Supporting Information for

Visible-Light Induced Metal-Free Intramolecular Reductive Cyclisations of Ketones with Alkynes and Allenes

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Table of Contents

General methods and materials	**S2-S3**
Optimization studies	**S4-S5**
Experimental details and characterization data	**S6-S39**
Unsuccessful results and up-scaling experiment	**S40**
Transformations	**S41-S44**
Experimental details for mechanistic studies	**S45-S48**
X-Ray crystal structure of 2l and 4a	**S49-S53**
References	**S54**
Copies of NMR spectra	**S55-S129**

General methods and materials

Reagents were purchased from commercial suppliers and used as received unless noted otherwise. The photocatalysts,[1] Hantzsch esters **HEH-1**[2] and **HEH-2**[3] were either commercially available or synthesized according to reported procedures.

Reactions were carried out in dry glassware under an argon atmosphere (Argon 5.0, Sauerstoffwerk Friedrichshafen). For this, the glassware was dried by heat gun under high vacuum (oil pump, 0.1 mbar), cooled to room temperature and backfilled with argon. An argon atmosphere in the reaction vessel was maintained throughout the reaction, unless noted otherwise. For the addition of solvents and reagents, syringes and cannula were flushed with argon three times prior to use. All yields are isolated yields, unless noted otherwise. For optimization studies in catalytic reactions, yields were determined from the ^{1}H-NMR spectrum of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

Solvents were bought in p.a. quality and used without further purification. Dry solvents for air/moisture sensitive reactions were bought from commercial suppliers and used as received. Toluene was freshly distilled over sodium/benzophenone. Solvents were evaporated at 40°C under reduced pressure using a *Heidolph Laborota 4001* rotatory evaporator system and a rotary vane pump (≥ 8 mbar) from Vaccubrand GmbH & Co. KG.

Thin layer chromatography (TLC) was performed on Macherey-Nagel silica gel 60 F254 aluminum plates (0.25 mm layer thickness). Compounds were visualized using UV light (λ = 254 nm) or by applying common staining solution and heating:

$KMnO_4$ stain: $KMnO_4$ (3.00 g), Na_2CO_3 (20.0 g), aq. NaOH solution (5 % w/v, 5.00 mL) in H_2O (300 mL).

MOPS stain: phosphomolybdic acid hydrate (25.0 g) in EtOH (250 mL).

Flash column chromatography was carried out using standard glass columns packed with a plug of cotton wool, sea sand (1-2 cm), silica gel 60 (Macherey-Nagel, 0.04-0.063 mm, 230-240 mesh) and sea sand (1-2 cm). Alternatively, purification was performed on an Ultra Performance Flash Purification System- *puriFlash® XS 420+* equipped with a PF-15C18HP/35G column.

Melting points (mp) were determined on a Stuart® SMP10 digital melting point apparatus and are uncorrected.

Nuclear magnetic resonance (NMR) spectra were measured on BRUKER Avance III HD 300 MHz, BRUKER Avance Neo 400 MHz and BRUKER Avance 500 MHz spectrometers. ^{1}H-NMR spectra were

measured at 300, 400 or 500 MHz, ^{13}C-NMR spectra were measured at 101 or 125 MHz, ^{19}F-NMR spectra were measure at 282, 377 or 471 MHz. All signals are referenced to the signal of the deuterated solvent (^{1}H-NMR: $CHCl_3$, δ = 7.26 ppm; DMSO-d_5, δ = 2.49 ppm, C_6D_6, δ = 7.15 ppm; ^{13}C-NMR: $^{13}CDCl_3$, δ = 77.1 ppm; DMSO-d_6, δ = 39.5 ppm, C_6D_6, δ = 128 ppm). ^{13}C-NMR spectra are ^{1}H broad band decoupled. Measurements on the BRUKER Avance Neo 400 MHz and BRUKER Avance 500 MHz spectrometers as well as all 2D experiments were performed in the institute's analytical department. NMR data are reported as follows: chemical shift (δ/*ppm*), multiplicity (s: singlet; d: doublet; t: triplet; q: quartett; p: pentett; m: multiplet; brs: broad signal), coupling constants (*J*/Hz), integration.

High resolution mass spectrometry (HRMS) experiments were performed on a Thermo Fisher Scientific Exactive^{TM} mass spectrometer (Orbitrap instrument). Samples were infused directly or via a LC/MS setup. Ionization was achieved by electrospray ionization (ESI, needle voltage 2.5-5.0 kV, ion transfer tube 250°C, sheath/auxiliary gas N_2) or atmospheric pressure chemical ionization (APCI, corona needle current 5-10 µA, vaporizer temperature 50-400°C, sheath gas N_2, auxiliary gas N_2/NH_3). All experiments were performed in the institute's analytic department. HRMS data are reported as follows: ionization method (ESI or APCI in positive or negative mode), chemical formula, $[ion]^{charge}$, mass to charge ratio (*m/z*): calculated value, found value.

Stern-Volmer quenching experiments were performed using a PerkinElmer LS55 Fluorescence Spectrometer.

Reaction Setup A reaction setup containing a 4.8 W, 3528 300 Blue LEDs strip as light source and a case fan as cooling system was used to run the catalysis,[4] see Figure 1.

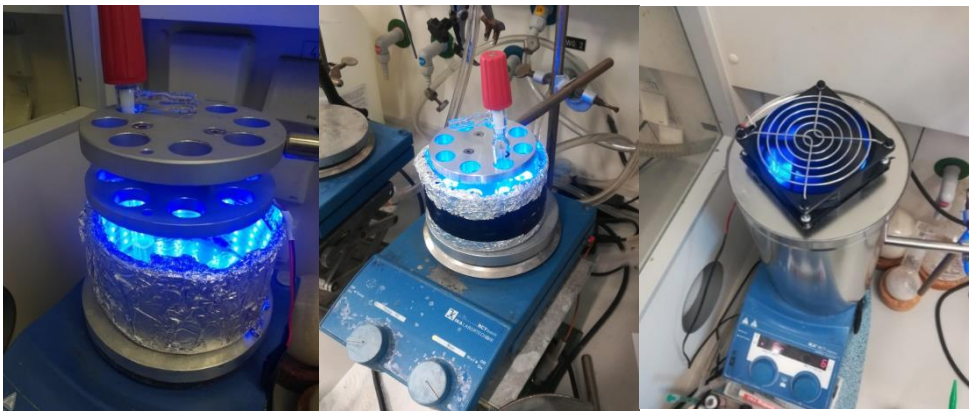
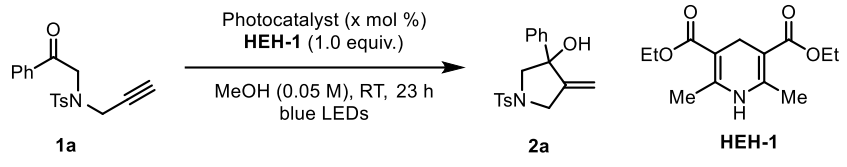
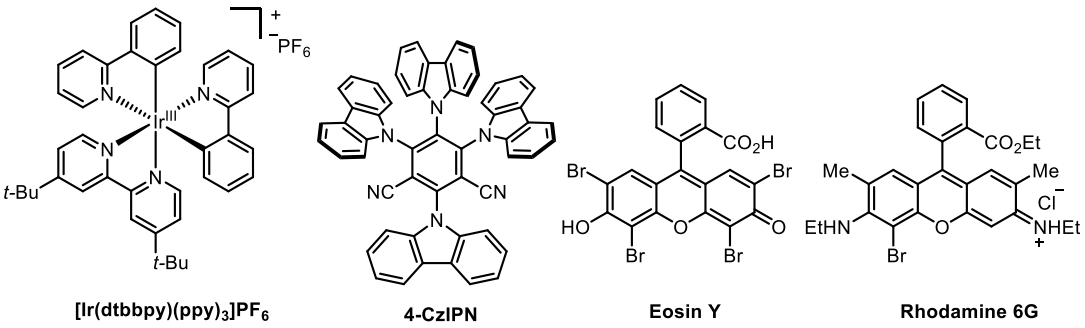


Figure 1: Reaction setup containing blue LED strips and a case fan.

Optimization studies

Table S1: *Screening of Photocatalysts in ketone-alkyne cyclization reaction*

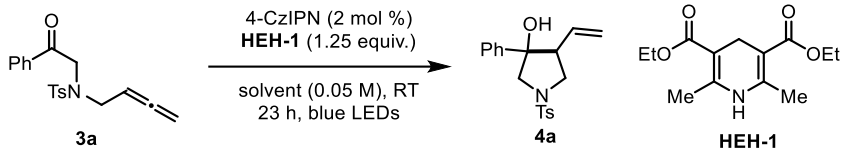




Entry[a]	Photocatalyst	x	Yield [%]
1	$[Ir(dtbbpy)(ppy)_2]PF_6$	0.5	66
2	$[Ir(ppy)_3]$	0.5	81
3	4-CzIPN	0.5	55
4	Eosin Y	0.5	24
5	Rhodamine 6G	0.5	--
6	4-CzIPN	1	70
7	**4-CzIPN**	**2**	**73**

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), Photocatalyst (x mol %), and **HEH-1** (1.0 equiv.) in MeOH (4 mL), irradiated by blue LEDs at rt. NMR yields are reported by using 1,3,5-trimethoxybenzene as internal standard, isolated yield is presented in parenthesis.

Table S2: *Screening of Photocatalysts in ketone-allene cyclization reaction*



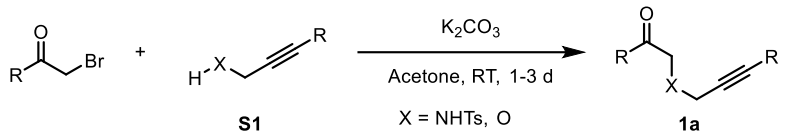
Entry[a]	solvent	Yield [%]	d.r.
1	MeCN	48	1.8:1
2	THF	53	1.7:1
3	EA	44	1.1:1
4	DCM	29	0.8:1

5	MeOH	65	2.5:1
6	DMA	64	2.5:1
7	1,4-Dioxane	38	1.1:1
8	toluene	31	1:1
9	DMF	80	2.5:1
10	DMSO	74	2.8:1
11[b]	**DMSO**	**74**	**3.5:1**

[a]Reaction conditions: 5-allenyl ketones **3a** (0.1 mmol), 4-CzIPN (2 mol %), and **HEH-1** (1.25 equiv.) in solvent (1 mL), irradiated by blue LEDs at rt. NMR yields are reported by using 1,3,5-trimethoxybenzene as internal standard. Diastereoselective ratio (d.r.) was determined by ^{1}H NMR spectroscopy of the crude mixture. [b]6 mL DMSO was used.

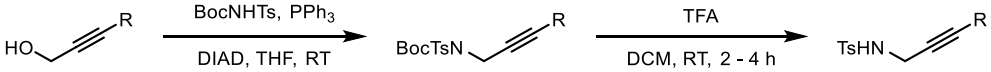
Experimental details and characterization data

General Procedure GP1 - Coupling of alkynes and α-haloacetophenones



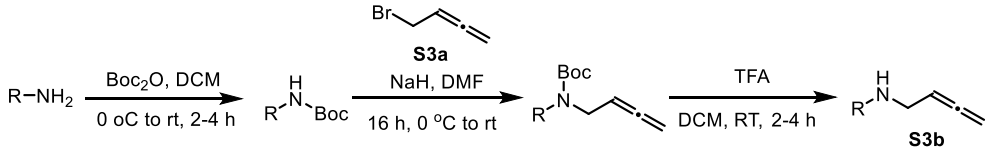
In a modified procedure,[5] α-haloacetophenone, alkynes **S1** and K_2CO_3 were suspended in acetone and it was stirred at rt until completion of the reaction was confirmed by TLC. H_2O was added and it was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure.

General Procedure GP2 - Synthesis of propargylic tosyl amides



tert-Butyl tosyl-carbamate and PPh_3 (1.5 equiv.) were dissolved in THF. After cooling to 0°C, propargylic alcohol (1.1 equiv.) and diisopropyl azodicarboxylate (1.1 equiv.) were added dropwise. The mixture was allowed to warm to rt and stirred overnight. The solvent was removed under reduced pressure. Propargylic tosyl carbamate was dissolved in CH_2Cl_2 and CF_3COOH (4.5 equiv.) was added dropwise. It was stirred at rt until completion of the reaction was confirmed by TLC. The solvent was evaporated under reduced pressure.

General Procedure GP3 - Synthesis of Allenyl propargylic tosyl amides

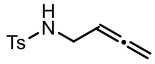


To a 1,2-dichloroethane (0.5 M) solution of amide (1.0 equiv.) were added Boc_2O (1.2 equiv.), triethylamine (1.1 equiv.), and dimethylaminopyridines (DMAP) (0.1 equiv.) at room temperature. The reaction mixture was stirred overnight and poured into water (20 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with 1 M HCl (50 mL), water (50 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was precipitated from n-hexane and filtered off to give the N-Boc-amine (quant).[6]

To a stirred suspension of NaH (60 % in oil, 1.0 equiv.) in DMF (0.5 M) at 0 °C was added N-Boc-amine (1 equiv.) as a solution in DMF (10 mL). The reaction mixture was stirred at room temperature for 30 min. **S3a**[7] (1.2 equiv.) was added dropwise at room temperature. The reaction mixture was stirred overnight and poured into H_2O (50 mL) and EtOAc (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (3 x 50 mL), dried over $MgSO_4$, filtered and concentrated. The crude material was purified by flash chromatography on silica gel to afford allene.[8]

To a DCM (0.5 M) solution of allenylamine (1.0 equiv.) was added dropwise trifluoroacetic acid (20 equiv.) at room temperature. The reaction mixture was stirred overnight and evaporated under reduced pressure. The crude material was purified by flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) to afford **S3b** as a white solid (quant).[8]

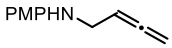
N-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide



S3b

Prepared according to the general procedure **GP3**, starting from 4-methylbenzenesulfonamide (1.7 g, 10 mmol, 1.0 equiv.). This compound has been reported already.[9]

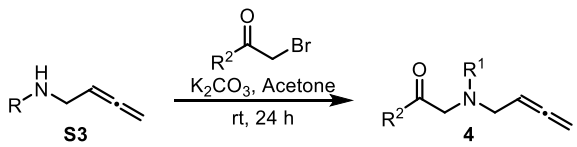
N-(buta-2,3-dien-1-yl)-4-methoxyaniline



S3c

Prepared according to the general procedure **GP3**, starting from 4-methoxyaniline (1.2 g, 10 mmol, 1.0 equiv.). This compound has been reported already.[9]

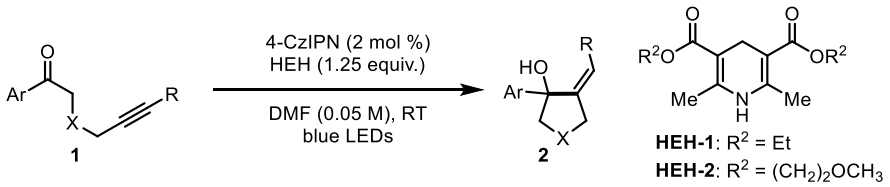
General Procedure GP4 - Coupling of allenes and α-haloacetophenones



To a solution of **S3** (1.0 equiv.) in acetone (0.2 M) was added K_2CO_3 (2.0 equiv.) followed by α-haloacetophenones (1.05 equiv.), and the mixture was stirred at room temperature for 16 h. The reaction was quenched with and the acetone was removed under reduced pressure. The resulting aqueous

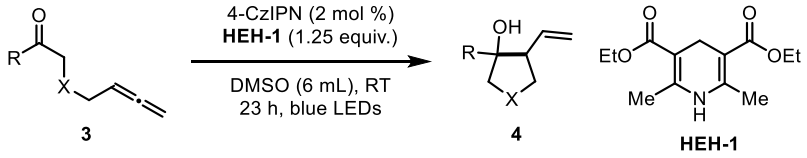
phase was extracted with EtOAc, and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (*n*-pentane/EtOAc) gave allene **4**.[9]

General Procedure GP5 - Photoredox-catalyzed ketone-alkyne coupling reaction



To an oven-dried Schlenk-tube equipped with magnetic stirring was charged with **1** (0.2 mmol), Hantzsch-ester **HEH** (0.25 mmol, 1.25 equiv.) and 4-CzIPN (2 mol %). The Schlenk tube was put on vacuum and backfilled with argon three times. DMF or MeOH (4 mL) was added and the reaction mixture was degassed twice before it was stirred at rt under blue LEDs light until completion of the reaction was confirmed by TLC. The solvent was evaporated under reduced pressure.

General Procedure GP6 - Photoredox-catalyzed ketone-allene coupling reaction

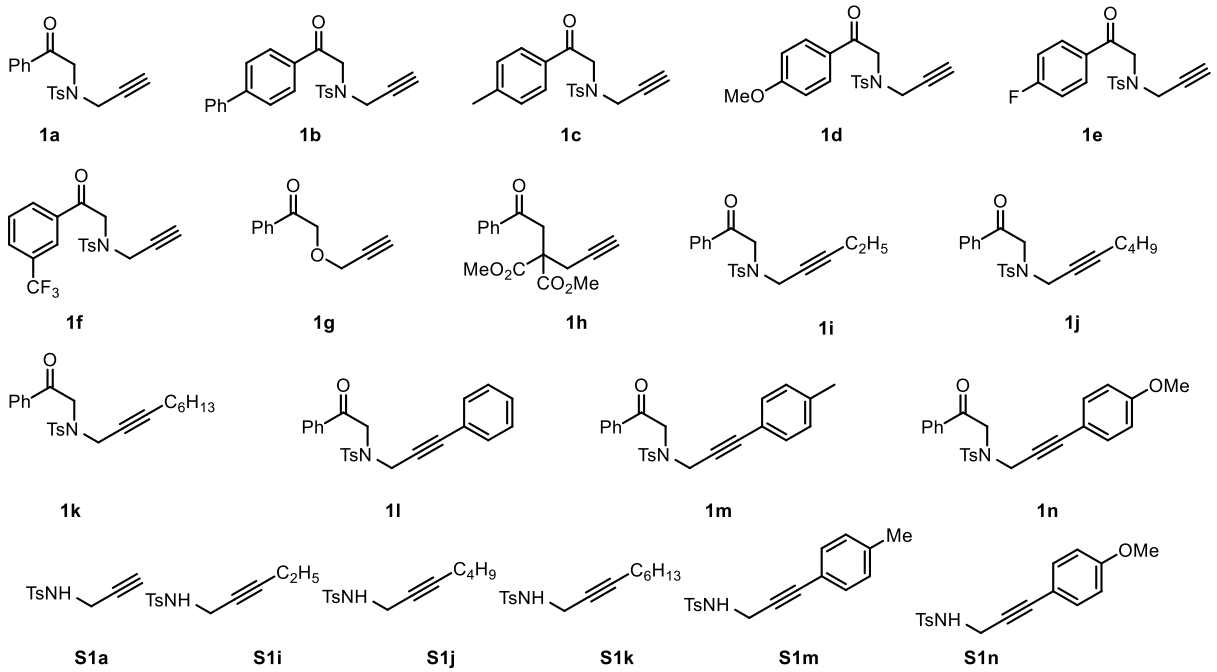


To an oven-dried Schlenk-tube equipped with magnetic stirring was charged with **3** (0.2 mmol), Hantzsch-ester **HEH-1** (63mg, 0.25 mmol, 1.25 equiv.) and 4-CzIPN (3.2 mg, 2 mol %). The Schlenk tube was put on vacuum and backfilled with argon three times. DMSO (6 mL) was added and then the mixture was stirred at room temperature under blue LEDs until completion of the reaction was confirmed by TLC. Then poured into water (40 mL), The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (3 x 40 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification of the residue by column chromatography (*n*-pentane/EtOAc) gave **4**.

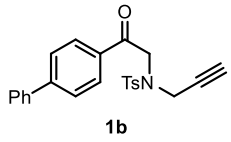
Reagent and Substrate Synthesis

5-alkynyl-ketones 1a,[5] 1c,[10] 1e,[10] 1g,[11] 1h,[12] 1l[10] were synthesized according to the corresponding literatures. Propargylic tosyl amides S1a,[13] S1i, [14] S1j, [15] S1m, [16] were synthesized according to reported procedure.

The others were synthesized according to the general procedure mentioned above.

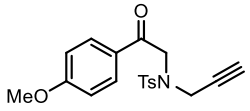


***N*-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b)**



According to **GP1** from propargylic tosyl amides (**S1a**) (500 mg, 2.39 mmol), 1-([1,1'-biphenyl]-4-yl)-2-bromoethan-1-one (986 mg, 3.58 mmol, 1.5 equiv.) and K_2CO_3 (495 mg, 3.58 mmol, 1.5 equiv.). After stirring in acetone (16 mL) for 2 days, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 50 mL). Flash chromatography on silica gel (7:3 *n*-pentane/Et_2O) provided the title compound as a white solid (318 mg, 33%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.55. **m.p.** = 136°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01-8.05 (m, 2H), 7.76-7.80 (m, 2H), 7.68-7.73 (m, 2H), 7.61-7.65 (m, 2H), 7.46-7.51 (m, 2H), 7.40-7.45 (m, 1H), 7.31-7.35 (m, 2H), 4.84 (d, *J* = 0.6 Hz, 2H), 4.30 (dd, *J* = 2.6, 0.7 Hz, 2H), 2.44 (s, 3H), 2.13 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.0, 146.7, 144.0, 139.8, 136.2, 133.6, 129.8, 129.2, 128.8, 128.6, 127.8, 127.6, 127.4, 76.7, 74.6, 51.7, 37.5, 21.7. **HR-MS**: *calcd.* for $C_{24}H_{21}NO_3S$: 404.1315 [$(M+H)^+$]; *found:* 404.1315 [$(M+H)^+$].

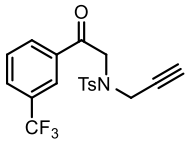
***N*-(2-(4-methoxyphenyl)-2-oxoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1d)**



1d

According to **GP1** from propargylic tosyl amides (**S1a**) (500 mg, 2.39 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one (821 mg, 3.58 mmol, 1.5 equiv.) and K_2CO_3 (495 mg, 3.58 mmol, 3.58 equiv.). After stirring in acetone (16 mL) for two days, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 50 mL). Flash chromatography on silica gel (1:1 *n*-pentane/Et_2O) provided the title compound as a white-yellow solid (558 mg, 59%). $\mathbf{R_f}$ (1:2 *n*-pentane/Et_2O) = 0.50. **m.p.** = 97°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.97 (m, 2H), 7.74-7.79 (m, 2H), 7.28-7.33 (m, 2H), 6.92-6.97 (m, 2H), 4.74 (d, *J* = 0.6 Hz, 2H), 4.27 (dd, *J* = 2.5, 0.6 Hz, 2H), 3.87 (s, 3H), 2.43 (s, 3H), 2.10 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.8, 164.2, 143.9, 136.3, 130.6, 129.7, 128.0, 127.8, 114.2, 76.8, 74.4, 55.7, 51.3, 37.5, 21.7. **HR-MS**: *calcd.* for $C_{19}H_{19}NO_4S$: 358.1108 [$(M+H)^+$]; *found:* 358.1107 [$(M+H)^+$].

4-Methyl-*N*-(2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfon-amide (1f)

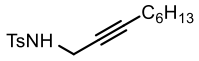


1f

According to **GP1** from propargylic tosyl amides (**S1a**) (500 mg, 2.39 mmol), 2-bromo-1-(3-(trifluoromethyl)phenyl)ethan-1-one (829 mg, 3.11 mmol, 1.3 equiv.) and K_2CO_3 (429 mg, 3.11 mmol, 1.3 equiv.). After stirring in acetone (18 mL) overnight, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 50 mL). Flash chromatography on silica gel (4:1 to 3:2 *n*-pentane/Et_2O) provided the title compound as yellow oil (821 mg, 87%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.65. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (dq, *J* = 1.7, 0.9 Hz, 1H), 8.16 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.87 (ddt, *J* = 7.8, 1.6, 0.9 Hz, 1H), 7.73-7.80 (m, 2H), 7.65 (tt, *J* = 7.8, 0.8 Hz, 1H), 7.31-7.38 (m, 2H), 4.79 (d, *J* = 0.7 Hz, 2H), 4.26 (dd, *J* = 2.6, 0.7 Hz, 2H), 2.45 (s, 3H), 2.12-2.16 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.5, 144.2, 135.9, 135.5, 131.7 (q, J_{C-F} = 33.0 Hz), 131.4, 130.4 (q, J_{C-F} = 3.7 Hz), 129.9, 129.7, 127.8, 125.1 (q, J_{C-F} = 3.7 Hz),

123.7 (q, $J_{C\text{-}F}$ = 272.6 Hz), 76.5, 74.9, 51.9, 37.7, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –62.87 (s). **HR-MS**: *calcd.* for $C_{19}H_{16}F_3NO_3S$: 418.0695 [$(M+Na)^+$]; *found:* 418.0697 [$(M+Na)^+$].

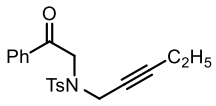
4-Methyl-*N*-(non-2-yn-1-yl)benzenesulfonamide (S1k)



S1k

According to **GP2** from BocNHTs. Flash chromatography on silica gel (3:1 *n*-pentane/Et_2O) provided the title compound as waxy oil (505 mg, 63%). **R_f** (1:1 *n*-pentane/Et_2O) = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.79 (m, 2H), 7.29-7.33 (m, 2H), 4.46 (s, 1H), 3.80 (dt, *J* = 5.9, 2.3 Hz, 2H), 2.43 (s, 3H), 1.95 (tt, *J* = 7.1, 2.3 Hz, 2H), 1.16-1.36 (m, 8H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.6, 137.0, 129.7, 127.5, 85.8, 74.1, 33.6, 31.4, 28.6, 28.4, 22.6, 21.6, 18.6, 14.1. **HR-MS**: *calcd.* for $C_{16}H_{23}NO_2S$: 294.1522 [$(M+H)^+$]; *found:* 294.1523 [$(M+H)^+$].

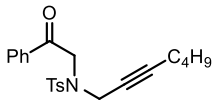
4-Methyl-*N*-(2-oxo-2-phenylethyl)-*N*-(pent-2-yn-1-yl)benzenesulfonamide (1i)



1i

According to **GP1** from **S1i** (750 mg, 3.16 mmol), 2-bromo-1-phenylethan-1-one (818 mg, 4.11 mmol, 1.3 equiv.) and K_2CO_3 (568 mg, 4.11 mmol, 1.3 equiv.). After stirring in acetone (22 mL) for 20 h, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 50 mL). Flash chromatography on silica gel (2:1 *n*-pentane/Et_2O) provided the title compound as a white-yellow solid (684 mg, 59%). **R_f** (2:1 *n*-pentane/Et_2O) = 0.45. **m.p.** = 66°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.99 (m, 2H), 7.73-7.80 (m, 2H), 7.54-7.61 (m, 1H), 7.43-7.51 (m, 2H), 7.28-7.33 (m, 2H), 4.74 (d, *J* = 0.7 Hz, 2H), 4.21 (td, *J* = 2.3, 0.7 Hz, 2H), 2.42 (s, 3H), 1.93 (qt, *J* = 7.5, 2.3 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 143.7, 136.3, 135.1, 133.8, 129.6, 128.8, 128.1, 127.8, 88.4, 71.8, 51.8, 38.0, 21.6, 13.5, 12.2. **HR-MS**: *calcd.* for $C_{20}H_{21}NO_3S$: 356.1315 [$(M+H)^+$]; *found:* 356.1315 [$(M+H)^+$].

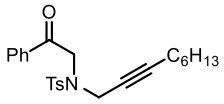
***N*-(hept-2-yn-1-yl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (1j)**



1j

According to **GP1** from **S1j** (462 mg, 1.74 mmol), 2-bromo-1-phenylethan-1-one (465 mg, 2.33 mmol, 1.2 equiv.) and K_2CO_3 (329 mg, 2.38 mmol, 1.4 equiv.). After stirring in acetone (15 mL) overnight, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 30 mL). Flash chromatography on silica gel (4:1 *n*-pentane/Et_2O) provided the title compound as a white-yellow solid (547 mg, 76%). $\mathbf{R_f}$ (2:1 *n*-pentane/Et_2O) = 0.40. **m.p.** = 69°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.99 (m, 2H), 7.74-7.79 (m, 2H), 7.56-7.63 (m, 1H), 7.45-7.52 (m, 2H), 7.29-7.33 (m, 2H), 4.75 (s, 2H), 4.22 (td, *J* = 2.3, 0.7 Hz, 2H), 2.44 (s, 3H), 1.94 (ddt, *J* = 6.9, 4.7, 2.3 Hz, 2H), 1.15-1.31 (m, 4H), 0.77-0.84 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.7, 143.7, 136.5, 135.2, 133.8, 129.7, 128.9, 128.2, 127.9, 87.3, 72.5, 51.9, 38.1, 30.5, 22.0, 21.7, 18.3, 13.6. **HR-MS**: *calcd.* for $C_{22}H_{26}NO_3S$: 384.1628 [$(M+H)^+$]; *found:* 384.1633 [$(M+H)^+$].

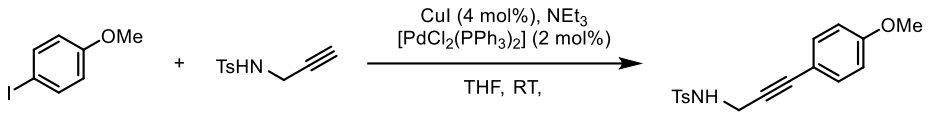
4-Methyl-*N*-(non-2-yn-1-yl)-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (1k)



1k

According to **GP1** from **S1k** (441 mg, 1.50 mmol), 2-bromo-1-phenylethan-1-one (421 mg, 2.12 mmol, 1.4 equiv.) and K_2CO_3 (297 mg, 2.15 mmol, 1.4 equiv.). After stirring in acetone (15 mL) overnight, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 30 mL). Flash chromatography on silica gel (4:1 *n*-pentane/Et_2O) provided the title compound as yellow oil (601 mg, 86%). $\mathbf{R_f}$ (2:1 *n*-pentane/Et_2O) = 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.99 (m, 2H), 7.74-7.80 (m, 2H), 7.56-7.63 (m, 1H), 7.44-7.52 (m, 2H), 7.29-7.35 (m, 2H), 4.75 (s, 2H), 4.23 (td, *J* = 2.3, 0.7 Hz, 2H), 2.43 (s, 3H), 1.94 (tt, *J* = 6.9, 2.3 Hz, 2H), 1.11-1.34 (m, 8H), 0.79-0.94 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.7, 143.7, 136.5, 135.2, 133.8, 129.7, 128.9, 128.2, 127.9, 87.3, 72.5, 51.8, 38.1, 31.4, 28.6, 28.5, 22.6, 21.7, 18.7, 14.2. **HR-MS**: *calcd.* for $C_{24}H_{29}NO_3S$: 412.1941 [$(M+H)^+$]; *found:* 412.1938 [$(M+H)^+$].

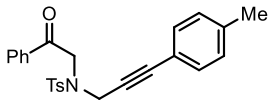
4-Methyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide (S1n)



S1a **S1n**

Propargyl amine **S1a** (500 mg, 2.39 mmol), 1-iodo-4-methoxybenzene (727 mg, 3.11 mmol, 1.3 equiv.), $[PdCl_2(PPh_3)_2]$ (33.5 mg, 47.8 µmol, 2 mol%) and CuI (18.2 mg, 95.6 µmol, 4 mol%) were suspended in THF (15 mL). NEt_3 (1 mL, 7.18 mmol, 3.0 equiv.) was added dropwise. After stirring at rt overnight, purification via flash chromatography on silica gel (1:1 *n*-pentane/Et_2O) provided the title compound as a yellow solid (382 mg, 51%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.40. **m.p.** = 125°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.84 (m, 2H), 7.24-7.43 (m, 2H), 7.06-7.11 (m, 2H), 6.74-6.80 (m, 2H), 4.85 (t, *J* = 6.1 Hz, 1H), 4.05 (dd, *J* = 6.1, 1.3 Hz, 2H), 3.79 (d, *J* = 1.3 Hz, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 143.8, 137.1, 133.2, 129.8, 127.6, 114.3, 113.9, 84.8, 82.0, 55.4, 34.0, 21.6. **HR-MS**: *calcd.* for $C_{17}H_{17}NO_3S$: 314.0856 [$(M-H)^-$]; *found:* 314.0856 [$(M-H)^-$].

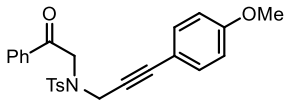
4-Methyl-*N*-(2-oxo-2-phenylethyl)-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1m)



1m

According to **GP1** from **S1m** (300 mg, 1.00 mmol), 2-bromo-1-phenylethan-1-one (199 mg, 1.00 mmol, 1.0 equiv.) and K_2CO_3 (138 mg, 1.00 mmol, 1.0 equiv.). After stirring in acetone (10 mL) overnight, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). Flash chromatography on silica gel (2:1 *n*-pentane/Et_2O) provided the title compound as a white solid (277 mg, 66%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.60. **m.p.** = 121°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-8.02 (m, 2H), 7.77-7.87 (m, 2H), 7.56-7.65 (m, 1H), 7.44-7.52 (m, 2H), 7.28-7.35 (m, 2H), 6.97-7.08 (m, 4H), 4.80 (d, *J* = 0.5 Hz, 2H), 4.48 (s, 2H), 2.40 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 143.8, 138.8, 136.3, 135.1, 133.9, 131.6, 129.8, 129.0, 128.9, 128.3, 127.8, 119.1, 86.5, 81.0, 52.0, 38.5, 21.6, 21.5. **HR-MS**: *calcd.* for $C_{25}H_{23}NO_3S$: 440.1291 [$(M+Na)^+$]; *found:* 440.1295 [$(M+Na)^+$].

***N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfon-amide (1n)**

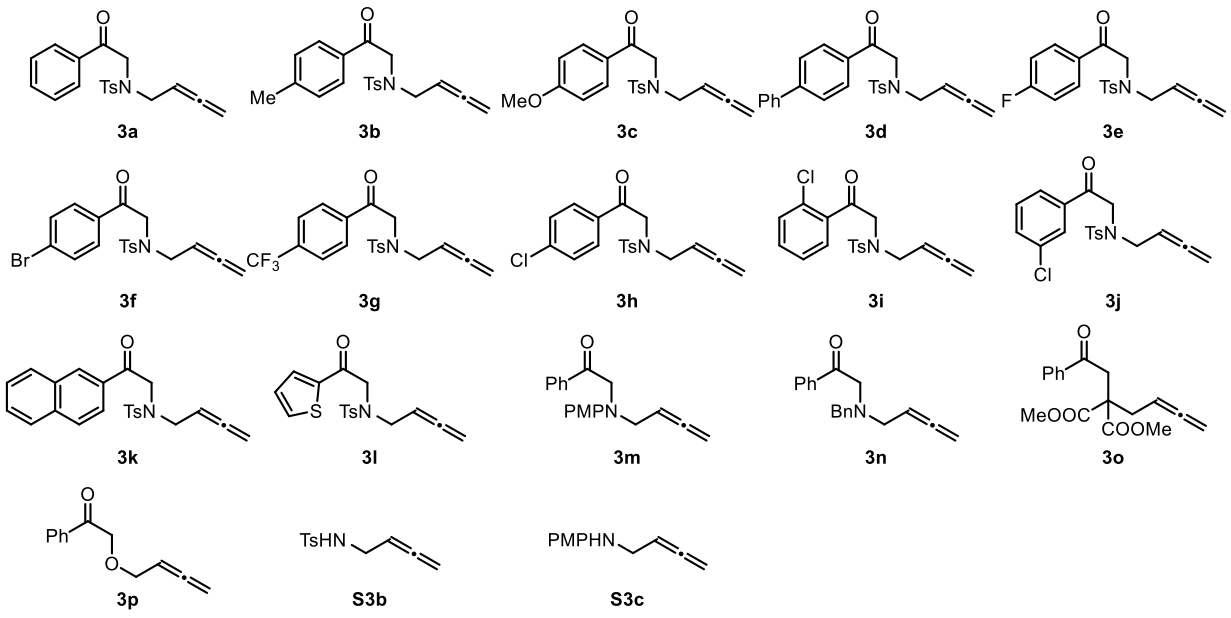


1n

According to **GP3** from **S1n** (300 mg, 951 μmol), 2-bromo-1-phenyl-ethan-1-one (189 mg, 951 μmol, 1.0 equiv.) and K_2CO_3 (131 mg, 951 μmol, 1.0 equiv.). After stirring in acetone (9 mL) overnight, it was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). Flash chromatography on silica gel (1:1 to 1:2 *n*-pentane/Et_2O) provided the title compound as a white solid (226 mg, 55%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.40. **m.p.** = 146°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95-8.00 (m, 2H), 7.79-7.83 (m, 2H), 7.56-7.63 (m, 1H), 7.44-7.51 (m, 2H), 7.29-7.33 (m, 2H), 7.02-7.08 (m, 2H), 6.73-6.77 (m, 2H), 4.80 (s, 2H), 4.47 (s, 2H), 3.78 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.6, 159.9, 143.9, 136.3, 135.1, 133.9, 133.2, 129.8, 128.9, 128.3, 127.9, 114.2, 113.9, 86.3, 80.3, 55.4, 52.0, 38.5, 21.7. **HR-MS**: *calcd.* for $C_{25}H_{23}NO_4S$: 456.1240 [(M+Na)$^+$]; *found:* 456.1245 [(M+Na)$^+$].

5-allenyl-ketones 3o, 3p were synthesized according to the corresponding literatures. Allenyl tosyl amides S3a-3c were synthesized according to reported procedure.

The others were synthesized according to the general procedure mentioned above.



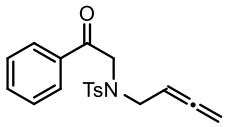
3a **3b** **3c** **3d** **3e**

3f **3g** **3h** **3i** **3j**

3k **3l** **3m** **3n** **3o**

3p **S3b** **S3c**

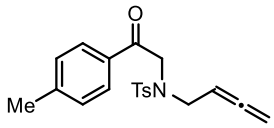
N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (3a)



3a

Prepared according to the general procedure **GP4**, starting from 2-Bromoacetophenone (1.04 g, 5.25 mmol, 1.05 equiv.) and **S3b** (1.12 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (1.1 g, 68%). $\mathbf{R_f}$ (5:1 *n*-pentane/EtOAc) = 0.4. This compound has been reported already.[9]

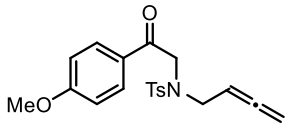
N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (3b)



3b

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-methylacetophenone (1.12 g, 5.25 mmol, 1.05 equiv.) and **S3b** (1.12 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (1.4 g, 80%). $\mathbf{R_f}$ (5:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 56 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.78-7.73 (m, 2H), 7.32-7.23 (m, 4H), 5.03-4.94 (m, 1H), 4.74 (s, 2H), 4.61 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.93 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 193.4, 144.6, 143.4, 137.1, 132.7, 129.6, 129.5, 128.1, 127.5, 85.7, 76.2, 51.9, 47.2, 21.7, 21.5. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO_3S^+$: 378.1134; *found*: 378.1140.

N-(buta-2,3-dien-1-yl)-N-(2-(4-methoxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide

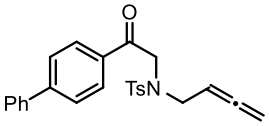


3c

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-methoxyacetophenone (1.20 g, 5.25 mmol, 1.05 equiv.) and **S3b** (1.12 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (1.3 g, 72%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 68 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 2H), 7.77-7.73 (m, 2H), 7.31-7.26 (m, 2H), 6.95-6.90 (m, 2H), 5.02-4.93 (m, 1H), 4.70 (s, 2H), 4.61 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.92 (dt, *J* = 7.2, 2.4 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 192.2, 164.0,

143.4, 137.1, 130.3, 129.6, 128.2, 127.5, 114.0, 85.7, 76.2, 55.5, 51.7, 47.3, 21.5. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO_4S^+$: 394.1083; *found*: 394.1085.

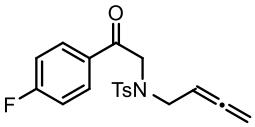
N-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-N-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide



3d

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-phenylacetophenone (0.58 g, 2.1 mmol, 1.05 equiv.) and **S3b** (0.45 g, 2.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1to 5:1) provided the title compound as white solid (0.76 g, 91%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 2H), 7.81-7.77 (m, 2H), 7.72-7.68 (m, 2H), 7.65-7.60 (m, 2H), 7.51-7.45 (m, 2H), 7.44-7.38 (m, 1H), 7.34-7.29 (m, 2H), 5.06-4.98 (m, 1H), 4.80 (s, 2H), 4.65 (dt, *J* = 6.8, 2.4 Hz, 2H), 3.97 (dt, *J* = 7.6, 2.4 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 193.5, 146.4, 143.5, 139.6, 137.0, 133.8, 129.6, 129.0, 128.6, 128.4, 127.5, 127.4, 127.3, 85.7, 76.3, 52.1, 47.3, 21.5. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{23}NNaO_3S^+$: 440.1291; *found*: 440.1299.

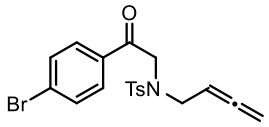
N-(buta-2,3-dien-1-yl)-N-(2-(4-fluorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide



3e

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-fluoroacetophenone (0.91 g, 4.2 mmol, 1.05 equiv.) and **S3b** (0.89 g, 4.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1to 5:1) provided the title compound as white solid (1.2 g, 84%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 63 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.76-7.72 (m, 2H), 7.32-7.27 (m, 2H), 7.16-7.09 (m, 2H), 4.98-4.91 (m, 1H), 4.69 (s, 2H), 4.63-4.59 (m, 2H), 4.24 (dt, *J* = 7.0, 2.5 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.8, 192.4, 166.0 (d, $J_{C\text{-}F}$ = 256.5 Hz), 143.6, 136.7, 131.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.8 (d, $J_{C\text{-}F}$ = 9.7 Hz), 129.7, 127.4, 116.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 85.5, 76.3, 52.1, 47.3, 21.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -103.7 (m). **HR-MS** (+ p ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}FNNaO_3S^+$: 382.0884; *found*: 382.0886.

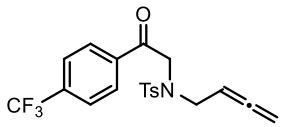
N-(2-(4-bromophenyl)-2-oxoethyl)-N-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide



3f

Prepared according to the general procedure **GP4**, starting from 2,4′-Dibromoacetophenone (0.58 g, 2.1 mmol, 1.05 equiv.) and **S3b** (0.45 g, 2.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (0.66 g, 78%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.76-7.71 (m, 2H), 7.63-7.58 (m, 2H), 7.33-7.27 (m, 2H), 4.99-4.90 (m, 1H), 4.67 (s, 2H), 4.62 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.90 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 193.2, 143.6, 136.8, 133.9, 132.2, 129.7, 129.6, 128.9, 127.5, 85.5, 76.3, 52.2, 47.4, 21.6. **HR-MS** (+ p ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}BrNNaO_3S^+$: 442.0083; *found*: 442.0081.

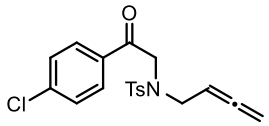
N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide



3g

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-(trifluoromethyl)acetophenone (0.56 g, 2.1 mmol, 1.05 equiv.) and **S3b** (0.45 g, 2.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (0.47 g, 57%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 66 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07-8.03 (m, 2H), 7.76-7.71 (m, 4H), 7.33-7.28 (m, 2H), 4.99-4.90 (m, 1H), 4.72 (s, 2H), 4.63 (dt, *J* = 6.8, 2.4 Hz, 2H), 3.90 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.9, 193.5, 143.8, 137.9, 136.6, 134.9 (q, J_{C-F} = 32.9 Hz), 129.8, 128.5, 127.5, 125.9 (q, J_{C-F} = 3.8 Hz), 123.5 (q, J_{C-F} = 273.8 Hz), 85.5, 76.4, 52.6, 47.6, 21.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.2 (s). **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}F_3NNaO_3S^+$: 432.0852; *found*: 432.0860.

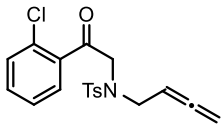
N-(buta-2,3-dien-1-yl)-N-(2-(4-chlorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide



3h

Prepared according to the general procedure **GP4**, starting from 2-Bromo-4′-chloroacetophenone (0.98 g, 4.2 mmol, 1.05 equiv.) and **S3b** (0.89 g, 4.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (1.2 g, 73%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.76-7.71 (m, 2H), 7.45-7.41 (m, 2H), 7.32-7.27 (m, 2H), 4.99-4.90 (m, 1H), 4.68 (s, 2H), 4.62 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.90 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 192.9, 143.6, 140.2, 136.8, 133.5, 129.7, 129.5, 129.1, 127.5, 85.5, 76.3, 52.2, 47.4, 21.5. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{18}ClNNaO_3S^+$: 398.0588; *found*: 398.0592.

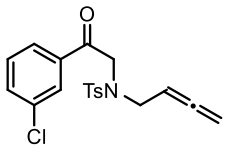
N-(buta-2,3-dien-1-yl)-N-(2-(2-chlorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide



3i

Prepared according to the general procedure **GP4**, starting from 2-Bromo-2′-chloroacetophenone (0.74 g, 3.15 mmol, 1.05 equiv.) and **S3b** (0.67 g, 3.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (0.62 g, 55%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (ddd, *J* = 2.0, 1.6, 0.4 Hz, 1H), 7.83 (ddd, *J* = 7.6, 1.6, 1.2 Hz, 1H), 7.77-7.73 (m, 2H), 7.57 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.46-7.40 (m, 1H), 7.34-7.29 (m, 2H), 5.02-4.94 (m, 1H), 4.70 (s, 2H), 4.65 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.92 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.0, 193.0, 143.7, 136.9, 136.7, 135.3, 133.7, 130.3, 129.8, 128.2, 127.6, 126.2, 85.7, 76.4, 52.3, 47.5, 21.6. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}ClNO_3S^+$: 376.0769; *found*: 376.0778.

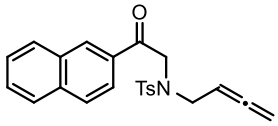
N-(buta-2,3-dien-1-yl)-N-(2-(3-chlorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide



3j

Prepared according to the general procedure **GP4**, starting from 2-Bromo-3′-chloroacetophenone (0.74 g, 3.15 mmol, 1.05 equiv.) and **S3b** (0.67 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (0.76 mg, 67%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 68 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 2H), 7.50 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.38-7.32 (m, 1H), 7.32-7.28 (m, 2H), 5.03-4.94 (m, 1H), 4.71-4.66 (m, 4H), 3.95 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.0, 197.3, 143.6, 137.1, 137.1, 132.4, 131.2, 130.6, 129.73, 129.5, 127.6, 127.2, 85.8, 76.5, 54.9, 47.5, 21.6. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}ClNO_3S^+$: 376.0769; *found*: 376.0776.

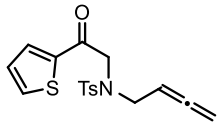
N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(naphthalen-2-yl)-2-oxoethyl)benzenesulfonamide



3k

Prepared according to the general procedure **GP4**, starting from 2-Bromo-2′-acetonaphthone (1.04 g, 4.2 mmol, 1.05 equiv.) and **S3b** (1.12 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (1 g, 64%). $\mathbf{R_f}$ (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.6 Hz, 1H), 7.98-7.94 (m, 2H), 7.90-7.84 (m, 2H), 7.82-7.78 (m, 2H), 7.64-7.53 (m, 2H), 7.33-7.28 (m, 2H), 5.07-4.99 (m, 1H), 4.91 (s, 2H), 4.63 (dt, *J* = 6.4, 2.4 Hz, 2H), 4.00 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 193.8, 143.5, 137.0, 135.8, 132.4, 129.8, 129.6, 128.8, 128.7, 127.8, 127.5, 127.0, 123.5, 85.7, 76.3, 52.1, 47.3, 21.5. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{21}NNaO_3S^+$: 414.1134; *found*: 414.1141.

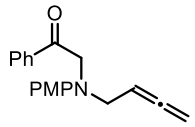
N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-oxo-2-(thiophen-2-yl)ethyl)benzenesulfonamide



3l

Prepared according to the general procedure **GP4**, starting from 2-(2-Bromoacetyl)thiophene (1.0 g, 4.2 mmol, 1.05 equiv.) and **S3b** (1.12 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (572.5 mg, 41%). **R_f** (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 58 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.77-7.73 (m, 2H), 7.67 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.32-7.27 (m, 2H), 7.15 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.03-4.94 (m, 1H), 4.6-4.61 (m, 4H), 3.92 (dt, *J* = 7.6, 2.4 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.9, 187.0, 143.6, 141.4, 136.8, 134.3, 132.6, 129.7, 128.4, 127.6, 85.5, 76.3, 52.3, 47.5, 21.6. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_3S_2^+$: 348.0723; *found*: 348.0726.

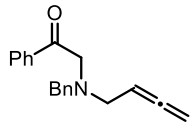
2-(buta-2,3-dien-1-yl(4-methoxyphenyl)amino)-1-phenylethan-1-one



3m

Prepared according to the general procedure **GP4**, starting from 2-Bromoacetophenone (853 mg, 4.2 mmol, 1.05 equiv.) and **S3c** (0.88 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (751 mg, 64%). **R_f** (4:1 *n*-pentane/EtOAc) = 0.4. **m.p.** = 65 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.63-7.57 (m, 1H), 7.52-7.46 (m, 2H), 6.83-6.78 (m, 2H), 6.71-6.65 (m, 2H), 5.28-5.20 (m, 1H), 4.75 (dt, *J* = 6.8, 2.8 Hz, 2H), 4.71 (s, 2H), 4.03 (dt, *J* = 6.8, 2.8 Hz, 2H), 3.74 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.2, 196.9, 152.4, 143.0, 135.7, 133.5, 128.8, 128.0, 115.2, 114.8, 87.2, 76.0, 57.6, 55.8, 51.5. **HR-MS** (+ p APCI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}NO_2^+$: 294.1489; *found*: 294.1491.

2-(benzyl(buta-2,3-dien-1-yl)amino)-1-phenylethan-1-one

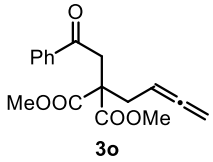


3n

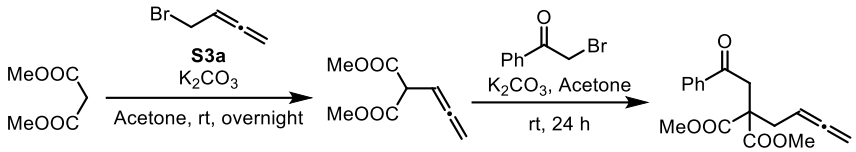
Prepared according to the general procedure **GP4**, starting from 2-Bromoacetophenone (564 mg, 2.83 mmol, 1.05 equiv.) and **S3d** (0.8 g, 5.0 mmol, 1.0 equiv.). Flash chromatography on silica gel (*n*-pentane/EtOAc 10:1 to 5:1) provided the title compound as white solid (634 mg, 84%). **R_f** (4:1 *n*-pentane/EtOAc) = 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 1H), 7.90-7.88 (m, 1H), 7.54-7.48 (m, 1H),

7.42-7.36 (m, 2H), 7.32-7.18 (m, 5H), 5.21-5.13 (m, 1H), 4.66 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.89 (s, 2H), 3.7 (s, 2H), 3.28 (dt, *J* = 7.2, 2.4 Hz, 2H), 3.74 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.9, 198.4, 138.5, 136.4, 133.1, 129.3, 128.5, 128.4, 127.3, 86.6, 75.0, 59.4, 58.2, 53.1. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}NO^+$: 278.1539; *found*: 278.1547.

dimethyl 2-(buta-2,3-dien-1-yl)-2-(2-oxo-2-phenylethyl)malonate



3o



S3e **3o**

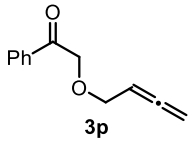
To a solution of dimethyl malonate (2.97 g, 22.5 mmol,1.5 equiv.) in acetone (0.5 M) was added K_2CO_3 (6.2 g, 45 mmol, 3.0 equiv.) followed by **S3a** (15 mmol, 1.0 equiv.), and the mixture was stirred at room temperature overnight. The reaction was quenched with H_2O (20 mL) and the acetone was removed under reduced pressure. The resulting aqueous phase was extracted with EtOAc (3 x 10 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (*n*-pentane/EtOAc 15:1 to 10 :1) gave *allene* **S3e** as colorless oil(0.64 g, 21%).

To a solution of sodium hydride (128 mg, 3.2 mmol, 60% in mineral oil) in DMF (10 mL) was added a solution of **S3e** (0.64 g, 3.2 mmol) in DMF (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 30 min, a solution of 2-Bromoacetophenone (796 mg, 4 mmol) in DMF (5 mL) was added. After stirring at room temperature overnight, the reaction was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 10:1 to 5:1) gave **3o** as colorless oil (742 mg, 76%).[17]

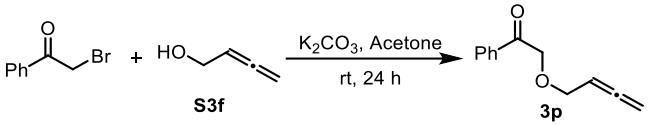
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 2H), 7.59-7.53 (m, 1H), 7.48-7.42 (m, 2H), 5.01-4.92 (m, 1H), 4.49 (dt, *J* = 6.4, 2.4 Hz, 2H), 3.74 (s, 6H), 2.82 (dt, *J* = 8.0, 2.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$)

δ 210.1, 196.7, 170.8, 136.6, 133.4, 128.7, 128.1, 84.7, 74.7, 55.7, 52.8, 41.3, 32.8. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}O_5^+$: 303.1227; *found*: 303.1227.

2-(buta-2,3-dien-1-yloxy)-1-phenylethan-1-one



3p

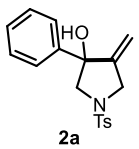


To a solution of **S3f**[7] (20 mmol, 1.0 equiv.) in acetone (0.5 M) was added K_2CO_3 (6.2 g, 45 mmol, 3.0 equiv.) followed by 2-Bromoacetophenone (3.98 g, 20 mmol, 1.0 equiv.), and the mixture was stirred at room temperature overnight. The reaction was quenched with H_2O (20 mL) and the acetone was removed under reduced pressure. The resulting aqueous phase was extracted with EtOAc (3 x 10 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (*n*-pentane/EtOAc 25:1 to 20 :1) gave *allene* **S3p** as colorless oil (0.95 g, 25%).[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (m, 2H), 7.59-7.53 (m, 1H), 7.48-7.42 (m, 2H), 5.31-5.23 (m, 1H), 4.81-4.76 (m, 2H), 4.76-4.74 (m, 2H), 4.20-4.16 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 196.2, 135.1, 133.5, 128.7, 127.9, 87.2, 75.9, 72.3, 69.3. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}O_2^+$: 189.0910; *found*: 189.0912.

Catalysis

4-Methylene-3-phenyl-1-tosylpyrrolidin-3-ol (2a)

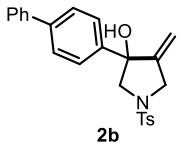


2a

According to **GP5** from **1a** (65.4 mg, 200 µmol) with 4-CzIPN (3.4 mg, 4.25 µmol, 2.1 mol%) and **HEH-1** (63.6 mg, 251 µmol, 1.25 equiv.) in DMF (4 mL) within 23 h. Flash chromatography on silica gel (3:1:1 *n*-pentane/Et_2O/CH_2Cl_2) provided the title compound as yellow oil (52.1 mg, 79%). **R_f** (3:1:1 *n*-

pentane/Et_2O/CH_2Cl_2) = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68-7.73 (m, 2H), 7.37-7.41 (m, 2H), 7.25-7.35 (m, 5H), 5.15 (t, *J* = 2.1 Hz, 1H), 4.98 (t, *J* = 2.4 Hz, 1H), 4.20 (dt, *J* = 14.2, 2.3 Hz, 1H), 3.97 (dt, *J* = 14.2, 2.3 Hz, 1H), 3.57 (d, *J* = 2.2 Hz, 2H), 2.44 (s, 3H), 2.40 (brs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 144.0, 141.1, 133.0, 129.9, 128.4, 128.0, 127.9, 126.1, 110.9, 80.6, 62.3, 51.7, 21.7. **HR-MS**: *calcd.* for $C_{18}H_{19}NO_3S$: 330.1158 [$(M+H)^+$]; *found:* 330.1158 [$(M+H)^+$].

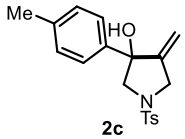
3-([1,1'-Biphenyl]-4-yl)-4-methylene-1-tosylpyrrolidin-3-ol (2b)



2b

According to **GP5** from **1b** (80.7 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-1** (63.4 mg, 250 µmol, 1.25 equiv.) in DMF (4 mL) within 14 h. Flash chromatography on silica gel (2:1 *c*-hexane/Et_2O) provided the title compound as yellow oil (72.9 mg, 90%). **R_f** (1:1 *c*-hexane/Et_2O) = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.75 (m, 2H), 7.51-7.60 (m, 4H), 7.41-7.49 (m, 4H), 7.30-7.39 (m, 3H), 5.17-5.20 (m, 1H), 5.06 (td, *J* = 2.5, 0.5 Hz, 1H), 4.23 (dt, *J* = 14.2, 2.2 Hz, 1H), 4.01 (dt, *J* = 14.3, 2.3 Hz, 1H), 3.62 (d, *J* = 1.0 Hz, 2H), 2.42 (s, 3H), 2.39 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.8, 144.0, 140.9, 140.6, 140.2, 133.2, 129.9, 129.0, 128.0, 127.6, 127.2, 127.1, 126.6, 111.0, 80.6, 62.3, 51.7, 21.7. **HR-MS**: *calcd.* for $C_{24}H_{24}NO_3S$: 406.1471 [$(M+H)^+$]; *found:* 406.1476 [$(M+H)^+$].

4-Methylene-3-(*p*-tolyl)-1-tosylpyrrolidin-3-ol (2c)

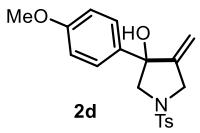


2c

According to **GP5** from **1c** (68.6 mg, 201 µmol) with 4-CzIPN (3.3 mg, 4.1 µmol, 2.1 mol%) and **HEH-1** (63.9 mg, 252 µmol, 1.26 equiv.) in DMF (4 mL) within 2 days. Flash chromatography on silica gel (3:1:1 *n*-pentane/Et_2O/CH_2Cl_2) provided the title compound as yellow oil (63.5 mg, 92%). **R_f** (1:1 *n*-pentane/Et_2O) = 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.73 (m, 2H), 7.26-7.34 (m, 4H), 7.09-7.15 (m, 2H), 5.14 (t, *J* = 2.1 Hz, 1H), 5.00 (t, *J* = 2.4 Hz, 1H), 4.19 (dt, *J* = 14.2, 2.2 Hz, 1H), 3.97 (dt, *J* = 14.2, 2.3 Hz, 1H), 3.56 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 143.9, 138.1,

137.8, 133.2, 129.9, 129.1, 128.0, 126.1, 110.7, 80.6, 62.3, 51.7, 21.7, 21.2. **HR-MS**: *calcd.* for $C_{19}H_{21}NO_3S$: 344.1315 [$(M+H)^+$]; *found:* 344.1315 [$(M+H)^+$].

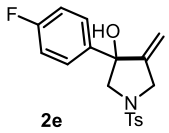
3-(4-Methoxyphenyl)-4-methylene-1-tosylpyrrolidin-3-ol (2d)



2d

According to **GP5** from **1d** (71.1 mg, 199 µmol) with 4-CzIPN (3.4 mg, 4.3 µmol, 2.1 mol%) and **HEH-1** (63.8 mg, 252 µmol, 1.26 equiv.) in DMF (4 mL) within 2 days. Flash chromatography on silica gel (3:1:1 *n*-pentane/Et_2O/CH_2Cl_2) provided the title compound as yellow oil (54.4 mg, 76%). $\mathbf{R_f}$ (1:2 *n*-pentane/Et_2O) = 0.65. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.72 (m, 2H), 7.29-7.33 (m, 4H), 6.81-6.86 (m, 2H), 5.14 (t, *J* = 2.1 Hz, 1H), 5.01 (t, *J* = 2.4 Hz, 1H), 4.18 (dt, *J* = 14.2, 2.2 Hz, 1H), 3.96 (dt, *J* = 14.2, 2.3 Hz, 1H), 3.80 (s, 3H), 3.55 (d, *J* = 3.4 Hz, 2H), 2.44 (s, 3H), 2.22 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 150.9, 143.9, 133.2, 133.1, 129.9, 128.0, 127.4, 113.8, 110.6, 80.4, 62.1, 55.4, 51.6, 21.7. **HR-MS**: *calcd.* for $C_{19}H_{21}NO_4S$: 382.1084 [$(M+Na)^+$]; *found:* 382.1083 [$(M+Na)^+$].

3-(4-Fluorophenyl)-4-methylene-1-tosylpyrrolidin-3-ol (2e)

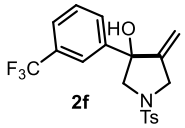


2e

According to **GP5** from **1e** (69.0 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-1** (63.3 mg, 250 µmol, 1.25 equiv.) in DMF (4 mL) within 13 h. The solvent was evaporated, and the residue was resolved in MeOH (2 mL) and H_2O (1 mL). KOH (112 mg, 2.00 mmol, 10 equiv.) was added and it was stirred overnight. The mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure. Flash chromatography on silica gel (2:3 *n*-pentane/Et_2O) provided the title compound as yellow oil (52.1 mg, 75%). $\mathbf{R_f}$ (2:3 *n*-pentane/Et_2O) = 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.73 (m, 2H), 7.29-7.40 (m, 4H), 6.94-7.02 (m, 2H), 5.16 (td, *J* = 2.1, 0.5 Hz, 1H), 4.99 (td, *J* = 2.5, 0.5 Hz, 1H), 4.15-4.24 (m, 1H), 3.96 (dt, *J* = 14.3, 2.3 Hz, 1H), 3.47-3.62 (m, 2H), 2.44 (s, 3H), 2.34 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 247.5 Hz), 150.8, 144.1, 136.91 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.1, 129.9, 128.1, 128.0,

115.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 111.0, 80.3, 62.4, 51.6, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.57 (m). **HR-MS**: *calcd.* for $C_{18}H_{18}FNO_3S$: 348.1064 [$(M+H)^+$]; *found:* 348.1066 [$(M+H)^+$].

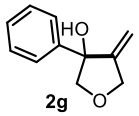
4-Methylene-1-tosyl-3-(3-(trifluoromethyl)phenyl)pyrrolidin-3-ol (2f)



2f

According to **GP4** from **1f** (79.3 mg, 201 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-1** (63.4 mg, 250 µmol, 1.25 equiv.) in DMF (4 mL) within 13 h. The solvent was evaporated, and the residue was resolved in MeOH (2 mL) and H_2O (1 mL). KOH (112 mg, 2.00 mmol, 10 equiv.) was added and it was stirred overnight. The mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure. Flash chromatography on silica gel (2:3 *n*-pentane/Et_2O) provided the title compound as yellow oil (56.7 mg, 71%). **R_f** (2:3 *n*-pentane/Et_2O) = 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.74 (m, 3H), 7.56 (ddddd, *J* = 10.4, 7.8, 2.0, 1.3, 0.7 Hz, 2H), 7.43 (tt, *J* = 7.8, 0.7 Hz, 1H), 7.31-7.36 (m, 2H), 5.20 (td, *J* = 2.1, 0.6 Hz, 1H), 4.97 (td, *J* = 2.5, 0.7 Hz, 1H), 4.25 (dt, *J* = 14.3, 2.3 Hz, 1H), 3.99 (dt, *J* = 14.4, 2.3 Hz, 1H), 3.62 (d, *J* = 10.7 Hz, 1H), 3.50 (d, *J* = 10.7 Hz, 1H), 2.48 (brs, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 144.3, 142.4, 133.0, 130.8 (q, *J* = 32.2 Hz), 130.0, 129.7, 128.9, 128.0, 124.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.4 Hz), 123.1 (q, *J* = 3.9 Hz), 111.7, 80.4, 62.6, 51.7, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.6 (s). **HR-MS**: *calcd.* for $C_{19}H_{18}F_3NO_3S$: 398.1032 [$(M+H)^+$]; *found:* 398.1034 [$(M+H)^+$].

4-Methylene-3-phenyltetrahydrofuran-3-ol (2g)

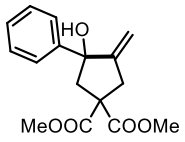


2g

According to **GP5** from **1g** (34.5 mg, 198 µmol) with 4-CzIPN (3.1 mg, 3.9 µmol, 2.0 mol%) and **HEH-1** (63.6 mg, 251 µmol, 1.27 equiv.) in DMF (4 mL) within 20 h. Flash chromatography on silica gel (5:1 *n*-pentane/Et_2O) provided the title compound as colourless oil (17.8 mg, 51%). **R_f** (1:2 *n*-pentane/Et_2O) = 0.65. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.55 (m, 2H), 7.34-7.40 (m, 2H), 7.27-7.32 (m, 1H), 5.17 (t, *J* = 2.2 Hz, 1H), 4.99-5.06 (m, 1H), 4.77 (dddd, *J* = 13.7, 2.6, 2.2, 0.7 Hz, 1H), 4.54 (dddd, *J* = 13.7, 2.7, 2.3, 0.8 Hz, 1H), 4.03-4.10 (m, 1H), 3.96 (dd, *J* = 9.6, 0.7 Hz, 1H); **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 155.4, 141.4, 128.3, 127.6, 126.2, 108.2, 82.2, 81.6, 71.8. **HR-MS**: *calcd.* for $C_{11}H_{12}O_4$: 194.1176 [$(M+NH_4)^+$]; *found:* 194.1179 [$(M+NH_4)^+$].

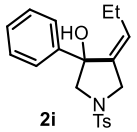
Dimethyl 3-hydroxy-4-methylene-3-phenylcyclopentane-1,1-dicarboxylate (2h)



2h

According to **GP5** from **1h** (58.2 mg, 202 µmol) with 4-CzIPN (3.3 mg, 4.1 µmol, 2.0 mol%) and **HEH-1** (63.3 mg, 250 µmol, 1.24 equiv.) in DMF (4 mL) for 3 days. Flash chromatography on silica gel (5:1 to 4:1 *n*-pentane/Et_2O) provided the title compound as colourless oil (28.3 mg, 49%). $\mathbf{R_f}$ (1:1 *n*-pentane/Et_2O) = 0.50. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.48 (m, 2H), 7.31-7.36 (m, 2H), 7.23-7.28 (m, 1H), 5.17 (ddd, *J* = 2.4, 1.8, 0.5 Hz, 1H), 4.87 (dd, *J* = 2.9, 2.0 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.50 (dq, *J* = 17.1, 1.9 Hz, 1H), 3.08 (dt, *J* = 17.1, 2.6 Hz, 1H), 2.81-2.88 (m, 1H), 2.70 (d, *J* = 14.3 Hz, 1H), 2.53 (brs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 171.9, 155.6, 144.3, 128.1, 127.3, 126.1, 111.7, 82.4, 57.9, 53.3, 53.1, 51.0, 40.6. **HR-MS**: *calcd.* for $C_{16}H_{18}O_5$: 273.112. [$(M-(OH^-))^+$]; *found:* 273.1128 [$(M-(OH^-))^+$].

(*Z*)-3-Phenyl-4-propylidene-1-tosylpyrrolidin-3-ol (2i)

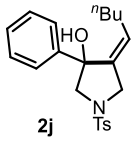


2i

According to **GP5** from **1i** (71.0 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-2** (78.3 mg, 250 µmol, 1.25 equiv.) in MeOH (4 mL) within 14 h. The isomers could be separated by flash chromatography on silica gel (4:1:1 to 3:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as colourless oil (60.9 mg, 85% for both isomers, *Z*/*E* = 11:1). $\mathbf{R_f}$ (4:1:1 *n*-pentane/Et_2O/CH_2Cl_2) = 0.30 (*Z*-isomer); 0.20 (*E*-isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.71 (m, 2H), 7.21-7.41 (m, 7H), 5.50 (tt, *J* = 7.7, 2.0 Hz, 1H), 4.13-4.19 (m, 1H), 3.74 (ddt, *J* = 13.1, 2.0 Hz, 1H), 3.61 (d, *J* = 10.4 Hz, 1H), 3.12 (dd, *J* = 10.4, 0.5 Hz, 1H), 2.49 (brs, 1H), 2.44 (s, 3H), 1.55-1.87 (m, 2H), 0.69 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 142.9, 140.1, 132.1, 130.7, 129.8, 128.3, 128.3, 127.4, 125.4, 80.2,

65.7, 53.9, 21.8, 21.6, 13.3. **HR-MS**: *calcd.* for $C_{20}H_{23}NO_3S$: 358.1471 [$(M+H)^+$]; *found:* 358.1471 [$(M+H)^+$].

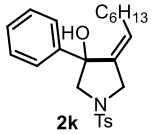
(*Z*)-4-Pentylidene-3-phenyl-1-tosylpyrrolidin-3-ol (2j)



2j

According to **GP5** from **1j** (77.2 mg, 201 µmol) with 4-CzIPN (3.3 mg, 4.1 µmol, 2.0 mol%) and **HEH-2** (78.6 mg, 251 µmol, 1.25 equiv.) in MeOH (4 mL) within 14 h. The isomers could be separated by flash chromatography on silica gel (5:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as colourless oil (62.0 mg, 80% for both isomers, *Z/E* = 11:1). $\mathbf{R_f}$ (4:1:1 *n*-pentane/Et_2O/CH_2Cl_2) = 0.40 (*Z*-isomer); 0.30 (*E*-isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.71 (m, 2H), 7.19-7.41 (m, 7H), 5.51 (tt, *J* = 7.7, 2.0 Hz, 1H), 4.12-4.21 (m, 1H), 3.74 (dqd, *J* = 13.1, 2.0, 0.5 Hz, 1H), 3.61 (dd, *J* = 10.4, 0.8 Hz, 1H), 3.12 (dd, *J* = 10.4, 0.5 Hz, 1H), 2.52 (brs, 1H), 2.44 (s, 3H), 1.56-1.81 (m, 2H), 0.93-1.16 (m, 4H), 0.62-0.70 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 143.0, 140.6, 131.9, 129.9, 129.3, 128.3, 128.3, 127.4, 125.4, 80.1, 65.8, 54.0, 31.0, 28.0, 22.3, 21.7, 13.8. **HR-MS**: *calcd.* for $C_{22}H_{27}NO_3S$: 386.1784 [$(M+H)^+$]; *found:* 386.1789 [$(M+H)^+$].

(*Z*)-4-Heptylidene-3-phenyl-1-tosylpyrrolidin-3-ol (2k)

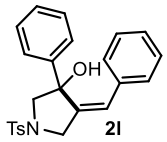


2k

According to **GP5** from **1k** (83.3 mg, 202 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-2** (78.4 mg, 250 µmol, 1.24 equiv.) in MeOH (4 mL) within 14 h. The isomers could be separated by flash chromatography on silica gel (5:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as colourless oil (63.5 mg, 76% for both isomers, *Z/E* = 9:1). $\mathbf{R_f}$ (4:1:1 *n*-pentane/Et_2O/CH_2Cl_2) = 0.40 (*Z*-isomer); 0.30 (*E*-isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.71 (m, 2H), 7.19-7.41 (m, 7H), 5.51 (tt, *J* = 7.4, 2.0 Hz, 1H), 4.16 (ddt, *J* = 13.2, 1.5, 0.7 Hz, 1H), 3.75 (dq, *J* = 13.1, 2.1 Hz, 1H), 3.56-3.65 (m, 1H), 3.14 (d, *J* = 10.4 Hz, 1H), 2.51 (brs, 1H), 2.44 (s, 3H), 1.53-1.84 (m, 2H), 0.92-1.20 (m, 8H), 0.79 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 143.1, 140.6, 132.1, 129.9, 129.3, 128.3, 128.3,

127.4, 125.4, 80.2, 65.8, 54.0, 31.6, 28.9, 28.8, 28.3, 22.6, 21.7, 14.1. **HR-MS**: *calcd.* for $C_{24}H_{31}NO_3S$: 414.2097 [$(M+H)^+$]; *found:* 414.2098 [$(M+H)^+$].

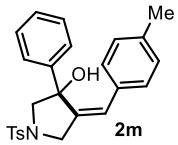
(*Z*)-4-Benzylidene-3-phenyl-1-tosylpyrrolidin-3-ol (2l)



2l

According to **GP5** from **1l** (80.5 mg, 200 µmol) with 4-CzIPN (3.4 mg, 4.3 µmol, 2.1 mol%) and **HEH-2** (78.1 mg, 249 µmol, 1.25 equiv.) in MeOH (4 mL) within 14 h. The isomers could be separated by flash chromatography on silica gel (5:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as white-yellow solid (74.2 mg, 92% for both isomers, *Z/E* = 14:1). $\mathbf{R_f}$ (3:1:1 *n*-pentane/Et_2O/CH_2Cl_2) = 0.55 (*Z*-isomer); 0.40 (*E*-isomer). **m.p.** = 180°C (decomposition). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.72 (m, 2H), 7.28-7.35 (m, 4H), 7.12-7.22 (m, 3H), 6.99-7.05 (m, 5H), 6.60 (t, *J* = 2.1 Hz, 1H), 4.25-4.38 (m, 1H), 4.10 (ddd, *J* = 14.0, 2.3, 0.6 Hz, 1H), 3.49-3.66 (m, 1H), 3.31 (dd, *J* = 10.1, 0.5 Hz, 1H), 2.79 (brs, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 142.2, 141.2, 134.6, 132.3, 129.9, 129.1, 128.3, 128.2, 128.0, 127.6, 127.6, 126.9, 125.7, 80.5, 65.4, 54.9, 21.7. **HR-MS**: *calcd.* for $C_{24}H_{23}NO_3S$: 406.1471 [$(M+H)^+$]; *found:* 406.1472 [$(M+H)^+$].

(*Z*)-4-(4-Methylbenzylidene)-3-phenyl-1-tosylpyrrolidin-3-ol (2m)

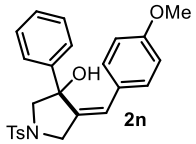


2m

According to **GP5** from **1m** (83.0 mg, 199 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-2** (78.4 mg, 250 µmol, 1.25 equiv.) in MeOH (4 mL) within 14 h. The isomers could be separated by flash chromatography on silica gel (5:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as yellow oil (77.6 mg, 93% for both isomers, *Z/E* = 12:1). $\mathbf{R_f}$ (3:1:1 *n*-pentane/Et_2O/CH_2Cl_2) = 0.60 (*Z*-isomer); 0.50 (*E*-isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.72 (m, 2H), 7.29-7.38 (m, 4H), 7.13-7.24 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.81-6.88 (m, 2H), 6.52-6.62 (m, 1H), 4.27 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.12 (dd, *J* = 14.1, 2.3 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 3.34 (dd, *J* = 9.9, 0.5 Hz, 1H), 2.77 (brs, 1H), 2.44 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 142.6, 140.2, 137.5, 132.2, 131.6,

129.8, 129.0, 128.8, 128.4, 128.2, 127.5, 126.7, 125.6, 80.4, 65.3, 54.9, 21.6, 21.2. **HR-MS**: *calcd.* for $C_{25}H_{25}NO_3S$: 420.1628 [$(M+H)^+$]; *found:* 420.1633 [$(M+H)^+$].

