Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Concise enantioselective synthesis of nonproteinogenic α-aminoacids via organocatalytic Mannich-type reaction

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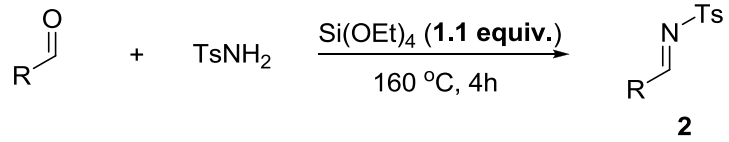
1. General information

The ^{1}H, ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. The high-resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer. The measurements were taken in the positive ion mode (interface capillary voltage 4500 V) in the mass range from m/z = 50 Da to m/z = 3000 Da; external and internal calibrations were done with the electrospray calibrant solution. Optical rotations were measured on a polarimeter JASCO P-2000 and calibrated with a pure solvent as a blank. HPLC analyses were performed on an HPLC system equipped with chiral stationary phase columns (AD-H, OD-H, OJ-H, AS-H), detection at 220 or 254 nm. Allomaltol **1** is commercially availble. Catalysts **I-VI, XI-XIV** were synthesized by reported procedures,[1-7] catalysts **VII-X** are commercially available. Reagents and solvents were purified according to standard methods. Solvents were removed from reaction mixtures by means of vacuum pomp ULVAC with efficiency 40 L min^{-1}.

2. General procedures for synthesis and characterization data of substrates 2.

Procedure A. (For R= Ar, het-Ar and Ad)

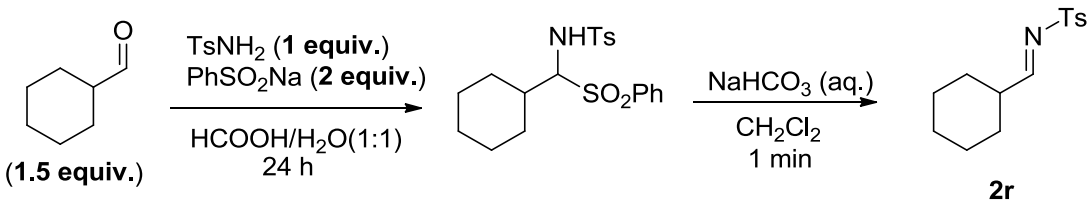


2

Tetraethoxysilane (2.43 mL, 11 mmol) was added to a suspension of corresponding aldehyde (10 mmol)[a] and toluenesulfonamide (1.62 g, 9.5 mmol) and the mixture was stirred at 160 °C with Dean-Stark trap under argon for 4 h. The raw product was recrystallized from EtOAc and dried under reduced pressure (10 torr) affording analytically pure product **2**.

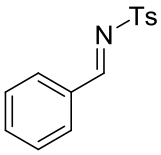
[a] for compounds **2a**, **2g** and **2q** the reactions were performed on the 20-mmol scale.

Procedure B. (For R= Cyclohexyl)



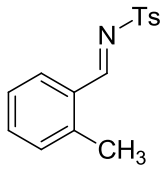
2r

To stirred solution of toluenesulfonamide (1.62 g, 9.5 mmol) and sodium phenylsulfinate (3.12 g, 19 mmol) in $HCOOH/H_2O$ (1:1, v/v, 40 mL) was added cyclohexylcarboxaldehyde (1.73 mL, 14.25 mmol) and stirred under argon for 24 h. The obtained white solid then filtrated, washed with hexane (50 mL) and water (100 mL), dried under high vacuum and used in next step without further purification. The obtained solid was dissolved in DCM (60 mL) and vigorously shacked with saturated $NaHCO_3$ solution (60 mL) in the separatory funnel for 1 minute, then the organic layer was separated, dried under Na_2SO_4, end concentrated under vacuum to obtain analytically pure imine **2r**.



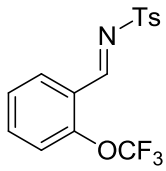
2a

N-Benzylidene-4-methylbenzenesulfonamide (2a). Colorless solid, yield 3.84 g (78 %), mp = 106-108 °C (lit.[8] 104-106 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.92 (t, *J* = 8.4 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H).



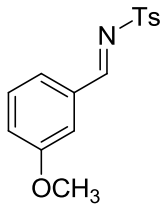
2b

4-Methyl-N-(2-methylbenzylidene)benzenesulfonamide (2b). Colorless solid, yield 2.26 g (87 %), mp = 93-95°C (lit.[9] 93-95 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32-7.27 (m, 2H), 2.63 (s, 3H), 2.46 (s, 3H).



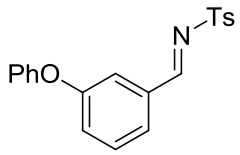
2c

4-Methyl-N-(2-(trifluoromethoxy)benzylidene)benzenesulfonamide (2c). Colorless solid, yield 2.25 g (69 %), mp = 125-127°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.43-7.37 (m, 4H), 2.46 (s, 3H). The NMR data are in accordance with literature.[9]



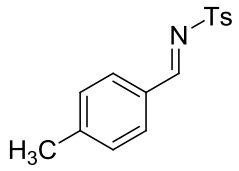
2d

N-(3-Methoxybenzylidene)-4-methylbenzenesulfonamide (2d). Colorless solid, yield 2.17 g (79 %), mp = 70-72°C (lit.[8] 71-72 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.49-7.35 (m, 5H), 7.18 (d, *J* = 7.0 Hz, 1H), 3.85 (s, 3H), 2.46 (s, 3H).



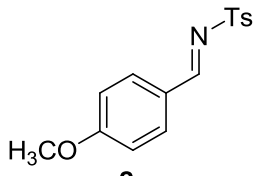
2e

4-Methyl-N-(3-phenoxybenzylidene)benzenesulfonamide (2e). Colorless solid, yield 2.70 g (81 %), mp = 89-91°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.56 (brs, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.41-7.34 (m, 4H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). All data in accordance with literature.[8]



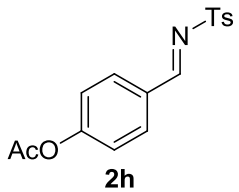
2f

4-Methyl-N-(4-methylbenzylidene)benzenesulfonamide (2f). Colorless solid, yield 2.10 g (81 %), mp = 114-116 ^{o}C (lit.[8] 115-116 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 6H).



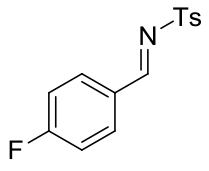
2g

N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (2g). Colorless solid, yield 4.50 g (82 %), mp = 125-127^{o}C (lit.[8] 124-125 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.91-7.88 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.44 (s, 3H).



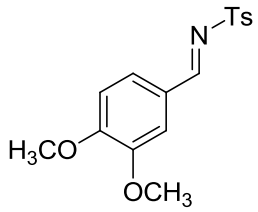
2h

4-((Tosylimino)methyl)phenyl acetate (2h). Colorless solid, yield 2.38 g (79 %), mp = 121-123^{o}C (lit.[11] 121-123 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 2.45 (s, 3H), 2.33 (s, 3H).



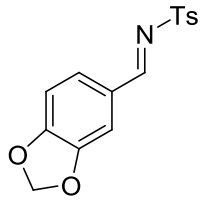
2i

N-(4-Fluorobenzylidene)-4-methylbenzenesulfonamide (2i). Colorless solid, yield 2.21 g (84 %), mp = 110-112^{o}C (lit.[8] 110-111 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.00-7.95 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (t, J_{F-H} = 8.4 Hz, 2H), 2.46 (s, 3H).



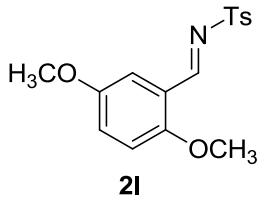
2j

N-(3,4-Dimethoxybenzylidene)-4-methylbenzenesulfonamide (2j) Colorless solid, yield 2.43 g (80 %), mp = 110-112°C (lit.[9] 110-112 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 2.45 (s, 3H).



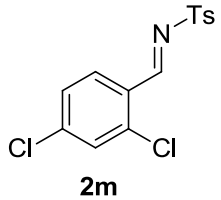
2k

N-(Benzo[d][1,3]dioxol-5-ylmethylene)-4-methylbenzenesulfonamide (2k). Colorless solid, yield 2.30 g (80 %), mp = 113-115°C (lit.[9] 114-115 °C). ^{1}H NMR (300 MHz, DMSO-*d6*) δ 9.01 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.68 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46-7.43 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 2H), 2.40 (s, 3H).



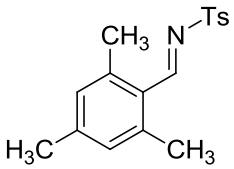
2l

N-(2,5-Dimethoxybenzylidene)-4-methylbenzenesulfonamide (2l). Colorless solid, yield 2.39 g (79 %), mp = 124-126°C (lit.[13] 125-126 °C). ^{1}H NMR (300 MHz, DMSO-*d6*) δ 9.32 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.34-7.29 (m, 2H), 7.21-7.18 (m, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 2.40 (s, 3H).



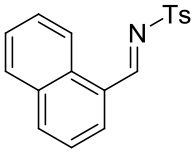
2m

N-(2,4-Dichlorobenzylidene)-4-methylbenzenesulfonamide (2m). Colorless solid, yield 2.34 g (75 %), mp = 111-113°C (lit.[10] 112-113 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 1.2 Hz, 1H), 7.39-7.32 (m, 3H), 2.46 (s, 3H).



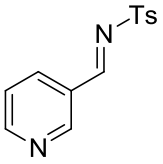
2n

4-Methyl-N-(2,4,6-trimethylbenzylidene)benzenesulfonamide (2n). Colorless solid, yield 2.03g (79 %), mp = 118-120°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 2.55 (s, 6H), 2.45 (s, 3H), 2.33 (s, 3H). The NMR data are in accordance with literature.[11]



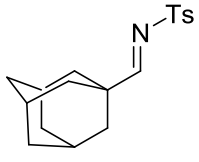
2o

4-Methyl-N-(naphthalen-1-ylmethylene)benzenesulfonamide (2o). Colorless solid, yield 2.41 g (82 %), mp = 133-135°C (lit.[8] 133-134 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.01 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.63-7.56 (m, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H).



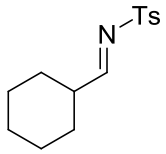
2p

4-Methyl-N-(pyridin-3-ylmethylene)benzenesulfonamide (2p). Colorless solid, yield 2.20 g (89 %), mp = 131-133°C (lit.[14] 131-132 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 9.06 (s, 1H), 8.82 (d, *J* = 4.4 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 7.8, 4.4 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).



2q

N-(Adamantan-1-ylmethylene)-4-methylbenzenesulfonamide (2q). Colorless solid, yield 4.22 g (70 %), mp = 80-82°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H), 2.06 (brs, 3H), 1.79-1.66 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.0, 144.4, 135.0, 129.7, 127.9, 40.0, 38.0, 36.3, 27.4, 21.6. HRMS (ESI) calculated for $C_{18}H_{23}NO_2S$ $[M+H]^+$ 317.1449, found 317.1446.



2r

N-(cyclohexylmethylene)-4-methylbenzenesulfonamide (2r). Colorless solid, yield 2.04 g (81 %), mp = 107-109°C (lit.[20] 109-110°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (brs, 4H), 1.90-1.62 (m, 5H), 1.39-1.19 (m, 5H).

3. Optimization of model catalytic reaction conditions

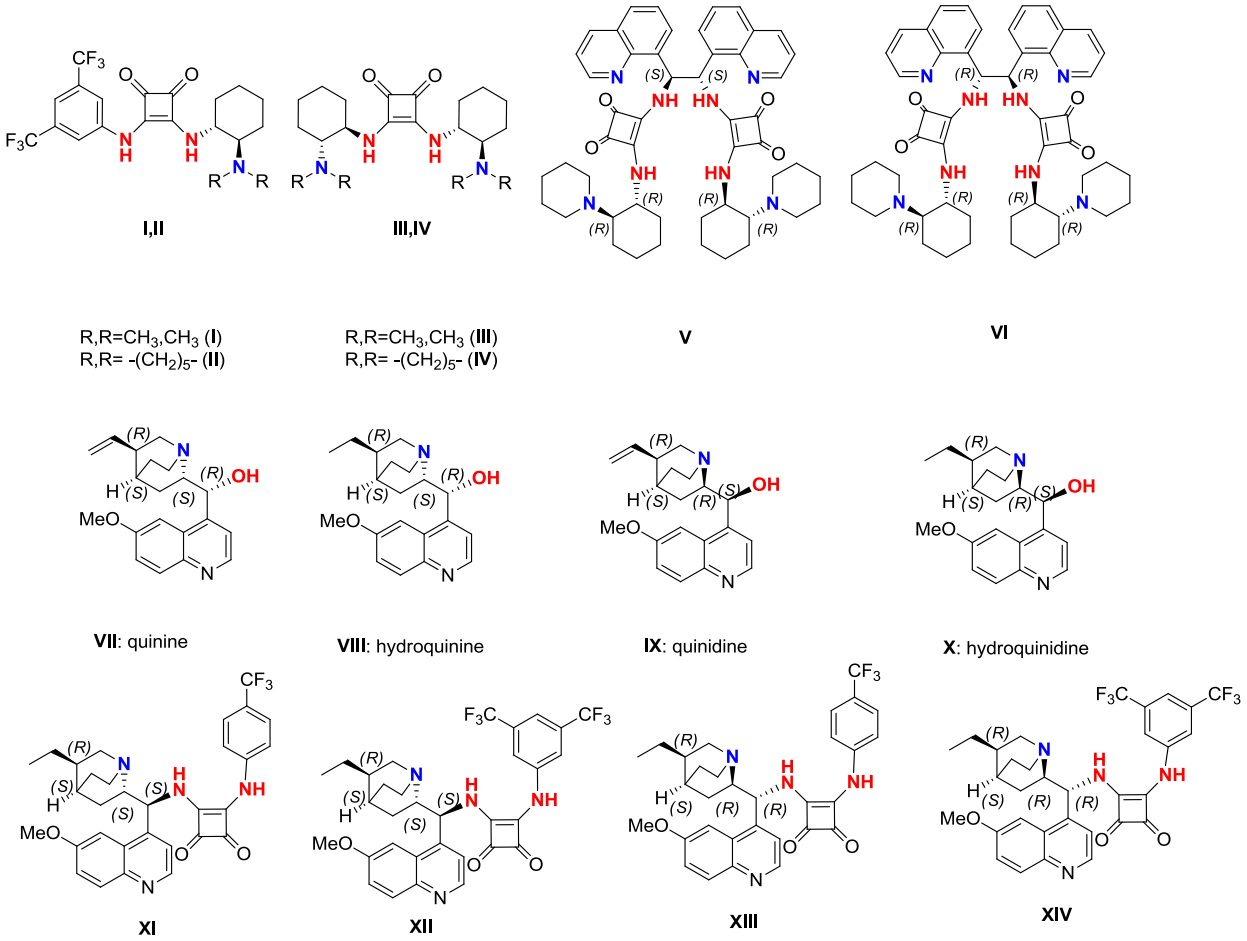
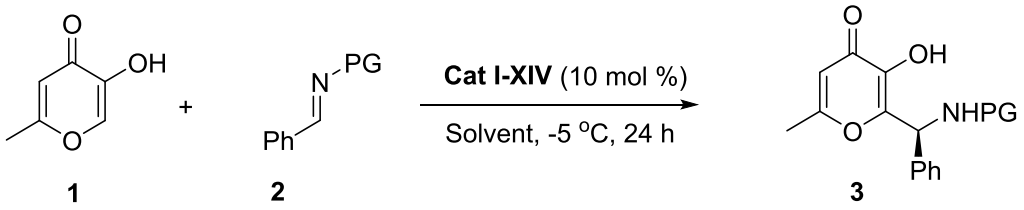


Figure S1. Selected bifinctional organocatalysts**.**

Available bifunctional tertiary amines **I** – **XIV**, having different spatial environments around the amino group (groups) essential for catalytic activity and stereoinduction, were selected as potential catalysts (**Table S1**). Amines **I** – **XIV** were examined in the model reaction of allomaltol (**1**) with *N*-tosylated benzaldimine (**2a**) in comparable conditions (DCM, catalyst loading 10 mol %, 24 h). In all the cases, adduct **3a** (*ent*-**3a** for **VII**, **VIII**, **XI**, and **XII**) (entries 1-14) was formed. The best enantioselectivity (83% *ee*) was attained in the presence of hydroquinidine-based squaramide **XIV**. Reactions in Et_2O, PhMe, 1,4-dioxane and EtOH gave inferior results (entries 15-18). In aqueous media the reaction did not occur (entry 19). Stereoinduction was improved to 94 % *ee* in THF (entry 20). The use of lower temperature, excess of imine **2a** or reduced catalyst loading (2.0 mol %) negatively affected the reaction yield and/or selectivity (entries 21-23). Reactions of allomaltol with imines **2a'** (PG = Boc) and **2a''** (PG = Nos) in the optimized conditions also did not afford satisfactory results (entries 24, 25). O-Benzylated allomaltol (**OBn-1**) did not react with **2a** in the proposed conditions.

Table S1. Optimization of the model reaction[a]



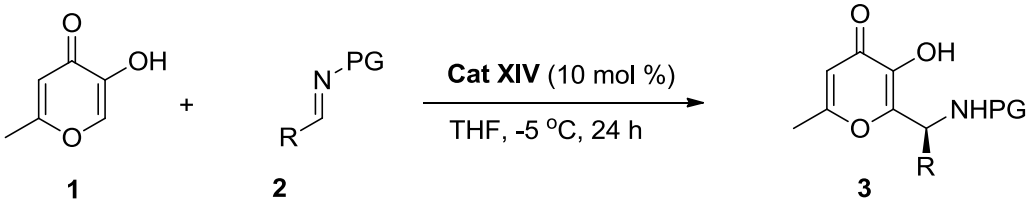
PG = Ts (**2a**, **3a**), Boc (**2a'**, **3a'**), Nos (**2a''**, **3a''**)

Entry	PG	Cat (10 mol %)	Solvent	Yield[b], **3a** (%)	*ee* [c] (%)
1	Ts	**I**	DCM	87	7
2	Ts	**II**	DCM	83	9
3	Ts	**III**	DCM	76	10
4	Ts	**IV**	DCM	78	3
5	Ts	**V**	DCM	34	61
6	Ts	**VI**	DCM	52	42
7	Ts	**VII**	DCM	78	-53[d]
8	Ts	**VIII**	DCM	74	-56[d]
9	Ts	**IX**	DCM	81	69
10	Ts	**X**	DCM	76	71
11	Ts	**XI**	DCM	71	-75[d]
12	Ts	**XII**	DCM	64	-80[d]
13	Ts	**XIII**	DCM	79	77
14	Ts	**XIV**	DCM	78	83
15	Ts	**XIV**	Et_2O	31	71
16	Ts	**XIV**	PhMe	83	76
17	Ts	**XIV**	1,4-dioxane	61	66
18	Ts	**XIV**	EtOH	90	68
19	Ts	**XIV**	H_2O	< 1	n.d.
20	Ts	**XIV**	THF	90	94
21[e]	Ts	**XIV**	THF	55	96
22[f]	Ts	**XIV**	THF	91	89

23[g]	Ts	**XIV**	THF	39	86
24[h]	Boc	**XIV**	THF	97	10
25[i]	Ns	**XIV**	THF	< 1	n.d.
26[j]	Ts	**XIV**	THF	< 1	n.d.

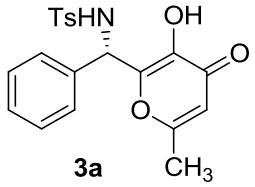
[a]Unless otherwise specified, the reactions were carried out with catalysts **I**-**XIV** (10 mol%), **1** (126 mg, 1 mmol) and **2a** (259 mg, 1 mmol) in the corresponding solvent (2 mL) at -5 ^{o}C. [b]Yield obtained after diluted by water and filtration. [c]HPLC data were obtained on the chiral phase (CHIRALPAK AD-H column, *n*-hexane/*i*-PrOH 80:20, flow rate 1.00 mL/min, 220 nm; $t_{(R)minor}$ = 12.3 min, $t_{(R)major}$ = 16.4 min). %). [d]*ent* -**3a** was formed in the reaction. [e]The reaction was carried out at -20 ^{o}C. [f]0.15 mmol of **2a** was used.[g] 2 mol% of **XIV** was used. [h]Imine **2a'** (0.1 mmol) was used as starting substrate. [i]Imine **2a''** (0.1 mmol) was used as starting substrate. [j]O-Benzylated allomaltol (**OBn-1**)[21] (0.1 mmol) was used instead of allomaltol as the nucleophilic component.

4. General procedure for synthesis and characterization data of Mannich adducts 3



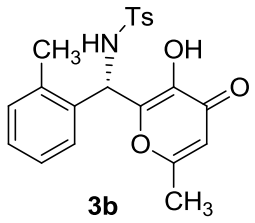
Catalyst **XIV** (63 mg, 0.1 mmol) was added to a solution of **1** (126 mg, 1.0 mmol) and corresponding aldimine **2** (1.0 mmol)[a] in THF (2 mL) and the reaction mixture was stirred at -5 °C for 24 h. Then it was diluted with water, the precipitated raw product **3** was filtrated and washed with Et_2O to afford analytically pure sample.

[a] Reactions with compounds **2a**, **2g** and **2q** were performed on the 15 mmol-scale.



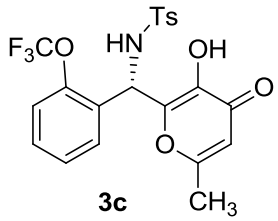
3a

(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (3a). Yellowish-brown solid, yield 5.19 g (90%), mp = 163-164 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.07 (brs, 1H), 8.80 (d, *J* = 9.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.36-7.31 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.94 (s, 1H), 5.77 (d, *J* = 9.8 Hz, 1H), 2.29 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.7, 146.7, 143.0, 141.3, 138.1, 129.4, 129.1, 128.3, 127.1, 126.7, 111.3, 53.1, 21.3, 19.3. HPLC data: 94% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 12.1 min, t_{major} = 14.9 min). $[\alpha]^{25}_D$ = +54.5 ° (*c* 0.85, CH_3OH). HRMS (ESI): calculated for $C_{20}H_{19}NO_5S$ $[M+H]^+$ 385.0984, found 385.0982.



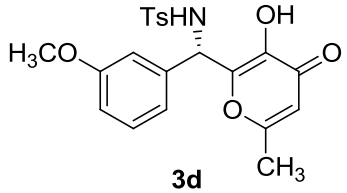
3b

(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(o-tolyl)methyl)-4-methylbenzenesulfonamide (3b). Colorless solid, yield 367 mg (92%), mp = 134-136 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.07 (brs, 1H), 8.69 (brs, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.21-7.18 (m, 5H), 5.96 (s, 2H), 2.36 (s, 3H), 2.29 (s, 3H), 2.08 (s, 3H) .^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 164.6, 146.4, 142.9, 141.3, 138.1, 136.4, 135.9, 130.8, 129.4, 128.2, 127.7, 126.7, 126.6, 111.2, 50.0, 21.3, 19.3. HPLC data: 93% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 20.3 min, t_{major} = 31.3 min). $[\alpha]^{25}_D$ = +38.3 ° (*c* 1.0, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{21}NO_5S$ $[M+H]^+$ 399.1140, found 399.1146.



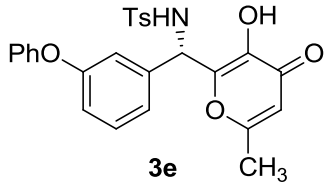
3c

(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(2-(trifluoromethoxy)phenyl)methyl)-4-methylbenzenesulfonamide (3c). Orange solid, yield 422 mg (90%), mp = 128-130 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.07 (brs, 1H), 8.85 (brs, 1H), 7.60-7.54 (m, 3H), 7.45-7.40 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.15 (s, 1H), 5.98 (s, 1H), 2.29 (s, 3H), 2.07 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 164.7, 146.0, 145.2, 143.0, 138.2, 130.4, 130.3, 130.0, 129.5, 127.8, 126.7, 120.5, 111.2, 60.2, 47.5, 21.3, 19.3, 14.5. HPLC data: 92% *ee* (Chiralpak OD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 19.4 min, t_{major} = 22.5 min). $[\alpha]^{25}_{D}$ = +29.0 ° (*c* 1.2, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{18}F_3NO_6S$ $[M+H]^+$ 469.0807, found 469.0811.



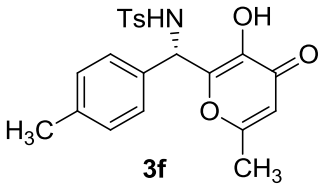
3d

(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(3-methoxyphenyl)methyl)-4-methyl-benzenesulfonamide (3d). Yellow solid, yield 365 mg (88%), mp = 124-126 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.00 (brs, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.26-7.18 (m, 3H), 6.86-6.83 (m, 3H), 5.94 (s, 1H), 5.72 (s, 1H), 3.71 (s, 3H), 2.28 (s, 3H), 2.08 (s, 3H).^{13}C (75 MHz, DMSO-d_6) δ 173.8, 164.5, 159.8, 146.8, 143.0, 141.4, 139.6, 138.1, 130.2, 129.4, 126.7, 119.3, 113.6, 112.8, 111.3, 55.5, 55.1, 21.3, 19.3. HPLC data: 91% *ee* (Chiralpak OD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 37.8 min, t_{major} = 45.7 min). $[\alpha]^{25}_{D}$ = +61.1 ° (*c* 1.3, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{21}NO_6S$ $[M+H]^+$ 415.1090, found 415,1088.

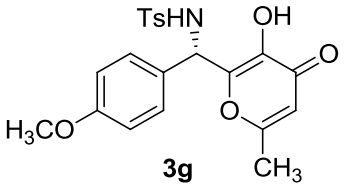


3e

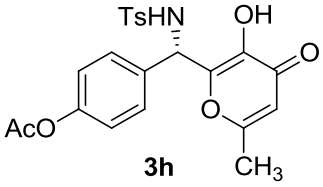
(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(3-phenoxyphenyl)methyl)-4-methyl-benzenesulfonamide (3e). Yellow solid, yield 424 mg (89%), mp = 134-136 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.11 (brs, 1H), 8.87 (brs, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.20-7.14 (m, 3H), 7.04-6.97 (m, 4H), 6.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.95 (s, 1H), 5.75 (s, 1H), 2.28 (s, 3H), 2.05 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 164.7, 157.3, 156.7, 146.4, 143.1, 141.4, 140.2, 138.0, 130.7, 130.5, 129.4, 126.7, 124.1, 122.1, 119.2, 118.2, 117.1, 111.3, 52.9, 21.3, 19.3. HPLC data: 92% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 13.7 min, t_{major} = 25.4 min). $[\alpha]^{25}_{D}$ = +51.5 ° (*c* 1.3, CH_3OH). HRMS (ESI): calculated for $C_{26}H_{23}NO_6S$ $[M+H]^+$ 477.1246, found 477.1249.



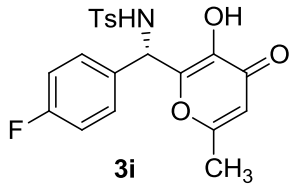
(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(p-tolyl)methyl)-4-methylbenzenesulfonamide (3f). Brown solid, yield 355 mg (89%), mp = 140-142 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.03 (brs, 1H), 8.77 (brs, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.20-7.11 (m, 6H), 5.93 (s, 1H), 5.72 (s, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.6, 146.9, 143.0, 141.2, 138.1, 137.5, 135.1, 129.6, 129.4, 127.0, 126.7, 111.2, 52.8, 21.3, 21.0, 19.3. HPLC data: 96% *ee* (Chiralpak OD-H, *n*-hexane : *i*-PrOH = 80 : 20; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 8.5 min, t_{major} = 12.3 min). $[\alpha]^{25}_{D}$ = +47.1 ° (*c* 1.1, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{21}NO_5S$ $[M+H]^+$ 399.1140, found 399.1144.



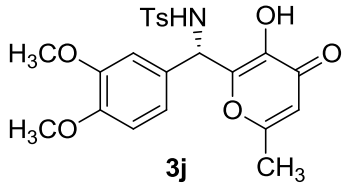
(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(4-methoxyphenyl)methyl)-4-methylbenzenesulfonamide (3g). Pink solid, yield 5.66 g (91%), mp = 144-146 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.03 (brs, 1H), 8.74 (brs, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.22-7.17 (m, 4H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.93 (s, 1H), 5.70 (s, 1H), 3.71 (s, 3H), 2.28 (s, 3H), 2.07 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.5, 159.3, 147.0, 143.0, 141.1, 138.1, 130.0, 129.4, 128.4, 126.7, 114.4, 111.2, 55.6, 52.5, 21.3, 19.3. HPLC data: 90% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 22.0 min, t_{major} = 28.5 min). $[\alpha]^{25}_{D}$ = +60.2 ° (*c* 0.9, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{21}NO_6S$ $[M+H]^+$ 415.1090, found 415.1092.



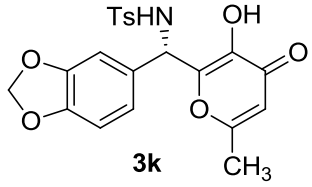
(*S*)-4-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(4-methylphenylsulfonamido)methyl)-phenyl acetate (3h). Yellow solid, yield 390 mg (88%), mp = 166-168 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.15 (brs, 1H), 8.85 (d, *J* = 9.6 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.34-7.31 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 5.77 (d, *J* = 9.6 Hz, 1H), 2.28 (s, 3H), 2.25 (s. 3H), 2.08 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 169.6, 164.7, 150.4, 146.4, 143.1, 141.3, 138.0, 135.5, 129.5, 128.3, 126.7, 122.5, 111.3, 52.6, 21.3, 21.2, 19.3. HPLC data: 95% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 25.2 min, t_{major} = 37.0 min). $[\alpha]^{25}_{D}$ = +53.2 ° (*c* 1.0, CH_3OH). HRMS (ESI): calculated for $C_{22}H_{21}NO_7S$ $[M+H]^+$ 443.1039, found 443.1045.



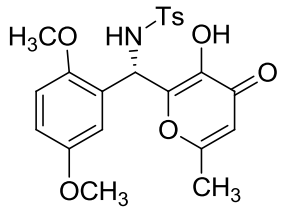
(*S*)-N-((4-Fluorophenyl)(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methyl-benzenesulfonamide (3i). Yellow solid, yield 346 mg (86%), mp = 150-151^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.06 (brs, 2H), 7.56 (d, J = 7.7 Hz, 2H), 7.33 (t, J_{F-H} = 7.7 Hz, 2H), 7.20-7.13 (m, 4H), 5.95 (s, 1H), 5.74 (s, 1H), 2.28 (s, 3H), 2.08 (s, 3H). ^{13}C (75 MHz, DMSO-d_6) δ 173.8, 164.6, 163.7, 160.4, 146.5, 143.0, 141.5, 138.1, 134.4, 129.5, 129.2 (d, J_{F-C} = 8.4 Hz), 126.7, 116.9 (d, J_{F-C} = 22.3 Hz), 111.3, 52.6, 21.3, 19.3. HPLC data: 97% *ee* (Chiralpak OJ-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{major}= 28.4 min, t_{major} = 34.6 min). $[\alpha]^{25}_{D}$ = +39.0 ° (*c* 0.9, CH_3OH). HRMS (ESI): calculated for $C_{20}H_{18}FNO_5S$ $[M+H]^+$ 403.0890, found 403.0894.



(*S*)-N-((3,4-Dimethoxyphenyl)(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methyl-benzenesulfonamide (3j). Pink solid, yield 410 mg (92%), mp = 137-139 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.05 (brs, 1H), 8.74 (brs, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.95 (s, 1H), 5.68 (s, 1H), 3.70 (s, 6H), 2.28 (s, 3H), 2.10 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 164.5, 149.1, 148.9, 147.1, 143.0, 140.9, 138.1, 130.1, 129.4, 126.7, 119.4, 112.1, 111.2, 110.9, 56.0, 55.9, 52.8, 21.3, 19.3. HPLC data: 89% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 17.7 min, t_{major} = 22.7 min). $[\alpha]^{25}_{D}$ = +39.1 ° (*c* 1.0, CH_3OH). HRMS (ESI): calculated for $C_{22}H_{23}NO_7S$ $[M+H]^+$ 445.1195, found 445.1198.

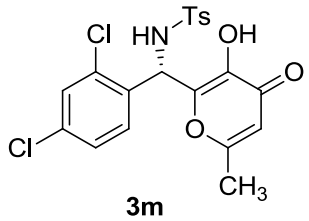


(*S*)-N-(Benzo[d][1,3]dioxol-5-yl(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (3k). Colorless solid, yield 407 mg (95%), mp = 137-139 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.10 (brs, 1H), 8.74 (brs, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.84-6.82 (m, 2H), 6.73 (d, J = 8.0 Hz, 1H), 5.98 (s, 2H), 5.95 (s, 1H), 5.66 (s, 1H), 2.28 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.6, 147.9, 147.3, 146.9, 143.0, 141.0, 138.0, 131.8, 129.4, 126.7, 120.6, 111.3, 108.6, 107.4, 101.6, 52.9, 21.3, 19.3. HPLC data: 92% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 27.7 min, t_{major} = 31.7 min). $[\alpha]^{25}_{D}$ = +29.1 ° (*c* 1.0, CH_3OH). HRMS (ESI): calculated for $C_{21}H_{19}NO_7S$ $[M+H]^+$ 429.0882, found 429.0883.



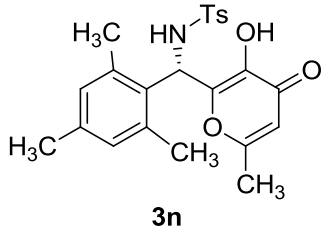
3l

(*S*)-N-((2,5-Dimethoxyphenyl)(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (3l). Pink solid, yield 409 mg (94%), mp = 129-131 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.81 (brs, 1H), 8.54 (brs, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 2.6 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.79 (dd, J = 9.0, 2.6 Hz, 1H), 6.18 (s, 1H), 5.97 (s, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.28 (s, 3H). 2.11 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 164.5, 153.5, 150.4, 146.7, 142.8, 141.1, 138.3, 129.3, 127.0, 126.7, 114.9, 114.0, 113.0, 111.1, 56.8, 55.8, 47.1, 21.3, 19.4. HPLC data: 92% *ee* (Chiralpak OJ-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{major}= 12.8 min, t_{minor} = 18.6 min). $[\alpha]^{25}_{D}$ = +69.5 ° (*c* 0.8, CH_3OH). HRMS (ESI): calculated for $C_{22}H_{23}NO_7S$ $[M+H]^+$ 445.1195, found 445.1195.



3m

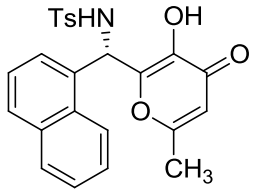
(*S*)-N-((2,4-Dichlorophenyl)(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (3m). Yellow solid, yield 389 mg (86%), mp = 170-172 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.08 (brs, 2H), 7.56-7.50 (m, 4H), 7.37 (dd, J = 8.4, 1.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.16 (s, 1H), 6.03 (s, 1H), 2.31 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 164.9, 144.9, 143.1, 141.9, 138.1, 134.6, 133.8, 133.4, 131.4, 129.6, 129.2, 128.0, 126.7, 111.4, 50.2, 21.4, 19.4. HPLC data: 96% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 21.8 min, t_{major} = 32.9 min). $[\alpha]^{25}_{D}$ = +29.1 ° (*c* 1.0, CH_3OH). HRMS (ESI): calculated for $C_{20}H_{17}Cl_2NO_5S$ $[M+H]^+$ 453.0204, found 453.0206.



3n

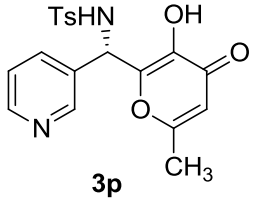
(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(mesityl)methyl)-4-methylbenzenesulfonamide (3n). Yellow solid, yield 384 mg (90%), mp = 134-136 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.92 (brs, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.75 (s, 2H), 6.08-6.04 (m, 2H), 2.34 (s, 3H), 2.21 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 163.8, 147.1, 142.9, 141.8, 138.7, 137.2, 137.1, 132.3, 130.2, 129.6, 126.9, 111.6, 50.8, 21.4, 20.7, 19.2. HPLC data: 95% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 80 : 20; 220 nm, flow rate: 1.0

mL/min, t_{minor}= 14.8 min, t_{major} = 18.1 min). $[\alpha]^{25}_{D}$ = +53.6 ° (*c* 1.2, CH_3OH). HRMS (ESI): calculated for $C_{23}H_{25}NO_5S$ $[M+H]^+$ 427.1453, found 427.1451.



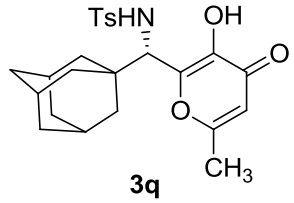
3o

(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(naphthalen-1-yl)methyl)-4-methyl-benzenesulfonamide (3o). Yellow solid, yield 392 mg (90%), mp = 160-162 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.06 (brs, 2H), 8.32 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.90 (t, *J* = 4.5 Hz, 1H), 7.64-7.54 (m, 4H), 7.46 (d, *J* = 4.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 5.96 (s, 1H), 2.30 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.8, 146.2, 143.1, 141.3, 138.1, 133.8, 133.7, 130.8, 129.5, 129.2, 129.1, 127.2, 126.7, 126.4, 125.8, 123.3, 111.4, 49.9, 21.4, 19.4. HPLC data: 91% *ee* (Chiralpak OJ-H, *n*-hexane : *i*-PrOH = 85 : 15; 220 nm, flow rate: 1.0 mL/min, t_{major}= 22.3 min, t_{minor} = 29.6 min). $[\alpha]^{25}_{D}$ = +53.6 ° (*c* 1.2, CH_3OH). HRMS (ESI): calculated for $C_{24}H_{21}NO_5S$ $[M+H]^+$ 435.1140, found 435.1137.



3p

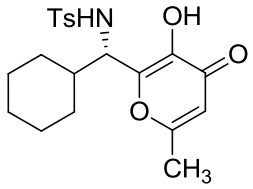
(*S*)-N-((3-Hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)(pyridin-3-yl)methyl)-4-methylbenzene-sulfonamide (3p). Brown solid, yield 340 mg (88%), mp = 160-162 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.00 (brs, 2H), 8.48 (brs, 1H), 7.72-7.70 (m, 1H), 7.63-7.49 (m, 2H), 7.41-7.31 (m, 1H), 7.22-7.19 (m, 2H), 5.98 (s, 1H), 5.80 (s, 1H), 2.29 (s, 3H), 2.09 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 164.9, 149.5, 148.2, 145.8, 143.3, 141.5, 137.8, 135.0, 133.8, 129.6, 126.7, 124.2, 111.4, 51.3, 21.3, 19.3. HPLC data: 97% *ee* (Chiralpak AD-H, *n*-hexane : *i*-PrOH = 70 : 30; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 8.9 min, t_{major} = 18.3 min). $[\alpha]^{25}_{D}$ = +38.1 ° (*c* 1.2, CH_3OH). HRMS (ESI): calculated for $C_{19}H_{18}N_2O_5S$ $[M+H]^+$ 386.0936, found 386.0938.



3q

N-((*S*)-(Adamantan-1-yl)(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methyl-benzenesulfonamide (3q). Colorless solid, yield 6.04 g (91%), mp = 111-113 °C .^{1}H NMR (300 MHz, DMSO-d_6) δ 8.55 (brs, 1H), 7.87 (brs, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.85 (s, 1H), 4.12 (d, *J* = 10.5 Hz, 1H), 2.23 (s, 3H), 2.08 (s, 3H), 1.99-1.86 (m, 3H), 1.69-1.52 (m, 9H), 1.45-1.41 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.1, 164.3, 145.7, 142.6, 138.2, 129.2, 126.5, 110.8, 37.5, 36.8, 28.1, 21.3, 19.4. HPLC data: 98% *ee* (Chiralpak OD-H, *n*-hexane : *i*-PrOH = 90 : 10; 220 nm, flow rate: 1.0 mL/min, t_{minor}= 11.9 min, t_{major} = 17.3 min).

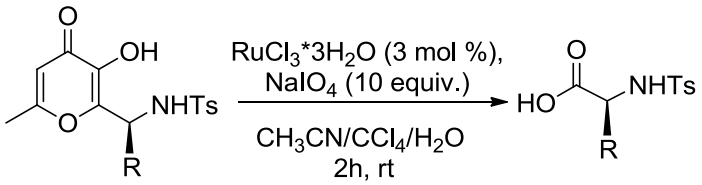
$[\alpha]^{25}_D$ = +23.1 ° (*c* 0.7, CH_3OH). HRMS (ESI): calculated for $C_{24}H_{29}NO_5S$ $[M+H]^+$ 443.1766, found 443.1769.



3r

(*S*)-N-(cyclohexyl(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (3r). Colorless solid, yield 384 mg (98%), mp = 98-100 ^oC .^1H NMR (300 MHz, DMSO-d_6) δ 8.64 (brs, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.87 (s, 1H), 4.29 (t, *J* = 8.8 Hz, 1H), 2.26 (s, 3H), 2.06 (s, 3H), 1.94 (d, *J* = 11.6 Hz, 1H), 1.67-1.57 (m, 4H), 1.33-0.83 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.3, 164.4, 146.7, 142.6, 142.1, 138.5, 129.3, 126.5, 110.9, 54.7, 29.8, 29.1, 26.2, 25.5, 21.3, 19.4. HPLC data: 13% *ee* (Chiralpak OD-H, *n*-hexane : *i*-PrOH = 80 : 20; 220 nm, flow rate: 1.0 mL/min, t_{major} = 6.1 min, t_{minor}= 8.6 min). $[\alpha]^{25}_D$ = +8.0° (*c* 0.9, CH_3OH). HRMS (ESI): calculated for $C_{24}H_{29}NO_5S$ $[M+H]^+$ 391.1453, found 391.1459.

