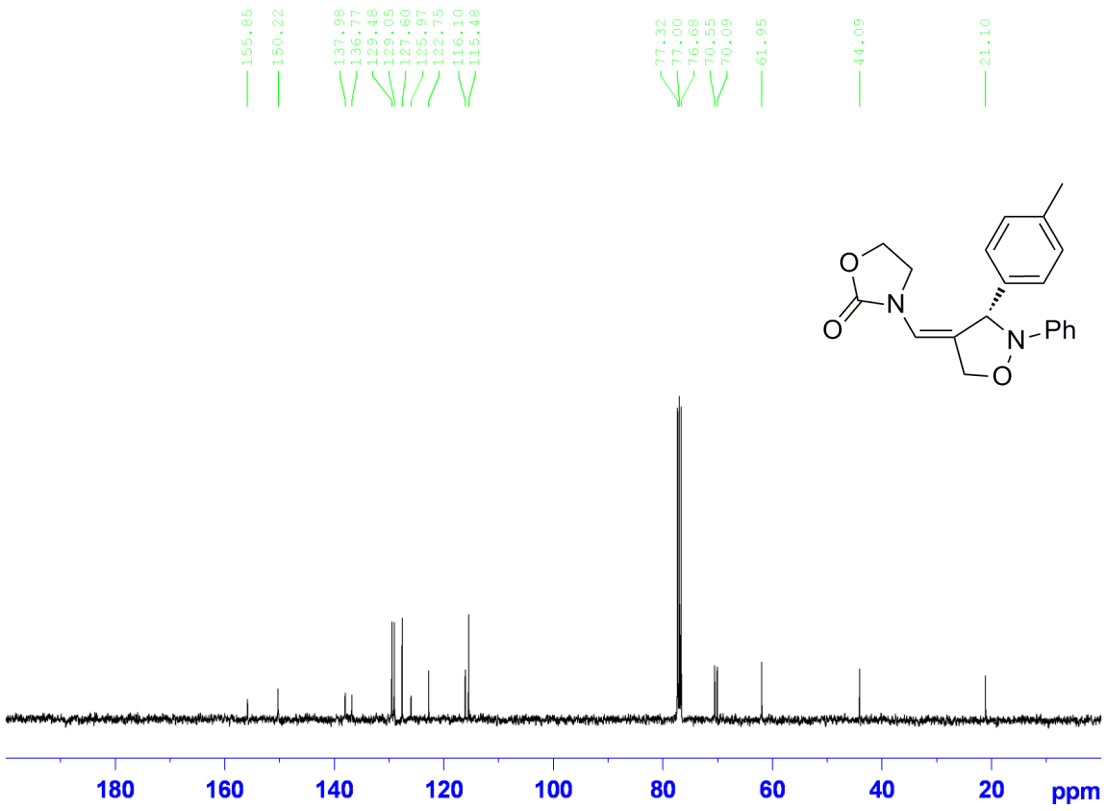




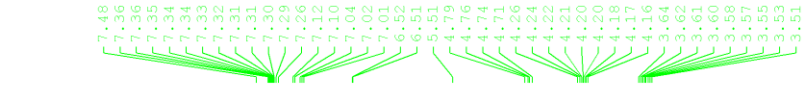
^{1}H NMR (400MHz, $CDCl_3$) of **3x**:

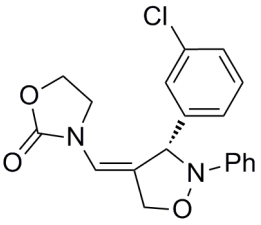


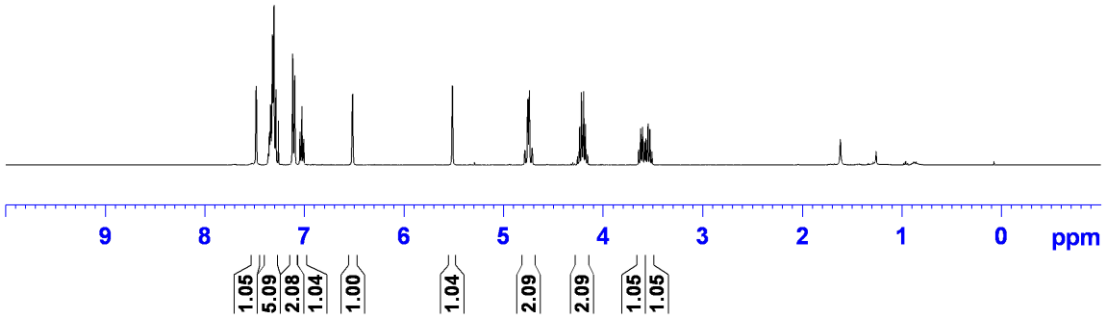
^{13}C NMR (100MHz, $CDCl_3$) of **3x**:



