Supporting Information

Dual-role of $PtCl_2$ Catalysis in the Intramolecular Cyclization of (Hetero)Aryl-Allenes for the Facile Construction of Substituted 2,3-Dihydropyrroles and Polyheterocyclic Skeletons

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CONTENTS

1. Additional References:

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2. General remarks. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. Unless otherwise noted, all reaction mixtures were stirred with a magnetic stir bar in flame-dried glassware under argon atmosphere. All the temperatures were referred to the used oil baths. Extracts were dried over $MgSO_4$ or Na_2SO_4 and solvents were removed in a rotary evaporator. TLC analysis of reaction mixtures was performed on Huanghai GF_{254} silica gel coated plates. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai GF254) and 250-400 mesh silica gel (Silicycle UltraPure silica gels). MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Infra-red spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. *J*-values are in Hz. Mass and HRMS spectra were recorded by EI, ESI, or MALDI method.

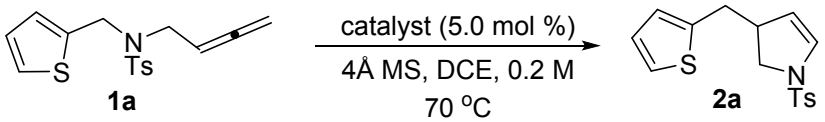
3. Condition optimization for the cyclization of allene 1a to 2a

General optimization screening conditions

To a flame dried Schlenk tube was added allene **1a** (0.20 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%), 4Å MS (100 mg) and the anhydrous solvent anisole (1.25 mL) under argon. The resulting solution was allowed to stir at 70 ^{o}C. When the reaction was complete as monitored by TLC, the solution was filtered through a short column with 250-400 mesh silica gel and condensed by rotary evaporation to yield the

crude product. In some cases, the reaction was carried out under CO atmosphere.

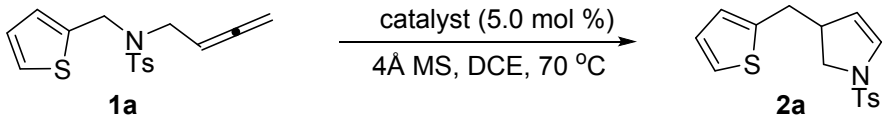
Table S1. Catalyst screening for the cyclization of allene 1a to 2a



entry[a]	catalyst	time (h)	yield[b] (%)
1	IPrAuCl/$AgNTf_2$	17	40
2	PPh_3AuCl/$AgNTf_2$	17	0
3	JohnphosAuOTf	17	3
4	JohnphosAu(MeCN)SbF_6	17	13
5	^{t}BuXphosAuOTf	17	7
6	JackiephosAuNTf_2	17	0
7	IPrAu(MeCN)SbF_6	17	30
8	$AgNTf_2$	17	0
9	$PtCl_2$	17	43
10	$PtCl_2$/CO	15	37
11	[Pt(COD)Cl_2]	17	41
12	[$Pt(PPh_3)_2Cl_2$]	17	8

[a]Reaction Conditions: **1a** (0.20 mmol), catalyst (5.0 mol%) and 4Å MS (100 mg) in DCE (1.0 mL) at 70 °C. [b]Determined by ^{1}H NMR using 1,3,5-trimethoxy benzene as an internal standard.

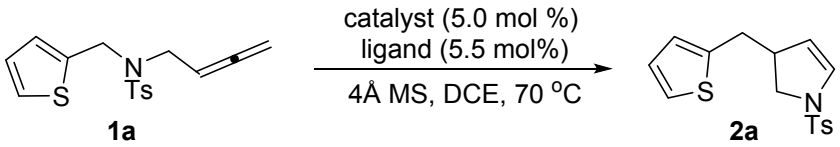
Table S2. Reaction condition screening for the Au-catalyzed cyclization of allene 1a to 2a



entry[a]	catalyst	concetration (M)	time (h)	yield[b] (%)
1	IPrAuCl/$AgNTf_2$	0.10	17	53
2	IPrAuCl/$AgNTf_2$	0.03	17	59
3	IPrAuCl/$AgBF_4$	0.03	17	12
4	IPrAuCl/NaBARF	0.03	17	30
5	SIPrAuCl/$AgNTf_2$	0.03	15	0

[a]Reaction Conditions: **1a** (0.20 mmol), catalyst (5.0 mol%) and 4Å MS (100 mg) in DCE at 70 °C. [b]Determined by ^{1}H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S3. Ligand screening for the $PtCl_2$-catalyzed cyclization of allene 1a to 2a

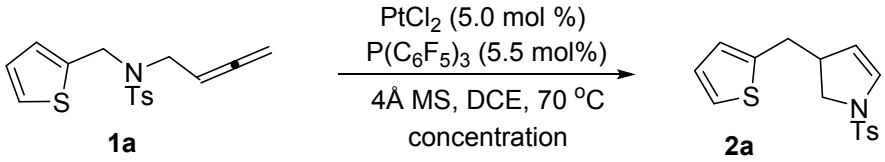


1a **2a**

entry[a]	catalyst	ligand	time (h)	yield[b] (%)
1	$PtCl_2$	$(2,4\text{-di-}^tBuC_6H_3O)_3P$	17	20
2	$PtCl_2$	$P(3,5\text{-}C_6H_3(CF_3)_2)_3$	39	28
3	$PtCl_2$	$P(C_6F_5)_3$	27	47

[a]Reaction Conditions: **1a** (0.20 mmol), $PtCl_2$ (5.0 mol%), ligand (5.5 mol%) and 4Å MS (100 mg) in DCE at 70 °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S4. Concentration screening for the $PtCl_2$-catalyzed cyclization of allene 1a to 2a

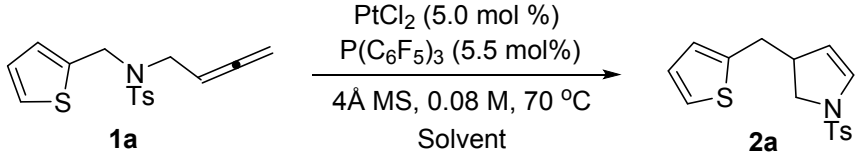


1a **2a**

entry[a]	concetration (M)	time (h)	yield[b] (%)
1	0.10	14	65
2	0.15	24	46
3	0.10	35	83
4	0.08	35	75

[a]Reaction Conditions: **1a** (0.20 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%) and 4 Å MS (100 mg) in DCE at 70 °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S5. Solvent screening for the $PtCl_2$-catalyzed cyclization of allene 1a to 2a

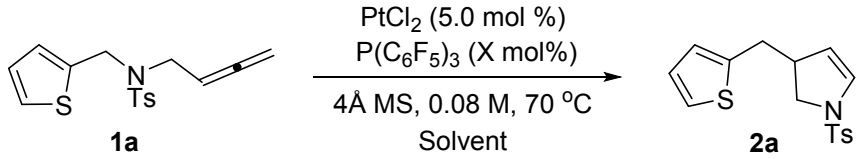


1a **2a**

entry[a]	solvent	time (h)	yield[b] (%)
1	toluene	35	>99 (96)[c]
2	*p*-xylene	30	95
3	**anisole**	**20**	**>99 (97)[c]**

[a]Reaction Conditions: **1a** (0.20 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%) and 4Å MS (100 mg) in solvent at 70 °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S6. Other conditions screening for the $PtCl_2$-catalyzed cyclization of allene 1a to 2a

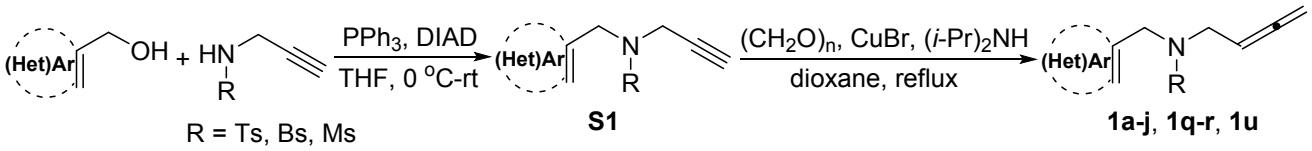


entry[a]	ligand	time (h)	yield[b] (%)
1	10 mol % $P(C_6F_5)_3$	35	75
2	5 mol % $P(C_6F_5)_3$	35	86

[a]Reaction Conditions: **1a** (0.20 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%) and 4Å MS (100 mg) in anisole (2.50 mL) at 70 °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

4. General procedure for synthesis of (hetero)aryl-allenes 1

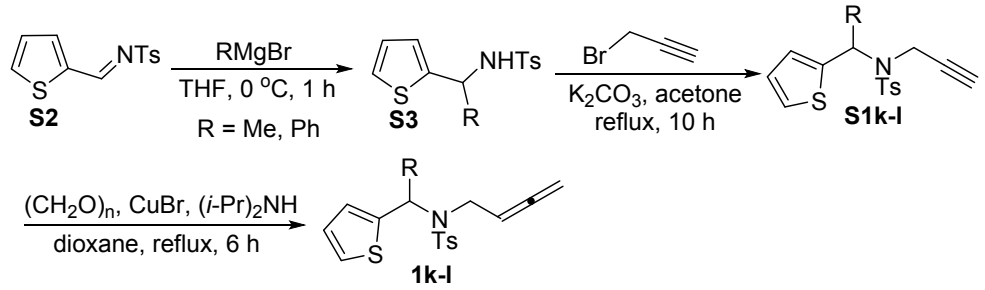
Procedure for synthesis of (hetero)aryl-allenes 1a-j, 1q-r and 1u



To a 100 mL flame and vacuum dried flask was added 2-thiophenemethanol (1.57 mL, 16.50 mmol), *N*-propargyl tosyl amine (3.13 g, 15.00 mmol), triphenylphosphine (4.32 g, 16.50 mmol) and anhydrous THF (17.00 mL) under Ar. Then, DIAD (2.17 mL, 11.00 mmol) was added dropwise at 0 °C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1), affording 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide **S1** (3.20 g, 10.50 mmol) in 70% yield.

To an oven-dried reaction tube was sequentially added **S1** (4.00 mmol), $(CH_2O)_n$ (12.00 mmol), CuBr (2.00 mmol) and diisopropylamine (8.00 mmol) in dioxane (4.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. Water (5.00 mL) and ether (10.00 mL) were added and then the aqueous solution was separated and extracted with ether (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1), affording 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(thiophen-2-yl methyl)benzenesulfonamide **1a-f**, **1q-r** and **1u**.

Procedure for synthesis of 1k-l

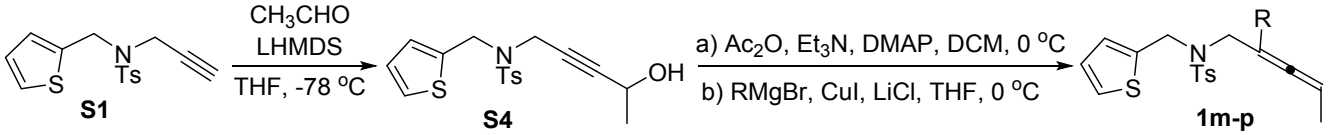


To a solution of (*E*)-4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide **S2**[1] (5.00 mmol) in THF (10.00 mL) was added RMgBr (5.50 mmol, 1.0 M in THF) within 20 min at 0 °C under an argon atmosphere. The resulting solution was allowed to stir at 0 °C for 1 h. Then, water was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered. The solvent was removed under reduced pressure, giving the crude product **S3**.

To the solution of **S3** (5.00 mmol) and K_2CO_3 (10.00 mmol) in acetone (10.00 mL) was added 3-bromoprop-1-yne (10.00 mmol) under an argon atmosphere. The resulting solution was allowed to stir at reflux for 10 h. After filtration, the solvent was removed under reduced pressure and the crude product was purified via a silica gel chromatography (PE/EA = 4/1), affording **S1k-l**.

To an oven-dried reaction tube was sequentially added **S1k-l** (4 mmol), $(CH_2O)_n$ (12.00 mmol), CuBr (2.00 mmol) and diisopropylamine (3.60 mmol) in dioxane (4.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. Water (5.00 mL) and ether (10.00 mL) were added and then the aqueous solution was separated and extracted with ether (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-10/1), affording **1k-l**.

Procedure for synthesis of 1m-p

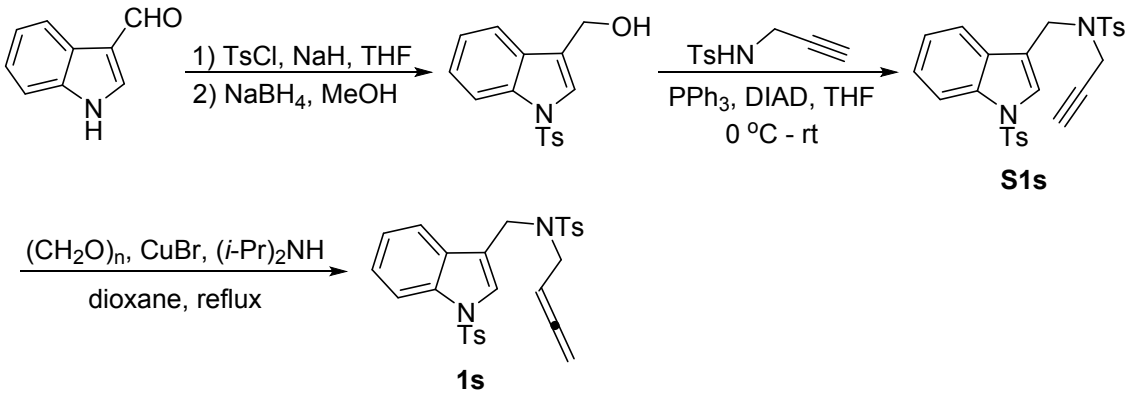


To a solution of 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide **S1** (10.00 mmol) in THF (100.00 mL) was added LHMDS (12.00 mmol, 1.0 M in THF) within 20 min at -78 °C under an argon atmosphere. The resulting solution was allowed to stir at -78 °C for 30 min before acetaldehyde (14.00 mmol) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and was stirred for 2 h. Then, a saturated NH_4Cl solution was added to quench the reaction. The reaction mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over anhydrous Na_2SO_4. After filtration over Na_2SO_4, the solvent was removed under reduced pressure. The crude product was purified via a silica gel chromatography (PE/EA = 4/1), affording *N*-(4-hydroxypent-2-yn-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide **S4** (3.49 g, 3.10 mmol) in > 99% yield.

To the solution of **S4** (3.00 mmol) and anhydrous Et_3N (9.00 mmol) in CH_2Cl_2 (15.00 mL) was added Ac_2O (3.90 mmol) within 10 min at 0 °C under an argon atmosphere. The resulting solution was allowed to warm up to room temperature and was stirred for 1 h. Then, water was added to quench the reaction. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered and the organic phase was purified by a flash column chromatography on silica gel to give the desired acetate.

To a flame dried three-neck flask was added anhydrous CuI (6.00 mmol), LiCl (6.00 mmol) and THF (15.00 mL) under an argon atmosphere. Then, the flask was cooled to 0 °C before RMgBr (6.00 mmol, 3.0 M in THF) was added at one portion into the flask under argon and the mixture was stirred for 15 min. Next, the reaction mixture was allowed to warm up to room temperature and a solution of the above acetate (3.00 mmol) in THF (15.00 mL) was added dropwise within 15 min. The resulting solution was allowed to stir for 2 h before saturated NH_4Cl solution was added to quench the reaction. The mixture was extracted with EtOAc (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered and the organic phase was concentrated under reduced pressure and the residue was purified via flash column chromatography on silica gel to give the desired 4-methyl-*N*-(2-methylpenta-2,3-dien-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamides **1m-p**.

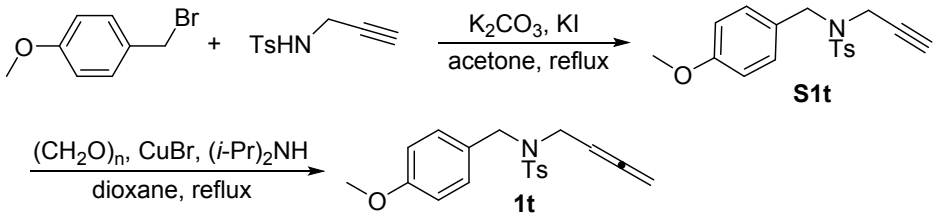
Procedure for synthesis of 1s



To a 100 mL flame and vacuum dried flask was added (1-tosyl-1*H*-indol-3-yl)methanol (903.00 mg, 3.00 mmol), *N*-propargyl tosyl amine (571.00 mg, 2.73 mmol), triphenylphosphine (716.00 mg, 2.73 mmol) and anhydrous THF (4.00 mL) under Ar. Then, DIAD (0.54 mL, 2.73 mmol) was added dropwise at 0 °C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-8/1), affording 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-((1-tosyl-1*H*-indol-3-yl)methyl)benzenesulfonamide **S1s** (1.04 g, 2.12 mmol) in 78% yield.

To an oven-dried reaction tube was sequentially added 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-((1-tosyl- 1*H*-indol-3-yl)methyl)benzenesulfonamide **S1s** (984.00 mg, 2.00 mmol), $(CH_2O)_n$ (150.00 mg, 12.00 mmol), CuBr (85.00 mg, 2.00 mmol), and diisopropylamine (0.50 mL, 3.60 mmol) in dioxane (4.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. Water (5.00 mL) and ether (10.00 mL) were added and then the aqueous solution was separated and extracted with ether (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-10/1), affording *N*-(buta-2,3-dien-1-yl)-4-methyl-*N*- ((1-tosyl-1*H*-indol-3-yl)methyl)benzenesulfonamide **1s** (728.00 mg, 1.44 mmol) in 72% yield.

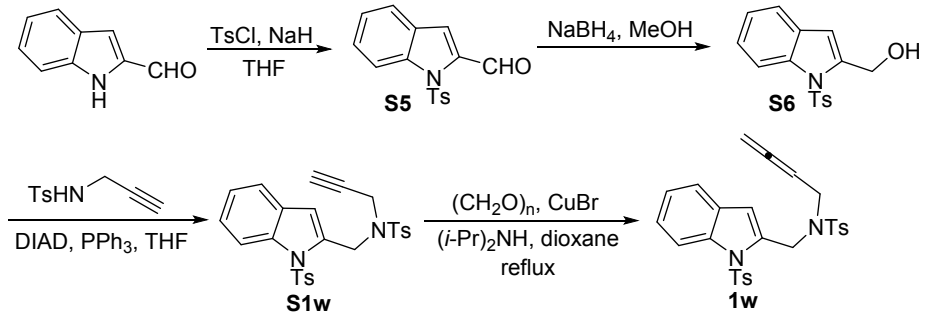
Procedure for synthesis of 1t



To a 50 mL flame and vacuum dried flask was added 4-methoxybenzyl bromide (1.32 mL, 9.00 mmol), *N*-propargyl tosyl amine (1.25 g, 6.00 mmol), K_2CO_3 (1.65 g, 12.00 mmol), KI (149.40 mg, 0.90 mmol) and acetone (18.00 mL) under an argon atmosphere. The resulting solution was allowed to stir at reflux overnight. After filtration, the solvent was removed under reduced pressure and the crude product was purified via a silica gel chromatography (PE/EA = 4/1), affording *N*-(4-methoxybenzyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1t** (1.68 g, 5.10 mmol) in 85% yield.

To an oven-dried reaction tube was sequentially added **S1t** (1.32 g, 4.00 mmol), $(CH_2O)_n$ (360.00 mg, 12.00 mmol), CuBr (286.00 mg, 2.00 mmol) and diisopropylamine (0.50 mL, 3.60 mmol) in dioxane (4.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. Water (5.00 mL) and ether (10.00 mL) were added and then the aqueous solution was separated and extracted with ether (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-10/1), affording *N*-(buta-2,3-dien-1-yl)-*N*-(4-methoxybenzyl)-4-methylbenzenesulfonamide **1t** (1.10 g, 3.20 mmol) in 80% yield.

Procedure for synthesis of 1w



To a 50 mL flame and vacuum dried flask was added 1*H*-indole-2-carbaldehyde (725.00 mg, 5.00 mmol) and anhydrous THF (10.00 mL) under an argon atmosphere. The resulting solution was cooled to 0 °C, then, NaH (220.00 mg, 5.50 mmol) was added slowly at 0 °C. The resulting mixture was warmed to room

temperature and stirred for 30 min. To the resulting solution at 0 °C was added a solution of 4-methylbenzenesulfonyl chloride (1.04 g, 5.50 mmol) in anhydrous THF (4.00 mL). The mixture was allowed to stir and warmed to room temperature over 3 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (5.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 8-1-6/1), affording 5-fluoro-1-tosyl-1*H*-indole-2-carbaldehyde **S5** (899.00 mg, 3.00 mmol) in 60% yield.

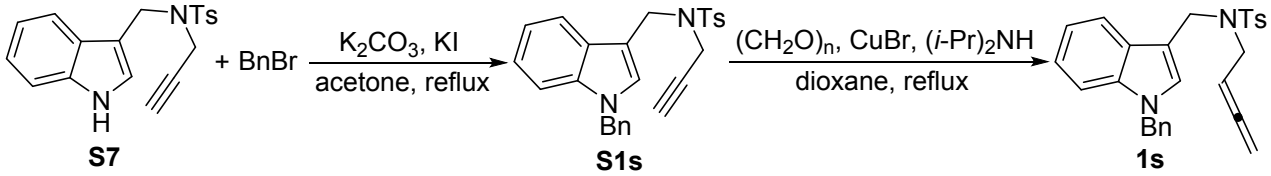
To a 50 mL flame and vacuum dried flask was added 1-tosyl-1*H*-indole-2-carbaldehyde **S5** (899.00 mg, 3.00 mmol) and MeOH (4.00 mL). The solution was cooled to 0 °C and $NaBH_4$ (113.49 mg, 3.00 mmol) was added slowly at 0 °C. The mixture was allowed to stir and warmed to room temperature over 2 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (3.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording (5-fluoro-1-tosyl-1*H*-indol-2-yl)methanol **S6** (903 mg, 3.00 mmol) in > 99% yield.

To a 50 mL flame and vacuum dried flask was added (1-tosyl-1*H*-indol-2-yl)methanol **S6** (903.00 mg, 3.00 mmol), *N*-propargyl tosyl amine (571.00 mg, 2.73 mmol), triphenylphosphine (716.00 mg, 2.73 mmol) and anhydrous THF (4.00 mL) under an argon atmosphere. Then, DIAD (0.54 mL, 2.73 mmol) was added dropwise at 0 °C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-8/1), affording *N*-((1-tosyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1w** (1.43 g, 2.90 mmol) in 96% yield.

To an oven-dried reaction tube was sequentially added *N*-((1-tosyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1w** (1.43 g, 2.90 mmol), $(CH_2O)_n$ (217.50 mg, 7.25 mmol), CuBr (124.41 mg, 0.87 mmol) and diisopropylamine (0.73 mL, 5.22 mmol) in dioxane (5.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as

monitored by TLC, it was cooled to room temperature. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 8/1), affording *N*-(buta-2,3-dien-1-yl)-*N*-((5-fluoro-1-tosyl-1*H*-indol-2-yl)methyl)-4-methylbenzenesulfonamide **1w** (777.00 mg, 1.53 mmol) in 53% yield.

Procedure for synthesis of 1x

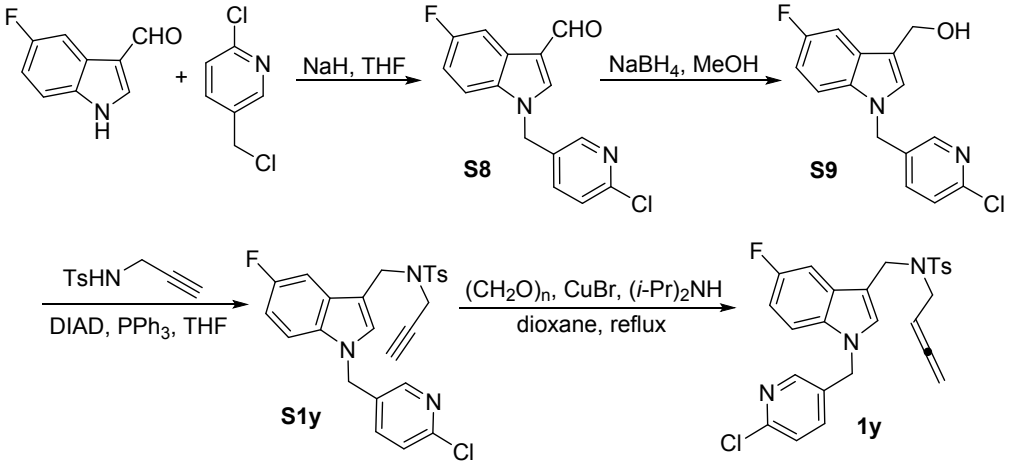


S7 **S1s** **1s**

To an oven-dried flask was sequentially added *N*-((1*H*-indol-3-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S7** (1.10 g, 3.26 mmol), K_2CO_3 (902.00 mg, 6.53 mmol), KI (54.00 mg, 0.33 mmol) and acetone (5.00 mL) under an argon atmosphere. To the mixture was added dropwise (bromomethyl)benzene (0.58 mL, 4.90 mmol) at room temperature and the resulting mixture was stirred under reflux overnight. When the reaction was complete as monitored by TLC, it was cooled to room temperature. The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 6/1), affording *N*-((1-benzyl-1*H*-indol-3-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1s** (1.28 g, 2.97 mmol) in 91% yield.

To an oven-dried reaction tube was sequentially added *N*-((1-benzyl-1*H*-indol-3-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1s** (428.00 mg, 1.00 mmol), $(CH_2O)_n$ (75.00 mg, 2.50 mmol), CuBr (73.00 mg, 0.50 mmol) and diisopropylamine (0.26 mL, 1.80 mmol) in dioxane (2.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. Water (5.00 mL) and ether (10.00 mL) were added and then the aqueous solution was separated and extracted with ether (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1), affording *N*-((1-benzyl-1*H*-indol-3-yl)methyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide **1s** (326.00 mg, 0.74 mmol) in 73% yield.

Procedure for synthesis of 1y



To a 100 mL flame and vacuum dried flask was added 5-fluoro-1*H*-indole-3-carbaldehyde (489.00 mg, 3.00 mmol) and anhydrous THF (30.00 mL) under an argon atmosphere. The resulting solution was cooled to 0 °C, then, NaH (180.00 mg, 4.50 mmol) was added slowly at 0 °C. The resulting mixture was warmed to room temperature and stirred for 30 min. To the resulting solution was added a solution of 2-chloro-5-(chloromethyl)pyridine (725.00 mg, 4.50 mmol) in anhydrous THF (10.00 mL) at 0 °C. The mixture was allowed to stir and warmed to room temperature over 3 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (10.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 15 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording 1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indole-3-carbaldehyde **S8** (634.00 mg, 2.20 mmol) in 73% yield.

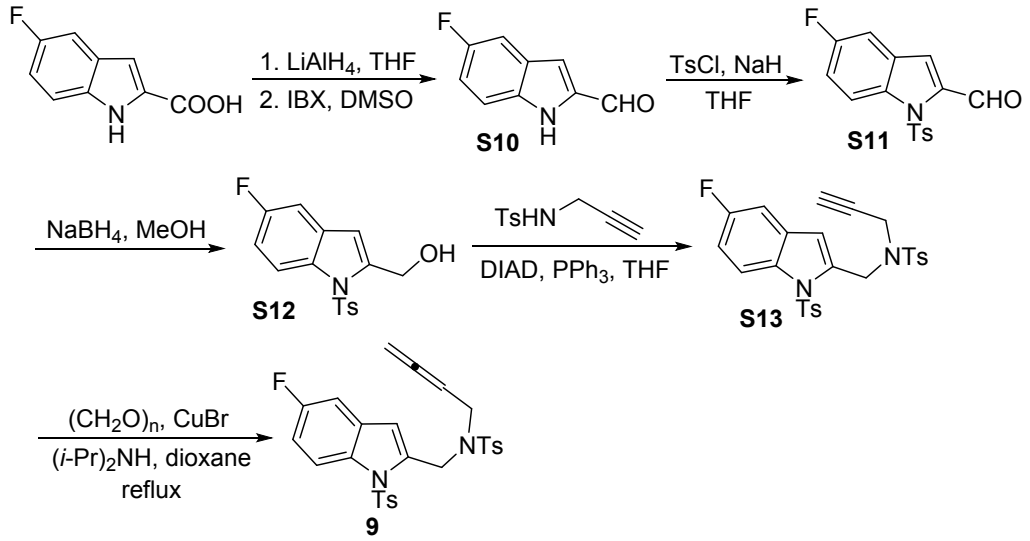
To a 50 mL flame and vacuum dried flask was added **S8** (634.00 mg, 2.20 mmol) and MeOH (5.00 mL). The resulting solution was cooled to 0 °C, then, $NaBH_4$ (70.00 mg, 1.76 mmol) was added slowly at 0 °C. The resulting mixture was warmed to room temperature and stirred for 2 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (3.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording (1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indol-3-yl)methanol **S9** (635.00 mg, 2.19 mmol).

To a 100 mL flame and vacuum dried flask was added (1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indol-3-yl)methanol **S9** (635.00 mg, 2.19 mmol), *N*-propargyl tosyl amine (418.00 mg, 2.00 mmol), triphenylphosphine (577.00 mg, 2.20 mmol) and anhydrous THF (4.00 mL) under an argon atmosphere. Then, DIAD (0.44 mL, 2.20 mmol) was added dropwise at 0 ^{o}C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-8/1), affording *N*-((1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indol-3-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S1y** (602.00 mg, 1.25 mmol) in 62% yield.

To an oven-dried reaction tube was sequentially added **S1y** (602.00 mg, 1.25 mmol), $(CH_2O)_n$ (93.00 mg, 3.13 mmol), CuBr (53.00 mg, 0.37 mmol) and diisopropylamine (0.31 mL, 2.25 mmol) in dioxane (2.00 mL) under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 8/1), affording *N*-(buta-2,3-dien-1-yl)-*N*-((1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indol -3-yl)methyl)-4-methylbenzenesulfonamide **1y** (452.00 mg, 0.90 mmol) in 72% yield.

5. General procedure for synthesis of compound 9 and 12

Synthesis of compound 9



To a 250 mL flame and vacuum dried flask was added 5-fluoro-1*H*-indole-2-carboxylic acid (5.37 g, 32.00 mmol) and anhydrous THF (150.00 mL) under an argon atmosphere. The resulting solution was cooled to 0 °C, then, $LiAlH_4$ (2.43 g, 64.00 mmol) was added slowly at 0 °C. The resulting mixture was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was quenched with water (20.00 mL) and filtered and the filtrate was concentrated under reduced pressure, affording the corresponding crude product.

To a 100 mL flame and vacuum dried flask was added above crude product, IBX (10.68 g, 38.16 mmol) and DMSO (45.00 mL). The resulting mixture was stirred at room temperature for 3 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (10.00 mL) and filtered. Then, the solution was washed with water (300.00 mL) and extracted with ethyl acetate (1 × 200 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording 5-fluoro-1*H*-indole-2-carbaldehyde **S10** (4.48 g, 27.49 mmol) in 86% yield.

To a 100 mL flame and vacuum dried flask was added 5-fluoro-1*H*-indole-2-carbaldehyde **S10** (3.20 g, 19.63 mmol) and anhydrous THF (40.00 mL) under an argon atmosphere. The resulting solution was cooled to 0 °C, then, NaH (942.00 mg, 23.55 mmol) was added slowly at 0 °C. The resulting mixture was warmed to room temperature and stirred for 30 min. To the resulting solution at 0 °C was added a

solution of 4-methylbenzenesulfonyl chloride (4.47 g, 23.55 mmol) in anhydrous THF (10.00 mL). The mixture was allowed to stir and warmed to room temperature over 3 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (10.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 30 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 8-1-6/1), affording 5-fluoro-1-tosyl-1*H*-indole-2-carbaldehyde **S11** (3.27 g, 10.33 mmol) in 52% yield.

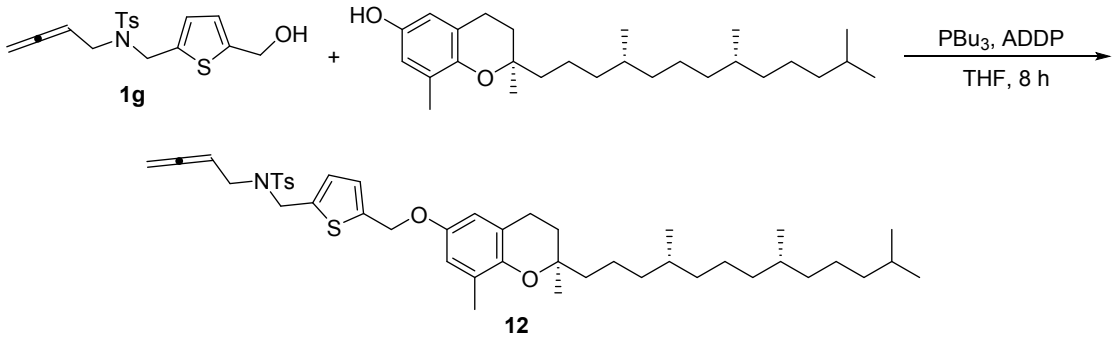
To a 50 mL flame and vacuum dried flask was added 5-fluoro-1-tosyl-1*H*-indole-2-carbaldehyde **S11** (3.27 g, 10.33 mmol) and MeOH (20.00 mL). The solution was cooled to 0 °C and $NaBH_4$ (471.00 mg, 12.39 mmol) was added slowly at 0 °C. The mixture was allowed to stir and warmed to room temperature over 2 h. When the reaction was complete as monitored by TLC, the solution was quenched with water (10.00 mL). The aqueous solution was separated and extracted with ethyl acetate (3 × 15 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording (5-fluoro-1-tosyl-1*H*-indol-2-yl)methanol **S12** (2.01 g, 6.30 mmol) in 61% yield.

To a 50 mL flame and vacuum dried flask was added (5-fluoro-1-tosyl-1*H*-indol-2-yl)methanol **S12** (319.00 mg, 1.00 mmol), *N*-propargyl tosyl amine (230.00 mg, 1.10 mmol), triphenylphosphine (288.00 mg, 1.10 mmol) and anhydrous THF (2.00 mL) under an argon atmosphere. Then, DIAD (0.22 mL, 1.10 mmol) was added dropwise at 0 °C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1-8/1), affording *N*-((5-fluoro-1-tosyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S13** (455.00 mg, 0.89 mmol) in 89% yield.

To an oven-dried reaction tube was sequentially added *N*-((5-fluoro-1-tosyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **S13** (453.00 mg, 0.89 mmol), $(CH_2O)_n$ (66.00 mg, 2.22 mmol), CuBr (38.00 mg, 0.27 mmol), and diisopropylamine (0.22 mL, 1.60 mmol) in dioxane (2.00 mL)

under an argon atmosphere. The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 8/1), affording *N*-(buta-2,3-dien-1-yl)-*N*-((5-fluoro-1-tosyl-1*H*-indol-2-yl)methyl)-4-methylbenzenesulfonamide **9** (224.00 mg, 0.43 mmol) in 48% yield.

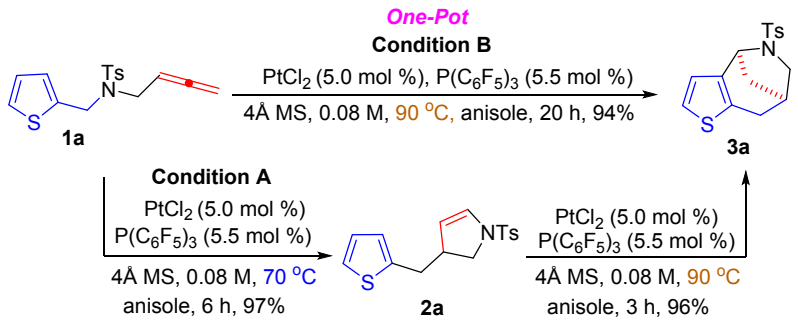
Synthesis of compound 12



To a 50 mL flame and vacuum dried flask was added *N*-(buta-2,3-dien-1-yl)-*N*-((5-(hydroxymethyl)thiophen-2-yl)methyl)-4-methylbenzenesulfonamide **1g** (200.00 mg, 0.57 mmol), (+)-δ-tocopherol (271.30 mg, 0.63 mmol), tributylphosphine (0.20 mL, 0.85 mmol) and anhydrous THF (2.00 mL) under an argon atmosphere. Then, ADDP (215.70 mg, 0.85 mmol) in anhydrous THF (2 mL) was added dropwise at 0 °C and the resulting solution was warmed to room temperature and stirred overnight. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1), affording (+)-δ-tocopherol derived allene **12** (208.30 mg, 0.25 mmol) in 45% yield.

6. General procedure for the $PtCl_2$-catalyzed tandem cyclization of allenes 1

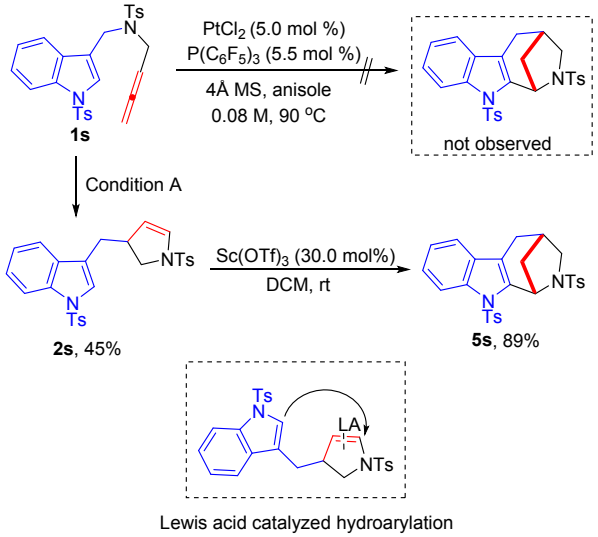
Scheme S1. One pot and stepwise synthesis of polyheterocycle **3a**



To a flame dried Schlenk tube was added **1** (0.10 mmol), $PtCl_2$ (5.00 mol%), $P(C_6F_5)_3$ (5.50 mol%), 4Å MS (50.00 mg) and the anhydrous anisole (1.25 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 90 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 8/1), affording the desired products **3**.

7. Cyclization of C3-indole-allene substrates

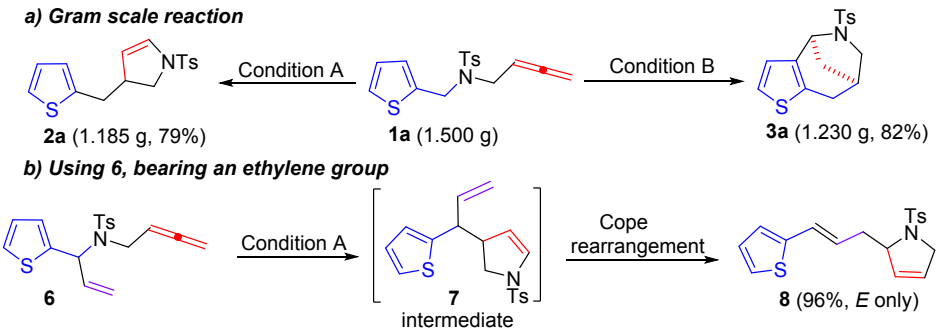
Scheme S2. Stepwise Cyclization of C3-indole-allene substrate **1s**



To a flame dried Schlenk tube was added **1s** or **1x-y** (0.20 mmol), $PtCl_2$ (5.00 mol%), $P(C_6F_5)_3$ (5.50 mol%), 4Å MS (100.00 mg) and the anhydrous anisole (2.50 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 8/1), affording the crude products.

To a flame dried Schlenk tube was added above-mentioned crude products in anhydrous DCM (3.00 mL), then $Sc(OTf)_3$ (0.30 equiv) was added into the reaction tube in one portion. The reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the residue was purified via a silica gel flash column chromatography (PE/EA = 4/1), affording the desired products **5s** and **5x-y**.

8. Procedure of transformations.

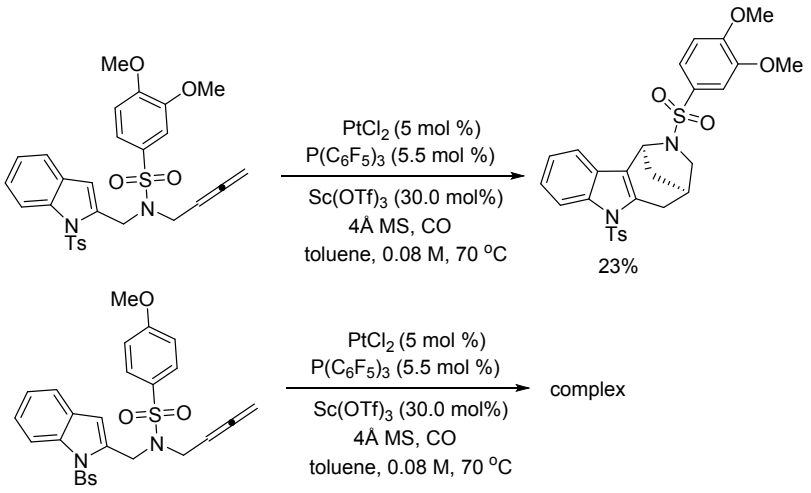


To a flame dried Schlenk tube was added **1a** (1.50 g, 4.70 mmol), $PtCl_2$ (61.00 mg, 0.23 mmol), $P(C_6F_5)_3$ (133.00 mg, 0.25 mmol), 4Å MS (2.30 g) and the anhydrous anisole (58 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 8/1), affording the desired product **2a** (1.18 g, 3.71 mmol) in 79% yield.

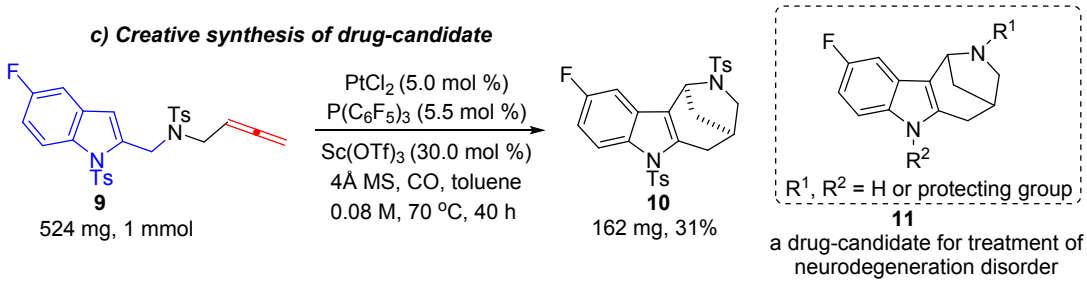
To a flame dried Schlenk tube was added **1a** (1.50 g, 4.70 mmol), $PtCl_2$ (61.00 mg, 0.23 mmol), $P(C_6F_5)_3$ (133.00 mg, 0.25 mmol), 4Å MS (2.30 g) and the anhydrous anisole (58 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 90 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 6/1), affording the desired product **3a** (1.23 g, 3.85 mmol) in 82% yield.

To a flame dried Schlenk tube was added **6** (34.00 mg, 0.10 mmol), $PtCl_2$ (1.25 mg, 0.005 mmol), $P(C_6F_5)_3$ (3.00 mg, 0.0055 mmol), 4Å MS (50 mg) and the anhydrous anisole (1.25 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 8/1), affording the desired product **8** (33.00 mg, 0.096 mmol) in 96% yield.

Scheme S3 Attempts to improve the yield by using substrates with more electron-rich protected N-groups.



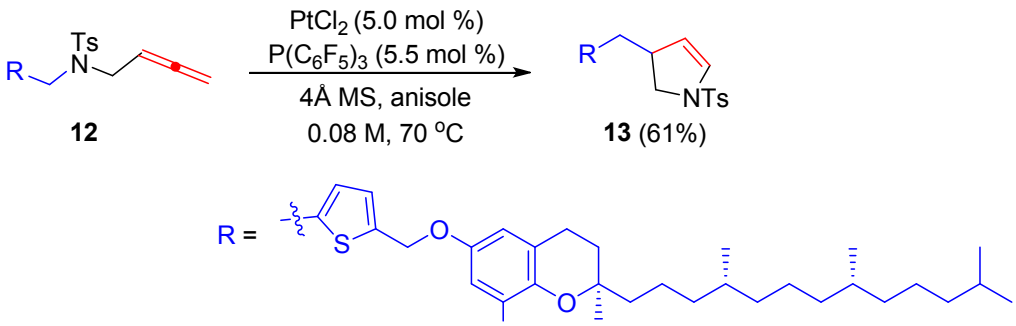
Using substrates with more electron-rich protected N-groups, however, the results were disappointing.



Previously, compounds of **11** were prepared through condensation of phenylhydrazine derivatives with bicyclic ketoamines under condition of the Fischer indole synthesis. However, the synthesis of bicyclic ketoamines needs multistep operations. Starting from **9**, the tandem cyclization proceeded smoothly to give **10** in 31% yield along with the recovery of **9** in 56% yield, whereas the reaction needed additional $Sc(OTf)_3$ (30.0 mol%) to improve the yield under CO (1.0 atm) atmosphere.

To a flame dried Schlenk tube was added indole-allene **9** (1.00 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%), $Sc(OTf)_3$ (30.0 mol%), 4Å MS (500 mg) and the anhydrous toluene (12.00 mL) under CO atmosphere. Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 4/1), affording the desired product **10**.

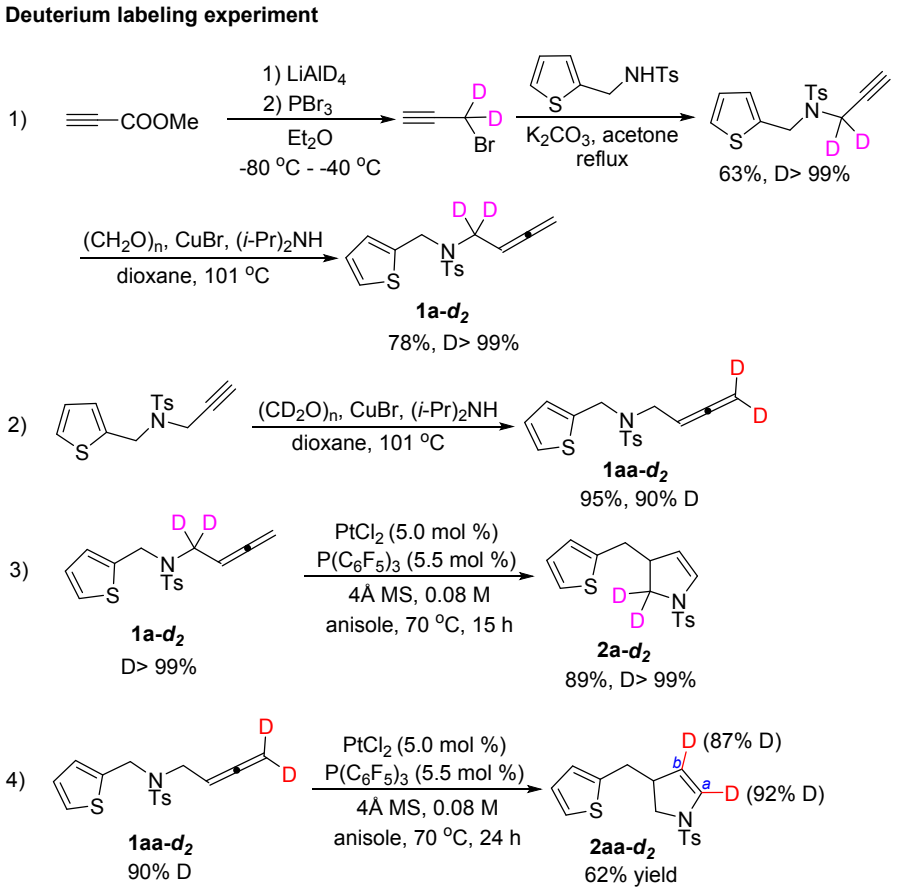
d) Application in (+)-δ-tocopherol derivative.

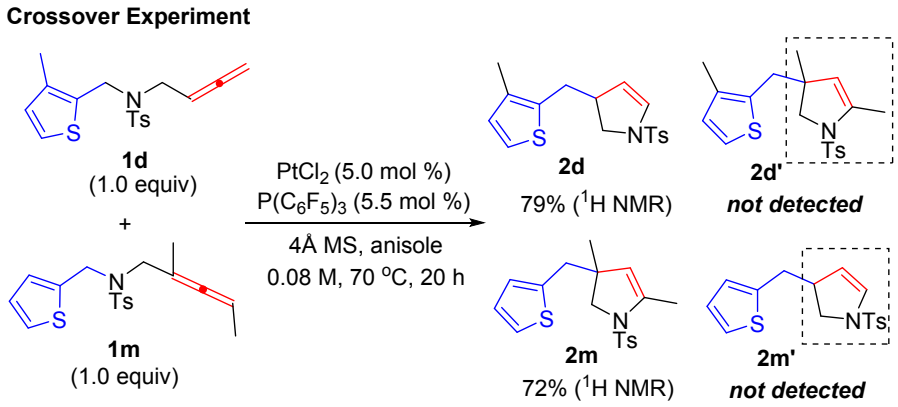


To a flame dried Schlenk tube was added (+)-δ-tocopherol derived allene **12** (0.10 mmol), $PtCl_2$ (5.0 mol%), $P(C_6F_5)_3$ (5.5 mol%), 4Å MS (50 mg) and the anhydrous anisole (1.25 mL). Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the crude product was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 4/1), affording the desired product **13**.

9. Deuterium labeling experiment and crossover experiment

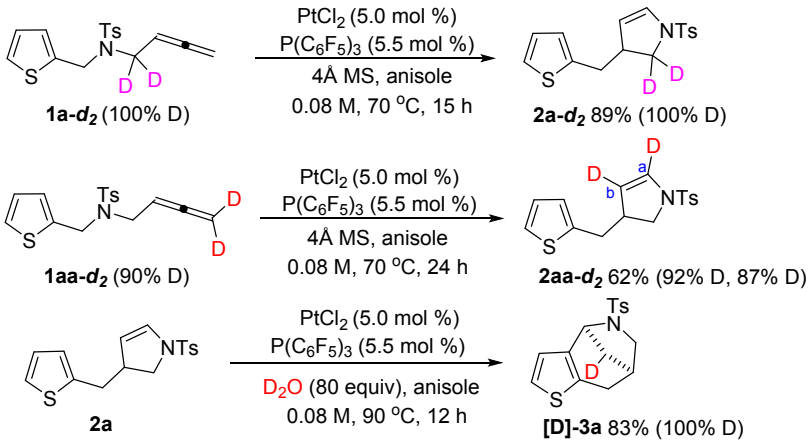
Deuterium labeling experiment





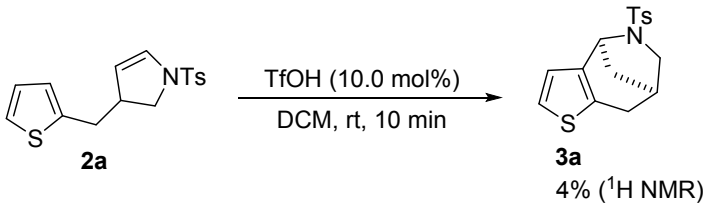
To a flame dried Schlenk tube was added **1d** (33.00 mg, 0.10 mmol), **1m** (34.00 mg, 0.10 mmol), $PtCl_2$ (3.00 mg, 0.005 mmol), $P(C_6F_5)_3$ (6.00 mg, 0.0055 mmol), 4Å MS (100 mg) and the anhydrous anisole (2.50 mL) under an argon atmosphere. Then, the resulting solution was allowed to stir at 70 °C. When the reaction was complete as monitored by TLC, the solution was purified via a silica gel flash column chromatography (PE/EA = 20/1 to 8/1), affording the product **2d** and **2m**.

Scheme S4 Deuterium Labeling Experiments.



As shown in Scheme S4, several deuterium labeling experiments were conducted to gain some insights into the reaction mechanism. The reactions **1a**-d_2 and **1aa**-d_2 showed that allyl hydrogens remain but a 1,2-H shift of the terminal vinyl protons occurs. Besides, we also carried out the reaction of unlabeled product **2a** in the presence of D_2O (80.0 eq), [D]-**3a** was formed in 83% yield along with 100% D content. We also confirmed that under the catalysis of Brønsted acid such as TfOH, only trace of **3a** was observed (see Scheme S5 in the Supporting Information), indicating that $PtCl_2$ as Lewis acid plays a major role in Friedel-Crafts type annulation.

Scheme S5 Compound **2a** was treated with a Brønsted acid.



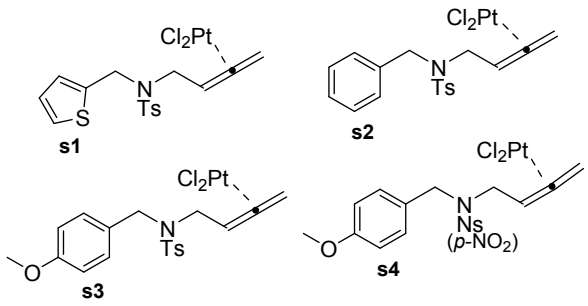
To a flame dried Schlenk tube was added **2a** (16.00 mg, 0.05 mmol) and DCM (0.25 mL), then, TfOH (0.4 μL, 0.005 mmol) was added into the flask under Ar. Then, the resulting solution was allowed to stir at room temperature for 10 min.

10. Computational details

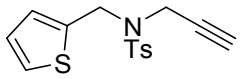
In order to understand the effects of substituents on the reaction outcomes, we calculated the NPA Charge on N in some reactant complexes at B3LYP/6-31+G(d) level. Switching thienyl moiety (**s1**) to phenyl moiety (**s2**), the NPA Charge on N atom decreased from -0.773 to -0.754. The decreased electron density on N atom probably leads to that the nucleophilic attack of N atom to allene is more difficult to happen and the desired product cannot be obtained. In the similar reason, varying NTs (**s1**) to NNs (**s4**), the NPA Charge on N atom decreased from -0.773 to -0.742; thus, the corresponding substrate cannot undergo this reaction. During the experiments, we found that the substrate having *p*-methoxylphenyl moiety can undergo the reaction smoothly. We also calculated the NPA Charge on N atom in **s3**, which is same as that in **s2**. This result indicates that the electron density of N atom is not sufficient to explain the observed reactivity. Subsequently, we calculated HOMO-LUMO energy gap. Although the electron density of N atom between **s2** and **s3** has no difference, the HOMO-LUMO energy gap in **s3** is decreased, which probably accounts for why **s3** can undergo the reaction smoothly. The more detailed mechanistic studies are still underway.

	NPA charge on N atom[a]	HOMO-LUMO
s1	-0.773	0.106
s2	-0.754	0.114
s3	-0.754	0.096
s4	-0.742	0.095

[a]Calculated at B3LYP/6-31+G(d) level

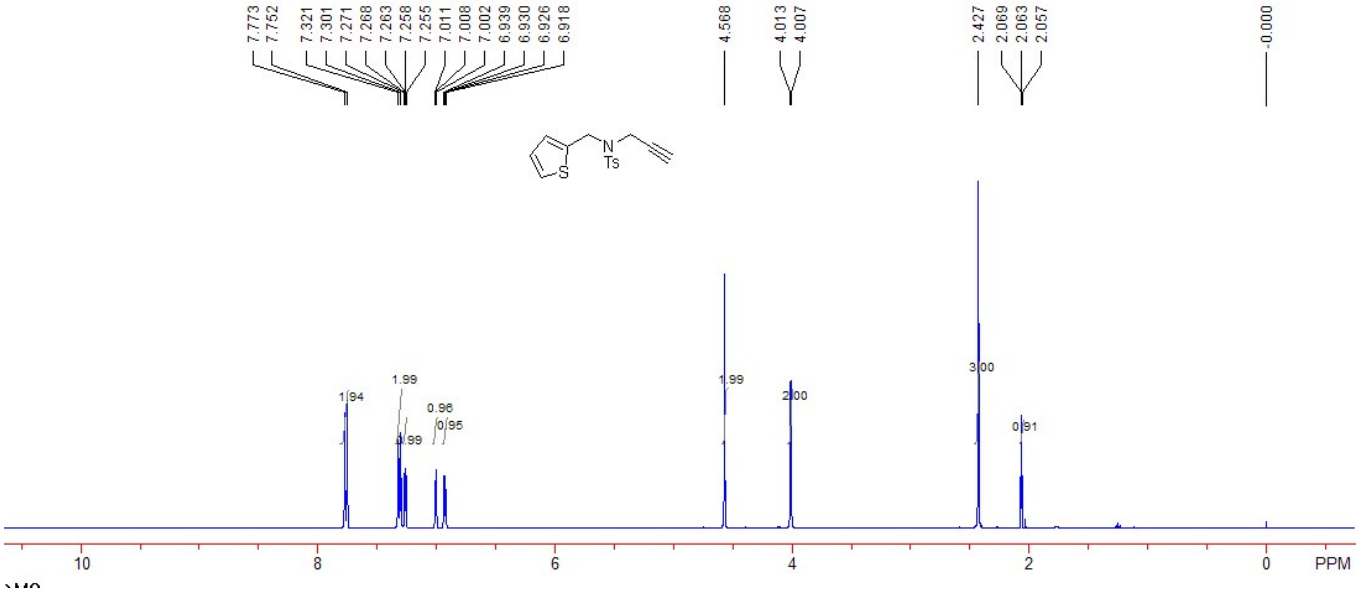


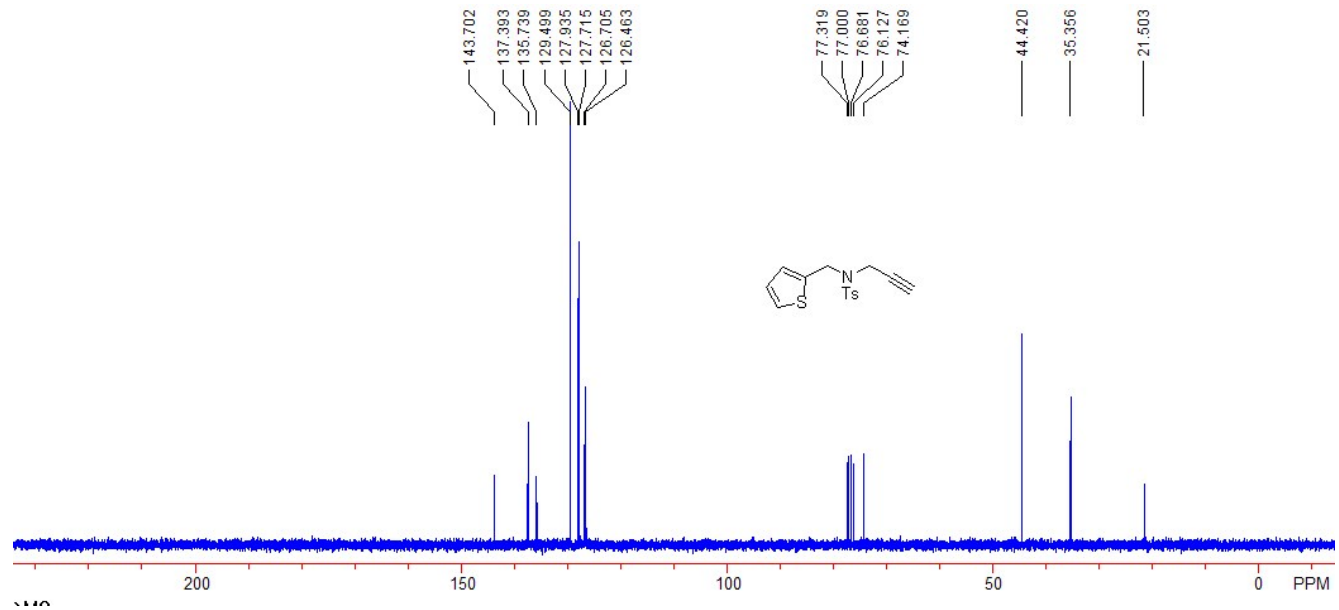
11. Characterization and spectra charts for compounds S1, S4 and S13

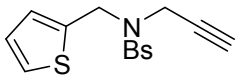


4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S1a

A white solid, 70% yield (3.20 g). M.p.: 78-80 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.06 (t, *J* = 2.4 Hz, 1H, CH), 2.43 (s, 3H, CH_3), 4.01 (d, *J* = 2.4 Hz, 2H, CH_2), 4.57 (s, 2H, CH_2), 6.93 (dd, *J* = 5.2, 3.6 Hz, 1H, ArH), 7.01 (d, *J* = 3.6 Hz, 1H, ArH), 7.26 (dd, *J* = 5.2, 1.6 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.4, 44.4, 74.2, 76.1, 126.5, 126.7, 127.7, 127.9, 129.5, 135.7, 137.4, 143.7. IR (CH_2Cl_2) ν 3270, 3104, 2975, 1717, 1598, 1343, 1328, 1159, 1091, 890, 817, 729, 659 cm^{-1}. MS (ESI) *m/z* (%): 323.08 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{15}H_{19}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 323.0882, found: 323.0879.

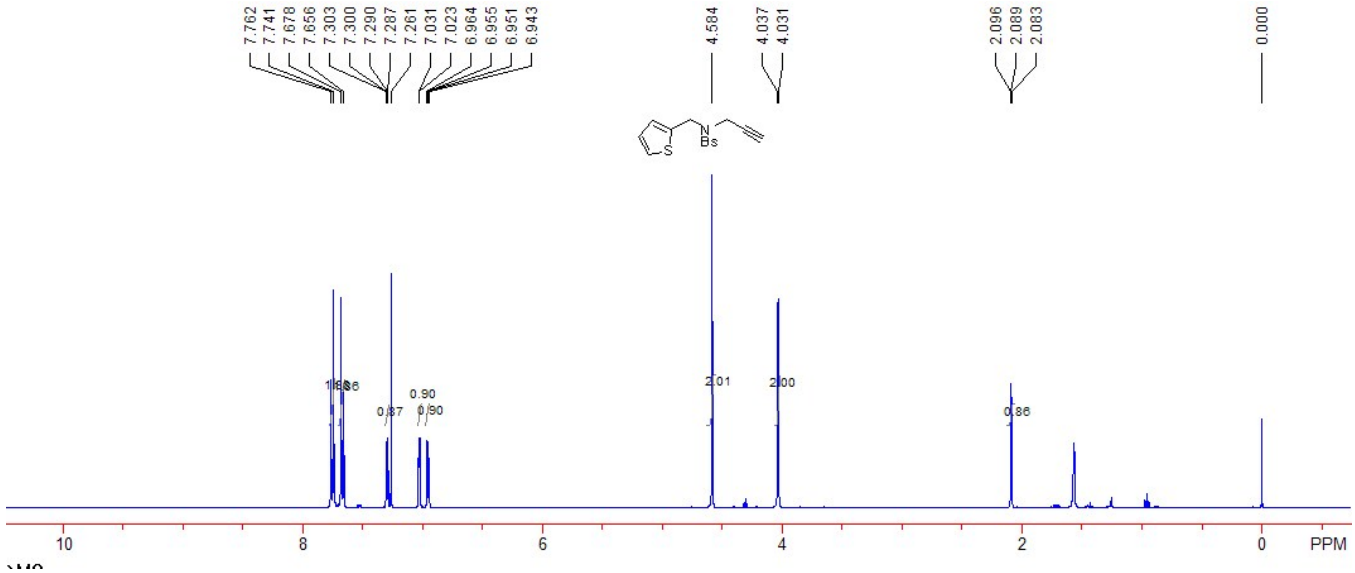


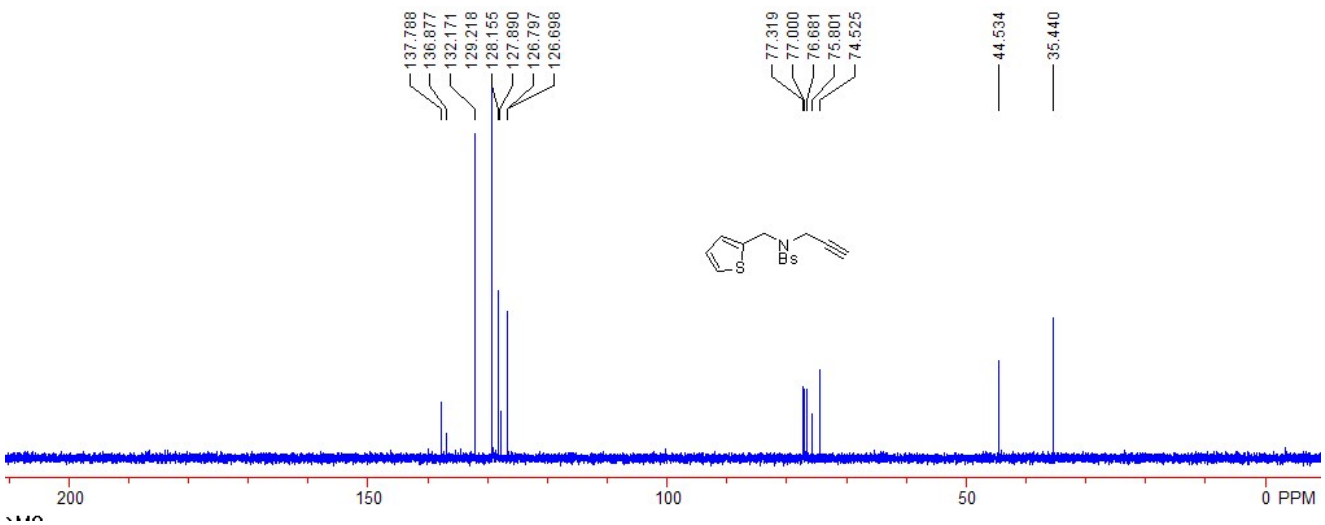


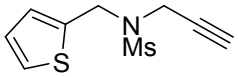


4-bromo-*N*-(prop-2-yn-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S1b

A white solid, 72% yield (879 mg). M.p.: 77-79 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.09 (t, *J* = 2.4 Hz, 1H, CH), 4.03 (d, *J* = 2.4 Hz, 2H, CH_2), 4.58 (s, 2H, CH_2), 6.95 (dd, *J* = 4.8, 3.2 Hz, 1H, ArH), 7.03 (dd, *J* = 3.2, 1.2 Hz, 1H, ArH), 7.30 (dd, *J* = 4.8, 1.2 Hz, 1H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH), 7.75 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 35.4, 44.5, 74.5, 75.8, 126.7, 126.8, 127.9, 128.1, 129.2, 132.2, 136.9, 137.8. IR (CH_2Cl_2) ν 3267, 3103, 1728, 1573, 1346, 1163, 1090, 891, 822, 730, 682, 614 cm^{-1}. MS (ESI) *m/z* (%): 386.98 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{14}H_{16}BrN_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 386.9831, found: 386.9829.

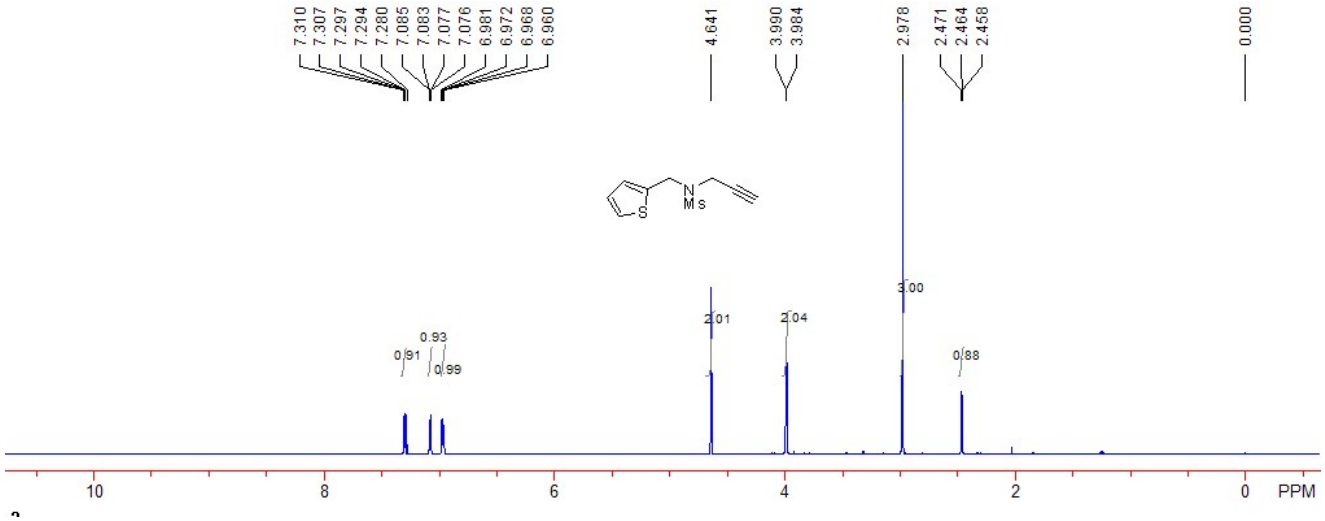


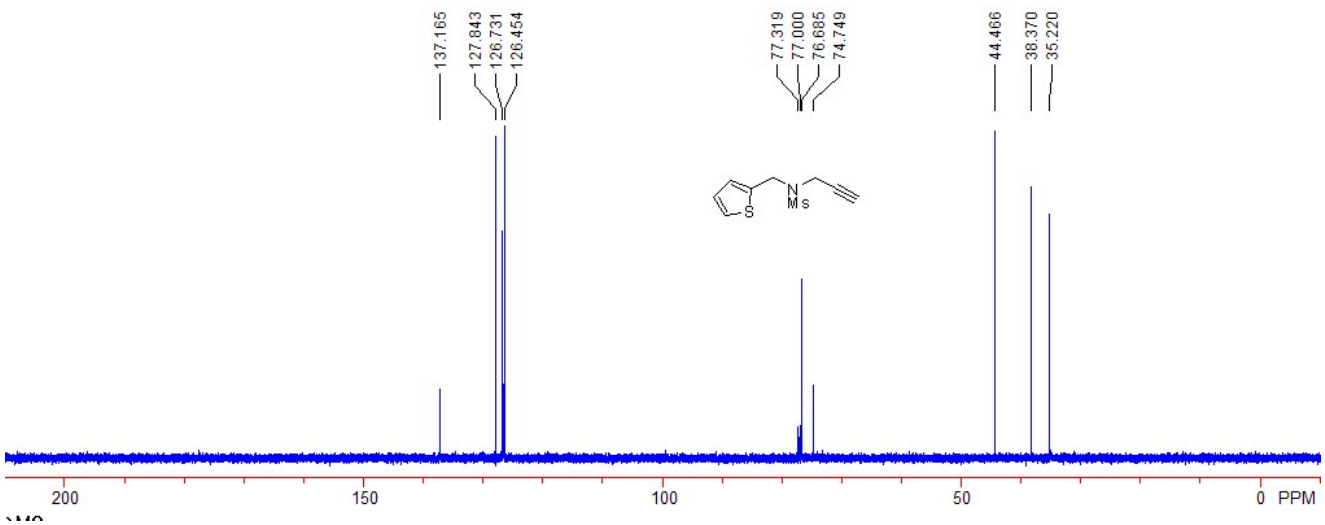


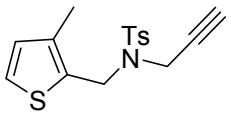


_N_-(prop-2-yn-1-yl)-_N_-(thiophen-2-ylmethyl)methanesulfonamide S1c

A white solid, 88% yield (1.20 g). M.p.: 69-71 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (t, J = 2.4 Hz, 1H, CH), 2.98 (s, 3H, CH_3), 3.98 (d, J = 2.4 Hz, 2H, CH_2), 4.64 (s, 2H, CH_2), 6.97 (dd, J = 5.2, 3.2 Hz, 1H, ArH), 7.07-7.09 (m, 1H, ArH), 7.30 (dd, J = 5.2, 1.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 35.2, 38.4, 44.5, 74.7, 76.7, 126.4, 126.7, 127.8, 137.2. IR (CH_2Cl_2) ν 3276, 2860, 1431, 1341, 1329, 1148, 1069, 894, 782, 704 cm^{-1}. MS (ESI) *m/z* (%): 247.05 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_9H_{15}N_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 247.0569, found: 247.0571.

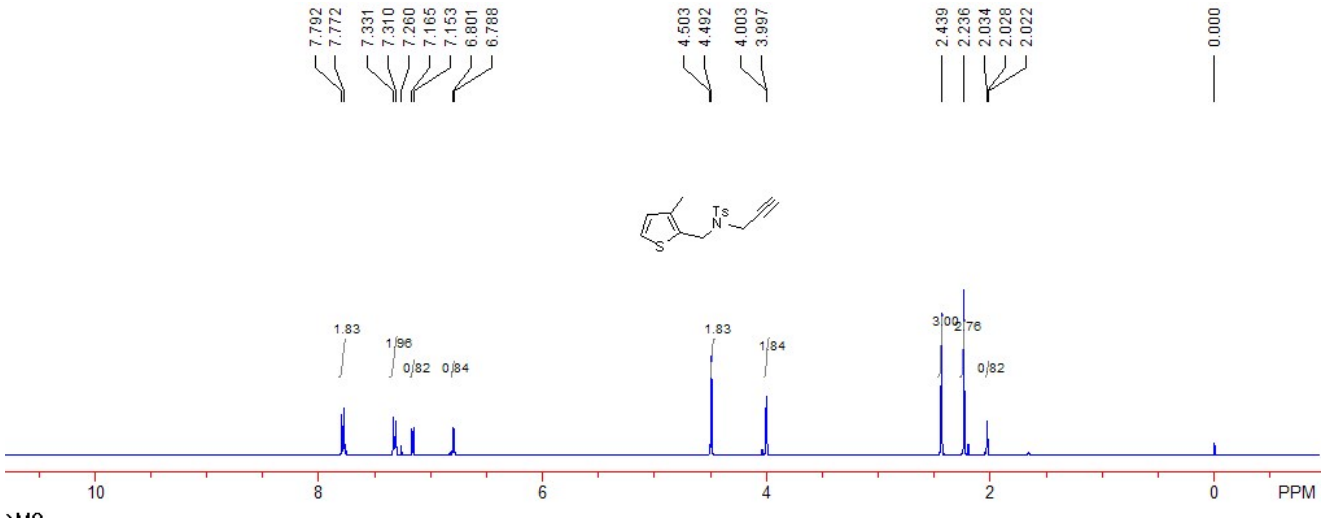


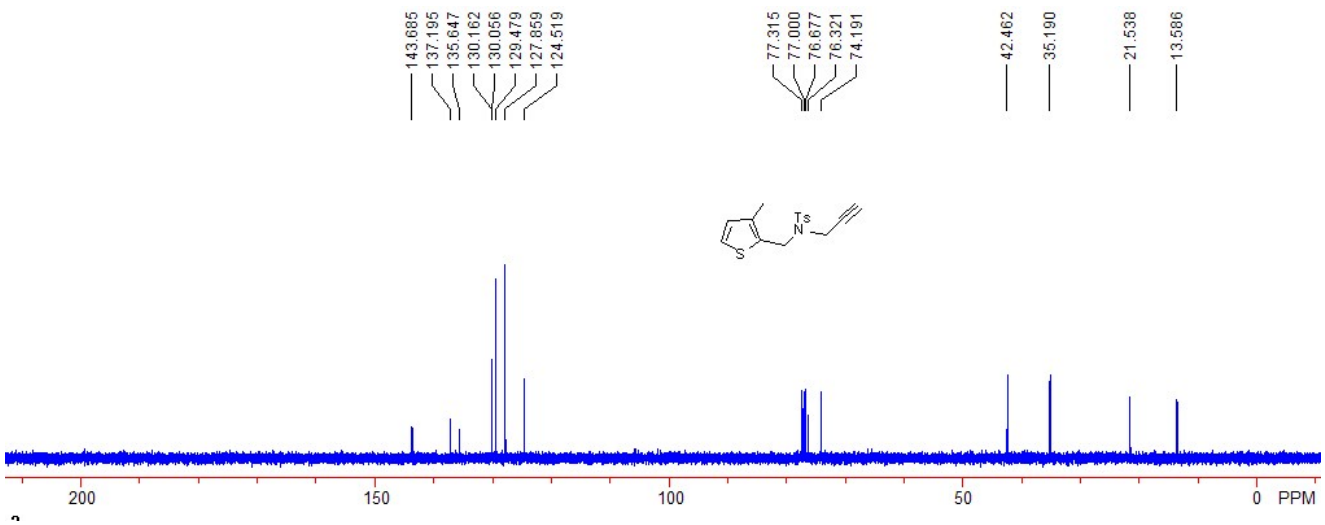


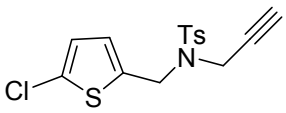


4-methyl-*N*-((3-methylthiophen-2-yl)methyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide S1d

A white solid, 43% yield (1.90 g). M.p.: 89-91 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03 (t, *J* = 2.4 Hz, 1H, CH), 2.24 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.00 (d, *J* = 2.4 Hz, 2H, CH_2), 4.49 (s, 2H, CH_2), 6.79 (d, *J* = 5.2 Hz, 1H, ArH), 7.15 (d, *J* = 5.2 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.78 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.6, 21.5, 35.2, 42.5, 74.2, 76.3, 124.5, 127.9, 129.5, 130.1, 130.2, 135.6, 137.2, 143.7. IR (CH_2Cl_2) ν 3258, 2865, 1598, 1340, 1329, 1161, 1090, 892, 810, 762, 724, 712, 658 cm^{-1}. MS (ESI) *m/z* (%): 337.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{16}H_{21}N_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 337.1039, found: 337.1041.

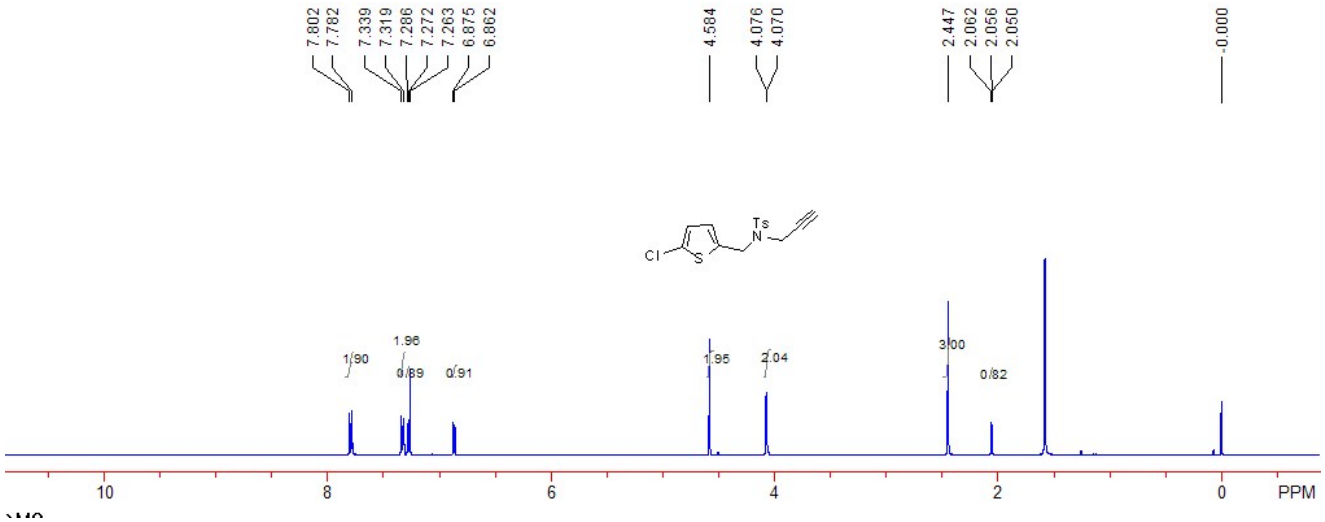


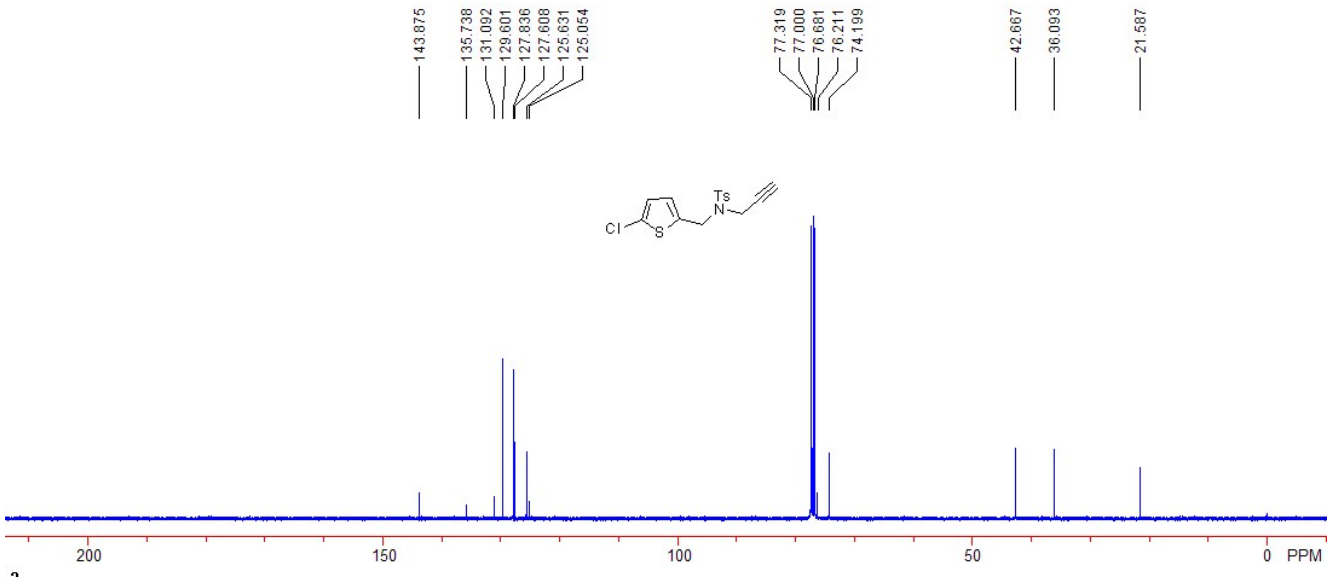


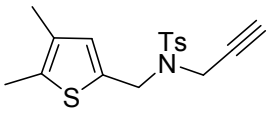


***N*-((5-chlorothiophen-2-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide S1e**

A white solid, 49% yield (998 mg). M.p.: 61-63 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.05 (t, J = 2.4 Hz, 1H, CH), 2.45 (s, 3H, CH_3), 4.07 (d, J = 2.4 Hz, 2H, CH_2), 4.58 (s, 2H, CH_2), 6.86 (d, J = 5.2 Hz, 1H, ArH), 7.28 (d, J = 5.2 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.79 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 36.1, 42.7, 74.2, 76.2, 125.0, 125.6, 127.6, 127.8, 129.6, 131.1, 135.7, 143.9. IR (CH_2Cl_2) ν 3292, 2356, 1597, 1442, 1349, 1329, 1160, 1096, 900, 813, 750, 713, 660 cm^{-1}. MS (ESI) *m/z* (%): 357.04 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{15}H_{18}ClN_2O_2S_2^{+1}(M+NH_4)^+$ requires 357.0493, found: 357.0494.

