

Supporting Information

Intramolecular Annulation of Aromatic Rings with *N*-Sulfonyl 1,2,3-triazoles: Divergent Synthesis of 3-Methylene-2,3-dihydrobenzofurans and 3-Methylene-2,3-dihydroindoles

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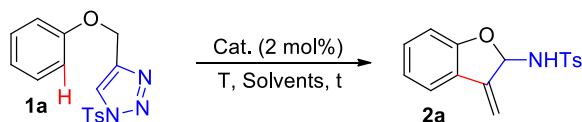
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1. General Remarks. MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. ^1H NMR spectra were recorded for solution in CDCl_3 with tetramethylsilane (TMS) as internal standard or $\text{DMSO}-d_6$. J -values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

2. Table S1. Optimization of the Reaction Conditions of 1a.

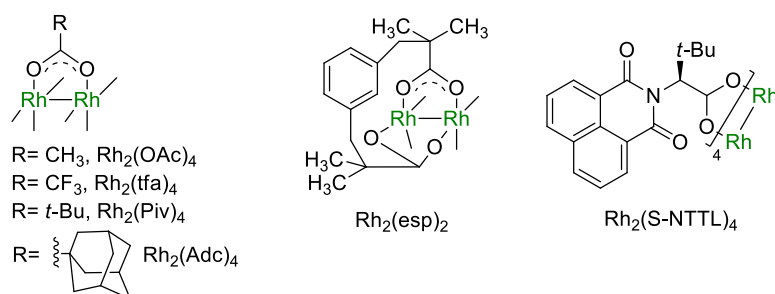


entry	cat.	T (°C)	solvent	time (h)	yield (%) ^b
					2a
1	Rh ₂ (Piv) ₄	80	DCM	2	35
2	Rh ₂ (OAc) ₄	80	DCM	2	30
3	Rh ₂ (esp) ₂	80	DCM	2	22
4	Rh ₂ (tfa) ₄	80	DCM	2	10
5	Rh ₂ (Adc) ₄	80	DCM	2	15
6	Rh ₂ (S-NTTL) ₄	80	DCM	2	NR
7	Rh ₂ (Piv) ₄	70	DCM	2	26
8	Rh ₂ (Piv) ₄	90	DCE	2	68
9	Rh₂(Piv)₄	90	DCE	3	95
10	Rh ₂ (Piv) ₄	110	DCE	3	80 ^c

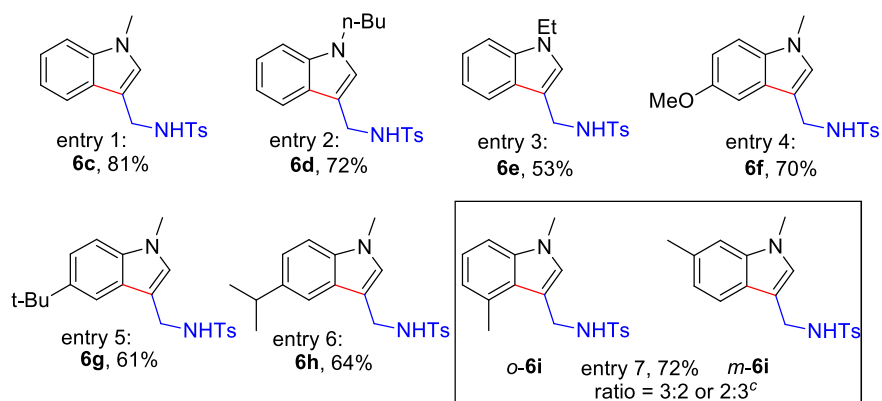
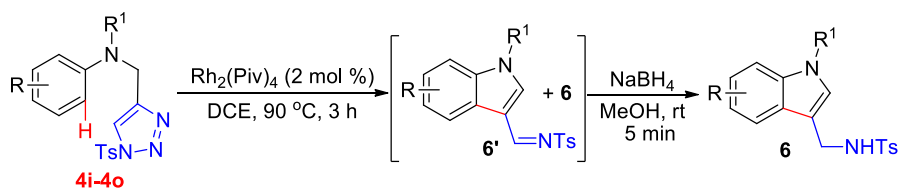
^a 0.2 mmol scale. Reaction conditions: under Ar, triazole, Rh(II) catalysts and solvent were stirred in a sealed tube. ^b Isolated yields.

^c Other complex product mixture was formed.

Rhodium(II) carboxylate catalysts employed in this study:

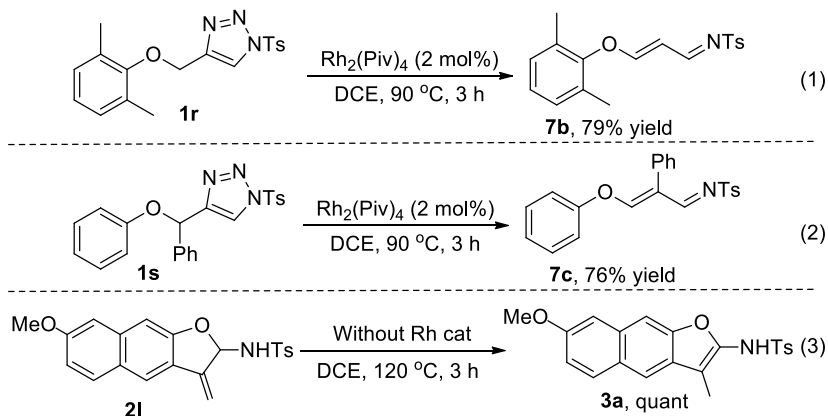


3. Table S2. Scope of the Reaction for the Synthesis of 6.

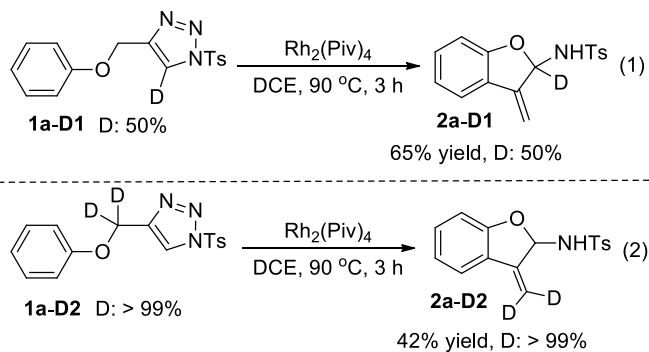


^a 0.2 mmol scale. Procedure: under Ar, triazole, Rh₂(Piv)₄ and DCE (2.0 mL) were stirred in a sealed tube at 90 °C for 3 h. ^b Isolated yields. ^c Determined by ¹H NMR.

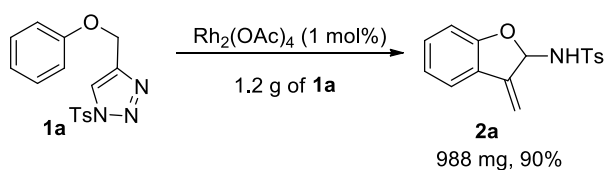
4. Scheme S1. Control Experiments.



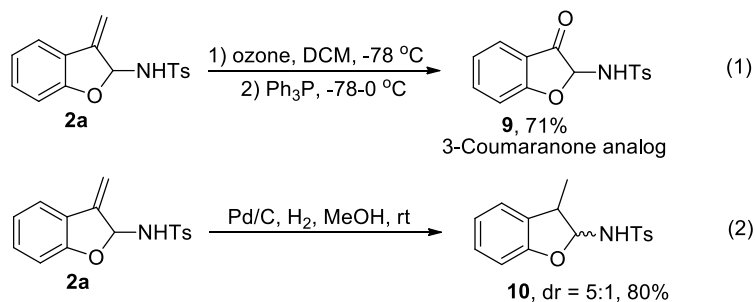
5. Scheme S2. Isotopic Labeling Experiments.



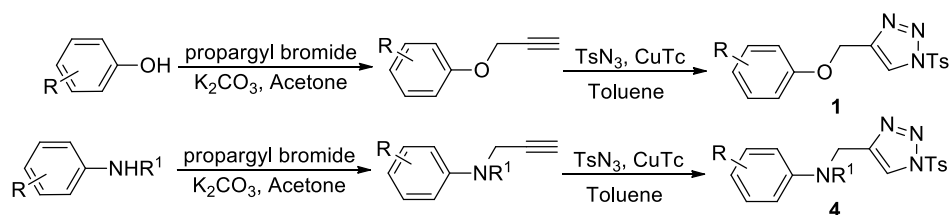
6. Scheme S3. Gram Scale Synthesis of 2a.



7. Scheme S4. Ozonization and Hydrogenation of 2a.



8. General procedure for the synthesis of triazoles **1** and **4**.

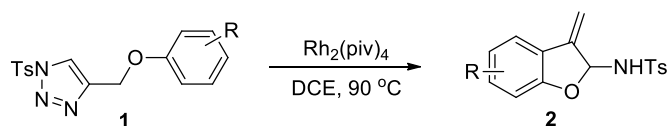


Phenol (10.0 mmol, 1.0 equiv) was suspended in acetone (20 mL), followed by addition of K_2CO_3 (20.0 mmol, 2.0 equiv). The suspension was stirred for 10 min, and then propargyl bromide (1.5 equiv) was added via syringe at room temperature. The reaction mixture was stirred for 5 h at room temperature, whereupon a deep-yellow mixture was obtained. The crude product was collected by filtration, which was used without purification in the next step, yield: >90% in most cases.

CuTc (0.2 mmol, 0.04 equiv) was added to a solution of the alkyne (5.0 mmol, 1.0 equiv) in toluene (10 mL). The reaction mixture was stirred for 3 min at room temperature, followed by addition of TsN_3 (6.0 mmol, 1.2 equiv) in one pot via syringe. The reaction mixture was stirred for 4 h at room temperature and then directly subjected to flash column chromatography (PE:EA = 6:1) to get the pure product **1**.

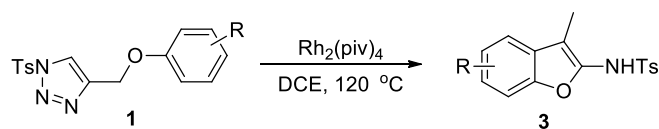
The synthesis of **4** follows the same procedure.

9. General procedure for the synthesis of **2**.



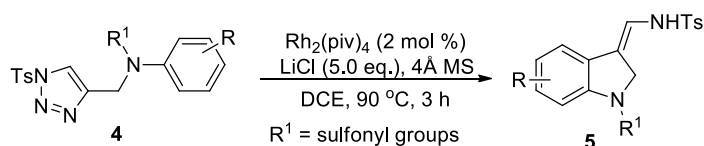
To a flame-dried flask were added the triazole (0.2 mmol, 1.0 equiv) and the $Rh_2(piv)_4$ (0.004 mmol, 0.02 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via syringe under Ar. The reaction mixture was stirred for 3 hour at 90 °C. Silica gel was added to the reaction mixture and the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography (PE:EA = 6:1) to afford the desired product **2**.

10. General procedure for the synthesis of **3**.



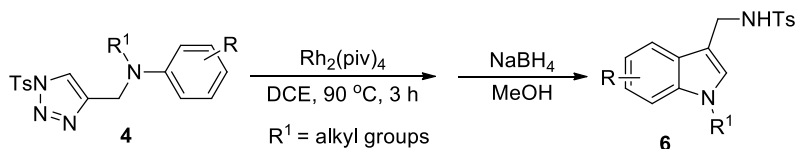
To a flame-dried flask were added the triazole (0.2 mmol, 1.0 equiv) and the $\text{Rh}_2(\text{piv})_4$ (0.004 mmol, 0.02 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via syringe under Ar. The reaction mixture was stirred for 3 hour at 120 °C. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (PE:EA = 6:1) to get the desired product.

11. General procedure for the synthesis of 5.



To a 10 ml flask were added the LiCl (1.0 mmol, 5 equiv) and the 4Å MS (50 mg), then the flask was flame and vacuum dried. Triazole (0.2 mmol, 1 equiv), $\text{Rh}_2(\text{piv})_4$ (0.002 mmol, 0.02 equiv) were added, and the flask was evacuated and backfilled with Ar for 3 times. DCE (2 mL) was added to this flask via syringe under Ar. The reaction mixture was stirred at 90 °C for 3 h. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography to give the desired product **5**.

12. General procedure for the synthesis of 6.



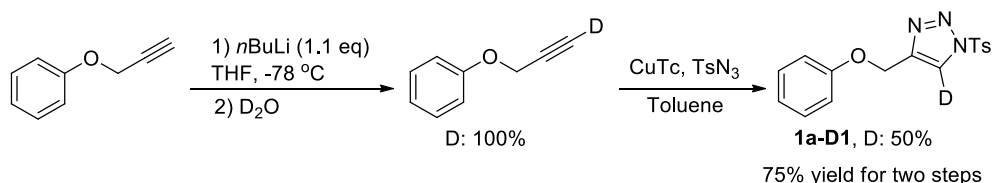
To a flame-dried flask were added the triazole (0.2 mmol, 1 equiv) and the $\text{Rh}_2(\text{piv})_4$ (0.002 mmol, 0.02 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2 mL) was added to this flask via syringe under Ar. The reaction mixture was stirred at 90 °C. After 3 hour, MeOH (1.0 mL) and NaBH_4 (4 mg, 0.1 mmol, 2 equiv) were added. The reaction mixture was stirred for additional 5 min. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under reduced pressure, the crude product was purified by silica gel

chromatography (PE:EA = 6:1) to give the desired products **6**.

13. General procedure for the synthesis of **7**.

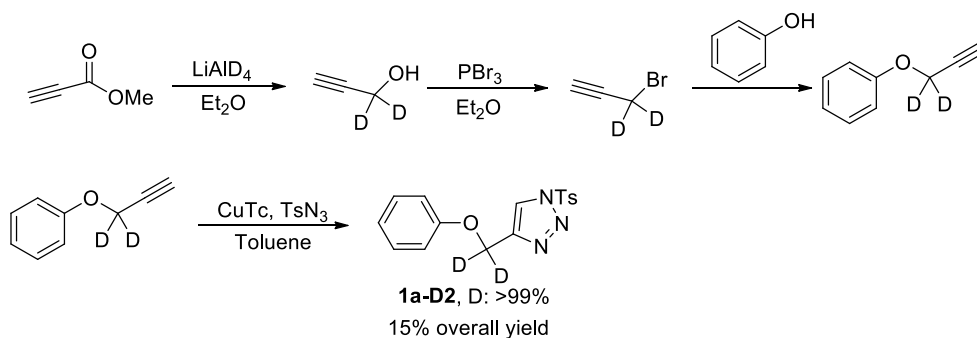
Follow the same procedure in the synthesis of **2** and **3**.

14. General procedure for the synthesis of **1a-D1**.



To a 25 mL flame dried flask were added prop-2-ynoxybenzene (1 mmol, 133 mg) and THF (5 mL). The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and then *n*BuLi (2.5 M, 0.44 mL) solution in hexane was added dropwise. After 2 h, D_2O (2 mmol, 40 mg) was added to quench the reaction. The reaction mixture was diluted with DCM and water. After extraction, the organic layers were dried, filtered and concentrated in vacuo. The obtained D-containing intermediate was used directly in the CuAAC reaction, following the same procedure depicted above. The corresponding product **1a-D1** was obtained in 75% yield over two steps.

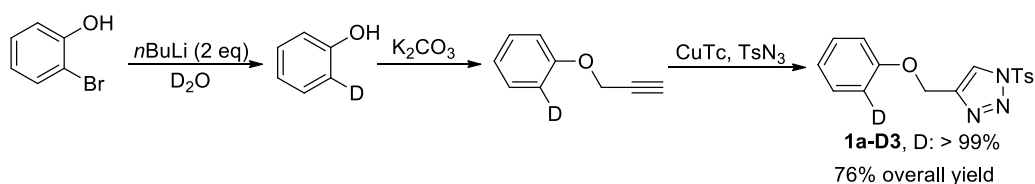
15. General procedure for the synthesis of **1a-D2**.



To a 100 mL flame dried flask charged with 15 mL Et_2O was added LiAlD_4 (12 mmol, 0.5 g) under Ar. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$, then methyl propiolate (15 mmol, 1.25 g) in Et_2O (5.0 mL) was added dropwise to this mixture at $-78\text{ }^{\circ}\text{C}$ for 2 h. The mixture was stirred for 5 h at $-40\text{ }^{\circ}\text{C}$, then the reaction was quenched by addition of water (5.0 mL). The mixture was extracted with small amount of Et_2O , dried, filtered to get the crude alcohol product solution. To the above alcohol solution in Et_2O was added PBr_3 (15 mmol, 4.1 g) at $0\text{ }^{\circ}\text{C}$. After 30 min, the reaction

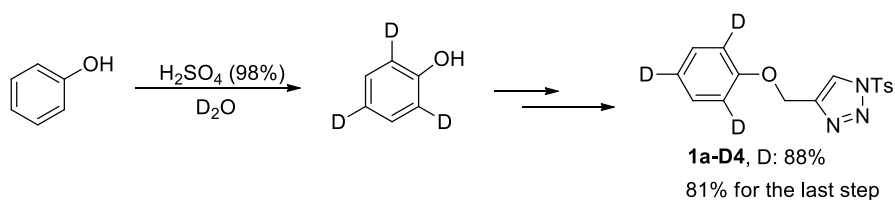
mixture was slowly quenched by water (5.0 mL). The resulting mixture was separated and the organic layer was dried and filtered. The mixture was carefully concentrated to about 2.0 mL and then treated with phenol (5 mmol, 448 μ L) and K_2CO_3 (10 mmol, 1.38 g) in acetone (15 mL). After 5 h, the solution was concentrated and purified by silica gel chromatography to yield the alkyne intermediate. Following the same CuAAC procedure, **1a-D2** was given in 15% overall yield, (D: >99%).

16. General procedure for the synthesis of **1a-D3**.



To a 100 mL flame dried flask was added *ortho*-Br-phenol (2.5 mmol, 432 mg), followed by addition of Et_2O (10 mL). The reaction mixture was cooled to 0 $^{\circ}C$, and then $nBuLi$ (2.5 M, 2.0 mL) in hexane was added dropwise. After 2 h, D_2O (0.5 mL) was added. The crude phenolic product was used in the next step without purification. The rest steps are identical as that depicted above to give **1a-D3** in 76% overall yield, (D: >99%).

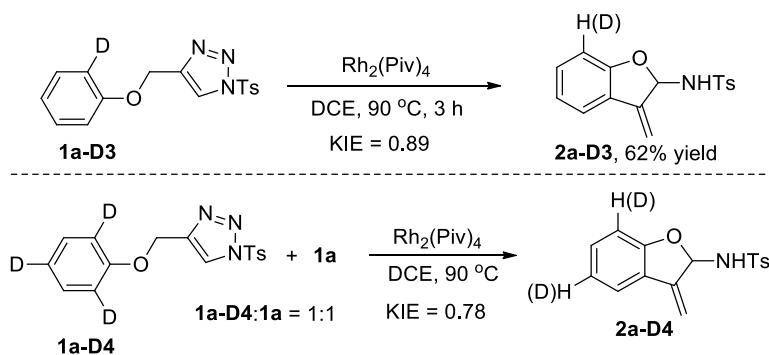
17. General procedure for the synthesis of **1a-D4**.



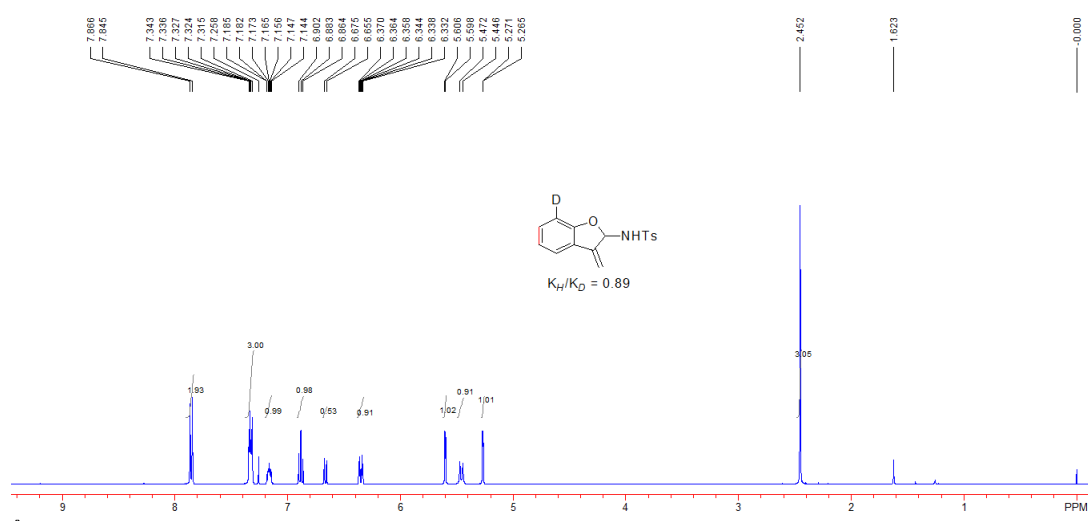
To a 10 mL flame dried flask was added D_2O (270 μ L, 5.0 mL), H_2SO_4 (98%, 0.6 mL, 10 mmol) was added slowly to the solution, followed by addition of phenol (10 mmol, 940 mg) to this mixture via a syringe under Ar. The reaction mixture was stirred for 8 h at 110 $^{\circ}C$. After cooling down; the reaction mixture was diluted with ice-water, extracted with EA. The solvent was removed to get the crude deuterated phenol, yield: quant.

The other steps were identical as that depicted above and **1a-D4** was obtained in 81% yield.

18. Intra-/Intermolecular Kinetic Isotopic Effects.



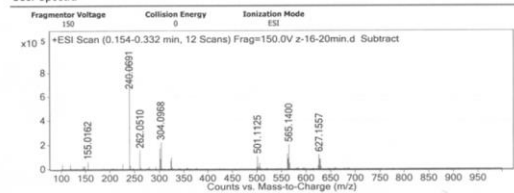
a) Intramolecular KIE investigation: Following the identical reaction procedure. Calculation of intramolecular k_H/k_D : $0.47/0.53 = 0.89$.



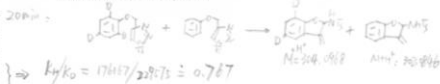
b) Intermolecular KIE investigation: To a flame-dried flask were added **1a-D4** (18 mg, 88% D) and **1a** (13 mg) and $\text{Rh}_2(\text{piv})_4$ (0.001 mmol, 0.01 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (1.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred at 90 °C. The reaction mixture was immediately subjected to HR Ms at 20 min and 60 min. Calculation of intramolecular k_H/k_D : 1) 20 min, $176167/229575 = 0.767$; 2) 60 min, $178121/231574 = 0.769$. Average: 0.77.

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Sample Name z-16-20min
User Name
Acquired Time 2013-11-20 4:09:27 PM
Instrument Agilent Technologies 6224 TOF LC/MS

User Spectra



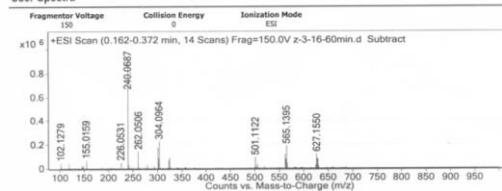
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262.051	1	165361.3	
302.0846	1	176167	
304.0968	1	229575.4	
326.0794	1	99350.1	
501.1125	1	109907.2	
563.128	1	131735.2	
565.14	1	209435.9	
627.1557	1	126527.5	



— End Of Report —

Data Filename z-3-16-60min.d
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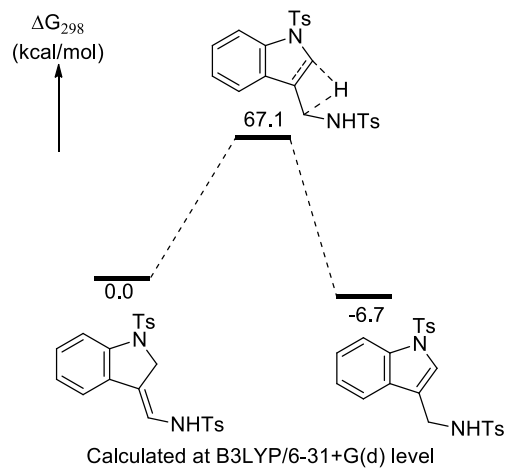


Peak List	m/z	z	Abund
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262.0506	1	147642.6	
302.0842	1	178121.6	
304.0964	1	231574.9	
326.079	1	97963.2	
501.1122	1	93973.9	
563.1274	1	120788.1	
565.1395	1	192362.1	
627.155	1	124615.6	

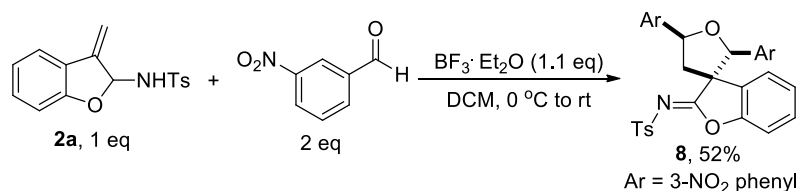


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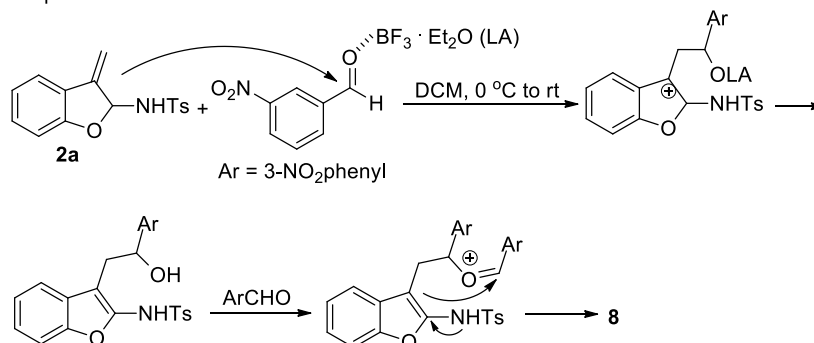
19. Figure S1. DFT Calculation Using 5a as a Model.



20. General procedure for the synthesis of 8.

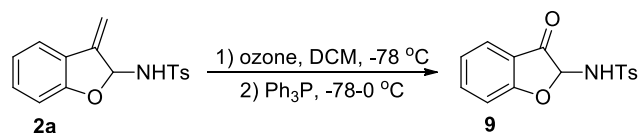


Proposed Mechanism:



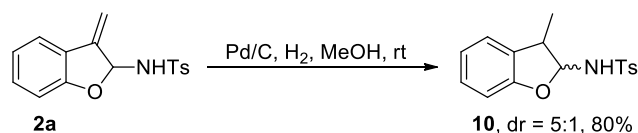
To a 10 mL flask were added **2a** (0.1 mmol, 31 mg), aldehyde (0.2 mmol, 30 mg) and DCM (2.0 mL). The reaction mixture was cooled to 0 °C and then BF₃·Et₂O (0.11 mmol, 15 mg) was added via a syringe. The reaction was slowly warmed to room temperature and stirred until **2a** was consumed. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give **8** (31 mg, 52%).

21. General procedure for the synthesis of **9**.



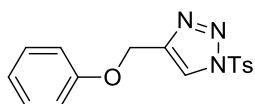
To a 20 mL flask were added **2a** (0.1 mmol, 30 mg) and DCM (3.0 mL) and the resulting mixture was stirred at -78 °C for 5 min then ozone was bubbled in until the solution maintained light blue. Then Ar was bubbled in to remove ozone. After Ph₃P (0.11 mmol, 29 mg) was added, the reaction mixture was slowly warmed to rt and stirred overnight. The mixture was concentrated under reduced pressure and the residue was purified by silica gel chromatography to give a white solid product **9** (21 mg, 71%).

22. General procedure for the synthesis of **10**.



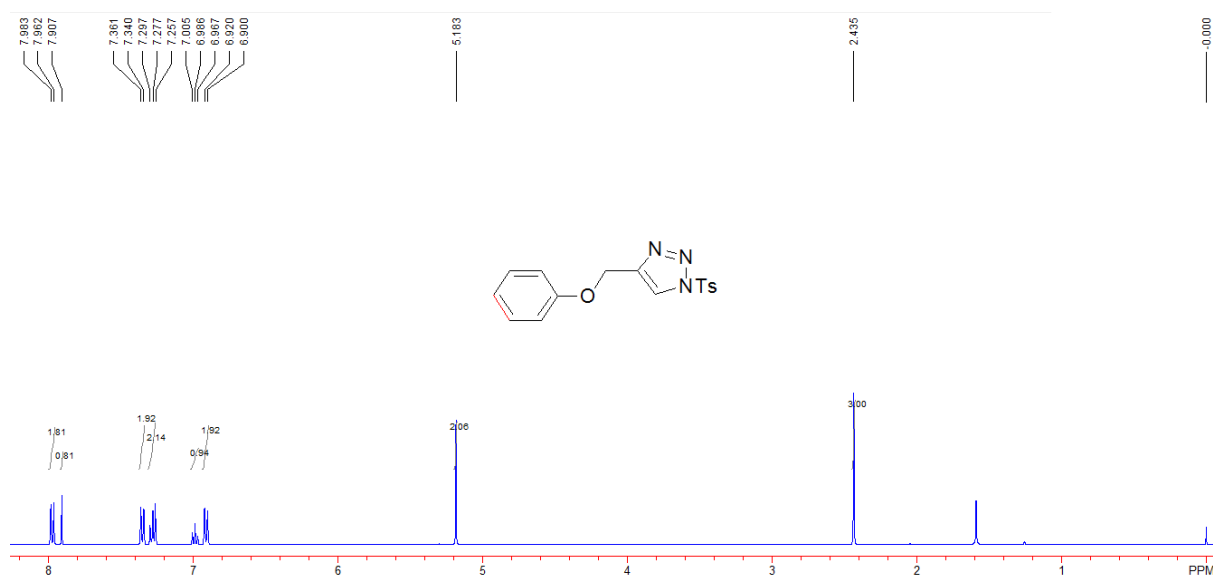
To a 10 mL flask were added **2a** (0.1 mmol, 30 mg), Pd/C (5 mg) and MeOH (3.0 mL) and the resulting mixture was stirred under an atmosphere of H₂ (1.0 atm) for 12 h. The mixture was concentrated under reduced pressure and the residue was purified by silica gel chromatography to give a white solid product **10** (24 mg, 80%).

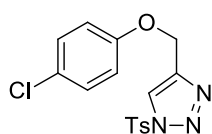
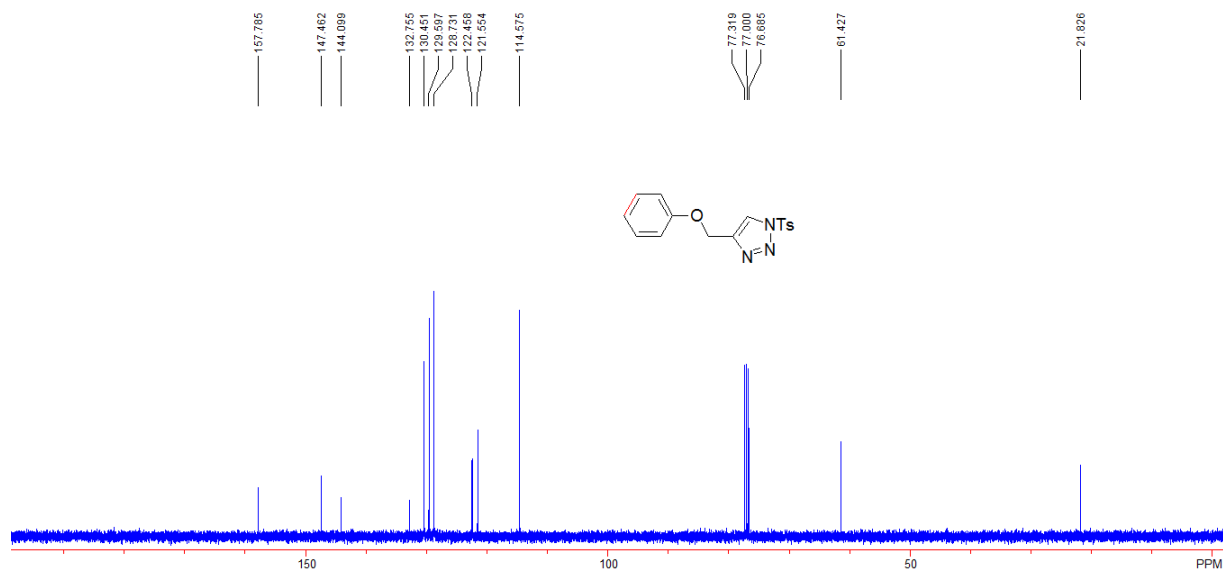
23. Characterization and spectra charts



4-Phenoxymethyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole **1a**.

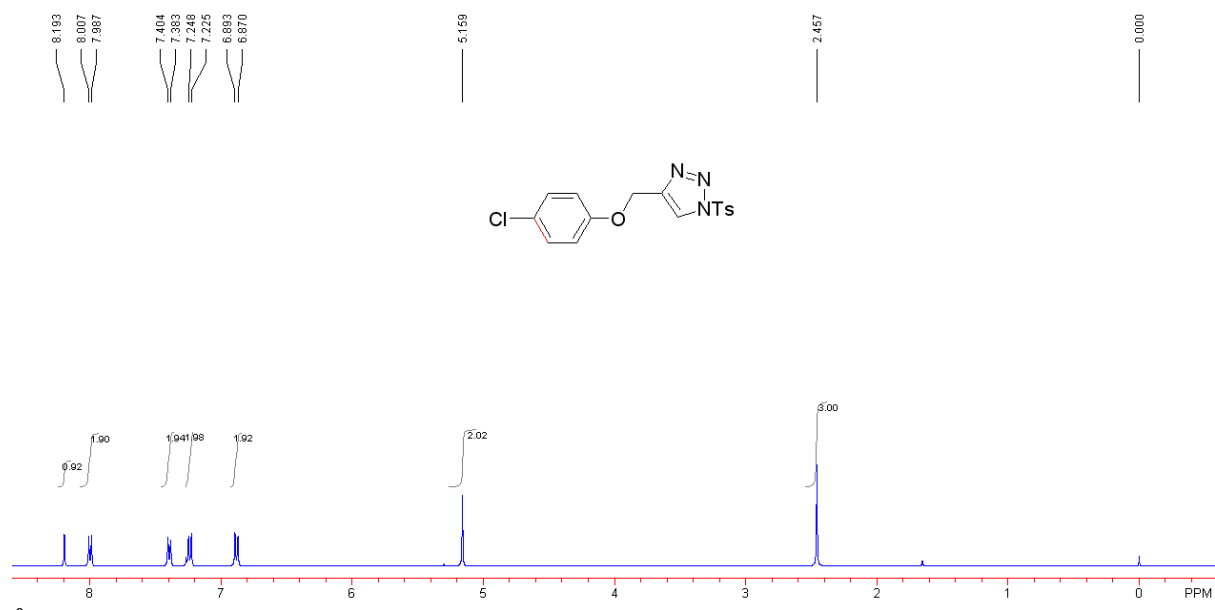
5.0 mmol scale, a white solid, 87% yield (1.44 g). m.p.: 94-96 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.43 (s, 3H, CH₃), 5.18 (s, 2H, CH₂), 6.91 (d, *J* = 8.0 Hz, 2H, Ar), 6.99 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.28 (dd, *J* = 8.0 Hz, 2H, Ar), 7.35 (d, *J* = 8.0 Hz, 2H, Ar), 7.90 (s, 1H, CH=), 7.97 (d, *J* = 8.0 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 61.4, 114.6, 121.6, 122.4, 128.7, 129.6, 130.4, 132.7, 144.1, 147.5, 157.8. IR (CH₂Cl₂) ν 1614, 1599, 1589, 1397, 1296, 1236, 1219, 1117, 1057, 1033, 1006, 992, 950, 886, 858, 840, 813, 705, 689, 681 cm⁻¹. HRMS (ESI) Calcd. for C₁₆H₁₆N₃O₃S⁺ (M⁺+H) requires 330.0907, found: 330.0913.

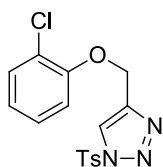
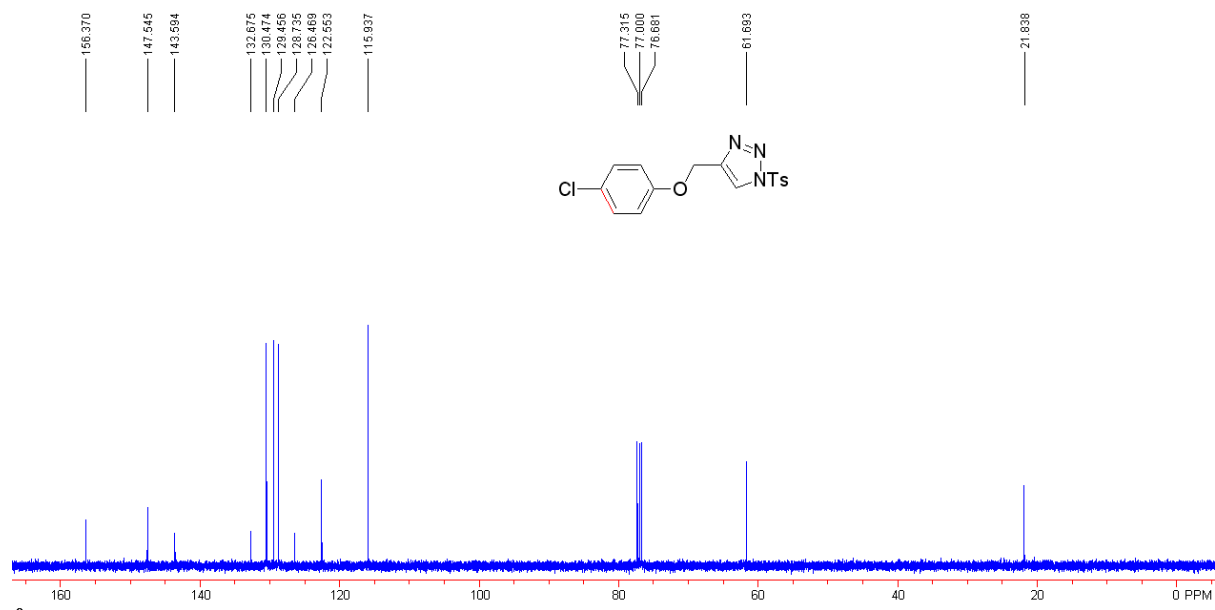




4-(4-Chlorophenoxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1b

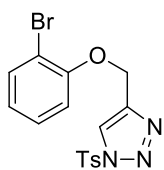
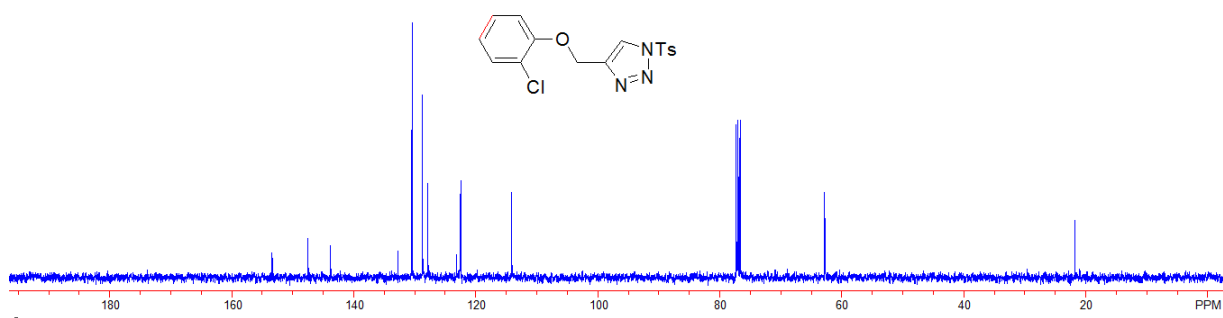
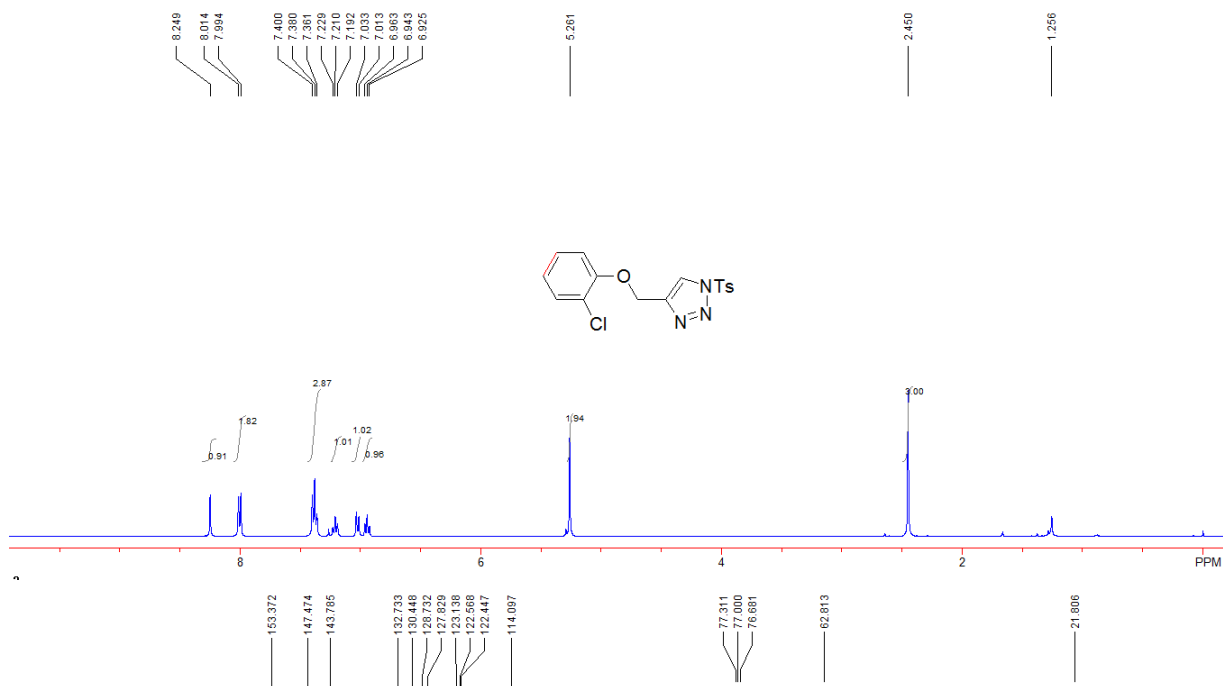
5.0 mmol scale, a white solid, 85% yield (1.55 g). M.p.: 151-153 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 5.16 (s, 2H, CH_2), 6.87 (d, $J = 8.0$ Hz, 2H, Ar), 7.23 (d, 2H, $J = 8.0$ Hz, Ar), 7.39 (d, $J = 8.0$ Hz, 2H, Ar), 7.99 (d, $J = 8.0$ Hz, 2H, Ar), 8.20 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.8, 61.7, 115.9, 122.6, 126.5, 128.7, 129.5, 130.5, 132.7, 143.6, 147.5, 156.4. IR (CH_2Cl_2) ν 3385, 1637, 1491, 1388, 1242, 1197, 1176, 1013, 970, 915, 802, 700, 672 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{15}\text{ClN}_3\text{O}_3\text{S}^+$ (M^++H) requires 364.0517, found: 364.0524.





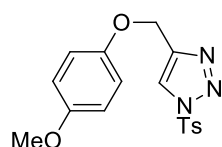
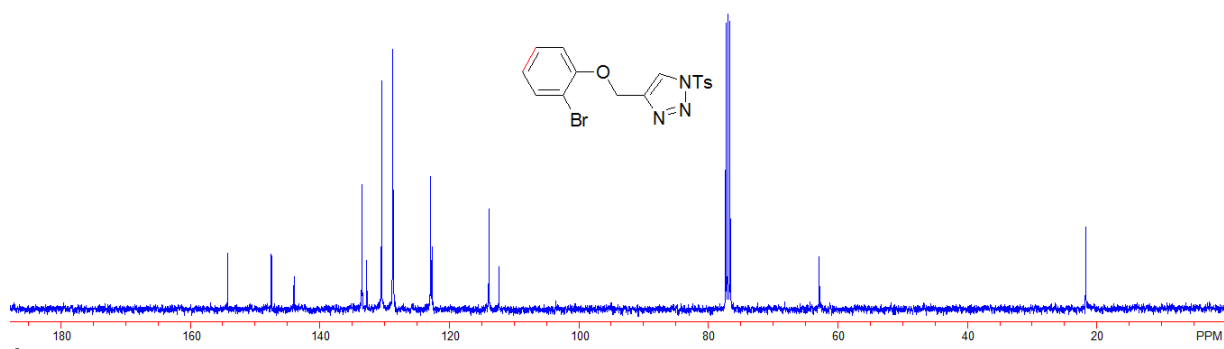
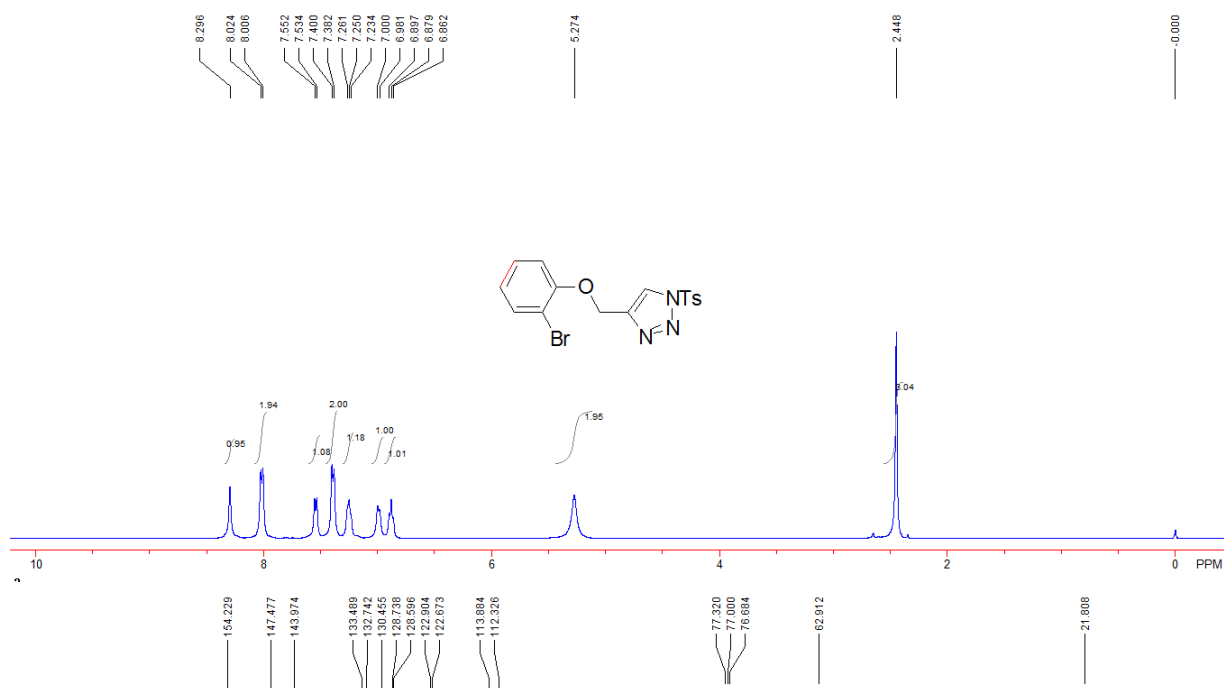
4-(2-Chlorophenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole **1c**

5.0 mmol scale, a white solid, 78% yield (1.42 g). M.p.: 146-148 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.45 (s, 3H, CH₃), 5.26 (s, 2H, CH₂), 6.94 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.02 (d, 1H, *J* = 8.0 Hz, Ar), 7.21 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.36-7.40 (m, 3H, Ar), 8.00 (d, *J* = 8.0 Hz, 2H, Ar), 8.25 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 62.8, 114.1, 122.4, 122.6, 123.1, 127.8, 128.7, 130.4, 132.7, 143.8, 147.5, 153.4. IR (CH₂Cl₂) ν 1592, 1488, 1405, 1273, 1193, 1135, 1122, 1067, 1008, 967, 809, 762, 742, 686, 669 cm⁻¹. MS (ESI) *m/z* (%): 330.1 (100) [M⁺+H]; HRMS (ESI) Calcd. for C₁₆H₁₅ClN₃O₃S⁺ (M⁺+H) requires 364.0517, found: 364.0523.



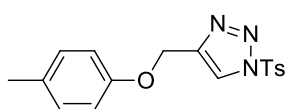
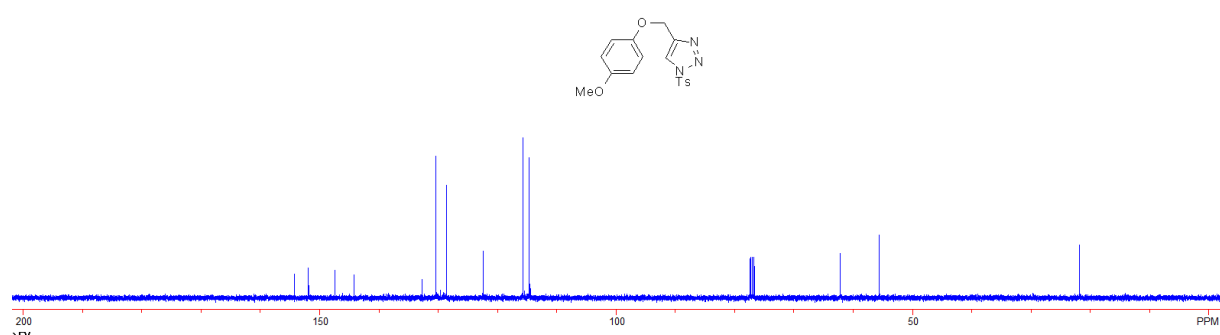
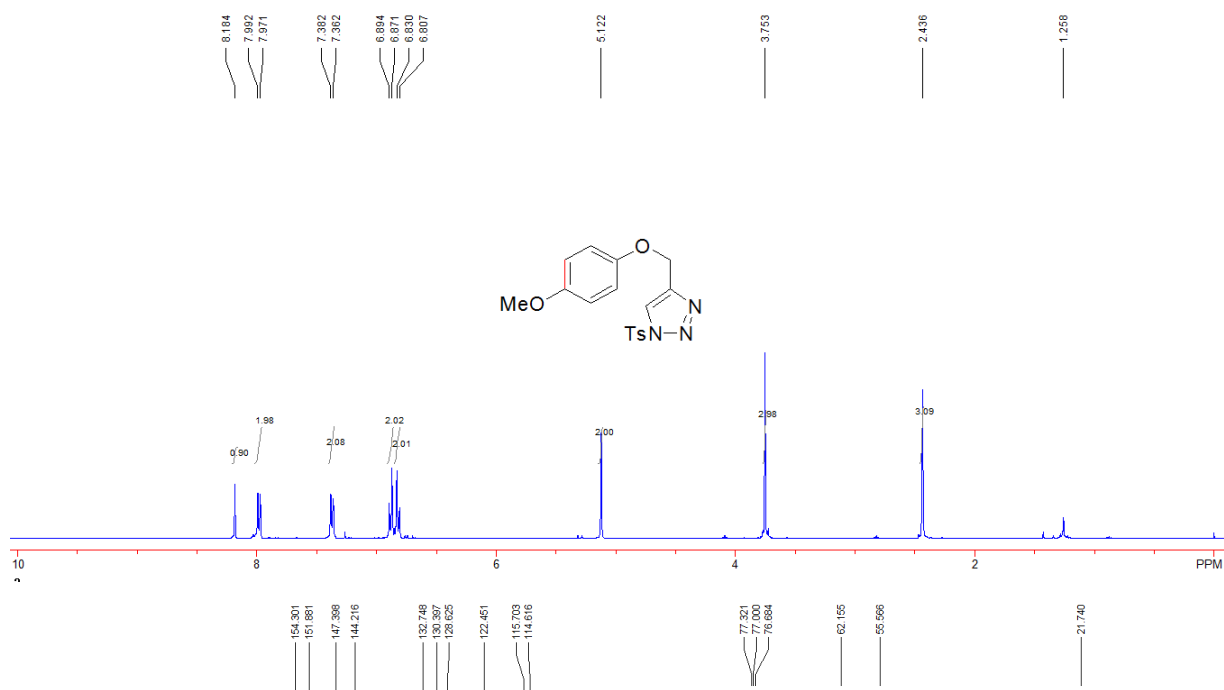
4-(2-Bromophenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole **1d**

5.0 mmol scale, a white solid, 79% yield (1.61 g). M.p.: 190-193 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.45 (s, 3H, CH₃), 5.27 (s, 2H, CH₂), 6.88 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 6.99 (d, *J* = 7.2 Hz, 1H, Ar), 7.23-7.27 (m, 1H, Ar), 7.39 (d, *J* = 7.2 Hz, 2H, Ar), 7.54 (d, *J* = 7.2 Hz, 1H, Ar), 8.01 (d, *J* = 7.2 Hz, 2H, Ar), 8.30 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 62.9, 112.3, 113.9, 122.7, 127.9, 128.6, 128.7, 130.4, 133.5, 144.0, 147.5, 154.2. IR (CH₂Cl₂) ν 3290, 1479, 1158, 1122, 1052, 1031, 1007, 849, 809, 708, 679, 665, 658 cm⁻¹. HRMS (ESI) Calcd. for C₁₆H₁₅BrN₃O₃S⁺ (M⁺+H) requires 408.0012, found: 408.0026.



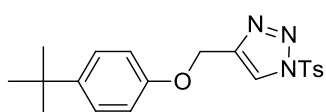
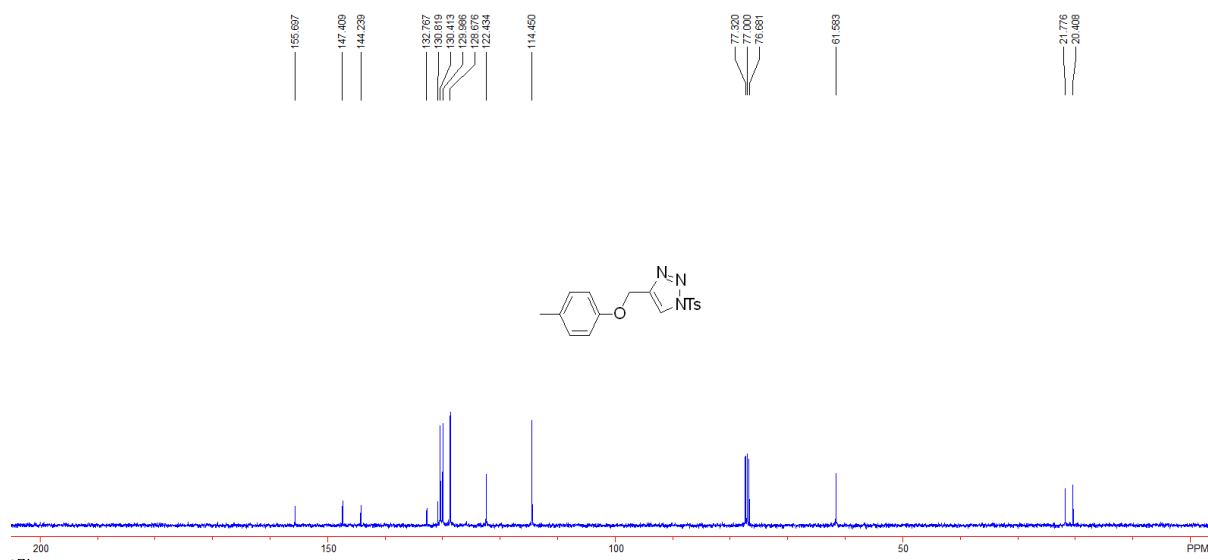
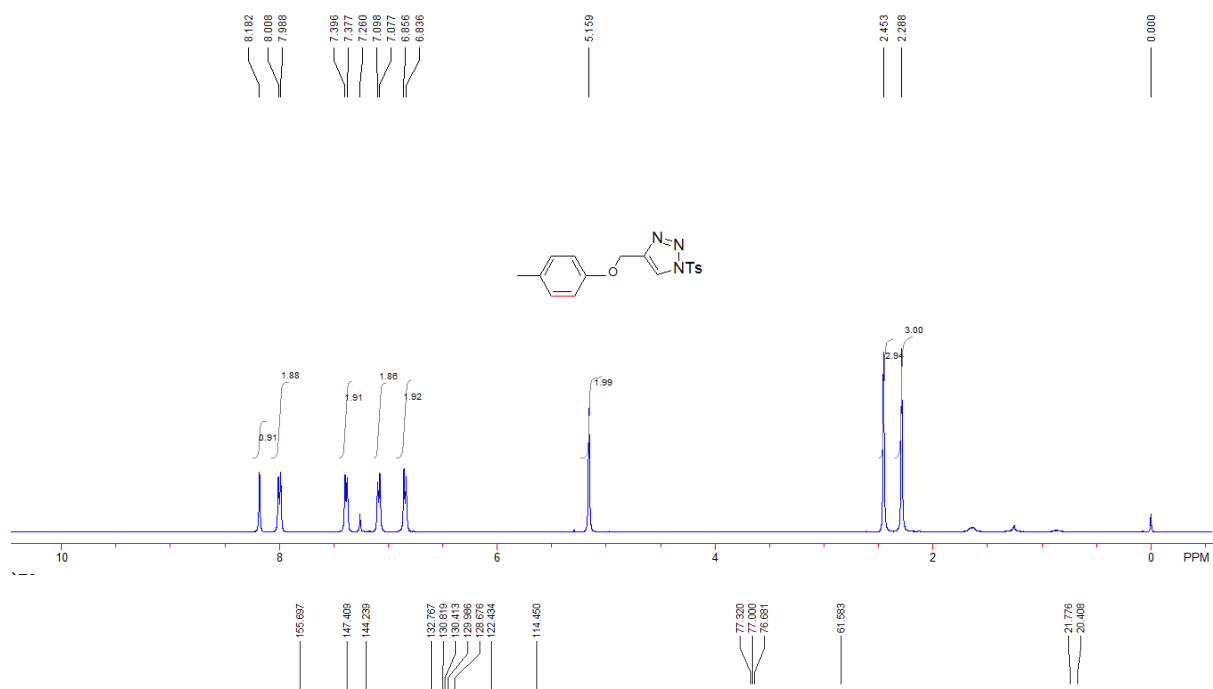
4-(4-Methoxyphenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole **1e**

5.0 mmol scale, a white solid, 76% yield (1.37 g). M.p.: 112-114 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.44 (s, 3H, CH₃), 3.75 (s, 3H, CH₃), 5.12 (s, 2H, CH₂), 6.82 (d, *J* = 9.2 Hz, 2H, Ar), 6.88 (d, *J* = 9.2 Hz, 2H, Ar), 7.37(d, *J* = 8.0 Hz, 2H, Ar), 7.98 (d, *J* = 8.0 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.7, 55.6, 62.1, 114.6, 115.7, 122.4, 128.6, 130.4, 132.7, 144.2, 147.4, 151.9, 154.3. IR (CH₂Cl₂) ν 3126, 3096, 2941, 1591, 1505, 1390, 1265, 1214, 1194, 1123, 1054, 1024, 1008, 990, 963, 841, 823, 814, 796, 700, 672 cm⁻¹. HRMS (ESI) Calcd. for C₁₇H₁₈N₃O₄S⁺ (M⁺+H) requires 360.1013, found: 360.1006.