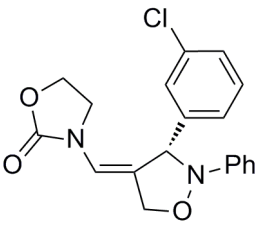
^{1}H NMR (400MHz, $CDCl_3$) of **3y**:

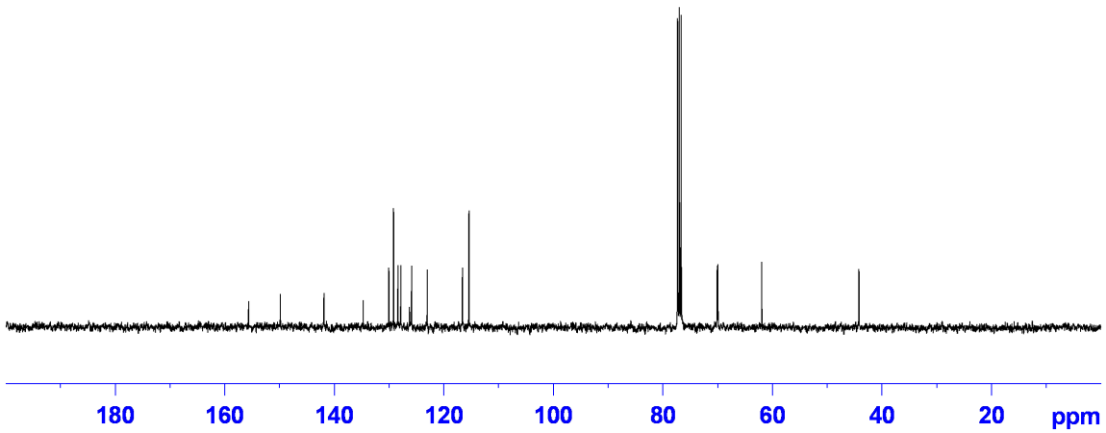




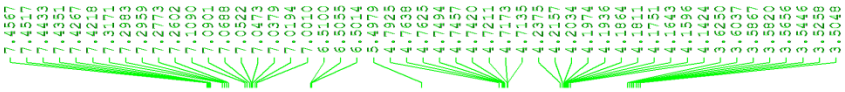


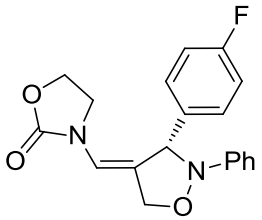
^{13}C NMR (100MHz, $CDCl_3$) of **3y**:

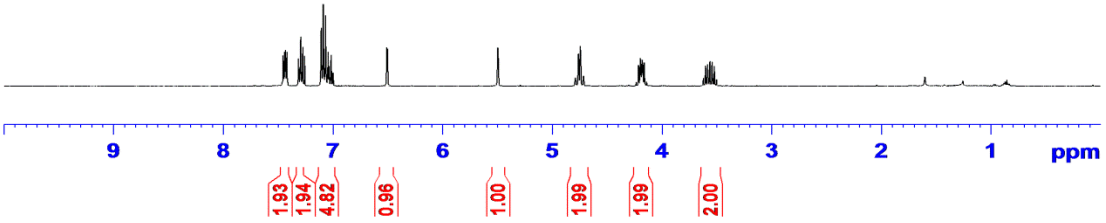




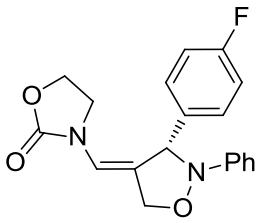
^{1}H NMR (400MHz, $CDCl_3$) of **3z**:

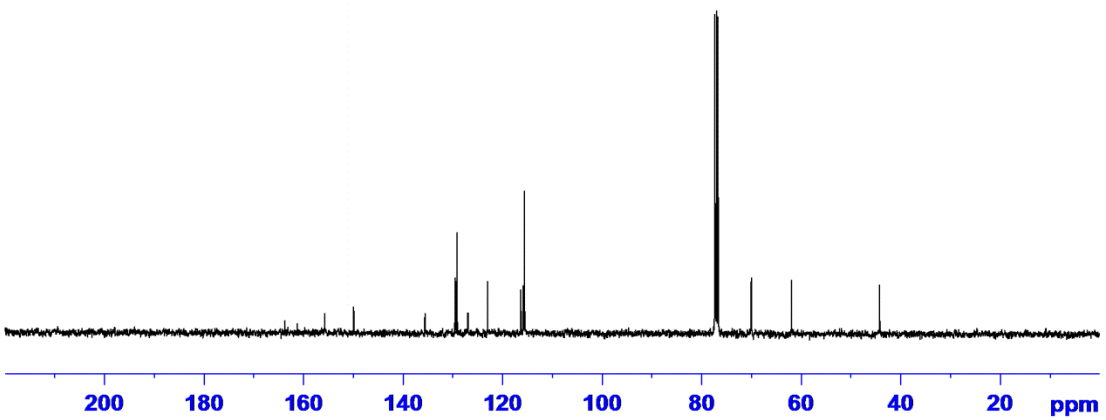




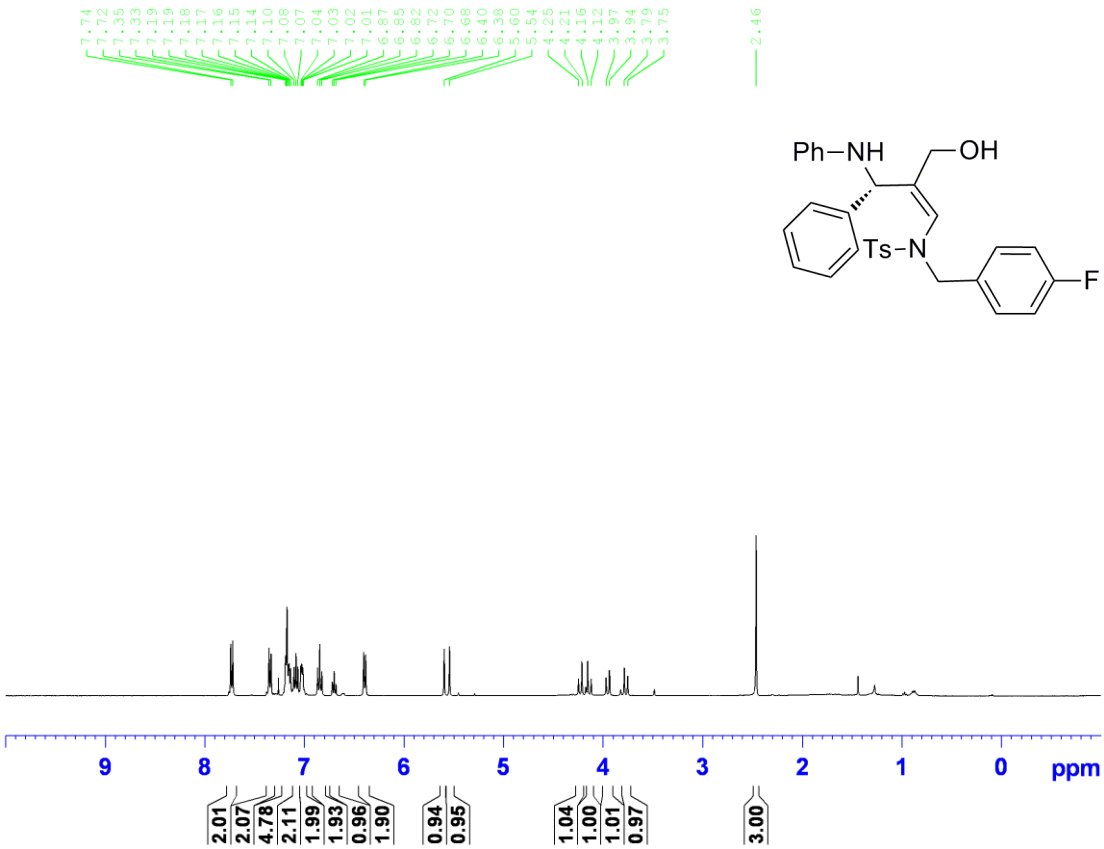


^{13}C NMR (100MHz, $CDCl_3$) of **3z**:

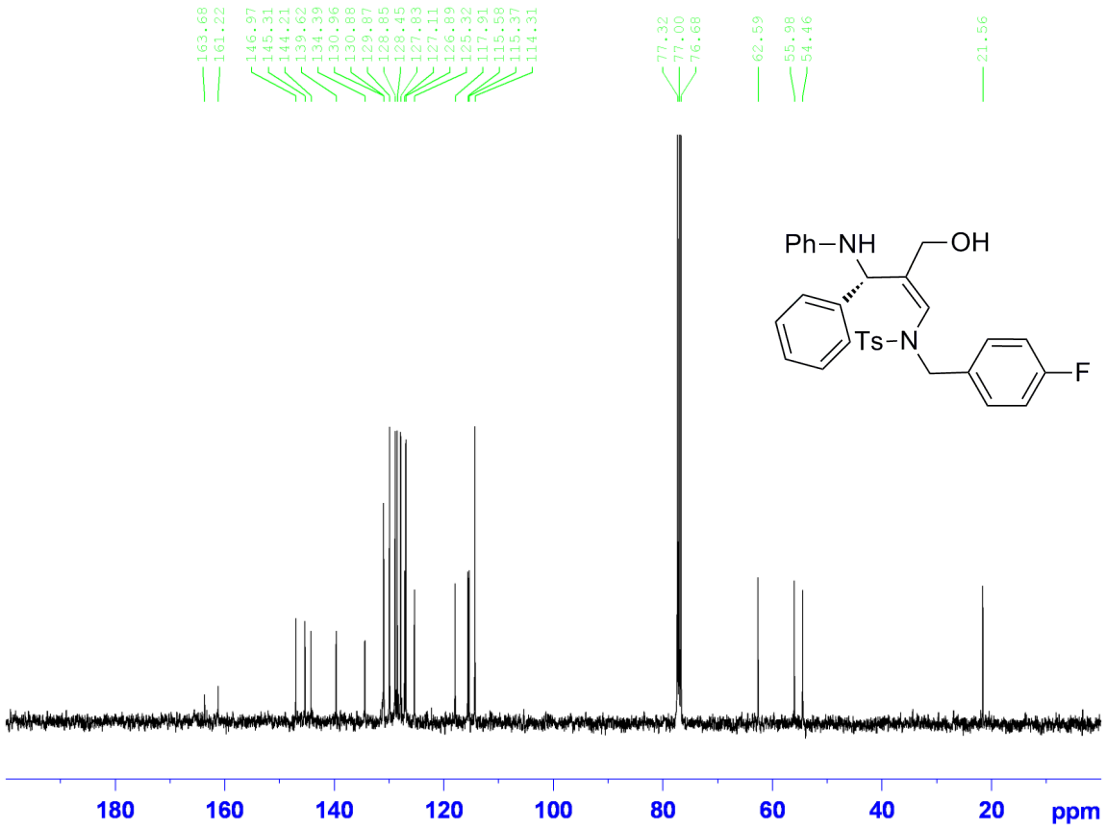




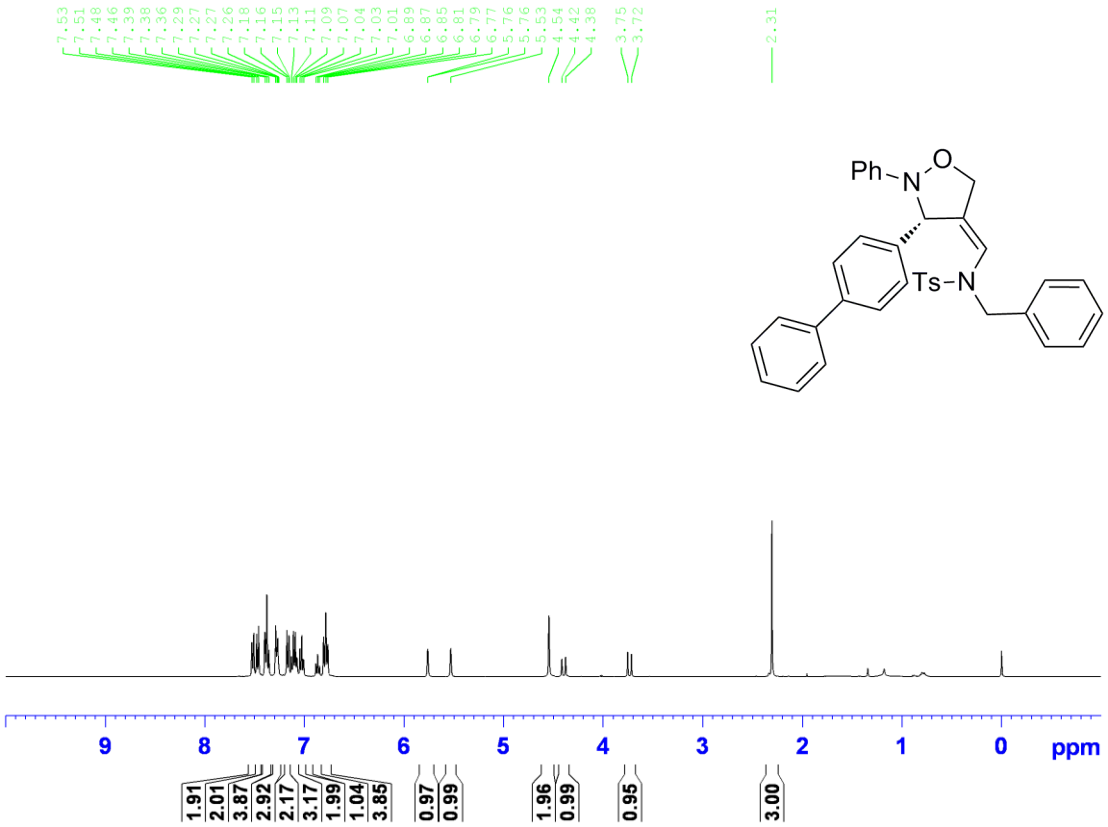
^{1}H NMR (400MHz, $CDCl_3$) of **4a**:



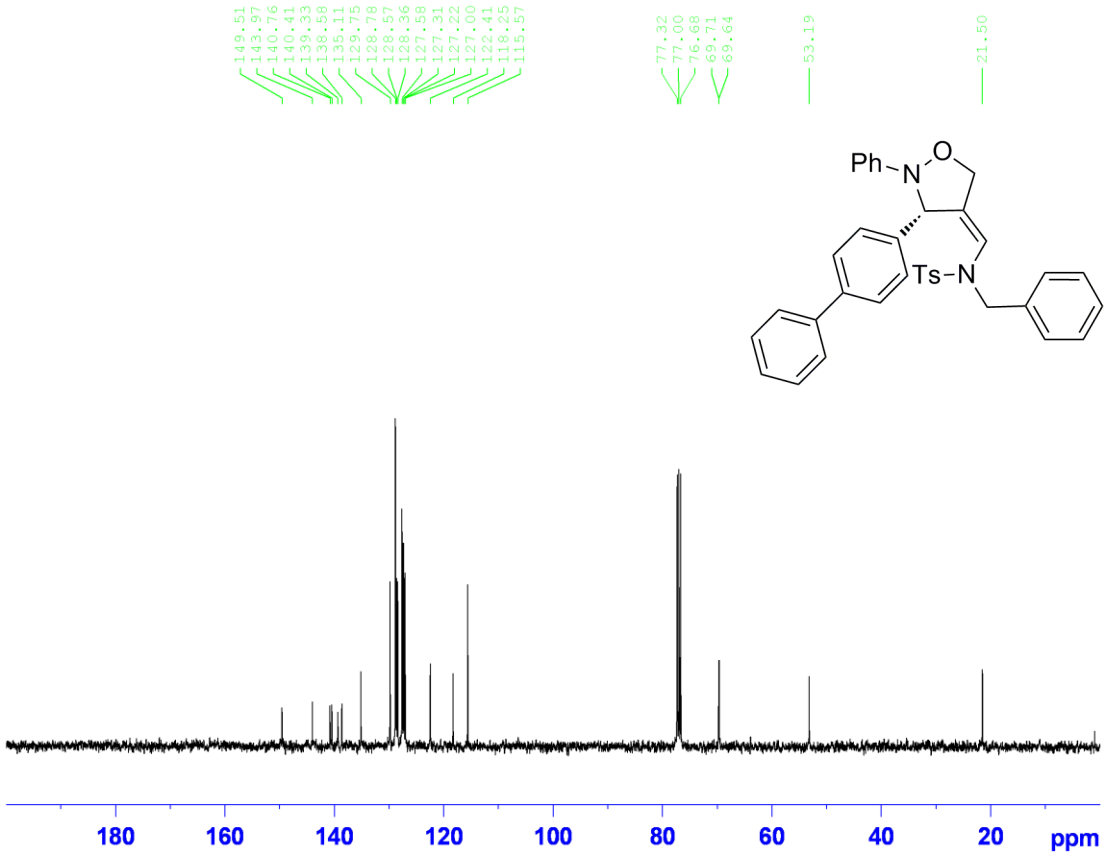
^{13}C NMR (100MHz, $CDCl_3$) of **4a**:



