Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2022

----Electronic Supplementary Information----

Enantioselective C–H bond functionalization of aromatic ketones with 1,6-enynes via photoredox/cobalt dual catalysis

Kakoli Maji‡, Pradip Ramdas Thorve‡, Pramod Rai and Biplab Maji*

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India

E-mail: bm@iiserkol.ac.in

Table of contents

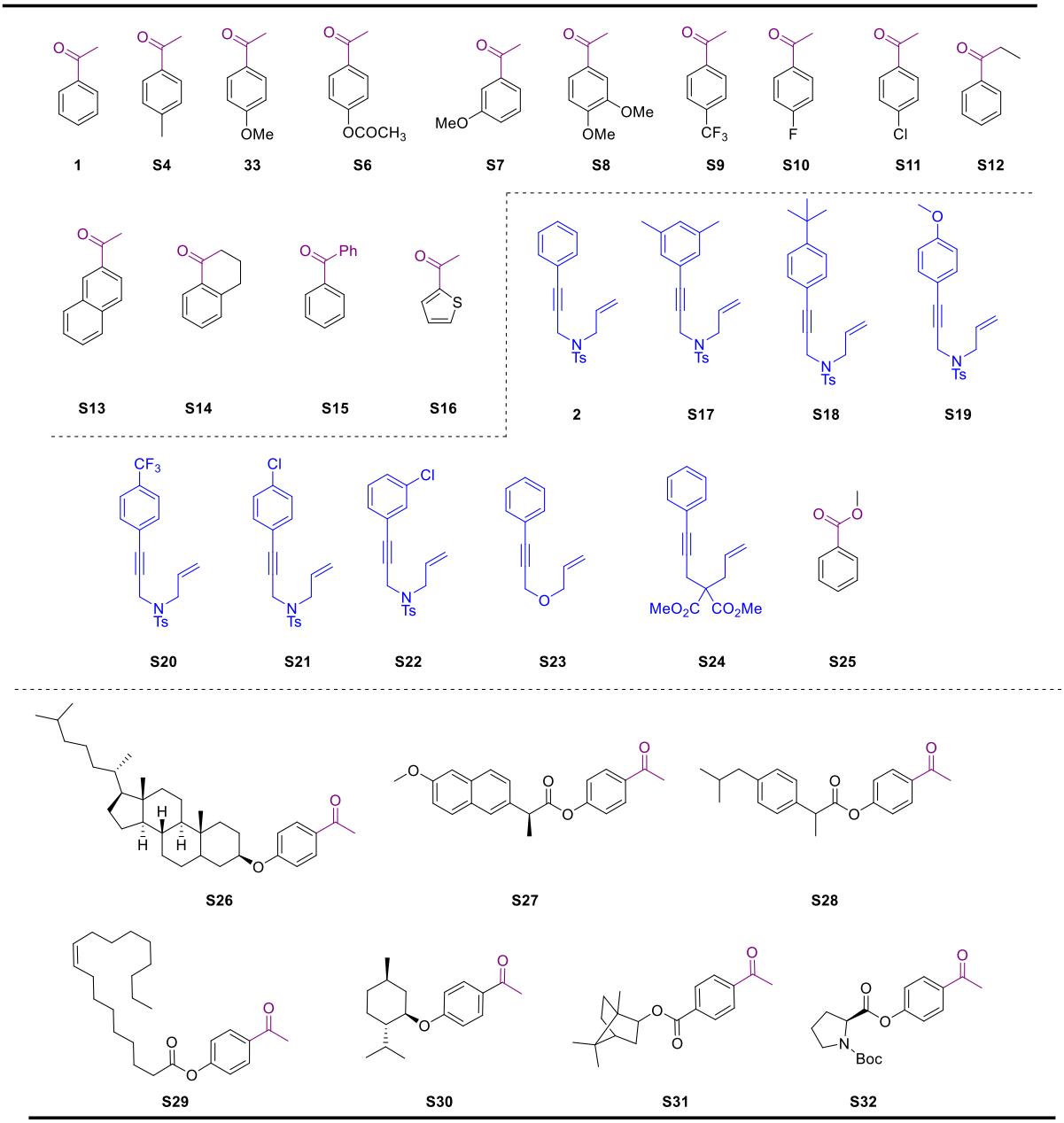
1. General information

All the reactions were performed in oven-dried glassware under an argon or nitrogen atmosphere using standard Schlenk techniques. Reaction temperatures are reported as the bath temperature surrounding the vessel unless otherwise stated. Non-halogenated solvents were dried over calcium hydride. All the solvents were degassed with argon and stored over activated molecular sieves (4 Å).

Analytics: ^{1}H, ^{13}C and ^{19}F NMR spectra has been recorded on Bruker (^{1}H: 500 MHz, ^{13}C $\{^{1}H\}$: 126 MHz, ^{19}F $\{^{1}H\}$: 470 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C $\{^{1}H\}$: 101 MHz, ^{19}F $\{^{1}H\}$: 376 MHz) and were referenced to the resonances of the solvent used. Multiplicities have been indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). FT-IR spectra were recorded by Perkin–Elmer FT–IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. HPLC was recorded on Waters HPLC with Photodiode Array Detector. Optical rotations were recorded using a 100 mm cell on Anton Paar Polarimeter (MCP 100) and are reported as follows: $[\alpha]_D^{RT}$ (c in mg per 1 mL solvent). For thin-layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used, and visualization was accomplished by UV light (254 nm), I_2, $KMnO_4$, and cerium molybdate.

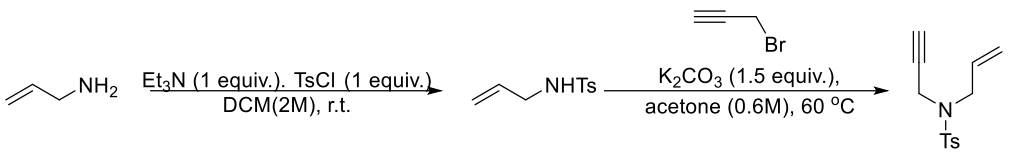
Chemicals. Commercially available chemicals were bought from Sigma–Aldrich, Alfa–Aesar, Avra Synthesis, BLD Pharma, and used without further purification. Dry solvents were prepared according to the standard procedure and degassed by freeze–pump–thaw cycles prior to use. No attempts were made to optimize yields for substrate, catalyst, and ligand.

2. Numbering of starting materials.



3. Synthesis of the starting materials

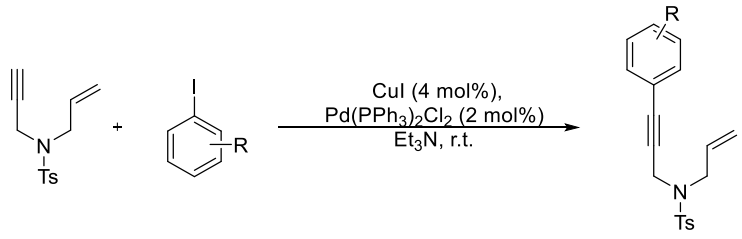
3.1. General procedure for preparation of internal alkynes:



99%

Allyl amine (1.1 equiv.) was dissolved in DCM (2 M). Et_3N (1 equiv.) was added to the solution and was cooled to 0 °C. *p*-Toluenesulfonyl chloride (1 equiv.) was added portion-wise at 0 °C. Then the reaction was stirred at room temperature until the complete conversion, checked by TLC. The reaction was quenched with $NaHCO_3$ and diluted with DCM. The aqueous layer was extracted with DCM three times. The organic layer was washed twice with water, dried over Na_2SO_4, filtered, and concentrated. The *N*-allyl-*p*-toluenesulfonamides were subjected to the next step with no further purification.

To a solution of *N*-allyl-*p*-toluenesulfonamides in acetone (0.6 M), K_2CO_3 (1.5 equiv.) was added. After that, propargyl bromide (1.5 equiv.) was added dropwise. The solution was stirred at rt to 60 °C until no starting material was observed on TLC. The reaction was filtered over a silica gel pad using ethyl acetate. The filtrate was concentrated in vacuo and columned in 5% EtOAc/hexanes to yield the *N*-allyl-4-methyl-*N*-(propargyl)benzenesulfonamide as a white solid.

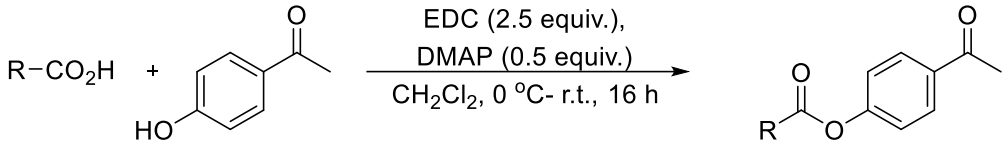


S17-S22

In a flame dried flask $PdCl_2(PPh_3)_2$ (2 mol %), and copper iodide (4 mol %) in Et_3N (2 mL/mmol) is taken. In the reaction mixture, **S2** and aryl iodide (1.2 equiv.) were added and stirred at room temperature to 60 °C until no starting material was observed on TLC, typically 24 hours. The reaction was quenched with saturated NH_4Cl, and diluted with EtOAc. The aqueous layer was extracted, washed, dried over Na_2SO_4, filtered, and concentrated. The 1,6-enynes were purified by flash chromatography, typically in 5-10% EtOAc/hexane.

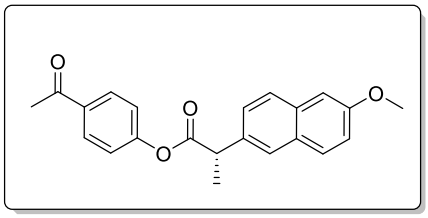
The characterization data are consistent with the literature values **2,**[1] **S17,**[2] **S18,**[3] **S19,**[1] **S21**,[2] **S20**,[2] **S22**,[3] **S23[1].**

3.2 General procedure for the preparation of substrates S27, S28, S29, S31, S32



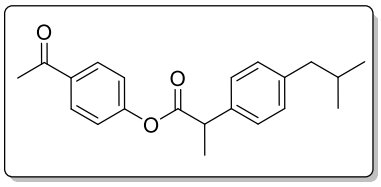
EDC (2.5 equiv.) and DMAP (0.5 equiv.) were added sequentially to an ice-cold solution of the 4'-hydroxy acetophenone (1.0 equiv.) and corresponding acid (2.5 equiv.) in CH_2Cl_2 (0.1 M). After 30 min, the ice-water cooling bath was removed, and the resulting suspension was stirred vigorously at room temperature for 16 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane/EtOAc) afforded the desired esters.

4-acetylphenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (S27):



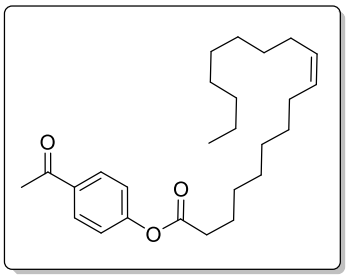
Purified by silica gel chromatography (R_f = 0.70, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield= 575 mg (55%, 1.65 mmol).^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.78 – 7.71 (m, 3H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.09 – 7.03 (m, 2H), 4.14 – 4.08 (m, 1H), 3.91 (s, 3H), 2.55 (s, 3H), 1.69 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.0, 172.8, 158.0, 154.7, 134.9, 134.0, 130.0, 129.5, 129.1, 127.6, 126.3, 126.1, 121.8, 119.4, 105.7, 77.5, 77.2, 76.8, 55.5, 45.7, 26.7, 18.6.

4-acetylphenyl 2-(4-isobutylphenyl)propanoate (S28):



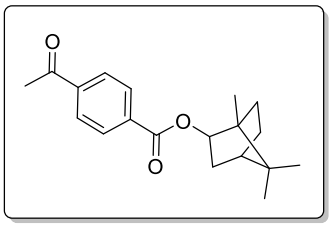
Purified by silica gel chromatography (R_f = 0.70, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield= 645 mg (66%, 1.99 mmol).^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.05 (m, 2H), 3.94 (q, *J* = 7.1 Hz, 1H), 2.56 (s, 3H), 2.46 (d, *J* = 7.1 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.61 (s, 3H), 0.90 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.00, 172.84, 154.74, 141.17, 136.99, 134.78, 129.99, 129.74, 127.33, 127.03, 121.77, 77.48, 77.16, 76.84, 45.44, 45.18, 30.33, 26.72, 22.52, 18.58.

4-acetylphenyl oleate (S29):



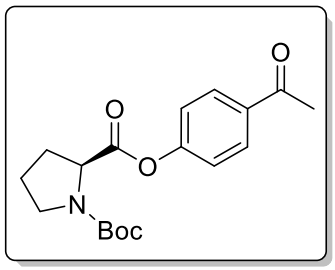
Purified by silica gel chromatography (R_f = 0.60, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield = 913 mg (76%, 2.28 mmol).[1]H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 5.49 – 5.30 (m, 2H), 2.62 – 2.53 (m, 5H), 2.05 – 1.97 (m, 4H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.19 (m, 20H), 0.90 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.95, 171.82, 154.63, 134.77, 130.20, 130.05, 129.82, 121.90, 77.49, 77.17, 76.85, 34.51, 32.04, 29.90, 29.80, 29.66, 29.46, 29.27, 29.20, 27.36, 27.28, 27.04, 26.71, 24.96, 22.81, 14.24.

(2*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-acetylbenzoate (S31) :



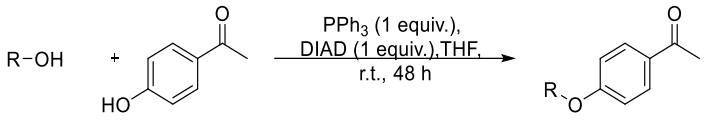
Purified by silica gel chromatography (R_f = 0.60, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield = 709 mg (79%, 2.36 mmol).[1]H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.5 Hz, 2H), 8.04 – 8.00 (m, 2H), 5.18 – 5.07 (m, 1H), 2.65 (s, 3H), 2.53 – 2.45 (m, 1H), 2.15 – 2.08 (m, 1H), 1.87–1.74 (m, 1H), 1.49 – 1.38 (m, 1H), 1.35 – 1.29 (m, 1H), 1.13 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 1.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.70, 166.09, 140.27, 134.81, 129.89, 128.35, 81.32, 77.41, 77.16, 76.91, 49.30, 48.09, 45.12, 37.03, 28.23, 27.54, 27.03, 19.86, 19.06, 13.77.

2-(4-acetylphenyl) 1-(tert-butyl) (S)-pyrrolidine-1,2-dicarboxylate (S32)[4]:



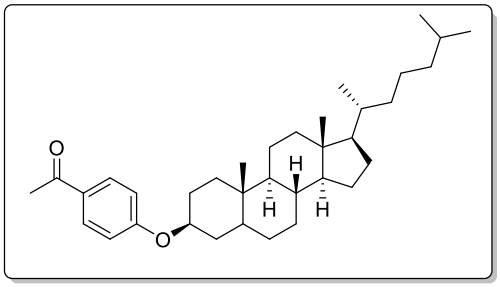
Purified by silica gel chromatography (R_f = 0.60, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield = 820 mg (82%, 2.46 mmol).[1]H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 12.8, 8.3 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 2H), 4.53 – 4.35 (m, 1H), 3.70 – 3.35 (m, 2H), 2.54 (d, *J* = 4.6 Hz, 3H), 2.42 – 2.23 (m, 1H), 2.18 – 2.07 (m, 1H), 2.04 – 1.83 (m, 2H), 1.42 (d, *J* = 8.8 Hz, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.9, 196.7, 171.1, 154.5, 154.2, 153.6, 134.8, 134.7, 130.0, 129.9, 121.7, 121.3, 80.3, 80.1, 77.5, 77.2, 76.8, 59.2, 59.1, 46.6, 46.4, 31.0, 29.9, 28.4, 26.6, 24.5, 23.7.

3.3 General procedure for the preparation of substrates S26 and S30



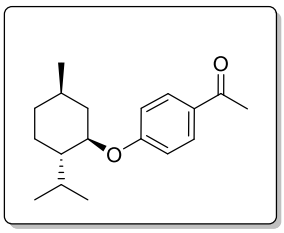
PPh_3 (1 equiv.) and DIAD (1 equiv.) were added sequentially to a solution of the 4'-hydroxy acetophenone (1.0 equiv.) and corresponding alcohol (1 equiv.) in THF (0.1 M). The resulting suspension was stirred vigorously at room temperature for 48 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (*n*-hexane/EtOAc) afforded the desired ethers.

1-(4-(((*3S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)phenyl)ethan-1-one (S26):



Purified by silica gel chromatography (R_f = 0.60, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield= 516 mg (51%, 1.02 mmol).[1]H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 9.0 Hz, 2H), 6.94 – 6.89 (m, 2H), 4.63 (m, 4.64 – 4.62, 1H), 2.54 (s, 3H), 2.01 – 1.75 (m, 3H), 1.74 – 1.45 (m, 10H), 1.41 – 1.26 (m, 6H), 1.25 – 1.05 (m, 9H), 1.04 – 0.95 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.4, 2.2 Hz, 6H), 0.83 (s, 3H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.9, 162.1, 130.8, 129.9, 115.4, 77.5, 77.2, 76.9, 72.6, 56.7, 56.5, 54.3, 42.8, 40.2, 39.8, 39.7, 36.3, 36.0, 35.6, 32.8, 32.1, 28.6, 28.4, 28.2, 26.5, 25.8, 24.3, 24.0, 23.0, 22.7, 21.0, 18.8, 12.2, 11.6.

1-(4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-one (S30):



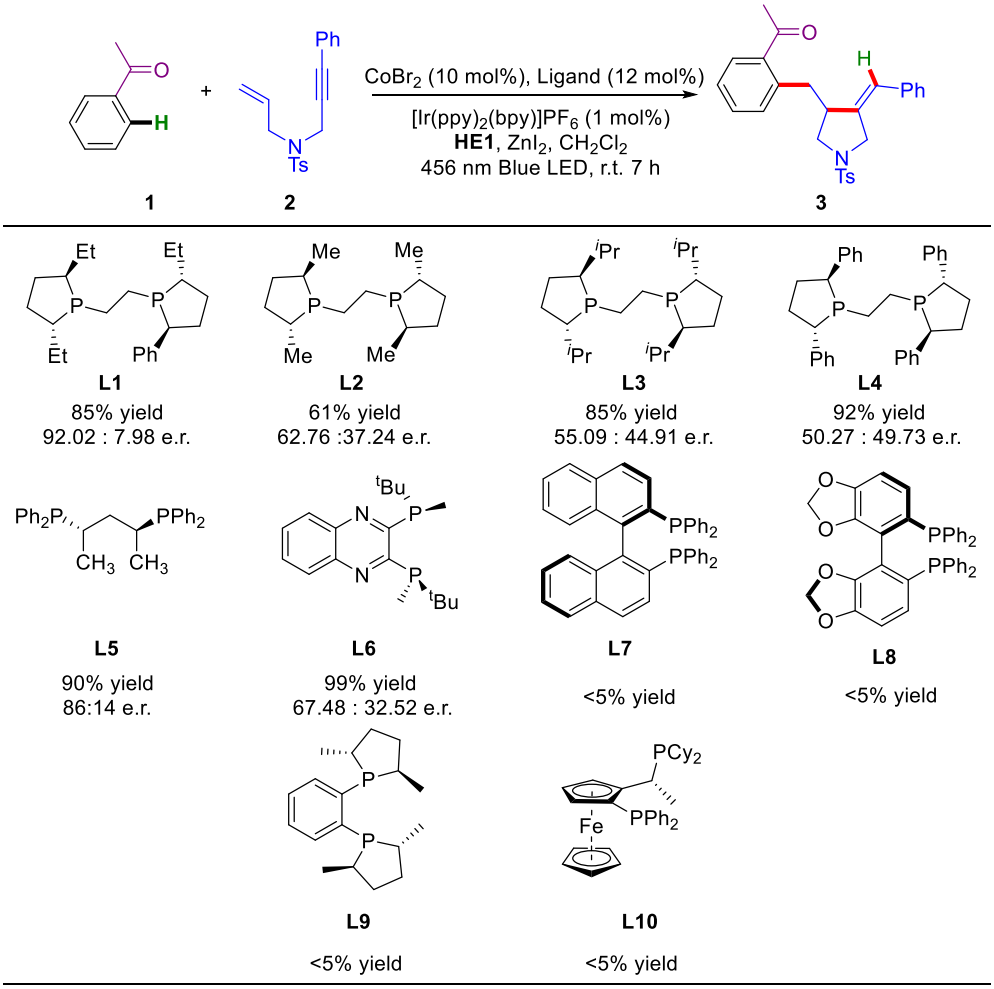
Purified by silica gel chromatography (R_f = 0.60, Eluent: Ethyl acetate/ Hexane in 5% mixture) Isolated yield= 130 mg (24%, 0.480 mmol).[1]H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.85 (m, 2H), 6.95 – 6.88 (m, 2H), 4.73 (q, *J* = 2.8 Hz, 1H), 2.54 (s, 3H), 2.11 – 2.04 (m, 1H), 1.81 – 1.74 (m, 2H), 1.71 – 1.51 (m, 4H), 1.09 – 0.99 (m, 2H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.83 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.9, 162.6, 130.8, 129.9, 115.0, 77.5, 77.2, 76.8, 73.8, 47.8, 37.7, 35.0, 29.4, 26.4, 26.3, 24.9, 22.4, 21.1, 20.9.

4. Detailed optimization for the enantioselective C–H bond functionalization reaction.

4.1.General procedure

In a 10 mL reaction tube, $CoBr_2$ (2.2 mg, 0.010 mmol) and **L2** (4.4 mg, 0.012 mmol) were taken inside a nitrogen-filled glove box. The mixture is stirred at r.t. for 1 h. Then **PC** (0.8 mg, 0.001 mmol), **HE** (6.2 mg, 0.02 mmol), ZnI_2 (6.4 mg, 0.02 mmol), **1** (14.4 mg, 0.12 mmol), and **2** (32.5 mg, 0.1 mmol) were added and the tube was closed and placed under blue LED irradiation at 456 nm. Upon completion, the reaction was quenched with water (2 mL), and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent. The enantiomeric ratio e.r. were determined by chiral HPLC chromatography using a Daicel Chiralpak IA-3 column (250 × 4.6 mm).

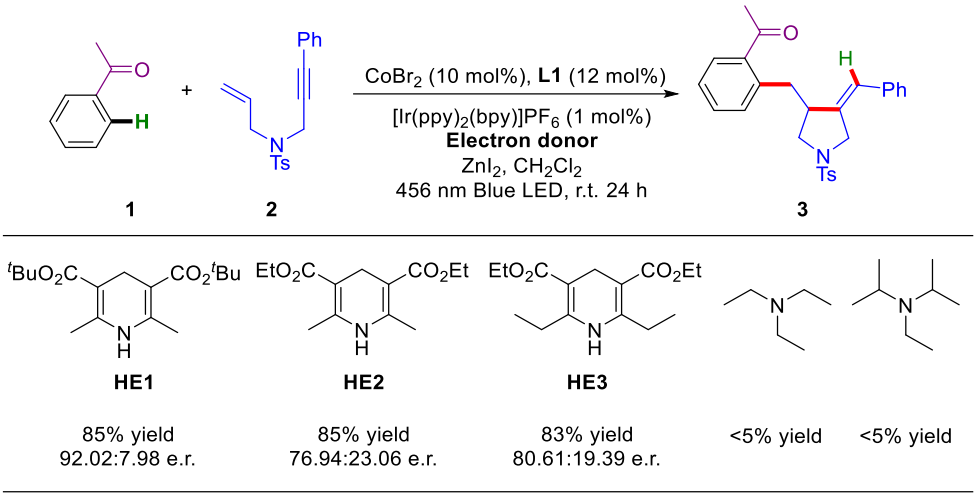
Table S1: Optimization of chiral ligands:



Reaction Conditions: **1** (0.12 mmol), **2** (0.1 mmol), $[Ir(ppy)_2bpy]PF_6$ (1 mol%), $CoBr_2$ (10 mol%), Ligand (12 mol%), Hantzsch ester **HE1** (20 mol%), ZnI_2 (20 mol%), 456 nm Blue LED

in CH_2Cl_2 (0.2 M) at room temperature under Ar. Isolated yield. Enantiomeric ratio e.r. determined by Chiral HPLC using a Daicel Chiralpak IA-3 column (250 × 4.6 mm).

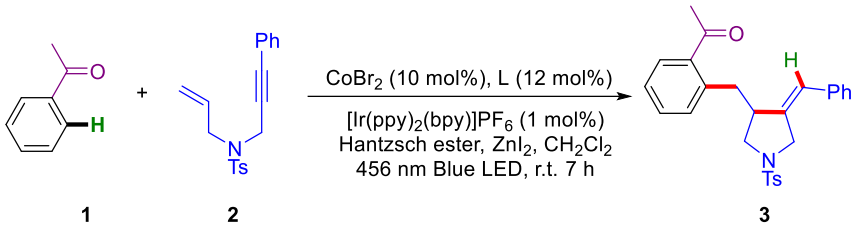
Table S2: Optimization of electron donor:



HE1	HE2	HE3		
85% yield 92.02:7.98 e.r.	85% yield 76.94:23.06 e.r.	83% yield 80.61:19.39 e.r.	<5% yield	<5% yield

Reaction Conditions: **1** (0.12 mmol), **2** (0.1 mmol), $[Ir(ppy)_2bpy]PF_6$ (1 mol%), $CoBr_2$ (10 mol%), Ligand (12 mol%), electron donor (20 mol%), ZnI_2 (20 mol%), 456 nm Blue LED in CH_2Cl_2 (0.2 M) at room temperature under Ar. Isolated yield. Eanantiomeric ration e.r. determined by Chiral HPLC using a Daicel Chiralpak IA-3 column (250 × 4.6 mm).

Table S3: Control experiments:



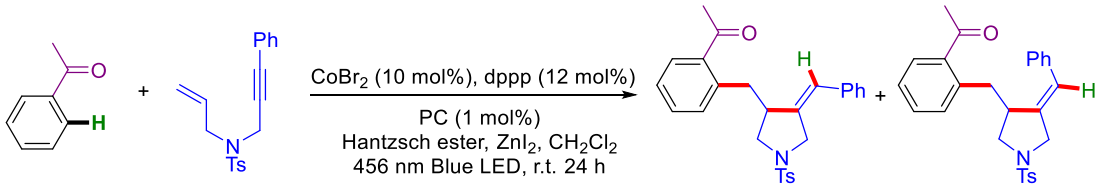
Entry	Deviation from above	Yield (%)
1	No $[Ir(ppy)_2(bpy)]PF_6$	5
2	No Hantzsch ester	11
3	No $CoBr_2$/L	<5
4	no light at 100 °C	<5
5	No ZnI_2	<5

Reaction Conditions: **1** (0.12 mmol), **2** (0.1 mmol), **PC** (1 mol%), $CoBr_2$ (10 mol%), **L** (12 mol%), **HE2** (0.2 mmol), ZnI_2 (20 mol%), Blue LED in CH_2Cl_2 (0.2 M) at room temperature under Ar. Isolated yields.

Table S4: Effect of photocatalyst:[5]

The effect of photocatalyst on the reaction outcome was checked. All the photocatalysts sufficiently reducing to reduce Co(II) ($E_{1/2}[Co^{II}/Co^{I}]$= −0.76 V vs SCE in MeCN for (dppbz)$CoBr_2$) gave moderate to a good yield of the product. However, an *E*/*Z* mixture of the exocyclic double bond in the product was observed. We reasoned triplet energy transfer (EnT) mediated post-reaction isomerization. Indeed, we observed a 50:50 mixture of **3**:**3'** with [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 having substantially higher triplet energy (E_T = 60.1 kcal mol^{-1}). In this regard, best result in terms of reactivity and E/Z selectivity was observed with [Ir(ppy)$_2$(bpy)]PF_6 as the photocatalyst.

To validate that the isomerization is occurring off-catalytic cycle via a triplet−triplet energy transfer, the isolated product **3** exclusively with *Z* isomer only was treated under standard reaction conditions with [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 as the photocatalyst for 24 h. As expected, the *Z*/*E* ratio was changed from >99:1 to 50:50, indicating that the isomerization occurs after the C−C bond formation.



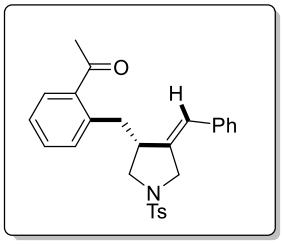
1 **2** **3** **3'**

Entry	Photocatalyst	$E_{1/2}$ ($PC^{\bullet-}$/PC) vs SCE	E_T (kcal mol^{-1})	Yield (%)	3aa/3aa'[b]
1	[Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6	-1.37	60.1	72	50:50
2	Ir(ppy)$_3$	-2.19	55.2	90	77:23
3	[Ir(ppy)$_2$(bpy)]PF_6	-1.44	53.1	99	87:13
4	[Ir(ppy)$_2$(dtbpy)]PF_6	-1.51	49.2	90	91:9
5[b]	[Ir(ppy)$_2$(bpy)]PF_6	-1.44	53.1	85	>99:1
6	4cZIPN	-1.21	53	69	91:9

Reaction Conditions: **1** (0.12 mmol), **2** (0.1 mmol), **PC** (1 mol%), $CoBr_2$ (10 mol%), dppp (12 mol%), **HE2** (0.1 mmol), ZnI_2 (20 mol%), 456 nm Blue LED in CH_2Cl_2 (0.2 M) at room temperature under Ar. Isolated yields. [a]Determined by ^{1}H NMR analysis. [b]7 h instead of 24 h. $E_{1/2}$ and E_T from ref. 7.

5. **Product characterization**.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (3):

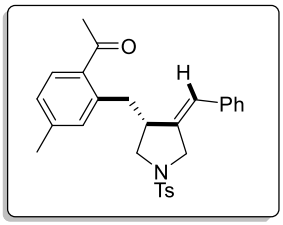


Purified by silica gel chromatography (R_f = 0.45, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield= 37.8 mg (85%, 0.085 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.43 (td, *J* = 7.4, 1.6 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.25 – 7.18 (m, 2H), 7.15 – 7.09 (m, 2H), 6.27 (q, *J* = 2.4 Hz, 1H), 4.33 – 4.28 (m, 1H), 4.02 (dd, *J* = 14.9, 2.5 Hz, 1H), 3.38 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.19 (dd, *J* = 9.0, 4.1 Hz, 1H), 3.14 – 3.10 (m, 1H), 3.04 (dd, *J* = 8.9, 6.3 Hz, 1H), 2.83 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.59 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.5, 143.7, 140.0, 137.1, 136.7, 132.9, 132.7, 132.0, 130.4, 129.8, 128.6, 128.4, 128.2, 127.9, 127.0, 126.8, 123.7, 77.5, 77.13, 76.8, 51.6, 50.8, 46.3, 38.4, 29.8, 29.7, 21.6.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +3.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 92:8, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.05 min, t_r (minor) = 20.37 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-methylphenyl)ethan-1-one (4):

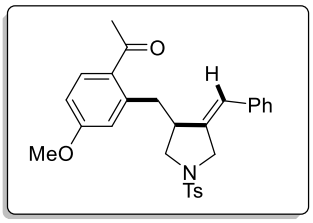


Purified by silica gel chromatography (R_f = 0.45, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 39 mg (85%, 0.085 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (dd, *J* = 8.1, 1.9 Hz, 3H), 7.37 – 7.28 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 6.8, 5.2 Hz, 3H), 7.00 (s, 1H), 6.30 (d, *J* = 2.2 Hz, 1H), 4.35 – 4.30 (m, 1H), 4.02 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.39 (dd, *J* = 12.7, 5.5 Hz, 1H), 3.18 (dd, *J* = 8.8, 4.1 Hz, 1H), 3.11 (p, *J* = 4.6 Hz, 1H), 3.03 (dd, *J* = 8.9, 6.4 Hz, 1H), 2.78 (dd, *J* = 12.5, 9.1 Hz, 1H), 2.57 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.8, 143.7, 142.8, 140.4, 140.2, 136.8, 134.1, 133.6, 133.0, 131.0, 129.8, 128.6, 128.2, 127.9, 127.4, 127.0, 123.7, 77.5, 77.2, 76.8, 51.5, 50.8, 46.2, 38.6, 29.5, 21.6, 21.6. **IR (ATR) ν** 1673 cm^{-1}, 1344 cm^{-1}, 1153 cm^{-1}, 663 cm^{-1}. **HRMS** calcd for $C_{16}H_{21}ClO_2Na$ $[M + Na]^+$ 303.1122, found 303.1138.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = –2.00°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 71:29, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 14.63 min, t_r (minor) = 12.27 min.

(*R, Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-methoxyphenyl)ethan-1-one (5):

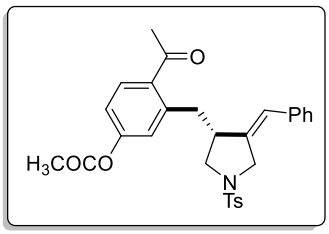


Purified by silica gel chromatography (R_f = 0.35, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 43.7 mg (92%, 0.092 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 7.15 – 7.11 (m, 2H), 6.81 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.70 (d, *J* = 2.9 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 4.38 – 4.28 (m, 1H), 3.97 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.85 (s, 3H), 3.48 (dd, *J* = 12.3, 5.5 Hz, 1H), 3.21 (dd, *J* = 9.3, 3.9 Hz, 1H), 3.17 – 3.09 (m, 1H), 2.96 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.79 (dd, *J* = 12.5, 9.5 Hz, 1H), 2.55 (s, 3H), 2.39 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.3, 162.2, 143.8, 143.6, 140.2, 136.8, 133.6, 132.9, 129.8, 129.1, 128.6, 128.2, 127.8, 127.0, 123.7, 118.0, 112.0, 77.5, 77.2, 76.8, 55.6, 51.3, 50.8, 45.9, 39.3, 29.3, 21.6. **IR (ATR) ν** 1665 cm^{-1}, 1344 cm^{-1}, 1245 cm^{-1}, 1153 cm^{-1}. **HRMS** calcd for $C_{28}H_{30}NO_4S$ $[M + H]^+$ 476.1890, found 476.1894.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = +1.67°

HPLC: Daicel Chiralpak AD-H Column, e.r. = 60:40, λ = 254 nm, hexane/isopropanol = 94:06, flow rate 1 mL/min, t_r (major) = 170.90 min, t_r (minor) = 161.53 min.

(*R,Z*)-4-acetyl-3-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl acetate (6):

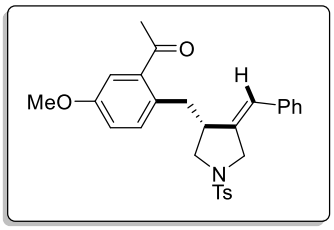


Purified by silica gel chromatography (R_f = 0.35, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 35.2 mg (70%, 0.07 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 11.5, 7.9 Hz, 4H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.16 – 7.10 (m, 3H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.31 (q, *J* = 2.4 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.99 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.40 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.20 (dd, *J* = 9.1, 3.8 Hz, 1H), 3.11 (t, *J* = 6.3 Hz, 1H), 3.04 (dd, *J* = 9.1, 6.3 Hz, 1H), 2.81 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.58 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 200.2, 169.0, 153.0, 143.8, 142.6, 139.9, 136.7, 134.6, 132.9, 132.1, 129.9, 128.6, 128.3, 127.9, 127.1, 125.5, 124.0, 119.9, 77.4, 77.2, 76.9, 51.6, 50.8, 46.2, 38.5, 29.7, 21.7, 21.31. **IR (ATR) ν** 2921 cm^{-1},1684 cm^{-1}, 1334 cm^{-1}, 1157 cm^{-1}. **HRMS** calcd for $C_{29}H_{30}NO_3S$ $[M + H]^+$ 504.1839, found 504.1832.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +6.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 77:23, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 26.37 min, t_r (minor) = 28.93 min.

(*R,Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-5-methoxyphenyl)ethan-1-one (7):

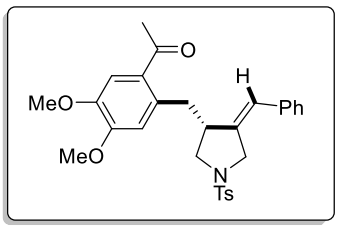


Purified by silica gel chromatography (R_f = 0.35, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 33.3 mg (70%, 0.070 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.25 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 3H), 6.96 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.26 (q, *J* = 2.2 Hz, 1H), 4.31 – 4.27 (m, 1H), 3.98 (dd, *J* = 15.0, 2.5 Hz, 1H), 3.84 (s, 3H), 3.26 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.16 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.10 – 3.04 (m, 1H), 2.99 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.73 (dd, *J* = 13.1, 9.1 Hz, 1H), 2.56 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.3, 158.1, 143.7, 140.2, 138.1, 136.8, 133.7, 132.9, 131.7, 129.8, 128.6, 128.2, 127.9, 127.0, 123.7, 116.6, 77.5, 77.2, 76.8, 55.6, 51.5, 50.8, 46.5, 37.6, 29.7, 21.6. **IR (ATR) ν** 1684 cm^{-1}, 1344 cm^{-1}, 1153 cm^{-1}. **HRMS** calcd for $C_{28}H_{30}NO_4S$ $[M + H]^+$ 476.1890, found 476.1892.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = +0.33°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 51.72 min, t_r (minor) = 42.07 min.

(*R,Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4,5-dimethoxyphenyl)ethan-1-one (8):

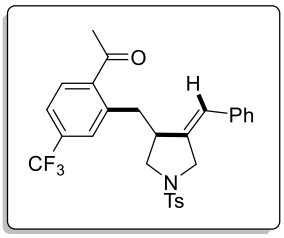


Purified by silica gel chromatography (R_f = 0.3, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 37.9 mg (75%, 0.075 mmol). ^{1}H NMR analysis after purification.**^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.73 (s, 1H), 6.33 (s, 1H), 4.42 (d, *J* = 14.8 Hz, 1H), 3.93 (d, *J* = 4.1 Hz, 6H), 3.91 – 3.86 (m, 1H), 3.40 – 3.29 (m, 2H), 3.14 (q, *J* = 7.7 Hz, 1H), 2.88 – 2.80 (m, 2H), 2.58 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.3, 151.8, 146.9, 143.8, 140.2, 136.7, 135.3, 132.7, 129.8, 128.7, 128.2, 127.8, 127.1, 123.9, 115.7, 114.0, 77.5, 77.2, 76.8, 56.3, 56.2, 51.1, 50.6, 46.4, 38.9, 29.4, 21.6. **IR (ATR) ν** 1673 cm^{-1}, 1344 cm^{-1}, 1150 cm^{-1}. **HRMS** calcd for $C_{29}H_{31}NO_5SNa$ $[M + Na]^+$ 505.1996, found 505.1966.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = +1.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 66:34, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 27.24 min, t_r (minor) = 33.68 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-(trifluoromethyl)phenyl)ethan-1-one (9):

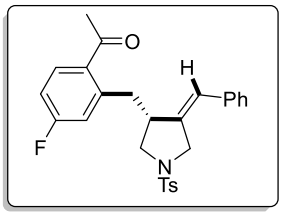


Purified by silica gel chromatography (R_f = 0.4, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 37 mg (72%, 0.072 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.58 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.11 (d, *J* = 2.8 Hz, 1H), 4.27 (dd, *J* = 14.5, 2.7 Hz, 1H), 4.03 (dd, *J* = 14.7, 2.4 Hz, 1H), 3.38 – 3.28 (m, 1H), 3.16 – 3.06 (m, 3H), 2.88 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.59 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 200.97, 143.91, 140.69, 140.42, 139.28, 136.38, 133.1(q, ^2J =32.5H), 130.01, 129.90, 129.1 (q, ^3J = 3.75 Hz), 128.67, 128.21, 127.88, 127.29, 124.26, 123.5 (q, ^3J = 3.75 Hz), 123.5 (q, ^1J = 271.25 Hz), 77.41, 77.16, 76.90, 51.72, 50.62, 46.39, 37.84, 30.0, 21.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.97. **IR (ATR) ν** 2923 cm^{-1},1690 cm^{-1}, 1328 cm^{-1}, 1161 cm^{-1}. **HRMS** calcd for $C_{28}H_{27}F_3NO_3S$ $[M + H]^+$ 514.1658, found 514.1651.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = –16.00°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 81:19, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 17.50 min, t_r (minor) = 14.07 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-fluorophenyl)ethan-1-one (10):



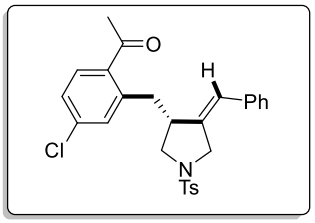
Purified by silica gel chromatography (R_f = 0.45, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 34.7 mg (75%, 0.075 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.33 (q, *J* = 7.7 Hz, 4H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.04 – 7.00 (m, 1H), 6.86 (dd, *J* = 9.5, 2.7 Hz, 1H), 6.27 (d, *J* = 3.0 Hz, 1H), 4.29 (dt, *J* = 14.7, 2.2 Hz, 1H), 4.04 (dd, *J* = 14.5, 2.5 Hz, 1H), 3.41 (dd, *J* = 12.8, 5.2 Hz, 1H), 3.17 – 3.06 (m, 3H), 2.81 (dd, *J* = 12.6, 8.2 Hz, 1H), 2.57 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 199.70, 164.19 (d, ^1J = 254.7 Hz), 144.02 (d, ^3J = 8.2 Hz), 143.85, 139.68, 136.58, 133.27 (d, ^3J = 3.1 Hz), 133.19, 133.12, 133.00, 129.87, 128.66, 128.23, 127.88, 127.18, 123.96, 119.45 (d, ^2J = 21.1 Hz), 113.68 (d, ^3J = 21.2 Hz)., 77.41, 77.16, 76.91, 51.55, 50.69, 46.07, 38.48, 29.65, 21.63.

IR (ATR) ν 1682 cm^{-1}, 1340 cm^{-1}, 1231 cm^{-1}, 1150 cm^{-1}. **HRMS** calcd for $C_{27}H_{27}FNO_3S$ [M + H]$^+$ 464.1690, found 464.1667.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +4.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 84:16, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.50 min, t_r (minor) = 22.69 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-chlorophenyl)ethan-1-one (11):

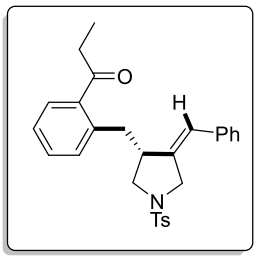


Purified by silica gel chromatography (R_f = 0.45, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 37 mg (77%, 0.077 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.4 Hz, 3H), 7.36 – 7.29 (m, 5H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16 – 7.10 (m, 3H), 6.23 (d, *J* = 3.0 Hz, 1H), 4.28 (dd, *J* = 12.9, 1.8 Hz, 1H), 4.04 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.17 – 3.06 (m, 3H), 2.82 – 2.74 (m, 1H), 2.56 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.2, 143.9, 142.3, 139.6, 138.0, 136.5, 135.3, 133.0, 132.5, 131.8, 129.9, 128.7, 128.2, 127.9, 127.2, 127.0, 124.0, 77.5, 77.2, 76.8, 51.6, 50.7, 46.2, 38.1, 29.7, 21.7. **IR (ATR) ν** 1684 cm^{-1}, 1338 cm^{-1}, 1159 cm^{-1}, 1593 cm^{-1}. **HRMS** calcd for $C_{27}H_{27}ClNO_3S$ [M + H]$^+$ 480.1395, found 480.1383.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +3.00°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 77:23, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.70 min, t_r (minor) = 16.90 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)propan-1-one (12):

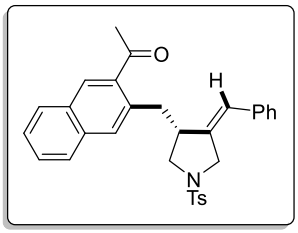


Purified by silica gel chromatography (R_f = 0.5, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 40 mg (87%, 0.087 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (t, *J* = 7.4 Hz, 3H), 7.41 (td, *J* = 7.4, 1.5 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.25 – 7.17 (m, 2H), 7.14 – 7.09 (m, 2H), 6.23 (d, *J* = 2.0 Hz, 1H), 4.31 – 4.26 (m, 1H), 4.03 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.29 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.19 – 3.11 (m, 2H), 3.08 – 3.01 (m, 1H), 2.94 (q, *J* = 7.3 Hz, 2H), 2.82 (dd, *J* = 13.0, 8.8 Hz, 1H), 2.40 (s, 3H), 1.19 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 204.8, 143.8, 139.9, 139.4, 137.7, 136.7, 132.8, 132.5, 131.5, 129.8, 129.2, 128.6, 128.2, 127.9, 127.1, 126.7, 123.8, 77.5, 77.2, 76.8, 51.7, 50.8, 46.4, 38.1, 34.8, 21.6, 8.6.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +8.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 86.5:13.5, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 15.01 min, t_r (minor) = 16.94 min.

(*R*,*Z*)-1-(3-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)naphthalen-2-yl)ethan-1-one (13):

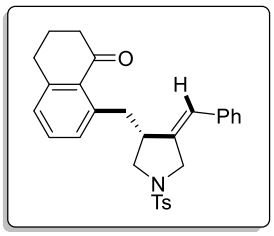


Purified by silica gel chromatography (R_f = 0.35, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 44.1 mg (89%, 0.089 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.57 – 7.51 (m, 1H), 7.36 – 7.28 (m, 4H), 7.23 (d, *J* = 14.5 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.37 (d, *J* = 2.0 Hz, 1H), 4.38 – 4.38 (m, 1H), 4.05 (dd, *J* = 14.7, 2.7 Hz, 1H), 3.61 (dd, *J* = 12.9, 5.1 Hz, 1H), 3.24 (dd, *J* = 9.0, 4.1 Hz, 1H), 3.20 – 3.14 (m, 1H), 3.05 – 2.92 (m, 2H), 2.73 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.2, 143.7, 140.3, 136.9, 136.1, 135.2, 134.7, 133.0, 132.2, 131.4, 131.3, 129.8, 128.8, 128.7, 128.6, 128.2, 128.0, 127.5, 127.0, 126.7, 123.8, 77.5, 77.2, 76.8, 51.5, 50.9, 46.2, 38.8, 29.6, 21.6. **IR (ATR) ν** 1684 cm^{-1}, 1334 cm^{-1}, 1157 cm^{-1}, 1091 cm^{-1}, **HRMS** calcd for $C_{31}H_{30}NO_3S$ $[M + H]^+$ 496.1941, found 496.1937.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +5.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 79:21, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 51.10 min, t_r (minor) = 29.49 min.

(*R*,*Z*)-8-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-3,4-dihydronaphthalen-1(2H)-one (14):



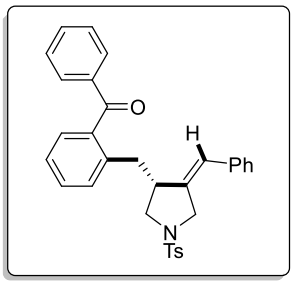
Purified by silica gel chromatography (R_f = 0.45, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 34.9 mg (74%, 0.074 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.28 (m, 5H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.39 (q, *J* = 2.3 Hz, 1H), 4.32 (dt, *J* = 14.6, 2.4 Hz, 1H), 4.01 (dd, *J* = 14.7, 2.5 Hz, 1H), 3.62 (dd, *J* = 12.4, 5.1 Hz, 1H), 3.19 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.12 (p, *J* = 4.6 Hz, 1H), 3.03 – 2.96 (m, 3H), 2.83 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.65 (td, *J* = 6.3, 2.7 Hz, 2H), 2.41 (s, 3H), 2.08 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 200.3, 146.6, 143.7, 142.4, 140.5, 136.9, 133.1, 132.7, 131.3, 130.9, 129.8, 128.6, 128.3, 128.1, 127.9, 127.0, 123.7, 77.4, 77.2, 76.9, 51.6,

50.9, 45.8, 41.3, 39.8, 31.3, 23.0, 21.7. **IR (ATR) ν** 2919 cm^{-1}, 2862 cm^{-1}, 1673 cm^{-1}, 1338 cm^{-1}, 1150 cm^{-1}. **HRMS** calcd for $C_{29}H_{30}NO_3S$ $[M + H]^+$ 472.1925, found 472.1941.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = –1.67°

HPLC: Daicel Chiralpak AD-H Column, e.r. = 78:20, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 43.50 min, t_r (minor) = 33.54 min.

(*R*,*Z*)-2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)(phenyl)methanone (15):

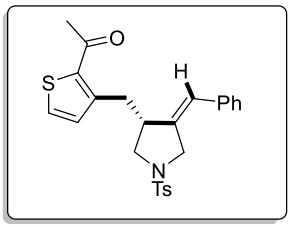


Purified by silica gel chromatography (R_f = 0.5, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 40.1 mg (79%, 0.079 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 8.2 Hz, 3H), 7.48 – 7.41 (m, 3H), 7.35 – 7.26 (m, 5H), 7.22 (dd, *J* = 10.1, 7.8 Hz, 3H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.07 (d, *J* = 2.8 Hz, 1H), 4.15 (dd, *J* = 15.0, 2.6 Hz, 1H), 4.00 (dd, *J* = 14.7, 2.8 Hz, 1H), 3.15 – 3.04 (m, 4H), 2.78 – 2.71 (m, 1H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.4, 143.8, 139.6, 138.7, 138.4, 137.9, 136.5, 133.5, 132.7, 131.5, 130.8, 130.4, 129.9, 129.6, 128.7, 128.6, 128.2, 127.9, 127.1, 126.1, 123.8, 77.5, 77.2, 76.9, 51.7, 50.8, 46.6, 37.1, 21.6.

$[\alpha]_D^{25}$(c = 0.1, $CHCl_3$) = –2.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 82:18, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.36 min, t_r (minor) = 22.98 min.

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)thiophen-3-yl)ethan-1-one (16)

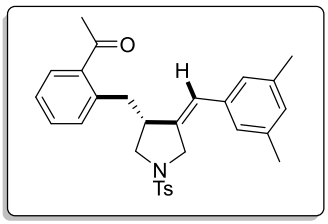


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 34 mg (76%, 0.076 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.30 (dd, *J* = 10.5, 8.0 Hz, 4H), 7.22 (dd, *J* = 14.4, 7.1 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 5.0 Hz, 1H), 6.24 (s, 1H), 4.27 (d, *J* = 14.7 Hz, 1H), 3.98 (d, *J* = 14.8 Hz, 1H), 3.36 (dd, *J* = 12.7, 5.2 Hz, 1H), 3.16 – 2.96 (m, 4H), 2.51 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 191.1, 147.0, 143.8, 139.8, 136.6, 135.9, 132.6, 130.0, 129.8, 128.6, 128.2, 127.9, 127.1, 123.8, 51.7, 50.7, 45.5, 34.2, 29.8, 21.6. **IR (ATR) ν** 1659 cm^{-1}, 1338 cm^{-1}, 1159 cm^{-1}, 1091 cm^{-1}. **HRMS** calcd for $C_{25}H_{26}NO_3S_2$ $[M + H]^+$ 452.1349, found 452.1337.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +2.33°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 61:39, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.74 min, t_r (minor) = 23.32min.

(*R*,*Z*)-1-(2-((4-(3,5-dimethylbenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (17)

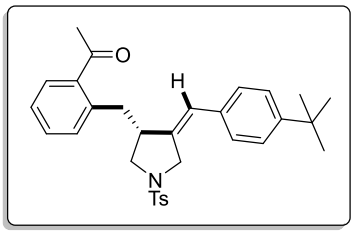


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 37.4 mg (79%, 0.079 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.77 (d, *J* = 6.5 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 1H), 6.87 (s, 1H), 6.74 (s, 2H), 6.21 (d, *J* = 1.2 Hz, 1H), 4.31 (d, *J* = 14.8 Hz, 1H), 4.01 (d, *J* = 14.8 Hz, 1H), 3.35 (dd, *J* = 12.7, 5.6 Hz, 1H), 3.18 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.14 – 3.05 (m, 1H), 3.02 (dd, *J* = 8.9, 6.4 Hz, 1H), 2.81 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.59 (s, 3H), 2.41 (s, 3H), 2.31 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 201.5, 143.7, 140.0, 139.5, 138.1, 137.2, 136.7, 132.7, 132.0, 130.4, 129.8, 128.9, 127.9, 126.8, 126.1, 124.0, 51.6, 50.7, 46.4, 38.4, 29.8, 21.6, 21.5. **IR (ATR) ν** 2921 cm^{-1}, 1667 cm^{-1}, 1350 cm^{-1}, 1253 cm^{-1}, 1157 cm^{-1}. **HRMS** calcd for $C_{29}H_{32}NO_3S$ $[M + H]^+$ 474.2097, found 474.2060.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = -2.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 84:16, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 11.44 min, t_r (minor) = 12.36 min.

(*R*,*Z*)-1-(2-((4-(4-(tert-butyl)benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (18)

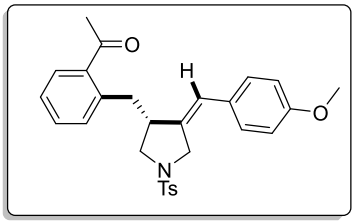


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 43 mg (86%, 0.086 mmol). 20 h. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 5.8 Hz, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.23 (s, 1H), 4.30 (d, *J* = 14.7 Hz, 1H), 4.01 (d, *J* = 14.7 Hz, 1H), 3.35 (dd, *J* = 12.8, 5.7 Hz, 1H), 3.18 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.14-3.09 (m, 1H), 3.01 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.82 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.59 (s, 3H), 2.41 (s, 3H), 1.32 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 200.5, 149.1, 142.7, 139.1, 138.2, 136.2, 132.9, 131.8, 131.0, 129.4, 128.8, 127.0, 126.9, 125.8, 124.6, 122.5, 50.6, 49.9, 45.4, 37.6, 33.7, 30.4, 28.8, 20.7. **IR (ATR) ν** 2960 cm^{-1}, 1678 cm^{-1}, 1346 cm^{-1}, 1167 cm^{-1}. **HRMS** calcd for $C_{31}H_{36}NO_3S$ $[M + H]^+$ 502.2410, found 502.2405.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +3.33°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 15.20min, t_r (minor) = 18.82 min.

(*R*,*Z*)-1-(2-((4-(4-methoxybenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (19):

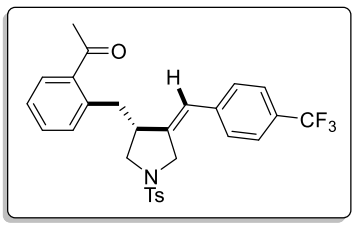


Purified by silica gel chromatography (R_f = 0.4), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 38 mg (80%, 0.080). ^{1}H NMR analysis after purification.**^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.45 – 7.41 (m, 1H), 7.36 – 7.28 (m, 3H), 7.21 – 7.17 (m, 1H), 7.09 – 7.02 (m, 2H), 6.90 – 6.83 (m, 2H), 6.20 (q, *J* = 2.3 Hz, 1H), 4.30 – 4.25 (m, 1H), 3.99 (dd, *J* = 14.8, 2.7 Hz, 1H), 3.81 (s, 3H), 3.37 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.17 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.12 – 3.06 (m, 1H), 3.01 (dd, *J* = 8.9, 6.4 Hz, 1H), 2.80 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.58 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.5, 158.6, 143.7, 140.1, 137.7, 137.2, 132.9, 132.7, 132.0, 130.3, 129.8, 129.5, 127.9, 126.8, 123.1, 114.1, 77.5, 77.2, 76.8, 55.4, 51.6, 50.8, 46.3, 38.4, 29.8, 21.6.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +5.00°

HPLC: Daicel Chiralpak AD-H Column, e.r. = 88:12, λ = 254 nm, hexane/isopropanol = 70:30, flow rate 1 mL/min, t_r (major) = 18.43 min, t_r (minor) = 21.69 min.

(*R*,*Z*)-1-(2-((1-tosyl-4-(4-(trifluoromethyl)benzylidene)pyrrolidin-3-yl)methyl)phenyl)ethan-1-one (20):

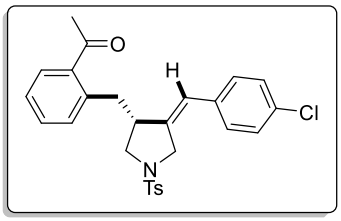


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 40.1 mg (78%, 0.078 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.80 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.38 – 7.29 (m, 3H), 7.20 (dd, *J* = 10.4, 7.8 Hz, 3H), 6.33 (q, *J* = 2.3 Hz, 1H), 4.33 – 4.28 (m, 1H), 3.99 (dd, *J* = 14.9, 2.6 Hz, 1H), 3.39 (dd, *J* = 12.8, 5.3 Hz, 1H), 3.24 – 3.13 (m, 2H), 3.08 – 2.99 (m, 1H), 2.82 (dd, *J* = 12.7, 9.1 Hz, 1H), 2.60 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 201.42, 143.91, 143.08, 140.18, 139.85, 136.92, 132.80, 132.72, 132.13, 130.61, 129.88, 128.85 (q, ^2J = 32.6 Hz), 128.33, 127.88, 126.97, 125.55 (q, ^3J = 3.9 Hz), 124.22 (q, ^1J = 271.9 Hz) 122.57, 77.41, 77.16, 76.90, 51.48, 50.78, 46.46, 38.53, 29.68, 21.62, **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.34.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +0.33°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 58:42, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 24.536min, t_r (minor) = 35.069min.

(*R*,*Z*)-1-(2-((4-(4-chlorobenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (21)

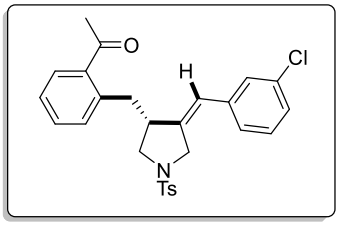


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 30 mg (63%, 0.063 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.79 (d, *J* = 7.3 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 6.7 Hz, 1H), 7.30 (dd, *J* = 8.2, 4.0 Hz, 4H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.23 (s, 1H), 4.26 (d, *J* = 14.6 Hz, 1H), 3.95 (d, *J* = 14.6 Hz, 1H), 3.37 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.18 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.14-3.09 (m, 1H), 3.01 (dd, *J* = 8.9, 6.4 Hz, 1H), 2.80 (dd, *J* = 12.5, 9.5 Hz, 1H), 2.59 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 201.5, 143.9, 140.9, 140.0, 137.0, 135.2, 132.90, 132.87, 132.8, 132.1, 130.5, 129.9, 129.5, 128.8, 127.9, 126.9, 122.6, 51.5, 50.8, 46.4, 38.5, 29.8, 29.7, 21.7. **IR (ATR) ν** 2915 cm^{-1}, 2359 cm^{-1}, 1673 cm^{-1}, 1492 cm^{-1}, 1340 cm^{-1}, 1153 cm^{-1}. **HRMS** calcd for $C_{27}H_{27}ClNO_3S$ $[M + H]^+$ 480.1395, found 480.1395.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +10.00°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 63:37, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 32.00 min, t_r (minor) = 35.04 min.

(*R*,*Z*)-1-(2-((4-(3-chlorobenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (22)



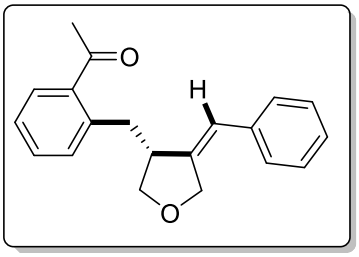
Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a whit solid. Isolated yield 38.4 mg (80%, 0.080 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 7.08 (s, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.22 (d, *J* = 1.4 Hz, 1H), 4.27 (d, *J* = 14.9 Hz, 1H), 3.97 (d, *J* = 14.9 Hz, 1H), 3.35 (dd, *J* = 12.7, 5.5 Hz, 1H), 3.19 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.15 - 3.09 (m, 1H), 3.02 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.80 (dd, *J* = 12.7, 9.1 Hz, 1H), 2.59 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 201.4, 143.9, 141.9, 139.9, 138.5, 137.0, 134.5, 133.9, 132.7, 132.1, 130.5, 129.9, 128.3, 127.9, 127.1, 126.9, 126.1, 122.6, 51.5, 50.7, 46.4, 38.5, 29.7, 21.6. **IR (ATR) ν** 2359 cm^{-1}, 1671 cm^{-1}, 1338

cm^{-1}, 1247 cm^{-1}, 1150 cm^{-1}. **HRMS** calcd for $C_{27}H_{27}ClNO_3S$ $[M + H]^+$ 480.1395, found 480.1380.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +0.67°

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 58:42, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 21.88 min, t_r (minor) = 23.14 min.

(*R*,*Z*)-1-(2-((4-benzylidenetetrahydrofuran-3-yl)methyl)phenyl)ethan-1-one (23)

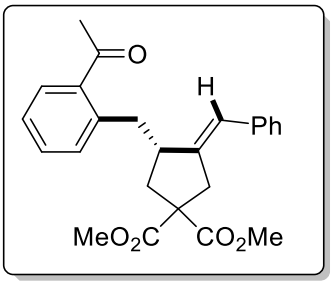


Purified by silica gel chromatography (R_f = 0.6), Eluent: Ethyl acetate/ Hexane in 8% mixture) appeared as a colourless liquid. Isolated yield 17.5 mg (60%, 0.060 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.77 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.28 – 7.20 (m, 2H), 7.14 – 7.09 (m, 2H), 6.30 – 6.26 (m, 1H), 4.77 – 4.72 (m, 1H), 4.61 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.79 – 3.71 (m, 2H), 3.44 (dd, *J* = 12.8, 6.1 Hz, 1H), 3.17 – 3.14 (m, 1H), 2.91 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.60 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 201.7, 144.6, 140.6, 137.6, 137.5, 132.6, 131.8, 130.2, 128.6, 128.5, 128.1, 126.6, 121.6, 77.5, 77.2, 76.9, 72.4, 70.3, 47.1, 38.2, 29.9.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = –12.33°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 9.24 min, t_r (minor) = 8.12 min.

dimethyl (*S*,*E*)-3-(2-acetylbenzyl)-4-benzylidenecyclopentane-1,1-dicarboxylate (24):



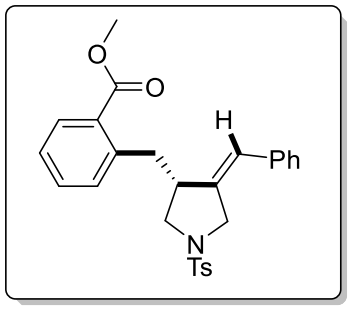
Purified by silica gel chromatography (R_f = 0.6), Eluent: Ethyl acetate/ Hexane in 10% mixture) appeared as a colourless liquid. Isolated yield 16.3 mg (40%, 0.040 mmol). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.35 – 7.26 (m, 6H), 7.19 (t, J = 7.4 Hz, 1H), 6.34 (d, J = 3.5 Hz, 1H), 3.73 (t, J = 1.9 Hz, 3H), 3.66 – 3.57 (m, 4H), 3.39 – 3.25 (m, 2H), 3.11 – 2.98 (m, 1H), 2.72 (dd, J = 13.3, 9.3 Hz, 1H), 2.60 (t, J = 2.0 Hz, 3H), 2.32 (dd, J = 13.1, 7.7 Hz, 1H), 1.92 (dd, J = 13.1, 9.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.0, 172.4, 172.1, 144.5, 140.7, 138.1, 137.8, 132.2, 131.6, 129.8, 128.6, 128.4, 126.4, 123.1, 59.4, 53.0, 52.9, 45.5, 39.3, 39.2, 29.9.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = –4.67°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 90:10, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 10.64 min, t_r (minor) = 8.73 min.

methyl (*R*,*Z*)-2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)benzoate (25):

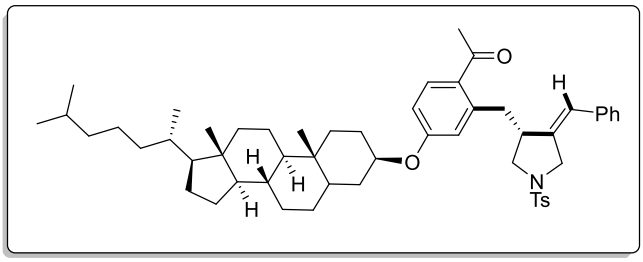


Purified by silica gel chromatography (R_f = 0.6), Eluent: Ethyl acetate/ Hexane in 12% mixture) appeared as a white solid. Isolated yield 18.5 mg (40%, 0.040 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.36 – 7.28 (m, 5H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 1.3 Hz, 2H), 6.21 (q, *J* = 2.3 Hz, 1H), 4.34 – 4.26 (m, 1H), 4.03 (dd, *J* = 14.8, 2.6 Hz, 1H), 3.88 (s, 3H), 3.48 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.20 – 3.16 (m, 1H), 3.16 – 3.09 (m, 1H), 3.05 (dd, *J* = 8.6, 6.1 Hz, 1H), 2.93 (dd, *J* = 12.8, 8.7 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.7, 143.8, 141.5, 140.0, 136.7, 133.0, 132.4, 132.3, 131.4, 129.8, 129.4, 128.7, 128.2, 127.9, 127.1, 126.8, 123.8, 52.1, 51.7, 50.8, 46.4, 38.5, 21.7.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +4.67°

HPLC: Daicel Chiralpak OD-H Column, e.r. = 76:24, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.44 min, t_r (minor) = 14.84 min.

1-(2-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)-4-(((3*R*,8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)phenyl)ethan-1-one (26):

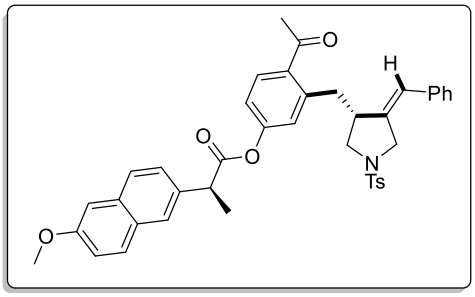


Purified by silica gel chromatography (R_f = 0.4, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 69.9 mg (84%, 0.084 mmol). d.r 1.6:1. ^{1}H NMR analysis after purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.7 Hz, 0.6H), 7.71 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.52 (dd, *J* = 8.7, 1.8 Hz, 0.4H), 7.36 – 7.28 (m, 3.4H), 7.22 (d, *J* = 7.3 Hz, 0.6H), 7.10 (dd, *J* = 17.9, 7.3 Hz, 2.4H), 6.96 (d, *J* = 7.4 Hz, 0.6H), 6.80 (dd, *J* = 8.7, 2.6 Hz, 0.6H), 6.71 – 6.61 (m, 1H), 6.56 (d, *J* = 2.7 Hz, 0.4H), 6.29 (s, 0.6H), 6.22 (s, 0.4H), 4.59 (d, *J* = 13.9 Hz, 1H), 4.34 – 4.22 (m, 1H), 4.04 – 3.97 (m, 0.6H), 3.81 – 3.76 (m, 0.4H), 3.71 (d, *J* = 5.5 Hz, 0.6H), 3.42 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.21 (dd, *J* = 9.1, 4.3 Hz, 0.6H), 3.17 – 3.07 (m, 1.4H), 3.04 (dd, *J* = 9.2, 6.5 Hz, 0.6H), 2.99 – 2.90 (m, 0.4H), 2.83 (dd, *J* = 12.4, 9.0 Hz, 0.6H), 2.55 (s, 2H), 2.41 (d, *J* = 6.8 Hz, 4H), 1.97 (d, *J* = 12.4 Hz, 1H), 1.83 (s, 2H), 1.65 (t, *J* = 12.4 Hz, 3H), 1.56 – 1.44 (m, 5H), 1.38 – 1.18 (m, 10H), 1.18 – 0.96 (m, 10H), 0.91 (dd, *J* = 6.6, 2.2 Hz, 3H), 0.86 (dd, *J* = 6.5, 2.3 Hz, 6H), 0.84 – 0.81 (m, 3H), 0.67 – 0.64 (m, 3H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 199.2, 160.8, 143.7, 140.2, 136.8, 133.7, 133.0, 129.8, 128.6, 128.5, 128.2, 127.9, 127.0, 123.8, 119.7, 119.5, 113.5, 113.4, 77.5, 77.2, 76.8, 72.6, 56.6, 56.4, 54.2, 51.7, 50.9, 46.0, 42.7, 40.2, 39.7, 39.6, 39.4, 36.3, 36.0, 35.9, 35.6, 32.9, 32.7, 32.1, 29.2, 28.6, 28.5, 28.4, 28.1, 27.0, 25.8, 25.7, 24.3, 24.0, 23.0, 22.7, 21.7, 20.9, 18.8, 12.2, 11.5. **IR (ATR) ν** 2929 cm^{-1}, 1669 cm^{-1}, 1595 cm^{-1}, 1344 cm^{-1}, 1231 cm^{-1}. **HRMS** calcd for $C_{54}H_{74}NO_4S$ $[M + H]^+$ 832.5319, found 832.5333.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +7.00°

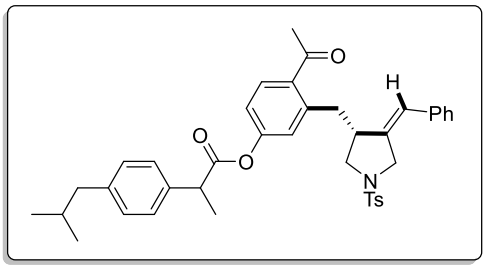
4-acetyl-3-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (27):



Purified by silica gel chromatography (R_f = 0.3), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 47 mg (70%, 0.070 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.72 (m, 4H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.33 – 7.29 (m, 2H), 7.22 (dd, *J* = 7.7, 5.6 Hz, 3H), 7.18 – 7.13 (m, 2H), 7.12 – 7.07 (m, 2H), 7.01 – 6.96 (m, 1H), 6.87 (t, *J* = 2.8 Hz, 1H), 6.22 (dd, *J* = 9.2, 3.1 Hz, 1H), 4.27 – 4.22 (m, 1H), 4.14 – 4.10 (m, 1H), 4.03 – 3.98 (m, 1H), 3.91 (s, 3H), 3.38 – 3.30 (m, 1H), 3.13 (dd, *J* = 8.0, 5.1 Hz, 1H), 3.09 – 3.01 (m, 2H), 2.79 – 2.72 (m, 1H), 2.53 (s, 3H), 2.36 (s, 3H), 1.69 (dd, *J* = 7.2, 3.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.1, 172.8, 158.0, 153.1, 143.7, 142.5, 139.8, 136.7, 134.9, 134.5, 134.0, 132.9, 132.0, 129.8, 129.5, 129.1, 128.6, 128.3, 127.9, 127.7, 127.1, 126.4, 126.1, 125.4, 125.3, 123.9, 119.7, 119.3, 105.8, 77.5, 77.2, 76.9, 55.5, 51.8, 51.7, 50.8, 5.15, 45.7, 38.3, 29.7, 21.6, 18.6. **IR (ATR) ν** 1754 cm^{-1}, 1682 cm^{-1}, 1603 cm^{-1}, 1340 cm^{-1}, 1157 cm^{-1}. **HRMS** calcd for $C_{41}H_{40}NO_6S$ $[M + H]^+$ 674.2571, found 674.2556.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +3.67°

4-acetyl-3-(((*S*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl 2-(4-isobutylphenyl)propanoate (28):

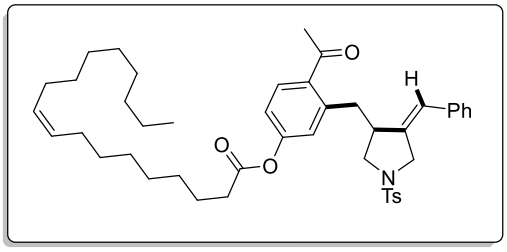


Purified by silica gel chromatography (R_f = 0.4), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 32.5 mg (50%, 0.050 mmol,). ^{1}H NMR analysis after purification.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 –

7.08 (m, 4H), 7.02 – 6.97 (m, 1H), 6.87 (t, *J* = 1.8 Hz, 1H), 6.23 (d, *J* = 7.0 Hz, 1H), 4.30 – 4.21 (m, 1H), 4.07 – 3.99 (m, 1H), 3.94 (q, *J* = 7.2 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.19 – 3.12 (m, 1H), 3.11 – 3.02 (m, 2H), 2.81 – 2.77 (m, 1H), 2.54 (s, 3H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.92 – 1.81 (m, 1H), 1.60 (dd, *J* = 7.1, 2.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 6H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.2, 172.8, 153.2, 143.7, 142.5, 141.1, 139.8, 137.0, 136.7, 134.4, 132.9, 131.9, 129.8, 129.7, 128.6, 128.3, 127.9, 127.3, 127.1, 125.4, 125.3, 123.9, 119.7, 77.5, 77.2, 76.8, 51.7, 51.7, 50.8, 46.2, 45.4, 45.2, 38.3, 30.3, 29.7, 22.5, 21.6, 18.7. **IR (ATR) ν** 2954 cm^{-1}, 1758 cm^{-1}, 1680 cm^{-1}, 1344 cm^{-1}, 1157 cm^{-1}. **HRMS** calcd for $C_{40}H_{44}NO_5S$ $[M + H]^+$ 650.2935, found 650.2925.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$(c=0.1, $CHCl_3$) = –3.33°

4-acetyl-3-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl oleate (29):

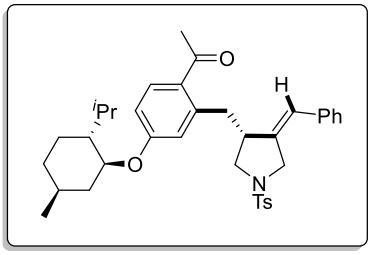


Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 40 mg (55%, 0.055 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.14 – 7.08 (m, 3H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.29 (t, *J* = 2.1 Hz, 1H), 5.40 – 5.31 (m, 2H), 4.32 – 4.27 (m, 1H), 4.01 (dd, *J* = 14.9, 2.5 Hz, 1H), 3.40 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.19 (dd, *J* = 9.0, 3.7 Hz, 1H), 3.13 – 3.03 (m, 2H), 2.82 (dd, *J* = 12.8, 8.6 Hz, 1H), 2.57 (d, *J* = 2.0 Hz, 5H), 2.40 (s, 3H), 2.02 (q, *J* = 6.6 Hz, 4H), 1.77 (q, *J* = 7.6 Hz, 2H), 1.38 – 1.19 (m, 20H), 0.87 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.1, 171.8, 153.1, 143.7, 142.6, 139.9, 136.7, 134.4, 132.9, 132.0, 130.2, 129.8, 128.60 128.3, 127.9, 127.1, 125.5, 123.9, 119.9, 77.5, 77.2, 76.9, 51.6, 50.8, 46.2, 38.4, 34.5, 32.0, 29.9, 29.8, 29.7, 29.4, 29.3, 29.2, 27.3, 27.3, 24.9, 22.8, 21.6, 14.2. IR (ATR) ν 2923 cm^{-1}, 2853 cm^{-1},1760 cm^{-1}, 1682 cm^{-1},1348 cm^{-1}, 1161 cm^{-1}. HRMS calcd for $C_{45}H_{60}NO_5S$ $[M + H]^+$ 726.4187, found 726.4169.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$(c=0.1, $CHCl_3$) = +0.67°

HPLC: Daicel Chiralpak AD-H Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 12.05 min, t_r (minor) = 13.30 min.

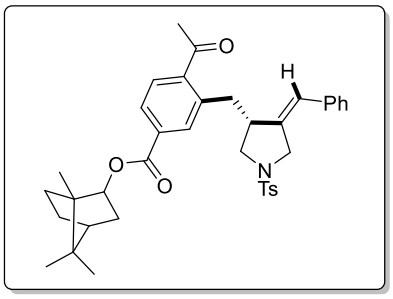
1-(2-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)-4-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-one (30):



Purified by silica gel chromatography (R_f = 0.5, Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 46 mg (77%, 0.077 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.68 (s, 2H), 7.33 – 7.27 (m, 4H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.10 (m, 2H), 6.83 – 6.77 (m, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.31 – 6.26 (m, 1H), 4.72 (d, *J* = 16.8 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.03 (dd, *J* = 14.6, 2.5 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.26 – 3.18 (m, 1H), 3.14 (s, 1H), 3.07 – 3.01 (m, 1H), 2.91 – 2.81 (m, 1H), 2.55 (s, 3H), 2.40 (s, 3H), 2.14 – 2.07 (m, 1H), 1.80 – 1.75 (m, 2H), 1.65 – 1.59 (m, 4H), 1.10 – 1.04 (m, 2H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.84 – 0.79 (m, 6H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.2, 161.1, 143.8, 143.7, 140.1, 136.8, 133.8, 133.0, 129.8, 128.6, 128.5, 128.3, 127.9, 127.0, 123.9, 123.8, 119.4, 113.1, 113.0, 77.5, 77.2, 76.8, 73.9, 51.7, 50.9, 50.8, 47.7, 46.0, 39.5, 39.4, 37.8, 37.8, 35.0, 29.4, 29.2, 26.4, 25.0, 24.9, 22.4, 22.3, 21.7, 21.1, 20.9. **IR (ATR) ν** 2940 cm^{-1}, 1667 cm^{-1}, 1601 cm^{-1}, 1348 cm^{-1}, 1241 cm^{-1}. **HRMS** calcd for $C_{37}H_{46}NO_4S$ $[M + H]^+$ 600.3142, found 600.3130.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = +10.67°

(1*S*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-acetyl-3-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)benzoate (31):



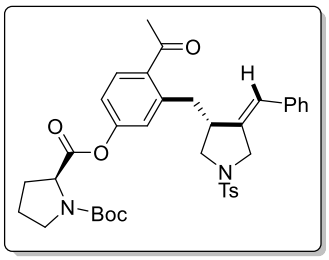
Purified by silica gel chromatography (R_f = 0.35), Eluent: Ethyl acetate/ Hexane in 15% mixture) appeared as a white solid. Isolated yield 48 mg (77%, 0.077 mmol). ^{1}H NMR analysis after purification. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.85 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.8, 3.6 Hz, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.11 (d, *J* = 9.7 Hz, 1H), 5.12 (d, *J* = 9.8 Hz, 1H), 4.24 (d, *J* = 14.7 Hz, 1H), 4.06 (d, *J* = 14.9 Hz, 1H), 3.35 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.17 – 3.09 (m, 3H), 2.89 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.59 (s, 3H), 2.42 (d, *J* = 12.8 Hz, 4H), 2.07 (td, *J* = 10.8, 4.1 Hz, 1H), 1.82 (d, *J* = 4.0 Hz, 1H), 1.76 (d, *J* = 4.8 Hz, 1H), 1.49 – 1.40 (m, 2H), 1.13 (dd, *J* = 13.7, 3.5 Hz, 1H), 0.97 (s, 3H), 0.92 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.5, 165.9, 143.8, 141.1, 139.8, 139.5, 136.5, 133.3, 133.0, 132.9, 129.9, 129.7, 128.7, 128.2, 127.9, 127.2, 124.0, 81.3, 77.5, 77.2, 76.8, 52.1, 52.0, 50.8, 49.3, 48.1, 46.4, 45.1, 37.6, 36.9,

30.1, 28.2, 27.6, 27.0, 22.8, 21.7, 19.9, 19.0, 13.8. **IR (ATR) ν** 2956 cm^{-1}, 1715 cm^{-1}, 1686 cm^{-1}, 1262 cm^{-1}, 1165 cm^{-1}. **HRMS** calcd for $C_{38}H_{43}NO_5SNa$ $[M + Na]^+$ 648.2754, found 648.2728.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = –5.67°

HPLC: Daicel Chiralpak IB-3 Column, e.r. = 83:17, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 12.54 min, t_r (minor) = 11.85 min.

2-(4-acetyl-3-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl) 1-(tert-butyl) (*S*)-pyrrolidine-1,2-dicarboxylate (32):



Purified by silica gel chromatography (R_f = 0.45), Eluent: Ethyl acetate in Hexane in 15% mixture) appeared as a white solid. Isolated yield 40 mg (61%, 0.061 mmol). ^{1}H NMR analysis after purification. d.r 1.2:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (dd, *J* = 17.1, 8.6 Hz, 1H), 7.69 (dd, *J* = 8.5, 2.3 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.07 (m, 3H), 6.98 – 6.96(m, 1H), 6.25 (d, *J* = 12.1 Hz, 0.44H), 6.22 (s, 0.55H), 4.51 (dd, *J* = 8.2, 4.0 Hz, 0.43H), 4.47 – 4.43 (m, 0.57H), 4.33 – 4.21 (m, 1H), 4.04 – 3.94 (m, 1H), 3.66 – 3.49 (m, 1.58H), 3.49 – 3.31 (m, 1.36H), 3.22 – 3.14 (m, 1H), 3.13 – 2.97 (m, 2H), 2.89 – 2.74 (m, 1H), 2.57 (s, 1.61H), 2.55 (s, 1.36H), 2.39 (s, 3H), 2.37 – 2.27 (m, 1H), 2.14 (td, *J* = 10.9, 5.7 Hz, 1H), 2.01 – 1.81 (m, 2H), 1.48 (s, 4H), 1.45 (s, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.2, 200.1, 171.2, 154.6, 153.7, 153.0, 152.8, 143.7, 142.6, 142.4, 139.7, 139.6, 136.6, 134.6, 132.8, 132.7, 132.1, 132.0, 129.8, 128.6, 128.2, 127.9, 127.1, 127.0, 125.2, 125.1, 124.0, 123.8, 119.9, 119.4, 80.4, 80.2, 77.5, 77.2, 76.8, 60.5, 59.2, 59.2, 51.7, 51.5, 50.7, 46.7, 46.5, 46.2, 38.3, 38.1, 31.0, 30.0, 29.8, 29.7, 28.5, 24.6, 23.8, 21.6, 14.3, 14.2. **IR (ATR) ν** 2923 cm^{-1}, 1768 cm^{-1}, 1682 cm^{-1}, 1393 cm^{-1}, 1159 cm^{-1}. **HRMS** calcd for $C_{37}H_{42}N_2O_7SNa$ $[M + Na]^+$ 681.2605, found 681.2570.

$[\alpha]_D^{25}$(c=0.1, $CHCl_3$) = –2.67°

6. Absolute stereochemistry determination via single-crystal X-ray diffraction

Single crystals of enantiomerically pure compounds **15** and **17** were obtained by slow diffusion from the methanol and ethyl acetate solution at room temperature. Intensity data were collected on an XtaLAB Synergy, Dualflex, HyPix3000 diffractometer. The crystal was kept at 99.99 K during the data collection. The software Olex2 was used for space group, structure determination, and refinements. The least-squares refinement techniques on F2 were performed until the model converged. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model.

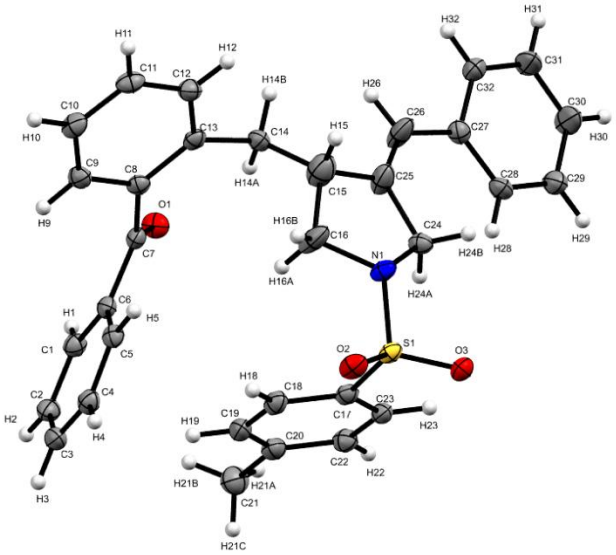


Figure S1 Molecular structure of **15**. (ORTEP view, 50% probability level). **(CCDC = 2131987).**

Crystal data and structure refinement for 15.

Identification code	KMC-KD-273
Empirical formula	$C_{32}H_{29}NO_3S$
Formula weight	507.62
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.92120(10)
b/Å	10.49310(10)
c/Å	12.89360(10)

α/°	74.3850(10)
β/°	86.4320(10)
γ/°	89.0320(10)
Volume/Å^3	1290.23(2)
Z	2
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	1.387
F(000)	536.0
Crystal size/mm^3	0.06 × 0.04 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.132 to 133.174
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	22997
Independent reflections	4508 [R_{int} = 0.0505, R_{sigma} = 0.0284]
Data/restraints/parameters	4508/0/335
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1387
Final R indexes [all data]	R_1 = 0.0597, wR_2 = 0.1396
Largest diff. peak/hole / e Å^{-3}	2.08/-0.68

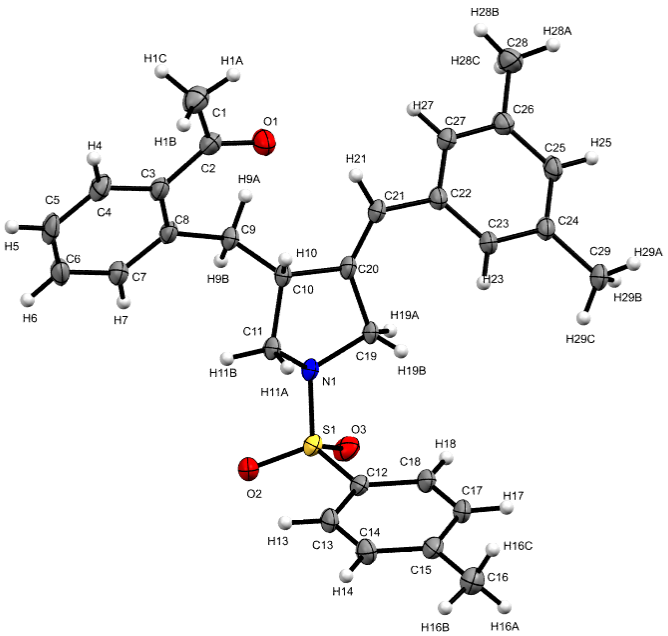


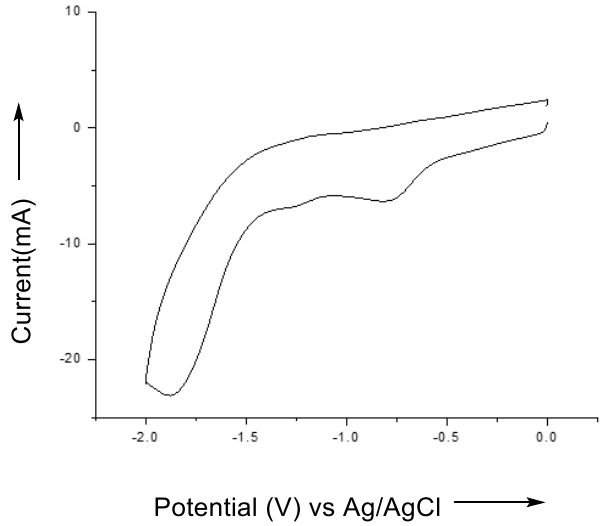
Figure S2 Molecular structure of **17**. (ORTEP view, 50% probability level). **(CCDC = 2131986).**

Identification code	KMC KD-277_1
Empirical formula	$C_{29}H_{31}NO_3S$
Formula weight	473.61
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0088(2)
b/Å	11.8283(2)
c/Å	12.2176(2)
α/°	109.579(2)
β/°	91.015(2)
γ/°	93.297(2)
Volume/Å^3	1223.64(4)
Z	2
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	1.419
F(000)	504.0
Crystal size/mm^3	0.06 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.686 to 133.166
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$
Reflections collected	20335
Independent reflections	4263 [R_{int} = 0.0668, R_{sigma} = 0.0392]
Data/restraints/parameters	4263/0/311
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1259
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1284
Largest diff. peak/hole / e Å^{-3}	0.51/-0.51

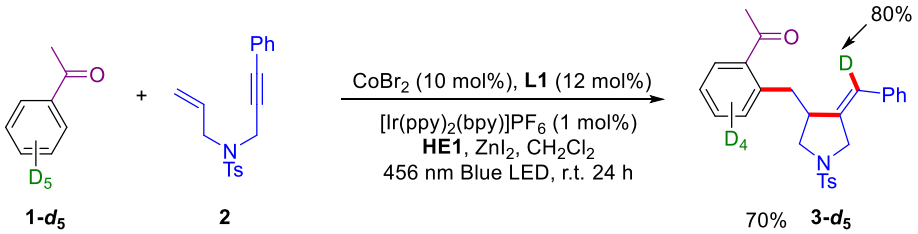
7. Mechanistic Investigations:

7.1. Cyclic voltammetry:

Cyclic Voltammetry was performed using a CHI 400A workstation at a rate of 0.05 V/s in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Polished glassy carbon, platinum wire, and Ag/AgCl (sat KCl) were used as the working, counter, and reference electrodes, respectively. To convert the potentials from Ag/AgCl (0.1 M KCl) to SCE, ferrocene was measured under the above conditions in CH_3CN, and 12 mV was added from the measured values. The $CoBr_2$(dppbz) complex was formed *in situ* by adding $CoBr_2$ (0.01 mmol) and dppbz (0.012 mmol) into acetonitrile (10 mL). The solutions were degassed with nitrogen gas for 15 mins and stirred for 2 h. As shown below, the first reduction peak ($E_{1/2}$ = –0.76 V vs SCE in CH_3CN) corresponds to the Co(II)/Co(I) couple.



7.2. Deuterium labelling study:

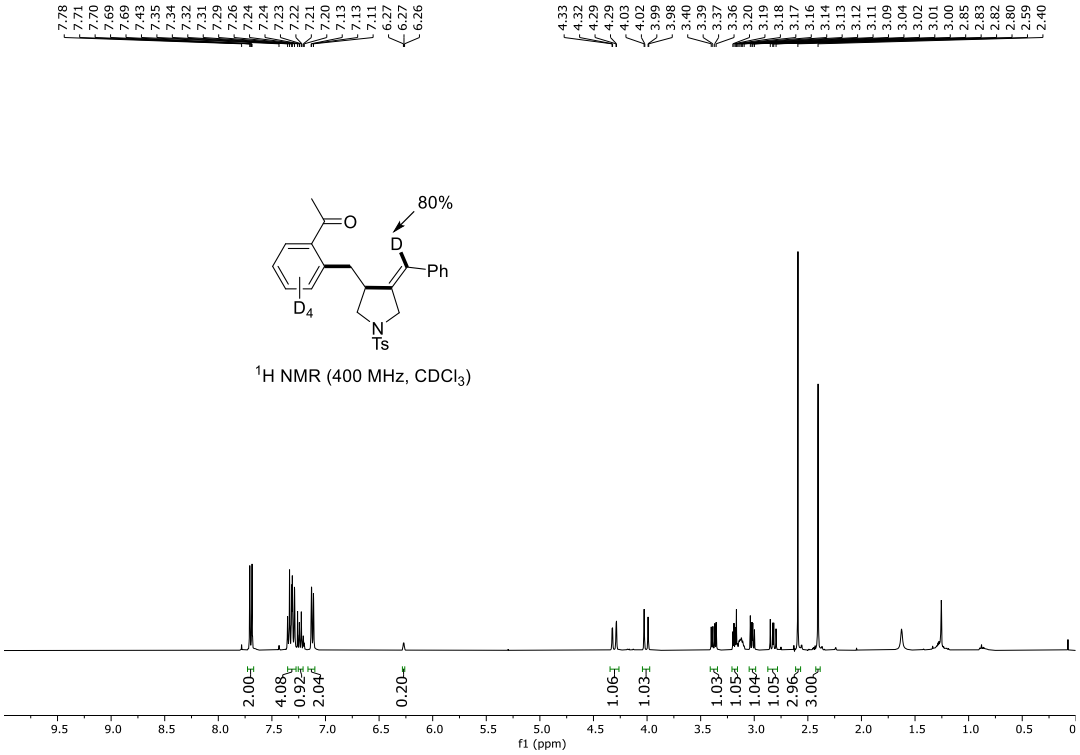


1-d_5 2 3-d_5

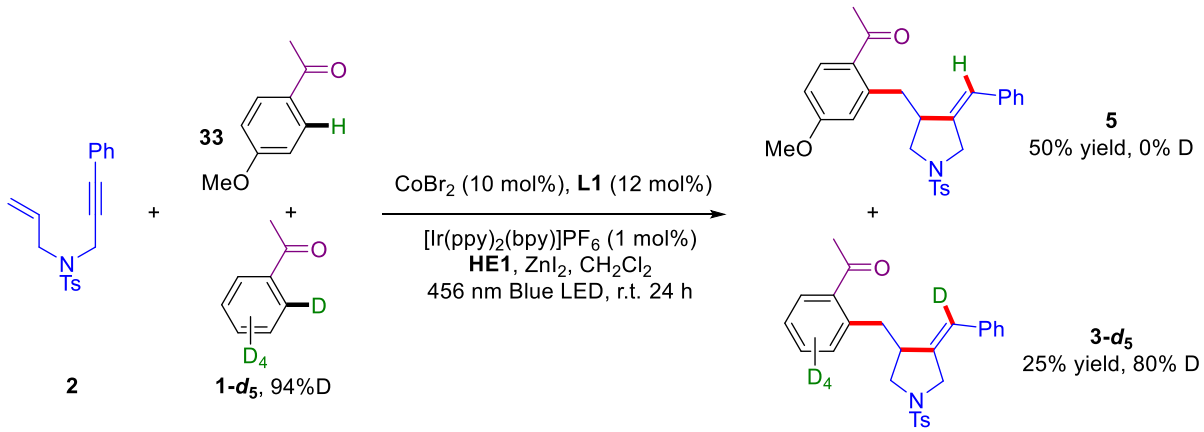
Experimental Procedure:

In a 10 mL reaction tube, $CoBr_2$ (0.010 mmol) and **L1** (0.012 mmol) were taken under argon atmosphere. Then **PC** (0.001 mmol), **HE1** (0.02 mmol), ZnI_2 (0.02 mmol), enyne **2** (0.1 mmol), and pentadeuteriated acetophenone **1-*d*$_5$** (0.12 mmol) were added and the tube was closed and

placed under blue LED irradiation at 456 nm. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water (2 mL), and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent. From the ^1H NMR study, 80% D incorporation at the exocyclic olefinic carbon was observed.



7.3. Deuterium crossover study:

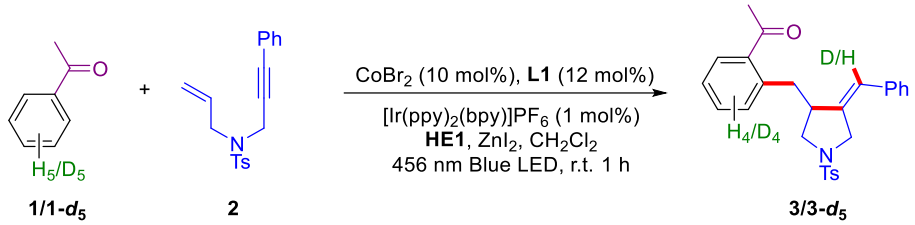


Experimental Procedure:

In a 10 mL reaction tube, $CoBr_2$ (0.020 mmol) and **L1** (0.024 mmol) were taken under argon atmosphere. Then **PC** (0.002 mmol), **HE1** (0.04 mmol), ZnI_2 (0.04 mmol), enyne **2** (0.2 mmol), 4-methoxy acetophenone **5** (0.12 mmol) and pentadeuteriated acetophenone **1-*d*$_5$** (0.12 mmol)

were added and the tube was closed and placed under blue LED irradiation at 456 nm. Upon completion, the reaction was quenched with water (2 mL), and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent. We have only observed the formation of **5** (50% yield, 0% D incorporation) and **3-*d*$_5$** (25% yield, 80% D incorporation). No crossover product formation was noticed.

7.4. Determination of the kinetic isotope effect.



Experimental Procedure:

In six different 10 mL sealed tube, $CoBr_2$ (0.010 mmol) and **L1** (0.012 mmol) **PC** (0.001 mmol), **HE1** (0.2 mmol), ZnI_2 (0.02 mmol), enyne **2** (0.1 mmol) and acetophenone **1** (0.12 mmol) a were added and the tube was closed and placed under blue LED irradiation at 456 nm. The reaction was quenched with water (2 mL), and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Analyzed the products via ^{1}H NMR spectrum using 1,3,5-trimethoxy benzene as an internal standard. An initial rate constant $k_H = 5.06\times 10^{-2}$ mmol/h was calculated.

The same analysis was repeated in deuterium acetophenone **1-*d*$_5$**. An initial rate constant $k_D = 1.75 \times 10^{-2}$ mmol/h was calculated.

The **KIE** = $\boldsymbol{k_H/k_D}$ = **2.9** was determined from the initial rates of such reaction.

Time (h)	**3** (mmol) from **1** and **2**	**3-*d*$_5$** (mmol) from **1-*d*$_5$** and **2**
0	0	0
0.16	0.011	0.003
0.33	0.02	0.006
0.5	0.025	0.008
0.6	0.028	0.011

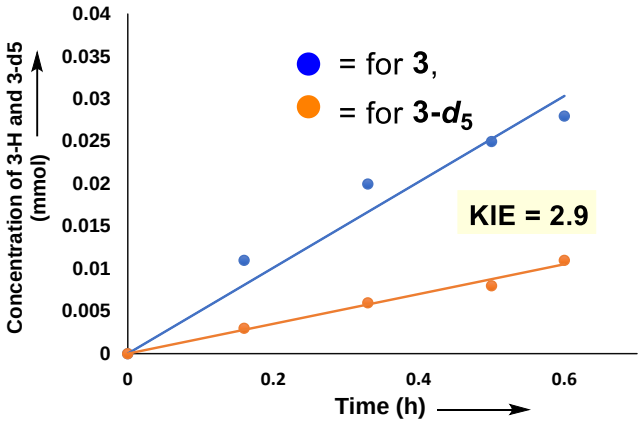
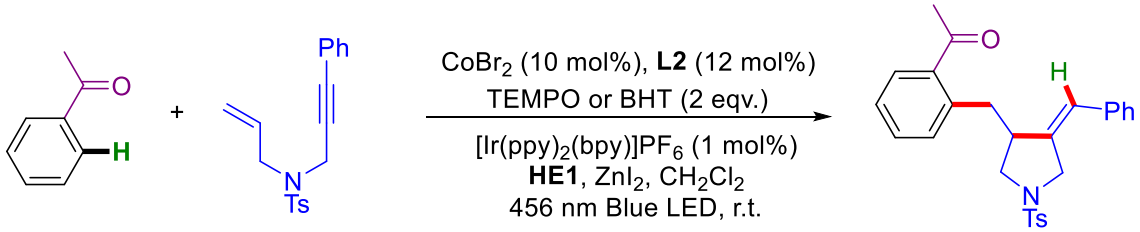


Figure S2. Determination of the kinetic isotope effect.

7.5. Radical quenching experiment:



1 2 3

TEMPO- 0%
BHT - 90%

Experimental Procedure:

In a 10 mL reaction tube, $CoBr_2$ (0.010 mmol) and **L1** (0.012 mmol) were taken under argon atmosphere. Then **PC** (0.001 mmol), **HE1** (0.2 mmol), ZnI_2 (0.02 mmol), corresponding enyne **2** (0.1 mmol), acetophenone **1** (0.12 mmol), and a radical quencher (2 mmol) were added, and the tube was closed and placed under blue LED irradiation at 456 nm. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water (2 mL), and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.

7.6. Stern-Volmer fluorescence quenching studies [6]

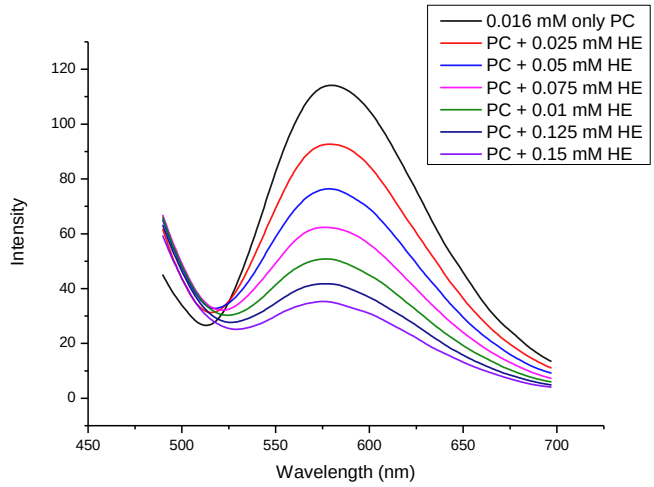
Rates of quenching (kq) were determined using Stern–Volmer kinetics (eq 1).

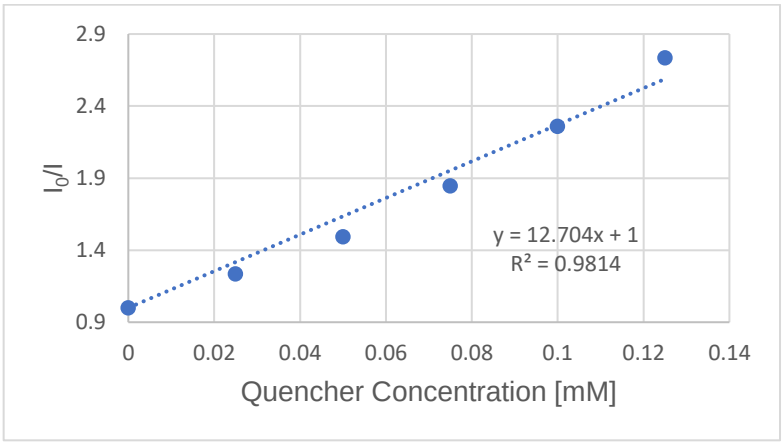
$$\frac{Io}{I} = k_q \tau_0 [\text{Quencher}] + 1 \ldots\ldots(1)$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst (390 ns for $[Ir(ppy)_2(bpy)(PF_6)]$[7] in acetonitrile).

Stern-Volmer fluorescence quenching studies were carried out using a 0.016 mM solution of $[Ir(ppy)_2(bpy)(PF_6)]$ (Cat.) in dichloromethane and variable concentrations of Hantzsch ester (HE). The samples were prepared in 3.5 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm inside an argon-filled glove bag. The solutions were irradiated at 390 nm, and the luminescence was measured at 585 nm.

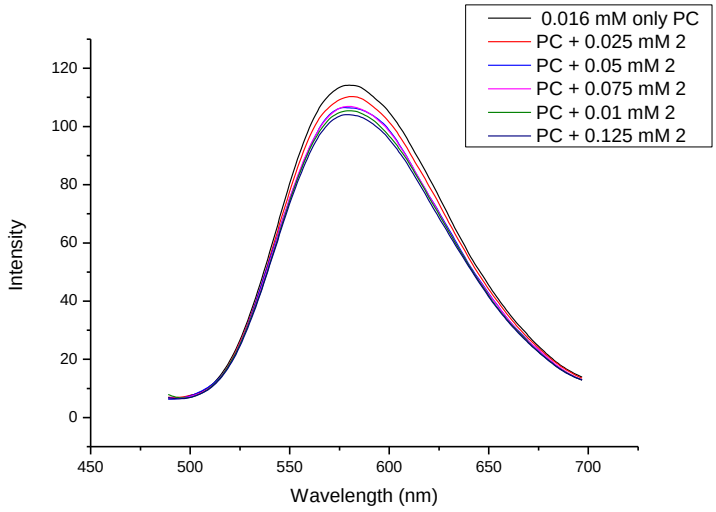
Luminescence spectra of $[Ir(ppy)_2bpy]PF_6$ with Hantzsch ester:

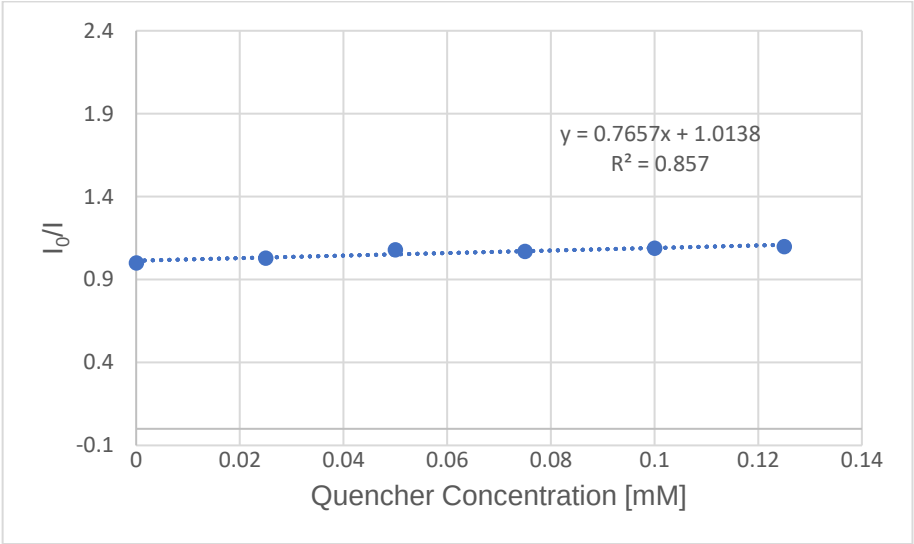




A linear Stern-Volmer plot was obtained at the variable concentration of Hantzsch ester. From the plot $k_q = 3.25\times10^7\ M^{-1}s^{-1}$ was obtained.

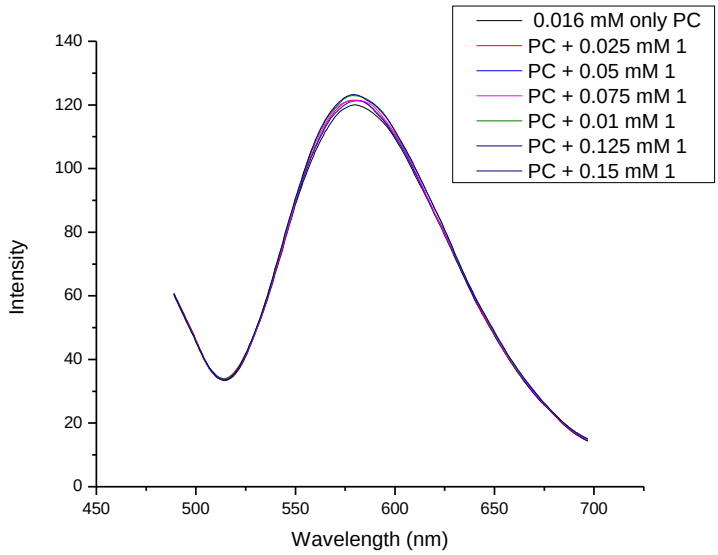
Luminescence spectra of [Ir(ppy)$_2$bpy]PF$_6$ with enyne 2:

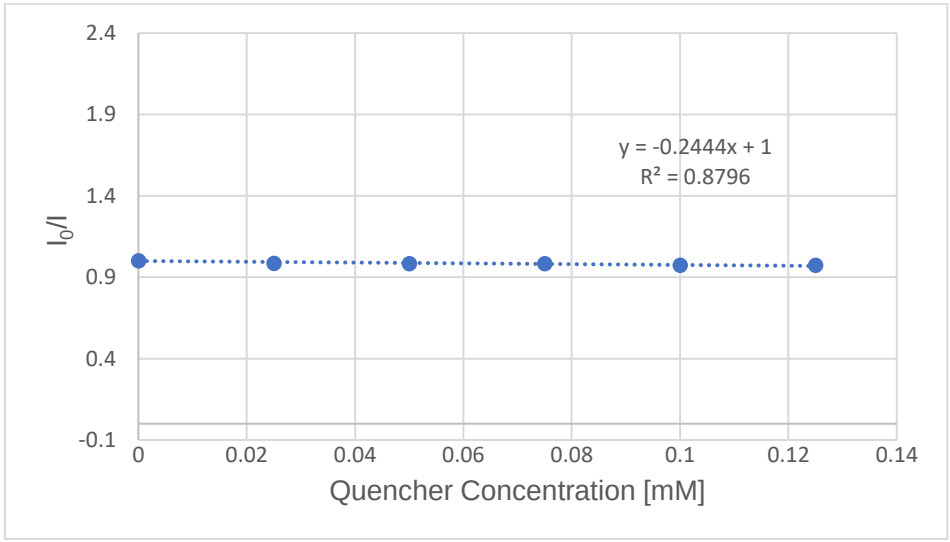




A linear Stern-Volmer plot was obtained at the variable concentration of enyne **2**. From the plot $k_q = 1.96\times10^6$ $M^{-1}s^{-1}$ was obtained.

Luminescence spectra of $[Ir(ppy)_2bpy]PF_6$ with acetophenone 1:

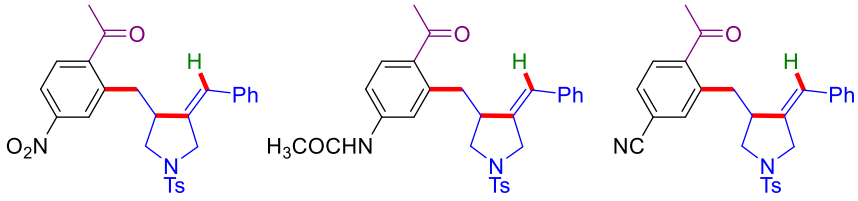




A linear Stern-Volmer plot was obtained at the variable concentration of **1**. From the plot k_q = 6.26×10^5 $M^{-1}s^{-1}$ was obtained.

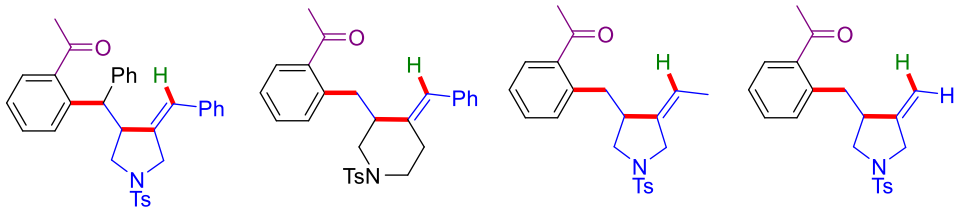
8. Unsuccessful substrates:

Acetophenones



0% conversion | 0% conversion | 0% conversion

1,6-enynes



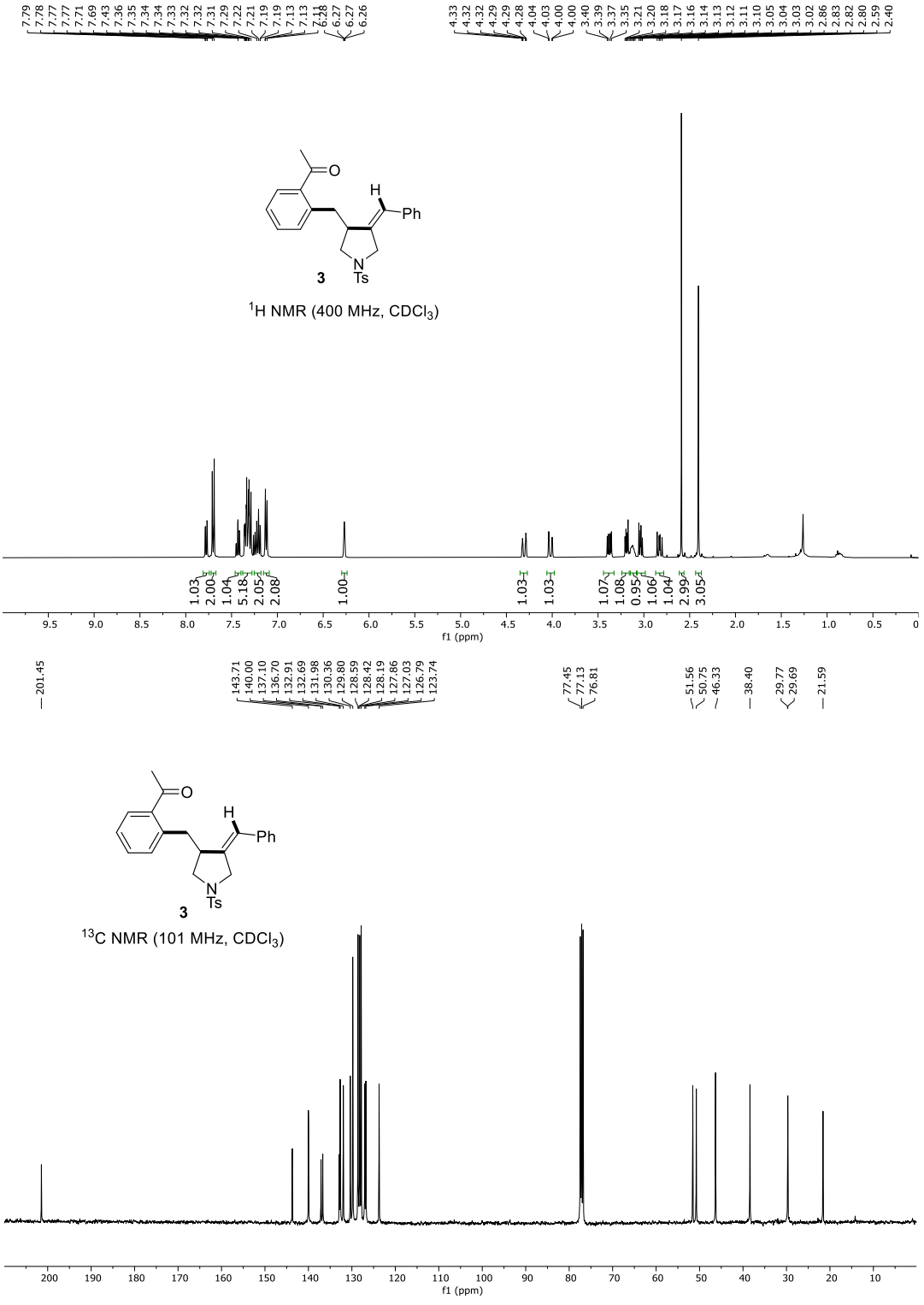
0% conversion | 12% yield | 0% conversion | 20% yield

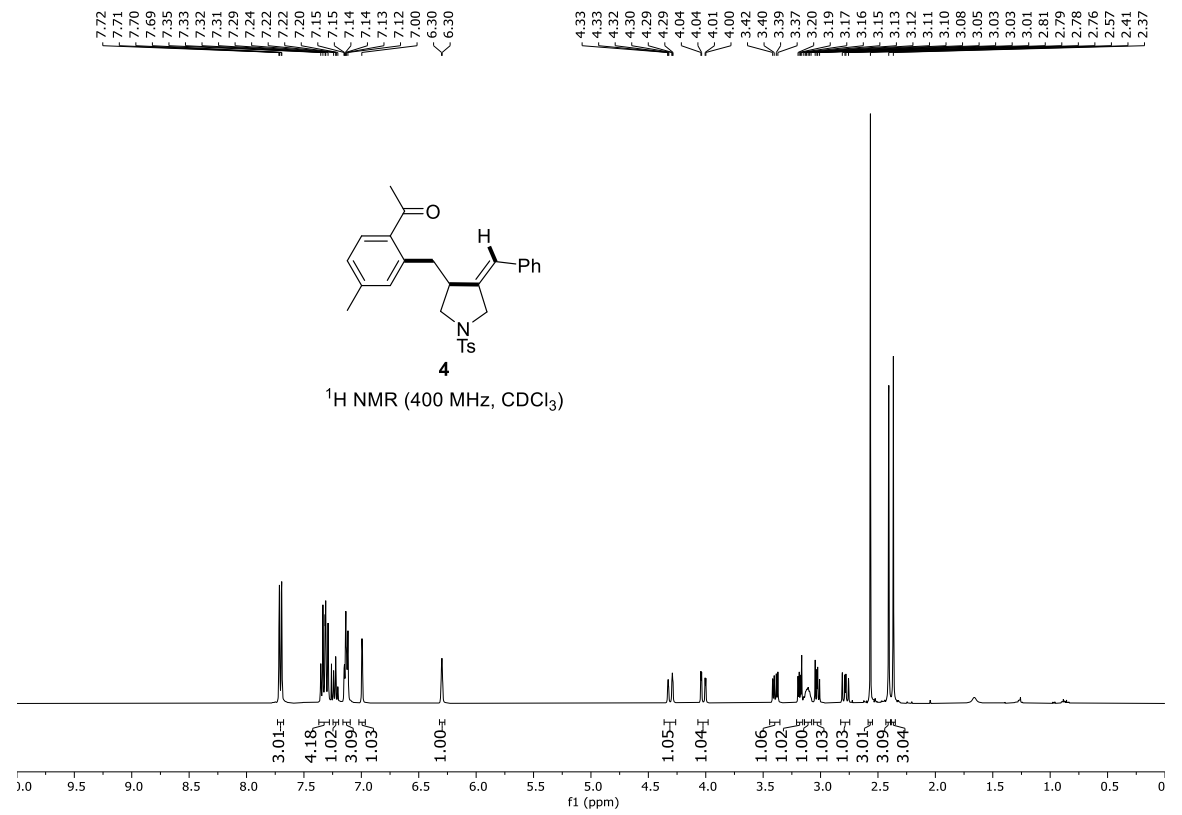
Reaction Conditions: **acetophenone** (0.12 mmol), **enyne** (0.1 mmol), **PC** (1 mol%), $CoBr_2$ (10 mol%), dppbz (12 mol%), **HE2** (0.1 mmol), ZnI_2 (20 mol%), 456 nm Blue LED in CH_2Cl_2 (0.2 M) at room temperature under Ar.

9. References

1. R. Santhoshkumar, S. Mannathan and C.-H. Cheng, *Org. Lett.*, 2014, **16**, 4208-4211.
2. A. Lin, Z.-W. Zhang and J. Yang, *Org. Lett.*, 2014, **16**, 386-389.
3. Y. You and S. Ge, *Angew. Chem. Int. Ed.*, 2021, **60**, 12046-12052.
4. R. Sun, Y. Qin and D. G. Nocera, *Angew. Chem. Int. Ed.*, 2020, **59**, 9527-9533.
5. X. Zhang and T. Rovis, *J. Am. Chem. Soc.*, 2021, **143**, 21211-21217.
6. P. Rai, K. Maji and B. Maji, *Org. Lett.*, 2019, **21**, 3755-3759.
7. J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson and S. Bernhard, *J. Am. Chem. Soc.*, 2005, **127**, 7502-7510.

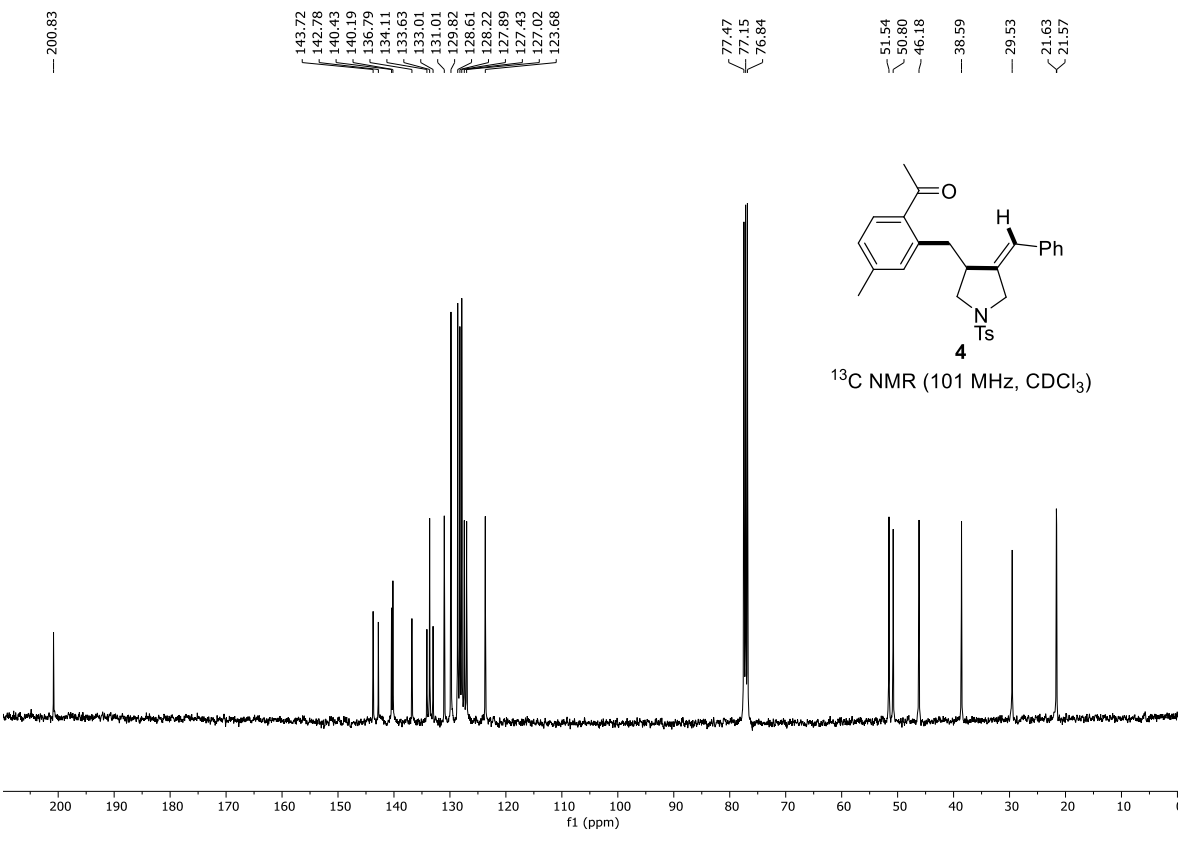
10. Copies of ^{1}H and ^{13}C NMR spectra





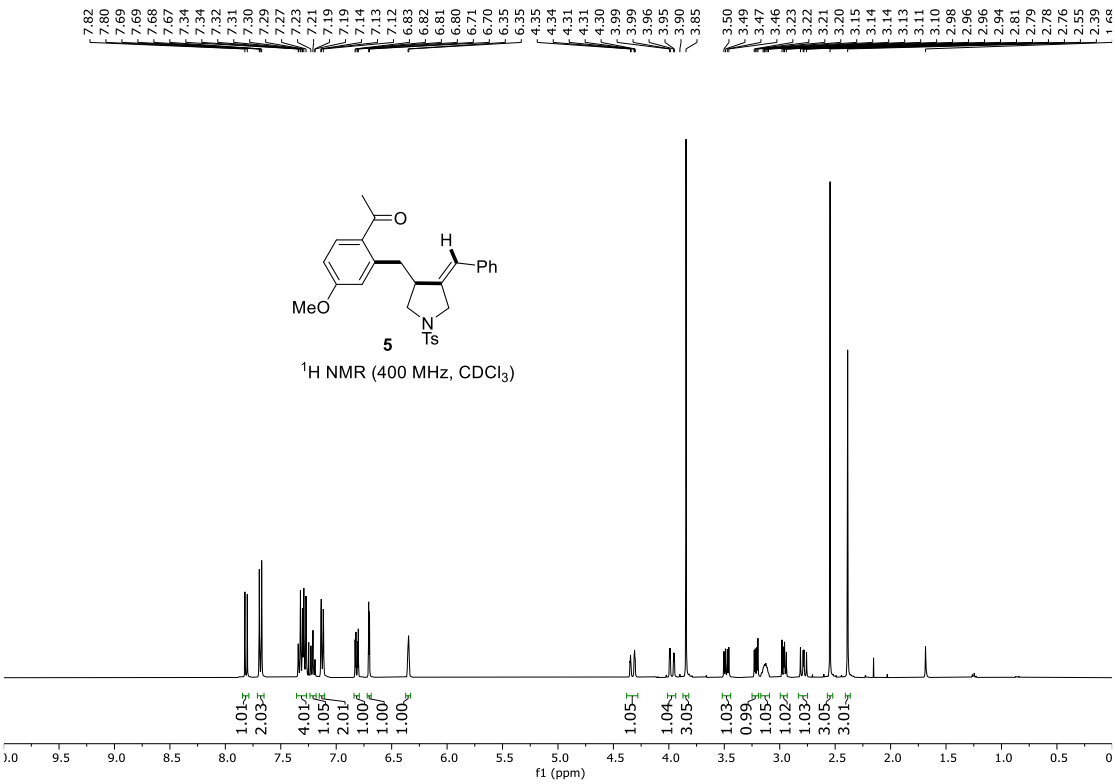
4

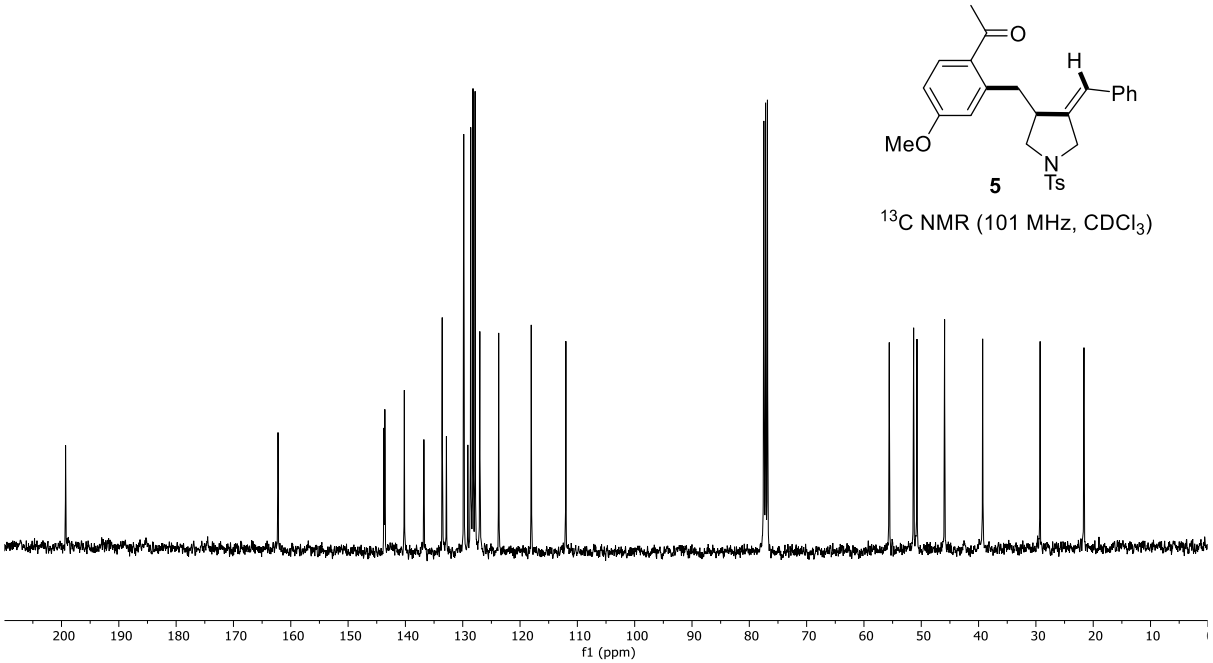
^{1}H NMR (400 MHz, $CDCl_3$)

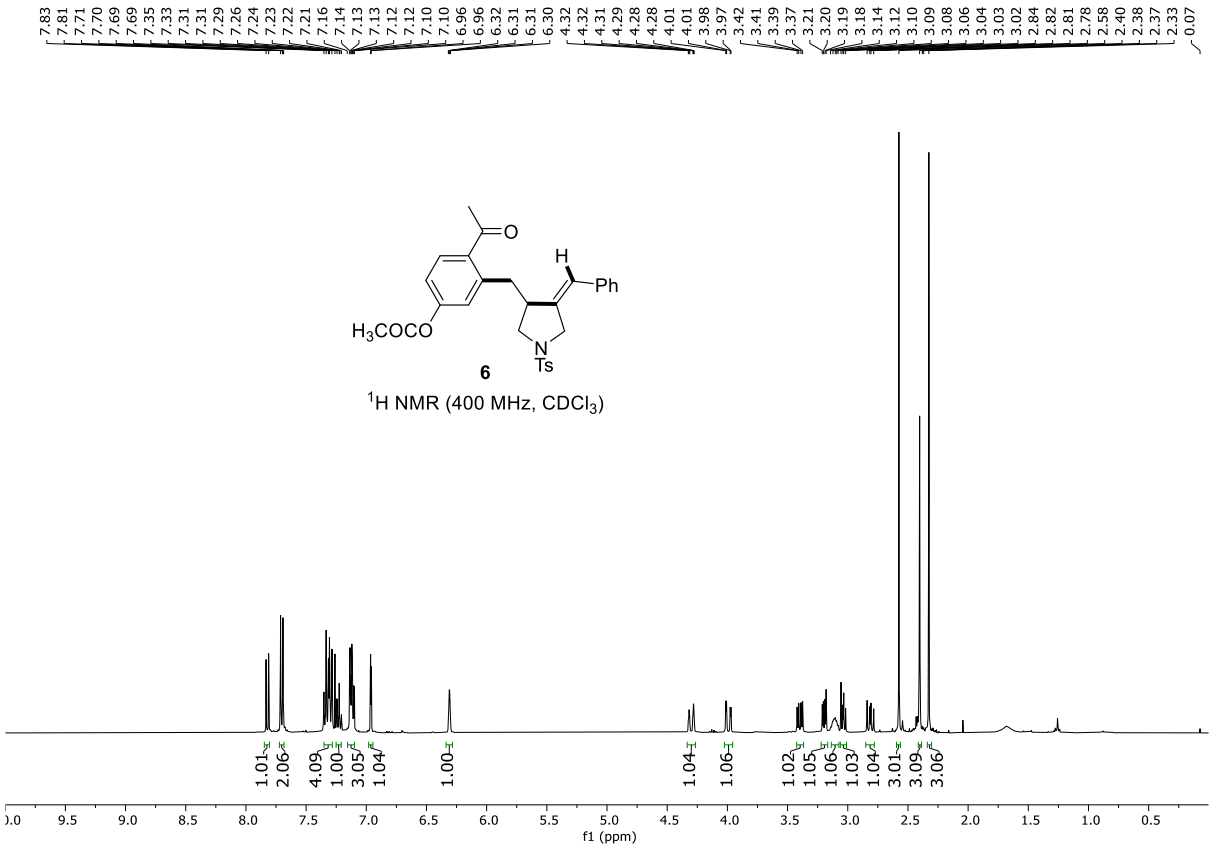


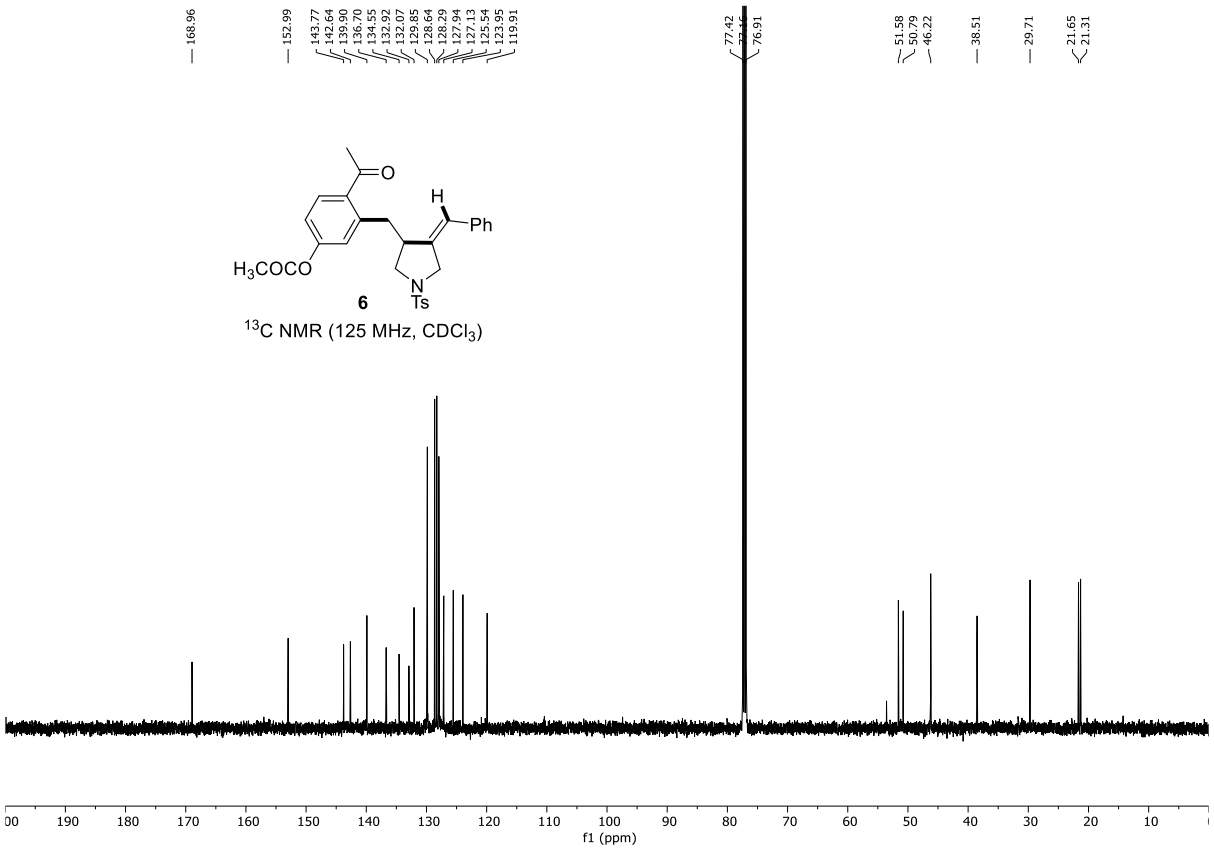
4

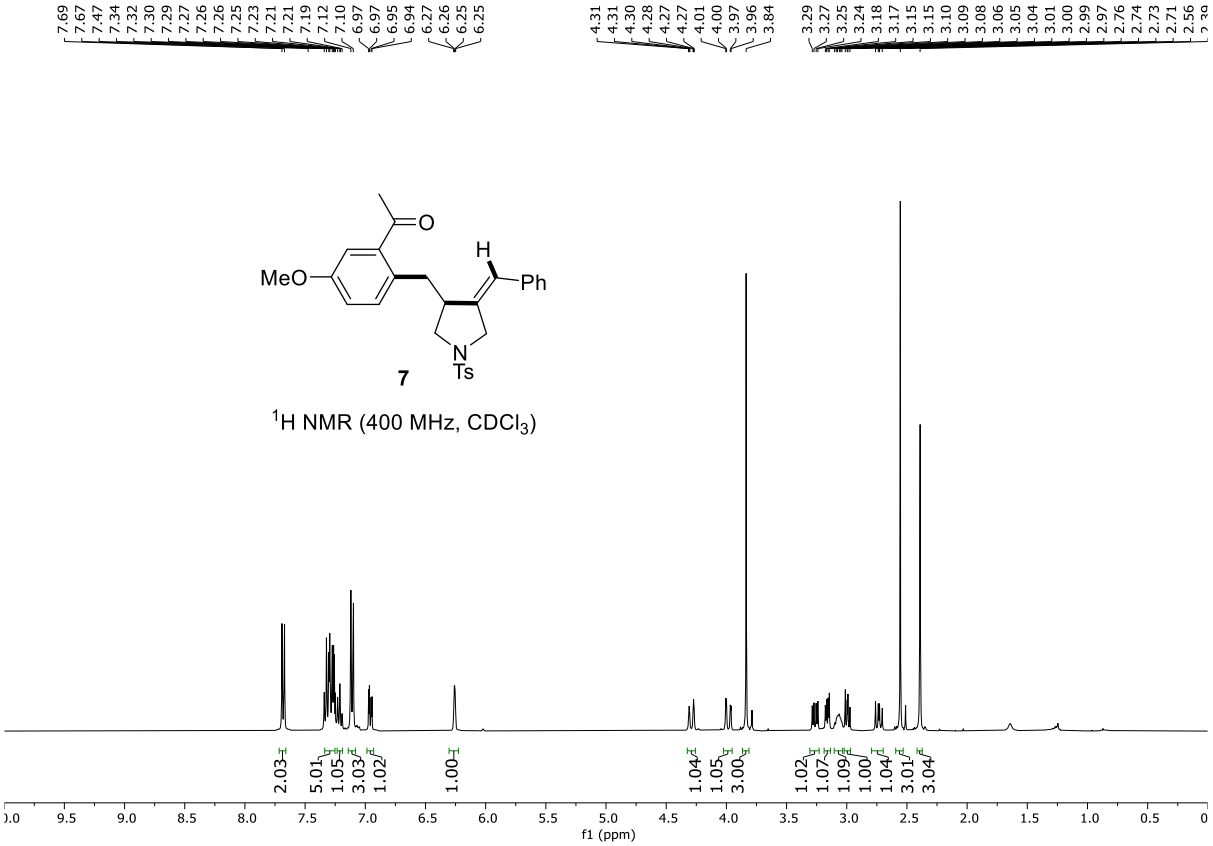
^{13}C NMR (101 MHz, $CDCl_3$)

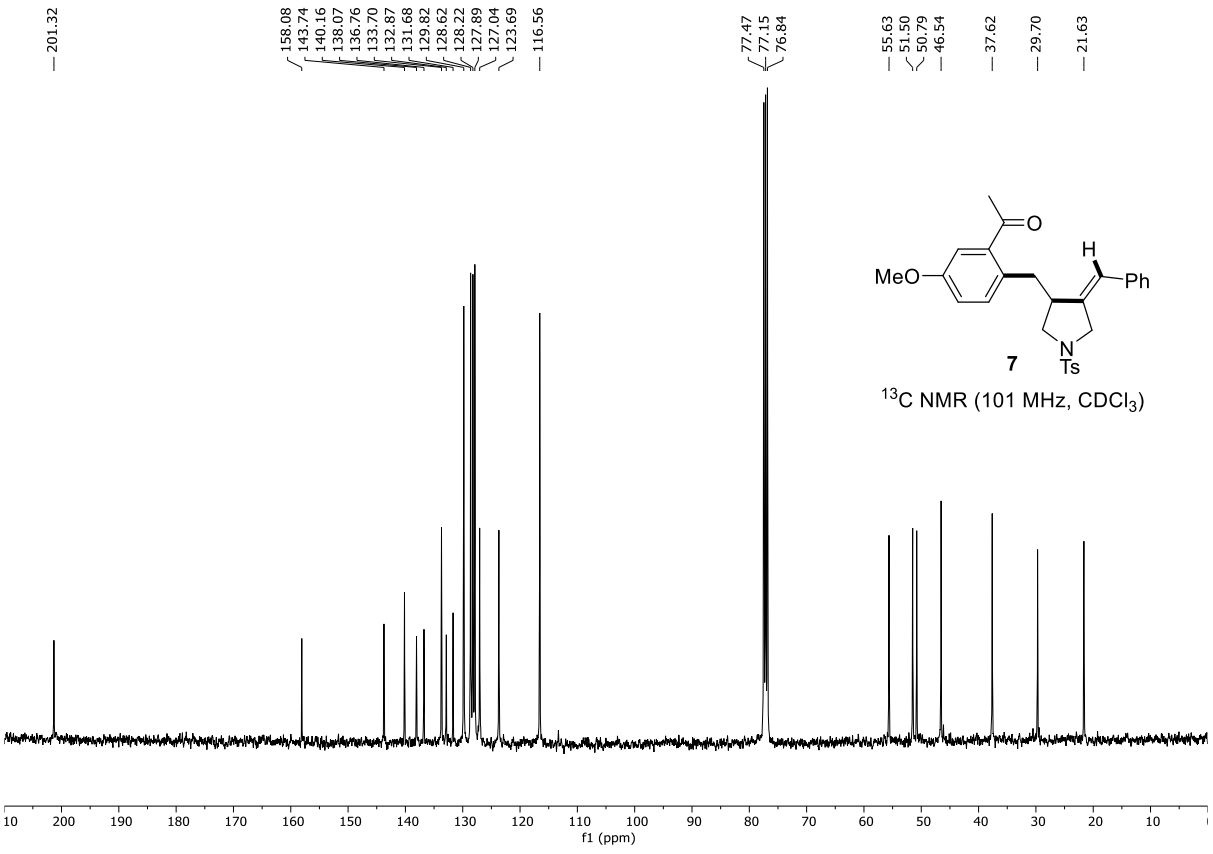

MeO
H
Ph
N
Ts
5
1H NMR (400 MHz, CDCl3)
f1 (ppm)

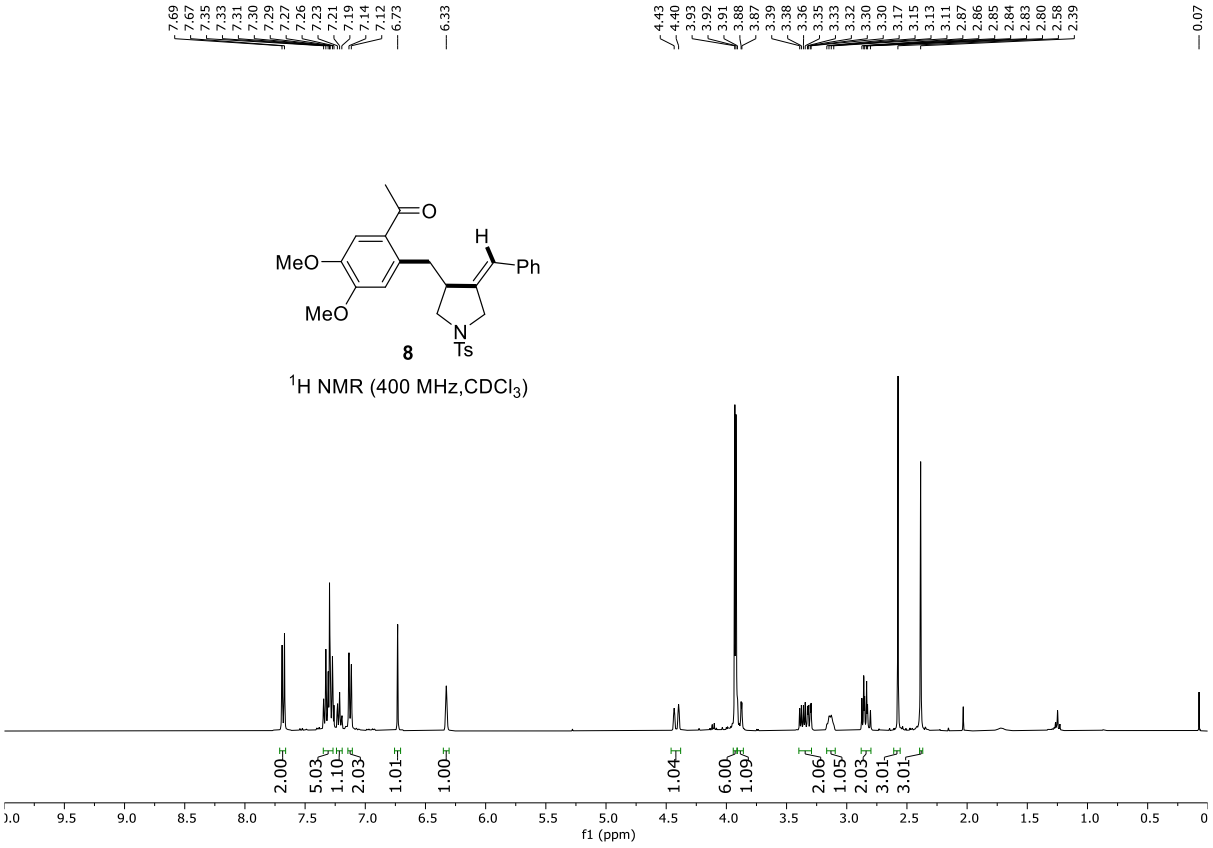

MeO
H
Ph
N
Ts
5
13C NMR (101 MHz, CDCl3)
f1 (ppm)

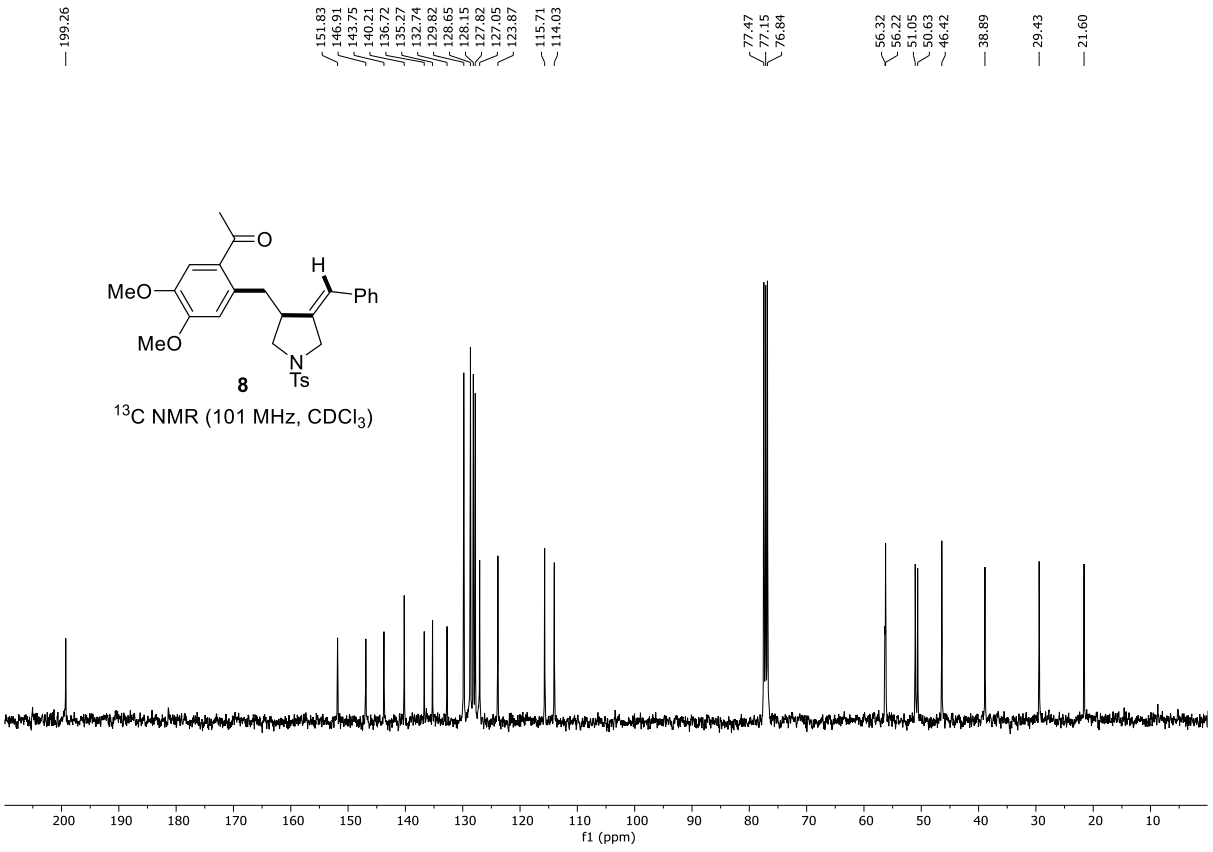

7.83 7.81 7.71 7.70 7.69 7.69 7.35 7.33 7.31 7.31 7.29 7.26 7.24 7.23 7.22 7.21 7.16 7.14 7.13 7.13 7.12 7.12 7.10 7.10 6.96 6.96 6.32 6.31 6.31 6.30
4.32 4.32 4.31 4.29 4.28 4.28 4.01 4.01 3.98 3.97 3.42 3.41 3.39 3.37 3.21 3.20 3.19 3.18 3.14 3.12 3.10 3.09 3.08 3.06 3.04 3.03 3.02 2.84 2.82 2.81 2.78 2.58 2.40 2.38 2.37 2.33 0.07
O
H
Ph
H3COCO
N
Ts
6
1H NMR (400 MHz, CDCl3)
1.01 2.06 4.09 1.00 3.05 1.04 1.00 1.04 1.06 1.02 1.05 1.06 1.03 1.04 3.01 3.09 3.06
f1 (ppm)

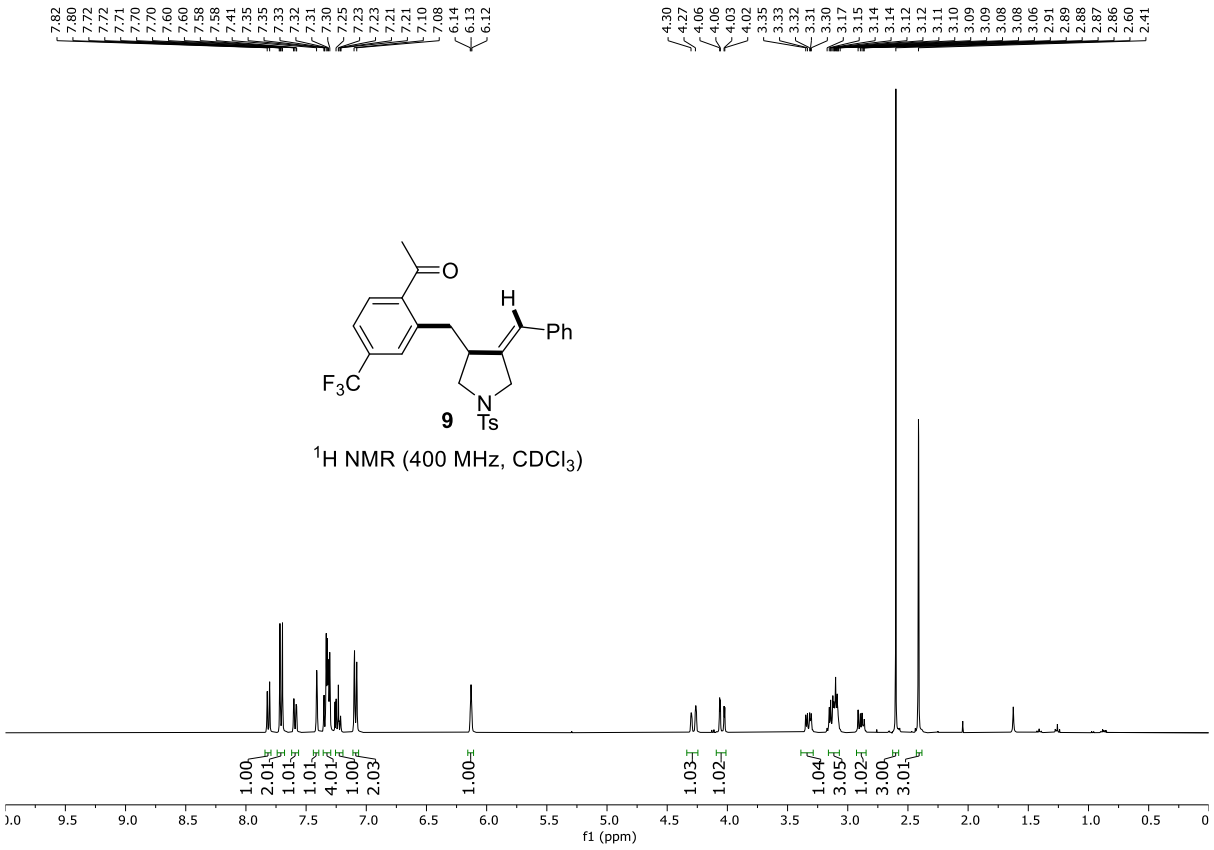

168.96 152.99 143.77 142.64 139.90 136.70 134.55 132.92 132.07 129.85 128.64 128.29 127.94 127.13 125.54 123.95 119.91
77.42 77.16 76.91
51.58 50.79 46.22 38.51 29.71 21.65 21.31
O
H
Ph
H3COCO
N
Ts
6
13C NMR (125 MHz, CDCl3)
f1 (ppm)

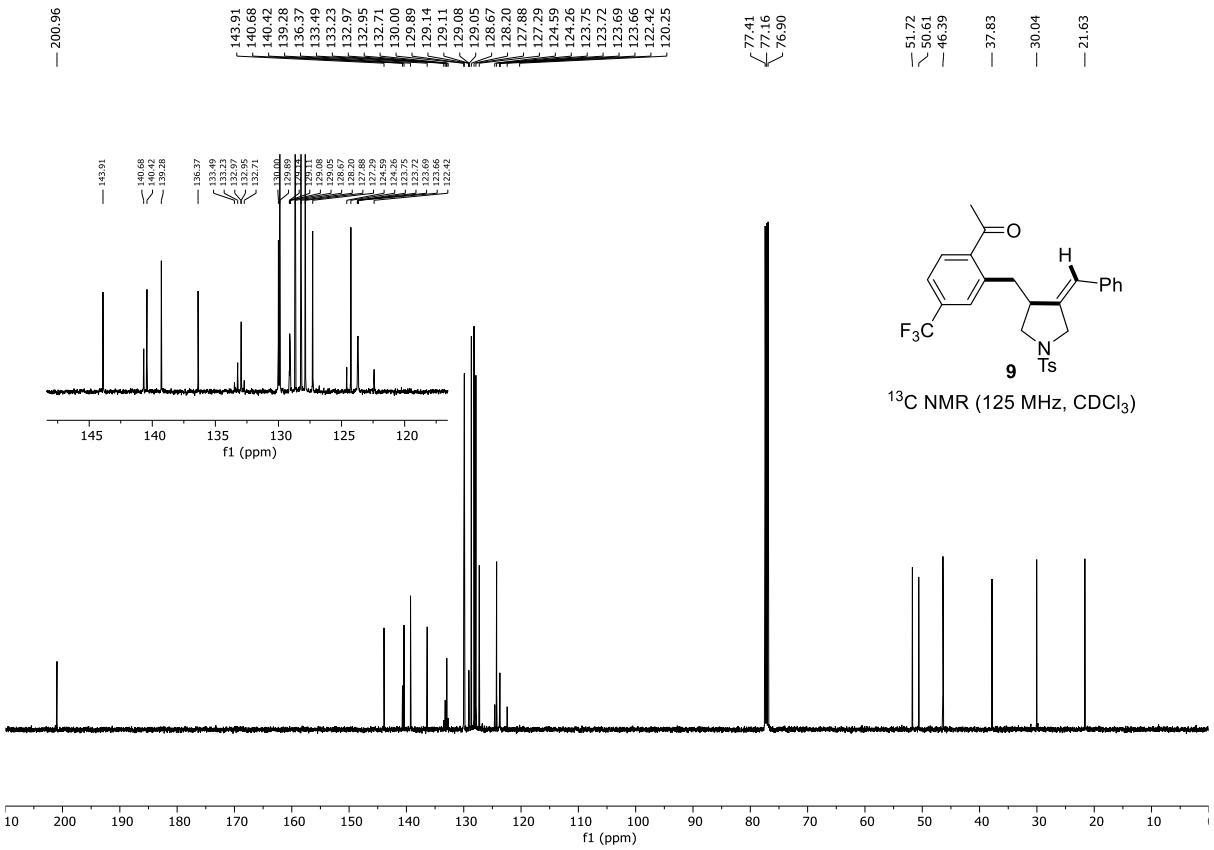

7.69 7.67 7.47 7.34 7.32 7.30 7.29 7.27 7.26 7.26 7.25 7.23 7.21 7.21 7.19 7.12 7.10 6.97 6.97 6.95 6.94 6.27 6.26 6.25 6.25
4.31 4.31 4.30 4.28 4.27 4.27 4.01 4.00 3.97 3.96 3.84
3.29 3.27 3.25 3.24 3.18 3.17 3.15 3.15 3.10 3.09 3.08 3.06 3.05 3.04 3.01 3.00 2.99 2.97 2.76 2.74 2.73 2.71 2.56
O
H
MeO
Ph
N
Ts
7
^{1}H NMR (400 MHz, $CDCl_3$)
2.03 5.01 1.05 3.03 1.02 1.00 1.04 1.05 3.00 1.02 1.07 1.09 1.00 1.04 3.01 3.04
f1 (ppm)

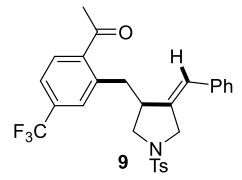

201.32
158.08 143.74 140.16 138.07 136.76 133.70 132.87 131.68 129.82 128.62 128.22 127.89 127.04 123.69 116.56
77.47 77.15 76.84
55.63 51.50 50.79 46.54 37.62 29.70 21.63
O
H
MeO
Ph
N
Ts
7
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


7.69
7.67
7.35
7.33
7.31
7.30
7.29
7.27
7.26
7.23
7.21
7.19
7.14
7.12
6.73
6.33
4.43
4.40
3.93
3.92
3.91
3.88
3.87
3.39
3.38
3.36
3.35
3.33
3.32
3.30
3.30
3.17
3.15
3.13
3.11
2.87
2.86
2.85
2.84
2.83
2.80
2.58
2.39
0.07
MeO
MeO
O
H
Ph
N
Ts
8
^{1}H NMR (400 MHz,CDCl$_3$)
2.00
5.03
1.10
2.03
1.01
1.00
1.04
6.00
1.09
2.06
1.05
2.03
3.01
3.01
f1 (ppm)


199.26
151.83
146.91
143.75
140.21
136.72
135.27
132.74
129.82
128.65
128.15
127.82
127.05
123.87
115.71
114.03
77.47
77.15
76.84
56.32
56.22
51.05
50.63
46.42
38.89
29.43
21.60
MeO
MeO
O
H
Ph
N
Ts
8
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

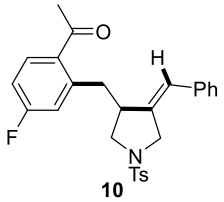

7.82
7.80
7.72
7.72
7.71
7.70
7.70
7.60
7.60
7.58
7.58
7.41
7.35
7.35
7.33
7.32
7.31
7.30
7.25
7.23
7.23
7.21
7.21
7.10
7.08
6.14
6.13
6.12
4.30
4.27
4.06
4.06
4.03
4.02
3.35
3.33
3.32
3.31
3.30
3.17
3.15
3.14
3.14
3.12
3.12
3.11
3.10
3.09
3.09
3.08
3.08
3.06
2.91
2.89
2.88
2.87
2.86
2.60
2.41
O
H
Ph
F3C
N
Ts
9
1H NMR (400 MHz, CDCl3)
1.00
2.01
1.01
1.01
4.01
1.00
2.03
1.00
1.03
1.02
1.04
3.05
1.02
3.00
3.01
f1 (ppm)


200.96
143.91
140.68
140.42
139.28
136.37
133.49
133.23
132.97
132.95
132.71
130.00
129.89
129.14
129.11
129.08
129.05
128.67
128.20
127.88
127.29
124.59
124.26
123.75
123.72
123.69
123.66
122.42
120.25
77.41
77.16
76.90
51.72
50.61
46.39
37.83
30.04
21.63
f1 (ppm)
O
H
Ph
F3C
N
Ts
9
13C NMR (125 MHz, CDCl3)



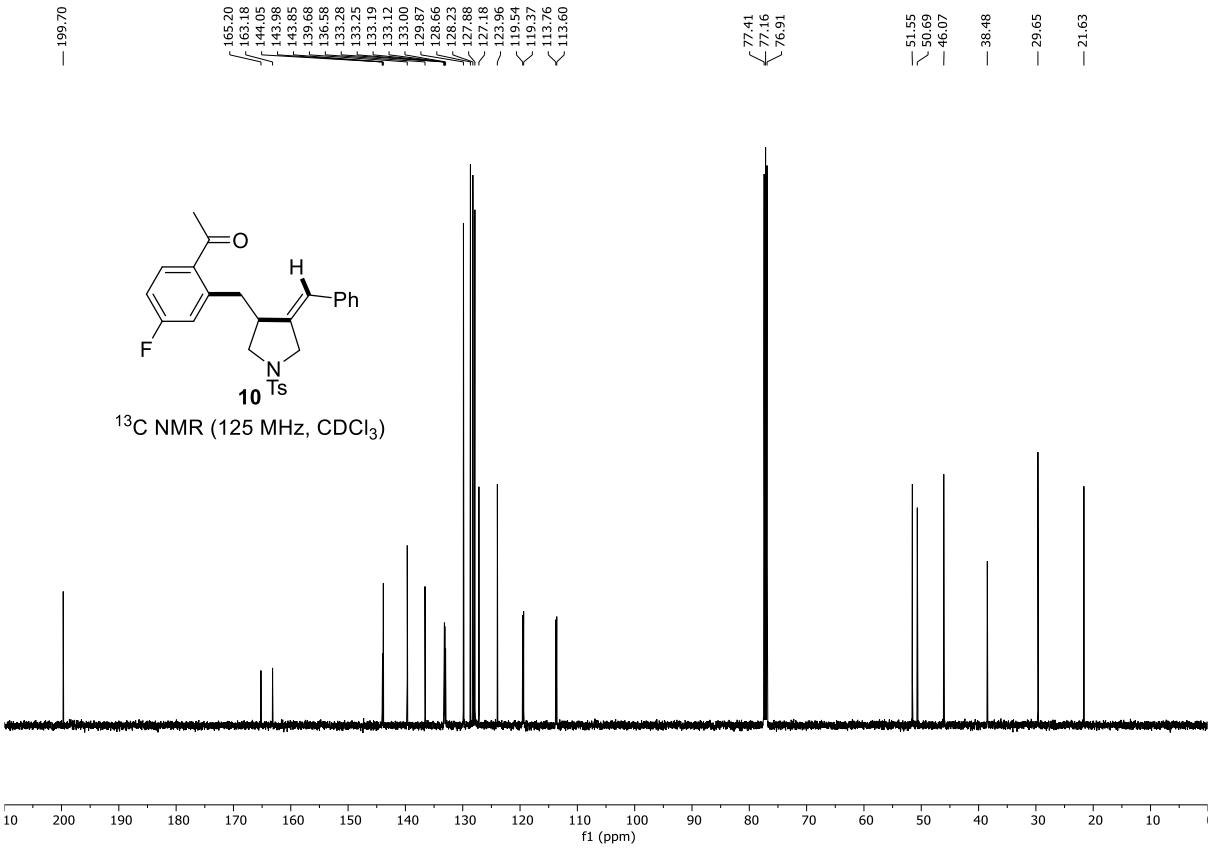
9

^{19}F NMR (376 MHz, $CDCl_3$)

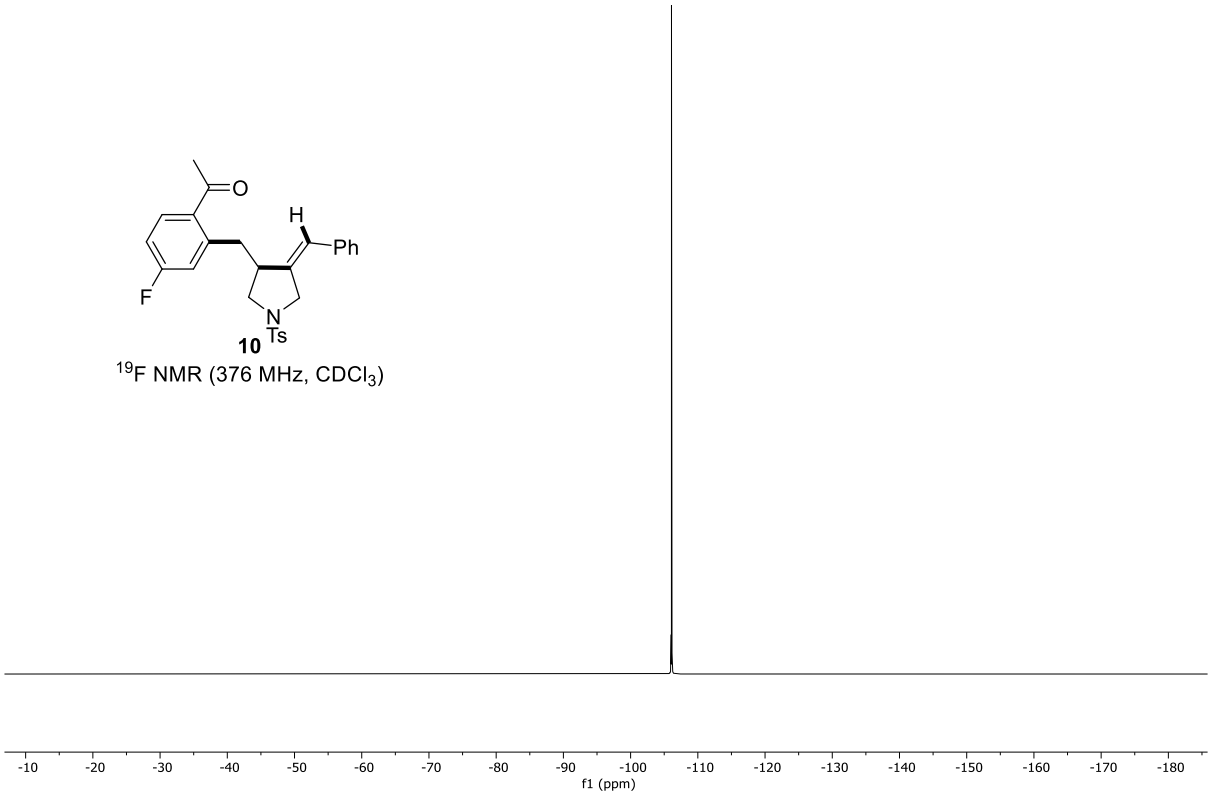


10

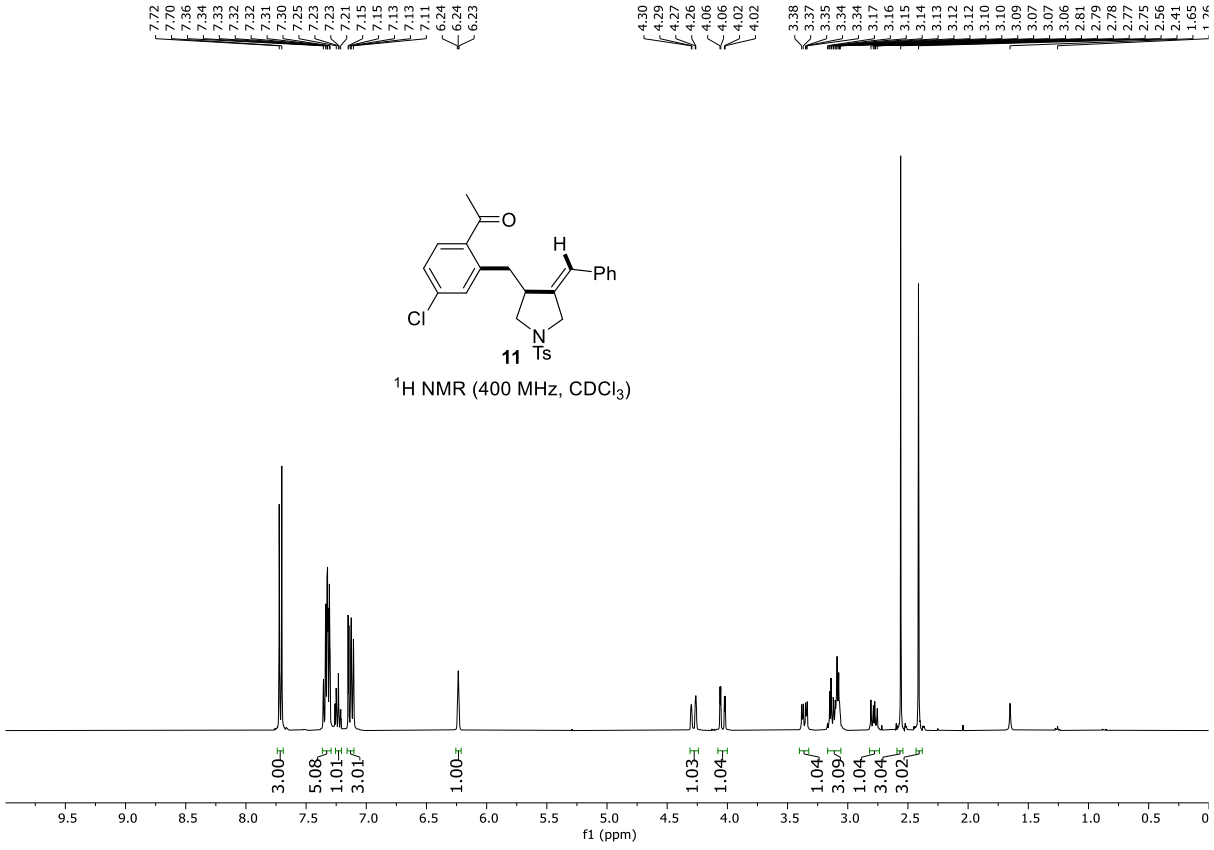
^{1}H NMR (400 MHz, $CDCl_3$)

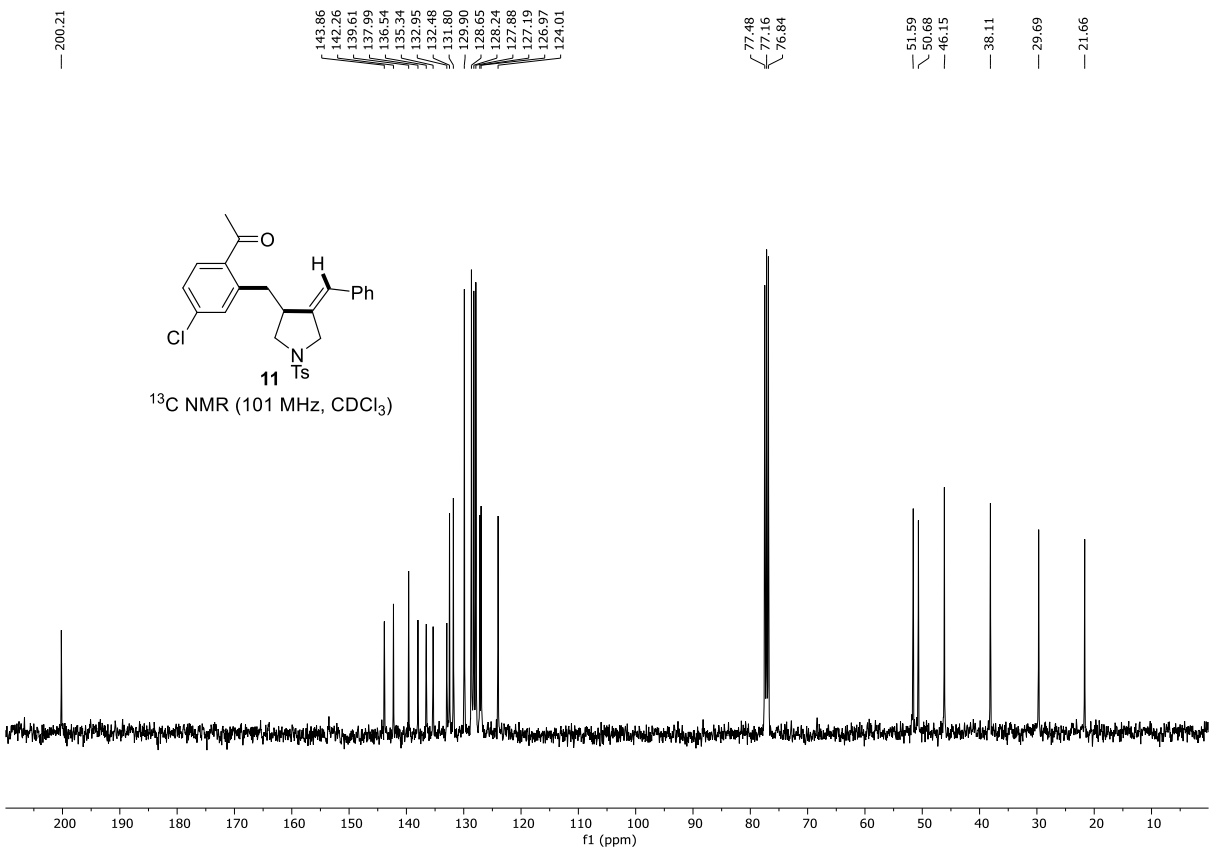


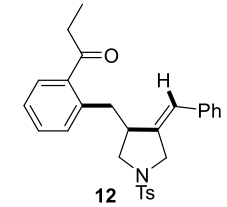
^{13}C NMR (125 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

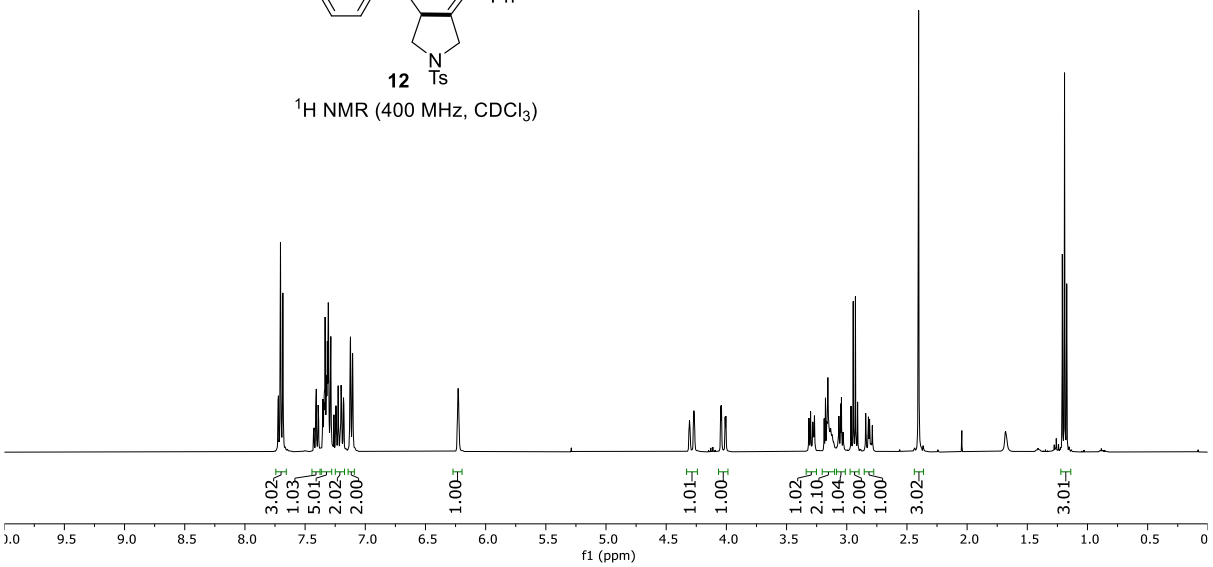

7.72 7.70 7.36 7.34 7.33 7.32 7.32 7.31 7.30 7.25 7.23 7.23 7.21 7.15 7.15 7.13 7.13 7.11 6.24 6.24 6.23
4.30 4.29 4.27 4.26 4.06 4.06 4.02 4.02
3.38 3.37 3.35 3.34 3.34 3.17 3.16 3.15 3.14 3.13 3.12 3.12 3.10 3.10 3.09 3.07 3.07 3.06 2.81 2.79 2.78 2.77 2.75 2.56 2.41 1.65
O
H
Ph
Cl
N
Ts
11
1H NMR (400 MHz, CDCl3)
3.00 5.08 1.01 3.01 1.00 1.03 1.04 1.04 3.09 1.04 3.04 3.02
f1 (ppm)

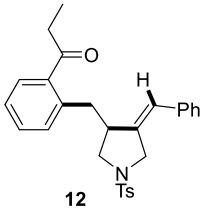

200.21
143.86 142.26 139.61 137.99 136.54 135.34 132.95 132.48 131.80 129.90 128.65 128.24 127.88 127.19 126.97 124.01
77.48 77.16 76.84
51.59 50.68 46.15 38.11 29.69 21.66
O
H
Ph
Cl
N
Ts
11
13C NMR (101 MHz, CDCl3)
f1 (ppm)



12

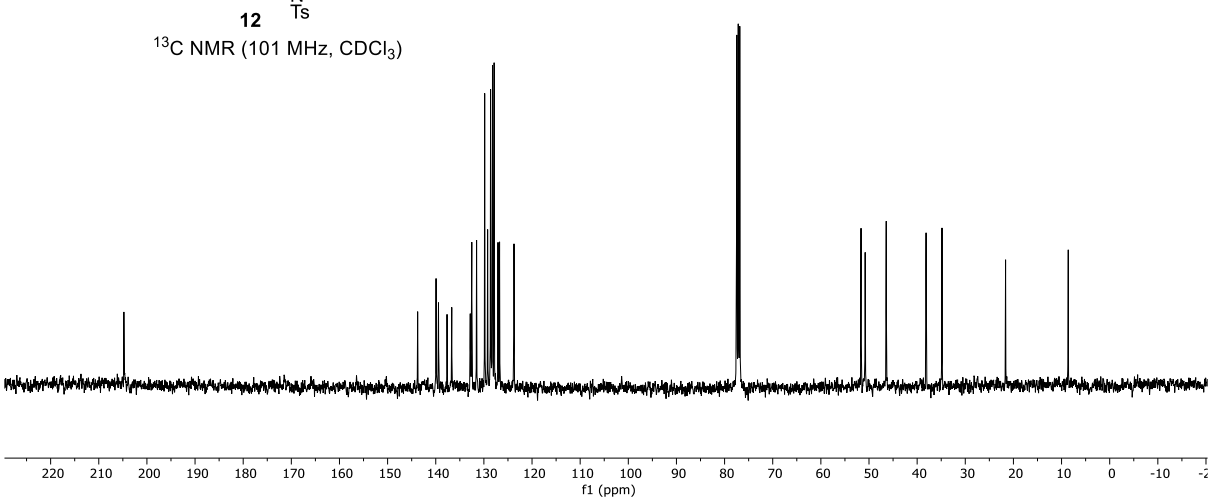
^{1}H NMR (400 MHz, $CDCl_3$)

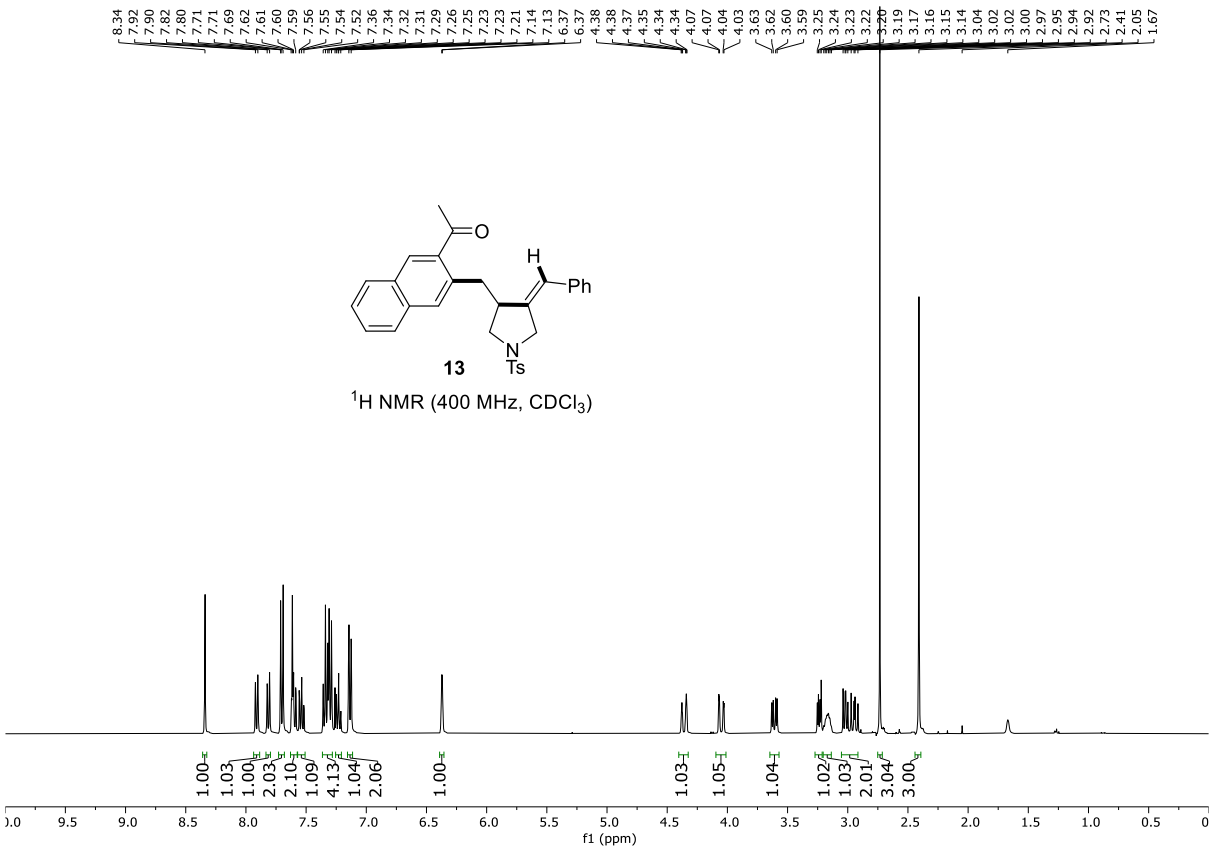




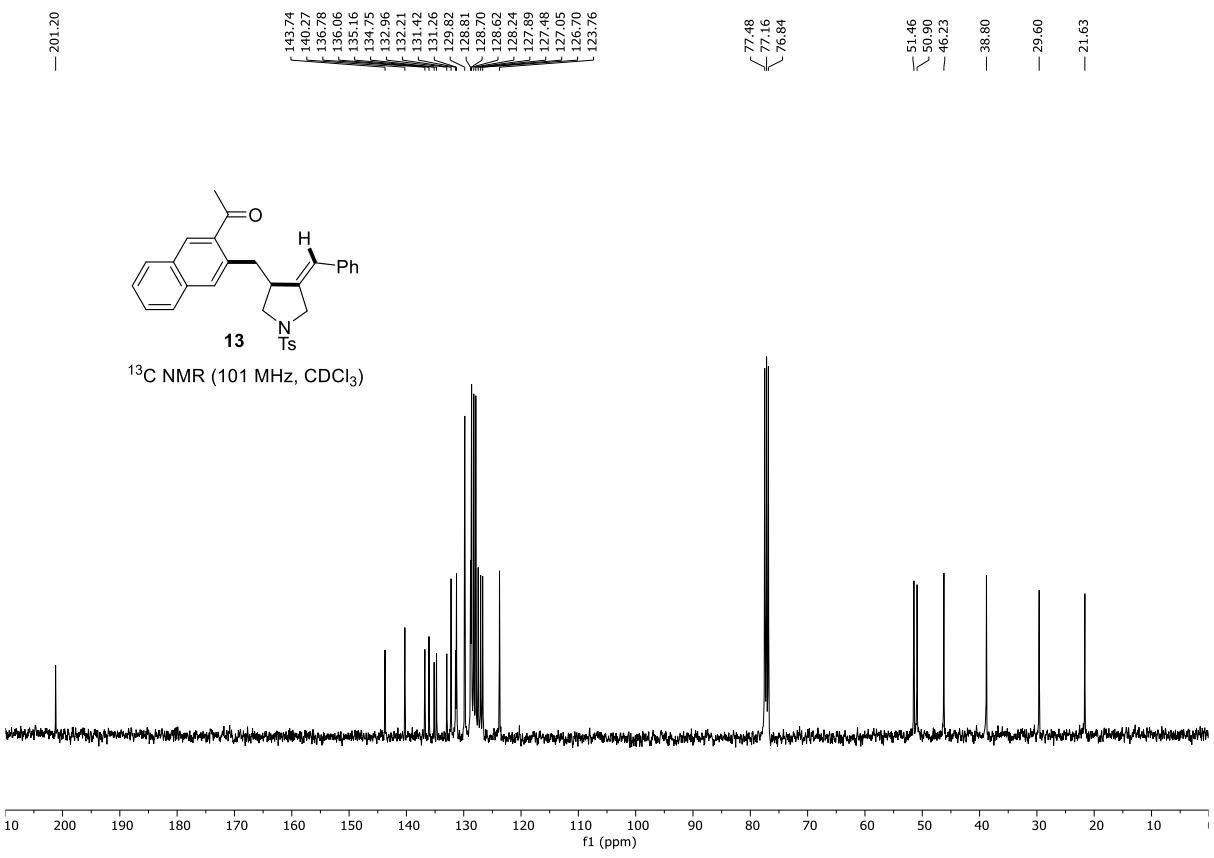
12

^{13}C NMR (101 MHz, $CDCl_3$)

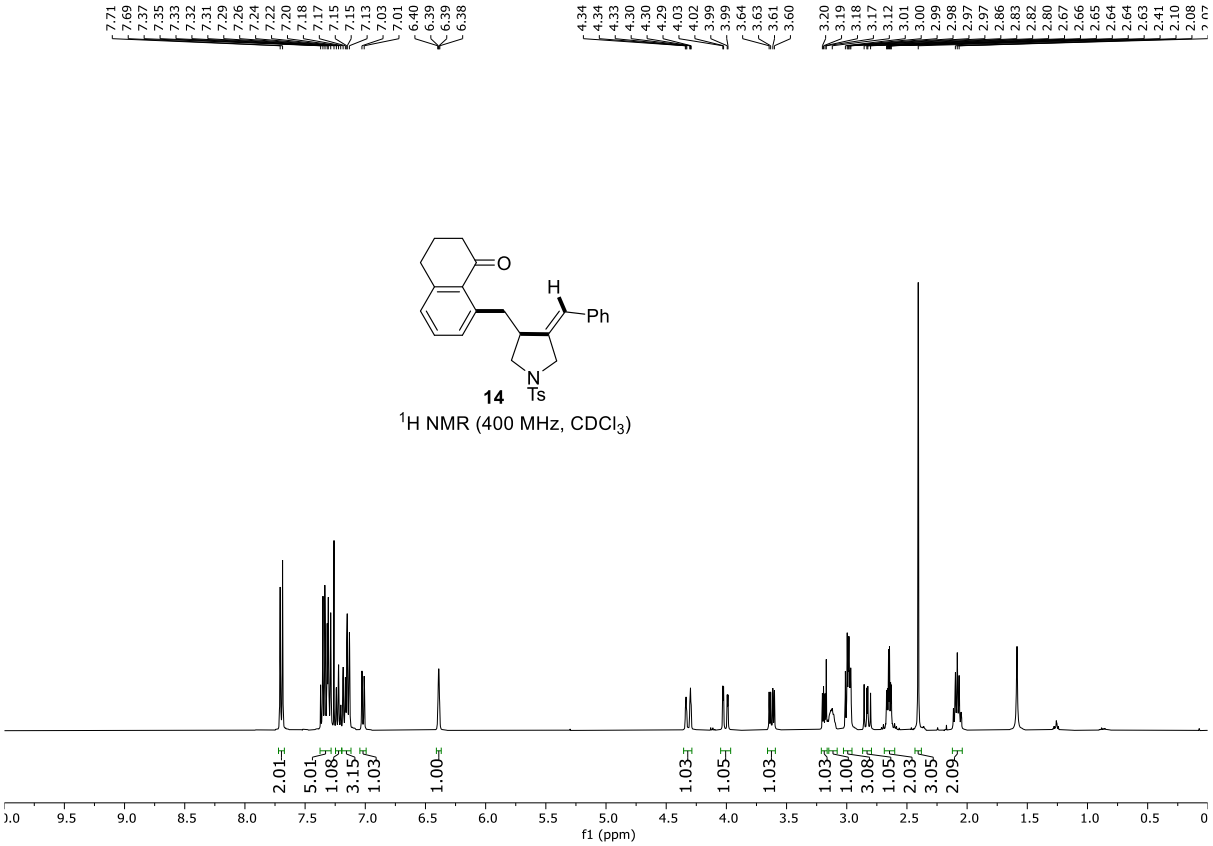


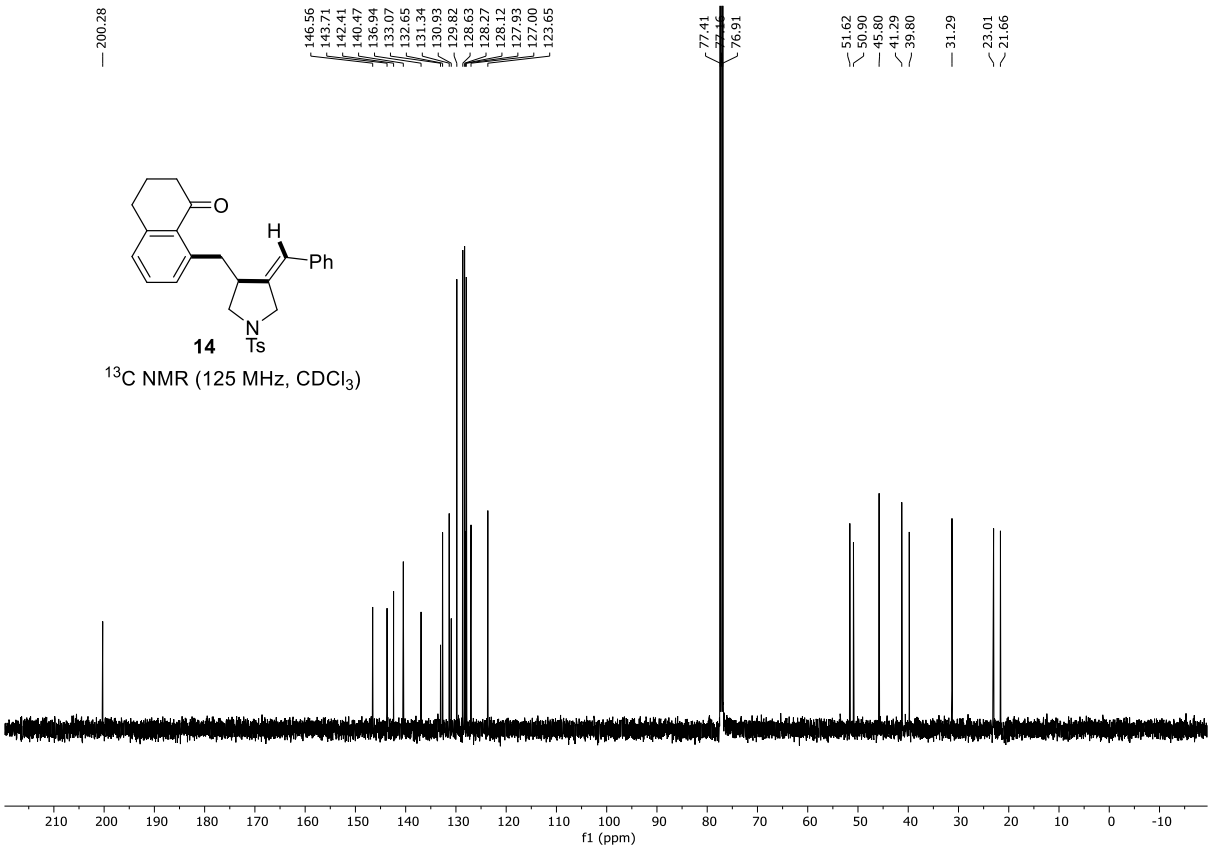


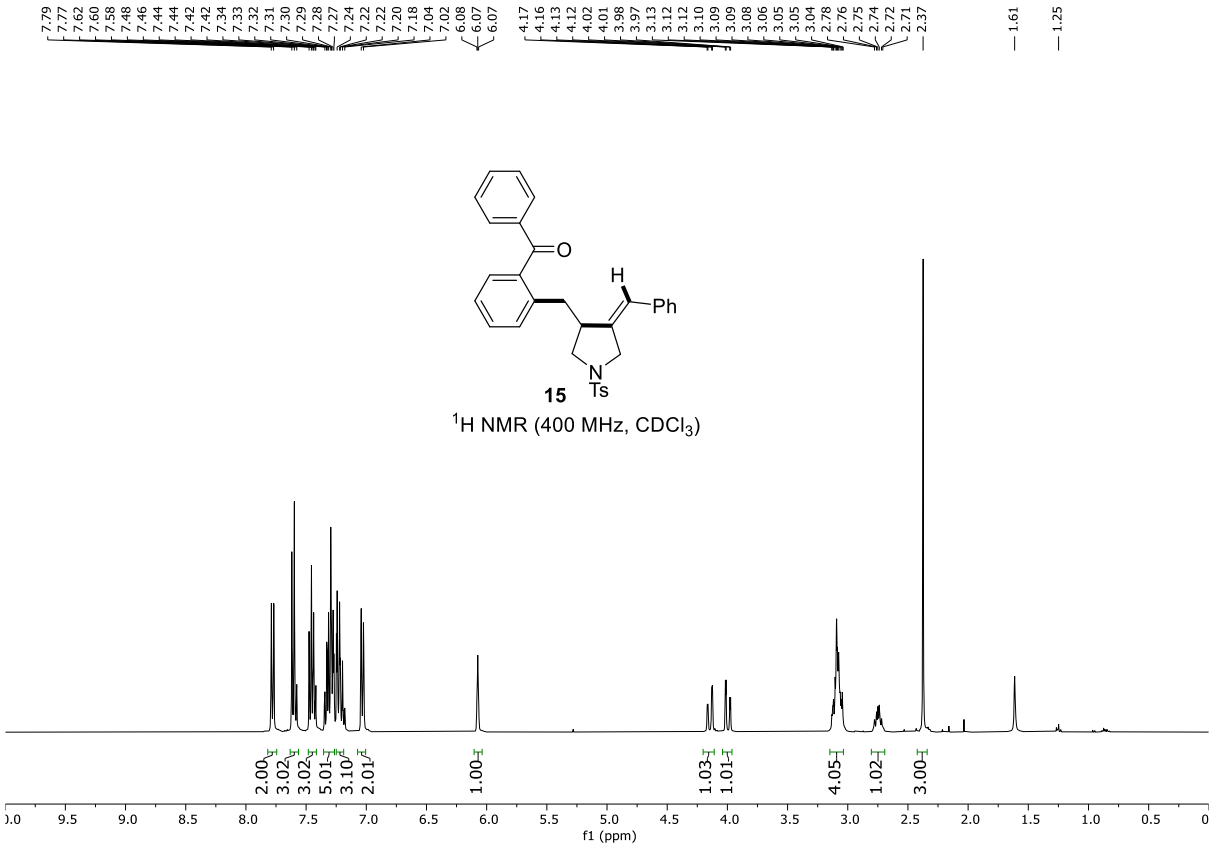
^{1}H NMR (400 MHz, $CDCl_3$)

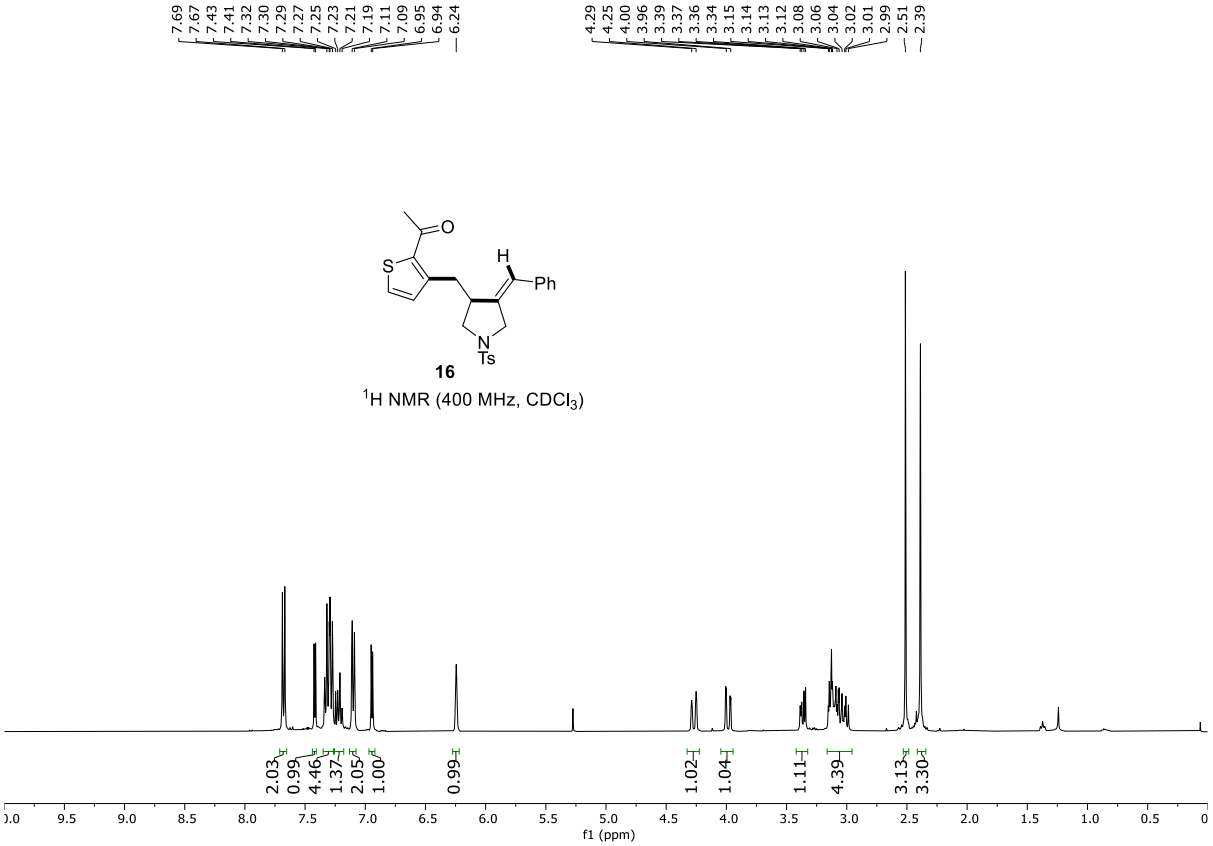


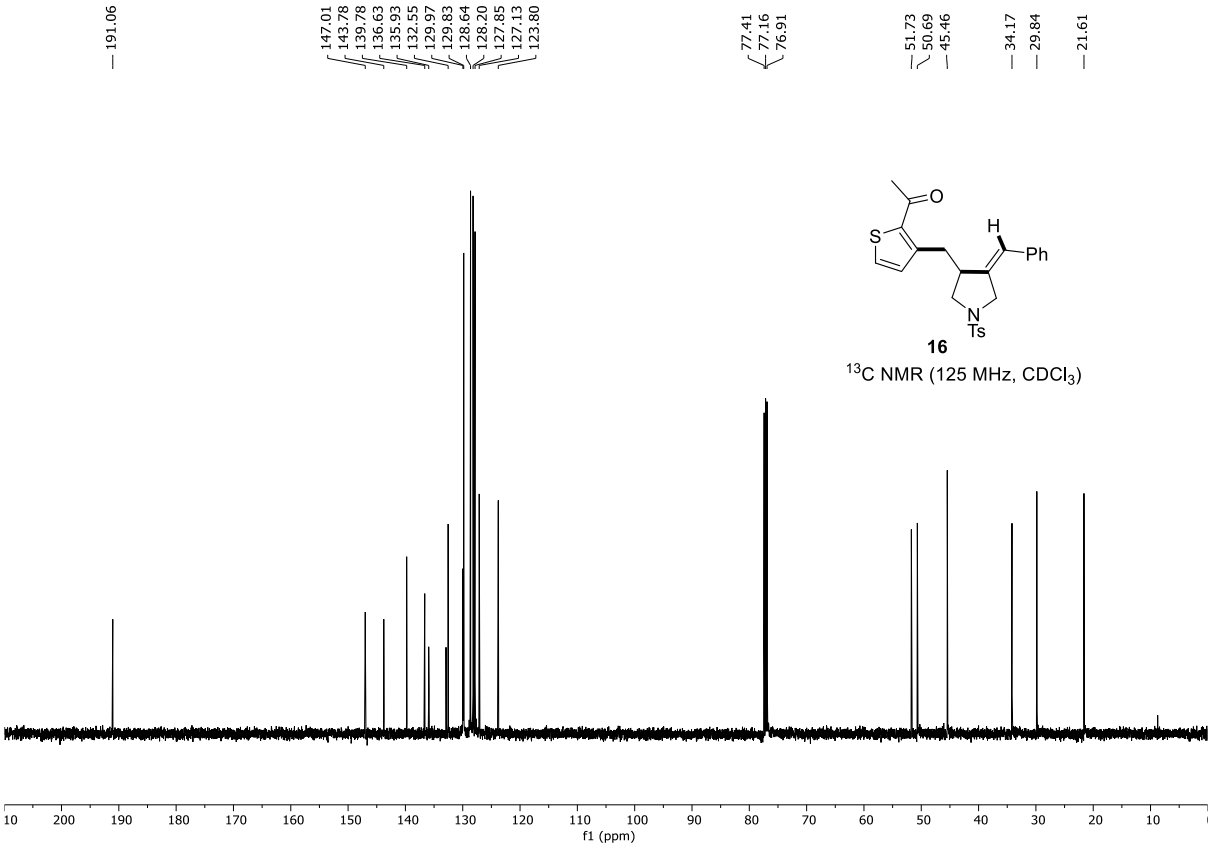
^{13}C NMR (101 MHz, $CDCl_3$)

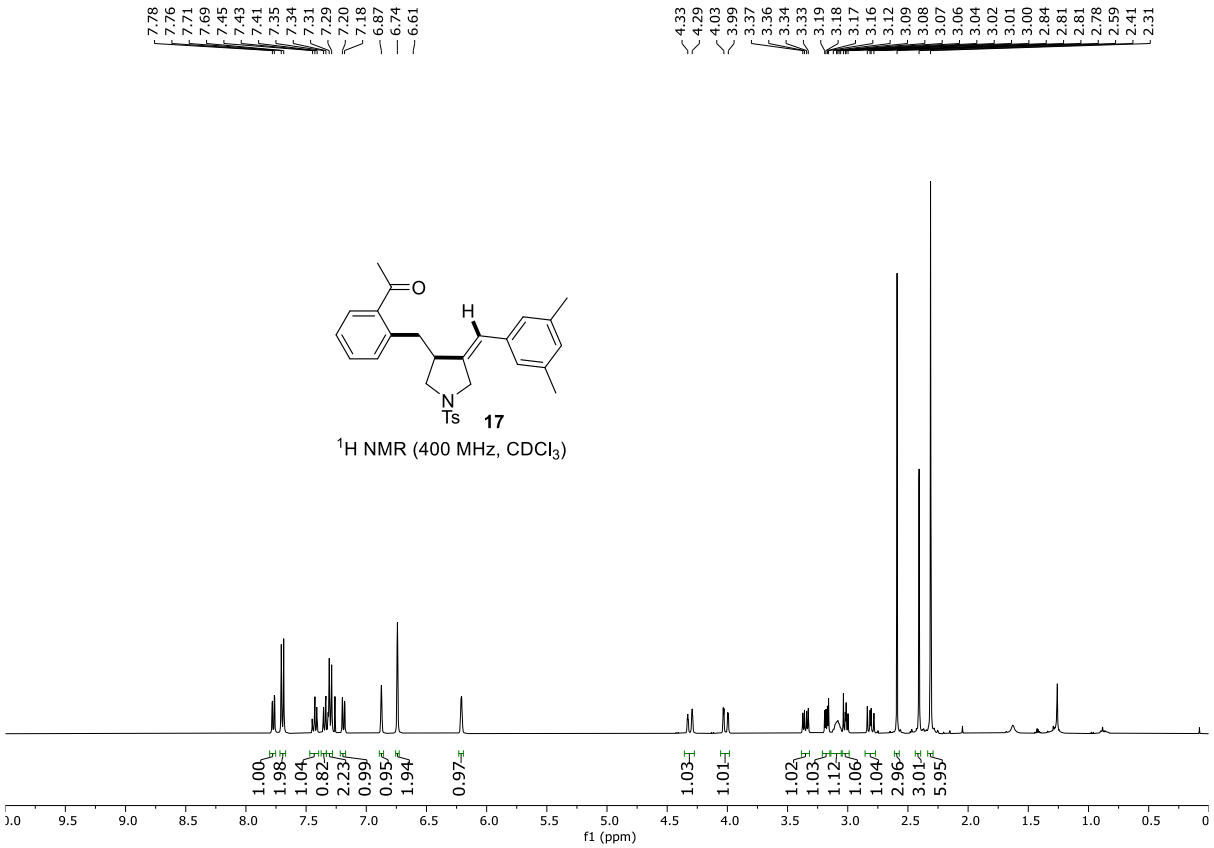

O
H
Ph
N
Ts
14
1H NMR (400 MHz, CDCl3)
f1 (ppm)

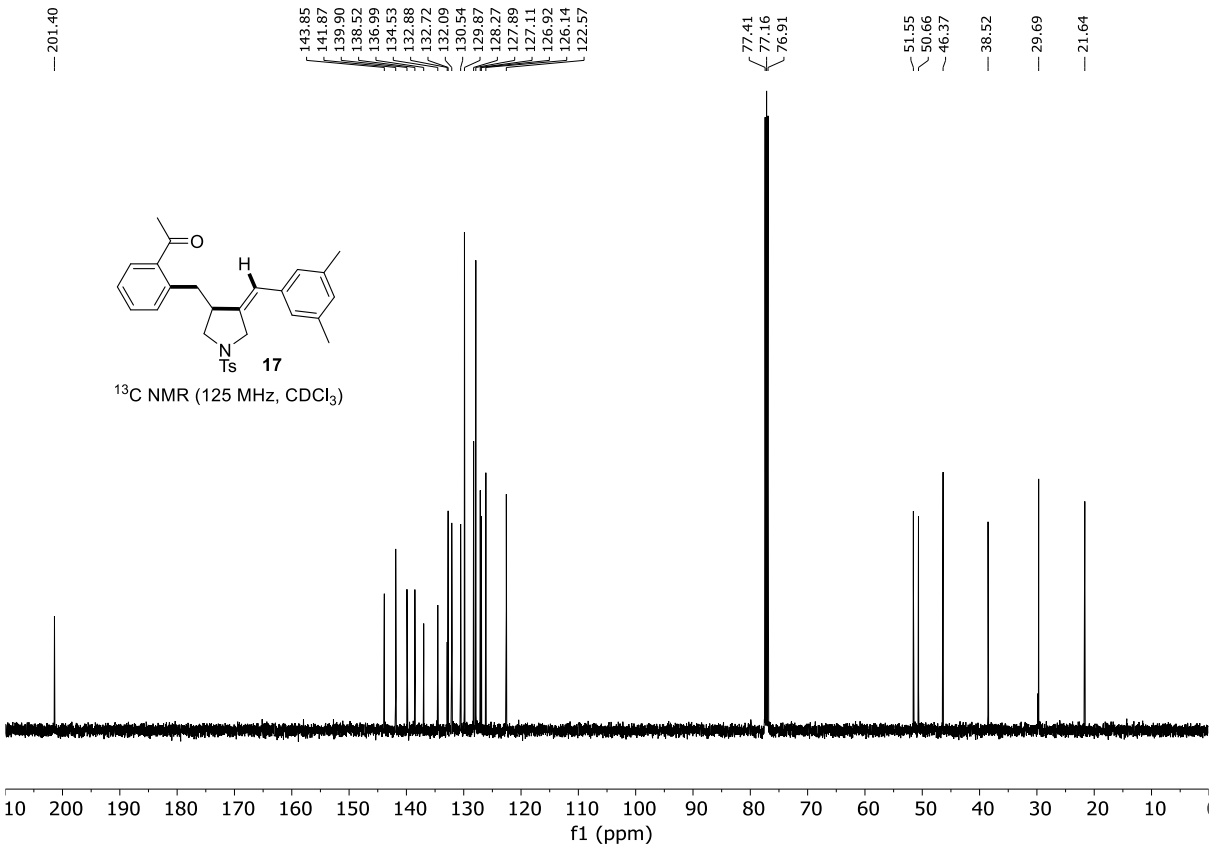

O
H
Ph
N
Ts
14
13C NMR (125 MHz, CDCl3)
f1 (ppm)

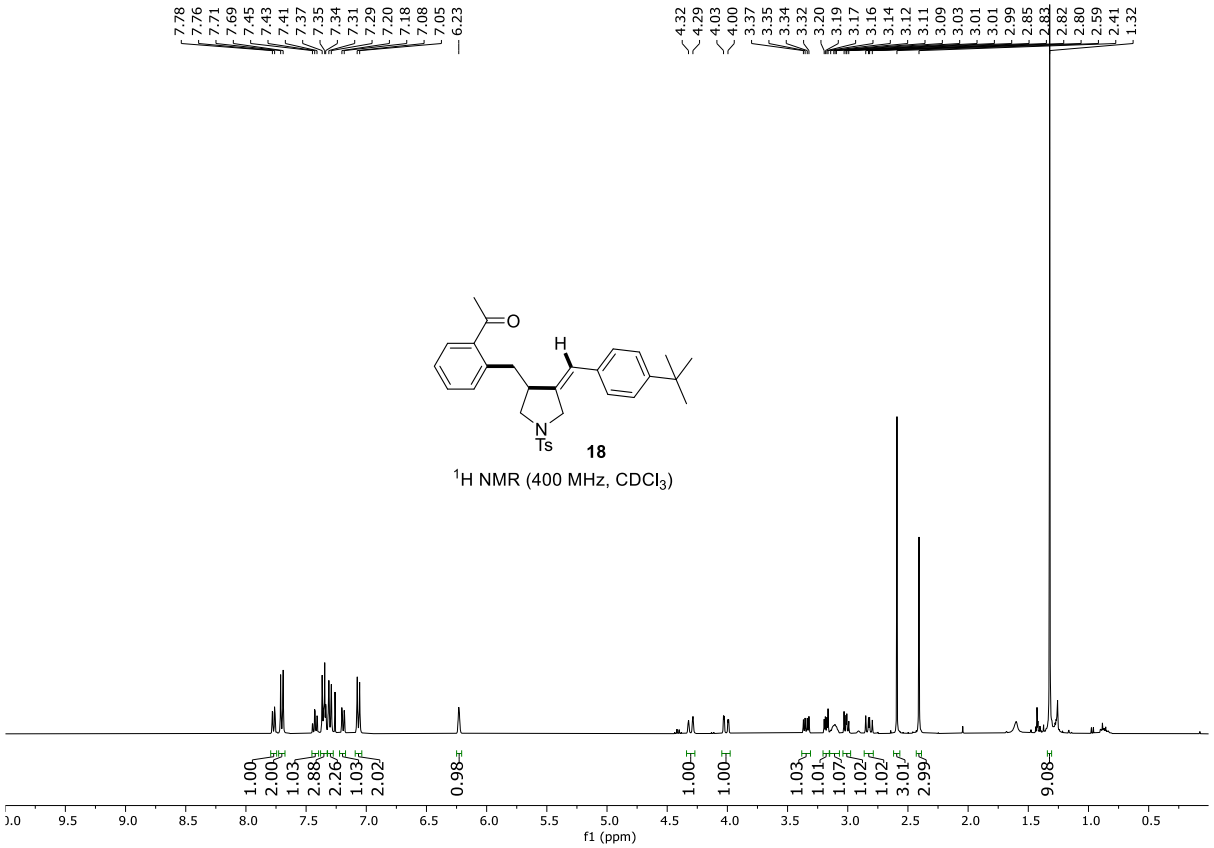

7.79 7.77 7.62 7.60 7.58 7.48 7.46 7.44 7.44 7.42 7.42 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.27 7.24 7.22 7.22 7.20 7.18 7.04 7.02 6.08 6.07 6.07
4.17 4.16 4.13 4.12 4.02 4.01 3.98 3.97 3.13 3.12 3.12 3.10 3.09 3.09 3.08 3.06 3.05 3.05 3.04 2.78 2.76 2.75 2.74 2.72 2.71 2.37
1.61 1.25
O
H
Ph
N
Ts
15
1H NMR (400 MHz, CDCl3)
2.00 3.02 3.02 5.01 3.10 2.01 1.00 1.03 1.01 4.05 1.02 3.00
f1 (ppm)
198.36
143.77 139.59 138.72 138.39 137.85 136.52 133.47 132.69 131.49 130.75 130.40 129.84 129.61 128.68 128.62 128.21 127.85 127.14 126.10 123.77
77.48 77.16 76.85
51.73 50.75 46.64
37.11
21.64
O
H
Ph
N
Ts
15
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.69
7.67
7.43
7.41
7.32
7.30
7.29
7.27
7.25
7.23
7.21
7.19
7.11
7.09
6.95
6.94
6.24
4.29
4.25
4.00
3.96
3.39
3.37
3.36
3.34
3.15
3.14
3.13
3.12
3.08
3.06
3.04
3.02
3.01
2.99
2.51
2.39
O
S
H
Ph
N
Ts
16
1H NMR (400 MHz, CDCl3)
2.03
0.99
4.46
1.37
2.05
1.00
0.99
1.02
1.04
1.11
4.39
3.13
3.30
f1 (ppm)

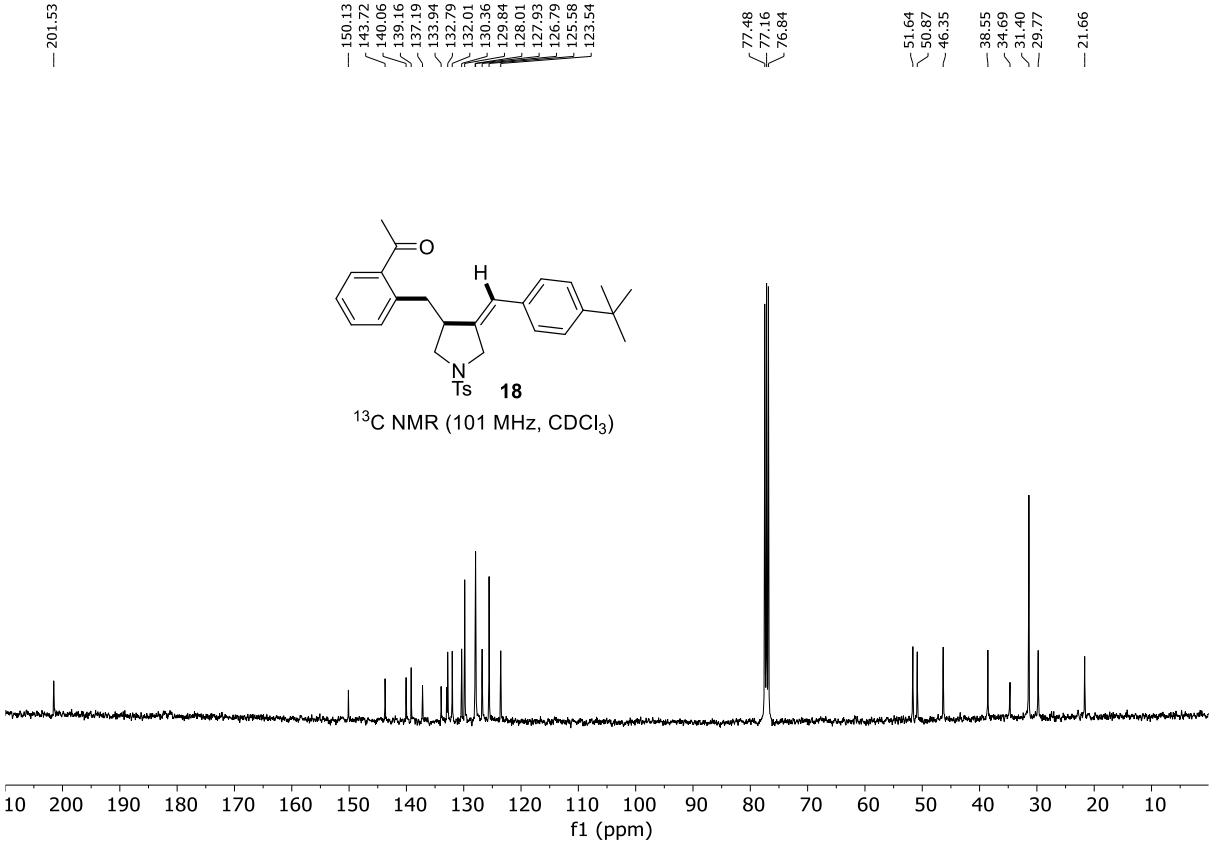

191.06
147.01
143.78
139.78
136.63
135.93
132.55
129.97
129.83
128.64
128.20
127.85
127.13
123.80
77.41
77.16
76.91
51.73
50.69
45.46
34.17
29.84
21.61
O
S
H
Ph
N
Ts
16
13C NMR (125 MHz, CDCl3)
f1 (ppm)


7.78
7.76
7.71
7.69
7.45
7.43
7.41
7.35
7.34
7.31
7.29
7.20
7.18
6.87
6.74
6.61
4.33
4.29
4.03
3.99
3.37
3.36
3.34
3.33
3.19
3.18
3.17
3.16
3.12
3.09
3.08
3.07
3.06
3.04
3.02
3.01
3.00
2.84
2.81
2.81
2.78
2.59
2.41
2.31
O
H
N
Ts
17
1H NMR (400 MHz, CDCl3)
1.00
1.98
1.04
0.82
2.23
0.99
0.95
1.94
0.97
1.03
1.01
1.02
1.03
1.12
1.06
1.04
2.96
3.01
5.95
f1 (ppm)

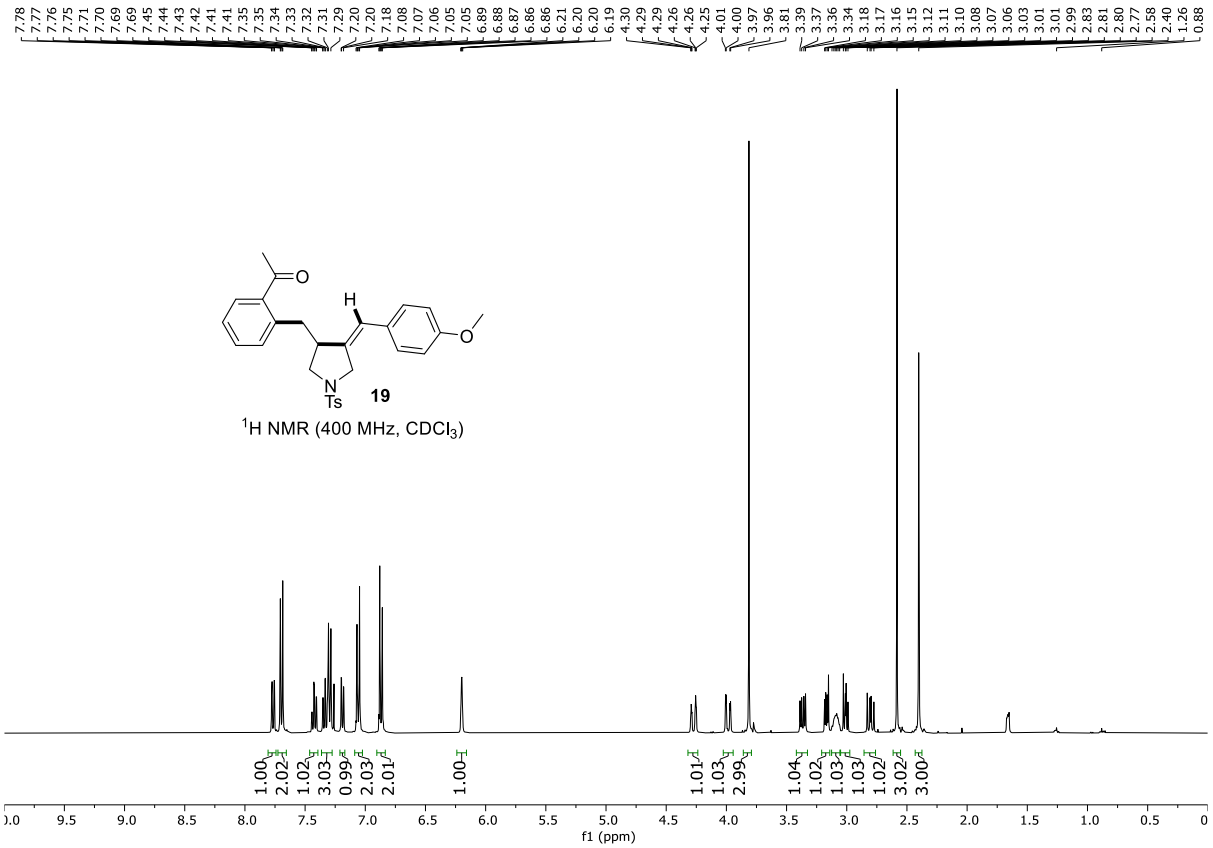

201.40
143.85
141.87
139.90
138.52
136.99
134.53
132.88
132.72
132.09
130.54
129.87
128.27
127.89
127.11
126.92
126.14
122.57
77.41
77.16
76.91
51.55
50.66
46.37
38.52
29.69
21.64
O
H
N
Ts
17
13C NMR (125 MHz, CDCl3)
f1 (ppm)

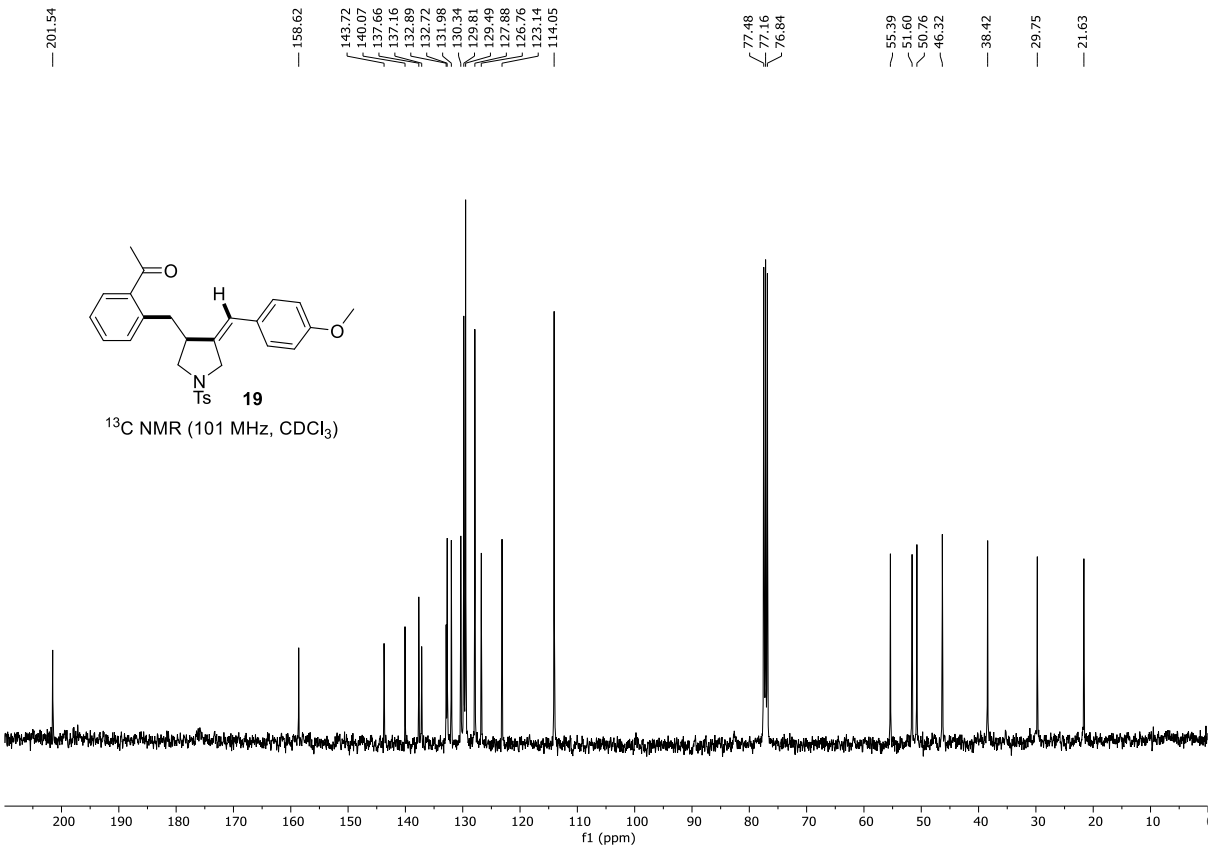


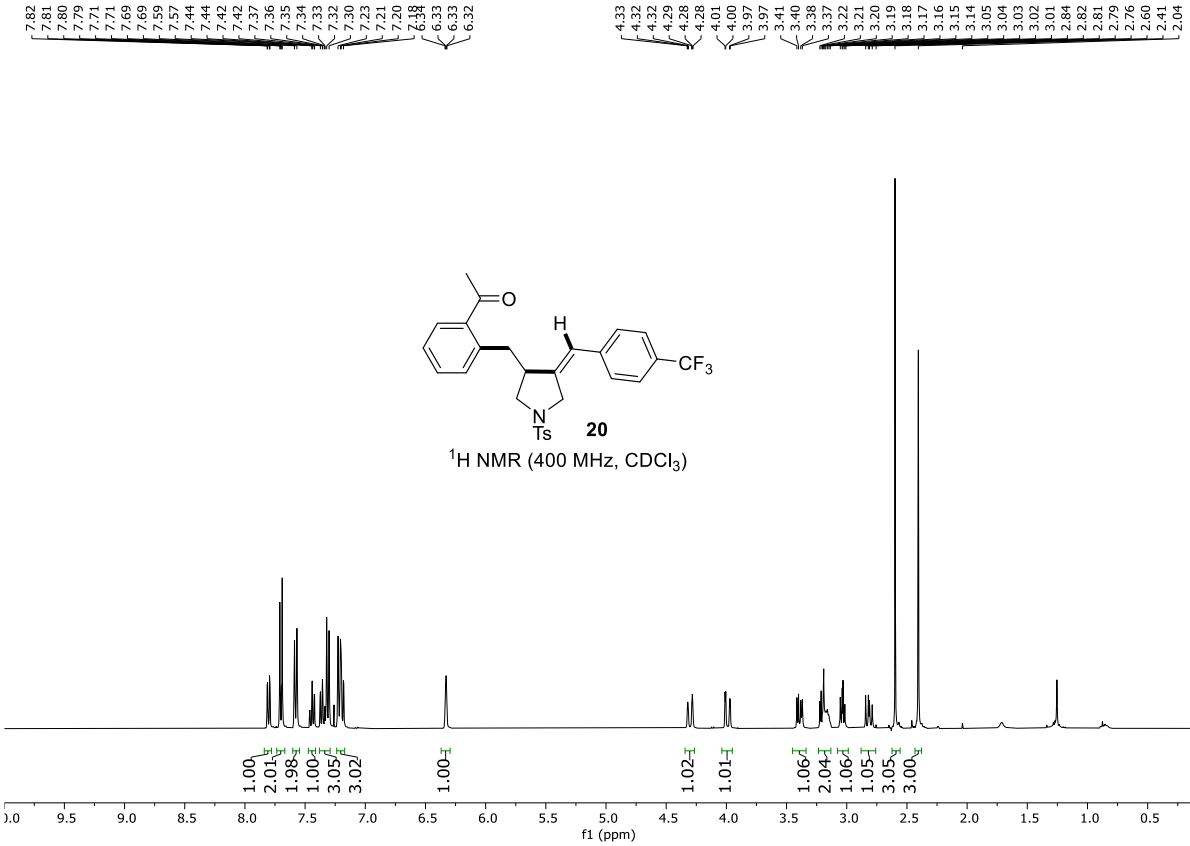
^{1}H NMR (400 MHz, $CDCl_3$)

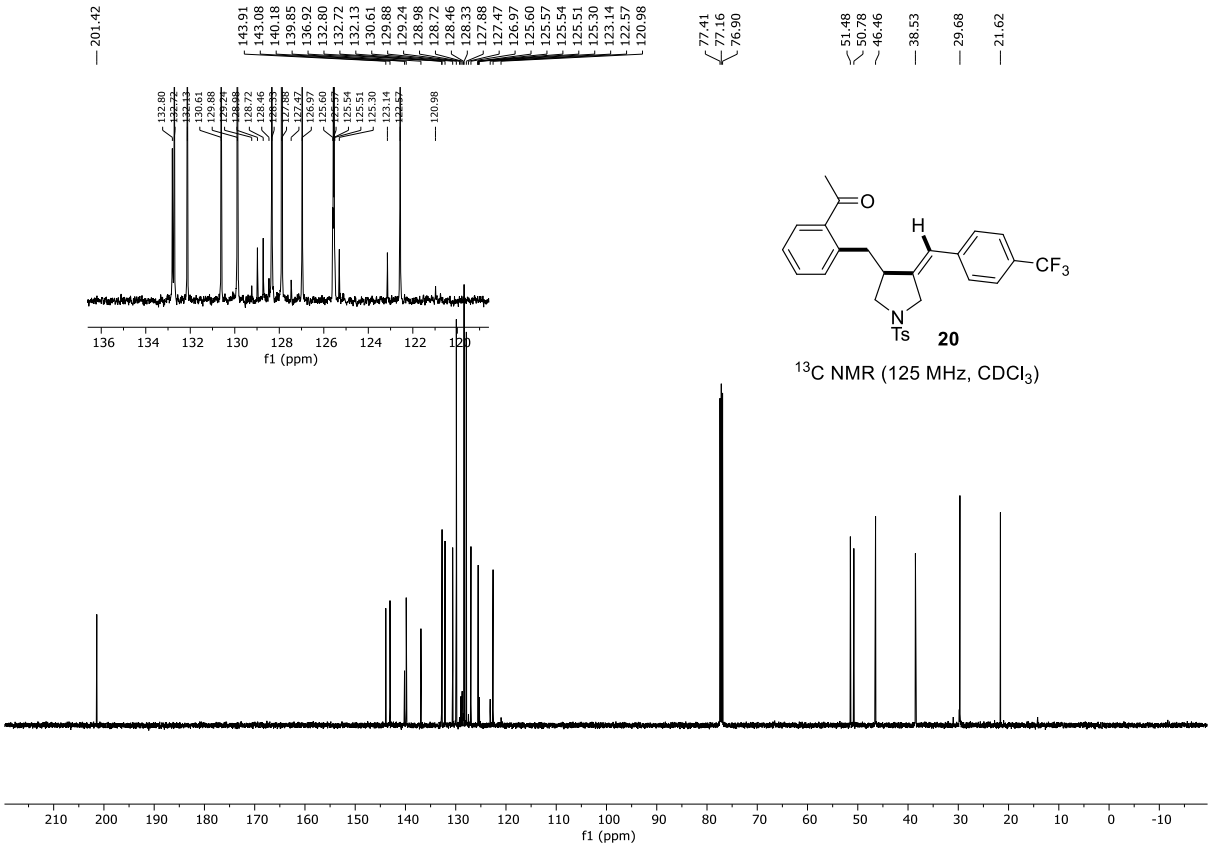


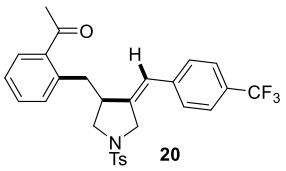
^{13}C NMR (101 MHz, $CDCl_3$)


7.78 7.77 7.76 7.75 7.71 7.70 7.69 7.69 7.45 7.44 7.43 7.42 7.41 7.41 7.35 7.35 7.34 7.33 7.32 7.31 7.29 7.20 7.20 7.18 7.08 7.07 7.06 7.05 7.05 6.89 6.88 6.87 6.86 6.86 6.21 6.20 6.20 6.19 4.30 4.29 4.29 4.26 4.26 4.25 4.01 4.00 3.97 3.96 3.81 3.39 3.37 3.36 3.34 3.18 3.17 3.16 3.15 3.12 3.11 3.10 3.08 3.07 3.06 3.03 3.01 3.01 2.99 2.83 2.81 2.80 2.77 2.58 2.40 1.26 0.88
O
H
O
N
Ts
19
1H NMR (400 MHz, CDCl3)
1.00 2.02 1.02 3.03 0.99 2.03 2.01 1.00 1.01 1.03 2.99 1.04 1.02 1.03 1.03 1.02 3.02 3.00
f1 (ppm)


201.54 158.62 143.72 140.07 137.66 137.16 132.89 132.72 131.98 130.34 129.81 129.49 127.88 126.76 123.14 114.05 77.48 77.16 76.84 55.39 51.60 50.76 46.32 38.42 29.75 21.63
O
H
O
N
Ts
19
13C NMR (101 MHz, CDCl3)
f1 (ppm)

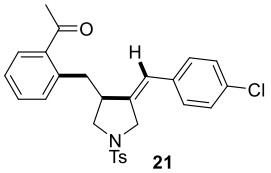

7.82 7.81 7.80 7.79 7.71 7.71 7.69 7.69 7.59 7.57 7.44 7.44 7.42 7.42 7.37 7.36 7.35 7.34 7.33 7.32 7.30 7.23 7.21 7.20 7.18 6.34 6.33 6.33 6.32
4.33 4.32 4.32 4.29 4.28 4.28 4.01 4.00 3.97 3.97 3.41 3.40 3.38 3.37 3.22 3.21 3.20 3.19 3.18 3.17 3.16 3.15 3.14 3.05 3.04 3.03 3.02 3.01 2.84 2.82 2.81 2.79 2.76 2.60 2.41 2.04
O
H
CF3
N
Ts
20
1H NMR (400 MHz, CDCl3)
1.00 2.01 1.98 1.00 3.05 3.02 1.00 1.02 1.01 1.06 2.04 1.06 1.05 3.05 3.00
f1 (ppm)


201.42
143.91 143.08 140.18 139.85 136.92 132.80 132.72 132.13 130.61 129.88 129.24 128.98 128.72 128.46 128.33 127.88 127.47 126.97 125.60 125.57 125.54 125.51 125.30 123.14 122.57 120.98
77.41 77.16 76.90
51.48 50.78 46.46
38.53
29.68
21.62
f1 (ppm)
O
H
CF3
N
Ts
20
13C NMR (125 MHz, CDCl3)
f1 (ppm)



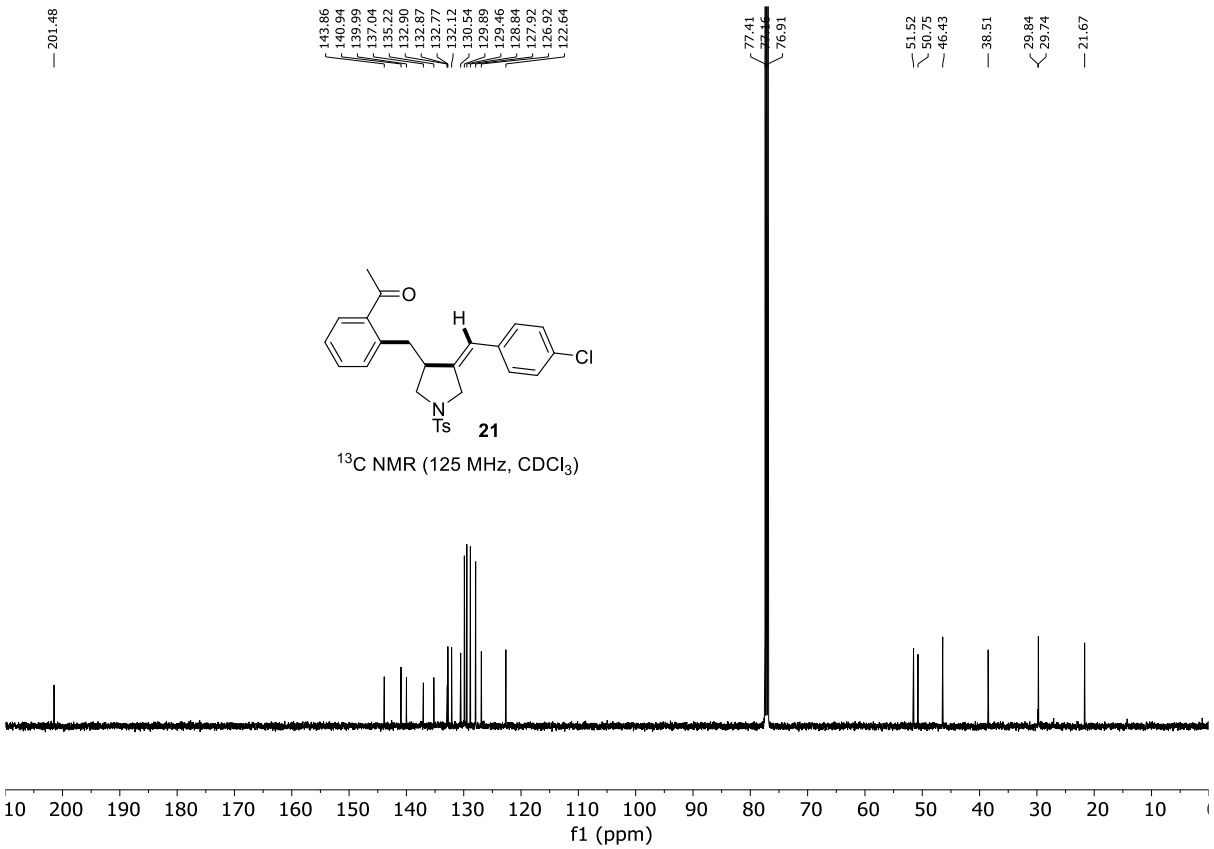
20

^{19}F NMR (376 MHz, $CDCl_3$)

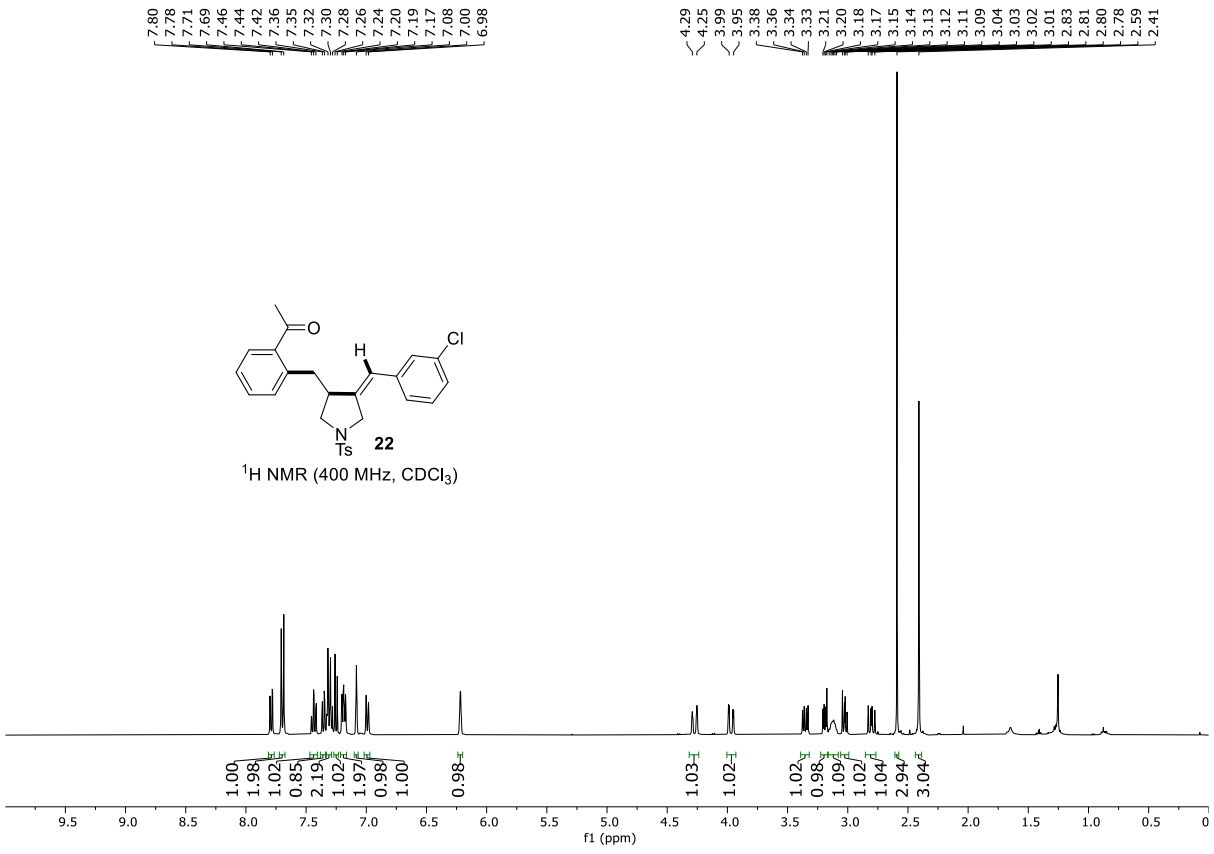


21

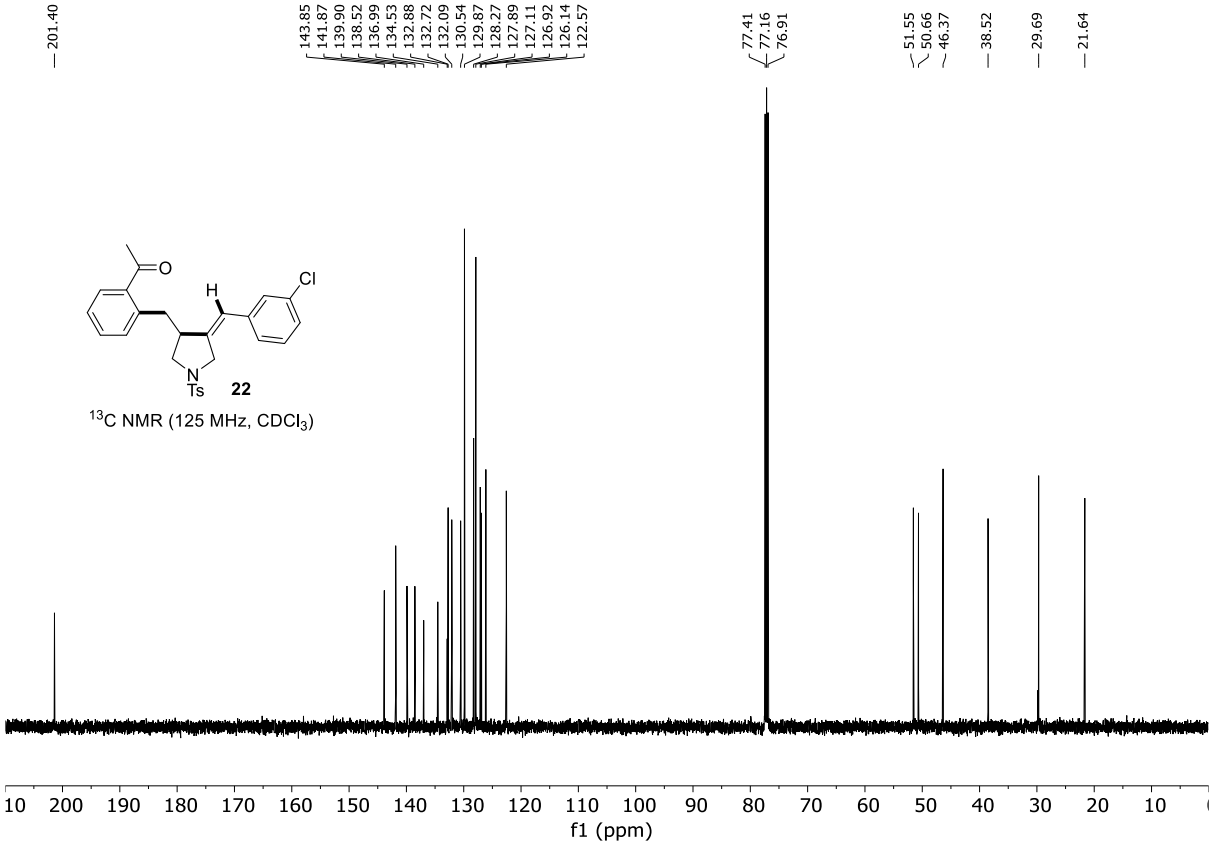
^{1}H NMR (400 MHz, $CDCl_3$)

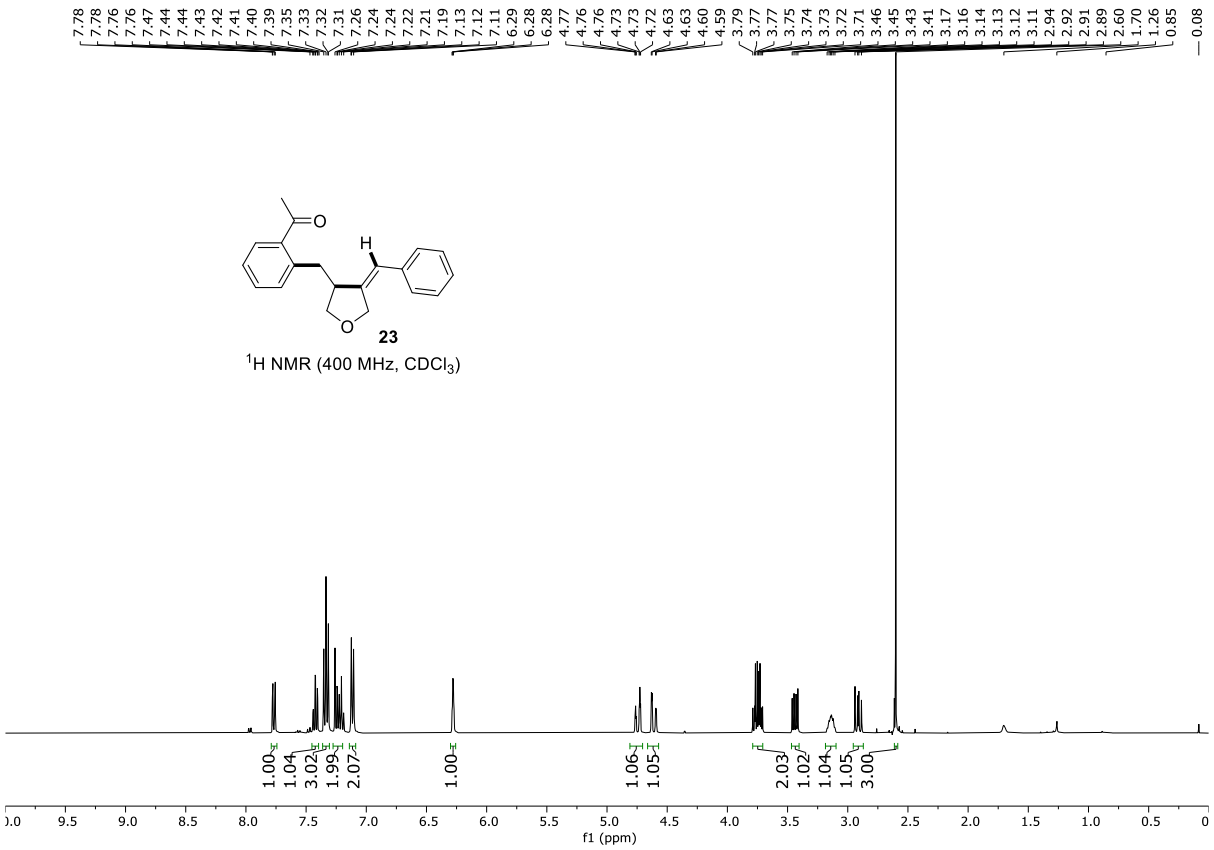


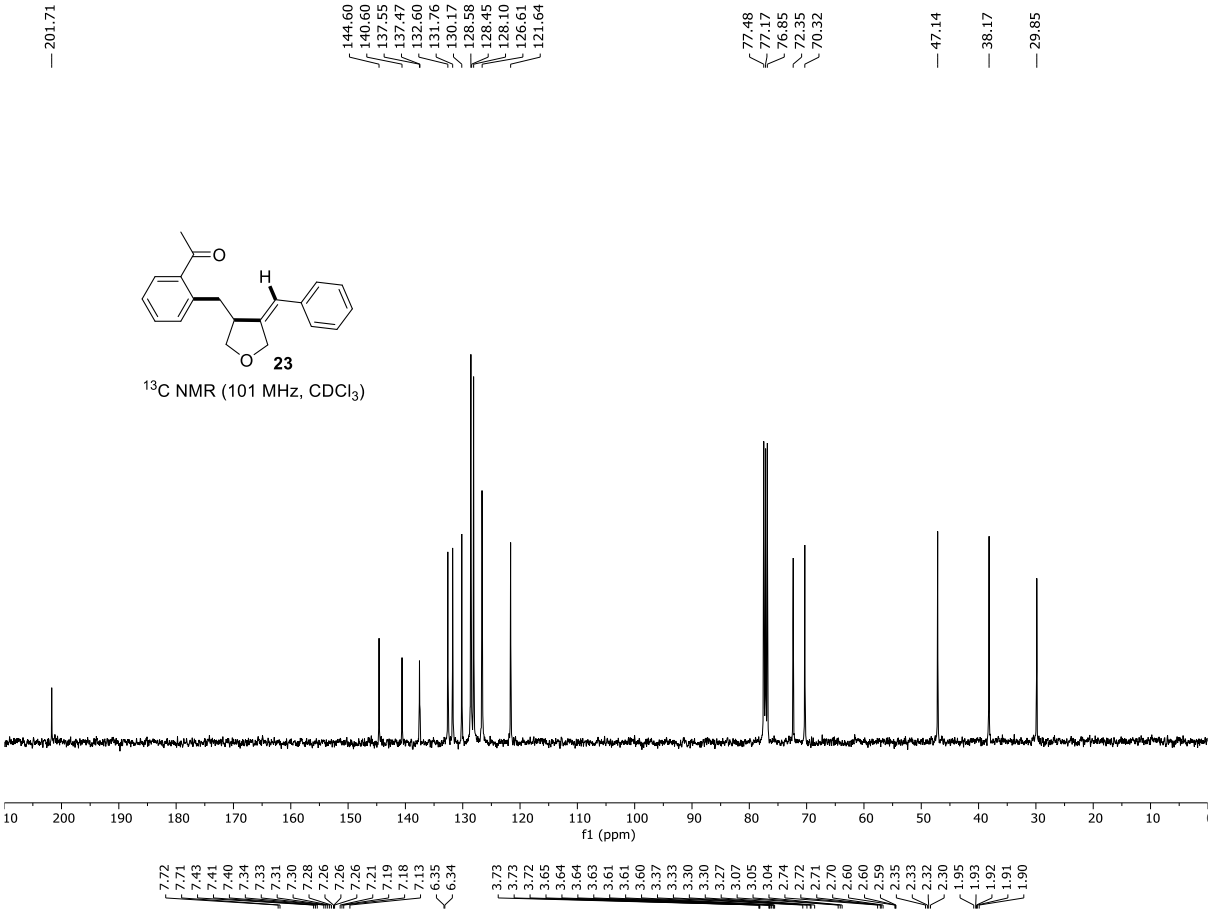
^{13}C NMR (125 MHz, $CDCl_3$)

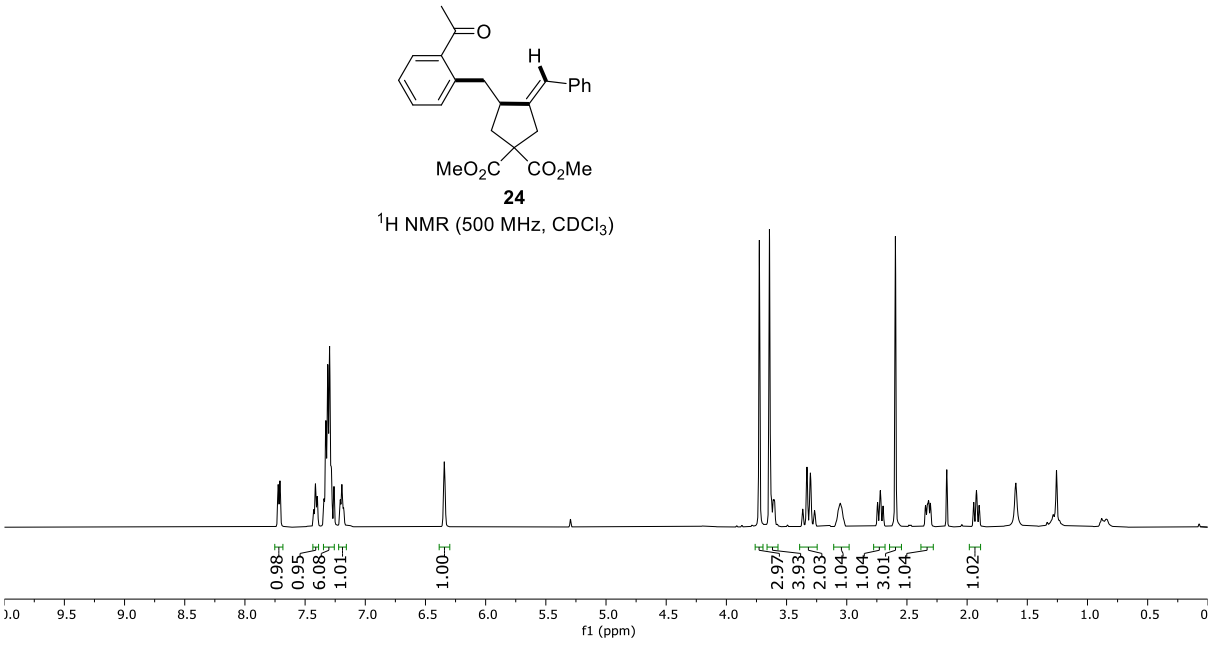


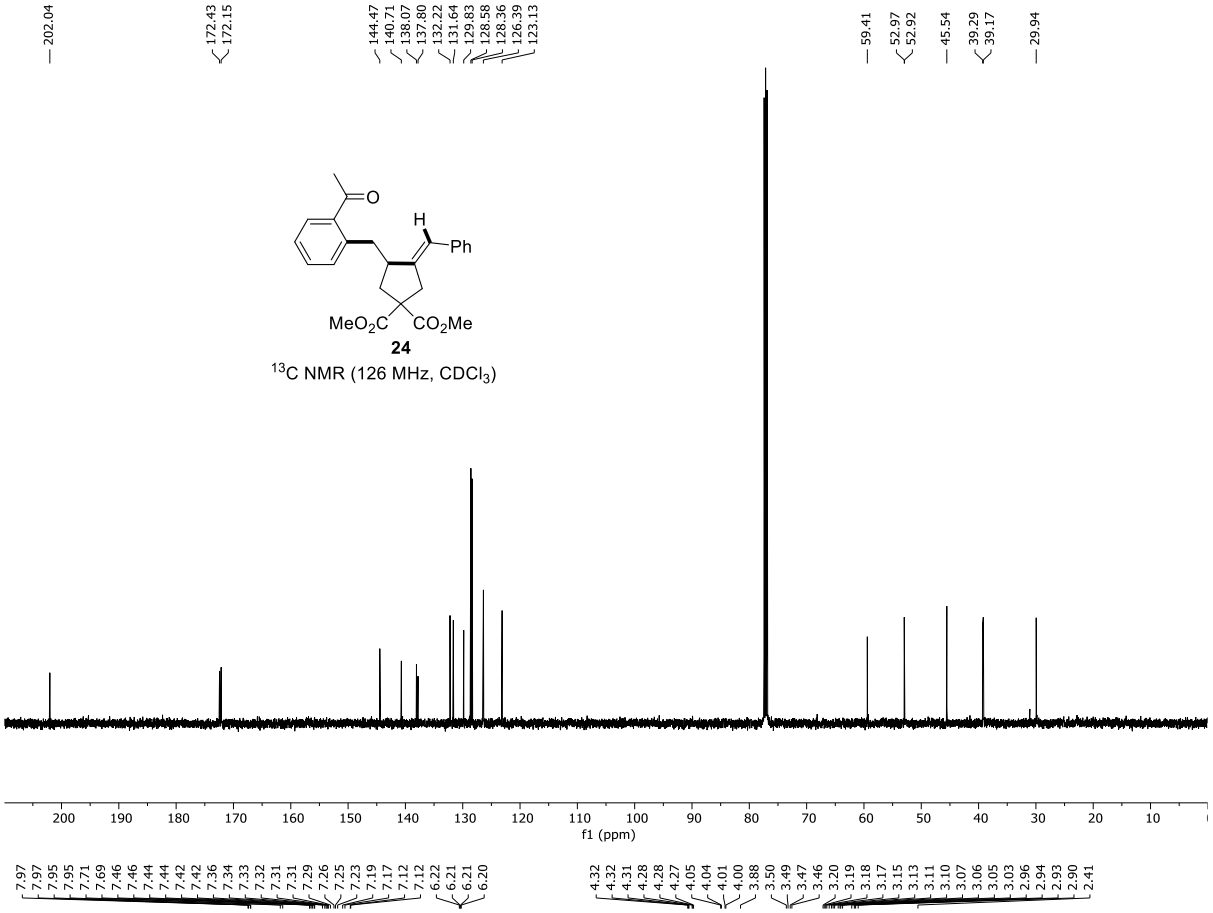
^{1}H NMR (400 MHz, $CDCl_3$)


201.40
143.85
141.87
139.90
138.52
136.99
134.53
132.88
132.72
132.09
130.54
129.87
128.27
127.89
127.11
126.92
126.14
122.57
77.41
77.16
76.91
51.55
50.66
46.37
38.52
29.69
21.64
O
H
Cl
N
Ts
22
13C NMR (125 MHz, CDCl3)
f1 (ppm)


7.78
7.78
7.76
7.76
7.76
7.47
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.35
7.33
7.32
7.31
7.26
7.24
7.24
7.22
7.21
7.19
7.13
7.12
7.11
6.29
6.28
4.77
4.76
4.76
4.73
4.73
4.72
4.63
4.63
4.60
4.59
3.79
3.77
3.77
3.75
3.74
3.73
3.72
3.71
3.46
3.45
3.43
3.41
3.17
3.16
3.14
3.13
3.12
3.11
2.94
2.92
2.91
2.89
2.60
1.70
1.26
0.85
0.08
O
H
O
23
1H NMR (400 MHz, CDCl3)
1.00
1.04
3.02
1.99
2.07
1.00
1.06
1.05
2.03
1.02
1.04
1.05
3.00
f1 (ppm)

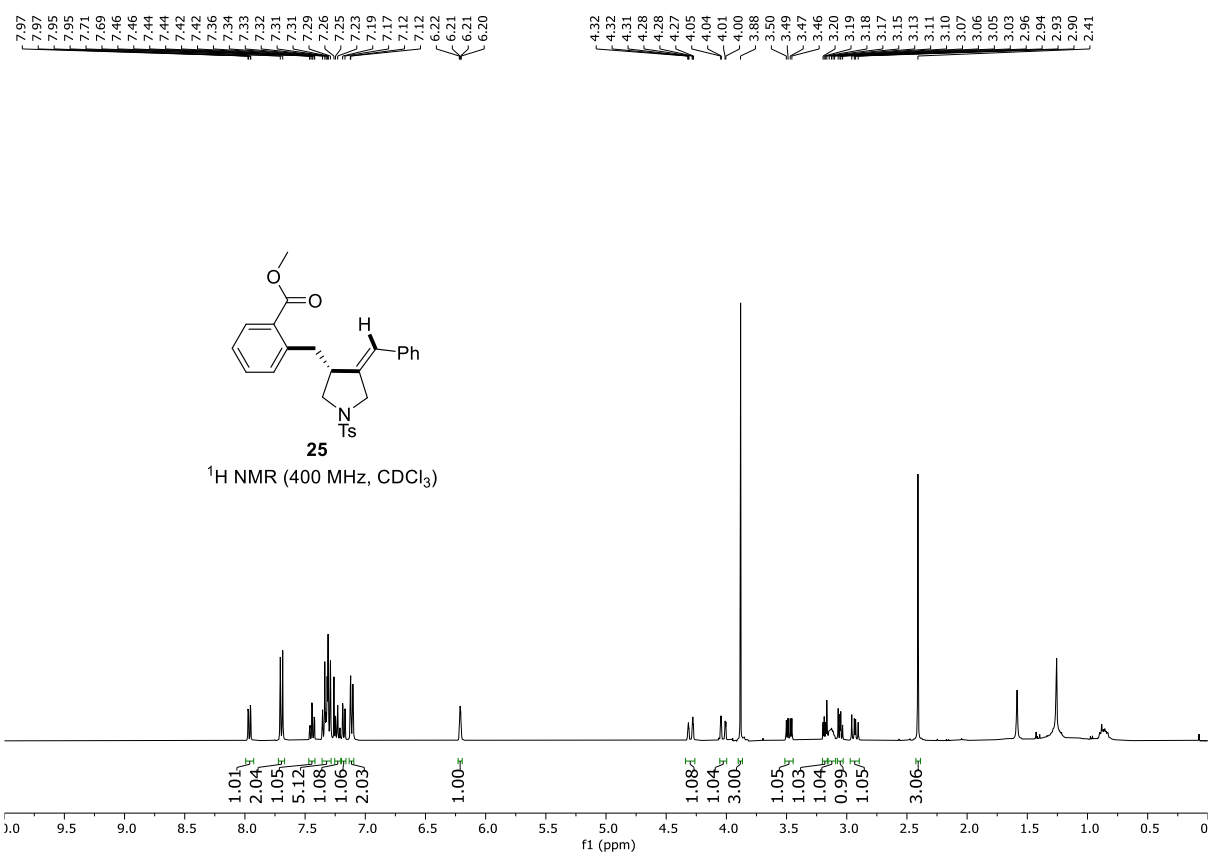

201.71
144.60
140.60
137.55
137.47
132.60
131.76
130.17
128.58
128.45
128.10
126.61
121.64
77.48
77.17
76.85
72.35
70.32
47.14
38.17
29.85
O
H
O
23
13C NMR (101 MHz, CDCl3)
f1 (ppm)
7.72
7.71
7.43
7.41
7.40
7.34
7.33
7.31
7.30
7.28
7.26
7.26
7.26
7.21
7.19
7.18
7.13
6.35
6.34
3.73
3.73
3.72
3.65
3.64
3.64
3.63
3.61
3.61
3.60
3.37
3.33
3.30
3.30
3.27
3.07
3.05
3.04
2.74
2.72
2.71
2.70
2.60
2.60
2.59
2.35
2.33
2.32
2.30
1.95
1.93
1.92
1.91
1.90


O
H
Ph
MeO2C
CO2Me
24
1H NMR (500 MHz, CDCl3)
0.98
0.95
6.08
1.01
1.00
2.97
3.93
2.03
1.04
1.04
3.01
1.04
1.02
f1 (ppm)



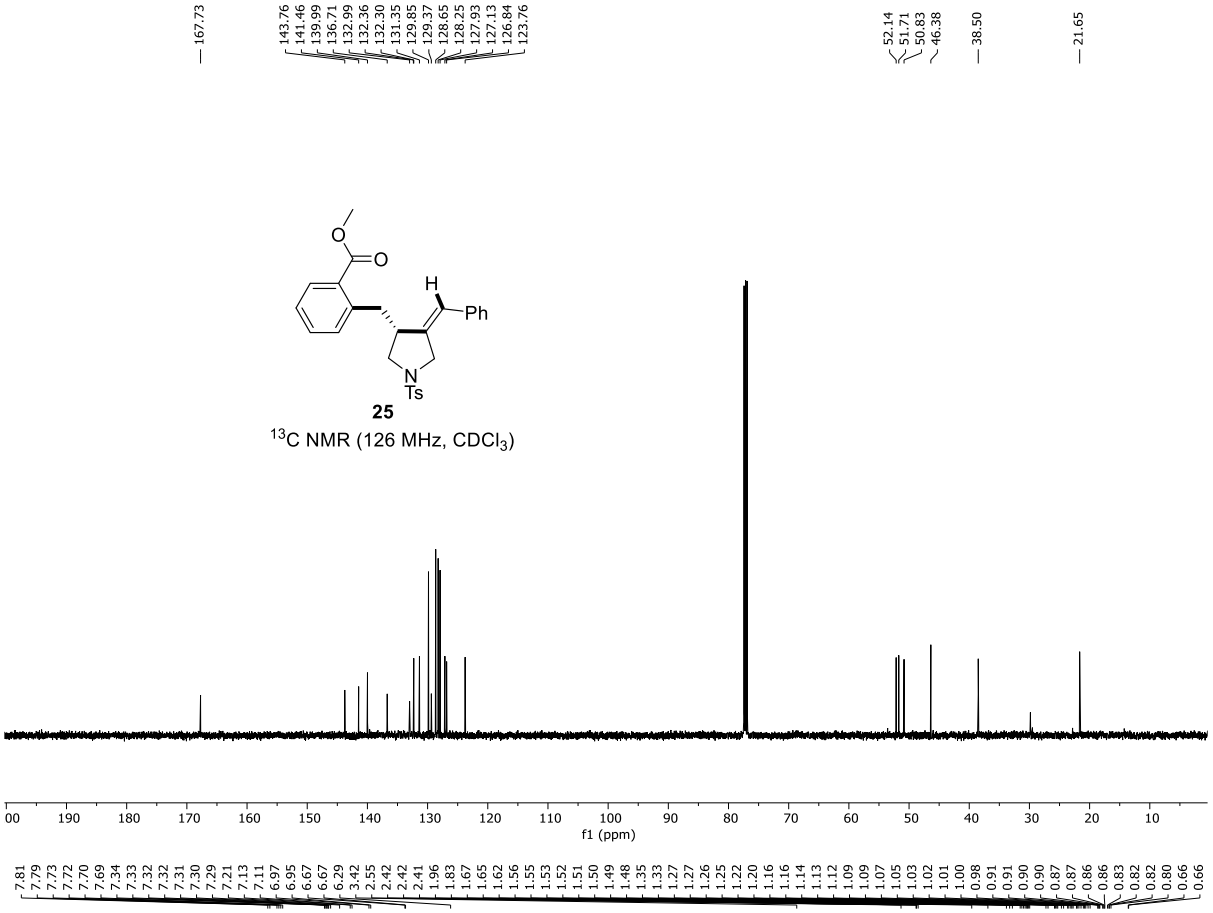
24

^{13}C NMR (126 MHz, $CDCl_3$)



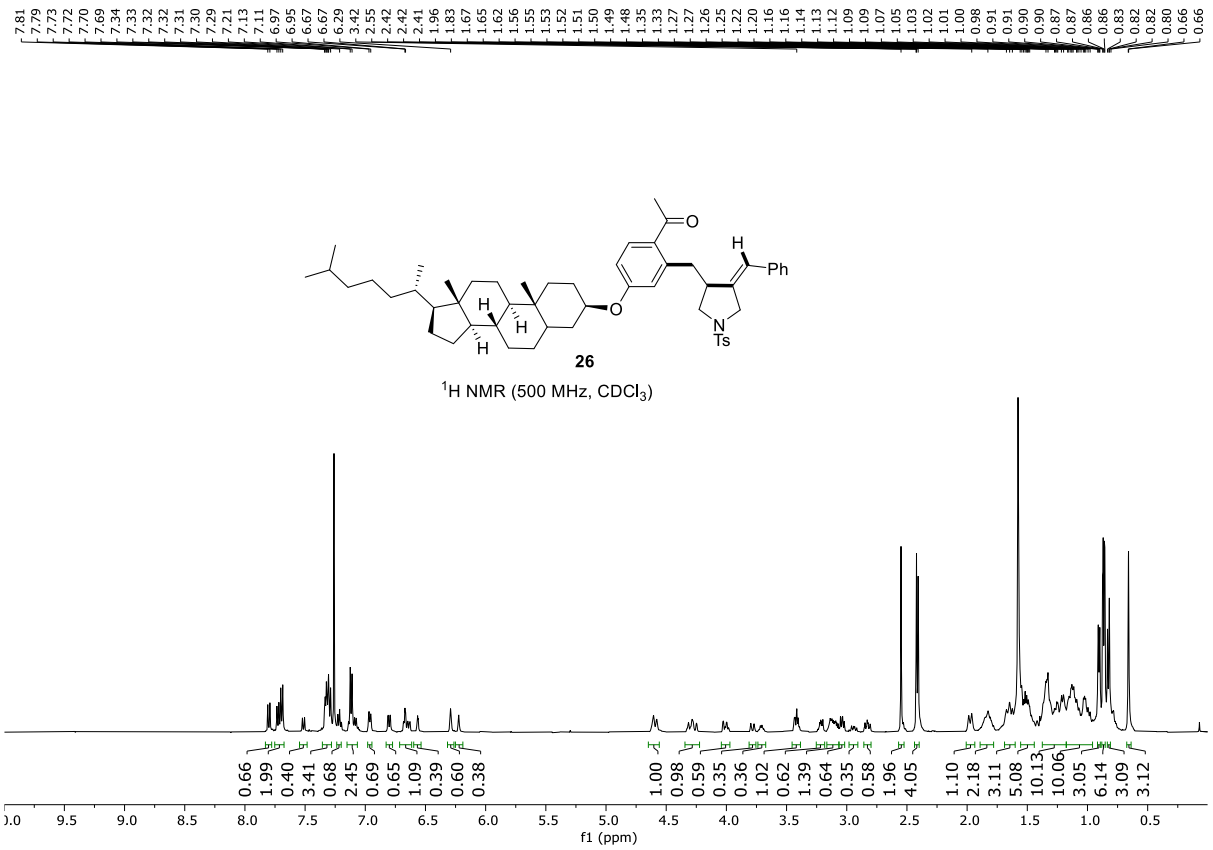
25

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



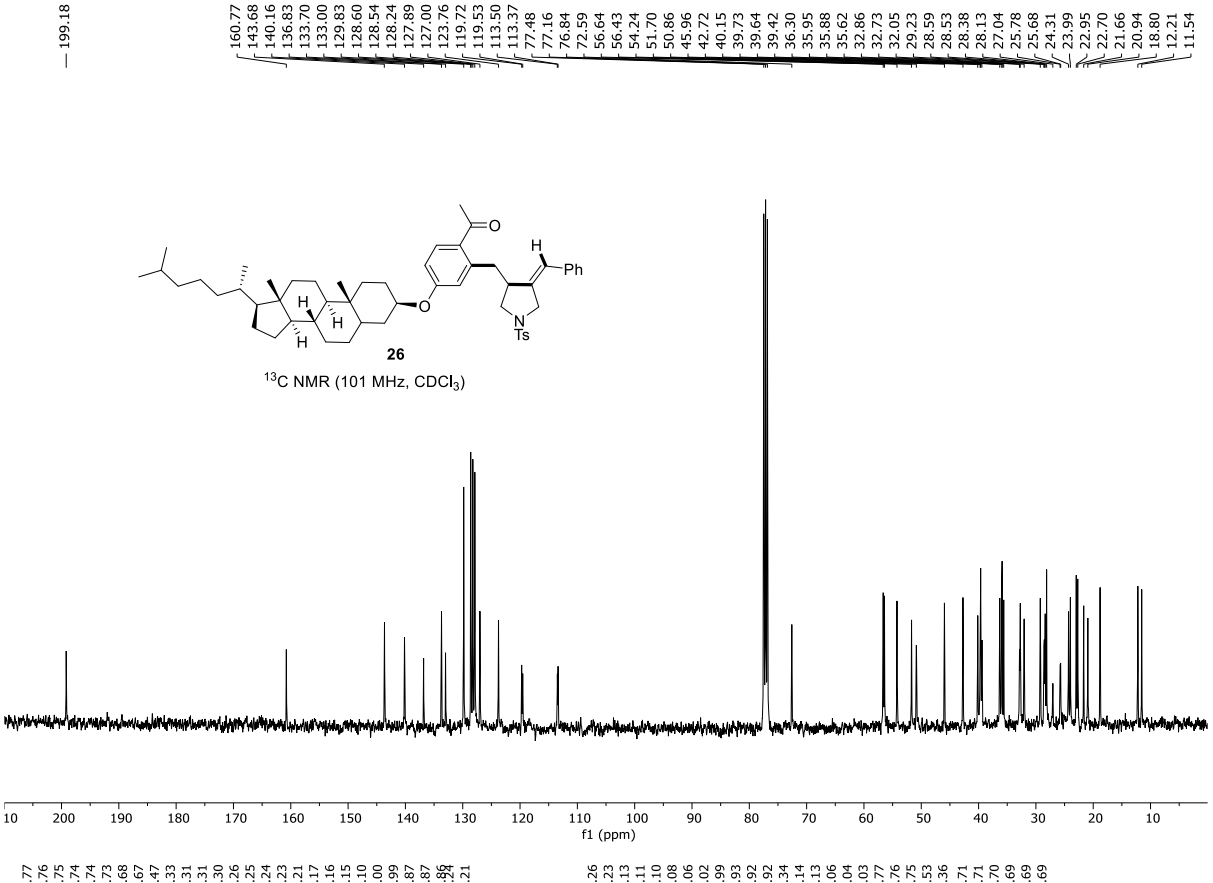
25

^{13}C NMR (126 MHz, $CDCl_3$)



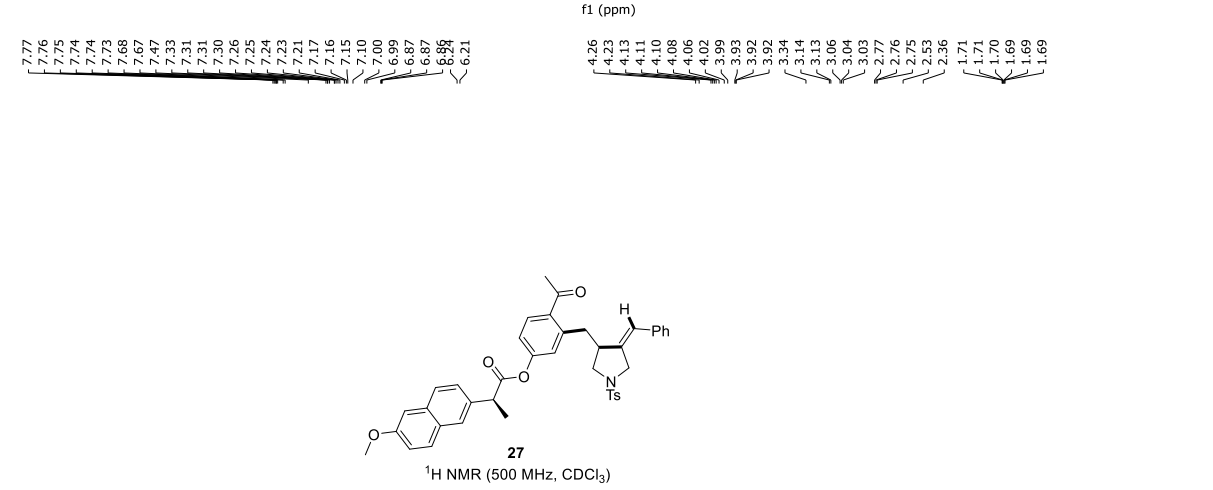
26

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



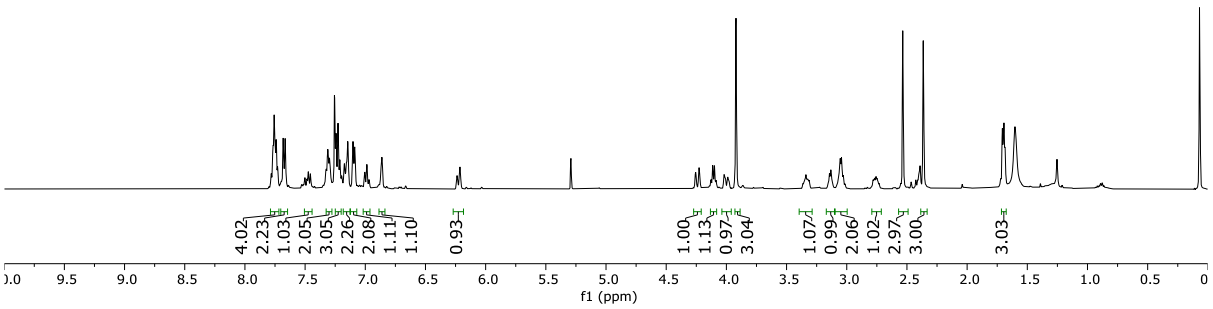
26

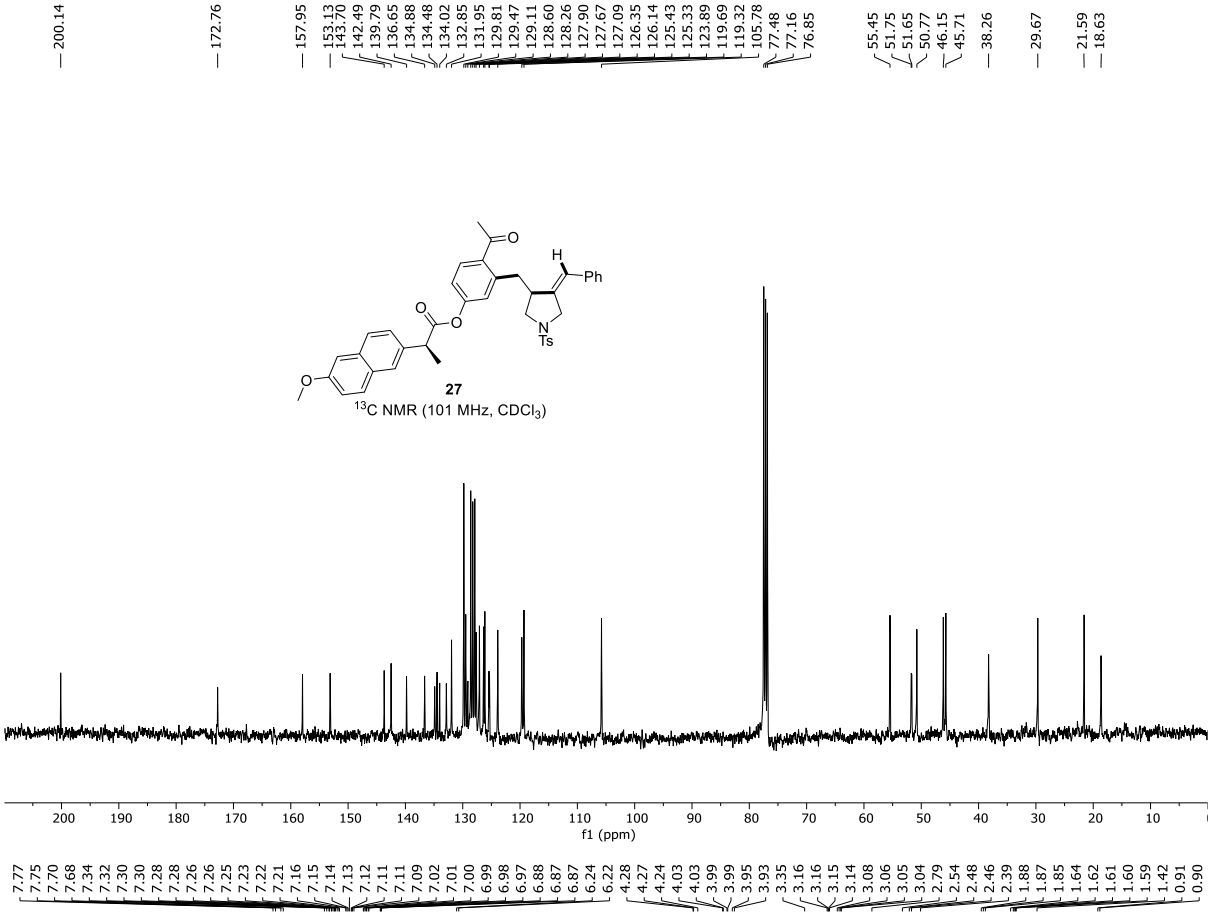
^{13}C NMR (101 MHz, $CDCl_3$)



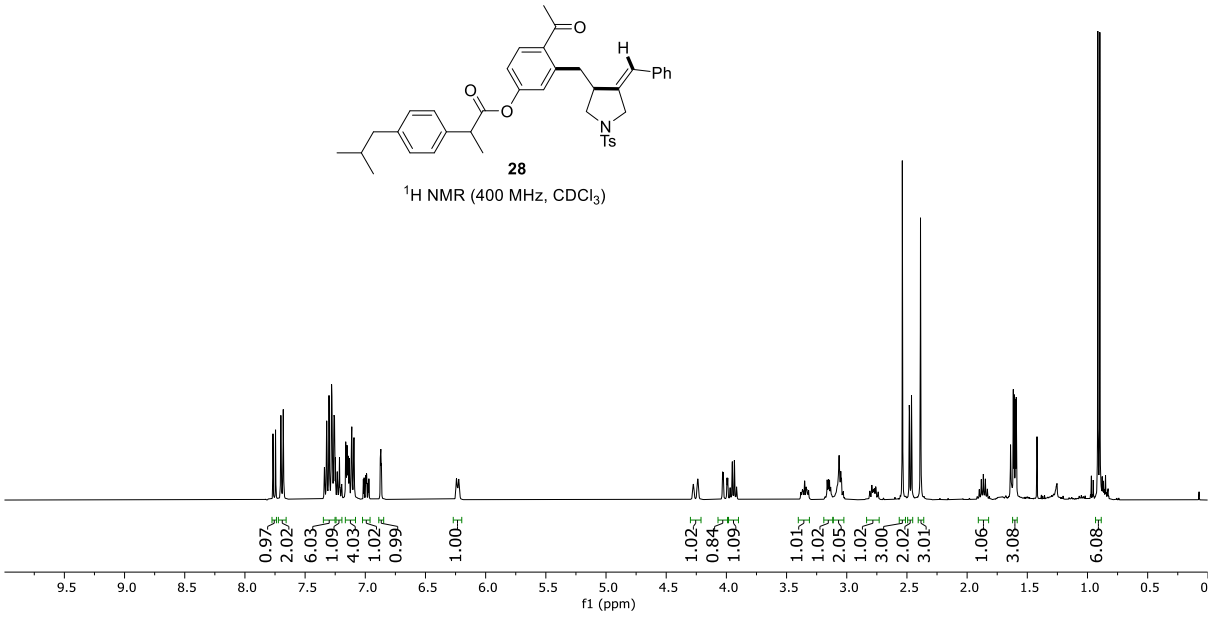
27

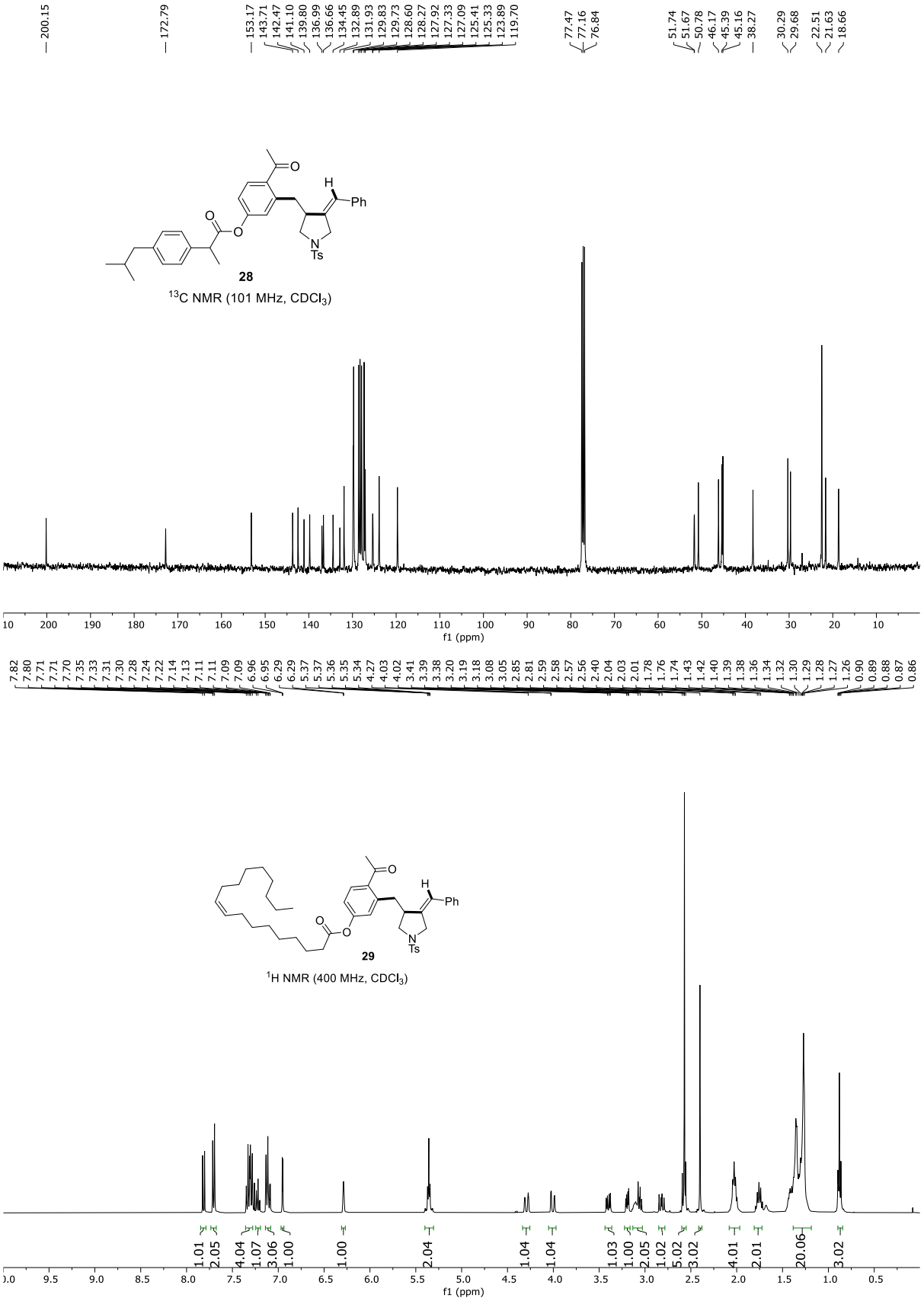
^{1}H NMR (500 MHz, $CDCl_3$)

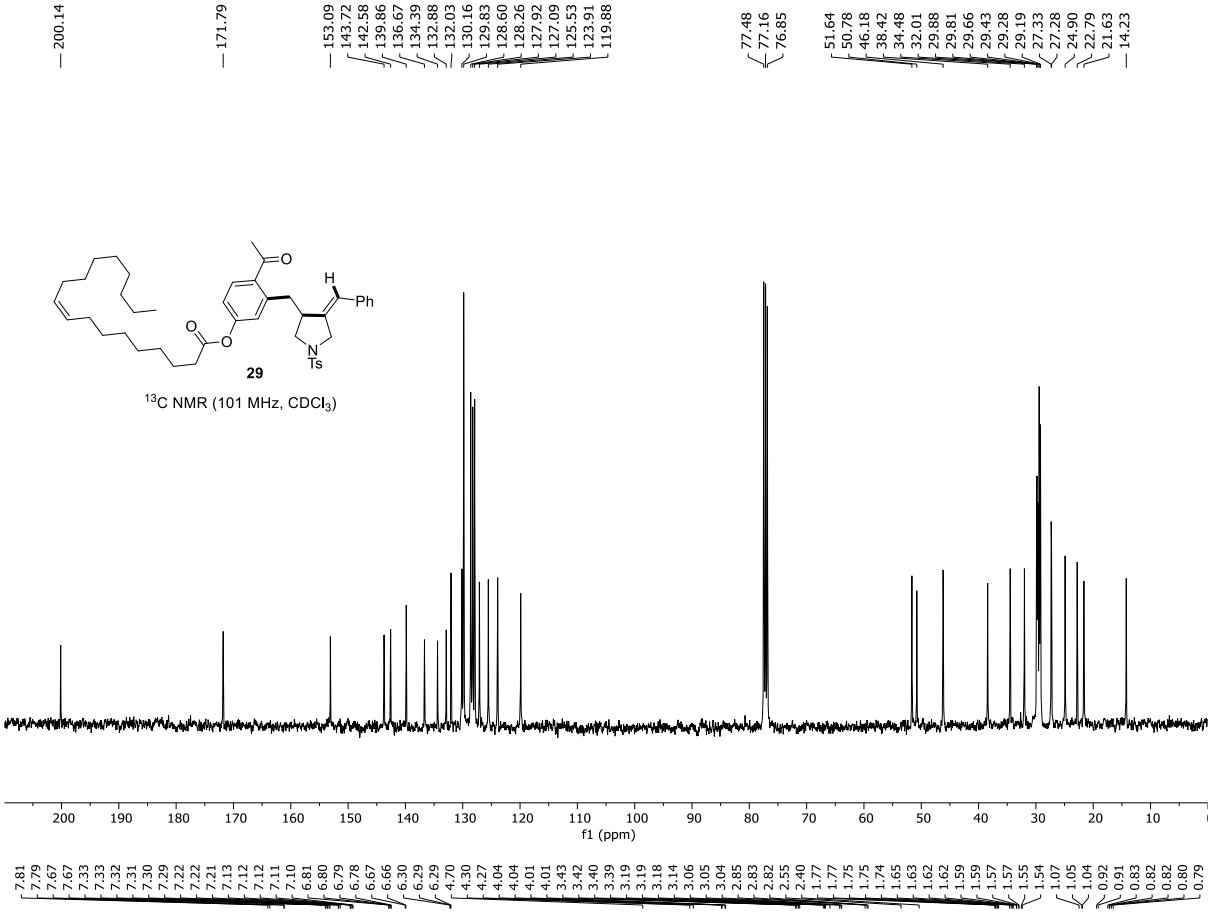



200.14
172.76
157.95
153.13
143.70
142.49
139.79
136.65
134.88
134.48
134.02
132.85
131.95
129.81
129.47
129.11
128.60
128.26
127.90
127.67
127.09
126.35
126.14
125.43
125.33
123.89
119.69
119.32
105.78
77.48
77.16
76.85
55.45
51.75
51.65
50.77
46.15
45.71
38.26
29.67
21.59
18.63
O
H
Ph
O
O
N
Ts
O
27
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

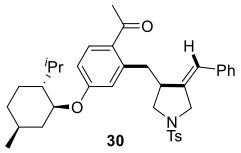
7.77
7.75
7.70
7.68
7.34
7.32
7.30
7.30
7.28
7.28
7.26
7.26
7.25
7.23
7.22
7.21
7.16
7.15
7.14
7.13
7.12
7.11
7.11
7.09
7.02
7.01
7.00
6.99
6.98
6.97
6.88
6.87
6.87
6.24
6.22
4.28
4.27
4.24
4.03
4.03
3.99
3.99
3.95
3.93
3.35
3.16
3.16
3.15
3.14
3.08
3.06
3.05
3.04
2.79
2.54
2.48
2.46
2.39
1.88
1.87
1.85
1.64
1.62
1.61
1.60
1.59
1.42
0.91
0.90

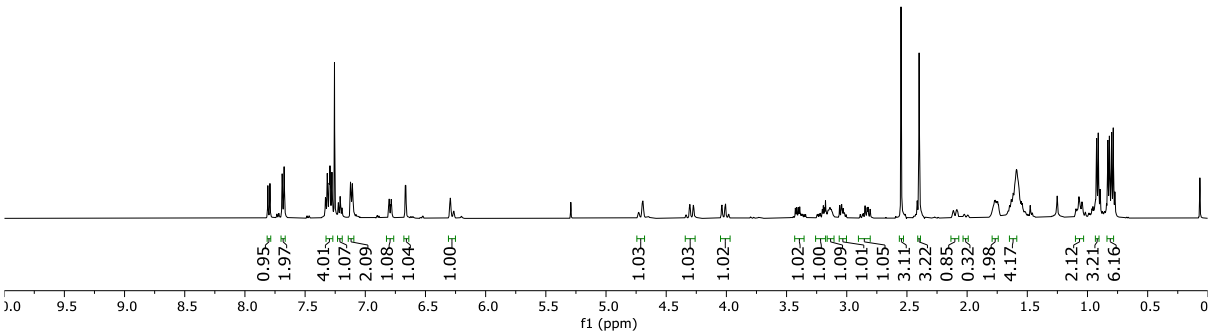

O
H
Ph
O
O
N
Ts
28
1H NMR (400 MHz, CDCl3)
0.97
2.02
6.03
1.09
4.03
1.02
0.99
1.00
1.02
0.84
1.09
1.01
1.02
2.05
1.02
3.00
2.02
3.01
1.06
3.08
6.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

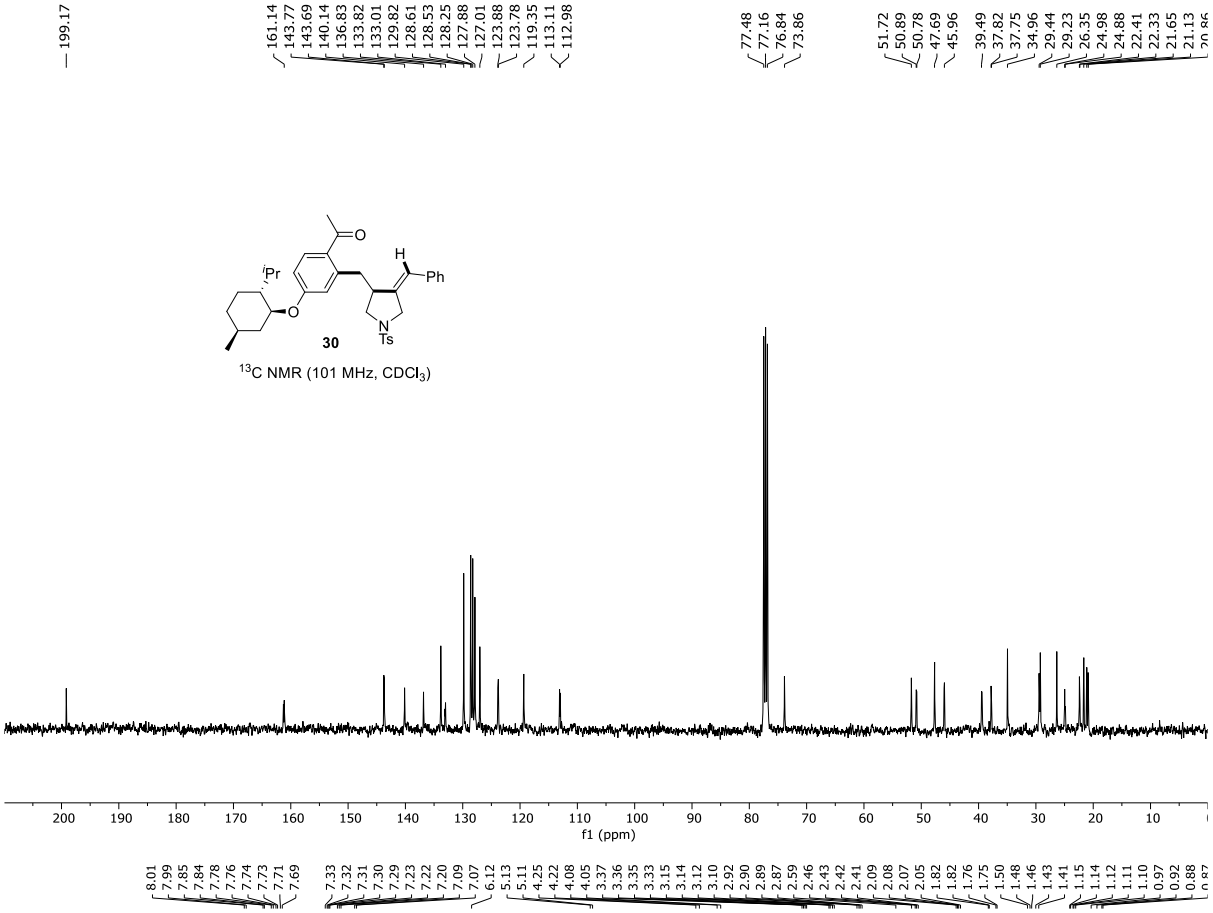

200.15
172.79
153.17
143.71
142.47
141.10
139.80
136.99
136.66
134.45
132.89
131.93
129.83
129.73
128.60
128.27
127.92
127.33
127.09
125.41
125.33
123.89
119.70
77.47
77.16
76.84
51.74
51.67
50.78
46.17
45.39
45.16
38.27
30.29
29.68
22.51
21.63
18.66
O
H
Ph
O
O
N
Ts
28
13C NMR (101 MHz, CDCl3)
f1 (ppm)
7.82
7.80
7.71
7.71
7.70
7.35
7.33
7.31
7.30
7.28
7.24
7.22
7.14
7.13
7.11
7.11
7.09
7.09
6.96
6.95
6.29
6.29
5.37
5.37
5.36
5.35
5.34
4.27
4.03
4.02
3.41
3.39
3.38
3.20
3.19
3.18
3.08
3.05
2.85
2.81
2.59
2.58
2.57
2.56
2.40
2.04
2.03
2.01
1.78
1.76
1.74
1.43
1.42
1.40
1.39
1.38
1.36
1.34
1.32
1.30
1.29
1.28
1.27
1.26
0.90
0.89
0.88
0.87
0.86
O
H
Ph
O
O
N
Ts
29
1H NMR (400 MHz, CDCl3)
1.01
2.05
4.04
1.07
3.06
1.00
1.00
2.04
1.04
1.04
1.03
1.00
2.05
1.02
5.02
3.02
4.01
2.01
20.06
3.02
f1 (ppm)


200.14
171.79
153.09
143.72
142.58
139.86
136.67
134.39
132.88
132.03
130.16
129.83
128.60
128.26
127.92
127.09
125.53
123.91
119.88
77.48
77.16
76.85
51.64
50.78
46.18
38.42
34.48
32.01
29.88
29.81
29.66
29.43
29.28
29.19
27.33
27.28
24.90
22.79
21.63
14.23
O
H
Ph
O
O
N
Ts
29
13C NMR (101 MHz, CDCl3)
f1 (ppm)

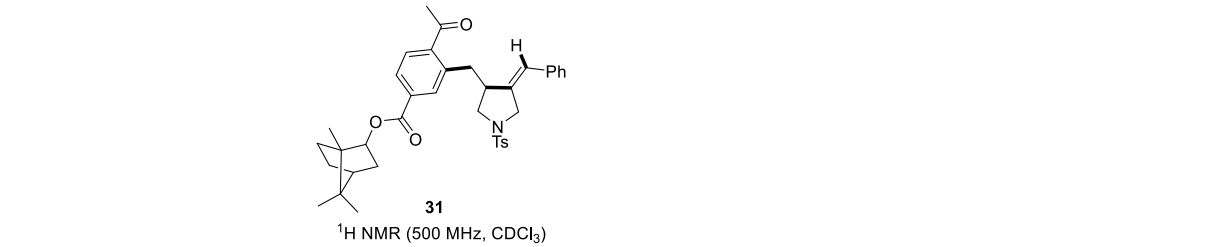
7.81
7.79
7.67
7.67
7.33
7.33
7.32
7.31
7.30
7.29
7.22
7.22
7.21
7.13
7.12
7.12
7.11
7.10
6.81
6.80
6.79
6.78
6.67
6.66
6.30
6.29
4.70
4.30
4.27
4.04
4.04
4.01
4.01
3.43
3.42
3.40
3.39
3.19
3.19
3.18
3.14
3.06
3.05
3.04
2.85
2.83
2.82
2.55
2.40
1.77
1.77
1.75
1.75
1.74
1.65
1.63
1.62
1.62
1.59
1.59
1.57
1.57
1.55
1.54
1.07
1.05
1.04
0.92
0.91
0.83
0.82
0.82
0.80
0.79

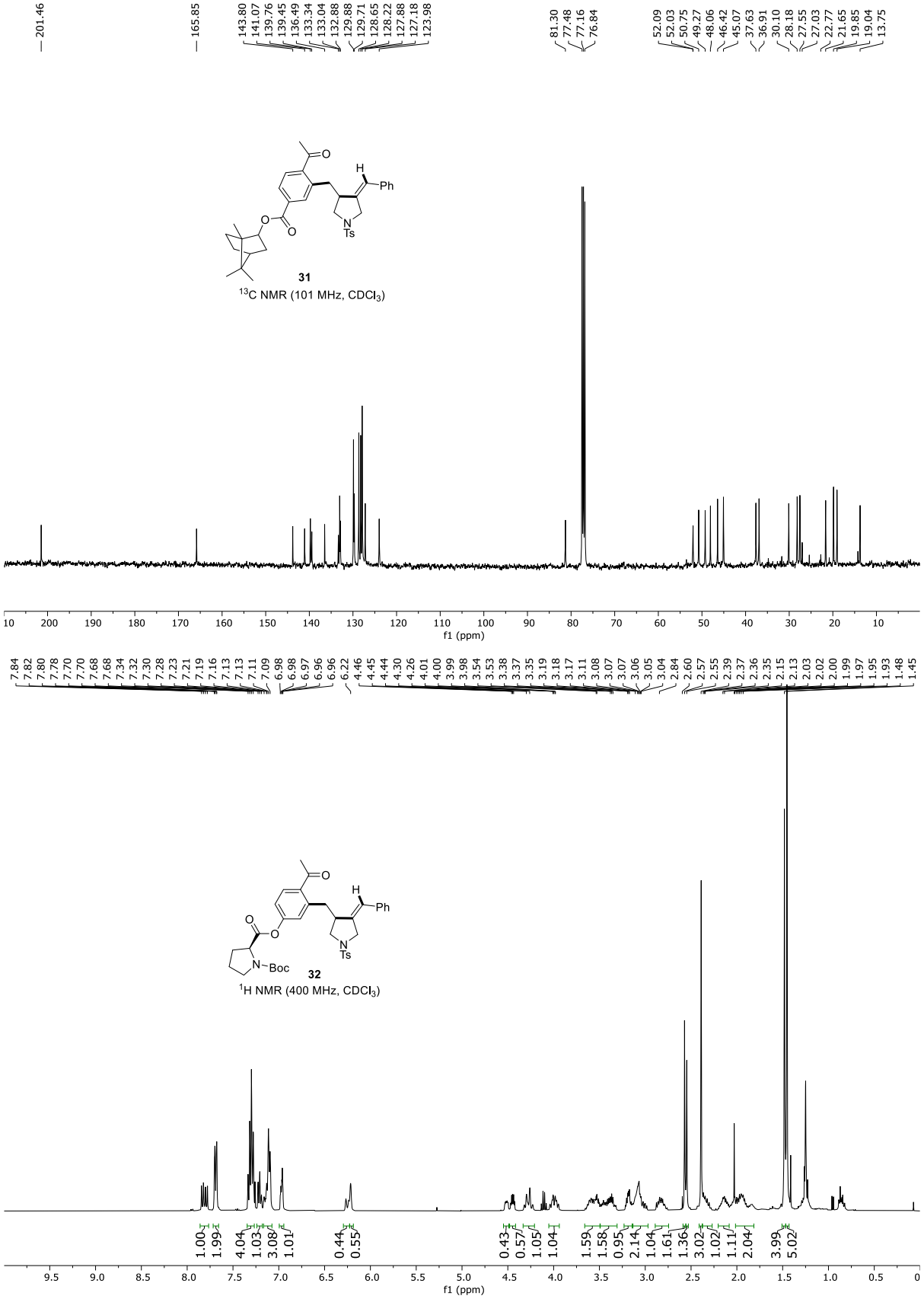

O
H
Ph
iPr
O
N
Ts
30
1H NMR (500 MHz, CDCl3)

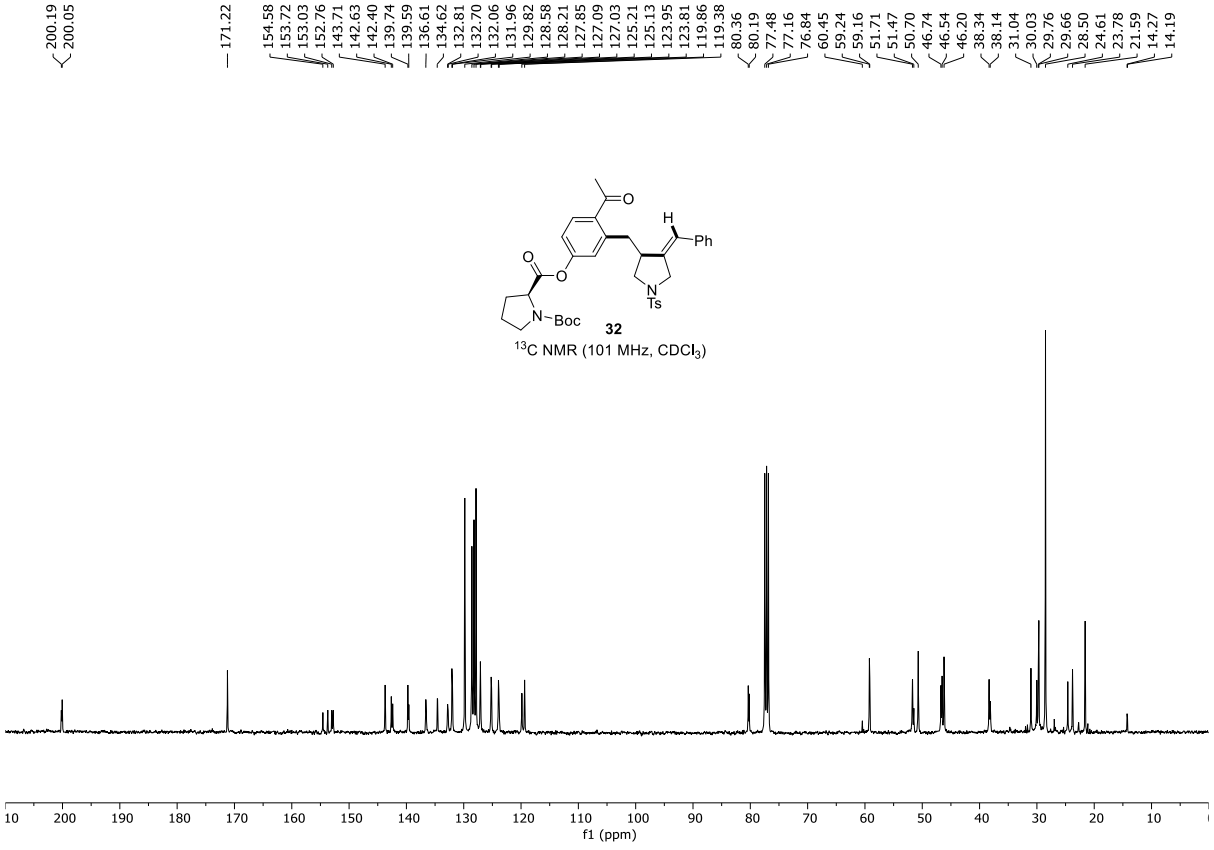

0.95
1.97
4.01
1.07
2.09
1.08
1.04
1.00
1.03
1.03
1.02
1.02
1.00
1.09
1.01
1.05
3.11
3.22
0.85
0.32
1.98
4.17
2.12
3.21
6.16
f1 (ppm)

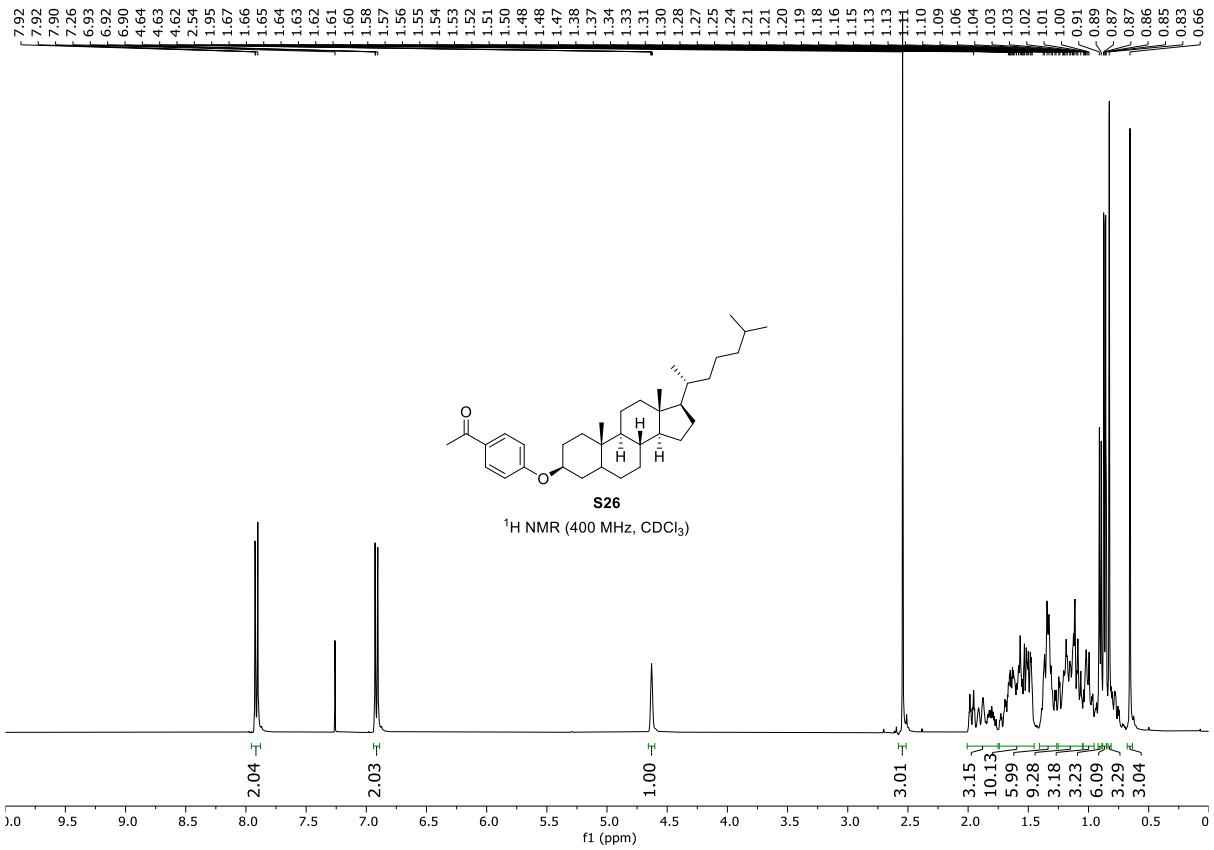

199.17
161.14
143.77
143.69
140.14
136.83
133.82
133.01
129.82
128.61
128.53
128.25
127.88
127.01
123.88
123.78
119.35
113.11
112.98
77.48
77.16
76.84
73.86
51.72
50.89
50.78
47.69
45.96
39.49
37.82
37.75
34.96
29.44
29.23
26.35
24.98
24.88
22.41
22.33
21.65
21.13
O
H
Ph
iPr
O
N
Ts
30
13C NMR (101 MHz, CDCl3)
f1 (ppm)

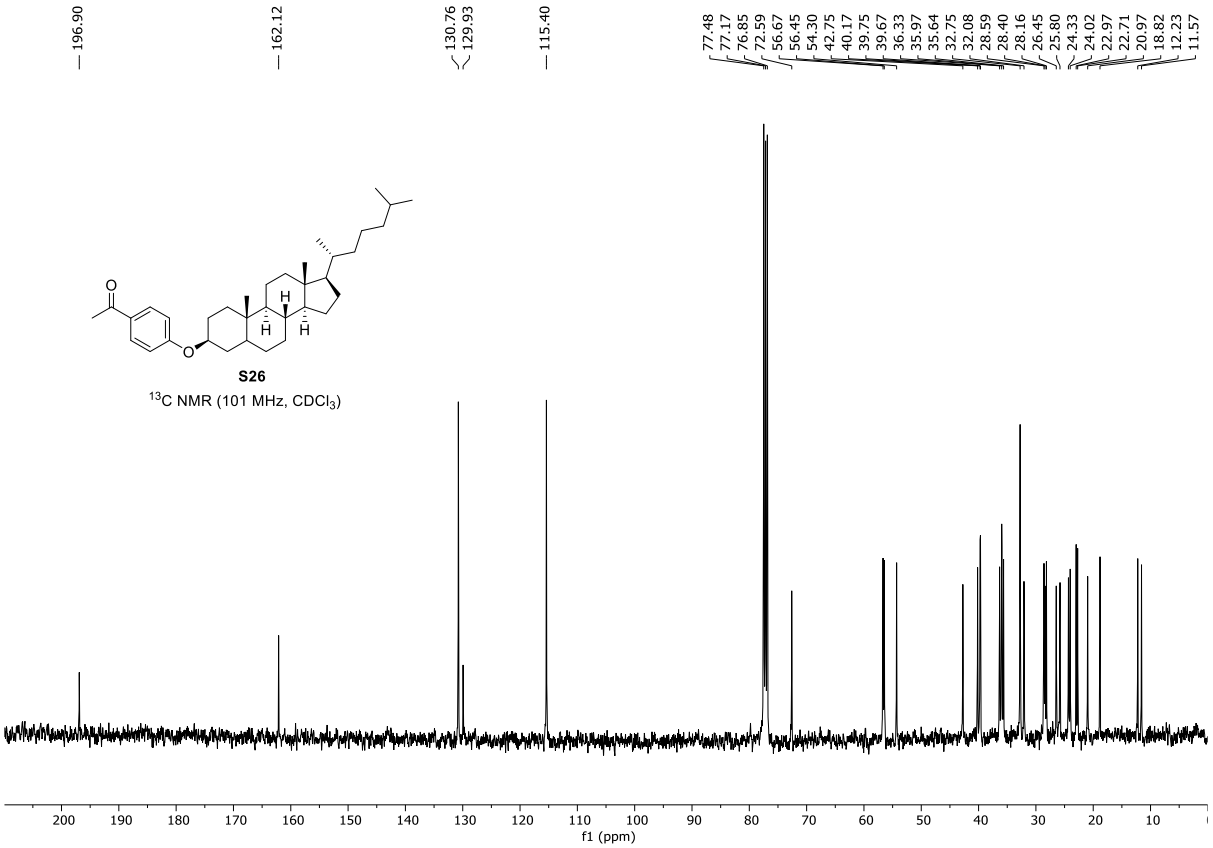
8.01
7.99
7.85
7.84
7.78
7.76
7.74
7.73
7.71
7.69
7.33
7.32
7.31
7.30
7.29
7.23
7.22
7.20
7.09
7.07
6.12
5.13
5.11
4.25
4.22
4.08
4.05
3.37
3.36
3.35
3.33
3.15
3.14
3.12
3.10
2.92
2.90
2.89
2.87
2.59
2.46
2.43
2.42
2.41
2.09
2.08
2.07
2.05
1.82
1.82
1.76
1.75
1.50
1.48
1.46
1.43
1.41
1.15
1.14
1.12
1.11
1.10
0.97
0.92
0.88


O
H
Ph
O
O
N
Ts
31
1H NMR (500 MHz, CDCl3)
1.02
1.01
1.23
2.09
4.10
1.08
2.12
1.02
1.04
1.02
1.06
1.06
3.12
1.15
3.15
4.05
1.31
1.00
1.20
2.10
1.18
3.00
6.25
f1 (ppm)


201.46
165.85
143.80
141.07
139.76
139.45
136.49
133.34
133.04
132.88
129.88
129.71
128.65
128.22
127.88
127.18
123.98
81.30
77.48
77.16
76.84
52.09
52.03
50.75
49.27
48.06
46.42
45.07
37.63
36.91
30.10
28.18
27.55
27.03
22.77
21.65
19.85
19.04
13.75
O
H
Ph
O
O
N
Ts
31
13C NMR (101 MHz, CDCl3)
f1 (ppm)
7.84
7.82
7.80
7.78
7.70
7.70
7.68
7.68
7.34
7.32
7.30
7.28
7.23
7.21
7.19
7.16
7.13
7.13
7.11
7.09
6.98
6.98
6.97
6.96
6.96
6.22
4.46
4.45
4.44
4.30
4.26
4.01
4.00
3.99
3.98
3.54
3.53
3.38
3.37
3.35
3.19
3.18
3.17
3.11
3.08
3.07
3.07
3.06
3.05
3.04
2.84
2.60
2.57
2.55
2.39
2.37
2.36
2.35
2.15
2.13
2.03
2.02
2.00
1.99
1.97
1.95
1.93
1.48
1.45
O
H
Ph
O
O
N
Ts
N
Boc
32
1H NMR (400 MHz, CDCl3)
1.00
1.99
4.04
1.03
3.08
1.01
0.44
0.55
0.43
0.57
1.05
1.04
1.59
1.58
0.95
2.14
1.04
1.61
1.36
3.02
1.02
1.11
2.04
3.99
5.02
f1 (ppm)

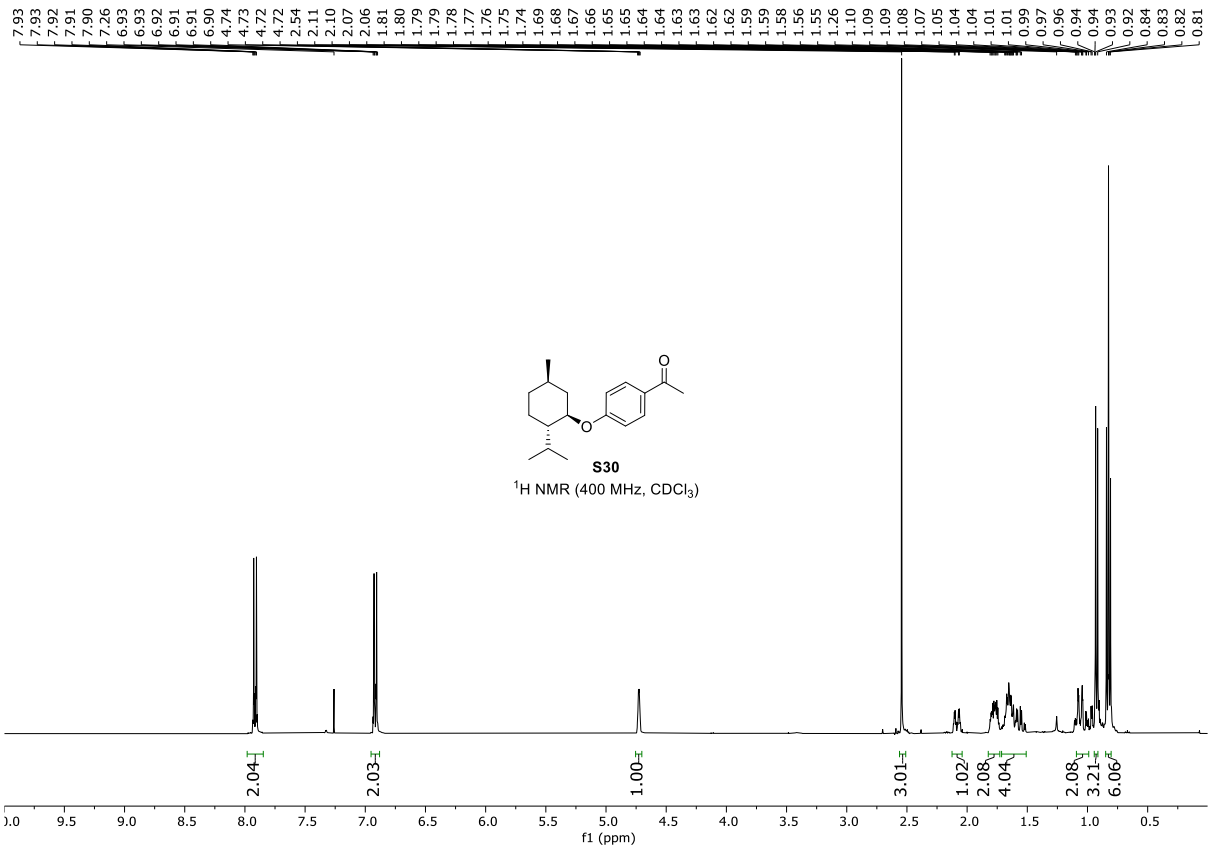

200.19
200.05
171.22
154.58
153.72
153.03
152.76
143.71
142.63
142.40
139.74
139.59
136.61
134.62
132.81
132.70
132.06
131.96
129.82
128.58
128.21
127.85
127.09
127.03
125.21
125.13
123.95
123.81
119.86
119.38
80.36
80.19
77.48
77.16
76.84
60.45
59.24
59.16
51.71
51.47
50.70
46.74
46.54
46.20
38.34
38.14
31.04
30.03
29.76
29.66
28.50
24.61
23.78
21.59
14.27
14.19
O
H
Ph
O
O
N
Ts
N
Boc
32
13C NMR (101 MHz, CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.92
7.92
7.90
7.26
6.93
6.92
6.90
4.64
4.63
4.62
2.54
1.95
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.48
1.48
1.47
1.38
1.37
1.34
1.33
1.31
1.30
1.28
1.27
1.25
1.24
1.21
1.21
1.20
1.19
1.18
1.16
1.15
1.13
1.13
1.11
1.10
1.09
1.06
1.04
1.03
1.03
1.02
1.01
1.00
0.91
0.89
0.87
0.87
0.86
0.85
0.83
0.66
O
H
H
H
O
S26
1H NMR (400 MHz, CDCl3)
2.04
2.03
1.00
3.01
3.15
10.13
5.99
9.28
3.18
3.23
6.09
3.29
3.04
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



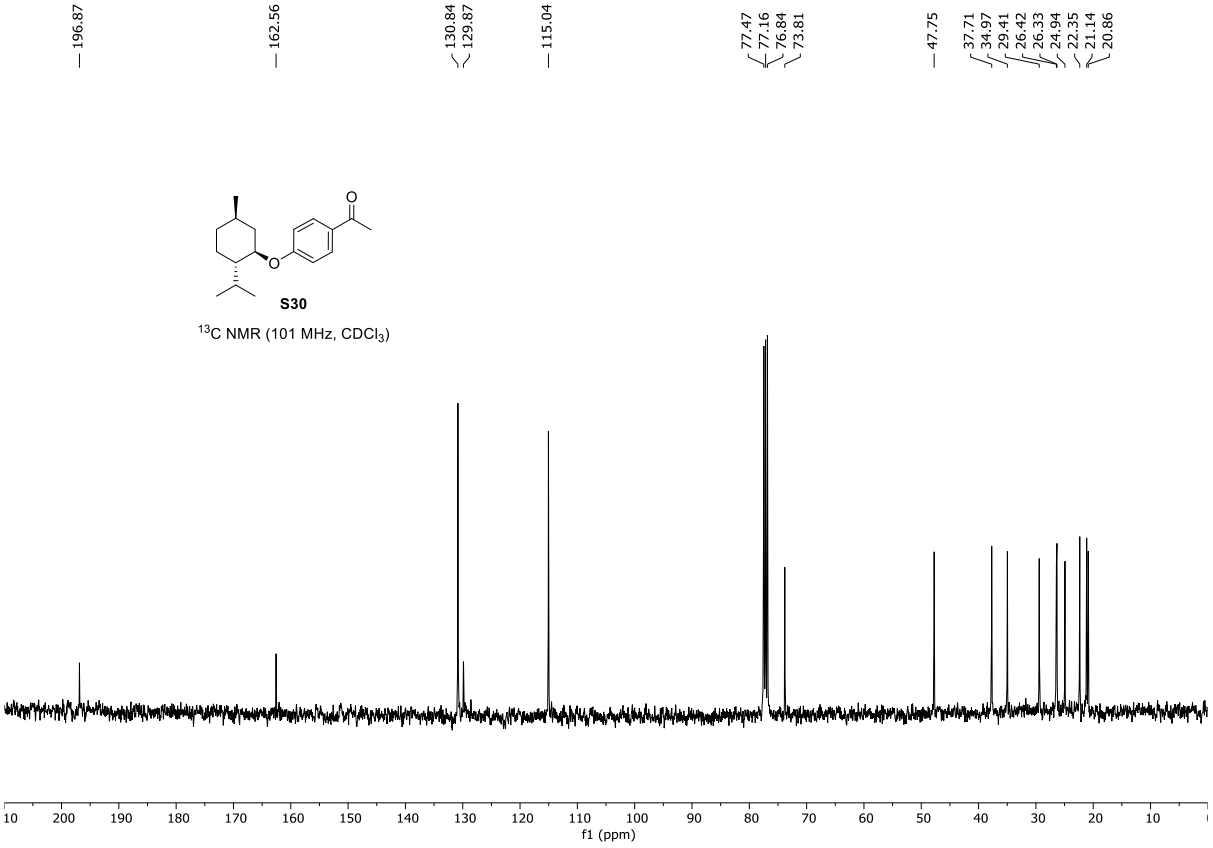
S26

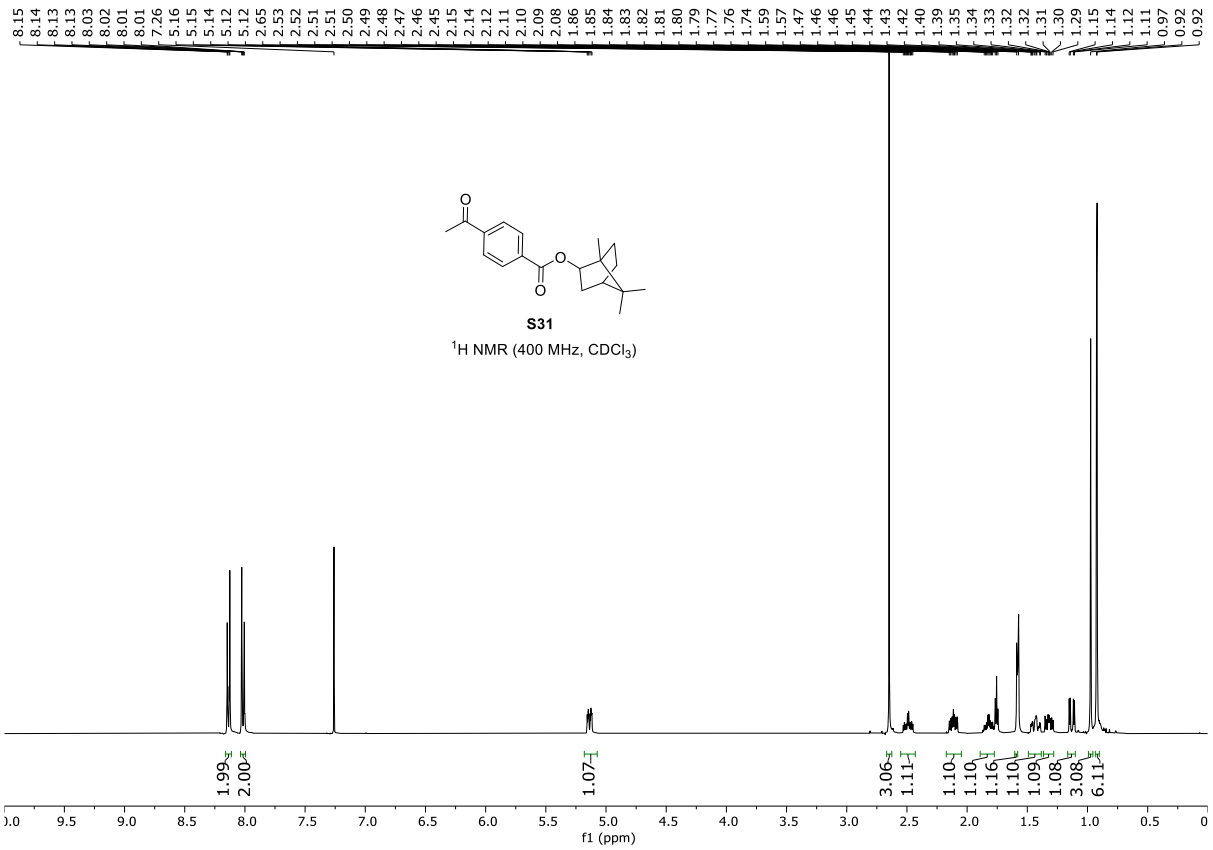
^{13}C NMR (101 MHz, $CDCl_3$)

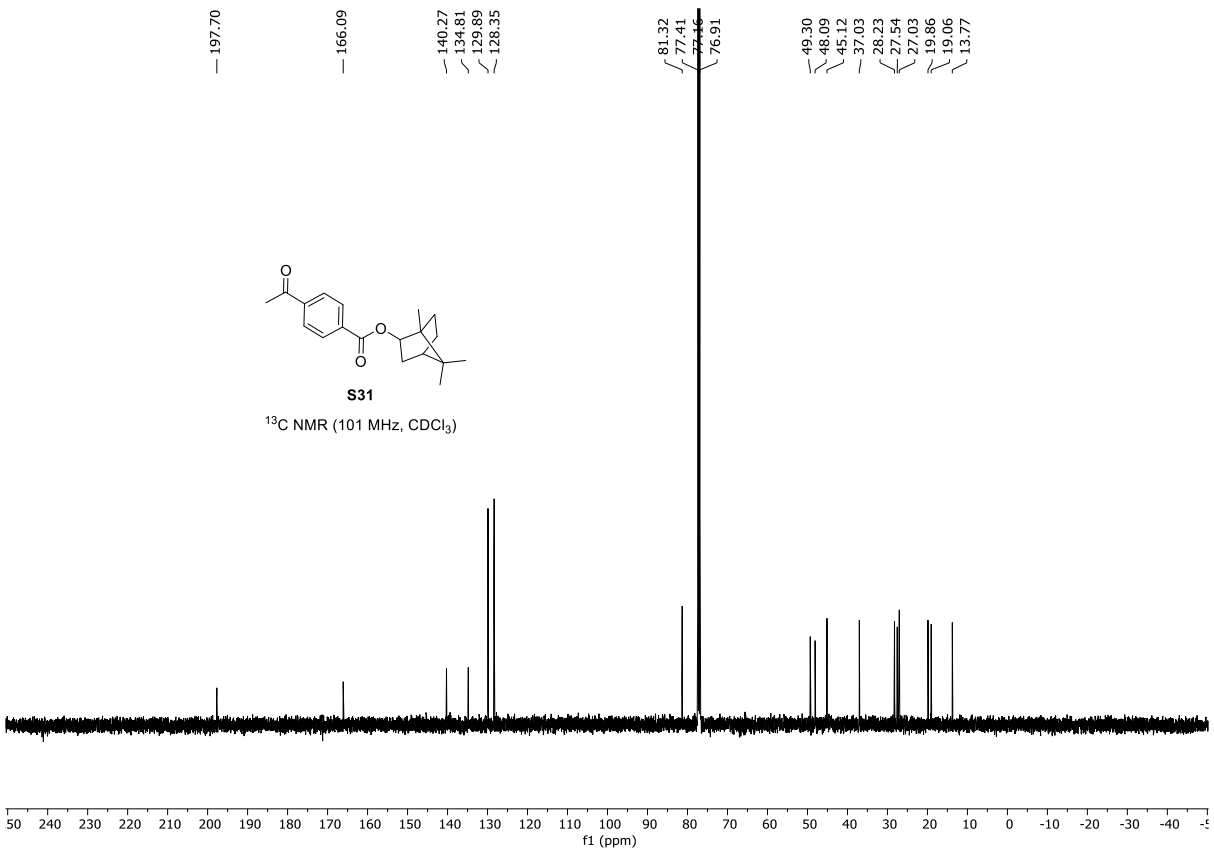


S30

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


196.87
162.56
130.84
129.87
115.04
77.47
77.16
76.84
73.81
47.75
37.71
34.97
29.41
26.42
26.33
24.94
22.35
21.14
20.86
S30
13C NMR (101 MHz, CDCl3)
f1 (ppm)


S31
1H NMR (400 MHz, CDCl3)
1.99
2.00
1.07
3.06
1.11
1.10
1.10
1.16
1.10
1.09
1.08
3.08
6.11
f1 (ppm)



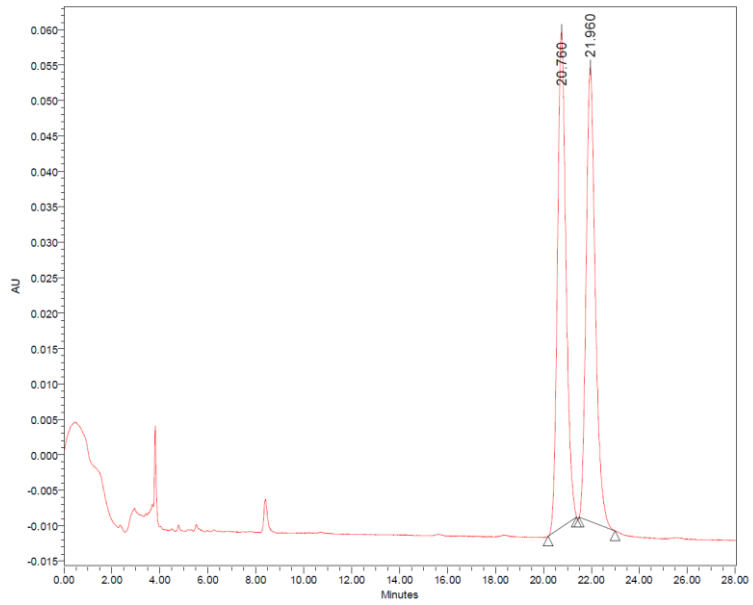
S31

^{13}C NMR (101 MHz, $CDCl_3$)

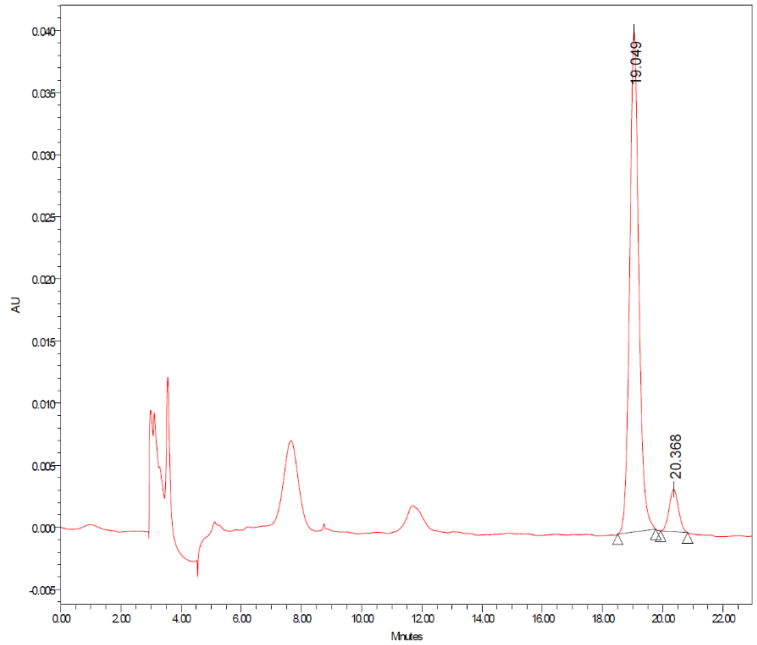
11. HPLC chromatogram of the products

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (3):

Daicel Chiralpak IA-3 Column, e.r. = 92:8, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.049 min, t_r (minor) = 20.368 min.



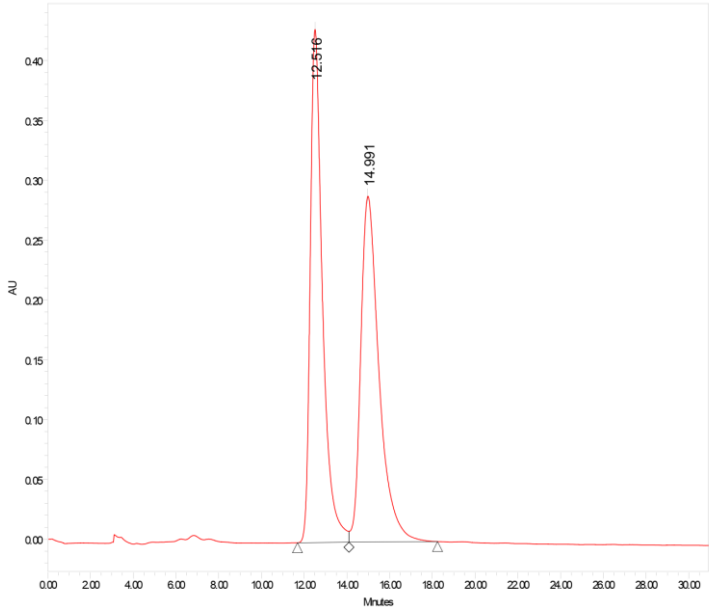
Entry	RT (min)	Height (μV)	Area (μV*sec)	%Area
1	21.960	64090	1709414	50.0
2	20.760	69899	1720458	50.0



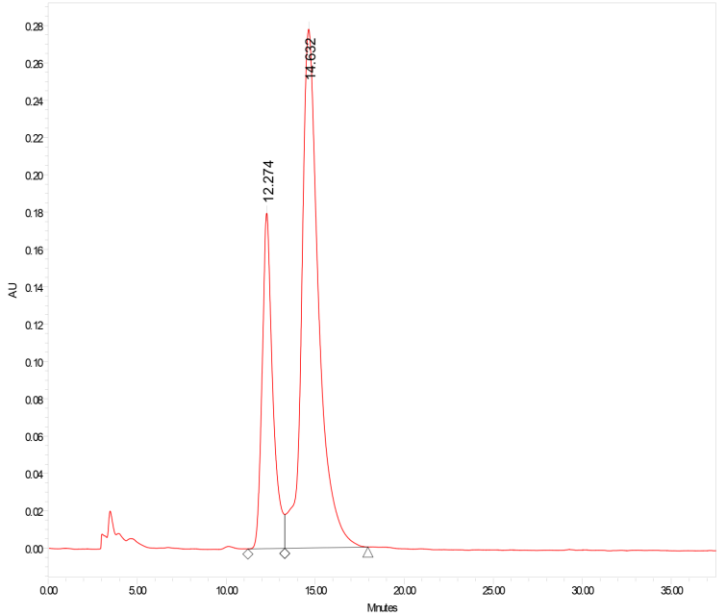
Entry	RT (min)	Height (μV)	Area (μV*sec)	%Area
1	20.368	3406	73353	8
2	19.049	40237	845875	92

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-methylphenyl)ethan-1-one (4):

HPLC: Daicel Chiralpak OD-H Column, e.r. = 71:29, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 14.632 min, t_r (minor) = 12.274 min.



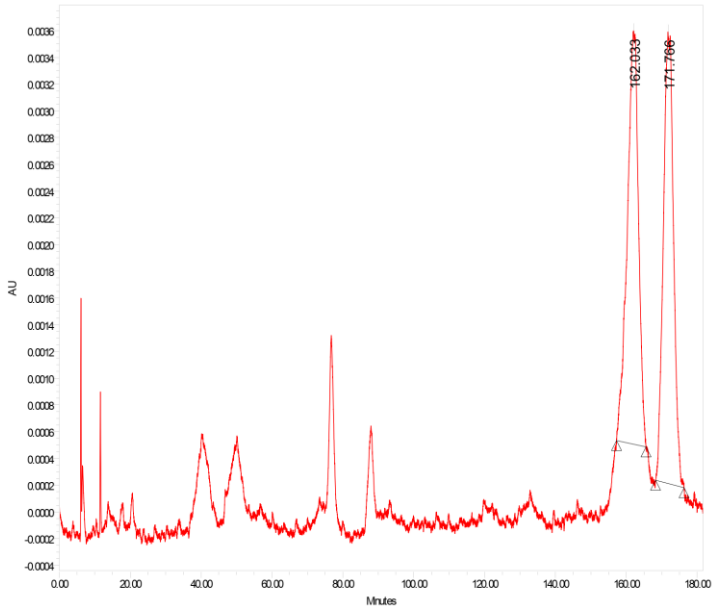
c	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	14.991	289113	17191674	50.26
2	12.516	428807	17011969	49.74



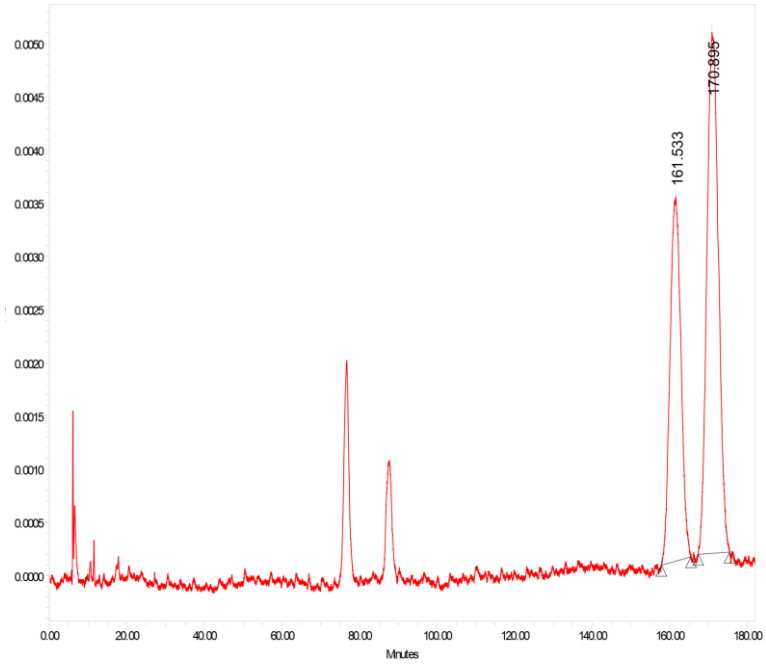
c	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	14.632	277917	18505711	71.35
2	12.274	179708	7431432	28.65

(*R*, *Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-methoxyphenyl)ethan-1-one (5):

HPLC: Daicel Chiralpak AD-H Column, e.r. = 60:40, λ = 254 nm, hexane/isopropanol = 94:06, flow rate 1 mL/min, t_r (major) = 170.895 min, t_r (minor) = 161.533 min.



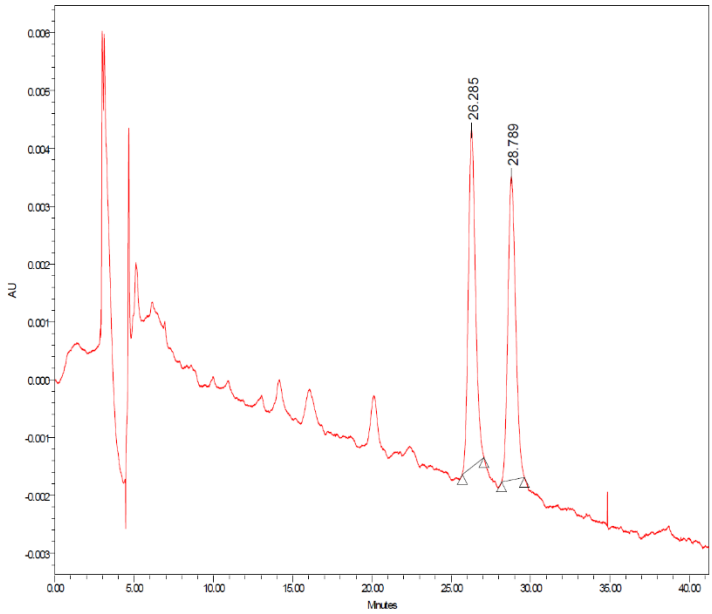
c	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	171.766	3378	674038	49.76
2	162.033	3092	680525	50.24



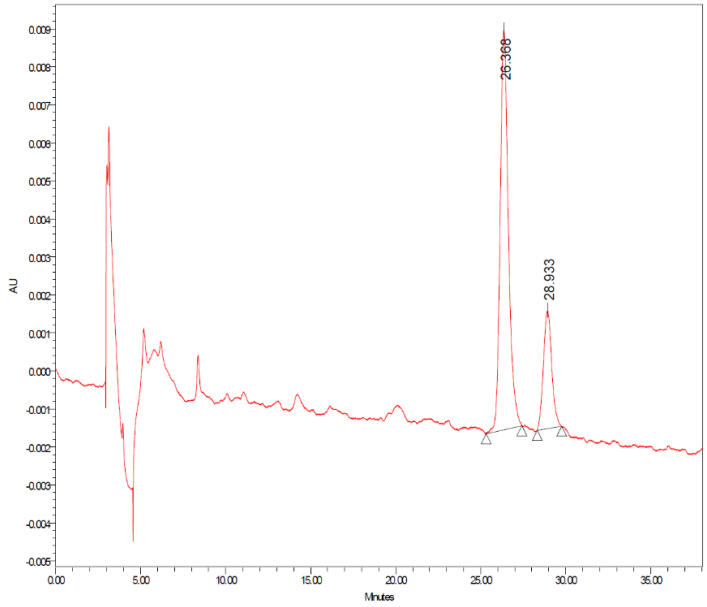
c	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	170.895	4896	1011691	60
2	161.533	3423	670641	40

(*R*,*Z*)-4-acetyl-3-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl acetate (6):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 77:23, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 26.368 min, t_r (minor) = 28.933/ min.

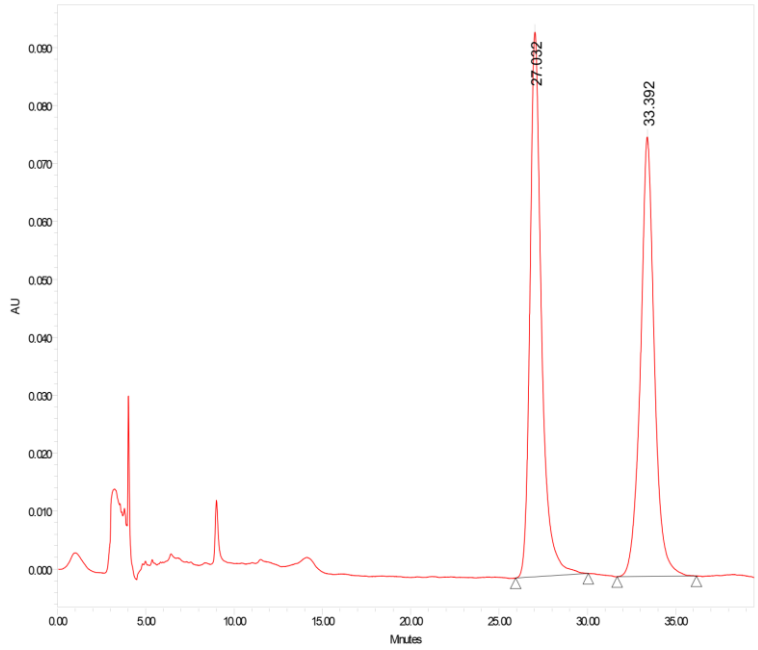


Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	28.789	5253	177589	49
2	26.285	5830	181782	51

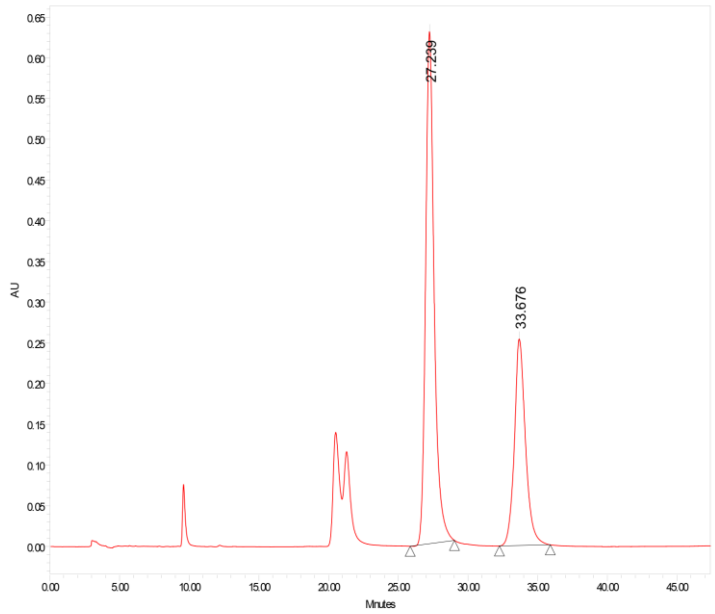


Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	28.933	3111	105426	23
2	26.368	10521	353660	77

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4,5-dimethoxyphenyl)ethan-1-one (7):



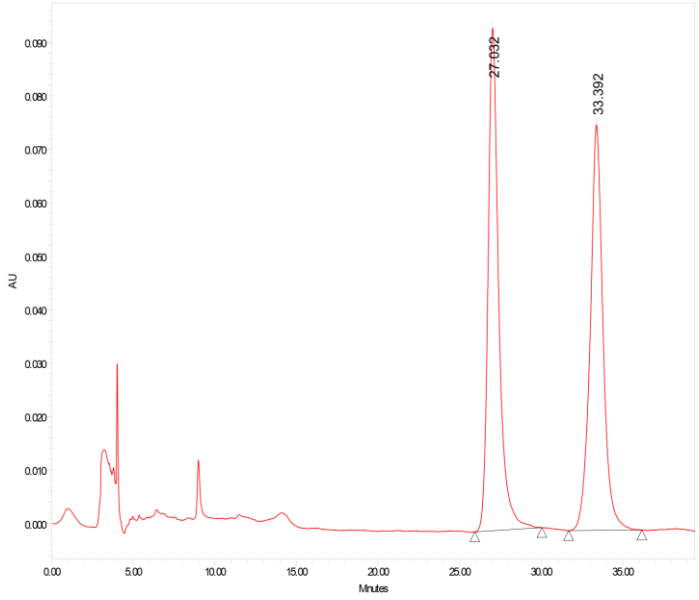
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	33.392	75828	4141012	49.30
2	27.032	93967	4259293	50.70



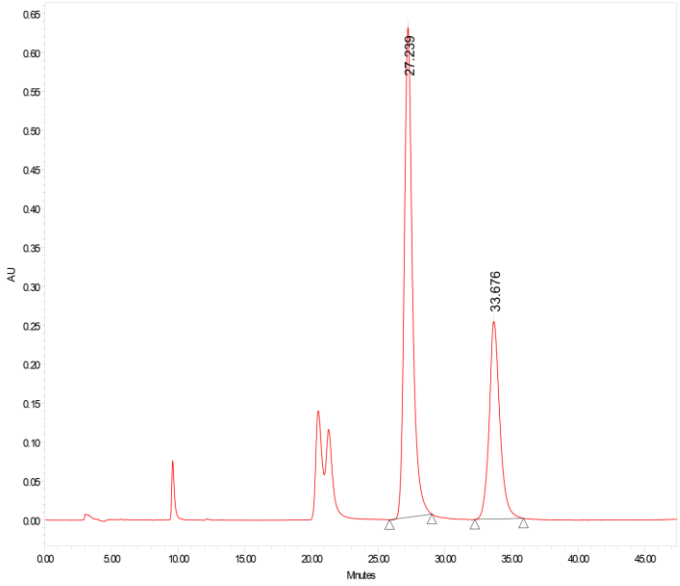
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	33.676	253605	14039507	34.38
2	27.239	628585	26798090	65.62

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4,5-dimethoxyphenyl)ethan-1-one (8):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 66:34, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 27.239 min, t_r (minor) = 33.676 min.



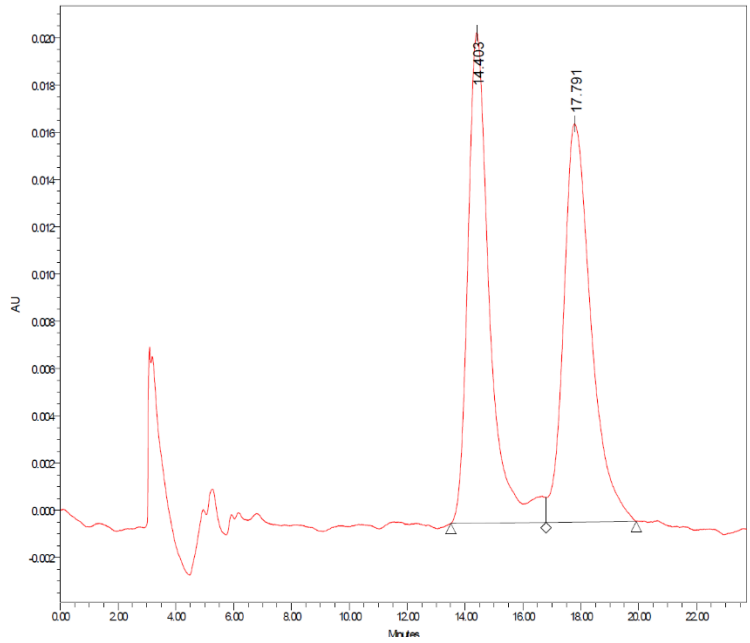
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	33.392	75828	4141012	49.30
2	27.032	93967	4259293	50.70



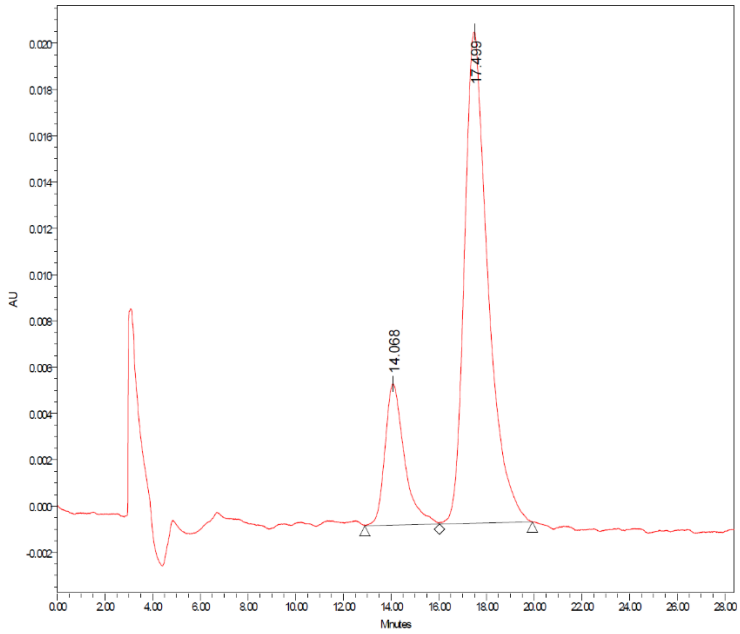
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	33.676	253605	14039507	34.38
2	27.239	628585	26798090	65.62

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-(trifluoromethyl)phenyl)ethan-1-one (9):

HPLC: Daicel Chiralpak OD-H Column, e.r. = 19:81, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 17.499 min, t_r (minor) = 14.068 min.



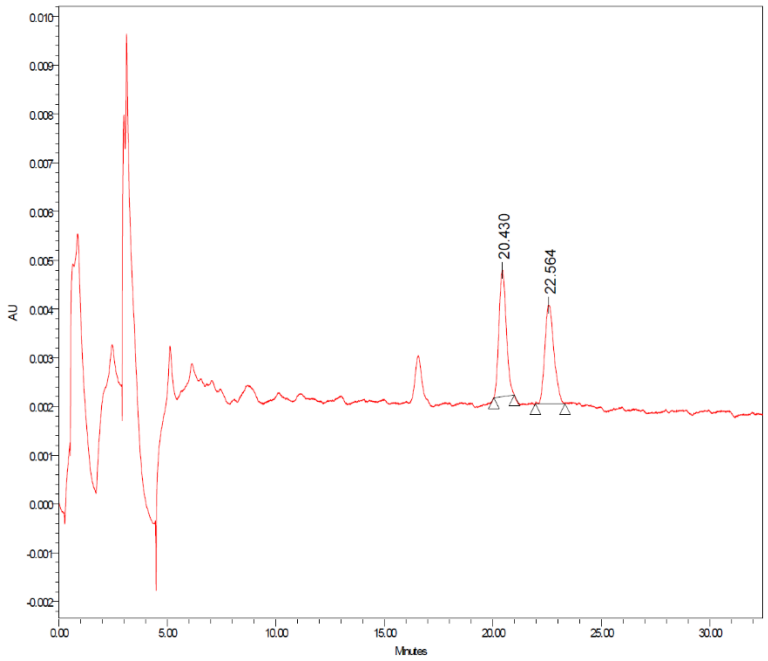
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	17.791	16858	1110029	50.5
2	14.403	20758	1089710	49.5



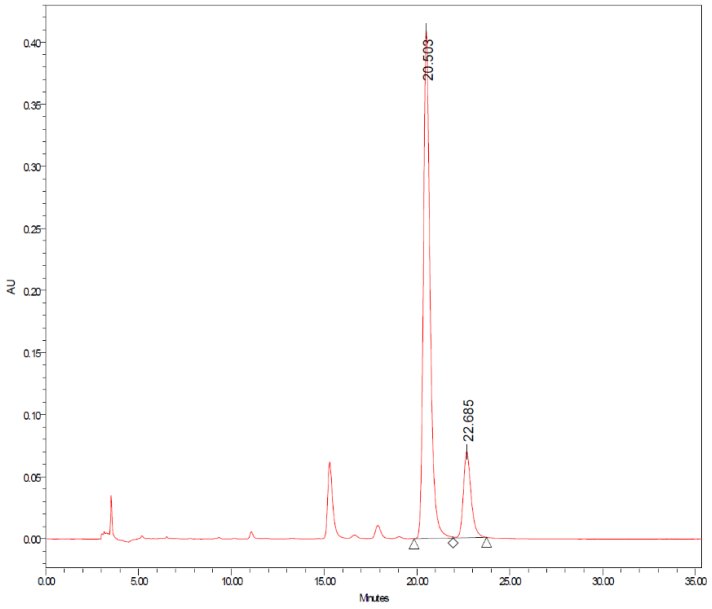
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	17.499	21224	1456241	81
2	14.068	6106	345609	19

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-fluorophenyl)ethan-1-one (10):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 84:16, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.503 min, t_r (minor) = 22.685 min.



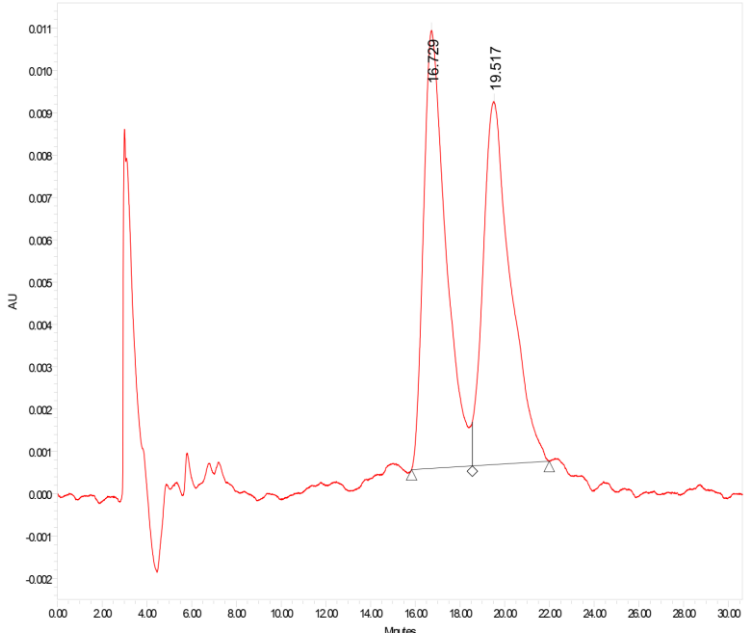
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	22.564	2021	59045	49
2	20.430	2599	60615	51



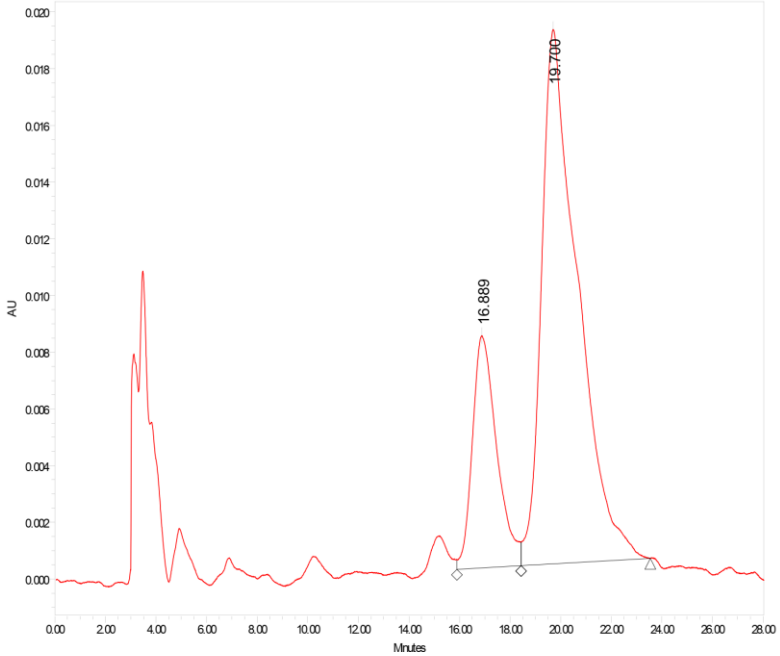
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	22.685	69378	1995514	16
2	20.503	409185	10251629	84

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-chlorophenyl)ethan-1-one (11):

HPLC: Daicel Chiralpak OD-H Column, e.r. = 77:23, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.700 min, t_r (minor) = 16.889 min.



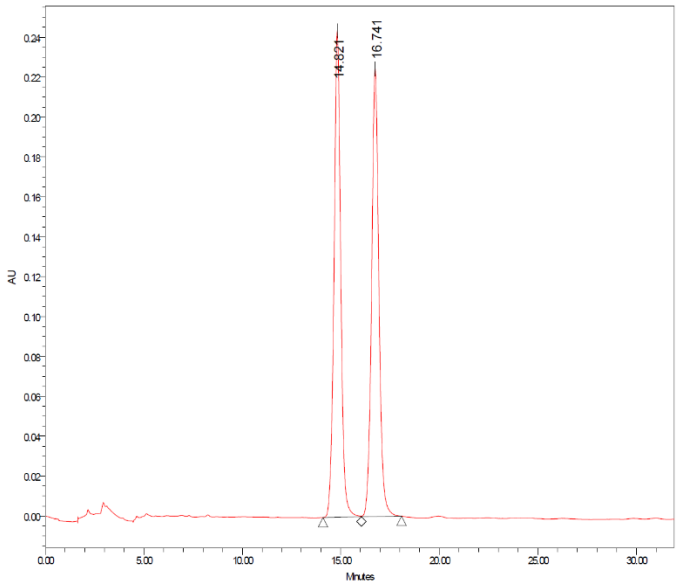
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	19.517	8574	732122	50.42
2	16.729	10343	719965	49.58



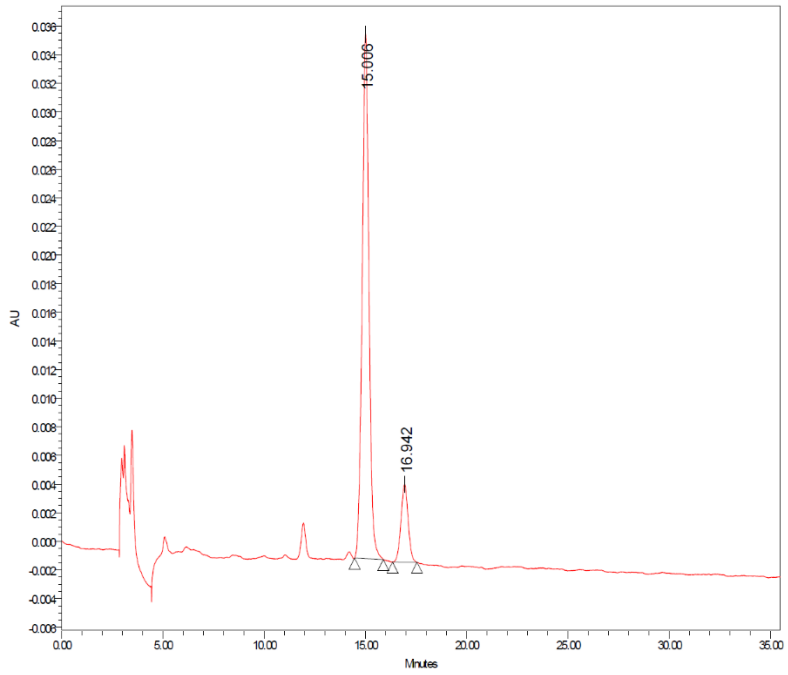
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	19.700	18847	1872102	77.37
2	16.889	8198	547587	22.63

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)propan-1-one (12):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 86.5:13.5, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 15.006 min, t_r (minor) = 16.942 min.



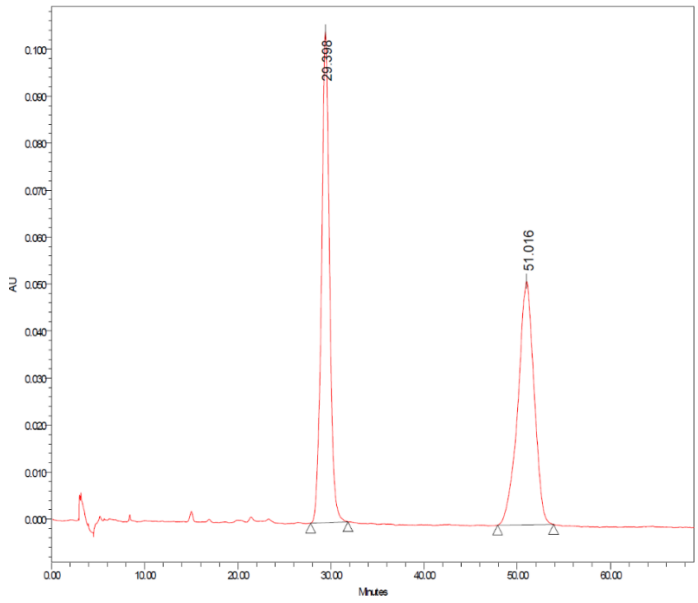
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	16.741	224471	5753738	50
2	14.821	243976	5788653	50



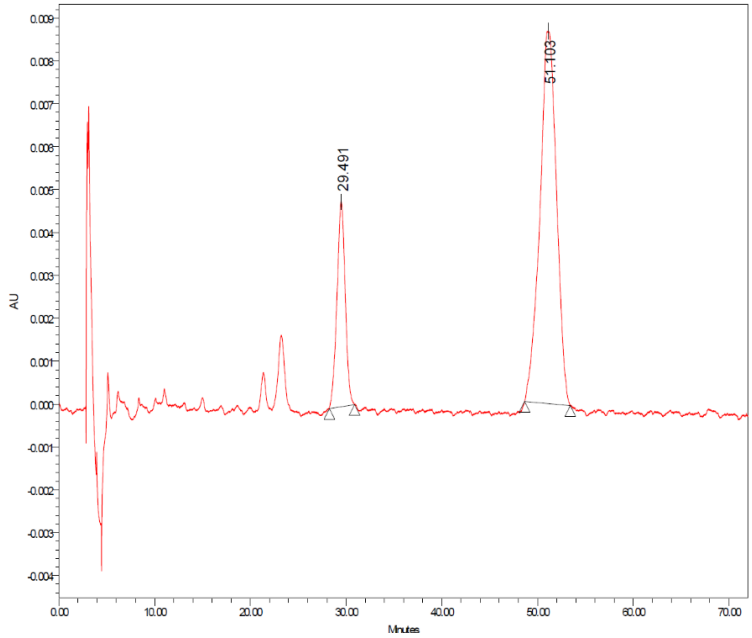
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	16.942	5428	133148	13.5
2	15.006	36644	851660	86.5

(*R*,*Z*)-1-(3-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)naphthalen-2-yl)ethan-1-one (13):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 22:79, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 51.103 min, t_r (minor) = 29.491 min.



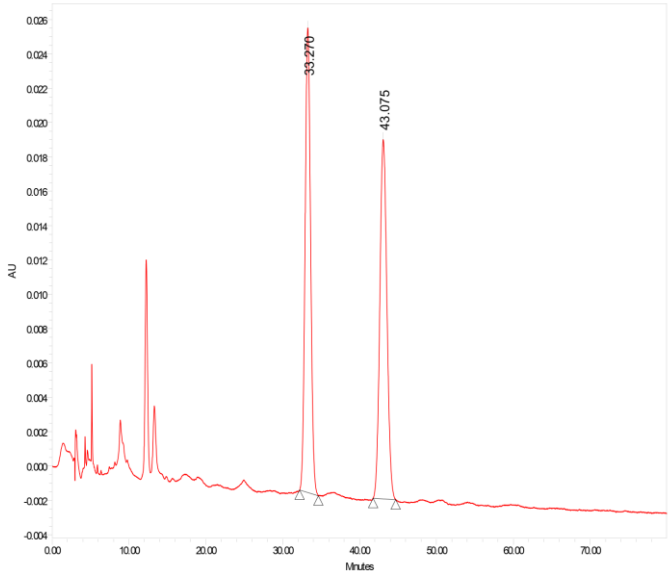
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	51.016	51805	6229928	50
2	29.398	104467	6257813	50



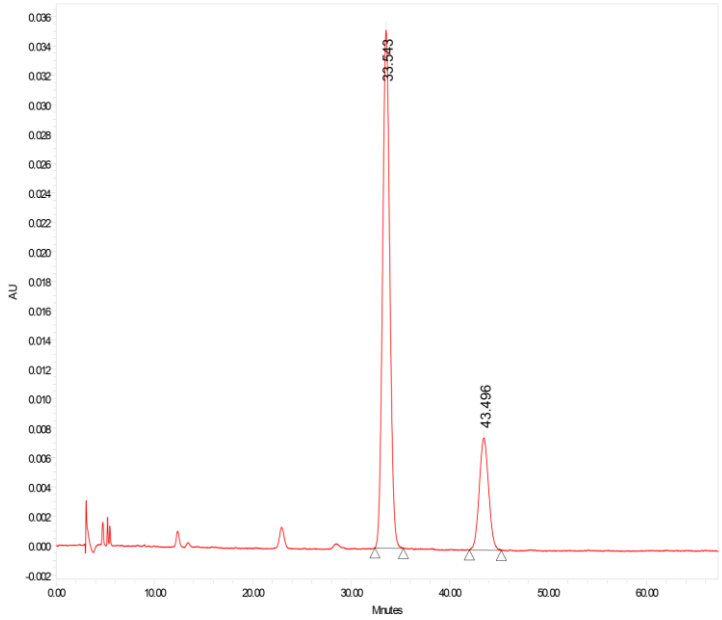
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	51.103	8685	1051378	79
2	29.491	4780	287160	21

(*R*,*Z*)-8-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-3,4-dihydronaphthalen-1(2H)-one (14):

HPLC: Daicel Chiralpak AD-H Column, e.r. = 78:20, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 43.496 min, t_r (minor) = 33.543 min.



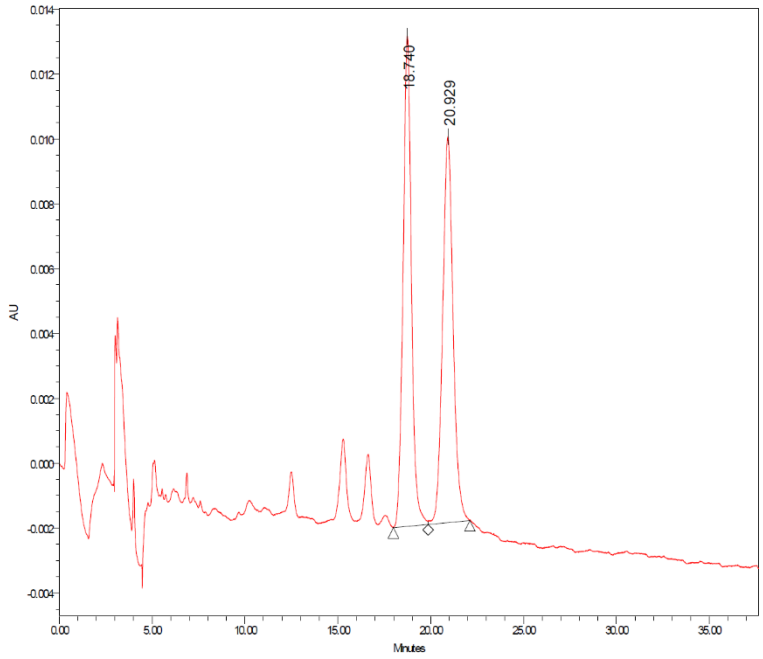
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	43.075	20923	1336459	49.79
2	33.270	27051	1347533	50.21



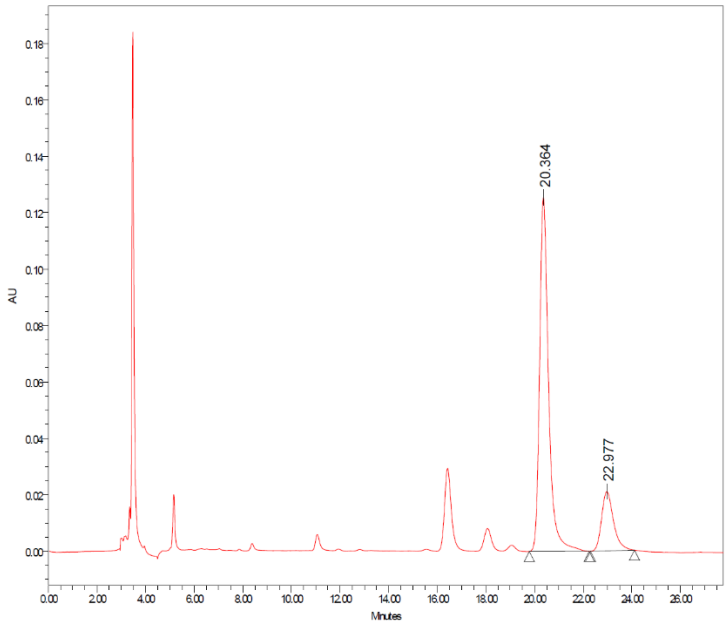
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	43.496	20923	7626	22.00
2	33.543	27051	35228	78.00

(*R*,*Z*)-2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)phenyl)(phenyl)methanone (15):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 82:18, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.364 min, t_r (minor) = 22.977 min.



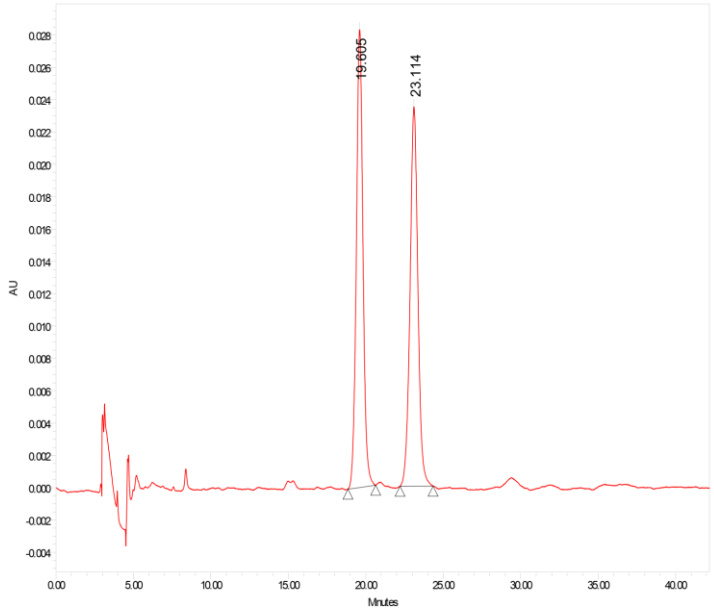
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	20.929	11905	467570	50
2	18.740	15123	470673	50



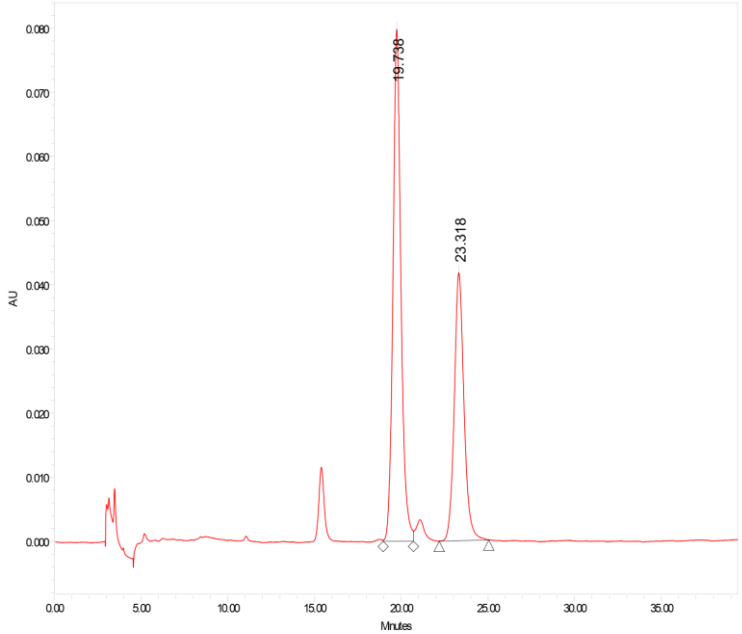
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	22.977	20986	715256	18
2	20.364	125536	3217302	82

(*R*,*Z*)-1-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)thiophen-3-yl)ethan-1-one (16)

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 61:39, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 19.738 min, t_r (minor) = 23.318min.



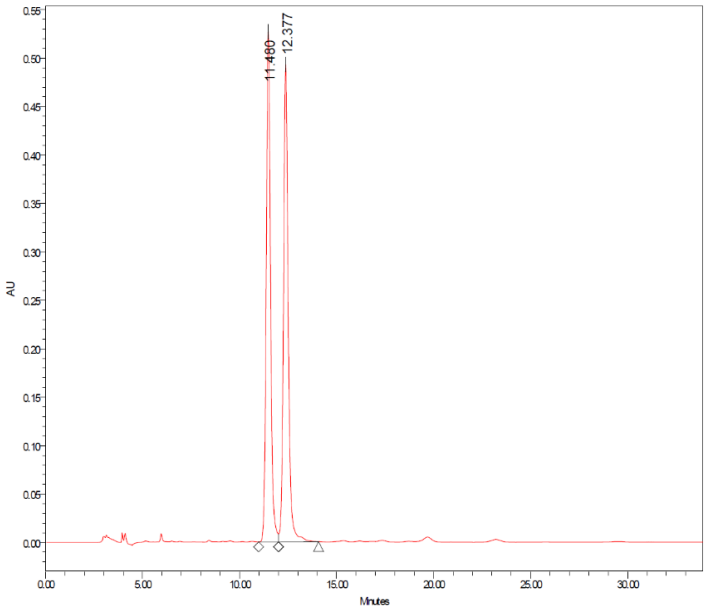
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	23.114	23464	824218	49.57
2	19.605	28316	838541	50.43



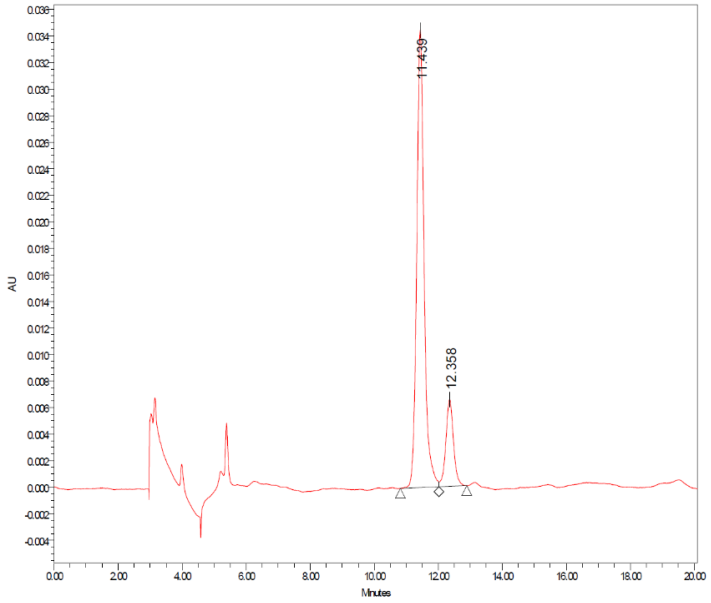
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	23.318	41763	1624774	39.00
2	19.738	79745	2541174	61.00

(*R*,*Z*)-1-(2-((4-(3,5-dimethylbenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (17):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 84:16, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 11.439 min, t_r (minor) = 12.358 min.



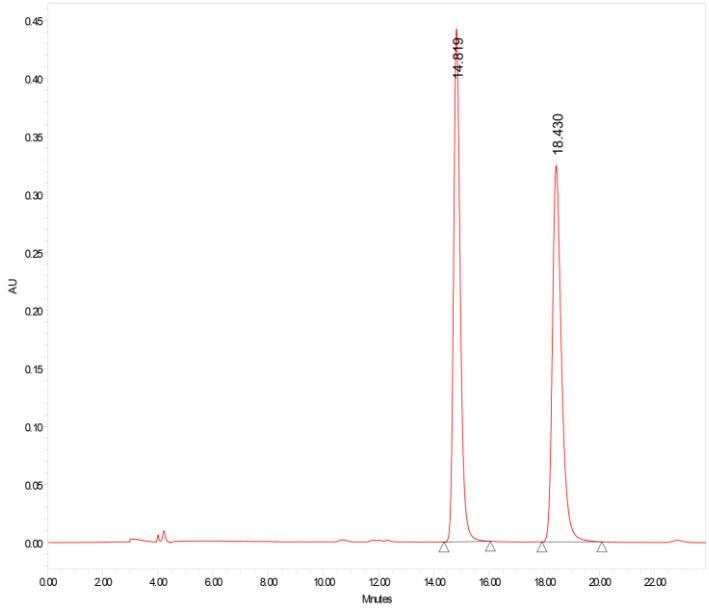
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	12.377	492597	8284531	50
2	11.480	526727	8096475	50



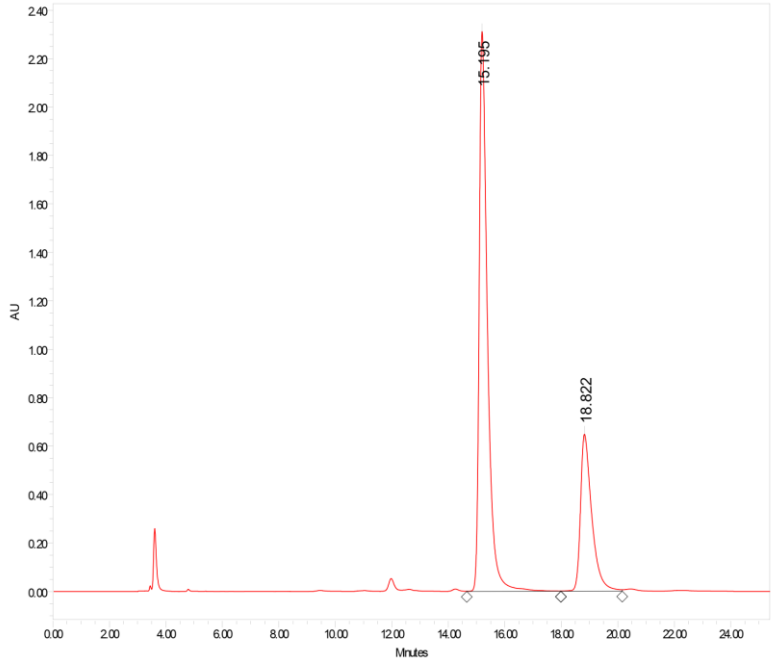
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	12.358	6535	108311	16
2	11.439	34474	549925	83

(*R*,*Z*)-1-(2-((4-(4-(tert-butyl)benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (18)

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 15.195min, t_r (minor) = 18.822min.



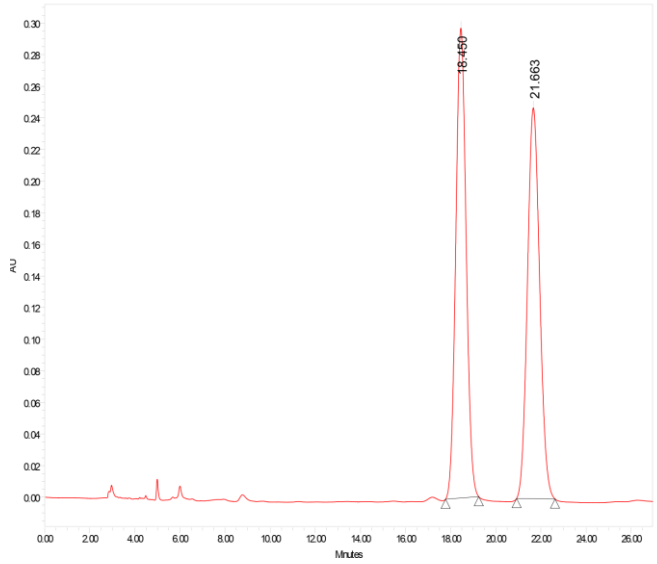
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	14.819	441864	7437579	50.15
2	18.430	324297	7393194	49.85



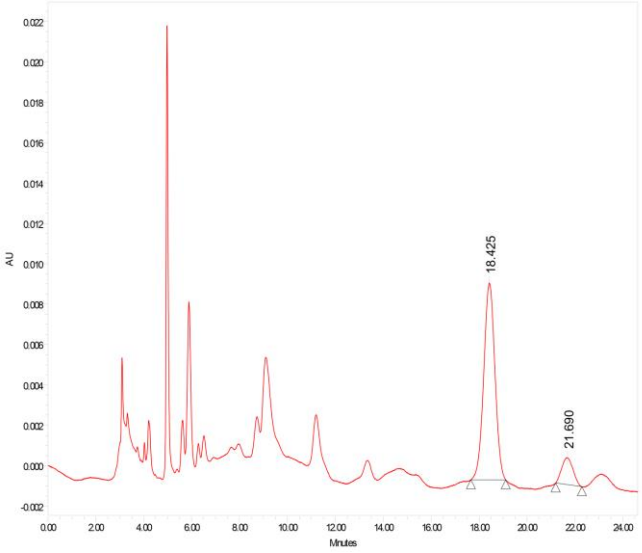
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	18.822	648282	17980295	27.71
2	15.195	2310749	46905503	72.29

(*R*,*Z*)-1-(2-((4-(4-methoxybenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (19):

HPLC: Daicel Chiralpak AD-H Column, e.r. = 88:12, λ = 254 nm, hexane/isopropanol = 70:30, flow rate 1 mL/min, t_r (major) = 18.425 min, t_r (minor) = 21.69 min.



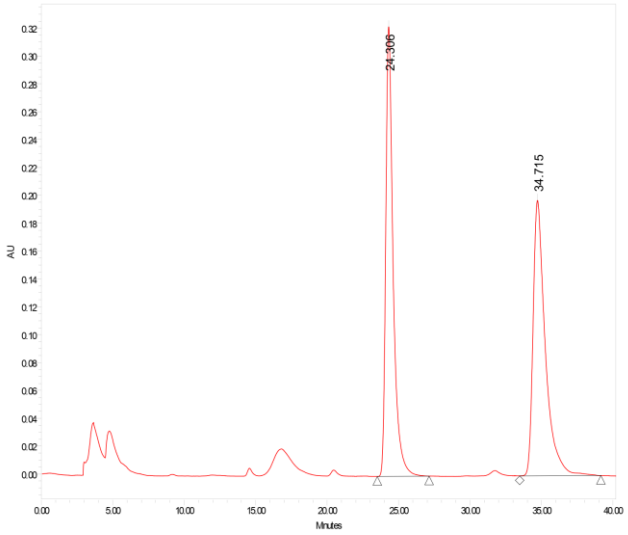
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	21.663	247274	9289093	49.60
2	18.450	297255	9437813	50.40



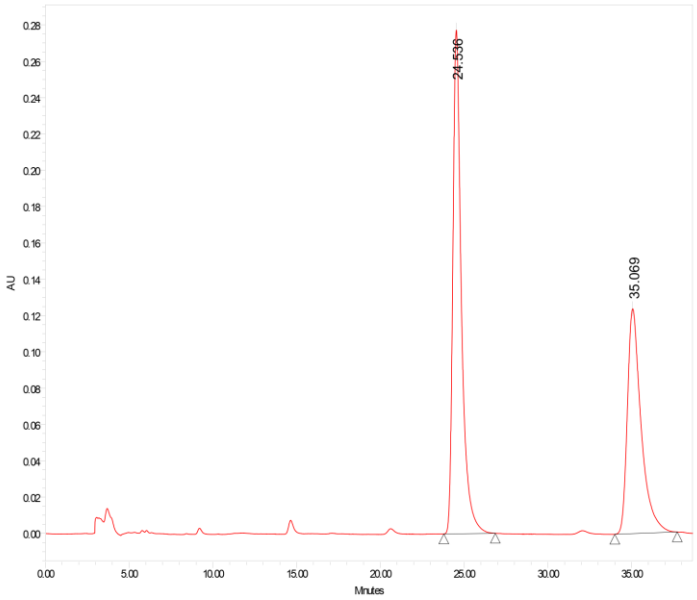
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	21.690	1330	43304	12.06
2	18.425	9742	315808	87.94

(*R*,*Z*)-1-(2-((1-tosyl-4-(4-(trifluoromethyl)benzylidene)pyrrolidin-3-yl)methyl)phenyl)ethan-1-one (20):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 58:42, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 24.536min, t_r (minor) = 35.069min.



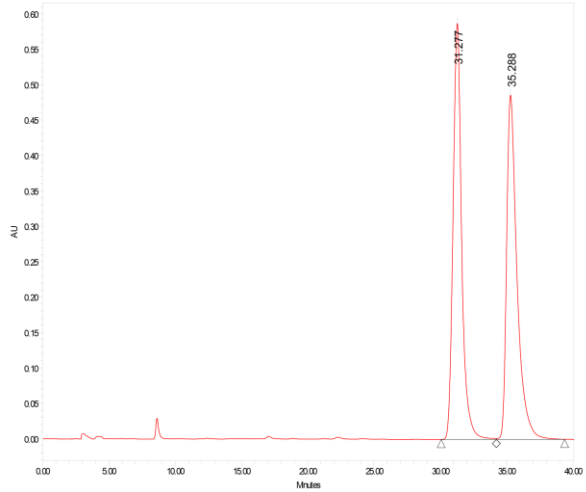
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	34.715	197686	11733921	50.30
2	24.306	322640	11594488	49.70



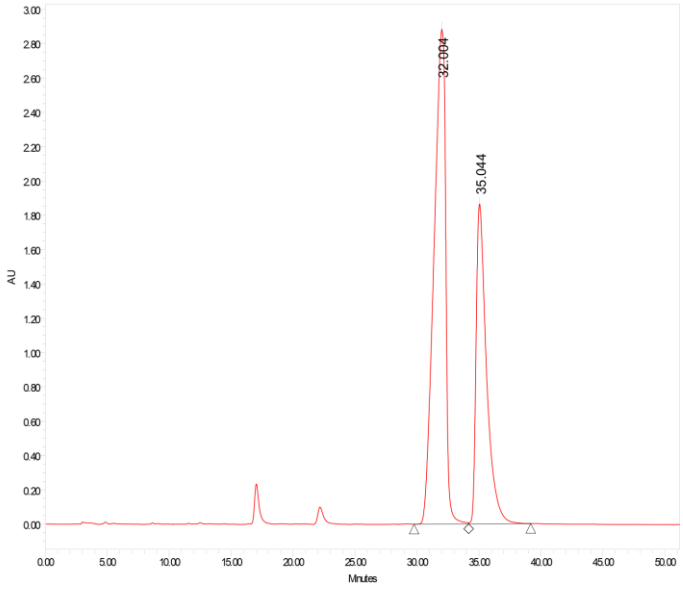
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	35.069	123814	7031255	41.71
2	24.536	277341	9826306	58.29

(*R*,*Z*)-1-(2-((4-(4-chlorobenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (21):

HPLC: Daicel Chiralpak IA-3 Column, e.r. = 63:37, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 32.004min, t_r (minor) = 35.044min.



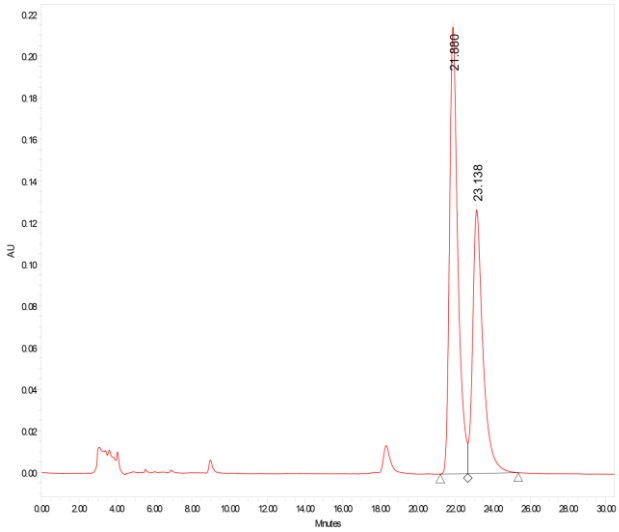
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	35.288	486151	26423851	49.87
2	31.277	587410	26560075	50.13



Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	35.044	1863517	108741330	36.63
2	32.004	2883769	18811092	63.37

(*R*,*Z*)-1-(2-((4-(3-chlorobenzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl)ethan-1-one (22):

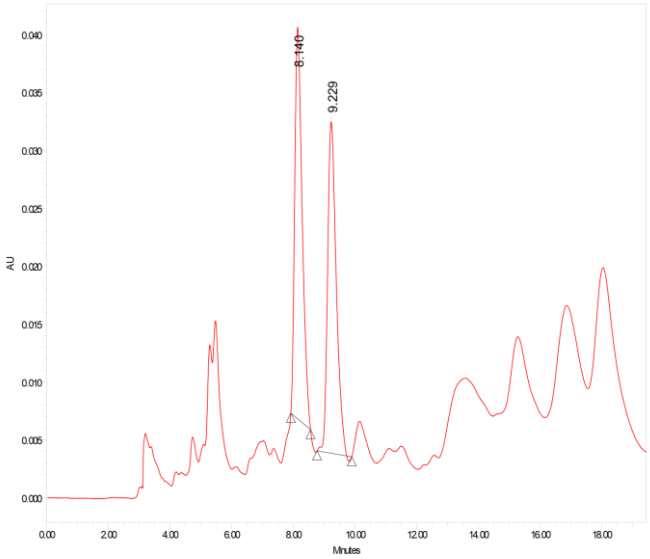
HPLC: Daicel Chiralpak IA-3 Column, e.r. = 58:42, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 21.880 min, t_r (minor) = 23.138 min.



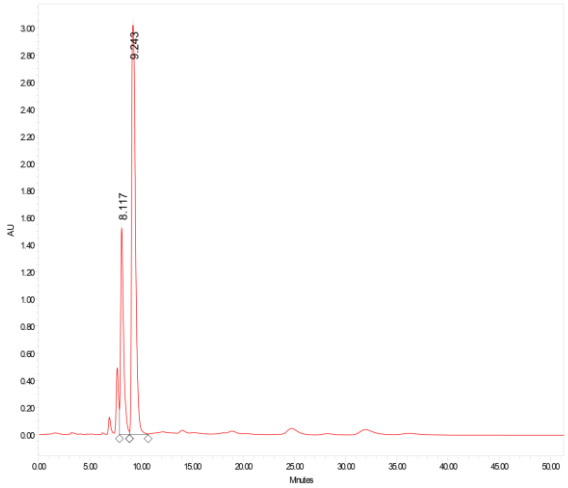
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	23.138	126501	4792196	42.09
2	21.880	214629	6592628	57.91

(*R*,*Z*)-1-(2-((4-benzylidenetetrahydrofuran-3-yl)methyl)phenyl)ethan-1-one (23)

HPLC: Daicel Chiralpak OD-H Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 9.243 min, t_r (minor) = 8.117 min.



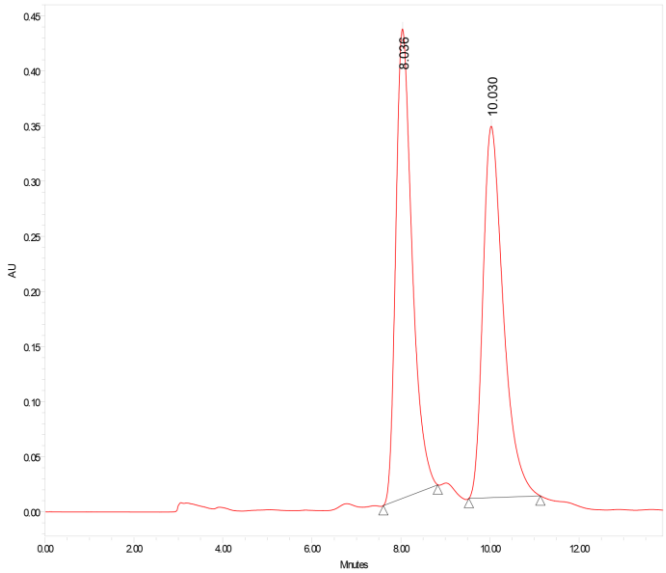
Entry	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	9.229	28624	560431	49.67
2	8.140	33802	567800	50.33



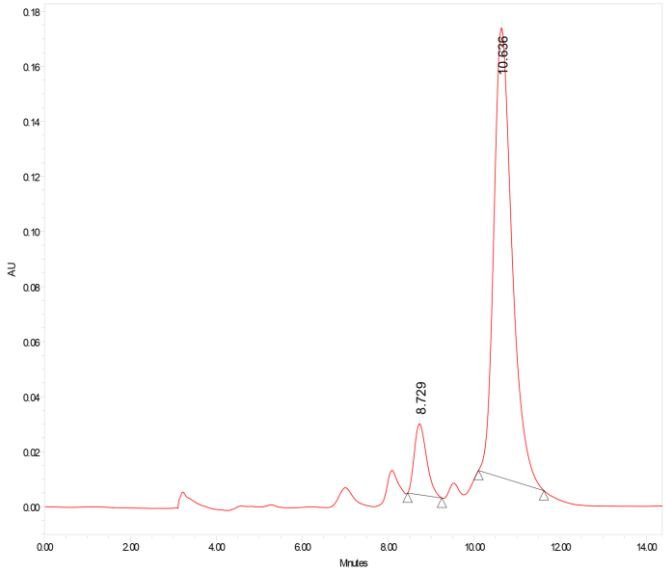
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	9.243	3021828	79624266	72.31
2	8.117	1522946	30494390	27.69

dimethyl (*S*,*E*)-3-(2-acetylbenzyl)-4-benzylidenecyclopentane-1,1-dicarboxylate (24):

HPLC: Daicel Chiralpak OD-H Column, e.r. = 90:10, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 10.636 min, t_r (minor) = 8.729 min.



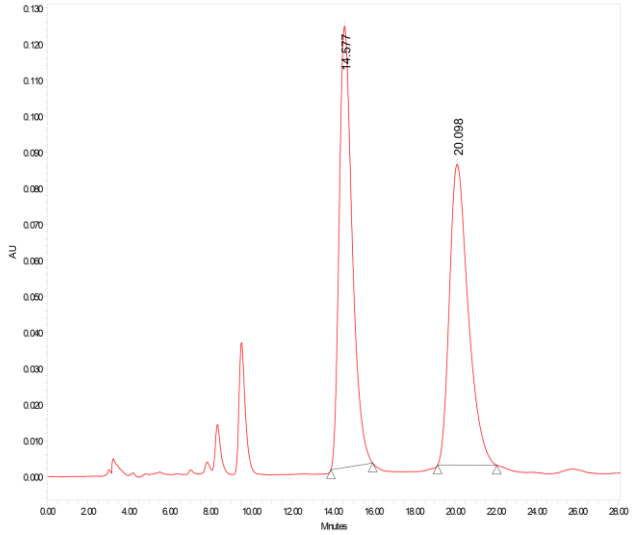
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	10.030	337028	10730371	49.73
2	8.036	425859	10845151	50.27



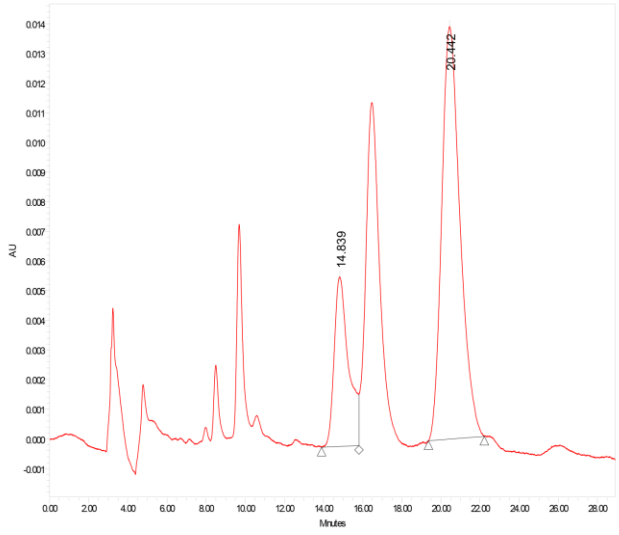
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	8.729	25778	510359	9.60
2	10.636	163330	4808145	90.40

methyl (*R*,*Z*)-2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)benzoate (25):

HPLC: Daicel Chiralpak OD-H Column, e.r. = 76:24, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 20.442 min, t_r (minor) = 14.839 min.



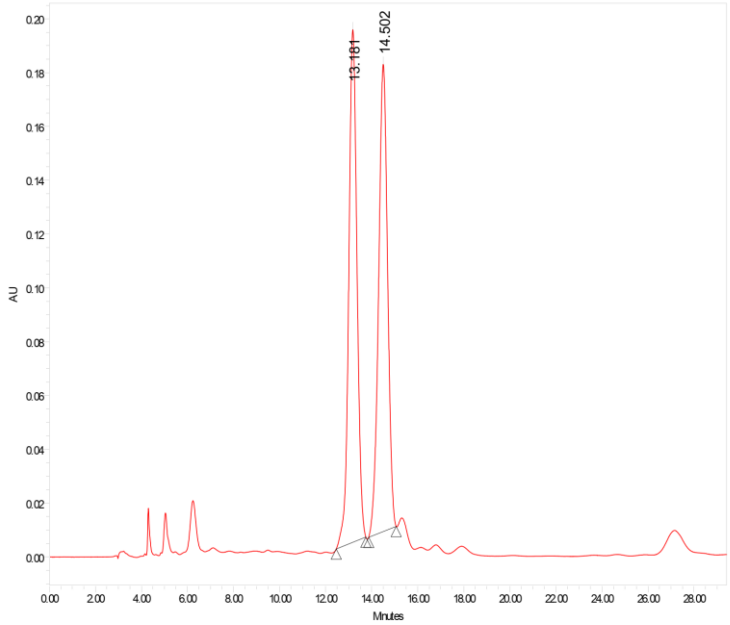
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	20.098	83455	5327187	49.57
2	14.577	122423	5420086	50.43



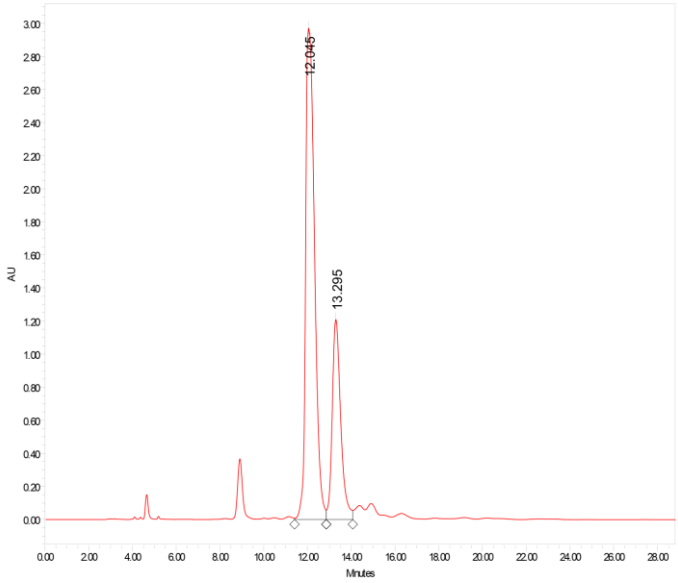
C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	20.442	13910	903538	75.56
2	14.839	5718	292190	24.44

4-acetyl-3-(((*R*)-4-((*Z*)-benzylidene)-1-tosylpyrrolidin-3-yl)methyl)phenyl oleate (29):

HPLC: Daicel Chiralpak AD-H Column, e.r. = 72:28, λ = 254 nm, hexane/isopropanol = 90:10, flow rate 1 mL/min, t_r (major) = 12.045 min, t_r (minor) = 13.295min.



C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	14.502	173637	4702762	49.96
2	13.181	190506	4709749	50.04



C	RT (min)	Height (µV)	Area (µV*sec)	%Area
1	13.295	1209354	32667207	28.04
2	12.045	2969572	83844367	71.96