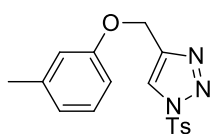
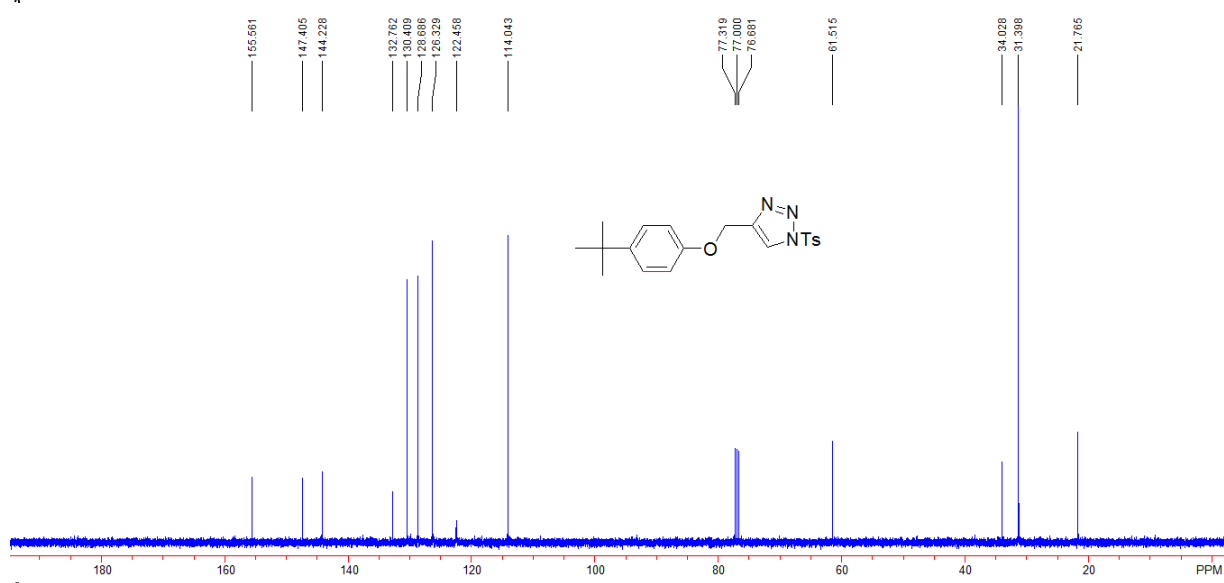
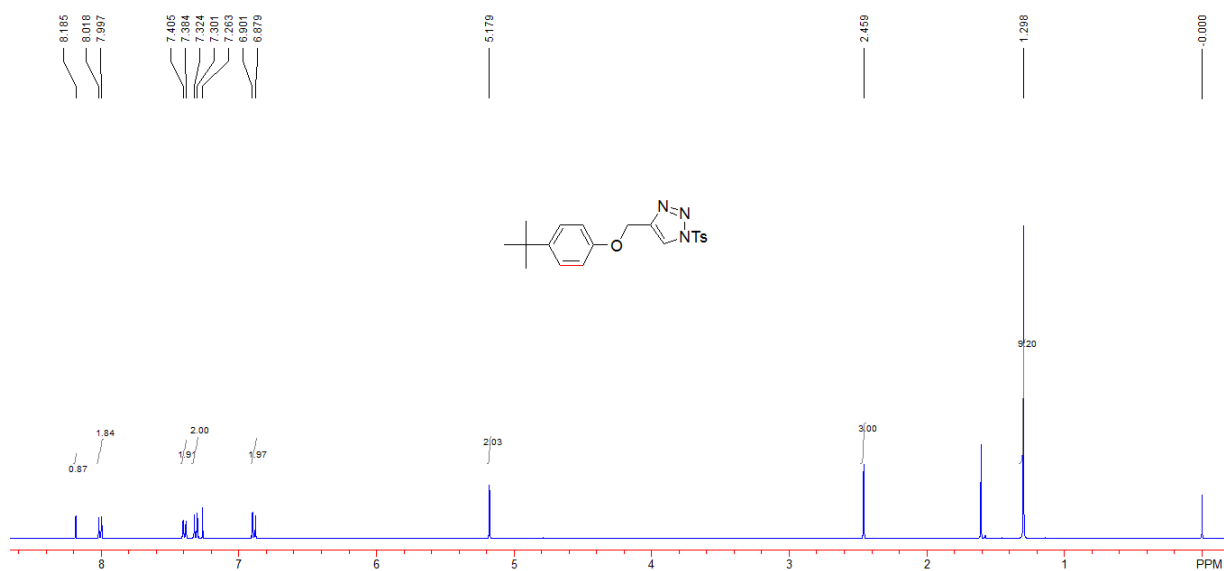
1-(Toluene-4-sulfonyl)-4-p-toloxymethyl-1H-[1,2,3]triazole 1f

5.0 mmol scale, a white solid, 75% yield (1.29 g). M.p.: 114 - 116 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.28 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 5.16 (s, 2H, CH₂), 6.84 (d, *J* = 8.0 Hz, 2H, Ar), 7.09 (d, *J* = 8.0 Hz, 2H, Ar), 7.39 (d, *J* = 7.6 Hz, 2H, Ar), 8.00 (d, *J* = 7.6 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 20.4, 21.8, 61.6, 114.5, 122.4, 128.7, 130.0, 130.4, 130.9, 132.8, 144.2, 147.4, 155.7. IR (CH₂Cl₂) ν 3133, 2924, 1614, 1509, 1399, 1232, 1196, 1054, 1010, 989, 966, 811, 792, 700, 672 cm⁻¹. HRMS (ESI) Calcd. for C₁₇H₁₈N₃O₃S (M+H⁺), requires 344.1063, found: 344.1072.



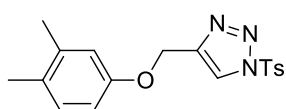
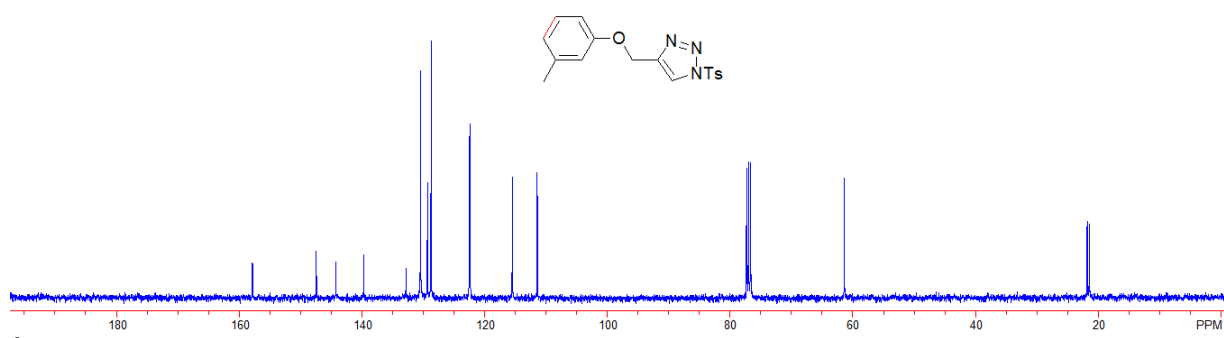
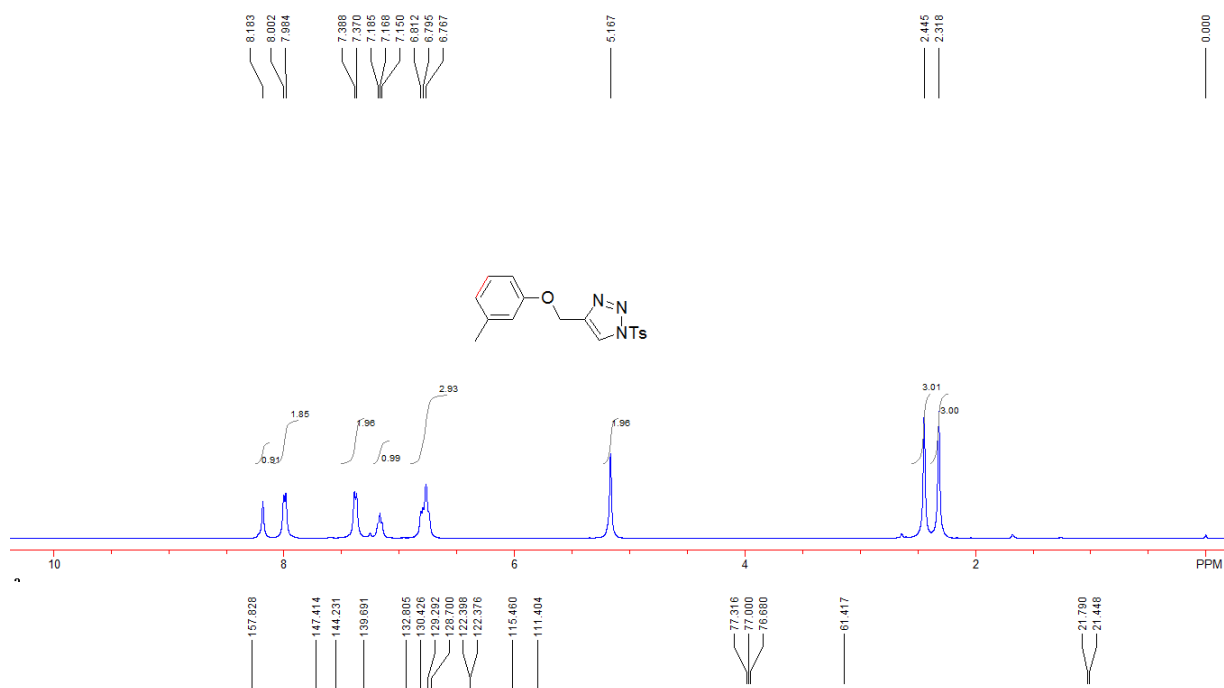
4-(4-Tert-butylphenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole **1g**

5.0 mmol scale, a white solid, 80% yield (1.54 g). M.p.: 128-130 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.30 (s, 9H, CH₃), 2.46 (s, 3H, CH₃), 5.18 (s, 2H, CH₂), 6.89 (d, *J* = 8.8 Hz, 2H, Ar), 7.31 (d, *J* = 8.8 Hz, 2H, Ar), 7.39 (d, *J* = 8.4 Hz, 2H, Ar), 8.00 (d, *J* = 8.4 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 31.4, 34.0, 61.5, 114.0, 122.5, 126.3, 128.7, 130.4, 132.8, 144.2, 147.4, 155.6. IR (CH₂Cl₂) ν 2954, 1607, 1514, 1385, 1242, 1208, 1194, 1182, 1121, 1093, 1047, 1011, 972, 857, 832, 811, 763, 701, 685 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₂₄N₃O₃S (M+H⁺), requires 386.1533, found: 386.1539.



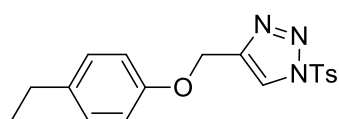
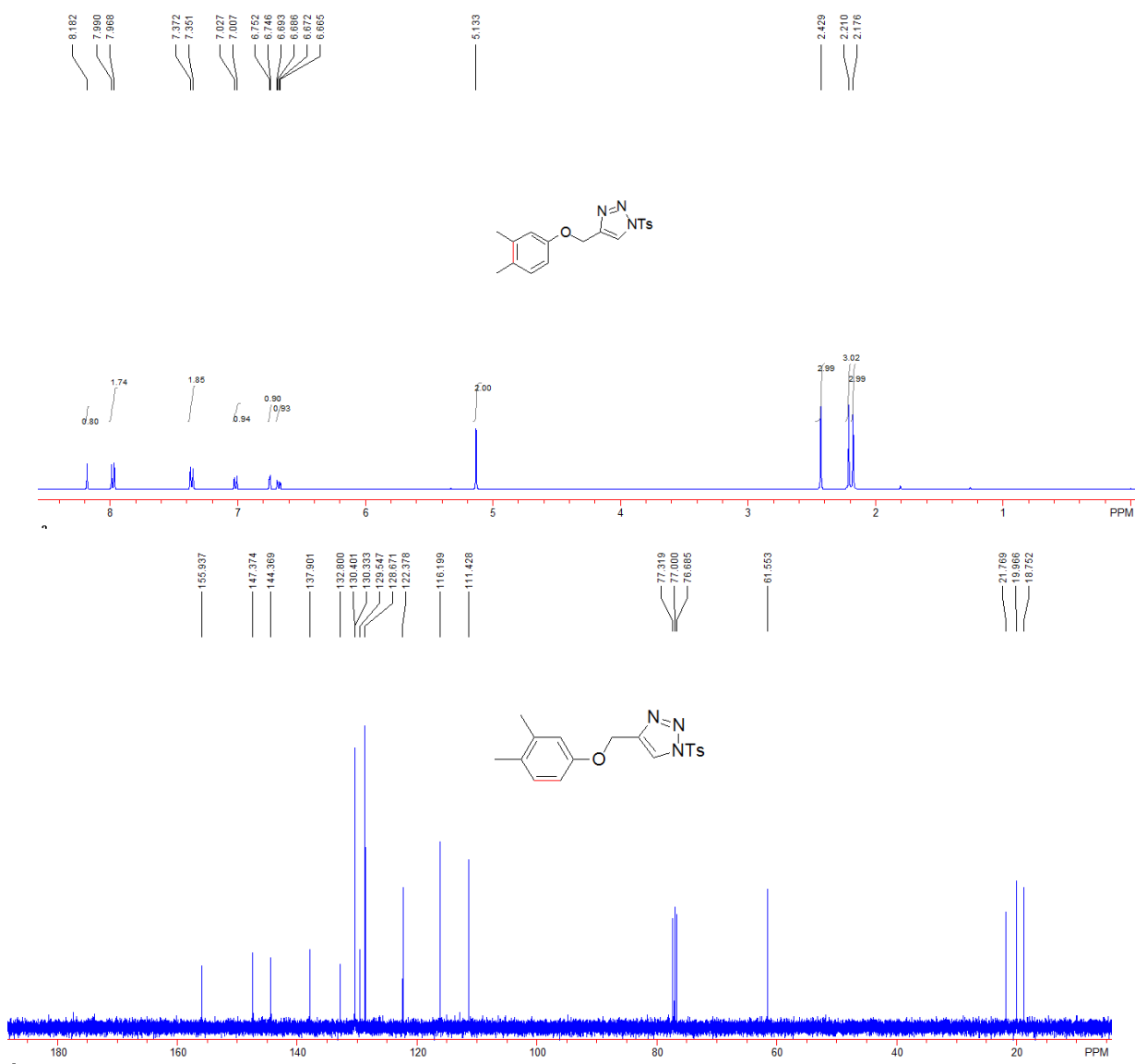
1-(Toluene-4-sulfonyl)-4-m-tolyloxymethyl-1H-[1,2,3]triazole **1h**

5.0 mmol scale, a white solid, 72% yield (1.24 g). M.p.: 135-137 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.32 (s, 3H, CH₃), 2.44 (s, 3H, CH₃), 5.17 (s, 2H, CH₂), 6.76-6.82 (m, 3H, Ar), 7.17 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.38 (d, *J* = 7.2 Hz, 2H, Ar), 7.99 (d, *J* = 7.2 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.4, 21.8, 61.4, 111.4, 115.5, 122.3, 122.4, 128.7, 129.3, 130.4, 132.8, 139.7, 144.2, 147.4, 157.8. IR (CH₂Cl₂) ν 3290, 1591, 1492, 1407, 1390, 1262, 1210, 1192, 1038, 970, 810, 781, 691, 673 cm⁻¹. HRMS (ESI) Calcd. for C₁₇H₁₈N₃O₃S⁺ (M⁺+H) requires 344.1063, found: 344.1073.



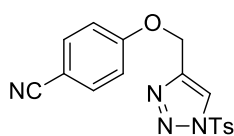
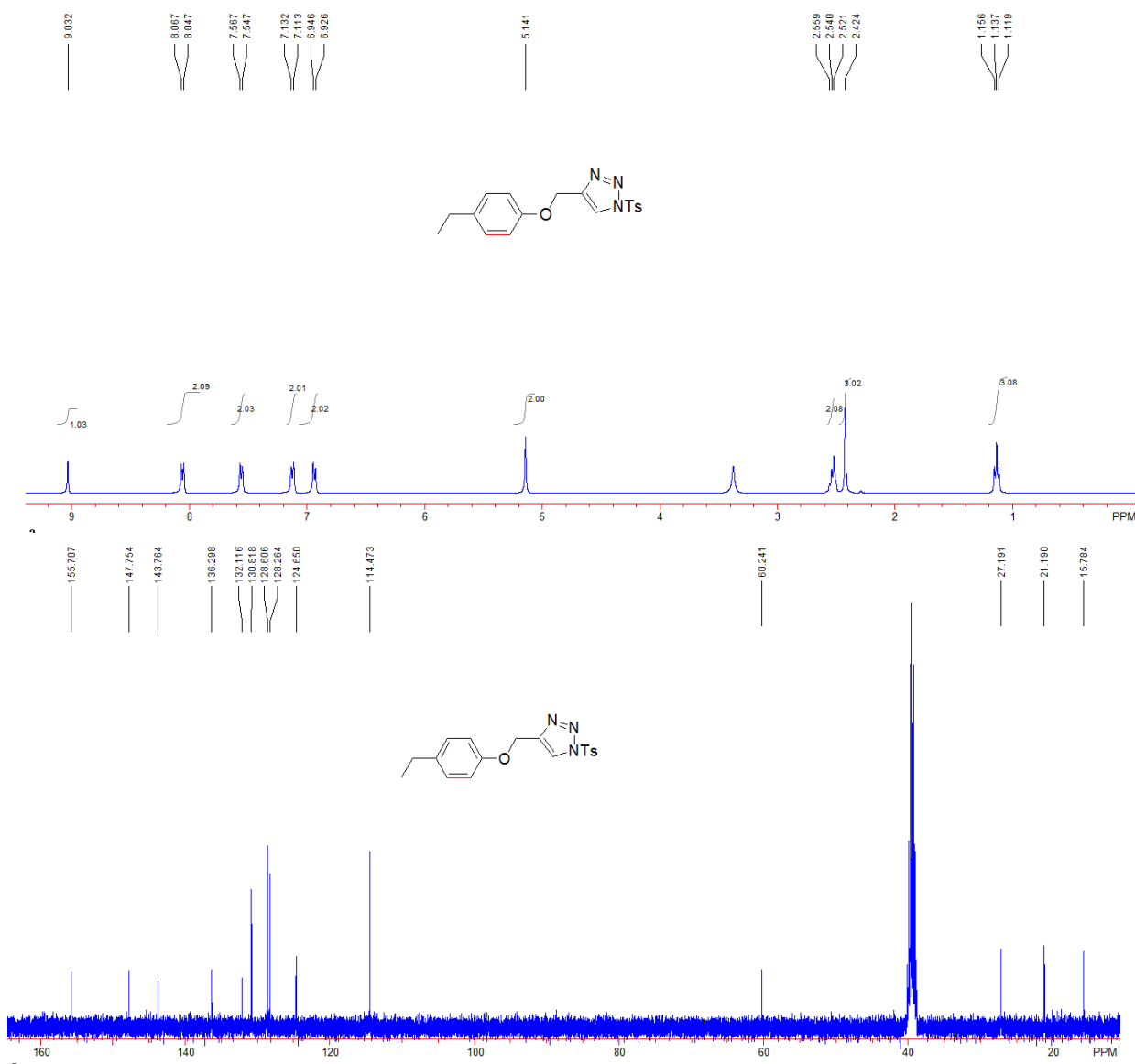
4-(3,4-Dimethylphenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1i

1.0 mmol scale, a white solid, 80% yield (286 mg). M.p.: 136-138 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.18 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 5.13 (s, 2H, CH₂), 6.68 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H, Ar), 6.75 (d, *J* = 2.8 Hz, 1H, Ar), 7.01 (d, *J* = 8.4 Hz, 1H, Ar), 7.36 (d, *J* = 8.4 Hz, 2H, Ar), 7.98 (d, *J* = 8.4 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 18.8, 20.0, 221.8, 61.6, 111.6, 116.2, 122.4, 128.7, 129.5, 130.3, 130.4, 132.8, 137.9, 144.4, 147.4, 155.9. IR (CH₂Cl₂) ν 3147, 2925, 1069, 1500, 1455, 1353, 1296, 1251, 1204, 1188, 1175, 1112, 1033, 1008, 918, 815, 778, 682, 662 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₂₀N₃O₃S (M+H⁺), requires 358.1220, found: 358.1214.



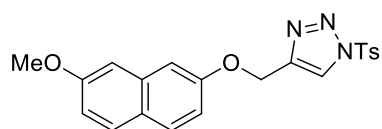
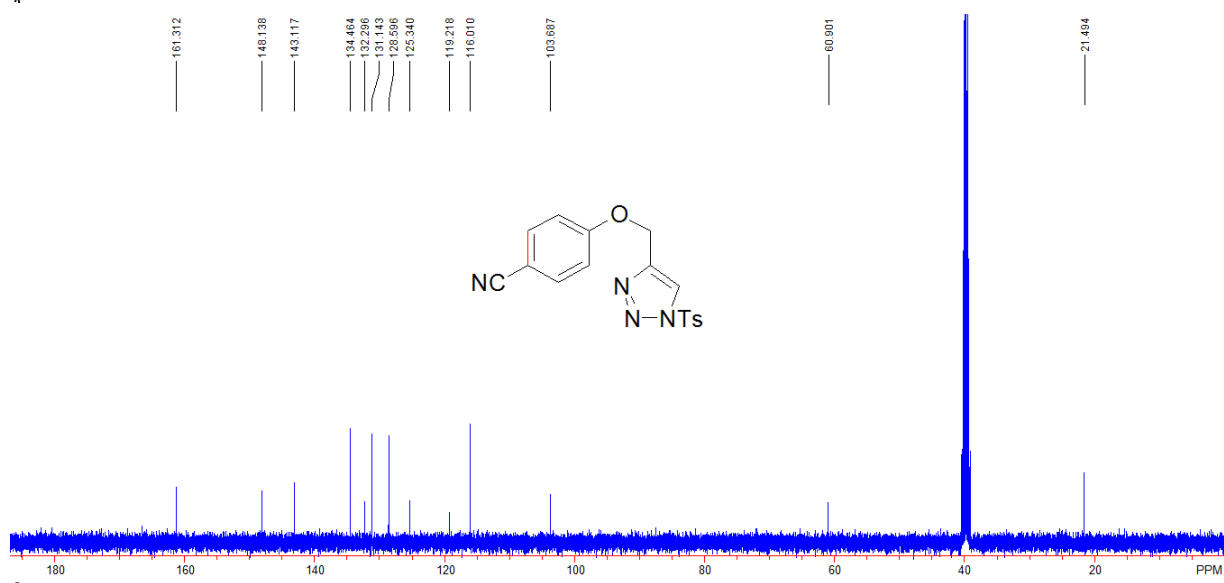
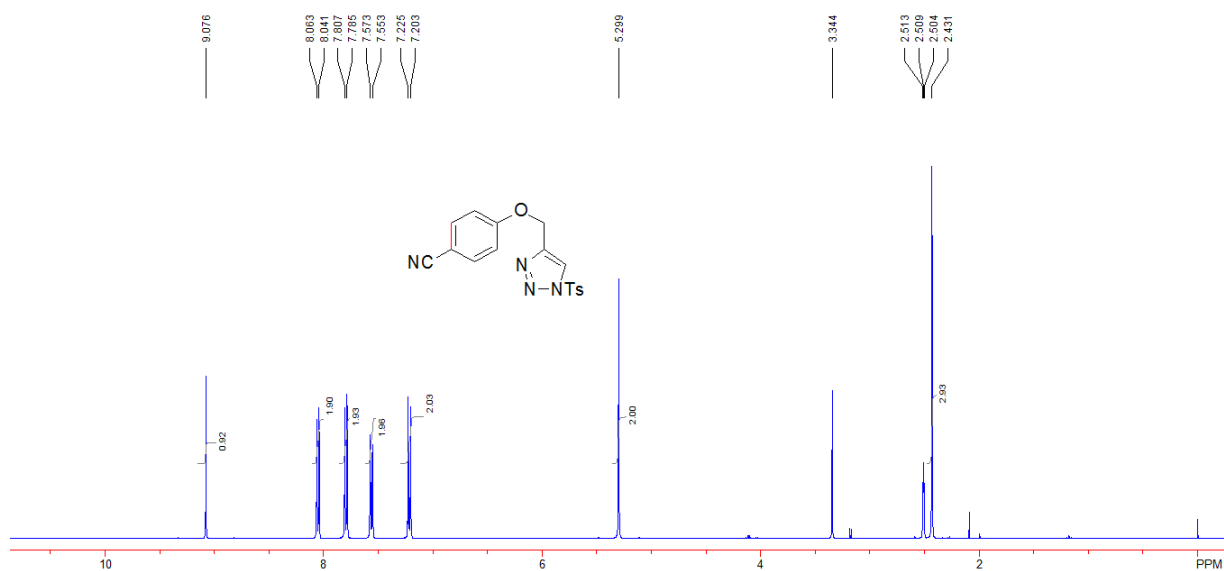
4-(4-Ethylphenoxy)methyl-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1j

1.0 mmol scale, a white solid, 89% yield (318 mg). M.p.: 95-97 °C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 1.14 (t, J = 7.6 Hz, 3H, CH₃), 2.42 (s, 3H, CH₃), 2.52 (q, J = 7.6 Hz, 2H, CH₂), 5.14 (s, 2H, CH₂), 6.93 (d, J = 8.0 Hz, 2H, Ar), 7.12 (d, J = 8.0 Hz, 2H, Ar), 7.55 (d, J = 8.0 Hz, 2H, Ar), 8.05 (d, J = 8.0 Hz, 2H, Ar), 9.03 (s, 1H, CH=). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 15.8, 21.2, 27.2, 60.2, 114.5, 124.6, 128.3, 128.6, 130.9, 132.1, 136.3, 143.8, 147.8, 155.7. IR (CH₂Cl₂) ν 3115, 1631, 1609, 1515, 1392, 1248, 1222, 1212, 1187, 1155, 1135, 1118, 1028, 1005, 876, 832, 820, 810, 766, 734, 685 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₂₀N₃O₃S (M+H⁺), requires 358.1220, found: 358.1211.



4-[1-(Toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzonitrile 1k

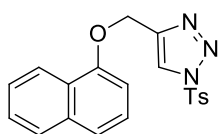
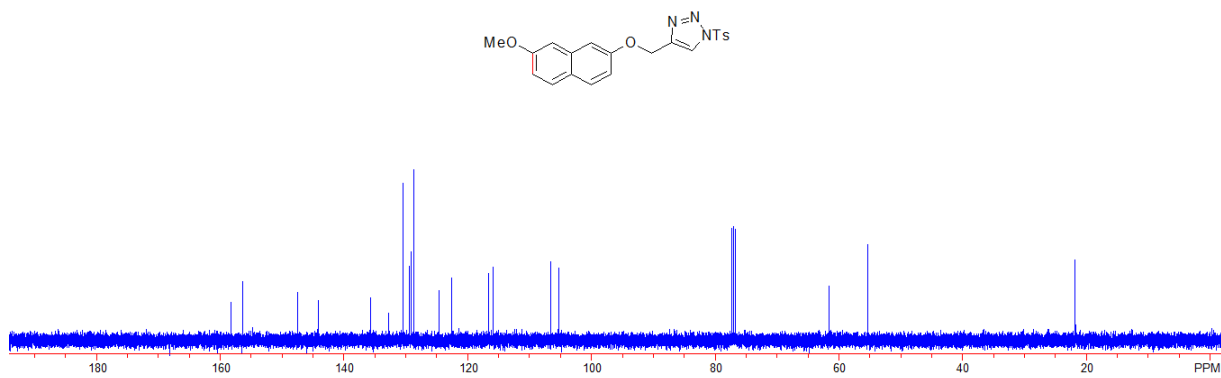
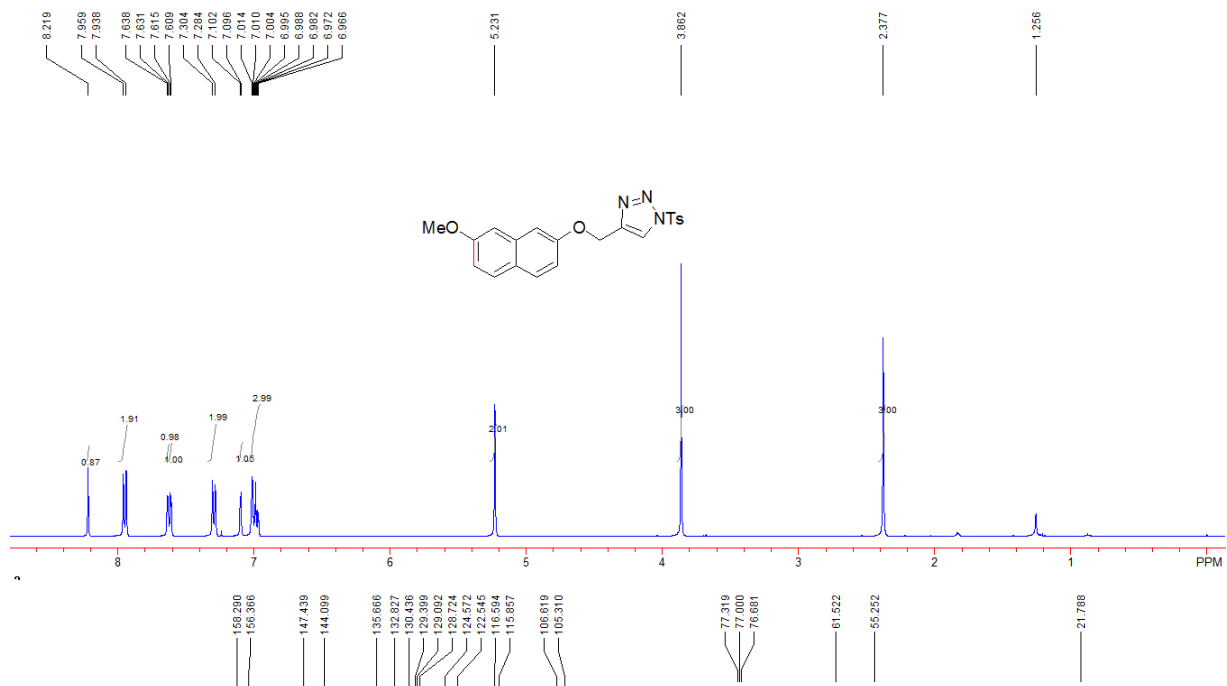
1.0 mmol scale, a white solid, 86% yield (305 mg). M.p.: 148-151 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 2.43 (s, 3H, CH₃), 5.30 (s, 2H, CH₂), 7.21 (d, *J* = 8.8 Hz, 2H, Ar), 7.56 (d, *J* = 8.8 Hz, 2H, Ar), 7.79 (d, *J* = 8.8 Hz, 2H, Ar), 8.05 (d, *J* = 8.8 Hz, 2H, Ar), 9.08 (s, 1H, CH=). ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 21.9, 60.9, 103.7, 116.0, 119.2, 125.3, 128.6, 131.1, 132.3, 134.5, 143.1, 148.1, 161.3. IR (CH₂Cl₂) ν 3115, 2315, 2295, 1611, 1602, 1344, 1272, 1258, 1221, 1187, 1135, 1128, 9805, 876, 832, 821, 810, 746, 734, 695 cm⁻¹. HRMS (ESI) Calcd. for C₁₇H₁₅N₄O₃S⁺ (M⁺+H) requires 355.0859, found: 355.0872.



5-(7-Methoxynaphthalen-2-yloxymethyl)-3H-pyrazole 11.

1.0 mmol scale, a white solid, 80% yield (328 mg). M.p.: 142-144 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.38 (s, 3H, CH₃), 3.87 (s, 3H, CH₃), 5.23 (s, 2H, CH₂), 6.96-7.02 (m, 3H, Ar), 7.10 (d, *J* = 2.4 Hz, 1H, Ar), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.61 (d, *J* = 2.4 Hz, 1H, Ar), 7.63 (d, *J* = 2.4 Hz, 1H, Ar), 7.94 (d, *J* = 8.4 Hz, 2H, Ar), 8.22 (s, 1H, CH=). ¹³C NMR δ (CDCl₃, 100 MHz, TMS) δ 21.8, 55.2, 61.5, 105.3, 106.6, 115.8, 116.6, 122.5, 124.6, 128.7, 129.1, 129.4, 130.4, 132.8, 135.7, 144.1, 147.4, 156.4, 158.3. IR (CH₂Cl₂) ν 3125, 2961, 2923, 1611, 1510, 1386, 1233, 1195, 1176, 1093, 1058, 1006, 984, 959, 824, 812, 780, 705, 681 cm⁻¹. HRMS (ESI) Calcd.

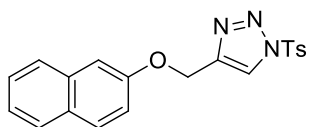
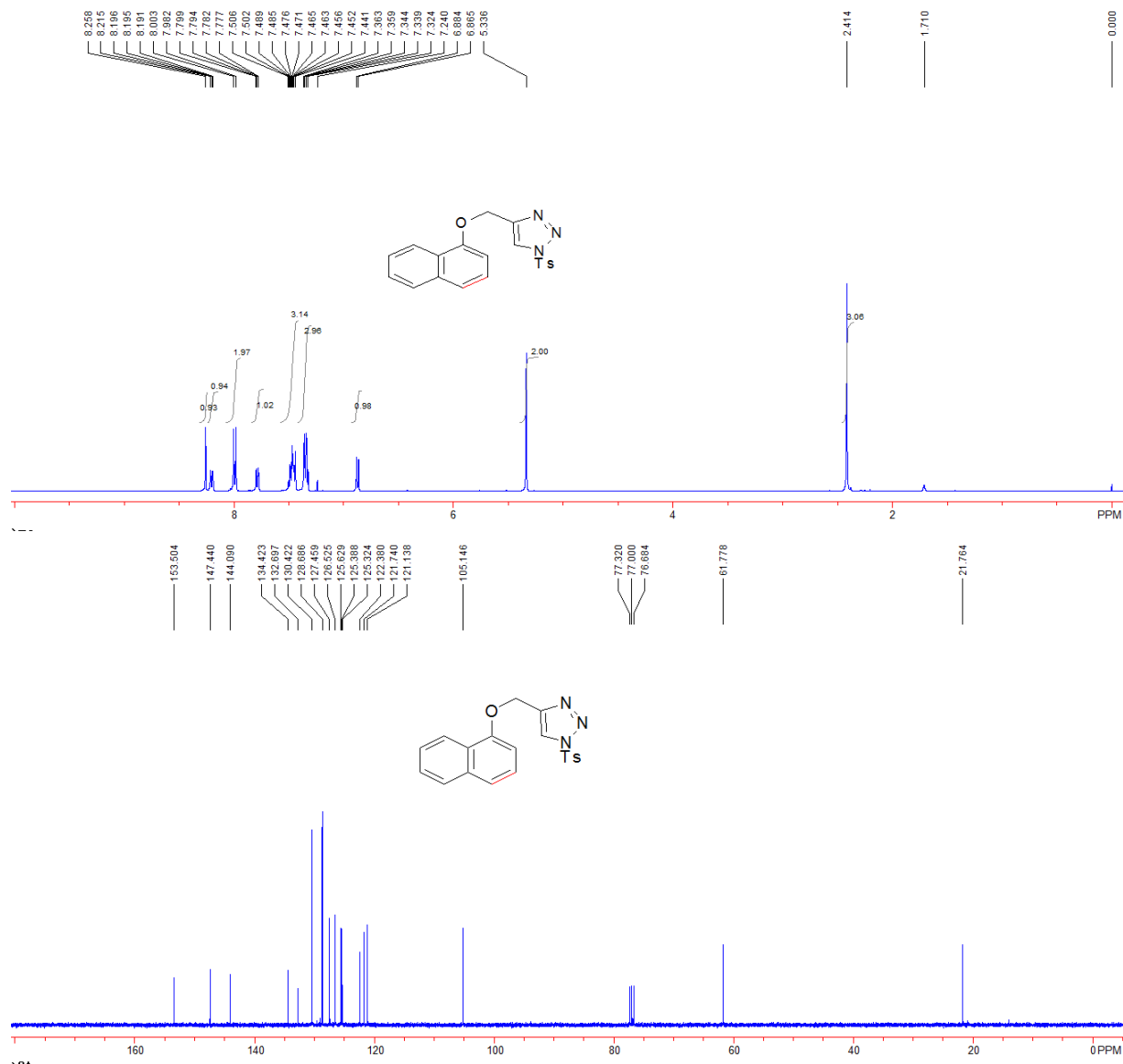
for C₂₁H₂₀N₃O₄S (M+H⁺), requires 410.1169, found: 410.1161.



4-(Naphthalen-1-yloxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1m

1.0 mmol scale, a white solid, 81% yield (308 mg). M.p.: 148-150 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.41 (s, 3H, CH₃), 5.34 (s, 2H, CH₂), 6.87 (d, *J* = 7.6 Hz, 1H, Ar), 7.24-7.27 (m, 3H, Ar), 7.44-7.51 (m, 3H, Ar), 7.79 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 1H, Ar), 7.99 (d, *J* = 8.4 Hz, 2H, Ar), 8.19-8.22 (m, 1H, Ar), 8.26 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 61.8, 105.1, 121.1, 121.7, 122.4, 125.3, 125.4, 125.6, 126.5, 127.5, 128.7, 130.4, 132.7, 134.4, 144.1, 147.4, 153.5. IR (CH₂Cl₂) ν 2012, 1976, 1576, 1507, 1272, 1229, 1157, 1123, 1109, 1031, 1006

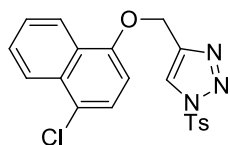
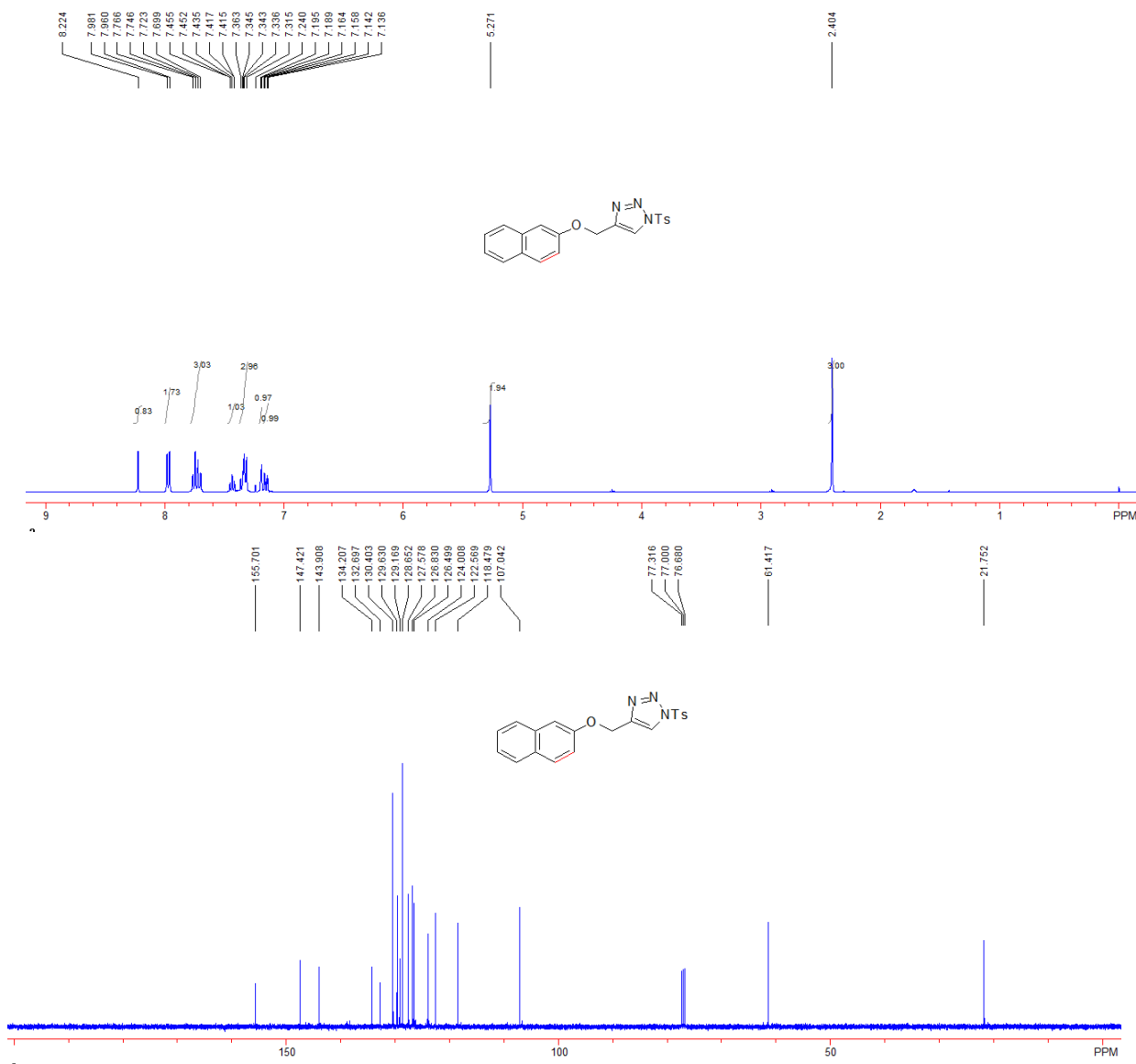
cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₁₈N₃O₃S (M+H⁺), requires 380.1063, found: 380.1059.



4-(Naphthalen-2-yloxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1n

1.0 mmol scale, a white solid, 88% yield (334 mg). M.p.: 144-147 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.40 (s, 3H, CH₃), 5.27 (s, 2H, CH₂), 7.15 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H, Ar), 7.19 (d, *J* = 2.4 Hz, 1H, Ar), 7.31-7.37 (m, 3H, Ar), 7.41-7.46 (m, 1H, Ar), 7.73 (m, 3H, Ar), 7.97 (d, *J* = 8.4 Hz, 2H, Ar), 8.22 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 61.4, 107.0, 118.5, 122.6, 124.0, 126.5, 126.8, 127.6, 128.6, 129.2, 129.6, 130.4, 132.7, 134.2, 143.9, 147.4, 155.7. IR (CH₂Cl₂) ν 1259, 1217, 1193, 1170, 1143, 1119, 1033, 1006, 988, 952, 917, 844,

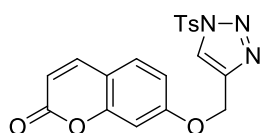
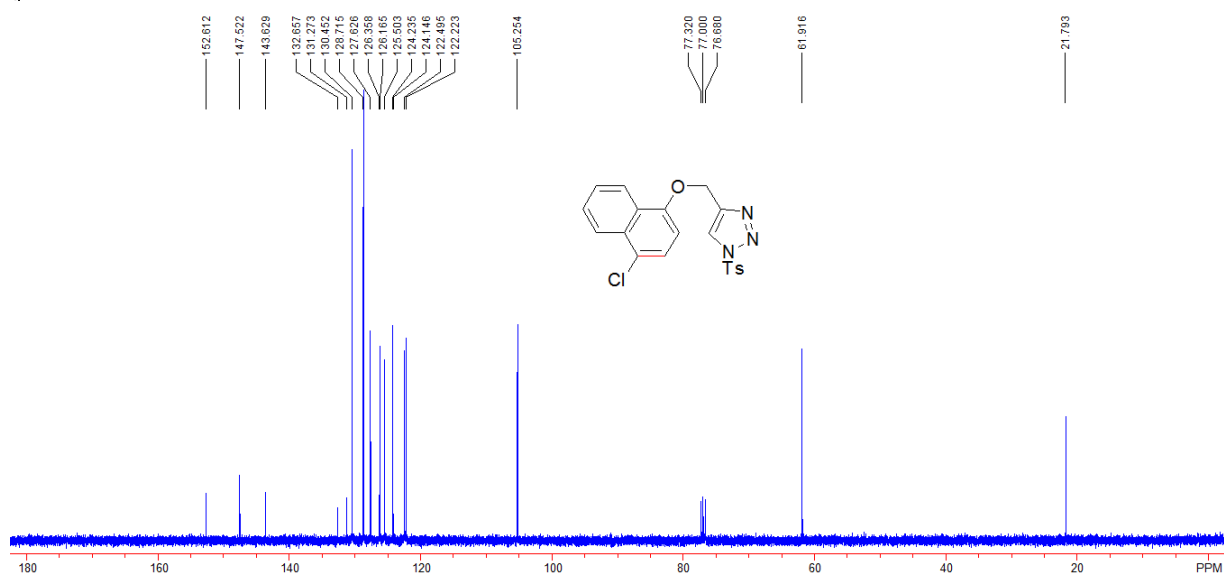
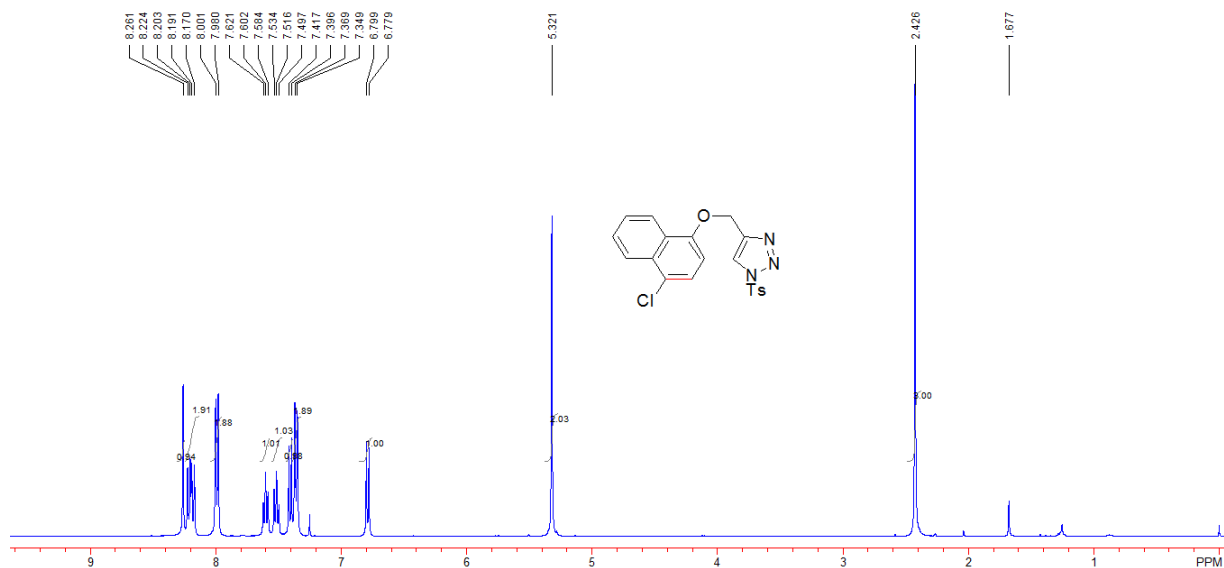
809, 796, 754, 740, 700, 681 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}^+$), requires 380.1063, found: 380.1060.



4-(4-Chloronaphthalen-1-yloxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 10

1.0 mmol scale, a white solid, 80% yield (331 mg). M.p.: 131-133 °C. ^1H NMR (CDCl₃, 400 MHz, TMS) δ 2.43 (s, 3H, CH₃), 5.32 (s, 2H, CH₂), 6.78 (d, J = 8.0, 1H, Ar), 7.35 (d, J = 8.0 Hz, 2H, Ar), 7.40 (d, J = 8.0 Hz, 1H, Ar), 7.52 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.60 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.99 (d, J = 8.4 Hz, 2H, Ar), 8.20 (dd, J = 8.4 Hz, J = 8.4 Hz, 2H, Ar), 8.26 (s, 1H, CH=). ^{13}C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 61.9, 105.3, 122.2, 122.5, 124.1,

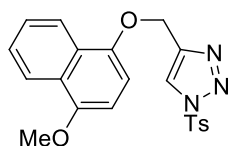
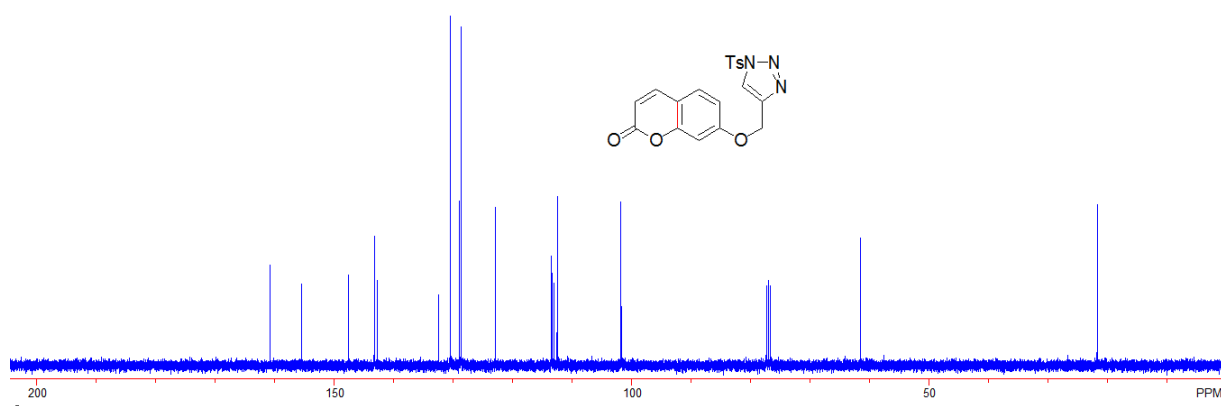
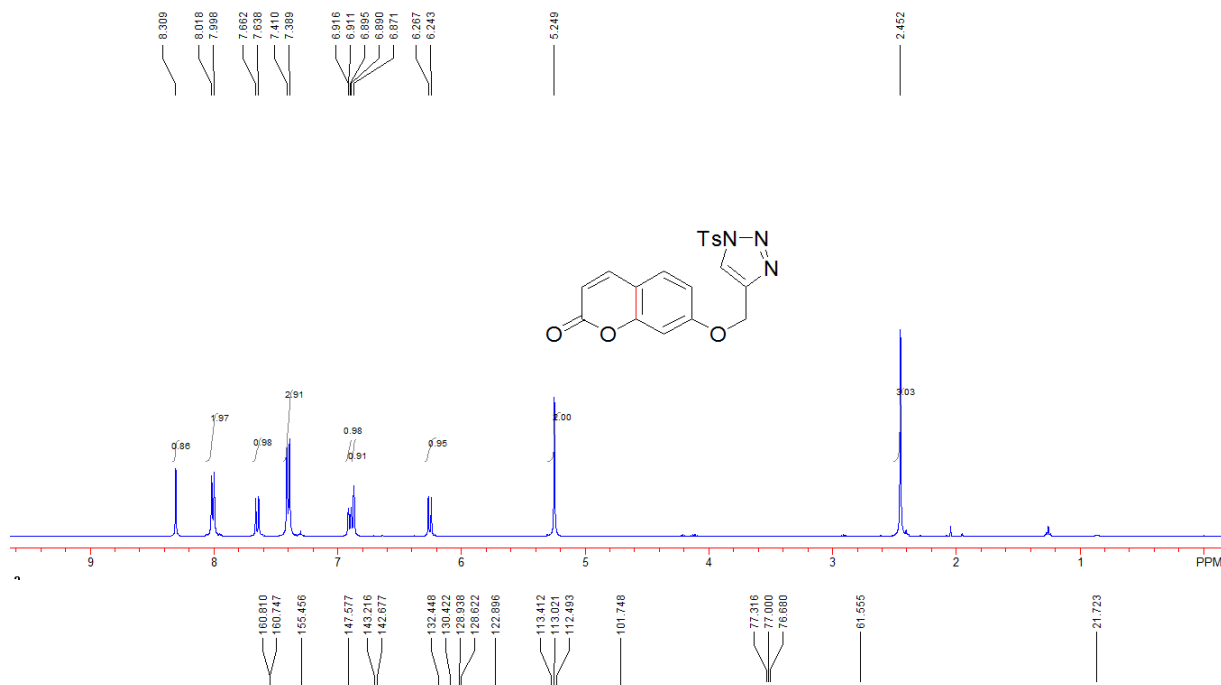
124.2, 125.5, 126.2, 126.4, 127.6, 128.7, 130.4, 131.3, 132.6, 143.6, 147.5, 152.6. IR (CH₂Cl₂) v 3124, 2960, 2920, 1609, 1520, 1376, 1238, 1199, 1175, 1093, 1059, 1008, 985, 957, 823, 802, 789, 715, 681 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₁₇ClN₃O₃S (M+H⁺), requires 414.0674, found: 414.0674.



7-[1-(Toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one 1p

1.0 mmol scale, a white solid, 84% yield (333 mg). M.p.: 175-177 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.45 (s, 3H, CH₃), 5.25 (s, 2H, CH₂), 6.25 (d, *J* = 9.6 Hz, 1H, Ar), 6.87 (s, 1H, Ar), 6.89-6.92 (m, 1H, Ar), 7.40 (d, *J* = 8.0 Hz, 3H, Ar), 7.65 (d, *J* = 9.6 Hz, 1H, Ar), 8.00 (d, *J* = 8.0

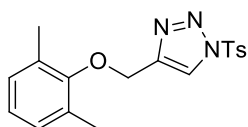
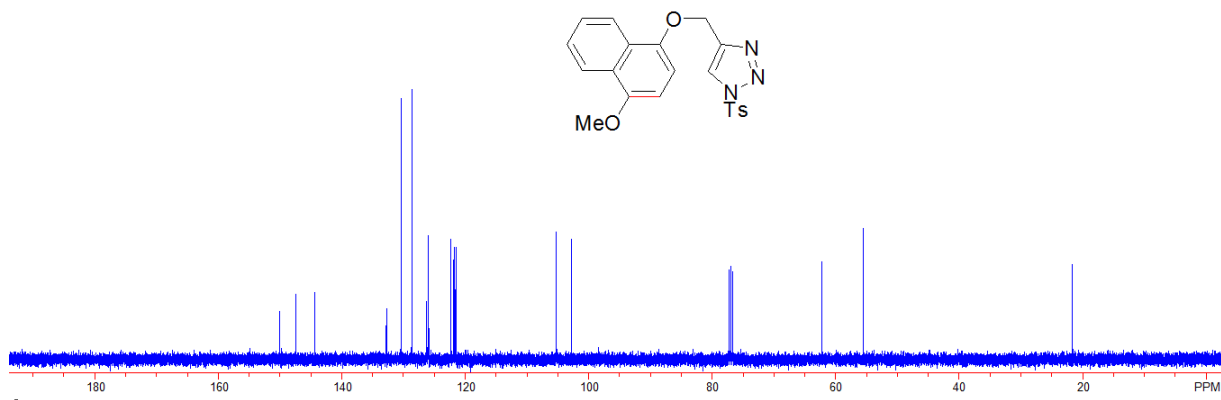
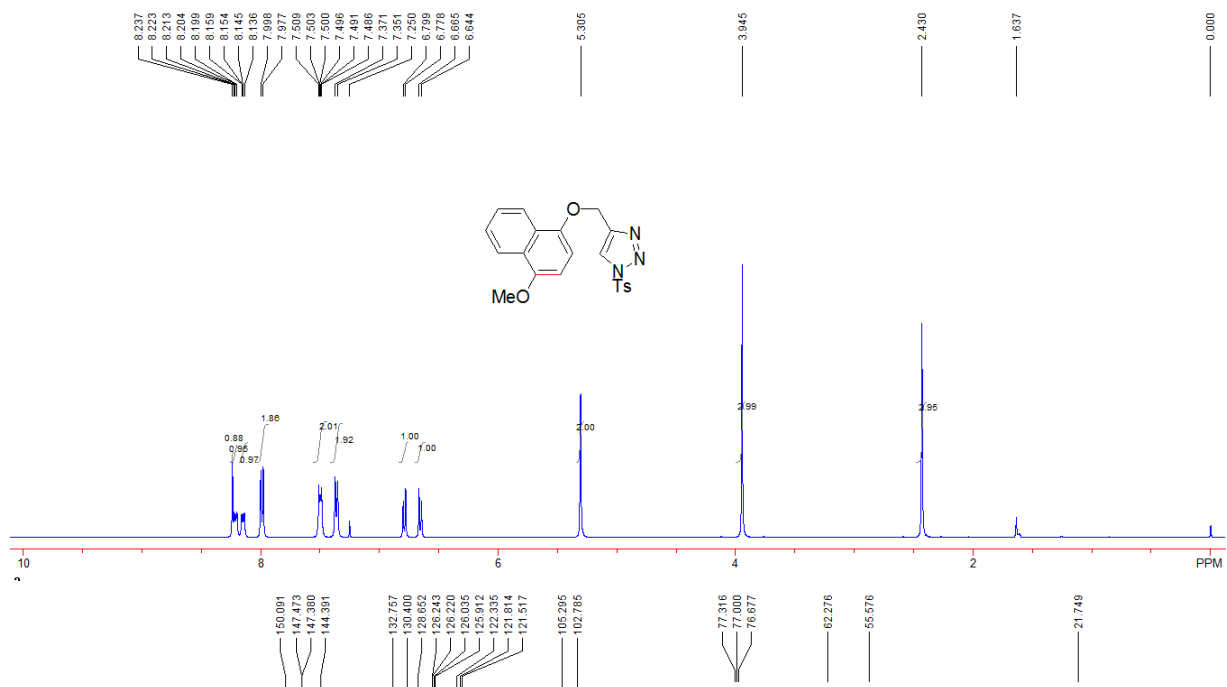
Hz, 2H, Ar), 8.31 (s, 1H, CH=). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.7, 61.6, 101.7, 112.5, 113.0, 113.4, 122.9, 128.6, 128.9, 130.4, 132.4, 142.7, 143.2, 147.6, 155.4, 160.7, 160.8. IR (CH_2Cl_2) ν 3124, 2162, 1718, 1612, 1389, 1278, 1178, 1158, 1123, 1029, 978, 849, 833, 782, 700, 669 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_3\text{O}_5\text{S}^+$ (M^++H) requires 398.0805, found: 398.0806.



4-(4-Methoxynaphthalen-1-yloxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1q

1.0 mmol scale, a white solid, 76% yield (311 mg). M.p.: 155-157 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.43 (s, 3H, CH_3), 3.94 (s, 3H, CH_3), 5.30 (s, 2H, CH_2), 6.65 (d, $J = 8.4$, 1H, Ar), 6.78 (d, $J = 8.4$ Hz, 1H, Ar), 7.36 (d, $J = 8.4$ Hz, 2H, Ar), 7.48-7.51 (m, 2H, Ar), 7.98 (d, $J = 8.4$

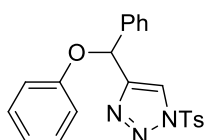
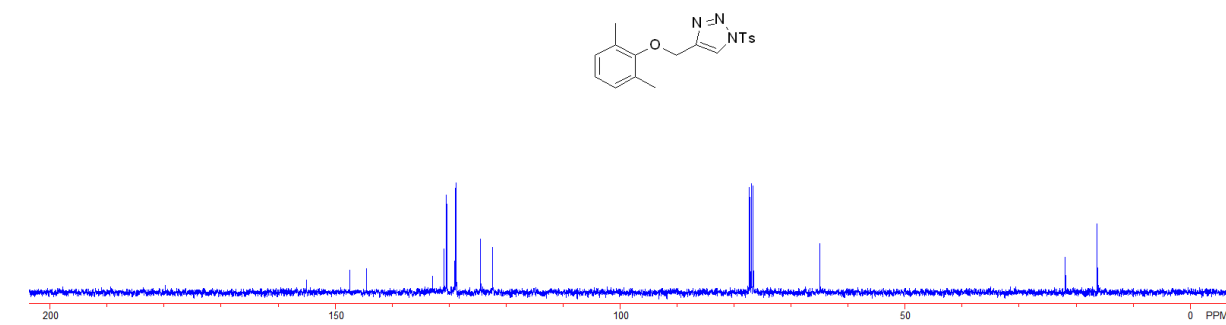
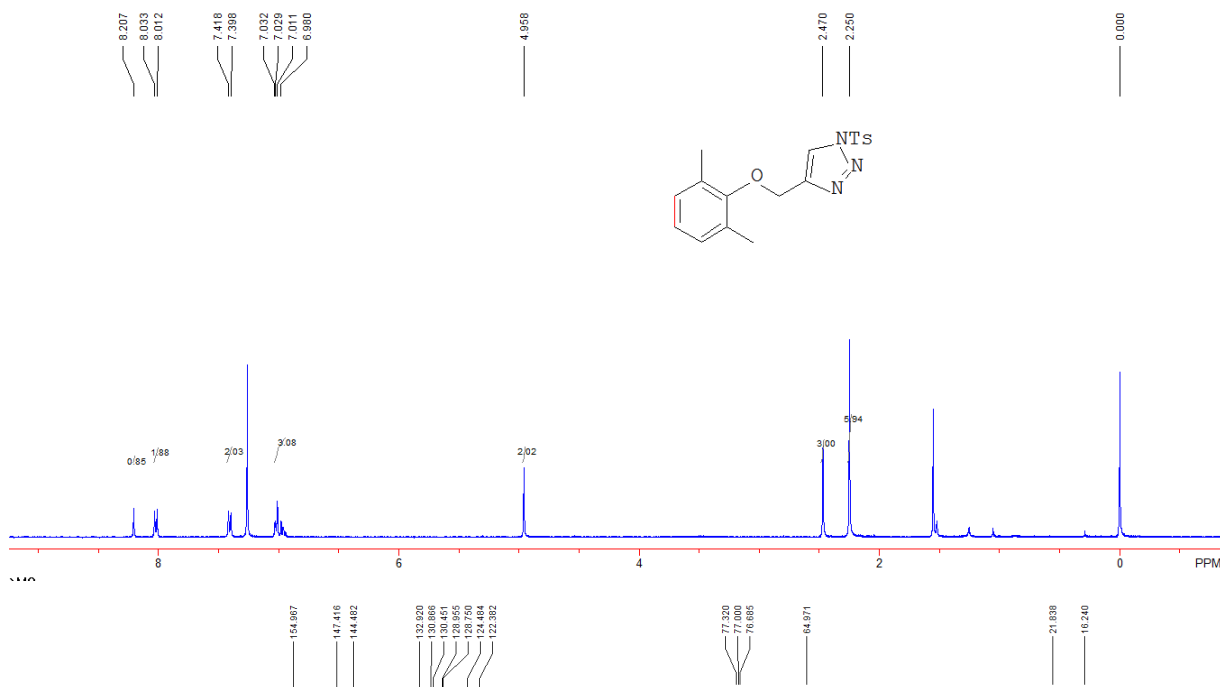
Hz, 2H, Ar), 8.13-8.16 (m, 1H, Ar), 8.19-8.23 (m, 1H, Ar), 8.24 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.7, 55.6, 62.3, 102.8, 105.3, 121.5, 121.8, 122.3, 125.9, 126.0, 126.2, 126.3, 128.6, 130.4, 132.7, 144.4, 147.4, 147.5, 150.1. IR (CH₂Cl₂) ν 3177, 3064, 1596, 1466, 1394, 1311, 1277, 1218, 1194, 1122, 1102, 1026, 972, 826, 754, 728, 690, 670 cm⁻¹. HRMS (ESI) Calcd. for C₂₁H₂₀N₃O₄S (M+H⁺), requires 410.1169, found: 410.1165.