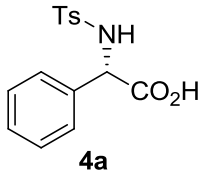
5. General procedure for synthesis and characterization data of *N*-Ts protected amino acids 4



3 **4**

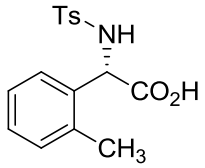
$NaIO_4$ (5 mmol, 1.07 g) and $RuCl_3*3H_2O$ (0.015 mmol, 4 mg) were successively added to a solution of adduct **3** (0.5 mmol)[a] in the $CH_3CN/CCl_4/H_2O$ (2:2:5) solvent system (5 mL) and the resulting mixture was stirred at ambient temperature for 2 h. Inorganic materials were filtrated off and the filtrate was extracted with EtOAc (3x5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure (10 torr). The crude product was recrystallized from 80% EtOH to afford analytically pure sample **4**.

[a] Reactions with compounds **3a, 3g** and **3q** were performed on the 10 mmol-scale.



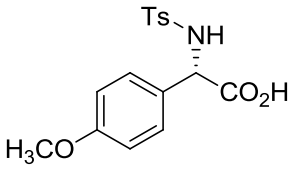
4a

(*S*)-2-(4-Methylphenylsulfonamido)-2-phenylacetic acid (**4a**). Colorless solid, yield 2.47 g (81%), mp = 175-176°C (lit.[15] 175-176 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.87 (brs, 1H), 8.62 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.29-7.27 (m, 7H), 4.87 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.5, 142.9, 138.7, 137.1, 129.7, 128.8, 128.4, 127.7, 127.0, 60.0, 21.4. $[\alpha]^{25}_D$ = +105 ° (94 % *ee*, *c* 1, CH_3OH), lit. [15]: $[\alpha]^{25}_D$ = +112 ° (100 % *ee*, *c* 4.3, CH_3OH). HRMS (ESI): calculated for $C_{15}H_{15}NO_4S$ $[M+H]^+$ 305.0722, found 305.0727.



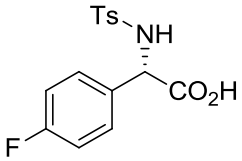
4b

(*S*)-2-(4-Methylphenylsulfonamido)-2-(o-tolyl)acetic acid (**4b**). Colorless solid, yield 127 mg (80%), mp = 172-174°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.88 (brs, 1H), 8.54 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.28-7.23 (m, 3H), 7.17-7.04 (m, 3H), 5.07 (d, J = 8.8 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.6, 142.9, 138.6, 136.0, 135.6, 130.7, 129.7, 128.3, 127.5, 127.0, 126.5, 56.3, 21.4, 19.3. $[\alpha]^{25}_D$ = +89 ° (*c* 1, CH_3OH). HRMS (ESI): calculated for $C_{16}H_{17}NO_4S$ $[M+H]^+$ 319.0878, found 319.0881.



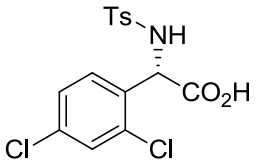
4g

(*S*)-2-(4-Methoxyphenyl)-2-(4-methylphenylsulfonamido)acetic acid (**4g**). Colorless solid, yield 2.68 g (80%), mp = 163-165°C . ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.53 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 7.18 (d, J = 7.3 Hz, 2H), 6.82 (d, J = 7.3 Hz, 2H), 4.80 (d, J = 8.8 Hz, 1H), 3.71 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.7, 159.4, 142.8, 138.7, 129.7, 129.0, 127.0, 114.2, 59.4, 55.6, 21.4. $[\alpha]^{25}_{D}$ = +93 ° (*c* 1, CH_3OH). HRMS (ESI): calculated for $C_{16}H_{17}NO_5S$ $[M+H]^+$ 335.0827, found 335.0824.



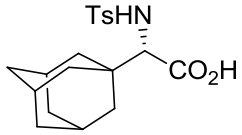
4i

(*S*)-2-(4-fluorophenyl)-2-(4-methylphenylsulfonamido)acetic acid (**4i**). Colorless solid, yield 124 mg (77%), mp = 144-146°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.63 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.33-7.25 (m, 4H), 7.07 (t, J_{F-H} = 8.9 Hz, 2H), 4.91 (d, J = 8.9 Hz, 1H), 2.33 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 171.3, 142.9, 138.6, 133.5, 129.9 (d, J_{F-C} = 8.4 Hz), 129.7, 127.0, 115.6 (d, J_{F-C} = 20.9 Hz), 59.2, 21.4. $[\alpha]^{25}_{D}$ = +73 ° (*c* 1, CH_3OH). HRMS (ESI): calculated for $C_{15}H_{14}FNO_4S$ $[M+H]^+$ 323.0628, found 323.0626.



4m

(*S*)-2-(2,4-Dichlorophenyl)-2-(4-methylphenylsulfonamido)acetic acid (**4m**). Colorless solid, yield 124 mg (82%), mp = 180-182°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.51 (brs, 1H), 7.55 (d, J = 8.0 Hz , 2H), 7.46 (d, J =1.2 Hz, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.28-7.22 (m, 3H), 5.19 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 143.0, 138.1, 135.0, 133.9, 133.4, 130.8, 129.6, 128.9, 127.8, 126.9, 56.4, 21.3. $[\alpha]^{25}_{D}$ = +68 ° (*c* 1, CH_3OH). HRMS (ESI): calculated for $C_{15}H_{13}Cl_2NO_4S$ $[M+H]^+$ 372.9942, found 372.9946.

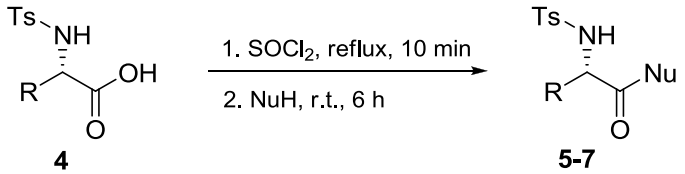


4q

(*S*)-2-(Adamantan-1-yl)-2-(4-methylphenylsulfonamido)acetic acid (**4q**). Colorless solid, yield 2.54 g (70%), mp = 140-142°C .^{1}H NMR (300 MHz, DMSO-d_6) δ 7.64 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.59 (brs, 1H), 4.40 (s, 1H), 2.36 (s. 3H), 2.04 (s, 3H), 1.72-1.61 (m, 9H), 1.54 (d, J = 12.3 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.4, 142.6, 138.1, 129.7,

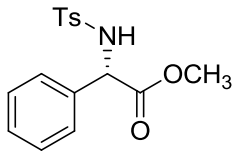
127.2, 62.8, 50.7, 40.6, 35.7, 31.4, 28.8, 21.4. $[\alpha]^{25}_{D}$ = +18 ° (*c* 0.6, CH_3OH). HRMS (ESI): calculated for $C_{19}H_{25}NO_4S$ $[M+H]^+$ 363.1504, found 363.1506.

6. General procedure for synthesis and characterization data of amino acid derivatives 5-7



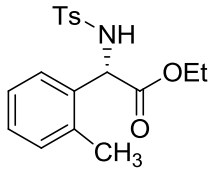
Nu = OAlk (**5**), NH_2 (**6**), (*S*)-PhCH(Me)NH (**7**)

Thionyl chloride (1.38 mmol, 100 μL) was added to *N*-tosylated amino acid **4** (0.3 mmol) and the mixture was refluxed for 10 min to obtain homogenous solution. Then it was concentrated under reduced pressure (10 torr) and corresponding nucleophile (0.5 mmol) was added to the residue. The resulting mixture was stirred for 6 h. For esters **5**, water (5 mL) was added to the reaction mixture, the resulting aqueous suspension was extracted with EtOAc (3x5 mL), the combined organic layer was dried and concentrated under reduced pressure (10 torr) to afford raw product **5**, which was purified by column chromatography on silica gel (hexanes-EtOAc). For amides **6** and **7**, the reaction mixture was diluted with diethyl ether (5 mL), the precipitated product was collected by filtration and dried in air to afford analytically pure sample.



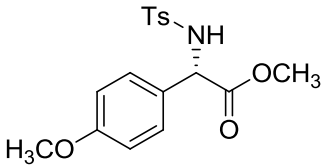
5a

(*S*)-Methyl 2-(4-methylphenylsulfonamido)-2-phenylacetate (5a). Colorless solid, yield 80 mg (84%), mp = 130-132°C(lit.[16] 132-133 °C) .^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.29-7.20 (m, 7H), 5.77 (d, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 143.5, 137.0, 135.3, 129.5, 128.8, 128.6, 127.2, 127.1, 59.4, 53.0, 21.0. $[\alpha]^{25}_D$ = +94 ° (94 % *ee*, *c* 1, $CHCl_3$), lit [16]: $[\alpha]^{25}_D$ = +102 ° (100 % *ee*, *c* 1.12, $CHCl_3$). HRMS (ESI): calculated for $C_{16}H_{17}NO_4S$ $[M+H]^+$ 319.0878, found 319.0881.



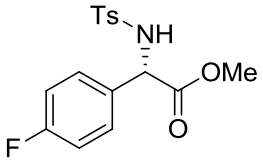
5b

(*S*)-Ethyl 2-(4-methylphenylsulfonamido)-2-(o-tolyl)acetate (5b). Colorless solid, yield 80 mg (80%), mp = 102-104°C (lit.[17] 102-103 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.20-7.10 (m, 4H), 7.06 (d, *J* = 3.5 Hz, 2H), 5.67 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.14-3.93 (m, 2H), 2.39 (s, 6H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 143.4, 137.0, 136.6, 133.8, 130.9, 129.4, 128.5, 127.1, 126.8, 126.3, 62.1, 56.2, 21.5, 19.3, 13.8. $[\alpha]^{25}_D$ = +89 ° (93% *ee*, *c* 1, $CHCl_3$), lit.[17] $[\alpha]^{25}_D$ = +99.5 ° (98 % *ee*, *c* 0.8, $CHCl_3$). HRMS (ESI): calculated for $C_{18}H_{21}NO_4S$ $[M+H]^+$ 347.1191, found 347.1193.



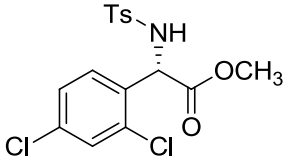
5g

(*S*)-Methyl 2-(4-methoxyphenyl)-2-(4-methylphenylsulfonamido)acetate (5g). Colorless solid, yield 84 mg (80%), mp = 140-142 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.70 (d, *J* = 7.8 Hz, 1H), 5.03 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.58 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 159.8, 143.4, 137.0, 129.5, 128.4, 127.3, 127.2, 114.2, 58.8, 55.3, 52.9, 21.5. $[\alpha]^{25}_{D}$ = +93 ° (91% *ee*, *c* 1, $CHCl_3$). HRMS (ESI): calculated for $C_{17}H_{19}NO_5S$ $[M+H]^+$ 349.0984, found 349.0986.



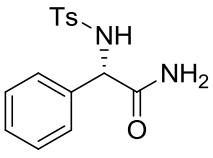
5i

(*S*)-Methyl 2-(4-fluorophenyl)-2-(4-methylphenylsulfonamido)acetate (5i). Colorless solid, yield 86 mg (85%), mp = 117-119 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.23-7.21 (m, 4H), 6.95 (t, J_{F-H} = 8.4 Hz, 2H), 5.82 (d, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 3.60 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 161.1, 143.7, 136.9, 131.2, 129.5, 129.0 (d, J_{F-C} = 8.4 Hz), 127.2, 115.8 (d, J_{F-C} = 21.8 Hz), 58.6, 53.1, 21.5. $[\alpha]^{25}_{D}$ = +74 ° (95% *ee*, *c* 1, $CHCl_3$). HRMS (ESI): calculated for $C_{16}H_{16}FNO_4S$ $[M+H]^+$ 337.0784, found 337.0786.



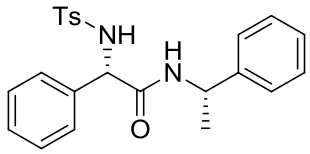
5m

(*S*)-Methyl 2-(2,4-dichlorophenyl)-2-(4-methylphenylsulfonamido)acetate (5m). Colorless solid, yield 99 mg (85%), mp = 135-137 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.21-7.16 (m, 3H), 7.12 (dd, *J* = 8.3, 1.8 Hz, 1H), 5.96 (d, *J* = 6.3 Hz, 1H), 5.40 (d, *J* = 6.3 Hz, 1H), 3.67 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 143.7, 136.6, 135.1, 134.2, 132.3, 130.8, 129.7, 129.4, 127.4, 127.1, 56.5, 53.5, 21.5. $[\alpha]^{25}_{D}$ = +50 ° (95 % *ee*, *c* 1, $CHCl_3$). HRMS (ESI): calculated for $C_{16}H_{15}Cl_2NO_4S$ $[M+H]^+$ 387.0099, found 387.0102.



6

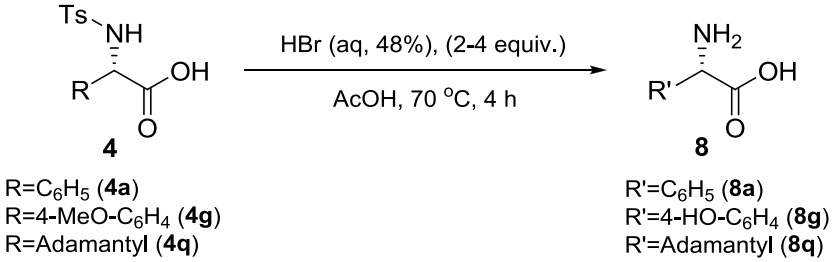
(*S*)-2-(4-Methylphenylsulfonamido)-2-phenylacetamide (6). Colorless solid, yield 93 mg (80%), mp = >200 °C (dec.). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.35 (d, J = 8.5 Hz, 1H), 7.62-7.59 (m, 2H), 7.46-7.06 (m, 9H), 4.91 (d, J = 8.5 Hz, 1H), 2.33 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 171.2, 142.7, 138.8, 138.5, 129.6, 128.5, 127.9, 127.5, 127.0, 59.9, 21.4. $[\alpha]^{25}_{D}$ = +87 ° (94% *ee*, *c* 1, DMSO). HRMS (ESI): calculated for $C_{15}H_{16}N_2O_3S$ $[M+H]^+$ 304.0882, found 304.0885.



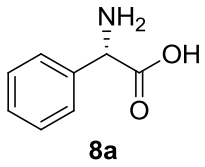
7

(*S*)-2-(4-Methylphenylsulfonamido)-2-phenyl-N-((*S*)-1-phenylethyl)acetamide (7). Colorless solid, yield 93 mg (76%), mp = 165-167 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (d, J = 7.9 Hz, 1H), 8.45 (d, J = 9.4 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.38-7.23 (m, 8H), 7.17 (d, J = 8.2 Hz, 4H), 5.07 (d, J = 9.4 Hz, 1H), 4.75-7.66 (m, 1H), 2.31 (s, 3H), 1.18 (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.4, 144.1, 142.7, 138.9, 138.6, 129.6, 128.7, 128.7, 127.9, 127.4, 127.2, 126.8, 126.4, 59.9, 48.4, 22.5, 21.4. $[\alpha]^{25}_{D}$ = +92 ° (*c* 0.75, $CHCl_3$). HRMS (ESI): calculated for $C_{23}H_{24}N_2O_3S$ $[M+H]^+$ 408.1508, found 408.1505.

7. General procedure for gram-scale synthesis and characterization data of amino acids 8

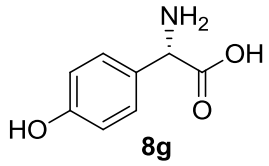


48% HBr (13 mmol, 2.2mL (for **4a**,**q**) or 26 mmol, 4.4mL (for **4g**)) was added to a stirred solution of corresponding *N*-tosylated amino acid **4** (6.5 mmol) in glacial acetic acid (5 mL) and the mixture was heated at 70 ^{o}C for 4 h. The resulting red solution was evaporated to dryness and the raw amino acid hydrobromide **8** • HBr was washed with acetone (3x5 mL). For purification, it was dissolved in water (2 mL) and converted to corresponding amino acid by careful neutralization with 25% aq. NH_3 to adjust pH 4-5. The precipitated **8** were filtered, washed with diethyl ether (3x5 mL) and dried in air. Amino acids **8** exhibited miserable solubility in organic solvents and water. Therefore, their NMR spectra were recorded in D_2O in the presence of 48% HBr and the HRMS data were obtained for corresponding hydrobromides.



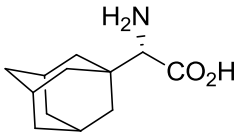
8a

(*S*)-Phehylglycine (8a). Colorless solid, yield 1.21 g (80%), mp >200 ^{o}C (dec.). ^{1}H NMR (300 MHz, D_2O, 48% HBr (1 drop)) δ 7.90 (s, 5H), 5.72 (s, 1H). $[\alpha]^{25}_{D}$ = +143 ° (94 % *ee*, *c* 1, HCl_{aq}) lit.[18] $[\alpha]^{25}_{D}$ = +152 ° (100 % *ee*, *c* 1, HCl_{aq}). HRMS (ESI): calculated for $C_8H_{10}BrNO_2[M+H]^+$ 230.9895, found 230.9897.



8g

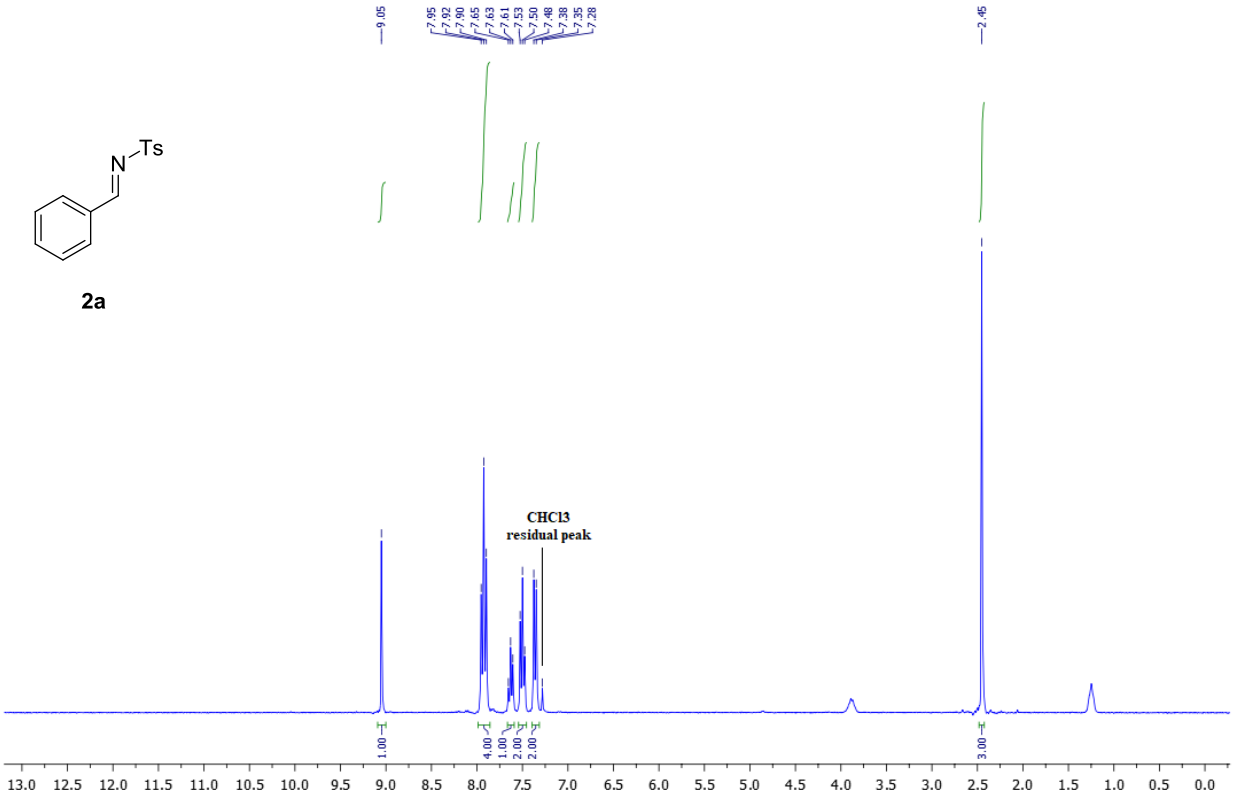
(*S*)-4-Hydroxyphehylglycine (8g). Yellowish solid, yield 1.19 g (74%), mp >200 ^{o}C (dec.). ^{1}H NMR (300 MHz, D_2O + 48% HBr (1 drop)) δ 7.68 (br. d, *J* = 8.7 Hz, 2H), 7.28 (br. d, *J* = 8.7 Hz, 2H), 5.53 (s, 1H). $[\alpha]^{25}_{D}$ = +145 ° (92 % *ee*, *c* 1, HCl_{aq}), lit.[18] $[\alpha]^{25}_{D}$ = +156 ° (100 % *ee*, *c* 1, HCl_{aq}) HRMS (ESI): calculated for $C_8H_{10}BrNO_3$ $[M+H]^+$ 246.9844, found 246.9847.

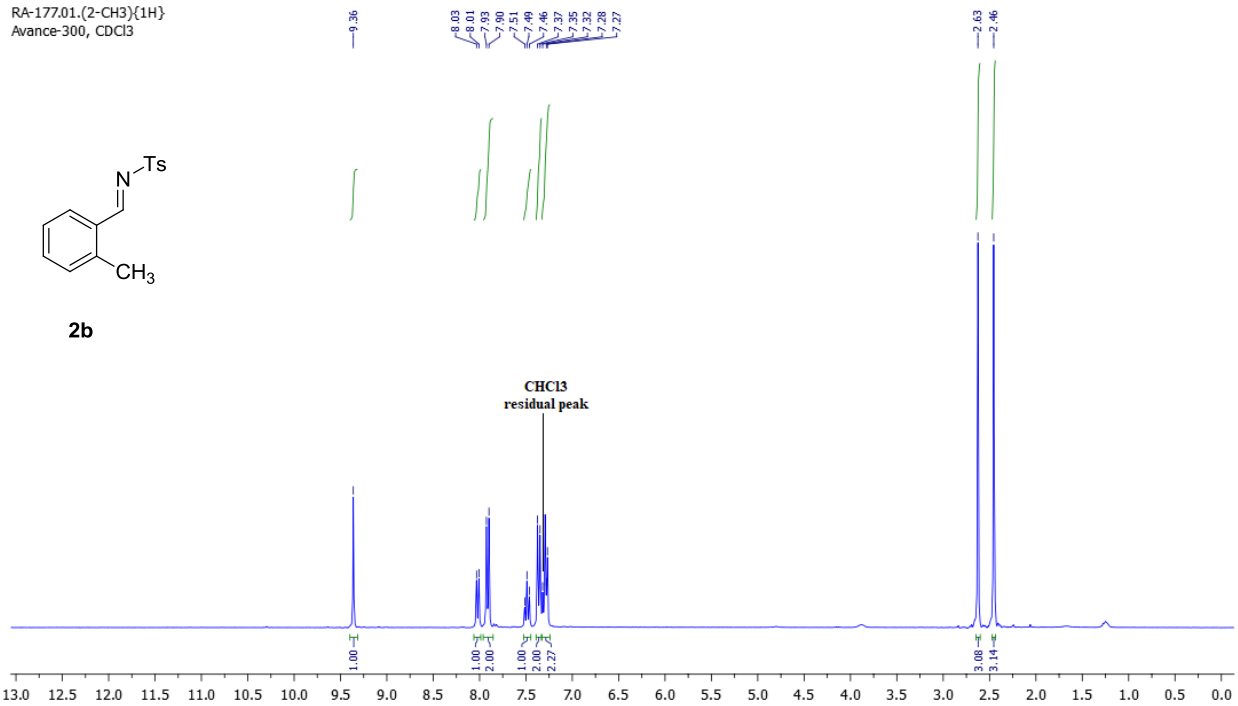


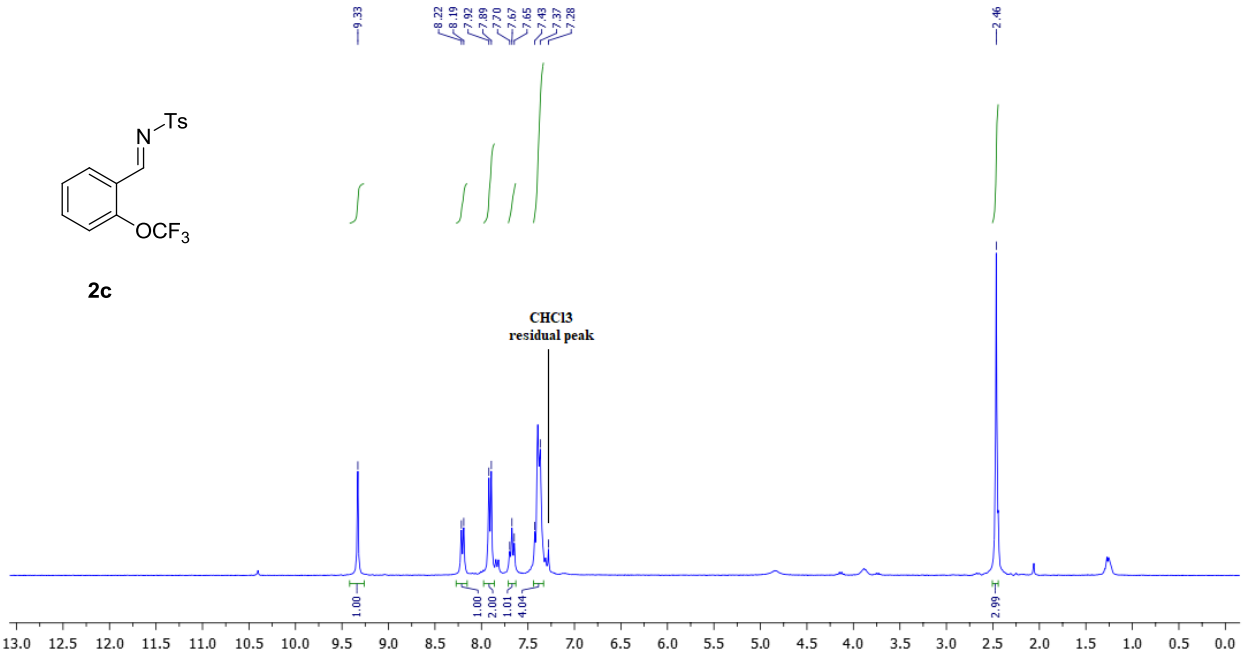
8q

(*S*)-Adamantylglycine (8q). Colorless solid, yield 1.37 g (73%), mp >200 ^{o}C (dec.). ^{1}H NMR (300 MHz, D_2O + 48% HBr (1 drop)) δ 3.52 (s, 1H), 2.08 (brs, 3H), 1.80-1.79 (m, 6H), 1.67 (br. d, *J* = 12.4 Hz, 3H), 1.58 (br. d, *J* = 12.4 Hz, 3H). $[\alpha]^{25}_{D}$ = +15.3 ° (98% *ee*, *c* 0.3, MeOH). lit.[19] $[\alpha]^{25}_{D}$ = +15.0 ° (100 % *ee*, *c* 0.53, MeOH). HRMS (ESI): calculated for $C_{12}H_{20}BrNO_2$ $[M+H]^+$ 289.0677, found 289.0674.

8. NMR pictures of prepared compounds



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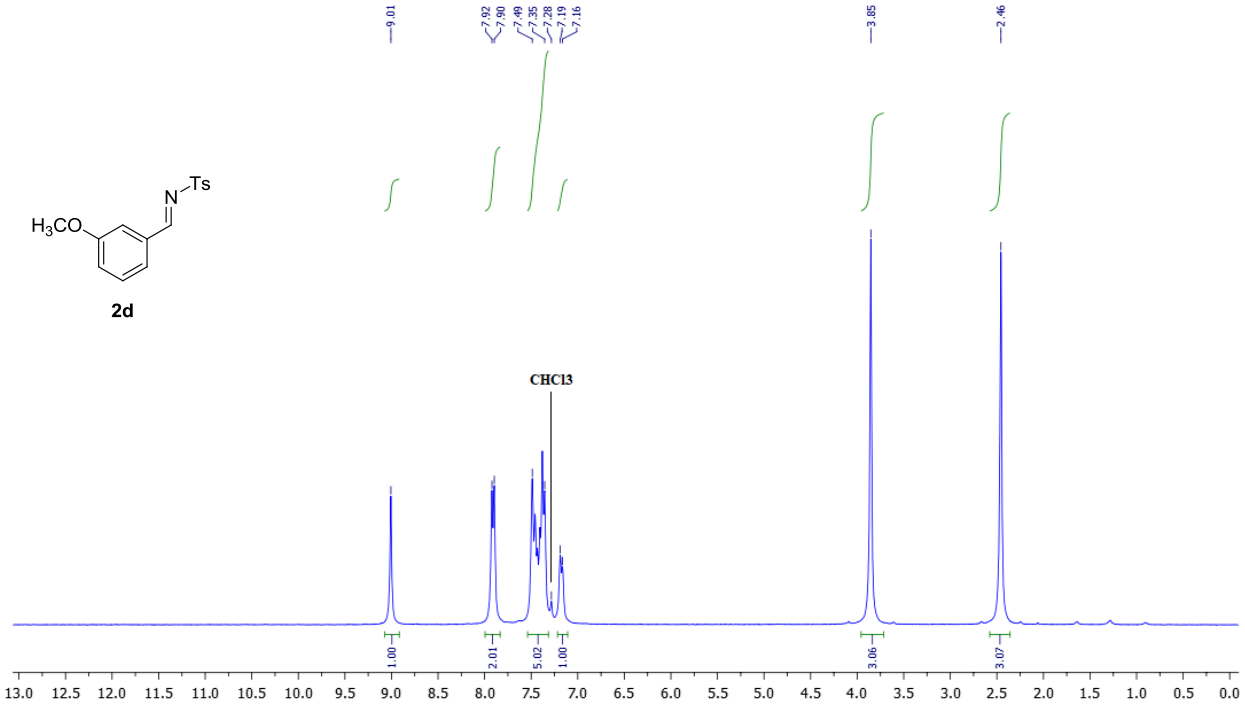
Ts
OCF3
2c
9.33
8.22
8.19
7.92
7.89
7.70
7.67
7.65
7.43
7.37
7.28
2.46
CHCl3
residual peak
1.00
1.00
2.00
1.01
4.04
2.99
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


N
Ts
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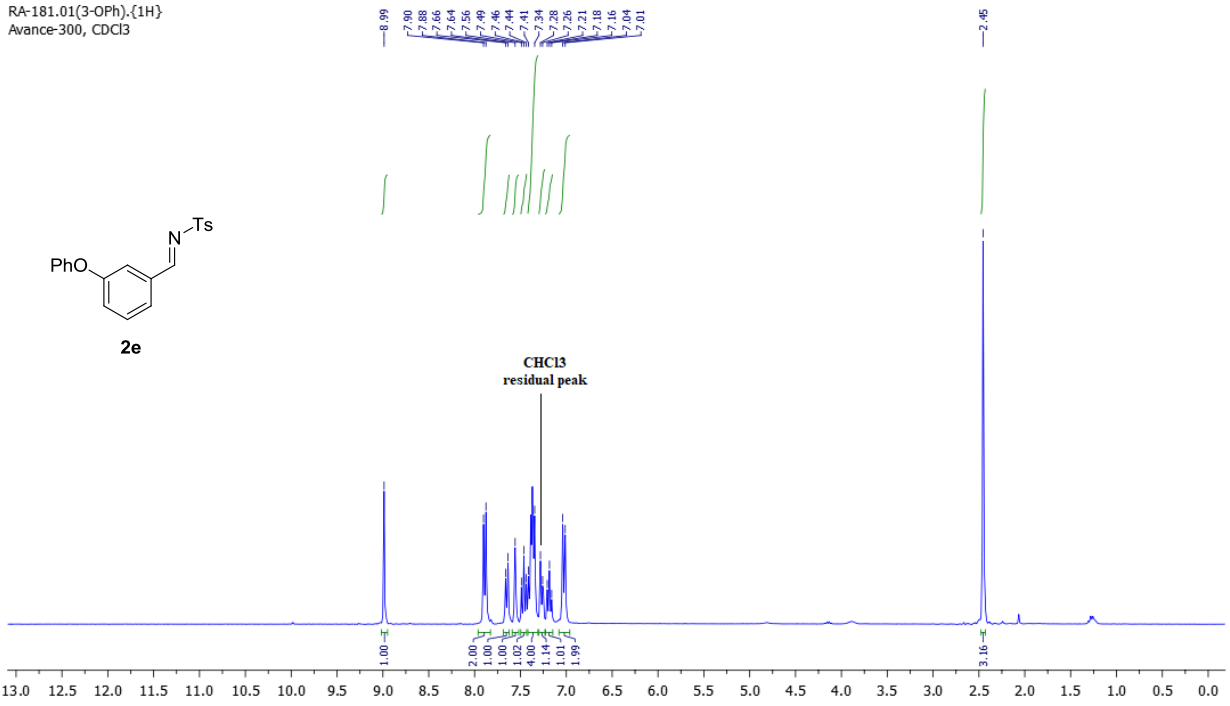
2d
9.01
7.92
7.90
7.49
7.35
7.28
7.19
7.16
3.85
2.46
CHCl3
1.00
2.01
5.02
1.00
3.06
3.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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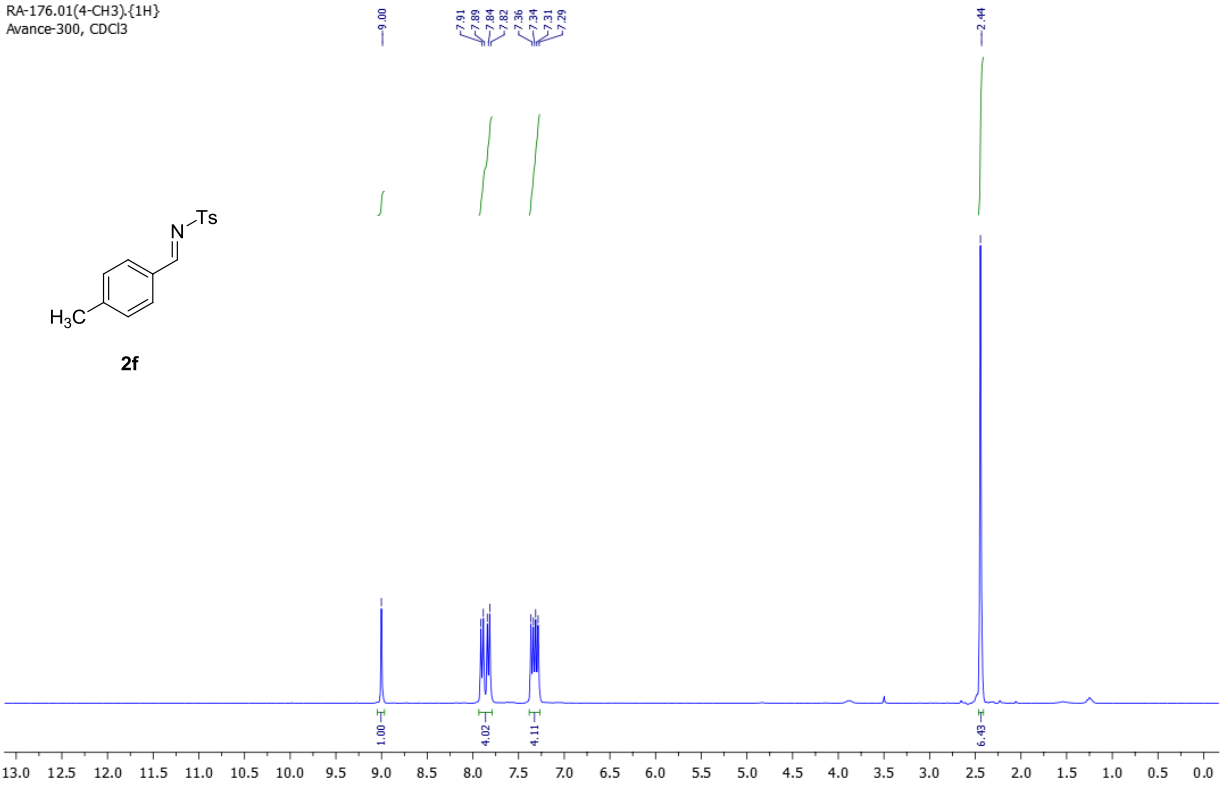
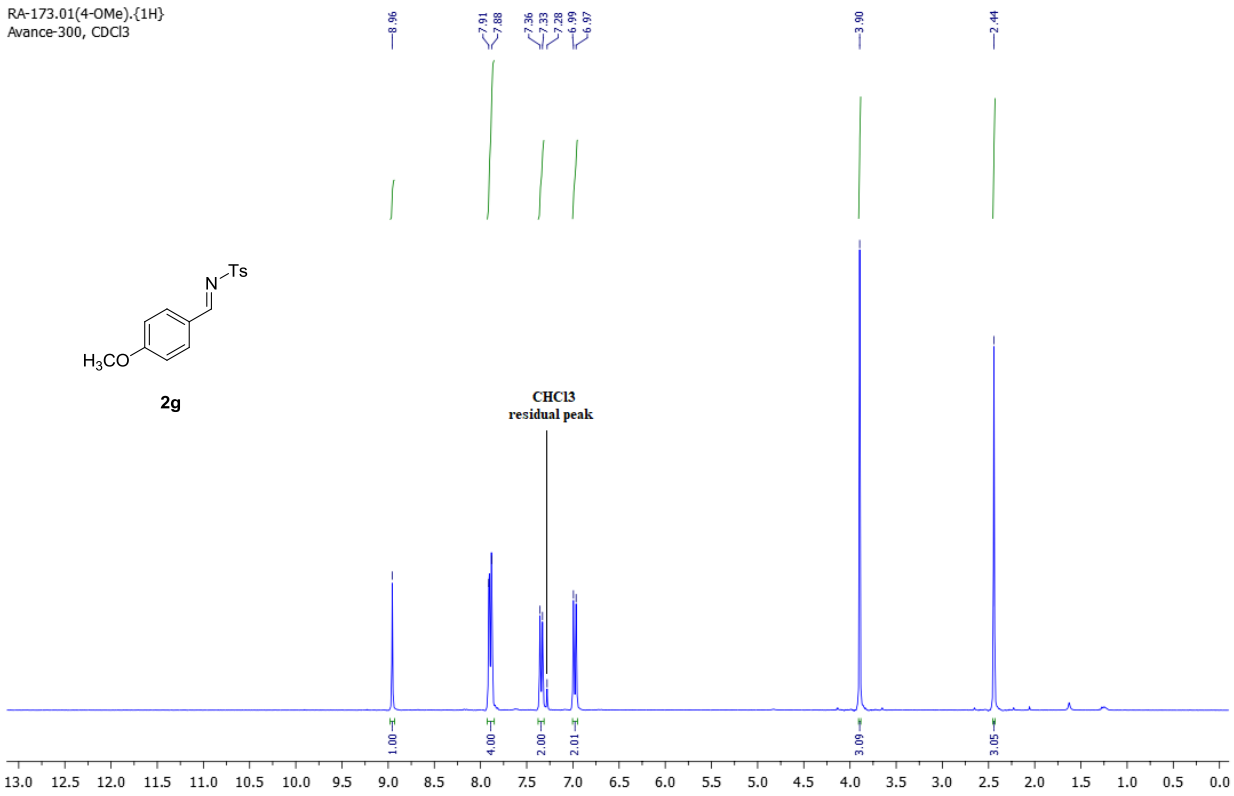
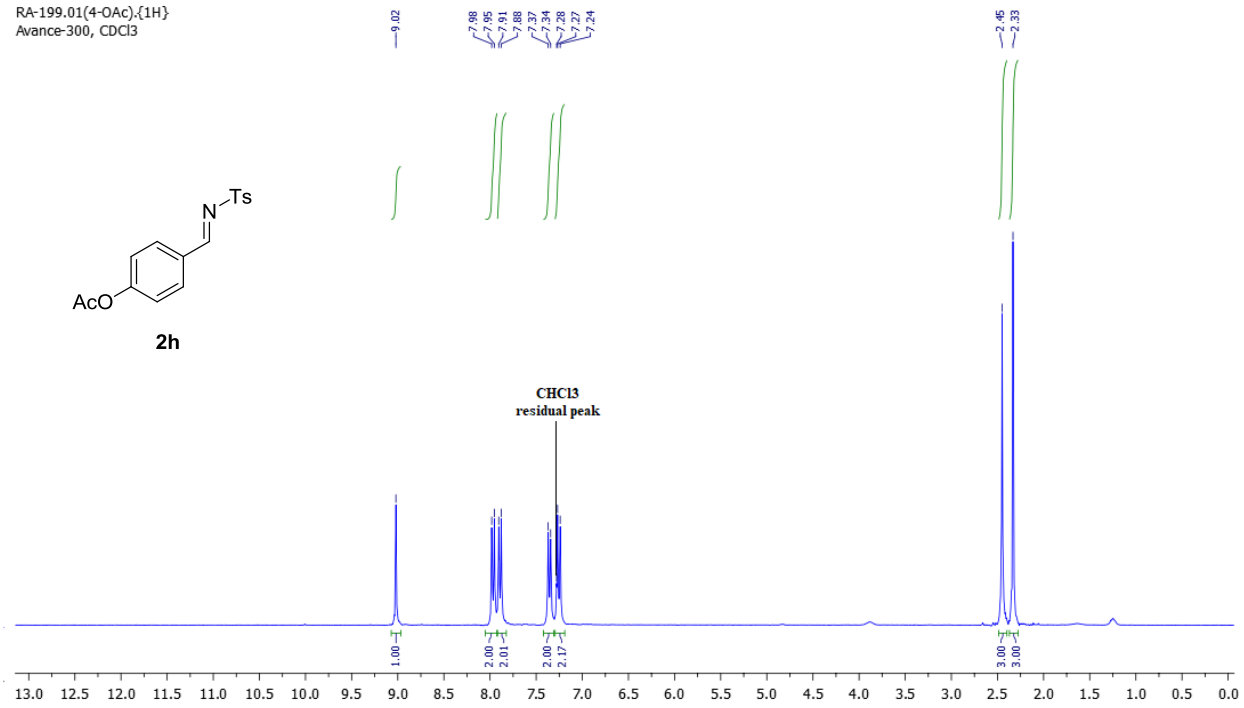
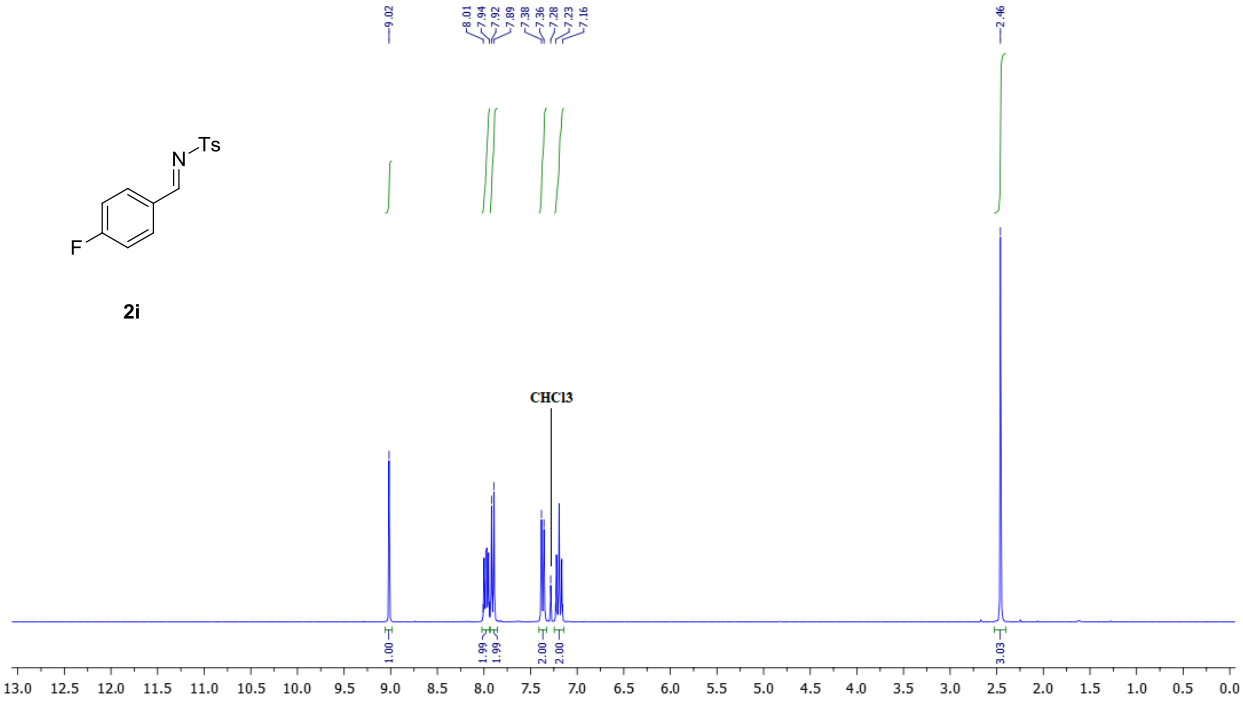
Avance-300, CDCl3
PhO
N
Ts
2e
CHCl3
residual peak


RA-176.01(4-CH3).{1H}
Avance-300, CDCl3
H3C
N
Ts
2f


RA-173.01(4-OMe).{1H}
Avance-300, CDCl3
8.96
7.91
7.88
7.36
7.33
7.28
6.99
6.97
3.90
2.44
Ts
N
H3CO
2g
CHCl3
residual peak
1.00
4.00
2.00
2.01
3.09
3.05
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


RA-199.01(4-OAc).{1H}
Avance-300, CDCl3
9.02
7.98
7.95
7.91
7.88
7.37
7.34
7.28
7.27
7.24
2.45
2.33
Ts
N
AcO
2h
CHCl3
residual peak
1.00
2.00
2.01
2.00
2.17
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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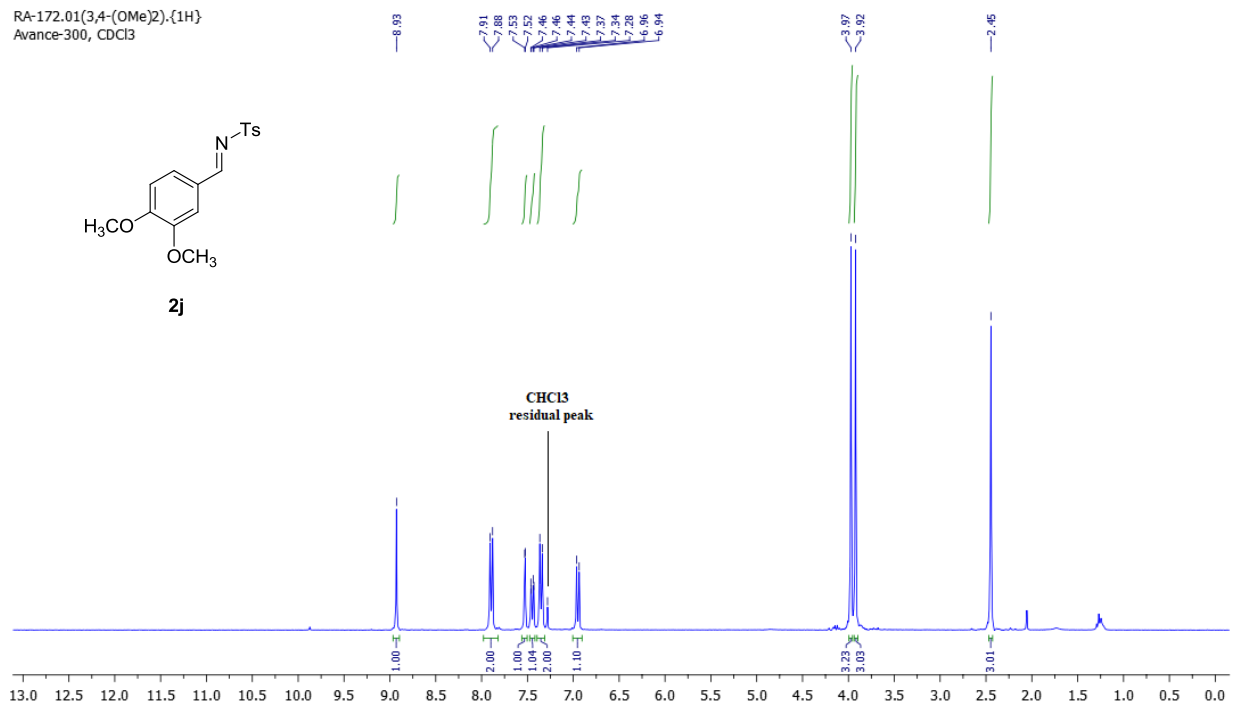
8.01
7.94
7.92
7.89
7.38
7.36
7.28
7.23
7.16
2.46
N
Ts
F
CHCl3
1.00
1.99
1.99
2.00
2.00
3.03
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2i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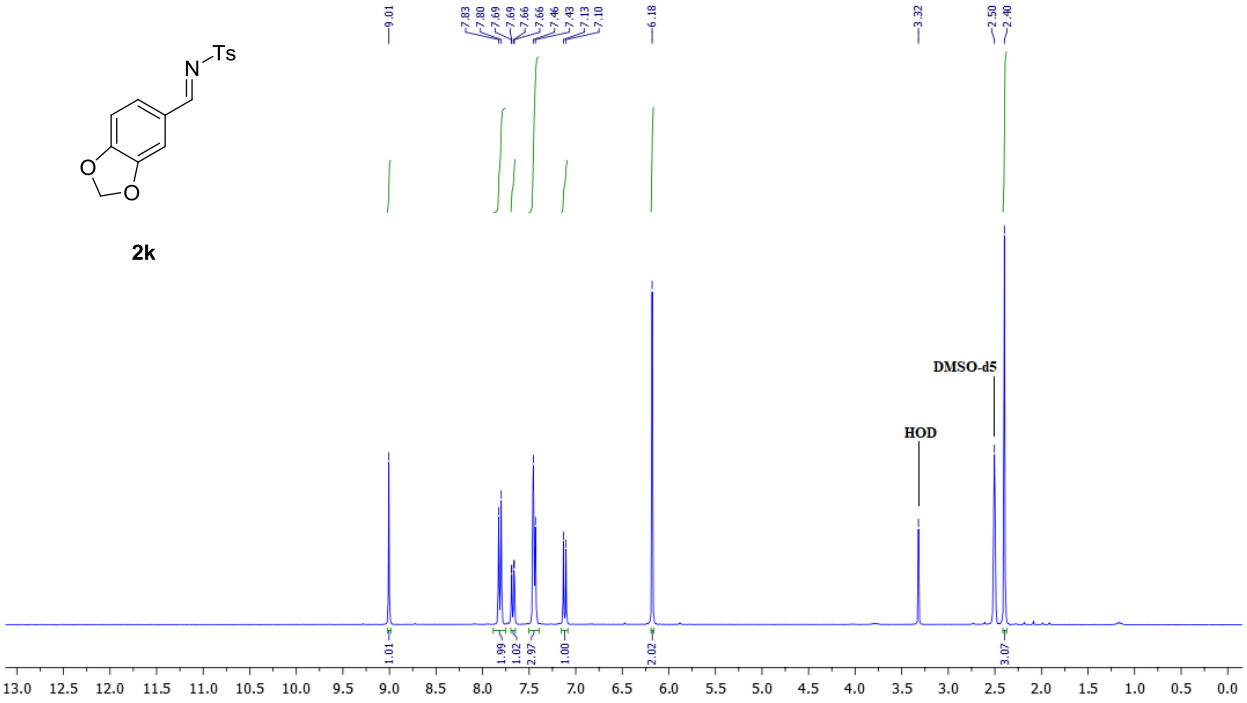
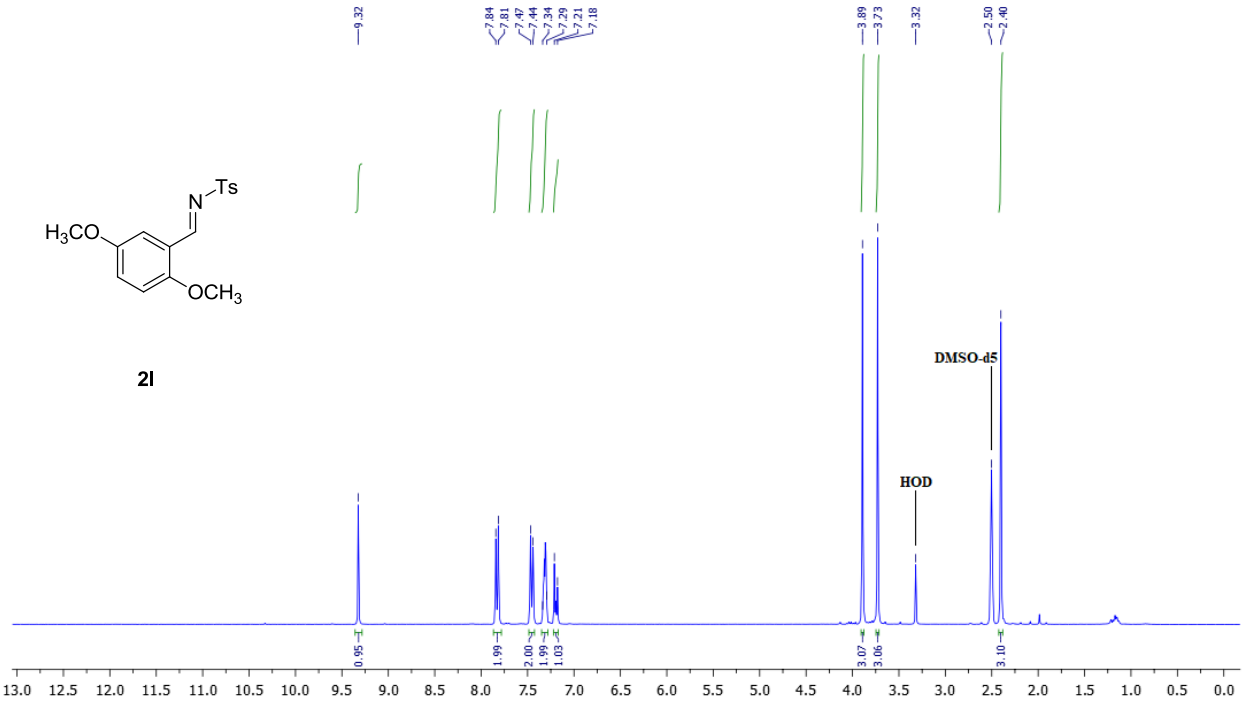
7.88
7.53
7.52
7.46
7.46
7.44
7.43
7.37
7.34
7.28
6.96
6.94
3.97
3.92
2.45
N
Ts
H3CO
OCH3
CHCl3
residual peak
1.00
2.00
1.00
1.04
2.00
1.10
3.23
3.03
3.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2j


N
Ts
O
O
9.01
7.83
7.80
7.69
7.69
7.66
7.66
7.46
7.43
7.13
7.10
6.18
3.32
2.50
2.40
DMSO-d5
HOD
1.01
1.99
1.02
2.97
1.00
2.02
3.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2k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Ts
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OCH3
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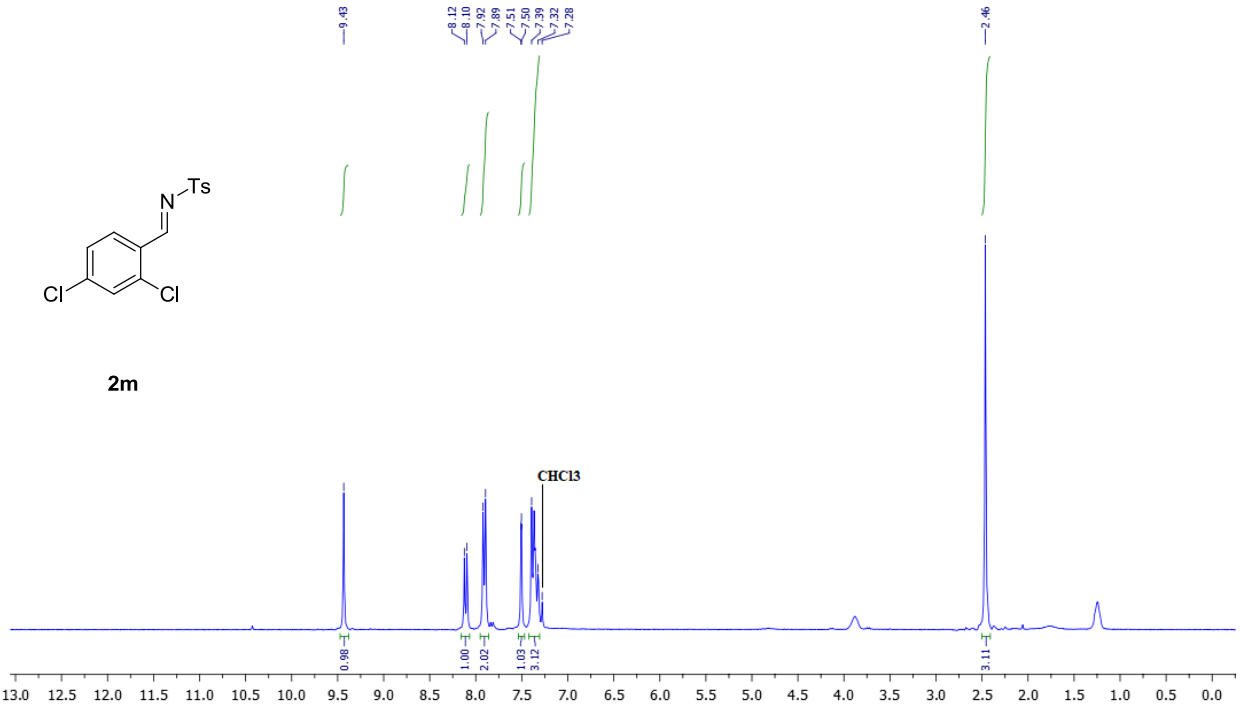
7.81
7.47
7.44
7.34
7.29
7.21
7.18
3.89
3.73
3.32
2.50
2.40
DMSO-d5
HOD
0.95
1.99
2.00
1.99
1.03
3.07
3.06
3.10
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2l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7.39
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7.28
2.46
N
Ts
Cl
Cl
CHCl3
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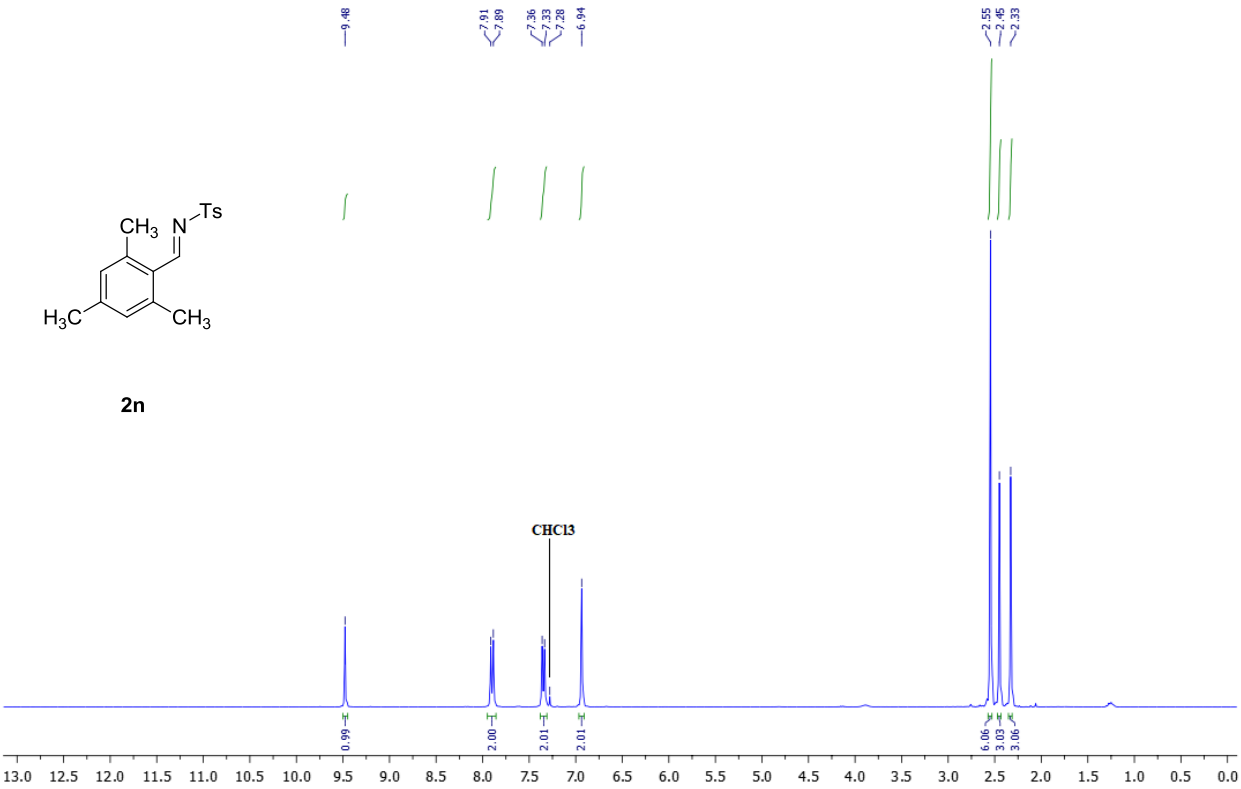
1.00
2.02
1.03
3.12
3.11
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2m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7.28
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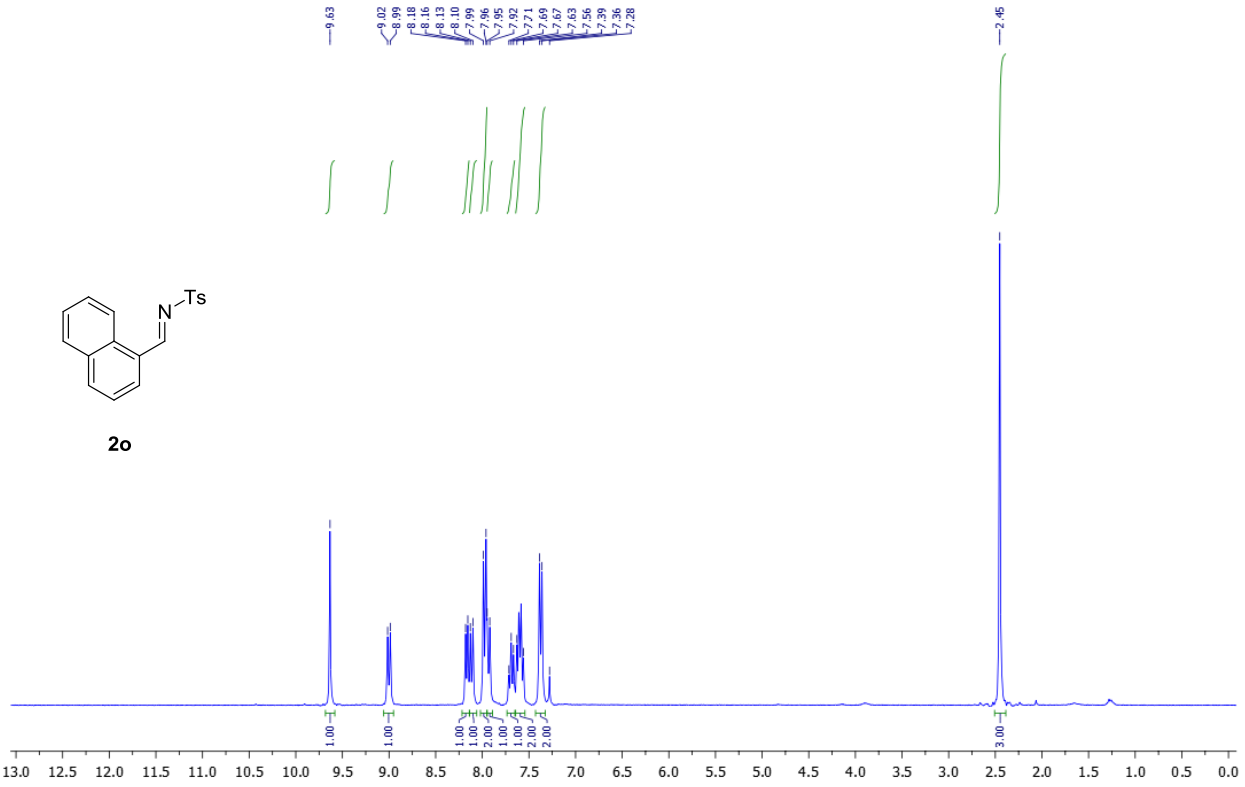
2.55
2.45
2.33
CH3
N
Ts
H3C
CH3
CHCl3
0.99
2.00
2.01
2.01
6.06
3.03
3.06
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2n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7.99
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7.95
7.92
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7.69
7.67
7.63
7.56
7.39
7.36
7.28
2.45
N
Ts
1.00
1.00
1.00
1.00
2.00
2.00
1.00
1.00
2.00
2.00
3.00
13.0
12.5
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6.5
6.0
5.5
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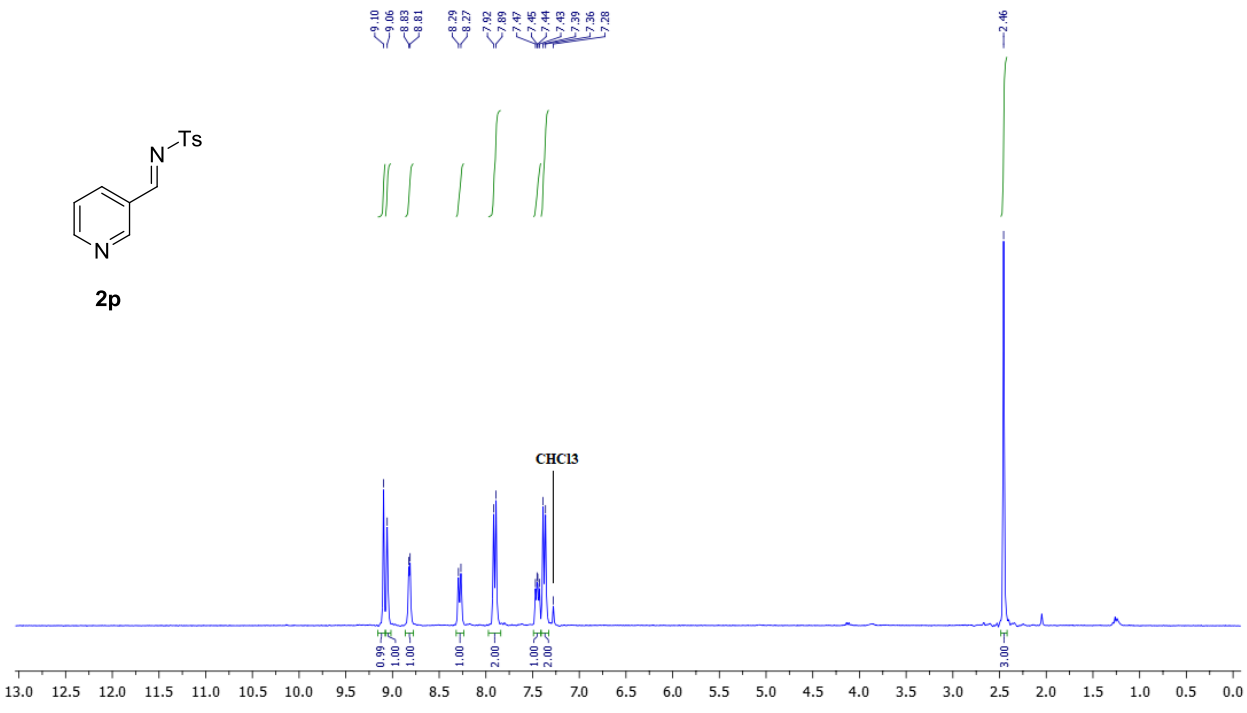
2o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8.27
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7.89
7.47
7.45
7.44
7.43
7.39
7.36
7.28
2.46
N
Ts
CHCl3
0.99
1.00
1.00
1.00
2.00
1.00
2.00
3.00
13.0
12.5
12.0
11.5
11.0
10.5
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6.5
6.0
5.5
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4.0
3.5
3.0
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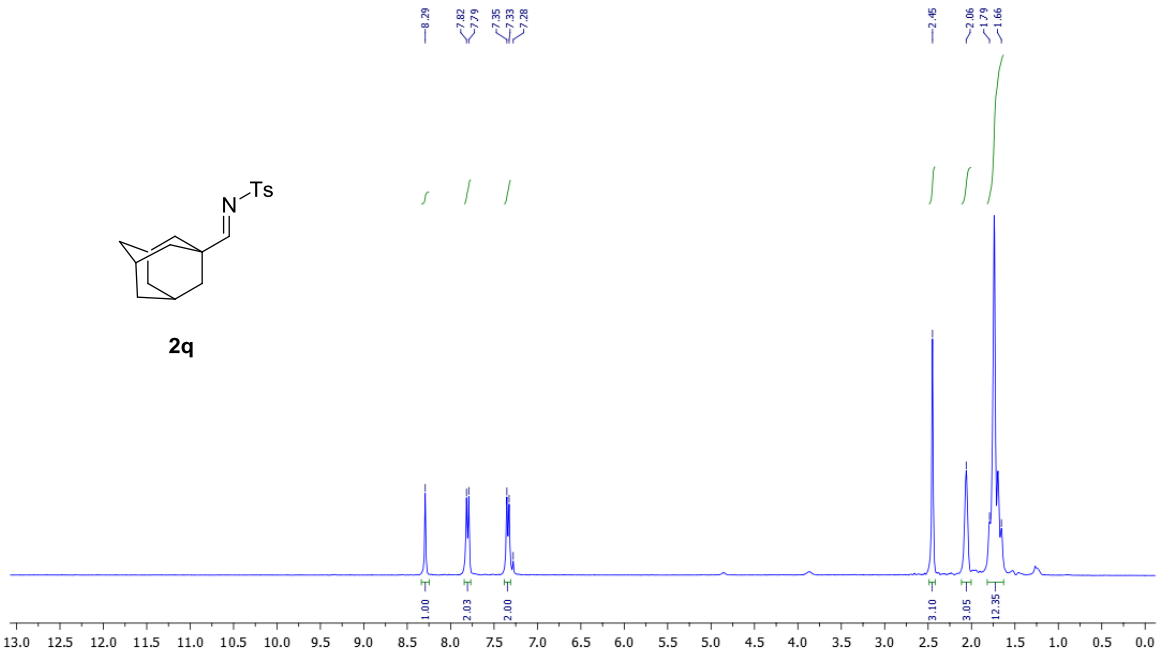
2.0
1.5
1.0
0.5
0.0

2p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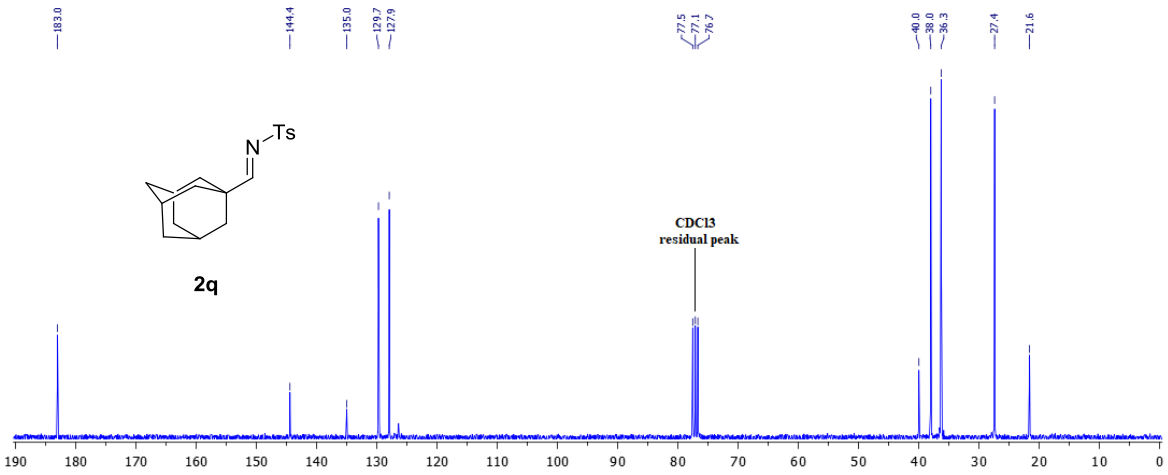
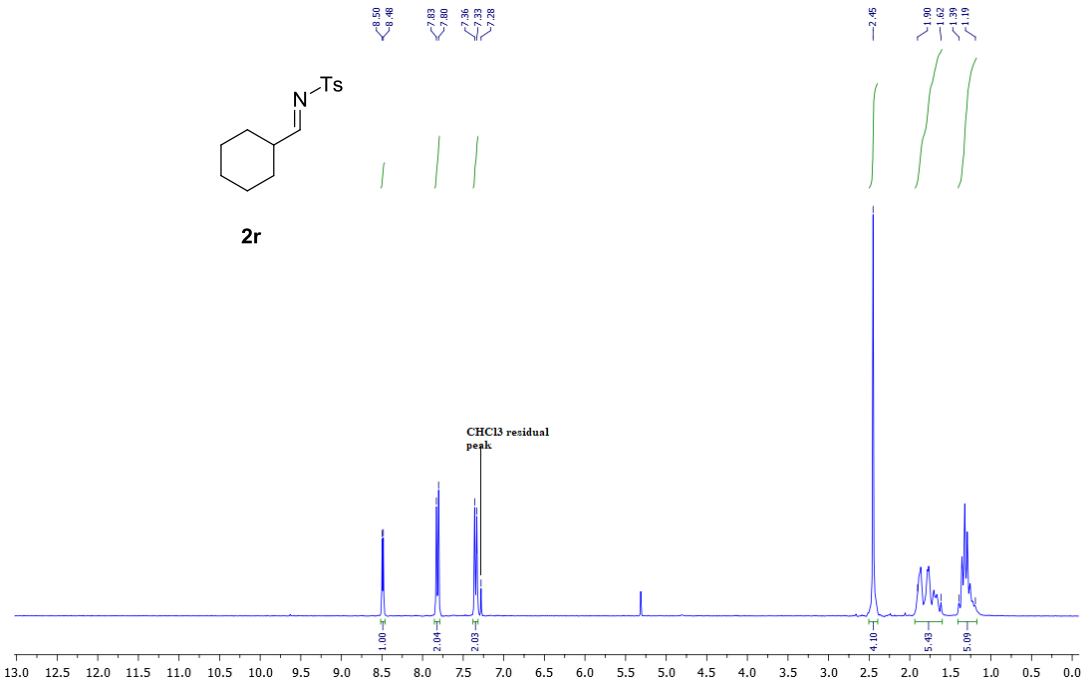
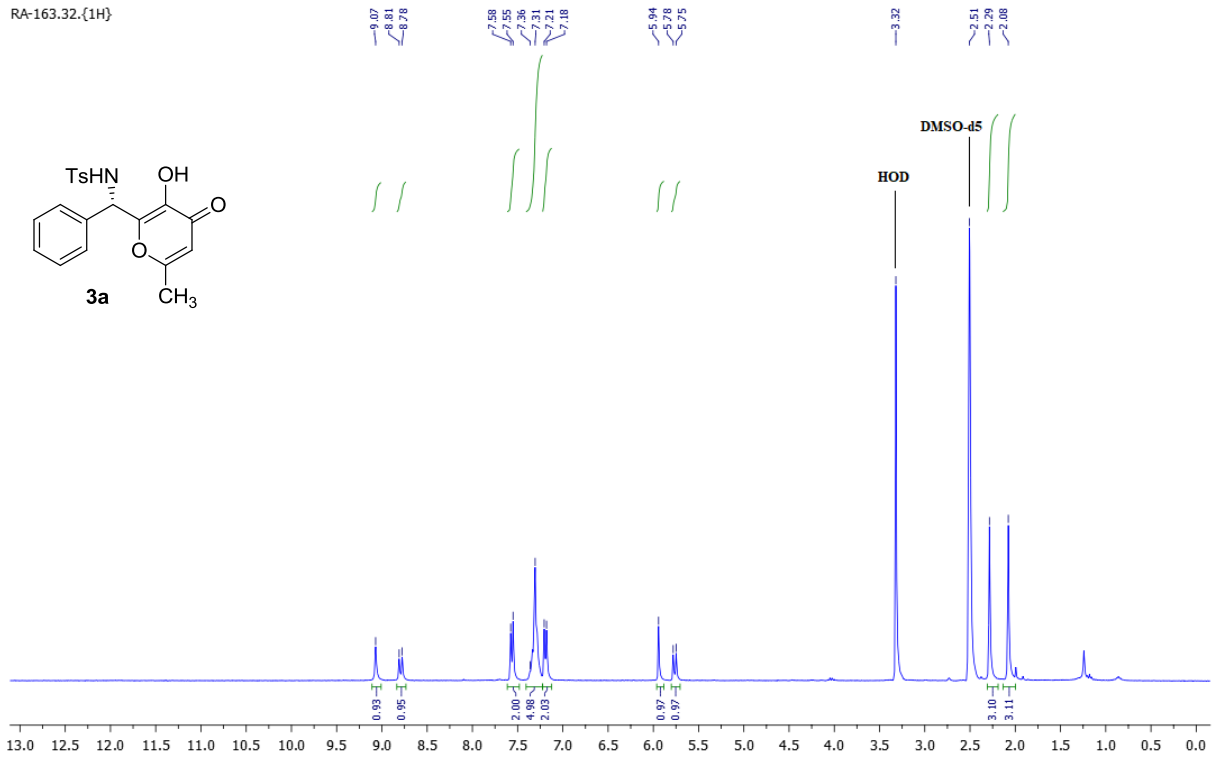
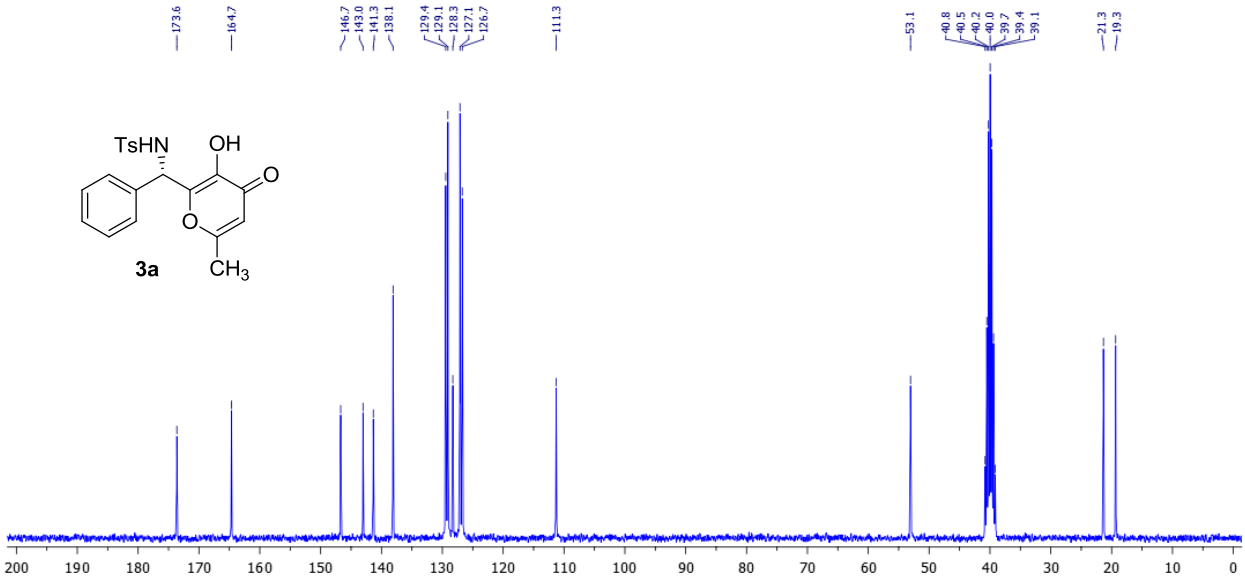
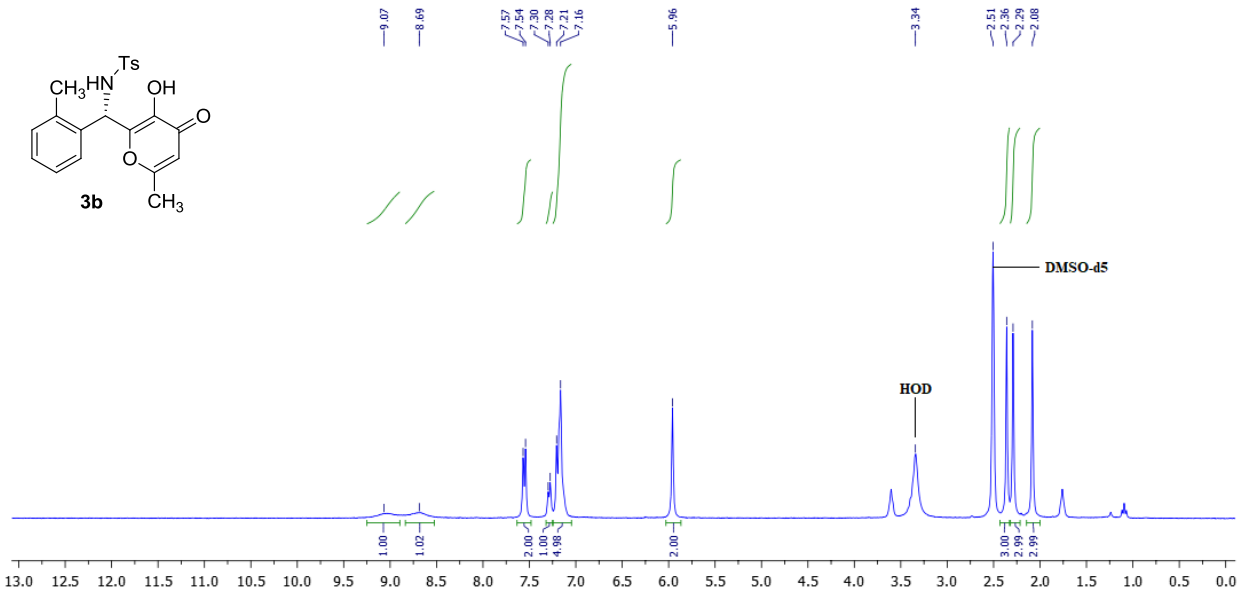
7.35
7.33
7.28
2.45
2.06
1.79
1.66
Ts
N
2q
1.00
2.03
2.00
3.10
3.05
12.35

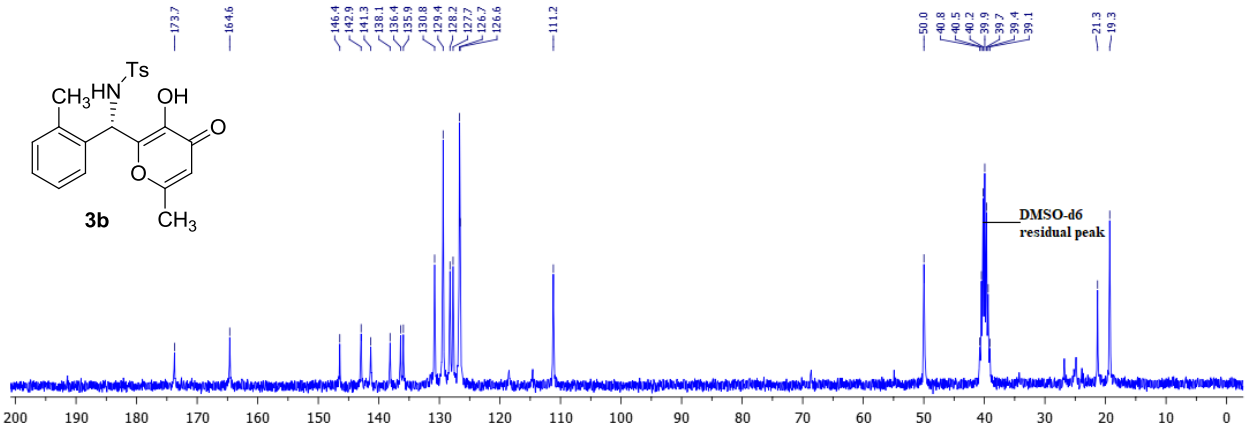

183.0
144.4
135.0
129.7
127.9
77.5
77.1
76.7
40.0
38.0
36.3
27.4
21.6
Ts
N
2q
CDCl3
residual peak

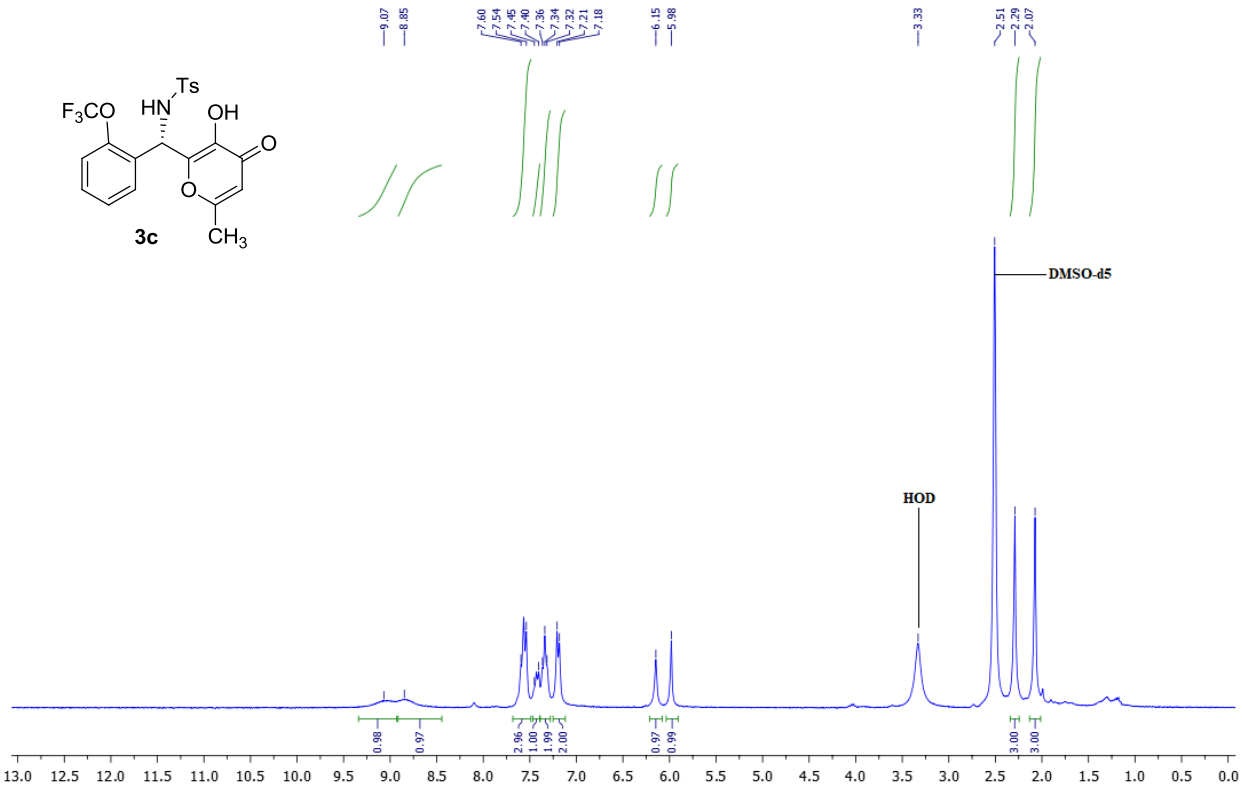

8.50
8.48
7.83
7.80
7.36
7.33
7.28
2.45
1.90
1.62
1.39
1.19
Ts
N
2r
CHCl3 residual
peak
1.00
2.04
2.03
4.10
5.43
5.09

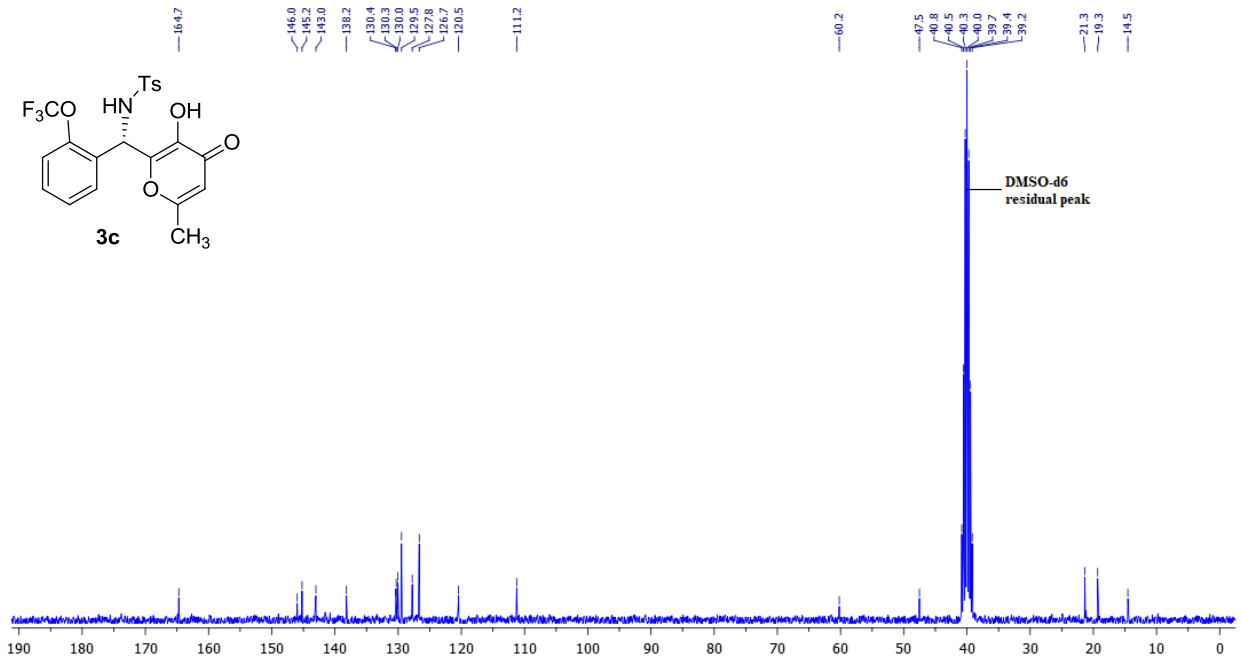

RA-163.32.{1H}
TsHN
OH
O
O
CH3
3a
HOD
DMSO-d5

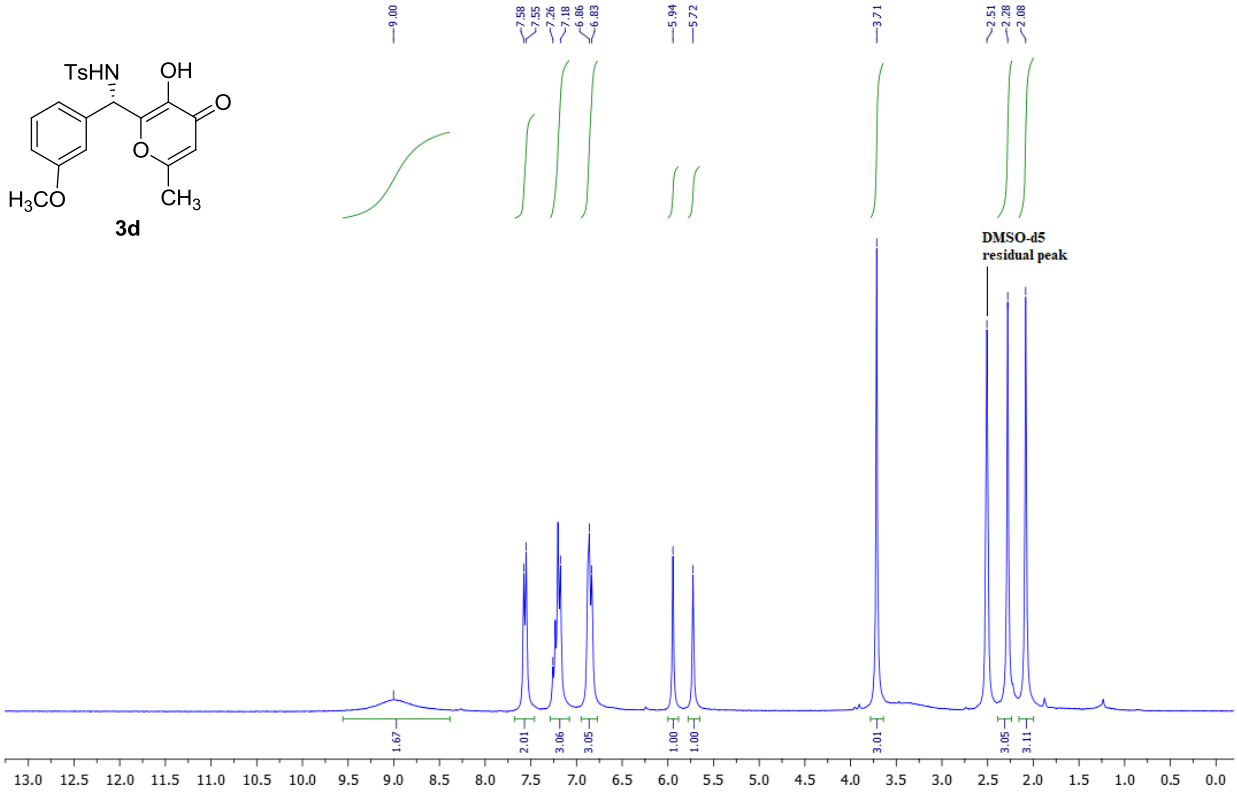

TsHN
OH
O
O
CH3
3a

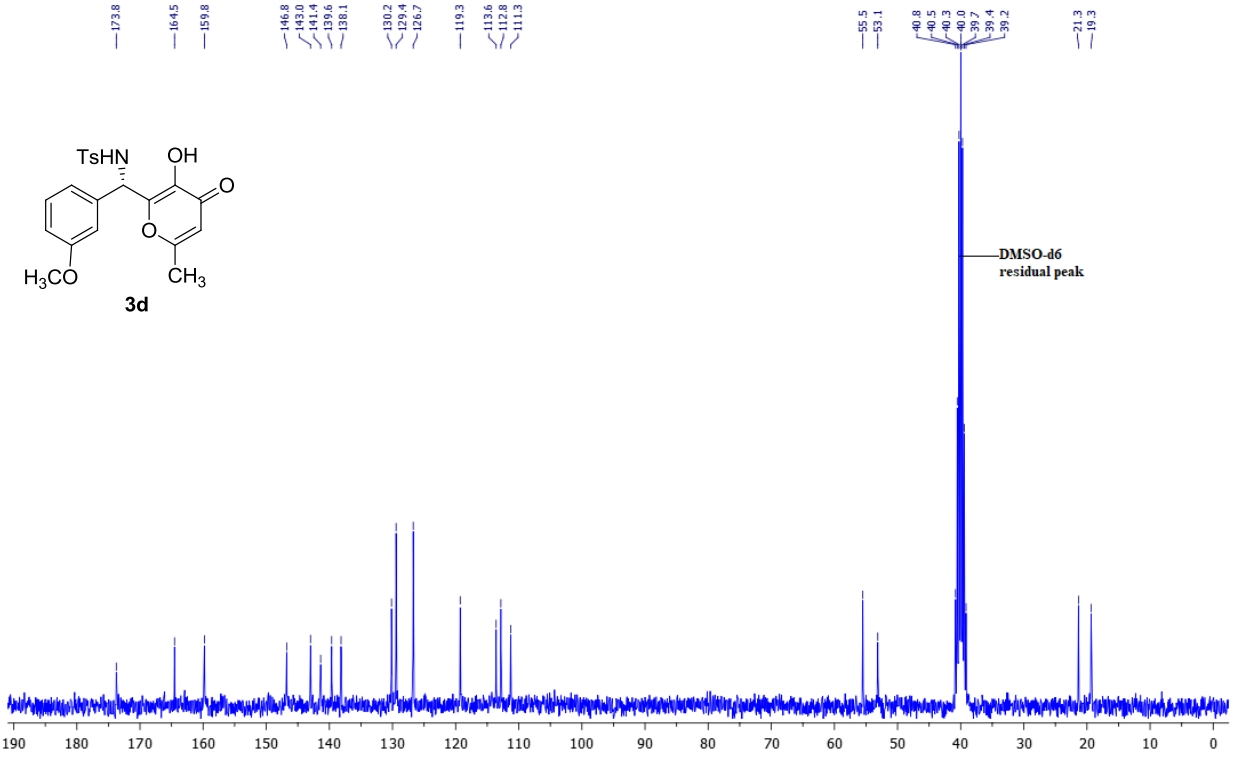

3b
DMSO-d5
HOD

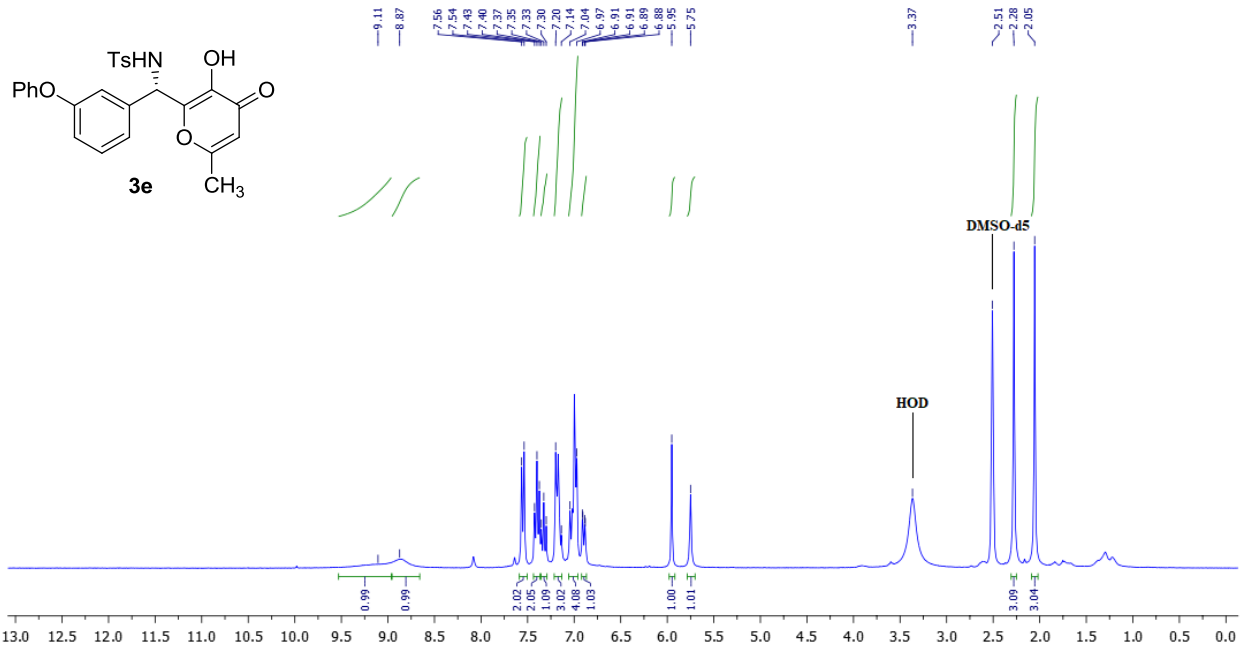

3b
DMSO-d6
residual peak

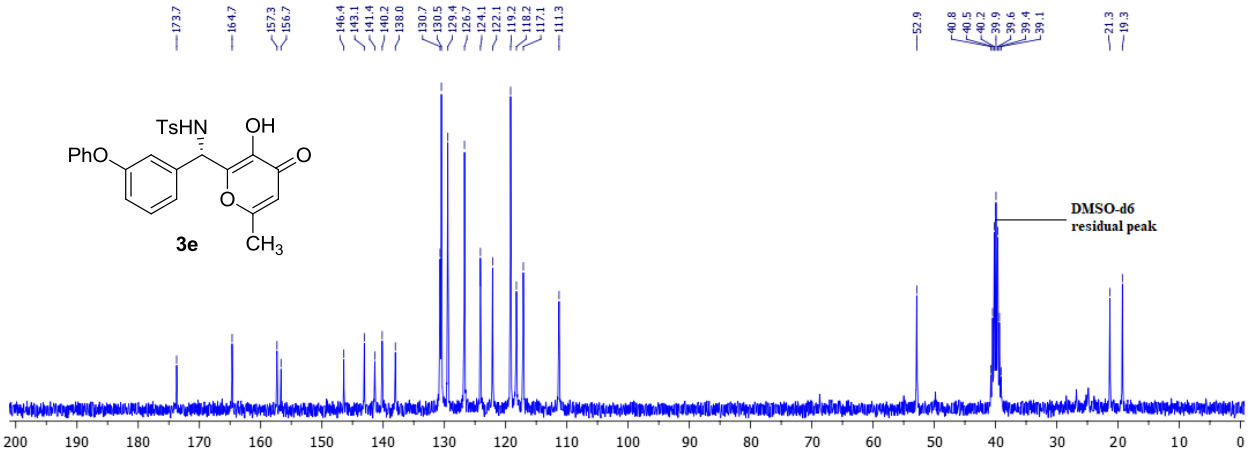

Ts
HN
OH
F3CO
O
O
CH3
3c
9.07
8.85
7.60
7.54
7.45
7.40
7.36
7.34
7.32
7.21
7.18
6.15
5.98
3.33
2.51
2.29
2.07
DMSO-d5
HOD
0.98
0.97
2.96
1.00
1.99
2.00
0.97
0.99
3.00
3.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

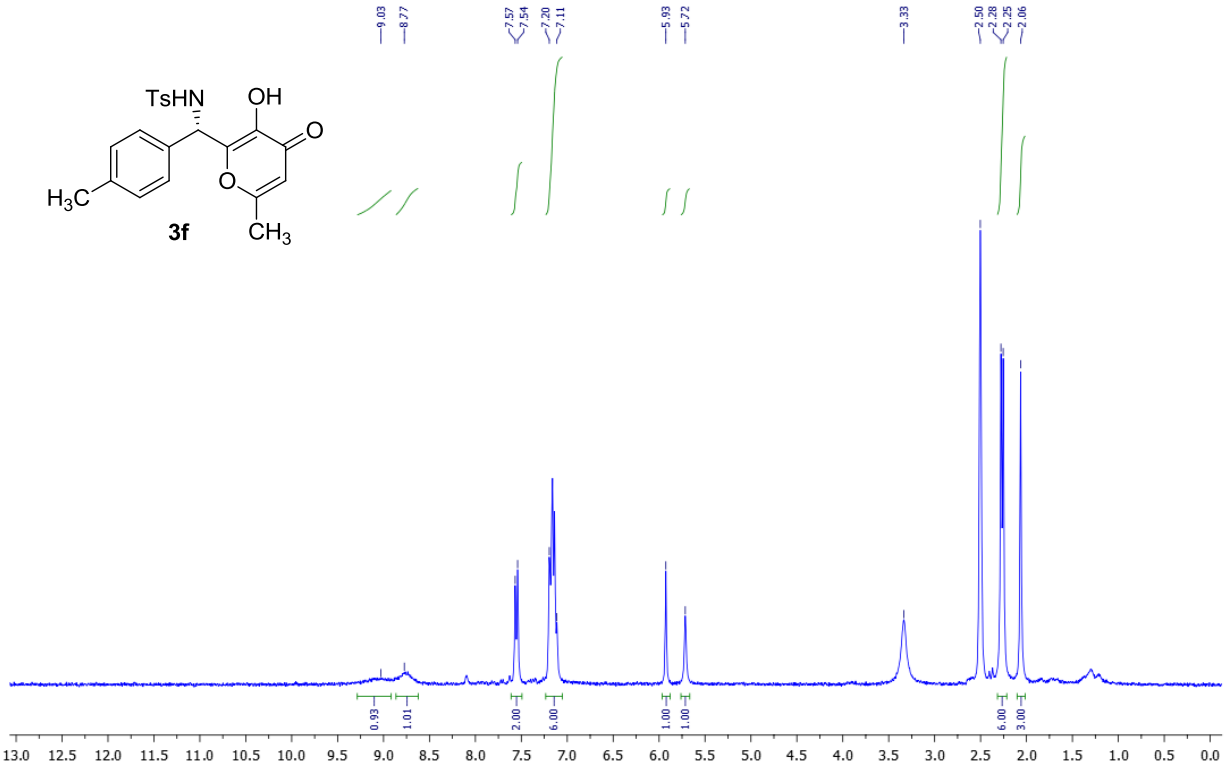

Ts
HN
OH
F3CO
O
O
CH3
3c
164.7
146.0
145.2
143.0
138.2
130.4
130.3
130.0
129.5
127.8
126.7
120.5
111.2
60.2
47.5
40.8
40.5
40.3
40.0
39.7
39.4
39.2
21.3
19.3
14.5
DMSO-d6
residual peak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

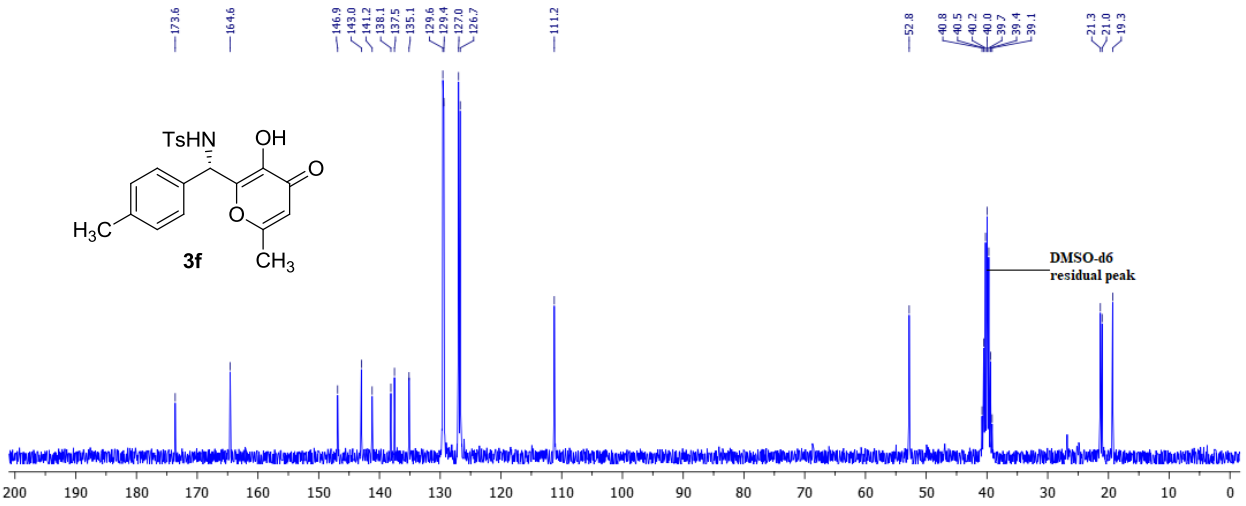

TsHN
OH
O
O
H3CO
CH3
3d
9.00
7.58
7.55
7.26
7.18
6.86
6.83
5.94
5.72
3.71
2.51
2.28
2.08
DMSO-d5
residual peak
1.67
2.01
3.06
3.05
1.00
1.00
3.01
3.05
3.11
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

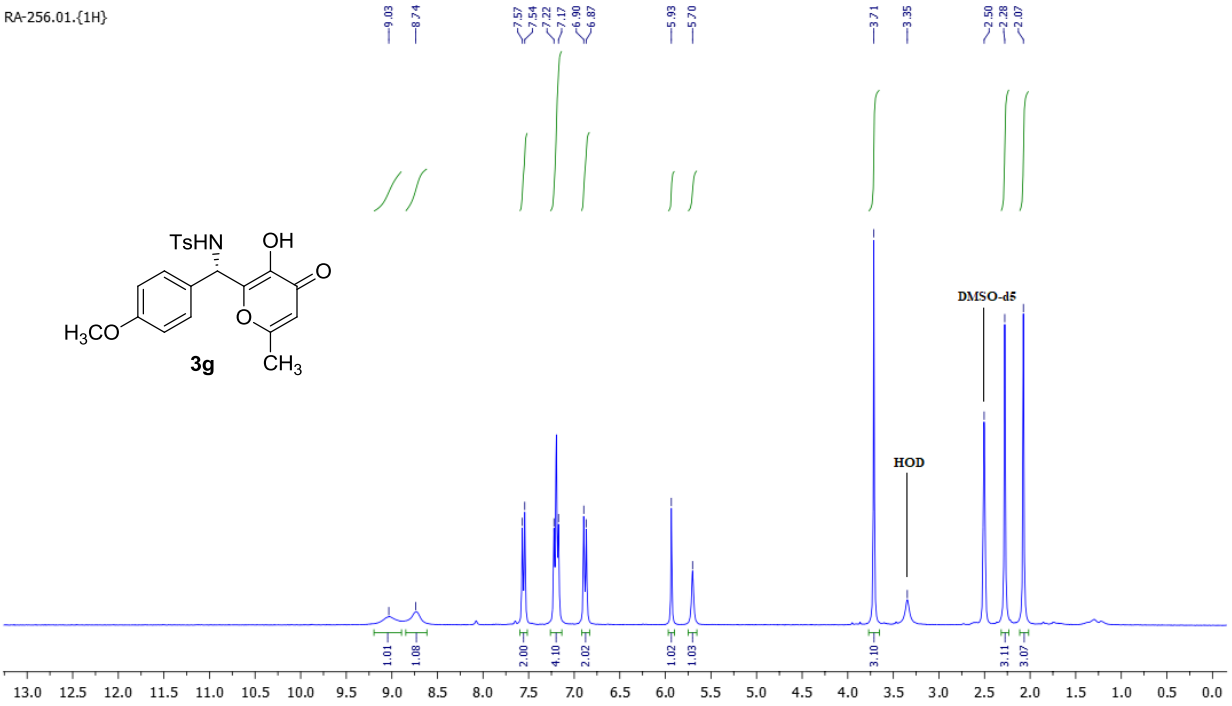

173.8
164.5
159.8
146.8
143.0
141.4
139.6
138.1
130.2
129.4
126.7
119.3
113.6
112.8
111.3
55.5
53.1
40.8
40.5
40.3
40.0
39.7
39.4
39.2
21.3
19.3
TsHN
OH
O
O
H3CO
CH3
3d
DMSO-d6
residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

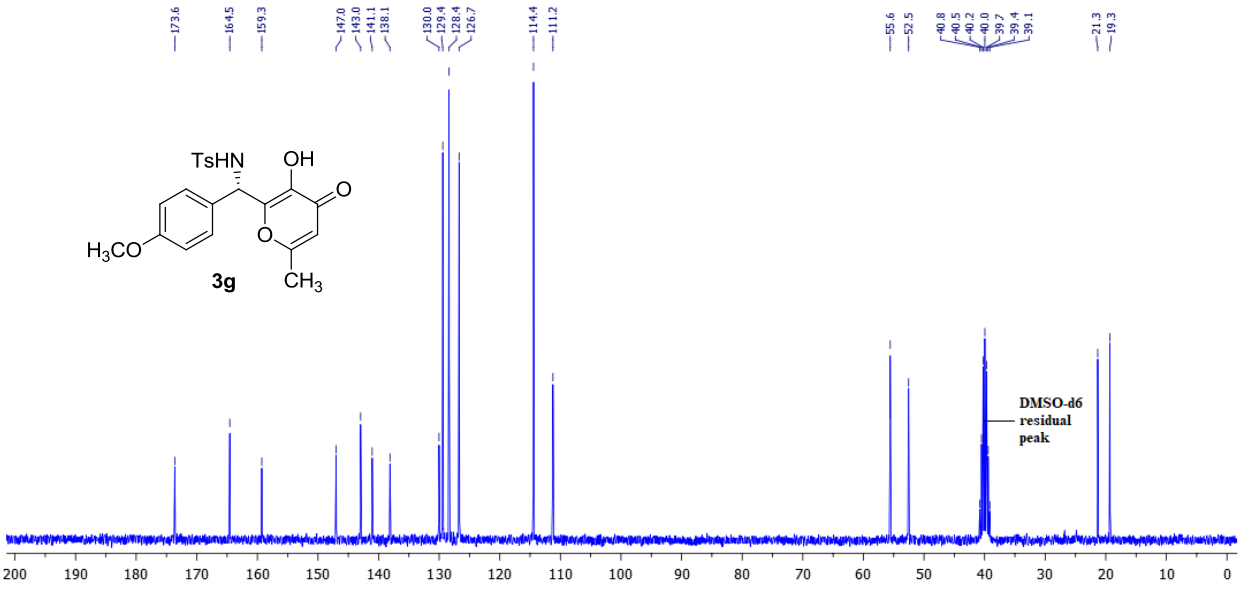

TsHN
OH
PhO
O
O
CH3
3e
DMSO-d5
HOD

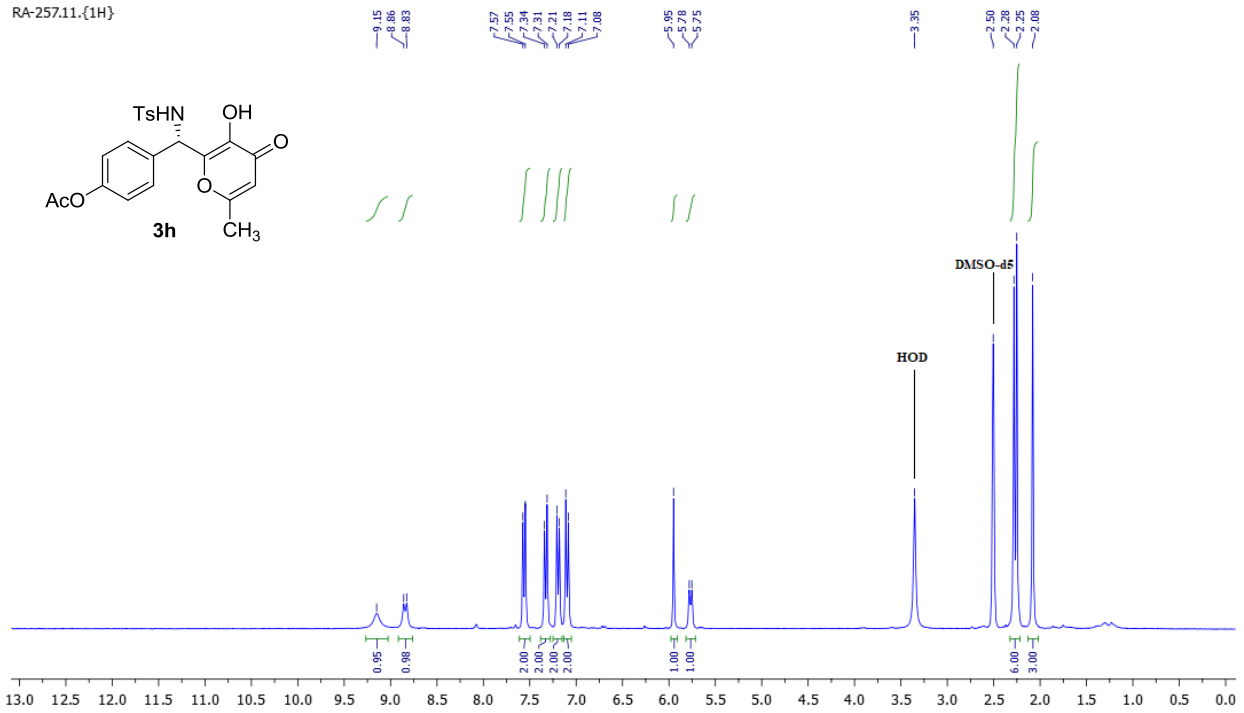

TsHN
OH
PhO
O
O
CH3
3e
DMSO-d6
residual peak

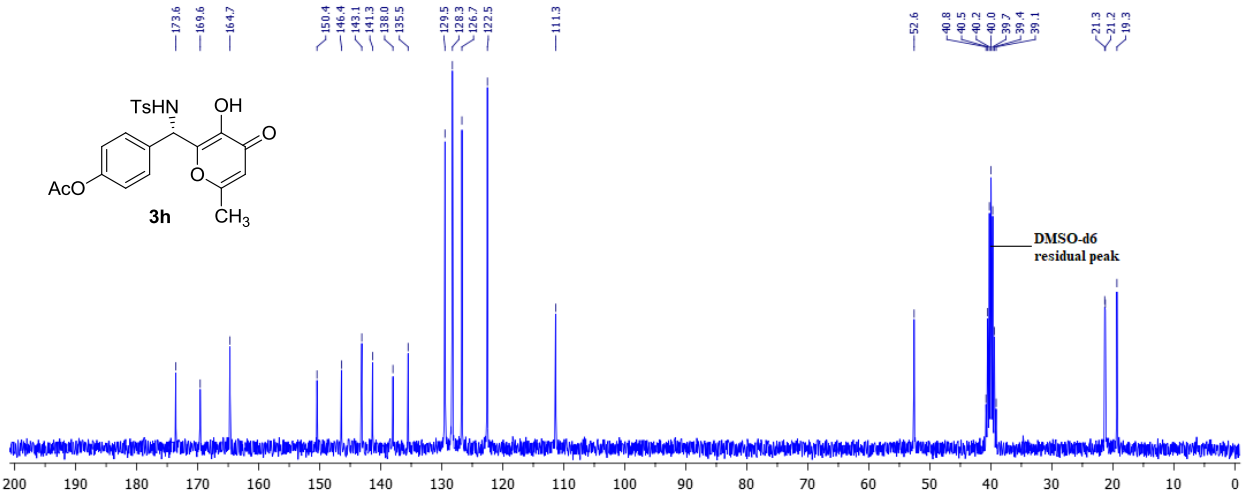

TsHN
OH
O
O
H_3C
CH_3
3f
9.03
8.77
7.57
7.54
7.20
7.11
5.93
5.72
3.33
2.50
2.28
2.25
2.06
0.93
1.01
2.00
6.00
1.00
1.00
6.00
3.00

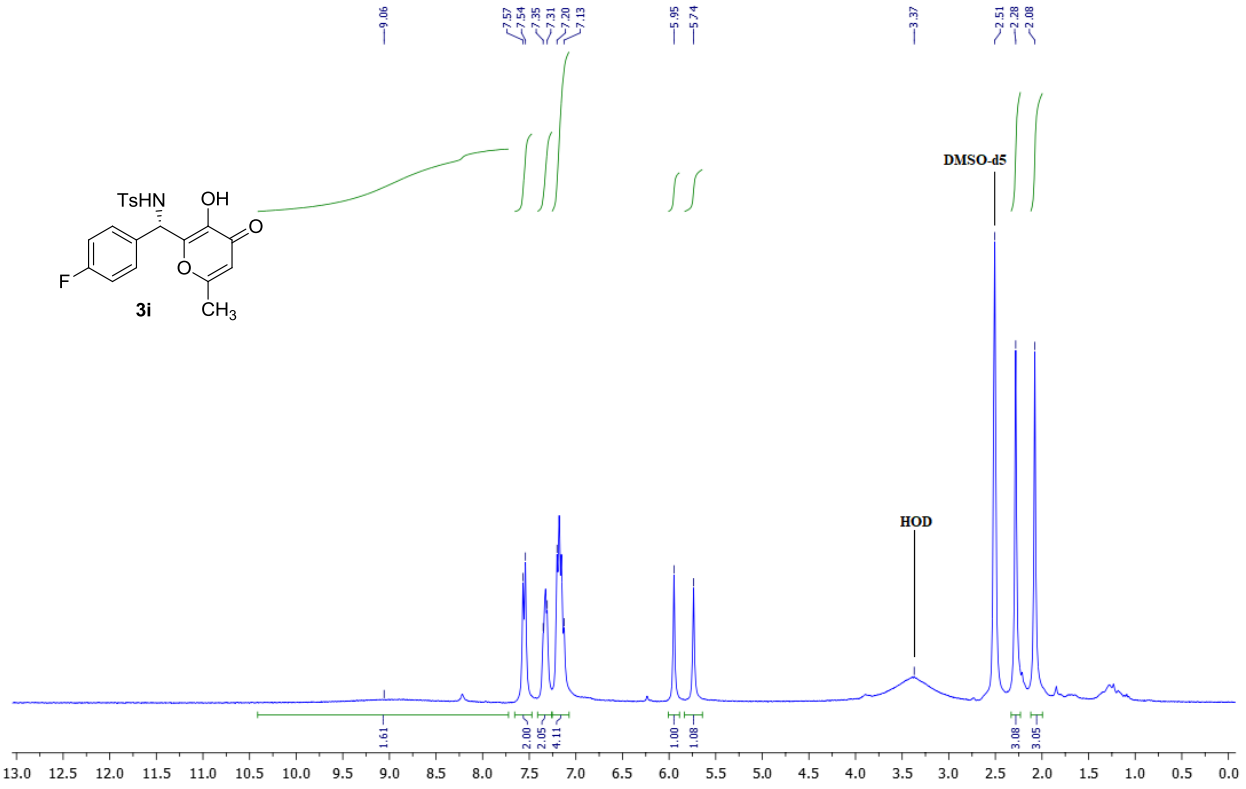

TsHN
OH
O
O
H_3C
CH_3
3f
173.6
164.6
146.9
143.0
141.2
138.1
137.5
135.1
130.6
129.4
127.0
126.7
111.2
52.8
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.3
21.0
19.3
DMSO-d6
residual peak

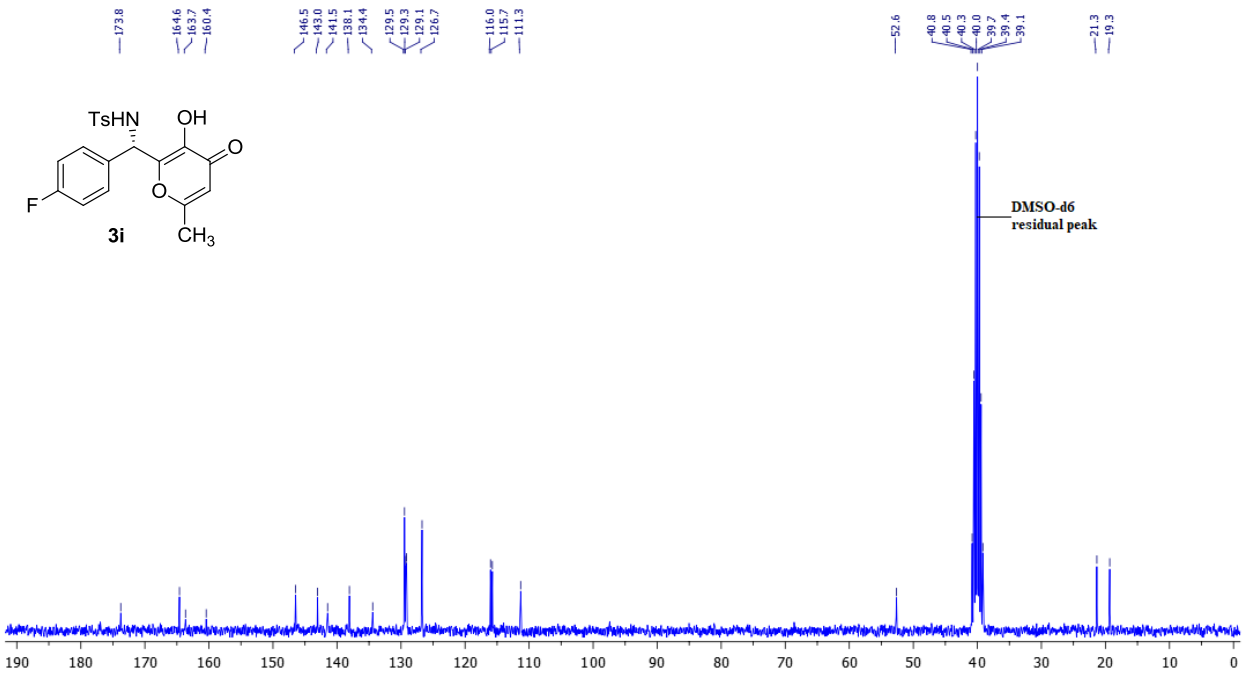

RA-256.01.{1H}
9.03
8.74
7.57
7.54
7.22
7.17
6.90
6.87
5.93
5.70
3.71
3.35
2.50
2.28
2.07
TsHN
OH
O
O
H3CO
CH3
3g
DMSO-d5
HOD
1.01
1.08
2.00
4.10
2.02
1.02
1.03
3.10
3.11
3.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

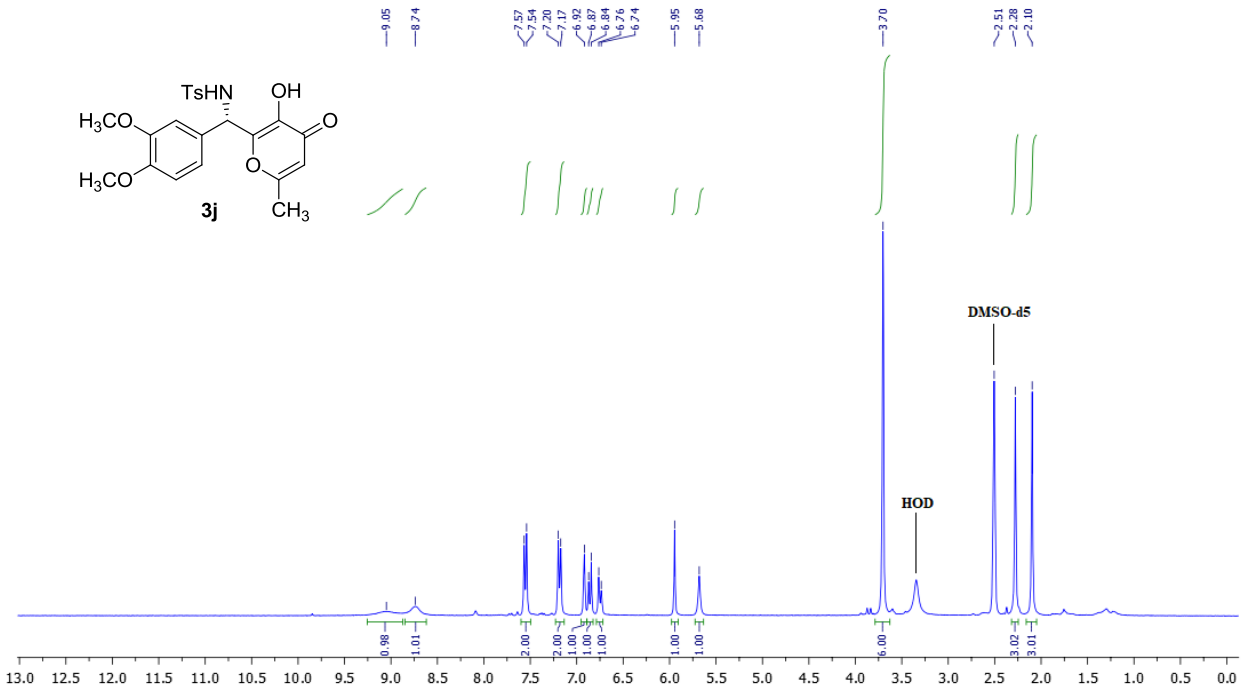

173.6
164.5
159.3
147.0
143.0
141.1
138.1
130.0
129.4
128.4
126.7
114.4
111.2
55.6
52.5
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.3
19.3
TsHN
OH
O
O
H3CO
CH3
3g
DMSO-d6
residual
peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

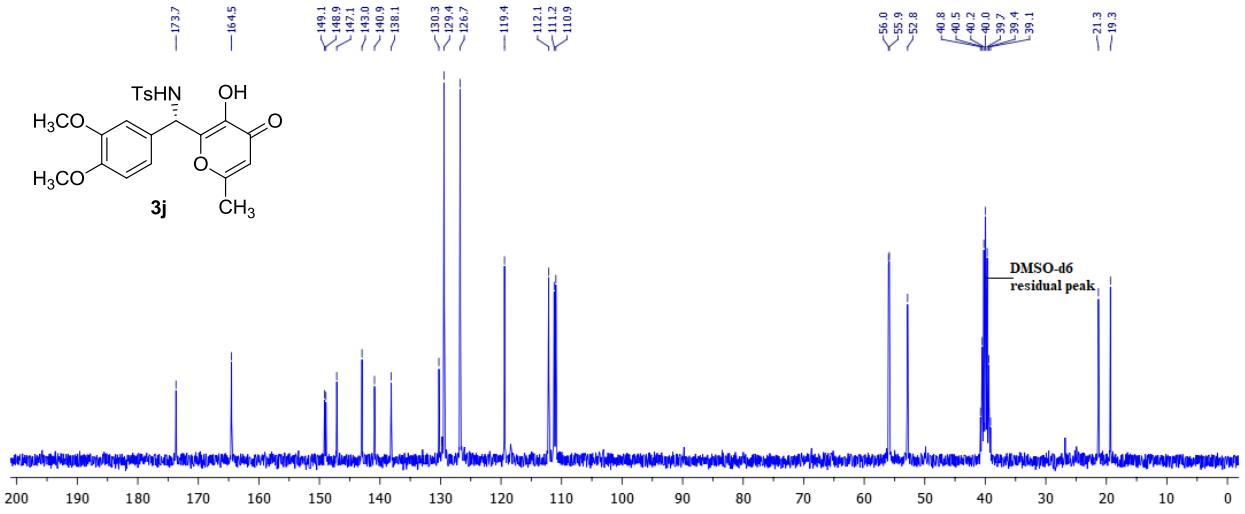

RA-257.11.{1H}
TsHN
OH
O
AcO
O
CH3
3h
9.15
8.86
8.83
7.57
7.55
7.34
7.31
7.21
7.18
7.11
7.08
5.95
5.78
5.75
3.35
2.50
2.28
2.25
2.08
DMSO-d5
HOD
0.95
0.98
2.00
2.00
2.00
2.00
1.00
1.00
6.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

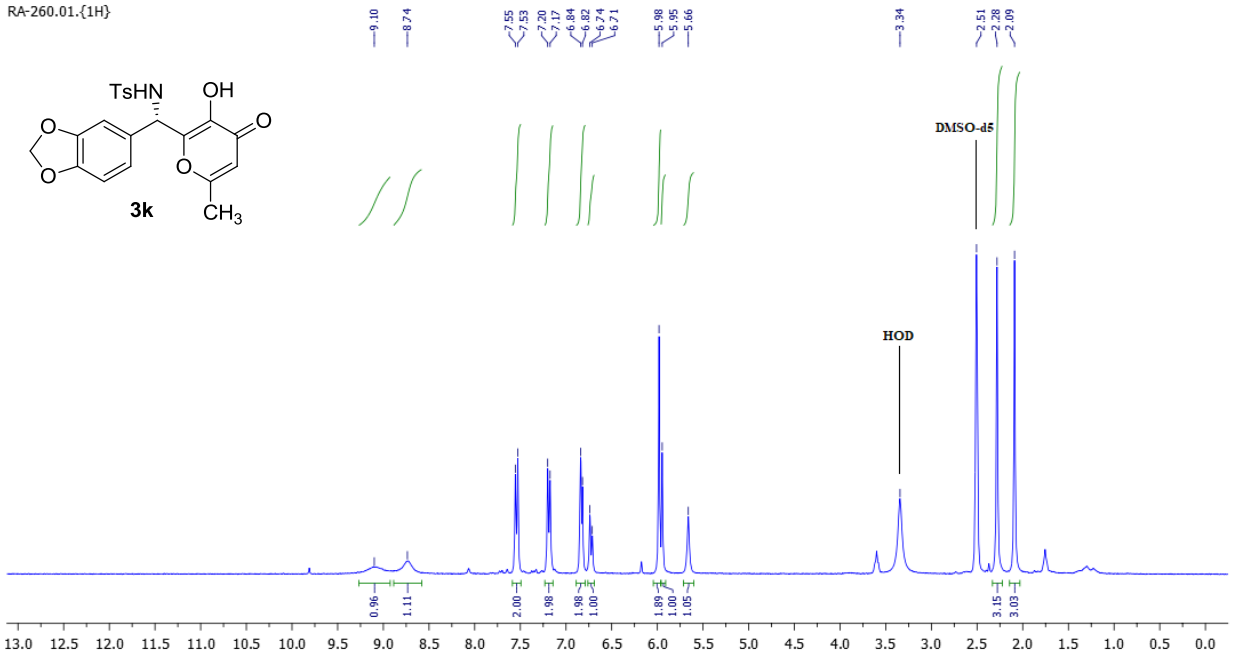

173.6
169.6
164.7
150.4
146.4
143.1
141.3
138.0
135.5
129.5
128.3
126.7
122.5
111.3
52.6
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.3
21.2
19.3
TsHN
OH
O
AcO
O
CH3
3h
DMSO-d6
residual peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

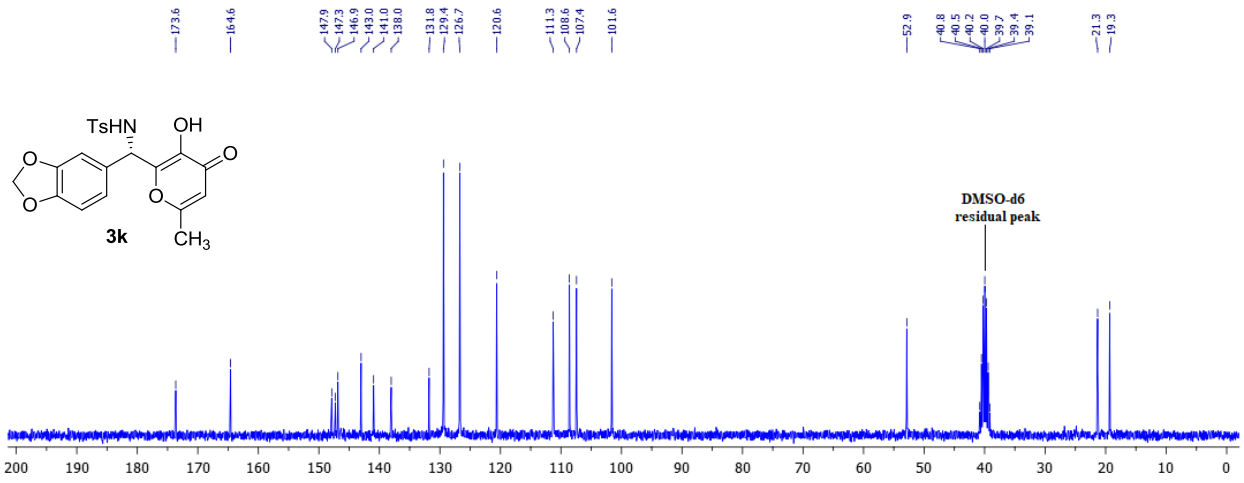

9.06
7.57
7.54
7.35
7.31
7.20
7.13
5.95
5.74
3.37
2.51
2.28
2.08
TsHN
OH
O
F
O
CH3
3i
DMSO-d5
HOD
1.61
2.00
2.05
4.11
1.00
1.08
3.08
3.05
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

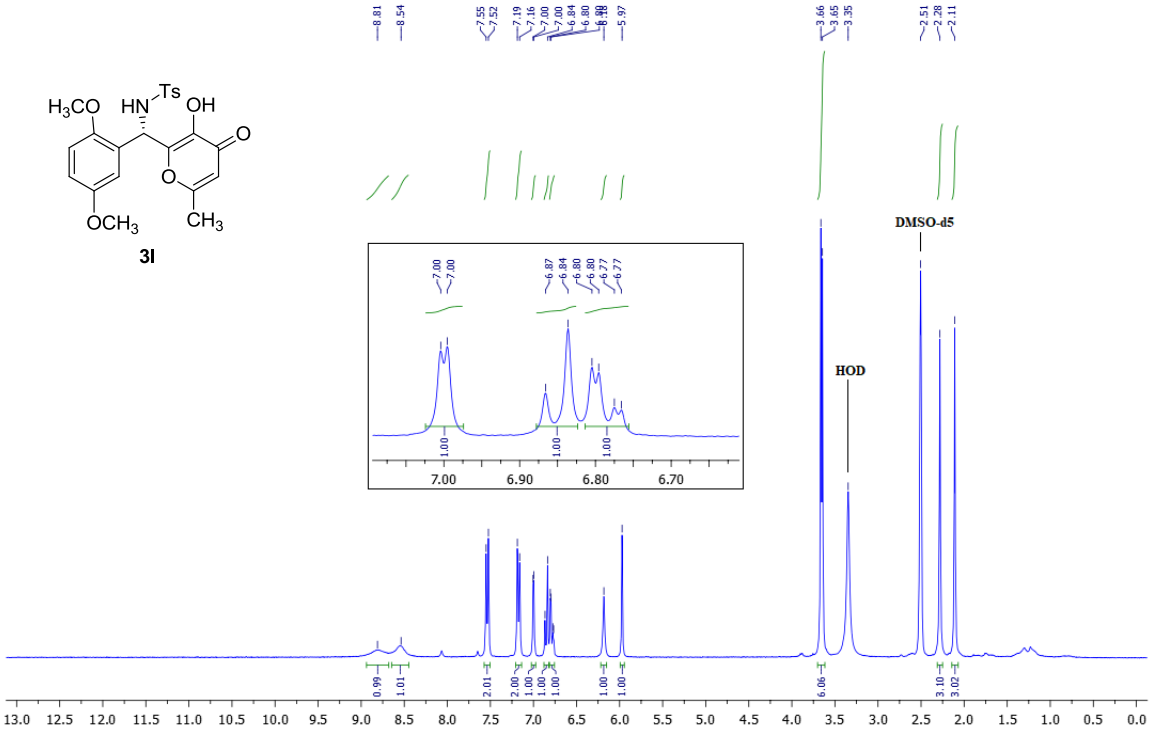

173.8
164.6
163.7
160.4
146.5
143.0
141.5
138.1
134.4
129.5
129.3
129.1
126.7
116.0
115.7
111.3
52.6
40.8
40.5
40.3
40.0
39.7
39.4
39.1
21.3
19.3
TsHN
OH
O
F
O
CH3
3i
DMSO-d6
residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

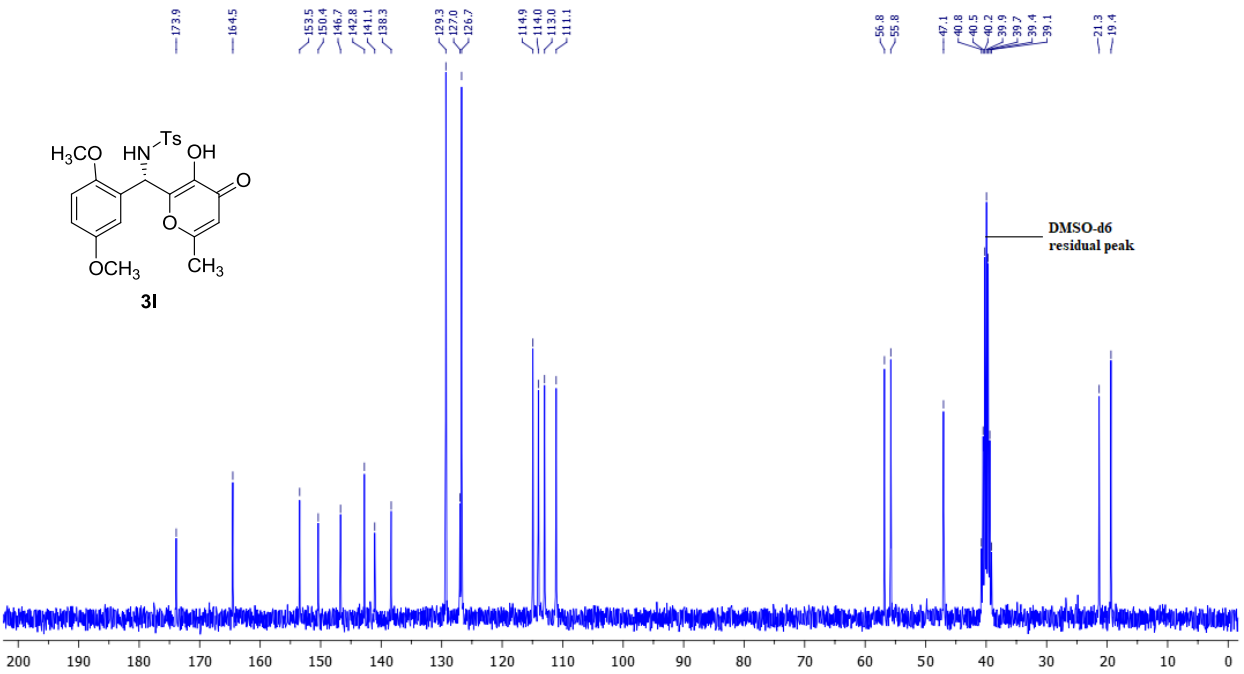

TsHN
OH
O
H3CO
H3CO
O
CH3
3j
9.05
8.74
7.57
7.54
7.20
7.17
6.92
6.87
6.84
6.76
6.74
5.95
5.68
3.70
2.51
2.28
2.10
DMSO-d5
HOD
0.98
1.01
2.00
2.00
1.00
1.00
1.00
1.00
1.00
6.00
3.02
3.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

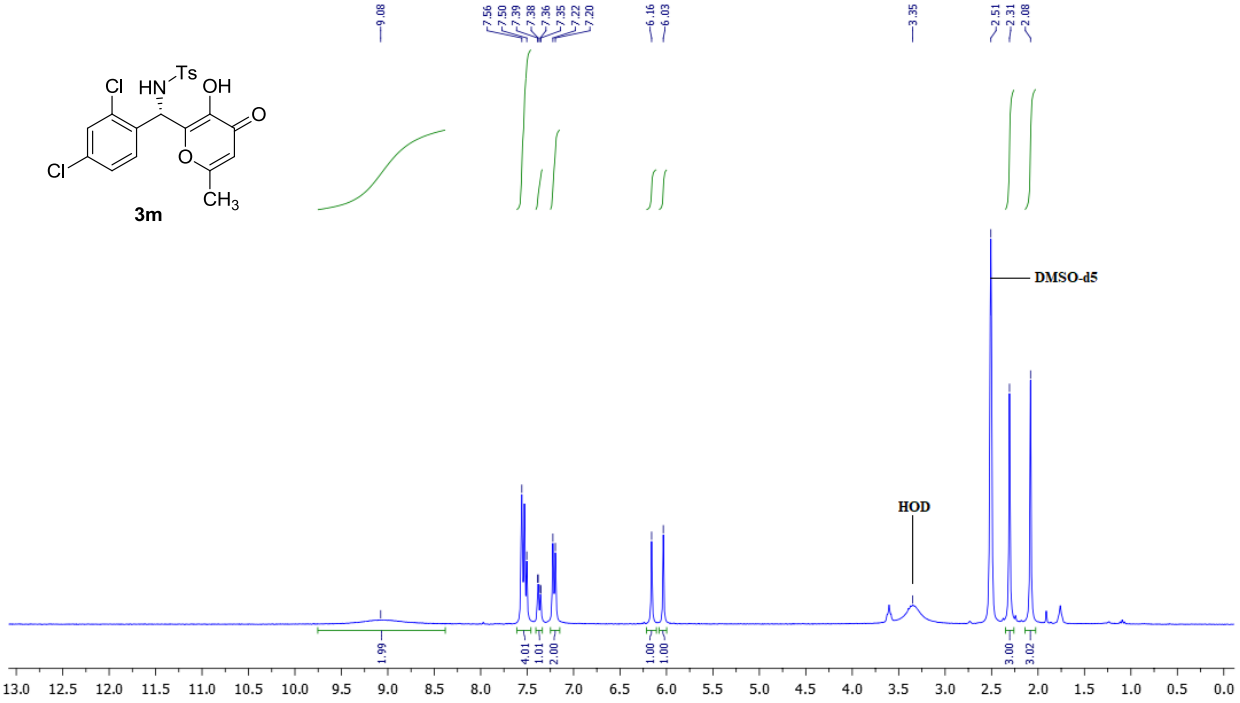

TsHN
OH
O
H3CO
H3CO
O
CH3
3j
173.7
164.5
149.1
148.9
147.1
143.0
140.9
138.1
130.3
129.4
126.7
119.4
112.1
111.2
110.9
56.0
55.9
52.8
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.3
19.3
DMSO-d6
residual peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

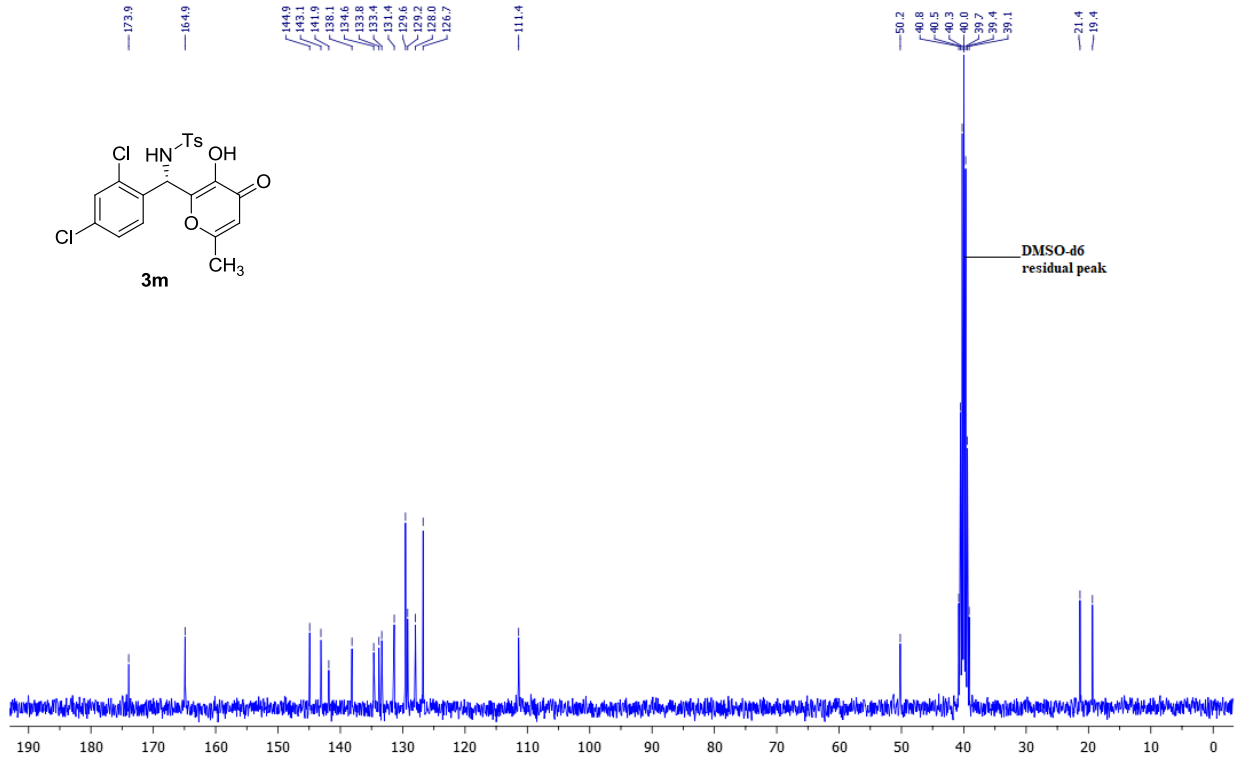

RA-260.01.{1H}
TsHN
OH
O
O
O
O
CH3
3k
9.10
8.74
7.55
7.53
7.20
7.17
6.84
6.82
6.74
6.71
5.98
5.95
5.66
3.34
2.51
2.28
2.09
DMSO-d5
HOD
0.96
1.11
2.00
1.98
1.98
1.00
1.89
1.00
1.05
3.15
3.03
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

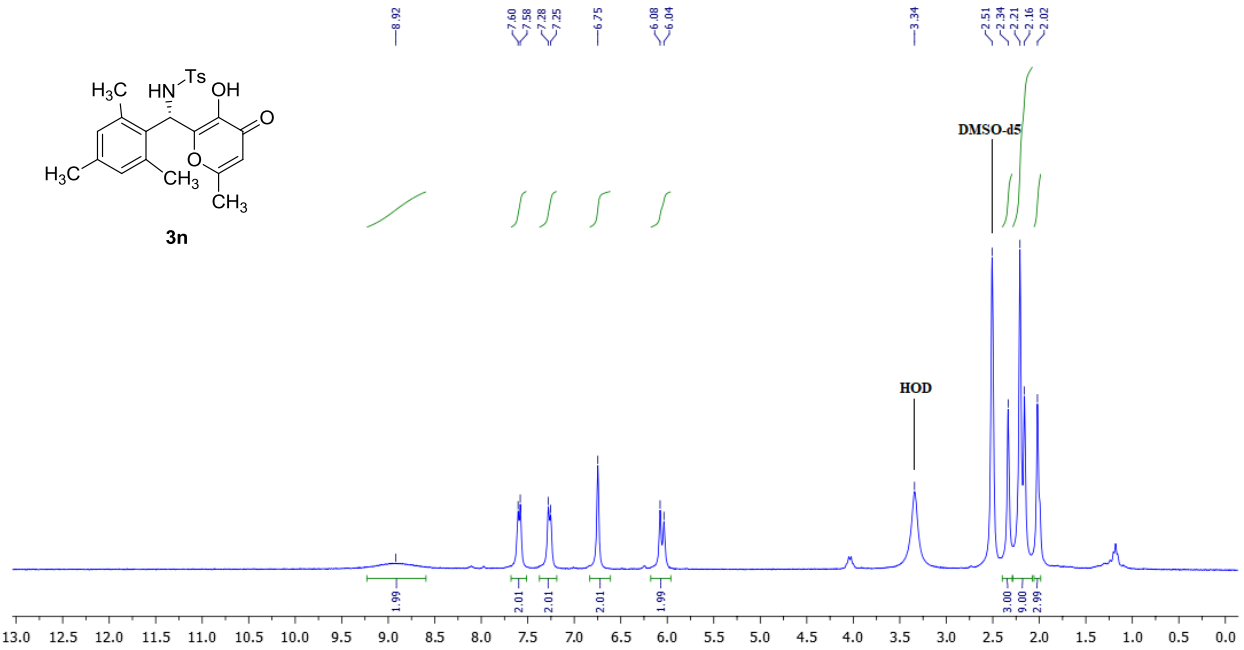

173.6
164.6
147.9
147.3
146.9
143.0
141.0
138.0
131.8
129.4
126.7
120.6
111.3
108.6
107.4
101.6
52.9
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.3
19.3
TsHN
OH
O
O
O
O
CH3
3k
DMSO-d6
residual peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


3l
DMSO-d5
HOD


3l
DMSO-d6
residual peak


Cl
HN
Ts
OH
O
Cl
O
CH3
3m
9.08
7.56
7.50
7.39
7.38
7.36
7.35
7.22
7.20
6.16
6.03
3.35
2.51
2.31
2.08
DMSO-d5
HOD
1.99
4.01
1.01
2.00
1.00
1.00
3.00
3.02
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


173.9
164.9
144.9
143.1
141.9
138.1
134.6
133.8
133.4
131.4
129.6
129.2
128.0
126.7
111.4
50.2
40.8
40.5
40.3
40.0
39.7
39.4
39.1
21.4
19.4
Cl
HN
Ts
OH
O
Cl
O
CH3
3m
DMSO-d6
residual peak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6.08
6.04
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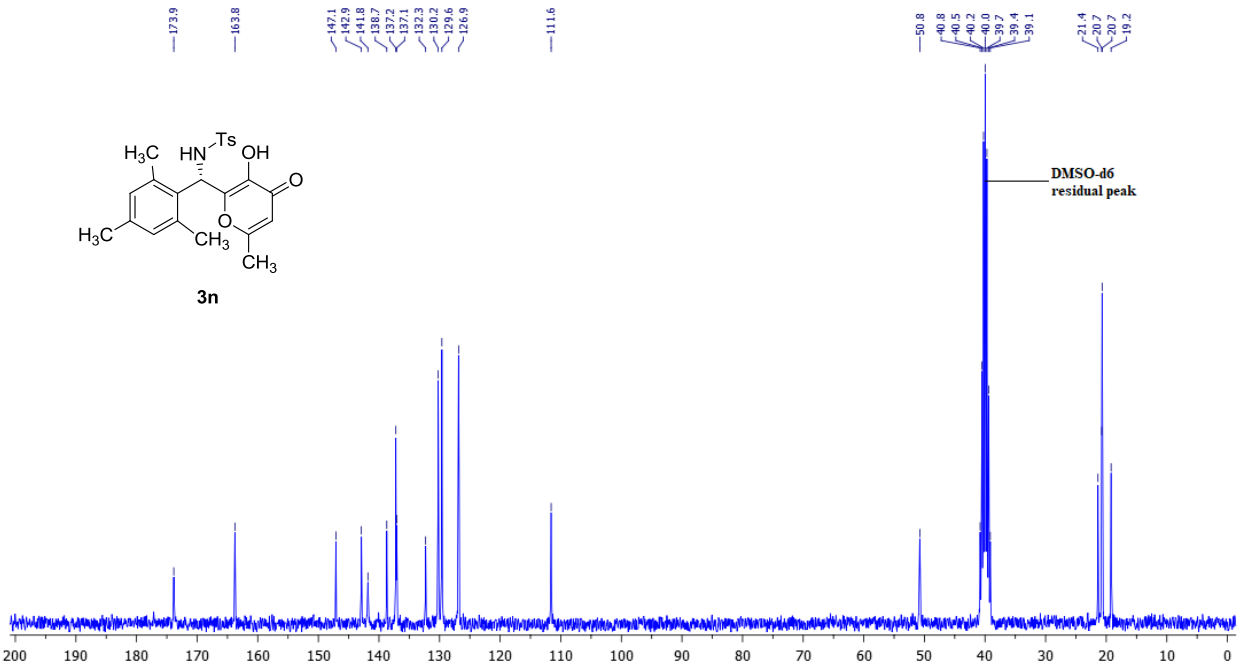
2.51
2.34
2.21
2.16
2.02
DMSO-d5
HOD
1.99
2.01
2.01
2.01
1.99
3.00
9.00
2.99
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

H3C
HN
Ts
OH
O
H3C
CH3
O
CH3

3n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163.8
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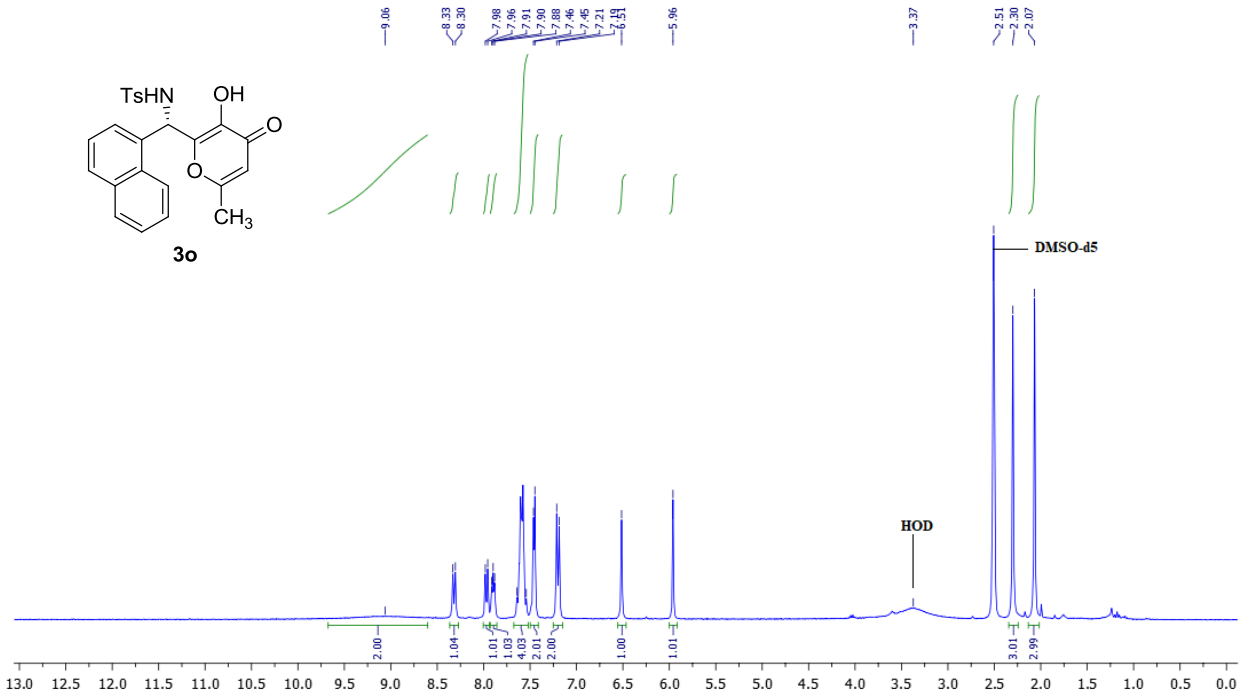
137.1
132.3
130.2
129.6
126.9
111.6
50.8
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.4
20.7
20.7
19.2
DMSO-d6
residual peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

H3C
HN
Ts
OH
O
H3C
CH3
O
CH3

3n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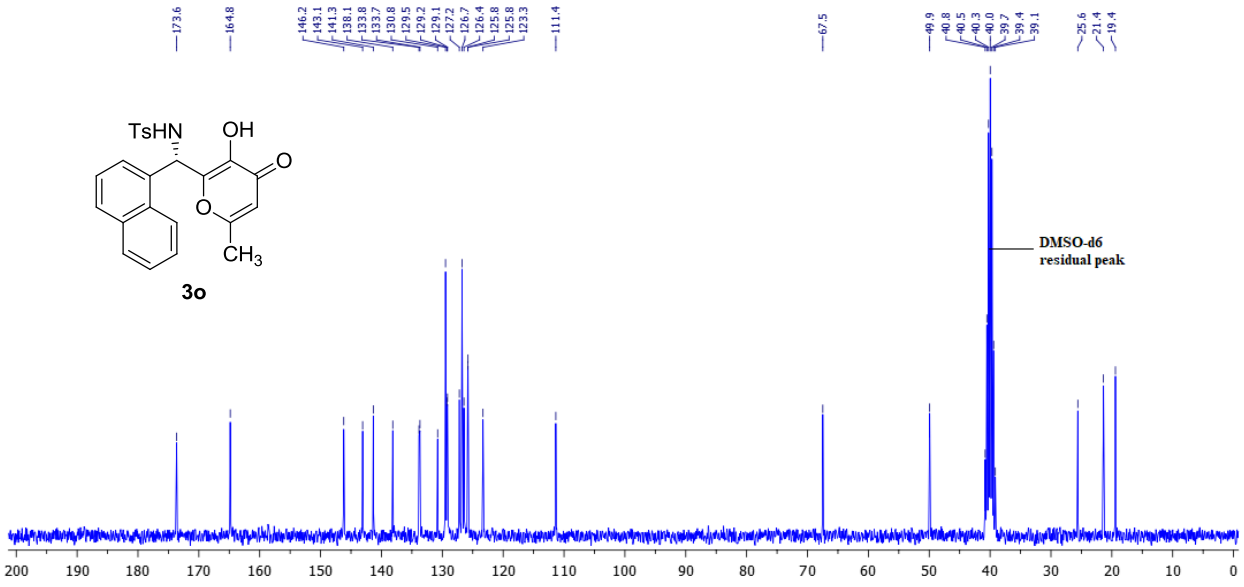
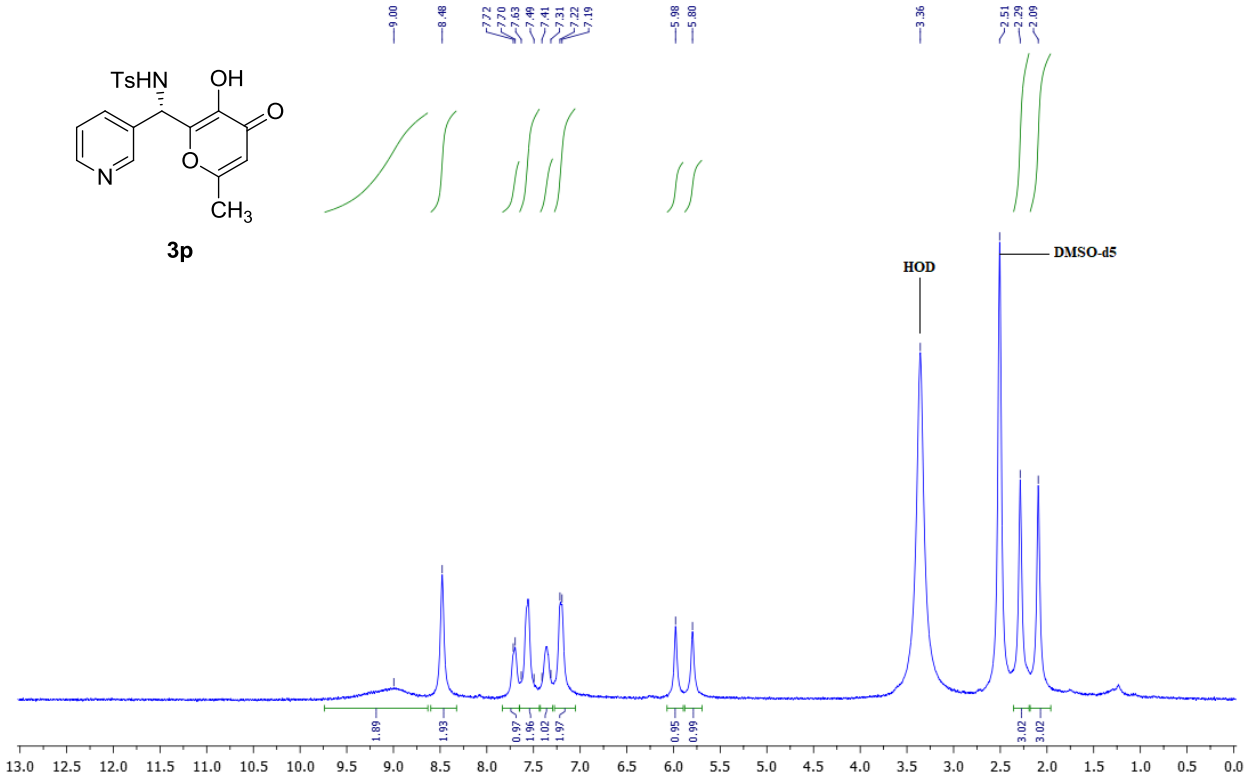
O
CH3
3o
DMSO-d5
HOD


TsHN
OH
O
O
CH3
3o
DMSO-d6
residual peak


TsHN
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O
N
O
CH3
3p
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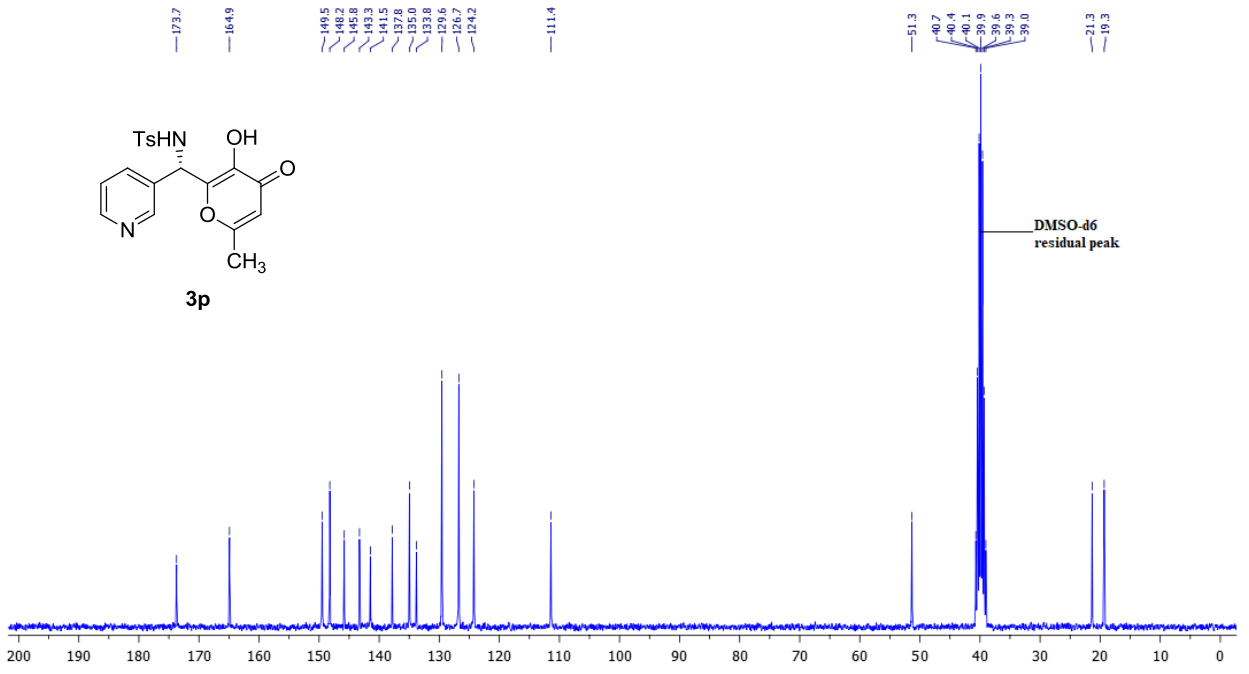
7.49
7.41
7.31
7.22
7.19
5.98
5.80
3.36
2.51
2.29
2.09
HOD
DMSO-d5
1.89
1.93
0.97
1.96
1.02
1.97
0.95
0.99
3.02
3.02
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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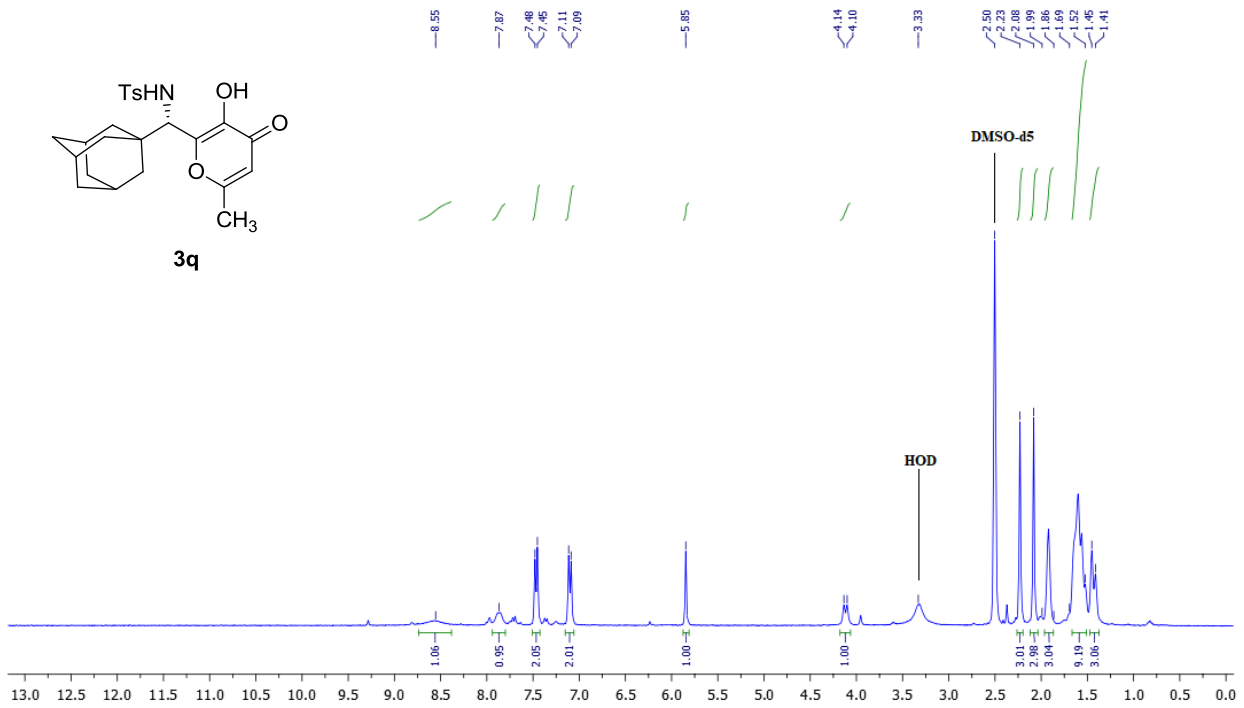
129.6
126.7
124.2
111.4
51.3
40.7
40.4
40.1
39.9
39.6
39.3
39.0
21.3
19.3
TsHN
OH
O
N
O
CH3
3p
DMSO-d6
residual peak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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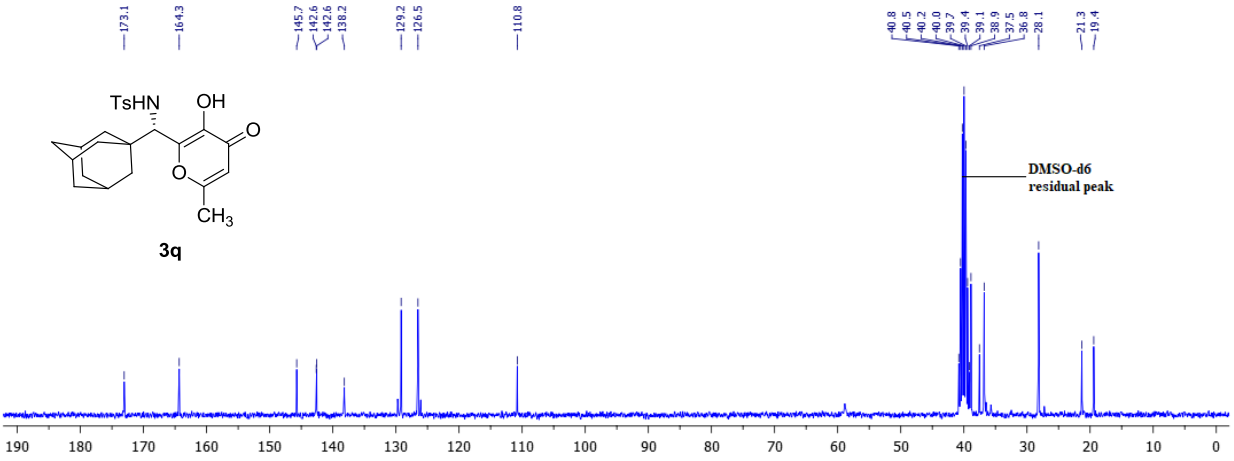
OH
O
O
CH3
3q
DMSO-d5
HOD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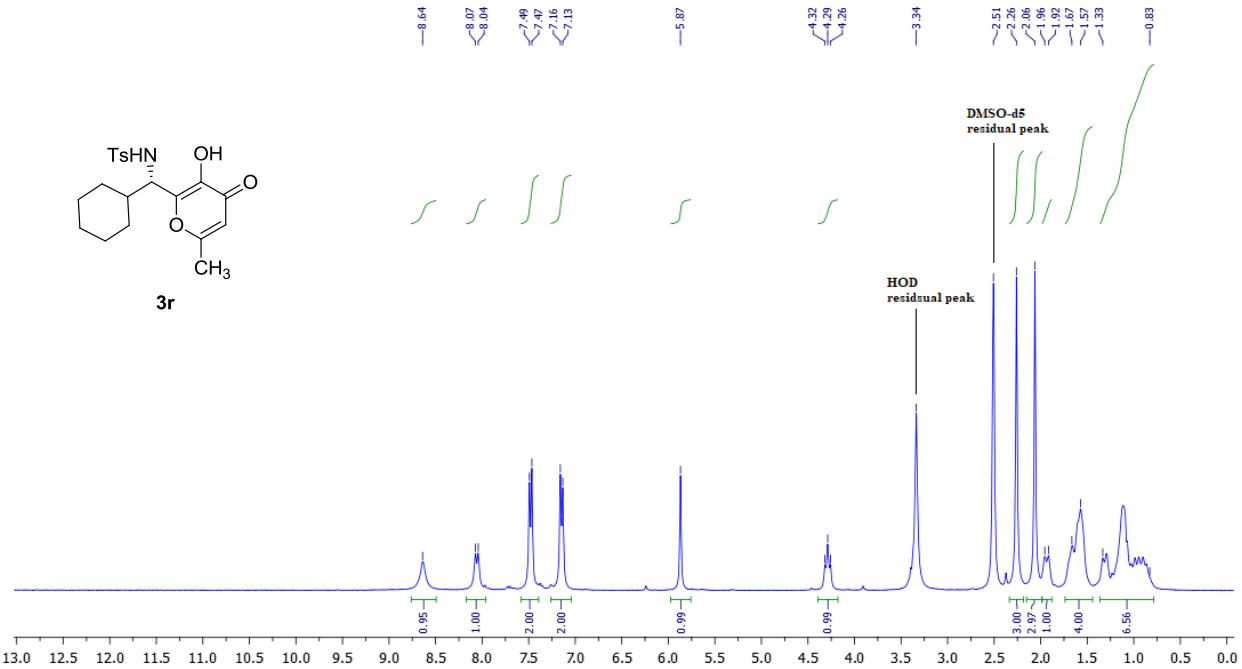
OH
O
O
CH3
3q
DMSO-d6
residual peak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OH
O
O
CH3
3r
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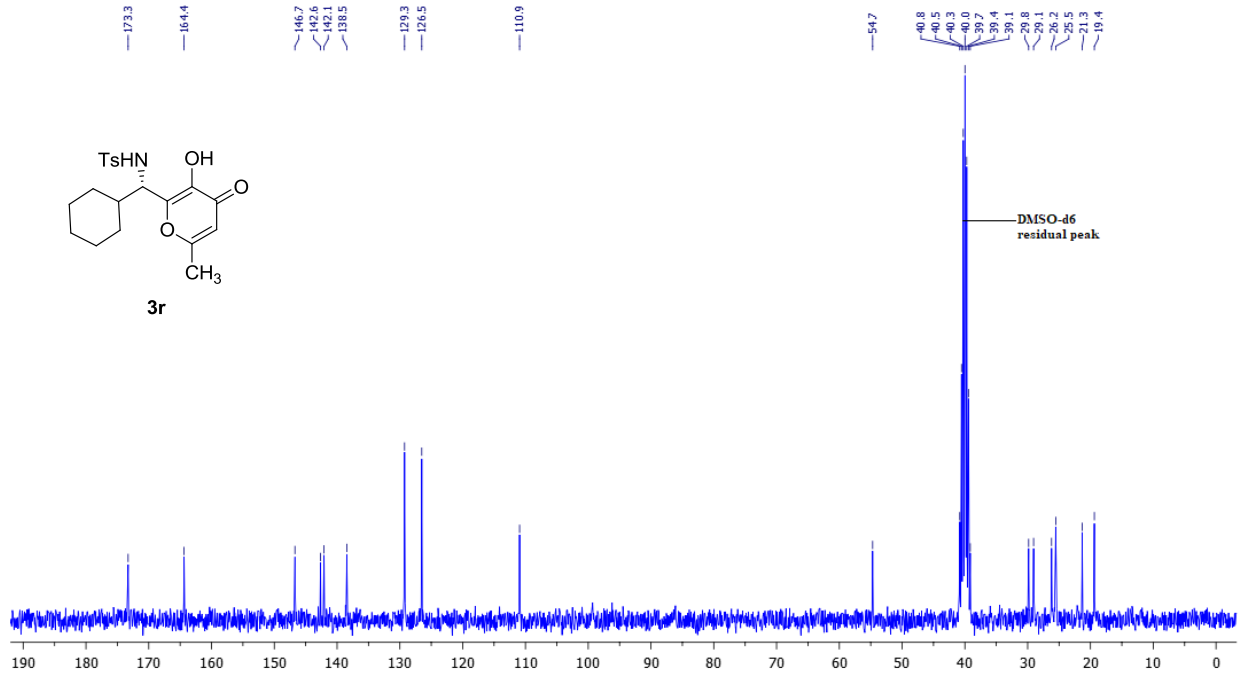
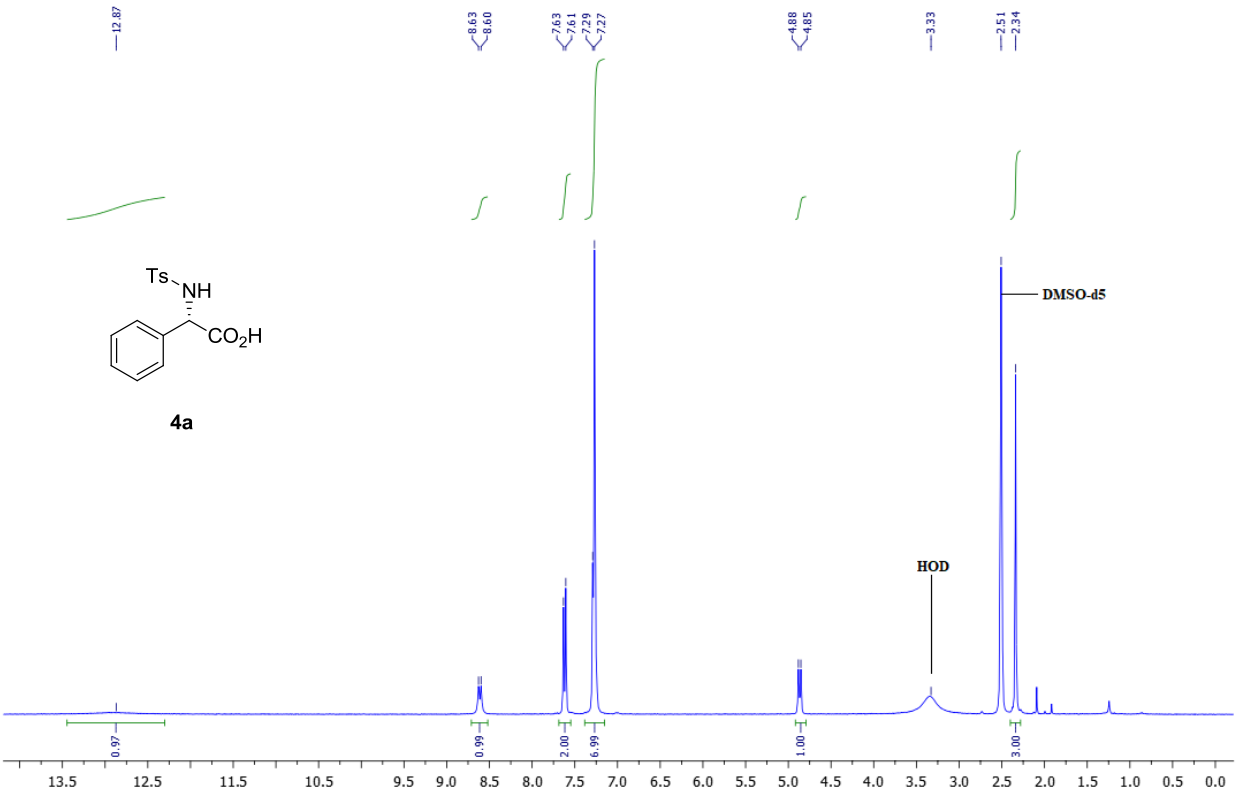
8.07
8.04
7.49
7.47
7.16
7.13
5.87
4.32
4.29
4.26
3.34
2.51
2.26
2.06
1.96
1.92
1.67
1.57
1.33
0.83
DMSO-d5
residual peak
HOD
residsual peak
0.95
1.00
2.00
2.00
0.99
0.99
3.00
2.97
1.00
4.00
6.56
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


TsHN
OH
O
O
CH3
3r
173.3
164.4
146.7
142.6
142.1
138.5
129.3
126.5
110.9
54.7
40.8
40.5
40.3
40.0
39.7
39.4
39.1
29.8
29.1
26.2
25.5
21.3
19.4
DMSO-d6
residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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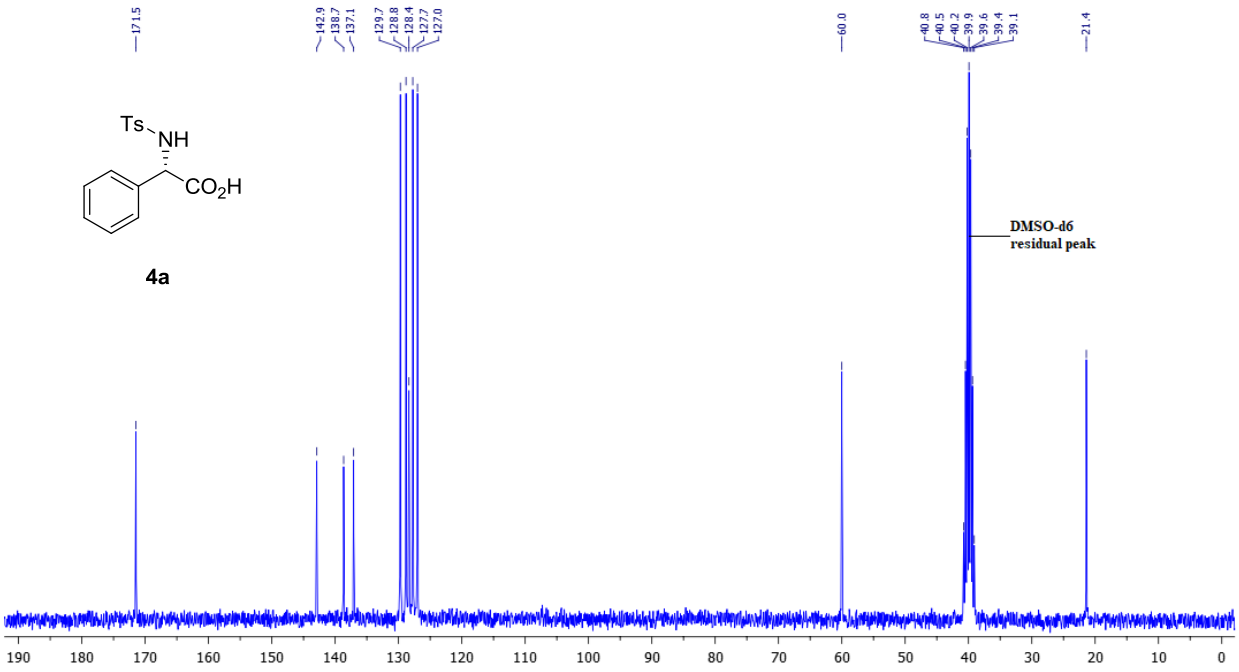
7.29
7.27
4.88
4.85
3.33
2.51
2.34
Ts
NH
CO2H
4a
DMSO-d5
HOD
0.97
0.99
2.00
6.99
1.00
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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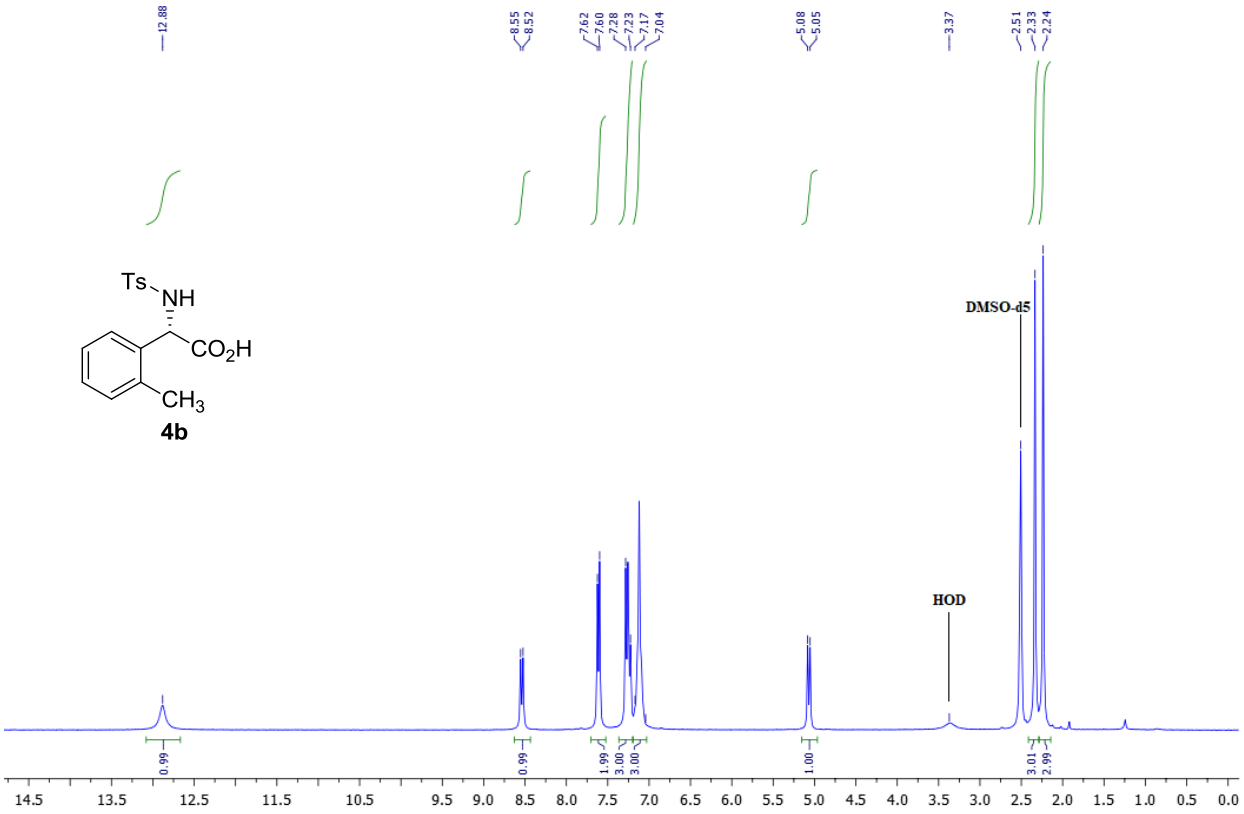
138.7
137.1
129.7
128.8
128.4
127.7
127.0
60.0
40.8
40.5
40.2
39.9
39.6
39.4
39.1
21.4
Ts
NH
CO2H
4a
DMSO-d6
residual peak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.55
8.52
7.62
7.60
7.28
7.23
7.17
7.04
5.08
5.05
3.37
2.51
2.33
2.24
Ts
NH
CO2H
CH3
4b
DMSO-d5
HOD
0.99
0.99
1.99
3.00
3.00
1.00
3.01
2.99
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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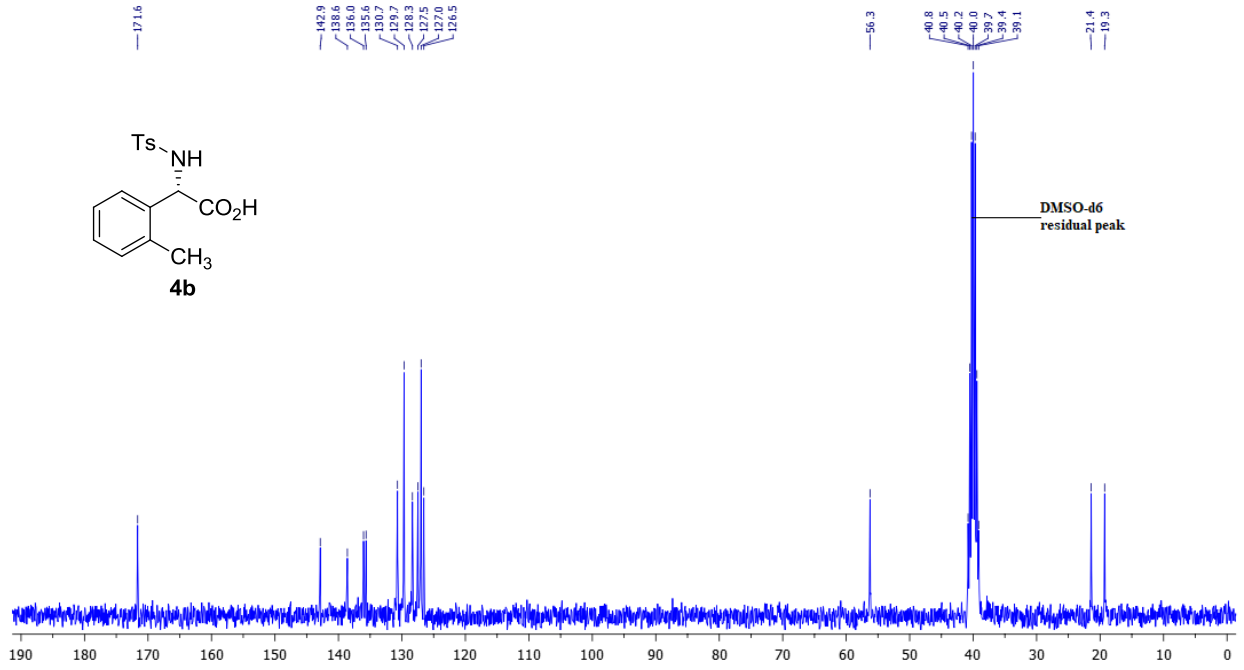
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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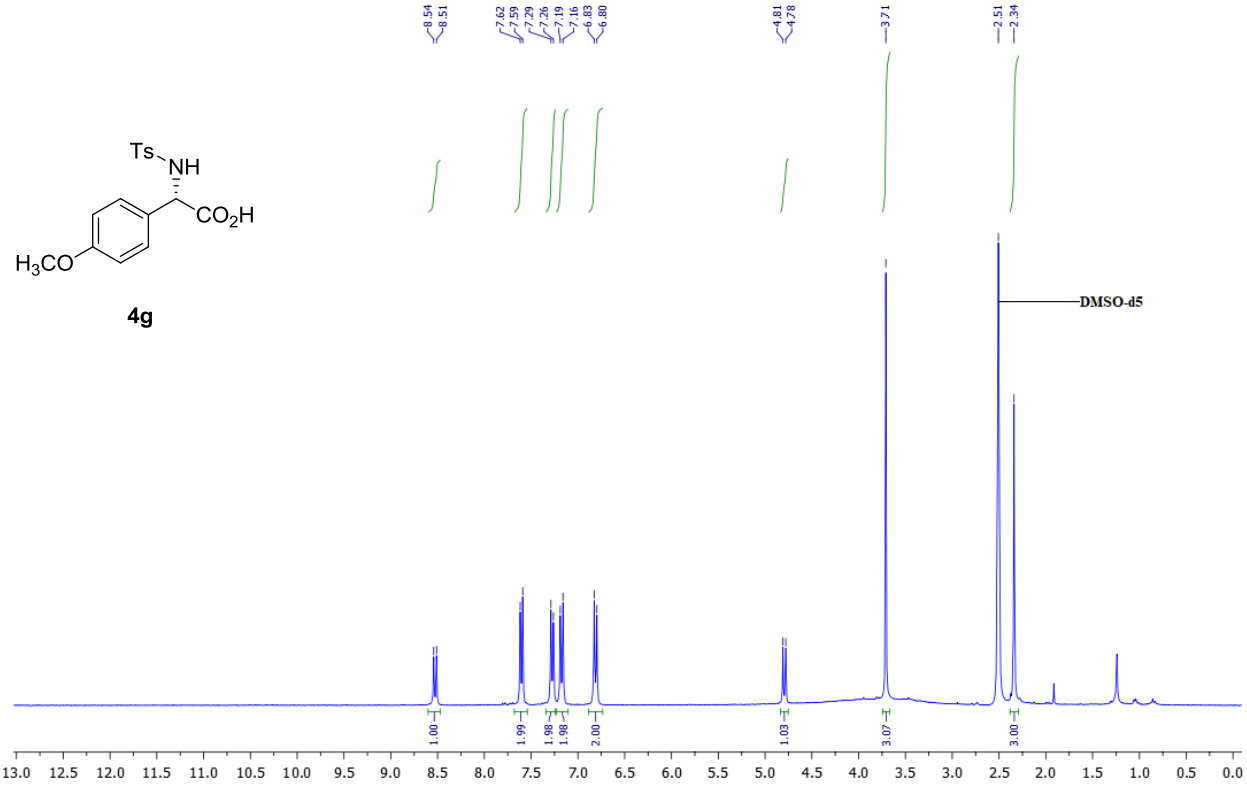
138.6
136.0
135.6
130.7
129.7
128.3
127.5
127.0
126.5
56.3
40.8
40.5
40.2
40.0
39.7
39.4
39.1
21.4
19.3
Ts
NH
CO2H
CH3
4b
DMSO-d6
residual peak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ts
NH
CO2H
H3CO
4g
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8.51
7.62
7.59
7.29
7.26
7.19
7.16
6.83
6.80
4.81
4.78
3.71
2.51
2.34
DMSO-d5
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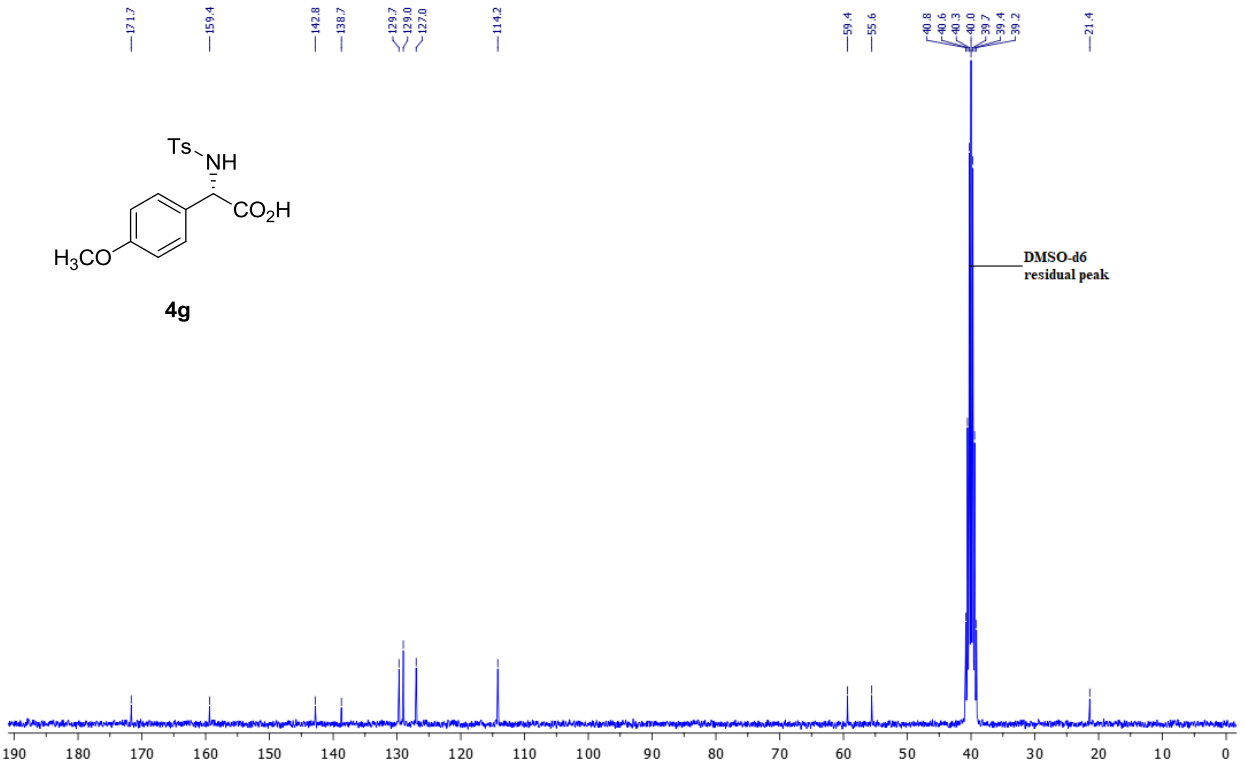
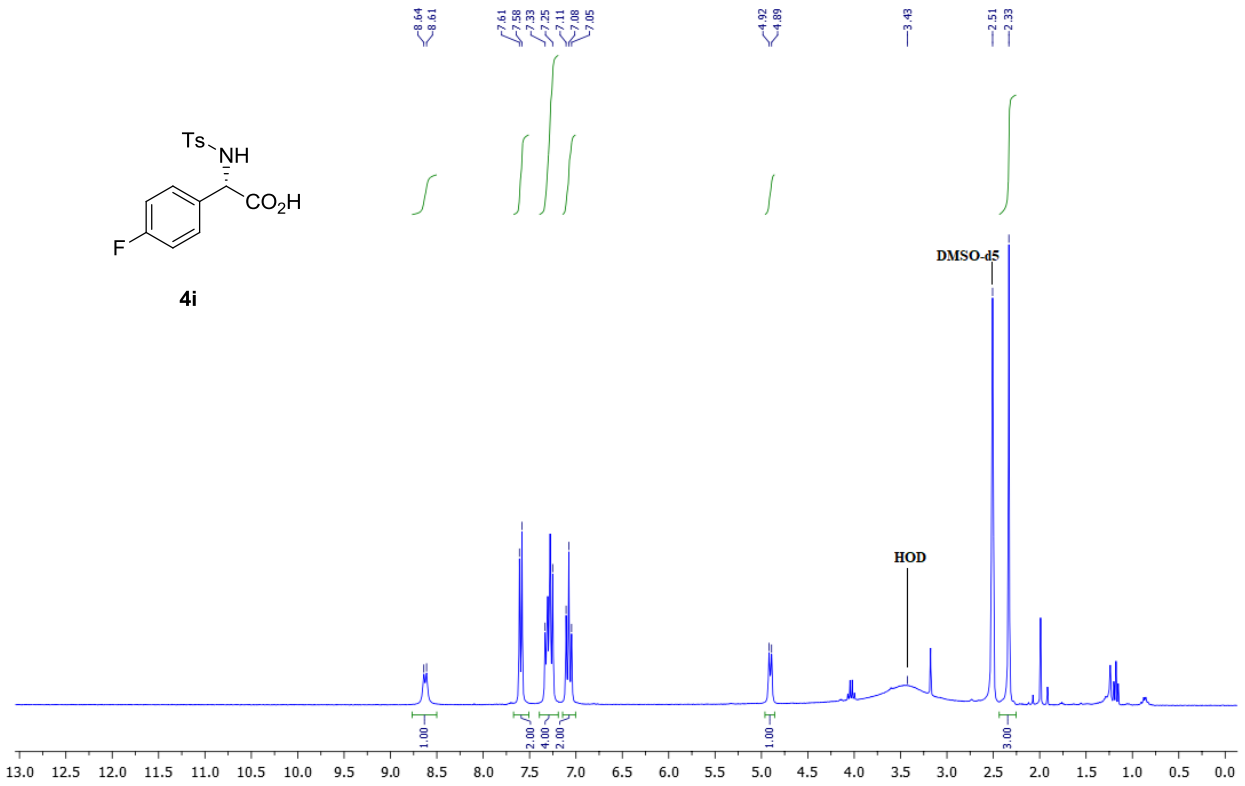
1.99
1.98
1.98
2.00
1.03
3.07
3.00


Ts
NH
CO2H
H3CO
4g
171.7
159.4
142.8
138.7
129.7
129.0
127.0
114.2
59.4
55.6
40.8
40.6
40.3
40.0
39.7
39.4
39.2
21.4
DMSO-d6
residual peak


Ts
NH
CO2H
F
4i
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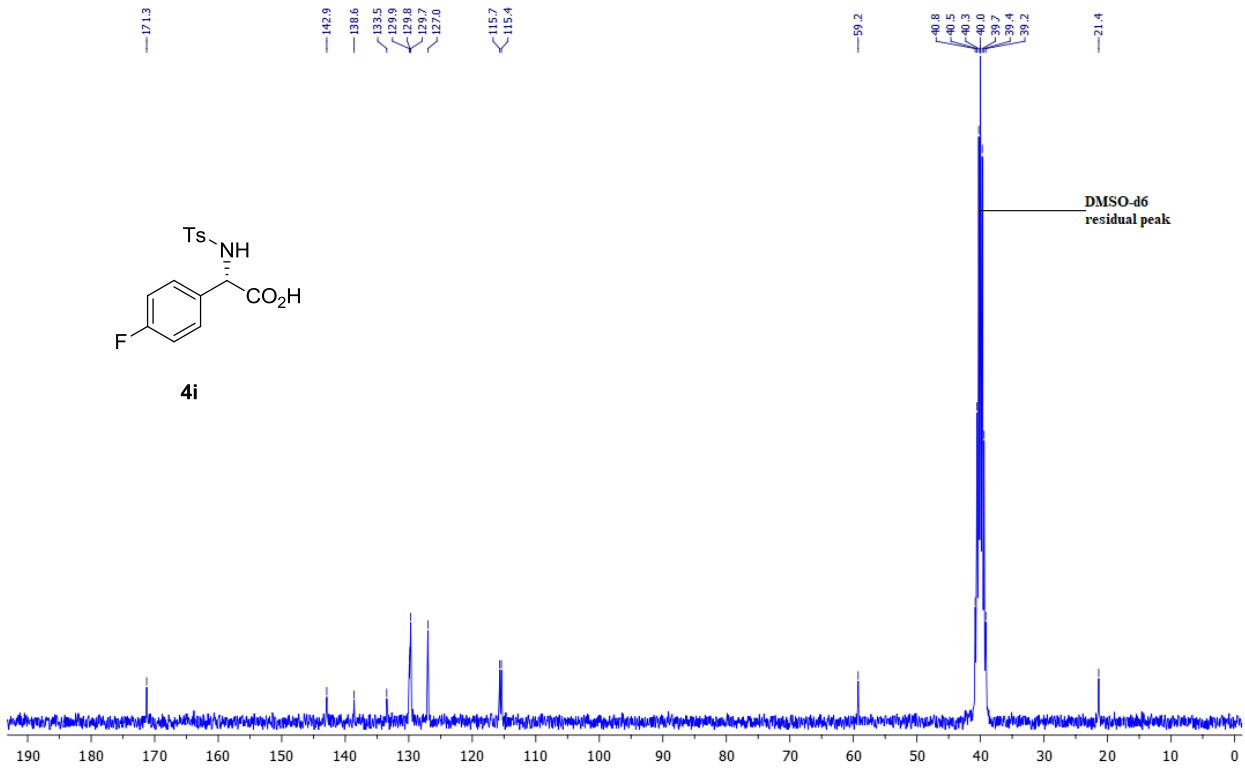
8.61
7.61
7.58
7.33
7.25
7.11
7.08
7.05
4.92
4.89
3.43
2.51
2.33
DMSO-d5
HOD
1.00
2.00
4.08
2.00
1.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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NH
CO2H
F
4i
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138.6
133.5
129.9
129.8
129.7
127.0
115.7
115.4
59.2
40.8
40.5
40.3
40.0
39.7
39.4
39.2
21.4
DMSO-d6
residual peak
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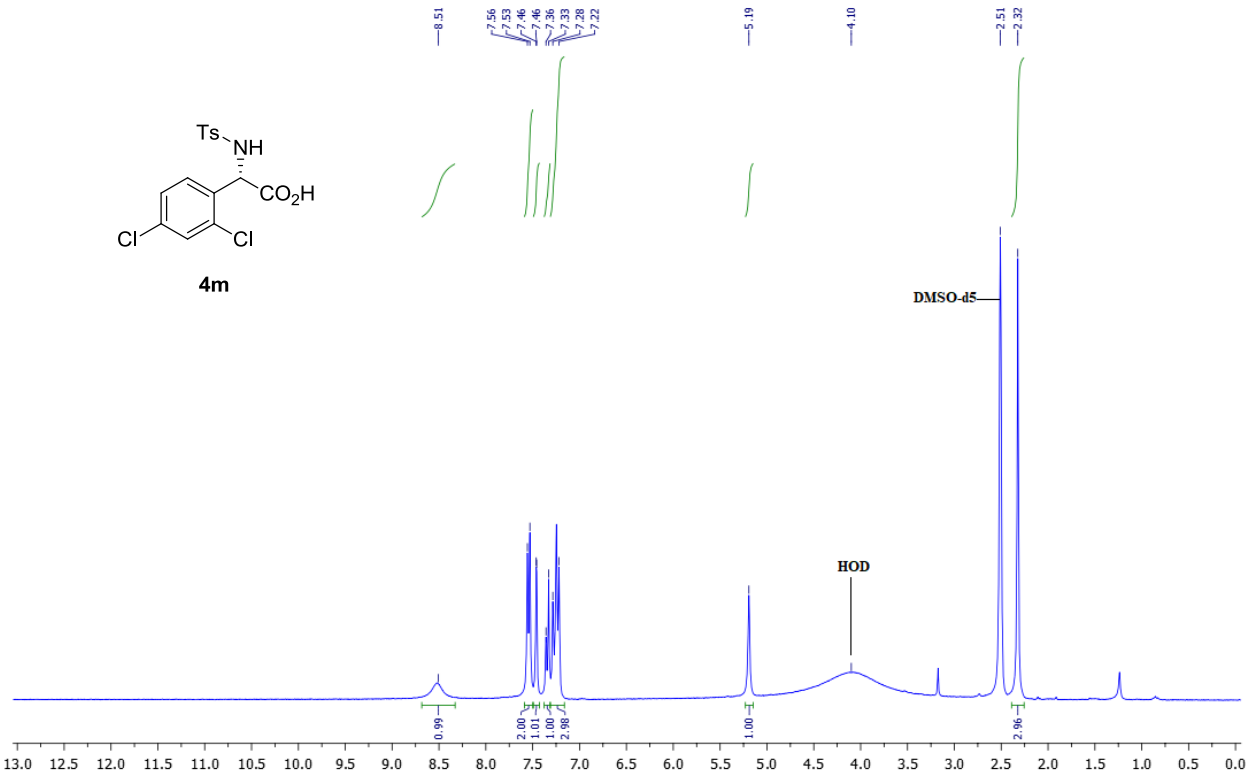
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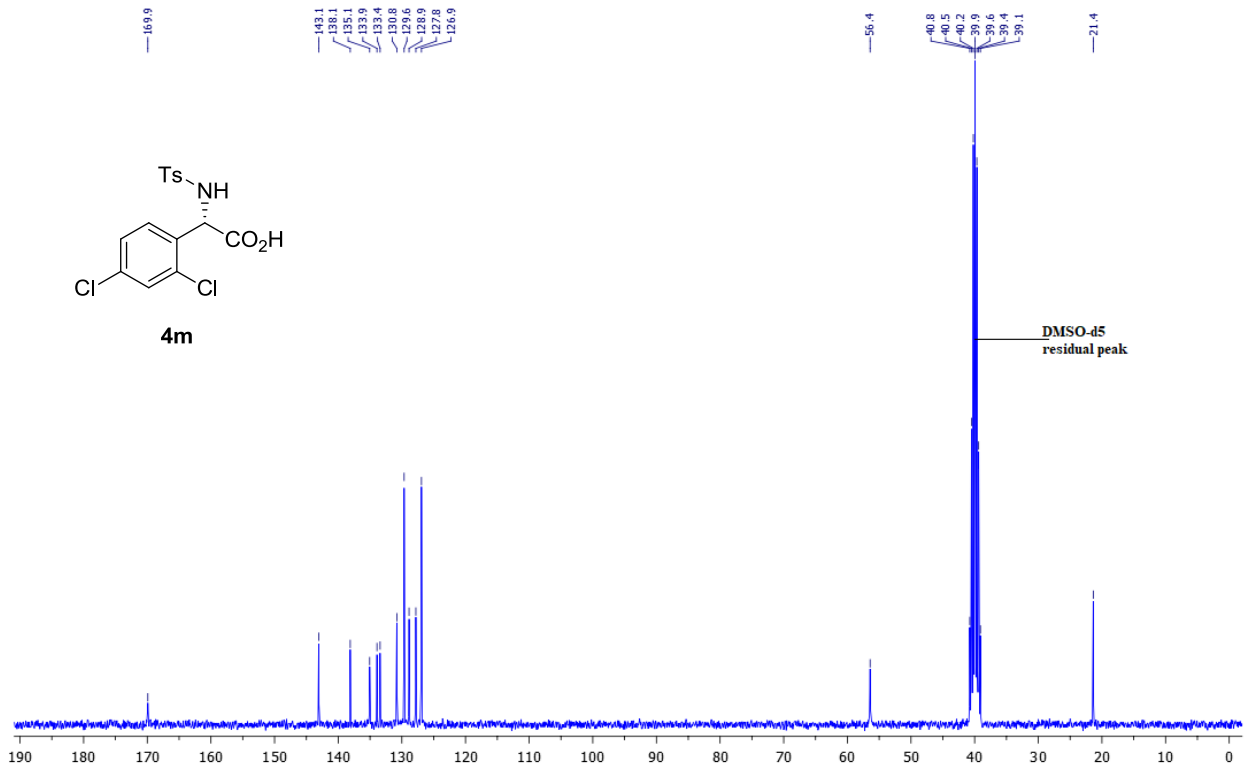
7.46
7.36
7.33
7.28
7.22
5.19
4.10
2.51
2.32
Ts
NH
CO2H
Cl
Cl
4m
DMSO-d5
HOD
0.99
2.00
1.01
1.00
2.98
1.00
2.96
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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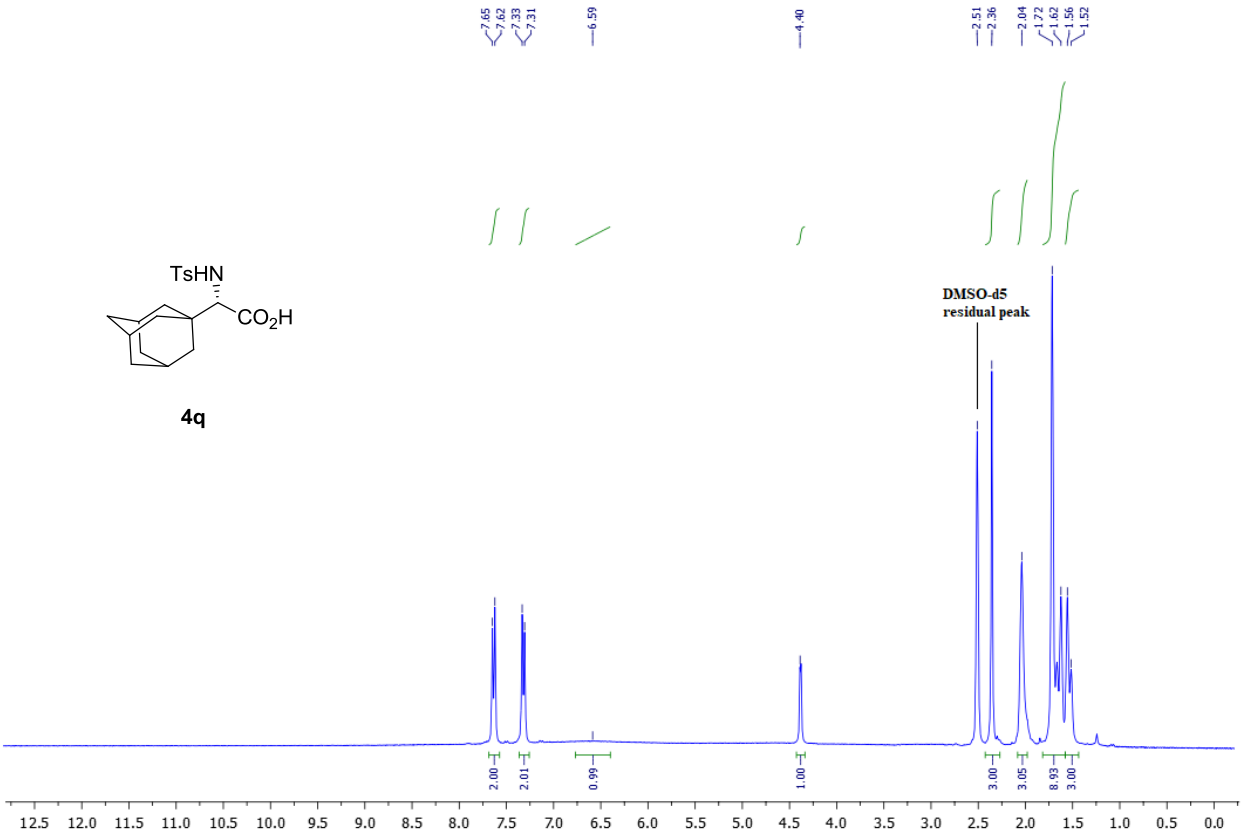
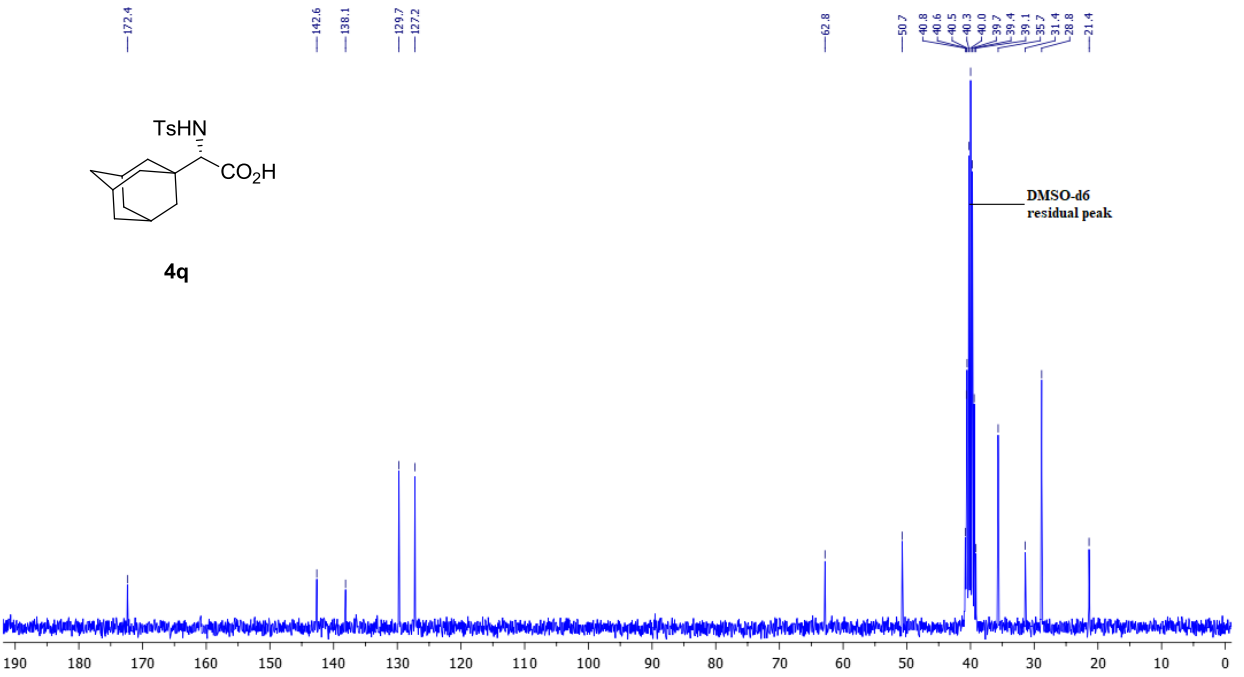
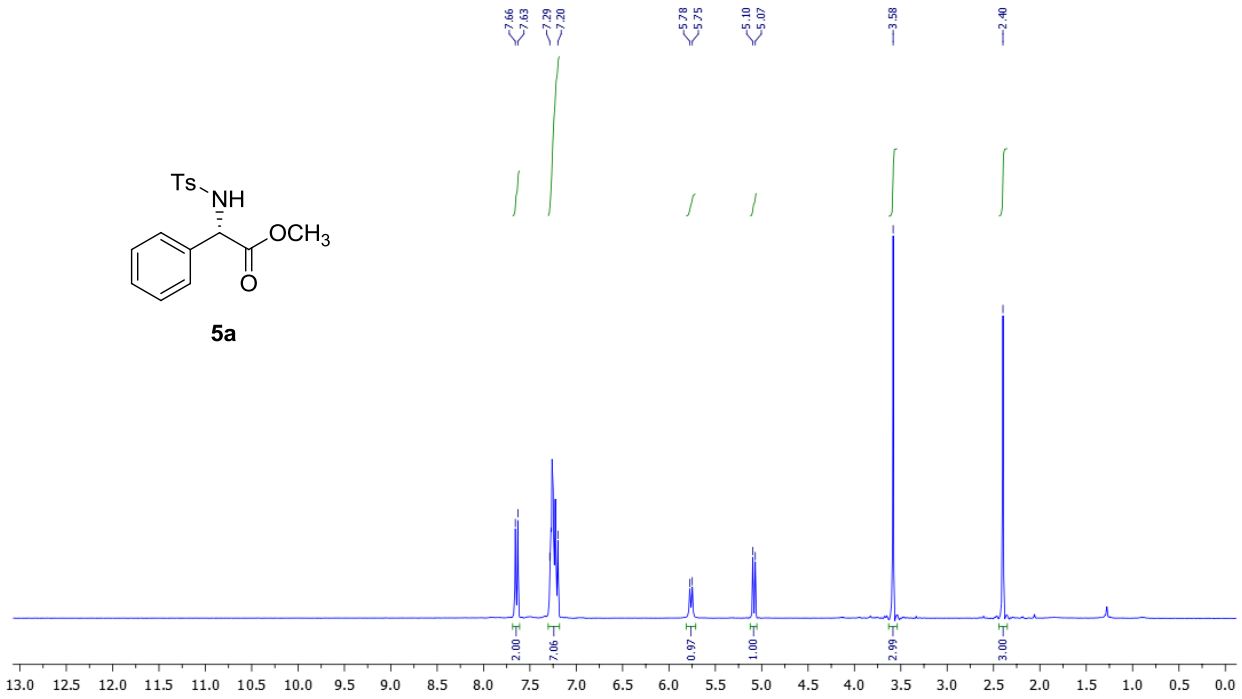
138.1
135.1
133.9
133.4
130.8
129.6
128.9
127.8
126.9
56.4
40.8
40.5
40.2
39.9
39.6
39.4
39.1
21.4
Ts
NH
CO2H
Cl
Cl
4m
DMSO-d5
residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


TsHN
CO2H
4q
DMSO-d5
residual peak


TsHN
CO2H
4q
DMSO-d6
residual peak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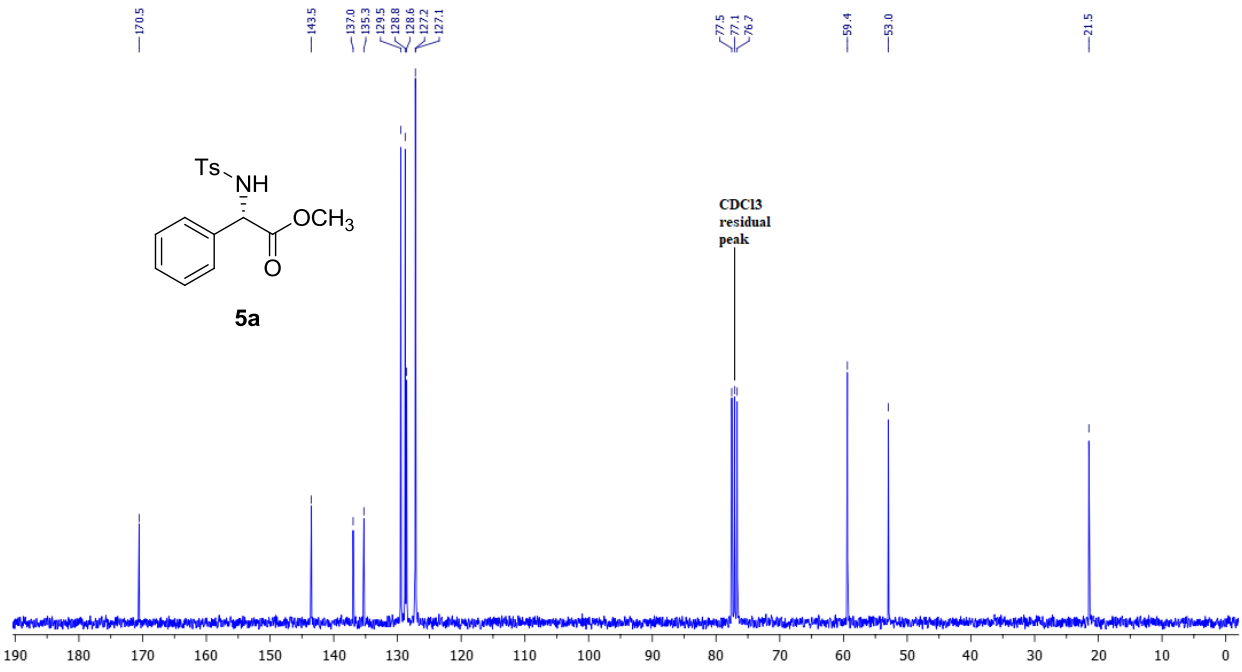
NH
OCH3
O
5a
7.66
7.63
7.29
7.20
5.78
5.75
5.10
5.07
3.58
2.40
2.00
7.06
0.97
1.00
2.99
3.00


Ts
NH
OCH3
O
5a
170.5
143.5
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135.3
129.5
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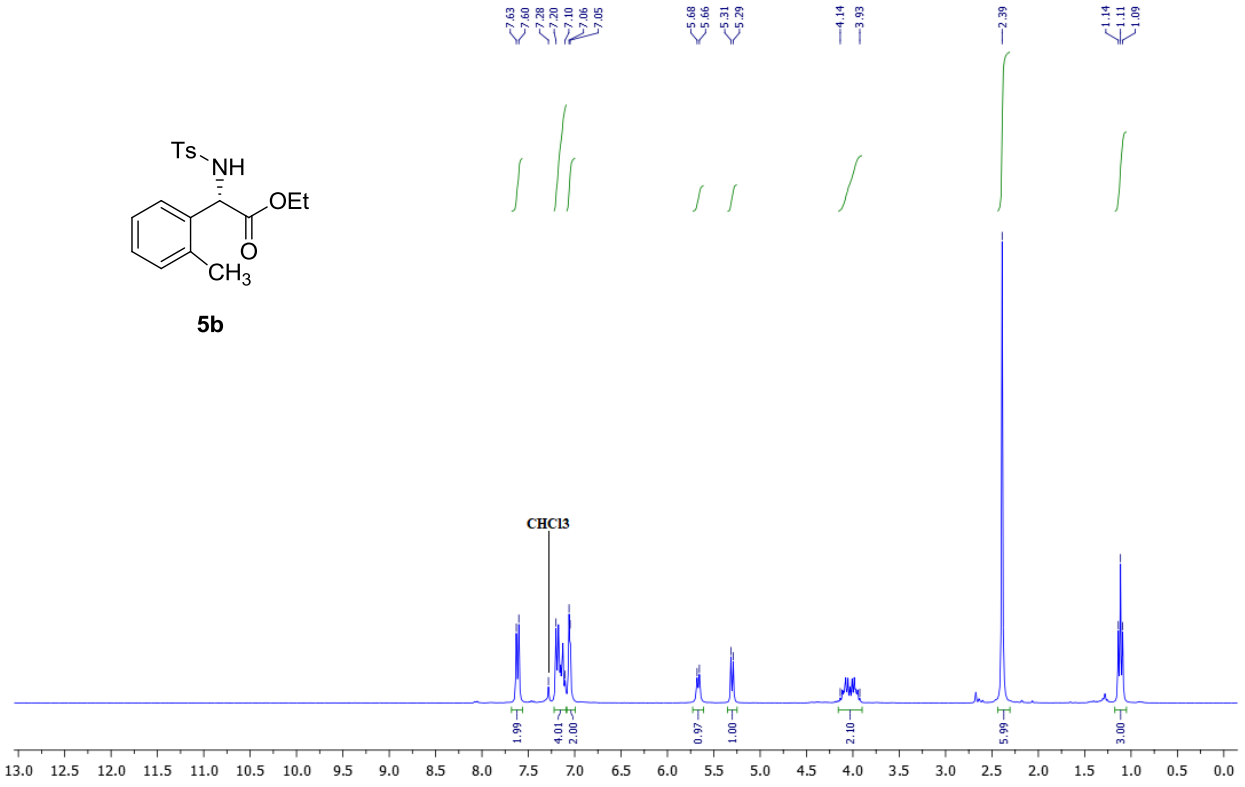
127.2
127.1
77.5
77.1
76.7
CDCl3
residual
peak
59.4
53.0
21.5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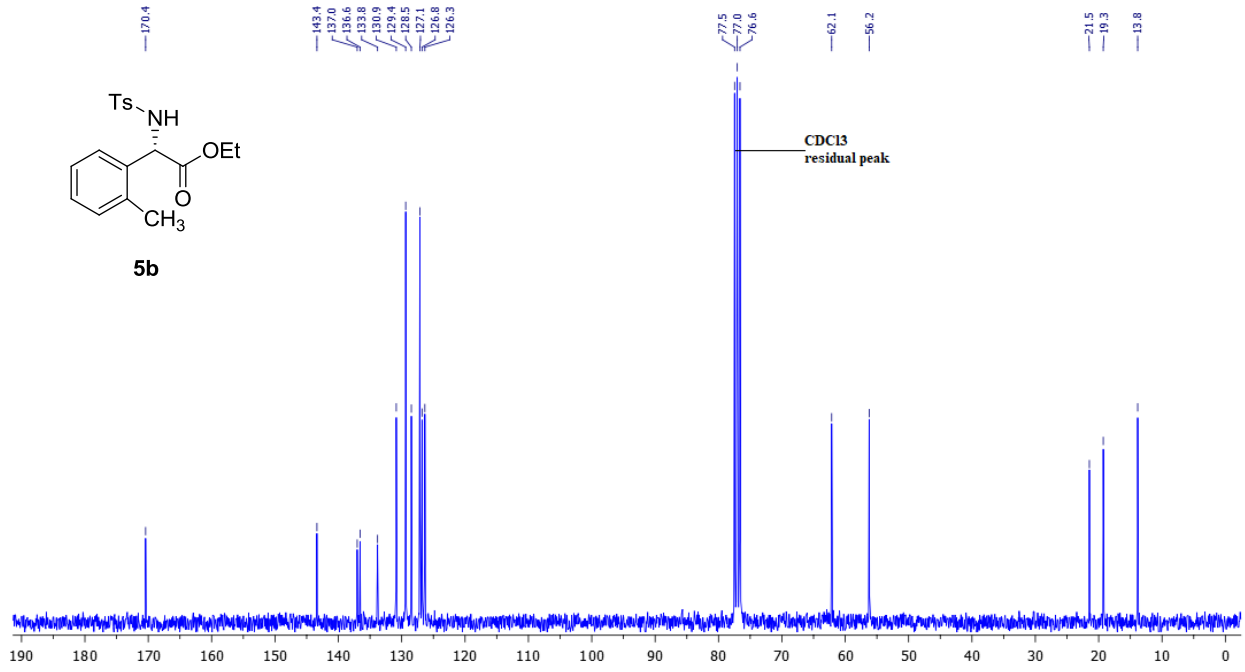
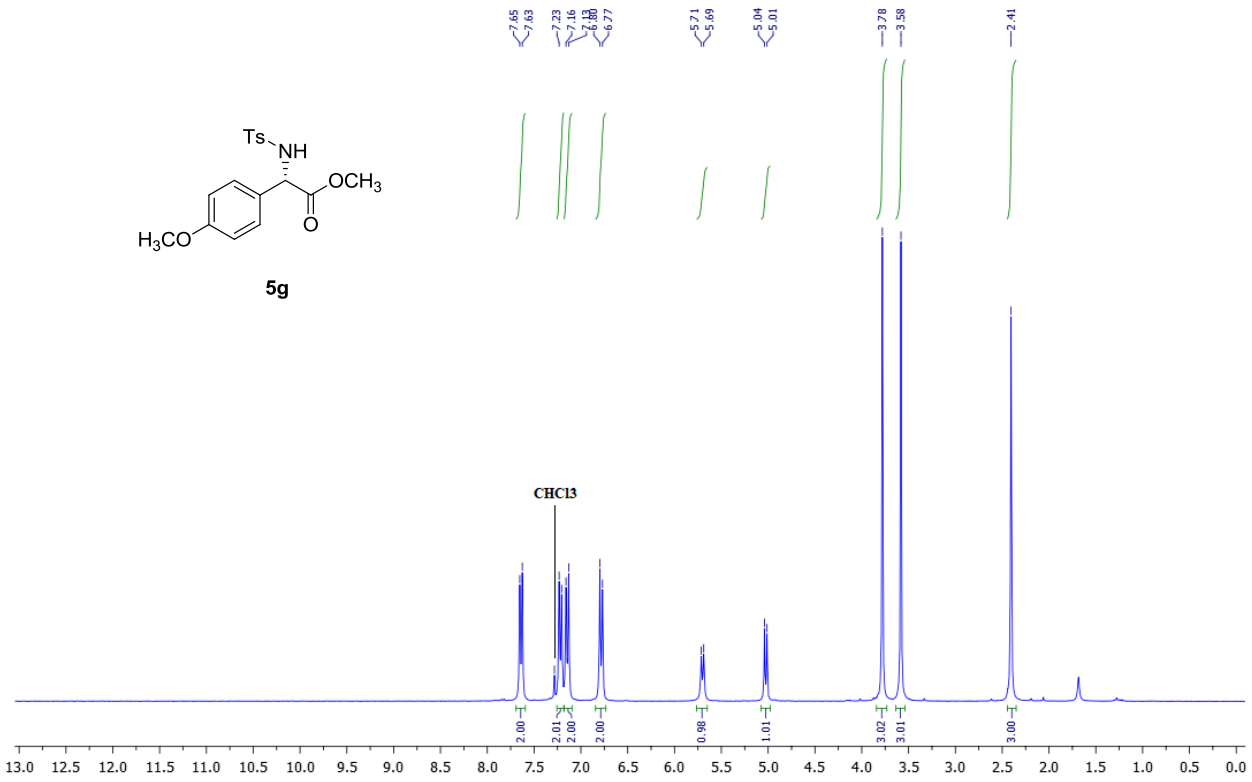
NH
OEt
O
CH3
5b
CHCl3


Ts
NH
OEt
O
CH3
5b
CDCl3
residual peak


Ts
NH
OCH3
O
H3CO
5g
7.65
7.63
7.23
7.16
7.13
6.80
6.77
5.71
5.69
5.04
5.01
3.78
3.58
2.41
CHCl3
2.00
2.01
2.00
2.00
0.98
1.01
3.02
3.01
3.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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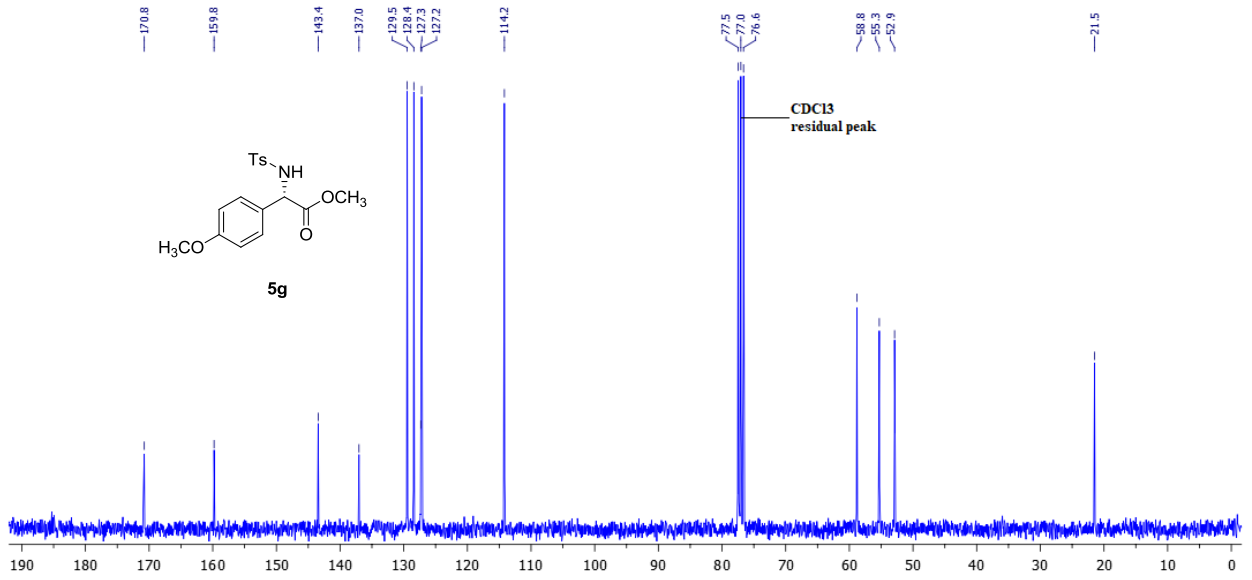
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159.8
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137.0
129.5
128.4
127.3
127.2
114.2
77.5
77.0
76.6
58.8
55.3
52.9
21.5
CDCl3
residual peak
Ts
NH
OCH3
O
H3CO
5g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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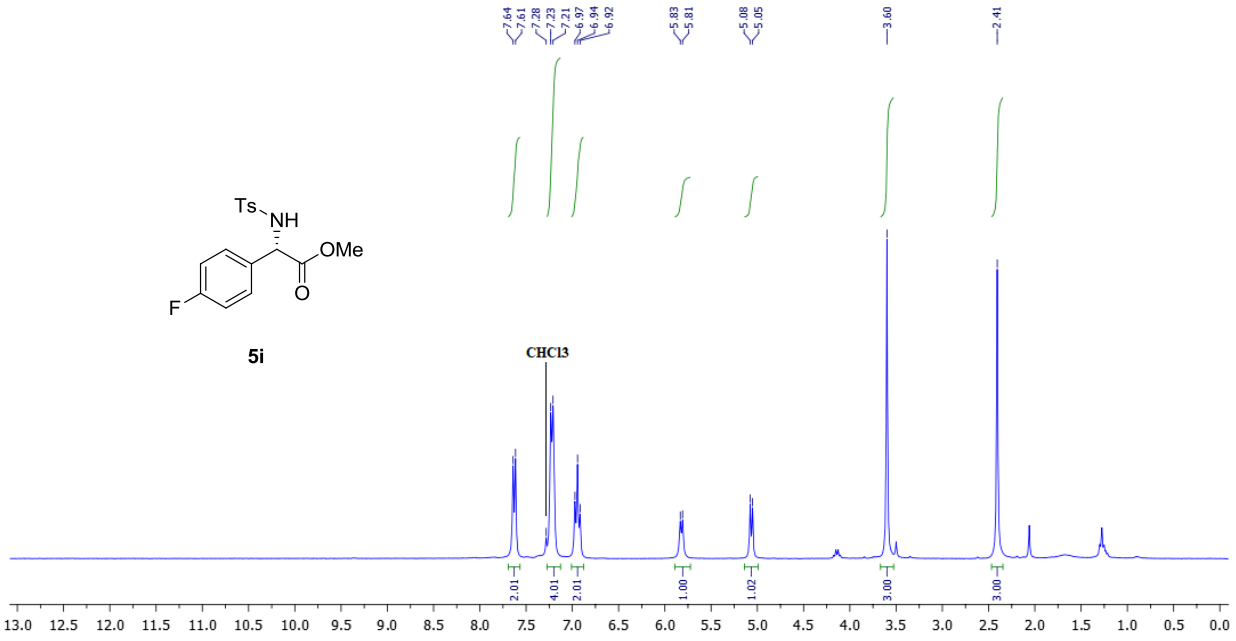
30
20
10
0


7.64
7.61
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7.23
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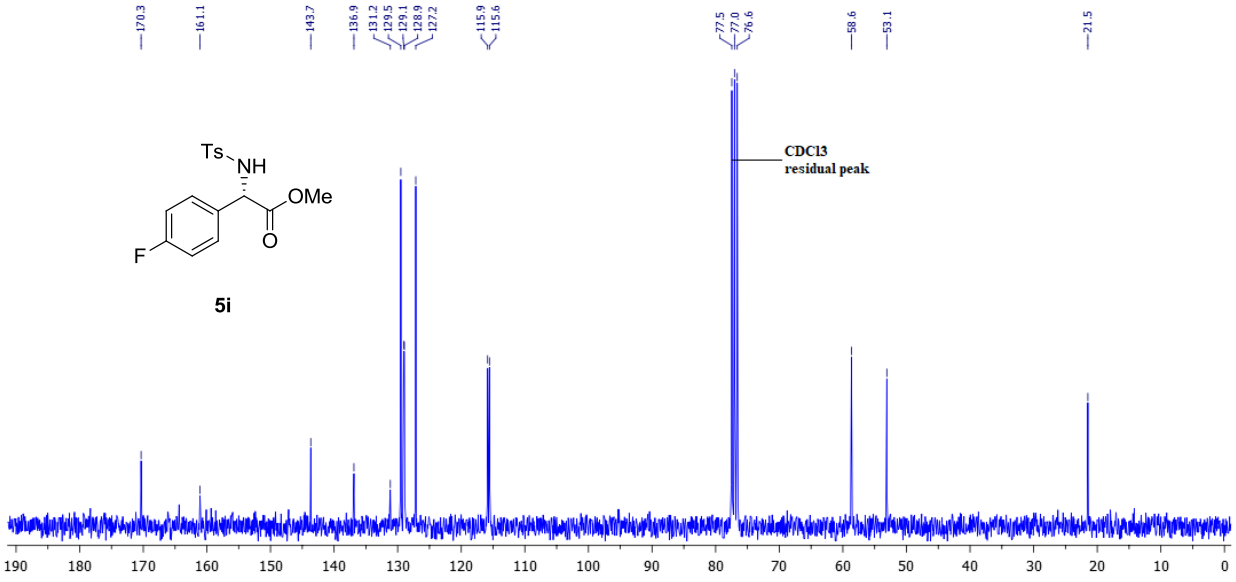
5.08
5.05
3.60
2.41
Ts
NH
OMe
O
F
5i
CHCl3
2.01
4.01
2.01
1.00
1.02
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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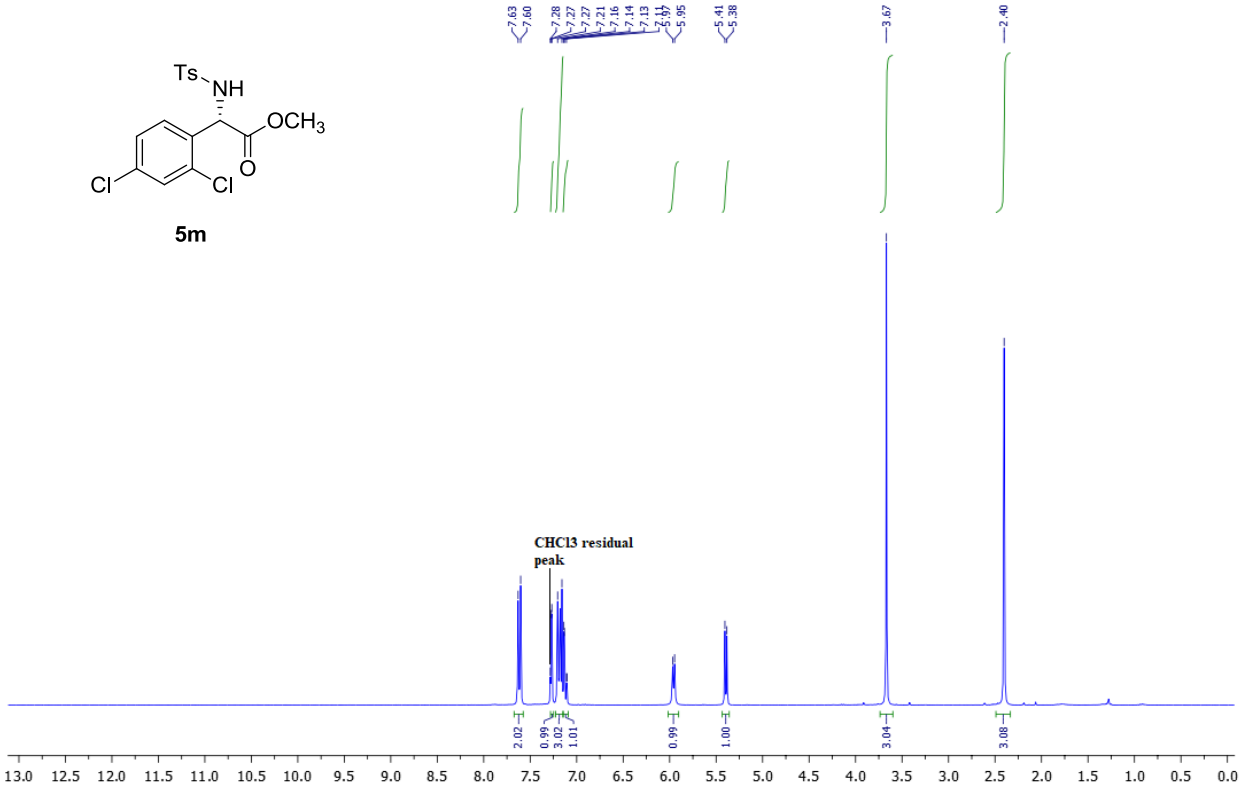
161.1
143.7
136.9
131.2
129.5
129.1
128.9
127.2
115.9
115.6
77.5
77.0
76.6
58.6
53.1
21.5
Ts
NH
OMe
O
F
5i
CDCl3
residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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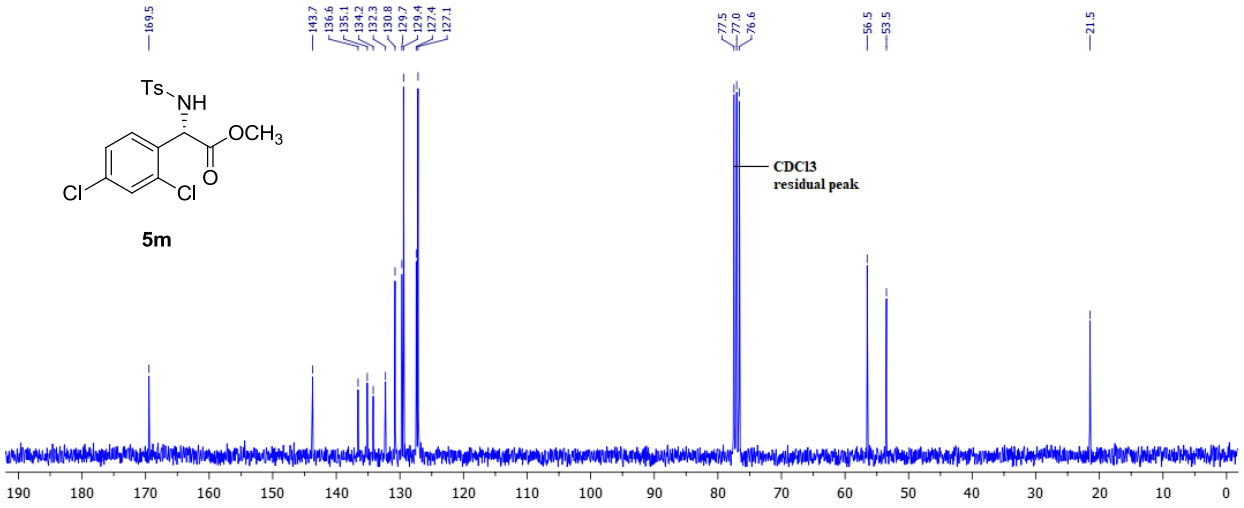
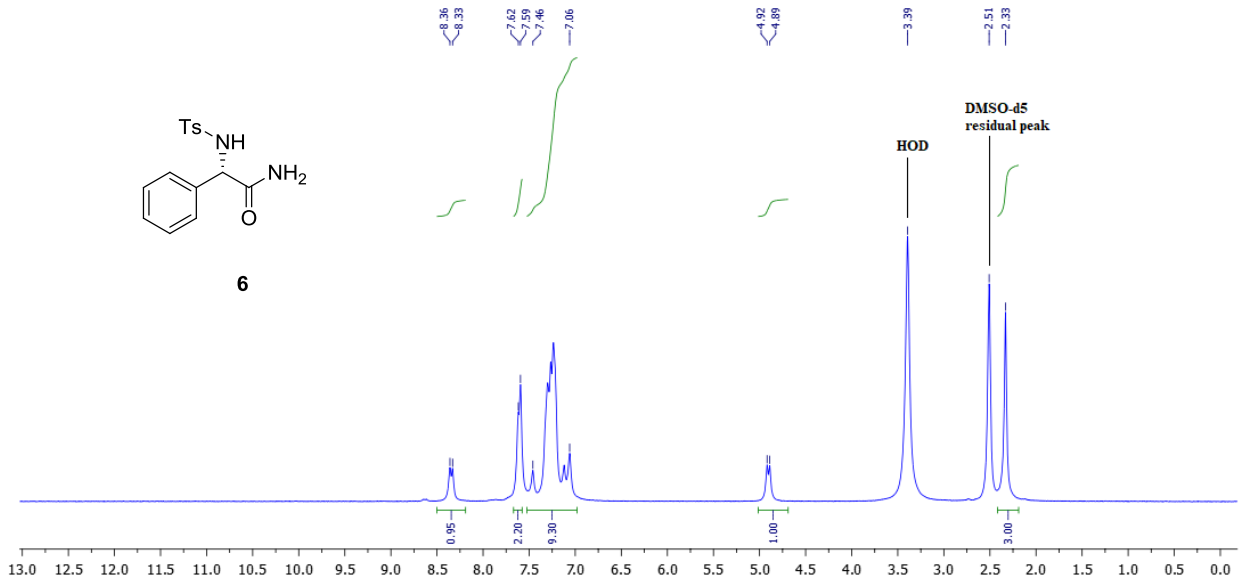
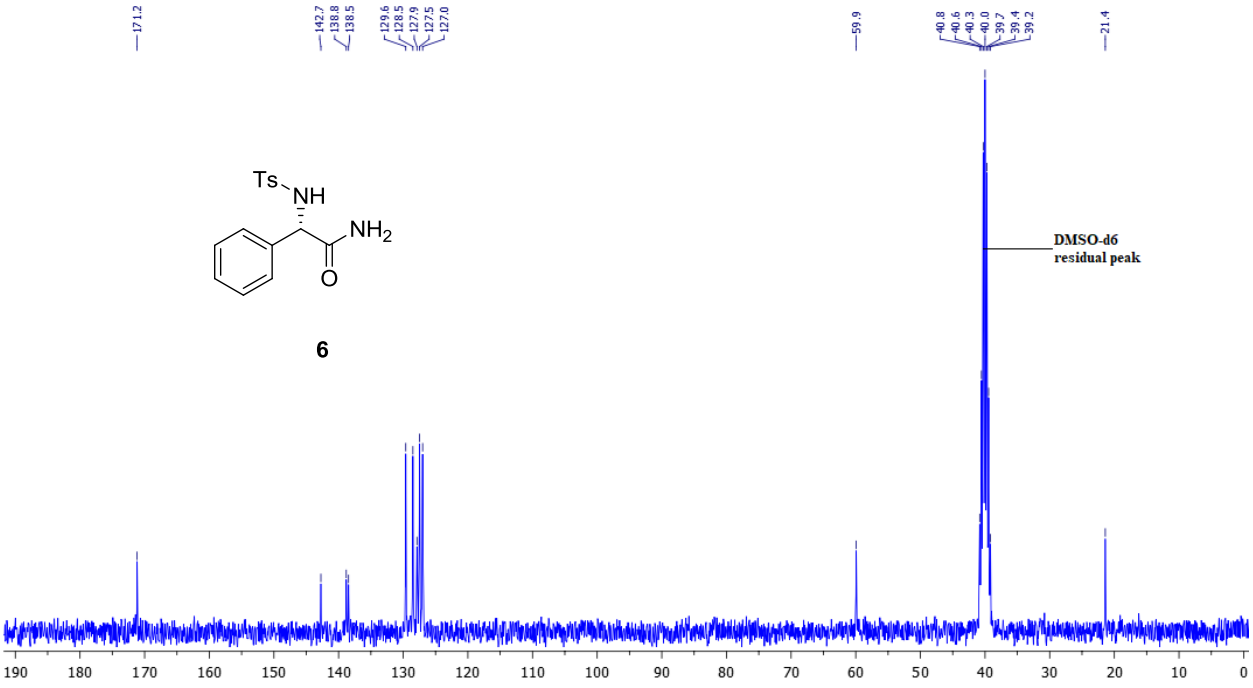
NH
OCH3
O
Cl
Cl
5m
7.63
7.60
7.28
7.27
7.27
7.27
7.21
7.16
7.14
7.13
5.97
5.95
5.41
5.38
3.67
2.40
CHCl3 residual peak
2.02
0.99
3.02
1.01
0.99
1.00
3.04
3.08
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


169.5
143.7
136.6
135.1
134.2
132.3
130.8
129.7
129.4
127.4
127.1
77.5
77.0
76.6
56.5
53.5
21.5
Ts
NH
OCH3
O
Cl
Cl
5m
CDCl3 residual peak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.36
8.33
7.62
7.59
7.46
7.06
4.92
4.89
3.39
2.51
2.33
HOD
DMSO-d5
residual peak
Ts
NH
NH2
O
0.95
2.20
9.30
1.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

6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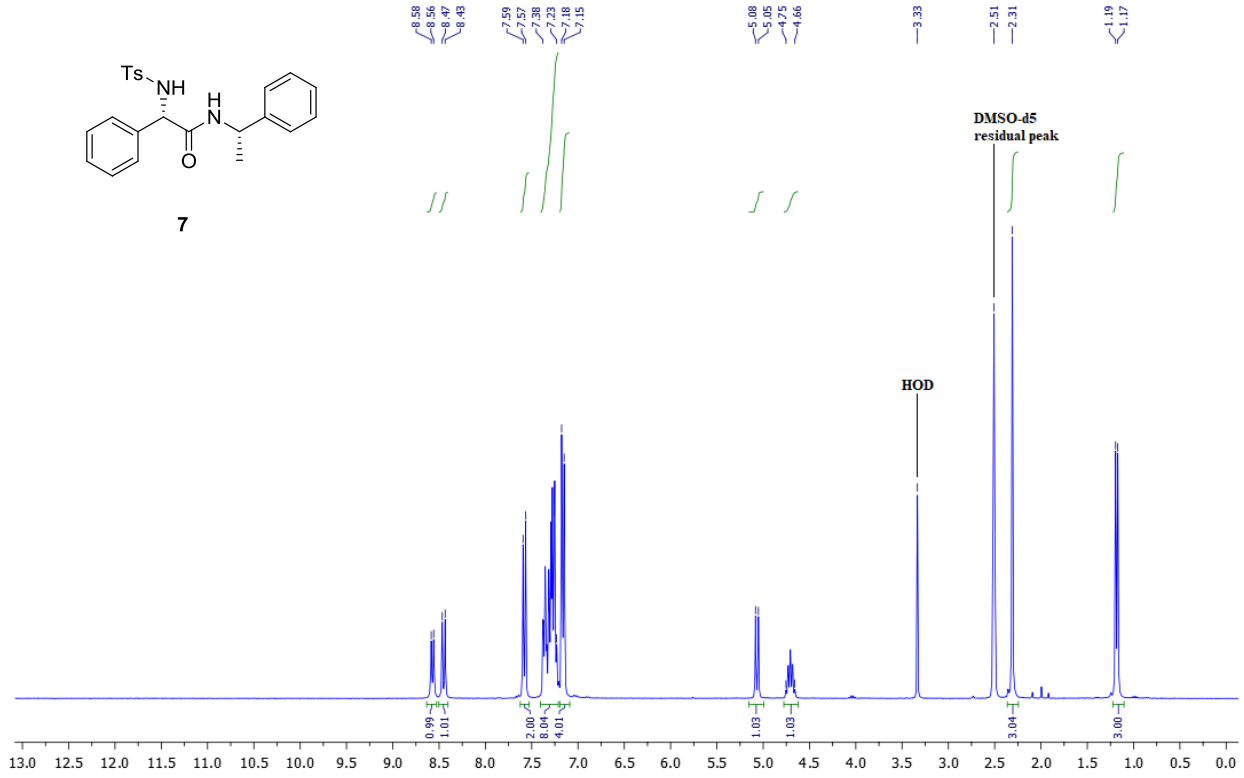
142.7
138.8
138.5
129.6
128.5
127.9
127.5
127.0
59.9
40.8
40.6
40.3
40.0
39.7
39.4
39.2
21.4
DMSO-d6
residual peak
Ts
NH
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

6


Ts
NH
H
N
O
7
8.58
8.56
8.47
8.43
7.59
7.57
7.38
7.23
7.18
7.15
5.08
5.05
4.75
4.66
3.33
2.51
2.31
1.19
1.17
DMSO-d5
residual peak
HOD
0.99
1.01
2.00
8.04
4.01
1.03
1.03
3.04
3.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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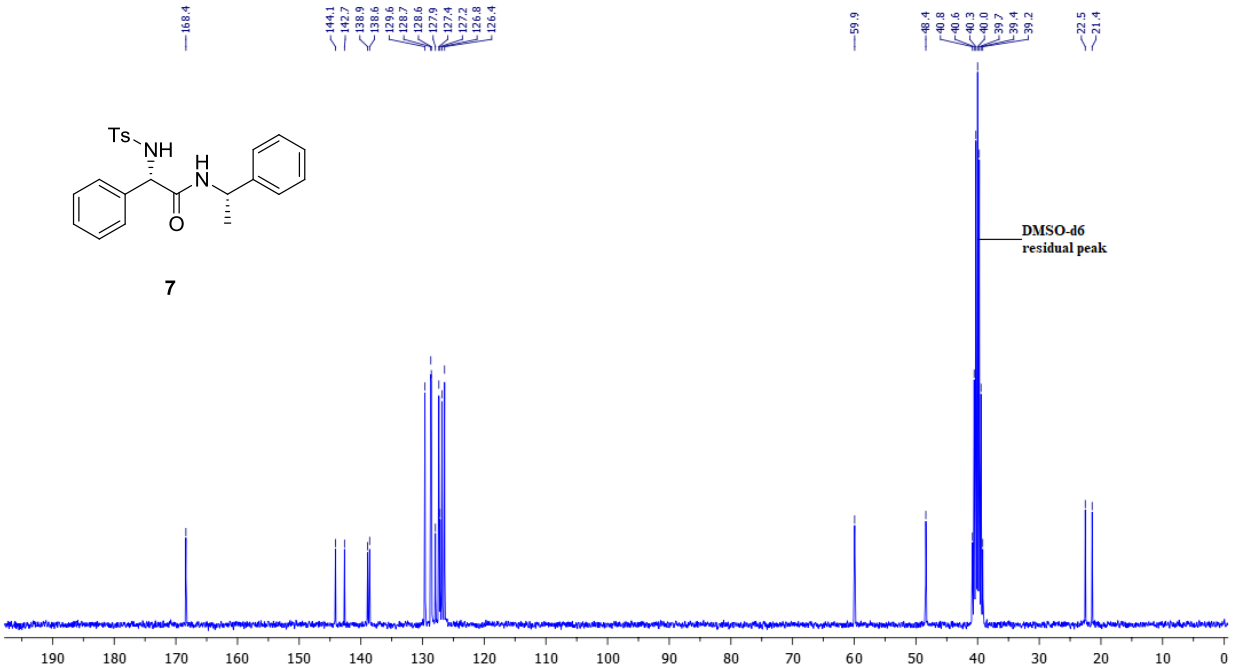
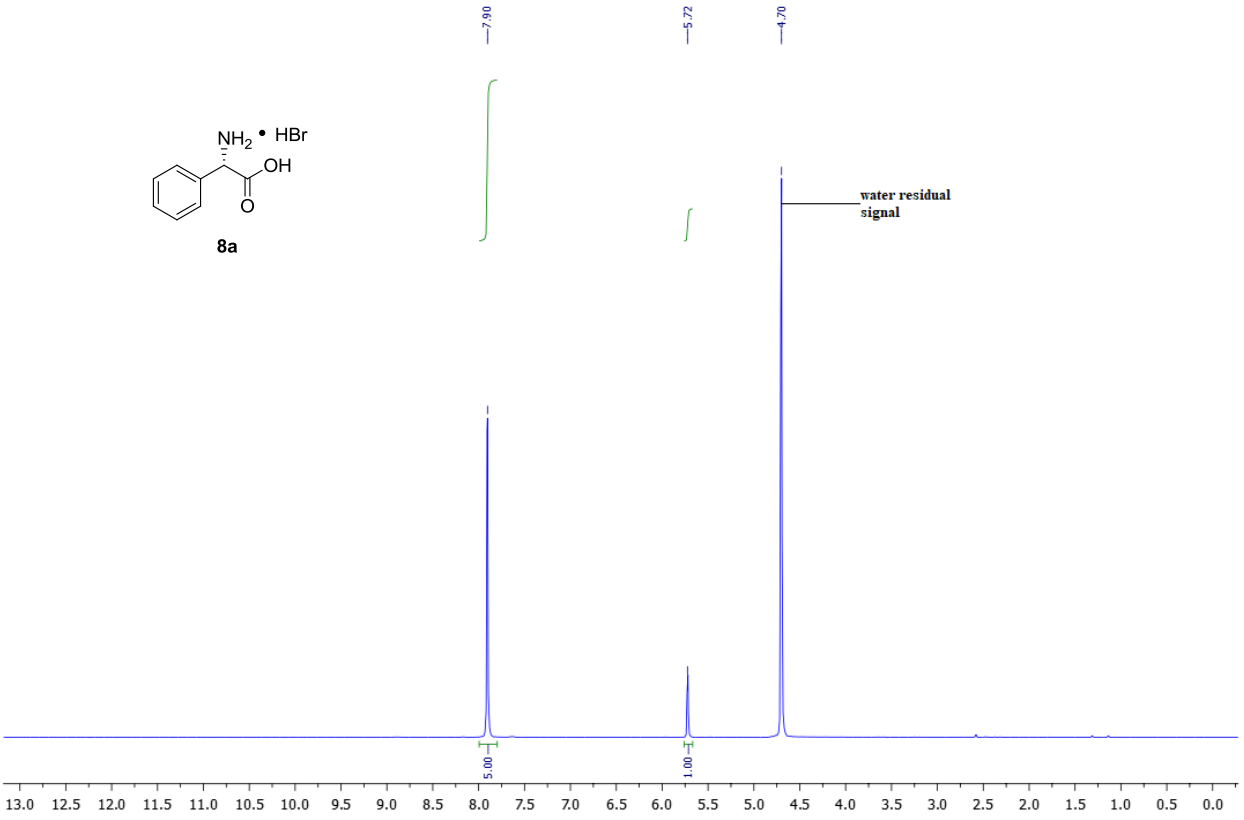
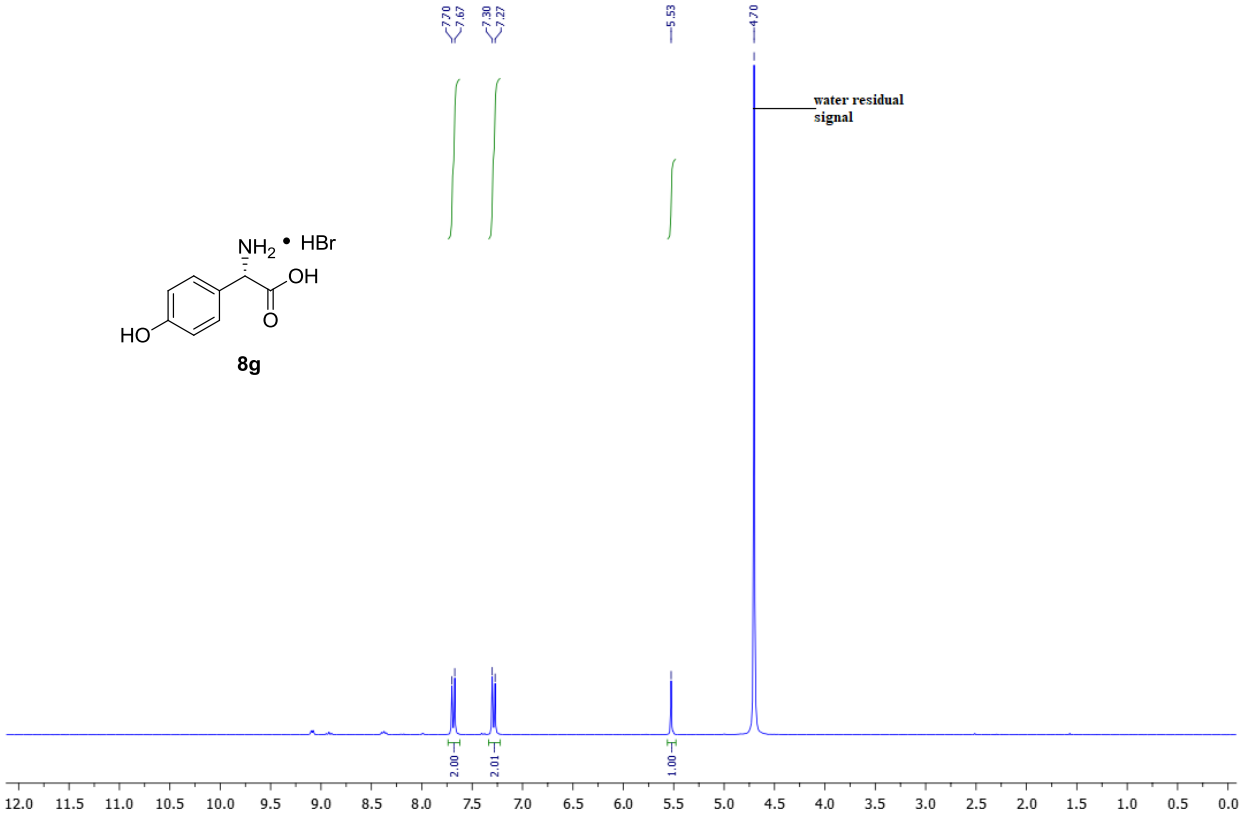
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

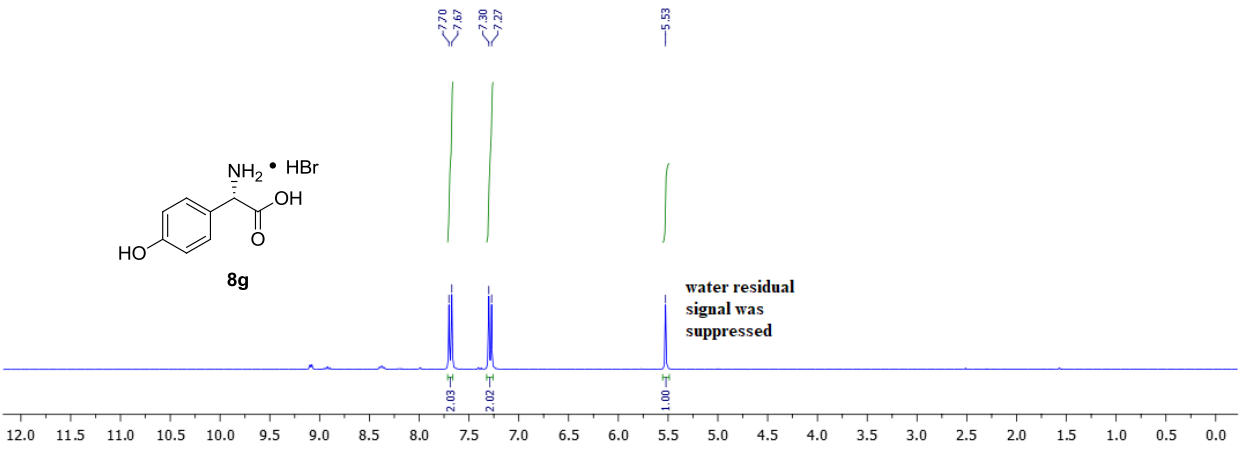

Ts
NH
H
N
O
7
168.4
144.1
142.7
138.9
138.6
129.6
128.7
128.6
127.9
127.4
127.2
126.8
126.4
59.9
48.4
40.8
40.6
40.3
40.0
39.7
39.4
39.2
22.5
21.4
DMSO-d6
residual peak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

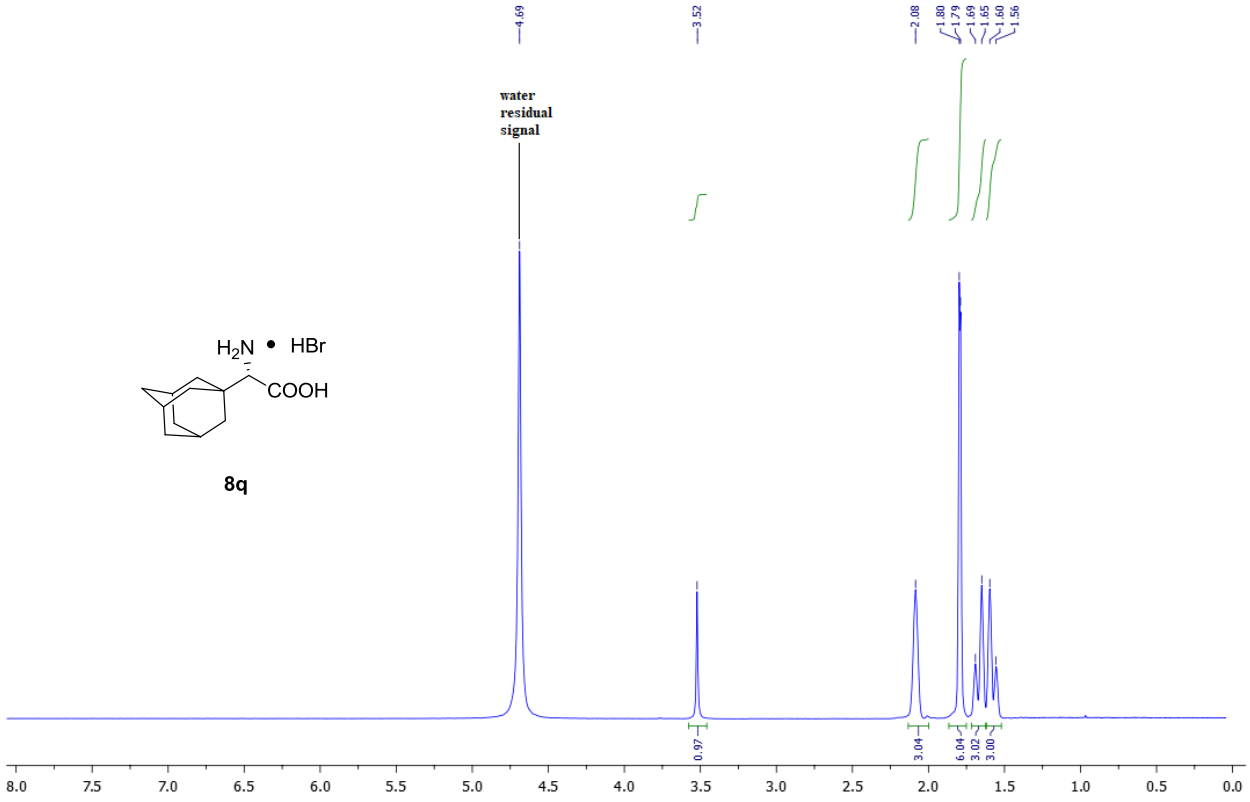

7.90
5.72
4.70
water residual signal
5.00
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

8a

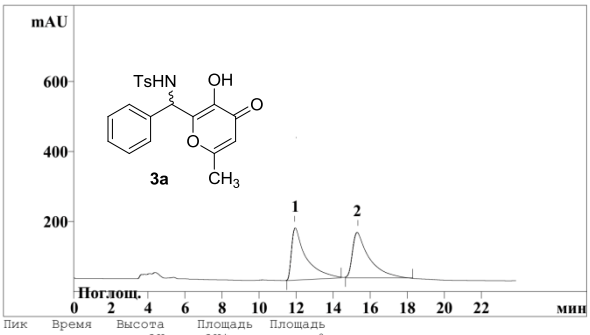

7.70
7.67
7.30
7.27
5.53
4.70
water residual signal
2.00
2.01
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

8g

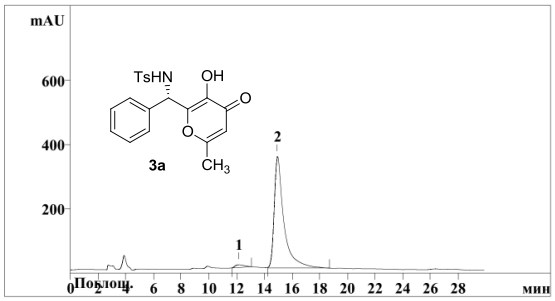

7.70
7.67
7.30
7.27
5.53
NH2 • HBr
OH
O
HO
8g
water residual
signal was
suppressed
2.03
2.02
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


4.69
3.52
2.08
1.80
1.79
1.69
1.65
1.60
1.56
water
residual
signal
H2N • HBr
COOH
8q
0.97
3.04
6.04
3.02
3.00
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

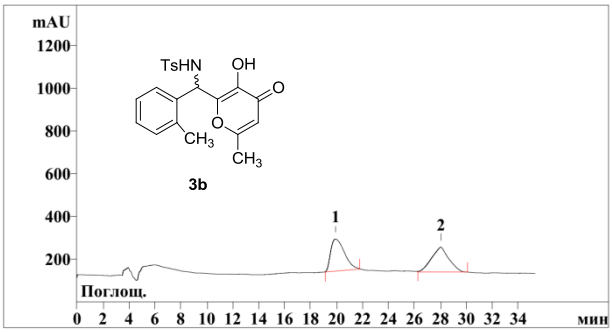
8. HPLC data for catalytic adducts 3



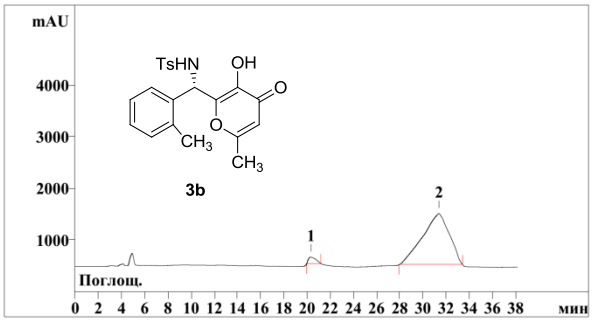
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	11.94	148.45	7966.75	49.89
2	15.29	128.63	8002.76	50.11
2	23.87	277.08	15969.51	100.00



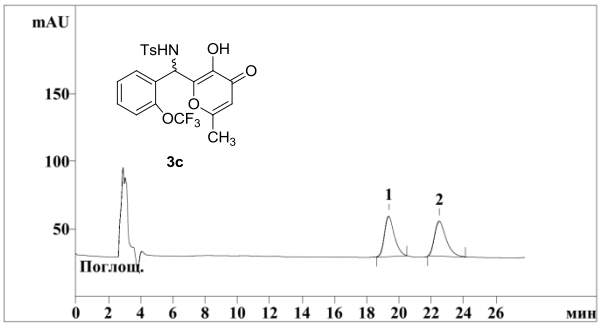
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.11	8.50	392.08	2.30
2	14.96	346.01	16670.61	97.70
2	29.88	354.51	17062.69	100.00



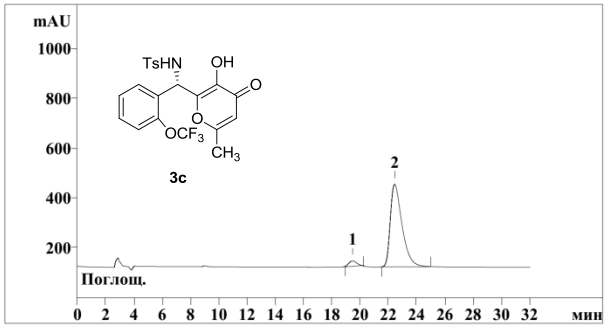
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	19.91	148.64	10808.82	50.82
2	28.02	114.64	10461.63	49.18
2	35.29	263.28	21270.45	100.00



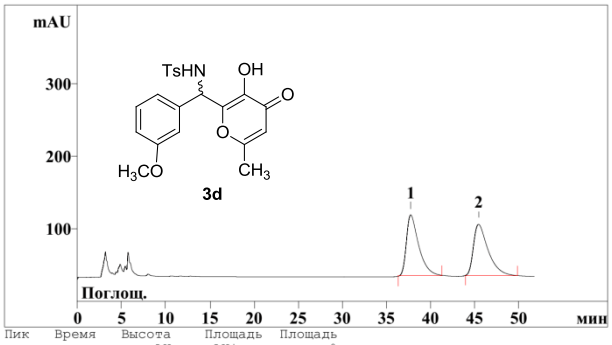
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	20.32	130.14	5856.92	3.54
2	31.37	987.36	159786.58	96.46
2	38.18	1117.50	165643.50	100.00



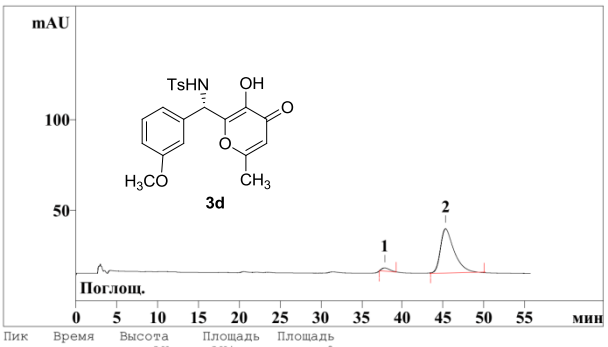
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	19.37	29.53	1254.13	49.14
2	22.5	26.06	1297.90	50.86
2	27.79	55.59	2552.03	100.00



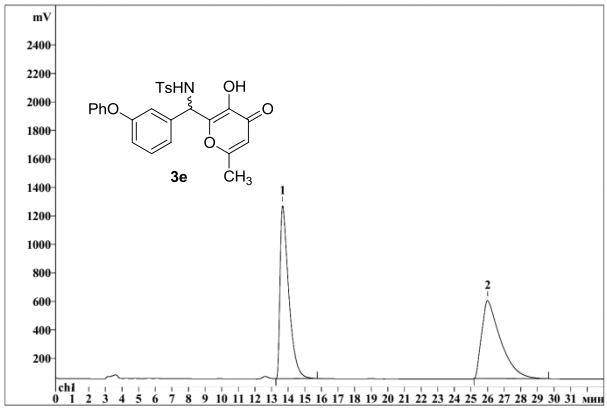
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	19.47	21.00	834.98	4.20
2	22.45	330.74	19061.64	95.80
2	32.04	351.74	19896.62	100.00



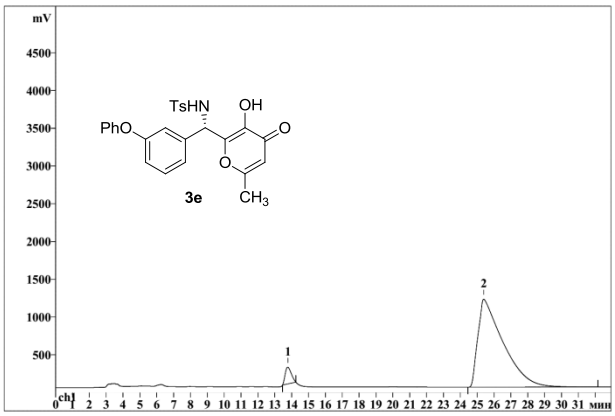
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	37.78	84.17	8213.57	50.18
2	45.75	70.55	8154.67	49.82
2	51.78	154.72	16368.24	100.00



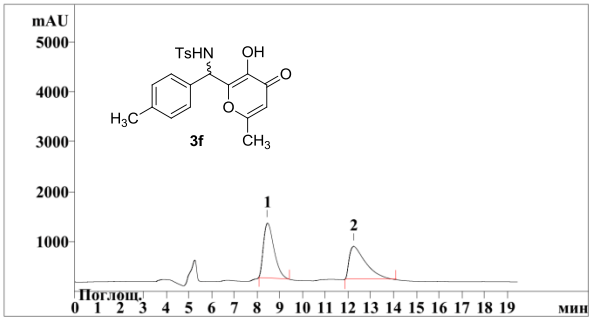
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	37.86	1.90	125.93	4.23
2	45.72	24.30	2853.60	95.77
2	55.73	26.20	2979.53	100.00



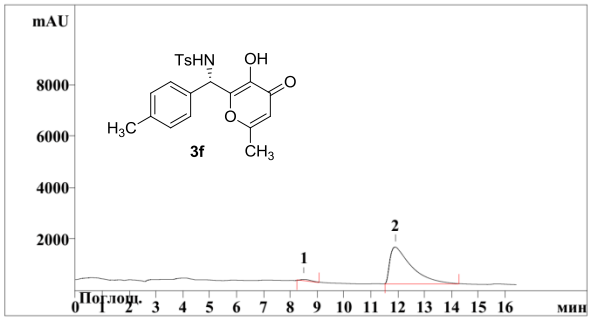
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	13.67	0.539	1213.64	68.91	43922.53	50.45
2	25.99	1.183	547.67	31.09	43138.33	49.55
2	33	0.861	1761.31	100.00	87060.86	100.00



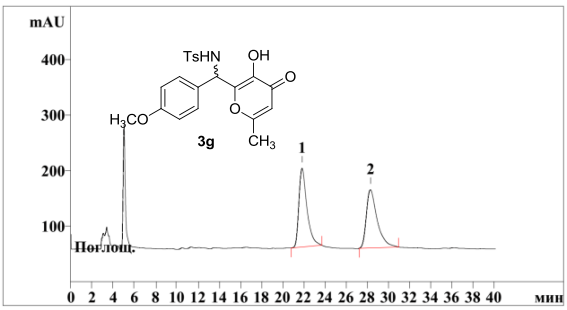
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	13.76	0.414	222.14	16.03	5590.78	4.41
2	25.39	1.574	1163.50	83.97	121116.08	95.59
2	32.94	0.994	1385.64	100.00	126706.85	100.00



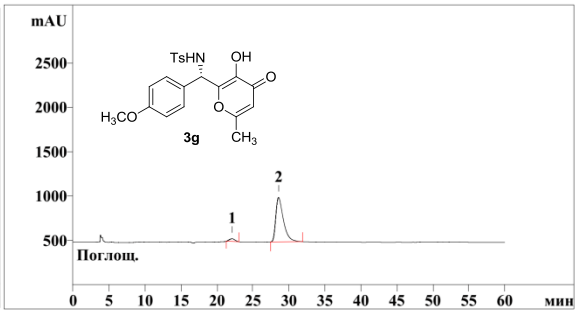
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.47	1092.64	35287.72	50.98
2	12.25	661.23	33928.30	49.02
2	19.45	1753.86	69216.03	100.00



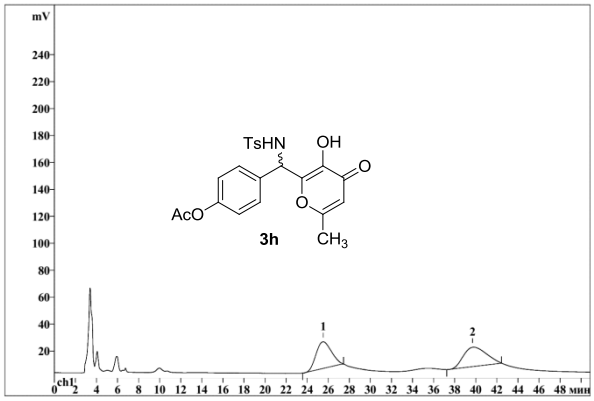
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.517	61.58	1579.64	1.97
2	11.9	1419.58	78477.76	98.03
2	16.42	1481.16	80057.39	100.00



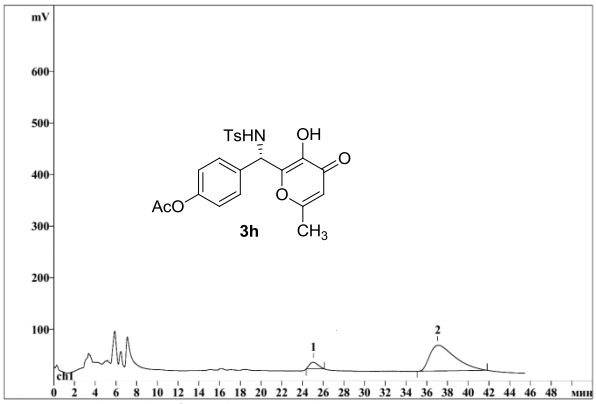
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	21.86	141.60	7541.28	50.28
2	28.33	104.87	7458.12	49.72
2	40.17	246.48	14999.40	100.00



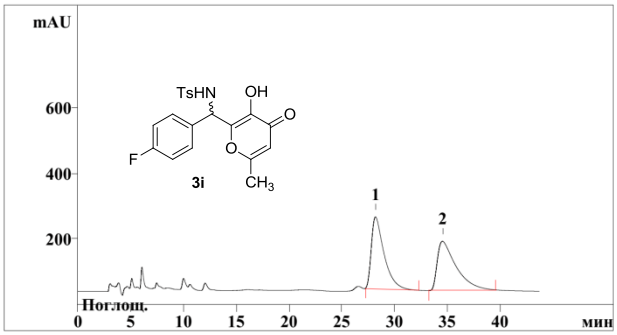
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	22.01	60.38	1570.39	4.09
2	28.55	500.17	36854.11	95.91
2	59.99	560.55	38424.50	100.00



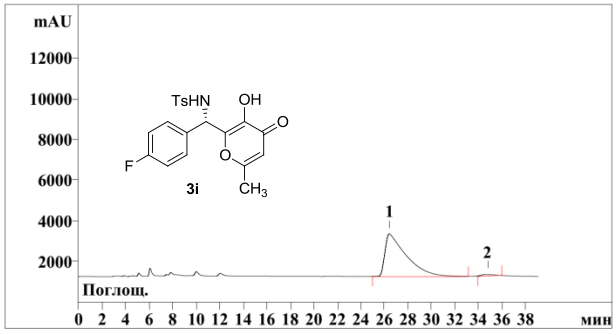
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	25.5	1.639	19.81	58.04	1999.48	48.19
2	39.71	2.491	14.32	41.96	2149.60	51.81
2	50.87	2.065	34.13	100.00	4149.08	100.00



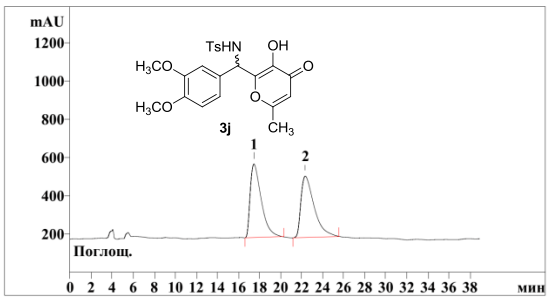
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	25.25	0.836	8.78	14.72	423.63	4.28
2	37.04	2.773	50.87	85.28	9480.81	95.72
2	45.23	1.805	59.66	100.00	9904.44	100.00



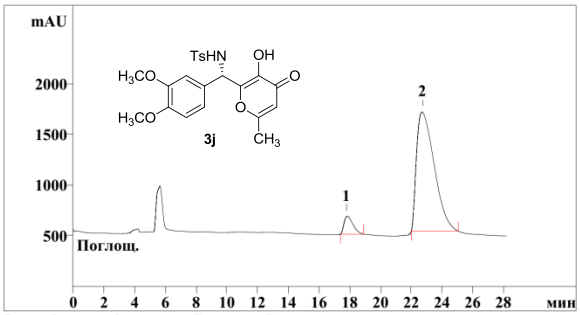
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	28.43	218.98	18410.31	49.64
2	34.58	150.43	18679.57	50.36
2	43.75	369.40	37089.88	100.00



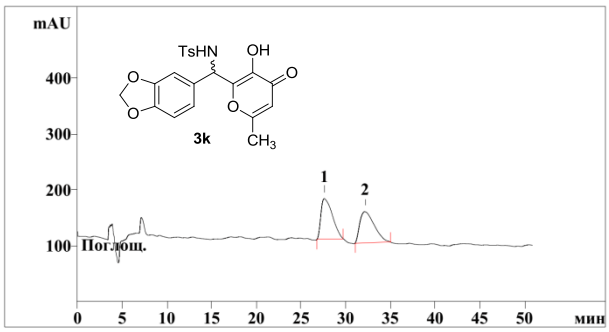
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	26.45	2084.53	259534.64	98.34
2	34.69	61.91	4380.16	1.66
2	39.09	2146.43	263914.81	100.00



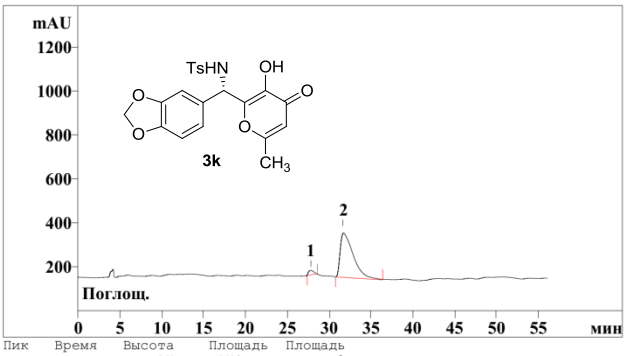
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	17.47	383.93	28203.04	50.27
2	22.35	320.44	27901.68	49.73
2	38.92	704.37	56104.72	100.00



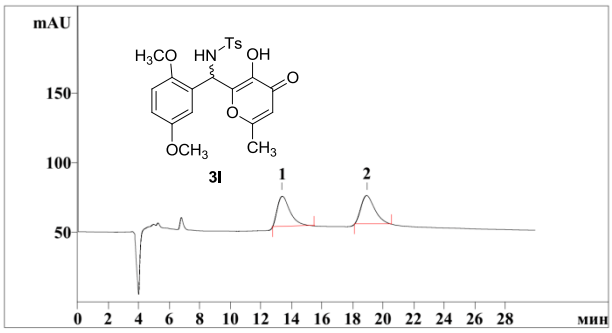
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	17.73	174.52	5415.88	5.44
2	22.71	1178.21	94196.65	94.56
2	28.22	1352.72	99612.53	100.00



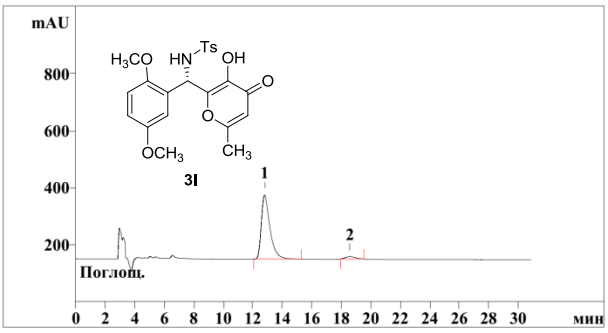
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	27.61	72.75	6451.26	50.91
2	32.15	55.58	6220.76	49.09
2	50.91	128.32	12672.02	100.00



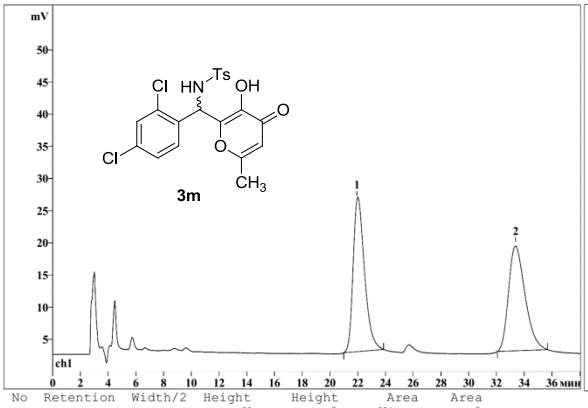
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	27.75	20.72	951.44	4.23
2	31.71	201.72	21542.41	95.77
2	56.06	222.44	22493.85	100.00



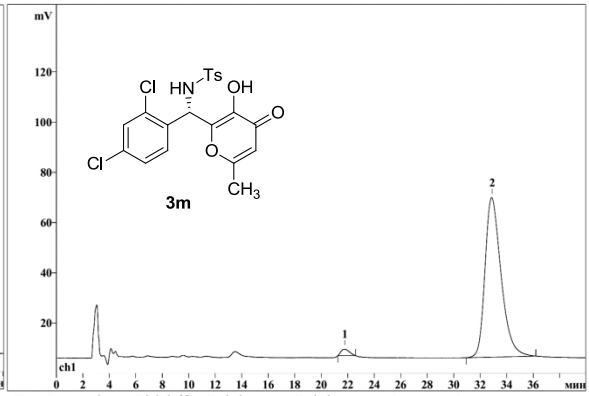
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	13.41	21.91	1286.69	49.89
2	18.93	20.54	1292.35	50.11
2	29.98	42.45	2579.04	100.00



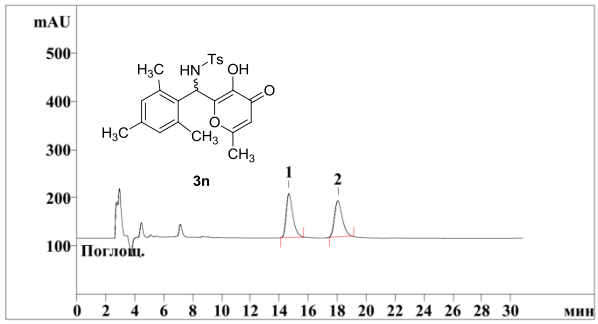
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	12.8	224.85	9207.80	95.84
2	18.59	8.28	400.08	4.16
2	30.88	233.14	9607.88	100.00



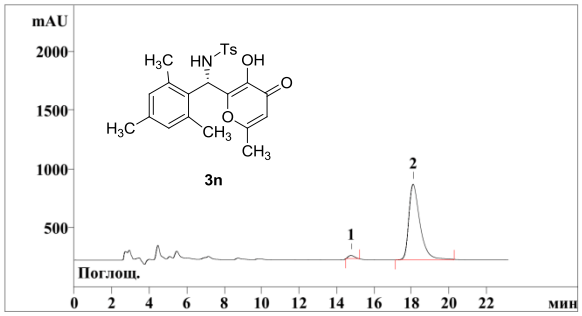
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	21.93	0.875	23.59	59.17	1365.87	50.34
2	33.37	1.279	16.28	40.83	1347.42	49.66
2	38.07	1.077	39.87	100.00	2713.29	100.00



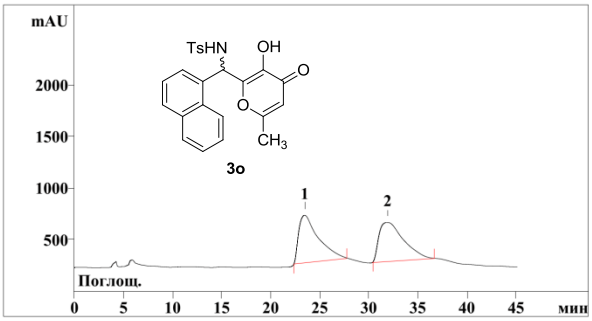
No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	21.77	0.734	2.56	3.87	112.55	2.06
2	32.86	1.272	63.50	96.13	5358.02	97.94
2	39.97	1.003	66.06	100.00	5470.57	100.00



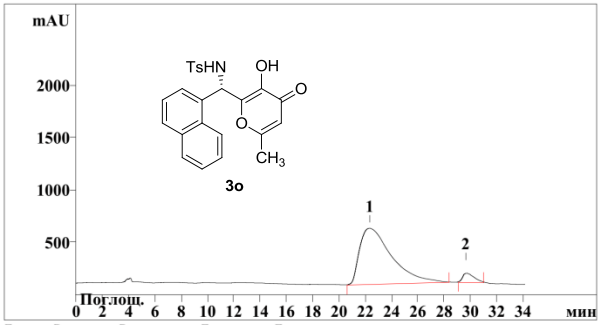
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	14.69	90.99	2903.04	50.63
2	18.06	75.00	2831.06	49.37
2	30.86	166.00	5734.10	100.00



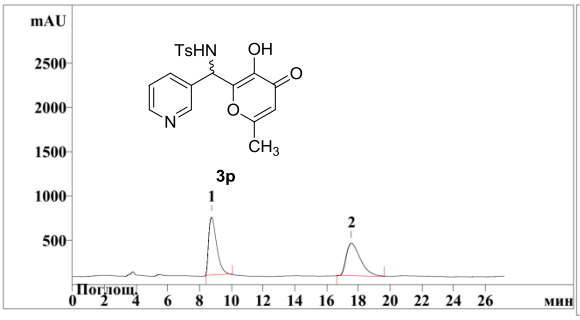
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	14.78	28.91	691.55	2.56
2	18.09	640.87	26316.78	97.44
2	23.17	669.78	27008.33	100.00



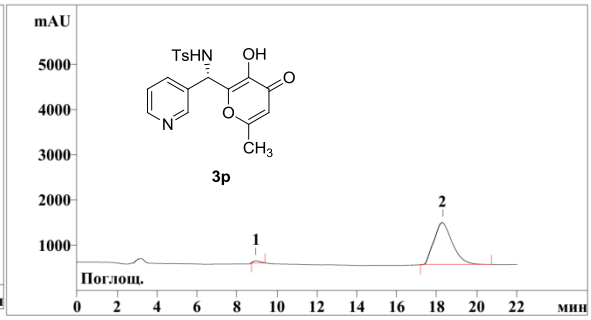
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	23.45	460.46	64110.53	49.69
2	31.84	374.77	64914.90	50.31
2	45.13	835.23	129025.42	100.00



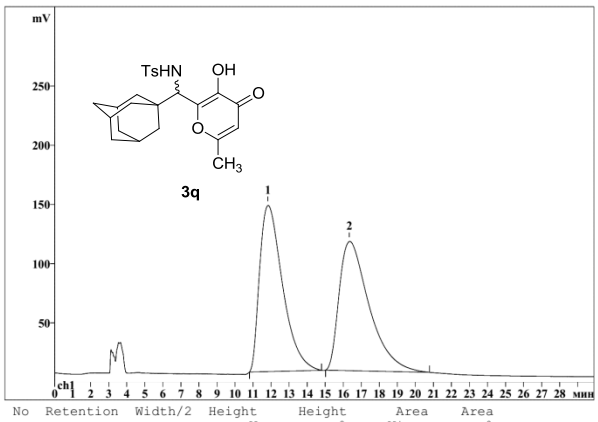
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	22.3	533.81	90302.24	95.44
2	29.6	75.88	4312.58	4.56
2	34.13	609.69	94614.82	100.00



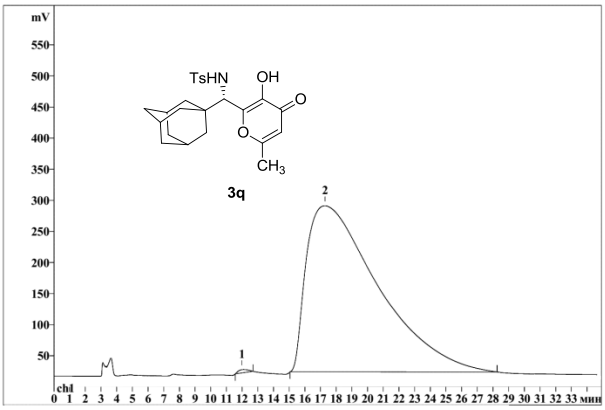
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.758	649.58	22845.54	50.27
2	17.57	367.37	22602.98	49.73
2	27.2	1016.95	45448.52	100.00



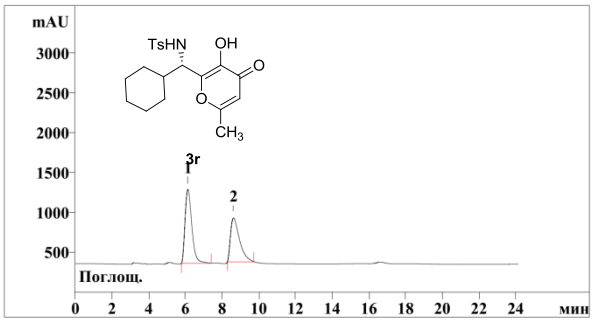
Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь %
1	8.959	44.55	1048.54	1.72
2	18.27	927.90	59711.65	98.28
2	22.02	972.45	60760.20	100.00



No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	11.83	1.369	140.16	56.23	12429.87	49.60
2	16.36	1.747	109.10	43.77	12628.84	50.40
2	29.9	1.558	249.27	100.00	25058.71	100.00



No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	11.96	0.746	5.29	1.94	226.13	0.27
2	17.28	4.885	267.13	98.06	84996.87	99.73
2	34.92	2.815	272.42	100.00	85223.00	100.00



Пик	Время мин	Высота mAU	Площадь mAU*сек	Площадь пика %
1	6.136	928.96	23776.79	56.387
2	8.626	545.17	18390.22	43.613
2	24.15	1474.12	42167.01	

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