

Supporting Information

**Diastereoselective intramolecular *O*-allylation with
alkynes using Palladium/Brønsted acid combined
catalysis: Access to substituted chiral oxazolidines**

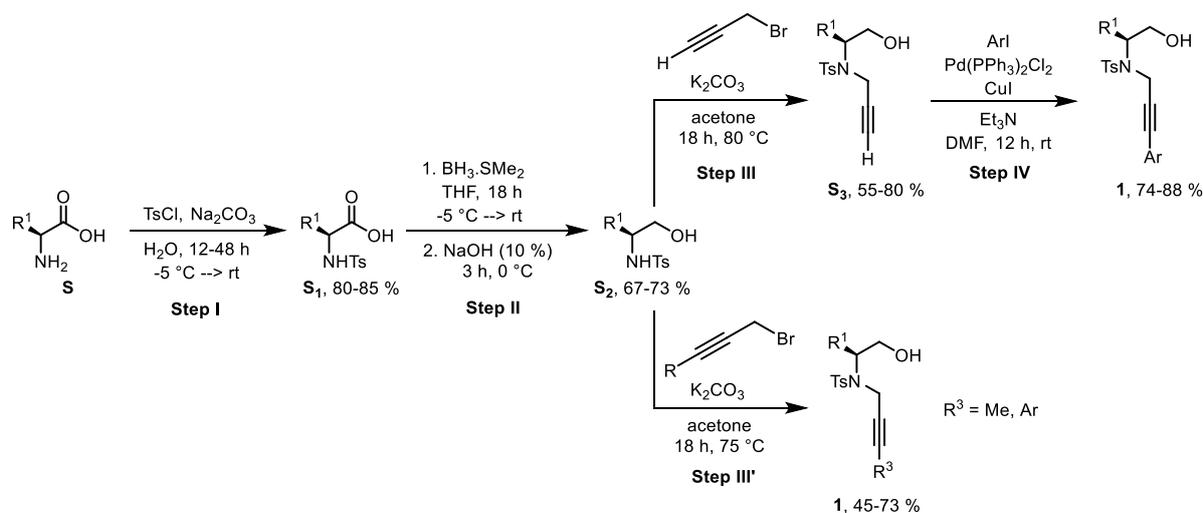
Table of Contents

1	General information:	S2
2	General procedure of substrate synthesis:	S3
3	General procedure for the diastereoselective intramolecular <i>O</i>-allylation with alkynes:	S8
4	Procedure for the gram-scale reaction:	S8
5	Characterisation data of final substrates:	S9
6	Characterisation data of cyclized products:	S20
7	Further derivatizations of product (2o):	S31
8	Deuterium-labelling experiment:	S33
9	X-ray crystallographic information of the product 2o:	S35
10	Crystal data of 2o:	S36
11	References:	S41
12	NMR spectral data of final substrate:	S42
13	NMR spectral data of cyclic products:	S76

1 General information:

The ^1H and ^{13}C spectra were recorded in CDCl_3 and DMSO at 297 K, and the chemical shifts (δ) are depicted in parts per million (ppm). The proton magnetic resonance (^1H NMR) and carbon magnetic resonance (^{13}C NMR) spectra were recorded at 400 MHz and 101 MHz respectively, and obtained using the Bruker AVANCE NEO Ascend 400 MHz FT-NMR instrument. The chemical shifts (δ) are depicted in parts per million (ppm) and the data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets). Splitting patterns that could not be interpreted are designated as multiplet (m). Coupling constants (J) are measured in Hertz (Hz). For ^1H NMR, the chemical shifts were calibrated in reference to tetramethylsilane (0 ppm), or the residual undeuterated solvents (CDCl_3 , 7.26 ppm or DMSO, 2.50 ppm). Data for ^{13}C NMR spectra were reported in a similar pattern. Singlet peaks in the ^{13}C NMR spectra were reported only with their chemical shifts. For ^{13}C NMR spectra, chemical shifts were calibrated in reference to the deuterated solvents (CDCl_3 , 77.1 ppm or DMSO, 39.5 ppm). High-resolution mass spectra (HRMS) were measured on a Xevo G2-XS QTOF Quadrupole Time-of-Flight Mass Spectrometer Waters instrument with an ESI ion source. X-ray crystallography was performed on a Rigaku XtaLab Synergy DW instrument. Chiral HPLC was performed on a WATERS e2695 Separation Module instrument. Unless otherwise specified, all commercial chemicals including enantiopure chiral amino acid and amino alcohols were used in their received form. Solvents were either dried and kept over molecular sieves (4 Å) after being distilled using CaH_2 or dried solvents were purchased commercially and used as such. Reactions above room temperature were carried out in an aluminium metal block. TLC Silica gel 60 F254 from Merck was used for the Thin Layer Chromatography. The results were observed using UV light and PMA stain. Silica gel with a mesh size of 100–200 was used for the silica gel column chromatography (Hyma).

2 General procedure of substrate synthesis:



Scheme S1. Synthesis of **1** from **S**.

STEP I (Synthesis of **S₁ from **S**):** A solution of amino acid (**S**) (1.0 equiv) and Na₂CO₃ (1.5 equiv) in H₂O (20 mL) was stirred at -5 °C for 5 min. TsCl (1.2 equiv) was added slowly in proportions over a period of 1 h and the reaction was stirred for 12-48 h at room temperature. After completion of reaction as indicated by TLC, the reaction was quenched with 5 M HCl solution till the pH < 2, then the mixture was extracted three times with EtOAc. The combined organic layers were washed with 1 M HCl, followed by brine, and dried over Na₂SO₄. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a DCM/MeOH = 99:1 to 90:10 solution as the eluting agent, resulting in the isolation of N-tosylated amino acid (**S**₁).¹

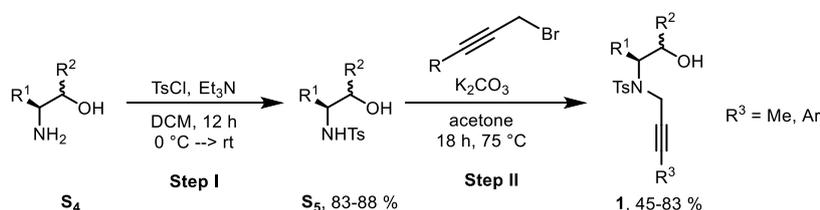
STEP II (Synthesis of **S₂ from **S**₁):** A solution of **S**₁ (1.0 equiv) in dry THF (15 mL) was stirred at -5 °C for 10 min. BH₃.SMe₂ (3.0 equiv) was added slowly over a period of 10 min and the reaction was stirred for 18 h at room temperature. After completion of reaction as indicated by TLC, the reaction was quenched with a 10 % NaOH solution and the mixture was again stirred below 0 °C for 3 h. The mixture was extracted three times with EtOAc. The combined organic layers were washed with brine, and dried over Na₂SO₄. Following filtration, the solvent was evaporated under reduced pressure. The isolated N-tosylated amino alcohol (**S**₂) was used directly in the next step without further purification.²

STEP III (Synthesis of **S₃ from **S**₂):** A solution of N-tosylated amino alcohol (**S**₂) (1.0 equiv), propargyl bromide (1.2 equiv) and K₂CO₃ (1.5 equiv) in acetone (20 mL) was stirred at 80 °C for 18 h. After completion of reaction as indicated by TLC, the reaction mixture was cooled to

room temperature. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a Hexane/EtOAc = 9:1 to 3:2 solution as the eluting agent, resulting in the isolation of **S₃**.³

STEP III' (Synthesis of **1 from **S₂**):** A solution of **S₂** (1.0 equiv), substituted propargyl bromide (1.2 equiv) and K₂CO₃ (1.5 equiv) in acetone (20 mL) was stirred at 75 °C for 18 h. After completion of reaction as indicated by TLC, the reaction mixture was cooled to room temperature. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a Hexane/EtOAc = 9:1 to 3:2 solution as the eluting agent, resulting in the isolation of **1**.³

STEP IV (Synthesis of **1 from **S₃**):** A solution of **S₃** (1.0 equiv), aryl iodide (1.1 equiv), Pd(PPh₃)₂Cl₂ (0.01 equiv), CuI (0.02 equiv) and Et₃N (3.0 equiv) in dry DMF (5 mL) was stirred at room temperature for 12 h. After completion of reaction as indicated by TLC, the reaction mixture was quenched with sat. NH₄Cl solution and extracted three times with EtOAc. The combined organic layers were washed with brine, and dried over Na₂SO₄. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a Hexane/EtOAc = 9:1 to 3:2 solution as the eluting agent, resulting in the isolation of **1**.



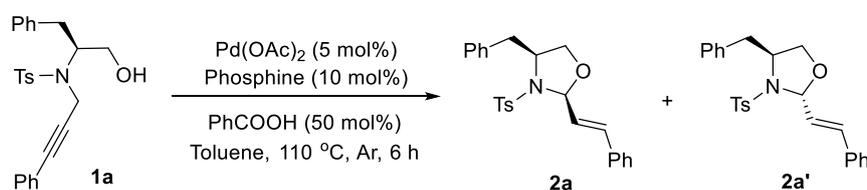
Scheme S2. Synthesis of **1** from **S₄**.

STEP I (Synthesis of **S₅ from **S₄**):** A solution of amino alcohol (**S₄**) (1.0 equiv) and TsCl (1.1 equiv) in dry DCM (20 mL) was stirred at 0 °C for 5 min. Et₃N (1.5 equiv) was added slowly and the reaction was stirred for 12 h at room temperature. After completion of reaction as indicated by TLC, the reaction was quenched with H₂O, and extracted three times with EtOAc. The combined organic layers were washed with brine, and dried over Na₂SO₄. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a Hexane/EtOAc = 3:2 to 1:1 solution as the eluting agent, resulting in the isolation of **S₅**.³

STEP II (Synthesis of **1 from **S**₅):** A solution of **S**₅ (1.0 equiv), substituted propargyl bromide (1.2 equiv) and K₂CO₃ (1.5 equiv) in acetone (20 mL) was stirred at 75 °C for 18 h. After completion of reaction as indicated by TLC, the reaction mixture was cooled to room temperature. Following filtration, the solvent was evaporated under reduced pressure. The crude mixture was purified using flash column chromatography on silica gel with a Hexane/EtOAc = 9:1 to 3:2 solution as the eluting agent, resulting in the isolation of **1**.³

Optimization of the reaction conditions for the synthesis of **2a**:

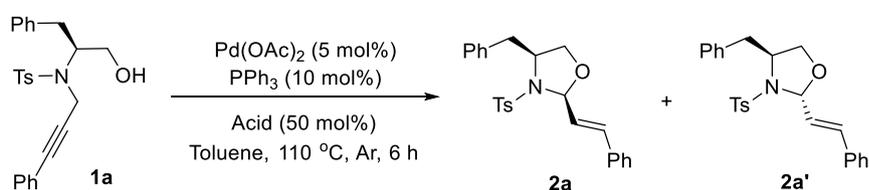
Table S1: Phosphine screening^a



Entry	Phosphine	Yield (%) ^b	Ratio (2a : 2a')
1	DPPP	46	52:48
2^c	CyJohnPhos	<5	-
3^c	ⁿ Bu ₃ P	18	35:65
4^c	P(2,4,6-trimethylphenyl) ₃	<5	-
5	ⁿ Oct ₃ P	29%	40:60
6	DPPBz	nr	-

^aReaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), phosphine (10 mol%), PhCOOH (50 mol%), and toluene (0.5 mL) were heated at 110 °C in a Schlenk tube under an Ar atmosphere for 6 h. ^bIsolated yield. ^c24h.

Table S2: Acid screening^a

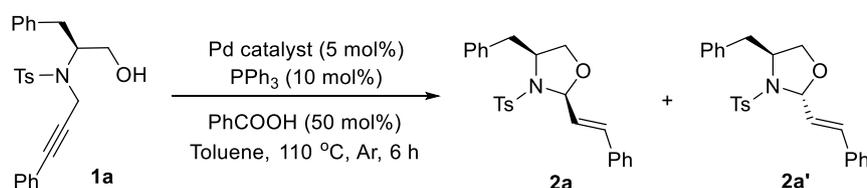


Entry	Acid	Yield (%) ^b	Ratio (2a : 2a')
1	CH ₃ COOH	71	91:9
2	DPP	59	88:12

3	(CH ₃) ₃ CCOOH	59	93:7
4	<i>p</i> -nitrobenzoic acid	41	93:7
5	CF ₃ COOH	46	90:10
6^c	PhCOOH	68	83:17

^aReaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), PPh₃ (10 mol%), acid (50 mol%), and toluene (0.5 mL) were heated at 110 °C in a Schlenk tube under an Ar atmosphere for 6 h. ^bIsolated yield. ^c15 mol% acid.

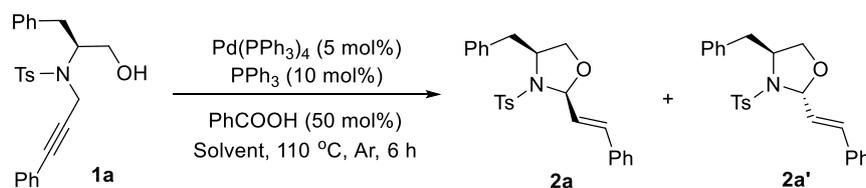
Table S3: Pd Catalyst screening^a



Entry	Pd catalyst	Phosphine	Yield (%) ^b	Ratio (2a:2a')
1	PdCl ₂	PPh ₃	<5	-
2^{c,d}	Pd(PPh ₃) ₄	PPh ₃	71	94:6
3	Pd(PPh ₃) ₄	--	62	94:6

^aReaction conditions: **1a** (0.2 mmol), Pd catalyst (5 mol%), PPh₃ (10 mol%), PhCOOH (50 mol%), and toluene (0.5 mL) were heated at 110 °C in a Schlenk tube under an Ar atmosphere for 6 h. ^bIsolated yield. ^c14h. ^dcatalyst loading 2.5 mol% and phosphine loading 5 mol%.

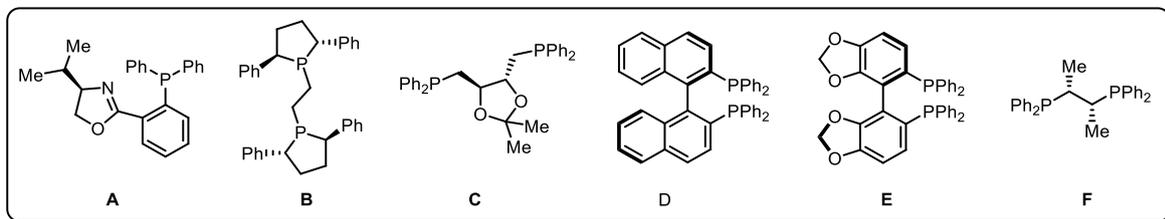
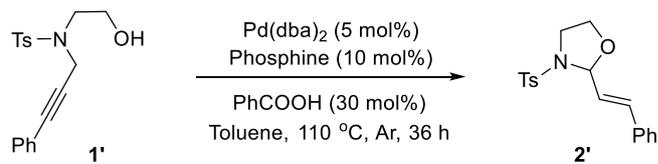
Table S4: Solvent screening^a



Entry	Solvent	Yield (%) ^b	Ratio (2a:2a')
1	THF	nr	-
2^c	Toluene-THF	63	72:28
3	Chlorobenzene	nr	-

^aReaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), PPh₃ (10 mol%), PhCOOH (50 mol%), and solvent (0.5 mL) were heated at 110 °C in a Schlenk tube under an Ar atmosphere for 6 h. ^bIsolated yield. ^cMixture solvent(1:1).

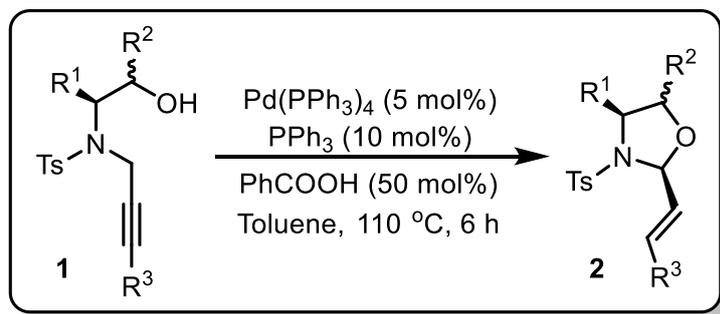
Table S5: Chiral phosphine screening with substrate 1^a



Entry	Phosphines	Yield (%) ^b	ee
1	A	nr	-
2	B	nr	-
3	C	34	racemic
4	D	nr	-
5 ^c	E	57	racemic
6	F	nr	-

^aReaction conditions: **1'** (0.2 mmol), $\text{Pd}(\text{dba})_2$ (5 mol%), phosphine (10 mol%), PhCOOH (30 mol%), and Toluene (0.5 mL) were heated at 110 °C in a Schlenk tube under an Ar atmosphere for 36 h. ^bIsolated yield. ^c9 h.

3 General procedure for the diastereoselective intramolecular *O*-allylation with alkynes:



Scheme S3

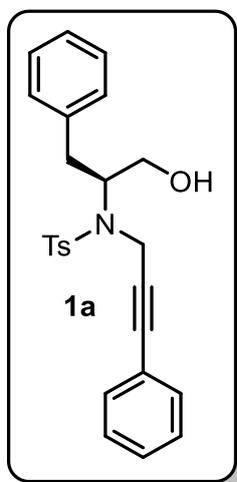
A flame-dried 10 mL Schlenk tube equipped with a stir bar was charged with **1** (0.2 mmol), Pd(PPh₃)₄ (0.01 mmol), PPh₃ (0.02 mmol), PhCOOH (0.1 mmol), dry and degassed toluene (0.5 mL) and capped with a glass stopper. The reaction mixture was vigorously stirred at 110 °C for 6 h under argon atmosphere. After completion of reaction as indicated by TLC, the reaction mixture was cooled to room temperature, diluted with EtOAc (10.0 mL) and washed with sat. NaHCO₃ followed by brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a dark residue. The crude mixture was purified by flash chromatography to give the pure product **2**.

4 Procedure for the gram-scale reaction:

A flame-dried 25 mL Schlenk tube equipped with a stir bar was charged with **1o** (1 g), Pd(PPh₃)₄ (129 mg), PPh₃ (59 mg), PhCOOH (136 mg), dry and degassed toluene (5 mL) and capped with a glass stopper. The reaction mixture was vigorously stirred at 110 °C for 6 h under argon atmosphere. After completion of reaction as indicated by TLC, the reaction mixture was cooled to room temperature, diluted with EtOAc (30.0 mL) and washed with sat. NaHCO₃ followed by brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a dark residue. The crude mixture was purified by flash chromatography (silica gel, hexane/EtOAc = 9:1 to 4:1) to give the pure solid product **2o** (884 mg, 88 %).

5 Characterisation data of final substrates:

(S)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-

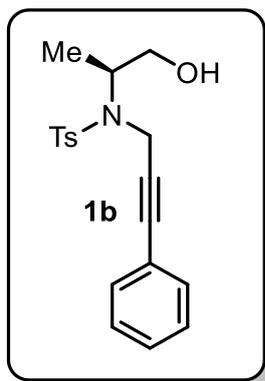


yl)benzenesulfonamide (**1a**). White solid; 85%; MP: 93-95 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.23 – 6.98 (m, 12H), 4.44 – 4.09 (m, 3H), 3.75 – 3.47 (m, 2H), 2.86 – 2.67 (m, 2H), 2.21 (s, 3H), 2.18 – 2.09 (m, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 143.4, 137.6, 137.5, 131.5, 129.5, 129.1, 128.7, 128.6, 128.3, 127.6, 126.6, 122.0, 85.0, 84.6, 62.2, 61.8, 36.8, 33.6, 21.4; HRMS (ESI) calculated for [M+Na]⁺ (C₂₅H₂₅O₃NSNa) *m/z* 442.1453, found 442.1469.

HPLC data for model substrate was checked to confirm no erosion in the enantiopurity during synthesis.

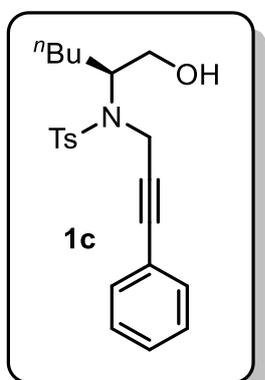
HPLC (IG-3 column, Hexane/Isopropanol = 80:20, 1.0 mL/min) *t_R* = 16.568 min (major), *t_R* = 18.545 min (minor), er: 99.72:0.28.

(S)-*N*-(1-hydroxypropan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1b**).



Yellow solid; 61%; MP: 69-71 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.18 (m, 7H), 4.45 – 4.26 (m, 2H), 4.20 – 4.09 (m, 1H), 3.76 – 3.67 (m, 1H), 3.63 – 3.54 (m, 1H), 2.56 (s, 1H), 2.33 (s, 3H), 1.12 (d, *J* = 7.0 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 143.4, 137.6, 131.4, 129.5, 128.5, 128.2, 127.4, 122.1, 85.1, 84.3, 64.4, 55.6, 32.9, 21.4, 14.6; HRMS (ESI) calculated for [M+Na]⁺ (C₁₉H₂₁O₃NSNa) *m/z* 366.1140, found 366.1136.

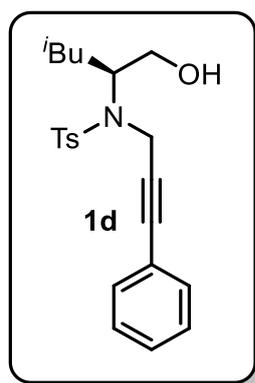
(S)-*N*-(1-hydroxyhexan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1c**).



Yellow oil; 58%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.16 (m, 7H), 4.47 – 4.37 (m, 1H), 4.30 – 4.20 (m, 1H), 4.03 – 3.93 (m, 1H), 3.73 – 3.57 (m, 2H), 2.40 (s, 1H), 2.31 (s, 3H), 1.47 (q, *J* = 7.4 Hz, 2H), 1.25 – 1.07 (m, 4H), 0.76 (t, *J* = 6.9 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 143.3, 137.7, 131.3, 129.3, 128.5, 128.2, 127.6, 122.0, 84.9, 84.1, 63.3, 60.3, 32.7, 28.5, 28.4, 22.4, 21.3, 13.7; HRMS (ESI) calculated for [M+Na]⁺ (C₂₂H₂₇O₃NSNa) *m/z* 408.1609, found

408.1624.

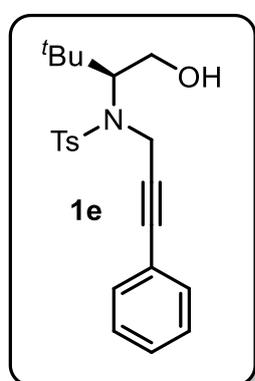
(S)-*N*-(1-hydroxy-4-methylpentan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-



yl)benzenesulfonamide (**1d**). Yellow oil; 45%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.31 – 7.17 (m, 7H), 4.47 – 4.35 (m, 1H), 4.34 – 4.22 (m, 1H), 4.14 – 4.03 (m, 1H), 3.74 – 3.55 (m, 2H), 2.44 (s, 1H), 2.31 (s, 3H), 1.58 – 1.41 (m, 2H), 1.31 – 1.23 (m, 1H), 0.86 – 0.78 (m, 6H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 143.3, 137.7, 131.3, 129.3, 128.5, 128.2, 127.7, 122.1, 85.0, 84.1, 63.4, 58.2, 38.0, 32.7, 24.5, 22.9, 22.1, 21.3; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{22}\text{H}_{27}\text{O}_3\text{NSNa}$) m/z

408.1609, found 408.1601.

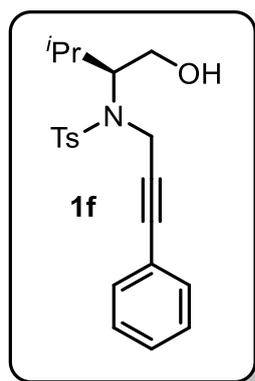
(S)-*N*-(1-hydroxy-3,3-dimethylbutan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-



yl)benzenesulfonamide (**1e**). White solid; 58%; MP: 91-93 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.23 – 7.15 (m, 3H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 7.2$ Hz, 2H), 4.57 – 4.44 (m, 1H), 4.30 – 4.18 (m, 1H), 3.93 – 3.73 (m, 3H), 2.20 (s, 3H), 1.73 (s, 1H), 0.95 (s, 9H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 143.5, 137.8, 131.5, 129.3, 128.8, 128.4, 128.3, 121.8, 84.9, 84.5, 68.5, 59.3, 34.7, 34.1, 28.6, 21.5; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{22}\text{H}_{27}\text{O}_3\text{NSNa}$) m/z 408.1609,

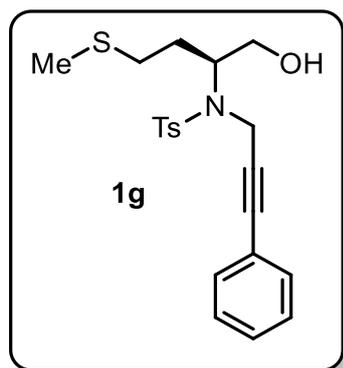
found 408.1606.

(S)-*N*-(1-hydroxy-3-methylbutan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-



yl)benzenesulfonamide (**1f**). Yellow oil; 68%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.14 (m, 7H), 4.65 – 4.50 (m, 1H), 4.17 – 4.06 (m, 1H), 3.85 – 3.67 (m, 3H), 2.33 (s, 3H), 2.00 – 1.80 (m, 2H), 0.99 (d, $J = 6.5$ Hz, 3H), 0.91 (d, $J = 6.7$ Hz, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 143.4, 138.0, 131.5, 129.3, 128.7, 128.3, 127.8, 121.8, 84.6, 84.4, 66.5, 61.8, 33.0, 27.5, 21.5, 20.6, 20.1; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{25}\text{O}_3\text{NSNa}$) m/z 394.1453, found 394.1468.

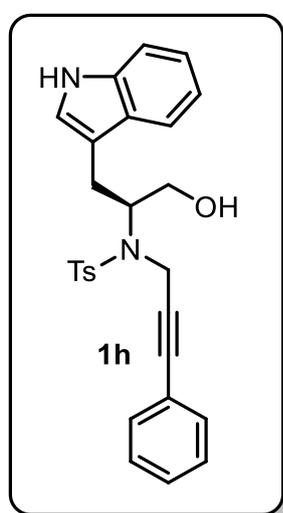
(*S*)-*N*-(1-hydroxy-4-(methylthio)butan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-



yl)benzenesulfonamide (**1g**). Yellow solid; 71%; MP: 94-96 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.09 (m, 7H), 4.41 – 4.19 (m, 2H), 4.12 – 4.01 (m, 1H), 3.68 – 3.53 (m, 2H), 2.39 – 2.21 (m, 6H), 1.90 (s, 3H), 1.84 – 1.63 (m, 2 H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.6, 137.6, 131.5, 129.5, 128.7, 128.3, 127.7, 122.0, 84.7, 84.5, 63.3, 59.3, 33.2, 30.9,

28.5, 21.5, 15.4; HRMS (ESI) calculated for [M+Na]⁺ (C₂₁H₂₅O₃NS₂Na) *m/z* 426.1174, found 426.1150.

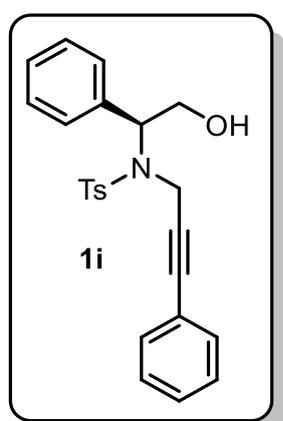
(*S*)-*N*-(1-hydroxy-3-(1*H*-indol-3-yl)propan-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-



yl)benzenesulfonamide (**1h**). Yellow solid; 68%; MP: 114-116 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.80 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.03 (m, 2H), 6.99 – 6.92 (m, 1H), 4.83 (t, *J* = 5.2 Hz, 1H), 4.53 – 4.39 (m, 2H), 4.13 (quint, *J* = 6.8 Hz, 1H), 3.65 – 3.48 (m, 2H), 3.19 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.93 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.31 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ 143.2, 138.2, 136.7, 131.6, 129.7, 129.1, 127.5, 127.4, 124.1, 122.6, 121.3, 118.8, 118.5, 111.9, 111.0, 87.3, 83.8, 61.9, 60.9, 33.8, 25.9,

21.4; HRMS (ESI) calculated for [M+H]⁺ (C₂₇H₂₇O₃N₂S) *m/z* 459.1742, found 459.1742.

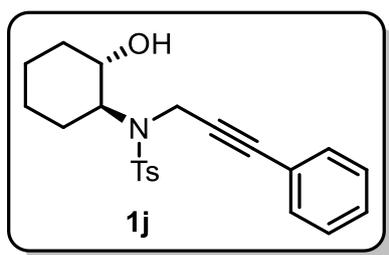
(*S*)-*N*-(2-hydroxy-1-phenylethyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide



(**1i**). Yellow oil; 73%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 7.18 – 7.15 (m, 2H), 5.32 – 5.22 (m, 1H), 4.59 – 4.50 (m, 1H), 4.30 – 4.22 (m, 1H), 4.17 – 4.08 (m, 1H), 3.98 – 3.90 (m, 1H), 2.37 (s, 3H), 2.02 – 1.94 (m, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.6, 137.8, 135.8, 131.5, 129.5, 128.8, 128.7, 128.4, 128.3, 128.0, 127.8, 121.8, 84.63, 84.59, 62.5, 62.0, 33.8, 21.5; HRMS (ESI) calculated for [M+Na]⁺ (C₂₄H₂₃O₃NSNa)

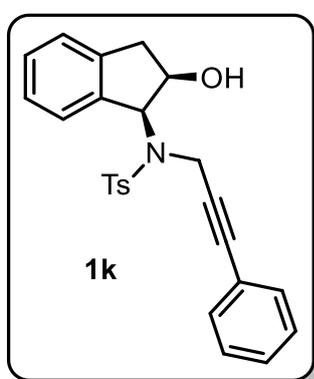
m/z 428.1296, found 428.1311.

N-((1S,2S)-2-hydroxycyclohexyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide



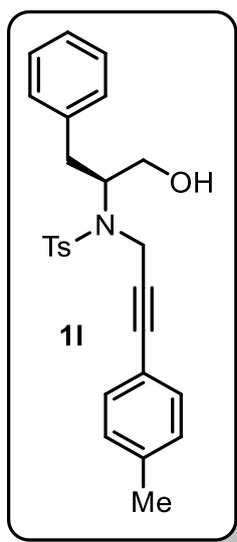
(**1j**). Yellow solid; 81%; MP: 98-100 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.09 (m, 7H), 4.44 – 4.34 (m, 1H), 4.26 – 4.16 (m, 1H), 3.63 – 3.51 (m, 2H), 2.32 – 2.18 (m, 4H), 2.08 – 1.98 (m, 1H), 1.68 – 1.57 (m, 3H), 1.53 – 1.40 (m, 1H), 1.31 – 1.10 (m, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.5, 137.7, 131.5, 129.5, 128.7, 128.4, 127.6, 122.0, 84.9, 84.7, 70.0, 64.4, 33.9, 33.1, 29.4, 25.4, 24.1, 21.5; HRMS (ESI) calculated for [M+Na]⁺ (C₂₂H₂₅O₃SNNa) *m/z* 406.1453, found 406.1462.

N-((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1k**).



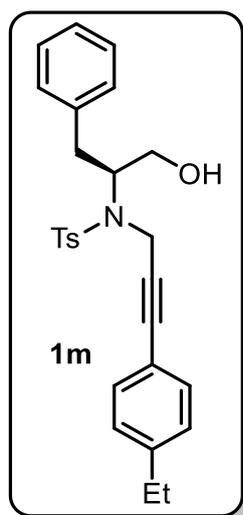
(**1k**). Yellow oil; 77%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.13 (m, 9H), 7.09 – 7.02 (m, 1H), 6.95 – 6.87 (m, 1H), 5.33 (d, *J* = 6.2 Hz, 1H), 4.74 – 4.63 (m, 1H), 4.36 – 4.07 (m, 2H), 3.23 – 2.94 (m, 3H), 2.29 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.3, 140.7, 137.5, 136.5, 131.2, 129.3, 128.7, 128.1, 127.9, 127.3, 126.6, 125.6, 125.2, 122.2, 85.7, 83.9, 72.9, 65.0, 39.3, 36.0, 21.2; HRMS (ESI) calculated for [M+Na]⁺ (C₂₅H₂₃O₃SNNa) *m/z* 440.1296, found 440.1295.

(S)-N-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (**1l**).



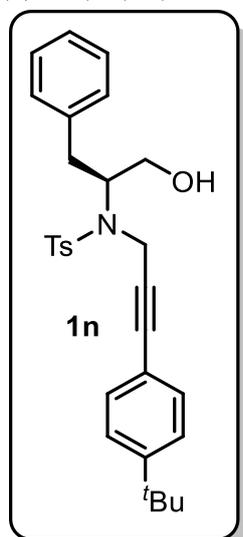
(**1l**). White solid; 81%; MP: 100-102 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.15 (m, 5H), 7.14 – 7.06 (m, 6H), 4.54 – 4.43 (m, 1H), 4.35 – 4.19 (m, 2H), 3.81 – 3.72 (m, 1H), 3.68 – 3.60 (m, 1H), 2.92 – 2.80 (m, 2H), 2.36 – 2.30 (m, 6H), 2.10 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.5, 139.0, 137.64, 137.61, 131.5, 129.6, 129.2, 129.1, 128.7, 127.7, 126.7, 119.0, 84.9, 84.3, 62.3, 61.9, 36.4, 33.7, 21.6; HRMS (ESI) calculated for [M+H]⁺ (C₂₆H₂₈NO₃S) *m/z* 434.1790, found 434.1801.

(*S*)-*N*-(3-(4-ethylphenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



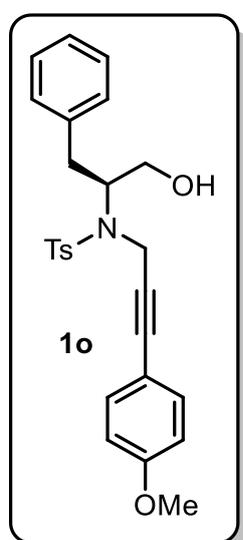
methylbenzenesulfonamide (1m). White solid; 81%; MP: 82-84 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.24 – 7.08 (m, 11H), 4.53 – 4.45 (m, 1H), 4.35 – 4.20 (m, 2H), 3.80 – 3.60 (m, 2H), 2.91 – 2.80 (m, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 2.33 (s, 3H), 2.20 – 2.13 (m, 1H), 1.20 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 145.2, 143.4, 137.64, 137.57, 131.6, 129.5, 129.2, 128.7, 127.9, 127.7, 126.7, 119.2, 84.9, 84.3, 62.2, 61.8, 36.3, 33.7, 28.8, 21.5, 15.4; HRMS (ESI) calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{27}\text{H}_{30}\text{O}_3\text{SN}$) m/z 448.1946, found 448.1956.

(*S*)-*N*-(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



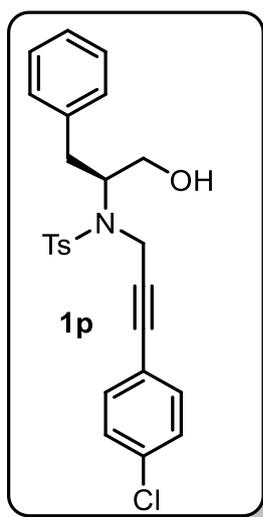
methylbenzenesulfonamide (1n). Yellow oil; 78%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.08 (m, 11H), 4.58 – 4.42 (m, 1H), 4.40 – 4.16 (m, 2H), 3.85 – 3.55 (m, 2H), 2.93 – 2.75 (m, 2H), 2.32 (s, 3H), 2.20 (s, 1H), 1.29 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 152.0, 143.4, 137.7, 137.6, 131.3, 129.5, 129.2, 128.7, 127.7, 126.7, 125.4, 119.0, 84.9, 84.3, 62.2, 61.8, 36.3, 34.8, 33.7, 31.2, 21.5; HRMS (ESI) calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{29}\text{H}_{34}\text{O}_3\text{NS}$) m/z 476.2259, found 476.2277.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-



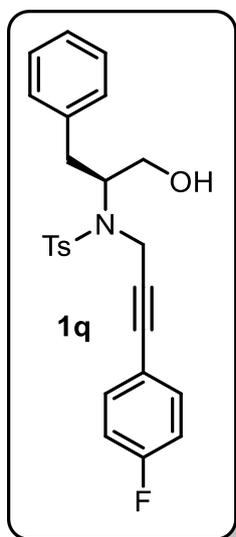
methylbenzenesulfonamide (1o). White solid; 86%; MP: 93-95 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.27 – 7.16 (m, 7H), 7.15 – 7.08 (m, 2H), 6.84 – 6.77 (m, 2H), 4.56 – 4.44 (m, 1H), 4.34 – 4.19 (m, 2H), 3.80 (s, 3H), 3.79 – 3.71 (m, 1H), 3.69 – 3.59 (m, 1H), 2.91 – 2.80 (m, 2H), 2.35 (s, 3H), 2.10 – 1.99 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 160.0, 143.5, 137.67, 137.65, 133.1, 129.6, 129.3, 128.8, 127.8, 126.8, 114.1, 84.8, 83.6, 62.3, 61.9, 55.4, 36.4, 33.7, 21.6; HRMS (ESI) calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{26}\text{H}_{28}\text{O}_4\text{NS}$) m/z 450.1739, found 450.1752.

(*S*)-*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



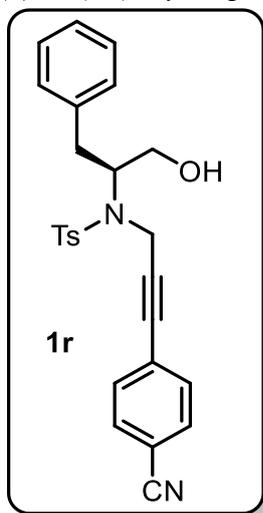
methylbenzenesulfonamide (1p). White solid; 80%; MP: 148-150 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.14 (m, 9H), 7.12 – 7.07 (m, 2H), 4.50 – 4.20 (m, 3H), 3.79 – 3.62 (m, 2H), 2.92 – 2.78 (m, 2H), 2.33 (s, 3H), 2.20 – 2.13 (m, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.5, 137.53, 137.46, 134.7, 132.8, 129.5, 129.1, 128.70, 128.67, 127.6, 126.7, 120.6, 86.1, 83.5, 62.3, 61.8, 36.2, 33.6, 21.5; HRMS (ESI) calculated for [M+H]⁺ (C₂₅H₂₅NO₃SCl) *m/z* 454.1244, found 454.1238.

(*S*)-*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



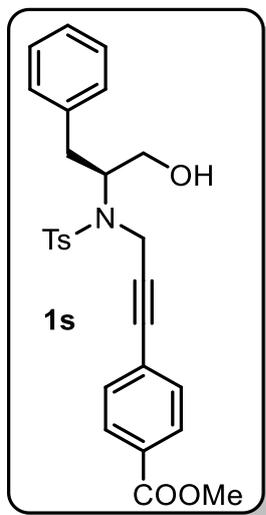
methylbenzenesulfonamide (1q). White solid; 83%; MP: 114-116 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.16 (m, 7H), 7.14 – 7.07 (m, 2H), 7.02 – 6.92 (m, 2H), 4.52 – 4.18 (m, 3H), 3.83 – 3.60 (m, 2H), 2.93 – 2.77 (m, 2H), 2.35 (s, 3H), 2.12 – 1.95 (m, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 162.9 (d, *J* = 251.5 Hz), 143.6, 137.57, 137.59, 133.6 (d, *J* = 8.1 Hz), 129.6, 129.2, 128.8, 127.7, 126.8, 118.2 (d, *J* = 4.0 Hz), 115.8 (d, *J* = 22.2 Hz), 84.8, 83.7, 62.4, 61.9, 36.4, 33.7, 21.6; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -110.1; HRMS (ESI) calculated for [M+H]⁺ (C₂₅H₂₅NO₃SF) *m/z* 438.1539, found 438.1359.

(*S*)-*N*-(3-(4-cyanophenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



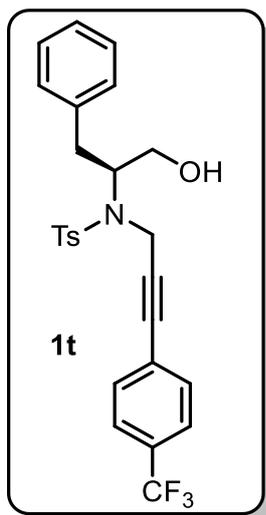
methylbenzenesulfonamide (1r). White solid; 80%; MP: 192-194 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.17 (m, 5H), 7.12 – 7.07 (m, 2H), 4.53 – 4.36 (m, 2H), 4.29 – 4.19 (m, 1H), 3.82 – 3.66 (m, 2H), 2.92 – 2.78 (m, 2H), 2.37 (s, 3H), 1.97 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.8, 137.4, 132.2, 132.1, 129.7, 129.2, 128.8, 127.7, 127.1, 126.9, 118.4, 112.2, 89.8, 83.0, 62.5, 61.8, 36.3, 33.8, 21.6; HRMS (ESI) calculated for [M+Na]⁺ (C₂₆H₂₄N₂O₃SNa) *m/z* 467.1405, found 467.1409.

methyll (S)-4-(3-((N-(1-hydroxy-3-phenylpropan-2-yl)-4-methylphenyl)sulfonamido)prop-1-



yn-1-yl)benzoate (1s). White solid; 75%; MP: 123-135 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.16 – 7.07 (m, 4H), 4.55 – 4.37 (m, 2H), 4.32 – 4.21 (m, 1H), 3.88 (s, 3H), 3.82 – 3.64 (m, 2H), 3.01 – 2.77 (m, 2H), 2.58 (s, 1H), 2.30 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 166.3, 143.3, 137.5, 137.3, 131.3, 129.7, 129.4, 129.3, 129.0, 128.5, 127.4, 126.8, 126.5, 88.3, 83.6, 62.2, 61.6, 52.2, 35.9, 33.6, 21.3; HRMS (ESI) calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{27}\text{H}_{28}\text{NO}_5\text{S}$) m/z 478.1688, found 478.1689.

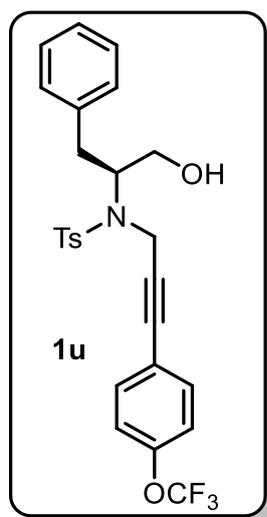
(S)-N-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-



1-yl)benzenesulfonamide (1t). White solid; 79%; MP: 166-168 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.25 – 7.15 (m, 5H), 7.14 – 7.07 (m, 2H), 4.55 – 4.34 (m, 2H), 4.31 – 4.20 (m, 1H), 3.83 – 3.64 (m, 2H), 2.96 – 2.79 (m, 2H), 2.35 (s, 3H), 2.04 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 143.7, 137.5, 131.9, 130.5 (q, J = 33.3 Hz), 129.6, 129.2, 128.8, 127.7, 126.9, 126.0 (q, J = 1.0 Hz), 125.4 (q, J = 3.0 Hz), 123.9 (q, J = 272.7 Hz), 87.7, 83.3, 62.4, 61.9, 36.3, 33.7, 21.6; $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3): δ -62.9; HRMS (ESI) calculated for $[\text{M}+\text{H}]^+$

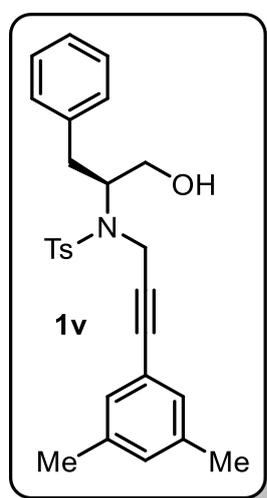
($\text{C}_{26}\text{H}_{25}\text{O}_3\text{SNF}_3$) m/z 488.1507, found 488.1523.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-*N*-(3-(4-(trifluoromethoxy)phenyl)prop-2-yn-1-yl)benzenesulfonamide (**1u**).



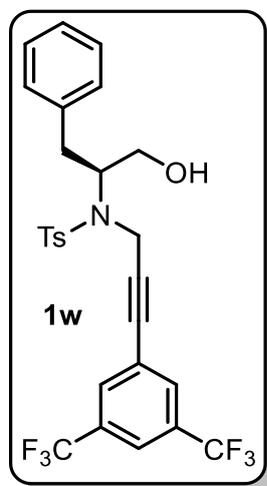
White solid; 74%; MP: 151-153 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.17 – 7.08 (m, 6H), 4.51 – 4.32 (m, 2H), 4.31 – 4.21 (m, 1H), 3.82 – 3.62 (m, 2H), 2.94 – 2.78 (m, 2H), 2.36 – 2.26 (m, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 149.1, 143.5, 137.6, 137.5, 133.1, 129.5, 129.1, 128.7, 127.6, 126.7, 121.0, 120.8, 120.4 (q, *J* = 258.6 Hz), 86.1, 83.2, 62.3, 61.8, 36.1, 33.6, 21.4; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -57.8; HRMS (ESI) calculated for [M+H]⁺ (C₂₆H₂₅NO₄SF₃) m/z 504.1456, found 504.1458.

(*S*)-*N*-(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



methylbenzenesulfonamide (**1v**). Yellow oil; 83%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.15 – 7.10 (m, 2H), 6.94 (s, 1H), 6.85 (s, 2H), 4.54 – 4.43 (m, 1H), 4.34 – 4.21 (m, 2H), 3.80 – 3.72 (m, 1H), 3.68 – 3.60 (m, 1H), 2.91 – 2.80 (m, 2H), 2.35 (s, 3H), 2.26 (s, 6H), 2.10 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.4, 138.0, 137.71, 137.68, 130.7, 129.5, 129.3, 129.2, 128.7, 127.7, 126.7, 121.7, 85.1, 84.2, 62.3, 61.9, 36.4, 33.7, 21.6, 21.1; HRMS (ESI) calculated for [M+H]⁺ (C₂₇H₃₀O₃NS) m/z 448.1946, found 448.1958.

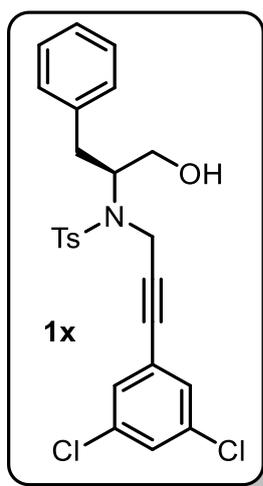
(*S*)-*N*-(3-(3,5-bis(trifluoromethyl)phenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-



4-methylbenzenesulfonamide (**1w**). White solid; 77%; MP: 105-109 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.79 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.63 (s, 2H), 7.24 – 7.11 (m, 7H), 4.55 – 4.41 (m, 2H), 4.38 – 4.29 (m, 1H), 3.81 – 3.69 (m, 2H), 2.98 – 2.88 (m, 1H), 2.86 – 2.79 (m, 1H), 2.59 (s, 1H), 2.33 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.8, 137.6, 137.5, 131.9 (q, *J* = 34.3 Hz), 131.4, 129.5, 129.1, 128.6, 127.6, 126.7, 124.7, 122.9 (q, *J* = 273.7 Hz), 121.9 (q, *J* = 4.0 Hz), 89.0, 81.4, 62.6, 61.7, 36.0, 33.6, 21.2; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -63.1;

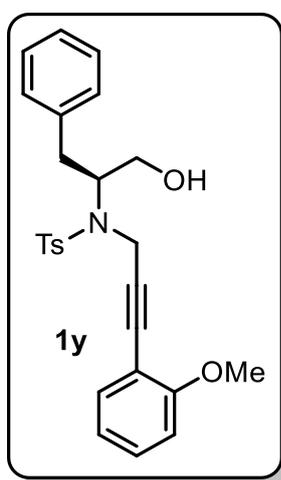
HRMS (ESI) calculated for [M+H]⁺ (C₂₇H₂₄O₃SNF₆) m/z 556.1381, found 556.1386.

(*S*)-*N*-(3-(3,5-dichlorophenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



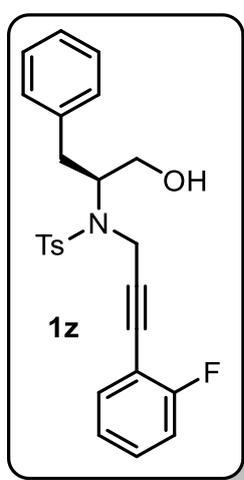
methylbenzenesulfonamide (**1x**). White solid; 81%; MP: 92-94 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.17 (m, 6H), 7.14 – 7.09 (m, 2H), 7.06 – 7.00 (m, 2H), 4.48 – 4.25 (m, 3H), 3.77 – 3.64 (m, 2H), 2.93 – 2.77 (m, 2H), 2.38 (s, 3H), 2.17 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.7, 137.6, 137.5, 134.9, 129.7, 129.6, 129.2, 129.0, 128.7, 127.6, 126.8, 124.9, 87.7, 81.9, 62.4, 61.8, 36.2, 33.6, 21.6; HRMS (ESI) calculated for [M+H]⁺ (C₂₅H₂₄O₃SNCl₂) *m/z* 488.0854, found 488.0851.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-



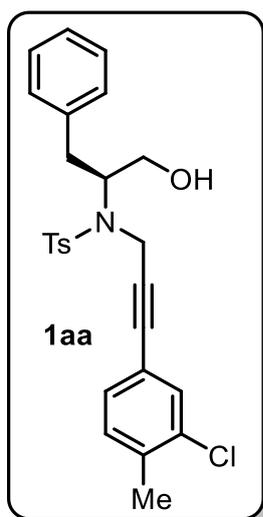
methylbenzenesulfonamide (**1y**). Yellow oil; 84%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.05 (m, 9H), 6.90 – 6.83 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.70 – 4.56 (m, 1H), 4.29 – 4.16 (m, 2H), 3.82 – 3.73 (m, 1H), 3.68 (s, 3H), 3.65 – 3.56 (m, 1H), 2.92 – 2.80 (m, 2H), 2.79 – 2.70 (m, 1H), 2.25 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 159.8, 143.0, 137.7, 137.6, 130.0, 129.1, 128.5, 127.7, 126.5, 120.4, 111.1, 110.3, 89.1, 80.8, 61.7, 55.3, 36.2, 22.4, 21.4; HRMS (ESI) calculated for [M+H]⁺ (C₂₆H₂₈NO₄S) *m/z* 450.1739, found 450.1723.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-



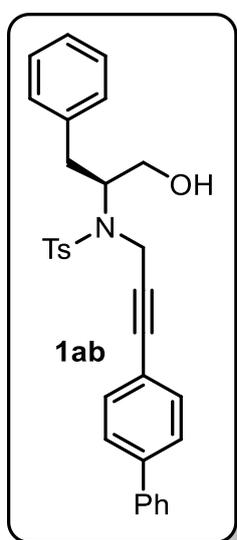
methylbenzenesulfonamide (**1z**). Yellow oil; 82%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.16 (m, 5H), 7.16 – 7.07 (m, 4H), 7.06 – 6.98 (m, 2H), 4.57 – 4.35 (m, 2H), 4.27 – 4.11 (m, 1H), 3.82 – 3.61 (m, 2H), 2.96 – 2.78 (m, 2H), 2.47 – 2.38 (m, 1H), 2.28 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 162.9 (d, *J* = 252.5 Hz), 143.5, 137.8, 137.4, 133.5, 130.5 (d, *J* = 8.1 Hz), 129.5, 129.2, 128.6, 127.6, 126.6, 124.1 (d, *J* = 4.0 Hz), 115.5 (d, *J* = 21.2 Hz), 110.7 (d, *J* = 16.2 Hz), 90.5 (d, *J* = 3.0 Hz), 78.2, 62.2, 61.8, 36.1, 33.8, 21.5; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -110.1; HRMS (ESI) calculated for [M+Na]⁺ (C₂₅H₂₄NO₃SFNa) *m/z* 460.1359, found 460.1371.

(*S*)-*N*-(3-(3-chloro-4-methylphenyl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



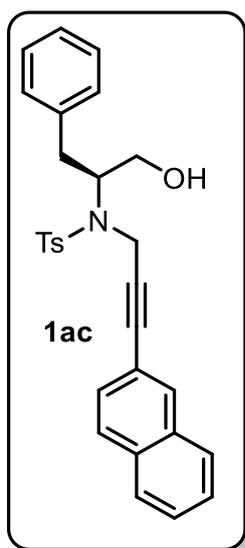
methylbenzenesulfonamide (1aa). White solid; 84%; MP: 100-102 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.09 (m, 9H), 7.05 – 7.00 (m, 1H), 4.53 – 4.20 (m, 3H), 3.79 – 3.61 (m, 2H), 2.92 – 2.77 (m, 2H), 2.41 – 2.30 (s, 6H), 2.18 – 2.11 (m, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 143.6, 137.6, 137.1, 134.2, 131.8, 130.9, 129.7, 129.5, 129.2, 128.7, 127.6, 126.7, 121.0, 85.5, 83.3, 62.3, 61.8, 36.2, 33.6, 21.5, 20.1; HRMS (ESI) calculated for [M+H]⁺ (C₂₆H₂₇NO₃SCl) *m/z* 468.1400, found 468.1404.

(*S*)-*N*-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-



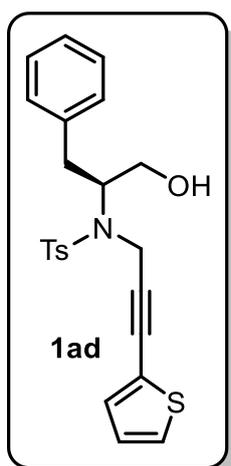
methylbenzenesulfonamide (1ab). White solid; 88%; MP: 99-101 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.16 (m, 5H), 7.15 – 7.10 (m, 2H), 4.57 – 4.47 (m, 1H), 4.40 – 4.21 (m, 2H), 3.85 – 3.62 (m, 2H), 2.94 – 2.81 (m, 2H), 2.34 (s, 3H), 2.21 – 2.06 (m, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 143.5, 141.5, 140.2, 137.62, 137.59, 132.0, 129.6, 129.2, 129.0, 128.7, 127.9, 127.7, 127.1, 127.0, 126.8, 120.9, 85.7, 84.6, 62.3, 61.9, 36.3, 33.7, 21.6; HRMS (ESI) calculated for [M+H]⁺ (C₃₁H₃₀O₃NS) *m/z* 496.1946, found 496.1965.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-*N*-(3-(naphthalen-2-yl)prop-2-yn-1-



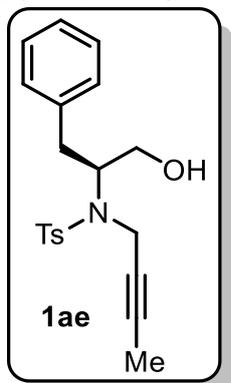
yl)benzenesulfonamide (**1ac**). White solid; 85%; MP: 111-113 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.81 – 7.65 (m, 6H), 7.49 – 7.40 (m, 2H), 7.28 – 7.07 (m, 8H), 4.56 – 4.23 (m, 3H), 3.85 – 3.62 (m, 2H), 2.97 – 2.78 (m, 2H), 2.45 – 2.33 (m, 1H), 2.24 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.3, 137.6, 137.5, 132.8, 132.7, 131.5, 129.4, 129.1, 128.6, 128.0, 127.7, 127.61, 127.57, 126.9, 126.7, 126.6, 119.3, 85.3, 84.9, 62.3, 61.8, 36.1, 33.7, 21.4; HRMS (ESI) calculated for [M+H]⁺ (C₂₉H₂₈NO₃S) m/z 470.1790, found 470.1810.

(*S*)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-



yl)benzenesulfonamide (**1ad**). Yellow solid; 79%; MP: 87-89 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.15 (m, 6H), 7.12 – 7.05 (m, 3H), 6.95 – 6.90 (m, 1H), 4.51 – 4.35 (m, 2H), 4.26 – 4.17 (m, 1H), 3.76 – 3.60 (m, 2H), 2.92 – 2.76 (m, 2H), 2.33 (s, 3H), 2.20 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.5, 137.6, 137.3, 132.4, 129.5, 129.1, 128.6, 127.6, 127.0, 126.6, 122.0, 89.0, 78.1, 62.2, 61.7, 36.2, 33.9, 21.5; HRMS (ESI) calculated for [M+H]⁺ (C₂₃H₂₄O₃NS₂) m/z 426.1198, found 426.1192.

(*S*)-*N*-(but-2-yn-1-yl)-*N*-(1-hydroxy-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide (**1ae**).

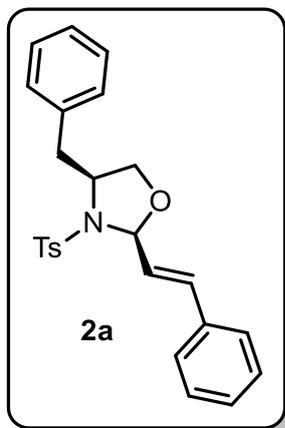


Yellow oil; 57%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.16 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 2H), 4.25 – 4.12 (m, 2H), 4.05 – 3.97 (m, 1H), 3.74 – 3.66 (m, 1H), 3.63 – 3.55 (m, 1H), 2.85 – 2.72 (m, 2H), 2.38 (s, 3H), 2.29 (s, 1H), 1.69 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.3, 137.6, 137.5, 129.3, 129.1, 128.5, 127.5, 126.5, 80.8, 75.1, 62.1, 61.5, 36.0, 33.1, 21.4, 3.3; HRMS (ESI) calculated for [M+Na]⁺

(C₂₀H₂₃O₃SNNa) m/z 380.1296, found 380.1294.

6 Characterisation data of cyclized products:

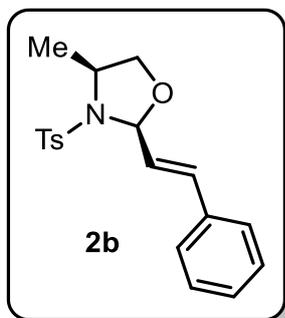
(2*S*,4*S*)-4-benzyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2a**). Yellow oil, 75 mg, 90%; column



chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.40 – 7.26 (m, 9H), 7.24 – 7.17 (m, 3H), 6.75 (d, $J = 15.9$ Hz, 1H), 6.05 (dd, $J = 15.9, 5.3$ Hz, 1H), 5.64 (d, $J = 5.2$ Hz, 1H), 4.03 – 3.92 (m, 1H), 3.80 – 3.73 (m, 1H), 3.51 – 3.44 (m, 1H), 3.28 – 3.20 (m, 1H), 2.88 – 2.80 (m, 1H), 2.39 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.3, 137.3, 135.9, 134.8, 134.0, 130.0, 129.6, 128.8, 128.7, 128.4, 128.0, 127.1, 126.9, 126.4, 91.7, 69.7, 60.6, 40.9, 21.7; HRMS (ESI) calculated for

$[\text{M}+\text{Na}]^+$ ($\text{C}_{25}\text{H}_{25}\text{O}_3\text{NSNa}$) m/z 442.1453, found 442.1468.

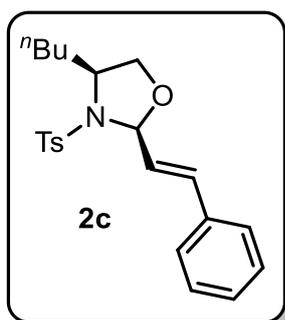
(2*S*,4*S*)-4-methyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2b**). White solid, 56 mg, 82%; MP: 142-



144 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.23 (m, 7H), 6.80 (d, $J = 15.9$ Hz, 1H), 6.16 (dd, $J = 15.9, 4.8$ Hz, 1H), 5.69 (d, $J = 4.7$ Hz, 1H), 3.85 (sxt, $J = 6.2$ Hz, 1H), 3.78 – 3.68 (m, 1H), 3.64 – 3.54 (m, 1H), 2.41 (s, 3H), 1.37 (d, $J = 6.3$ Hz, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.2, 135.9, 134.7, 133.8, 130.0, 128.7,

128.4, 128.0, 127.1, 126.7, 91.3, 72.0, 55.3, 21.7, 20.4; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{19}\text{H}_{21}\text{O}_3\text{NSNa}$) m/z 366.1140, found 366.1163.

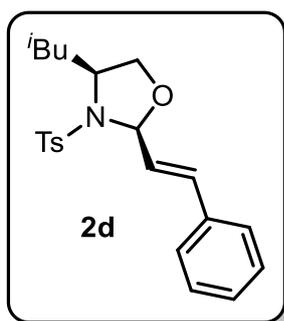
(2*S*,4*S*)-4-butyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2c**). White solid, 60 mg, 78%; MP: 112-114



°C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.24 (m, 5H), 6.77 (d, $J = 15.9$ Hz, 1H), 6.14 (dd, $J = 15.9, 4.9$ Hz, 1H), 5.68 (d, $J = 4.8$ Hz, 1H), 3.79 – 3.70 (m, 1H), 3.70 – 3.63 (m, 1H), 3.63 – 3.53 (m, 1H), 2.42 (s, 3H), 1.93 – 1.81 (m, 1H), 1.60 – 1.49 (m, 1H), 1.38 – 1.22 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C $\{^1\text{H}\}$

NMR (101 MHz, CDCl_3): δ 144.2, 136.0, 134.9, 133.7, 130.0, 128.7, 128.4, 128.0, 127.1, 126.7, 91.3, 70.6, 59.6, 34.7, 28.3, 22.6, 21.7, 14.1; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{22}\text{H}_{27}\text{O}_3\text{NSNa}$) m/z 408.1609, found 408.1639.

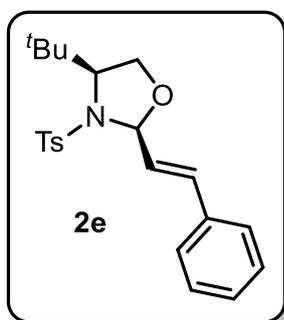
(2*S*,4*S*)-4-isobutyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2d**). White solid, 61 mg, 79%; MP: 126-



128 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.24 (m, 7H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 4.6 Hz, 1H), 5.71 (d, *J* = 4.5 Hz, 1H), 3.88 – 3.75 (m, 1H), 3.68 – 3.55 (m, 2H), 2.43 (s, 3H), 1.85 – 1.74 (m, 1H), 1.71 – 1.61 (m, 1H), 1.47 – 1.37 (m, 1H), 0.99 – 0.87 (m, 6H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 144.2,

135.9, 134.8, 133.5, 129.9, 128.6, 128.3, 127.9, 127.0, 126.7, 91.1, 70.9, 57.9, 44.0, 25.2, 23.0, 22.3, 21.6; HRMS (ESI) calculated for [M+H]⁺ (C₂₂H₂₈O₃NS) m/z 386.1790, found 386.1768.

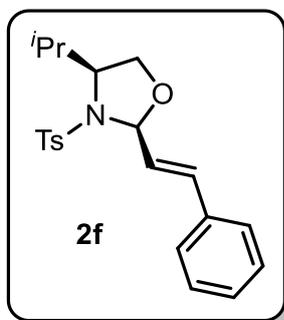
(2*S*,4*S*)-4-(*tert*-butyl)-2-((*E*)-styryl)-3-tosyloxazolidine (**2e**). White solid, 58 mg, 75%; MP:



116-118 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.25 (m, 7H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 5.5 Hz, 1H), 5.48 (d, *J* = 5.4 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.69 – 3.59 (m, 1H), 3.26 – 3.14 (m, 1H), 2.40 (s, 3H), 0.99 (s, 9H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 144.4, 136.1, 134.7, 134.2, 130.0, 128.7, 128.6,

128.3, 127.1, 126.1, 92.6, 68.2, 67.7, 34.2, 27.5, 21.7; HRMS (ESI) calculated for [M+H]⁺ (C₂₂H₂₈O₃NS) m/z 386.1790, found 386.1815.