4-(2,6-Dimethylphoxymethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1r

6.4 mmol scale, a white solid, 93% yield (2.1 g). M.p.: 120-122 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.25 (s, 6H, CH₃), 2.47 (s, 3H, CH₃), 4.96 (s, 2H, CH₂), 6.98-7.03 (m, 3H, Ar), 7.41 (dd,

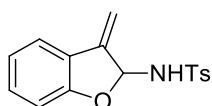
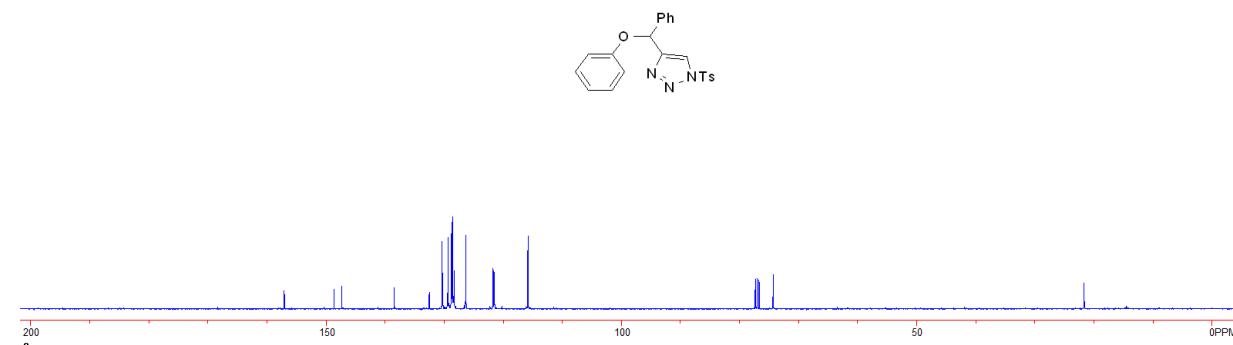
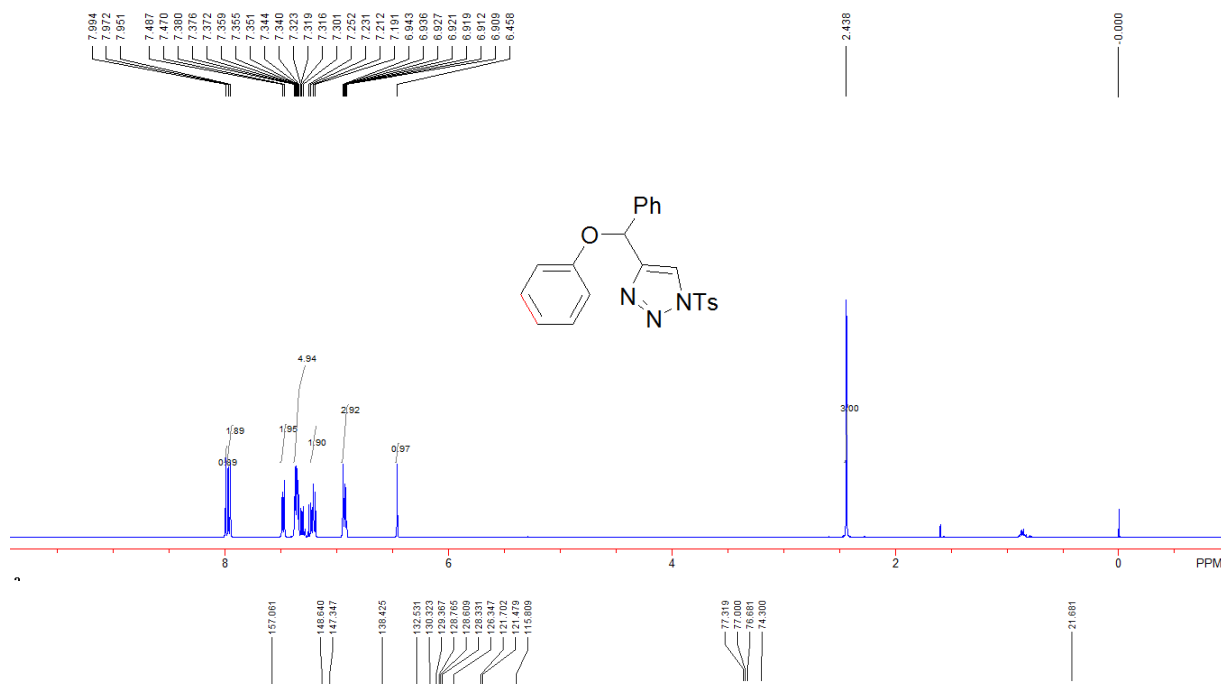
$J = 8.0$ Hz, 2H, Ar), 8.02 (d, $J = 8.0$ Hz, 2H, Ar), 8.21 (s, 1H, CH=). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 16.2, 21.8, 65.0, 122.4, 124.5, 128.7, 129.0, 130.4, 130.9, 133.0, 144.5, 147.4, 155.0. IR (CH_2Cl_2) ν 2921, 2848, 1456, 1366, 1345, 1319, 1302, 1237, 1163, 1152, 1086, 1050 965, 924, 823, 804, 790, 663 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_3\text{S}^+$ (M^++H) requires 358.1220, found: 358.1220



4-(Phenoxyphenylmethyl)-1-(toluene-4-sulfonyl)-1H-[1,2,3]triazole 1s

0.4 mmol scale, a white solid, 83% yield (134 mg). M.p.: 142-144 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 6.46 (s, 1H, CH), 6.90-6.95 (m, 3H, Ar), 7.19-7.24 (m, 2H, Ar),

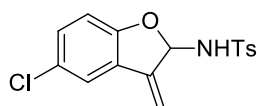
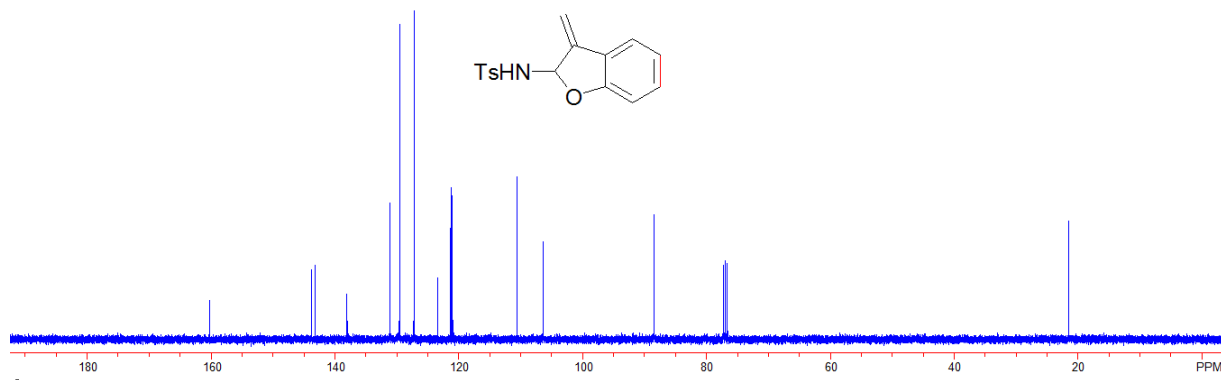
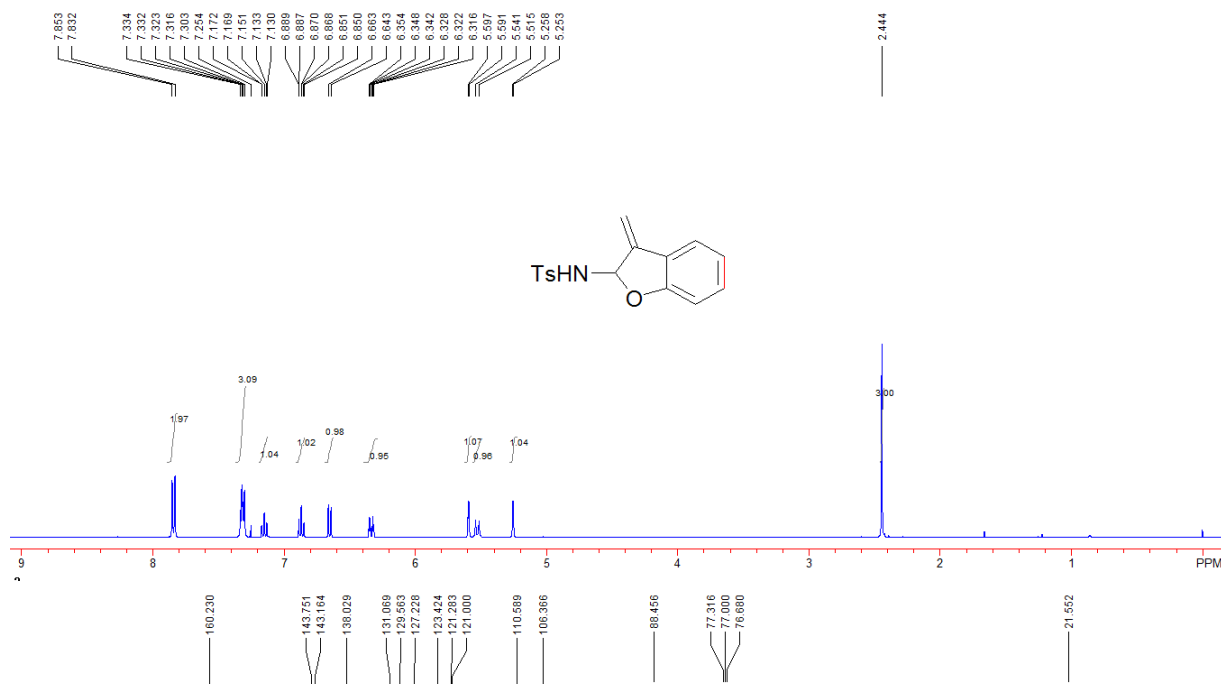
7.30-7.38 (m, 5H, Ar), 7.48 (d, $J = 8.4$ Hz, 2H, Ar), 7.96 (d, 2H, $J = 8.4$ Hz, Ar). 7.99 (s, 1H, CH=), ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.7, 74.3, 115.8, 121.5, 121.7, 126.3, 128.3, 128.6, 128.8, 129.4, 130.3, 132.5, 138.4, 147.3, 148.6, 157.1. IR (CH_2Cl_2) ν 2954, 2922, 2853 1458, 1376, 1259, 1024, 804 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_3\text{S}^+$ ($\text{M}^+ + \text{H}$) requires 406.1220, found: 406.1223.



4-Methyl-N-(3-methylene-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide 2a.

0.2 mmol scale, a white solid, 95% yield (57 mg). M.p.: 161-163 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 5.26 (d, $J = 2.0$ Hz, 1H, CH=), 5.53 (d, $J = 10.4$ Hz, 1H, NH), 5.60 (d, $J = 2.0$ Hz, 1H, CH=), 6.37 (dt, $J = 2.0\text{Hz}$, $J = 10.4$ Hz, 1H, CH), 6.65 (d, $J = 8.0$ Hz, 1H, Ar),

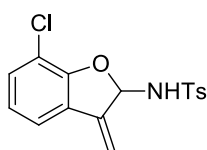
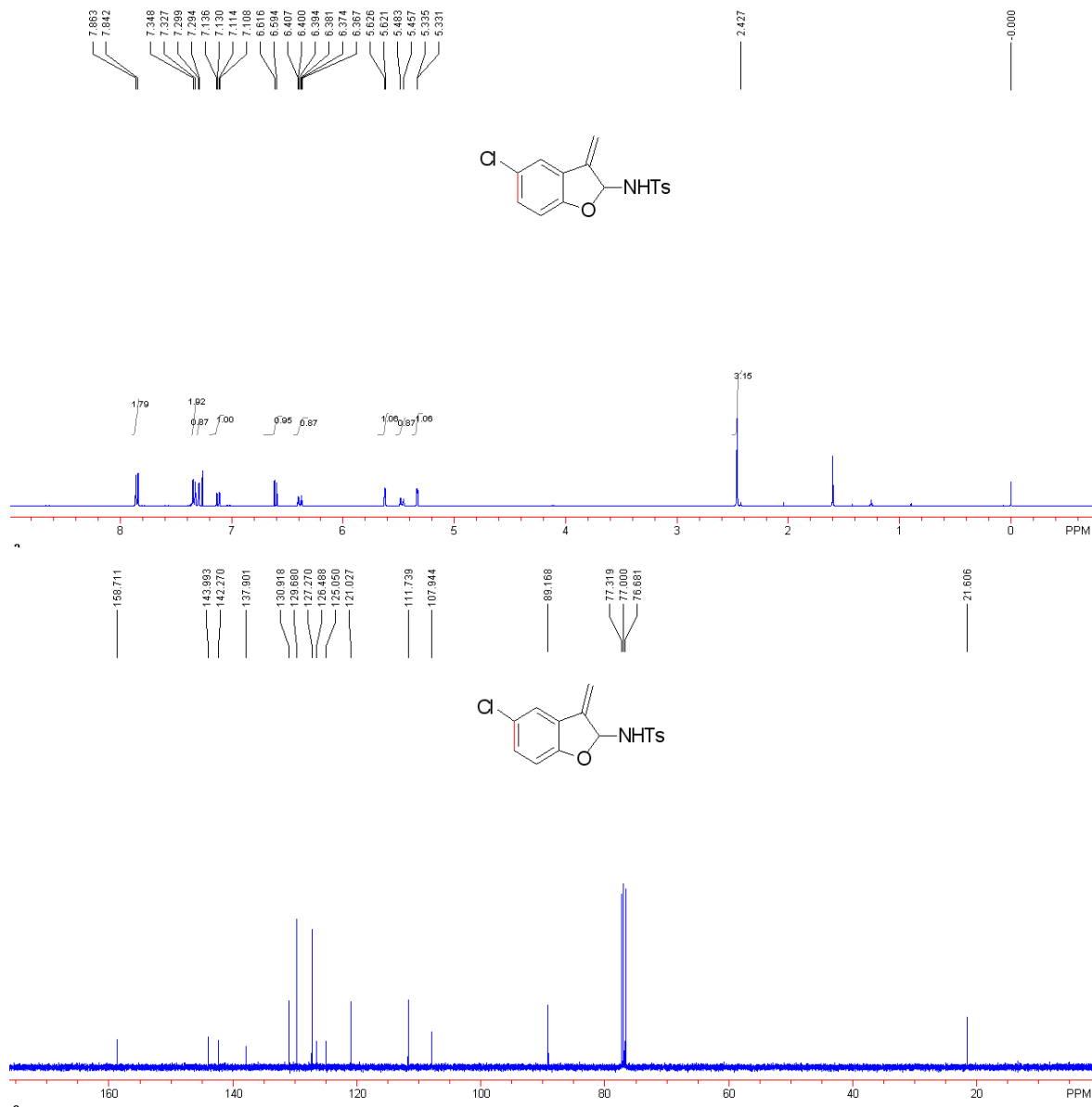
6.85-6.90 (m, 1H, Ar), 7.13-7.18 (m, 1H, Ar), 7.30-7.34 (m, 3H, Ar), 7.84 (d, $J = 8.4$ Hz, 2H, Ar).
 ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 21.6, 88.4, 106.4, 110.6, 121.0, 121.3, 123.4, 127.2, 129.6, 131.1, 138.0, 143.2, 143.8, 160.2. IR (CH_2Cl_2) ν 3355, 3260, 1596, 1450, 1387, 1337, 1299, 1231, 1157, 1090, 1017, 900, 847, 811, 759, 745, 702, 692, 665 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{16}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) requires 302.0845, found: 302.0848.



N-(5-Chloro-3-methylene-2,3-dihydrobenzofuran-2-yl)-4-methylbenzenesulfonamide **2b**

0.2 mmol scale, a white solid, 72% yield (48 mg). M.p.: 191-193 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.43 (s, 3H, CH_3), 5.33 (d, $J = 2.4$ Hz, 1H, $\text{CH}=\text{C}$), 5.46 (d, $J = 10.8$ Hz, 1H, NH), 5.62 (d, $J = 2.4$ Hz, 1H, $\text{CH}=\text{C}$), 6.37 (dt, $J = 10.8$ Hz, $J = 2.4$ Hz, 1H, CH), 6.59 (d, $J = 8.8$ Hz, 1H, Ar),

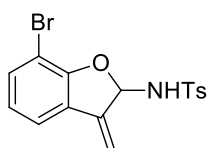
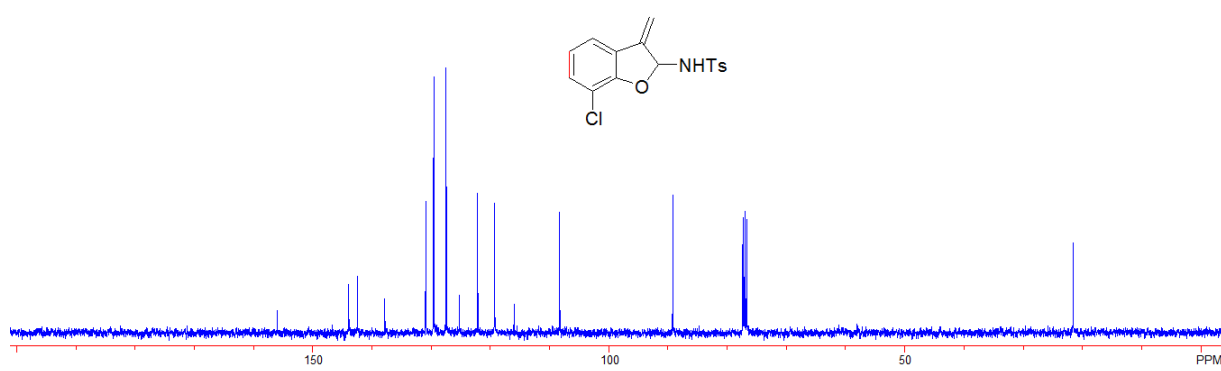
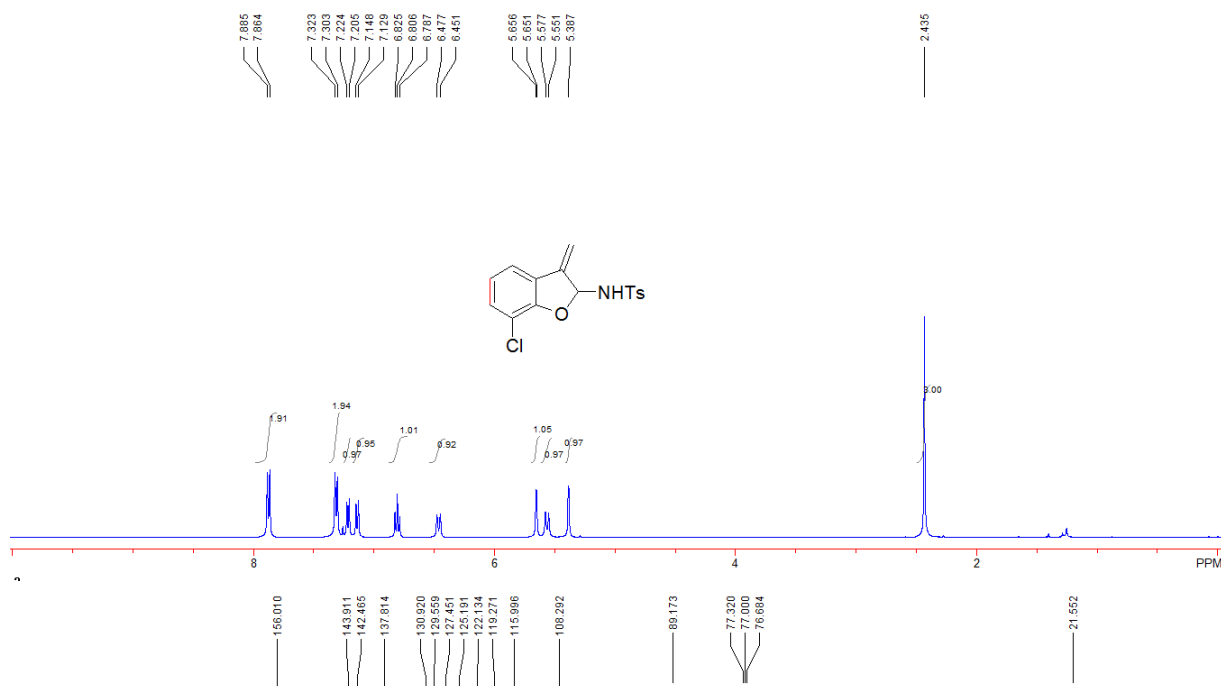
7.12 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H, Ar), 7.29 (d, $J = 2.4$ Hz, 1H, Ar), 7.33 (d, $J = 8.0$ Hz, 2H, Ar), 7.85 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 89.2, 107.9, 111.8, 121.0, 125.1, 126.5, 127.3, 129.7, 130.9, 137.9, 142.3, 144.0, 158.7. IR (CH_2Cl_2) ν 3201, 2912, 1570, 1338, 1321, 1283, 1159, 1002, 904, 845, 763, 692, 669 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{15}\text{ClINO}_3\text{S}^+$ (M^+H) requires 336.0456, found: 336.0456.



N-(7-Chloro-3-methylene-2,3-dihydrobenzofuran-2-yl)-4-methylbenzenesulfonamide 2c

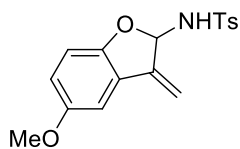
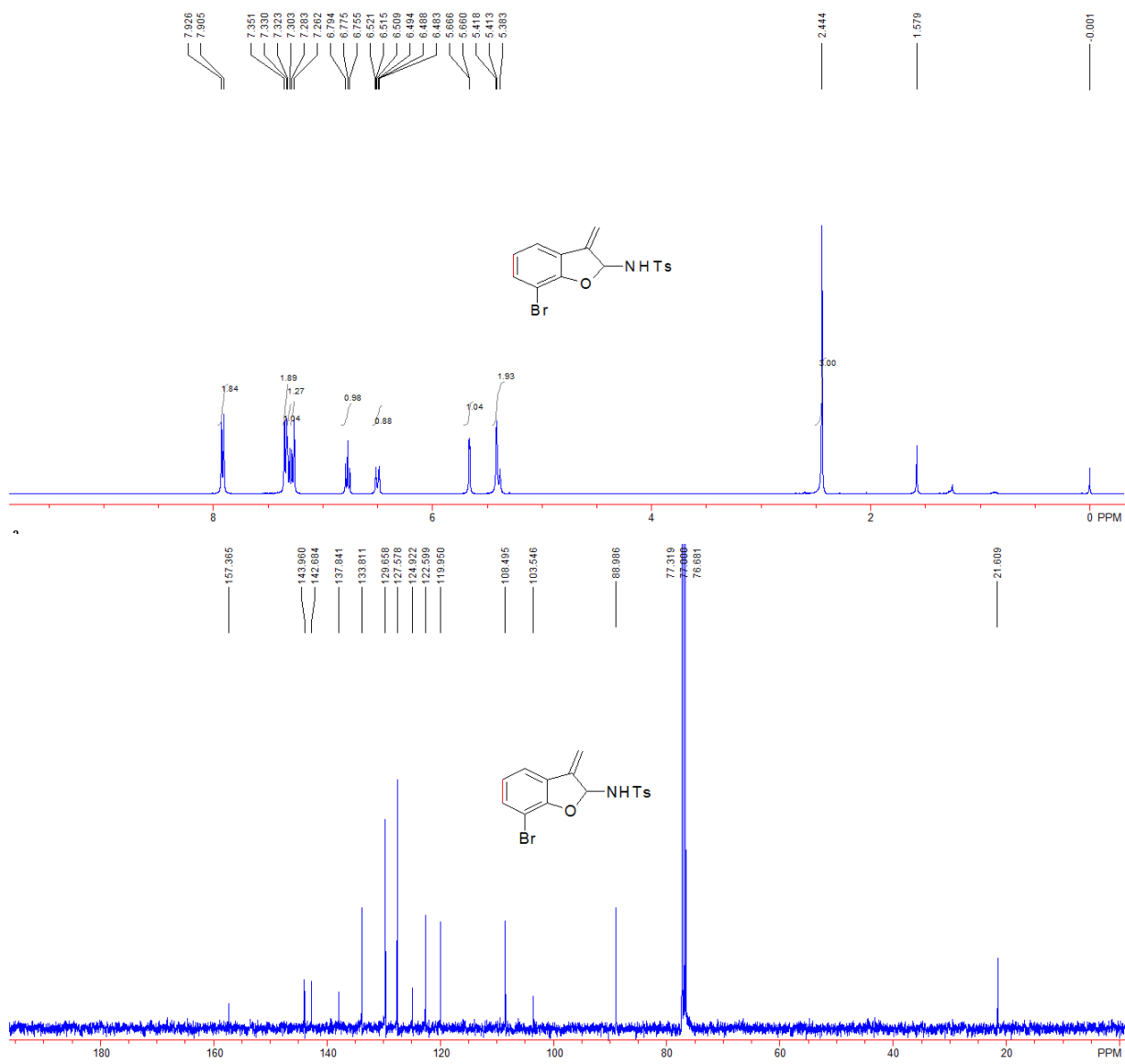
0.2 mmol scale, a white solid, 43% yield (29 mg). M.p.: 152-154 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz,

TMS) δ 2.44 (s, 3H, CH₃), 5.39 (s, 1H, CH=), 5.56 (d, $J = 10.4$ Hz, 1H, NH), 5.65 (d, $J = 2.0$ Hz, 1H, CH=), 6.46 (d, $J = 10.4$ Hz, 1H, CH), 6.81 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H, Ar), 7.14 (d, $J = 7.6$ Hz, 1H, Ar), 7.21 (d, $J = 7.6$ Hz, 1H, Ar), 7.31 (d, 2H, $J = 8.0$ Hz, Ar), 7.87 (d, $J = 8.0$ Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 89.2, 108.3, 116.0, 119.3, 122.1, 125.2, 127.5, 129.6, 130.9, 137.8, 142.5, 143.9, 156.0. IR (CH₂Cl₂) ν 3256, 2922, 1600, 1438, 1337, 1293, 1159, 1078, 1051, 904, 815, 785, 692, 670 cm⁻¹. HRMS (ESI) Calcd. for C₁₆H₁₅ClNO₃S (M⁺+H) requires 336.0456, found: 336.0445.



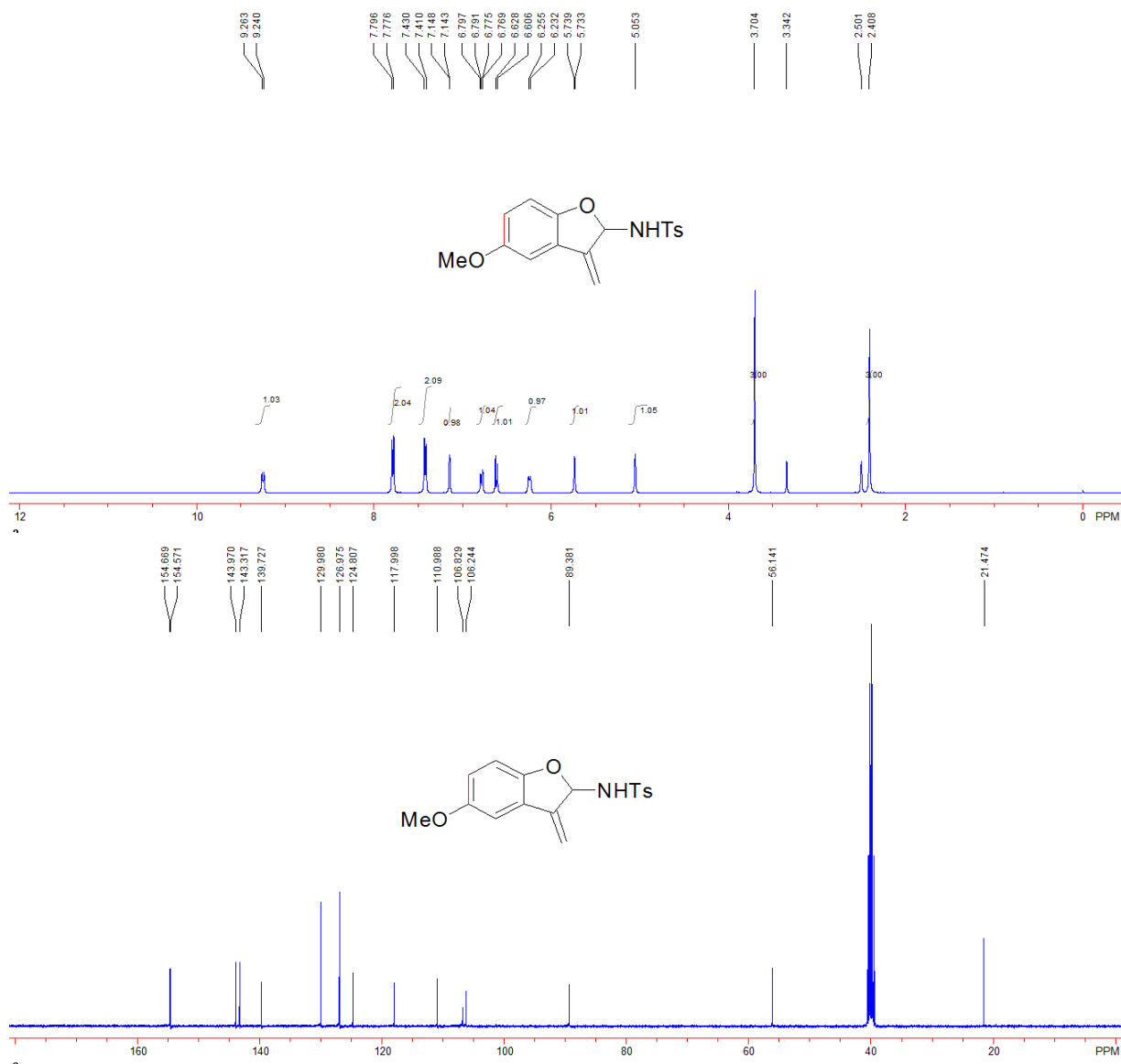
N-(7-Bromo-3-methylene-2,3-dihydrobenzofuran-2-yl)-4-methylbenzenesulfonamide 2d

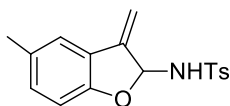
0.2 mmol scale, a white solid, 45% yield (34 mg). M.p.: 194-196 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 5.38-5.42 (m, 2H, $\text{CH}=\text{, NH}$), 5.66 (d, $J = 2.4$ Hz, 1H, $\text{CH}=\text{}$), 6.50 (dt, $J = 10.4$ Hz, $J = 2.4$ Hz, 1H, CH), 6.78 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H, Ar), 7.27 (d, $J = 8.0$ Hz, 1H, Ar), 7.31 (d, $J = 8.0$ Hz, 1H, Ar), 7.34 (d, $J = 8.4$ Hz, 2H, Ar), 7.91 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 89.0, 103.5, 108.5, 120.0, 122.6, 124.9, 127.6, 129.7, 133.8, 137.8, 142.7, 144.0, 157.4. IR (CH_2Cl_2) ν 3246, 2923, 1649, 1598, 1579, 1435, 1336, 1292, 1213, 1159, 1116, 1086, 922, 902, 813, 783, 744, 692, 652 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{15}\text{BrNO}_3\text{S}$ ($\text{M}^+ + \text{H}$) requires 379.9951, found: 379.9963.



N-(5-Methoxy-3-methylene-2,3-dihydrobenzofuran-2-yl)-4-methylbenzenesulfonamide 2e

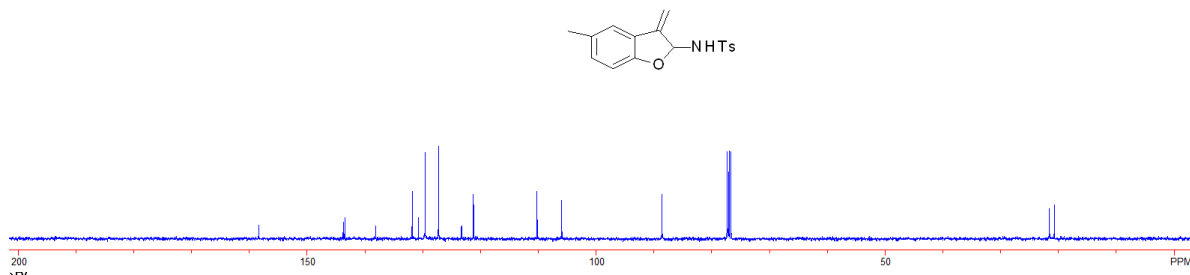
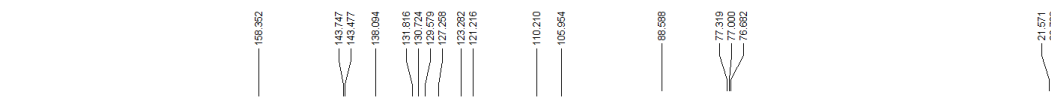
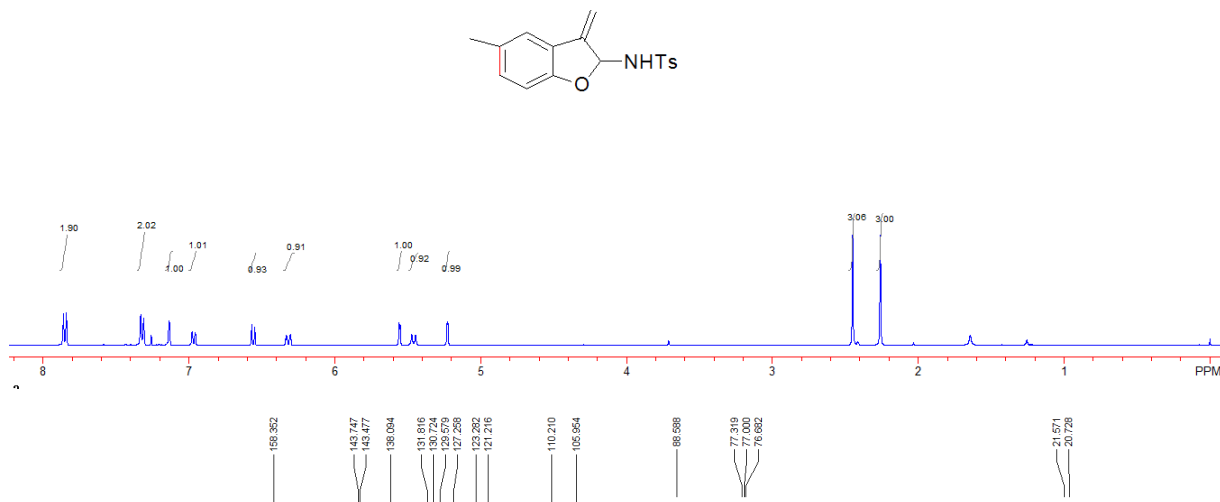
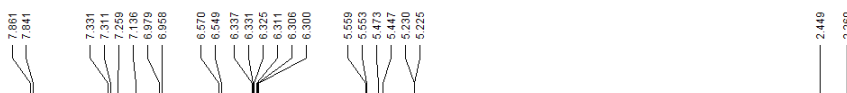
0.2 mmol scale, a white solid, 65% yield (43 mg). M.p.: 213-214°C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 2.41 (s, 3H, CH₃), 3.70 (s, 3H, CH₃), 5.05 (s, 1H, CH₂=), 5.74 (d, J = 2.4 Hz, 1H, CH=), 6.24 (d, J = 9.2 Hz, 1H, CH), 6.61 (d, J = 8.8 Hz, 1H, Ar), 6.78 (dd, J = 9.2 Hz, J = 2.4 Hz, 1H, Ar), 7.14 (d, J = 2.4 Hz, 1H, Ar), 7.42 (d, J = 8.0 Hz, 2H, Ar), 7.78 (d, J = 8.0 Hz, 2H, Ar), 9.25 (d, J = 9.2 Hz, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz, TMS) δ 21.5, 56.1, 89.4, 106.2, 106.8, 111.0, 118.0, 124.8, 127.0, 130.0, 139.7, 143.3, 144.0, 154.6, 154.7. IR (CH₂Cl₂) ν 3272, 1644, 1599, 1485, 1446, 1336, 1308, 1288, 1160, 1110, 1090, 1026, 958, 933, 906, 810, 799, 750, 703, 690, 673, 661 cm^{-1} . HRMS (ESI) Calcd. for C₁₇H₁₈NO₄S (M⁺+H) requires 332.0952, found: 332.0951.

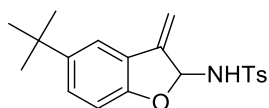




4-Methyl-N-(5-methyl-3-methylene-2,3-dihydro-benzofuran-2-yl)-benzenesulfonamide 2f.

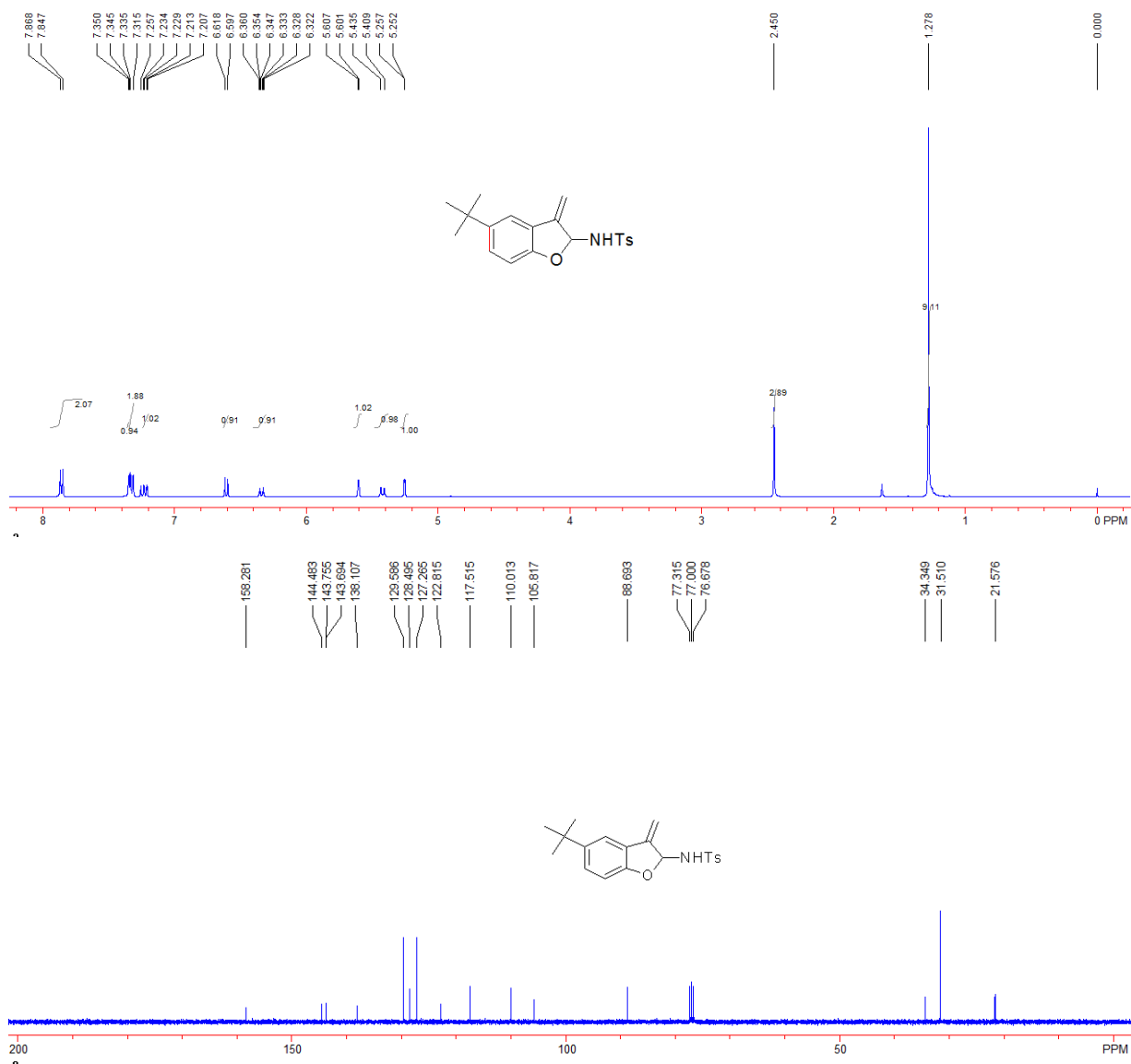
0.2 mmol scale, a white solid, 76% yield (48 mg). M.p.: 133-135 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.26 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 5.23 (d, *J* = 2.0 Hz, 1H, CH=), 5.46 (d, *J* = 10.4 Hz, 1H, NH), 5.62 (d, *J* = 2.0 Hz, 1H, CH=), 6.37 (dt, *J* = 10.0 Hz, *J* = 2.0 Hz, 1H, CH), 6.56 (d, *J* = 8.4 Hz, 1H, Ar), 6.96 (d, *J* = 8.4 Hz, 1H, Ar), 7.14 (s, 1H, Ar), 7.32 (d, *J* = 8.0 Hz, 2H, Ar), 7.85 (d, *J* = 8.0 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 20.7, 21.6, 88.6, 106.0, 110.2, 121.2, 123.3, 127.3, 129.6, 130.7, 131.8, 138.1, 143.5, 143.7, 158.4. IR (CH₂Cl₂) ν 3355, 3258, 2922, 1651, 1486, 1450, 1339, 1295, 1157, 1116, 1090, 1035, 933, 916, 810, 793, 692, 662 cm⁻¹. HRMS (ESI) Calcd. for C₁₇H₁₈NO₃S (M⁺+H) requires 316.1002, found: 316.1005.

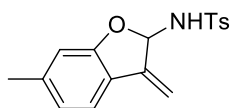




4-Methyl-N-(5-tert-butyl-3-methylene-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide 2g.

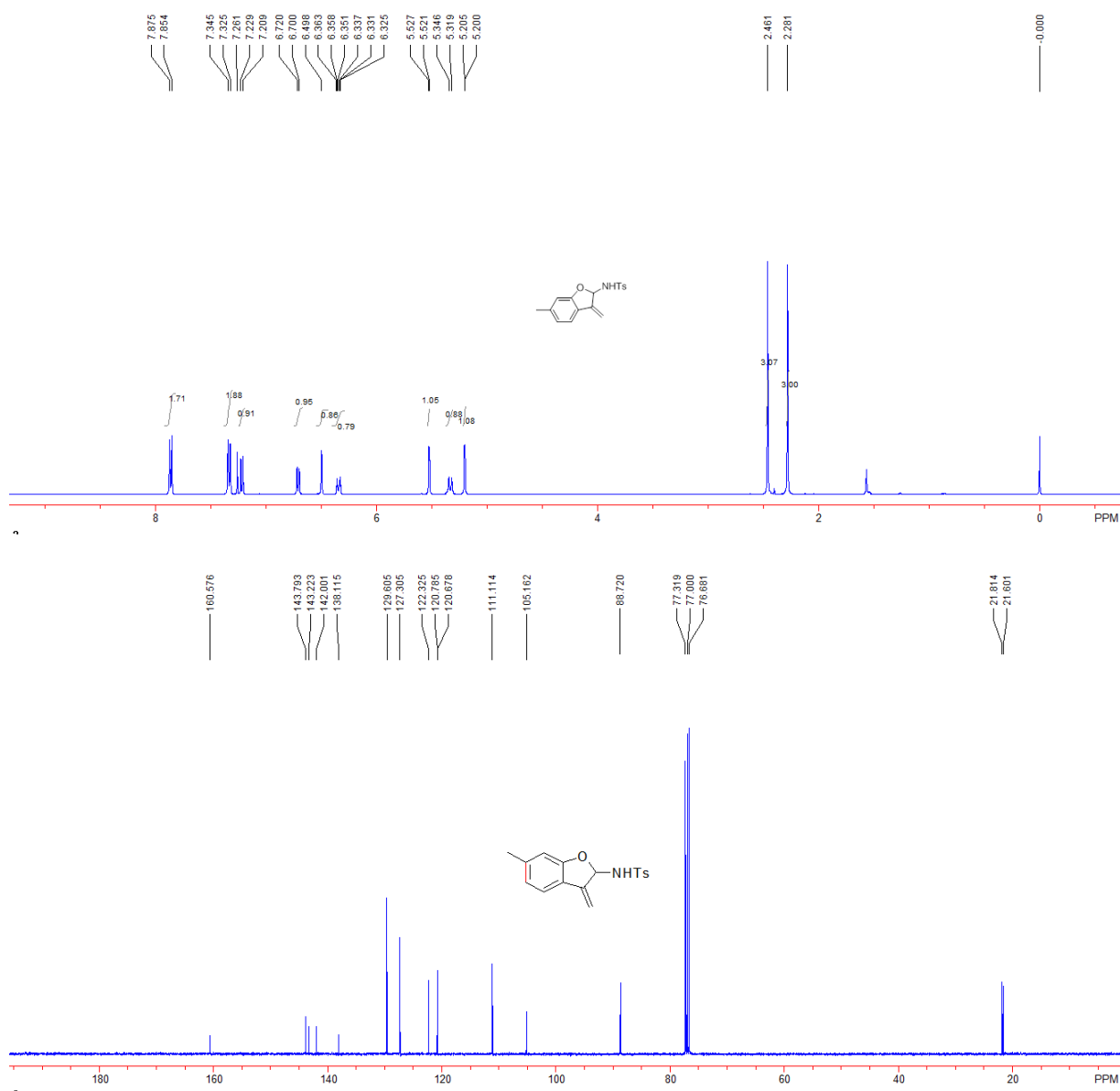
0.2 mmol scale, a white solid, 99% yield (70 mg). M.p.: 140-142 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.28 (s, 9H, CH_3), 2.45 (s, 3H, CH_3), 5.25 (d, $J = 2.4$ Hz, 1H, $\text{CH}=\text{}$), 5.42 (d, $J = 10.4$ Hz, 1H, NH), 5.60 (d, $J = 2.4$ Hz, 1H, $\text{CH}=\text{}$), 6.34 (dt, $J = 10.4$ Hz, $J = 2.4$ Hz, 1H, CH), 6.60 (d, $J = 8.4$ Hz, 1H, Ar), 7.22 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H, Ar), 7.32-7.35 (m, 3H, Ar), 7.85 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 31.5, 34.3, 88.7, 105.8, 110.0, 117.5, 122.8, 127.3, 128.5, 129.6, 138.1, 143.7, 143.8, 144.5, 158.3. IR (CH_2Cl_2) ν 3284, 1597, 1453, 1337, 1309, 1269, 1232, 1159, 1138, 1119, 1090, 918, 901, 812, 783, 679, 668 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{24}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) requires 358.1471, found: 358.1479.

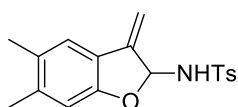




4-Methyl-N-(6-methyl-3-methylene-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide **2h**

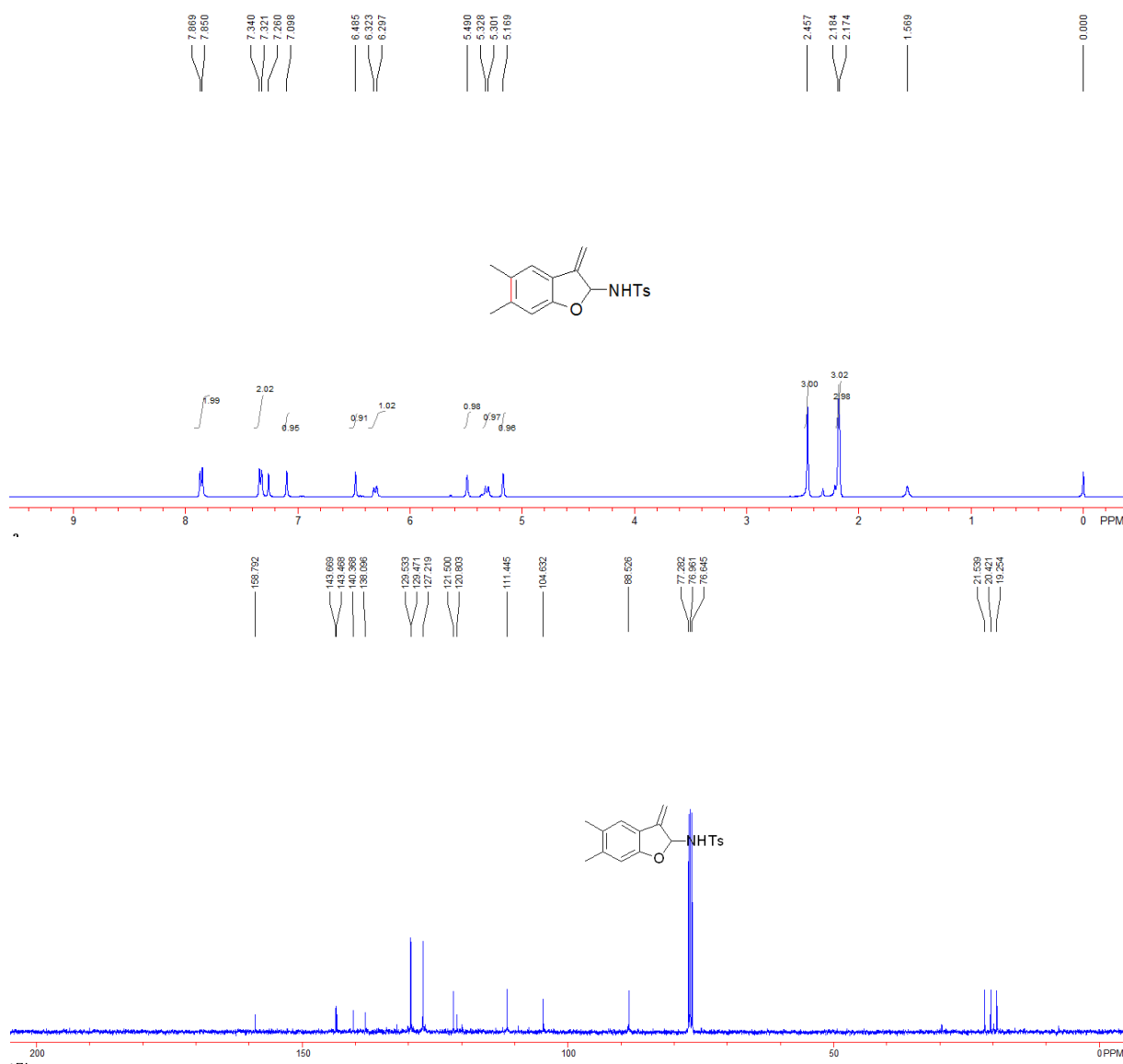
0.2 mmol scale, a white solid, 82% yield (52 mg). M.p.: 142-145 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.28 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.20 (d, $J = 2.4$ Hz, 1H, $\text{CH}_2=$), 5.33 (d, $J = 10.8$ Hz, 1H, NH), 5.52 (d, $J = 2.4$ Hz, 1H, $\text{CH}=$), 6.34 (dt, $J = 10.8$ Hz, $J = 2.4$ Hz, 1H, CH), 6.50 (s, 1H, Ar), 6.71 (d, $J = 8.0$ Hz, 1H, Ar), 7.22 (d, $J = 8.0$ Hz, 1H, Ar), 7.33 (d, $J = 8.0$ Hz, 2H, Ar), 7.86 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 21.8, 88.7, 105.2, 111.1, 120.7, 120.8, 122.3, 127.3, 129.6, 138.1, 142.0, 143.2, 143.8, 160.5. IR (CH_2Cl_2) ν 2925, 1596, 1422, 1339, 1162, 1090, 994, 905, 765, 728, 665 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{18}\text{BNO}_3\text{S}$ (M^+H) requires 316.1002, found: 316.1006.

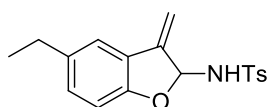




4-Methyl-N-(4,5-diethyl-3-methylene-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide 2i.

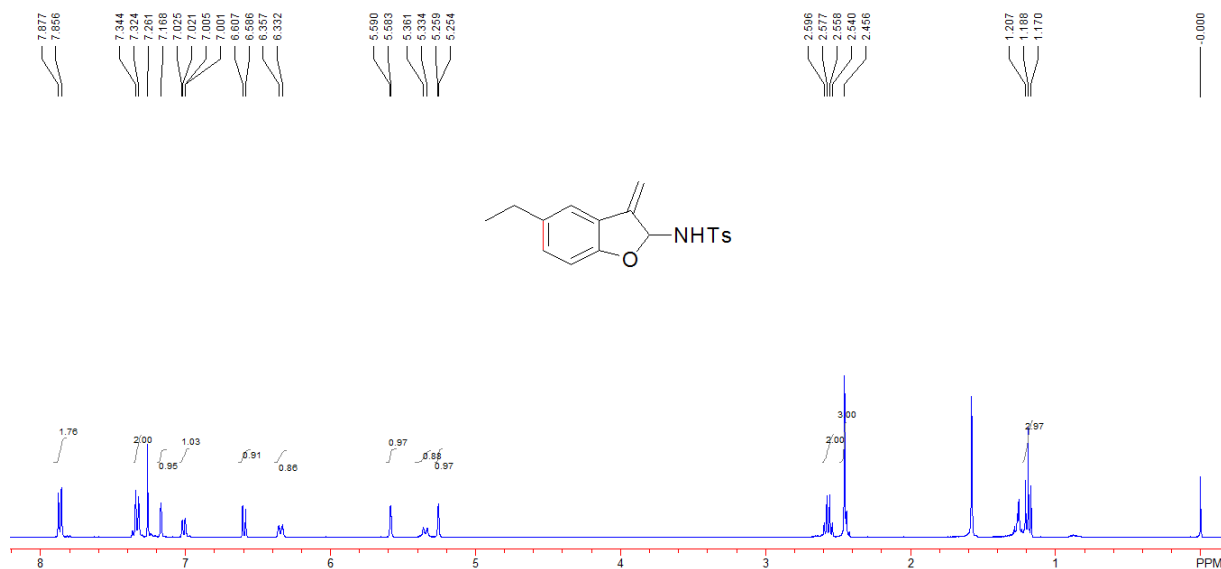
0.2 mmol scale, a white solid, 85% yield (56 mg). M.p.: 140-142 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.17 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.17 (s, 1H, $\text{CH}=\text{C}$), 5.32 (d, $J = 10.8$ Hz, 1H, NH), 5.48 (s, 1H, $\text{CH}=\text{C}$), 6.31 (d, $J = 10.8$ Hz, 1H, CH), 6.48 (s, 1H, Ar), 7.10 (s, 1H, Ar), 7.33 (d, 2H, $J = 8.0$ Hz, Ar), 7.86 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 19.3, 20.5, 21.6, 88.6, 104.7, 111.5, 120.8, 121.5, 127.3, 129.5, 129.6, 138.1, 140.4, 143.5, 143.7, 158.8. IR (CH_2Cl_2) ν 3275, 2922, 2853, 1618, 1483, 1338, 1327, 1292, 1179, 1161, 1107, 1087, 1044, 923, 907, 889, 811, 704, 685, 671 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) requires 330.1158, found: 330.1161.

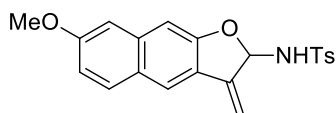
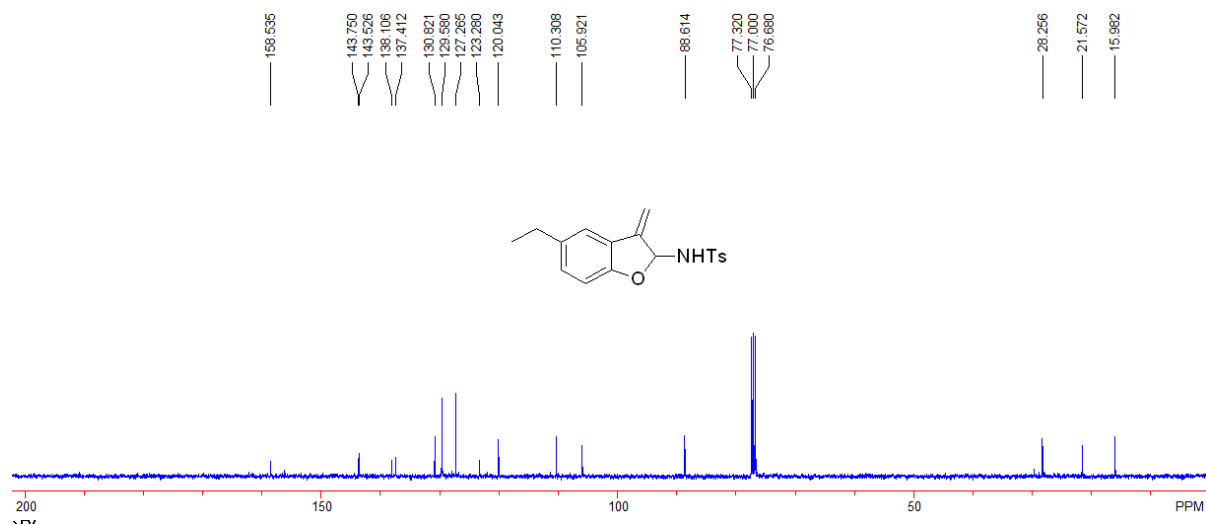




4-Methyl-N-(5-ethyl-3-methylene-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide 2j.

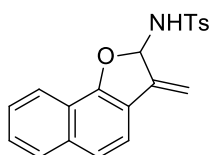
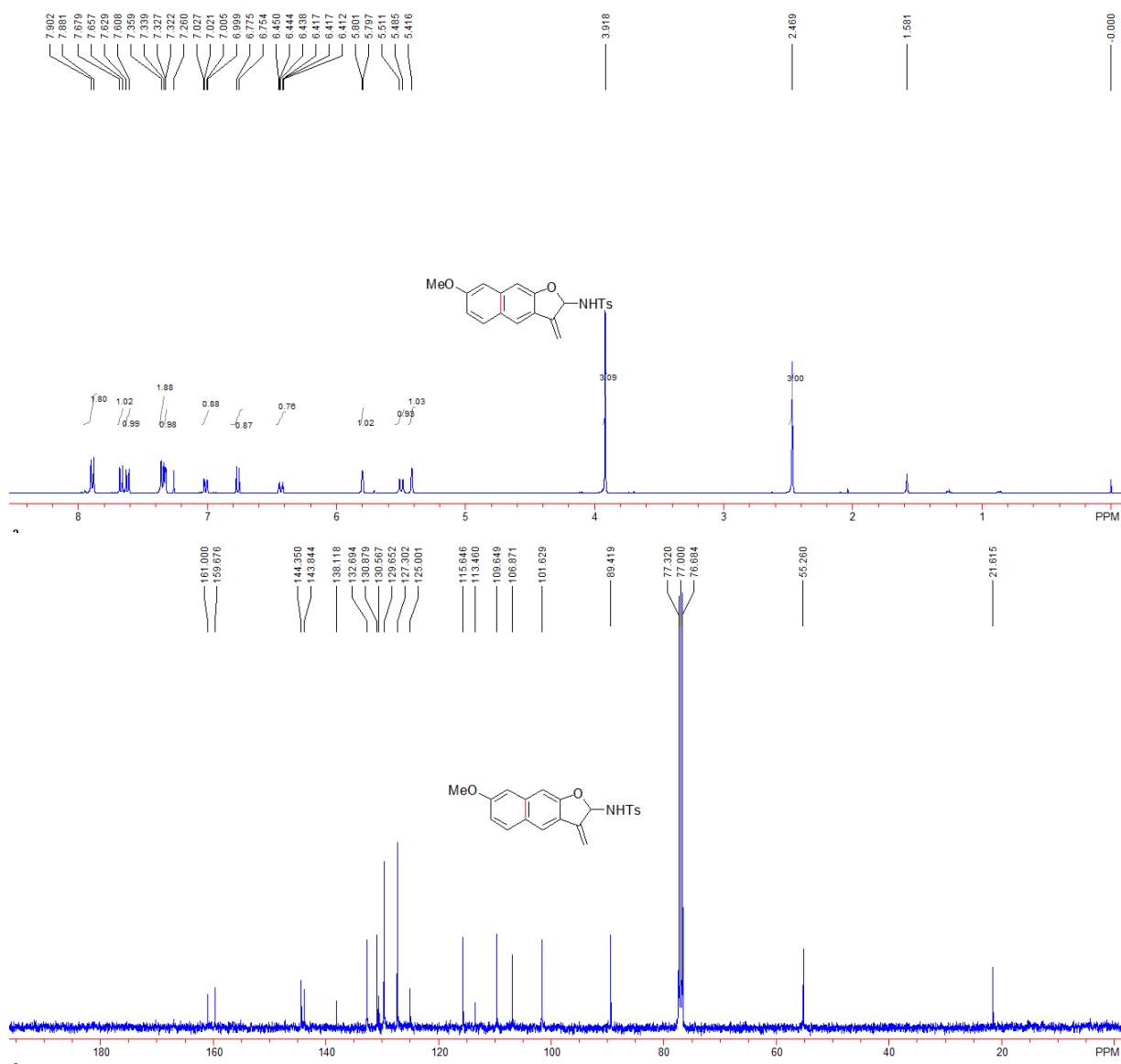
0.2 mmol scale, a white solid, 83% yield (55 mg). M.p.: 136-138 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.19 (t, $J = 7.2\text{ Hz}$, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.56 (q, $J = 7.2\text{ Hz}$, 2H, CH_2), 5.26 (d, $J = 2.0\text{ Hz}$, 1H, $\text{CH}=\text{)$, 5.35 (d, $J = 10.8\text{ Hz}$, 1H, NH), 5.59 (d, $J = 2.0\text{ Hz}$, 1H, $\text{CH}=\text{)$, 6.34 (d, 10.8 Hz, 1H, CH), 6.59 (d, $J = 8.4\text{ Hz}$, 1H, Ar), 7.01 (dd, $J = 8.0\text{ Hz}$, $J = 1.6\text{ Hz}$, 1H, Ar), 7.17 (s, 1H, Ar), 7.33 (d, 2H, $J = 8.0\text{ Hz}$, Ar), 7.86 (d, $J = 8.0\text{ Hz}$, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 16.0, 21.6, 28.3, 88.6, 105.9, 110.3, 120.0, 123.3, 127.3, 129.6, 130.8, 137.4, 138.1, 143.5, 143.8, 158.5. IR (CH_2Cl_2) ν 3272, 2956, 2924, 2853, 1484, 1454, 1343, 1162, 1120, 1091, 1028, 954, 871, 815, 687, 660 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) requires 330.1158, found: 330.1153.