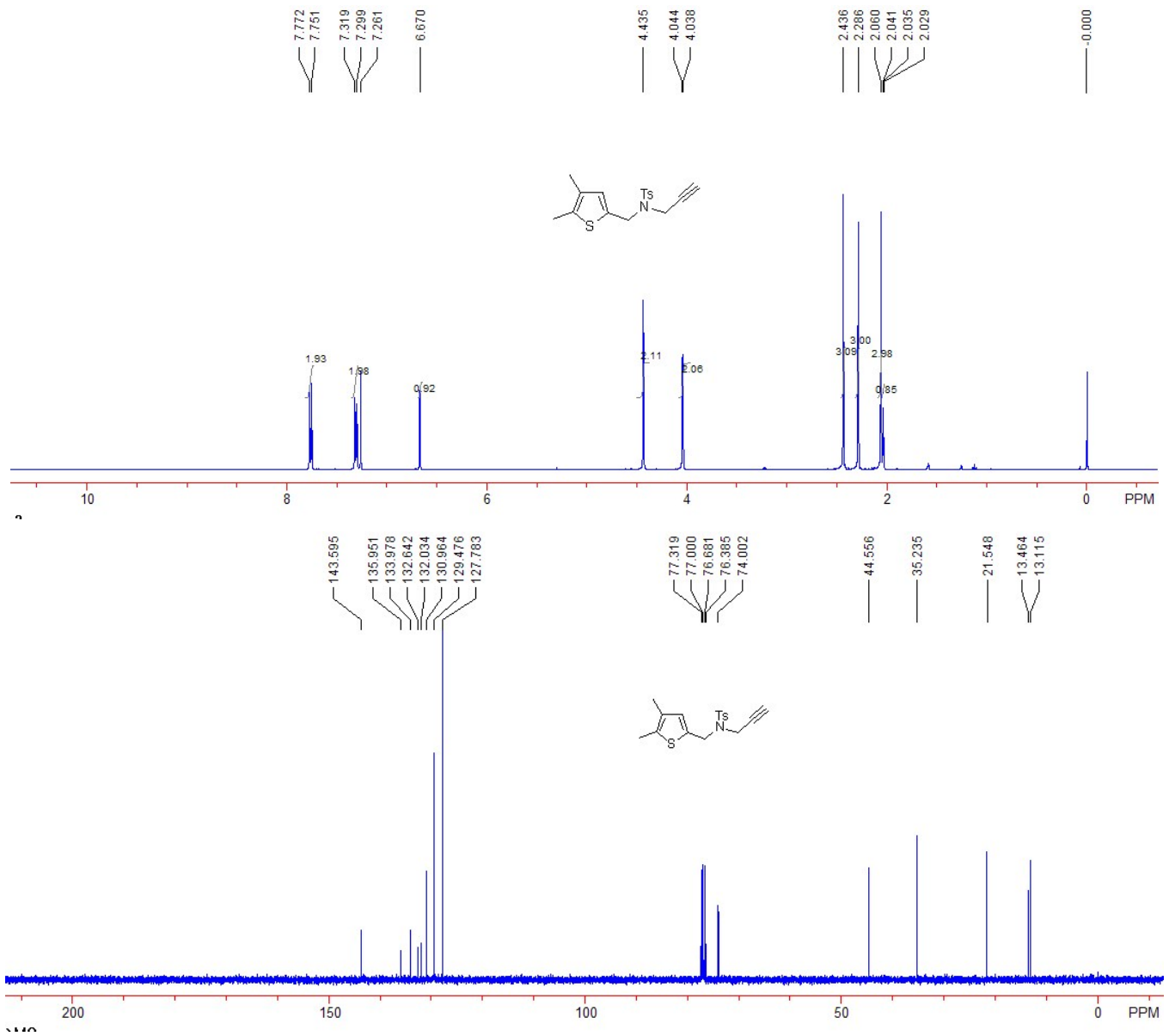


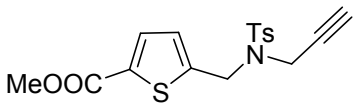




_N_-((4,5-dimethylthiophen-2-yl)methyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1f

A pale yellow liquid, 74% yield (344 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.04 (t, J = 2.4 Hz, 1H, CH), 2.06 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.04 (d, J = 2.4 Hz, 2H, CH_2), 4.44 (s, 2H, CH_2), 6.67 (s, 1H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.76 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 13.5, 21.6, 35.2, 44.6, 74.0, 76.4, 127.8, 129.5, 131.0, 132.0, 132.6, 134.0, 136.0, 143.6. IR (CH_2Cl_2) ν 3291, 2921, 2834, 1662, 1557, 1449, 1358, 1326, 1174, 1112, 1028, 945, 843, 706, 665 cm^{-1}. MS (ESI) *m/z* (%): 351.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 351.1195, found: 351.1186.

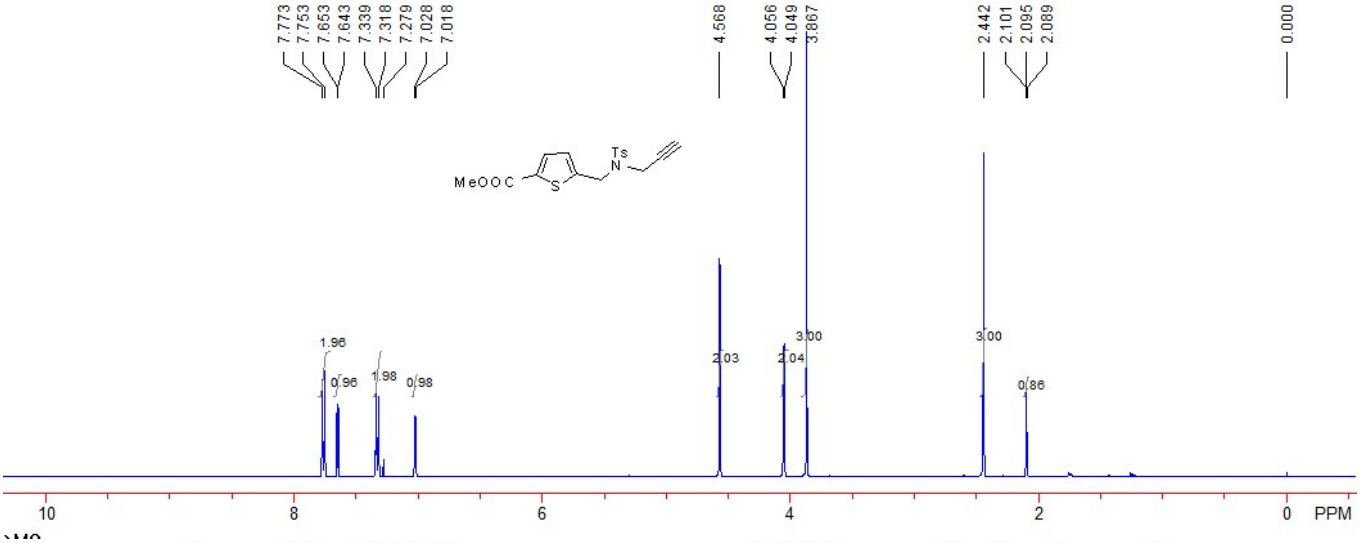


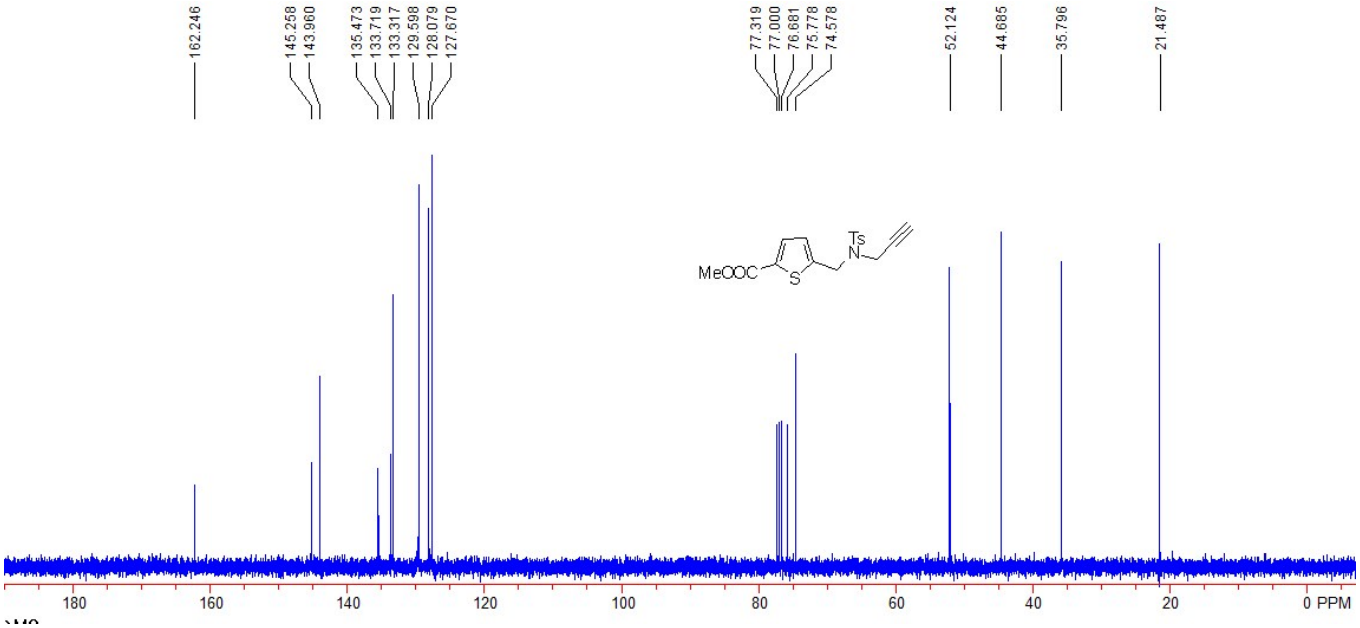


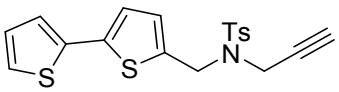
Methyl 5-(((4-methyl-*N*-(prop-2-yn-1-yl)phenyl)sulfonamido)methyl)thiophene-2-carboxylate S1h

A white solid, 90% yield (1.9 g). M.p.: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.10 (t, *J* = 2.4 Hz, 1H, CH), 2.44 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 4.05 (d, *J* = 2.4 Hz, 2H, CH_2), 4.57 (s, 2H, CH_2), 7.02 (d, *J* = 4.0 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 4.0 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.8, 44.7, 52.1, 74.6, 75.8, 127.7, 128.1, 129.6, 133.3, 133.7, 135.5, 144.0, 145.3, 162.2. IR (CH_2Cl_2) ν 3297, 1714, 1469, 1162, 1087, 893, 747, 662 cm^{-1}. MS (ESI) *m/z* (%): 381.09 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For

$C_{17}H_{21}N_2O_4S_2^{+1}[M+NH_4]^+$ requires 381.0937, found: 381.0935.



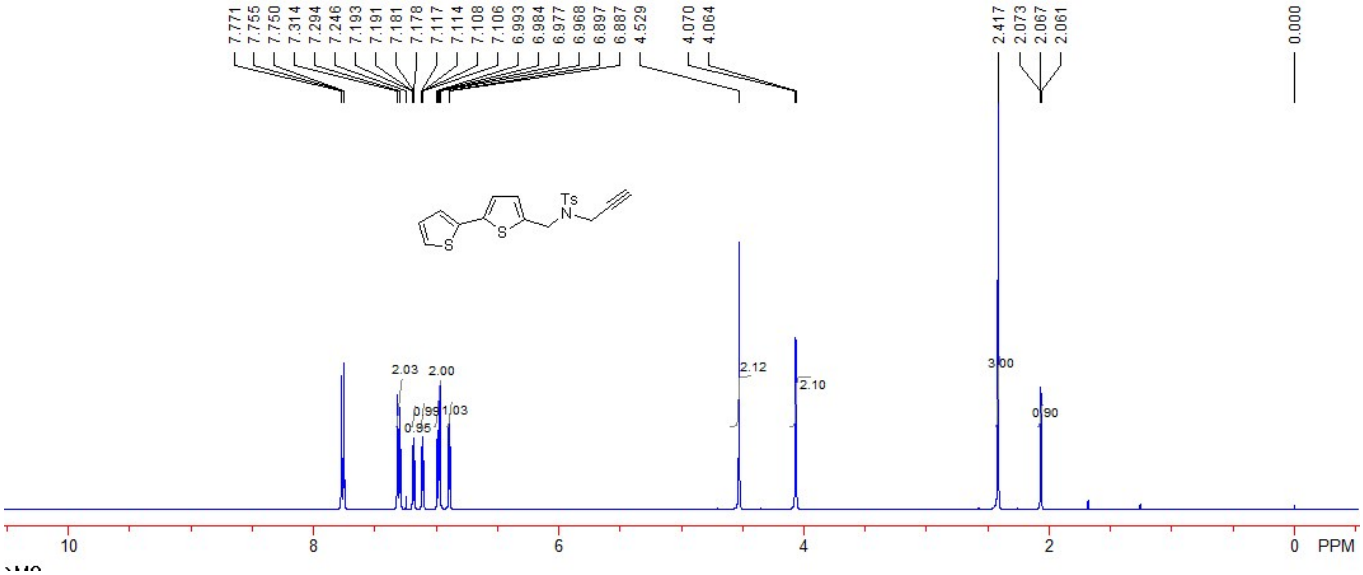


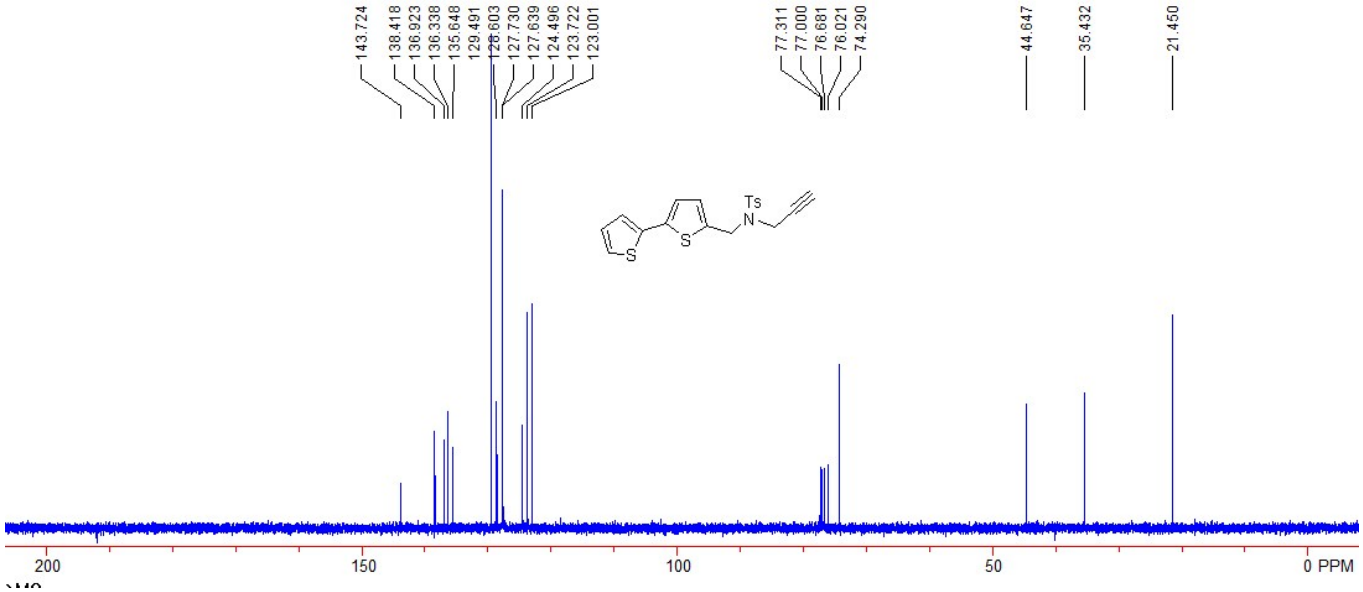


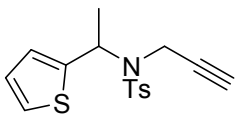
_N_-([2,2'-bithiophen]-5-ylmethyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1j

A white solid, 71% yield (897.7 mg). M.p.: 124-126 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.07 (t, J = 2.4 Hz, 1H, CH), 2.42 (s, 3H, CH_3), 4.06 (d, J = 2.4 Hz, 2H, CH_2), 4.53 (s, 2H, CH_2), 6.89 (d, J = 4.0 Hz, 1H, ArH), 6.96-7.00 (m, 2H, ArH), 7.11 (dd, J = 3.6, 1.2 Hz, 1H, ArH), 7.19 (dd, J = 4.8, 1.2 Hz, 1H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.76 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.4, 44.6, 74.3, 76.0, 123.0, 123.7, 124.5, 127.6, 127.7, 128.6, 129.5, 135.6, 136.3, 136.9, 138.4, 143.7. IR (CH_2Cl_2) ν 3285, 3104, 2916, 1370, 1328, 1157, 1090, 896, 812, 712, 679 cm^{-1}. MS (ESI) *m/z*

(%): 405.07 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{21}N_2O_2S_3^{+1}[M+NH_4]^+$ requires 405.0760, found: 405.0759.



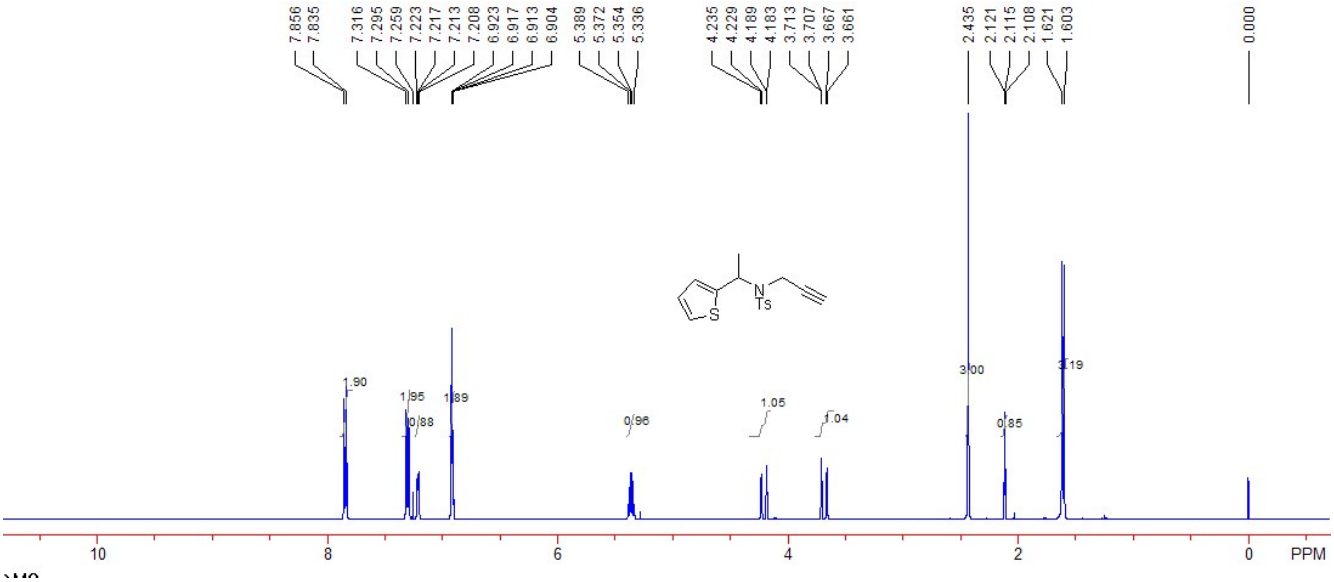


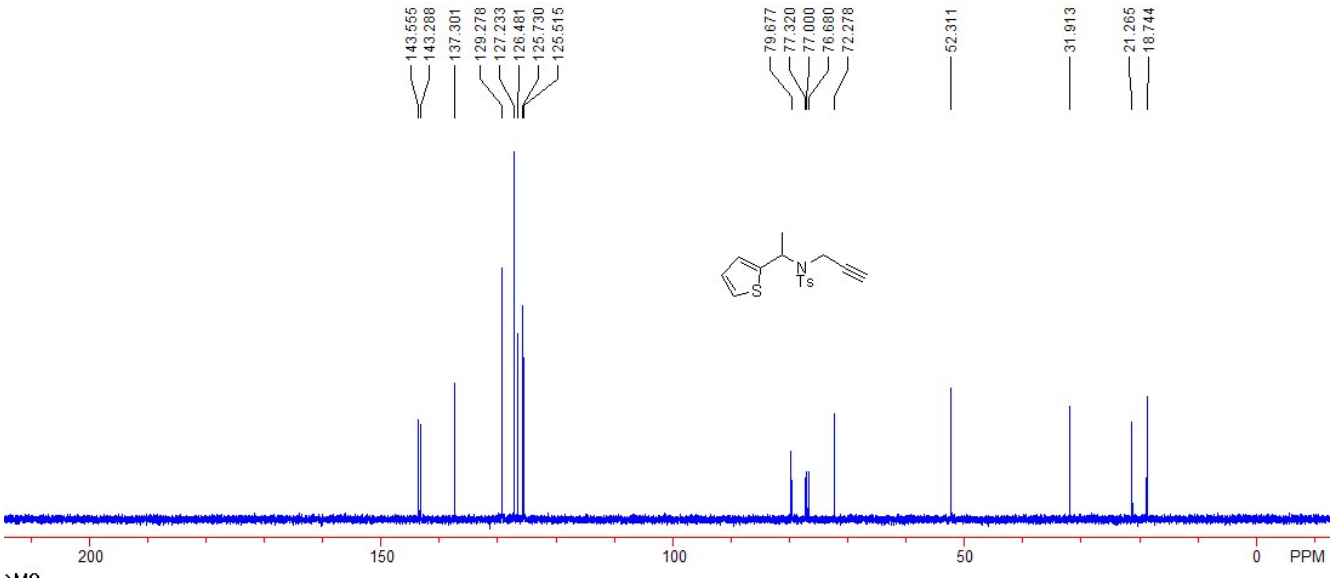


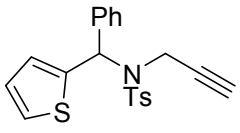
4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(thiophen-2-yl)ethyl)benzenesulfonamide S1k

A white solid, 78% yield (1.20 g). M.p.: 64-66 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.61 (d, J = 7.2 Hz, 3H, CH_3), 2.11 (t, J = 2.4 Hz, 1H, CH), 2.44 (s, 3H, CH_3), 3.68 (dd, J = 18.4, 2.4 Hz, 1H, CH_2), 4.20 (dd, J = 18.4, 2.4 Hz, 1H, CH_2), 5.36 (q, J = 7.2 Hz, 1H, CH), 6.90-6.93 (m, 2H, ArH), 7.21 (dd, J = 4.0, 2.0 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.84 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100

MHz, TMS) δ 18.8, 21.3, 31.9, 52.3, 72.3, 79.7, 125.5, 125.7, 126.5, 127.2, 129.3, 137.3, 143.3, 143.6. IR (CH_2Cl_2) ν 3288, 2954, 2921, 2851, 1735, 1597, 1494, 1349, 1185, 1161, 1092, 929, 898, 750, 658 cm^{-1}. MS (ESI) *m/z* (%): 337.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{16}H_{21}N_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 337.1039, found: 337.1041.



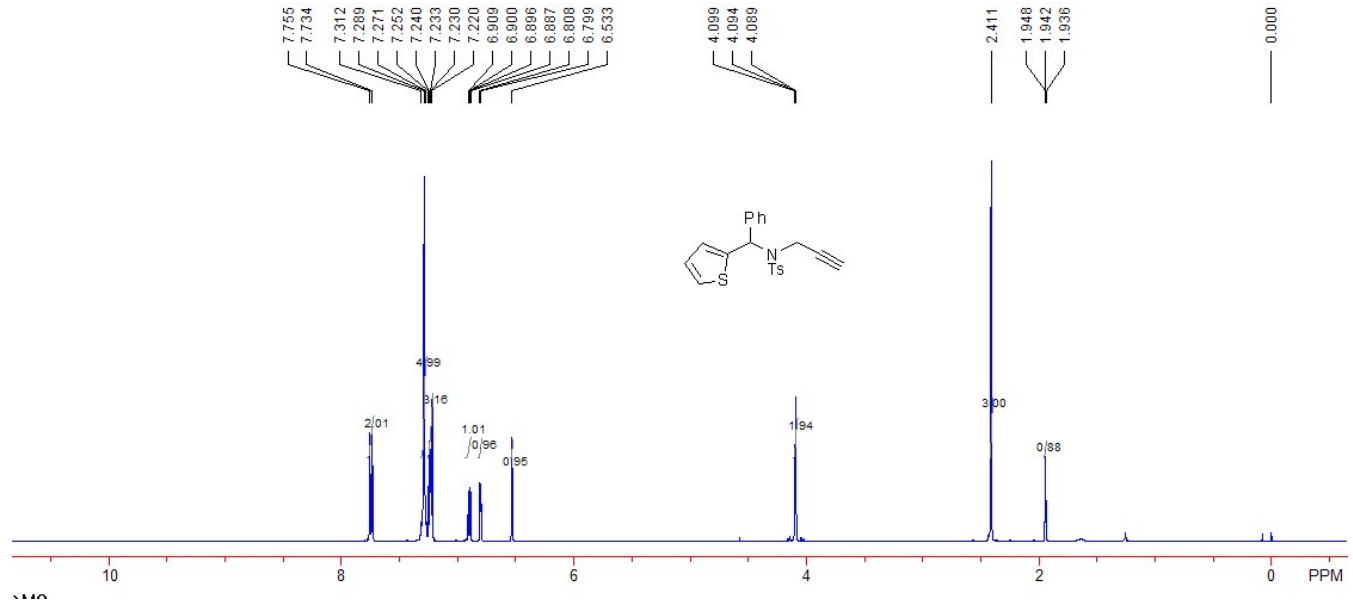


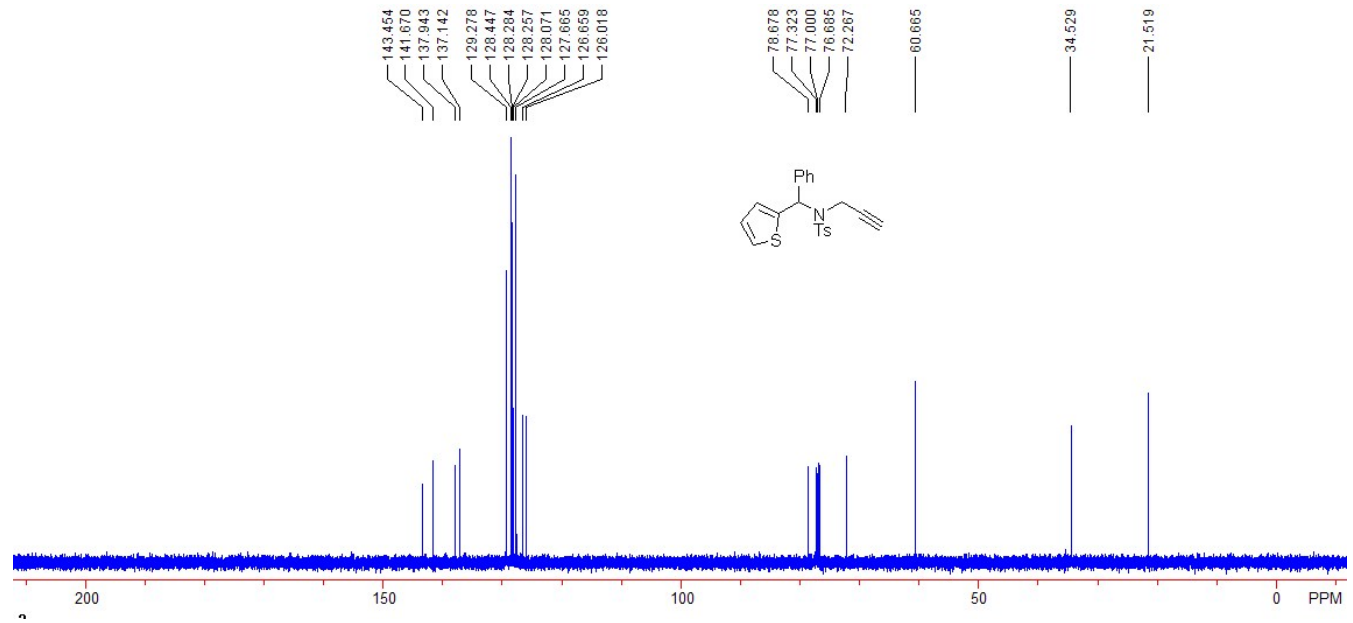


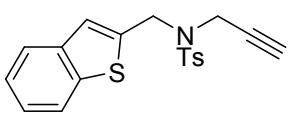
4-methyl-*N*-(phenyl(thiophen-2-yl)methyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide S1l

A white solid, 99% yield (755 mg). M.p.: 130-132 °C. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.94 (t, *J* = 2.4 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 4.08-4.10 (m, 2H, CH_2), 6.53 (s, 1H, CH), 6.81 (d, *J* = 3.6 Hz, 1H,

ArH), 6.90 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.22-7.26 (m, 3H, ArH), 7.29 (s, 5H, ArH), 7.74 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 34.5, 60.7, 72.3, 78.7, 126.0, 126.7, 127.7, 128.1, 128.25, 128.28, 128.44, 129.3, 137.1, 137.9, 141.7, 143.4. IR (CH_2Cl_2) ν 3276, 2960, 2925, 2854, 1597, 1495, 1337, 1159, 1091, 904, 813, 747, 699, 663 cm^{-1}. MS (ESI) *m/z* (%): 399.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{21}H_{23}N_2O_2S_2^{+1}$ $[M+NH_4]^+$ requires 399.1195, found: 399.1197.



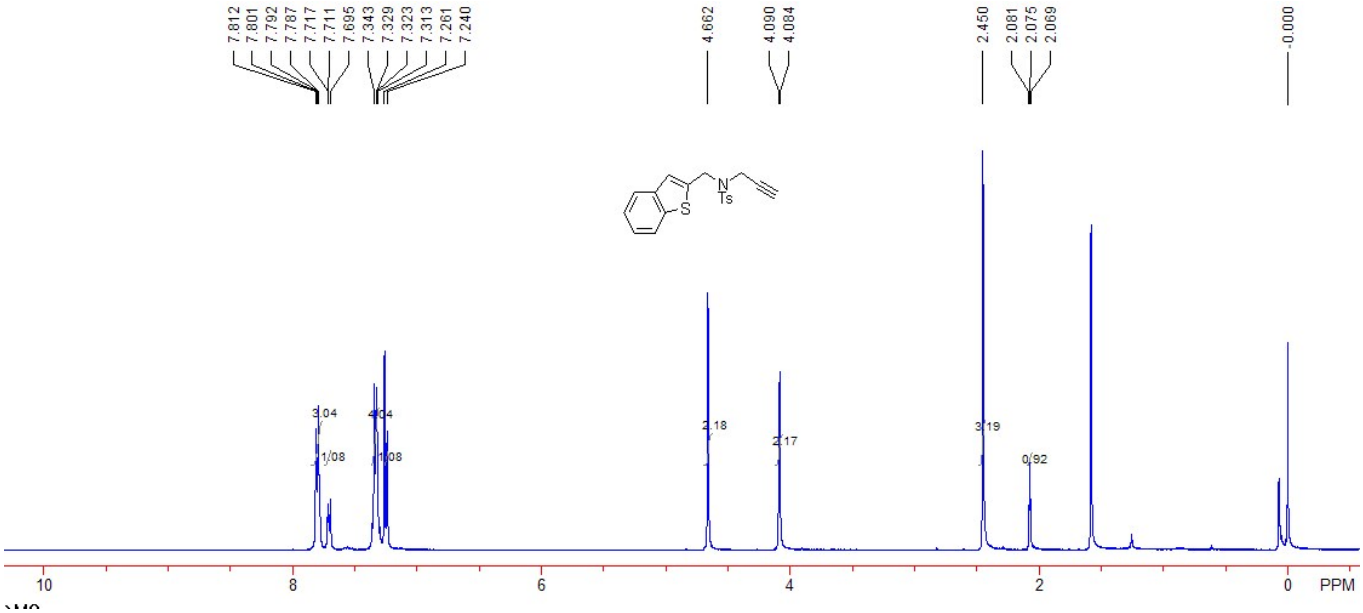


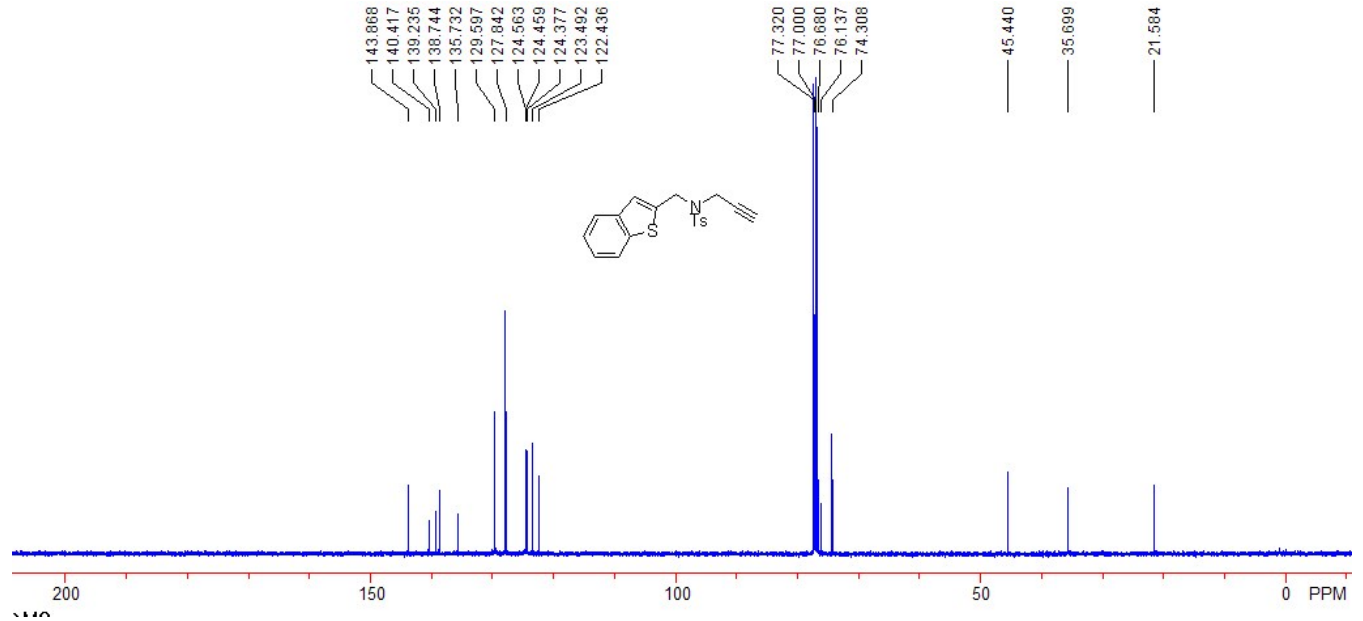


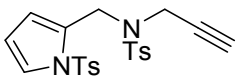
_N_-(benzo[_b_]thiophen-2-ylmethyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1q

A white solid, 57% yield (1.20 g). M.p.: 90-92 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.08 (t, J = 2.4

Hz, 1H, CH), 2.45 (s, 3H, CH_3), 4.08 (d, J = 2.4 Hz, 2H, CH_2), 4.66 (s, 2H, CH_2), 7.24 (s, 1H, ArH), 7.31-7.35 (m, 4H, ArH), 7.71 (dd, J = 4.8, 2.4 Hz, 1H, ArH), 7.77-7.82 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.7, 45.4, 74.3, 76.1, 122.4, 123.5, 124.4, 124.5, 124.6, 127.8, 129.6, 135.7, 138.7, 139.2, 140.4, 143.9. IR (CH_2Cl_2) ν 3296, 3248, 2970, 2909, 2359, 1599, 1436, 1347, 1330, 1261, 1159, 1095, 935, 810, 752, 660 cm^{-1}. MS (ESI) *m/z* (%): 373.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{21}N_2O_2S_2^{+1}(M+NH_4)^+$ requires 373.1039, found: 373.1033.



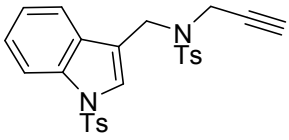




4-methyl-*N*-(prop-2-yn-1-yl)-*N*-((1-tosyl-1*H*-pyrrol-2-yl)methyl)benzenesulfonamide S1r

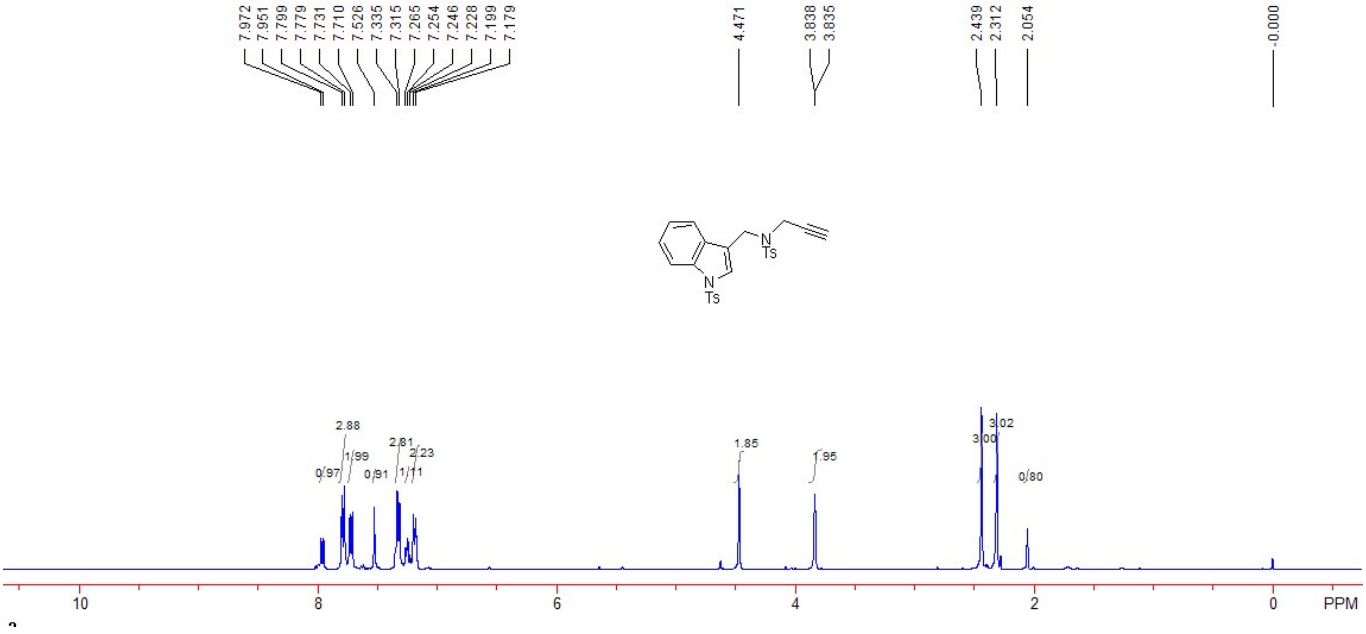
A white solid, 86% yield (1.10 g).

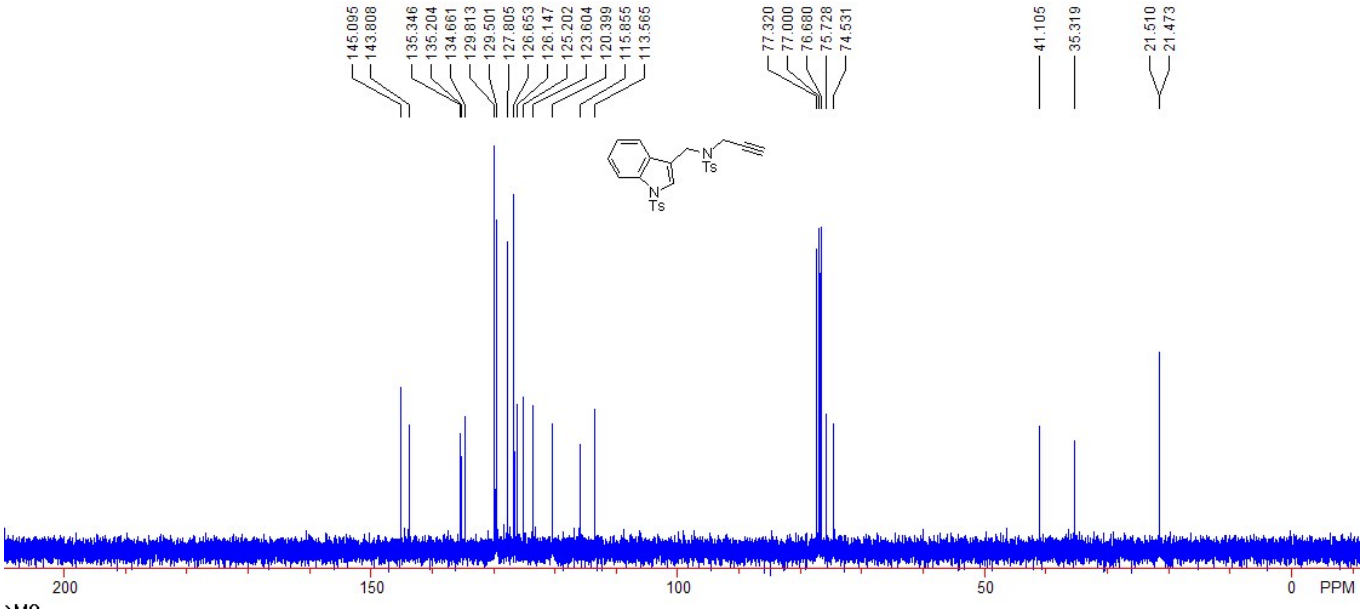
The preparation of substrate **S1r** has been detailed in the reference.[2]

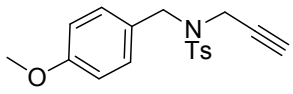


4-methyl-*N*-(prop-2-yn-1-yl)-*N*-((1-tosyl-1*H*-indol-3-yl)methyl)benzenesulfonamide S1s

A white solid, 89% yield (2.60 g). M.p.: 77-79 °C (this starting material is quite labile and it will contain some impurity when it is stored in refrigerator). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.04 (t, *J* = 2.4 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.84 (d, *J* = 2.4 Hz, 2H, CH_2), 4.47 (s, 2H, CH_2), 7.20 (d, *J* = 8.4 Hz, 2H, ArH), 7.24-7.27 (m, 1H, ArH), 7.31-7.34 (m, 3H, ArH), 7.52 (s, 1H, ArH), 7.72 (d, *J* = 8.4 Hz, 2H, ArH), 7.77-7.80 (m, 3H, ArH), 7.96 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.47, 21.51, 35.3, 41.1, 74.5, 75.7, 113.6, 115.9, 120.4, 123.6, 125.2, 126.1, 126.6, 127.8, 129.5, 129.8, 134.7, 135.2, 135.3, 143.8, 145.1. IR (CH_2Cl_2) ν 3262, 2921, 2338, 1597, 1450, 1363, 1331, 1158, 1097, 975, 811, 703, 660 cm^{-1}. MS (ESI) *m/z* (%): 510.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{26}H_{28}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 510.1516, found: 510.1518.



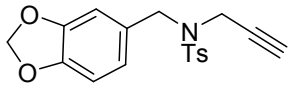




_N_-(4-methoxybenzyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1t

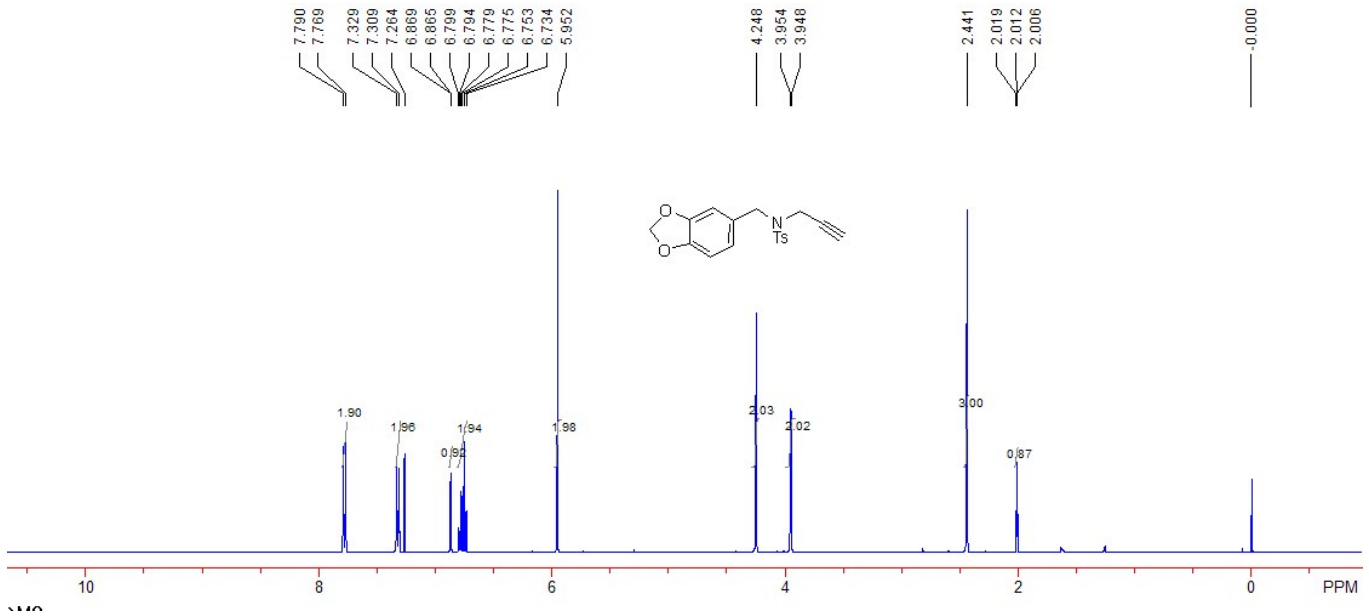
A white solid, 95% yield (2.00 g).

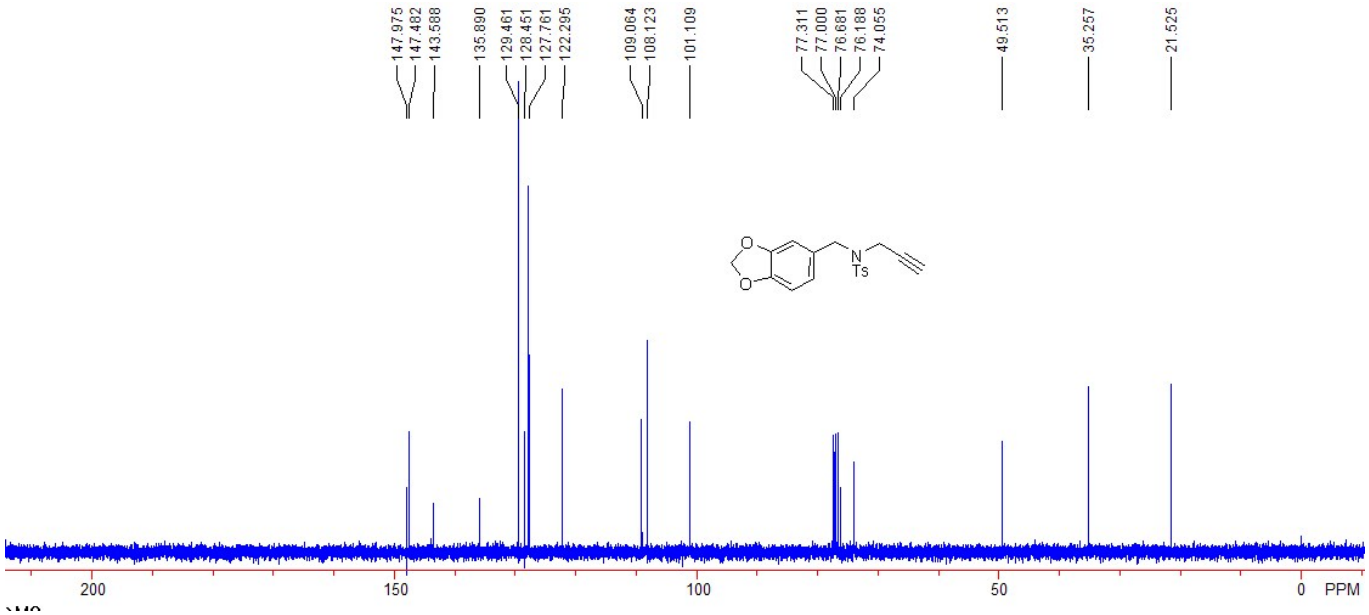
The preparation of substrate **S1t** has been detailed in the reference.[3]

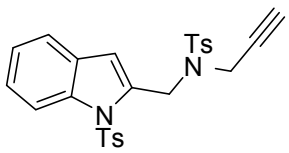


_N_-(benzo[_d_][1,3]dioxol-5-ylmethyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1u

A white solid, 64% yield (883 mg). M.p.: 140-142 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.01 (t, J = 2.4 Hz, 1H, CH), 2.44 (s, 3H, CH_3), 3.95 (d, J = 2.4 Hz, 2H, CH_2), 4.25 (s, 2H, CH_2), 5.95 (s, 2H, CH_2), 6.73-6.80 (m, 2H, ArH), 6.87 (d, J = 1.6 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.78 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.3, 49.5, 74.1, 76.2, 101.1, 108.1, 109.1, 122.3, 127.8, 128.4, 129.5, 135.9, 143.6, 147.5, 148.0. IR (CH_2Cl_2) ν 3300, 2921, 1612, 1493, 1454, 1345, 1325, 1159, 1091, 927, 901, 813, 755, 662 cm^{-1}. MS (ESI) *m/z* (%): 361.12 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{21}N_2O_4S^{+1}[M+NH_4]^+$ requires 361.1217, found: 361.1217.



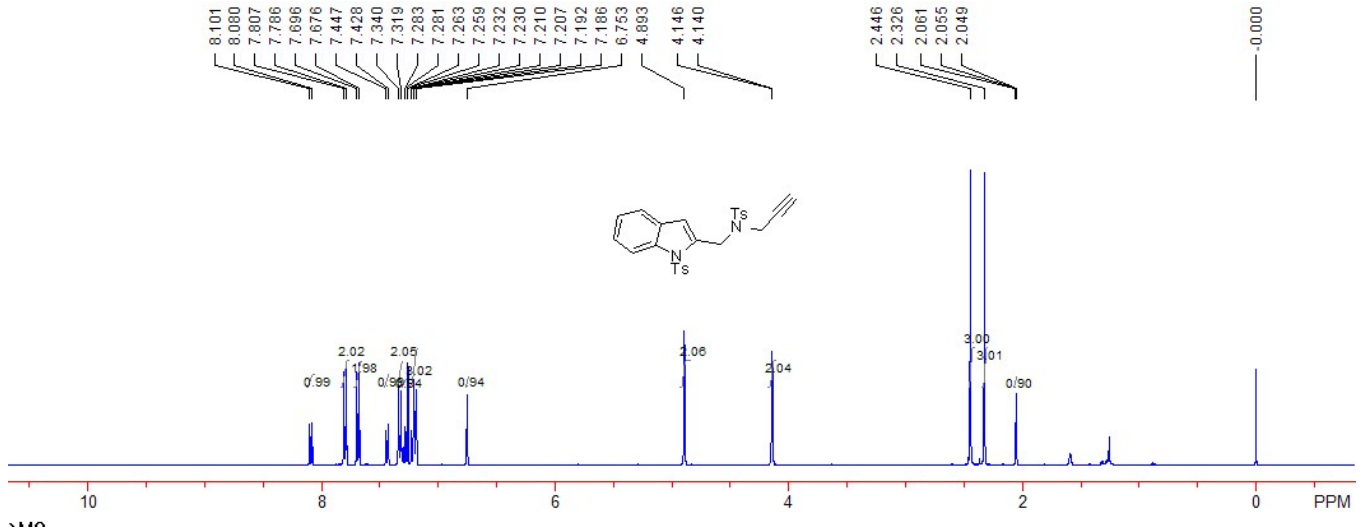


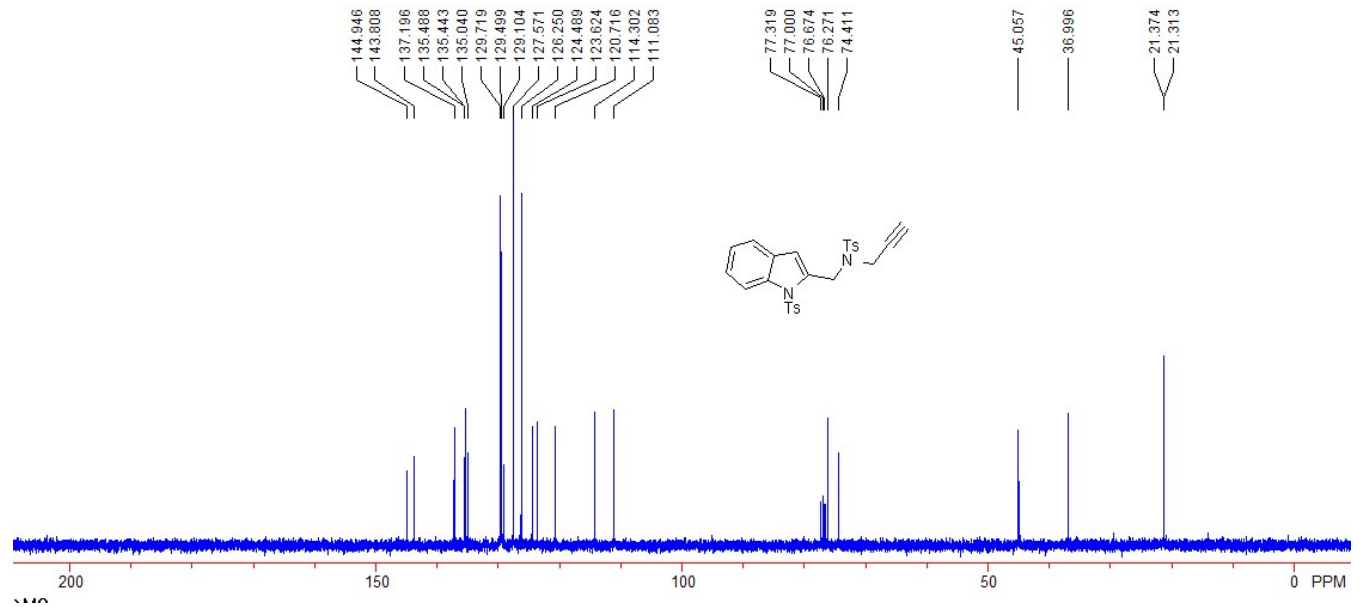


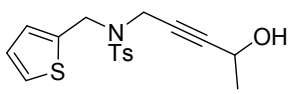
4-methyl-*N*-(prop-2-yn-1-yl)-*N*-((1-tosyl-1*H*-indol-2-yl)methyl)benzenesulfonamide S1w

A white solid, 51% yield (179 mg). M.p.: 60-63 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.05 (t, *J* = 2.4 Hz, 1H, CH), 2.33 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.15 (d, *J* = 2.4 Hz, 2H, CH_2), 4.89 (s, 2H, CH_2), 6.75 (s, 1H, ArH), 7.18-7.24 (m, 3H, ArH), 7.26-7.31 (m, 1H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.43 (d, *J* = 7.6 Hz, 1H, ArH), 7.68 (d, *J* = 8.0 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 2H, ArH), 8.09 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 21.4, 37.0, 45.1, 74.4, 76.3, 111.1, 114.3, 120.7, 123.6,

124.5, 126.2, 127.6, 129.1, 129.5, 129.7, 135.0, 135.4, 135.5, 137.2, 143.8, 144.9. IR (CH_2Cl_2) ν 3304, 2922, 1596, 1453, 1369, 1305, 1155, 1090, 937, 814, 703, 661 cm^{-1}. MS (ESI) *m/z* (%): 510.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{26}H_{28}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 510.1516, found: 510.1516.



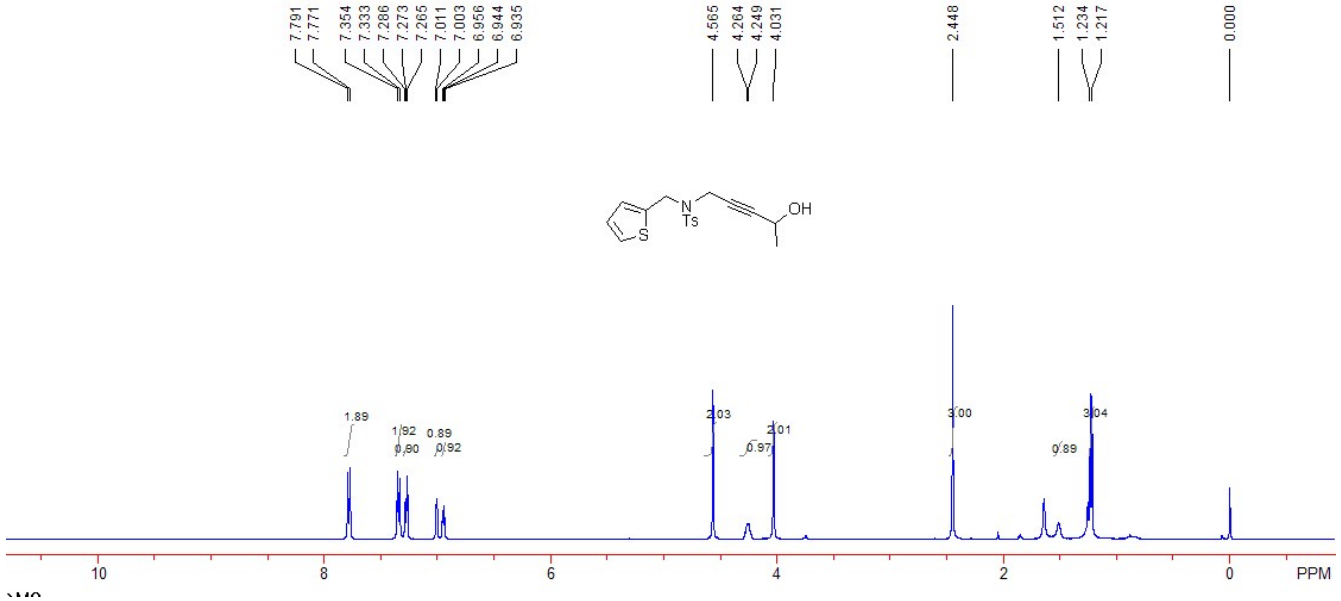


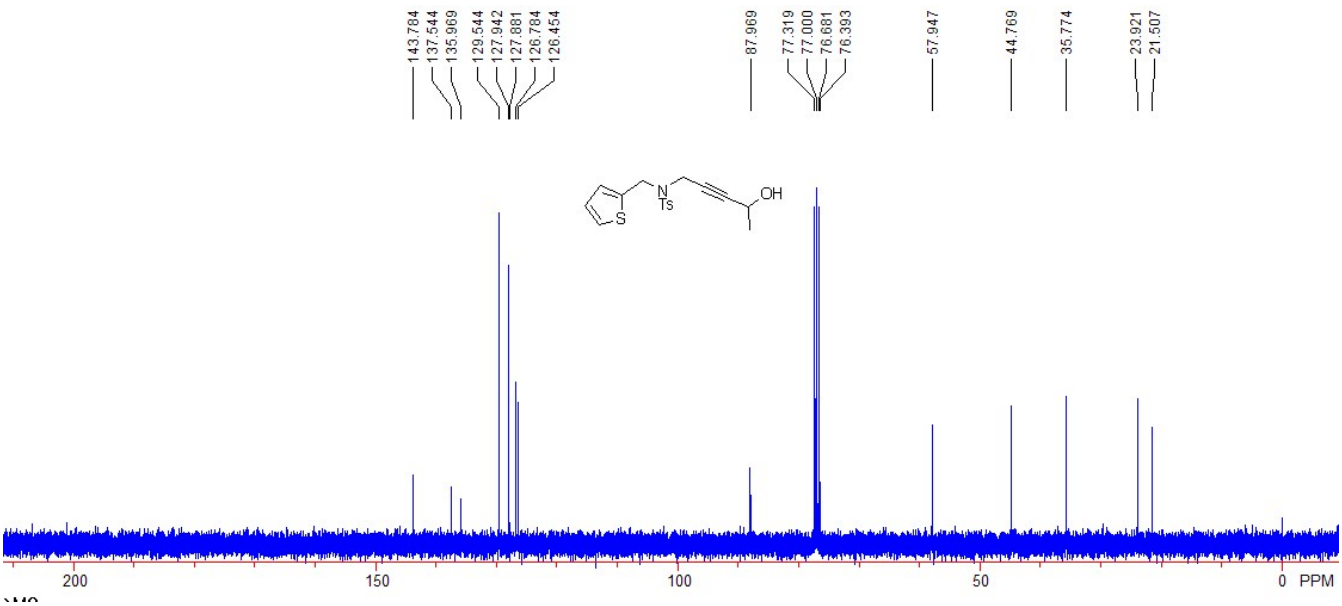


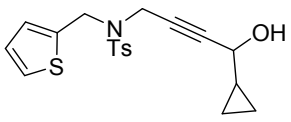
***N*-(4-hydroxypent-2-yn-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S4a**

A white liquid, 98% yield (3.49 g). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.22 (d, *J* = 6.8 Hz, 3H, CH_3), 1.51 (br, 1H, OH), 2.45 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 4.25 (d, *J* = 6.4 Hz, 1H, CH), 4.57 (s, 2H, CH_2), 6.94 (dd, *J* = 4.8, 3.6 Hz, 1H, ArH), 7.01 (d, *J* = 3.6 Hz, 1H, ArH), 7.28 (d, *J* = 4.8 Hz, 1H, ArH), 7.34 (d, *J* = 8.0 Hz, 2H, ArH), 7.78 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 24.0,

35.8, 44.8, 58.0, 76.4, 88.0, 126.4, 126.8, 127.9, 128.0, 129.5, 136.0, 137.5, 143.8. IR (CH_2Cl_2) ν 3279, 1713, 1436, 1342, 1326, 1152, 1082, 965, 897, 853, 784, 706 cm^{-1}. MS (ESI) *m/z* (%): 367.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 367.1145, found: 367.1145.



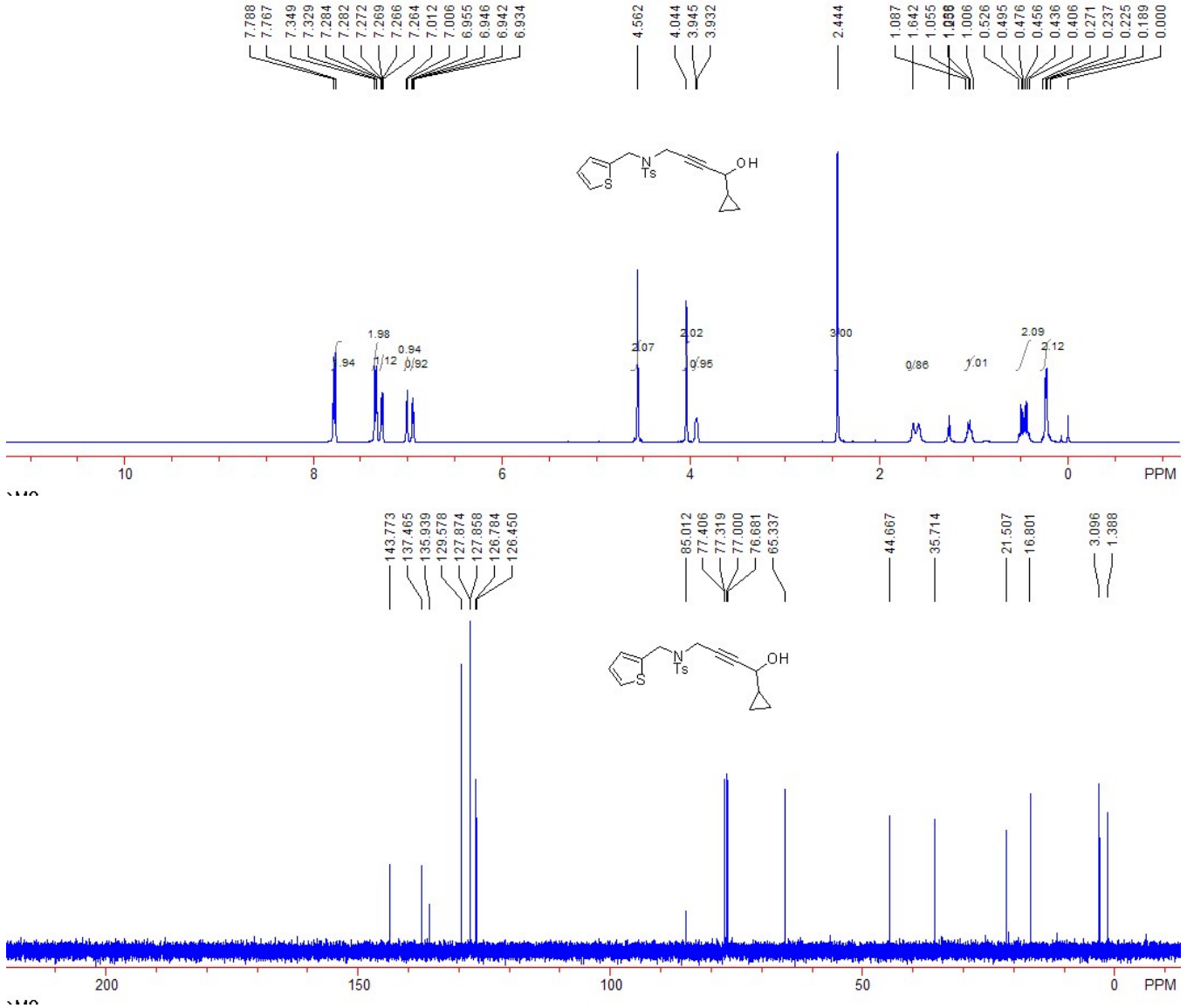


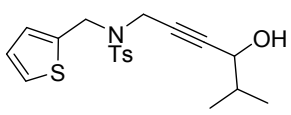


***N*-(4-cyclopropyl-4-hydroxybut-2-yn-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S4b**

A white liquid, 91% yield (5.11 g). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.18-0.28 (m, 2H, CH_2), 0.40-0.53 (m, 2H, CH_2), 1.00-1.09 (m, 1H, CH), 1.61 (d, *J* = 24.8 Hz, 1H, OH), 2.44 (s, 3H, CH_3), 3.94 (d, *J* =

5.2 Hz, 1H, CH), 4.04 (s, 2H, CH_2), 4.56 (s, 2H, CH_2), 6.94 (dd, *J* = 4.8, 3.2 Hz, 1H, ArH), 7.01 (d, *J* = 2.4 Hz, 1H, ArH), 7.27 (dd, *J* = 5.2, 1.2 Hz, 1H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.77 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.4, 3.1, 16.8, 21.5, 35.7, 44.7, 65.3, 77.4, 85.0, 126.4, 126.8, 127.86, 127.87, 129.6, 135.9, 137.5, 143.8. IR (CH_2Cl_2) ν 3502, 2921, 2851, 1597, 1436, 1347, 1328, 1158, 1092, 900, 854, 745, 705 cm^{-1}. MS (ESI) *m/z* (%): 393.13 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{25}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 393.1301, found: 393.1305.

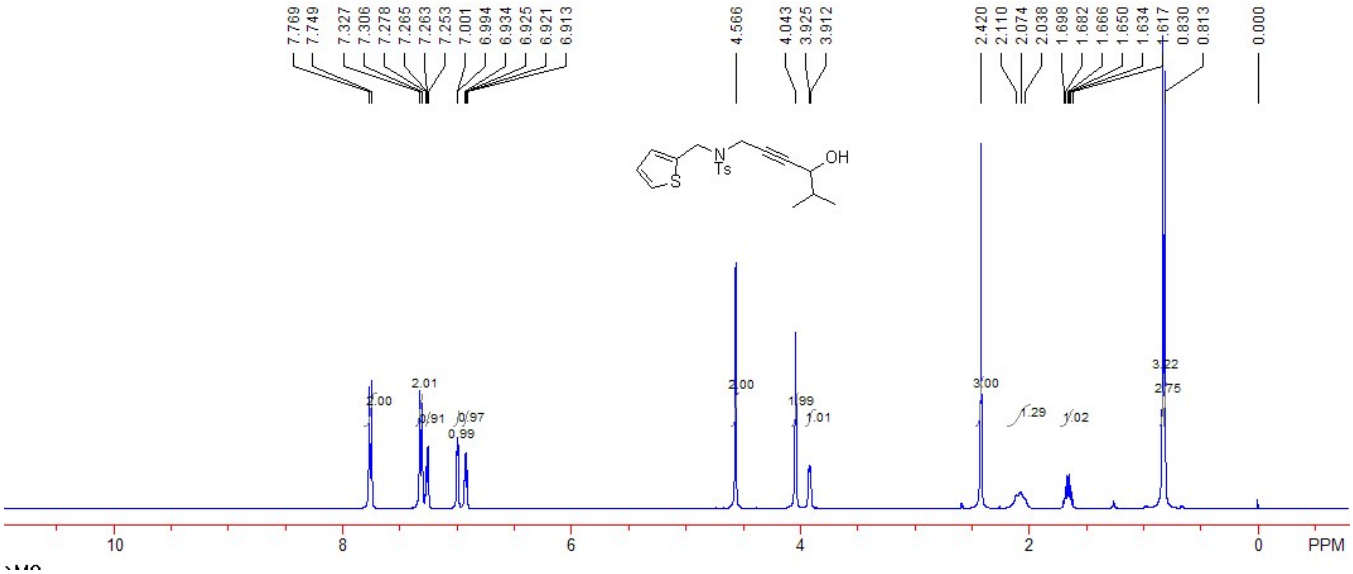


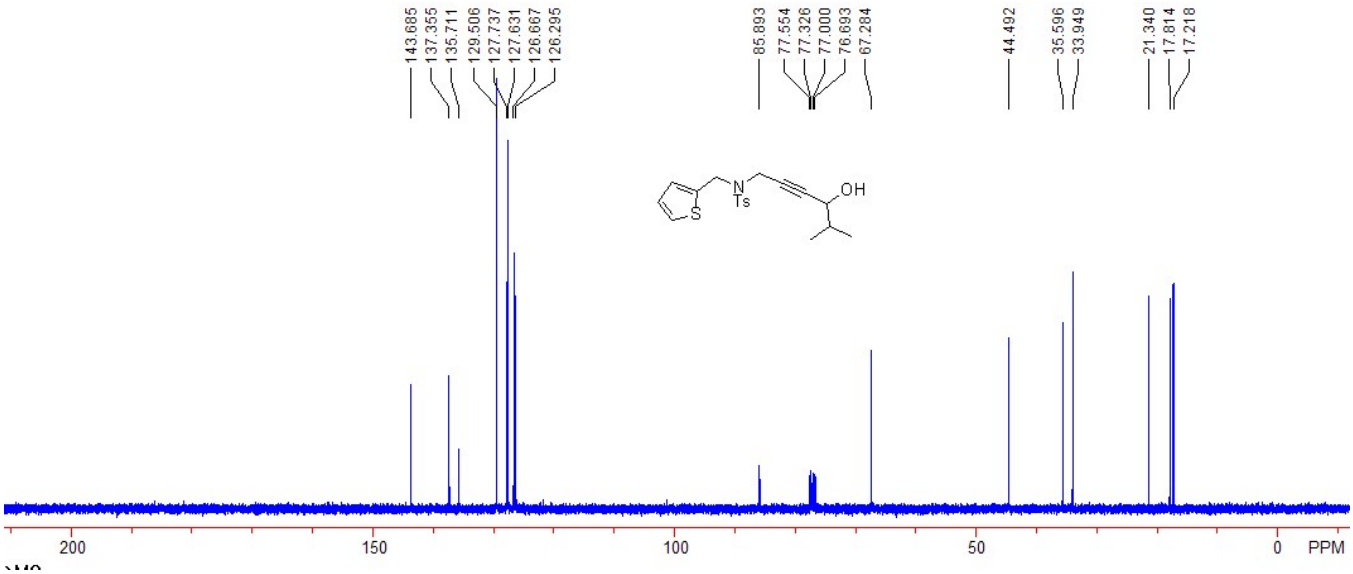


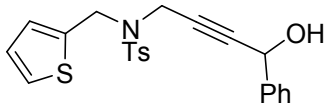
_N_-(4-hydroxy-5-methylhex-2-yn-1-yl)-4-methyl-_N_-(thiophen-2-ylmethyl)benzenesulfonamide S4c

A white liquid, 71% yield (2.69 g). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.81 (s, 3H, CH_3), 0.83 (s, 3H,

CH_3), 1.61-1.70 (m, 1H, CH_2), 2.11 (br, 1H, OH), 2.42 (s, 3H, CH_3), 3.92 (d, *J* = 5.2 Hz, 1H, CH), 4.04 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 6.92 (dd, *J* = 4.8, 3.2 Hz, 1H, ArH), 7.00 (d, *J* = 2.8 Hz, 1H, ArH), 7.27 (d, *J* = 4.8 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.75 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.2, 17.8, 21.3, 33.9, 35.6, 44.5, 67.3, 77.5, 85.9, 126.3, 126.7, 127.6, 127.7, 129.5, 135.7, 137.3, 143.7. IR (CH_2Cl_2) ν 3675, 2967, 2901, 1407, 1260, 1119, 867, 797, 662 cm^{-1}. MS (ESI) *m/z* (%): 395.14 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{27}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 395.1458, found: 395.1459.

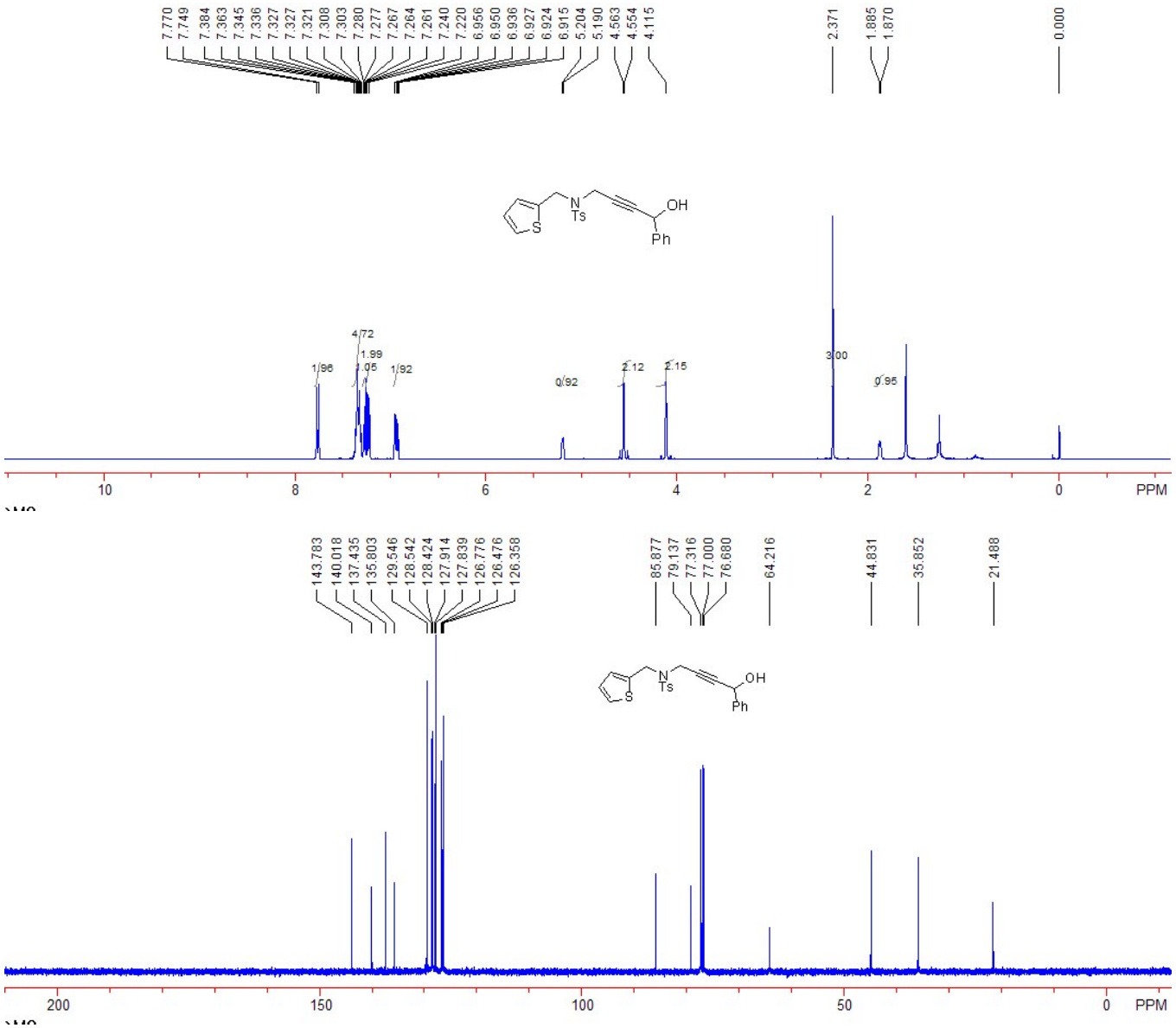


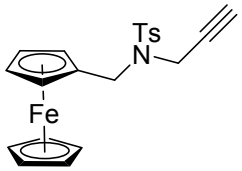




***N*-(4-hydroxy-4-phenylbut-2-yn-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S4d**

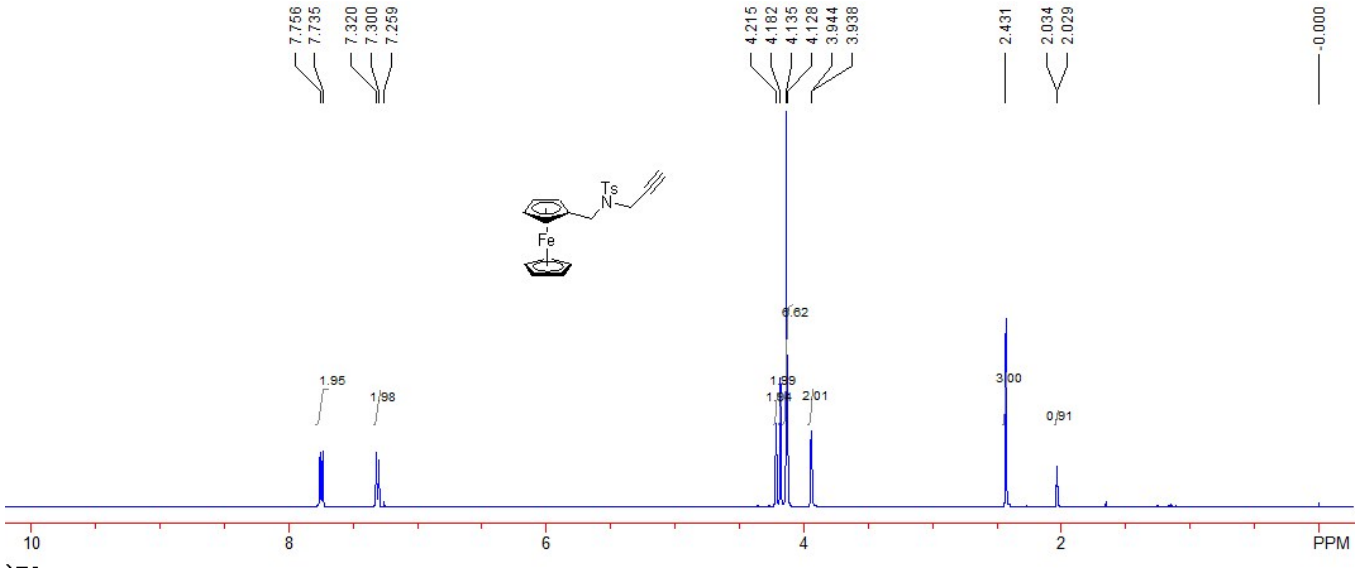
A white liquid, 58% yield (2.38 g). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.88 (br, 1H, OH), 2.37 (s, 3H, CH_3), 4.12 (s, 2H, CH_2), 4.55 (d, J = 3.6 Hz, 2H, CH_2), 5.20 (d, J = 5.6 Hz, 1H, CH), 6.91-6.96 (m, 2H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.26-7.28 (m, 1H, ArH), 7.30-7.39 (m, 5H, ArH), 7.76 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.9, 44.8, 64.2, 79.1, 85.9, 126.4, 126.5, 126.8, 127.84, 127.91, 128.5, 128.6, 129.5, 135.8, 137.4, 140.0, 143.8. IR (CH_2Cl_2) ν 3521, 3285, 2967, 2919, 2861, 1598, 1494, 1225, 1160, 898, 746, 661 cm^{-1}. MS (ESI) *m/z* (%): 429.13 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{22}H_{25}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 429.1301, found: 429.1302.

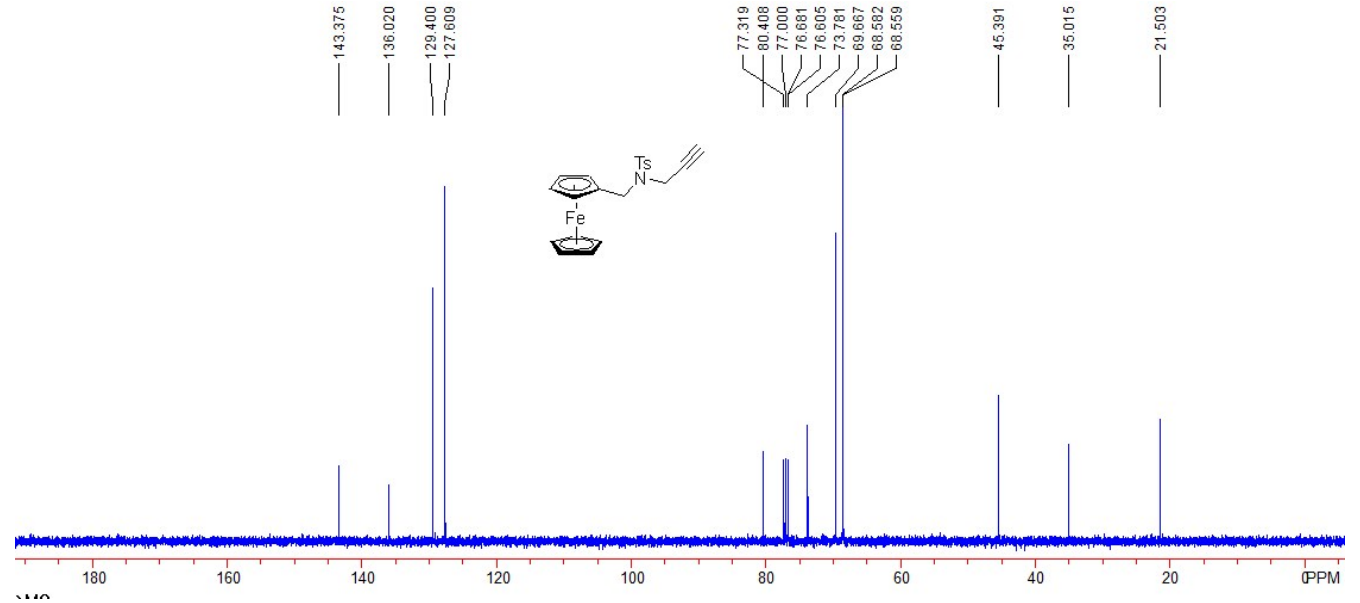


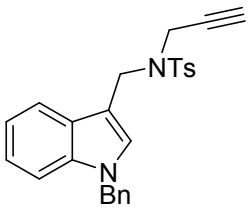


2-(((4-methyl-*N*-(prop-2-yn-1-yl)phenyl)sulfonamido)methyl)ferrocene S1v

A yellow solid, 67% yield (826.7 mg). M.p.: 94-96 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03 (t, J = 2.0 Hz, 1H, CH), 2.43 (s, 3H, CH_3), 3.94 (d, J = 2.4 Hz, 2H, CH_2), 4.12-4.14 (m, 7H), 4.18 (s, 2H, CH_2), 4.18 (s, 2H, CH_2), 4.22 (s, 2H), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.74 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.0, 45.4, 68.5, 68.6, 69.7, 73.8, 76.6, 80.4, 127.6, 129.4, 136.0, 143.4. IR (CH_2Cl_2) ν 3294, 2921, 1597, 1347, 1130, 1057, 886, 768, 659 cm^{-1}. MS (ESI) *m/z* (%): 405.06 (100) $[M]^+$; HRMS (ESI) Calcd. For $C_{21}H_{21}O_2N^{54}FeS^{+1}[M]^+$ requires 405.0684, found: 405.0684.