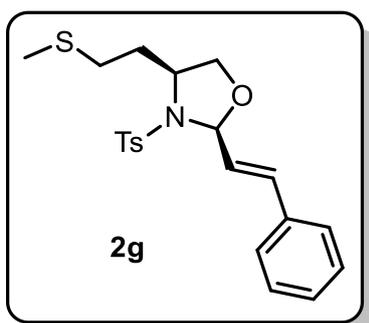
(2*S*,4*S*)-4-isopropyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2f**). White solid, 51 mg, 69%; MP: 117-



119 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.33 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 15.9, 5.0 Hz, 1H), 5.61 (d, *J* = 5.0 Hz, 1H), 3.82 – 3.77 (m, 1H), 3.58 – 3.52 (m, 1H), 3.41 – 3.34 (m, 1H), 2.40 (s, 3H), 1.96 – 1.84 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.7 Hz,

3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 144.3, 136.0, 135.0, 133.6, 130.0, 128.7, 128.4, 128.1, 127.0, 126.6, 91.5, 68.3, 65.2, 31.5, 21.7, 19.9, 18.6; HRMS (ESI) calculated for [M+Na]⁺ (C₂₁H₂₅O₃NSNa) m/z 394.1453, found 394.1473.

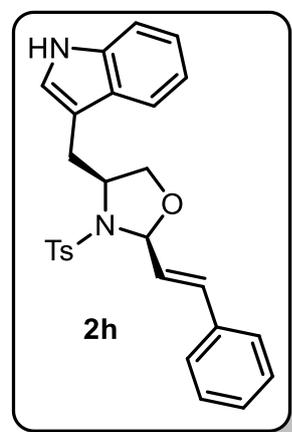
(2*S*,4*S*)-4-(2-(methylthio)ethyl)-2-((*E*)-styryl)-3-tosyloxazolidine (**2g**). White solid, 58 mg,



72%; MP: 110-112 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.24 (m, 7H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9, 4.8 Hz, 1H), 5.67 (d, *J* = 4.8 Hz, 1H), 4.02 (m, 1H), 3.72 – 3.63 (m, 1H), 3.60 – 3.50 (m, 1H), 2.68 – 2.52 (m, 2H), 2.42 (s, 3H), 2.18 – 2.06 (m, 4H), 1.87 –

1.74 (m, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.4, 135.8, 134.6, 133.8, 130.1, 128.7, 128.4, 128.1, 127.1, 126.5, 91.4, 70.6, 58.2, 33.9, 30.6, 21.7, 15.5; HRMS (ESI) calculated for [M+Na]⁺ (C₂₁H₂₅O₃NS₂Na) m/z 426.1174, found 426.1185.

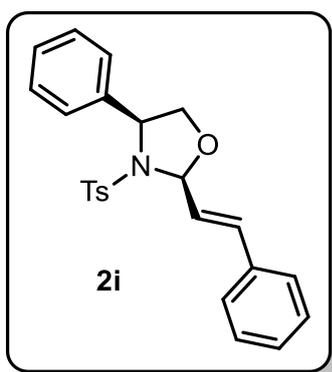
(2*S*,4*S*)-4-((1*H*-indol-3-yl)methyl)-2-((*E*)-styryl)-3-tosyloxazolidine (**2h**). Yellow oil, 78 mg,



85%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 8.08 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.69 (m, 1H), 7.37 – 7.30 (m, 5H), 7.30 – 7.27 (m, 2H), 7.24 – 7.13 (m, 3H), 7.00 – 6.95 (m, 1H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 5.3 Hz, 1H), 5.65 (d, *J* = 5.2 Hz, 1H), 4.15 – 4.07 (m, 1H), 3.82 – 3.75 (m, 1H), 3.46 – 3.34 (m, 2H), 3.06 – 2.95 (m, 1H), 2.37 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.2, 136.3, 135.8, 134.7, 133.8, 130.0, 128.6, 128.3, 127.9, 127.4, 127.0, 126.6,

122.8, 122.3, 119.8, 118.9, 111.5, 111.4, 91.7, 70.1, 59.7, 30.8, 21.6; HRMS (ESI) calculated for [M+H]⁺ (C₂₇H₂₇O₃N₂S) m/z 459.1742, found 459.1745.

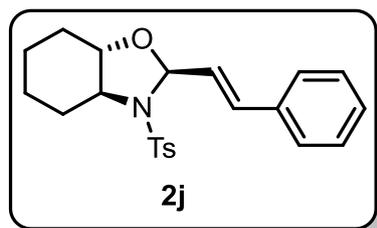
(2*S*,4*S*)-4-phenyl-2-((*E*)-styryl)-3-tosyloxazolidine (**2i**). Yellow oil, 60 mg, 74%; column



chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.27 (m, 11H), 7.25 – 7.22 (m, 1H), 6.83 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 5.5 Hz, 1H), 5.86 (d, *J* = 5.4 Hz, 1H), 4.87 (t, *J* = 6.2 Hz, 1H), 4.13 – 4.06 (m, 1H), 4.02 – 3.97 (m, 1H), 2.40 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.2, 139.1, 125.9, 135.2, 134.5, 129.9, 128.8, 128.7, 128.5, 128.1, 127.12, 127.10, 125.9, 92.2,

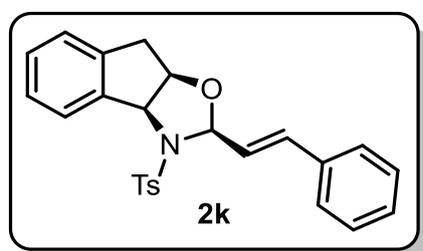
73.5, 62.7, 21.7; HRMS (ESI) calculated for [M+Na]⁺ (C₂₄H₂₃O₃NSNa) m/z 428.1296, found 428.1311.

(2*S*,3*aS*,7*aS*)-2-((*E*)-styryl)-3-tosyl-3,3,8,8-tetrahydrobenzo[*d*]oxazole (**2j**). Yellow oil, 66 mg, 86%;



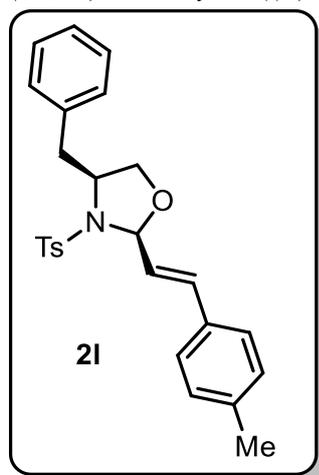
column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.28 – 7.21 (m, 4H), 7.20 – 7.15 (m, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 4.4 Hz, 1H), 5.50 (d, *J* = 4.4 Hz, 1H), 3.54 – 3.44 (m, 1H), 2.51 – 2.34 (m, 5H), 2.02 – 1.94 (m, 1H), 1.77 – 1.67 (m, 2H), 1.43 – 1.15 (m, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.3, 136.1, 133.4, 132.7, 130.0, 128.7, 128.2, 127.1, 127.0, 90.5, 80.9, 64.9, 29.9, 29.3, 24.1, 23.5, 21.7; HRMS (ESI) calculated for [M+Na]⁺ (C₂₂H₂₅O₃SNNa) *m/z* 406.1453, found 406.1444.

(2*S*,3*aS*,8*aR*)-2-((*E*)-styryl)-3-tosyl-3,3*a*,8,8*a*-tetrahydro-2*H*-indeno[1,2-*d*]oxazole (**2k**).



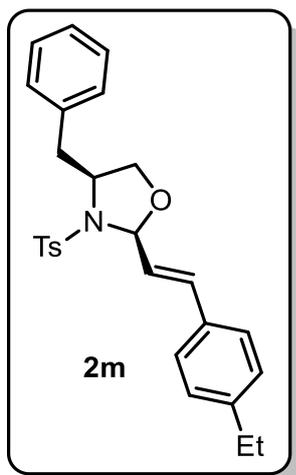
White solid, 59 mg, 71%; MP: 148-150 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.14 – 7.05 (m, 4H), 7.02 – 6.95 (m, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.66 (d, *J* = 6.6 Hz, 1H), 5.45 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.34 (d, *J* = 5.5 Hz, 1H), 4.37 – 4.25 (m, 1H), 3.08 – 2.91 (m, 2H), 2.33 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.5, 140.1, 135.8, 135.3, 133.8, 130.1, 129.0, 128.4, 128.13, 128.08, 127.7, 126.9, 126.3, 125.3, 93.0, 81.5, 67.7, 38.1, 21.7; HRMS (ESI) calculated for [M+Na]⁺ (C₂₅H₂₃O₃SNNa) *m/z* 440.1296, found 440.1303.

(2*S*,4*S*)-4-benzyl-2-((*E*)-4-methylstyryl)-3-tosyl-oxazolidine (**2l**). White solid, 80 mg, 92%;



MP: 110-112 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.26 (m, 6H), 7.24 – 7.10 (m, 5H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.02 (dd, *J* = 15.8, 5.3 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.81 – 3.73 (m, 1H), 3.52 – 3.44 (m, 1H), 3.31 – 3.20 (m, 1H), 2.90 – 2.80 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.3, 138.4, 137.8, 134.9, 134.0, 133.1, 130.1, 129.6, 129.4, 128.8, 128.0, 127.1, 127.0, 125.3, 91.9, 69.7, 60.7, 41.0, 21.7, 21.4; HRMS (ESI) calculated for [M+Na]⁺ (C₂₆H₂₇O₃NSNa) *m/z* 456.1609, found 456.1619.

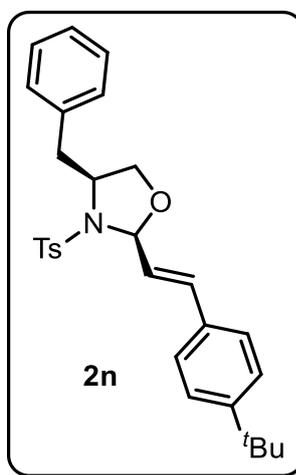
(2*S*,4*S*)-4-benzyl-2-((*E*)-4-ethylstyryl)-3-tosyloxazolidine (**2m**). White solid, 81 mg, 91%; MP:



86-88 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.26 (m, 6H), 7.25 – 7.15 (m, 5H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.02 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.65 (d, *J* = 5.2 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.81 – 3.73 (m, 1H), 3.53 – 3.43 (m, 1H), 3.32 – 3.20 (m, 1H), 2.90 – 2.80 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 144.8, 144.3, 137.4, 134.8, 133.9, 133.4, 130.0, 129.6, 128.8, 128.2, 128.0, 127.1, 126.9, 125.4, 91.8, 69.7, 60.7, 40.9, 28.8, 21.7, 15.6; HRMS (ESI)

calculated for [M+Na]⁺ (C₂₇H₂₉O₃NSNa) *m/z* 470.1766, found 470.1777.

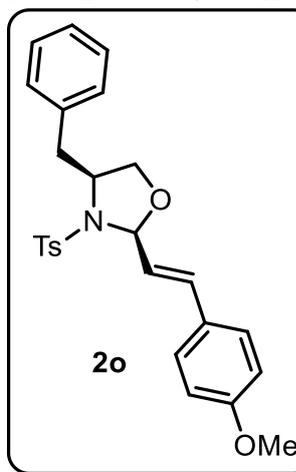
(2*S*,4*S*)-4-benzyl-2-((*E*)-4-(*tert*-butyl)styryl)-3-tosyloxazolidine (**2n**). White solid, 84 mg, 88%;



MP: 113-115 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.26 (m, 8H), 7.25 – 7.16 (m, 3H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.8, 5.1 Hz, 1H), 5.66 (d, *J* = 5.1 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.81 – 3.73 (m, 1H), 3.53 – 3.45 (m, 1H), 3.31 – 3.21 (m, 1H), 2.89 – 2.78 (m, 1H), 2.40 (s, 3H), 1.33 (s, 9H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 151.5, 144.2, 137.3, 134.8, 133.7, 133.0, 129.9, 129.4, 128.7, 127.9, 126.82, 126.76, 125.5, 125.4, 91.7, 69.6, 60.6, 40.9, 34.7, 31.3, 21.6; HRMS (ESI) calculated for [M+H]⁺

(C₂₉H₃₄O₃NS) *m/z* 476.2259, found 476.2274.

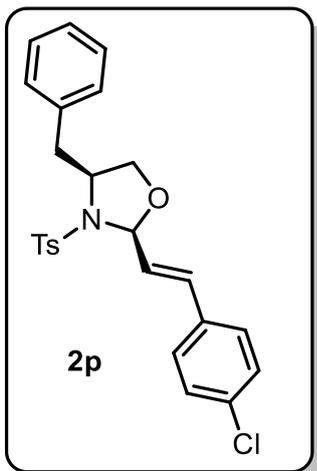
(2*S*,4*S*)-4-benzyl-2-((*E*)-4-methoxystyryl)-3-tosyloxazolidine (**2o**). White solid, 83 mg, 92%;



MP: 140-142 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.26 (m, 6H), 7.25 – 7.17 (m, 3H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 5.4 Hz, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.85 – 3.75 (m, 4H), 3.51 – 3.42 (m, 1H), 3.31 – 3.21 (m, 1H), 2.90 – 2.80 (m, 1H), 2.40 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 159.9, 144.3, 137.3, 134.8, 133.6, 130.0, 129.6, 128.8, 128.6, 128.4, 128.0, 126.9, 124.1, 114.1, 92.0, 69.6, 60.6, 55.4, 40.9, 21.7; HRMS (ESI)

calculated for [M+Na]⁺ (C₂₆H₂₇O₄NSNa) *m/z* 472.1558, found 472.1570.

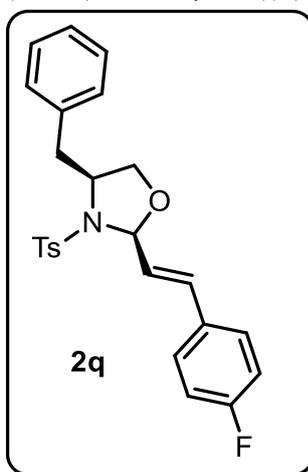
(2*S*,4*S*)-4-benzyl-2-((*E*)-4-chlorostyryl)-3-tosyloxazolidine (**2p**). White solid, 75 mg, 83%;



MP: 92-94 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 8H), 7.25 – 7.18 (m, 3H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.02 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.62 (d, *J* = 5.1 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.81 – 3.73 (m, 1H), 3.52 – 3.44 (m, 1H), 3.28 – 3.18 (m, 1H), 2.92 – 2.82 (m, 1H), 2.41 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.4, 137.2, 134.7, 134.4, 134.1, 132.7, 130.1, 129.7, 128.9, 128.8, 128.3, 128.0, 127.1, 127.0, 91.5, 69.7, 60.6, 40.8, 21.7; HRMS (ESI) calculated for [M+H]⁺ (C₂₅H₂₅O₃NSCl) m/z

454.1244, found 454.1257.

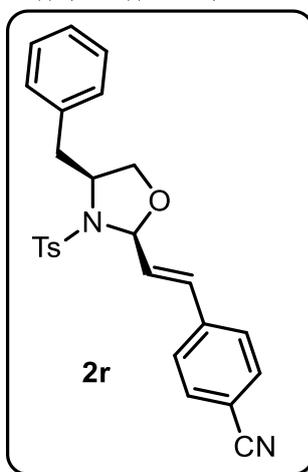
(2*S*,4*S*)-4-benzyl-2-((*E*)-4-fluorostyryl)-3-tosyloxazolidine (**2q**). White solid, 75 mg, 86%;



MP: 87-89 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.25 – 7.17 (m, 3H), 7.07 – 6.99 (m, 2H), 6.72 (d, *J* = 15.9 Hz, 1H), 5.97 (dd, *J* = 15.9, 5.3 Hz, 1H), 5.61 (d, *J* = 5.2 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.81 – 3.74 (m, 1H), 3.53 – 3.43 (m, 1H), 3.28 – 3.19 (m, 1H), 2.91 – 2.82 (m, 1H), 2.42 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 248.5 (d, *J* = 248.5 Hz), 144.4, 137.3, 134.7, 132.8, 132.1 (d, *J* = 4.0 Hz), 130.1, 129.7, 128.81, 128.78, 128.7, 128.0, 127.0, 126.2 (d, *J* = 2.0 Hz), 115.6

(d, *J* = 22.2 Hz), 91.7, 69.7, 60.7, 40.8, 21.7; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -113.3; HRMS (ESI) calculated for [M+Na]⁺ (C₂₅H₂₄O₃NSFNa) m/z 460.1359, found 460.1353.

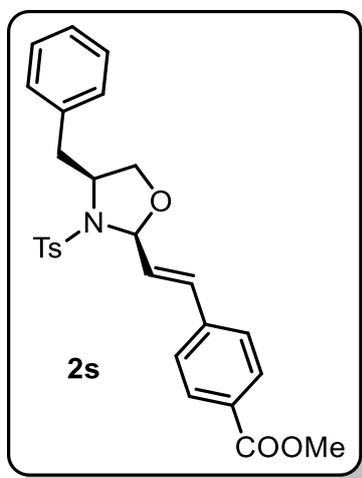
4-((*E*)-2-((2*S*,4*S*)-4-benzyl-3-tosyloxazolidin-2-yl)vinyl)benzonitrile (**2r**). Yellow oil, 71 mg,



80%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 5.0 Hz, 1H), 5.63 (d, *J* = 5.0 Hz, 1H), 4.0 – 3.91 (m, 1H), 3.82 – 3.75 (m, 1H), 3.53 – 3.45 (m, 1H), 3.26 – 3.17 (m, 1H), 2.92 – 2.82 (m, 1H), 2.43 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.6, 140.4, 137.0, 134.3, 132.5, 131.9, 130.4, 130.2, 129.7, 128.8, 128.0, 127.6, 127.0, 118.9, 111.7, 91.1, 69.7, 60.6,

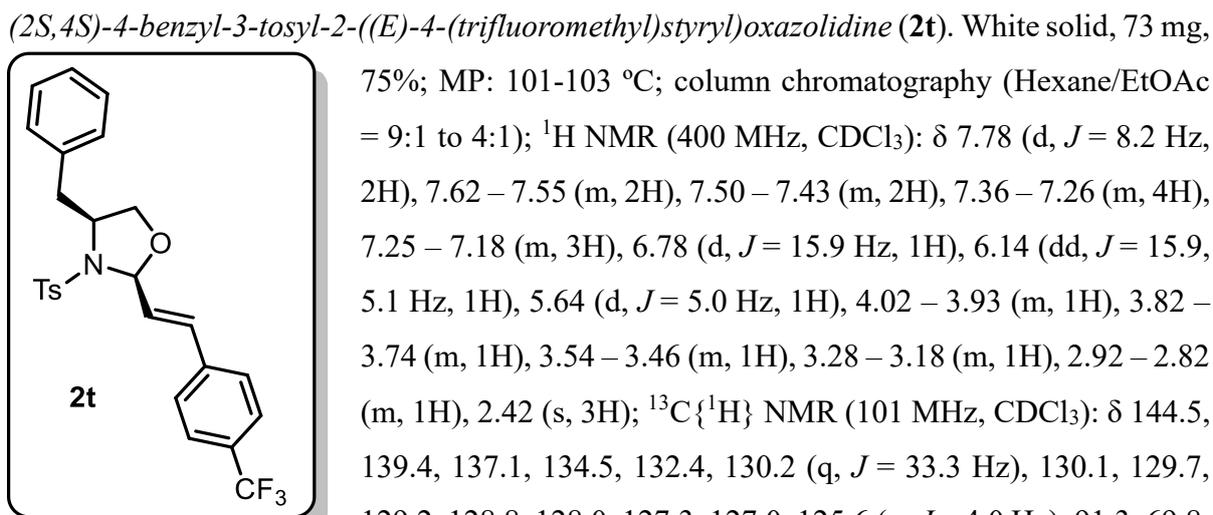
40.6, 21.7; HRMS (ESI) calculated for $[M+Na]^+$ ($C_{26}H_{24}O_3N_2SNa$) m/z 467.1405, found 467.1421.

methyl 4-((E)-2-((2S,4S)-4-benzyl-3-tosyloxazolidin-2-yl)vinyl)benzoate (2s). White solid, 77



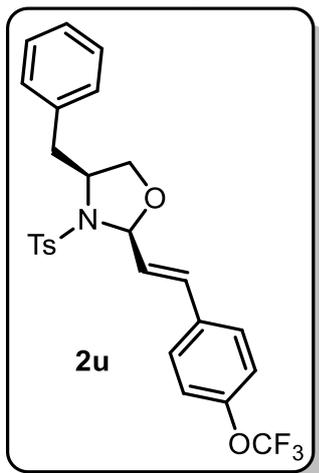
mg, 81%; MP: 107-109 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); 1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.24 – 7.17 (m, 3H), 6.78 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 5.2 Hz, 1H), 5.64 (d, J = 5.1 Hz, 1H), 4.02 – 3.90 (m, 4H), 3.82 – 3.75 (m, 1H), 3.53 – 3.46 (m, 1H), 3.29 – 3.18 (m, 1H), 2.93 – 2.84 (m, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.8, 144.4, 140.3, 137.1, 134.5, 132.7, 130.1, 130.0, 128.74, 129.66,

129.1, 128.7, 128.0, 127.0, 91.3, 69.7, 60.5, 52.2, 40.6, 21.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{27}H_{28}O_5NS$) m/z 478.1688, found 478.1707.



(2S,4S)-4-benzyl-3-tosyl-2-((E)-4-(trifluoromethyl)styryl)oxazolidine (2t). White solid, 73 mg, 75%; MP: 101-103 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); 1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.2 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.50 – 7.43 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 6.78 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 5.1 Hz, 1H), 5.64 (d, J = 5.0 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.82 – 3.74 (m, 1H), 3.54 – 3.46 (m, 1H), 3.28 – 3.18 (m, 1H), 2.92 – 2.82 (m, 1H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.5, 139.4, 137.1, 134.5, 132.4, 130.2 (q, J = 33.3 Hz), 130.1, 129.7, 129.2, 128.8, 128.0, 127.3, 127.0, 125.6 (q, J = 4.0 Hz), 91.3, 69.8, 60.6, 40.7, 21.7; $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$): δ -62.6; HRMS (ESI) calculated for $[M+Na]^+$ ($C_{26}H_{24}O_3NSF_3Na$) m/z 510.1327, found 510.1341.

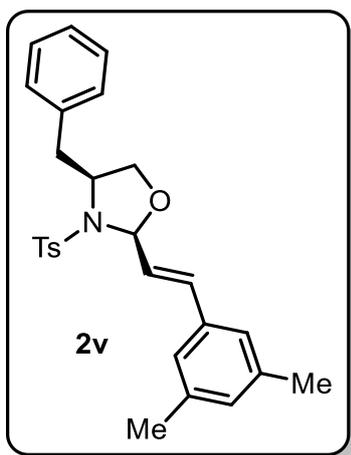
(2*S*,4*S*)-4-benzyl-3-tosyl-2-((*E*)-4-(trifluoromethoxy)styryl)oxazolidine (**2u**). White solid, 83



mg, 83%; MP: 98-100 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.26 (m, 4H), 7.25 – 7.16 (m, 5H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.62 (d, *J* = 5.2 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.82 – 3.73 (m, 1H), 3.53 – 3.44 (m, 1H), 3.29 – 3.19 (m, 1H), 2.93 – 2.80 (m, 1H), 2.40 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 149.0, 144.4, 137.1, 134.54, 134.50, 132.3, 130.0, 129.6, 128.7, 128.3, 127.9, 127.5, 126.9, 121.0, 120.5 (q, *J* = 258.6 Hz), 91.4, 69.6,

60.5, 40.7, 21.6; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -57.8; HRMS (ESI) calculated for [M+Na]⁺ (C₂₆H₂₄O₄NSF₃Na) m/z 526.1276, found 526.1279.

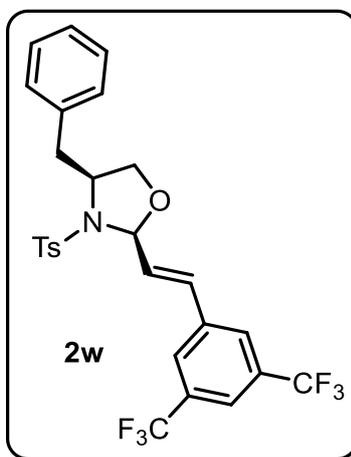
(2*S*,4*S*)-4-benzyl-2-((*E*)-3,5-dimethylstyryl)-3-tosyloxazolidine (**2v**). White solid, 79 mg, 88%;



MP: 134-136 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.00 (s, 2H), 6.92 (s, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.03 (dd, *J* = 15.8, 5.2 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.82 – 3.73 (m, 1H), 3.52 – 3.43 (m, 1H), 3.30 – 3.22 (m, 1H), 2.90 – 2.80 (m, 1H), 2.41 (s, 3H), 2.32 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.3, 138.1, 137.4, 135.8, 134.8, 134.1, 130.1, 130.0, 129.6, 128.8, 128.0, 126.9, 126.0, 125.0, 91.8, 69.7, 60.6,

40.9, 21.7, 21.4; HRMS (ESI) calculated for [M+H]⁺ (C₂₇H₃₀O₃NS) m/z 448.1946, found 448.1949.

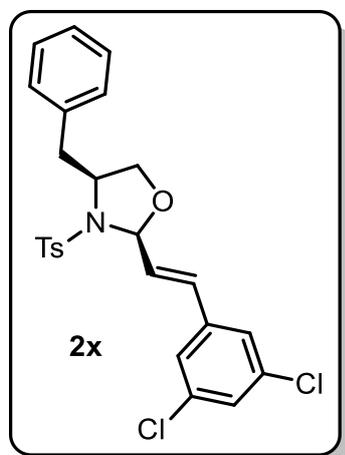
(2*S*,4*S*)-4-benzyl-2-((*E*)-3,5-bis(trifluoromethyl)styryl)-3-tosyloxazolidine (**2w**). White solid,



91 mg, 82%; MP: 83-85 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.76 (m, 3H), 7.74 (s, 2H), 7.38 – 7.19 (m, 7H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.9, 5.1 Hz, 1H), 5.61 (d, *J* = 5.1 Hz, 1H), 4.05 – 3.94 (m, 1H), 3.86 – 3.77 (m, 1H), 3.60 – 3.50 (m, 1H), 3.22 – 3.11 (m, 1H), 3.02 – 2.91 (m, 1H), 2.43 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.6, 137.9, 136.7, 134.2, 132.0 (q, *J* = 33.3 Hz), 130.6, 130.5, 130.1, 129.9, 128.6, 127.9, 127.0, 126.8 (q, *J* = 3.0 Hz), 123.3 (q, *J* = 273.7 Hz),

121.6 (q, $J = 4.0$ Hz), 90.9, 69.5, 60.3, 40.1, 21.6; $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3): δ -63.0; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{27}\text{H}_{23}\text{O}_3\text{NSF}_6\text{Na}$) m/z 578.1201, found 578.1190.

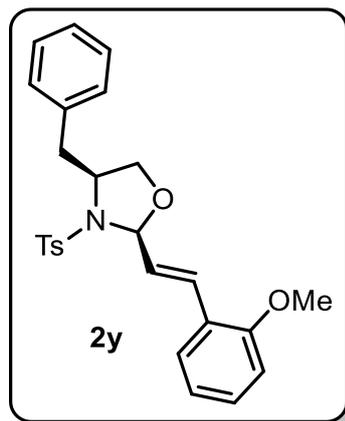
(2*S*,4*S*)-4-benzyl-2-((*E*)-3,5-dichlorostyryl)-3-tosyloxazolidine (**2x**). White solid, 77 mg, 79%;



MP: 149-151 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.0$ Hz, 2H), 7.42 – 7.14 (m, 10H), 6.58 (d, $J = 15.8$ Hz, 1H), 5.96 (dd, $J = 15.9, 5.2$ Hz, 1H), 5.59 (d, $J = 5.1$ Hz, 1H), 4.05 – 3.91 (m, 1H), 3.84 – 3.71 (m, 1H), 3.59 – 3.45 (m, 1H), 3.26 – 3.11 (m, 1H), 2.99 – 2.83 (m, 1H), 2.42 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.5, 138.9, 136.9, 135.2, 134.4, 131.1, 130.1, 129.9, 129.5, 128.8, 128.1, 128.0, 127.1, 125.4, 91.1, 69.6, 60.4, 40.4, 21.7; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{25}\text{H}_{23}\text{O}_3\text{NSNaCl}_2$)

m/z 510.0673, found 510.0687.

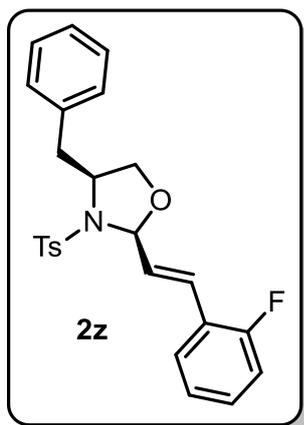
(2*S*,4*S*)-4-benzyl-2-((*E*)-2-methoxystyryl)-3-tosyloxazolidine (**2y**). Yellow oil, 82 mg, 91%;



column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 7.9$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.27 (m, 4H), 7.25 – 7.17 (m, 4H), 7.11 (d, $J = 16.0$ Hz, 1H), 6.96 – 6.90 (m, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.11 (dd, $J = 16.0, 5.3$ Hz, 1H), 5.66 (d, $J = 5.4$ Hz, 1H), 4.04 – 3.96 (m, 1H), 3.85 (s, 3H), 3.81 – 3.76 (m, 1H), 3.50 – 3.45 (m, 1H), 3.31 – 3.24 (m, 1H), 2.91 – 2.83 (m, 1H), 2.39 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 157.3, 144.2, 137.5, 135.0, 130.0,

129.6, 129.5, 129.2, 128.8, 128.0, 127.6, 126.9, 126.7, 124.9, 120.6, 111.0, 92.1, 69.7, 60.7, 55.6, 41.0, 21.7; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{26}\text{H}_{27}\text{O}_4\text{NSNa}$) m/z 472.1558, found 472.1575.

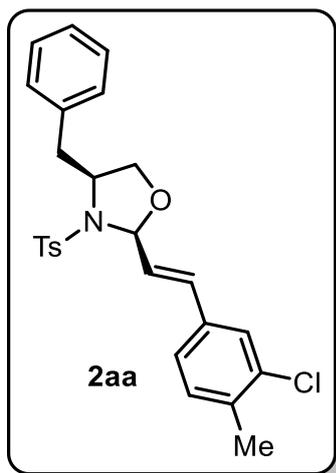
(2*S*,4*S*)-4-benzyl-2-((*E*)-2-fluorostyryl)-3-tosyloxazolidine (**2z**). White solid, 74 mg, 85%; MP:



121-123 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 7.8$ Hz, 2H), 7.45 – 7.38 (m, 1H), 7.34 – 7.26 (m, 4H), 7.26 – 7.16 (m, 4H), 7.14 – 7.08 (m, 1H), 7.07 – 7.01 (m, 1H), 6.91 (d, $J = 16.1$ Hz, 1H), 6.16 (dd, $J = 16.0, 5.2$ Hz, 1H), 5.63 (d, $J = 5.2$ Hz, 1H), 4.04 – 3.95 (m, 1H), 3.82 – 3.75 (m, 1H), 3.52 – 3.45 (m, 1H), 3.29 – 3.21 (m, 1H), 2.91 – 2.82 (m, 1H), 2.40 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 160.6 (d, $J = 251.5$ Hz), 144.4, 137.3, 134.7, 130.1, 129.8 (d, $J = 8.1$ Hz), 129.6, 128.9 (d, $J = 5.1$ Hz), 128.1 (d, $J = 3.0$ Hz), 128.0,

126.9, 126.4 (d, $J = 4.0$ Hz), 124.2 (d, $J = 3.0$ Hz), 123.7 (d, $J = 12.1$ Hz), 115.9 (d, $J = 22.2$ Hz), 91.7, 69.7, 60.6, 40.9, 21.7; ^{19}F $\{^1\text{H}\}$ NMR (377 MHz, CDCl_3): δ -117.0; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{25}\text{H}_{24}\text{O}_3\text{NSFNa}$) m/z 460.1359, found 460.1367.

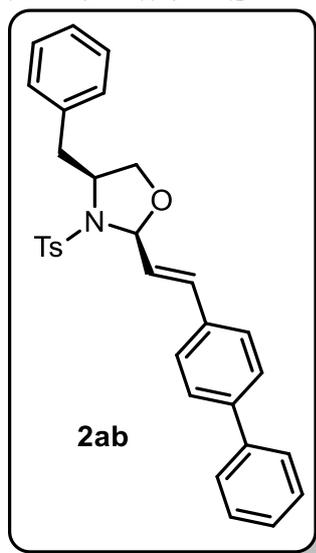
(2*S*,4*S*)-4-benzyl-2-((*E*)-3-chloro-4-methylstyryl)-3-tosyloxazolidine (**2aa**). Yellow oil, 78 mg,



84%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.27 (m, 5H), 7.25 – 7.10 (m, 5H), 6.65 (d, $J = 15.9$ Hz, 1H), 5.97 (dd, $J = 15.9, 5.4$ Hz, 1H), 5.61 (d, $J = 5.3$ Hz, 1H), 4.02 – 3.94 (m, 1H), 3.80 – 3.74 (m, 1H), 3.53 – 3.45 (m, 1H), 3.26 – 3.18 (m, 1H), 2.90 – 2.81 (m, 1H), 2.41 (s, 3H), 2.37 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.4, 137.2, 136.1, 135.2, 134.7, 132.5, 131.1, 130.1, 129.7, 128.8, 128.0, 1287.4, 127.0, 126.9, 125.4, 91.6, 69.7, 60.6, 40.7, 21.7, 20.0; HRMS (ESI) calculated

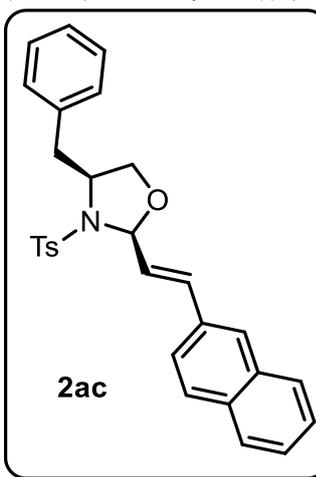
for $[\text{M}+\text{H}]^+$ ($\text{C}_{26}\text{H}_{27}\text{O}_3\text{NSCl}$) m/z 468.1400, found 468.1425.

(2*S*,4*S*)-2-((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-4-benzyl-3-tosyloxazolidine (**2ab**). Yellow oil,



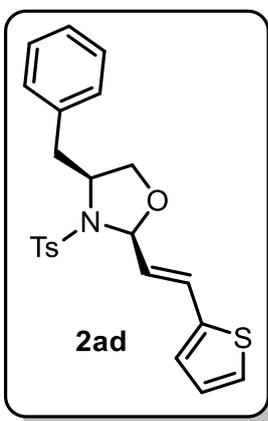
80 mg, 81%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, $J = 8.2$ Hz, 2H), 7.63 – 7.56 (m, 4H), 7.48 – 7.42 (m, 4H), 7.38 – 7.34 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.17 (m, 3H), 6.80 (d, $J = 15.8$ Hz, 1H), 6.10 (dd, $J = 15.8, 5.2$ Hz, 1H), 5.67 (d, $J = 5.1$ Hz, 1H), 4.04 – 3.95 (m, 1H), 3.83 – 3.76 (m, 1H), 3.54 – 3.46 (m, 1H), 3.32 – 3.23 (m, 1H), 2.92 – 2.82 (m, 1H), 2.41 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.2, 141.1, 140.6, 137.2, 124.8, 134.7, 133.4, 130.0, 129.5, 128.8, 128.7, 127.9, 127.5, 127.3, 127.0, 126.9, 126.3, 91.6, 69.6, 60.6, 40.8, 21.6; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{31}\text{H}_{29}\text{O}_3\text{NSNa}$) m/z 518.1766, found 518.1797.

(2*S*,4*S*)-4-benzyl-2-((*E*)-2-(naphthalen-2-yl)vinyl)-3-tosyloxazolidine (**2ac**). White solid, 74



mg, 79%; MP: 141-143 $^\circ\text{C}$; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.86 – 7.74 (m, 6H), 7.56 (d, $J = 8.5$ Hz, 1H), 7.50 – 7.43 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 6.92 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.8, 5.2$ Hz, 1H), 5.70 (d, $J = 5.2$ Hz, 1H), 4.06 – 3.95 (m, 1H), 3.86 – 3.77 (m, 1H), 3.56 – 3.46 (m, 1H), 3.34 – 3.22 (m, 1H), 2.95 – 2.84 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.3, 137.3, 134.8, 134.0, 133.6, 133.4, 133.3, 130.1, 129.7, 129.6, 128.8, 128.3, 128.2, 128.0, 127.8, 127.5, 127.0, 126.7, 126.5, 126.3, 123.9, 91.8, 69.7, 60.6, 40.9, 21.7; HRMS (ESI) calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{29}\text{H}_{27}\text{O}_3\text{NSNa}$) m/z 492.1609, found 492.1613.

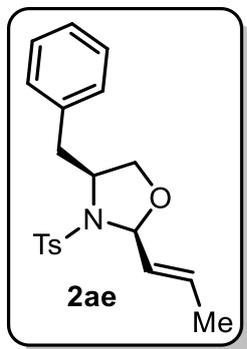
(2*S*,4*S*)-4-benzyl-2-((*E*)-2-(thiophen-2-yl)vinyl)-3-tosyloxazolidine (**2ad**). Yellow oil, 69 mg,



81%; column chromatography (Hexane/EtOAc = 9:1 to 4:1); ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.17 (m, 4H), 7.04 – 7.00 (m, 1H), 7.00 – 6.96 (m, 1H), 6.89 (d, $J = 15.7$ Hz, 1H), 5.90 (dd, $J = 15.6, 5.1$ Hz, 1H), 5.61 (d, $J = 5.1$ Hz, 1H), 4.00 – 3.93 (m, 1H), 3.79 – 3.73 (m, 1H), 3.50 – 3.44 (m, 1H), 3.29 – 3.22 (m, 1H), 2.88 – 2.80 (m, 1H), 2.41 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 144.4, 140.9, 137.3, 134.8, 130.1, 129.6, 128.8, 128.0, 127.6, 127.3, 127.1, 127.0, 125.7, 125.5, 91.4, 69.8,

60.7, 40.9, 21.7; HRMS (ESI) calculated for $[M+Na]^+$ ($C_{23}H_{23}O_3NS_2Na$) m/z 448.1017, found 448.1039.

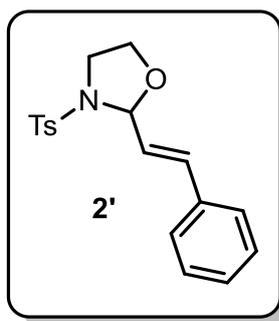
(2*S*,4*S*)-4-benzyl-2-((*E*)-prop-1-en-1-yl)-3-tosyloxazolidine (**2ae**). White solid, 58 mg, 81%;



MP: 83-85 °C; column chromatography (Hexane/EtOAc = 9:1 to 4:1); 1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.1 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 7.21 – 7.17 (m, 2H), 6.00 – 5.89 (m, 1H), 5.49 – 5.41 (m, 1H), 5.40 – 5.35 (m, 1H), 3.95 – 3.87 (m, 1H), 3.73 – 3.67 (m, 1H), 3.38 – 3.32 (m, 1H), 3.25 – 3.18 (m, 1H), 2.85 – 2.76 (m, 1H), 2.42 (s, 3H), 1.74 (d, J = 6.4 Hz, 3H); ^{13}C $\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.1, 137.3, 134.7, 131.4, 129.9, 129.4, 128.7, 127.8, 127.7, 126.8,

91.8, 69.2, 60.6, 40.9, 21.6, 17.6; HRMS (ESI) calculated for $[M+Na]^+$ ($C_{20}H_{23}O_3NSNa$) m/z 380.1296, found 380.1303.

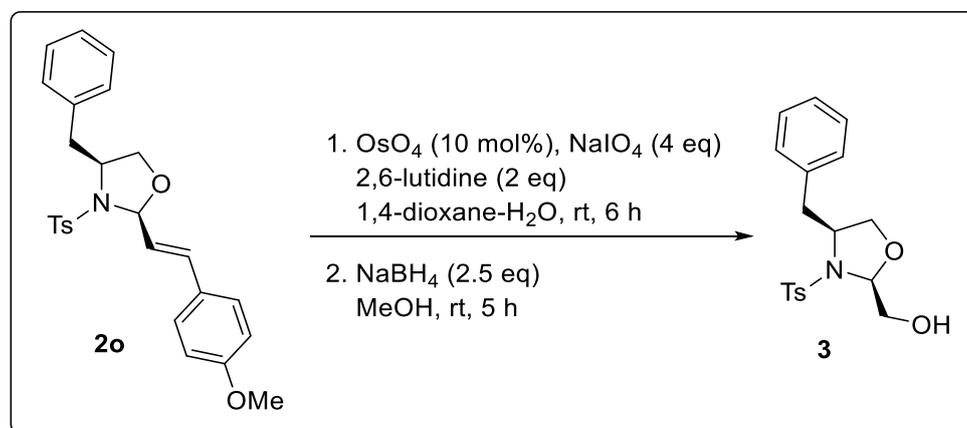
(*E*)-2-styryl-3-tosyloxazolidine (**2'**). Colourless oil, 55 mg, 83%; column chromatography



(Hexane/EtOAc = 9:1 to 4:1); 1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.1 Hz, 2H), 7.41 – 7.26 (m, 7H), 6.76 (d, J = 15.8 Hz, 1H), 6.11 (dd, J = 15.9 Hz, 4.6 Hz, 1H), 5.77 (d, J = 4.6 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.61 – 3.44 (m, 3H), 2.43 (s, 3H); ^{13}C $\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.4, 135.9, 134.8, 133.4, 130.0, 128.7, 128.4, 128.0, 127.1, 125.6, 90.5, 65.4, 46.4, 21.7; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{20}O_3NS$) m/z 330.1164, found 380.1157.

7 Further derivatizations of product (2o):

7.1 Synthesis of alcohol 3 from 2o:

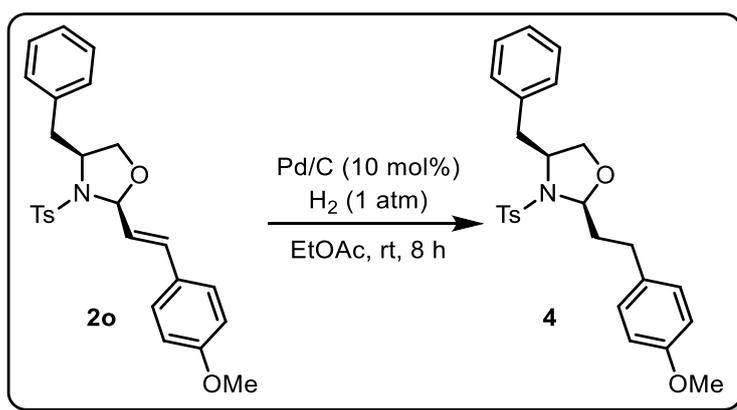


Scheme S4

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with solution of (2*S*,4*S*)-4-benzyl-2-((*E*)-4-methoxystyryl)-3-tosyloxazolidine (**2o**) (0.1 mmol) in 1,4-dioxane:H₂O (1.0 mL, v/v = 3:1), followed by addition of 2,6-lutidine (0.2 mmol), OsO₄ (0.01 mmol) and NaIO₄ (0.4 mmol). The reaction was stirred at room temperature for 6 h. After completion of reaction as indicated by TLC, the reaction mixture was quenched by Na₂S₂O₃ and the mixture was extracted three times with DCM. After combining the organic layers, it was washed with brine, and dried over Na₂SO₄. Following filtration, the solvent was evaporated under reduced pressure to afford the corresponding aldehyde. To the solution of crude aldehyde in dry MeOH (1.0 mL), NaBH₄ (0.25 mmol) was added. The reaction was stirred at room temperature for 5 h. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, Hexane/EtOAc = 4:1 to 1:1) to give product **3** as colourless oil.

((2*S*,4*S*)-4-benzyl-3-tosyloxazolidin-2-yl)methanol (**3**). Colourless oil, 19 mg, 55 %; column chromatography (Hexane /EtOAc = 4:1 to 1:1); ¹H NMR (400 MHz, CDCl₃): δ 7.79 – 7.72 (m, 2H), 7.36 – 7.27 (m, 4H), 7.25 – 7.17 (m, 3H), 4.99 – 4.93 (m, 1H), 3.90 – 3.82 (m, 1H), 3.77 – 3.66 (m, 3H), 3.30 – 3.22 (m, 1H), 3.19 – 3.11 (m, 1H), 2.91 – 2.82 (m, 1H), 2.42 (s, 3H), 2.28 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.7, 137.0, 133.5, 130.2, 129.6, 128.8, 128.0, 127.0, 91.9, 69.2, 64.7, 60.8, 40.6, 21.7; HRMS (ESI) calculated for [M+Na]⁺ (C₁₈H₂₁O₄NSNa) m/z 370.1089; found 370.1094.

7.2 Synthesis of hydrogenated product **4** from **2o**:



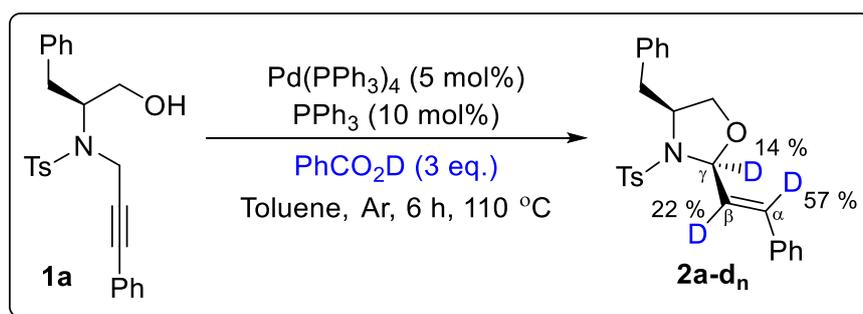
Scheme S5

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with (2*S*,4*S*)-4-benzyl-2-((*E*)-4-methoxystyryl)-3-tosyloxazolidine (**2o**) (0.1 mmol), Pd/C (0.01 mmol) and EtOAc (0.5 mL) under Ar atmosphere. Subsequently, the Schlenk tube was subjected to three cycles of backfilling with hydrogen gas (H₂). The reaction was stirred at room temperature under H₂

atmosphere for 8 h. After completion of reaction as indicated by TLC, solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, Hexane/EtOAc = 9:1 to 4:1) to give product **4** as colourless oil.

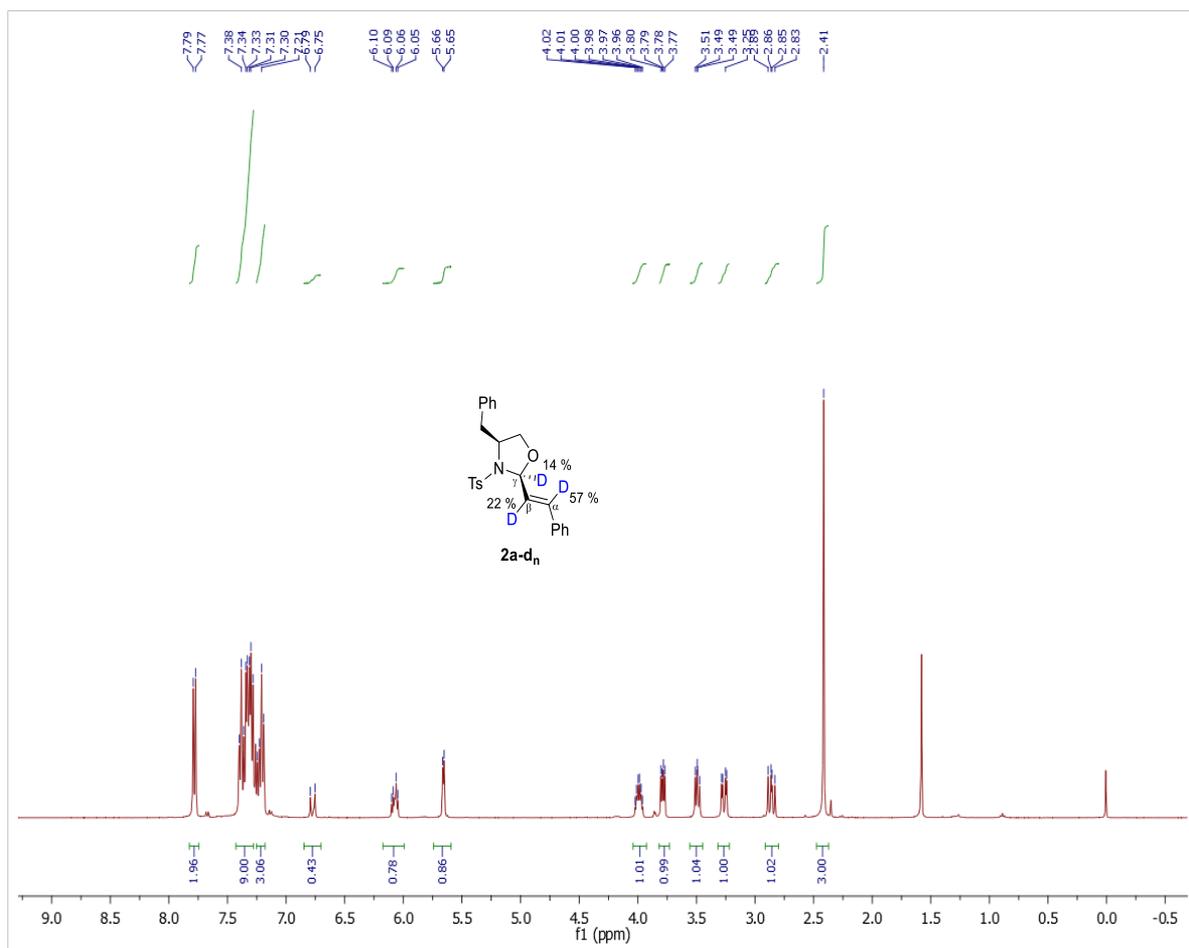
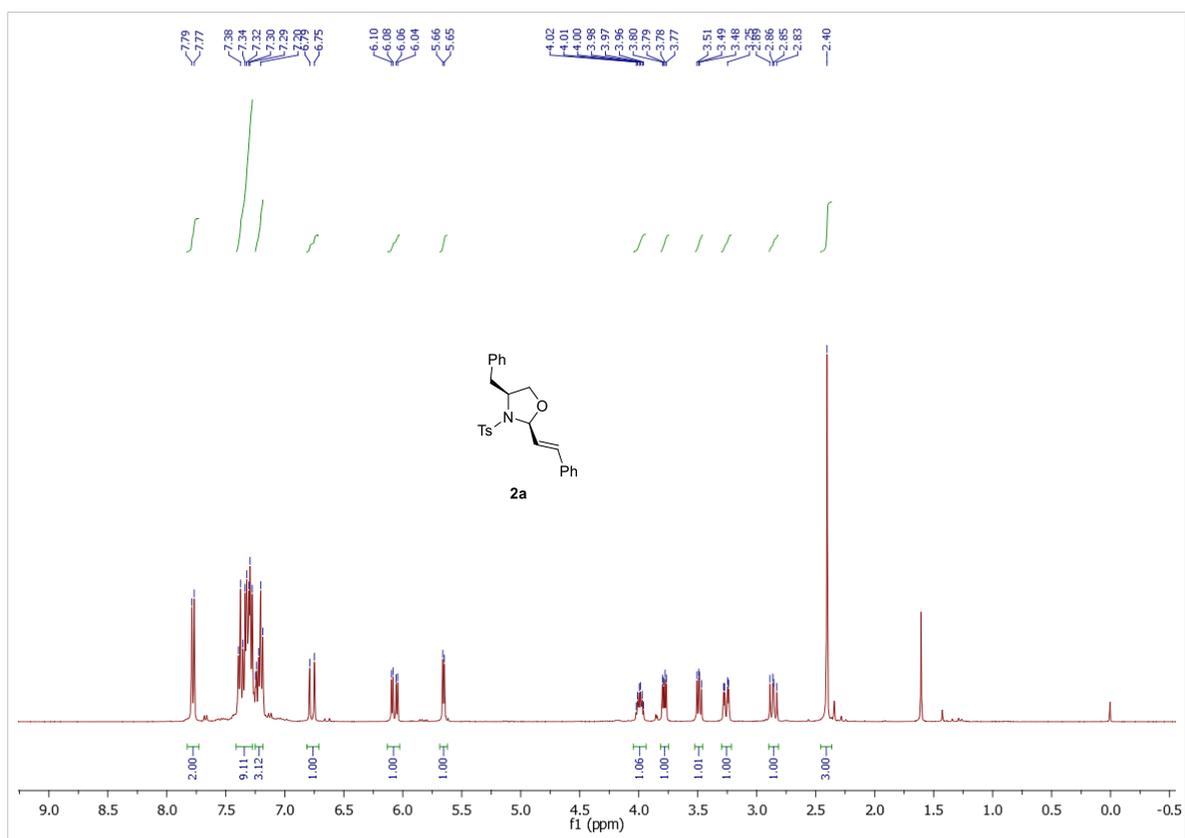
(2*S*,4*S*)-4-benzyl-2-(4-methoxyphenethyl)-3-tosyloxazolidine (**4**). Colourless oil, 32 mg, 71%; column chromatography (Hexane /EtOAc = 9:1 to 4:1); ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.95 – 4.86 (m, 1H), 3.88 – 3.80 (m, 4H), 3.71 (dd, *J* = 9.0, 3.3 Hz, 1H), 3.24 – 3.14 (m, 2H), 2.87 – 2.74 (m, 2H), 2.72 – 2.62 (m, 1H), 2.41 (s, 3H), 2.26 – 2.16 (m, 1H), 2.02 – 1.91 (m, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 158.1, 144.2, 137.6, 134.3, 133.3, 130.0, 129.64, 129.56, 128.8, 128.0, 126.9, 114.0, 92.0, 69.0, 60.9, 55.5, 41.4, 37.7, 29.9, 21.7; HRMS (ESI) calculated for [M+Na]⁺ (C₂₆H₂₉O₄NSNa) *m/z* 474.1715; found 474.1743.

8 Deuterium-labelling experiment:



Scheme S6

A flame dried 10 mL Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol), Pd(PPh₃)₄ (0.01 mmol), PPh₃ (0.02 mmol), PhCOOD (0.6 mmol), dry and degassed toluene (0.5 mL) and capped with a glass stopper. The reaction mixture was vigorously stirred at 110 °C for 6 h under argon atmosphere. After completion of reaction as indicated by TLC, the reaction mixture was cooled to room temperature, diluted with EtOAc (10.0 mL) and washed with sat. NaHCO₃ followed by brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a dark residue. The crude mixture was purified by flash chromatography (silica gel, hexane/EtOAc = 9:1 to 4:1) to give the pure product **2a-d_n**. The α-, β-, and γ- positions were found to be deuterated in the ratios of 57 %, 22 % and 14 %, respectively.



9 X-ray crystallographic information of the product 2o:

Crystal (**2o**) suitable for X-ray crystallography was obtained from recrystallization of the solid in DCM and hexane combination using solvent diffusion method at room temperature.

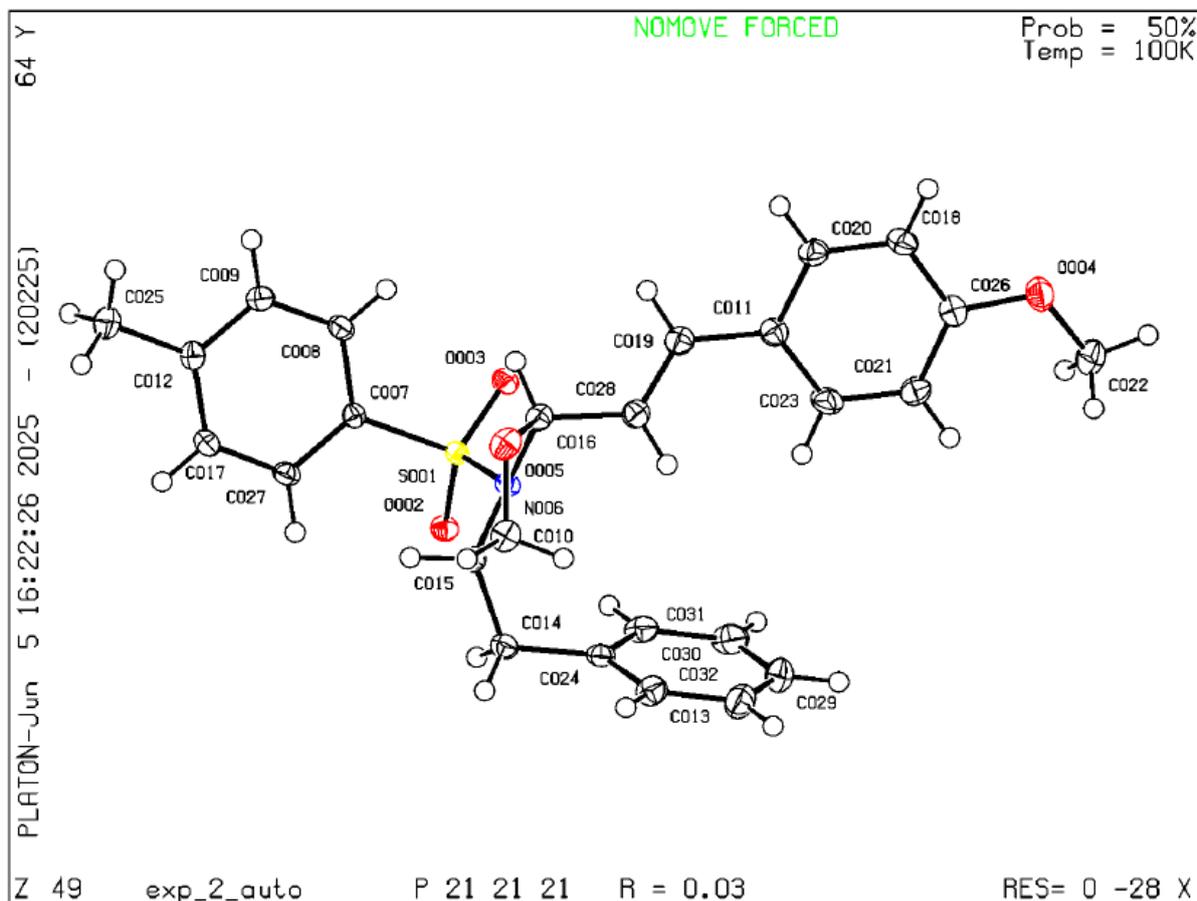


Figure S1. ORTEP view of **2o** with thermal ellipsoids drawn at 50% probability level.

10 Crystal data of 2o:

Table S6 Crystal data and structure refinement for exp_2_auto.

Identification code	exp_2_auto
Empirical formula	C ₂₆ H ₂₇ NO ₄ S
Formula weight	449.575
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.360(5)
b/Å	10.914(5)
c/Å	28.239(5)
α/°	90.000(5)
β/°	90.000(5)
γ/°	90.000(5)
Volume/Å ³	2268.4(19)
Z	4
ρ _{calc} /g/cm ³	1.316
μ/mm ⁻¹	0.176
F(000)	953.1
Crystal size/mm ³	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4 to 59.06
Index ranges	-6 ≤ h ≤ 9, -14 ≤ k ≤ 11, -35 ≤ l ≤ 24
Reflections collected	8924
Independent reflections	4875 [R _{int} = 0.0124, R _{sigma} = 0.0195]
Data/restraints/parameters	4875/0/291
Goodness-of-fit on F ²	1.038
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0279, wR ₂ = 0.0711
Final R indexes [all data]	R ₁ = 0.0293, wR ₂ = 0.0723
Largest diff. peak/hole / e Å ⁻³	0.29/-0.35
Flack parameter	-0.012(17)

Table S7 Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for exp_2_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
S001	1155.4 (4)	4315.6 (3)	7077.22 (10)	12.95 (7)
O002	641.4 (13)	3128.7 (9)	6900.5 (3)	16.9 (2)
O003	311.1 (13)	5399.0 (8)	6892.0 (3)	17.7 (2)
O004	5457.6 (16)	9928.5 (10)	4779.2 (4)	26.5 (2)
O005	5704.1 (13)	5382.4 (9)	7353.7 (4)	21.9 (2)
N006	3320.9 (14)	4455.6 (10)	6970.1 (4)	14.3 (2)
C007	842.3 (15)	4297.1 (12)	7694.8 (4)	13.7 (2)

Table S7 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for exp_2_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
C008	349.7 (18)	5377.0 (12)	7924.3 (5)	17.3 (3)
C009	138.2 (19)	5371.0 (12)	8412.0 (5)	18.7 (3)
C010	6317.4 (18)	4204.8 (14)	7199.3 (5)	20.8 (3)
C011	4646.1 (19)	8026.9 (13)	6043.7 (5)	18.8 (3)
C012	452.9 (18)	4313.6 (13)	8677.2 (5)	17.7 (3)
C013	6991 (2)	2851.8 (14)	6098.6 (5)	22.6 (3)
C014	4760.9 (19)	2422.3 (12)	6756.5 (5)	18.7 (3)
C015	4581.8 (18)	3460.4 (12)	7118.2 (5)	16.1 (2)
C016	4189.4 (17)	5668.8 (13)	7062.3 (5)	17.2 (3)
C017	919.0 (19)	3239.2 (13)	8437.9 (5)	18.9 (3)
C018	4904 (2)	9922.8 (13)	5594.0 (5)	21.4 (3)
C019	4260.2 (19)	7402.9 (13)	6493.5 (5)	19.9 (3)
C020	4610.9 (19)	9311.2 (14)	6019.2 (5)	20.8 (3)
C021	5291 (2)	7977.5 (14)	5199.9 (5)	23.7 (3)
C022	5392 (2)	9286.2 (17)	4338.8 (5)	31.2 (3)
C023	5000 (2)	7381.2 (13)	5626.4 (5)	23.5 (3)
C024	5199.9 (19)	2822.2 (12)	6257.7 (5)	18.0 (3)
C025	284 (2)	4334.6 (15)	9207.0 (5)	25.2 (3)
C026	5218.3 (18)	9251.9 (14)	5182.5 (5)	20.1 (3)
C027	1109.9 (18)	3218.3 (12)	7949.7 (5)	17.0 (2)
C028	4712.8 (19)	6257.5 (13)	6602.6 (5)	19.7 (3)
C029	6022 (3)	3514.3 (15)	5328.4 (5)	32.0 (4)
C030	3829 (2)	3155.0 (13)	5941.6 (5)	22.6 (3)
C031	4238 (2)	3499.7 (15)	5480.8 (6)	30.0 (4)
C032	7403 (2)	3184.5 (15)	5636.7 (6)	28.5 (3)

Table S8 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for exp_2_auto. The anisotropic displacement factor exponent takes the form: - $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S001	13.12 (14)	11.83 (14)	13.90 (13)	-0.68 (11)	-0.77 (11)	0.25 (12)
O002	17.8 (5)	14.4 (4)	18.6 (5)	-3.6 (4)	-1.4 (3)	-2.1 (4)
O003	19.6 (5)	16.1 (5)	17.3 (4)	3.5 (4)	-1.5 (4)	2.4 (4)
O004	37.3 (6)	23.0 (5)	19.1 (5)	-5.8 (5)	-0.8 (4)	2.1 (4)
O005	20.1 (5)	26.3 (5)	19.3 (5)	-4.5 (4)	-2.7 (4)	-5.5 (4)
N006	13.9 (5)	12.3 (5)	16.7 (5)	-0.4 (4)	0.1 (4)	0.5 (4)
C007	12.4 (6)	14.1 (6)	14.5 (5)	-0.9 (5)	0.0 (4)	0.9 (5)
C008	19.2 (6)	13.0 (6)	19.6 (6)	1.4 (5)	-0.1 (5)	2.0 (5)
C009	20.1 (7)	16.3 (6)	19.8 (6)	1.2 (5)	1.6 (5)	-1.6 (5)
C010	15.6 (6)	26.3 (7)	20.4 (6)	-0.7 (6)	-2.2 (5)	-0.8 (6)

Table S8 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for exp_2_auto. The anisotropic displacement factor exponent takes the form: - $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C011	18.6 (6)	17.5 (6)	20.2 (7)	-2.5 (5)	-0.9 (5)	-0.5 (5)
C012	16.4 (6)	19.7 (6)	16.8 (6)	-1.2 (5)	0.4 (5)	1.8 (5)
C013	22.2 (7)	25.1 (7)	20.5 (7)	2.5 (6)	-1.5 (5)	-1.3 (6)
C014	19.3 (6)	15.7 (6)	21.1 (7)	2.5 (5)	0.9 (5)	1.3 (5)
C015	15.4 (6)	17.8 (6)	14.9 (6)	2.2 (5)	-0.4 (5)	1.2 (5)
C016	16.9 (6)	17.2 (6)	17.5 (6)	-4.6 (5)	1.1 (5)	-3.6 (6)
C017	21.6 (7)	15.0 (6)	20.0 (6)	0.4 (5)	0.8 (5)	3.5 (5)
C018	24.5 (7)	15.1 (6)	24.7 (7)	-0.7 (5)	-1.7 (5)	-0.8 (5)
C019	20.9 (7)	19.0 (7)	19.8 (7)	-4.2 (5)	-0.2 (5)	-3.3 (5)
C020	23.1 (7)	18.3 (6)	20.9 (6)	-1.0 (6)	0.4 (5)	-3.1 (6)
C021	31.1 (8)	21.0 (7)	19.1 (7)	-2.4 (6)	-0.6 (6)	-5.1 (6)
C022	43.8 (9)	32.2 (8)	17.6 (7)	-0.3 (8)	2.0 (6)	0.4 (7)
C023	31.4 (8)	14.4 (6)	24.8 (7)	-2.8 (6)	-2.2 (6)	-2.5 (6)
C024	22.1 (7)	13.3 (6)	18.5 (6)	2.3 (5)	-1.2 (5)	-2.3 (5)
C025	31.1 (8)	27.1 (7)	17.3 (7)	2.2 (7)	1.2 (5)	1.5 (6)
C026	19.0 (6)	21.5 (7)	19.7 (6)	-3.0 (6)	-2.5 (5)	2.3 (6)
C027	17.9 (6)	11.9 (5)	21.1 (6)	-0.2 (5)	1.0 (5)	-0.1 (5)
C028	19.9 (7)	18.1 (6)	21.1 (7)	-5.1 (5)	3.3 (5)	-1.6 (5)
C029	49.3 (10)	30.0 (8)	16.9 (7)	3.3 (8)	3.1 (7)	2.4 (6)
C030	23.1 (7)	21.7 (7)	22.9 (7)	5.4 (6)	-3.7 (6)	-4.3 (5)
C031	39.2 (9)	29.1 (8)	21.8 (7)	12.8 (7)	-9.4 (6)	-3.5 (6)
C032	29.8 (8)	31.1 (8)	24.5 (7)	-3.0 (7)	6.4 (6)	-1.5 (7)

Table S9 Bond lengths for exp_2_auto.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
S001	O002	1.4388 (11)	C012	C017	1.396 (2)
S001	O003	1.4345 (11)	C012	C025	1.5015 (18)
S001	N006	1.6295 (15)	C013	C024	1.393 (2)
S001	C007	1.7592 (13)	C013	C032	1.387 (2)
O004	C022	1.4284 (18)	C014	C015	1.5311 (19)
O004	C026	1.3686 (17)	C014	C024	1.510 (2)
O005	C010	1.4302 (18)	C016	C028	1.4988 (19)
O005	C016	1.4204 (17)	C017	C027	1.3858 (19)
N006	C015	1.4887 (17)	C018	C020	1.391 (2)
N006	C016	1.4931 (17)	C018	C026	1.393 (2)
C007	C008	1.3930 (18)	C019	C028	1.330 (2)
C007	C027	1.3941 (18)	C021	C023	1.386 (2)
C008	C009	1.386 (2)	C021	C026	1.393 (2)
C009	C012	1.395 (2)	C024	C030	1.395 (2)

Table S9 Bond lengths for exp_2_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C010	C015	1.531 (2)	C029	C031	1.382 (3)
C011	C019	1.4688 (19)	C029	C032	1.386 (2)
C011	C020	1.404 (2)	C030	C031	1.388 (2)
C011	C023	1.398 (2)			

Table S10 Bond angles for exp_2_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O003	S001	O002	120.12 (5)	C010	C015	N006	100.07 (10)
N006	S001	O002	106.09 (6)	C014	C015	N006	113.96 (11)
N006	S001	O003	106.18 (6)	C014	C015	C010	114.87 (11)
C007	S001	O002	107.40 (6)	N006	C016	O005	104.00 (10)
C007	S001	O003	108.32 (6)	C028	C016	O005	113.23 (10)
C007	S001	N006	108.25 (6)	C028	C016	N006	109.83 (11)
C026	O004	C022	117.08 (12)	C027	C017	C012	121.34 (12)
C016	O005	C010	105.60 (10)	C026	C018	C020	119.59 (13)
C015	N006	S001	119.29 (9)	C028	C019	C011	126.00 (13)
C016	N006	S001	118.01 (8)	C018	C020	C011	121.27 (13)
C016	N006	C015	109.34 (10)	C026	C021	C023	119.59 (13)
C008	C007	S001	119.05 (10)	C021	C023	C011	121.66 (13)
C027	C007	S001	120.21 (10)	C014	C024	C013	120.67 (12)
C027	C007	C008	120.73 (12)	C030	C024	C013	118.17 (13)
C009	C008	C007	119.18 (12)	C030	C024	C014	121.16 (13)
C012	C009	C008	121.24 (12)	C018	C026	O004	115.59 (13)
C015	C010	O005	105.02 (10)	C021	C026	O004	124.28 (13)
C020	C011	C019	120.14 (13)	C021	C026	C018	120.12 (13)
C023	C011	C019	122.10 (13)	C017	C027	C007	119.05 (12)
C023	C011	C020	117.73 (13)	C019	C028	C016	122.64 (13)
C017	C012	C009	118.41 (12)	C032	C029	C031	119.88 (15)
C025	C012	C009	120.56 (13)	C031	C030	C024	120.90 (14)
C025	C012	C017	121.03 (13)	C030	C031	C029	120.10 (14)
C032	C013	C024	121.05 (14)	C029	C032	C013	119.91 (15)
C024	C014	C015	115.28 (11)				

Table S11 Torsion angles for exp_2_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S001	N006	C015	C010	151.20 (11)	C009	C008	C007	C027	0.42 (15)
S001	N006	C015	C014	85.68 (10)	C009	C012	C017	C027	1.47 (15)
S001	N006	C016	O005	127.87 (9)	C010	O005	C016	C028	-85.73 (11)

Table S11 Torsion angles for exp_2_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S001	N006	C016	C028	110.66 (10)	C010	C015	N006	C016	-11.07 (11)
S001	C007	C008	C009	178.70 (10)	C010	C015	C014	C024	-63.04 (13)
S001	C007	C027	C017	177.67 (10)	C011	C019	C028	C016	177.02 (13)
O002	S001	N006	C015	-50.66 (8)	C011	C020	C018	C026	0.74 (16)
O002	S001	N006	C016	172.59 (8)	C011	C023	C021	C026	-0.51 (18)
O002	S001	C007	C008	-148.27 (9)	C013	C024	C014	C015	94.55 (14)
O002	S001	C007	C027	32.61 (8)	C013	C024	C030	C031	0.34 (17)
O003	S001	N006	C015	-179.52 (8)	C013	C032	C029	C031	-0.59 (19)
O003	S001	N006	C016	43.73 (8)	C014	C015	N006	C016	134.19 (11)
O003	S001	C007	C008	-17.15 (8)	C014	C024	C013	C032	178.15 (14)
O003	S001	C007	C027	163.73 (9)	C014	C024	C030	C031	178.78 (14)
O004	C026	C018	C020	178.79 (12)	C015	N006	C016	C028	108.63 (11)
O004	C026	C021	C023	178.96 (15)	C015	C010	O005	C016	-41.73 (11)
O005	C010	C015	N006	31.35 (10)	C015	C014	C024	C030	-86.36 (13)
O005	C010	C015	C014	153.83 (10)	C018	C020	C011	C019	177.56 (13)
O005	C016	N006	C015	-12.83 (11)	C018	C020	C011	C023	0.48 (16)
O005	C016	C028	C019	114.83 (12)	C018	C026	O004	C022	166.90 (14)
N006	S001	C007	C008	97.58 (9)	C018	C026	C021	C023	1.76 (16)
N006	S001	C007	C027	-81.54 (8)	C019	C011	C023	C021	177.40 (14)
N006	C015	C014	C024	51.61 (12)	C020	C011	C019	C028	160.52 (13)
N006	C016	O005	C010	33.44 (11)	C020	C011	C023	C021	-0.59 (16)
N006	C016	C028	C019	129.41 (11)	C020	C018	C026	C021	-1.87 (17)
C007	S001	N006	C015	64.36 (8)	C021	C026	O004	C022	13.78 (18)
C007	S001	N006	C016	-72.40 (8)	C023	C011	C019	C028	21.53 (17)
C007	C008	C009	C012	1.60 (15)	C024	C013	C032	C029	1.11 (18)
C007	C027	C017	C012	0.47 (15)	C024	C030	C031	C029	0.16 (17)
C008	C007	C027	C017	-1.44 (14)	C025	C012	C017	C027	178.81 (13)
C008	C009	C012	C017	-2.53 (16)	C030	C024	C013	C032	-0.98 (16)
C008	C009	C012	C025	177.75 (13)	C030	C031	C029	C032	-0.03 (19)

Table S12 Hydrogen atom coordinates ($\text{\AA}\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2\times 10^3$) for exp_2_auto.

Atom	x	y	z	U(eq)
H008	165.1 (18)	6093.1 (12)	7752.4 (5)	20.7 (3)

Table S12 Hydrogen atom coordinates ($\text{\AA}\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2\times 10^3$) for exp_2_auto.

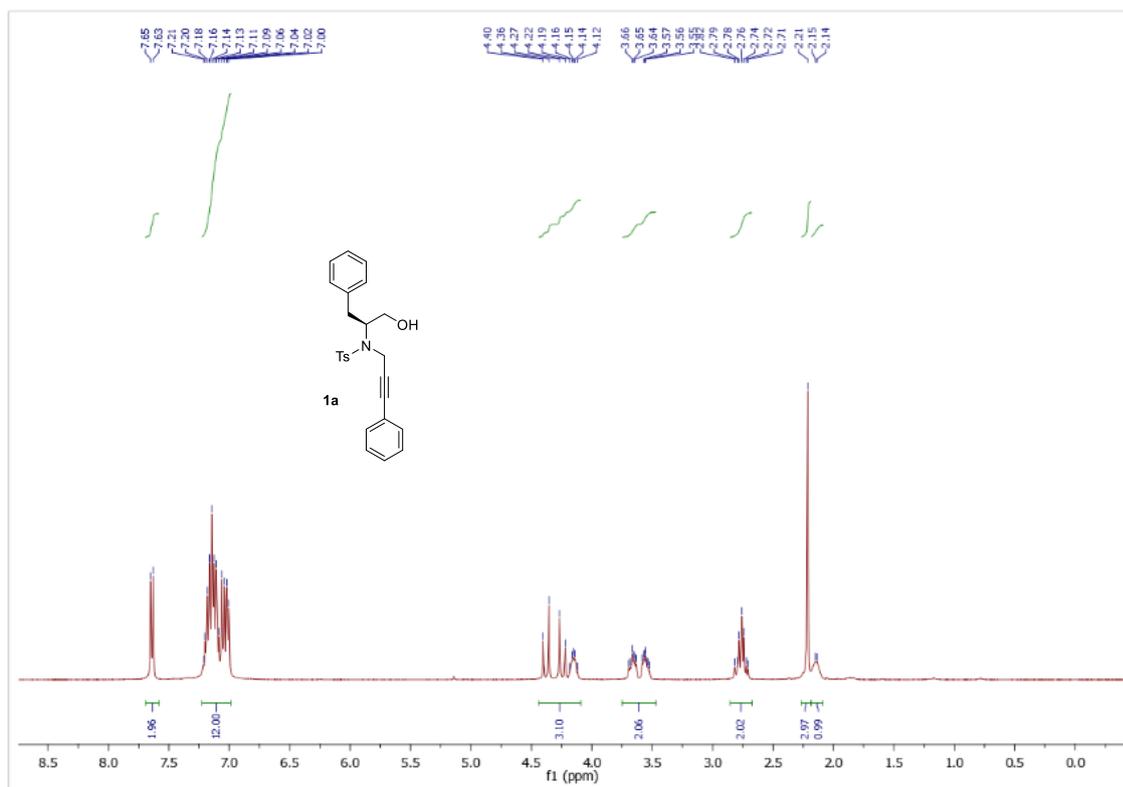
Atom	x	y	z	U(eq)
H009	-220.2 (19)	6085.3 (12)	8565.4 (5)	22.5 (3)
H01a	7011.5 (18)	4274.1 (14)	6908.5 (5)	24.9 (3)
H01b	7072.2 (18)	3822.9 (14)	7439.1 (5)	24.9 (3)
H013	7926 (2)	2645.2 (14)	6305.3 (5)	27.1 (4)
H01c	5706.0 (19)	1867.6 (12)	6863.2 (5)	22.5 (3)
H01d	3629.7 (19)	1966.5 (12)	6750.9 (5)	22.5 (3)
H015	4169.9 (18)	3120.5 (12)	7421.0 (5)	19.3 (3)
H016	3344.8 (17)	6200.2 (13)	7234.8 (5)	20.6 (3)
H017	1105.1 (19)	2522.9 (13)	8609.5 (5)	22.7 (3)
H018	4890 (2)	10774.5 (13)	5584.5 (5)	25.7 (3)
H019	3642.7 (19)	7850.0 (13)	6723.0 (5)	23.9 (3)
H020	4387.5 (19)	9761.8 (14)	6292.6 (5)	24.9 (3)
H021	5534 (2)	7529.6 (14)	4927.0 (5)	28.4 (4)
H02a	5412 (18)	9864.1 (18)	4082.6 (5)	46.8 (5)
H02b	6425 (10)	8752 (9)	4315 (2)	46.8 (5)
H02c	4297 (9)	8811 (9)	4323 (2)	46.8 (5)
H023	5041 (2)	6529.8 (13)	5635.1 (5)	28.2 (4)
H02d	525 (16)	5147 (3)	9321.1 (6)	37.8 (4)
H02e	-925 (5)	4097 (10)	9295.9 (5)	37.8 (4)
H02f	1142 (11)	3773 (8)	9342.7 (5)	37.8 (4)
H027	1412.2 (18)	2495.1 (12)	7794.4 (5)	20.4 (3)
H028	5380.9 (19)	5803.7 (13)	6384.9 (5)	23.6 (3)
H029	6295 (3)	3744.9 (15)	5019.5 (5)	38.5 (4)
H030	2625 (2)	3145.8 (13)	6041.2 (5)	27.1 (3)
H031	3311 (2)	3721.3 (15)	5274.3 (6)	36.0 (4)
H032	8603 (2)	3186.2 (15)	5534.2 (6)	34.2 (4)

11 References:

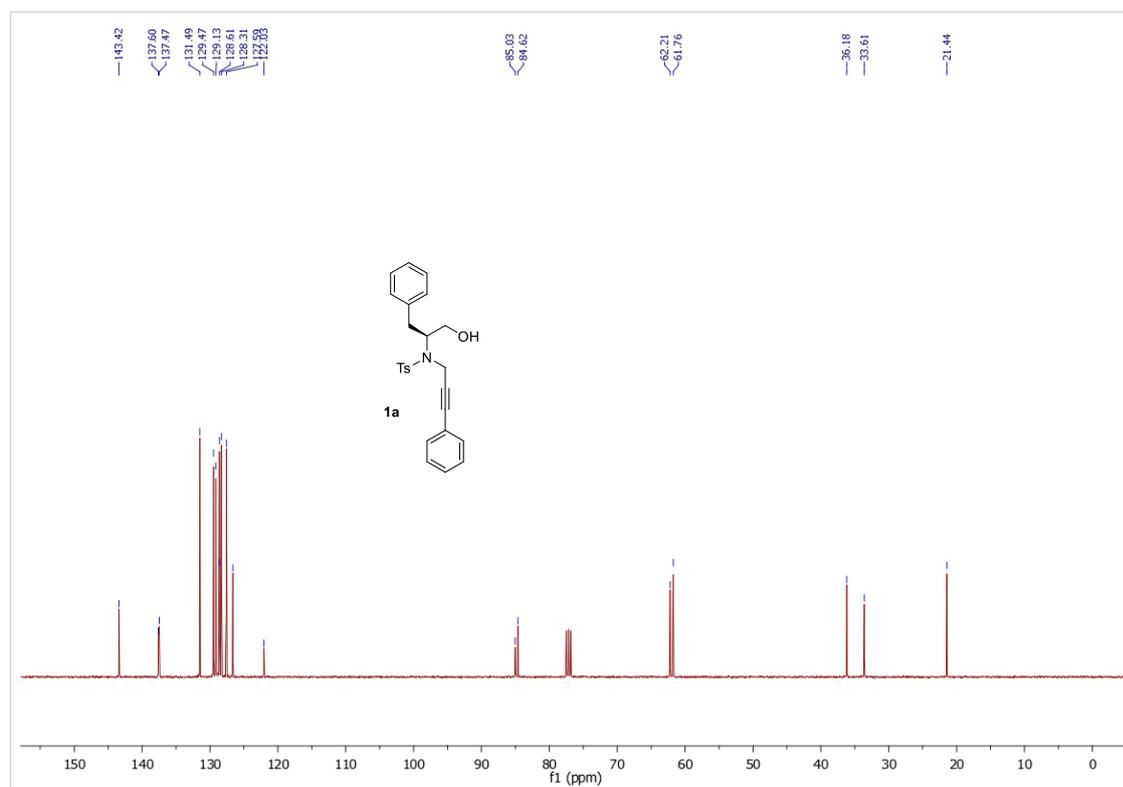
- (1) a) D. I. Ugwu, U. C. Okoro and N. K. Mishra, *PLoS ONE*, 2018, **13**, e0191234; b) J. L. M. Matos, S. Vasquez-Cespedes, J. Gu and R. A. Shenvi, *J. Am. Chem. Soc.*, 2018, **140**, 16976-16981; c) A. V. Malkov, Z. Bourhani, and P. Kocovsky, *Org. Biomol. Chem.*, 2005, **3**, 3194-3200.
- (2) D. Craig, S. R. J. Spreadbury and A. J. P. White, *Chem. Commun.*, 2020, **56**, 9803-9806.
- (3) a) J. S. Gharpure, D. Kalita, S. Somani and J. Pal, *Org. Biomol. Chem.*, 2024, **22**, 5529-5533; b) A. Z. Halimehjani and B. Breit, *Chem. Commun.*, 2023, **59**, 4376-4379.

12 NMR spectral data of final substrate:

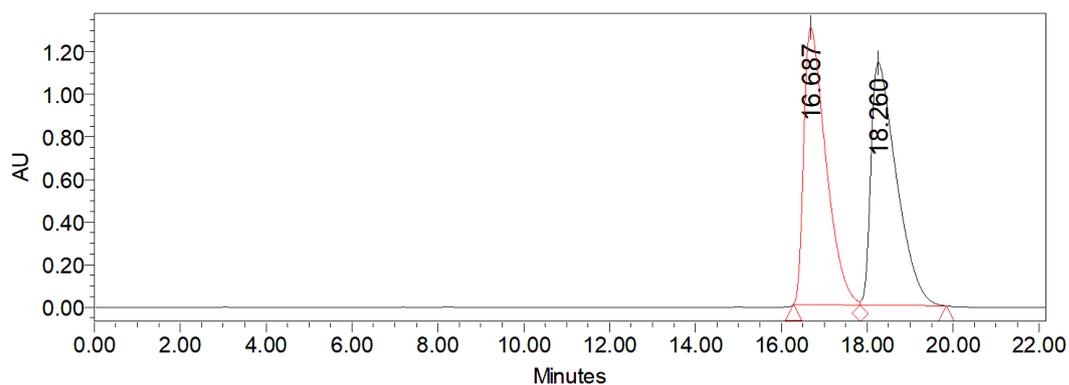
^1H NMR of **1a** (400 MHz, CDCl_3)



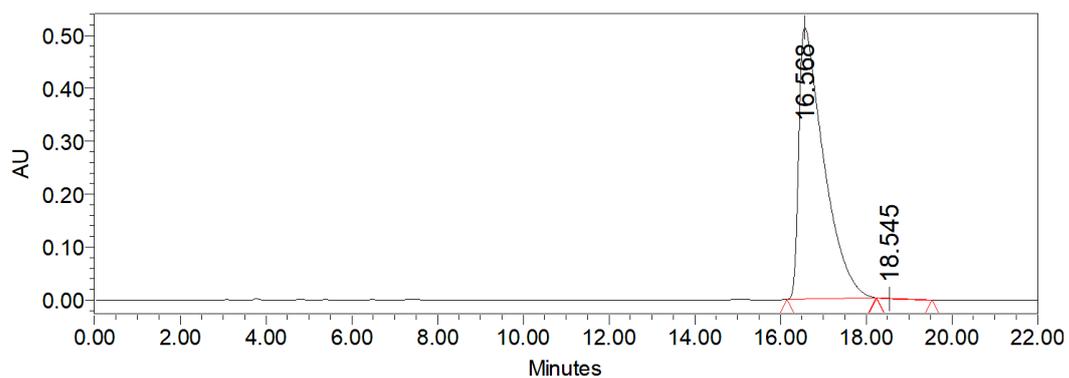
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1a** (101 MHz, CDCl_3)



HPLC spectra of **1a** (101 MHz, CDCl₃)

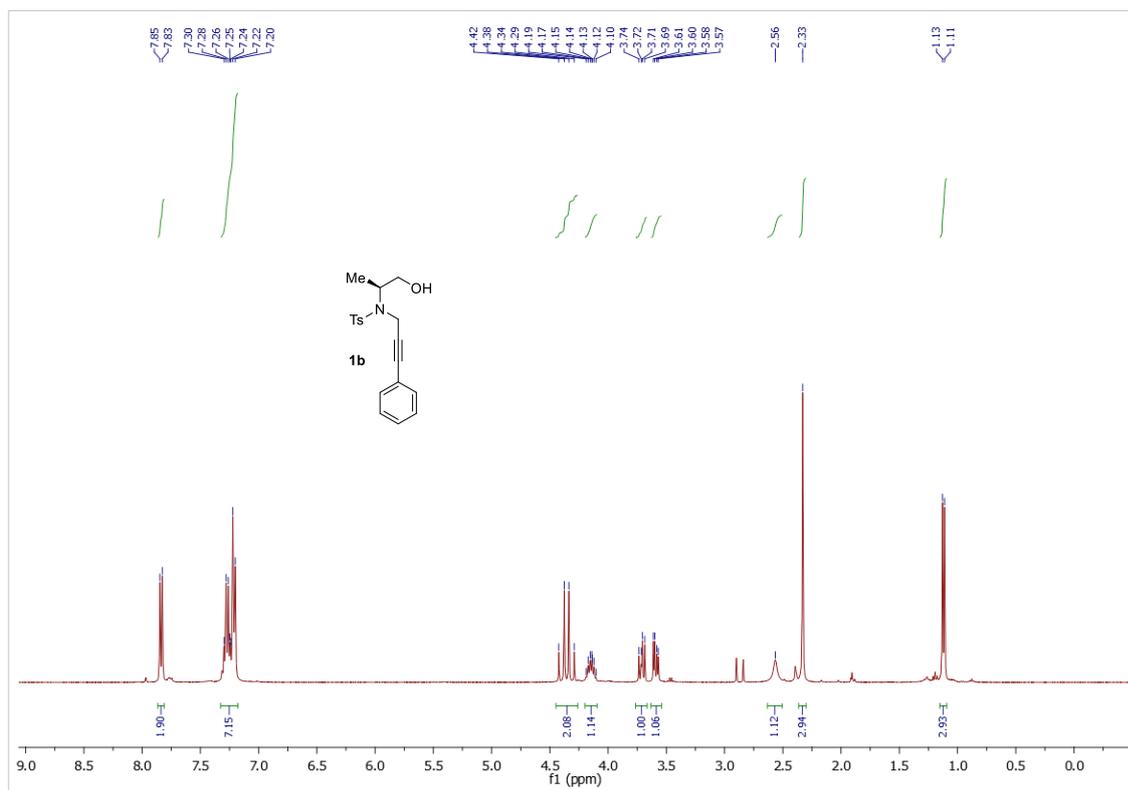


S.No.	Retention Time	Area	% Area
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2	18.260	47062347	50.30

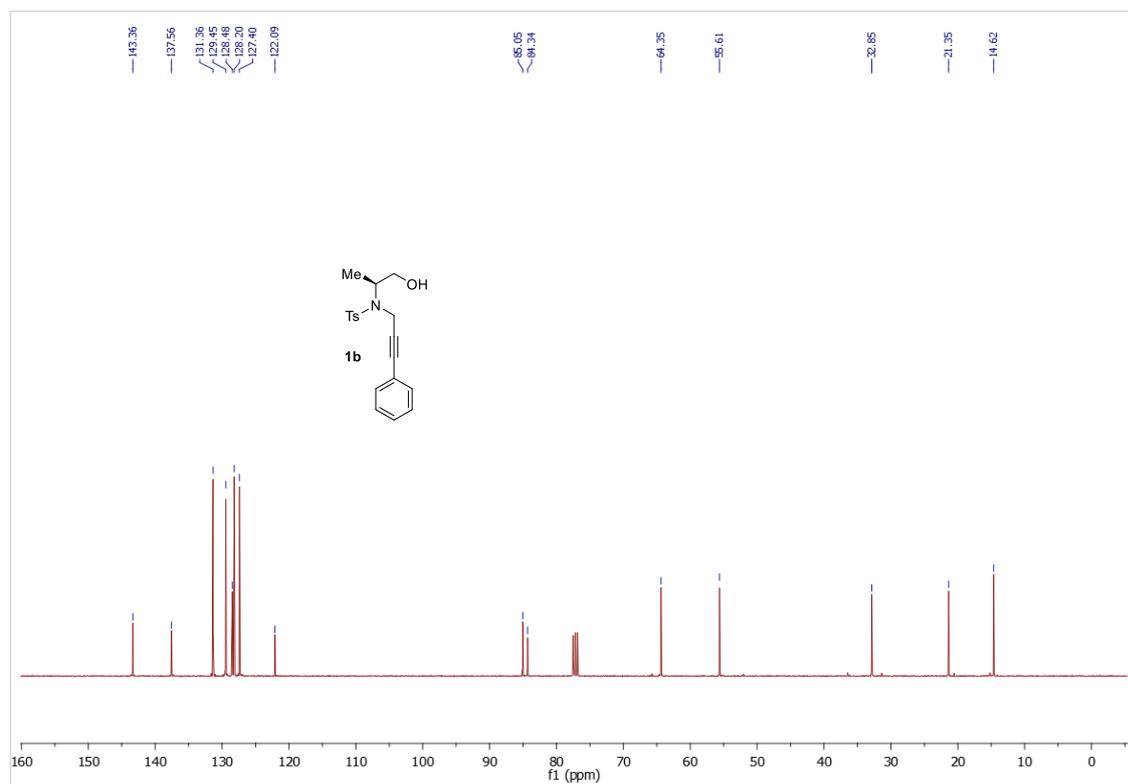


S.No.	Retention Time	Area	%
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2	18.545	57320	0.28

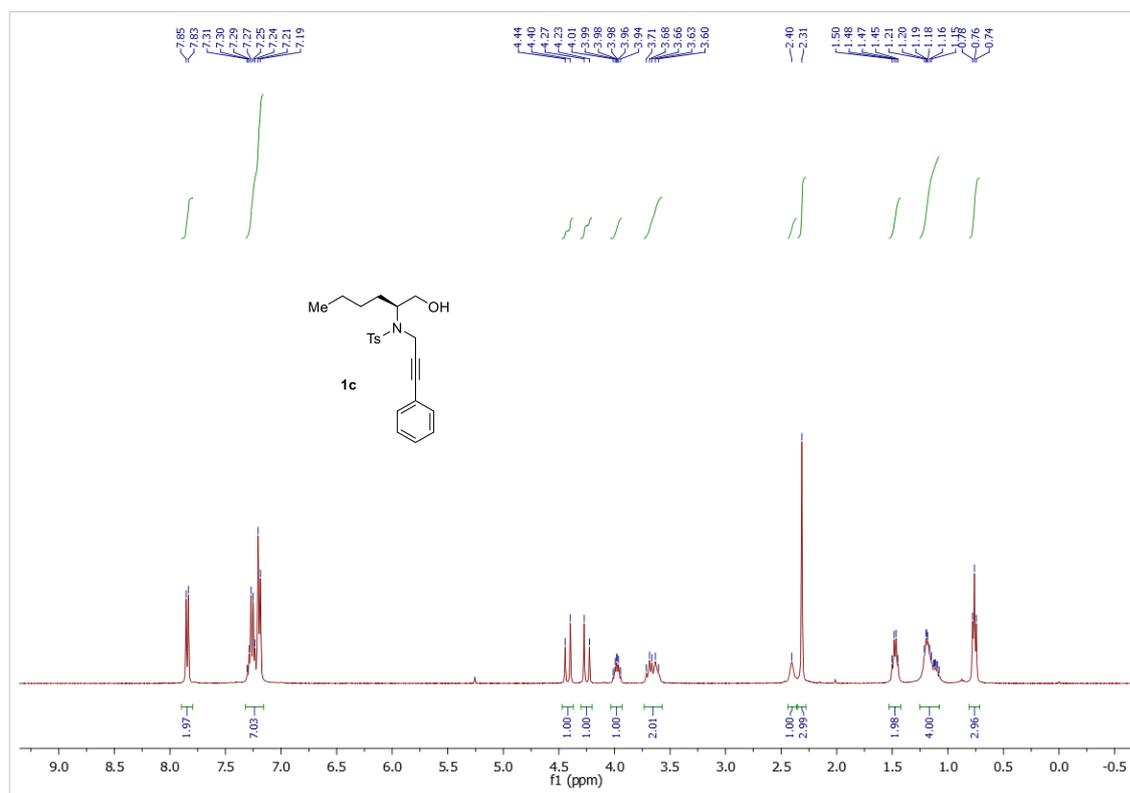
^1H NMR of **1b** (400 MHz, CDCl_3)



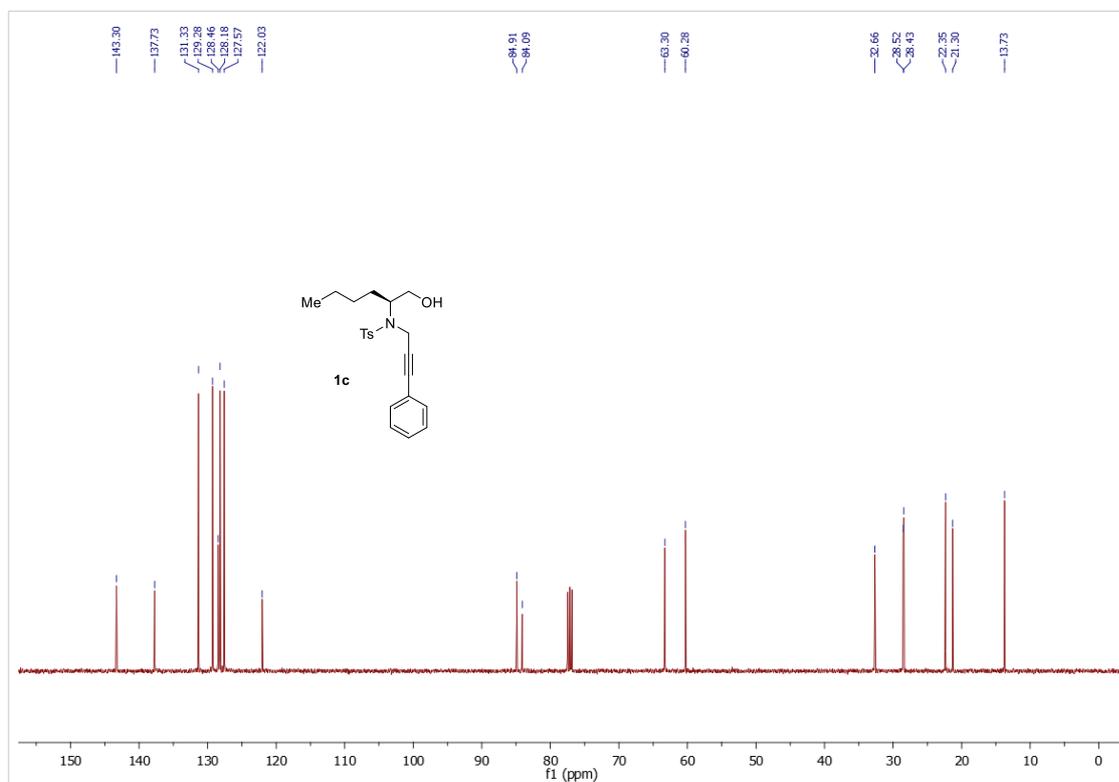
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1b** (101 MHz, CDCl_3)



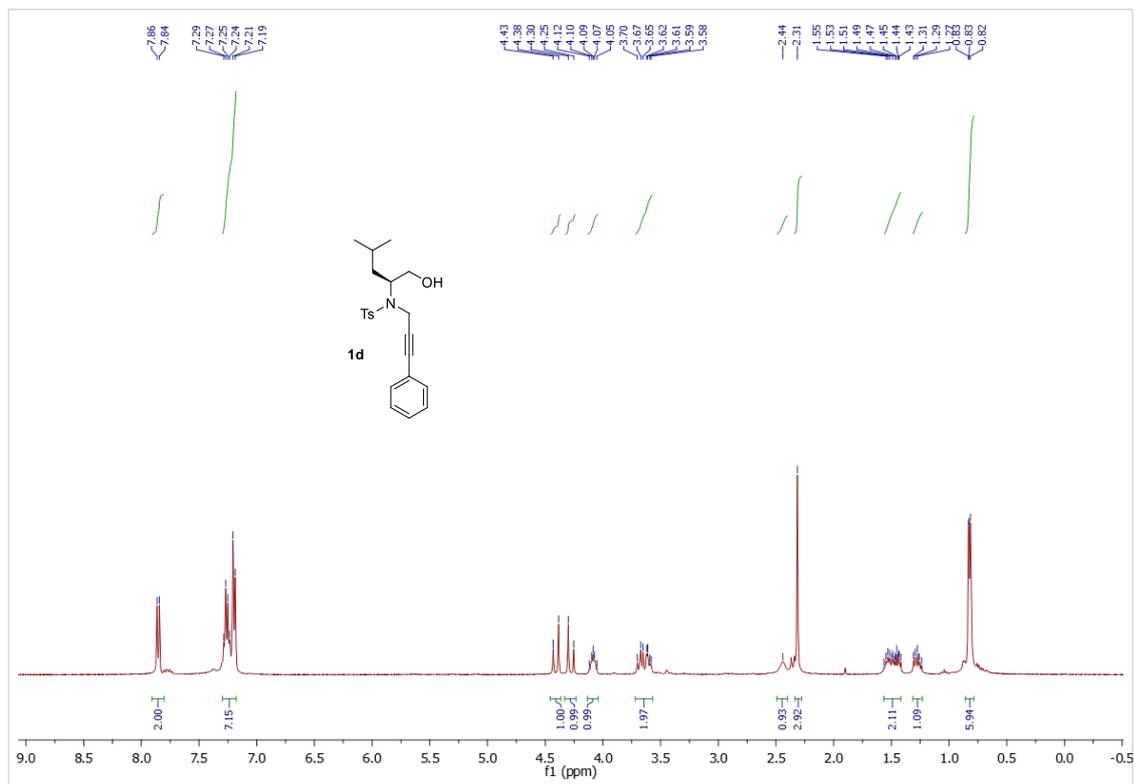
^1H NMR of **1c** (400 MHz, CDCl_3)



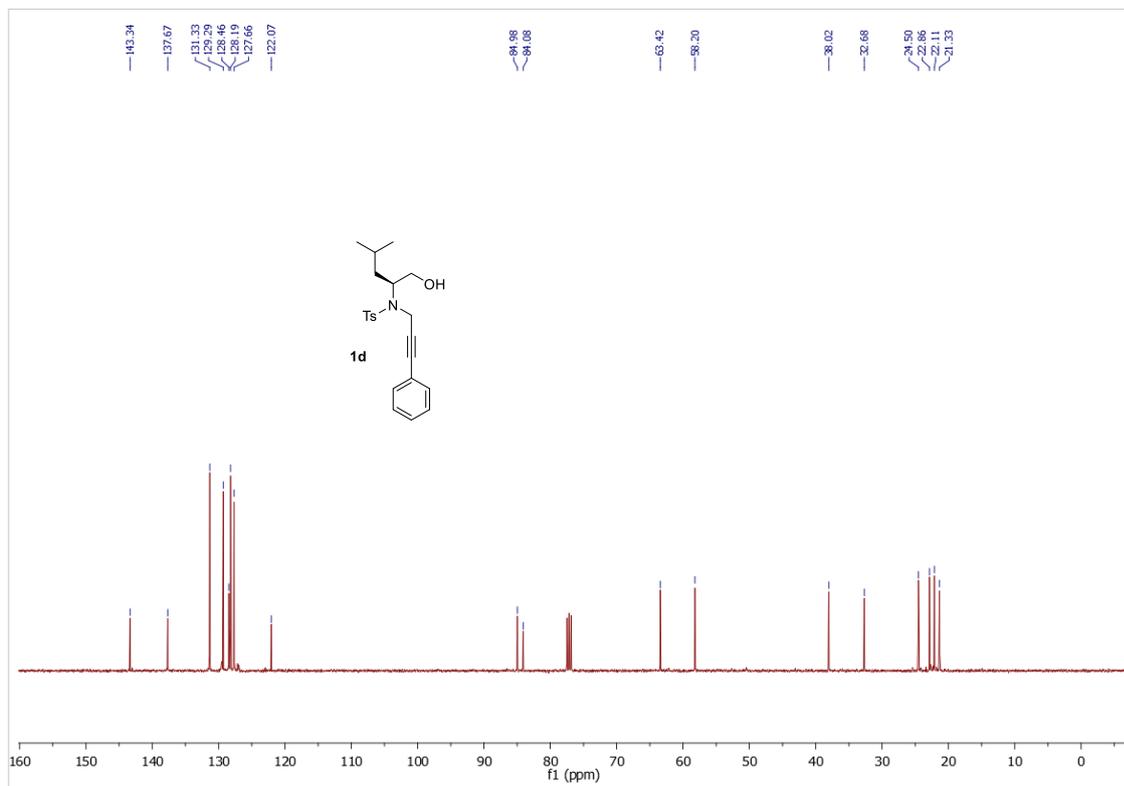
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1c** (101 MHz, CDCl_3)



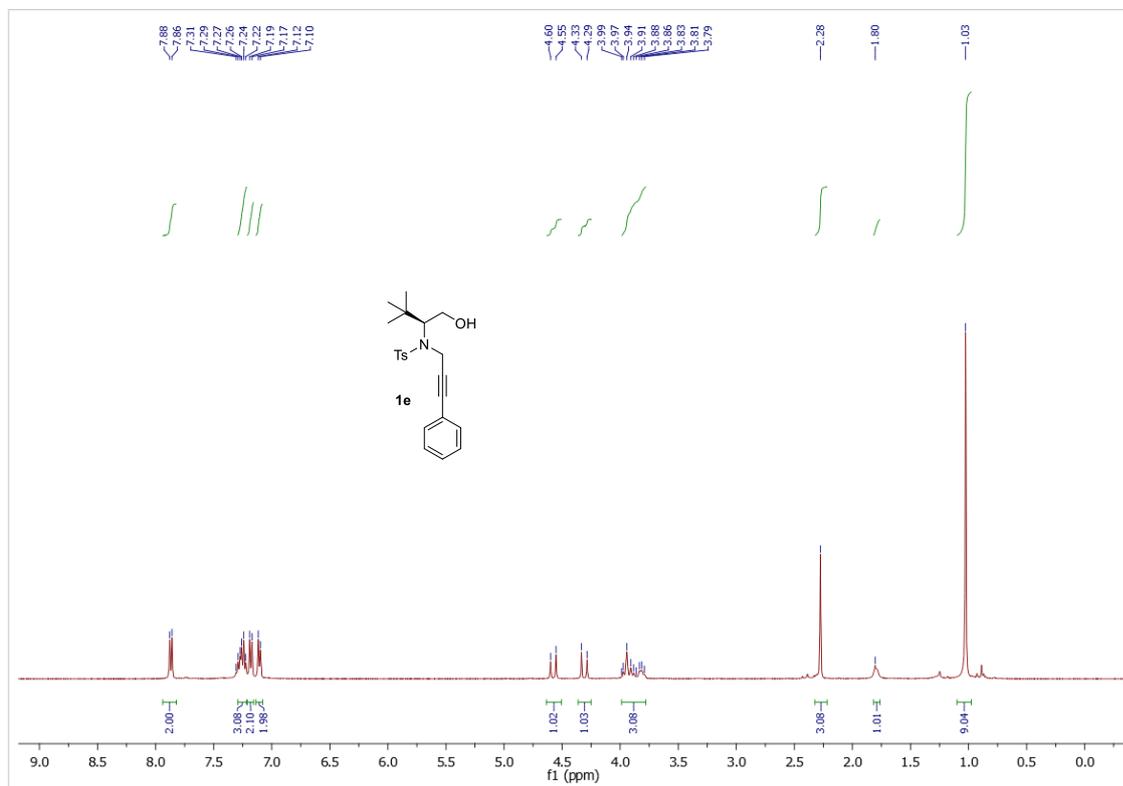
^1H NMR of **1d** (400 MHz, CDCl_3)



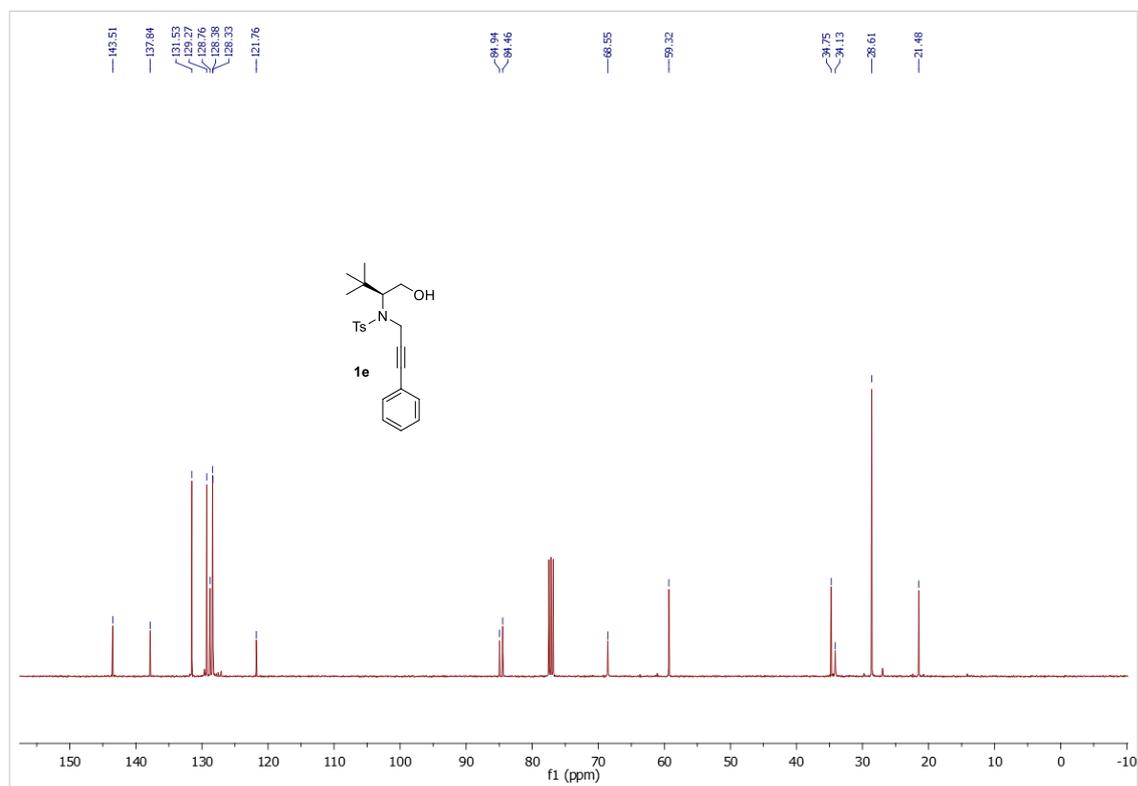
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1d** (101 MHz, CDCl_3)



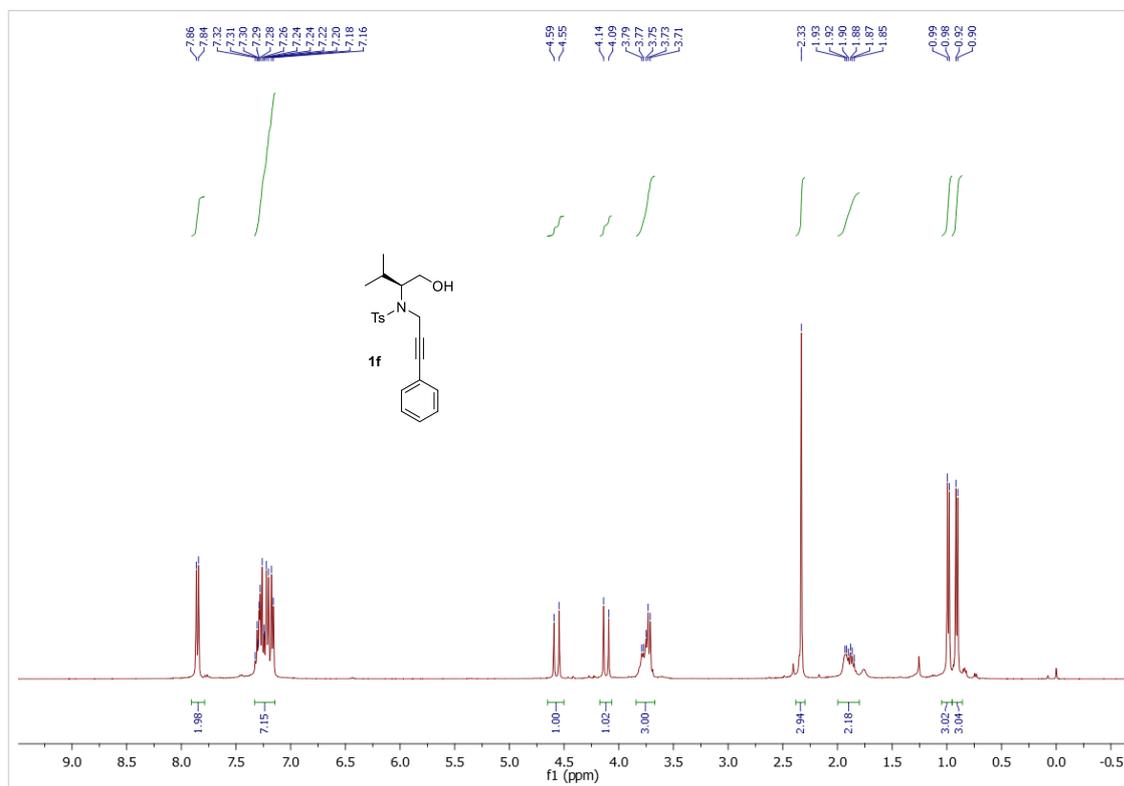
^1H NMR of **1e** (400 MHz, CDCl_3)



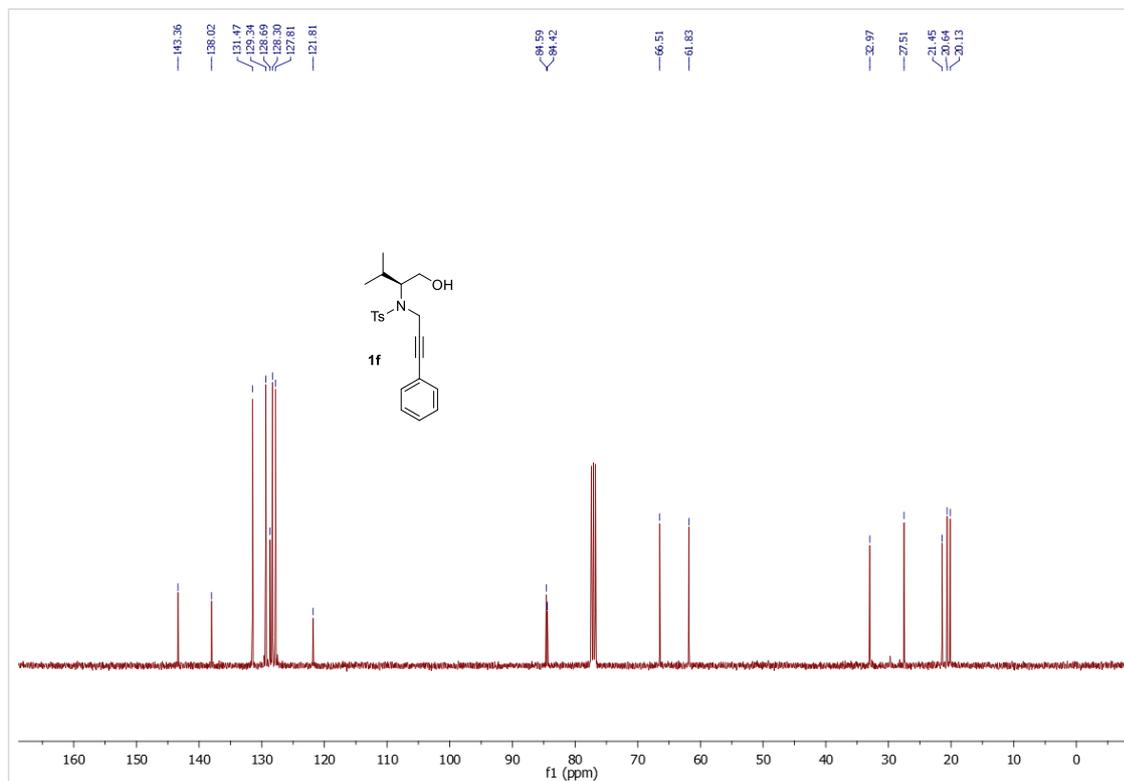
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1e** (101 MHz, CDCl_3)



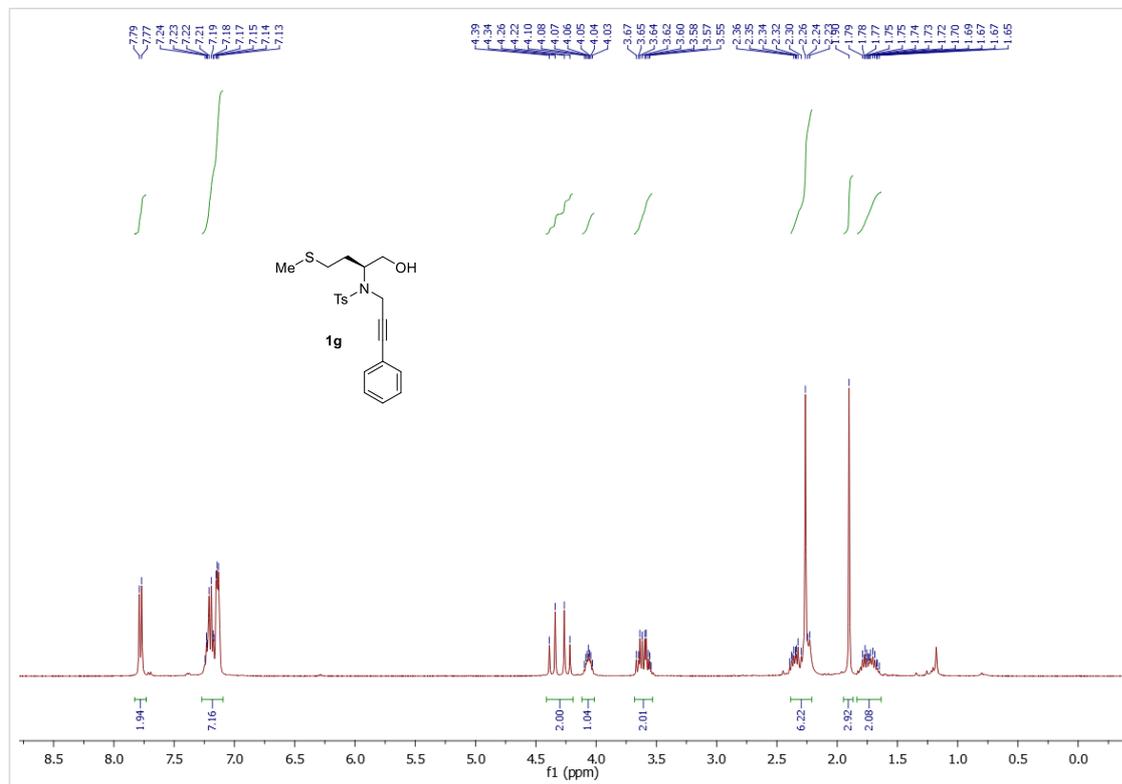
^1H NMR of **1f** (400 MHz, CDCl_3)



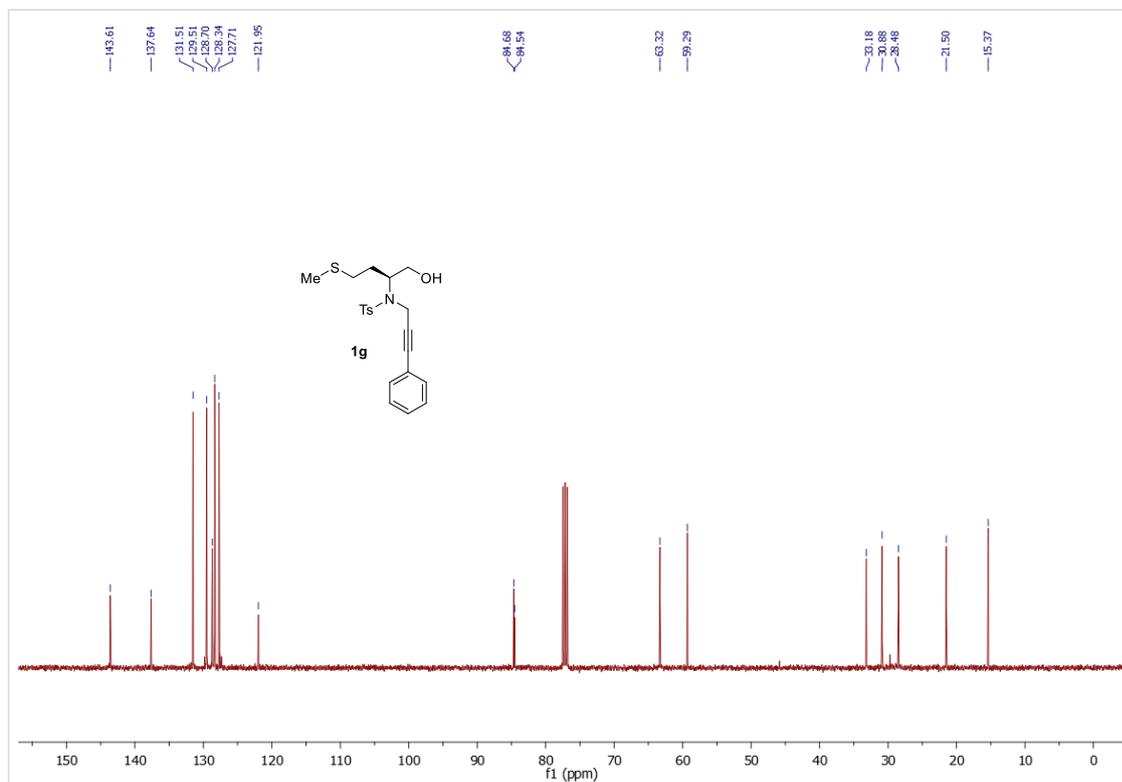
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1f** (101 MHz, CDCl_3)



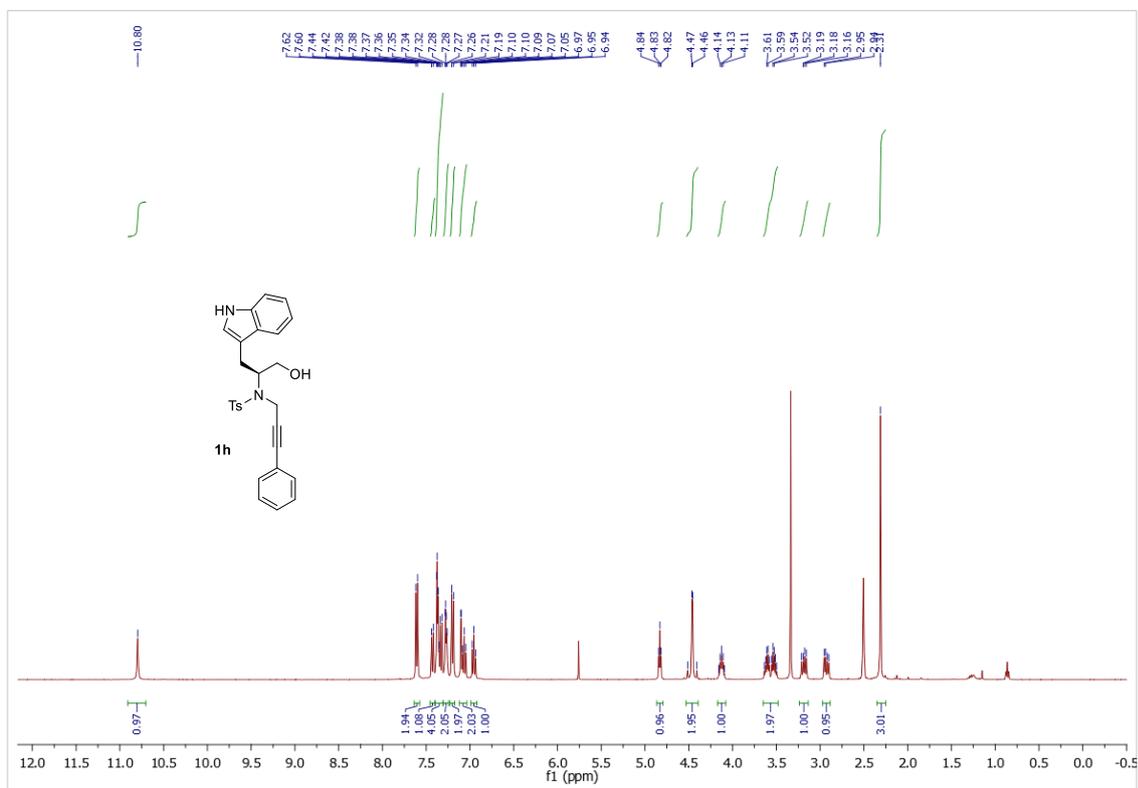
^1H NMR of **1g** (400 MHz, CDCl_3)



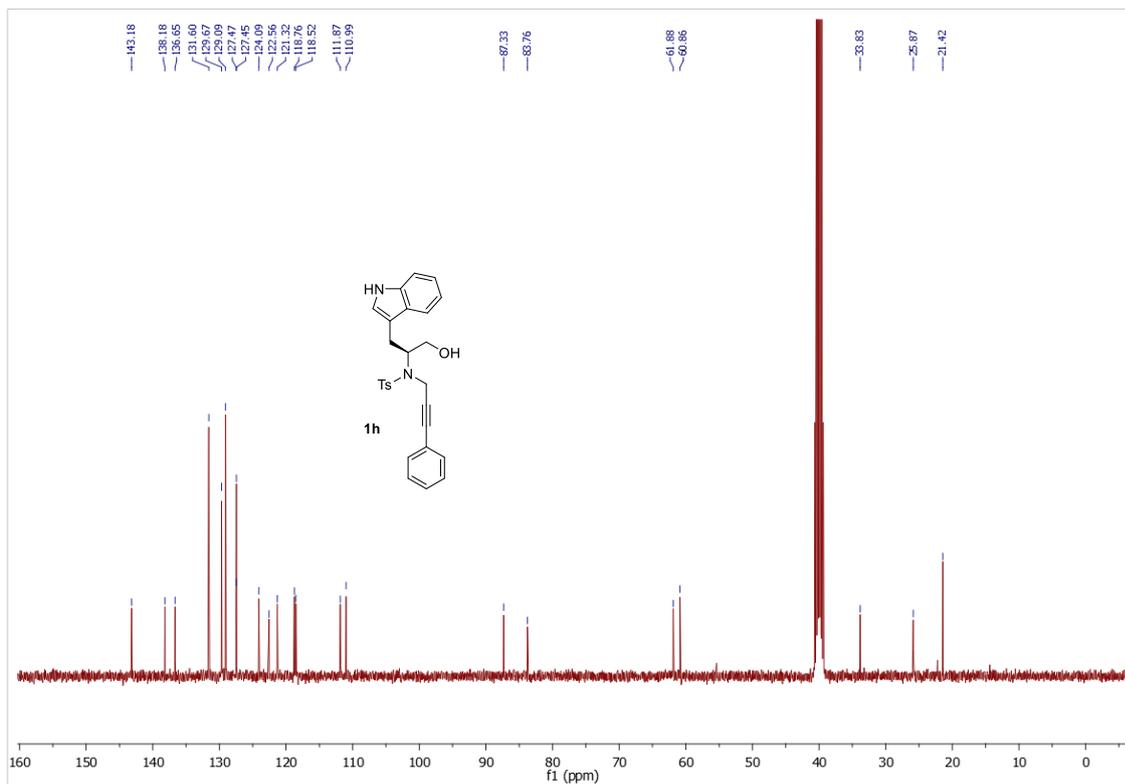
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1g** (101 MHz, CDCl_3)



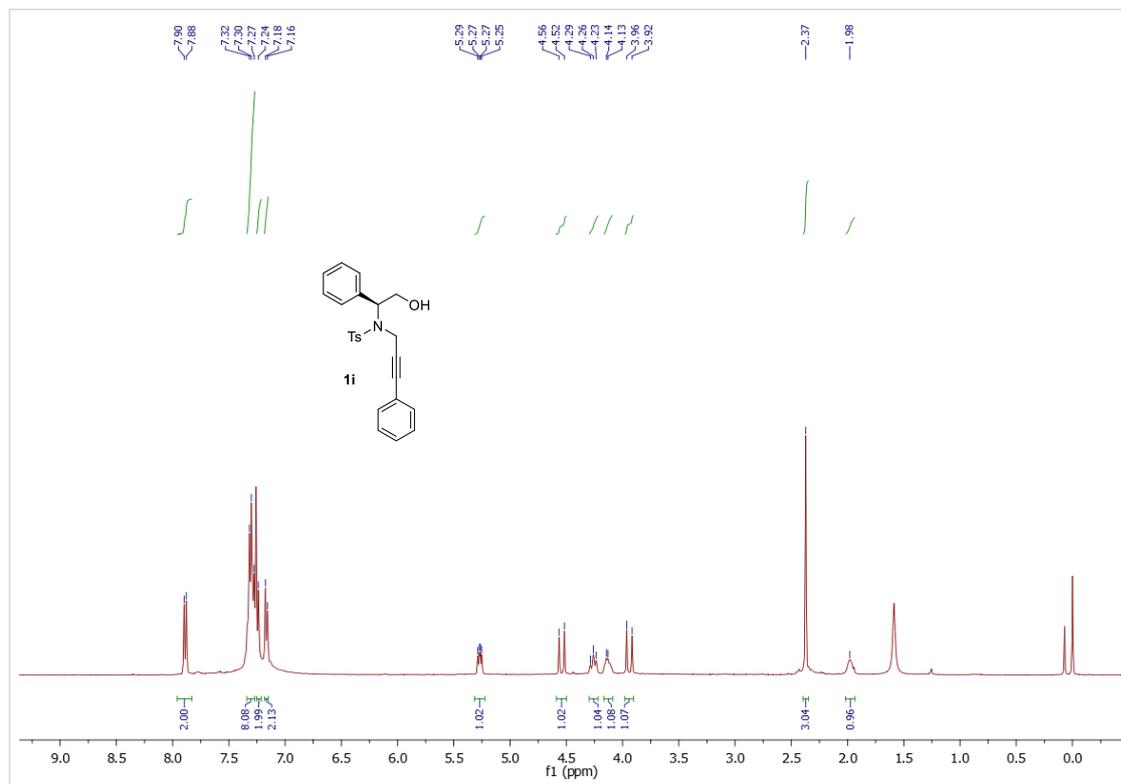
^1H NMR of **1h** (400 MHz, DMSO- d_6)



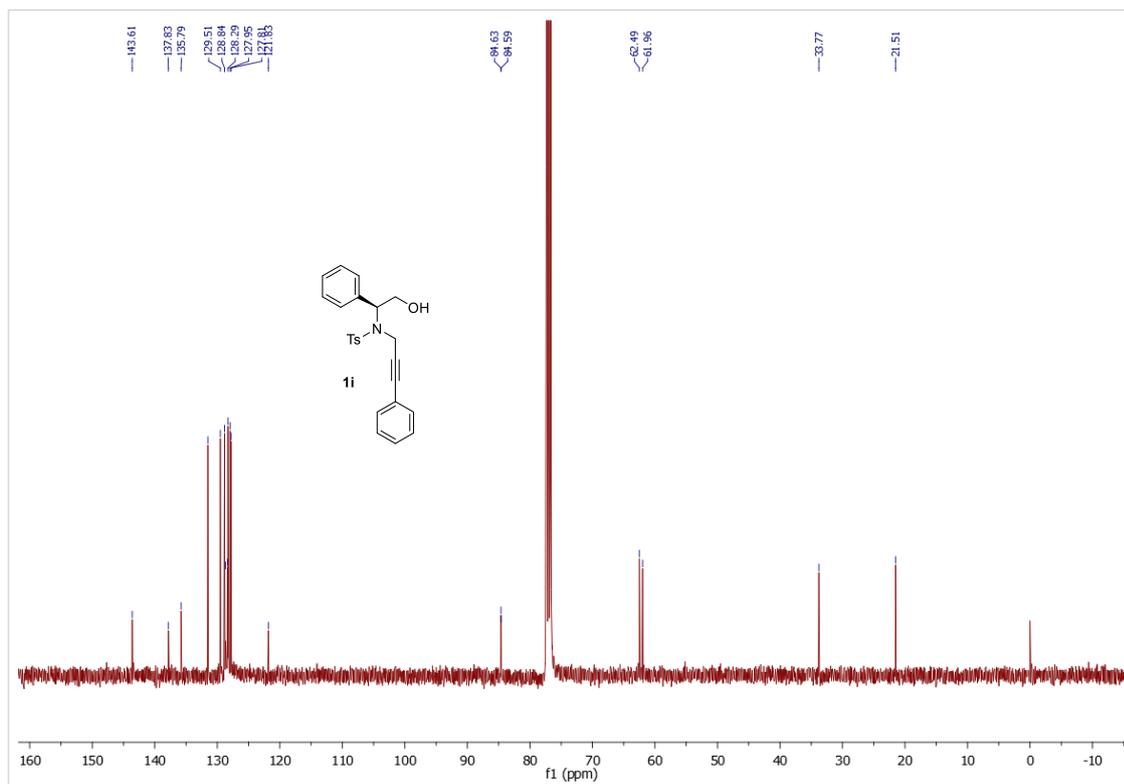
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1h** (400 MHz, DMSO- d_6)



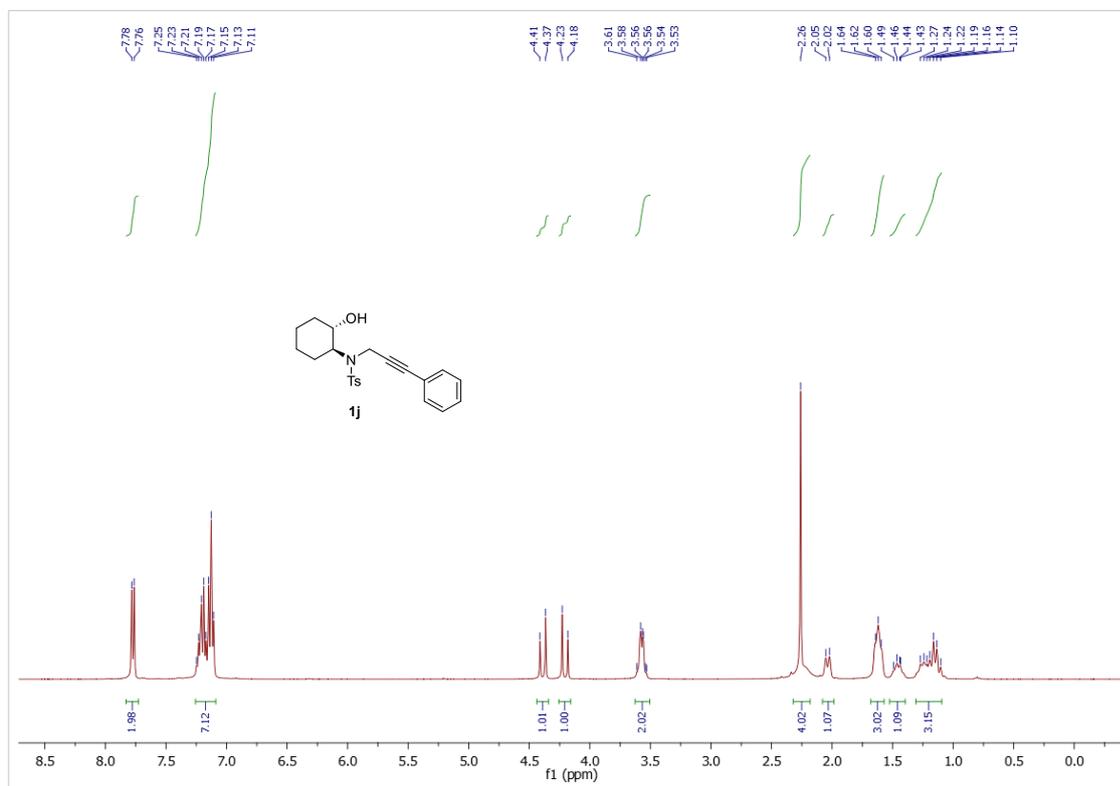
^1H NMR of **1i** (400 MHz, CDCl_3)



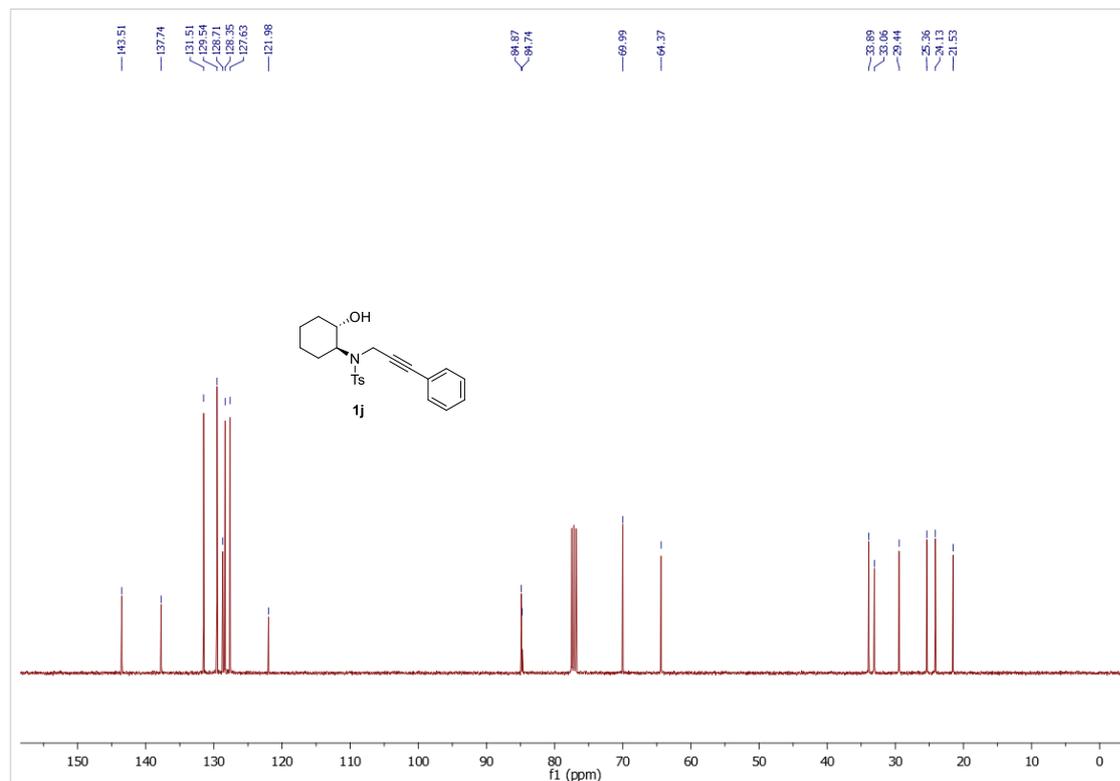
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1i** (101 MHz, CDCl_3)



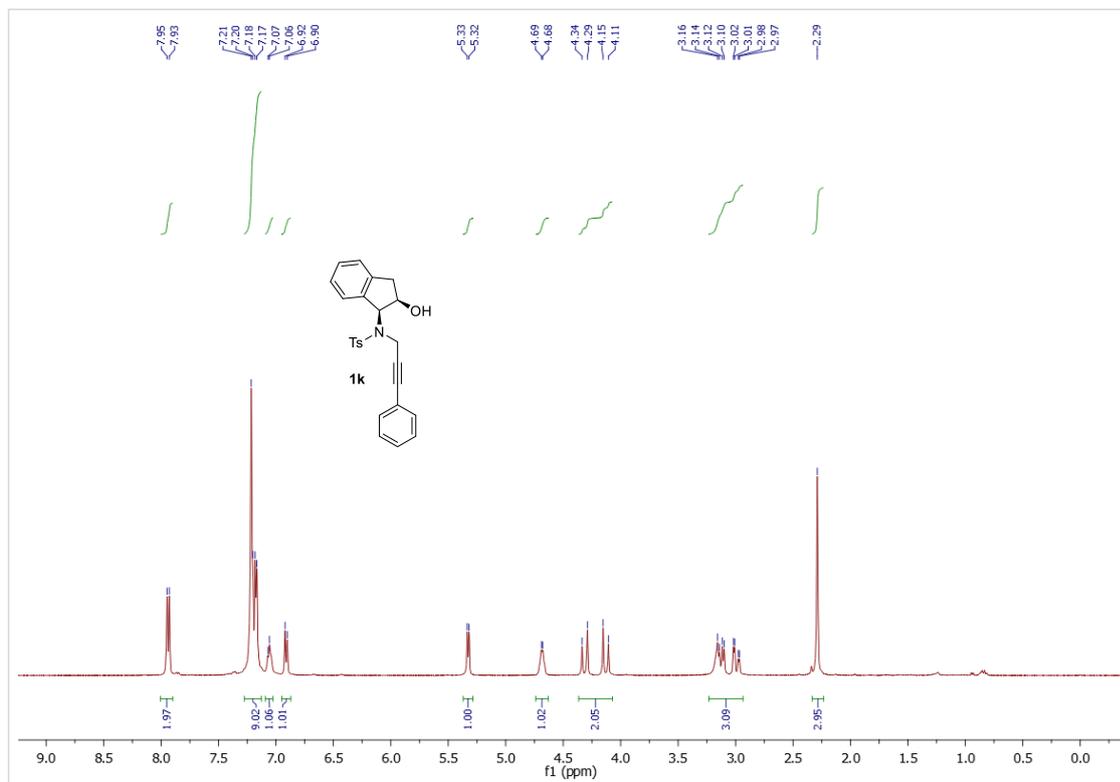
^1H NMR of **1j** (400 MHz, CDCl_3)



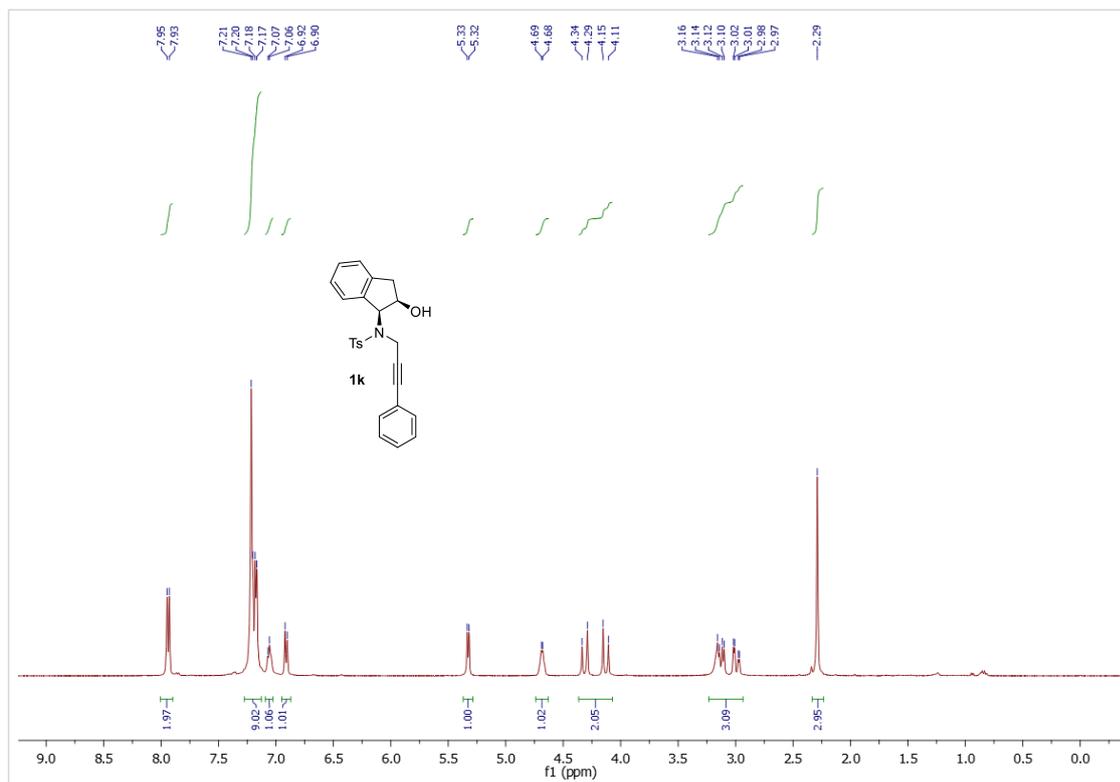
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1j** (101 MHz, CDCl_3)



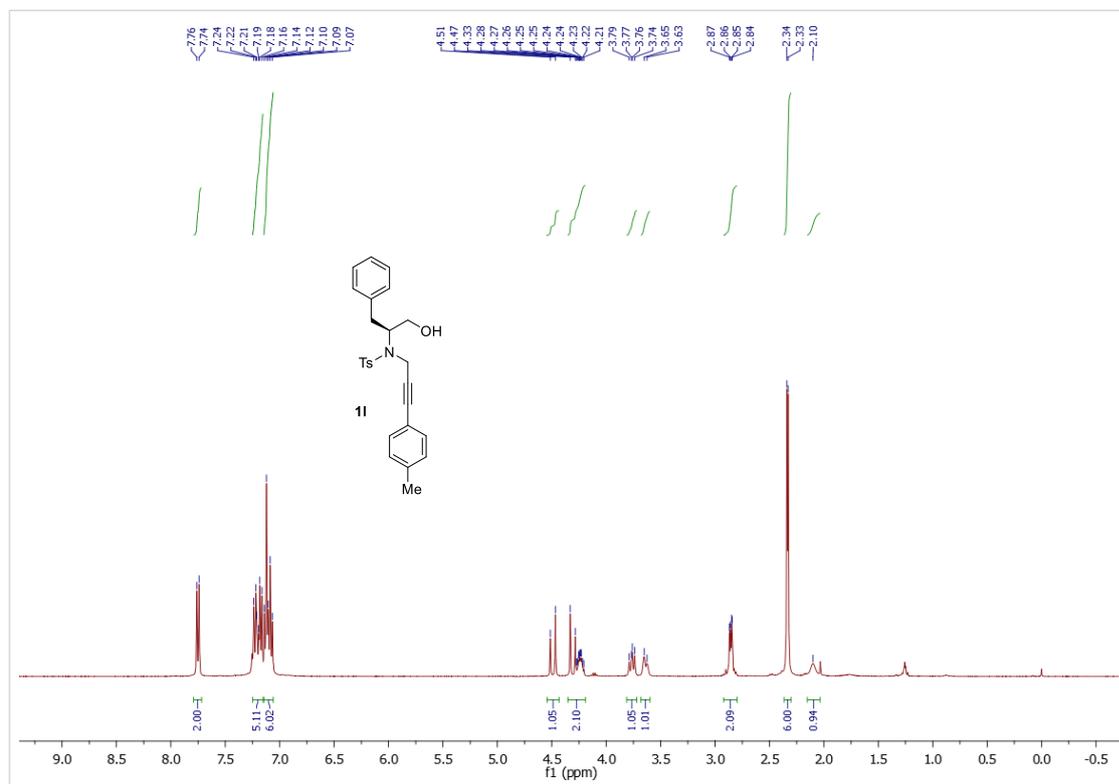
^1H NMR of **1k** (400 MHz, CDCl_3)



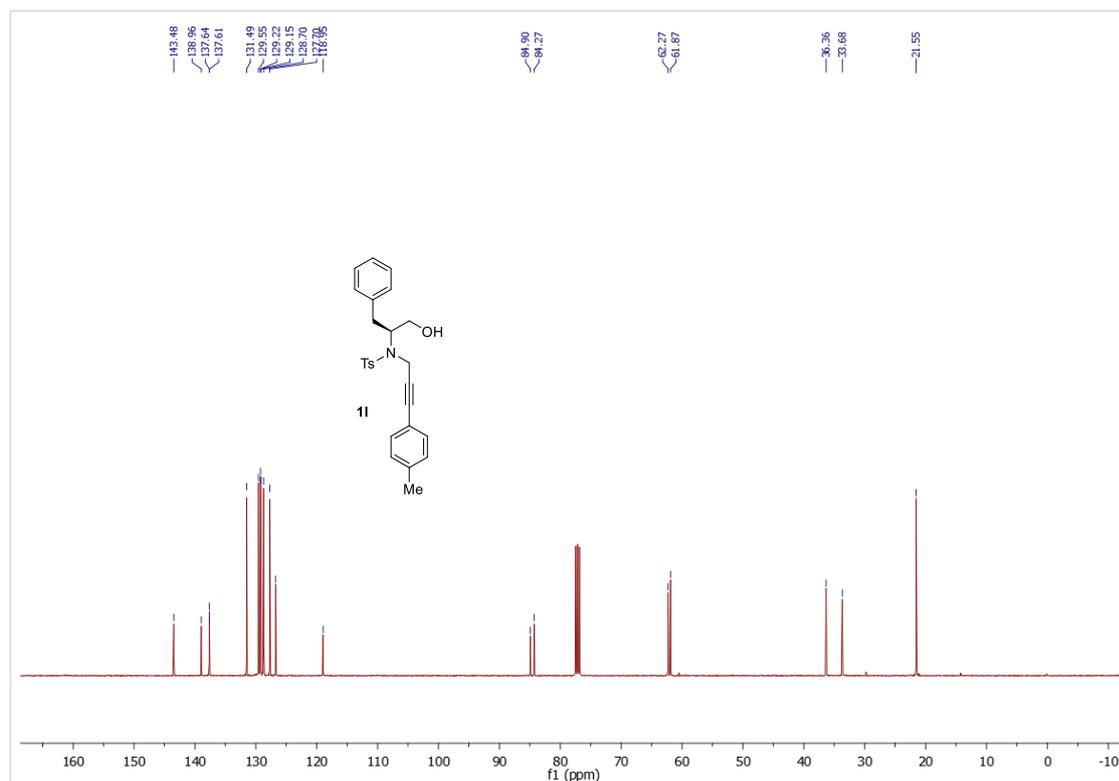
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1k** (101 MHz, CDCl_3)



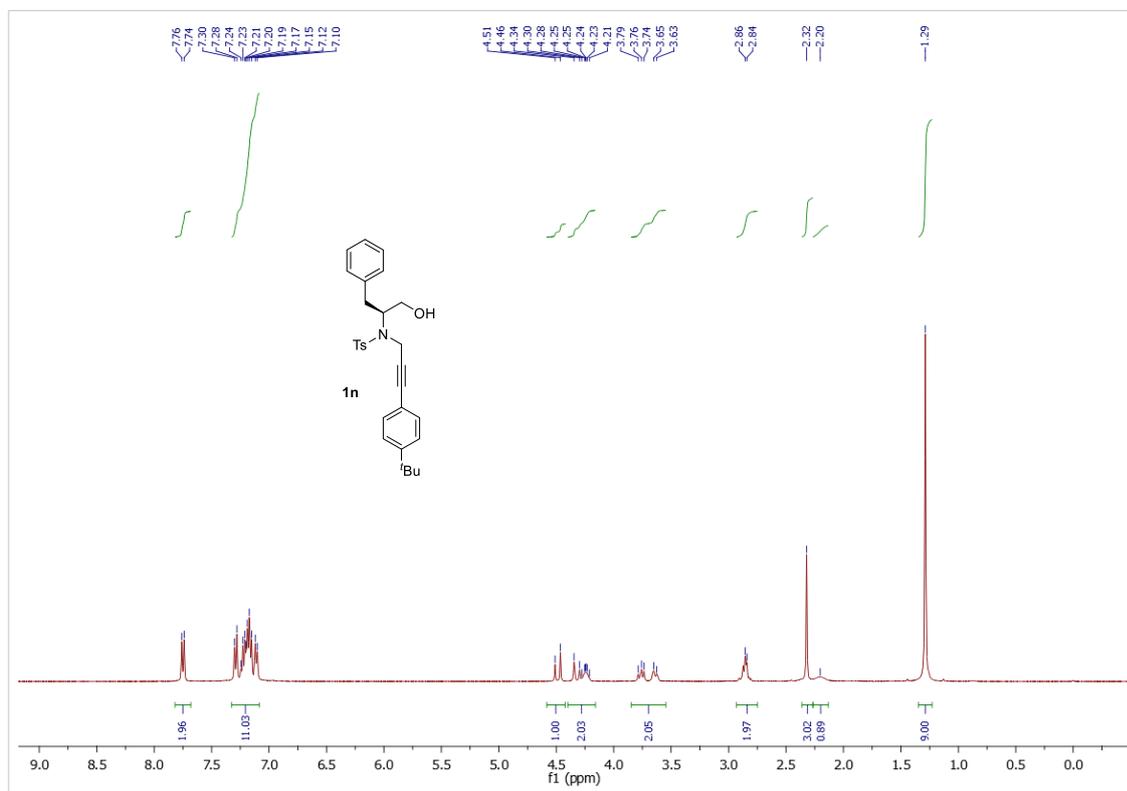
^1H NMR of **11** (400 MHz, CDCl_3)



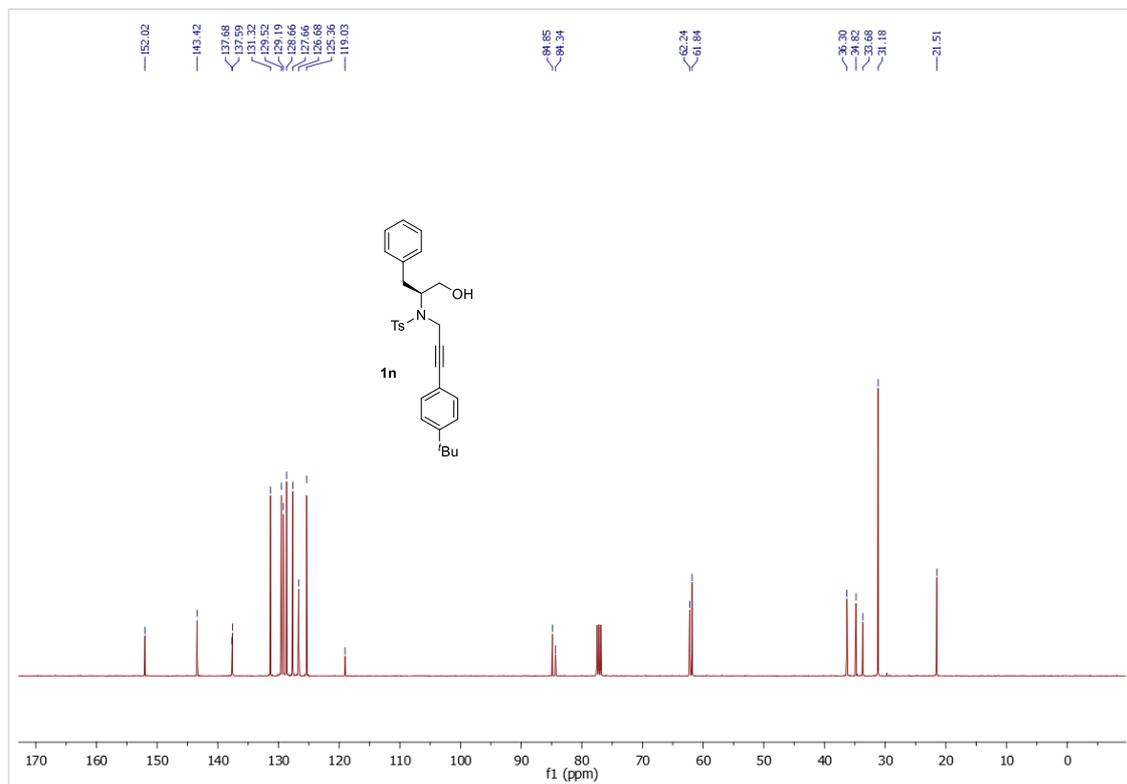
$^{13}\text{C}\{^1\text{H}\}$ NMR of **11** (101 MHz, CDCl_3)



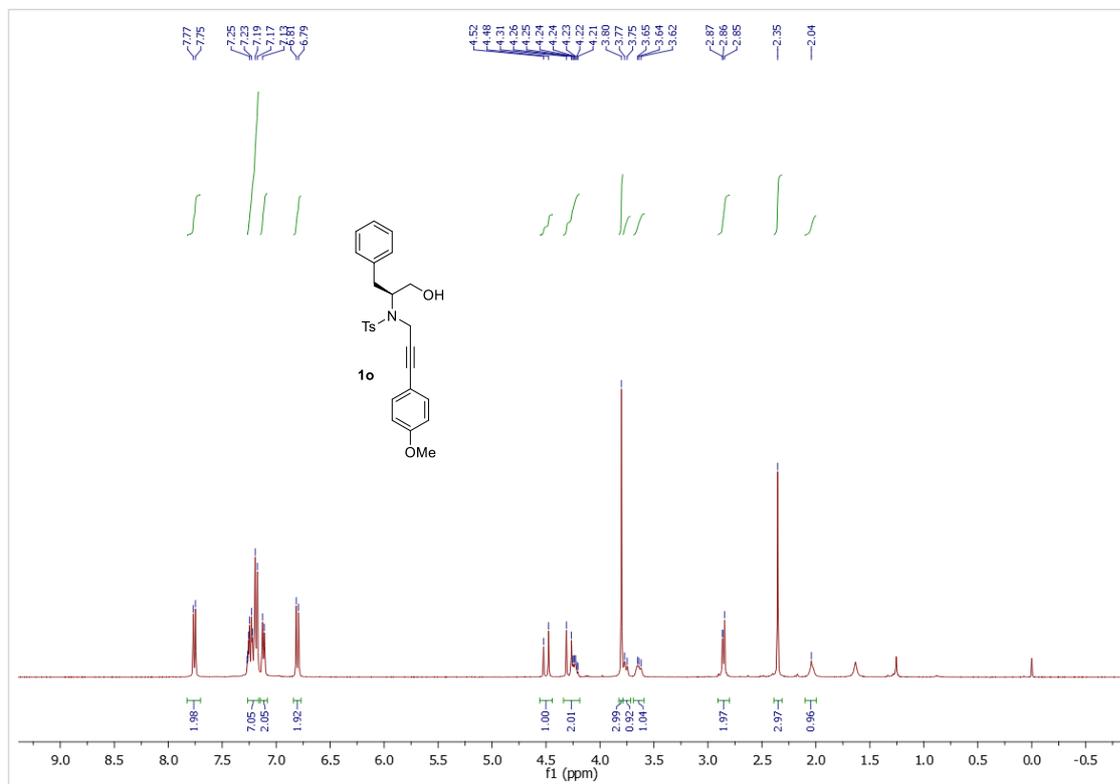
^1H NMR of **1n** (400 MHz, CDCl_3)



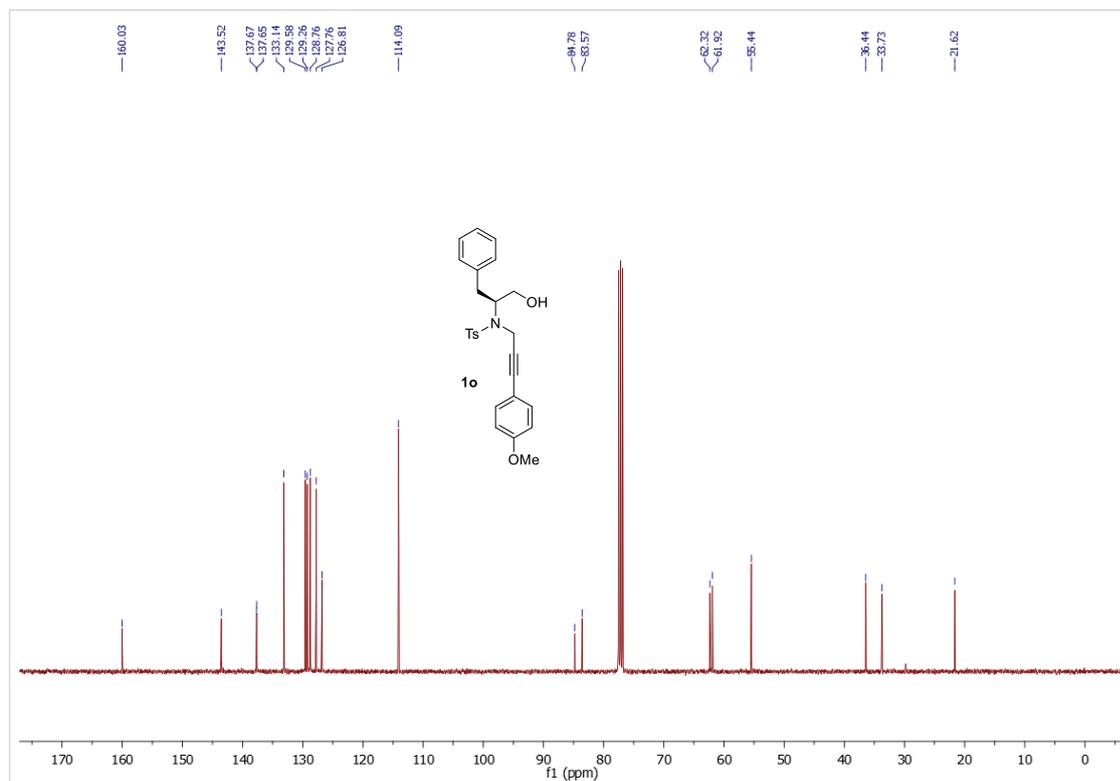
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1n** (101 MHz, CDCl_3)



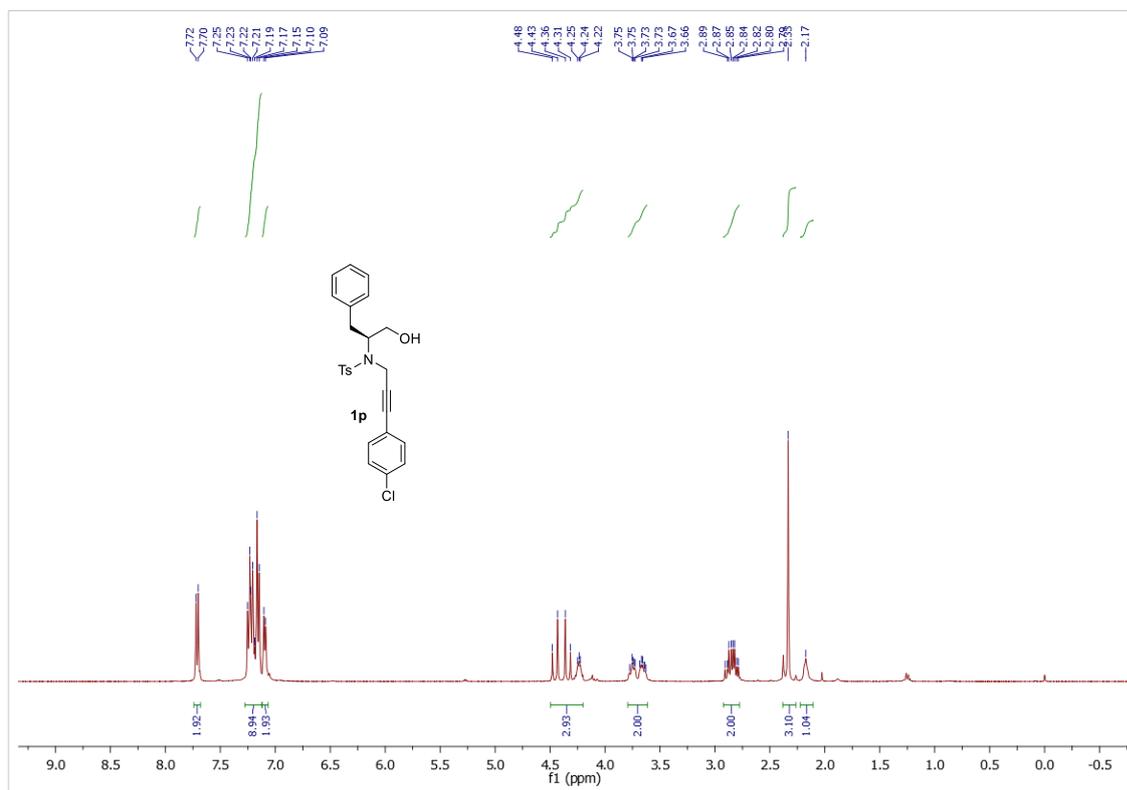
^1H NMR of **1o** (400 MHz, CDCl_3)



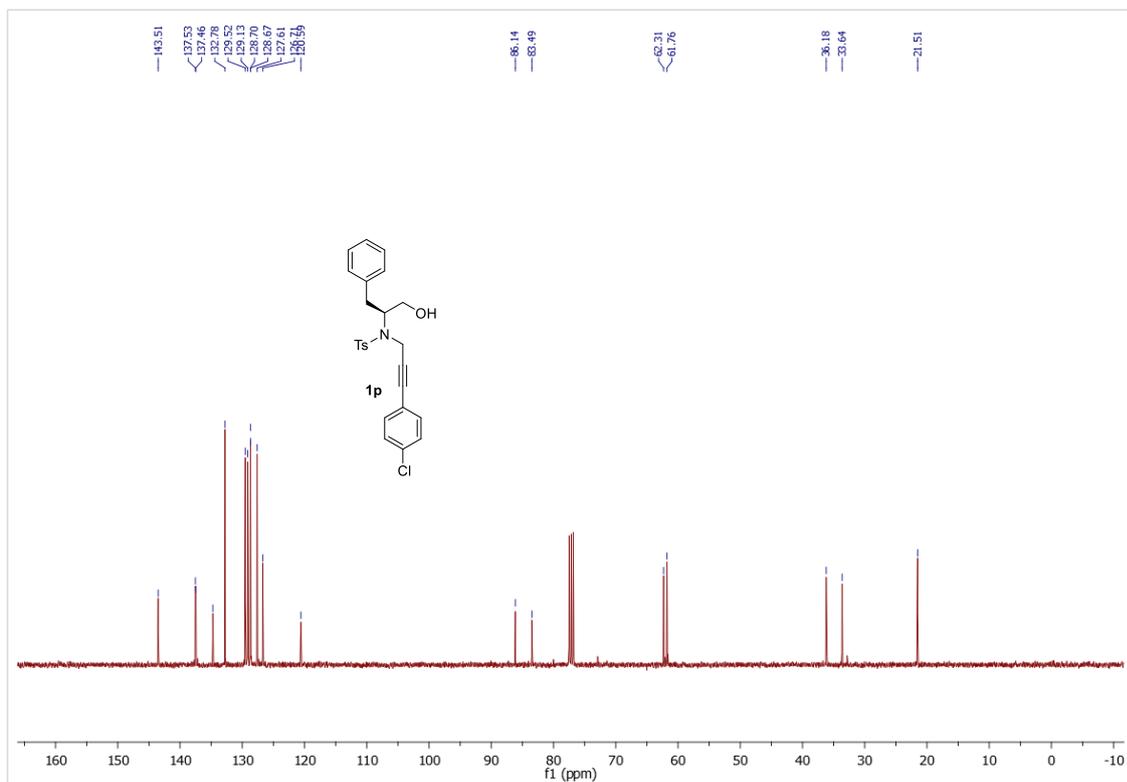
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1o** (101 MHz, CDCl_3)



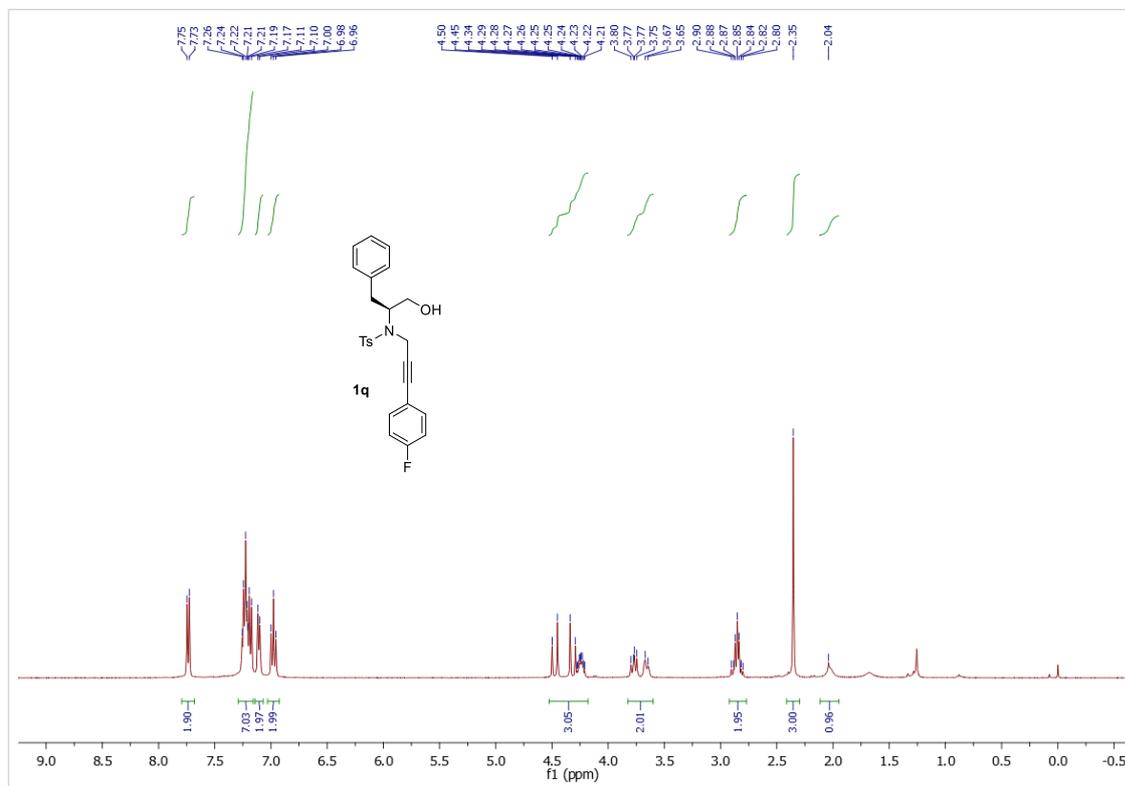
^1H NMR of **1p** (400 MHz, CDCl_3)



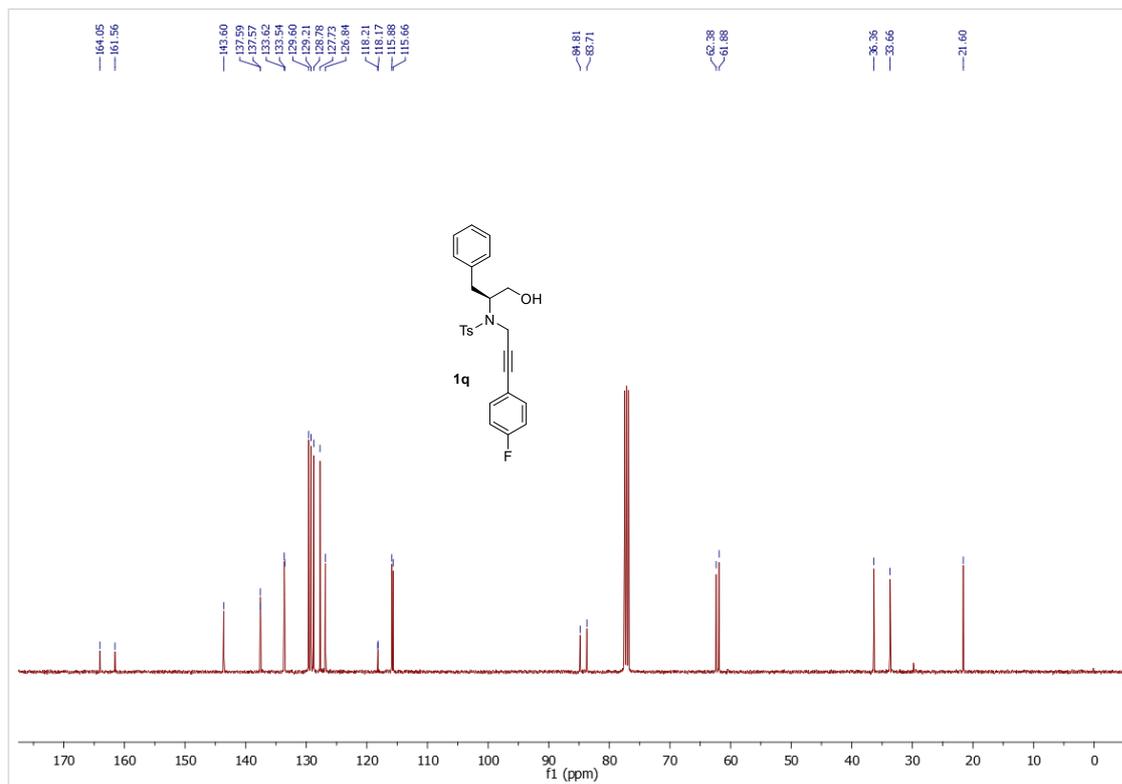
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1p** (101 MHz, CDCl_3)



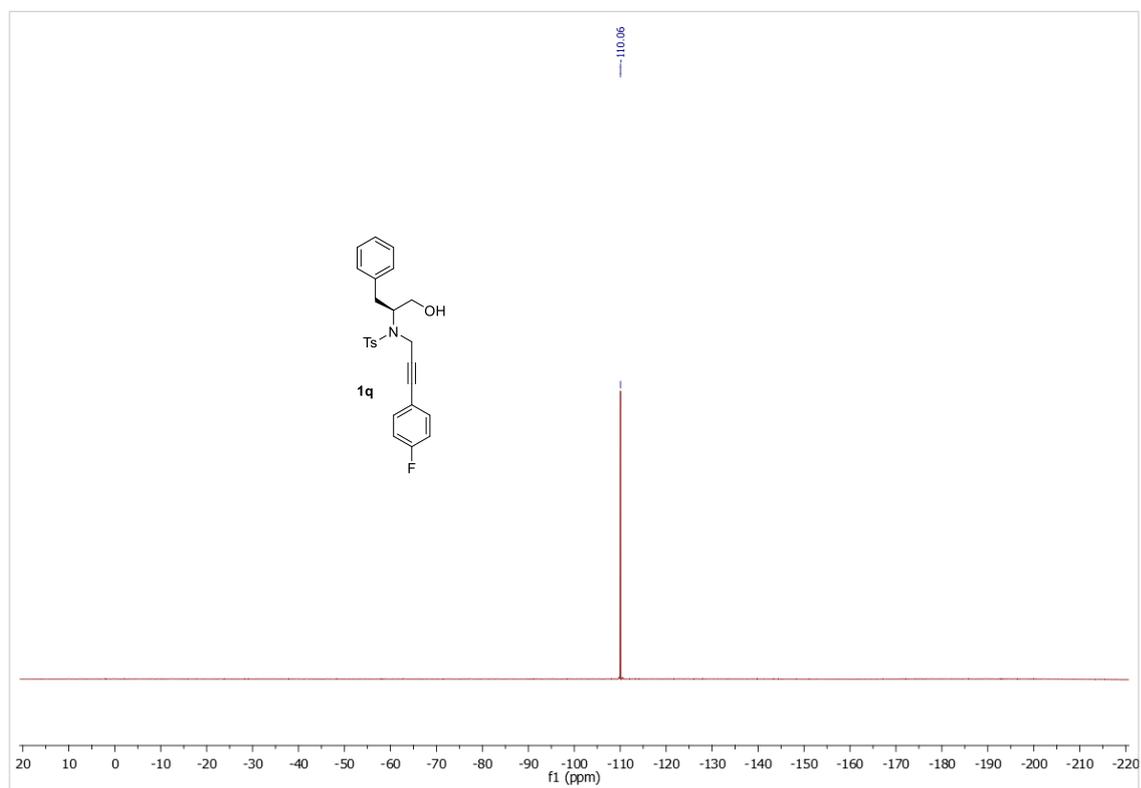
^1H NMR of **1q** (400 MHz, CDCl_3)



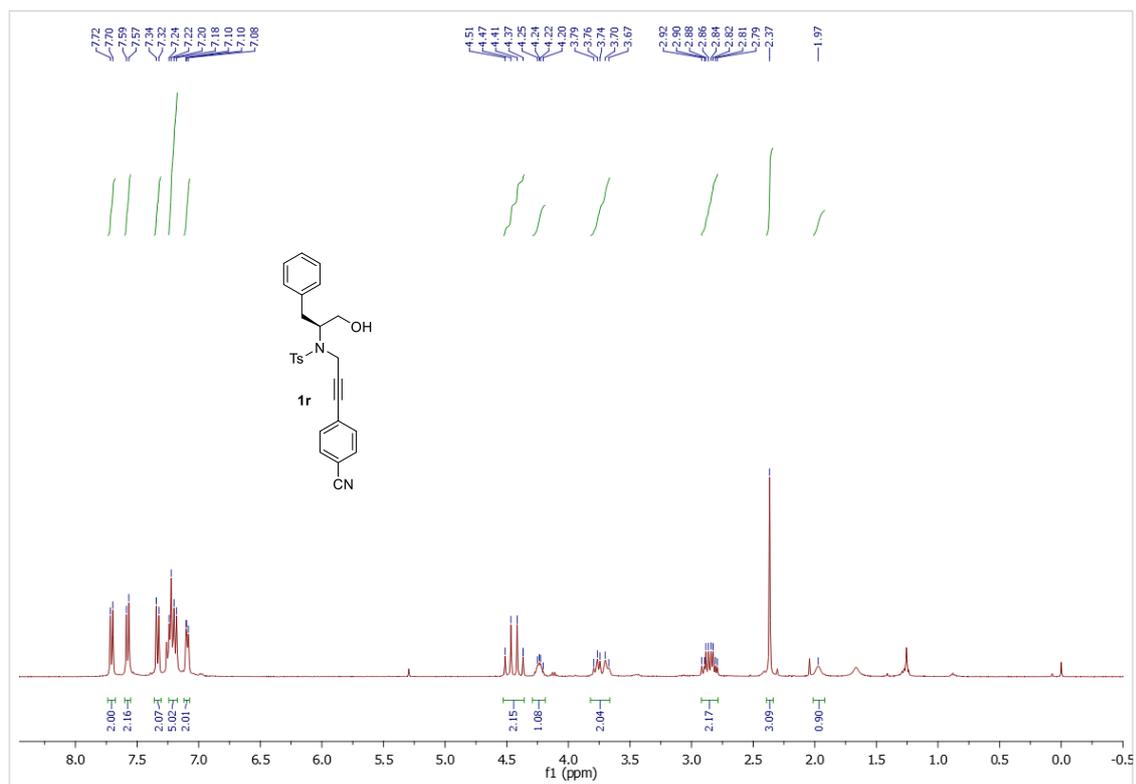
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1q** (101 MHz, CDCl_3)



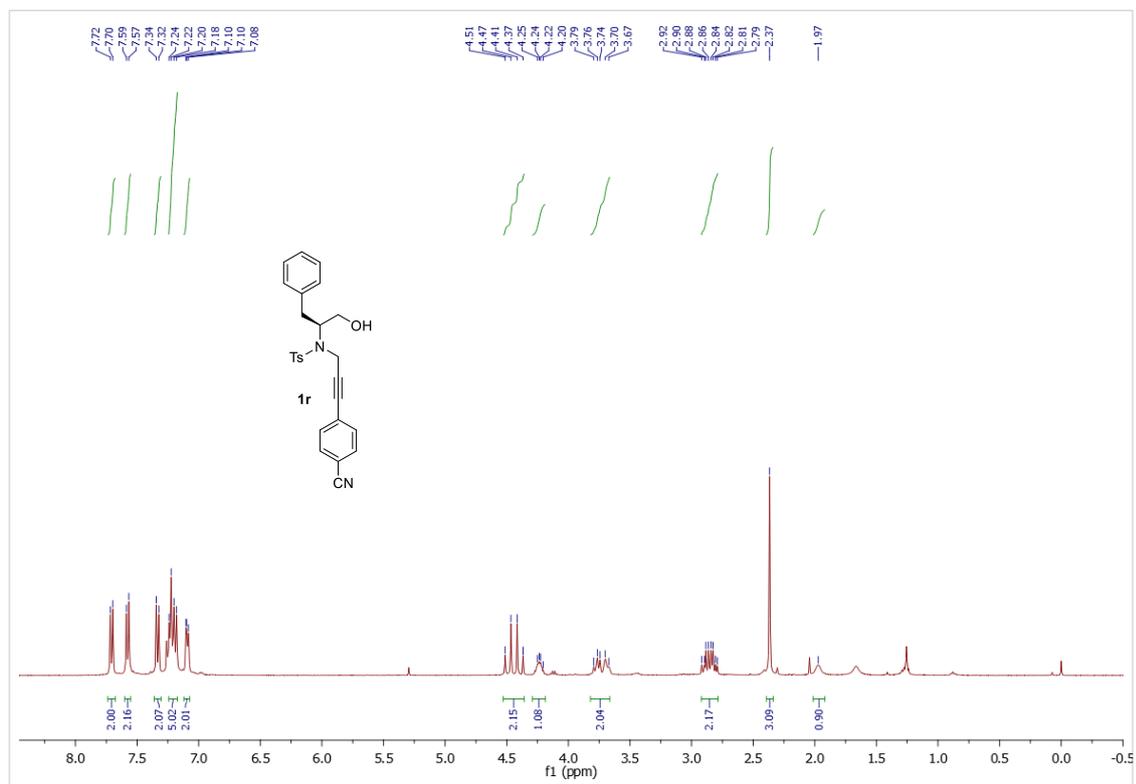
$^{19}\text{F}\{^1\text{H}\}$ NMR of **1q** (101 MHz, CDCl_3)



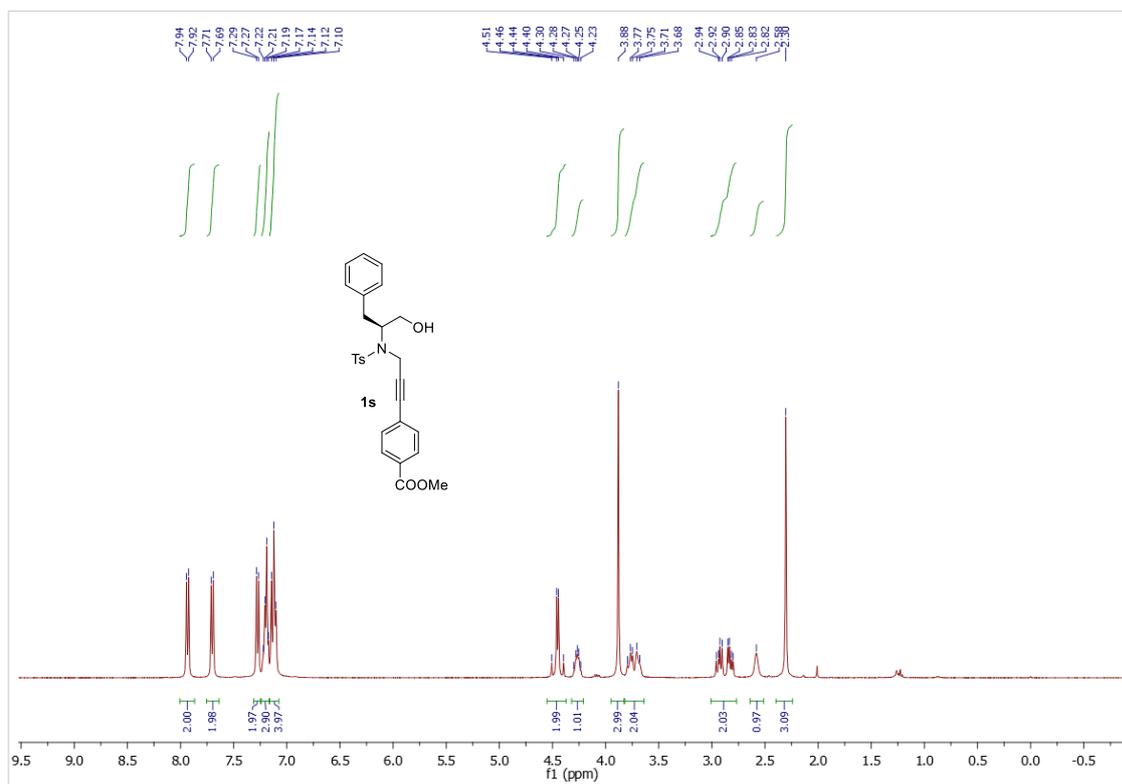
^1H NMR of **1r** (400 MHz, CDCl_3)



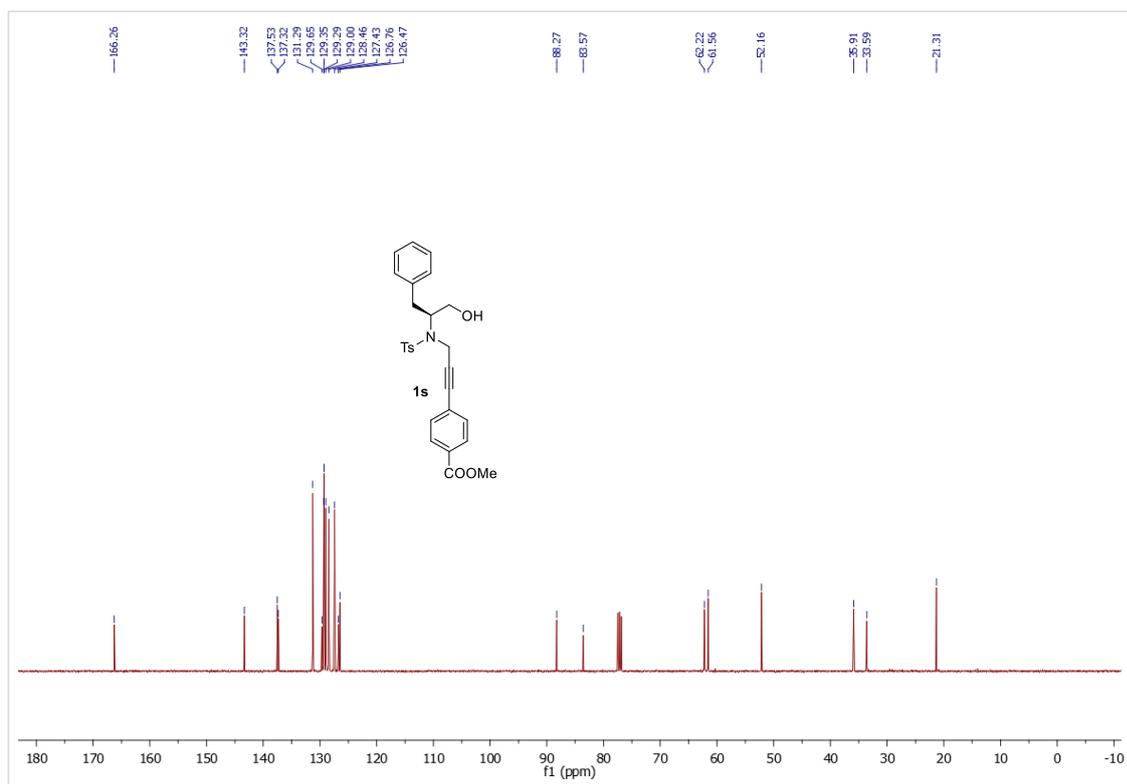
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1r** (101 MHz, CDCl_3)



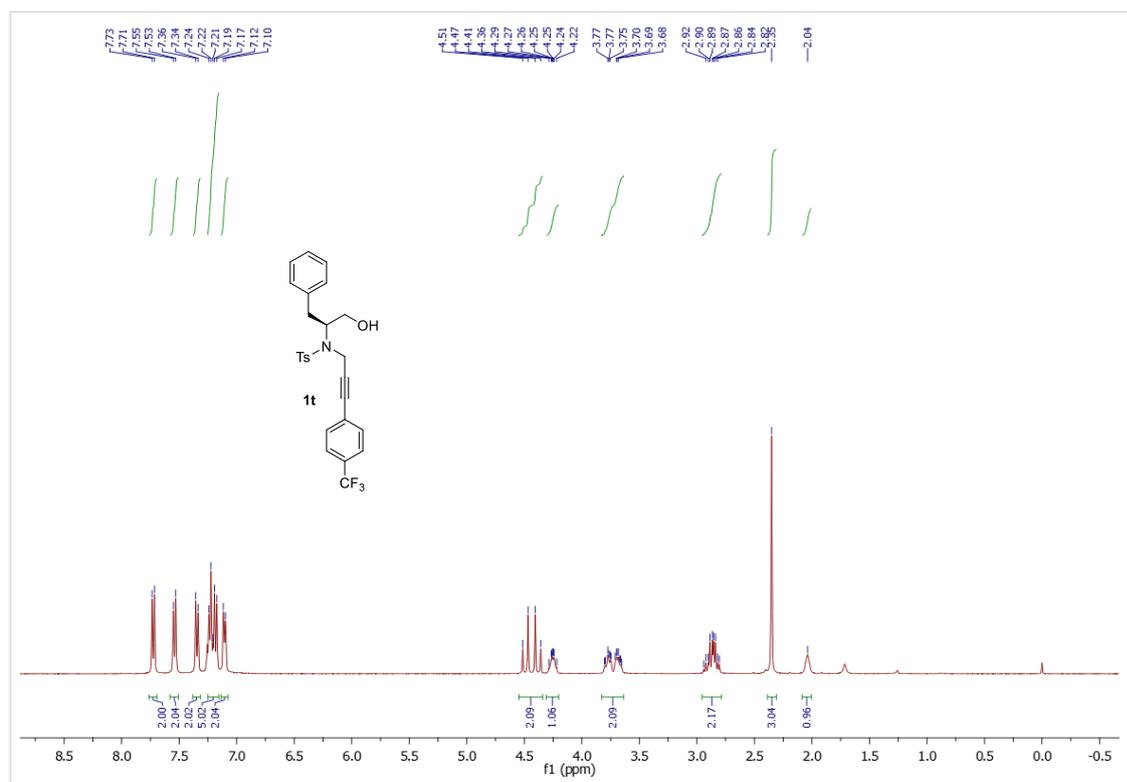
^1H NMR of **1s** (400 MHz, CDCl_3)



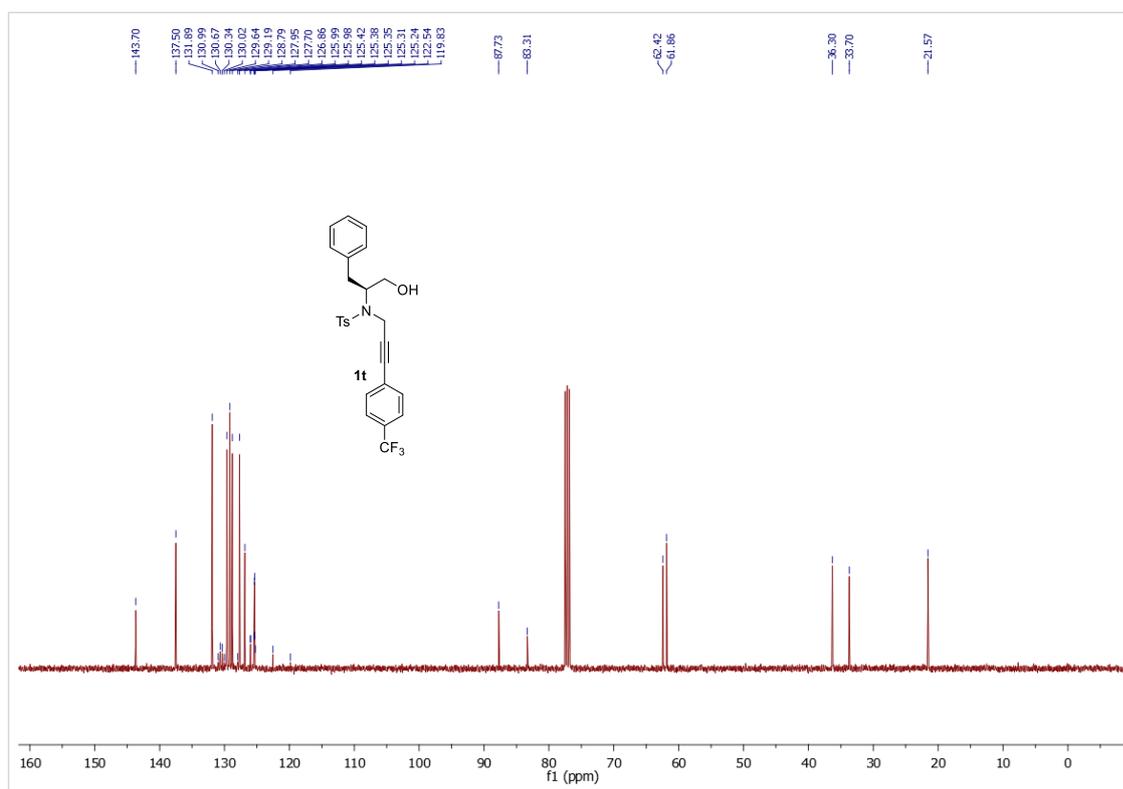
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1s** (101 MHz, CDCl_3)



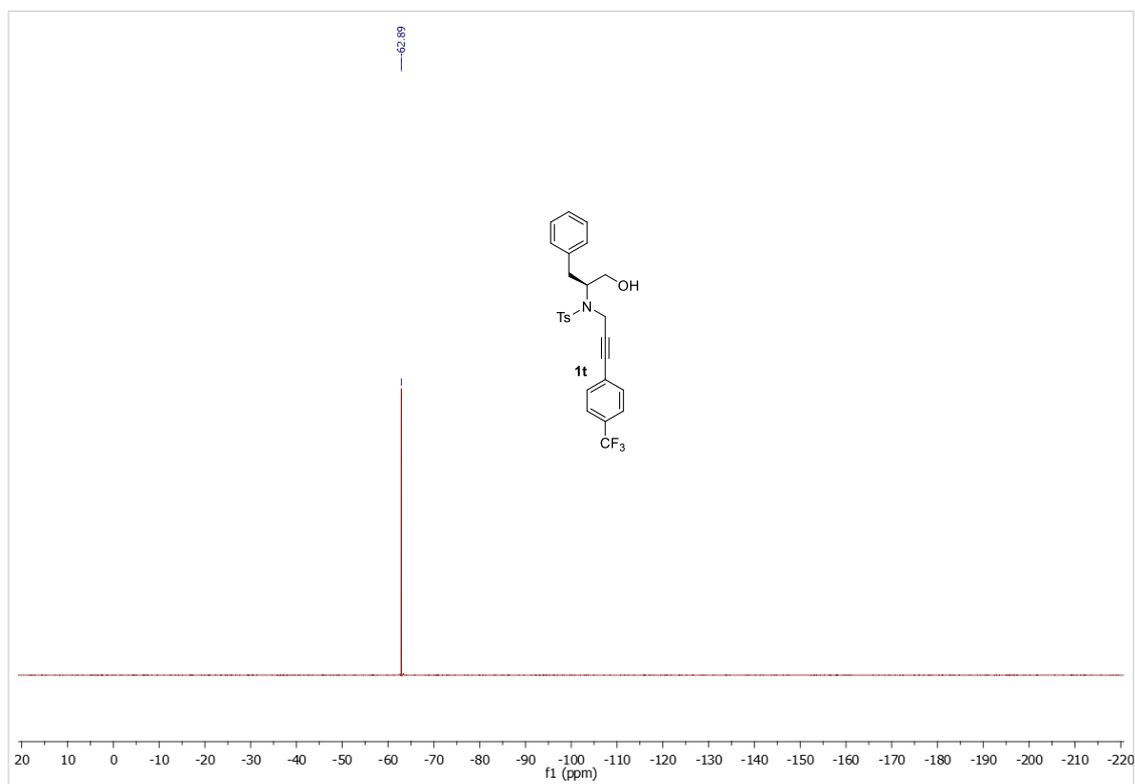
^1H NMR of **1t** (400 MHz, CDCl_3)



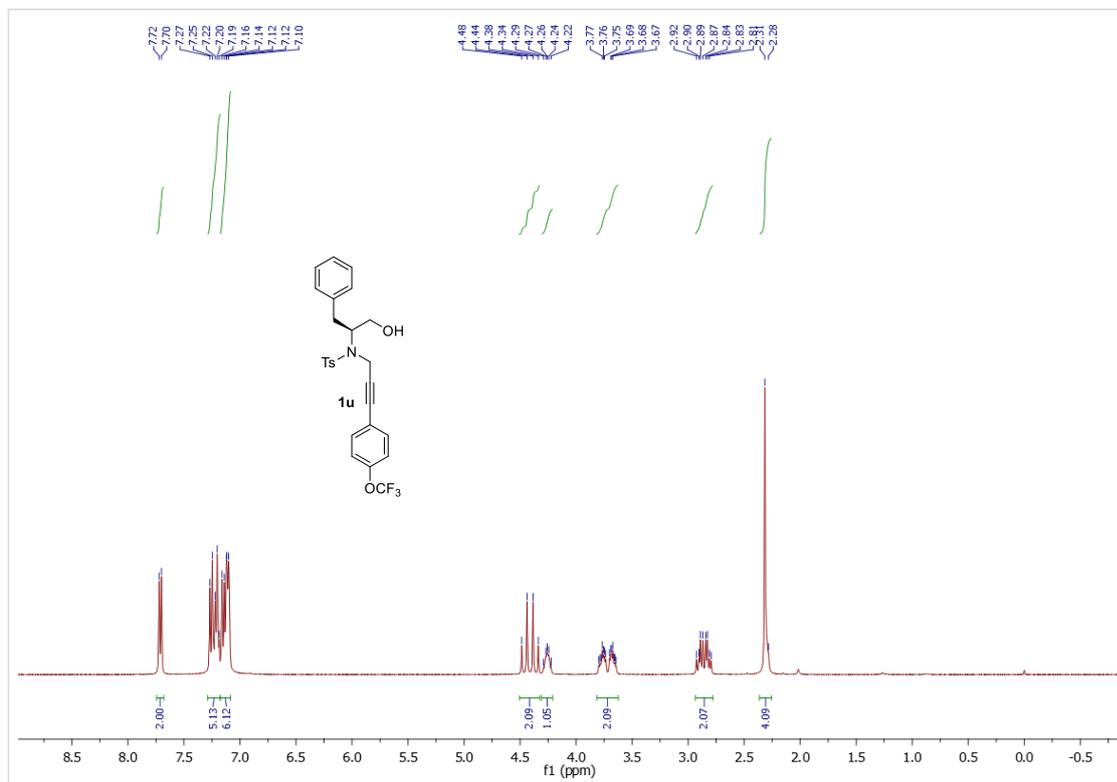
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1t** (101 MHz, CDCl_3)



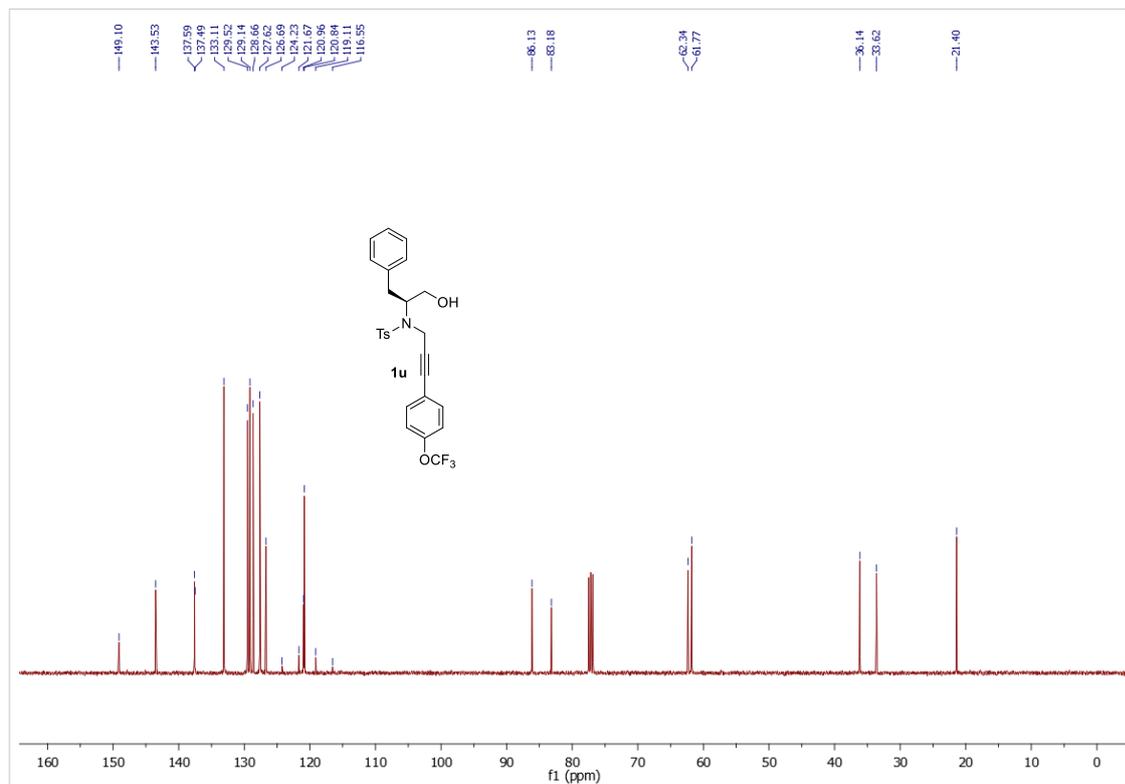
$^{19}\text{F}\{^1\text{H}\}$ NMR of **1t** (101 MHz, CDCl_3)



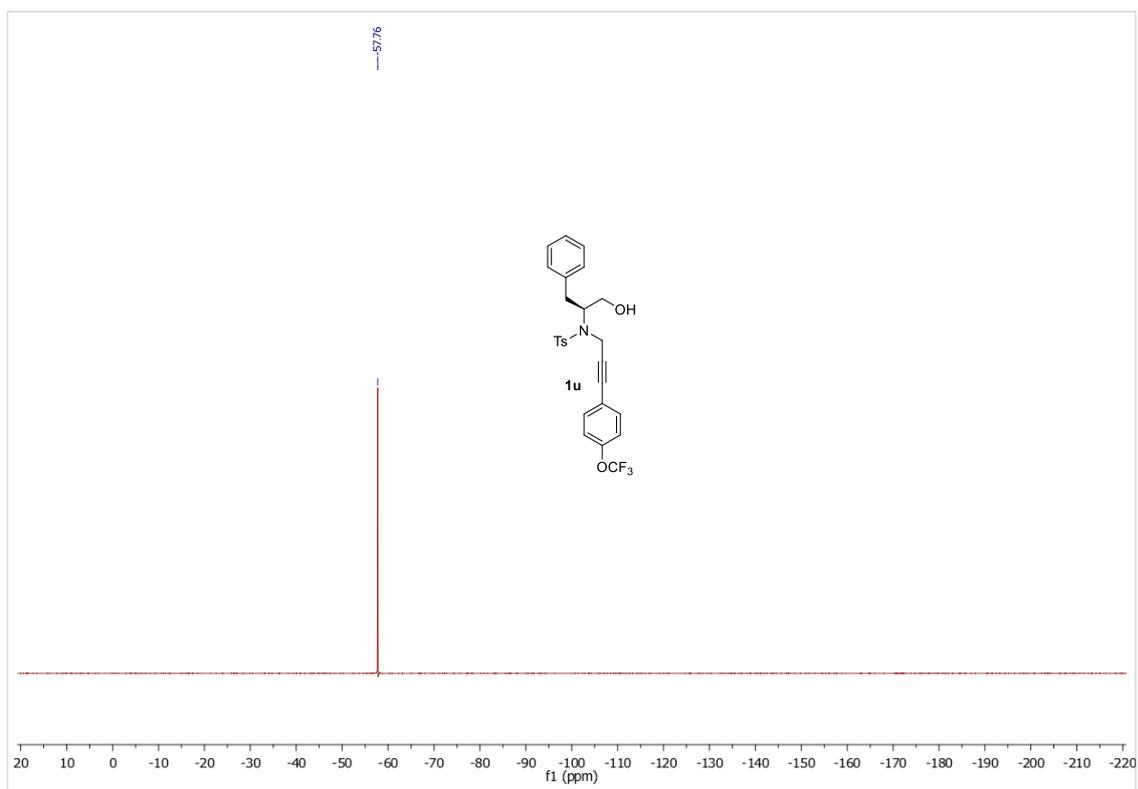
^1H NMR of **1u** (400 MHz, CDCl_3)



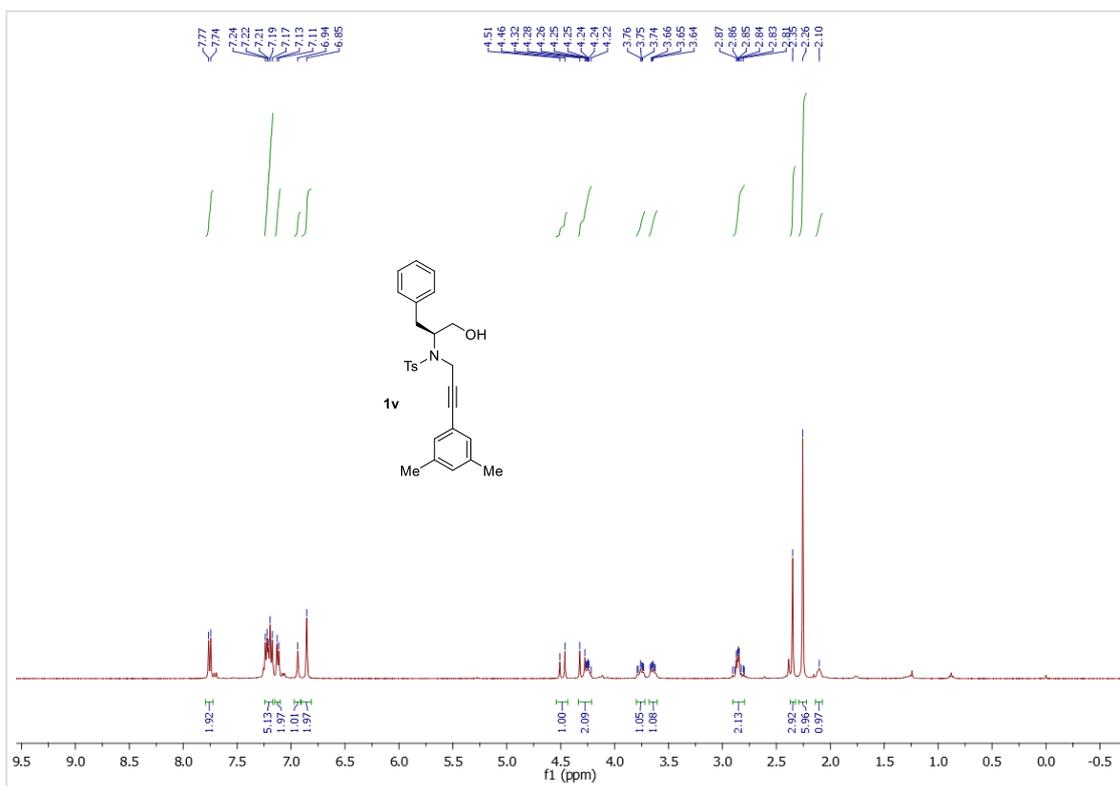
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1u** (101 MHz, CDCl_3)



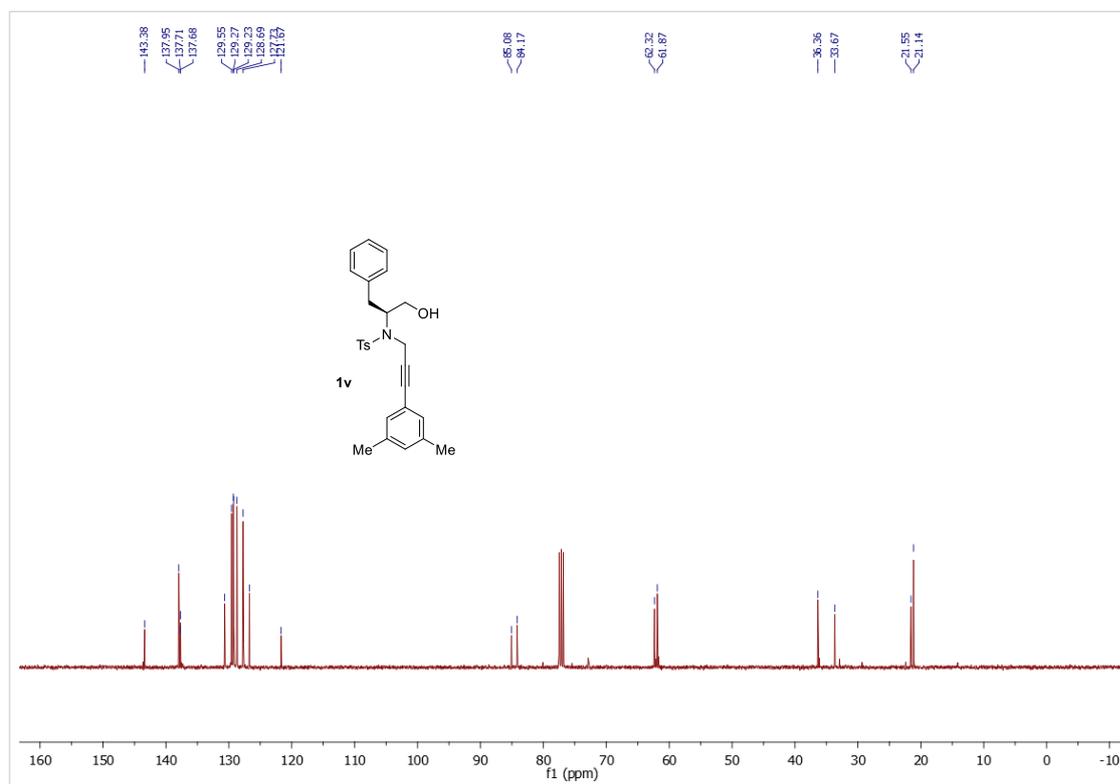
$^{19}\text{F}\{^1\text{H}\}$ NMR of **1u** (101 MHz, CDCl_3)



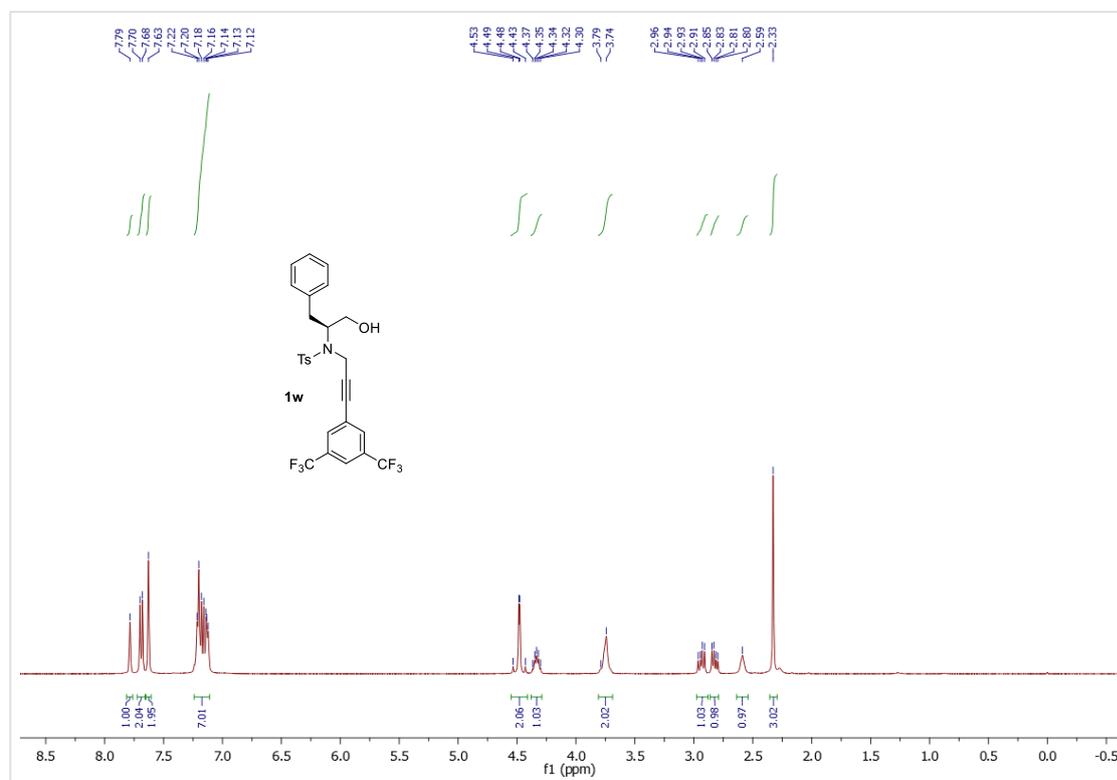
^1H NMR of **1v** (400 MHz, CDCl_3)



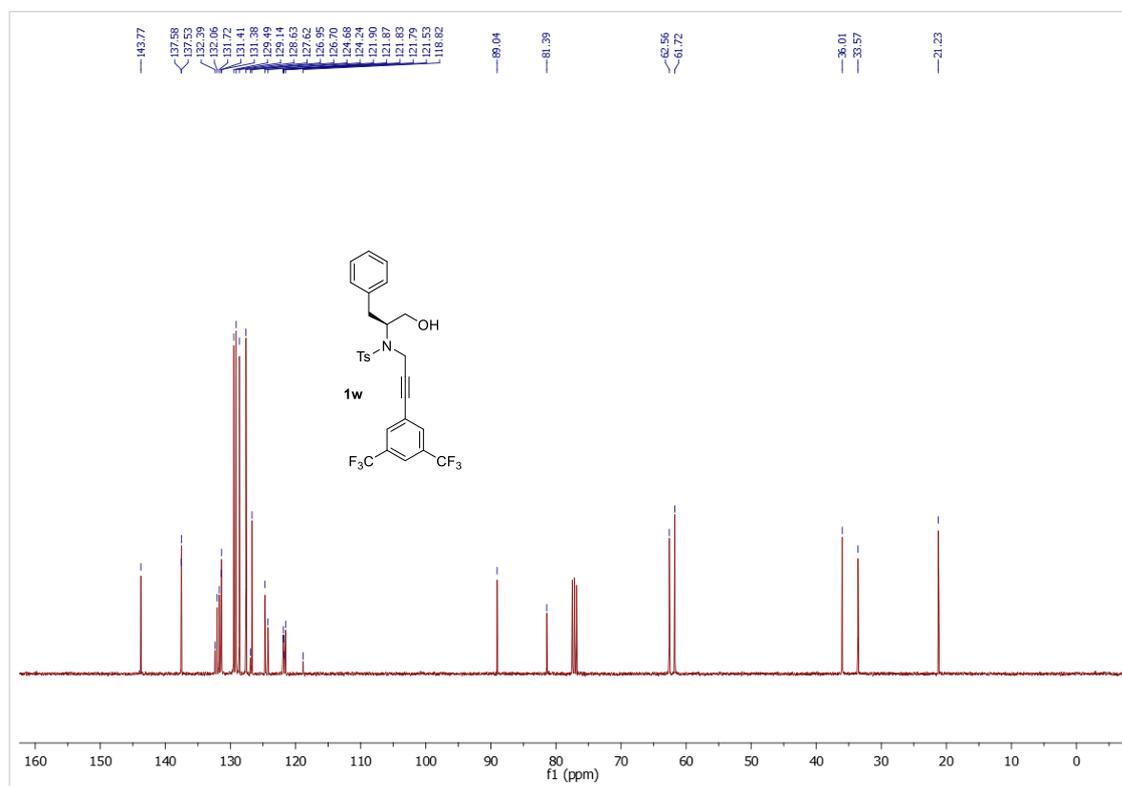
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1v** (101 MHz, CDCl_3)



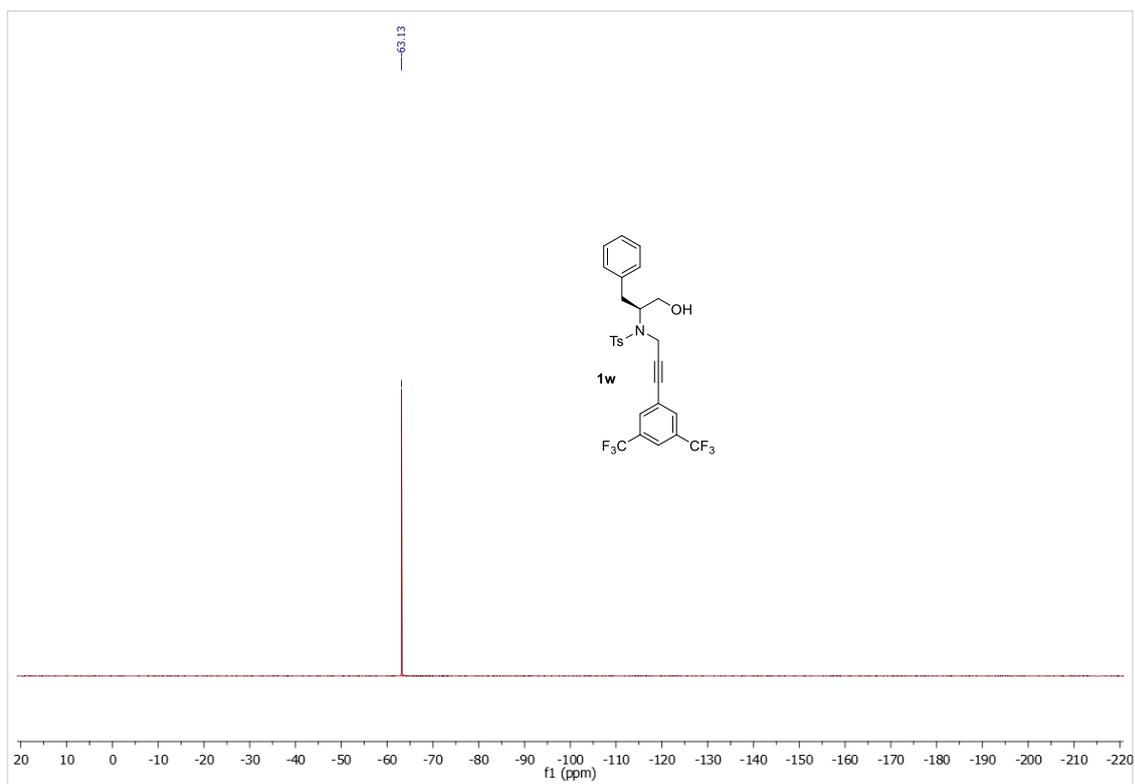
^1H NMR of **1w** (400 MHz, CDCl_3)



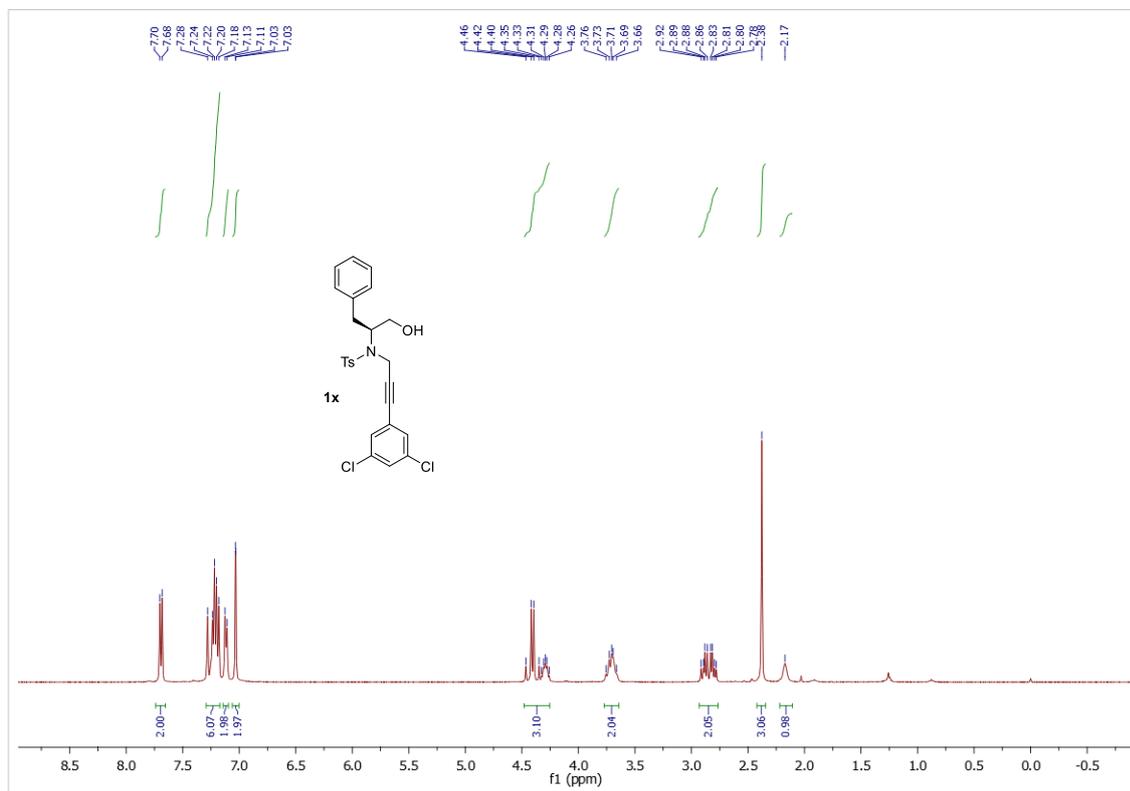
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1w** (101 MHz, CDCl_3)



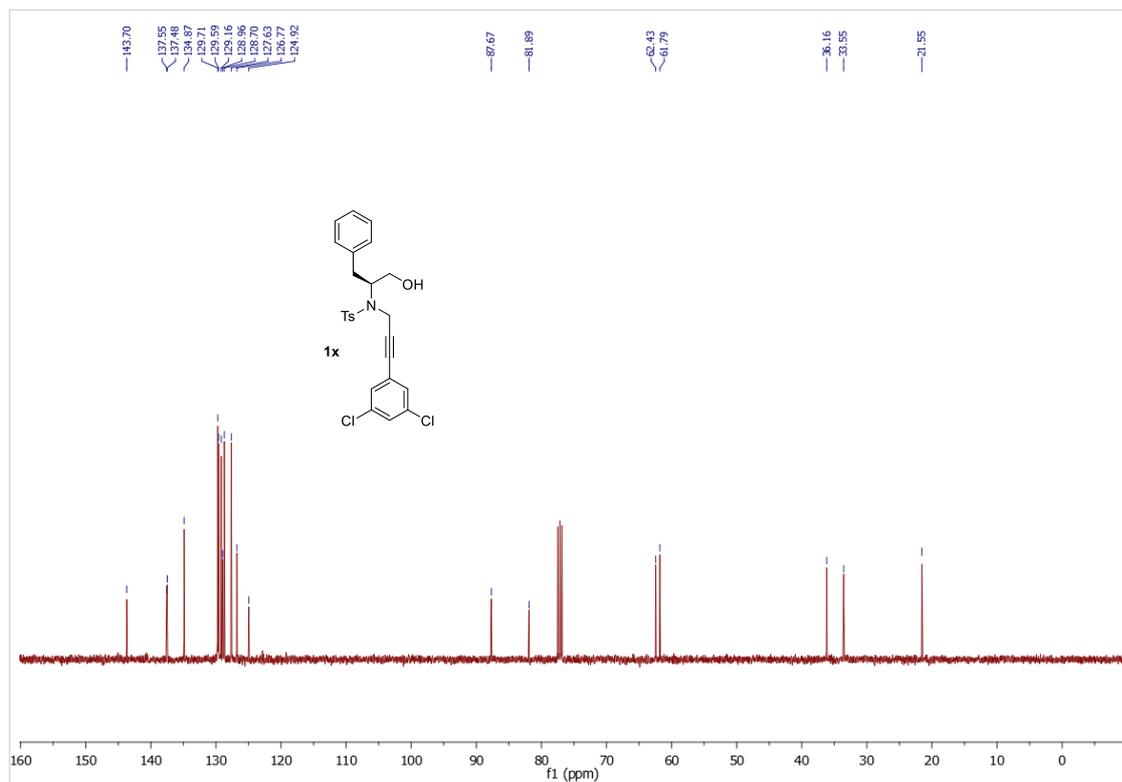
$^{19}\text{F}\{^1\text{H}\}$ NMR of **1w** (101 MHz, CDCl_3)



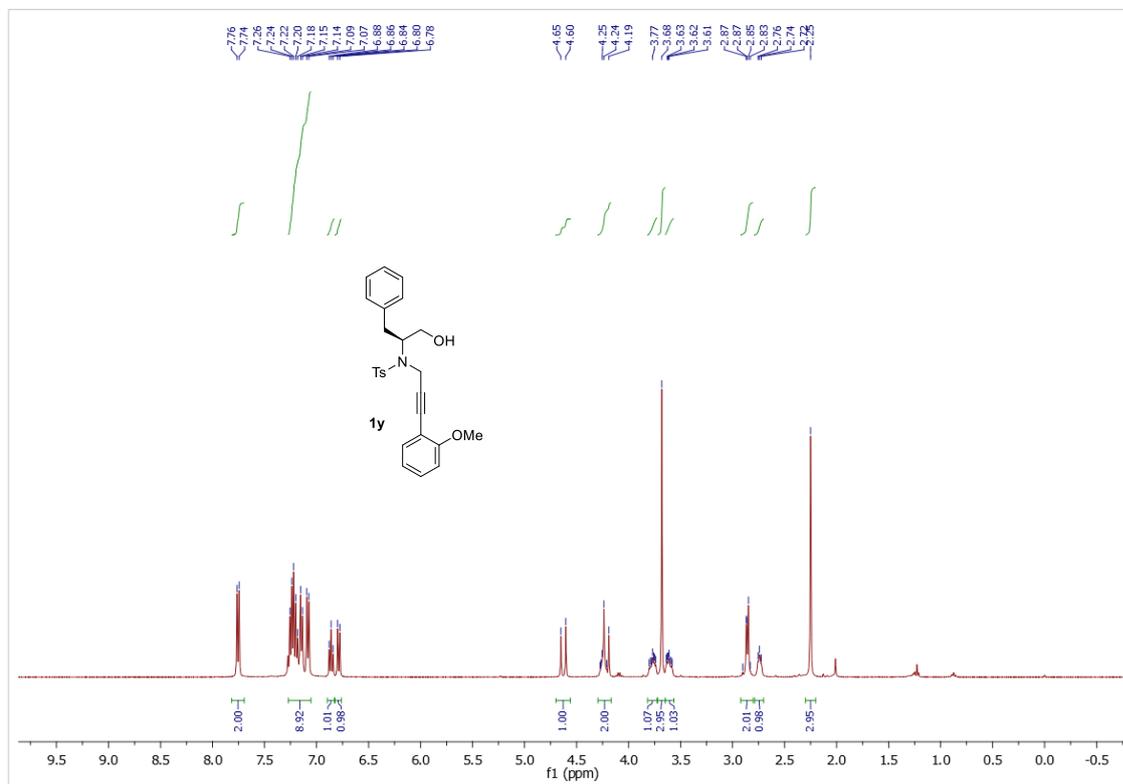
^1H NMR of **1x** (400 MHz, CDCl_3)



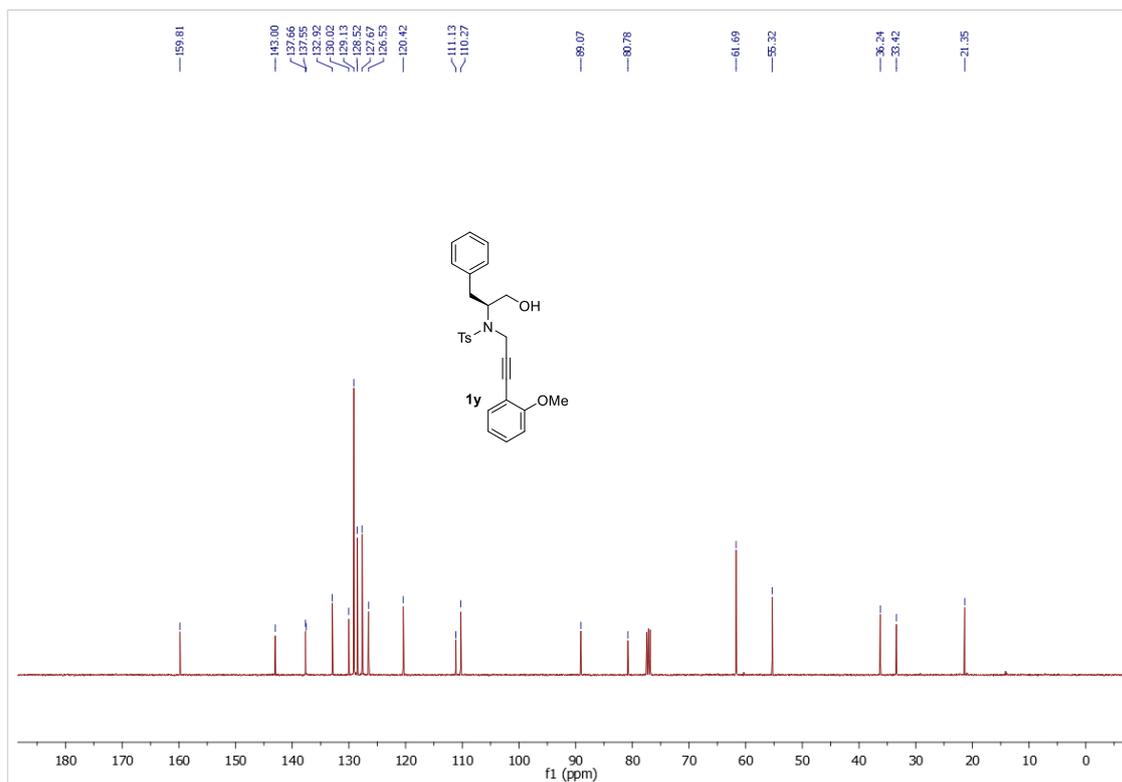
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1x** (101 MHz, CDCl_3)



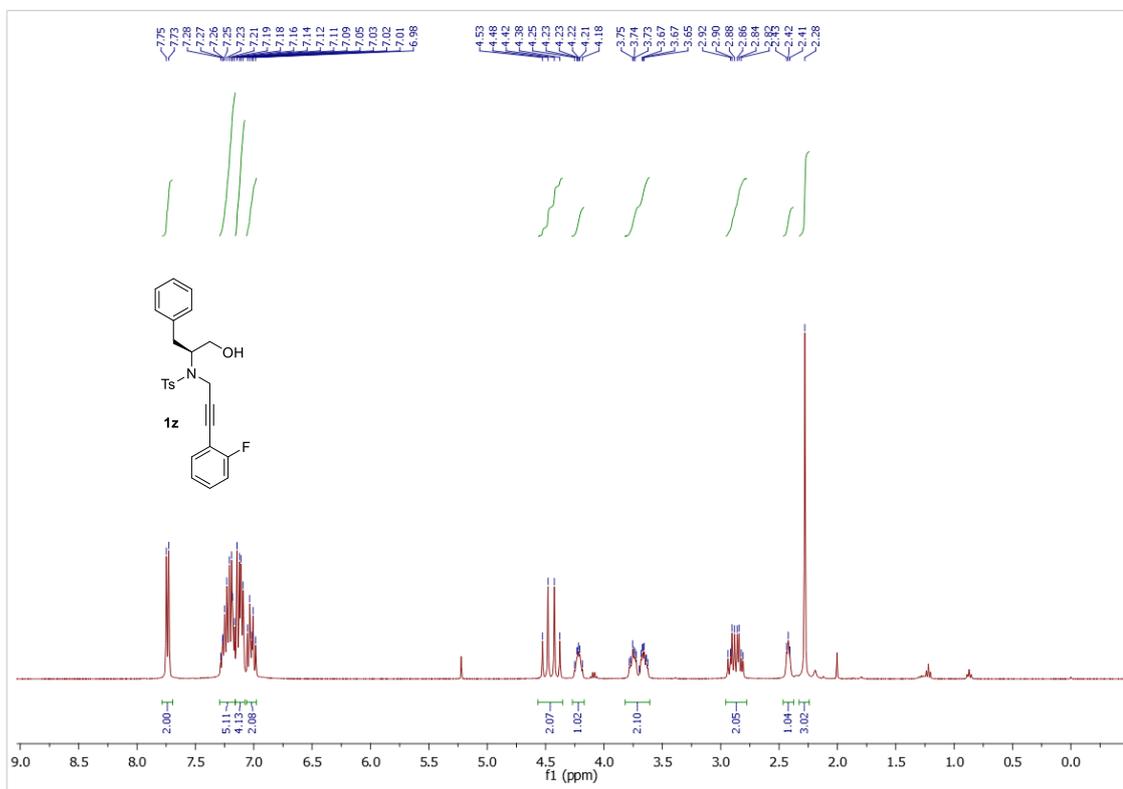
^1H NMR of **1y** (400 MHz, CDCl_3)



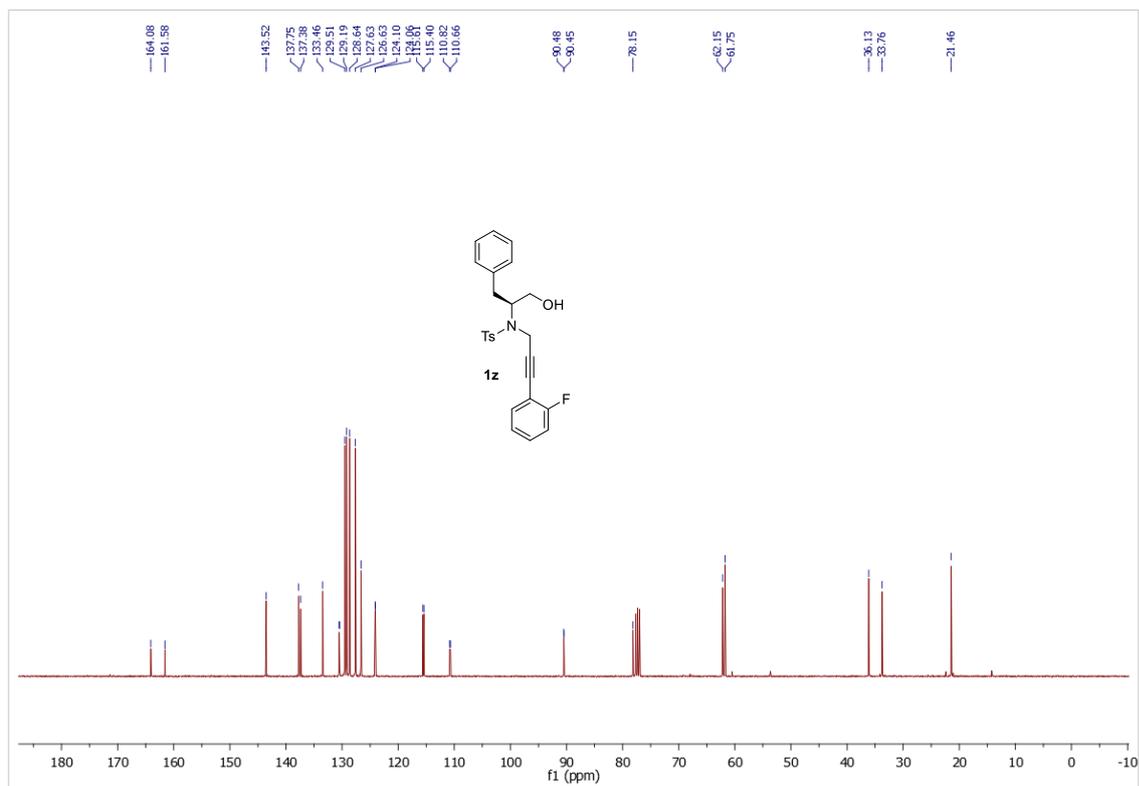
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1y** (101 MHz, CDCl_3)



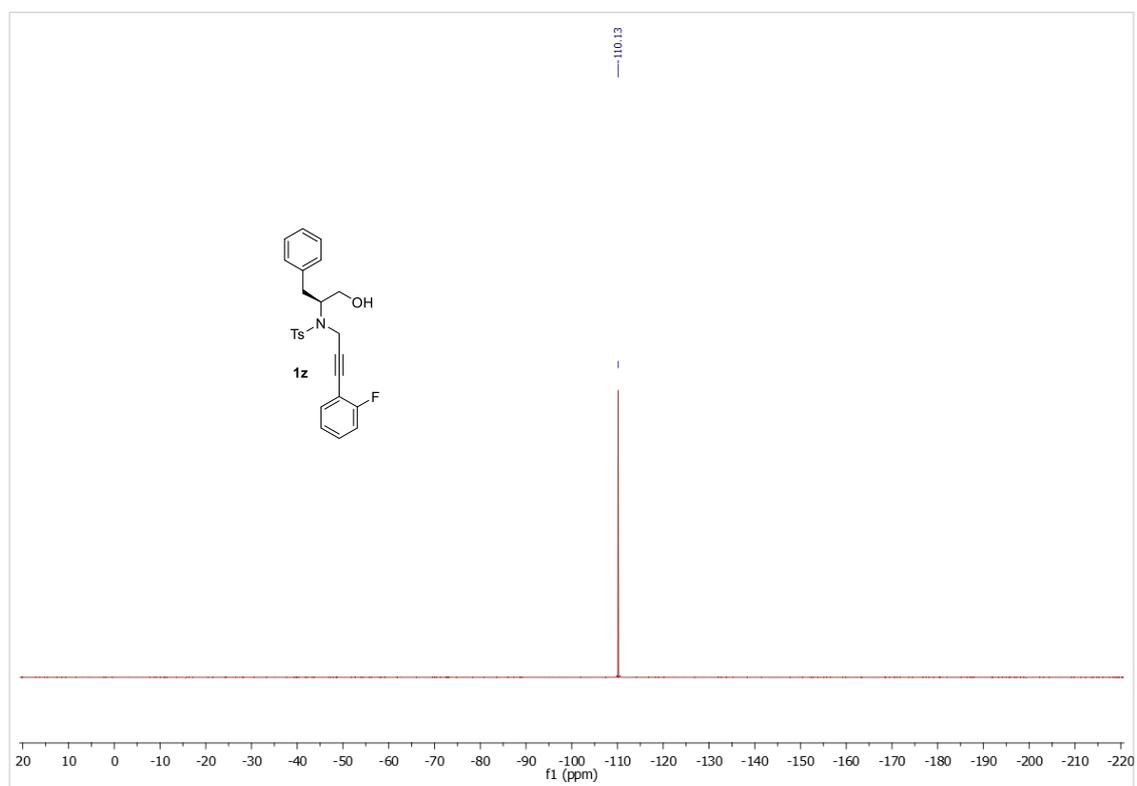
^1H NMR of **1z** (400 MHz, CDCl_3)



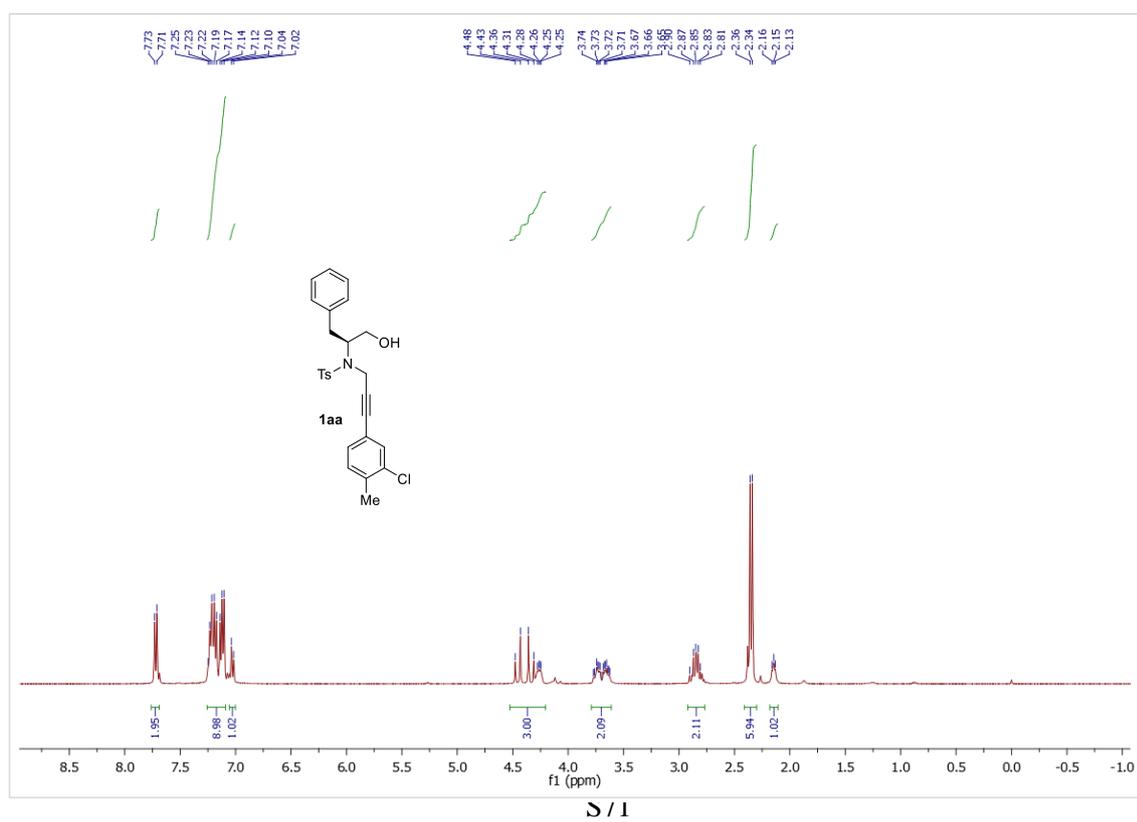
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1z** (101 MHz, CDCl_3)



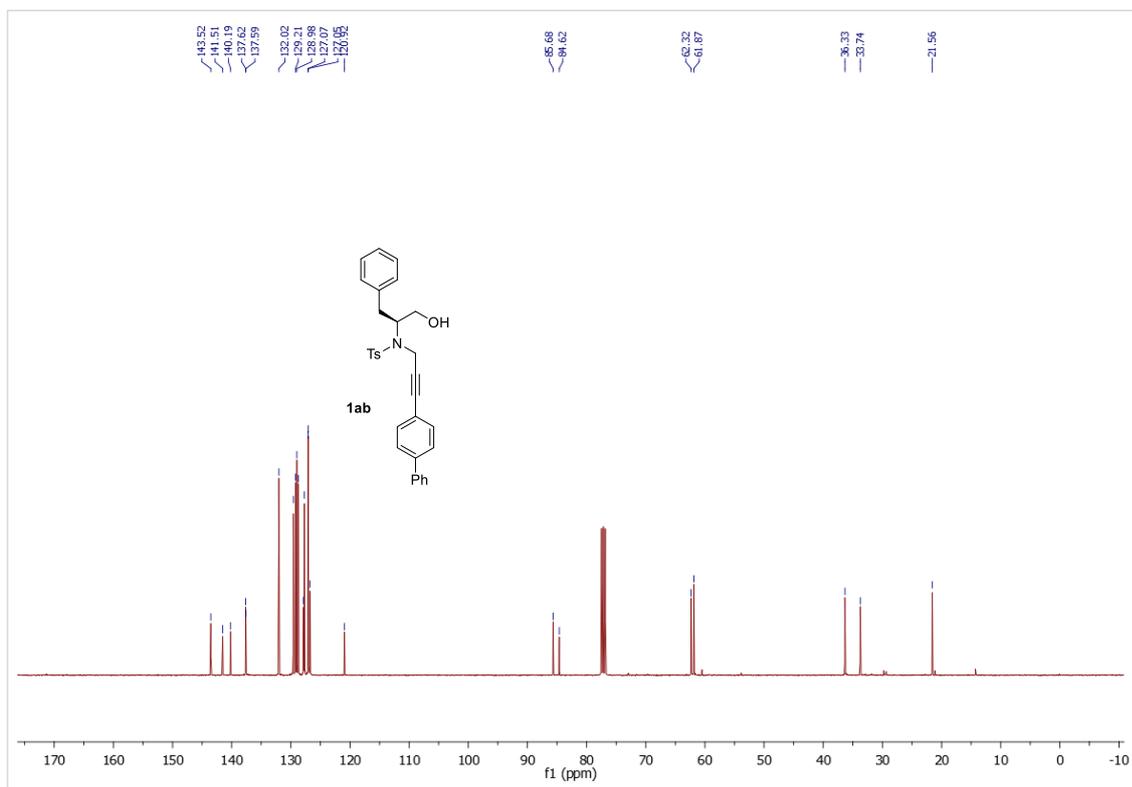
$^{19}\text{F}\{^1\text{H}\}$ NMR of **1z** (101 MHz, CDCl_3)



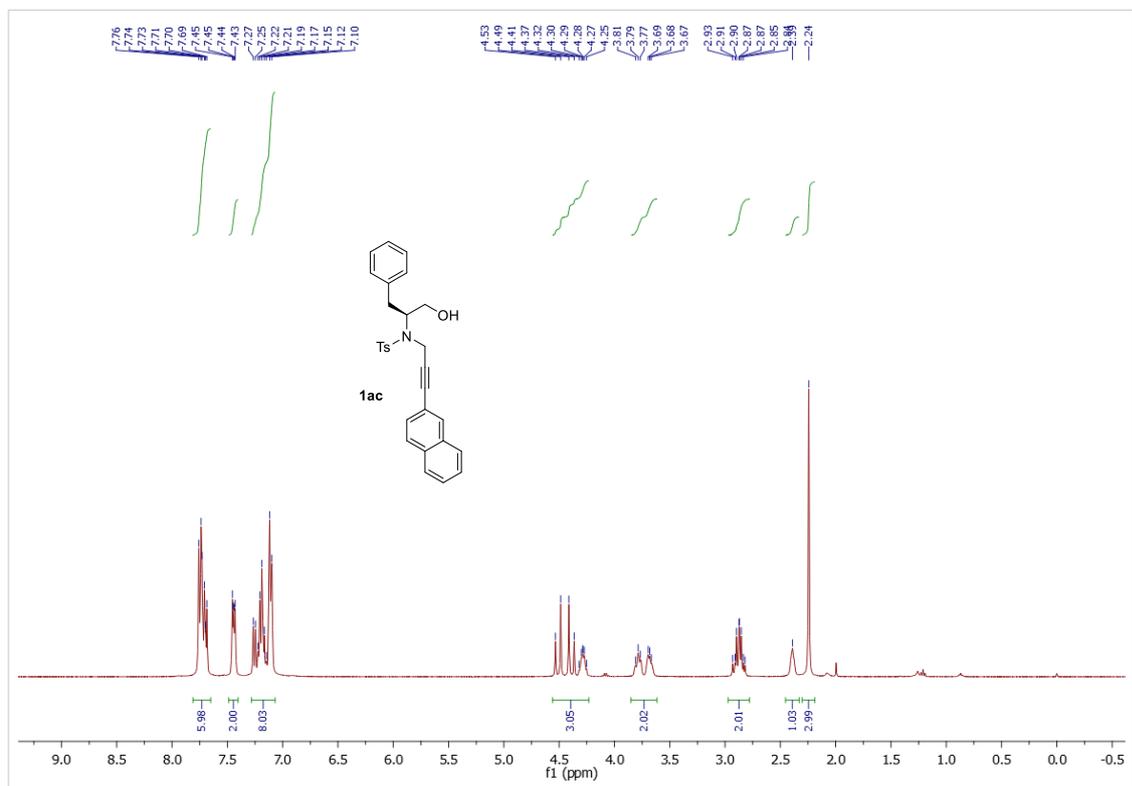
^1H NMR of **1aa** (400 MHz, CDCl_3)



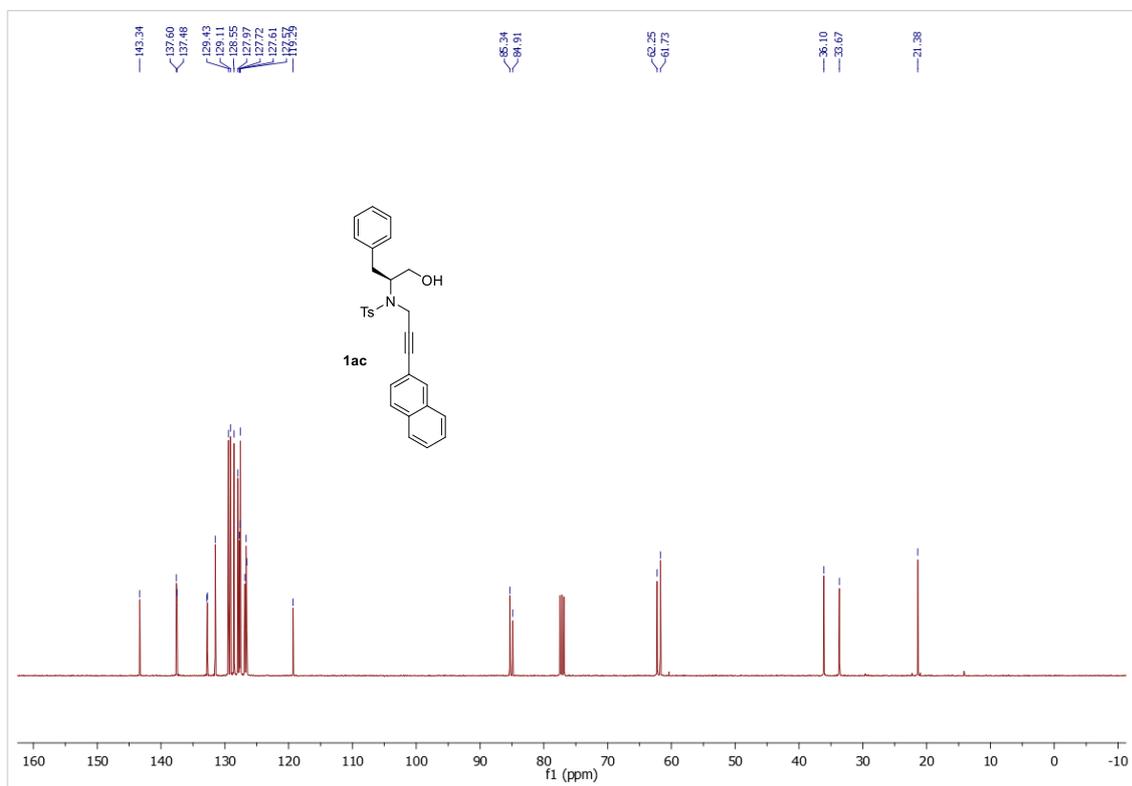
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1ab** (101 MHz, CDCl_3)



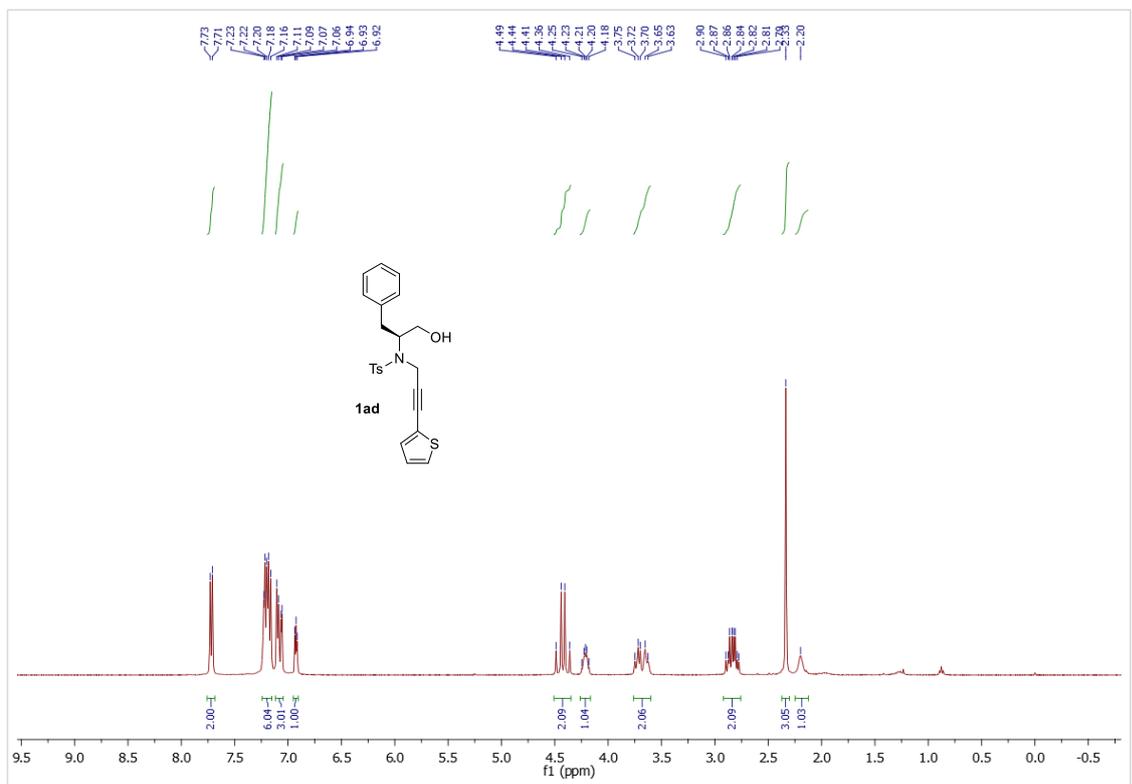
^1H NMR of **1ac** (400 MHz, CDCl_3)



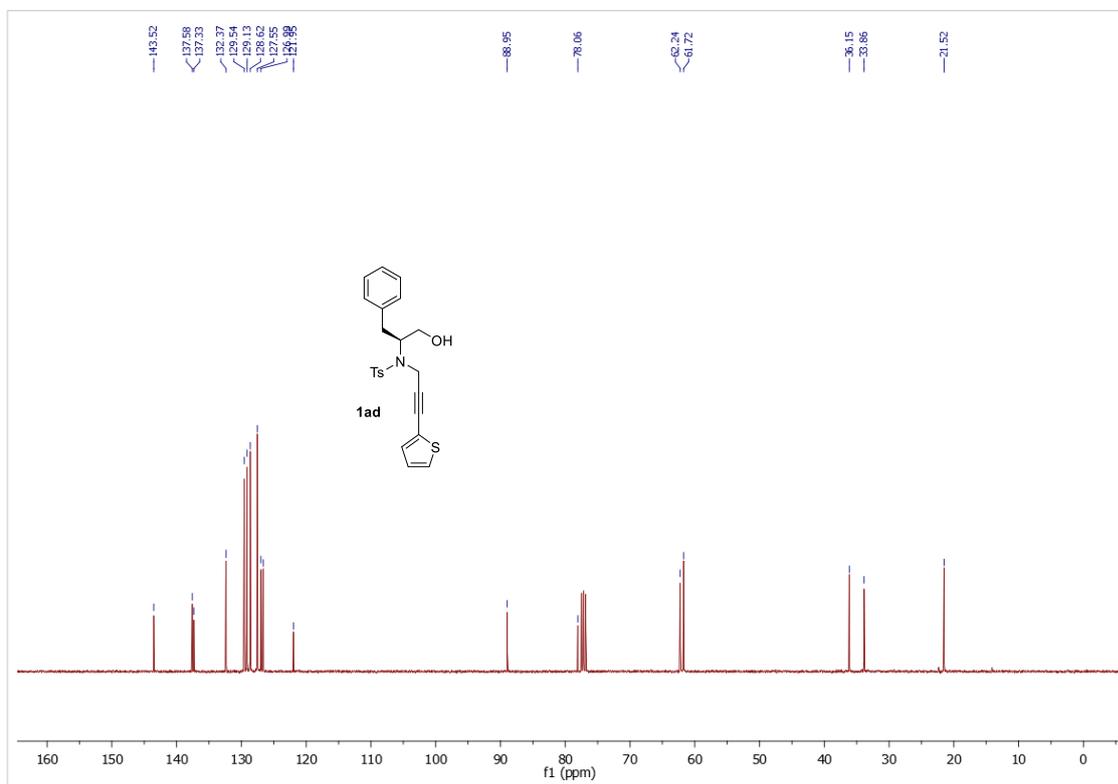
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1ac** (101 MHz, CDCl_3)



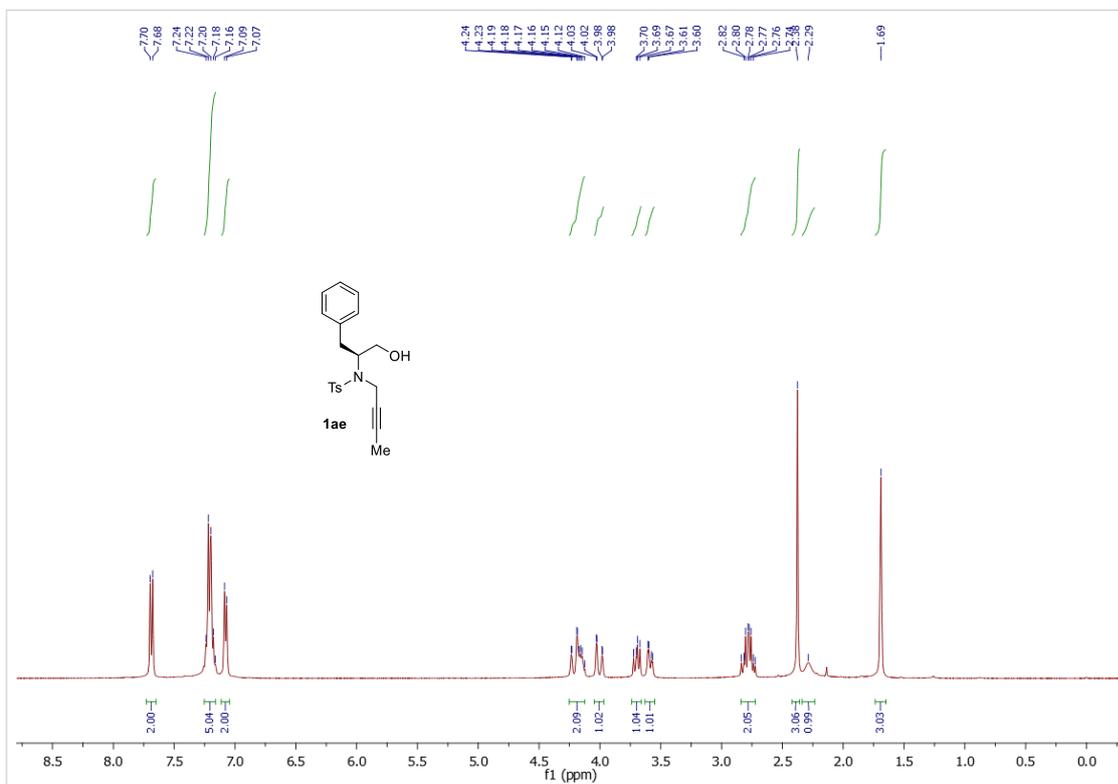
^1H NMR of **1ad** (400 MHz, CDCl_3)



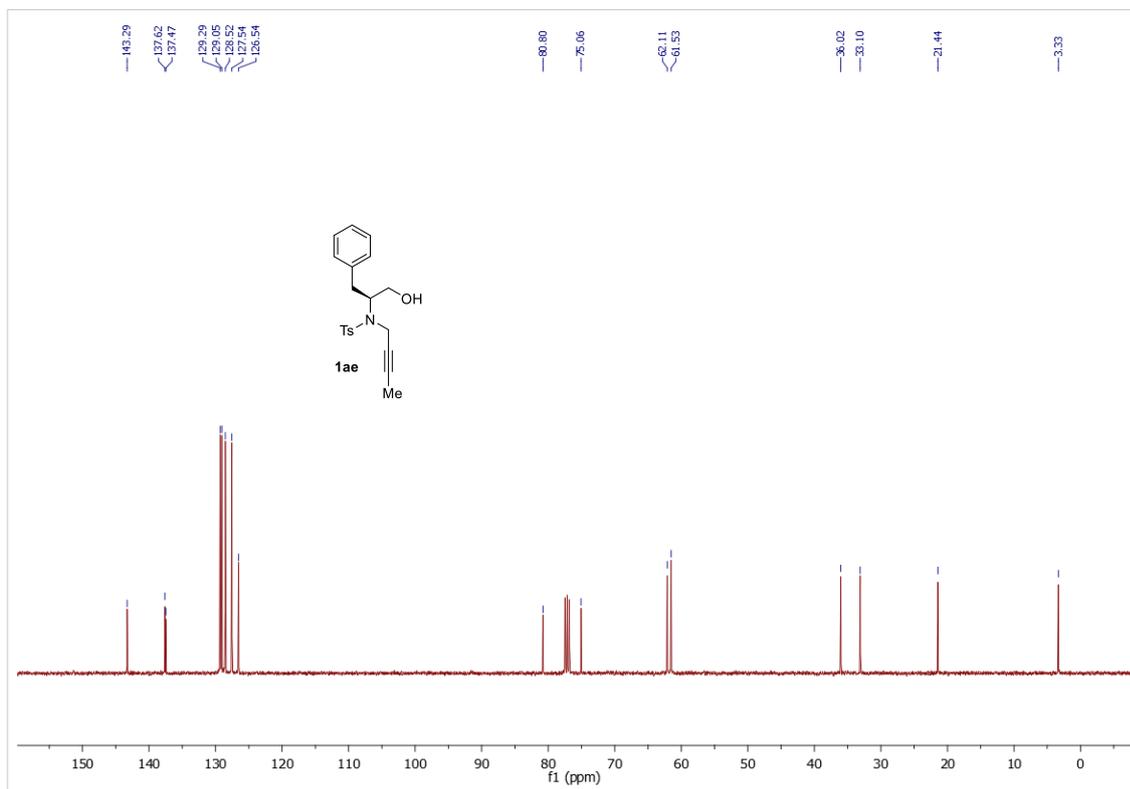
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1ad** (101 MHz, CDCl_3)



^1H NMR of **1ae** (400 MHz, CDCl_3)

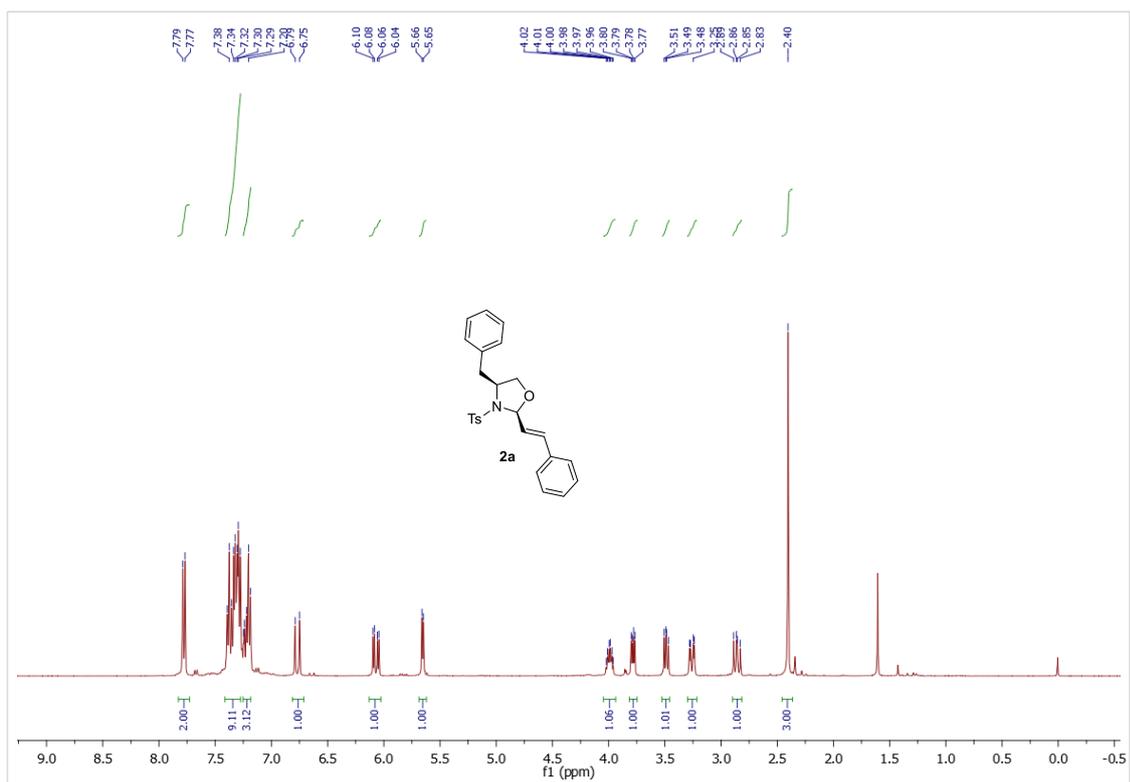


$^{13}\text{C}\{^1\text{H}\}$ NMR of **1ae** (101 MHz, CDCl_3)

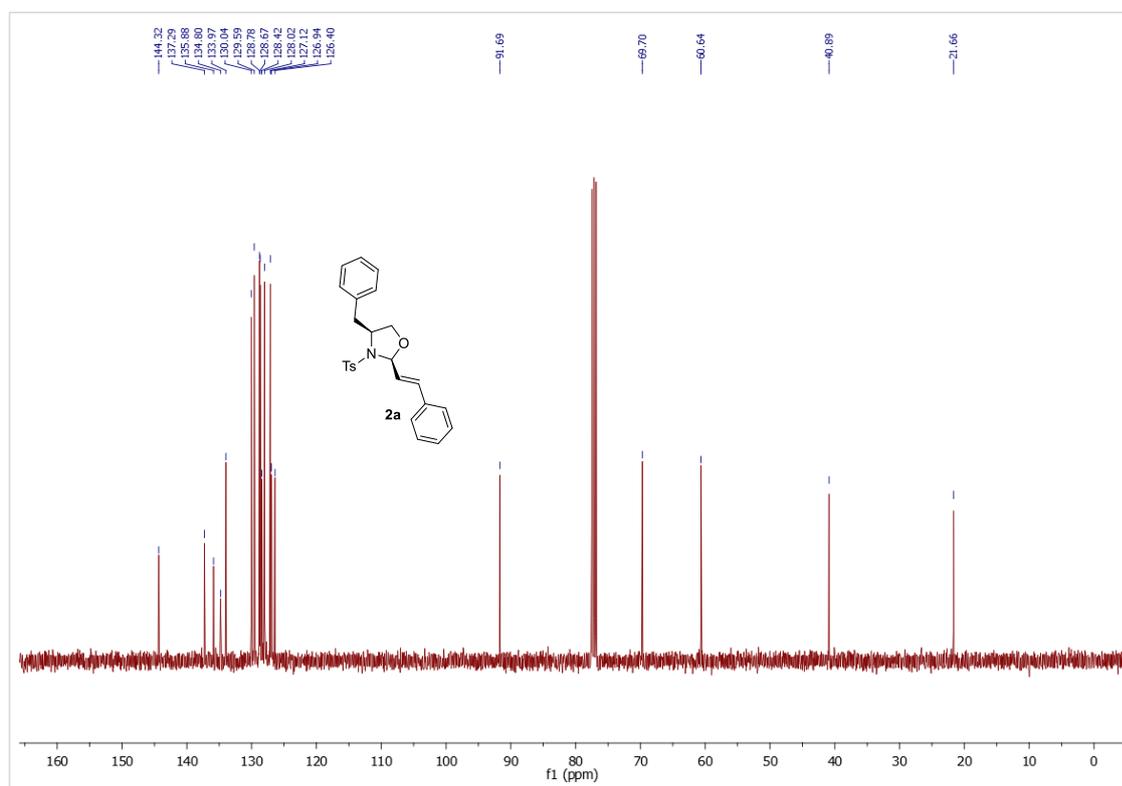


13 NMR spectral data of cyclic products:

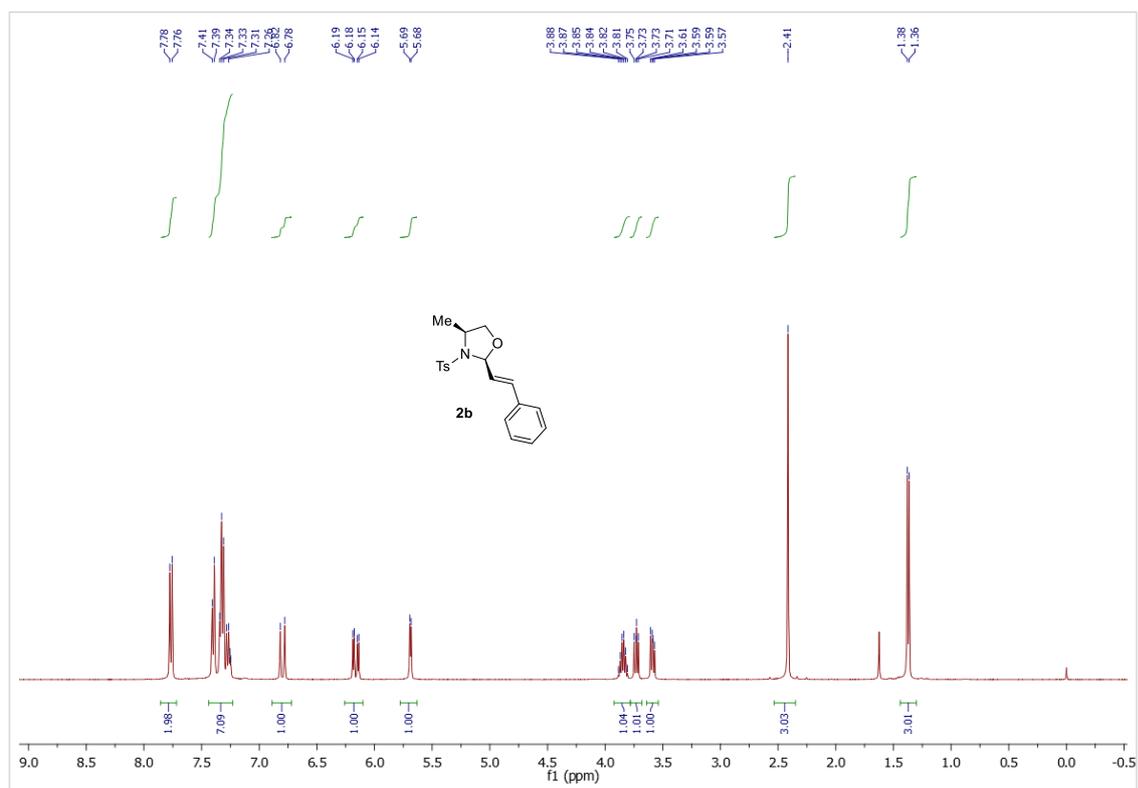
^1H NMR of **2a** (400 MHz, CDCl_3)



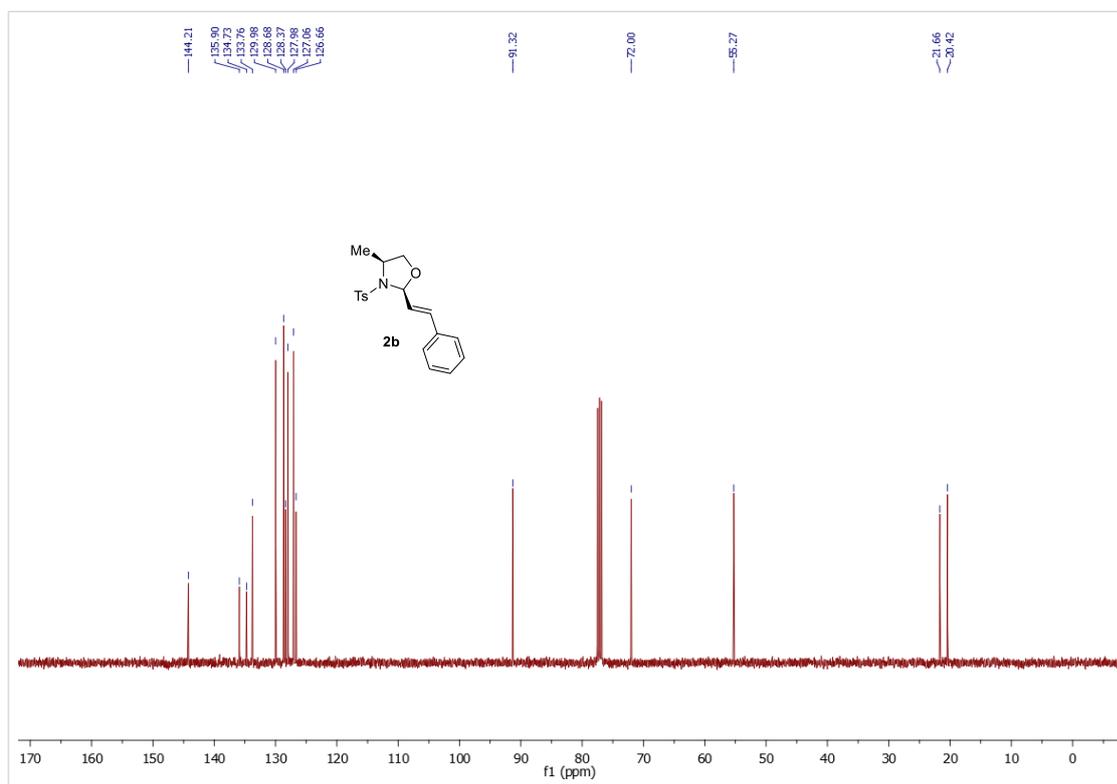
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2a** (101 MHz, CDCl_3)



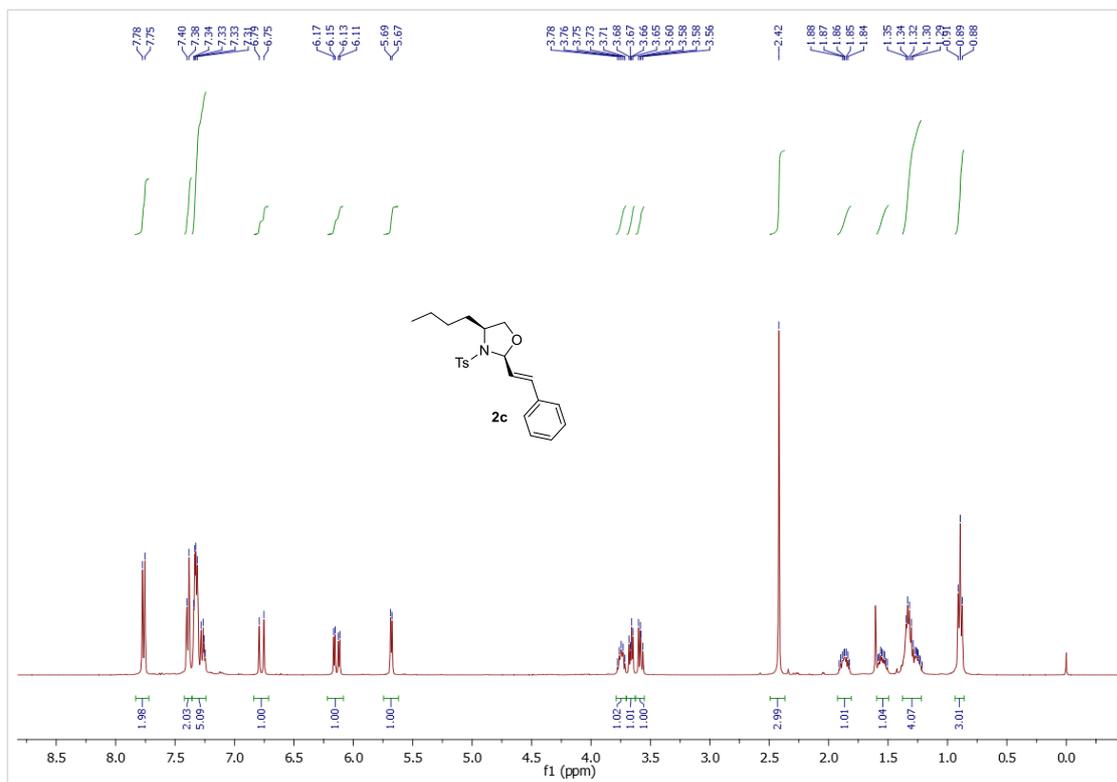
^1H NMR of **2b** (400 MHz, CDCl_3)



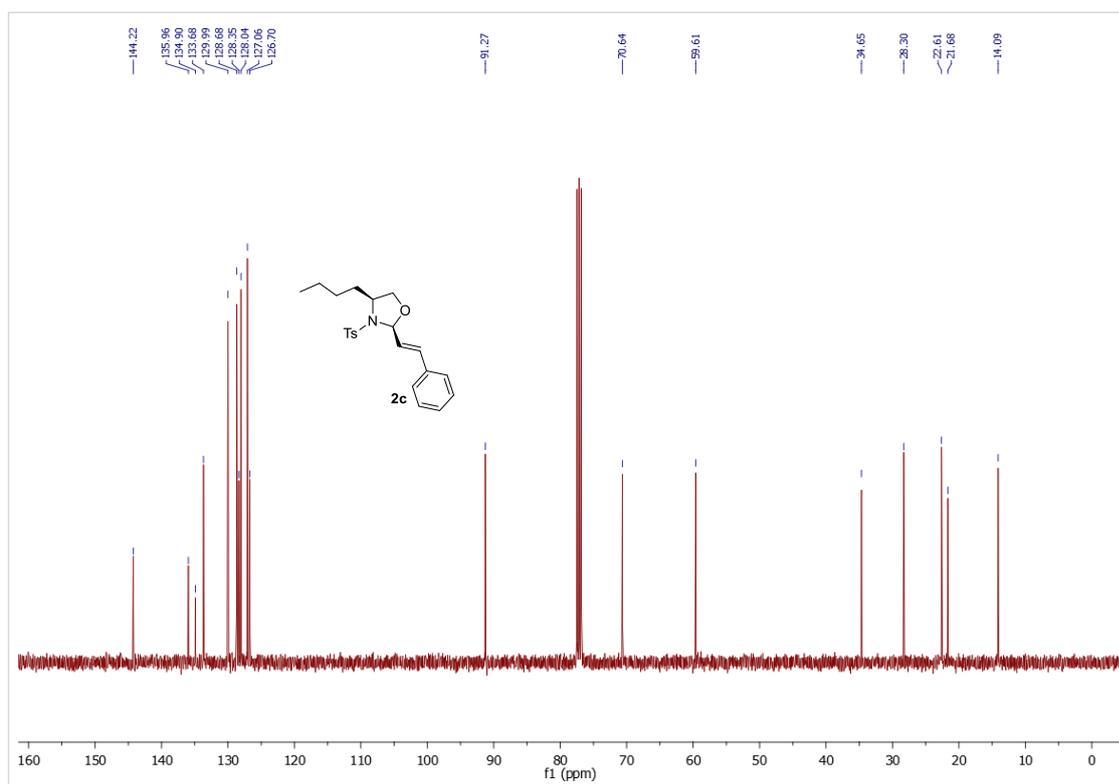
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2b** (101 MHz, CDCl_3)



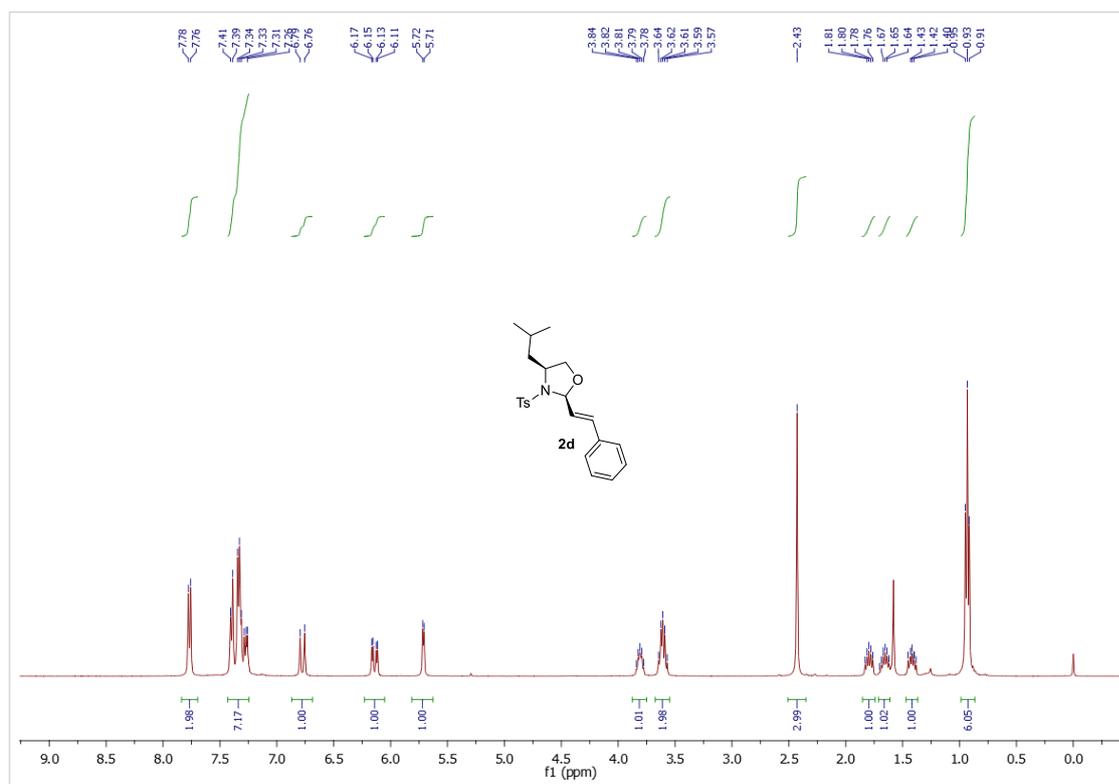
^1H NMR of **2c** (400 MHz, CDCl_3)



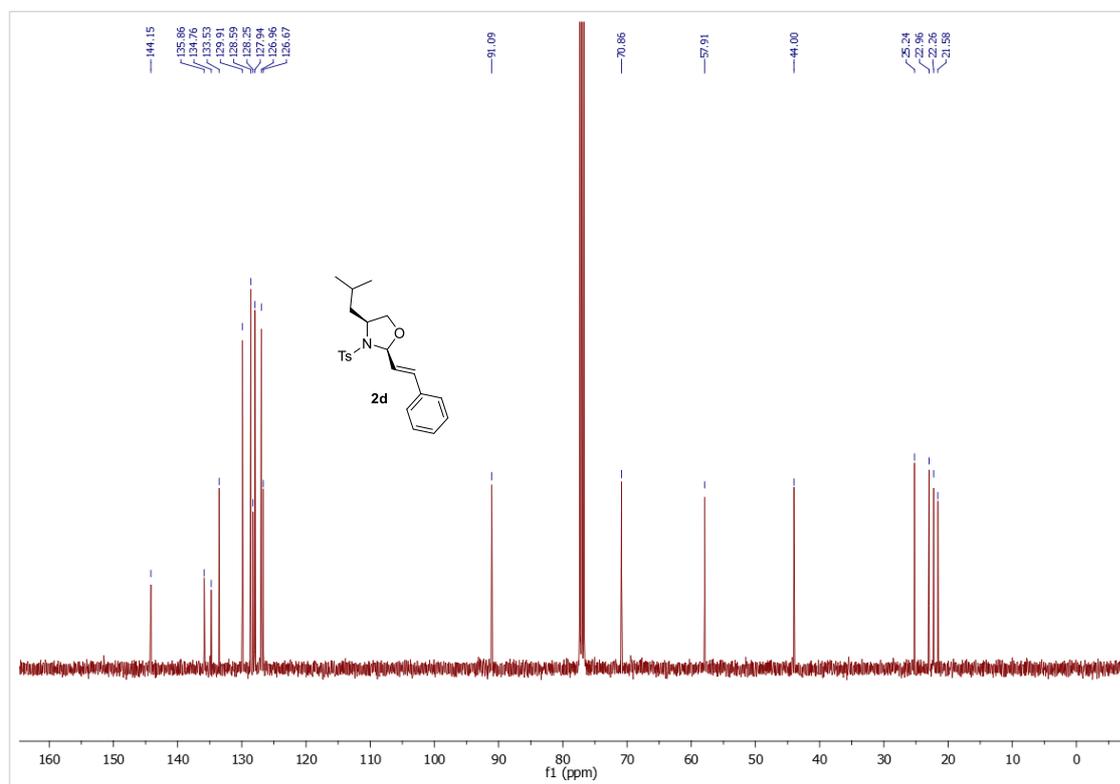
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2c** (101 MHz, CDCl_3)



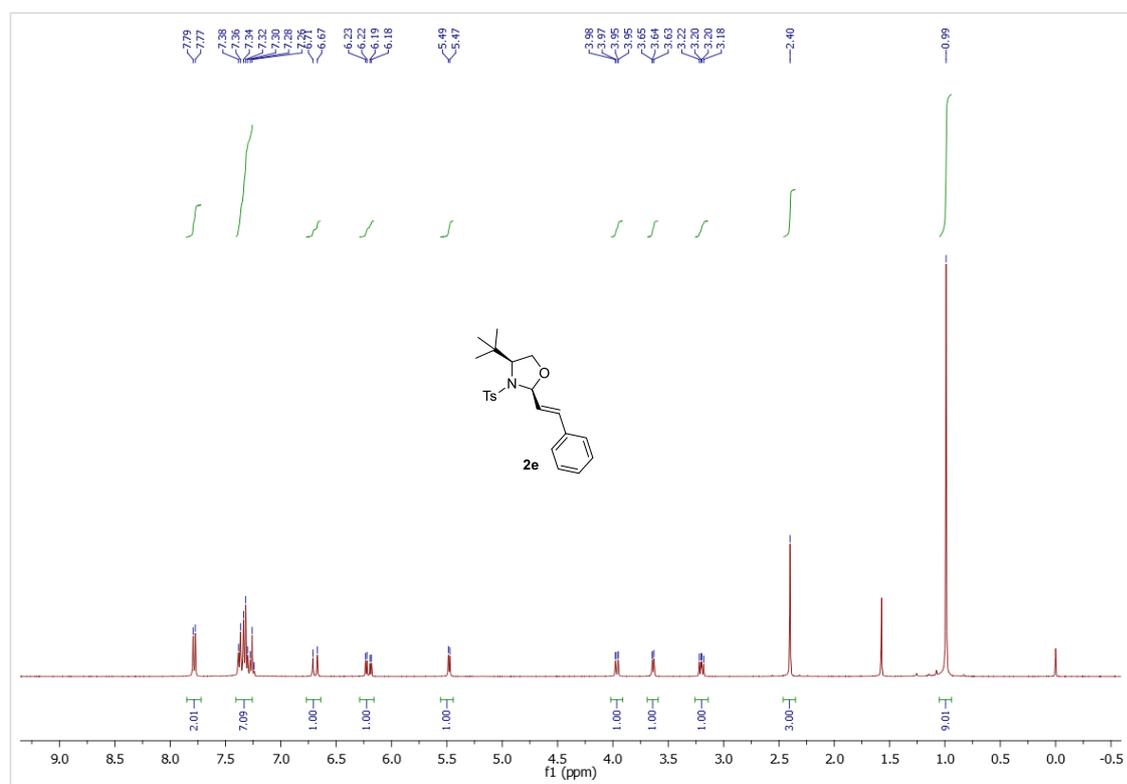
^1H NMR of **2d** (400 MHz, CDCl_3)



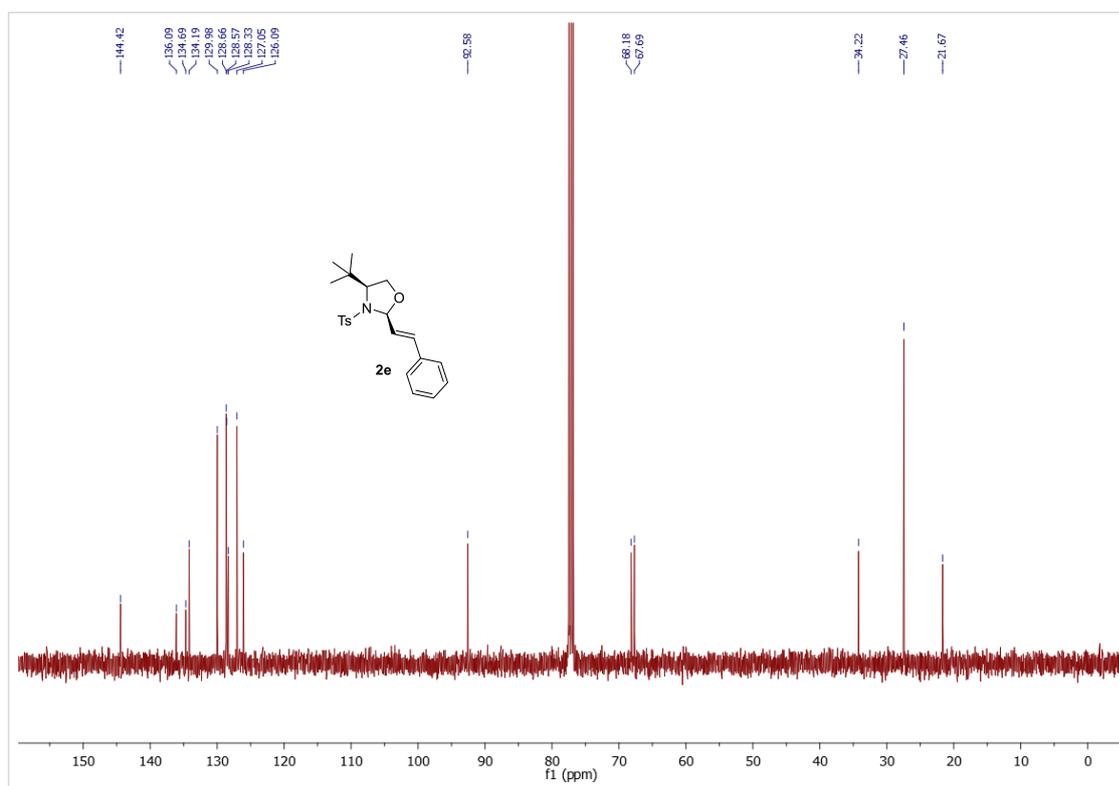
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2d** (101 MHz, CDCl_3)



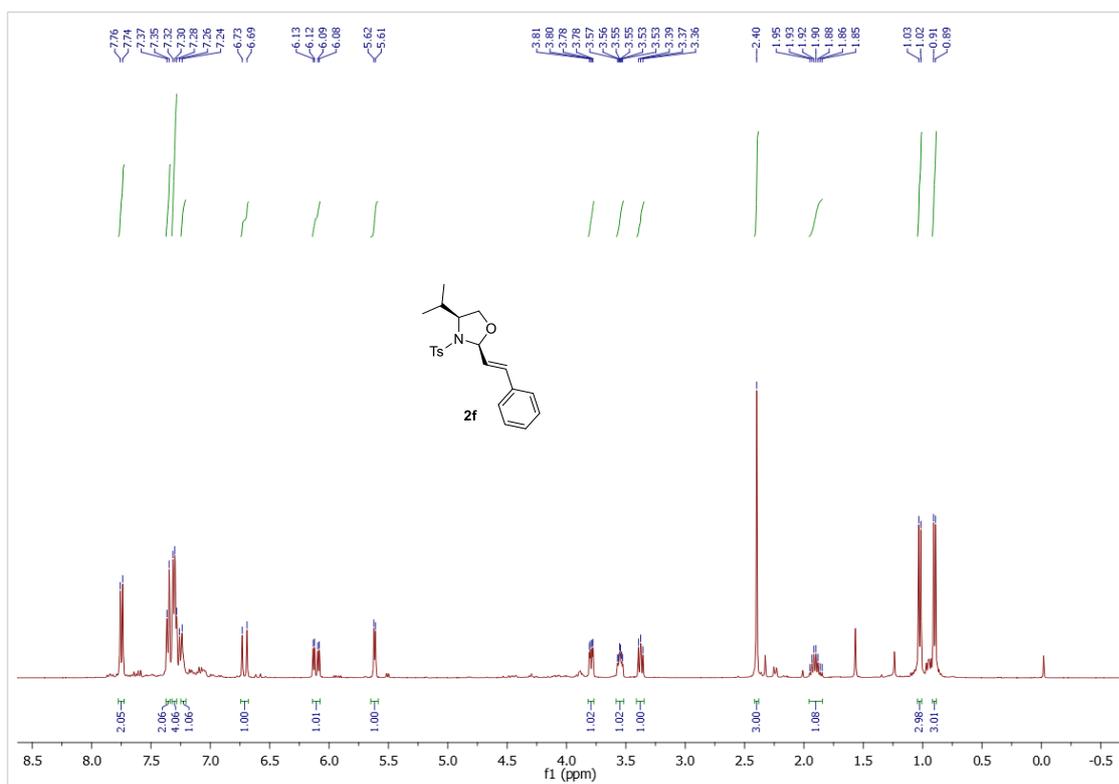
^1H NMR of **2e** (400 MHz, CDCl_3)



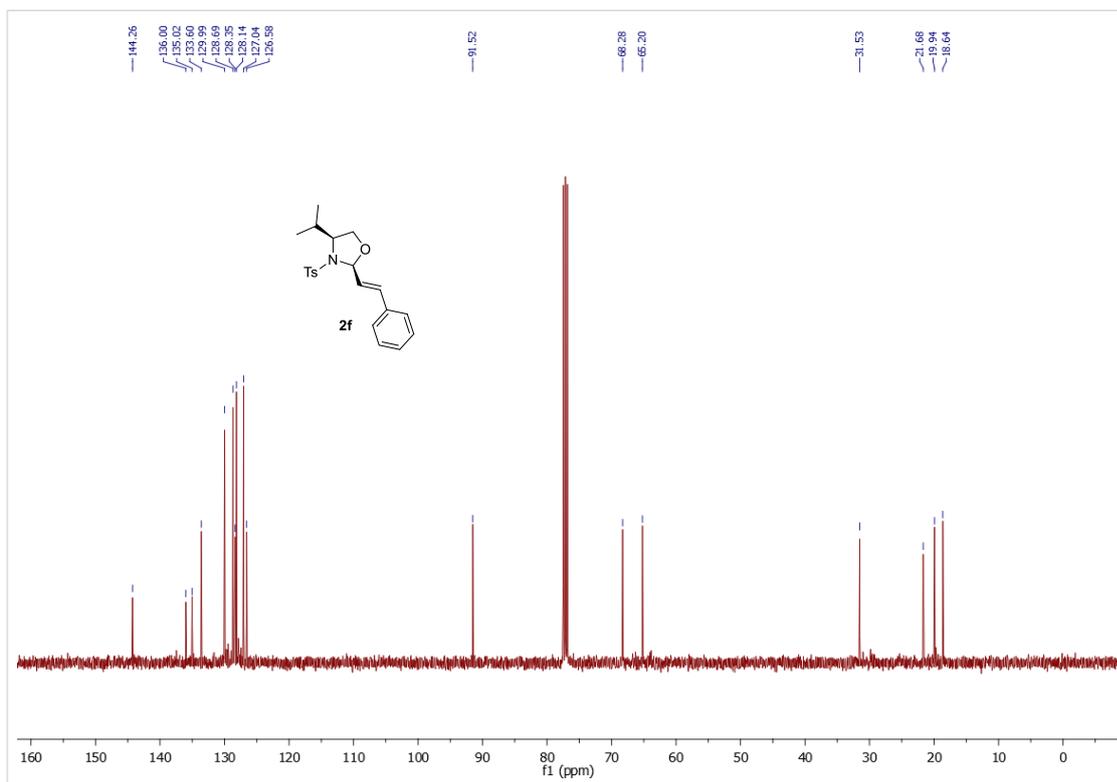
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2e** (101 MHz, CDCl_3)



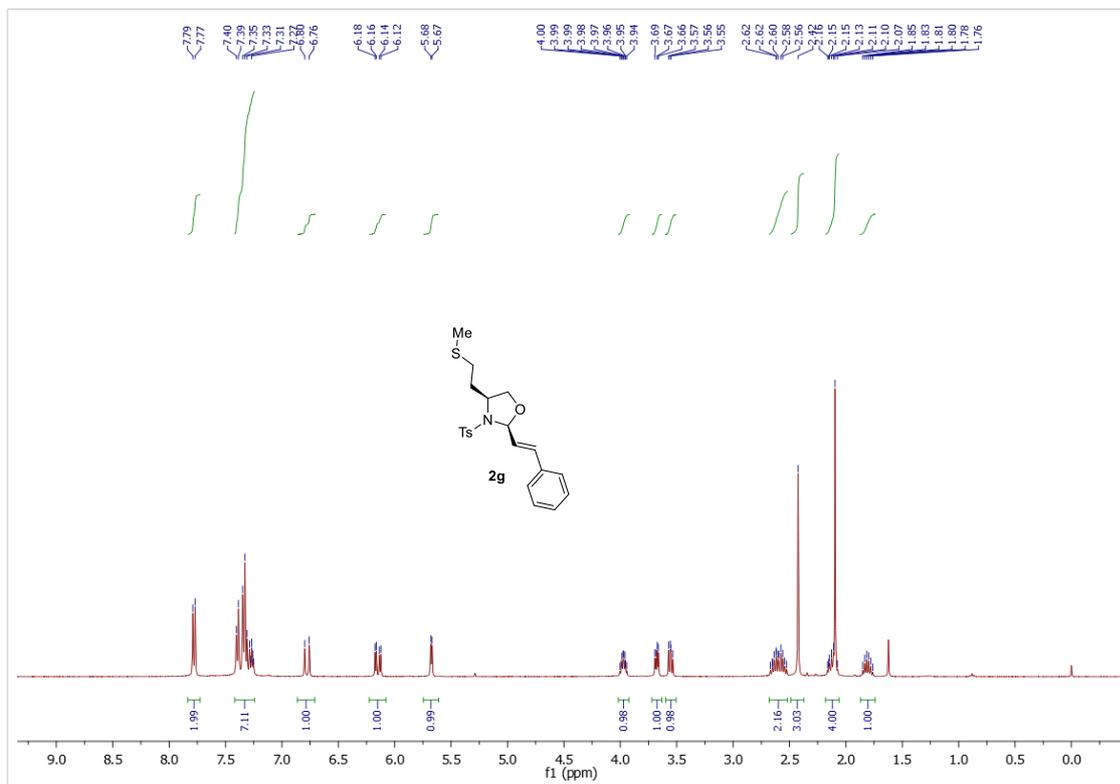
^1H NMR of **2f** (400 MHz, CDCl_3)



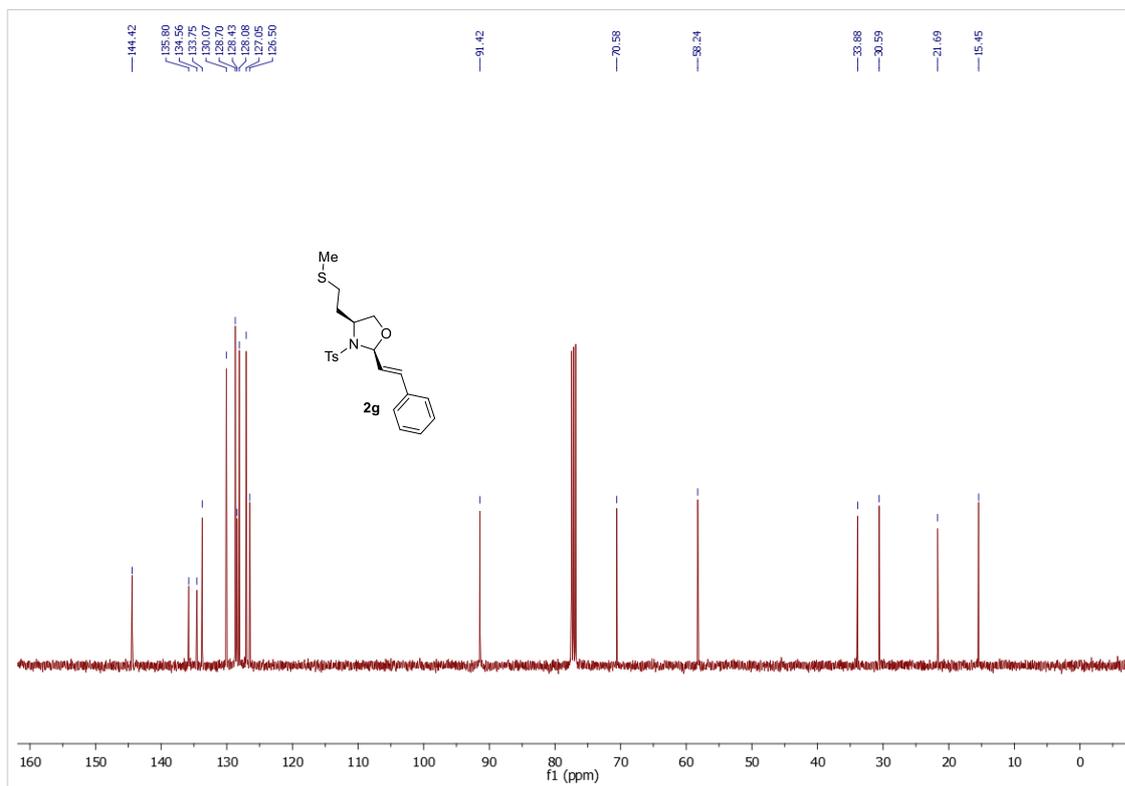
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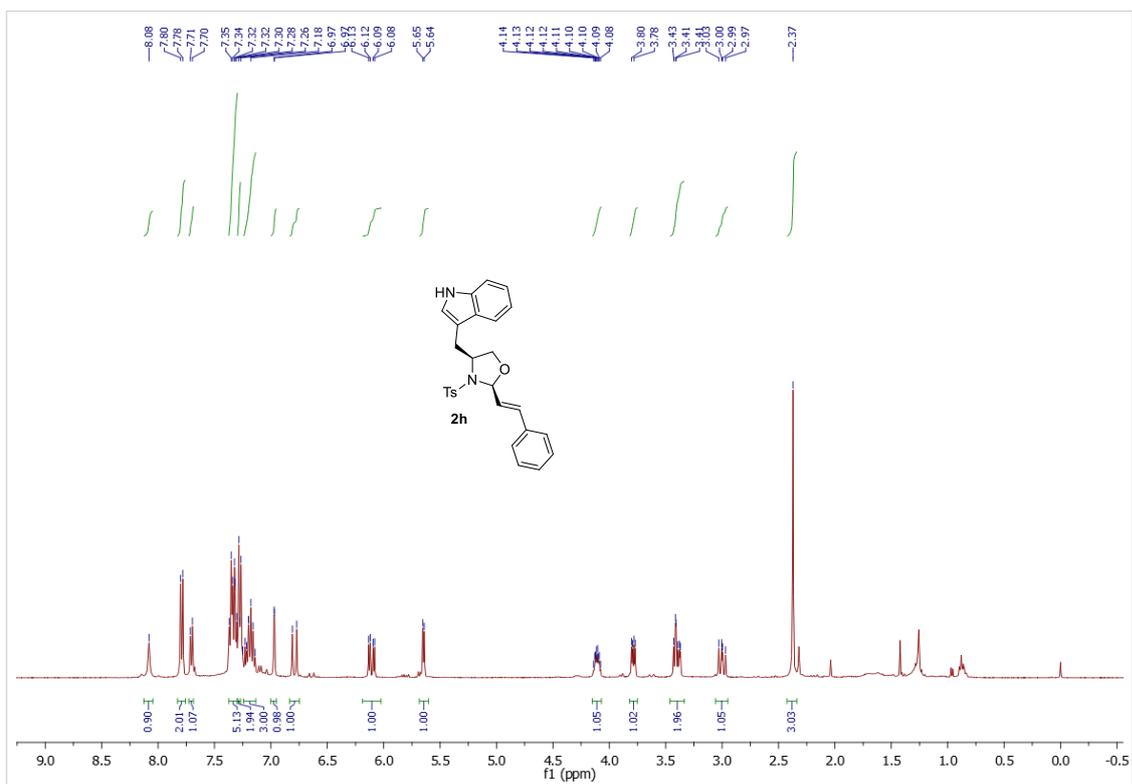
^1H NMR of **2g** (400 MHz, CDCl_3)



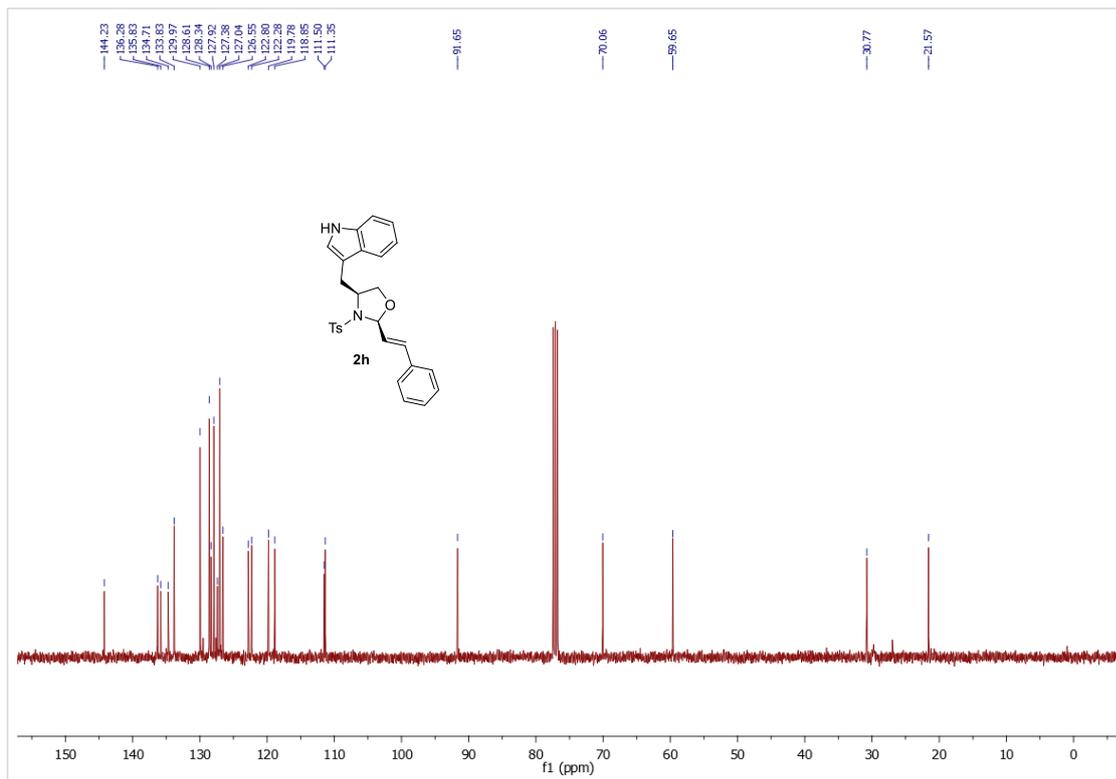
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2g** (101 MHz, CDCl_3)



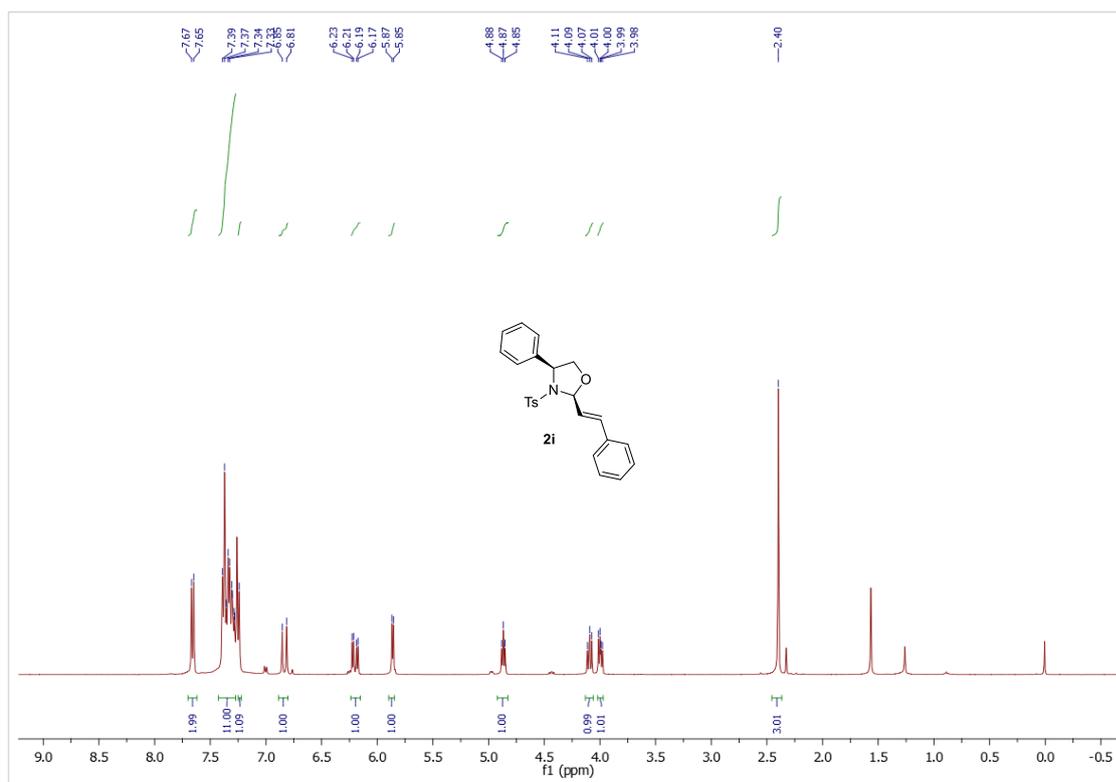
^1H NMR of **2h** (400 MHz, CDCl_3)



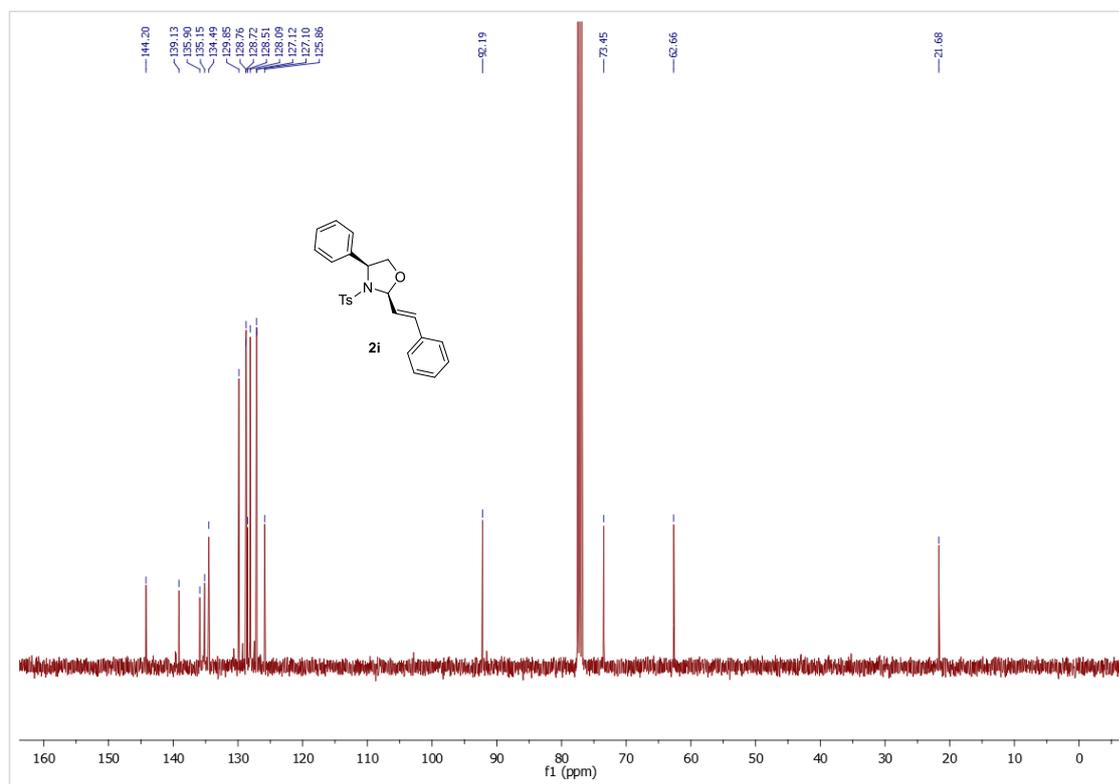
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2h** (101 MHz, CDCl_3)



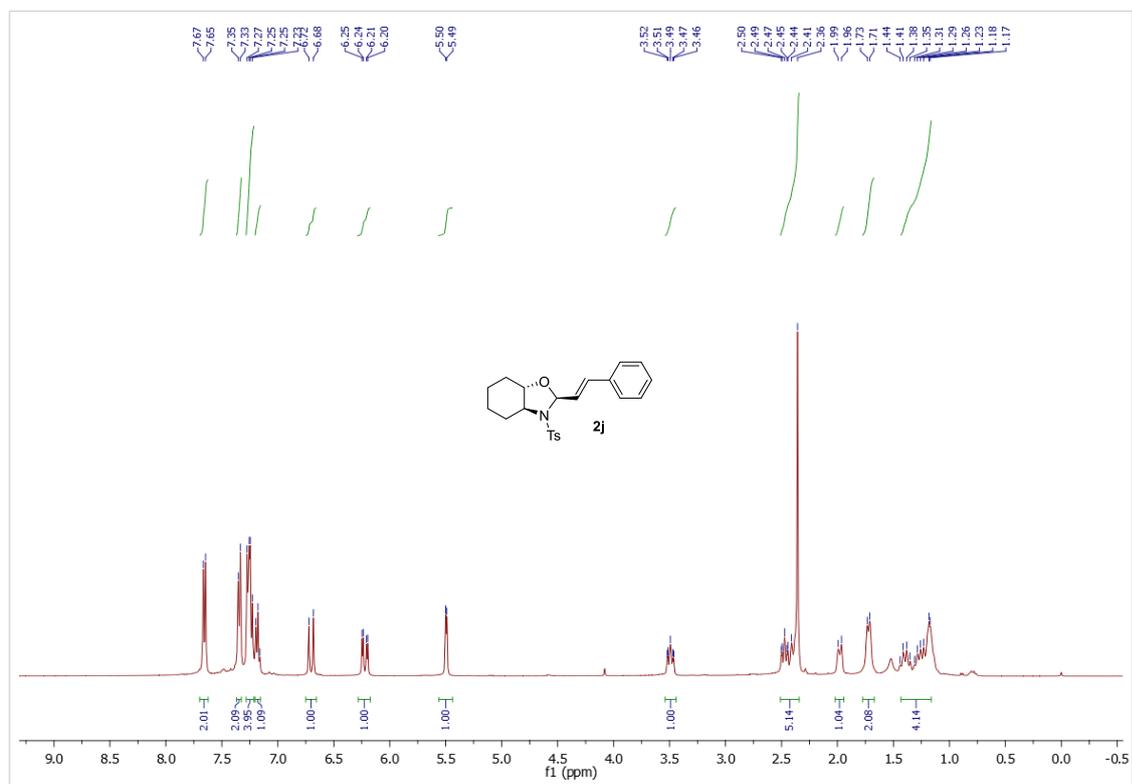
^1H NMR of **2i** (400 MHz, CDCl_3)



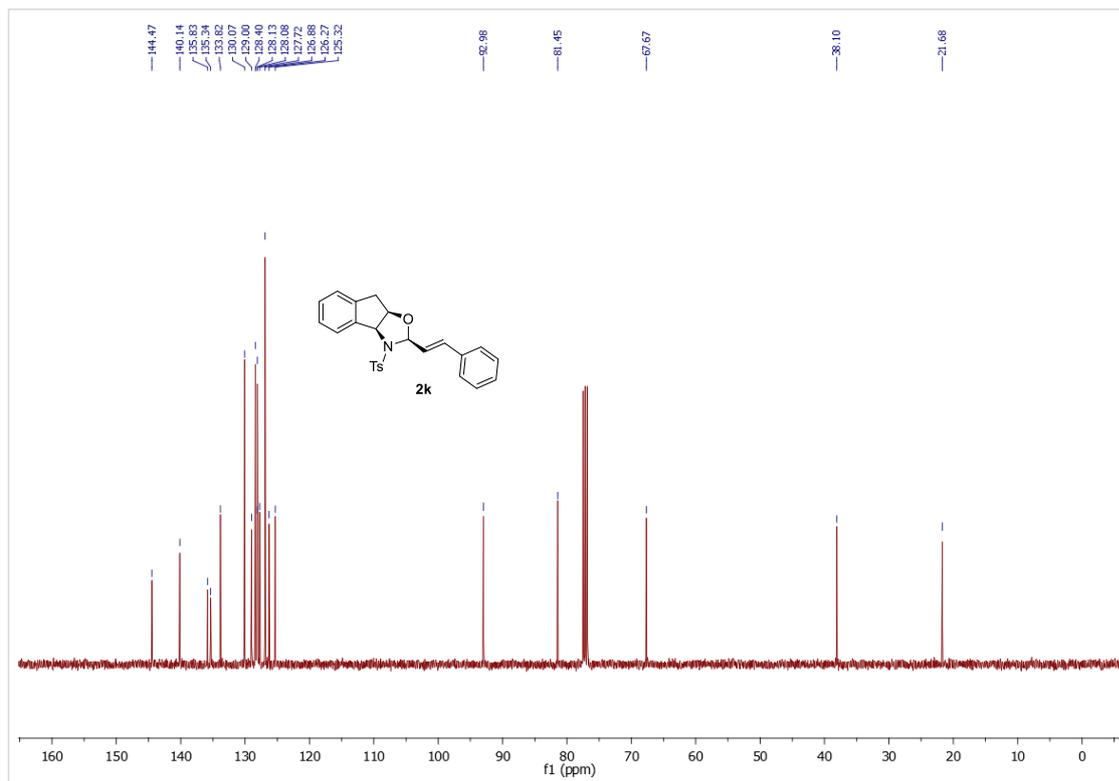
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2i** (101 MHz, CDCl_3)



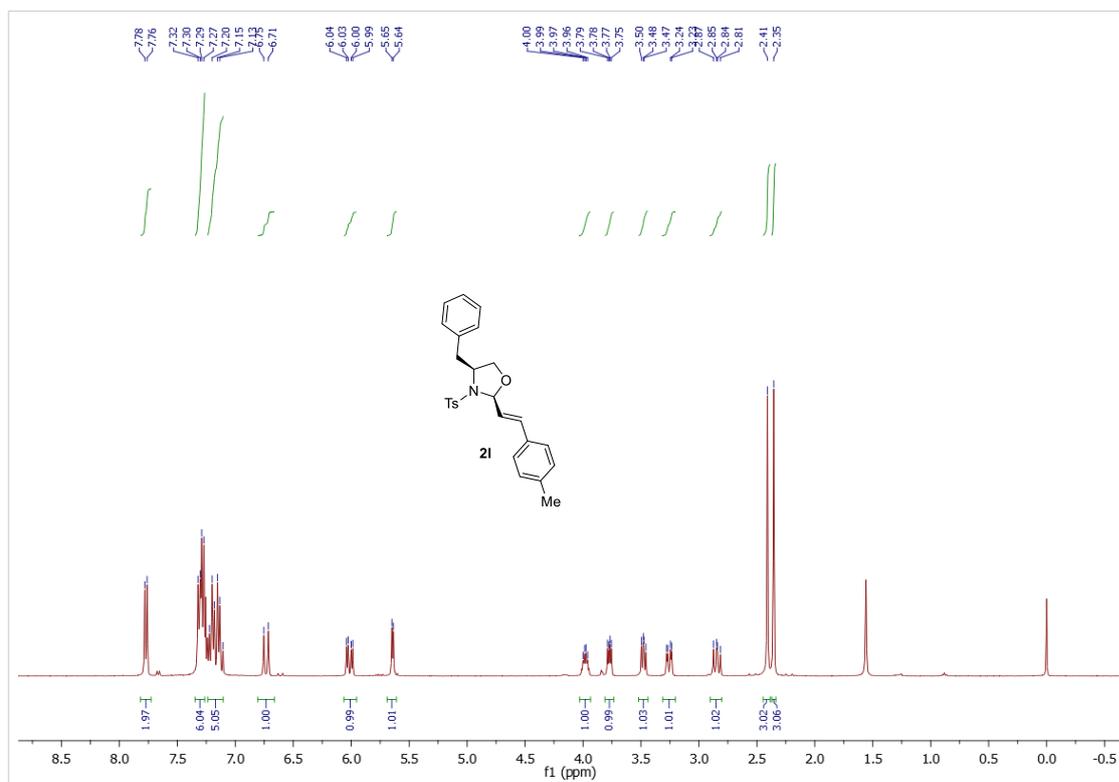
^1H NMR of **2j** (400 MHz, CDCl_3)



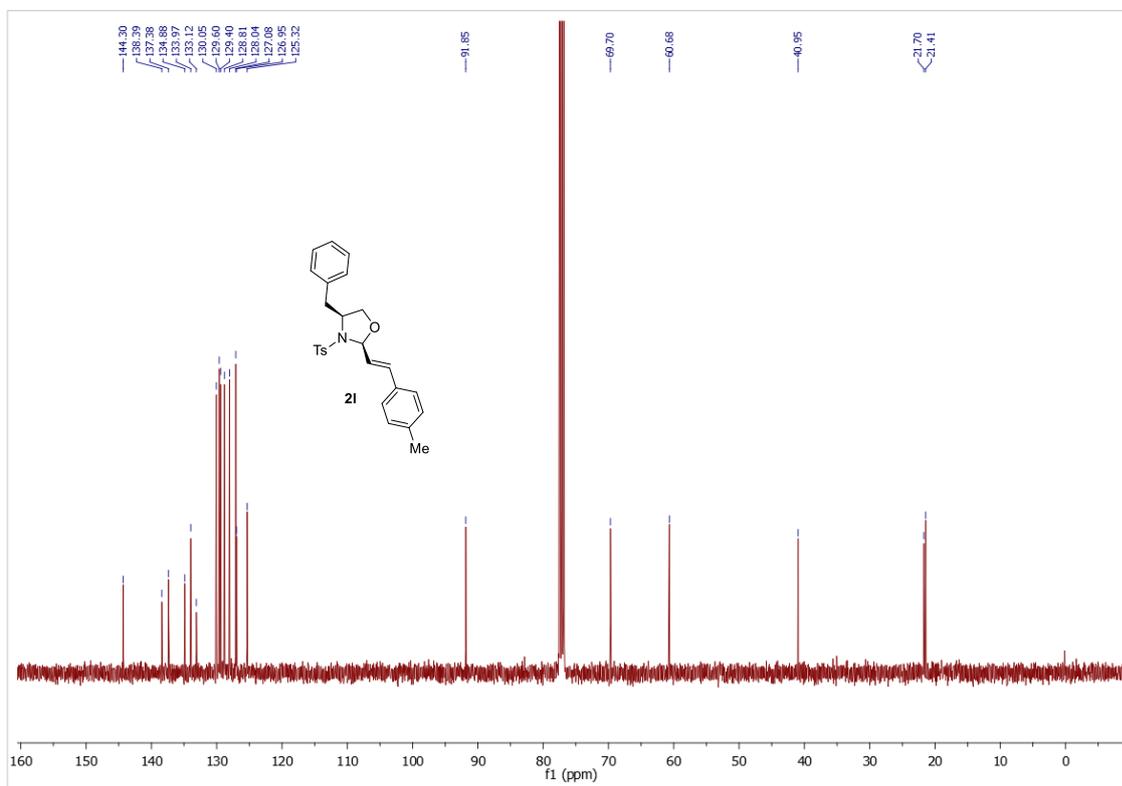
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2k** (101 MHz, CDCl_3)



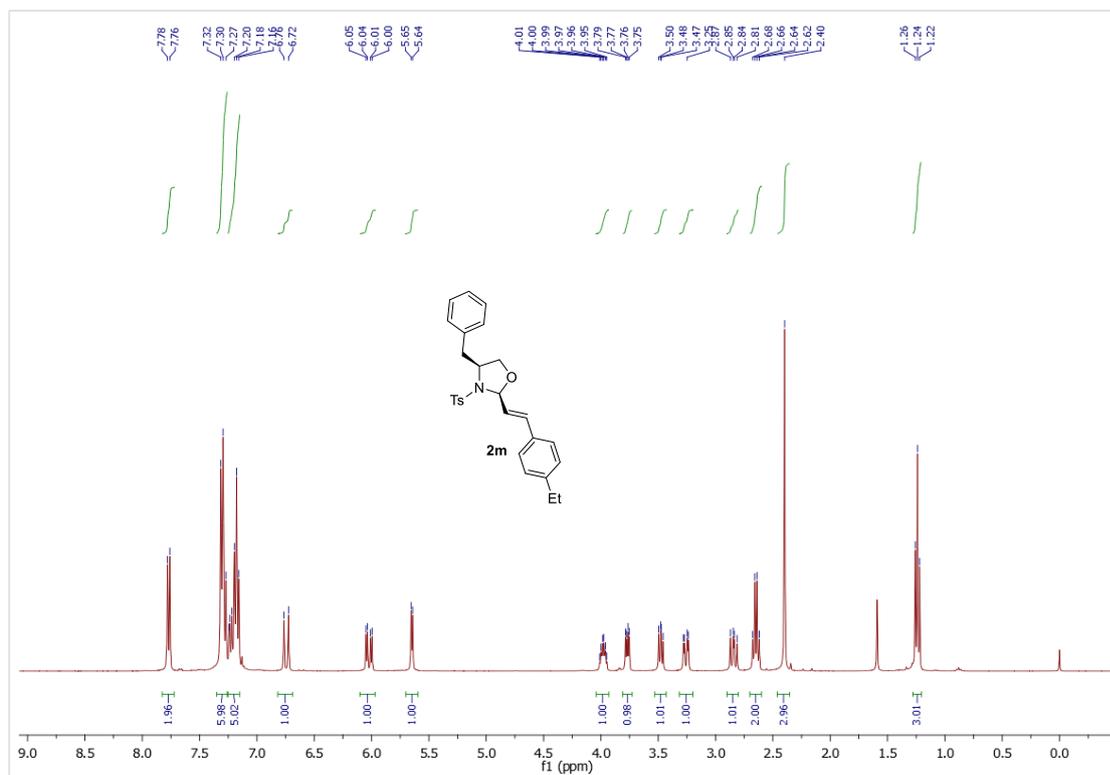
^1H NMR of **2l** (400 MHz, CDCl_3)



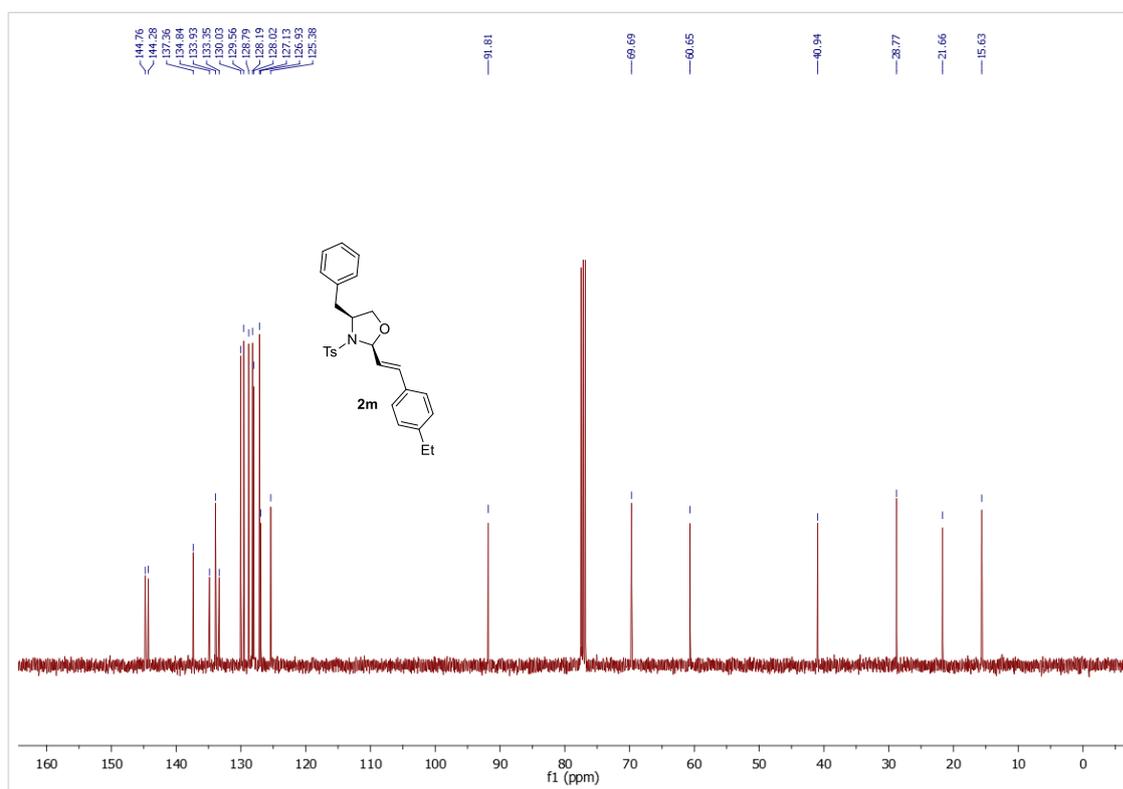
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2l** (101 MHz, CDCl_3)



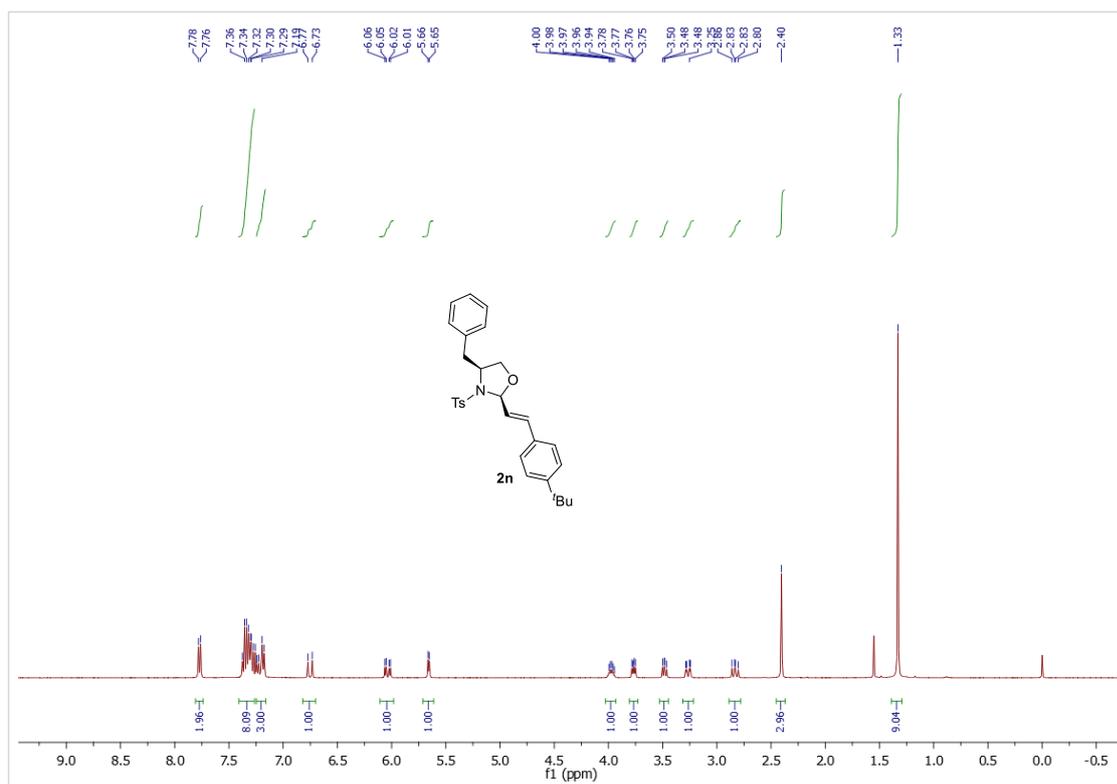
^1H NMR of **2m** (400 MHz, CDCl_3)



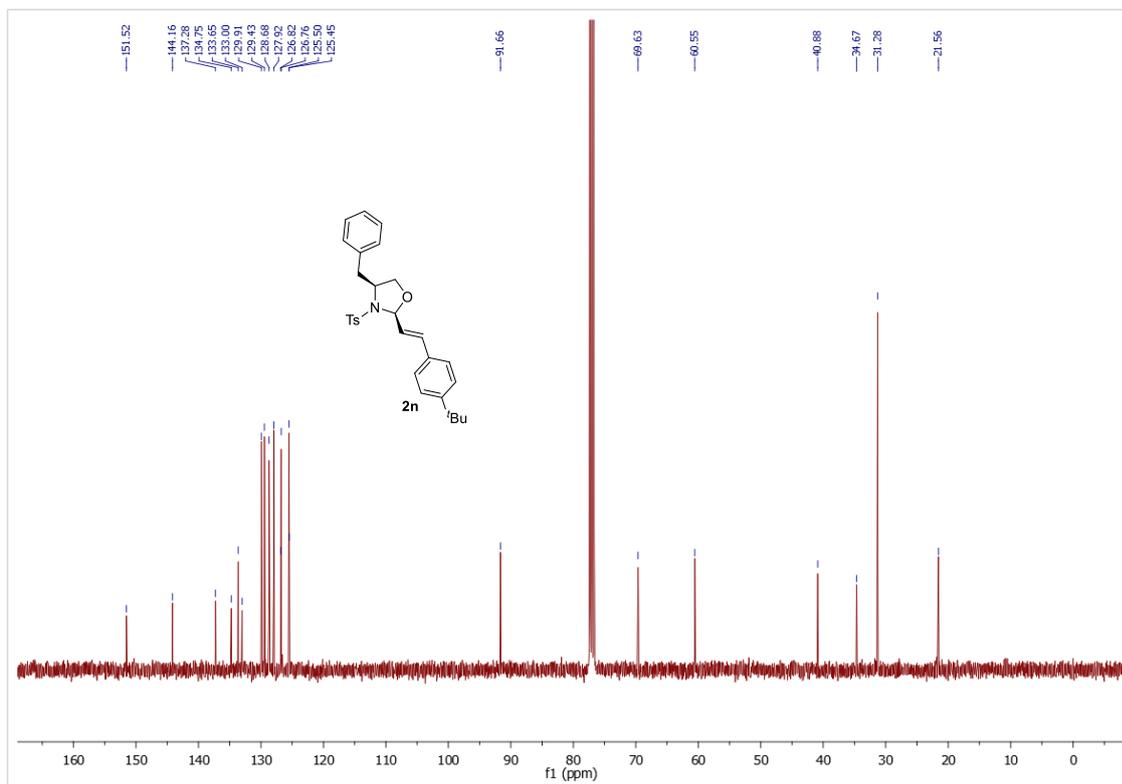
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2m** (101 MHz, CDCl_3)



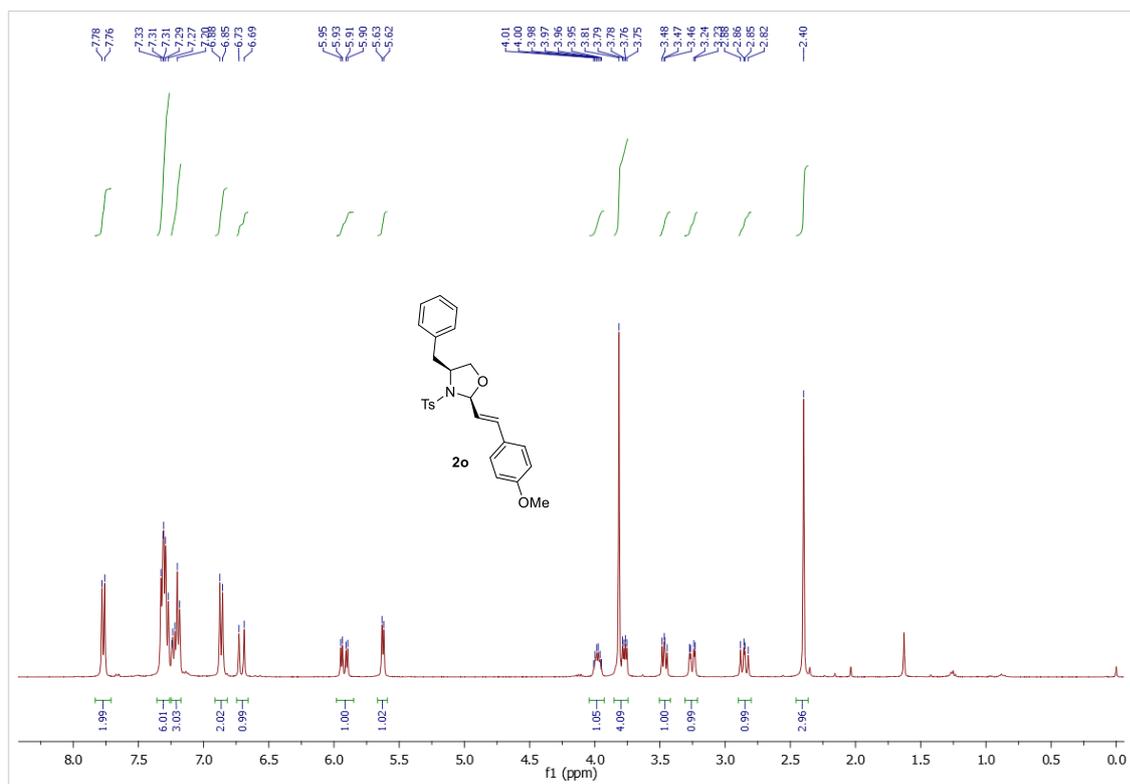
^1H NMR of **2n** (400 MHz, CDCl_3)



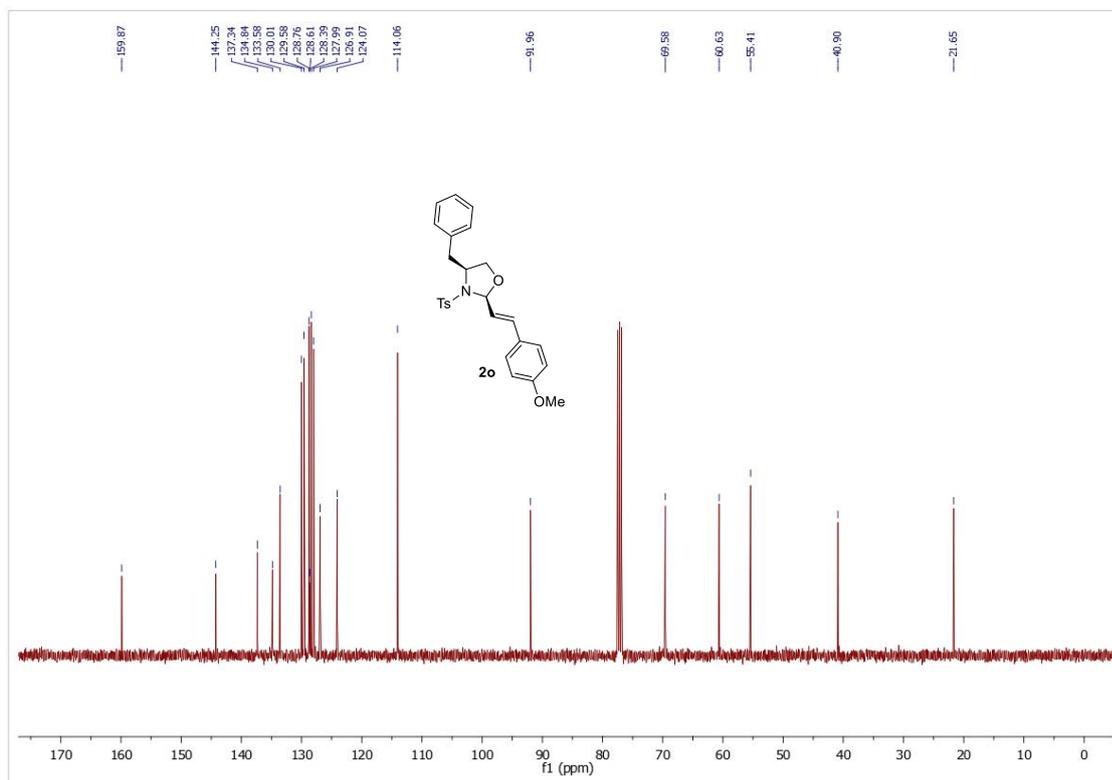
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2n** (101 MHz, CDCl_3)



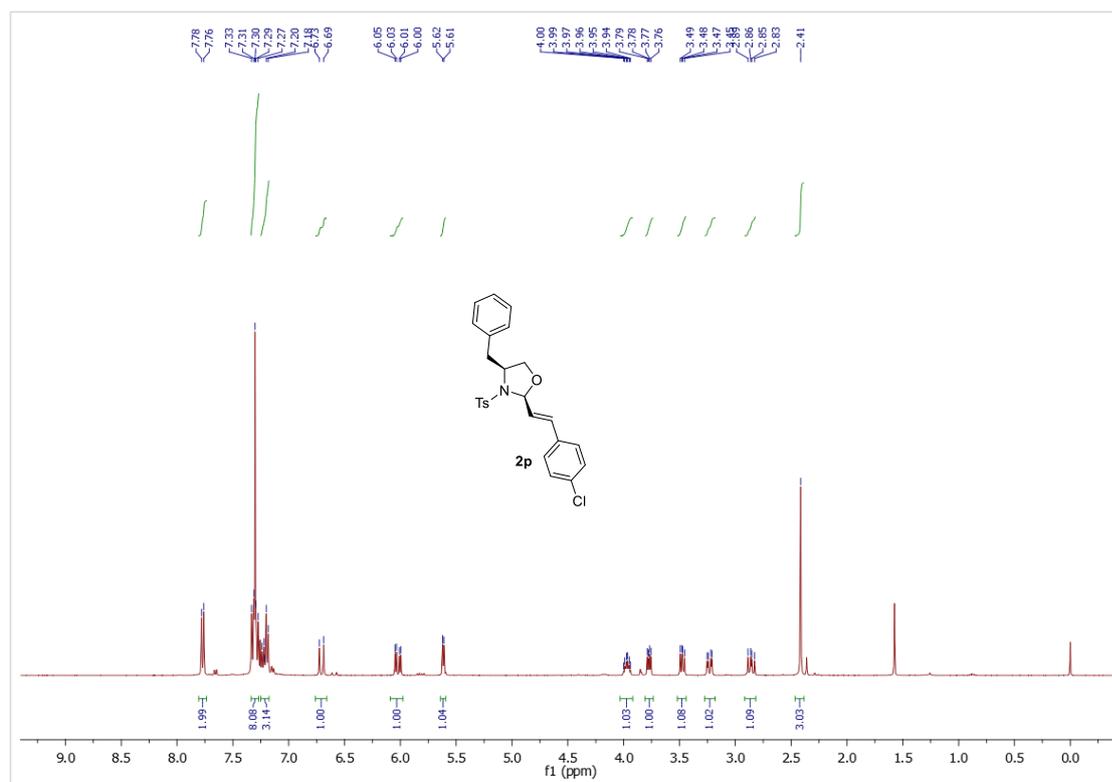
^1H NMR of **2o** (400 MHz, CDCl_3)



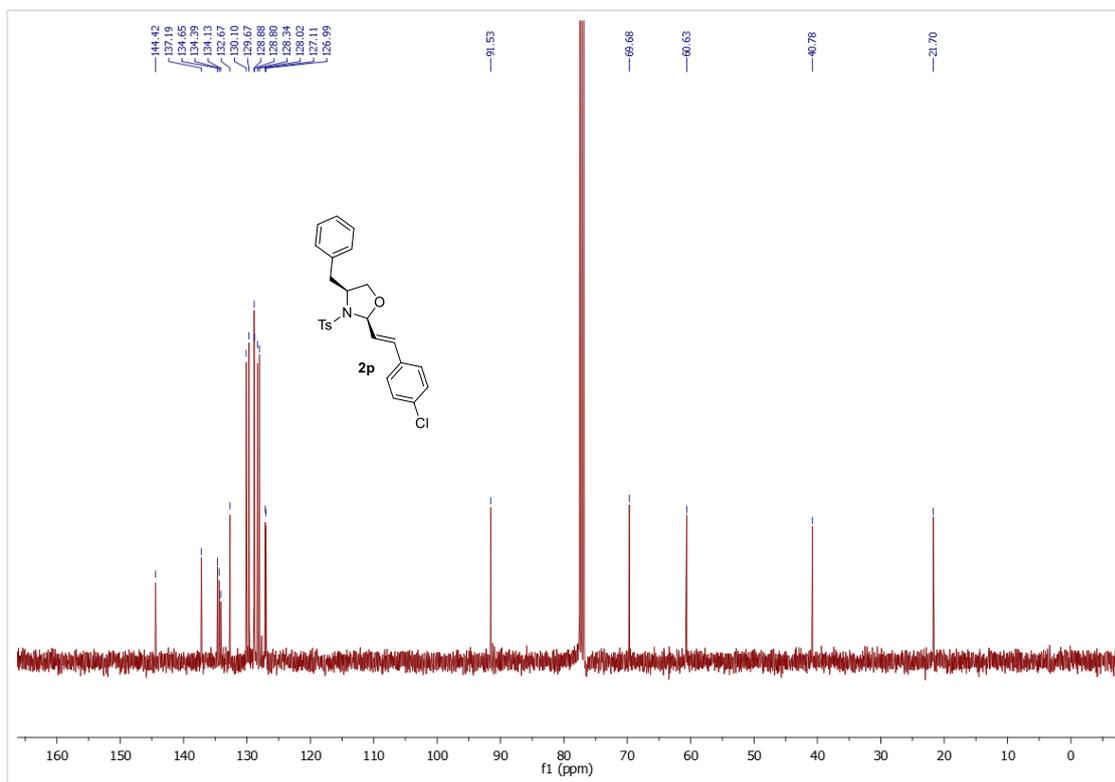
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2o** (101 MHz, CDCl_3)



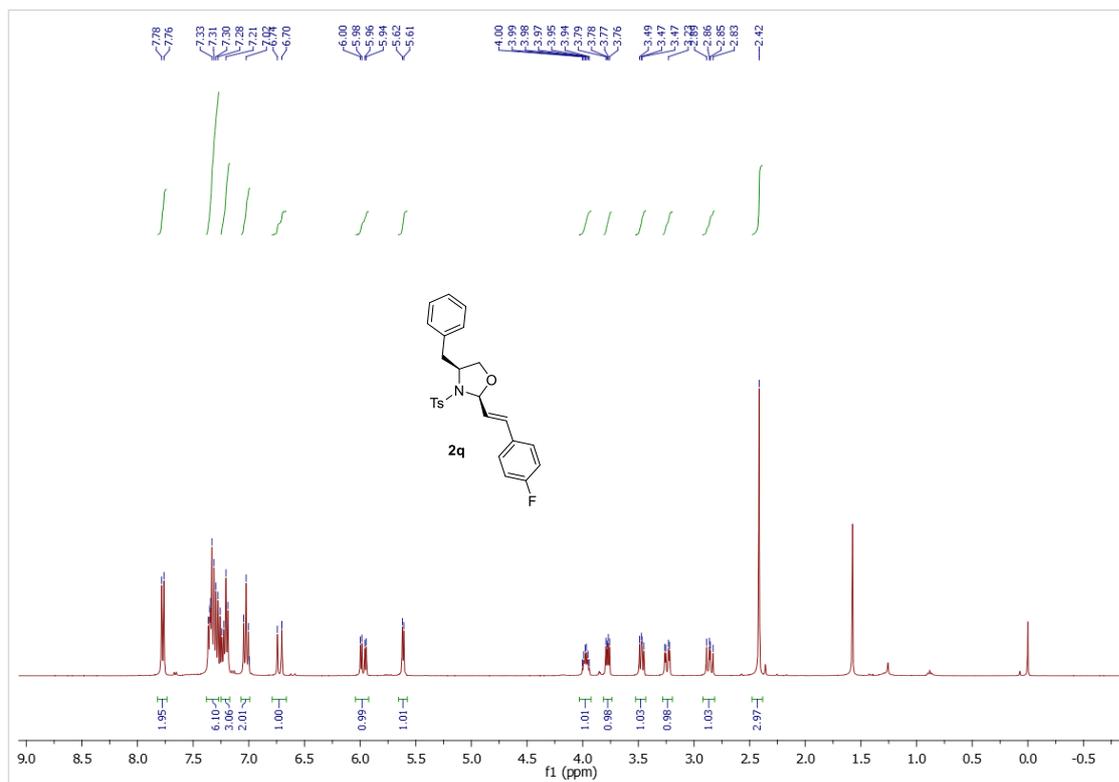
^1H NMR of **2p** (400 MHz, CDCl_3)



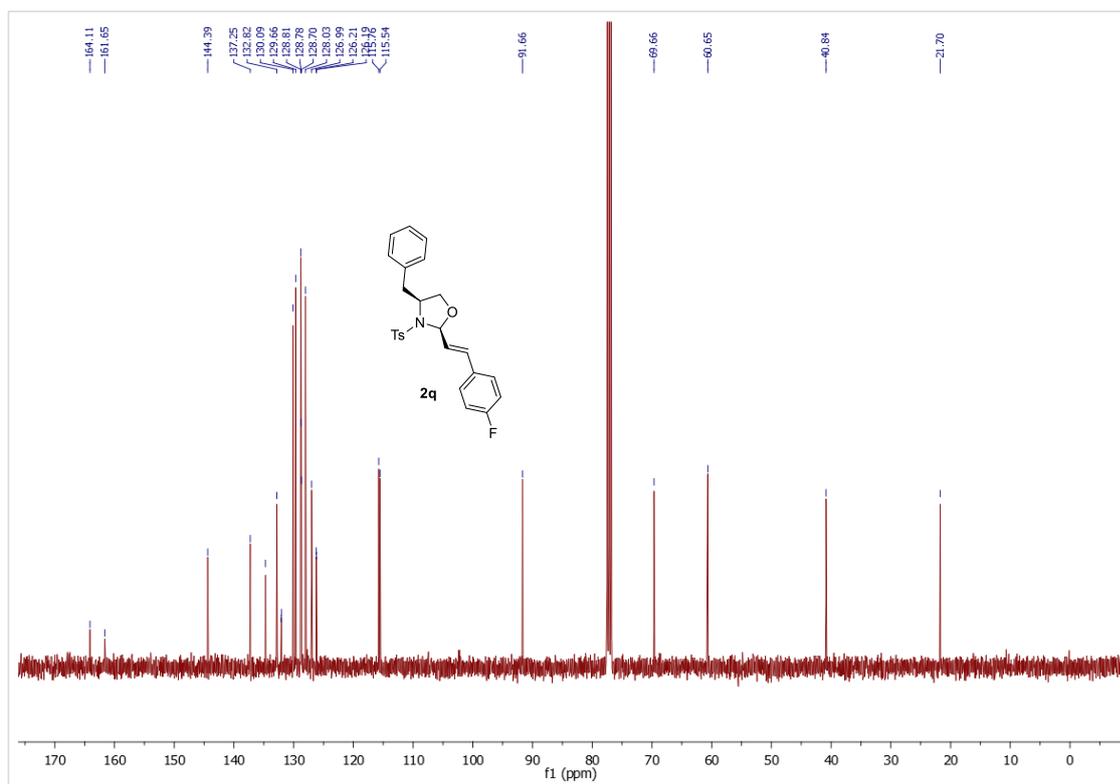
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2p** (101 MHz, CDCl_3)



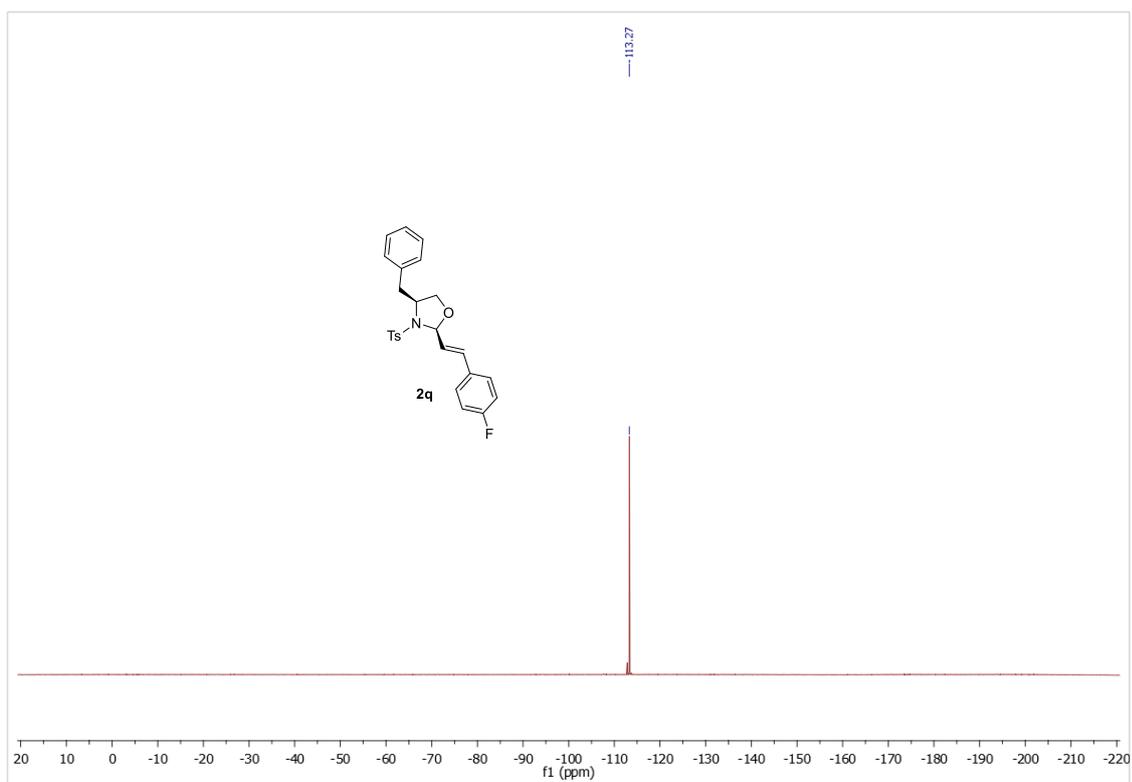
^1H NMR of **2q** (400 MHz, CDCl_3)



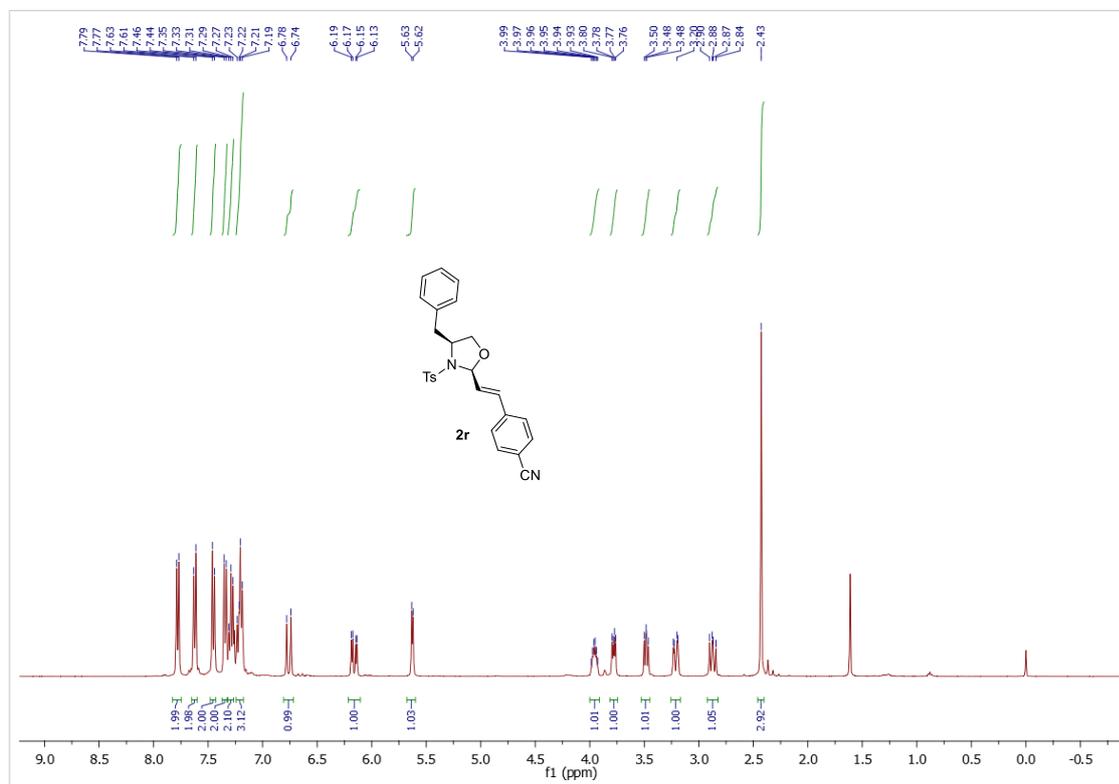
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2q** (101 MHz, CDCl_3)



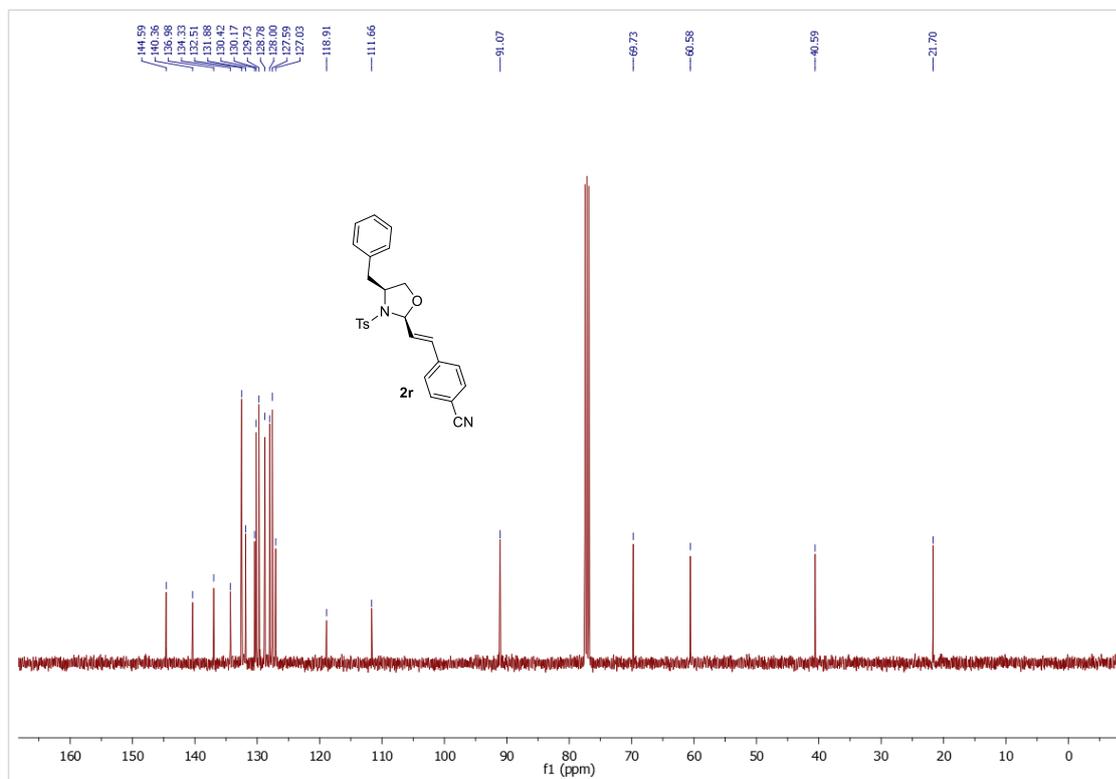
$^{19}\text{F}\{^1\text{H}\}$ NMR of **2q** (400 MHz, CDCl_3)



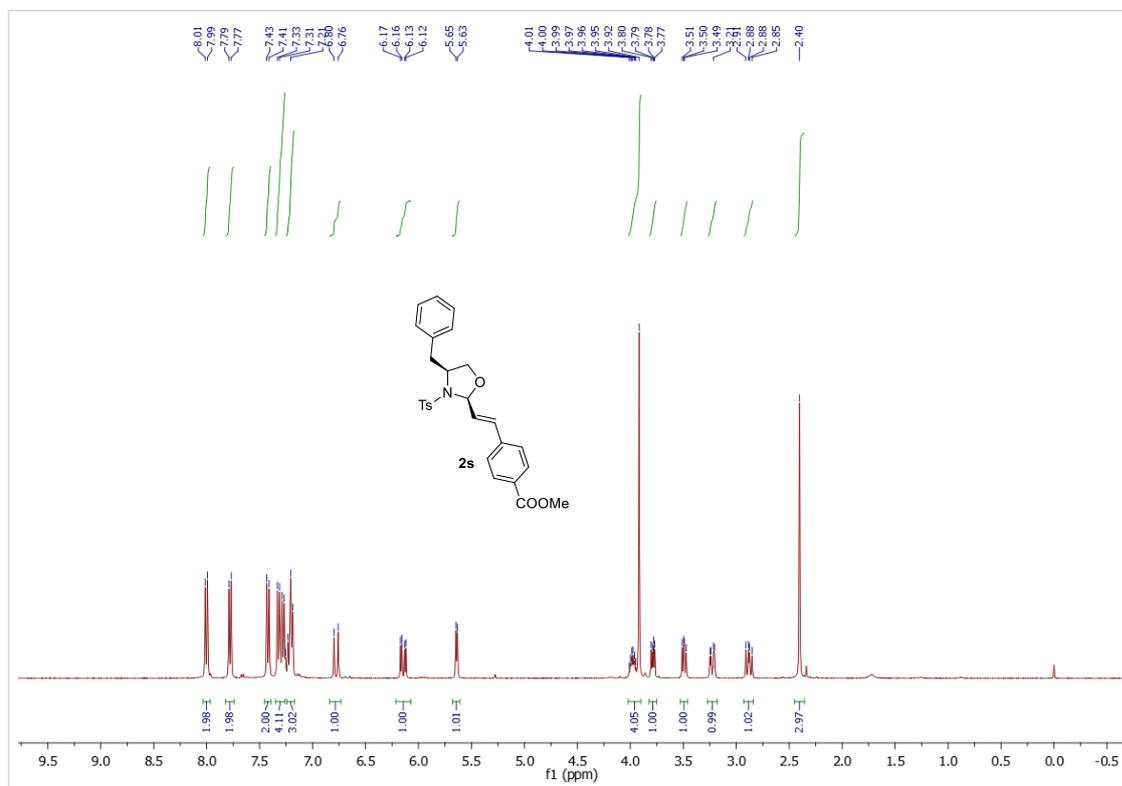
^1H NMR of **2r** (400 MHz, CDCl_3)



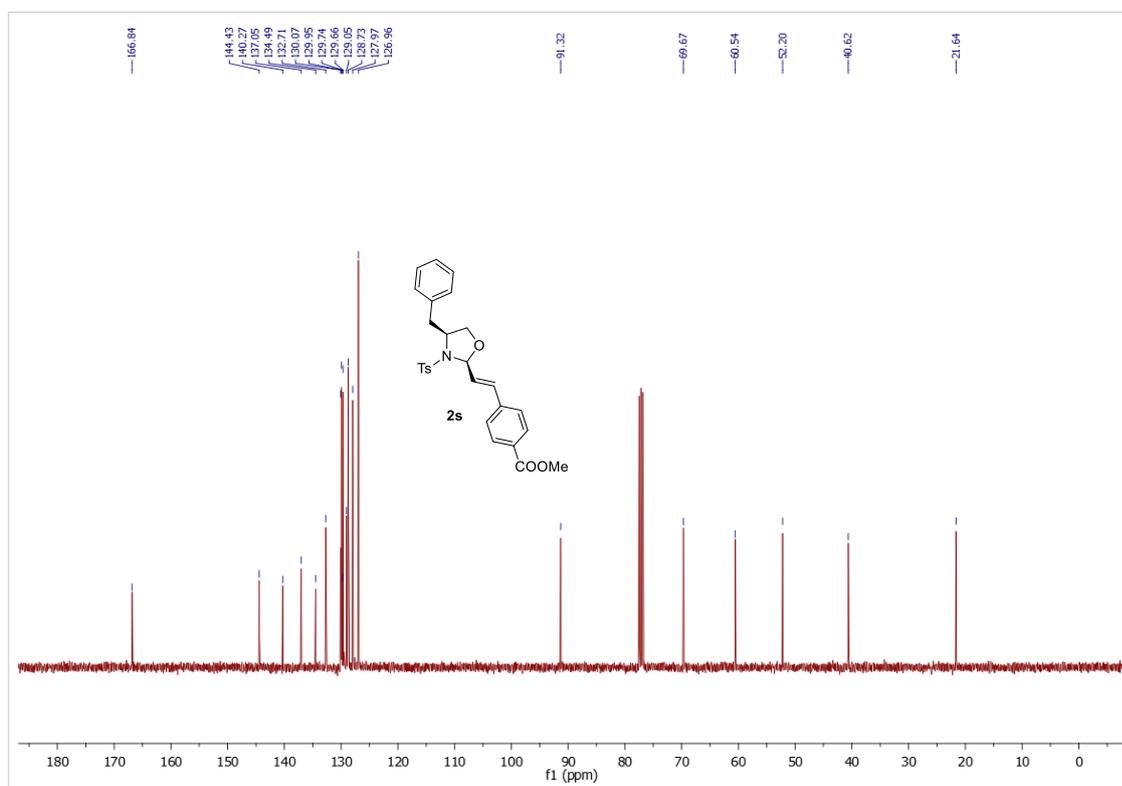
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2r** (101 MHz, CDCl_3)



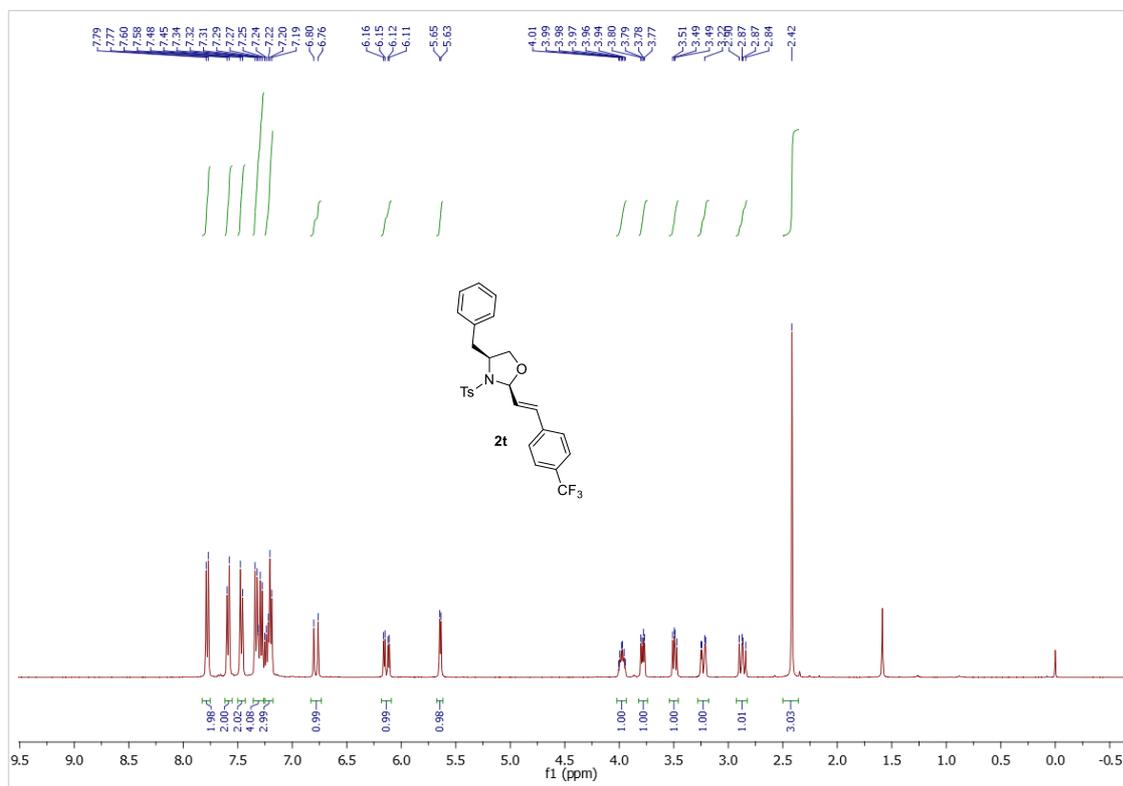
^1H NMR of **2s** (400 MHz, CDCl_3)



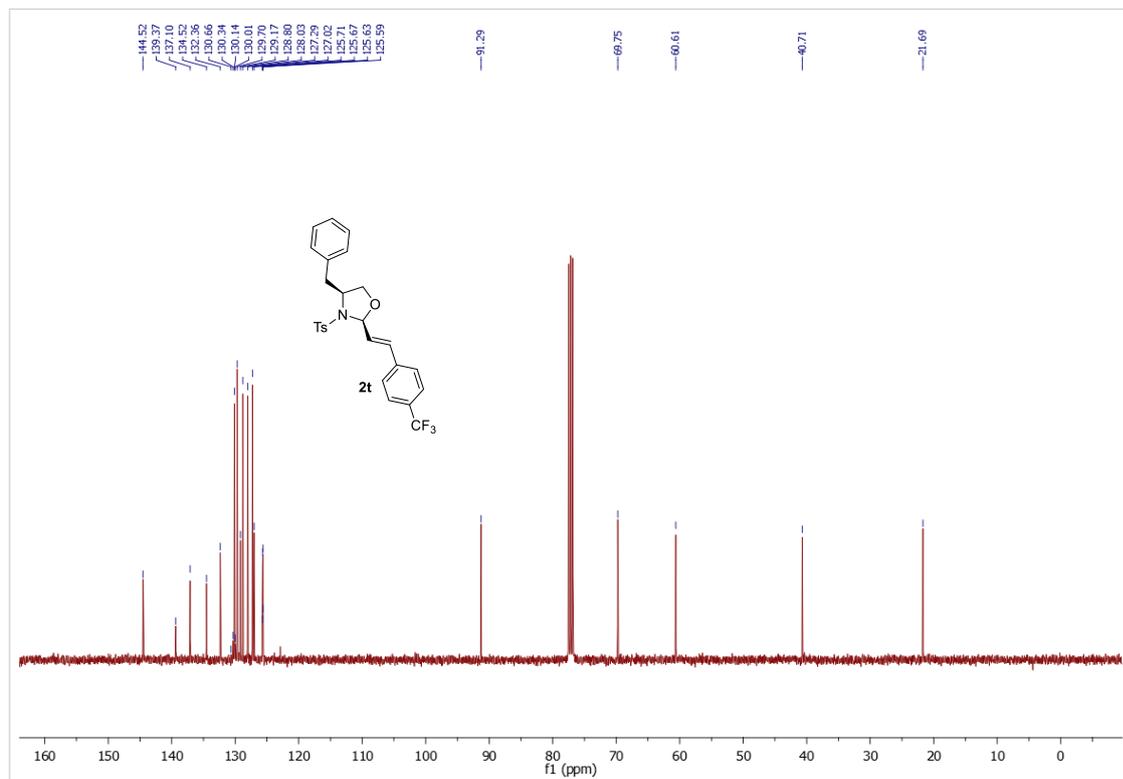
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2s** (101 MHz, CDCl_3)



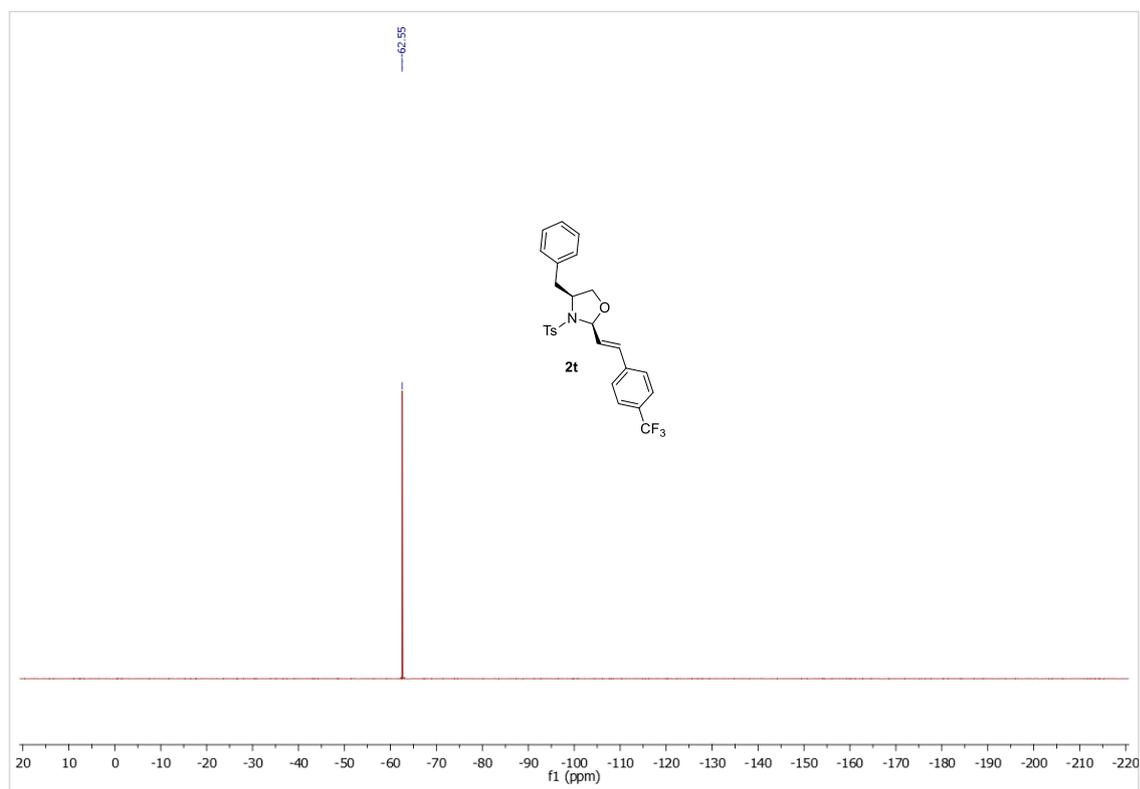
^1H NMR of **2t** (400 MHz, CDCl_3)



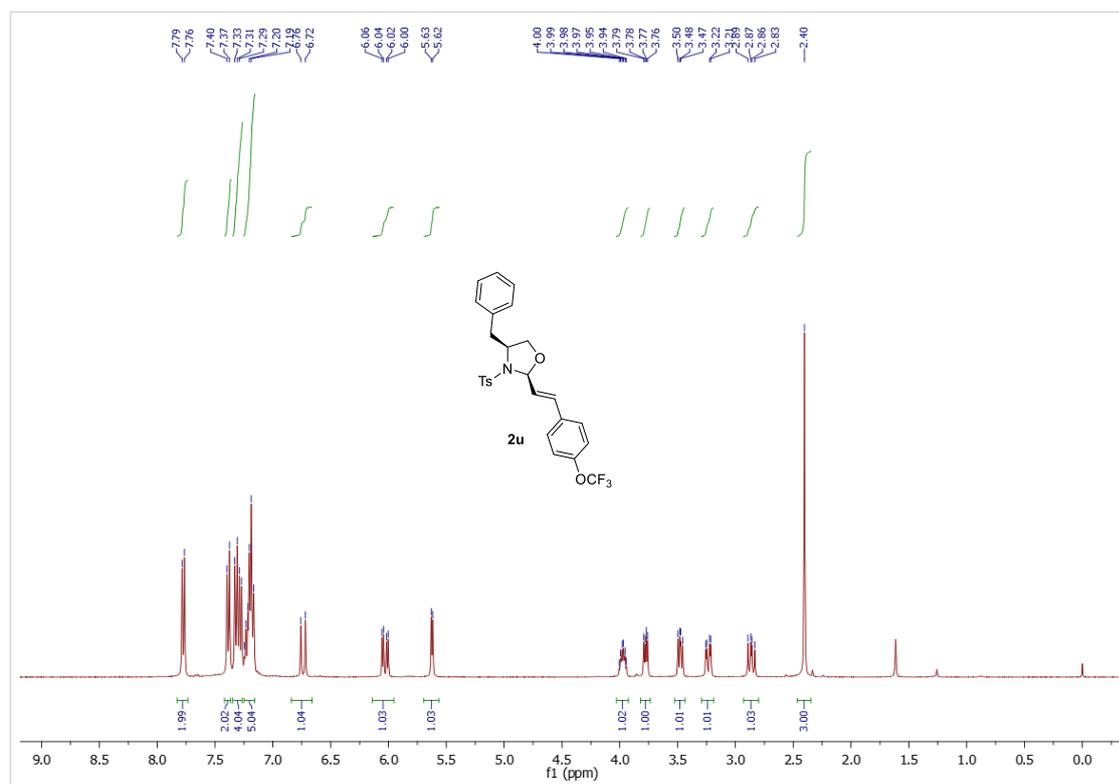
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2t** (101 MHz, CDCl_3)



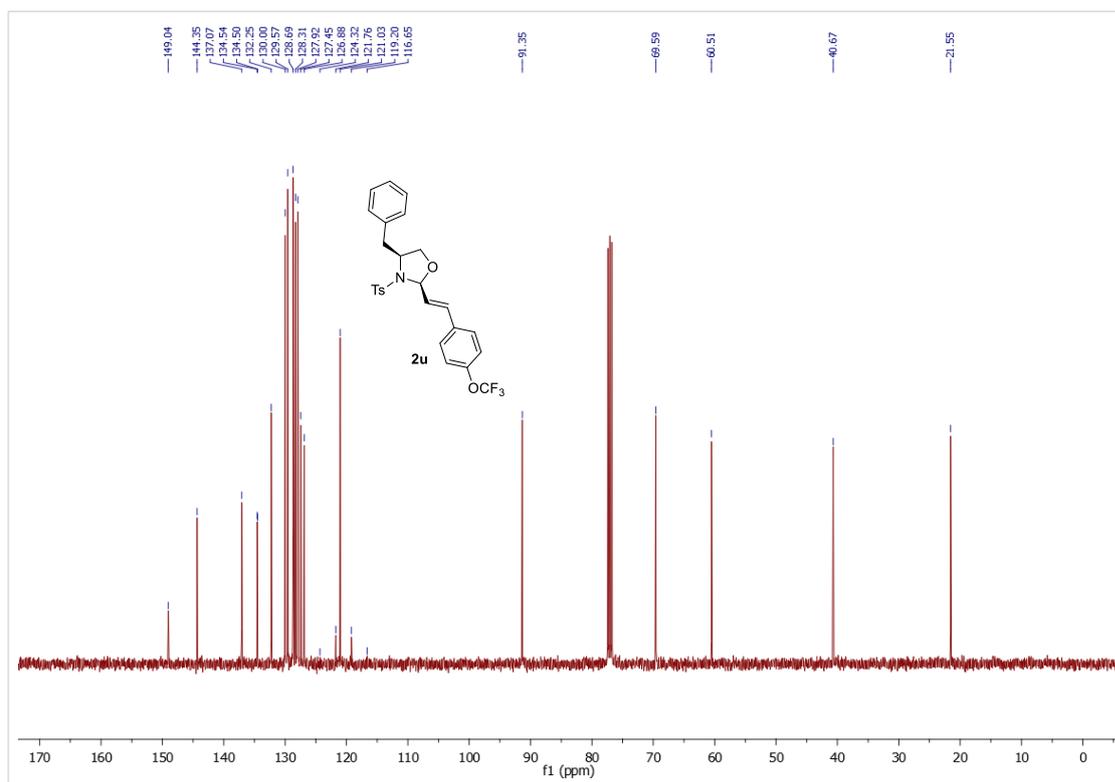
$^{19}\text{F}\{^1\text{H}\}$ NMR of **2t** (400 MHz, CDCl_3)



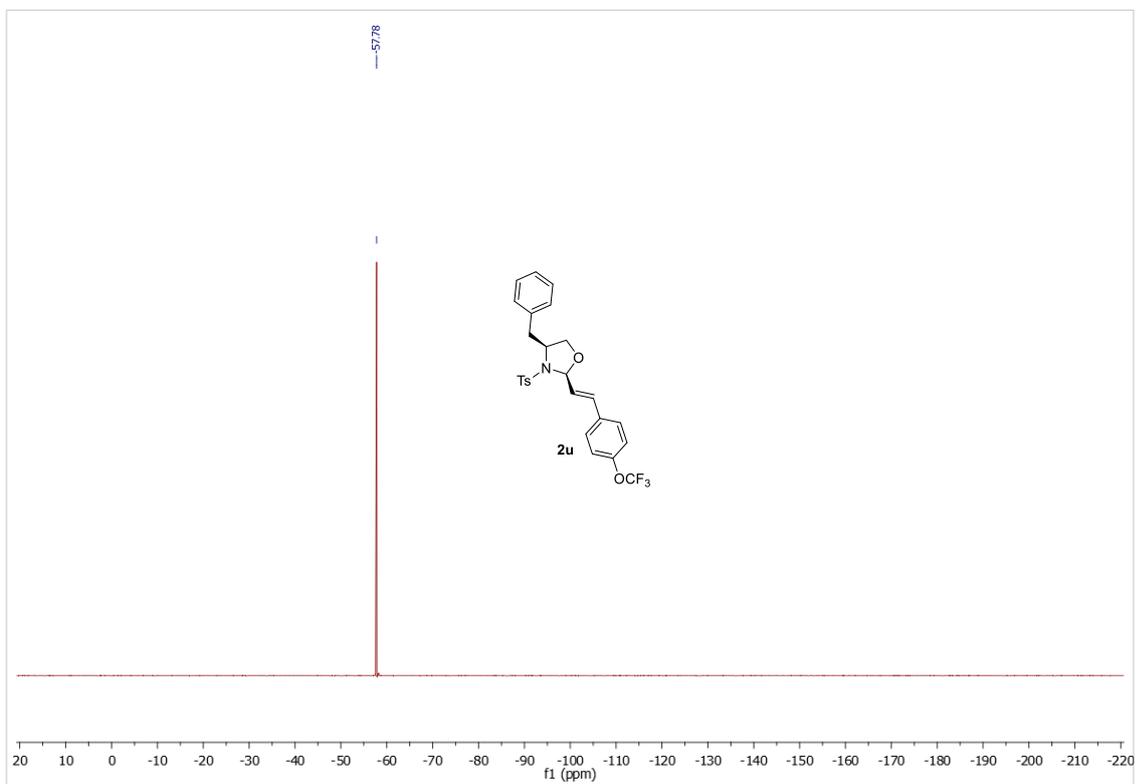
^1H NMR of **2u** (400 MHz, CDCl_3)



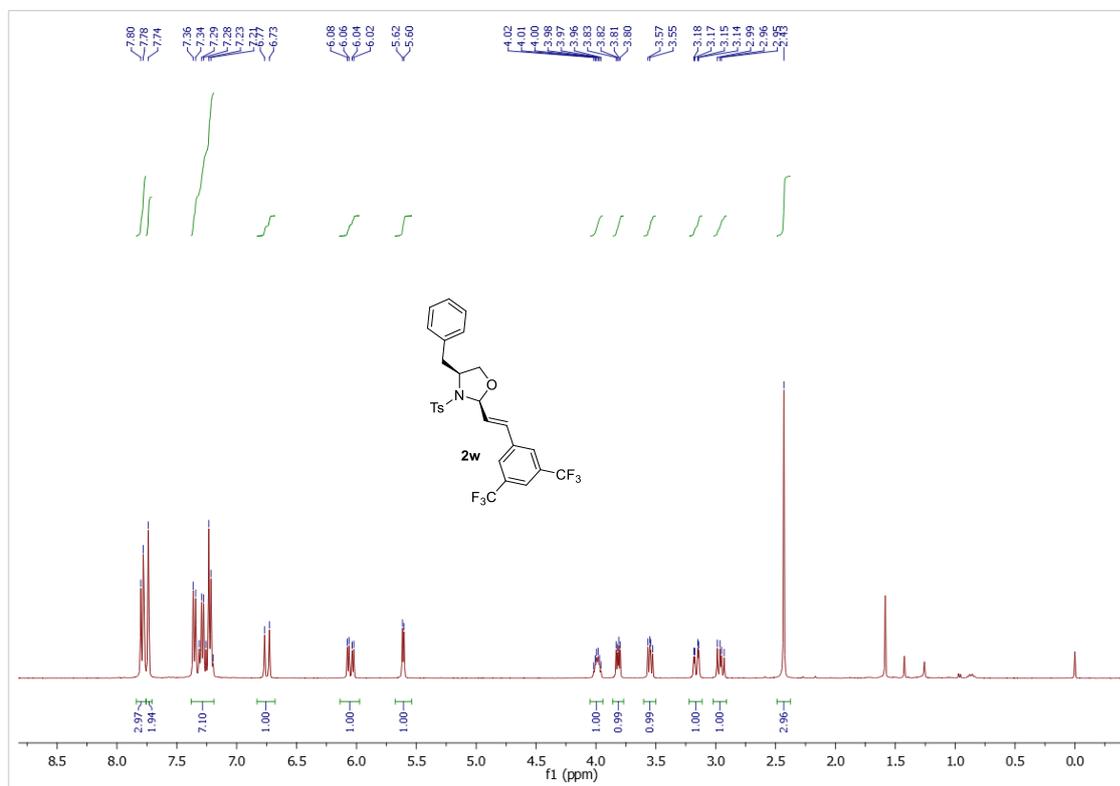
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2u** (101 MHz, CDCl_3)