N-(7-Methoxy-3-methylene-2,3-dihydrophtho[2,3-b]furan-2-yl)-4-methylbenzenesulfonamide 2l

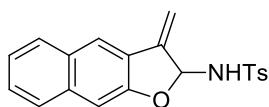
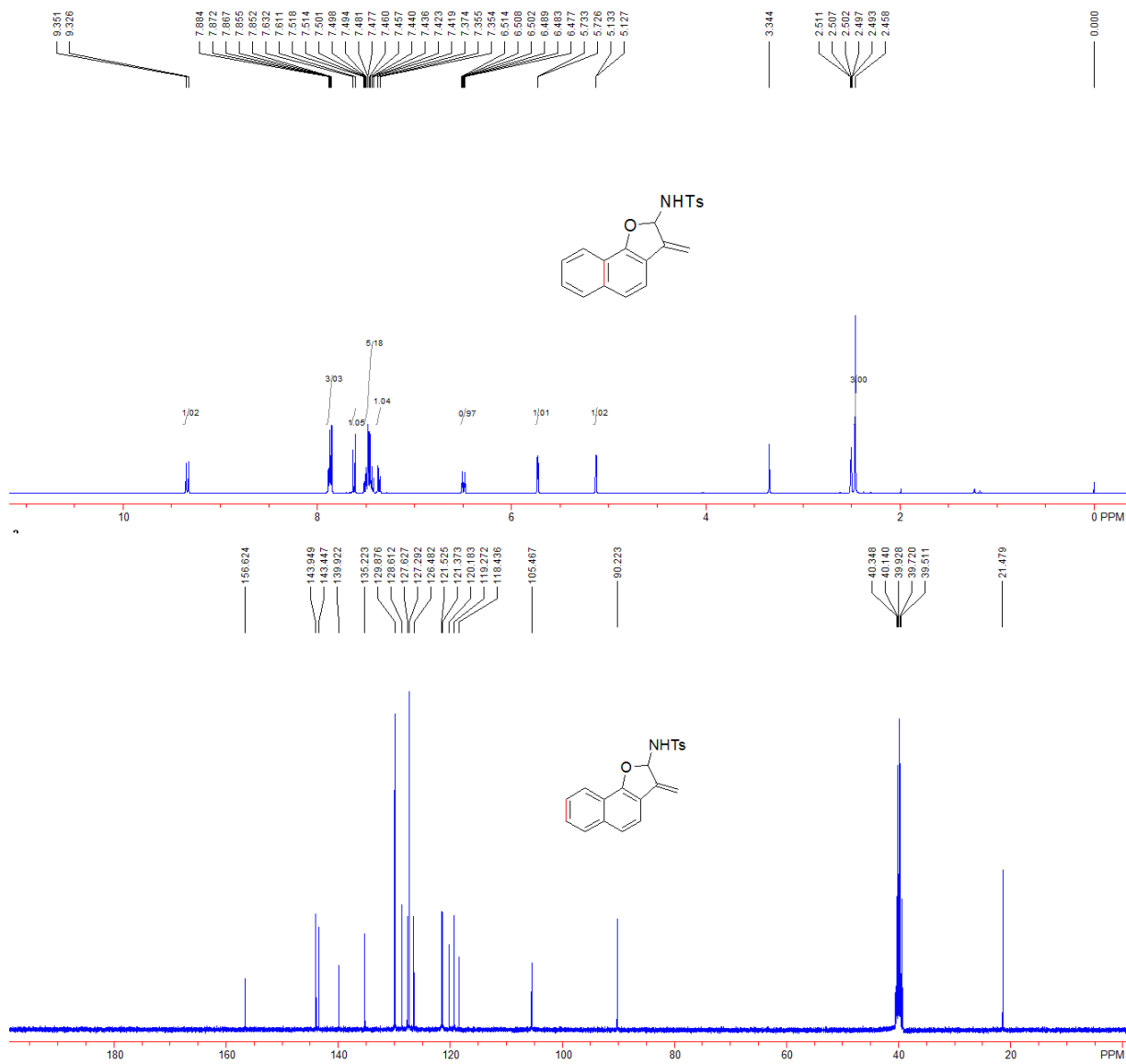
0.2 mmol scale, a white solid, 80% yield (61 mg). M.p.: 150-152 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 5.42 (s, 1H, CH_2), 5.50 (d, $J = 10.4$ Hz, 1H, NH), 5.80 (d, $J = 1.6$ Hz, 1H, CH_2), 6.42 (dt, $J = 10.4$ Hz, $J = 1.6$ Hz, 1H, CH), 6.76 (d, $J = 8.4$ Hz, 1H, Ar), 7.01 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H, Ar), 7.35 (d, $J = 2.4$ Hz, 1H, Ar), 7.34 (d, $J = 8.0$ Hz, 2H, Ar), 7.61 (d, $J = 8.4$ Hz, 1H, Ar), 7.66 (d, $J = 8.4$ Hz, 1H, Ar), 7.89 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 55.3, 89.4, 101.6, 106.9, 109.6, 113.5, 115.6, 125.0, 127.3, 129.6, 130.6, 130.9, 132.7, 138.1, 143.8, 144.3, 159.7, 161.0. IR (CH_2Cl_2) ν 3243, 2925, 1619, 1519, 1352, 1336, 1223, 1159, 1103, 1086, 927, 907, 828, 813, 695, 665 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{21}\text{H}_{20}\text{NO}_4\text{S}$ ($\text{M}^+\text{+H}$) requires 382.1108, found: 382.1109.



4-Methyl-N-(3-methylene-2,3-dihydro-2H-naphtho[1,2-*b*]furan-2-yl)benzenesulfonamide 2m.

0.2 mmol scale, a white solid, 85% yield (60 mg). M.p.: 153-156 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 2.46 (s, 3H, CH₃), 5.13 (d, *J* = 2.4 Hz, 1H, CH₂), 5.73 (d, *J* = 2.4 Hz, 1H, CH₂), 6.49 (dt, *J* = 10.0 Hz, *J* = 2.4 Hz, 1H, CH), 7.35-7.38 (m, 1H, Ar), 7.41-7.52 (m, 5H, Ar), 7.62 (d, *J* = 8.4 Hz, 1H, Ar), 7.85-7.89 (m, 3H, Ar), 9.34 (d, *J* = 10.0 Hz, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz, TMS) δ 21.5, 90.2, 105.5, 118.4, 119.3, 120.2, 121.4, 121.5, 126.5, 127.3, 127.6, 128.6, 129.9, 135.2, 139.9, 143.4, 143.9, 156.6. IR (CH₂Cl₂) ν 3252, 1578, 1519, 1440, 1388, 1340, 1294, 1185, 1160, 1105, 1088, 1069, 910, 894, 811, 705, 697, 677, 661 cm⁻¹. HRMS (ESI) Calcd.

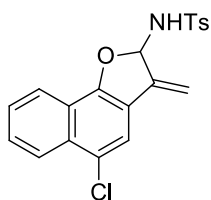
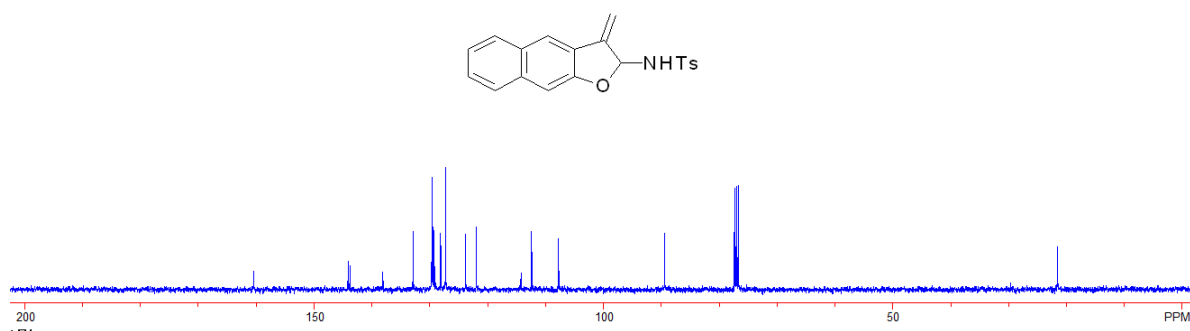
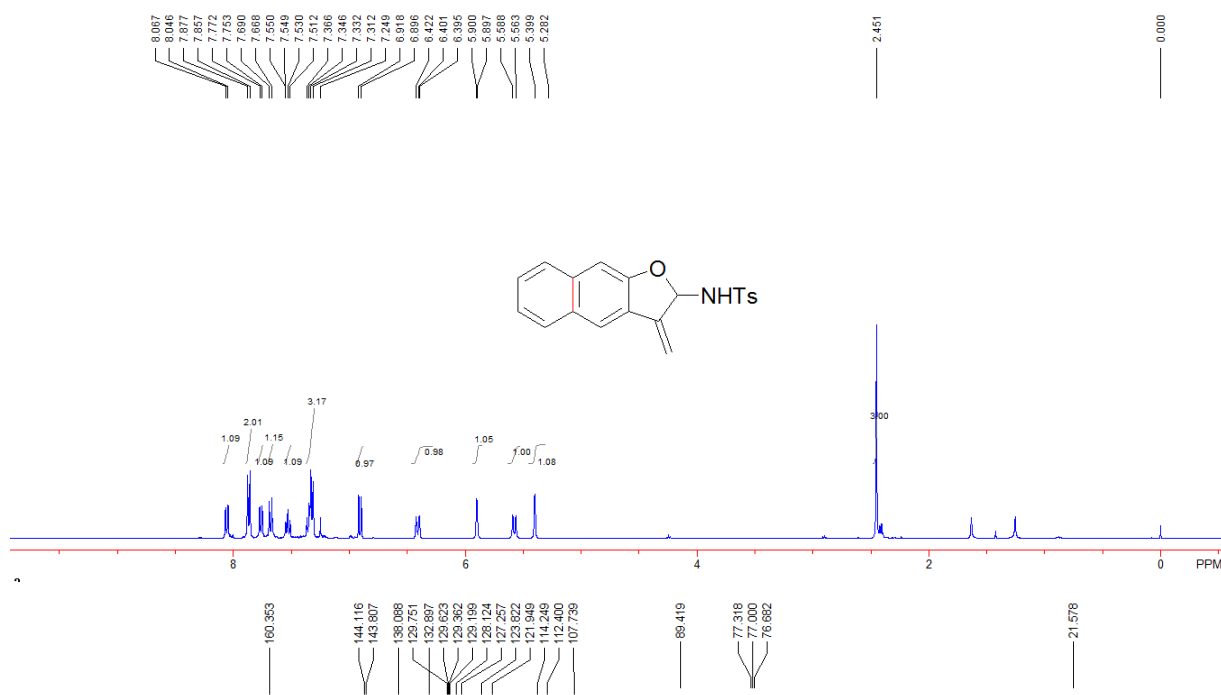
for C₂₀H₁₈NO₃S (M⁺+H) requires 352.1002, found: 352.0996.



4-Methyl-N-(3-methylene-2,3-dihydro-1-benzofuran-2-yl)benzenesulfonamide **2n**

0.2 mmol scale, a white solid, 83% yield (58 mg). M.p.: 150-152 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.45 (s, 3H, CH₃), 5.40 (s, 1H, CH₂), 5.57 (d, *J* = 10.4 Hz, 1H, NH), 5.90 (s, 1H, CH₂), 6.41 (dt, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H, CH), 6.91 (d, *J* = 8.8 Hz, 1H, Ar), 7.31-7.37 (m, 3H, Ar), 7.51-7.55 (m, 1H, Ar), 7.68 (d, *J* = 8.8 Hz, 1H, Ar), 7.76 (d, *J* = 8.0 Hz, 1H, Ar), 7.86 (d, *J* = 8.0 Hz, 2H, Ar), 8.05 (d, *J* = 8.4 Hz, 1H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 89.4, 107.7, 112.4, 114.2, 121.9, 123.8, 127.2, 128.1, 129.2, 129.4, 129.6, 129.8, 132.9, 138.1, 143.8, 144.1, 160.4. IR (CH₂Cl₂) ν 3273, 2921, 1597, 1392, 1331, 1306, 1290, 1182, 1162, 1129, 1088, 815,

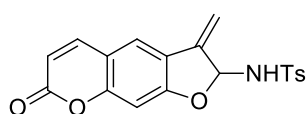
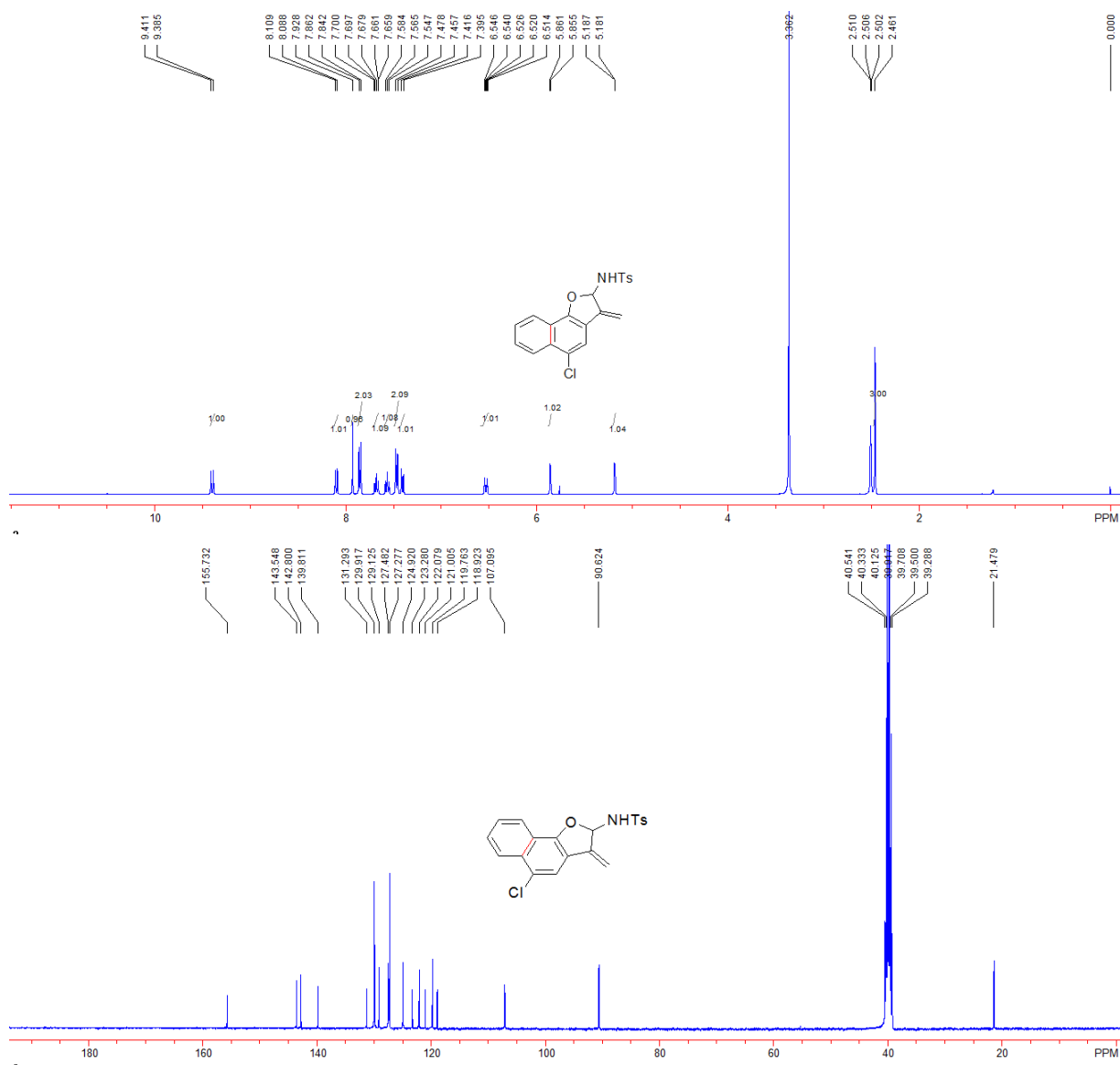
772, 746, 704, 680, 664 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{NO}_3\text{S}$ ($\text{M}^+\text{+H}$) requires 352.1002, found: 352.0997.



N-(5-Chloro-3-methylene-2,3-dihydro-1-benzofuran-2-yl)-4-methylbenzenesulfonamide 20.

0.2 mmol scale, a white solid, 72% yield (55 mg). m.p.: 143-145 °C. ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) δ 2.46 (s, 3H, CH_3), 5.19 (d, $J = 2.4$ Hz, 1H, CH_2), 5.85 (d, $J = 2.4$ Hz, 1H, CH_2), 6.53 (dt, $J = 10.4$ Hz, $J = 2.4$ Hz, 1H, CH), 7.40 (d, $J = 8.4$ Hz, 1H, Ar), 7.46 (d, $J = 8.0$ Hz, 2H, Ar), 7.56

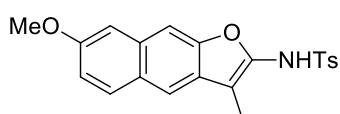
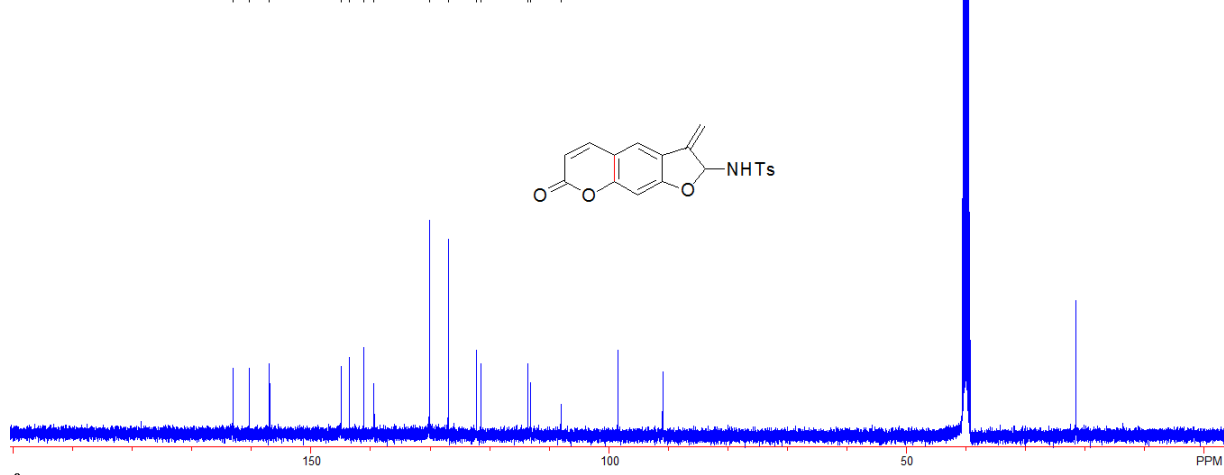
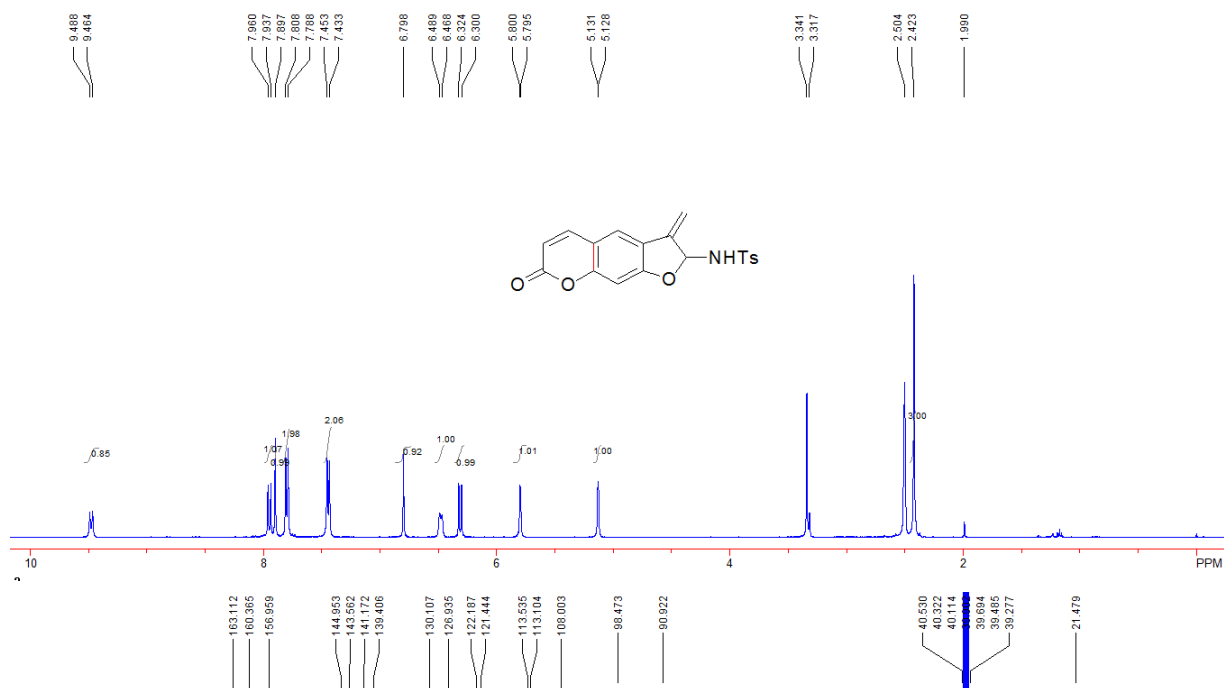
(dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H, Ar), 7.68 (ddd, $J = 8.4$ Hz, $J = 8.4$ Hz, $J = 1.2$ Hz, 1H, Ar), 7.85 (d, $J = 8.0$ Hz, 2H, Ar), 7.93 (s, 1H, Ar), 8.09 (d, $J = 8.4$ Hz, 1H, Ar), 9.39 (d, $J = 10.4$ Hz, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 21.5, 90.6, 107.1, 118.9, 119.8, 121.0, 122.1, 123.3, 124.9, 127.3, 127.5, 129.1, 129.9, 131.3, 139.8, 142.8, 143.5, 155.7. IR (CH $_2$ Cl $_2$) ν 3270, 1592, 1391, 1332, 1305, 1292, 1182, 1161, 1125, 1079, 812, 760, 749, 701, 681, 665 cm^{-1} . HRMS (ESI) Calcd. for C $_{20}$ H $_{17}$ ClNO $_3$ S (M $^+$ +H) requires 386.0612, found: 386.0612.



4-Methyl-N-(3-methylene-7-oxo-2,3-dihydro-7H-furo[3,2-g]chromen-2-yl)benzenesulfonamide 2p

0.2 mmol scale, a white solid, 61% yield (45 mg). M.p.: 210-212 °C. ^1H NMR (DMSO- d_6 , 400

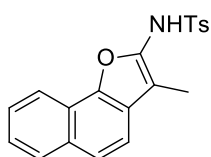
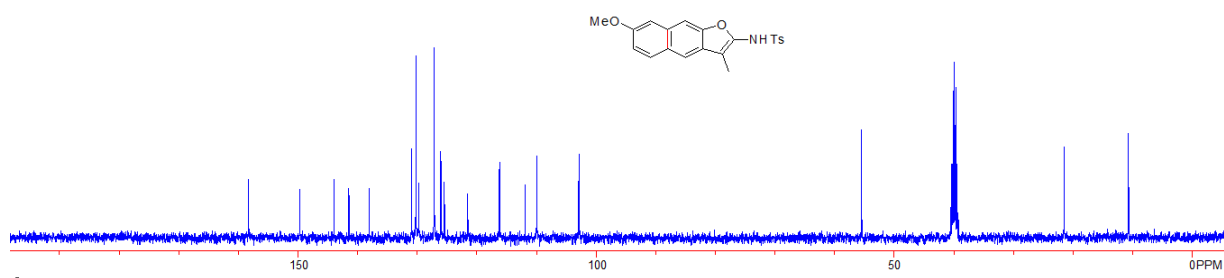
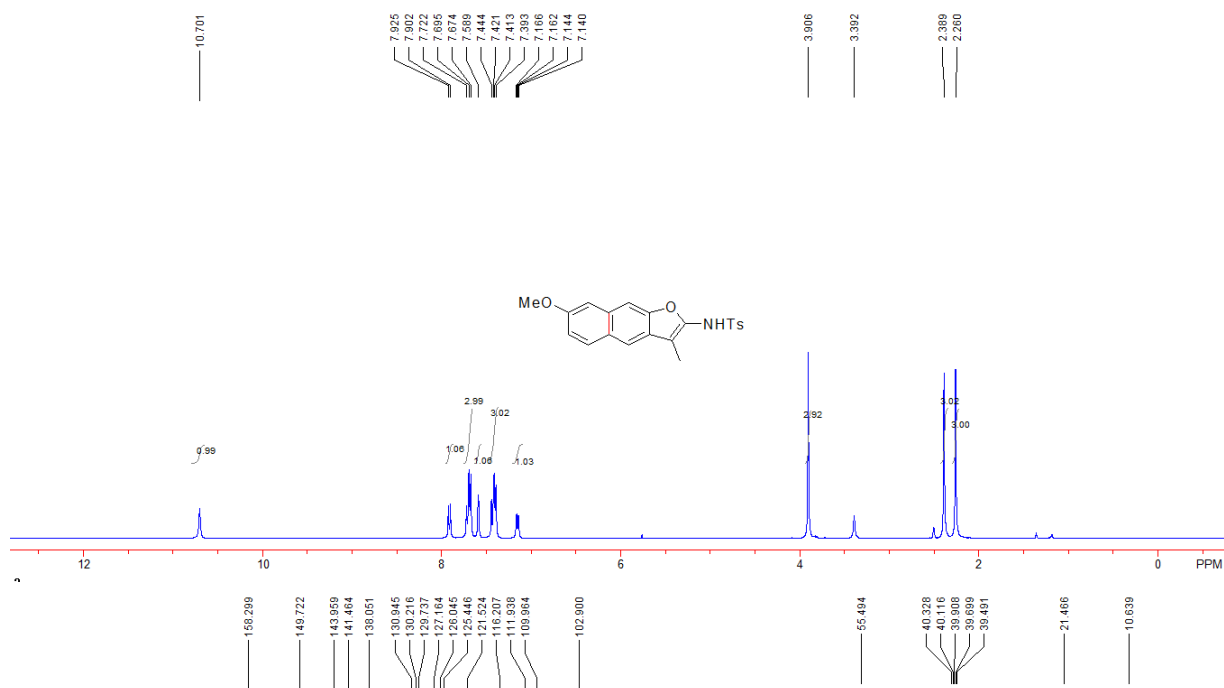
MHz) δ 2.42 (s, 3H, CH₃), 5.13 (d, J = 1.6 Hz, 1H, CH=), 5.80 (d, J = 1.6 Hz, 1H, CH=), 6.31 (d, J = 9.6 Hz, 1H, Ar), 6.47 (d, J = 8.4 Hz, 1H, CH), 6.80 (s, 1H, Ar), 7.44 (d, J = 8.0 Hz, 2H, Ar), 7.79 (d, J = 8.0 Hz, 2H, Ar), 7.90 (s, 1H, Ar), 7.95 (d, J = 13.2 Hz, 1H, Ar), 9.47 (d, J = 9.6 Hz, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 21.5, 90.9, 98.5, 108.0, 113.1, 113.5, 121.4, 122.2, 126.9, 130.1, 139.4, 141.2, 143.6, 145.0, 157.0, 160.4, 163.1. IR (CH₂Cl₂) ν 3270, 2162, 1710, 1685, 1336, 1200, 1145, 1110, 1011, 943, 906, 860, 769, 740, 699, 667 cm⁻¹. HRMS (ESI) Calcd. for C₁₉H₁₆NO₅S (M⁺+H) requires 370.0744, found: 370.0741.



N-(7-Methoxy-3-methylnaphtho[2,3-b]furan-2-yl)-4-methylbenzenesulfonamide 3a.

0.2 mmol scale, a white solid, 81% yield (62 mg). M.p.: 156-158 °C. ¹H NMR (DMSO-*d*₆, 400

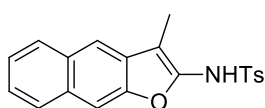
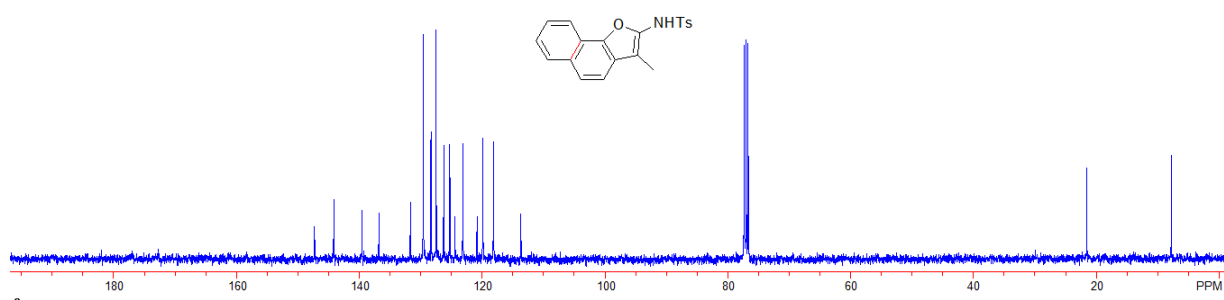
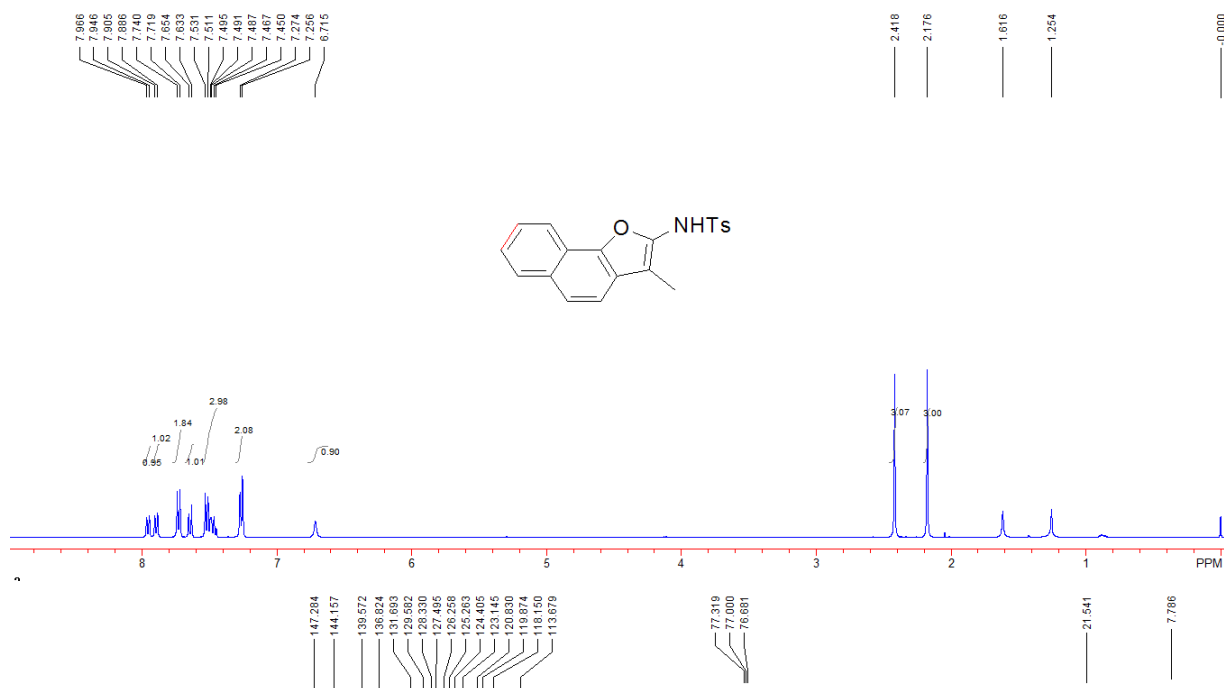
MHz) δ 2.26 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 7.15 (dd, $J = 1.6$ Hz, $J = 8.8$ Hz, 1H, Ar), 7.39-7.45 (m, 3H, Ar), 7.59 (s, 1H, Ar), 7.67-7.73 (m, 3H, Ar), 7.91 (d, $J = 8.8$ Hz, 1H, Ar), 10.70 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 10.6, 21.5, 55.5, 102.9, 110.0, 111.9, 116.2, 121.5, 125.4, 126.0, 127.2, 129.7, 130.2, 130.9, 138.1, 141.5, 144.0, 149.7, 158.3. IR (CH₂Cl₂) ν 3243, 2925, 1618, 1472, 1372, 1319, 1158, 1076, 1409, 938, 908, 825, 768, 720, 695, 665 cm⁻¹. HRMS (ESI) Calcd. for C₂₁H₂₀NO₄S (M⁺ + H) requires 382.1108, found: 382.1108.



4-Methyl-N-(3-methylnaphtho[1,2-*b*]furan-2-yl)benzenesulfonamide 3b.

0.2 mmol scale, a white solid, 83% yield (58 mg). M.p.: 156-158 °C. ¹H NMR (CDCl₃, 400 MHz,

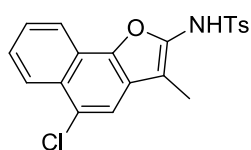
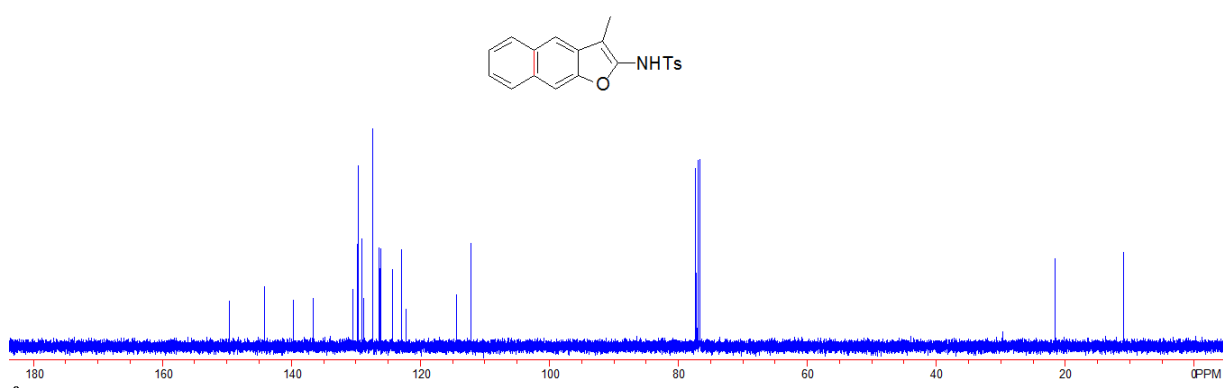
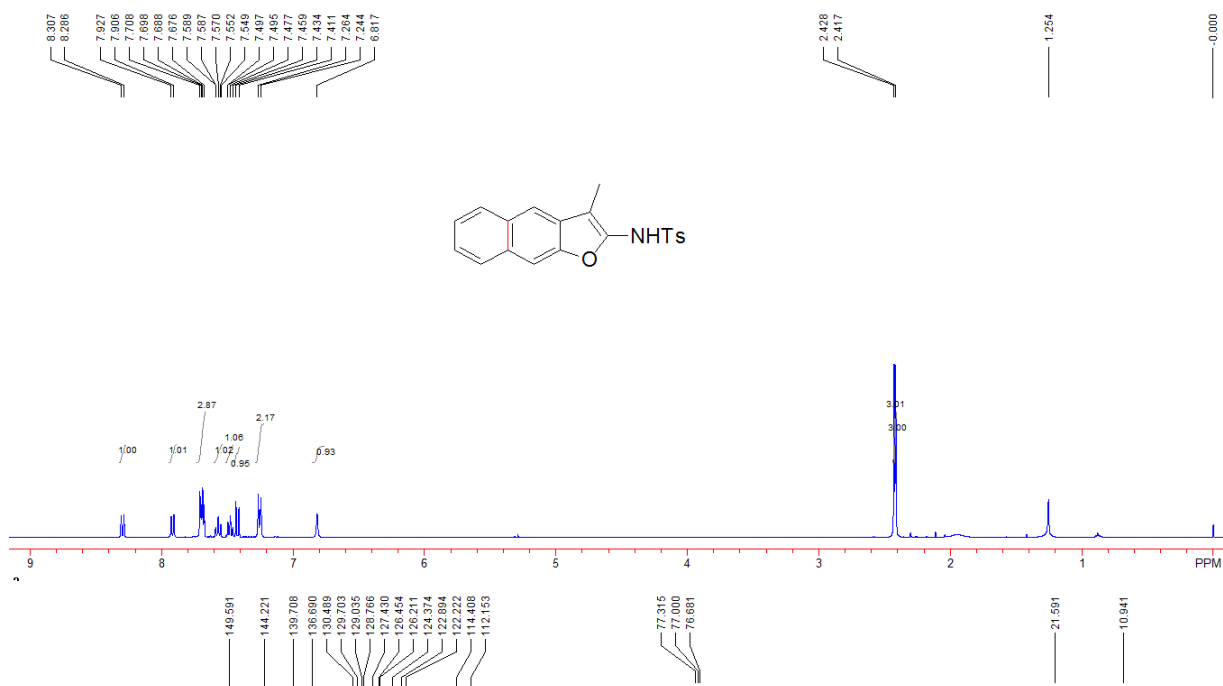
TMS) δ 2.18 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 6.72 (s, 1H, NH), 7.26 (d, $J = 7.2$ Hz, 2H, Ar), 7.45-7.54 (m, 3H, Ar), 7.64 (d, $J = 8.4$ Hz, 1H, Ar), 7.73 (d, $J = 8.4$ Hz, 2H, Ar), 7.89 (d, $J = 8.0$ Hz, 1H, Ar), 7.95 (d, $J = 8.0$ Hz, 1H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 7.8, 21.5, 113.7, 118.2, 119.9, 120.8, 123.1, 124.4, 125.3, 126.3, 127.5, 128.3, 129.6, 131.7, 136.8, 139.6, 144.2, 147.3. IR (CH₂Cl₂) ν 3273, 1392, 1331, 1182, 1162, 1129, 1114, 1088, 858, 814, 772, 746, 704, 694, 680, 664 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₂₁N₂O₃S (M⁺ +NH₄) requires 369.1267, found: 369.1261.



4-Methyl-N-(3-methylnaphtho[2,3-*b*]furan-2-yl)benzenesulfonamide 3c.

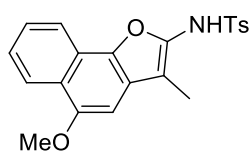
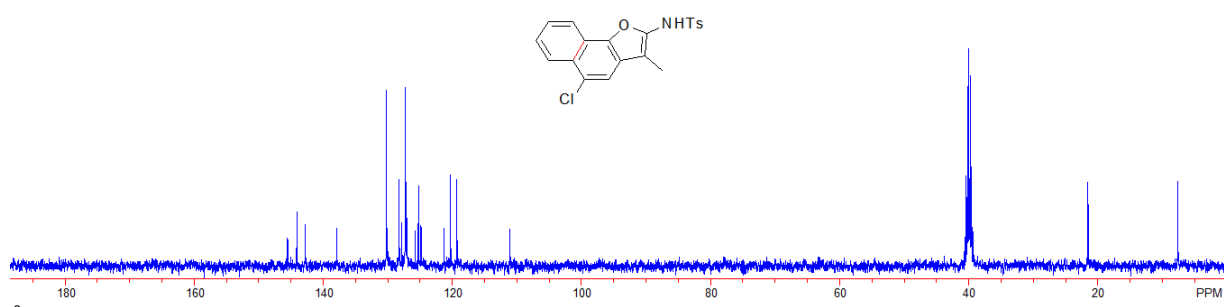
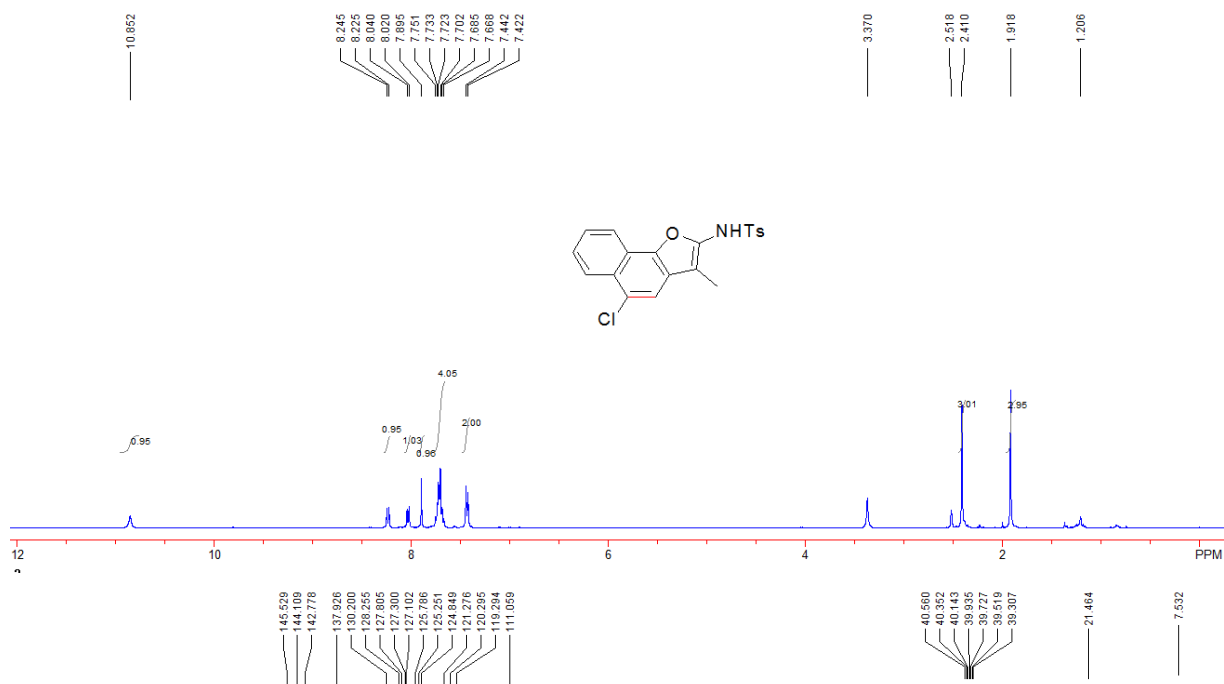
0.2 mmol scale, a white solid, 88% yield (62 mg). M.p.: 156-158 °C. ¹H NMR (CDCl₃, 400 MHz,

TMS) δ 2.42 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 6.82 (s, 1H, NH) 7.25 (d, $J = 8.0$ Hz, 2H, Ar), 7.42 (d, $J = 9.2$ Hz, 1H, Ar), 7.45-7.50 (m, 1H, Ar), 7.54-7.59 (m, 1H, Ar), 7.67-7.71 (m, 3H, Ar), 7.91 (d, $J = 8.4$ Hz, 1H, Ar), 8.29 (d, $J = 8.4$ Hz, 1H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 10.9, 21.6, 112.2, 114.4, 122.2, 122.9, 124.4, 126.2, 126.4, 127.4, 128.8, 129.0, 129.7, 130.5, 136.7, 139.7, 144.2, 149.6. IR (CH₂Cl₂) ν 3267, 2911, 1596, 1389, 1329, 1301, 1290, 1187, 1160, 1129, 1079, 820, 782, 746, 725, 670, 665 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₂₁N₂O₃S (M⁺ +NH₄) requires 369.1267, found: 369.1269.



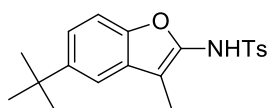
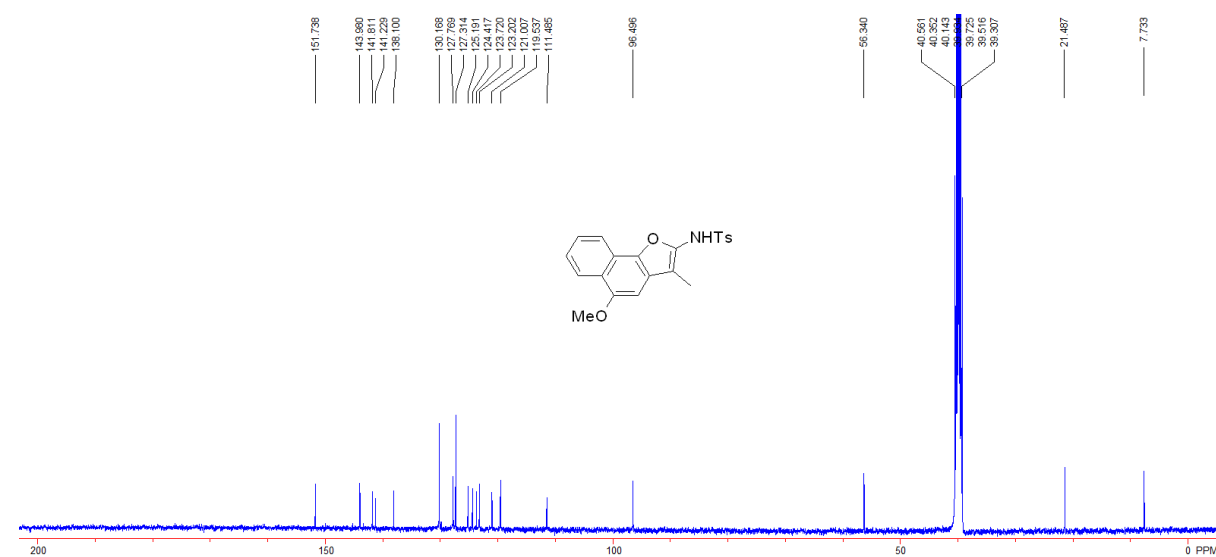
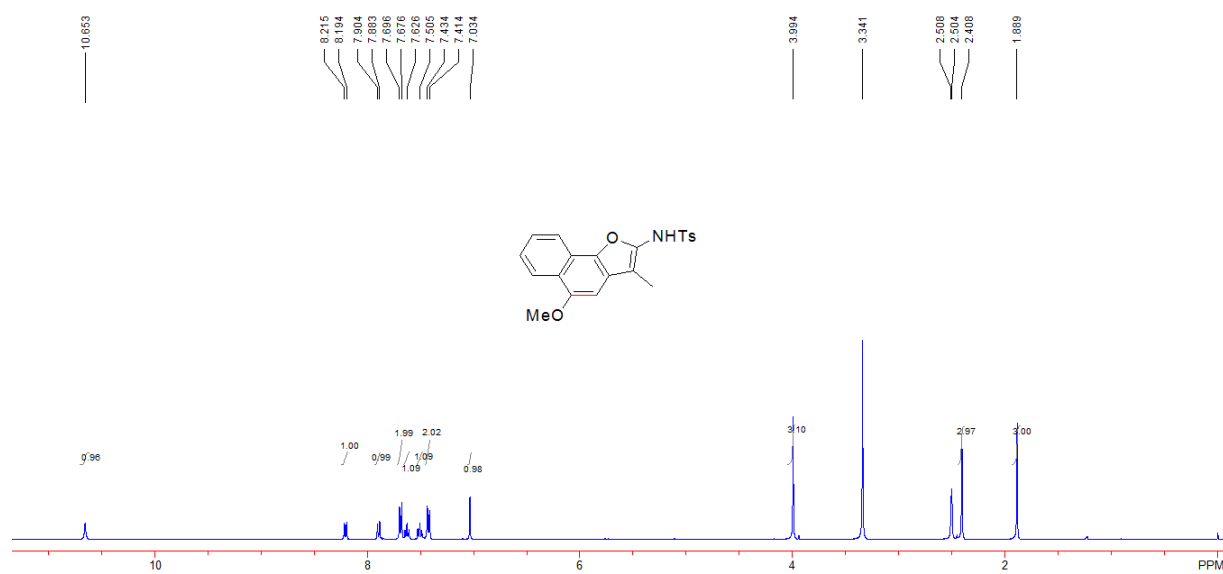
N-(5-Chloro-3-methylnaphtho[1,2-b]furan-2-yl)-4-methylbenzenesulfonamide 3d.

0.2 mmol scale, a white solid, 50% yield (39 mg). M.p.: 146-148 °C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 1.92 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 7.43 (d, J = 8.0 Hz, 2H, Ar), 7.66-7.76 (m, 4H, Ar), 7.89 (s, 1H, Ar), 8.03 (d, J = 8.0 Hz, 1H, Ar), 8.23 (d, J = 8.0 Hz, 1H, Ar), 10.85 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 7.5, 21.5, 111.0, 119.3, 120.3, 121.3, 124.8, 125.3, 125.8, 127.1, 127.3, 127.8, 128.3, 130.2, 137.9, 142.8, 144.1, 145.5. IR (CH₂Cl₂) ν 3245, 1592, 1447, 1338, 1151, 1107, 1087, 908, 895, 882, 870, 762, 745, 688, 665 cm^{-1} . HRMS (ESI) Calcd. for C₂₀H₂₀ClN₂O₃S (M⁺ + NH₄) requires 403.0878, found: 403.0878.



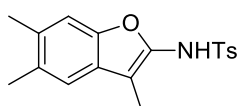
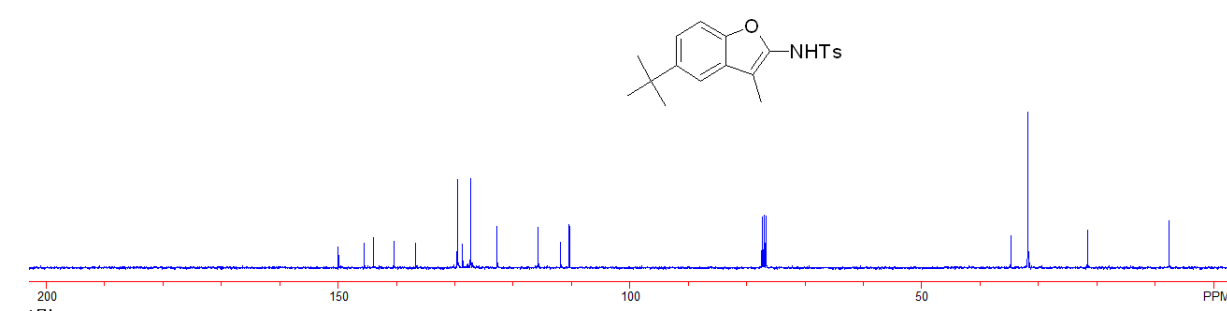
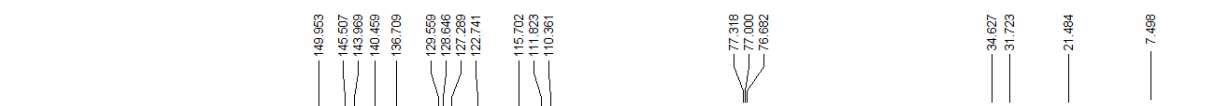
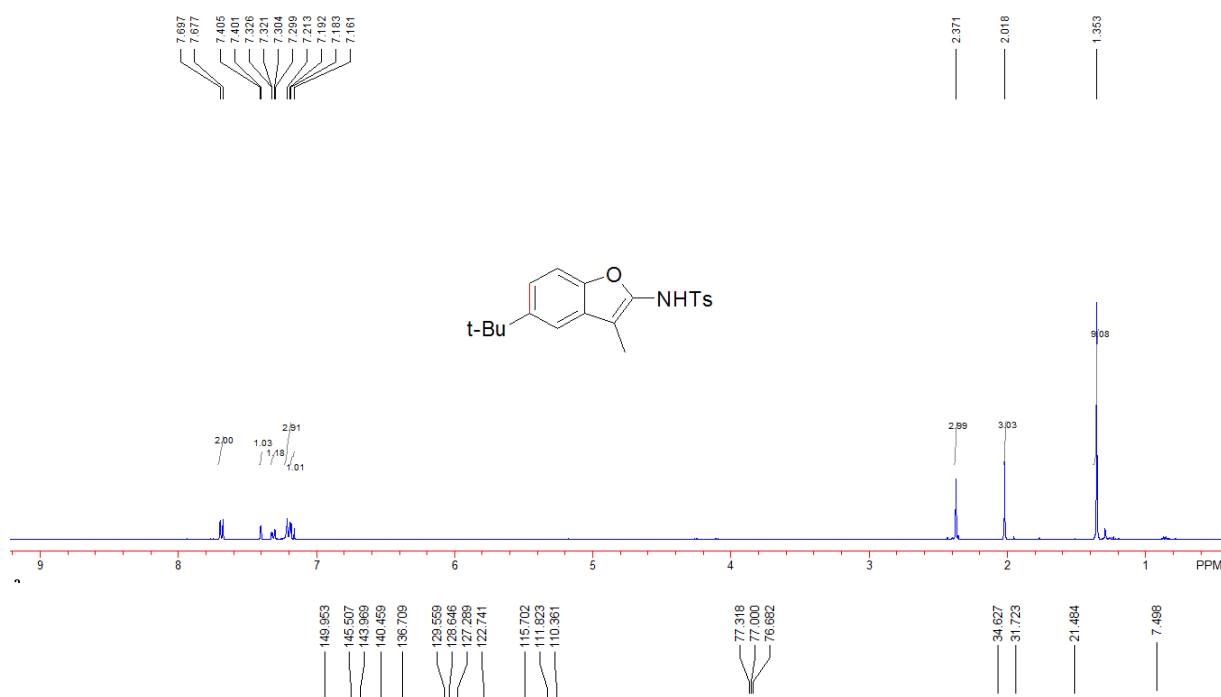
N-(5-Methoxy-3-methylnaphtho[1,2-b]furan-2-yl)-4-methylbenzenesulfonamide 3e.

0.2 mmol scale, a white solid, 82% yield (62 mg). M.p.: 164-166 °C. ^1H NMR (DMSO- d_6 , 400 MHz, TMS) δ 1.89 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 3.99 (s, 3H, CH₃), 7.03 (s, 1H, Ar), 7.42 (d, J = 8.0 Hz, 1H, Ar), 7.51 (dd, J = 8.4 Hz, J = 8.4 Hz, 3H, Ar), 7.63 (dd, J = 8.4 Hz, J = 8.4 Hz, 3H, Ar), 7.65-7.70 (m, 2H, Ar), 7.89 (d, J = 8.4 Hz, 1H, Ar), 8.20 (d, J = 8.4 Hz, 1H, Ar), 10.65 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz, TMS) δ 7.7, 21.5, 56.3, 96.5, 111.5, 119.5, 121.0, 123.2, 123.7, 124.4, 125.2, 127.3, 127.8, 130.2, 138.1, 141.2, 141.8, 144.0, 151.7. IR (CH₂Cl₂) ν 3258, 2921, 2162, 1647, 1592, 1452, 1434, 1335, 1301, 1223, 1158, 1106, 1090, 1070, 949, 914, 833, 810, 761, 703, 691, 666 cm^{-1} . HRMS (ESI) Calcd. for C₂₁H₂₀NO₄S (M⁺ + H) requires 382.1108, Found: 382.1108.



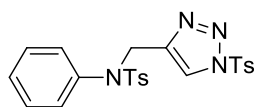
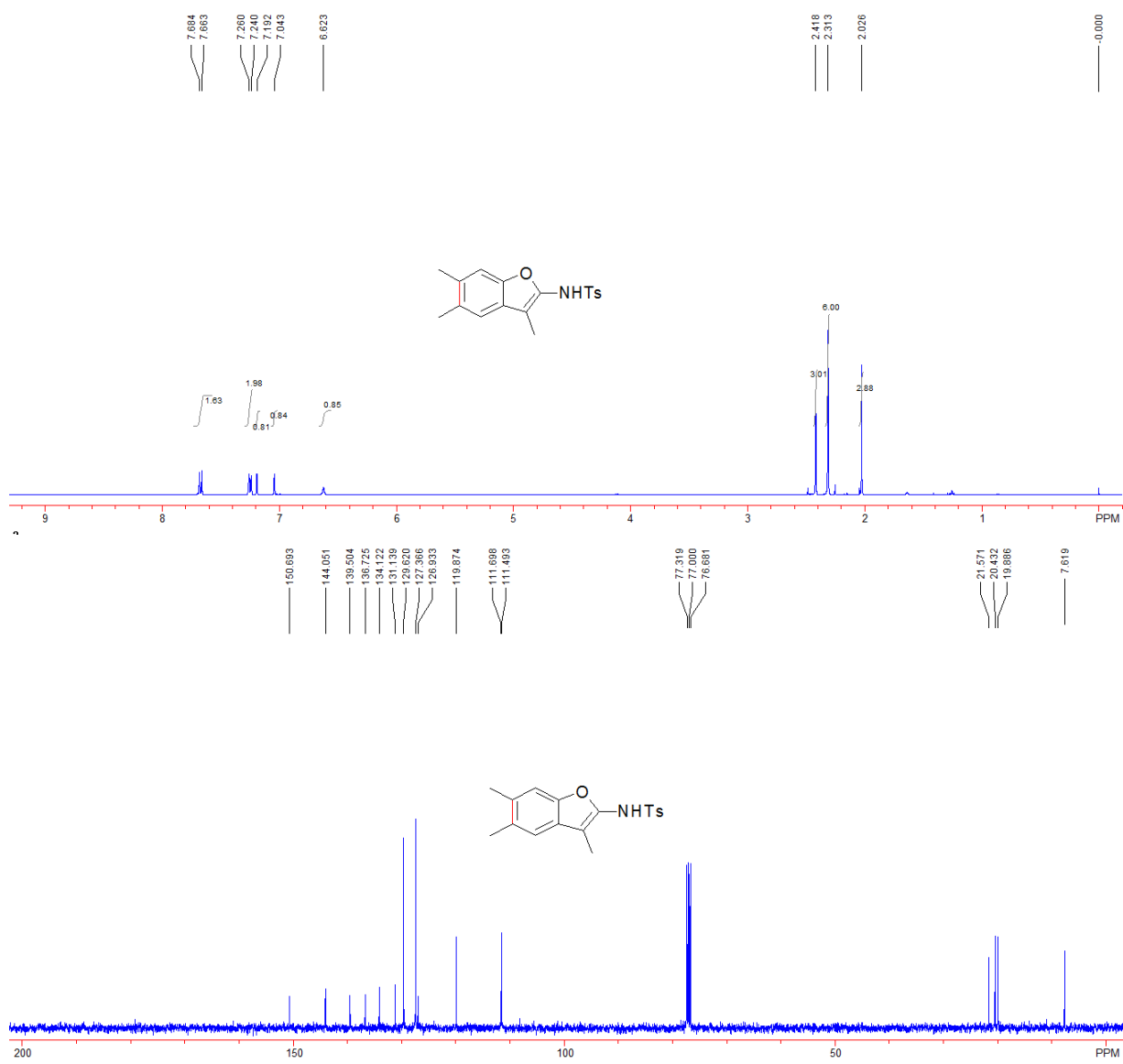
N-(5-tert-Butyl-3-methylbenzofuran-2-yl)-4-methylbenzenesulfonamide 3f

0.2 mmol scale, a white solid, 64% yield (46 mg). M.p.: 155-157 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.35 (s, 9H, CH_3), 2.02 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.17 (d, $J = 8.8$ Hz, 1H, Ar), 7.19-7.21 (m, 3H), 7.31 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H, Ar), 7.40 (d, $J = 2.0$ Hz, 1H, Ar), 6.60 (d, $J = 8.4$ Hz, 1H, Ar), 7.68 (d, $J = 8.0$ Hz 1H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 7.5, 21.5, 31.7, 34.6, 110.4, 111.8, 115.7, 122.7, 127.3, 128.6, 129.6, 136.7, 140.5, 144.0, 145.5, 150.0. IR (CH_2Cl_2) ν 3283, 1590, 1455, 1327, 1311, 1268, 1231, 1160, 1138, 1117, 1091, 918, 903, 810, 782, 677, 662 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{NH}_4$) $^+$ requires 375.1737, found: 375.1733.



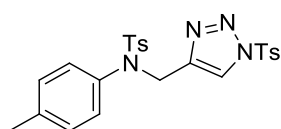
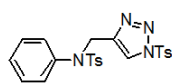
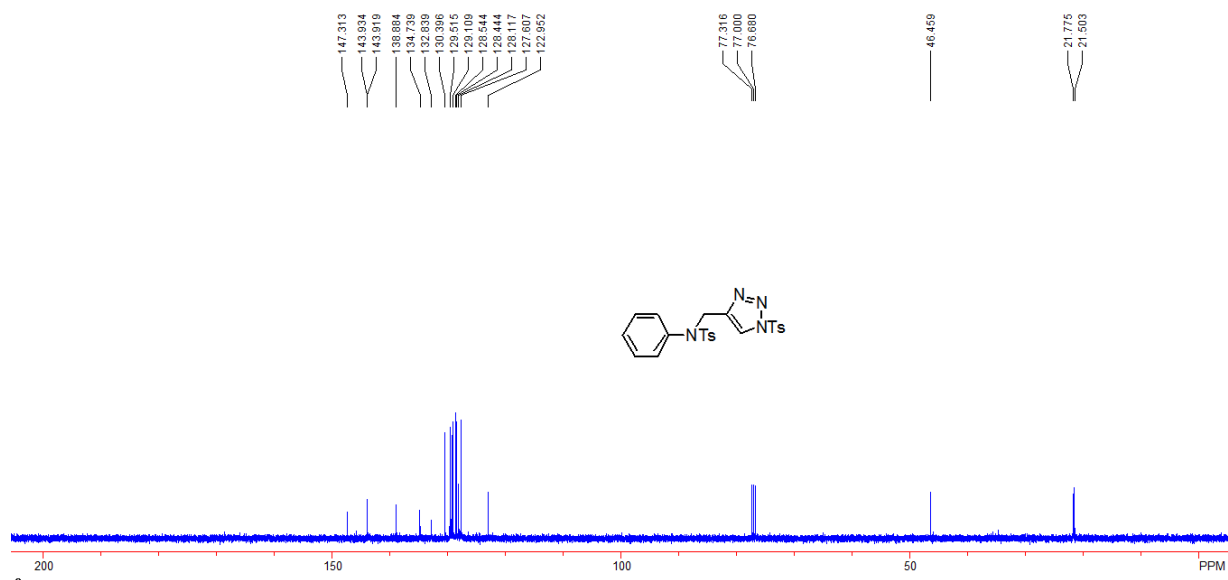
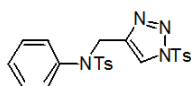
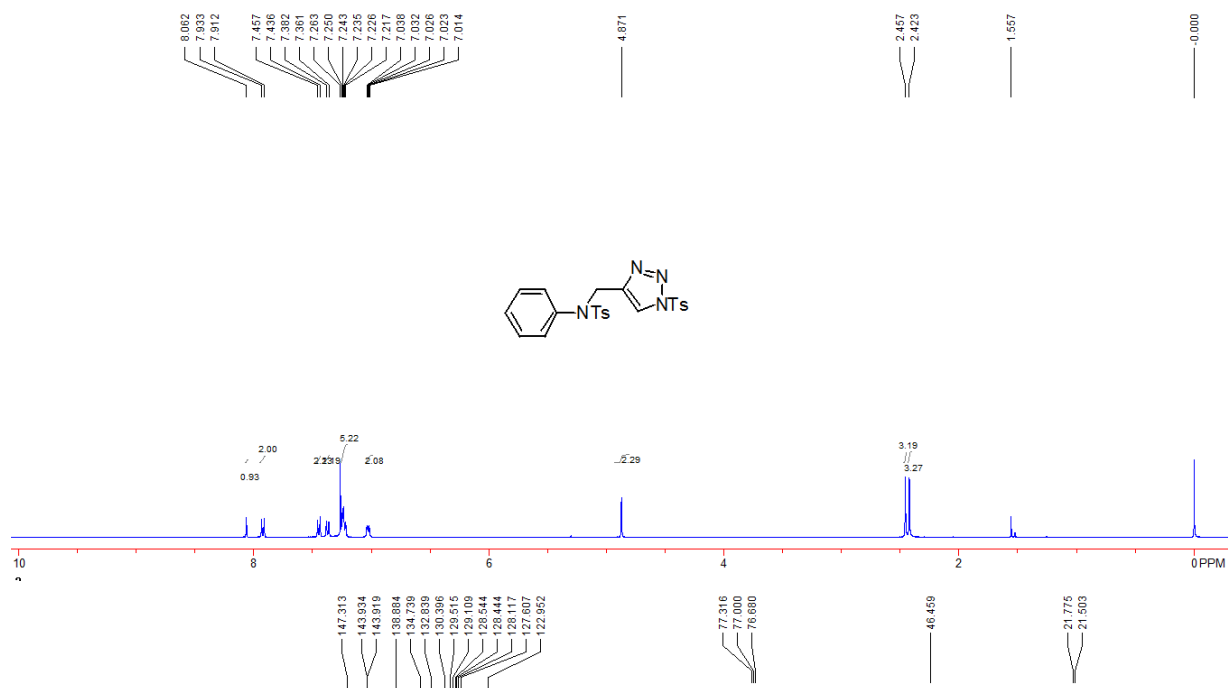
4-Methyl-N-(3,5,6-trimethylbenzofuran-2-yl)benzenesulfonamide 3g.

0.3 mmol scale, a white solid, 71% yield (70 mg). M.p.: 174-176 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.03 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 2.42 (s, 3H, CH_3), 6.62 (s, 1H, NH), 7.04 (s, 1H, Ar), 7.19 (s, 1H, Ar), 7.25 (d, $J = 8.0$ Hz, 2H, Ar), 7.67 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 7.6, 19.9, 20.4, 21.6, 111.5, 111.7, 119.9, 126.9, 127.4, 129.6, 131.1, 134.1, 136.7, 139.5, 144.0, 150.7. IR (CH_2Cl_2) ν 3224, 2857, 1629, 1593, 1460, 1407, 1333, 1163, 1088, 842, 812, 675, 661 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}^+\text{+H}$) requires 330.1158, found: 330.1153.



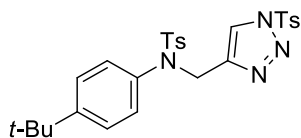
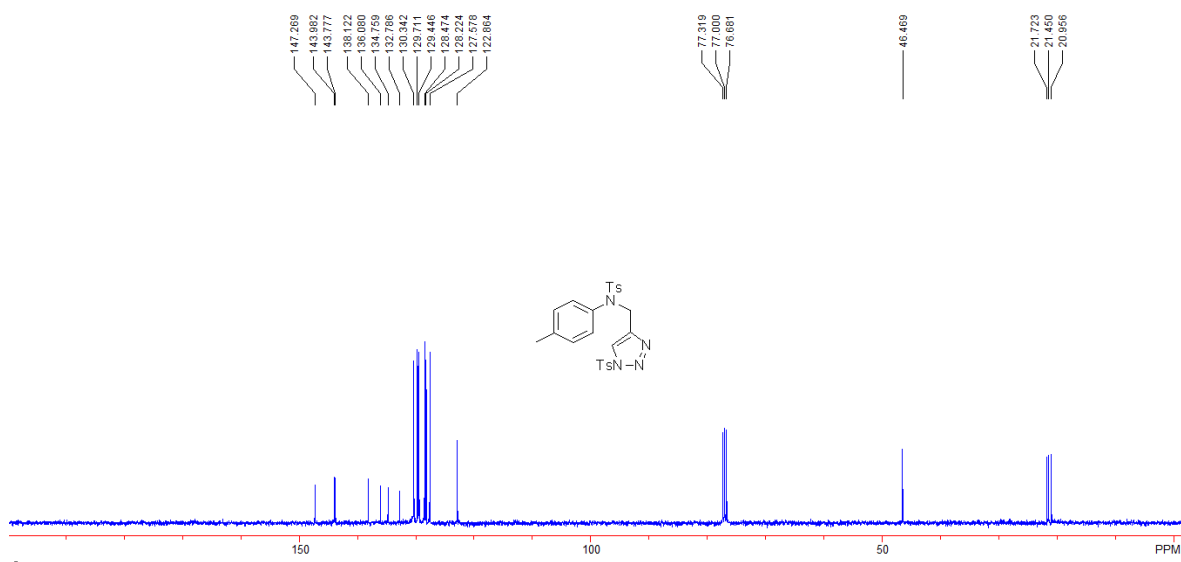
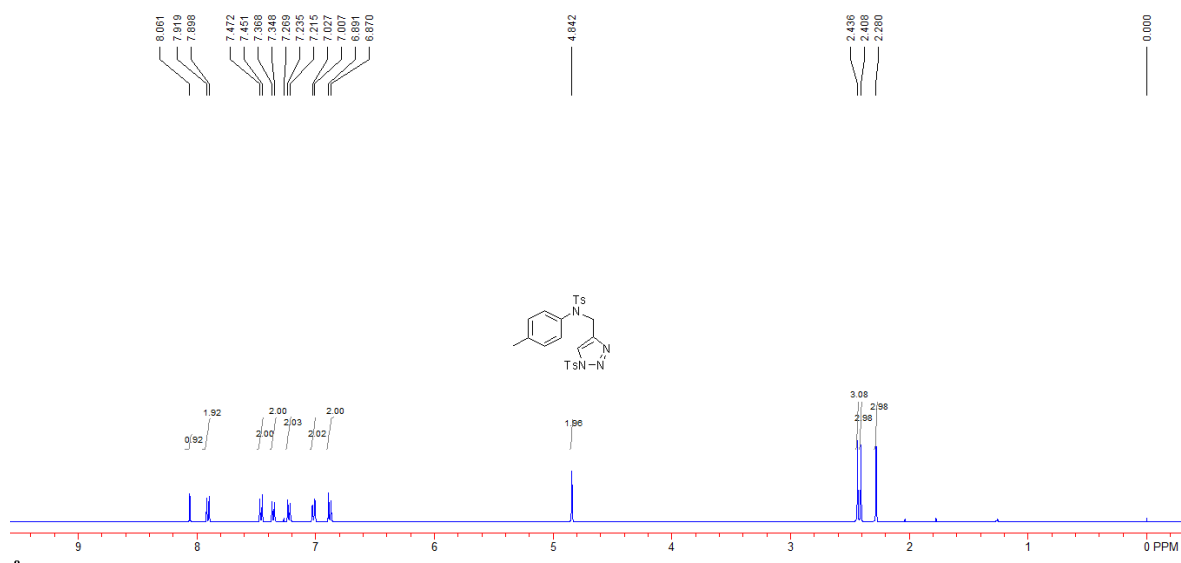
4-methyl-N-phenyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4a.

10.0 mmol scale, a white solid, 83% yield (4.00 g). m.p.: 134-136 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.42 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 4.87 (s, 2H, CH_2), 7.01-7.04 (m, 2H, Ar), 7.21-7.27 (m, 5H, Ar), 7.37 (d, $J = 8.4$ Hz, 2H, Ar), 7.44 (d, $J = 8.4$ Hz, 2H, Ar), 7.92 (d, $J = 8.4$ Hz, 2H, Ar), 8.06 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 21.8, 46.5, 123.0, 127.7, 128.1, 128.4, 128.5, 129.1, 129.5, 130.4, 132.8, 134.7, 138.9, 143.92, 143.93, 147.3. IR (CH_2Cl_2) ν 3051, 1594, 1494, 1454, 1396, 1346, 1310, 1272, 1198, 1184, 1162, 1124 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_4\text{O}_4\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 483.1155, found: 483.1166.



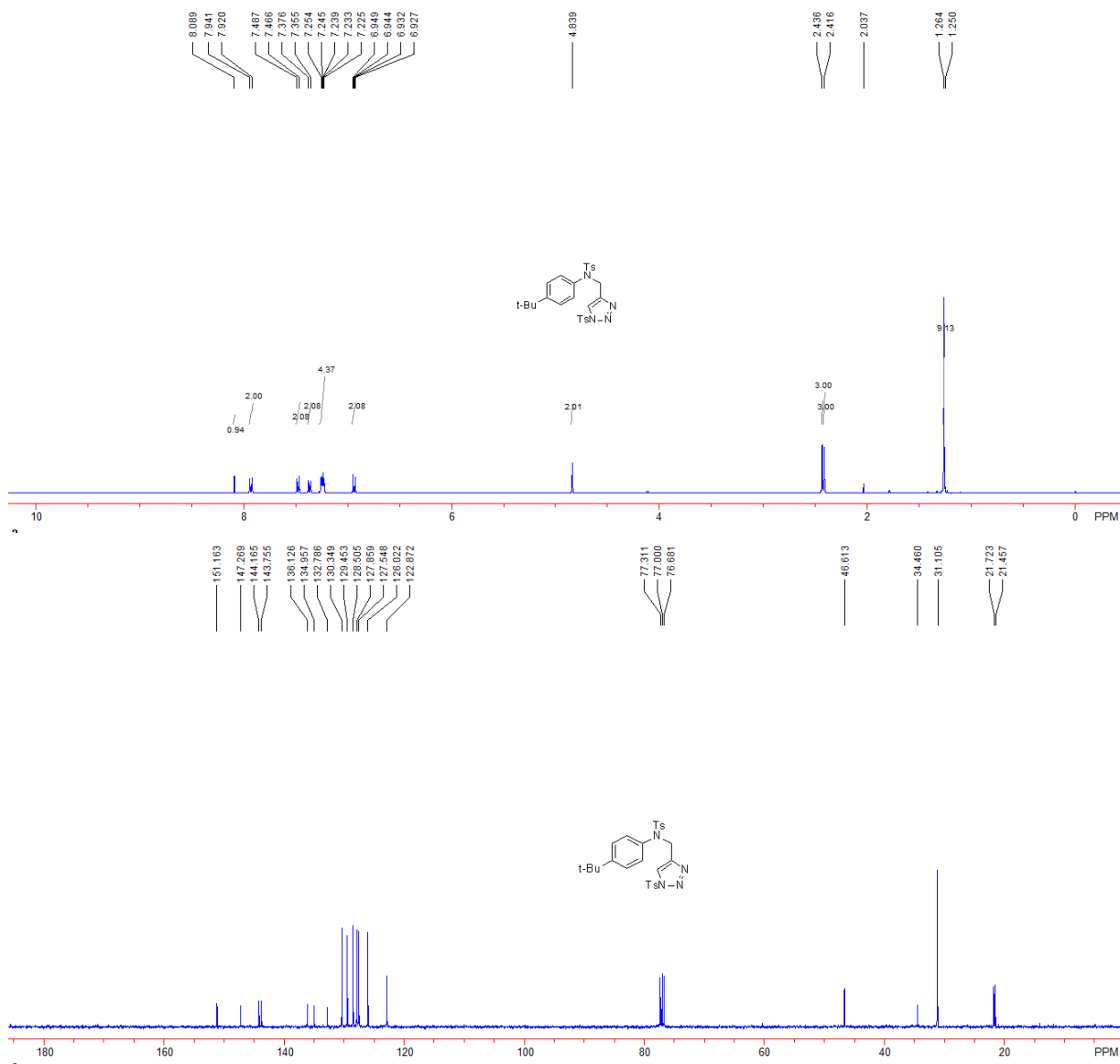
4-methyl-N-(p-tolyl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4b.

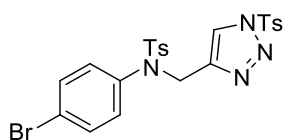
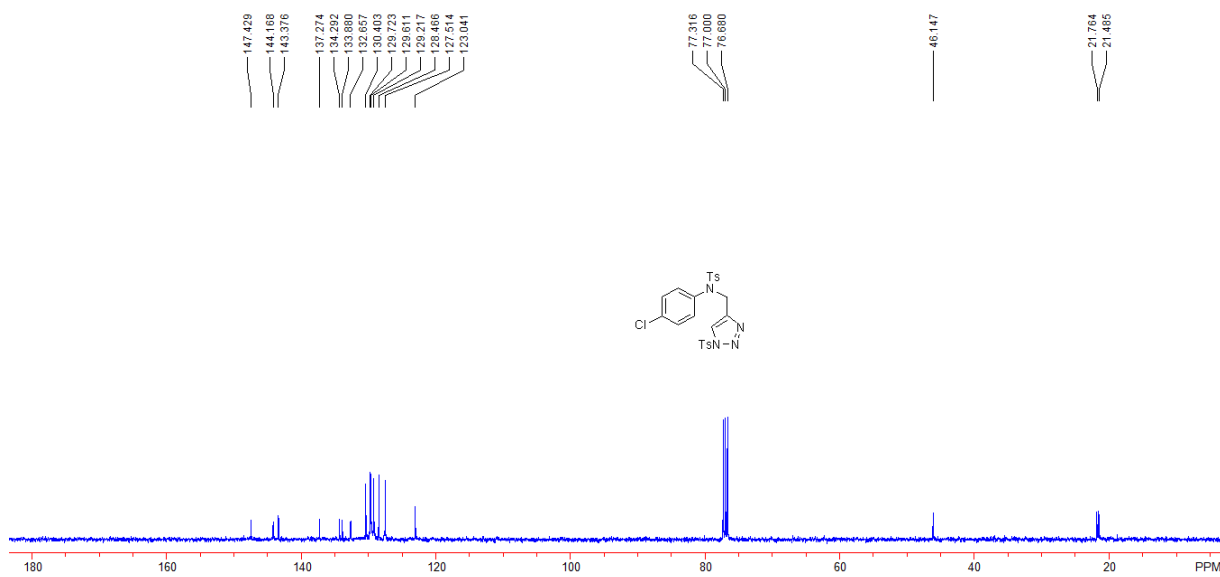
10.0 mmol scale, a white solid, 79% yield (3.92 g). m.p.: 115-117 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.28 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.84 (s, 2H, CH_2), 6.88 (d, $J = 8.4$ Hz, 2H, Ar), 7.02 (d, $J = 8.4$ Hz, 2H, Ar), 7.22 (d, $J = 8.0$ Hz, 2H, Ar), 7.35 (d, $J = 8.0$ Hz, 2H, Ar), 7.46 (d, $J = 8.4$ Hz, 2H, Ar), 7.91 (d, $J = 8.4$ Hz, 2H, Ar), 8.06 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.0, 21.4, 21.7, 46.5, 122.9, 127.6, 128.2, 128.5, 129.4, 129.7, 130.3, 132.8, 134.8, 136.1, 138.1, 143.8, 144.0, 147.3. IR (CH_2Cl_2) ν 3133, 3040, 2971, 1590, 1512, 1389, 1346, 1197, 1183, 1163, 1090, 1075, 1011, 977, 869, 825, 813, 800, 654 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_4\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 497.1312, found: 497.1314.



N-(4-(tert-butyl)phenyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4c.

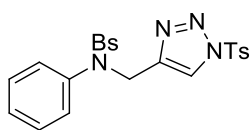
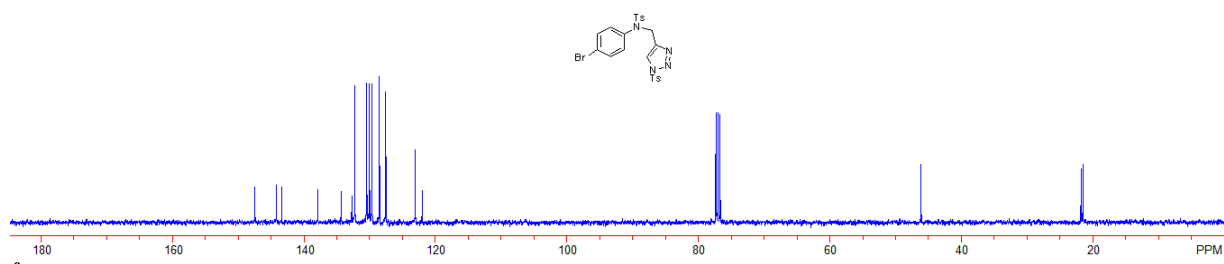
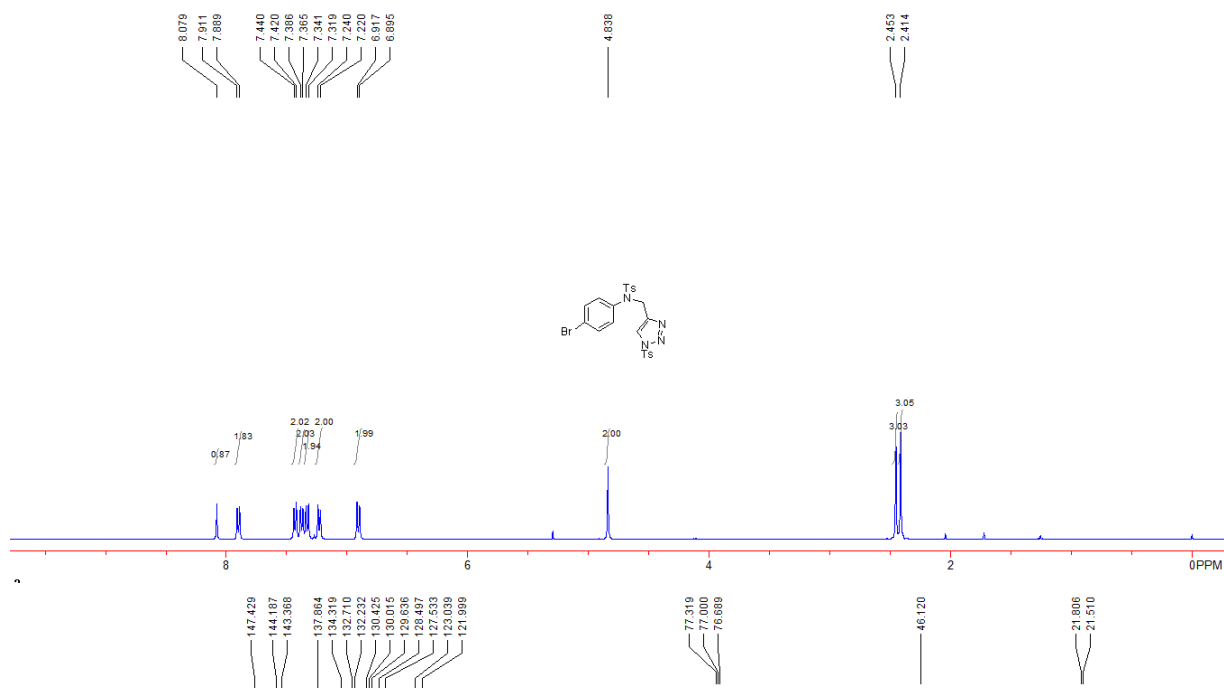
10.0 mmol scale, a white solid, 81% yield (4.36 g). m.p.: 142-146 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.26 (s, 9H, CH_3), 2.42 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.84 (s, 2H, CH_2), 6.94 (dd, $J = 6.0$ Hz, $J = 2.0$ Hz, 2H, Ar), 7.22-7.26 (m, 4H, Ar), 7.36 (d, $J = 8.4$ Hz, 2H, Ar), 7.47 (d, $J = 8.4$ Hz, 2H, Ar), 7.93 (d, $J = 8.4$ Hz, 2H, Ar), 8.09 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 21.7, 31.1, 34.5, 46.6, 122.9, 126.0, 127.5, 127.8, 128.5, 129.4, 130.3, 132.8, 134.9, 136.1, 143.8, 144.2, 147.3, 151.2. IR (CH_2Cl_2) ν 2959. 282, 1597, 1510. 1393, 1305, 1195, 1180, 1161, 1091, 1010, 970, 872, 813, 702, 667 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{27}\text{H}_{31}\text{N}_4\text{O}_4\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 539.1781, found: 539.1781.





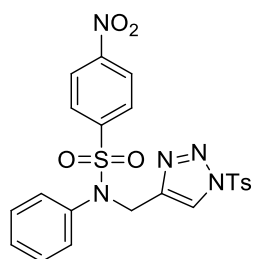
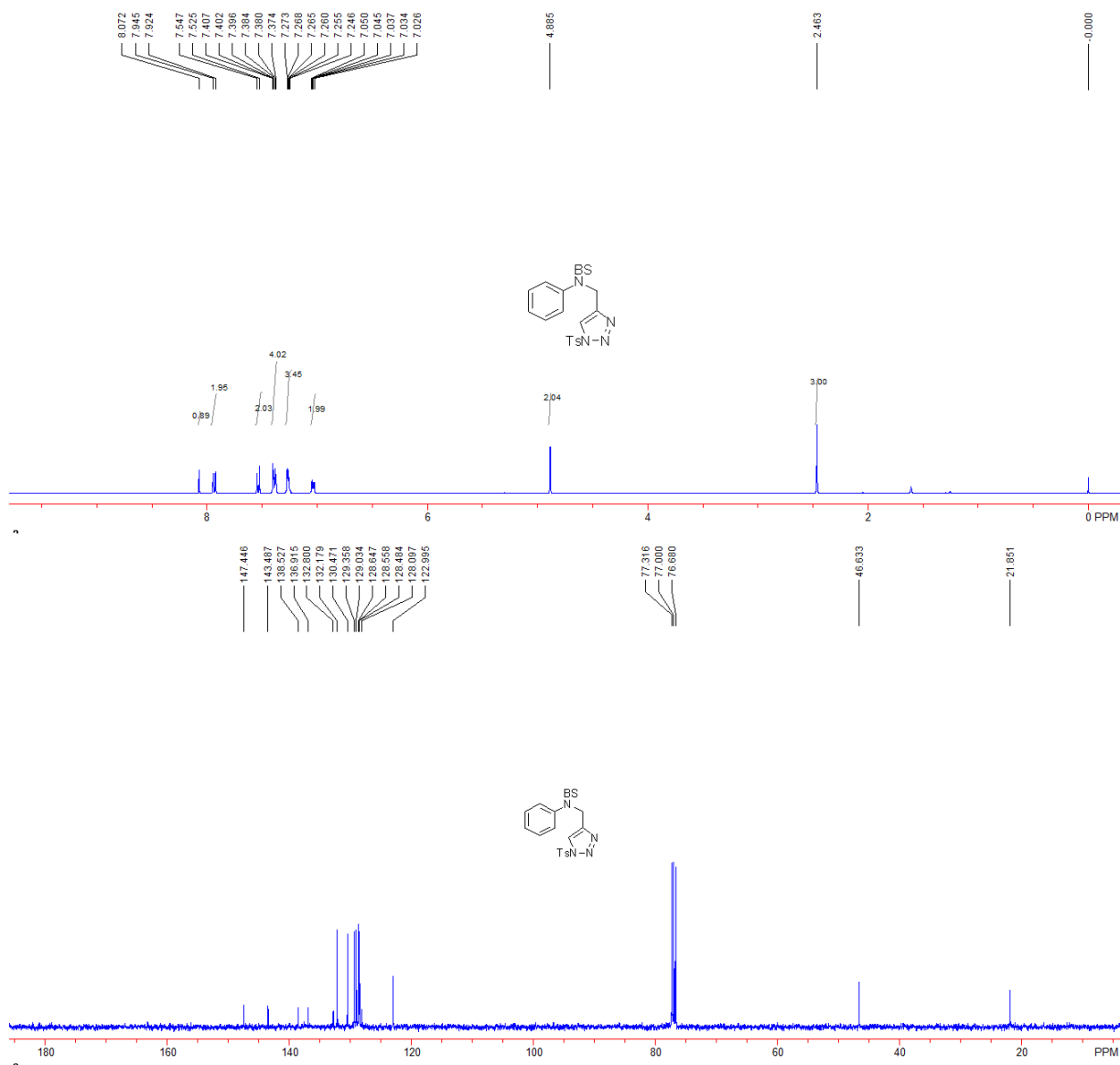
**N-(4-bromophenyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide
4e.**

10.0 mmol scale, a white solid, 72% yield (4.03 g). m.p.: 157-159 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.41 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.84 (s, 2H, CH_2), 6.90 (d, $J = 8.4$ Hz, 2H, Ar), 7.23 (d, $J = 8.0$ Hz, 2H, Ar), 7.33 (d, $J = 8.4$ Hz, 2H, Ar), 7.37 (d, $J = 8.4$ Hz, 2H, Ar), 7.43 (d, $J = 8.0$ Hz, 2H, Ar), 7.90 (d, $J = 8.4$ Hz, 2H, Ar), 8.08 (s, 1H, CH=). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 21.8, 46.1, 122.0, 123.0, 127.5, 128.5, 129.6, 130.0, 130.4, 132.2, 132.7, 134.3, 137.9, 143.4, 144.2, 147.4. IR (CH_2Cl_2) ν 3138, 3069, 2923, 1593, 1487, 1383, 1336, 1300, 1194, 1179, 1161, 1098, 1010, 975, 860, 815, 745, 711, 699, 686, 665 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{22}\text{BrN}_4\text{O}_4\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 561.0260, found: 561.0261.



4-bromo-N-phenyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4f.

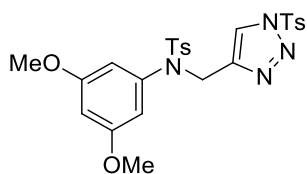
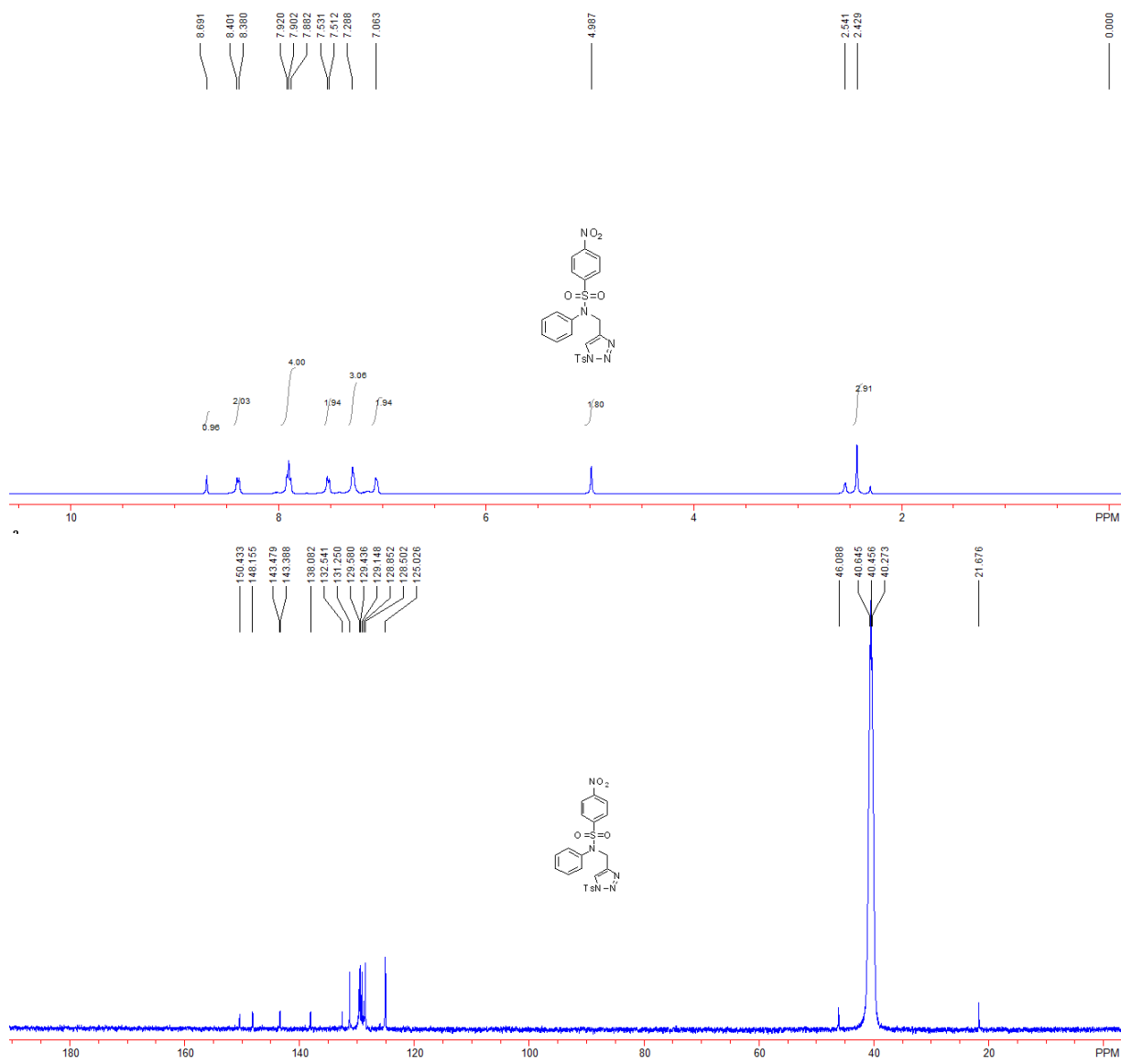
10.0 mmol scale, a white solid, 78% yield (4.26 g). m.p.: 170-172 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.46 (s, 3H, CH₃), 4.88 (s, 2H, CH₂), 7.02-7.05 (m, 2H, Ar), 7.24-7.28 (m, 3H, Ar), 7.37-7.41 (m, 4H, Ar), 7.53 (d, *J* = 8.4 Hz, 2H, Ar), 7.93 (d, *J* = 8.4 Hz, 2H, Ar), 8.07 (s, 1H, CH=). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.8, 46.6, 123.0, 128.1, 128.5, 128.6, 128.7, 129.0, 129.4, 130.5, 132.2, 132.8, 136.9, 138.5, 143.5, 147.4. IR (CH₂Cl₂) ν 3142, 3052, 1595, 1566, 1490, 1396, 1348, 1213, 1200, 1186, 1163, 1089, 1017, 1008, 989, 874, 817, 746, 718, 668 cm⁻¹. HRMS (ESI) Calcd. for C₂₂H₂₀BrN₄O₄S₂⁺ (M+H⁺) requires 547.0104, found: 547.0107.



4-nitro-N-phenyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4g.

10.0 mmol scale, a yellow solid, 97% yield (4.98 g). m.p.: 181-183 °C. ¹H NMR (DMSO-d₆, 400 MHz, TMS) δ 2.43 (s, 3H, CH₃), 4.99 (s, 2H, CH₂), 7.06 (s, 2H, Ar), 7.29 (s, 3H, Ar), 7.52 (d, *J* = 7.6 Hz, 2H, Ar), 7.88-7.92 (m, 4H, Ar), 8.39 (d, *J* = 8.4 Hz, 2H, Ar), 8.69 (s, 1H, CH=). ¹³C NMR (DMSO-d₆, 100 MHz, TMS) δ 21.7, 46.1, 125.0, 128.5, 128.8, 129.1, 129.4, 129.6, 131.2, 132.5, 138.1, 143.4, 143.5, 148.2, 150.4. IR (CH₂Cl₂) ν 3133, 3109, 3060, 1591, 1524, 1396, 1345, 1215,

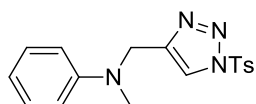
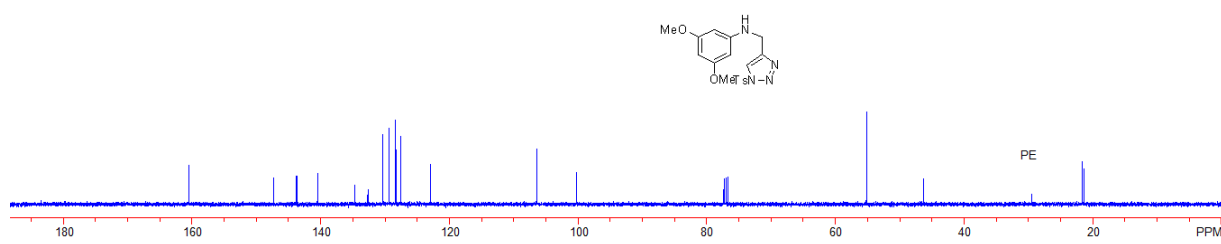
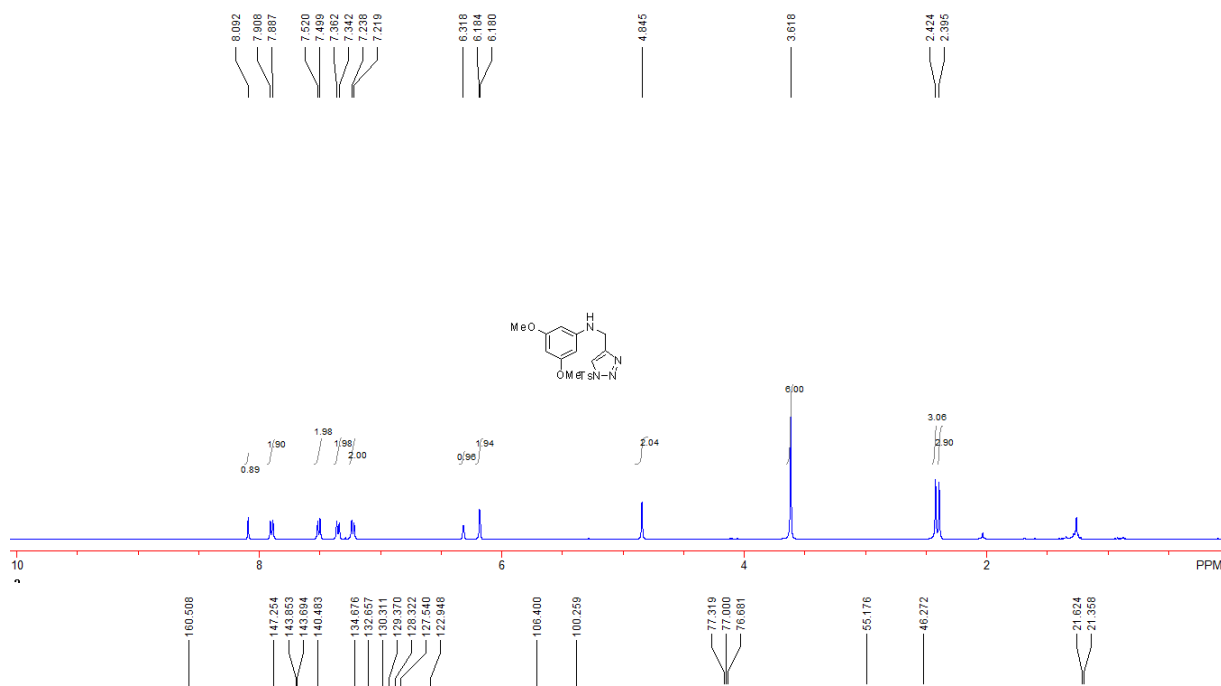
1201, 1187, 1164, 1089, 1017, 995, 877, 853, 751, 737, 681, 668 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_5\text{O}_6\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 514.0850, found: 514.0852.



N-(3,5-dimethoxyphenyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4h.

10.0 mmol scale, a white solid, 72% yield (3.90 g). m.p.: 120-122 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.39 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.61 (s, 6H, CH_3), 4.84 (s, 2H, CH_2), 6.18 (d, $J = 1.6$ Hz, 2H, Ar), 6.32 (s, 1H, Ar), 7.23 (d, $J = 7.6$ Hz, 2H, Ar), 7.35 (d, $J = 8.0$ Hz, 2H, Ar),

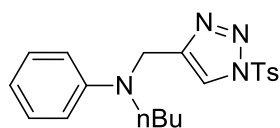
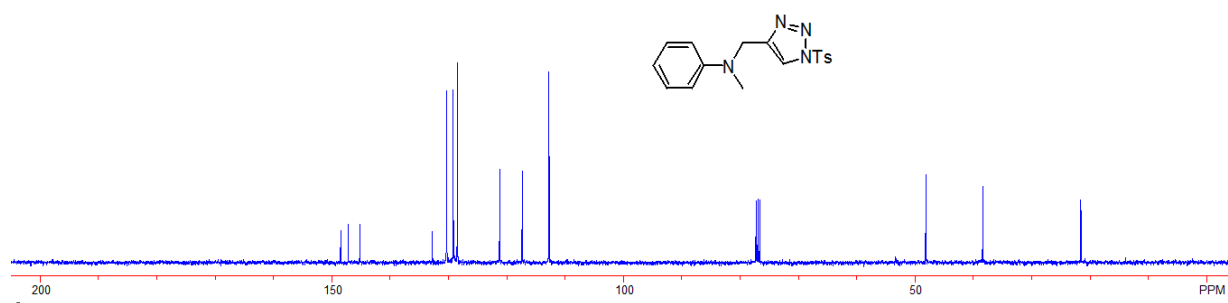
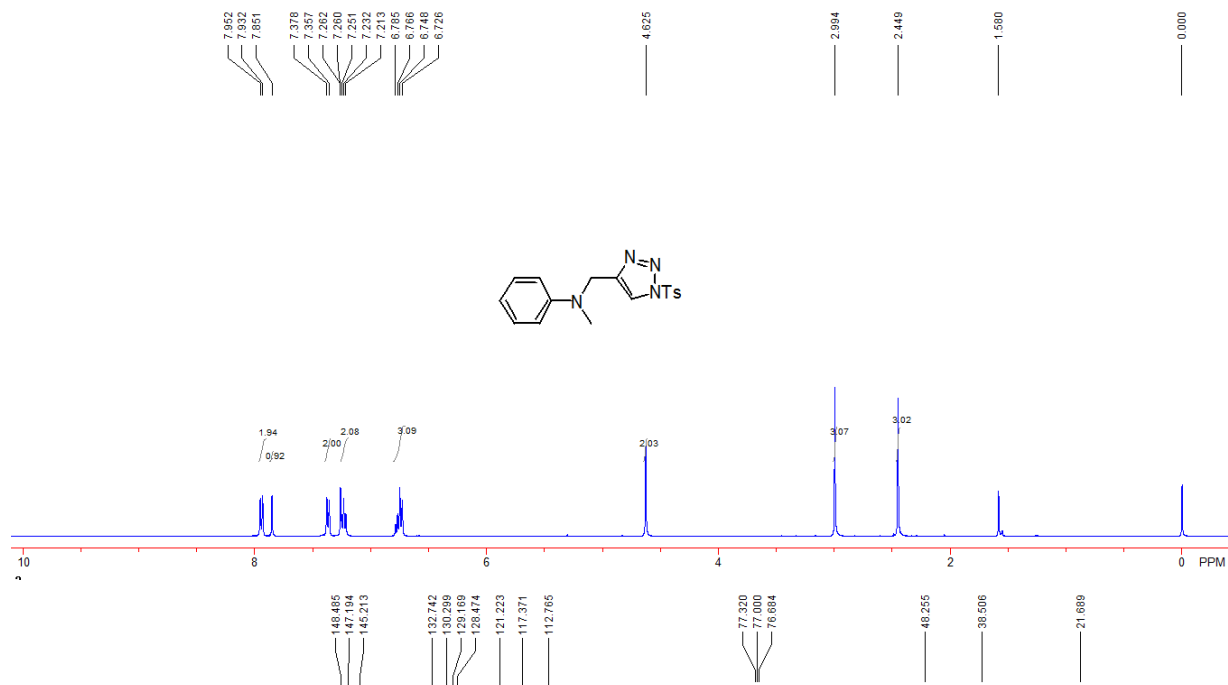
7.51 (d, $J = 7.6$ Hz, 2H, Ar), 7.90 (d, $J = 8.0$ Hz, 2H, Ar), 8.09 (s, 1H, CH=). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.4, 21.6, 46.3, 55.2, 100.2, 106.4, 122.9, 127.5, 128.3, 129.4, 130.3, 132.6, 134.7, 140.5, 143.7, 143.8, 147.2, 160.5. IR (CH_2Cl_2) ν 3121, 2963, 2843, 1736, 1606, 1591, 1427, 1345, 1208, 1185, 1150, 1091, 1055, 1034, 989, 927, 811, 700, 664 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O}_6\text{S}_2^+$ ($\text{M}+\text{H}^+$) requires 543.1367, found: 543.1369.



N-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4i.

5.0 mmol scale, a yellow solid, 75% yield (1.35 g). m.p.: 91-93 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 4.63 (d, 2H, CH_2), 6.72-6.79 (m, 3H, Ar), 7.24 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 2H, Ar), 7.37 (d, $J = 8.0$ Hz, 2H, Ar), 7.85 (s, 1H, CH=), 7.94 (d, $J = 8.0$

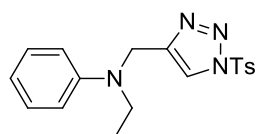
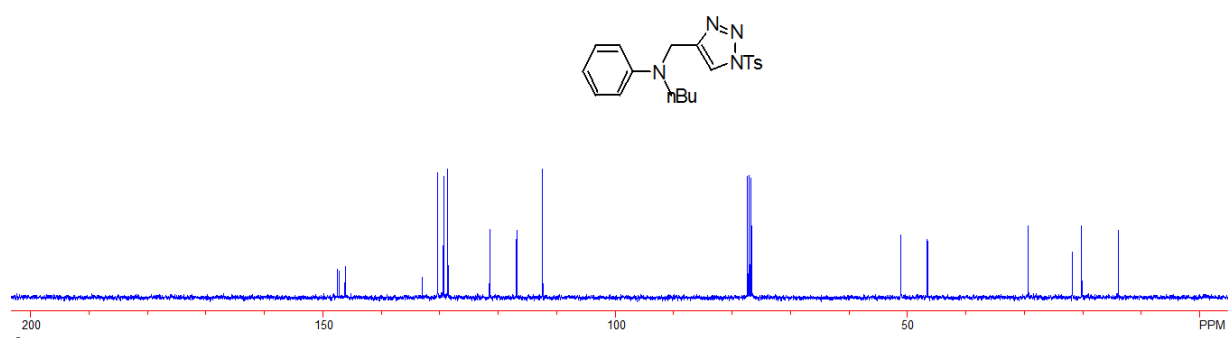
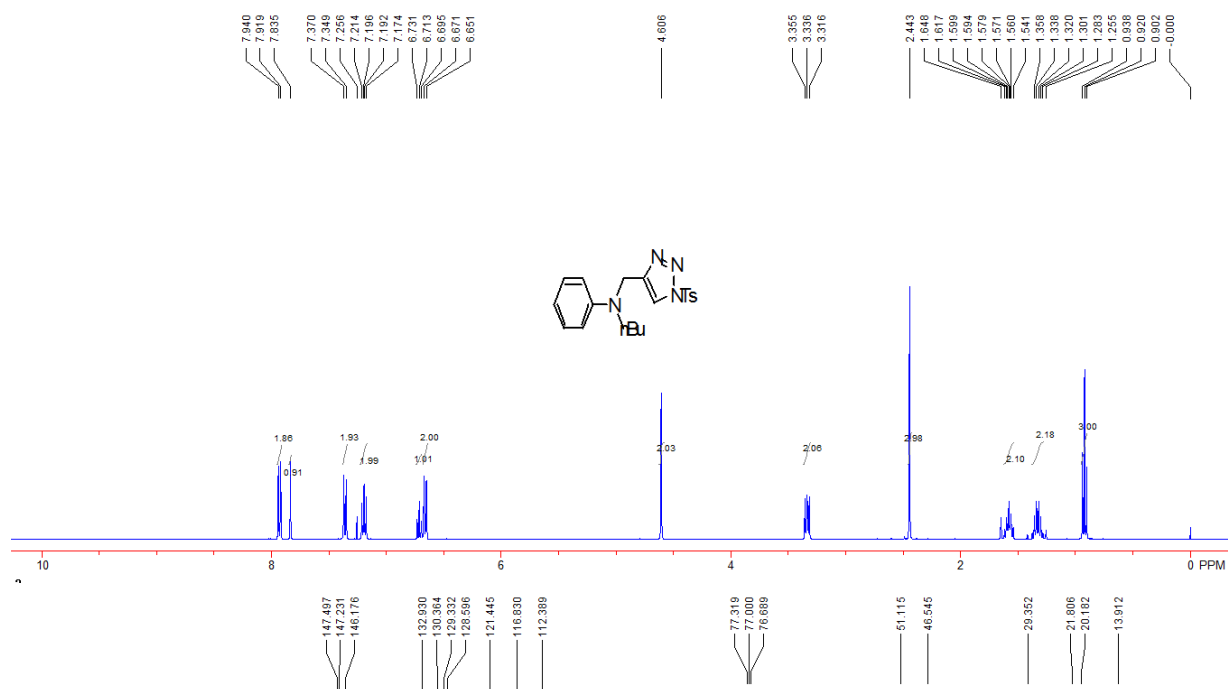
Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.8, 38.7, 48.4, 112.9, 117.5, 121.4, 128.6, 129.3, 130.4, 132.9, 145.4, 147.4, 148.6. IR (CH_2Cl_2) ν 3125, 1592, 1505, 1383, 1299, 1265, 1222, 1194, 1176, 1010, 978, 964, 810, 765, 739, 700, 668 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_4\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 343.1223, found: 343.1218.



N,3-dimethyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4j.

10.0 mmol scale, a white solid, 81% yield (3.11 g). m.p.: 107-109 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 0.92 (t, $J = 7.2$ Hz, 3H, CH_3), 1.29-1.38 (m, 2H, CH_2), 1.54-1.62 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 3.34 (t, $J = 7.2$ Hz, 2H, CH_2), 4.61 (s, 2H, CH_2), 6.66 (d, $J = 8.0$ Hz, 2H, Ar), 6.71 (dd,

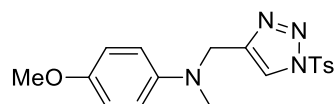
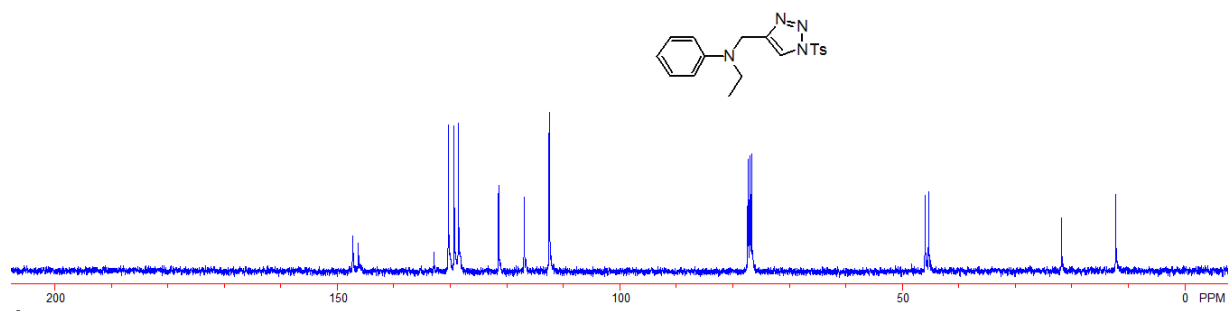
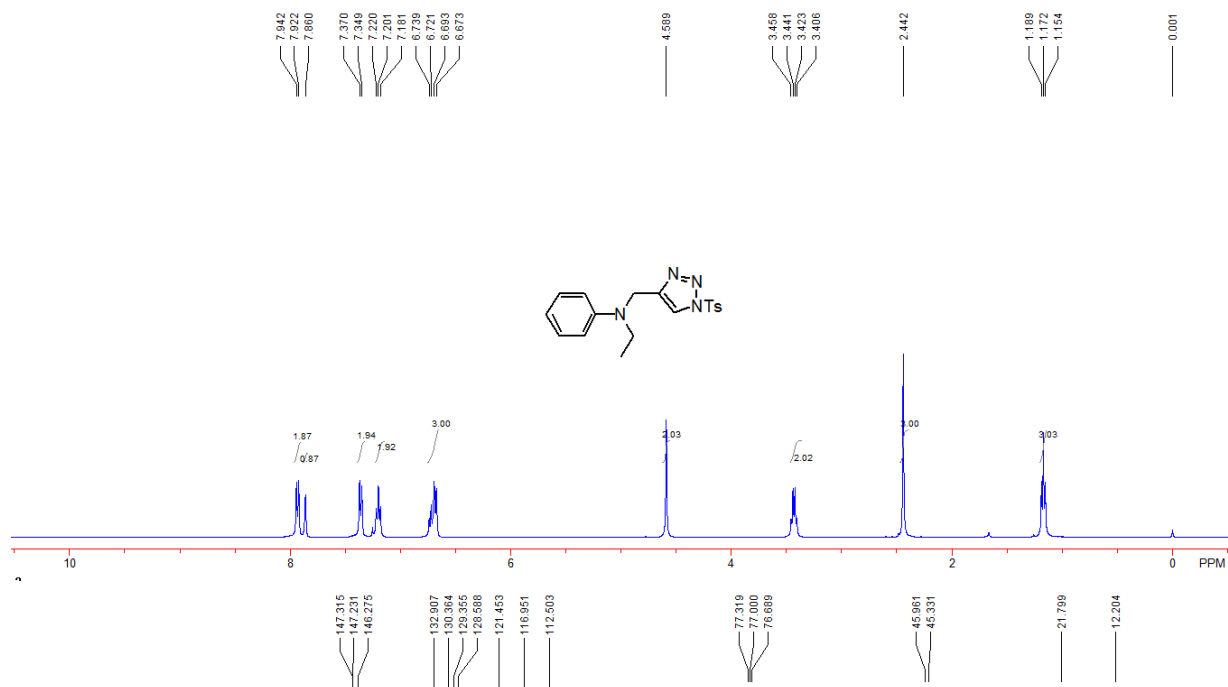
$J = 7.2$ Hz, $J = 7.2$ Hz, 1H, Ar), 7.19 (d, $J = 8.0$ Hz, 1H, Ar), 7.20 (d, $J = 8.0$ Hz, 1H, Ar), 7.36 (d, $J = 8.4$ Hz, 2H, Ar), 7.84 (s, 1H, CH=), 7.93 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.0, 20.2, 21.9, 29.4, 46.6, 51.2, 112.4, 116.9, 121.5, 128.7, 129.4, 130.4, 133.0, 146.2, 147.3, 147.5. IR (CH_2Cl_2) ν 3153, 2959, 2927, 1596, 1504, 1390, 1193, 1177, 1091, 1007 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_4\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 385.1693, found: 385.1694.



N-ethyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4k.

10.0 mmol scale, a white solid, 82% yield (2.93 g). m.p.: 90-92 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.17 (t, $J = 7.2$ Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.43 (q, $J = 7.2$ Hz, 2H, CH_2), 4.59 (d,

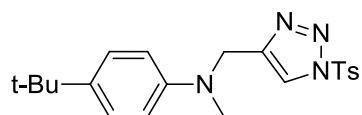
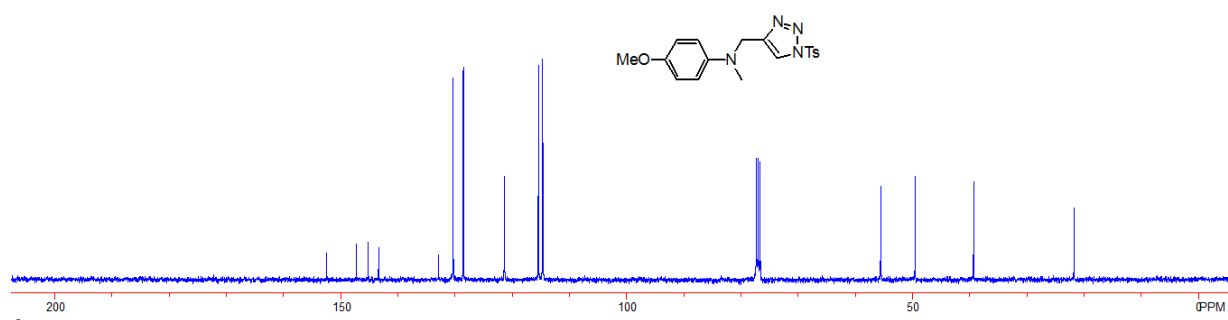
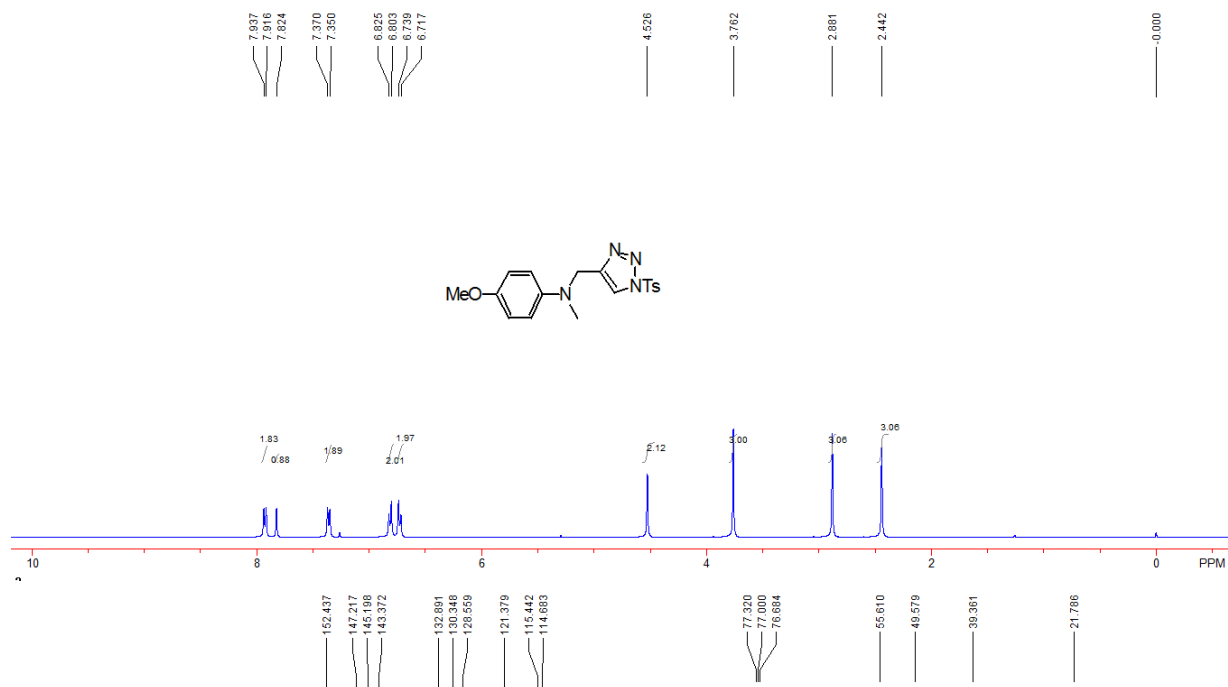
2H, CH₂), 6.72-6.74 (m, 3H, Ar), 7.20 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 2H, Ar), 7.36 (d, *J* = 8.0 Hz, 2H, Ar), 7.86 (s, 1H, CH=), 7.93 (d, *J* = 8.0 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 12.3, 21.9, 45.4, 46.0, 112.6, 117.0, 121.5, 128.7, 129.4, 130.4, 133.0, 146.3, 147.3, 147.4. IR (CH₂Cl₂) ν 3149, 3060, 2971, 1596, 1505, 1389, 1247, 1193, 1174, 1090, 1005, 968 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₂₁N₄O₂S⁺ (M+H⁺) requires 357.1380, found: 357.1380.



4-methoxy-N-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4l.