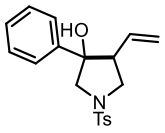
(*Z*)-4-(4-Methoxybenzylidene)-3-phenyl-1-tosylpyrrolidin-3-ol (2n)



2n

According to **GP5** from **1n** (86.0 mg, 198 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2.0 mol%) and **HEH-1** (62.8 mg, 248 µmol, 1.25 equiv.) in MeOH (4 mL) within 16 h. The isomers could be separated by flash chromato-graphy on silica gel (4:1:1 *n*-pentane/Et_2O/CH_2Cl_2). The title compound was obtained as yellow oil (81.1 mg, 94% for both isomers, *Z*/*E* = 10:1). $\mathbf{R_f}$ (1:2 *n*-pentane/Et_2O) = 0.55 (*Z*-isomer); 0.50 (*E*-isomer). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.70 (m, 2H), 7.30-7.34 (m, 4H), 7.14-7.22 (m, 3H), 6.94-7.01 (m, 2H), 6.54-6.57 (m, 2H), 6.53 (t, *J* = 2.2 Hz, 1H), 4.29 (dd, *J* = 13.9, 1.9 Hz, 1H), 4.06 (dd, *J* = 13.9, 2.3 Hz, 1H), 3.67 (s, 3H), 3.57 (d, *J* = 10.0 Hz, 1H), 3.27 (d, *J* = 10.1 Hz, 1H), 2.79 (brs, 1H), 2.44 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 144.2, 142.1, 138.8, 132.1, 130.6, 129.9, 128.4, 128.3, 127.6, 127.1, 126.6, 125.7, 113.5, 80.4, 65.6, 55.3, 55.0, 21.7. **HR-MS**: *calcd.* for $C_{25}H_{25}NO_4S$: 436.1577 [$(M+H)^+$]; *found:* 436.1582 [$(M+H)^+$].

3-phenyl-1-tosyl-4-vinylpyrrolidin-3-ol (4a)



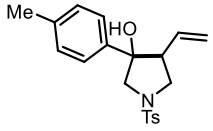
4a

According to **GP6** from **3a** (68.3 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (3:1 *n*-pentane/EtOAc) provided the title compound (50.8 mg, 74%). $\mathbf{R_f}$ (4:1 *n*-pentane/ EtOAc) = 0.4.

4a-1, **major**: white solid, **m.p.** = 127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.65 (m, 2H), 7.30-7.15 (m, 7H), 5.50 (ddd, *J* = 14.0, 8.4, 5.2 Hz, 1H), 5.08-5.03 (m, 1H), 4.95-4.88 (m, 1H), 3.69-3.62 (m, 1H), 3.61-3.50 (m, 2H), 3.36 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.05-2.97 (m, 1H), 2.36 (s, 3H), 2.06-1.97(m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 140.6, 134.1, 131.0, 129.7, 128.5, 127.7, 127.6, 125.2, 120.1, 81.1, 62.0, 52.6, 50.3, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_3S^+$: 366.1134; *found*: 366.1143.

4a-2, **minior**: yellow solid, **m.p.** = 118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.37-7.33 (m, 2H), 7.33-7.24 (m, 5H), 5.11 (ddd, *J* = 14.0, 8.4, 6.4 Hz, 1H), 4.93 (dt, *J* = 13.6, 1.2 Hz, 1H), 4.89 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 3.7 (d, *J* = 8.4 Hz 1H), 3.73 (dd, *J* = 8.0, 5.6 Hz, 1H), 3.54 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.40 (dd, *J* = 7.6, 3.6 Hz, 1H), 2.93-2.87 (m, 1H), 2.44 (s, 3H), 1.99-1.92 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 140.1, 134.6, 134.2, 129.8, 128.5, 128.3, 127.6, 126.2, 118.0, 82.1, 57.5, 53.5, 51.3, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_3S^+$: 366.1134; *found*: 366.1137.

3-(p-tolyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4b)



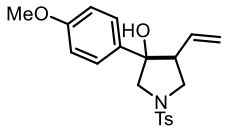
4b

According to **GP6** from **3b** (71.0 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 50 h. Flash chromatography on silica gel (3:1 *n*-pentane/EtOAc) provided the title compound (59.2 mg, 83%). $\mathbf{R_f}$ (4:1 *n*-pentane/ EtOAc) = 0.4.

4b-1, **major**: white solid, **m.p.** = 103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.37-7.32 (m, 2H), 7.25-7.20(m, 2H), 7.16-7.11 (m, 2H), 5.58 (ddd, *J* = 17.2, 10.8, 6.8 Hz, 1H), 5.15 (dt, *J* = 10.8, 1.2 Hz, 1H), 5.01 (dt, *J* = 17.6, 1.2 Hz, 1H), 3.73 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.66-3.62 (m, 1H), 3.60-3.56 (m, 1H), 3.44(dd, *J* = 10.8, 9.6 Hz, 1H), 3.13-3.05(m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 1.86 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 137.7, 137.6, 134.4, 131.2, 129.8, 129.3, 127.7, 125.1, 120.1, 81.1, 62.1, 52.5, 50.3, 21.6, 21.0. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_3S^+$: 358.1471; *found:* 358.1471.

4b-2, **minior**: yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.36-7.32 (m, 2H), 7.17-7.13 (m, 2H), 7.13-7.08 (m, 2H), 5.12 (ddd, *J* = 14.0, 8.4, 6.4 Hz, 1H), 4.93 (dt, *J* = 13.6, 1.2 Hz, 1H), 4.90-4.86 (m, 1H), 3.96-3.92 (m, 1H), 3.72 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.55-3.51 (m, 1H), 3.41-3.36 (m, 1H), 2.91-2.85 (m, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 2.01-1.93 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 138.0, 137.2, 134.8, 134.2, 129.8, 129.2, 127.6, 126.1, 117.8, 81.9, 57.5, 53.3, 51.3, 21.6, 21.1. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_3S^+$: 358.1471; *found:* 358.1470.

3-(4-methoxyphenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4c)



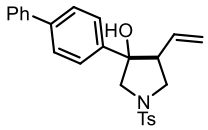
4c

According to **GP6** from **3c** (74.3 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 72 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (33.6 mg, 45%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4c-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.37-7.32 (m, 2H), 7.29-7.26(m, 1H), 7.26-7.24 (m, 1H), 6.88-6.83 (m, 2H), 5.59 (ddd, *J* = 17.2, 10.8, 6.8 Hz, 1H), 5.16 (dt, *J* = 10.4, 1.6 Hz, 1H), 5.02 (dt, *J* = 17.2, 1.6 Hz, 1H), 3.79 (s, 3H), 3.73 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.65-3.60 (m, 1H), 3.59-3.55 (m, 1H), 3.43 (dd, *J* = 10.8, 9.2 Hz, 1H), 3.13-3.04 (m, 1H), 2.45 (s, 3H), 1.77 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 143.6, 134.4, 132.7, 131.3, 129.8, 127.7, 126.5, 120.2, 114.0, 81.0, 62.0, 55.4, 52.4, 50.3, 21.7. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_4S^+$: 374.1421; *found*: 374.1421.

4c-2, **minior**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.37-7.32 (m, 2H), 7.22-7.17 (m, 2H), 6.85-6.80 (m, 2H), 5.13 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 4.97-4.87 (m, 2H), 3.93 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.72 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.52 (dd, *J* = 10.4, 0.8 Hz, 1H), 3.39 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.91-2.83 (m, 1H), 2.44 (s, 3H), 1.87 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 143.7, 134.9, 134.4, 132.3, 129.8, 127.6, 127.5, 117.8, 113.8, 81.8, 57.6, 55.3, 53.5, 51.4, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_4S^+$: 396.1240; *found*: 396.1245.

3-([1,1'-biphenyl]-4-yl)-1-tosyl-4-vinylpyrrolidin-3-ol (4d)



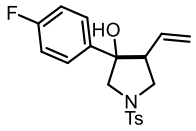
4d

According to **GP6** from **3d** (83.5 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (63.1 mg, 75%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4d-1, **major**: white solid, **m.p.** = 133 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.60-7.54 (m, 4H), 7.47-7.40 (m, 4H), 7.38-7.32 (m, 3H), 5.63 (ddd, *J* = 17.6, 10.8, 6.8 Hz, 1H), 5.17 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.04 (dt, *J* = 17.6, 1.2 Hz, 1H), 3.77 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.74-3.69 (m, 1H), 3.68-3.63 (m,

1H), 3.48 (dd, *J* = 10.8, 9.6 Hz, 1H), 3.18-3.09 (m, 1H), 2.45 (s, 3H), 2.14 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 140.6, 140.3, 139.7, 134.3, 131.1, 129.8, 128.8, 127.6, 127.5, 127.1, 127.0, 125.7, 120.1, 81.1, 62.0, 52.7, 50.4, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{25}NNaO_3S^+$: 442.1447; *found*: 442.1445.

3-(4-fluorophenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4e)



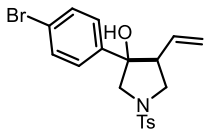
4e

According to **GP6** from **3c** (71.9 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (52.8 mg, 73%). **R_f** (3:1 *n*-pentane/ EtOAc) = 0.4.

4e-1, **major**: yellow solid, **m.p.** = 112 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.35-7.28 (m, 4H), 7.02-6.95 (m, 2H), 5.56 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 5.13 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.98 (dt, *J* = 17.5, 1.0 Hz, 1H), 3.70 (dd, *J* = 14.5, 7.5 Hz, 1H), 3.63-3.56 (m, 2H), 3.41 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.06-2.99 (m, 1H), 2.43 (s, 3H), 2.17 (brs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, J_{C-F} = 247.8 Hz), 143.7, 136.5 (d, J_{C-F} = 3.3 Hz), 134.0, 130.9, 129.8, 127.6, 127.1 (d, J_{C-F} = 8.7 Hz), 120.3, 115.3 (d, J_{C-F} = 20.8 Hz), 80.8, 61.9, 52.8, 50.3, 21.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.7 (m). **HR-MS** (- p ESI) *m/z*: $[M-H]^-$ Calcd for $C_{19}H_{19}FNO_3S^-$: 360.1075; *found*: 360.1073.

4e-2, **minior**: yellow solid, **m.p.** = 107 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.37-7.33 (m, 2H), 7.28-7.23 (m, 2H), 7.01-6.95 (m, 2H), 5.09 (ddd, *J* = 17.5, 10.5, 8.0 Hz, 1H), 4.5-4.88 (m, 2H), 3.2 (d, *J* = 10.5 Hz, 1H), 3.72 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.52 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.36 (dd, *J* = 9.5, 4.5 Hz, 1H), 2.89-2.83 (m, 1H), 2.45 (s, 3H), 2.07-1.99 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 249.0 Hz), 143.8, 136.0 (d, J_{C-F} = 4.0 Hz), 134.4, 134.1, 129.9, 128.1 (d, J_{C-F} = 7.6 Hz), 127.6, 118.3, 115.3 (d, J_{C-F} = 21.9 Hz), 81.6, 57.7, 53.6, 51.2, 21.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.6 (m). **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}FNNaO_3S^+$: 384.1040; *found*: 3841042.

3-(4-bromophenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4f)

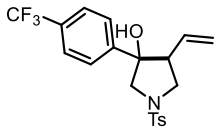


4f

According to **GP6** from **3c** (84.1 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (67.6 mg, 80%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4f-1, **major**: white solid, **m.p.** = 116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.71 (m, 2H), 7.46-7.40 (m, 2H), 7.36-7.31 (m, 2H), 7.24-7.19 (m, 2H), 5.55 (ddd, *J* = 17.6, 10.4, 6.8 Hz, 1H), 5.13 (dt, *J* = 10.8, 1.2 Hz, 1H), 4.98 (dt, *J* = 17.6, 1.2 Hz, 1H), 3.70 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.63-3.55 (m, 2H), 3.41 (dd, *J* = 10.8, 9.6 Hz, 1H), 3.06-2.97 (m, 1H), 2.44 (s, 3H), 2.13 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 139.8, 134.1, 131.6, 130.8, 129.8, 127.6, 127.1, 121.9, 120.4, 80.9, 61.8, 52.9, 50.3, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}BrNO_3S^+$: 422.0420; *found*: 422.0426.

1-tosyl-3-(4-(trifluoromethyl)phenyl)-4-vinylpyrrolidin-3-ol (4g)



4g

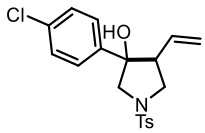
According to **GP6** from **3c** (81.9 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (65.9 mg, 80%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4g-1, **major**: yellow solid, **m.p.** = 106 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.59-7.55 (m, 2H), 7.49-6.45 (m, 2H), 7.36-7.32 (m, 2H), 5.55 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 5.13 (ddd, *J* = 10.5, 2.5, 1.5 Hz, 1H), 4.97 (ddd, *J* = 17.5, 2.5, 1.5 Hz, 1H), 3.2 (dd, *J* = 9.0, 8.0 Hz, 1H), 3.67-3.60 (m, 2H), 3.44 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.10-3.03 (m, 1H), 2.44 (s, 3H), 2.36-2.31(m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 143.9, 133.9, 130.5, 130.0 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.9, 127.6, 125.8, 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.5 Hz), 120.6, 81.0, 61.9, 53.1, 50.3, 21.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.6 (s). **HR-MS** (- p ESI) *m/z*: $[M-H]^-$ Calcd for $C_{20}H_{19}F_3NO_3S^-$: 410.1043; *found*: 410.1034.

4g-2, **minior**: white solid, **m.p.** = 136 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.57-7.53 (m, 2H), 7.43-7.39 (m, 2H), 7.38-7.34 (m, 2H), 5.06 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 4.96-4.90 (m, 2H), 3.9 (d, *J* = 11.0 Hz, 1H), 3.74 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.55 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.36 (dd, *J* = 10.0,

5.0 Hz, 1H), 2.93-2.87 (m, 1H), 2.46 (s, 3H), 2.20-2.15 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 144.0, 133.9, 133.9, 130.4 (q, J_{C-F} = 32.4 Hz), 130.0, 127.6, 126.7, 125.4 (q, J_{C-F} = 3.9 Hz), 124.0 (q, J_{C-F} = 272.5 Hz), 118.7, 81.7, 57.8, 53.9, 51.1, 21.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62. (s). **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{21}F_3NO_3S^+$: 412.1189; *found*: 412.1191.

3-(4-chlorophenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4h)



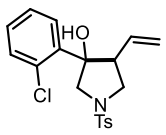
4h

According to **GP6** from **3c** (75.2 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 48 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (68.4 mg, 90%). **R_f** (3:1 *n*-pentane/ EtOAc) = 0.4.

4h-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.27 (m, 4H), 5.55 (ddd, *J* = 17.6, 10.8, 6.8 Hz, 1H), 5.14 (dt, *J* = 10.8, 1.2 Hz, 1H), 4.98 (dt, *J* = 17.6, 1.2 Hz, 1H), 3.71 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.64-3.56 (m, 2H), 3.42 (dd, *J* = 10.8, 9.6 Hz, 1H), 3.07-2.99 (m, 1H), 2.44 (s, 3H), 2.13-2.07 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 139.3, 134.2, 133.7, 130.8, 129.8, 128.7, 127.6, 126.8, 120.4, 80.9, 61.9, 52.9, 50.3, 21.6. **HR-MS** (- p ESI) *m/z*: $[M-H]^-$ Calcd for $C_{19}H_{19}ClNO_3S^-$: 376.0780; *found*: 376.0779.

4h-2, **minior**: white solid, **m.p.** = 85 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77-7.73 (m, 2H), 7.37-7.33 (m, 2H), 7.27-7.23 (m, 2H), 7.23-7.18 (m, 2H), 5.07 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 4.94- 4.88 (m, 2H), 3.89 (d, *J* = 10.5 Hz, 1H), 3.70 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.51 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.33 (dd, *J* = 9.5, 5.0 Hz, 1H), 2.88-2.82 (m, 1H), 2.44 (s, 3H), 2.26-2.19 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 138.8, 134.2, 134.1, 134.0, 129.9, 128.6, 127.7, 127.6, 118.4, 81.5, 57.7, 53.6, 51.2, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}ClNO_3S^+$: 378.0925; *found*: 378.0927.

3-(2-chlorophenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4i)

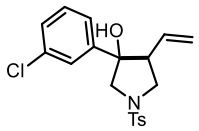


4i

According to **GP6** from **3c** (75.2 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (54.7 mg, 72%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4i-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.38-7.32 (m, 3H), 7.28-7.19 (m, 3H), 5.55 (ddd, *J* = 17.6, 10.8, 6.8 Hz, 1H), 5.17 (ddd, *J* = 10.8, 2.4, 1.2 Hz, 1H), 5.01 (ddd, *J* = 17.6, 2.4, 1.2 Hz, 1H), 3.74 (dd, *J* = 9.6, 8.0 Hz, 1H)), 3.65-3.56 (m, 2H), 3.43 (dd, *J* = 11.2, 9.6 Hz, 1H), 3.11-3.01 (m, 1H), 2.45 (s, 3H), 2.00-1.91 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 143.0, 134.7, 134.2, 130.6, 129.9, 128.1, 127.7, 125.8, 123.4, 120.7, 80.9, 62.0, 52.8, 50.2, 21.7. **HR-MS** (- p ESI) *m/z*: $[M-H]^-$ Calcd for $C_{19}H_{19}ClNO_3S^-$: 376.0780; *found*: 376.077.

3-(3-chlorophenyl)-1-tosyl-4-vinylpyrrolidin-3-ol (4j)



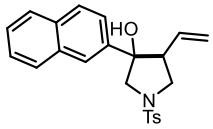
4j

According to **GP6** from **3c** (75.2 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (67.3 mg, 89%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4j-1, **major**: white solid, **m.p.** = 116 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.58-7.53 (m, 1H), 7.37-7.32 (m, 3H), 7.25-7.21 (m, 2H), 5.68-5.58 (m, 1H), 5.22-5.18 (m, 1H), 5.11 (dt, *J* = 17.2, 1.2 Hz, 1H), 4.03-3.98 (m, 1H), 3.76- 3.67 (m, 3H), 3.44-3.36 (m, 1H), 2.45 (s, 3H), 2.44 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 137.4, 134.3, 131.8, 131.7, 131.6, 129.8, 129.5, 128.5, 127.7, 127.2, 120.3, 80.8, 59.0, 50.4, 49.2, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}ClNO_3S^+$: 378.0925; *found*: 378.0925.

4j-2, **minior**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.37-7.33 (m, 1H), 7.33-7.29 (m, 2H), 7.25-7.15 (m, 3H), 5.24 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 5.03 (dt, *J* = 17.2, 1.2 Hz, 1H), 4.82 (ddd, *J* = 10.4, 1.6, 0.8 Hz, 1H), 4.08 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.78-3.75 (m, 1H), 3.74 (dd, *J* = 3.6, 2.4 Hz, 1H), 3.72-3.66 (m, 1H), 3.54 (dd, *J* = 9.2, 0.8 Hz, 1H), 2.76-2.73 (m, 1H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 136.8, 135.0, 134.4, 132.7, 131.5, 129.7, 129.6, 128.3, 127.7, 127.2, 117.3, 83.0, 56.1, 51.3, 51.0, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}ClNNaO_3S^+$: 400.0745; *found*: 400.0746.

3-(naphthalen-2-yl)-1-tosyl-4-vinylpyrrolidin-3-ol (4k)

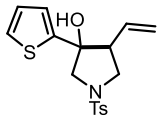


4k

According to **GP6** from **3b** (78.3 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (3:1 *n*-pentane/EtOAc) provided the title compound as (65.8 mg, 83%). $\mathbf{R_f}$ (4:1 *n*-pentane/ EtOAc).

4k-1, **major**: white solid, **m.p.** = 132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.0 Hz 1H), 7.83-7.77 (m, 5H), 7.51-7.46 (m, 2H), 7.39-7.33 (m, 3H), 5.59 (ddd, *J* = 17.5, 10.5, 6.5 Hz, 1H), 5.13 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.00 (dt, *J* = 17.5, 1.5 Hz, 1H), 3.81- 3.76 (m, 2H), 3.67-3.64 (m, 1H), 3.49 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.25-3.17 (m, 1H), 2.46 (s, 3H), 2.14-2.10 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7, 138.0, 134.2, 133.0, 132.7, 131.0, 129.8, 128.4, 128.2, 127.6, 127.6, 126.5, 126.4, 124.6, 123.0, 120.3, 81.4, 62.0, 52.6, 50.3, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{23}NNaO_3S^+$: 416.1291; *found*: 416.1293.

3-(thiophen-2-yl)-1-tosyl-4-vinylpyrrolidin-3-ol (4l)



4l

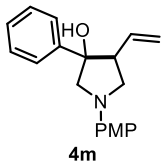
According to **GP6** from **3c** (69.5 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 24 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (45.6 mg, 65%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4l-1, **major**: yellow solid, **m.p.** = 122 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.36-7.31 (m, 2H), 7.22 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.92 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.69 (ddd, *J* = 17.2, 10.8, 7.2 Hz, 1H), 5.22 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.09 (dt, *J* = 17.6, 1.2 Hz, 1H), 3.74-3.65 (m, 3H), 3.42 (dd, *J* = 10.8, 9.6 Hz, 1H), 3.08-2.99 (m, 1H), 2.44 (s, 3H), 2.13 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 143.7, 134.3, 130.9, 129.8, 127.6, 127.2, 125.2, 123.8, 120.8, 80.0, 62.2, 53.6, 50.3, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{19}NNaO_3S_2^+$: 372.0699; *found*: 372.0701.

4l-2, **minior**: brown solid, **m.p.** = 107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.36-7.32 (m, 2H), 7.23 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.92 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.84 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.32-

5.22 (m, 1H), 5.02- 4.94 (m, 2H), 3.88 (d, *J* = 10.8 Hz, 1H), 3.70 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.53 (dd, *J* = 10.4, 0.8 Hz, 1H), 3.43 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.88-2.81 (m, 1H), 2.44 (s, 3H), 2.29 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 143.8, 134.3, 134.2, 129.8, 127.6, 126.9, 125.6, 124.4, 118.3, 80.9, 58.7, 54.3, 51.2, 21.6. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{19}NNaO_3S_2^+$: 372.0699; *found*: 372.0704.

1-(4-methoxyphenyl)-3-phenyl-4-vinylpyrrolidin-3-ol (4m)



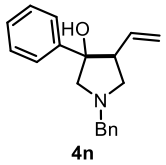
4m

According to **GP6** from **3c** (58.7 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 72 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (37.5 mg, 63%). **R_f** (3:1 *n*-pentane/ EtOAc) = 0.4.

4m-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58- 7.53 (m, 2H), 7.43-7.37 (m, 2H), 7.34-7.28 (m, 1H), 6.90-6.84 (m, 2H), 6.59-6.50 (m, 2H), 5.84 (ddd, *J* = 17.2, 10.8, 7.2 Hz, 1H), 5.23 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.16 (dt, *J* = 17.6, 1.6 Hz, 1H), 3.77 (s, 3H), 3.76-3.71 (m, 1H), 3.66-3.54 (m, 3H), 3.43-3.33 (m, 1H), 2.22 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 142.5, 142.2, 133.0, 128.5, 127.5, 125.5, 119.4, 115.3, 112.5, 81.5, 63.7, 56.1, 52.8, 51.3. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_2^+$: 296.1645; *found*: 296.1652.

4m-2, **minior**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H), 6.94- 6.88 (m, 2H), 6.67-6.56 (m, 2H), 5.35-5.22 (m, 1H), 5.10-5.02 (m, 1H), 4.99-4.94 (m, 1H), 3.97-3.91 (m, 1H), 3.79 (s, 3H), 3.77-3.70 (m, 1H), 3.67-3.63 (m, 1H), 3.29-3.18 (m, 2H), 2.50-2.34 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 141.8, 141.8, 135.8, 128.4, 127.8, 126.2, 117.5, 115.3, 112.6, 81.8, 60.2, 56.1, 54.4, 52.3. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_2^+$: 296.1645; *found*: 296.1648.

1-benzyl-3-phenyl-4-vinylpyrrolidin-3-ol (4n)

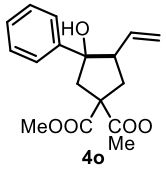


4n

According to **GP6** from **3c** (55.5 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 48 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (22.8 mg, 41%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4n-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.39-7.30 (m, 6H), 7.29-7.21 (m, 2H), 5.85 (ddd, *J* = 17.6, 10.4, 7.2 Hz, 1H), 5.11 (ddd, *J* = 10.4, 1.6, 1.2 Hz, 1H), 4.96 (ddd, *J* = 17.6, 1.6, 1.2 Hz, 1H), 3.85-3.75 (m, 2H), 3.20-3.12 (m, 1H), 3.10-3.04 (m, 1H), 2.99-2.92 (m, 3H), 2.67 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 138.8, 134.7, 128.8, 128.4, 128.2, 127.2, 127.1, 125.3, 117.9, 81.6, 68.7, 60.2, 56.9, 54.1. **HR-MS** (+ p ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO^+$: 280.1696; *found*: 280.1703.

3-hydroxy-3-phenyl-4-vinylcyclopentane-1,1-dicarboxylate (4o)



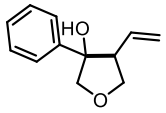
4o

According to **GP6** from **3c** (60.4 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 72 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (37.4 mg, 61%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

4o-1, **major**: yellow solid, **m.p.** = 127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.38-7.32 (m, 2H), 7.28-7.22 (m, 1H), 5.67 (ddd, *J* = 17.2, 10.8, 6.4 Hz, 1H), 5.13 (dt, *J* = 10.8, 1.6 Hz, 1H), 5.07 (dt, *J* = 17.6, 1.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.16-3.08 (m, 1H), 2.82-2.57 (m, 4H), 2.28 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 173.2, 143.5, 134.2, 128.3, 127.2, 125.3, 118.6, 83.3, 57.6, 53.9, 53.1, 53.1, 50.2, 36.9. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{20}NaO_5^+$: 327.1203; *found*: 327.1207.

4o-2, **minior**: yellow solid, **m.p.** = 110 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.69-7.64 (m, 2H), 7.62-7.57 (m, 1H), 5.69-5.61 (m, 1H), 5.21 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.5, 2.0, 1.0 Hz, 1H), 4.14 (s, 3H), 4.12 (s, 3H), 3.37-3.28 (m, 3H), 3.16-3.11 (m, 1H), 2.80-2.77 (m, 1H), 2.77-2.72 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 172.7, 142.6, 138.0, 128.2, 127.6, 126.4, 116.0, 85.1, 58.4, 55.5, 53.3, 53.1, 45.0, 38.0. **HR-MS** (+ p APCI) *m/z*: $[M-OH]^+$ Calcd for $C_{17}H_{19}O_4$: 287.1278; *found*: 287.1284.

3-phenyl-4-vinyltetrahydrofuran-3-ol (4p)



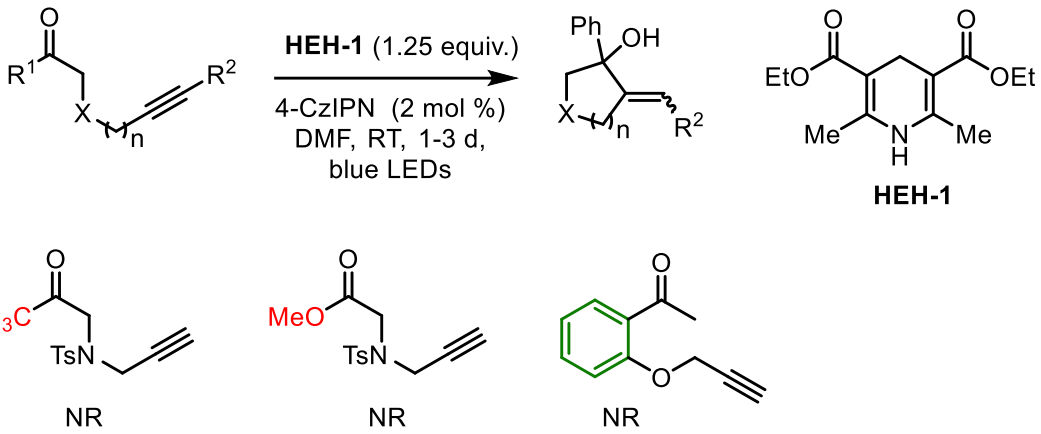
4p

According to **GP6** from **3c** (37.6 mg, 200 µmol) with 4-CzIPN (3.2 mg, 4.0 µmol, 2 mol%) and **HEH-1** (63.6 mg, 250 µmol, 1.25 equiv.) in DMSO (6 mL) within 48 h. Flash chromatography on silica gel (2:1 *n*-pentane/EtOAc) provided the title compound (28.7 mg, 75%). $\mathbf{R_f}$ (3:1 *n*-pentane/ EtOAc) = 0.4.

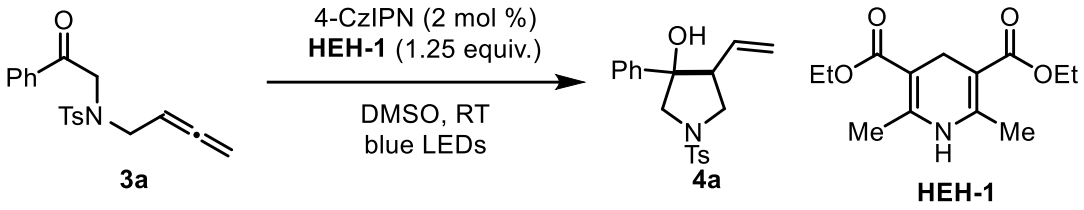
4p-1, **major**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.40-7.34 (m, 2H), 7.31-7.26 (m, 1H), 5.79 (ddd, *J* = 17.6, 10.4, 7.2 Hz, 1H), 5.21 (dt, *J* = 10.4, 1.6 Hz, 1H), 5.09 (dt, *J* = 17.6, 1.2 Hz, 1H), 4.22 (t, *J* = 8.4 Hz, 1H), 4.10-4.01 (m, 3H), 3.32-3.24 (m, 1H), 2.33 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 131.8, 128.5, 127.5, 125.4, 119.8, 82.4, 81.5, 71.4, 54.5. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2^+$: 191.1067; *found*: 191.1064.

4p-2, **minior**: colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.27 (m, 1H), 5.25 (ddd, *J* = 17.2, 10.4, 8.8 Hz, 1H), 5.02 (ddd, *J* = 16.8, 2.0, 1.2 Hz, 1H), 4.92 (ddd, *J* = 10.0, 1.6, 0.8 Hz, 1H), 4.38-4.30 (m, 2H), 4.04 (dd, *J* = 8.8, 0.4 Hz, 1H), 3.83 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.16-3.08 (m, 1H), 2.27 (brs, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 135.7, 128.4, 127.9, 126.5, 117.3, 83.4, 77.5, 72.4, 55.7. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2^+$: 191.1067; *found*: 191.1064.

Unsuccessful results

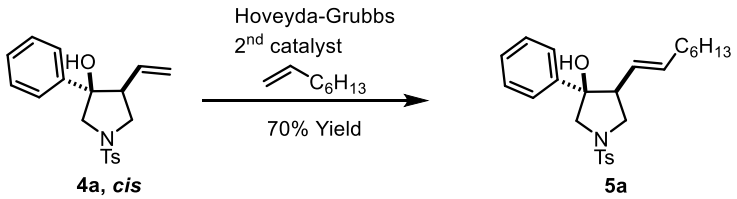


Up-scaling experiment



According to **GP6** from **3a** (1.07 g, 3 mmol) with 4-CzIPN (48 mg, 0.6 mmol, 2 mol%) and **HEH-1** (954 mg, 3. mmol, 1.25 equiv.) in DMSO (60 mL) within 24 h. Flash chromatography on silica gel (3:1 n-pentane/EtOAc) provided the title compound (752.1 mg, 73%, dr = 3:1).

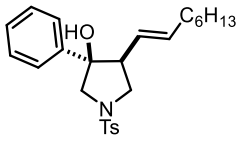
Transformations



4a, ***cis*** **5a**

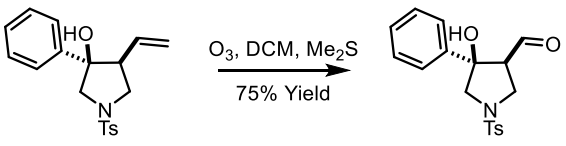
4a (34.3 mg, 0.1 mmol, 1 eq.) was dissolved in CH_2Cl_2 (1 ml) and 1-Octene (94 µl, 0.6 mmol, 6 eq.) and Hoveyda-Grubbs catalyst 2nd generation (6.2 mg, 10 µmol, 10 mol %) were added in sequence at room temperature. After reaction mixture was stirred for 24 h under 40 °C, saturated $NaHCO_3$ (aq) was added and was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The crude product was purified by flash column silica gel chromatography (5:1 *n*-pentane/EtOAc) provided **5a** as colorless oil (29.0 mg, 70%). $\mathbf{R_f}$ (5:1 *n*-pentane/ EtOAc) = 0.4.

4-((E)-oct-1-en-1-yl)-3-phenyl-1-tosylpyrrolidin-3-ol



5a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.37-7.30 (m, 6H), 5.40 (dtd, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.13 (ddt, *J* = 15.5, 6.5, 1.5 Hz, 1H), 3.72 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.65 (dd, *J* = 11.5, 1.5 Hz, 1H), 3.60-3.56 (m, 1H), 3.38 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.11-3.04 (m, 1H), 2.45 (s, 3H), 1.96-1.84 (m, 2H), 1.84-1.79 (m, 1H), 1.63-1.58 (m, 1H), 1.30-1.09 (m, 8H), 0.85 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.6, 141.0, 137.2, 134.3, 129.8, 128.5, 127.7, 125.3, 121.9, 81.2, 61.9, 51.8, 50.7, 32.8, 31.6, 29.1, 28.7, 22.6, 21.7, 14.1. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{34}NO_3S^+$: 428.2254; *found*: 428.2251.

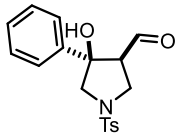


4a **5b**

4a (34.3 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to -78 °C. Ozone was bubbled then directly in the solution. After the reaction showed a blue color, the vial was degassed with N_2 until disappearance of the blue color occurred. After reductive work up with Me_2S (1 mL), the mixture was allowed to warm to room

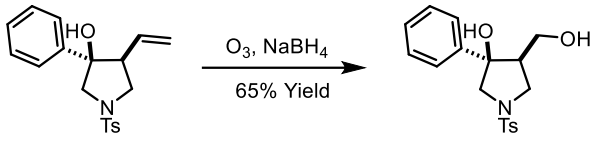
temperature and the volatiles removed under reduced pressure. The crude product was purified by flash column silica gel chromatography (2:1 *n*-pentane/EtOAc) provided **5b** as colorless oil (25.9 mg, 75%). **R_f** (3:1 *n*-pentane/ EtOAc) = 0.3.

4-hydroxy-4-phenyl-1-tosylpyrrolidine-3-carbaldehyde



5b

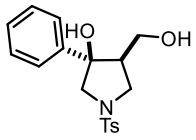
^{1}H NMR (500 MHz, C_6D_6) δ 9.10 (d, *J* = 0.5 Hz, 1H), 7.76-7.71 (m, 2H), 7.13-7.05 (m, 4H), 7.04-7.00 (m, 1H), 6.89-6.85 (m, 2H), 3.91 (t, *J* = 9.5 Hz, 1H), 3.53 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.49 (d, *J* = 11.5 Hz, 1H), 3.41 (d, *J* = 11.0 Hz, 1H), 2.85 (br, 1H), 2.70-2.65 (m, 1H), 1.92 (brs, 3H); **^{13}C NMR** (126 MHz, C_6D_6) δ 197.8, 143.6, 140.6, 134.6, 129.9, 128.8, 128.3, 128.1, 125.5, 81.4, 63.1, 60.2, 46.7, 21.1. **HR-MS** (+ p APCI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{19}NNaO_4S^+$: 368.0927; *found*: 368.0932.



4a **5c**

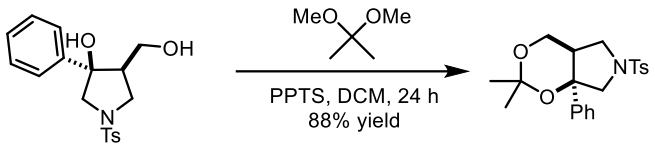
4a (34.3 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to -78 °C. Ozone was bubbled then directly in the solution. After the reaction showed a blue color, the vial was degassed with N_2 until disappearance of the blue color occurred. To the reaction mixture was further added methanol (2 mL) and $NaBH_4$ (22.7 mg, 0.6 mmol, 6 equiv.) at 0 °C, warmed to room temperature, stirred for 2 h and quenched by 1M HCl. The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated under reducer pressure. The crude product was purified by flash column silica gel chromatography (1:1 *n*-pentane/EtOAc) provided **5c** as white solid (22.7 mg, 65%). **R_f** (1:1 *n*-pentane/ EtOAc) = 0.3. **m.p.** = 93 °C.

4-(hydroxymethyl)-3-phenyl-1-tosylpyrrolidin-3-ol



5c

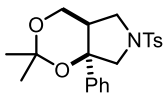
^{1}H NMR (500 MHz, C_6D_6) δ 7.89-7.85 (m, 2H), 7.23-7.18 (m, 2H), 7.12-7.07 (m, 2H), 7.05-7.00 (m, 1H), 6.92-6.87 (m, 2H), 4.34-4.24 (m, 1H), 3.87-3.80 (m, 1H), 3.76-3.70 (m, 1H), 3.64 (dd, *J* = 11.0, 1.5 Hz, 1H), 3.54 (d, *J* = 11.0 Hz, 1H), 3.35-3.20 (m, 2H), 2.60-2.33 (m, 1H), 2.03-1.95 (m, 1H), 1.90 (s, 3H); **^{13}C NMR** (126 MHz, C_6D_6) δ 143.2, 141.7, 134.9, 129.8, 128.5, 128.1, 127.5, 125.7, 82.5, 63.4, 58.7, 49.7, 48.8, 21.2. **HR-MS** (- p ESI) *m/z*: $[M-H]^-$ Calcd for $C_{18}H_{20}NO_4S^-$: 346.1119; *found*: 346.1117.



5c **5d**

To a solution of **5c** (17.4 mg, 0.05 mmol) in DCM (2 mL) were added 2,2- dimethoxypropane (32 µL, 0.25 mmol) and PPTS (1.2 mg, 10 % mmol) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. To the mixture was added saturated NH_4Cl solution at 0 °C, and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine (10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by flash column silica gel chromatography (5:1 *n*-pentane/EtOAc) provided **5d** as colorless oil(17.0 mg, 88%). **R_f** (10:1 *n*-pentane/ EtOAc) = 0.3.

7a-phenyl-6-tosylhexahydro-[1,3]dioxino[4,5-c]pyrrole



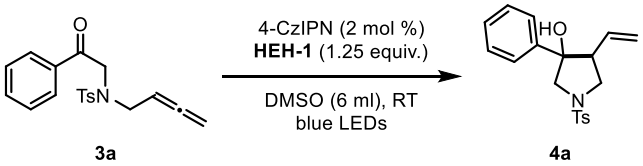
5d

^{1}H NMR (500 MHz, C_6D_6) δ 7.91-7.87 (m, 2H), 7.06-7.00 (m, 3H), 6.95-6.90 (m, 2H), 6.87-6.83 (m, 2H), 3.87 (dd, *J* = 10.5, 9.0 Hz, 1H), 3.81 (d, *J* = 11.5 Hz, 1H), 3.63-3.54 (m, 2H), 3.18 (d, *J* = 11.5 Hz, 1H), 3.17-3.12 (m, 1H), 2.16-2.08 (m, 1H), 1.91 (s, 3H), 0.92 (s, 3H), 0.61 (s, 3H).**^{13}C NMR** (126 MHz, C_6D_6)

δ 142.6, 141.4, 135.9, 129.5, 128.7, 128.3, 128.3, 125.6, 98.9, 80.0, 64.7, 56.0, 49.1, 36.5, 30.2, 22.9, 21.0. **HR-MS** (+ p ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{25}NNaO_4S^+$: 410.1397; *found*: 410.1399.

Mechanistic studies

On/Off studies



3a **4a**

Following the general procedure **GP6**. To an oven-dried Schlenk-tube equipped with magnetic stirring was charged with **3a** (68.3 mg, 0.2 mmol, 1.0 equiv.), Hantzsch-ester **HEH-1** (63mg, 0.25 mmol, 1.25 equiv.), 4-CzIPN (3.2 mg, 2 mol %) and 1,3,5-trimethoxybenzene (11.2 mg, 0.06 mmol, 33 mol %). The Schlenk tube was put on vacuum and backfilled with argon three times. DMSO-d_6 (6 mL) was added by syringe under a flow of argon. After stirring for a minute, the resulting pale-yellow solution (0.6 ml) was transferred to NMR tube by syringe under a flow of argon. The NMR tube was sealed by a screw cap and the resulting mixture was placed approximately 2.5 cm away from one 34 W blue LEDs and irradiated and stirred at room temperature. For each indicated time the yield of product (**4a**) was monitored by ^{1}H NMR.

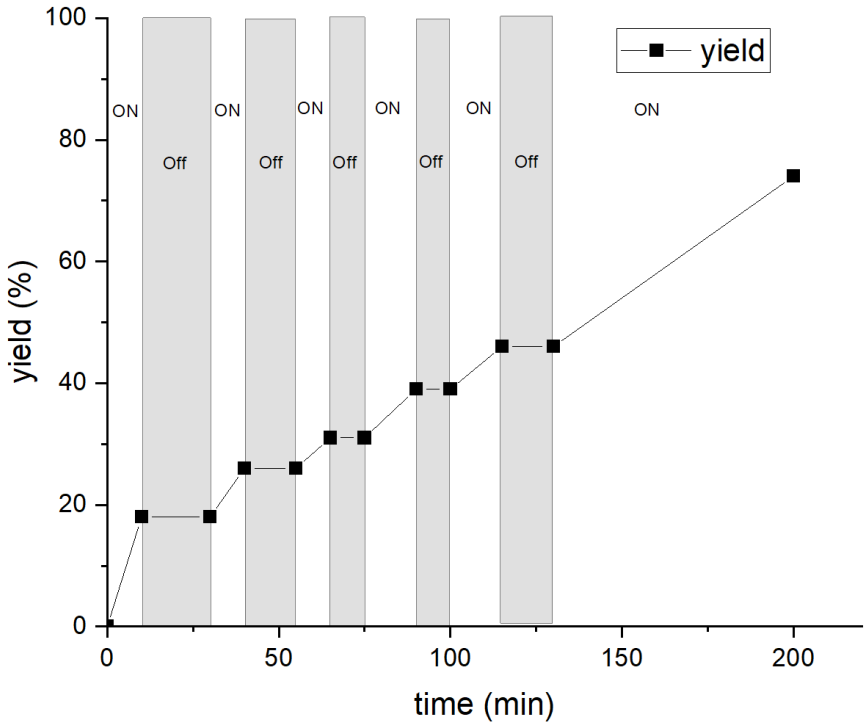


Figure S2. Monitor the formation of **4a** with light on/off.

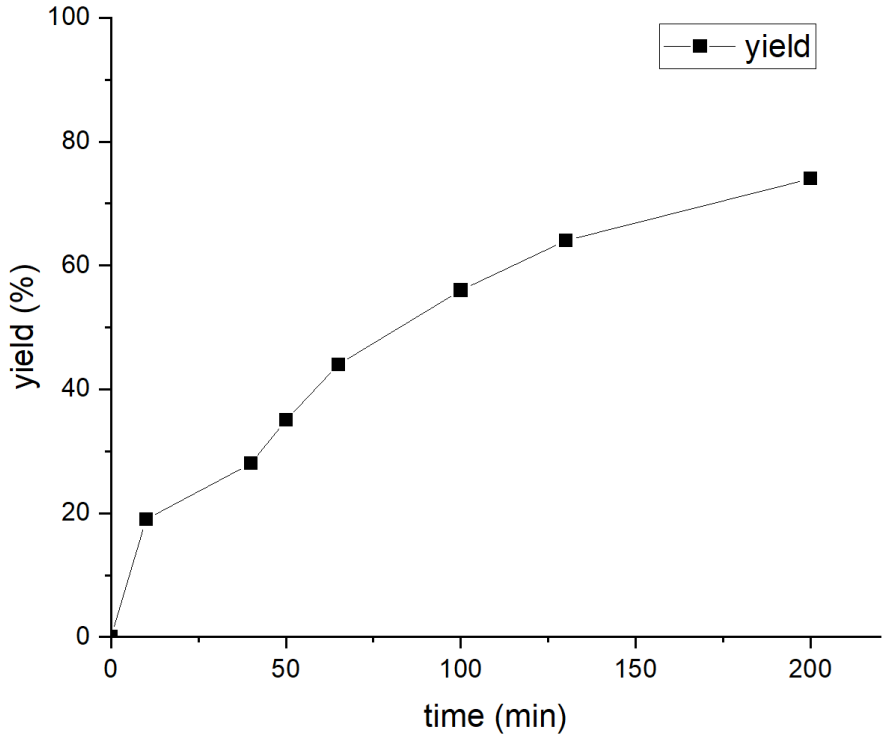


Figure S3. Monitor the formation of **4a** under continuous irradiation

The acid and base doping experiments

Following the general procedure **GP5**. To an oven-dried Schlenk-tube equipped with magnetic stirring was charged with **2a** (65.4 mg, 0.2 mmol, 1.0 equiv.), Hantzsch-ester **HEH-1** (63.6mg, 0.25 mmol, 1.25 equiv.), 4-CzIPN (3.4 mg, 2 mol %), diphenyl phosphate (25.0 mg, 0.10 mmol, 0.5 equiv.) or pyridinium 4-toluenesulfonate (PPTS) (25.1 mg, 0.10 mmol, 0.5 equiv.) or sodium acetate (NaOAc) (8.2 mg, 0.10 mmol, 0.5 equiv.), and 1,3,5-trimethoxybenzene (11.2 mg, 0.06 mmol, 33 mol %). The Schlenk tube was put on vacuum and backfilled with argon three times. DMF-d_7 (4 mL) was added by syringe under a flow of argon. After stirring for a minute, the resulting pale-yellow solution (0.6 mL) was transferred to NMR tube by syringe under a flow of argon. The NMR tube was sealed by a screw cap and the resulting mixture was placed approximately 2.5 cm away from one 34 W blue LEDs and irradiated and stirred at room temperature. For each indicated time the yield of product (**2a**) was monitored by ^{1}H NMR.

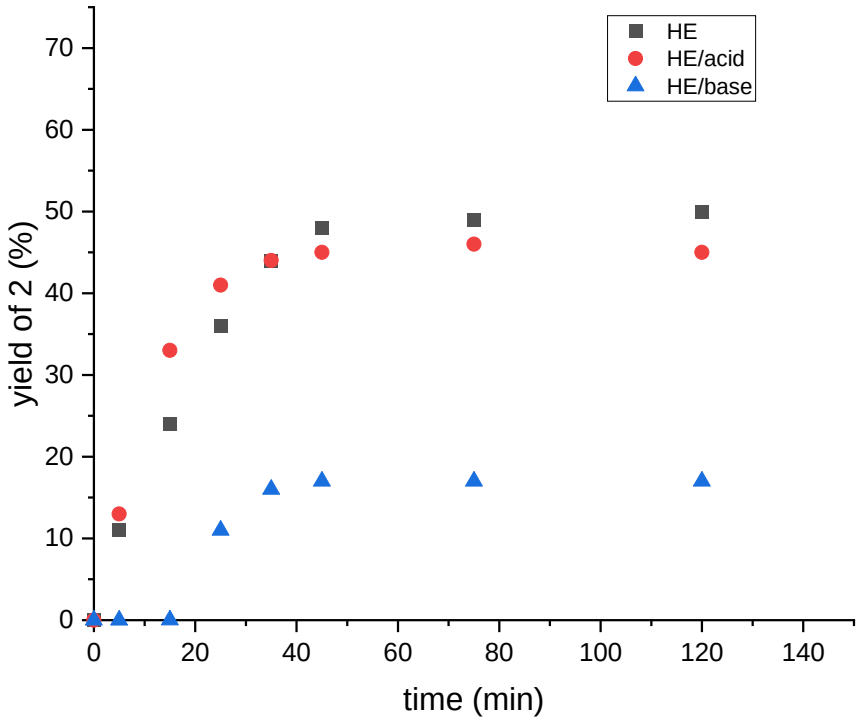


Figure S4. Monitor the formation of **2a** with HE or HE/**diphenyl phosphate** or HE/**NaOAc**

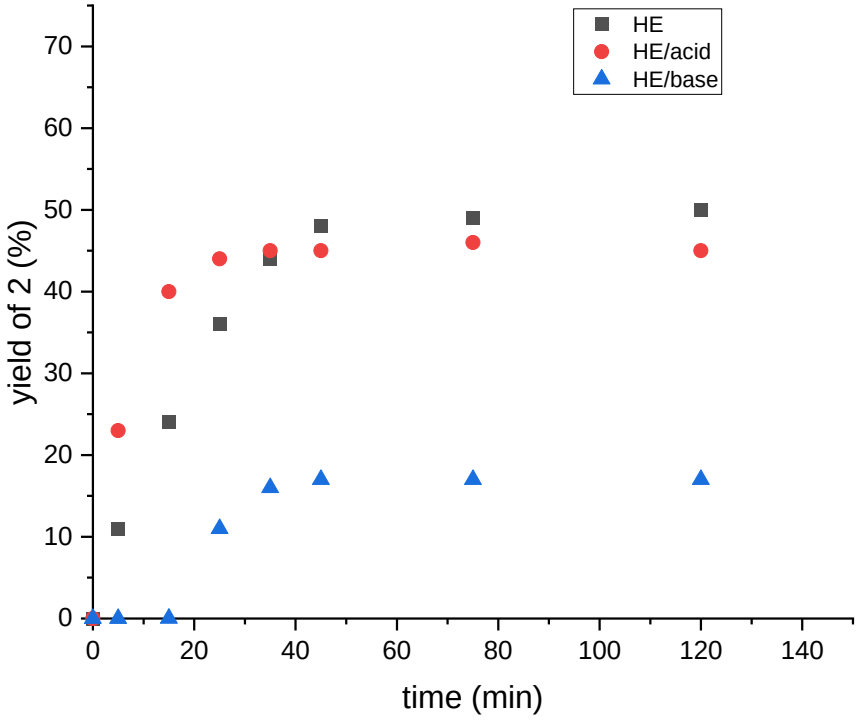


Figure S5. Monitor the formation of **2a** with HE or HE/**PPTS** or HE/**NaOAc**

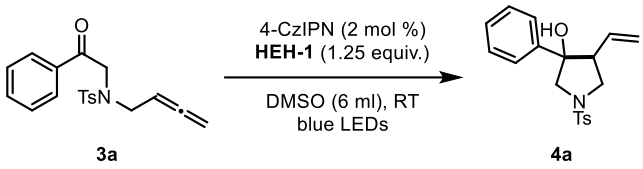
Quantum yield measurements

Determination of the light intensity of the blue LEDs

The photon flux of blue LEDs was determined by standard ferrioxalate actinometry.[11]

$$photo\ flux\ (Einstein \cdot s\text{-}1) = 1.03 \times 10^{-6}$$

Measurement of quantum yield:



3a **4a**

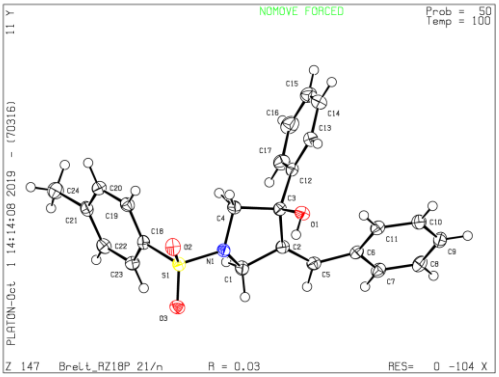
To an oven-dried Schlenk-tube equipped with magnetic stirring was charged with **3** (0.2 mmol), Hantzsch-ester **HEH-1** (63mg, 0.25 mmol, 1.25 equiv.) and 4-CzIPN (3.2 mg, 2 mol %). The Schlenk tube was put on vacuum and backfilled with argon three times. DMSO (6 mL) was added and The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 2.5 cm away from one 34 W blue LEDs and irradiated and stirred for 30 min at room temperature. Then poured into water (40 mL), The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (3 x 40 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure and residue was purified with column chromatography on silica gel afford the corresponding product after drying in vacuo. The product (**4a**) was obtained with 17.8 mg (52.0 μmol). The quantum yield calculation is then as following:

$$\Phi = \frac{\text{moles of produt}}{\text{moles of absorbed photons}} = \frac{\text{moles of produt}}{\text{flux} \cdot \text{t} \cdot \text{f}}$$

Where flux is the photon flux determined by ferrioxalate actinometry (1.03 × 10–6 Einstein/s), t is the time (1800 s), and f is the fraction of light absorbed by 4-CzIPN at 450 nm. A 1 × 10^{-3} M solution of [**PC1**] in DMSO was prepared, and the absorbance of the solutionat 450 nm was 2.080. The fraction of light absorbed at 450 nm was calculated: f = 1.0000 – 10^{-A} = 1.0000 –$10^{-2.080}$ = 0.99.

$$\Phi = \frac{\text{moles of produt}}{\text{moles of absorbed photons}} = \frac{\text{moles of produt}}{\text{flux} \cdot \text{t} \cdot \text{f}} = \frac{52.0 \times 10^{-5}}{1.03 \times 10^{-6} \cdot 1800 \cdot 0.99} = 0.28$$

X-Ray crystal structure of 2l



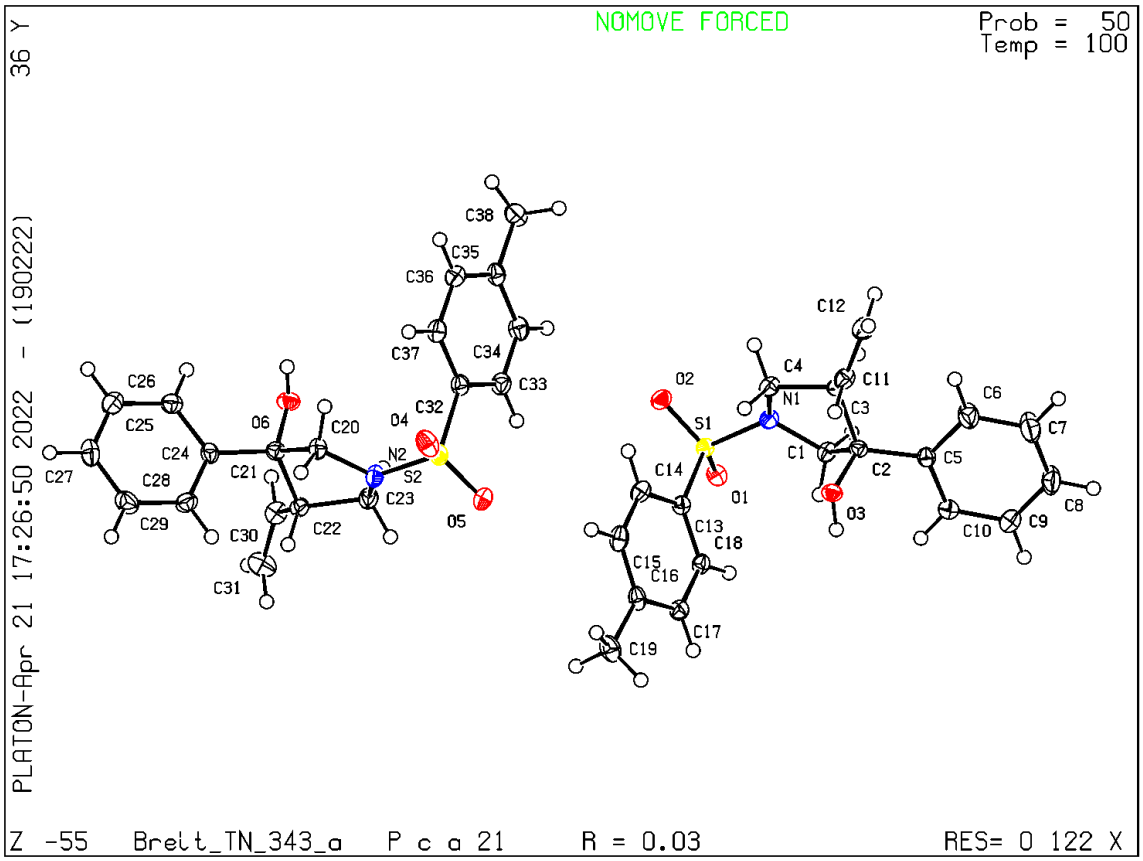
The compund was crystallized from DCM/pentane by solvent layering The data for Breit_RZ188FA_a-finalcif.cif were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used CuK_α radiation, λ = 1.54184 Å. All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 was applied. The structure were solved by direct methods using SHELXT 2014/5 (Sheldrick, 2014) and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1957120 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S3. Crystal data and structure refinement for Breit_RZ188FA_a-finalcif.cif

CCDC number	1957120
Empirical formula	$C_{24}H_{23}NO_3S$
Formula weight	405.49
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	14.9992(11)
b [Å]	6.4237(5)
c [Å]	21.1674(18)
α [Å]	90
β [Å]	95.605(4)
γ [Å]	90
Volume [Å^3]	2029.7(3)
Z	4

ρ_{calc} [g/cm^3]	1.327
μ [mm^{-1}]	1.621
F(000)	856
Crystal size [mm^3]	0.150×0.050×0.030
Crystal colour	colourless
Crystal shape	needle
Radiation	CuK_α (λ=1.54184)
2Θ range [°]	6.92 to 144.98
Index ranges	-18 ≤ h ≤ 18
	-7 ≤ k ≤ 7
	-25 ≤ l ≤ 26
Reflections collected	117377
Independent reflections	4007
	R_{int} = 0.0465
	R_{sigma} = 0.0104
Completeness to θ = 67.684°	100.00
Data / Restraints / Parameters	4007/0/266
Goodness-of-fit on F^2	1.036
Final R indexes	R_1 = 0.0295
[I≥2σ(I)]	wR_2 = 0.0778
Final R indexes	R_1 = 0.0326
[all data]	wR_2 = 0.0802
Largest peak/hole [eÅ^3]	0.41/-0.42
Extinction coefficient	0.00052(11)

X-Ray crystal structure of 4a-1



Crystals were obtained at room temperature by slow diffusion of pentane into a solution of the compound dissolved in dichloromethane by the aid of layering. The data for Breit_TN_343_a were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[20,21] The structure were solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3.[22,23] All non-hydrogen atoms were refined with an isotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[24] CCDC 2167993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[25]

Table S4. Crystal data and structure refinement for Breit_TN_343_a

CCDC number	2167993
Empirical formula	$C_{19}H_{21}NO_3S$
Formula weight	343.43
Temperature [K]	100(2)
Crystal system	orthorhombic
Space group (number)	$Pca2_1$ (29)
a [Å]	20.050(4)
b [Å]	16.600(3)
c [Å]	10.280(2)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	3421.4(11)
Z	8
ρ_{calc} [gcm^{-3}]	1.333
μ [mm^{-1}]	0.206
F(000)	1456
Crystal size [mm^3]	0.338×0.301×0.054
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2Θ range [°]	3.19 to 61.10 (0.70 Å)
Index ranges	-28 ≤ h ≤ 28
	-23 ≤ k ≤ 23

	-14 ≤ l ≤ 14
Reflections collected	228692
Independent reflections	10470
	R_{int} = 0.0627
	R_{sigma} = 0.0199
Completeness to	100.0 %
Θ = 25.242°	
Data / Restraints /	10470/1/439
Parameters	
Goodness-of-fit on F^2	1.046
Final *R* indexes	R_1 = 0.0342
[I≥2σ(I)]	wR_2 = 0.0860
Final *R* indexes	R_1 = 0.0378
[all data]	wR_2 = 0.0889
Largest peak/hole	0.45/-0.28
[eÅ^{-3}]	
Flack X parameter	0.297(11)

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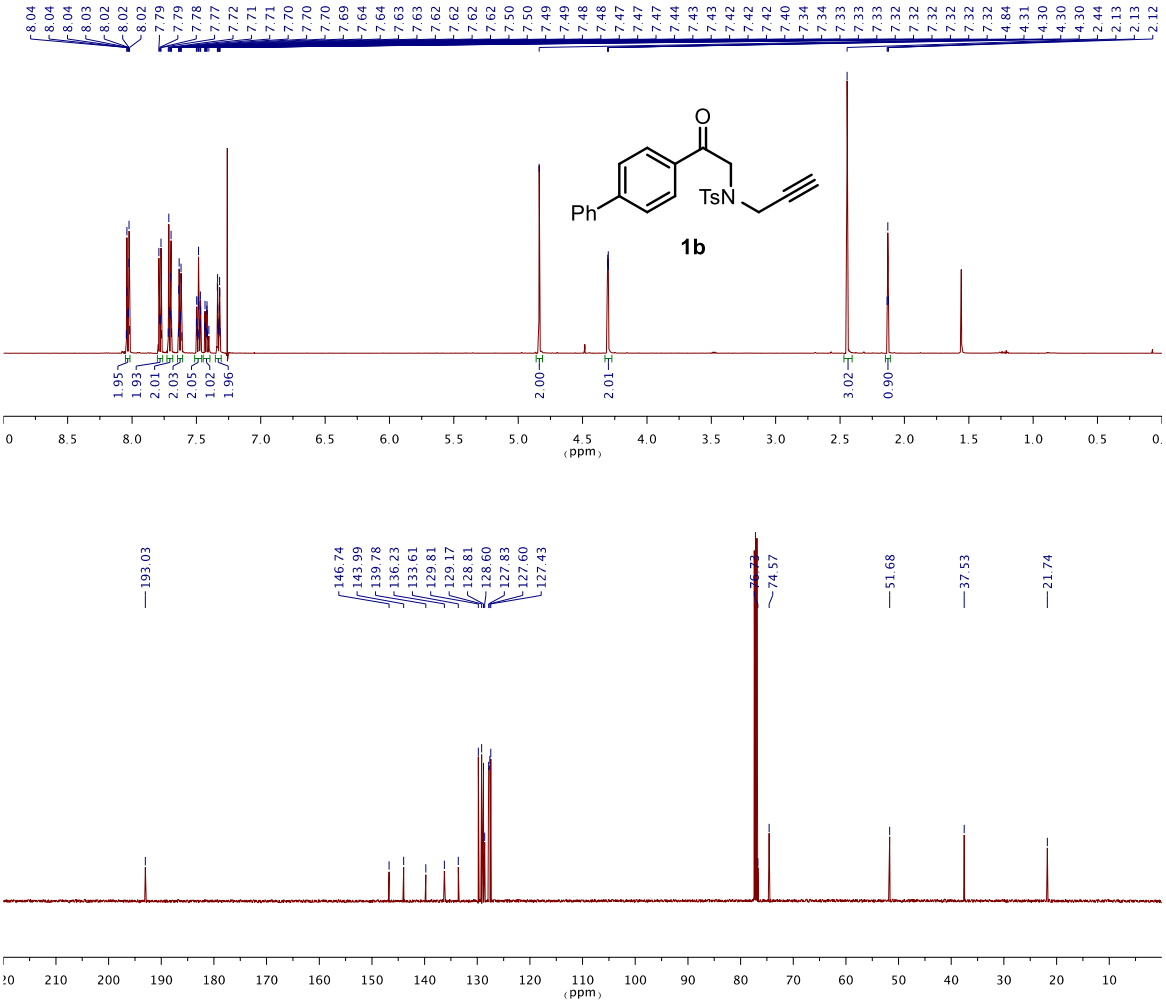
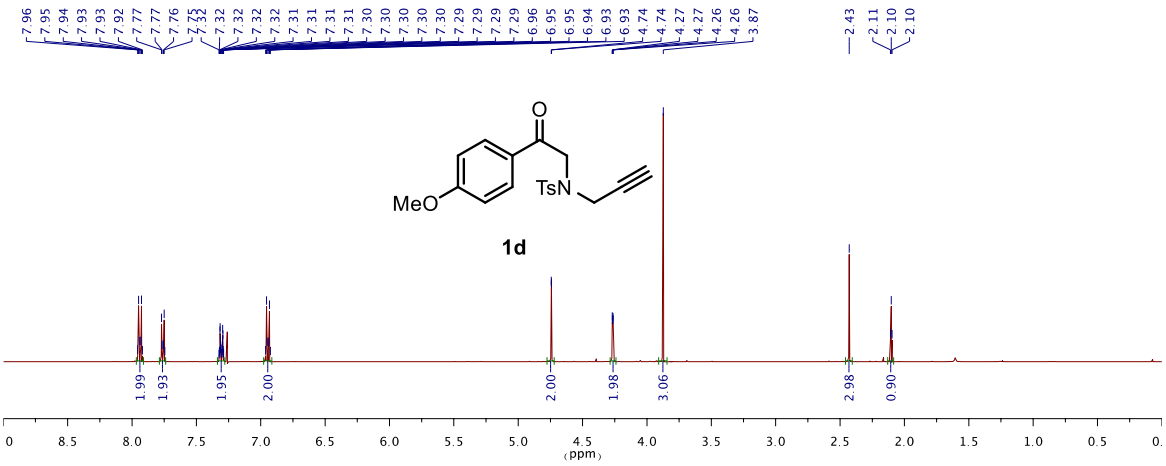
^{1}H, ^{13}C, ^{19}F NMR spectra

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7.93
7.93
7.92
7.77
7.77
7.76
7.75
7.32
7.32
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7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.30
7.29
7.29
7.29
7.29
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6.95
6.95
6.94
6.93
6.93
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4.74
4.27
4.27
4.26
4.26
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2.11
2.10
2.10
O
MeO
TsN
1d
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1.93
1.95
2.00
2.00
1.98
3.06
2.98
0.90
0
8.5
8.0
7.5
7.0
6.5
6.0
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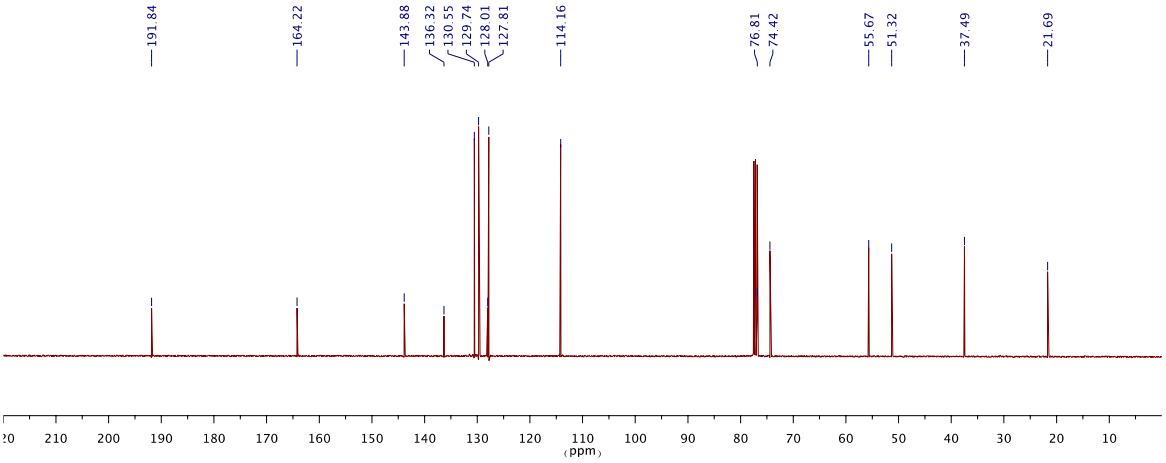
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74.42
55.67
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37.49
21.69
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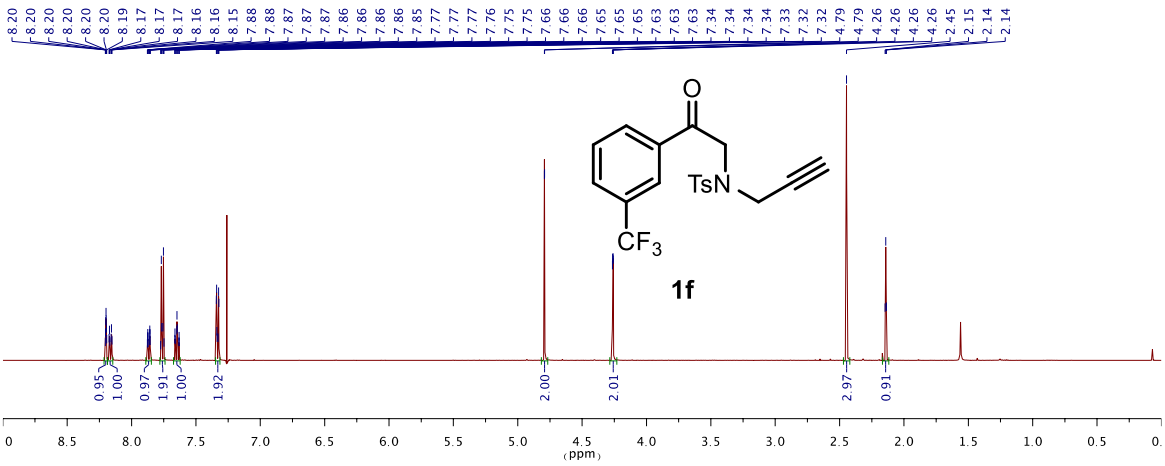
40
30
20
10
ppm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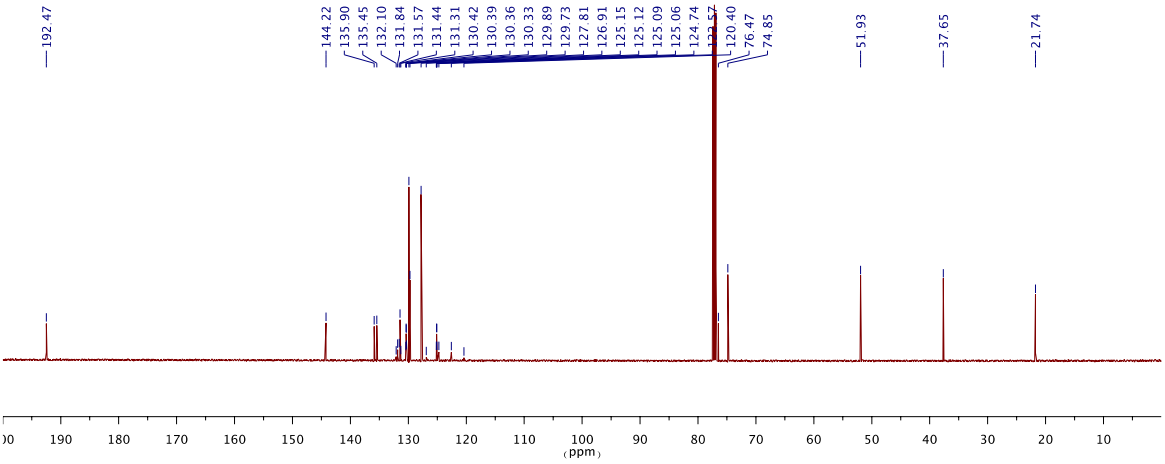
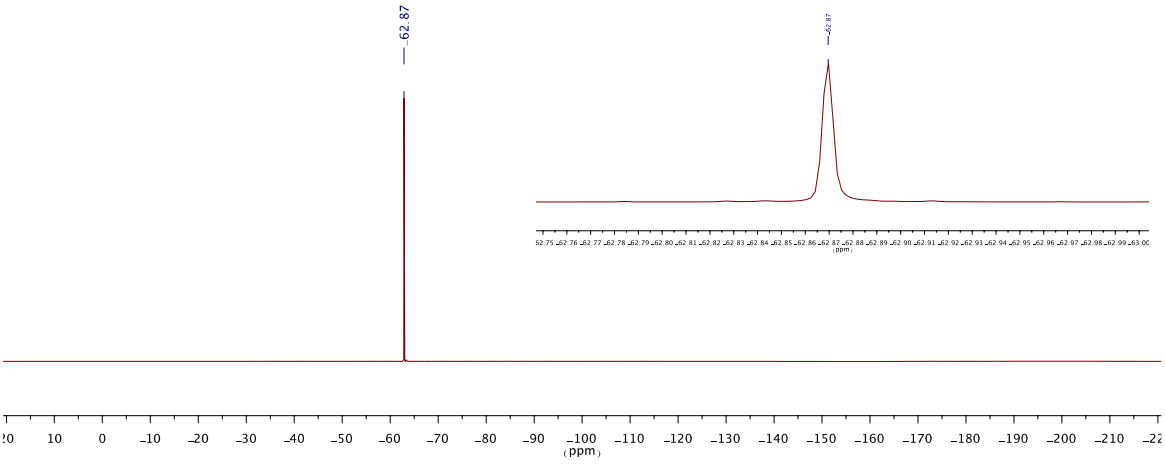
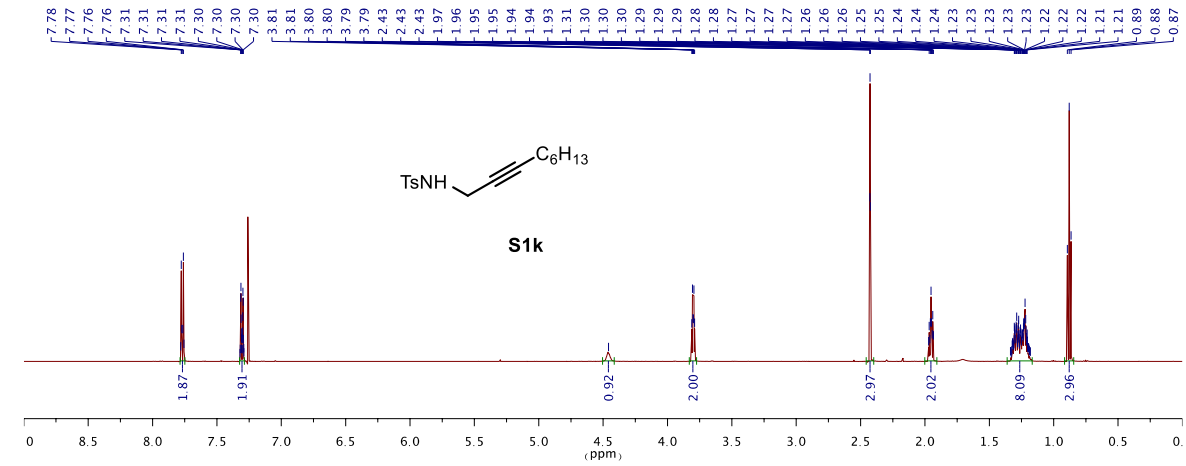
CF3
1f