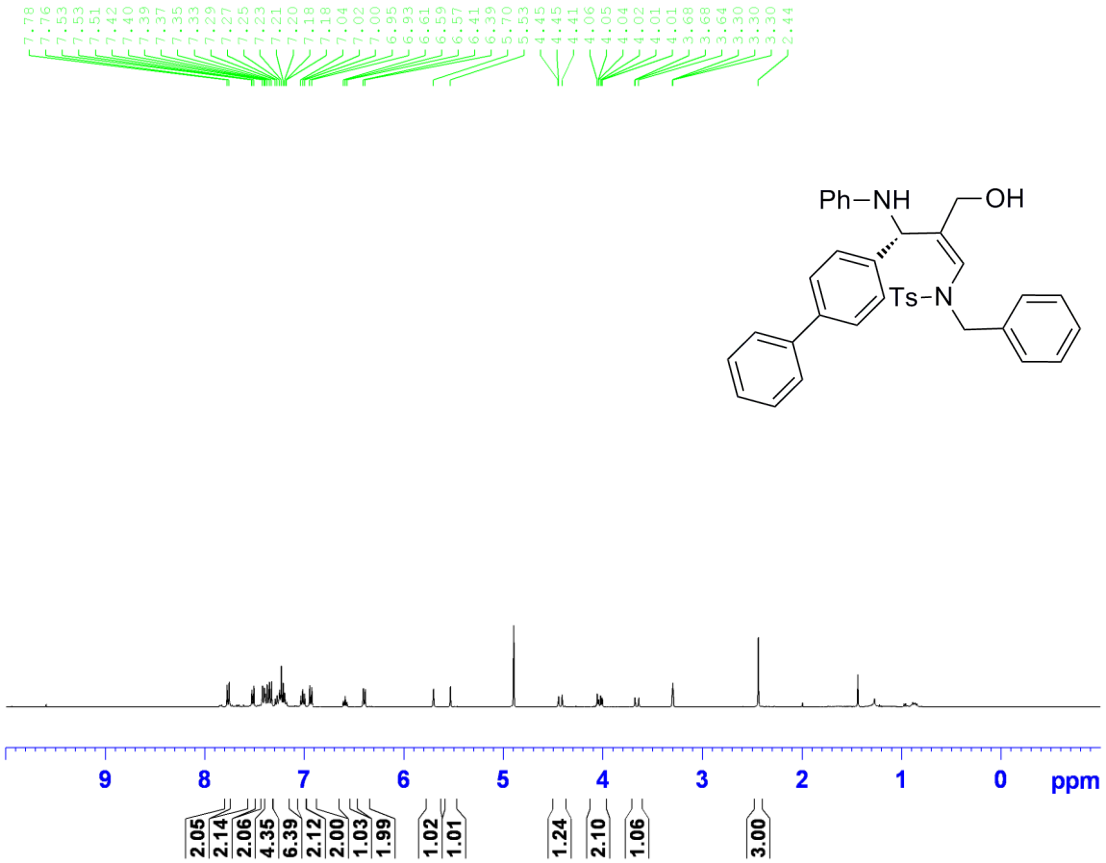
^{1}H NMR (400MHz, $CDCl_3$) of **5**:



^{13}C NMR (100MHz, $CDCl_3$) of **5**:



^{1}H NMR (400MHz, MeOD-d_4) of **6**:



^{13}C NMR (100MHz, MeOD-d_4) of **6**: