Supporting Information

Silver-catalyzed stereospecific (3+3)-cross-dimerization of oxaziridines with aziridines: divergent access to functionalized oxadiazines

Table of Contents

General Information. $AgNTf_2$ (96%), AgOTf (≥99%), $AgBF_4$ (98%), AgOAc (99%), $Cu(OTf)_2$ (98%), $Ni(OTf)_2$ (96%), $Yb(OTf)_3$ (99.99%), $Zn(OTf)_2$ (98%), $Ni(ClO_4)_2$•$6H_2O$, , $Pd(PPh_3)_4$ (99%), $PdCl_2(PPh_3)_2$ (98%), CuI (98%), 3-chloroperbenzoic acid (≤77%), chloramine-T trihydrate (98%), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (≥99.0%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (98%), (*R*)-(-)-2-phenylglycinol (98%), (*S*)-(+)-2-phenylglycinol (98%) of Aldrich, SRL Chemicals, BLD pharm and TCI Chemicals were used as received. Tetrahydrofuran (THF), toluene, $(CH_2Cl)_2$, CH_2Cl_2, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF) and CH_3CN were dried prior to use according to the standard procedure. Merck silica gel G/GF 254 plates used for analytical TLC and SRL silica gel (100-200 mesh) used for column chromatography. NMR (^1H, $^{13}C\{^1H\}$ and ^{19}F) spectra have been recorded with Bruker Avance III 600, 500 and 400 MHz spectrometers using $CDCl_3$ and DMSO-d_6 as solvent with Me_4Si as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in ppm and in Hz, respectively, and peak patterns are shown as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets. Melting points have been determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra have been collected on Perkin Elmer IR spectrometer. HPLC analysis has been carried out using Waters-2489 with Daicel CHIRAPAK AD-H and YMC Chiral ART Cellulose-SC columns utilizing *iso*-propanol and hexane as eluent. Optical rotation was determined using a Rudolph Autopol I Automatic Polarimeter. Quadrupole time-of-flight electrospray ionization (ESI) mass spectrometer (Agilent 6546) has been used for HRMS. Single crystal X-ray data have been collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure has been solved by direct method using 'SHELXL-2019/1 and SHELXL 2018/3 (Göttingen, Germany).

Sample Preparation for Crystal Growth. The compounds (±)-**3ka** and (±)-**4pa** were dissolved in 1 mL of CH_3CN and kept for slow evaporation. Block shaped crystal was formed which was subjected to X-ray diffraction analysis.

Crystal Data and Structure Refinement for (±)-**3ka**

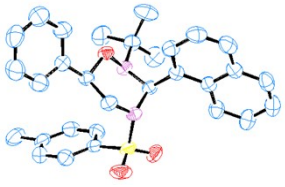


Figure S1. ORTEP diagram of 2-(*tert*-butyl)-3-(naphthalen-1-yl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-**3ka** (CCDC 2426695) with 50% ellipsoid. H-omitted for clarity.

Identification code	(±)-**3ka**
Empirical formula	'C30 H32 N2 O3 S'
Formula weight	501.64
Crystal habit, colour	Block/Colourless
Temperature, *T*/K	293 K
Wavelength, λ/Å	0.71073
Crystal system	'monoclinic'
Space group	' P 21/c'
Unit cell dimensions	a = 8.1277(10) Å b = 14.3667(13) Å c = 22.6619(18) Å α = 90 β = 96.681(9) γ = 90
Volume, *V*/Å^3	2628.2(5)
Z	4
Calculated density, Mg·m^{-3}	1.268
Absorption coefficient, μ/mm^{-1}	0.157
F(000)	1068
θ range for data collection	2.29 to 28.73°
Limiting indices	-10 ≤ h ≤ 9, –19 ≤ k ≤ 9, –28 ≤ l ≤ 29
Reflection collected / unique	5933/4034
Refinement method	'SHELXL-2019/1 (Sheldrick, 2019)'
Data / restraints / parameters	5933/0/ 330
Goodness–of–fit on F^2	1.041
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0571, wR2 = 0.1339
R indices (all data)	R1 = 0.0874, wR2 = 0.1617

Crystal Data and Structure Refinement for (±)-4pa

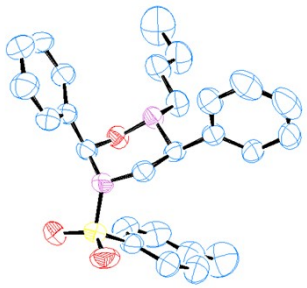


Figure S2. ORTEP diagram of 2-butyl-3,6-diphenyl-5-tosyl-1,2,5-oxadiazinane (±)-**4pa** (CCDC 2426708) with 50% ellipsoid. H-omitted for clarity.

Identification code	(±)-**4pa**
Empirical formula	'C26 H30 N2 O3 S'
Formula weight	450.58
Crystal habit, colour	Block/Colourless
Temperature, *T*/K	296 K
Wavelength, λ/Å	0.71073
Crystal system	'monoclinic'
Space group	'I 1 a 1'
Unit cell dimensions	a = 8.1212(9) Å b = 29.253(3) Å c = 11.1577(11) Å α = 90 β = 110.143(7) γ = 90
Volume, *V*/Å^3	2488.6(5)
Z	4
Calculated density, Mg·m^{-3}	1.203
Absorption coefficient, μ/mm^{-1}	0.159
F(000)	960
θ range for data collection	1.39 to 25.05°
Limiting indices	-9 ≤ h ≤ 9, –34 ≤ k ≤ 34, –13 ≤ l ≤ 13
Reflection collected / unique	4399/3132
Refinement method	'SHELXL 2018/3 (Sheldrick, 2015)'

Data / restraints / parameters	4399/2/ 292
Goodness−of−fit on F^2	1.013
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0350, wR2 = 0.0833
R indices (all data)	R1 = 0.0588, wR2 = 0.0985

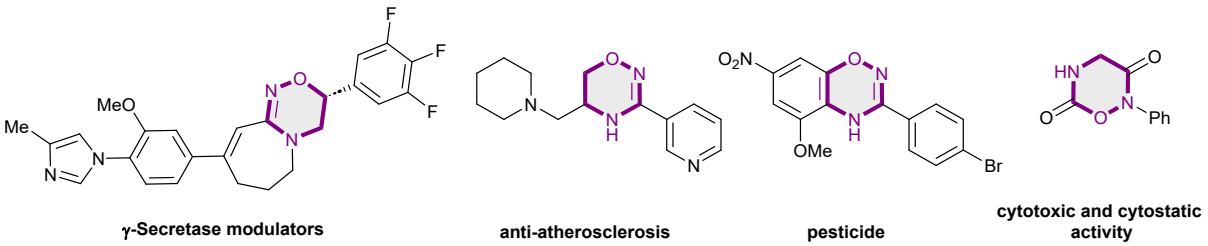
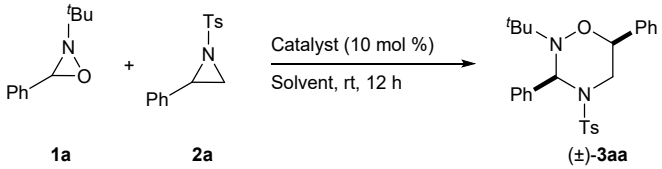


Figure S3. Examples of biologically important [1,2,4]/[1,2,5]-oxadiazine scaffolds.

Table S1. Optimization of the Reaction Conditions[a]

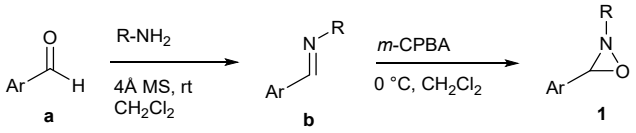


Entry	Catalyst (10 mol %)	Solvent	Yield [(±)-**3aa**, (%)][b]
1	$Ni(OTf)_2$	$(CH_2Cl)_2$	45
2	$Cu(OTf)_2$	$(CH_2Cl)_2$	68
3	AgOTf	$(CH_2Cl)_2$	70
4	$Zn(OTf)_2$	$(CH_2Cl)_2$	54
5	$Yb(OTf)_3$	$(CH_2Cl)_2$	60
6	$Ni(ClO_4)_2•6H_2O$	$(CH_2Cl)_2$	35
7	**$AgNTf_2$**	**$(CH_2Cl)_2$**	**82**
8	$AgBF_4$	$(CH_2Cl)_2$	55
9	AgOAc	$(CH_2Cl)_2$	n.r.
10	AgTFA	$(CH_2Cl)_2$	40
11	$AgNTf_2$	CH_2Cl_2	77
12	$AgNTf_2$	toluene	35
13	$AgNTf_2$	DMSO	n.r.
14	$AgNTf_2$	DMF	n.r.

15	$AgNTf_2$	CH_3CN	20
16	$AgNTf_2$	THF	trace
17[c]	$AgNTf_2$	$(CH_2Cl)_2$	62
18	-	$(CH_2Cl)_2$	n.r.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (10 mol %), solvent (2 mL), rt, 12 h. [b]Yield of the isolated product. [c]At 80 °C. n.r. = no reaction.

Scheme S1. **General Procedure for the Synthesis of Oxaziridines 1**[1a,1c]

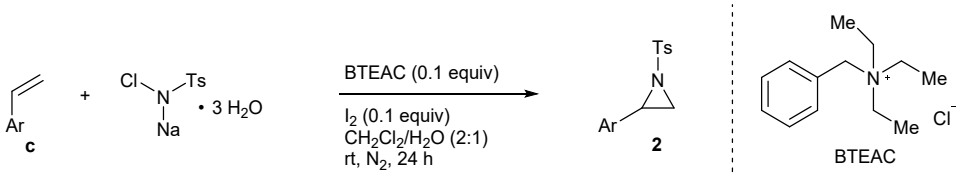


Step 1 (Scheme S1): To a stirred solution of aldehyde **a** (3 mmol, 1 equiv) and 4Å molecular sieves (3g) in CH_2Cl_2 (9 mL), appropriate amine (12 mmol, 4 equiv) was added dropwise and the resulting mixture was allowed to stir at room temperature for 6 h. After completion (monitored by TLC), the molecular sieves were removed by filtration and the solvent was evaporated to give imine **b** which was used for the next step without further purification.

Step 2 (Scheme S1): To a stirred solution of imine **b** (2 mmol, 1 equiv) in CH_2Cl_2 (4 mL), a solution of *m*-CPBA (4 mmol, 2 equiv) in CH_2Cl_2 (4 mL) was added dropwise at 0 °C. The resulting mixture was stirred at same temperature for 24 h. After completion (monitored by TLC), the resulting mixture was treated with saturated Na_2SO_3 (2 x 5 mL) and Na_2CO_3 (2 x 5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give **1**.

Oxaziridines **1m**[1b],**1o**[1b] and **1s**[1b] prepared according to the reported procedures.

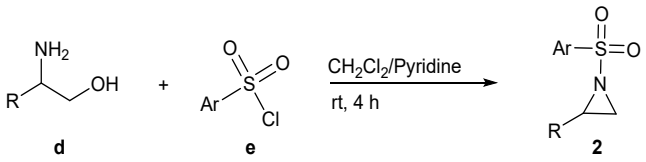
Scheme S2. General Procedure for the Synthesis of Aziridines 2a-h, 2n and 2o[2]



To a stirred solution of the alkene **c** (2 mmol, 1 equiv) and benzyltriethylammonium chloride (BTEAC) (0.2 mmol, 0.1 equiv) in CH_2Cl_2/H_2O (2:1, 15 mL), were added chloramine T

trihydrate (2.4 mmol, 1.2 equiv) and iodine (0.2 mmol, 0.1 equiv) at room temperature under N_2 atmosphere and the resulting mixture was allowed to stir for 24 h. After completion (monitored by TLC), the reaction mixture was washed with saturated $Na_2S_2O_3$ (2 x 10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give **2a**-**h**, **2n** and **2o**.

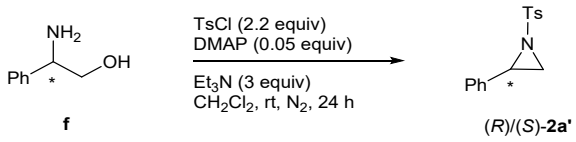
Scheme S3. General Procedure for the Synthesis of Aziridines 2i-m, 2p and 2t[2b]



To a stirred solution of amino alcohol **d** (3 mmol, 1 equiv) in CH_2Cl_2/pyridine (2:1, 3.15 mL) was added the appropriate sulfonyl chloride **e** (9 mmol, 3 equiv) in one portion at 0 °C. The resultant mixture was warmed to room temperature and allowed to stir for 4 h. After completion (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (30 mL), and washed with aqueous 2 N HCl (3 x 10 mL). The combined aqueous layers were extracted with CH_2Cl_2 (1 x 20 mL). The organic layer was then washed with aqueous 2 N KOH (3 x 10 mL). The combined basic layers were then extracted with CH_2Cl_2 (1 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give **2i**-**m**, **2p** and **2t**.

Aziridines **2q**[2a], **2r**[2e] and **2s**[2e] were prepared according to the reported procedure.

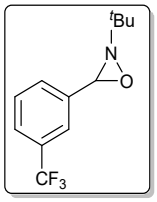
Scheme S4. Synthesis of Aziridines (*R*)/(*S*)-2a′[2e]



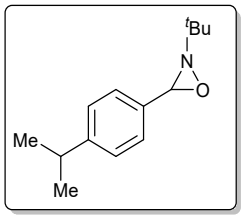
To a stirred solution of (*R*)/(*S*)-2-phenylglycinol **f** (1 mmol, 1 equiv, 137 mg), TsCl (2.2 mmol, 2.2 equiv, 420 mg) and DMAP (0.05 mmol, 0.05 equiv, 6 mg) in CH_2Cl_2 (20 mL) at 0 °C was added a solution of Et_3N (3.0 mmol, 3 equiv, 303 mg) in CH_2Cl_2 (5 mL). The resultant mixture was warmed to room temperature and allowed to stir for 24 h under N_2 atmosphere. After completion (monitored by TLC), the mixture was treated with a saturated NH_4Cl (20 mL) and

extracted with CH_2Cl_2 (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate (9:1) as eluent to afford (*R*)/(*S*)**2a′**.

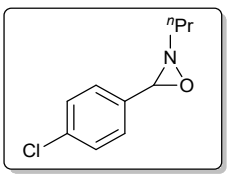
Characterization Data of Starting Materials



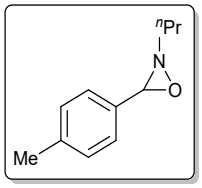
2-(*tert*-Butyl)-3-(3-(trifluoromethyl)phenyl)-1,2-oxaziridine 1d. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane R_f = 0.50; colorless liquid; yield 61% (448 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.65-7.61 (m, 2H), 7.51-7.47 (m, 1H), 4.73 (s, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 131.3 (q, *J* = 32.4 Hz), 131.1, 129.1, 126.7 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 270.6 Hz), 124.7 (q, *J* = 3.8 Hz), 73.0, 58.8, 25.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.675; FT-IR (neat) 2928, 1329, 1166, 1127, 1070, 803, 699 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{15}F_3NO$: 246.1100, found: 246.1102.



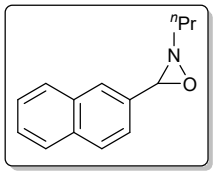
2-(*tert*-Butyl)-3-(4-isopropylphenyl)-1,2-oxaziridine 1j. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane R_f = 0.48; colorless liquid; yield 65% (427 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 1H), 2.95-2.88 (m, 1H), 1.35 (d, *J* = 7.2 Hz, 6H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 133.1, 127.6, 126.6, 73.7, 58.4, 34.1, 25.4, 24.0; FT-IR (neat) 2961, 1608, 1459, 1362, 1260, 824, 767 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{22}NO$: 220.1696, found: 220.1697.



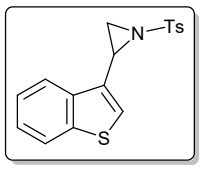
3-(4-Chlorophenyl)-2-propyl-1,2-oxaziridine 1t. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane R_f = 0.55; colorless liquid; yield 70% (413 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.356-7.350 (m, 4H), 4.46 (s, 1H), 2.96-2.91 (m, 1H), 2.74-2.69 (m, 1H), 1.78-1.71 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 133.6, 129.0, 128.8, 79.8, 64.0, 21.4, 12.0; FT-IR (neat) 2924, 1675, 1609, 1512, 1376, 1184, 814, 654 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{10}H_{13}ClNO$: 198.0680, found: 198.0679.



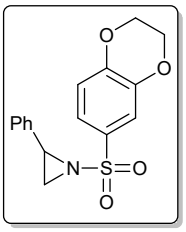
2-Propyl-3-(*p*-tolyl)-1,2-oxaziridine 1u. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane R_f = 0.60; colorless liquid; yield 72% (382 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.45 (s, 1H), 2.94-2.89 (m, 1H), 2.76-2.71 (m, 1H), 2.36 (s, 3H), 1.79-1.71 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.0, 129.3, 127.6, 80.6, 64.0, 21.4, 21.3, 12.0; FT-IR (neat) 2964, 1679, 1490, 1378, 1091, 1013, 825, 522 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{11}H_{16}NO$: 178.1226, found: 178.1225.



3-(Naphthalen-2-yl)-2-propyl-1,2-oxaziridine 1v. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane R_f = 0.48; colorless liquid; yield 55% (351 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87-7.83 (m, 3H), 7.53-7.49 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 4.66 (s, 1H), 3.02-2.97 (m, 1H), 2.83-2.77 (m, 1H), 1.83-1.76 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4, 133.0, 132.5, 128.6, 128.2, 128.2, 127.9, 126.9, 126.5, 124.0, 80.8, 64.1, 21.4, 12.0; FT-IR (neat) 2926, 1682, 1624, 1373, 1189, 819, 748 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO$: 214.1226, found: 214.1224.



2-(Benzo[b]thiophen-3-yl)-1-tosylaziridine 2o. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.43; sticky liquid; yield 39% (256 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8 Hz, 2H), 7.84-7.81 (m, 4H), 7.37-7.33 (m, 4H), 7.25 (d, *J* = 7.6 Hz), 4.03-4.00 (m, 1H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.55 (d, *J* = 4.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 140.6, 137.8, 134.9, 130.5, 129.9, 128.2, 124.9, 124.6, 124.5, 122.9, 121.8, 36.6, 34.7, 21.8; FT-IR (neat) 2923, 1596, 1430, 1323, 1160, 1091, 901, 718 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_2S_2$: 330.0617, found: 330.0605.

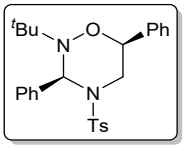


1-((2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)sulfonyl)-2-phenylaziridine 2t. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 154-155 °C; yield 35% (332 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.4 Hz, 1H), 7.47-7.44 (m, 1H), 7.30-7.25 (m, 3H), 7.23-7.21 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.30 (m, 4H), 3.74 (dd, *J* = 7.2, 4.4 Hz, 1H), 2.94 (d, *J* = 7.2 Hz, 1H), 2.37 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 143.6, 135.2, 130.1, 128.6, 128.3, 126.6, 121.7, 117.9, 117.7, 64.6, 64.2, 41.0, 36.1; FT-IR (KBr) 2956, 1594, 1498, 1458, 1326, 1190, 1015, 775 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO_4S$: 318.0795, found: 318.0779.

General Procedure for the Synthesis of [1,2,4]/[1,2,5]-Oxadiazines. Oxaziridine **1** (0.2 mmol, 1.0 equiv), aziridine **2** (0.2 mmol, 1.0 equiv) and $AgNTf_2$ (7.7 mg, 0.02 mmol, 0.1 equiv) were stirred in $(CH_2Cl)_2$ (2.0 mL, 0.1 M) at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (5 mL) and passed through a short pad of celite using CH_2Cl_2 (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3**/**4**.

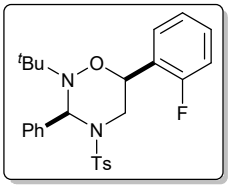
General Procedure for the Stereospecific Synthesis of [1,2,4]/[1,2,5]-Oxadiazines. Oxaziridine **1** (0.2 mmol, 1.0 equiv), (*R*)/(*S*)-**2a′** (0.2 mmol, 1.0 equiv) and $AgNTf_2$ (7.7 mg, 0.02 mmol, 0.1 equiv) were stirred in $(CH_2Cl)_2$ (2.0 mL, 0.1 M) at room temperature for 12 h. The purification was performed as above in general procedure to afford **3′**/**4′**. Then HPLC analysis was carried out using Daicel CHIRALPAK AD-H and YMC Chiral ART Cellulose-SC columns utilizing *iso*-propanol and hexane as eluent.

Characterization Data of Products

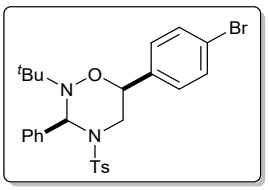


(3*S*,6*S*)-2-(*tert*-Butyl)-3,6-diphenyl-4-tosyl-1,2,4-oxadiazinane 3aa′. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 136-137 °C; yield 80% (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.40-7.37 (m, 2H), 7.35-7.33 (m, 1H), 7.31-7.28 (m, 5H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.06

(s, 1H), 4.74 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.83 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.42-3.37 (m, 1H), 2.38 (s, 3H), 0.98 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.3, 139.0, 138.3, 137.5, 129.7, 129.4, 128.7, 128.45, 128.40, 128.3, 127.7, 125.8, 78.6, 72.3, 58.3, 45.5, 26.8, 21.6; FT-IR (KBr) 2970, 2922, 2856, 1345, 1160, 959, 659 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$: 451.2050, found: 451.2055; $[\alpha]_D^{20.9}$ = +60 (c = 0.02, $CHCl_3$); HPLC: 94% *ee* [CHIRALPAK AD-H, hexane/^{i}PrOH = 98:02, flow rate: 1 mL /min, λ = 254 nm, t_R = 16.27 min (major), 20.51 min (minor)]: **(3*R*,6*R*)-2-(*tert*-Butyl)-3,6-diphenyl-4-tosyl-1,2,4-oxadiazinane 3aa′′.** Colorless solid; $[\alpha]_D^{21.0}$ = -10 (c = 0.01, $CHCl_3$); HPLC: 92% *ee* [CHIRALPAK AD-H, hexane/^{i}PrOH = 98:02, flow rate: 1 mL /min, λ = 254 nm, t_R = 16.46 min (minor), 20.95 min (major)].

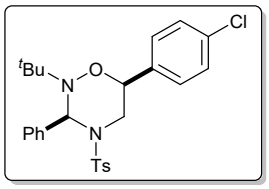


2-(*tert*-Butyl)-6-(2-fluorophenyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ab. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 224-225 °C; yield 65% (61 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz,1H), 7.33-7.29 (m, 4H), 7.26-7.24 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.07-7.03 (m, 1H), 6.06 (s, 1H), 4.87 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.94 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.44-3.39 (m, 1H), 2.40 (s, 3H), 0.95 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.6 (d, $J_{C\text{-}F}$ = 245.7 Hz), 143.4, 139.0, 137.6, 129.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.6, 129.4, 128.4, 128.3, 127.8, 127.0 (d, $J_{C\text{-}F}$ = 4.2 Hz), 125.6 (d, $J_{C\text{-}F}$ = 14.0 Hz), 124.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.2 Hz), 73.4, 72.5, 58.2, 44.6, 26.7, 21.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.431; FT-IR (KBr) 2922, 1493, 1455, 1345, 1162, 959, 705, 661 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{30}FN_2O_3S$: 469.1956, found: 469.1958.

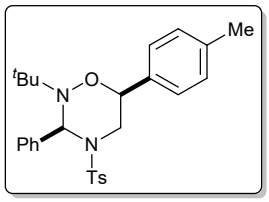


6-(4-Bromophenyl)-2-(*tert*-butyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ac. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 168-169 °C; yield 70% (74 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 3H), 7.18-7.17 (m, 4H), 6.04 (s, 1H), 4.70 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.81 (dd, *J* = 14.0, 3.0 Hz, 1H), 3.35-3.30 (m, 1H), 2.38 (s, 3H), 0.97 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.4, 138.8,

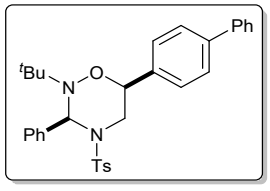
137.3, 137.1, 131.9, 129.5, 129.4, 128.5, 128.4, 127.6, 127.5, 122.3, 78.0, 72.2, 58.4, 45.3, 26.7, 21.6; FT-IR (KBr) 2926, 1488, 1343, 1162, 1010, 959, 703 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{30}BrN_2O_3S$: 529.1155, found: 529.1158.



2-(*tert*-Butyl)-6-(4-chlorophenyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ad. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; mp 185-186 °C; yield 69% (67 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.68 (m, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30-7.28 (m, 3H), 7.24-7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.05 (s, 1H), 4.72 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.81 (dd, *J* = 14.0, 3.0 Hz, 1H), 3.36-3.31 (m, 1H), 2.38 (s, 3H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.4, 138.9, 137.3, 136.6, 134.3, 129.6, 129.4, 129.0, 128.5, 128.4, 127.6, 127.2, 78.0, 72.2, 58.4, 45.4, 26.7, 21.6; FT-IR (KBr) 2924, 1490, 1340, 1162, 959, 814, 656 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{30}ClN_2O_3S$: 485.1660, found: 485.1666.

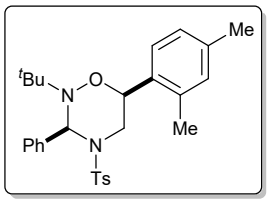


2-(*tert*-Butyl)-3-phenyl-6-(*p*-tolyl)-4-tosyl-1,2,4-oxadiazinane (±)-3ae. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 159-160 °C; yield 78% (73 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79-7.78 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.35-7.32 (m, 4H), 7.25-7.23 (m, 5H), 6.10 (s, 1H), 4.76 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.87 (dd, *J* = 14.0, 2.5 Hz, 1H), 3.48-3.43 (m, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 1.03 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.2, 139.1, 138.2, 137.5, 135.2, 129.7, 129.4, 129.3, 128.4, 128.2, 127.7, 125.9, 78.5, 72.3, 58.3, 45.5, 26.7, 21.6, 21.3; FT-IR (KBr) 2927, 1340, 1162, 959, 702, 659 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{33}N_2O_3S$: 465.2206, found: 465.2206.

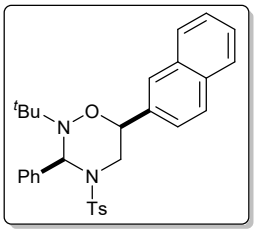


6-([1,1'-Biphenyl]-4-yl)-2-(*tert*-butyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3af. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 180-181 °C; yield 76% (80 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.74

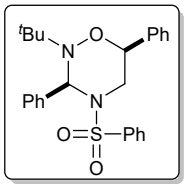
(m, 2H), 7.62-7.57 (m, 6H), 7.46-7.43 (m, 2H), 7.39-7.36 (m, 3H), 7.30-7.29 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.79 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.88 (dd, *J* = 14.0, 3.0 Hz, 1H), 3.46-3.41 (m, 1H), 2.39 (s, 3H), 1.00 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.3, 141.4, 140.7, 139.0, 137.4, 137.1, 129.7, 129.4, 129.0, 128.4, 128.3, 127.7, 127.6, 127.5, 127.2, 126.3, 78.4, 72.3, 58.4, 45.5, 26.8, 21.6; FT-IR (KBr) 2924, 1488, 1340, 1162, 959, 761, 664 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{35}N_2O_3S$: 527.2363, found: 527.2366.



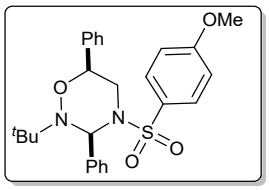
2-(*tert*-Butyl)-6-(2,4-dimethylphenyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ag. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 169-170 °C; yield 75% (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz,1H), 6.98 (s, 1H), 6.10 (s, 1H), 4.85 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.70 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.44-3.39 (m, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.14 (s, 3H), 0.97 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.3, 139.2, 138.1, 137.7, 135.4, 133.3, 131.5, 129.7, 129.3, 128.4, 128.2, 127.9, 127.1, 125.4, 75.9, 72.4, 58.2, 44.5, 26.8, 21.6, 21.1, 19.1; FT-IR (KBr) 2925, 1452, 1344, 1161, 959, 703, 659 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{35}N_2O_3S$: 479.2363, found: 479.2367.



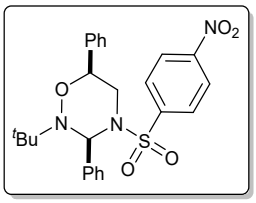
2-(*tert*-Butyl)-6-(naphthalen-2-yl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ah. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 147-148 °C; yield 79% (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.83 (m, 3H), 7.77-7.76 (m, 3H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.52-7.49 (m, 2H), 7.42 (m, 1H), 7.30-7.29 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H),), 6.09 (s, 1H), 4.92 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.95 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.51-3.46 (m, 1H), 2.38 (s, 3H), 1.02 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.3, 139.0, 137.4, 135.6, 133.29, 133.26, 129.7, 129.4, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 126.5, 126.4, 124.7, 123.8, 78.6, 72.3, 58.4, 45.5, 26.8, 21.6; FT-IR (KBr) 2975, 2926, 1341, 1161, 957, 815, 660 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{33}N_2O_3S$: 501.2206, found: 501.2208.



2-(*tert*-Butyl)-3,6-diphenyl-4-(phenylsulfonyl)-1,2,4-oxadiazinane (±)-3ai. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 172-173 °C; yield 70% (61 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 4H), 7.52-7.48 (m, 1H), 7.41-7.34 (m, 5H), 7.31-7.28 (m, 5H), 6.05 (s, 1H), 4.73 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.87 (dd, *J* = 17.5, 4.0 Hz, 1H), 3.44-3.38 (m, 1H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 140.2, 138.8, 138.1, 132.5, 129.6, 128.8, 128.45, 128.47, 128.40, 127.6, 125.9, 78.6, 72.4, 58.3, 45.6, 26.7; FT-IR (KBr) 2924, 1452, 1348, 1164, 959, 735, 696, 594 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{29}N_2O_3S$: 437.1893, found: 437.1898.

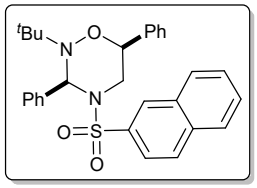


2-(*tert*-Butyl)-4-((4-methoxyphenyl)sulfonyl)-3,6-diphenyl-1,2,4-oxadiazinane (±)-3aj. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.42; colorless solid; mp 204-205 °C; yield 72% (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 2H), 7.35-7.28 (m, 6H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.05 (s, 1H), 4.75 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.83-3.79 (m, 4H), 3.40-3.35 (m, 1H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.8, 139.0, 138.2, 131.9, 129.77, 129.70, 128.7, 128.4, 128.39, 128.33, 125.8, 113.9, 78.5, 72.3, 58.3, 55.7, 45.5, 26.7; FT-IR (KBr) 2972, 2932, 1597, 1495, 1340, 1157, 958, 702 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_4S$: 467.1999, found: 467.2001.

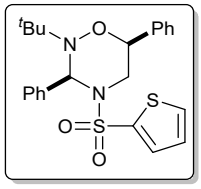


2-(*tert*-Butyl)-4-((4-nitrophenyl)sulfonyl)-3,6-diphenyl-1,2,4-oxadiazinane (±)-3ak. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.44; colorless solid; mp 179-180 °C; yield 81% (78 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.43-7.40 (m, 2H), 7.38-7.37 (m, 1H), 7.34-7.30 (m, 3H), 7.28-7.26 (m, 2H), 6.03 (s, 1H), 4.89 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.91 (dd, *J* = 13.5, 3.5 Hz, 1H), 3.41-3.36 (m, 1H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.8, 145.6, 138.2, 137.6, 129.6, 128.9, 128.8, 128.7, 128.66, 128.63, 125.9, 123.8,

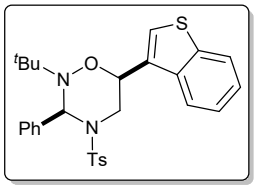
78.9, 72.8, 58.7, 45.8, 26.7; FT-IR (KBr) 2975, 2924, 1528, 1350, 1162, 949, 738, 611 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{28}N_3O_5S$: 482.1744, found: 482.1748.



2-(*tert*-Butyl)-4-(naphthalen-2-ylsulfonyl)-3,6-diphenyl-1,2,4-oxadiazinane (±)-3al. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 131-132 °C; yield 76% (74 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.86-7.83 (m, 3H), 7.76-7.74 (m, 2H), 7.69-7.68 (m, 1H), 7.62-7.55 (m, 2H), 7.38-7.35 (m, 2H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.28-7.26 (m, 5H), 6.14 (s, 1H), 4.75 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.92 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.45-3.40 (m, 1H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.8, 138.1, 137.1, 134.7, 132.1, 129.6, 129.2, 128.95, 128.91, 128.7, 128.48, 128.44, 128.42, 127.9, 127.4, 125.8, 123.0, 78.7, 72.4, 58.4, 45.6, 26.7; FT-IR (KBr) 2972, 2927, 1333, 1160, 960, 702, 657 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{31}N_2O_3S$: 487.2050, found: 487.2053.

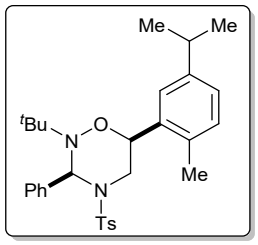


2-(*tert*-Butyl)-3,6-diphenyl-4-(thiophen-2-ylsulfonyl)-1,2,4-oxadiazinane (±)-3am. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 129-130 °C; yield 73% (65 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.51 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.37-7.34 (m, 4H), 7.31-7.29 (m, 3H), 6.99-6.97 (m, 1H), 6.06 (s, 1H), 4.84 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.93 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.49-3.43 (m, 1H), 1.00 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.0, 138.6, 138.1, 132.3, 131.8, 129.7, 128.8, 128.5, 128.4, 127.1, 125.8, 78.6, 72.6, 58.4, 45.7, 26.7; FT-IR (KBr) 2974, 1453, 1352, 1157, 1014, 959, 732, 666 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{27}N_2O_3S_2$: 443.1458, found: 443.1449.

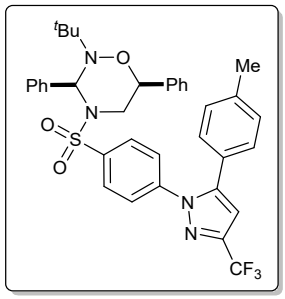


6-(Benzo[*b*]thiophen-3-yl)-2-(tert-butyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ao. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 151-152 °C; yield 59% (60 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87

(m, 1H), 7.77-7.75 (m, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.61-7.59 (m, 1H), 7.47 (s, 1H), 7.40-7.37 (m, 2H), 7.31-7.29 (m, 3H), 7.24 (d, J = 8 Hz, 2H), 6.13 (s, 1H), 5.10 (dd, J = 11.2, 2.8 Hz), 3.96 (dd, J = 14.0, 3.2 Hz), 3.64-3.59 (m, 1H), 2.40 (s, 3H), 1.00 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.5, 140.4, 139.0, 137.5, 137.4, 133.1, 129.6, 129.5, 128.5, 128.4, 127.8, 124.8, 124.5, 123.2, 123.0, 121.7, 73.9, 72.6, 58.4, 44.4, 26.9, 21.6; FT-IR (KBr) 2925, 1455, 1346, 1161, 955, 817, 733 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{31}N_2O_3S_2$: 507.1771, found: 507.1780.

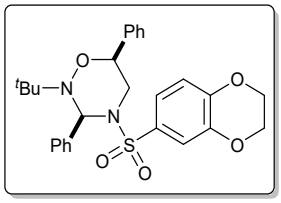


2-(*tert*-Butyl)-6-(5-isopropyl-2-methylphenyl)-3-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ar. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; yellow solid; mp 186-187 °C; yield 78% (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.33-7.32 (m, 4H), 7.23 (d, J = 7.5 Hz, 2H), 7.11-7.07 (m, 2H), 6.12 (s, 1H), 4.85 (dd, J = 11.0, 3.0 Hz, 1H), 3.72 (dd, J = 15.5, 3.5 Hz, 1H), 3.47-3.42 (m, 1H), 2.96-2.88 (m, 1H), 2.40 (s, 3H), 2.14 (s, 3H), 1.27 (d, J = 7.0 Hz, 6H), 0.99 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 146.9, 143.3, 139.2, 137.8, 136.1, 132.6, 130.6, 129.7, 129.3, 128.4, 128.2, 127.9, 126.3, 123.5, 75.9, 72.3, 58.2, 44.4, 33.8, 26.8, 24.2, 24.0, 21.6, 18.7; FT-IR (KBr) 2960, 1457, 1348, 1162, 959, 748, 659 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{39}N_2O_3S$: 507.2676, found: 507.2675.

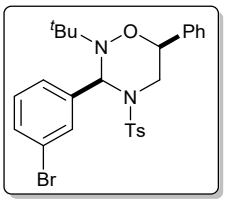


2-(*tert*-Butyl)-3,6-diphenyl-4-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonyl)-1,2,4-oxadiazinane (±)-3as. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless solid; mp 247-248 °C; yield 69% (91 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 4H), 7.43-7.34 (m, 5H), 7.30-7.29 (m, 5H), 7.08-7.03 (m, 4H), 6.71 (s, 1H), 6.04 (s, 1H), 4.75 (dd, J = 11.6, 3.2 Hz, 1H), 3.84 (dd, J = 14.0, 3.2 Hz, 1H), 3.43-3.37 (m, 1H), 2.28 (s, 3H), 0.98 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 145.2, 144.5 (q, $J_{C\text{-}F}$ = 38.5 Hz), 142.4, 139.83, 139.82, 138.6, 137.8, 129.8, 129.6, 128.9, 128.8,

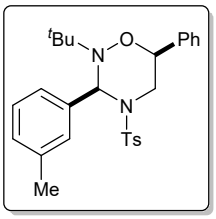
128.63, 128.60, 128.59, 128.53, 125.89, 125.84, 125.3, 123.8 (q, $J_{C\text{-}F}$ = 267.7 Hz), 106.4, 78.6, 72.6, 58.4, 45.7, 26.7, 21.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.430; FT-IR (KBr) 2927, 1470, 1358, 1236, 1164, 1099, 755 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{36}H_{36}F_3N_4O_3S$: 661.2455, found: 661.2462.



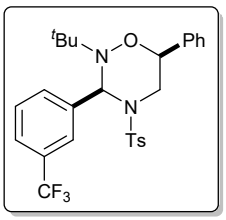
2-(*tert*-Butyl)-4-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)sulfonyl)-3,6-diphenyl-1,2,4-oxadiazinane (±)-3at. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.42; colorless solid; mp 188-189 °C; yield 70% (69 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.41-7.38 (m, 2H), 7.35-7.31 (m, 3H), 7.29-7.28 (m, 3H), 7.26-7.24 (m, 1H), 7.19 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.02 (s, 1H), 4.76 (dd, *J* = 11.0, 2.5 Hz, 1H), 4.28-4.24 (m, 4H), 3.82 (dd, *J* = 14.0, 3.0 Hz, 1H), 3.41-3.36 (m, 1H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.2, 143.3, 138.9, 138.3, 132.7, 129.7, 128.8, 128.4, 128.38, 128.32, 125.8, 121.3, 117.5, 117.4, 78.5, 72.3, 64.6, 64.2, 58.3, 45.6, 26.7; FT-IR (KBr) 2927, 1494, 1285, 1253, 1155, 958, 699 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{31}N_2O_5S$: 495.1948, found: 495.1956.



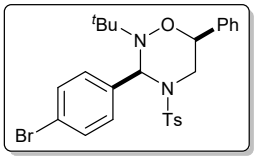
3-(3-Bromophenyl)-2-(*tert*-butyl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ba. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; mp 174-175 °C; yield 65% (69 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.43-7.38 (m, 3H), 7.36-7.33 (m, 1H), 7.29-7.28 (m, 2H), 7.23-7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 5.99 (s, 1H), 4.73 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.85 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.37-3.32 (m, 1H), 2.40 (s, 3H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.5, 141.1, 137.9, 137.2, 132.5, 131.3, 130.0, 129.5, 128.8, 128.5, 128.1, 127.6, 125.9, 122.4, 78.7, 71.4, 58.4, 45.5, 26.8, 21.6; FT-IR (KBr) 2924, 1345, 1162, 959, 748, 659, 583 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{30}BrN_2O_3S$: 529.1155, found: 529.1158.



2-(*tert*-Butyl)-6-phenyl-3-(*m*-tolyl)-4-tosyl-1,2,4-oxadiazinane (±)-3ca. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 184-185 °C; yield 77% (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3H), 7.44 (s, 1H), 7.40-7.37 (m, 2H), 7.35-7.29 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.17-7.14 (m, 1H), 7.11-7.09 (m, 1H), 6.01 (s, 1H), 4.71 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.83 (dd, *J* = 14.5, 3.5 Hz, 1H), 3.43-3.38 (m, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.2, 138.8, 138.3, 137.9, 137.4, 130.3, 129.3, 128.9, 128.7, 128.3, 128.2, 127.7, 126.7, 125.8, 78.5, 72.3, 58.3, 45.6, 26.8, 21.66, 21.62; FT-IR (KBr) 2978, 2924, 1344, 1161, 964, 744, 661 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{33}N_2O_3S$: 465.2206, found: 465.2211.

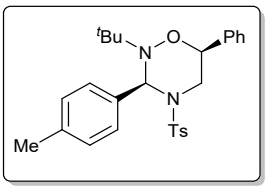


2-(*tert*-Butyl)-6-phenyl-4-tosyl-3-(3-(trifluoromethyl)phenyl)-1,2,4-oxadiazinane (±)-3da. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 128-129 °C; yield 70% (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.61-7.55 (m, 3H), 7.44-7.33 (m, 4H), 7.29-7.27 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.10 (s, 1H), 4.74 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.85 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.35-3.28 (m, 1H), 2.39 (s, 3H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.6, 139.8, 137.8, 137.1, 132.8, 130.7 (q, $J_{C\text{-}F}$ = 32.2 Hz), 129.5, 129.0, 128.9, 128.6, 127.5, 126.3 (q, $J_{C\text{-}F}$ = 4.1 Hz), 125.9, 125.18 (q, $J_{C\text{-}F}$ = 270.7 Hz) 125.10 (q, $J_{C\text{-}F}$ = 3.6 Hz), 78.9, 71.4, 58.4, 45.6, 26.8, 21.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.752; FT-IR (KBr) 2978, 2924, 1329, 1163, 1127, 964, 745, 664 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{30}F_3N_2O_3S$: 519.1924, found: 519.1933.

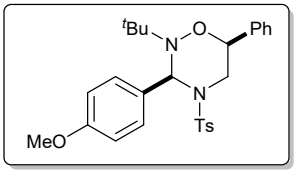


3-(4-Bromophenyl)-2-(*tert*-butyl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ea. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.42; colorless solid; mp 149-150 °C; yield 75% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59

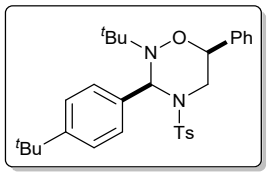
(m, 4H), 7.42-7.32 (m, 5H), 7.28-7.26 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 1H), 4.71 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.85 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.36-3.29 (m, 1H), 2.40 (s, 3H), 0.99 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.5, 138.0, 137.9, 137.2, 131.5, 131.2, 129.5, 128.8, 128.5, 127.6, 125.8, 122.5, 78.5, 71.5, 58.4, 45.4, 26.8, 21.6; FT-IR (KBr) 2978, 1485, 1345, 1161, 959, 745, 659, 585 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{30}BrN_2O_3S$: 529.1155, found: 529.1162.



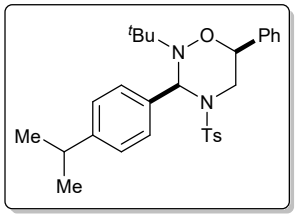
(3*S*,6*S*)-2-(*tert*-Butyl)-6-phenyl-3-(*p*-tolyl)-4-tosyl-1,2,4-oxadiazinane 3fa′. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 197-198 °C; yield 82% (76 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 4H), 7.40-7.37 (m, 2H), 7.34-7.32 (m, 1H), 7.30-7.29 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.02 (s, 1H), 4.70 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.81 (dd, *J* = 13.8, 3.0 Hz, 1H), 3.40-3.36 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 0.98 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 143.2, 138.3, 138.0, 137.4, 136.0, 129.5, 129.3, 129.0, 128.7, 128.3, 127.7, 125.8, 78.5, 72.2, 58.2, 45.6, 26.7, 21.6, 21.2; FT-IR (KBr) 2922, 1343, 1161, 959, 750, 659, 593 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{33}N_2O_3S$: 465.2206, found: 465.2208; $[\alpha]_D^{21.0}$ = +50 (c = 0.02, $CHCl_3$); HPLC: 94% *ee* [YMC Chiral ART Cellulose-SC, hexane/^{i}PrOH = 95:05, flow rate: 1 mL /min, λ = 254 nm, t_R = 12.94 min (major), 18.95 min (minor)].



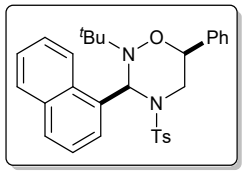
2-(*tert*-Butyl)-3-(4-methoxyphenyl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ga. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.42; colorless solid; mp 195-196 °C; yield 84% (81 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 4H), 7.41-7.33 (m, 3H), 7.30-7.28(m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.01 (s, 1H), 4.72 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.83-3.80 (m, 4H), 3.40-3.34 (m, 1H), 2.38 (s, 3H), 0.97 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.5, 143.2, 138.3, 137.4, 131.3, 130.8, 129.3, 128.7, 128.3, 127.7, 125.8, 113.7, 78.5, 71.9, 58.2, 55.3, 45.5, 26.7, 21.6; FT-IR (KBr) 2920, 1345, 1156, 942, 756, 720, 658 cm^{-1}; ; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{33}N_2O_4S$: 481.2156; found: 481.2158.



2-(*tert*-Butyl)-3-(4-(*tert*-butyl)phenyl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ha. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; colorless solid; mp 164-165 °C; yield 79% (80 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.40-7.38 (m, 2H), 7.35-7.31 (m, 3H), 7.27-7.26 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 4.77 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.84 (dd, *J* = 13.5, 3.0 Hz, 1H), 3.40-3.35 (m, 1H), 2.35 (s, 3H), 1.30 (s, 9H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.3, 143.0, 138.4, 137.3, 135.7, 129.3, 129.2, 128.7, 128.3, 127.7, 125.8, 125.2, 78.6, 72.2, 58.3, 45.7, 34.6, 31.4, 26.7, 21.5; FT-IR (KBr) 2965, 1346, 1163, 960, 730, 661, 592 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{39}N_2O_3S$: 507.2676, found: 507.2686.

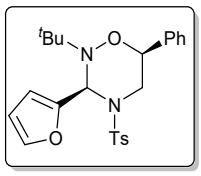


2-(*tert*-Butyl)-3-(4-isopropylphenyl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ja. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 131-132 °C; yield 76% (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41-7.37 (m, 2H), 7.35-7.30 (m, 3H), 7.15-7.10 (m, 4H), 6.01 (s, 1H), 4.76 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.84 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.39-3.33 (m, 1H), 2.90-2.84 (m, 1H), 2.36 (s, 3H), 1.24 (d, *J* = 7.6 Hz, 6H) 0.97 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.0, 143.0, 138.4, 137.3, 136.1, 129.6, 129.3, 128.7, 128.3, 127.7, 126.3, 125.8, 78.5, 72.3, 58.3, 45.7, 33.9, 26.7, 24.1, 24.0, 21.6; FT-IR (KBr) 2963, 1345, 1162, 960, 814, 661, 548 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{37}N_2O_3S$: 493.2519, found: 493.2519.

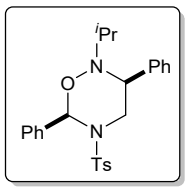


2-(*tert*-Butyl)-3-(naphthalen-1-yl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane (±)-3ka. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 229-230 °C; yield 74% (74 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.67-7.64 (m, 1H), 7.54-7.51 (m, 1H), 7.42-7.31 (m, 6H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.15 (s, 1H), 4.76-4.74 (m, 1H),

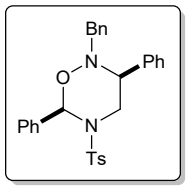
3.72-3.69 (m, 1H), 3.58-3.53 (m, 1H), 2.38 (s, 3H), 1.02 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.6, 138.3, 137.6, 134.2, 134.1, 131.2, 129.4, 129.2, 129.1, 128.9, 128.8, 128.4, 128.1, 127.1, 126.0, 125.7, 124.5, 123.7, 78.4, 65.9, 58.4, 45.4, 27.0, 21.6; FT-IR (KBr) 2974, 1346, 1159, 944, 810, 741, 664 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{33}N_2O_3S$: 501.2206, found: 501.2215.



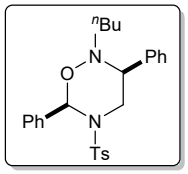
(3*S*,6*S*)-2-(*tert*-Butyl)-3-(furan-2-yl)-6-phenyl-4-tosyl-1,2,4-oxadiazinane 3la′. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; thick liquid; yield 85% (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.38-7.35 (m, 2H), 7.33-7.30 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.336-6.330 (m, 1H), 6.25-6.24 (m, 1H), 6.16 (s, 1H), 4.80 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.81 (dd, *J* = 13.0, 2.5 Hz, 1H), 3.29-3.24 (m, 1H), 2.37 (s, 3H), 0.96 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 150.4, 143.2, 141.3, 138.3, 136.7, 129.3, 128.7, 128.4, 127.6, 126.0, 110.6, 110.2, 78.6, 66.0, 58.2, 46.7, 26.0, 21.6; FT-IR (neat) 2978, 1347, 1223, 1161, 965, 748, 659 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{29}N_2O_4S$: 441.1843, found: 441.1847; $[\alpha]_D^{21.0}$ = +135 (c = 0.02, $CHCl_3$); HPLC: 95% *ee* [YMC Chiral ART Cellulose-SC, hexane/^{i}PrOH = 96:04, flow rate: 1 mL /min, λ = 254 nm, t_R = 17.14 min (major), 20.52 min (minor)].



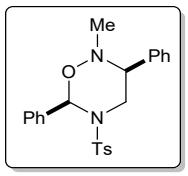
2-Isopropyl-3,6-diphenyl-5-tosyl-1,2,5-oxadiazinane (±)-4na. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 163-164 °C; yield 65% (57 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.44-7.39 (m, 4H), 7.35-7.32 (m, 1H), 7.18-7.17 (m, 3H), 6.87-6.85 (m, 2H), 6.83 (s, 1H), 3.71-3.65 (m, 1H), 3.44-3.38 (m, 2H), 2.61-2.56 (m, 1H), 2.50 (s, 3H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.57 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 143.9, 138.2, 137.7, 129.9, 128.8, 128.33, 128.31, 128.2, 127.8, 127.6, 127.4, 86.0, 61.5, 51.8, 47.5, 21.7, 21.2, 12.2; FT-IR (KBr) 2975, 2932, 1345, 1165, 959, 738, 687 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{29}N_2O_3S$: 437.1893, found: 437.1896.



2-Benzyl-3,6-diphenyl-5-tosyl-1,2,5-oxadiazinane (±)-4oa. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 166-167 °C; yield 70% (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 3H), 7.24-7.18 (m, 6H), 7.10-7.08 (m, 2H), 7.02-7.00 (m, 2H), 6.96-6.94 (m, 2H), 6.72 (s, 1H), 3.73-3.64 (m, 2H), 3.45-3.38 (m, 1H), 3.26 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.21 (d, *J* = 13.6 Hz, 1H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.0, 138.2, 137.7, 137.0, 136.7, 130.2, 129.9, 129.0, 128.5, 128.15, 128.13, 127.9, 127.7, 127.4, 127.2, 86.1, 65.9, 59.7, 47.4, 21.8; FT-IR (KBr) 2927, 1493, 1345, 1165, 1020, 746, 570 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{29}N_2O_3S$: 485.1893, found: 485.1894.

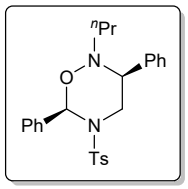


2-Butyl-3,6-diphenyl-5-tosyl-1,2,5-oxadiazinane (±)-4pa. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 133-134 °C; yield 68% (61 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 4H), 7.35-7.32 (m, 1H), 7.18-7.17 (m, 3H), 6.85-6.82 (m, 3H), 3.68-3.65 (m, 1H), 3.39-3.34 (m, 1H), 3.12 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.51 (s, 3H), 2.38-2.32 (m, 1H), 2.20-2.15 (m, 1H), 1.45-1.37 (m, 1H), 1.22-1.12 (m, 1H), 1.04-0.84 (m, 2H), 0.76 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.0, 138.4, 137.9, 137.7, 129.9, 128.8, 128.37, 128.35, 128.1, 127.9, 127.6, 127.2, 86.1, 66.3, 55.6, 47.4, 28.2, 21.8, 20.3, 13.9; FT-IR (KBr) 2926, 1434, 1346, 1132, 1036, 754, 661 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$: 451.2050, found: 451.2059.

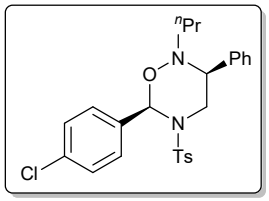


2-Methyl-3,6-diphenyl-5-tosyl-1,2,5-oxadiazinane (±)-4qa. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 165-166 °C; yield 67% (55 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.54-7.52 (m, 2H), 7.44-7.40 (m, 4H), 7.36-7.32 (m, 1H), 7.19-7.15 (m, 3H), 6.85-6.83 (m, 2H), 6.80 (s, 1H), 3.68 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.38-3.31 (m, 1H), 2.99 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.51 (s, 3H), 2.23 (s,

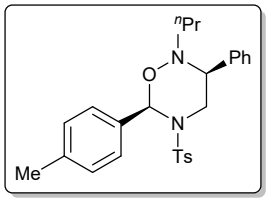
3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 144.1, 137.9, 137.8, 137.6, 129.9, 128.8, 128.54, 128.52, 128.1, 127.9, 127.6, 127.1, 86.3, 68.1, 47.1, 43.7, 21.8; FT-IR (KBr) 2922, 1345, 1165, 961, 750, 570 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3S$: 409.1580, found: 409.1571.



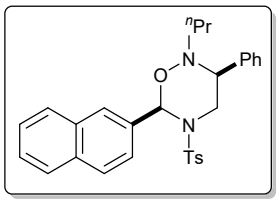
(3*S*,6*R*)-3,6-Diphenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane 4ra′. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.54; thick liquid; yield 68% (59 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 4H), 7.35-7.32 (m, 1H), 7.18-7.17 (m, 3H), 6.85-6.82 (m, 3H), 3.68 (dd, *J* = 14.5, 2.0 Hz, 1H), 3.39-3.34 (m, 1H), 3.11 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.51 (s, 3H), 2.30-2.25 (m, 1H), 2.19-2.14 (m, 1H), 1.57-1.51 (m, 2H), 0.68 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 144.0, 138.4, 137.8, 137.7, 129.9, 128.8, 128.4, 128.3, 128.1, 127.9, 127.6, 127.2, 86.1, 66.4, 57.8, 47.3, 21.8, 19.4, 11.7; FT-IR (neat) 2962, 2927, 1488, 1345, 1167, 972, 697 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{29}N_2O_3S$: 437.1893, found: 437.1897; $[\alpha]_D^{21.0}$ = +45 (c = 0.02, $CHCl_3$); HPLC: 97% *ee* [YMC Chiral ART Cellulose-SC, hexane/^{i}PrOH = 96:04, flow rate: 1 mL /min, λ = 254 nm, t_R = 16.23 min (minor), 18.67 min (major)].



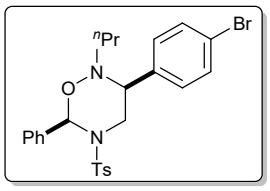
(3*S*,6*R*)-6-(4-Chlorophenyl)-3-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane 4ta′. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.52; thick liquid; mp 172-173 ^{o}C; yield 65% (61 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.20-7.19 (m, 3H), 6.85-6.82 (m, 2H), 6.77 (s, 1H), 3.67 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.34-3.27 (m, 1H), 3.08 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.51 (s, 3H), 2.31-2.24 (m, 1H), 2.18-2.12 (m, 1H), 1.54-1.47 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 144.2, 138.2, 137.7, 136.3, 133.8, 129.9, 128.89, 128.82, 128.6, 128.4, 128.1, 127.5, 85.7, 66.3, 57.8, 47.3, 21.8, 19.4, 11.7; FT-IR (neat) 2962, 2924, 1488, 1348, 1162, 972, 674 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{28}ClN_2O_3S$: 471.1504, found: 471.1504; $[\alpha]_D^{20.6}$ = +35 (c = 0.02, $CHCl_3$); HPLC: 95% *ee* [YMC Chiral ART Cellulose-SC, hexane/^{i}PrOH = 96:04, flow rate: 1 mL /min, λ = 254 nm, t_R = 15.41 min (minor), 17.78 min (major)].



(3*S*,6*R*)-3-Phenyl-2-propyl-6-(p-tolyl)-5-tosyl-1,2,5-oxadiazinane 4ua′. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.56; thick liquid; mp 134-135 °C; yield 67% (60 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.42-7.40 (m, 4H), 7.21-7.16 (m, 5H), 6.86-6.85 (m, 2H), 6.78 (s, 1H), 3.67 (dd, *J* = 15.0, 3.0 Hz, 1H), 3.40-3.35 (m, 1H), 3.11 (dd, *J* = 11.5, 3.0 Hz, 1H), 2.50 (s, 3H), 2.39 (s, 3H), 2.30-2.24 (m, 1H), 2.18-2.13 (m, 1H), 1.56-1.50 (m, 2H), 0.69 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.9, 138.5, 137.9, 137.5, 134.6, 129.8, 129.1, 128.7, 128.3, 128.1, 127.6, 127.1, 86.1, 66.5, 57.8, 47.3, 21.8, 21.3, 19.4, 11.7; FT-IR (neat) 2924, 1254, 1165, 973, 738, 705 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$: 451.2050, found: 451.2056; $[\alpha]_D^{20.7}$ = +20 (c = 0.02, $CHCl_3$); HPLC: 93% *ee* [YMC Chiral ART Cellulose-SC, hexane/^{i}PrOH = 96:04, flow rate: 1 mL /min, λ = 254 nm, t_R = 15.35 min (minor), 17.29 min (major)].

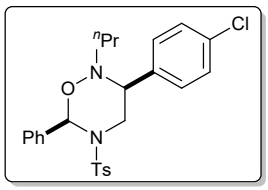


6-(Naphthalen-2-yl)-3-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-4va. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 189-190 °C; yield 70% (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.89-7.84 (m, 3H), 7.68-7.65 (m, 1H), 7.52-7.50 (m, 2H), 7.45-7.43 (m, 2H), 7.16-7.12 (m, 3H), 6.97 (s, 1H), 6.81-6.80 (m, 2H), 3.74 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.49-3.42 (m, 1H), 3.13 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.53 (s, 3H), 2.33-2.17 (m, 2H), 1.66-1.59 (m, 2H), 0.68 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.1, 138.4, 137.9, 135.3, 133.3, 133.1, 129.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 126.3, 126.2, 126.1, 125.2, 86.3, 66.5, 57.9, 47.5, 21.8, 19.5, 11.8; FT-IR (KBr) 2927, 1343, 1165, 809, 748, 682, 560 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{31}N_2O_3S$: 487.2050, found: 487.2056.

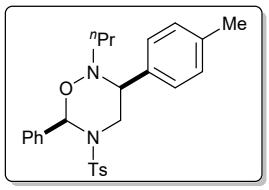


3-(4-Bromophenyl)-6-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-4rc. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.54; colorless solid; mp

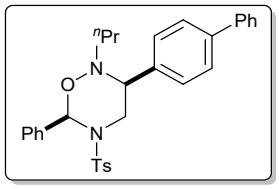
180-181 °C; yield 75% (77 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.42-7.39 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 3.65 (dd, *J* = 15.0, 3.0 Hz, 1H), 3.33-3.28 (m, 1H), 3.11 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.50 (s, 3H), 2.26-2.14 (m, 2H), 1.56-1.51 (m, 2H), 0.69 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.1, 137.7, 137.47, 137.45, 132.0, 129.9, 129.2, 128.4, 128.1, 127.9, 127.2, 122.2, 86.1, 65.8, 57.9, 47.1, 21.8, 19.4, 11.7; FT-IR (KBr) 2975, 2924, 1485, 1343, 1162, 959, 661 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{28}BrN_2O_3S$: 515.0999, found: 515.1000.



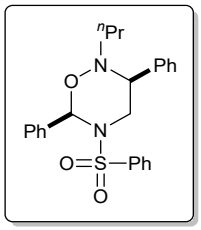
3-(4-Chlorophenyl)-6-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-4rd. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 119-120 °C; yield 79% (74 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 4H), 7.36-7.32 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.81-6.78 (m, 3H), 3.67-3.62 (m, 1H), 3.34-3.27 (m, 1H), 3.13 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.50 (s, 3H), 2.27-2.13 (m, 2H), 1.55-1.49 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.1, 137.8, 137.5, 136.9, 134.1, 129.9, 129.0, 128.9, 128.4, 128.1, 128.0, 127.2, 86.1, 65.8, 57.9, 47.2, 21.8, 19.4, 11.7; FT-IR (KBr) 2963, 1490, 1345, 1167, 1017, 971, 704 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{28}ClN_2O_3S$: 471.1504, found: 471.1509.



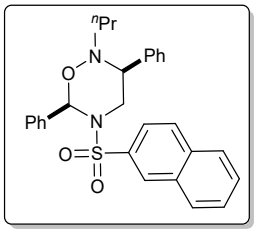
6-Phenyl-2-propyl-3-(*p*-tolyl)-5-tosyl-1,2,5-oxadiazinane (±)-4re. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.53; colorless solid; mp 138-139 °C; yield 77% (69 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 4H), 7.35-7.31 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.80 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.67-3.62 (m, 1H), 3.38-3.32 (m, 1H), 3.09 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.50 (s, 3H), 2.32-2.25 (m, 4H), 2.18-2.12 (m, 1H), 1.54-1.49 (m, 2H), 0.68 (d, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.9, 138.1, 137.9, 137.8, 135.4, 129.9, 129.4, 128.4, 128.1, 127.8, 127.5, 127.2, 86.1, 66.2, 57.8, 47.4, 21.8, 21.2, 19.4, 11.7; FT-IR (KBr) 2927, 1345, 1164, 1020, 969, 814, 656 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$: 451.2050, found: 451.2047.



3-([1,1'-Biphenyl]-4-yl)-6-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-4rf. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 149-150 °C; yield 71% (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.57-7.55 (m, 2H), 7.50-7.48 (m, 2H), 7.44-7.37 (m, 8H), 7.35-7.30 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 3.37-3.69 (m, 1H), 3.44-3.37 (m, 1H), 3.18 (dd, *J* = 10.8, 3.2 Hz, 1H), 2.52 (s, 3H), 2.38-2.31 (m, 1H), 2.24-2.18 (m, 1H), 1.56-1.53 (m, 2H), 0.71 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.0, 141.2, 140.5, 137.9, 137.7, 137.4, 129.9, 128.9, 128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 127.2, 127.1, 86.1, 66.2, 57.9, 47.3, 21.8, 19.5, 11.8; FT-IR (KBr) 2927, 1347, 1164, 1019, 971, 695, 569 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{31}H_{33}N_2O_3S$: 513.2206, found: 513.2201.

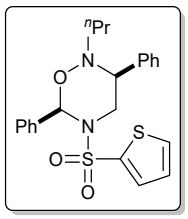


3,6-Diphenyl-5-(phenylsulfonyl)-2-propyl-1,2,5-oxadiazinane (±)-4ri. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 119-120 °C; yield 70% (59 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.71-7.62 (m, 3H), 7.56-7.54 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.18-7.17 (m, 3H), 6.84-6.82 (m, 3H), 3.70-3.65 (m, 1H), 3.42-3.36 (m, 1H), 3.04 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.30-2.23 (m, 1H), 2.17-2.10 (m, 1H), 1.56-1.49 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 140.8, 138.3, 137.6, 133.2, 129.3, 128.8, 128.4, 128.3, 128.1, 127.9, 127.6, 127.2, 86.2, 66.4, 57.8, 47.4, 19.4, 11.7; FT-IR (KBr) 2924, 1493, 1348, 1167, 1032, 720, 585 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{27}N_2O_3S$: 423.1737, found: 423.1735.

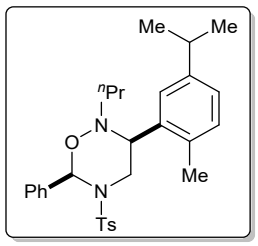


5-(Naphthalen-2-ylsulfonyl)-3,6-diphenyl-2-propyl-1,2,5-oxadiazinane (±)-4rl. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 129-130 °C; yield 68% (64 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s,

1H), 8.10-7.98 (m, 4H), 7.72-7.66 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.36-7.33 (m, 1H), 7.16-7.12 (m, 3H), 6.91 (s, 1H), 6.77 (d, *J* = 7.0 Hz, 2H), 3.77 (dd, *J* = 15.0, 1.5 Hz, 1H), 3.44-3.39 (m, 1H), 3.09 (dd, *J* = 11.0, 2.5 Hz, 1H), 2.24-2.18 (m, 1H), 2.11-2.06 (m, 1H), 1.52-1.45 (m, 2H), 0.63 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 138.3, 137.6, 135.1, 132.4, 129.6, 129.4, 129.3, 129.1, 128.7, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.2, 123.3, 86.2, 66.6, 57.8, 47.4, 19.4, 11.7; FT-IR (KBr) 2924, 1450, 1340, 1165, 1020, 969, 748, 656 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{29}N_2O_3S$: 473.1893, found: 473.1888.

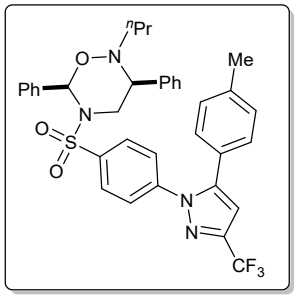


3,6-Diphenyl-2-propyl-5-(thiophen-2-ylsulfonyl)-1,2,5-oxadiazinane (±)-4rm. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.49; colorless solid; mp 149-150 °C; yield 69% (59 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.78 (m, 1H), 7.73-7.72 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.36-7.34 (m, 1H), 7.23-7.19 (m, 4H), 6.92-6.90 (m, 2H), 6.82 (s, 1H), 3.80 (dd, *J* = 14.5, 1.5 Hz, 1H), 3.46-3.41 (m, 1H), 3.20 (dd, *J* = 11.5, 3.0 Hz, 1H), 2.35-2.29 (m, 1H), 2.23-2.18 (m, 1H), 1.62-1.57 (m, 2H), 0.70 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 141.5, 138.3, 137.4, 133.1, 132.6, 128.8, 128.4, 128.0, 127.9, 127.6, 127.2, 86.3, 66.6, 57.9, 47.6, 19.4, 11.7; FT-IR (KBr) 2924, 1452, 1353, 1160, 1022, 969, 697, 590 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_3S_2$: 429.1301, found: 429.1305.



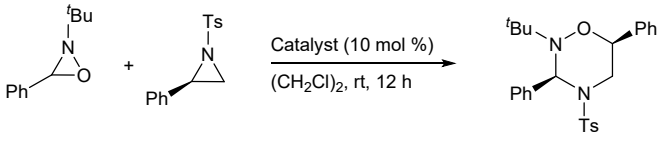
3-(5-Isopropyl-2-methylphenyl)-6-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-4rr. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 124-125 °C; yield 70% (69 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.44-7.38 (m, 4H), 7.36-7.33 (m, 1H), 6.96-6.90 (m, 2H), 6.87 (s, 1H), 6.65 (s, 1H), 3.60-3.56 (m, 1H), 3.49-3.46 (m, 1H), 3.36-3.30 (m, 1H), 2.66-2.60 (m, 1H), 2.48 (s, 3H), 2.31-2.19 (m, 2H), 1.96 (s, 3H), 1.68-1.60 (m, 1H), 1.50-1.42 (m, 1H), 1.01 (t, *J* = 7.6 Hz, 6H), 0.69 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ

147.1, 143.9, 137.9, 137.8, 136.5, 132.5, 130.3, 129.8, 128.3, 128.2, 127.8, 127.3, 125.5, 125.1, 86.1, 61.4, 57.4, 46.5, 33.5, 24.1, 23.7, 21.7, 19.5, 18.9, 11.9; FT-IR (KBr) 2960, 2927, 1452, 1345, 1162, 1017, 972, 733, 572 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{37}N_2O_3S$: 493.2519, found: 493.2502.



3,6-Diphenyl-2-propyl-5-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonyl)-1,2,5-oxadiazinane (±)-4rs. Analytical TLC on silica gel, 1:15 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 195-196 °C; yield 65% (84 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37-7.34 (m, 1H), 7.21-7.14 (m, 7H), 6.85 (d, *J* = 6.5 Hz, 2H), 6.80 (s, 1H), 6.77 (s, 1H), 3.71 (dd, *J* = 15.0, 2.5 Hz, 1H), 3.44-3.39 (m, 1H), 3.18 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.36 (s, 3H), 2.34-2.29 (m, 1H), 2.22-2.17 (m, 1H), 1.56-1.53 (m, 2H), 0.71 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.4, 144.5 (q, J_{C-F} = 38.6 Hz), 142.8, 140.4, 139.9, 138.1, 137.2, 129.9, 128.98, 128.93, 128.91, 128.5, 128.1, 127.6, 127.1, 126.0, 125.6, 122.2 (q, J_{C-F} = 267.5 Hz), 106.7, 86.3, 66.7, 57.9, 47.5, 21.4, 19.6, 11.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.409; FT-IR (KBr) 2927, 1470, 1365, 1237, 1165, 1020, 973, 699 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{35}H_{34}F_3N_4O_3S$: 647.2298, found: 647.2295.

Table S2. Effect of Catalysts on Stereospecific Synthesis of Oxadiazines.[a]

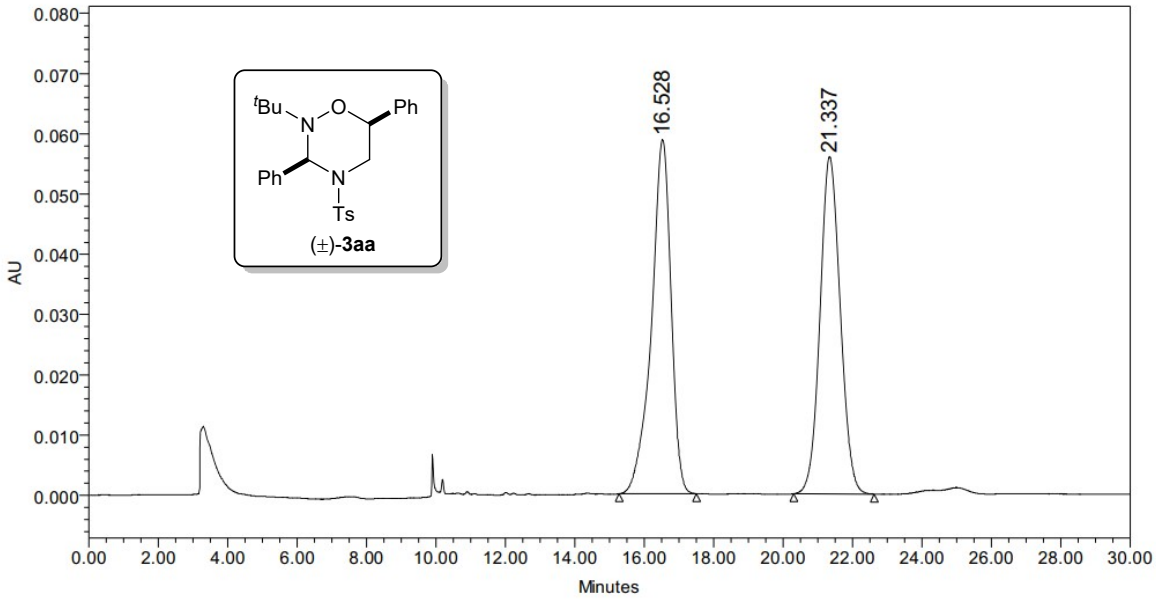


1a (*R*)-**2a'** (3*S*,6*S*)-**3aa'**

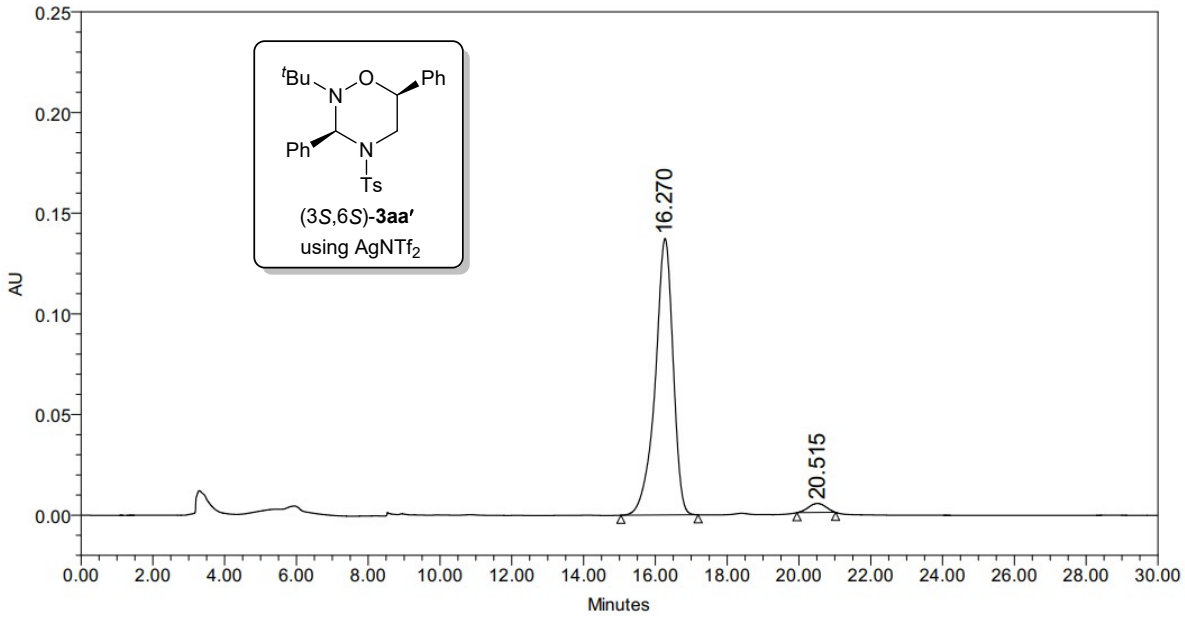
Entry	Catalyst (10 mol %)	Yield (**3aa′**, (%))[b]	ee (%)[c]
1	$Cu(OTf)_2$	64	9
2	$Ni(OTf)_2$	48	19
3	$Zn(OTf)_2$	52	20
4	$Yb(OTf)_3$	58	17
5	$AgNTf_2$	80	94
6	AgOTf	72	94
7	$AgBF_4$	54	94

[a]Reaction conditions: **1a** (0.2 mmol), (*R*)-**2a′** (0.2 mmol), catalyst (10 mol %), $(CH_2Cl)_2$ (2 mL), room temperature, 12 h. [b]Yield of the isolated product. [c]ee assigned by HPLC analysis.

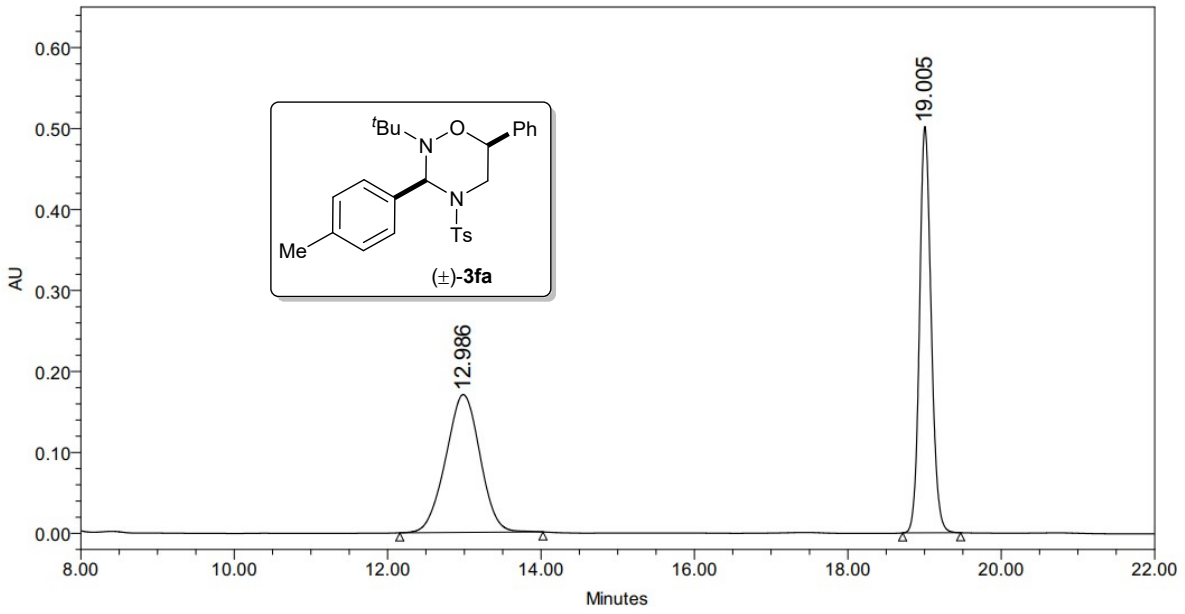
HPLC Chromatograms



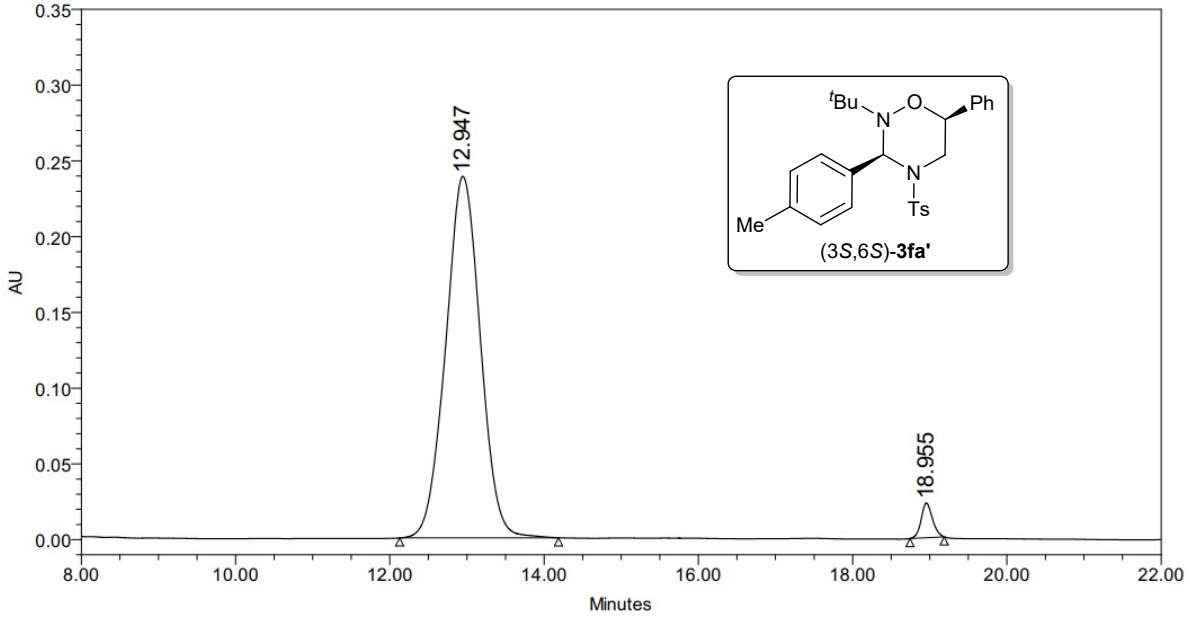
	RT	Area	% Area	Height
1	16.528	2283323	50.36	58808
2	21.337	2250846	49.64	56028



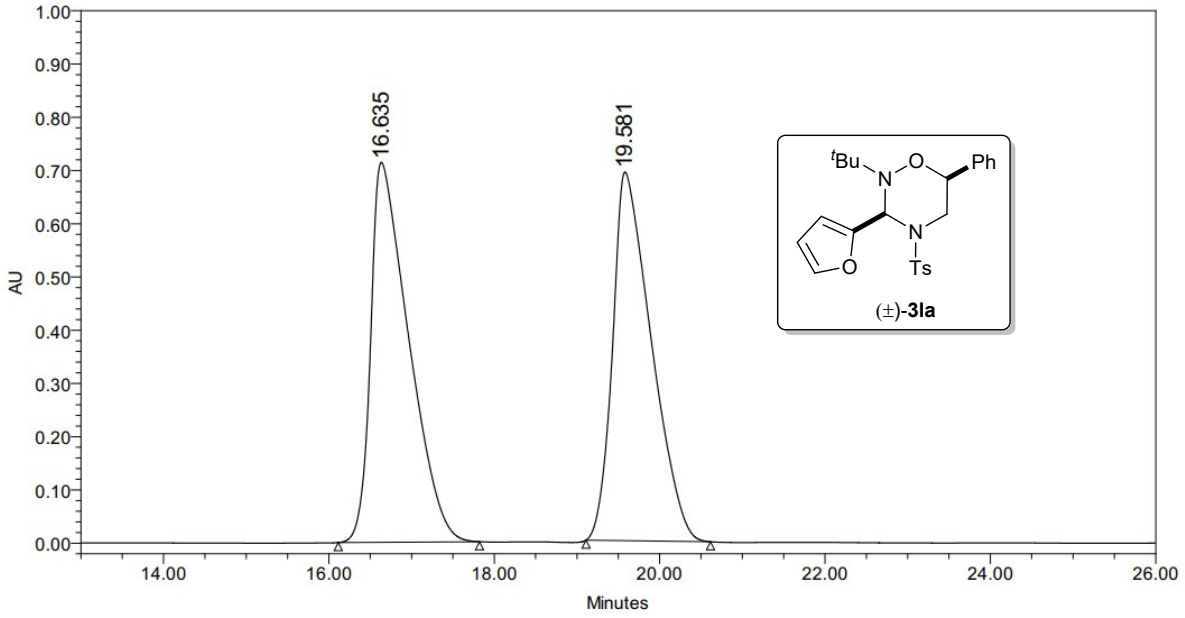
	RT	Area	% Area	Height
1	16.270	4757767	96.92	137350
2	20.515	151218	3.08	4496



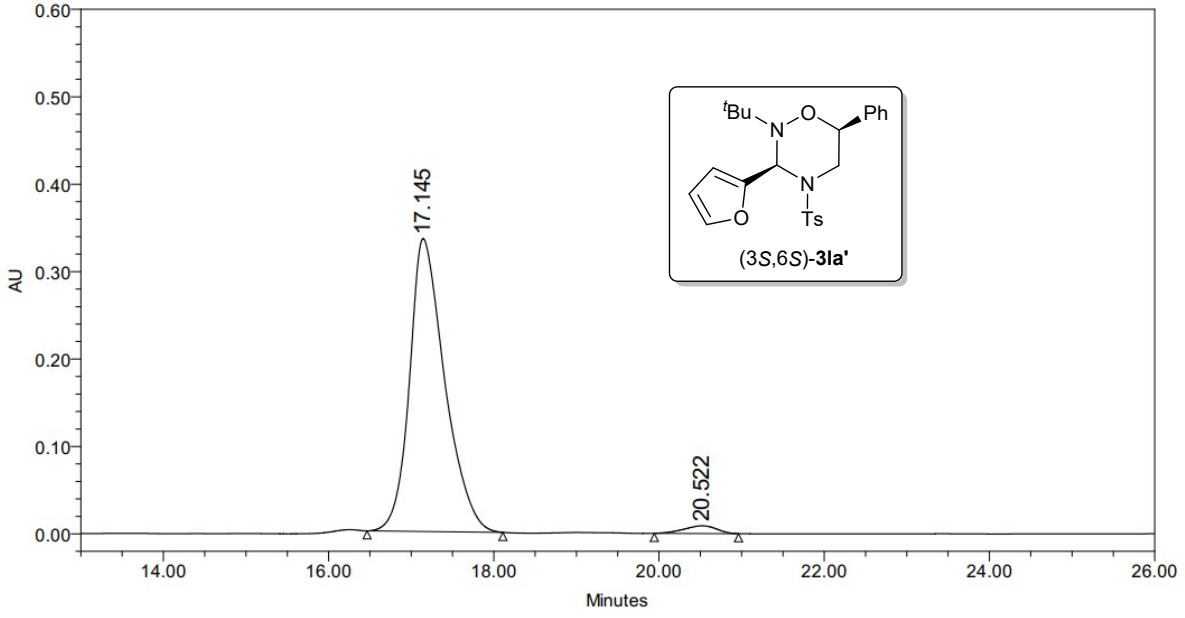
	RT	Area	% Area	Height
1	12.986	5301573	50.02	170333
2	19.005	5297004	49.98	501763



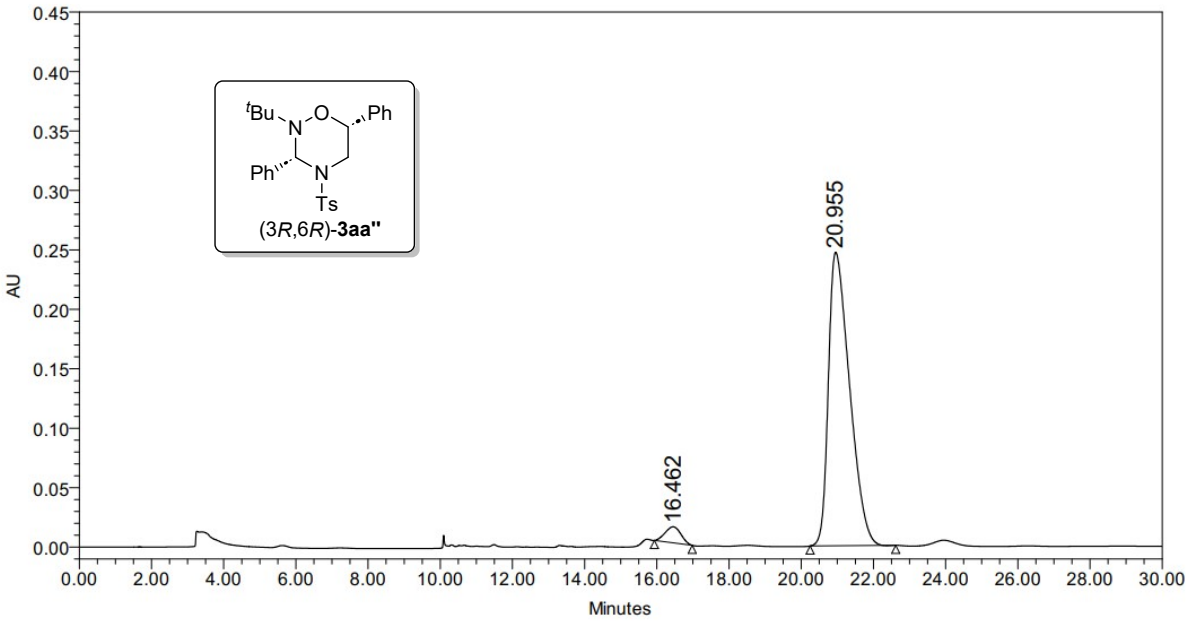
	RT	Area	% Area	Height
1	12.947	7458812	96.98	238617
2	18.955	232301	3.02	22886



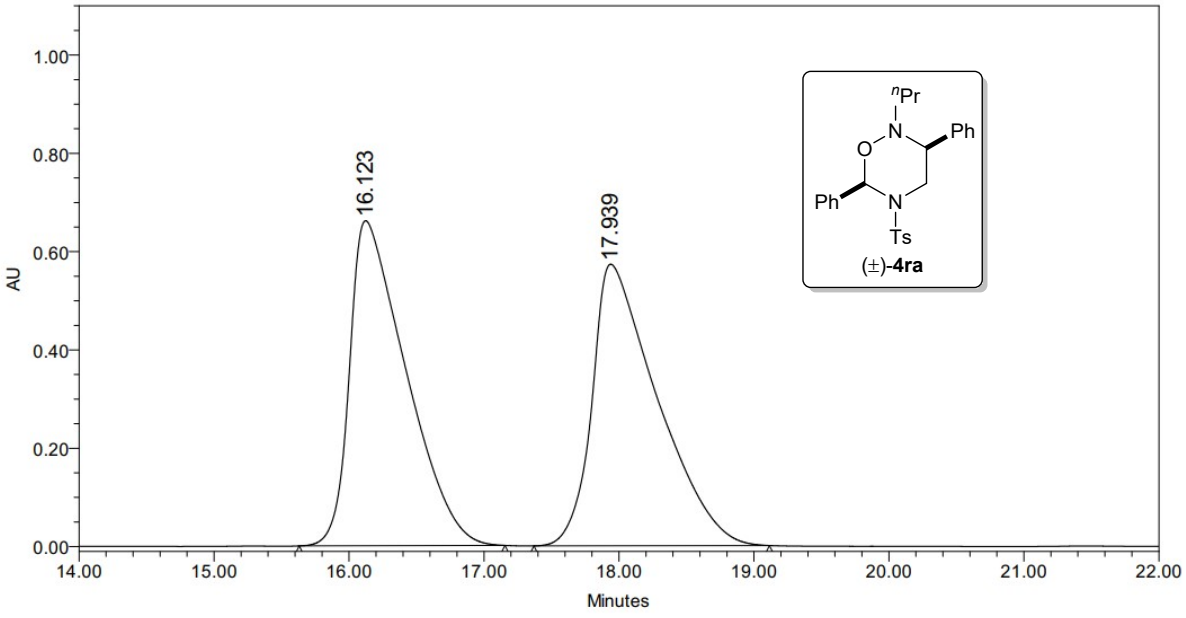
	RT	Area	% Area	Height
1	16.635	22774044	50.34	713491
2	19.581	22470876	49.66	692300



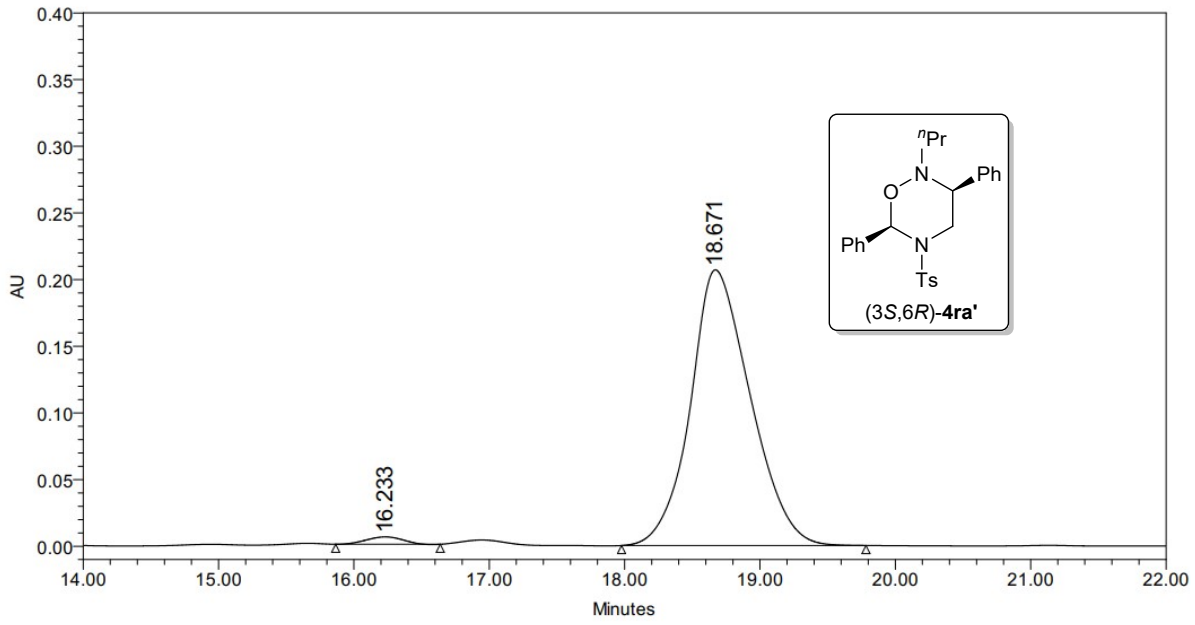
	RT	Area	% Area	Height
1	17.145	9926375	97.63	335037
2	20.522	240870	2.37	8775



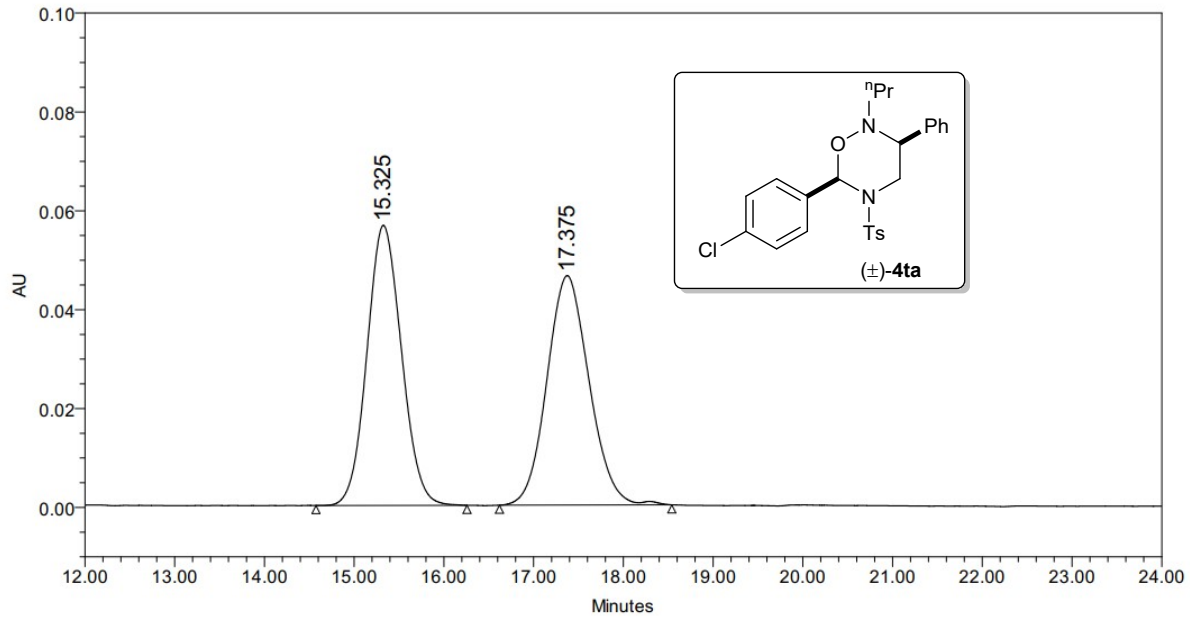
	RT	Area	% Area	Height
1	16.462	411949	3.94	13569
2	20.955	10054895	96.06	246925



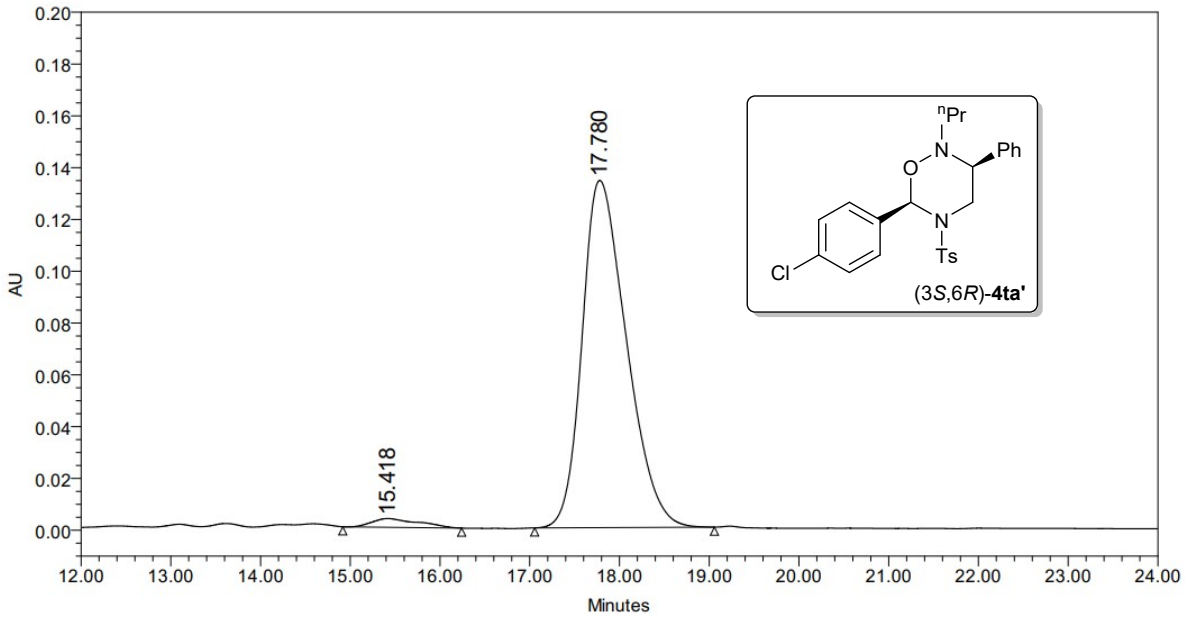
	RT	Area	% Area	Height
1	16.123	19201900	49.95	661326
2	17.939	19241134	50.05	572813



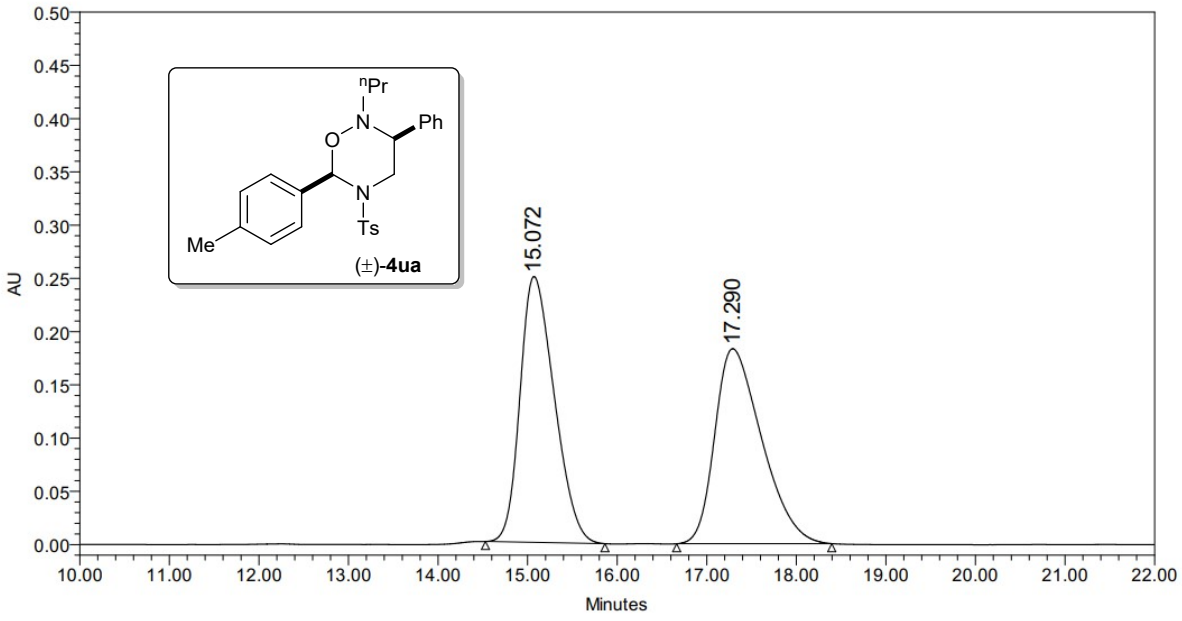
	RT	Area	% Area	Height
1	16.233	104334	1.61	5529
2	18.671	6374938	98.39	206772



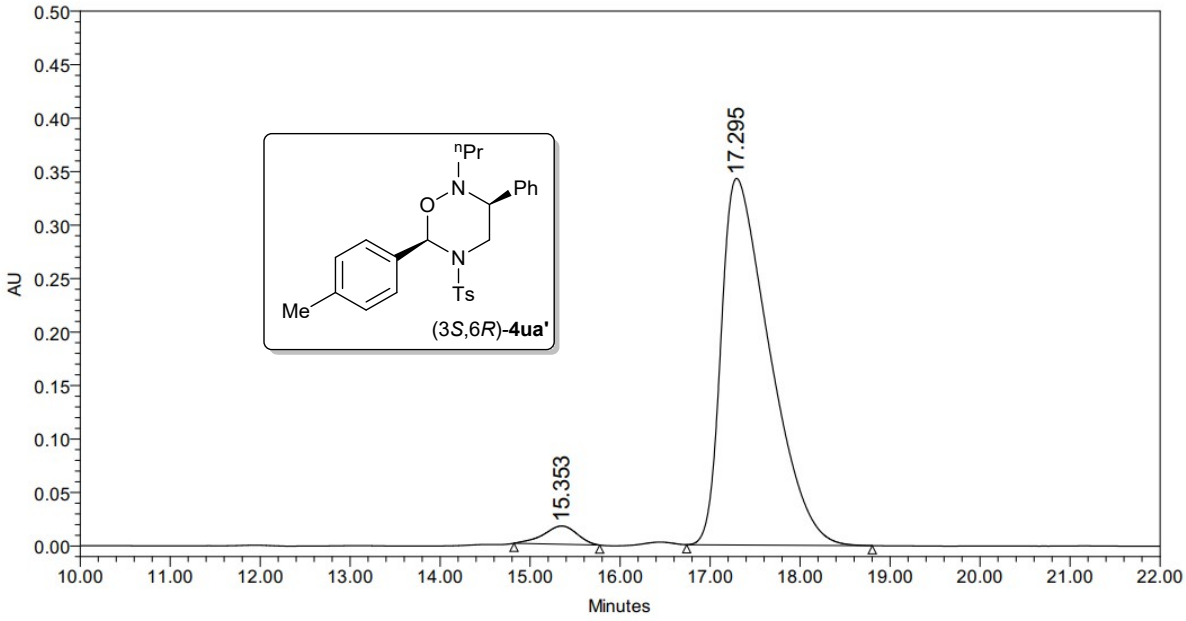
	RT	Area	% Area	Height
1	15.325	1515891	50.03	56660
2	17.375	1514349	49.97	46419



	RT	Area	% Area	Height
1	15.418	122067	2.58	3383
2	17.780	4601233	97.42	134022

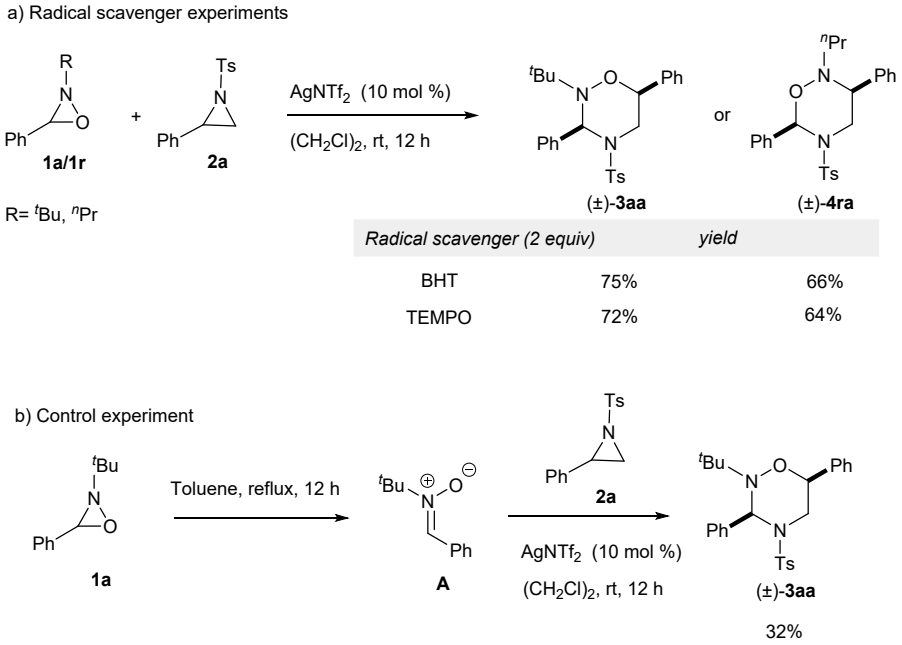


	RT	Area	% Area	Height
1	15.072	6638380	49.92	249692
2	17.290	6658336	50.08	183131



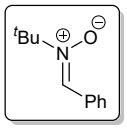
	RT	Area	% Area	Height
1	15.353	440053	3.34	17070
2	17.295	12752831	96.66	342679

Scheme S5. Mechanistic Studies

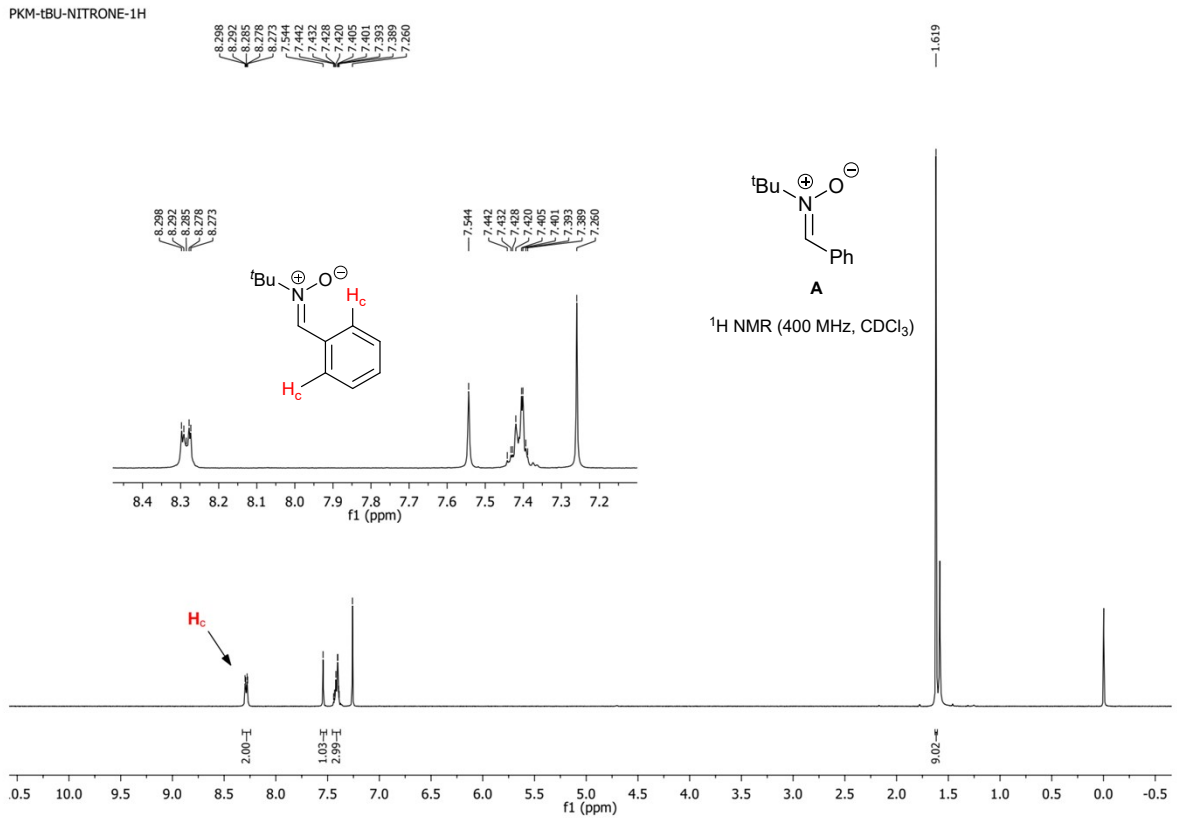


Radical Scavenger Experiments (Scheme S5a). Substrate **1a**/**1r** (0.2 mmol, 1 equiv), **2a** (54.6 mg, 0.2 mmol, 1 equiv), $AgNTf_2$ (7.7 mg, 0.02 mmol, 0.1 equiv) and TEMPO/BHT (0.4 mmol, 2 equiv) were stirred in $(CH_2Cl)_2$ (2 mL, 0.1 M) at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (5 mL) and passed through a short pad of celite using CH_2Cl_2 (10 mL). Evaporation of the solvent gave a residue that was

purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford (±)-**3aa**/(±)-**4ra**.



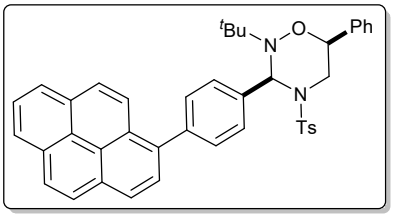
Preparation of **(*Z*)-*N*-*tert*-Butyl-1-phenylmethanimine oxide A**.[3] 2-(*tert*-Butyl)-3-phenyl-1,2-oxaziridine **1a** (177 mg, 1 mmol, 1 equiv) was stirred in toluene (10 mL, 1.0 M) under reflux for 12 h air. The resultant reaction mixture was cooled to room temperature and the solvent was evaporated to give nitrone **A** in 95% yield (168 mg). Colourless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.27 (m, 2H), 7.54 (s, 1H), 7.44-7.38 (m, 3H), 1.61 (s, 9H).



Control Experiment Scheme S5b. The nitrone A (0.2 mmol, 35 mg), aziridine **2a** (0.2 mmol, 54 mg) and $AgNTf_2$ (10 mol %, 7.7 mg) were stirred in $(CH_2Cl)_2$ (2 mL) at room temperature under nitrogen atmosphere 12 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and passed through a short pad of celite using CH_2Cl_2 (10 mL). Evaporation of the solvent gave a residue which was purified using ethyl acetate and hexane as eluent to give (±)-**3aa** in 32% yield (29 mg).

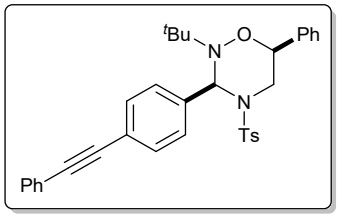
Scale-up Synthesis of (±)-**3ea.** Substrate **1e** (765 mg, 3 mmol, 1.0 equiv), **2a** (819 mg, 3 mmol, 1.0 equiv) and $AgNTf_2$ (116.3 mg, 0.3 mmol, 0.1 equiv) were stirred in $(CH_2Cl)_2$ (30 mL, 0.1 M) at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (20 mL) and passed through a short pad of celite using CH_2Cl_2 (50 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to yield (±)-**3ea** in 68% yield (1.07 g).

Scale-up Synthesis of (±)-**4rc.** Substrate **1r** (489 mg, 3 mmol, 1.0 equiv), **2c** (1.05 g, 3 mmol, 1.0 equiv) and $AgNTf_2$ (116.3 mg, 0.3 mmol, 0.1 equiv) were stirred in $(CH_2Cl)_2$ (30 mL, 0.1 M) at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (20 mL) and passed through a short pad of celite using CH_2Cl_2 (50 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to yield (±)-**4rc** in 66% yield (1.01 g).

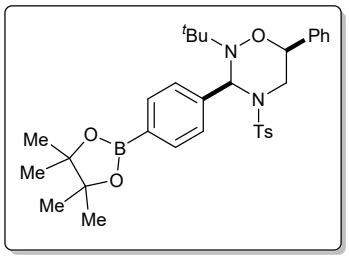


2-(*tert*-Butyl)-6-phenyl-3-(4-(pyren-1-yl)phenyl)-4-tosyl-1,2,4-oxadiazinane (±)-5. In a pressure tube, a mixture of compound (±)-**3ea** (52 mg, 0.1 mmol, 1.0 equiv), pyrene-1-boronic acid (25 mg, 0.1 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (3.5 mg, 0.003 mmol, 0.03 equiv), Na_2CO_3 (11 mg, 0.1 mmol, 1.0 equiv) and H_2O (25 µL) in toluene: EtOH (1:1, 1 mL) was stirred at 100 °C in an oil bath for 12 h under argon atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite using CH_2Cl_2 (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give (±)-**5** in 82% yield (53 mg). Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; brown solid; mp 193-194 °C; yield 82% (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.15 (m, 4H), 8.13-8.07 (m, 3H), 8.06-8.00 (m, 2H), 7.96-7.91 (m, 3H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.43-7.33 (m, 5H), 7.24 (s, 1H), 6.20 (s, 1H), 4.84 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.97 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.57-3.50 (m, 1H), 2.40 (s, 3H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.4, 141.2, 138.2, 137.8, 137.3, 137.2, 131.6, 131.1, 130.8, 130.6, 129.7, 129.4, 128.8, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 126.2, 125.8, 125.3, 125.2, 125.1, 125.0, 124.8, 78.6, 72.2, 58.5, 45.7, 26.9, 21.7;

FT-IR (KBr) 2967, 2926, 1595, 1344, 1161, 960, 845, 660 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{42}H_{39}N_2O_3S$: 651.2676, found: 651.2677.

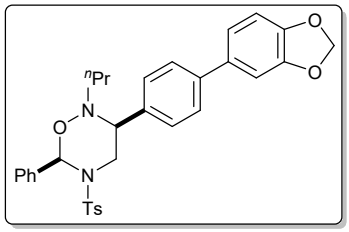


2-(*tert*-Butyl)-6-phenyl-3-(4-(phenylethynyl)phenyl)-4-tosyl-1,2,4-oxadiazinane (±)-6.[4] In a pressure tube, a mixture of (±)-**3ea** (52 mg, 0.1 mmol, 1 equiv), phenylacetylene (20.4 mg, 0.1 mmol, 2 equiv), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol, 0.1 equiv), CuI (1.9 mg, 0.01 mmol, 0.1 equiv) and Et_3N (70 μL, 0.5 mmol, 5 equiv) in DMF (1 mL) was stirred at 60 °C in an oil bath for 30 h under argon atmosphere. After completion, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (2 x 5 mL) and water (1 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate/hexane as an eluent to afford (±)-**6** in 85% (47 mg) yield. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.42; orange solid; mp 190-191 °C; yield 85% (47 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.54-7.53 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.42-7.35 (m, 6H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.75 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.86 (dd, *J* = 14.5, 3.5 Hz, 1H), 3.38 (t, *J* = 12.5 Hz, 1H), 2.40 (s, 3H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.5, 139.0, 138.0, 137.2, 131.7, 131.6, 129.6, 129.4, 128.8, 128.5, 128.4, 127.6, 125.8, 123.3, 123.2, 90.2, 89.0, 78.6, 71.8, 58.3, 45.5, 26.8, 21.6; FT-IR (KBr) 2926, 1496, 1344, 1263, 1162, 1031, 952, 758, 662 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{34}H_{35}N_2O_3S$: 551.2363, found: 551.2347.



2-(*tert*-Butyl)-6-phenyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-tosyl-1,2,4-oxadiazinane (±)-7.[4] In a pressure tube, a mixture of (±)-**3ea** (52 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (25 mg, 0.1 mmol, 1.0 equiv), KOAc (20 mg, 0.2 mmol, 2.0 equiv) and $Pd(dppf)Cl_2•CH_2Cl_2$ (4 mg, 0.005 mmol, 0.05 equiv) in THF (2 mL) was stirred at 100 °C in an oil bath for 4 h under N_2 atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short

pad of celite using CH_2Cl_2 (15 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as an eluent to give (±)-**7** in 72% yield (42 mg). Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 198-199 °C; yield 72% (42 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.39-7.33 (m, 3H), 7.30-7.28 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 4.73 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.81-3.78 (m, 1H), 3.37 (t, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 1.34 (s, 12H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.2, 141.8, 138.2, 137.3, 134.8, 129.4, 129.0, 128.7, 128.4, 127.6, 125.9, 83.9, 78.7, 72.1, 58.3, 45.6, 26.8, 25.0, 24.9, 21.6; FT-IR (KBr) 2924, 1360, 1162, 1094, 961, 662, 544 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{42}BN_2O_5S$: 577.2902, found: 577.2887.

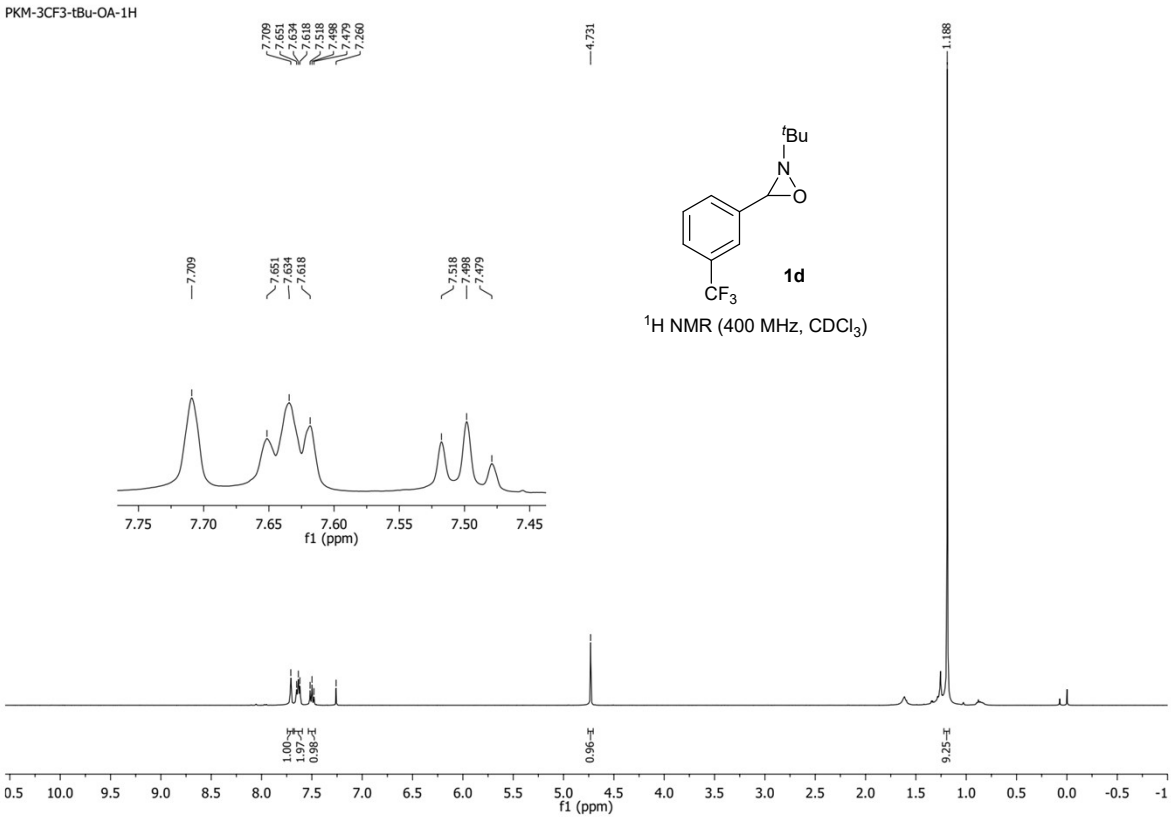


3-(4-(Benzo[d][1,3]dioxol-5-yl)phenyl)-6-phenyl-2-propyl-5-tosyl-1,2,5-oxadiazinane (±)-8. In a pressure tube, a mixture of (±)-**4rc** (51 mg, 0.1 mmol, 1.0 equiv), benzo[d][1,3]dioxol-5-ylboronic acid (16.6 mg, 0.1 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (3.5 mg, 0.003 mmol, 0.03 equiv), Na_2CO_3 (11 mg, 0.1 mmol, 1.0 equiv) and H_2O (25 μL) in toluene: EtOH (1:1, 1 mL) was stirred at 100 °C in an oil bath for 12 h under N_2 atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite using CH_2Cl_2 (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give (±)-**8** in 89% yield (50 mg). Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 156-157 °C; yield 89% (50 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.43-7.40 (m, 4H), 7.36-7.31 (m, 3H), 6.96-6.94 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.84-6.83 (m, 2H), 5.97 (s, 2H), 3.71-3.67 (m, 1H), 3.42-3.36 (m, 1H), 3.17-3.14 (m, 1H), 2.51 (s, 3H), 2.36-2.30 (m, 1H), 2.22-2.17 (m, 1H), 1.60-1.53 (m, 2H), 0.70 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.1, 147.2, 143.9, 140.8, 137.7, 137.5, 136.9, 134.7, 129.8, 128.3, 128.0, 127.8, 127.7, 127.1, 127.0, 120.5, 108.6, 107.4, 101.1, 86.0, 66.0, 57.7, 47.2, 21.6, 19.3, 11.6; FT-IR (KBr) 2962, 2927, 1480, 1345, 1226, 1038, 806, 740 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{33}N_2O_5S$: 557.2105, found: 557.2112.

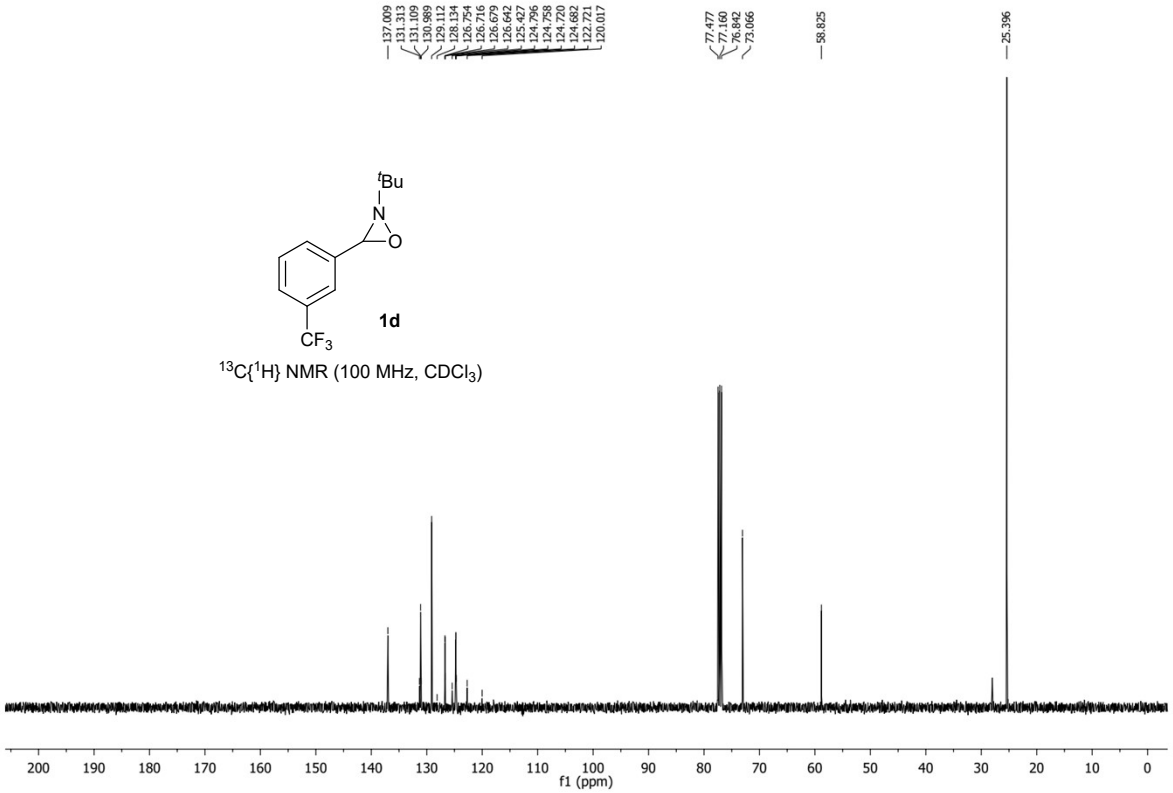
References

1. (a) A. Kivrak and R. C. Larock, *J. Org. Chem.,* 2010, **75**, 7381; (b) J. Kraïem, D. Ghedira and T. Ollevier, *Green Chem.*, 2016, **18**, 4859. (c) G. S. Jang, J. Lee, J. Seo and S. K. Woo, *Org. Lett.*, 2017, **19**, 6448.
2. (a) Y. Du, Y. Wu, A.-H. Liu and L.-N. He, *J. Org. Chem.*, 2008, **73**, 4709; (b) C. -Y. Huang and A. G. Doyle, *J. Am. Chem. Soc*., 2012, **134**, 9541; (c) R. Li, B. Li, H. Zhang, C.-W. Ju, Y. Qin, X.-S. Xue and D. Zhao, *Nat. Chem*., 2021, **13**, 1006; (d) D. Higuchi, S. Matsubara, H. Kadowaki, D. Tanaka and K. Murakami, *Chem*. *Eur*. *J*., 2023, **29**, e202301071; (e) S. Kar, P. K. Maharana, T. Punniyamurthy and V. Trivedi, *Org. Lett*., 2023, **25**, 8850.
3. M. Fabio, L. Ronzini and L. Troisi, *Tetrahedron*, 2007, **63**, 12896.
4. C. Chen, C. Ni, J.-H. Song, L.-Y. Ding, X.-X. Zhang, H. Guo, K. Wang, Z. Chen and B. Zhu, *ACS Catal.,* 2024, **14**, 12181.

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra

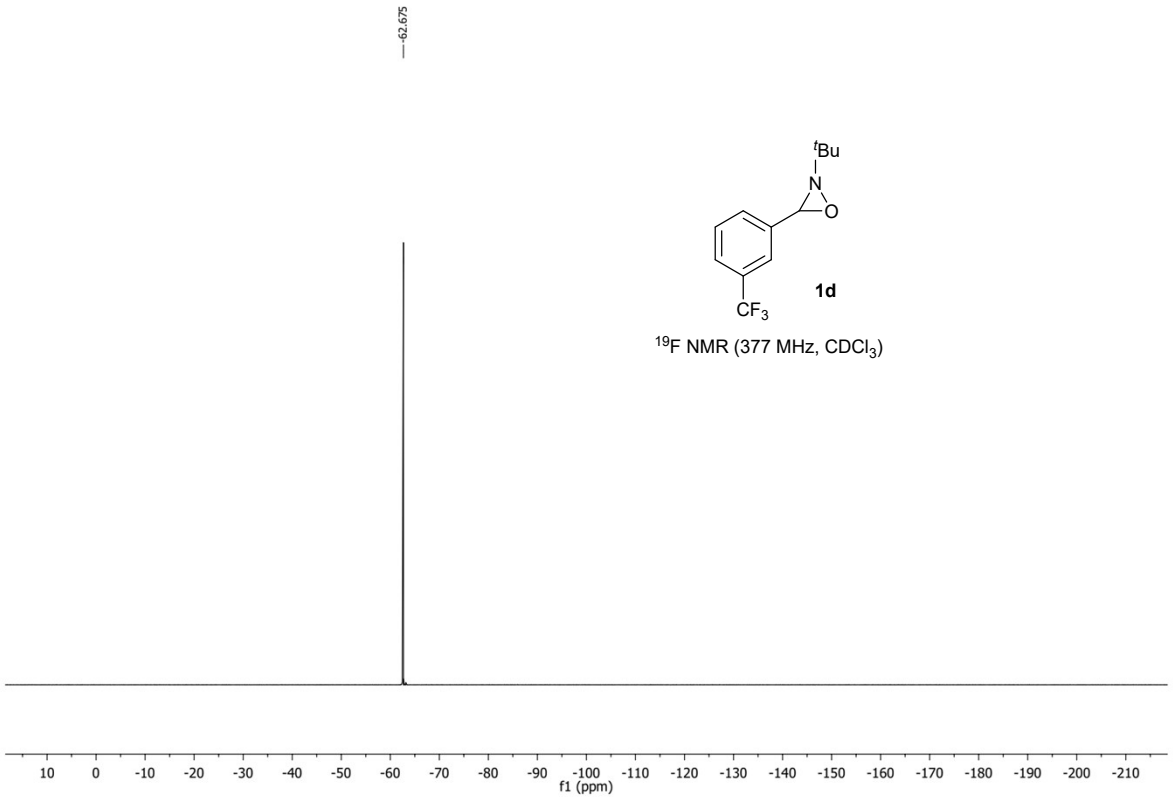


PKM-3CF3-tBu-OA-13C



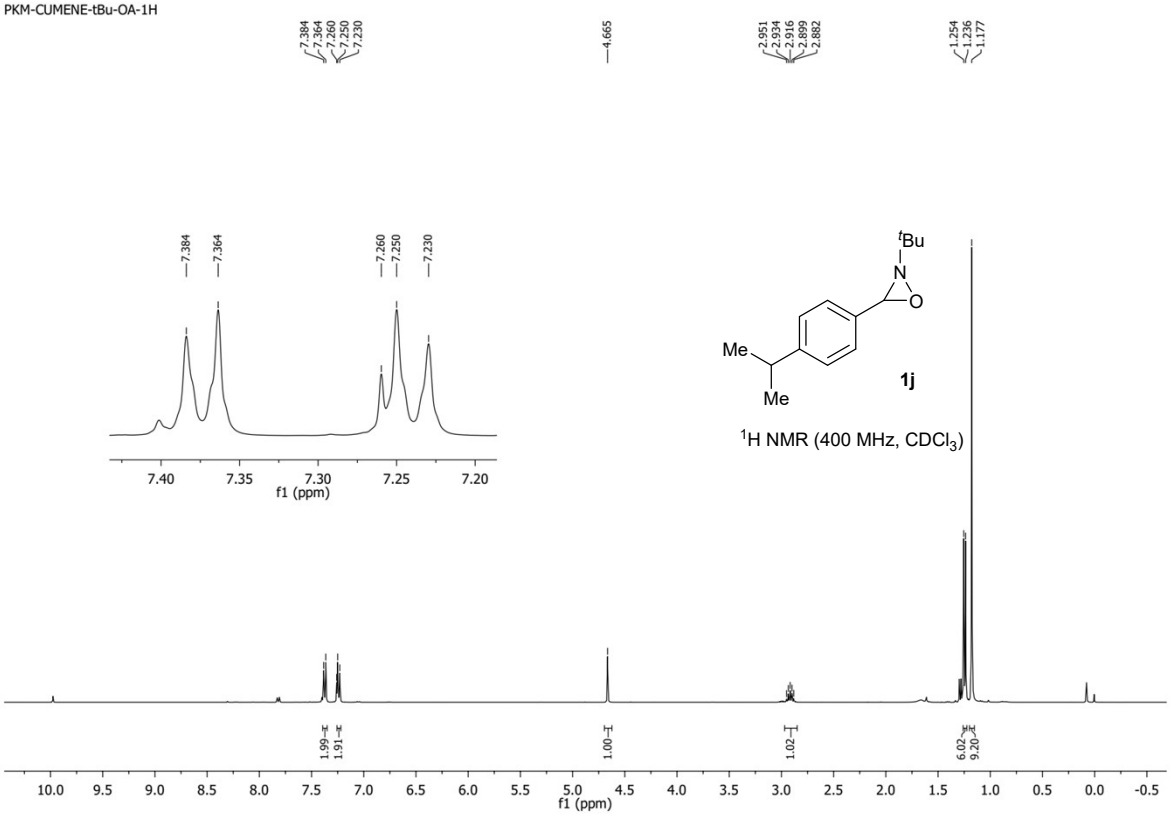
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

PKM-3CF3-OA-19F



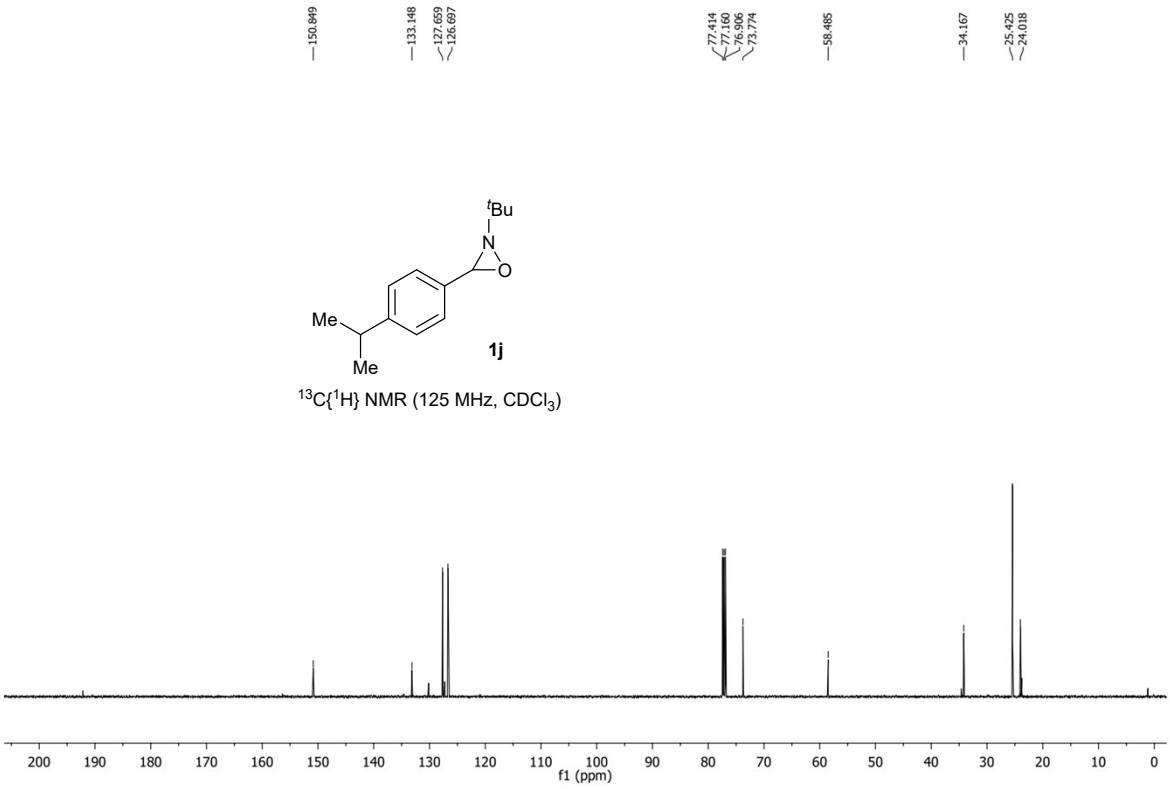
^{19}F NMR (377 MHz, $CDCl_3$)

PKM-CUMENE-tBu-OA-1H



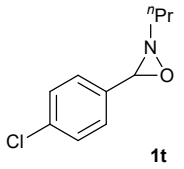
^{1}H NMR (400 MHz, $CDCl_3$)

PKM-CUMENE-tBu-OA-13C



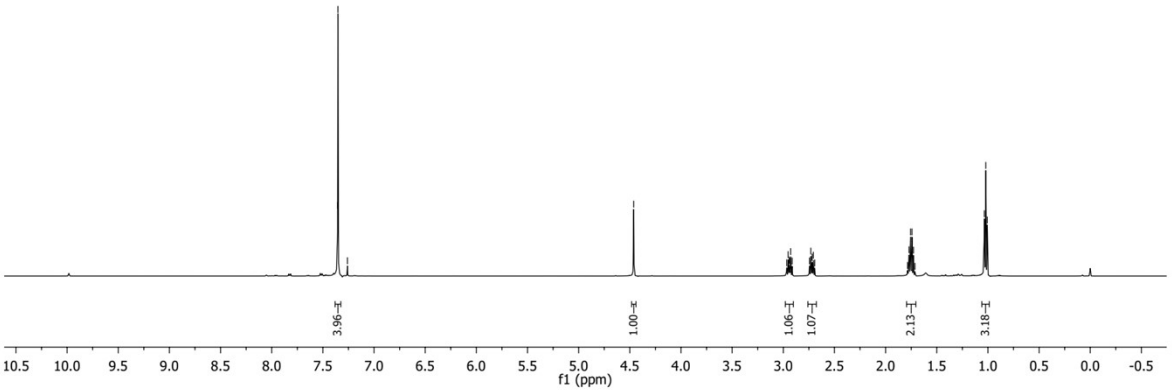
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-4Cl-NPr-OA-1H

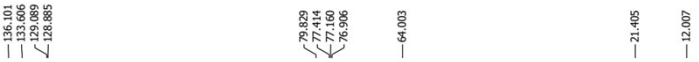


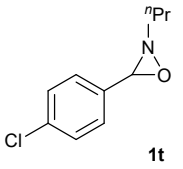
1t

^{1}H NMR (500 MHz, $CDCl_3$)



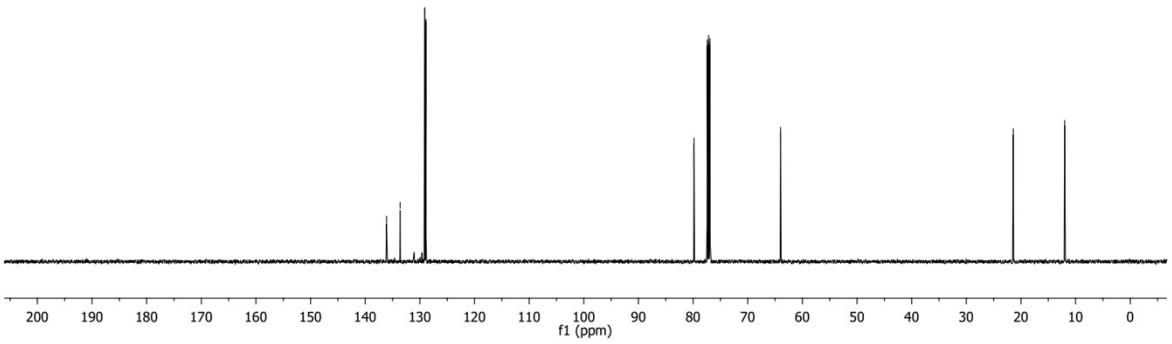
PKM-4Cl-NPr-OA-13c



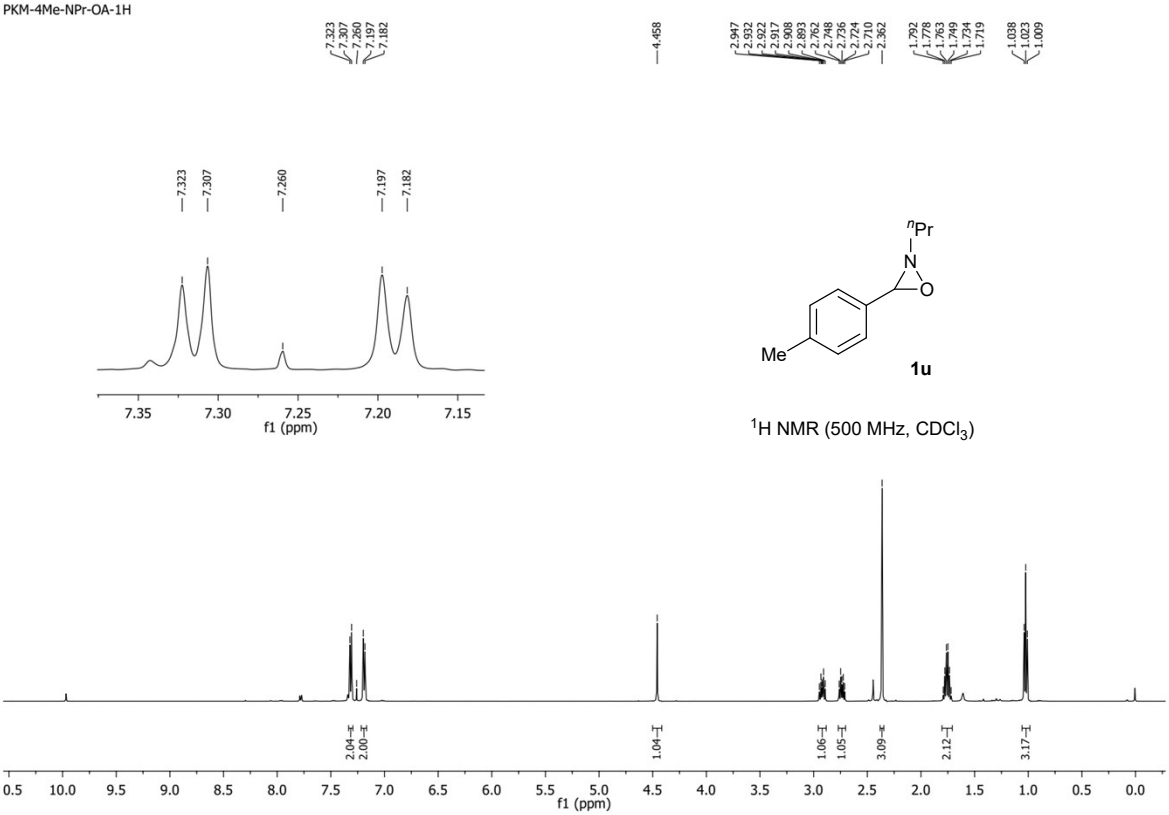


1t

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



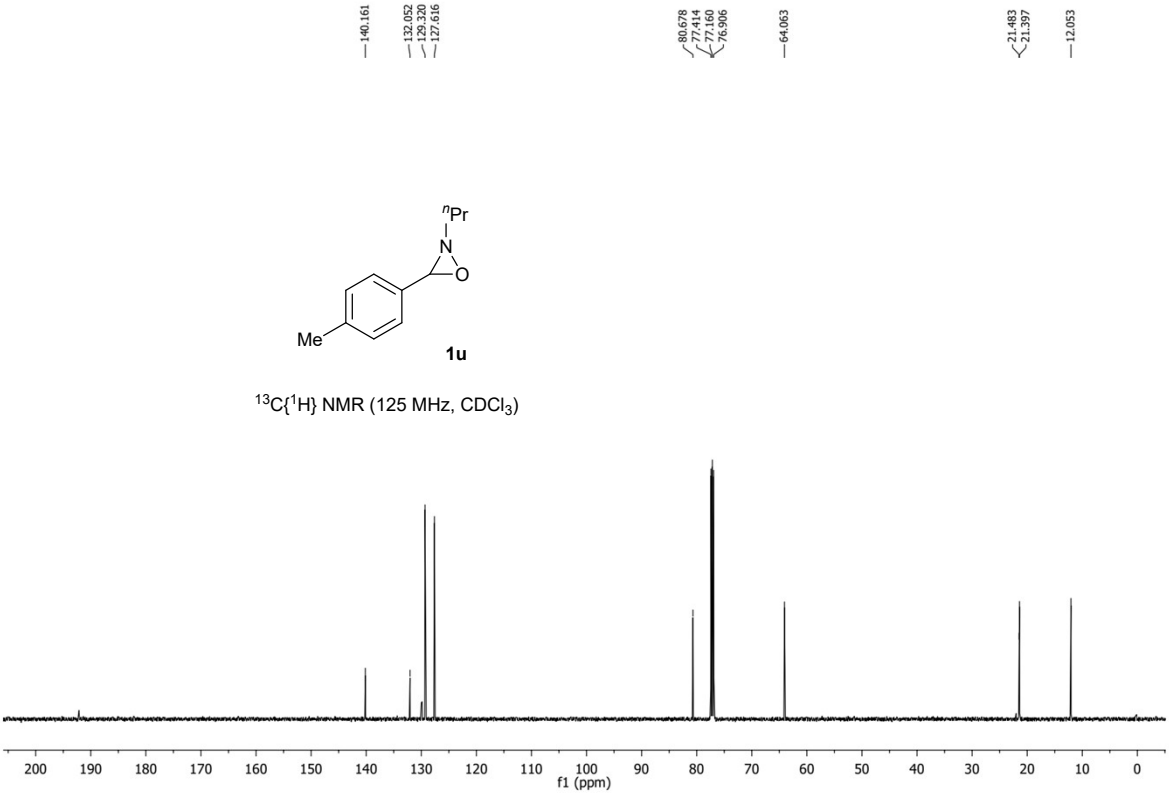
PKM-4Me-NPr-OA-1H



1u

^{1}H NMR (500 MHz, $CDCl_3$)

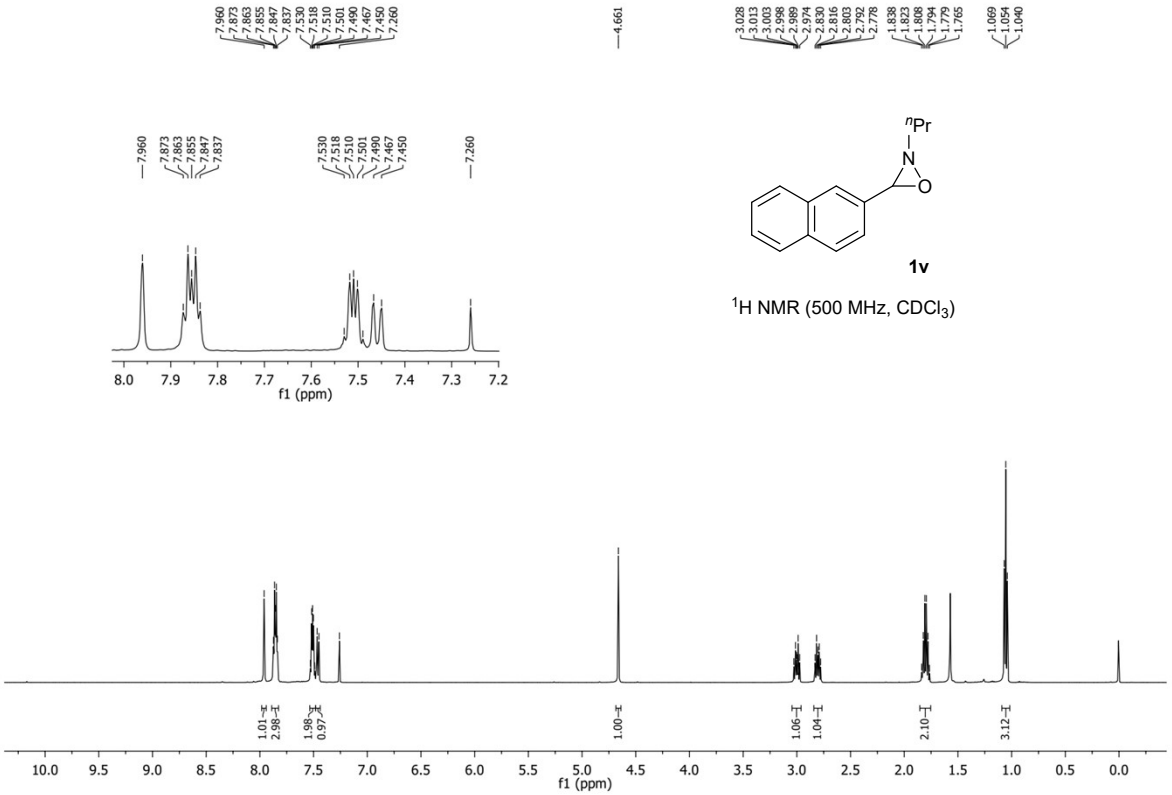
PKM-4Me-NPr-OA-13C



1u

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

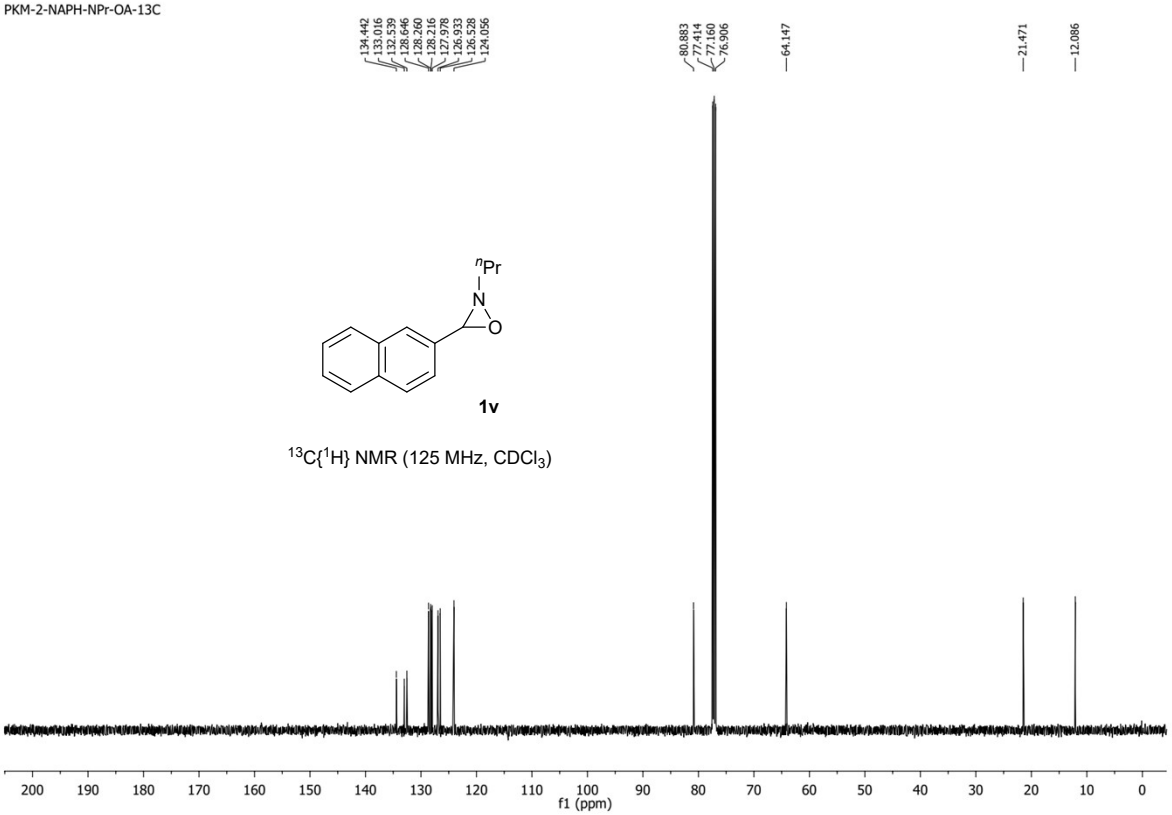
PKM-2-NAPH-NPr-OA-1H



1v

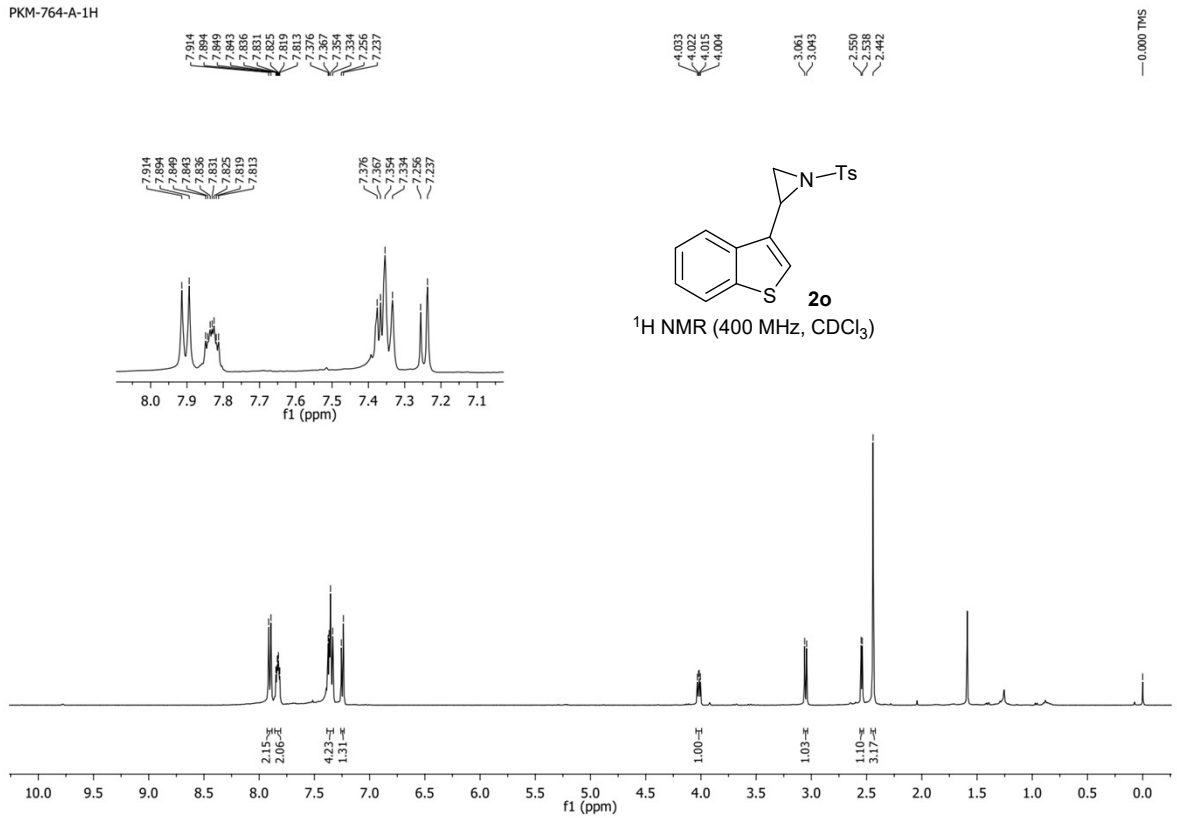
^{1}H NMR (500 MHz, $CDCl_3$)

PKM-2-NAPH-NPr-OA-13C

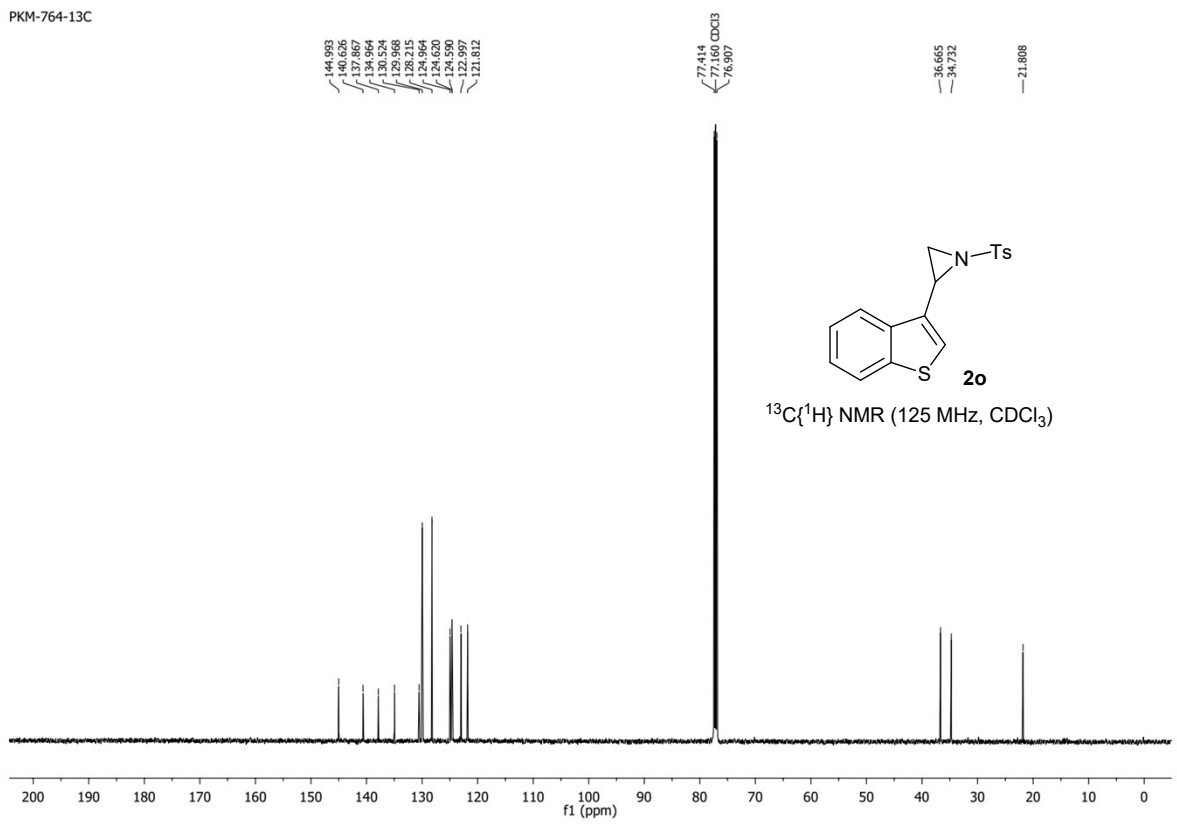


1v

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

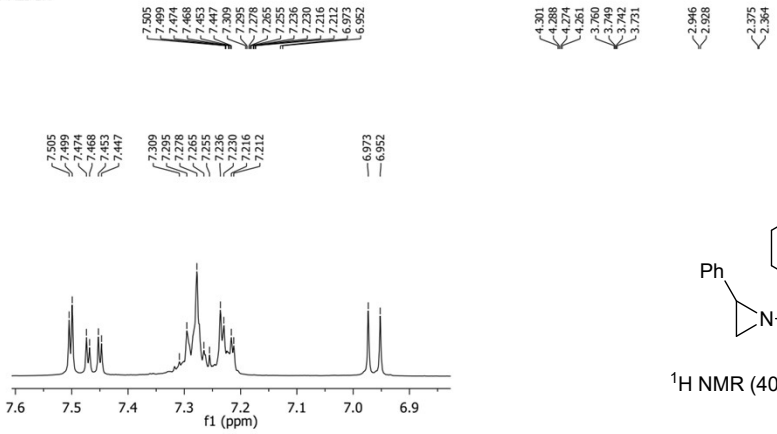


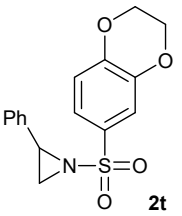
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

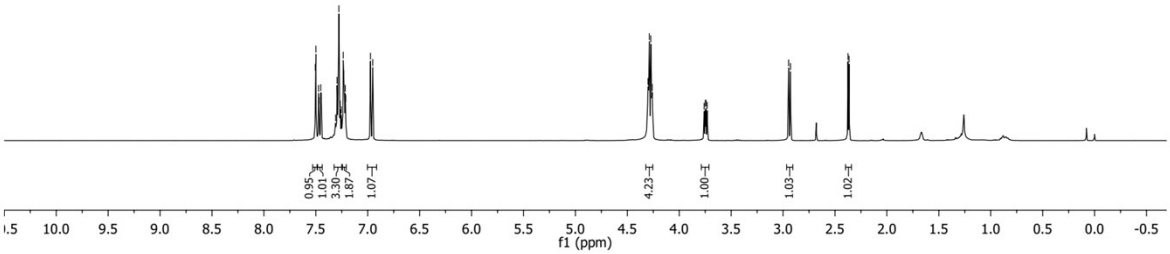
PKM-DIOXOLO-AZI-1H



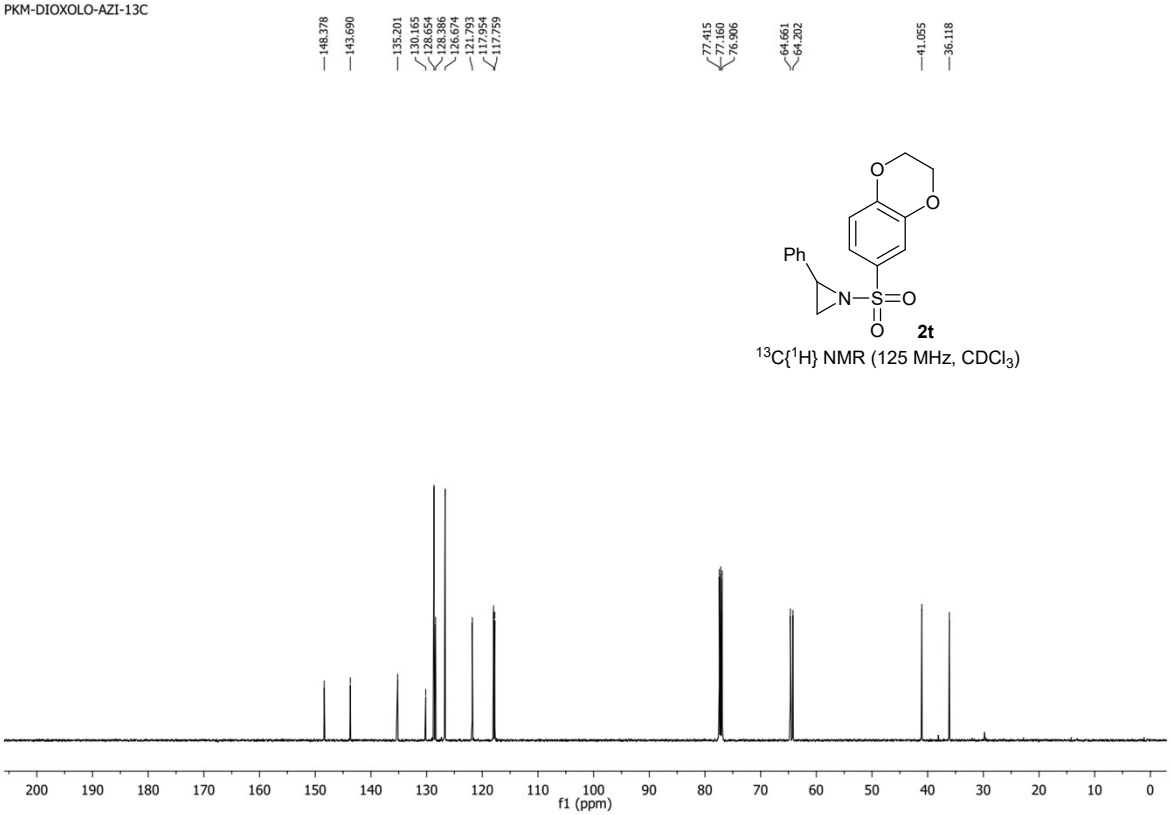


2t

^{1}H NMR (400 MHz, $CDCl_3$)

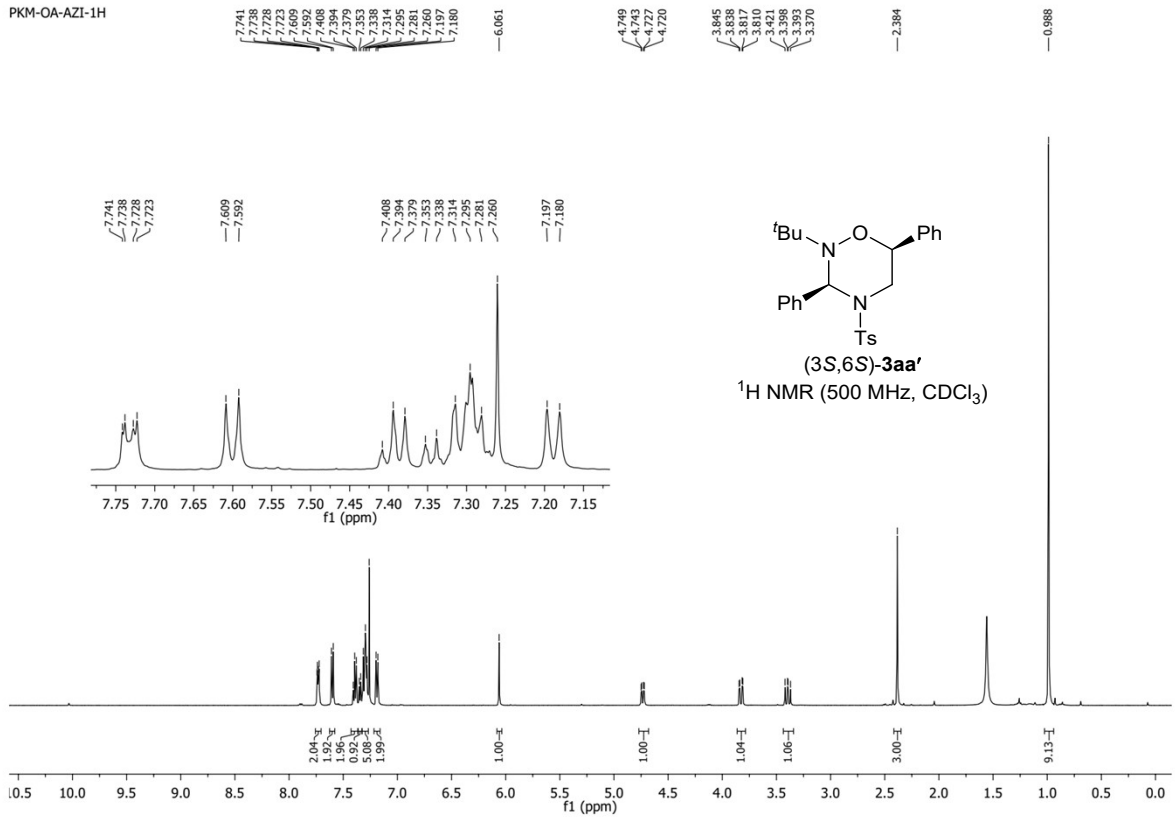


PKM-DIOXOLO-AZI-13C



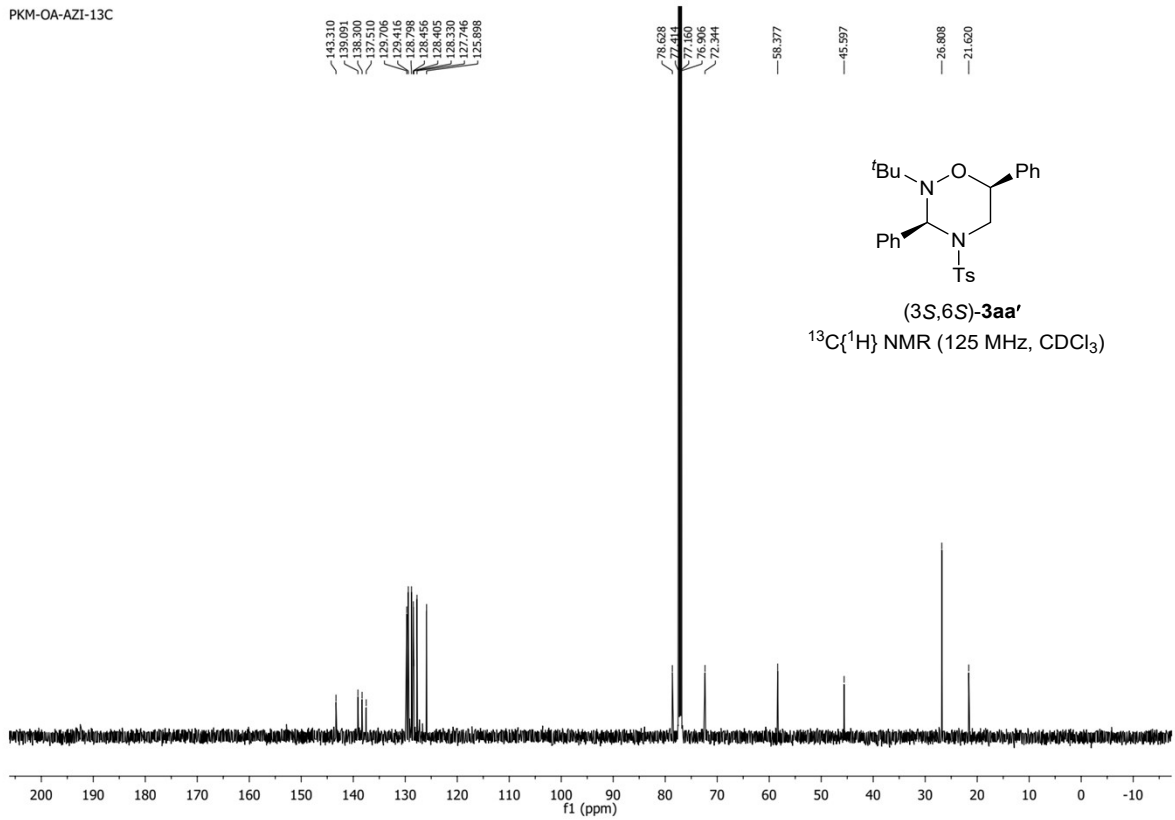
2t

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



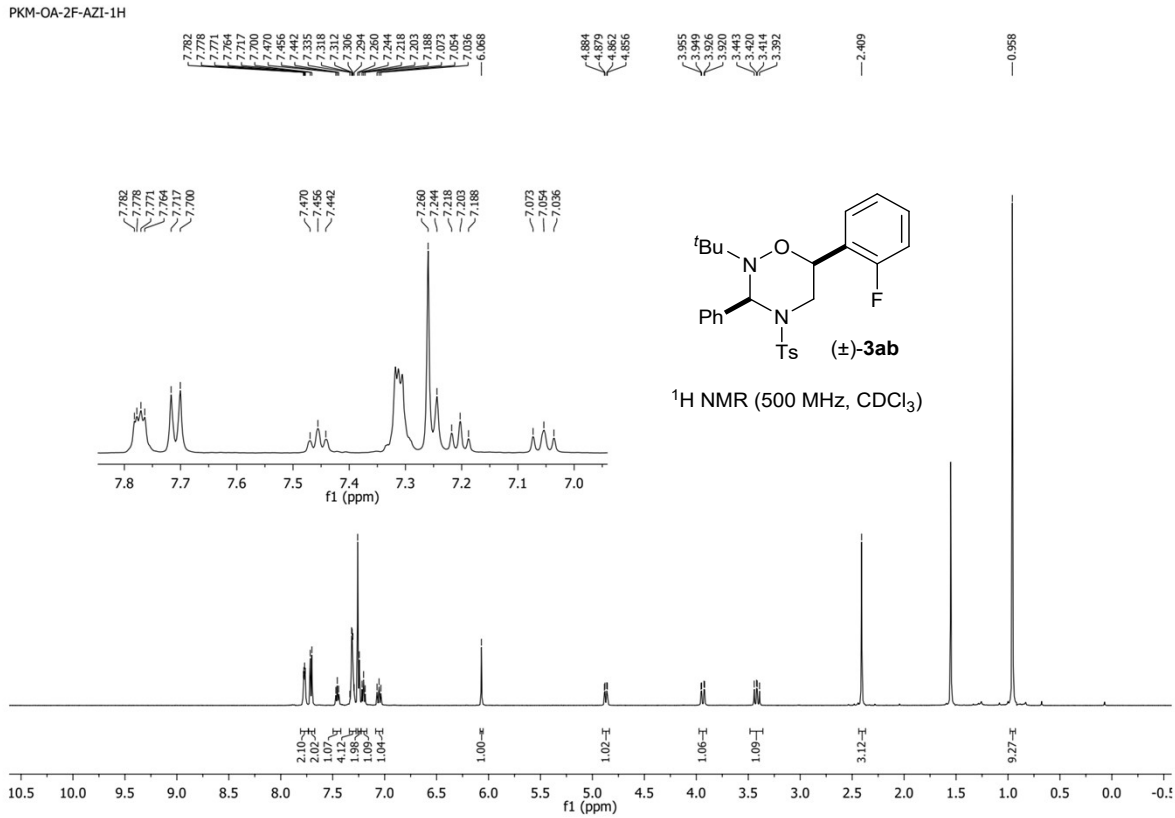
(3*S*,6*S*)-**3aa′**

^{1}H NMR (500 MHz, $CDCl_3$)



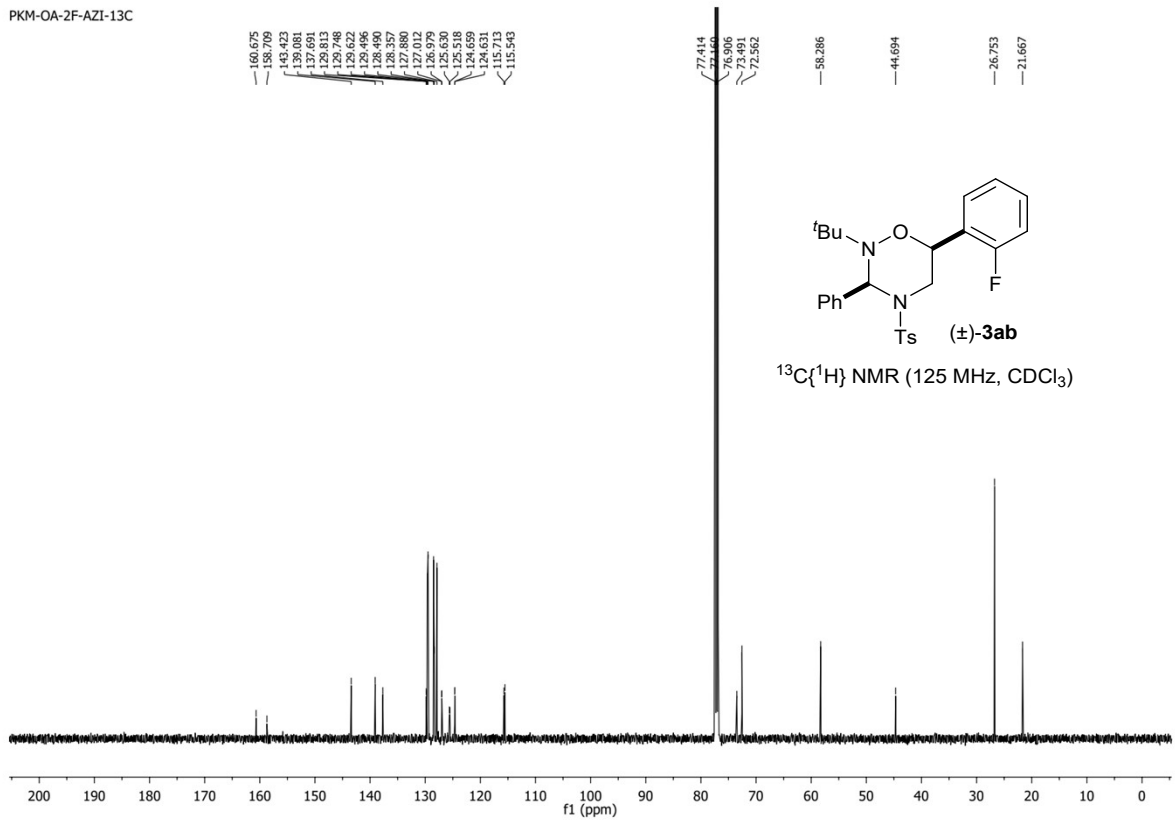
(3*S*,6*S*)-**3aa′**

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



(±)-**3ab**

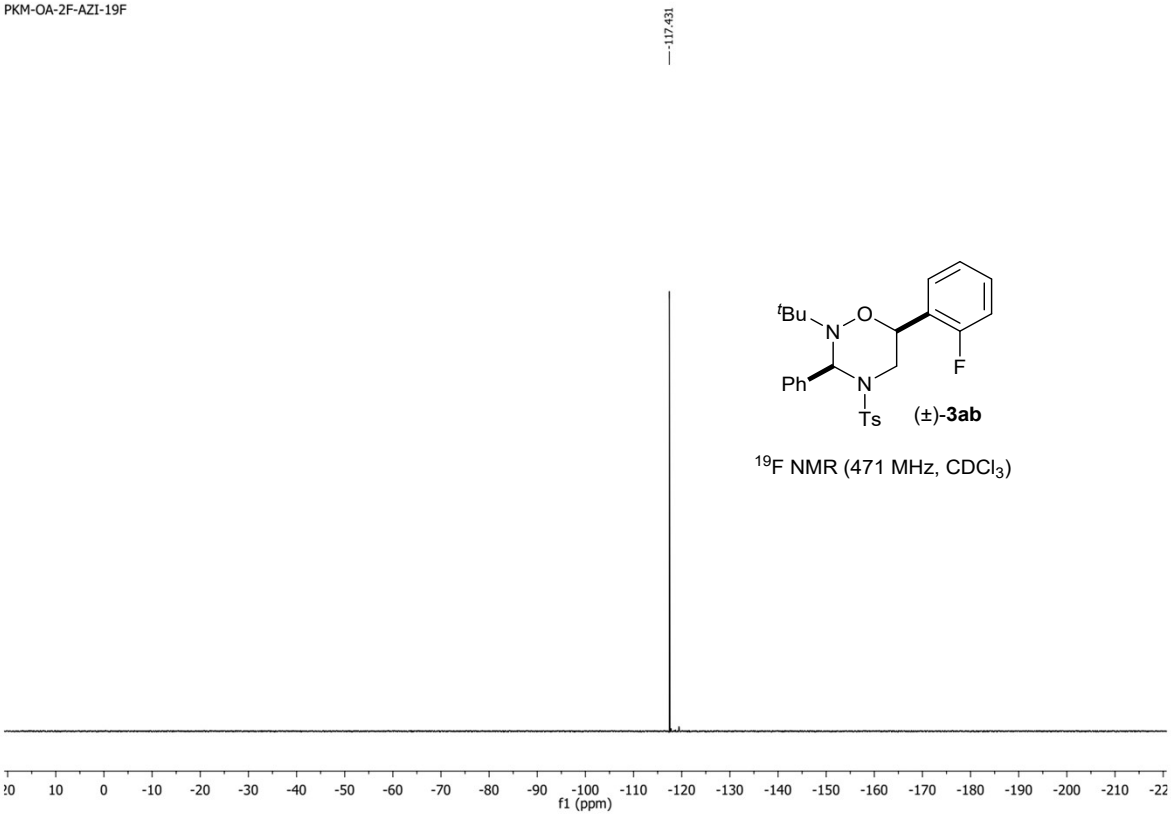
^{1}H NMR (500 MHz, $CDCl_3$)



(±)-**3ab**

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

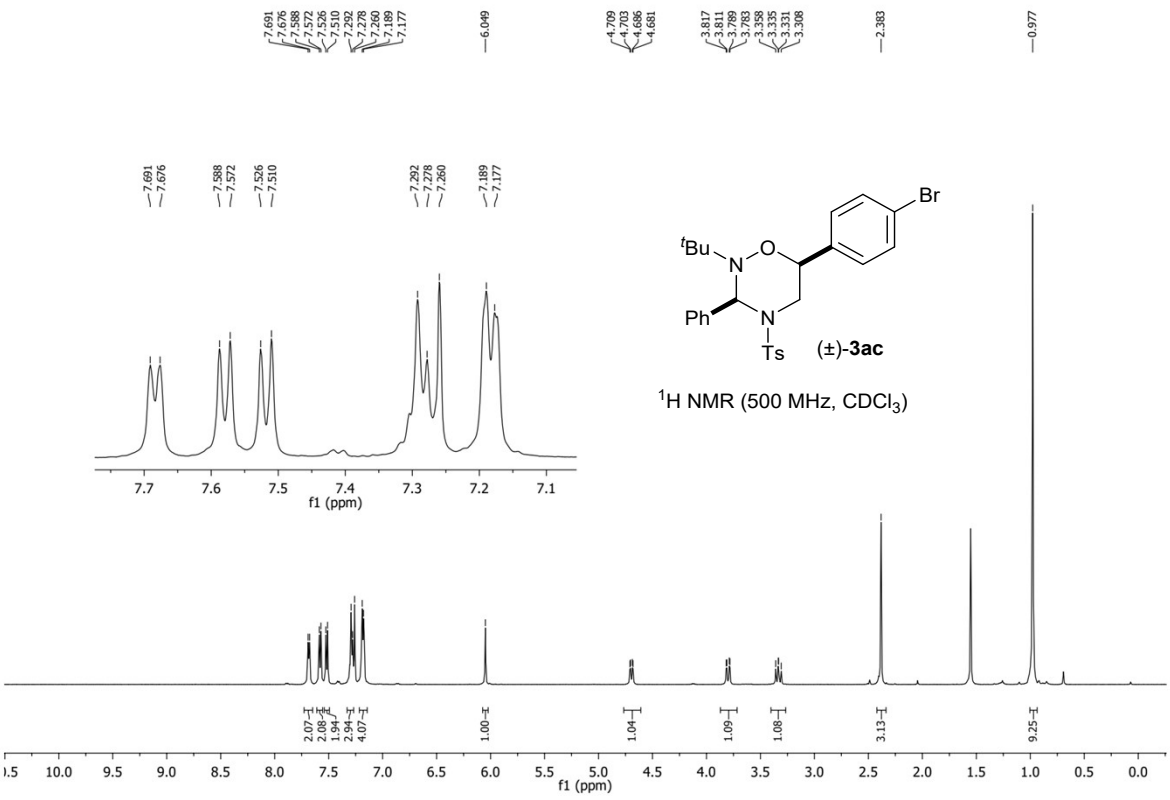
PKM-OA-2F-AZI-19F



(±)-**3ab**

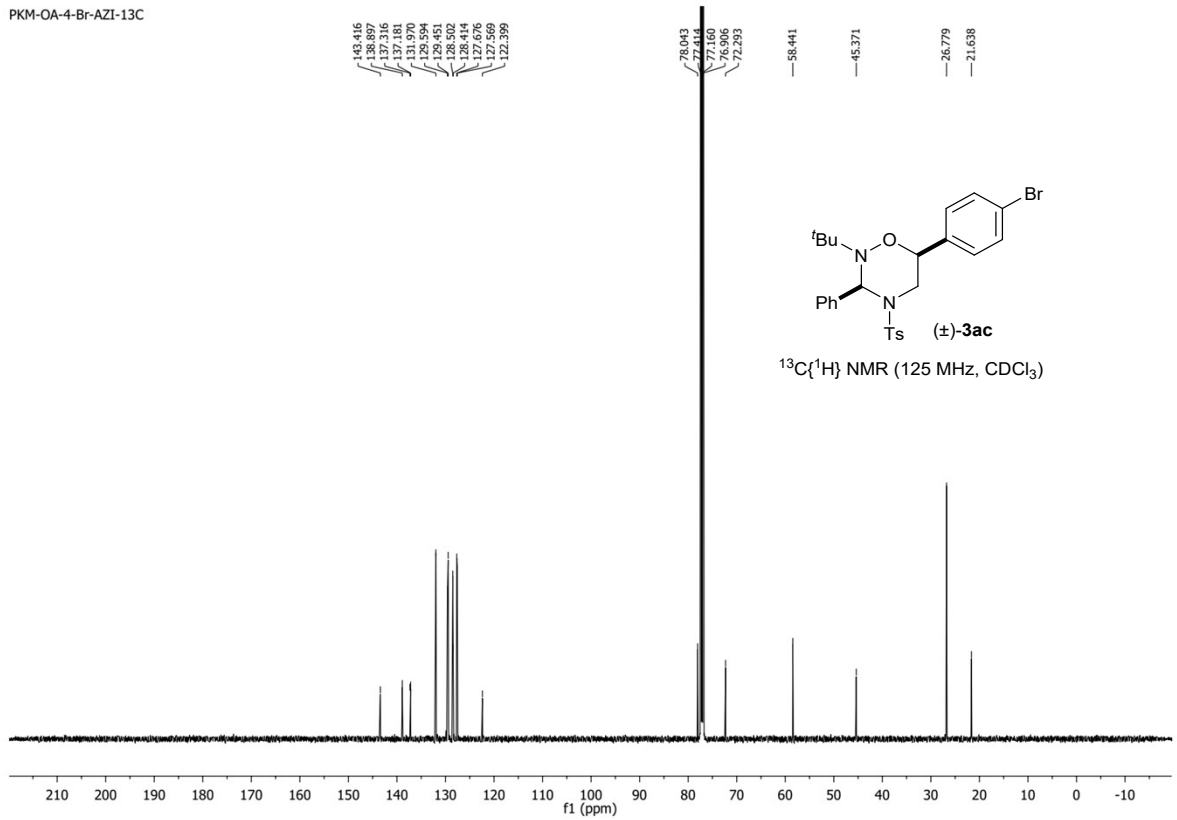
^{19}F NMR (471 MHz, $CDCl_3$)

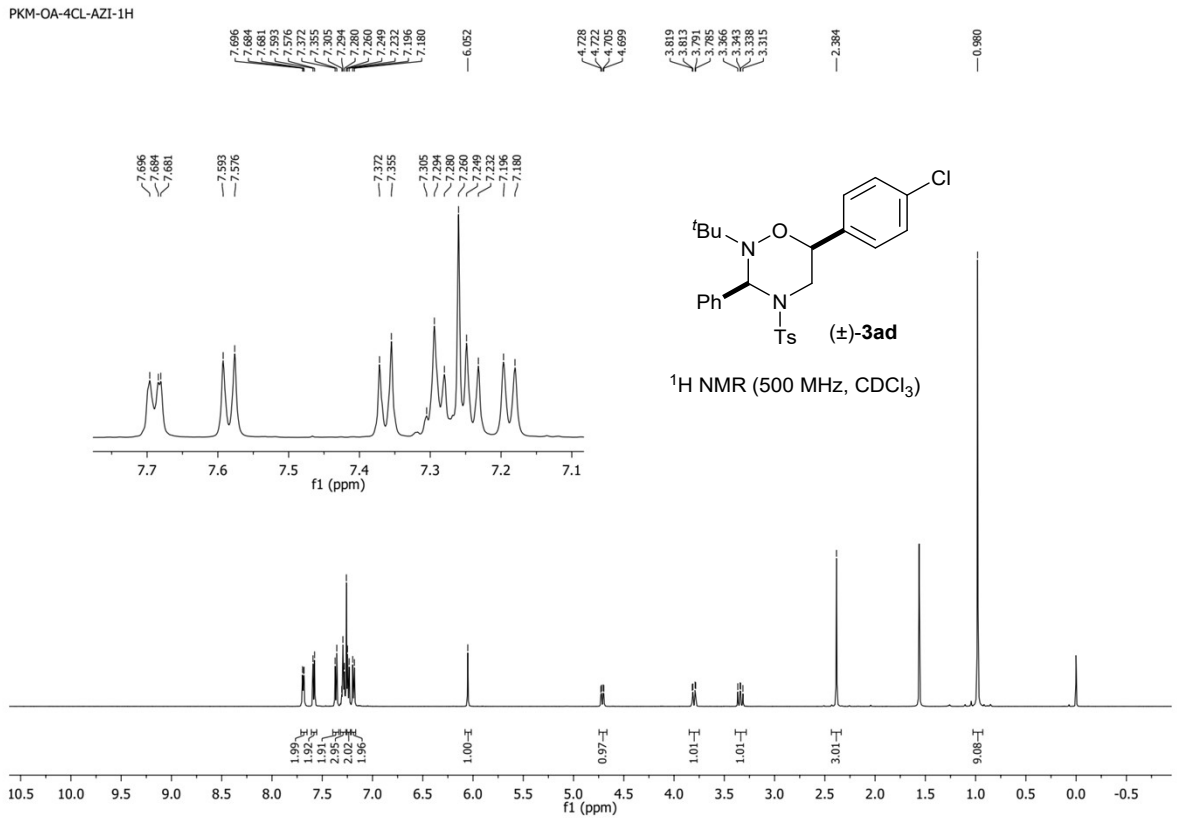
PKM-OA-4-Br-AZI-1H

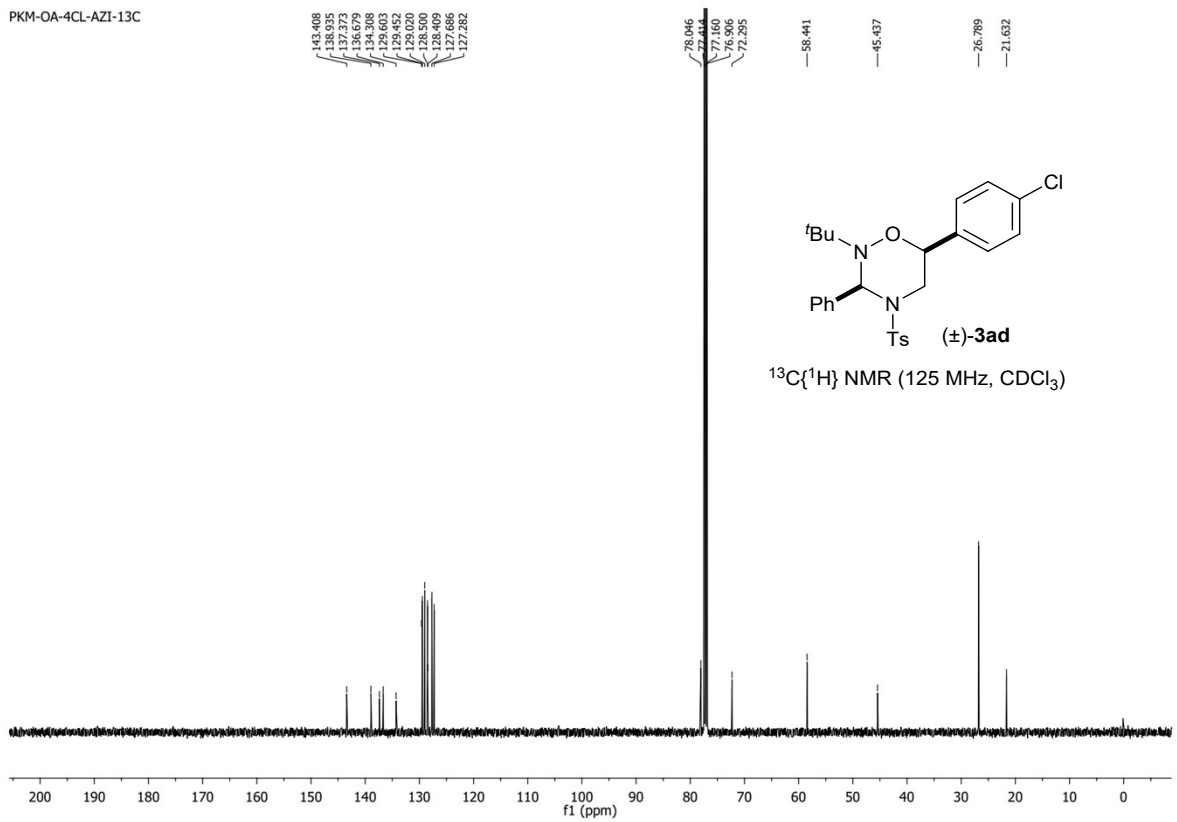


(±)-**3ac**

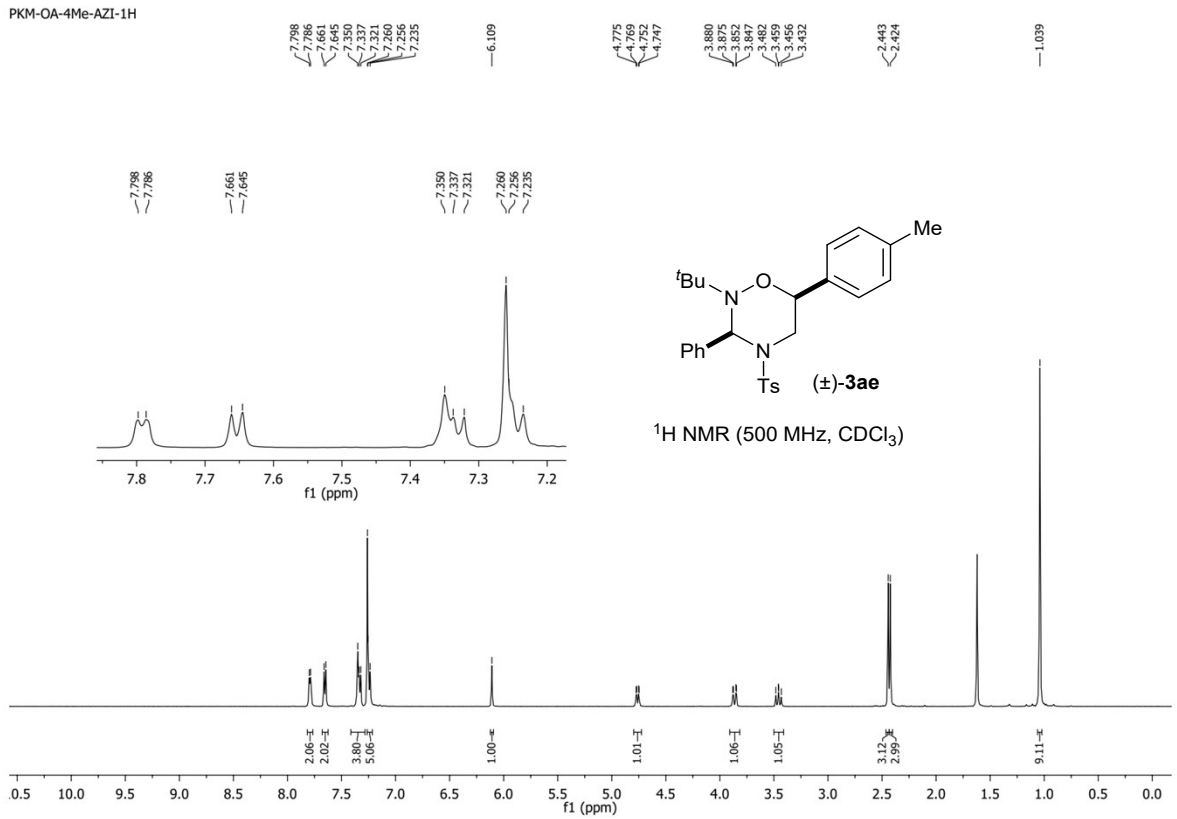
^{1}H NMR (500 MHz, $CDCl_3$)


PKM-OA-4-Br-AZI-13C
143.416
138.897
137.316
137.181
131.970
129.594
129.451
128.502
128.414
127.676
127.569
122.399
78.043
77.414
77.160
76.906
72.293
58.441
45.371
26.779
21.638
Br
tBu
N
O
Ph
N
Ts
(±)-3ac
13C{1H} NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

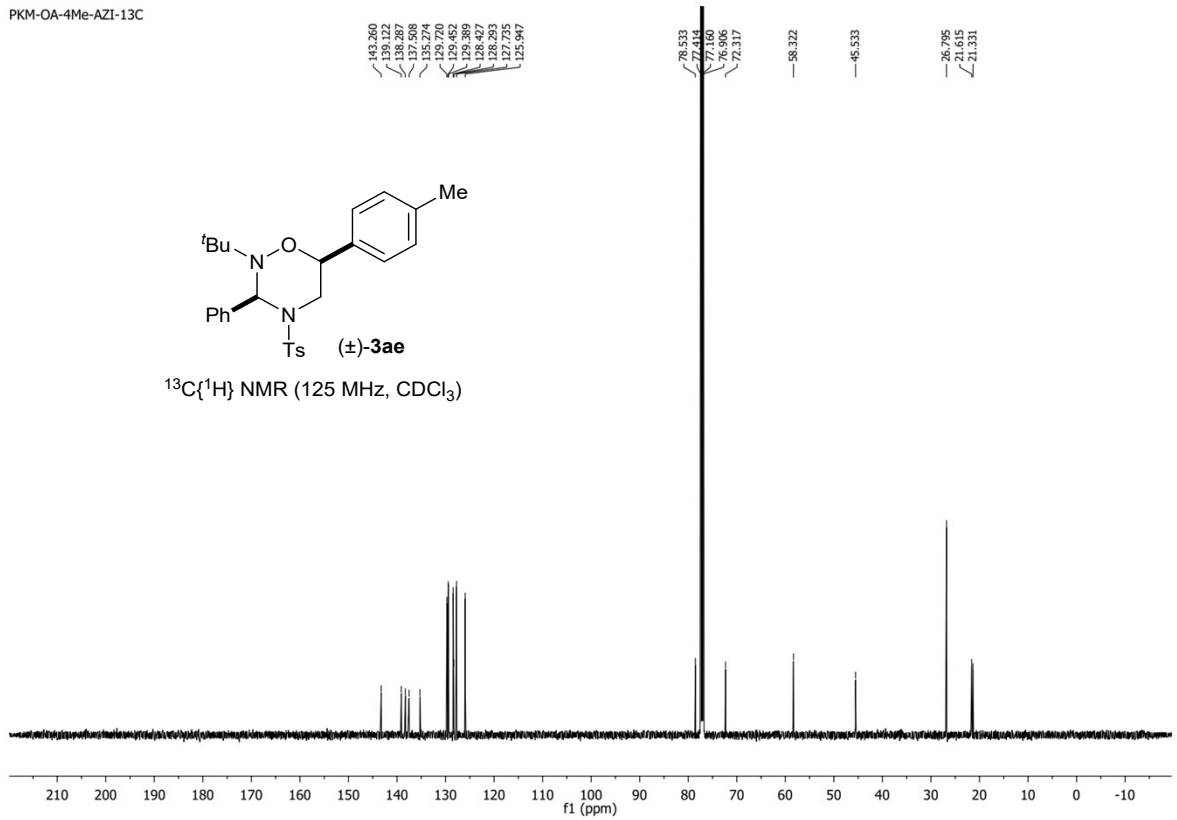

PKM-OA-4CL-AZI-1H
7.696
7.684
7.681
7.593
7.576
7.372
7.355
7.305
7.294
7.280
7.260
7.249
7.232
7.196
7.180
6.052
4.728
4.722
4.705
4.699
3.819
3.813
3.791
3.785
3.366
3.343
3.338
3.315
2.384
0.980
Cl
tBu
N
O
Ph
N
Ts
(±)-3ad
1H NMR (500 MHz, CDCl3)
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.99
1.92
1.91
2.95
2.02
1.96
1.00
0.97
1.01
1.01
3.01
9.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



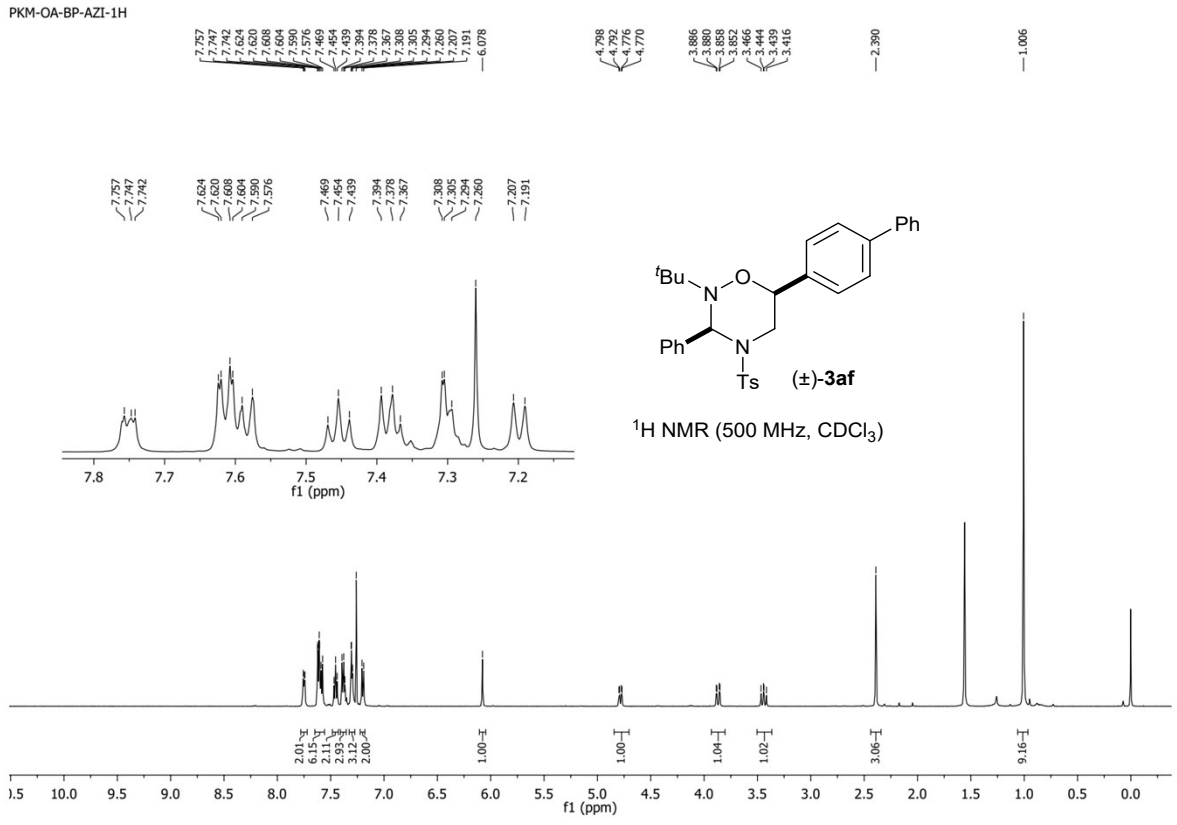
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



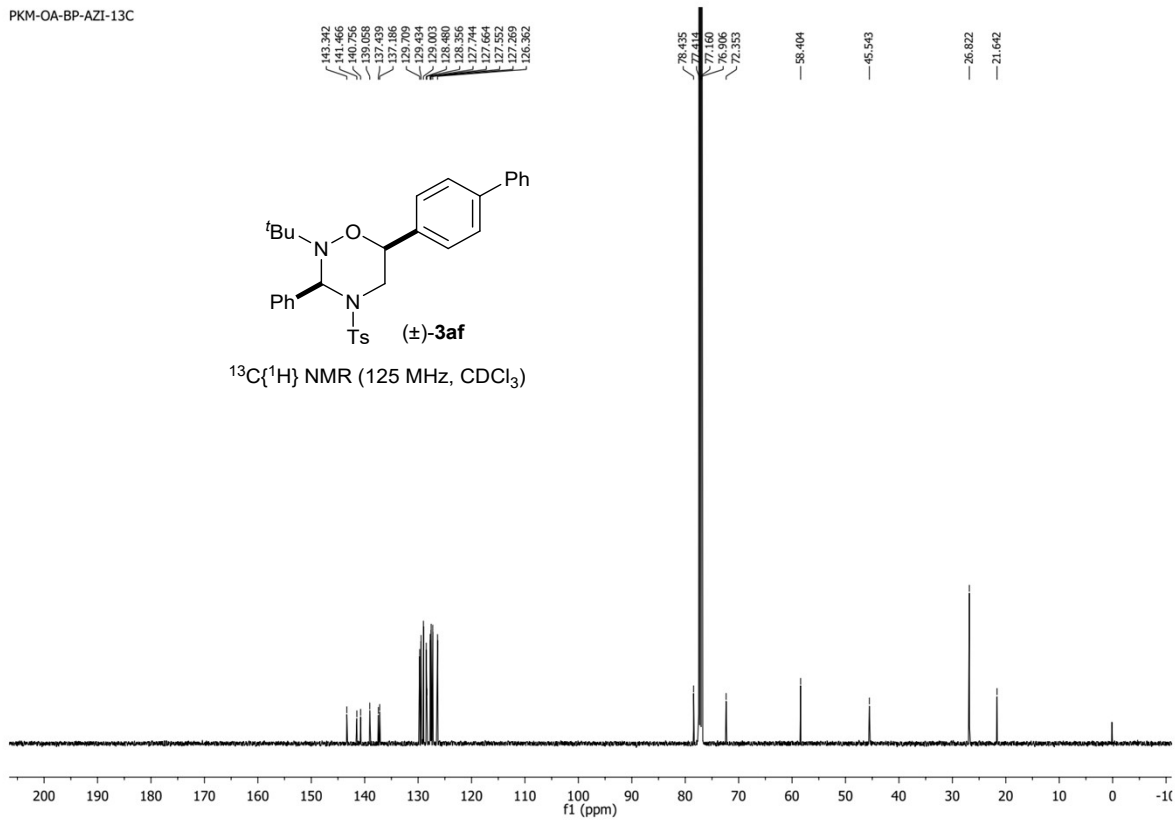
^{1}H NMR (500 MHz, $CDCl_3$)

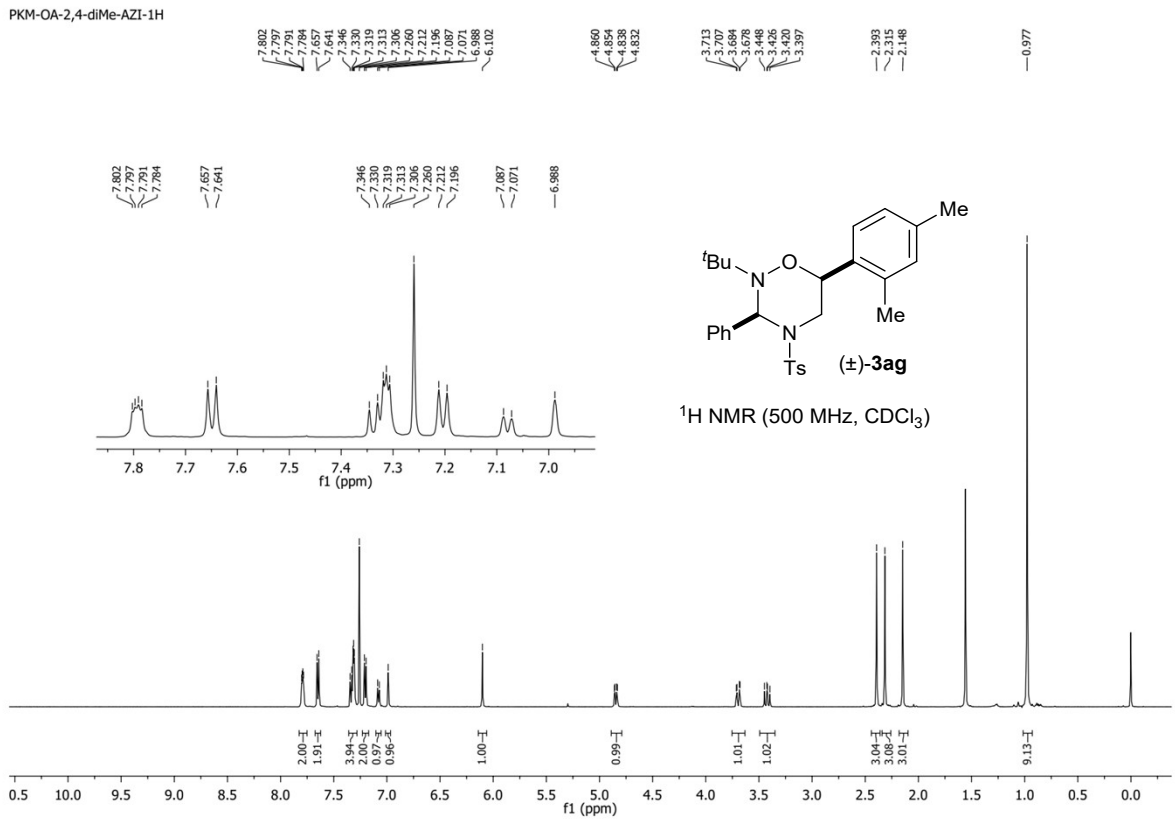


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

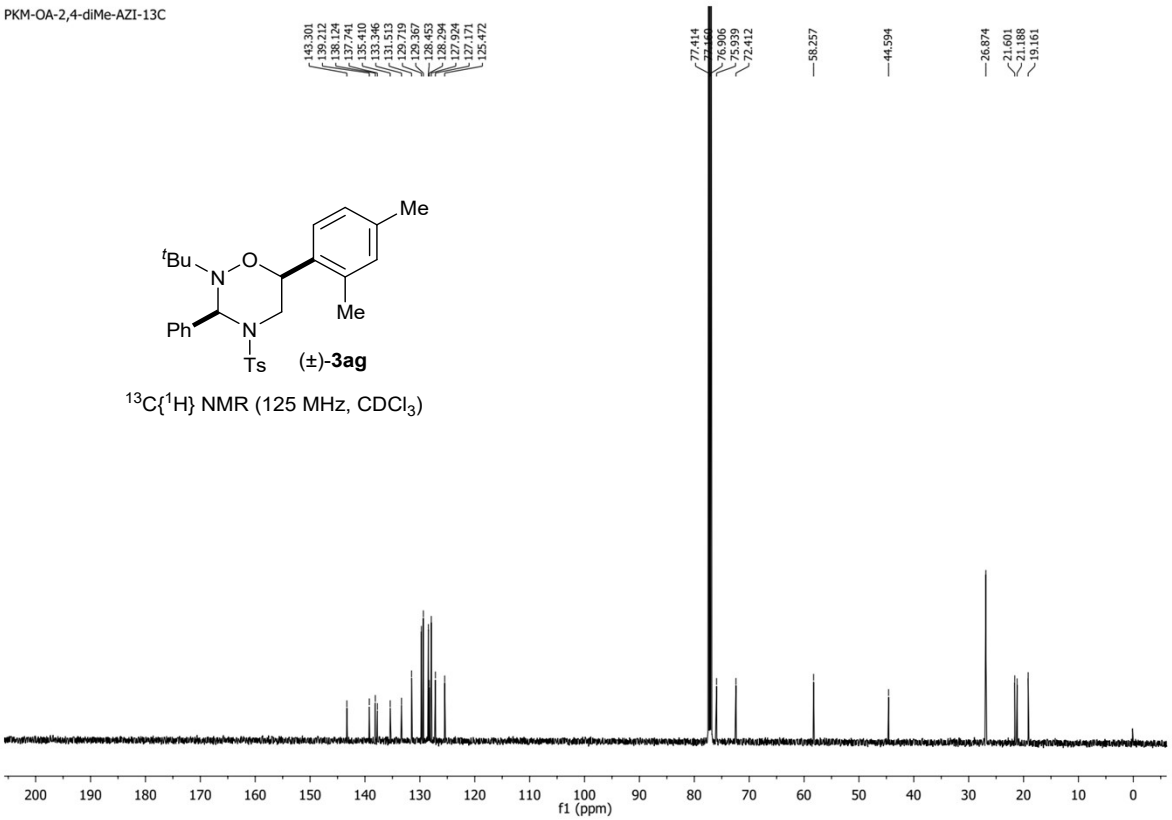


^{1}H NMR (500 MHz, $CDCl_3$)


PKM-OA-BP-AZI-13C
143.342
141.466
140.756
139.058
137.439
137.186
129.709
129.434
129.003
128.480
128.356
127.744
127.664
127.552
127.269
126.362
78.435
77.414
77.160
76.906
72.353
58.404
45.543
26.822
21.642
Ph
tBu
N
O
Ph
N
Ts
(±)-3af
13C{1H} NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PKM-OA-2,4-diMe-AZI-1H
7.802
7.797
7.791
7.784
7.657
7.641
7.346
7.330
7.319
7.313
7.306
7.260
7.212
7.196
7.087
7.071
6.988
6.102
4.860
4.854
4.838
4.832
3.713
3.707
3.684
3.678
3.448
3.426
3.420
3.397
2.393
2.315
2.148
0.977
Me
Me
tBu
N
O
Ph
N
Ts
(±)-3ag
1H NMR (500 MHz, CDCl3)
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.00
1.91
3.94
2.00
0.97
0.96
1.00
0.99
1.01
1.02
3.04
3.08
3.01
9.13
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

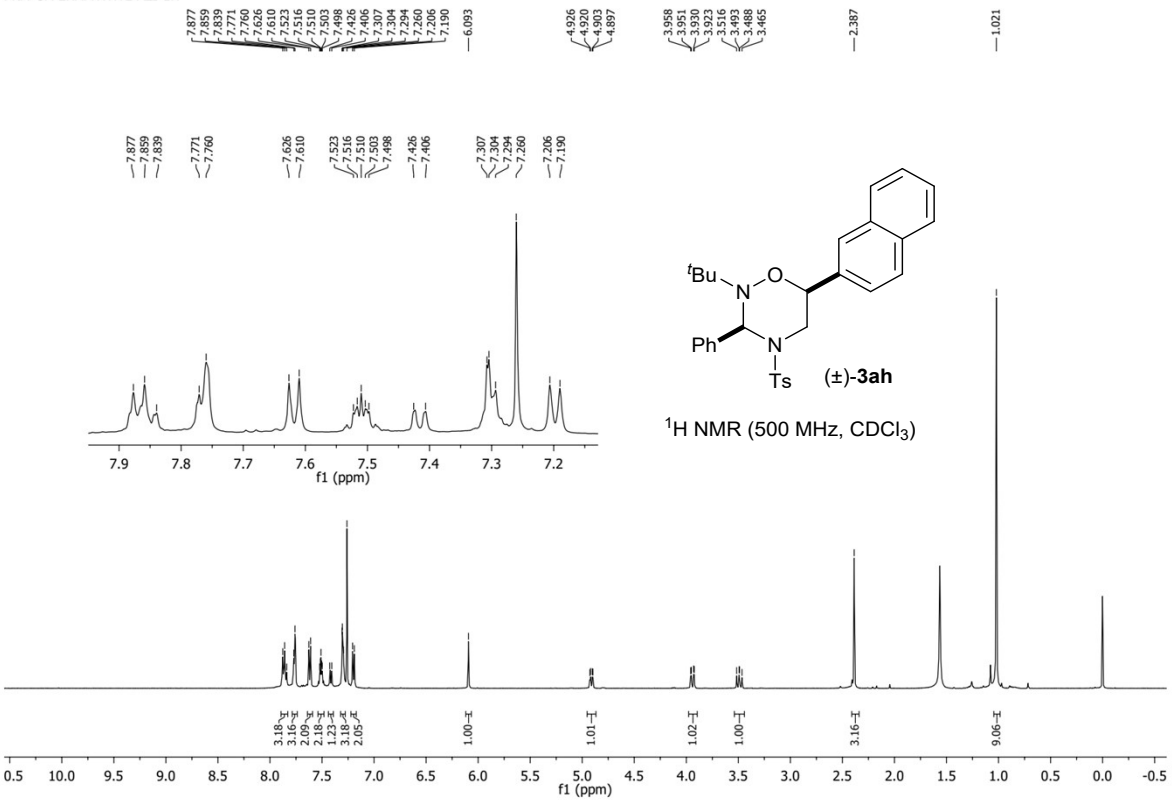
PKM-OA-2,4-diMe-AZI-13C



(±)-**3ag**

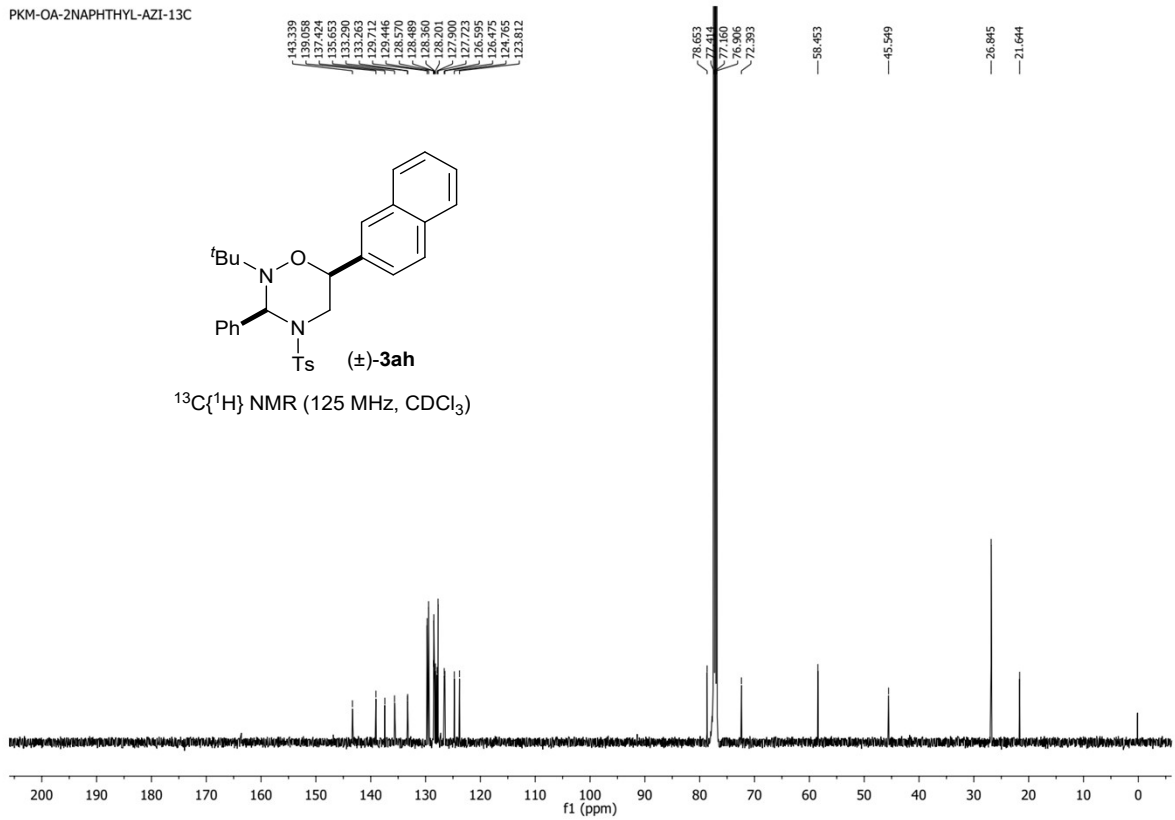
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-OA-2NAPHTHYL-AZI-1H



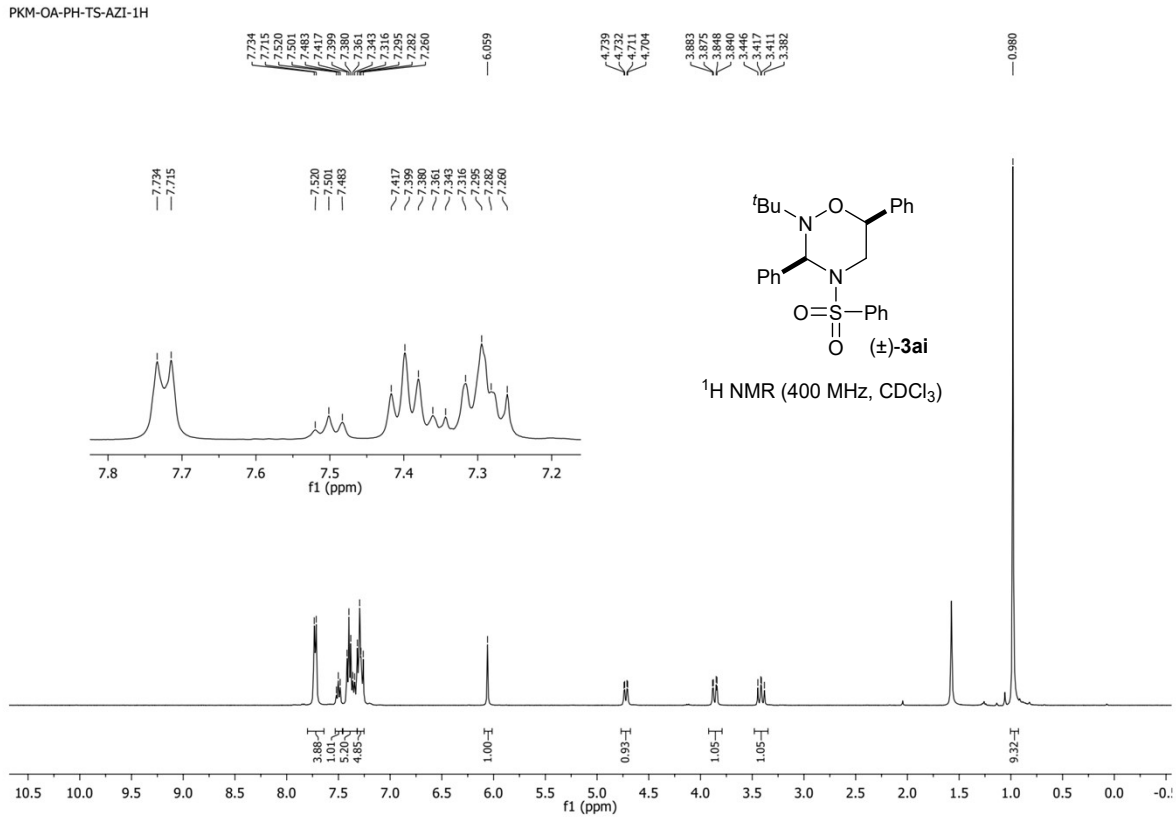
(±)-**3ah**

^{1}H NMR (500 MHz, $CDCl_3$)



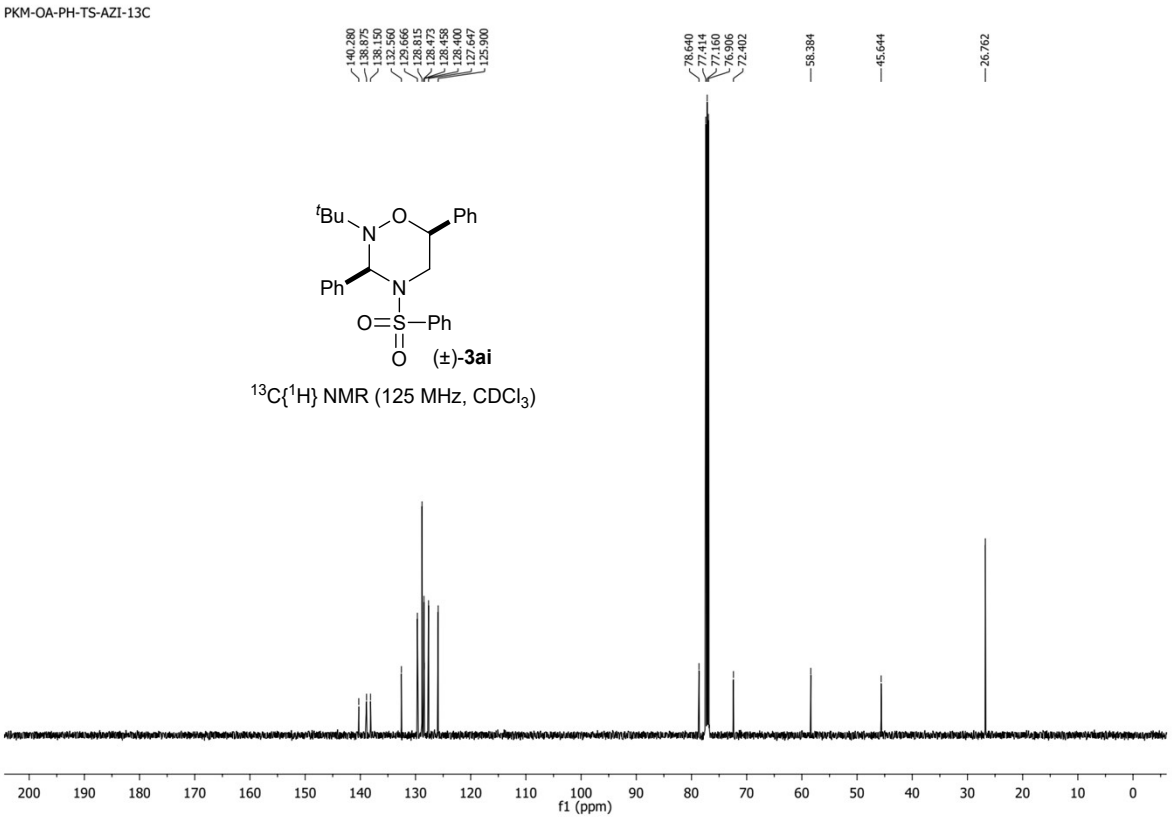
(±)-**3ah**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



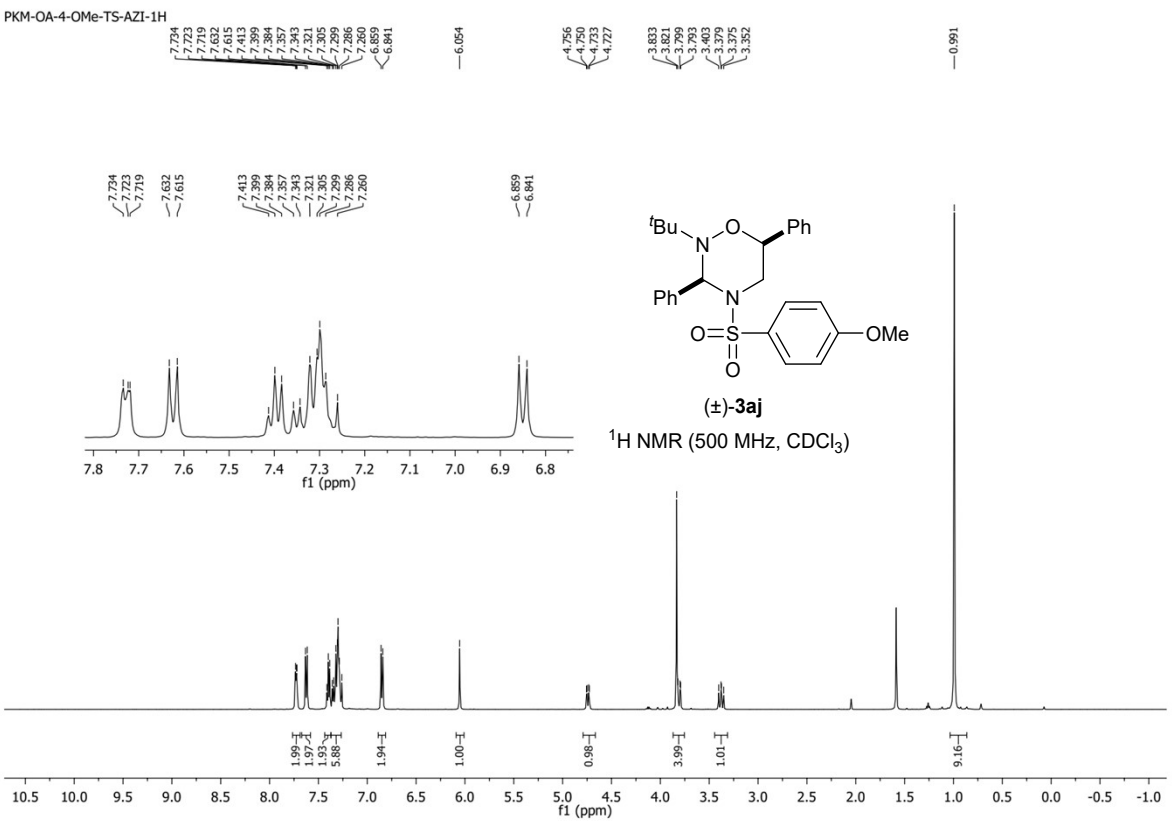
(±)-**3ai**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**3ai**

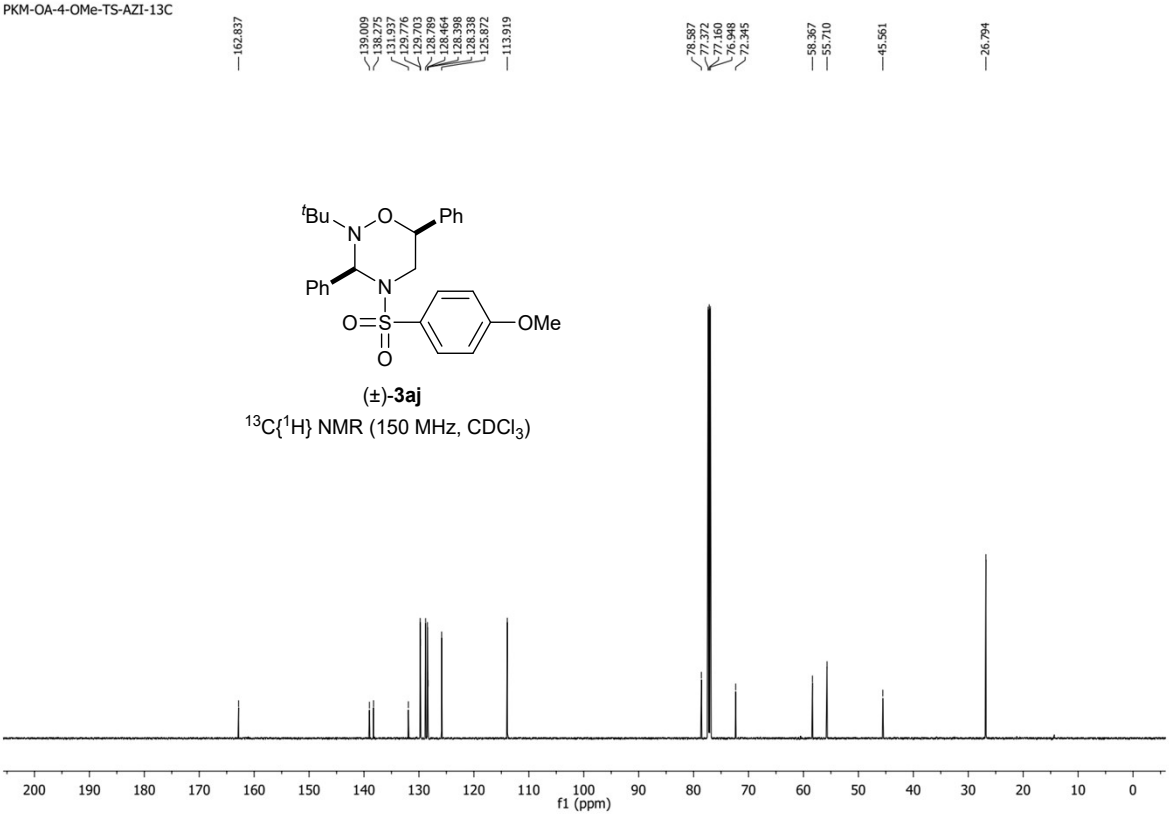
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**3aj**

^{1}H NMR (500 MHz, $CDCl_3$)

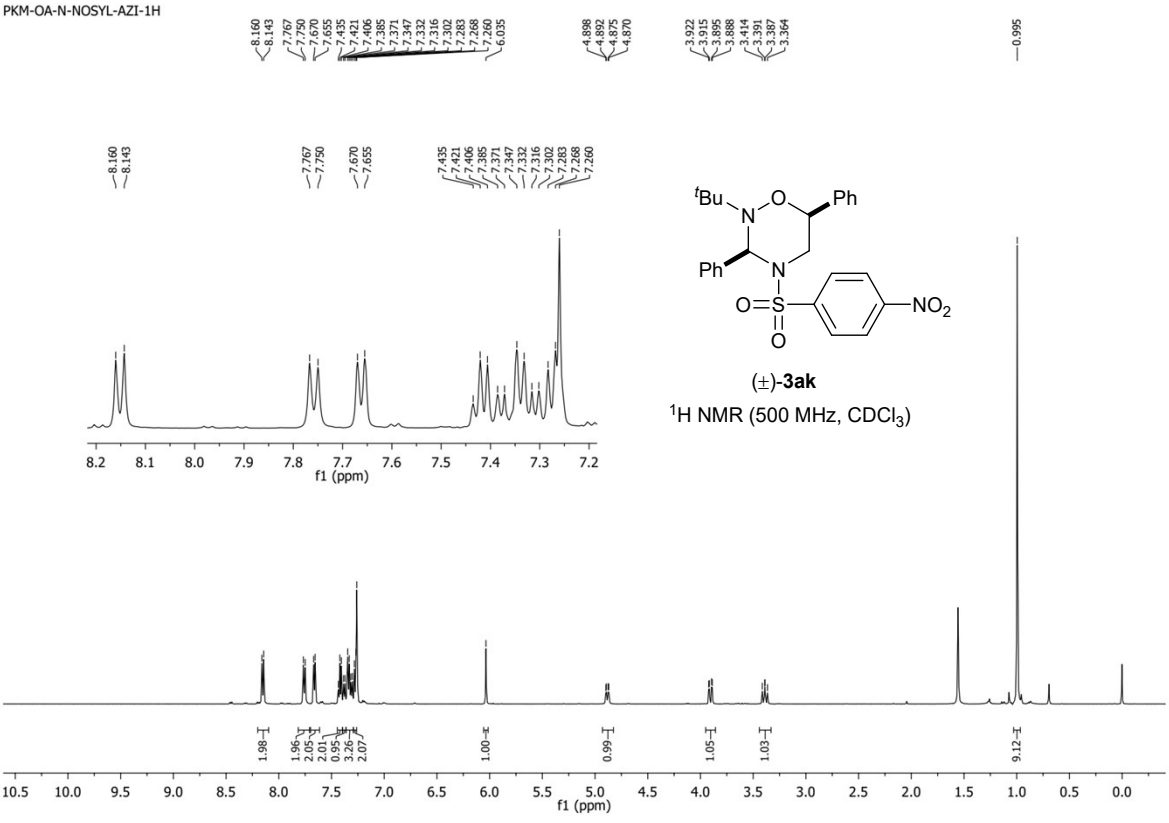
PKM-OA-4-OMe-TS-AZI-13C



(±)-**3aj**

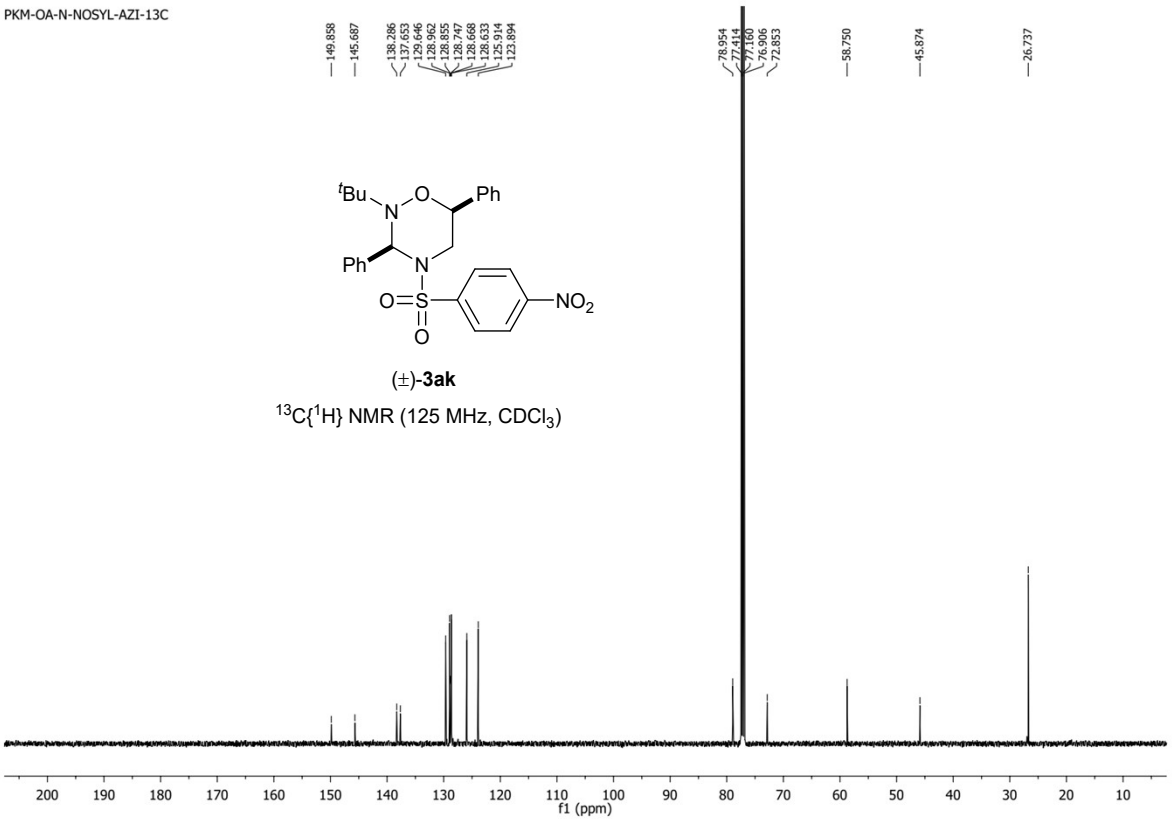
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

PKM-OA-N-NOSYL-AZI-1H



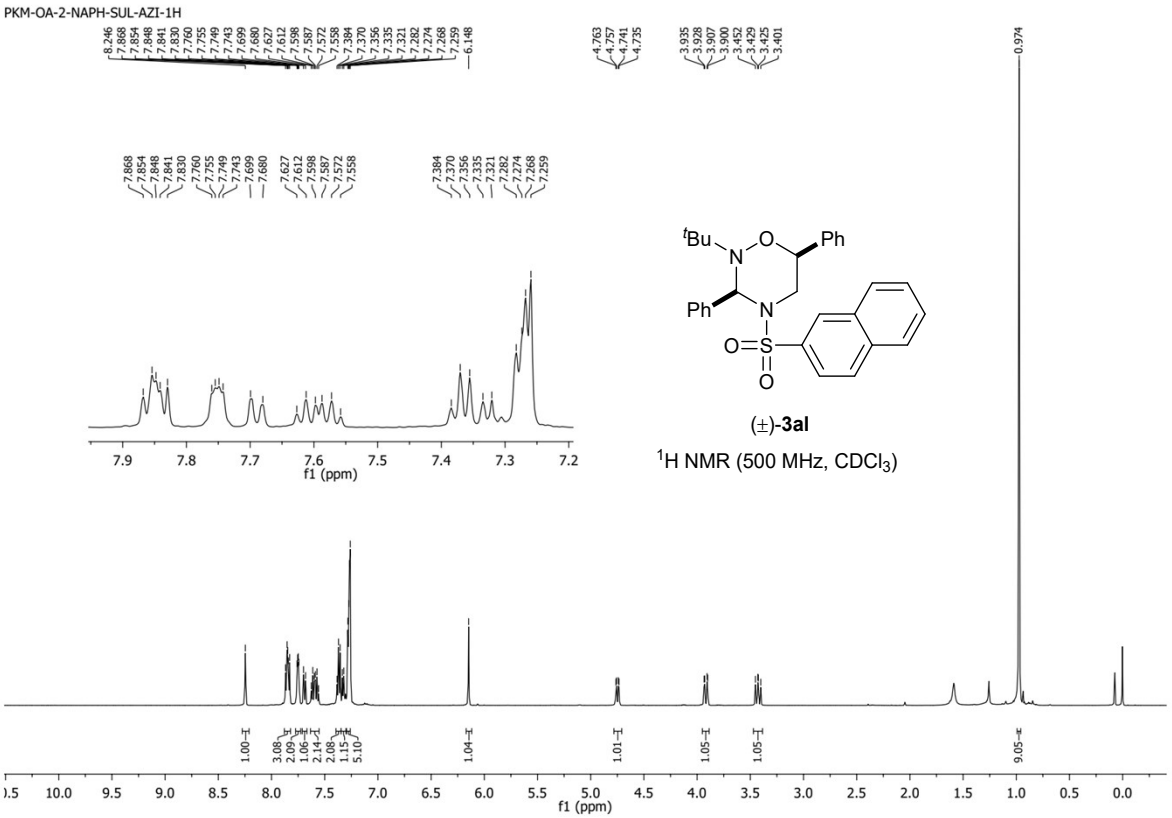
(±)-**3ak**

^{1}H NMR (500 MHz, $CDCl_3$)



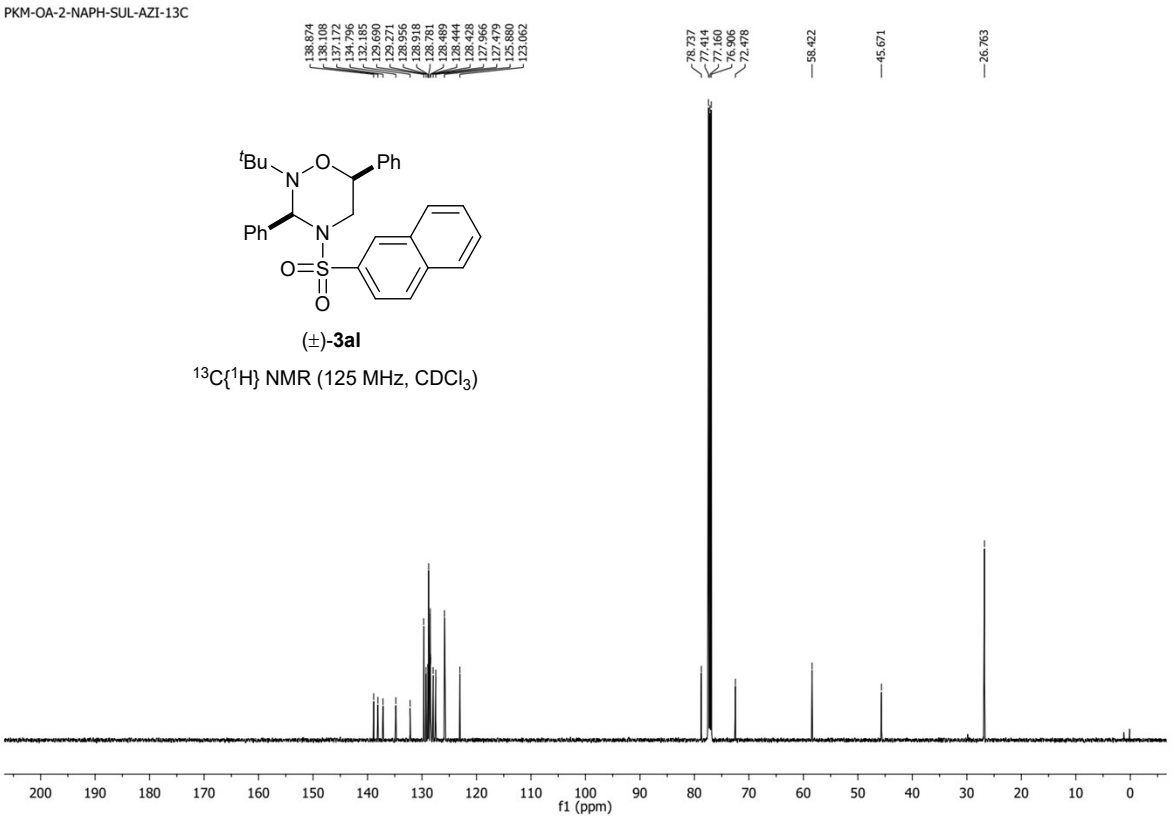
(±)-**3ak**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



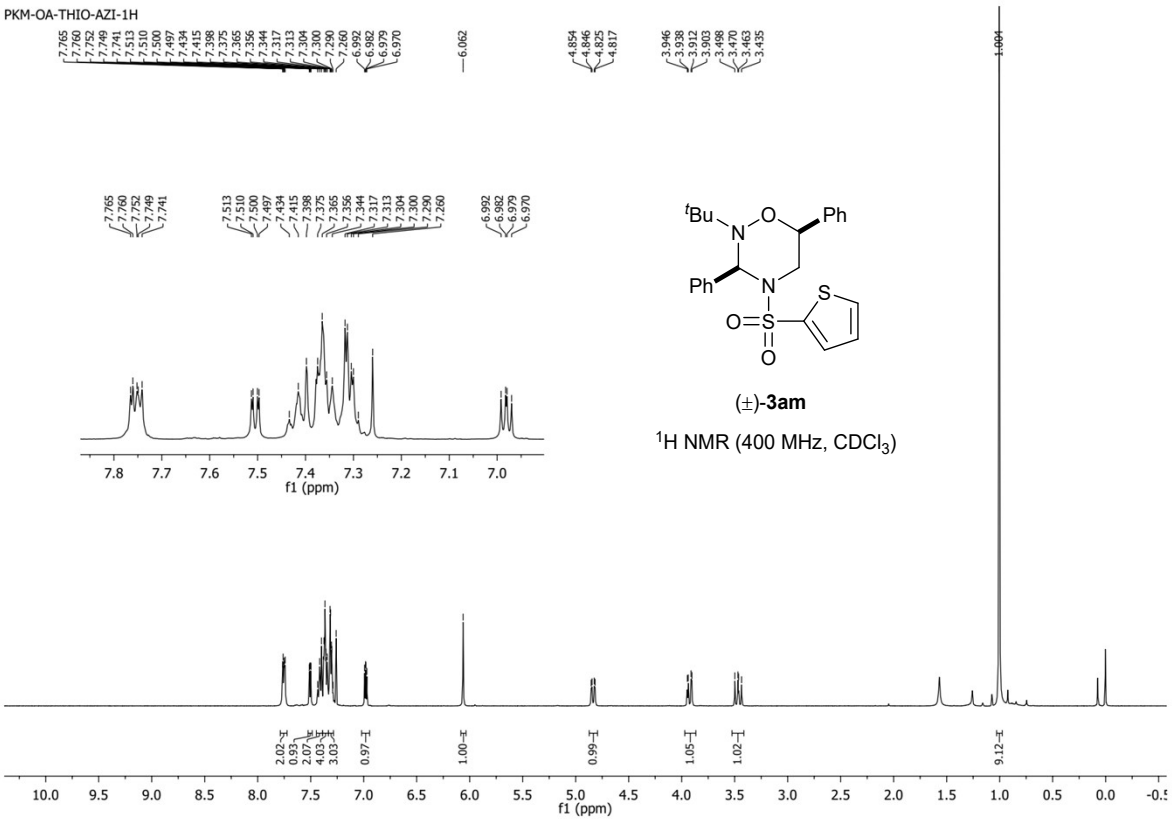
(±)-**3al**

^{1}H NMR (500 MHz, $CDCl_3$)



(±)-**3al**

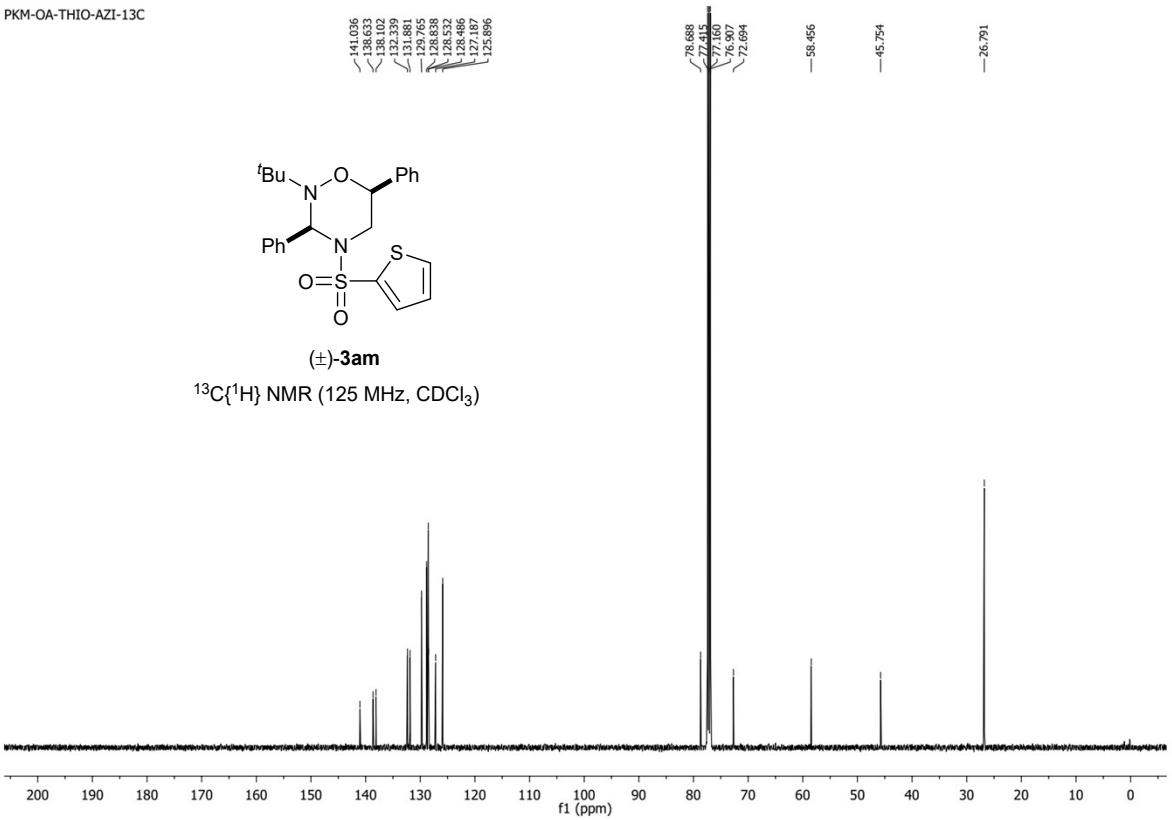
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**3am**

^{1}H NMR (400 MHz, $CDCl_3$)

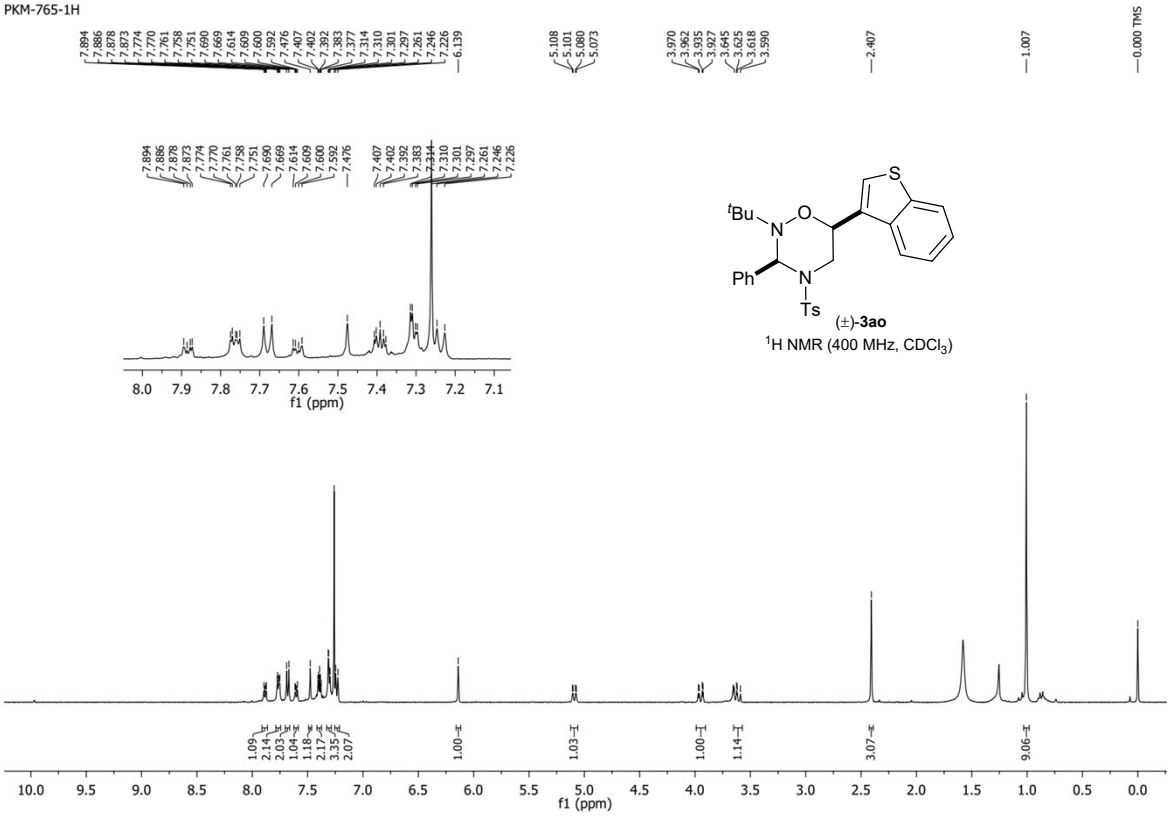
PKM-OA-THIO-AZI-13C



(±)-**3am**

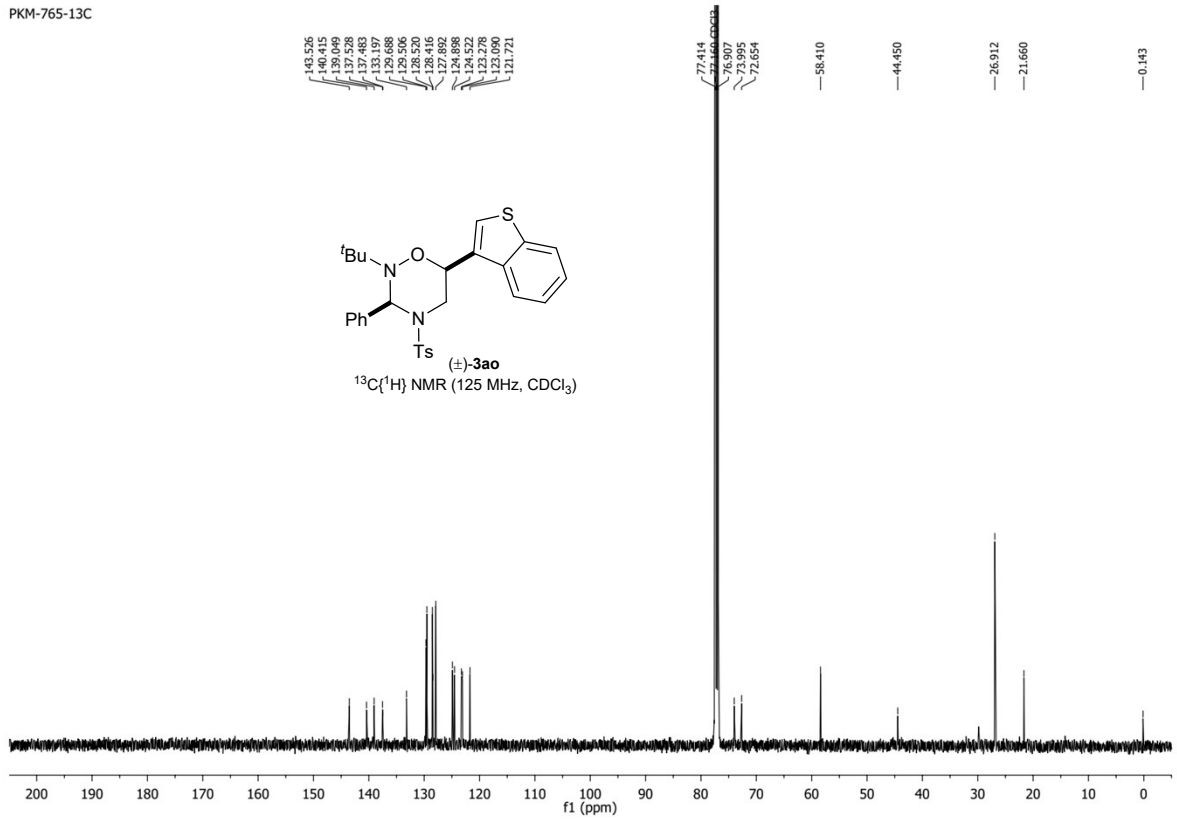
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-765-1H



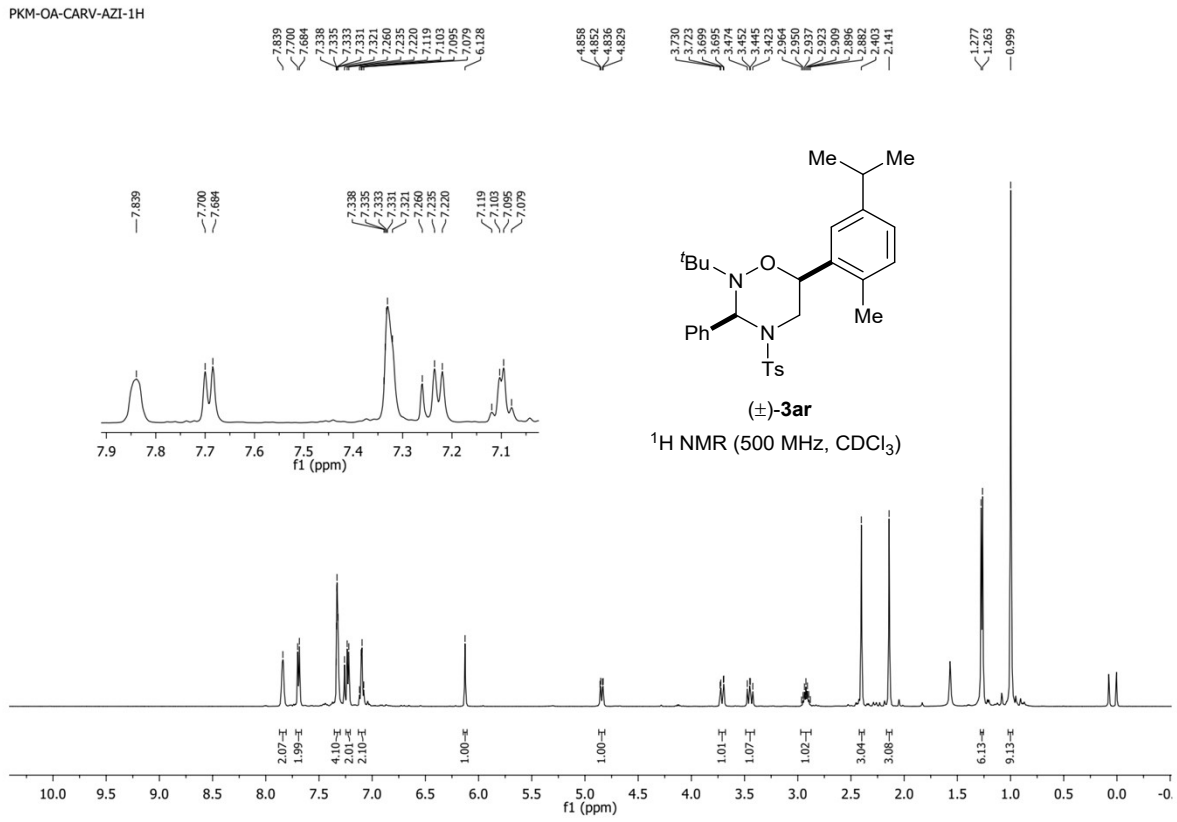
(±)-**3ao**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**3ao**

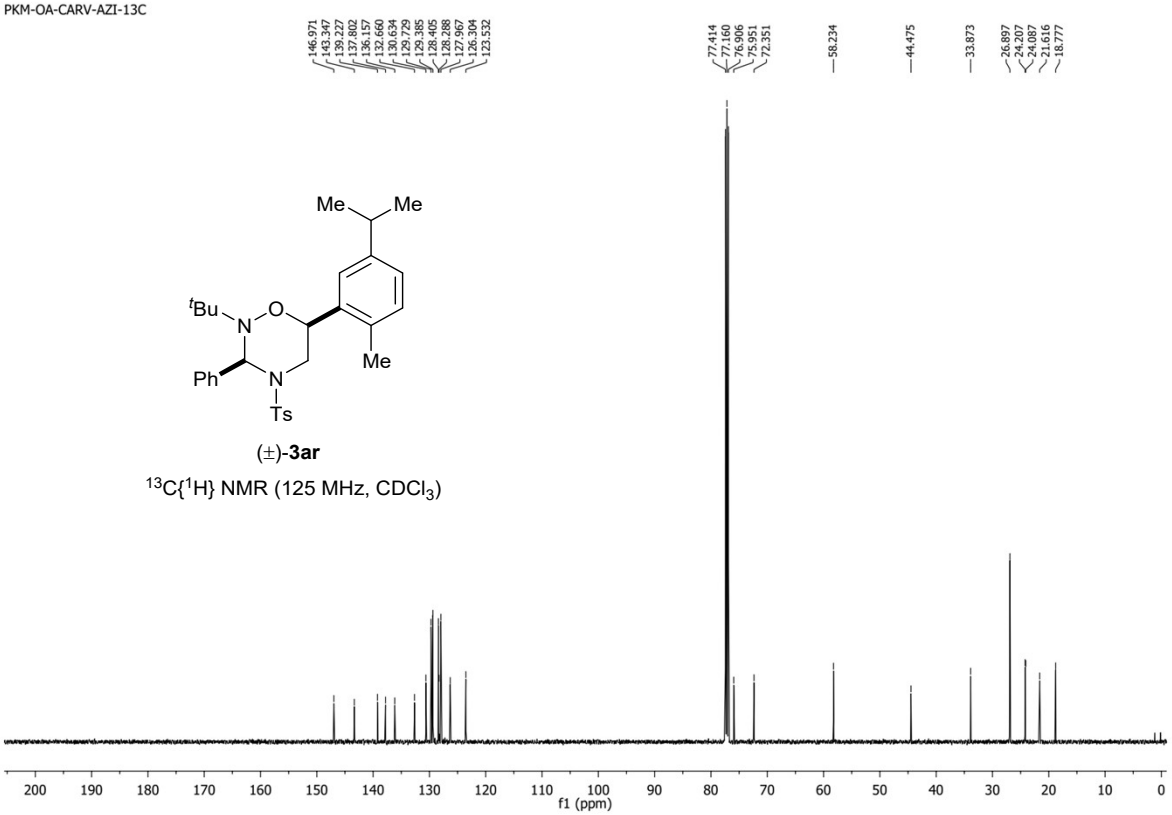
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**3ar**

^{1}H NMR (500 MHz, $CDCl_3$)

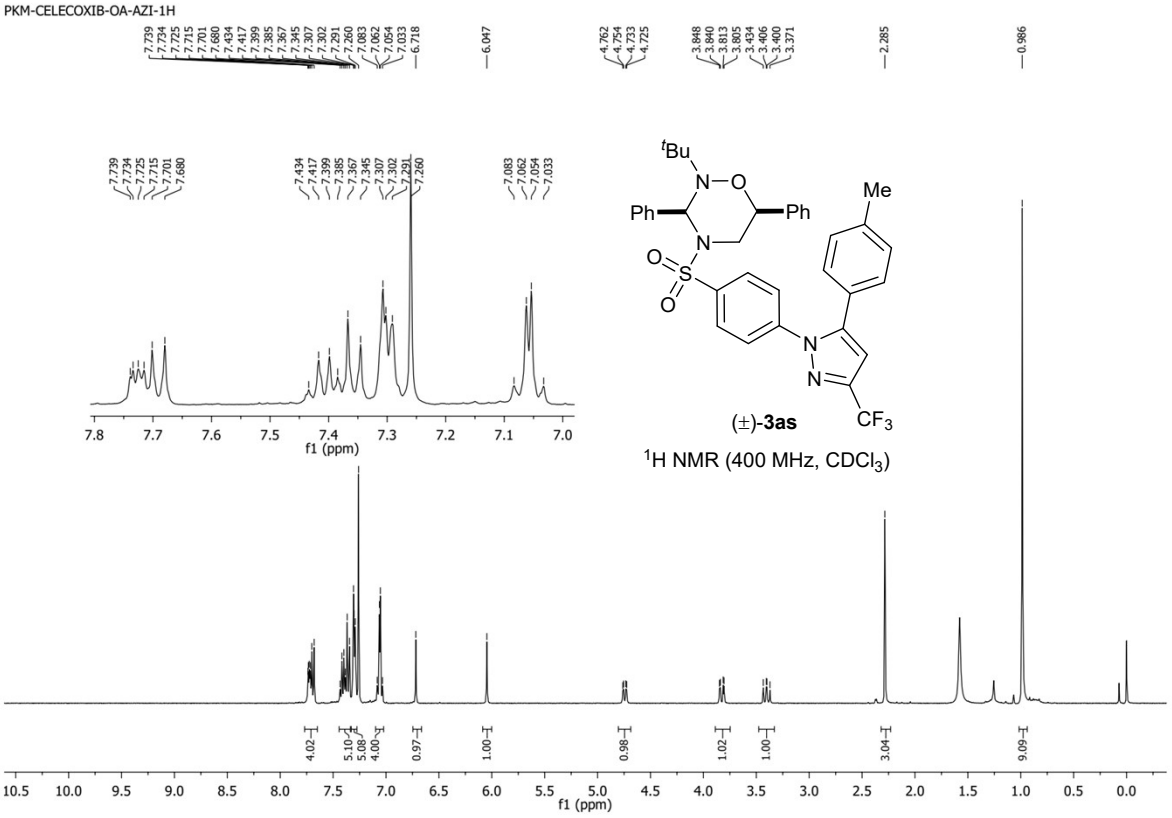
PKM-OA-CARV-AZI-13C



(±)-**3ar**

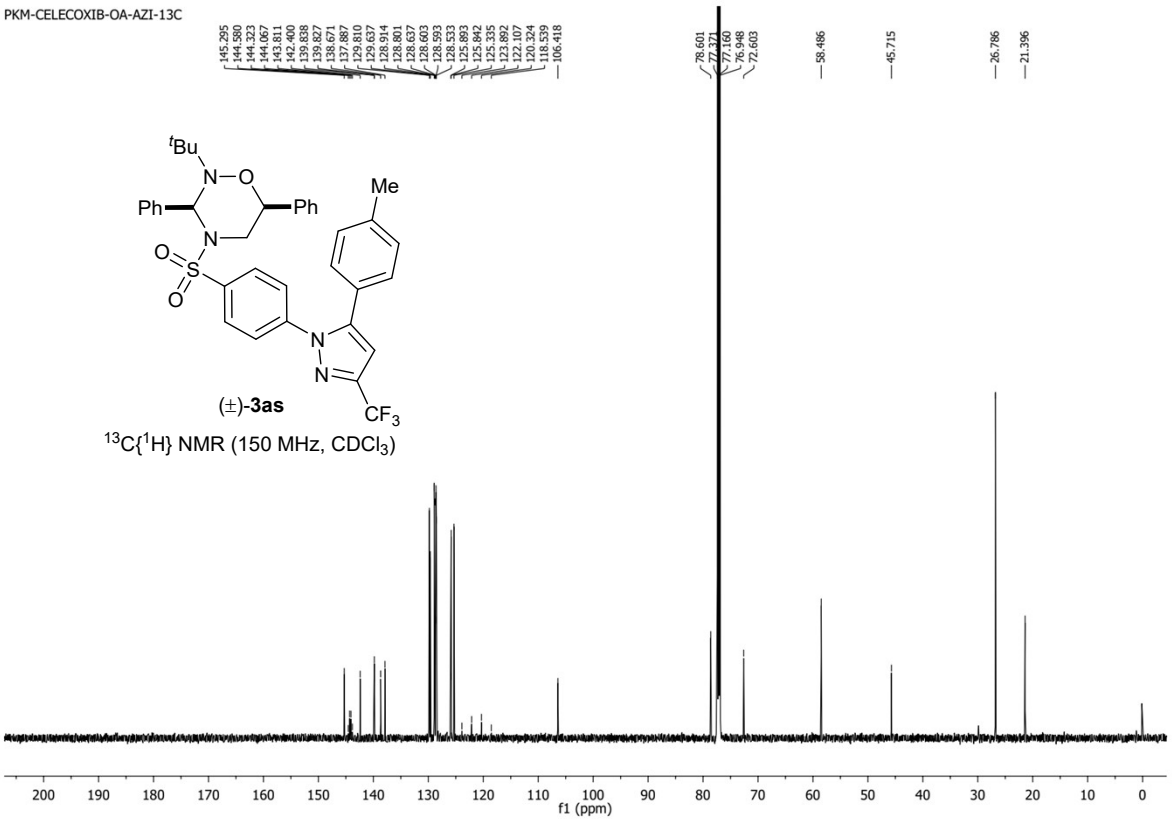
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-CELECOXIB-OA-AZI-1H



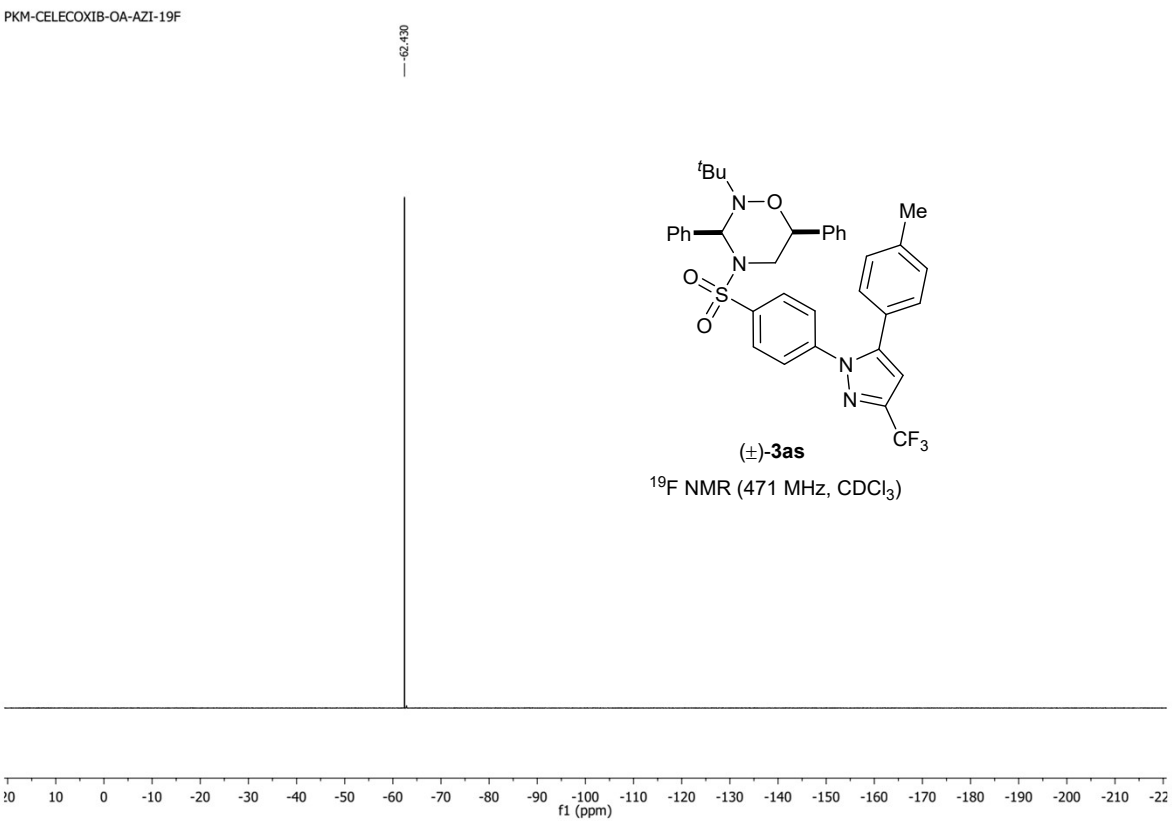
(±)-**3as**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**3as**

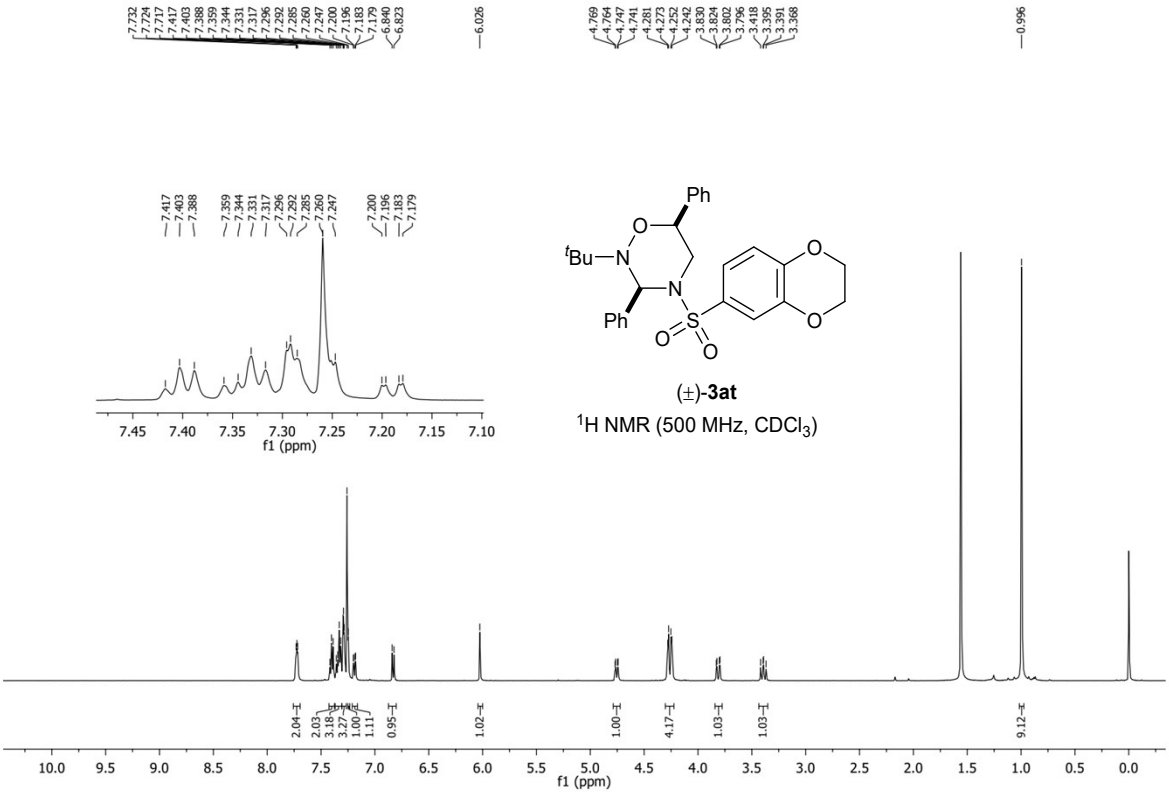
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



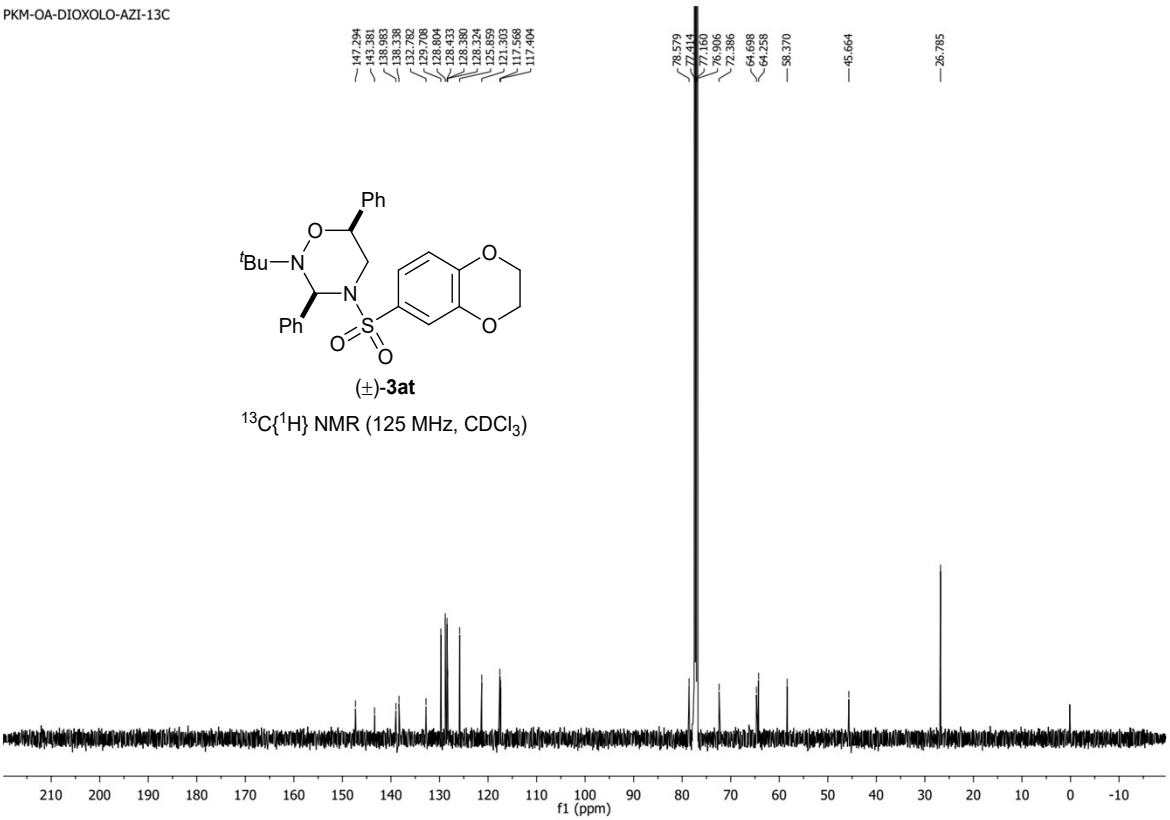
(±)-**3as**

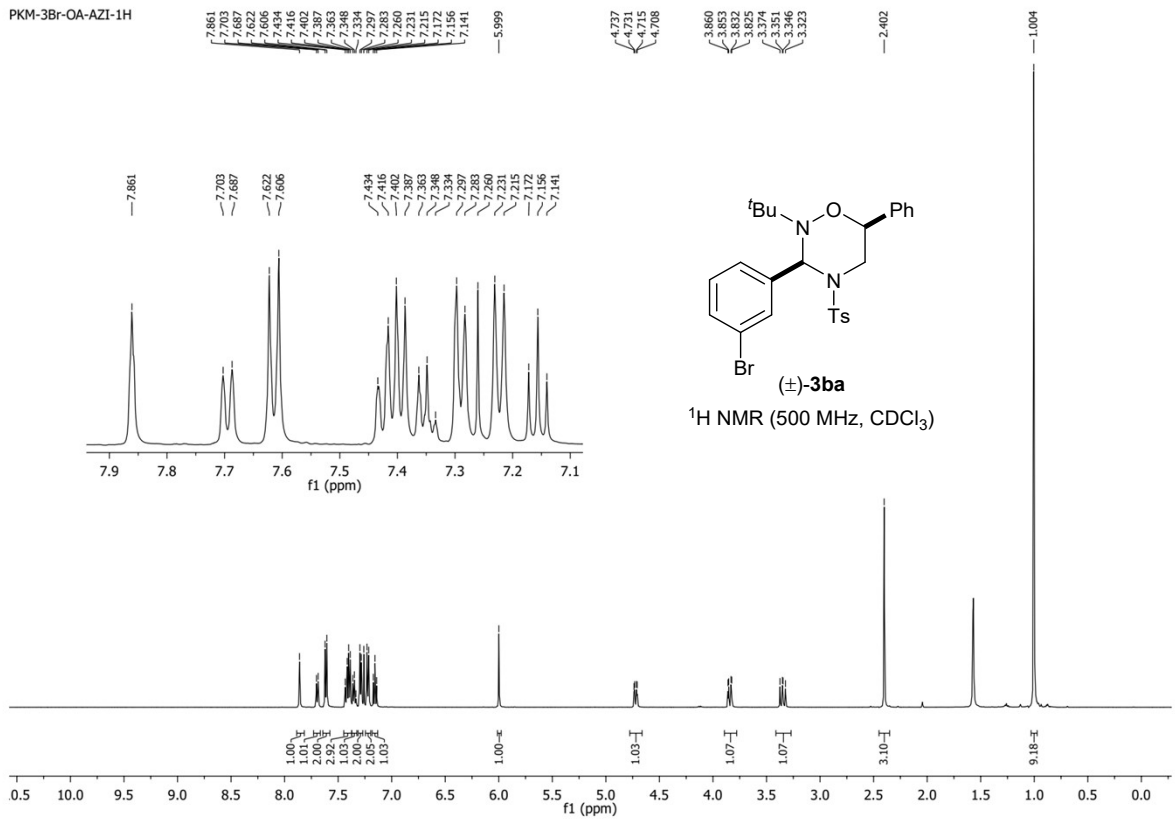
^{19}F NMR (471 MHz, $CDCl_3$)

PKM-TBU-OA-DIOXOLO-AZI-1H



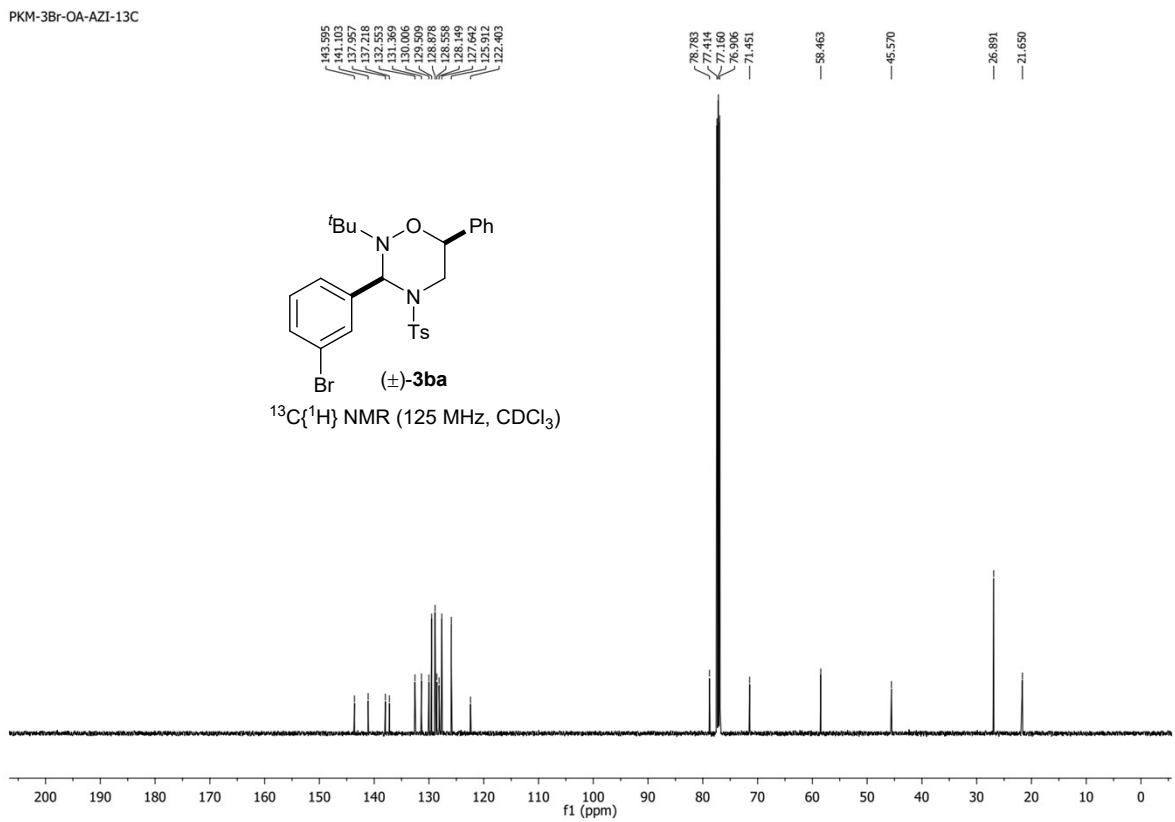
PKM-OA-DIOXOLO-AZI-13C





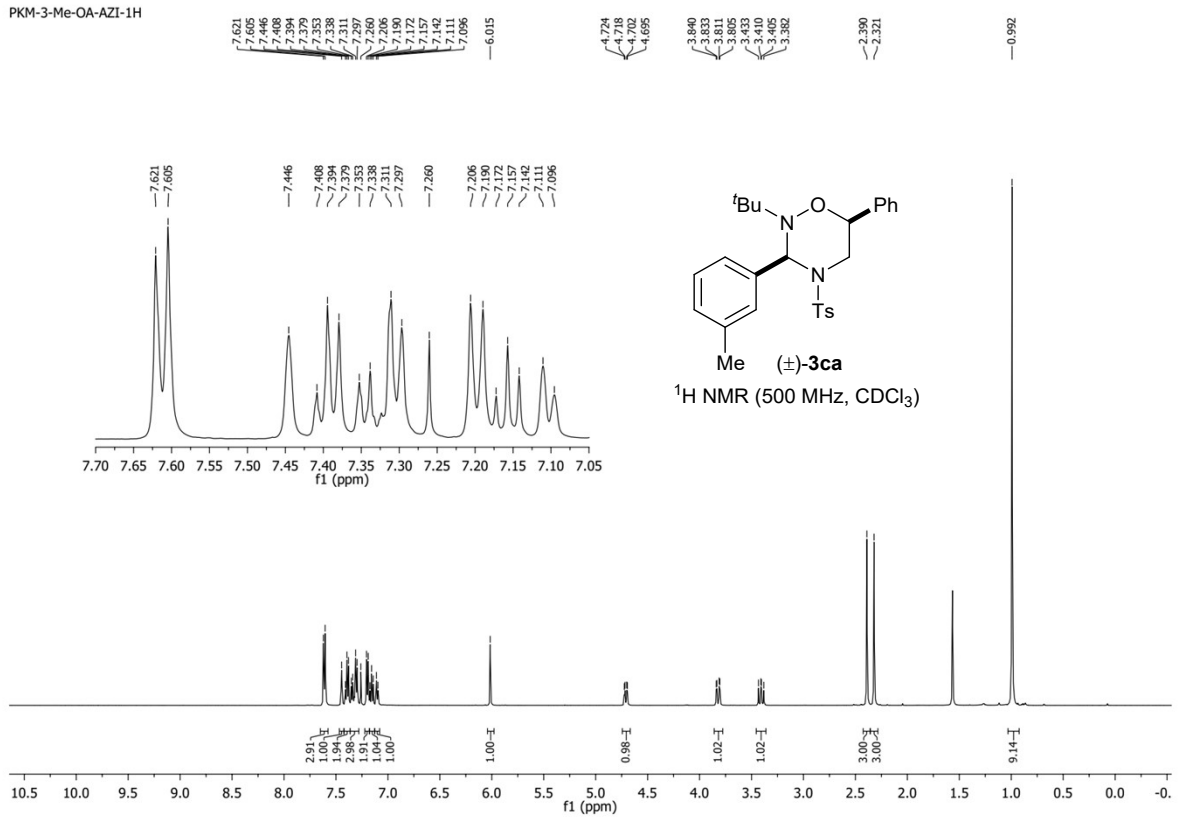
(±)-**3ba**

^{1}H NMR (500 MHz, $CDCl_3$)



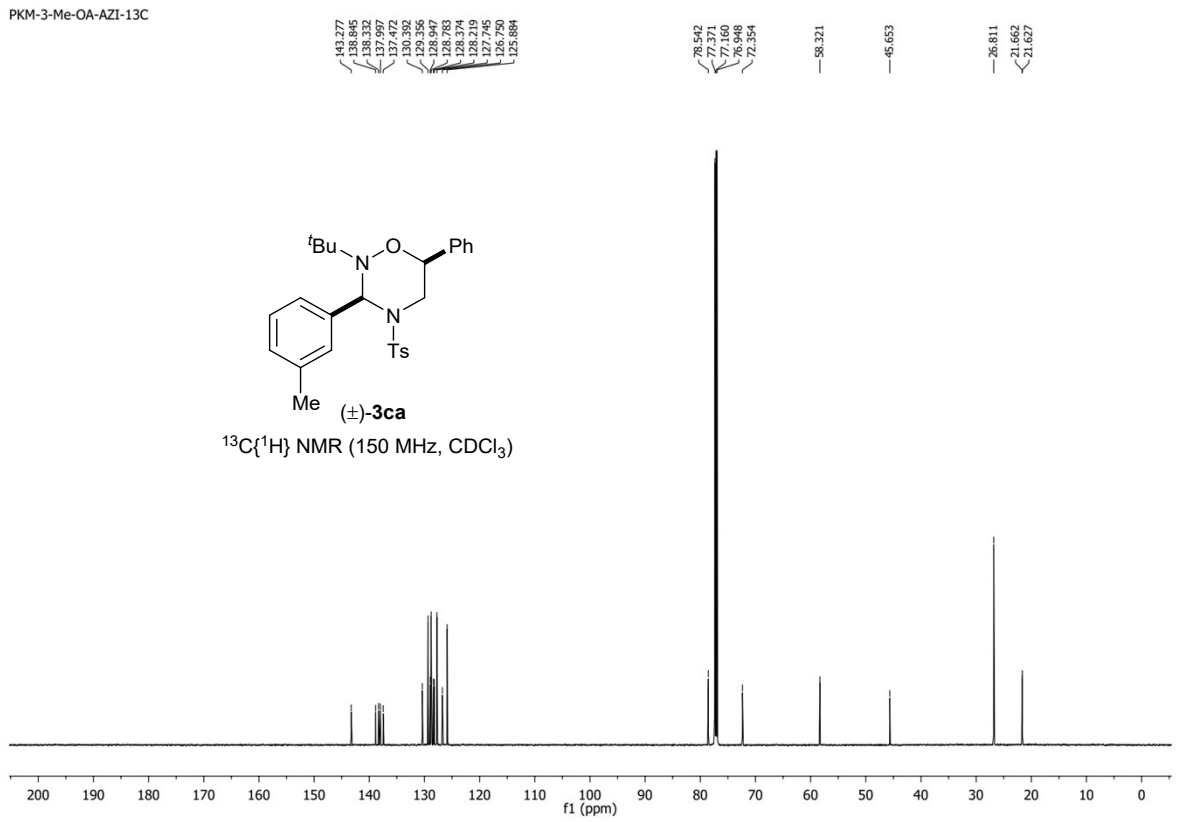
(±)-**3ba**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



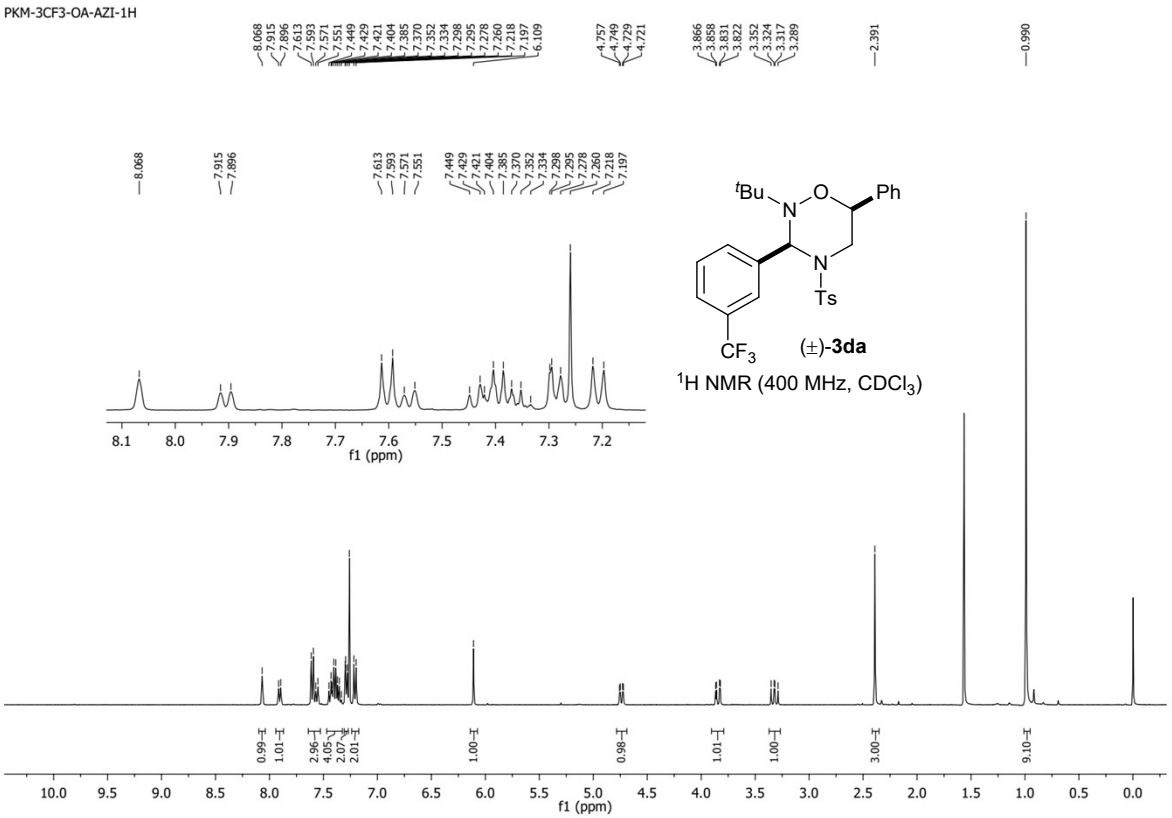
(±)-**3ca**

^{1}H NMR (500 MHz, $CDCl_3$)



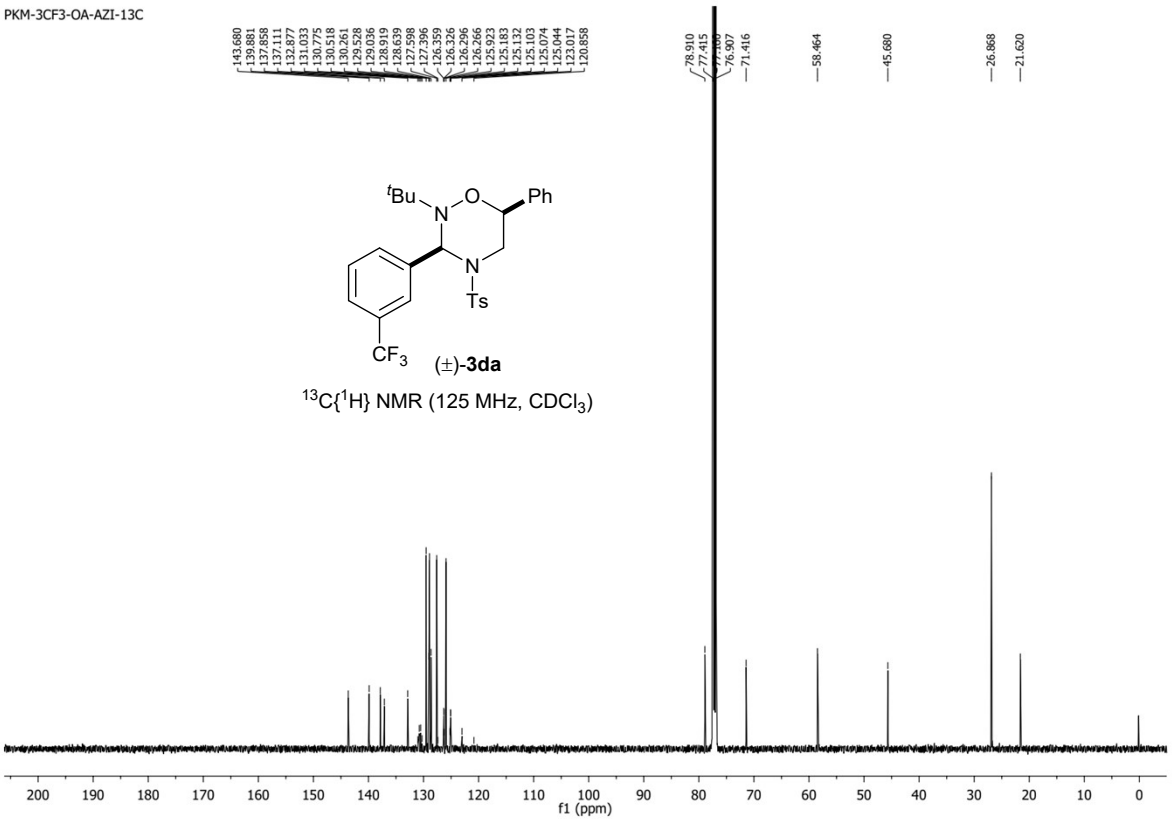
(±)-**3ca**

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$)



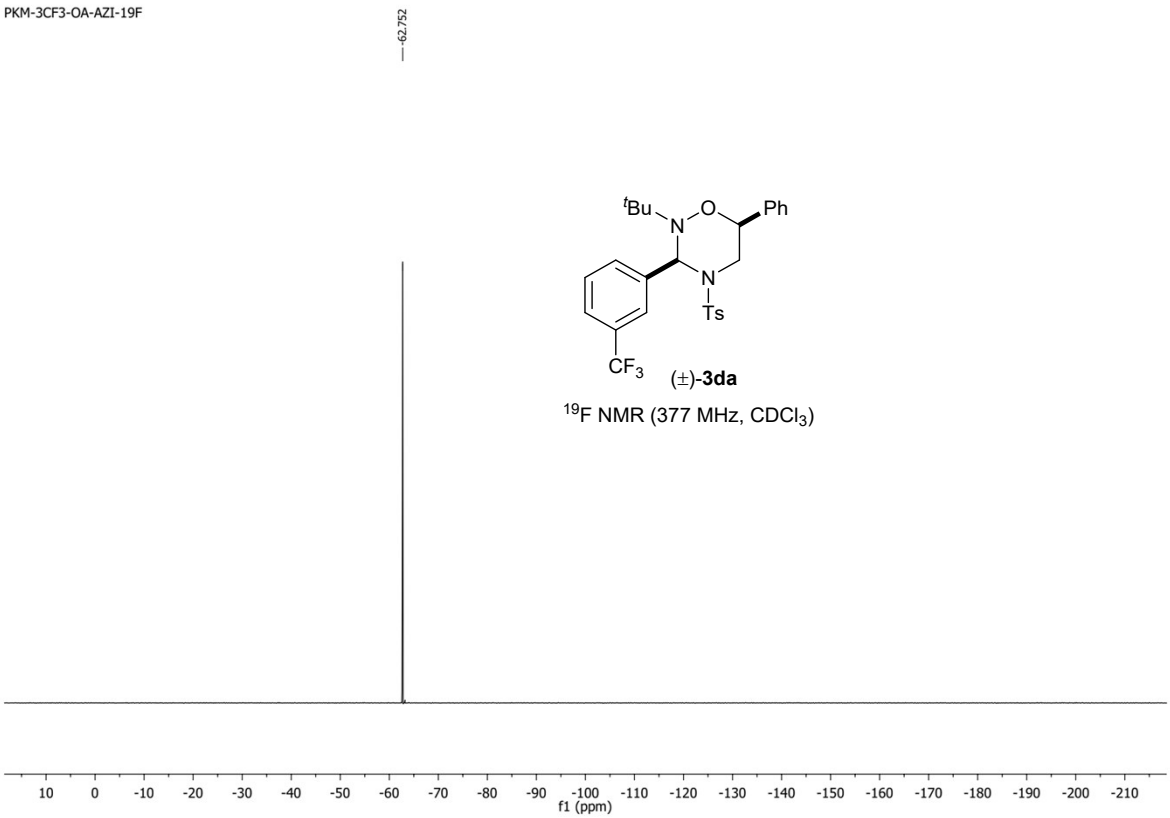
(±)-**3da**

^{1}H NMR (400 MHz, $CDCl_3$)



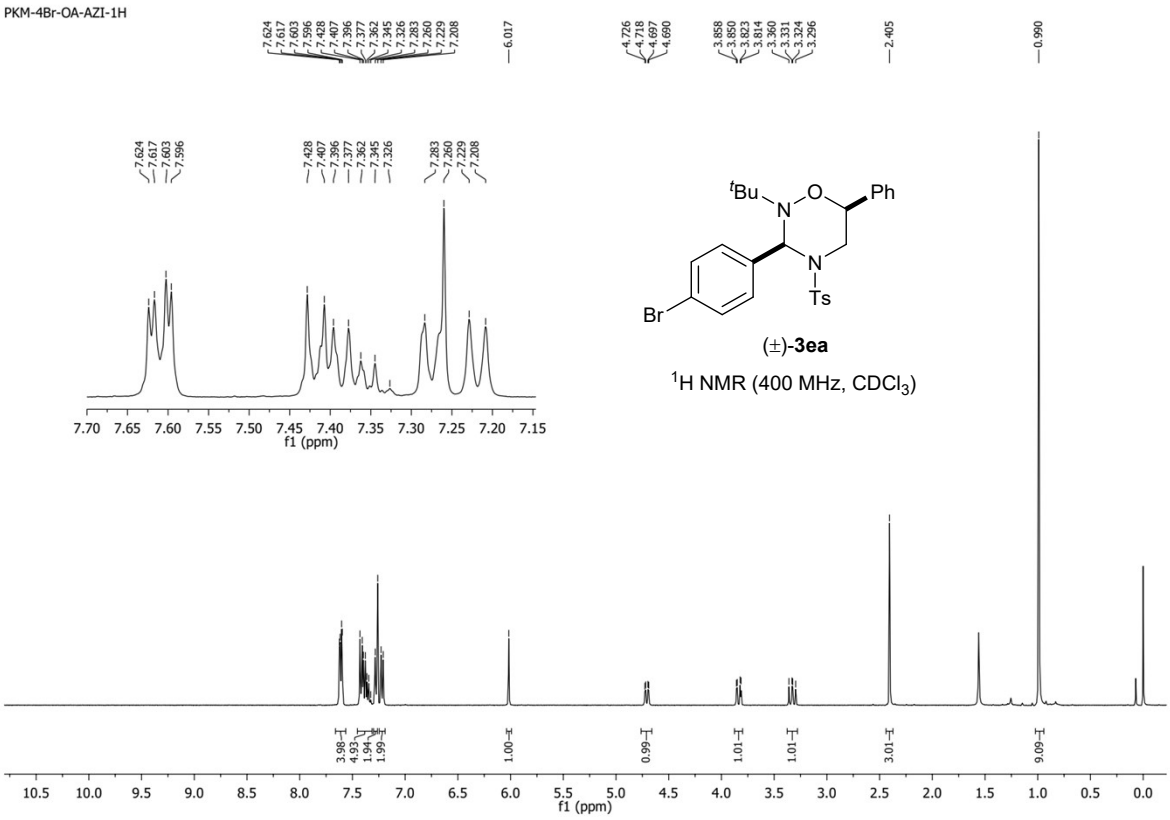
(±)-**3da**

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**3da**

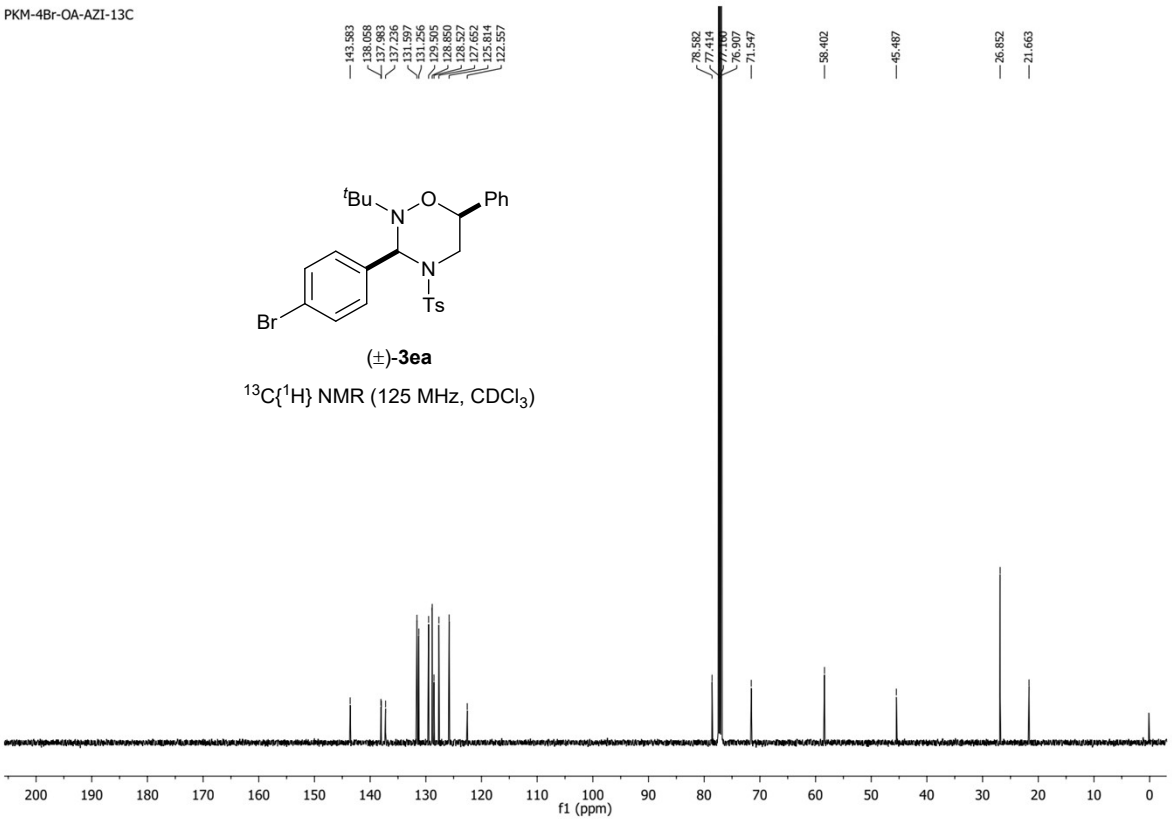
^{19}F NMR (377 MHz, $CDCl_3$)



(±)-**3ea**

^{1}H NMR (400 MHz, $CDCl_3$)

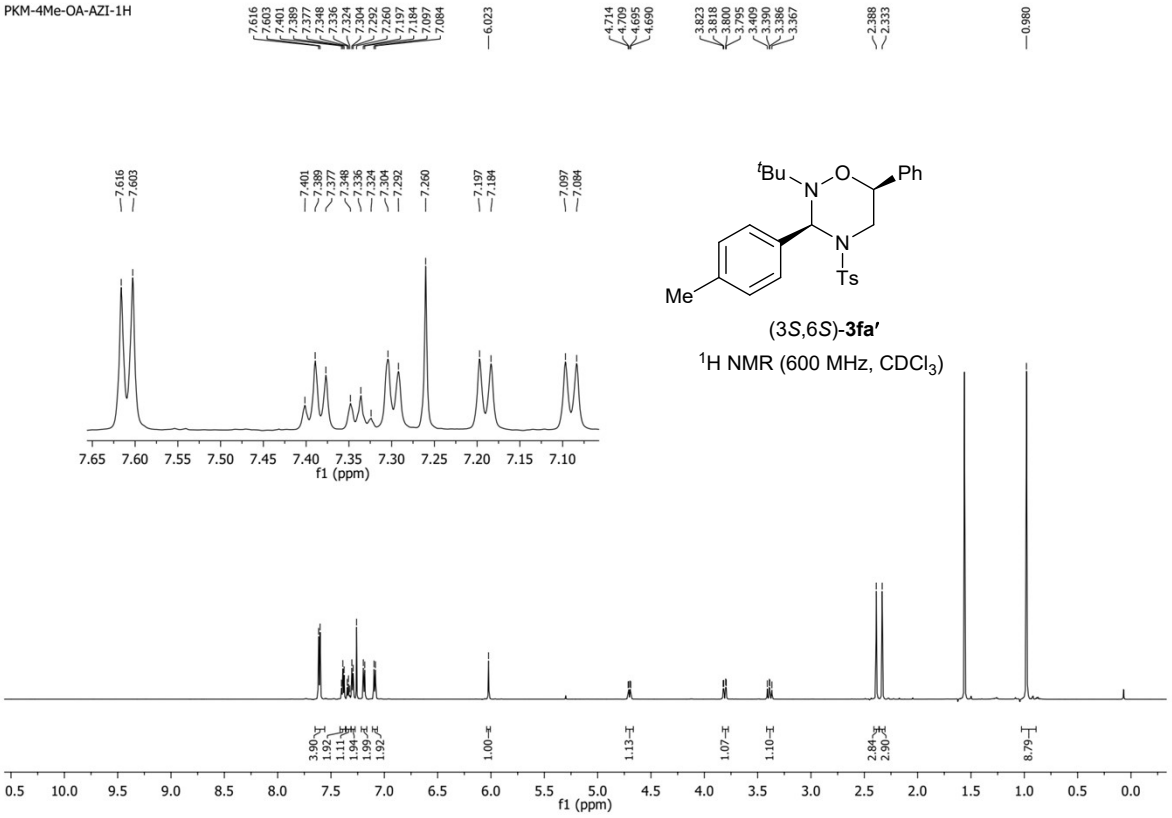
PKM-4Br-OA-AZI-13C



(±)-**3ea**

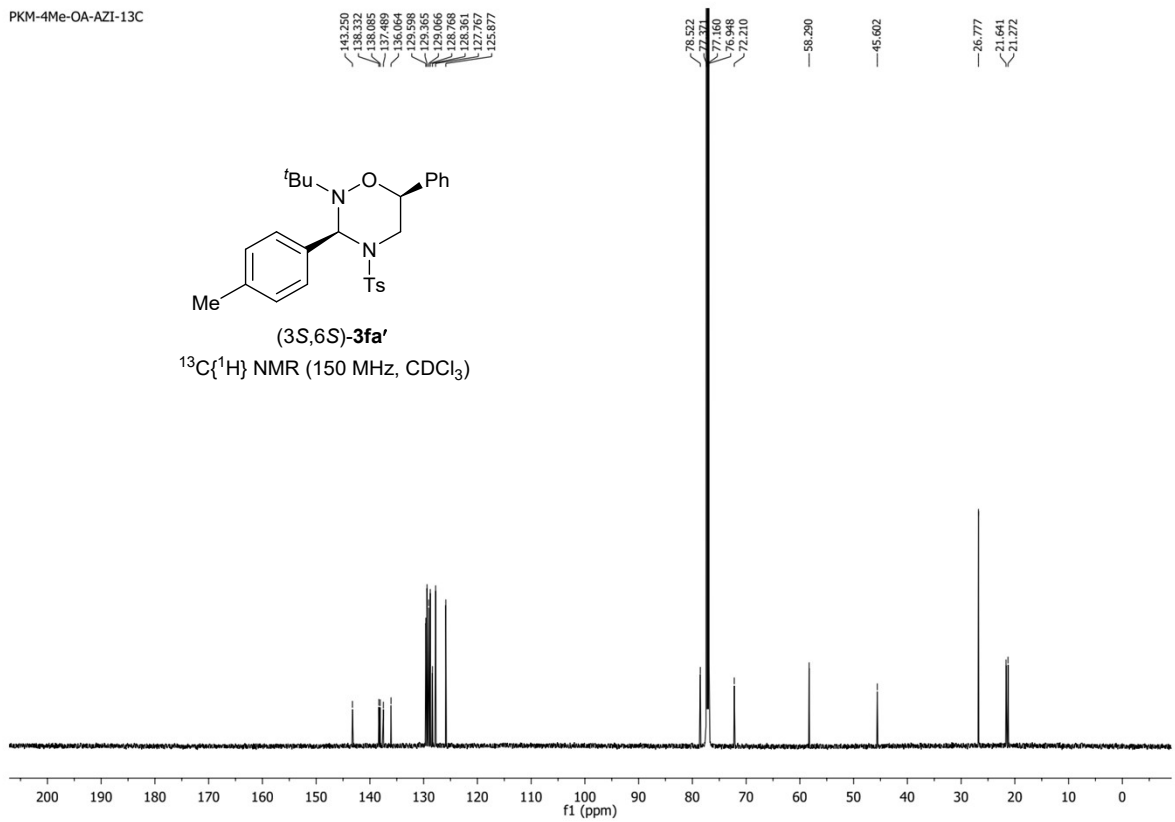
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-4Me-OA-AZI-1H



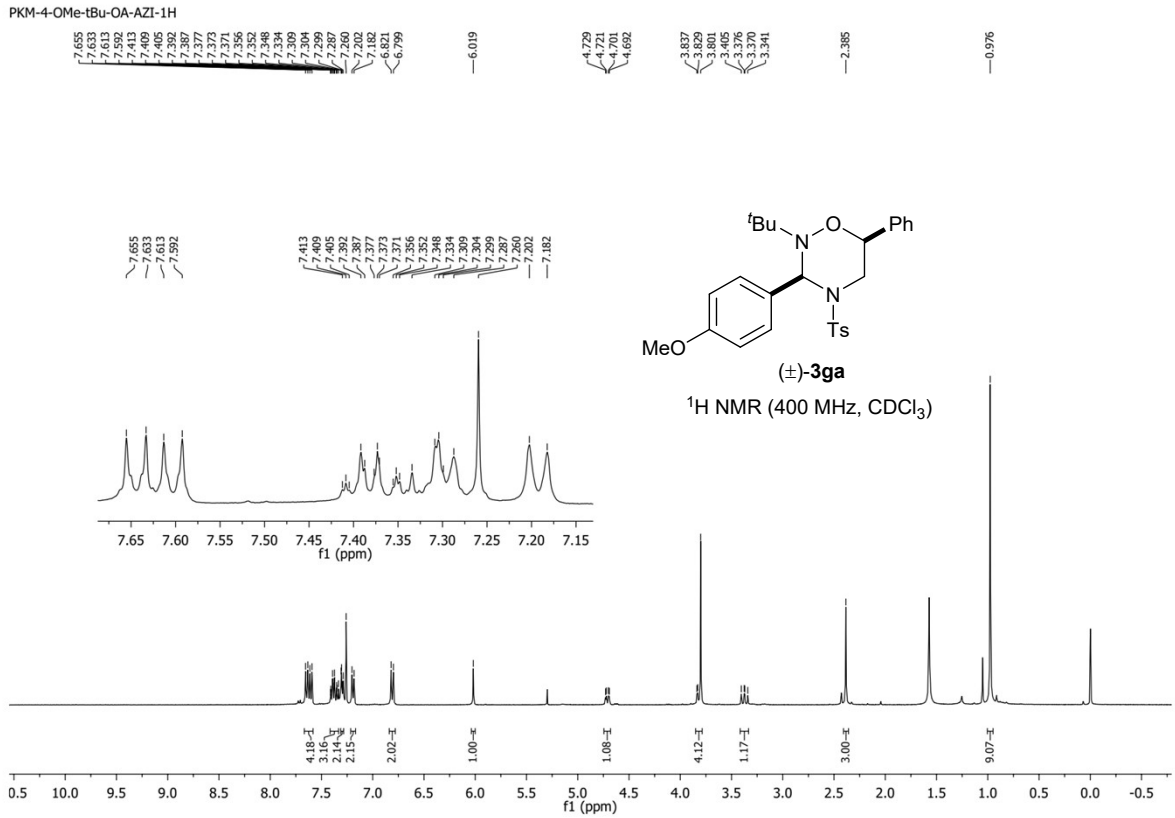
(3*S*,6*S*)-**3fa′**

^{1}H NMR (600 MHz, $CDCl_3$)



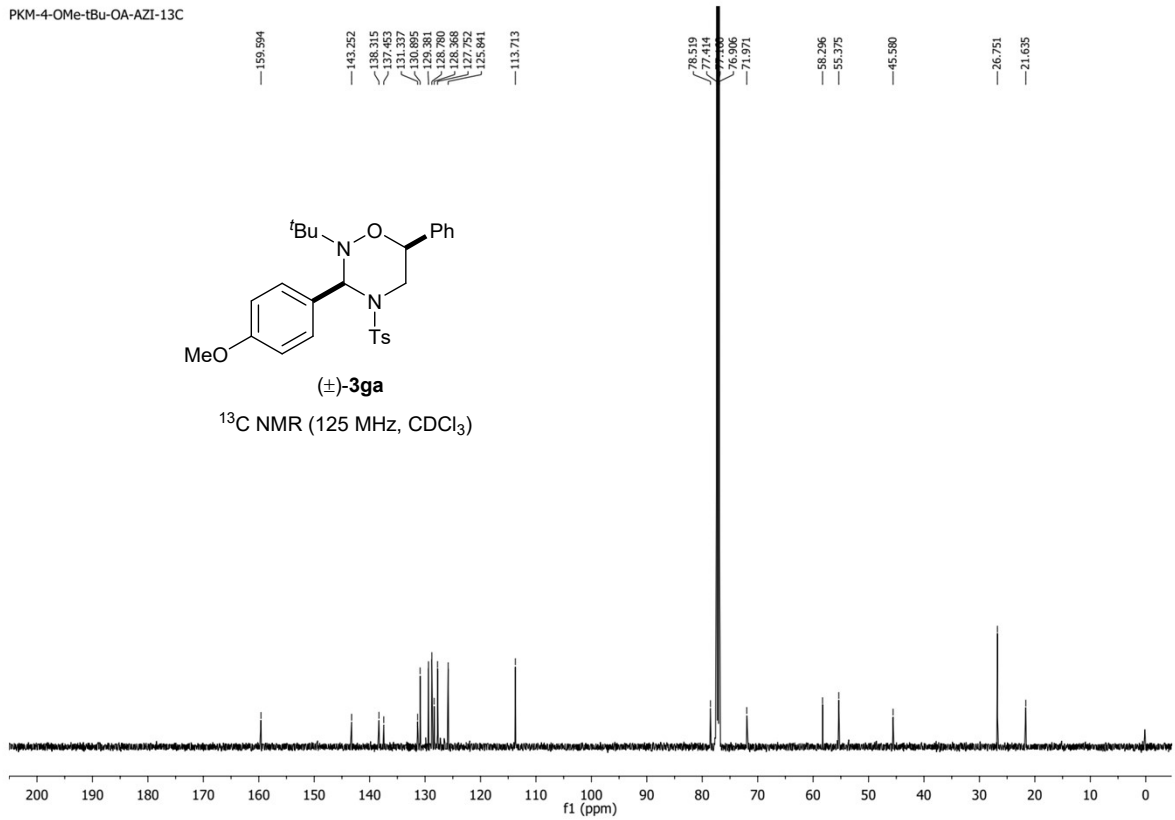
(3*S*,6*S*)-**3fa′**

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



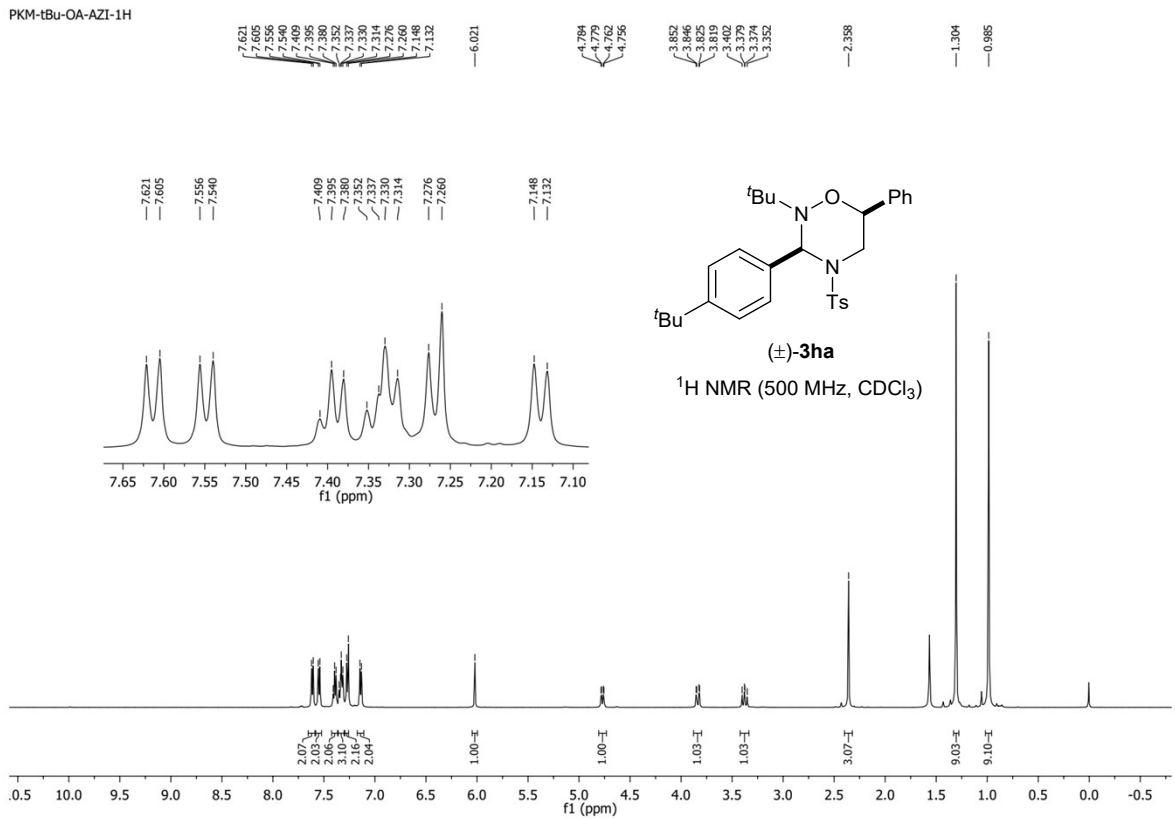
(±)-**3ga**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**3ga**

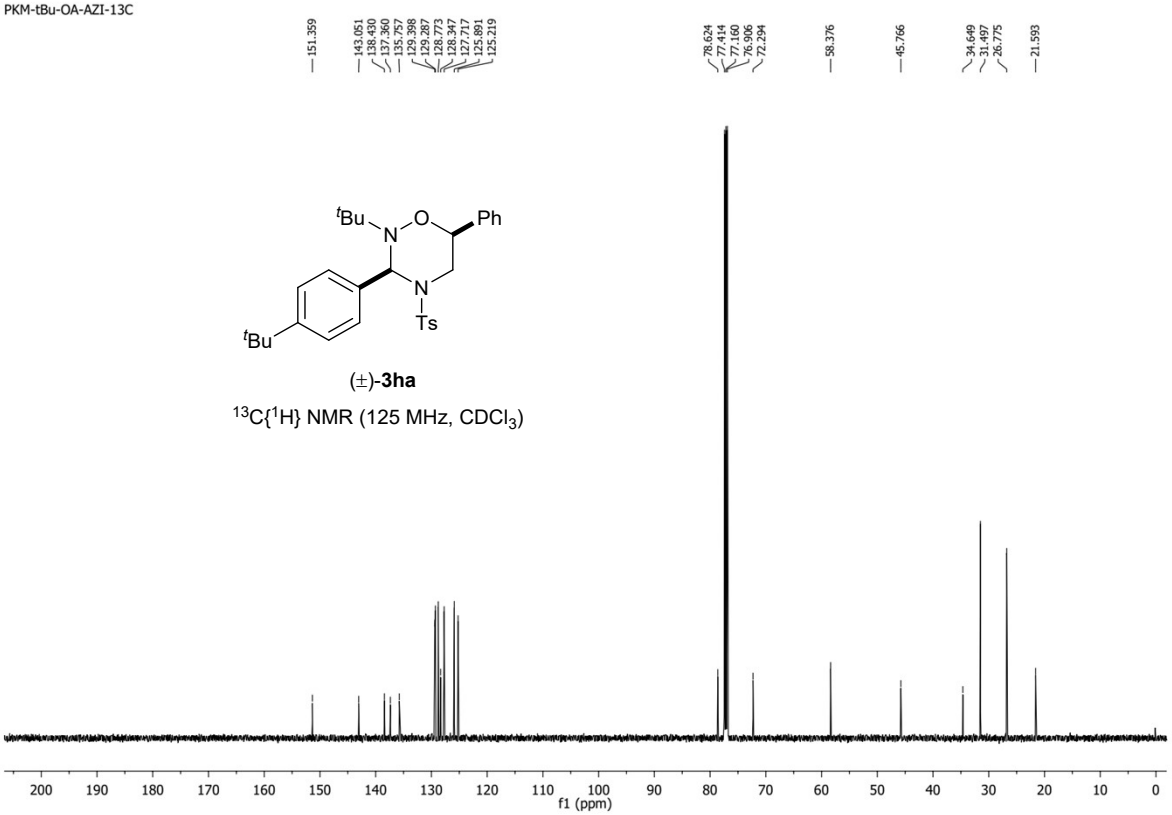
^{13}C NMR (125 MHz, $CDCl_3$)



(±)-**3ha**

^{1}H NMR (500 MHz, $CDCl_3$)

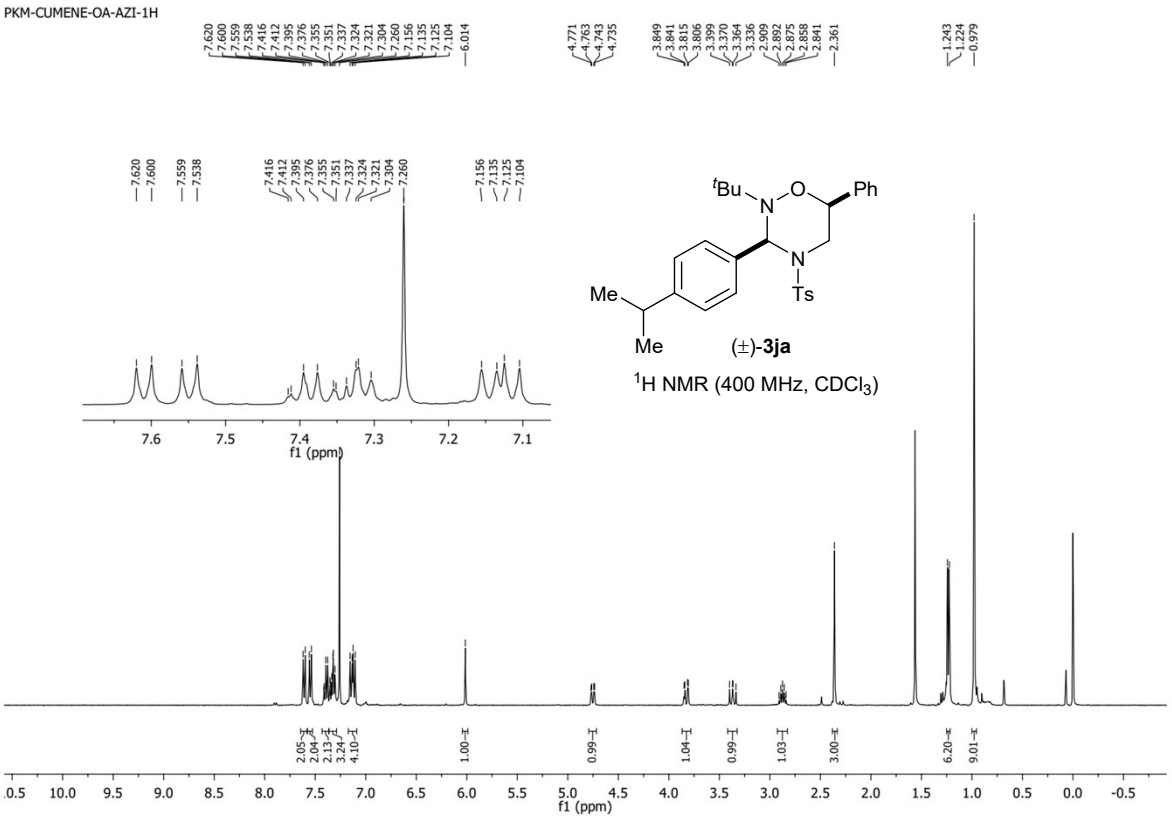
PKM-tBu-OA-AZI-13C



(±)-**3ha**

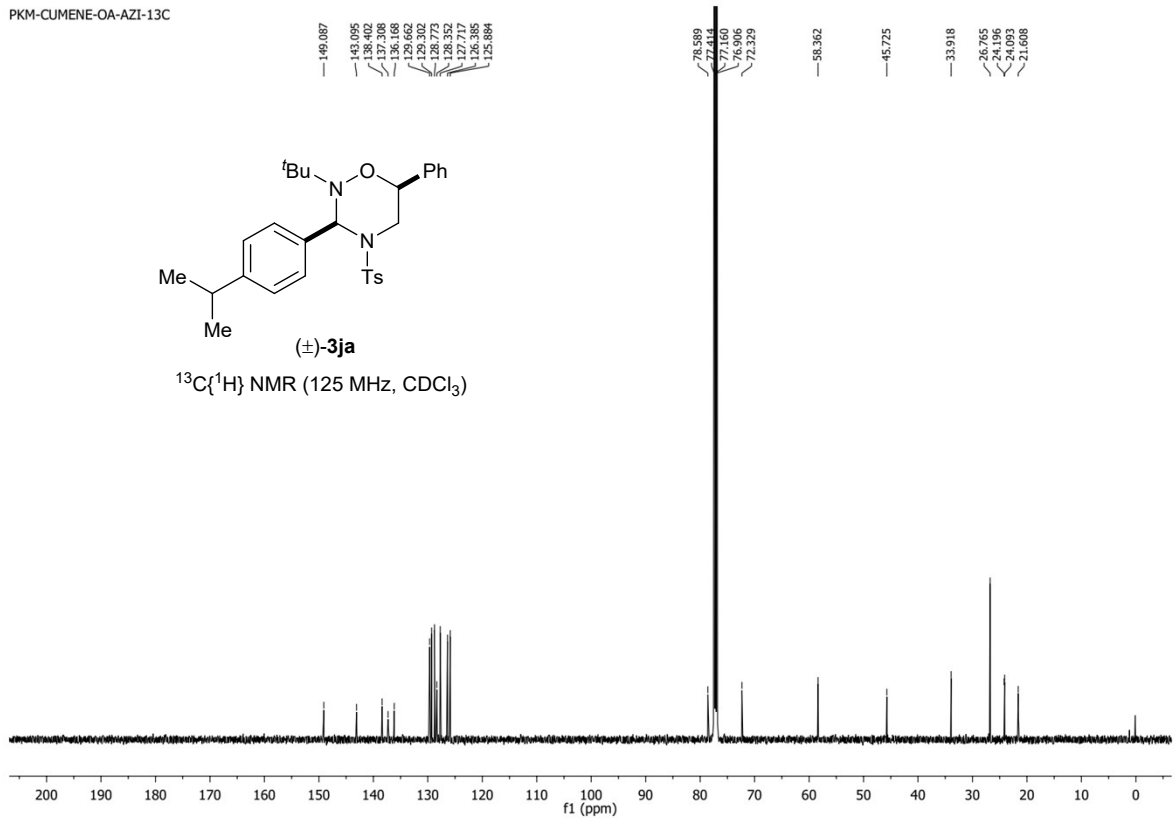
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-CUMENE-OA-AZI-1H



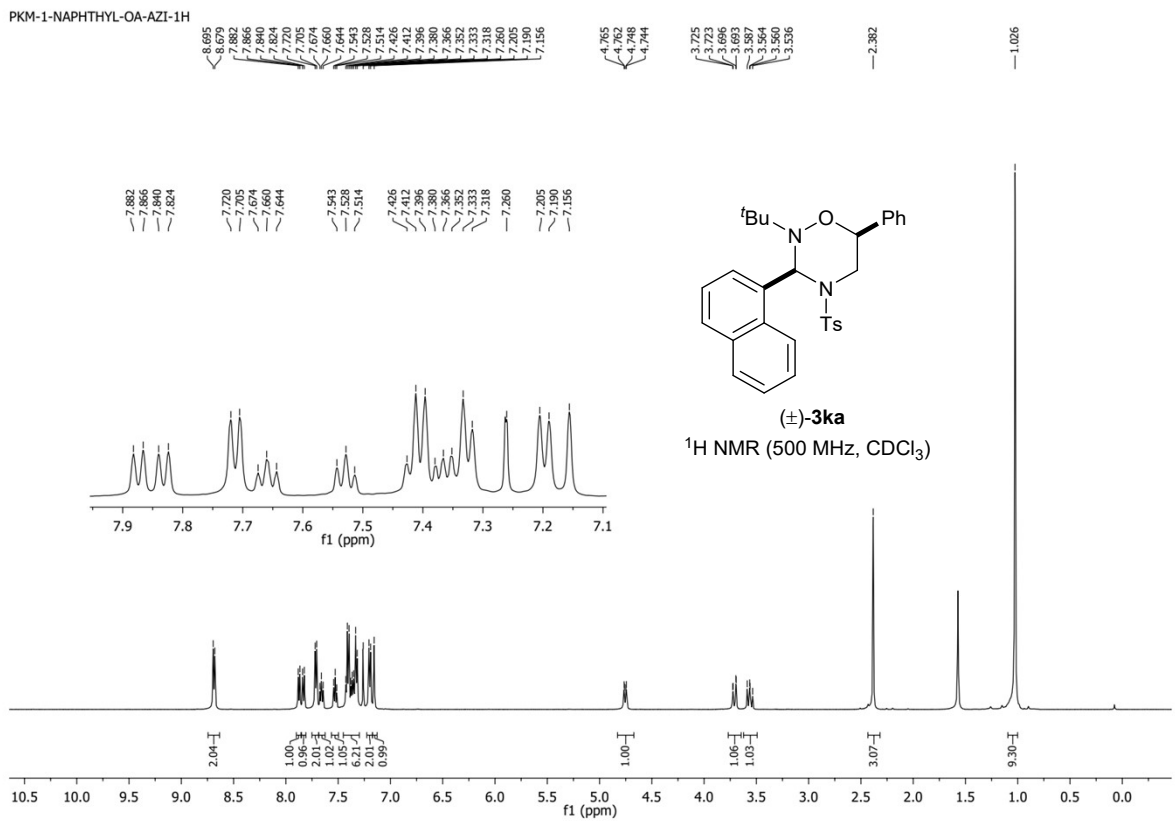
(±)-**3ja**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**3ja**

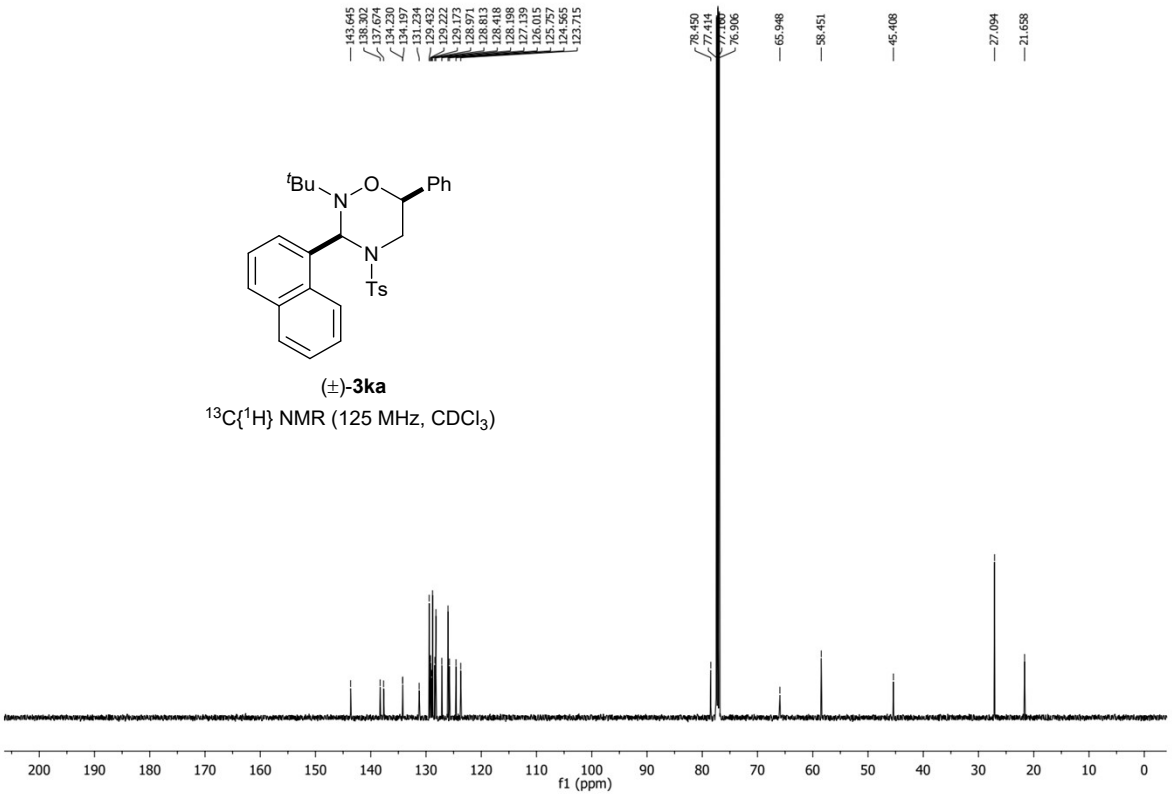
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**3ka**

^{1}H NMR (500 MHz, $CDCl_3$)

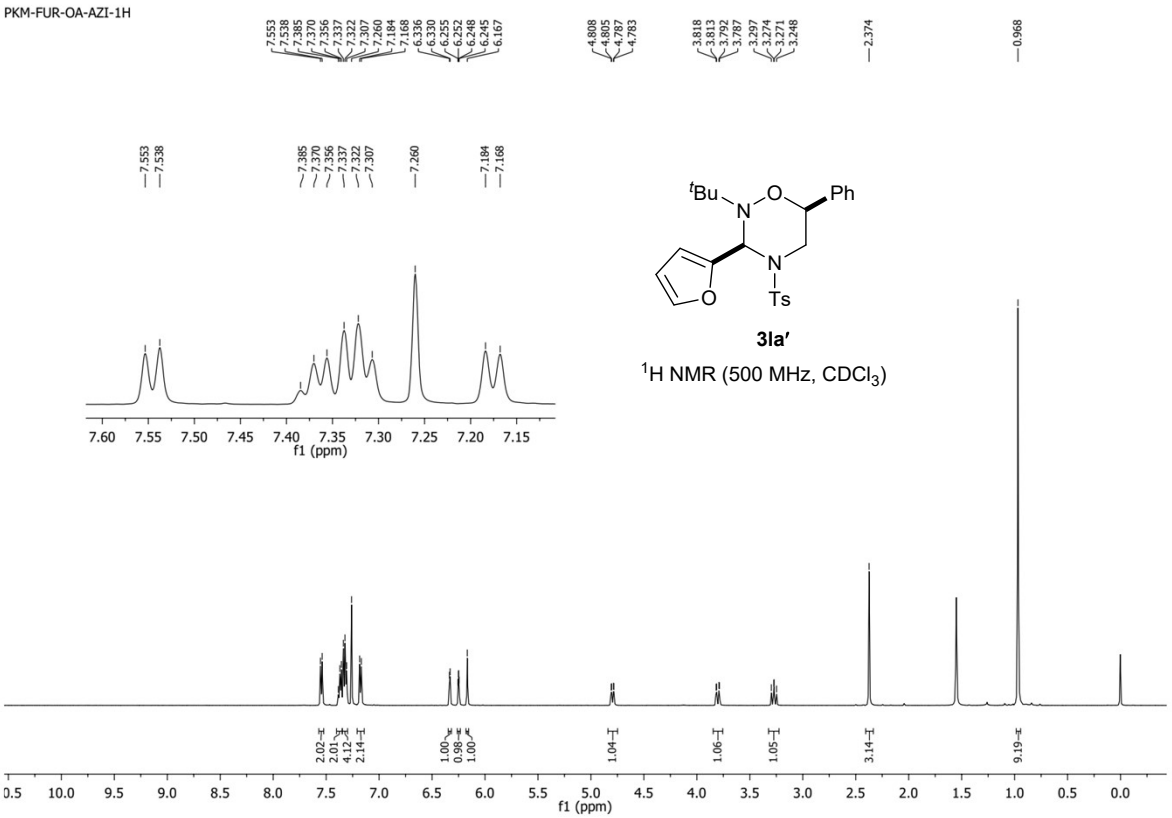
PKM-1-NAPHTHYL-OA-AZI-13C



(±)-**3ka**

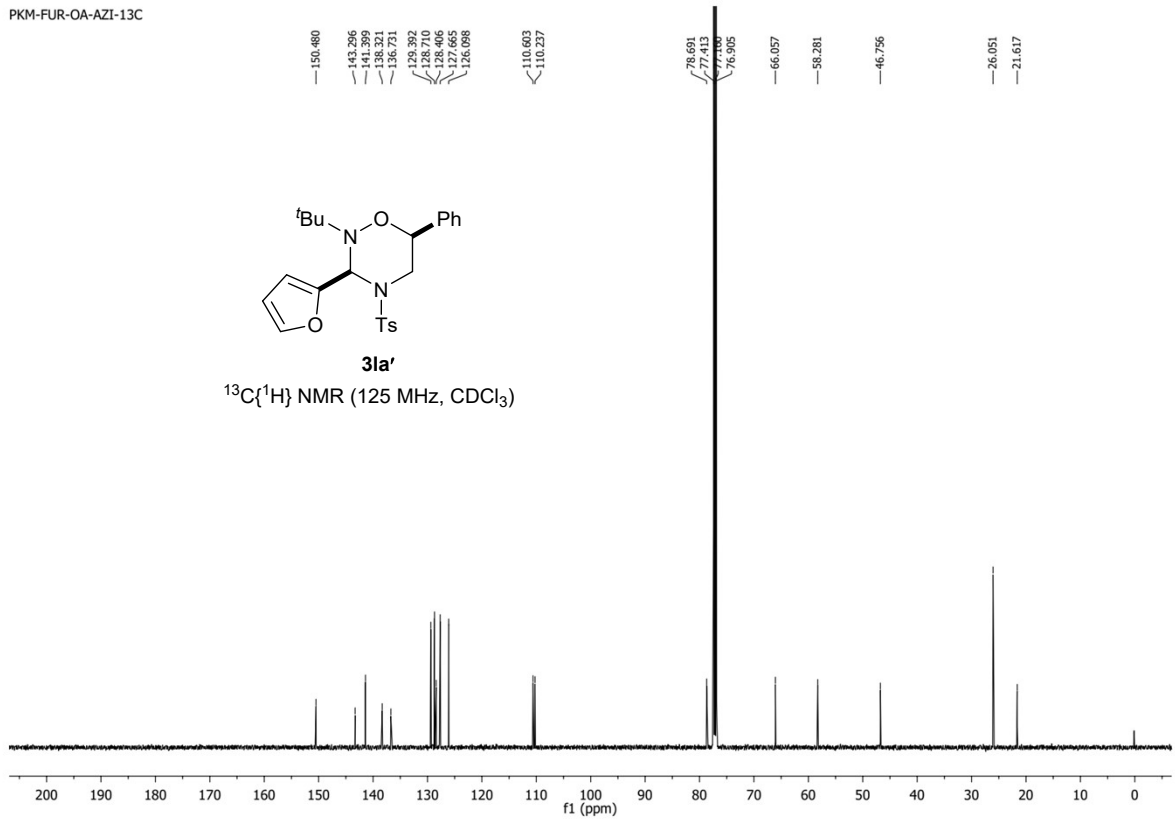
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-FUR-OA-AZI-1H



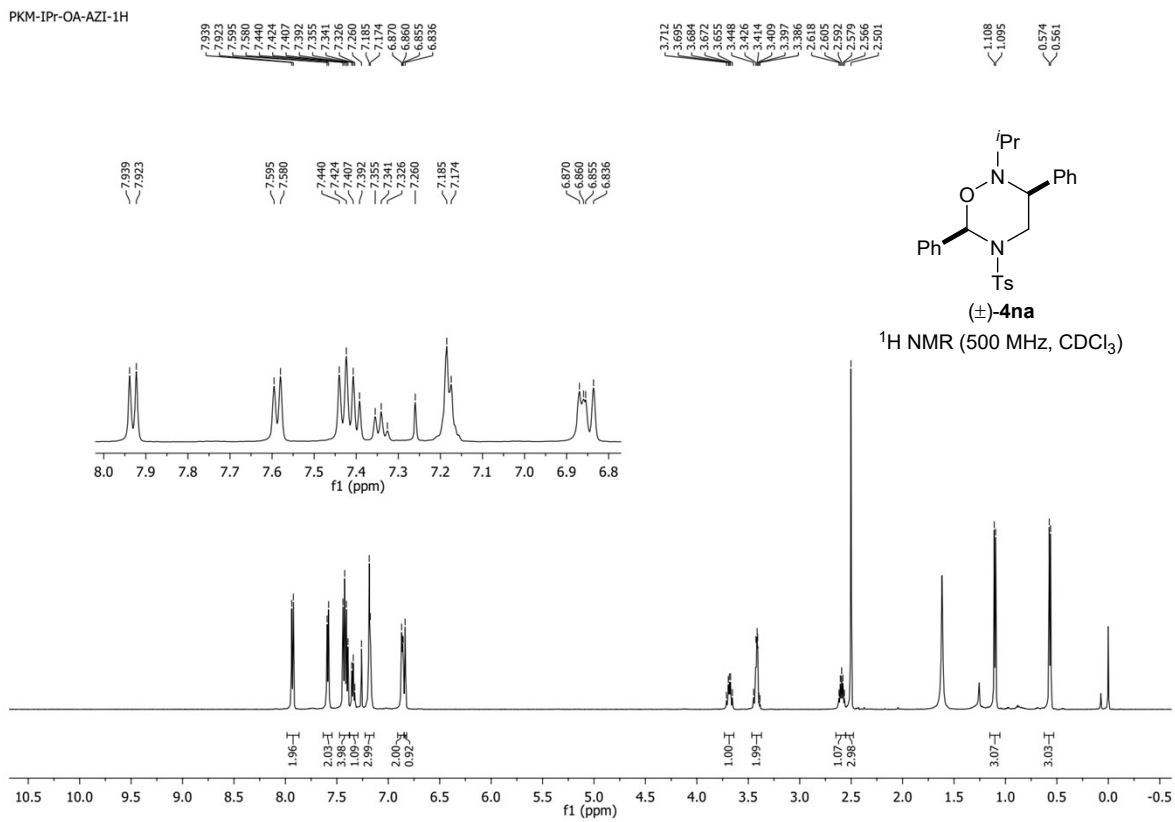
3la′

^{1}H NMR (500 MHz, $CDCl_3$)



3la′

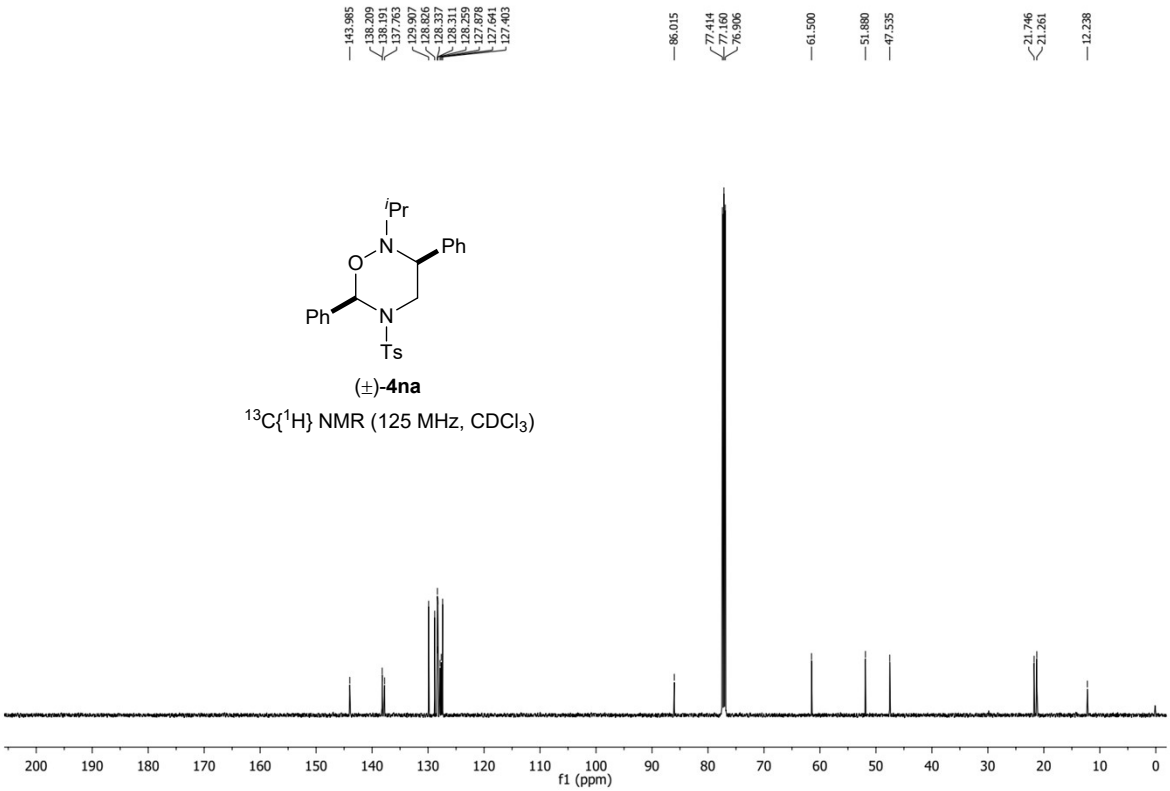
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**4na**

^{1}H NMR (500 MHz, $CDCl_3$)

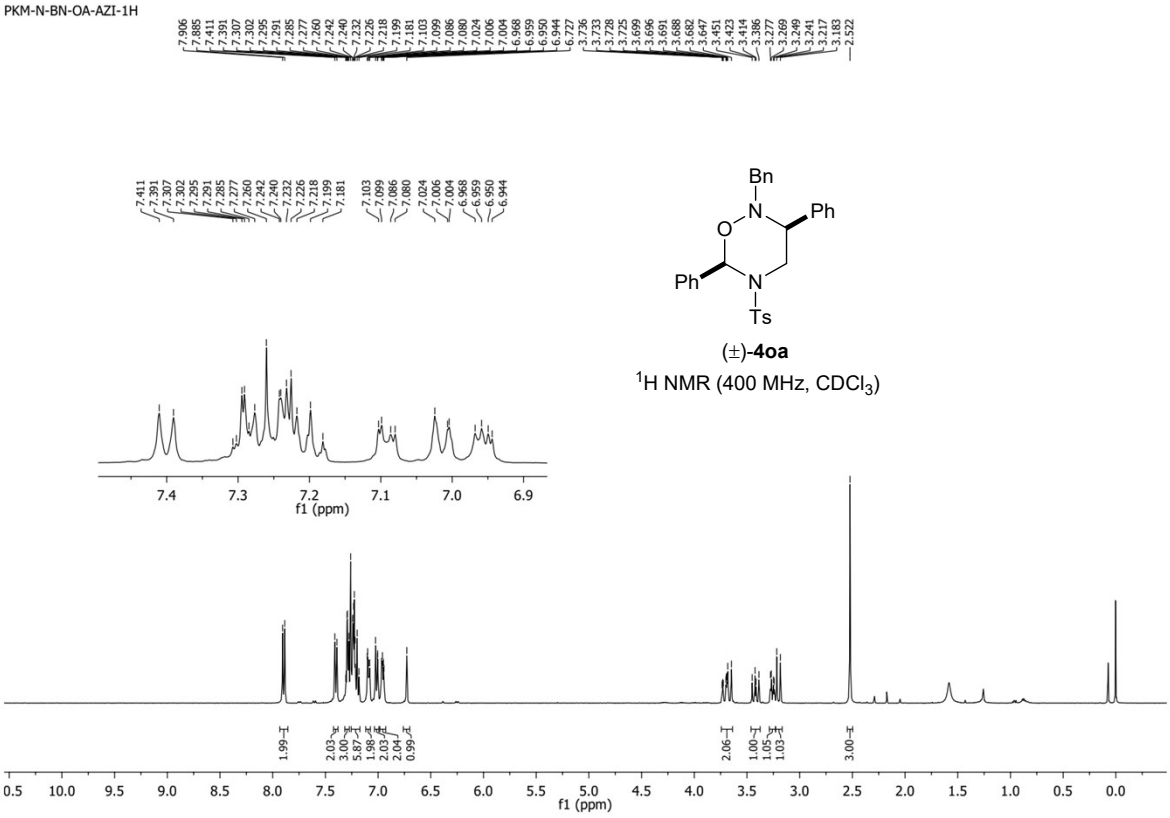
PKM-IPr-OA-AZI-13C



(±)-**4na**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

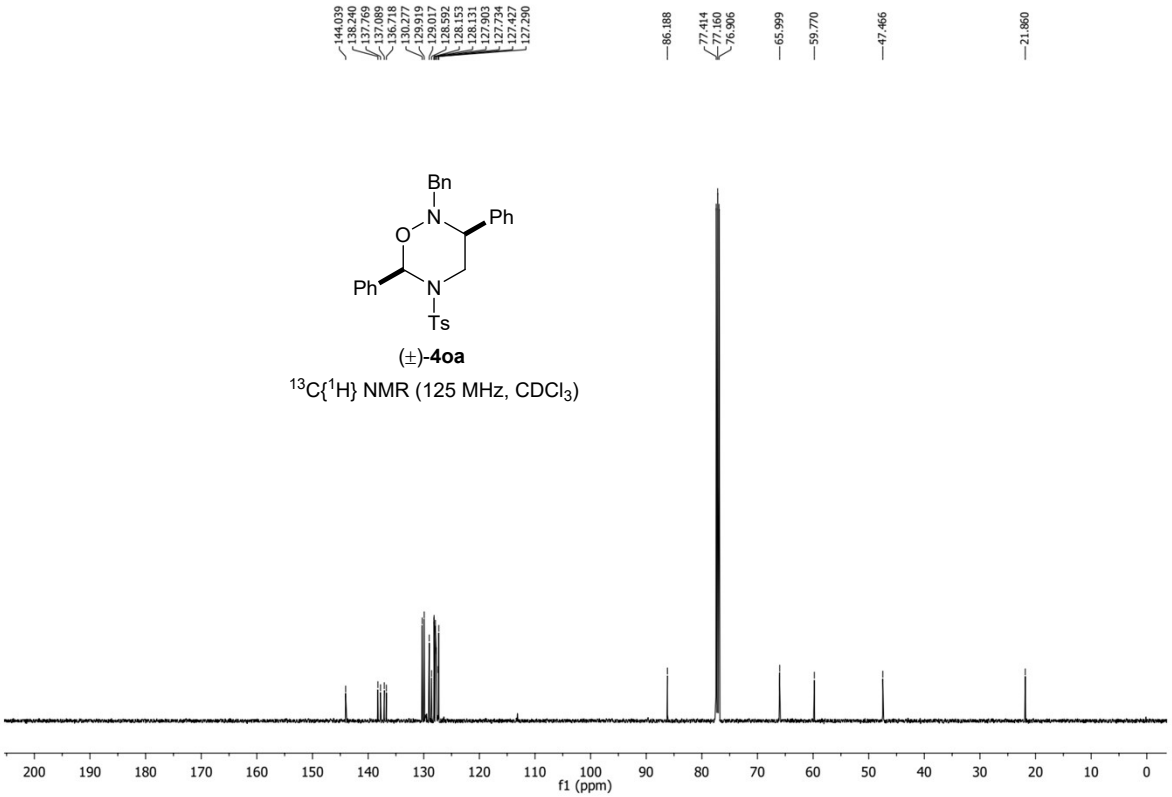
PKM-N-BN-OA-AZI-1H



(±)-**4oa**

^{1}H NMR (400 MHz, $CDCl_3$)

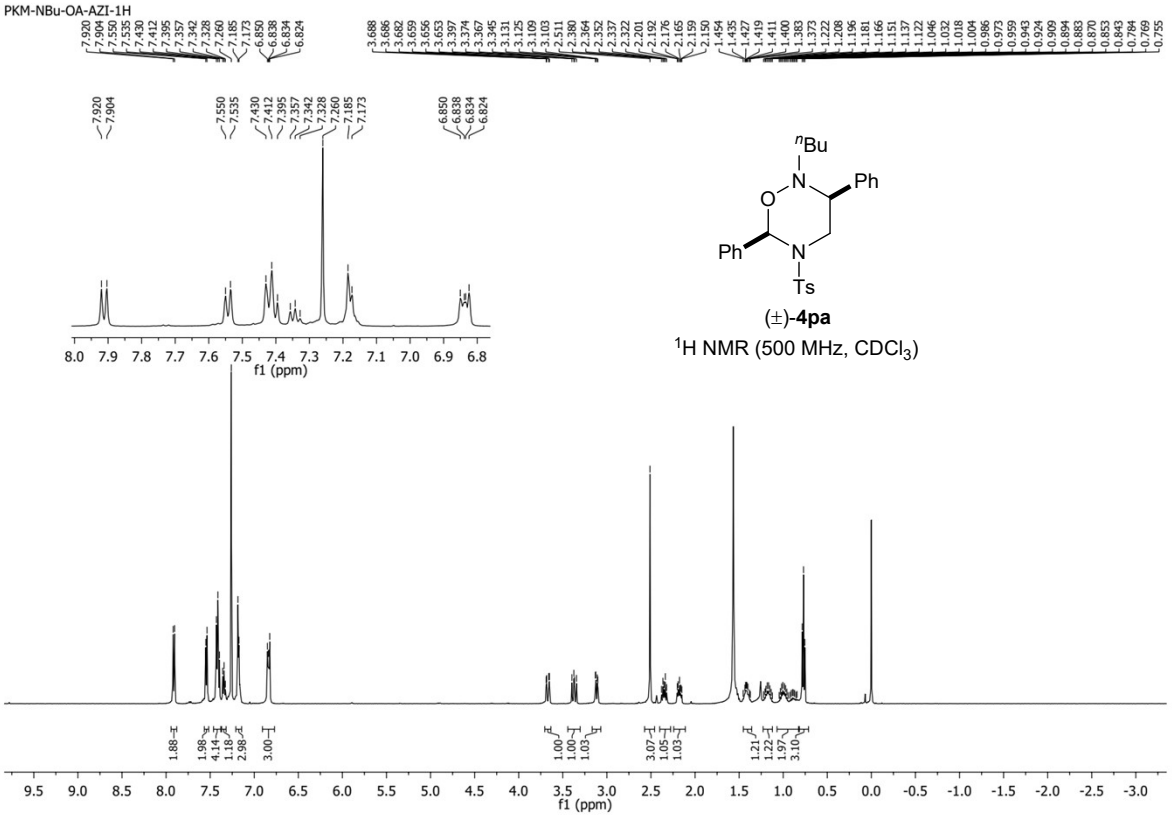
PKM-N-BN-OA-AZI-13C



(±)-**4oa**

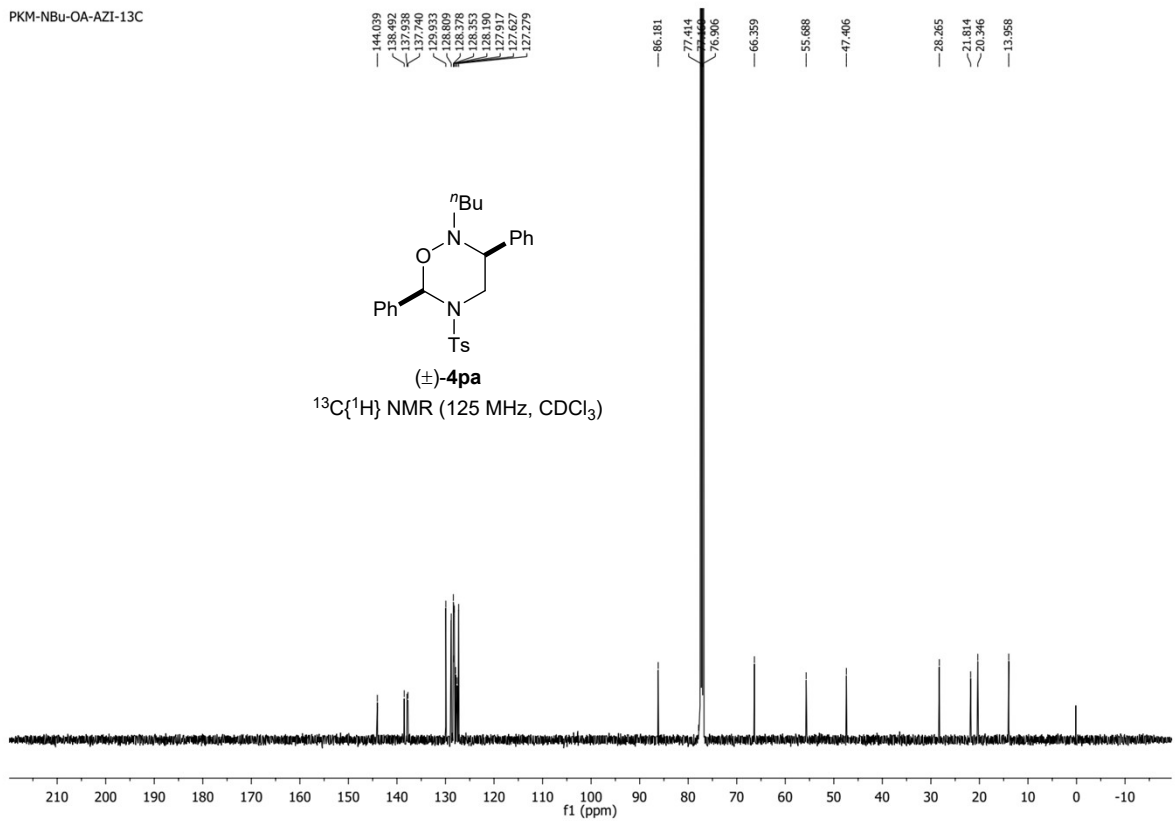
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-NBu-OA-AZI-1H



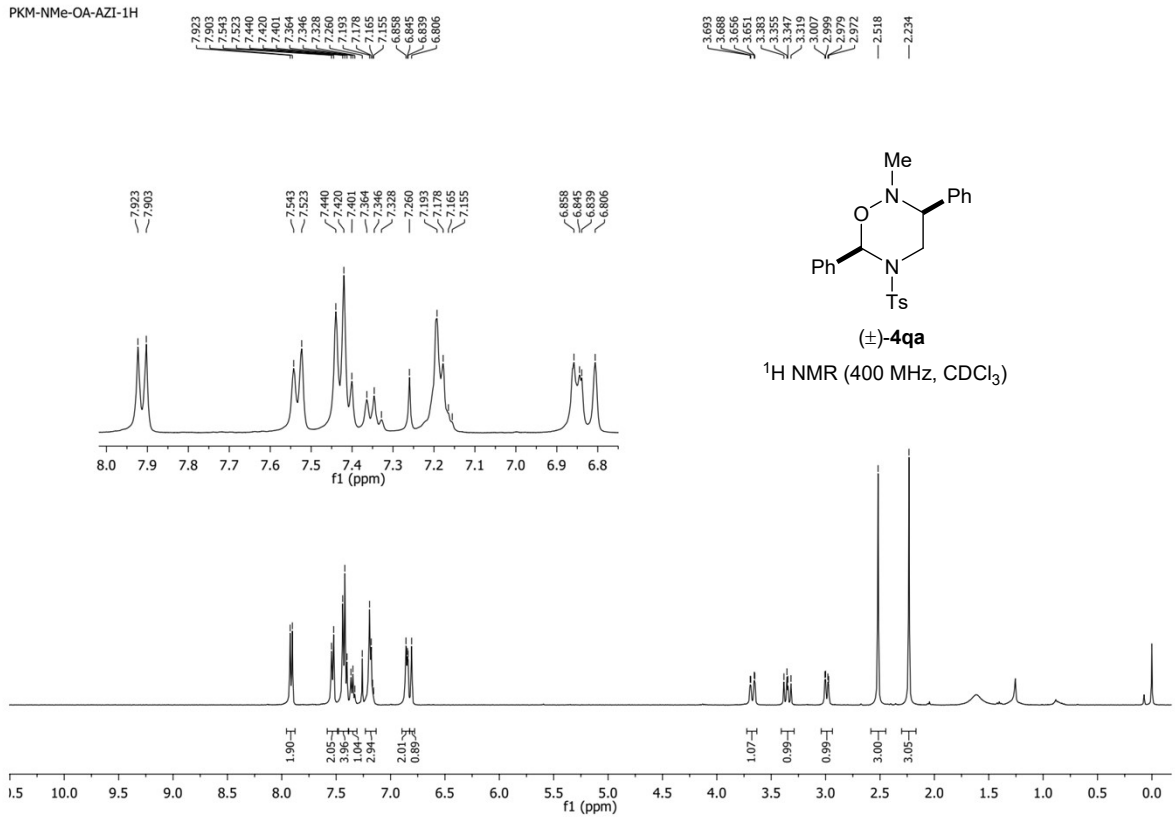
(±)-**4pa**

^{1}H NMR (500 MHz, $CDCl_3$)



(±)-**4pa**

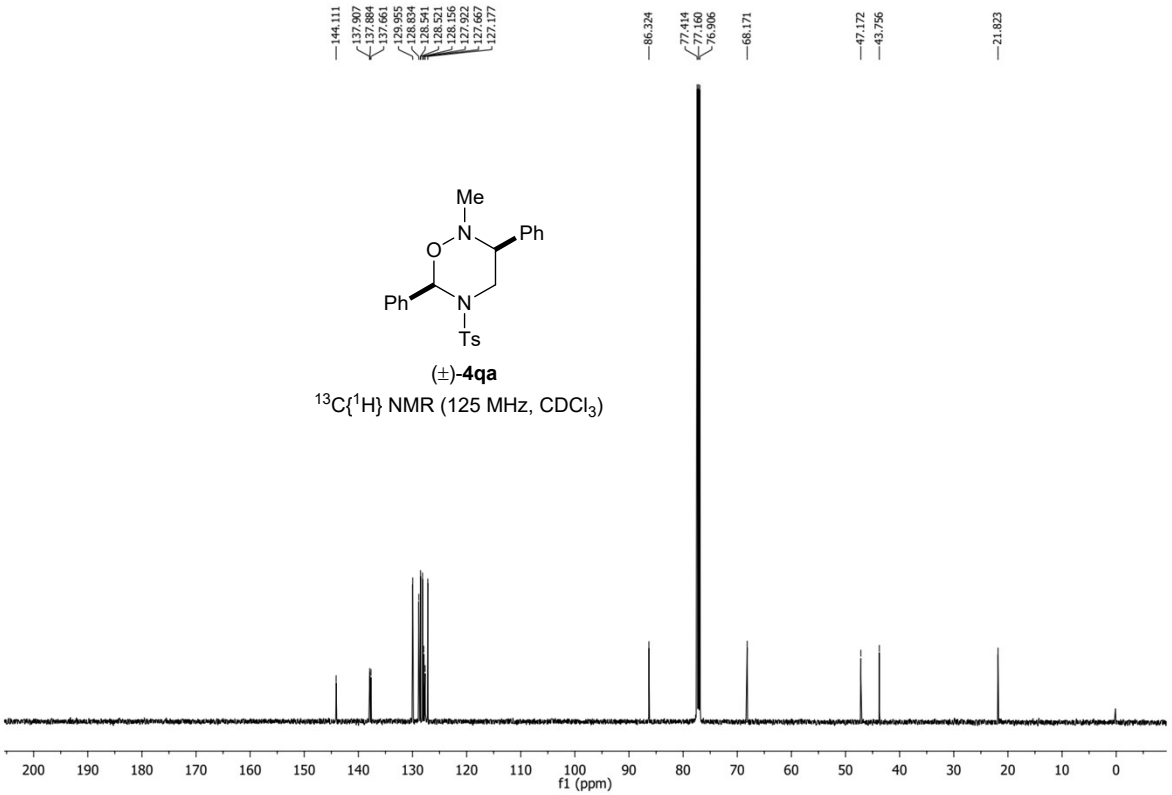
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**4qa**

^{1}H NMR (400 MHz, $CDCl_3$)

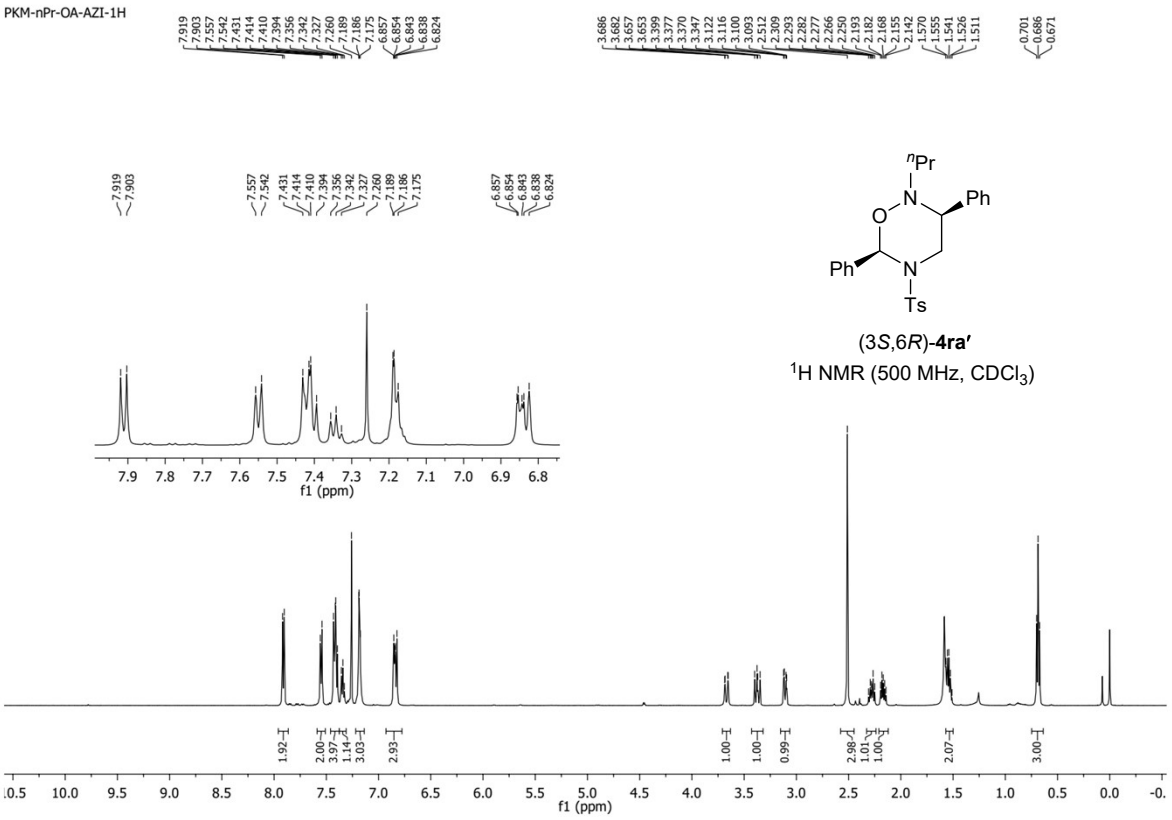
PKM-NMe-OA-AZI-13C



(±)-**4qa**

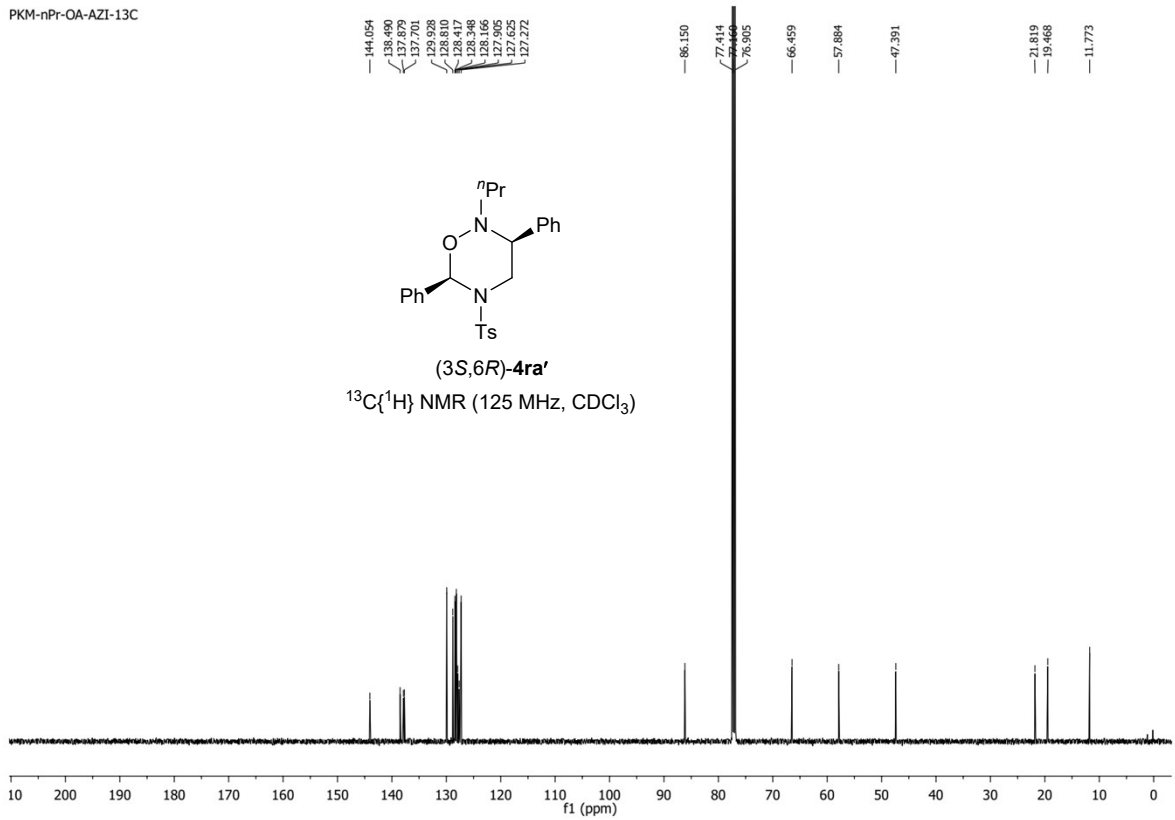
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-nPr-OA-AZI-1H



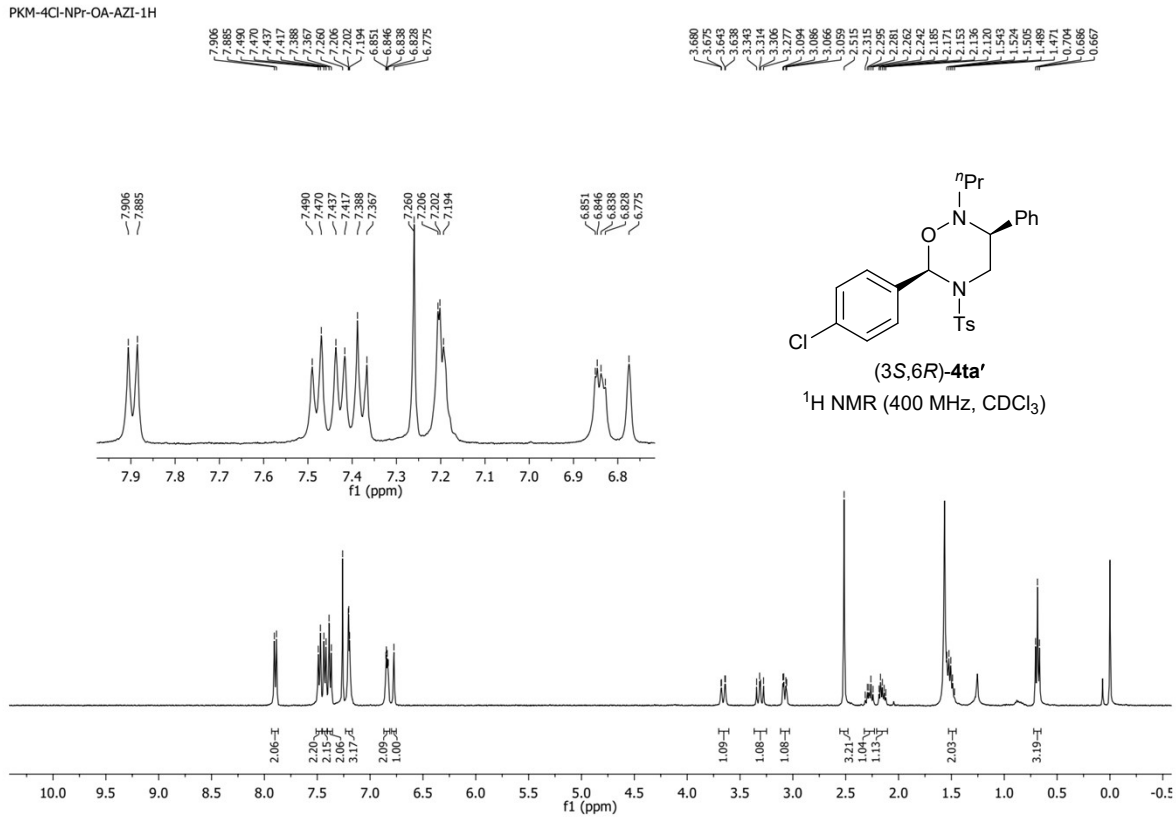
(3*S*,6*R*)-**4ra′**

^{1}H NMR (500 MHz, $CDCl_3$)



(3*S*,6*R*)-**4ra′**

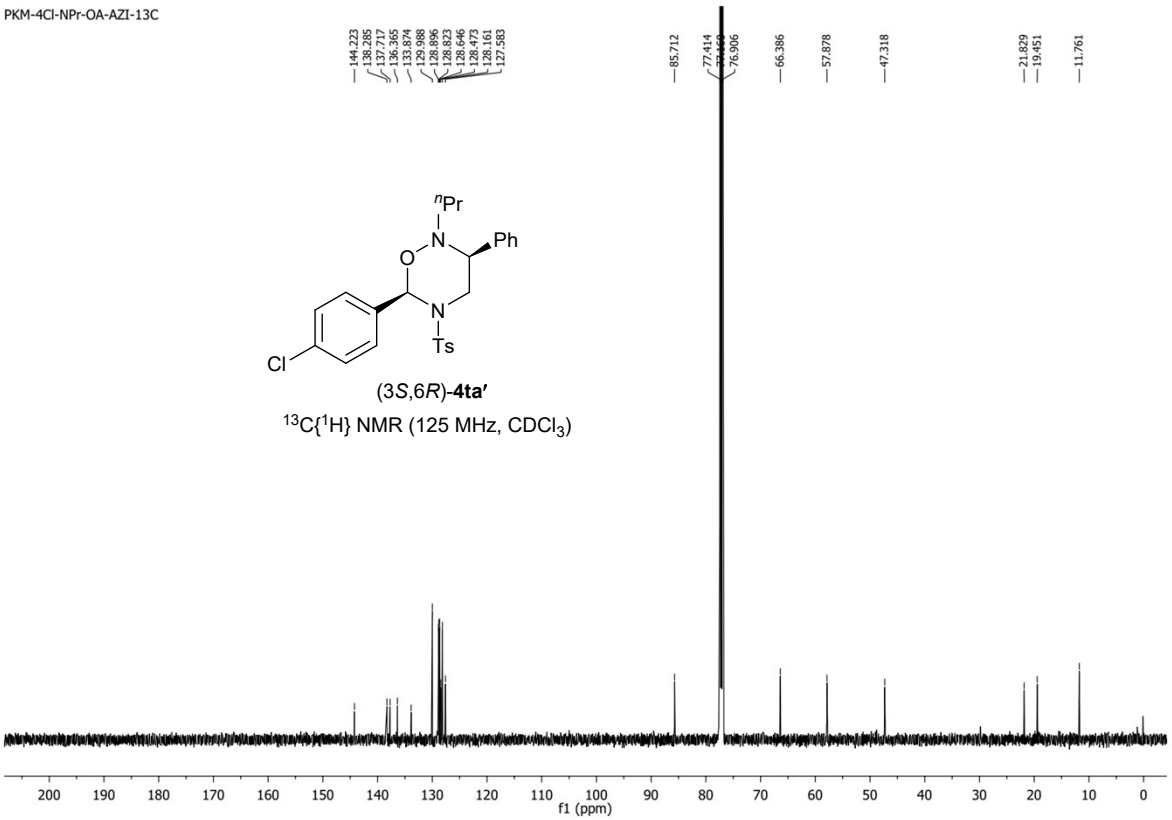
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(3*S*,6*R*)-**4ta′**

^{1}H NMR (400 MHz, $CDCl_3$)

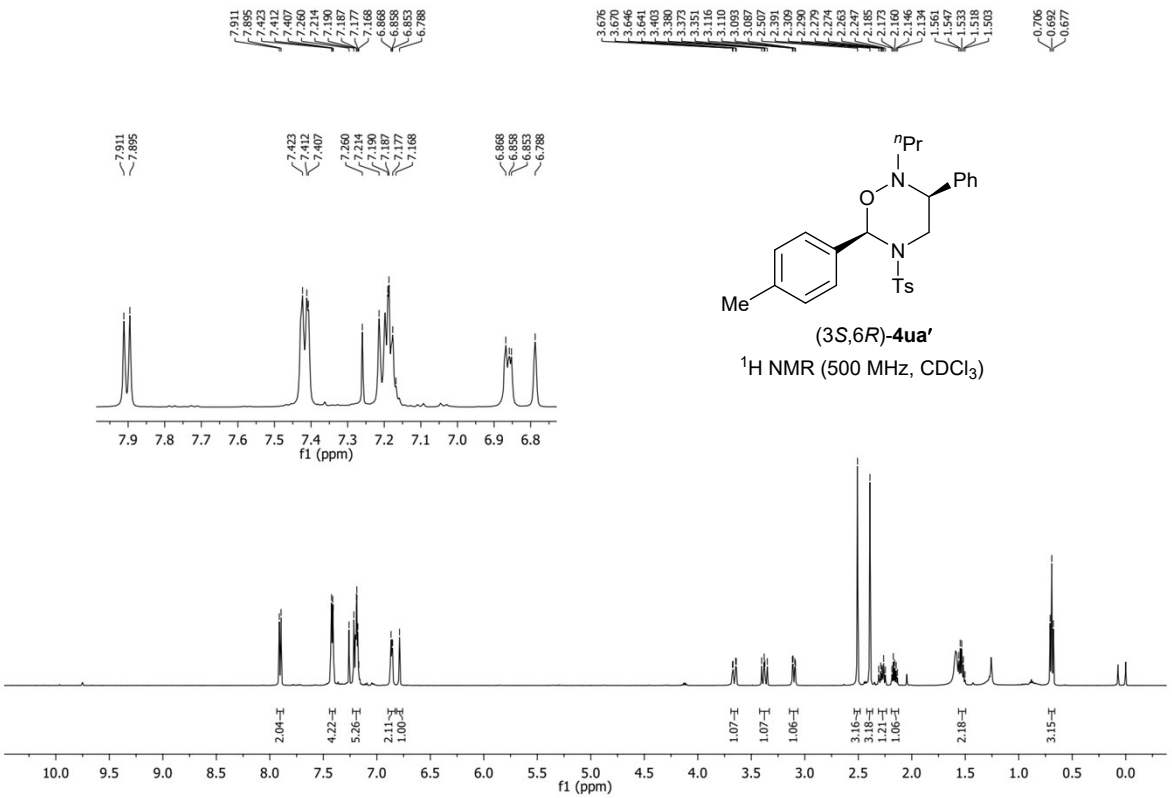
PKM-4Cl-NPr-OA-AZI-13C



(3*S*,6*R*)-**4ta′**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

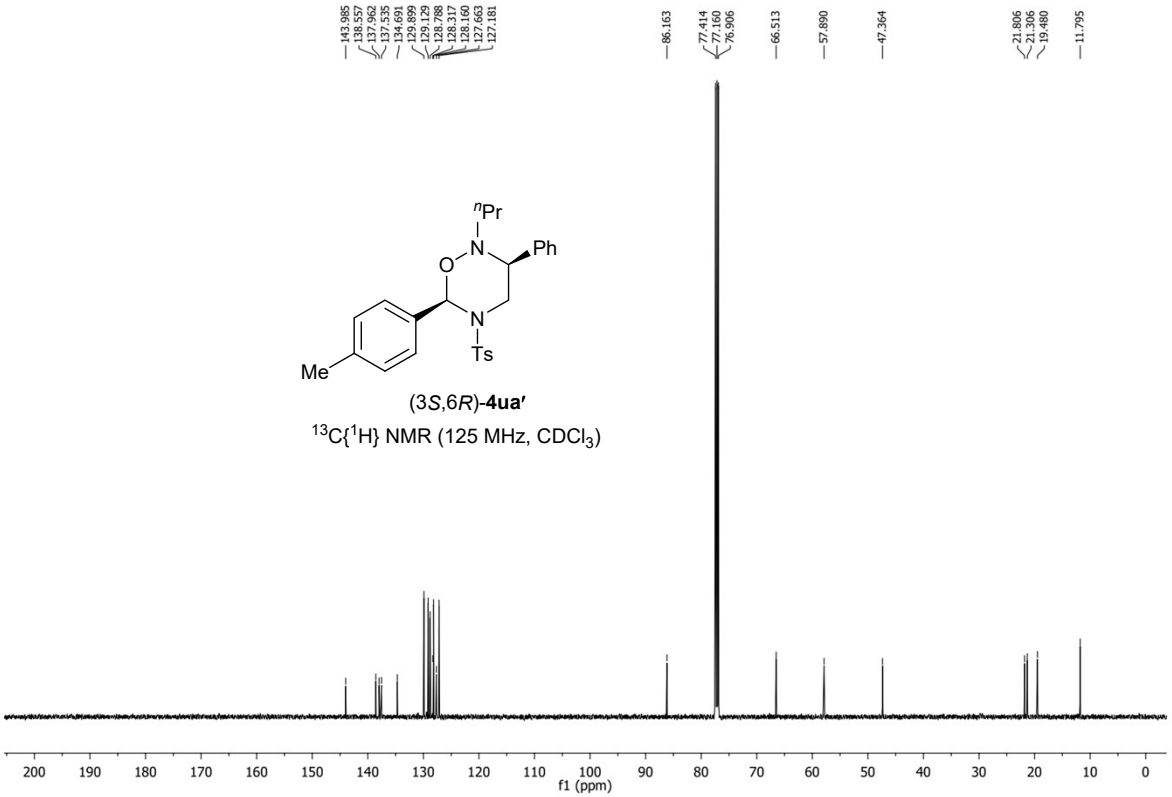
PKM-4Me-NPr-OA-AZI-1H



(3*S*,6*R*)-**4ua′**

^{1}H NMR (500 MHz, $CDCl_3$)

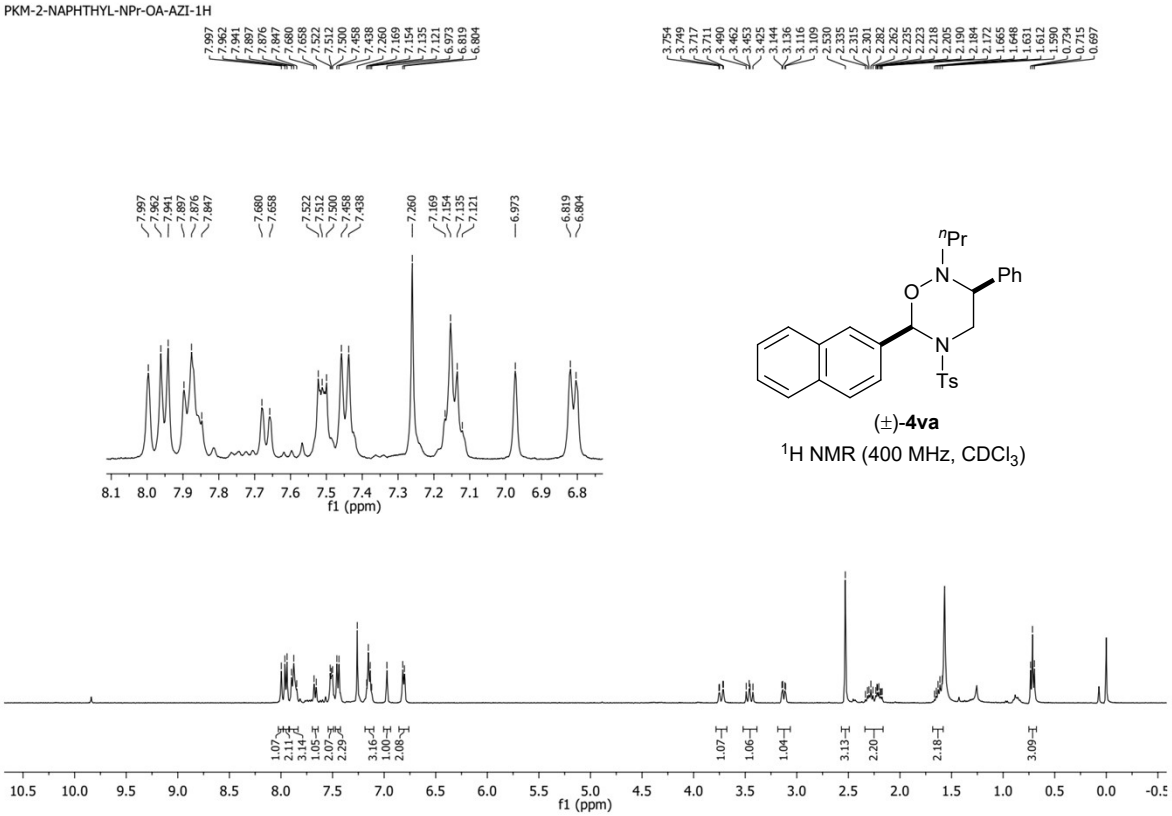
PKM-4Me-NPr-OA-AZI-13C



(3*S*,6*R*)-**4ua′**

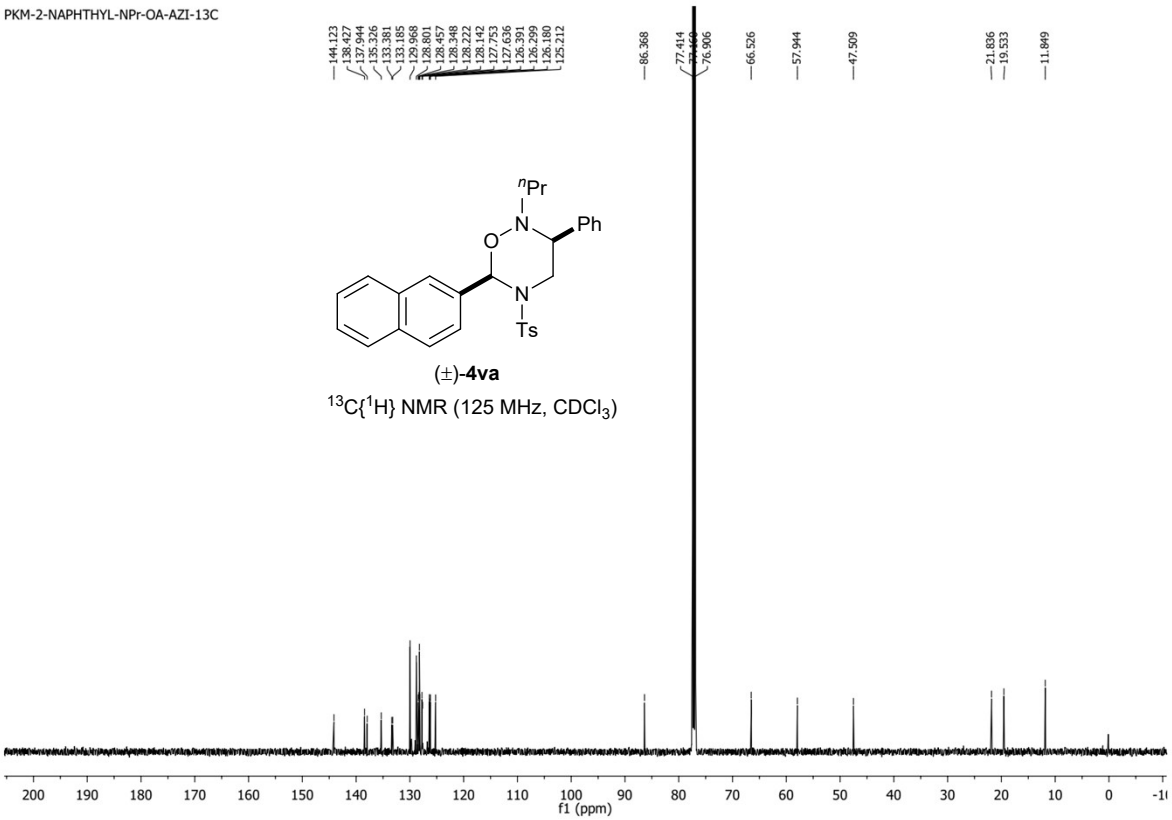
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-2-NAPHTHYL-NPr-OA-AZI-1H



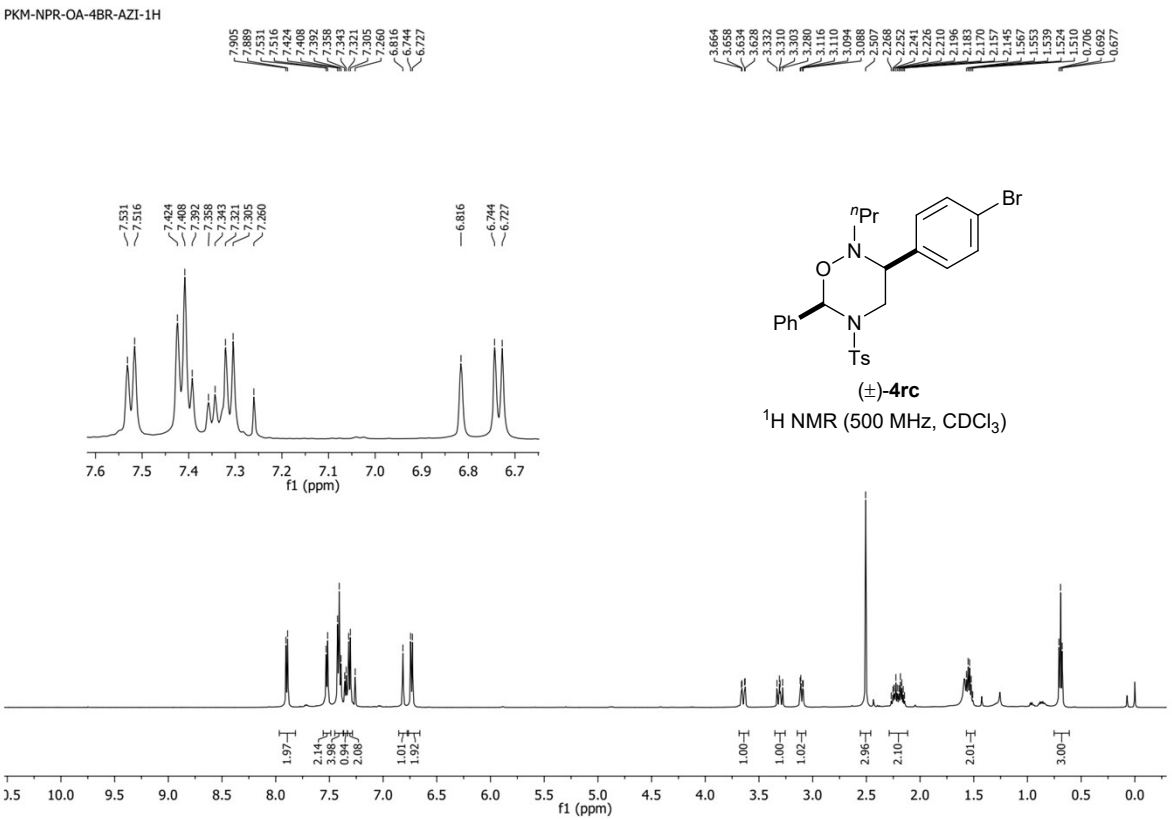
(±)-**4va**

^{1}H NMR (400 MHz, $CDCl_3$)



(±)-**4va**

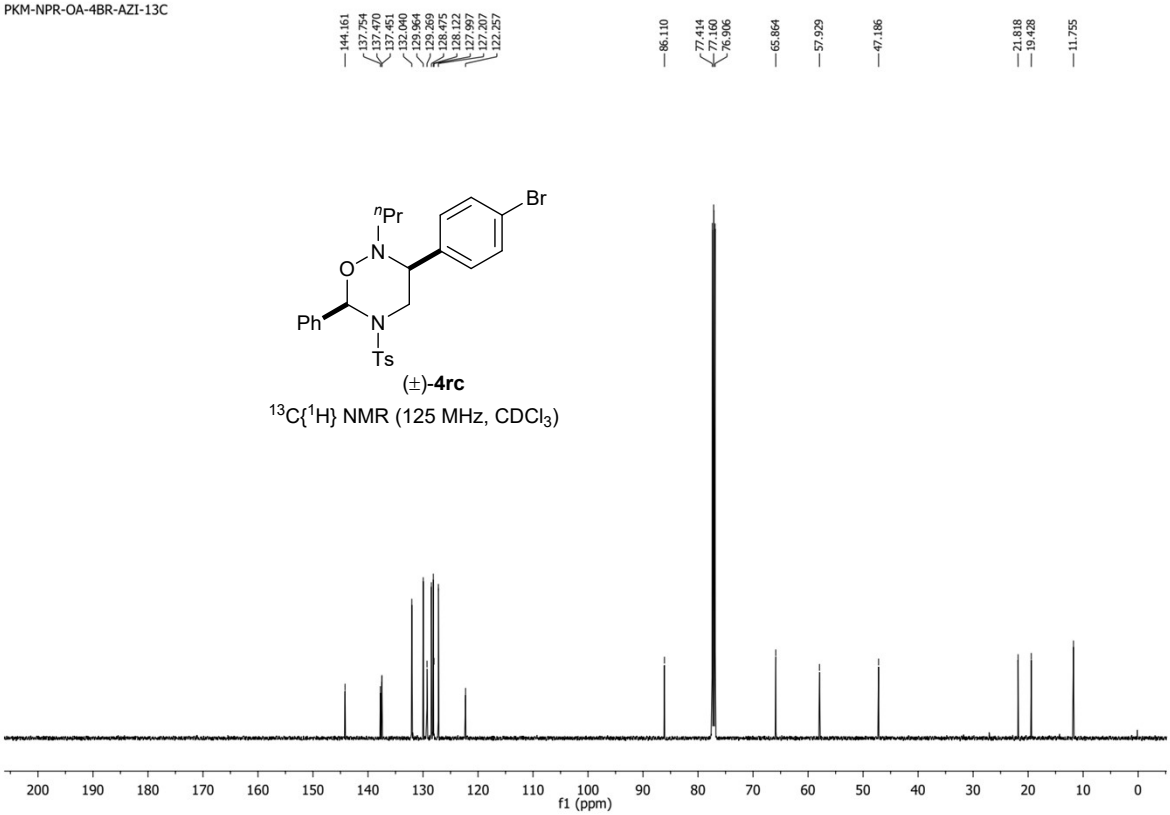
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**4rc**

^{1}H NMR (500 MHz, $CDCl_3$)

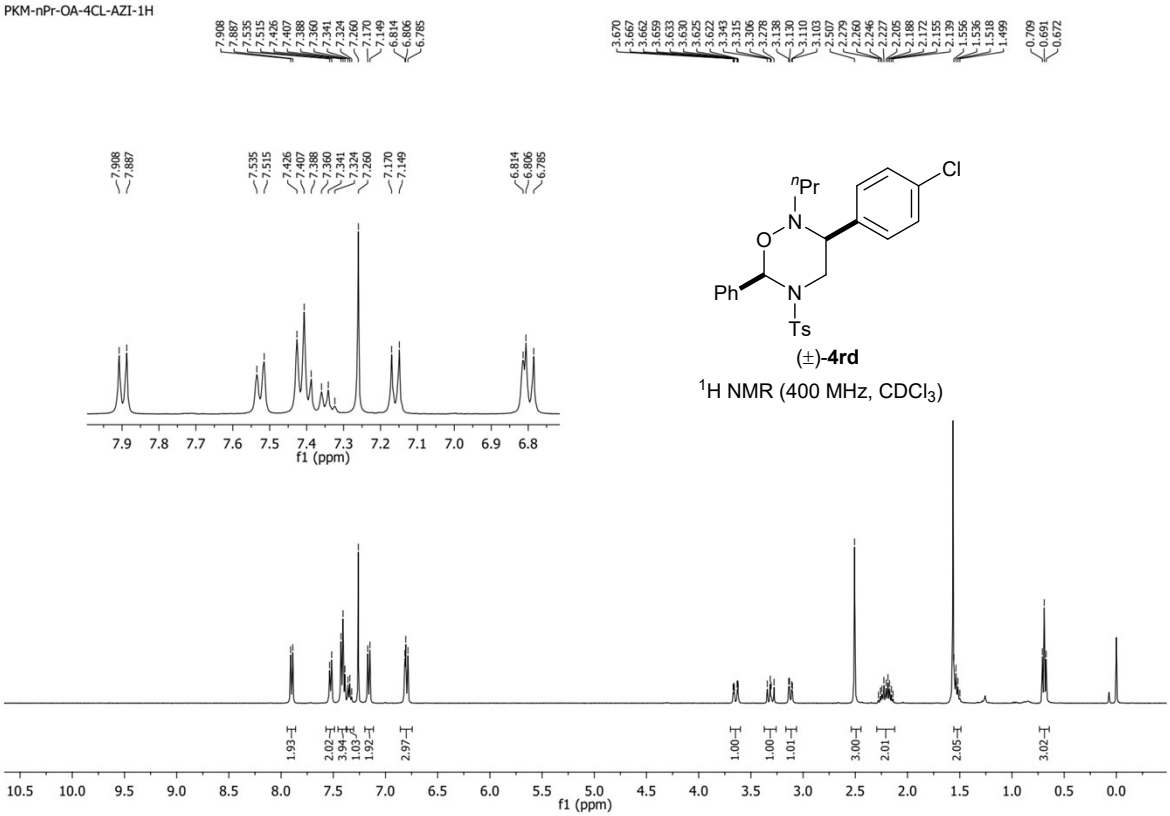
PKM-NPR-OA-4BR-AZI-13C



(±)-**4rc**

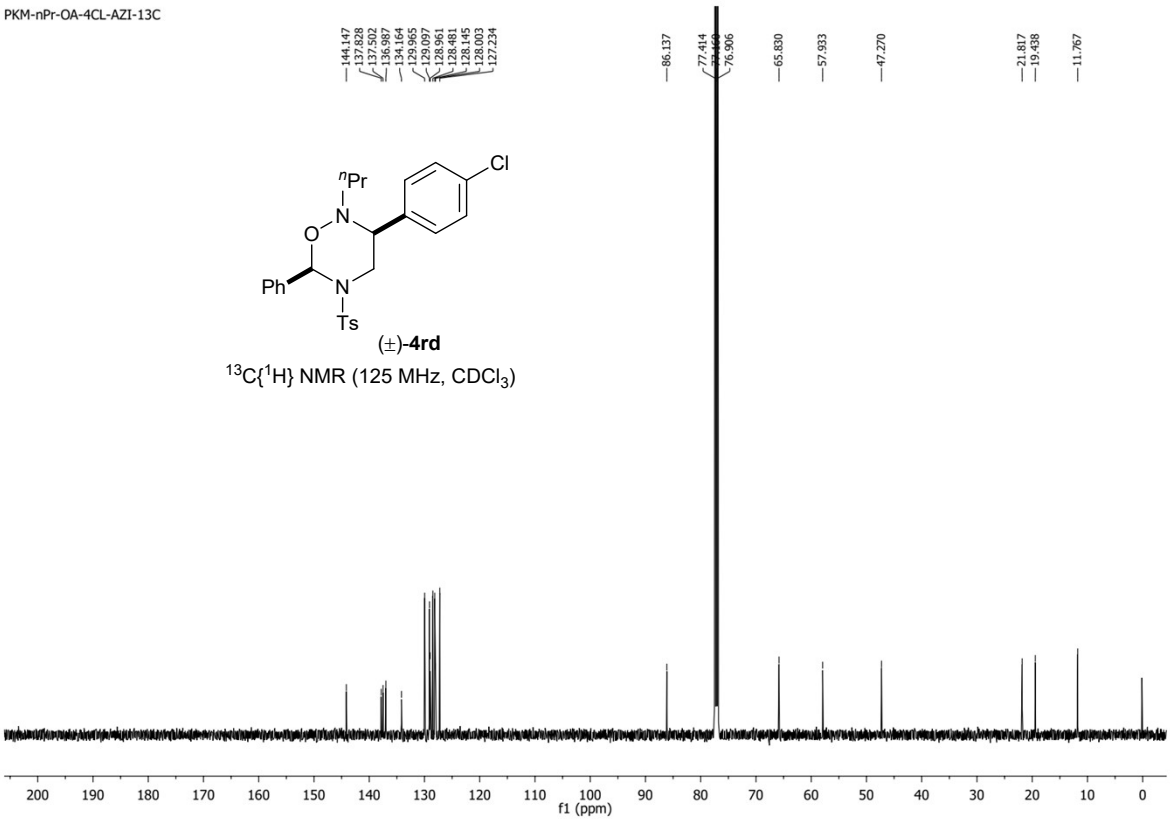
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-nPr-OA-4CL-AZI-1H



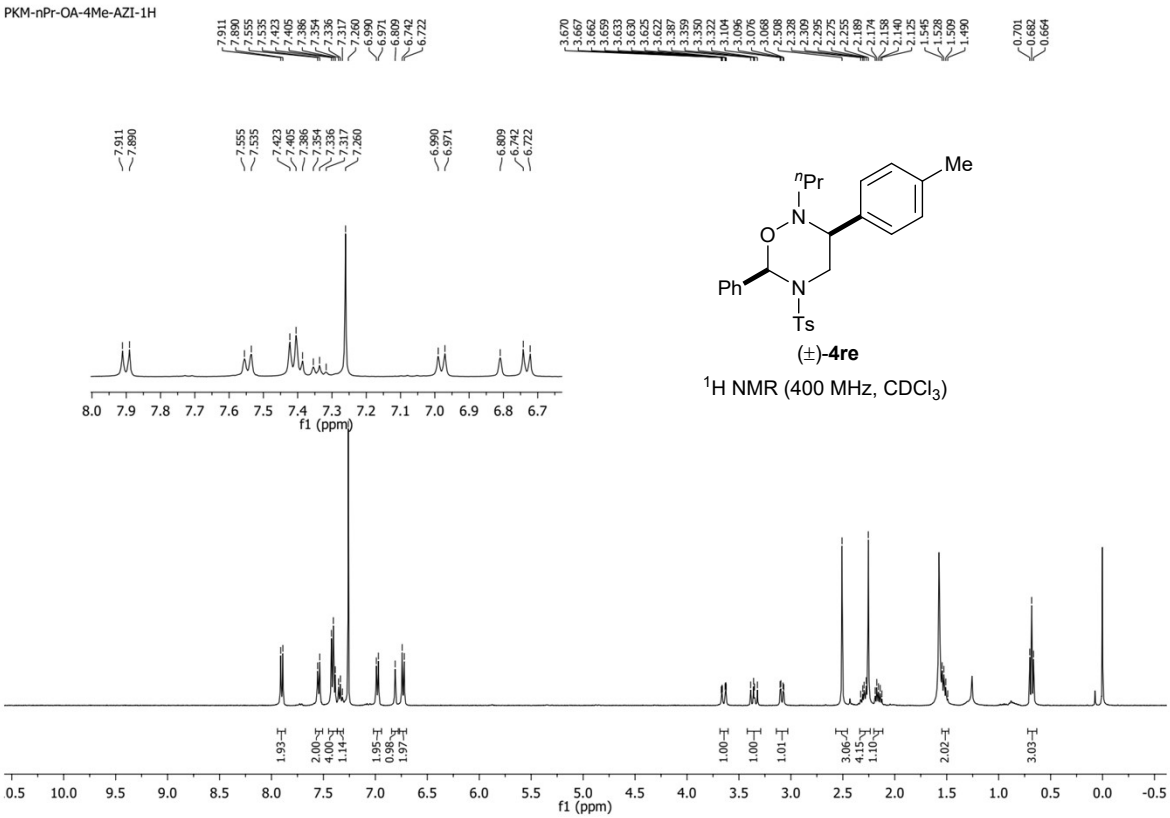
(±)-**4rd**

^{1}H NMR (400 MHz, $CDCl_3$)



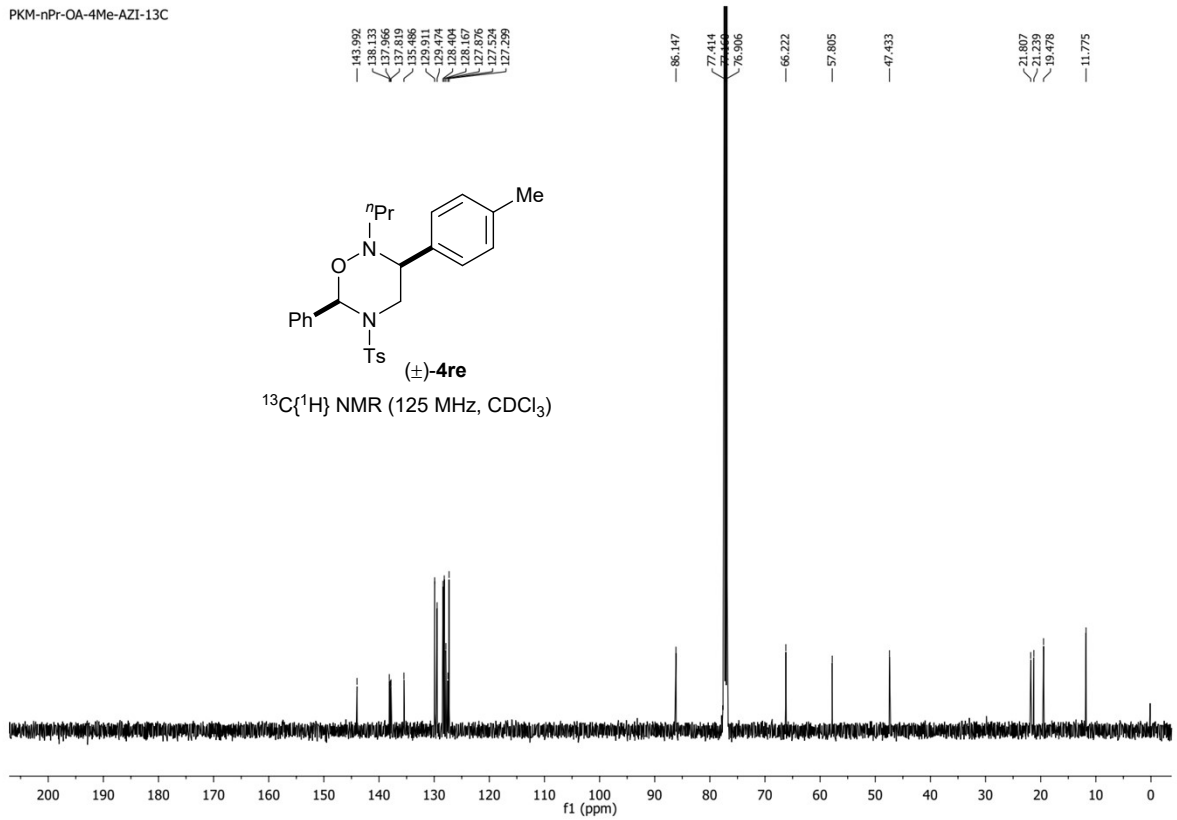
(±)-**4rd**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



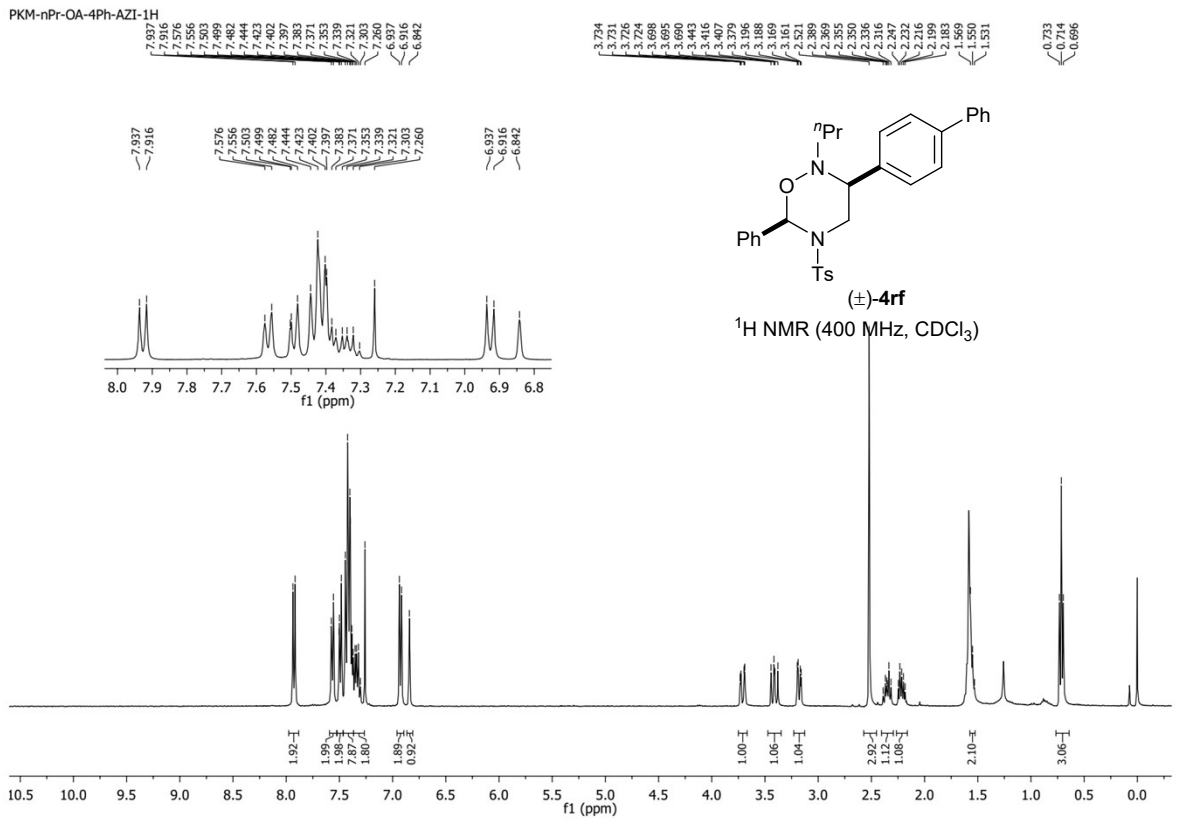
(±)-**4re**

^{1}H NMR (400 MHz, $CDCl_3$)



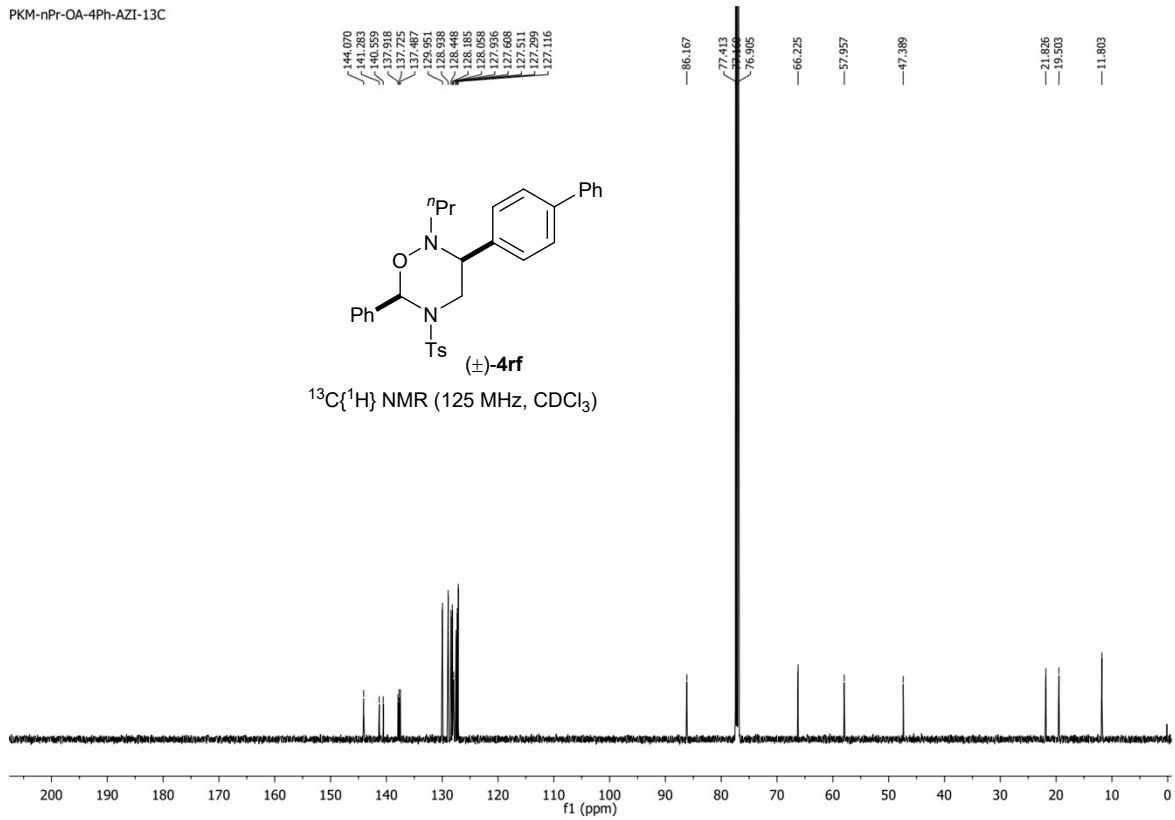
(±)-**4re**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



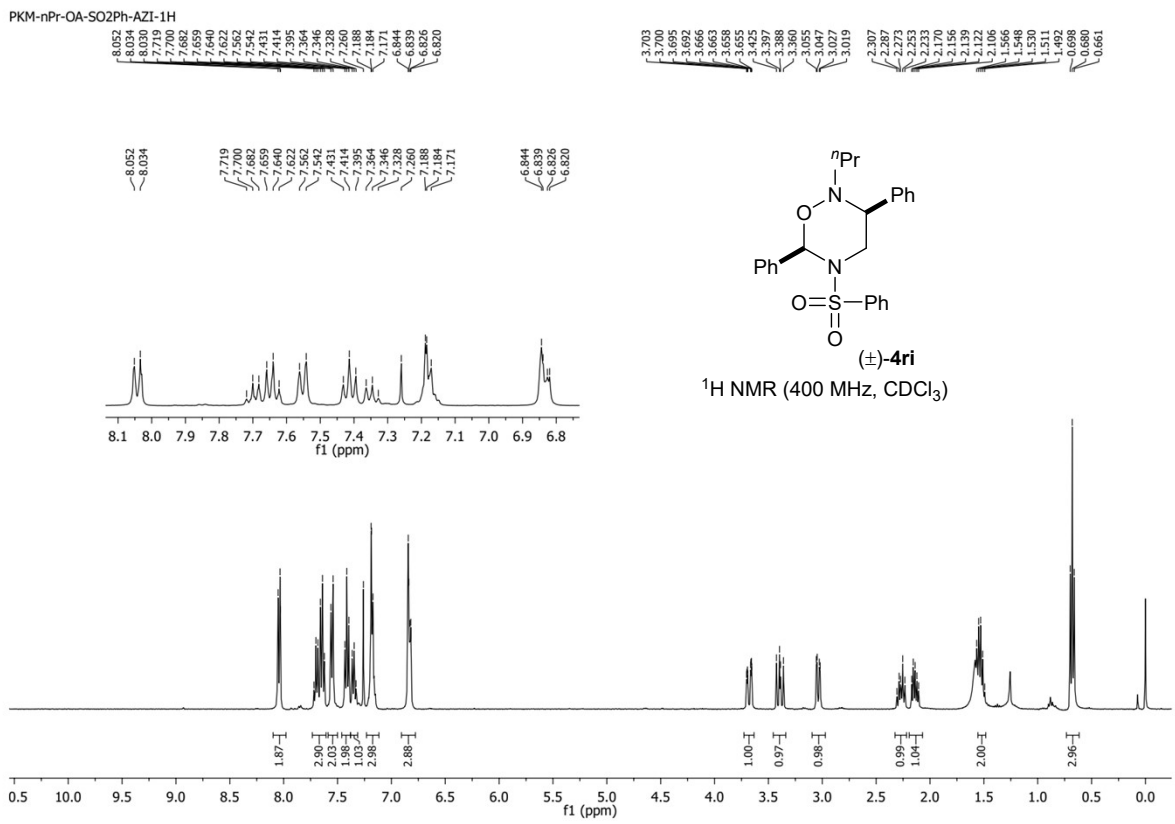
(±)-**4rf**

^{1}H NMR (400 MHz, $CDCl_3$)



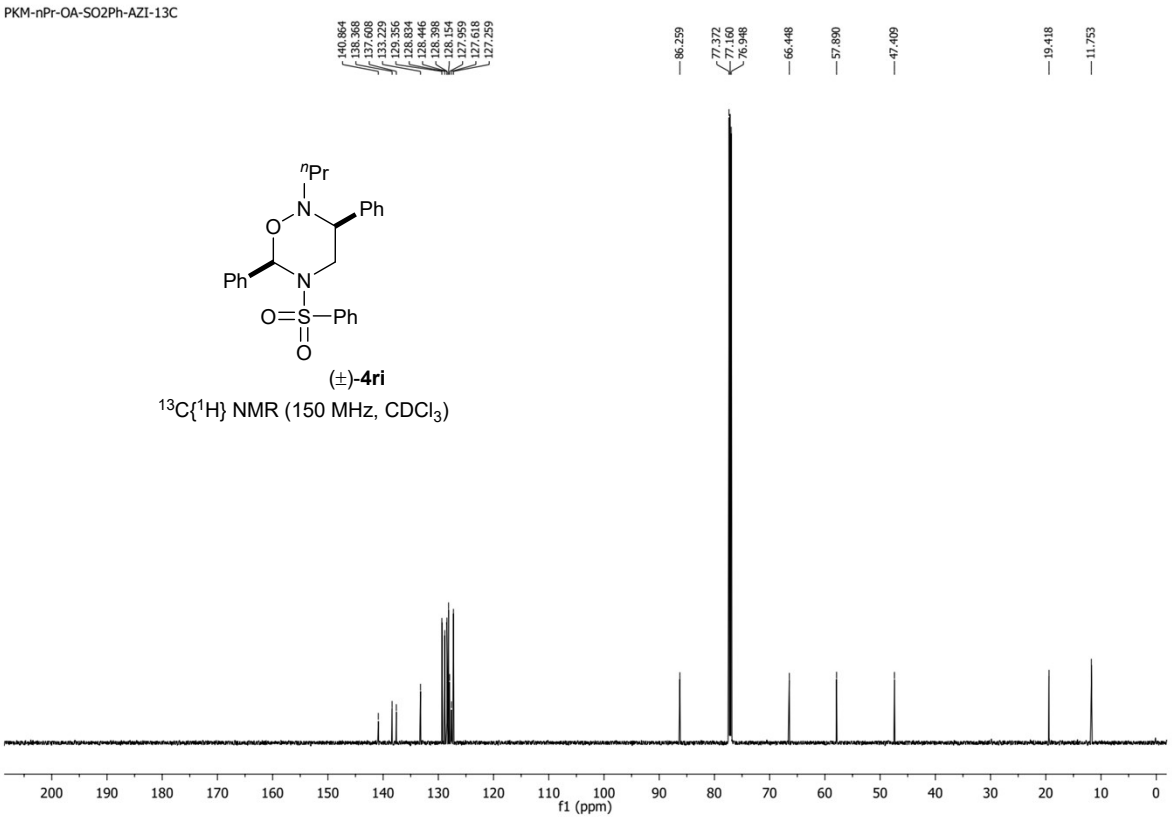
(±)-**4rf**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



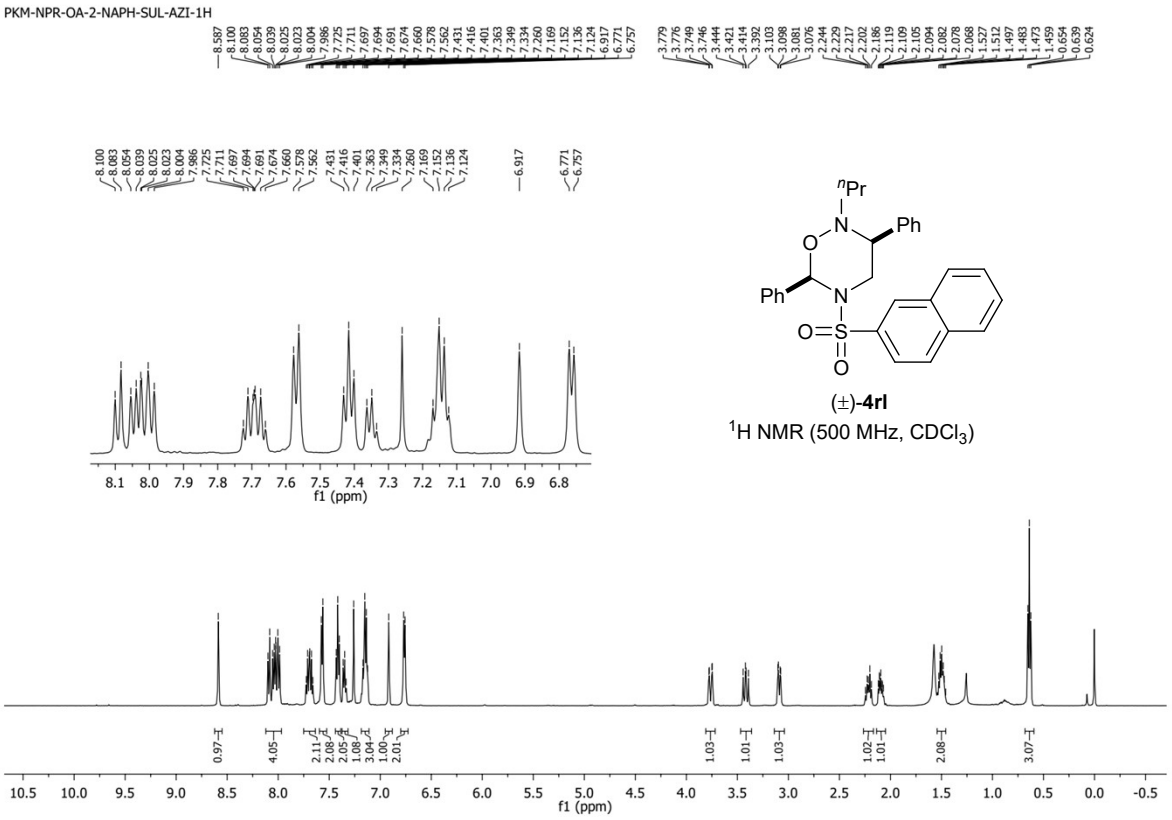
(±)-**4ri**

^{1}H NMR (400 MHz, $CDCl_3$)



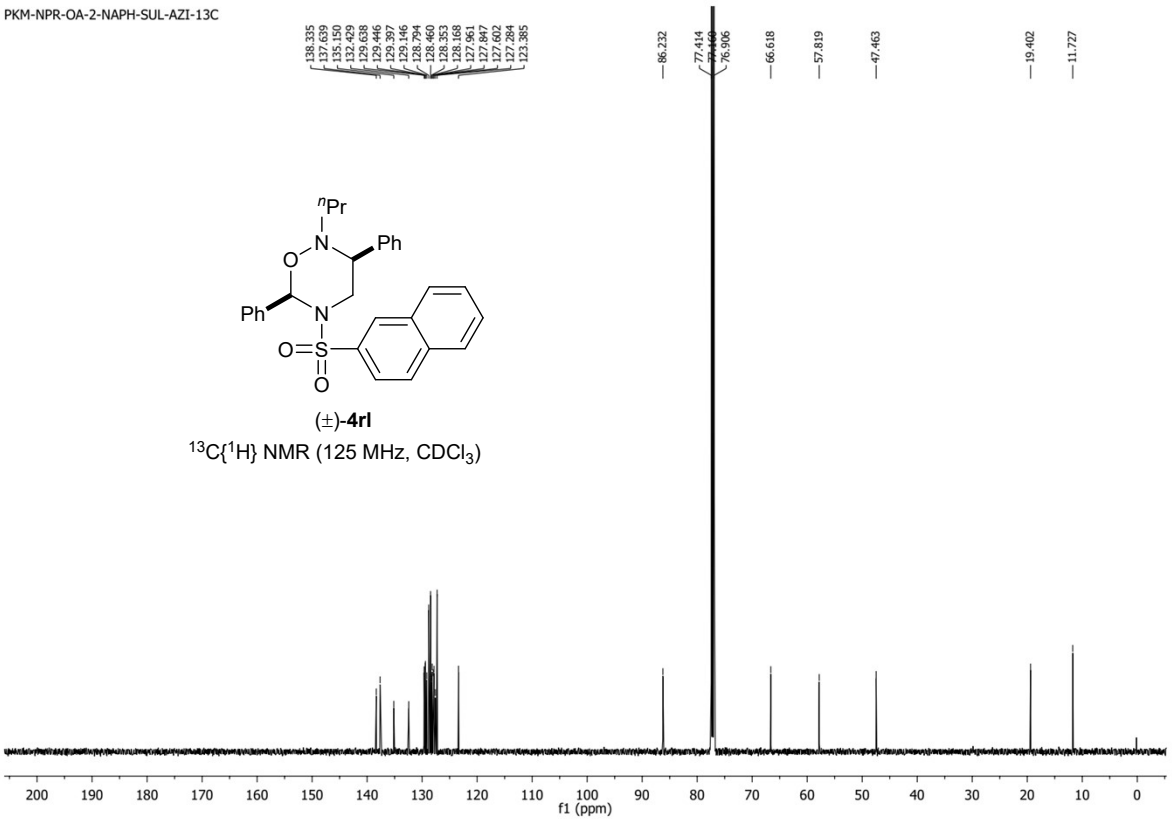
(±)-**4ri**

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



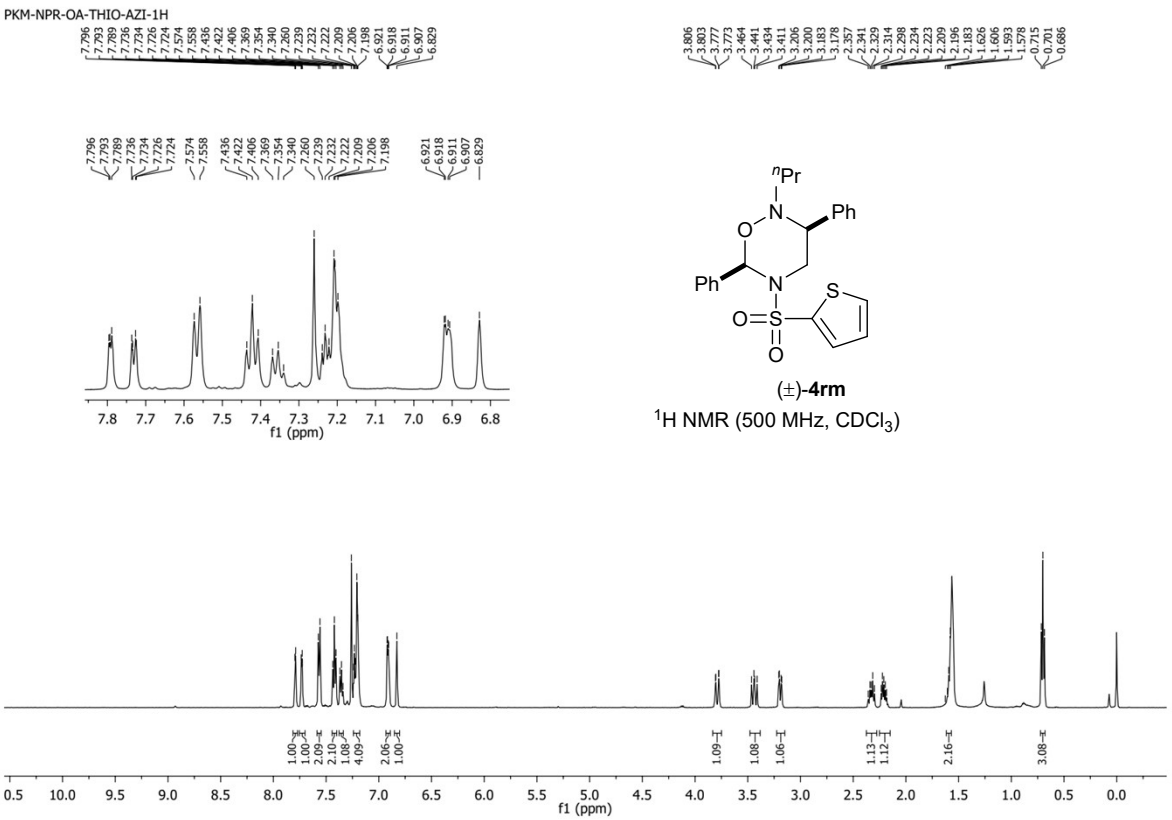
(±)-**4rl**

^{1}H NMR (500 MHz, $CDCl_3$)



(±)-**4rl**

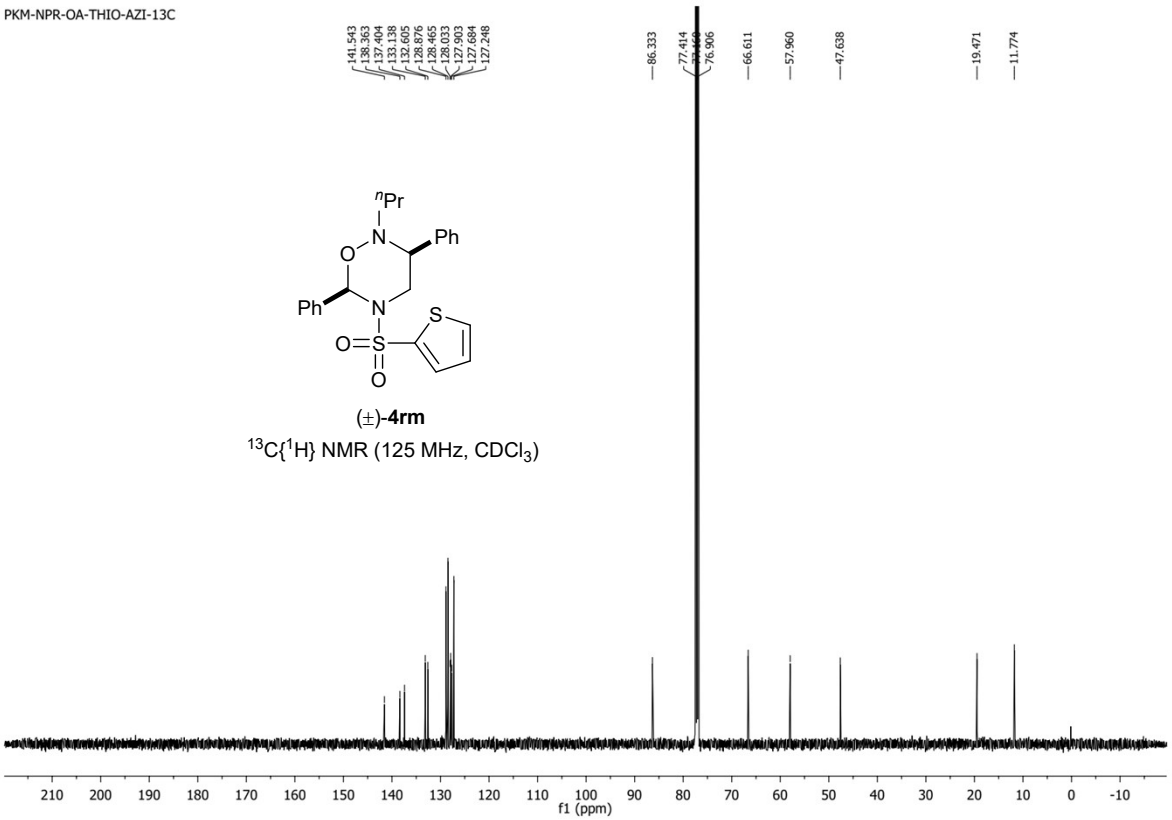
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



(±)-**4rm**

^{1}H NMR (500 MHz, $CDCl_3$)

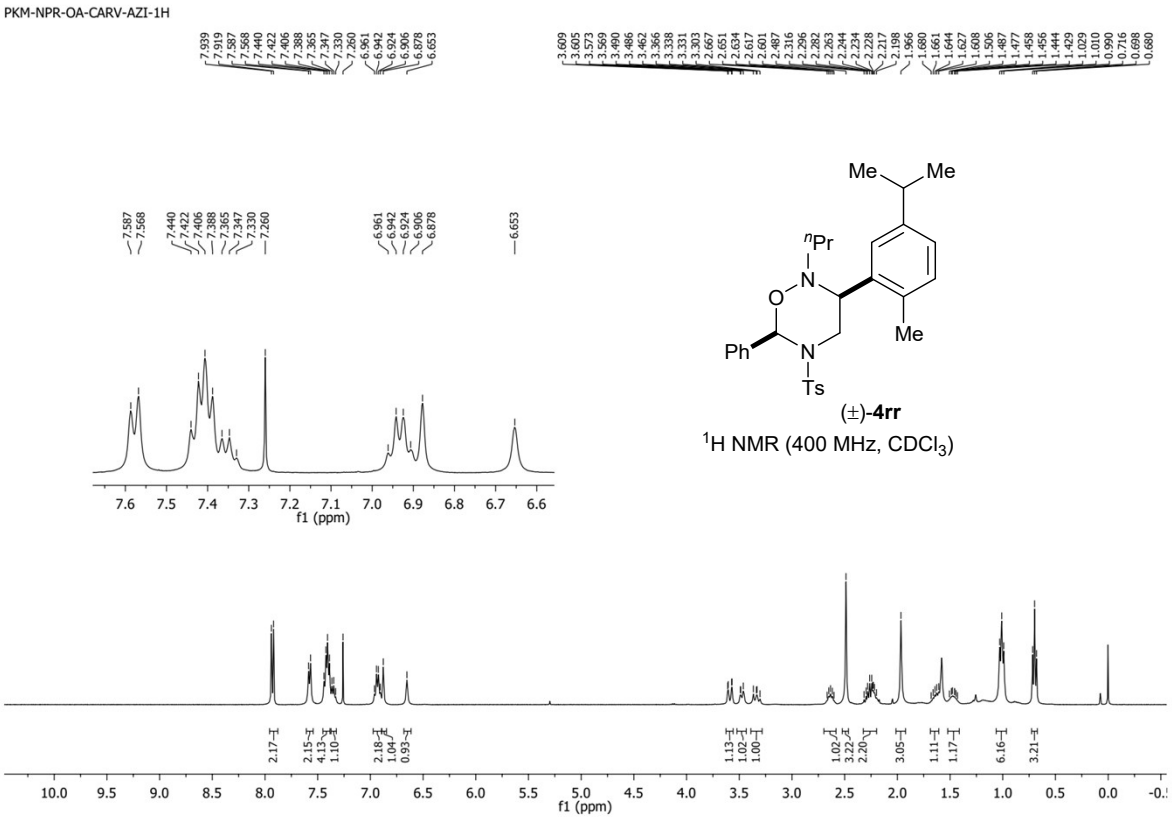
PKM-NPR-OA-THIO-AZI-13C



(±)-**4rm**

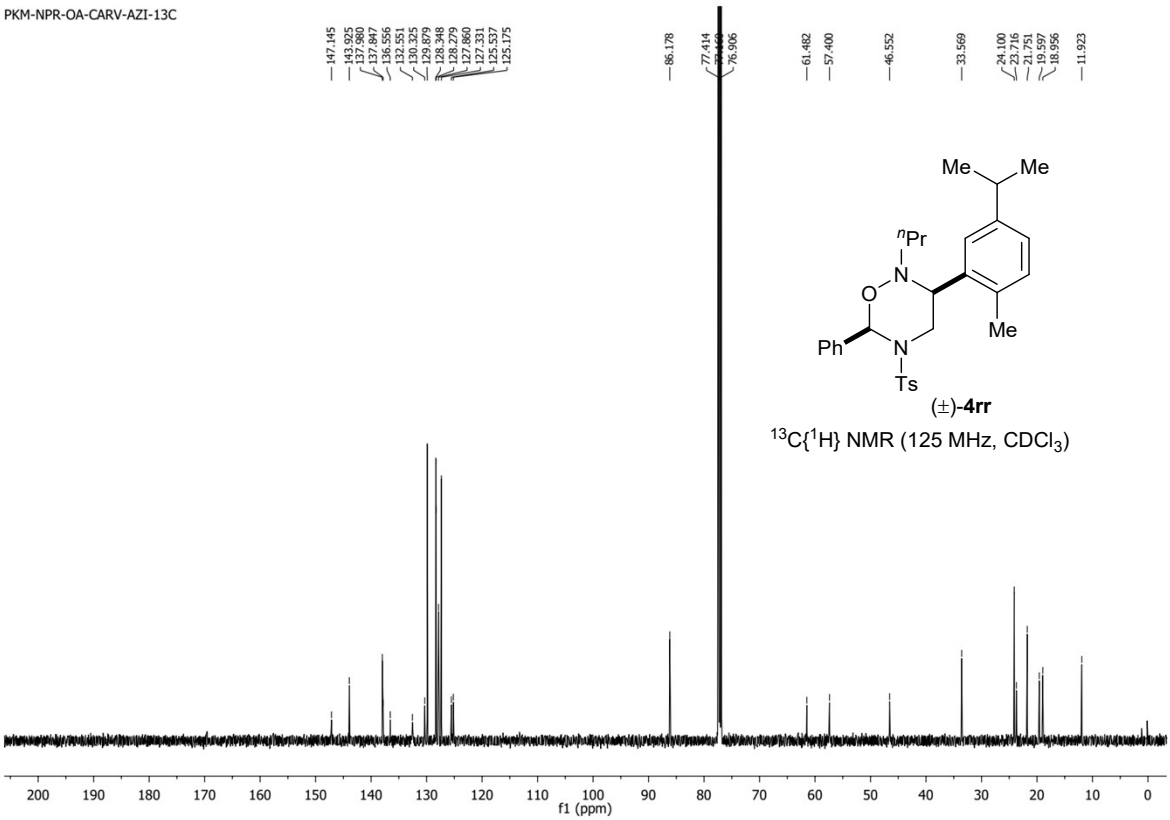
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

PKM-NPR-OA-CARV-AZI-1H



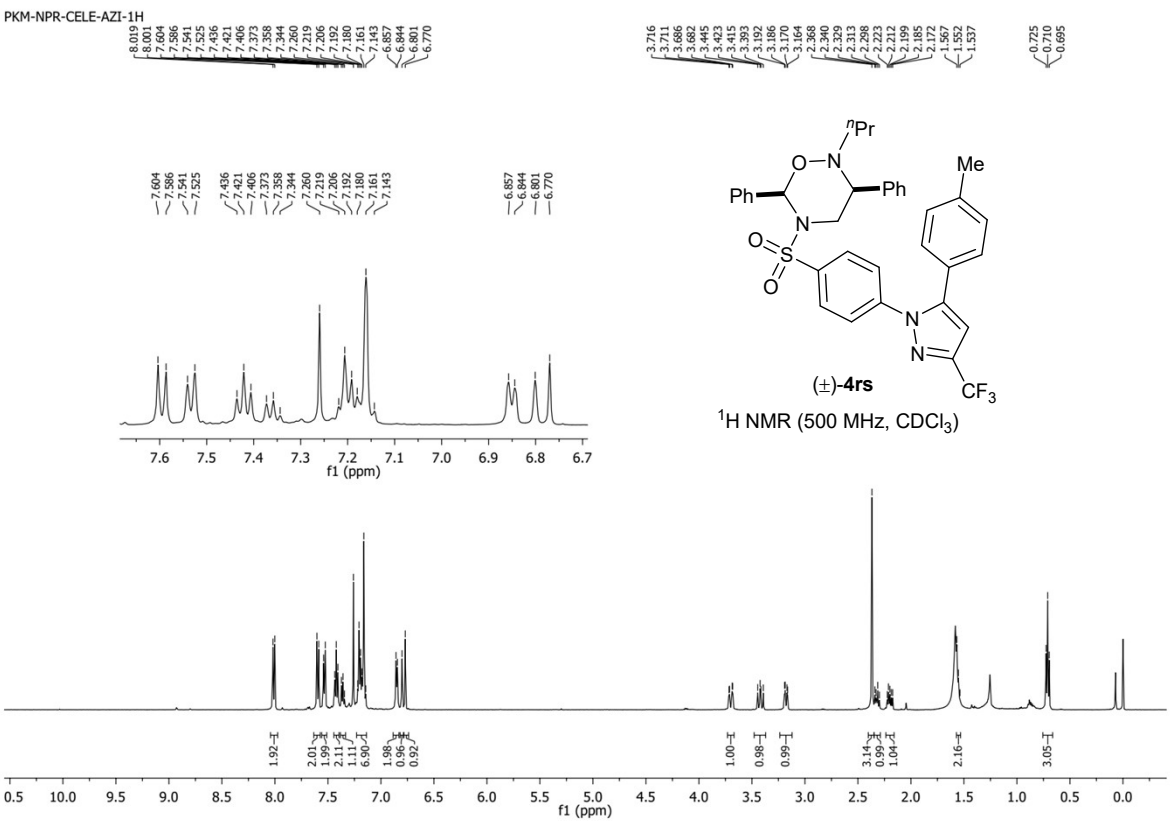
(±)-**4rr**

^{1}H NMR (400 MHz, $CDCl_3$)



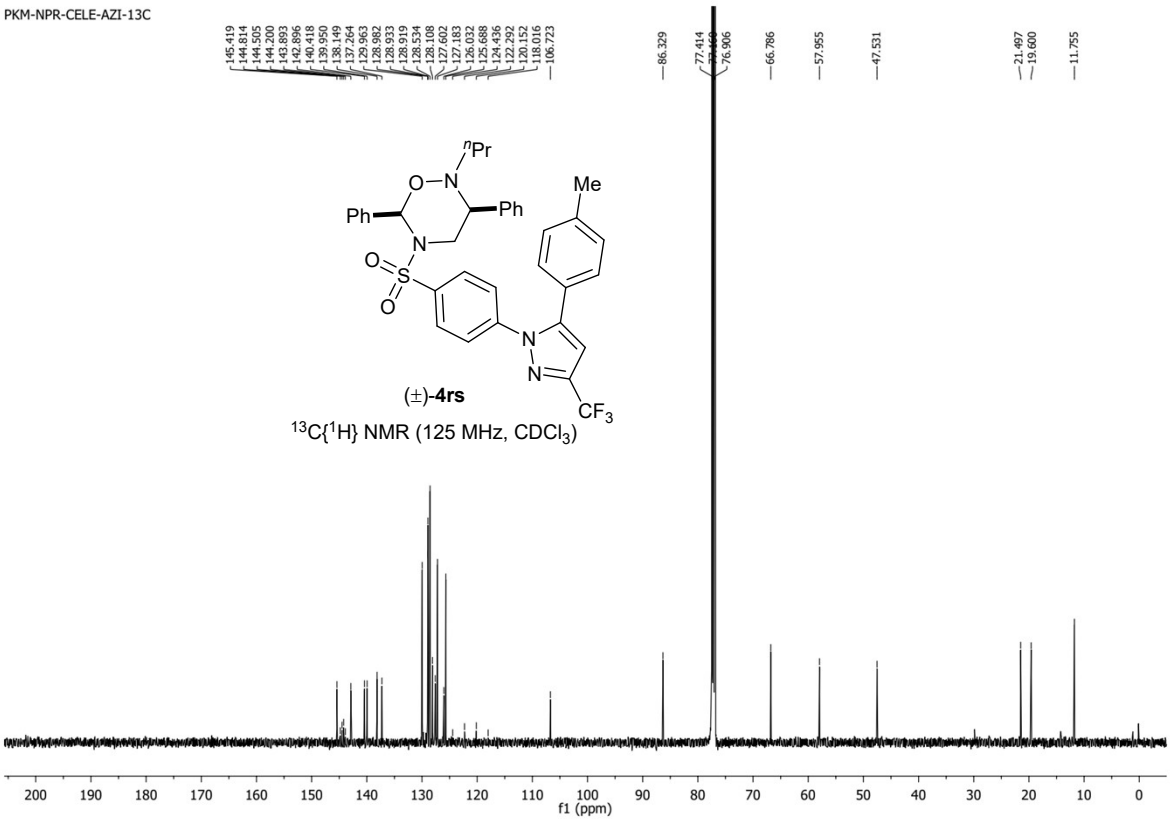
(±)-**4rr**

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



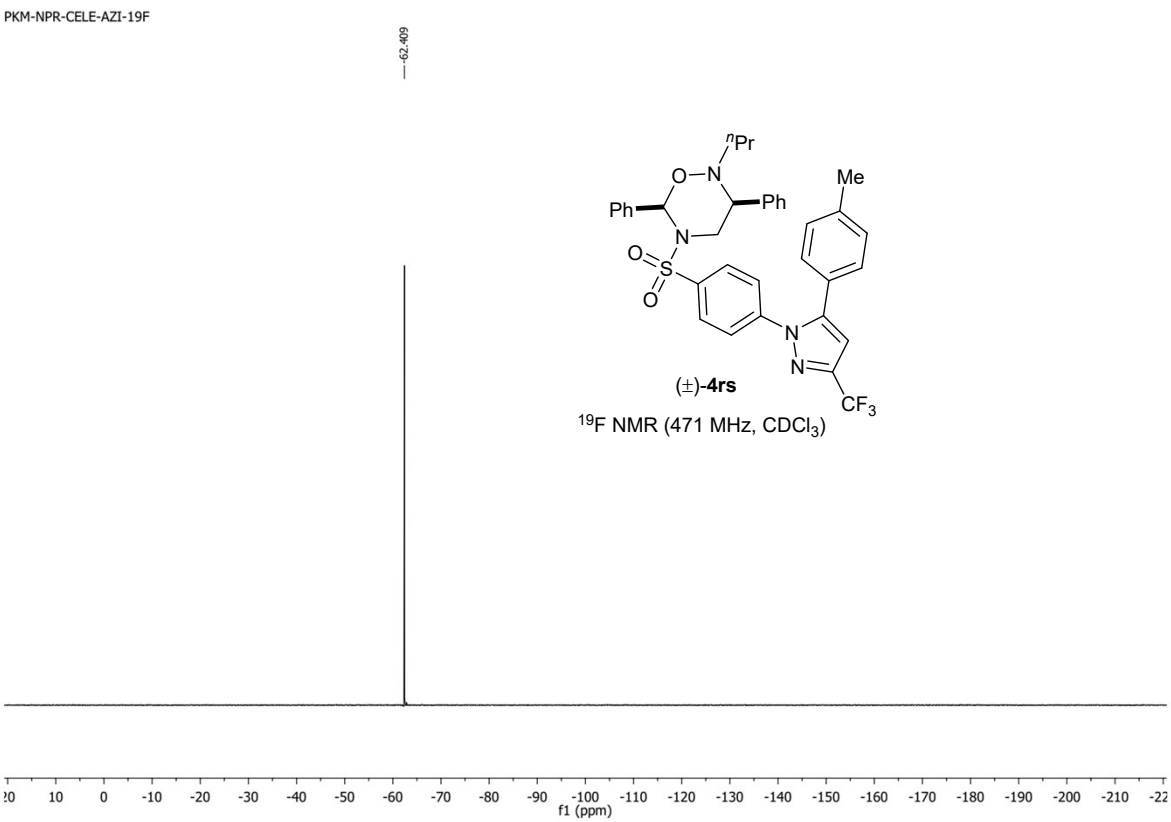
(±)-**4rs**

^{1}H NMR (500 MHz, $CDCl_3$)



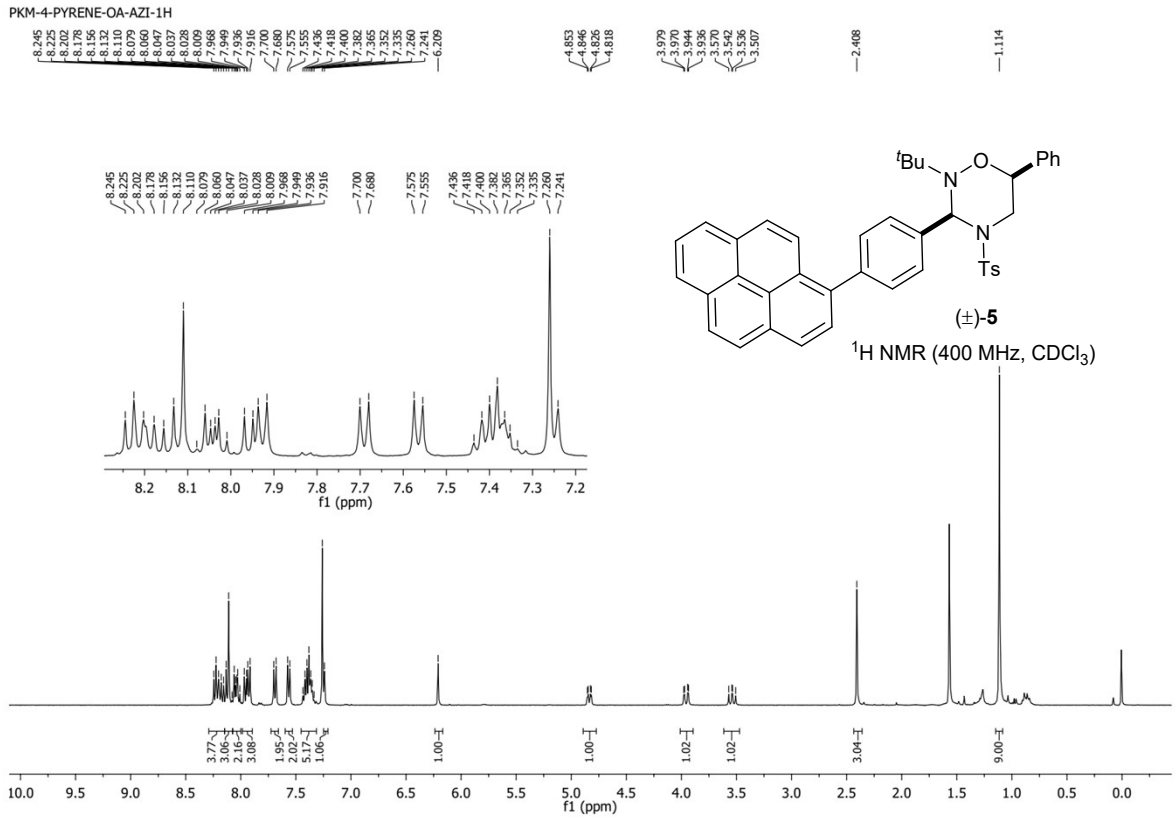
(±)-**4rs**

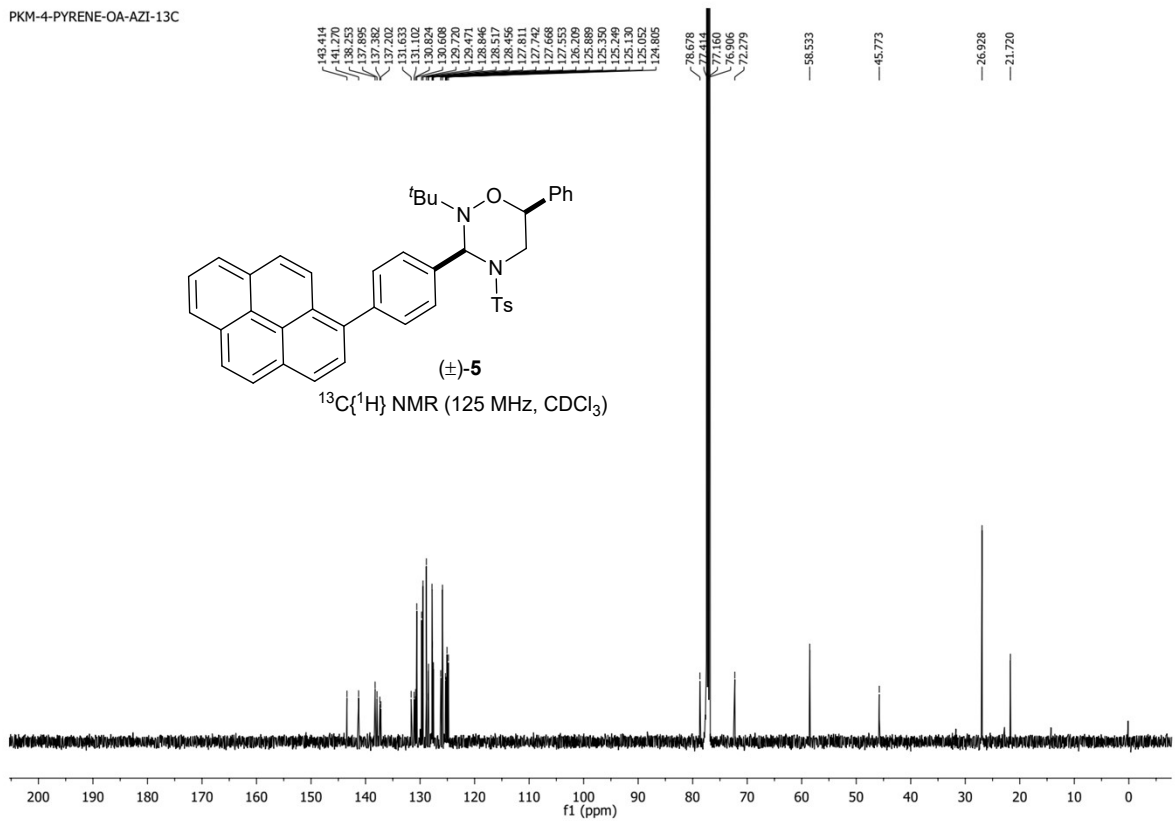
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

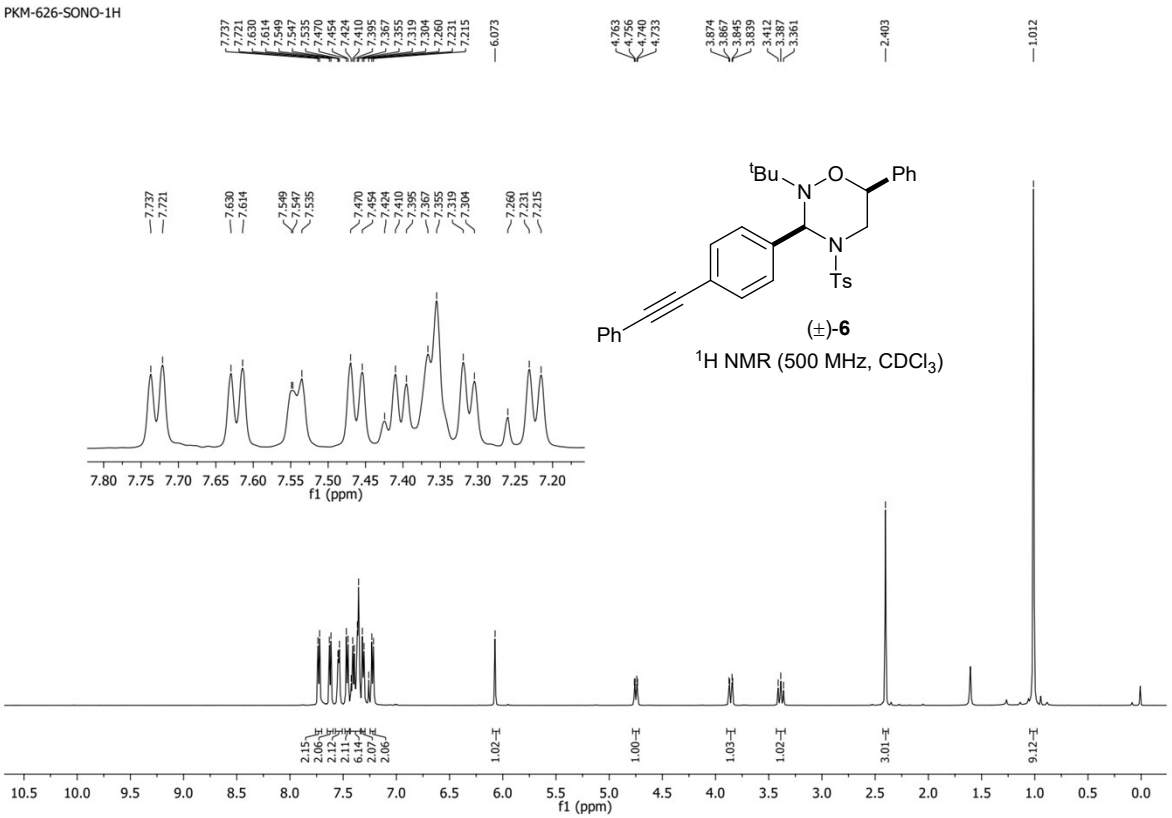


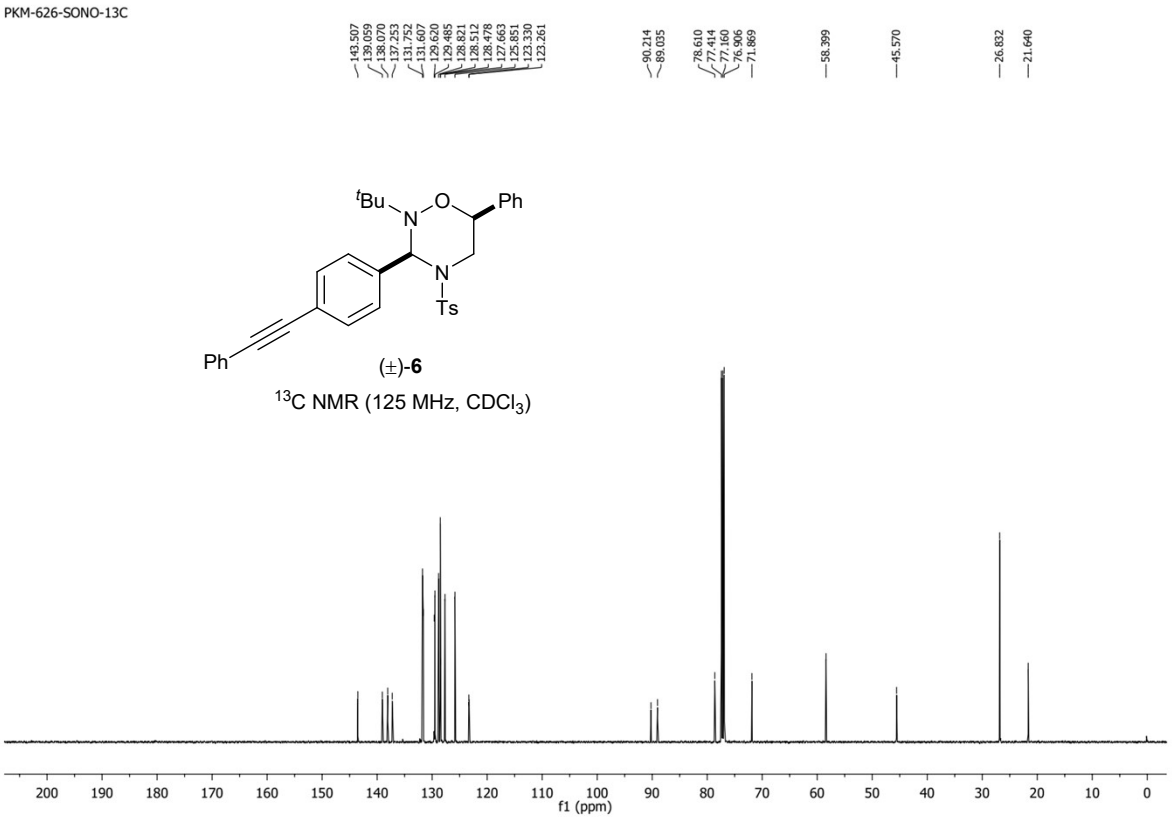
(±)-**4rs**

^{19}F NMR (471 MHz, $CDCl_3$)

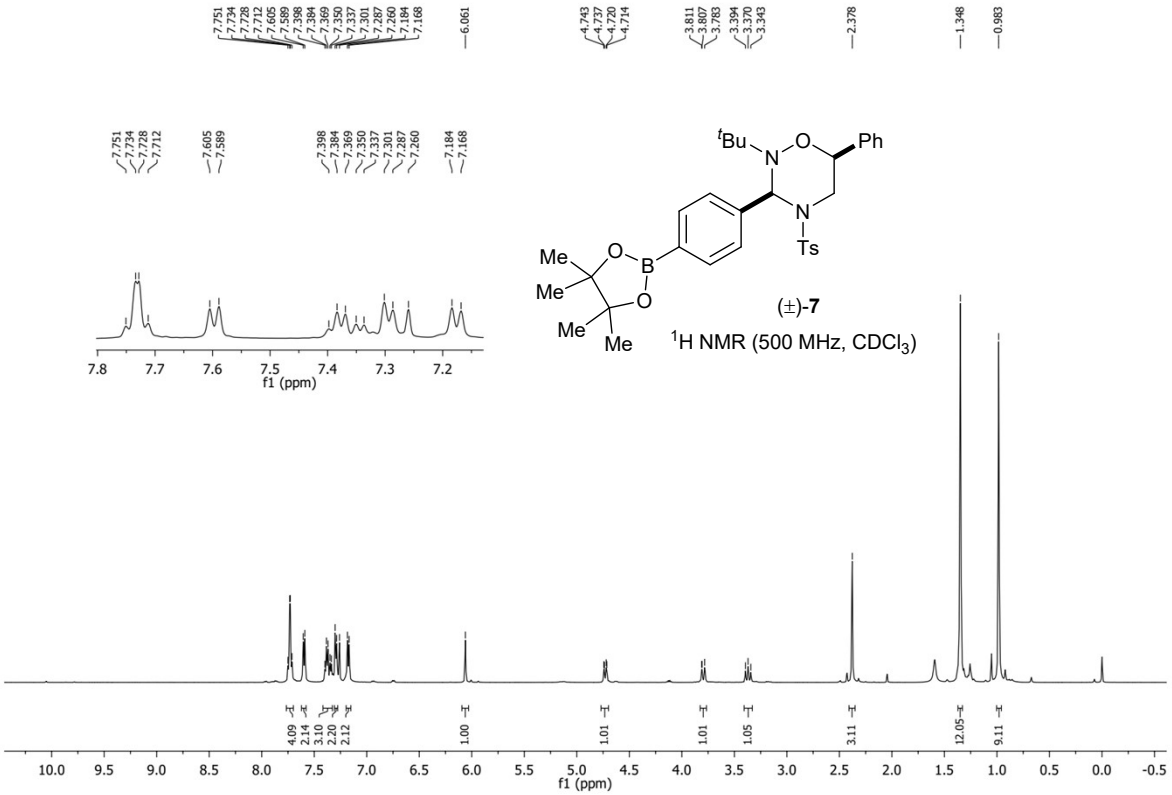

PKM-4-PYRENE-OA-AZI-1H
tBu
N
O
Ph
N
Ts
(±)-5
1H NMR (400 MHz, CDCl3)
f1 (ppm)


PKM-4-PYRENE-OA-AZI-13C
tBu
N
O
Ph
N
Ts
(±)-5
13C{1H} NMR (125 MHz, CDCl3)
f1 (ppm)


PKM-626-SONO-1H
7.737
7.721
7.630
7.614
7.549
7.547
7.535
7.470
7.454
7.424
7.410
7.395
7.367
7.355
7.319
7.304
7.260
7.231
7.215
6.073
4.763
4.756
4.740
4.733
3.874
3.867
3.845
3.839
3.412
3.387
3.361
2.403
1.012
tBu
N
O
Ph
N
Ts
Ph
(±)-6
1H NMR (500 MHz, CDCl3)
f1 (ppm)


PKM-626-SONO-13C
143.507
139.059
138.070
137.253
131.752
131.607
129.620
129.485
128.821
128.512
128.478
127.663
125.851
123.330
123.261
90.214
89.035
78.610
77.414
77.160
76.906
71.869
58.399
45.570
26.832
21.640
tBu
N
O
Ph
N
Ts
Ph
(±)-6
13C NMR (125 MHz, CDCl3)
f1 (ppm)

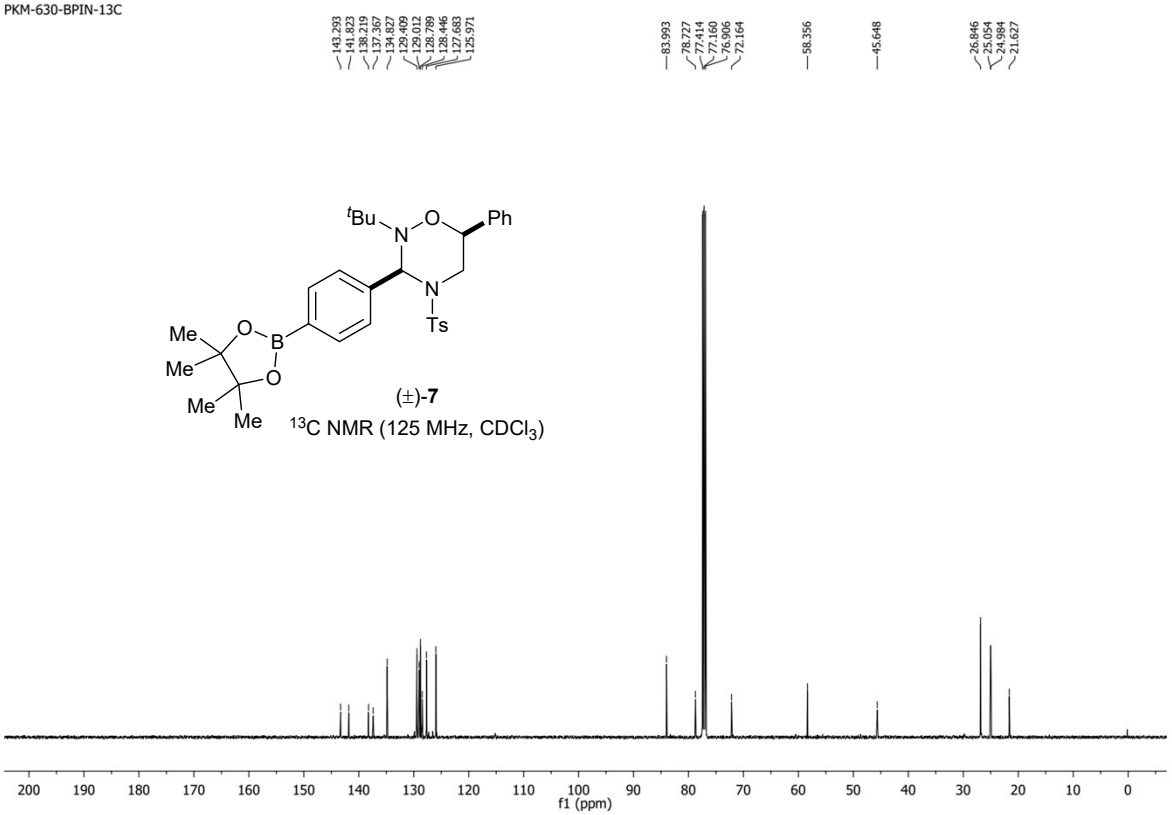
PKM-630-BPIN-1H



(±)-**7**

^{1}H NMR (500 MHz, $CDCl_3$)

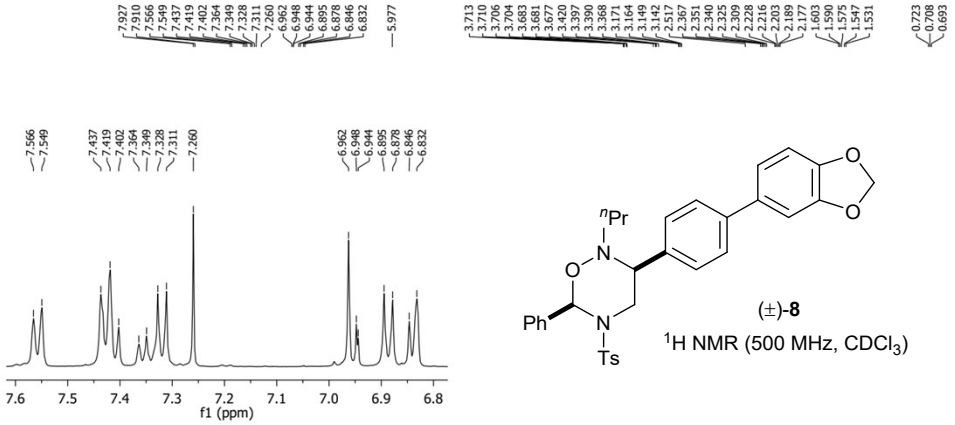
PKM-630-BPIN-13C



(±)-**7**

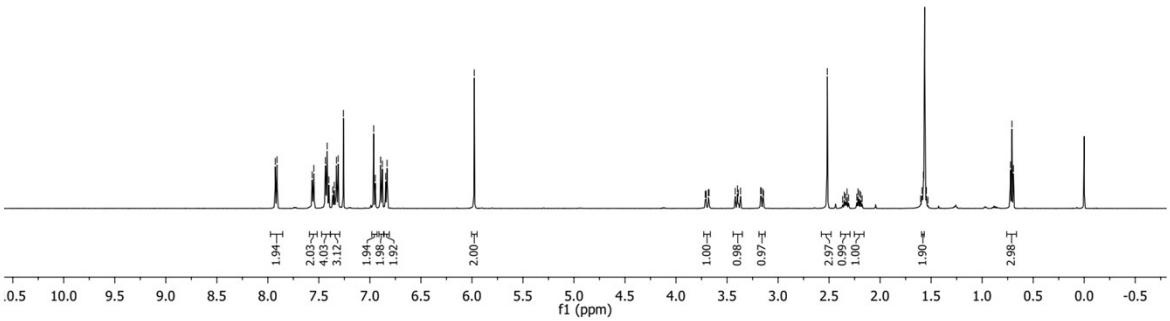
^{13}C NMR (125 MHz, $CDCl_3$)

PKM-499-NPR-SESA-APP-1H

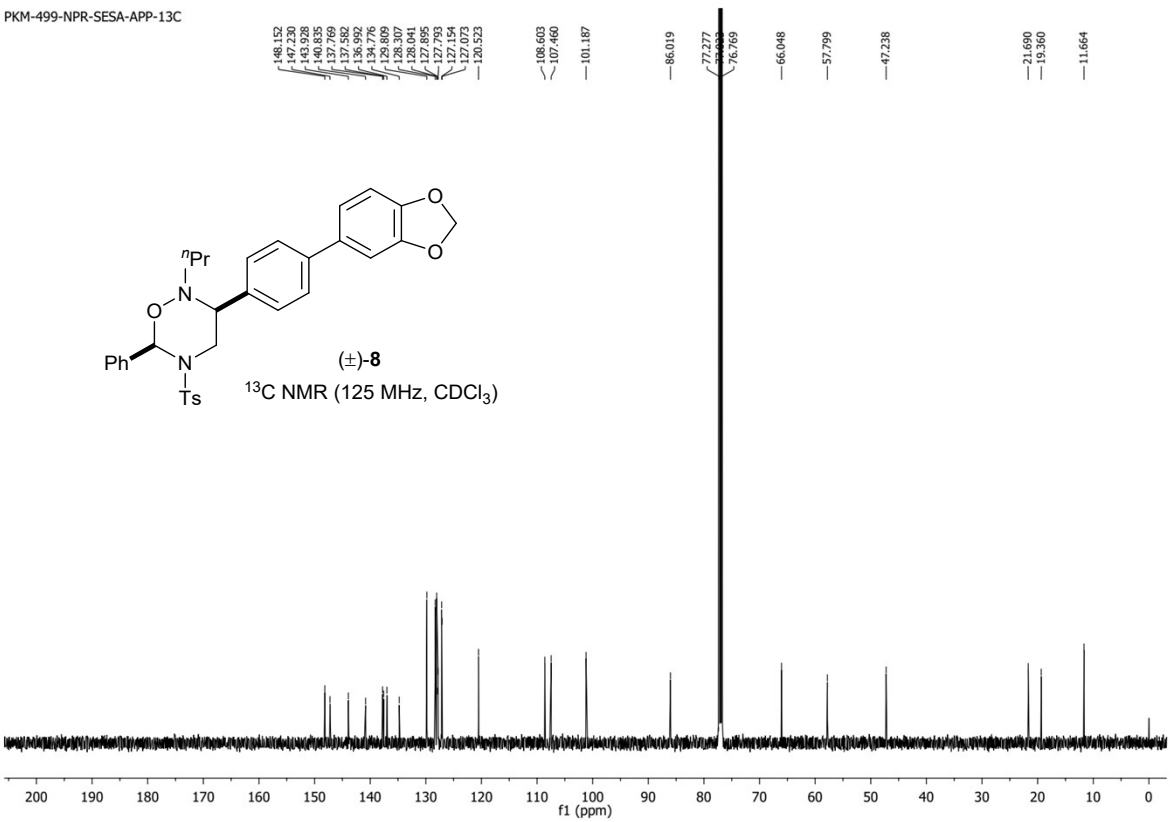


(±)-**8**

^{1}H NMR (500 MHz, $CDCl_3$)



PKM-499-NPR-SESA-APP-13C



(±)-**8**

^{13}C NMR (125 MHz, $CDCl_3$)