10.0 mmol scale, a white solid, 74% yield (2.75 g). m.p.: 81-83 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.44 (s, 3H, CH₃), 2.88 (s, 3H, CH₃), 3.76 (s, 3H, CH₃), 4.53 (s, 2H, CH₂), 6.73 (d, *J* =

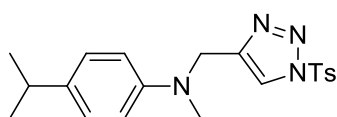
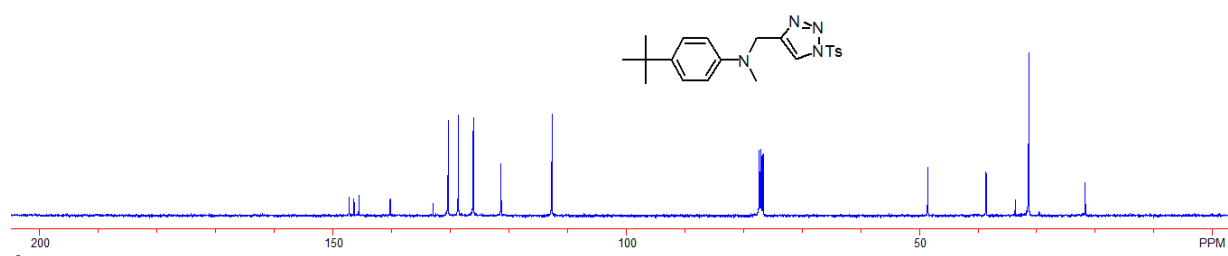
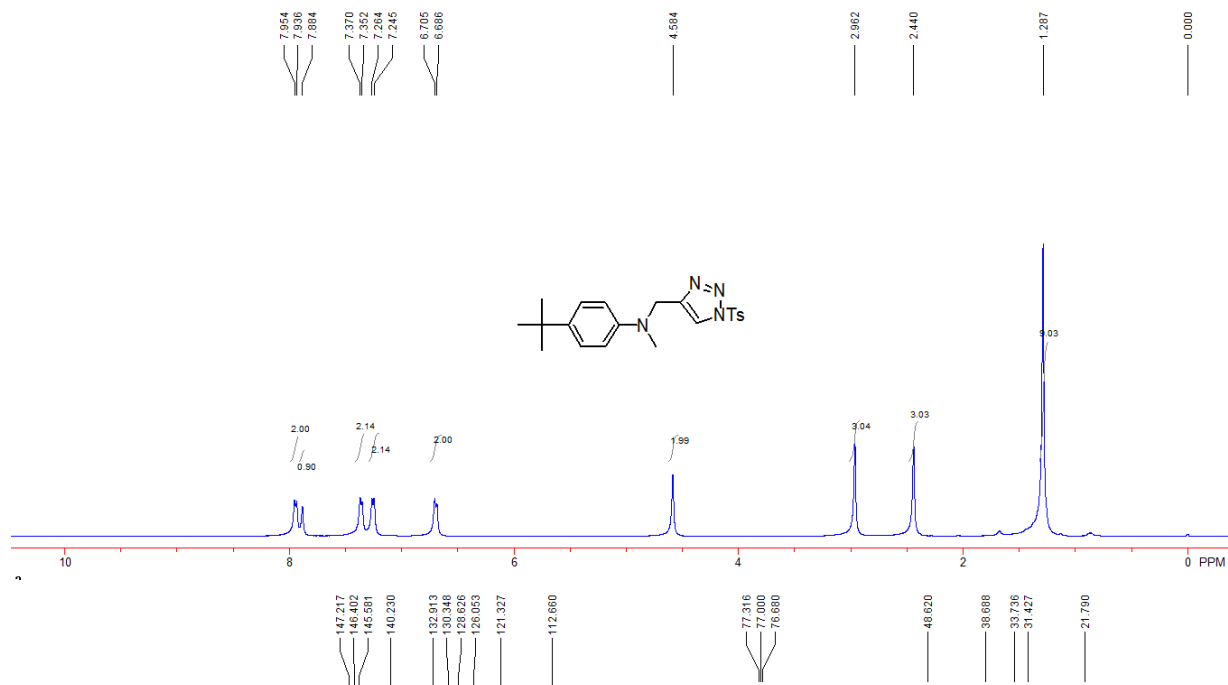
8.8 Hz, 2H, Ar), 6.81 (d, $J = 8.8$ Hz, 2H, Ar), 7.36 (d, $J = 8.0$ Hz, 2H, Ar), 7.82 (s, 1H, CH=), 7.93 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.8, 39.4, 49.6, 55.6, 114.7, 115.4, 121.4, 128.6, 130.3, 132.9, 143.4, 145.2, 147.2, 152.4. IR (CH_2Cl_2) ν 3137, 2927, 1590, 1510, 1389, 1241, 1193, 1174, 1090, 1035, 1009 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_4\text{O}_3\text{S}^+$ ($\text{M}+\text{H}^+$) requires 373.1329, found: 373.1329.



4-*tert*-butyl-N-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4m.

10.0 mmol scale, a white solid, 83% yield (3.30 g). m.p.: 105-107 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.29 (s, 9H, 3CH₃), 2.44 (s, 3H, CH₃), 2.96 (s, 3H, CH₃), 4.58 (s, 2H, CH₂), 6.70 (d, $J = 7.6$ Hz, 2H, Ar), 7.25 (d, $J = 7.6$ Hz, 2H, Ar), 7.36 (d, $J = 7.6$ Hz, 2H, Ar), 7.88 (s, 1H,

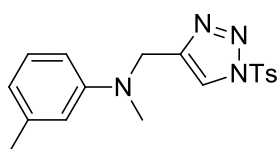
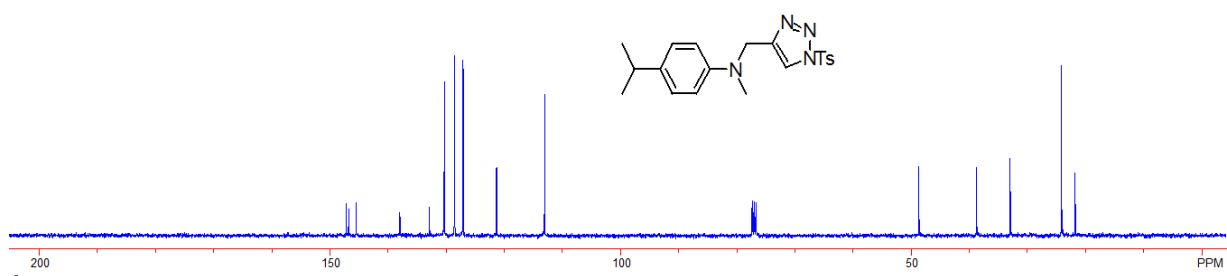
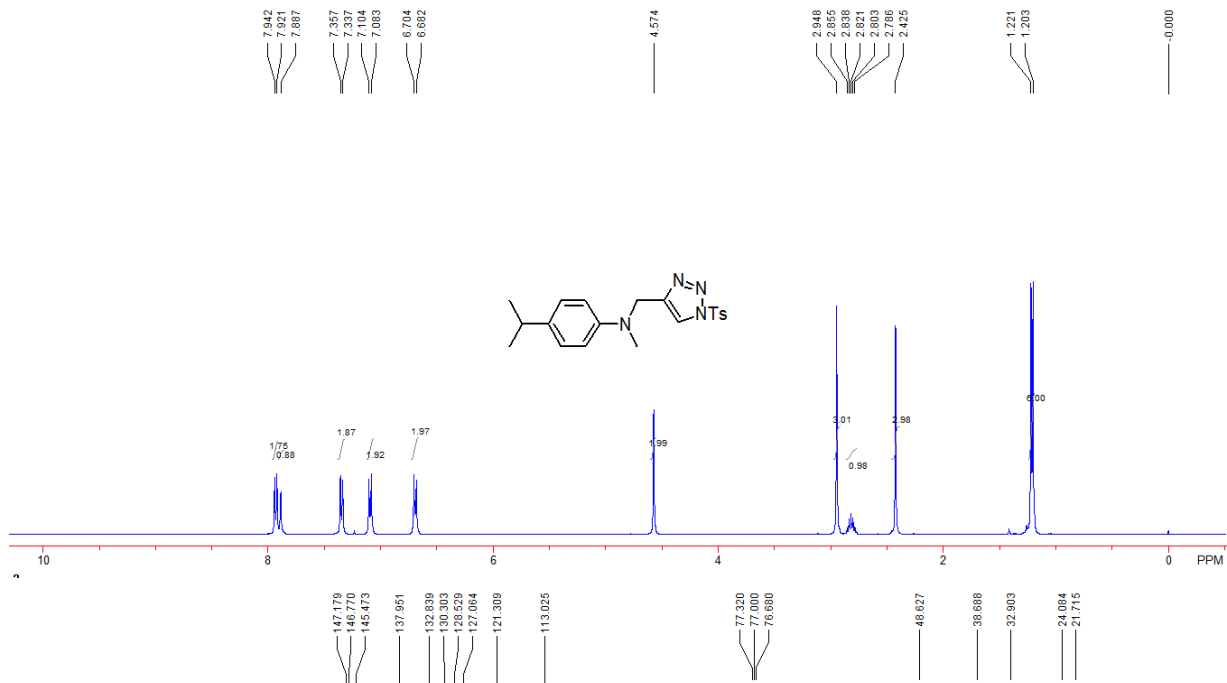
CH=), 7.94 (d, $J = 7.6$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.8, 31.5, 33.8, 38.7, 48.7, 112.7, 121.4, 126.1, 128.7, 130.4, 132.9, 140.3, 145.6, 146.4, 147.3. IR (CH_2Cl_2) ν 2960, 2866, 1613, 1594, 1519, 1393, 1251, 1194, 1178, 1091, 1010 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_4\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 399.1849, found: 399.1847.



N,3-dimethyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine **4n**.

10.0 mmol scale, a white solid, 94% yield (3.61 g). m.p.: 108-110 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.21 (d, $J = 7.2$ Hz, 6H, 2CH_3), 2.43 (s, 3H, CH_3), 2.79-2.86 (m, 1H, CH), 2.95 (s, 3H, CH_3), 4.57 (s, 2H, CH_2), 6.69 (d, $J = 8.4$ Hz, 2H, Ar), 7.09 (d, $J = 8.4$ Hz, 2H, Ar), 7.35 (d, $J =$

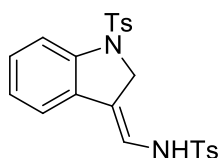
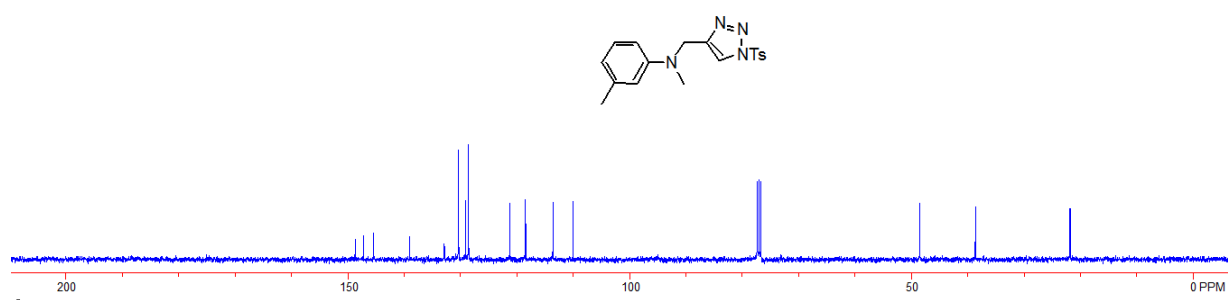
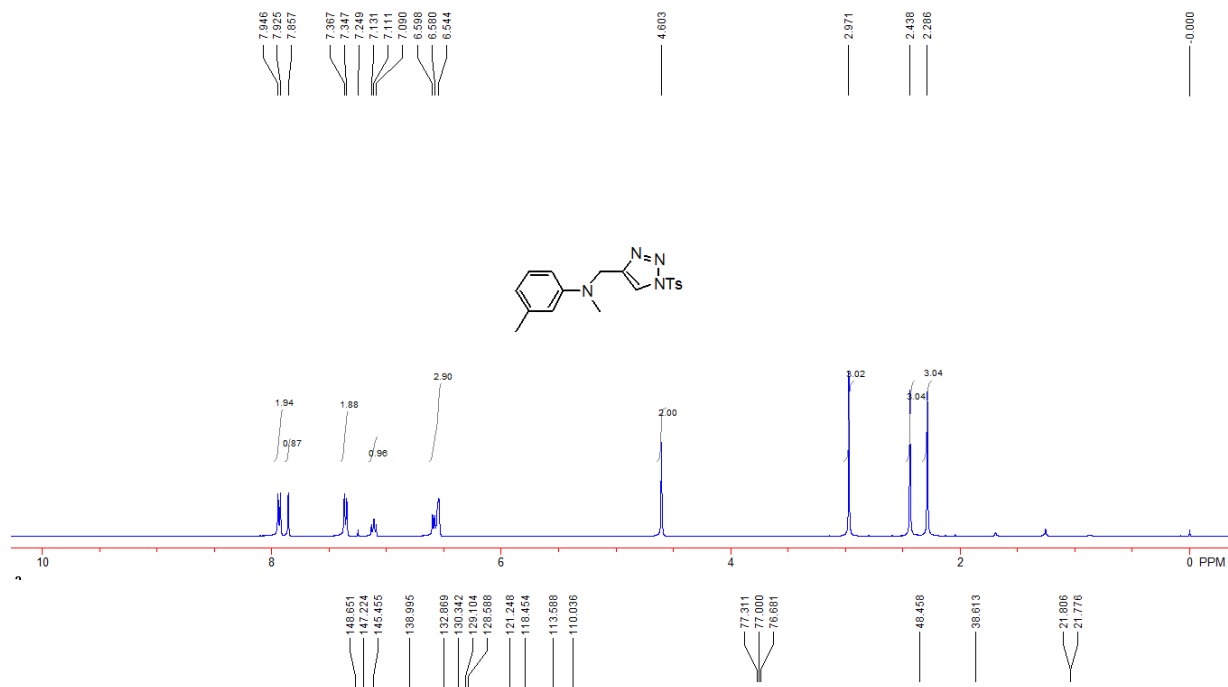
8.0 Hz, 1H, Ar), 7.89 (s, 1H, CH=), 7.93 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.7, 24.1, 32.9, 38.7, 48.6, 113.0, 121.3, 127.1, 128.5, 130.3, 132.8, 137.9, 145.5, 146.8, 147.2. IR (CH_2Cl_2) ν 3010, 2966, 1603, 1597, 1522, 1299, 1251, 1189, 1179, 1084, 1006 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_4\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 385.1693, found: 385.1694.



N,3-dimethyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenamine 4o.

10.0 mmol scale, a white solid, 76% yield (2.71 g). m.p.: 110-112 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.29 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 4.60 (s, 2H, CH_2), 6.54-6.60 (m, 3H, Ar), 7.11 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H, Ar), 7.36 (d, $J = 8.0$ Hz, 2H, Ar), 7.86 (s, 1H, CH=),

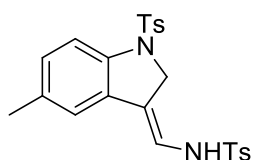
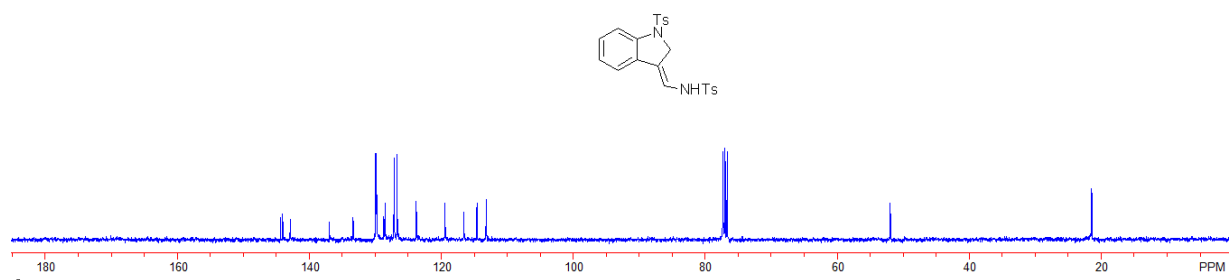
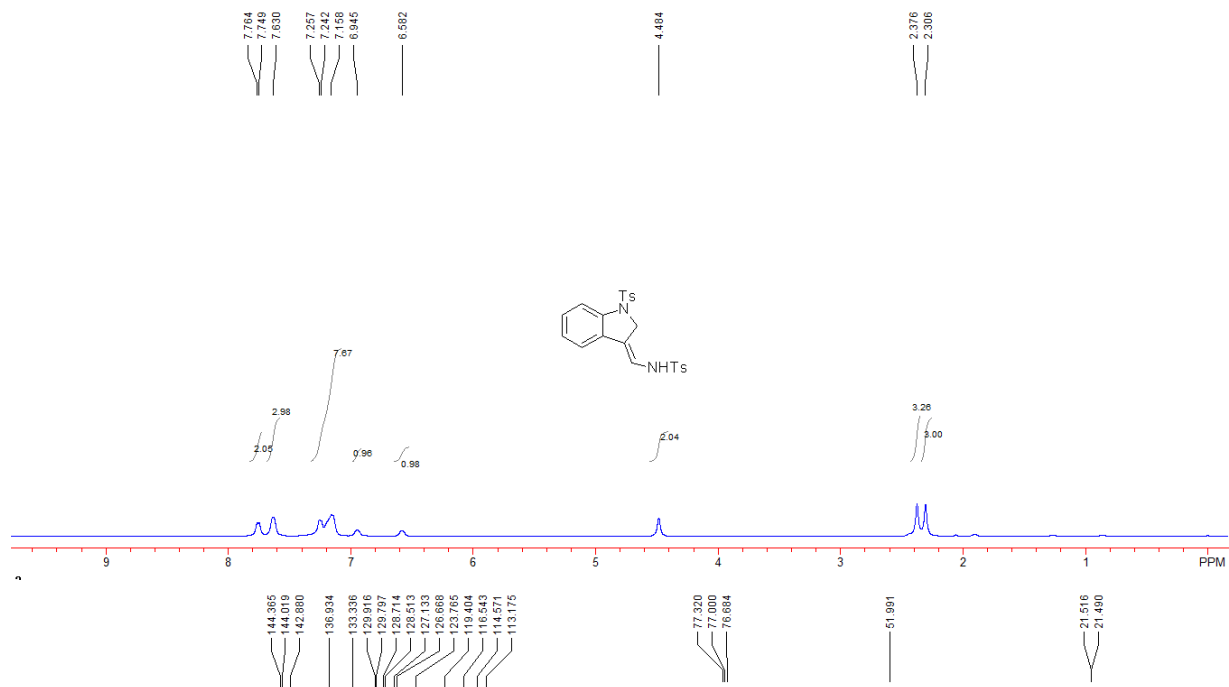
7.93 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.86, 21.89, 38.7, 48.5, 110.1, 113.7, 118.5, 121.3, 128.7, 129.2, 130.4, 133.0, 139.1, 145.5, 147.3, 148.7. IR (CH_2Cl_2) ν 3149, 3052, 2919, 1601, 1581, 1497, 1391, 1193, 1177, 1090, 1007 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_4\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 357.1380, found: 357.1380.



4-methyl-N-((1-tosyl-1H-indol-3-yl)methyl)benzenesulfonamide 5a

0.2 mmol scale, a white solid, 82% yield (74 mg). m.p.: 111-113 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.31 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.48 (s, 2H, CH_2), 6.58 (s, 1H, NH), 6.94 (s, 1H, Ar), 7.15-7.26 (m, 7H, Ar), 7.63 (s, 3H, Ar), 7.76 (d, $J = 6.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100

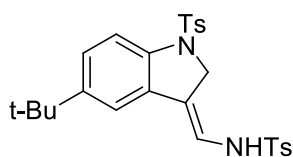
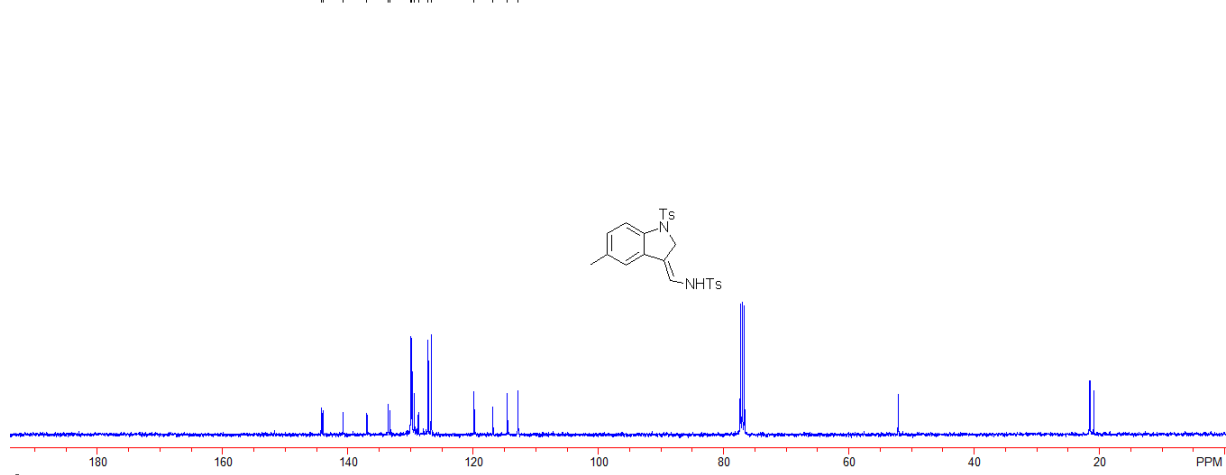
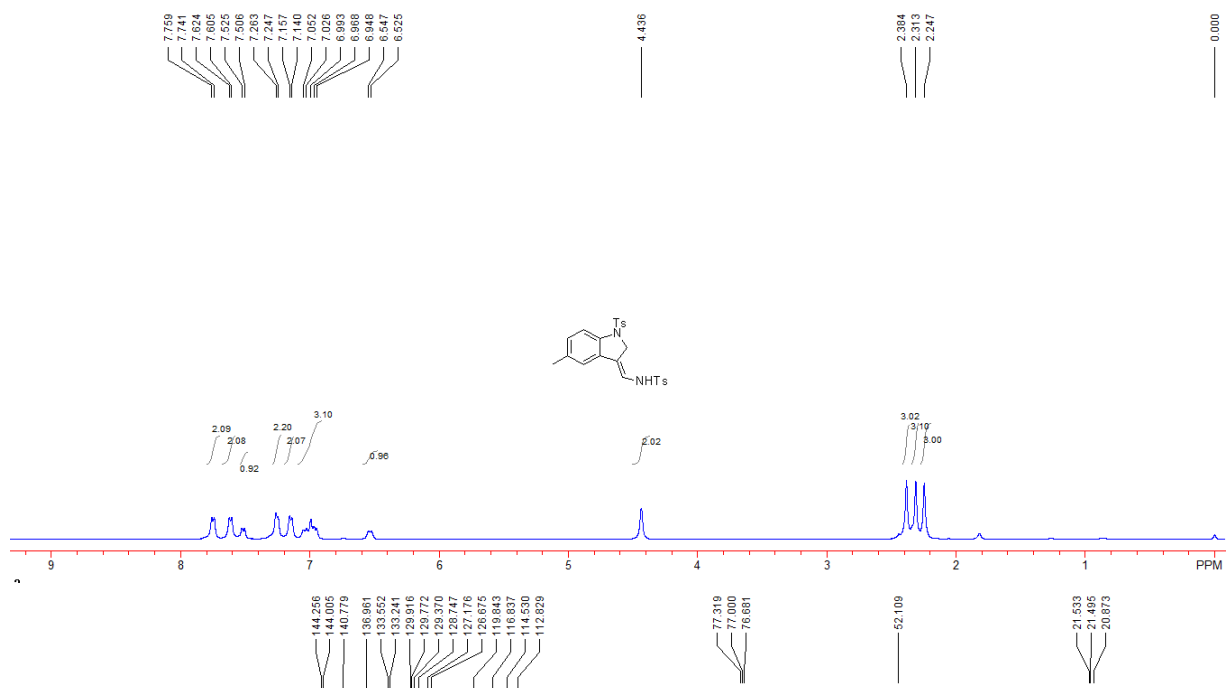
MHz, TMS) δ 21.49, 21.52, 52.0, 113.2, 114.6, 116.5, 119.4, 123.8, 126.7, 127.1, 128.5, 128.7, 129.8, 129.9, 133.3, 136.9, 142.9, 144.0, 144.4. IR (CH₂Cl₂) ν 3151, 3069, 1674, 1595, 1445, 1343, 1304, 1234, 1154 cm⁻¹. HRMS (ESI) Calcd. for C₂₃H₂₆N₃O₄S₂⁺ (M+NH₄⁺) requires 472.1359, found: 472.1375.



(Z)-4-methyl-N-((5-methyl-1-tosylindolin-3-ylidene)methyl)benzenesulfonamide 5b

0.2 mmol, a white solid, 70% yield (66 mg). m.p.: 121-123 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.25 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 4.44 (s, 2H, CH₂), 6.53 (d, *J* = 8.8 Hz, 1H, CH=), 6.94-7.00 (m, 2H, Ar), 7.04 (d, *J* = 8.8 Hz, 1H, NH), 7.15 (d, *J* = 6.8 Hz, 2H, Ar), 7.25

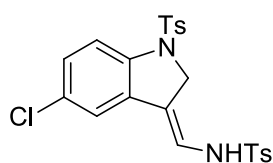
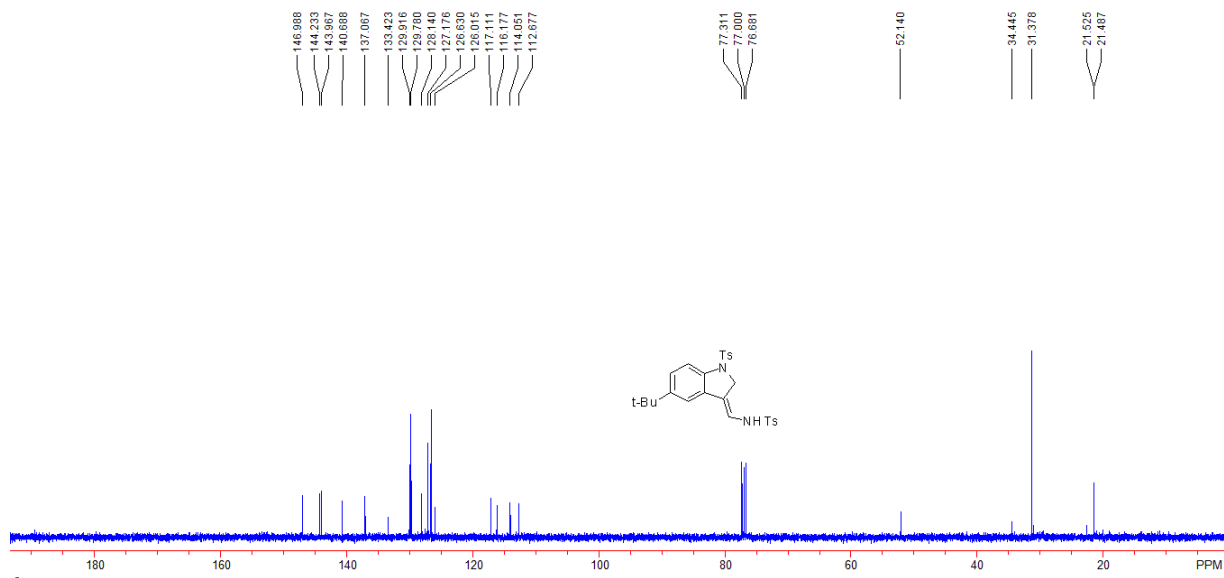
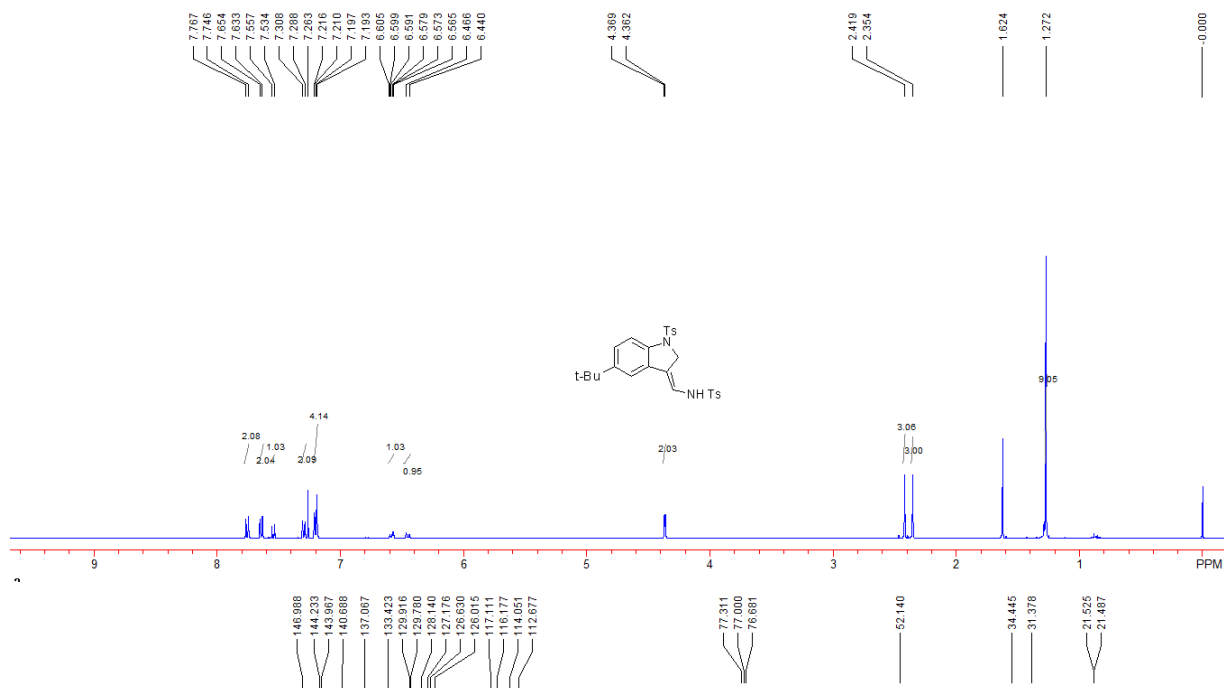
(d, $J = 6.8$ Hz, 2H, Ar), 7.51 (d, $J = 7.6$ Hz, 1H, Ar), 7.61 (d, $J = 7.6$ Hz, 2H, Ar), 7.75 (d, $J = 7.6$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 20.9, 21.5, 21.6, 52.1, 112.8, 114.5, 116.8, 119.8, 126.7, 127.2, 128.7, 129.4, 129.8, 129.9, 133.2, 133.6, 137.0, 140.8, 144.0, 144.2. IR (CH_2Cl_2) ν 3243, 2923, 2862, 1682, 1597, 1481, 1428, 1351, 1339, 1162, 1150, 1128, 1089, 1049, 905, 805, 751, 731, 667 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_4\text{S}_2^+$ ($\text{M}+\text{NH}_4^+$) requires 486.1516, found: 486.1517.



(Z)-N-((5-(tert-butyl)-1-tosylindolin-3-ylidene)methyl)-4-methylbenzenesulfonamide 5c

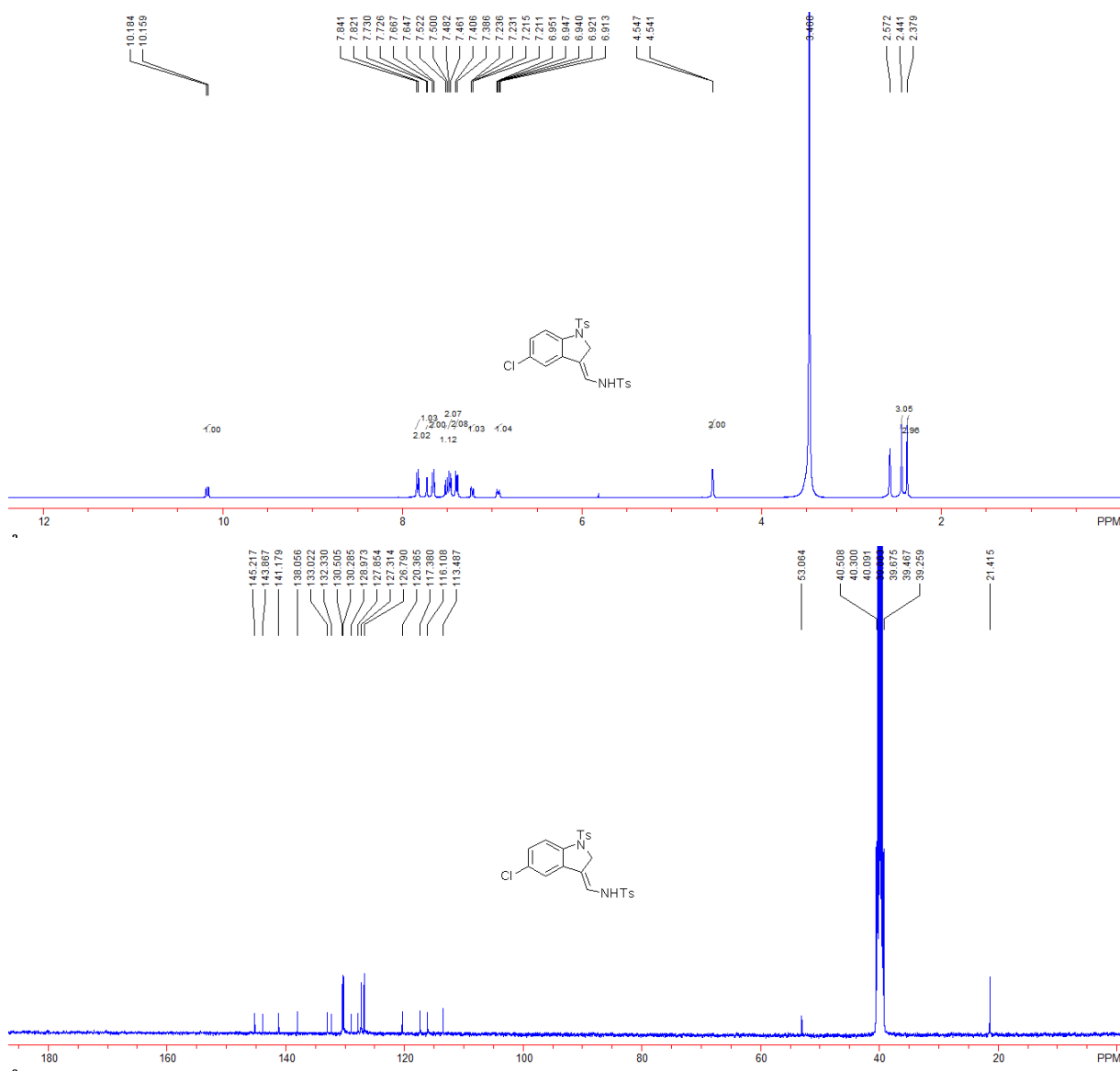
0.2 mmol, a white solid, 61% yield (62 mg). m.p.: 125-127 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS)

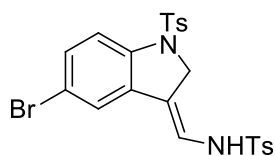
δ 1.27 (s, 9H, 3CH₃), 2.35 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 4.37 (d, J = 2.8 Hz, 2H, CH₂), 6.45 (d, J = 10.4 Hz, 1H, NH), 6.59 (dt, J = 10.4 Hz, J = 2.8 Hz, 1H, CH=), 7.19-7.22 (m, 4H, Ar), 7.30 (d, J = 8.0 Hz, 2H, Ar), 7.54 (d, J = 9.2 Hz, 1H, Ar), 7.64 (d, J = 8.4 Hz, 2H, Ar), 7.75 (d, J = 8.4 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 21.6, 31.4, 34.4, 52.1, 112.7, 114.1, 116.2, 117.1, 126.0, 126.6, 127.2, 128.1, 129.8, 129.9, 133.4, 137.1, 140.7, 144.0, 144.2, 147.0. IR (CH₂Cl₂) ν 2955, 2922, 2850, 1677, 1594, 1481, 1439, 1340, 1156, 1087, 1056, 902, 812, 738, 666 cm⁻¹. HRMS (ESI) Calcd. for C₂₇H₃₄N₃O₄S₂⁺ (M+NH₄⁺) requires 528.1985, found: 528.1986.



(Z)-N-((5-chloro-1-tosylindolin-3-ylidene)methyl)-4-methylbenzenesulfonamide 5d

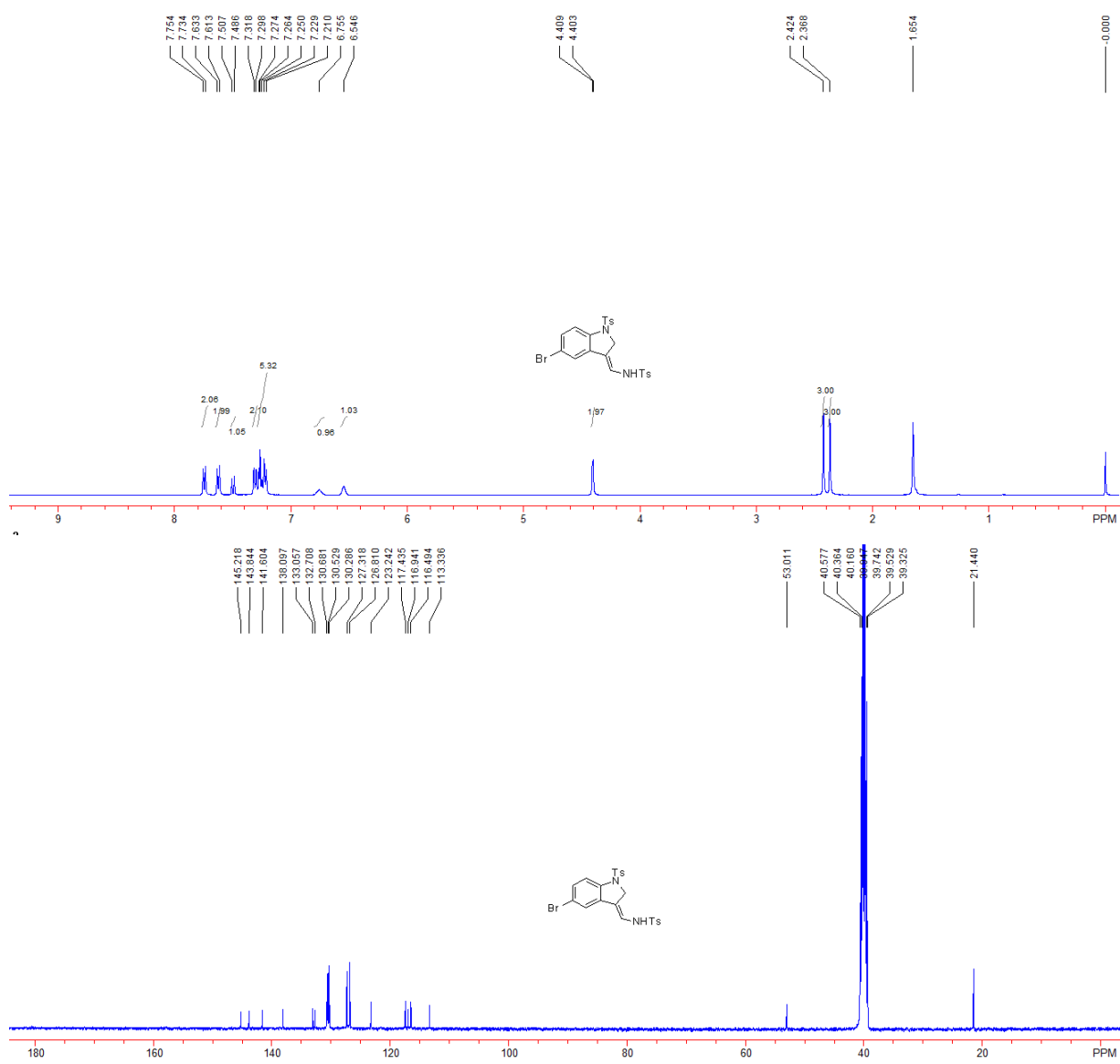
0.2 mmol scale, a white solid, 58% yield (57 mg). m.p.: 135-136°C. ¹H NMR (DMSO-d₆, 400 MHz, TMS) δ 2.38 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 4.54 (d, *J* = 2.4 Hz, 2H, CH₂), 6.93 (dt, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H, CH=), 7.22 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H, Ar), 7.39 (d, *J* = 8.0 Hz, 2H, Ar), 7.47 (d, *J* = 8.4 Hz, 2H, Ar), 7.51 (d, *J* = 8.4 Hz, 1H, Ar), 7.66 (d, *J* = 8.0 Hz, 2H, Ar), 7.73 (d, *J* = 2.0 Hz, 1H, Ar), 7.83 (d, *J* = 8.0 Hz, 2H, Ar), 10.17 (d, *J* = 10.4 Hz, 1H, NH). ¹³C NMR (DMSO-d₆, 100 MHz, TMS) δ 21.4, 53.1, 113.5, 116.1, 117.4, 120.4, 126.8, 127.3, 127.8, 129.0, 130.3, 130.5, 132.3, 133.0, 138.0, 141.2, 143.9, 145.2. IR (CH₂Cl₂) ν 3238, 2927, 2854, 1598, 1485, 1467, 1323, 1311, 1151, 1128, 1084, 813, 793, 666 cm⁻¹. HRMS (ESI) Calcd. for C₂₃H₂₂ClN₂O₄S₂⁺ (M+H⁺) requires 489.0704, found: 489.0708.

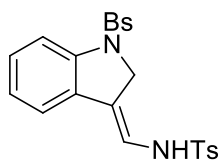




(Z)-N-((5-bromo-1-tosylindolin-3-ylidene)methyl)-4-methylbenzenesulfonamide 5e

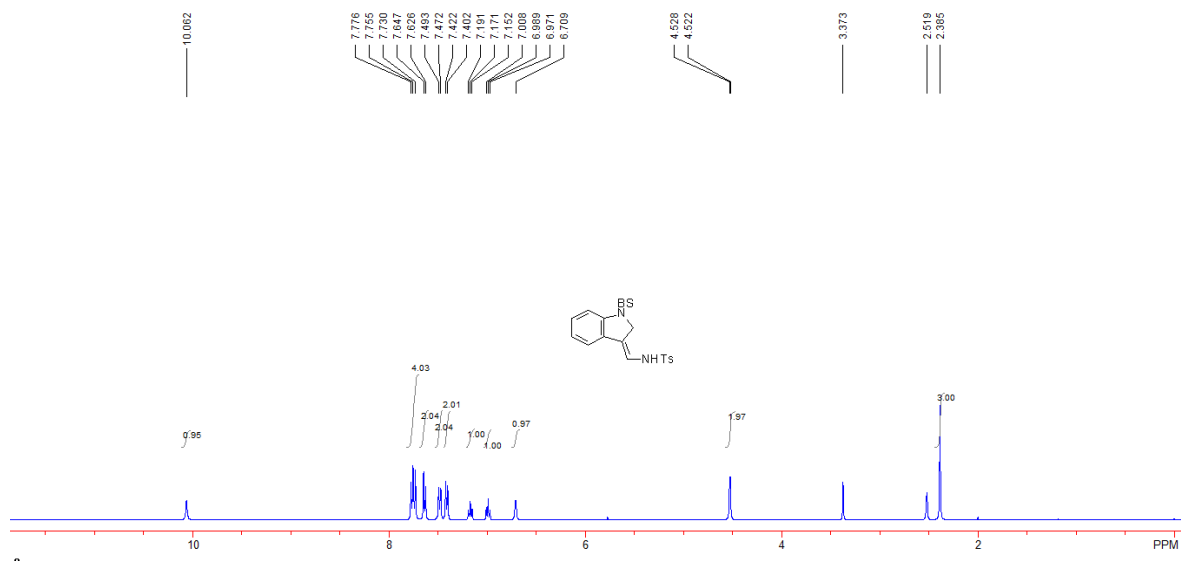
0.2 mmol, a white solid, 60% yield (64 mg). m.p.: 138-140 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.37 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.40 (d, $J = 2.4$ Hz, 2H, CH_2), 6.55 (s, 1H, NH), 6.76 (s, 1H, $\text{CH}=\text{)$, 7.21-7.28 (m, 4H, Ar), 7.31 (d, $J = 8.0$ Hz, 2H, Ar), 7.50 (d, $J = 8.0$ Hz, 1H, Ar), 7.62 (d, $J = 8.0$ Hz, 2H, Ar), 7.74 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz, TMS) δ 21.4, 53.0, 113.3, 116.5, 116.9, 117.4, 123.2, 126.8, 127.3, 130.3, 130.5, 130.7, 132.7, 133.0, 138.1, 141.6, 143.8, 145.2. IR (CH_2Cl_2) ν 3231, 3060, 2870, 1678, 1469, 1430, 1362, 1352, 1181, 1151, 1125, 1087, 1057, 1042, 903, 810, 704, 685, 664 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{25}\text{BrN}_3\text{O}_4\text{S}_2^+$ ($\text{M}+\text{NH}_4^+$) requires 550.0464, found: 550.0465.

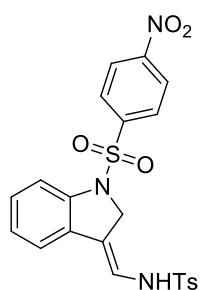
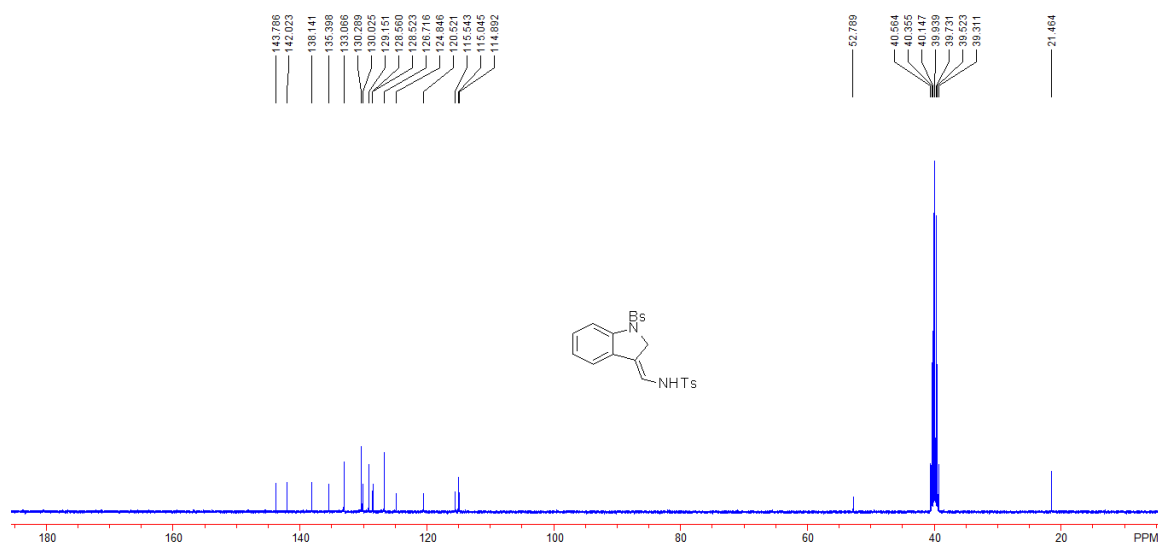




(Z)-N-((1-((4-bromophenyl)sulfonyl)indolin-3-ylidene)methyl)-4-methylbenzenesulfonamide
5f

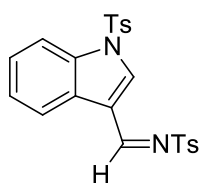
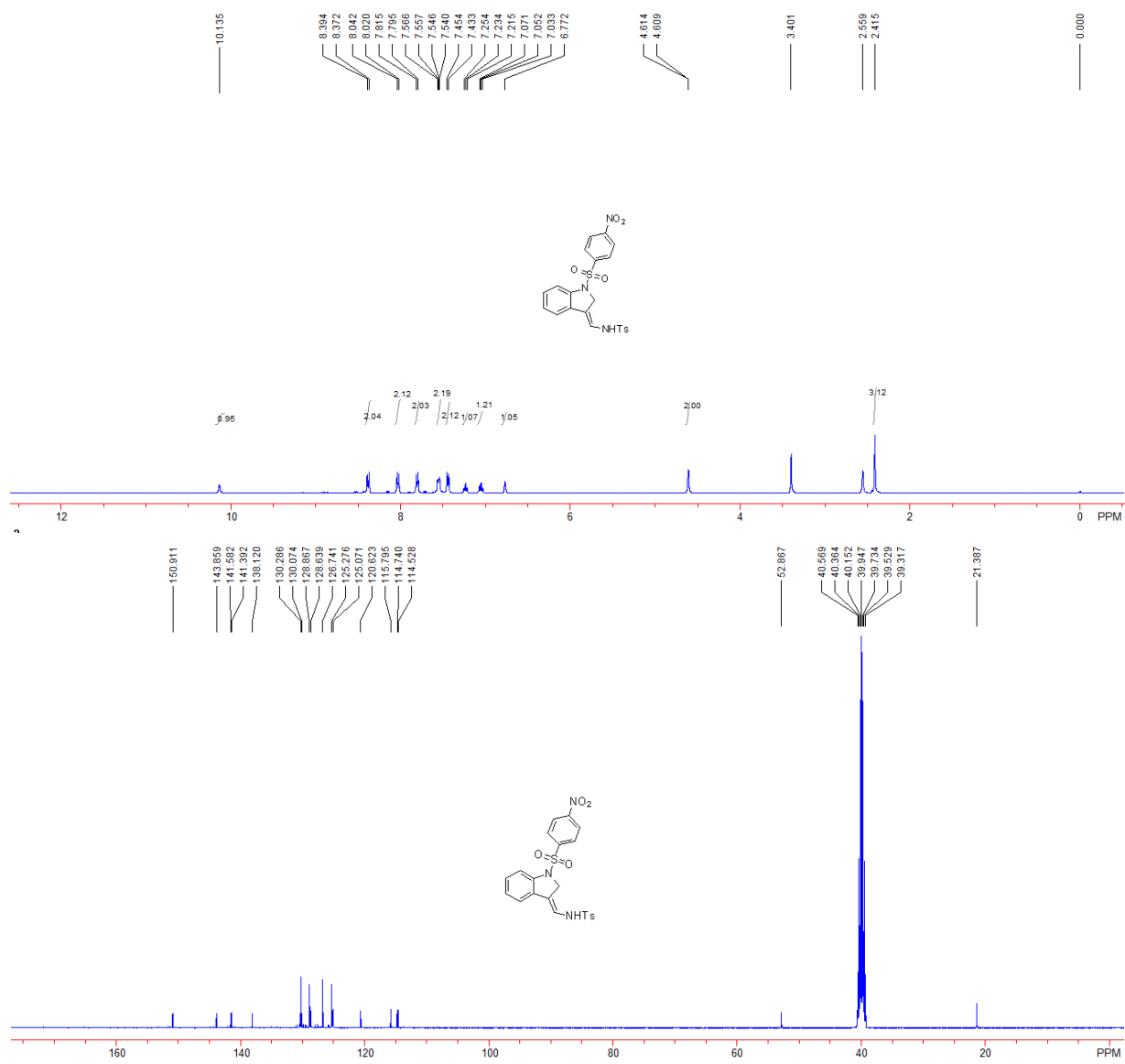
0.2 mmol, a white solid, 71% yield (74 mg). m.p.: 147-149 °C. ^1H NMR (DMSO- d_6 , 400 MHz, TMS) δ 2.38 (s, 3H, CH₃), 4.52 (d, J = 2.4 Hz, 2H, CH₂), 6.71 (s, 1H, CH=), 6.99 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.17 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.48 (d, J = 8.0 Hz, 2H, Ar), 7.63 (d, J = 8.0 Hz, 2H, Ar), 7.73-7.78 (m, 4H, Ar), 10.06 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz, TMS) δ 21.5, 52.8, 114.9, 115.0, 115.5, 120.5, 124.8, 126.7, 128.5, 128.6, 129.2, 130.0, 130.3, 133.1, 135.4, 138.1, 142.0, 143.8. IR (CH₂Cl₂) ν 3069, 2927, 2858, 1673, 1697, 1571, 1318, 1289, 1151, 1126, 1082, 1069, 1009, 900, 810, 773, 744, 699, 672 cm^{-1} . HRMS (ESI) Calcd. for C₂₂H₂₀BrN₂O₄S₂⁺ (M+H⁺) requires 519.0042, found: 519.0042.





(Z)-4-methyl-N-((1-((4-nitrophenyl)sulfonyl)-1H-indol-3-yl)methyl)benzenesulfonamide 5g

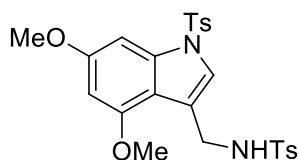
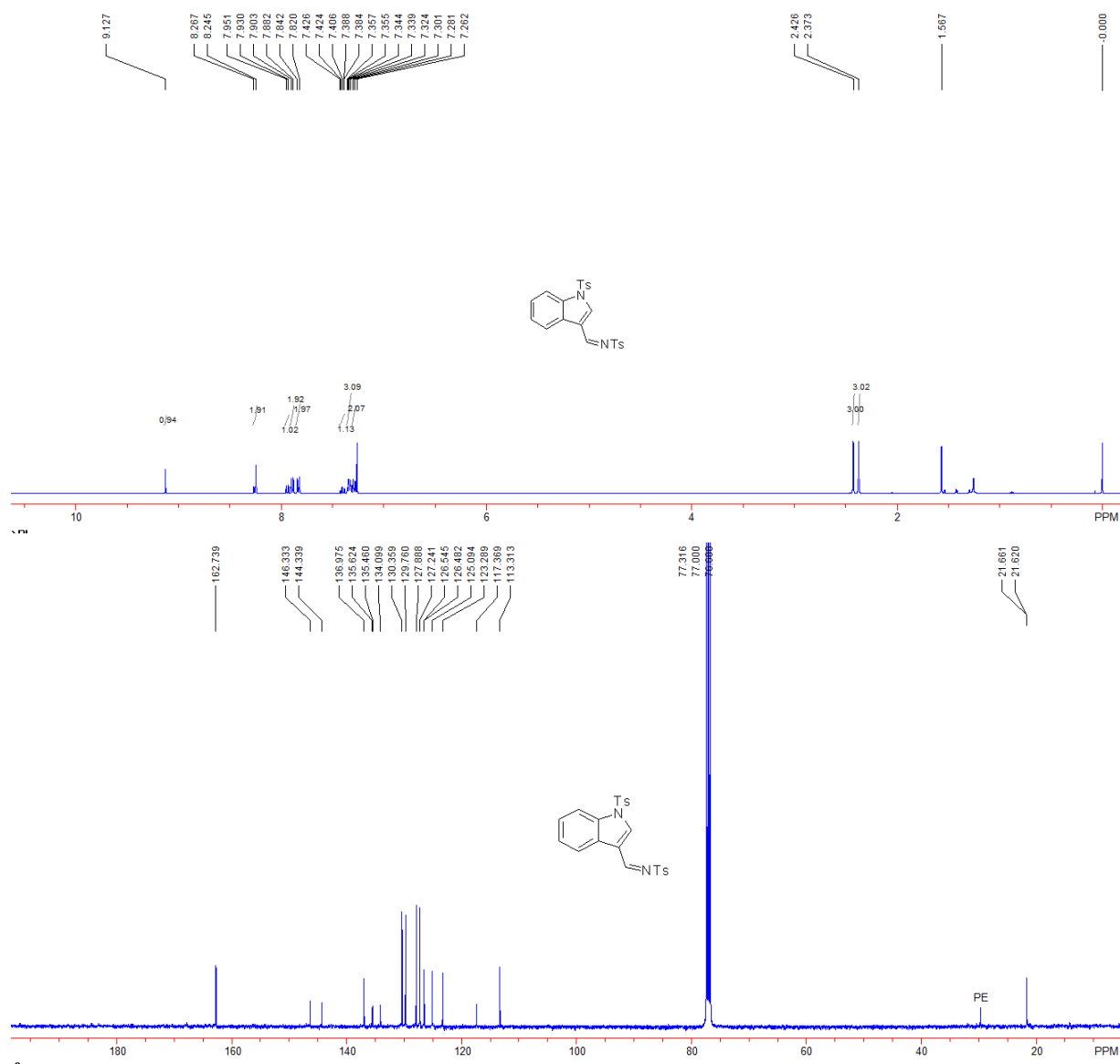
0.2 mmol scale, a yellow solid, 49% yield (48 mg). m.p.: 148-150 °C. ¹H NMR (DMSO-*d*₆, 400 MHz, TMS) δ 2.42 (s, 3H, CH₃), 4.61 (d, *J* = 2.0 Hz, 2H, CH₂), 6.77 (s, 1H, CH=), 7.05 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.23 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.44 (d, *J* = 7.6 Hz, 2H, Ar), 7.55 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 2H, Ar), 7.80 (d, *J* = 8.0 Hz, 2H, Ar), 8.03 (d, *J* = 8.4 Hz, 2H, Ar), 8.38 (d, *J* = 8.4 Hz, 2H, Ar), 10.14 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz, TMS) δ 21.4, 52.9, 114.5, 114.7, 115.8, 120.6, 125.1, 125.3, 126.7, 128.6, 128.9, 130.1, 130.3, 138.1, 141.4, 141.6, 143.8, 150.9. IR (CH₂Cl₂) ν 3251, 2919, 2854, 1675, 1597, 1529, 1348, 1335, 1291, 1150, 1121, 1084, 1040, 853, 758, 746, 670 cm⁻¹. HRMS (ESI) Calcd. for C₂₂H₂₀N₃O₆S₂⁺ (M+H⁺) requires 486.0788, found: 486.0788.



4-methyl-N-((1-tosyl-1H-indol-3-yl)methylene)benzenesulfonamide 6a'

0.2 mmol scale, a white solid, 30% yield (27 mg). m.p.: 108-110 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.37 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.32-7.36 (m, 3H, Ar), 7.38-7.43 (m, 1H, Ar), 7.83 (d, *J* = 8.4 Hz, 2H, Ar), 7.89 (d, *J* = 8.4 Hz, 2H, Ar), 7.94 (d, *J* = 8.4 Hz, 1H, Ar), 8.24 (s, 1H, Ar), 8.26 (d, *J* = 8.4 Hz, 1H, Ar), 9.13 (s, 1H, CH=NTs). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 21.7, 113.3, 117.4, 123.3, 125.1, 126.5, 126.6, 127.2, 127.9,

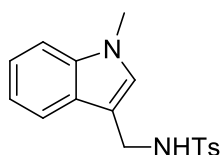
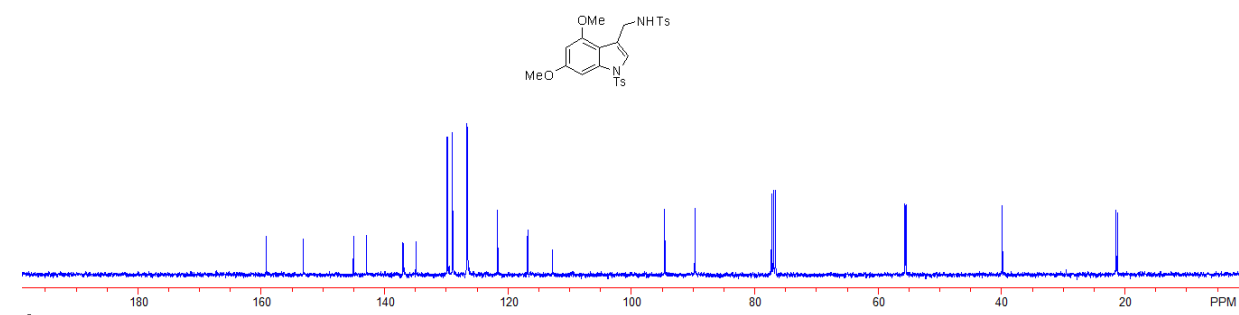
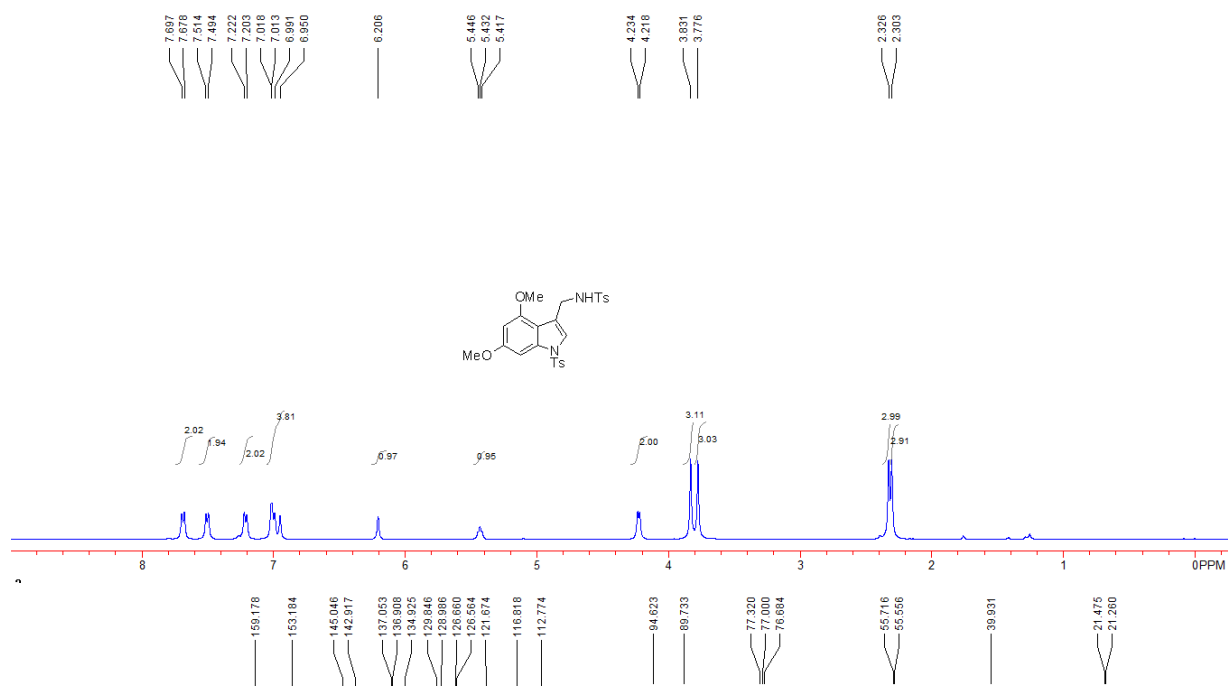
129.8, 130.4, 134.1, 135.5, 135.6, 137.0, 144.3, 146.3, 162.7. IR (CH₂Cl₂) v 3153, 2959, 2927, 1596, 1504, 1390, 1193, 1177, 1091, 1007 cm⁻¹. HRMS (ESI) Calcd. for C₂₃H₂₁N₂O₄S₂⁺ (M+H⁺) requires 453.0904, found: 453.0909.



N-((4,6-dimethoxy-1-tosyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6b

0.2 mmol scale, a yellow solid, 85% yield (88 mg). m.p.: 145-147 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.30 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 3.78 (s, 3H, CH₃), 3.83 (s, 3H, CH₃), 4.22 (d, *J* = 6.4 Hz, 2H, CH₂), 5.43 (t, *J* = 6.4 Hz, 1H, NH), 6.21 (s, 1H, Ar), 6.95-7.02 (m, 4H, Ar), 7.21 (d, *J* = 7.6 Hz, 2H, Ar), 7.50 (d, *J* = 8.0 Hz, 2H, Ar), 7.69 (d, *J* = 7.6 Hz, 2H, Ar). ¹³C NMR

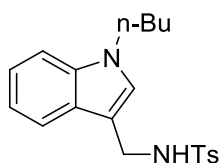
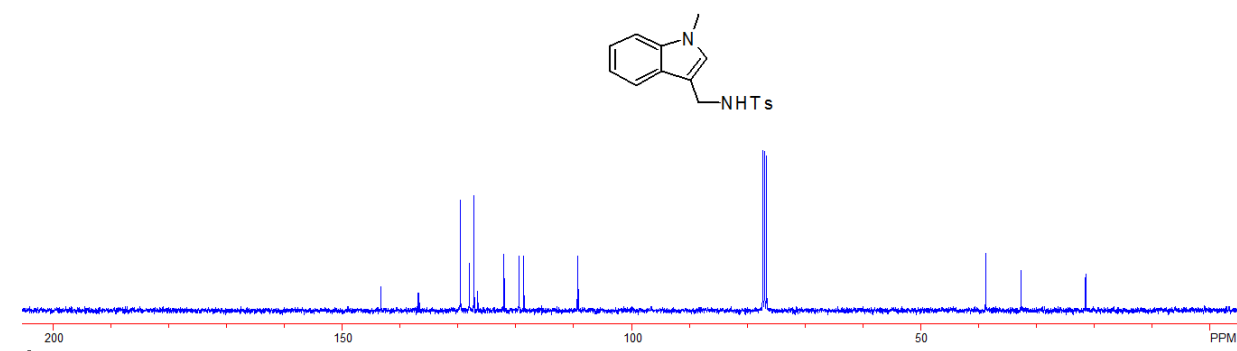
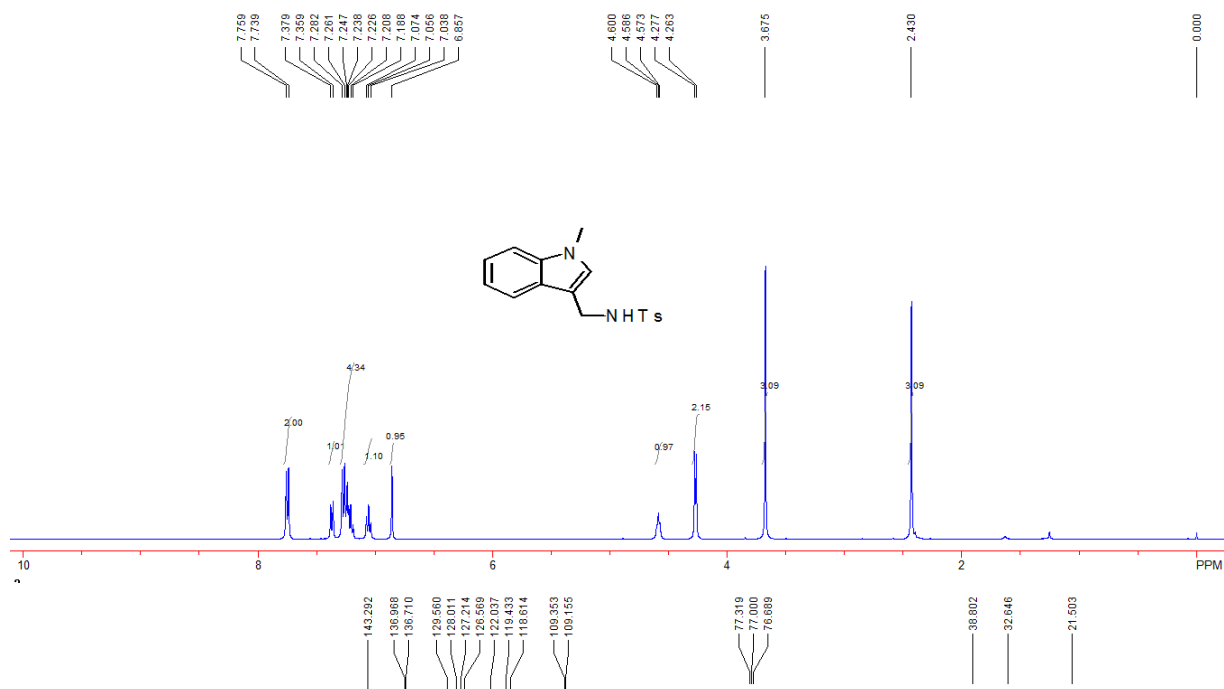
(CDCl₃, 100 MHz, TMS) δ 21.3, 21.5, 39.9, 55.6, 55.7, 89.7, 94.6, 112.8, 116.8, 121.7, 126.6, 126.7, 129.0, 129.8, 134.9, 136.9, 137.0, 142.9, 145.0, 153.2, 159.2. IR (CH₂Cl₂) ν 3283, 3109, 2842, 1594, 1463, 1420, 1357, 1343, 1321, 1257, 1206, 1159, 1117, 1096, 1087, 1040, 822, 811, 791, 669 cm⁻¹. HRMS (ESI) Calcd. for C₂₅H₃₀N₃O₆S₂⁺ (M+NH₄⁺) requires 532.1571, found: 532.1572.



4-methyl-N-((1-methyl-1H-indol-3-yl)methyl)benzenesulfonamide 6c.

0.2 mmol scale, a white solid, 81% yield (51 mg). m.p.: 172-174 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.43 (s, 3H, CH₃), 3.68 (s, 3H, CH₃), 4.27 (d, *J* = 5.6 Hz, 2H, CH₂), 4.59 (t, *J* = 5.6 Hz,

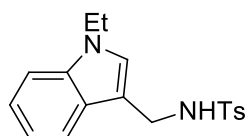
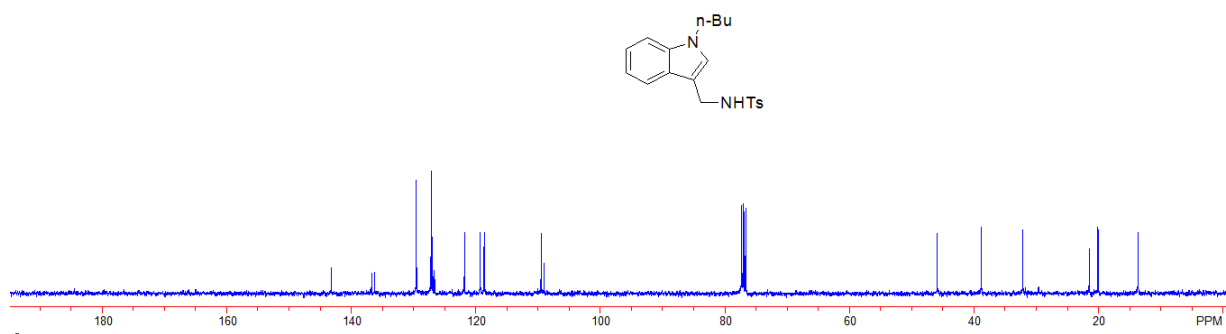
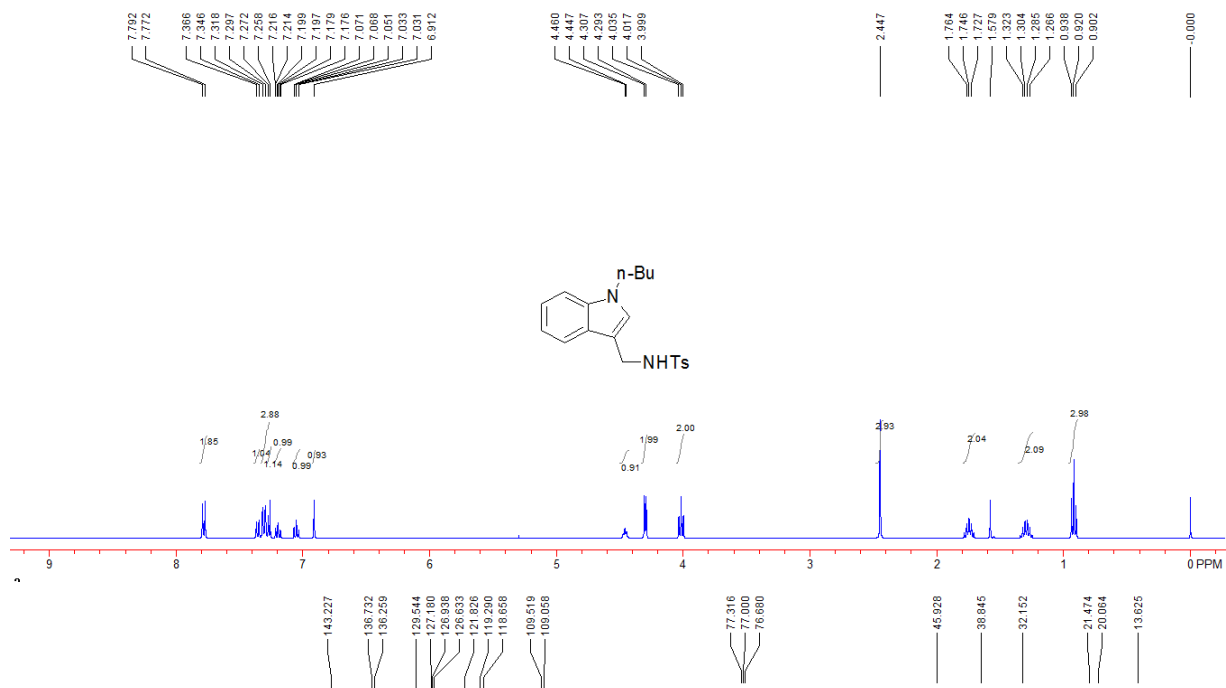
1H), 6.86 (s, 1H, Ar), 7.06 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 1H, Ar), 7.18-7.29 (m, 4H, Ar), 7.37 (d, $J = 8.0$ Hz, 1H, Ar), 7.75 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 32.7, 38.9, 109.2, 109.4, 118.7, 119.5, 122.1, 126.6, 127.3, 128.1, 129.6, 136.8, 137.0, 143.3. IR (CH_2Cl_2) ν 3303, 2952, 2923, 1597, 1476, 1405, 1330, 1302, 1157 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 315.1162, found: 315.1163.



N-((1-butyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6d.

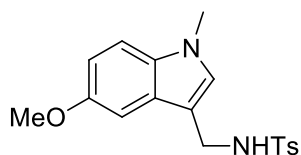
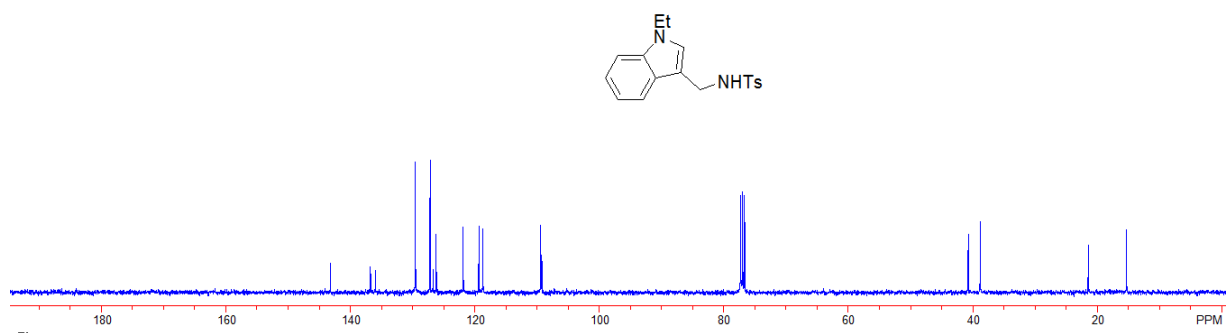
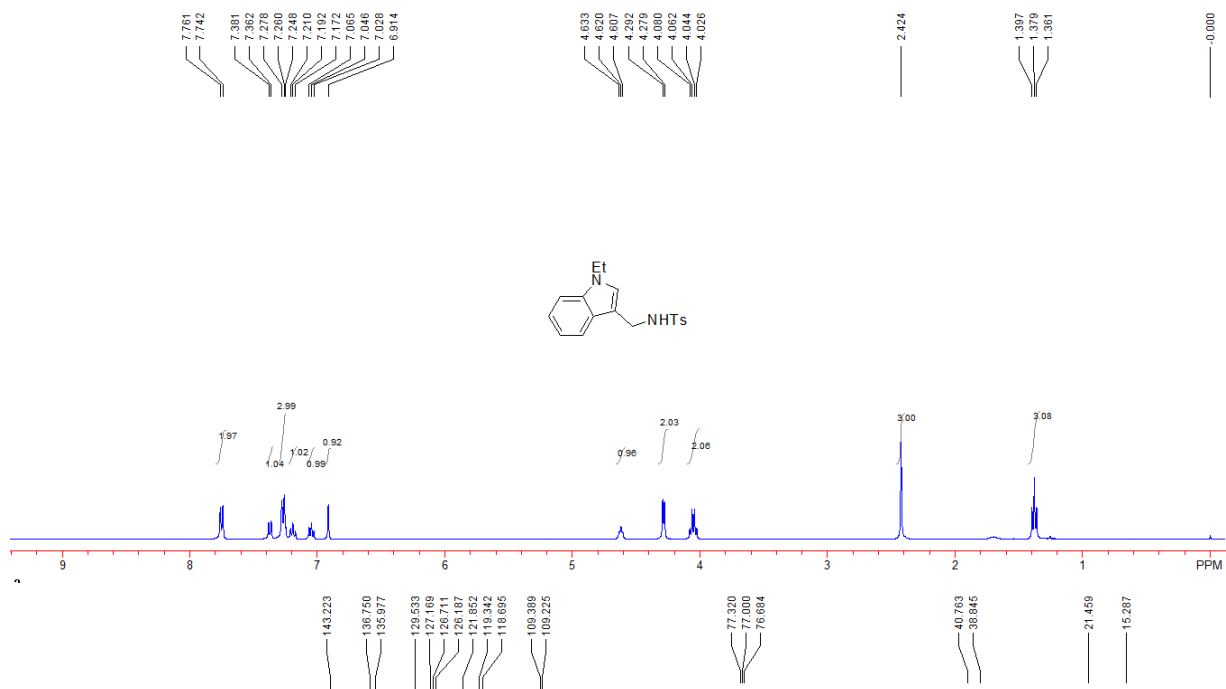
0.2 mmol scale, a white solid, 72% yield (51 mg). m.p.: 149-151 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 0.92 (t, $J = 7.2$ Hz, 3H, CH_3), 1.26-1.33 (m, 2H, CH_2), 1.70-1.79 (m, 2H, CH_2), 2.45 (s,

3H, CH₃), 4.02 (t, *J* = 7.2 Hz, 2H, CH₂), 4.30 (d, *J* = 5.6 Hz, 2H, CH₂), 4.46 (t, *J* = 5.6 Hz, 1H, NH), 6.91 (s, 1H, Ar), 7.05 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.20 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 7.27-7.32 (m, 3H, Ar), 7.35 (d, *J* = 8.0 Hz, 1H, Ar), 7.78 (d, *J* = 8.0 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 13.6, 20.1, 21.5, 32.2, 38.8, 45.9, 109.0, 109.5, 118.6, 119.3, 121.8, 126.6, 126.9, 127.2, 129.5, 136.2, 136.7, 143.2. IR (CH₂Cl₂) ν 3287, 3044, 2953, 1594, 1548, 1469, 1333, 1303, 1155, 1091, 1018, 815, 738, 705, 673, 658 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₂₅N₂O₂S⁺ (M+H⁺) requires 357.1631, found: 357.1633.



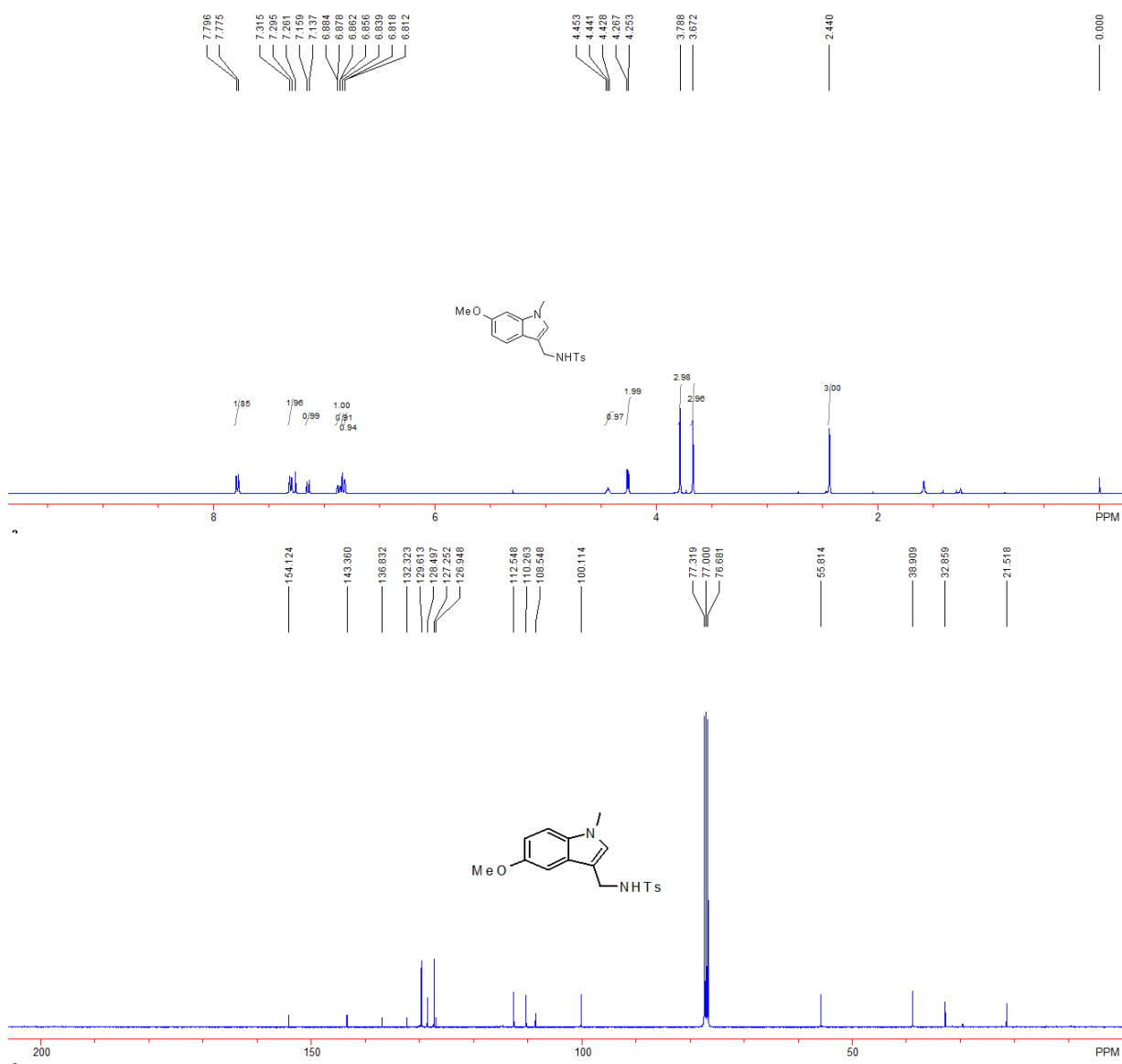
N-((1-ethyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6e.

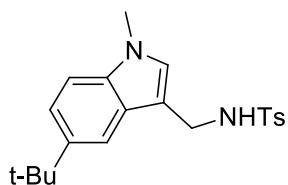
0.2 mmol scale, a brown solid, 53% yield (35 mg). m.p.: 122-124 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.38 (t, $J = 7.2$ Hz, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.05 (q, $J = 7.2$ Hz, 2H, CH_2), 4.28 (d, $J = 5.6$ Hz, 2H, CH_2), 4.61 (t, $J = 5.6$ Hz, 1H, NH), 6.92 (s, 1H, Ar), 7.05 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H, Ar), 7.19 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H, Ar), 7.24-7.28 (m, 3H, Ar), 7.37 (d, $J = 7.6$ Hz, 1H, Ar), 7.75 (d, $J = 7.6$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 15.3, 21.5, 38.8, 40.8, 109.2, 109.4, 118.7, 119.3, 121.8, 126.2, 126.7, 127.2, 129.5, 136.0, 136.8, 143.2. IR (CH_2Cl_2) ν 3283, 2971, 1594, 1470, 1461, 1320, 1153, 1091, 1043, 1014, 813, 738, 653 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H}^+$) requires 329.1318, found: 329.1319.



N-((5-methoxy-1-methyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6f.

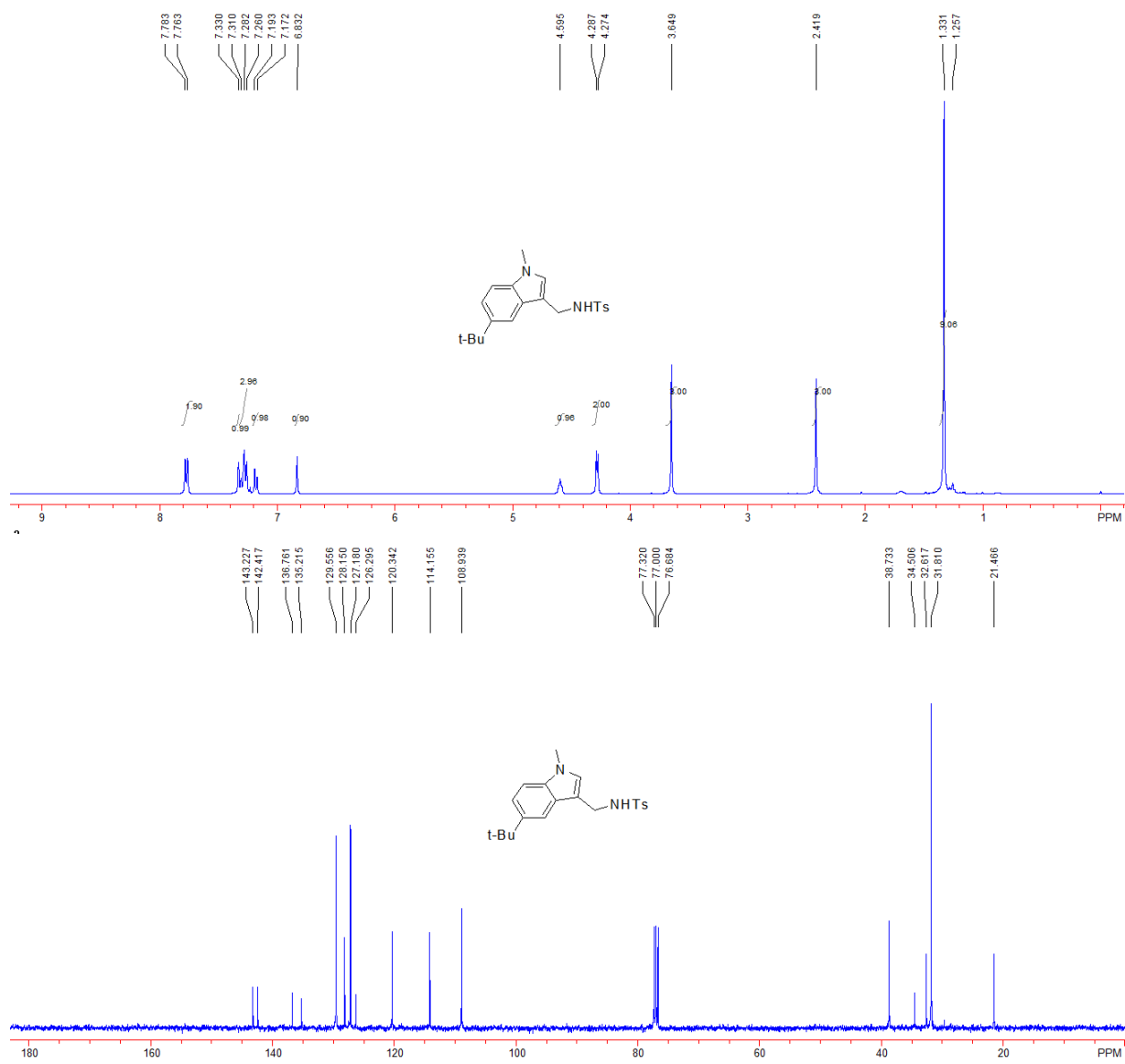
0.2 mmol scale, a white solid, 70% yield (48 mg). m.p.: 182-184 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 3.67 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 4.26 (d, $J = 5.6$ Hz, 2H, CH_2), 4.44 (t, $J = 5.6$ Hz, 1H, NH), 6.81 (d, $J = 2.4$ Hz, 1H, Ar), 6.84 (s, 1H, Ar), 6.87 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H, Ar), 7.15 (d, $J = 8.8$ Hz, 1H, Ar), 7.30 (d, $J = 8.4$ Hz, 2H, Ar), 7.78 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 32.9, 38.9, 55.8, 100.1, 108.5, 110.3, 112.5, 126.9, 127.3, 128.5, 129.6, 132.3, 136.8, 143.4, 154.1. IR (CH_2Cl_2) ν 3300, 2952, 2923, 1617, 1509, 1492, 1425, 1321, 1304, 1221, 1156 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}^+$) requires 345.1267, found: 345.1268.

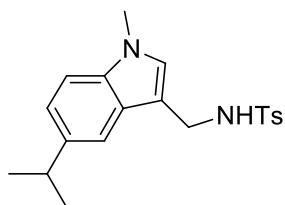




N-((5-tert-butyl-1-methyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6g.

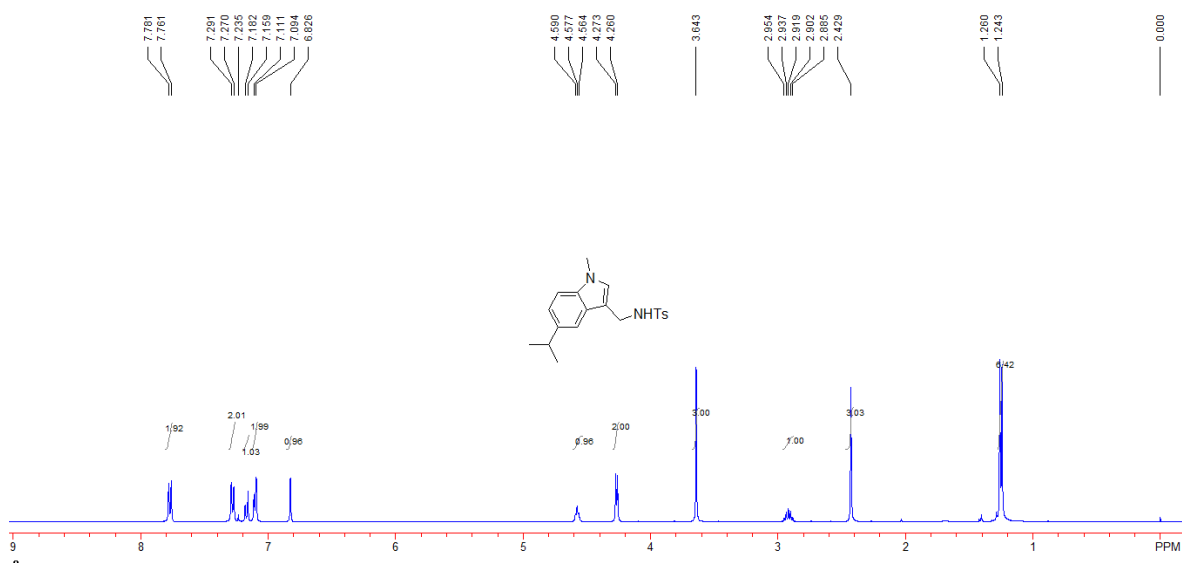
0.2 mmol scale, a white solid, 61% yield (45 mg). m.p.: 165-167 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.33 (s, 9H, CH₃), 2.42 (s, 3H, CH₃), 3.65 (s, 3H, CH₃), 4.28 (d, *J* = 5.6 Hz, 2H, CH₂), 4.59 (t, *J* = 5.6 Hz, 1H, NH), 6.83 (s, 1H, Ar), 7.18 (d, *J* = 8.8 Hz, 1H, Ar), 7.26-7.32 (m, 3H, Ar), 7.33 (s, 1H, Ar), 7.77 (d, *J* = 8.4 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 31.8, 32.6, 34.5, 38.7, 108.9, 114.2, 120.3, 126.3, 127.2, 128.1, 129.6, 135.2, 136.8, 142.4, 143.2. IR (CH₂Cl₂) ν 2957, 2906, 2862, 1613, 1520, 1490, 1321, 1302, 1155, 1059, 1038, 812, 734, 707 cm⁻¹. HRMS (ESI) Calcd. for C₂₁H₂₇N₂O₂S⁺ (M+H⁺) requires 371.1788, found: 371.1787.

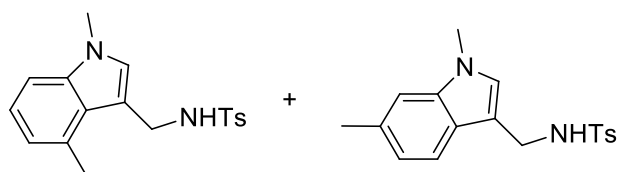
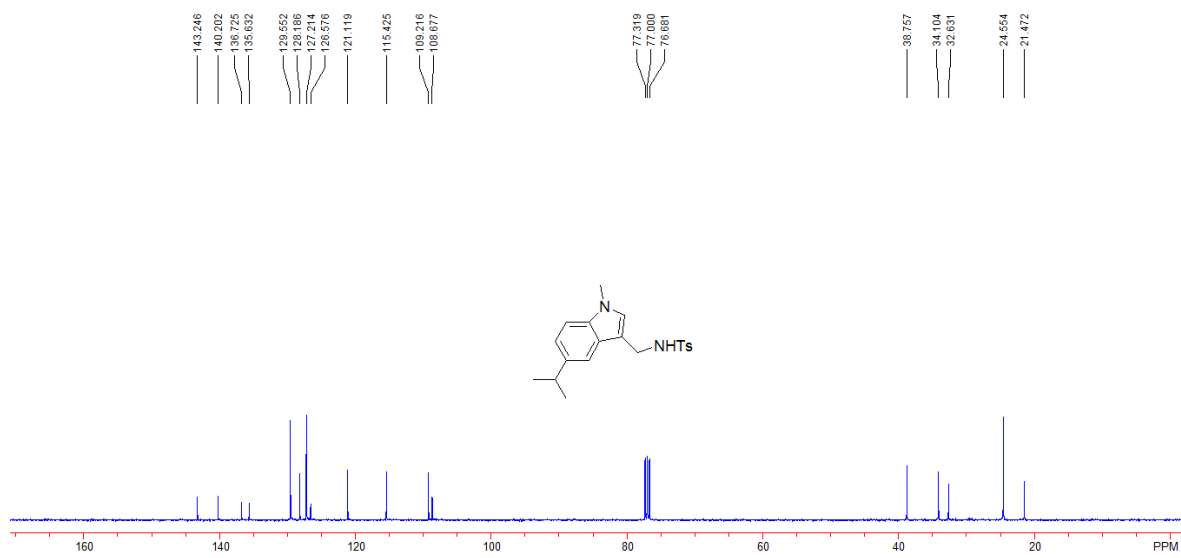




N-((5-isopropyl-1-methyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide 6h.

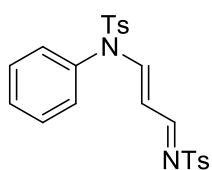
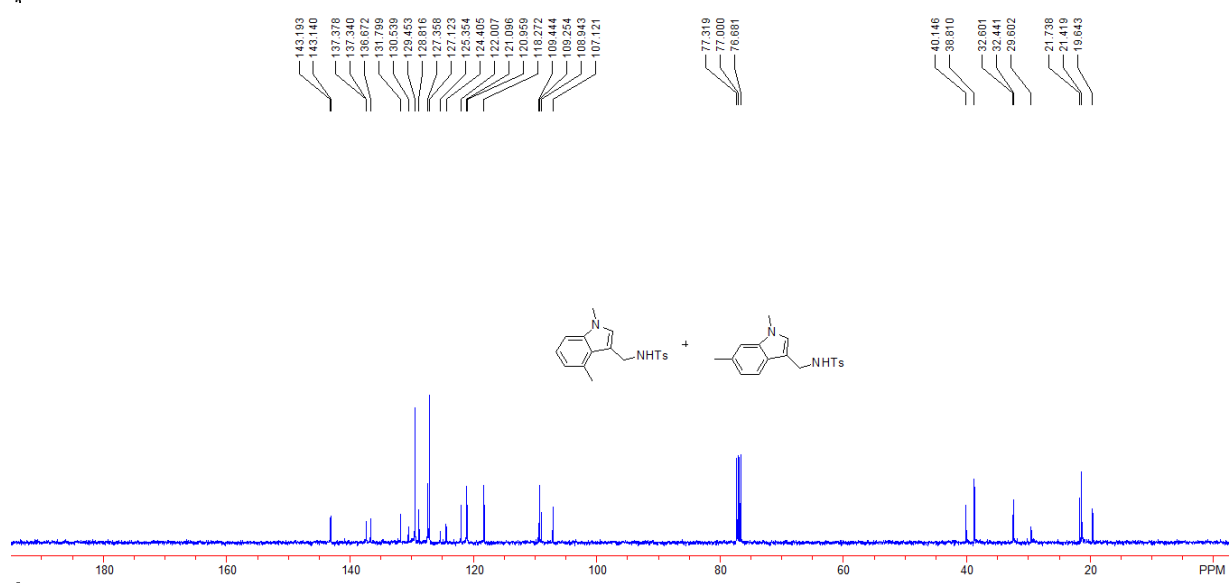
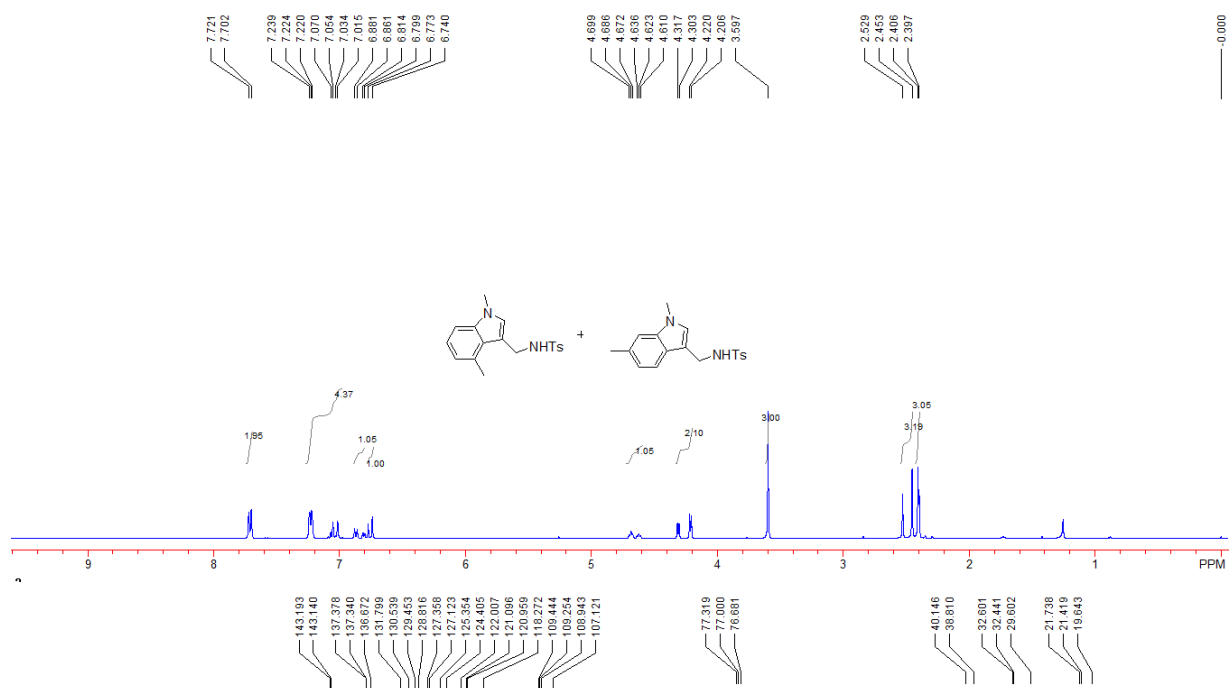
0.2 mmol scale, a white solid, 64% yield (46 mg). m.p.: 150-152 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.25 (d, *J* = 6.8 Hz, 6H, CH₃), 2.43 (s, 3H, CH₃), 2.86-2.98 (m, 1H, CH), 3.64 (s, 3H, CH₃), 4.27 (d, *J* = 5.2 Hz, 2H, CH₂), 4.58 (t, *J* = 5.2 Hz, 1H, NH), 6.83 (s, 1H, Ar), 7.10 (d, *J* = 6.8 Hz, 2H, Ar), 7.17 (d, *J* = 9.2 Hz, 1H, Ar), 7.28 (d, *J* = 8.4 Hz, 2H, Ar), 7.77 (d, *J* = 8.4 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 24.6, 32.6, 34.1, 38.8, 108.7, 109.2, 115.4, 121.1, 126.6, 127.2, 128.2, 129.6, 135.6, 136.7, 140.2, 143.2. IR (CH₂Cl₂) ν 3289, 2956, 2867, 1593, 1551, 1491, 1456, 1380, 1329, 1288, 1157, 1093, 1040, 871, 789, 665 cm⁻¹. HRMS (ESI) Calcd. for C₂₀H₂₅N₂O₂S⁺ (M+H⁺) requires 357.1631, found: 357.1636.





N-((1,4-dimethyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide **and**
N-((1,6-dimethyl-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide *o*-6i or *m*-6i

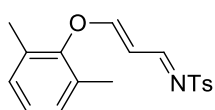
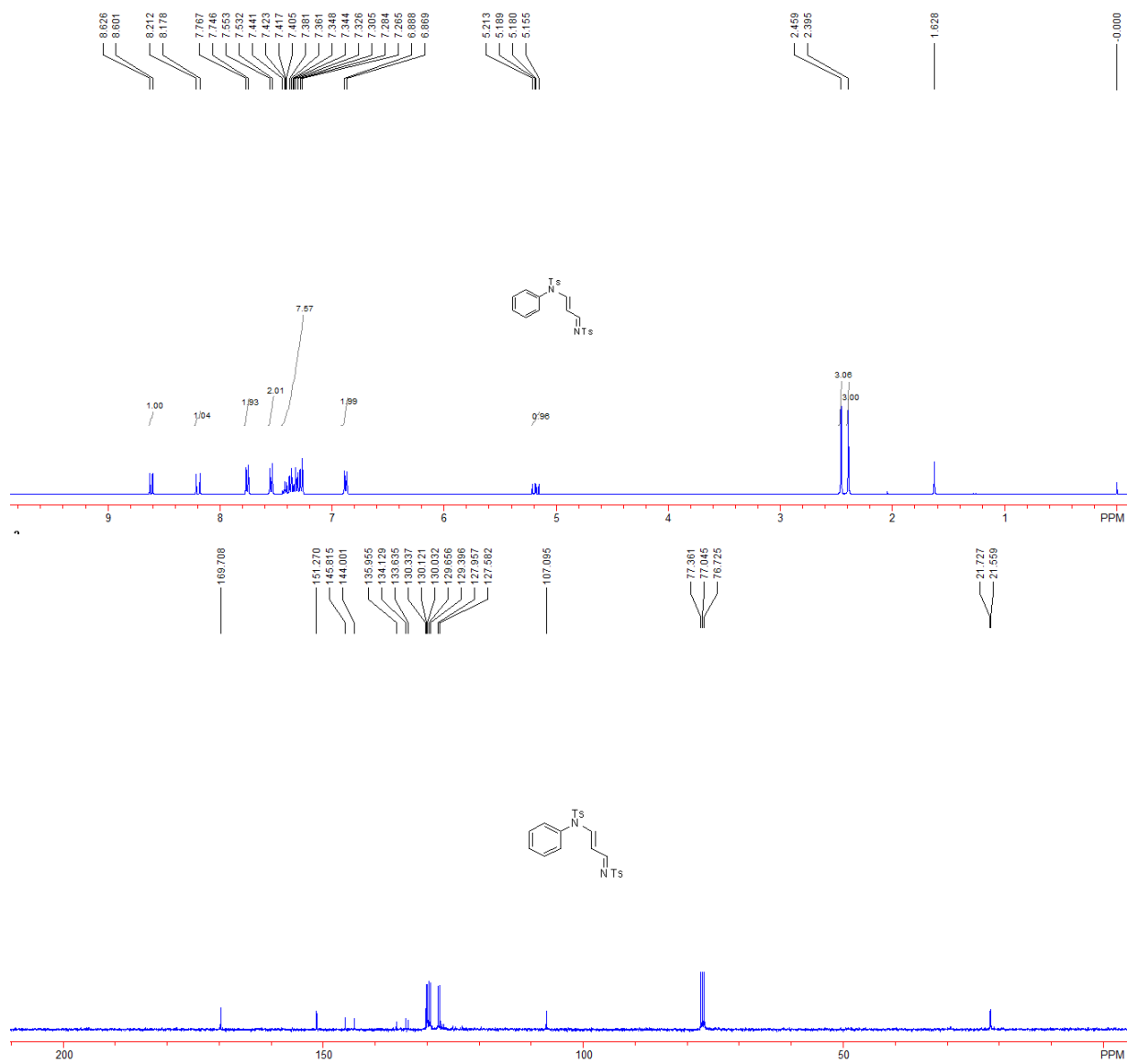
0.2 mmol scale, a white solid, 72% yield (52 mg). m.p.: 122-124 °C. Two isomers with ratio: 3:2 or 2: 3. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.39-2.41 (m, 3H, CH₃), 2.45-2.53 (m, 3H, CH₃), 3.60 (s, 3H, CH₃), 4.20-4.32 (m, 2H, CH₂), 4.61-4.70 (m, 1H, NH), 6.74-6.78 (m, 1H, Ar), 6.79-6.89 (m, 1H, Ar), 7.01-7.24 (m, 4H, Ar), 7.71 (d, *J* = 7.6 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 19.6, 21.4, 21.7, 29.6, 32.4, 32.6, 38.8, 40.1, 107.1, 108.9, 109.2, 109.4, 118.3, 120.9, 121.1, 122.0, 124.4, 125.4, 127.1, 127.4, 128.8, 129.4, 130.5, 131.8, 136.7, 137.3, 137.4, 143.1, 143.2. IR (CH₂Cl₂) ν 3280, 2921, 1597, 1474, 1417, 1323, 1155, 1092, 1035, 802, 746, 666 cm⁻¹. HRMS (ESI) Calcd. for C₂₈H₂₀N₂O₂S⁺ (M+H⁺) requires 328.1245, found: 328.1247.



4-methyl-N-phenyl-N-((1E)-3-(tosylimino)prop-1-en-1-yl)benzenesulfonamide 7a

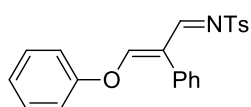
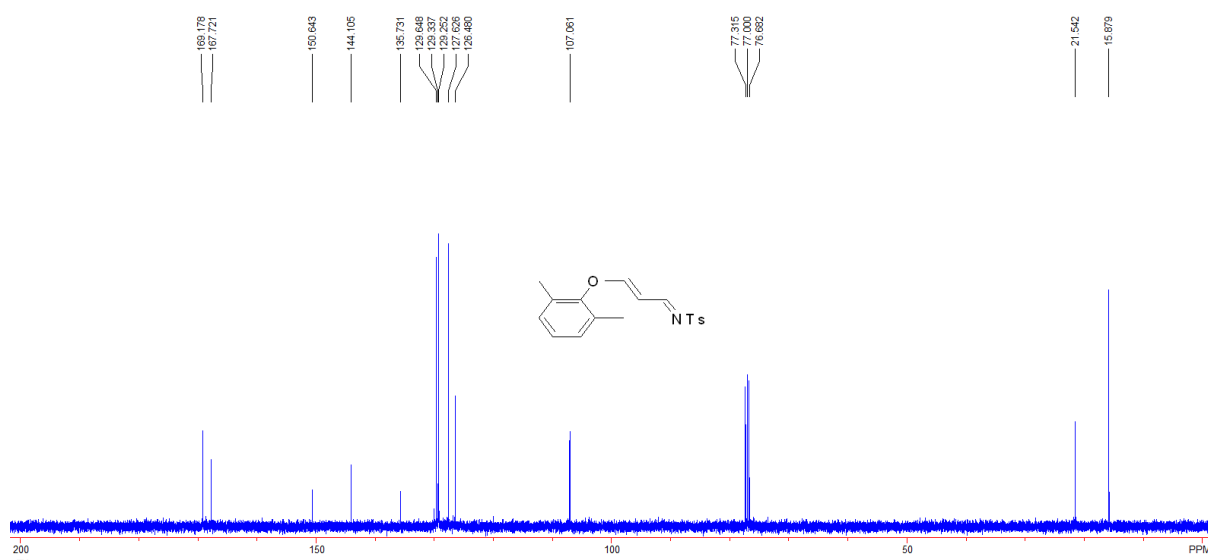
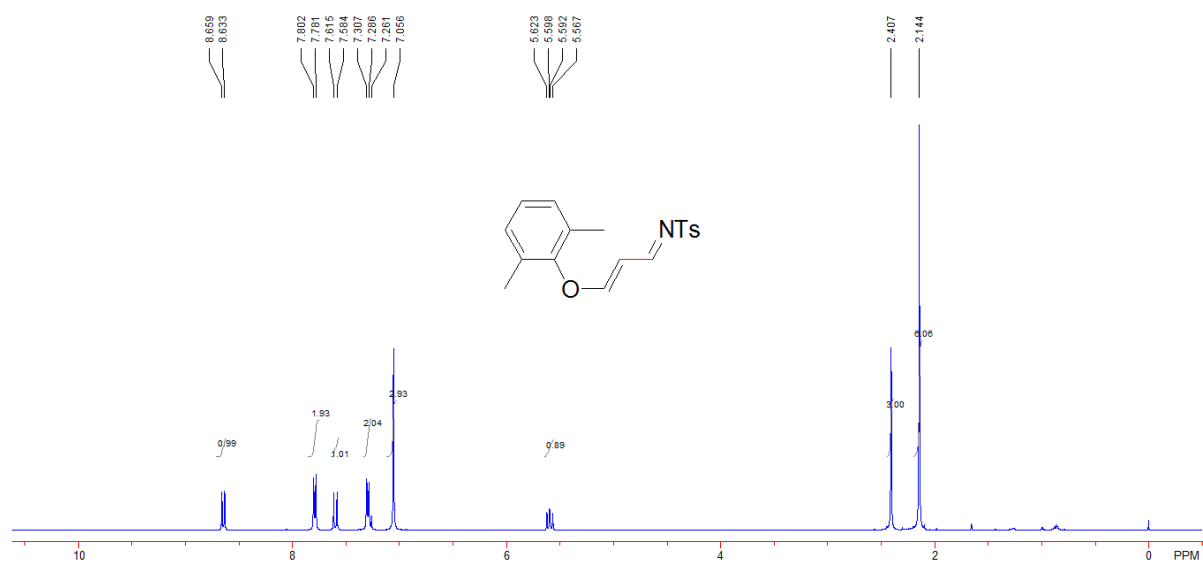
0.2 mmol, a white solid, 11% yield (10 mg). ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.40 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 5.18 (dd, *J* = 14.2 Hz, *J* = 10.0 Hz, 1H, CH=), 6.88 (d, *J* = 7.6 Hz, 2H, Ar), 7.26-7.45 (m, 7H, Ar), 7.54 (d, *J* = 8.4 Hz, 2H, Ar), 7.76 (d, *J* = 8.4 Hz, 2H, Ar), 8.20 (d, *J* = 14.2 Hz, 1H, =CH), 8.61 (d, *J* = 10.0 Hz, 1H, CH=N). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 21.7, 107.1, 127.6, 127.9, 129.4, 129.6, 130.0, 130.1, 130.3, 133.6, 134.1, 135.9, 144.0, 145.8, 151.3, 169.7. IR (CH₂Cl₂) ν 3056, 2923, 1609, 1568, 1489, 1370, 1322, 1264, 1171, 1154, 1129, 1084, 825, 812, 734, 702, 673, 664 cm⁻¹. HRMS (ESI) Calcd. for C₂₃H₂₃N₂O₄S₂⁺ (M+H⁺) requires

455.1100, found: 455.1101.



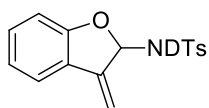
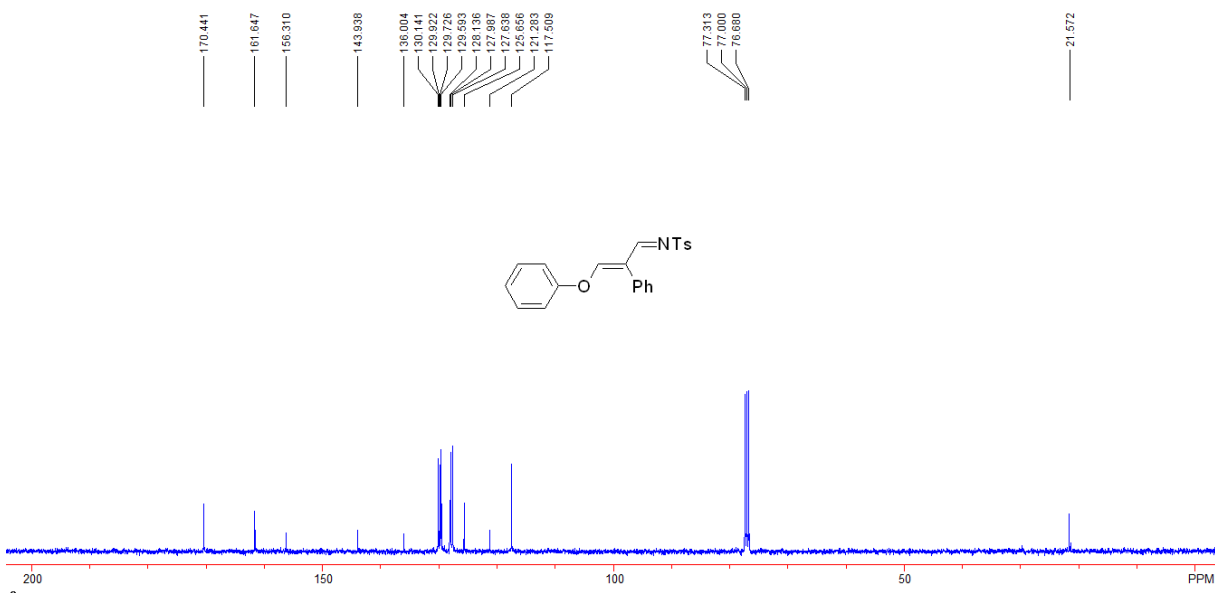
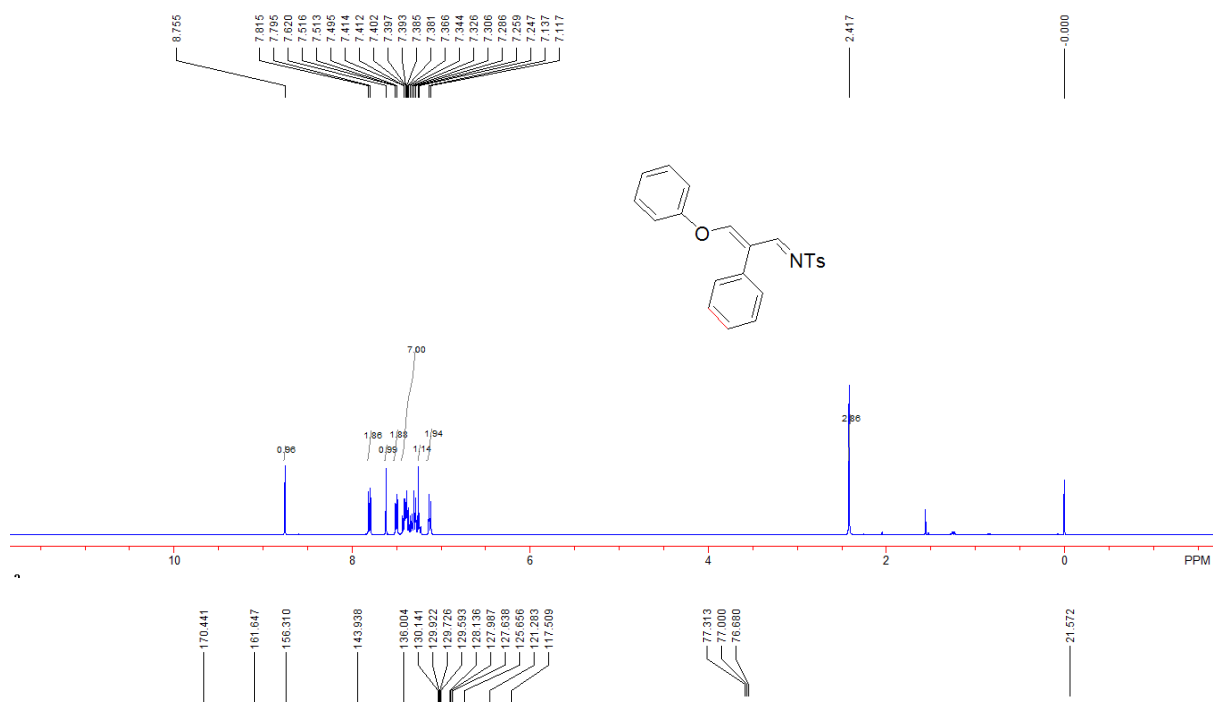
N-[3-(2,6-Dimethylphenoxy)allylidene]-4-methylbenzenesulfonamide 7b

0.2 mmol scale, a white solid, 79% yield (52 mg). M.p.: 120-122 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.14 (s, 6H, 2CH₃), 2.41 (s, 3H, CH₃), 5.59 (dd, *J* = 12.4 Hz, *J* = 10.0 Hz, 1H, CH=), 7.06 (s, 3H, Ar), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.60 (d, *J* = 12.4 Hz, 1H, CH=), 7.79 (d, *J* = 8.0 Hz, 2H, Ar), 8.64 (d, *J* = 10.0 Hz, 1H, CH=N). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 15.9, 21.5, 107.1, 126.5, 127.6, 129.2, 129.3, 129.6, 135.7, 144.1, 150.6, 167.7, 169.2. IR (CH₂Cl₂) ν 2962, 2848, 1616, 1434, 1396, 1347, 1306, 1242, 1147, 1080, 1032, 1012 856, 703 661 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₂₀NO₃S⁺ (M⁺+H) requires 330.1158, found: 330.1163.

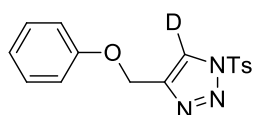
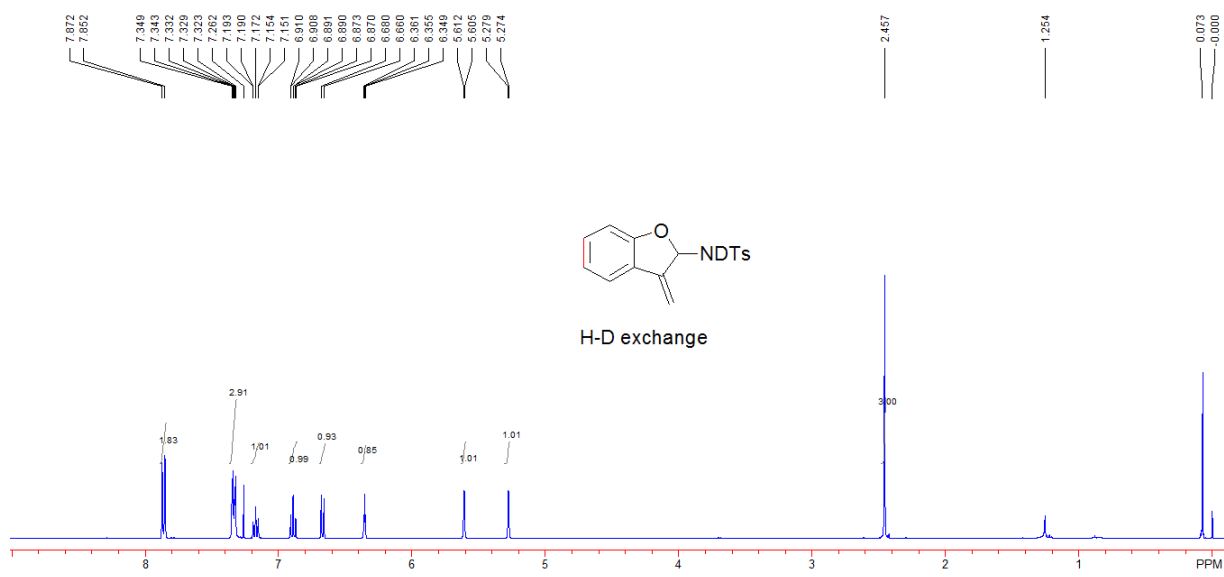


4-Methyl-N-(3-phenoxy-2-phenylallylidene)benzenesulfonamide **7c**

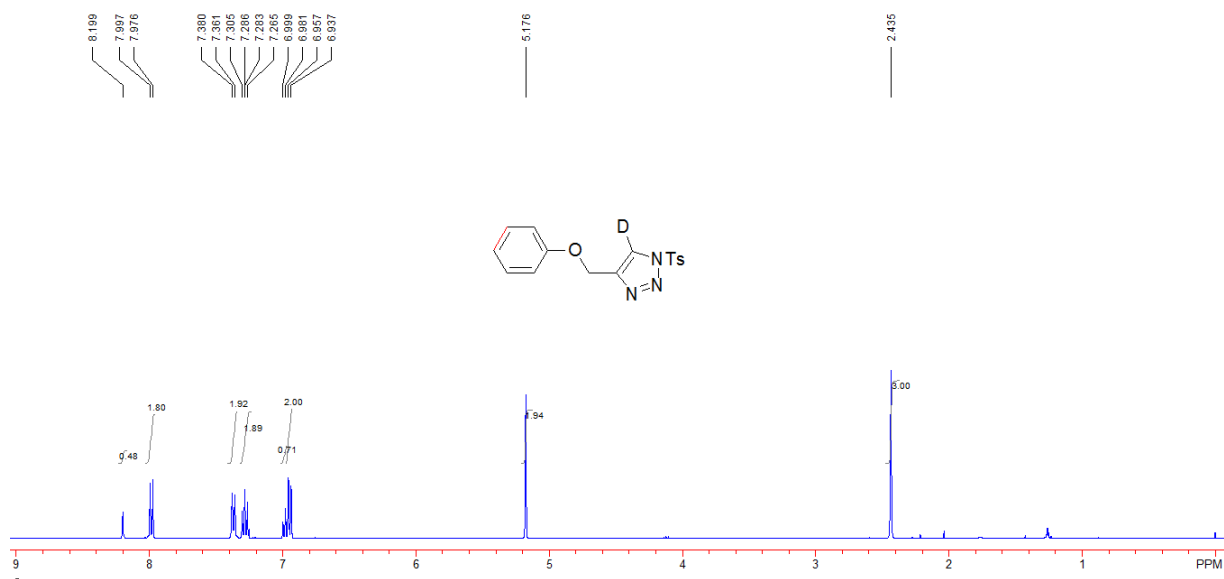
0.25 mmol scale, a white solid, 76% yield (72 mg). M.p.: 150-152 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.42 (s, 3H, CH_3), 7.12 (d, $J = 8.0$ Hz, 2H, Ar), 7.24-7.42 (m, 8H, Ar), 7.49-7.52 (m, 2H, Ar), 7.62 (s, 1H, $\text{CH}=\text{N}$), 7.80 (d, $J = 8.0$ Hz, 2H, Ar), 8.76 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.6, 117.5, 121.3, 125.6, 127.6, 128.0, 128.1, 129.6, 129.7, 129.9, 130.1, 136.0, 143.9, 156.3, 161.6, 170.4. IR (CH_2Cl_2) ν 2922, 1765, 1629, 1584, 1486, 1311, 1288, 1182, 1152, 1118, 1087, 857, 812, 765, 712, 692, 657 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_3\text{S}^+$ (M^++H) requires 378.1158, found: 378.1162.

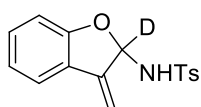
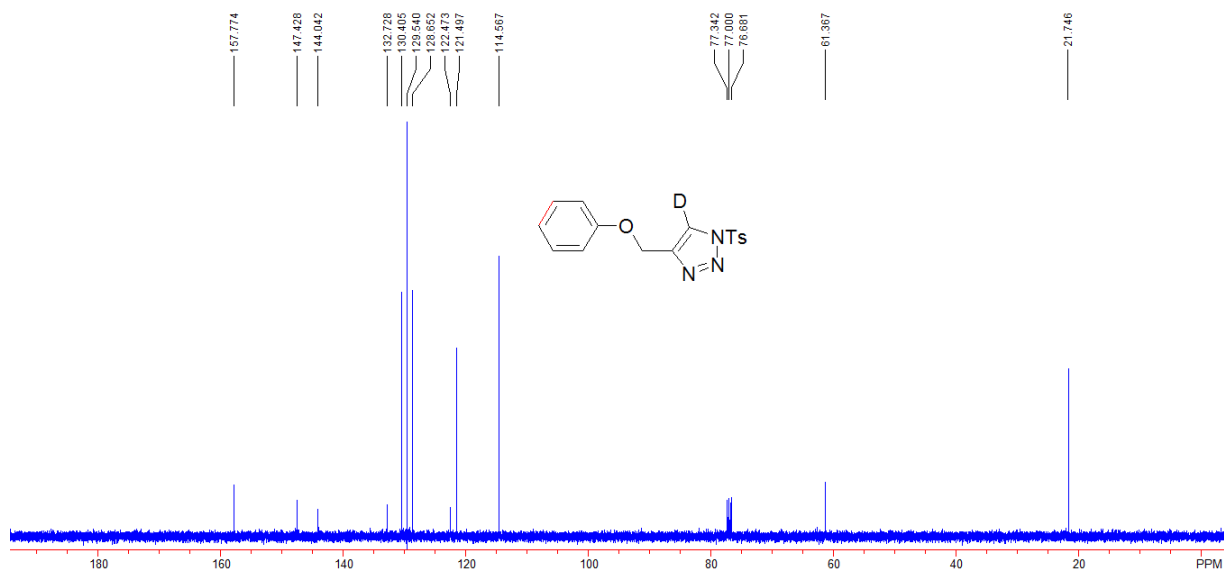


H-D exchange ¹H NMR. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.46 (s, 3H, CH₃), 5.28 (d, *J* = 2.4 Hz, 1H, CH₂), 5.61 (d, *J* = 2.4 Hz, 1H, CH₂), 6.36 (t, *J* = 2.4 Hz, 1H, CH), 6.67 (d, *J* = 8.0 Hz, 1H, Ar), 6.87-6.91 (m, 1H, Ar), 7.15-7.20 (m, 1H, Ar), 7.32-7.35 (m, 3H, Ar), 7.86 (d, *J* = 8.0 Hz, 2H, Ar).

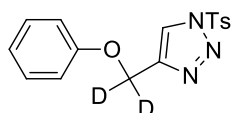
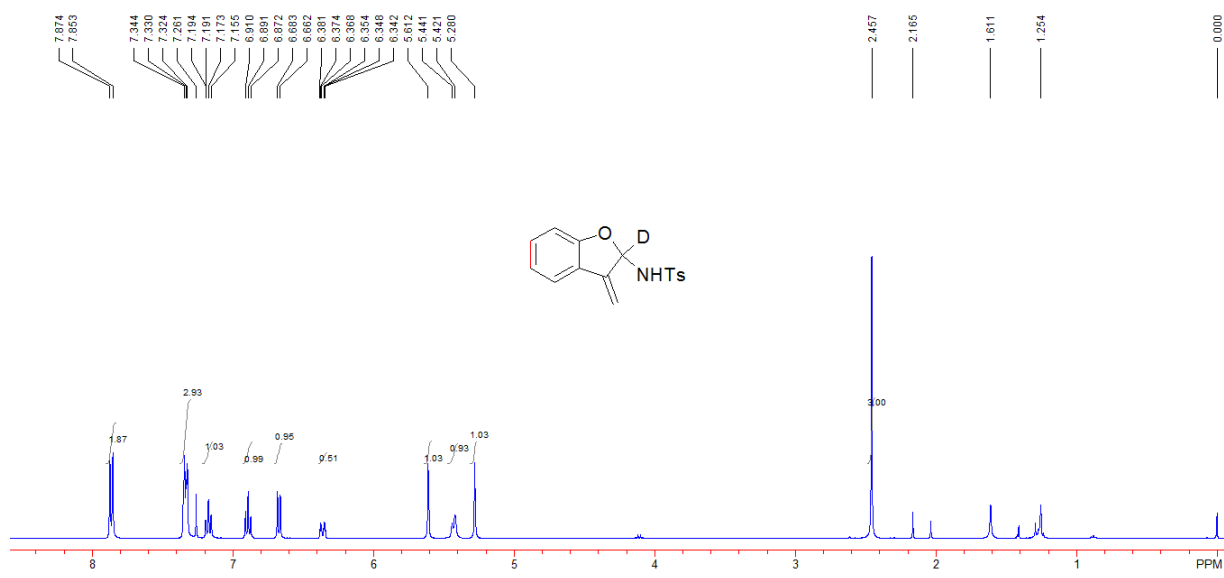


1a-D1. D contain: 50%, 1 mmol scale, a white solid, 75% overall yield (247 mg). ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 5.18 (s, 2H, CH_2), 6.94 (d, $J = 8.0$ Hz, 2H, Ar), 6.90 (d, $J = 8.0$ Hz, 1H, Ar), 7.26-7.31 (m, 2H, Ar), 7.37 (d, $J = 8.0$ Hz, 2H, Ar), 7.98 (d, $J = 8.0$ Hz, 2H, Ar), 8.20 (s, 0.5H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.7, 61.4, 114.6, 121.5, 122.5, 128.6, 129.5, 130.4, 132.7, 144.0, 147.4, 157.8. HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{15}\text{DN}_3\text{O}_3\text{S}^+$ ($\text{M}^+\text{+H}$) requires 331.0969, found: 331.0967.



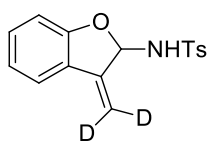
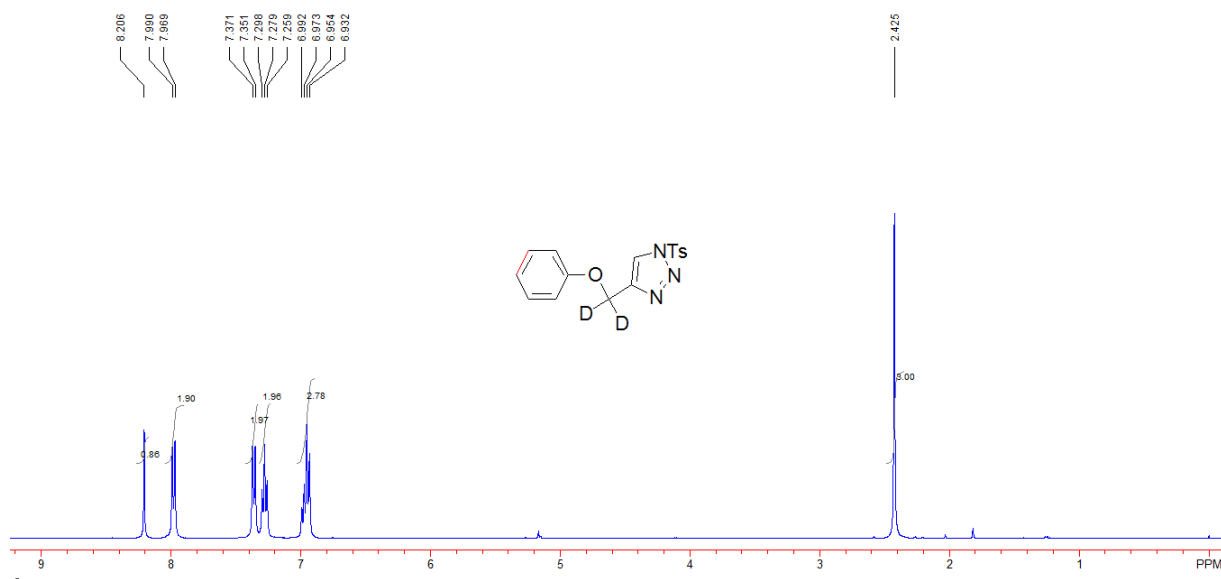


2a-D1. 0.2 mmol scale, a white solid, 68% yield (41 mg). ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.46 (s, 3H, CH₃), 5.28 (s, 1H, CH=), 5.42-5.44 (m, 1H, NH), 5.61 (s, 1H, CH=), 6.36 (dt, *J* = 10.0 Hz, *J* = 2.4 Hz, 0.5H, CH), 6.67 (d, *J* = 8.4 Hz, 1H, Ar), 6.89 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.15-7.20 (m, 1H, Ar), 7.32-7.35 (m, 3H, Ar), 7.86 (d, *J* = 8.4 Hz, 2H, Ar). HRMS (ESI) Calcd. for C₁₆H₁₅DNO₃S (M⁺+H) requires 303.0907, found: 303.0901.

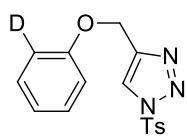
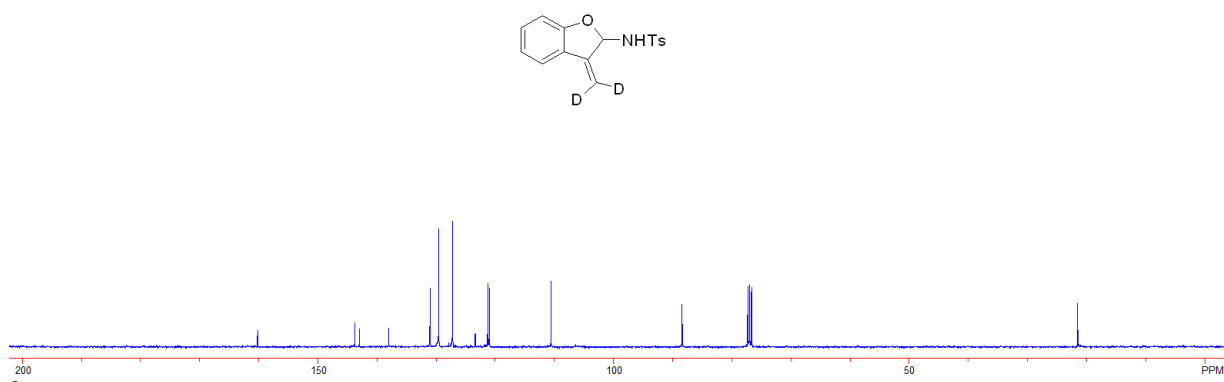
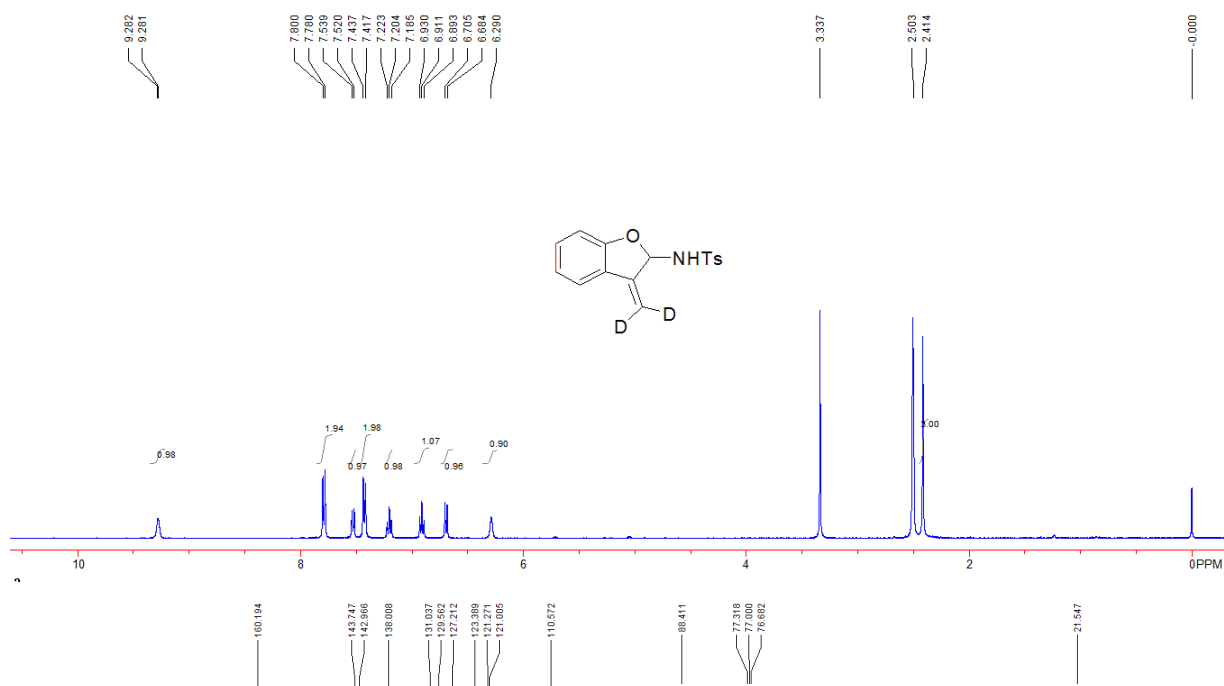


1a-D2. D: > 99%, a white solid, 15% overall yield (745 mg). ¹H NMR (CDCl₃, 400 MHz, TMS)

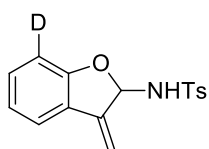
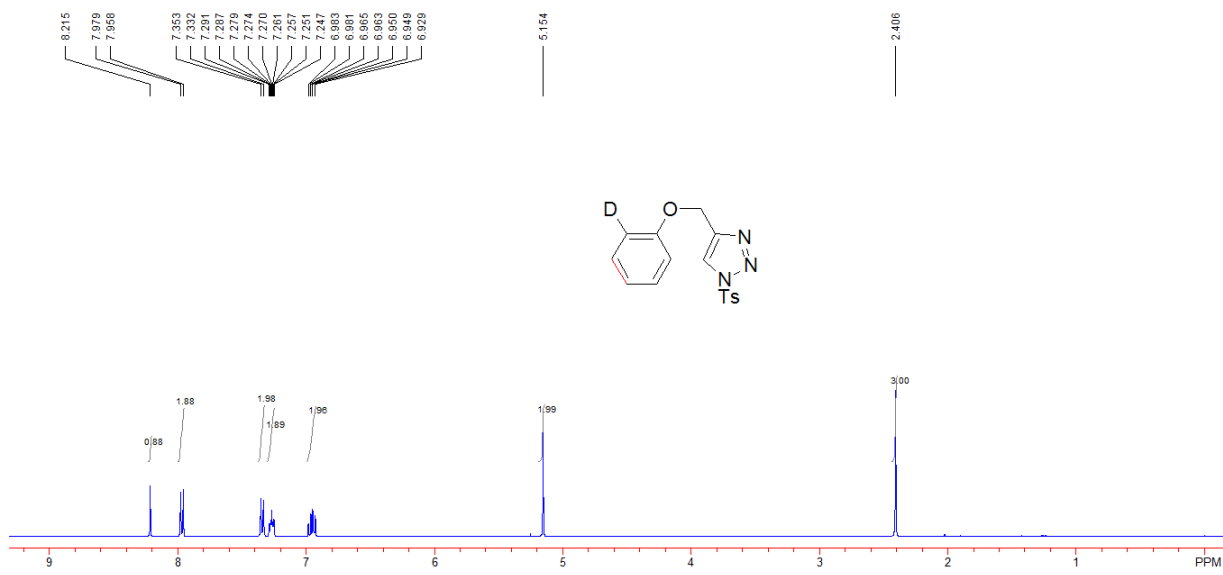
δ 2.42 (s, 3H, CH₃), 6.93-6.70 (m, 3H, Ar), 7.28 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 2H, Ar), 7.36 (d, $J = 8.4$ Hz, 2H, Ar), 7.98 (d, $J = 8.4$ Hz, 2H, Ar), 8.21 (s, 1H, CH=). HRMS (ESI) Calcd. for C₁₆H₁₄D₂N₃O₃S⁺ (M⁺+H) requires 332.1032, found: 332.1033.



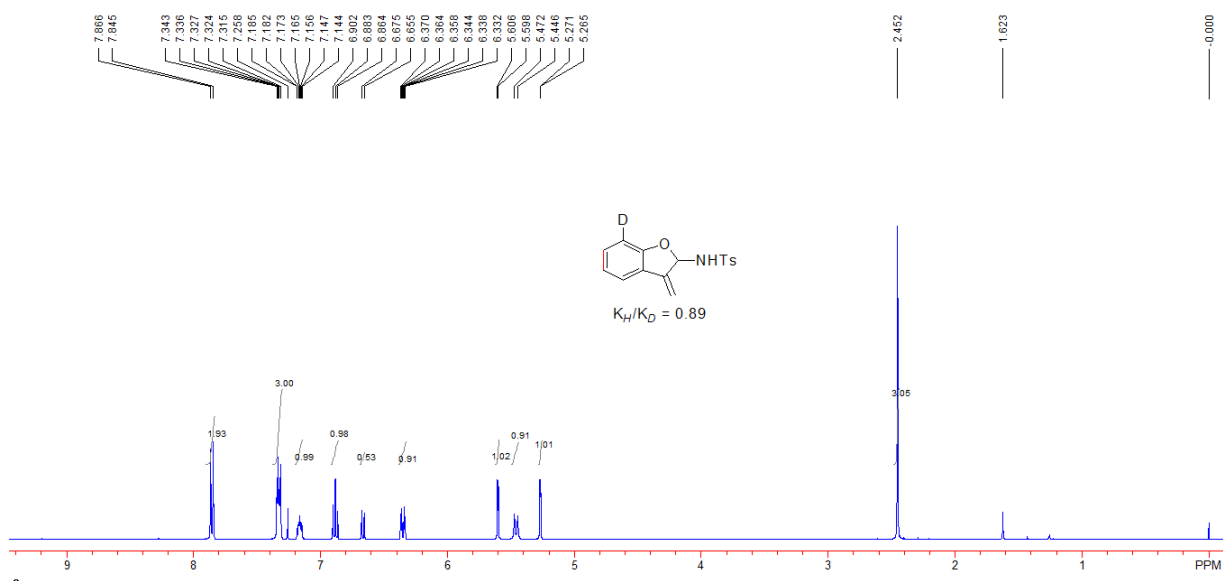
2a-D2. D: > 99%. 0.3 mmol scale, a white solid, 42% yield (38 mg). ¹H NMR (DMSO-*d*₆, 400 MHz, TMS) δ 2.41 (s, 3H, CH₃), 6.29 (s, 1H, CH), 6.69 (d, $J = 8.0$ Hz, 1H, Ar), 6.91 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H, Ar), 7.20 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H, Ar), 7.42 (d, $J = 8.0$ Hz, 2H, Ar), 7.53 (d, $J = 8.0$ Hz, 1H, Ar), 7.79 (d, $J = 8.0$ Hz, 2H, Ar), 9.28 (d, $J = 0.4$ Hz, 1H, NH). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 88.4, 110.6, 121.0, 121.3, 123.4, 127.2, 129.6, 131.0, 138.0, 143.0, 143.8, 160.2. HRMS (ESI) Calcd. for C₁₆H₁₄D₂NO₃S (M⁺+H) requires 304.0967, found: 304.0890.

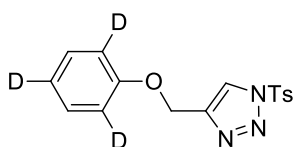
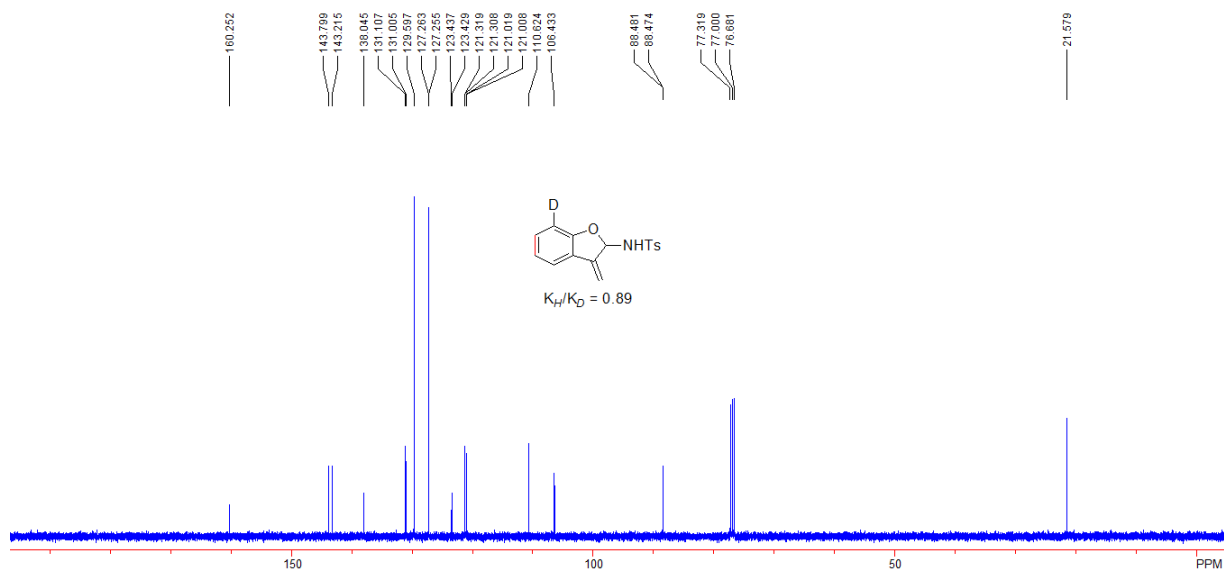


1a-D3. 2.5 mmol scale, a white solid, 76% overall yield (627 mg). $^1\text{H NMR}$ (CDCl₃, 400 MHz, TMS) δ 2.41 (s, 3H, CH₃), 5.15 (s, 2H, CH₂), 6.92-6.99 (m, 2H, Ar), 7.24-7.31 (m, 2H, Ar), 7.34 (d, $J = 8.4$ Hz, 2H, Ar), 7.96 (d, $J = 8.4$ Hz, 2H, Ar), 8.22 (s, 1H, CH=). HRMS (ESI) Calcd. for C₁₆H₁₅DN₃O₃S⁺ (M⁺+H) requires 331.0976, found: 331.0969.

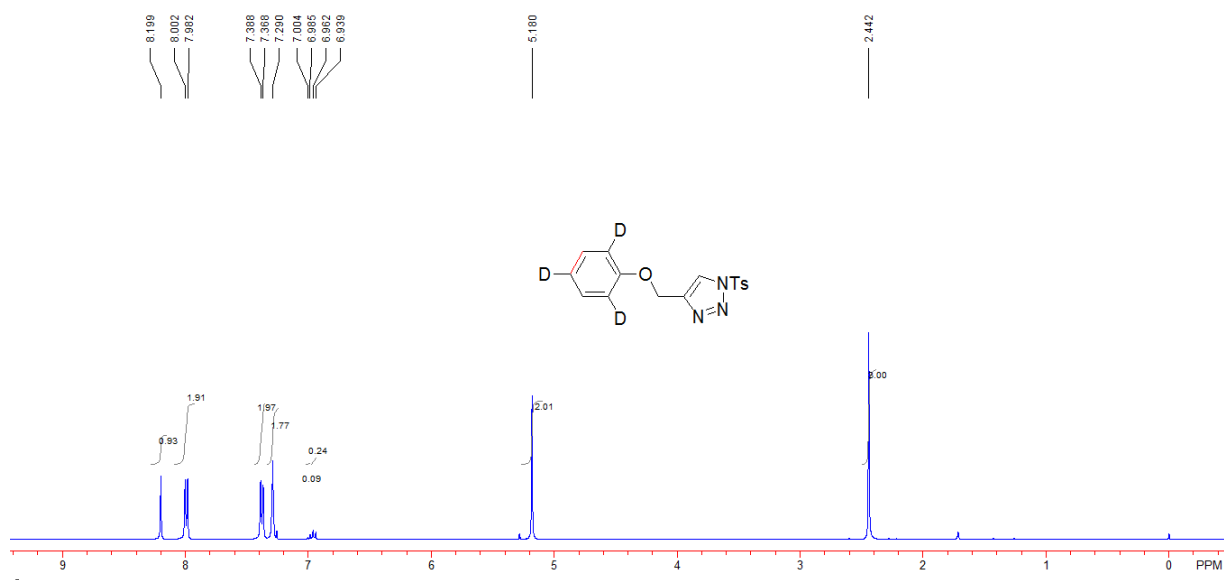


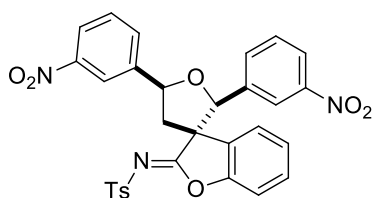
2a-D3. 0.24 mmol scale, a white solid, 62% yield (45 mg). ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.45 (s, 3H, CH₃), 5.27 (d, *J* = 2.4 Hz, 1H, CH=), 5.45 (d, *J* = 9.6 Hz, 1H, NH), 5.60 (d, *J* = 2.4 Hz, 1H, CH=), 6.35 (dt, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H, CH), 6.66 (d, *J* = 8.0 Hz, 0.53H, Ar), 6.88 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.14-7.19 (m, 1H, Ar), 7.31-7.35 (m, 3H, Ar), 7.85 (d, *J* = 8.0 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 88.47, 88.48, 106.4, 110.6, 121.0, 122.1, 121.31, 121.32, 123.42, 123.43, 127.25, 127.26, 129.6, 131.0, 131.1, 138.0, 143.2, 143.8, 160.3. HRMS (ESI) Calcd. for C₁₆H₁₅DNO₃S (M⁺+H) requires 303.0907, found: 303.0899.





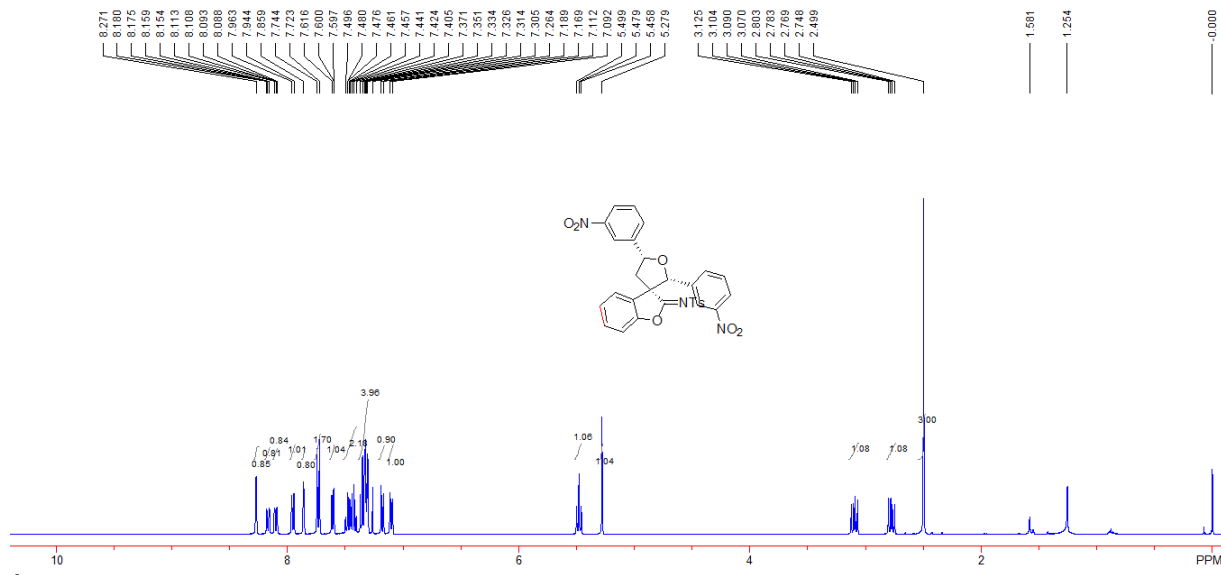
1a-D4. D: 88%, 1 mmol scale, a white solid, 81% yield for last step (269 mg). ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 5.18 (s, 2H, CH_2), 6.95 (d, $J = 7.6$ Hz, 0.24H, Ar), 7.00 (d, $J = 7.6$ Hz, 0.09H, Ar), 7.29 (s, 2H, Ar), 7.37 (d, $J = 8.0$ Hz, 2H, Ar), 7.99 (d, $J = 8.0$ Hz, 2H, Ar), 8.20 (s, 1H, $\text{CH}=\text{N}$). HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{13}\text{D}_3\text{N}_3\text{O}_3\text{S}^+$ ($\text{M}^+ + \text{H}$) requires 333.1092, found: 333.1085.

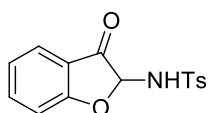
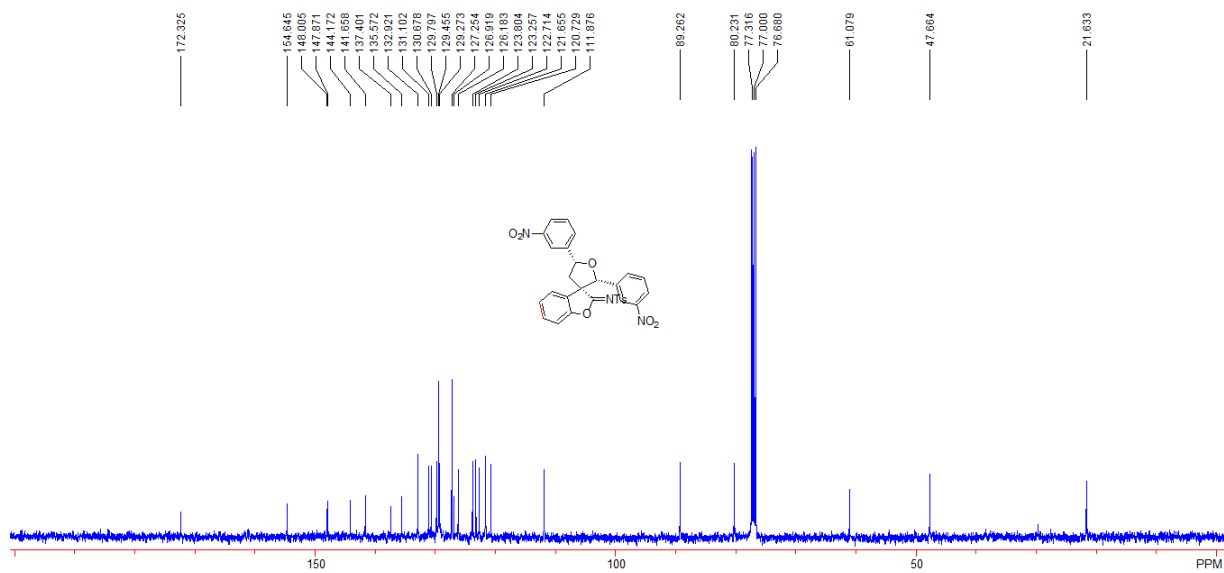




(Z)-N-2',5'-bis(3-nitrophenyl)-4',5'-dihydro-2H,2'H-spiro[benzofuran-3,3'-furan]-2-ylidene-4-methylbenzenesulfonamide 8.

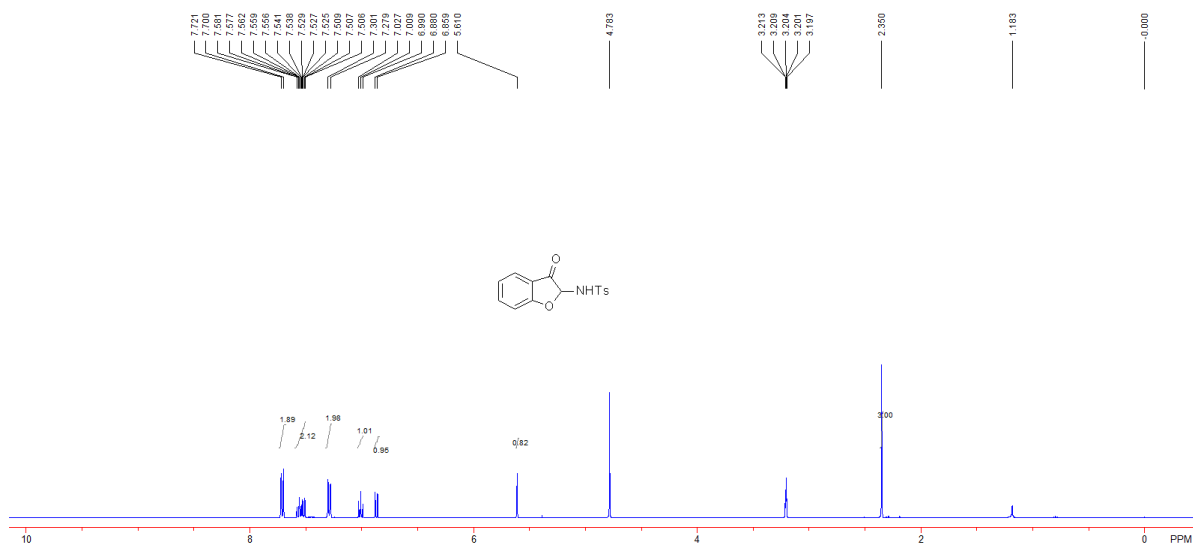
0.2 mmol scale, a white solid, 62 mg, 52% yield. m.p.: 231-232 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.50 (s, 3H, CH₃), 2.78 (dd, *J* = 8.0 Hz, *J* = 14.0 Hz, 1H, CH₂), 3.10 (dd, *J* = 8.0 Hz, *J* = 14.0 Hz, 1H, CH₂), 5.28 (s, 1H, CH), 5.48 (t, *J* = 8.0 Hz, 1H, CH), 7.10 (d, *J* = 8.0 Hz, 1H, Ar), 7.18 (d, *J* = 8.0 Hz, 1H, Ar), 7.26-7.38 (m, 4H, Ar), 7.40-7.50 (m, 2H, Ar), 7.59-7.62 (m, 1H, Ar), 7.73 (d, *J* = 8.0 Hz, 2H, Ar), 7.86 (s, 1H, Ar), 7.95 (d, *J* = 8.0 Hz, 1H, Ar), 8.10 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H, Ar), 8.17 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H, Ar), 8.27 (s, 1H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 47.7, 61.1, 80.2, 89.3, 111.9, 120.7, 121.6, 122.7, 123.2, 123.8, 126.2, 126.9, 127.2, 129.3, 129.4, 129.8, 130.7, 131.1, 132.9, 135.6, 137.4, 141.6, 144.2, 147.9, 148.0, 154.6, 172.3. IR (CH₂Cl₂) ν 1700, 1525, 1457, 1345, 1318, 1156, 1079, 1064, 753, 702, 680, 668. HRMS (ESI) Calcd. for C₃₀H₂₇N₄O₈S⁺ (M+NH₄)⁺ requires 603.1544, found: 603.1543.

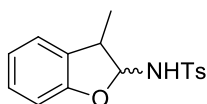
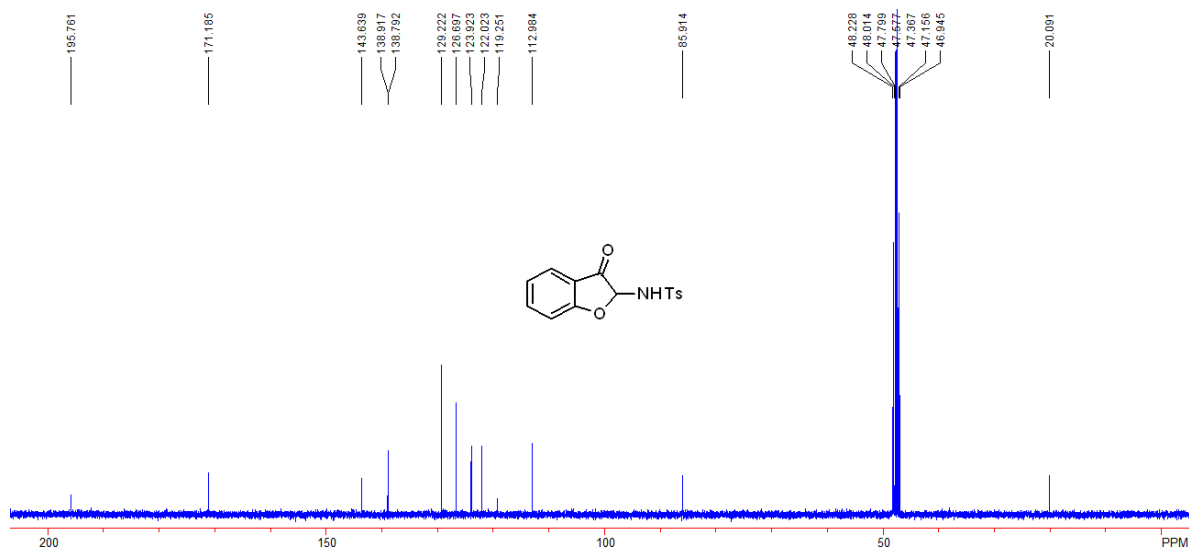




4-methyl-*N*-(3-oxo-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide **9**

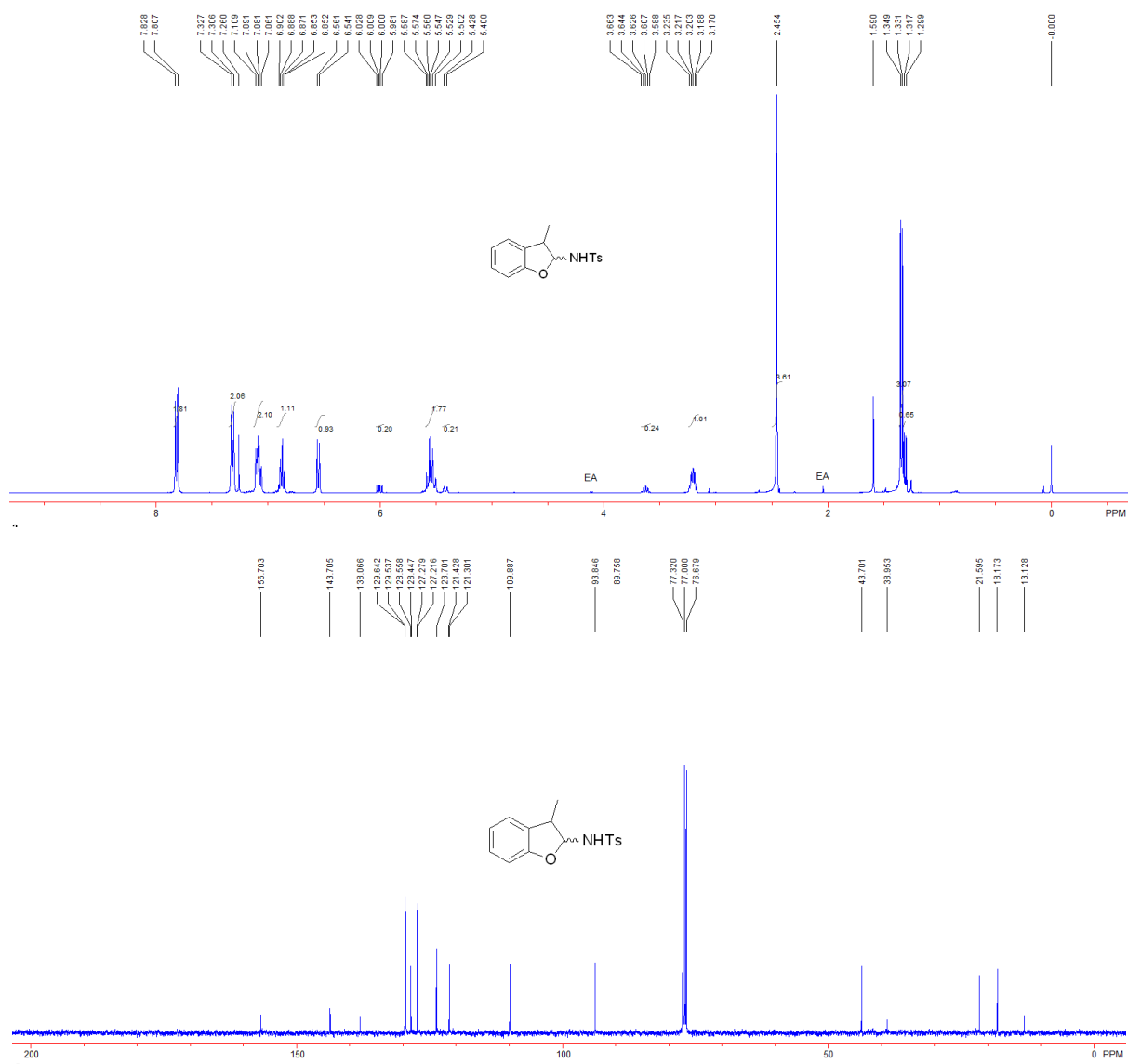
0.1 mmol scale, a white solid, 71% yield (22 mg). M.p.: 145-147 °C. ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.35 (s, 3H, CH₃), 6.46 (s, 1H, CH), 5.61 (s, 1H, CH), 6.87 (d, *J* = 8.4 Hz, 1H, Ar), 7.01 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H, Ar), 7.29 (d, *J* = 8.4 Hz, 2H, Ar), 7.50-7.58 (m, 2H, Ar). 7.71 (d, *J* = 8.4 Hz, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 20.1, 85.9, 113.0, 119.3, 122.0, 123.9, 126.7, 129.2, 138.8, 138.9, 143.6, 171.2, 195.8. IR (CH₂Cl₂) ν 3271, 2931, 1710, 1615, 1597, 1462, 1343, 1324 cm⁻¹. HRMS (ESI) Calcd. for C₁₅H₁₇N₂O₄S⁺ (M⁺+H) requires 321.0904, found: 321.0900.





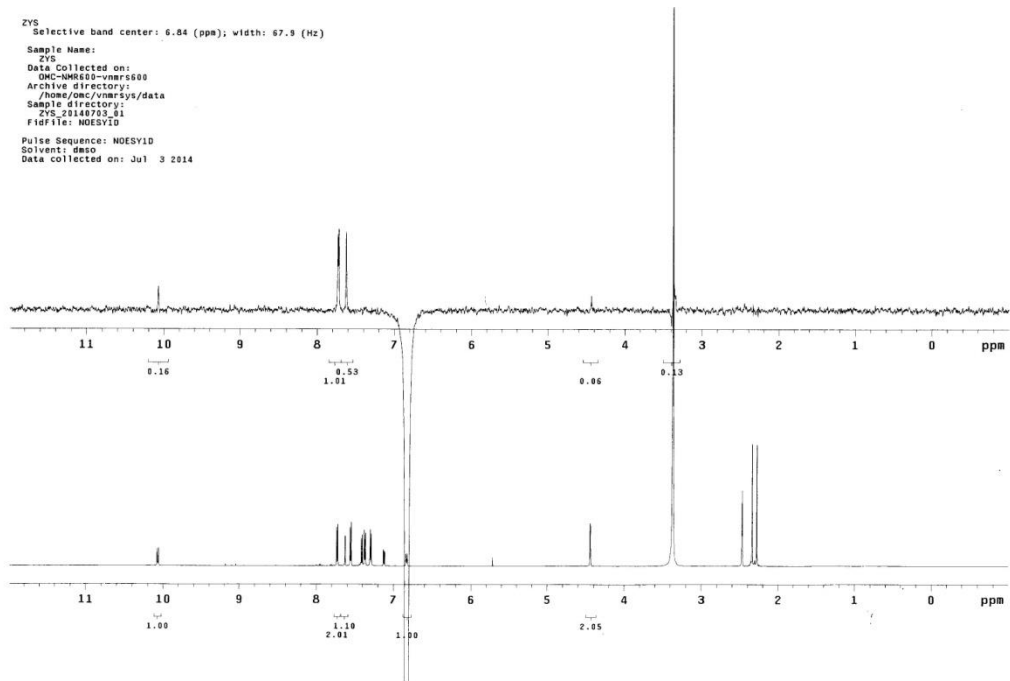
4-Methyl-N-(3-methyl-2,3-dihydrobenzofuran-2-yl)benzenesulfonamide 10

0.1 mmol scale, a white solid, 80% yield (24 mg). M.p.: 125-127 °C. A mixture of isomers, dr: around 5:1. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.30 (d, $J = 7.2$ Hz, 0.6H), 1.34 (d, $J = 7.2$ Hz, 3H), 2.45 (s, 3.6H), 3.17-3.24 (m, 1H, CH), 3.58-3.66 (m, 0.2H), 5.41 (d, $J = 11.2$ Hz, 0.2H), 5.50-5.59 (m, 2H), 6.00 (dd, $J = 11.2$ Hz, $J = 7.6$ Hz, 0.2H), 6.55 (d, $J = 8.0$ Hz, 1H). 6.85-6.90 (m, 1H), 7.06-7.11 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 13.1, 18.2, 21.6, 39.0, 43.7, 89.8, 93.9, 109.9, 121.3, 121.4, 123.7, 127.2, 127.3, 128.5, 128.6, 129.5, 129.6, 138.1, 143.6, 143.7, 156.7. IR (CH_2Cl_2) ν 3275, 2963, 2925, 1598, 1478, 1452, 1329, 1162, 1091 cm^{-1} . HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{18}\text{NO}_3\text{S}^+$ ($\text{M}^+ + \text{H}$) requires 304.1002, found: 304.0992.

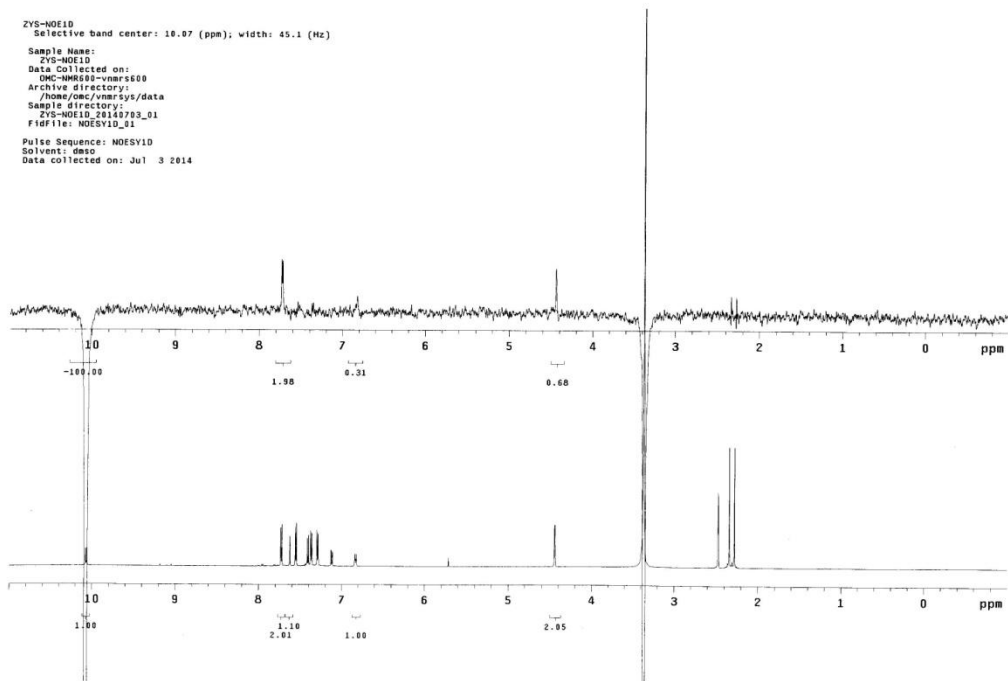


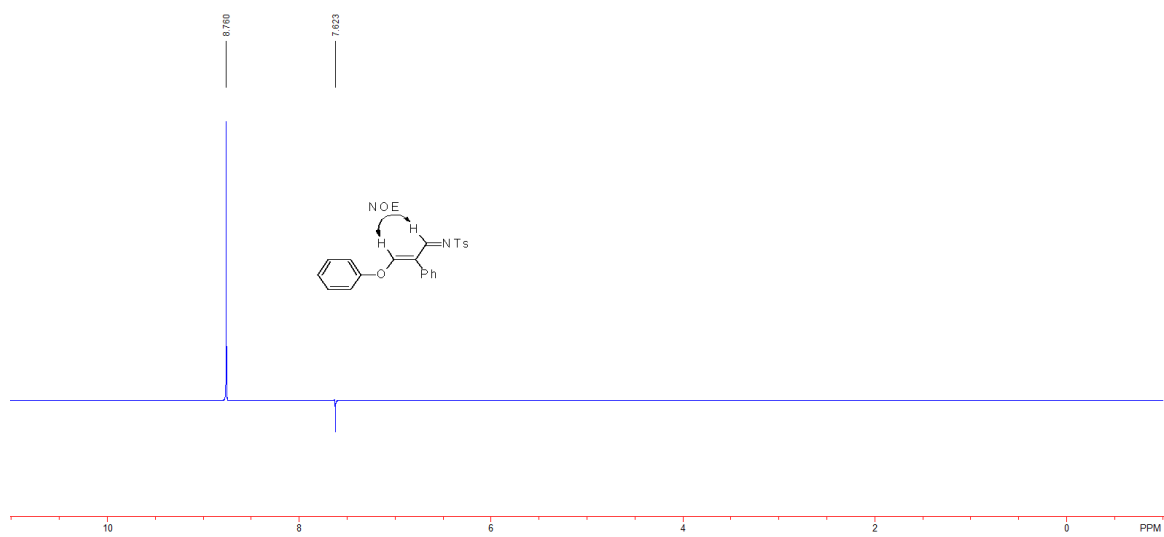
24. NOE of Compound 5d and 7c:

ZYS
Selective band center: 6.84 (ppm); width: 67.9 (Hz)
Sample Name:
ZYS
Data Collected on:
DMC-NMR600-vmr500
Archive directory:
/home/omc/vmr500/data
Sample directory:
ZYS_20140703_01
FidFile: NOESY10
Pulse Sequence: NOESY10
Solvent: dms0
Data collected on: Jul 3 2014



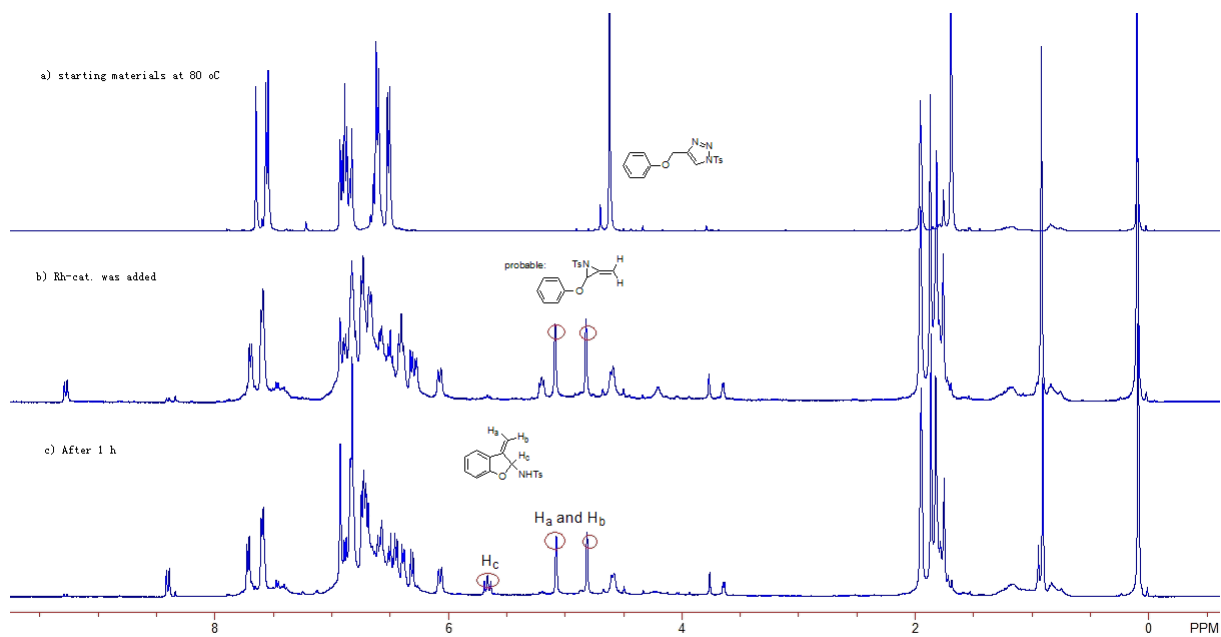
ZYS-NOE10
Selective band center: 10.07 (ppm); width: 45.1 (Hz)
Sample Name:
ZYS-NOE10
Data Collected on:
DMC-NMR600-vmr500
Archive directory:
/home/omc/vmr500/data
Sample directory:
ZYS-NOE10_20140703_01
FidFile: NOESY10_01
Pulse Sequence: NOESY10
Solvent: dms0
Data collected on: Jul 3 2014



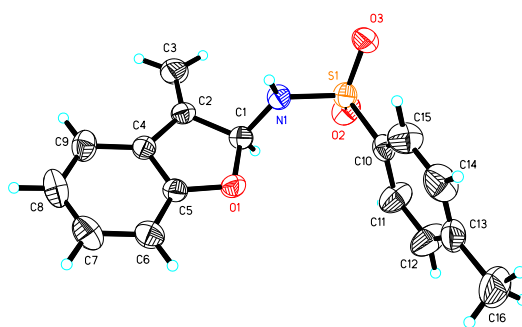


25. In situ high temperature (80 °C) ^1H NMR tests.

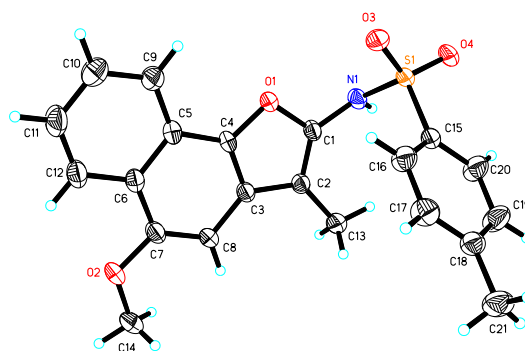
Note: This is not the standard reaction conditions!!!



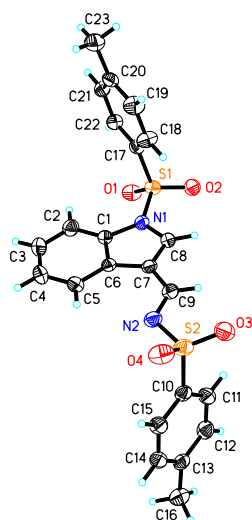
26. X-ray data of products **2a**, **3e**, **6a'**, **7a** and **8**.



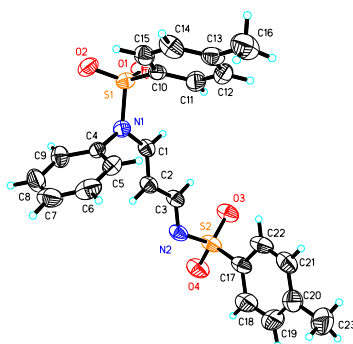
The crystal data of **2a** have been deposited in CCDC with number 966827. Empirical Formula: $C_{16}H_{15}NO_3S$; Formula Weight: 301.35; Crystal Color, Habit: colorless; Crystal System: Monoclinic; Crystal size: 0.212 x 0.164 x 0.078; Lattice Parameters: $a = 13.2128(15)\text{\AA}$, $b = 5.2286(6)\text{\AA}$, $c = 22.078(2)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90.021(2)^\circ$, $\gamma = 90^\circ$, $V = 1525.2(3)\text{\AA}^3$; Space group: $P2(1)/n$; $Z = 4$; $D_{calc} = 1.312\text{ g/cm}^3$; $F_{000} = 632$; Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0494$; $wR2 = 0.1274$.



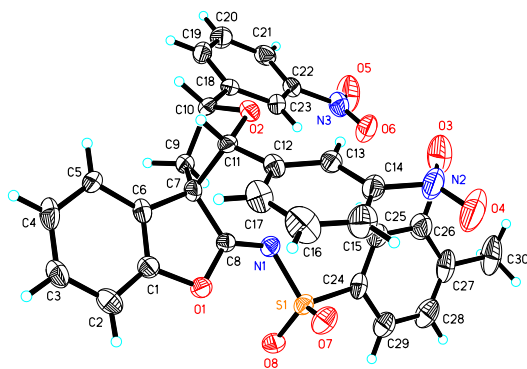
The crystal data of **3e** have been deposited in CCDC with number 969393. Empirical Formula: $C_{21}H_{19}NO_4S$; Formula Weight: 381.43; Crystal Color, Habit: colorless; Crystal System: Triclinic; Crystal size: 0.186 x 0.169 x 0.121; Lattice Parameters: $a = 8.1851(9)\text{\AA}$, $b = 11.3028(13)\text{\AA}$, $c = 11.9273(14)\text{\AA}$, $\alpha = 79.944(3)^\circ$, $\beta = 72.676(2)^\circ$, $\gamma = 78.178(2)^\circ$, $V = 1023.4(2)\text{\AA}^3$; Space group: $P-1$; $Z = 2$; $D_{calc} = 1.238\text{ g/cm}^3$; $F_{000} = 400$; Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0610$; $wR2 = 0.1518$.



The crystal data of **6a** have been deposited in CCDC with number 969179. Empirical Formula: $C_{23}H_{20}N_2O_4S_2$; Formula Weight: 452.53; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.165 x 0.100 mm; Crystal System: Pn2(1); Lattice Parameters: $a = 8.0251(6)\text{\AA}$, $b = 25.4919(18)\text{\AA}$, $c = 10.5814(8)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2164.7(3)\text{\AA}^3$; Space group: Pna2(1); $Z = 4$; $D_{calc} = 1.389\text{ g/cm}^3$; $F_{000} = 944$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0403$, $wR2 = 0.0823$.



The crystal data of **7a** have been deposited in CCDC with number 1012006. Empirical formula: $C_{23}H_{22}N_2O_4S_2$, Formula weight: 454.54, Temperature: 293(2) K, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: $a = 10.559(3)\text{\AA}$, $\alpha = 63.538(6)^\circ$, $b = 10.991(3)\text{\AA}$, $\beta = 78.349(6)^\circ$, $c = 11.719(3)\text{\AA}$, $\gamma = 71.093(6)^\circ$. Volume: $1149.3(5)\text{\AA}^3$, $Z = 2$, Density (calculated): 1.314 Mg/m^3 , $F(000)$: 476, Crystal size: 0.211 x 0.154 x 0.113 mm³, Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0844$, $wR2 = 0.2928$.



The crystal data of **8** have been deposited in CCDC with number 989483. Empirical Formula: $C_{30}H_{23}N_3O_8S$; Formula Weight: 585.57; Crystal Color, Habit: colorless; Crystal System: Monoclinic; Crystal size: 0.221 x 0.175 x 0.133; Lattice Parameters: $a = 11.441(2)\text{\AA}$, $b = 15.055(3)\text{\AA}$, $c = 15.927(3)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 97.324(4)^\circ$, $\gamma = 90^\circ$, $V = 2721.0(0)\text{\AA}^3$; Space group: $P21/n$; $Z = 4$; $D_{calc} = 1.429\text{ g/cm}^3$; $F_{000} = 1216$; Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0624$; $wR2 = 0.1463$.