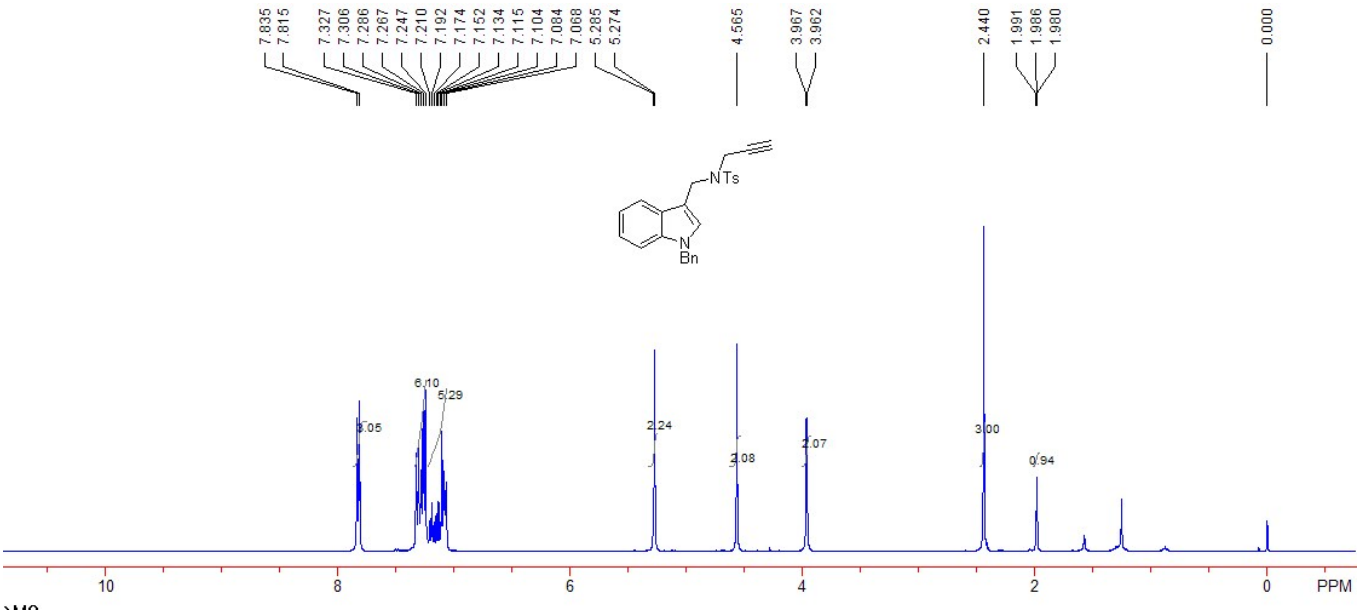


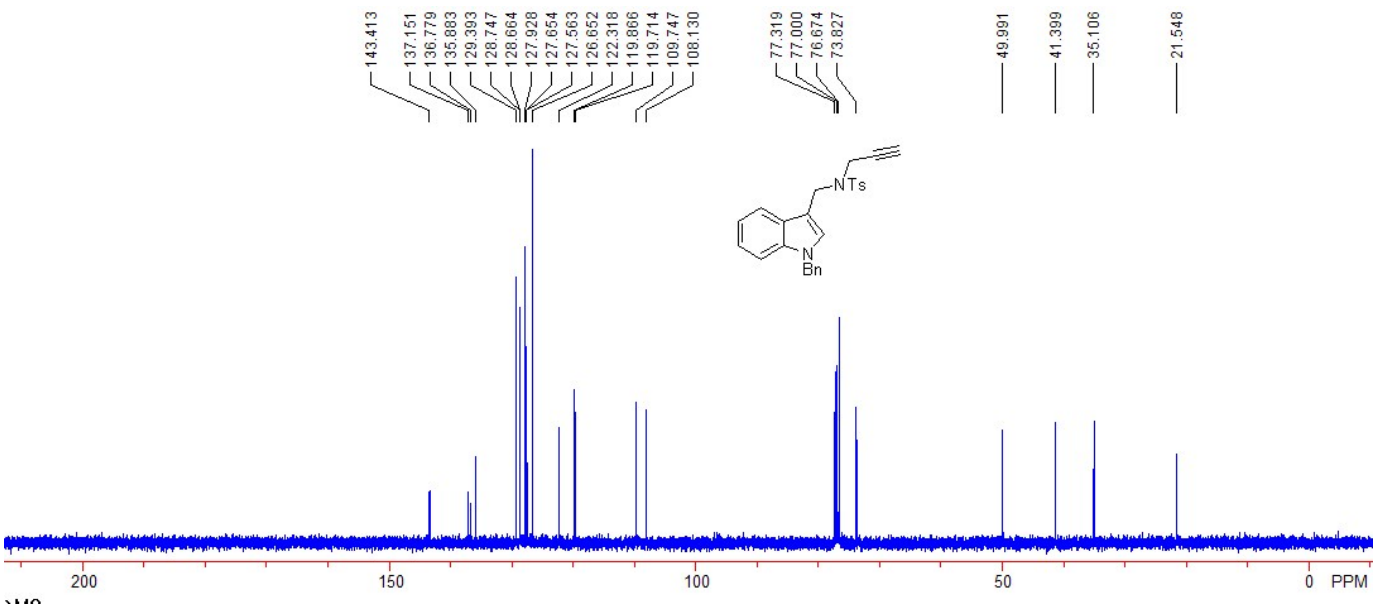


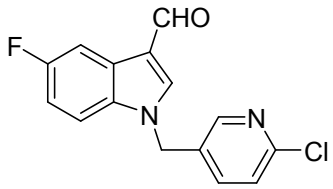


_N_-((1-benzyl-1_H_-indol-3-yl)methyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S1x

A white solid, 51% yield (428 mg). M.p.: 88-90 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.99 (t, J = 2.4 Hz, 1H, CH), 2.44 (s, 3H, CH_3), 3.96 (d, J = 2.4 Hz, 2H, CH_2), 4.57 (s, 2H, CH_2), 5.27 (s, 2H, CH_2), 7.07 -7.21 (m, 5H, ArH), 7.24-7.33 (m, 6H, ArH), 7.81-7.84 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.1, 41.4, 50.0, 73.8, 76.7, 108.1, 109.7, 119.7, 119.9, 122.3, 126.6, 127.56, 127.65, 127.9, 128.66, 128.75, 129.4, 135.9, 136.8, 137.1, 143.4. IR (CH_2Cl_2) ν 3287, 3031, 2920, 1661, 1597, 1555, 1467, 1345, 1160, 1092, 1015, 892, 773, 707, 661 cm^{-1}. MS (ESI) *m/z* (%): 446.18 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{26}H_{28}N_3O_2S^{+1}[M+NH_4]^+$ requires 446.1897, found: 446.1896.

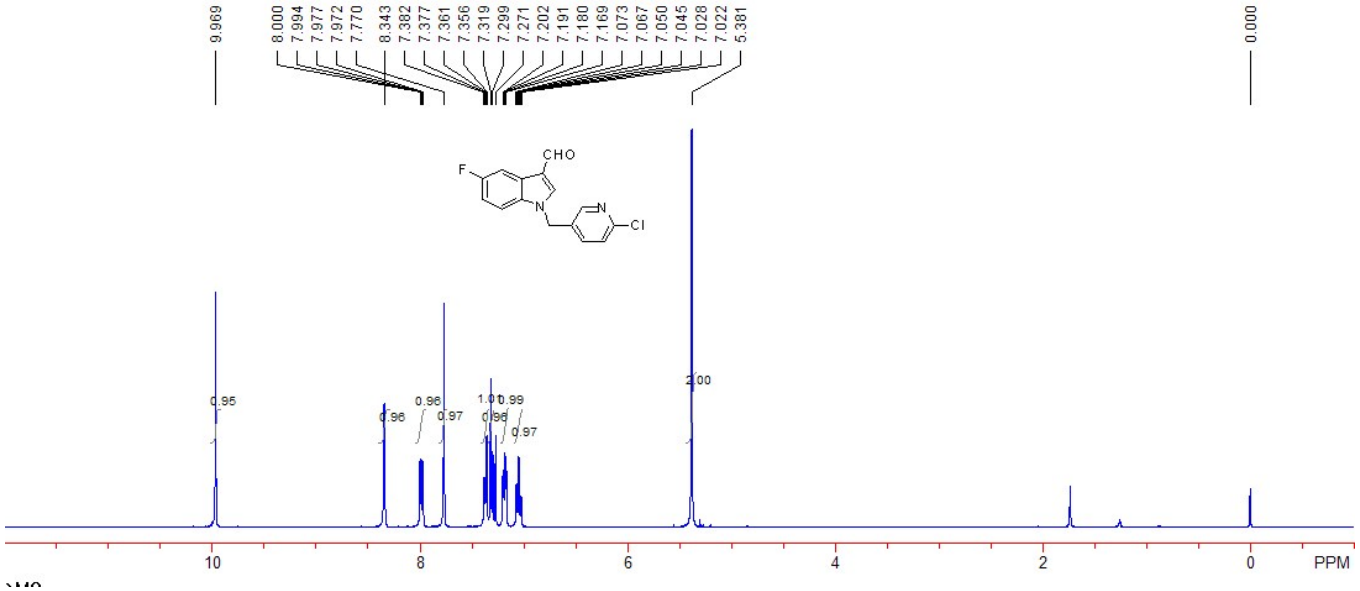






1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indole-3-carbaldehyde S8

A white solid, 73% yield (634 mg). M.p.: 172-174 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 5.38 (s, 2H, CH_2), 7.02-7.08 (m, 1H, ArH), 7.19 (dd, *J* = 8.4, 4.4 Hz, 1H, ArH), 7.30 (d, *J* = 8.0 Hz, 1H, ArH), 7.37 (dd, *J* = 8.4, 2.0 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.98 (dd, *J* = 8.8, 2.0 Hz, 1H, ArH), 8.34 (s, 1H, ArH), 9.97 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 48.0, 107.9 (d, *J* = 24.3 Hz), 110.9 (d, *J* = 9.8 Hz), 113.0 (d, *J* = 26.5 Hz), 118.8 (d, *J* = 4.6 Hz), 124.9, 126.2 (d, *J* = 10.7 Hz), 129.8, 133.4, 137.3, 138.8, 148.3, 151.9, 159.9 (d, *J* = 239.1 Hz), 184.3. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.4. IR (CH_2Cl_2) ν 3099, 2814, 1659, 1466, 1383, 1246, 1169, 1103, 1028, 912, 826, 734, 697 cm^{-1}. MS (ESI) m/z (%): 289.05 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{11}ClFN_2O^{+1}[M+H]^+$ requires 289.0538, found: 289.0539.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7.972
7.770
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7.271
7.202
7.191
7.180
7.169
7.073
7.067
7.050
7.045
7.028
7.022
5.381
0.000
CHO
F
N
Cl
0.95
0.96
0.96
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0.99
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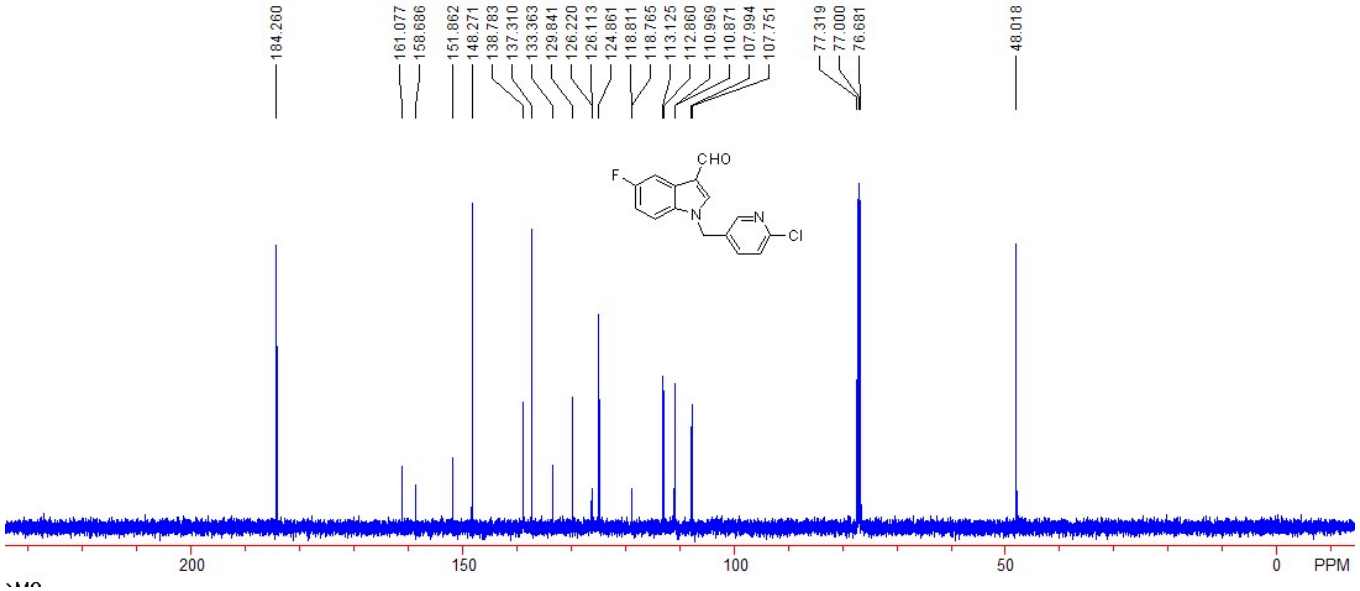
2.00
10
8
6
4
2
0
PPM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126.113
124.861
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118.765
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112.860
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110.871
107.994
107.751
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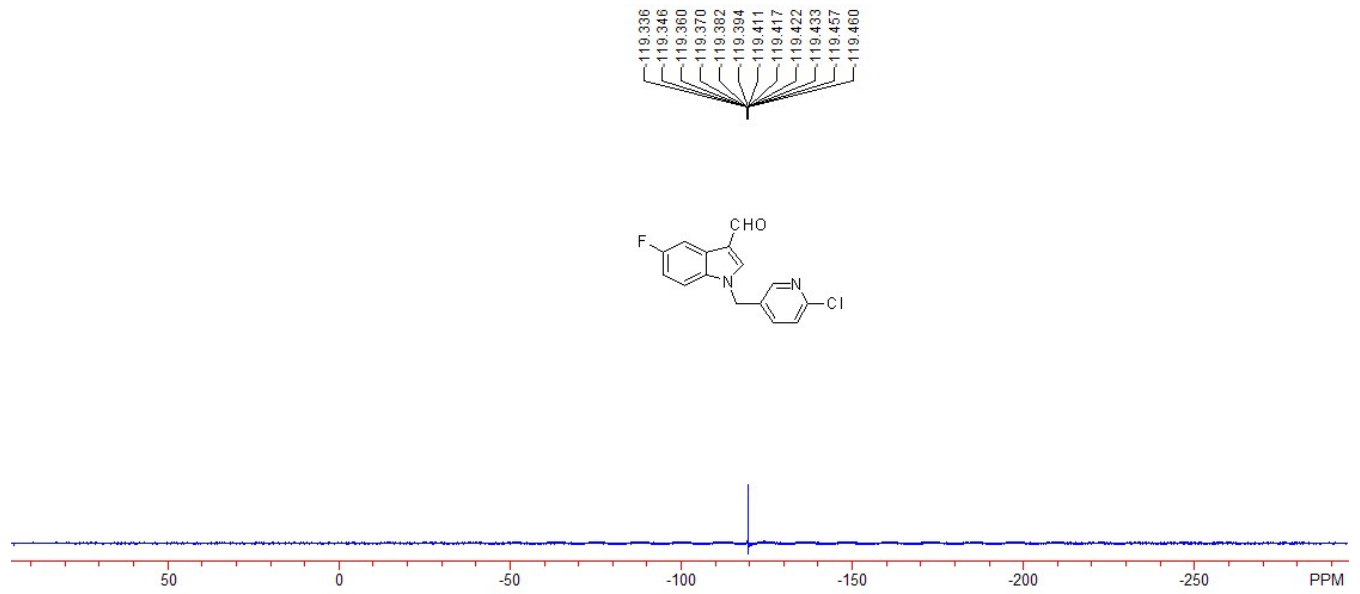
77.000
76.681
48.018
CHO
F
N
Cl
200
150
100
50
0
PPM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F
N
Cl
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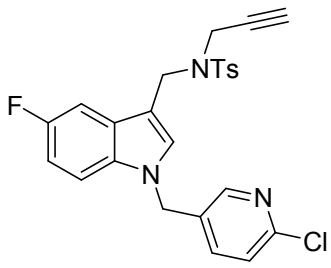
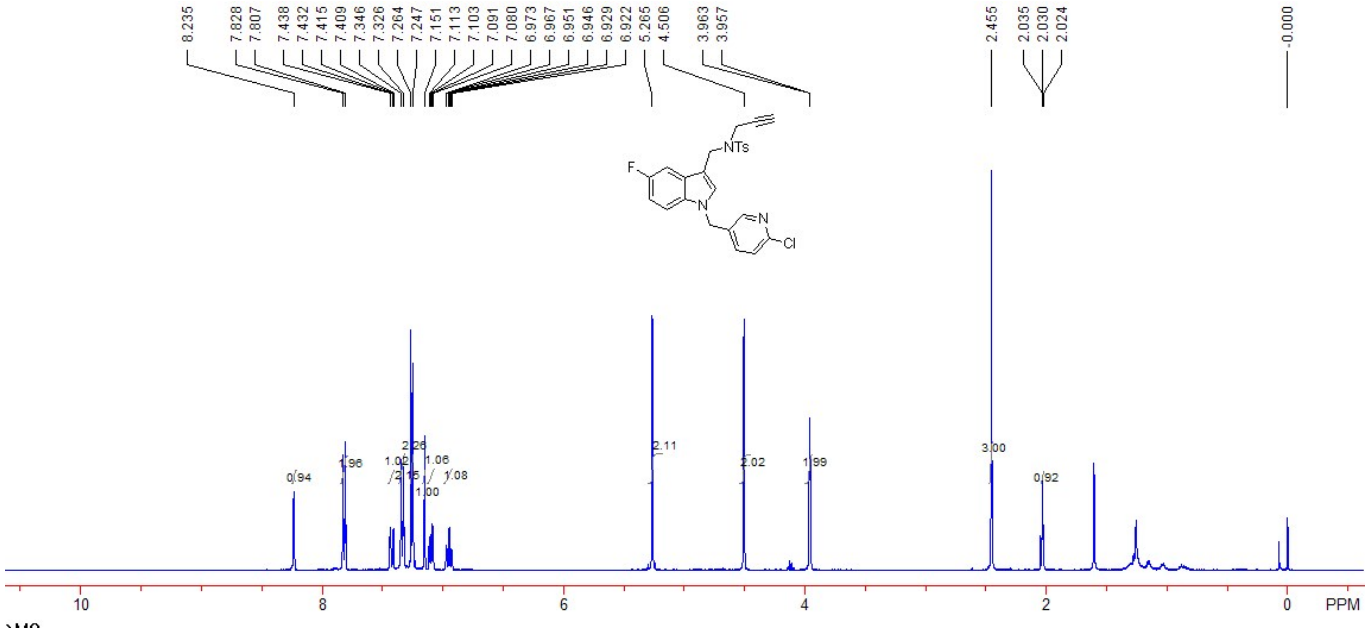
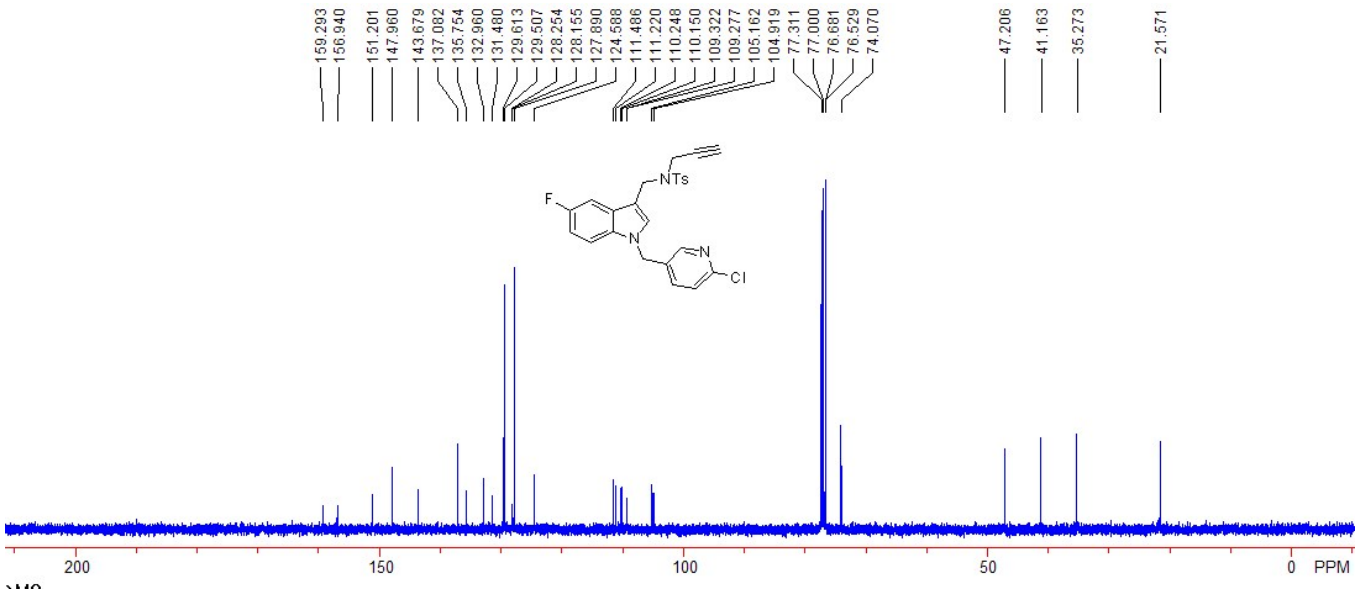
PPM

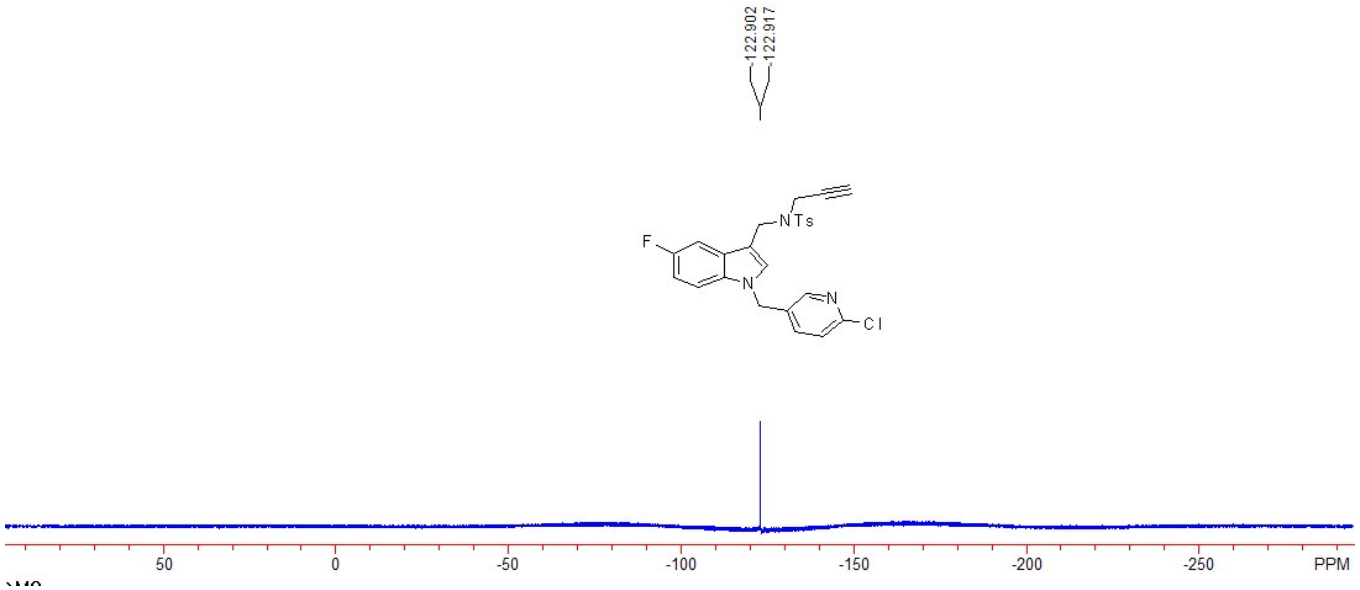


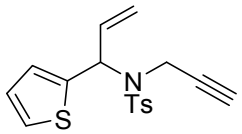
***N*-((1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1*H*-indol-3-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide S1y**

A white solid, 62% yield (602 mg). M.p.: 132-134 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03 (t, *J* = 2.4 Hz, 1H, CH), 2.45 (s, 3H, CH_3), 3.96 (d, *J* = 2.4 Hz, 2H, CH_2), 4.51 (s, 2H, CH_2), 5.26 (s, 2H, CH_2), 6.92-6.98 (m, 1H, ArH), 7.10 (dd, *J* = 4.4, 9.2 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.25 (d, *J* = 6.8 Hz, 2H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (dd, *J* = 2.4, 9.2 Hz, 1H, ArH), 7.81 (d, *J* = 8.0 Hz, 2H, ArH), 8.23 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.3, 41.2, 47.2, 74.1, 76.5, 105.0 (d, *J* = 23.8 Hz), 109.3 (d, *J* = 4.8 Hz), 110.2 (d, *J* = 9.5 Hz), 111.3 (d, *J* = 26.5 Hz), 124.6, 127.9, 128.2 (d, *J* = 9.9 Hz), 129.5, 129.6, 131.5, 133.0, 135.7, 137.1, 143.7, 148.0, 151.2, 158.0 (d, *J* = 235.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -122.9. IR (CH_2Cl_2) ν 3299, 2982, 1586, 1486, 1461, 1387, 1240, 1160, 1023, 908, 815, 798, 661 cm^{-1}. MS (ESI) m/z (%): 482.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{25}H_{22}ClFN_3O_2S^{+1}[M+H]^+$ requires 482.1100, found: 482.1100.





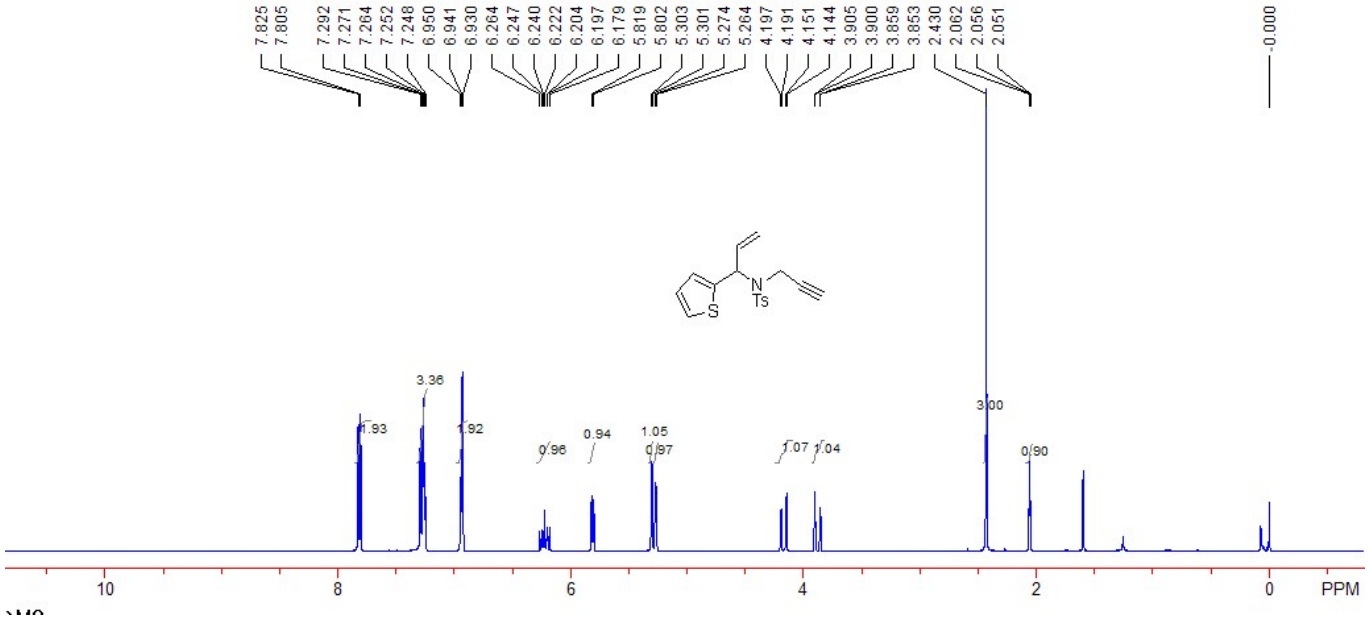


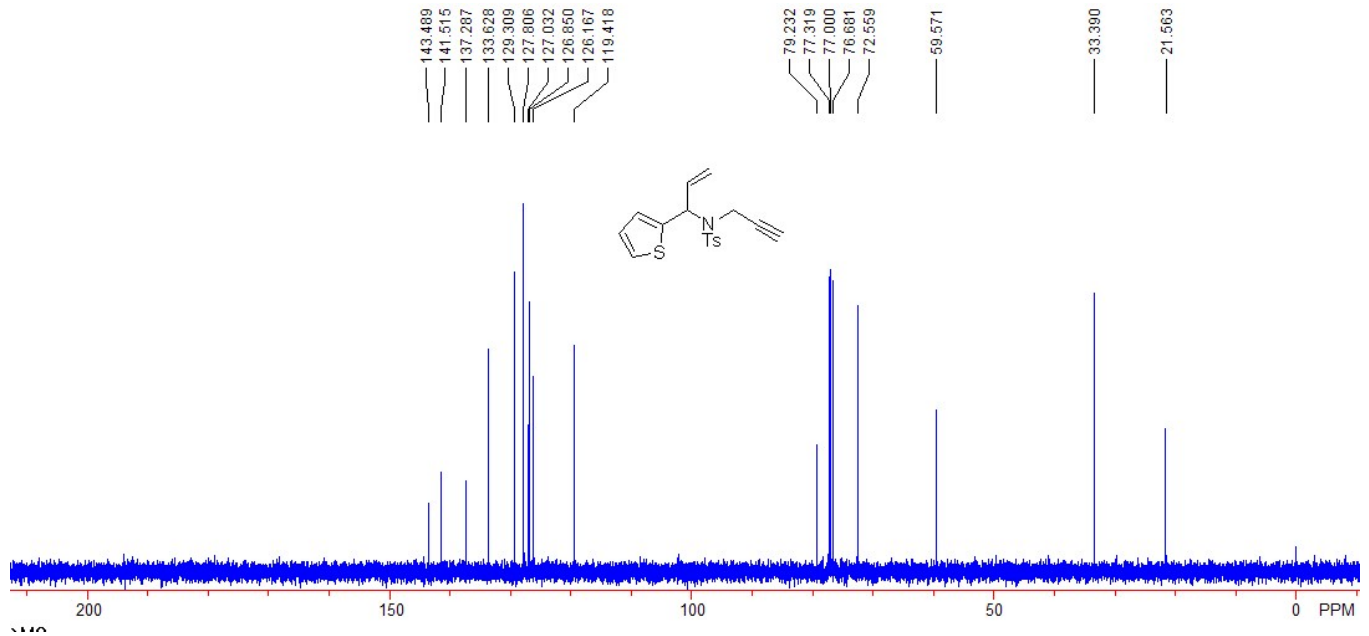


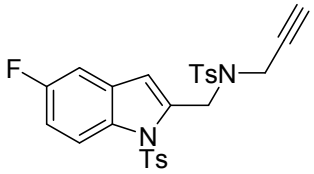
4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(thiophen-2-yl)allyl)benzenesulfonamide S1z

A white solid, 90% yield (708 mg). M.p.: 70-72 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.06 (t, *J* = 2.4 Hz, 1H, CH), 2.43 (s, 3H, CH_3), 3.87 (dd, *J* = 18.8, 2.4 Hz, 1H, CH_2), 4.17 (dd, *J* = 18.8, 2.4 Hz, 1H, CH_2), 5.26 (d, *J* = 4.0 Hz, 1H, CH), 5.30 (d, *J* = 0.8 Hz, 1H, =CH_2), 5.81 (d, *J* = 6.8 Hz, 1H, =CH_2), 6.23 (ddd, *J* = 20.8, 13.2, 3.2 Hz, 1H, =CH), 6.92-6.95 (m, 2H, ArH), 7.25 (dd, *J* = 6.0, 1.6 Hz, 1H, ArH), 7.28 (d, *J* = 8.0 Hz, 2H, ArH), 7.81 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 33.4,

59.6, 72.6, 79.2, 119.4, 126.2, 126.8, 127.0, 127.8, 129.3, 133.6, 137.3, 141.5, 143.5. IR (CH_2Cl_2) ν 3301, 2853, 1597, 1423, 1345, 1330, 1158, 1090, 1049, 894, 812, 712, 667 cm^{-1}. MS (ESI) *m/z* (%): 349.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{21}N_2O_2S_2^{+1}(M+NH_4)^+$ requires 349.1039, found: 337.1034.



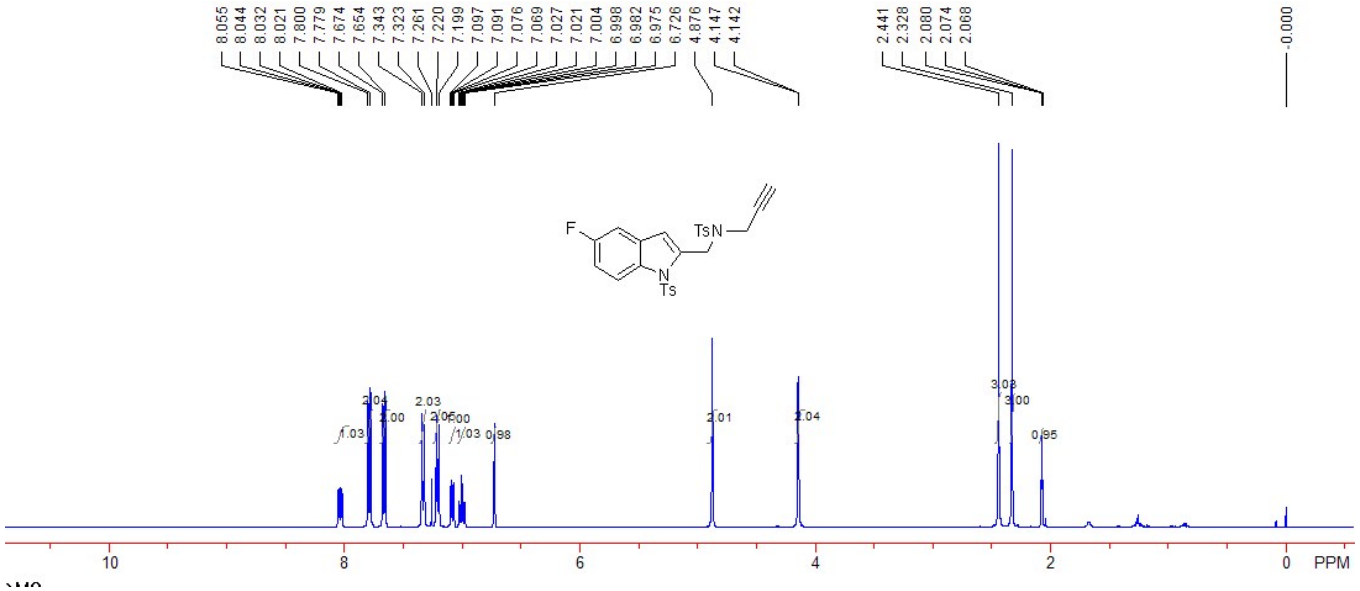


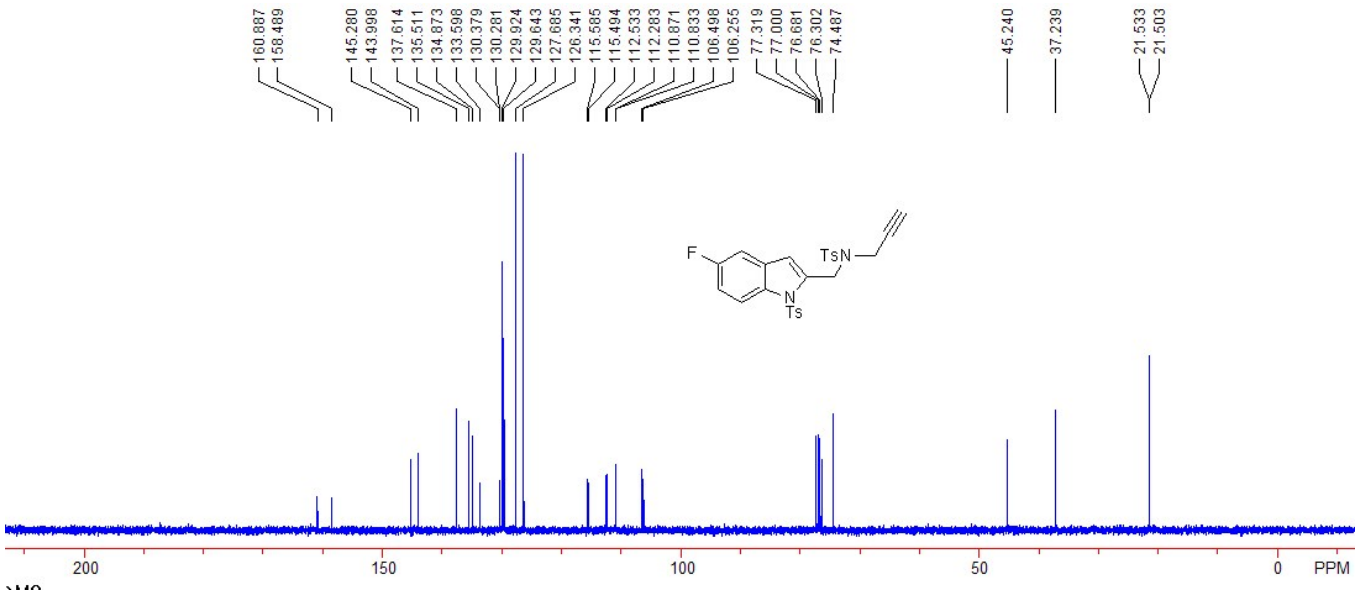


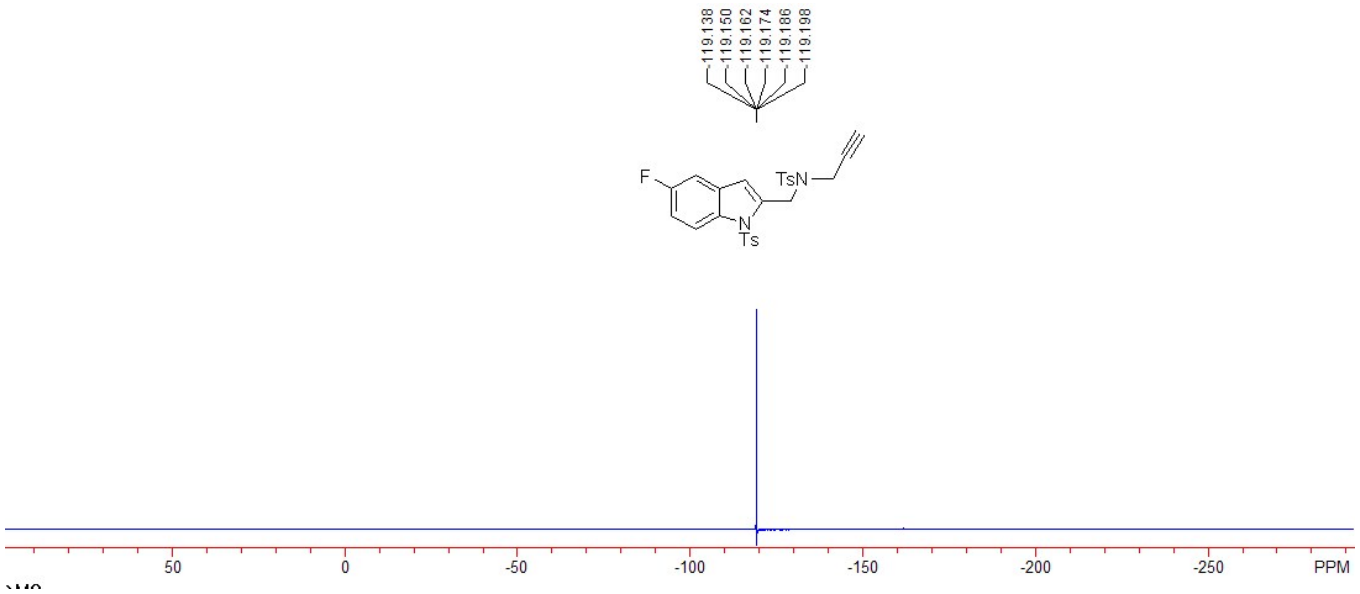
_N_-((5-fluoro-1-tosyl-1_H_-indol-2-yl)methyl)-4-methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide S13

A white solid, 81% yield (455 mg). M.p.: 135-138 ºC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.07 (t, *J* =

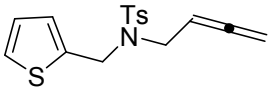
2.4 Hz, 1H, CH), 2.33 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.14 (d, *J* = 2.4 Hz, 2H, CH_2), 4.88 (s, 2H, CH_2), 6.73 (s, 1H, CH_2), 7.00 (td, *J* = 8.4, 2.4 Hz, 1H, ArH), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 2H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 2H, ArH), 8.03 (dd, *J* = 8.8, 4.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.51, 21.54, 37.2, 45.2, 74.5, 76.3, 106.3 (d, *J* = 23.8 Hz), 110.8 (d, *J* = 3.9 Hz), 112.4 (d, *J* = 25.1 Hz), 115.5 (d, *J* = 9.2 Hz), 126.3, 127.7, 129.6, 129.9, 130.3 (d, *J* = 10.1 Hz), 133.6, 134.9, 135.5, 137.6, 144.0, 145.3, 159.7 (d, *J* = 239.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.1. IR (CH_2Cl_2) ν 3275, 2918, 1597, 1467, 1339, 1159, 1091, 908, 816, 766, 661 cm^{-1}. MS (ESI) m/z (%): 528.14 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{26}H_{27}FN_3O_4S_2^{+1}[M+NH_4]^+$ requires 528.1422, found: 528.1423.





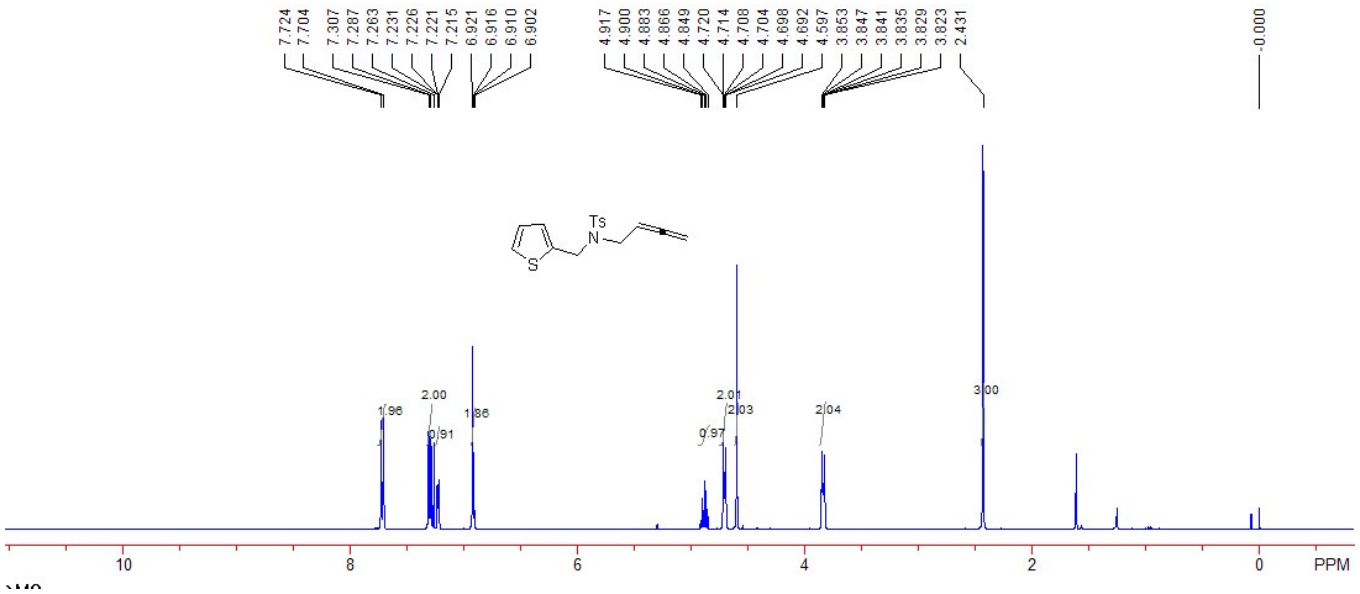


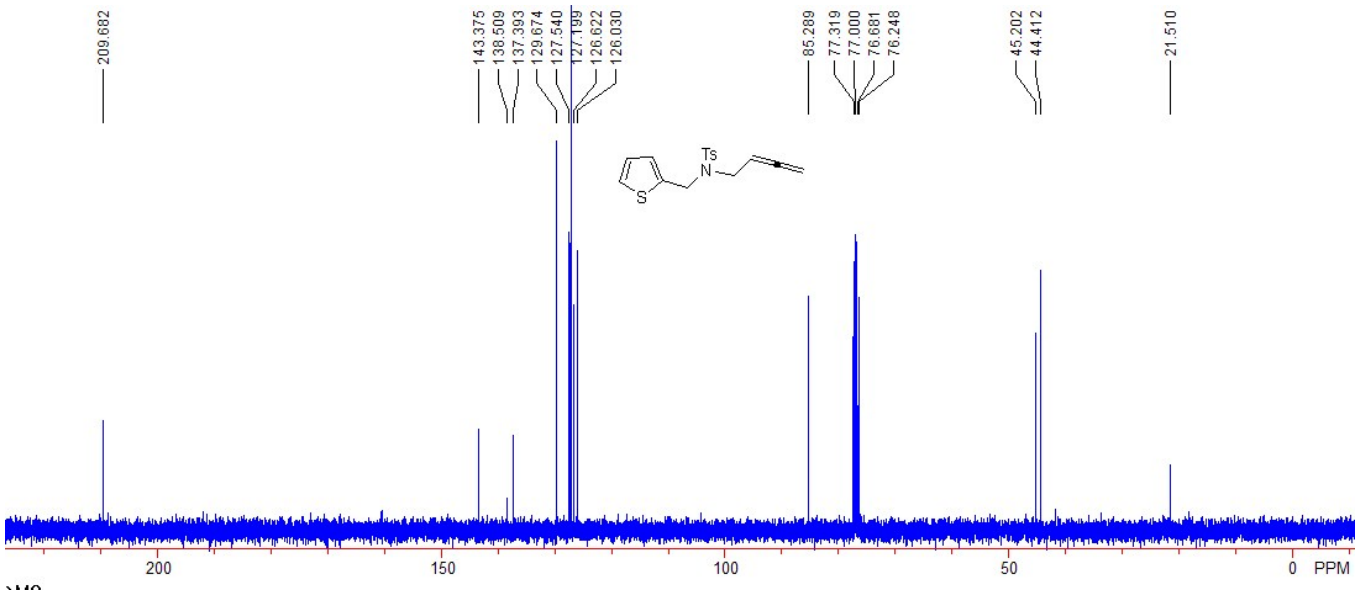
12. Characterization and spectra charts for compounds 1, 6, 9 and 12

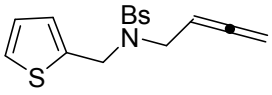


***N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1a**

A white solid, 79% yield (1.01 g). M.p.: 44-46 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 3.83 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.60 (s, 2H, CH_2), 4.71 (dt, *J* = 6.4, 2.4 Hz, 2H, =CH_2), 4.84-4.92 (m, 1H, =CH), 6.90-6.93 (m, 2H, ArH), 7.22 (dd, *J* = 4.4, 2.0 Hz, 1H, ArH), 7.29 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 44.4, 45.2, 76.2, 85.3, 126.0, 126.6, 127.2, 127.5, 129.7, 137.4, 138.5, 143.4, 209.7. IR (CH_2Cl_2) ν 2960, 2923, 2852, 1950, 1342, 1159, 1092, 896, 852, 707, 658 cm^{-1}. MS (ESI) *m/z* (%): 320.07 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{18}NO_2S_2^{+1}[M+H]^+$ requires 320.0773, found: 320.0771.



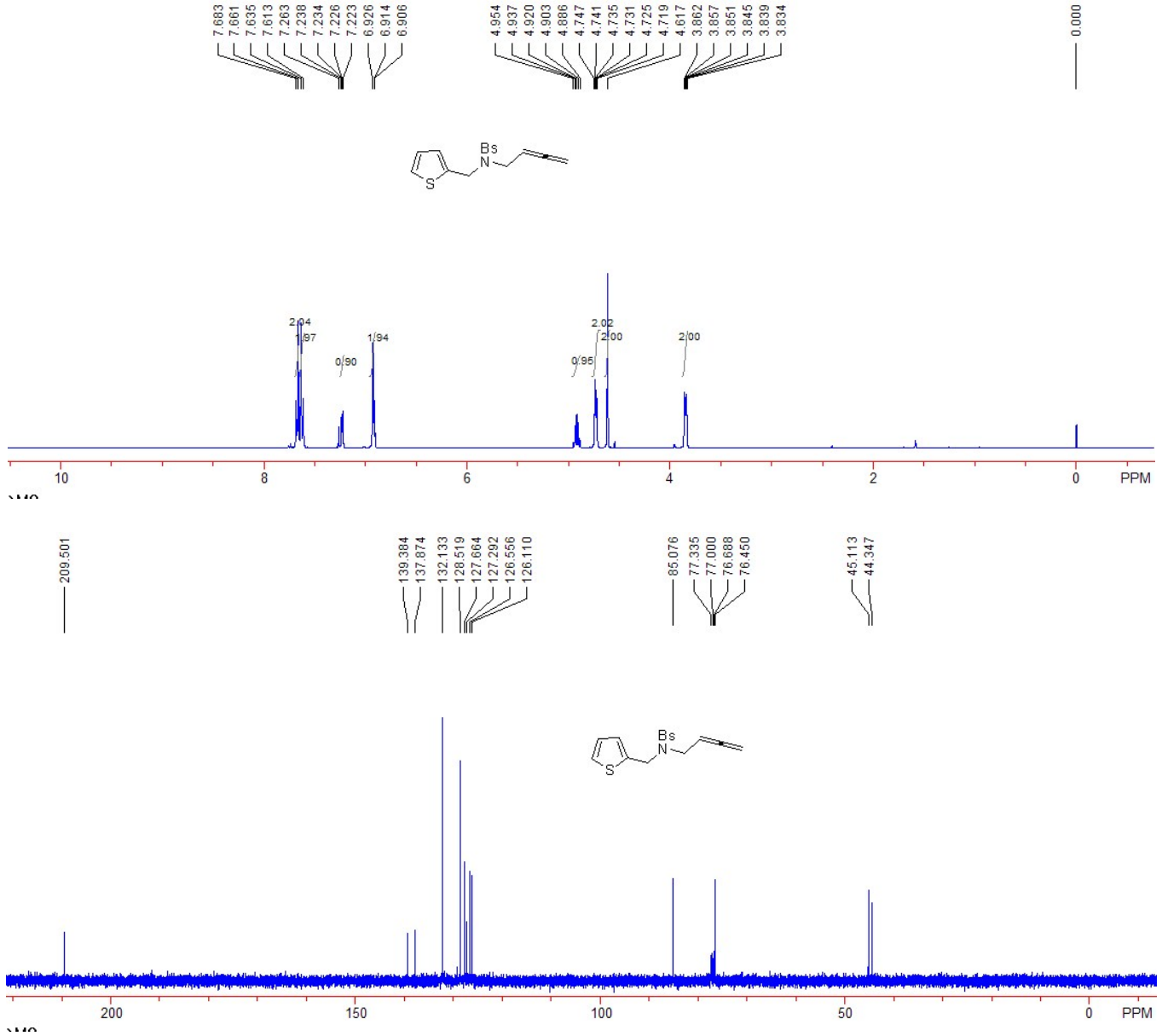


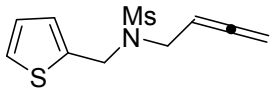


4-bromo-*N*-(buta-2,3-dien-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1b

A white solid, 76% yield (578 mg). M.p.: 83-85 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.85 (dt, J = 7.2, 2.4 Hz, 2H, CH_2), 4.62 (s, 2H, CH_2), 4.73 (dt, J = 6.4, 2.4 Hz, 2H, =CH_2), 4.88-4.96 (m, 1H, =CH), 6.90-6.93 (m, 2H, ArH), 7.23 (dd, J = 4.4, 1.6 Hz, 1H, ArH), 7.62 (d, J = 8.8 Hz, 2H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 44.3, 45.1, 76.5, 85.1, 126.1, 126.6, 127.3, 127.7, 128.5, 132.1, 137.9, 139.4, 209.5. IR (CH_2Cl_2) ν 3094, 2921, 2857, 1597, 1955, 1574, 1330, 1089, 1068, 1092, 906, 822, 723, 610 cm^{-1}. MS (ESI) *m/z* (%): 383.97 (100) $[M+H]^+$; HRMS (ESI) Calcd. For

$C_{15}H_{15}NO_2BrS_2^{+1}[M+H]^+$ requires 383.9722, found: 383.9720.

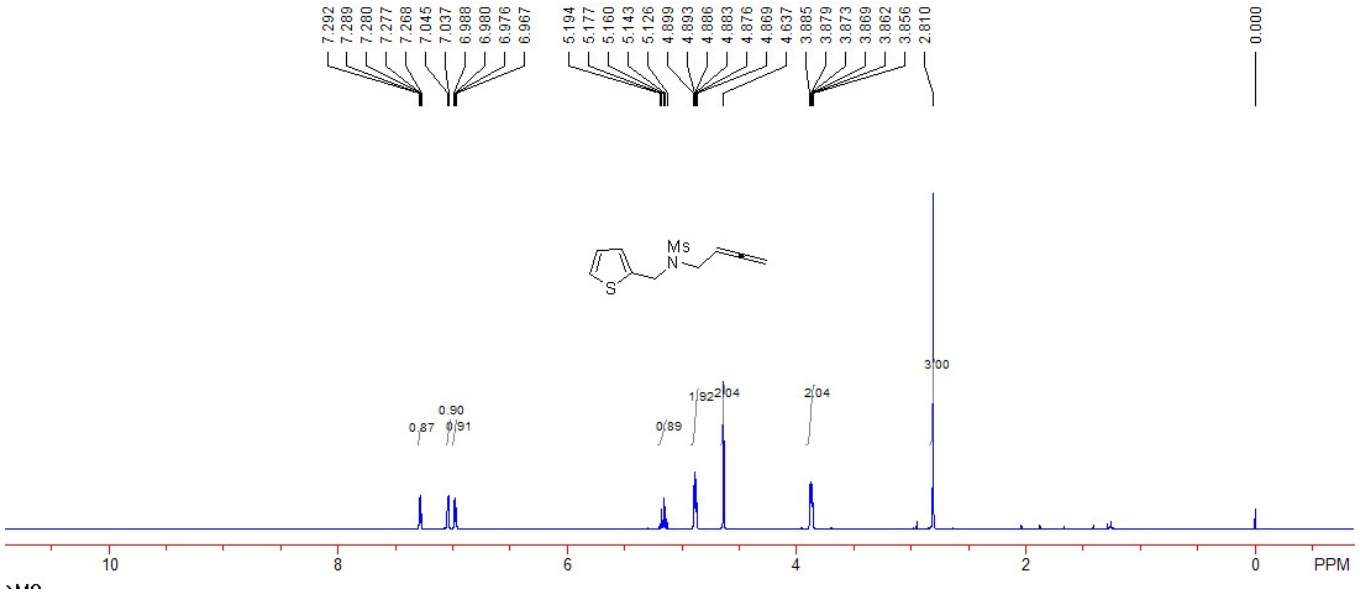


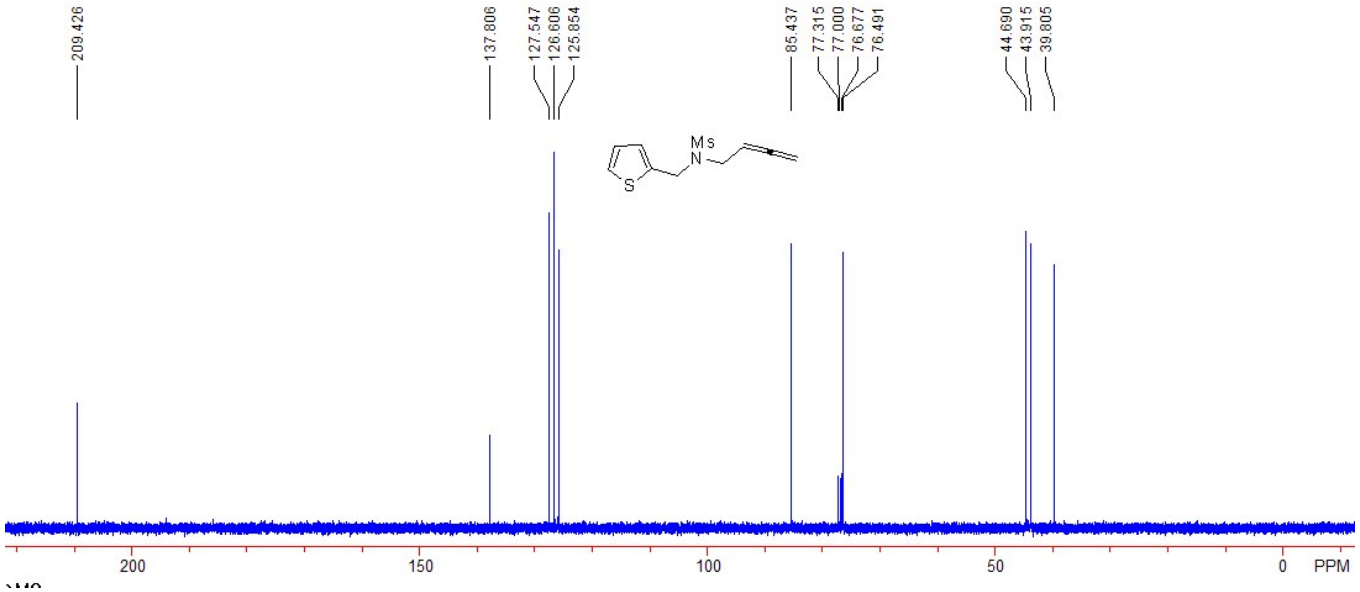


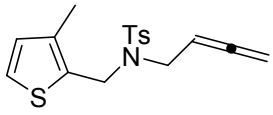
_N_-(buta-2,3-dien-1-yl)-_N_-(thiophen-2-ylmethyl)methanesulfonamide 1c

A white solid, 53% yield (256 mg). M.p.: 68-70 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.81 (s, 3H, CH_3), 3.87 (dt, J = 6.8, 2.4 Hz, 2H, CH_2), 4.64 (s, 2H, CH_2), 4.88 (dt, J = 6.8, 2.8 Hz, 2H, =CH_2), 5.12-5.20 (m, 1H, =CH), 6.98 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.04 (d, J = 3.2 Hz, 1H, ArH), 7.28 (dd, J = 4.8, 1.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 39.8, 43.9, 44.7, 76.5, 85.4, 125.9, 126.6, 127.5, 137.8, 209.4. IR (CH_2Cl_2) ν 2994, 1953, 1436, 1322, 1262, 1144, 1082, 962, 850, 783, 701 cm^{-1}. MS (ESI)

m/z (%): 261.07 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{10}H_{17}N_2O_2S_2^{+1}[M+ NH_4]^+$ requires 261.0726, found: 261.0727.



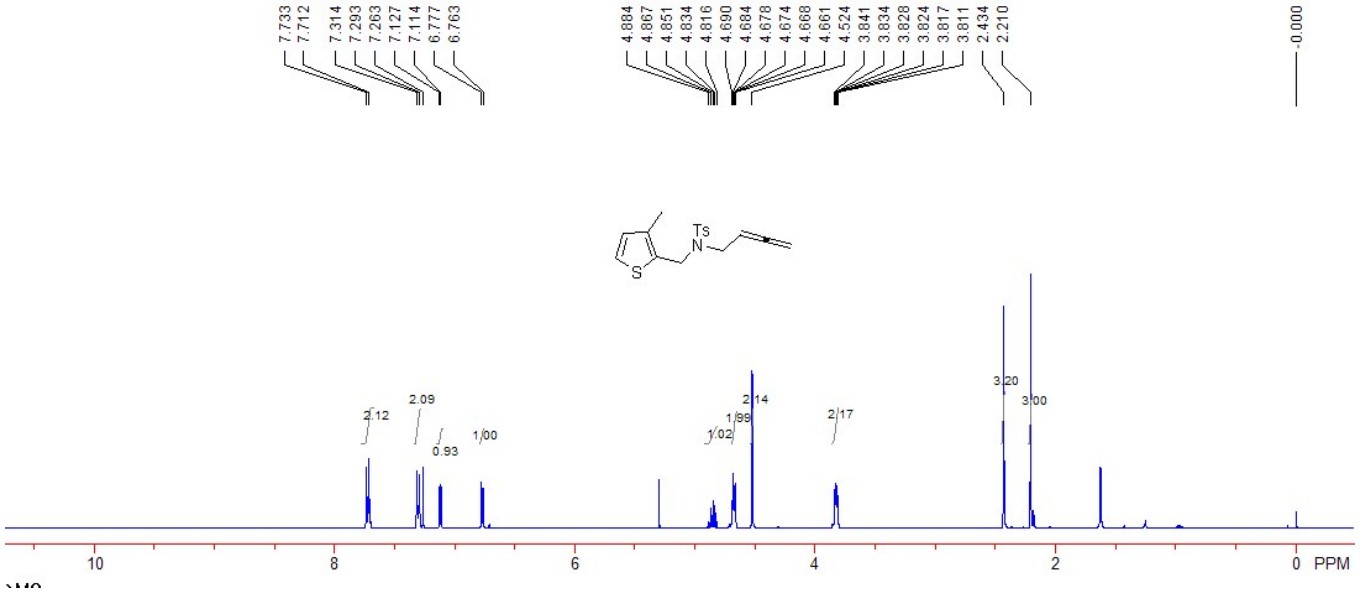


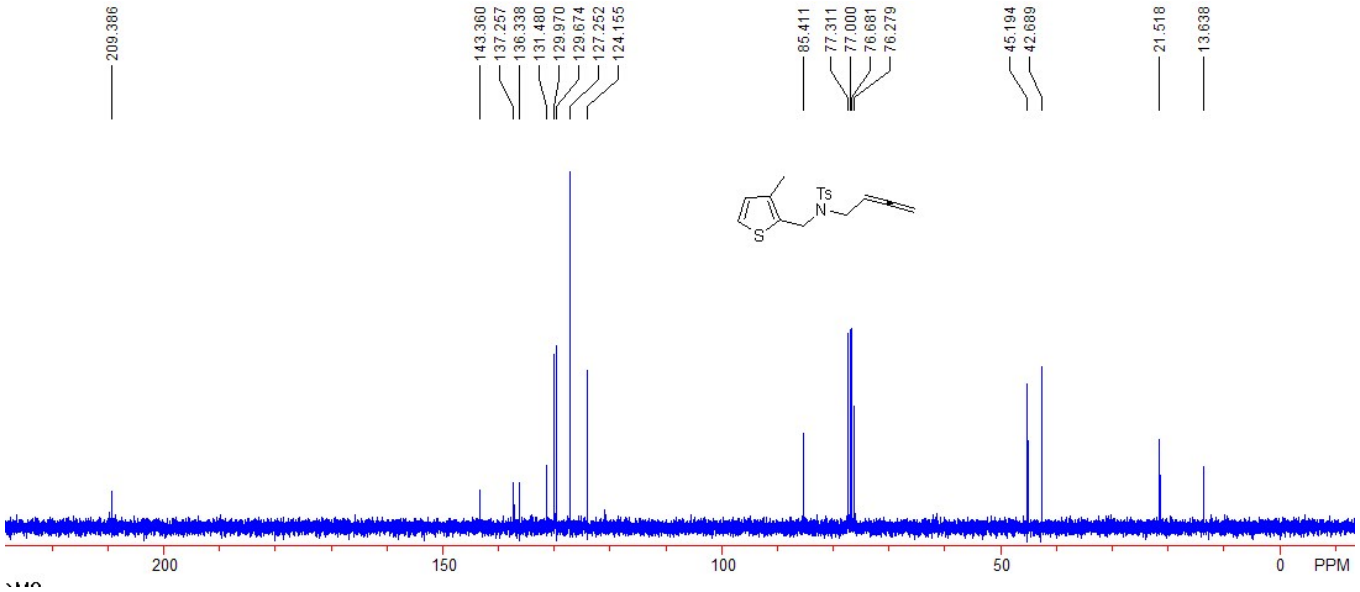


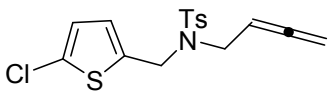
_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-((3-methylthiophen-2-yl)methyl)benzenesulfonamide 1d

A white solid, 91% yield (1.50 g). M.p.: 77-79 ^oC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.82 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.52 (s, 2H, CH_2), 4.67 (dt, *J* = 6.4, 2.4 Hz, 2H, $=CH_2$), 4.81-4.89 (m, 1H, =CH), 6.77 (d, *J* = 4.8 Hz, 1H, ArH), 7.12 (d, *J* = 4.8 Hz, 1H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 21.5, 42.7,

45.2, 76.3, 85.4, 124.1, 127.2, 129.7, 130.0, 131.5, 136.3, 137.2, 143.4, 209.4. IR (CH_2Cl_2) ν 2943, 2924, 2860, 1952, 1595, 1441, 1340, 1301, 1160, 1104, 1087, 947, 818, 719, 655 cm^{-1}. MS (ESI) *m/z* (%): 351.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 351.1195, found: 351.1196.



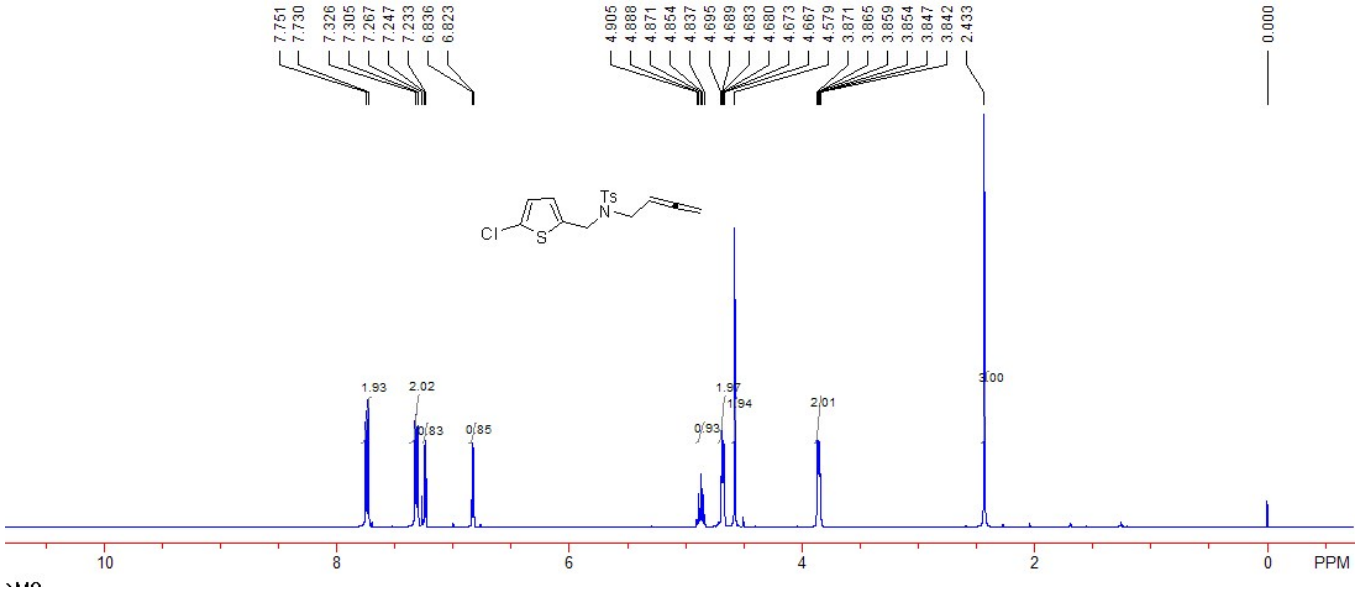


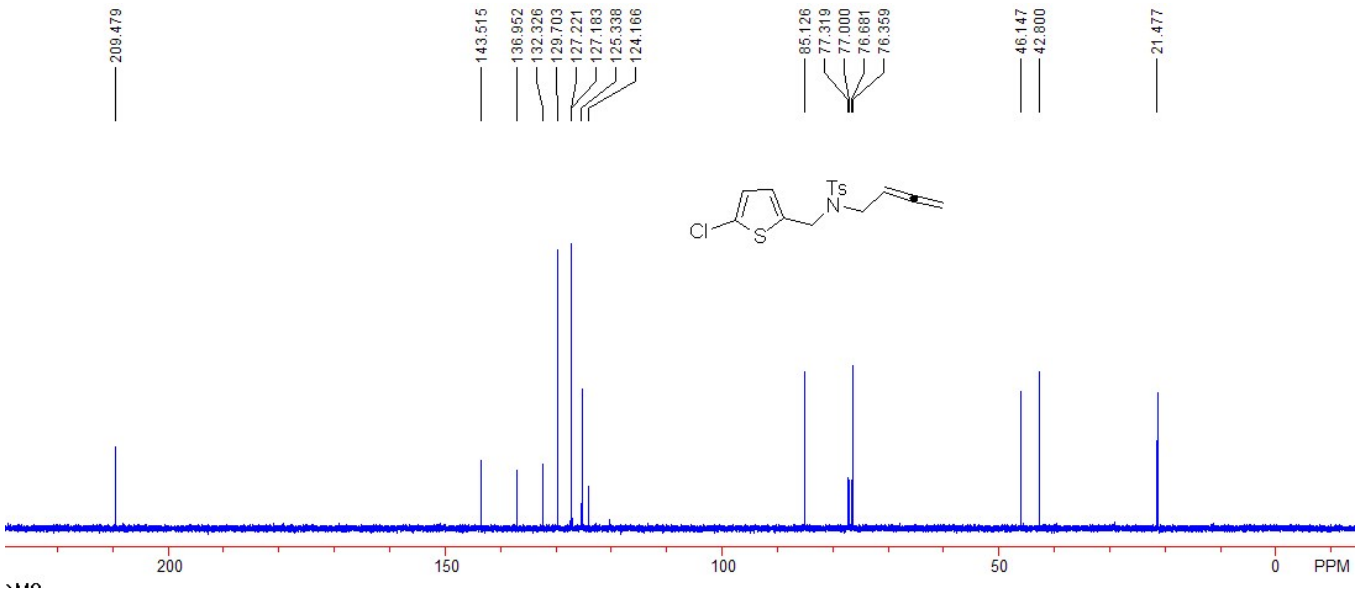


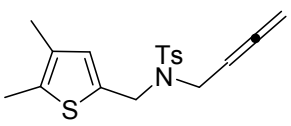
_N_-(buta-2,3-dien-1-yl)-_N_-((5-chlorothiophen-2-yl)methyl)-4-methylbenzenesulfonamide 1e

A white solid, 58% yield (594 mg). M.p.: 72-74 °C. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 3.86 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.58 (s, 2H, CH_2), 4.68 (dt, *J* = 6.4, 2.4 Hz, 2H, $=CH_2$), 4.83-

4.91 (m, 1H, =CH), 6.83 (d, J = 5.2 Hz, 1H, ArH), 7.24 (d, J = 5.6 Hz, 1H, ArH), 7.31 (d, J = 8.4 Hz, 2H, ArH), 7.74 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 42.8, 46.1, 76.4, 85.1, 124.2, 125.3, 127.18, 127.22, 129.7, 132.3, 137.0, 143.5, 209.5. IR (CH_2Cl_2) ν 3124, 2942, 2851, 1954, 1595, 1437, 1339, 1159, 1096, 930, 815, 746, 656 cm^{-1}. MS (ESI) *m/z* (%): 354.03 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{17}ClNO_2S_2{}^{+1}[M+H]^+$ requires 354.0384, found: 354.0384.



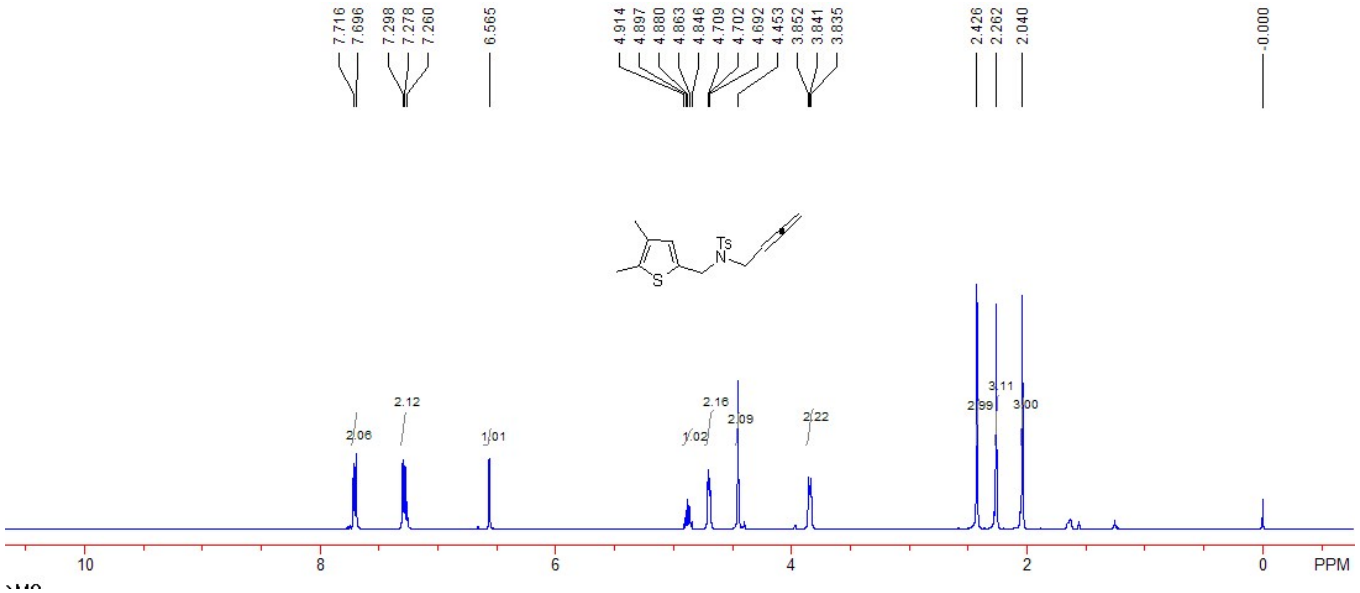


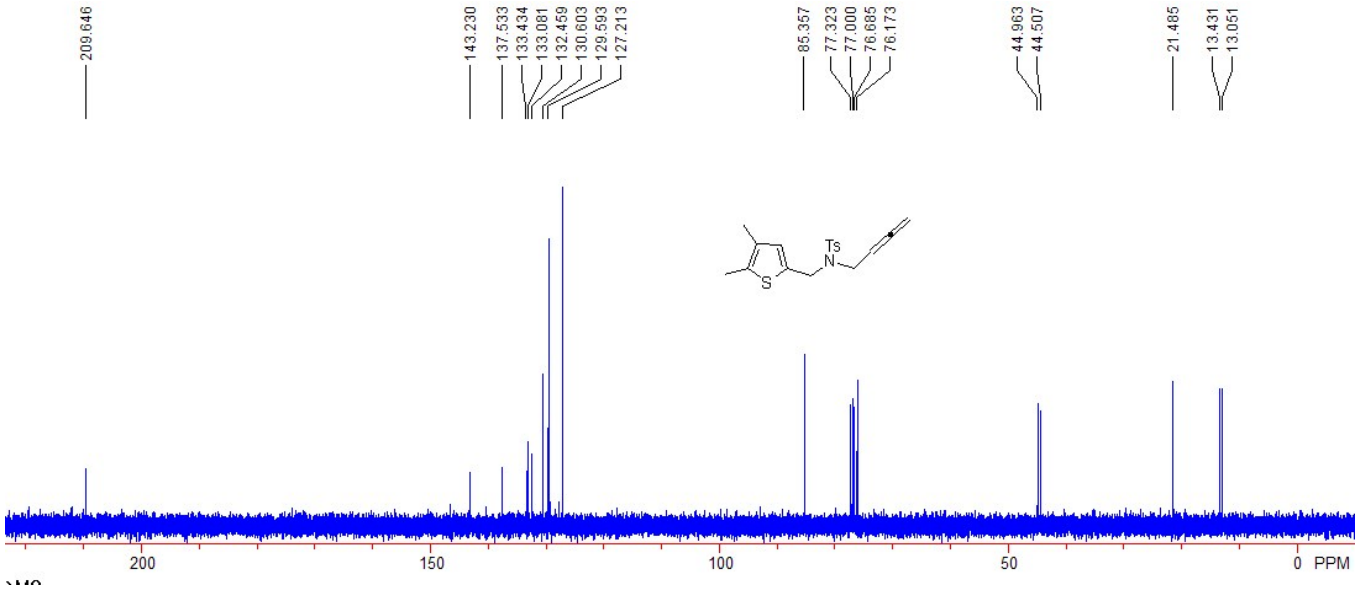


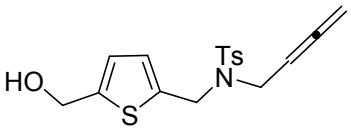
N-(buta-2,3-dien-1-yl)-N-((4,5-dimethylthiophen-2-yl)methyl)-4-methylbenzenesulfonamide 1f

A white solid, 59% yield (206 mg). M.p.: 73-75 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.04 (s, 3H,

CH_3), 2.26 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.84 (dt, J = 7.2, 2.4 Hz, 2H, CH_2), 4.45 (s, 2H, CH_2), 4.70 (dt, J = 7.2, 2.4 Hz, 2H, =CH_2), 4.84-4.92 (m, 1H, =CH), 6.57 (s, 1H, ArH), 7.28 (d, J = 8.0 Hz, 2H, ArH), 7.70 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 13.4, 21.5, 44.5, 45.0, 76.2, 85.4, 127.2, 129.6, 130.6, 132.4, 133.1, 133.4, 137.5, 143.2, 209.6. IR (CH_2Cl_2) ν 2985, 2920, 2860, 1956, 1597, 1493, 1335, 1158, 1091, 923, 818, 758, 660 cm^{-1}. MS (ESI) *m/z* (%): 365.13 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{25}N_2O_2S_2^{+1}[M+ NH_4]^+$ requires 365.1352, found: 365.1349.



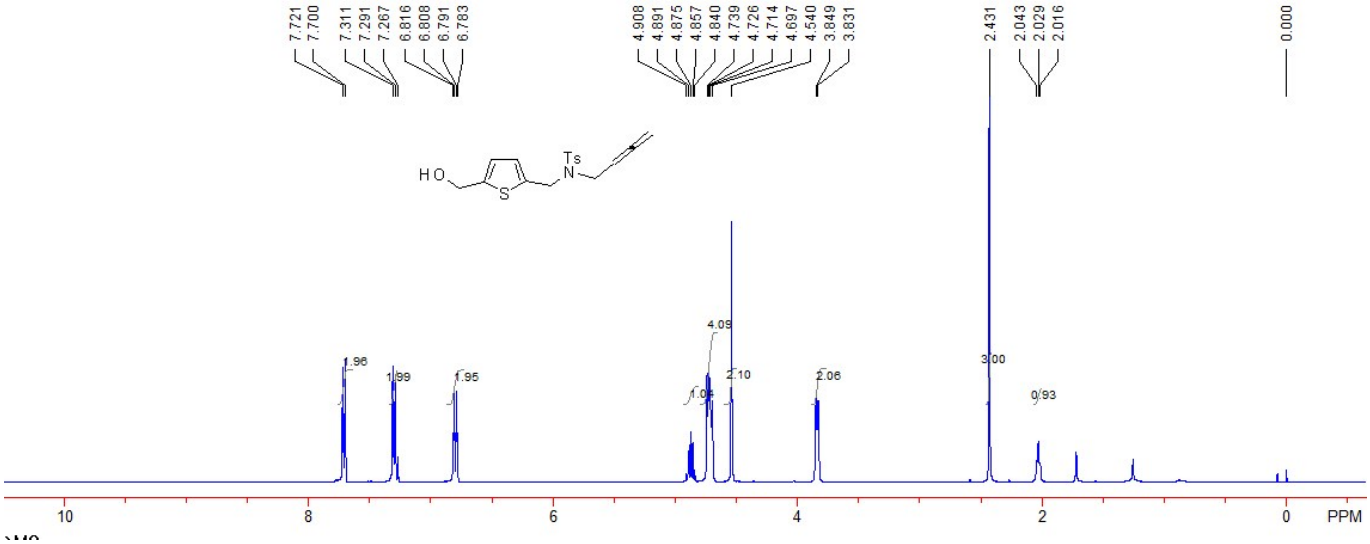


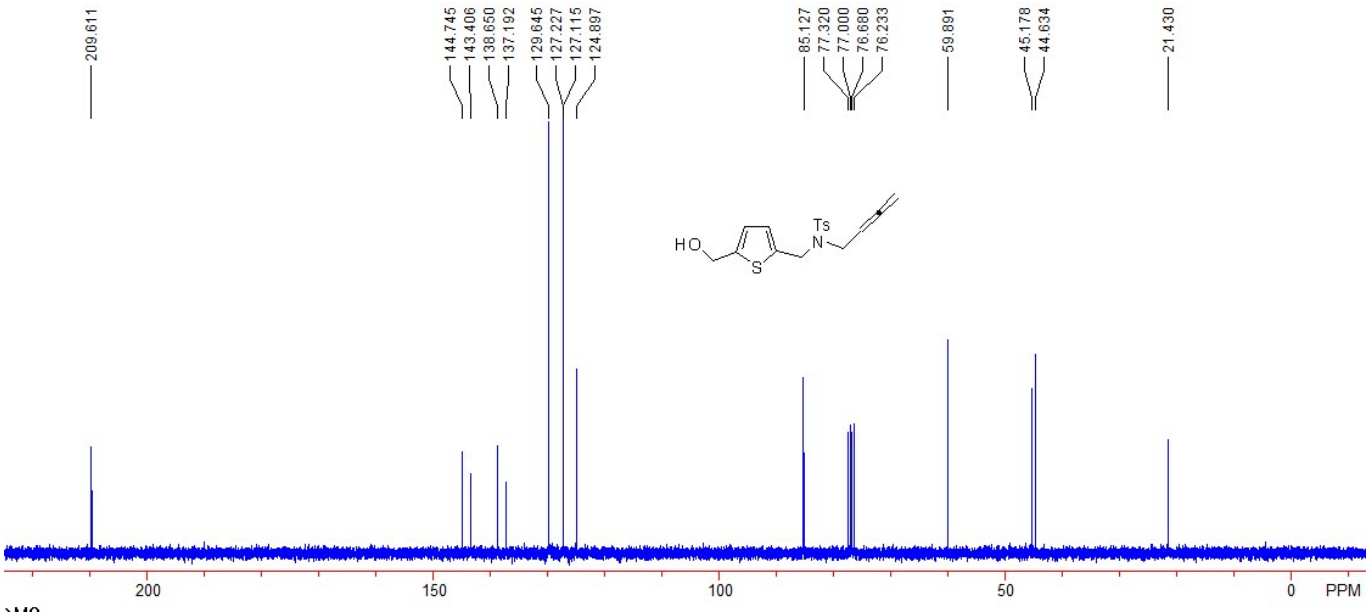


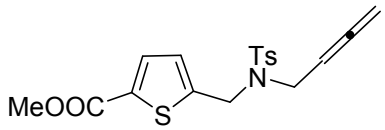
***N*-(buta-2,3-dien-1-yl)-*N*-((5-(hydroxymethyl)thiophen-2-yl)methyl)-4-methylbenzenesulfonamide**

1g

A white liquid, 61% yield (107.3 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03 (t, *J* = 1.2 Hz, 1H, OH), 2.43 (s, 3H, CH_3), 3.83 (d, *J* = 7.2 Hz, 2H, CH_2), 4.54 (s, 2H, CH_2), 4.69-4.74 (m, 4H, CH_2), 4.84-4.91 (m, 1H, =CH), 6.78-6.82 (m, 2H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 44.6, 45.2, 59.9, 76.2, 85.1, 124.9, 127.1, 127.2, 129.6, 137.2, 138.7, 143.4, 144.7, 209.6. IR (CH_2Cl_2) ν 3395, 2922, 1954, 1597, 1343, 1333, 1154, 1091, 895, 810, 750, 656 cm^{-1}. MS (ESI) *m/z* (%): 367.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 367.1145, found: 367.1144.

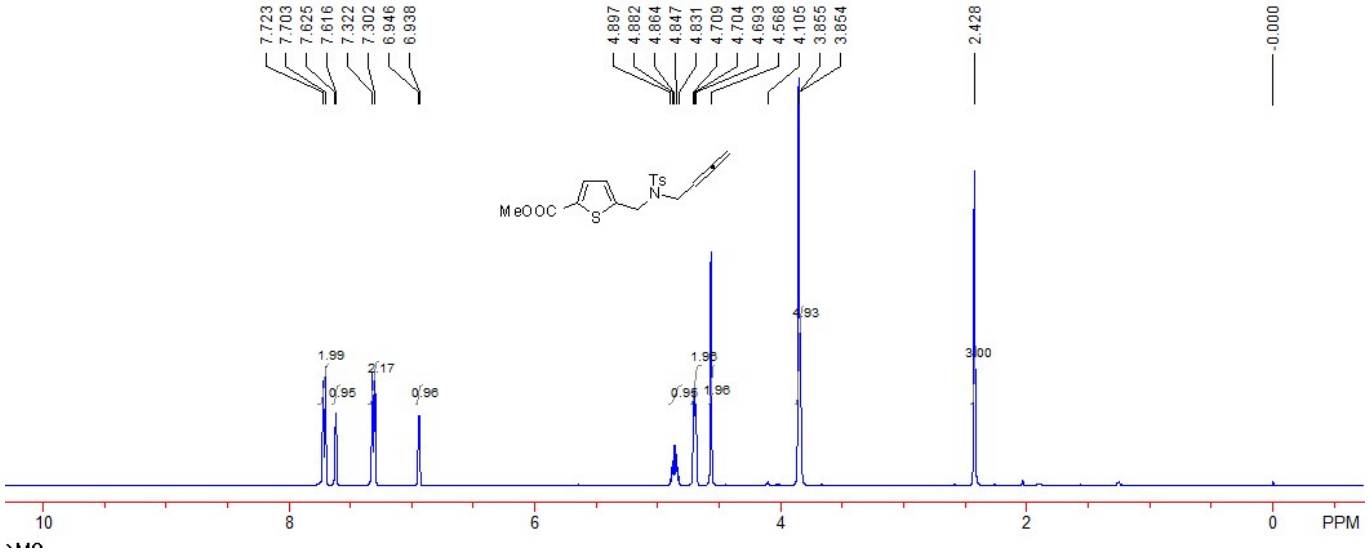


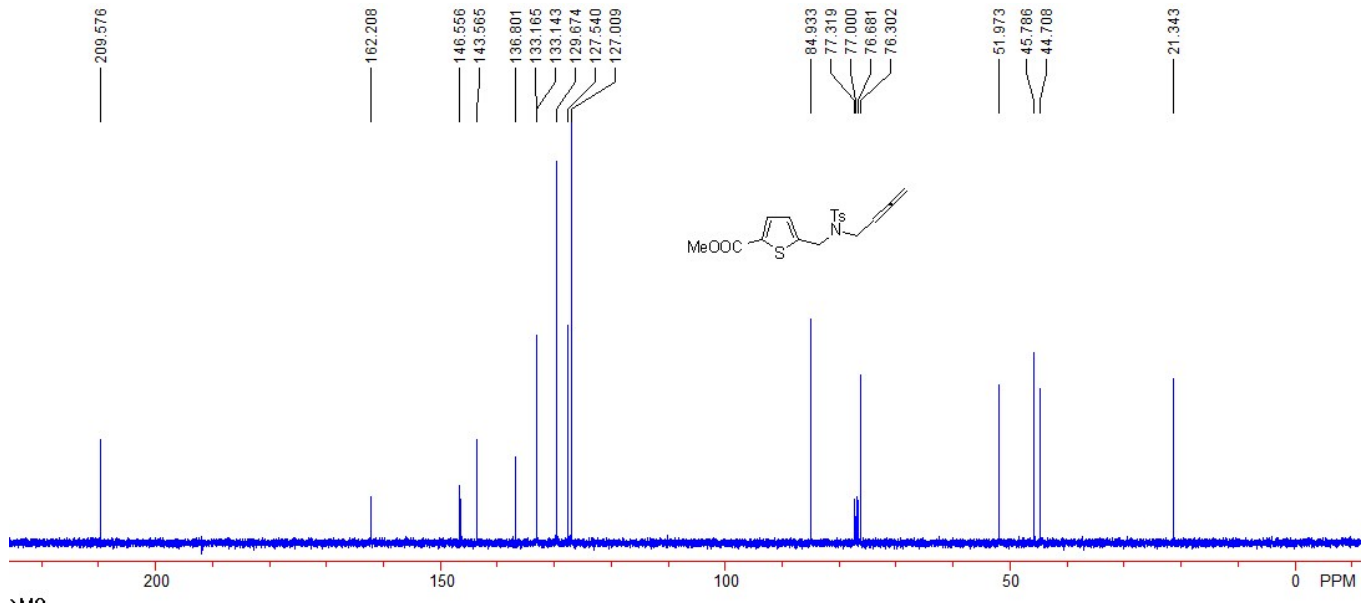


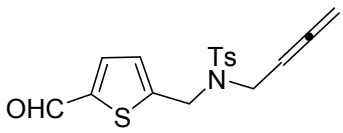


Methyl 5-(((*N*-(buta-2,3-dien-1-yl)-4-methylphenyl)sulfonamido)methyl)thiophene-2-carboxylate 1h

A white liquid, 53% yield (1.0 g). M.p.: 93-95 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 3.85-3.86 (m, 5H, CH_2), 4.57 (s, 2H, CH_2), 4.69-4.71 (m, 2H, CH_2), 4.83-4.90 (m, 1H, =CH), 6.94 (d, *J* = 3.2 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.61-7.63 (m, 1H, ArH), 7.71 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 44.7, 45.8, 52.0, 76.3, 84.9, 127.0, 127.5, 129.7, 133.1, 133.2, 136.8, 143.6, 146.6, 162.2, 209.6. IR (CH_2Cl_2) ν 2923, 1952, 1702, 1461, 1328, 1160, 1031, 841, 733, 657 cm^{-1}. MS (ESI) *m/z* (%): 395.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{23}N_2O_4S_2^{+1}[M+NH_4]^+$ requires 395.1094, found: 395.1092.

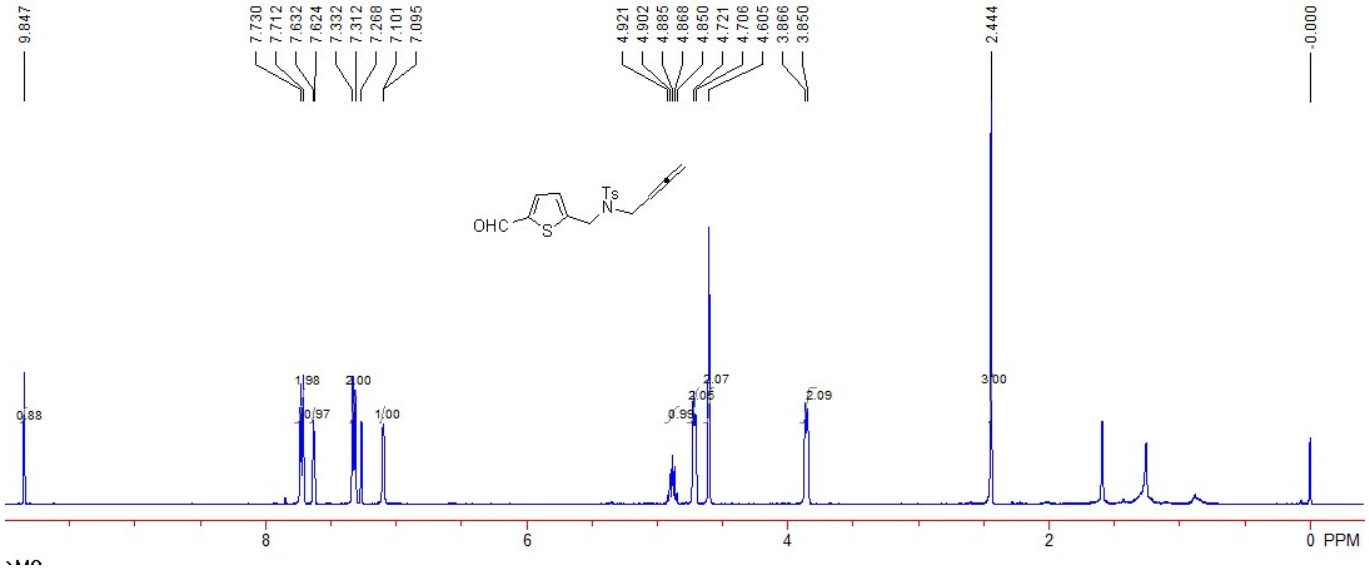


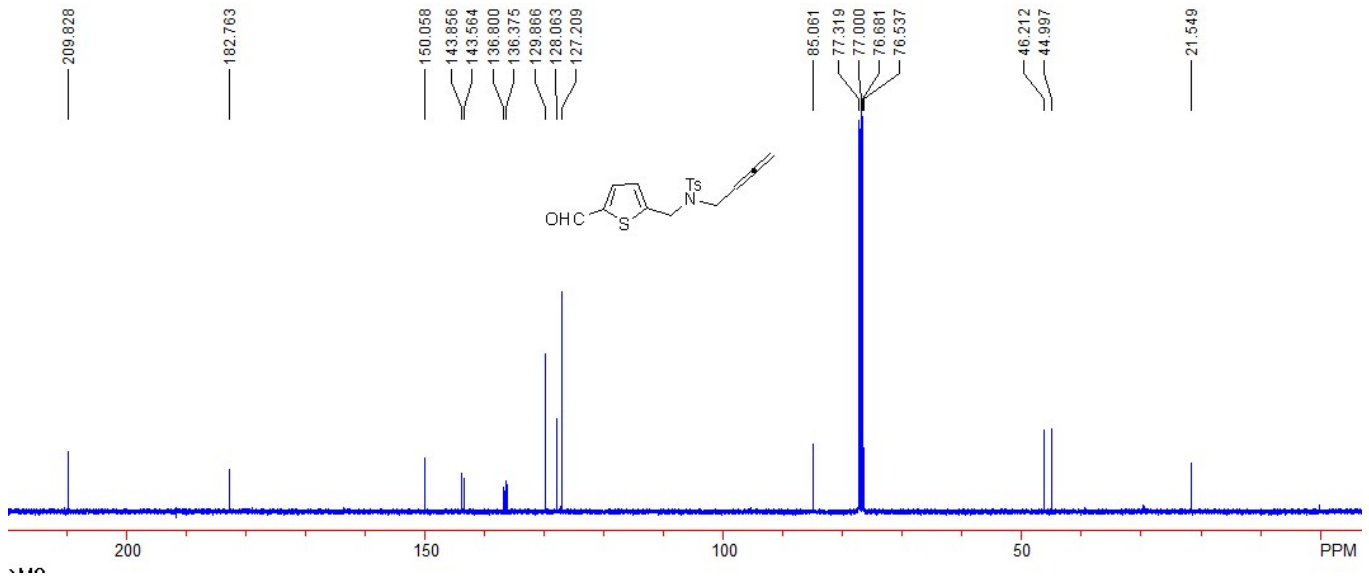


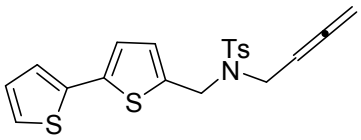


***N*-(buta-2,3-dien-1-yl)-*N*-((5-formylthiophen-2-yl)methyl)-4-methylbenzenesulfonamide 2i**

A white liquid, 60% yield (208.2 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 3.85-3.87 (m, 2H, CH_2), 4.61 (s, 2H, CH_2), 4.70-4.73 (m, 2H, CH_2), 4.85-4.93 (m, 1H, =CH), 7.09-7.11 (m, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.62-7.64 (m, 1H, ArH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH), 9.85 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 45.0, 46.2, 76.5, 85.1, 127.2, 128.1, 129.9, 136.4, 136.8, 143.6, 143.9, 150.1, 182.8, 209.8. IR (CH_2Cl_2) ν 2923, 1952, 1598, 1461, 1310, 1160, 1093, 840, 733, 657 cm^{-1}. MS (ESI) *m/z* (%): 395.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{23}N_2O_4S_2^{+1}[M+NH_4]^+$ requires 395.1094, found: 395.1092.

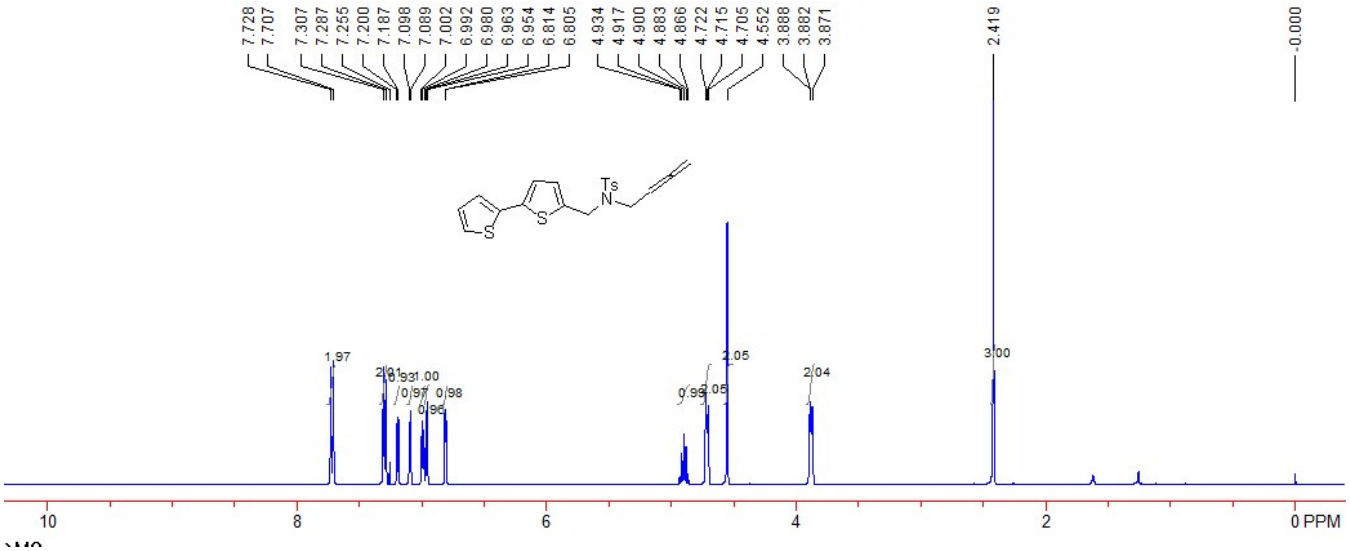


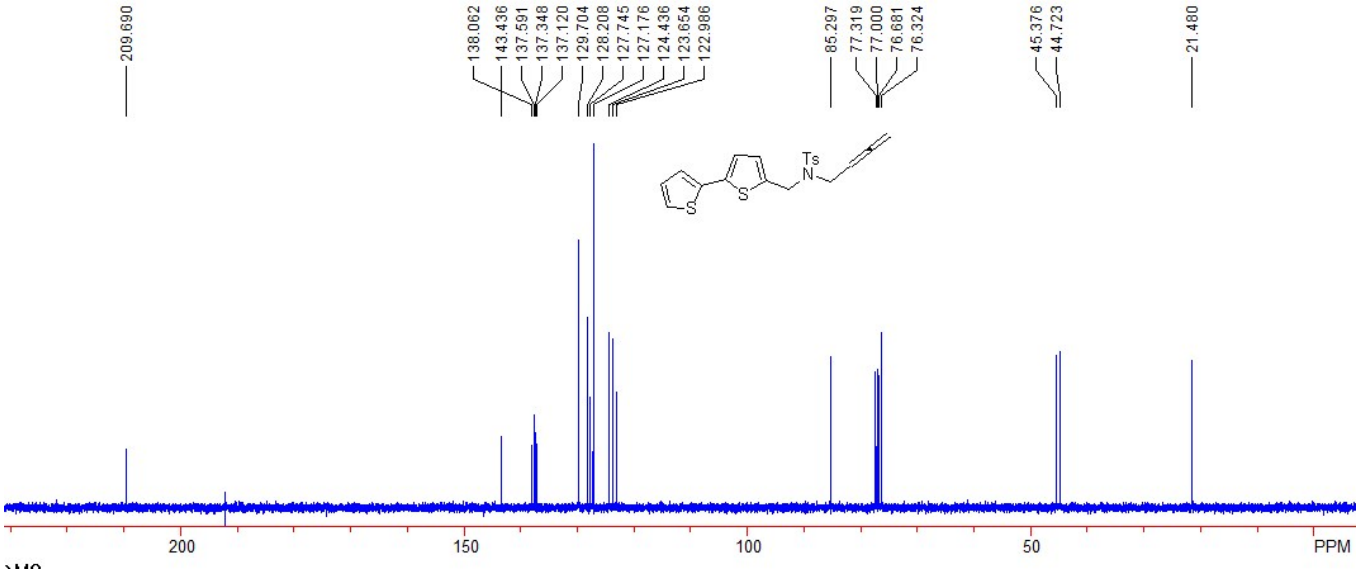


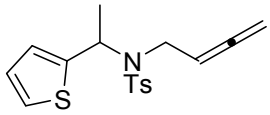


***N*-([2,2'-bithiophen]-5-ylmethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1j**

A white solid, 81% yield (653.2 mg). M.p.: 80-82 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 3.87-3.89 (m, 2H, CH_2), 4.55 (s, 2H, CH_2), 4.70-4.73 (m, 2H, CH_2), 4.86-4.94 (m, 2H, CH_2), 6.80-6.82 (m, 1H, ArH), 6.96 (d, *J* = 3.6 Hz, 1H, ArH), 6.98-7.01 (m, 1H, ArH), 7.09 (d, *J* = 3.6 Hz, 1H, ArH), 7.19 (d, *J* = 5.2 Hz, 1H, ArH), 7.29 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 44.7, 45.4, 76.3, 85.3, 123.0, 123.7, 124.4, 127.2, 127.7， 128.2, 129.7, 137.1, 137.3, 137.6, 138.1, 143.4, 209.7. IR (CH_2Cl_2) ν 3100, 2917, 1956, 1378, 1156, 1091, 851, 771, 656 cm^{-1}. MS (ESI) *m/z* (%): 419.09 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{20}H_{23}N_2O_2S_3^{+1}[M+NH_4]^+$ requires 419.0916, found: 419.0916.

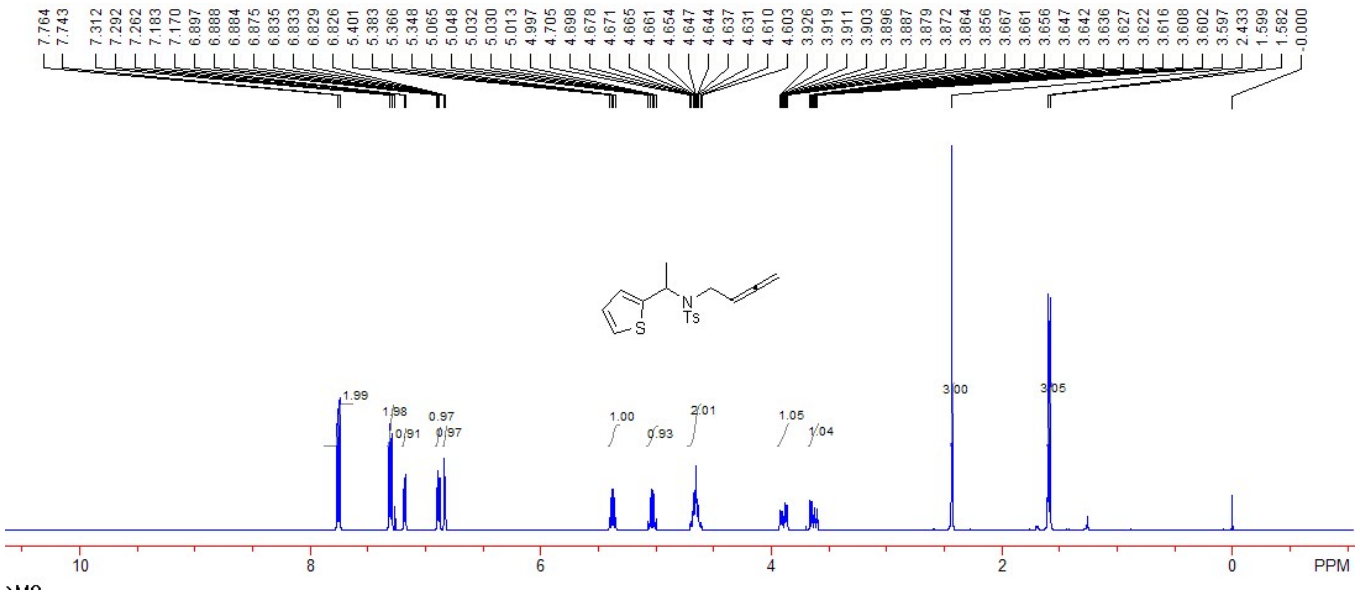


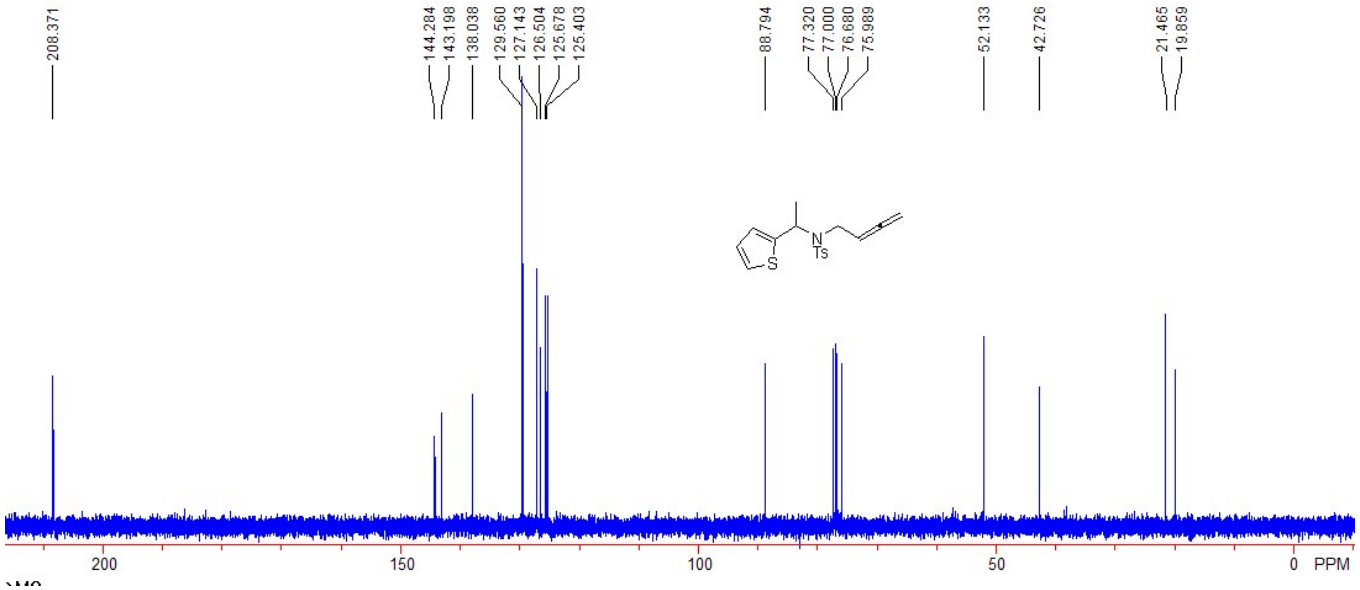


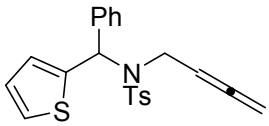


_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-(1-(thiophen-2-yl)ethyl)benzenesulfonamide 1k

A white solid, 55% yield (547 mg). M.p.: 56-58 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.59 (d, J = 6.8 Hz, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.59-3.67 (m, 1H, CH_2), 3.85-3.93 (m, 1H, CH_2), 4.60-4.71 (m, 2H, =CH_2), 4.99-5.07 (m, 1H, =CH), 5.37 (q, J = 7.2 Hz, 1H, CH), 6.83 (dd, J = 4.8, 1.2 Hz, 1H, ArH), 6.88 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.18 (d, J = 5.2 Hz, 1H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.75 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.9, 21.5, 42.7, 52.1, 76.0, 88.8, 125.4, 125.7, 126.5, 127.1, 129.6, 138.0, 143.2, 144.3, 208.3. IR (CH_2Cl_2) ν 3290, 2926, 1955, 1598, 1493, 1336, 1154, 1099, 1046, 982, 813, 702, 658 cm^{-1}. MS (ESI) *m/z* (%): 351.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 351.1195, found: 351.1193.



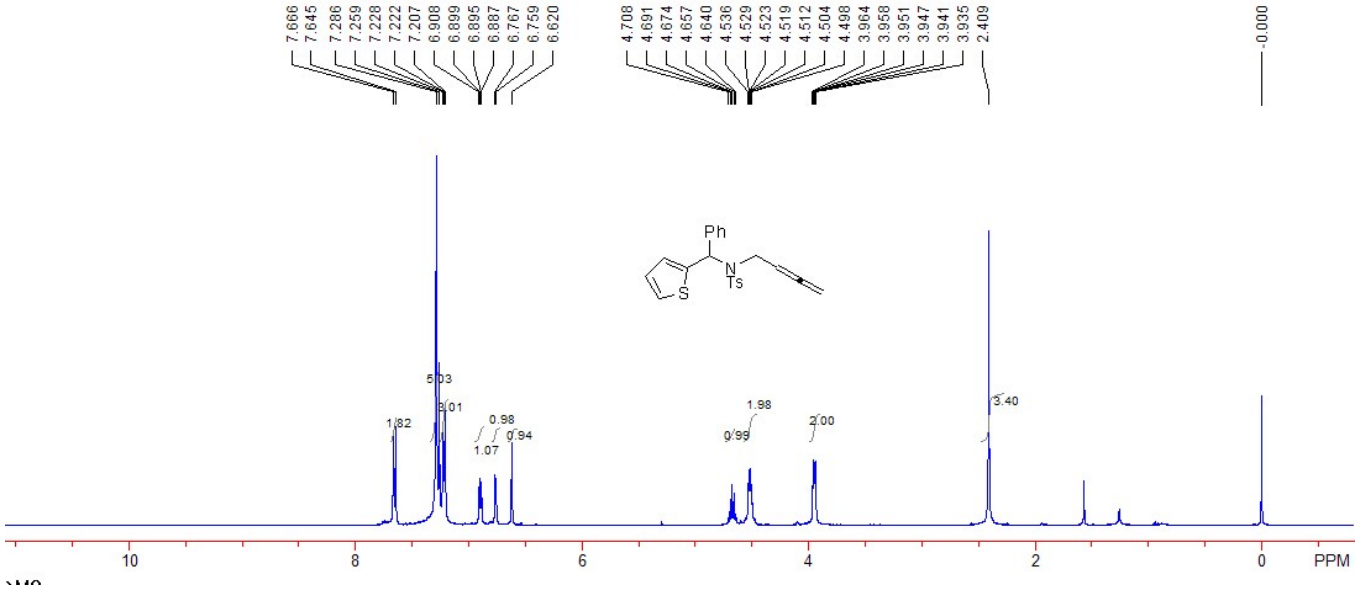


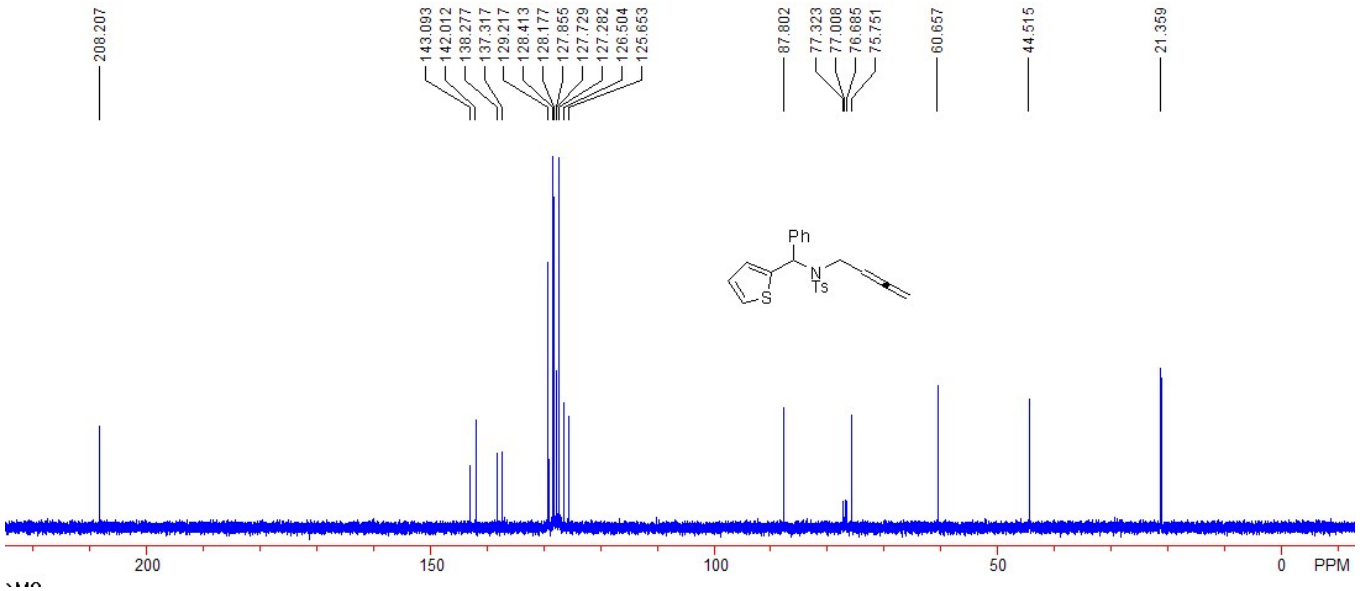


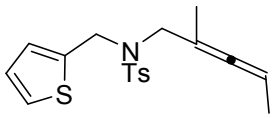
_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-(phenyl(thiophen-2-yl)methyl)benzenesulfonamide 1l

A white solid, 45% yield (358 mg). M.p.: 122-124 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H, CH_3), 3.95 (dt, J = 7.2, 2.4 Hz, 2H, CH_2), 4.52 (dt, J = 7.2, 2.4 Hz, 2H, =CH_2), 4.64-4.71 (m, 1H, =CH), 6.62 (s, 1H, ArH), 6.76 (d, J = 3.2 Hz, 1H, ArH), 6.89 (dd, J = 4.8, 3.2 Hz, 1H, ArH), 7.20-7.23 (m, 3H, ArH), 7.25-7.29 (m, 5H, ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 44.5, 60.7, 75.8, 87.8, 125.7, 126.5, 127.3, 127.7, 127.9, 128.2, 128.4, 129.2, 137.3, 138.3, 142.0, 143.1,

208.2. IR (CH_2Cl_2) ν 3102, 2930, 1606, 1495, 1348, 1330, 1167, 1123, 1066, 999, 816, 707, 663 cm^{-1}. MS (ESI) *m/z* (%): 413.13 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{22}H_{25}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 413.1352, found: 413.1351.



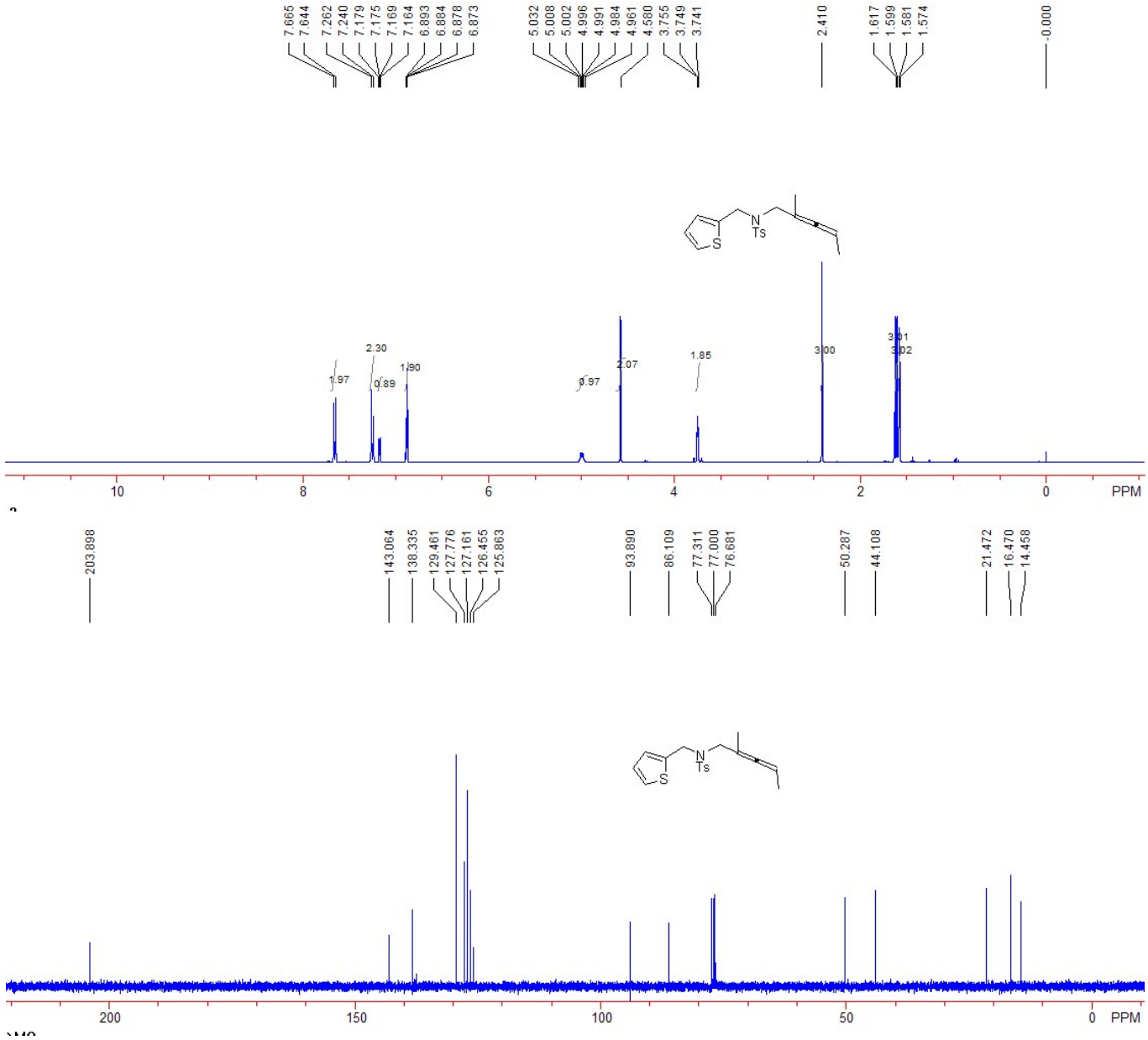


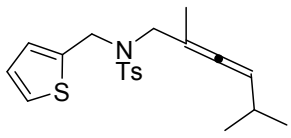


4-methyl-*N*-(2-methylpenta-2,3-dien-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1m

A white liquid, 39% yield (683 mg). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.57 (d, *J* = 3.2 Hz, 3H, CH_3), 1.60 (d, *J* = 7.2 Hz, 3H, CH_3), 2.41 (s, 3H, CH_3), 3.70-3.80 (m, 2H, CH_2), 4.58 (s, 2H, CH_2), 4.96-5.04 (m, 1H, =CH), 6.87-6.90 (m, 2H, ArH), 7.17 (dd, *J* = 4.4, 2.4 Hz, 1H, ArH), 7.25 (d, *J* = 8.0 Hz, 2H, ArH),

7.65 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.5, 16.5, 21.5, 44.1, 50.3, 86.1, 93.9, 125.9, 126.4, 127.2, 127.8, 129.5, 137.6, 138.3, 143.1, 203.9. IR (CH_2Cl_2) ν 2922, 1726, 1598, 1440, 1331, 1155, 1092, 898, 702, 655 cm^{-1}. MS (ESI) *m/z* (%): 348.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 348.1086, found: 348.1089.

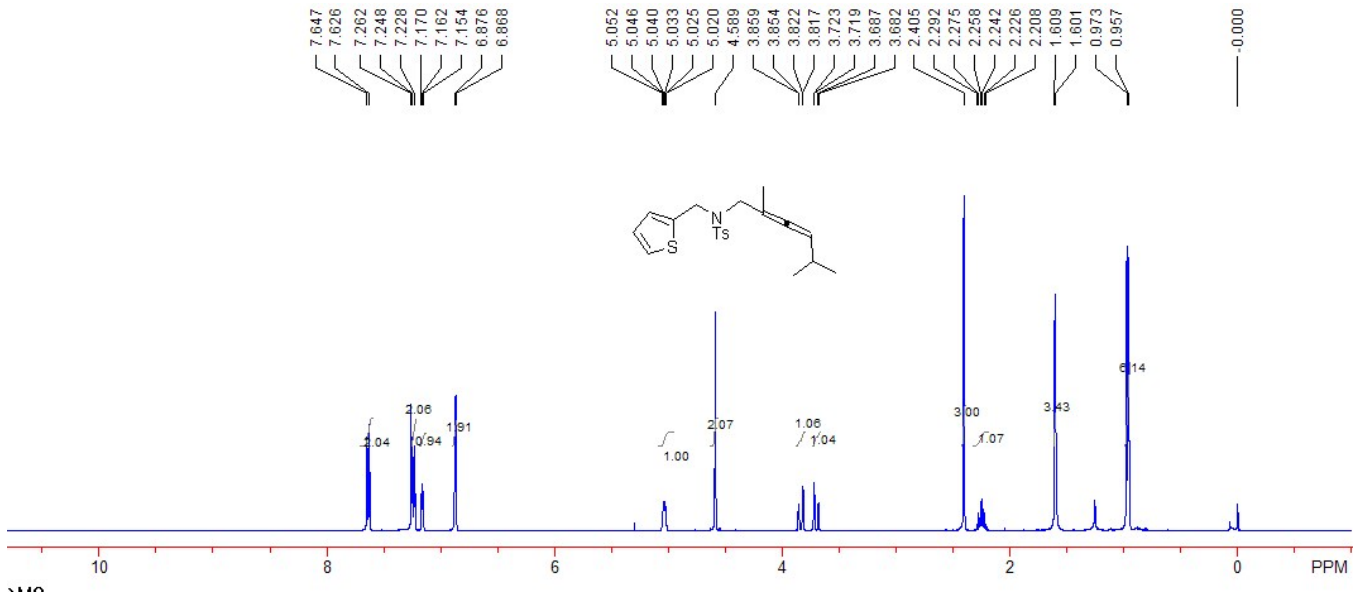


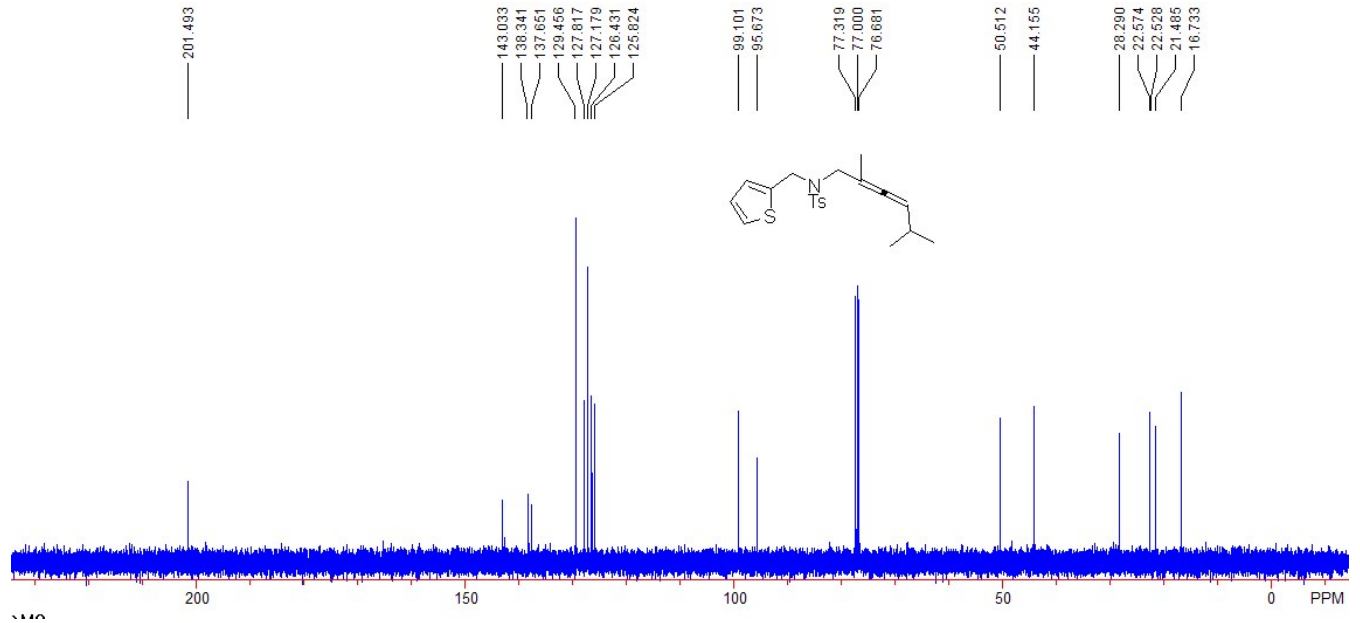


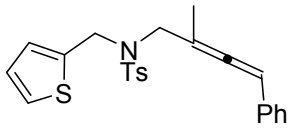
***N*-(2,5-dimethylhexa-2,3-dien-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1n**

A white liquid, 54% yield (389 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.95-0.98 (m, 6H, CH_3), 1.61 (s,

3H, CH_3), 2.20-2.30 (m, 1H, CH), 2.41 (s, 3H, CH_3), 3.70 (dd, *J* = 14.8, 2.0 Hz, 1H, CH_2), 3.83 (dd, *J* = 14.8, 2.0 Hz, 1H, CH_2), 4.59 (s, 2H, CH_2), 5.01-5.06 (m, 1H, =CH), 6.86-6.88 (m, 2H, ArH), 7.16 (dd, *J* = 3.2, 3.2 Hz, 1H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.63 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.7, 21.5, 22.5, 22.6, 28.3, 44.2, 50.5, 95.7, 99.1, 125.8, 126.4, 127.2, 127.8, 129.4, 137.6, 138.3, 143.0, 201.5. IR (CH_2Cl_2) ν 2960, 2926, 2870, 1727, 1598, 1445, 1158, 1092, 901, 703, 658 cm^{-1}. MS (ESI) *m/z* (%): 376.14 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{20}H_{26}NO_2S_2^{+1}[M+H]^+$ requires 376.1399, found: 376.1402.

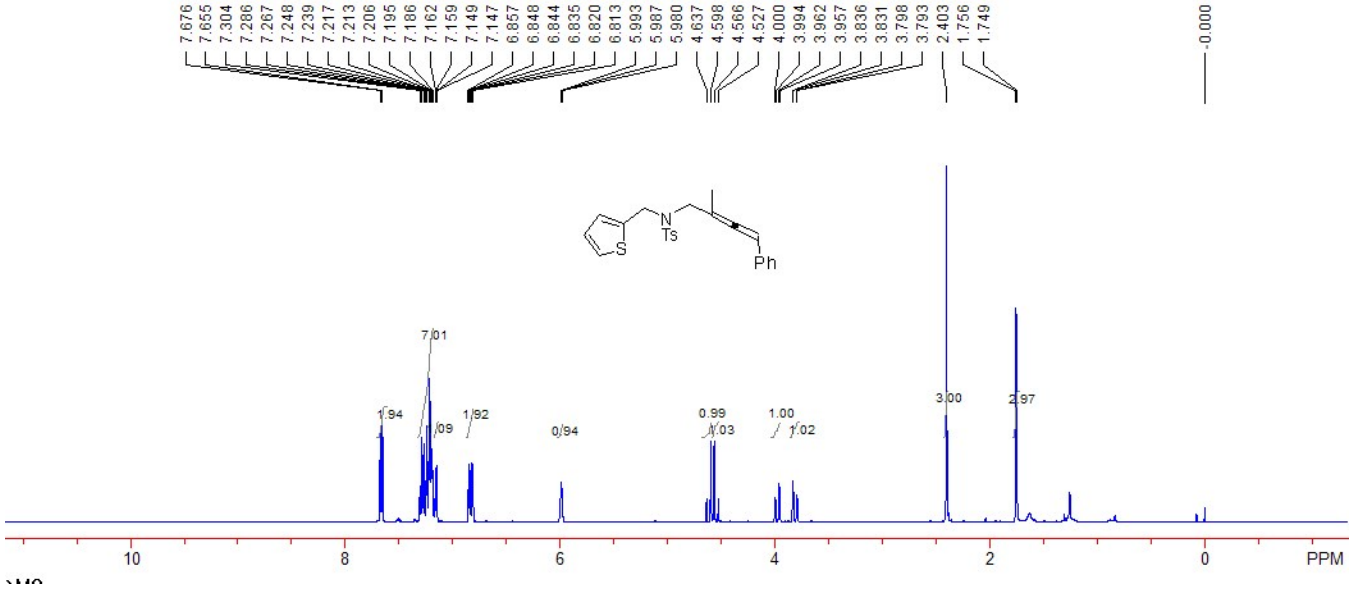


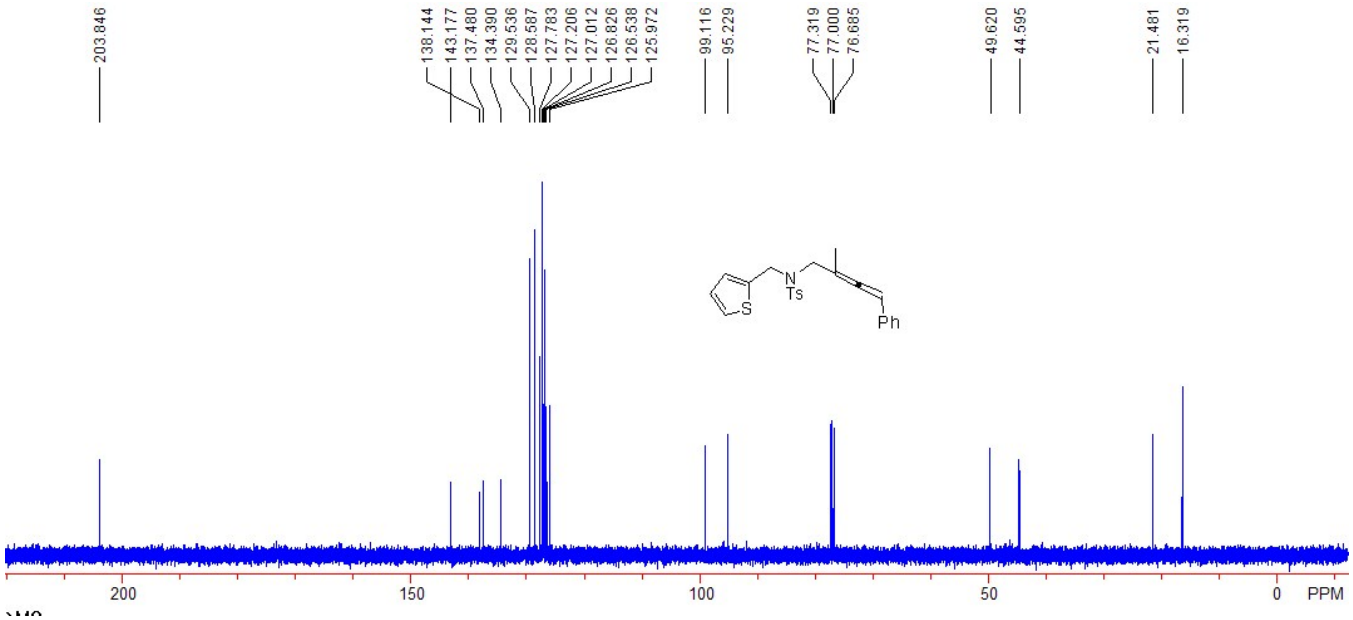


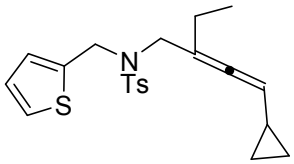


4-methyl-*N*-(2-methyl-4-phenylbuta-2,3-dien-1-yl)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1o

A white liquid, 21% yield (428 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.75 (d, *J* = 2.8 Hz, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.81 (dd, *J* = 15.2, 2.0 Hz, 1H, CH_2), 3.98 (dd, *J* = 15.2, 2.0 Hz, 1H, CH_2), 4.54 (d, *J* = 15.6 Hz, 1H, CH_2), 4.61 (d, *J* = 15.6 Hz, 1H, CH_2), 5.97-6.00 (m, 1H, =CH), 6.81-6.86 (m, 2H, ArH), 7.15 (dd, *J* = 5.2, 1.2 Hz, 1H, ArH), 7.18-7.31 (m, 7H, ArH), 7.66 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.3, 21.5, 44.6, 49.6, 95.2, 99.1, 126.0, 126.5, 126.8, 127.0, 127.2, 127.8, 128.6, 129.5, 134.4, 137.5, 138.1, 143.2, 203.8. IR (CH_2Cl_2) ν 2919, 1952, 1597, 1496, 1332, 1155, 1091, 899, 693, 656 cm^{-1}. MS (ESI) *m/z* (%): 427.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{23}H_{27}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 427.1508, found: 427.1512.



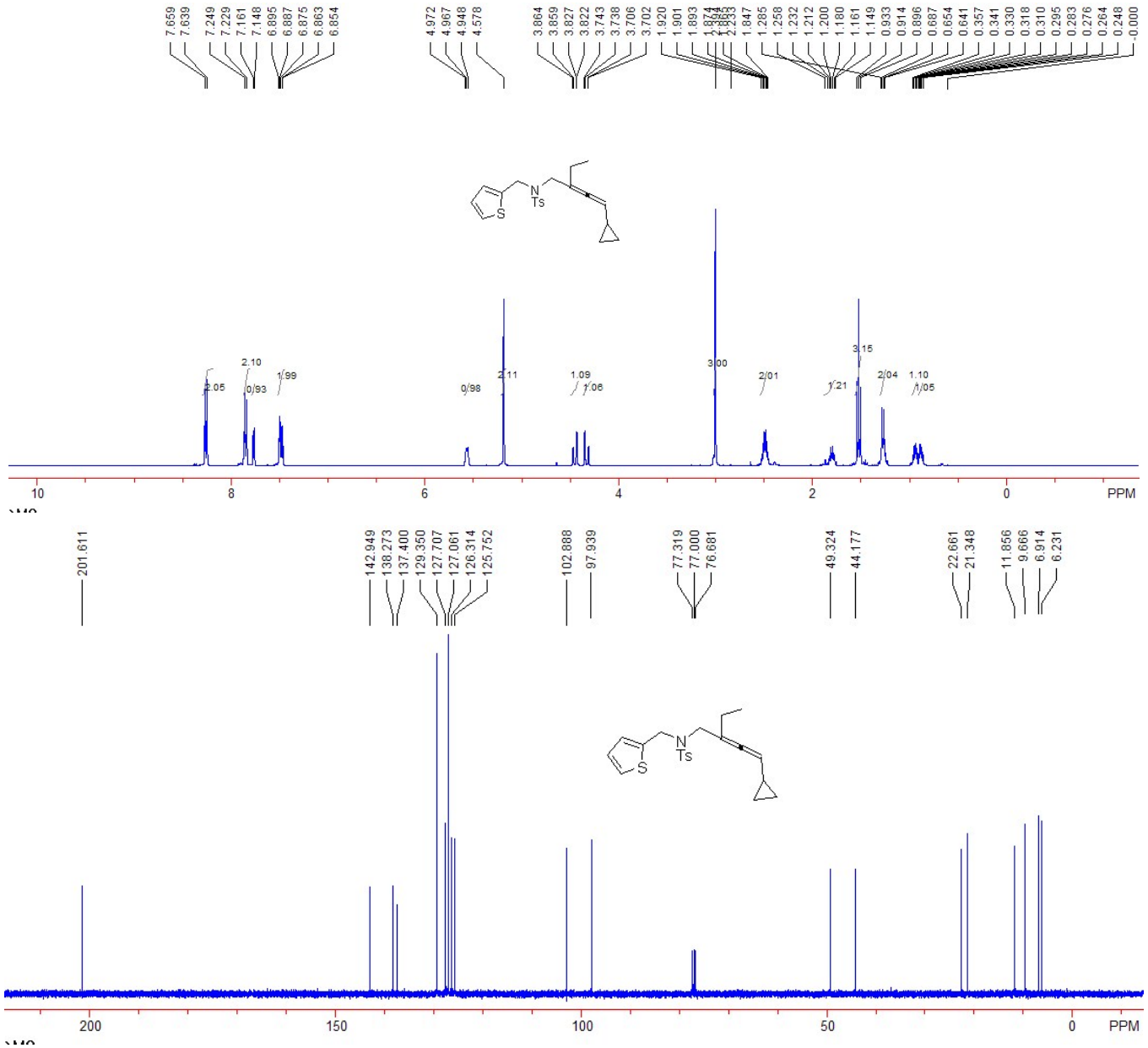


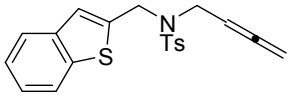


***N*-(4-cyclopropyl-2-ethylbuta-2,3-dien-1-yl)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide**

1p

A white liquid, 56% yield (648 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.24-0.30 (m, 1H, CH_2), 0.31-0.36 (m, 1H, CH_2), 0.64-0.69 (m, 2H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3H, CH_3), 1.14-1.26 (m, 1H, CH_2), 1.84-1.92 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.72 (dd, *J* = 14.8, 2.0 Hz, 1H, CH_2), 3.84 (dd, *J* = 14.8, 2.0 Hz, 1H, CH_2), 4.58 (s, 2H, CH_2), 4.94-4.98 (m, 1H, =CH), 6.85-6.90 (m, 2H, ArH), 7.15 (d, *J* = 5.2 Hz, 1H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.64 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.2, 6.9, 9.7, 11.9, 21.4, 22.7, 44.2, 49.3, 98.0, 102.9, 125.7, 126.3, 127.1, 127.7, 129.3, 137.4, 138.3, 143.0, 201.6. IR (CH_2Cl_2) ν 3080, 3003, 1598, 1441, 1346, 1157, 1092, 946, 703, 658 cm^{-1}. MS (ESI) *m/z* (%): 388.14 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{21}H_{26}NO_2S_2^{+1}[M+H]^+$ requires 388.1399, found: 388.1400.

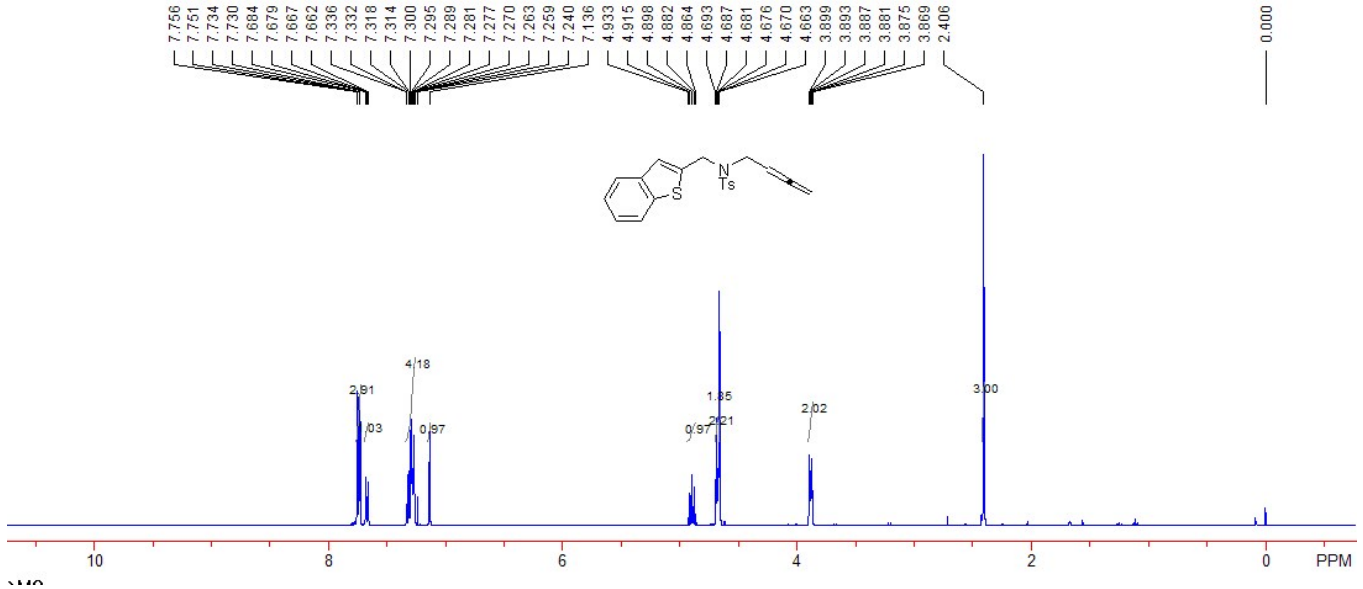


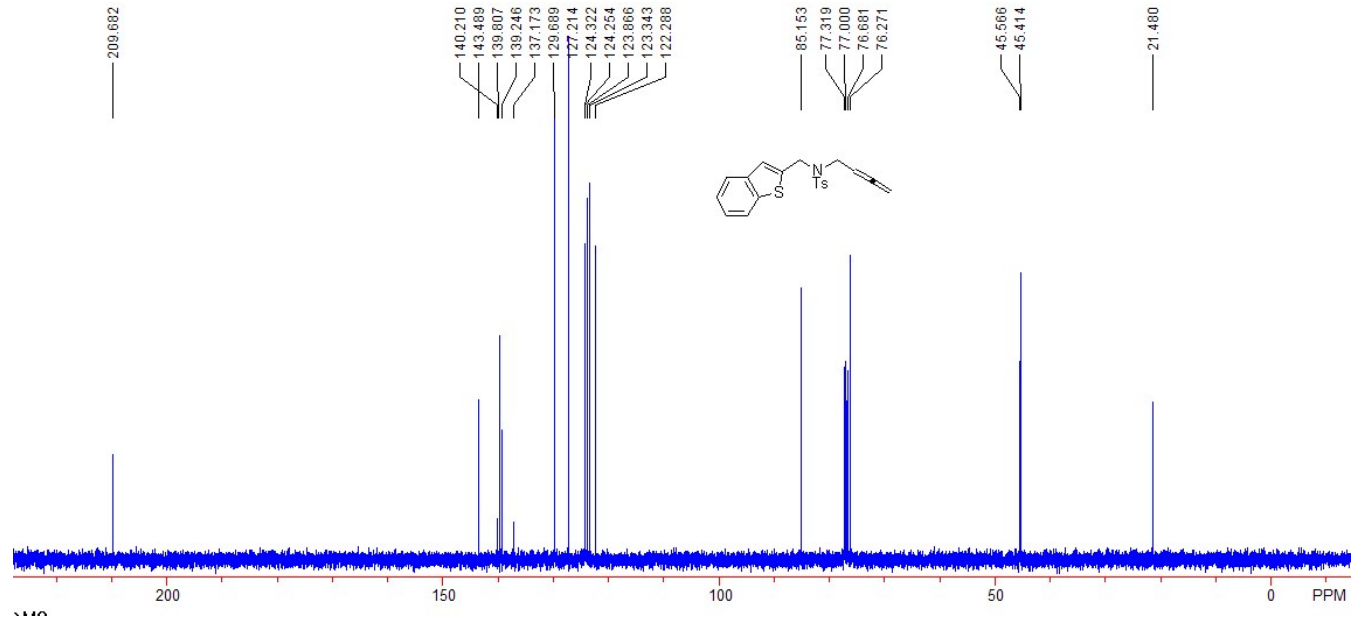


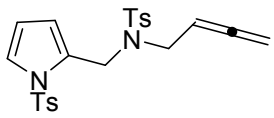
_N_-(benzo[_b_]thiophen-2-ylmethyl)-_N_-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1q

A white solid, 57% yield (1.1 g). M.p.: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H, CH_3), 3.88 (dt, J = 7.2, 2.4 Hz, 2H, CH_2), 4.66 (s, 2H, CH_2), 4.68 (dt, J = 7.2, 2.4 Hz, 2H, =CH_2), 4.86-4.94 (m, 1H, =CH), 7.14 (s, 1H, ArH), 7.26-7.34 (m, 4H, ArH), 7.67 (dd, J = 6.8, 2.0 Hz, 1H, ArH), 7.73-7.76 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 45.4, 45.6, 76.3, 85.2, 122.3, 123.3, 123.9, 124.2, 124.3, 127.2, 129.7, 137.2, 139.2, 139.8, 140.2, 143.5, 209.5. IR (CH_2Cl_2) ν 3056, 2964, 2924, 1958, 1598, 1435, 1335, 1160, 1092, 899, 726, 655 cm^{-1}. MS (ESI) *m/z* (%): 387.11 (100) $[M+NH_4]^+$; HRMS

(ESI) Calcd. For $C_{20}H_{23}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 387.1195, found: 387.1196.



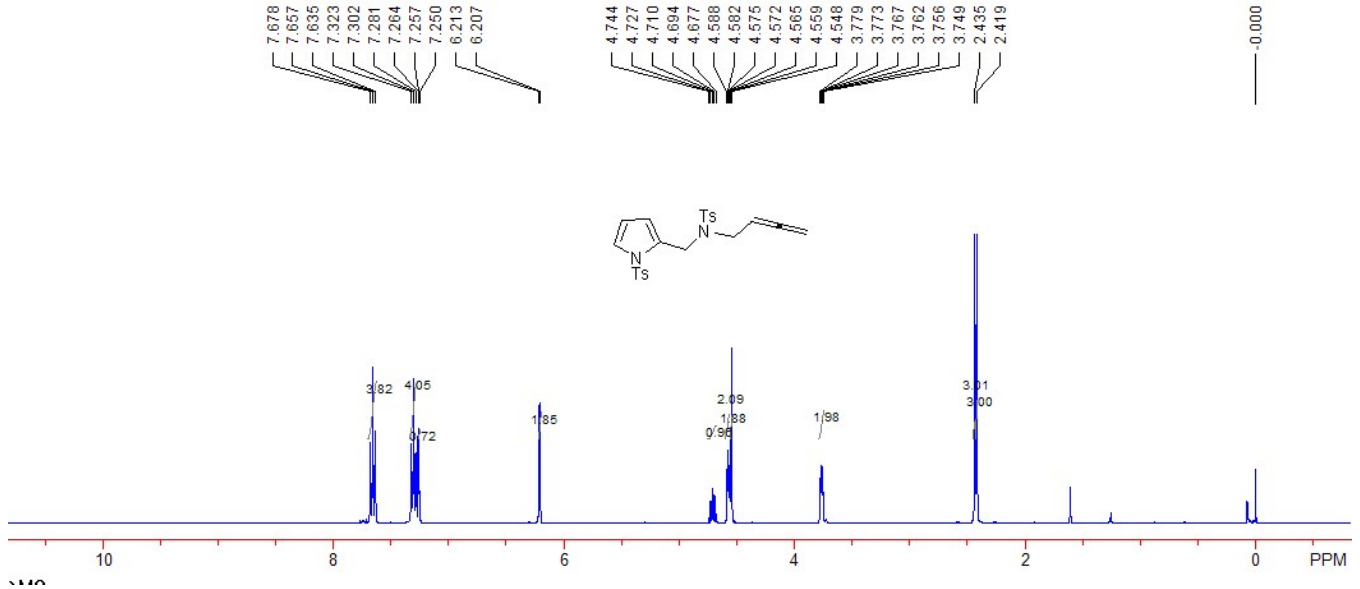


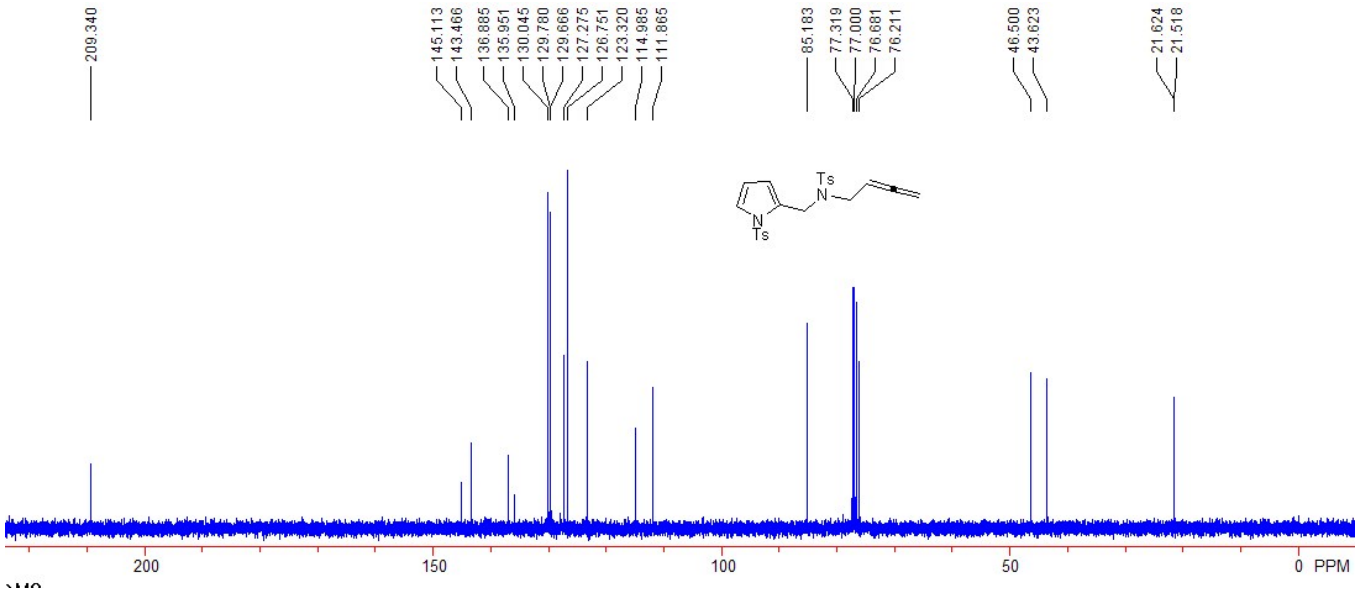


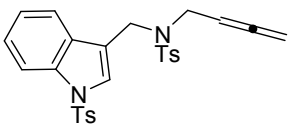
_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-((1-tosyl-1_H_-pyrrol-2-yl)methyl)benzenesulfonamide 1r

A white solid, 66% yield (600 mg). M.p.: 86-88 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.76 (dt, J = 7.2, 2.4 Hz, 2H, CH_2), 4.55 (s, 2H, CH_2), 4.57 (dt, J = 6.4, 2.4 Hz, 2H, =CH_2), 4.67-4.75 (m, 1H, =CH), 6.21 (d, J = 2.8 Hz, 2H, ArH), 7.25 (d, J = 2.8 Hz, 1H, ArH), 7.26-7.33 (m, 4H, ArH), 7.63-7.68 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.6, 43.6, 46.5, 76.2, 85.2, 111.9, 115.0, 123.3, 126.7, 127.3, 129.7, 129.8, 130.0, 136.0, 136.9, 143.5, 145.1, 209.3. IR

(CH_2Cl_2) ν 3090, 2941, 1955, 1597, 1401, 1342, 1157, 1191, 1017, 926, 813, 724, 669 cm^{-1}. MS (ESI) *m/z* (%): 457.12 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{23}H_{25}N_2O_4S_2^{+1}[M+H]^+$ requires 457.1250, found: 457.1249.



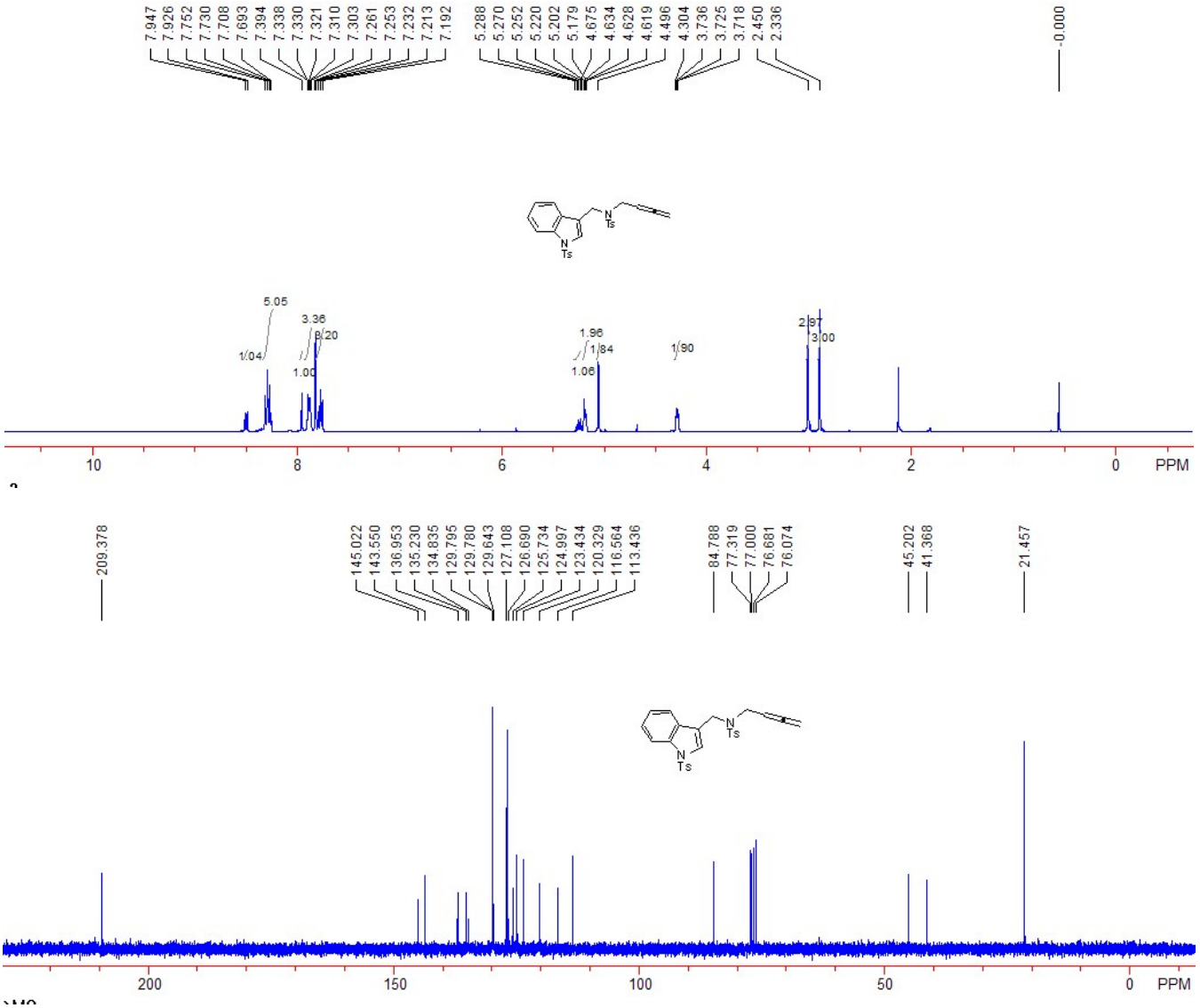


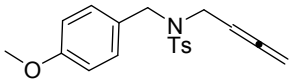


***N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-((1-tosyl-1*H*-indol-3-yl)methyl)benzenesulfonamide 1s**

A white solid, 72% yield (728 mg). M.p.: 142-144 °C (this starting material is quite labile and it will contain some impurity when it is stored in refrigerator). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.72 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.50 (s, 2H, CH_2), 4.62 (dt, *J* = 6.4, 2.4 Hz,

2H, $=CH_2$), 4.65-4.72 (m, 1H, =CH), 7.18-7.25 (m, 3H, ArH), 7.29-7.34 (m, 3H, ArH), 7.40 (s, 1H, ArH), 7.69-7.75 (m, 5H, ArH), 7.93 (d, *J* =8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 41.4, 45.2, 76.1, 84.8, 113.5, 116.6, 120.4, 123.5, 125.0, 125.7, 126.7, 127.1, 129.7, 129.81, 129.83, 134.9, 135.2, 137.0, 143.6, 145.0, 209.4. IR (CH_2Cl_2) ν 2937, 2861, 1953, 1597, 1447, 1363, 1338, 1171, 1158, 1099, 977, 891, 703, 611 cm^{-1}. MS (ESI) *m/z* (%): 524.16 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{30}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 524.1672, found: 524.1671.

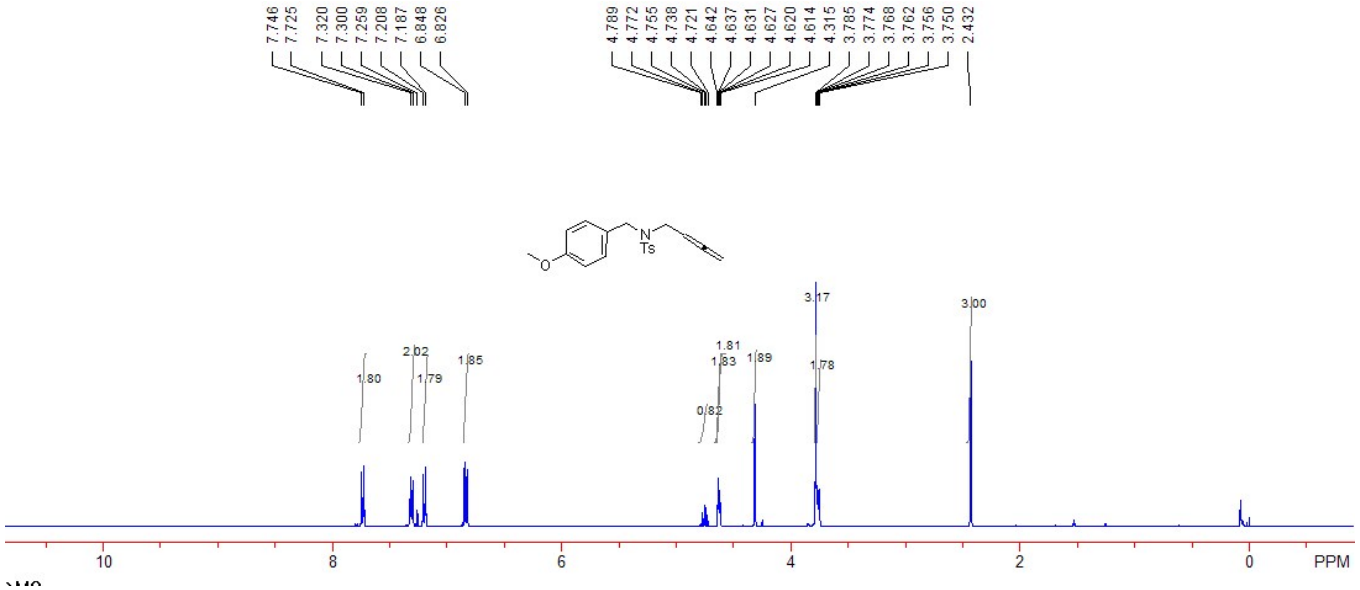


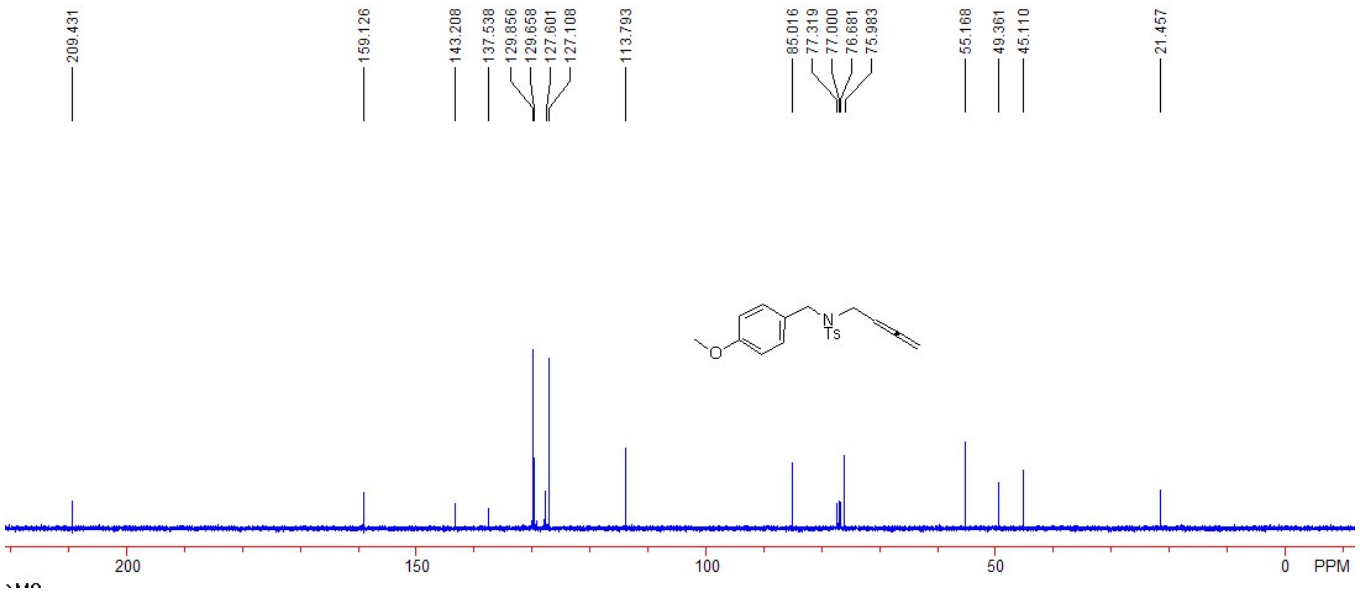


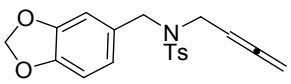
***N*-(buta-2,3-dien-1-yl)-*N*-(4-methoxybenzyl)-4-methylbenzenesulfonamide 1t**

A white solid, 80% yield (1.1 g). M.p.: 67-69 °C. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 3.76 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 3.79 (s, 3H, CH_3), 4.32 (s, 2H, CH_2), 4.62 (dt, *J* = 6.4, 2.4 Hz, 2H,

=CH_2), 4.72-4.79 (m, 1H, =CH), 6.83 (d, *J* =8.8 Hz, 2H, ArH), 7.19 (d, *J* = 8.8 Hz, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.73 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 45.1, 49.4, 55.2, 76.0, 85.0, 113.8, 127.1, 127.6, 129.6, 129.9, 137.5, 143.2, 159.1, 209.4. IR (CH_2Cl_2) ν 3273, 2917, 2849, 1955, 1612, 1513, 1337, 1249, 1160, 1091, 924, 820, 745, 659 cm^{-1}. MS (ESI) *m/z* (%): 361.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{25}N_2O_3S^{+1}[M+NH_4]^+$ requires 361.1580, found: 361.1583.



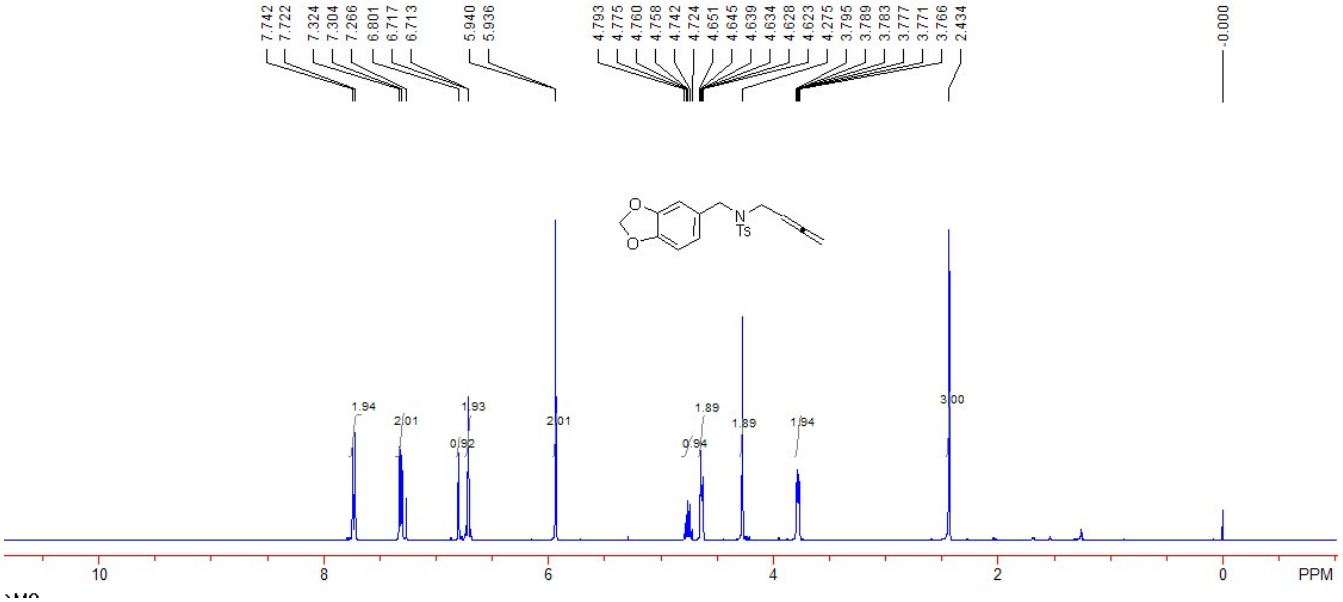


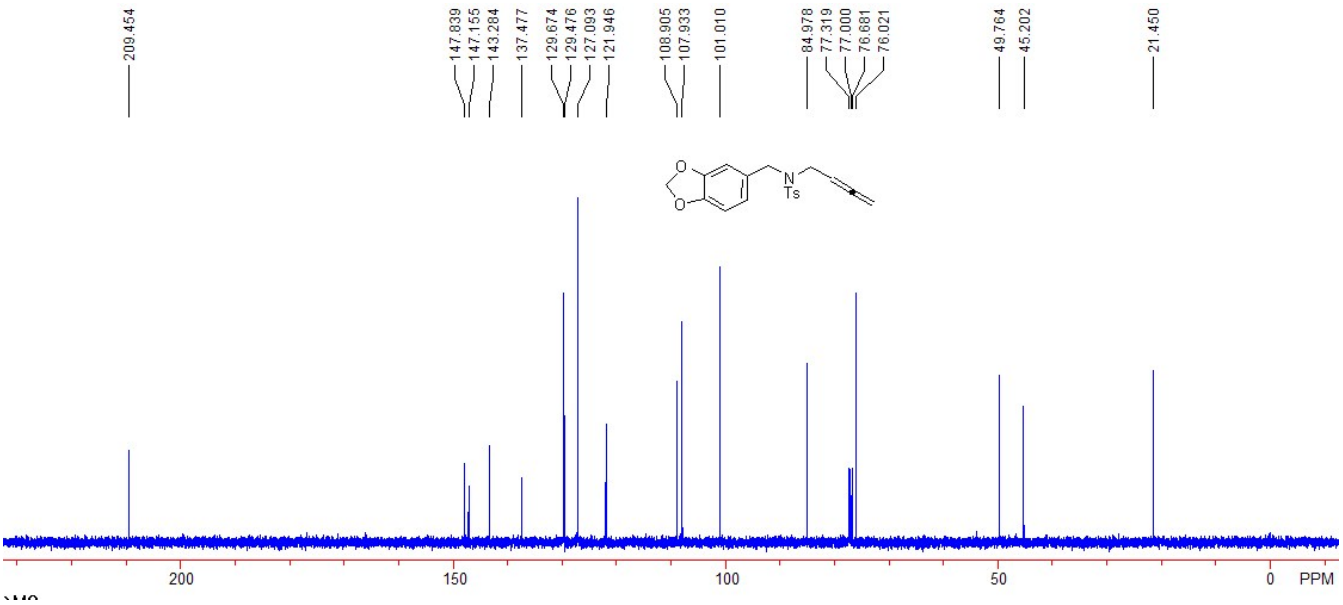


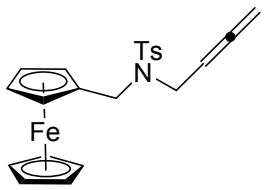
***N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1u**

A white solid, 61% yield (837 mg). M.p.: 105-107 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H,

CH_3), 3.78 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.28 (s, 2H, CH_2), 4.63 (dt, *J* = 7.2, 2.4 Hz, 2H, =CH_2), 4.72-4.80 (m, 1H, =CH), 5.94 (d, *J* = 2.4 Hz, 2H, CH_2), 6.70-6.72 (m, 2H, ArH), 6.80 (s, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.73 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 45.2, 49.8, 76.0, 85.0, 101.0, 107.9, 108.9, 121.9, 127.1, 129.5, 129.7, 137.5, 143.3, 147.1, 147.8, 209.4. IR (CH_2Cl_2) ν 2961, 2922, 2855, 1957, 1596, 1496, 1447, 1333, 1154, 1091, 935, 857, 755, 680 cm^{-1}. MS (ESI) *m/z* (%): 358.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{19}H_{20}NO_4S^{+1}[M+H]^+$ requires 358.1108, found: 358.1103.

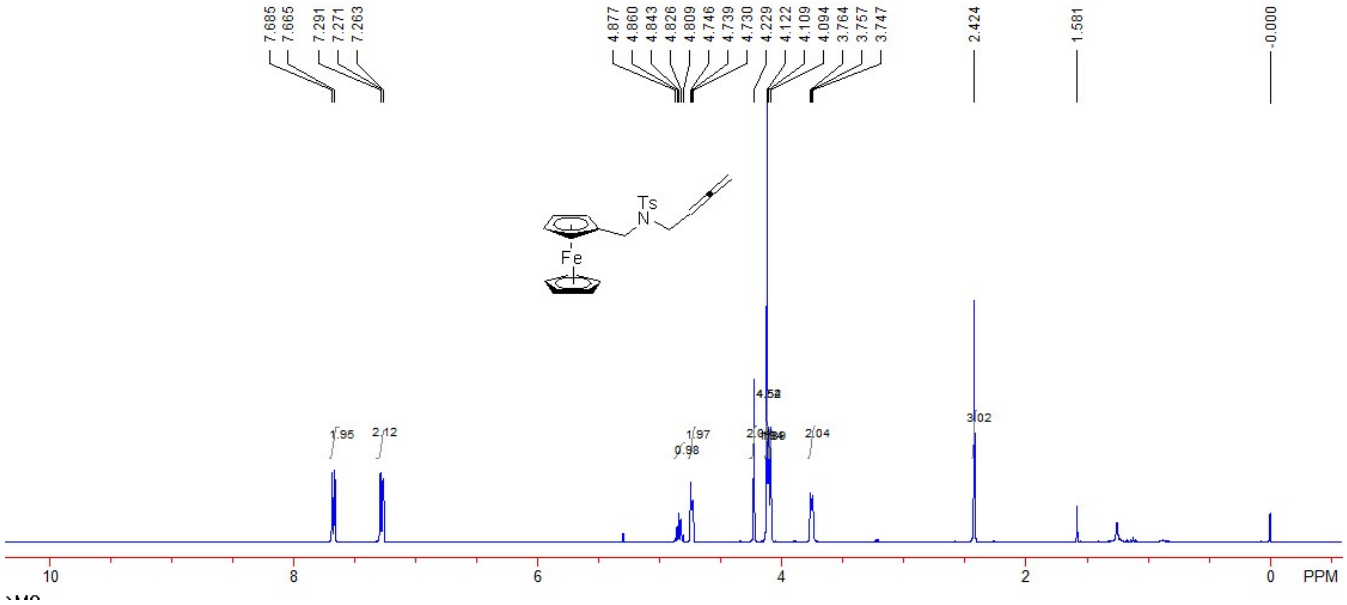


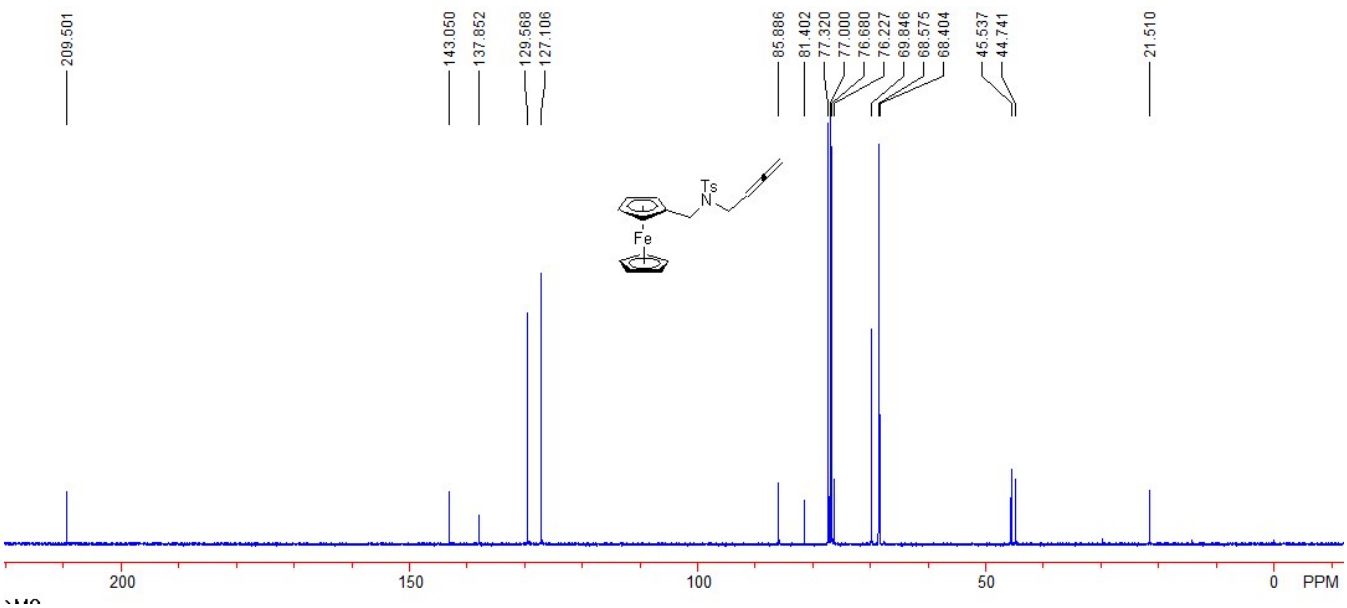


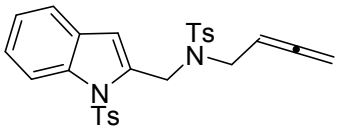


5-(((N-(buta-2,3-dien-1-yl)-4-methylphenyl)sulfonamido)methyl) ferrocene 1v

A yellow solid, 53% yield (111.8 mg). M.p.: 102-104 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 3.74-3.77 (m, 2H, CH_2), 4.09 (s, 2H, CH), 4.11 (s, 2H, CH), 4.12 (s, 5H, CH), 4.23 (s, 2H), 4.73-4.75 (m, 2H, CH_2), 4.80-4.88 (m, 1H, =CH), 7.28 (d, J = 8.0 Hz, 2H, ArH), 7.67 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 44.7, 45.5, 68.4, 68.6, 69.8, 76.2, 81.4, 85.9, 127.1, 129.6, 137.9, 143.1, 209.5. IR (CH_2Cl_2) ν 3093, 2927, 1952, 1376, 1334, 1157, 1024, 812, 766, 657 cm^{-1}. MS (ESI) *m/z* (%): 419.08 (100) $[M]^+$; HRMS (ESI) Calcd. For $C_{22}H_{23}O_2N^{54}FeS^{+1}[M]^+$ requires 419.0840, found: 419.0841.

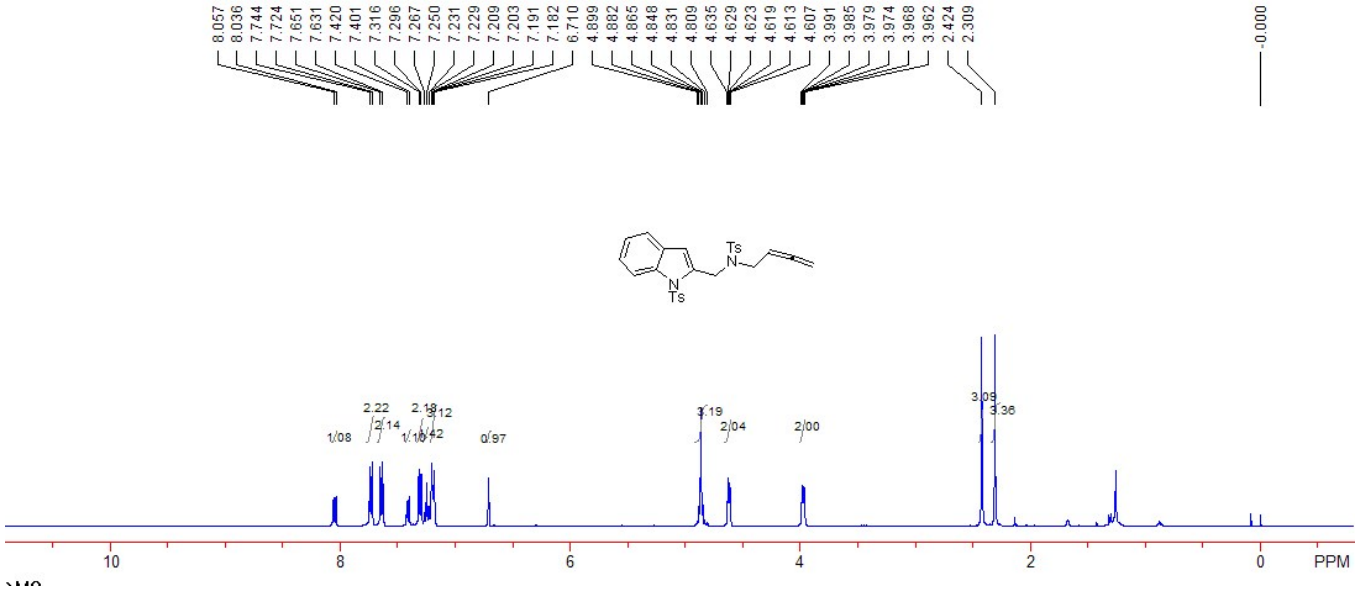


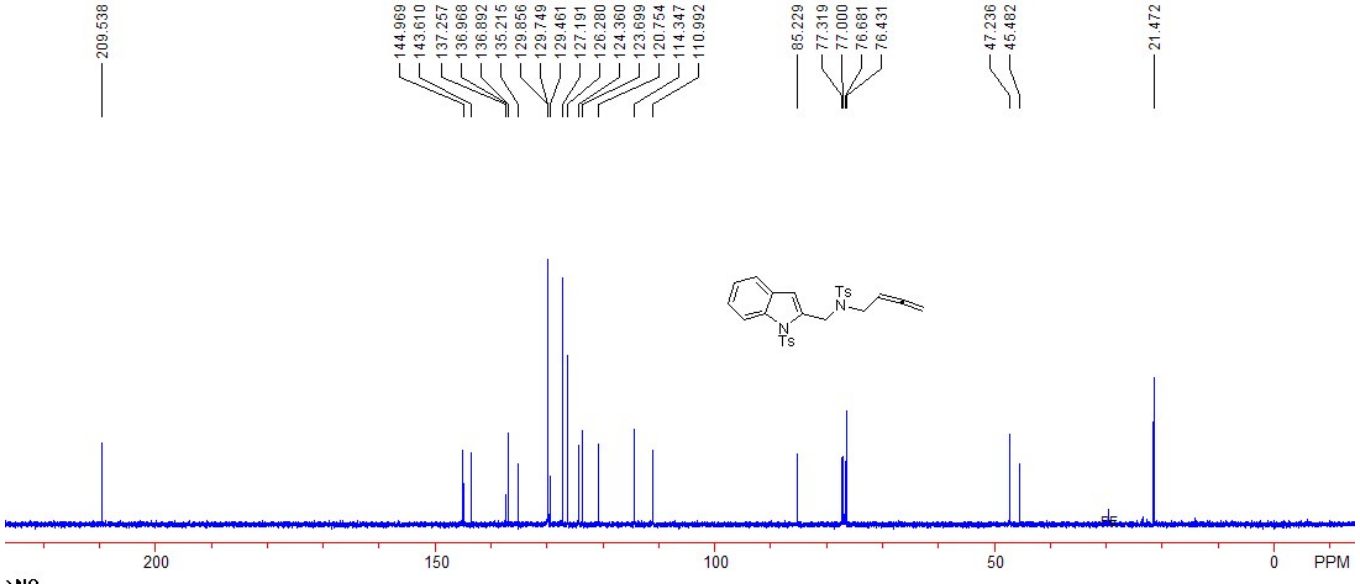


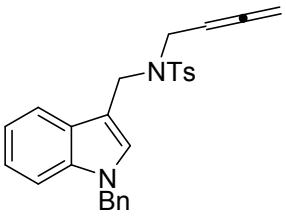


_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-((1-tosyl-1_H_-indol-2-yl)methyl)benzenesulfonamide 1w

A white liquid, 53% yield (777 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.98 (dt, *J* = 6.8, 2.4 Hz, 2H, CH_2), 4.62 (dt, *J* = 6.4, 2.4 Hz, 2H, =CH_2), 4.87 (s, 2H, CH_2), 4.80-4.90 (m, 1H, =CH), 6.71 (s, 1H, ArH), 7.18-7.21 (m, 3H, ArH), 7.22-7.27 (m, 1H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 7.41 (d, *J* = 7.6 Hz, 1H, ArH), 7.64 (d, *J* = 8.0 Hz, 2H, ArH), 7.73 (d, *J* =8.0 Hz, 2H, ArH), 8.04 (d, *J* =8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 45.5, 47.2, 76.4, 85.2, 111.0, 114.3, 120.8, 123.7, 124.4, 126.3, 127.2, 129.5, 129.7, 129.9, 135.2, 136.9, 137.0, 137.3, 143.6, 145.0, 209.5. IR (CH_2Cl_2) ν 2959, 2923, 2853, 1954, 1596, 1494, 1366, 1339, 1172, 1156, 1090, 925, 850, 748, 658 cm^{-1}. MS (ESI) *m/z* (%): 507.14 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{27}N_2O_4S_2^{+1}[M+H]^+$ requires 507.1407, found: 507.1407



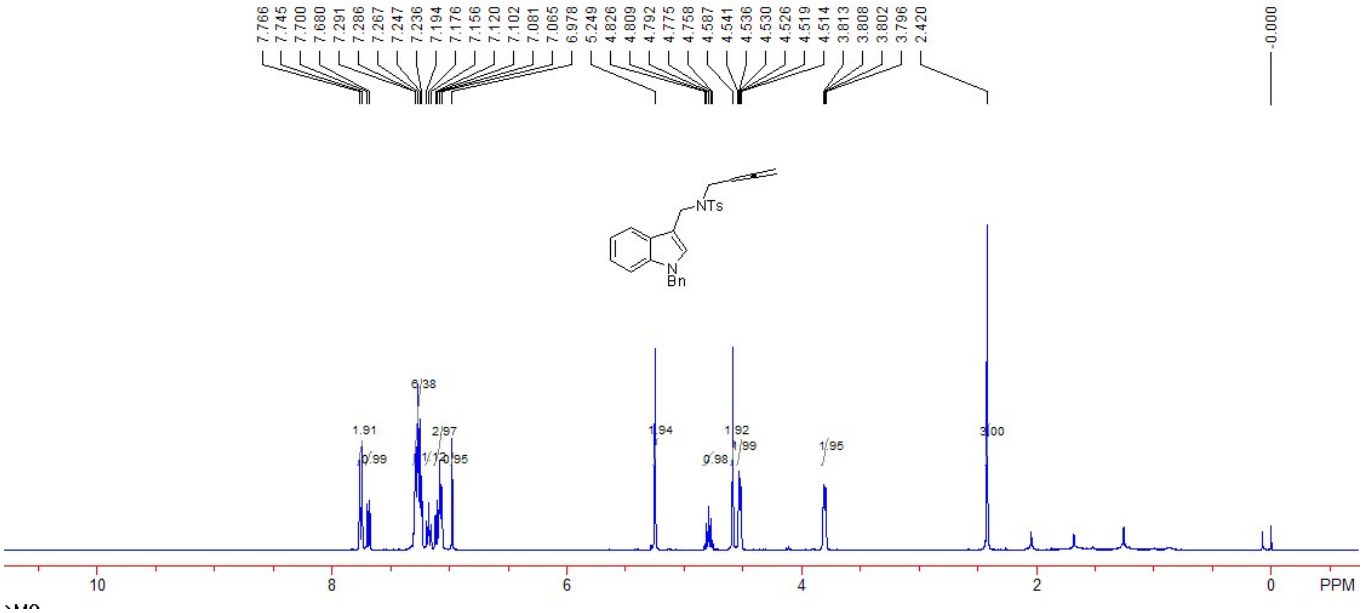


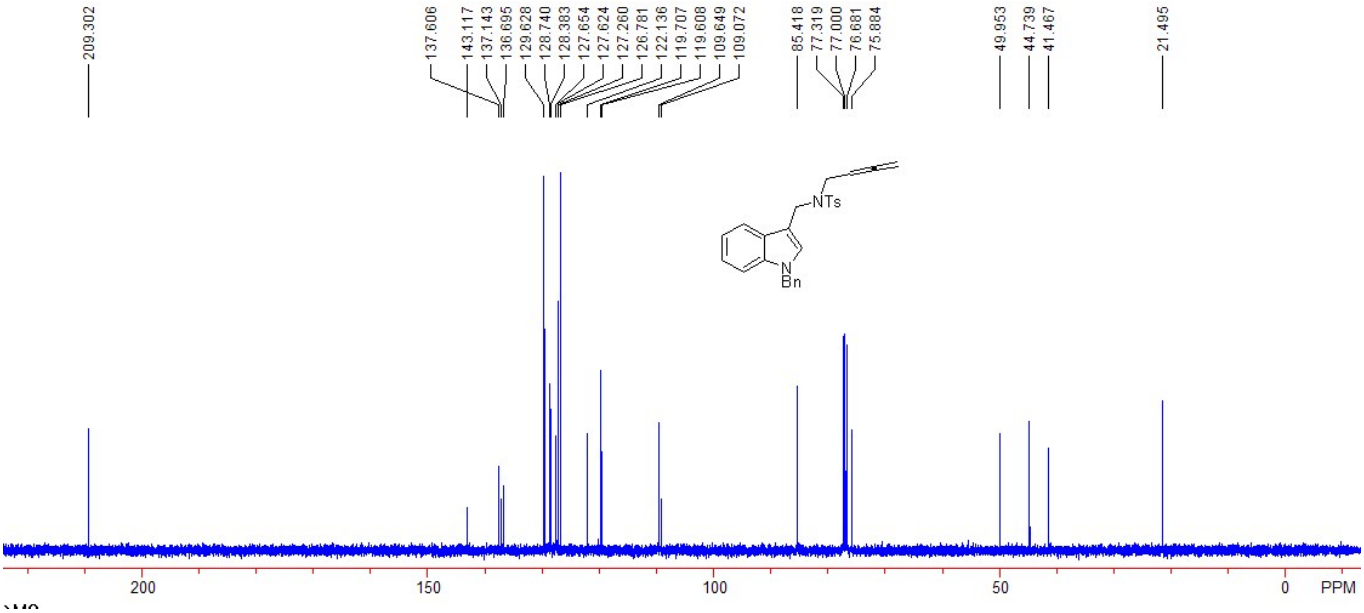


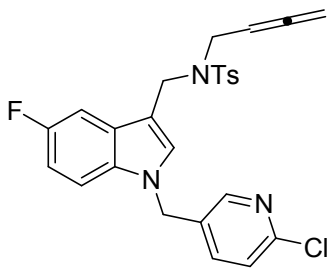
***N*-((1-benzyl-1*H*-indol-3-yl)methyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1x**

A white solid, 73% yield (326 mg). M.p.: 49-51 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 3.80 (dt, *J* = 7.2, 2.4 Hz, 2H, CH_2), 4.53 (dt, *J* = 6.4, 2.4 Hz, 2H, =CH_2), 4.59 (s, 2H, CH_2), 4.75-4.83 (m, 1H, =CH), 5.25 (s, 2H, CH_2), 6.98 (s, 1H, ArH), 7.06-7.12 (m, 3H, ArH), 7.15-7.20 (m, 1H, ArH), 7.23-7.30 (m, 6H, ArH), 7.69 (d, *J* =8.0 Hz, 1H, ArH), 7.75 (d, *J* =8.0 Hz, 2H, ArH). ^{13}C NMR

($CDCl_3$, 100 MHz, TMS) δ 21.5, 41.5, 44.7, 49.9, 75.9, 85.4, 109.1, 109.6, 119.6, 119.7, 122.1, 126.8, 127.2, 127.62, 127.65, 128.4, 128.7, 129.6, 136.7, 137.1, 137.6, 143.1, 209.3. IR (CH_2Cl_2) ν 3060, 2922, 2848, 1953, 1598, 1467, 1336, 1157, 1092, 924, 892, 743, 658 cm^{-1}. MS (ESI) *m/z* (%): 460.20 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{30}N_3O_2S^{+1}[M+NH_4]^+$ requires 460.2053, found: 460.2053.

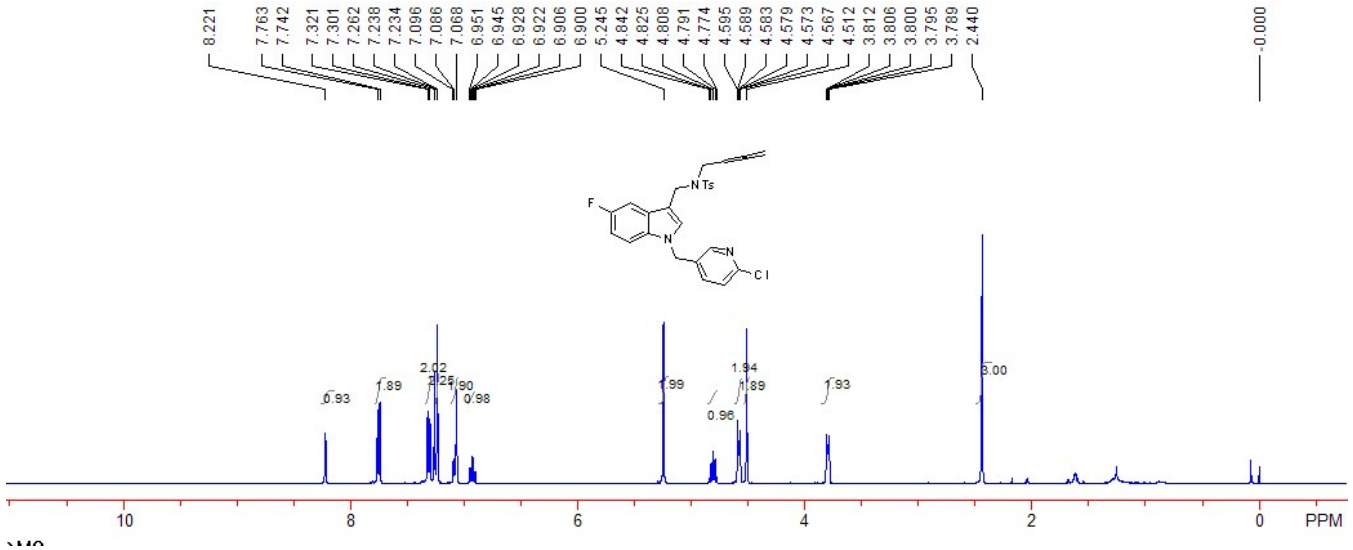


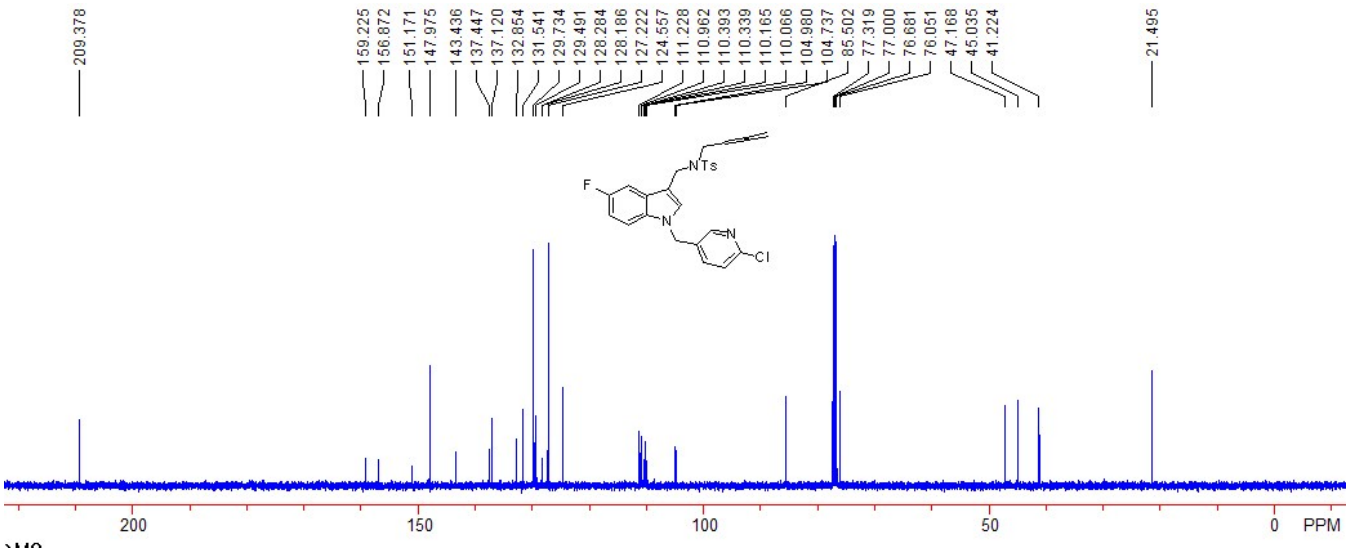


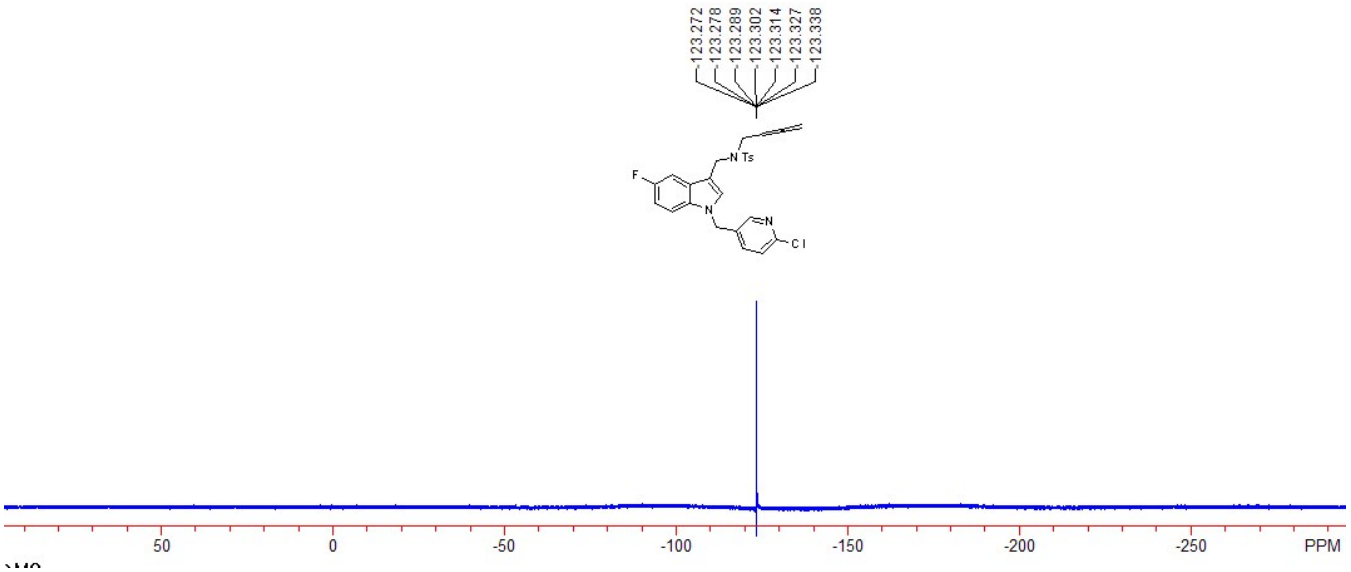


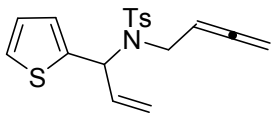
***N*-(buta-2,3-dien-1-yl)-*N*-((1-((6-chloropyridin-3-yl)methyl)-5-fluoro-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 1y**

A white liquid, 72% yield (452 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 3.78-3.82 (m, 2H, CH_2), 4.51 (s, 2H, CH_2), 4.56-4.60 (m, 2H, =CH_2), 4.77-4.85 (m, 1H, =CH), 5.24 (s, 2H, CH_2), 6.92 td, *J* = 9.2, 2.8 Hz, 1H, ArH), 7.06-7.10 (m, 2H, ArH), 7.23-7.24 (m, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.75 (d, *J* = 8.4 Hz, 2H, ArH), 8.22 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 41.2, 45.0, 47.2, 76.1, 85.5, 104.9 (d, *J* = 24.3 Hz), 110.1 (d, *J* = 9.9 Hz), 110.4 (d, *J* = 5.4 Hz), 111.1 (d, *J* = 26.6 Hz), 124.6, 127.2, 128.2 (d, *J* = 9.8 Hz), 129.5, 129.7, 131.5, 132.9, 137.1, 137.4, 143.4, 148.0, 151.2, 158.0 (d, *J* = 235.3 Hz), 209.4. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -123.3. IR (CH_2Cl_2) ν 3063, 2925, 1954, 1586, 1486, 1459, 1333, 1255, 1194, 1156, 1092, 908, 852, 744, 657 cm^{-1}. MS (ESI) m/z (%): 496.12 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{26}H_{24}ClFN_3O_2S^{+1}[M+H]^+$ requires 496.1256, found: 496.1255.





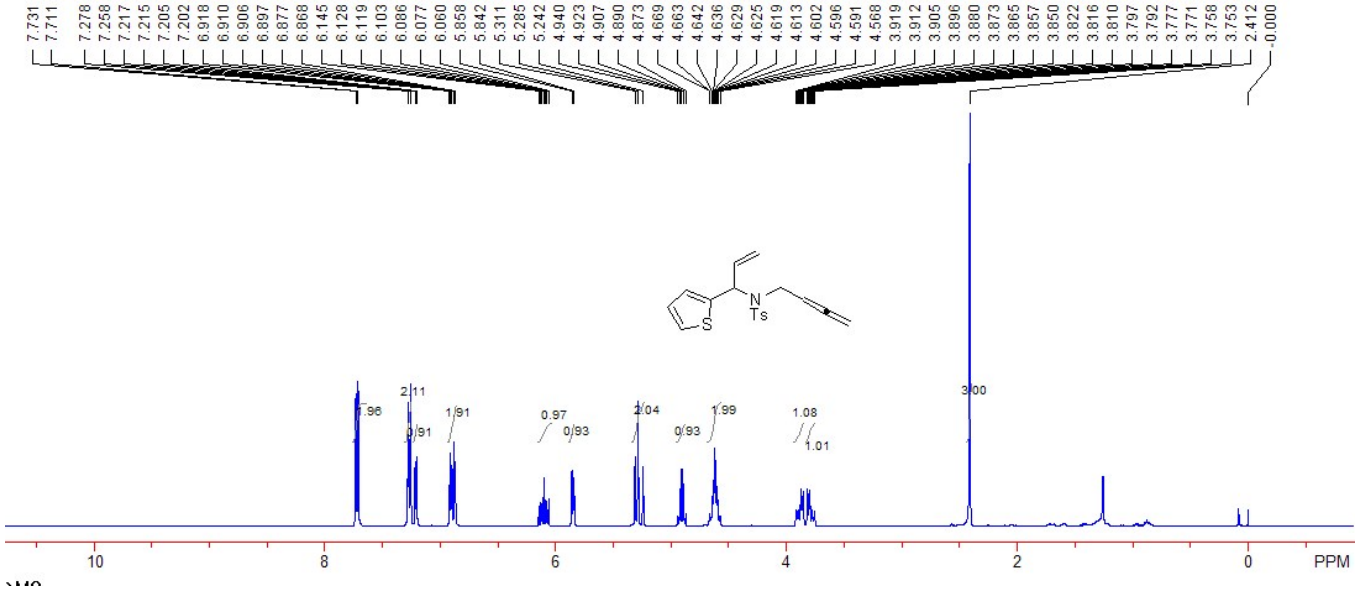


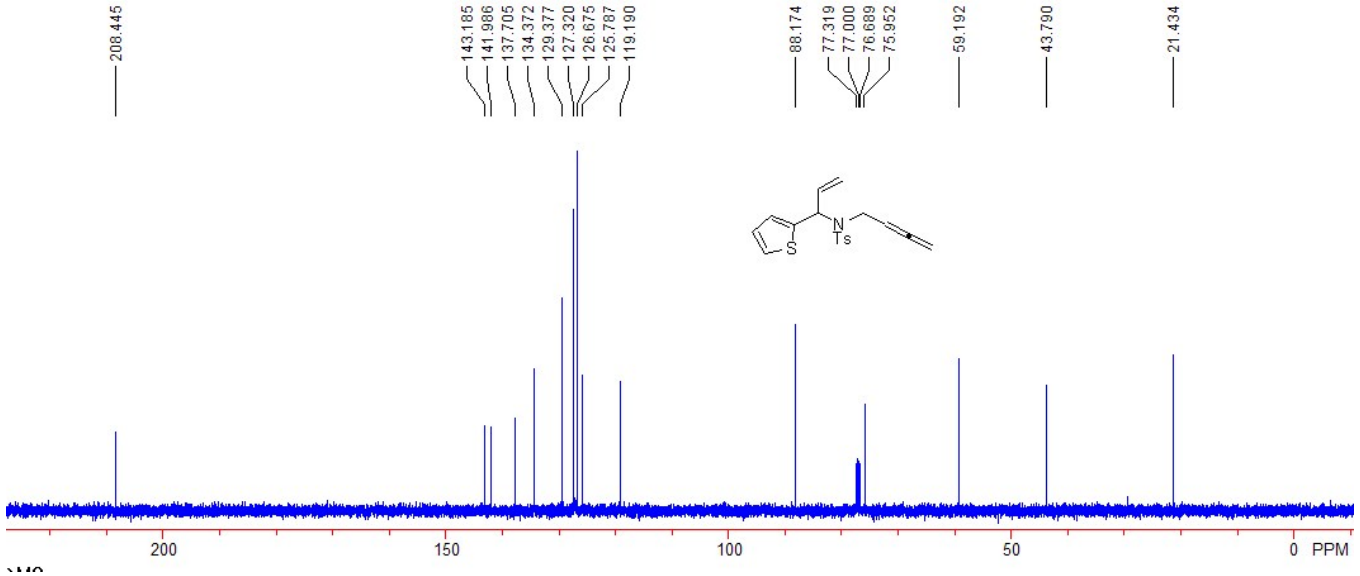


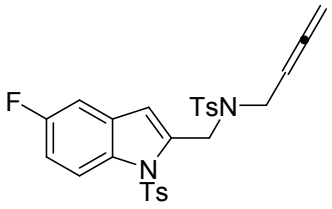
_N_-(buta-2,3-dien-1-yl)-4-methyl-_N_-(1-(thiophen-2-yl)allyl)benzenesulfonamide 6

A white solid, 59% yield (409 mg). M.p.: 66-68 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H, CH_3), 3.75-3.83 (m, 1H, CH_2), 3.85-3.92 (m, 1H, CH_2), 4.56-4.67 (m, 2H, =CH_2), 4.87-4.95 (m, 1H, =CH), 5.24-5.32 (m, 2H, =CH), 5.85 (d, J = 6.4 Hz, 1H, ArH), 6.06-6.15 (m, 1H, =CH), 6.86-6.92 (m, 2H, ArH), 7.21 (dd, J = 5.2, 1.2 Hz, 1H, ArH), 7.26 (d, J = 8.0 Hz, 2H, ArH), 7.72 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 43.8, 59.2, 76.0, 88.2, 119.2, 125.8, 126.7, 127.3, 129.4, 134.4, 137.7, 142.0, 143.2, 208.4. IR (CH_2Cl_2) ν 3089, 2986, 1958, 1596, 1436, 1332, 1188, 1088, 980, 812, 718, 666 cm^{-1}. MS (ESI) *m/z* (%): 363.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For

$C_{18}H_{23}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 363.1195, found: 363.1192.



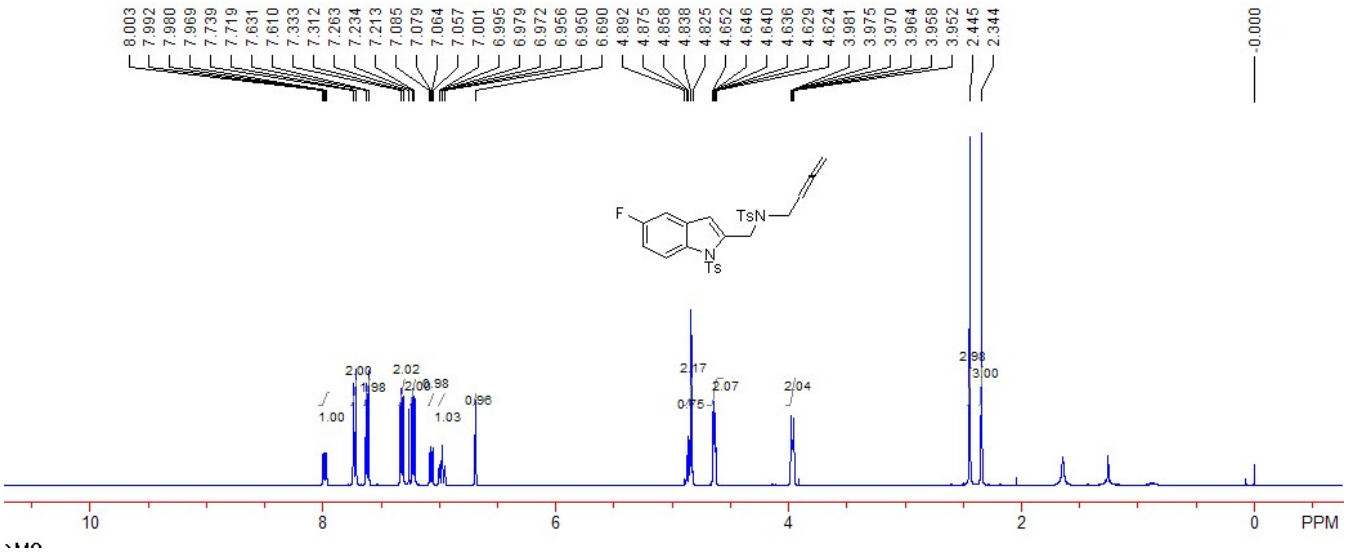


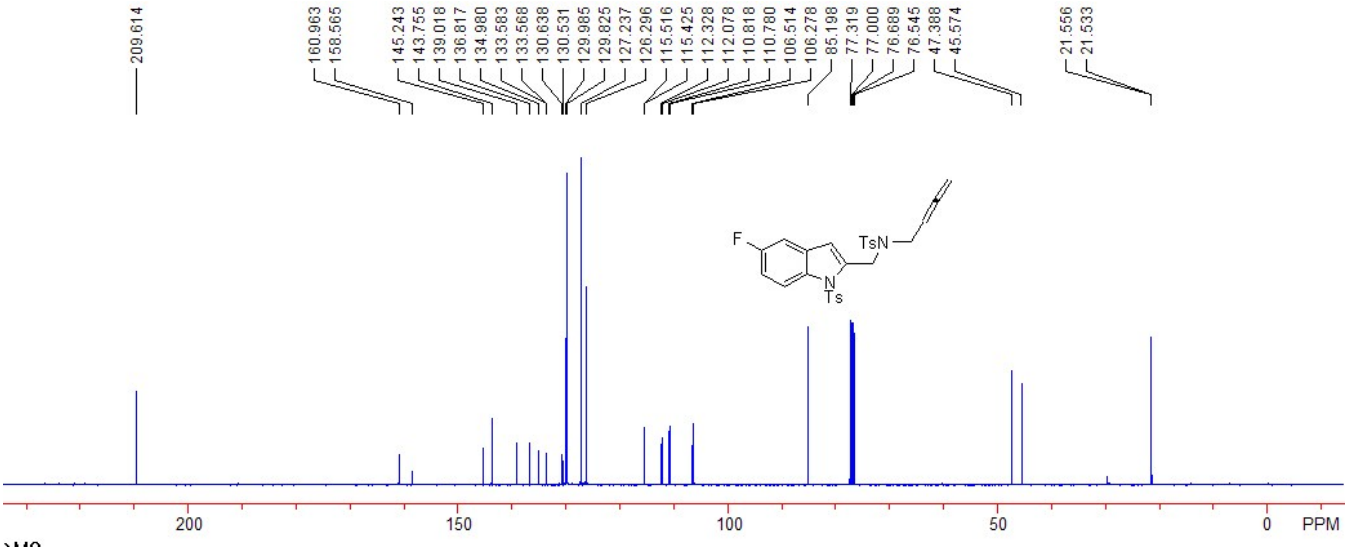


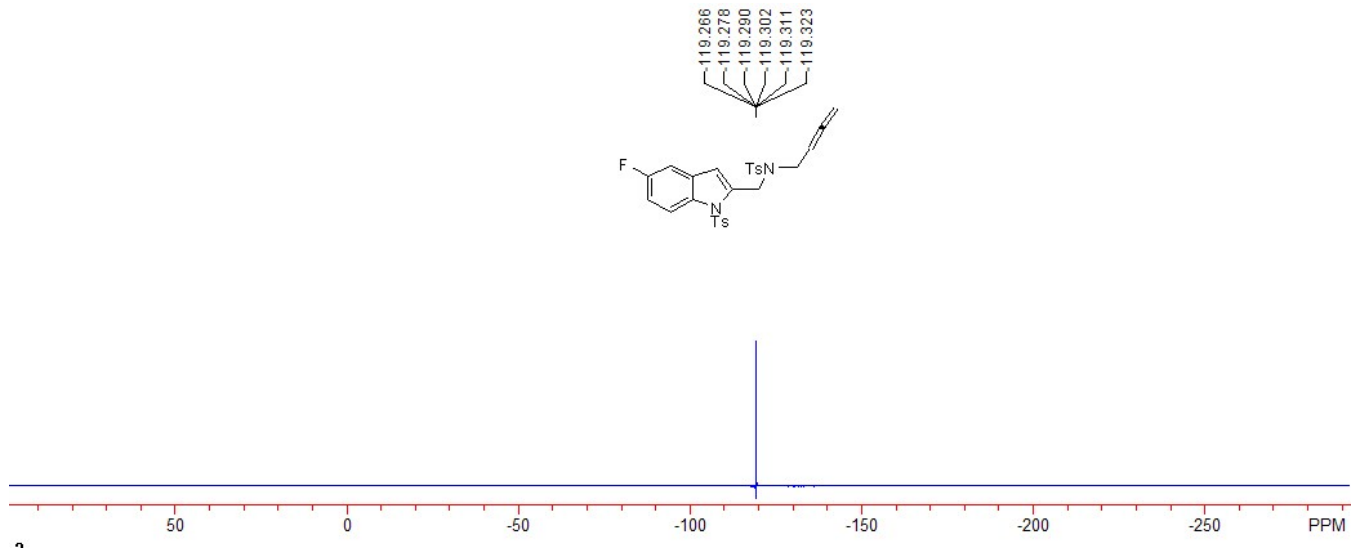
***N*-(buta-2,3-dien-1-yl)-*N*-((5-fluoro-1-tosyl-1*H*-indol-2-yl)methyl)-4-methylbenzenesulfonamide 9**

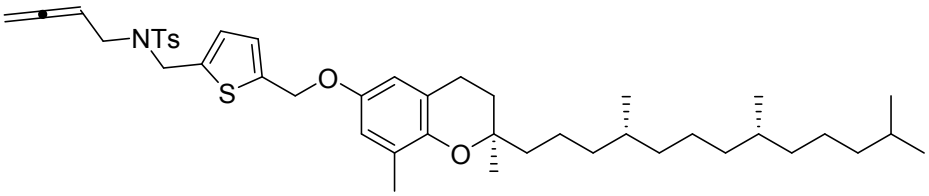
A white solid, 48% yield (224 mg). M.p.: 141-144 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.95-3.99 (m, 2H, CH_2), 4.62-4.66 (m, 2H, =CH_2), 4.84 (s, 2H, CH_2), 4.82-4.90 (m, 1H, =CH), 6.69 (s, 1H, ArH), 6.97 (td, *J* = 8.8, 2.4 Hz, 1H, ArH), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H, ArH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.62 (d, *J* = 8.0 Hz, 2H, ArH), 7.72 (d, *J* =

8.0 Hz, 2H, ArH), 7.99 (dd, J = 8.8, 4.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.6, 45.6, 47.4, 76.5, 85.2, 106.4 (d, J = 23.8 Hz), 110.8 (d, J = 3.9 Hz), 112.2 (d, J = 25.1 Hz), 115.4 (d, J = 9.2 Hz), 126.3, 127.2, 129.8, 130.0, 130.6 (d, J = 10.1 Hz), 133.6, 135.0, 136.8, 139.0, 143.7, 145.2, 159.8 (d, J = 239.4 Hz), 209.6. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.3. IR (CH_2Cl_2) ν 2954, 2923, 2362, 1598, 1467, 1370, 1346, 1178, 1161, 1093, 876, 769, 668 cm^{-1}. MS (ESI) m/z (%): 525.13 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{26}FN_2O_4S_2^{+1}[M+H]^+$ requires 525.1313, found: 525.1314.

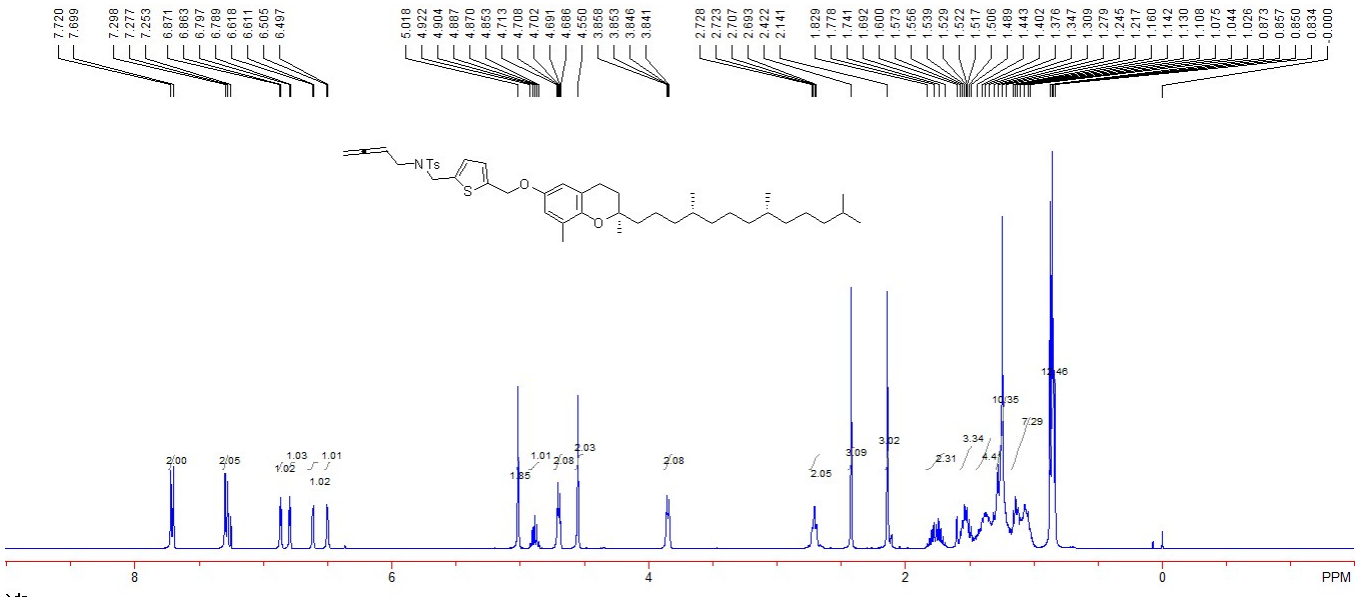


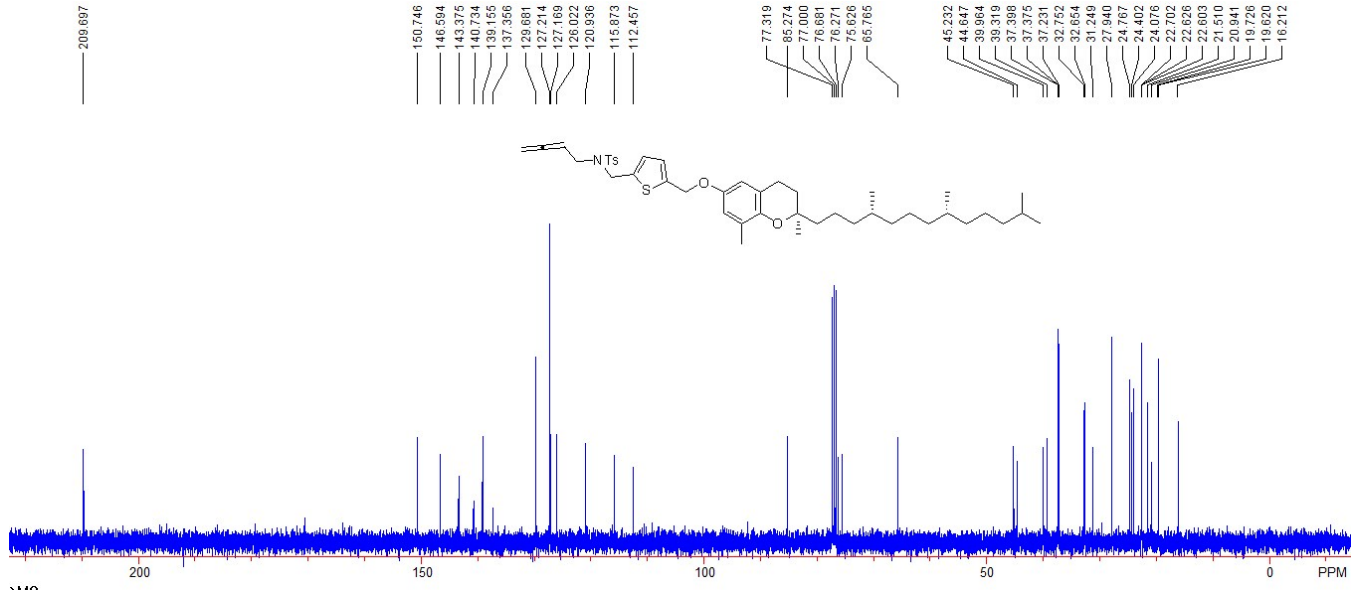




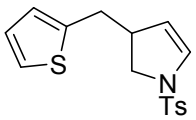


Compound 12. A yellow liquid, 45% yield (208 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.83-0.88 (m, 12H), 1.02-1.16 (m, 7H), 1.21-1.28 (m, 10H), 1.34-1.45 (m, 4H), 1.48-1.58 (m, 3H), 1.69-1.83 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.69-2.73 (m, 2H, CH_2), 3.84-3.86 (m, 2H, CH_2), 4.55 (s, 2H, CH_2), 4.68-4.72 (m, 2H, CH_2), 4.85-4.93 (m, 1H, =CH), 5.02 (s, 2H, CH_2), 6.50 (d, *J* = 3.2 Hz, 1H, ArH), 6.62 (d, *J* = 2.8 Hz, 1H, ArH), 6.79 (d, *J* = 3.2 Hz, 1H, ArH), 6.86 (d, *J* = 3.2 Hz, 1H, ArH), 7.28 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.2, 19.6, 19.7, 20.9, 21.5, 22.60, 22.62, 22.7, 24.1, 24.4, 24.8, 27.9, 31.2, 32.7, 32.8, 35.6, 37.2, 37.38, 37.40, 39.3, 40.0, 44.6, 45.2, 65.8, 75.6, 76.3, 85.3, 112.5, 115.9, 120.9, 126.0, 127.17, 127.21, 129.7, 137.4, 139.2, 140.7, 143.4, 146.6, 150.7, 209.7. IR (CH_2Cl_2) ν 2924, 2866, 1954, 1598, 1479, 1341, 1217, 1158, 1092, 1037, 812, 753, 657 cm^{-1}. MS (ESI) m/z (%): 751.45 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{44}H_{67}N_2O_4S_2$ $[M+NH_4]^+$ requires 751.4537, found: 751.4532.





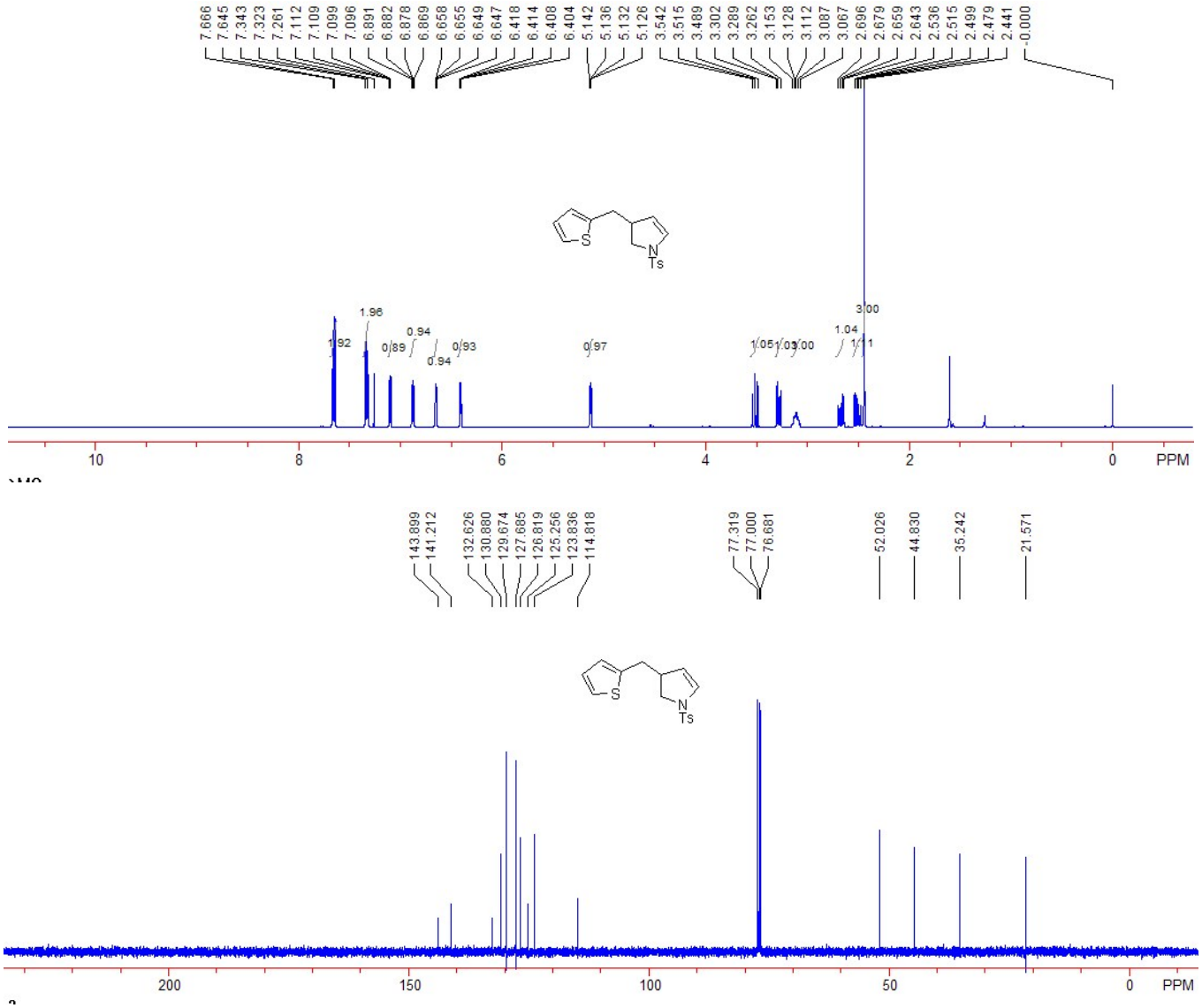
13. Characterization and spectra charts for compounds 2

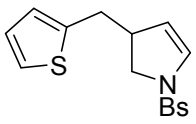


3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2a

A white solid, 97% yield (31 mg). M.p.: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 2.50 (dd, J = 15.2, 8.0 Hz, 1H, CH_2), 2.66 (dd, J = 14.4, 6.4 Hz, 1H, CH_2), 3.07-3.15 (m, 1H, CH), 3.28 (dd, J = 10.8, 5.6 Hz, 1H, CH_2), 3.51 (dd, J = 10.4, 10.4 Hz, 1H, CH_2), 5.13 (dd, J = 4.0, 2.8 Hz, 1H, =CH), 6.41 (dd, J = 4.4, 1.6 Hz, 1H, =CH), 6.65 (d, J = 3.2 Hz, 1H, ArH), 6.87 (dd, J = 5.2, 3.2 Hz, 1H, ArH), 7.10 (d, J = 4.8 Hz, 1H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH). ^{13}C

NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.2, 44.8, 52.0, 114.8, 123.8, 125.2, 126.8, 127.6, 129.6, 130.8, 132.6, 141.2, 143.9. IR (CH_2Cl_2) ν 2957, 2923, 2854, 1728, 1597, 1491, 1351, 1164, 1092, 914, 814, 707, 664 cm^{-1}. MS (ESI) *m/z* (%): 320.07 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{18}NO_2S_2^{+1}[M+H]^+$ requires 320.0773, found: 320.0775.

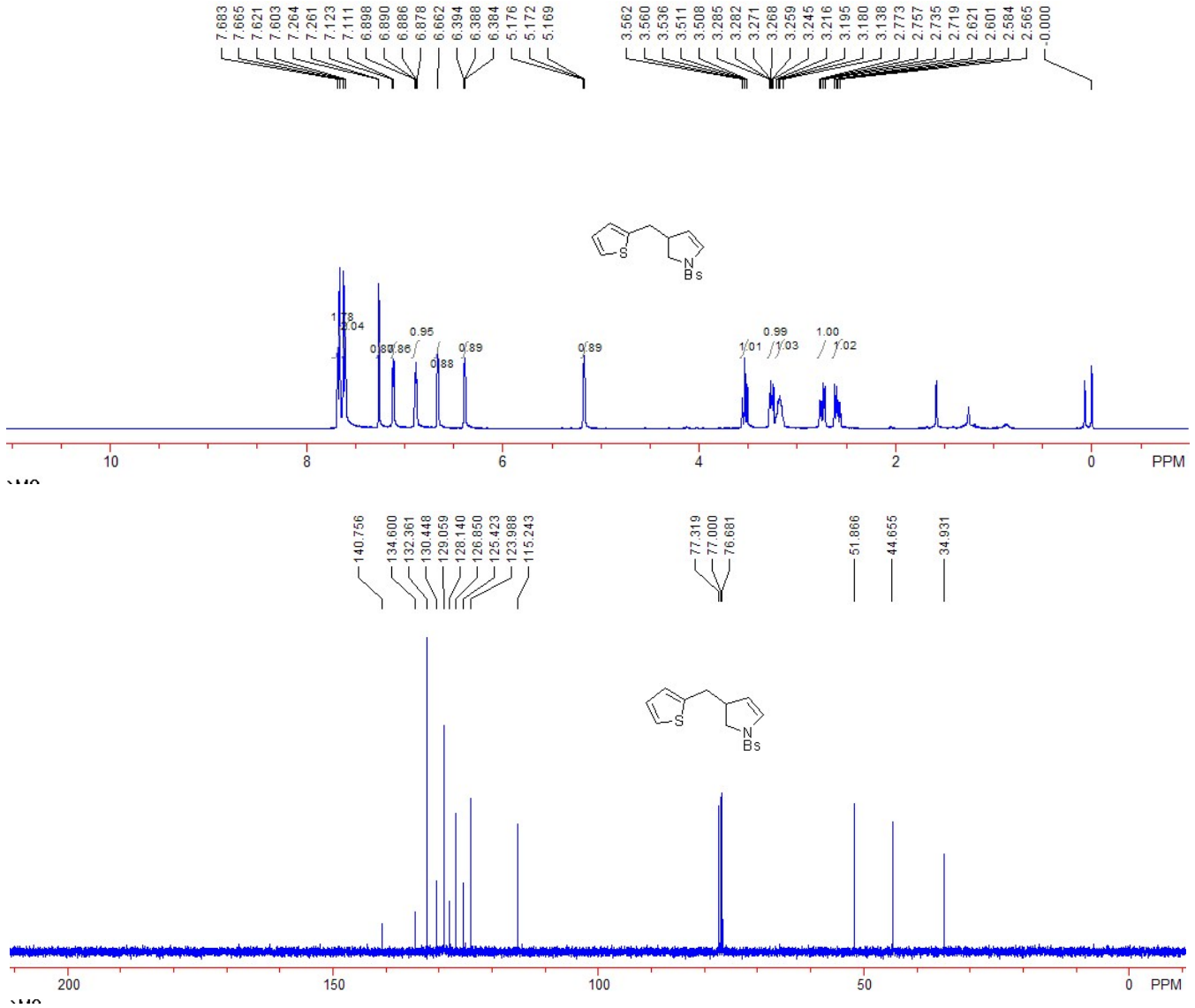


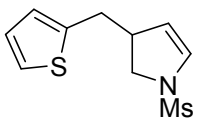


1-((4-bromophenyl)sulfonyl)-3-(thiophen-2-ylmethyl)-2,3-dihydro-1*H*-pyrrole 2b

A white liquid, 97% yield (37 mg). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.59 (dd, *J* = 14.4, 7.6 Hz, 1H, CH_2), 2.74 (dd, *J* = 15.2, 6.4 Hz, 1H, CH_2), 3.13-3.22 (m, 1H, CH), 3.26 (dd, *J* = 10.4, 5.6 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.4, 10.4 Hz, 1H, CH_2), 5.17 (dd, *J* = 2.8, 1.6 Hz, 1H, =CH), 6.39 (dd, *J* = 4.0, 1.6 Hz, 1H,

=CH), 6.66 (s, 1H, ArH), 6.89 (dd, J = 4.8, 3.2 Hz, 1H, ArH), 7.12 (d, J = 4.8 Hz, 1H, ArH), 7.61 (d, J = 8.8 Hz, 2H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 34.9, 44.7, 51.9, 115.2, 124.0, 125.4, 126.8, 128.1, 129.1, 130.4, 132.4, 134.6, 140.7. IR (CH_2Cl_2) ν 3089, 2926, 1613, 1574, 1471, 1389, 1354, 1170, 1068, 1008, 821, 741, 702 cm^{-1}. MS (ESI) *m/z* (%): 383.97 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{15}NO_2BrS_2^{+1}[M+H]^+$ requires 383.9722, found: 383.9720.

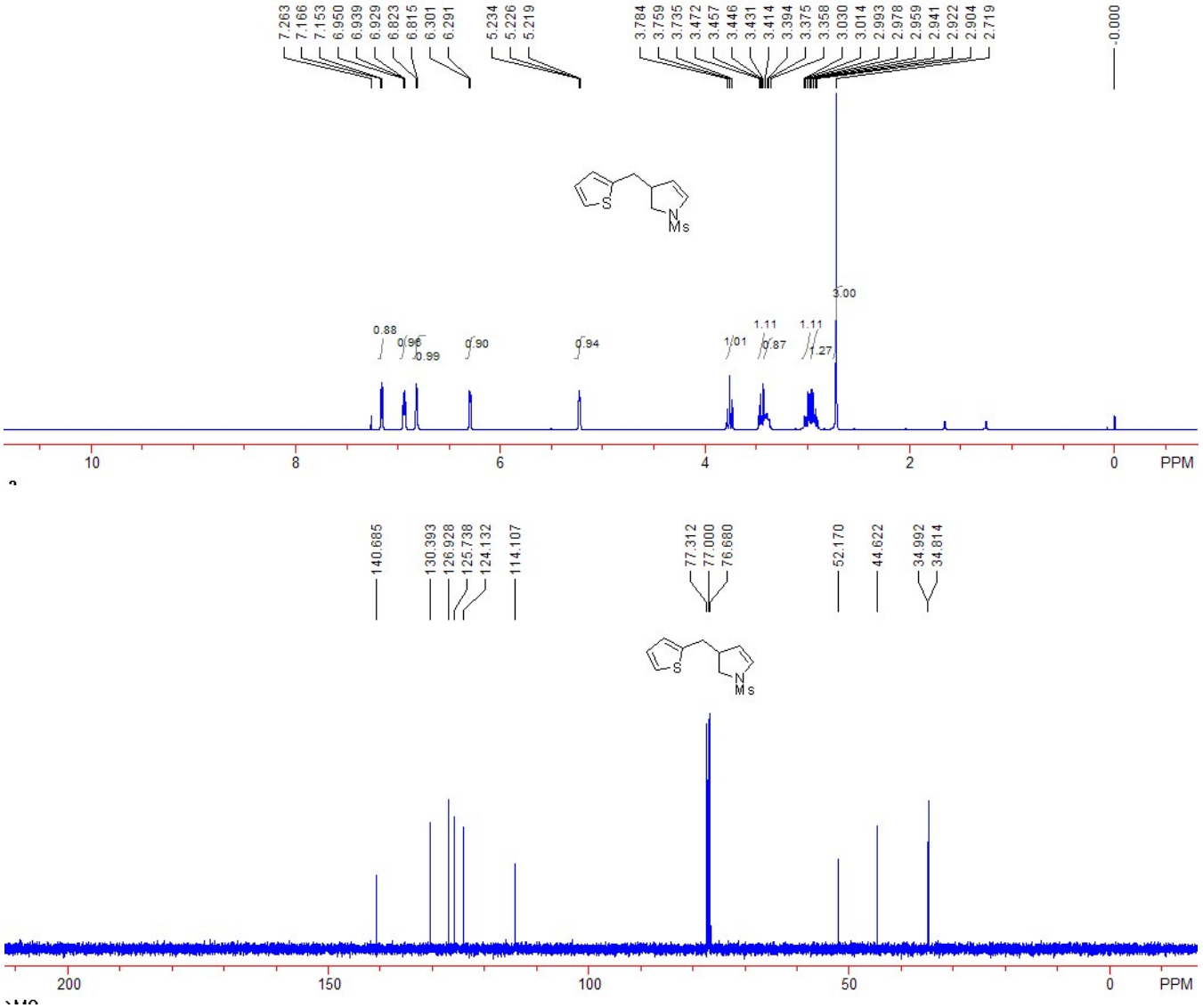


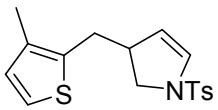


1-(methylsulfonyl)-3-(thiophen-2-ylmethyl)-2,3-dihydro-1*H*-pyrrole 2c

A white liquid, 92% yield (22 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.72 (s, 3H, CH_3), 2.93 (dd, J = 14.8, 7.2 Hz, 1H, CH_2), 3.00 (dd, J = 14.8, 6.0 Hz, 1H, CH_2), 3.35-3.45 (m, 1H, CH), 3.46 (dd, J = 10.4,

6.0 Hz, 1H, CH_2), 3.76 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.23 (dd, *J* = 3.2, 2.8 Hz, 1H, =CH), 6.30 (d, *J* = 4.0 Hz, 1H, =CH), 6.82 (d, *J* = 3.2 Hz, 1H, ArH), 6.94 (dd, *J* = 4.4, 4.0 Hz, 1H, ArH), 7.16 (d, *J* = 5.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 34.8, 35.0, 44.6, 52.2, 114.1, 124.1, 125.7, 126.9, 130.4, 140.7. IR (CH_2Cl_2) ν 3105, 2928, 1612, 1469, 1437, 1340, 1155, 1072, 960, 850, 759, 703 cm^{-1}. HRMS (ESI) Calcd. For $C_{10}H_{17}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 261.0726, found: 261.0727.

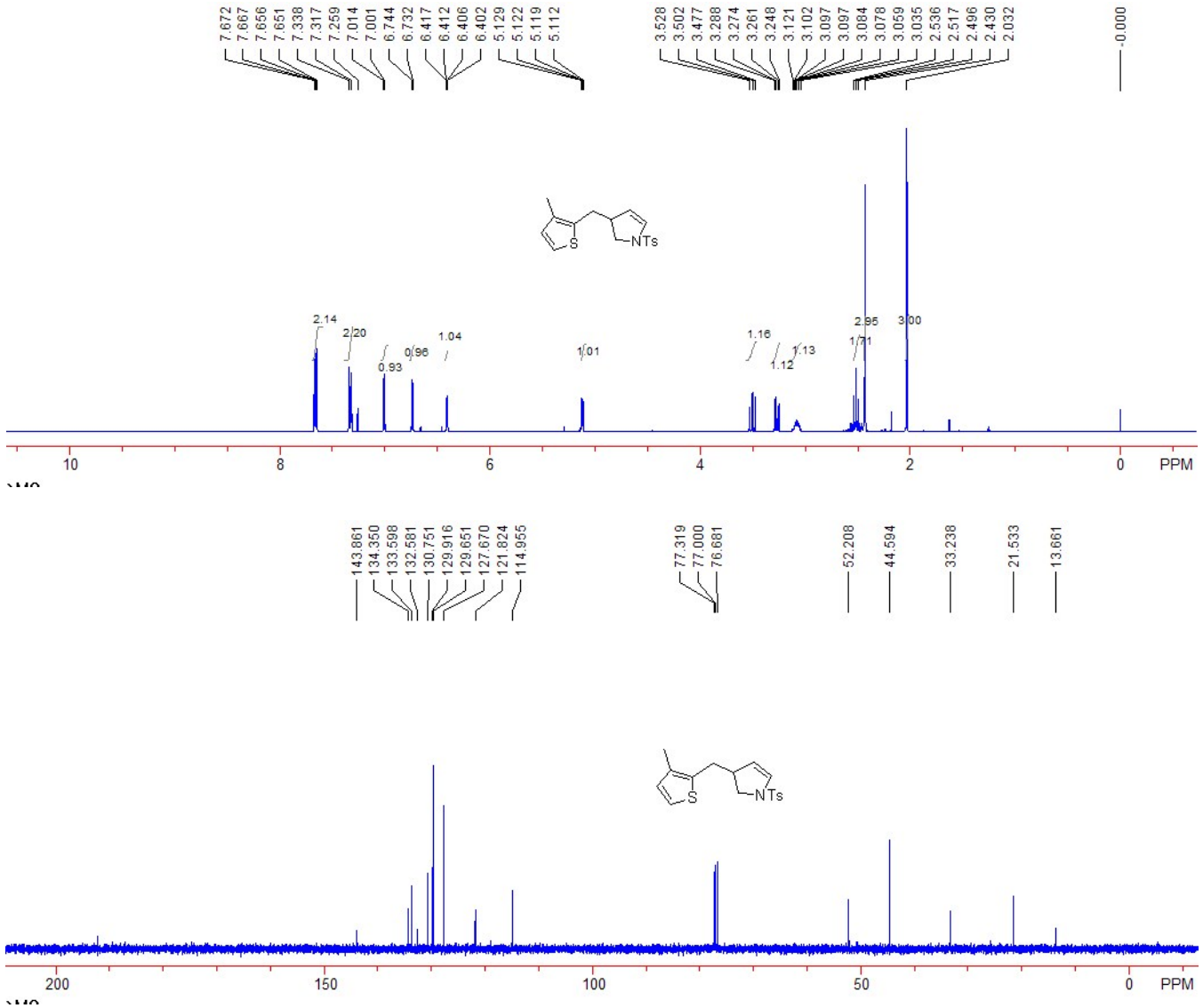


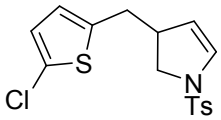


3-((3-methylthiophen-2-yl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2d

A white liquid, 96% yield (32 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.52 (dd, *J* = 8.0, 8.0 Hz, 2H, CH_2), 3.03-3.13 (m, 1H, CH), 3.26 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2),

3.50 (dd, J = 10.0, 10.0 Hz, 1H, CH_2), 5.12 (dd, J = 4.0, 2.8 Hz, 1H, =CH), 6.41 (dd, J = 2.4, 1.6 Hz, 1H, =CH), 6.74 (d, J = 4.8 Hz, 1H, ArH), 7.00 (d, J = 5.2 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.66 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 21.5, 33.2, 44.6, 52.2, 115.0, 121.8, 127.7, 129.6, 129.9, 130.7, 132.6, 133.6, 134.3, 143.9. IR (CH_2Cl_2) ν 2924, 1597, 1461, 1352, 1165, 1090, 927, 814, 707, 666 cm^{-1}. MS (ESI) *m/z* (%): 334.09 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{17}H_{20}NO_2S_2^{+1}[M+H]^+$ requires 334.0930, found: 334.0931.

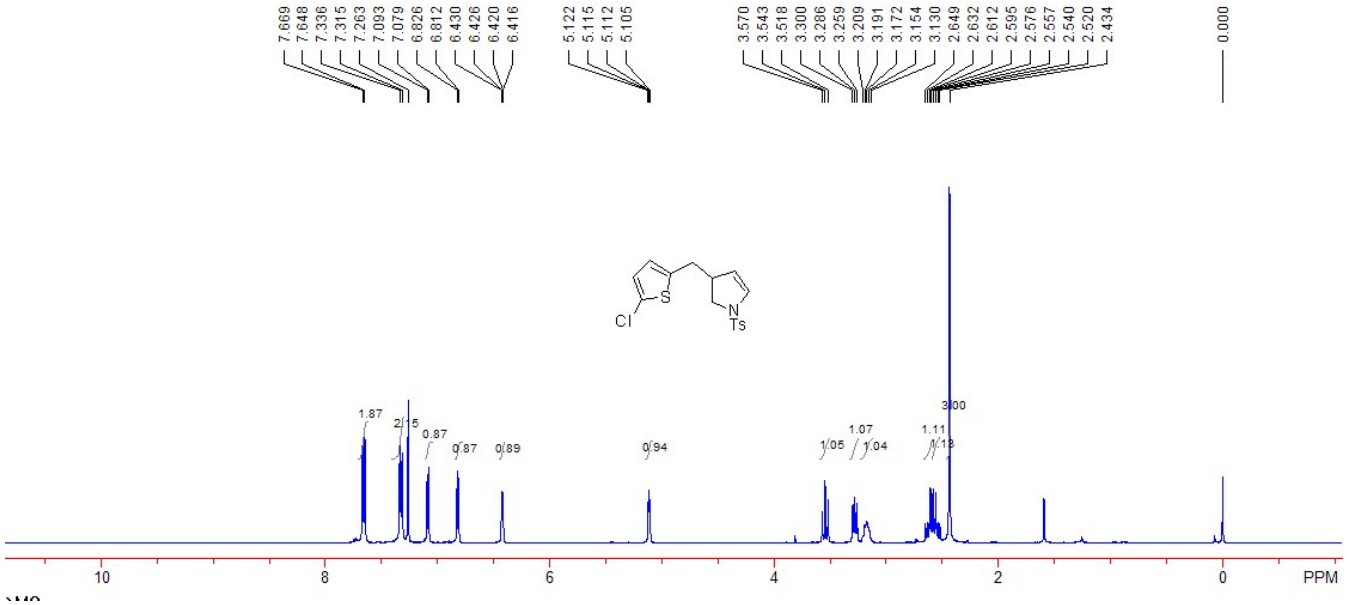


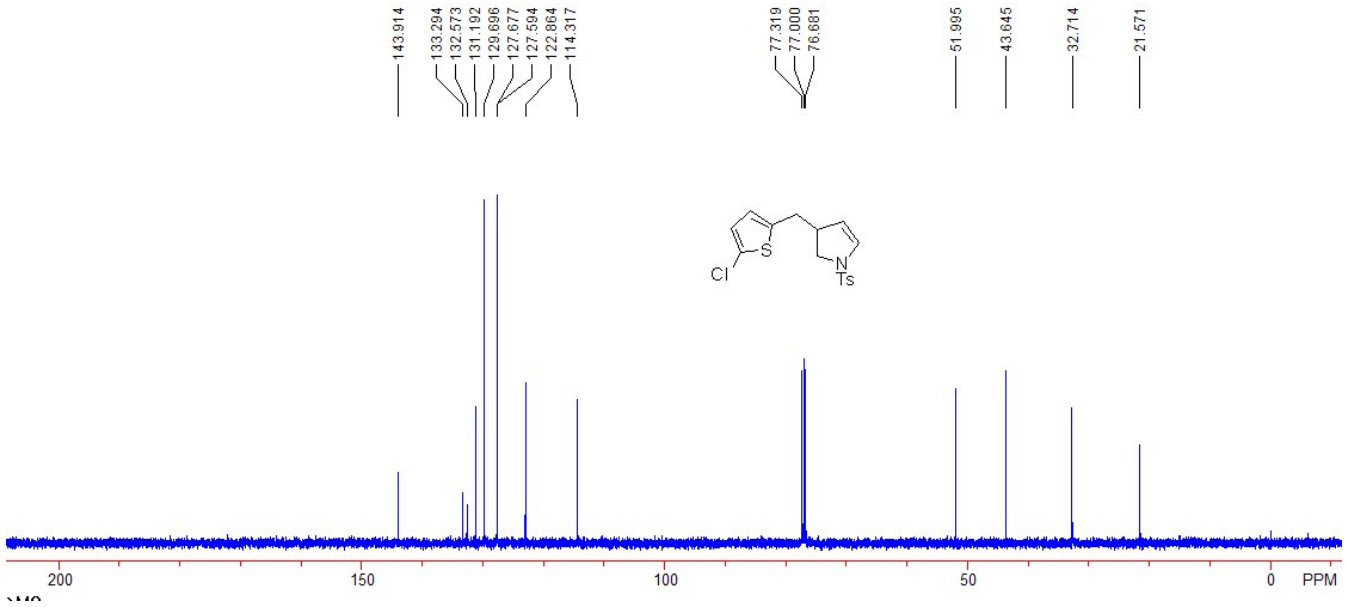


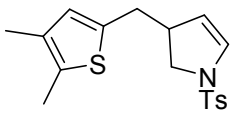
3-((5-chlorothiophen-2-yl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2e

A white liquid, 88% yield (31 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 2.55 (dd, J =

14.8, 8.0 Hz, 1H, CH_2), 2.62 (dd, *J* = 14.8, 6.8 Hz, 1H, CH_2), 3.13-3.21 (m, 1H, CH), 3.28 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.12 (dd, *J* = 4.0, 2.8 Hz, 1H, =CH), 6.41 (dd, *J* = 4.0, 1.6 Hz, 1H, =CH), 6.82 (d, *J* = 5.6 Hz, 1H, ArH), 7.08 (d, *J* = 5.6 Hz, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.7, 43.6, 52.0, 114.3, 122.9, 123.0, 127.6, 127.7, 129.7, 131.2, 132.6, 133.3, 143.9. IR (CH_2Cl_2) ν 2923, 1725, 1597, 1350, 1160, 1089, 912, 813, 706, 663 cm^{-1}. MS (ESI) *m/z* (%): 354.03 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{17}ClNO_2S_2^{+1}[M+H]^+$ requires 354.0384, found: 354.0385.

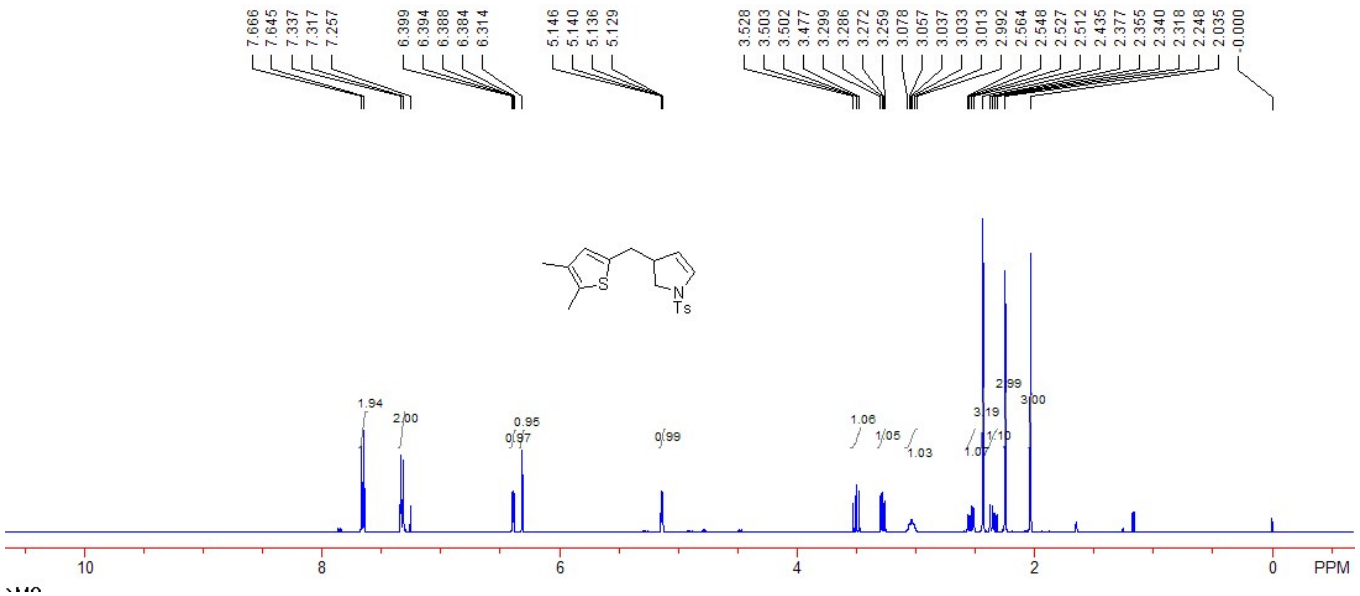


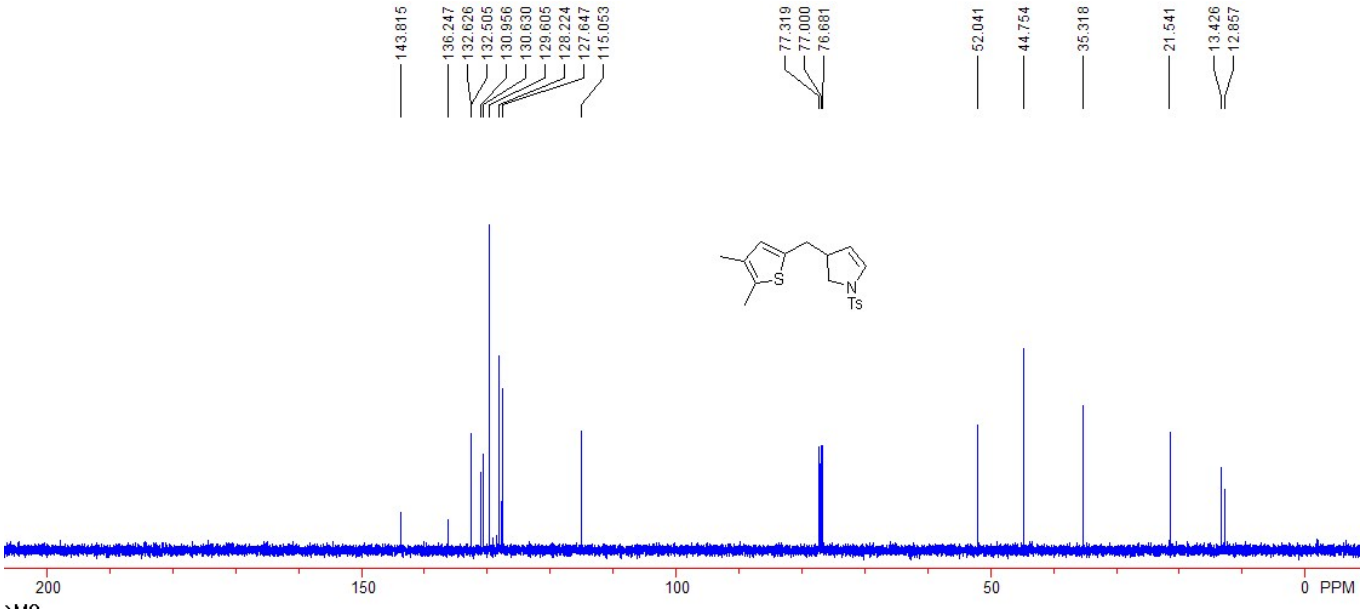


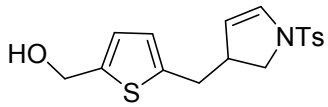


3-((4,5-dimethylthiophen-2-yl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2f

A white liquid, 92% yield (32 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.04 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.35 (dd, *J* = 14.8, 8.8 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.54 (dd, *J* = 14.8, 6.0, Hz, 1H, CH_2), 3.02-3.08 (m, 1H, CH), 3.28 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.50 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.13 (dd, *J* = 4.4, 2.8 Hz, 1H, =CH), 6.32 (s, 1H, =CH), 6.39 (dd, *J* = 4.0, 1.2 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.9, 13.4, 21.6, 35.3, 44.8, 52.1, 115.1, 127.7, 128.2, 129.6, 130.6, 131.0, 132.5, 132.6, 136.3, 143.8. IR (CH_2Cl_2) ν 2918, 1597, 1493, 1352, 1164, 1092, 902, 814, 707, 665 cm^{-1}. MS (ESI) *m/z* (%): 348.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 348.1086, found: 348.1085.

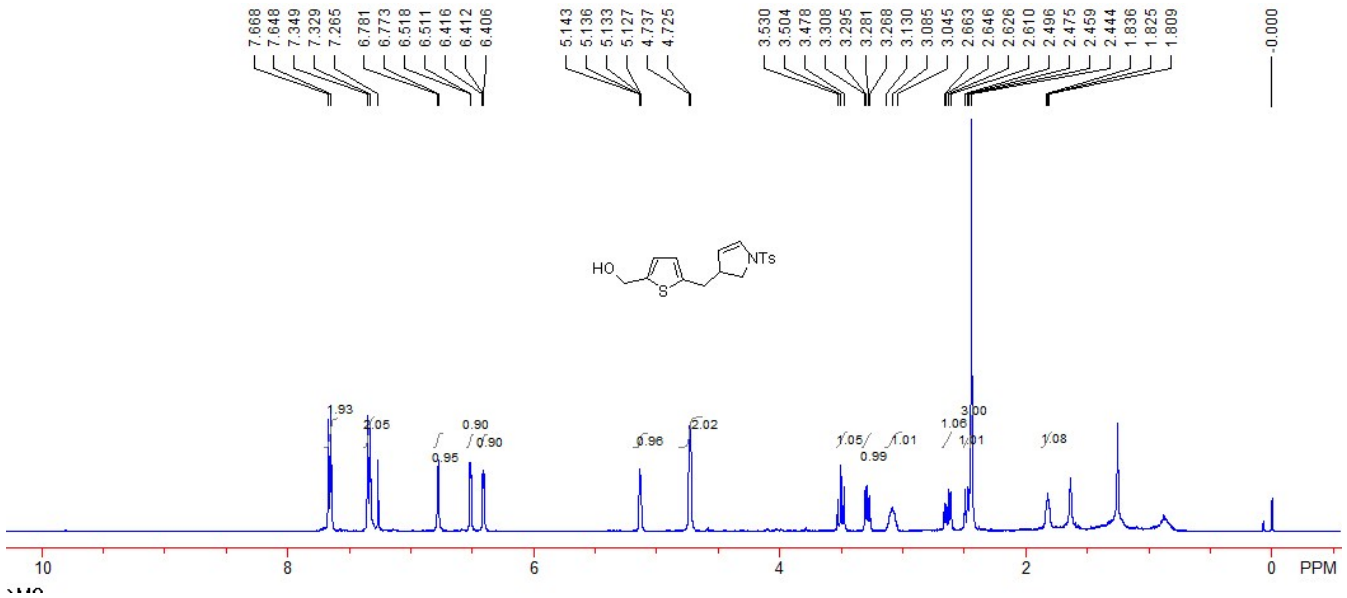


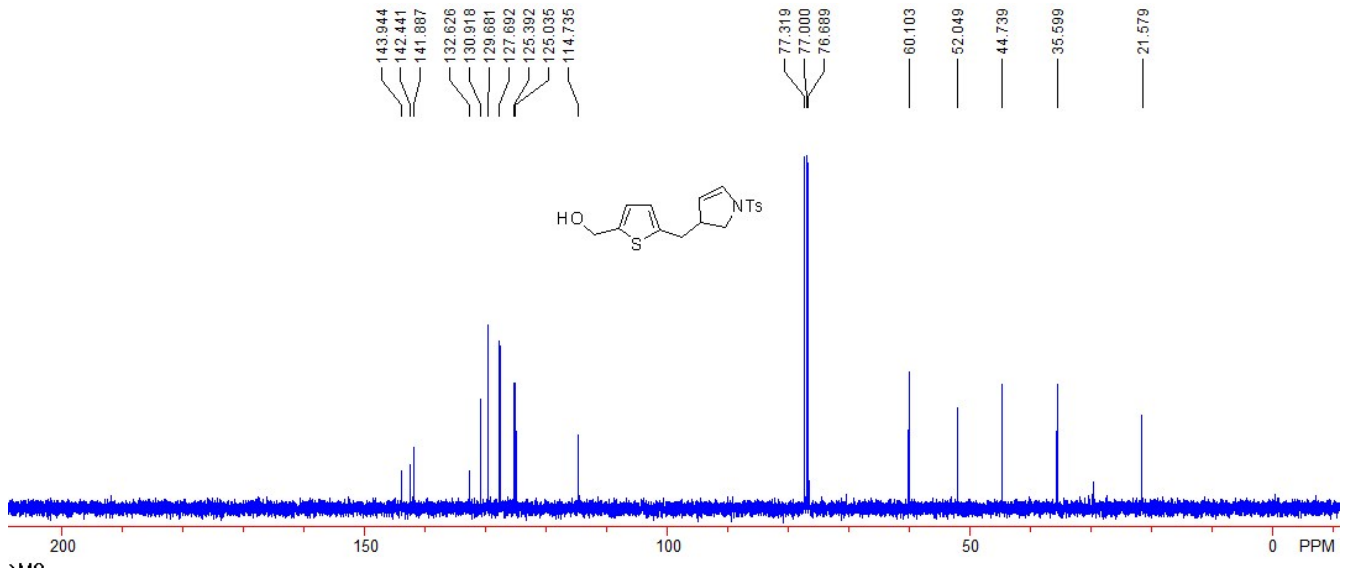


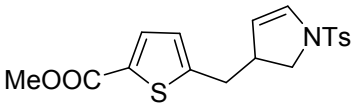


(5-((1-tosyl-2,3-dihydro-1*H*-pyrrol-3-yl)methyl)thiophen-2-yl)methanol 2g

A white liquid, 70% yield (24 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.80-1.84 (m, 1H, OH), 2.44 (s, 3H, CH_3), 2.45-2.50 (m, 1H, CH_2), 2.63 (dd, *J* = 12.0, 6.4 Hz, 1H, CH_2), 3.04-3.13 (m, 1H, CH_2), 3.28 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2), 3.50 (dd, *J* = 10.8, 10.8 Hz, 1H, CH_2), 4.73 (d, *J* = 4.8 Hz, 2H, CH_2), 5.13 (dd, *J* = 3.6, 2.4 Hz, 1H, =CH), 6.40-6.42 (m, 1H, =CH), 6.51 (d, *J* = 2.8 Hz, 1H, ArH), 6.78 (d, *J* = 2.8 Hz, 1H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 44.7, 52.0, 60.1, 114.7, 125.0, 125.4, 127.7, 129.7, 130.9, 132.6, 141.9, 142.4, 143.9. IR (CH_2Cl_2) ν 2916, 2853, 1610, 1510, 1463, 1351, 1245, 1164, 1032, 812, 663 cm^{-1}. MS (ESI) *m/z* (%): 367.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{17}H_{23}N_2O_3S_2^{+1}[M+NH_4]^+$ requires 367.1145, found: 367.1143.



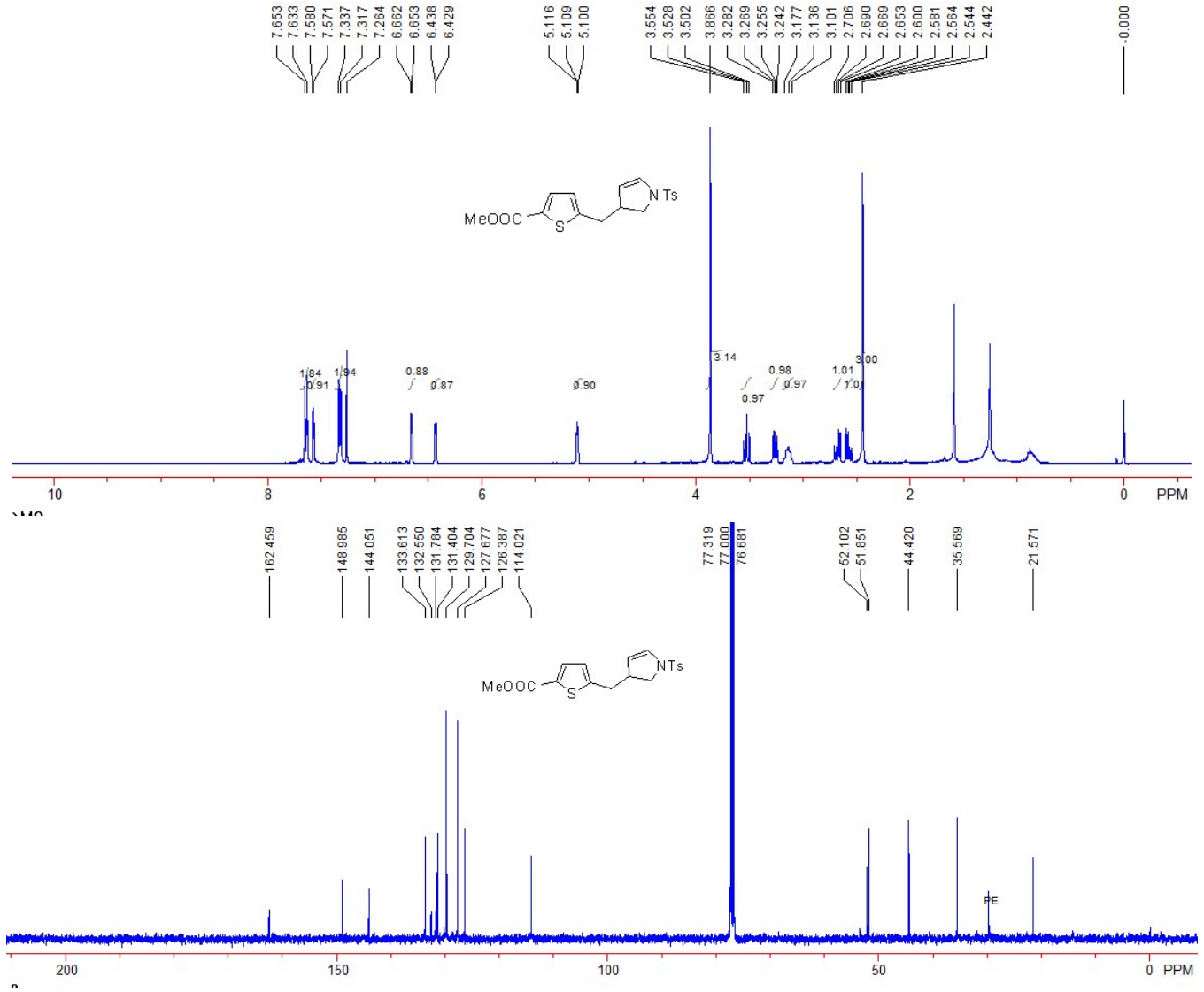


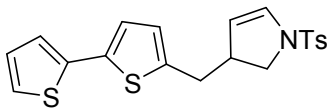


Methyl 5-((1-tosyl-2,3-dihydro-1*H*-pyrrol-3-yl)methyl)thiophene-2-carboxylate 2h

A white liquid, 31% yield (23 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 2.57 (dd, *J* = 14.4, 8.0 Hz, 1H, CH_2), 2.67 (dd, *J* = 14.8, 6.0 Hz, 1H, CH_2), 3.10-3.18 (m, 1H, CH), 3.26 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.53 (dd, *J* = 10.8, 10.8 Hz, 1H, CH_2), 3.87 (s, 3H, CH_3), 5.11 (dd, *J* = 3.6, 2.8 Hz, 1H, =CH), 6.43 (d, *J* = 3.6 Hz, 1H, ArH), 6.66 (d, *J* = 3.6 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.57 (d, *J* = 3.6 Hz, 1H, ArH), 7.64 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 44.4, 51.9, 52.1, 114.0, 126.4, 127.7, 129.7, 131.4, 131.8, 132.6, 133.6, 144.1, 149.0, 162.5. IR

(CH_2Cl_2) ν 2923, 1707, 1597, 1460, 1351, 1164, 1092, 910, 814, 707, 664 cm^{-1}. MS (ESI) *m/z* (%): 395.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{23}N_2O_4S_2^{+1}[M+ NH_4]^+$ requires 395.1094, found: 395.1092.

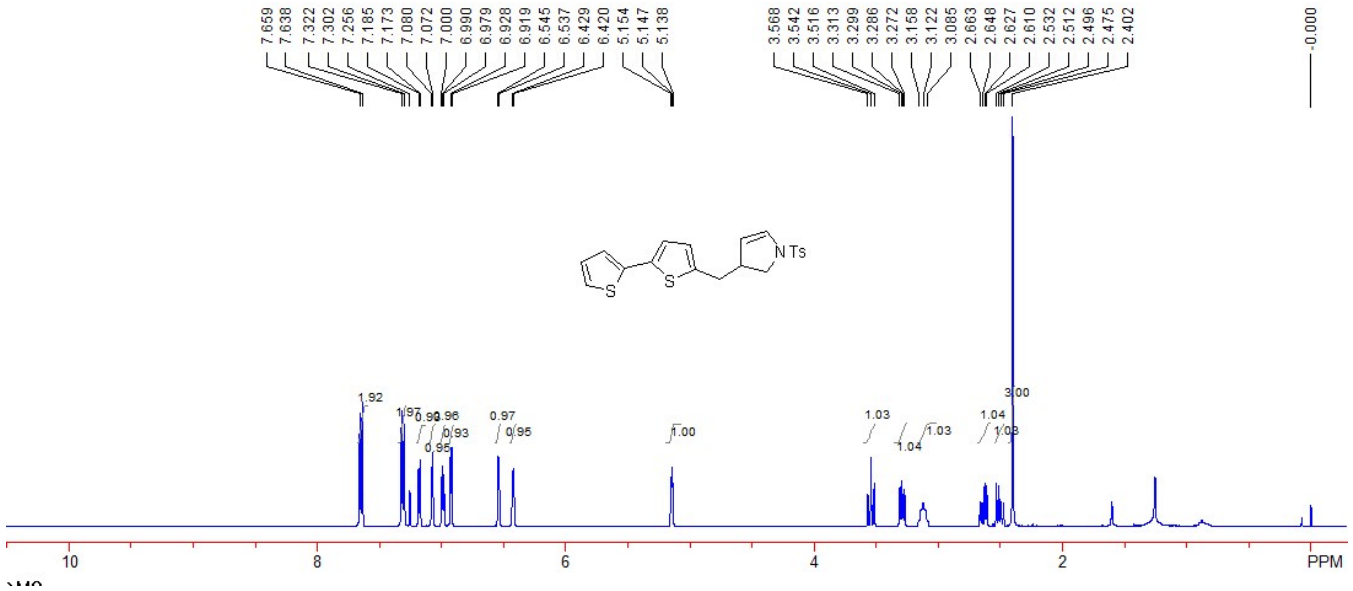


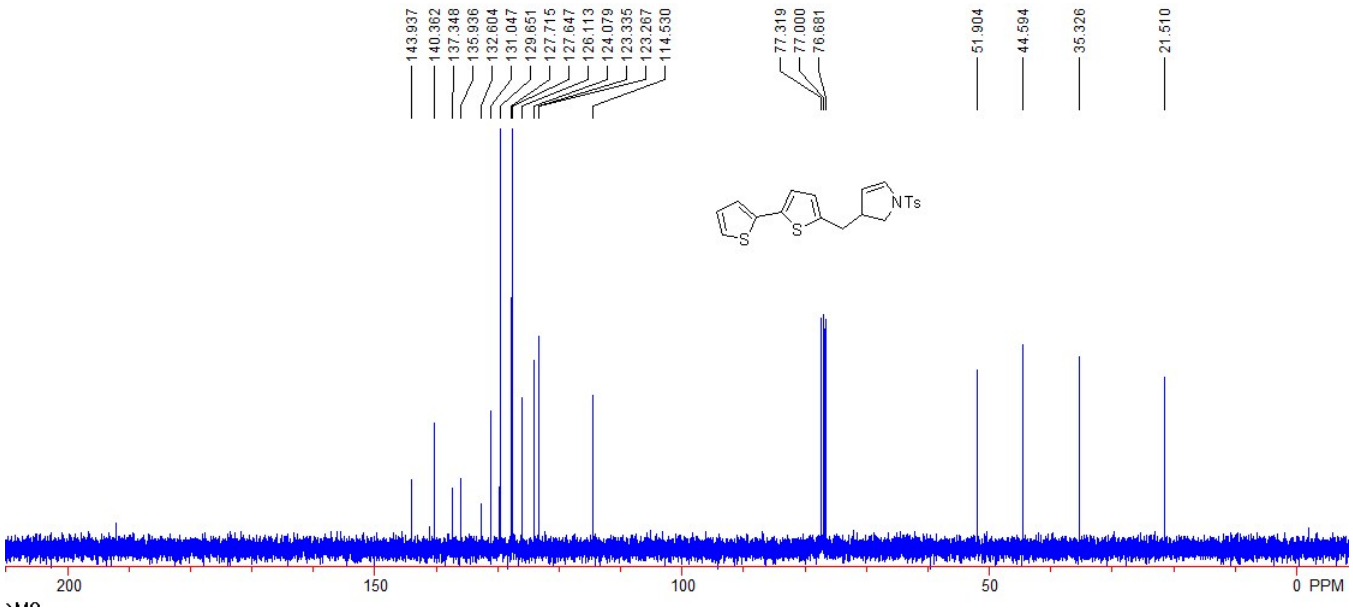


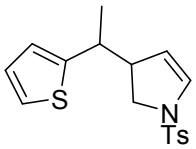
3-([2,2'-bithiophen]-5-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2j

A white liquid, 70% yield (56.1 mg). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H, CH_3), 2.50 (dd, *J* = 14.4, 8.0 Hz, 1H, CH_2), 2.63 (dd, *J* = 15.2, 6.8 Hz, 1H, CH_2), 3.08-3.16 (m, 1H, CH), 3.29 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.8, 10.8 Hz, 1H, CH_2), 5.15 (dd, *J* = 3.6, 2.8 Hz, 1H, =CH), 6.43 (d, *J* = 3.6 Hz, 1H, ArH), 6.54 (d, *J* = 3.6 Hz, 1H, ArH), 6.92 (d, *J* = 3.6 Hz, 1H, ArH), 6.97-7.00 (m, 1H, ArH), 7.07-7.08 (m, 1H, ArH), 7.18 (d, *J* = 4.8 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.64 (d, *J* = 8.0 Hz,

2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.3, 44.6, 51.9, 114.5, 123.27, 123.34, 124.1, 126.1, 127.6, 127.7, 129.7, 131.0, 132.6, 135.9, 137.3, 140.4, 143.9. IR (CH_2Cl_2) ν 3113, 2921, 1616, 1346, 1165, 1035, 898, 826, 704, 665 cm^{-1}. MS (ESI) *m/z* (%): 419.09 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{20}H_{23}N_2O_2S_3^{+1}[M+ NH_4]^+$ requires 419.0916, found: 419.0916.



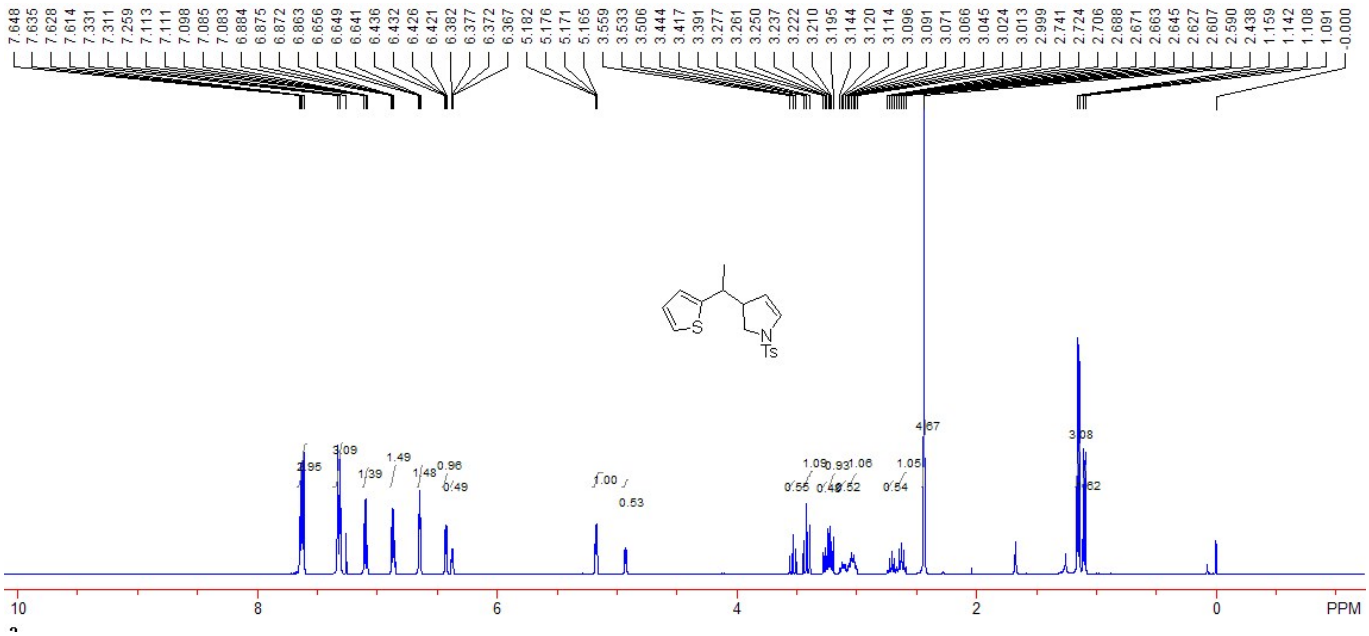


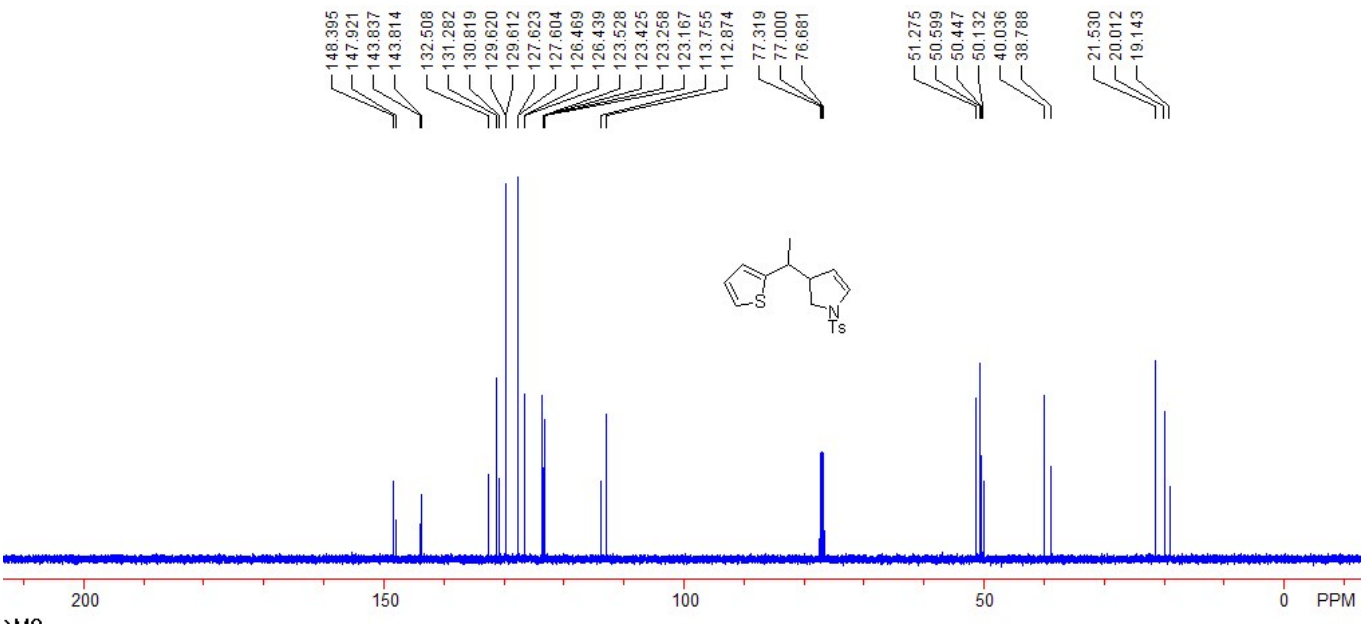


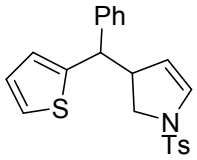
3-(1-(thiophen-2-yl)ethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2k

A white liquid, 93% yield (31 mg, dr: 2/1). Major product: ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.15 (d, *J*

= 6.8 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.61 (dd, *J* = 14.8, 6.8 Hz, 1H, CH_2), 3.00-3.08 (m, 1H, CH), 3.21 (dd, *J* = 10.8, 6.0 Hz, 1H, CH_2), 3.42 (dd, *J* = 10.4, 10.4 Hz, 1H, CH_2), 5.17 (dd, *J* = 4.4, 2.4, Hz, 1H, =CH), 6.43 (dd, *J* = 4.4, 2.0 Hz, 1H, =CH), 6.64-6.66 (m, 1H, ArH), 6.87 (dd, *J* = 4.8, 3.6 Hz, 1H, ArH), 7.10 (d, *J* = 5.2 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.62 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.5, 40.0, 50.6, 51.3, 112.9, 123.3, 123.5, 126.5, 127.6, 129.6, 131.3, 132.5, 143.8, 148.4. Minor product: ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.10 (d, *J* = 6.8 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.71 (dd, *J* = 14.8, 6.8 Hz, 1H, CH_2), 3.09-3.15 (m, 1H, CH), 3.26 (dd, *J* = 6.0, 10.8 Hz, 1H, CH_2), 3.53 (dd, *J* = 10.4, 10.4 Hz, 1H, CH_2), 4.93 (dd, *J* = 4.4, 2.4 Hz, 1H, =CH), 6.37 (dd, *J* = 4.4, 2.0 Hz, 1H, =CH), 6.64-6.66 (m, 1H, ArH), 6.86 (dd, *J* = 4.8, 3.6, Hz, 1H, ArH), 7.08 (d, *J* = 5.2 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.64 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 20.0, 38.8, 50.1, 50.4, 113.8, 123.2, 123.4, 126.4, 127.6, 129.6, 130.8, 143.8, 147.0. IR (CH_2Cl_2) ν 2969, 1597, 1494, 1349, 1162, 1090, 996, 814, 735, 664 cm^{-1}. MS (ESI) *m/z* (%): 334.09 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{17}H_{20}NO_2S_2^{+1}[M+H]^+$ requires 334.0930, found: 334.0932.

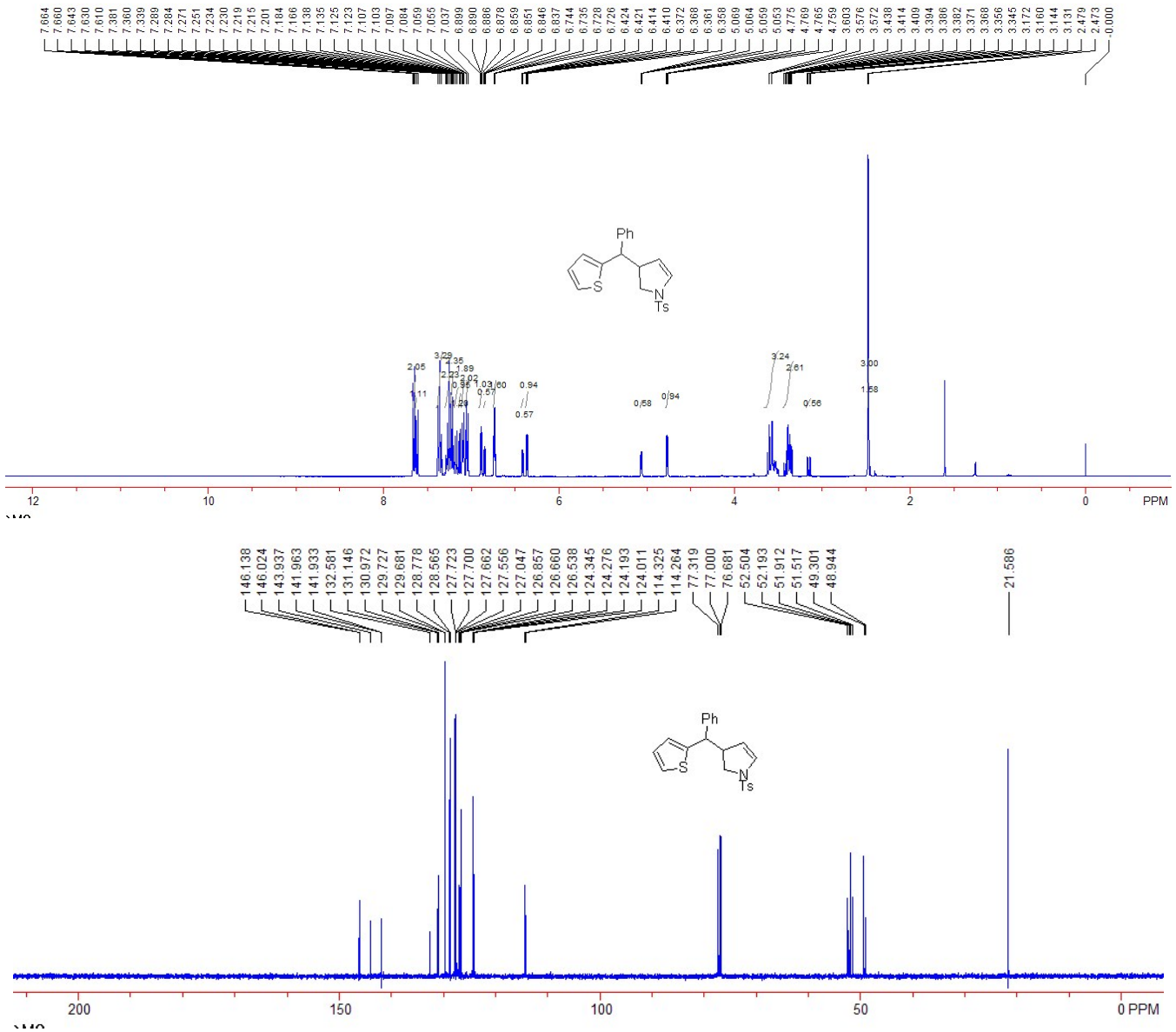


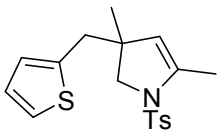




3-(phenyl(thiophen-2-yl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2l

A pale yellow solid, 68% yield (27 mg, dr : 2/1). M.p.: 56-58 ^{o}C. Major product: ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.49 (s, 3H, CH_3), 3.34-3.44 (m, 2H, CH_2), 3.52-3.63 (m, 2H, CH), 4.77 (dd, *J* = 4.0, 2.4 Hz, 1H, =CH), 6.37 (dd, *J* = 3.2, 1.2 Hz, 1H, =CH), 6.74 (s, 1H, ArH), 6.89 (dd, *J* = 5.2, 4.0 Hz, 1H, ArH), 7.05 (d, *J* = 8.0 Hz, 2H, ArH), 7.09-7.24 (m, 4H, ArH), 7.37 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 49.3, 52.0, 52.6, 114.3, 124.2, 124.4, 126.7, 126.9, 127.6, 127.8, 128.6, 129.8, 131.0, 132.7, 142.0, 144.0, 146.2. Minor product: ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.49 (s, 3H, CH_3), 3.15 (dd, *J* = 11.6, 5.2 Hz, 1H, CH_2), 3.34-3.44 (m, 1H, CH_2), 3.52-3.63 (m, 2H, CH_2), 5.06 (dd, *J* = 4.0, 2.0 Hz, 1H, =CH), 6.42 (dd, *J* = 4.4, 2.0 Hz, 1H, =CH), 6.74 (s, 1H, ArH), 6.85 (dd, *J* = 4.8, 3.6 Hz, 1H, ArH), 7.05 (d, *J* = 8.0 Hz, 2H, ArH), 7.09-7.24 (m, 4H, ArH), 7.37 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 49.0, 51.6, 52.2, 114.3, 124.0, 124.2, 126.7, 127.1, 127.70, 127.74, 128.8, 131.2, 142.0, 144.0, 146.1. IR (CH_2Cl_2) ν 2923, 1597, 1493, 1352, 1163, 1090, 997, 813, 734, 664 cm^{-1}. MS (ESI) *m/z* (%): 396.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{22}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 396.1086, Found: 396.1087.

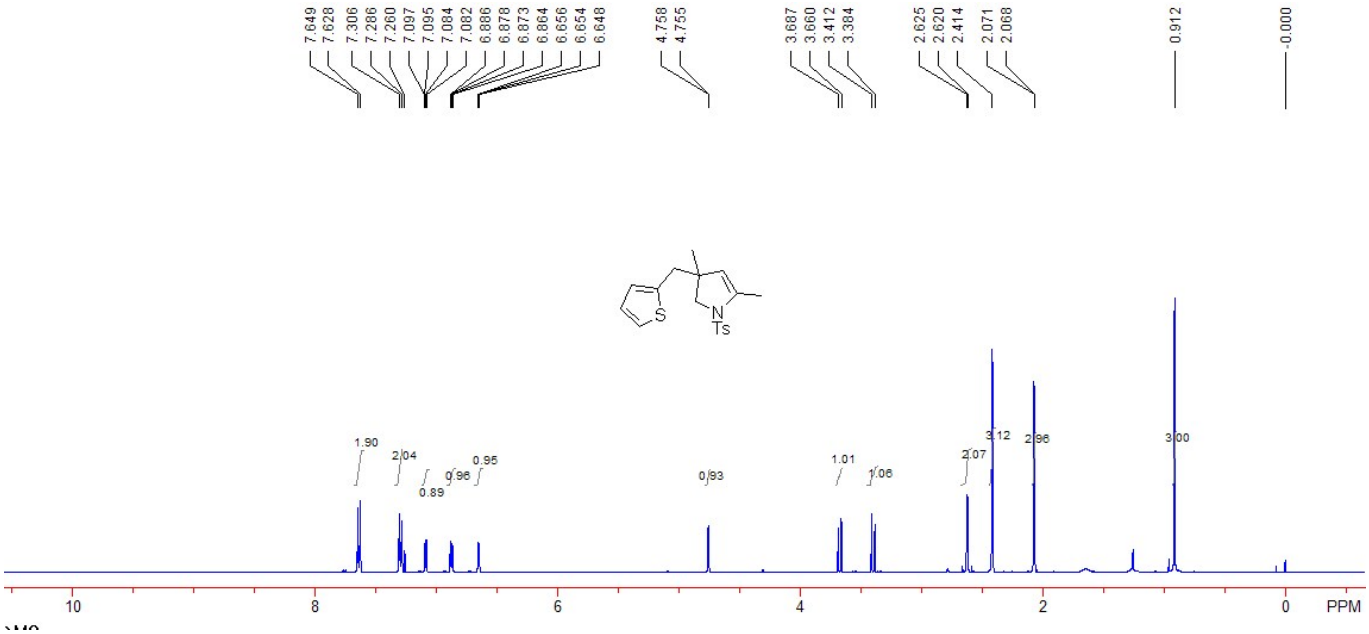


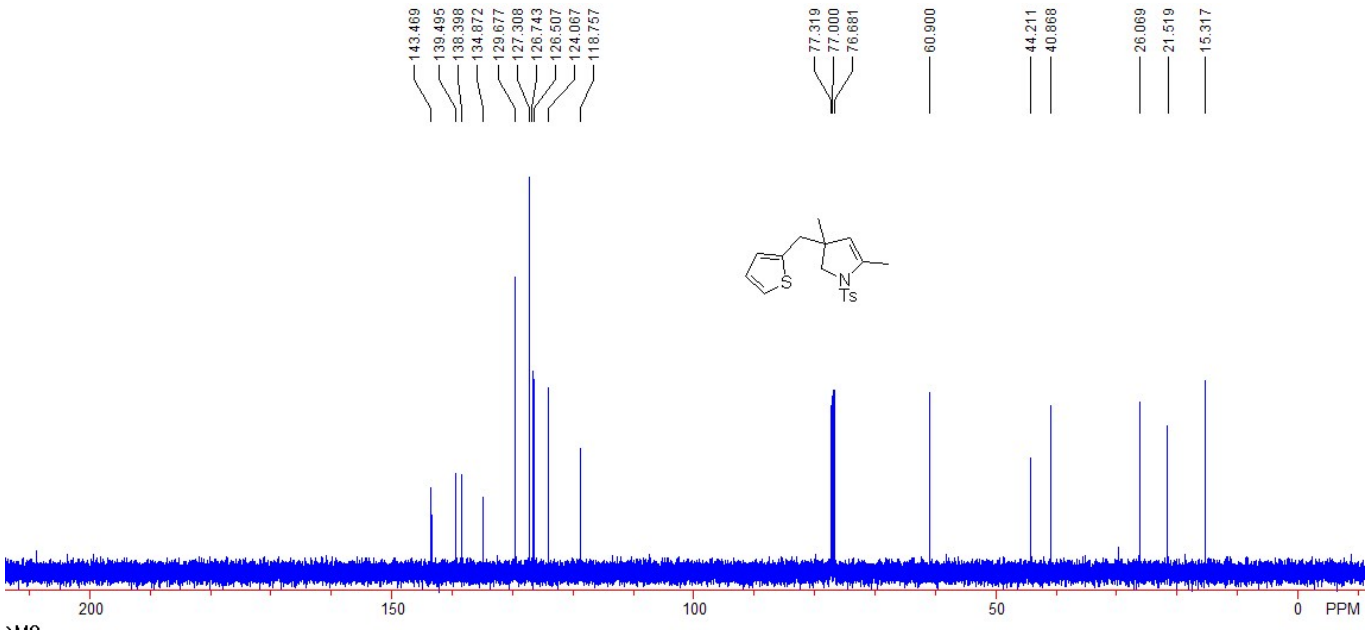


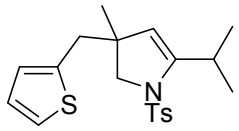
3,5-dimethyl-3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2m

A white liquid, 75% yield (26 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.91 (s, 3H, CH_3), 2.07 (d, J = 1.2 Hz, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.62 (d, J = 2.4 Hz, 2H, CH_2), 3.40 (d, J = 11.2 Hz, 1H, CH_2), 3.67 (d, J = 11.2 Hz, 1H, CH_2), 4.76 (d, J = 1.2 Hz, 1H, =CH), 6.65 (dd, J = 2.4, 0.8 Hz, 1H, ArH), 6.87 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.09 (dd, J = 5.2, 0.8 Hz, 1H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 7.64 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.3, 21.5, 26.1, 40.9, 44.2, 60.9, 118.8, 124.1, 126.5, 126.7, 127.3, 129.7, 134.9, 138.4, 139.5, 143.5. IR (CH_2Cl_2) ν 2960, 2925, 1658, 1597, 1435, 1346,

1162, 1092, 1036, 813, 717, 658 cm^{-1}. MS (ESI) *m/z* (%): 348.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 348.1086, found: 348.1088.



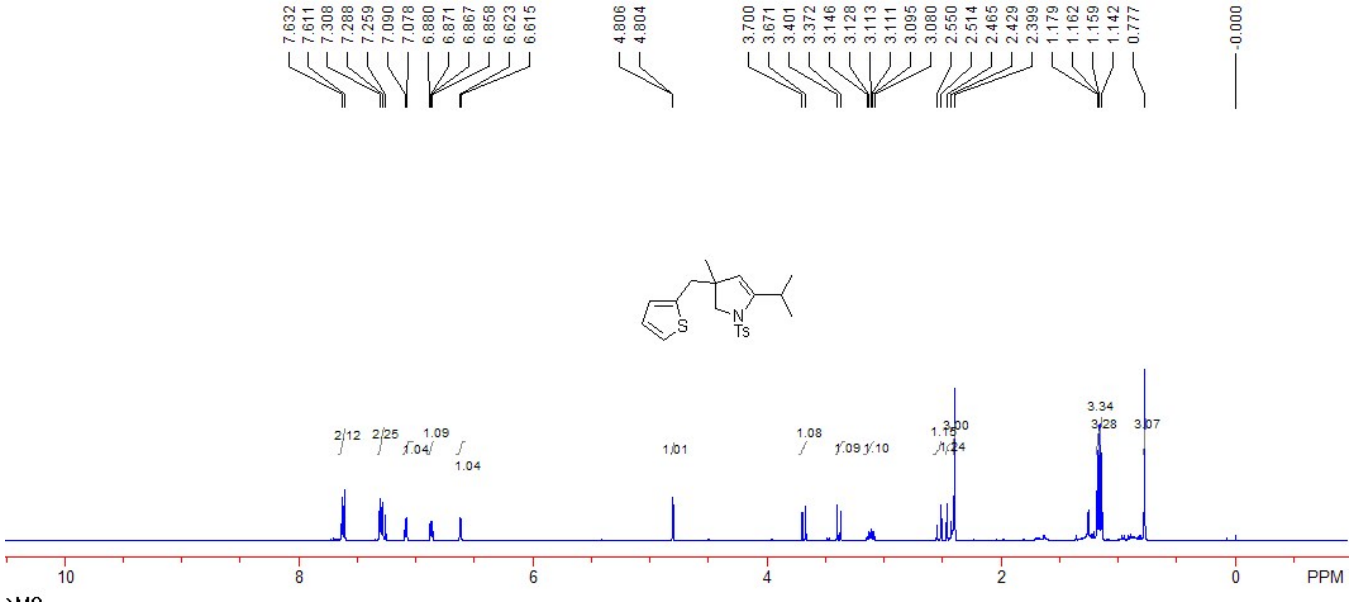


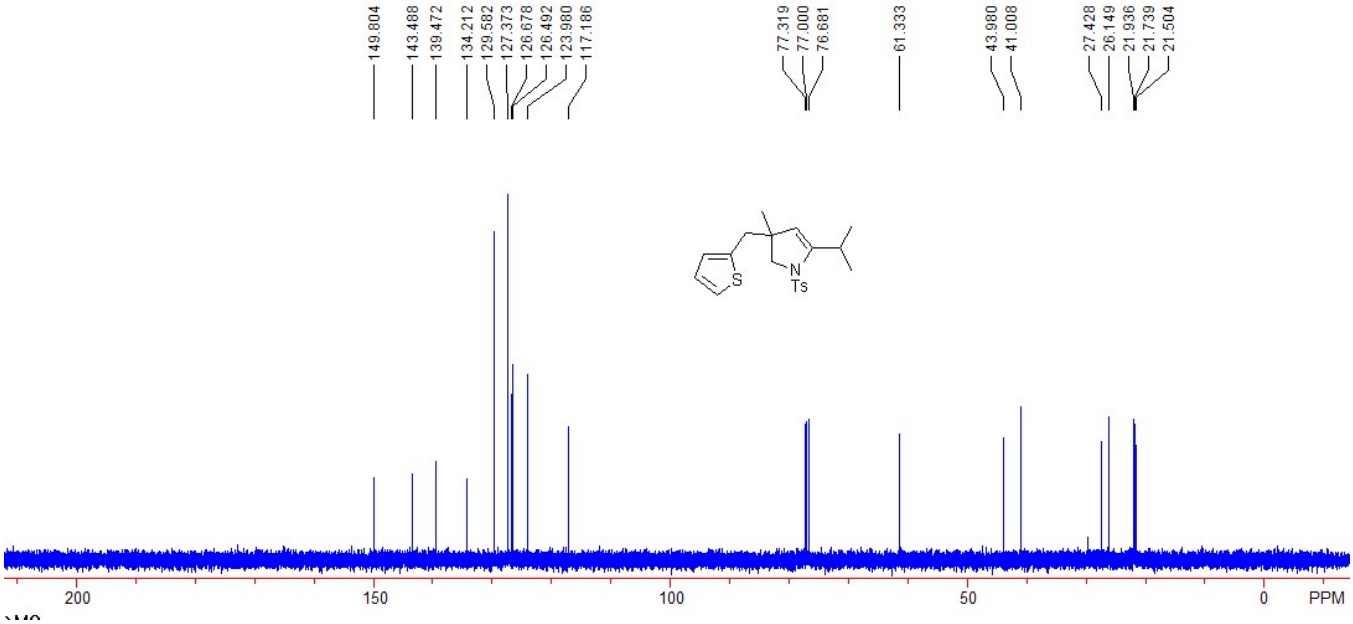


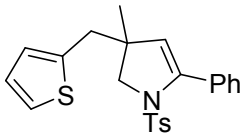
5-isopropyl-3-methyl-3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2n

A white liquid, 80% yield (30 mg). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.78 (s, 3H, CH_3), 1.15 (d, J = 6.8 Hz, 3H, CH_3), 1.17 (d, J = 6.8 Hz, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.44 (d, J = 14.4 Hz, 1H, CH_2), 2.53

(d, J = 14.4 Hz, 1H, CH_2), 3.07-3.15 (m, 1H, CH), 3.39 (d, J = 11.6 Hz, 1H, CH_2), 3.69 (d, J = 11.6 Hz, 1H, CH_2), 4.80 (d, J = 0.8 Hz, 1H, =CH), 6.62 (d, J = 3.2 Hz, 1H, ArH), 6.87 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.08 (d, J = 4.8 Hz, 1H, ArH), 7.29 (d, J = 8.0 Hz, 2H, ArH), 7.62 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.7, 21.9, 26.2, 27.4, 41.0, 44.0, 61.3, 117.2, 124.0, 126.5, 126.7, 127.4, 129.6, 134.2, 139.5, 143.5, 149.8. IR (CH_2Cl_2) ν 3674, 2966, 2926, 2872, 1645, 1598, 1454, 1348, 1165, 1091, 812, 716, 659 cm^{-1}. MS (ESI) *m/z* (%): 376.14 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{20}H_{26}NO_2S_2^{+1}[M+H]^+$ requires 376.1399, found: 376.1401.

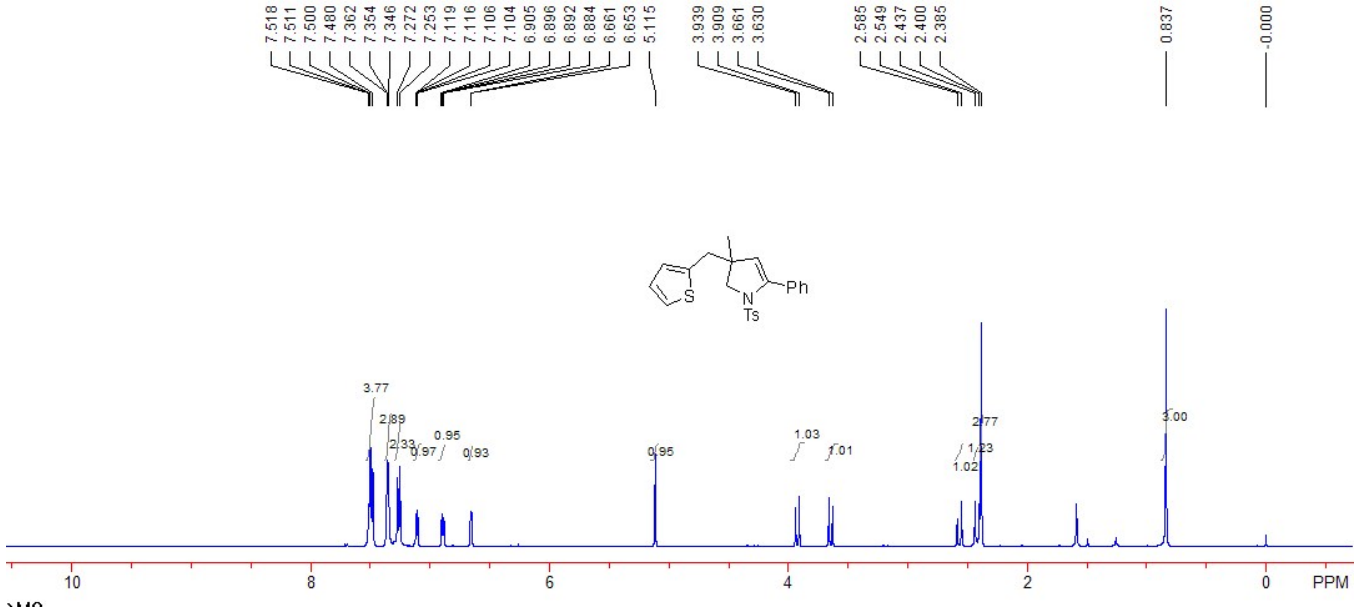


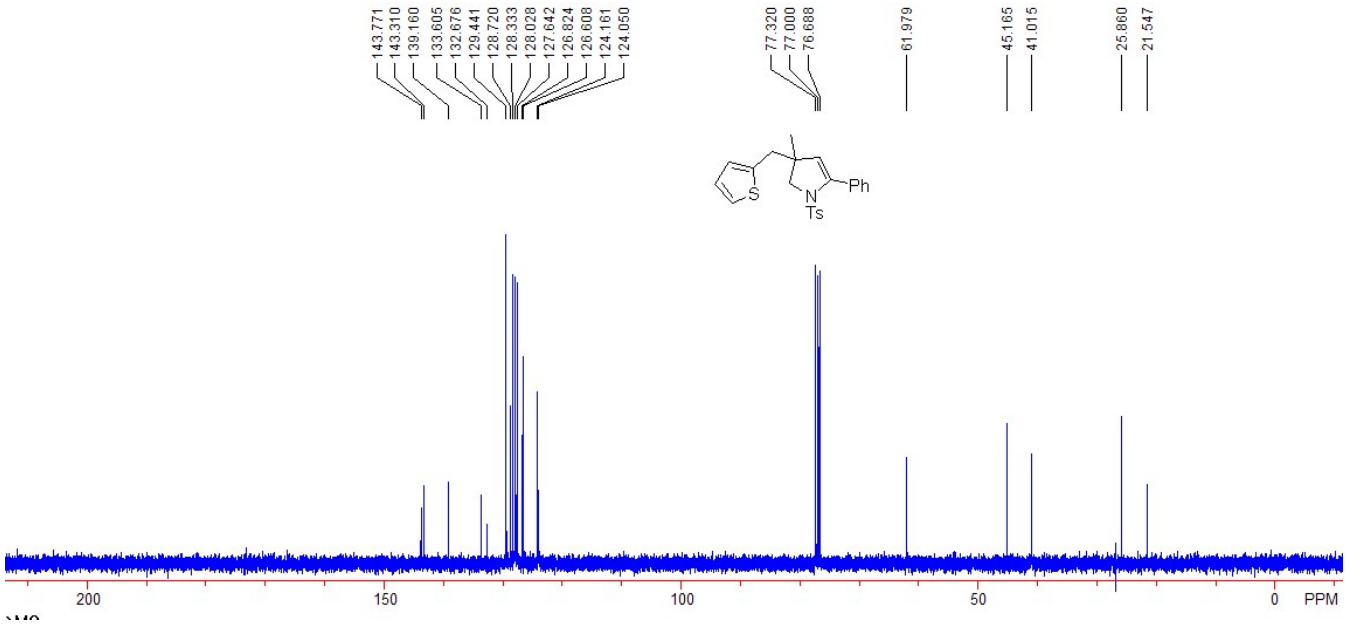


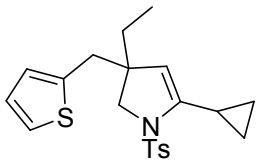


3-methyl-5-phenyl-3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2o

A white liquid, 73% yield (30 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.84 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.42 (d, *J* = 14.8 Hz, 1H, CH_2), 2.57 (d, *J* = 14.8 Hz, 1H, CH_2), 3.65 (d, *J* = 12.0 Hz, 1H, CH_2), 3.92 (d, *J* = 12.0 Hz, 1H, CH_2), 5.12 (s, 1H, =CH), 6.66 (d, *J* = 3.2 Hz, 1H, ArH), 6.89 (dd, *J* = 4.8, 3.2 Hz, 1H, ArH), 7.11 (dd, *J* = 4.8, 0.8 Hz, 1H, ArH), 7.26 (d, *J* = 7.6 Hz, 2H, ArH), 7.34-7.37 (m, 3H, ArH), 7.47-7.52 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 25.9, 41.0, 45.2, 62.0, 124.1, 124.2, 126.6, 126.8, 127.6, 128.0, 128.3, 128.7, 129.4, 132.7, 133.6, 139.1, 143.3, 143.8. IR (CH_2Cl_2) ν 2923, 1685, 1597, 1446, 1354, 1165, 1090, 1029, 813, 716, 660 cm^{-1}. MS (ESI) *m/z* (%): 410.12 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{23}H_{24}NO_2S_2^{+1}[M+H]^+$ requires 410.1243, found: 410.1243.

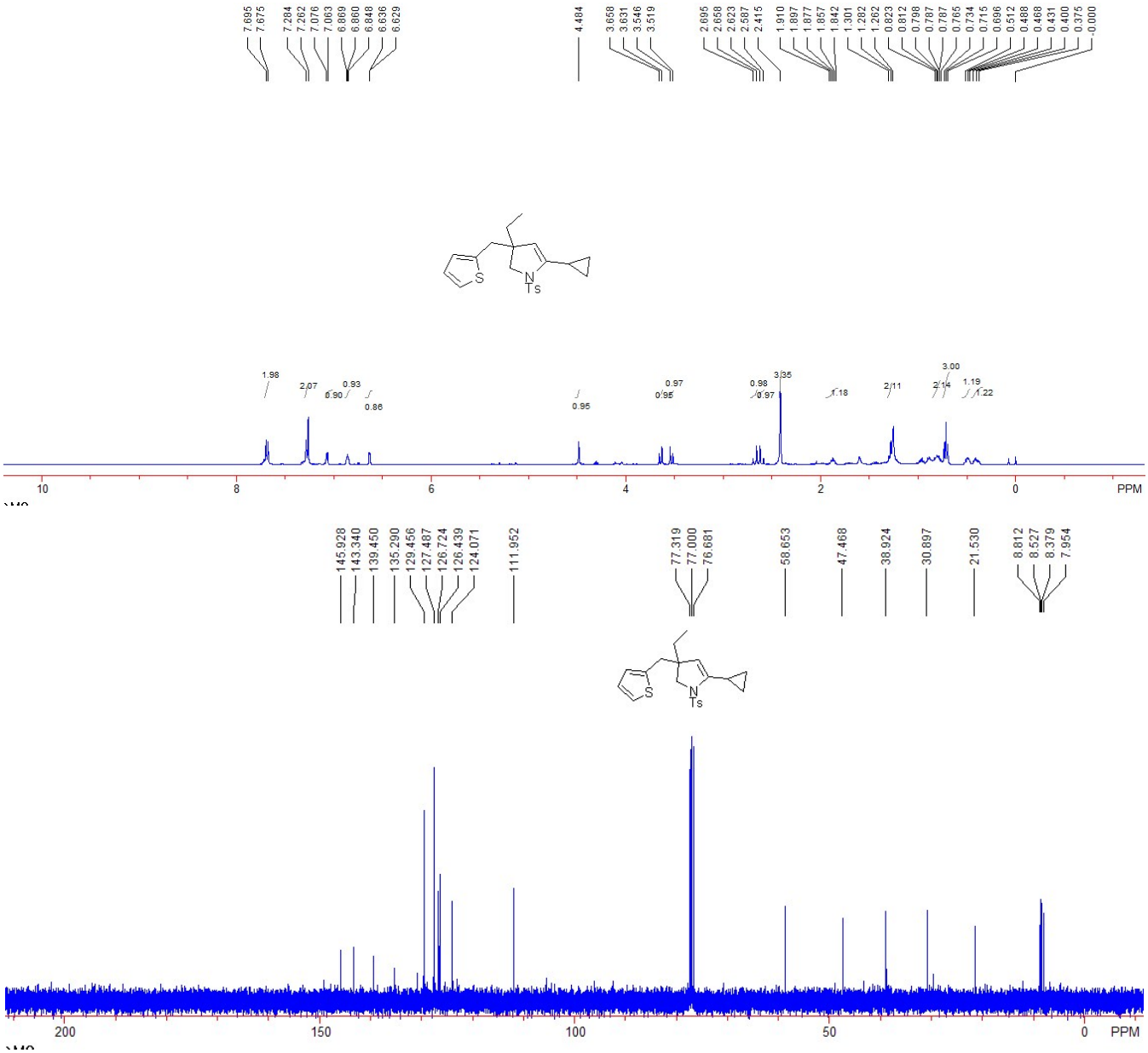


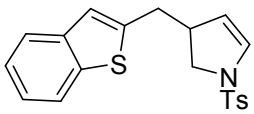




5-cyclopropyl-3-ethyl-3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2p

A white liquid, 52% yield (20 mg) (This product is quite labile and it will contain some impurity when it is stored in refrigerator). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.37-0.44 (m, 1H, CH_2), 0.46-0.53 (m, 1H, CH_2), 0.69-0.74 (m, 3H, CH_3), 0.76-0.83 (m, 2H, CH_2), 0.94-0.99 (m, 1H, CH_2), 1.25-1.29 (m, 2H, CH_2), 1.84-1.92 (m, 1H, CH), 2.42 (s, 3H, CH_3), 2.58-2.70 (m, 1H, CH_2), 3.53 (d, *J* = 10.8 Hz, 1H, CH_2), 3.64 (d, *J* = 10.8 Hz, 1H, CH_2), 4.49 (s, 1H, =CH), 6.63 (d, *J* = 2.8 Hz, 1H, ArH), 6.86 (dd, *J* = 4.8, 3.6 Hz, 1H, ArH), 7.07 (d, *J* = 4.8 Hz, 1H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH), 7.68 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 8.0, 8.4, 8.5, 8.8, 21.5, 30.9, 39.0, 47.5, 58.7, 112.0, 124.1, 126.4, 126.7, 127.5, 129.5, 135.3, 139.5, 143.3, 145.9. IR (CH_2Cl_2) ν 3674, 2970, 2922, 1727, 1459, 1348, 1305, 1162, 1092, 900, 813, 712, 659 cm^{-1}. MS (ESI) *m/z* (%): 388.14 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{21}H_{26}NO_2S_2^{+1}[M+H]^+$ requires 388.1399, found: 388.1402.

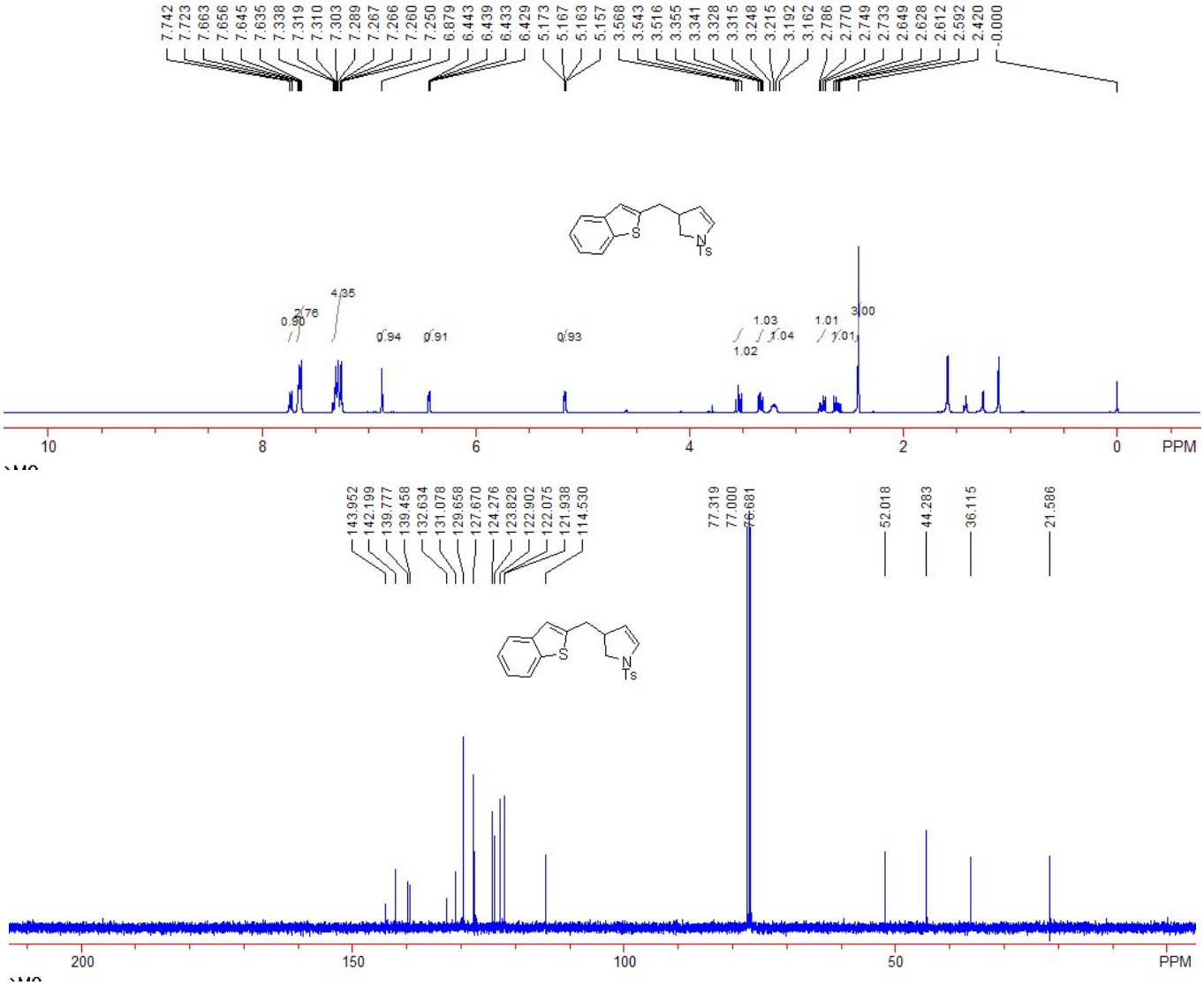


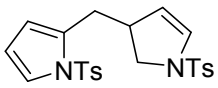


3-(benzo[*b*]thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2q

A white solid, 64% yield (24 mg). M.p.: 81-83 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 2.61 (dd, *J* = 14.8, 8.0 Hz, 1H, CH_2), 2.75 (dd, *J* = 14.8, 6.8 Hz, 1H, CH_2), 3.16-3.26 (m, 1H, CH), 3.33 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.16 (dd, *J* = 3.6, 2.4 Hz, 1H, =CH), 6.43 (dd, *J* = 4.4, 1.6 Hz, 1H, =CH), 6.87 (s, 1H, ArH), 7.24-7.34 (m, 4H, ArH), 7.63-7.67 (m, 3H, ArH), 7.73 (d, *J* = 8.0 Hz, 1H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 36.1, 44.3, 52.0, 114.5, 121.9, 122.1, 122.9, 123.8, 124.3, 127.7, 129.6, 131.1, 132.6, 139.4, 139.8, 142.2, 143.9. IR (CH_2Cl_2) ν

3059, 2924, 2853, 1598, 1487, 1437, 1338, 1159, 1092, 997, 816, 748, 668 cm^{-1}. MS (ESI) *m/z* (%): 370.09 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{20}H_{20}NO_2S_2^{+1}[M+H]^+$ requires 370.0930, Found: 370.0931.

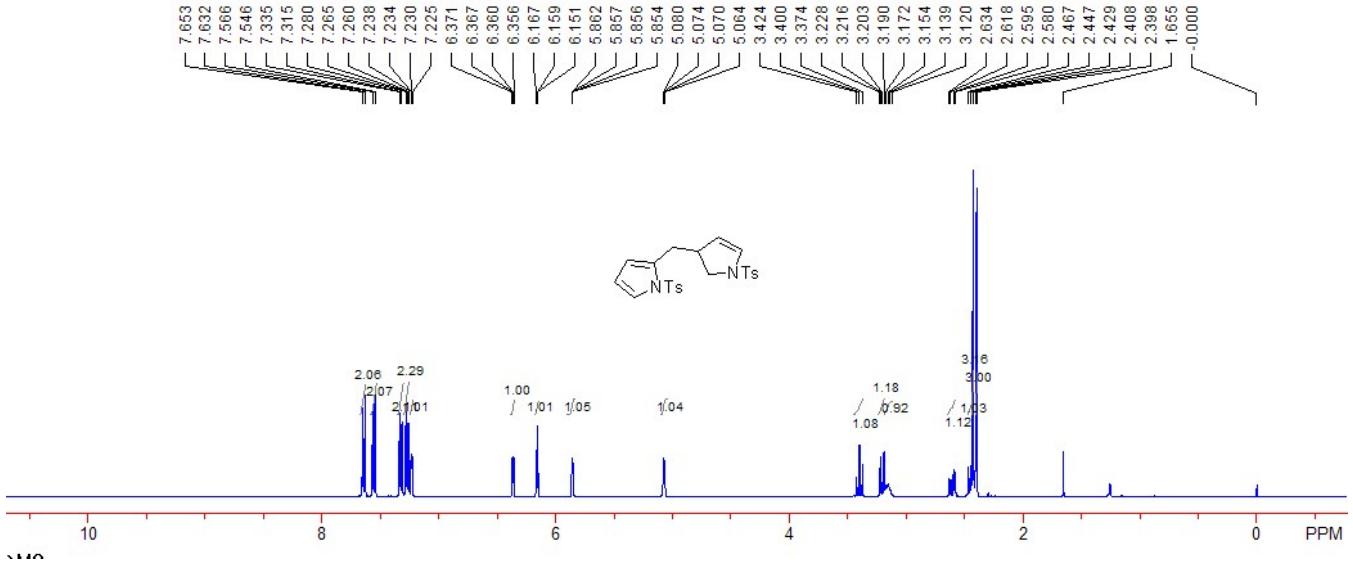


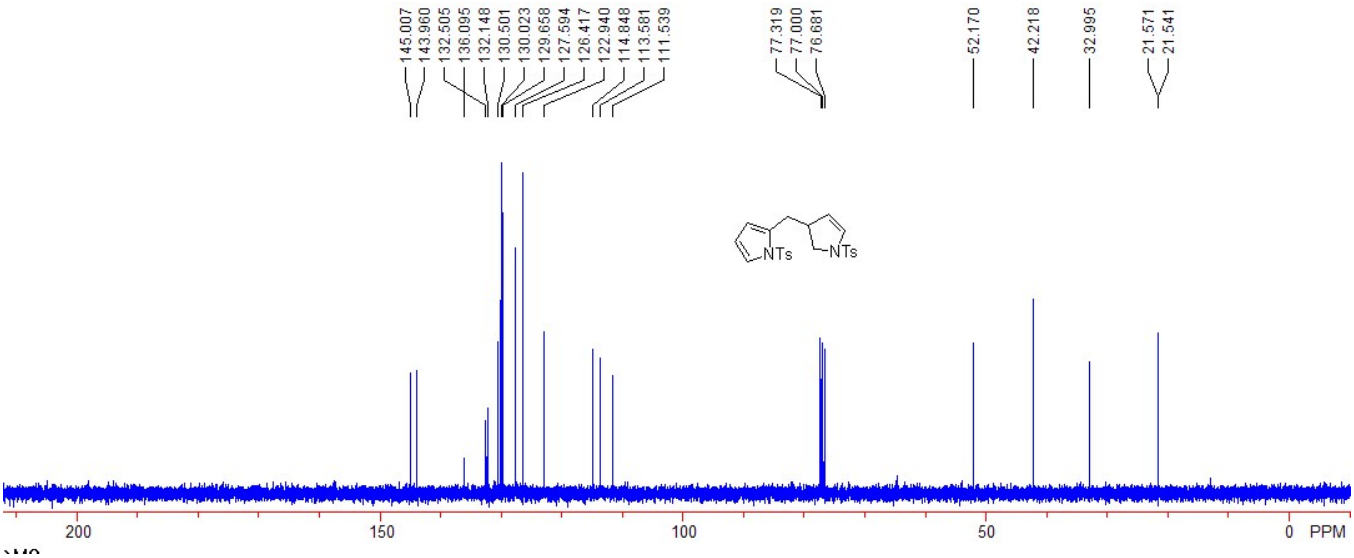


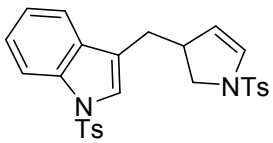
1-tosyl-2-((1-tosyl-2,3-dihydro-1*H*-pyrrol-3-yl)methyl)-1*H*-pyrrole 2r

A white solid, 67% yield (32 mg). M.p.: 51-53 ^oC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.44-2.47 (m, 1H, CH_2), 2.60 (dd, *J* = 15.2, 5.6 Hz, 1H, CH_2), 3.11-3.18 (m, 1H, CH), 3.21 (dd, *J* = 10.4, 5.2 Hz, 1H, CH_2), 3.40 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.07 (dd, *J* = 4.0, 2.8 Hz, 1H, =CH), 5.86 (s, 1H, =CH), 6.16 (dd, *J* = 3.2, 3.2 Hz, 1H, ArH), 6.37 (dd, *J* = 4.0, 1.2 Hz, 1H, ArH), 7.23 (dd, *J* = 3.2, 1.6 Hz, 1H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.55 (d, *J* =

8.4 Hz, 2H, ArH), 7.64 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.56, 21.59, 33.0, 42.2, 52.2, 111.5, 113.6, 114.8, 123.0, 126.4, 127.6, 129.7, 130.0, 130.5, 132.2, 132.5, 136.1, 144.0, 145.0. IR (CH_2Cl_2) ν 2922, 2851, 1754, 1597, 1493, 1353, 1306, 1166, 1122, 1090, 1007, 813, 719, 667 cm^{-1}. MS (ESI) *m/z* (%): 474.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{23}H_{28}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 474.1516, found: 474.1518.



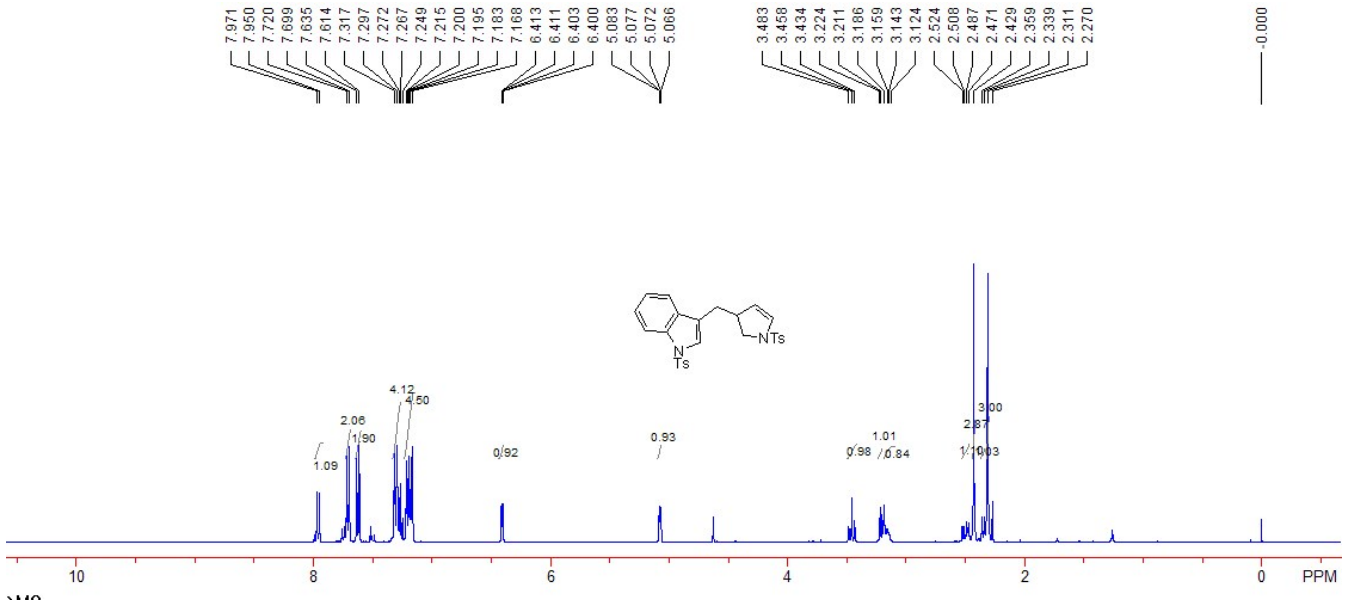


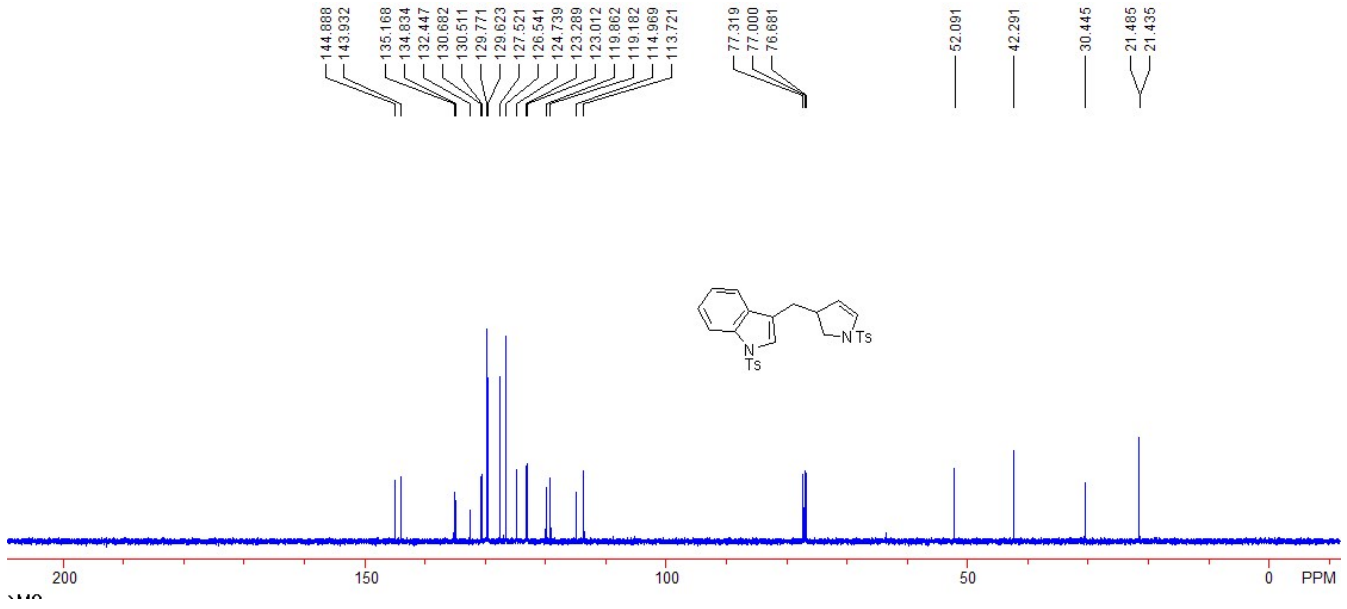


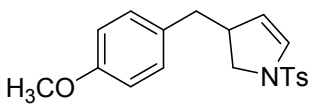
1-tosyl-2-((1-tosyl-2,3-dihydro-1*H*-pyrrol-3-yl)methyl)-1*H*-indole 2s

A white solid, 45% yield (23 mg). M.p.: 78-80 °C (This product is quite labile and it will contain some

impurity when it is stored in refrigerator). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H, CH_3), 2.33 (dd, *J* = 15.2, 8.0 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3), 2.49 (dd, *J* = 14.8, 6.4 Hz, 1H, CH_2), 3.11-3.19 (m, 1H, CH), 3.21 (dd, *J* = 10.4, 5.2 Hz, 1H, CH_2), 3.46 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.07 (dd, *J* = 4.4, 2.4 Hz, 1H, =CH), 6.40 (dd, *J* = 4.4, 1.2 Hz, 1H, =CH), 7.16-7.22 (m, 4H, ArH), 7.26-7.32 (m, 4H, ArH), 7.62 (d, *J* = 8.4 Hz, 2H, ArH), 7.71 (d, *J* = 8.4 Hz, 2H, ArH), 7.96 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.5, 30.5, 42.3, 52.1, 113.7, 115.0, 119.2, 119.9, 123.0, 123.3, 124.7, 126.5, 127.5, 129.6, 129.77, 129.79, 130.5, 130.7, 132.4, 134.8, 135.2, 143.9, 144.9. IR (CH_2Cl_2) ν 2922, 1597, 1493, 1447, 1353, 1169, 1120, 917, 813, 746, 667 cm^{-1}. MS (ESI) *m/z* (%): 524.16 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{30}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 524.1672, found: 524.1673.

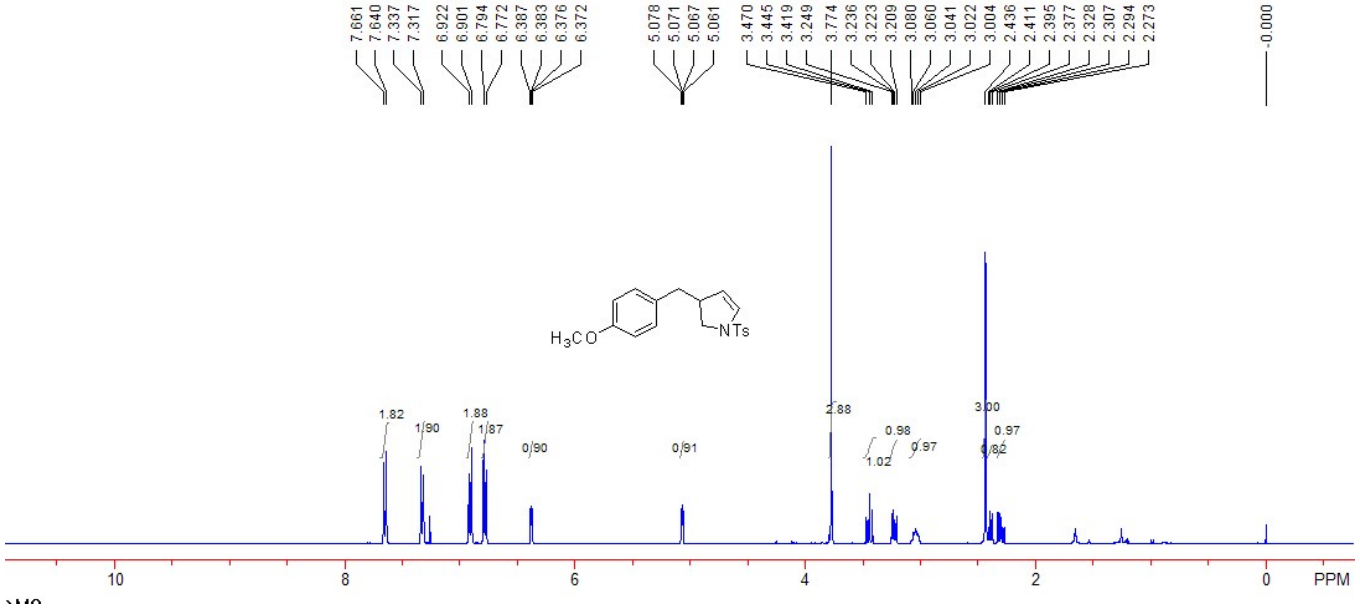


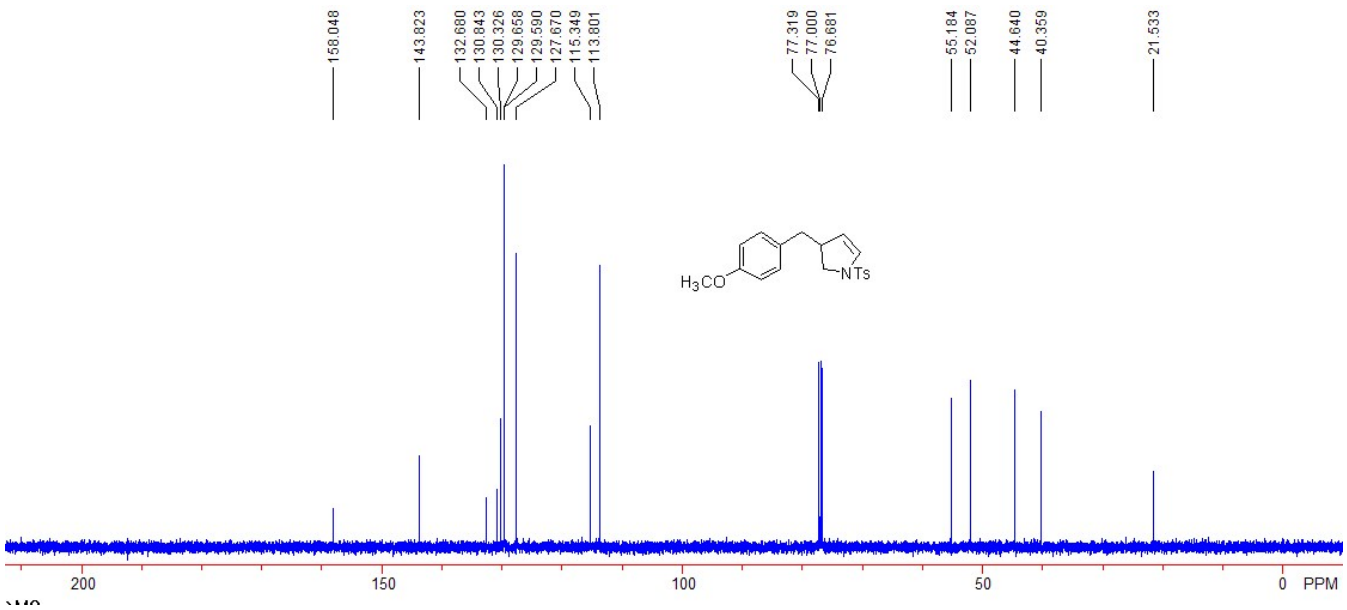


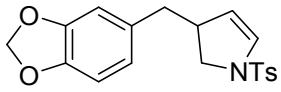


3-(4-methoxybenzyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2t

A white liquid, 76% yield (26 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.30 (dd, *J* = 13.6, 8.0 Hz, 1H, CH_2), 2.38 (dd, *J* = 13.6, 7.2 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3), 3.00-3.08 (m, 1H, CH), 3.23 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.44 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 3,77 (s, 3H, CH_3), 5.07 (dd, *J* = 4.0, 2.8 Hz, 1H, =CH), 6.38 (dd, *J* = 3.6, 1.2 Hz, 1H, =CH), 6.78 (d, *J* = 8.4 Hz, 2H, ArH), 6.91 (d, *J* = 8.4 Hz, 2H, ArH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.64 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 40.4, 44.7, 52.1, 55.2, 113.8, 115.3, 127.7, 129.6, 129.7, 130.3, 130.8, 132.7, 143.8, 158.0. IR (CH_2Cl_2) ν 3661, 2970, 2922, 1612, 1464, 1348, 1163, 1035, 814, 707, 665 cm^{-1}. MS (ESI) *m/z* (%): 344.13 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{19}H_{22}NO_3S^{+1}[M+H]^+$ requires 344.1315, found: 344.1308.

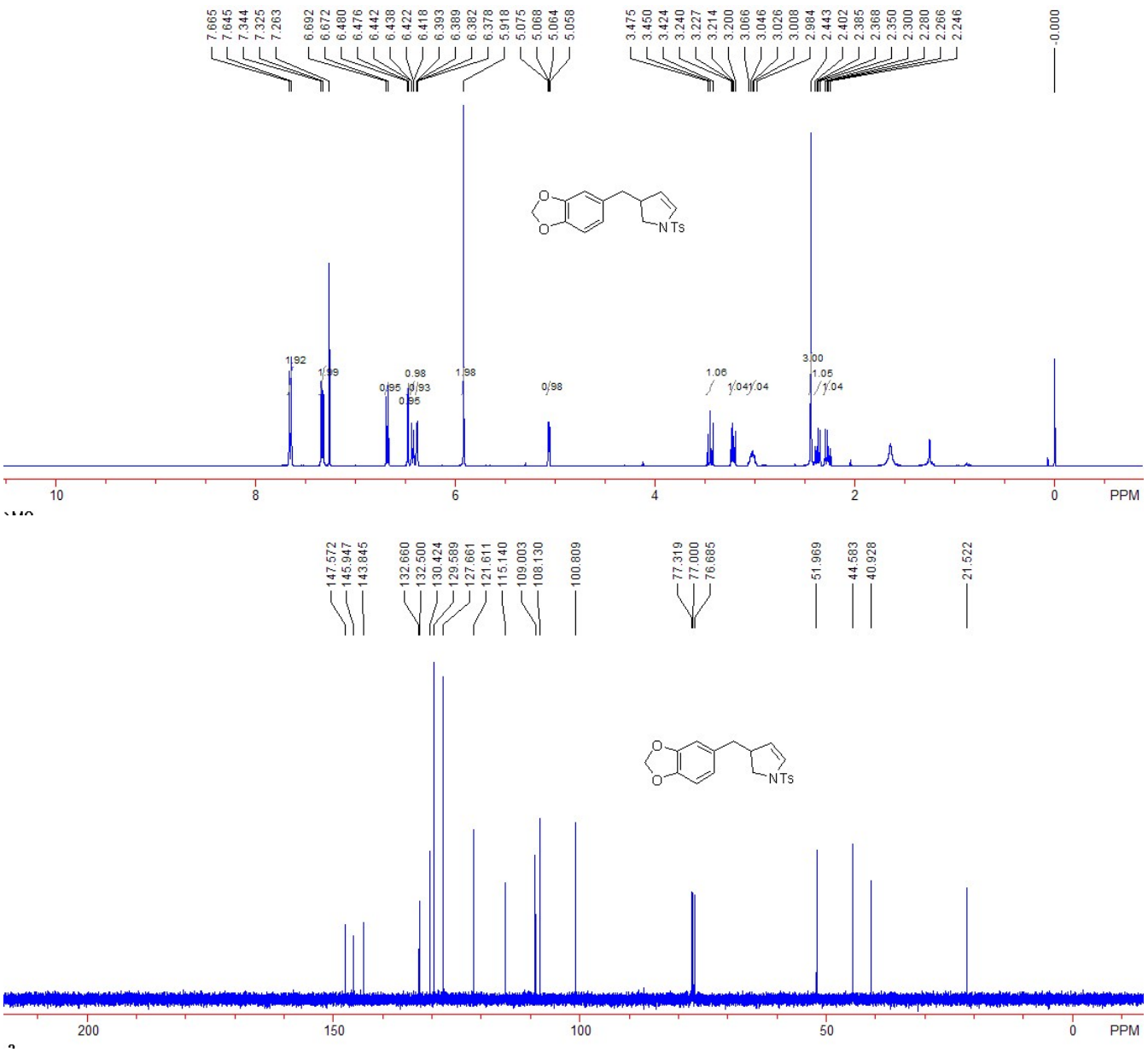


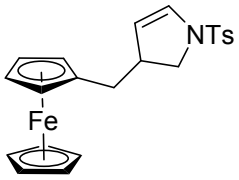




3-(benzo[*d*][1,3]dioxol-5-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole 2u

A white liquid, 84% yield (30 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.26 (dd, *J* = 13.6, 8.4 Hz, 1H, CH_2), 2.37 (dd, *J* = 13.6, 7.2 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 3.00-3.07 (m, 1H, CH), 3.21 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2), 3.45 (dd, *J* = 10.4, 10.4 Hz, 1H, CH_2), 5.07 (dd, *J* = 4.0, 2.4 Hz, 1H, =CH), 5.92 (s, 2H, CH_2), 6.38 (dd, *J* = 4.0, 1.6 Hz, 1H, =CH), 6.42 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 6.48 (s, 1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.65 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 40.9, 44.6, 52.0, 100.8, 108.1, 109.0, 115.1, 121.6, 127.7, 129.6, 130.4, 132.5, 132.7, 143.8, 145.9, 147.6. IR (CH_2Cl_2) ν 2959, 2925, 2874, 1598, 1503, 1443, 1350, 1164, 1093, 1038, 926, 813, 707, 665 cm^{-1}. MS (ESI) *m/z* (%): 358.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{19}H_{20}NO_4S^{+1}[M+H]^+$ requires 358.1108, found: 358.1109.

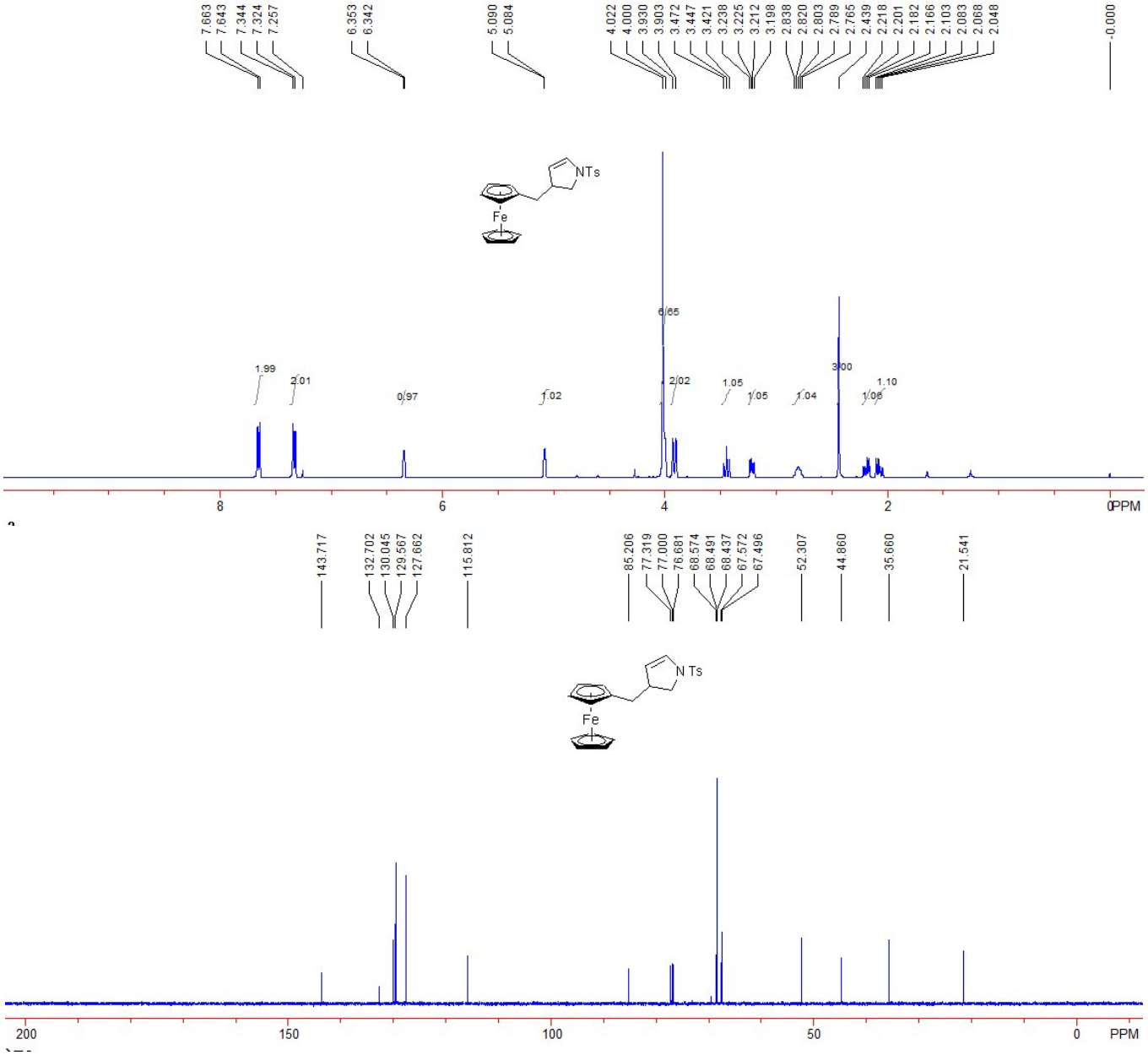




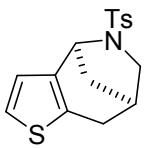
((1-tosyl-2,3-dihydro-1*H*-pyrrol-3-yl)methyl) ferrocene 2v

A yellow liquid, 71% yield (59.6 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.07 (dd, *J* = 14.0, 8.0 Hz, 1H, CH_2), 2.19 (dd, *J* = 14.0, 6.4 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.76-2.84 (m, 1H, CH), 3.22 (dd, *J* = 10.8, 5.6 Hz, 1H, CH_2), 3.45 (dd, *J* = 10.4, 10.4 Hz, 1H, CH_2), 3.92 (d, *J* = 10.8 Hz, 2H, CH_2), 4.00-4.03 (m, 7H, CH), 5.09 (dd, *J* = 3.6, 2.8 Hz, 1H, =CH), 6.35 (d, *J* = 4.4 Hz, 1H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H,

ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.7, 44.9, 52.3, 67.5, 67.6, 68.4, 68.5, 68.6, 85.2, 115.8, 127.7, 129.6, 130.0, 132.7, 143.7. IR (CH_2Cl_2) ν 3094, 2919, 1597, 1493, 1349, 1162, 1091, 999, 812, 707, 662 cm^{-1}. MS (ESI) *m/z* (%): 419.08 (100) $[M]^+$; HRMS (ESI) Calcd. For $C_{22}H_{23}O_2N^{54}FeS^{+1}[M+H]^+$ requires 419.0840, found: 419.0844.

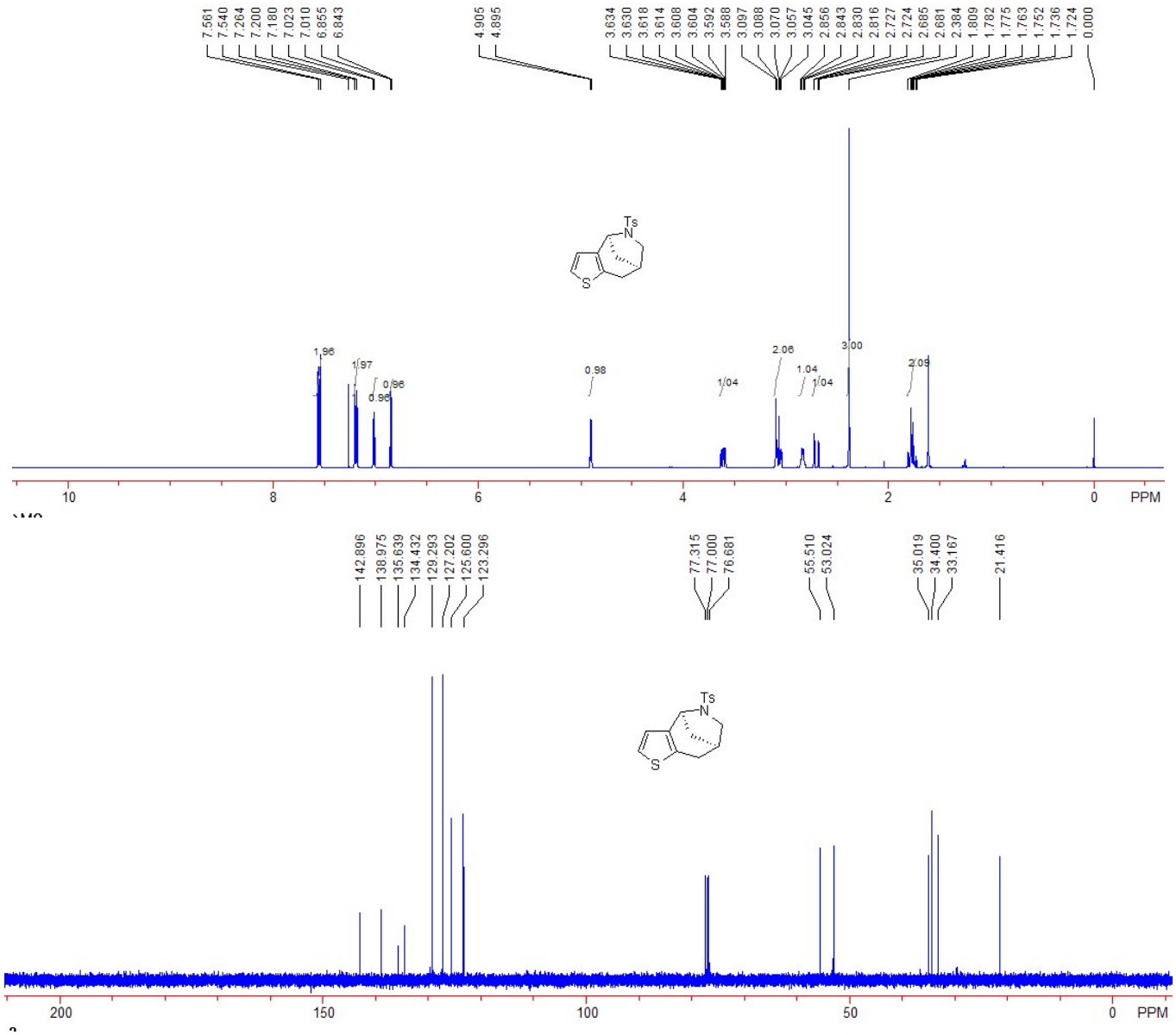


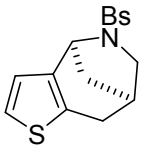
14. Characterization and spectra charts for compounds 3 and 5



5-tosyl-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine 3a

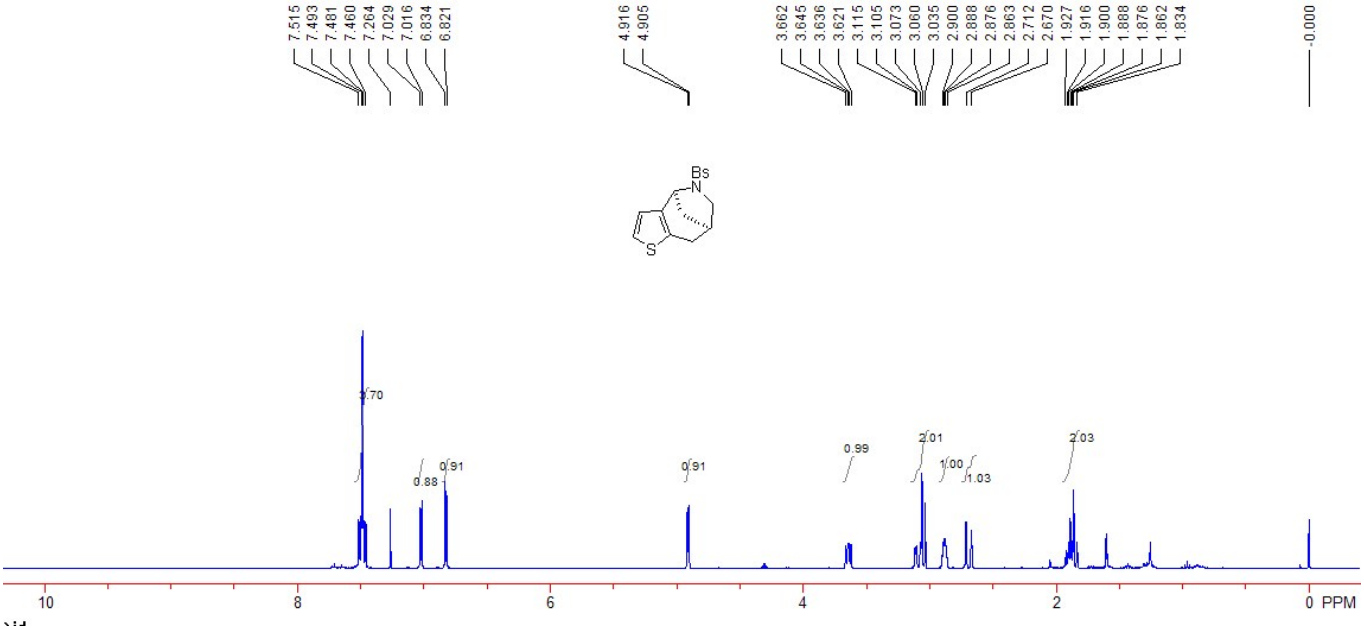
A pale yellow solid, 94% yield (30 mg). M.p.: 51-53 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.72-1.81 (m, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.69 (d, *J* = 16.8 Hz, 1H, CH_2), 2.81-2.85 (m, 1H, CH_2), 3.03-3.10 (m, 2H, CH_2), 3.58-3.63 (m, 1H, CH_2), 4.89 (d, *J* = 4.8 Hz, 1H, CH_2), 6.84 (d, *J* = 5.2 Hz, 1H, ArH), 7.01 (d, *J* = 5.2 Hz, 1H, ArH), 7.18 (d, *J* = 8.0 Hz, 2H, ArH), 7.54 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 33.2, 34.4, 35.0, 53.0, 55.5, 123.3, 125.6, 127.2, 129.3, 134.4, 135.6, 139.0, 142.9. IR (CH_2Cl_2) ν 3102, 2929, 2853, 1606, 1458, 1348, 1311, 1167, 1092, 999, 817, 708, 664 cm^{-1}. MS (ESI) *m/z* (%): 320.07 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{18}NO_2S_2^{+1}[M+H]^+$ requires 320.0773, found: 320.0775.

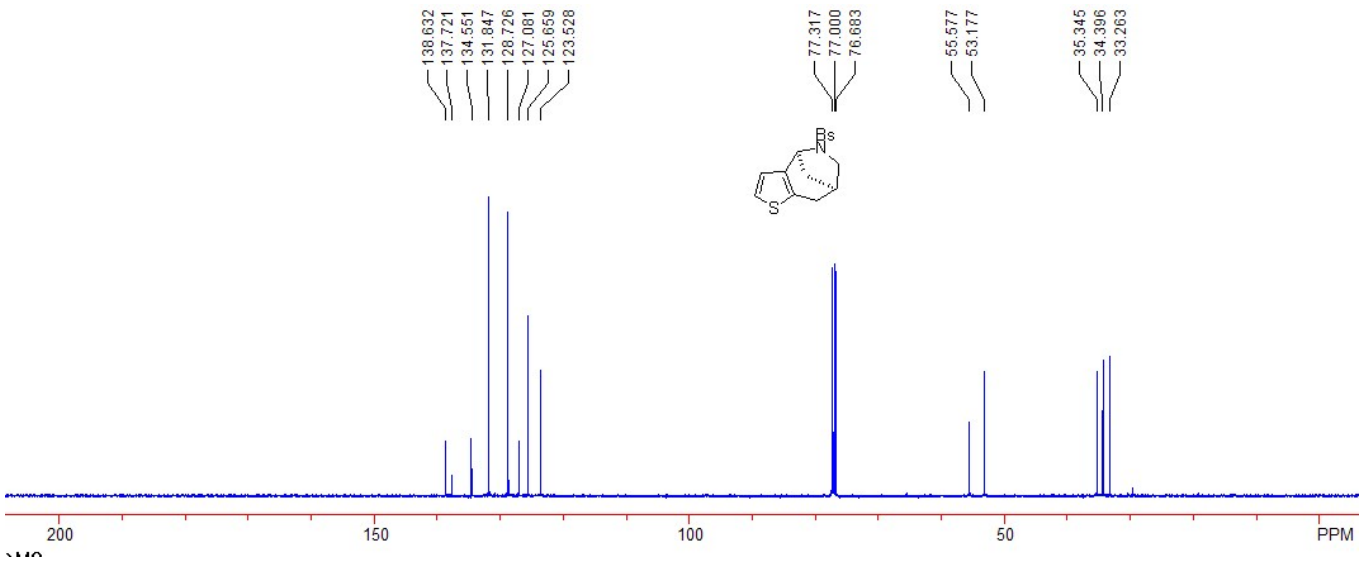


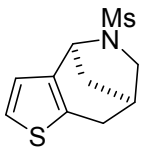


5-((4-bromophenyl)sulfonyl)-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine 3b

A pale yellow liquid, 19% yield (15 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.83-1.92 (m, 2H, CH_2), 2.69 (d, J = 16.8 Hz, 1H, CH_2), 2.86-2.90 (m, 1H, CH_2), 3.03-3.12 (m, 2H, CH_2), 3.62-3.67 (m, 1H, CH_2), 4.91 (d, J = 4.4 Hz, 1H, CH_2), 6.82 (d, J = 5.2 Hz, 1H, ArH), 7.02 (d, J = 5.2 Hz, 1H, ArH), 7.46-7.52 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.3, 34.4, 35.3, 53.2, 55.6, 123.5, 125.7, 127.1, 128.7, 131.8, 134.6, 137.7, 138.6. IR (CH_2Cl_2) ν 2952, 1574, 1471, 1341, 1153, 1092, 1008, 933, 851, 704, 671 cm^{-1}. MS (ESI) *m/z* (%): 383.97 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{15}BrNO_2S_2{}^{+1}[M+H]^+$ requires 383.9722, found: 383.9721.

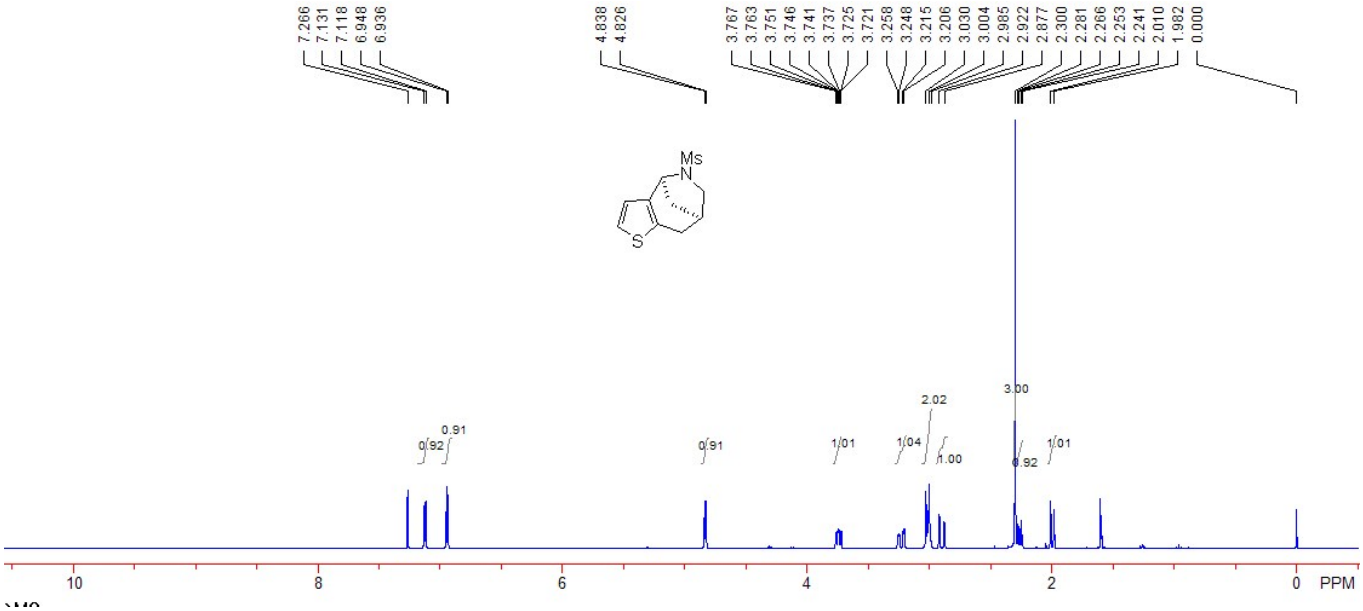


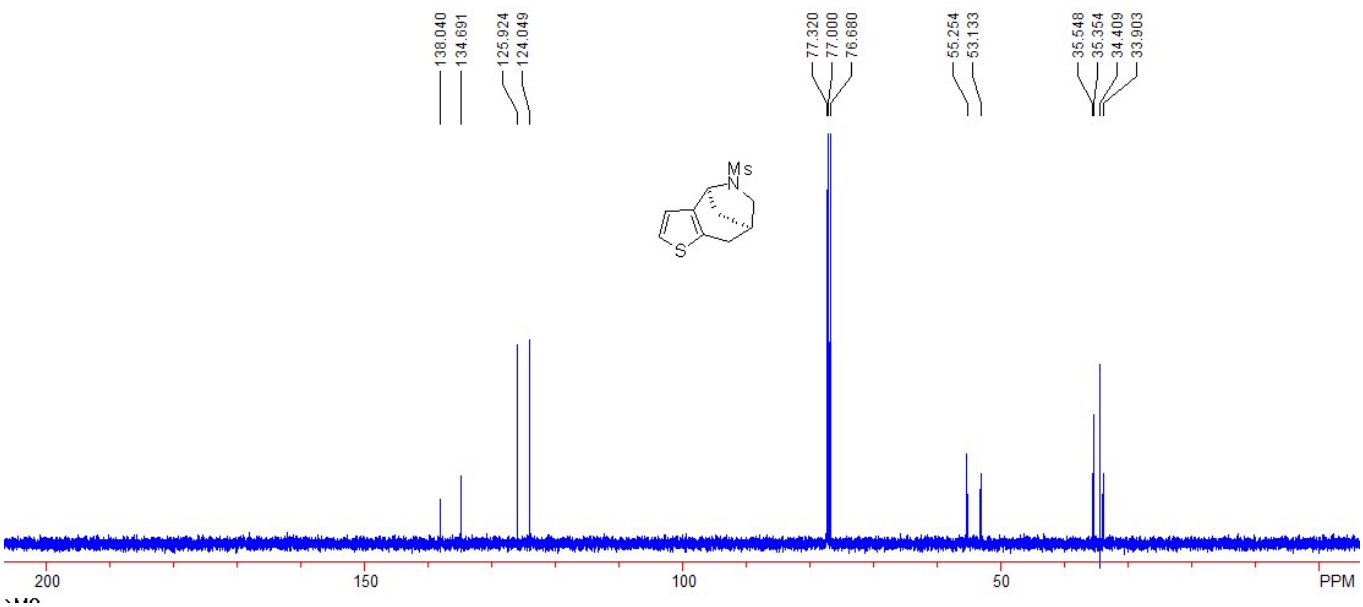


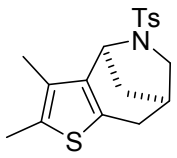


5-(methylsulfonyl)-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine 3c

A pale yellow liquid, 11% yield (5 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.98-2.01 (m, 1H, CH_2), 2.24-2.29 (m, 1H, CH_2), 2.30 (s, 3H, CH_3), 2.90 (d, J = 18.0 Hz, 1H, CH_2), 2.98-3.03 (m, 2H, CH_2), 3.20-3.26 (m, 1H, CH_2), 3.72-3.77 (m, 1H, CH_2), 4.83 (d, J = 4.8 Hz, 1H, CH_2), 6.94 (d, J = 4.8 Hz, 1H, ArH), 7.12 (d, J = 4.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.9, 34.4, 35.4, 35.5, 53.1, 55.3, 124.0, 125.9, 134.7, 138.0. IR (CH_2Cl_2) ν 2949, 1327, 1197, 1147, 1071, 961, 756, 669 cm^{-1}. MS (ESI) *m/z* (%): 244.04 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{10}H_{14}NO_2S_2^{+1}[M+H]^+$ requires 244.0460, found: 244.0464.

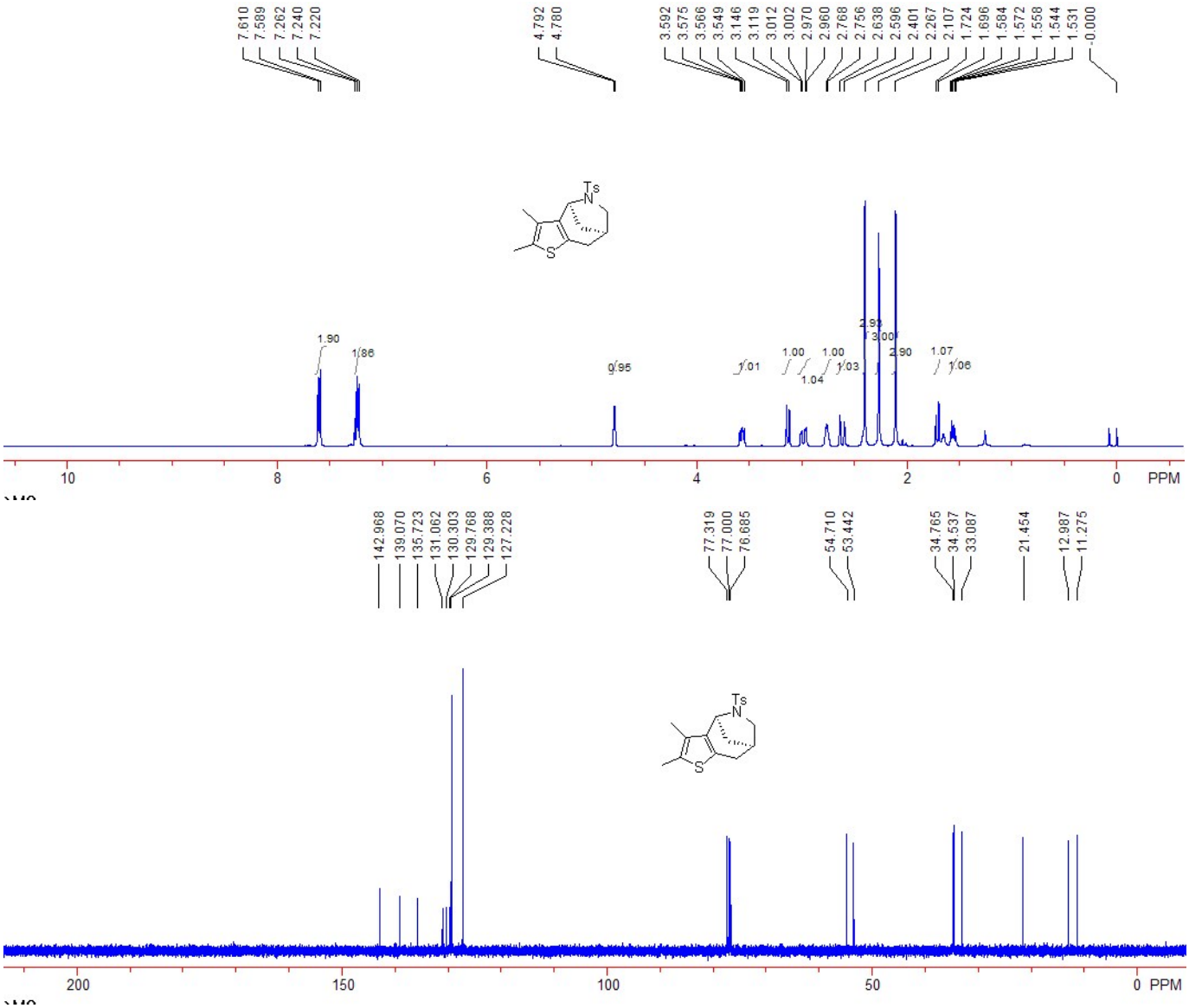


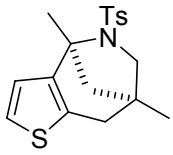




2,3-dimethyl-5-tosyl-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine 3f

A white solid, 69% yield (24 mg). M.p.: 140-142 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.53-1.59 (m, 1H, CH_2), 1.69-1.73 (m, 1H, CH_2), 2.11 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.61 (d, J = 16.8 Hz, 1H, CH_2), 2.74-2.77 (m, 1H, CH), 2.98 (dd, J = 16.8, 4.0 Hz, 1H, CH_2), 3.13 (d, J = 10.8 Hz, 1H, CH_2), 3.57 (dd, J = 10.4, 6.8 Hz, 1H, CH_2), 4.78 (d, J = 4.8 Hz, 1H, CH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.60 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.3, 13.0, 21.5, 33.1, 34.5, 34.8, 53.4, 54.7, 127.2, 129.4, 129.8, 130.3, 131.1, 135.7, 139.1, 143.0. IR (CH_2Cl_2) ν 3673, 2972, 2901, 1451, 1406, 1339, 1155, 1056, 895, 814, 708, 667 cm^{-1}. MS (ESI) *m/z* (%): 348.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 348.1086, found: 348.1089.

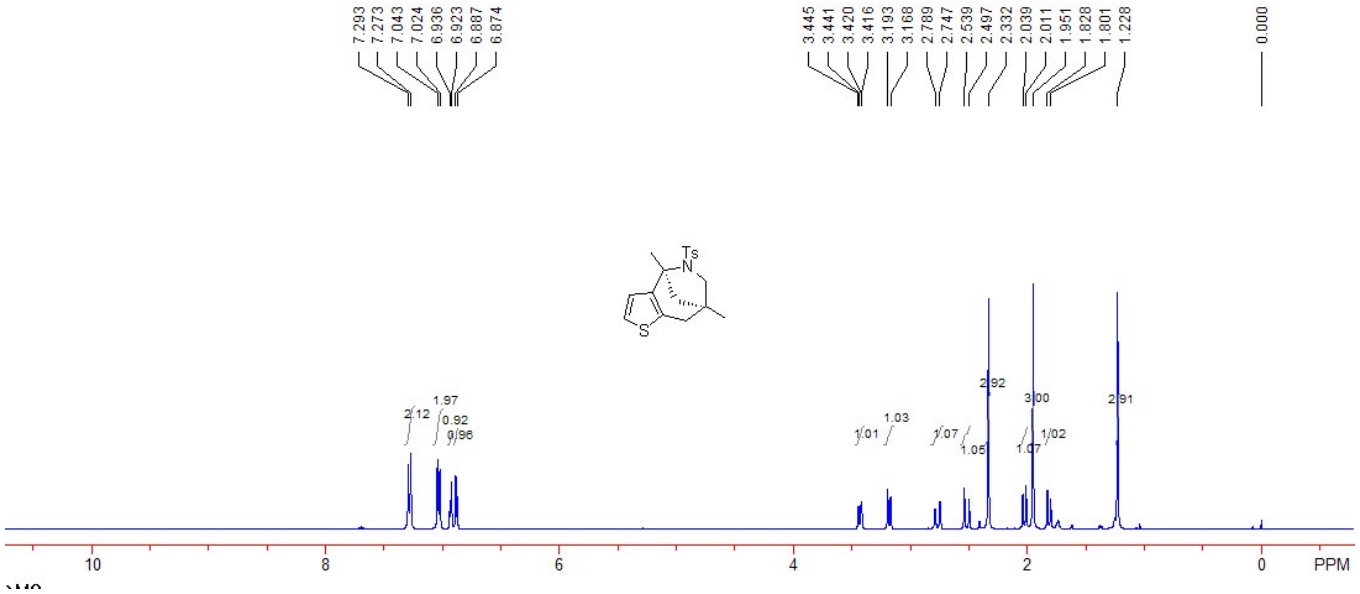


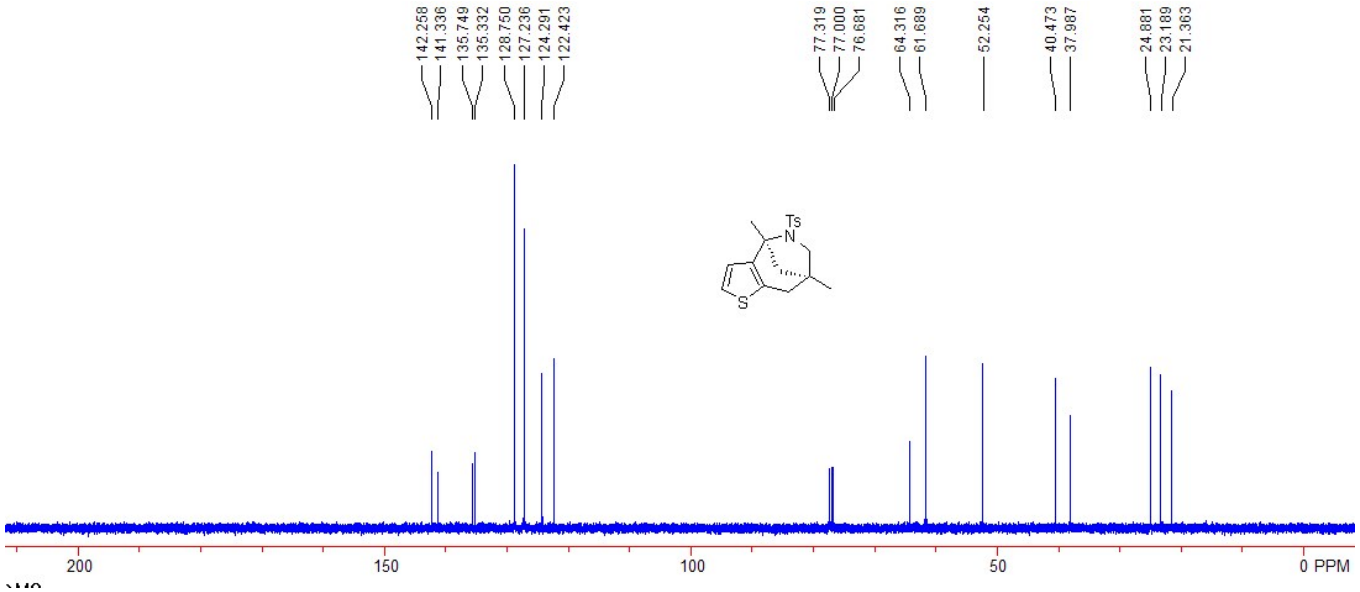


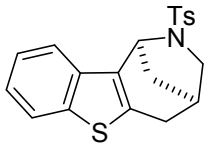
4,7-dimethyl-5-tosyl-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine 3m

A pale yellow solid, 81% yield (28 mg). M.p.: 125-127 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (s, 3H, CH_3), 1.81 (d, J = 10.8 Hz, 1H, CH_2), 1.95 (s, 3H, CH_3), 2.02 (d, J = 10.8 Hz, 1H, CH_2), 2.33 (s, 3H, CH_3), 2.52 (d, J = 16.8 Hz, 1H, CH_2), 2.76 (d, J = 16.8 Hz, 1H, CH_2), 3.17 (d, J = 10.0 Hz, 1H, CH_2), 3.43 (dd, J = 10.0, 1.6 Hz, 1H, CH_2), 6.88 (d, J = 5.2 Hz, 1H, ArH), 6.93 (d, J = 5.2 Hz, 1H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 7.28 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 23.2, 24.9, 38.0, 40.5, 52.3, 61.7, 64.3, 122.4, 124.3, 127.2, 128.8, 135.3, 135.7, 141.3, 142.3. IR (CH_2Cl_2) ν

2960, 2925, 2853, 1599, 1326, 1090, 805, 720, 672 cm^{-1}. MS (ESI) *m/z* (%): 348.10 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S_2^{+1}[M+H]^+$ requires 348.1086, found: 348.1088.



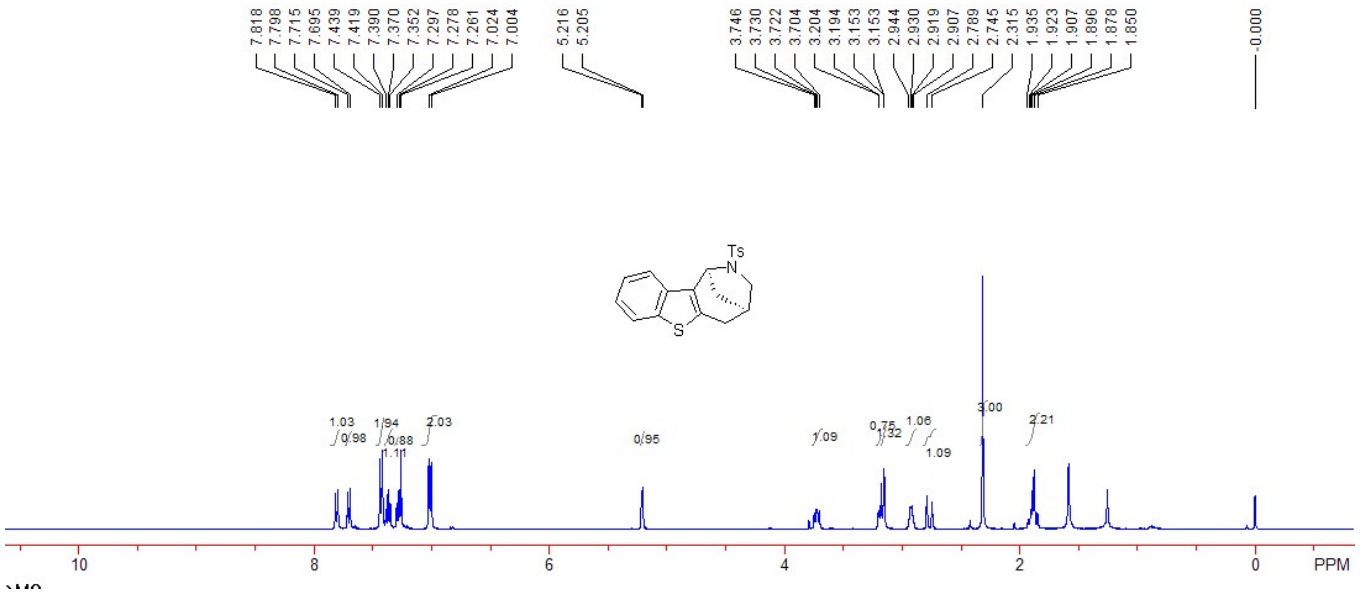


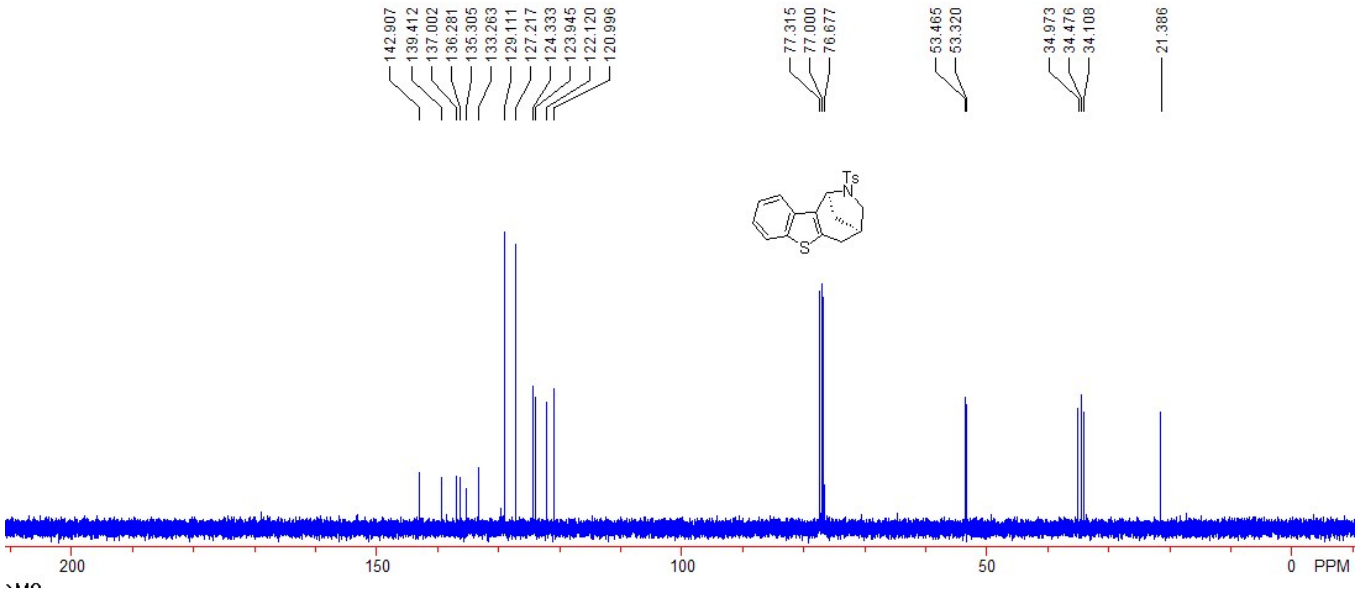


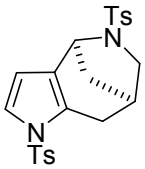
2-tosyl-2,3,4,5-tetrahydro-1*H*-1,4-methanobenzo[4,5]thieno[3,2-*c*]azepine 3q

A pale yellow solid, 78% yield (29 mg). M.p.: 126-128 ^oC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.85-1.94 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.76 (d, J = 17.6 Hz, 1H, CH_2), 2.91-2.94 (m, 1H, CH_2), 3.15-3.21 (m, 2H, CH_2), 3.72 (dd, J = 10.4, 6.8 Hz, 1H, CH_2), 5.21 (d, J = 4.4 Hz, 1H, CH_2), 7.01 (d, J = 8.0 Hz, 2H,

ArH), 7.28 (d, *J* = 8.0 Hz, 1H, ArH), 7.37 (dd, *J* = 8.0, 8.0 Hz, 1H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.70 (d, *J* = 8.0 Hz, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 34.1, 34.5, 35.0, 53.3, 53.5, 121.0, 122.1, 123.9, 124.3, 127.2, 129.1, 133.3, 135.3, 136.3, 137.0, 139.4, 142.9. IR (CH_2Cl_2) ν 2923, 1594, 1466, 1340, 1156, 1093, 948, 814, 731, 667 cm^{-1}. MS (ESI) *m/z* (%): 370.09 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{20}H_{20}NO_2S_2^{+1}[M+H]^+$ requires 370.0930, found: 370.0933.

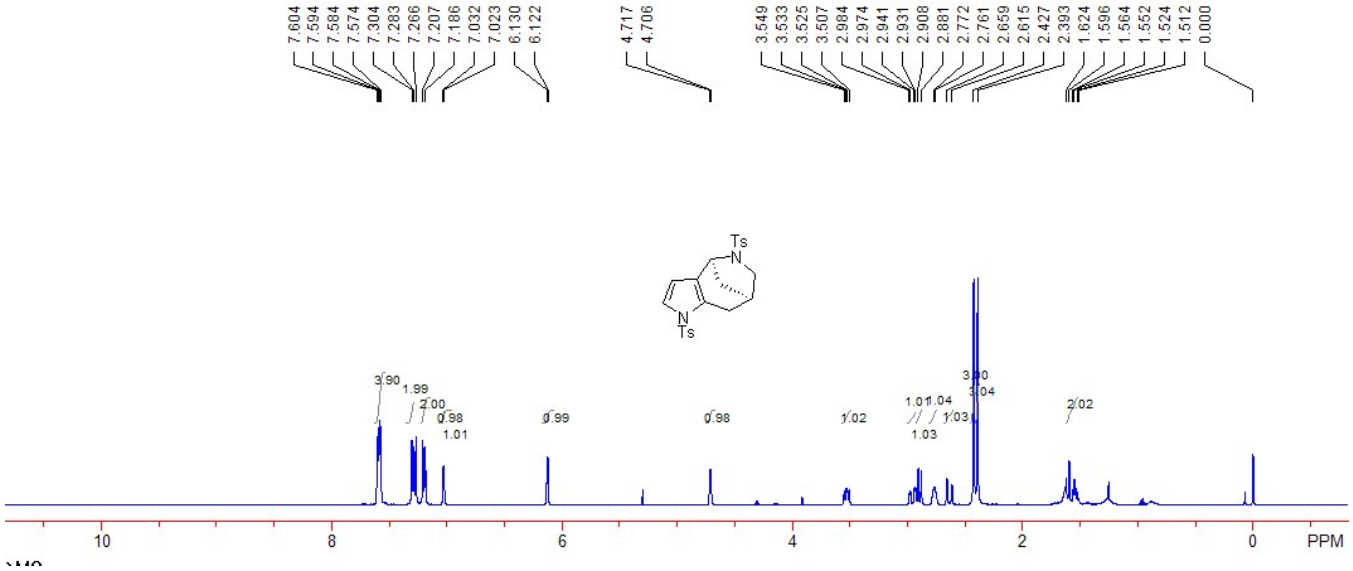


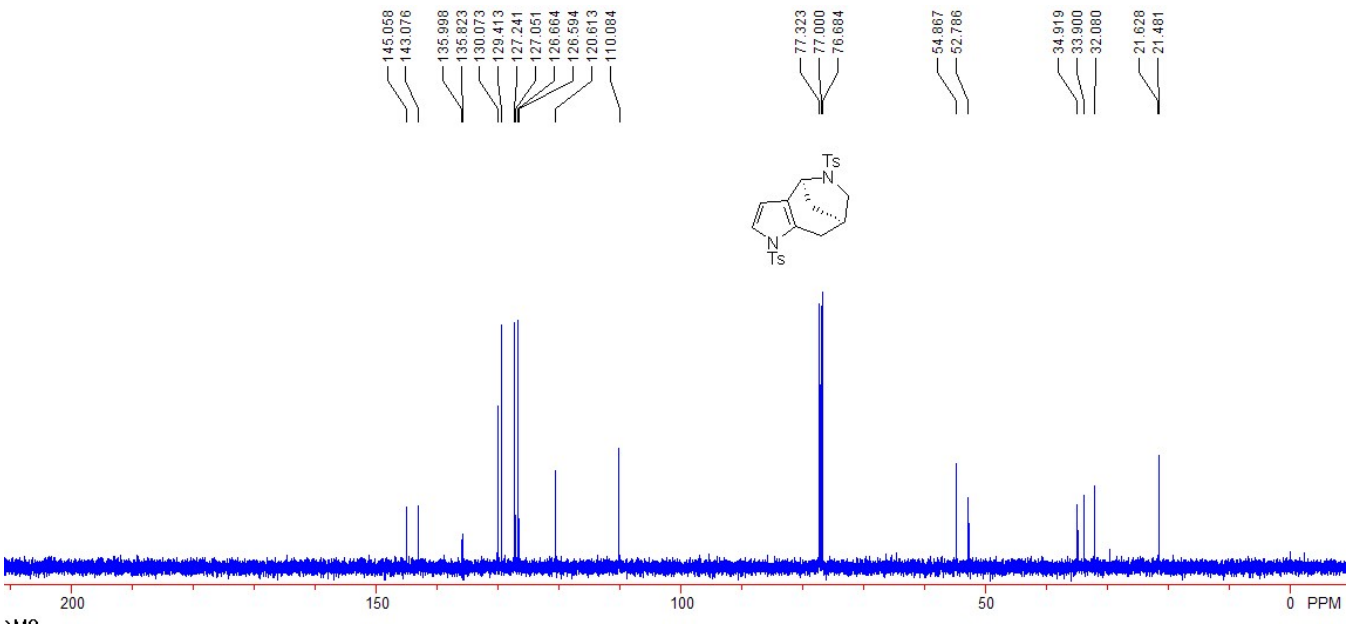


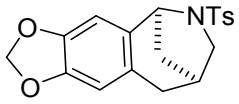


1,5-ditosyl-1,4,5,6,7,8-hexahydro-4,7-methanopyrrolo[3,2-*c*]azepine 3r

A white solid, 86% yield (40 mg). M.p.: 56-58 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.51-1.63 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.63 (d, J = 17.6 Hz, 1H, CH_2), 2.74-2.79 (m, 1H, CH_2), 2.89 (d, J = 10.8 Hz, 1H, CH_2), 2.96 (dd, J = 13.2, 4.0 Hz, 1H, CH_2), 3.53 (dd, J = 10.4, 7.2 Hz, 1H, CH_2), 4.71 (d, J = 4.4 Hz, 1H, CH_2), 6.13 (d, J = 3.2 Hz, 1H, ArH), 7.03 (d, J = 3.2 Hz, 1H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.29 (d, J = 8.0 Hz, 2H, ArH), 7.57-7.61 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.6, 32.1, 33.9, 34.9, 52.8, 54.9, 110.1, 120.6, 126.6, 126.7, 127.0, 127.2, 129.4, 130.1, 135.8, 136.0, 143.1, 145.0. IR (CH_2Cl_2) ν 2954, 2925, 2857, 1597, 1489, 1353, 1163, 1091, 813, 735, 667 cm^{-1}. MS (ESI) *m/z* (%): 457.12 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{23}H_{25}N_2O_4S_2^{+1}[M+H]^+$ requires 457.1250, found: 457.1254.

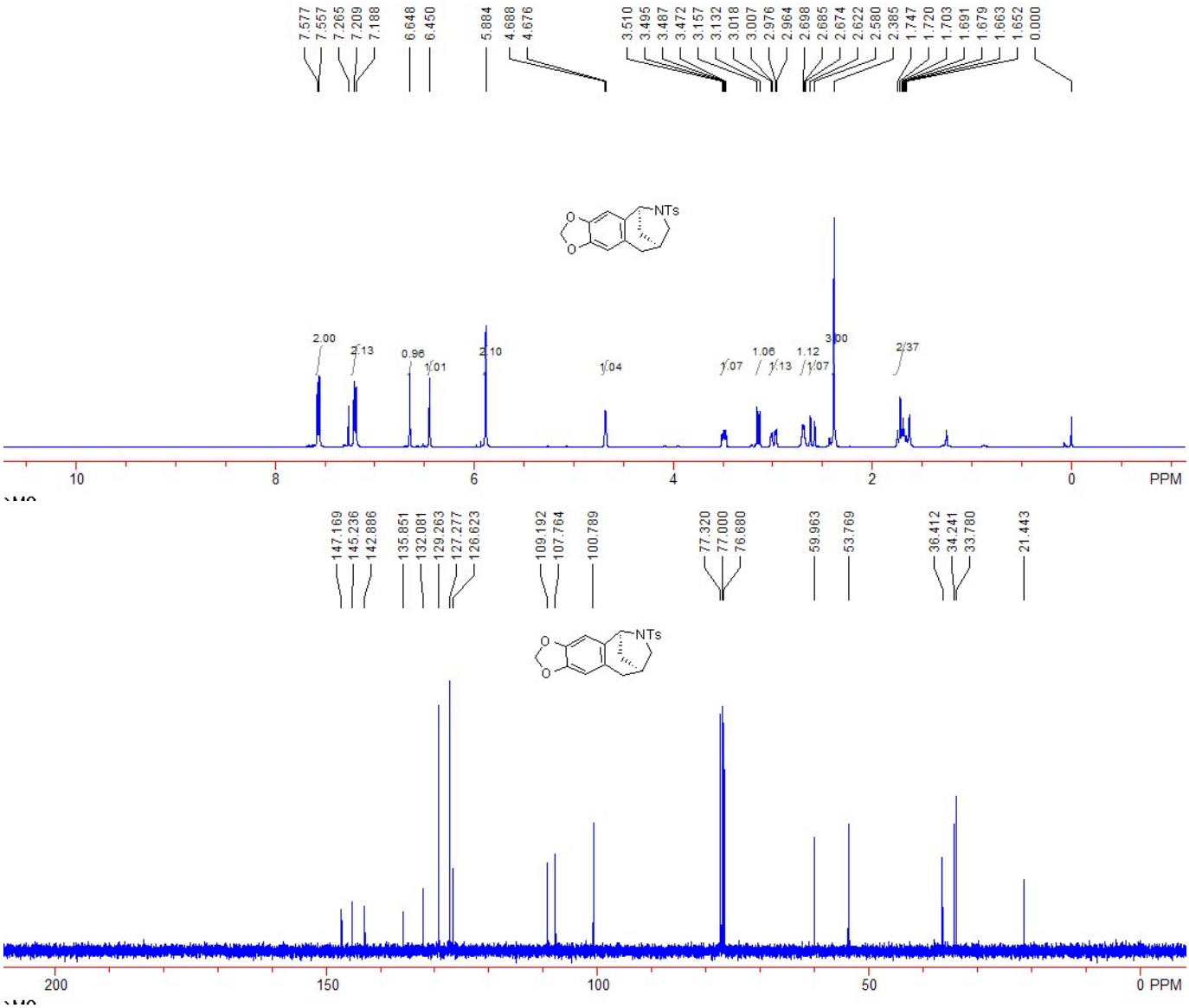


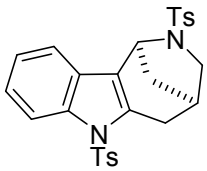




6-tosyl-6,7,8,9-tetrahydro-5*H*-5,8-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]azepine 3u

A pale yellow solid, 67% yield (24 mg). M.p.: 194-196 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.65-1.75 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.60 (d, J = 16.8 Hz, 1H, CH_2), 2.68-2.72 (m, 1H, CH_2), 2.98 (dd, J = 17.2, 4.8 Hz, 1H, CH_2), 3.14 (d, J = 10.0 Hz, 1H, CH_2), 3.49 (dd, J = 9.2, 6.0 Hz, 1H, CH_2), 4.68 (d, J = 4.8 Hz, 1H, CH_2), 5.89 (s, 2H, CH_2), 6.45 (s, 1H, ArH), 6.65 (s, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.56 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.8, 34.2, 36.4, 53.8, 60.0, 100.8, 107.8, 109.2, 126.6, 127.3, 129.3, 132.1, 135.8, 142.9, 145.2, 147.2. IR (CH_2Cl_2) ν 3674, 2971, 2922, 1487, 1306, 1157, 1088, 935, 817, 709, 670 cm^{-1}. MS (ESI) *m/z* (%): 358.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{19}H_{20}NO_4S^{+1}[M+H]^+$ requires 358.1108, found: 358.1110.

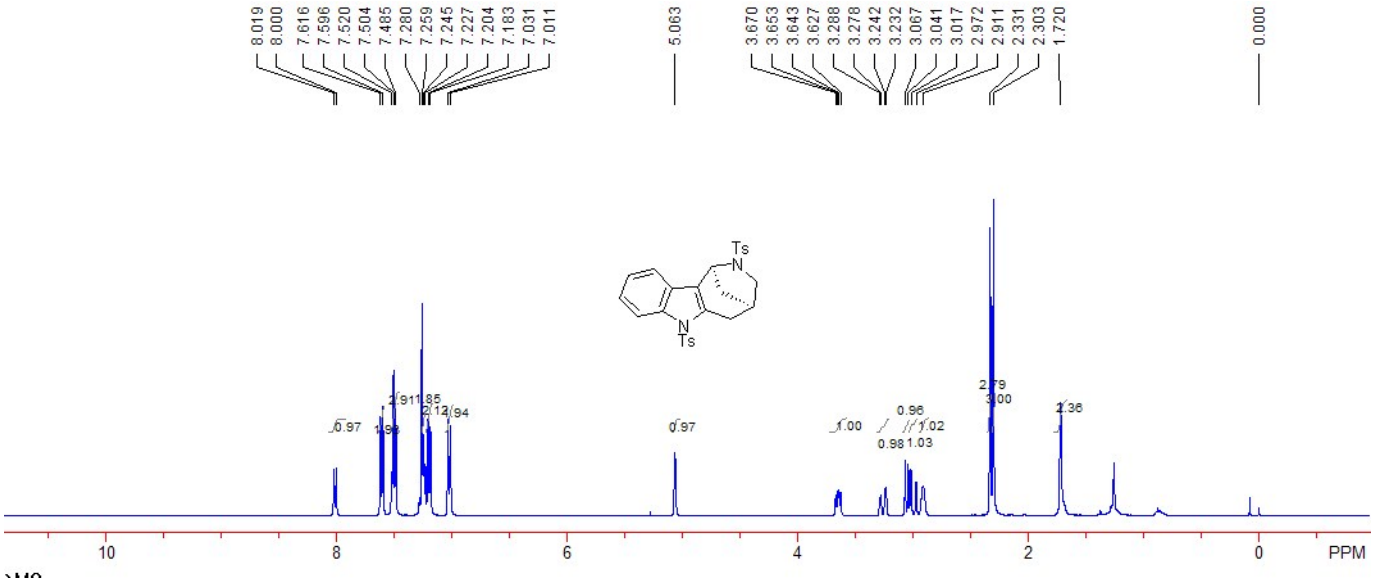


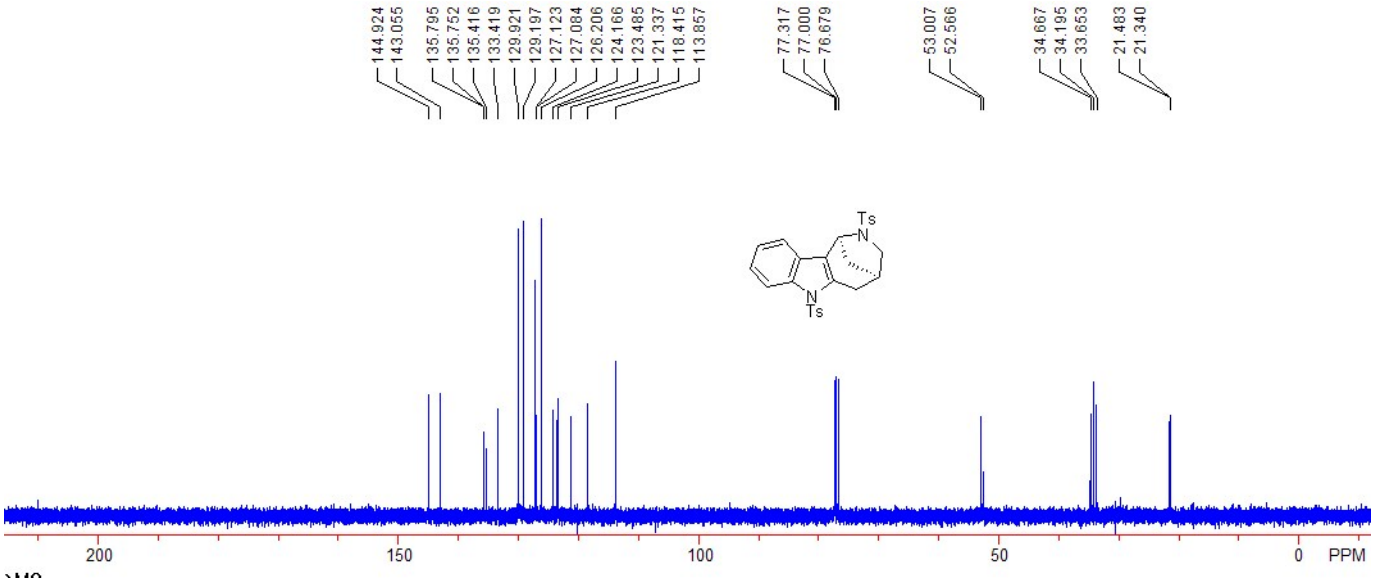


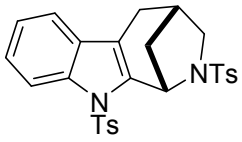
2,6-ditosyl-1,2,3,4,5,6-hexahydro-1,4-methanoazepino[4,3-*b*]indole 3w

A white solid, 0.2 mmol, 36% yield (36 mg), recovered of **1w** (55 mg, 55%). M.p.: 100-102 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.71-1.73 (m, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.89-2.92 (m, 1H, CH_2), 2.99 (d, J = 18.4 Hz, 1H, CH_2), 3.05 (d, J = 10.8 Hz, 1H, CH_2), 3.26 (dd, J = 17.2, 3.6 Hz, 1H, CH_2), 3.66 (dd, J = 10.4, 6.8 Hz, 1H, CH_2), 5.06 (d, J = 3.2 Hz, 1H, CH_2), 7.02 (d, J = 8.0 Hz, 2H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.22-7.26 (m, 2H, ArH), 7.48-7.53 (m, 3H, ArH), 7.60 (d, J = 8.0 Hz, 2H, ArH), 8.01 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 21.5, 33.7, 34.2, 34.7,

52.6, 53.0, 113.9, 118.5, 121.4, 123.6, 124.2, 126.3, 127.1, 127.2, 129.2, 130.0, 133.4, 135.5, 135.8, 135.9, 143.1, 145.0. IR (CH_2Cl_2) ν 2961, 2921, 2852, 2323, 1596, 1450, 1337, 1153, 1087, 979, 813, 743, 661 cm^{-1}. MS (ESI) *m/z* (%): 524.16 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{30}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 524.1672, found: 524.1673.



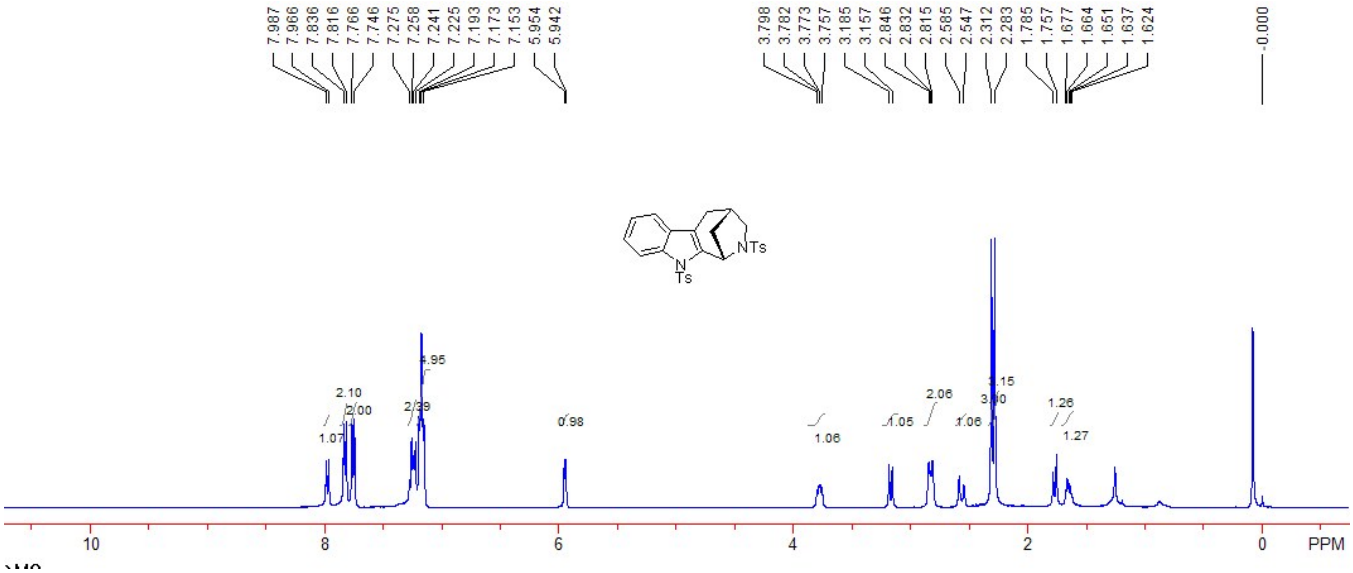


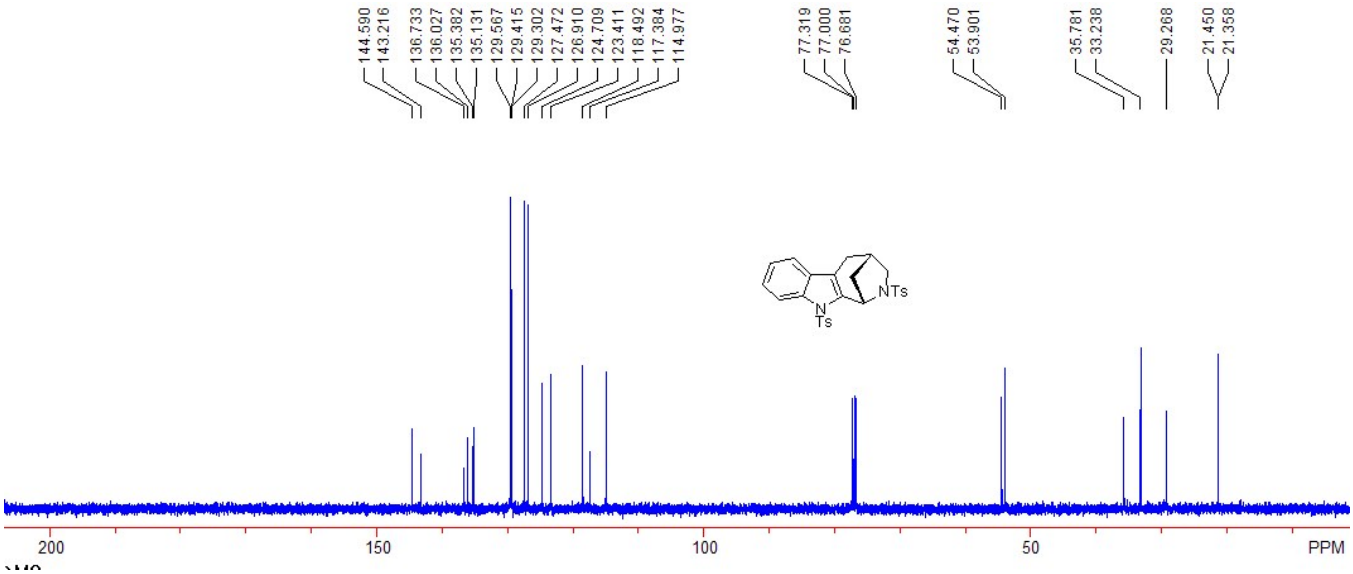


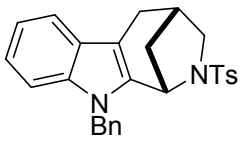
2,10-ditosyl-1,2,3,4,5,10-hexahydro-1,4-methanoazepino[3,4-*b*]indole 5s

A white solid, 40% yield for two steps (21 mg). M.p.: 160-162 °C. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.62-1.68 (m, 1H, CH_2), 1.75-1.79 (m, 1H, CH_2), 2.28 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.57 (d, *J* = 15.2

Hz, 1H, CH_2), 2.81-2.85 (m, 2H, CH), 3.17 (d, *J* = 11.2 Hz, 1H, CH_2), 3.78 (dd, *J* = 10.4, 6.4 Hz, 1H, CH_2), 5.95 (d, *J* = 4.8 Hz, 1H, CH), 7.15-7.20 (m, 5H, ArH), 7.22-7.28 (m, 2H, ArH), 7.75 (d, *J* = 8.0 Hz, 2H, ArH), 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.97 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.5, 29.3, 33.2, 35.8, 53.9, 54.5, 115.0, 117.4, 118.5, 123.4, 124.7, 126.9, 127.5, 129.3, 129.4, 129.6, 135.1, 135.4, 136.0, 136.7, 143.2, 144.6. IR (CH_2Cl_2) ν 2923, 2158, 1661, 1557, 1409, 1343, 1260, 1019, 927, 658 cm^{-1}. MS (ESI) *m/z* (%): 524.17 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{30}N_3O_4S_2^{+1}[M+NH_4]^+$ requires 524.1672, found: 524.1674.

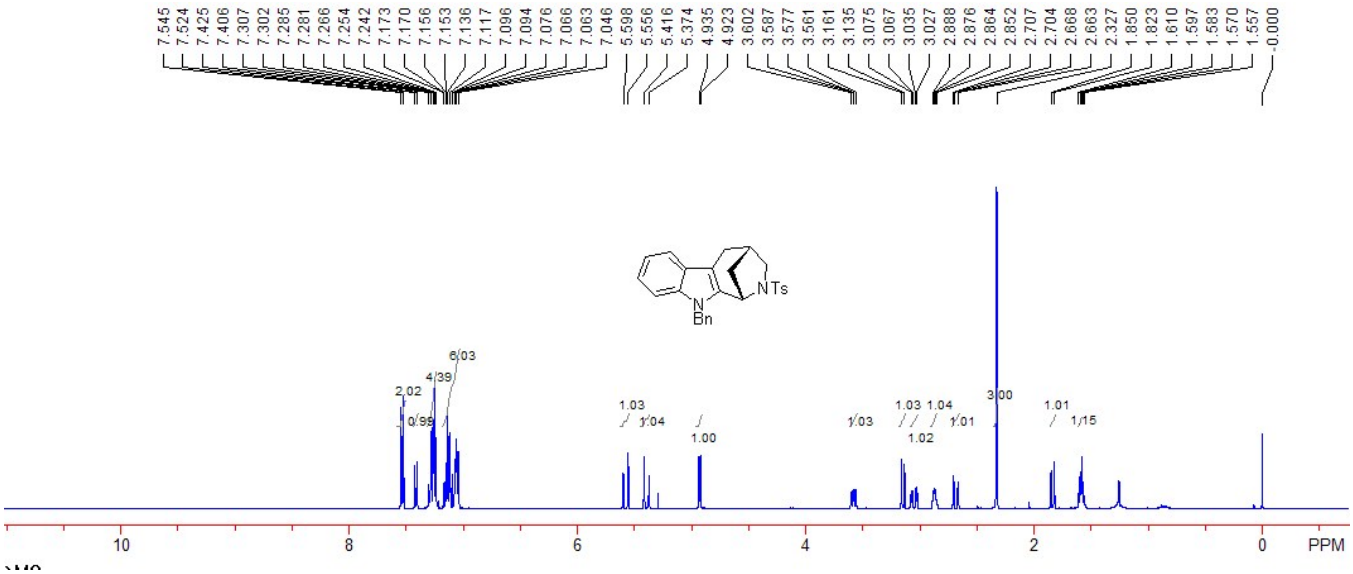


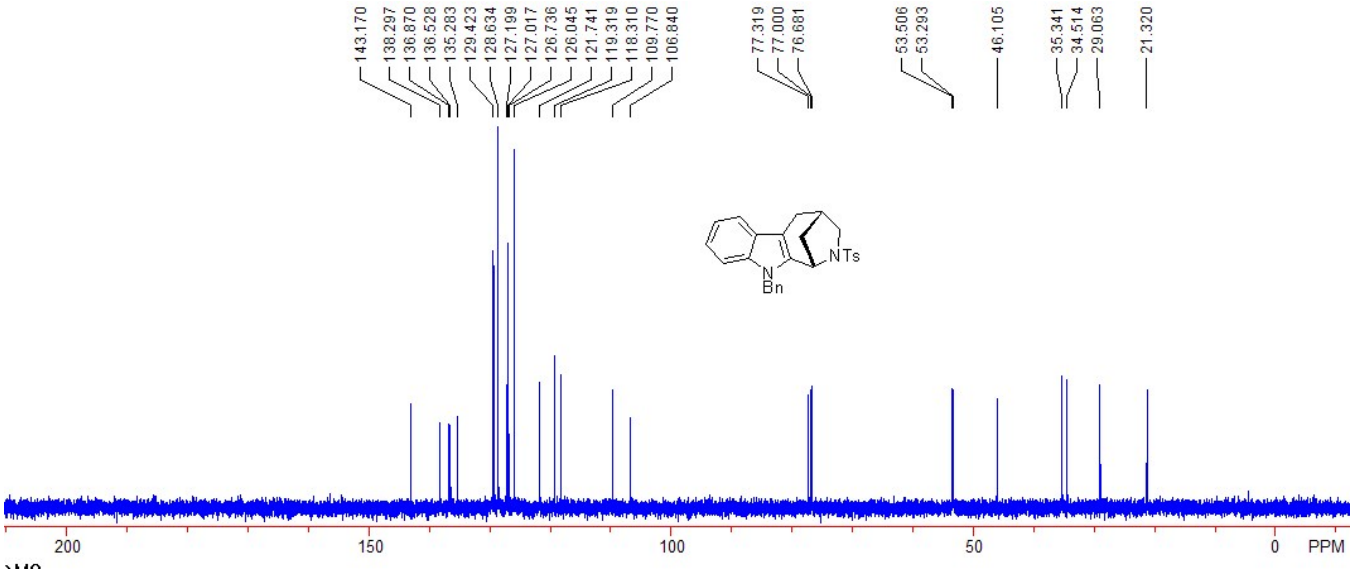


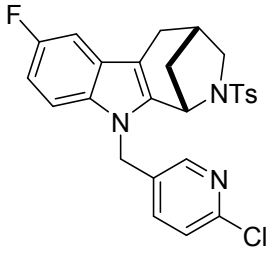


10-benzyl-2-tosyl-1,2,3,4,5,10-hexahydro-1,4-methanoazepino[3,4-*b*]indole 5x

A white solid, 0.20 mmol, 46% yield for two steps (42 mg). M.p.: 153-155 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.51-1.57 (m, 1H, CH_2), 1.79-1.83 (m, 1H, CH_2), 2.30 (s, 3H, CH_3), 2.66 (d, *J* = 16.0 Hz, 1H, CH_2), 2.83-2.85 (m, 1H, CH), 3.03 (dd, *J* = 16.0, 4.0 Hz, 1H, CH_2), 3.14 (d, *J* = 10.4 Hz, 1H, CH_2), 3.56 (dd, *J* = 10.4, 6.8 Hz, 1H, CH_2), 4.92 (d, *J* = 4.8 Hz, 1H, CH), 5.38 (d, *J* = 17.2 Hz, 1H, CH_2), 5.57 (d, *J* = 17.2 Hz, 1H, CH_2), 7.03-7.16 (m, 6H, ArH), 7.20-7.29 (m, 4H, ArH), 7.41 (d, *J* = 7.6 Hz, 1H, ArH), 7.53 (d, *J* = 7.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 29.1, 34.5, 35.3, 46.1, 53.3, 53.5, 106.8, 109.8, 118.3, 119.3, 121.7, 126.0, 126.7, 127.0, 127.2, 128.6, 129.4, 135.3, 136.5, 136.9, 138.3, 143.2. IR (CH_2Cl_2) ν 3062, 3034, 2923, 2848, 1597, 1495, 1455, 1342, 1315, 1304, 1199, 1153, 1125, 1087, 816, 780, 724, 698, 666 cm^{-1}. MS (ESI) *m/z* (%): 443.17 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{27}N_2O_2S^{+1}[M+H]^+$ requires 443.1788, found: 443.1787.

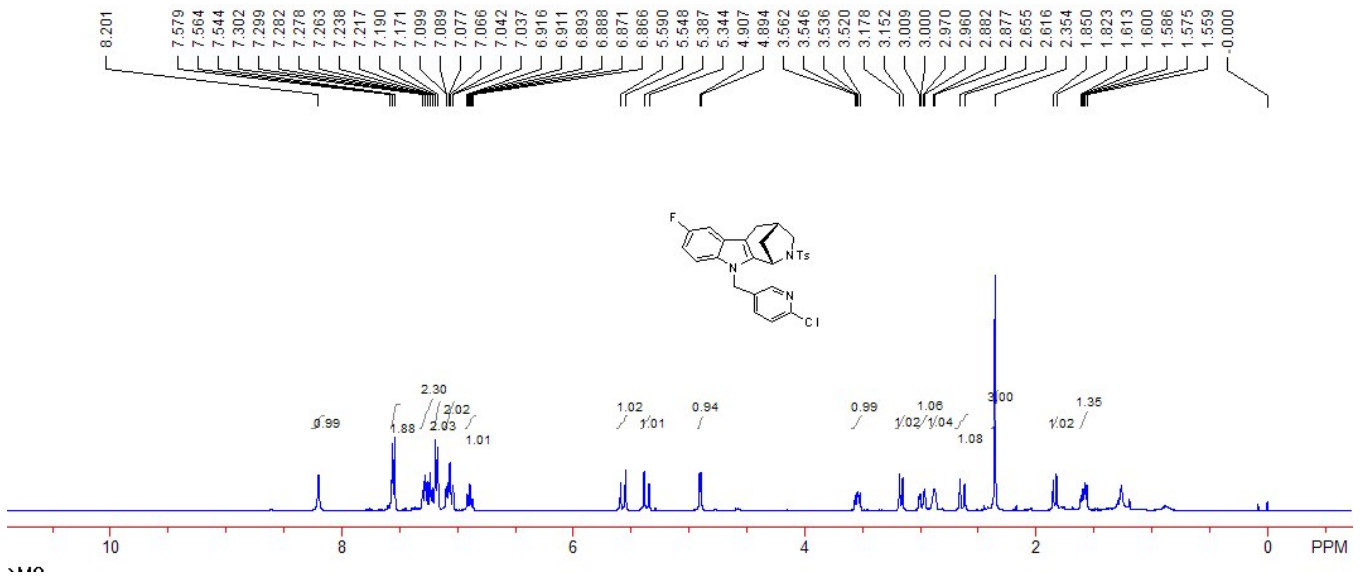


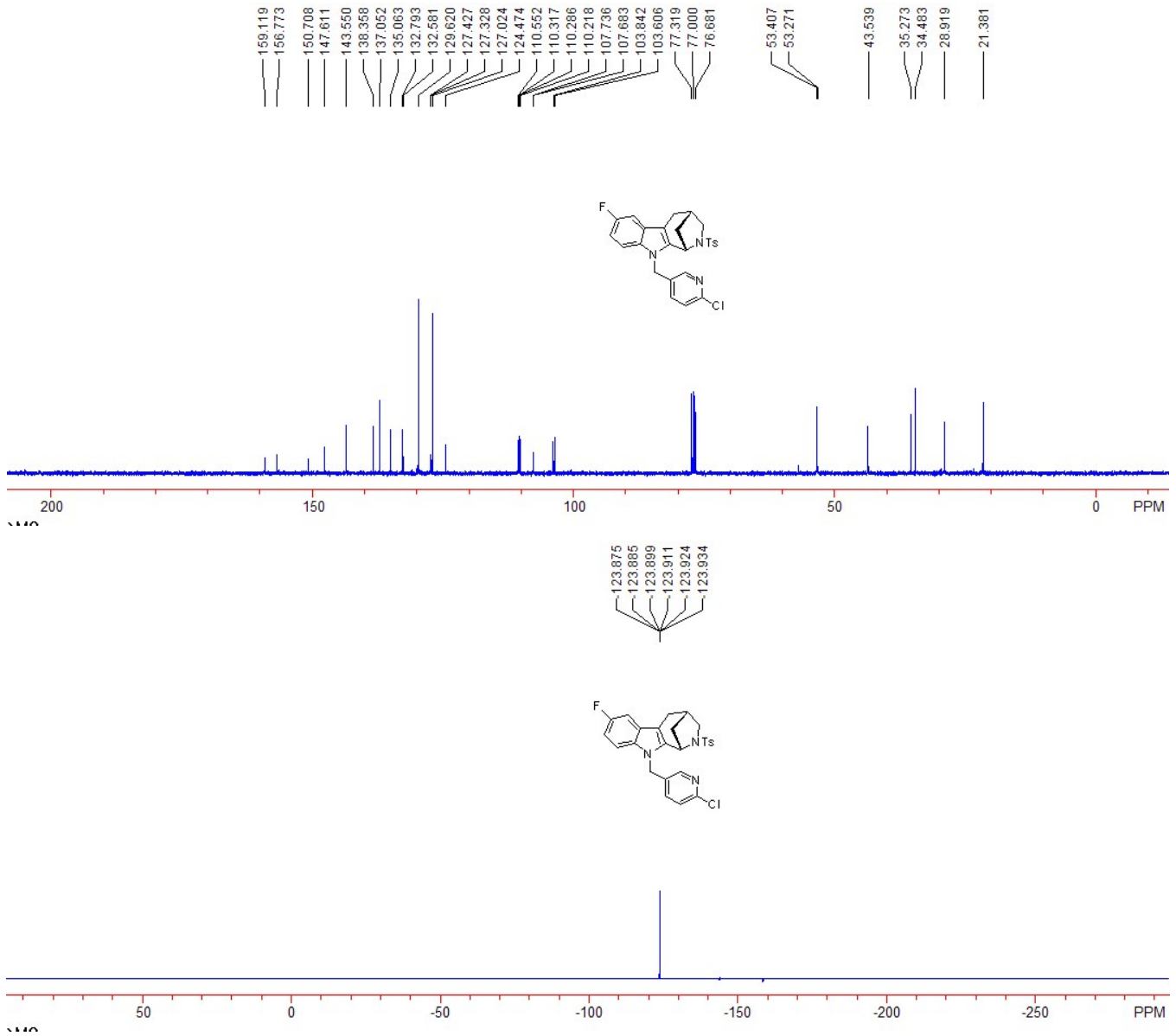




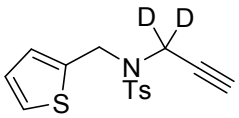
10-((6-chloropyridin-3-yl)methyl)-7-fluoro-2-tosyl-1,2,3,4,5,10-hexahydro-1,4-methanoazepino[3,4-*b*]indole 5y

A white solid, 0.20 mmol, 64% yield for two steps (64 mg). M.p.: 145-147 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.55-1.62 (m, 1H, CH_2), 1.82-1.85 (m, 1H, CH_2), 2.35 (s, 3H, CH_3), 2.63 (d, J = 16.0 Hz, 1H, CH_2), 2.85-2.89 (m, 1H, CH), 3.98 (dd, J = 16.0, 3.6 Hz, 1H, CH_2), 3.16 (d, J = 10.4 Hz, 1H, CH_2), 3.54 (dd, J = 10.4, 6.4 Hz, 1H, CH_2), 4.90 (d, J = 5.2 Hz, 1H, CH), 5.36 (d, J = 17.2 Hz, 1H, CH_2), 5.57 (d, J = 17.2 Hz, 1H, CH_2), 6.86-6.92 (m, 1H, ArH), 7.03-7.10 (m, 2H, ArH), 7.18 (d, J = 7.6 Hz, 2H, ArH), 7.22 (d, J = 8.0 Hz, 1H, ArH), 7.29 (d, J = 6.8 Hz, 1H, ArH), 7.55 (d, J = 8.0Hz, 2H, ArH), 8.20 (s, 1H, ArH). δ 21.4, 28.9, 34.5, 35.3, 43.5, 53.3, 53.4, 103.7 (d, J = 23.3 Hz), 107.7 (d, J = 4.7Hz), 110.2 (d, J = 6.9Hz), 110.4 (d, J = 23.3Hz), 124.5, 127.0, 127.4 (d, J = 9.7Hz), 129.6, 132.6, 132.8, 135.1, 137.0, 138.4, 143.5, 147.6, 150.7, 157.9 (d, J = 234.7Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -123.9. IR (CH_2Cl_2) ν 2972, 2886, 1625, 1587, 1483, 1459, 1338, 1301, 1195, 1155, 1090, 1046, 986, 880, 811, 664 cm^{-1}. MS (ESI) *m/z* (%): 496.12 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{26}H_{24}ClFN_3O_2S^{+1}[M+H]^+$ requires 496.1256, found: 496.1257.



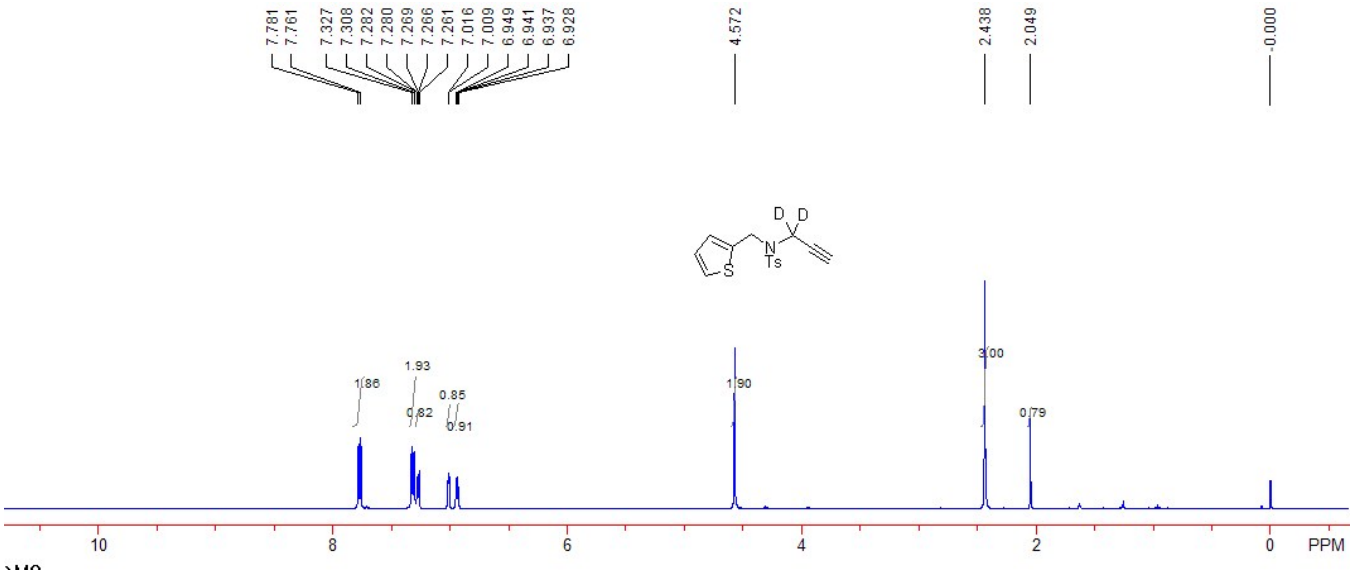


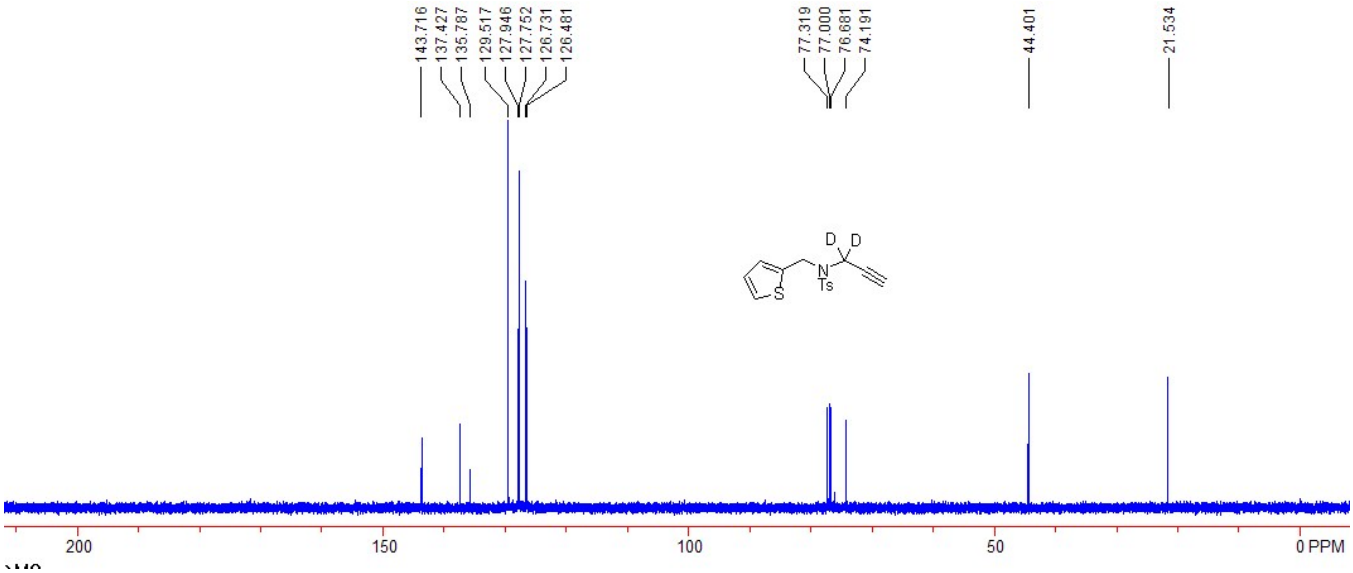
15. Characterization and spectra charts for compounds S1a-d_2, 1a-d_2, 2a-d_2, 1aa-d_2, 2aa-d_2

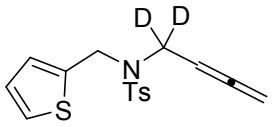


4-methyl-*N*-(prop-2-yn-1-yl-1,1-d_2)-*N*-(thiophen-2-ylmethyl)benzenesulfonamide S1a-d_2

A white solid, 63% yield (201 mg). M.p.: 78-80 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.05 (s, 1H, CH), 2.44 (s, 3H, CH_3), 4.57 (s, 2H, CH_2), 6.94 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 7.01 (d, J = 2.8 Hz, 1H, ArH), 7.27 (dd, J = 5.6, 1.2 Hz, 1H, ArH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.77 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 44.4, 74.2, 126.5, 126.7, 127.8, 127.9, 129.5, 135.8, 137.4, 143.7.



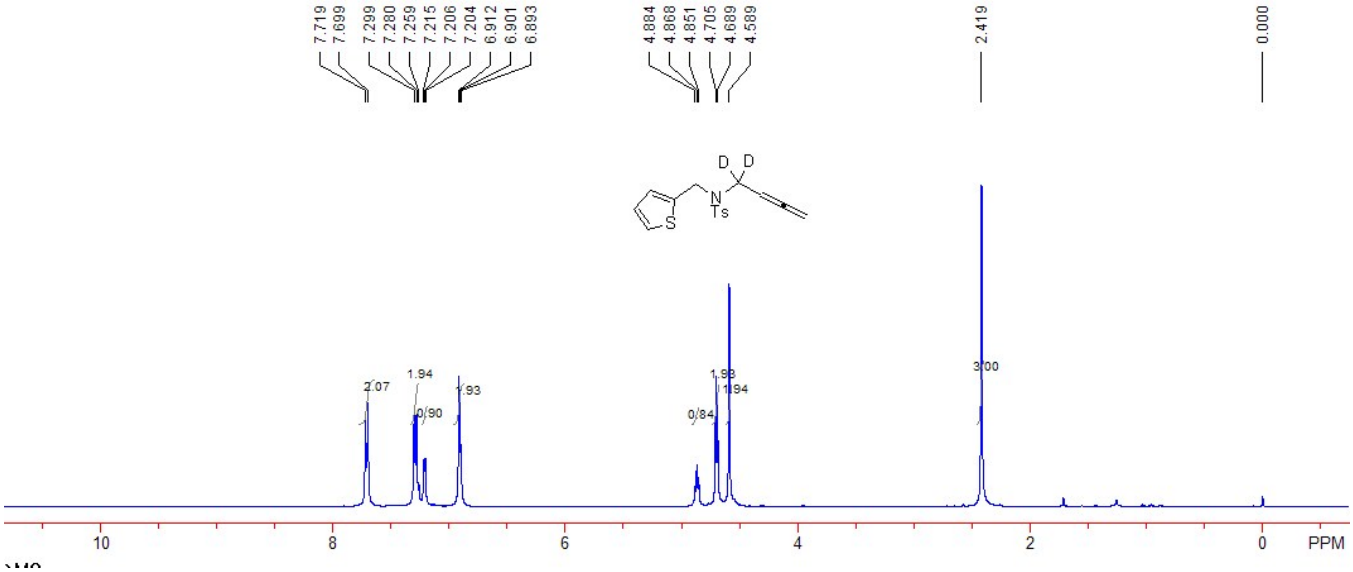


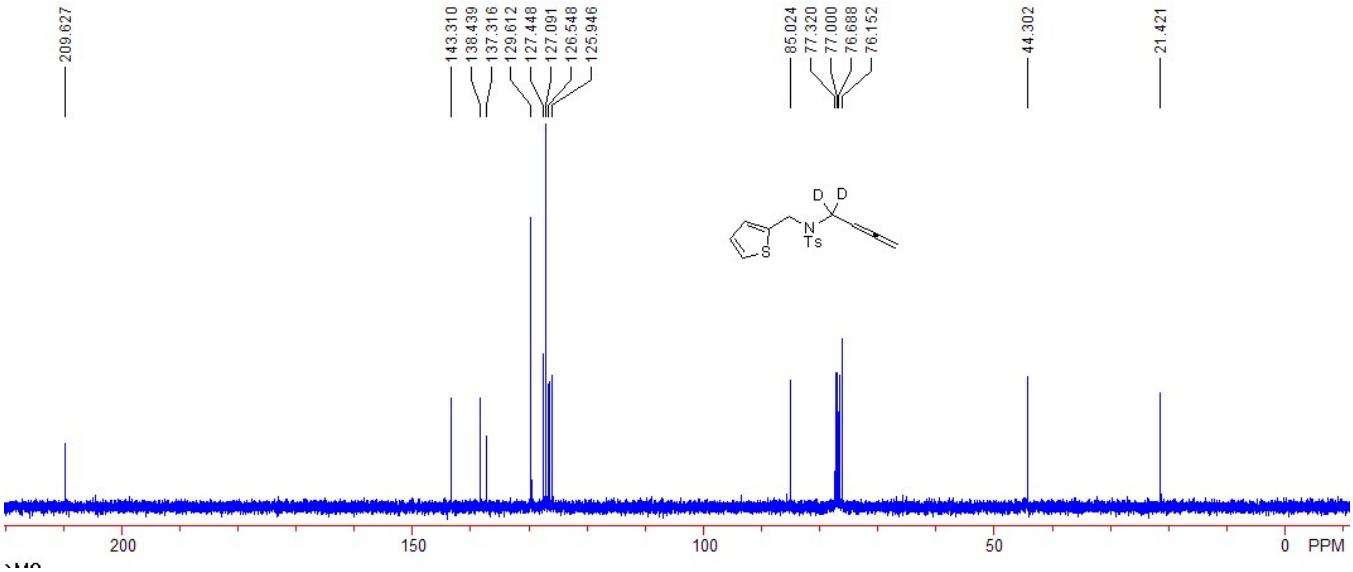


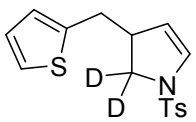
***N*-(buta-2,3-dien-1-yl-1,1-d_2)-4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide 1a-d_2**

A white liquid, 78% yield (81 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 4.59 (s, 2H, CH_2), 4.69 (d, J = 6.4 Hz, 2H, =CH_2), 4.87 (t, J = 6.4 Hz, 1H, =CH), 6.89-6.92 (m, 2H, ArH), 7.21 (d, J = 3.6 Hz, 1H, ArH), 7.29 (d, J = 8.0 Hz, 2H, ArH), 7.71 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 44.3, 76.2, 85.0, 126.0, 126.5, 127.1, 127.4, 129.6, 137.3, 138.4, 143.3, 209.6. IR (CH_2Cl_2) ν 3109, 2960, 2922, 2856, 1957, 1724, 1598, 1439, 1159, 1095, 919, 853, 725, 655 cm^{-1}. MS (ESI) *m/z* (%): 322.08 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{16}D_2NO_2S_2^{+1}[M+H]^+$ requires

322.0899, found: 322.0899.



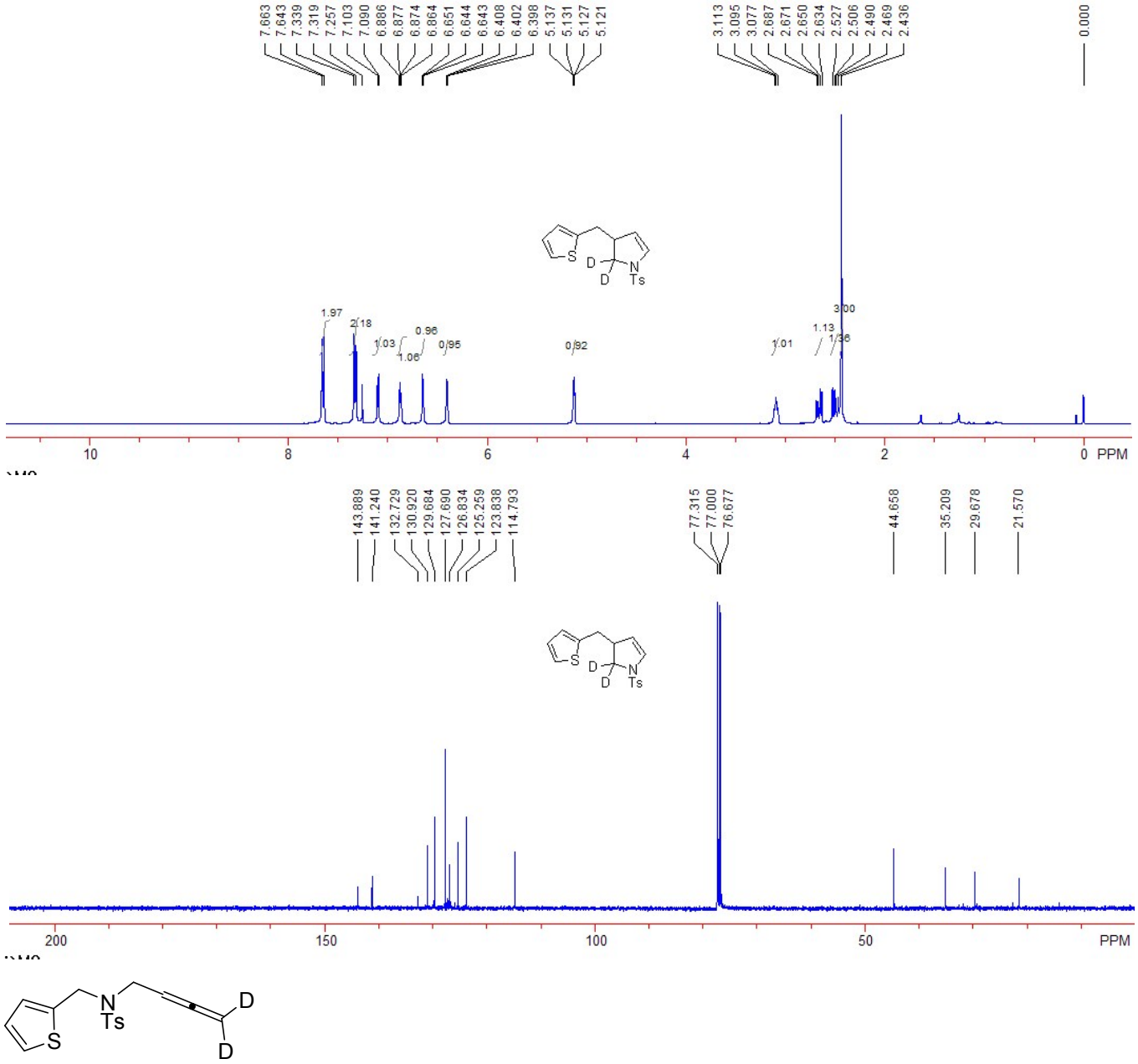




3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole-2,2-*d*$_2$ 2a-d$_2$

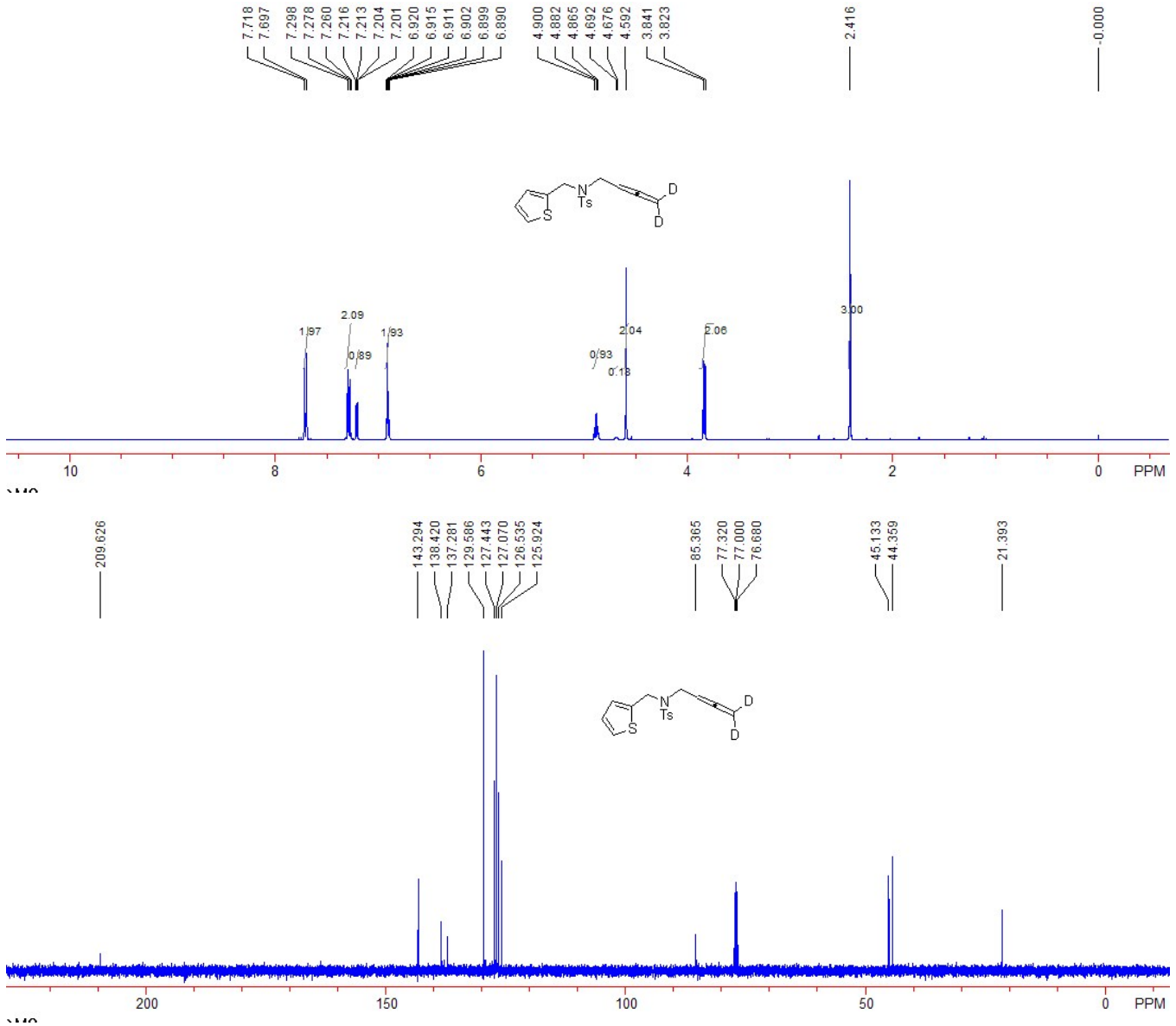
A white solid, 89% yield (57 mg). M.p.: 81-83 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 2.50 (dd, *J* = 15.2, 8.0 Hz, 1H, CH_2), 2.66 (dd, *J* = 14.4, 6.4 Hz, 1H, CH_2), 3.07-3.12 (m, 1H, CH), 5.13 (dd, *J* = 4.0, 2.4 Hz, 1H, =CH), 6.41 (dd, *J* = 4.0, 1.6 Hz, 1H, =CH), 6.65 (d, *J* = 3.2 Hz, 1H, ArH), 6.87 (dd, *J* = 5.2, 3.2 Hz, 1H, ArH), 7.10 (d, *J* = 4.8 Hz, 1H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 30.0, 35.2, 44.7, 114.8, 123.8, 125.3, 126.8, 127.7, 129.7, 130.9, 132.7, 141.2, 143.9. MS (ESI) *m/z* (%): 322.09 (100) $[M+H]^+$; HRMS (ESI) Calcd.

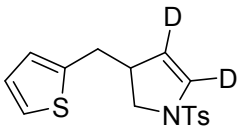
For $C_{16}H_{16}D_2NO_2S_2^{+1}[M+H]^+$ requires 322.0899, found: 322.0900.



_N_-(buta-2,3-dien-1-yl-4,4-d_2)-4-methyl-_N_-(thiophen-2-ylmethyl)benzenesulfonamide 1aa-d_2

A white liquid, 95% yield (289 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 3.83 (d, J = 7.2 Hz, 2H, CH_2), 4.60 (s, 2H, CH_2), 4.70 (s, 0.20 H, =CH_2), 4.89 (t, J = 7.2 Hz, 1H, =CH), 6.89-6.92 (m, 2H, ArH), 7.22 (dd, J = 4.4, 1.6 Hz, 1H, ArH), 7.29 (d, J = 8.0 Hz, 2H, ArH), 7.71 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 44.4, 45.1, 85.4, 126.0, 126.6, 127.1, 127.5, 129.6, 137.3, 138.5, 143.3, 209.7. IR (CH_2Cl_2) ν 3088, 2921, 2856, 2215, 1940, 1596, 1330, 1152, 1091, 918, 858, 701, 657 cm^{-1}. MS (ESI) m/z (%): 322.09 (100) [M+H]+; HRMS (ESI) Calcd. For $C_{16}H_{16}D_2NO_2S_2^{+1}(M+H)^+$ requires 322.0899, found: 322.0901.

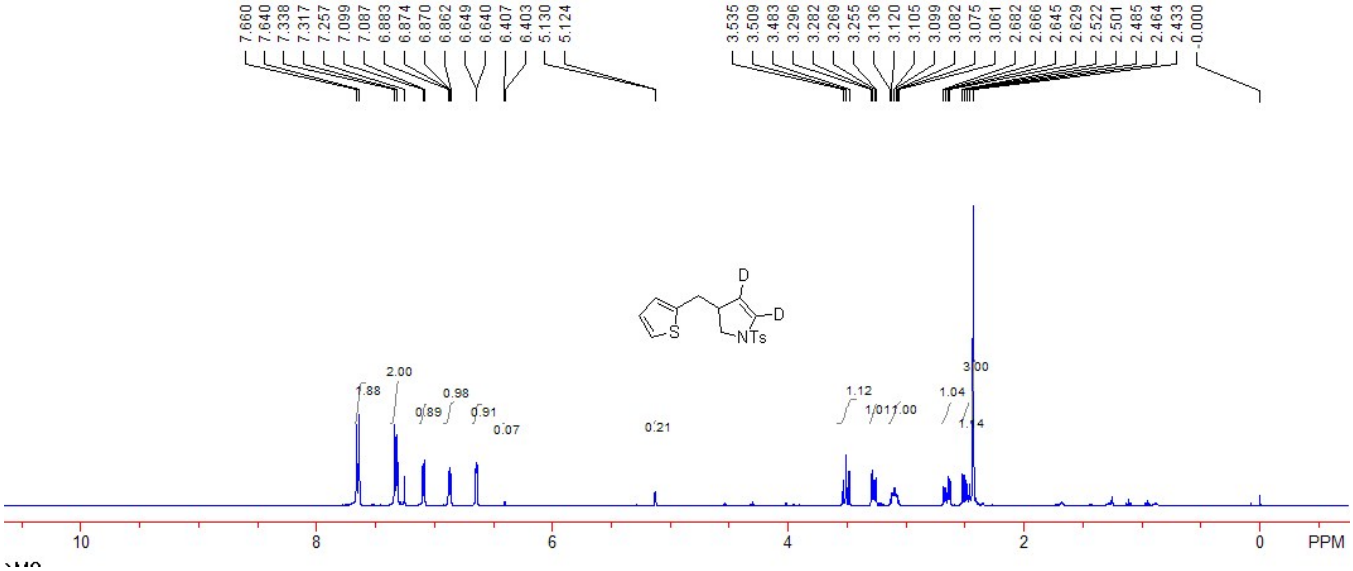


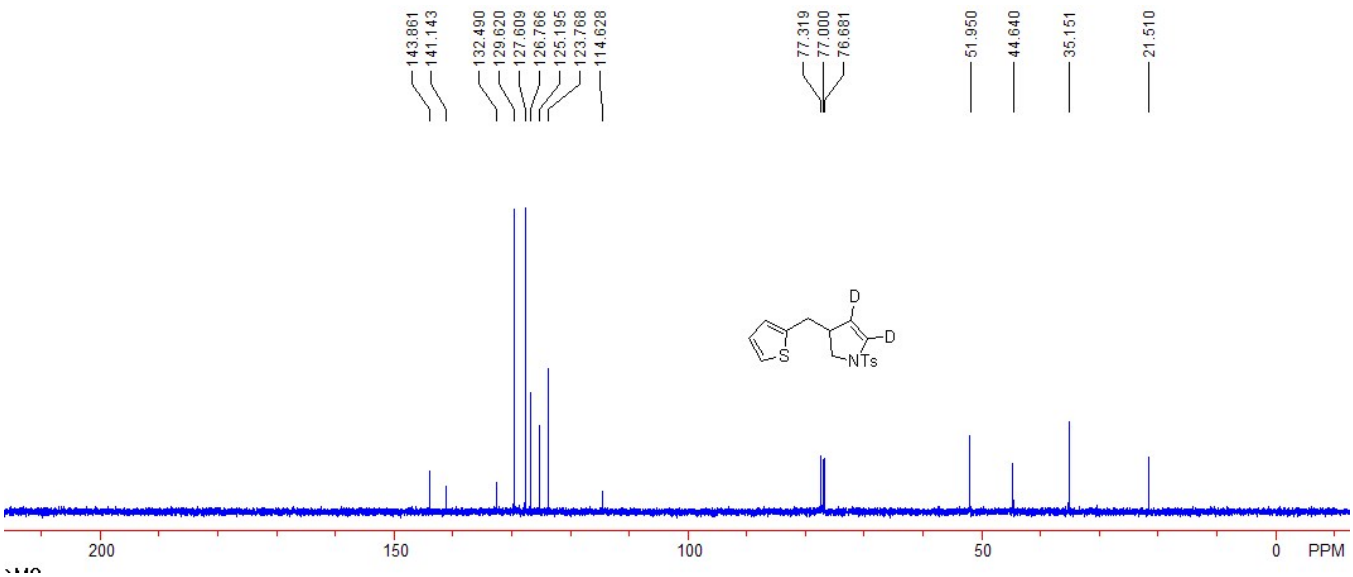


3-(thiophen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole-4,5-d_2 2aa-d_2

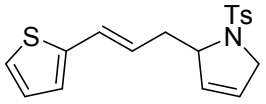
A white solid, 63% yield (40 mg). M.p.: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H, CH_3), 2.49 (dd, J = 14.8, 8.4 Hz, 1H, CH_2), 2.66 (dd, J = 14.8, 6.4 Hz, 1H, CH_2), 3.06-3.14 (m, 1H, CH), 3.27 (dd, J = 10.8, 5.6 Hz, 1H, CH_2), 3.51 (dd, J = 10.4, 10.4 Hz, 1H, CH_2), 5.12 (d, J = 2.4 Hz, 0.21H, =CH), 6.41 (d, J = 1.6 Hz, 0.07 H, ArH), 6.65 (d, J = 3.6 Hz, 1H, ArH), 6.87 (dd, J = 4.8, 3.2 Hz, 1H, ArH), 7.09 (d, J = 4.8 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.2, 44.6, 52.0, 114.6, 123.8, 125.2, 126.8, 127.6, 129.6, 132.5, 141.1, 143.9. IR (CH_2Cl_2) ν 3067, 2955, 2923, 2854, 2323, 1596, 1493, 1349, 1163, 1096, 960, 814, 705, 662

cm^{-1}. MS (ESI) *m/z* (%): 322.08 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{16}D_2NO_2S_2^{+1}[M+H]^+$ requires 322.0899, found: 322.0898.





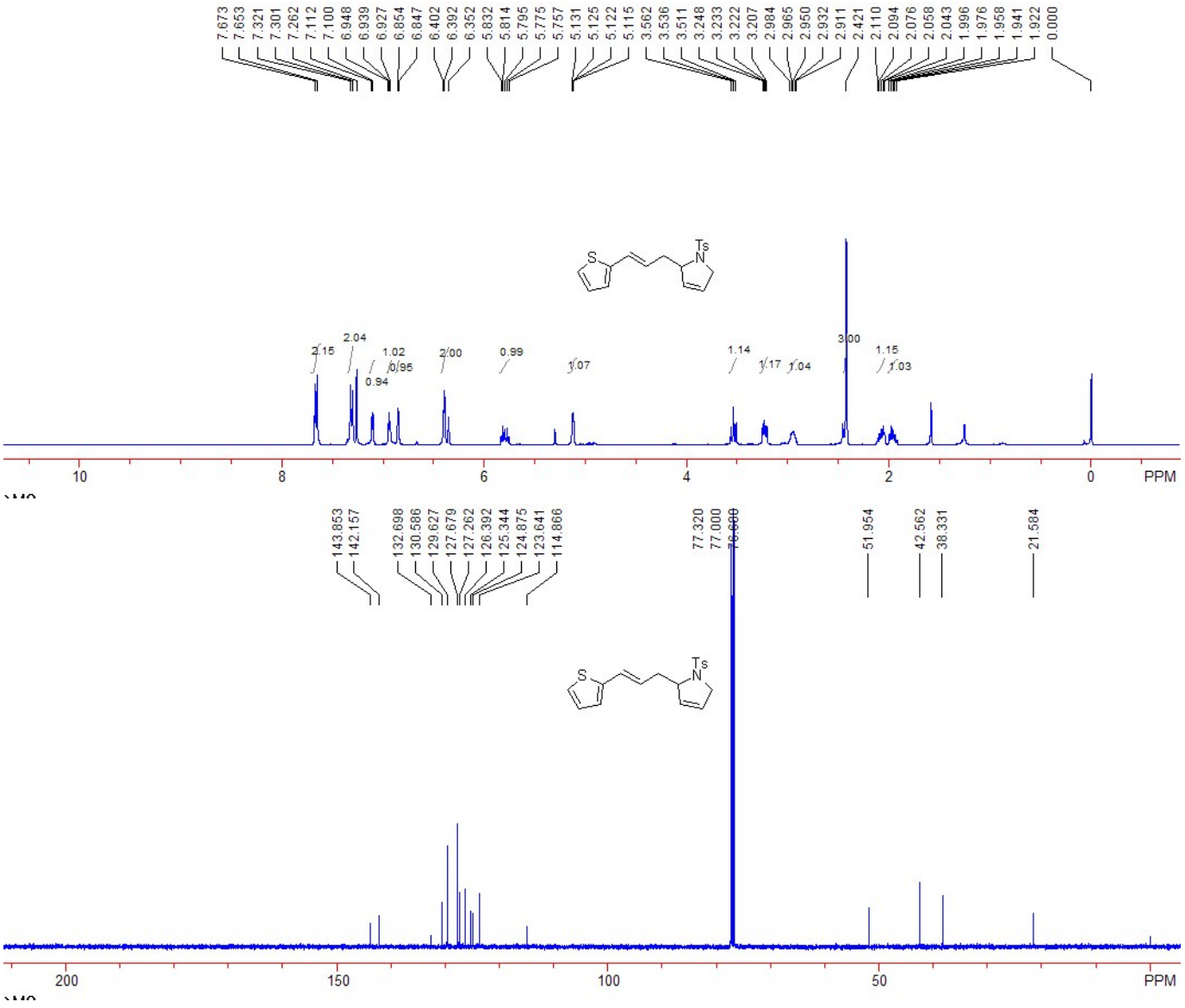
16. Characterization and spectra charts for compound 8, 10 and 13

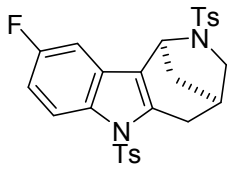


(*E*)-2-(3-(thiophen-2-yl)allyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole 8

A white liquid, 96% yield (33 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.92-2.00 (m, 1H, CH_2), 2.04-2.11 (m, 1H, CH_2), 2.42 (s, 3H, CH_3), 2.91-2.99 (m, 1H, CH_2), 3.22 (dd, *J* = 10.4, 6.0 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.0, 10.0 Hz, 1H, CH_2), 5.12 (dd, *J* = 4.0, 2.8 Hz, 1H, =CH), 5.75-5.84 (m, 1H, =CH), 6.35-6.41 (m, 2H, =CH), 6.85 (d, *J* = 2.8 Hz, 1H, ArH), 6.94 (dd, *J* = 4.8, 3.6 Hz, 1H, ArH), 7.11 (d, *J* = 4.8 Hz, 1H,

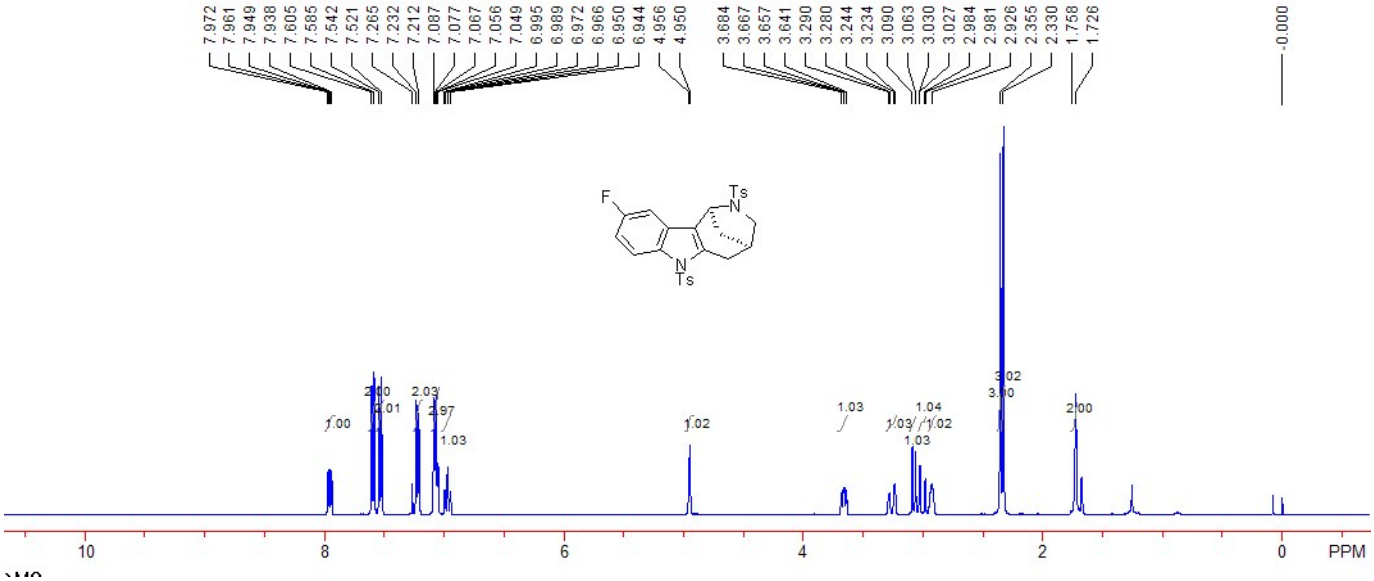
ArH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.66 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 38.3, 42.6, 52.0, 114.86, 114.88, 123.6, 124.9, 125.3, 126.4, 127.3, 127.7, 129.6, 130.6, 132.7, 142.2, 143.9. IR (CH_2Cl_2) ν 3512, 2920, 1597, 1348, 1159, 1089, 956, 813, 705, 664 cm^{-1}. MS (ESI) *m/z* (%): 363.11 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{18}H_{23}N_2O_2S_2^{+1}[M+NH_4]^+$ requires 363.1195, Found: 363.1195.

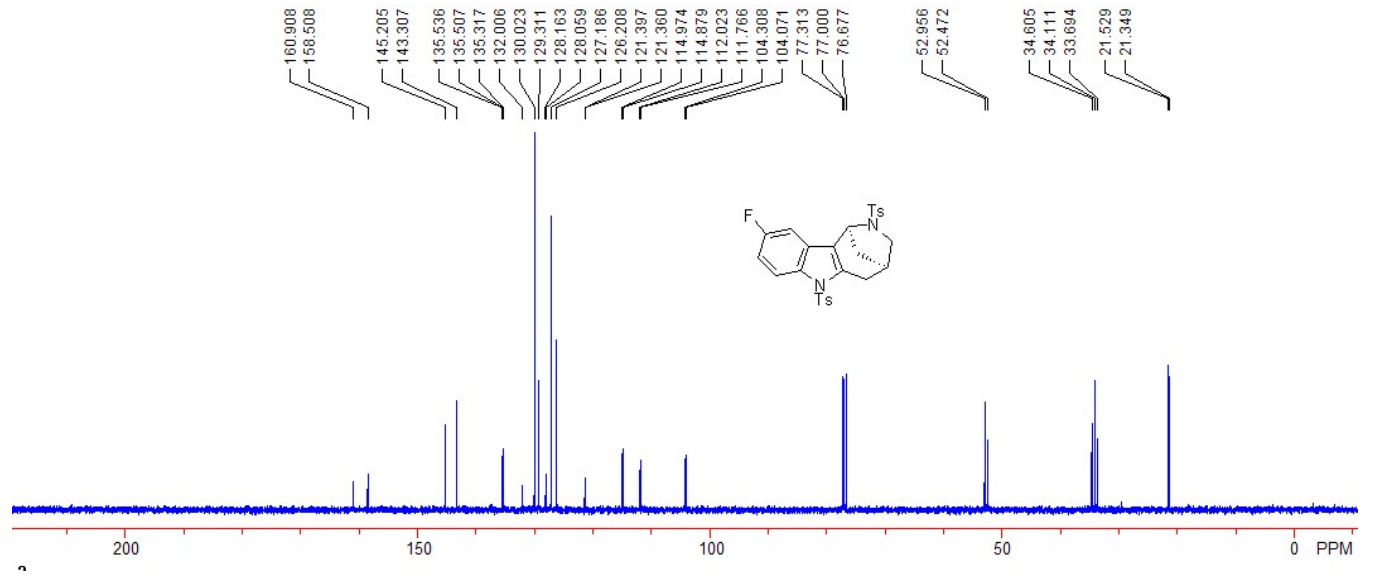


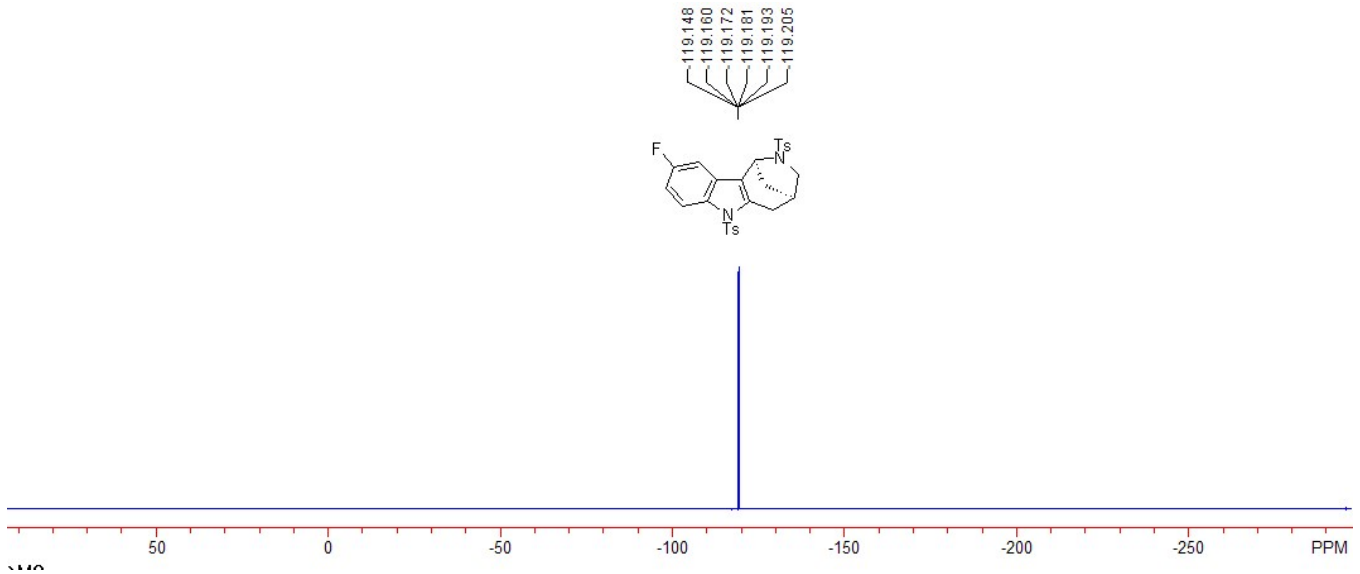


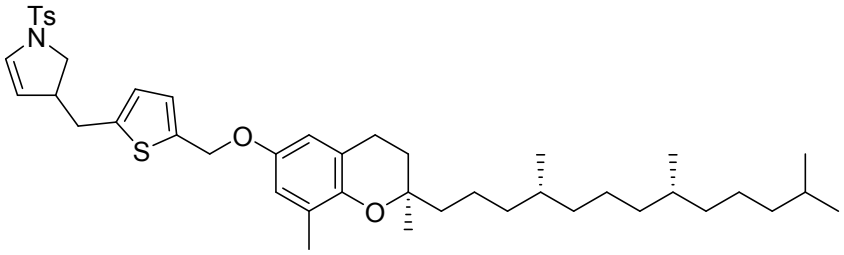
9-fluoro-2,6-ditosyl-1,2,3,4,5,6-hexahydro-1,4-methanoazepino[4,3-*b*]indole 10

A white solid, 1.0 mmol, 31% yield (162 mg), recovered of **9** (294 mg, 56%). M.p.: 90-93 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.72-1.76 (m, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.92-2.94 (m, 1H, CH_2), 3.01 (d, *J* = 18.4 Hz, 1H, CH_2), 3.07 (d, *J* = 10.8 Hz, 1H, CH_2), 3.26 (dd, *J* = 18.0, 4.0 Hz, 1H, CH_2), 3.66 (dd, *J* = 10.8, 6.8 Hz, 1H, CH_2), 4.95 (d, *J* = 2.8 Hz, 1H, CH_2), 6.94-7.00 (m, 1H, ArH), 7.04-7.09 (m, 3H, ArH), 7.22 (d, *J* = 8.0 Hz, 2H, ArH), 7.53 (d, *J* = 8.0 Hz, 2H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.95 (dd, *J* = 9.2, 4.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.6, 33.8, 34.2, 34.7, 52.5, 53.0, 104.2 (d, *J* = 24.2 Hz), 112.0 (d, *J* = 25.1 Hz), 115.0 (d, *J* = 9.2 Hz), 121.4 (d, *J* = 4.0 Hz), 126.2, 127.3, 128.2 (d, *J* = 10.0 Hz), 129.3, 130.1, 132.1, 135.5 (d, *J* = 32.8 Hz), 143.3, 145.2, 159.8 (d, *J* = 239.7 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.1. IR (CH_2Cl_2) ν 2924, 1732, 1597, 1493, 1187, 1089, 811, 704, 658 cm^{-1}. MS (ESI) m/z (%): 542.15 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{29}FN_3O_4S_2^{+1}[M+NH_4]^+$ requires 542.1578, found: 542.1578.

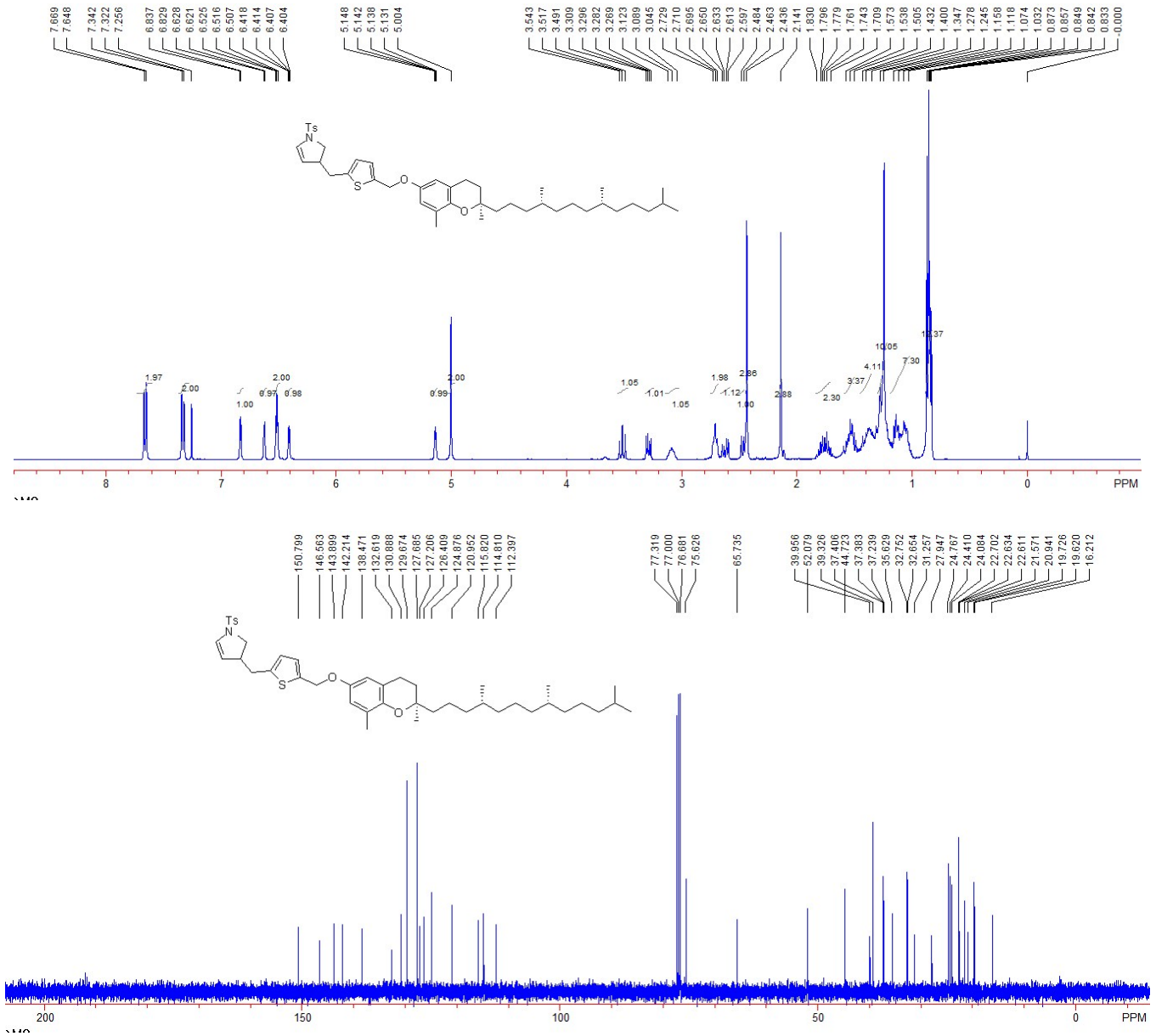




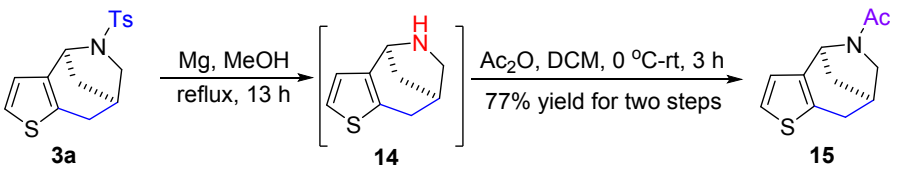




Compound 13. A yellow liquid, 61% yield (45 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.83-0.88 (m, 12H), 1.00-1.16 (m, 7H), 1.22-1.28 (m, 10H), 1.33-1.44 (m, 4H), 1.48-1.58 (m, 3H), 1.69-1.83 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.44-2.49 (m, 1H, CH_2), 2.62 (dd, *J* = 14.8, 6.4 Hz, 1H, CH_2), 2.69-2.74 (m, 2H, CH_2), 3.04-3.13 (m, 1H, CH_2), 3.29 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2), 3.52 (dd, *J* = 10.8, 10.8 Hz, 1H, CH_2), 5.00 (s, 2H, CH_2), 5.14 (dd, *J* = 4.4, 2.8 Hz, 1H, =CH), 6.41 (dd, *J* = 4.0, 1.2 Hz, 1H, ArH), 6.50-6.53 (m, 2H, ArH), 6.62 (d, *J* = 2.8 Hz, 1H, ArH), 6.83 (d, *J* = 2.8 Hz, 1H, ArH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.2, 19.6, 19.7, 20.9, 21.6, 22.61, 22.63, 22.7, 24.1, 24.4, 24.8, 27.9, 31.3, 32.7, 32.8, 35.6, 37.2, 37.38, 37.40, 39.3, 40.0, 44.7, 52.1, 65.7, 75.6, 112.4, 114.8, 115.8, 121.0, 124.9, 126.4, 127.2, 127.7, 129.7, 130.9, 132.6, 138.5, 142.2, 143.9, 146.6, 150.8. IR (CH_2Cl_2): ν 2925, 2867, 1609, 1464, 1377, 1219, 1166, 1092, 854, 735, 666 cm^{-1}; MS (ESI) m/z (%): 751.45 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{44}H_{67}N_2O_4S_2$ $[M+NH_4]^+$ requires 751.4537, found: 751.4534.

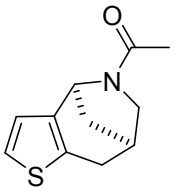


17. Additional experiments on the transformation of 3a and the additional deuterium labeling experiments as well as their characterization and spectra charts



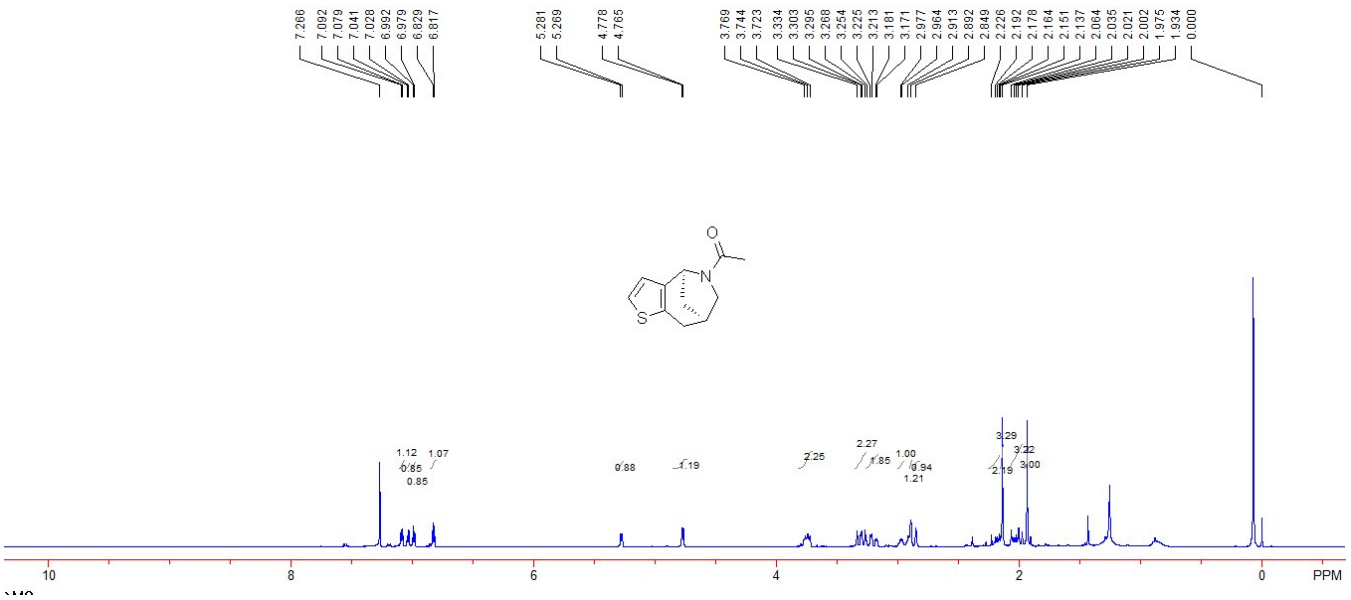
To a flame dried Schlenk tube was added a solution of **3a** (32.00 mg, 0.10 mmol) in MeOH (2.00 mL), then magnesium dust (24.00 mg, 1.00 mmol) was added into the reaction tube in one portion. The reaction mixture was stirred at reflux for 13 h. When the reaction was complete as monitored by TLC, the

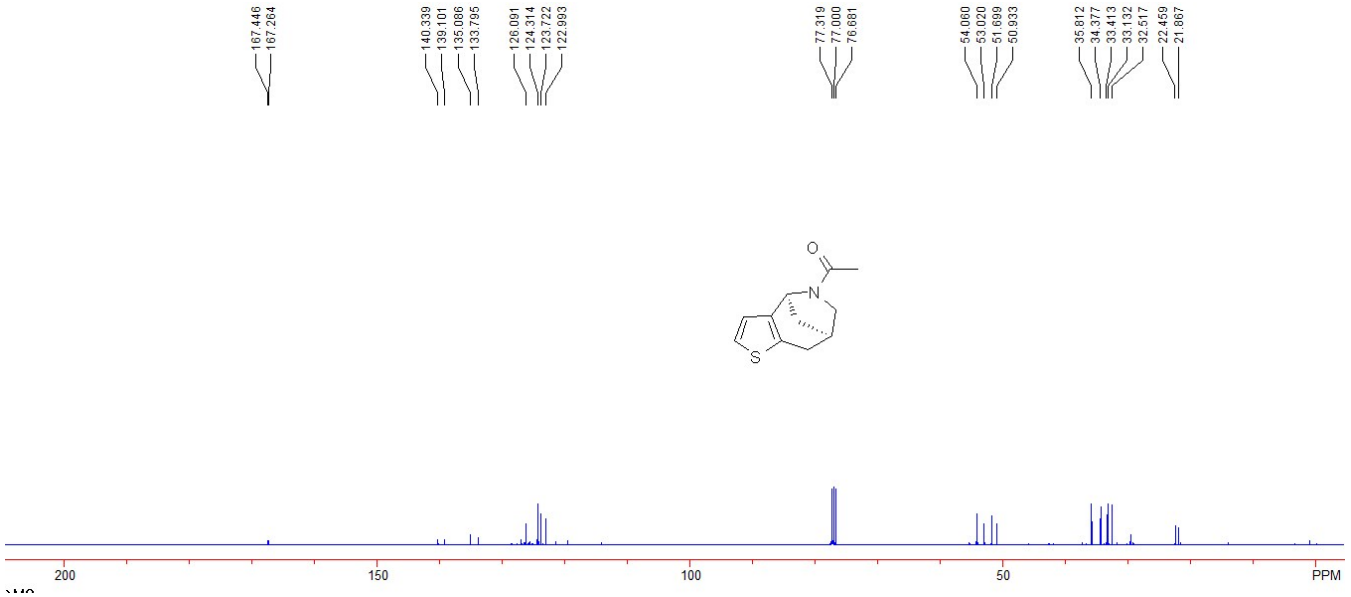
reaction was diluted with ether and carefully quenched with H_2O (10.00 mL). The product was extracted with DCM (10 mL x 3), and the combined organic extracts were washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used directly for next step without further purification. The above residue was dissolved in anhydrous DCM (1.00 mL) and transferred to a 10 mL, round-bottom flask equipped with a rubber septum and nitrogen inlet needle. The solution was cooled at 0 °C, and Ac_2O (6.10 mg, 6.00 μL, 0.06 mmol) were added. The resulting mixture was stirred at room temperature overnight. The reaction was added by a 2.00 N HCl solution (2.00 mL). The mixture was extracted with DCM (5 mL x 3), and the combined organic solution was washed with brine (10 mL), dried with $MgSO_4$, filtered and evaporated to give the desired product **15** as a pale yellow oil (15.00 mg, 72% for two steps, producty **15** was a pair of rotamers in a ratio of 1:1).



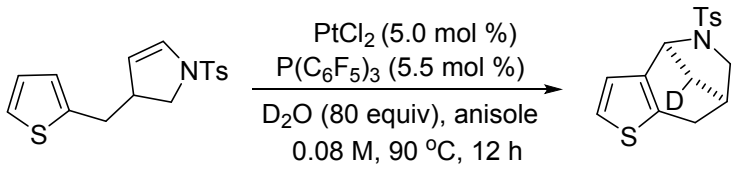
1-(7,8-dihydro-4*H*-4,7-methanothieno[3,2-*c*]azepin-5(6*H*)-yl)ethanone 15

A pale yellow liquid. 72% yield for two steps (15.00 mg), **13** was a pair of rotamers in a ratio of 1:1. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.14 (s, 3H, CH_3), 2.15-2.23 (m, 2H, CH_2), 2.86 (d, J = 17.2 Hz, 1H, CH_2), 2.95-2.99 (m, 1H, CH_2), 3.26-3.34 (m, 2H, CH_2), 3.72-3.77 (m, 1H, CH_2), 4.77 (d, J = 5.2 Hz, 1H, CH_2), 6.82 (d, J = 4.8 Hz, 1H, ArH), 7.08 (d, J = 4.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.5, 33.1, 34.4, 35.8, 51.7, 54.1, 123.7, 126.1, 135.1, 140.3, 167.4. IR (CH_2Cl_2) ν 3078, 2928, 2848, 1623, 1417, 1354, 1155, 1033, 852, 716, 647 cm^{-1}. MS (ESI) *m/z* (%): 208.07 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{11}H_{14}NOS^{+1}(M+H)^+$ requires 208.0791, found: 208.0792.





Additional deuterium labeling experiments



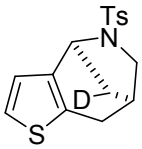
2a **[D]-3a**

83% yield

100% D

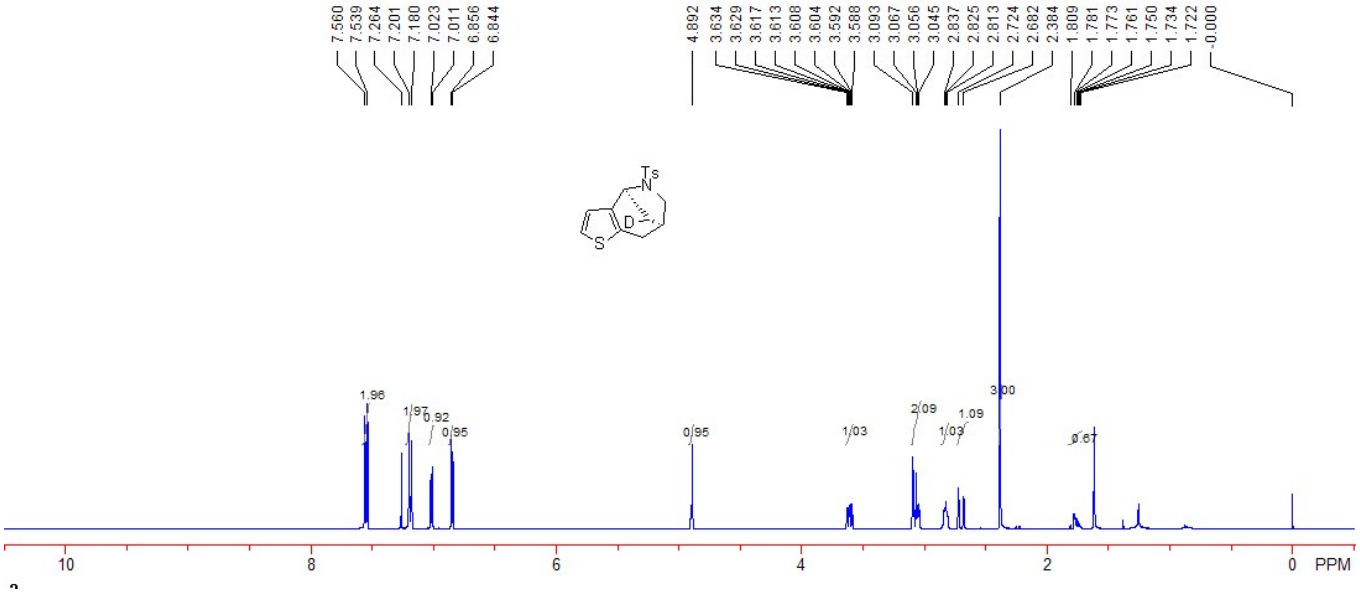
To a flame dried Schlenk tube was added **1a** (0.10 mmol), $PtCl_2$ (5.00 mol%), $P(C_6F_5)_3$ (5.50 mol%), D_2O (8.00 mmol) and anisole (1.20 mL) under argon. Then, the resulting solution was allowed to stir at 90 °C for 12 h. The mixture was purified by flash column chromatography on Al_2O_3 (PE/EA= 15/1-6/1) to give

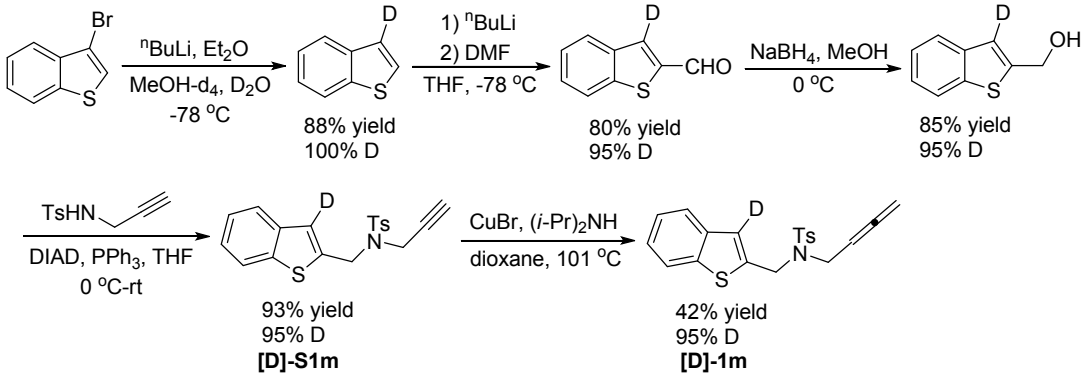
the desired products **[D]-3a**.

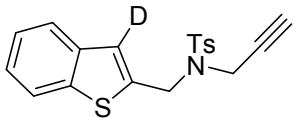


5-tosyl-5,6,7,8-tetrahydro-4*H*-4,7-methanothieno[3,2-*c*]azepine-9-*d* [D]-2a

A pale yellow solid, 83% yield (26 mg). 100% D. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.70-1.80 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.69 (d, J = 16.8 Hz, 1H, CH_2), 2.81-2.84 (m, 1H, CH_2), 3.04-3.10 (m, 2H, CH_2), 3.58-3.64 (m, 1H, CH_2), 4.89 (s, 1H, CH_2), 6.84 (d, J = 5.2 Hz, 1H, ArH), 7.01 (d, J = 4.8 Hz, 1H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.54 (d, J = 8.0 Hz, 2H, ArH).

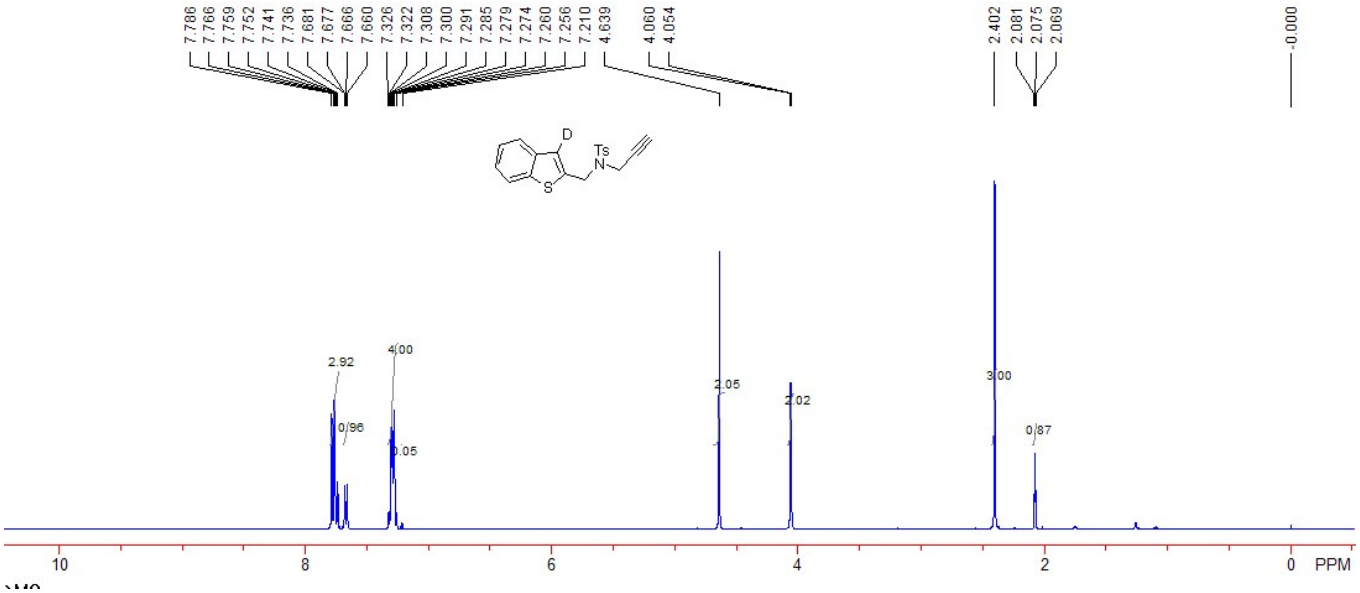


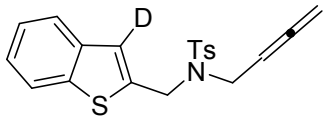




***N*-((benzo[*b*]thiophen-2-yl-3-*d*)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide [D]-S1m**

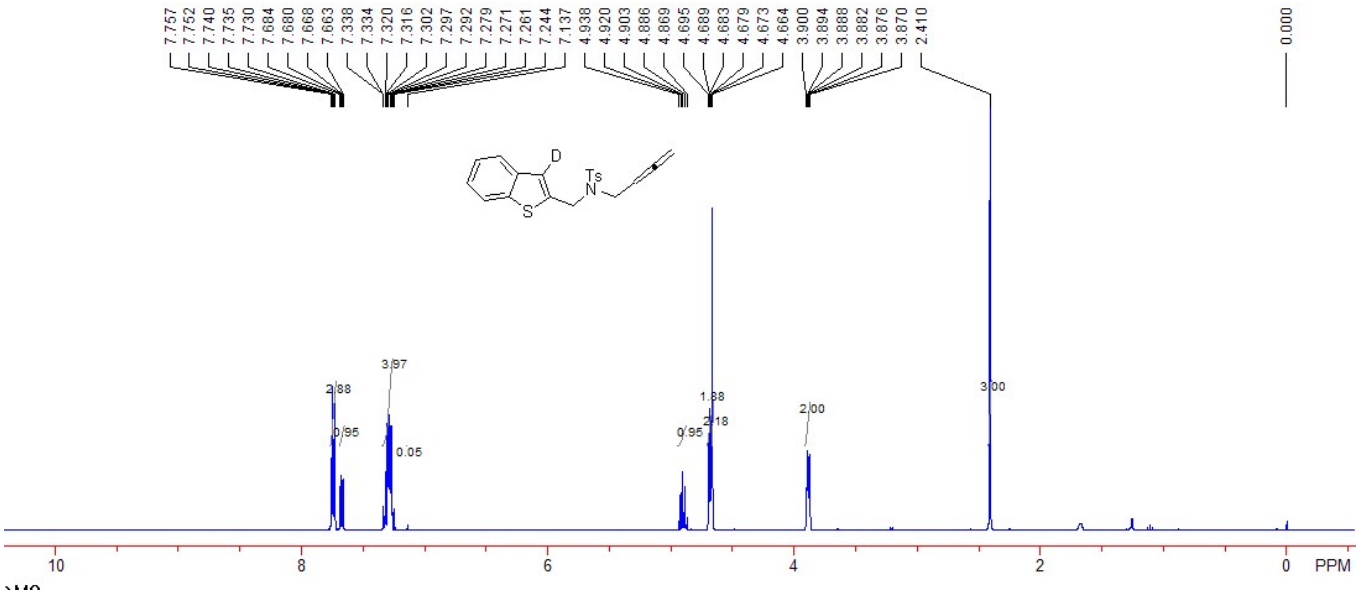
A white solid, 95% yield (997 mg), 95% D. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.08 (t, J = 2.4 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 4.06 (d, J = 2.4 Hz, 2H, CH_2), 4.64 (s, 2H, CH_2), 7.21 (s, 0.05H, ArH), 7.25-7.33 (m, 4H, ArH), 7.66-7.69 (m, 1H, ArH), 7.73-7.79 (m, 3H, ArH). MS (ESI) *m/z* (%): 374.10 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{19}H_{20}DN_2O_2S_2^{+1}(M+NH_4)^+$ requires 374.1102, found: 374.1096.

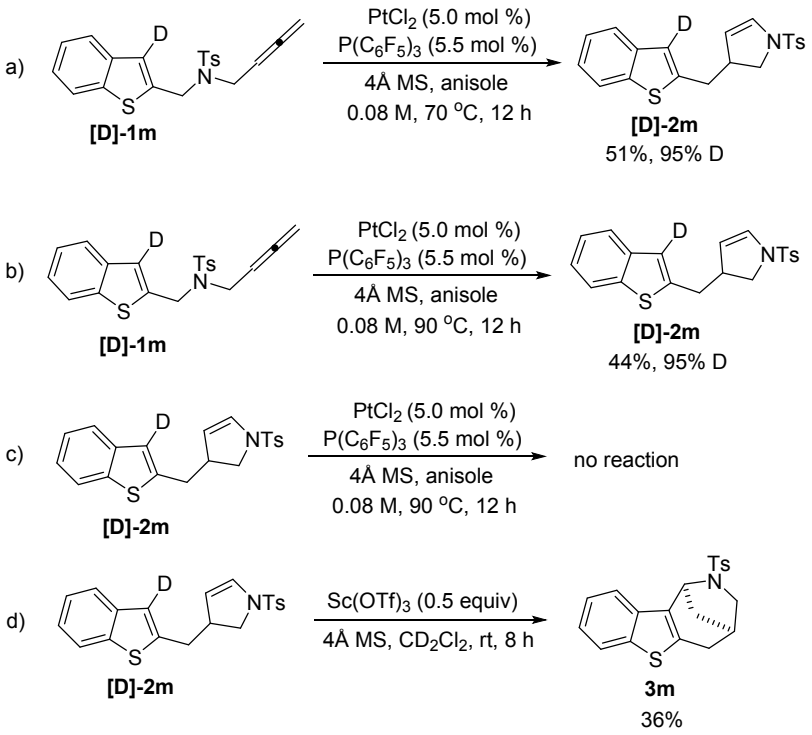




***N*-((benzo[*b*]thiophen-2-yl-3-*d*)methyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide [D]-1m**

A white solid, 42% yield (389 mg), 95% D. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H, CH_3), 3.87-3.90 (m, 2H, CH_2), 4.66 (s, 2H, CH_2), 4.67-4.70 (m, 2H, =CH_2), 4.87-4.94 (m, 1H, =CH), 7.14 (s, 0.05H, ArH), 7.26-7.34 (m, 4H, ArH), 7.66-7.69 (m, 1H, ArH), 7.73-7.76 (m, 3H, ArH). MS (ESI) *m/z* (%): 388.12 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{20}H_{22}DN_2O_2S_2^{+1}(M+NH_4)^+$ requires 388.1258, found: 388.1251.



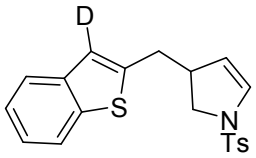


To a flame dried Schlenk tube was added **[D]-1m** (0.30 mmol), $PtCl_2$ (5.00 mol%), $P(C_6F_5)_3$ (5.50 mol%), 4Å MS (150 mg) and anisole (3.75 mL) under argon. Then, the resulting solution was allowed to stir at 70 °C or 90 °C for 12 h. The mixture was purified by a flash column chromatography on silica gel (PE/EA= 15/1-8/1) to give the desired products **[D]-2m** and **[D]-1m**.

To a flame dried Schlenk tube was added **[D]-2m** (0.10 mmol), $PtCl_2$ (5.00 mol%), $P(C_6F_5)_3$ (5.50 mol%), 4Å MS (50 mg) and anisole (1.25 mL) under argon. Then, the resulting solution was allowed to stir at 90

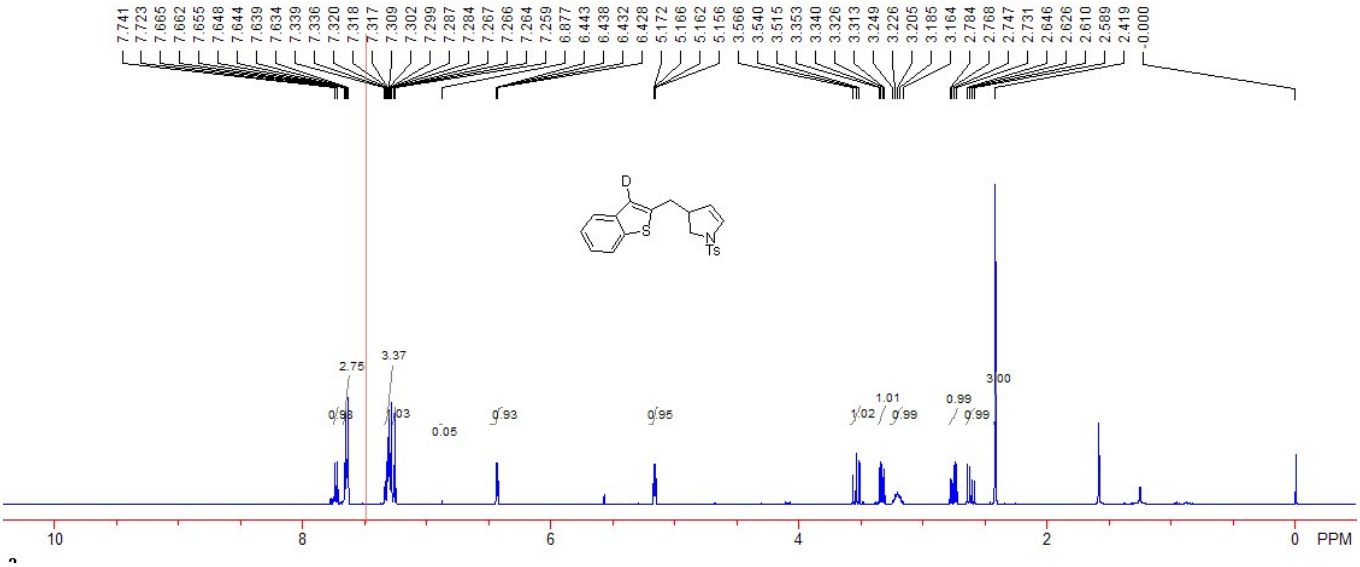
°C for 12 h. The mixture was purified by a flash column chromatography on silica gel (PE/EA= 15/1-8/1) to give the desired product **[D]-2m**.

To a flame dried Schlenk tube was added $Sc(OTf)_3$ (0.05 mmol) and 4Å MS (50 mg), then, it was dried by hot-gun for 5 min. **[D]-2m** (0.10 mmol) and CD_2Cl_2 (1.20 mL) were added into the flask in a glove box. Then, the resulting solution was allowed to stir at room temperature in a glove box overnight. The mixture was purified by a flash column chromatography on silica gel (PE/EA= 8/1) to give the desired product **3m**.

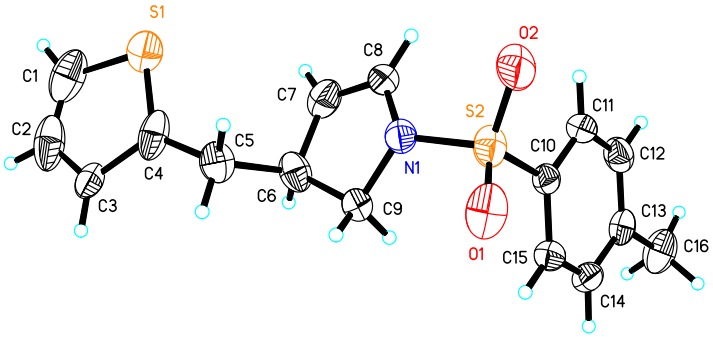


3-((benzo[*b*]thiophen-2-yl-3-*d*)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole [D]-2m

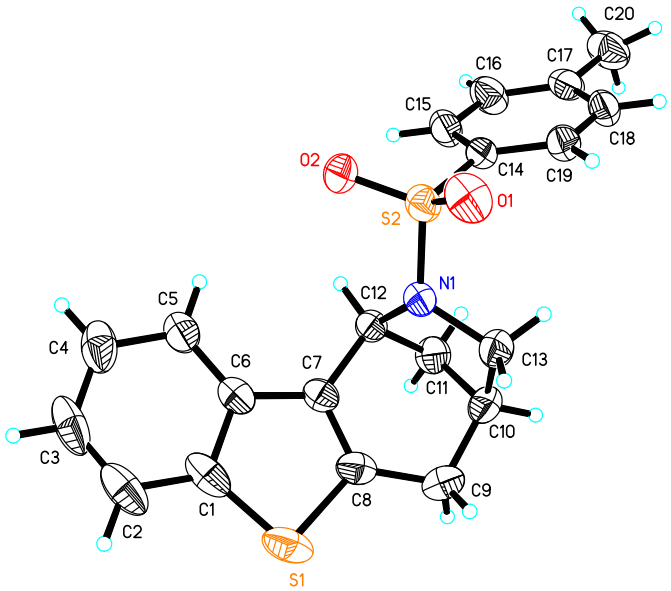
0.3 mmol scale, a white solid, 51% yield (57 mg), 95% D. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H, CH_3), 2.61 (dd, *J* = 14.8, 8.0 Hz, 1H, CH_2), 2.75 (dd, *J* = 14.8, 6.8 Hz, 1H, CH_2), 3.16-3.25 (m, 1H, CH), 3.34 (dd, *J* = 10.8, 5.2 Hz, 1H, CH_2), 3.54 (dd, *J* = 10.8, 10.0 Hz, 1H, CH_2), 5.16 (dd, *J* = 3.6, 2.4 Hz, 1H, =CH), 6.43 (dd, *J* = 4.4, 1.6 Hz, 1H, =CH), 6.88 (s, 0.05H, ArH), 7.25-7.34 (m, 4H, ArH), 7.63-7.67 (m, 3H, ArH), 7.73 (d, *J* = 8.0 Hz, 1H, CH_2).



18. X-ray crystallographic information of product 2a, 3q and 5x

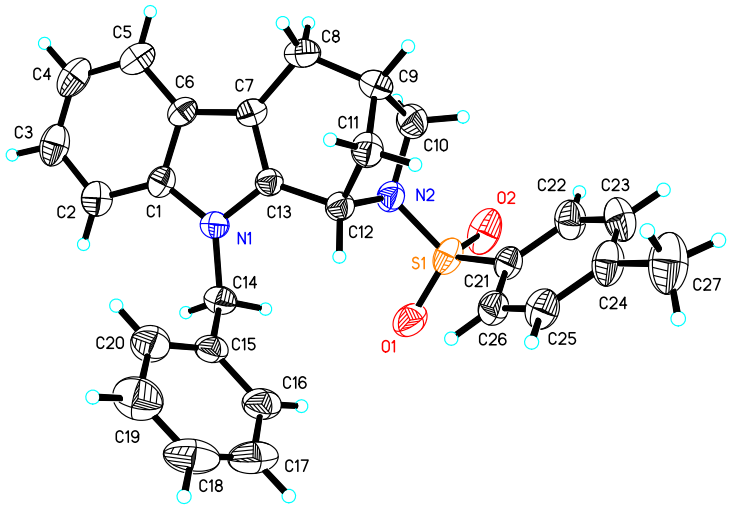


The crystal data of **2a** have been deposited in CCDC with number 995123. Empirical formula: $C_{16}H_{17}NO_2S_2$, Formula weight: 319.42, Temperature: 319.42 K, Crystal system: Monoclinic, Space group: P21/c, Unit cell dimensions: a = 16.677(4) Å, α = 90°; b = 8.1292(16) Å, β = 98.956(4)°; c = 11.693(2) Å, γ = 90°. Volume: 1565.9(6) $Å^3$, Z = 4, Density (calculated): 1.355 Mg/m^3, F(000): 672, Crystal size: 0.211 x 0.165 x 0.121 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0721, wR2 = 0.2027.



The crystal data of **3q** have been deposited in CCDC with number 1414546. Empirical formula: $C_{20}H_{19}NO_2S_2$, Formula weight: 369.48, Temperature: 293(2) K, Crystal system: Monoclinic, Space group: C 2/c, Unit cell dimensions: a = 25.934(5) Å, α = 90°; b = 8.1289(14) Å, β = 104.645(3)°; c = 17.387(3)

Å, γ = 90°. Volume: 3546.3(11) $Å^3$, Z = 8, Density (calculated): 1.384 Mg/m^3, F(000): 1552, Crystal size: 0.21 x 0.15 x 0.12 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0524, wR2 = 0.1261.



The crystal data of **5x** have been deposited in CCDC with number 1449115. Empirical Formula: $C_{27}H_{26}N_2O_2S$; Formula Weight: 442.56; Crystal Color, colorless; Crystal Dimensions: 0.170 x 0.150 x 0.100 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 14.945(2)Å, b = 16.857(3)Å, c = 18.059(3)Å, α = 90°, β = 90°, γ = 90°, V = 4549.7(12)$Å^3$; Space group: P b c a; Z = 8; D_{calc} = 1.292 g/cm^3; F_{000} = 1872; Final R indices [I>2sigma(I)] R1 = 0.0490, wR2 = 0.1021.

19. References:

[1] James H. Wynne, Stacy E.Price, Jeffrey R. Rorer and Wayne M. Stalick, *Synth. Commun*., 2003, **33**, 341.

[2] A. S. K. Hashmi, J. P. Weyrauch, E. Kurpejovic, T. M. Frost, B. Miehlich, W. Frey and J. W. Bats, *Chem. -Eur. J.*, 2006, **12**, 5806.

[3] W. Huang, Q. S. Shen, J. l. Wang and X. G. Zhou, *J. Org. Chem.*, 2008, **73**, 1586.