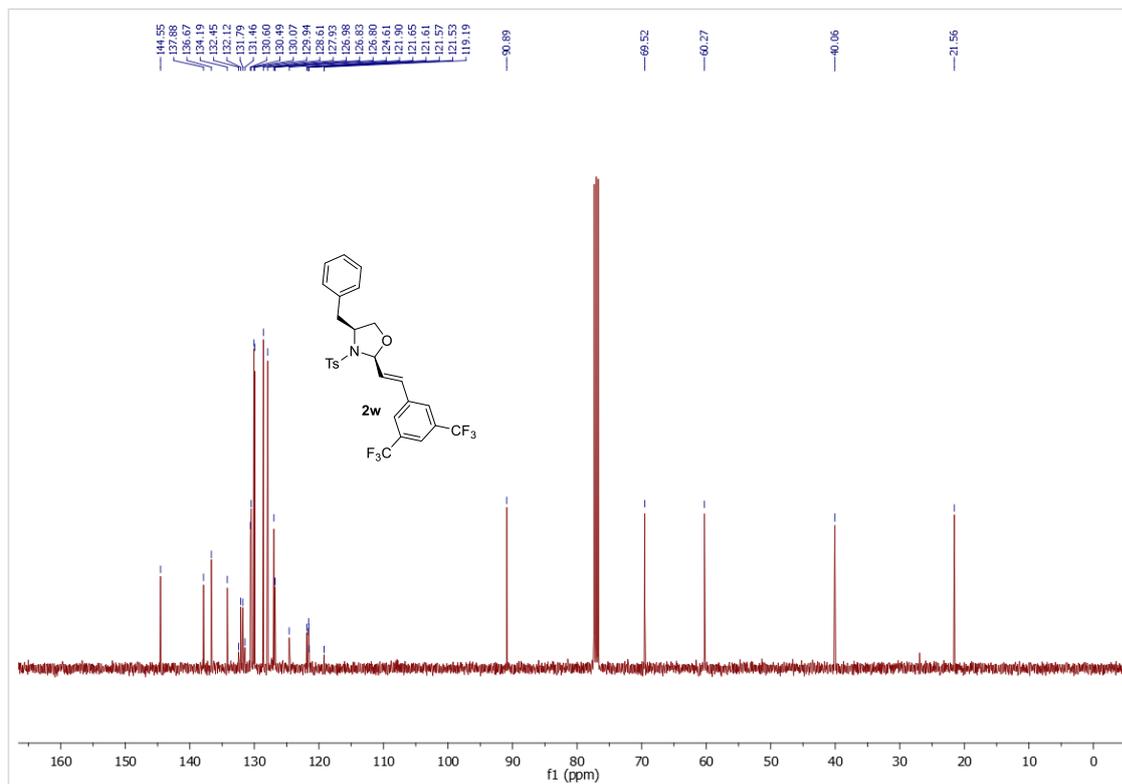
$^{19}\text{F}\{^1\text{H}\}$ NMR of **2u** (400 MHz, CDCl_3)



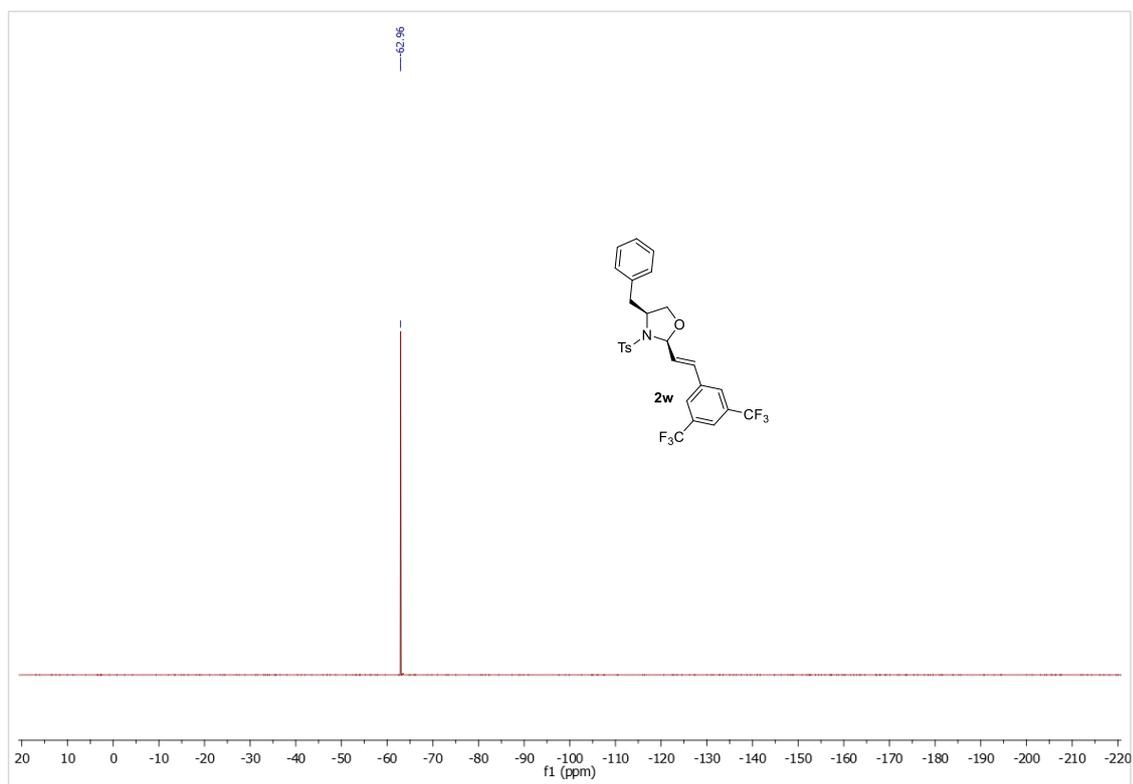
^1H NMR of **2w** (400 MHz, CDCl_3)



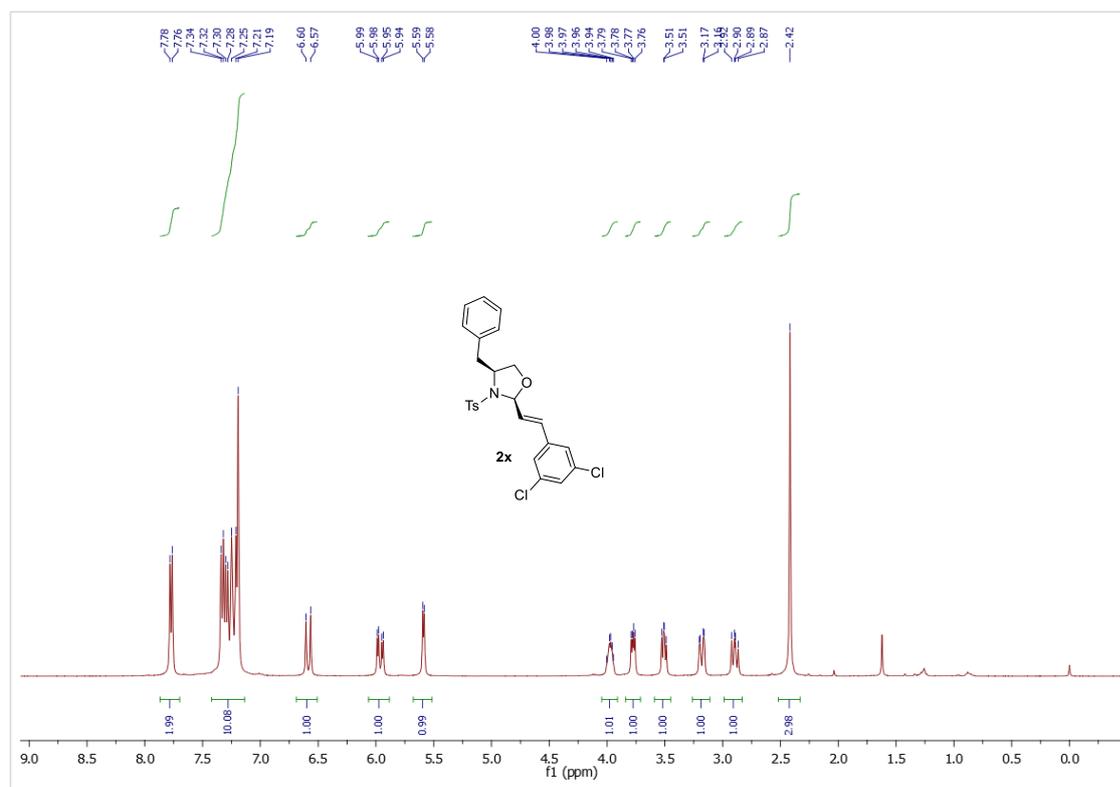
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2w** (101 MHz, CDCl_3)



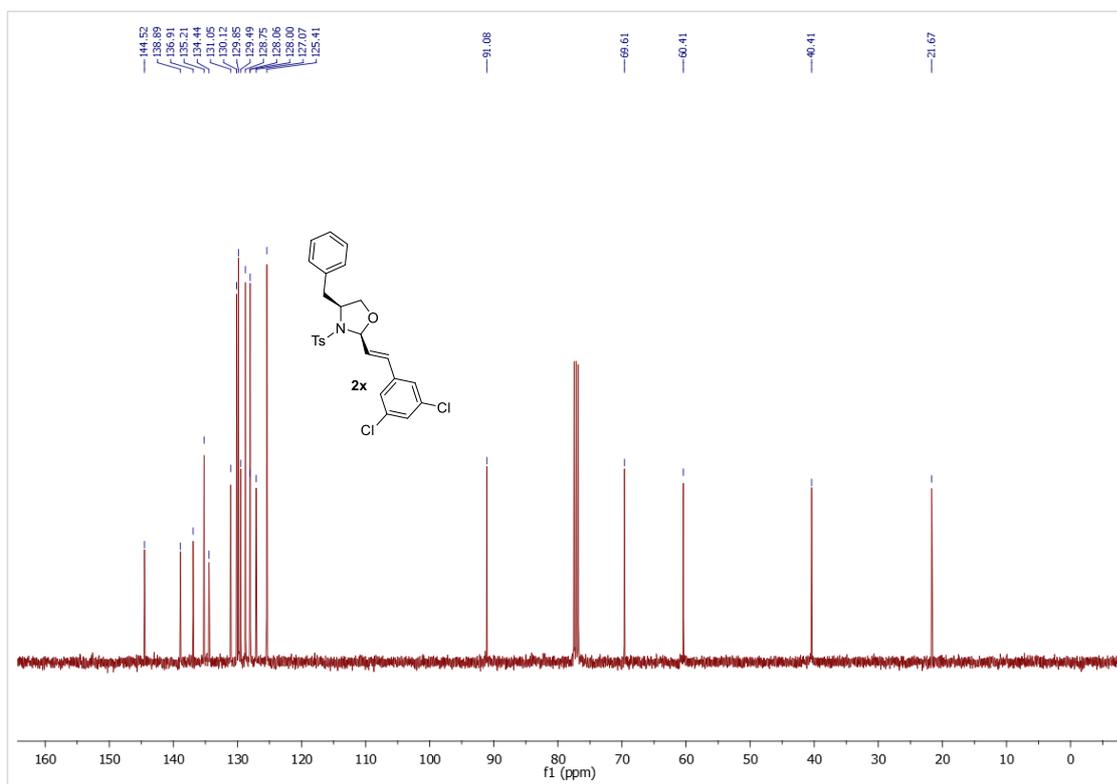
$^{19}\text{F}\{^1\text{H}\}$ NMR of **2w** (400 MHz, CDCl_3)



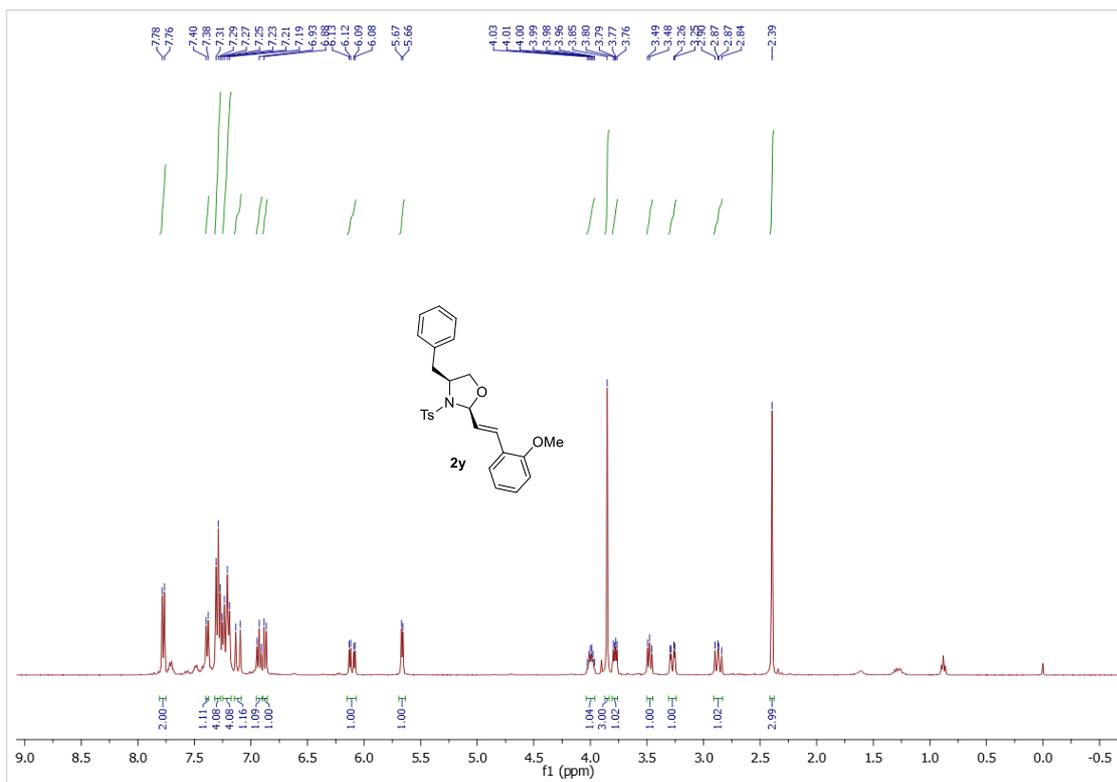
^1H NMR of **2x** (400 MHz, CDCl_3)



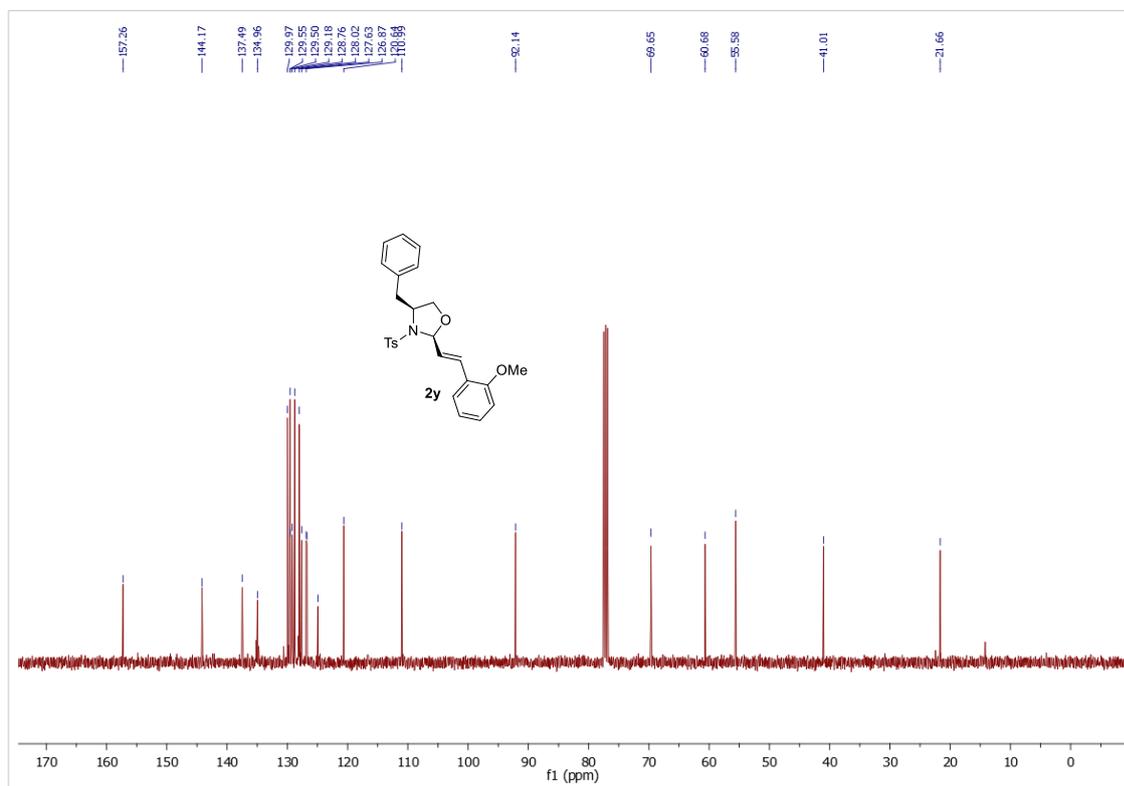
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2x** (101 MHz, CDCl_3)



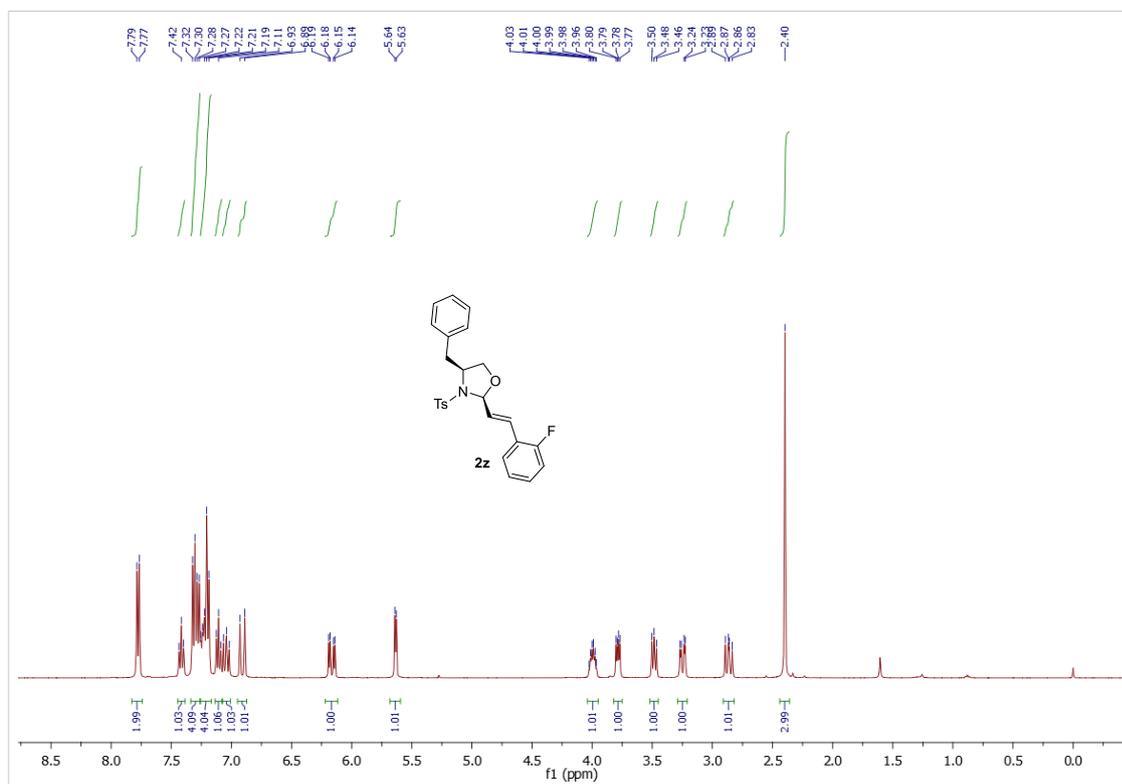
^1H NMR of **2y** (400 MHz, CDCl_3)



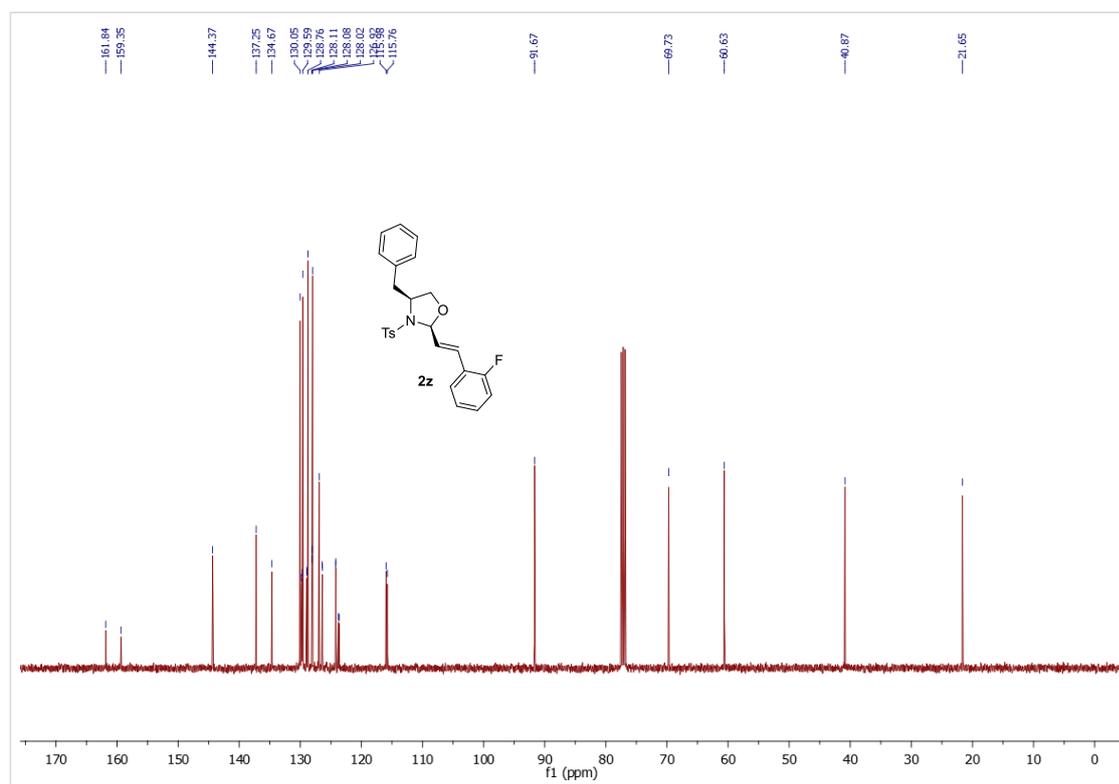
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2y** (101 MHz, CDCl_3)



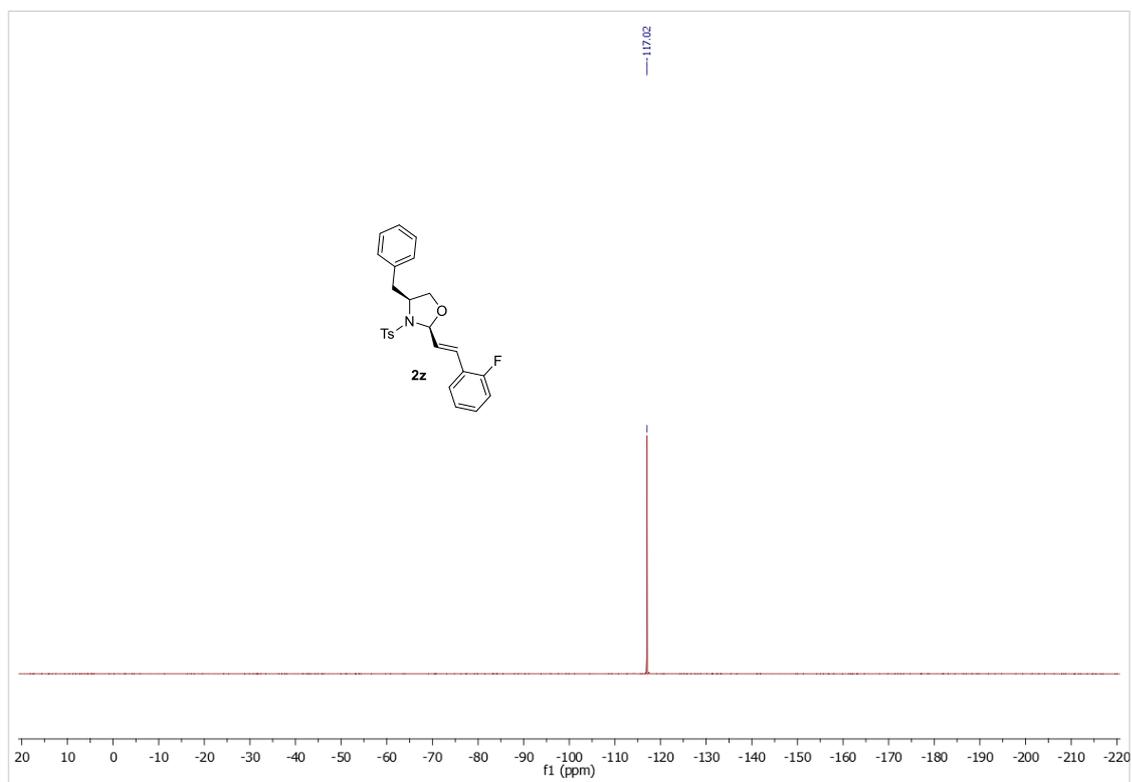
^1H NMR of **2z** (400 MHz, CDCl_3)



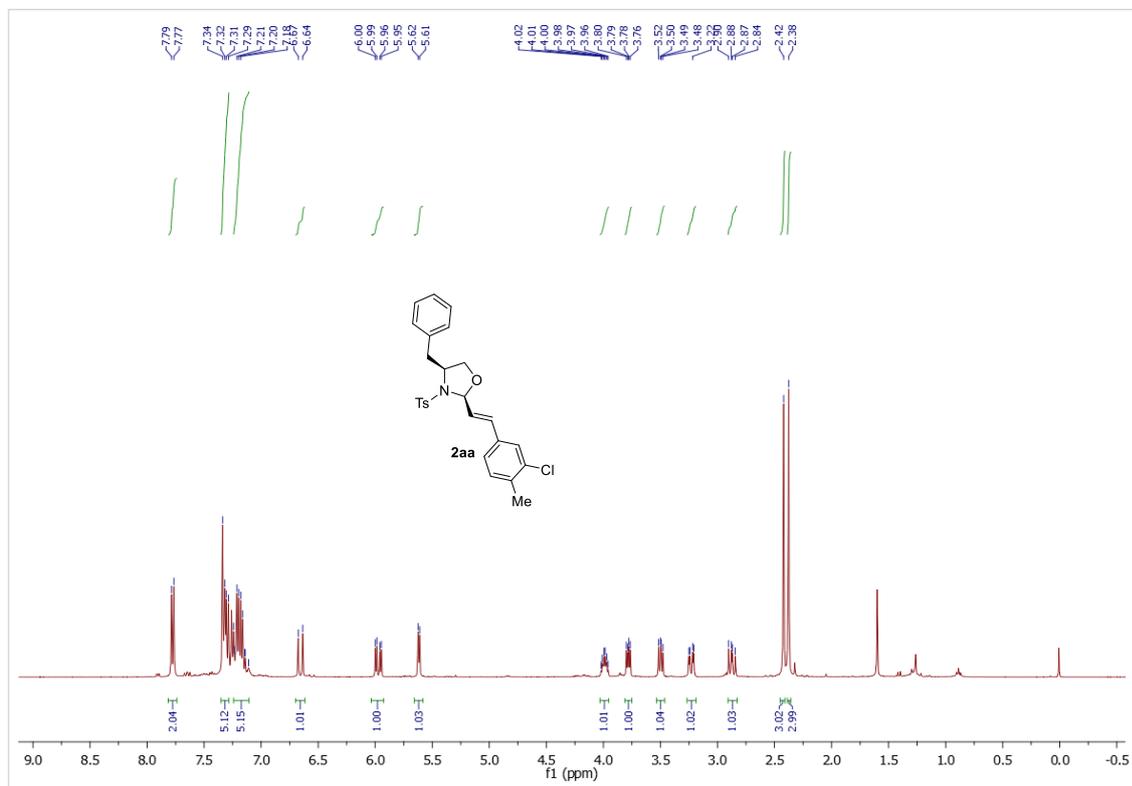
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2z** (101 MHz, CDCl_3)



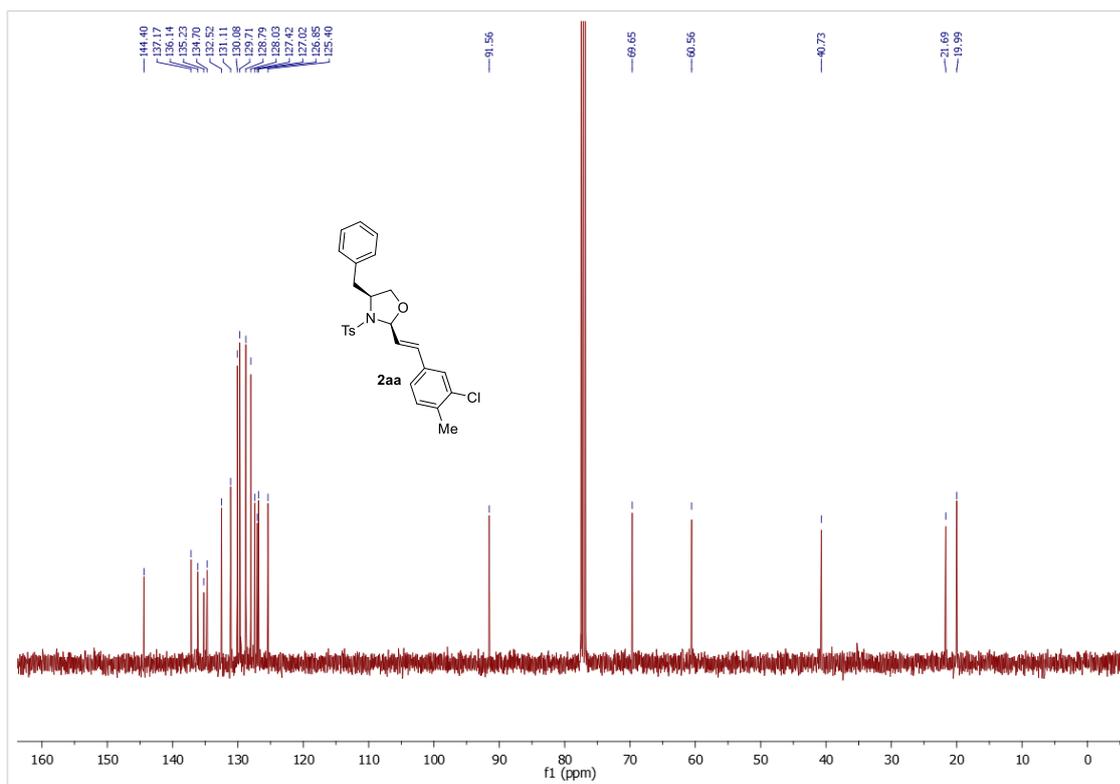
$^{19}\text{F}\{^1\text{H}\}$ NMR of **2z** (400 MHz, CDCl_3)



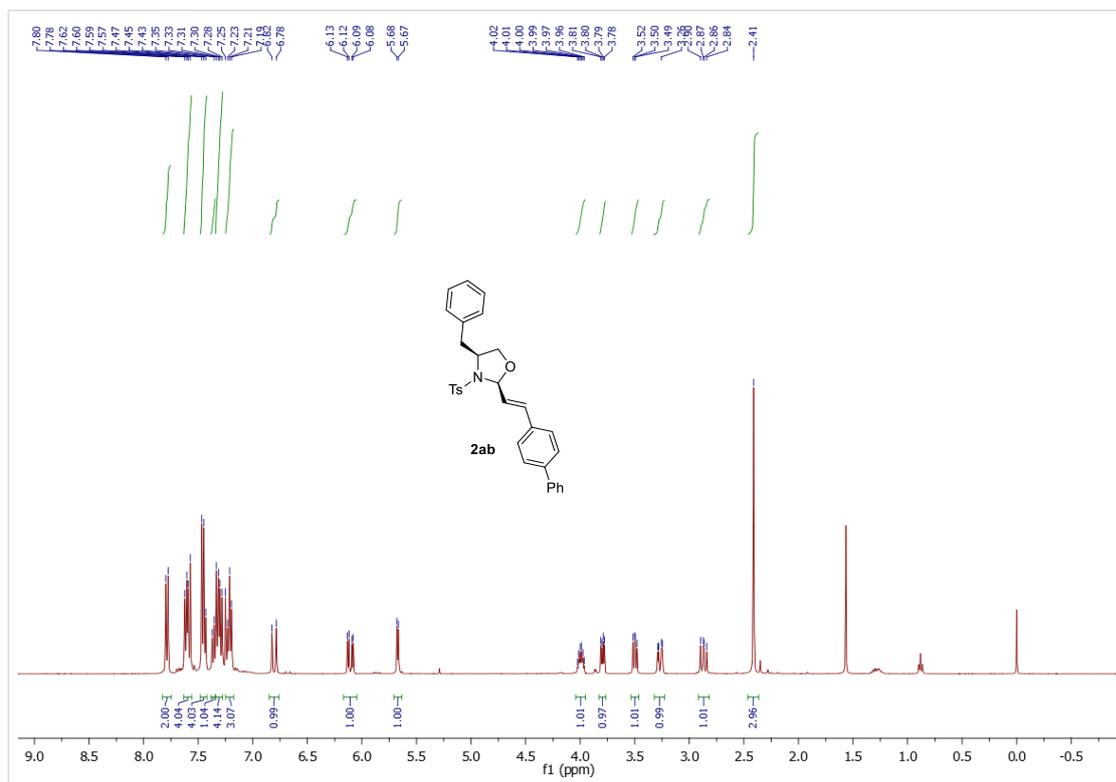
^1H NMR of **2aa** (400 MHz, CDCl_3)



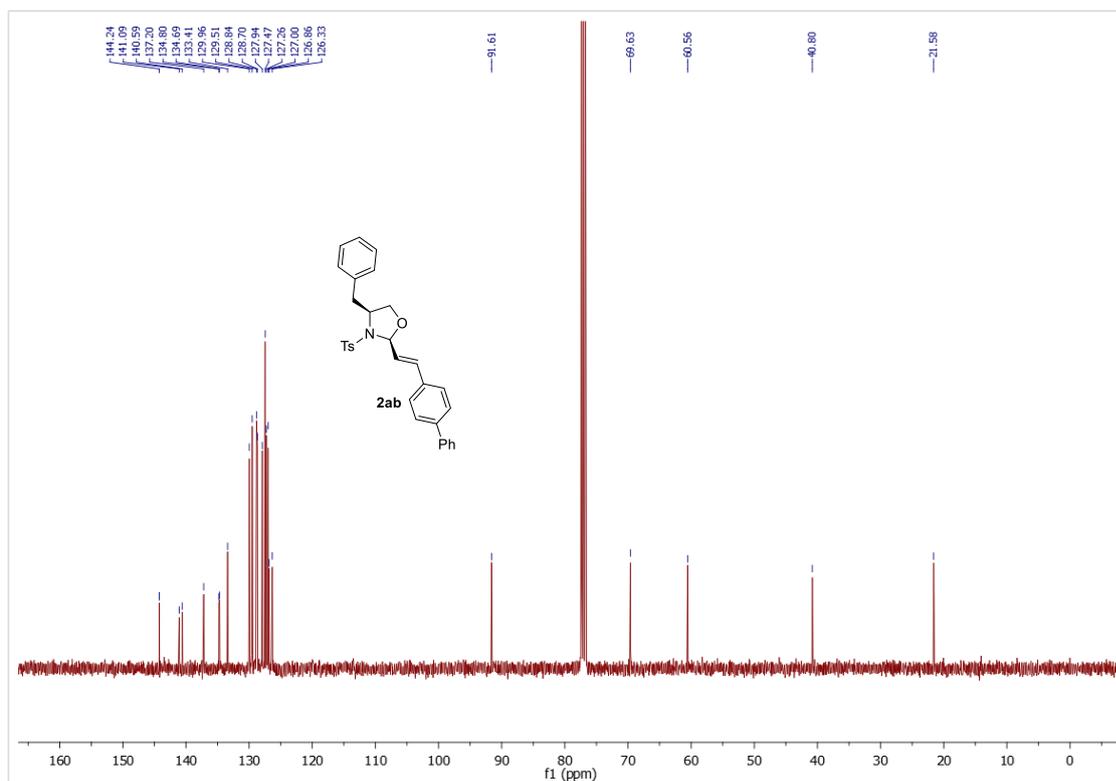
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2aa** (101 MHz, CDCl_3)



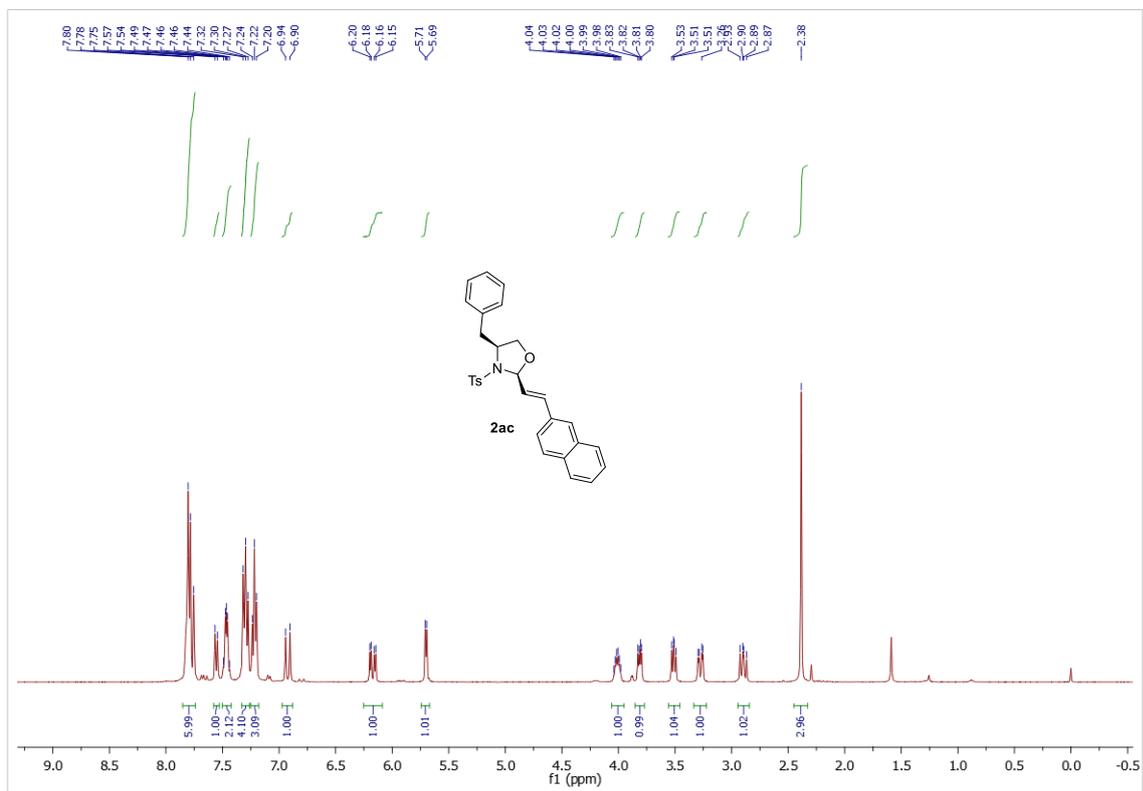
^1H NMR of **2ab** (400 MHz, CDCl_3)



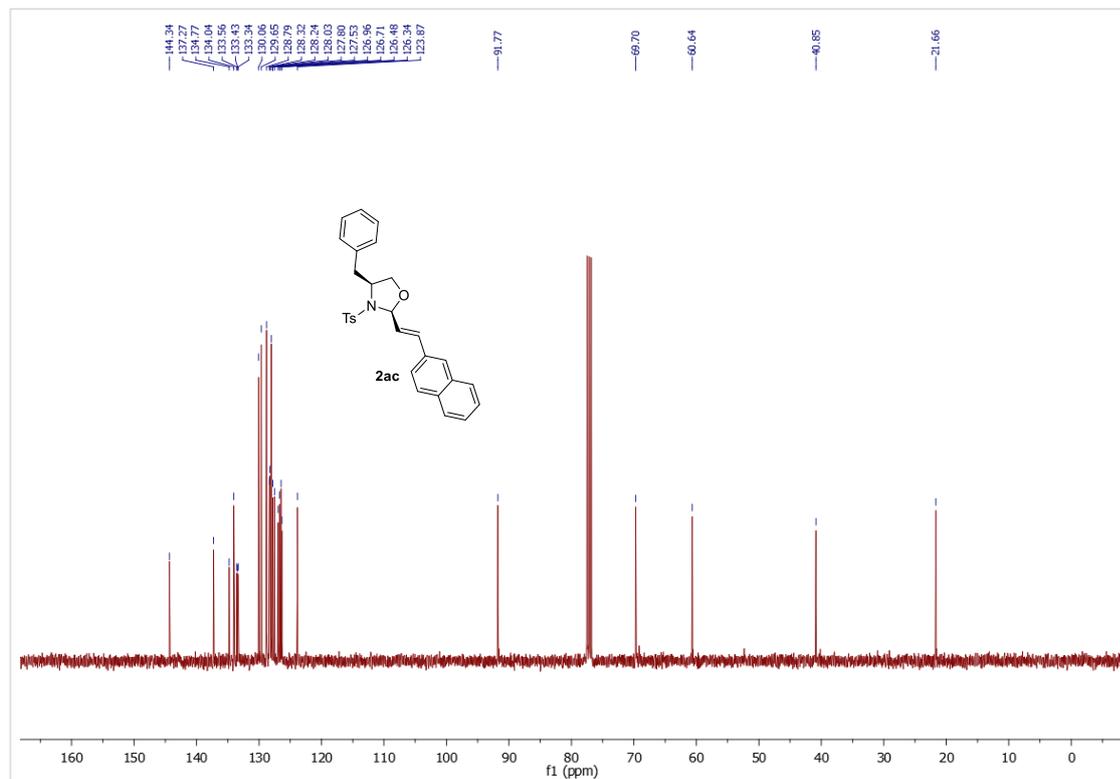
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2ab** (101 MHz, CDCl_3)



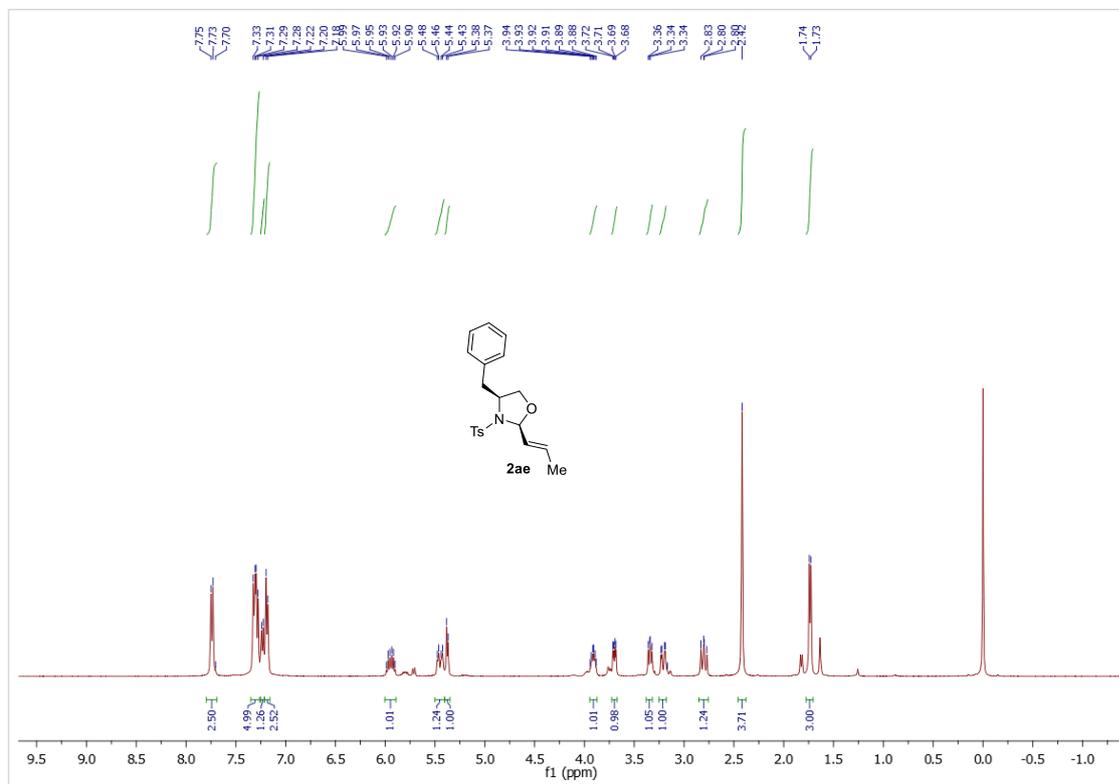
^1H NMR of **2ac** (400 MHz, CDCl_3)



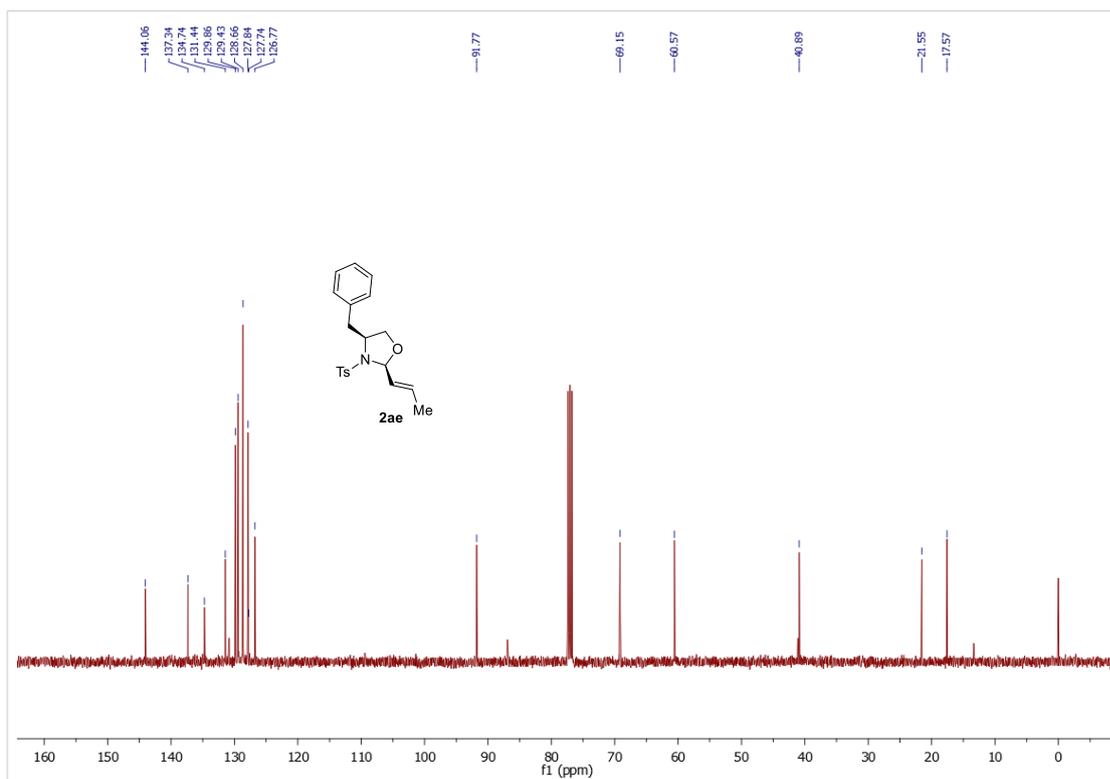
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2ac** (101 MHz, CDCl_3)



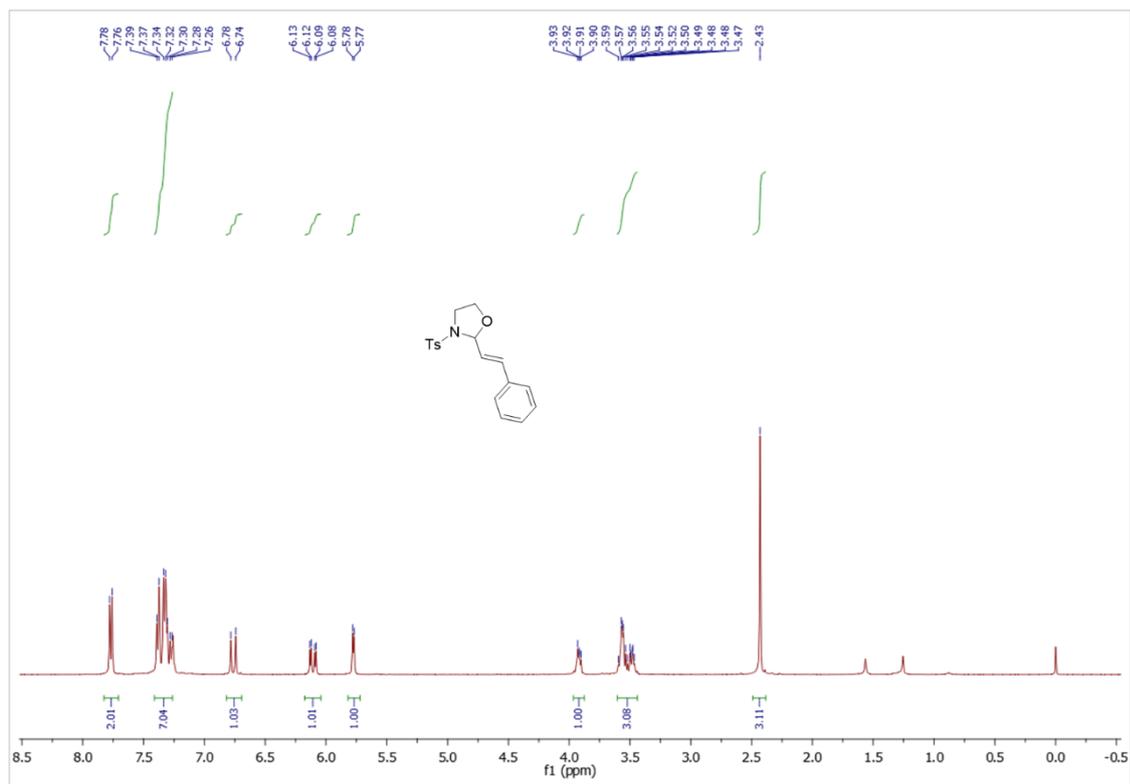
^1H NMR of **2ae** (400 MHz, CDCl_3)



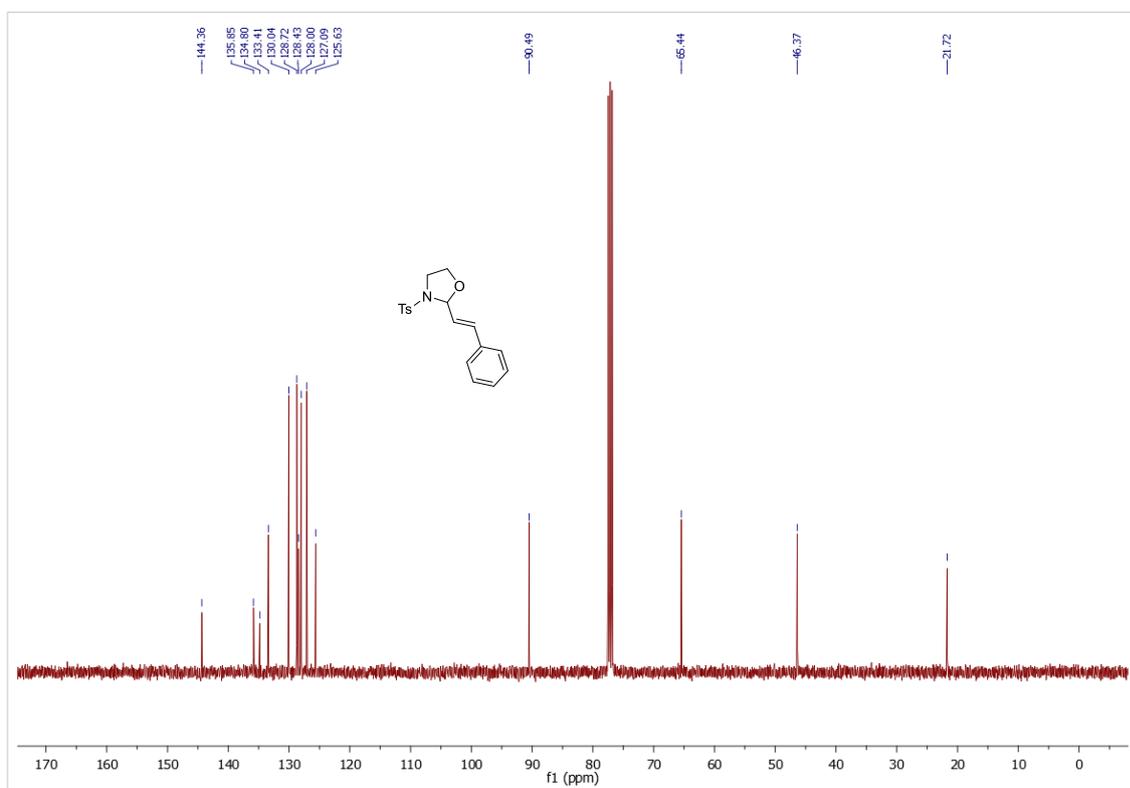
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2ae** (101 MHz, CDCl_3)



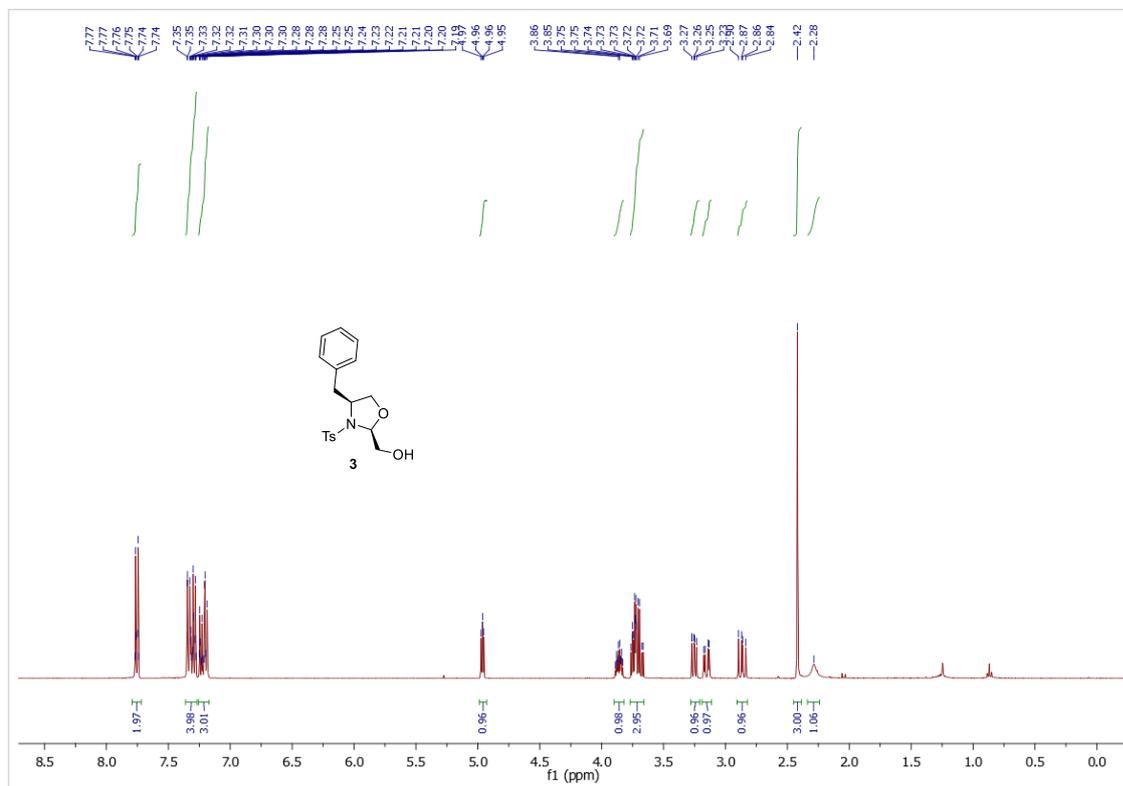
^1H NMR of **2'** (400 MHz, CDCl_3)



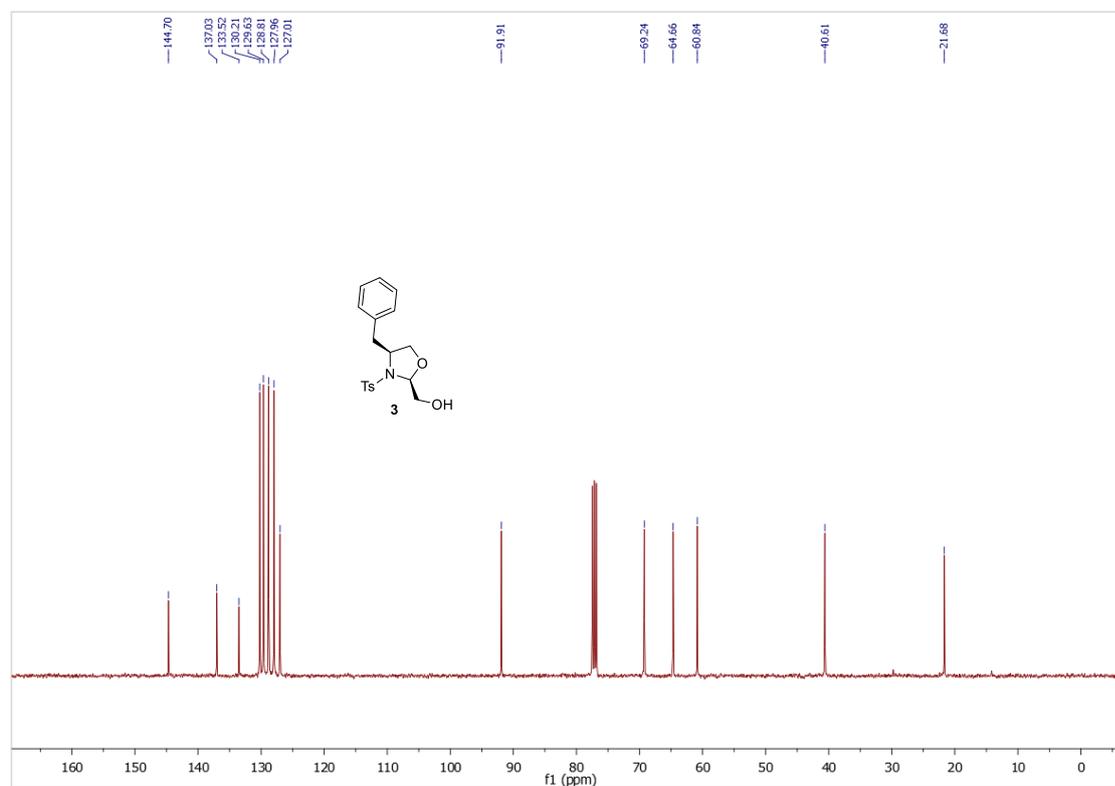
$^{13}\text{C}\{^1\text{H}\}$ NMR of **2'** (101 MHz, CDCl_3)



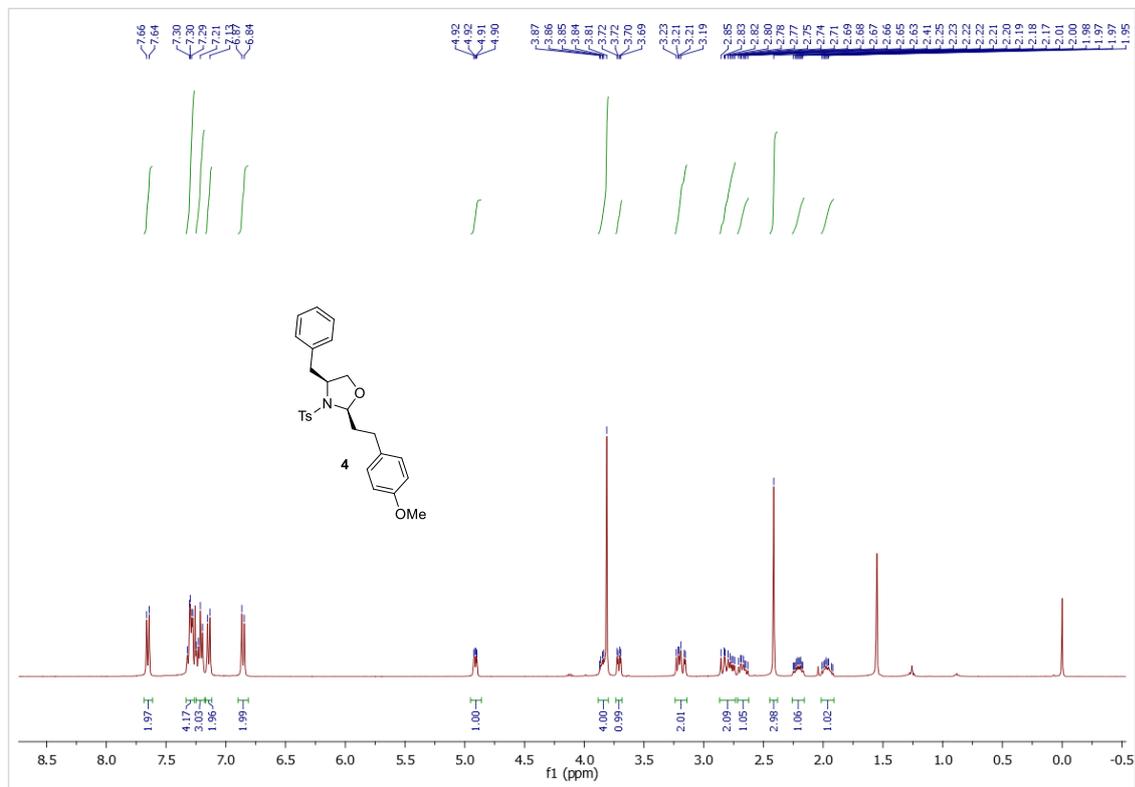
^1H NMR of **3** (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR of **3** (101 MHz, CDCl_3)



^1H NMR of **4** (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR of **4** (101 MHz, CDCl_3)