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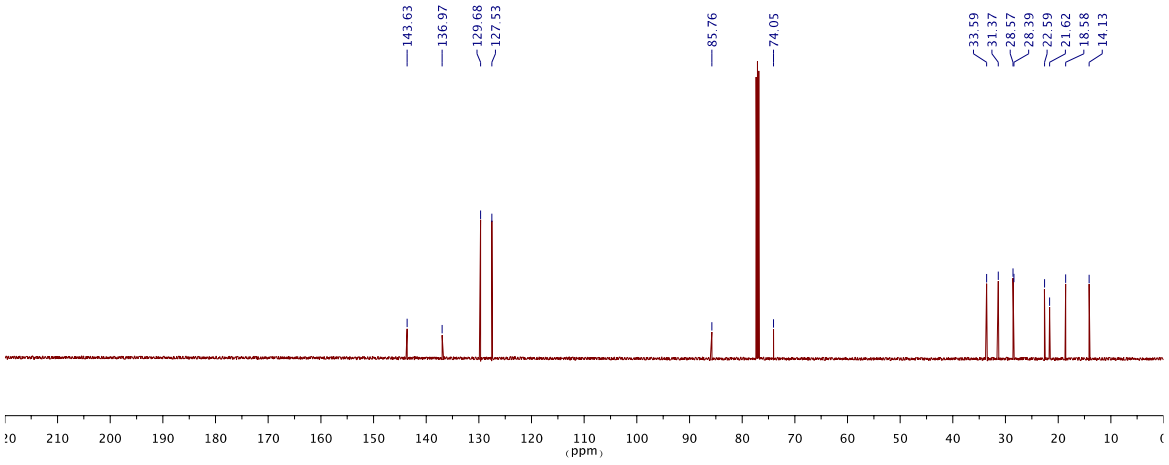
3.81 3.81 3.80 3.80 3.79 3.79 2.43 2.43 2.43 1.97 1.96 1.95 1.95 1.94 1.94 1.93 1.31 1.30 1.30 1.30 1.29 1.29 1.29 1.28 1.28 1.27 1.27 1.27 1.27 1.26 1.26 1.26 1.25 1.25 1.24 1.24 1.24 1.23 1.23 1.23 1.23 1.23 1.22 1.22 1.22 1.21 1.21 0.89 0.88 0.87
TsNH
C6H13
S1k
1.87
1.91
0.92
2.00
2.97
2.02
8.09
2.96
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
(ppm)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18.58
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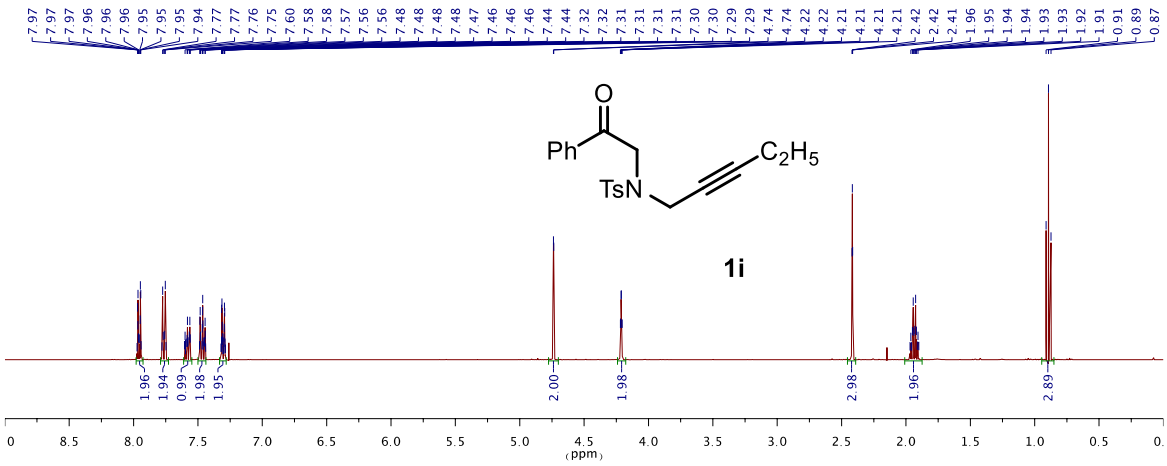
(ppm)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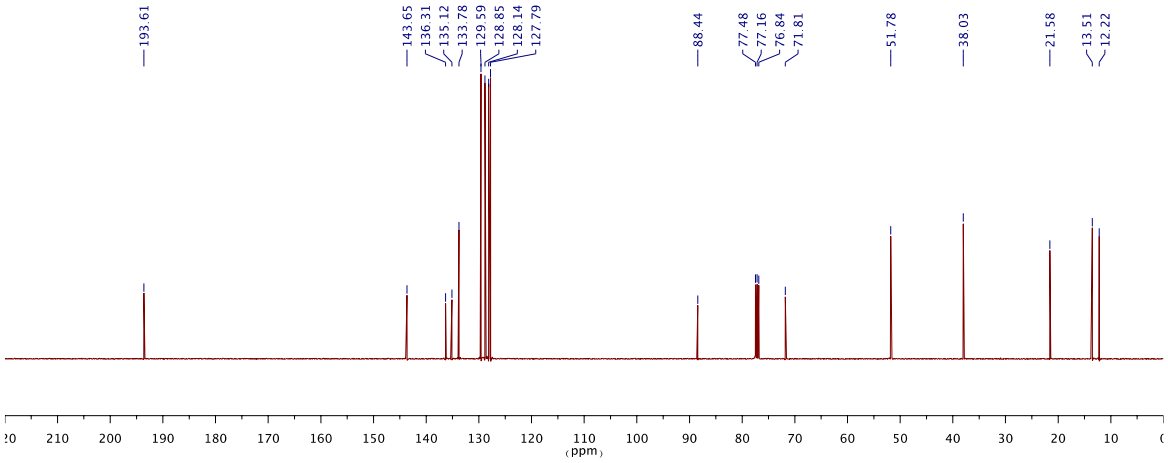
O
Ph
TsN
C2H5
1i
1.96 1.94 0.99 1.98 1.95 2.00 1.98 2.98 1.96 2.89
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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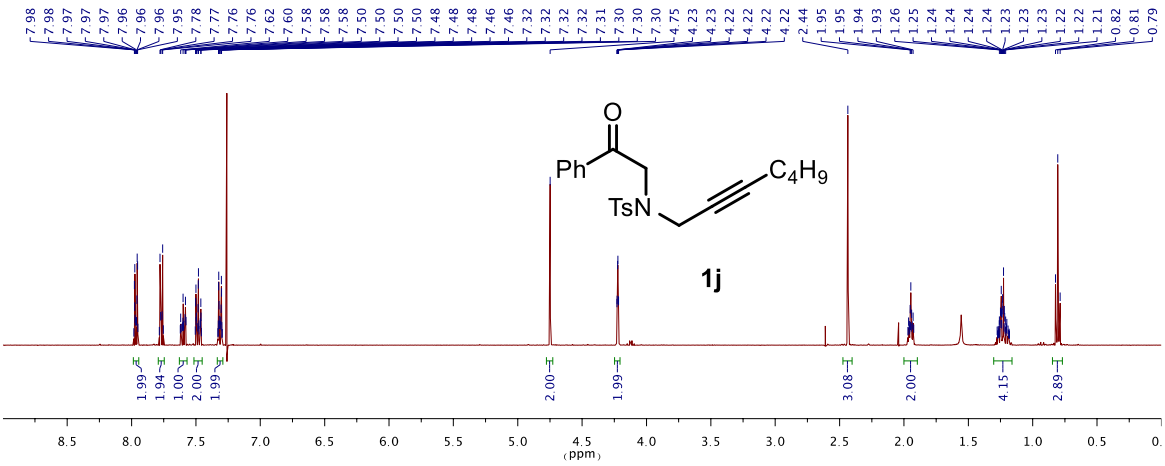
88.44
77.48 77.16 76.84 71.81
51.78
38.03
21.58
13.51 12.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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O
Ph
TsN
C4H9
1j
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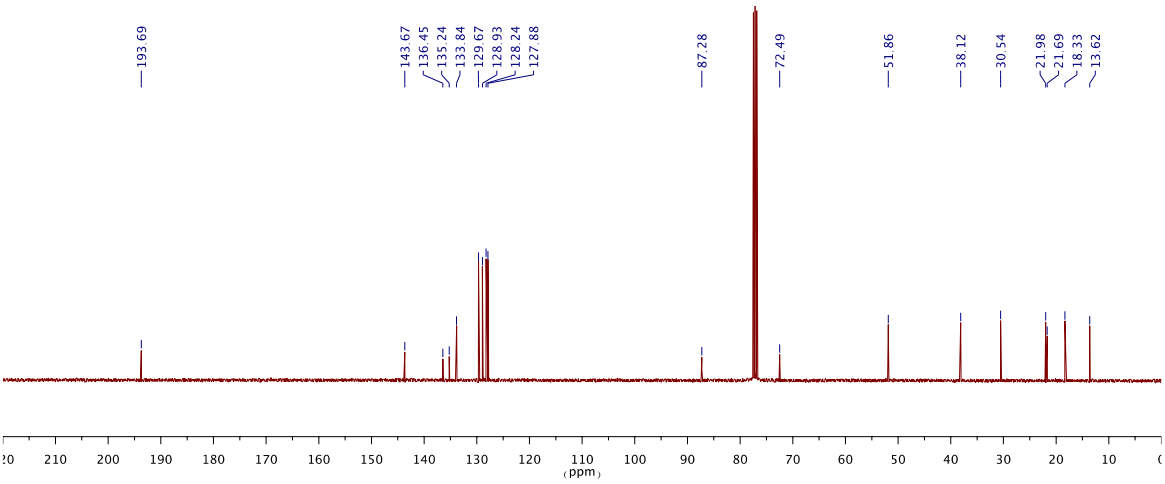
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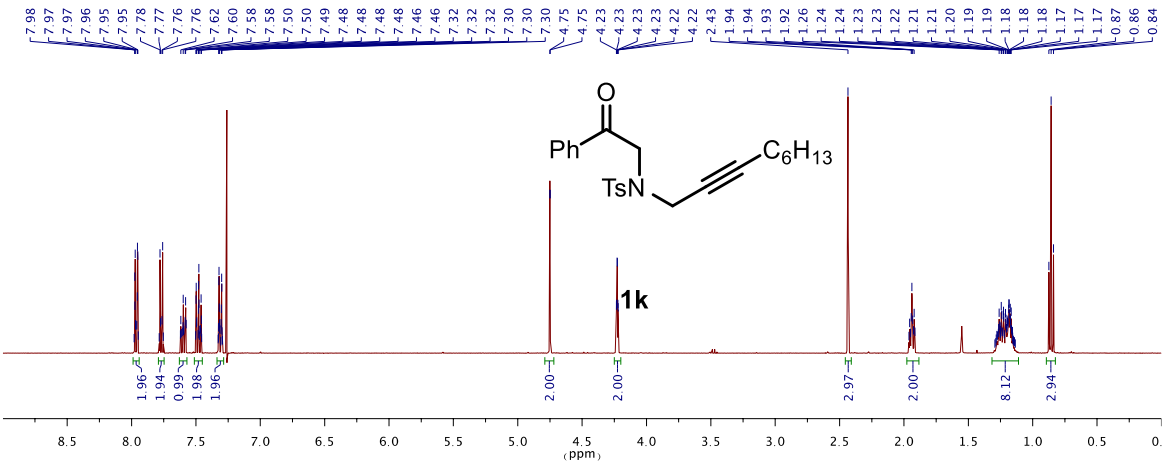
87.28
72.49
51.86
38.12
30.54
21.98 21.69 18.33 13.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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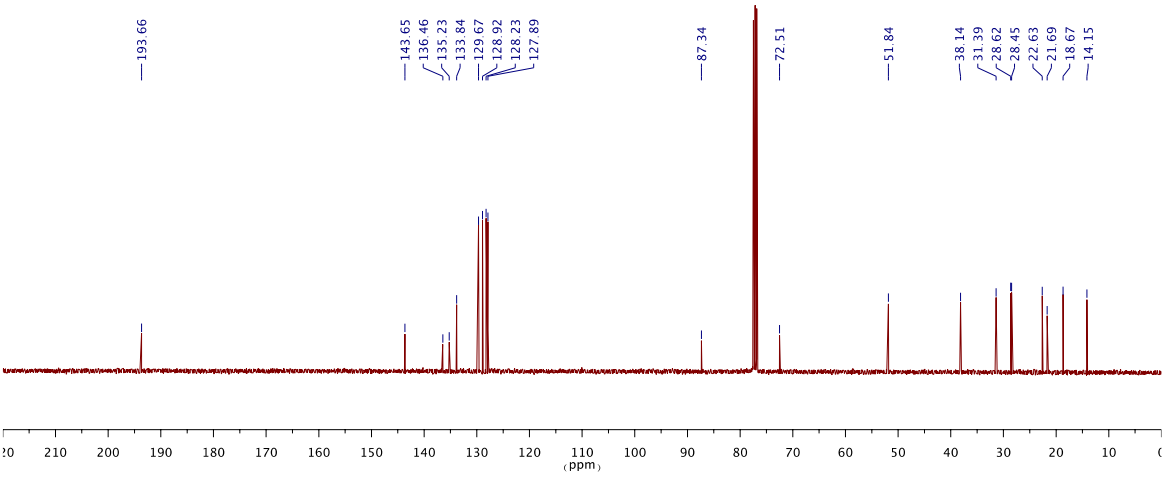
O
Ph
TsN
C6H13
1k
1.96 1.94 0.99 1.98 1.96 2.00 2.00 2.97 2.00 8.12 2.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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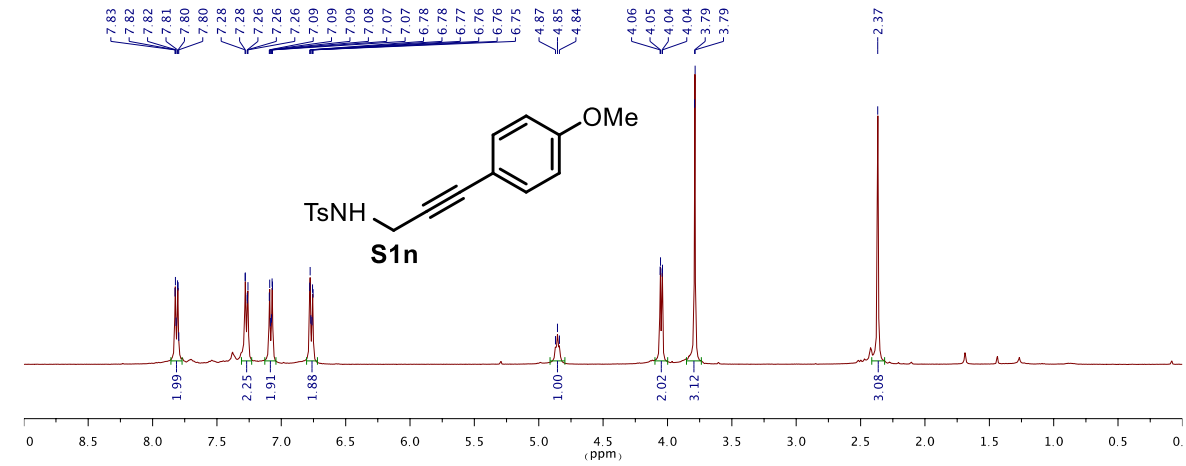
87.34 72.51 51.84 38.14 31.39 28.62 28.45 22.63 21.69 18.67 14.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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7.09
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7.08
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6.77
6.76
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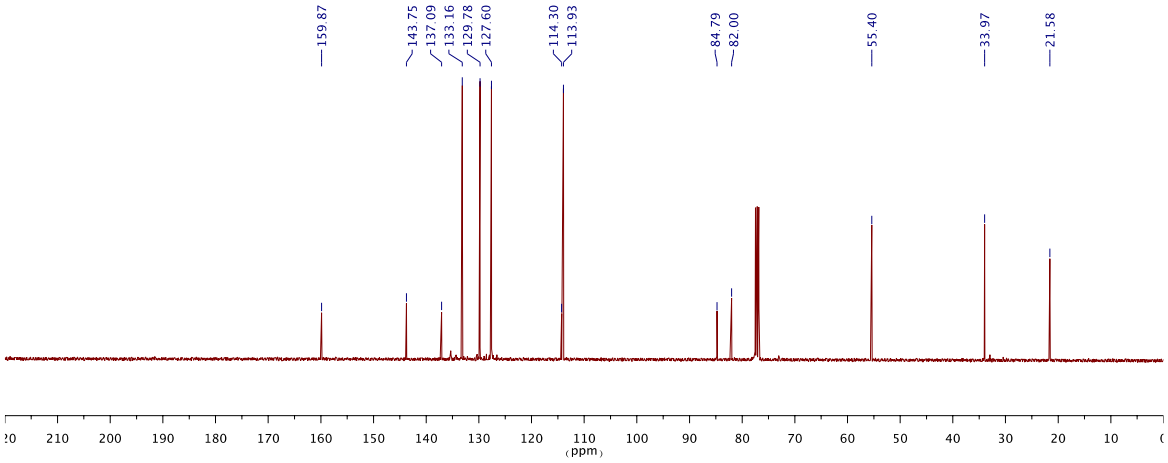
3.08
ppm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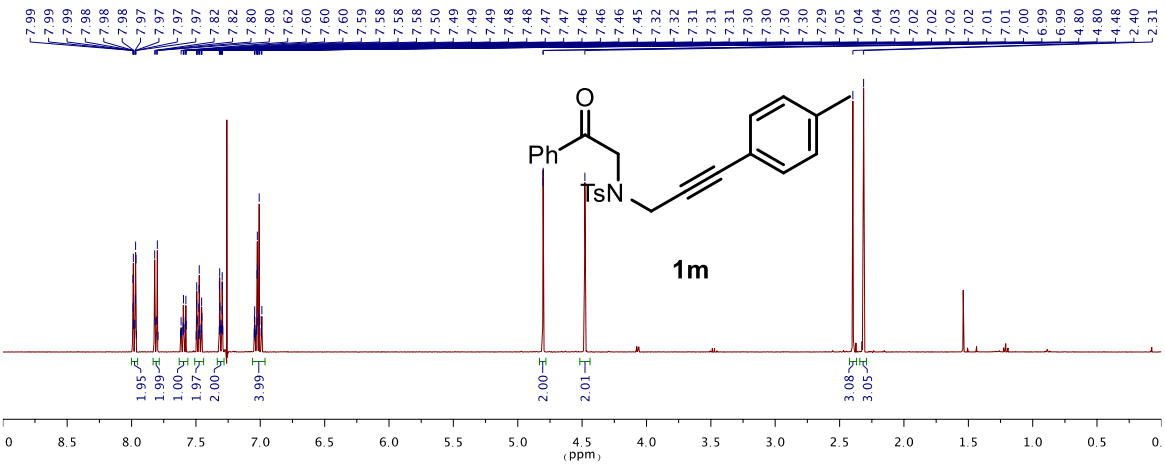
33.97
21.58
ppm


O
Ph
TsN
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2.00
2.01
3.08
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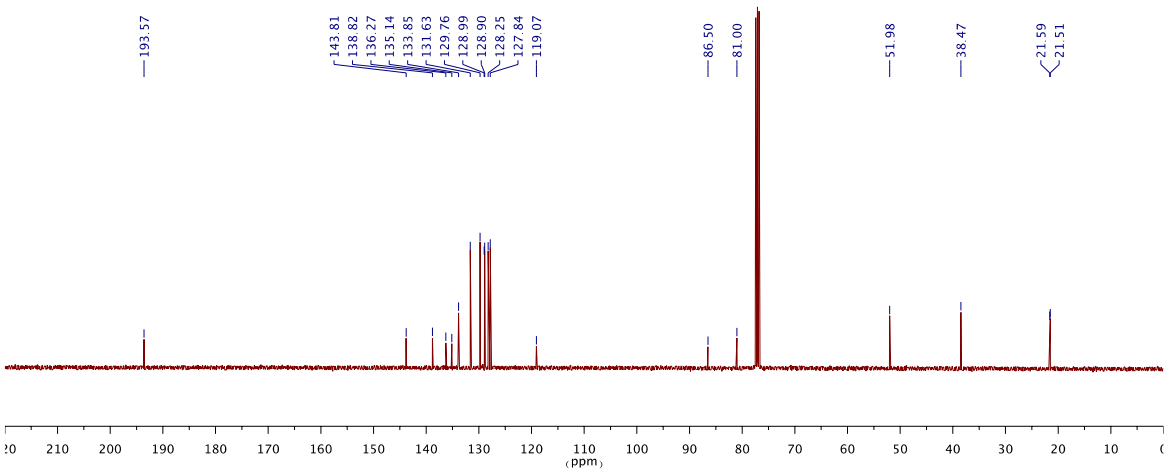
(ppm)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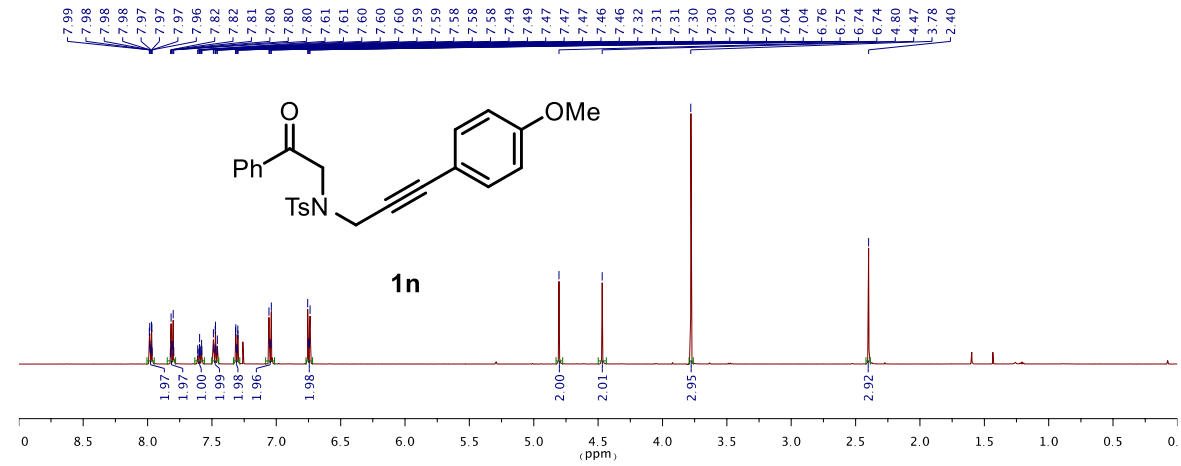
(ppm)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Ph
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OMe
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2.00
2.01
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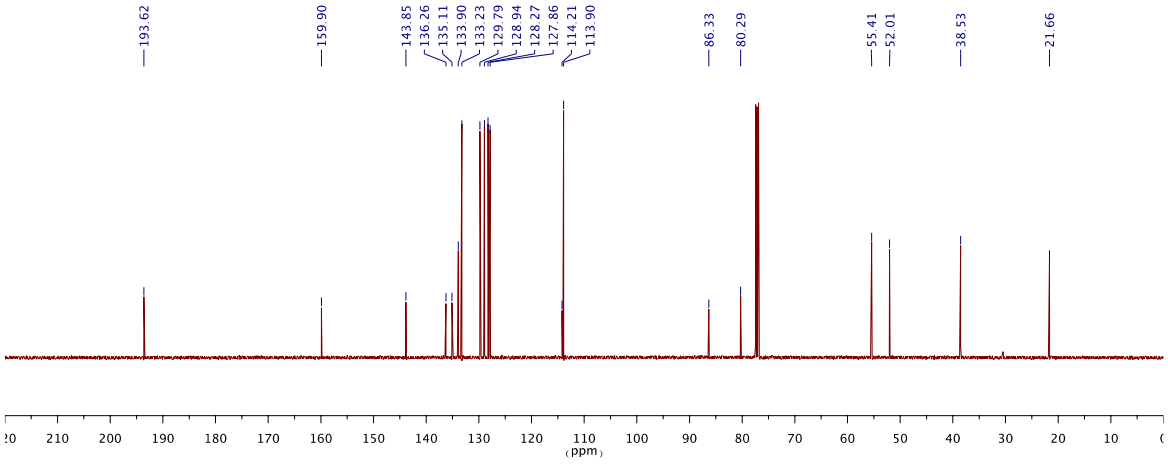
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52.01
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21.66
210
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60
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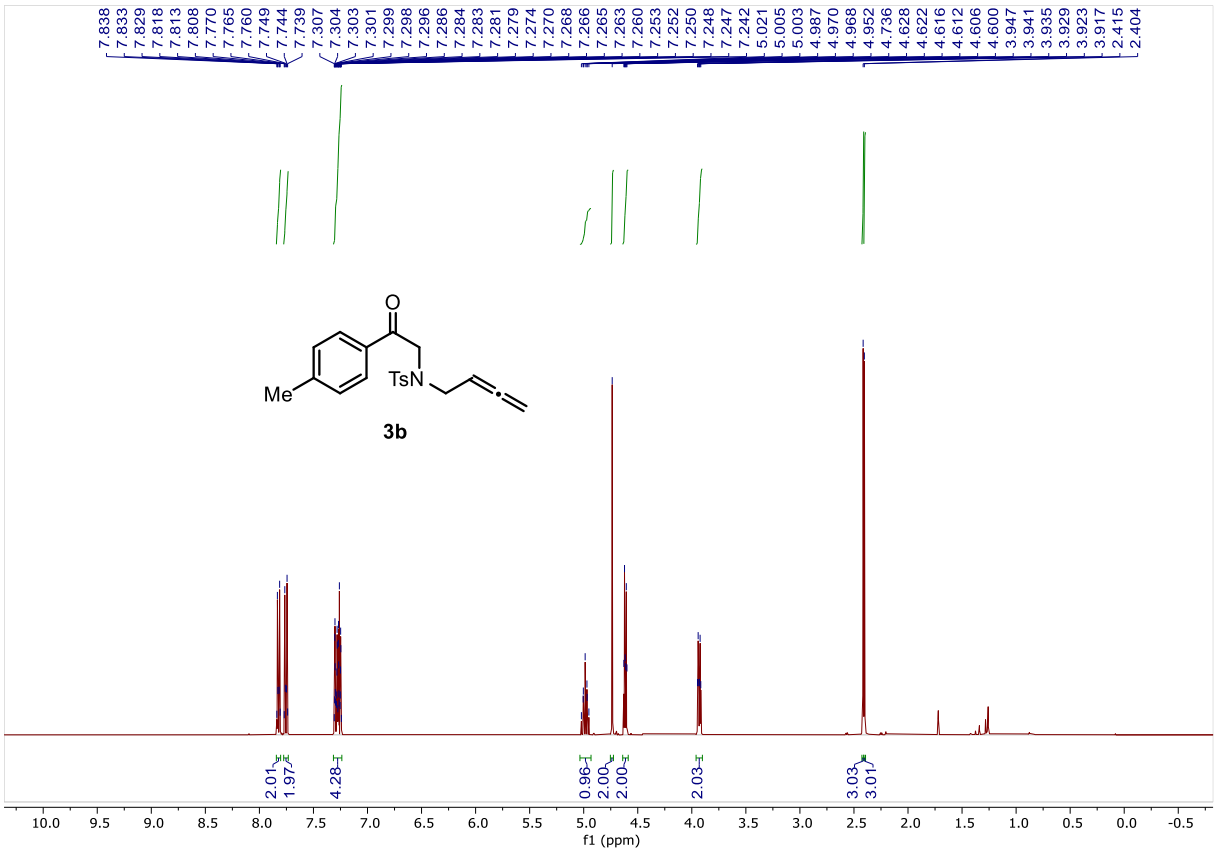
20
10
(ppm)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O
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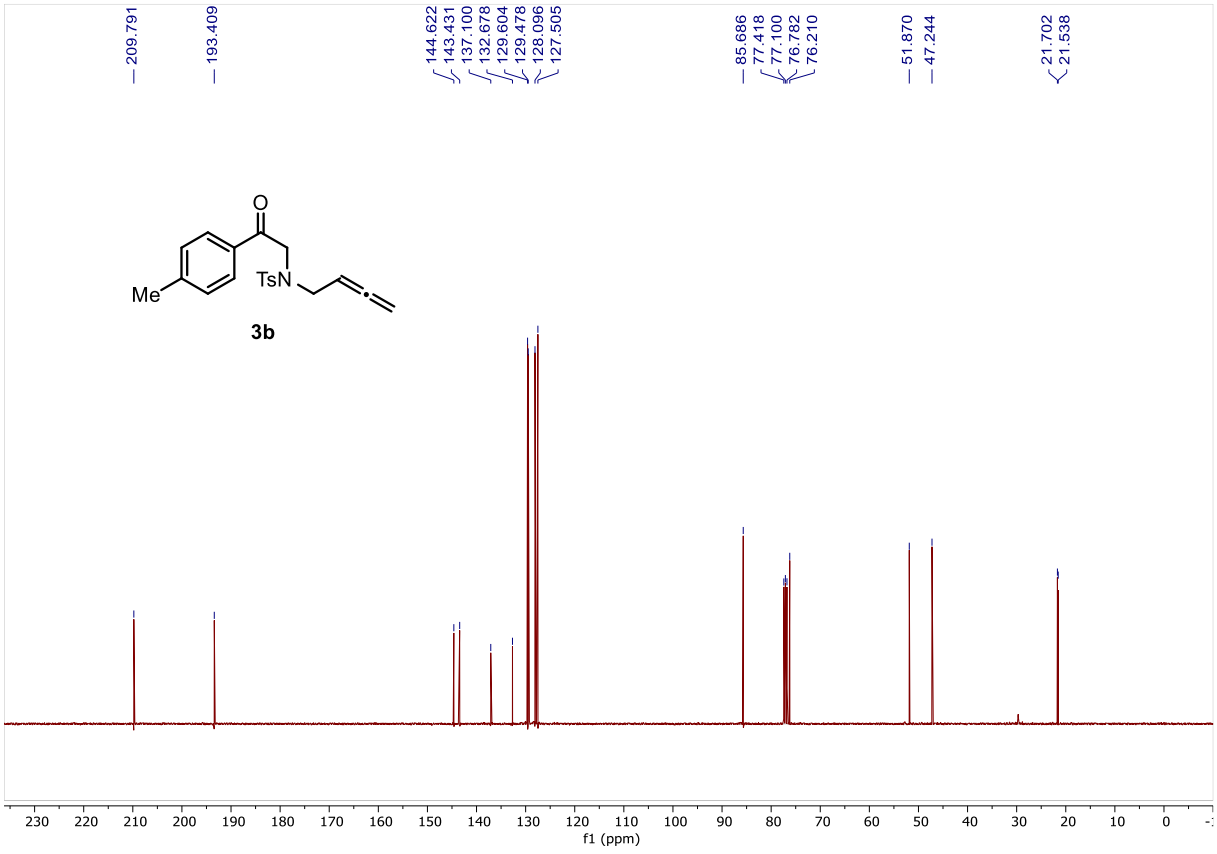
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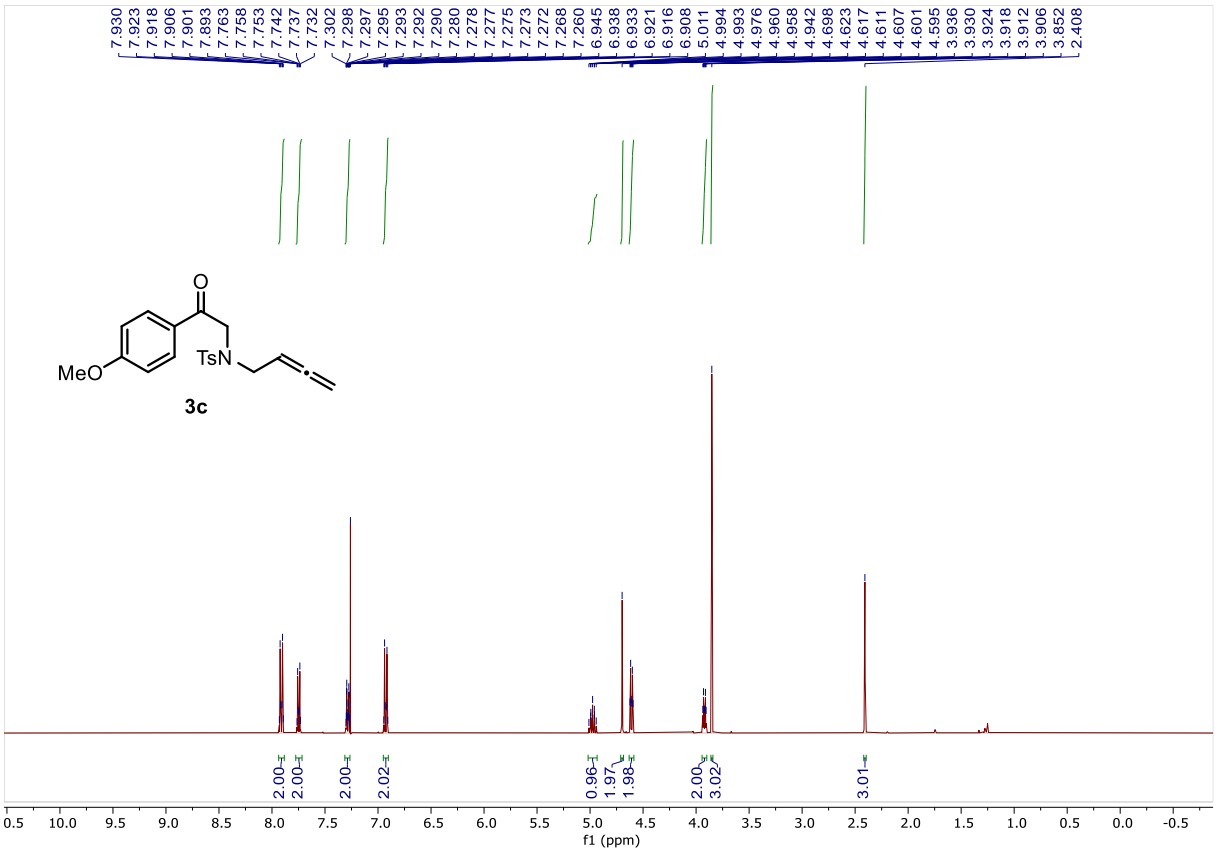
Me
3b
f1 (ppm)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4.623
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4.601
4.595
3.936
3.930
3.924
3.918
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3.906
3.852
2.408
O
TsN
MeO
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2.00
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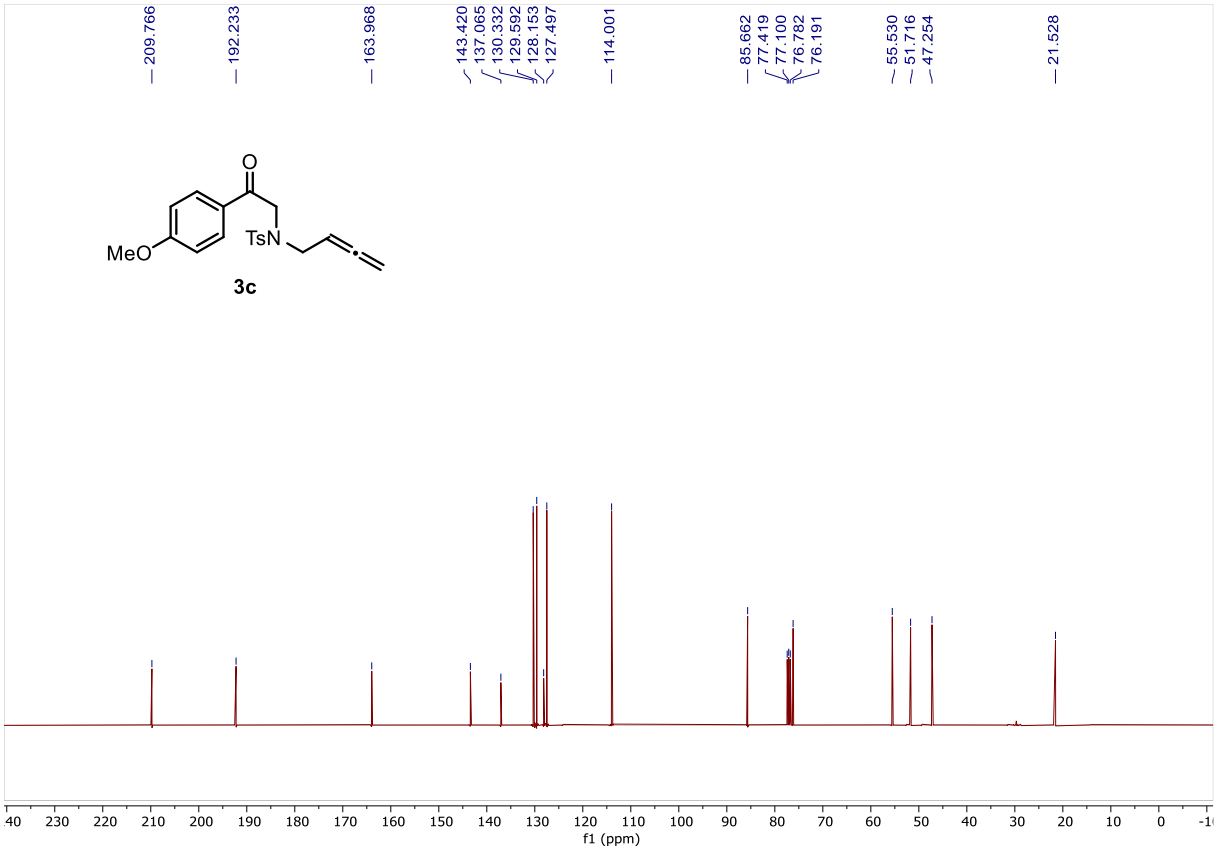
f1 (ppm)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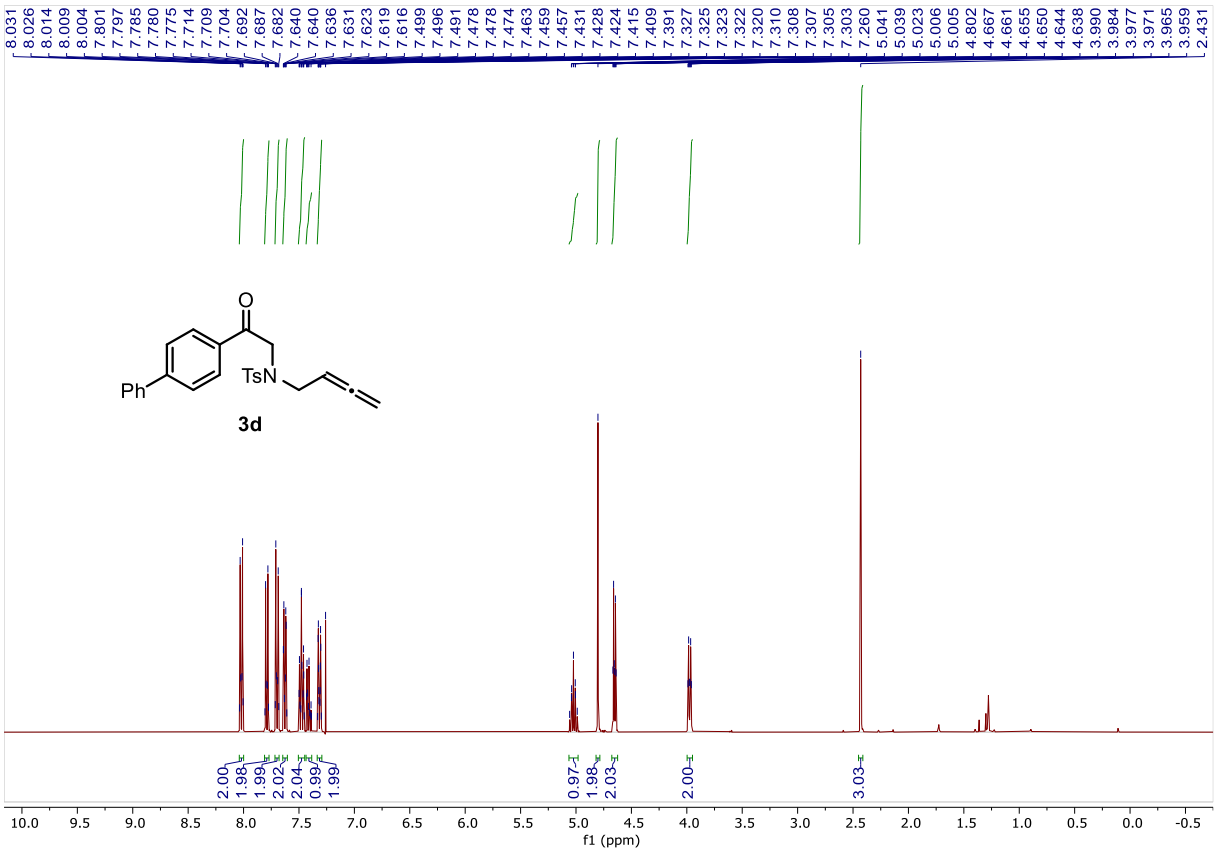
TsN
MeO
3c
f1 (ppm)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7.636
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7.616
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7.457
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7.303
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3.959
2.431
O
TsN
Ph
3d
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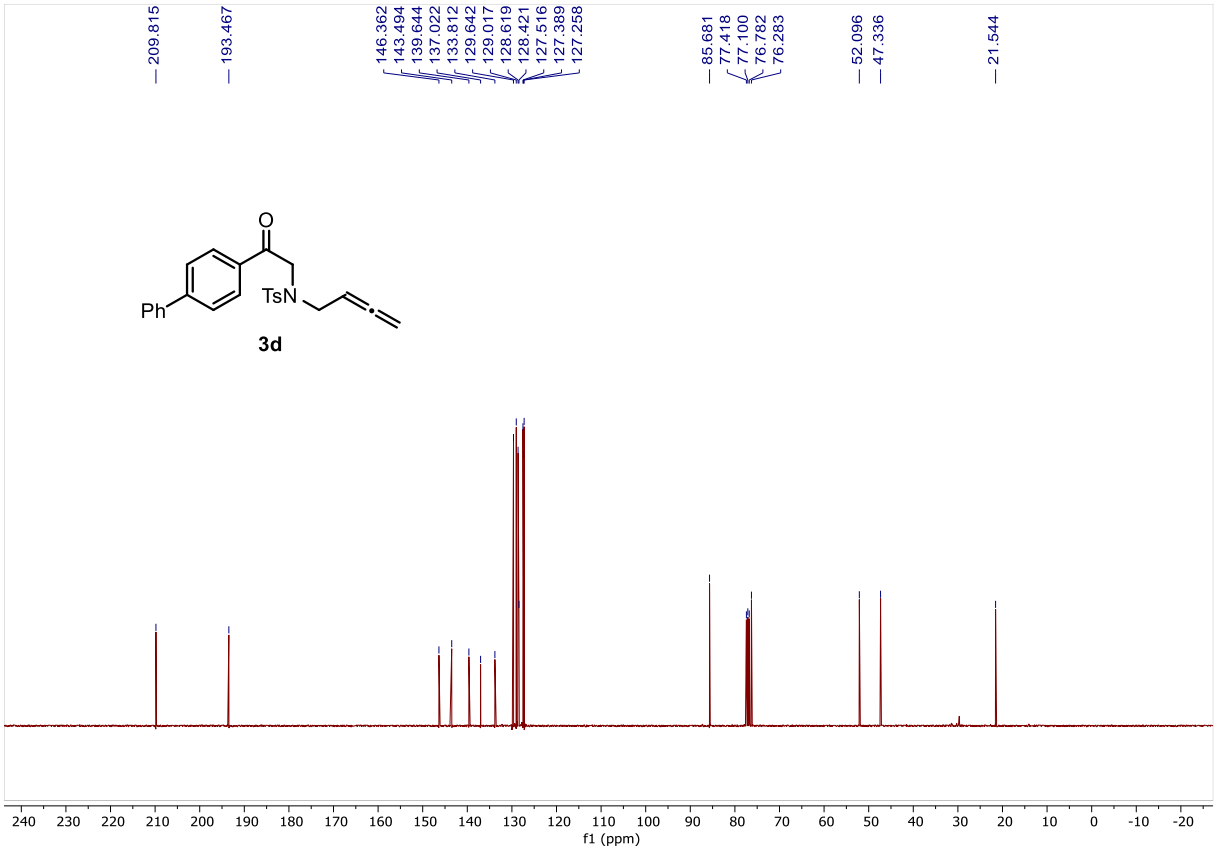
f1 (ppm)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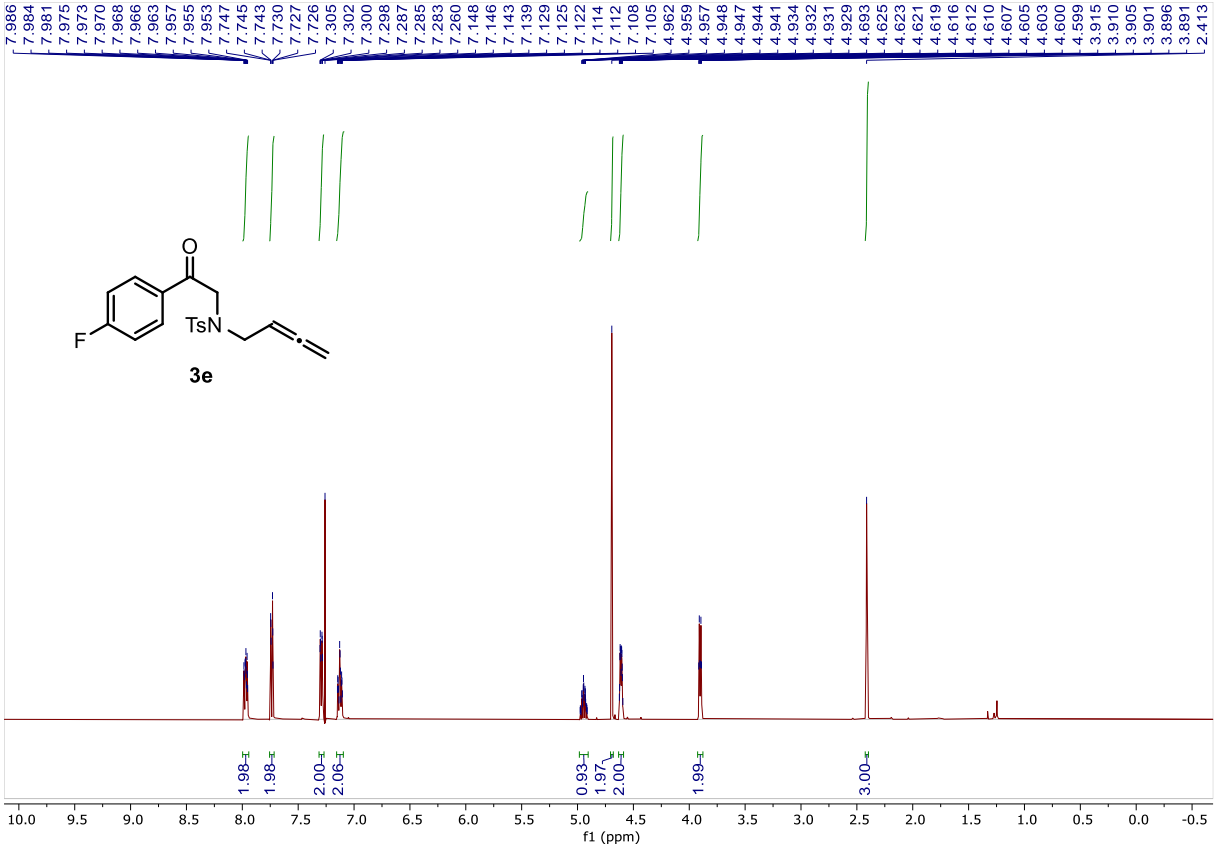
TsN
Ph
3d
f1 (ppm)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7.283
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7.108
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4.957
4.948
4.947
4.944
4.941
4.934
4.932
4.931
4.929
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4.625
4.623
4.621
4.619
4.616
4.612
4.610
4.607
4.605
4.603
4.600
4.599
3.915
3.910
3.905
3.901
3.896
3.891
2.413
O
TsN
F
3e
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1.98
2.00
2.06
0.93
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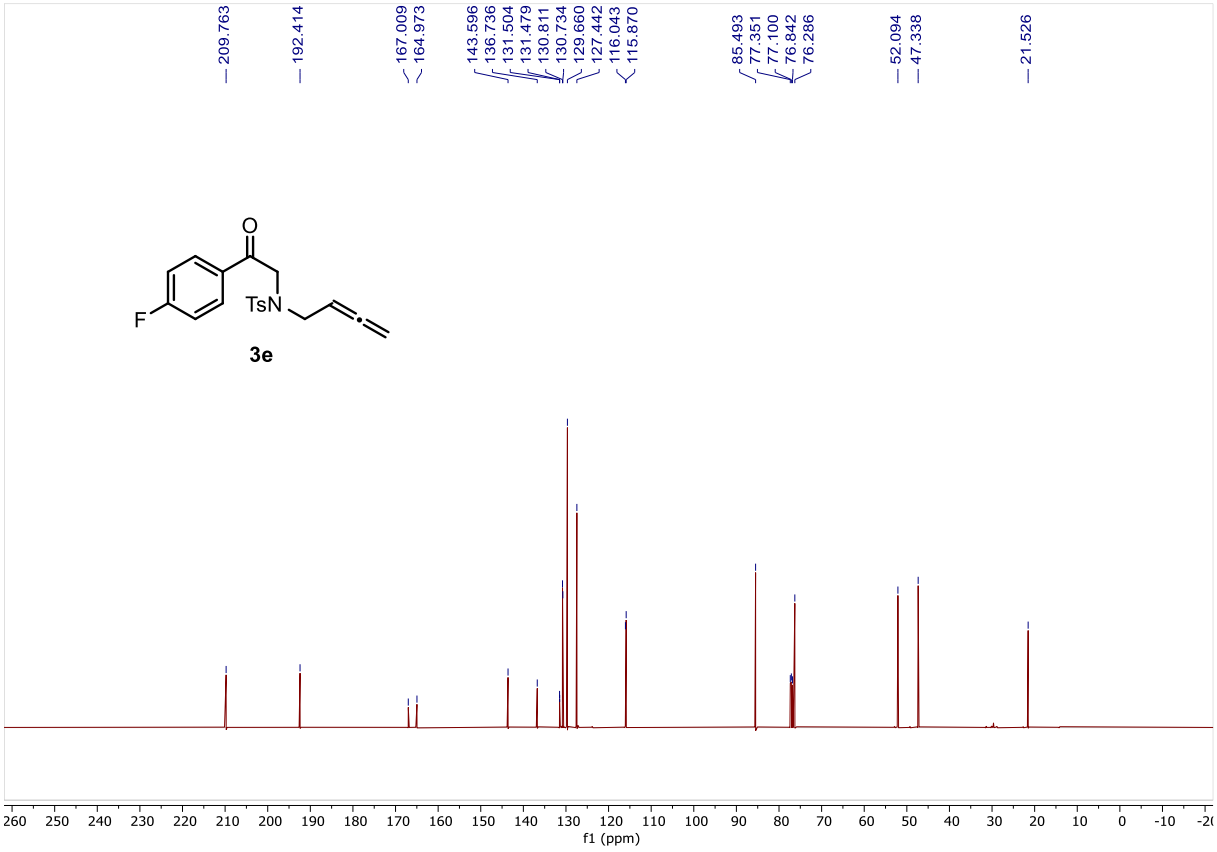
2.00
1.99
3.00
f1 (ppm)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116.043
115.870
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76.286
52.094
47.338
21.526
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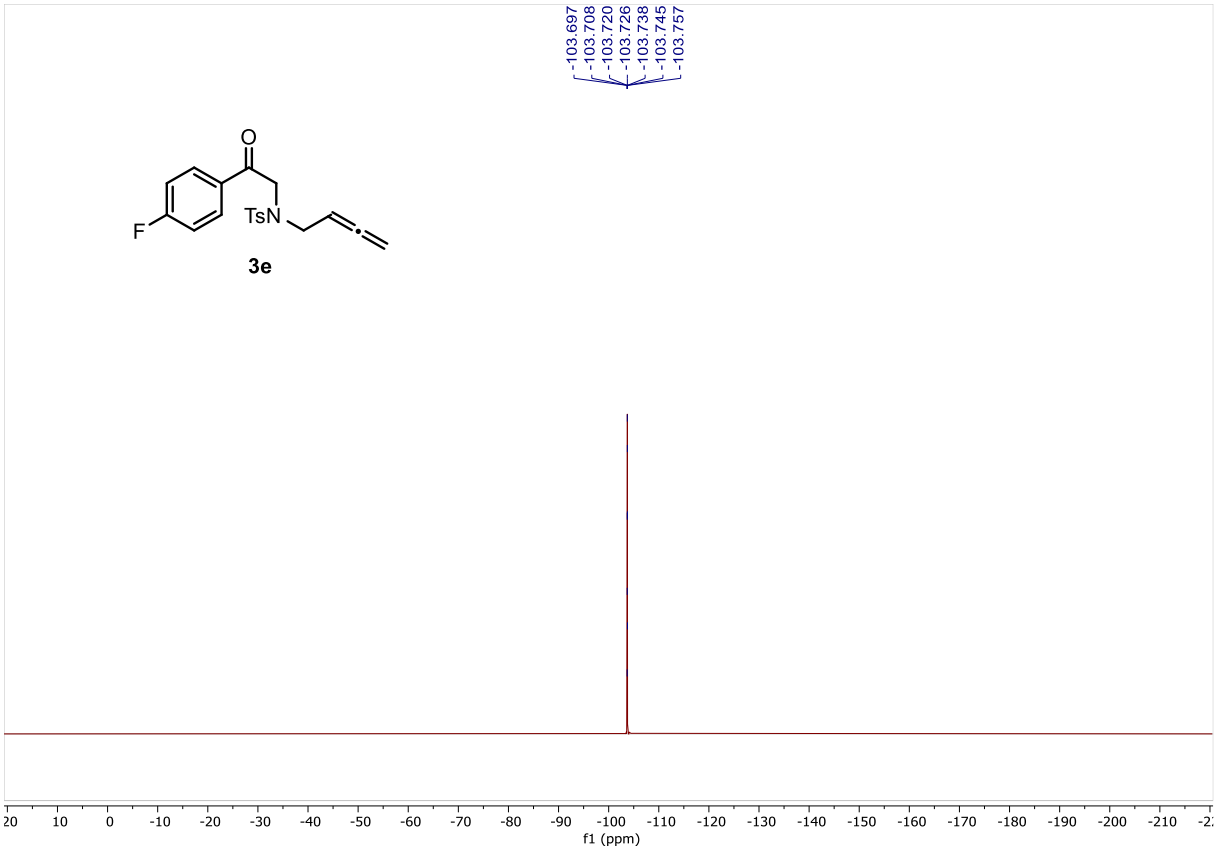
TsN
F
3e
f1 (ppm)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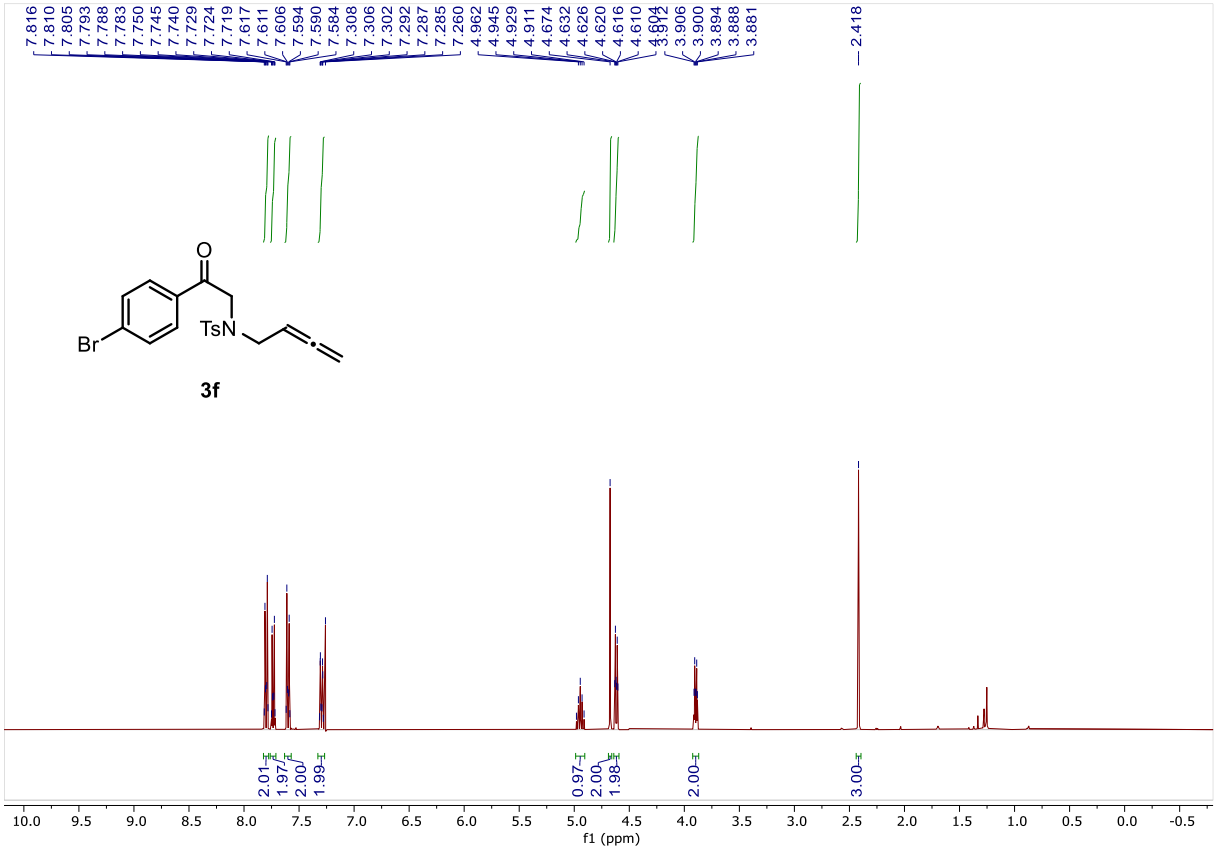
O
F
TsN
3e
f1 (ppm)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7.719
7.617
7.611
7.606
7.594
7.590
7.584
7.308
7.306
7.302
7.292
7.287
7.285
7.260
4.962
4.945
4.929
4.911
4.674
4.632
4.626
4.620
4.616
4.610
4.604
3.912
3.906
3.900
3.894
3.888
3.881
2.418
O
Br
TsN
3f
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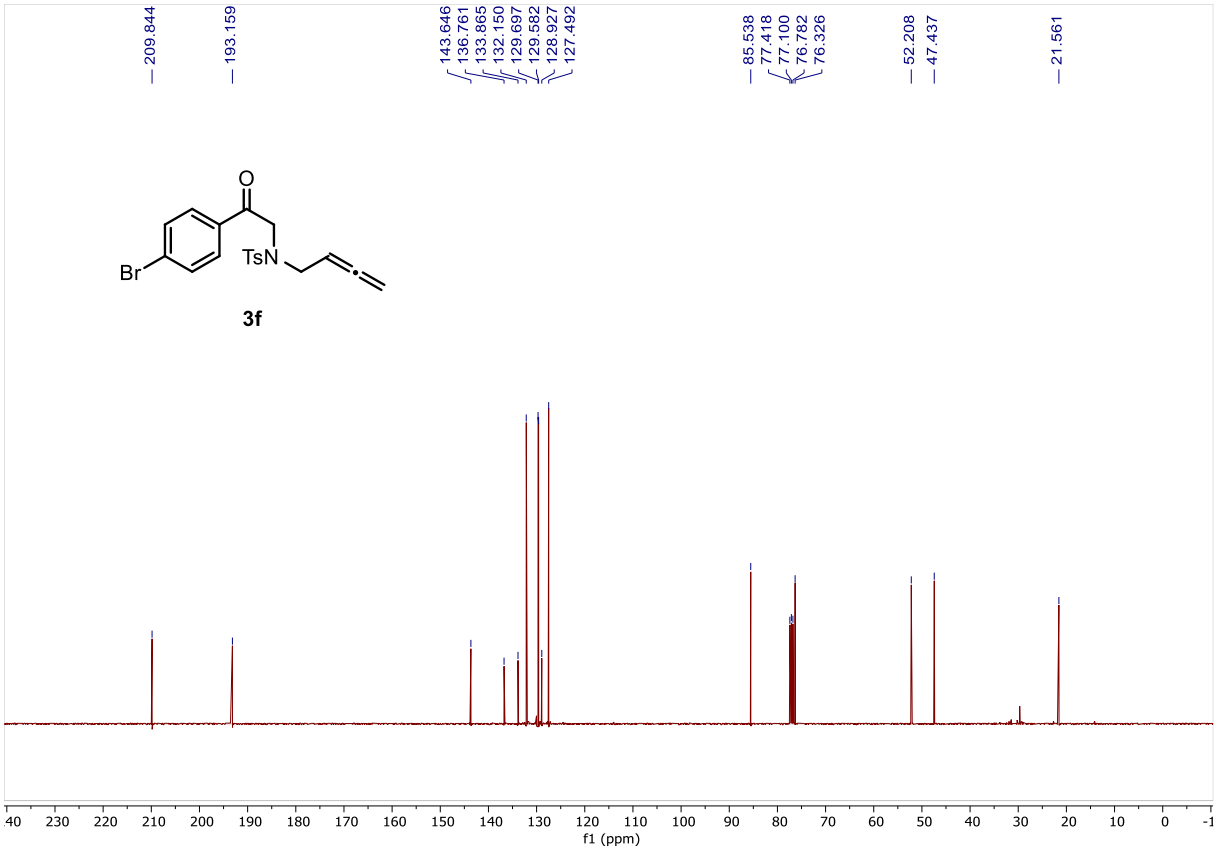
1.99
0.97
2.00
1.98
2.00
3.00
f1 (ppm)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76.782
76.326
52.208
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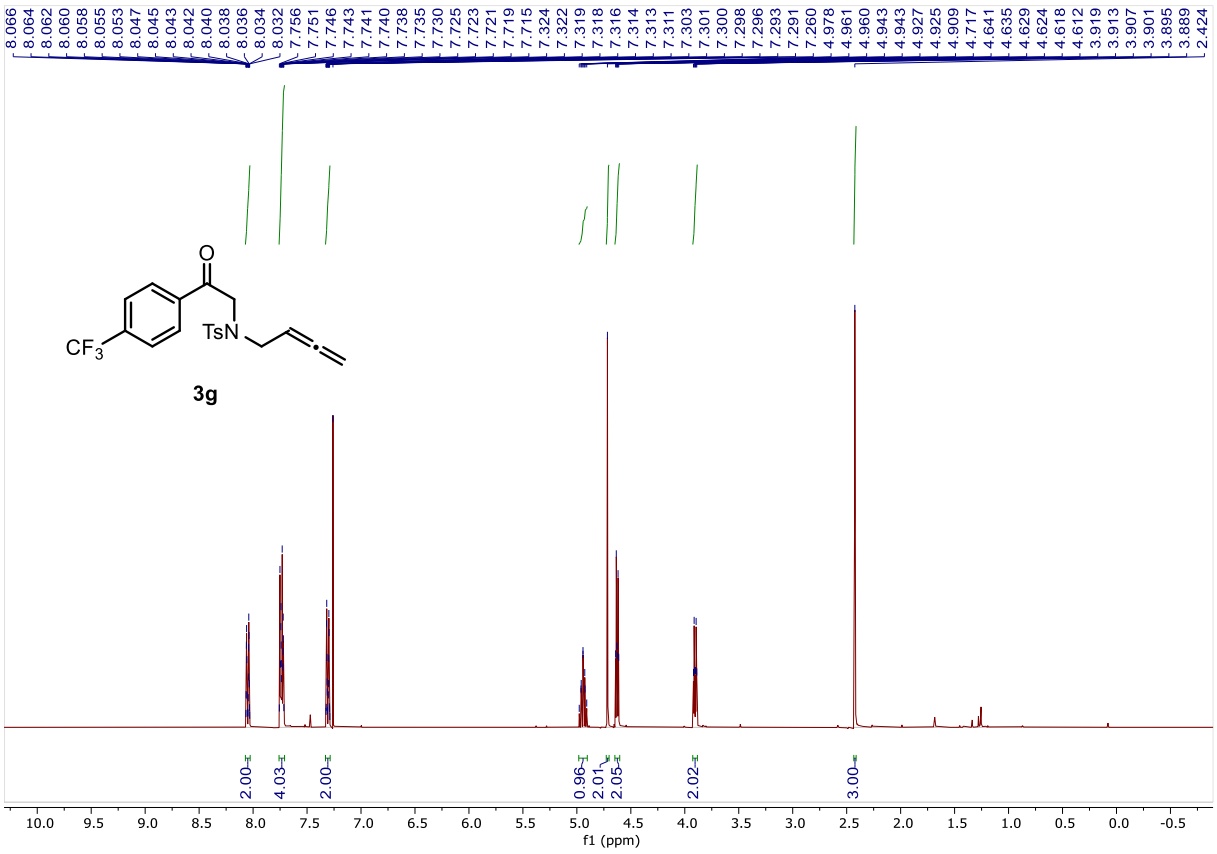
21.561
O
TsN
Br
f1 (ppm)

3f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7.740
7.738
7.735
7.730
7.725
7.723
7.721
7.719
7.715
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7.322
7.319
7.318
7.316
7.314
7.313
7.311
7.303
7.301
7.300
7.298
7.296
7.293
7.291
7.260
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4.961
4.960
4.943
4.943
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4.909
4.717
4.641
4.635
4.629
4.624
4.618
4.612
3.919
3.913
3.907
3.901
3.895
3.889
2.424
O
TsN
CF3
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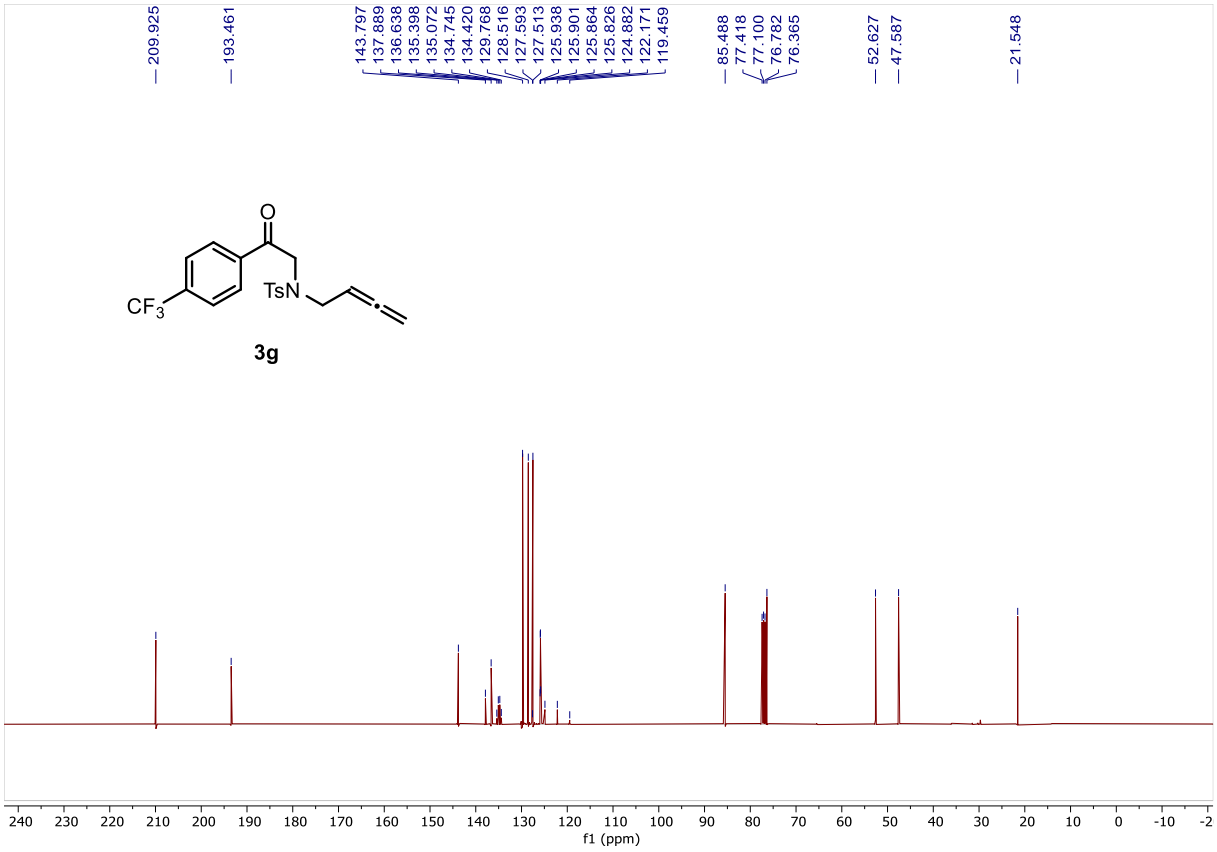
4.03
2.00
0.96
2.01
2.05
2.02
3.00
f1 (ppm)

3g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127.513
125.938
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125.864
125.826
124.882
122.171
119.459
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76.782
76.365
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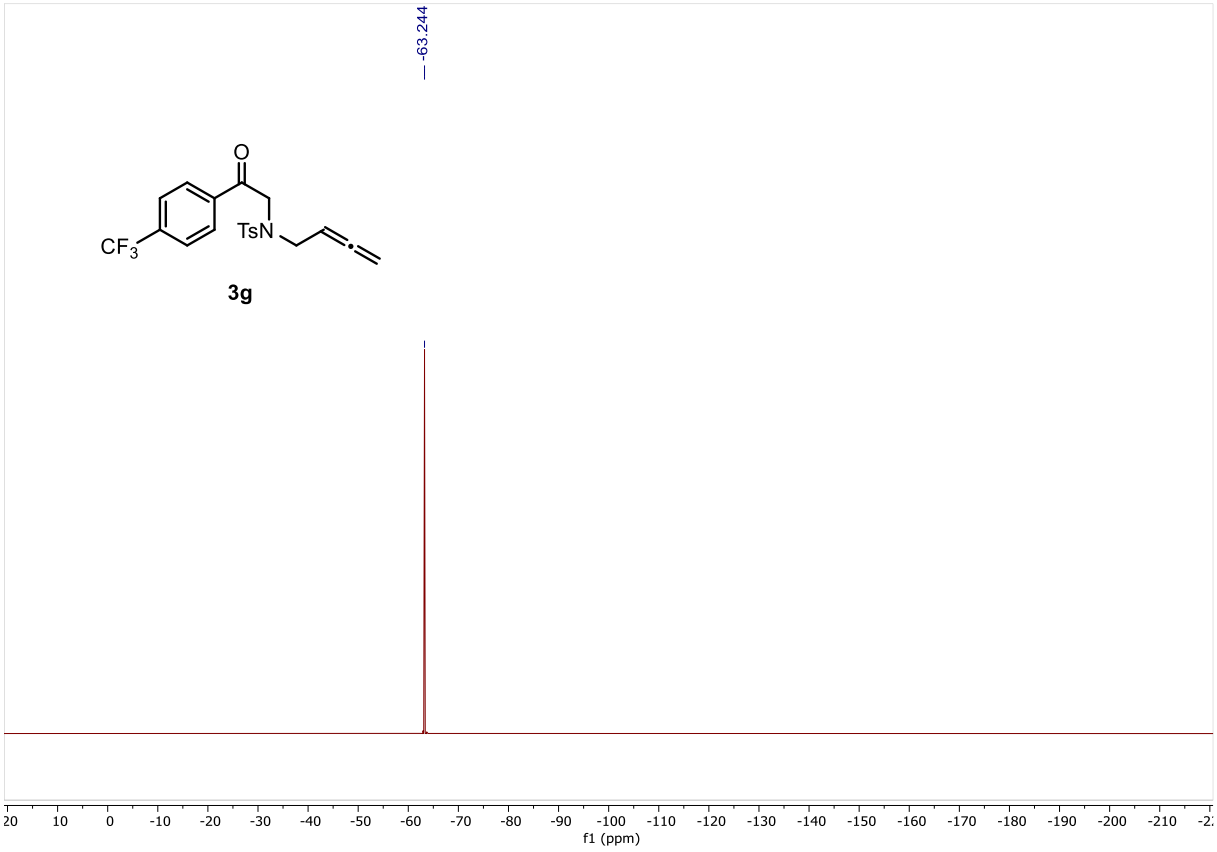
O
TsN
CF3
3g
f1 (ppm)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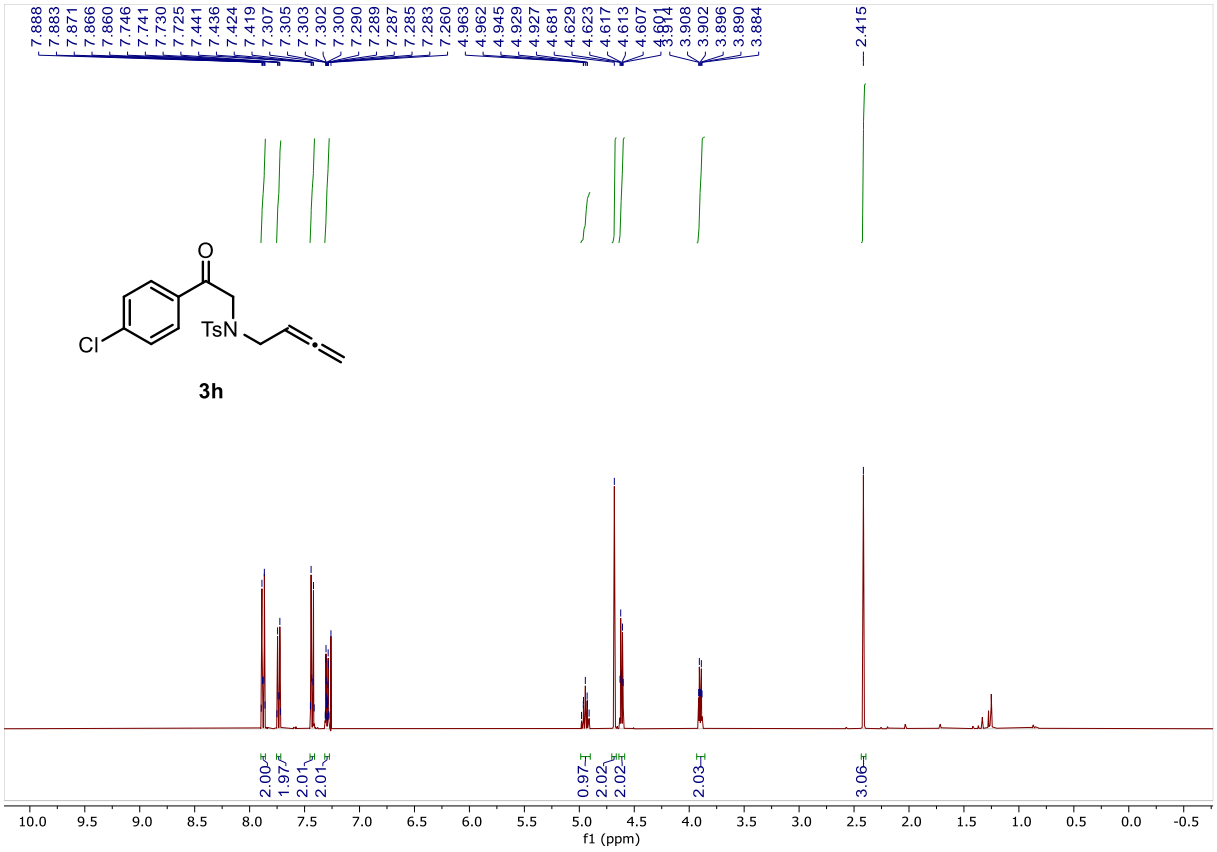
O
TsN
CF3
3g
f1 (ppm)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7.283
7.260
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4.945
4.929
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4.607
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3.902
3.896
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O
TsN
Cl
3h
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2.01
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2.02
2.03
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7.0
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6.0
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5.0
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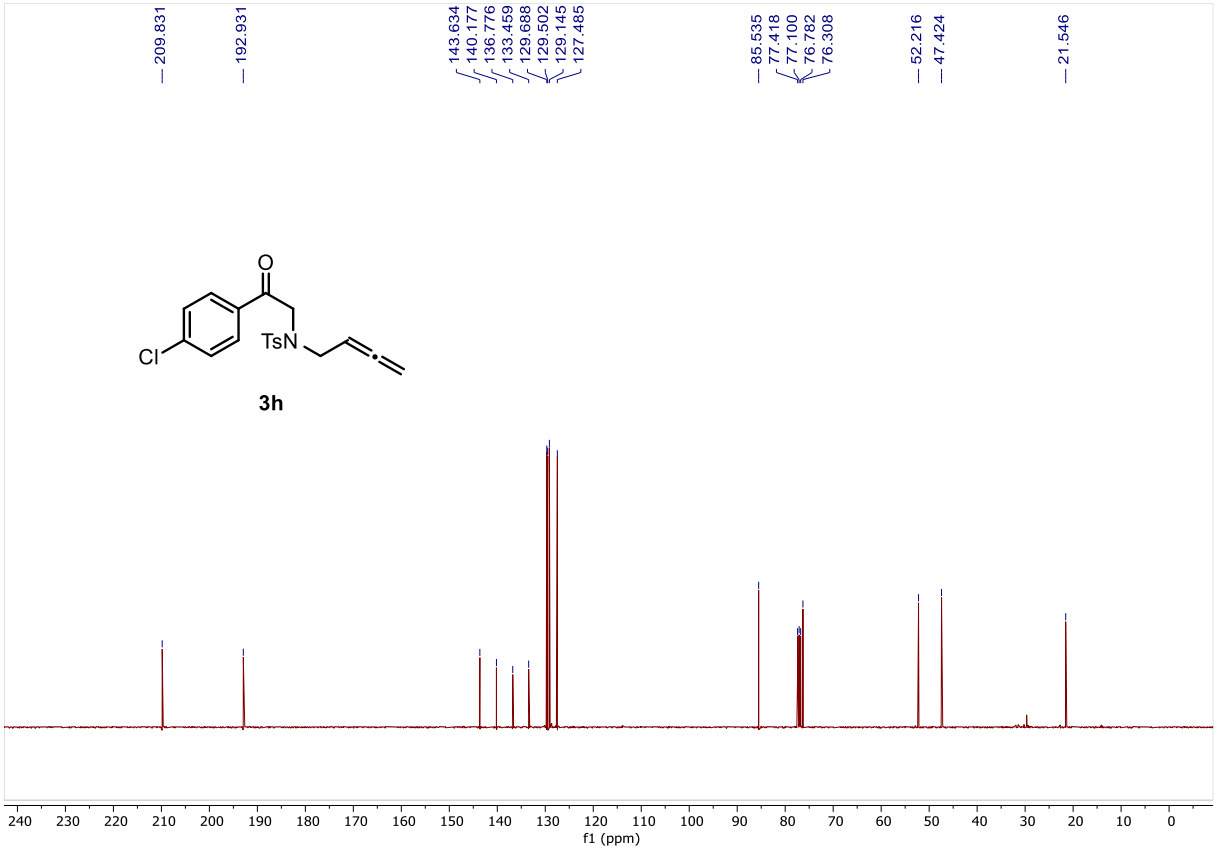
f1 (ppm)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76.782
76.308
52.216
47.424
21.546
O
TsN
Cl
3h
240
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220
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200
190
180
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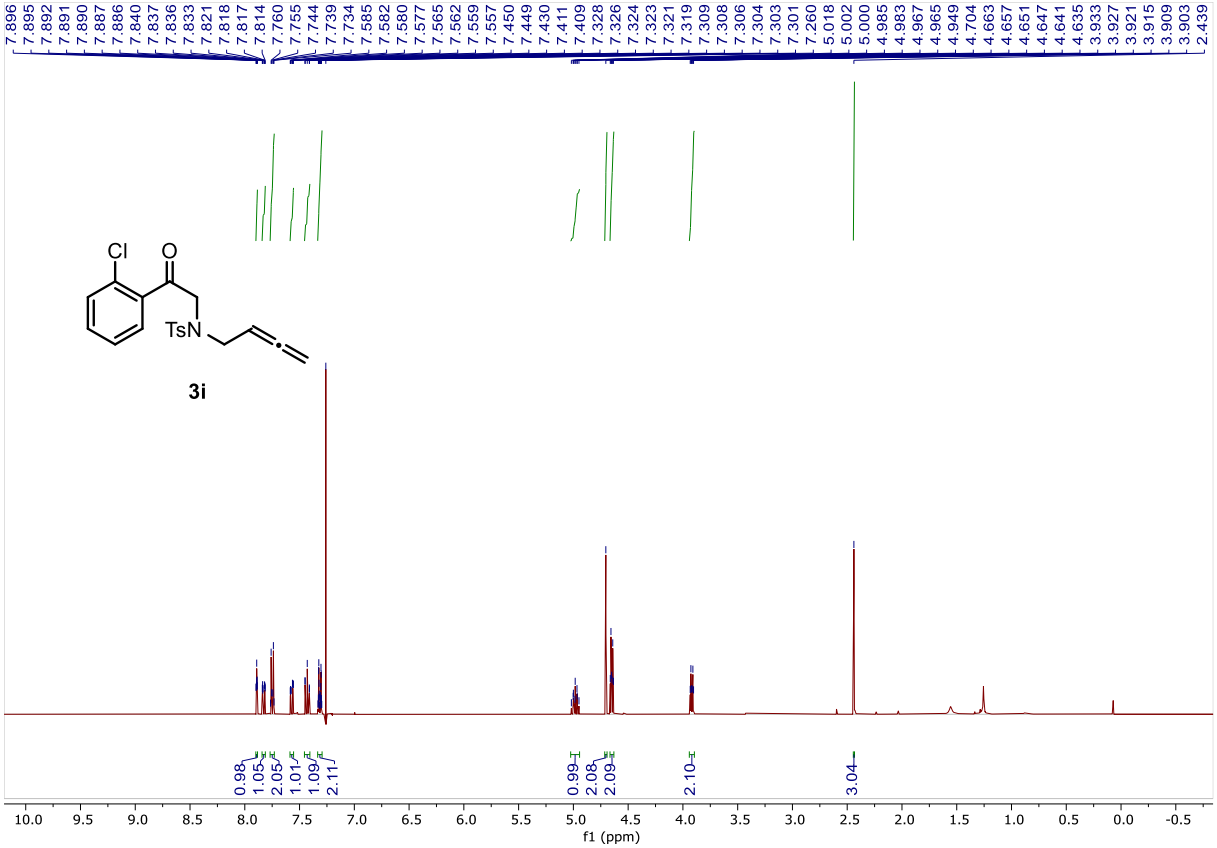
f1 (ppm)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7.821
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7.817
7.814
7.760
7.755
7.744
7.739
7.734
7.585
7.582
7.580
7.577
7.565
7.562
7.559
7.557
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7.449
7.430
7.411
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7.324
7.323
7.321
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7.308
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5.002
5.000
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4.635
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3.927
3.921
3.915
3.909
3.903
2.439
Cl
O
TsN
3i
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2.05
1.01
1.09
2.11
0.99
2.08
2.09
2.10
3.04
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7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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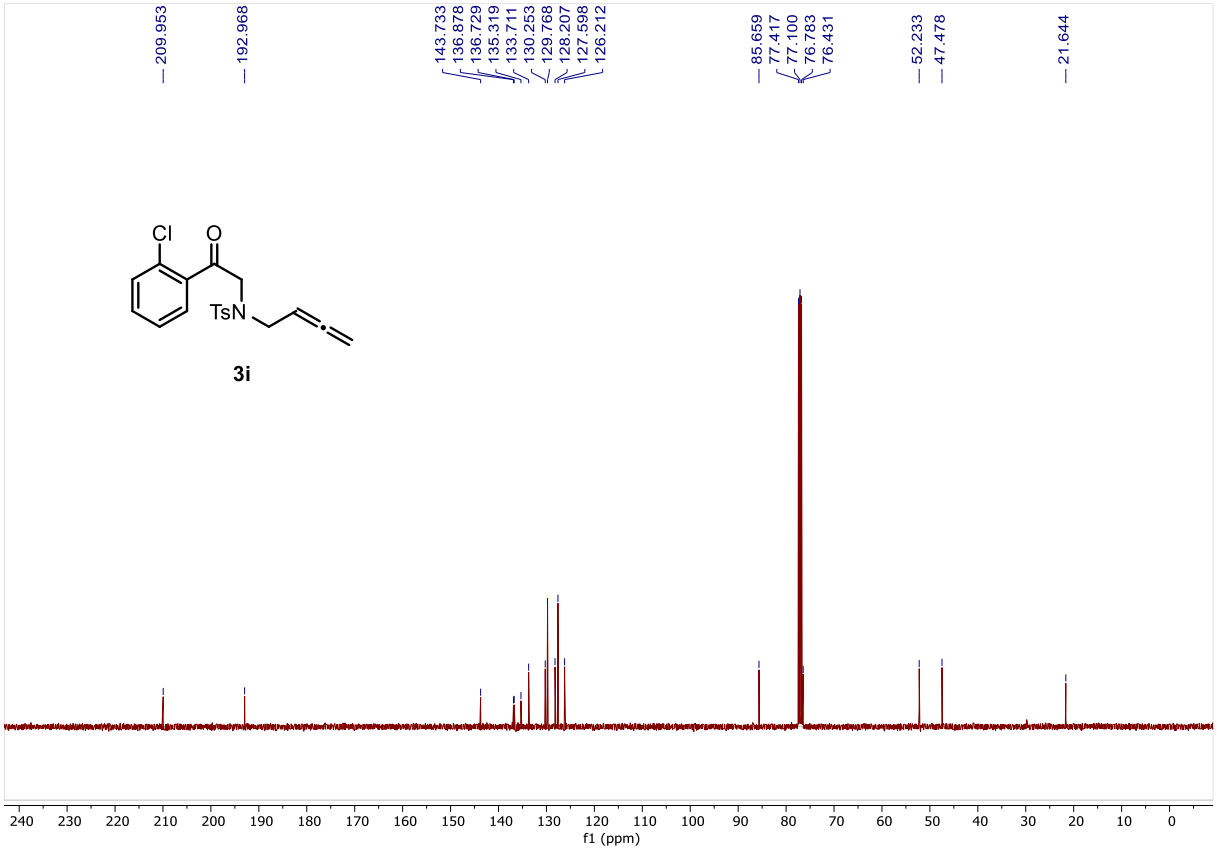
f1 (ppm)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77.100
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76.431
52.233
47.478
21.644
Cl
O
TsN
3i
240
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220
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200
190
180
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50
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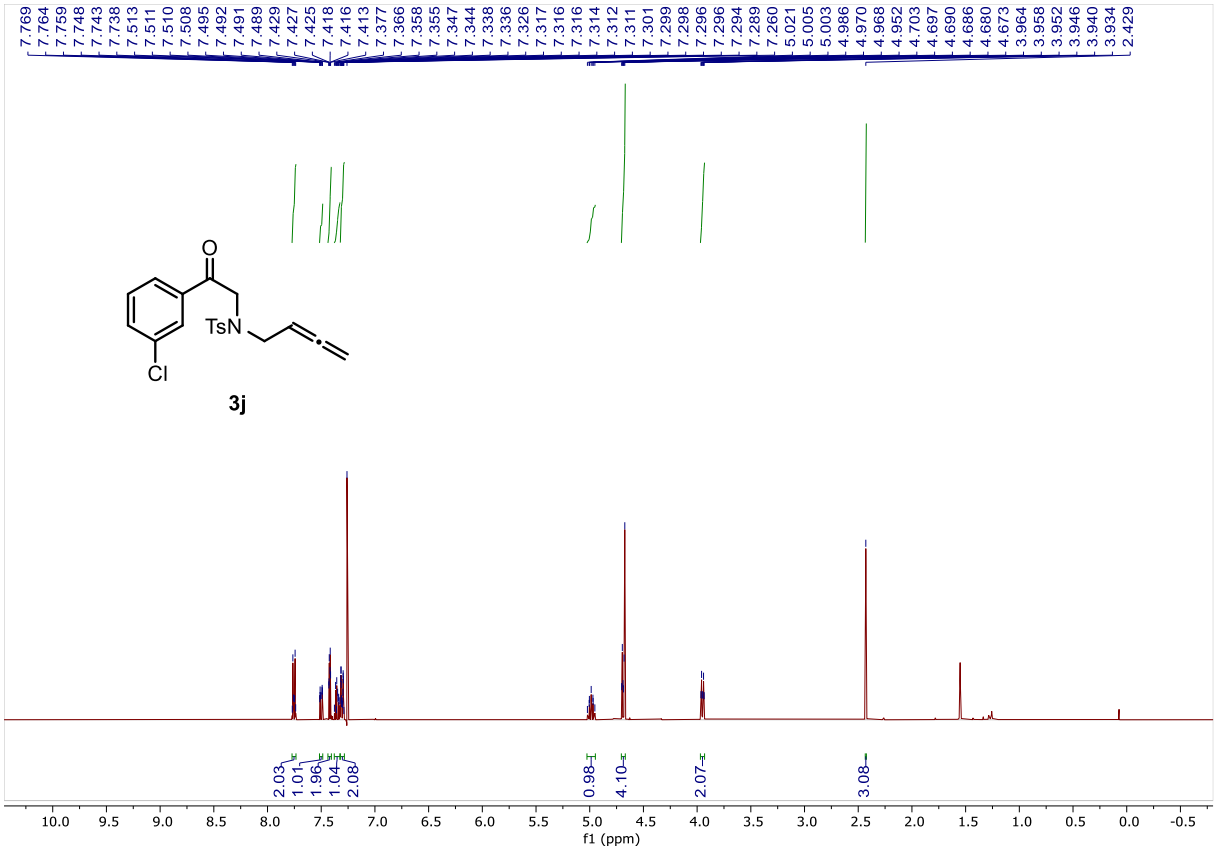
f1 (ppm)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7.316
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7.312
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3.940
3.934
2.429
O
TsN
Cl
3j
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1.04
2.08
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4.10
2.07
3.08
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8.0
7.5
7.0
6.5
6.0
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5.0
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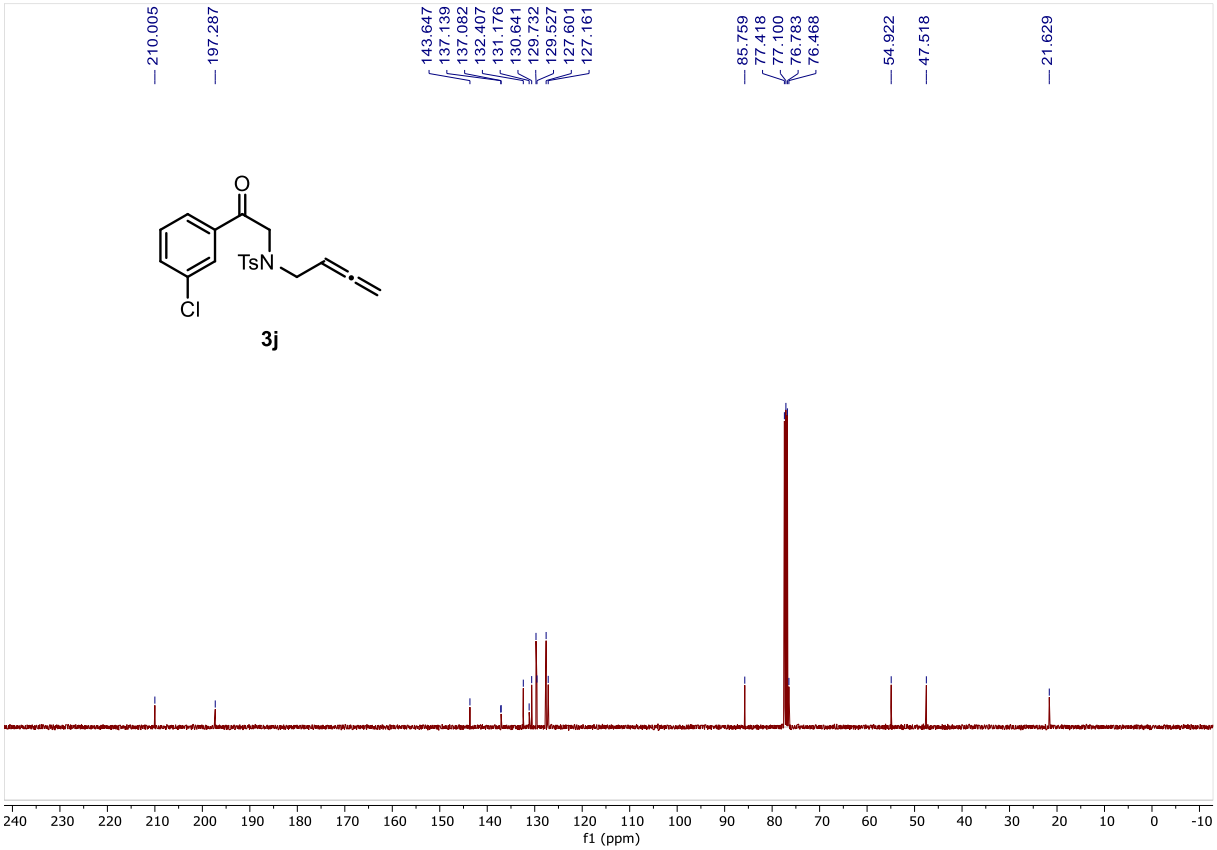
f1 (ppm)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127.161
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77.418
77.100
76.783
76.468
54.922
47.518
21.629
O
TsN
Cl
3j
240
230
220
210
200
190
180
170
160
150
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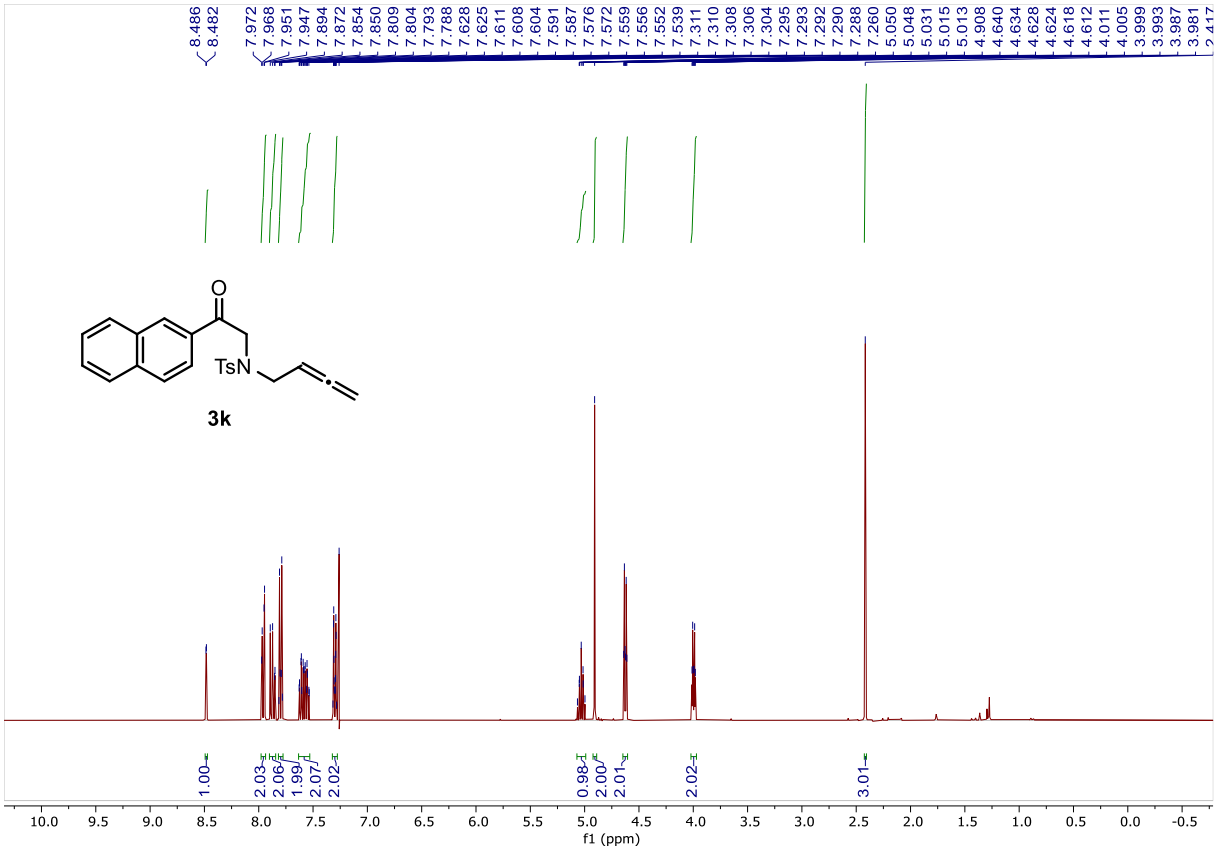
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.539
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7.308
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7.293
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7.290
7.288
7.260
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O
TsN
3k
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2.06
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2.07
2.02
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2.02
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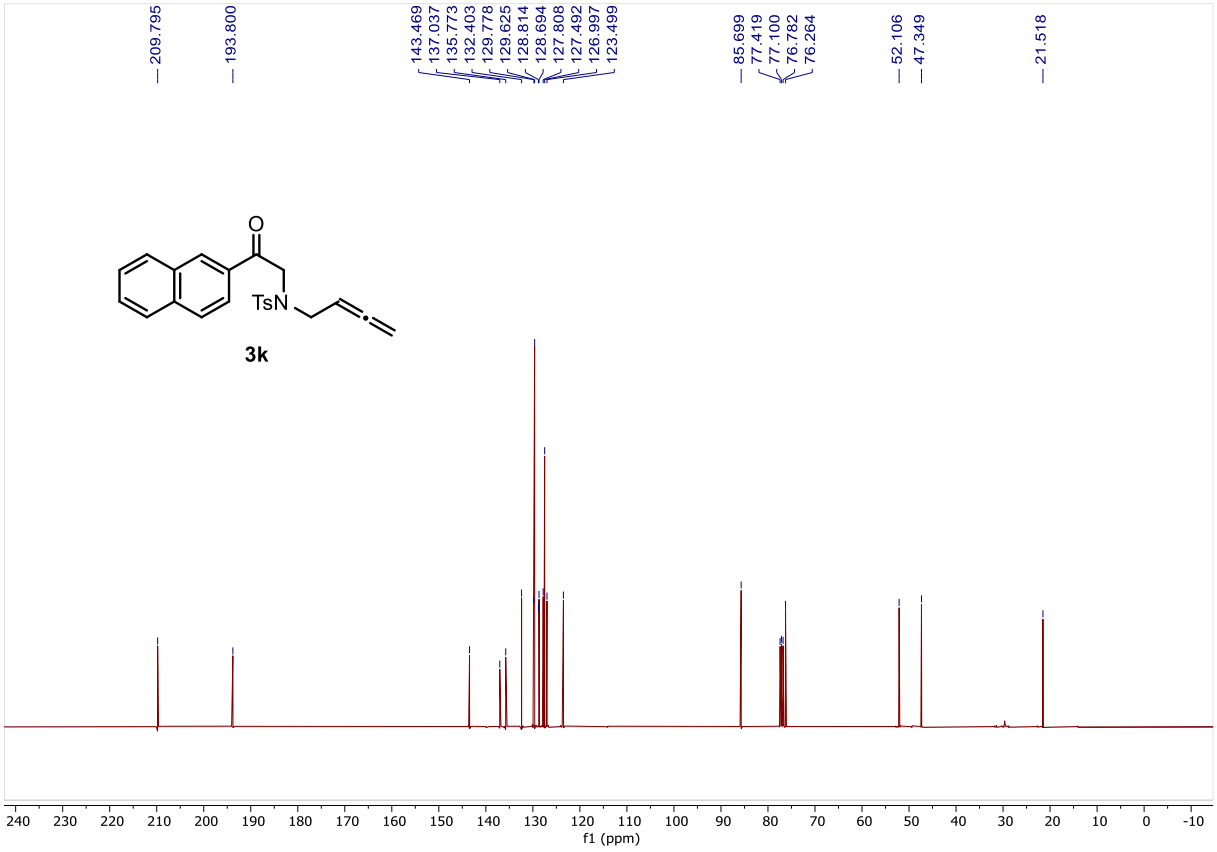
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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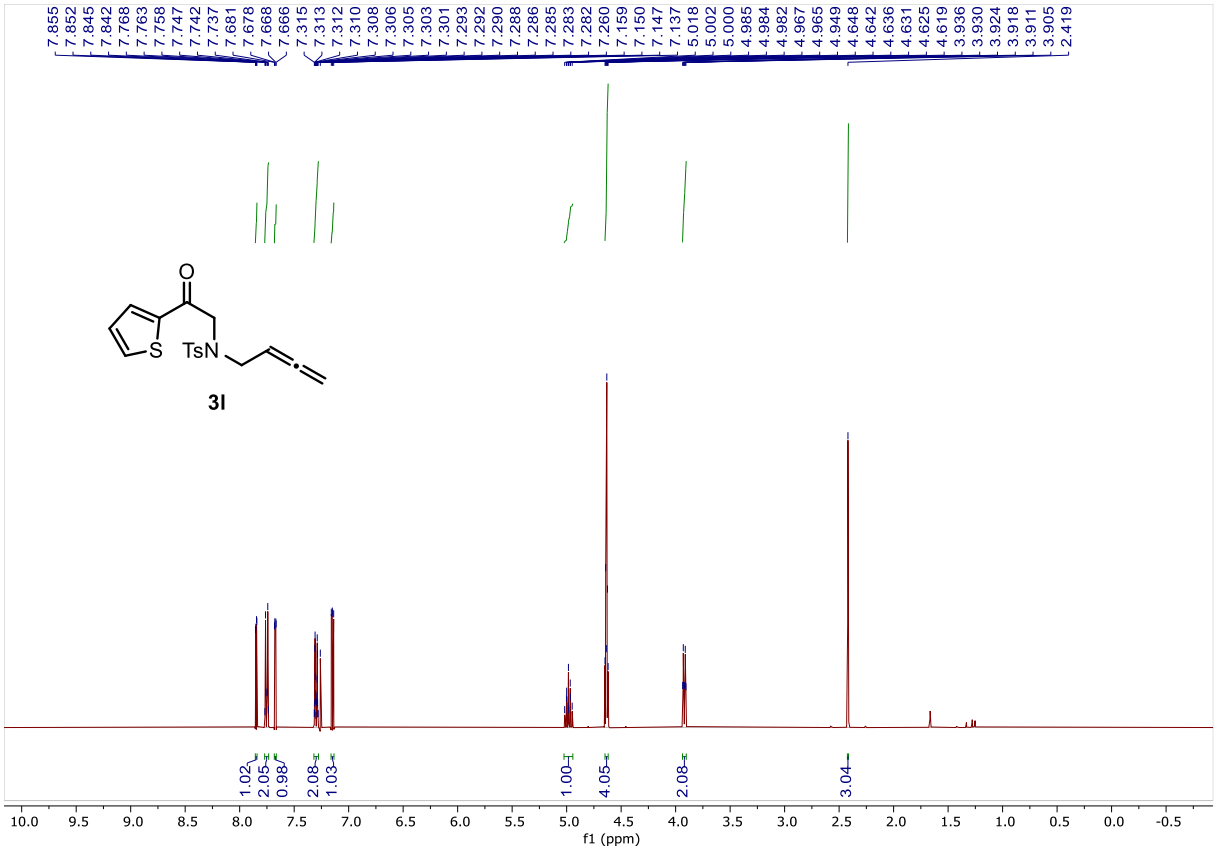
143.469
137.037
135.773
132.403
129.778
129.625
128.814
128.694
127.808
127.492
126.997
123.499
85.699
77.419
77.100
76.782
76.264
52.106
47.349
21.518
O
TsN
3k
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.855
7.852
7.845
7.842
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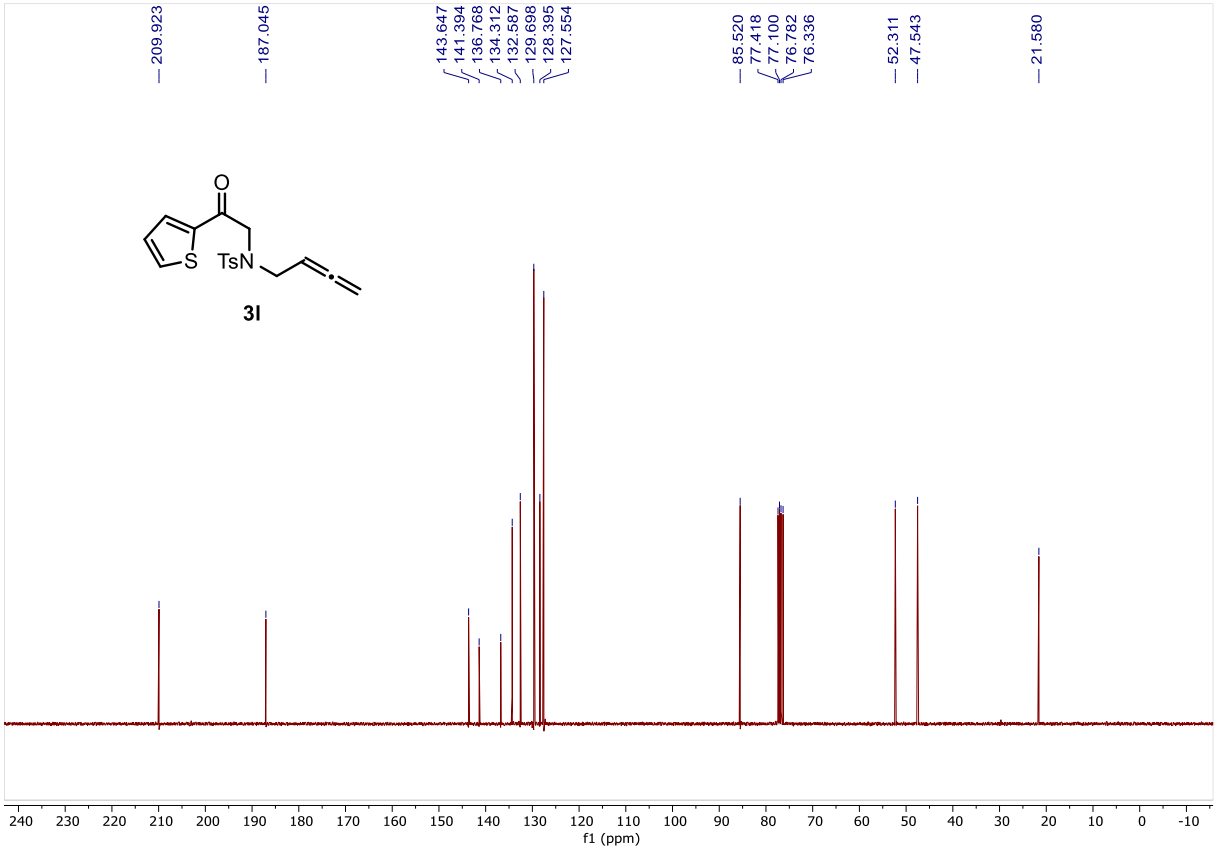
7.763
7.758
7.747
7.742
7.737
7.681
7.678
7.668
7.666
7.315
7.313
7.312
7.310
7.308
7.306
7.305
7.303
7.301
7.293
7.292
7.290
7.288
7.286
7.285
7.283
7.282
7.260
7.159
7.150
7.147
7.137
5.018
5.002
5.000
4.985
4.984
4.982
4.967
4.965
4.949
4.648
4.642
4.636
4.631
4.625
4.619
3.936
3.930
3.924
3.918
3.911
3.905
2.419
O
S
TsN
3l
1.02
2.05
0.98
2.08
1.03
1.00
4.05
2.08
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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187.045
143.647
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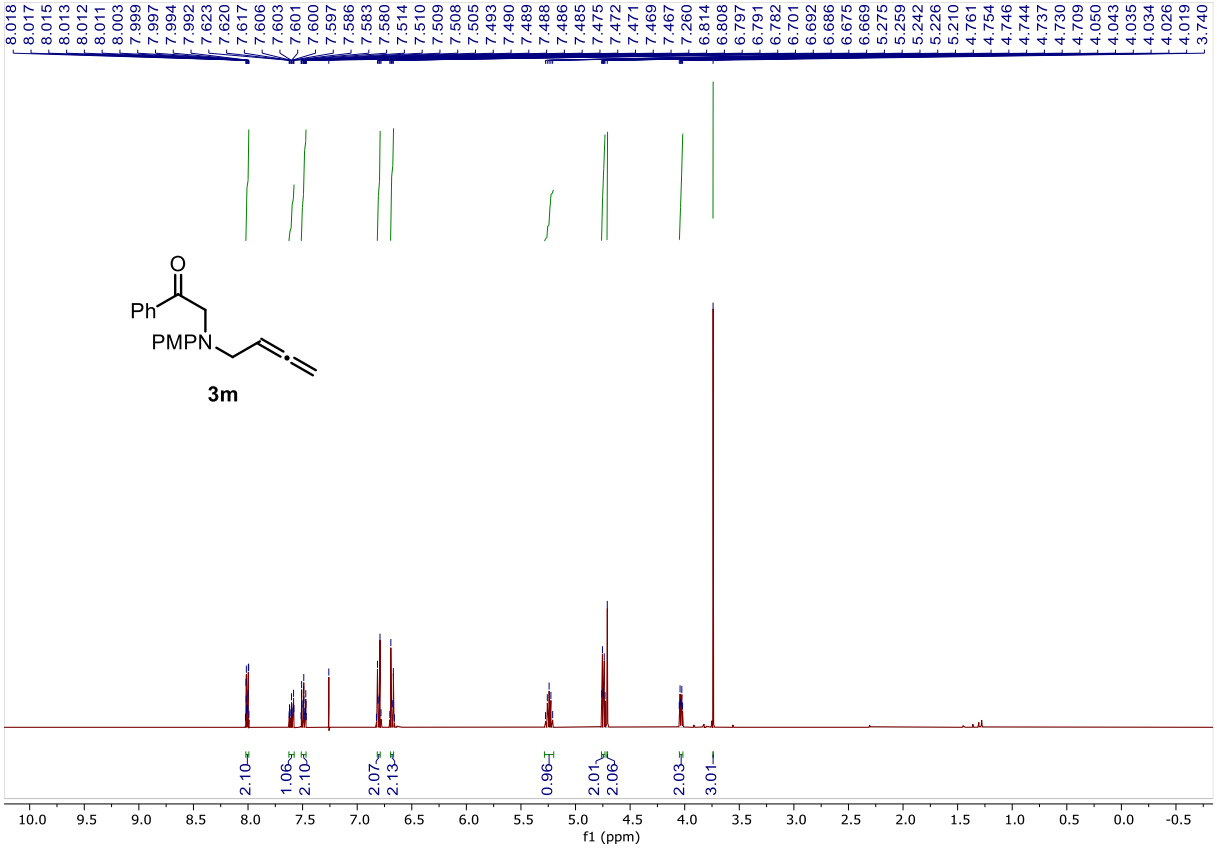
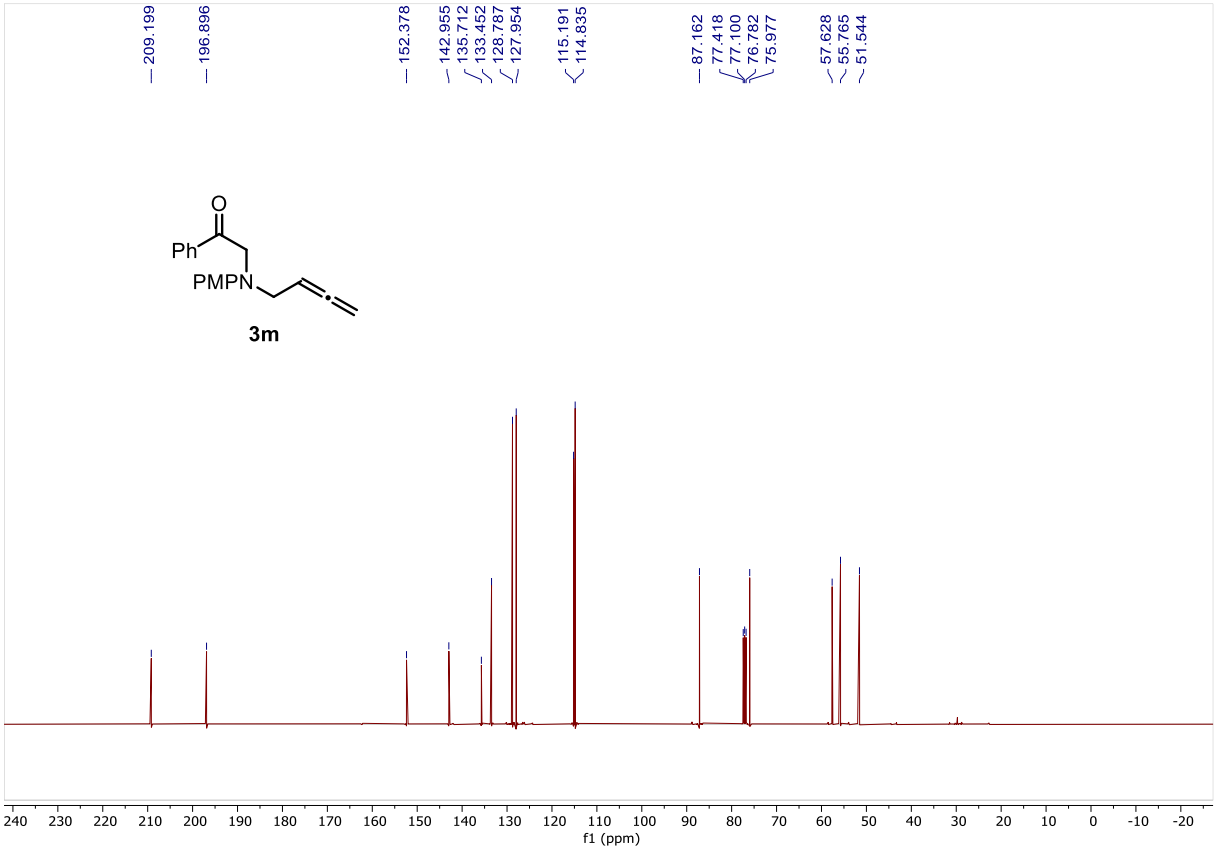
136.768
134.312
132.587
129.698
128.395
127.554
85.520
77.418
77.100
76.782
76.336
52.311
47.543
21.580
O
S
TsN
3l
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.018
8.017
8.015
8.013
8.012
8.011
8.003
7.999
7.997
7.994
7.992
7.623
7.620
7.617
7.606
7.603
7.601
7.600
7.597
7.586
7.583
7.580
7.514
7.510
7.509
7.508
7.505
7.493
7.490
7.489
7.488
7.486
7.485
7.475
7.472
7.471
7.469
7.467
7.260
6.814
6.808
6.797
6.791
6.782
6.701
6.692
6.686
6.675
6.669
5.275
5.259
5.242
5.226
5.210
4.761
4.754
4.746
4.744
4.737
4.730
4.709
4.050
4.043
4.035
4.034
4.026
4.019
3.740
O
Ph
PMPN
3m
2.10
1.06
2.10
2.07
2.13
0.96
2.01
2.06
2.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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196.896
152.378
142.955
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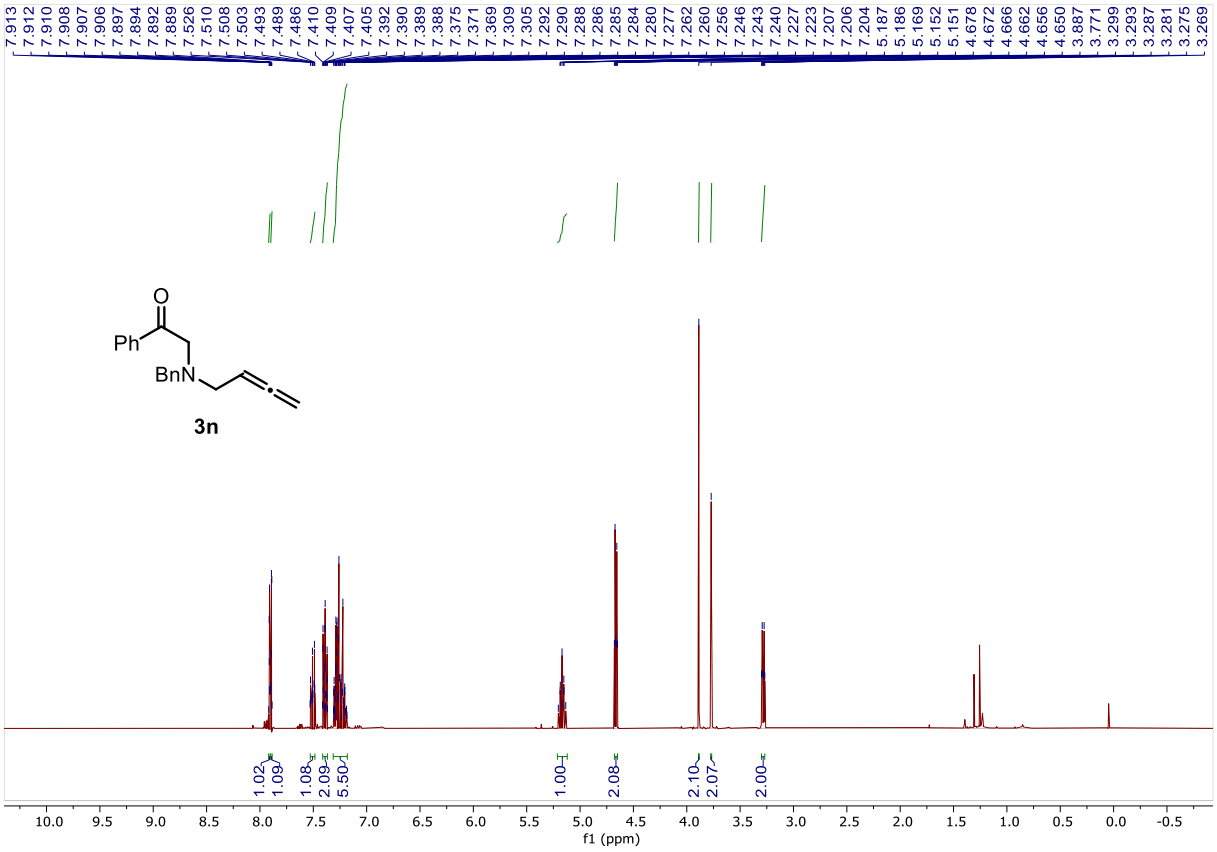
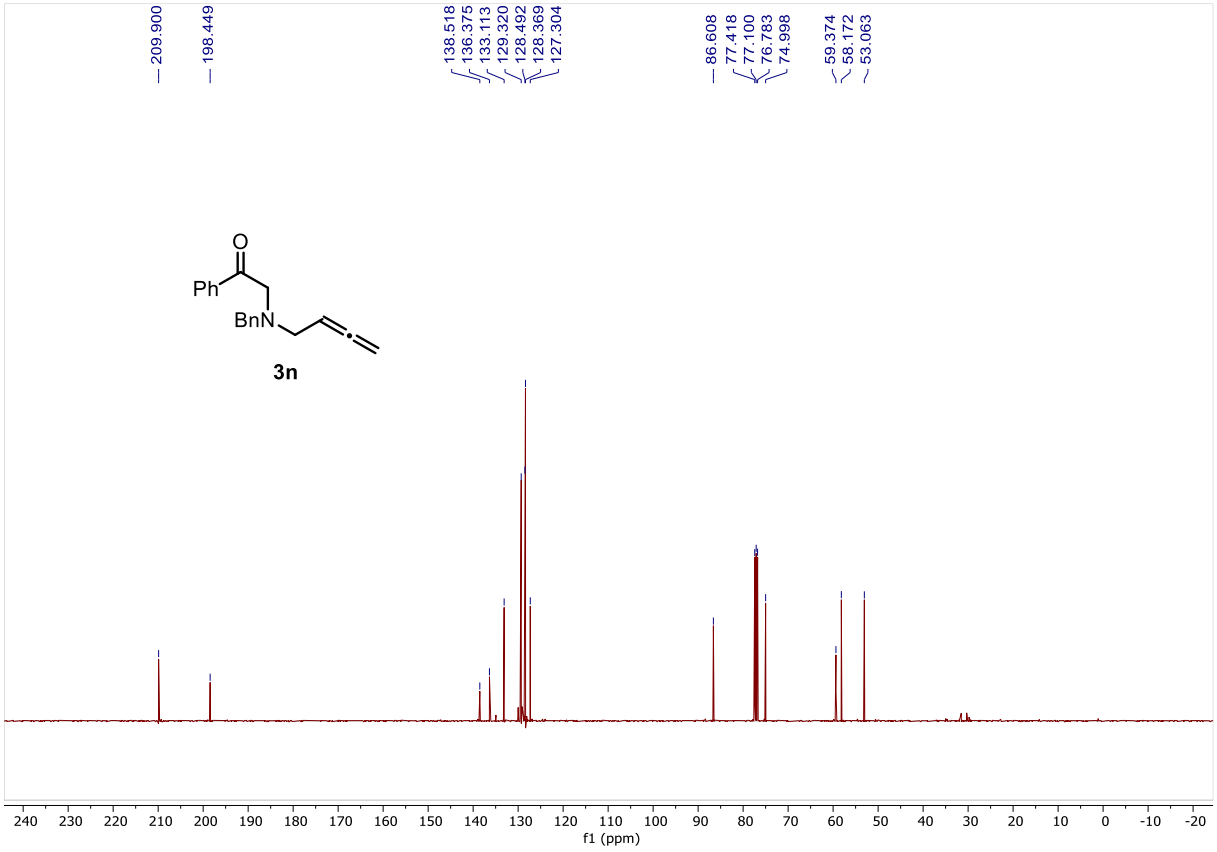
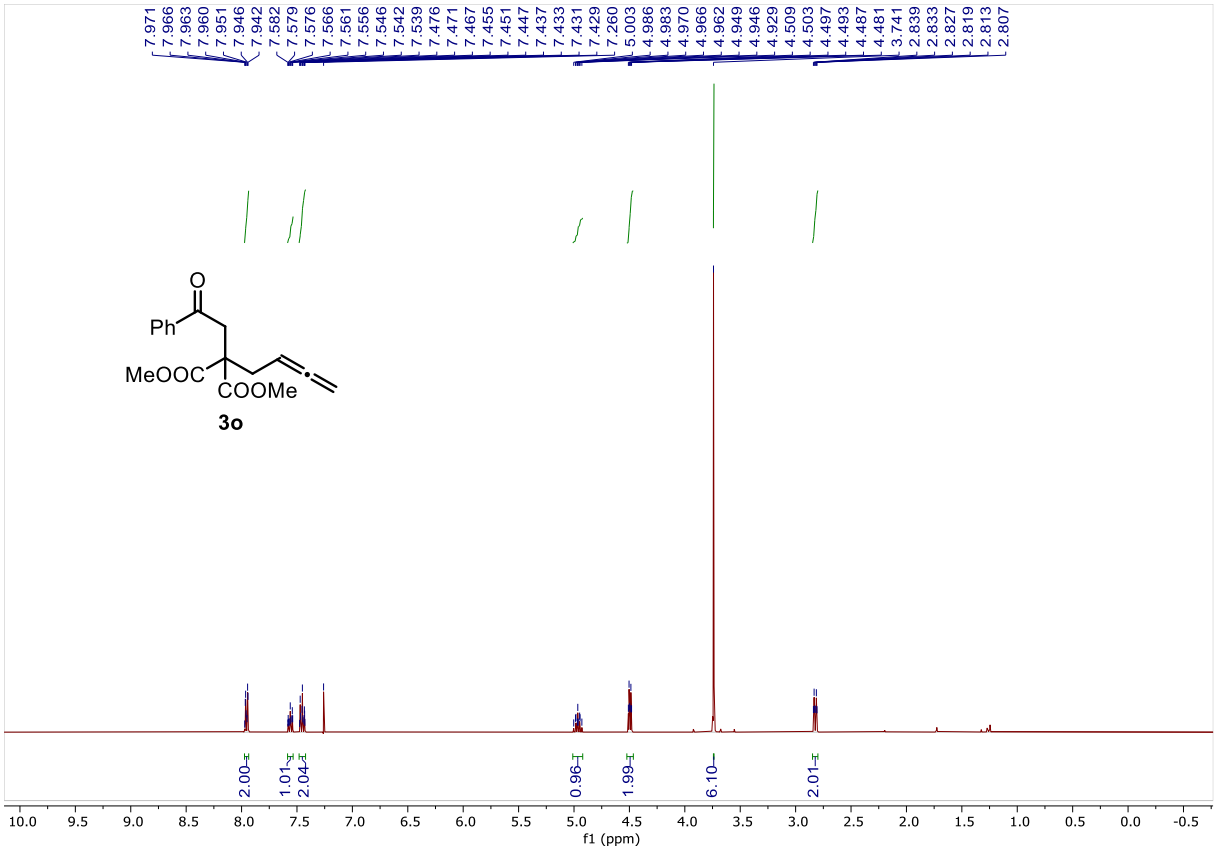
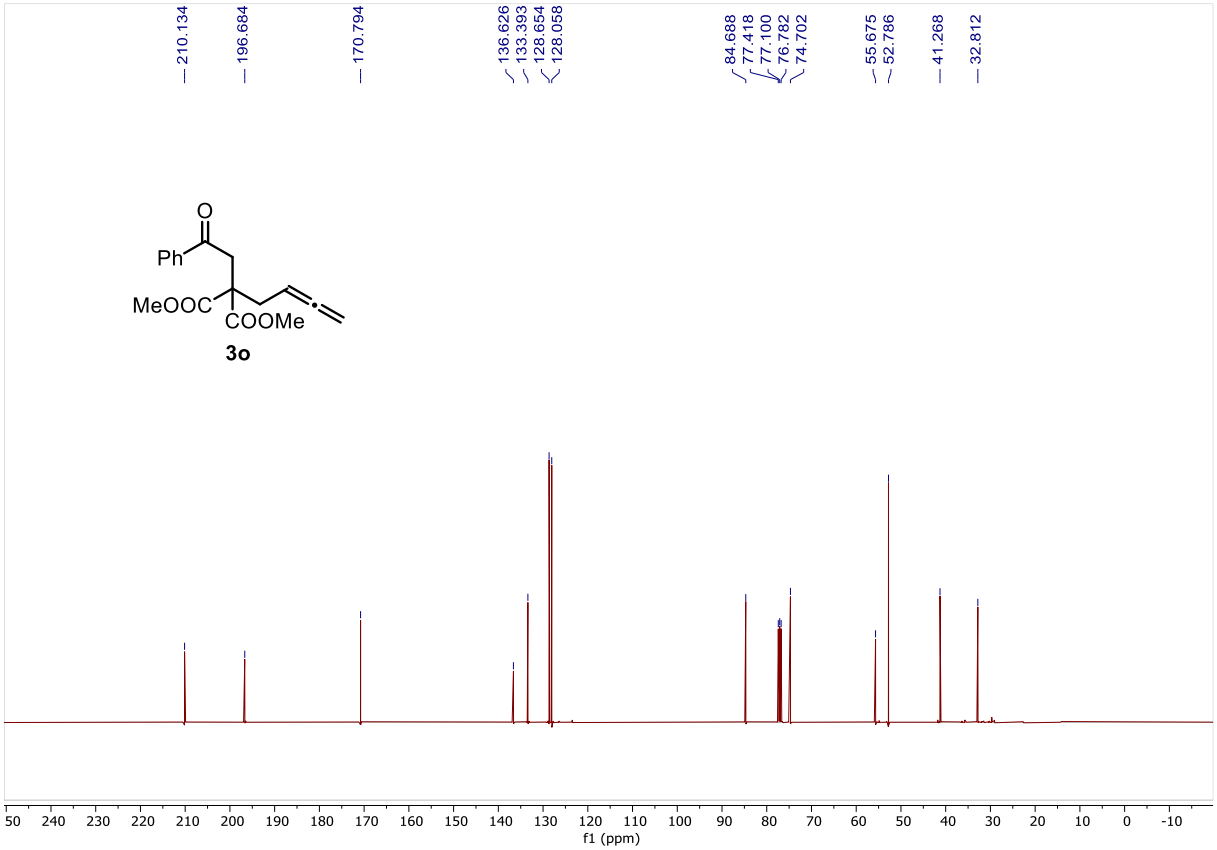
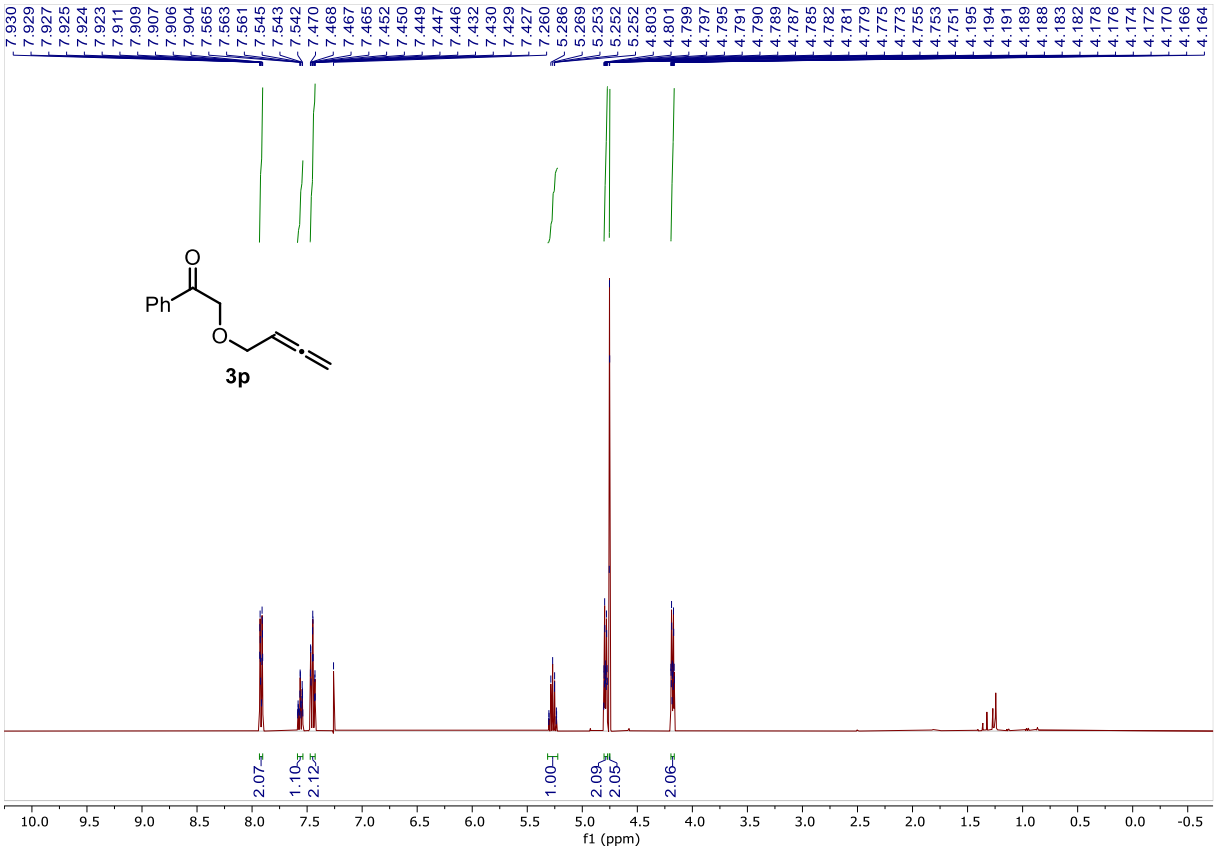
127.954
115.191
114.835
87.162
77.418
77.100
76.782
75.977
57.628
55.765
51.544
O
Ph
PMPN
3m
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

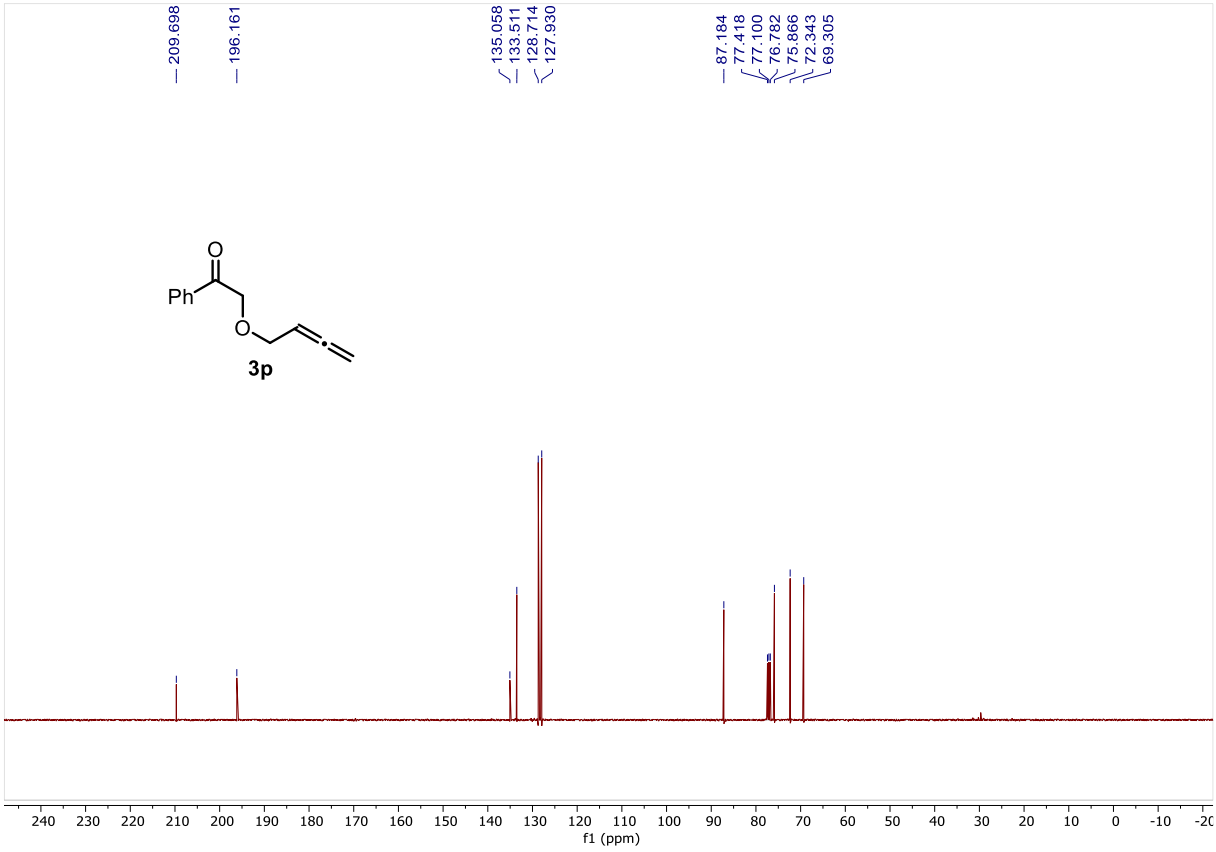

7.913 7.912 7.910 7.908 7.907 7.906 7.897 7.894 7.892 7.889 7.526 7.510 7.508 7.503 7.493 7.489 7.486 7.410 7.409 7.407 7.405 7.392 7.390 7.389 7.388 7.375 7.371 7.369 7.309 7.305 7.292 7.290 7.288 7.286 7.285 7.284 7.280 7.277 7.262 7.260 7.256 7.246 7.243 7.240 7.227 7.223 7.207 7.206 7.204 5.187 5.186 5.169 5.152 5.151 4.678 4.672 4.666 4.662 4.656 4.650 3.887 3.771 3.299 3.293 3.287 3.281 3.275 3.269
O
Ph
BnN
3n
1.02 1.09 1.08 2.09 5.50 1.00 2.08 2.10 2.07 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

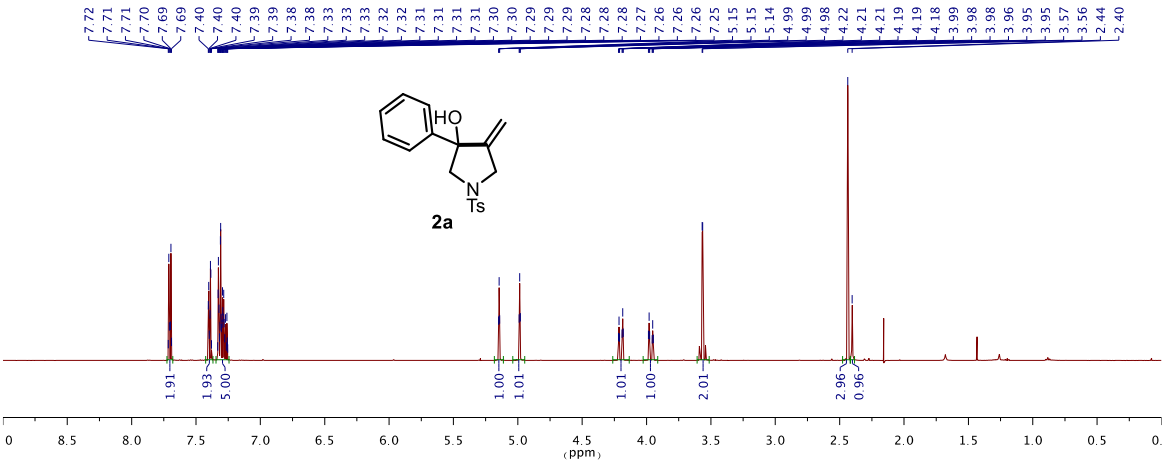

209.900 198.449 138.518 136.375 133.113 129.320 128.492 128.369 127.304 86.608 77.418 77.100 76.783 74.998 59.374 58.172 53.063
O
Ph
BnN
3n
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

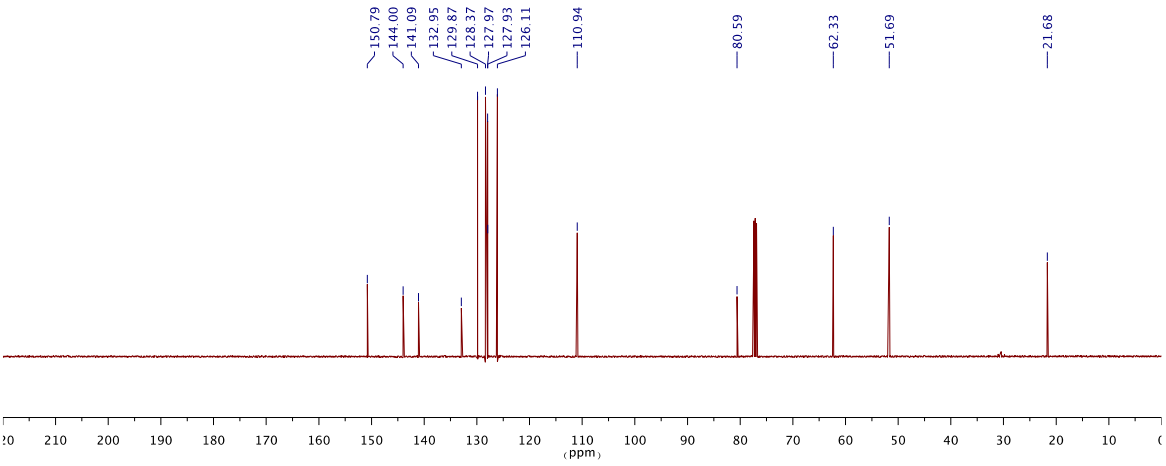

7.971
7.966
7.963
7.960
7.951
7.946
7.942
7.582
7.579
7.576
7.566
7.561
7.556
7.546
7.542
7.539
7.476
7.471
7.467
7.455
7.451
7.447
7.437
7.433
7.431
7.429
7.260
5.003
4.986
4.983
4.970
4.966
4.962
4.949
4.946
4.929
4.509
4.503
4.497
4.493
4.487
4.481
3.741
2.839
2.833
2.827
2.819
2.813
2.807
O
Ph
MeOOC
COOMe
3o
2.00
1.01
2.04
0.96
1.99
6.10
2.01
f1 (ppm)

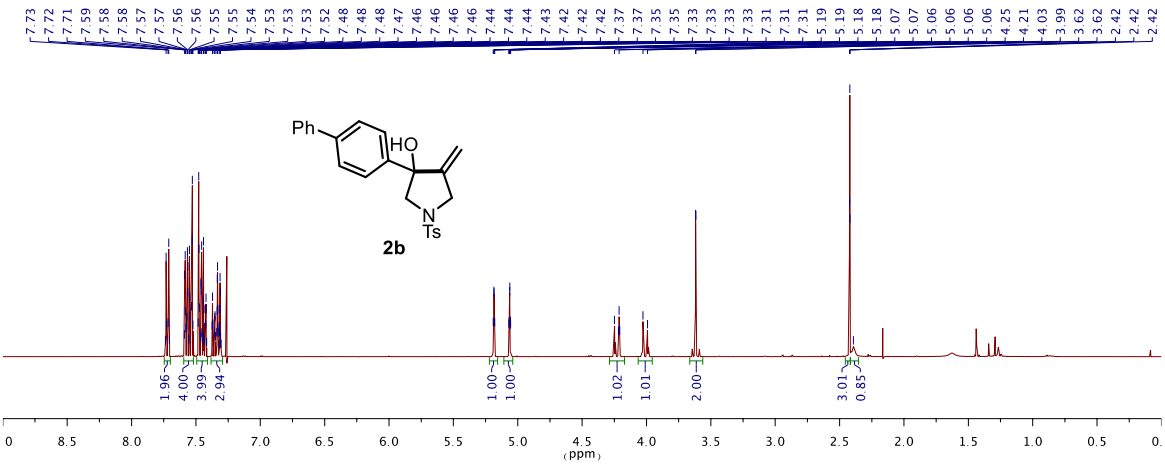

210.134
196.684
170.794
136.626
133.393
128.654
128.058
84.688
77.418
77.100
76.782
74.702
55.675
52.786
41.268
32.812
O
Ph
MeOOC
COOMe
3o
f1 (ppm)

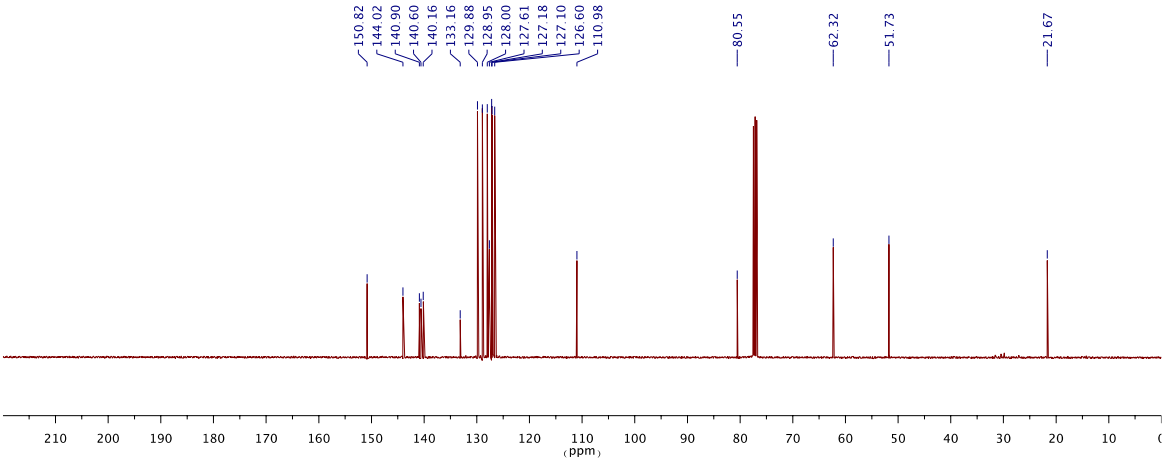

7.930
7.929
7.927
7.925
7.924
7.923
7.911
7.909
7.907
7.906
7.904
7.565
7.563
7.561
7.545
7.543
7.542
7.470
7.468
7.467
7.465
7.452
7.450
7.449
7.447
7.446
7.432
7.430
7.429
7.427
7.260
5.286
5.269
5.253
5.252
5.252
4.803
4.801
4.799
4.797
4.795
4.791
4.790
4.789
4.787
4.785
4.782
4.781
4.779
4.775
4.773
4.755
4.753
4.751
4.195
4.194
4.191
4.189
4.188
4.183
4.182
4.178
4.176
4.174
4.172
4.170
4.166
4.164
O
Ph
O
3p
2.07
1.10
2.12
1.00
2.09
2.05
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

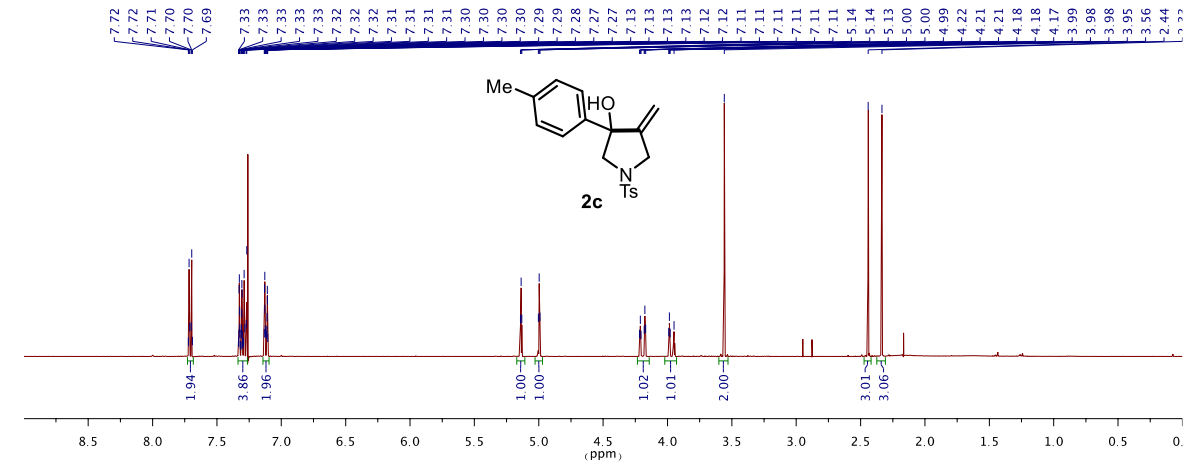

209.698
196.161
135.058
133.511
128.714
127.930
87.184
77.418
77.100
76.782
75.866
72.343
69.305
O
Ph
O
3p
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

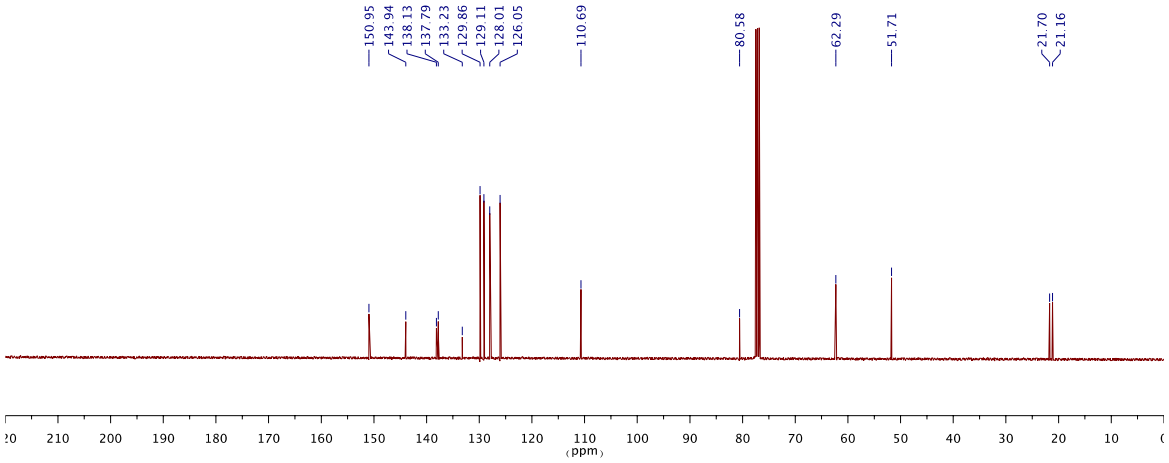

7.72 7.71 7.71 7.70 7.69 7.69 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.26 7.26 7.26 7.25 5.15 5.15 5.14 4.99 4.99 4.98 4.22 4.21 4.21 4.19 4.19 4.18 3.99 3.98 3.98 3.96 3.95 3.95 3.57 3.56 2.44 2.40
HO
N
Ts
2a
1.91 1.93 5.00 1.00 1.01 1.01 1.00 2.01 2.96 0.96
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.
(ppm)

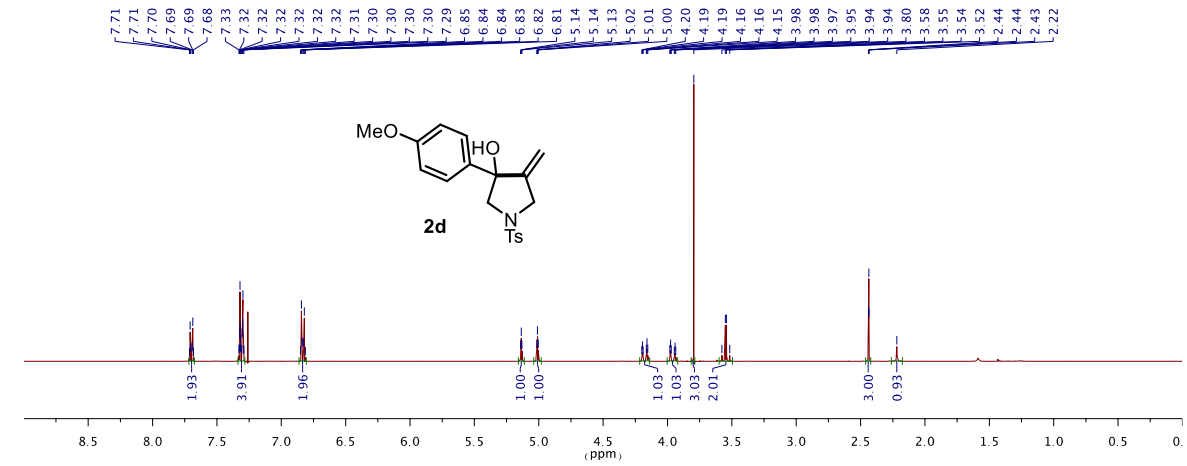

150.79 144.00 141.09 132.95 129.87 128.37 127.97 127.93 126.11 110.94 80.59 62.33 51.69 21.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

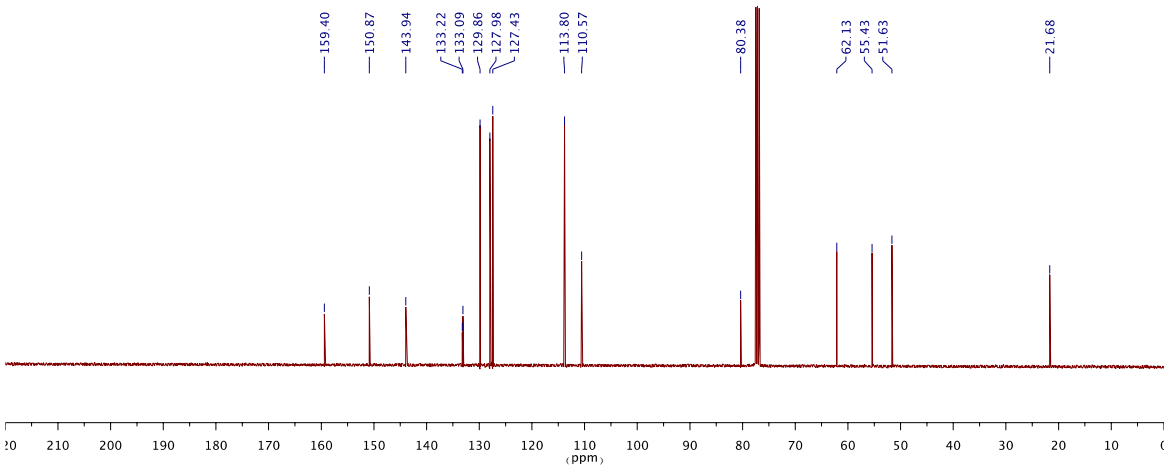

Ph
HO
N
Ts
2b
1.96
4.00
3.99
2.94
1.00
1.00
1.02
1.01
2.00
3.01
0.85
(ppm)

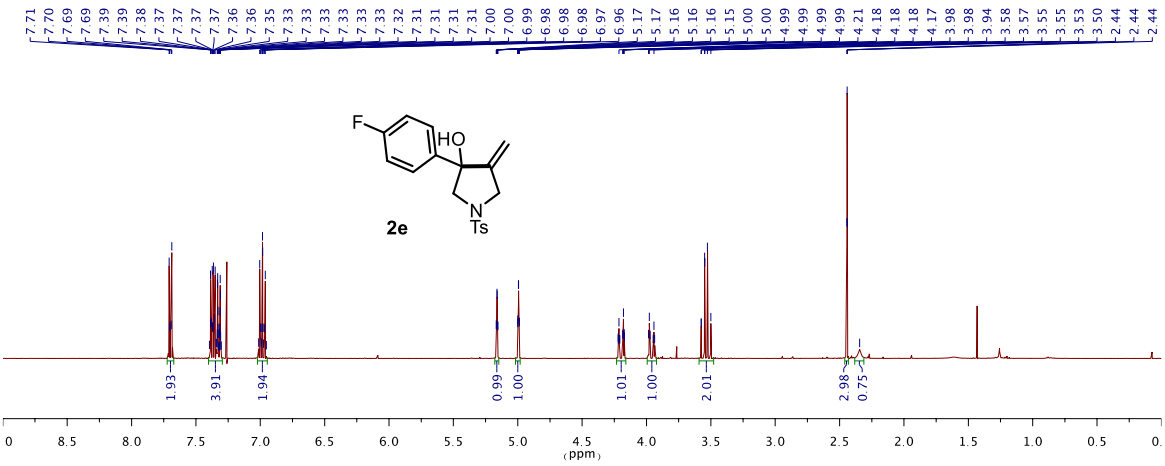

150.82
144.02
140.90
140.60
140.16
133.16
129.88
128.95
128.00
127.61
127.18
127.10
126.60
110.98
80.55
62.32
51.73
21.67
(ppm)

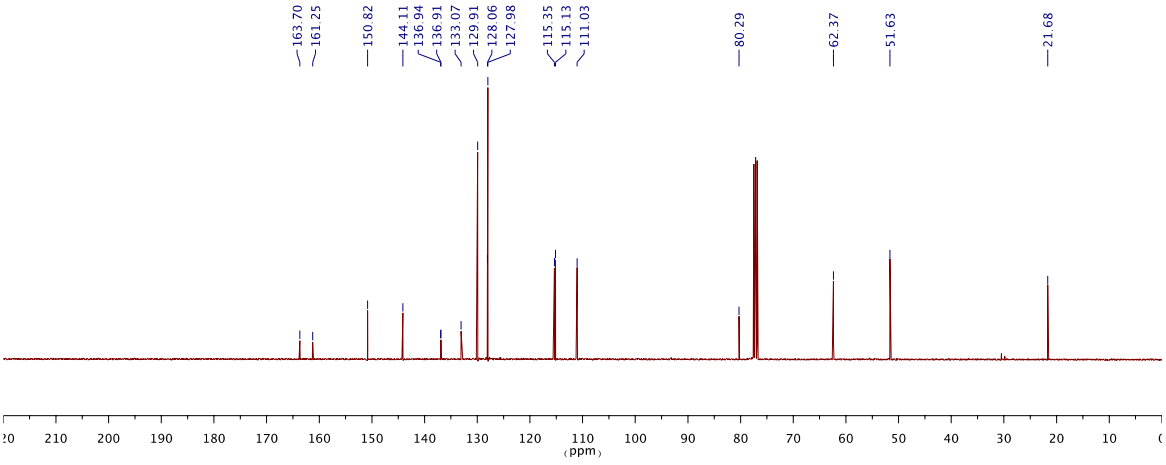

Me
HO
N
Ts
2c
1.94
3.86
1.96
1.00
1.00
1.02
1.01
2.00
3.01
3.06
ppm

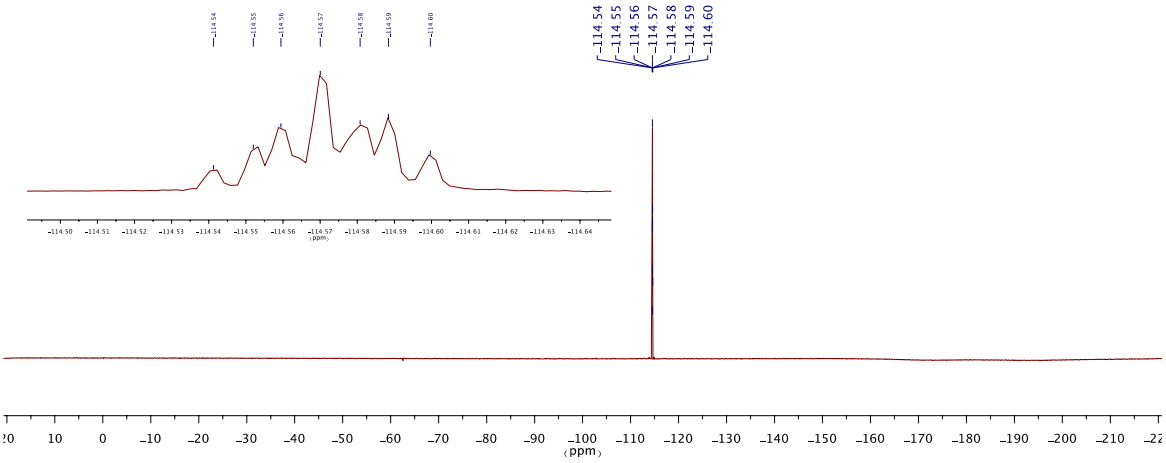

150.95
143.94
138.13
137.79
133.23
129.86
129.11
128.01
126.05
110.69
80.58
62.29
51.71
21.70
21.16
ppm

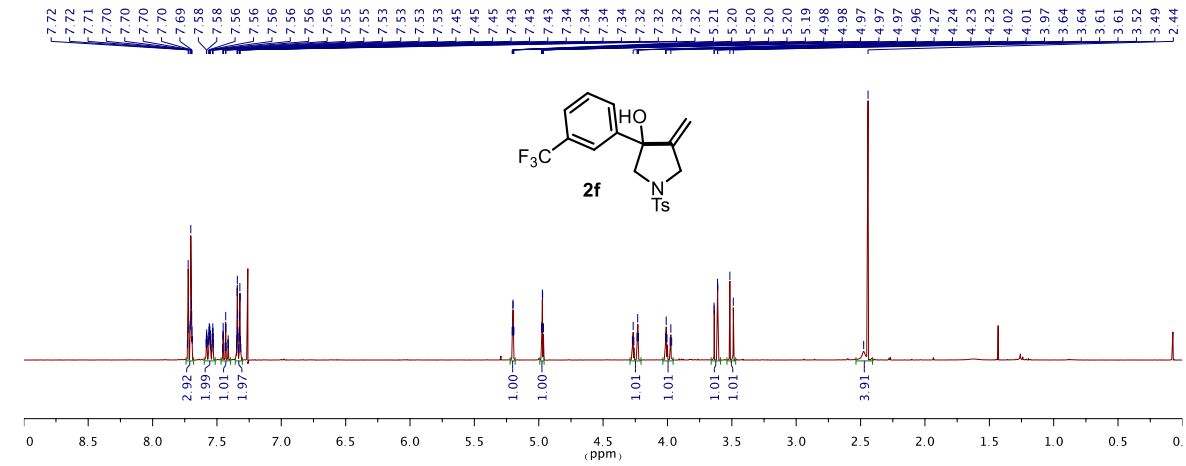

MeO
HO
N
Ts
2d
1.93
3.91
1.96
1.00
1.00
1.03
1.03
3.03
2.01
3.00
0.93
(ppm)

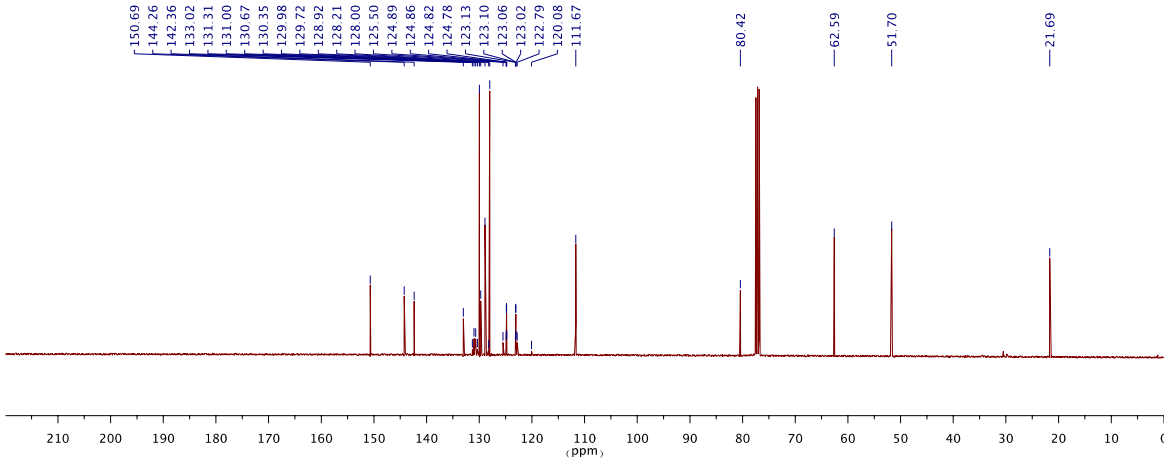

159.40
150.87
143.94
133.22
133.09
129.86
127.98
127.43
113.80
110.57
80.38
62.13
55.43
51.63
21.68
(ppm)

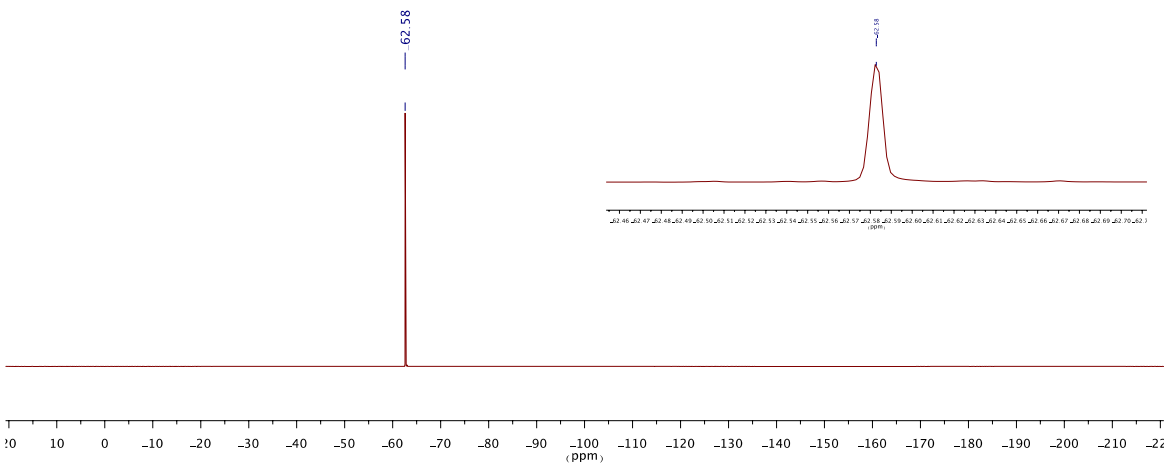

F
HO
N
Ts
2e
1.93
3.91
1.94
0.99
1.00
1.01
1.00
2.01
2.98
0.75
(ppm)

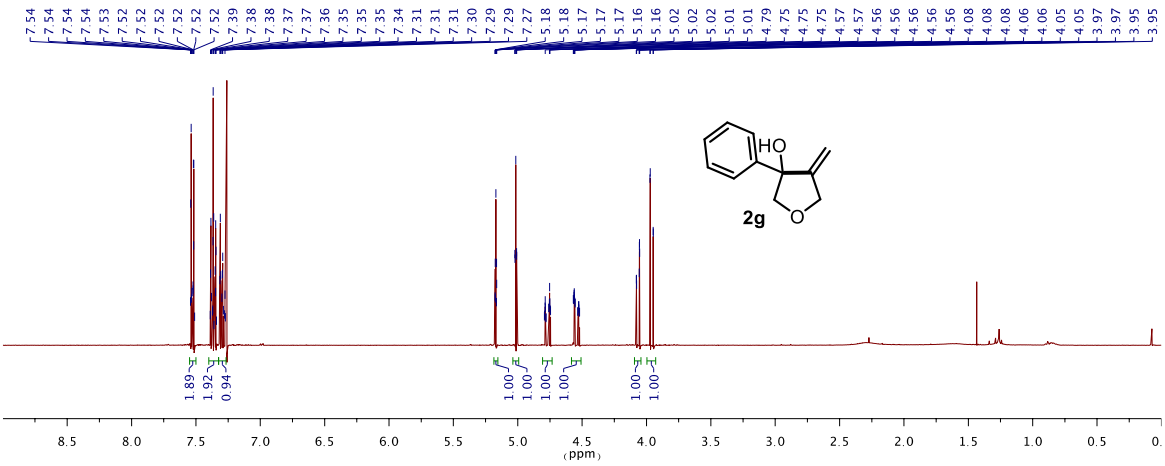

163.70
161.25
150.82
144.11
136.94
136.91
133.07
129.91
128.06
127.98
115.35
115.13
111.03
80.29
62.37
51.63
21.68
(ppm)

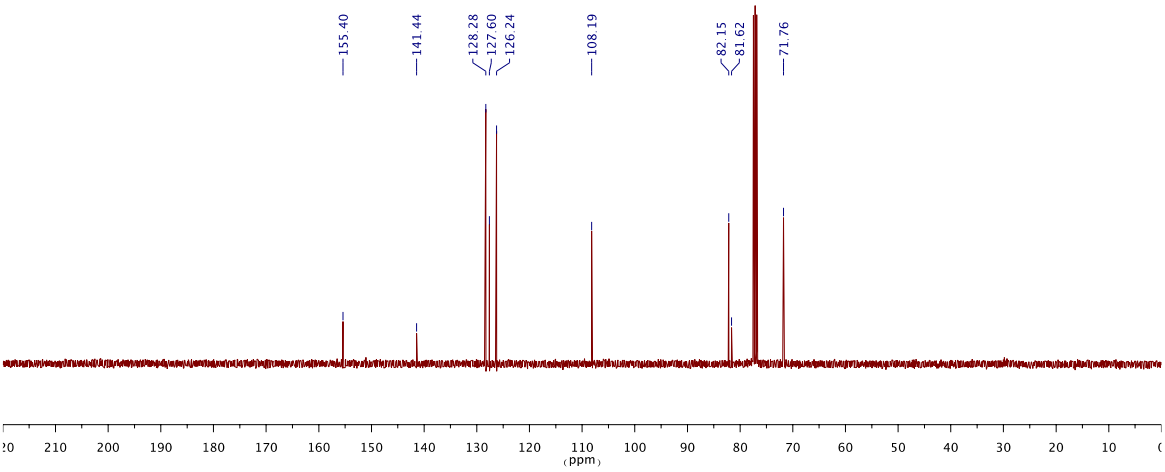

-114.54
-114.55
-114.56
-114.57
-114.58
-114.59
-114.60
(ppm)

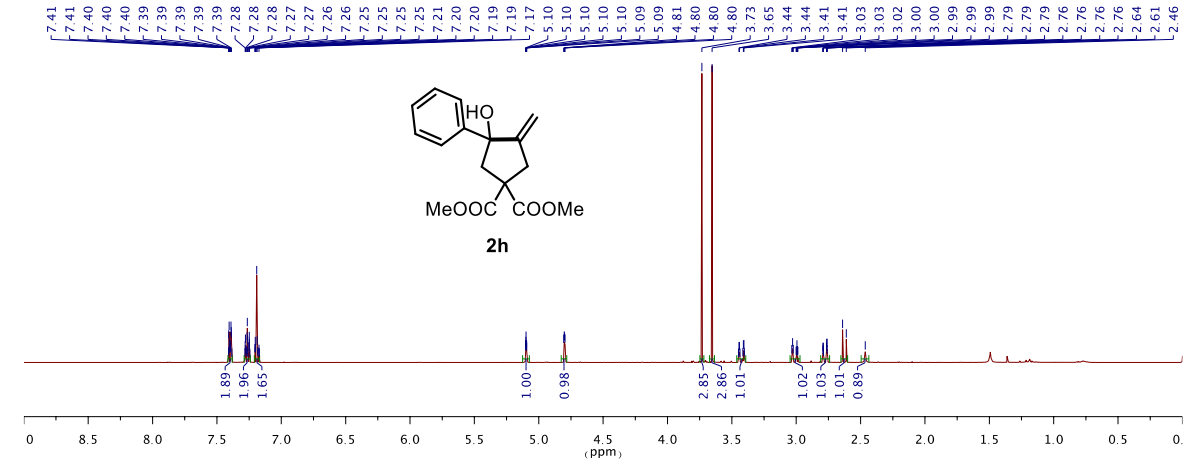

HO
F3C
N
Ts
2f

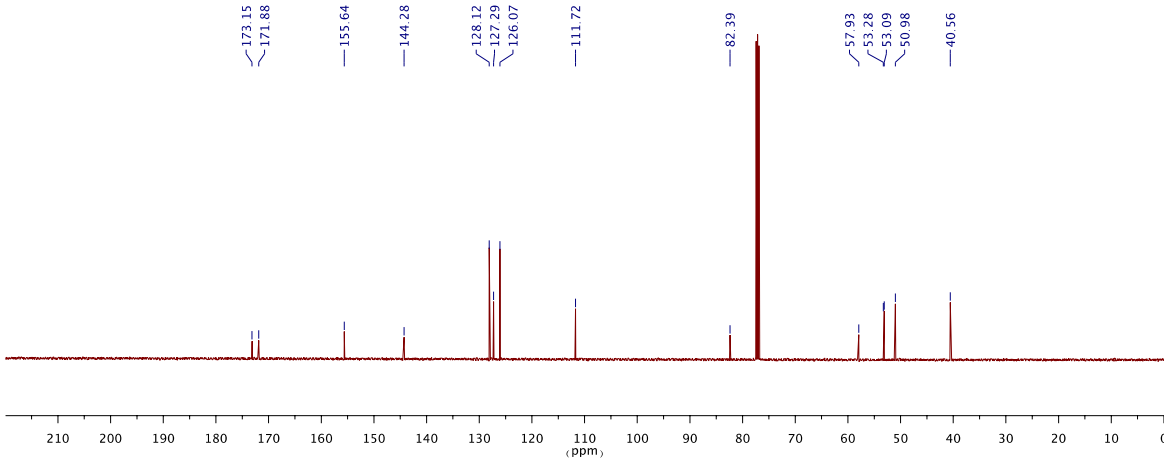


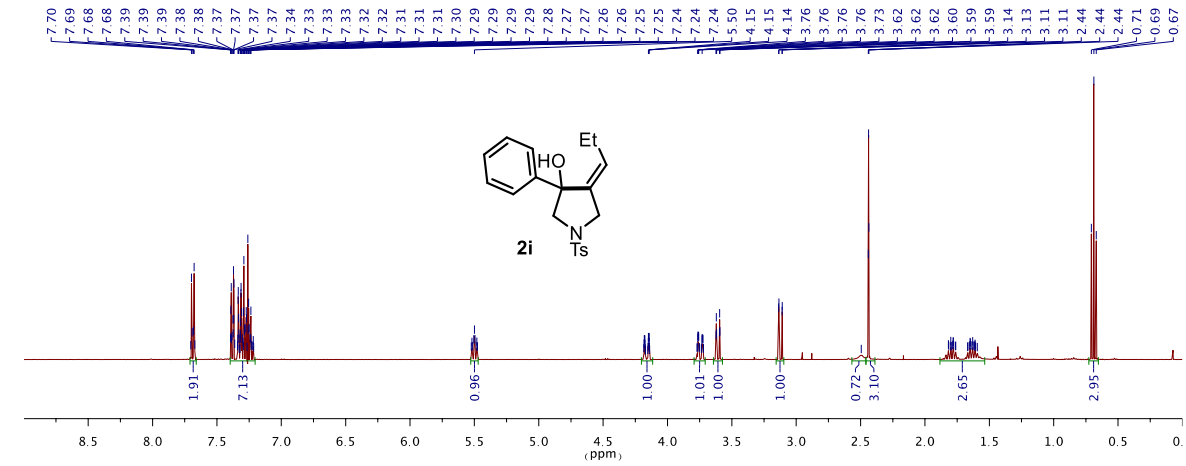


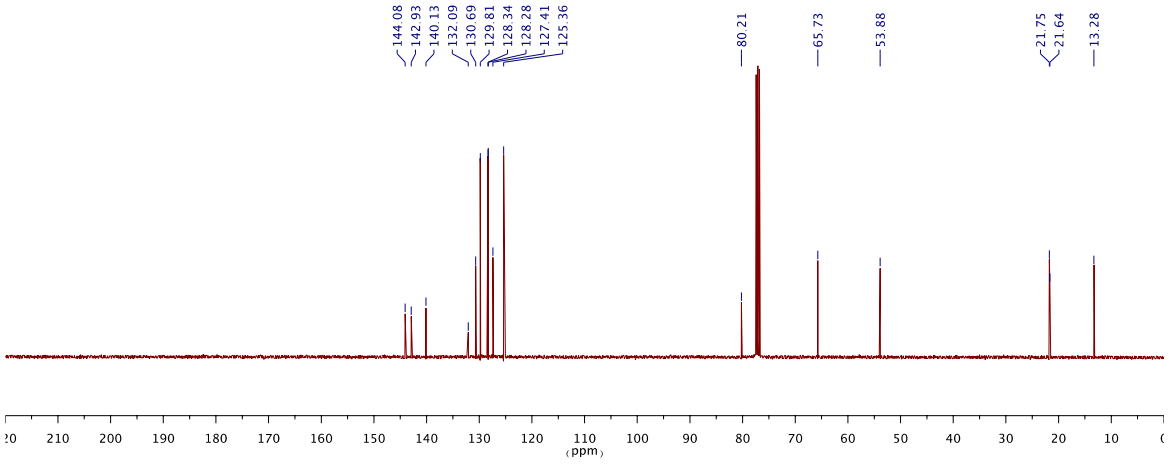

HO
O
2g
1.89
1.92
0.94
1.00
1.00
1.00
1.00
1.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

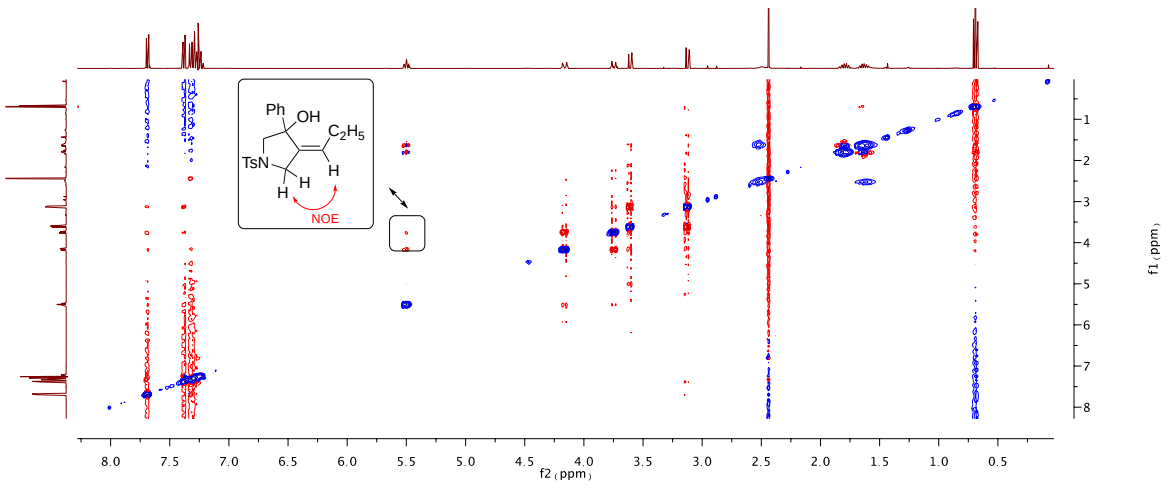

155.40
141.44
128.28
127.60
126.24
108.19
82.15
81.62
71.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

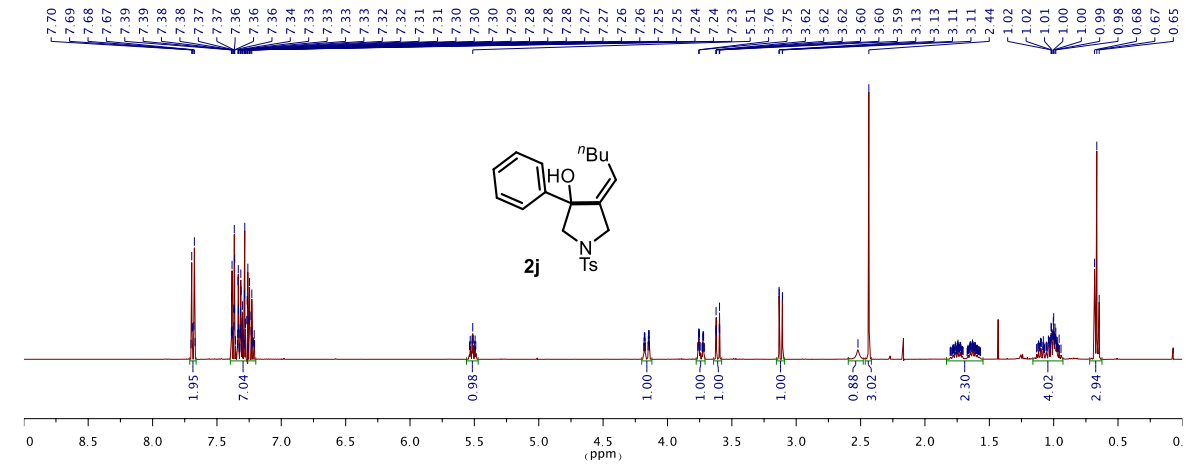

HO
MeOOC COOMe
2h
1.89
1.96
1.65
1.00
0.98
2.85
2.86
1.01
1.02
1.03
1.01
0.89
(ppm)

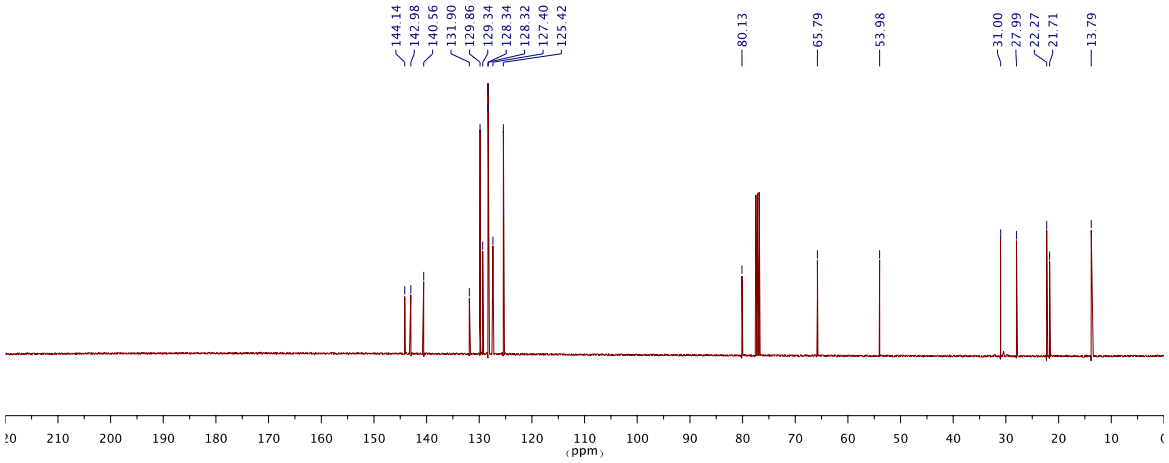

173.15
171.88
155.64
144.28
128.12
127.29
126.07
111.72
82.39
57.93
53.28
53.09
50.98
40.56
(ppm)

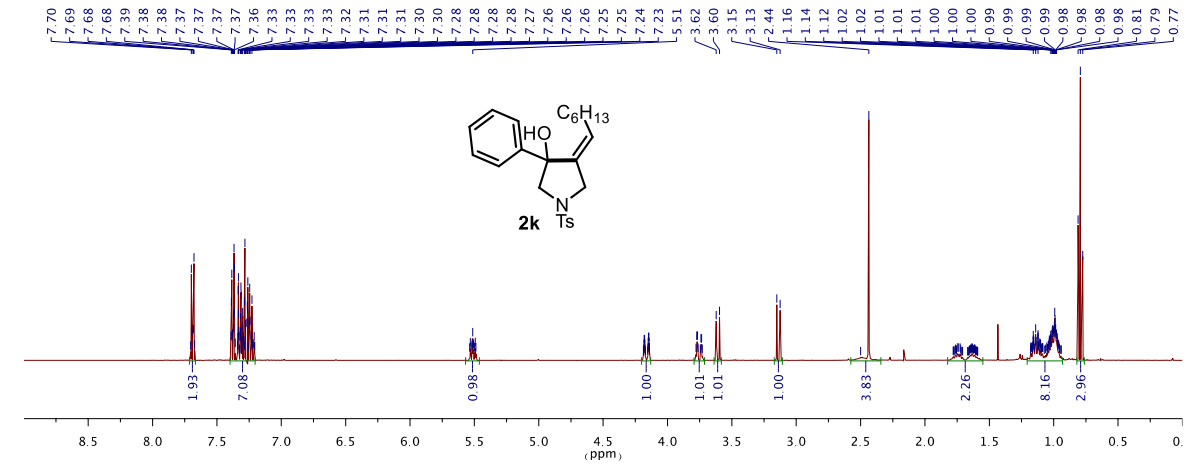

Et
HO
N
Ts
2i

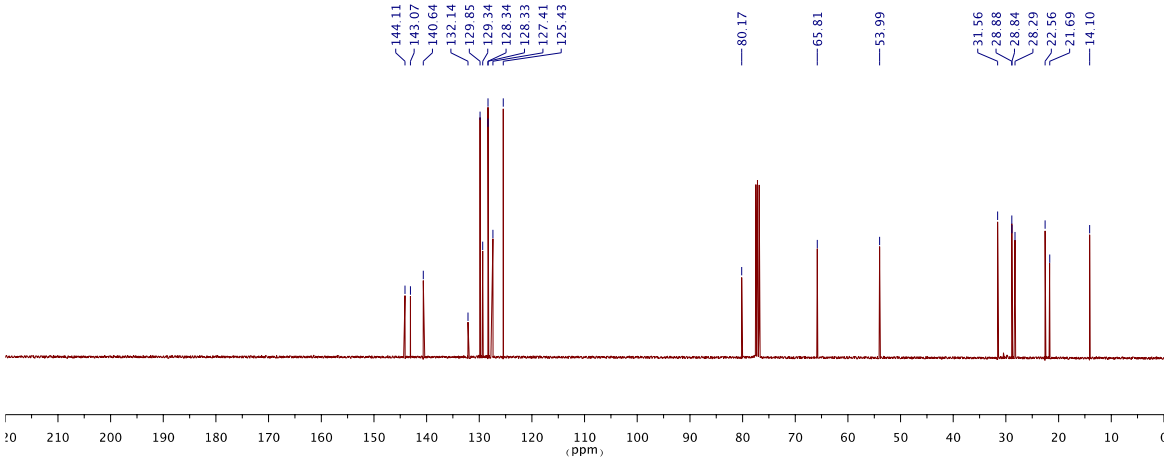


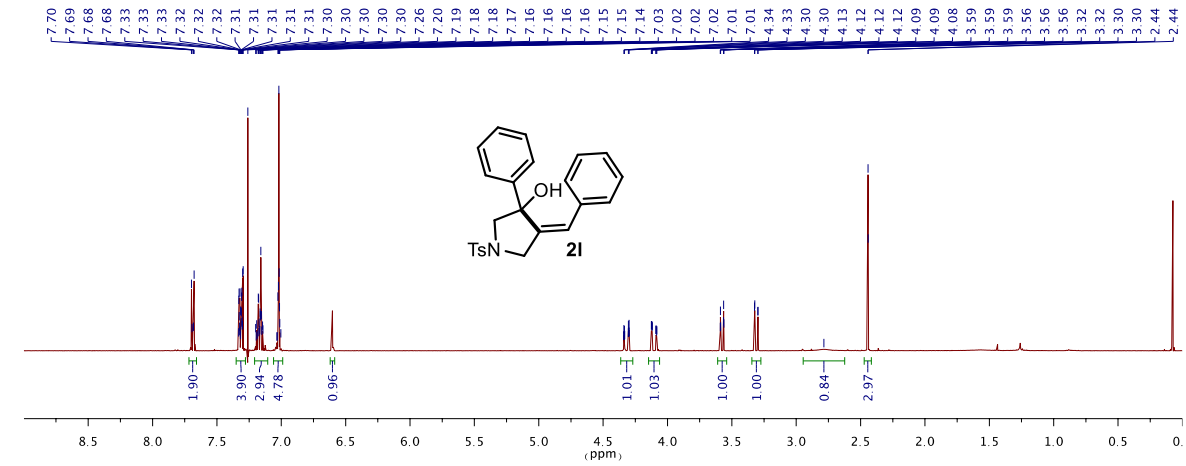

Ph
OH
C2H5
TsN
H
H
H
NOE

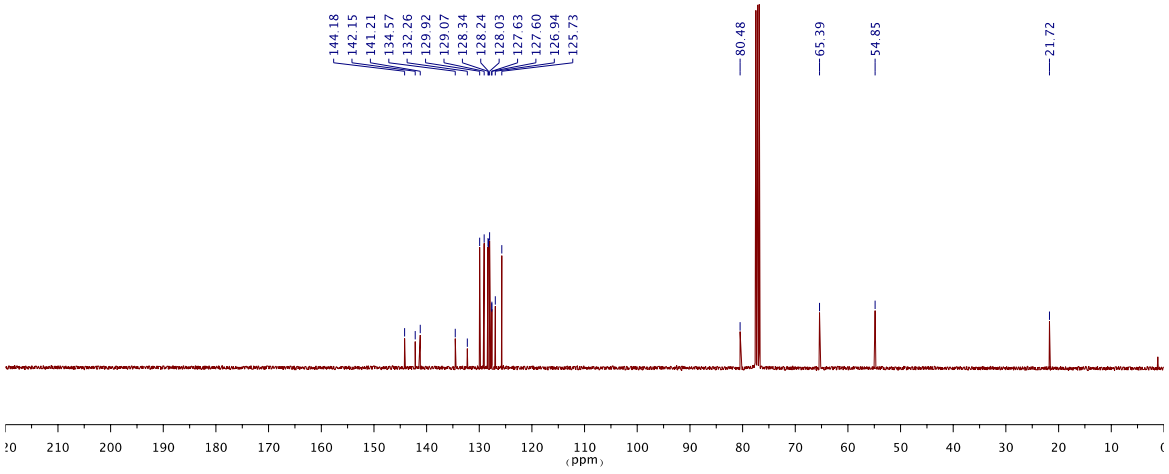

7.70 7.69 7.68 7.67 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.23 5.51 3.76 3.75 3.62 3.62 3.60 3.60 3.59 3.13 3.13 3.11 3.11 2.44 1.02 1.02 1.01 1.00 1.00 0.99 0.98 0.68 0.67 0.65
HO
nBu
N
Ts
2j
1.95 7.04 0.98 1.00 1.00 1.00 1.00 0.88 3.02 2.30 4.02 2.94
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
(ppm)

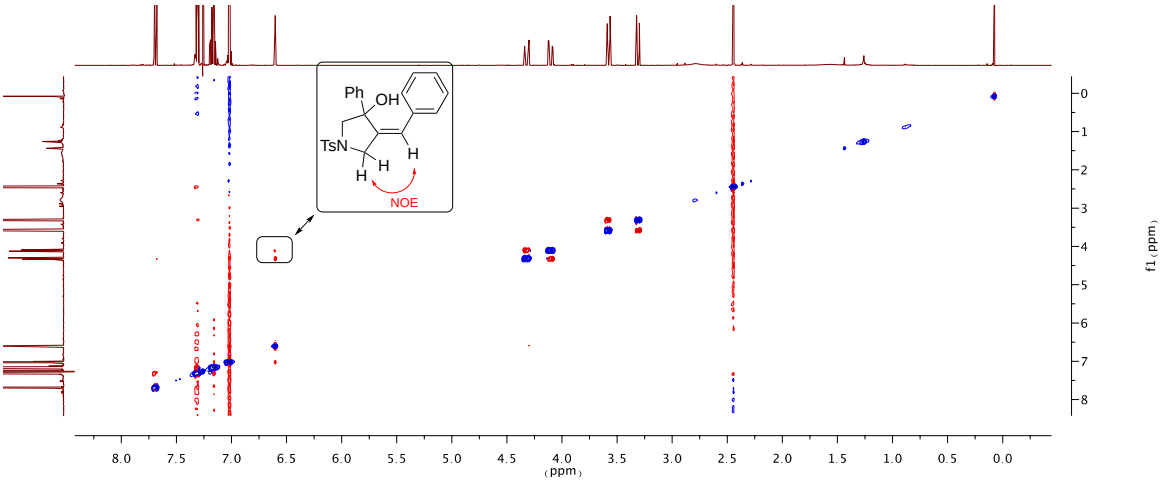

144.14 142.98 140.56 131.90 129.86 129.34 128.34 128.32 127.40 125.42 80.13 65.79 53.98 31.00 27.99 22.27 21.71 13.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

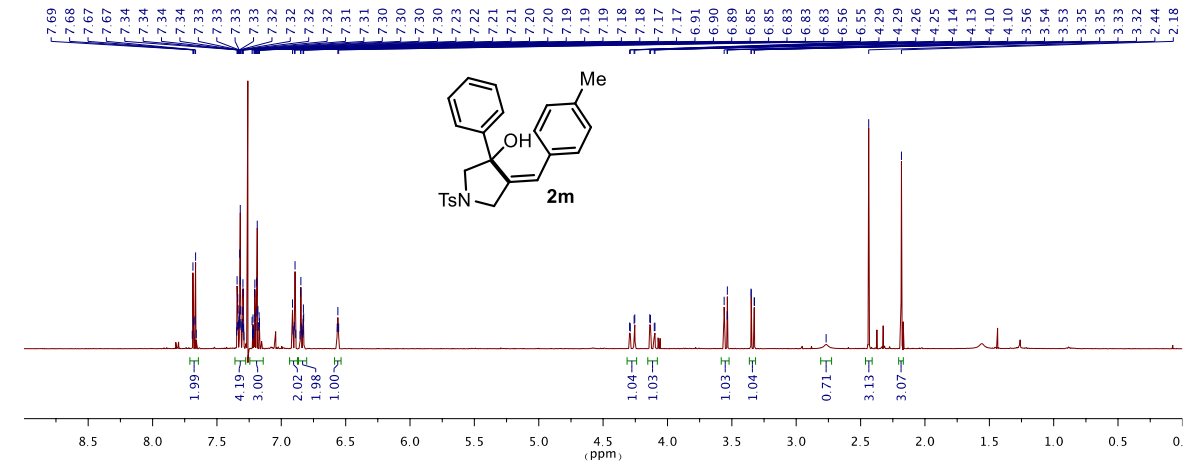

7.70 7.69 7.68 7.68 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.28 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.23 5.51 3.62 3.60 3.15 3.13 2.44 1.16 1.14 1.12 1.02 1.02 1.01 1.01 1.01 1.00 1.00 1.00 0.99 0.99 0.99 0.99 0.98 0.98 0.98 0.98 0.81 0.79 0.77
C6H13
HO
N
Ts
2k
1.93 7.08 0.98 1.00 1.01 1.01 1.00 3.83 2.26 8.16 2.96
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
(ppm)

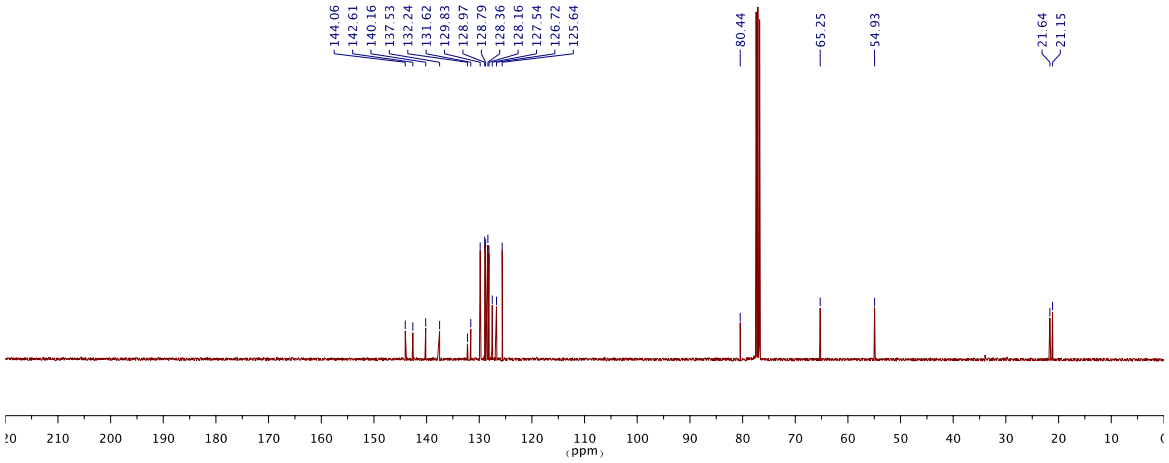

144.11 143.07 140.64 132.14 129.85 129.34 128.34 128.33 127.41 125.43
80.17 65.81 53.99
31.56 28.88 28.84 28.29 22.56 21.69 14.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

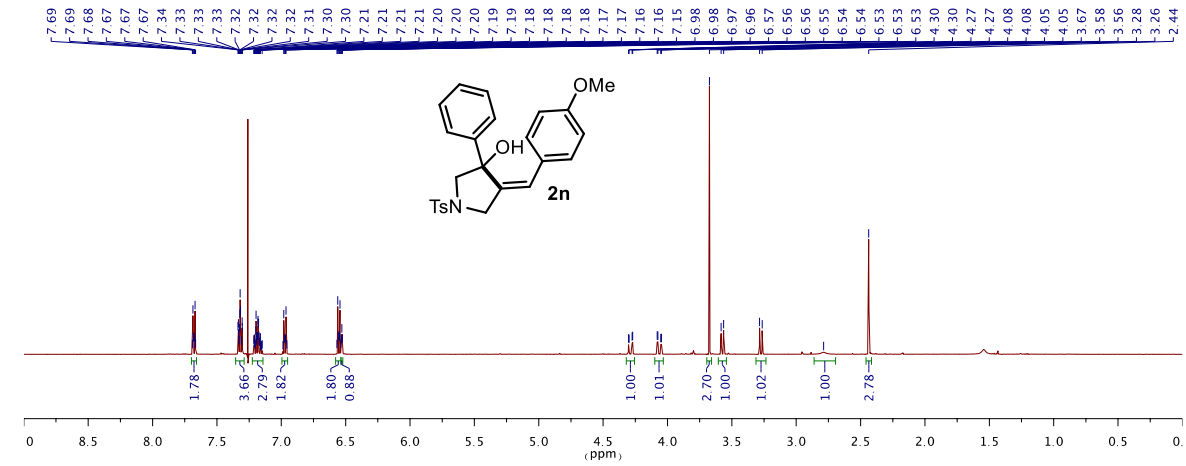

OH
TsN
2l
1.90
3.90
2.94
4.78
0.96
1.01
1.03
1.00
1.00
0.84
2.97
(ppm)

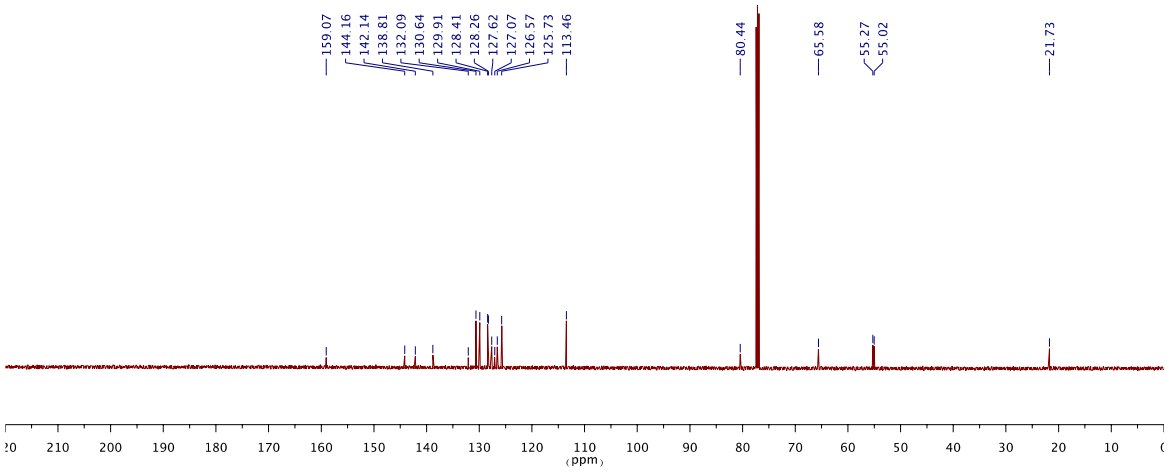

144.18
142.15
141.21
134.57
132.26
129.92
129.07
128.34
128.24
128.03
127.63
127.60
126.94
125.73
80.48
65.39
54.85
21.72
(ppm)

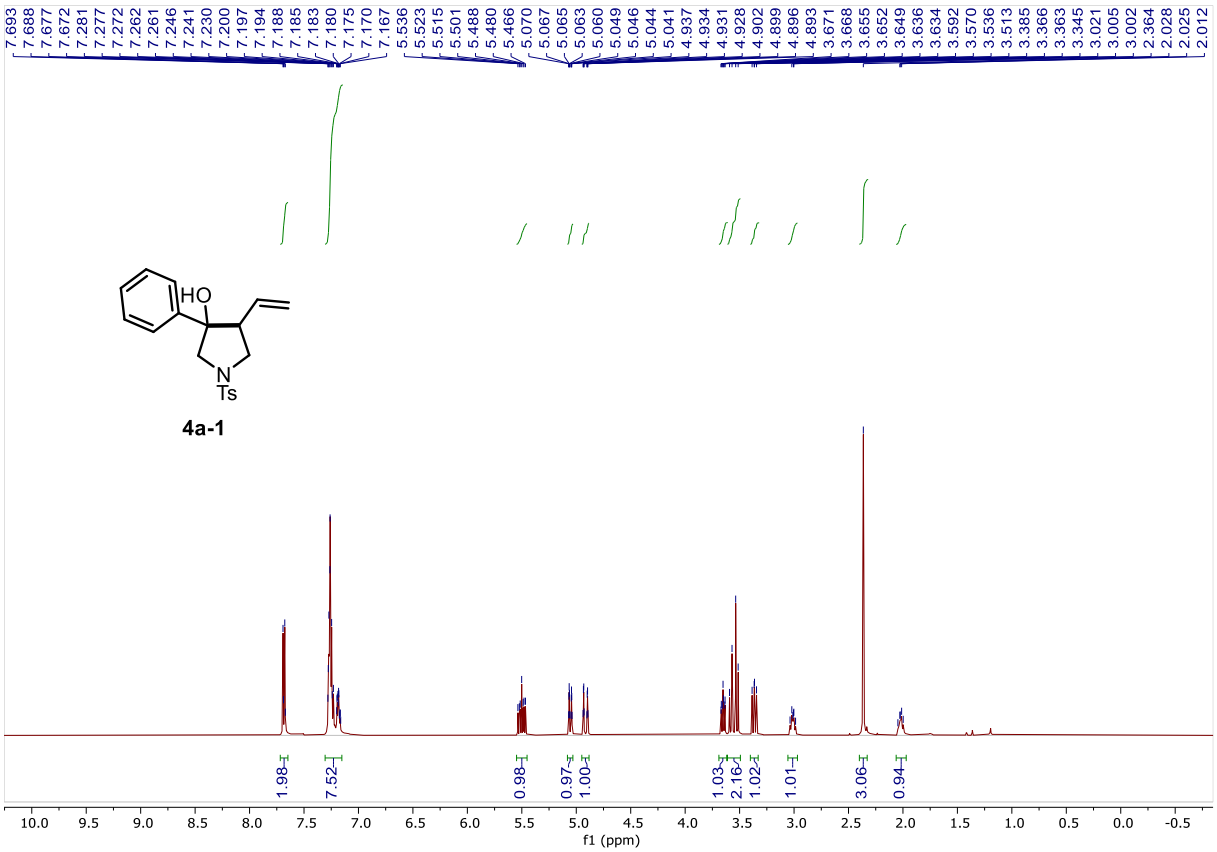

Ph
OH
TsN
H
H
H
NOE
(ppm)
f1 (ppm)

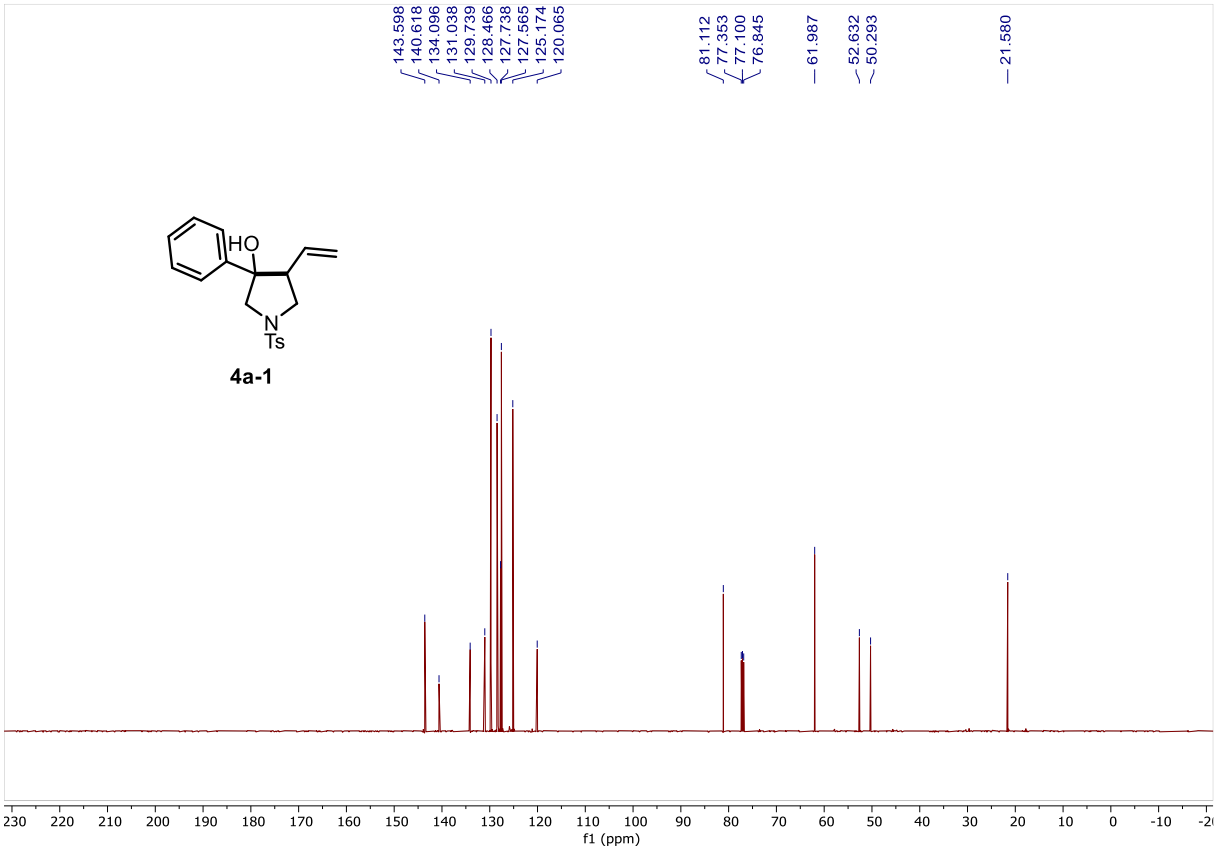

Me
OH
TsN
2m
(ppm)

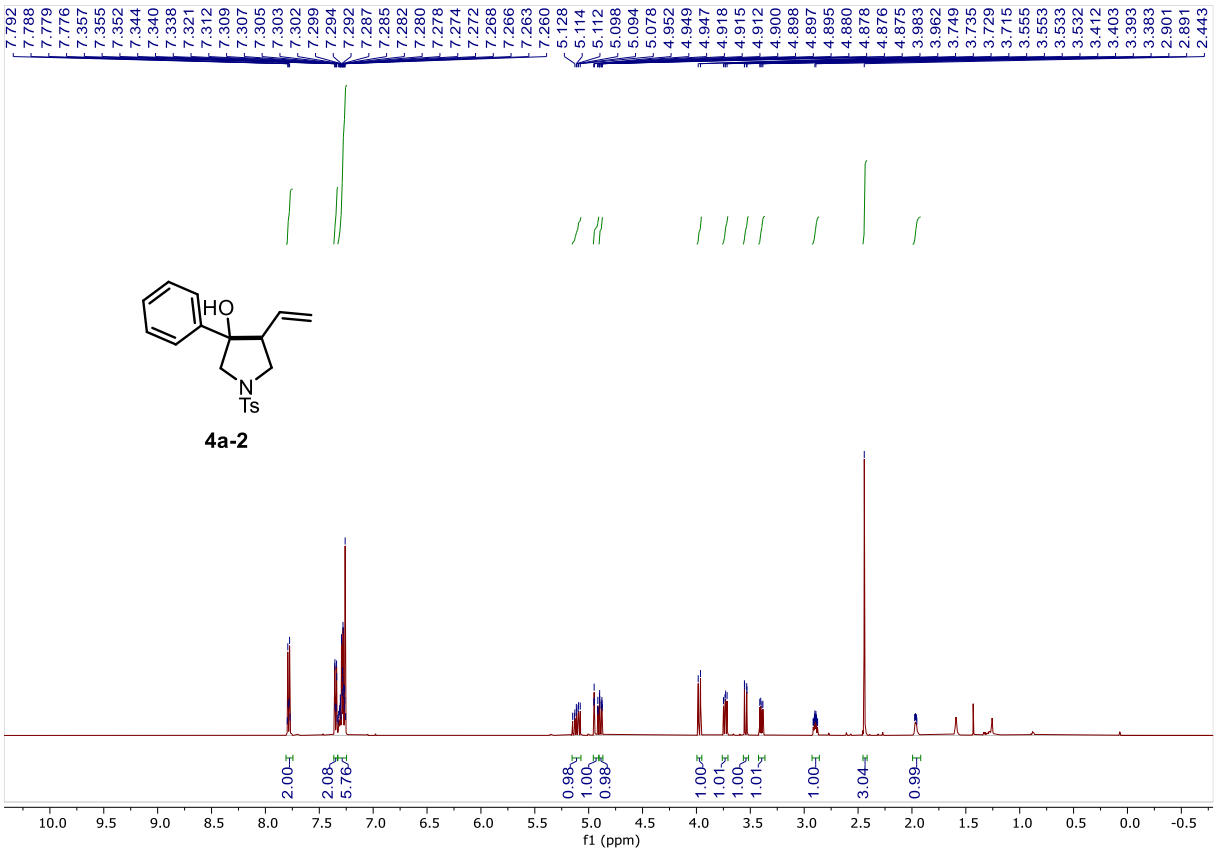

(ppm)

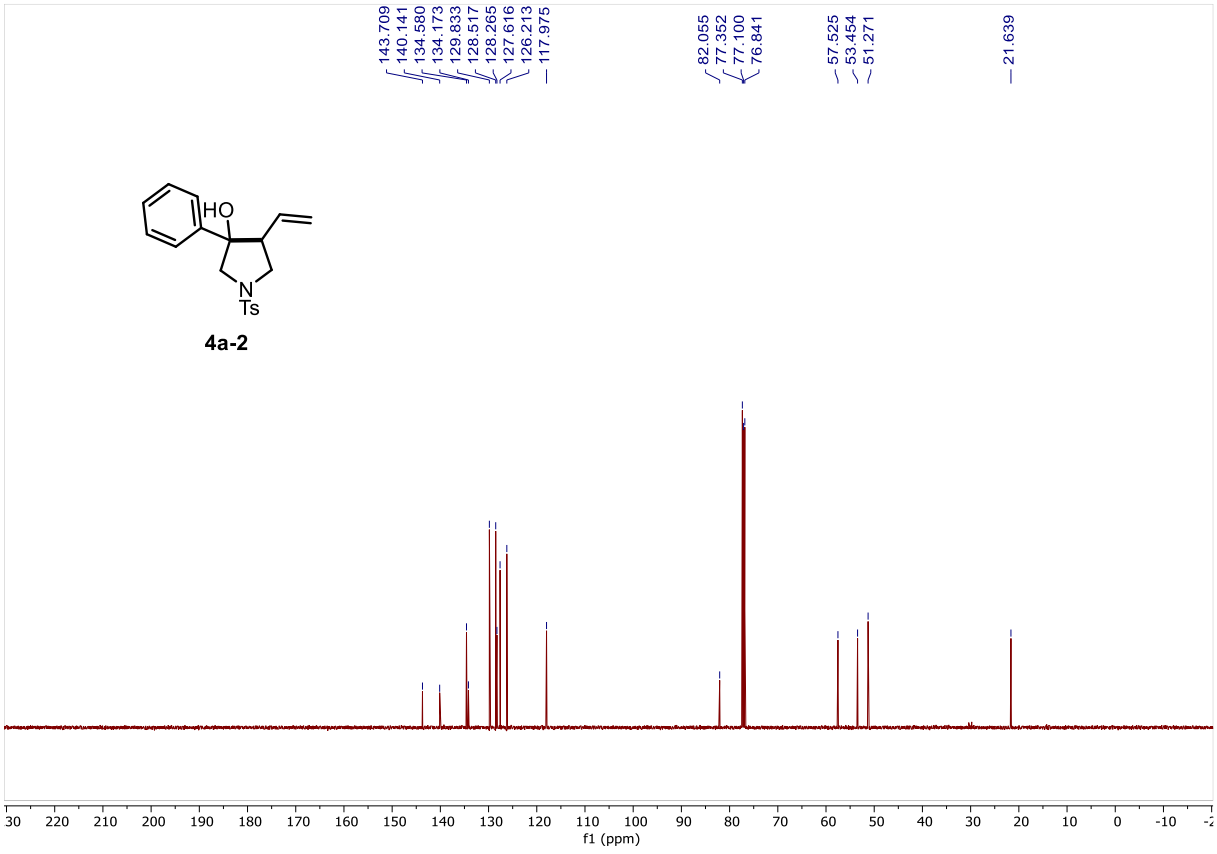

OMe
OH
TsN
2n
1.78
3.66
2.79
1.82
1.80
0.88
1.00
1.01
2.70
1.00
1.02
1.00
2.78
(ppm)

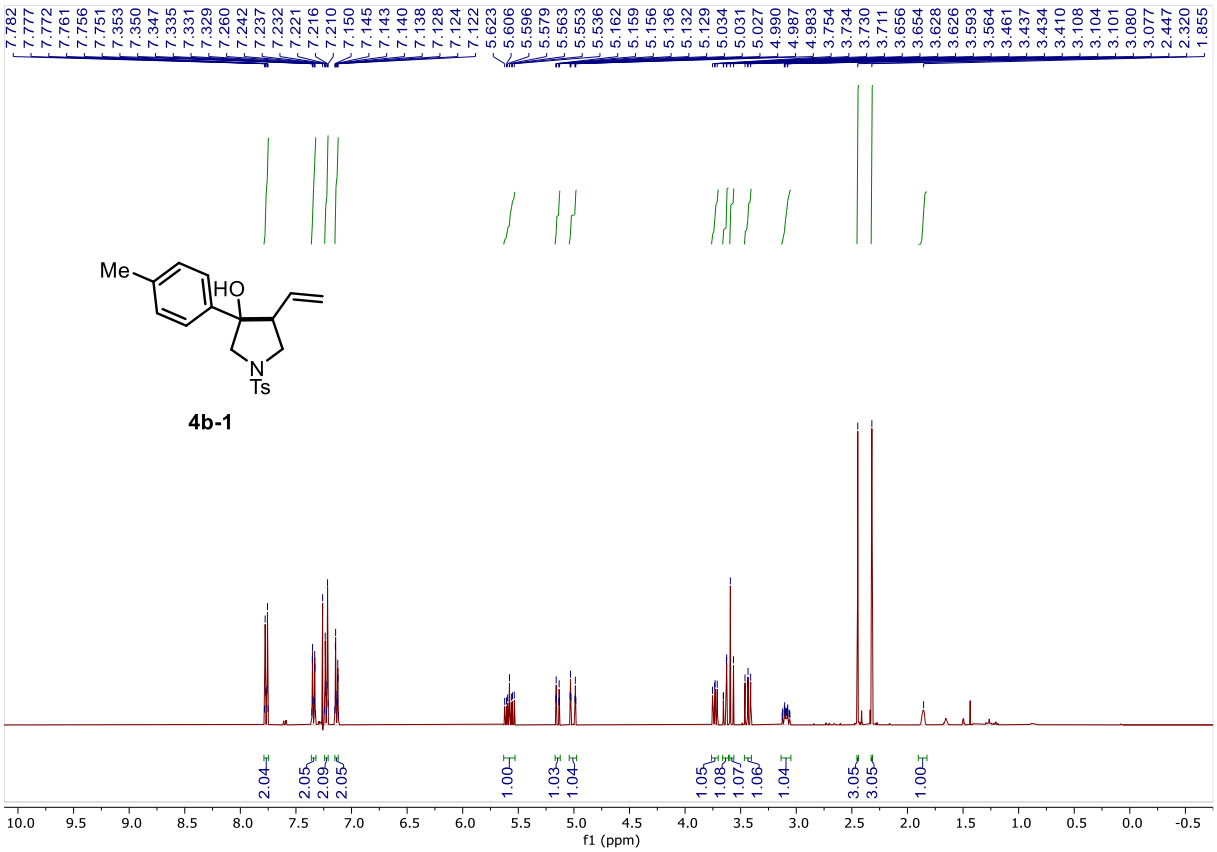

159.07
144.16
142.14
138.81
132.09
130.64
129.91
128.41
128.26
127.62
127.07
126.57
125.73
113.46
80.44
65.58
55.27
55.02
21.73
(ppm)

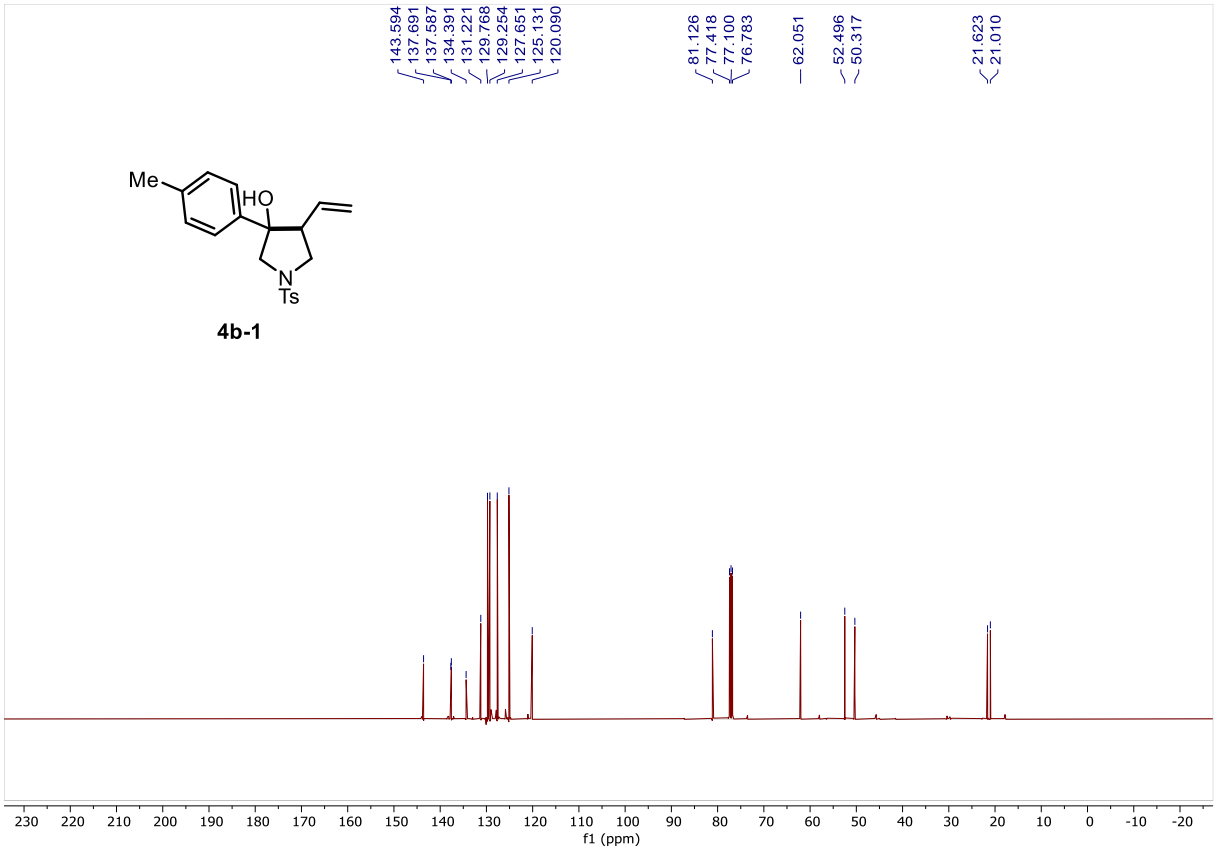

7.693
7.688
7.677
7.672
7.281
7.277
7.272
7.262
7.261
7.246
7.241
7.230
7.200
7.197
7.194
7.188
7.185
7.183
7.180
7.175
7.170
7.167
5.536
5.523
5.515
5.501
5.488
5.480
5.466
5.070
5.067
5.065
5.063
5.060
5.049
5.046
5.044
5.041
4.937
4.934
4.931
4.928
4.902
4.899
4.896
4.893
3.671
3.668
3.655
3.652
3.649
3.636
3.634
3.592
3.570
3.536
3.513
3.385
3.366
3.363
3.345
3.021
3.005
3.002
2.364
2.028
2.025
2.012
HO
N
Ts
4a-1
1.98
7.52
0.98
0.97
1.00
1.03
2.16
1.02
1.01
3.06
0.94
f1 (ppm)

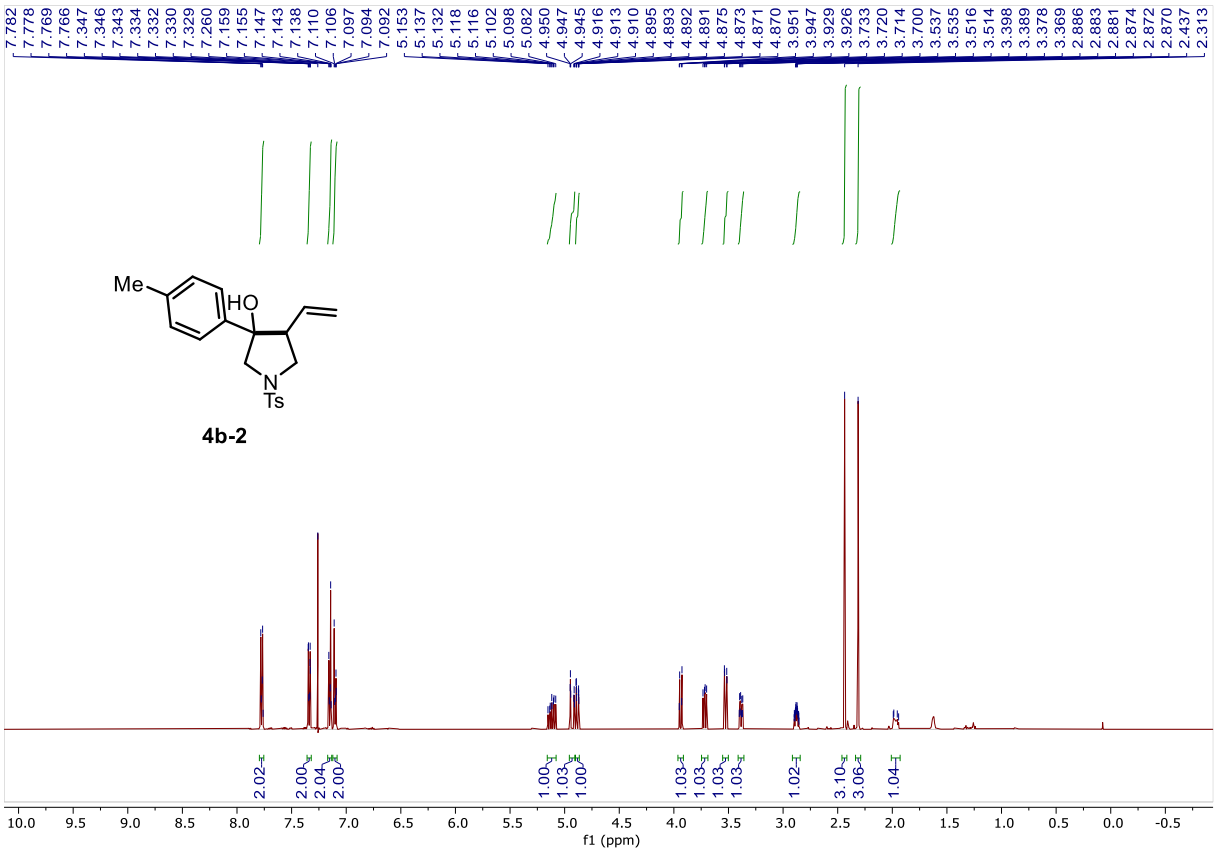

143.598
140.618
134.096
131.038
129.739
128.466
127.738
127.565
125.174
120.065
81.112
77.353
77.100
76.845
61.987
52.632
50.293
21.580
HO
N
Ts
4a-1
f1 (ppm)

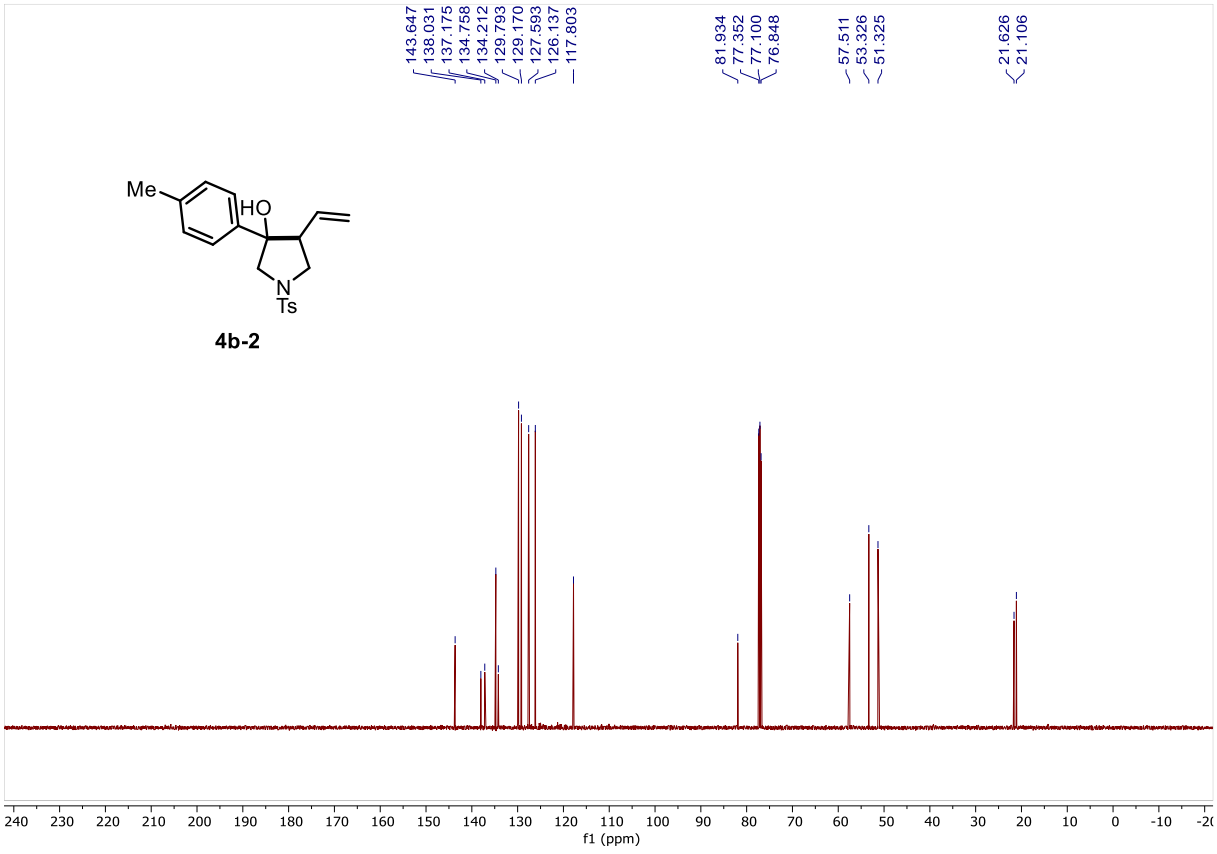

7.792
7.788
7.779
7.776
7.357
7.355
7.352
7.344
7.340
7.338
7.321
7.312
7.309
7.307
7.305
7.303
7.302
7.299
7.294
7.292
7.287
7.285
7.282
7.280
7.278
7.274
7.272
7.268
7.266
7.263
7.260
5.128
5.114
5.112
5.098
5.094
5.078
4.952
4.949
4.947
4.918
4.915
4.912
4.900
4.898
4.897
4.895
4.880
4.878
4.876
4.875
3.983
3.962
3.749
3.735
3.729
3.715
3.555
3.553
3.533
3.532
3.412
3.403
3.393
3.383
2.901
2.891
2.443
HO
N
Ts
4a-2
2.00
2.08
5.76
0.98
1.00
0.98
1.00
1.01
1.00
1.01
1.00
3.04
0.99
f1 (ppm)

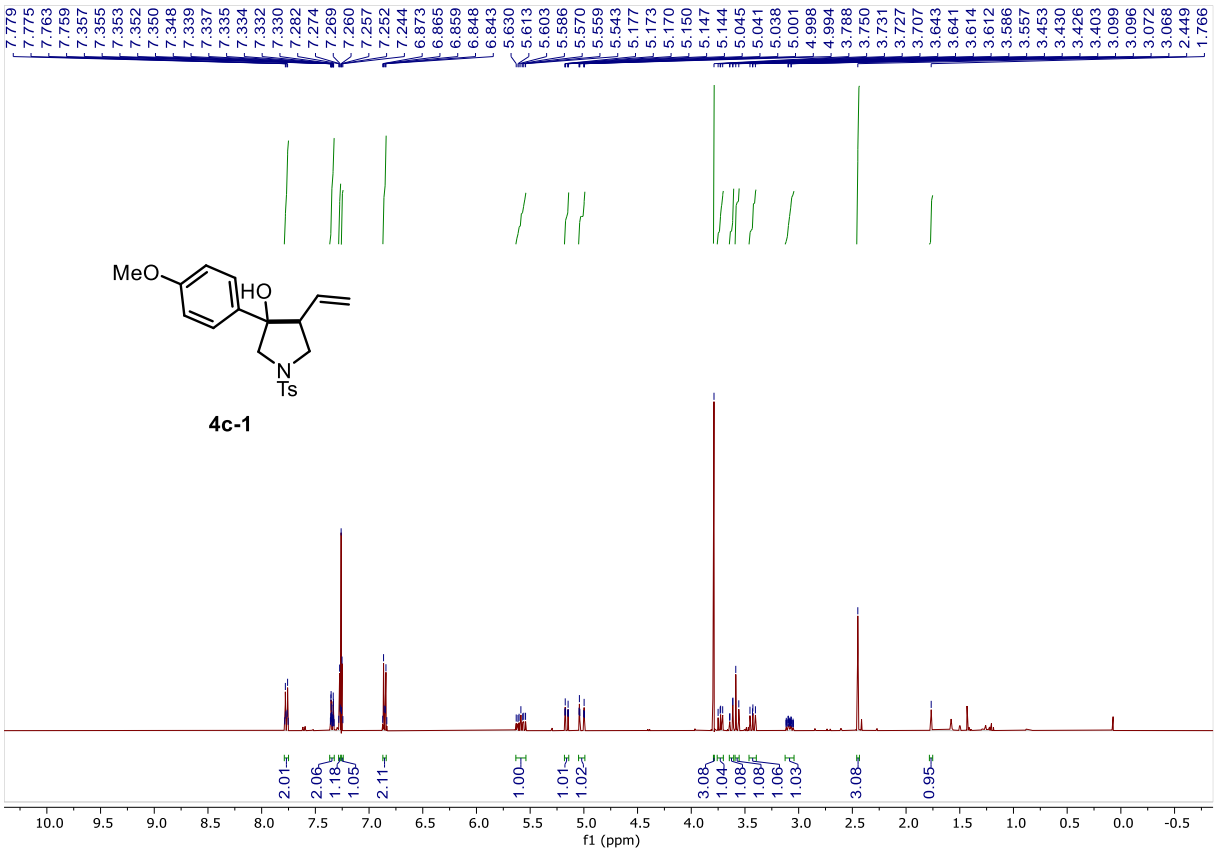

143.709
140.141
134.580
134.173
129.833
128.517
128.265
127.616
126.213
117.975
82.055
77.352
77.100
76.841
57.525
53.454
51.271
21.639
HO
N
Ts
4a-2
f1 (ppm)


7.782
7.777
7.772
7.761
7.756
7.751
7.353
7.350
7.347
7.335
7.331
7.329
7.260
7.242
7.237
7.232
7.221
7.216
7.210
7.150
7.145
7.143
7.140
7.138
7.128
7.124
7.122
5.623
5.606
5.596
5.579
5.563
5.553
5.536
5.162
5.159
5.156
5.136
5.132
5.129
5.034
5.031
5.027
4.990
4.987
4.983
3.754
3.734
3.730
3.711
3.656
3.654
3.628
3.626
3.593
3.564
3.461
3.437
3.434
3.410
3.108
3.104
3.101
3.080
3.077
2.447
2.320
1.855
Me
HO
N
Ts
4b-1
2.04
2.05
2.09
2.05
1.00
1.03
1.04
1.05
1.08
1.07
1.06
1.04
3.05
3.05
1.00
f1 (ppm)

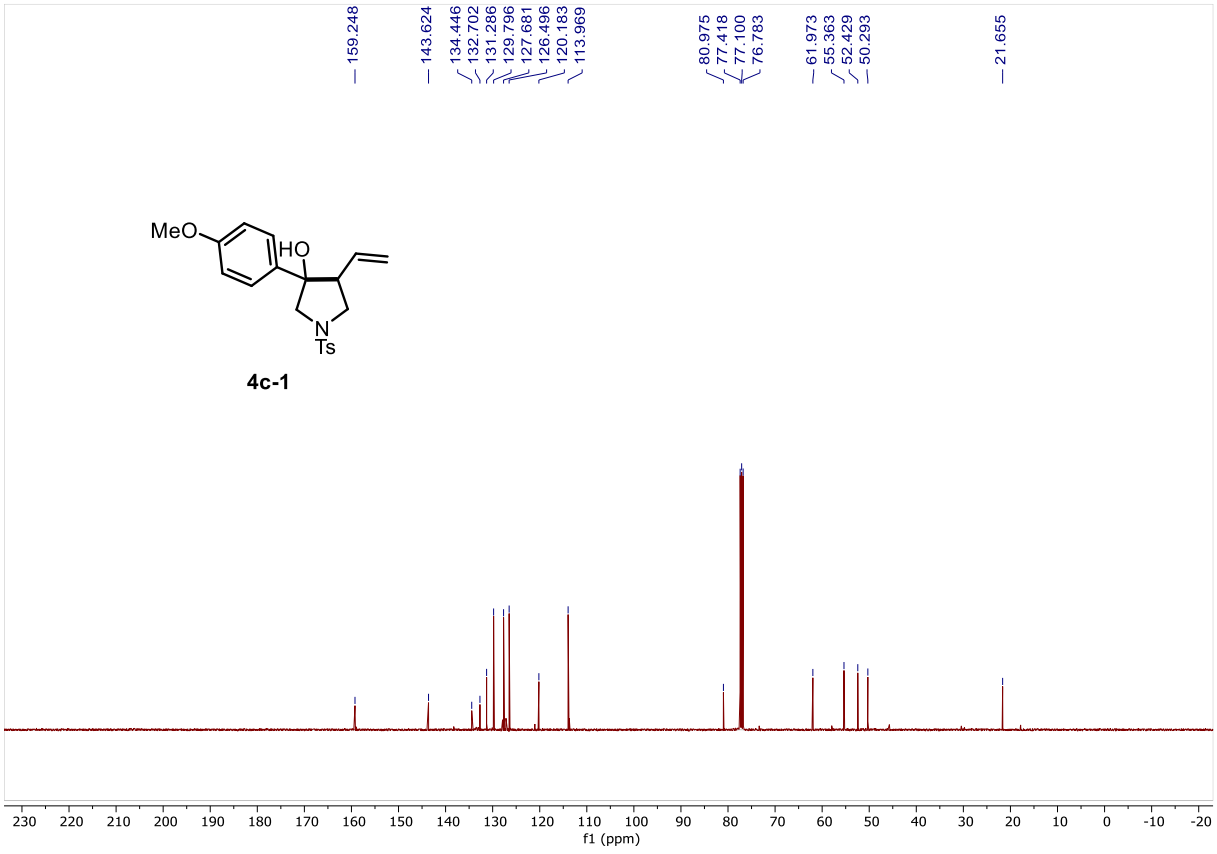

143.594
137.691
137.587
134.391
131.221
129.768
129.254
127.651
125.131
120.090
81.126
77.418
77.100
76.783
62.051
52.496
50.317
21.623
21.010
Me
HO
N
Ts
4b-1
f1 (ppm)


7.782 7.778 7.769 7.766 7.347 7.346 7.343 7.334 7.332 7.330 7.329 7.260 7.159 7.155 7.147 7.143 7.138 7.110 7.106 7.097 7.094 7.092
5.153 5.137 5.132 5.118 5.116 5.102 5.098 5.082 4.950 4.947 4.945 4.916 4.913 4.910 4.895 4.893 4.892 4.891 4.875 4.873 4.871 4.870
3.951 3.947 3.929 3.926 3.733 3.720 3.714 3.700 3.537 3.535 3.516 3.514 3.398 3.389 3.378 3.369 2.886 2.883 2.881 2.874 2.872 2.870 2.437 2.313
Me
HO
N
Ts
4b-2
2.02 2.00 2.04 2.00 1.00 1.03 1.00 1.03 1.03 1.03 1.02 3.10 3.06 1.04
f1 (ppm)

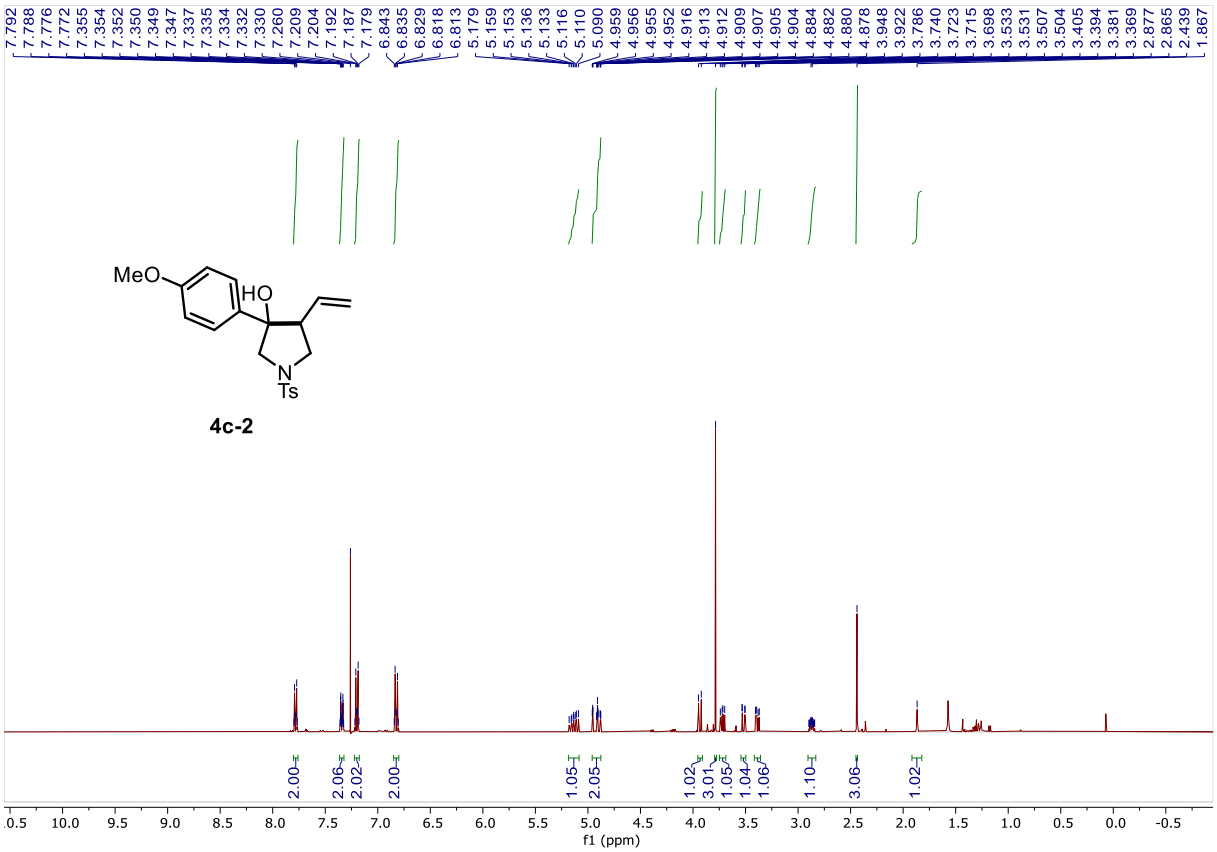

143.647 138.031 137.175 134.758 134.212 129.793 129.170 127.593 126.137 117.803
81.934 77.352 77.100 76.848
57.511 53.326 51.325
21.626 21.106
Me
HO
N
Ts
4b-2
f1 (ppm)

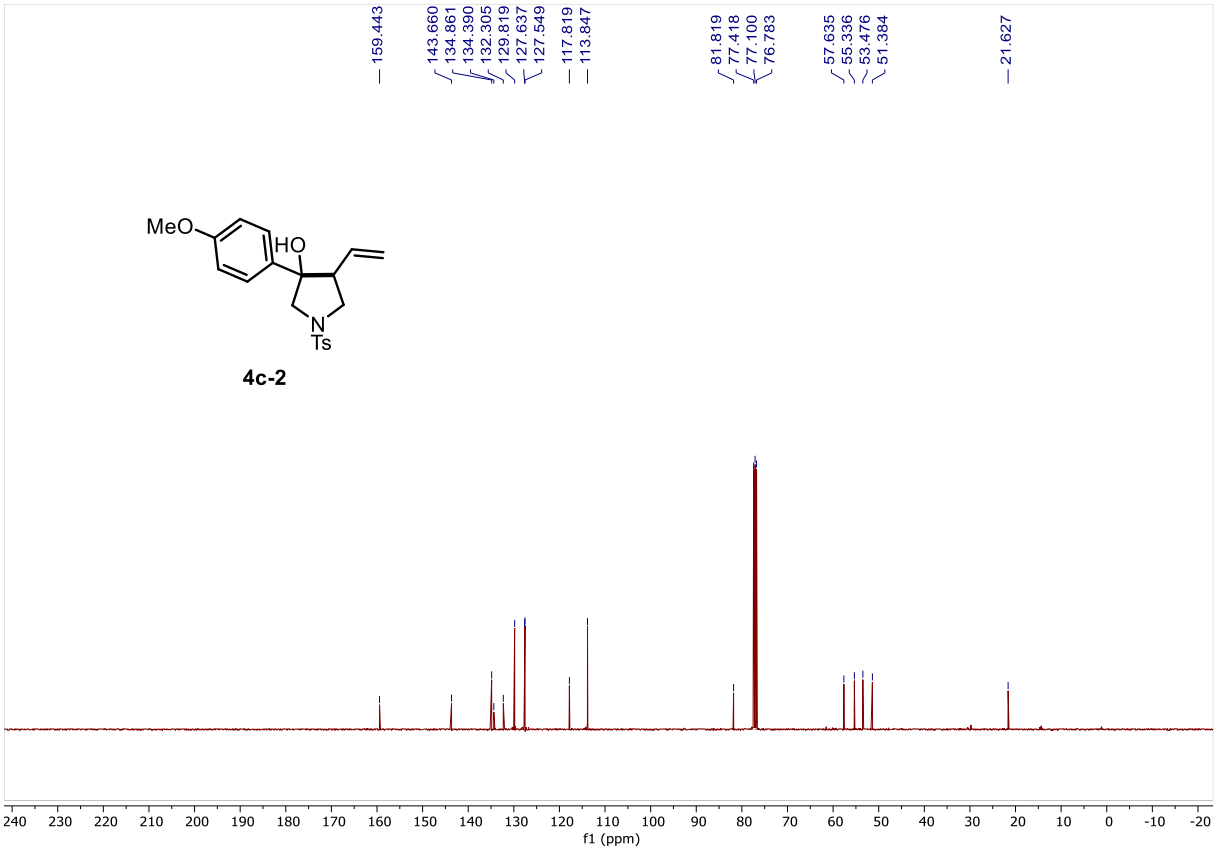

7.779
7.775
7.763
7.759
7.357
7.355
7.353
7.352
7.350
7.348
7.339
7.337
7.335
7.334
7.332
7.330
7.282
7.274
7.269
7.260
7.257
7.252
7.244
6.873
6.865
6.859
6.848
6.843
5.630
5.613
5.603
5.586
5.570
5.559
5.543
5.177
5.173
5.170
5.150
5.147
5.144
5.045
5.041
5.038
5.001
4.998
4.994
3.788
3.750
3.731
3.727
3.707
3.643
3.641
3.614
3.612
3.586
3.557
3.453
3.430
3.426
3.403
3.099
3.096
3.072
3.068
2.449
1.766
MeO
HO
N
Ts
2.01
2.06
1.18
1.05
2.11
1.00
1.01
1.02
3.08
1.04
1.08
1.08
1.06
1.03
3.08
0.95
f1 (ppm)

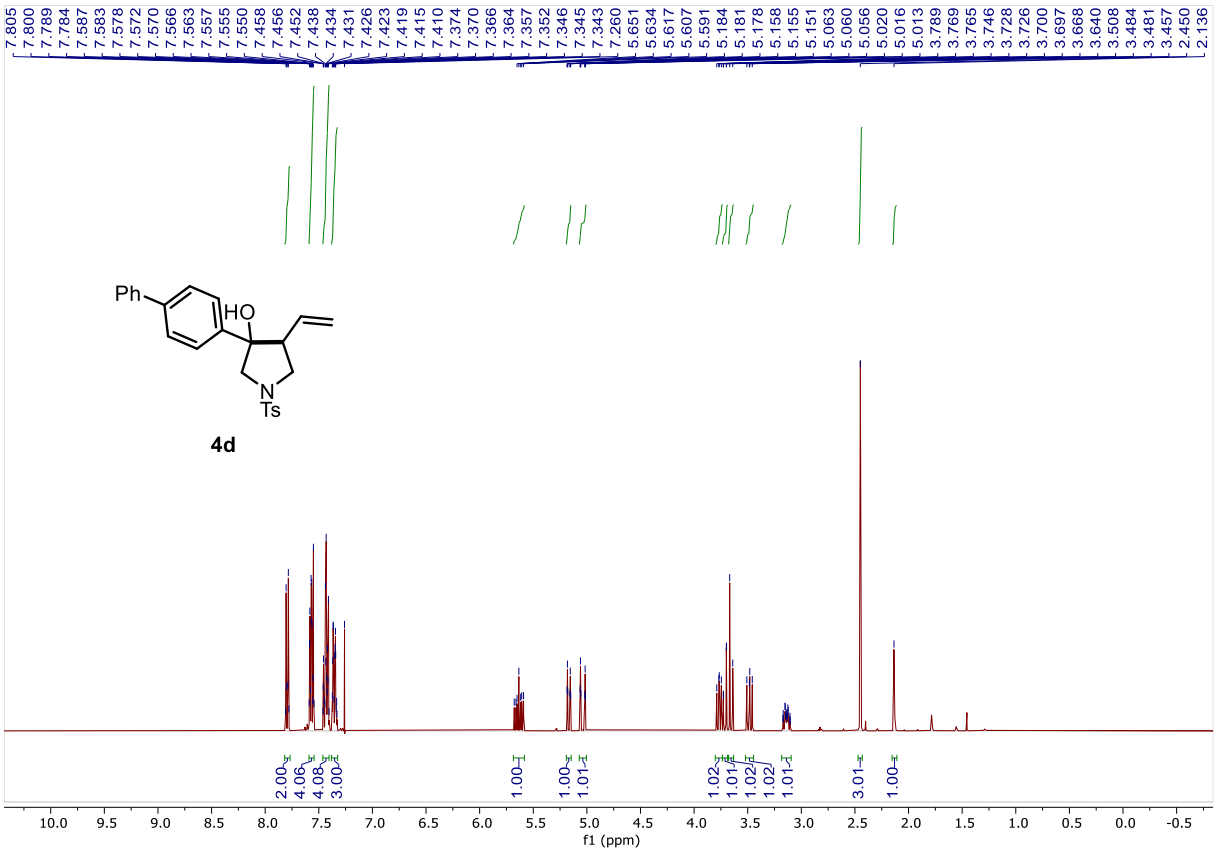
4c-1


159.248
143.624
134.446
132.702
131.286
129.796
127.681
126.496
120.183
113.969
80.975
77.418
77.100
76.783
61.973
55.363
52.429
50.293
21.655
MeO
HO
N
Ts
f1 (ppm)

4c-1


MeO
HO
N
Ts
4c-2
f1 (ppm)


MeO
HO
N
Ts
4c-2
f1 (ppm)


7.805
7.800
7.789
7.784
7.587
7.583
7.578
7.572
7.570
7.566
7.563
7.557
7.555
7.550
7.458
7.456
7.452
7.438
7.434
7.431
7.426
7.423
7.419
7.415
7.410
7.374
7.370
7.366
7.364
7.357
7.352
7.346
7.345
7.343
7.260
5.651
5.634
5.617
5.607
5.591
5.184
5.181
5.178
5.158
5.155
5.151
5.063
5.060
5.056
5.020
5.016
5.013
3.789
3.769
3.765
3.746
3.728
3.726
3.700
3.697
3.668
3.640
3.508
3.484
3.481
3.457
2.450
2.136
Ph
HO
N
Ts
4d
2.00
4.06
4.08
3.00
1.00
1.00
1.01
1.02
1.01
1.02
1.02
1.01
3.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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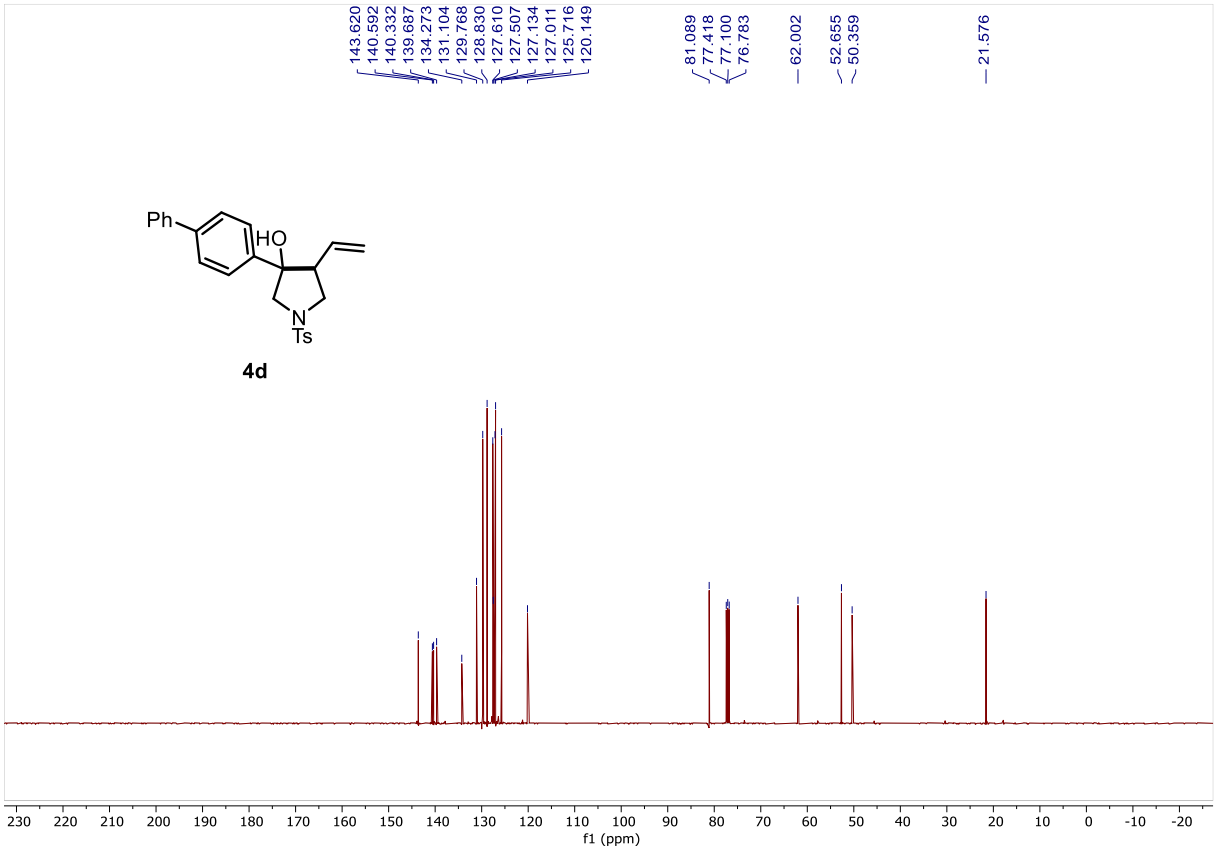
f1 (ppm)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127.134
127.011
125.716
120.149
81.089
77.418
77.100
76.783
62.002
52.655
50.359
21.576
Ph
HO
N
Ts
4d
230
220
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
20
10
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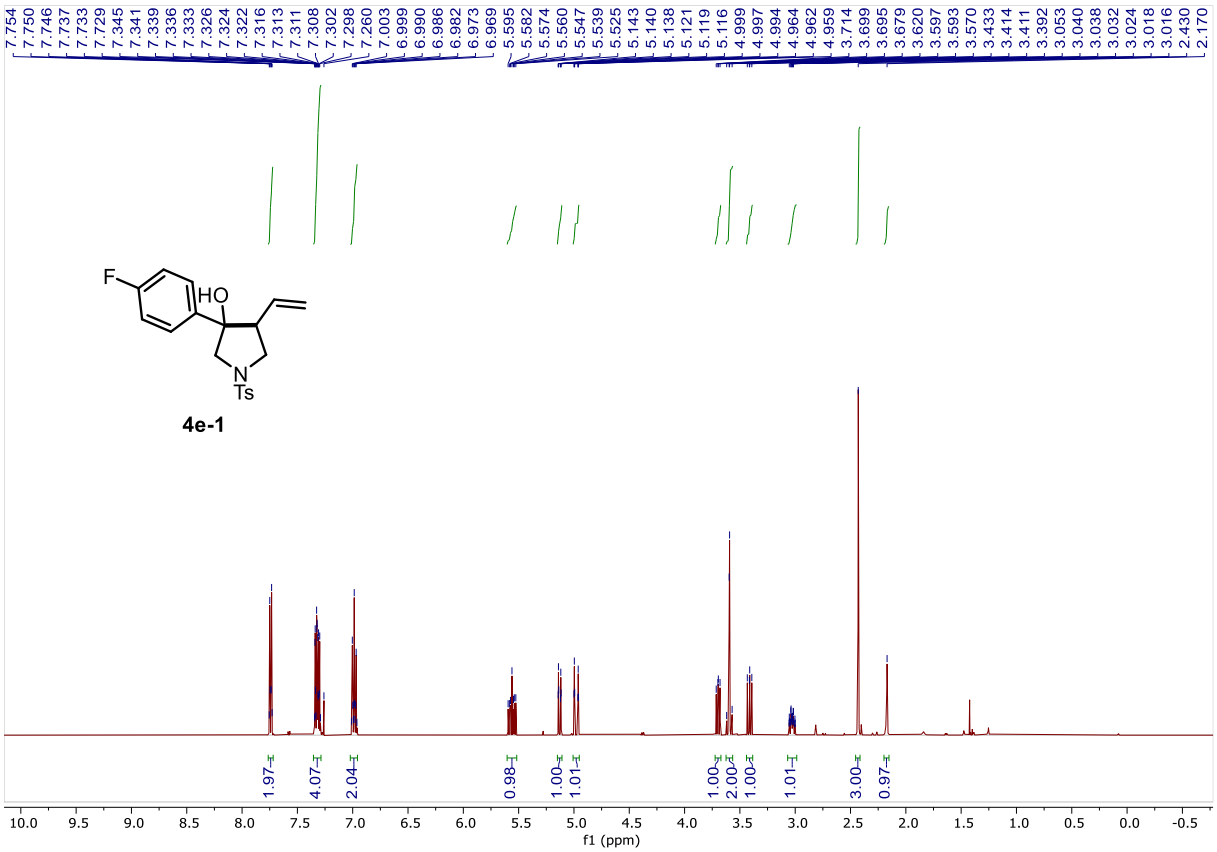
-10
-20
f1 (ppm)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7.324
7.322
7.316
7.313
7.311
7.308
7.302
7.298
7.260
7.003
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6.990
6.986
6.982
6.973
6.969
5.595
5.582
5.574
5.560
5.547
5.539
5.525
5.143
5.140
5.138
5.121
5.119
5.116
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4.997
4.994
4.964
4.962
4.959
3.714
3.699
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3.620
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3.593
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3.433
3.414
3.411
3.392
3.053
3.040
3.038
3.032
3.024
3.018
3.016
2.430
2.170
F
HO
N
Ts
4e-1
1.97
4.07
2.04
0.98
1.00
1.01
1.00
2.00
1.00
1.01
3.00
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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0.5
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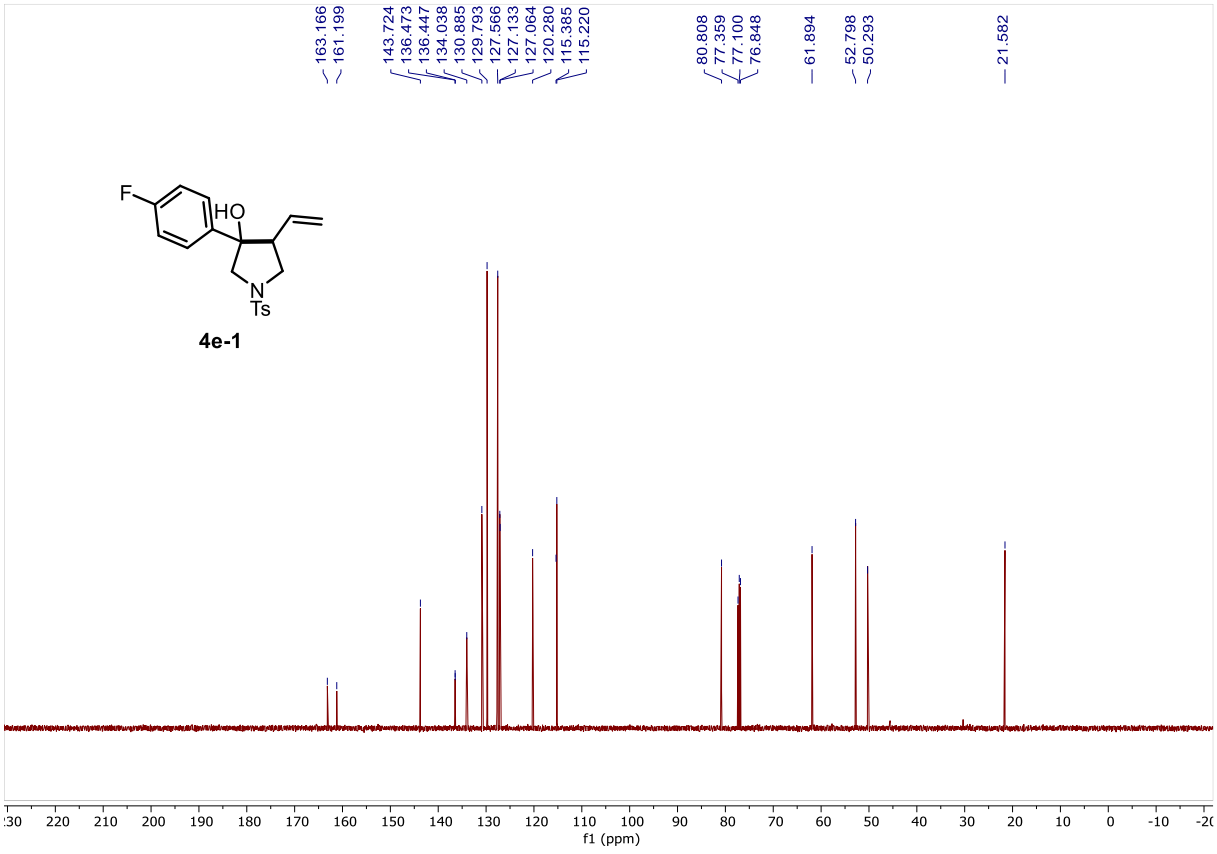
f1 (ppm)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115.385
115.220
80.808
77.359
77.100
76.848
61.894
52.798
50.293
21.582
F
HO
N
Ts
4e-1
220
210
200
190
180
170
160
150
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120
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100
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80
70
60
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40
30
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0
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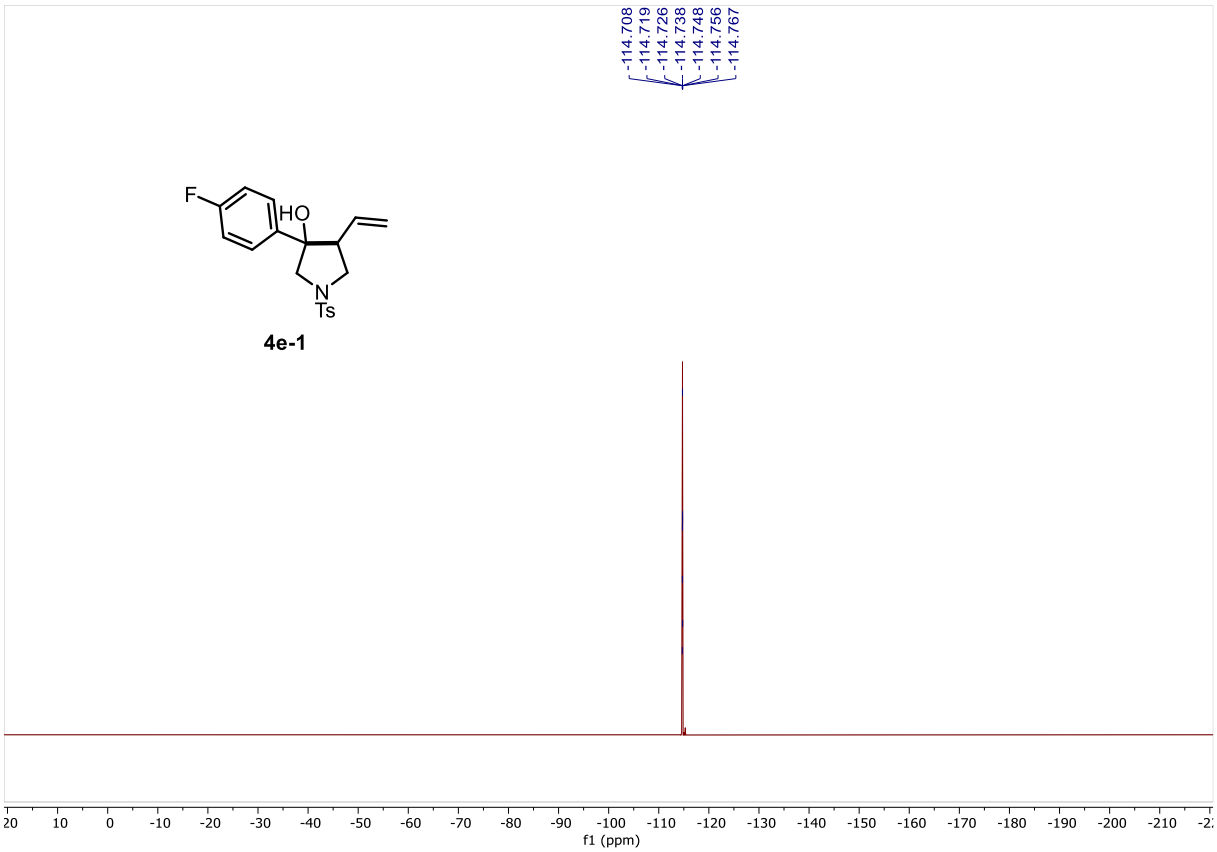
f1 (ppm)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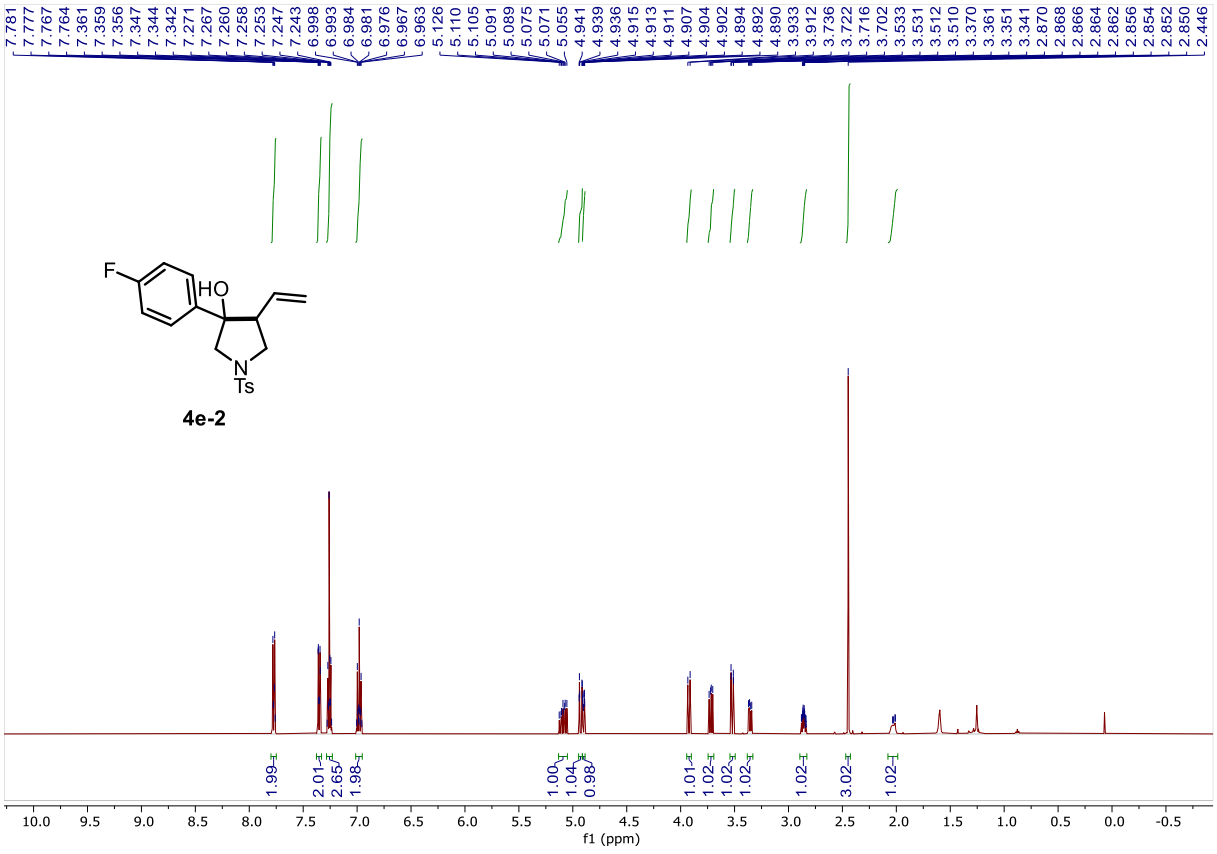
-114.767
F
HO
N
Ts
f1 (ppm)

4e-1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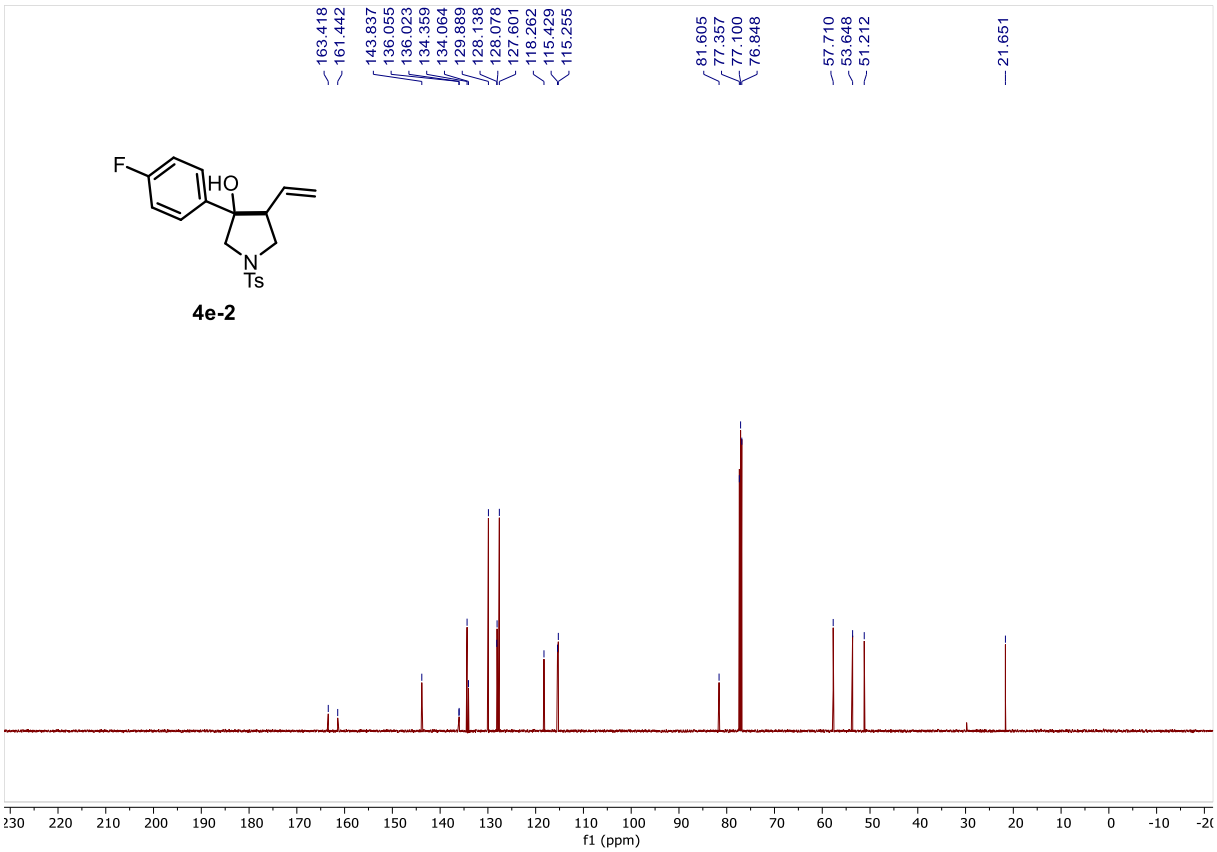
7.344
7.342
7.271
7.267
7.260
7.258
7.253
7.247
7.243
6.998
6.993
6.984
6.981
6.976
6.967
6.963
5.126
5.110
5.105
5.091
5.089
5.075
5.071
5.055
4.941
4.939
4.936
4.915
4.913
4.911
4.907
4.904
4.902
4.894
4.892
4.890
3.933
3.912
3.736
3.722
3.716
3.702
3.533
3.531
3.512
3.510
3.370
3.361
3.351
3.341
2.870
2.868
2.866
2.864
2.862
2.856
2.854
2.852
2.850
2.446
F
HO
N
Ts
1.99
2.01
2.65
1.98
1.00
1.04
0.98
1.01
1.02
1.02
1.02
1.02
3.02
1.02
f1 (ppm)

4e-2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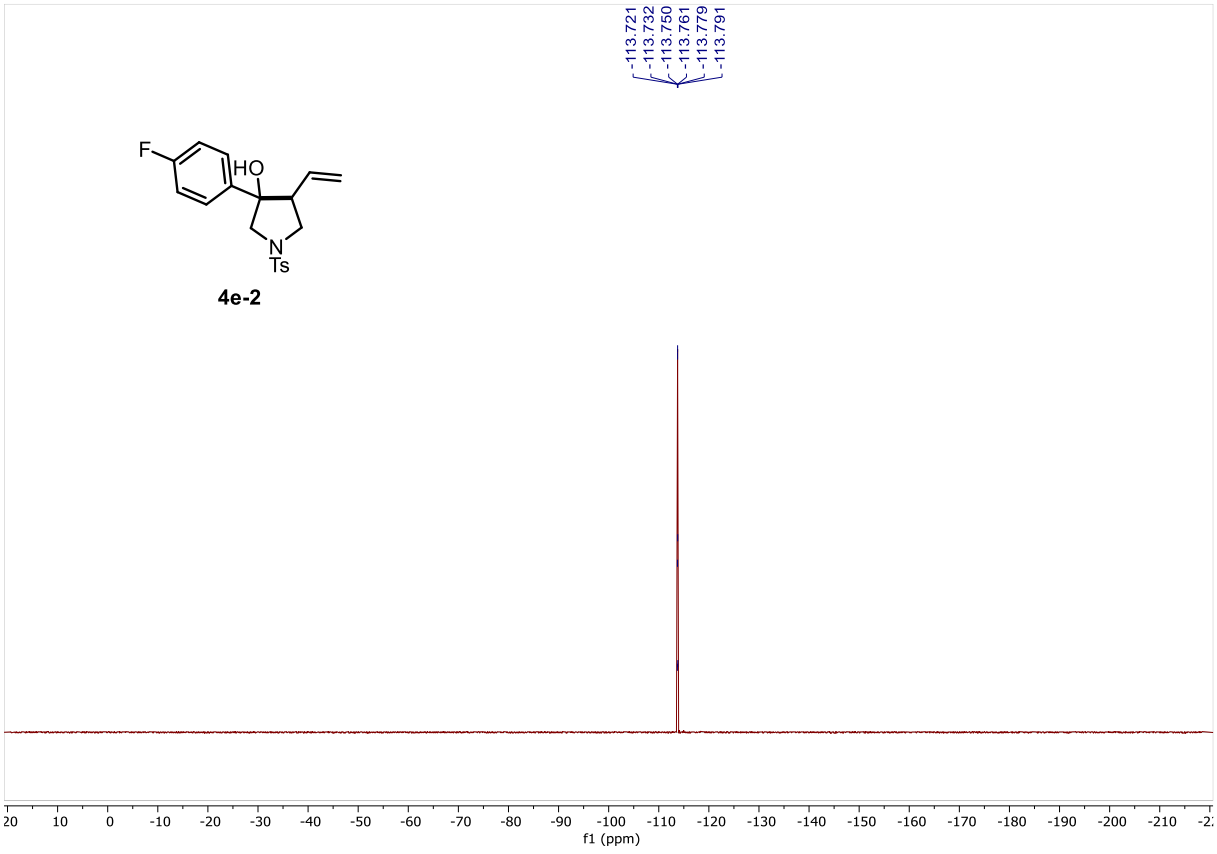
134.359
134.064
129.889
128.138
128.078
127.601
118.262
115.429
115.255
81.605
77.357
77.100
76.848
57.710
53.648
51.212
21.651
F
HO
N
Ts
4e-2
f1 (ppm)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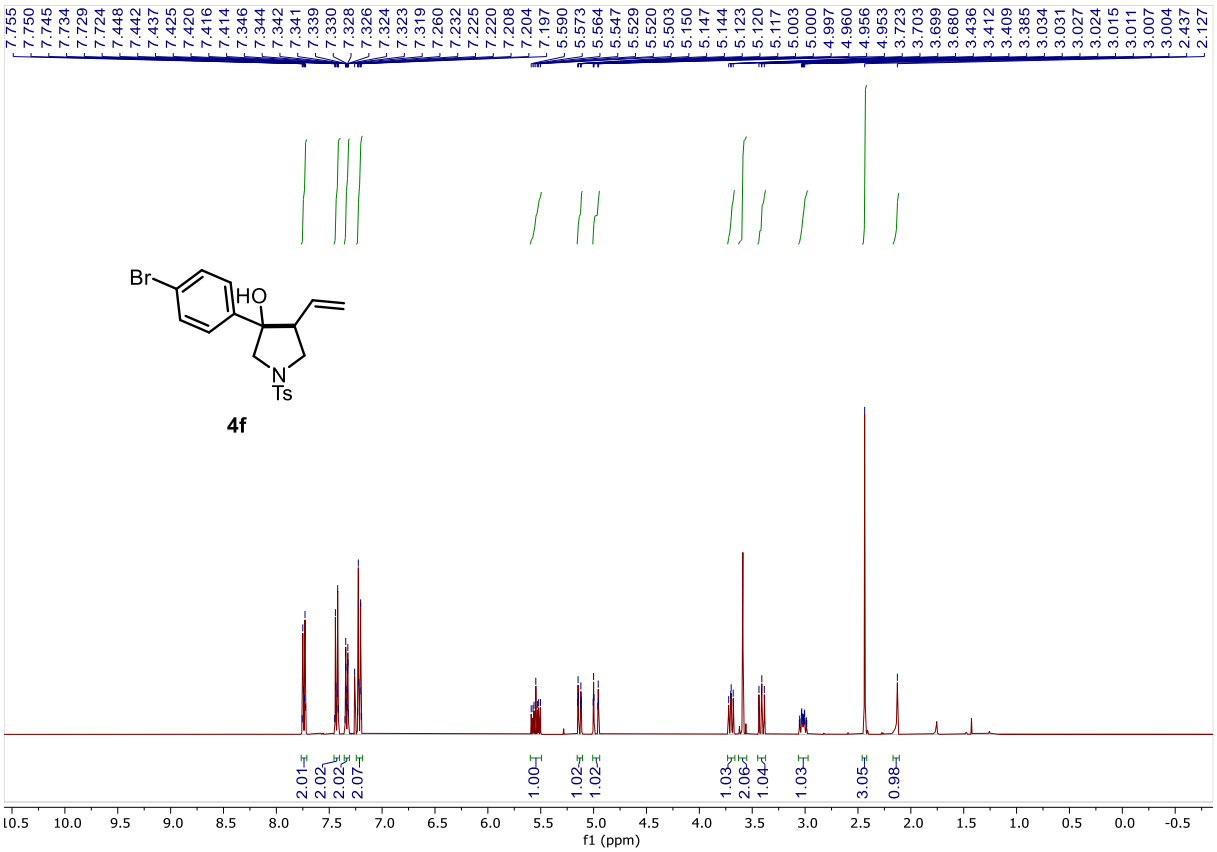
-113.750
-113.761
-113.779
-113.791
F
HO
N
Ts
4e-2
f1 (ppm)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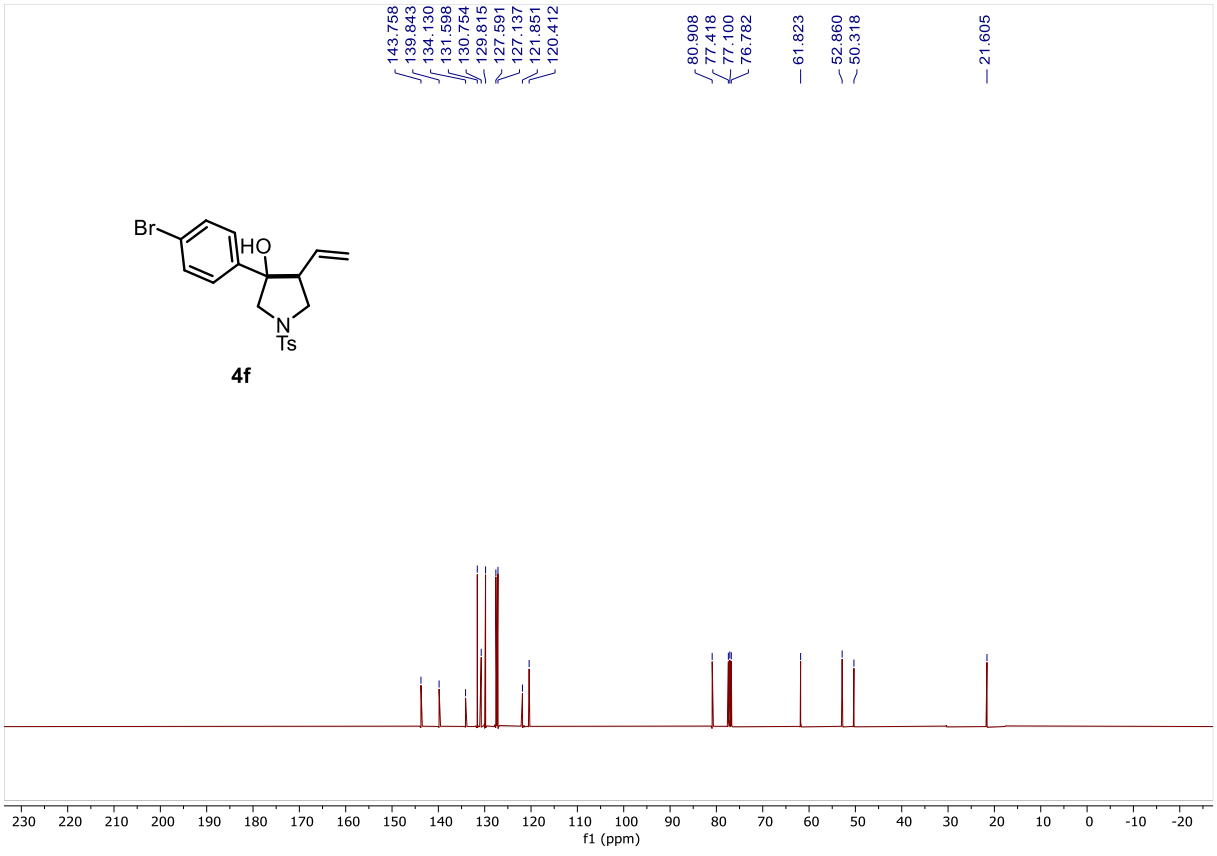
7.420
7.416
7.414
7.346
7.344
7.342
7.341
7.339
7.330
7.328
7.326
7.324
7.323
7.319
7.260
7.232
7.225
7.220
7.208
7.204
7.197
5.590
5.573
5.564
5.547
5.529
5.520
5.503
5.150
5.147
5.144
5.123
5.120
5.117
5.003
5.000
4.997
4.960
4.956
4.953
3.723
3.703
3.699
3.680
3.436
3.412
3.409
3.385
3.034
3.031
3.027
3.024
3.015
3.011
3.007
3.004
2.437
2.127
Br
HO
N
Ts
4f
2.01
2.02
2.02
2.07
1.00
1.02
1.02
1.03
2.06
1.04
1.03
3.05
0.98
f1 (ppm)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127.137
121.851
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80.908
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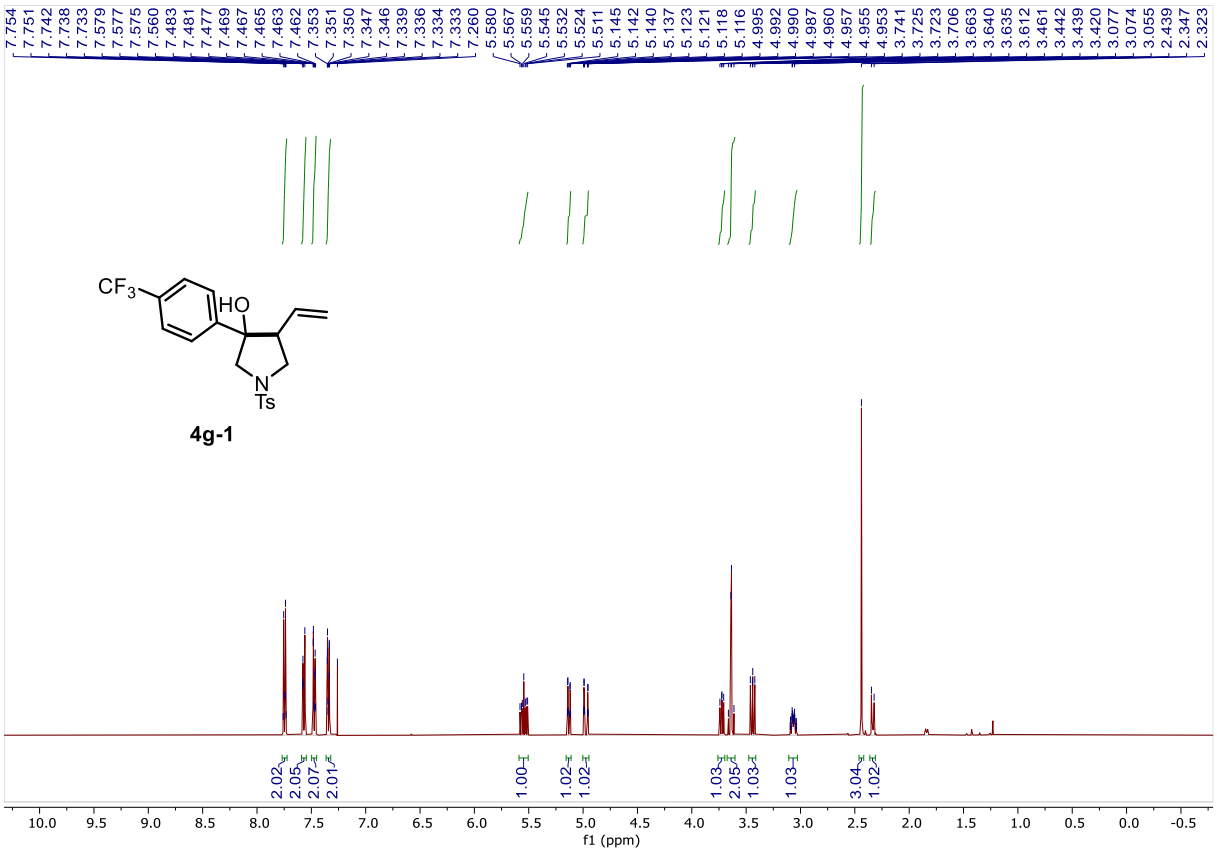
77.100
76.782
61.823
52.860
50.318
21.605
Br
HO
N
Ts
4f
f1 (ppm)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7.467
7.465
7.463
7.462
7.353
7.351
7.350
7.347
7.346
7.339
7.336
7.334
7.333
7.260
5.580
5.567
5.559
5.545
5.532
5.524
5.511
5.145
5.142
5.140
5.137
5.123
5.121
5.118
5.116
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4.992
4.990
4.987
4.960
4.957
4.955
4.953
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3.725
3.723
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3.663
3.640
3.635
3.612
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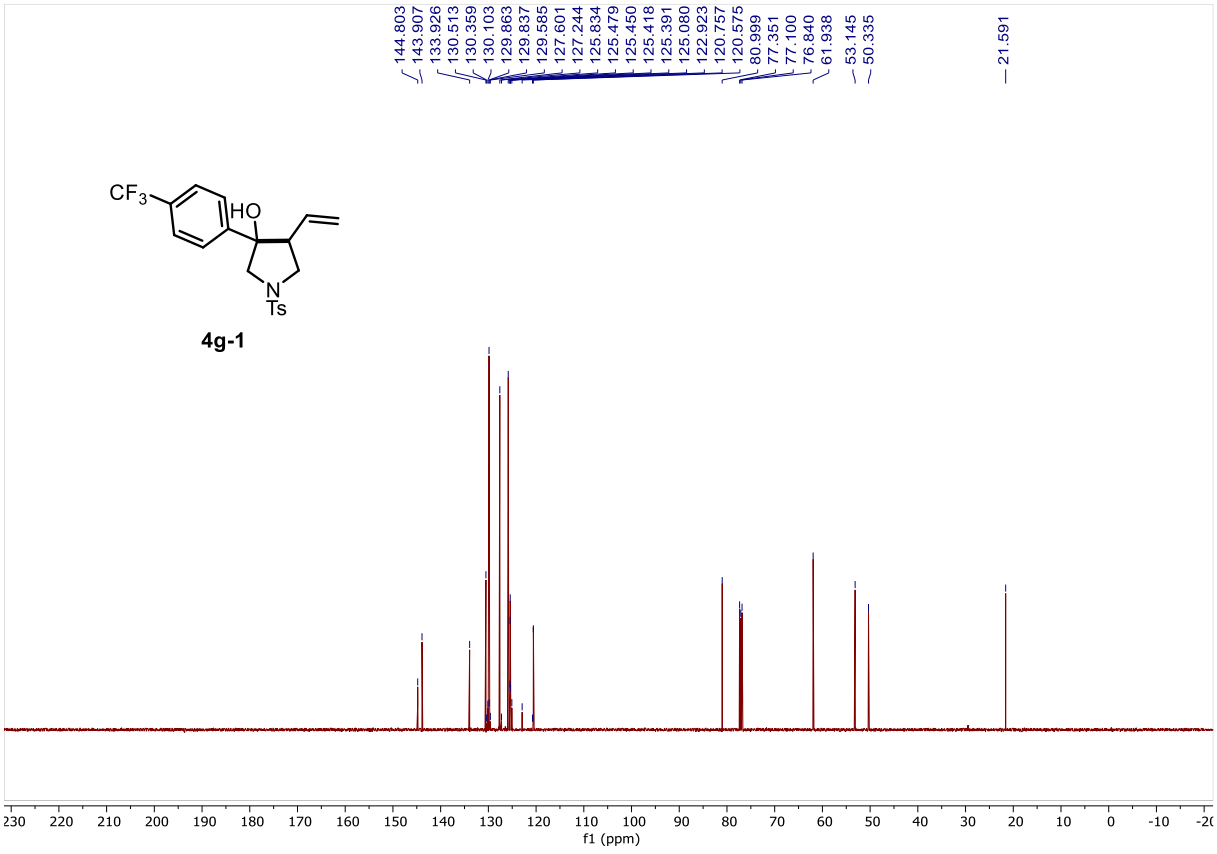
3.442
3.439
3.420
3.077
3.074
3.055
2.439
2.347
2.323
CF3
HO
N
Ts
4g-1
2.02
2.05
2.07
2.01
1.00
1.02
1.02
1.03
2.05
1.03
1.03
3.04
1.02
f1 (ppm)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127.244
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125.479
125.450
125.418
125.391
125.080
122.923
120.757
120.575
80.999
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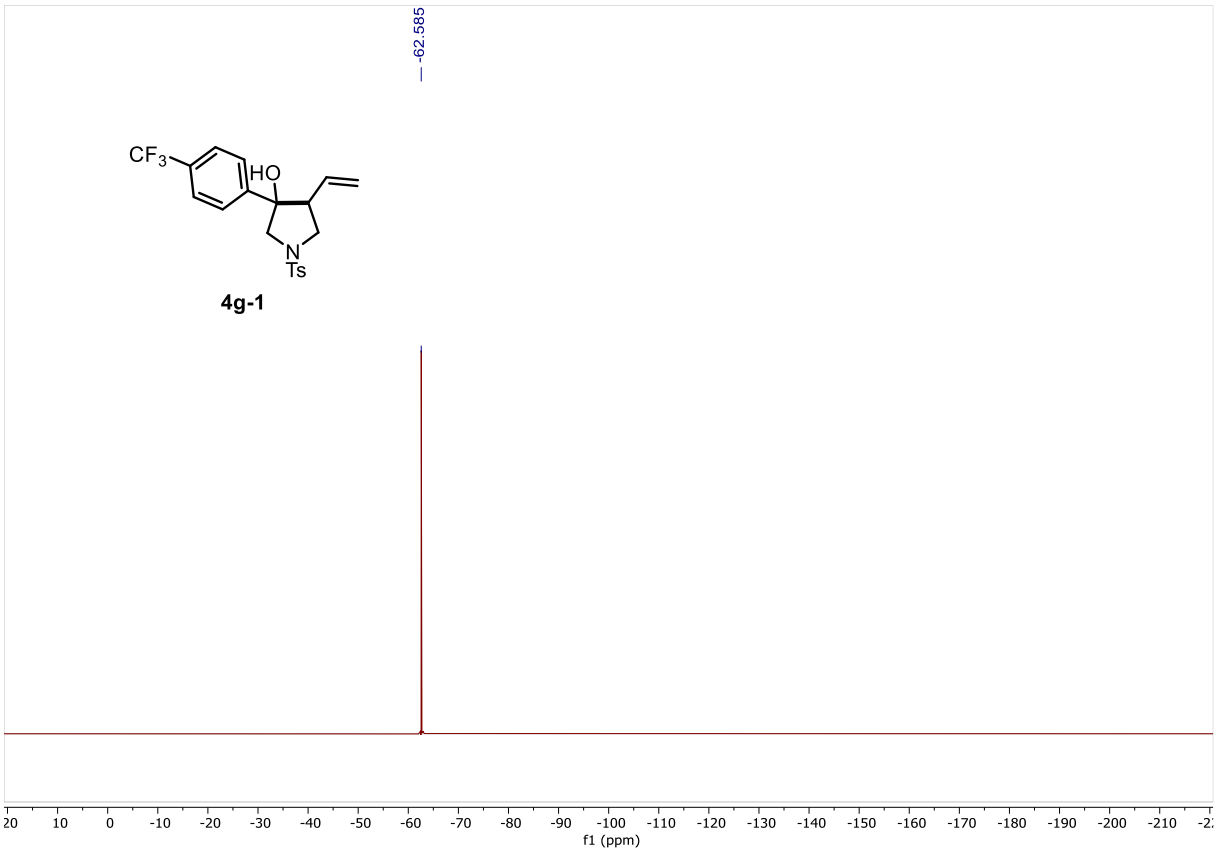
76.840
61.938
53.145
50.335
21.591
CF3
HO
N
Ts
4g-1
f1 (ppm)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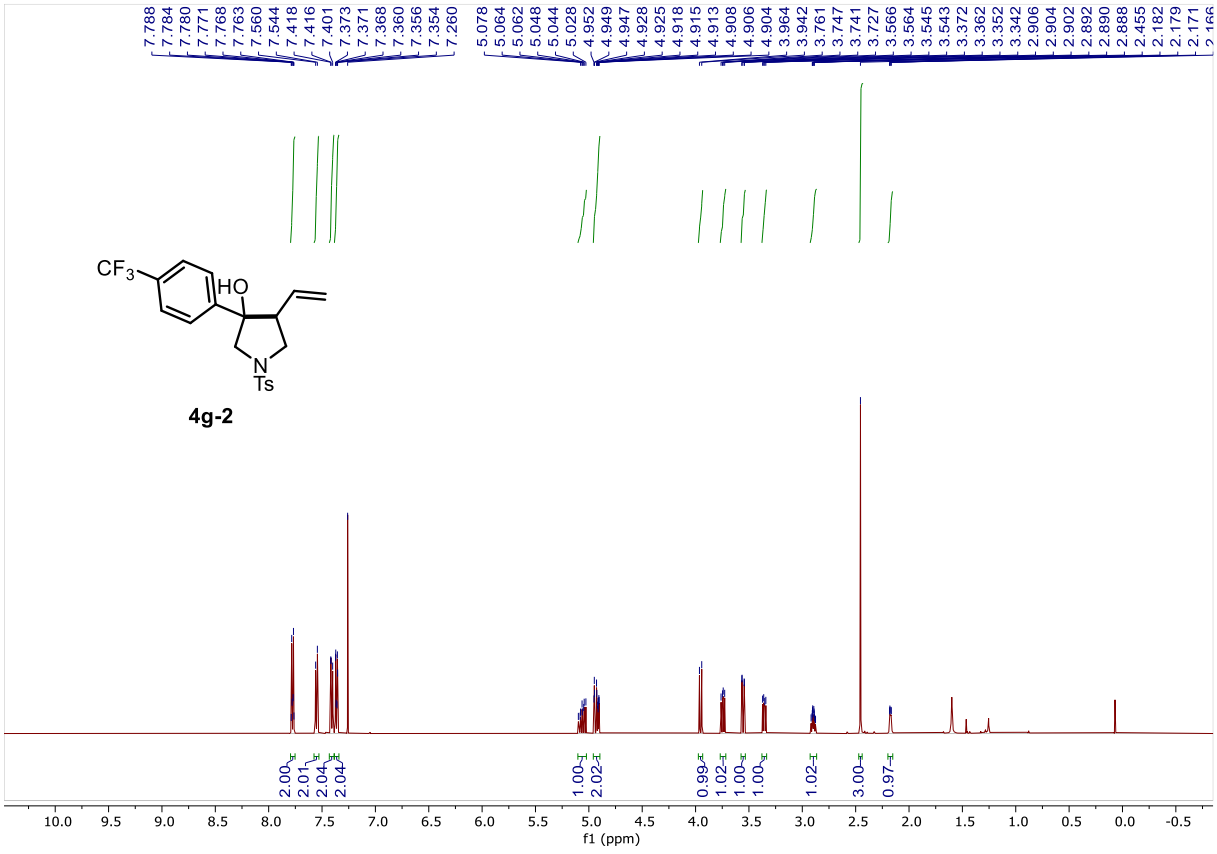
N
Ts
4g-1
f1 (ppm)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7.371
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7.354
7.260
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5.048
5.044
5.028
4.952
4.949
4.947
4.928
4.925
4.918
4.915
4.913
4.908
4.906
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3.942
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3.362
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3.342
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2.902
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2.890
2.888
2.455
2.182
2.179
2.171
CF3
HO
N
Ts
4g-2
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2.01
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2.04
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1.02
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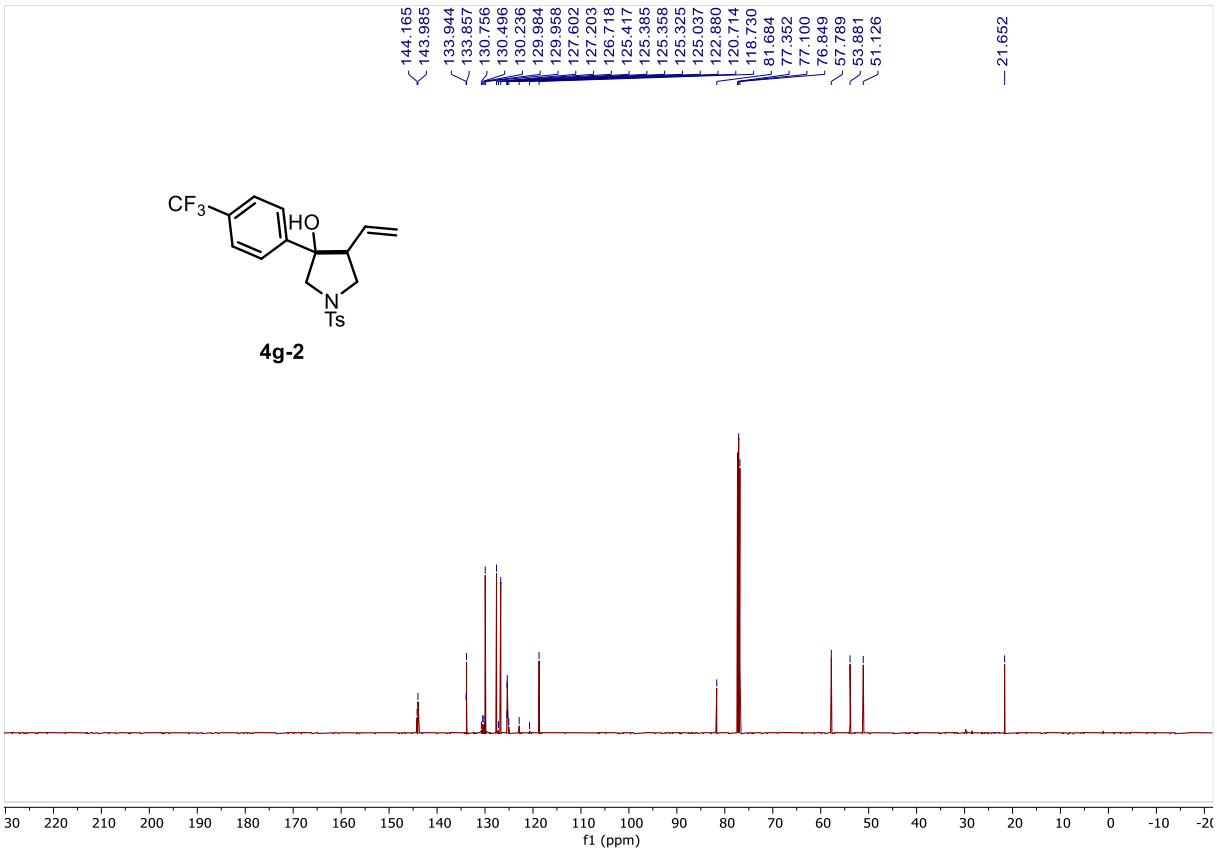
1.00
1.02
3.00
0.97
f1 (ppm)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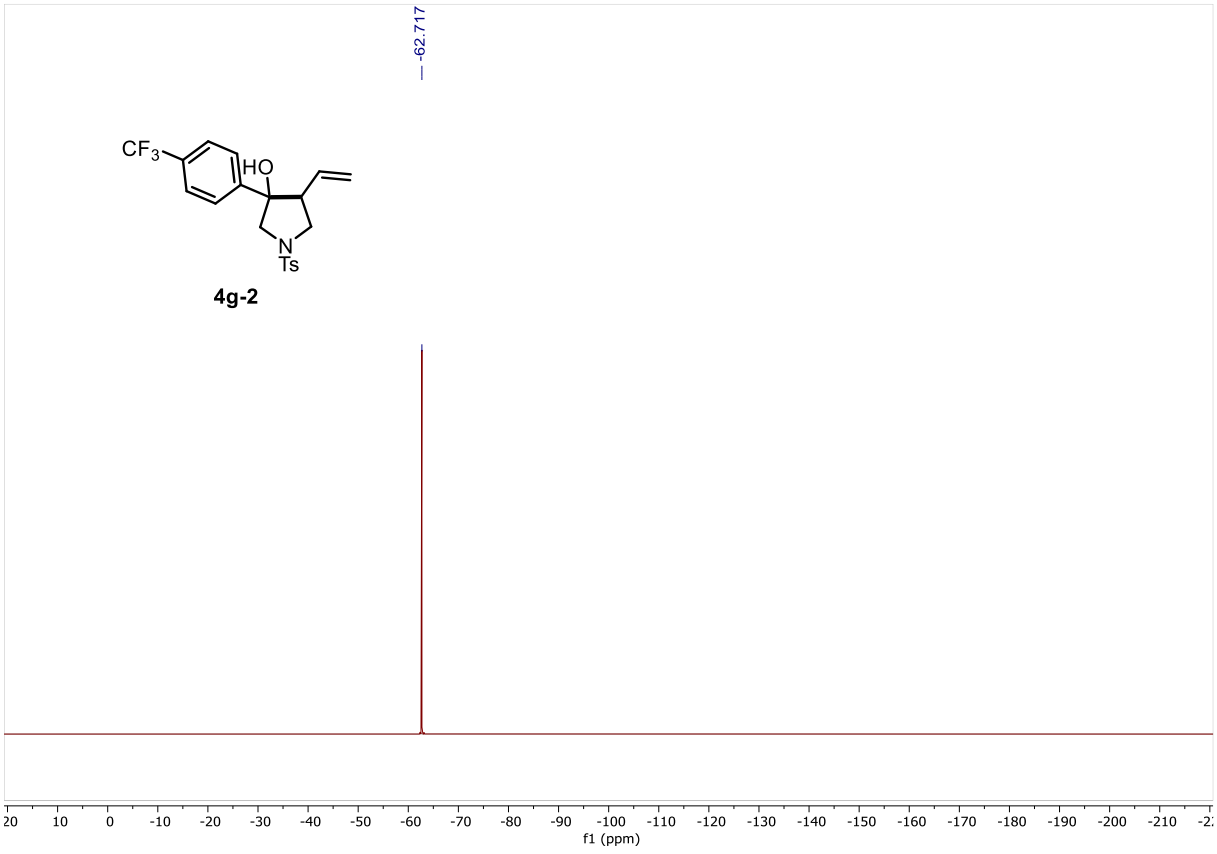
126.718
125.417
125.385
125.358
125.325
125.037
122.880
120.714
118.730
81.684
77.352
77.100
76.849
57.789
53.881
51.126
21.652
CF3
HO
N
Ts
4g-2
f1 (ppm)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4g-2
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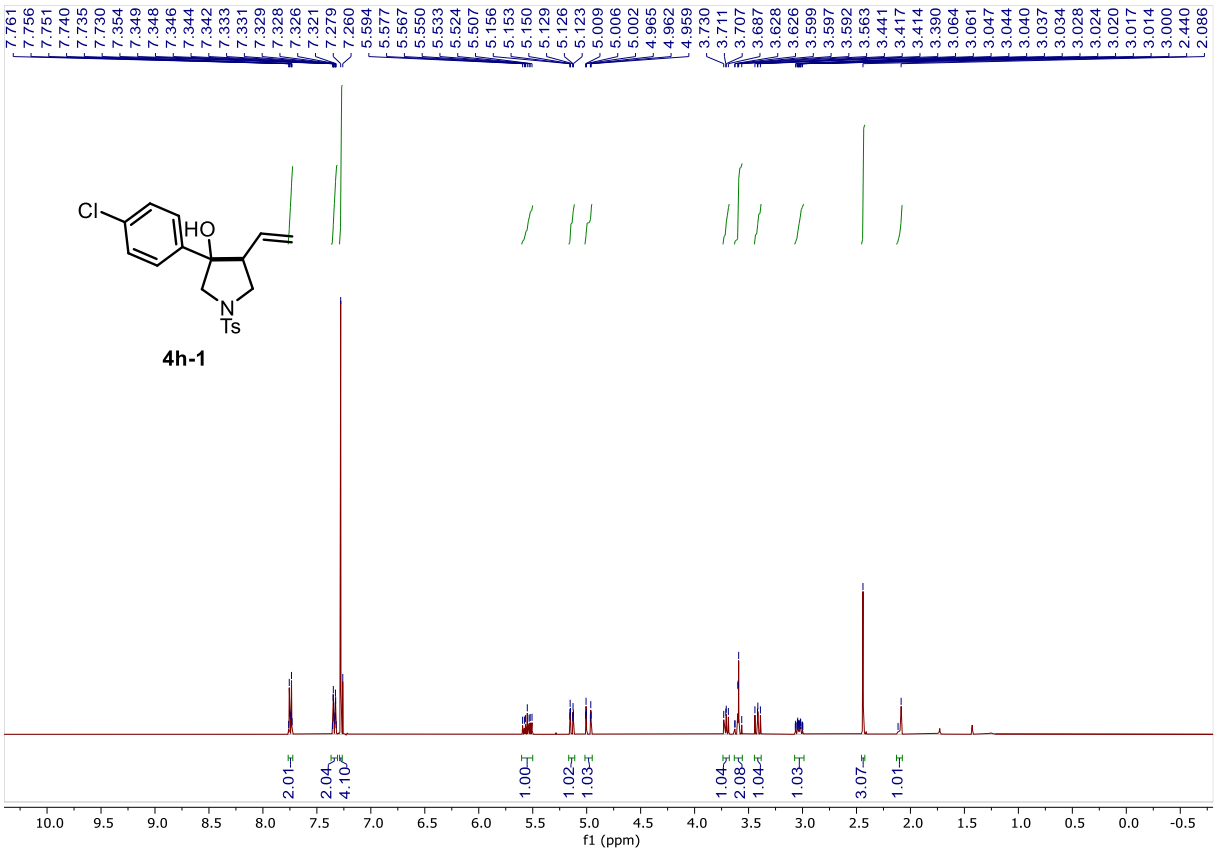
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7.342
7.333
7.331
7.329
7.328
7.326
7.321
7.279
7.260
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5.567
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5.533
5.524
5.507
5.156
5.153
5.150
5.129
5.126
5.123
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5.006
5.002
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3.040
3.037
3.034
3.028
3.024
3.020
3.017
3.014
3.000
2.440
2.086
Cl
HO
N
Ts
4h-1
2.01
2.04
4.10
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1.02
1.03
1.04
2.08
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1.03
3.07
1.01
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8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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2.5
2.0
1.5
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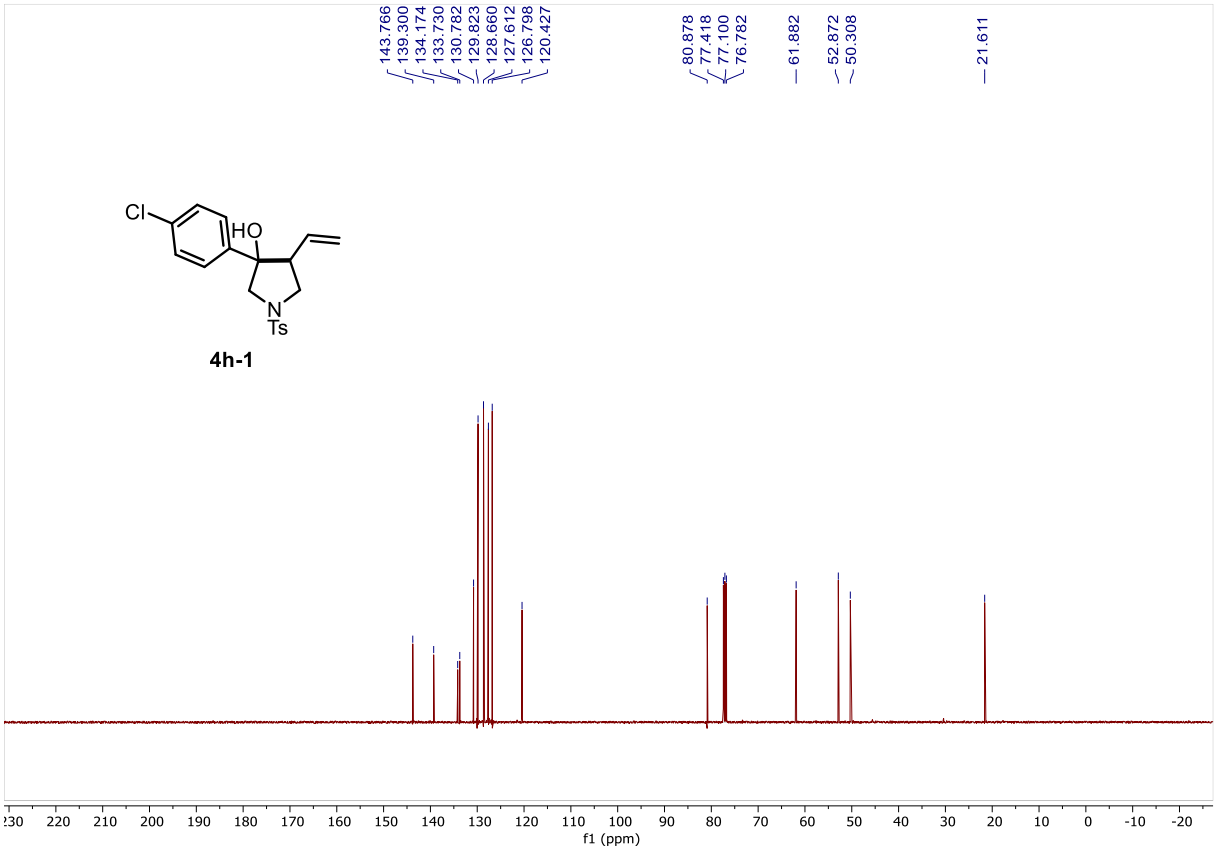
0.5
0.0
-0.5
f1 (ppm)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127.612
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80.878
77.418
77.100
76.782
61.882
52.872
50.308
21.611
Cl
HO
N
Ts
4h-1
230
220
210
200
190
180
170
160
150
140
130
120
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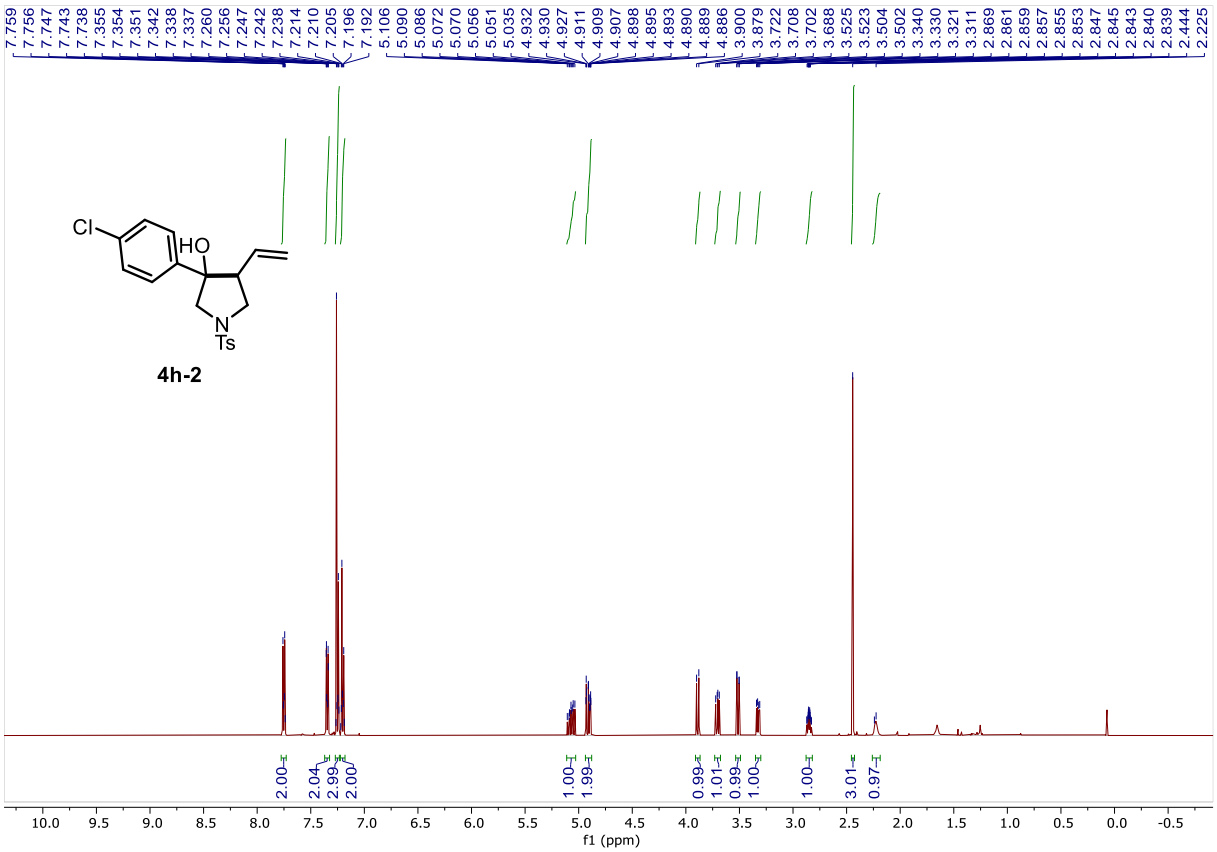
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.256
7.247
7.242
7.238
7.214
7.210
7.205
7.196
7.192
5.106
5.090
5.086
5.072
5.070
5.056
5.051
5.035
4.932
4.930
4.927
4.911
4.909
4.907
4.898
4.895
4.893
4.890
4.889
4.886
3.900
3.879
3.722
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3.702
3.688
3.525
3.523
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3.502
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2.847
2.845
2.843
2.840
2.839
2.444
2.225
Cl
HO
N
Ts
4h-2
2.00
2.04
2.99
2.00
1.00
1.99
0.99
1.01
0.99
1.00
1.00
3.01
0.97
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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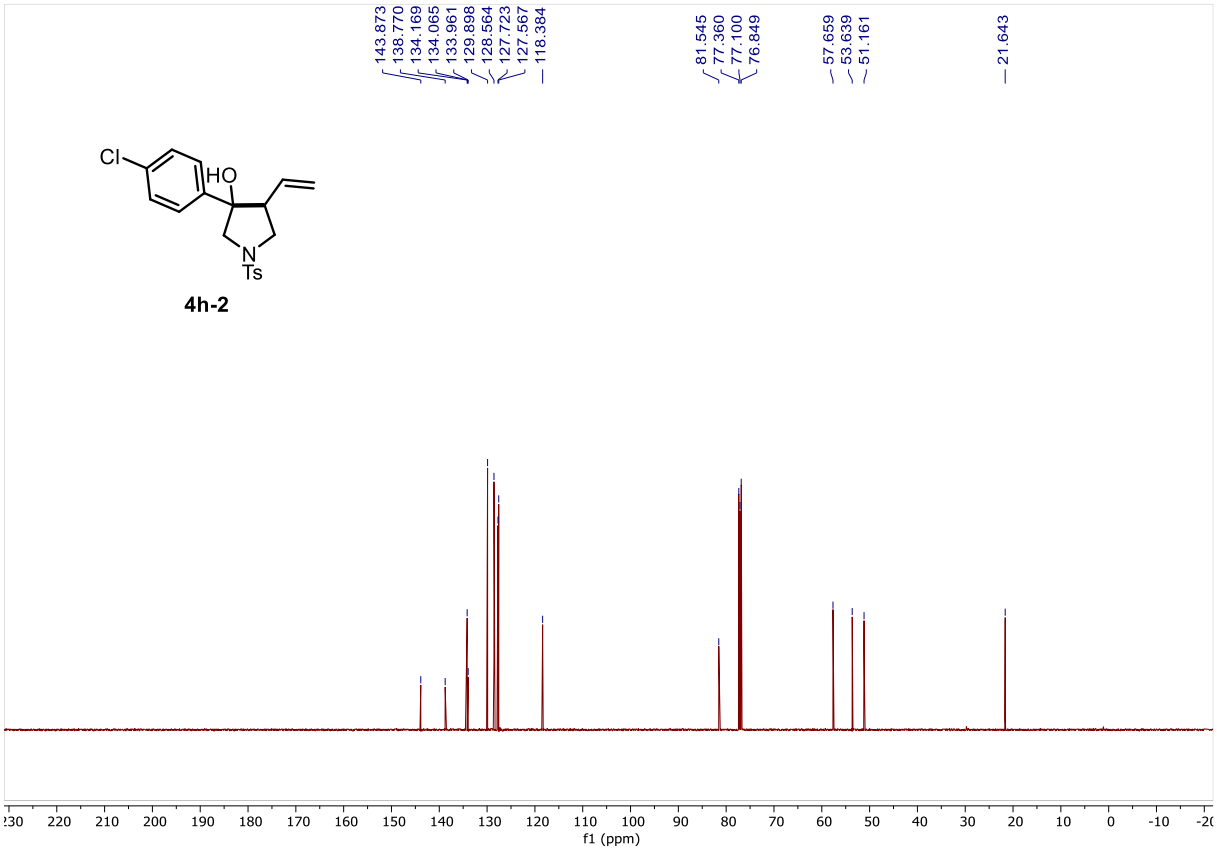
0.5
0.0
-0.5
f1 (ppm)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127.723
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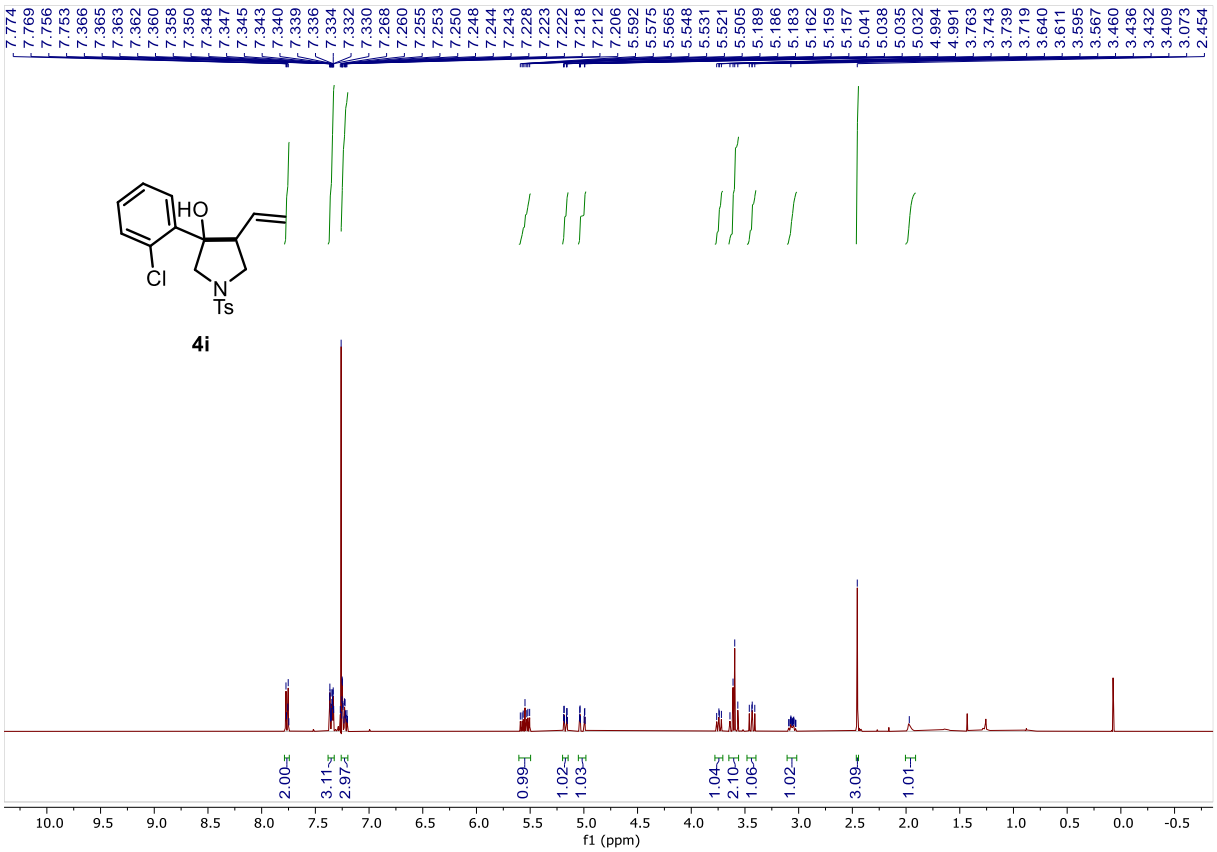
81.545
77.360
77.100
76.849
57.659
53.639
51.161
21.643
Cl
HO
N
Ts
4h-2
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.347
7.345
7.343
7.340
7.339
7.336
7.334
7.332
7.330
7.268
7.260
7.255
7.253
7.250
7.248
7.244
7.243
7.228
7.223
7.222
7.218
7.212
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5.575
5.565
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5.505
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5.186
5.183
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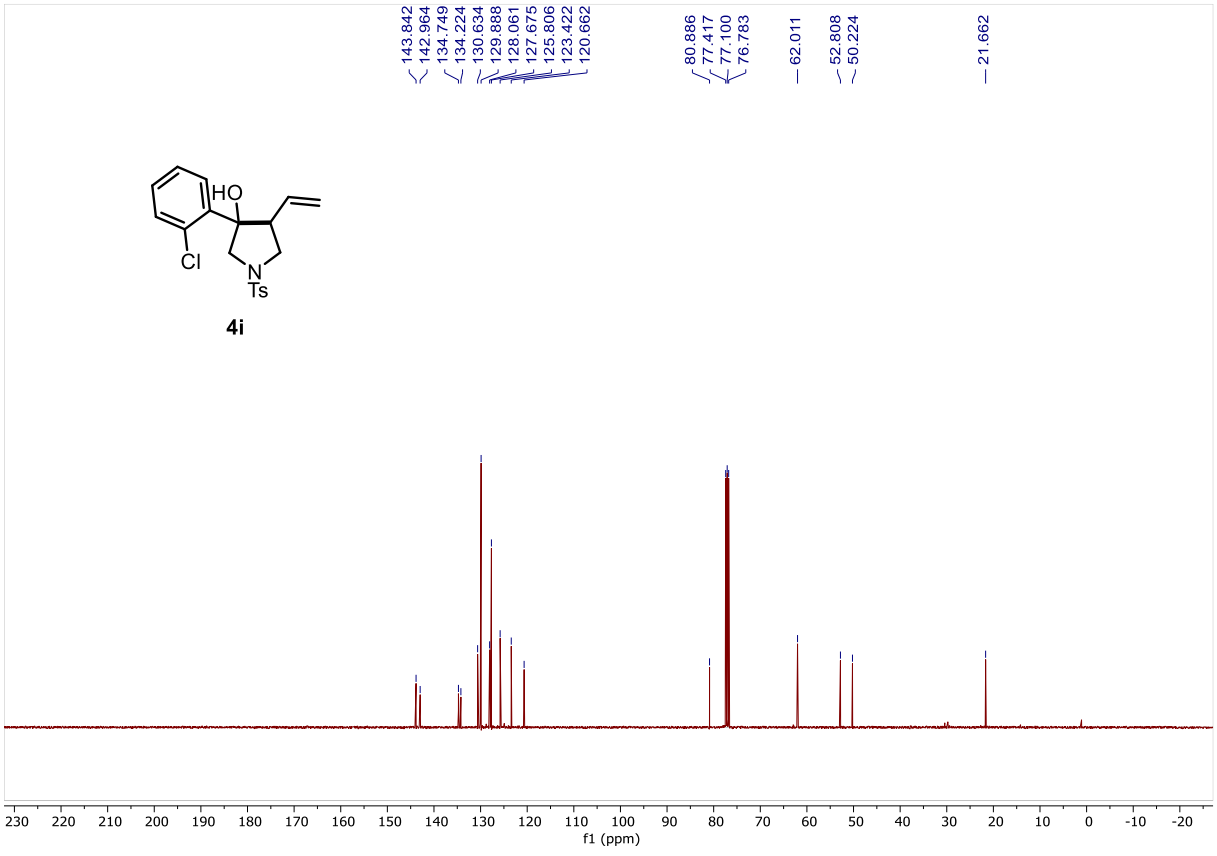
3.436
3.432
3.409
3.073
2.454
HO
Cl
N
Ts
4i
2.00
3.11
2.97
0.99
1.02
1.03
1.04
2.10
1.06
1.02
3.09
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.749
134.224
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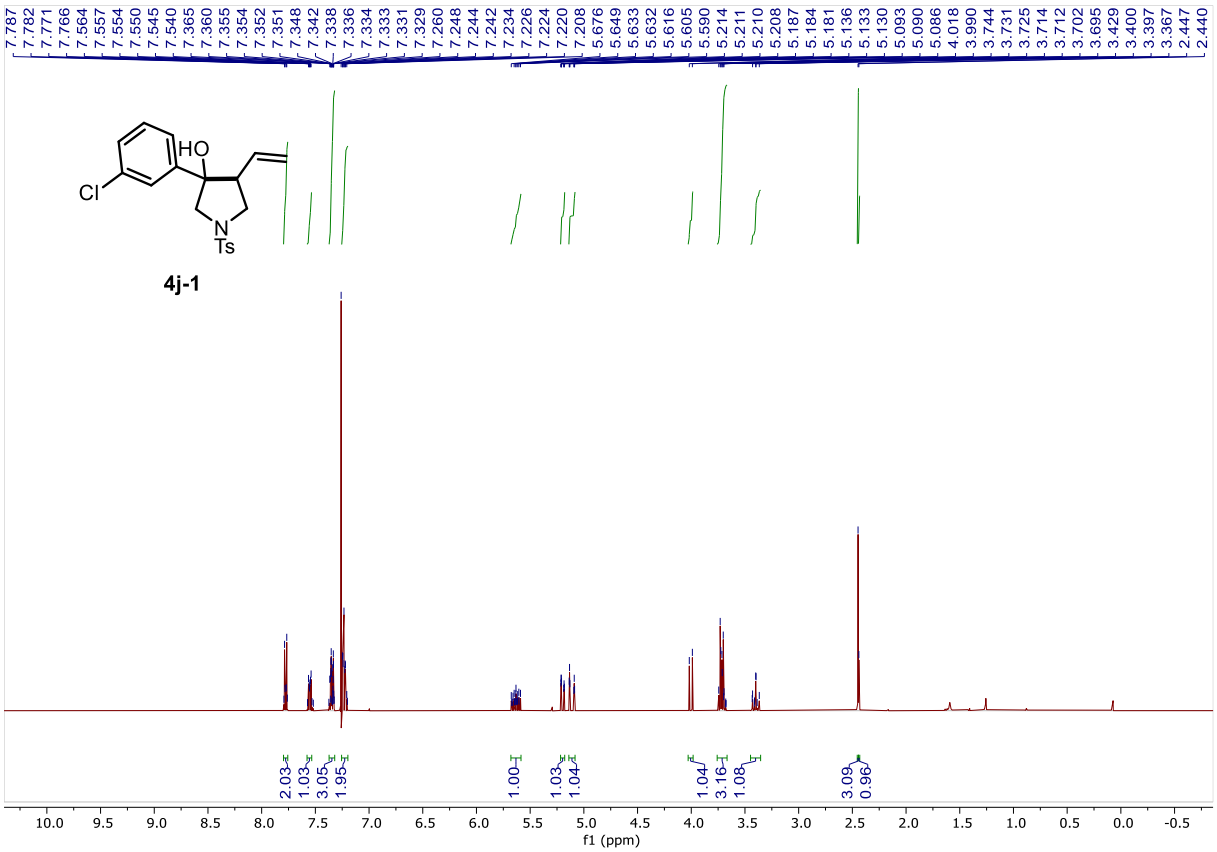
129.888
128.061
127.675
125.806
123.422
120.662
80.886
77.417
77.100
76.783
62.011
52.808
50.224
21.662
HO
Cl
N
Ts
4i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.782
7.771
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7.554
7.550
7.545
7.540
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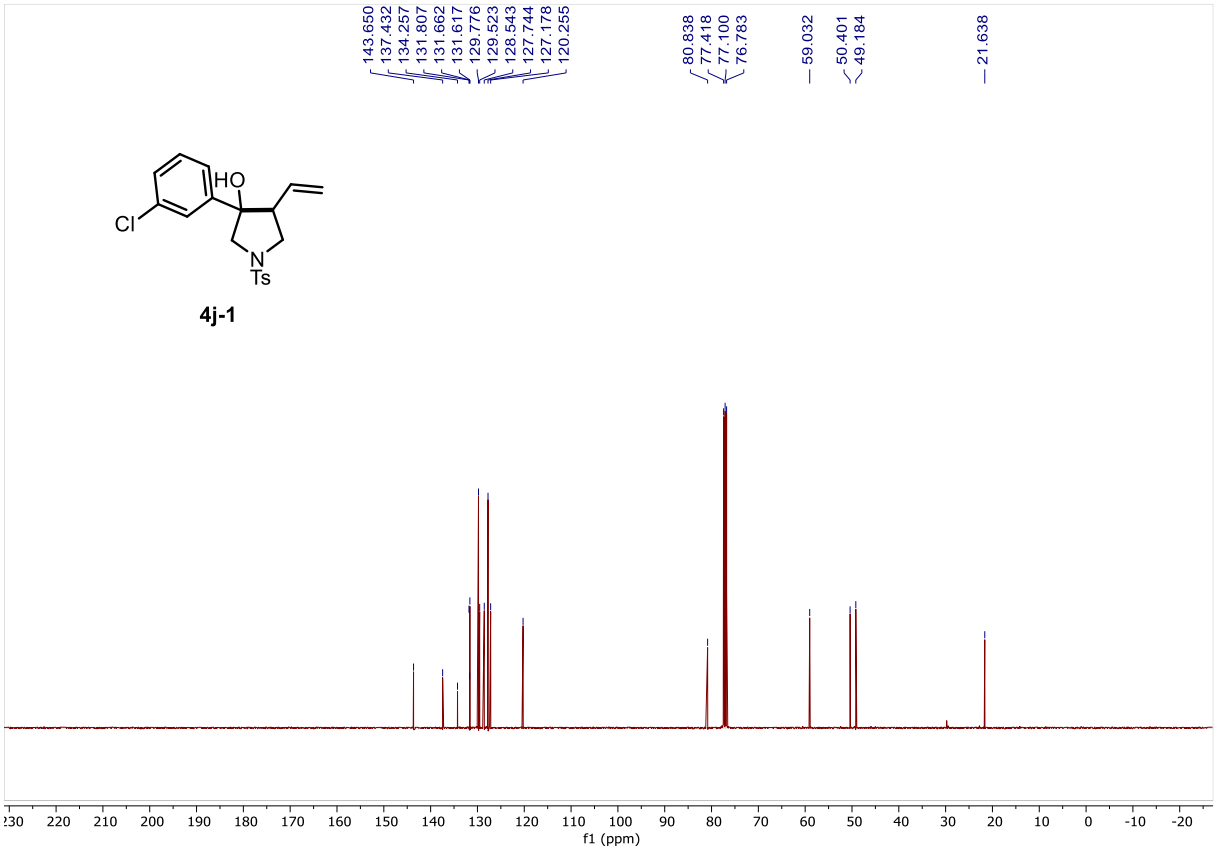
7.360
7.355
7.354
7.352
7.351
7.348
7.342
7.338
7.336
7.334
7.333
7.331
7.329
7.260
7.248
7.244
7.242
7.234
7.226
7.224
7.220
7.208
5.676
5.649
5.633
5.632
5.616
5.605
5.590
5.214
5.211
5.210
5.208
5.187
5.184
5.181
5.136
5.133
5.130
5.093
5.090
5.086
4.018
3.990
3.744
3.731
3.725
3.714
3.712
3.702
3.695
3.429
3.400
3.397
3.367
2.447
2.440
HO
Cl
N
Ts
4j-1
2.03
1.03
3.05
1.95
1.00
1.03
1.04
1.04
3.16
1.08
3.09
0.96
f1 (ppm)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137.432
134.257
131.807
131.662
131.617
129.776
129.523
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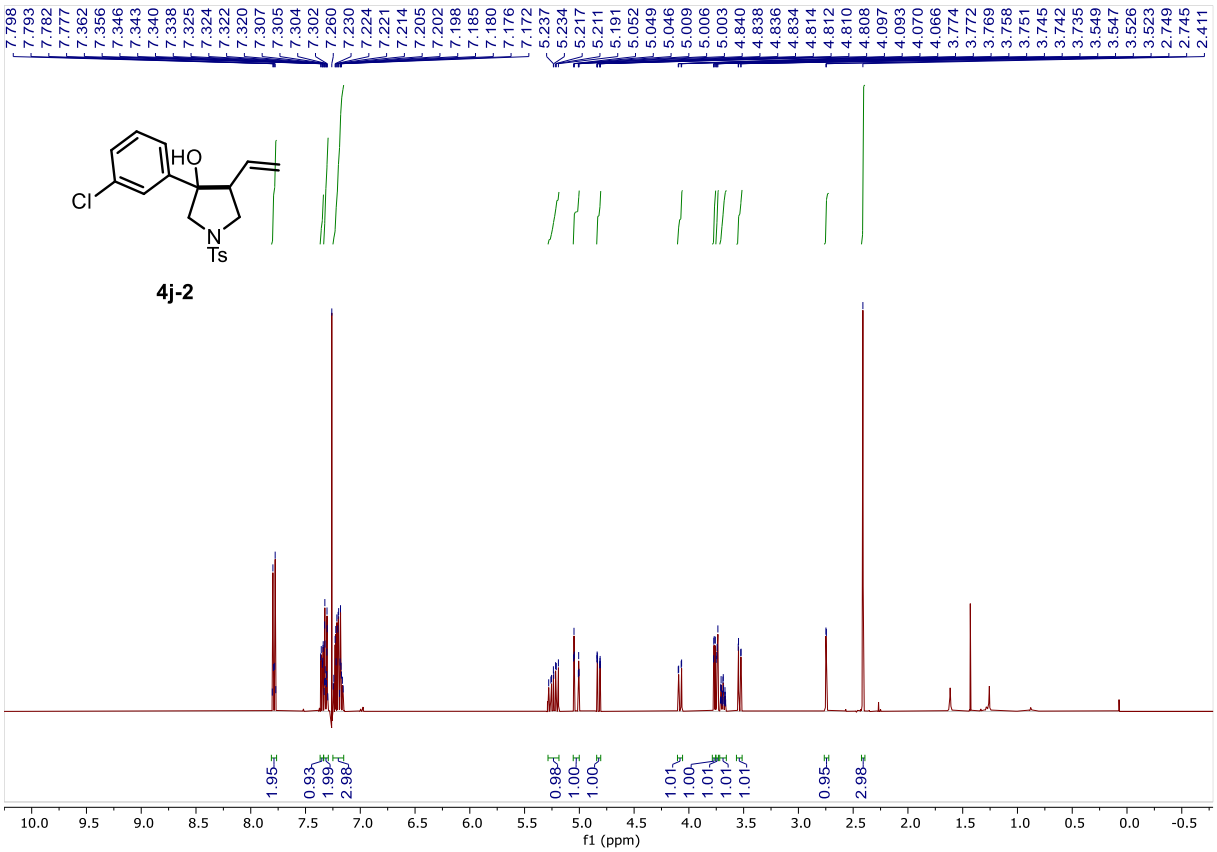
127.744
127.178
120.255
80.838
77.418
77.100
76.783
59.032
50.401
49.184
21.638
HO
Cl
N
Ts
4j-1
f1 (ppm)


7.798 7.793 7.782 7.777 7.362 7.356 7.346 7.343 7.340 7.338 7.325 7.324 7.322 7.320 7.307 7.305 7.304 7.302 7.260 7.230 7.224 7.221 7.214 7.205 7.202 7.198 7.185 7.180 7.176 7.172 5.237 5.234 5.217 5.211 5.191 5.052 5.049 5.046 5.009 5.006 5.003 4.840 4.838 4.836 4.834 4.814 4.812 4.810 4.808 4.097 4.093 4.070 4.066 3.774 3.772 3.769 3.758 3.751 3.745 3.742 3.735 3.549 3.547 3.526 3.523 2.749 2.745 2.411
HO
Cl
N
Ts
4j-2
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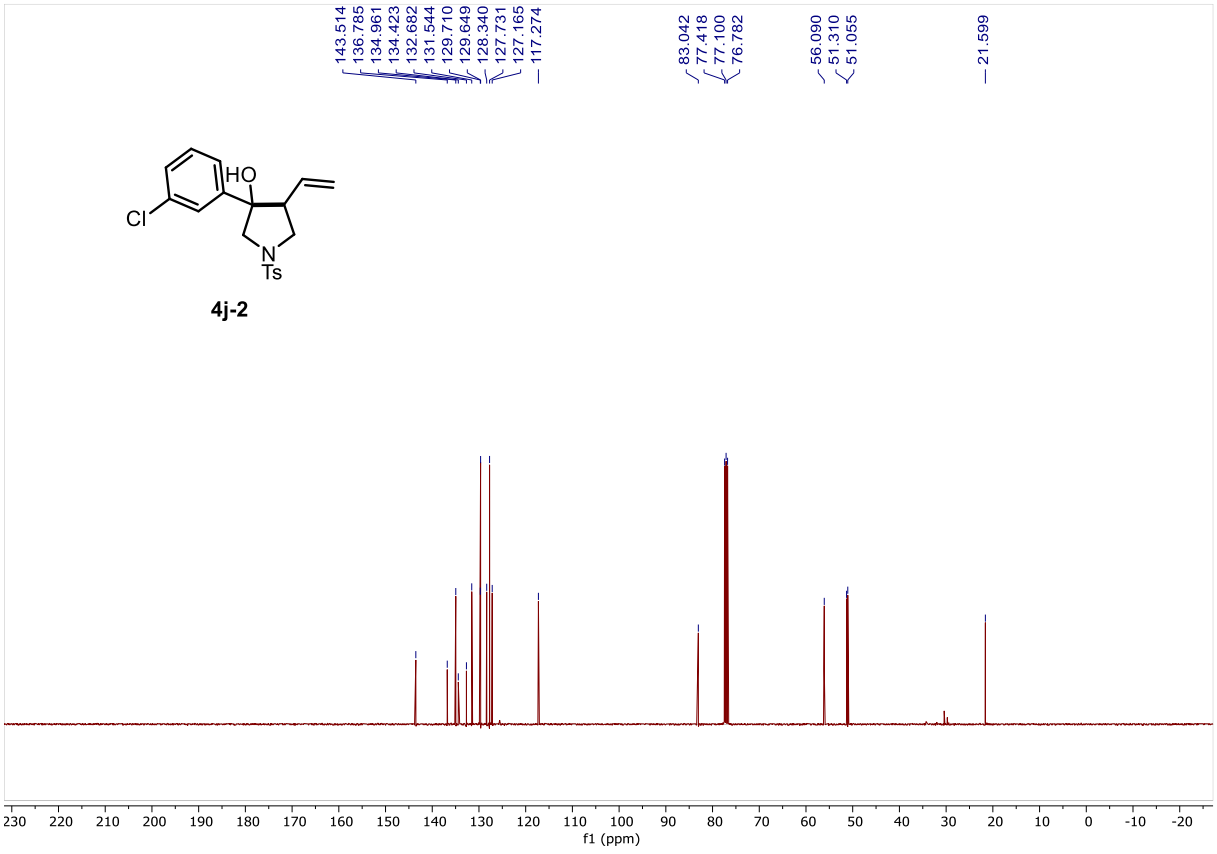
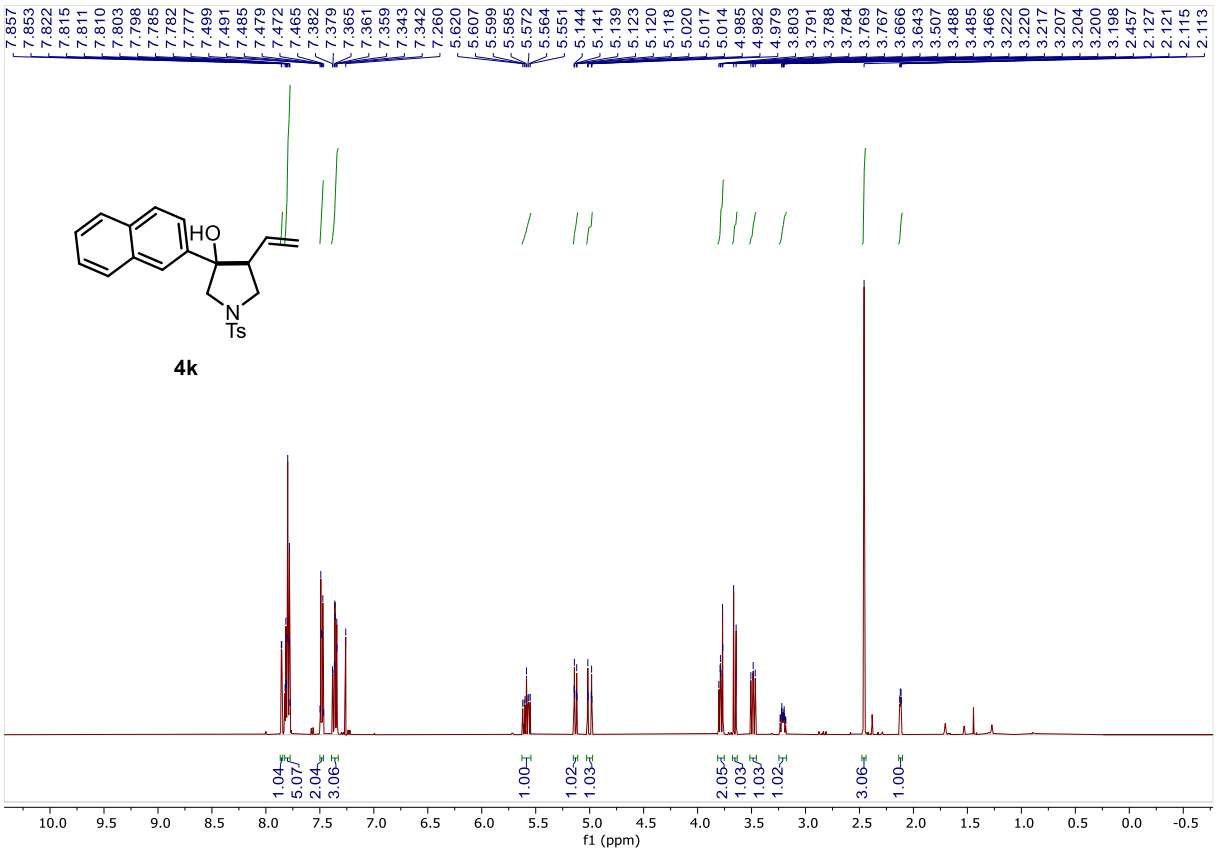
f1 (ppm)


143.514 136.785 134.961 134.423 132.682 131.544 129.710 129.649 128.340 127.731 127.165 117.274
83.042 77.418 77.100 76.782
56.090 51.310 51.055
21.599
HO
Cl
N
Ts
4j-2
f1 (ppm)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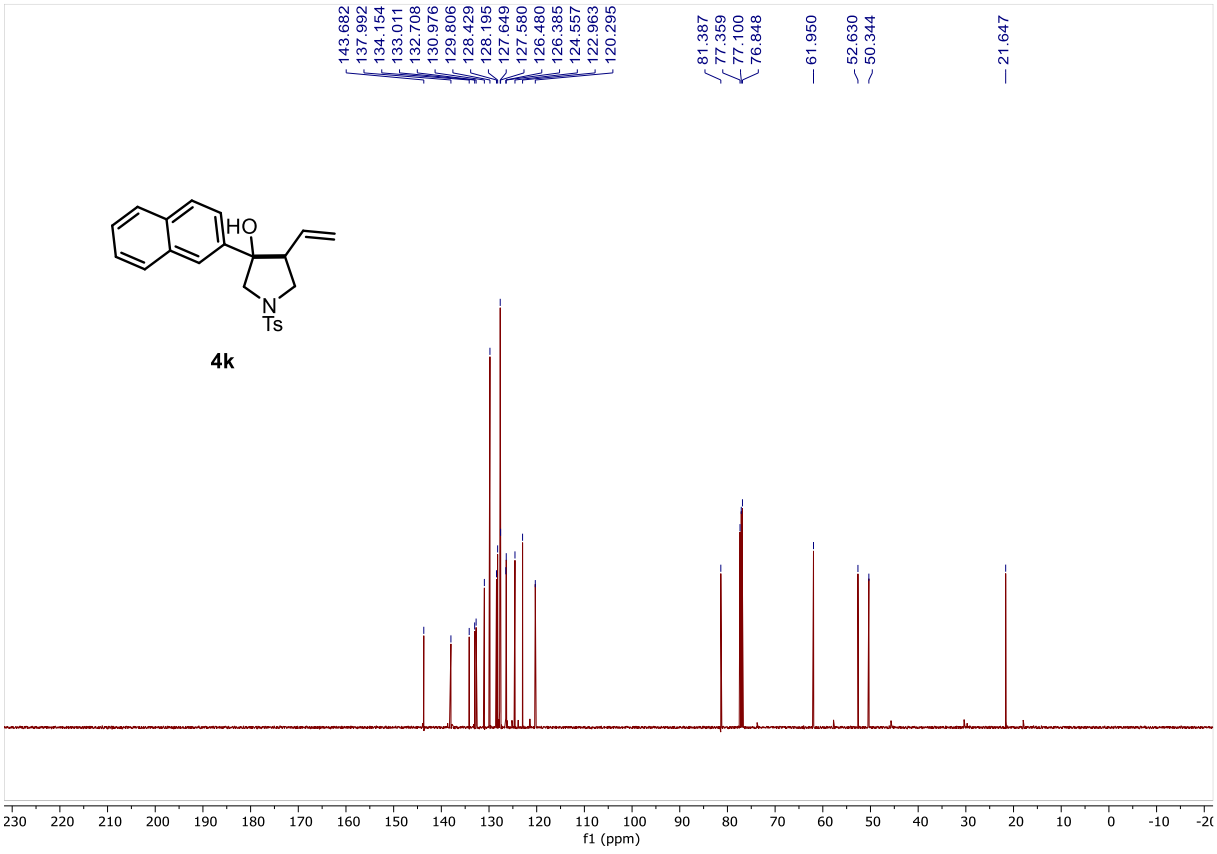
7.853
7.822
7.815
7.811
7.810
7.803
7.798
7.785
7.782
7.777
7.499
7.491
7.485
7.479
7.472
7.465
7.382
7.379
7.365
7.361
7.359
7.343
7.342
7.260
5.620
5.607
5.599
5.585
5.572
5.564
5.551
5.144
5.141
5.139
5.123
5.120
5.118
5.020
5.017
5.014
4.985
4.982
4.979
3.803
3.791
3.788
3.784
3.769
3.767
3.666
3.643
3.507
3.488
3.485
3.466
3.222
3.220
3.217
3.207
3.204
3.200
3.198
2.457
2.127
2.121
2.115
2.113
HO
N
Ts
4k
1.04
5.07
2.04
3.06
1.00
1.02
1.03
2.05
1.03
1.03
1.02
3.06
1.00
f1 (ppm)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137.992
134.154
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132.708
130.976
129.806
128.429
128.195
127.649
127.580
126.480
126.385
124.557
122.963
120.295
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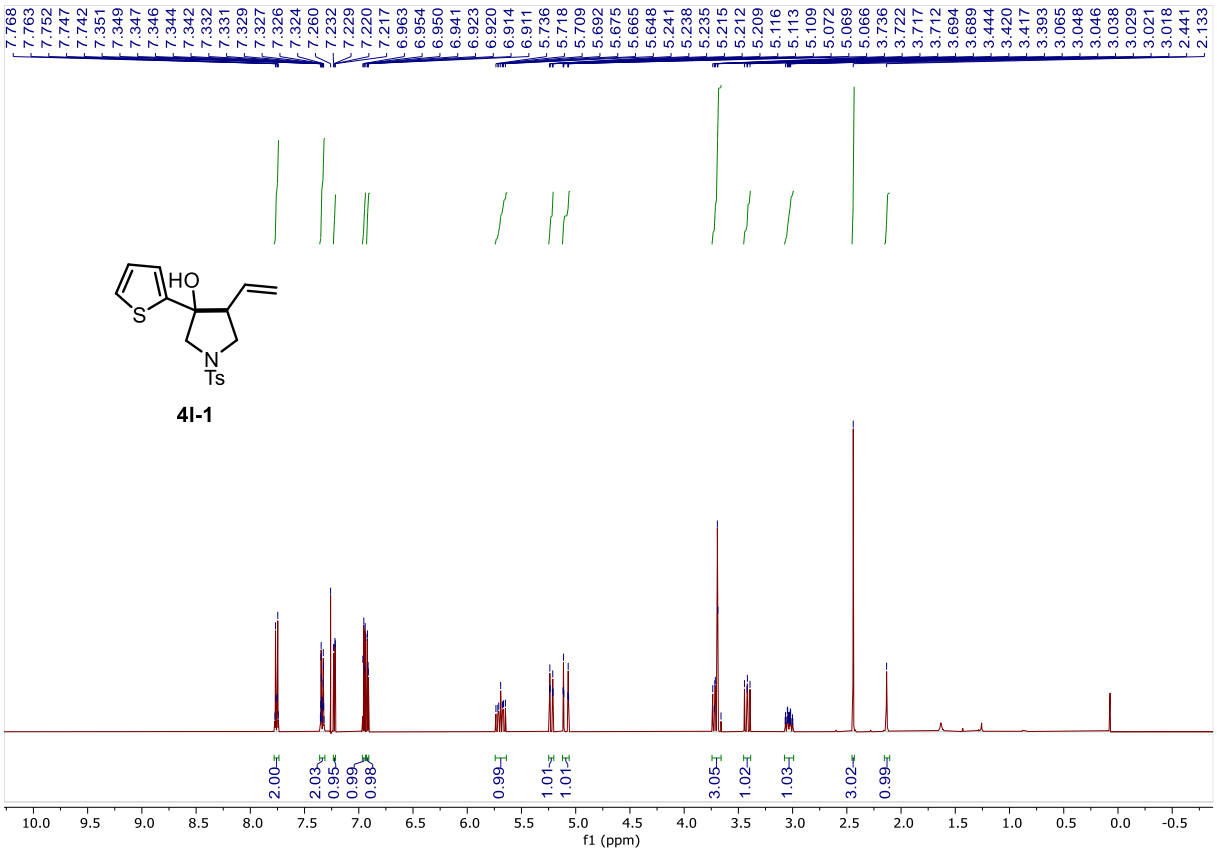
77.100
76.848
61.950
52.630
50.344
21.647
HO
N
Ts
4k
f1 (ppm)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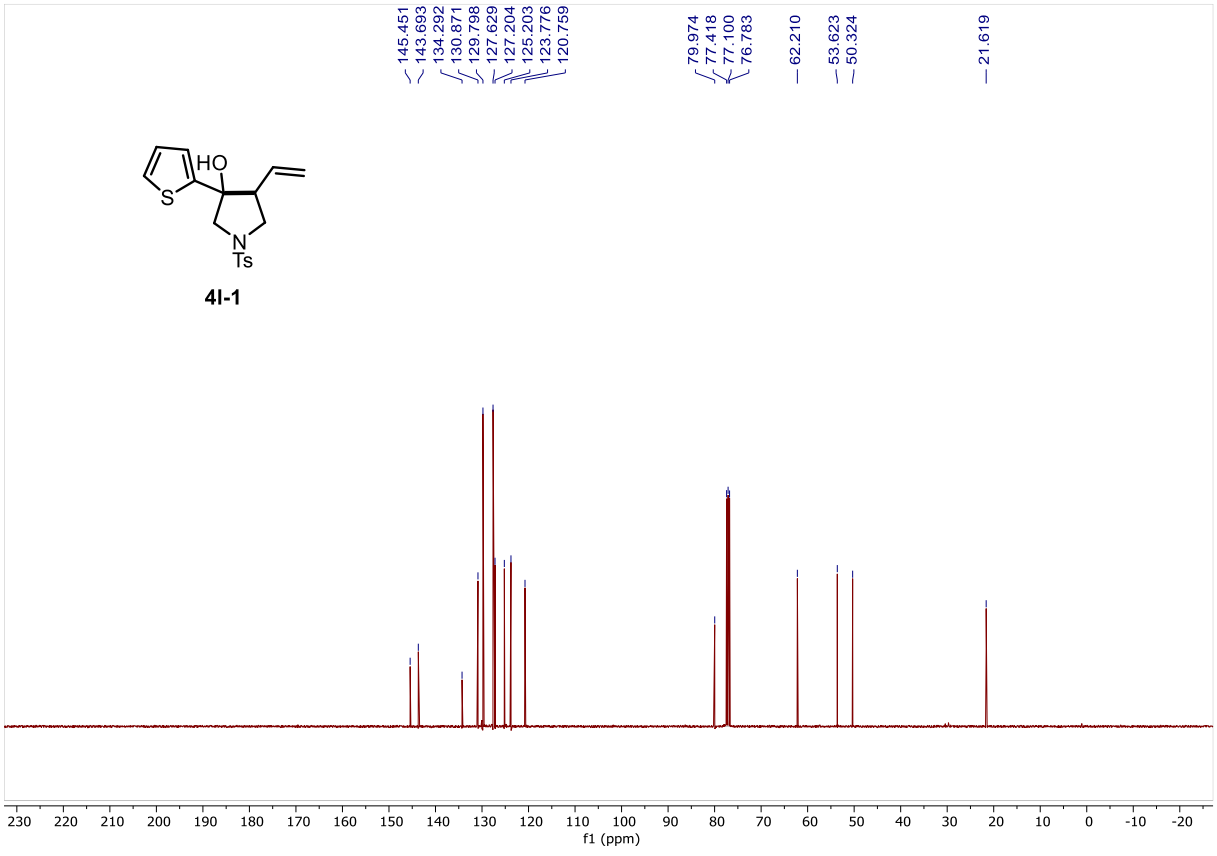
7.349
7.347
7.346
7.344
7.342
7.332
7.331
7.329
7.327
7.326
7.324
7.260
7.232
7.229
7.220
7.217
6.963
6.954
6.950
6.941
6.923
6.920
6.914
6.911
5.736
5.718
5.709
5.692
5.675
5.665
5.648
5.241
5.238
5.235
5.215
5.212
5.209
5.116
5.113
5.109
5.072
5.069
5.066
3.736
3.722
3.717
3.712
3.694
3.689
3.444
3.420
3.417
3.393
3.065
3.048
3.046
3.038
3.029
3.021
3.018
2.441
2.133
HO
S
N
Ts
2.00
2.03
0.95
0.99
0.98
0.99
1.01
1.01
3.05
1.02
1.03
3.02
0.99
f1 (ppm)

4l-1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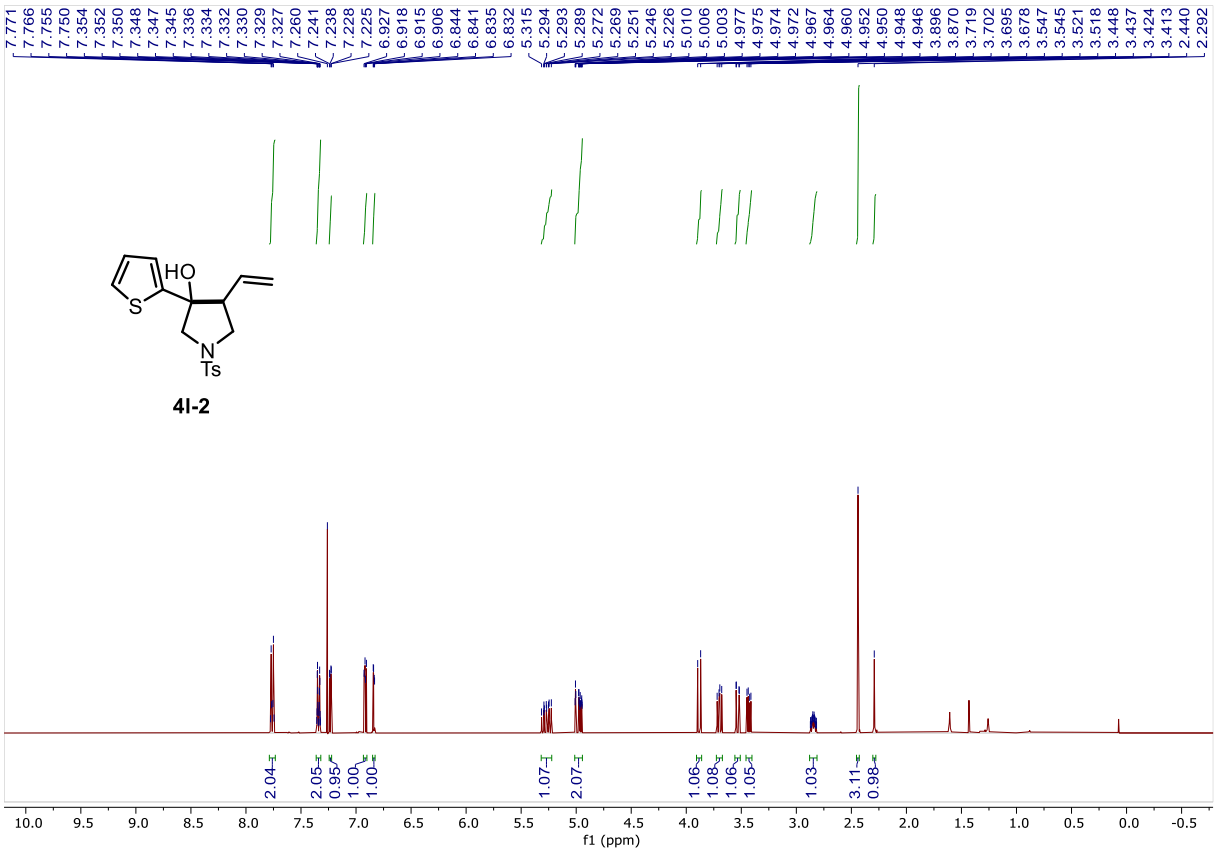
143.693
134.292
130.871
129.798
127.629
127.204
125.203
123.776
120.759
79.974
77.418
77.100
76.783
62.210
53.623
50.324
21.619
HO
S
N
Ts
f1 (ppm)

4l-1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7.755
7.750
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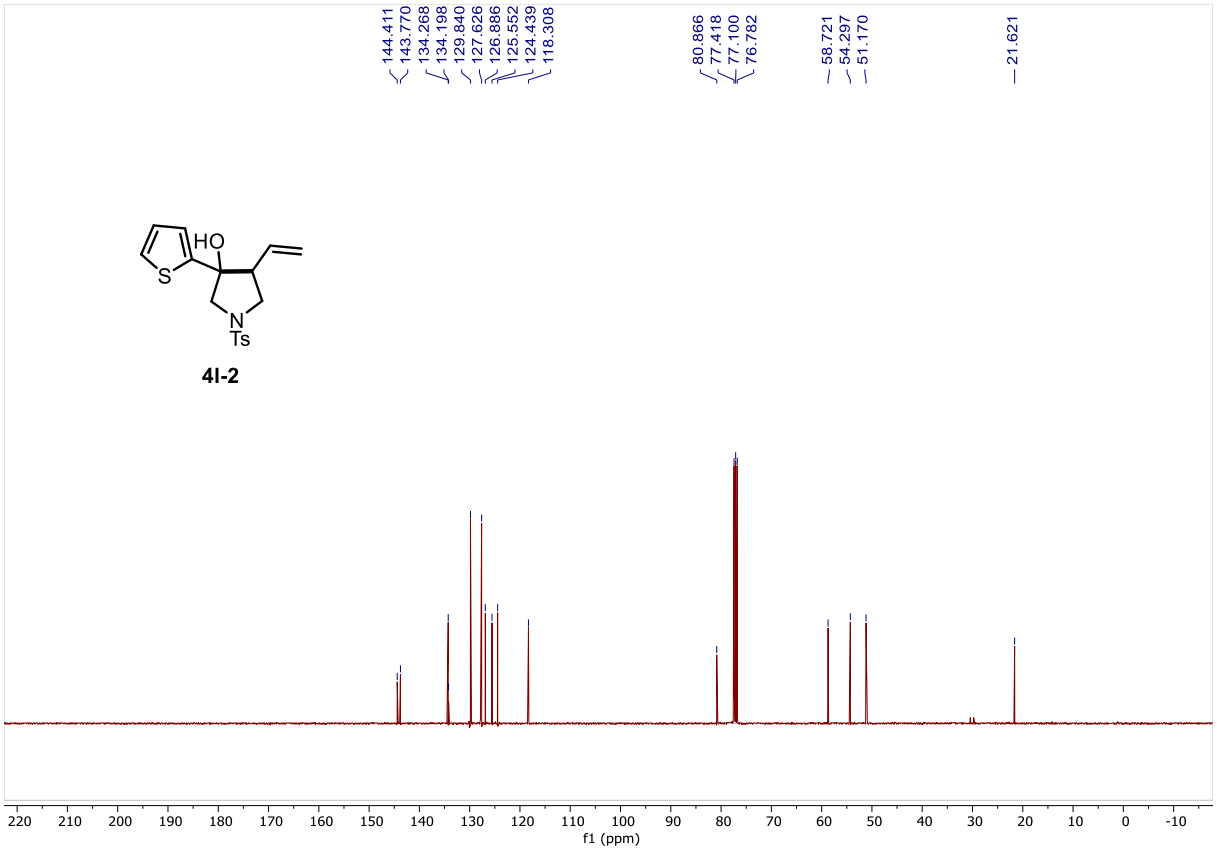
7.352
7.350
7.348
7.347
7.345
7.336
7.334
7.332
7.330
7.329
7.327
7.260
7.241
7.238
7.228
7.225
6.927
6.918
6.915
6.906
6.844
6.841
6.835
6.832
5.315
5.294
5.293
5.289
5.272
5.269
5.251
5.246
5.226
5.010
5.006
5.003
4.977
4.975
4.974
4.972
4.967
4.964
4.960
4.952
4.950
4.948
4.946
3.896
3.870
3.719
3.702
3.695
3.678
3.547
3.545
3.521
3.518
3.448
3.437
3.424
3.413
2.440
2.292
HO
S
N
Ts
4l-2
2.04
2.05
0.95
1.00
1.00
1.07
2.07
1.06
1.08
1.06
1.05
1.03
3.11
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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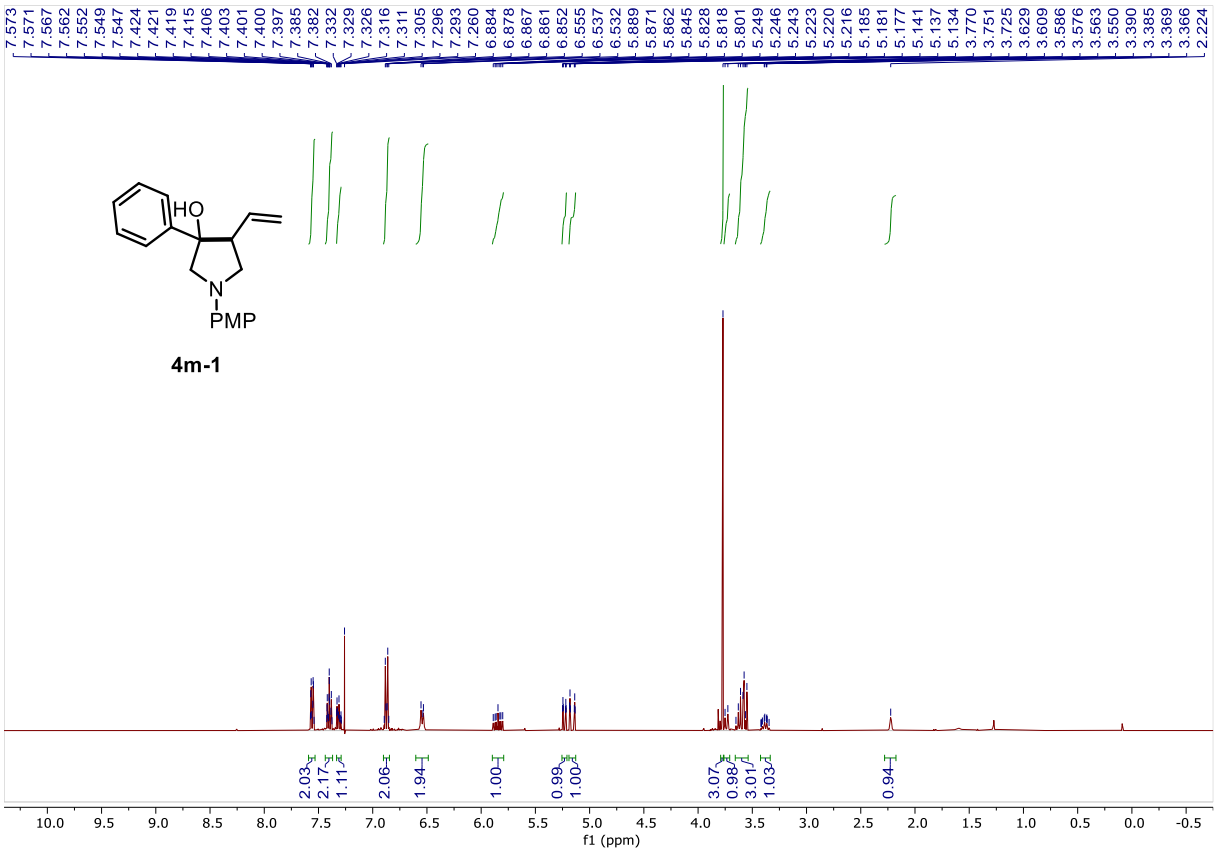
143.770
134.268
134.198
129.840
127.626
126.886
125.552
124.439
118.308
80.866
77.418
77.100
76.782
58.721
54.297
51.170
21.621
HO
S
N
Ts
4l-2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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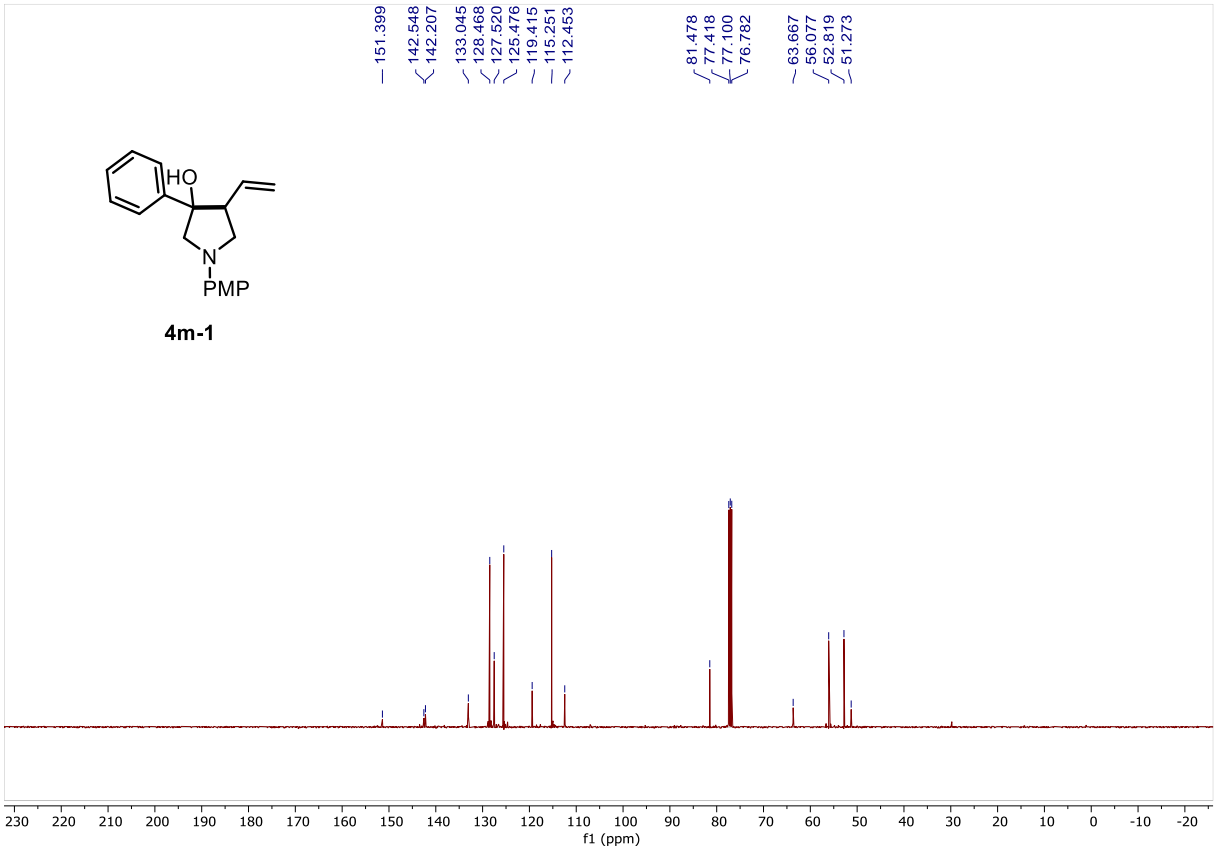
7.571
7.567
7.562
7.552
7.549
7.547
7.424
7.421
7.419
7.415
7.406
7.403
7.401
7.400
7.397
7.385
7.382
7.332
7.329
7.326
7.316
7.311
7.305
7.296
7.293
7.260
6.884
6.878
6.867
6.861
6.852
6.555
6.537
6.532
5.889
5.871
5.862
5.845
5.828
5.818
5.801
5.249
5.246
5.243
5.223
5.220
5.216
5.185
5.181
5.177
5.141
5.137
5.134
3.770
3.751
3.725
3.629
3.609
3.586
3.576
3.563
3.550
3.390
3.385
3.369
3.366
2.224
HO
N
PMP
4m-1
2.03
2.17
1.11
2.06
1.94
1.00
0.99
1.00
3.07
0.98
3.01
1.03
0.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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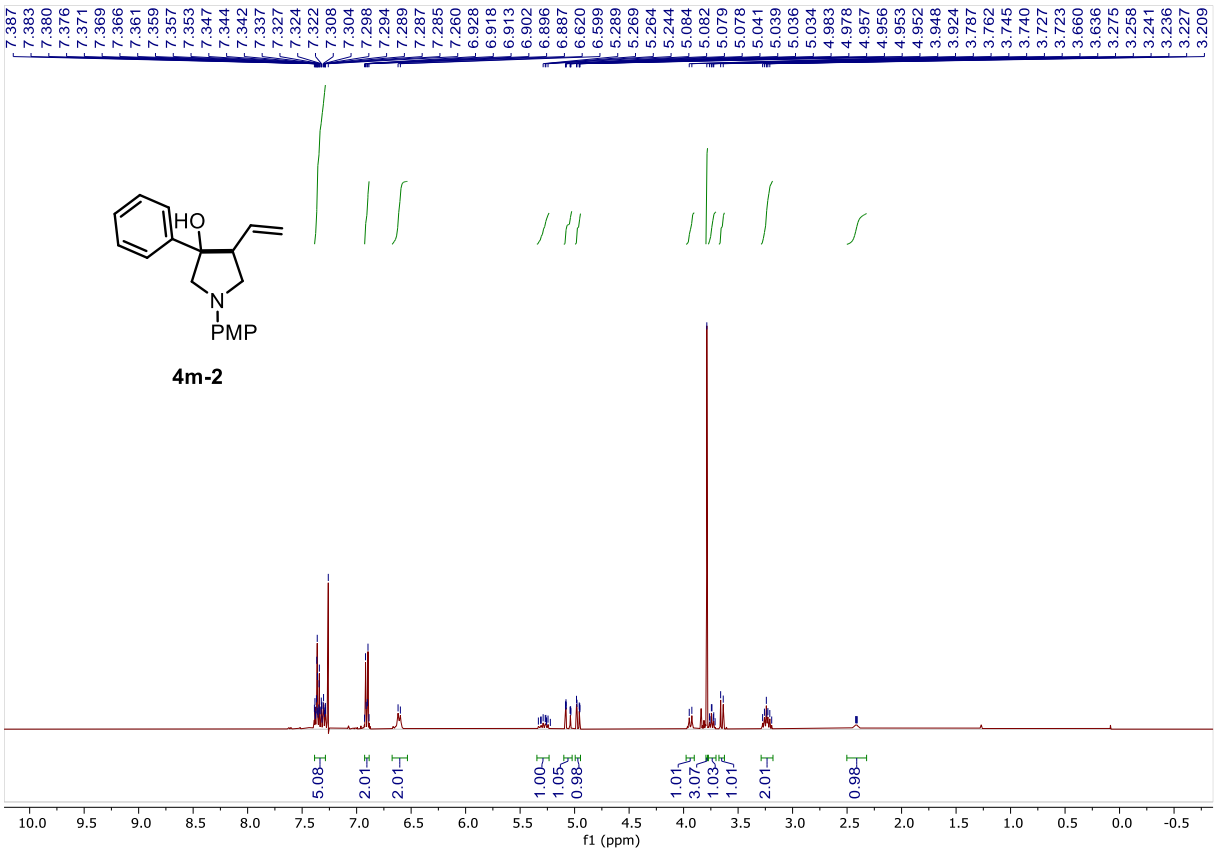
128.468
127.520
125.476
119.415
115.251
112.453
81.478
77.418
77.100
76.782
63.667
56.077
52.819
51.273
HO
N
PMP
4m-1
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.369
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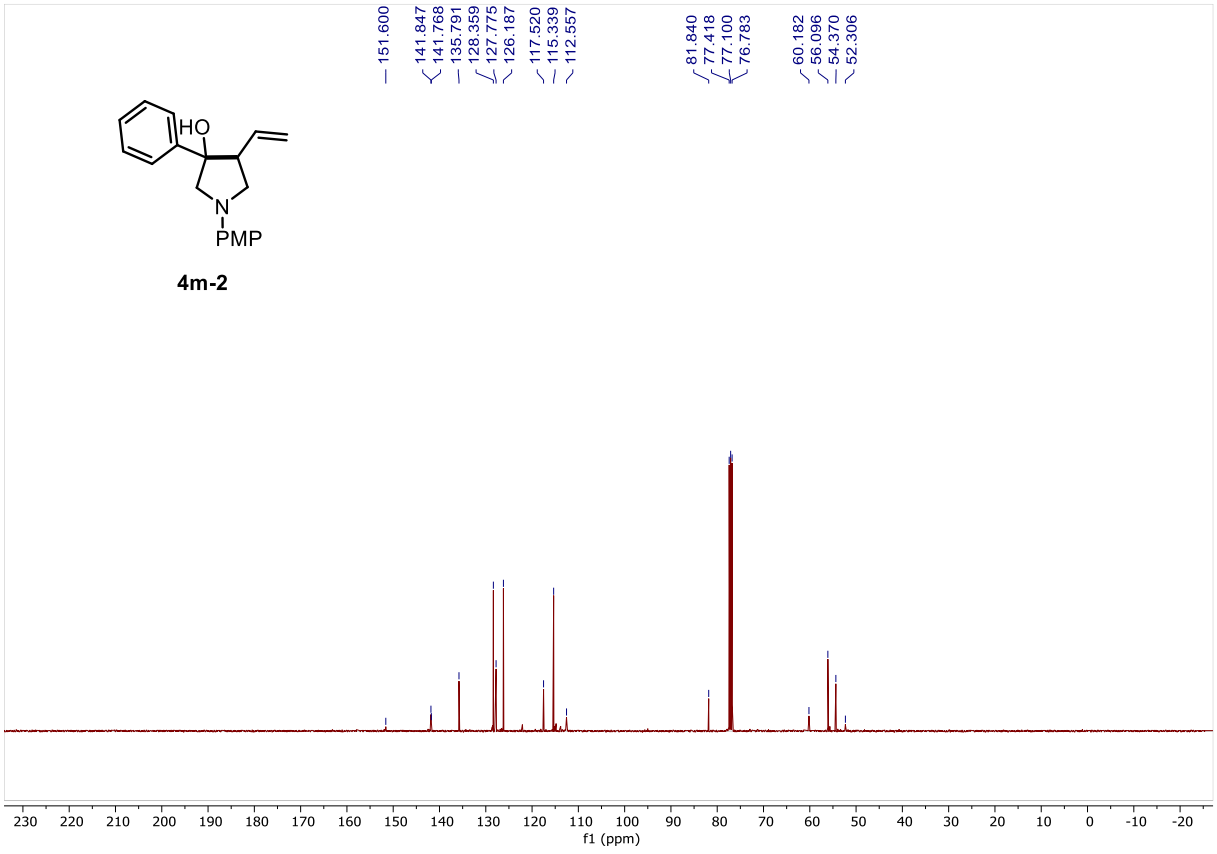
7.361
7.359
7.357
7.353
7.347
7.344
7.342
7.337
7.327
7.324
7.322
7.308
7.304
7.298
7.294
7.289
7.287
7.285
7.260
6.928
6.918
6.913
6.902
6.896
6.887
6.620
6.599
5.289
5.269
5.264
5.244
5.084
5.082
5.079
5.078
5.041
5.039
5.036
5.034
4.983
4.978
4.957
4.956
4.953
4.952
3.948
3.924
3.787
3.762
3.745
3.740
3.727
3.723
3.660
3.636
3.275
3.258
3.241
3.236
3.227
3.209
HO
N
PMP
4m-2
5.08
2.01
2.01
1.00
1.05
0.98
1.01
3.07
1.03
1.01
2.01
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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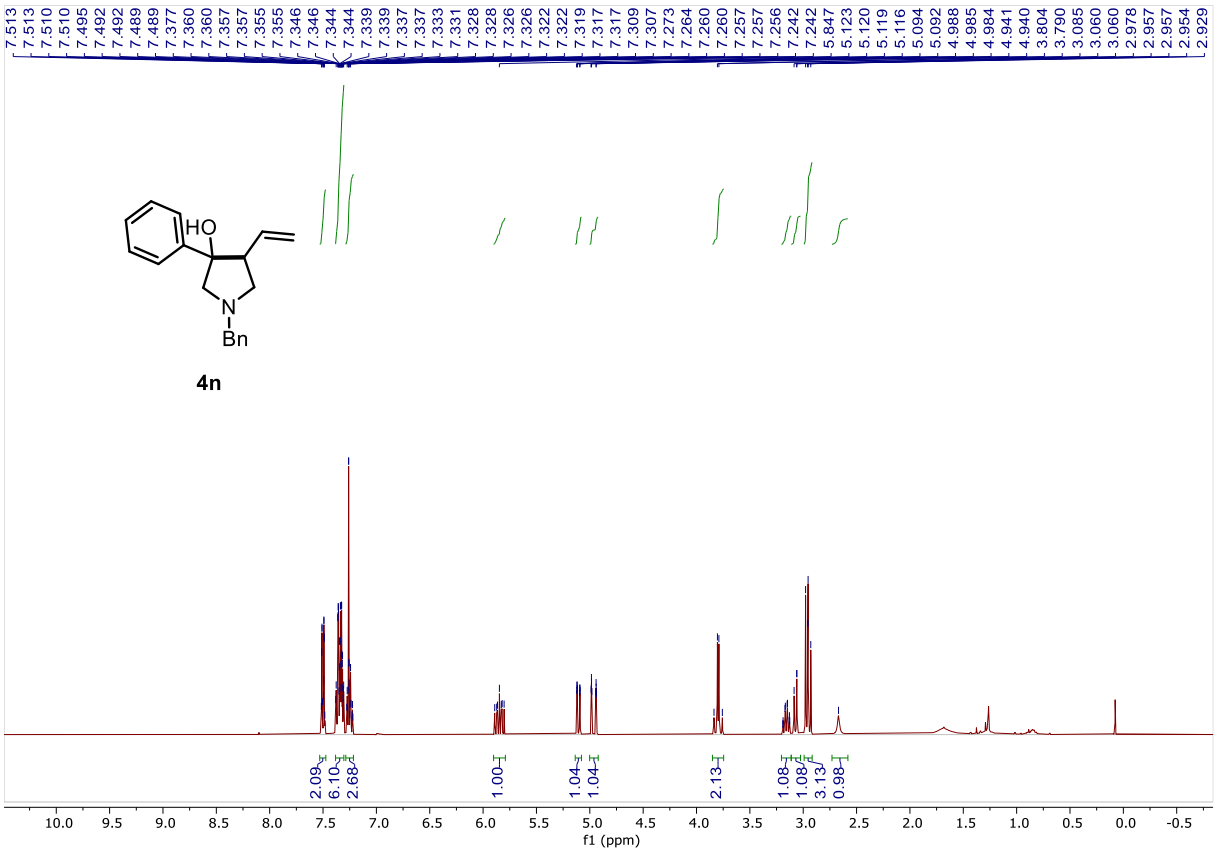
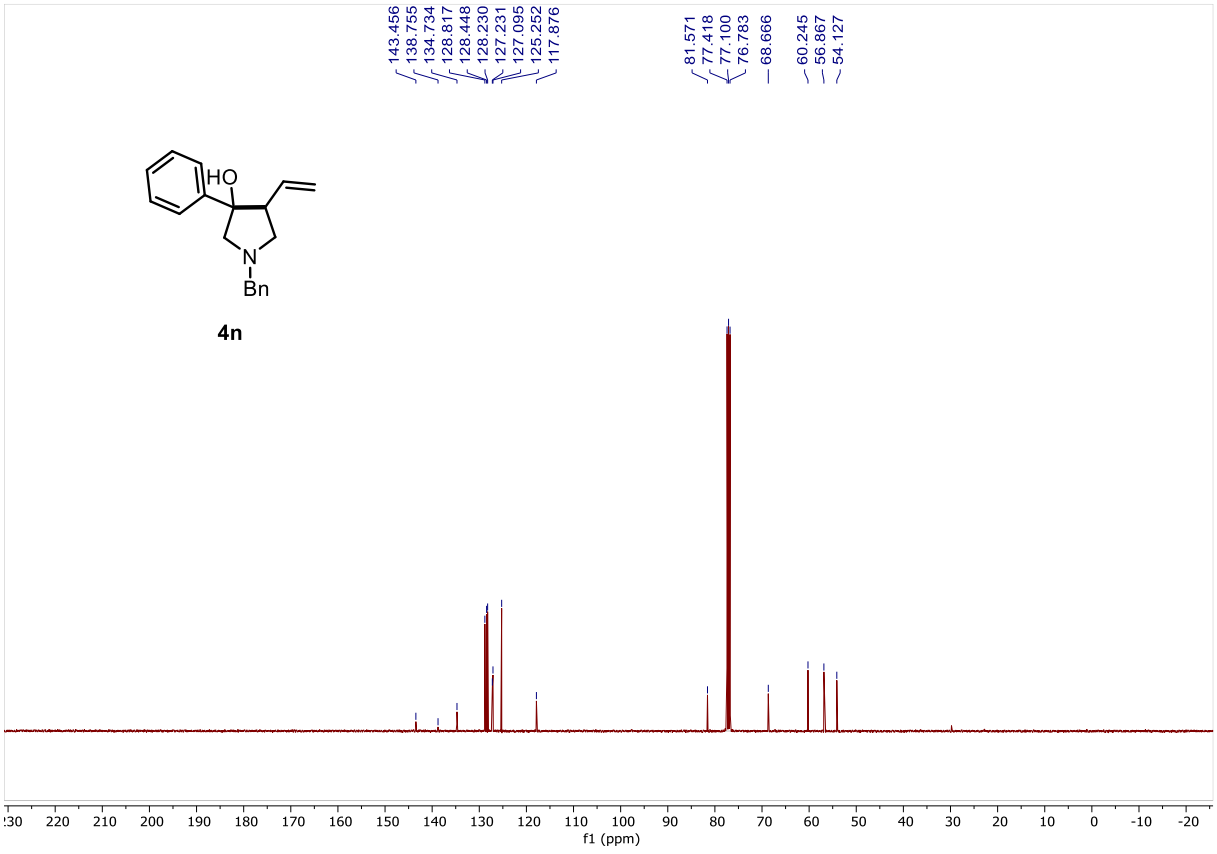
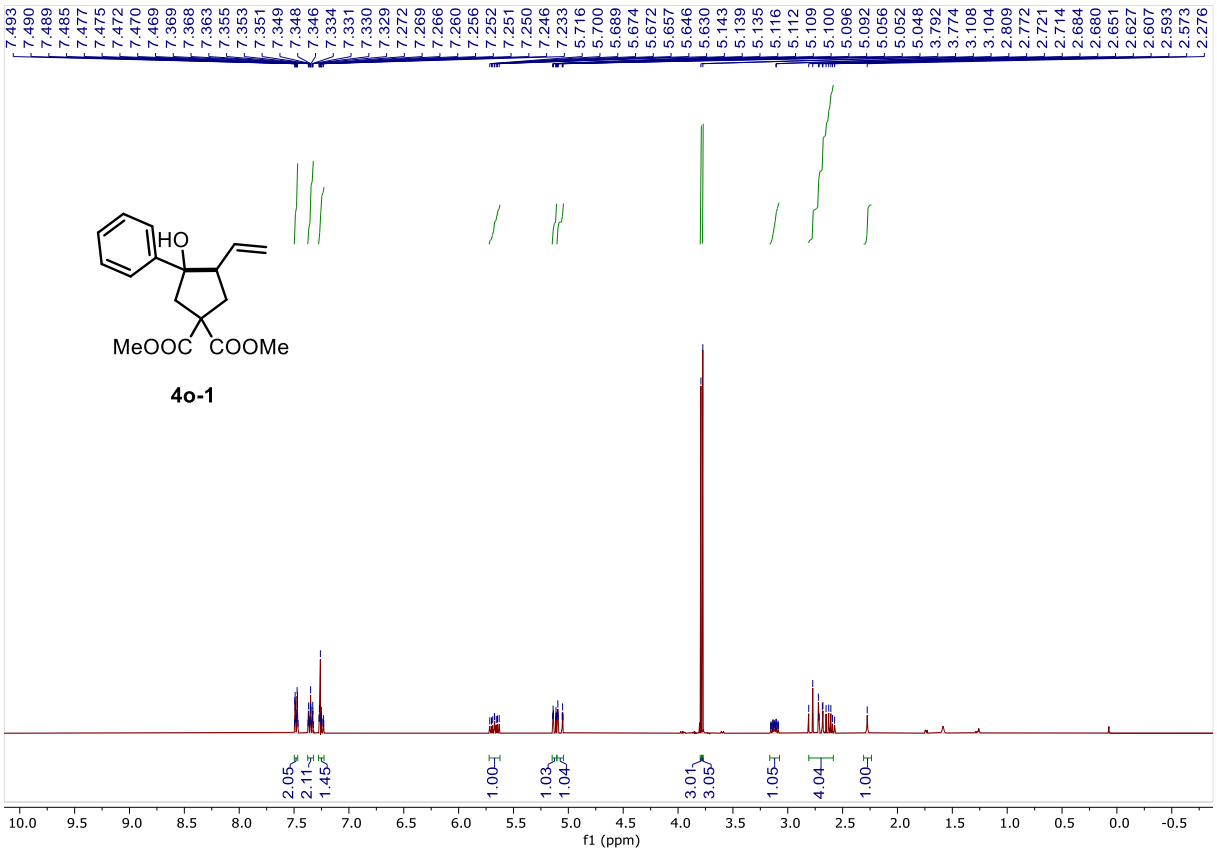
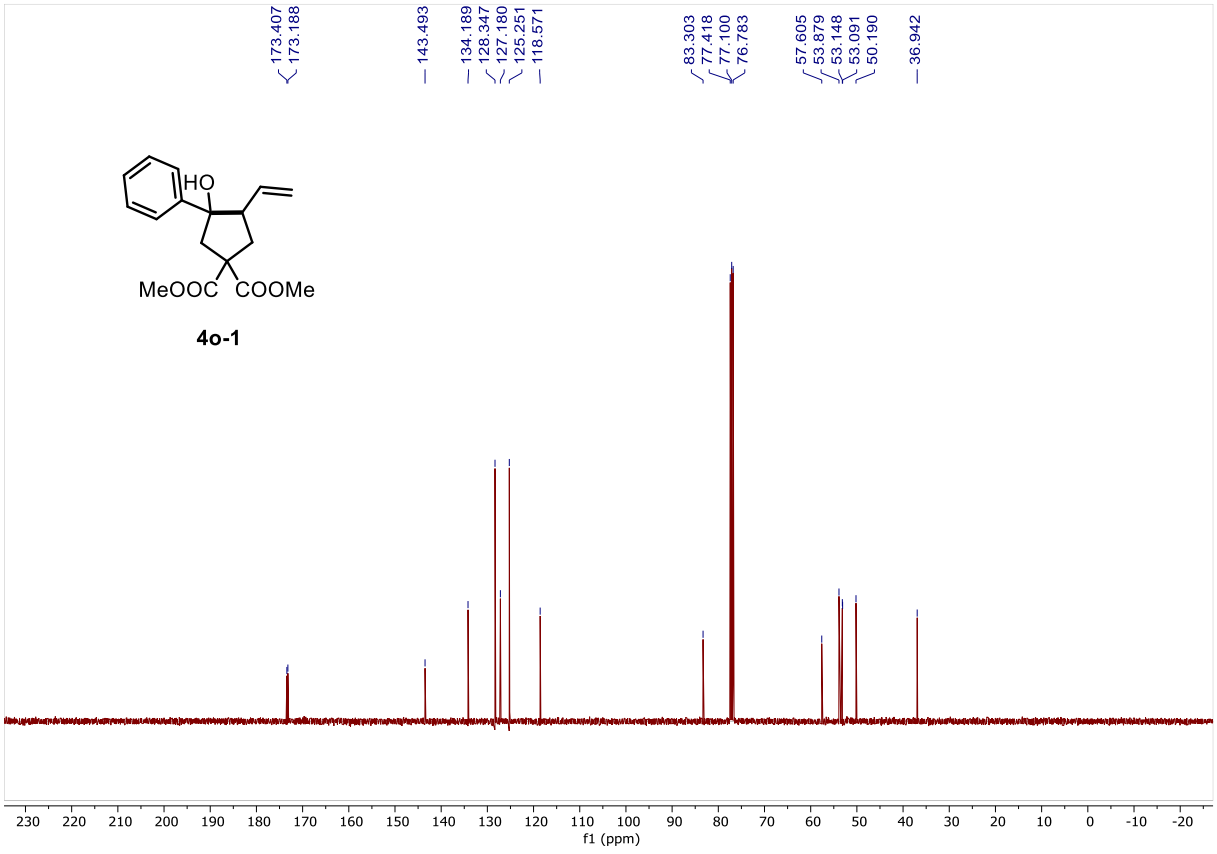
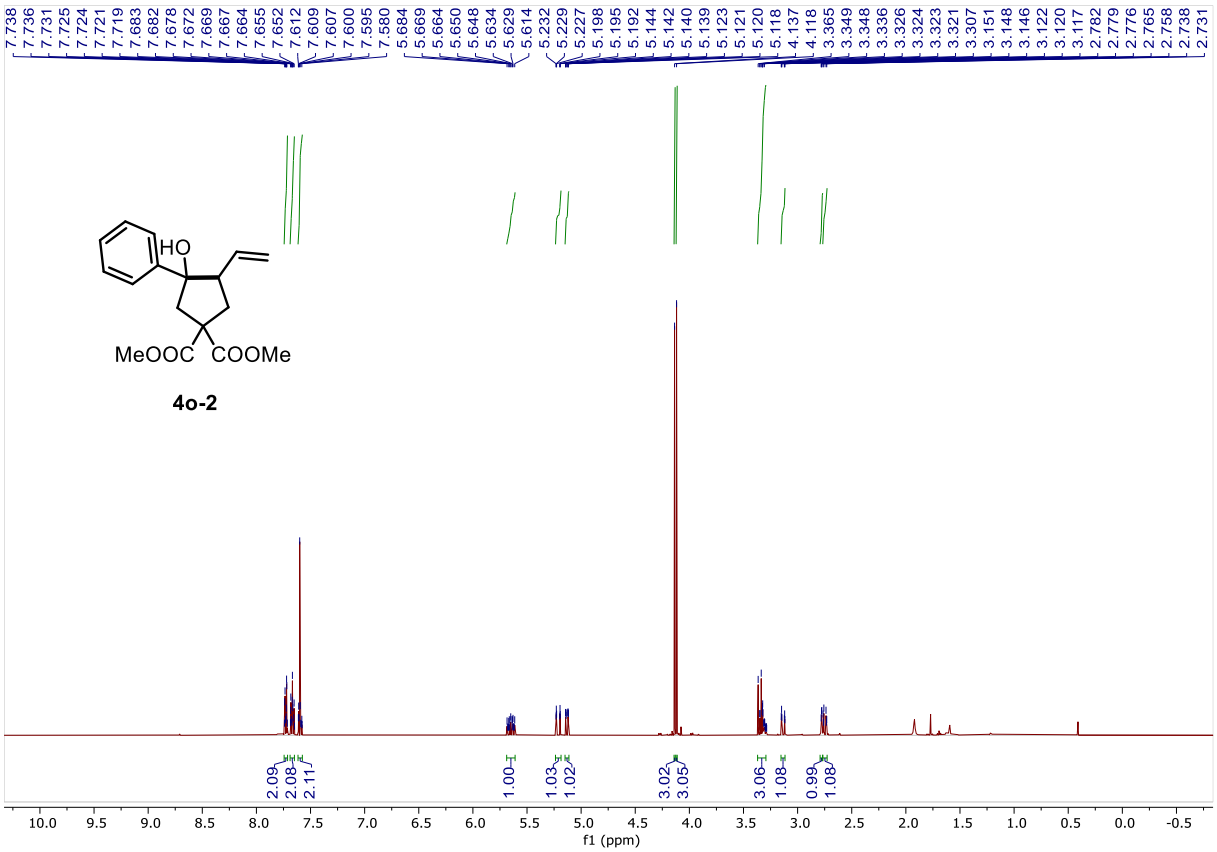
141.768
135.791
128.359
127.775
126.187
117.520
115.339
112.557
81.840
77.418
77.100
76.783
60.182
56.096
54.370
52.306
HO
N
PMP
4m-2
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

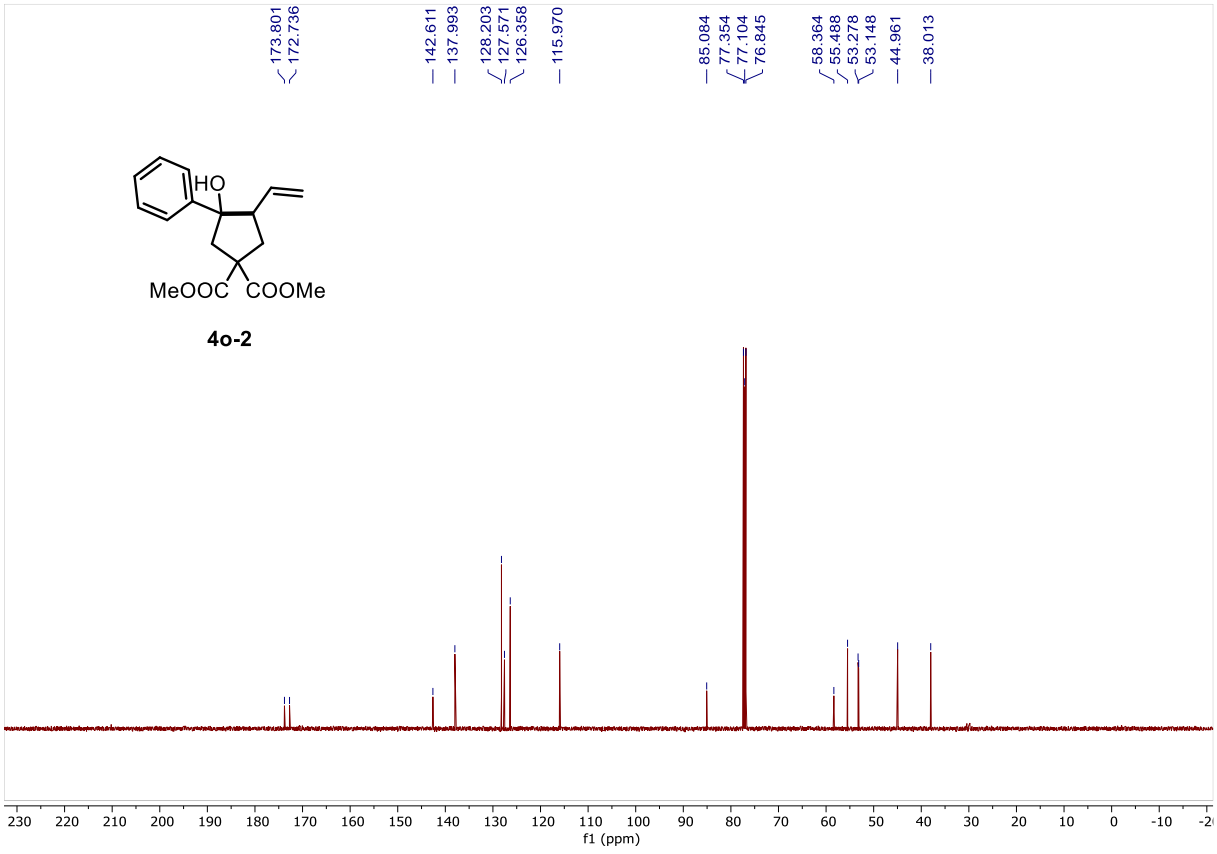

HO
N
Bn
4n
f1 (ppm)

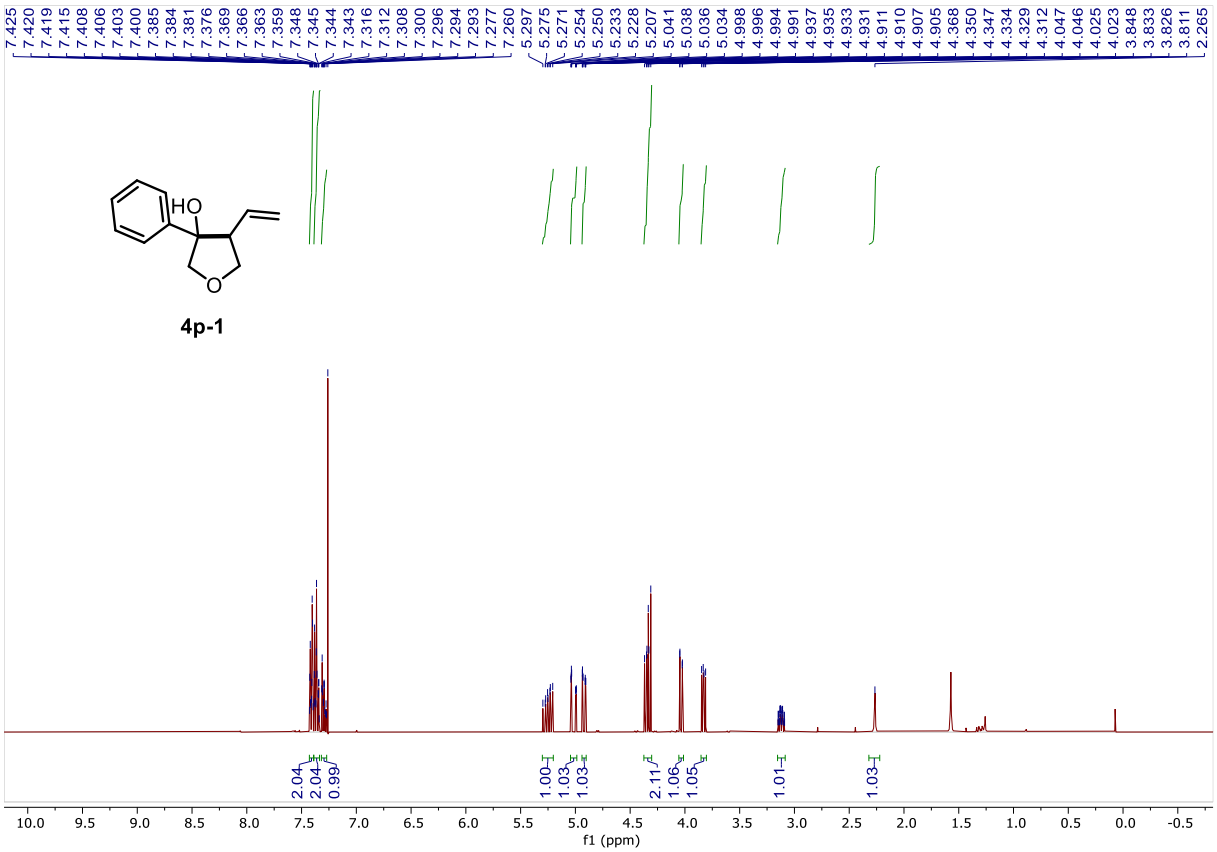

HO
N
Bn
4n
f1 (ppm)


HO
MeOOC COOMe
4o-1
f1 (ppm)


HO
MeOOC COOMe
4o-1
f1 (ppm)


HO
MeOOC COOMe
4o-2
f1 (ppm)


HO
MeOOC COOMe
4o-2
f1 (ppm)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7.400
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7.384
7.381
7.376
7.369
7.366
7.363
7.359
7.348
7.345
7.344
7.343
7.316
7.312
7.308
7.300
7.296
7.294
7.293
7.277
7.260
5.297
5.275
5.271
5.254
5.250
5.233
5.228
5.207
5.041
5.038
5.036
5.034
4.998
4.996
4.994
4.991
4.937
4.935
4.933
4.931
4.911
4.910
4.907
4.905
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4.350
4.347
4.334
4.329
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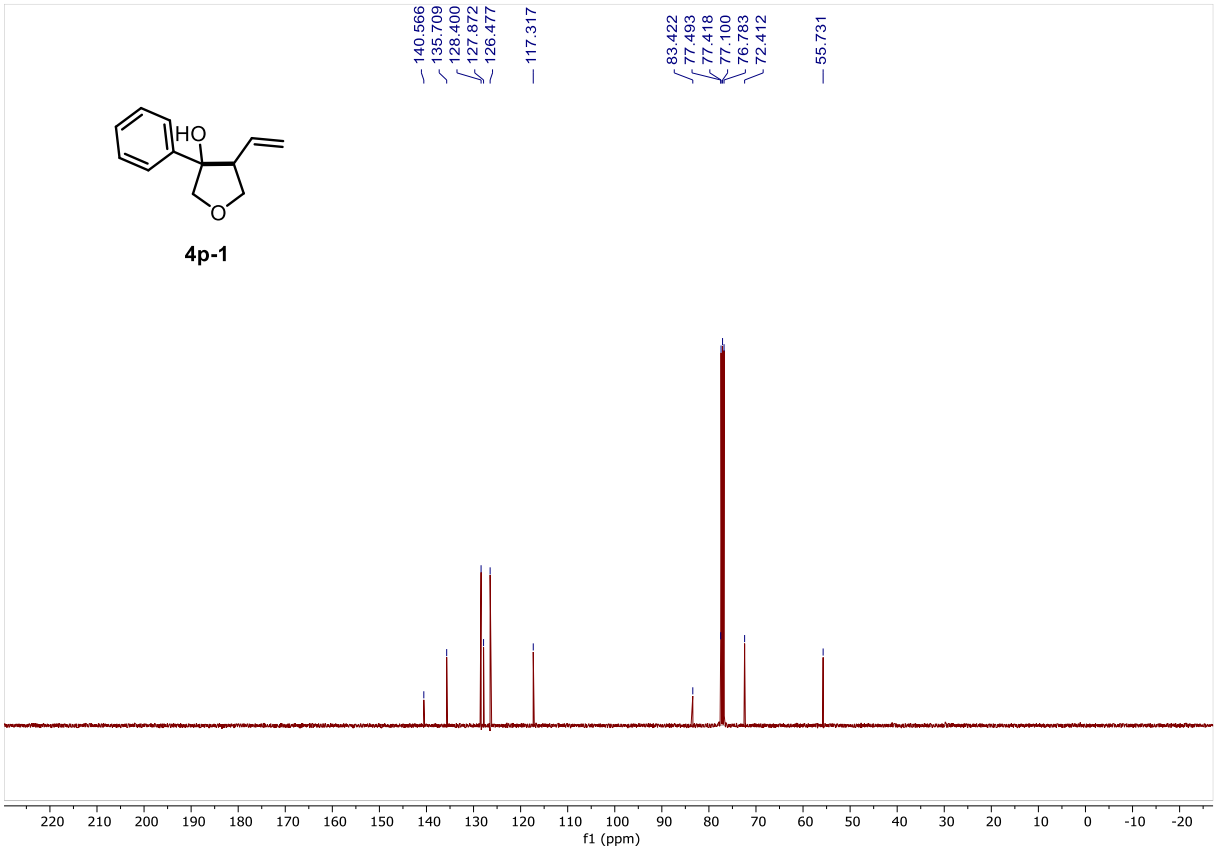
4.046
4.025
4.023
3.848
3.833
3.826
3.811
2.265
HO
O
4p-1
2.04
2.04
0.99
1.00
1.03
1.03
2.11
1.06
1.05
1.01
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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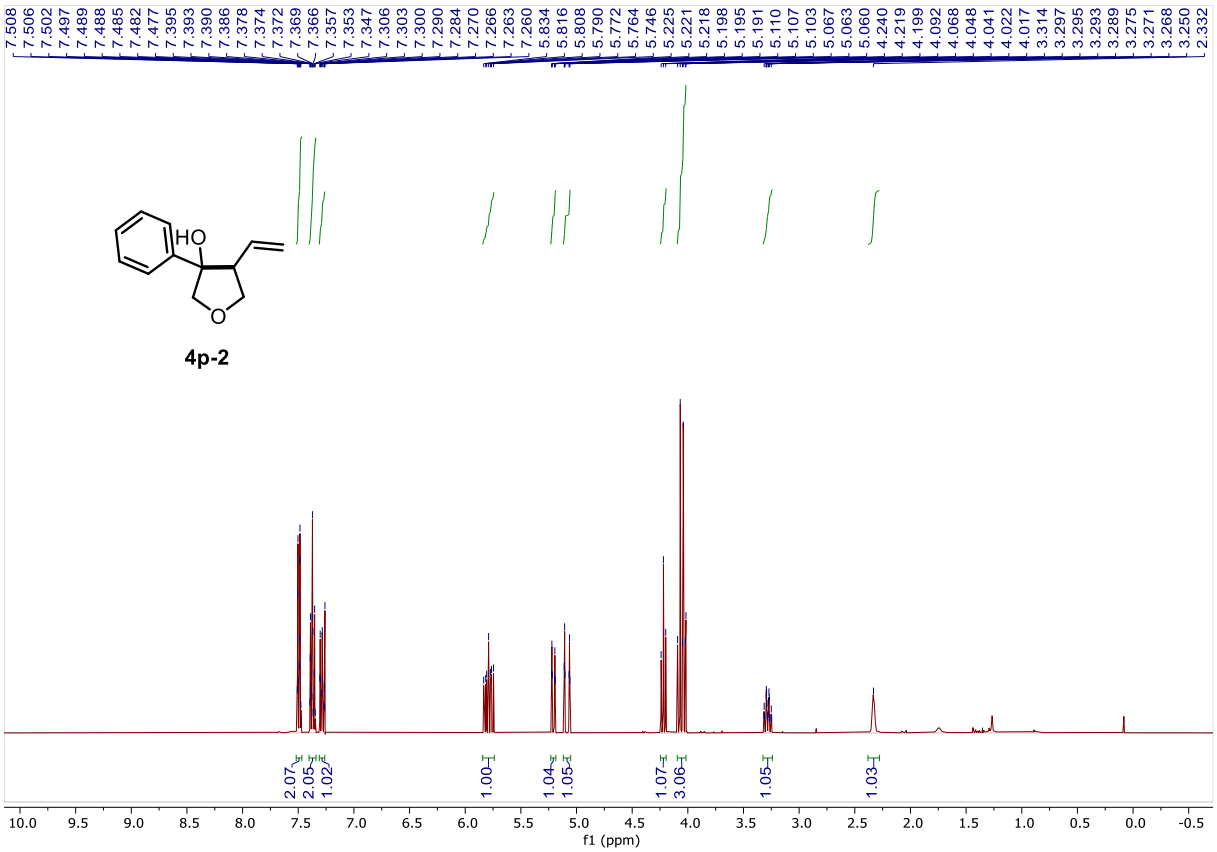
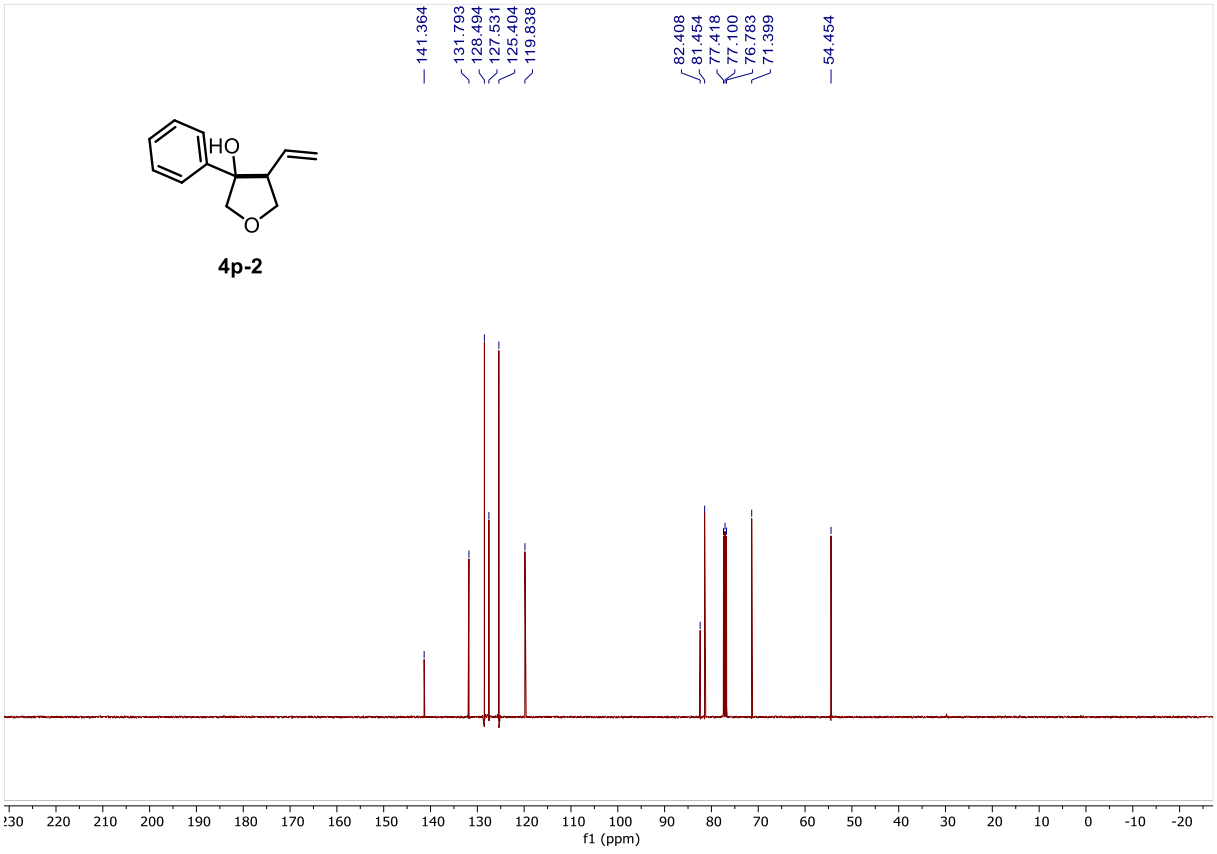
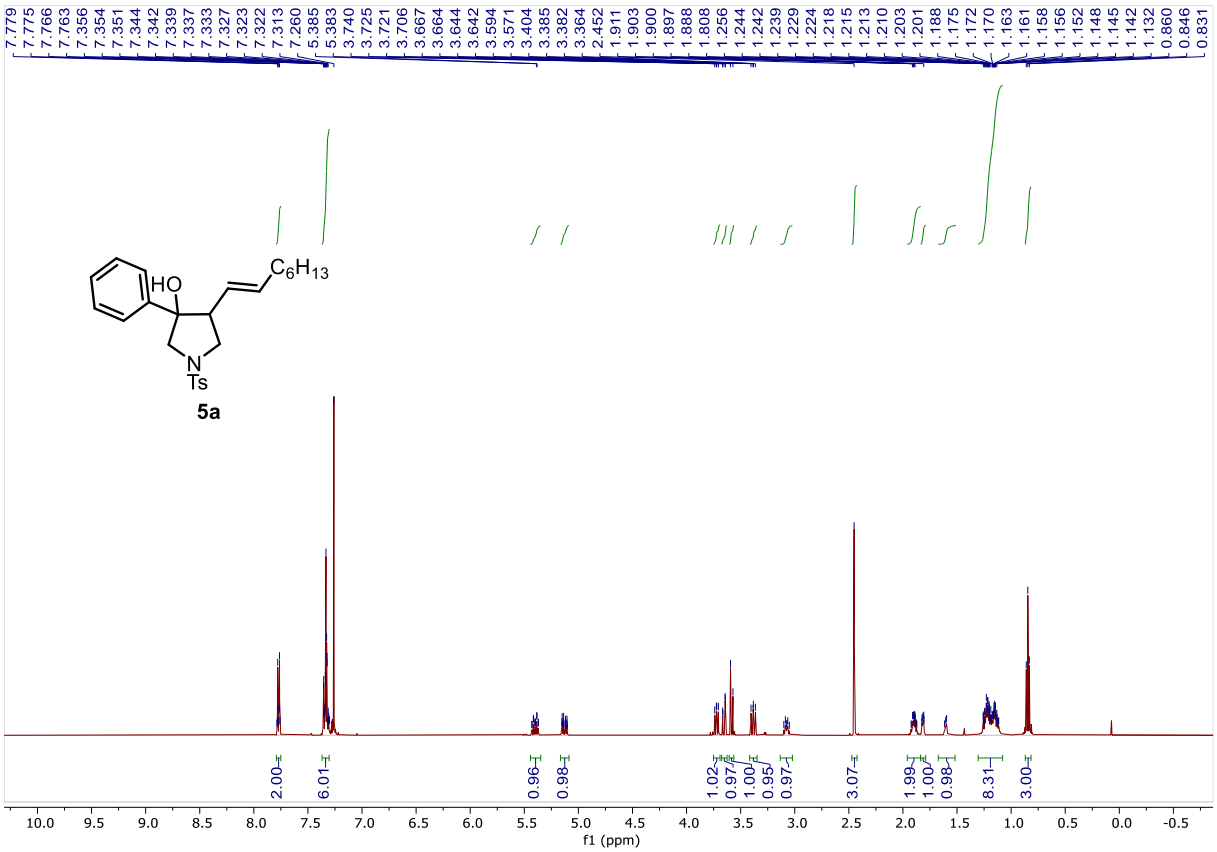
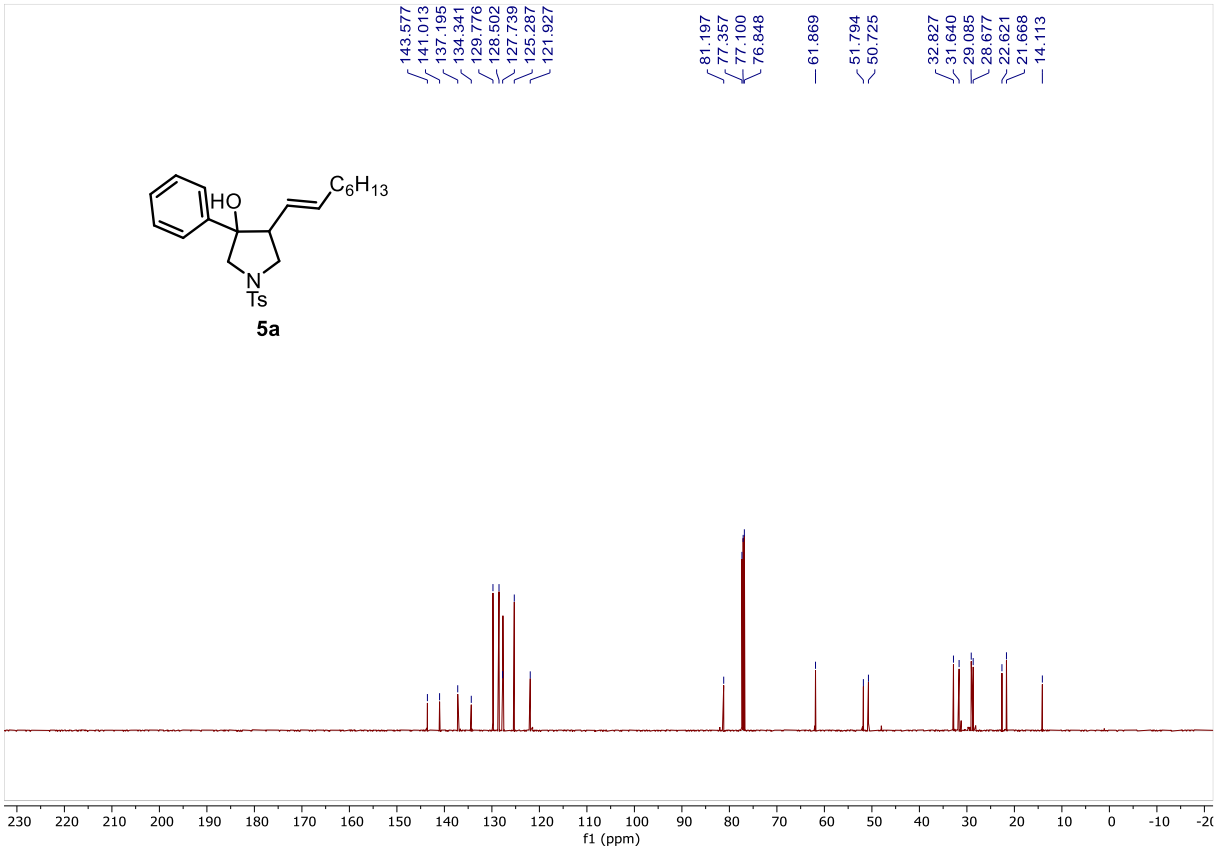
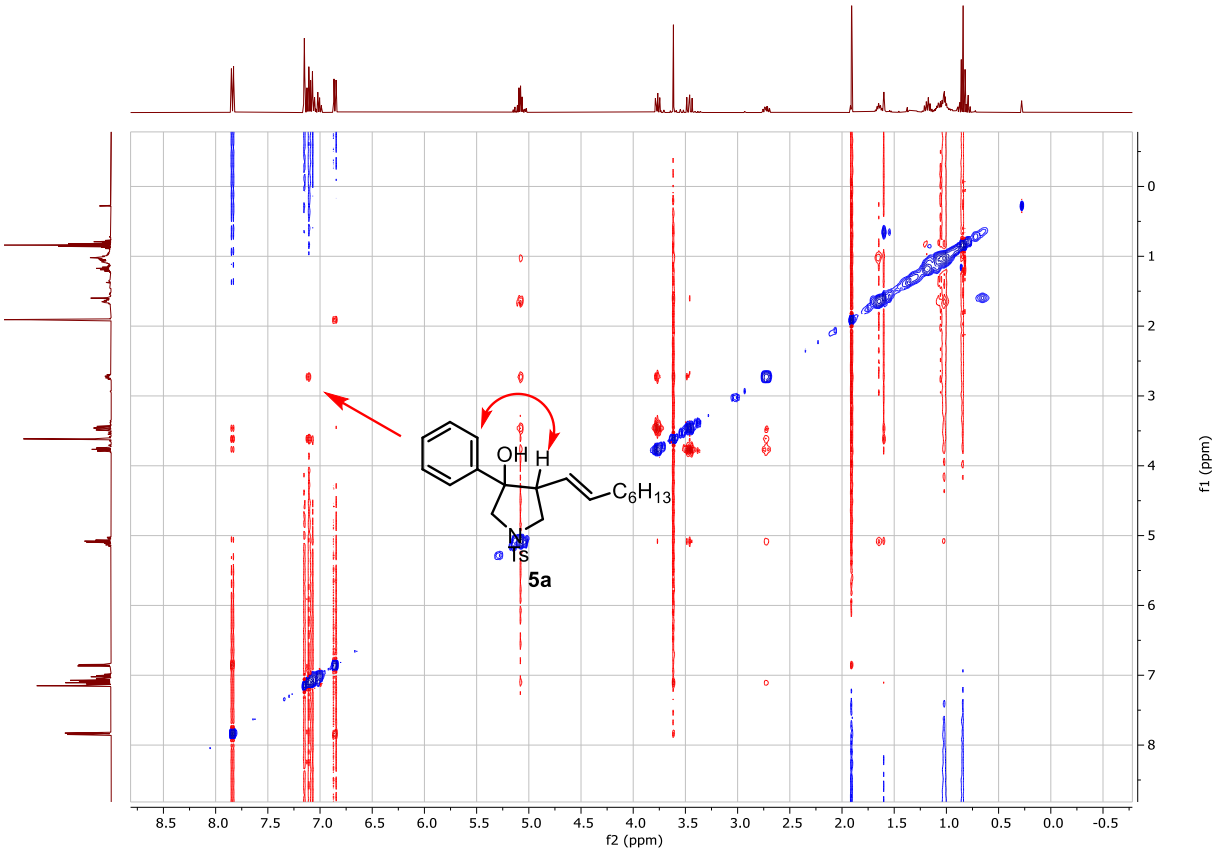
135.709
128.400
127.872
126.477
117.317
83.422
77.493
77.418
77.100
76.783
72.412
55.731
HO
O
4p-1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

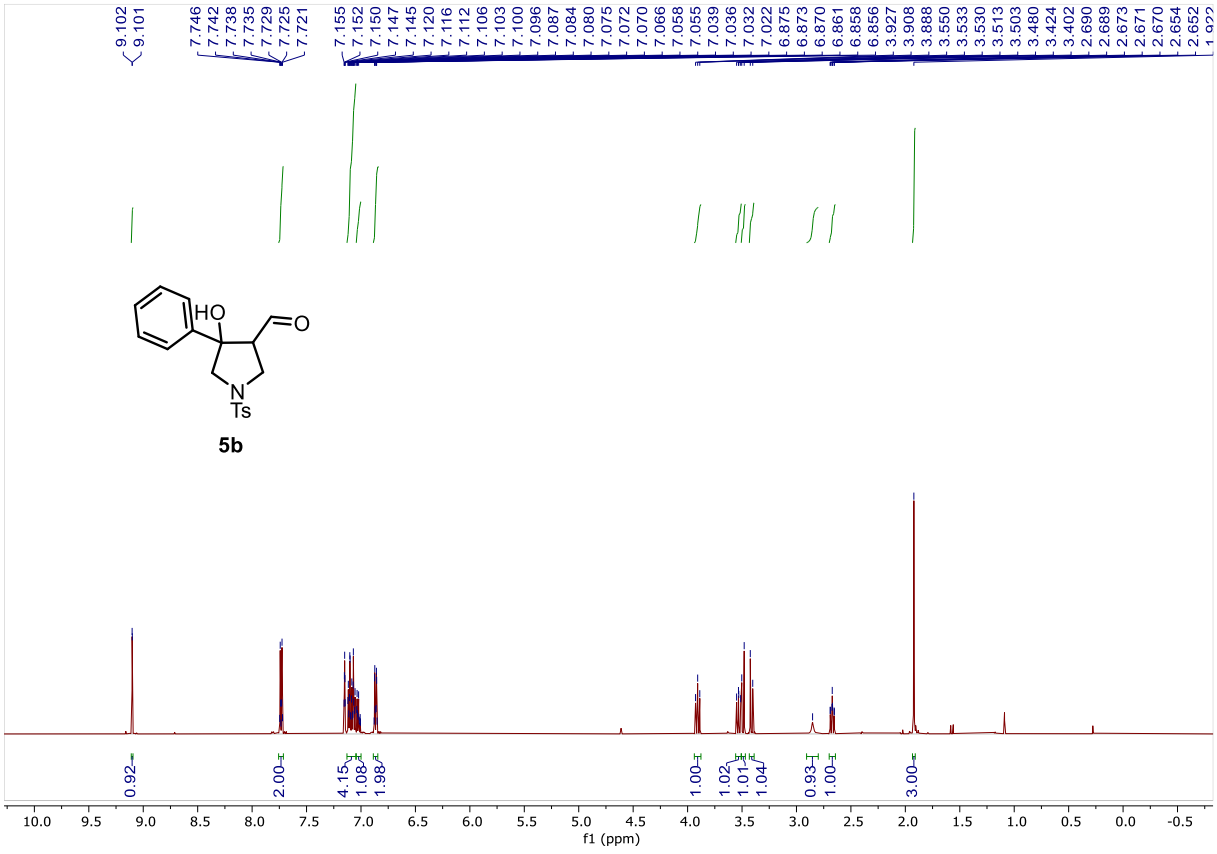

7.508
7.506
7.502
7.497
7.489
7.488
7.485
7.482
7.477
7.395
7.393
7.390
7.386
7.378
7.374
7.372
7.369
7.366
7.357
7.353
7.347
7.306
7.303
7.300
7.290
7.284
7.270
7.266
7.263
7.260
5.834
5.816
5.808
5.790
5.772
5.764
5.746
5.225
5.221
5.218
5.198
5.195
5.191
5.110
5.107
5.103
5.067
5.063
5.060
4.240
4.219
4.199
4.092
4.068
4.048
4.041
4.022
4.017
3.314
3.297
3.295
3.293
3.289
3.275
3.271
3.268
3.250
2.332
HO
O
4p-2
2.07
2.05
1.02
1.00
1.04
1.05
1.07
3.06
1.05
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

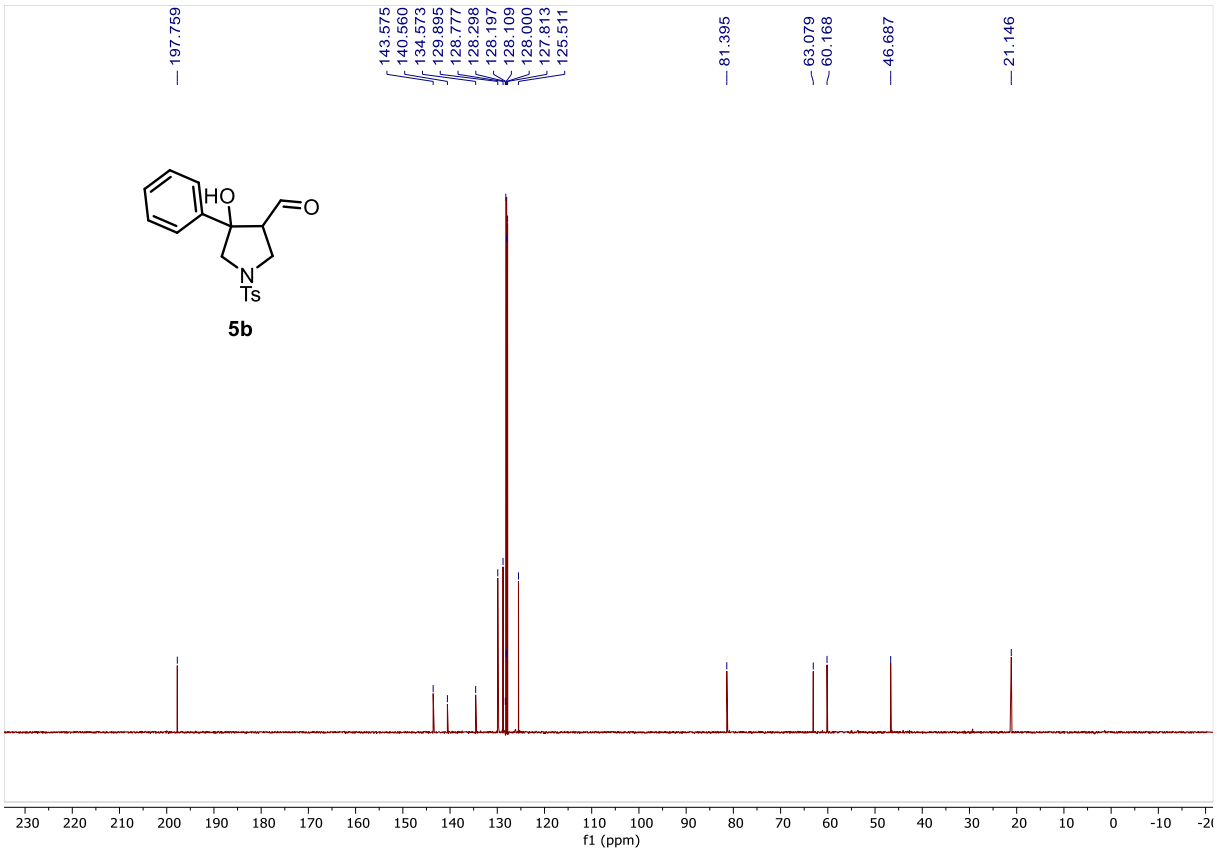

141.364
131.793
128.494
127.531
125.404
119.838
82.408
81.454
77.418
77.100
76.783
71.399
54.454
HO
O
4p-2
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

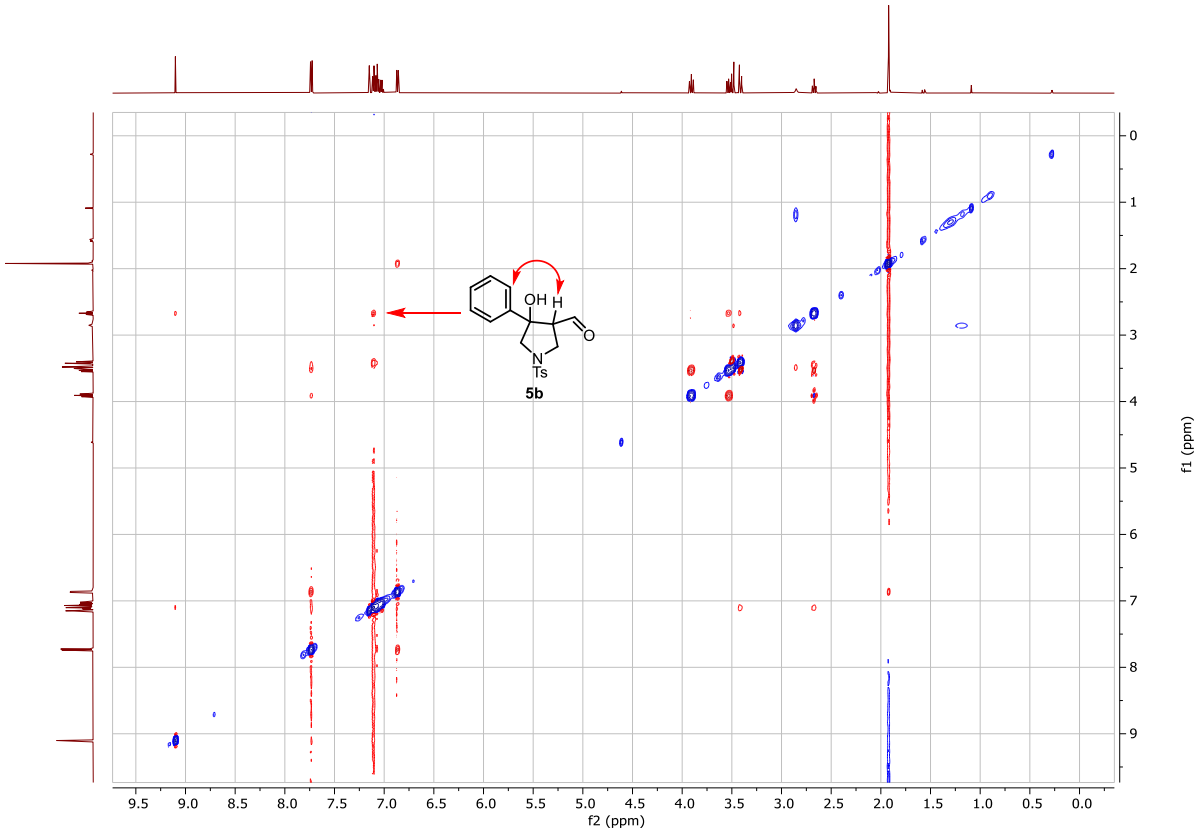

7.779
7.775
7.766
7.763
7.356
7.354
7.351
7.344
7.342
7.339
7.337
7.333
7.327
7.323
7.322
7.313
7.260
5.385
5.383
3.740
3.725
3.721
3.706
3.667
3.664
3.644
3.642
3.594
3.571
3.404
3.385
3.382
3.364
2.452
1.911
1.903
1.900
1.897
1.888
1.808
1.256
1.244
1.242
1.239
1.229
1.224
1.218
1.215
1.213
1.210
1.203
1.201
1.188
1.175
1.172
1.170
1.163
1.161
1.158
1.156
1.152
1.148
1.145
1.142
1.132
0.860
0.846
0.831
HO
C6H13
N
Ts
5a
2.00
6.01
0.96
0.98
1.02
0.97
1.00
0.95
0.97
3.07
1.99
1.00
0.98
8.31
3.00
f1 (ppm)

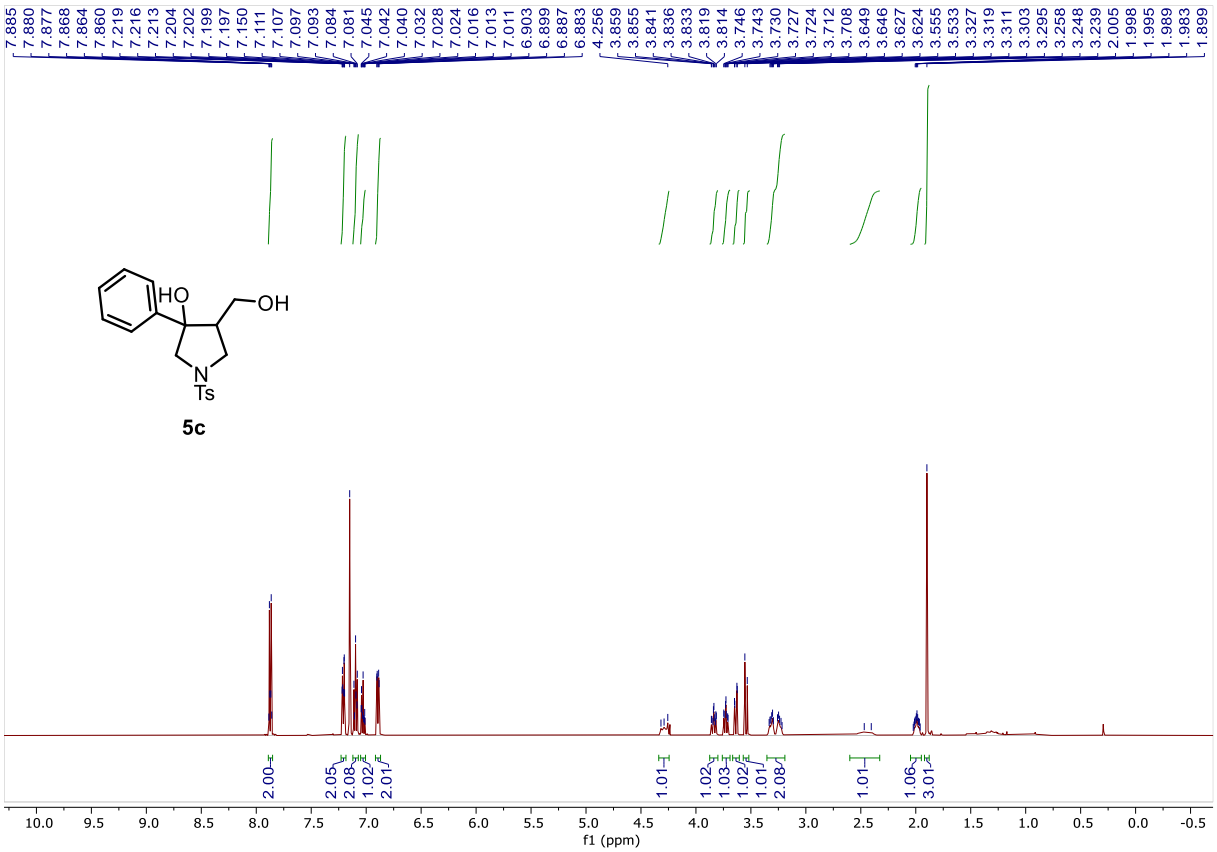

143.577
141.013
137.195
134.341
129.776
128.502
127.739
125.287
121.927
81.197
77.357
77.100
76.848
61.869
51.794
50.725
32.827
31.640
29.085
28.677
22.621
21.668
14.113
HO
C6H13
N
Ts
5a
f1 (ppm)

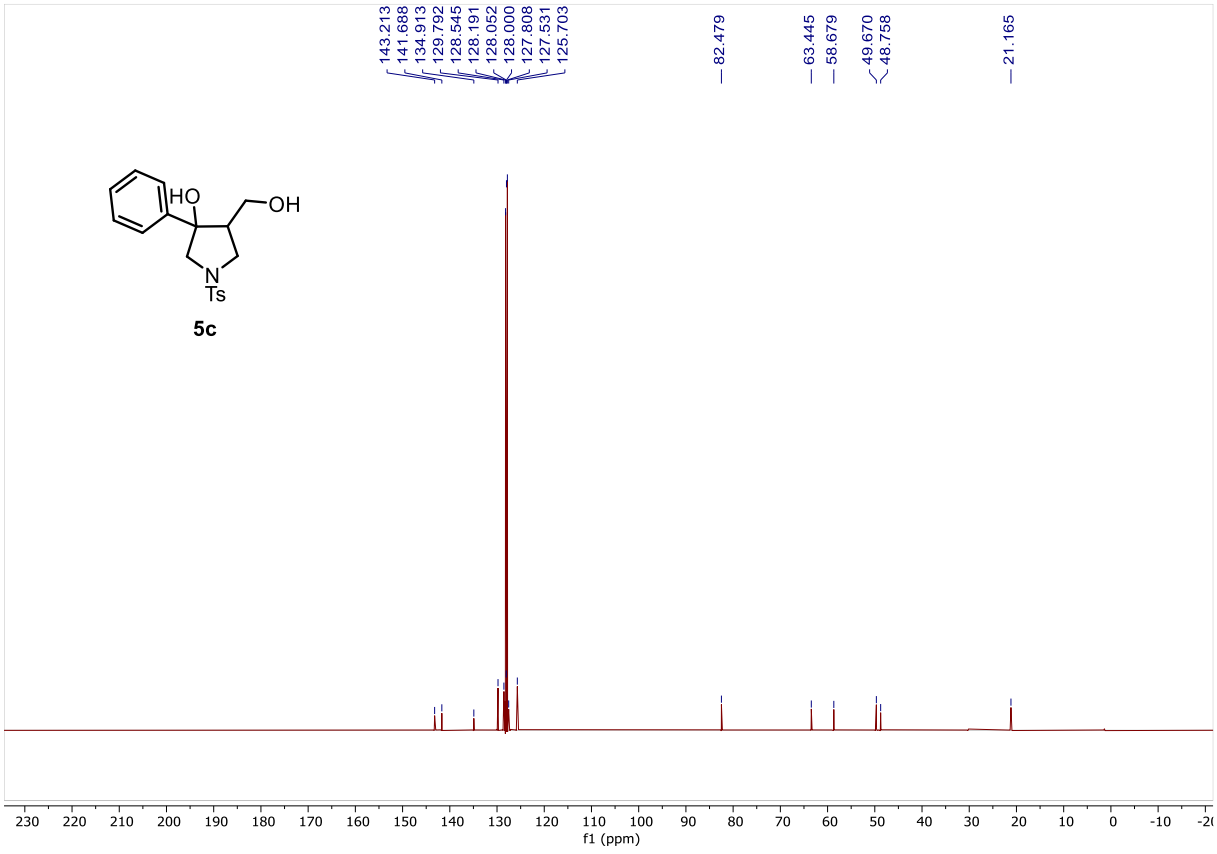

OH
H
C_6H_{13}
N
Ts
5a
f2 (ppm)
f1 (ppm)

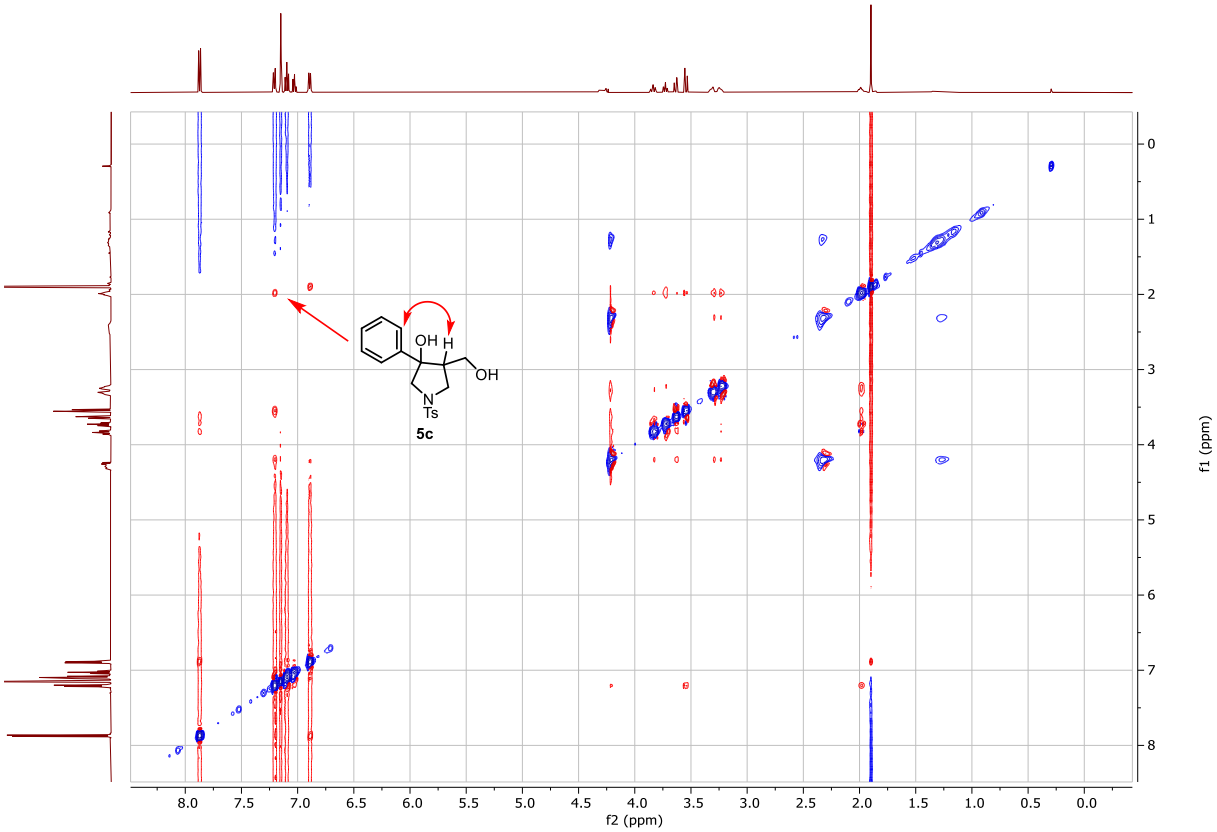

HO
O
N
Ts
5b
f1 (ppm)

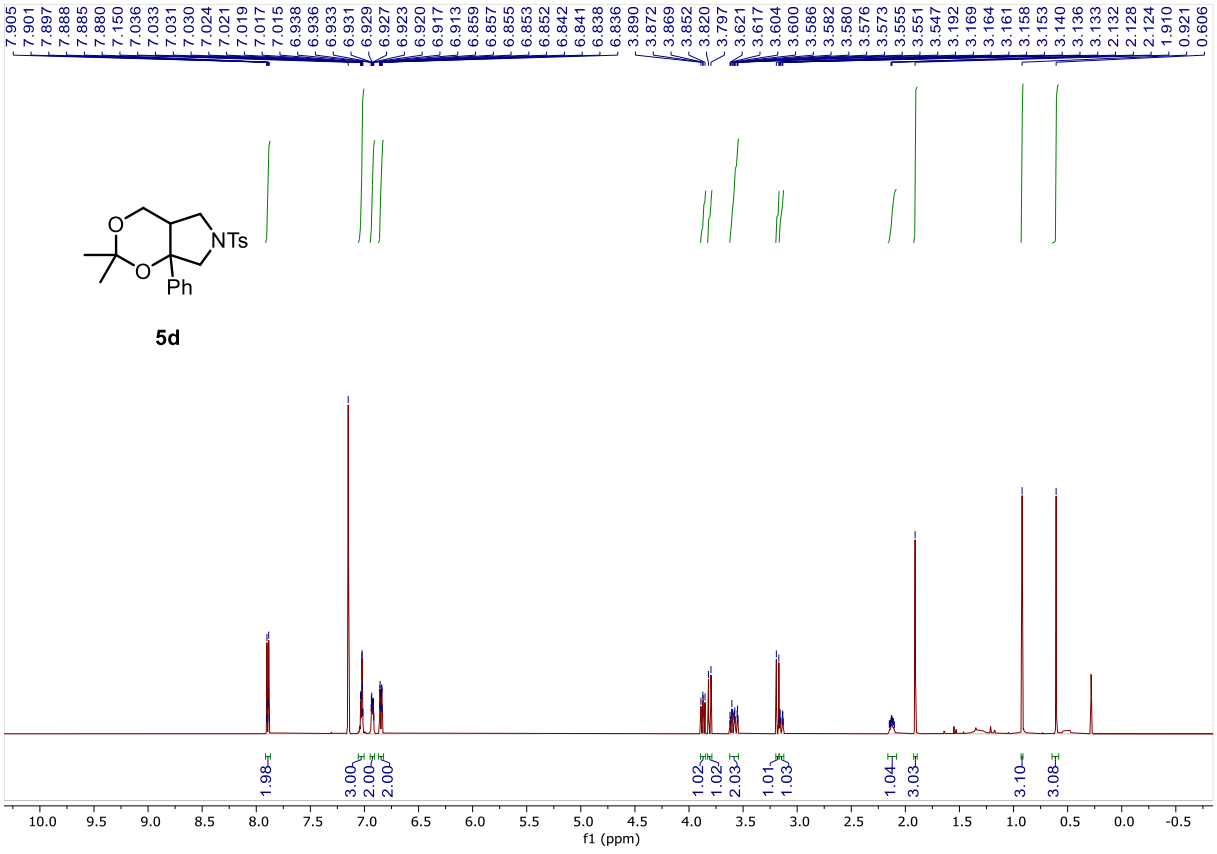

197.759
143.575
140.560
134.573
129.895
128.777
128.298
128.197
128.109
128.000
127.813
125.511
81.395
63.079
60.168
46.687
21.146
HO
O
N
Ts
5b
f1 (ppm)

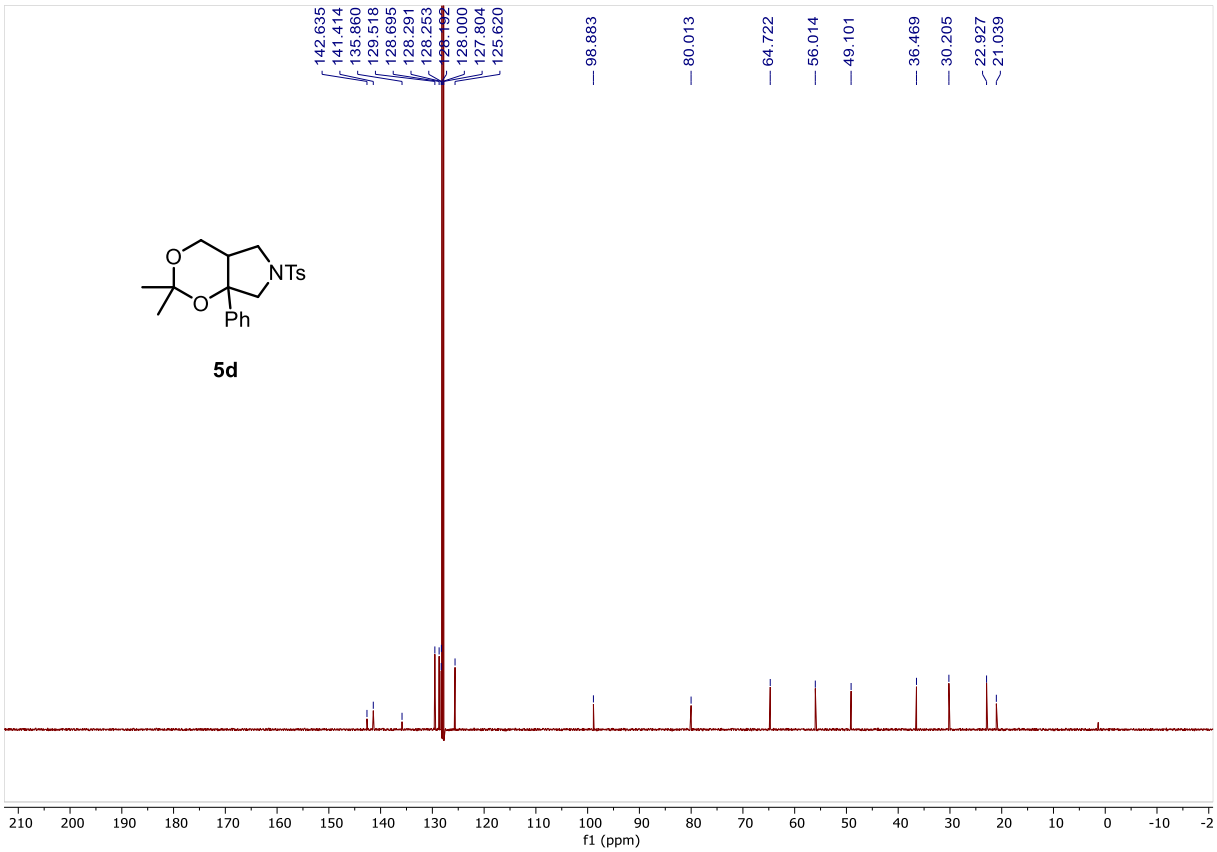

OH
H
O
N
Ts
5b
f2 (ppm)
f1 (ppm)

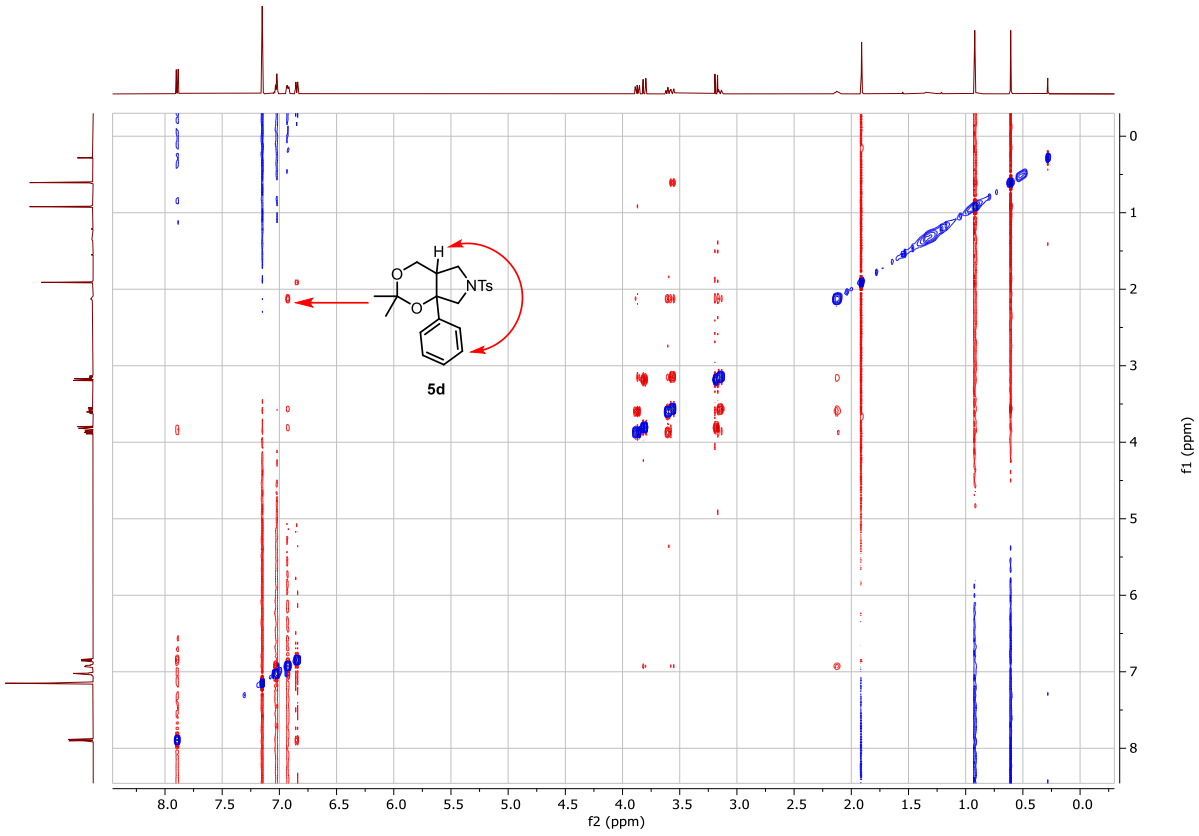

7.885
7.880
7.877
7.868
7.864
7.860
7.219
7.216
7.213
7.204
7.202
7.199
7.197
7.150
7.111
7.107
7.097
7.093
7.084
7.081
7.045
7.042
7.040
7.032
7.028
7.024
7.016
7.013
7.011
6.903
6.899
6.887
6.883
4.256
3.859
3.855
3.841
3.836
3.833
3.819
3.814
3.746
3.743
3.730
3.727
3.724
3.712
3.708
3.649
3.646
3.627
3.624
3.555
3.533
3.327
3.319
3.311
3.303
3.295
3.258
3.248
3.239
2.005
1.998
1.995
1.989
1.983
1.899
HO
OH
N
Ts
5c
2.00
2.05
2.08
1.02
2.01
1.01
1.02
1.03
1.02
1.01
2.08
1.01
1.06
3.01
f1 (ppm)


143.213
141.688
134.913
129.792
128.545
128.191
128.052
128.000
127.808
127.531
125.703
82.479
63.445
58.679
49.670
48.758
21.165
HO
OH
N
Ts
5c
f1 (ppm)


OH
H
OH
N
Ts
5c
f2 (ppm)
f1 (ppm)


7.905
7.901
7.897
7.888
7.885
7.880
7.150
7.036
7.033
7.031
7.030
7.024
7.021
7.019
7.017
7.015
6.938
6.936
6.933
6.931
6.929
6.927
6.923
6.920
6.917
6.913
6.859
6.857
6.855
6.853
6.852
6.842
6.841
6.838
6.836
3.890
3.872
3.869
3.852
3.820
3.797
3.621
3.617
3.604
3.600
3.586
3.582
3.580
3.576
3.573
3.555
3.551
3.547
3.192
3.169
3.164
3.161
3.158
3.153
3.140
3.136
3.133
2.132
2.128
2.124
1.910
0.921
0.606
O
O
NTs
Ph
5d
1.98
3.00
2.00
2.00
1.02
1.02
2.03
1.01
1.03
1.04
3.03
3.10
3.08
f1 (ppm)


142.635
141.414
135.860
129.518
128.695
128.291
128.253
128.192
128.000
127.804
125.620
98.883
80.013
64.722
56.014
49.101
36.469
30.205
22.927
21.039
NTs
Ph
5d
f1 (ppm)


H
NTs
5d
f2 (ppm)
f1 (ppm)