# Supporting Information

## Pd-Catalyzed Decarboxylative 1,4-Addition Reactions of Benzofuran-based Azadienes with Allyl Phenyl Carbonates

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## 1. General Information

Proton ($^{1}$H) and carbon ($^{13}$C) NMR spectra were recorded on 400 MHz instrument (400 MHz for $^{1}$H NMR, 100 MHz for $^{13}$C NMR) and calibrated using tetramethylsilane (TMS) as internal reference. High resolution mass spectra (HRMS) were recorded under electrospray ionization (ESI) conditions. The melting point of compounds was determined by a melting point instrument. Flash column chromatography was performed on silica gel (0.035-0.070 mm) using compressed air. Thin layer chromatography (TLC) was carried out on 0.25 mm SDS silica gel coated glass plates (60F254). Eluted plates were visualized using a 254 nm UV lamp. Unless otherwise indicated, all reagents were commercially available and used without further purification. All solvents were distilled from the appropriate drying agents immediately before using. Allyl phenyl carbonates **1a–1k** were synthesized according to the reported procedures.[1] Benzofuran-bases azadienes **2a–2g** were prepared according to literature procedures.[2]

## 2. X-Ray Crystallographic Analysis of Product 3aa

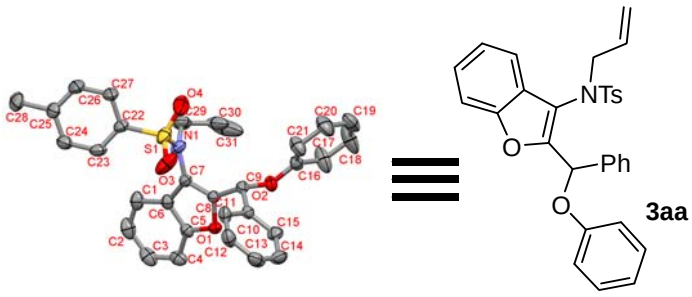



**Figure 1.** X-ray single crystal structure of **3aa** (with thermal ellipsoids shown at the 50% probability level)

| | |
|---|---|
| Identification code | **3aa** |
| Empirical formula | $C_{31}H_{27}NO_4S$ |
| Formula weight | 509.59 |
| Temperature/K | 113.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.3471(7) |
| b/Å | 11.5677(8) |
| c/Å | 12.0428(7) |
| α/° | 83.169(5) |
| β/° | 72.223(6) |
| γ/° | 71.119(6) |
| Volume/Å$^3$ | 1298.42(16) |
| Z | 2 |

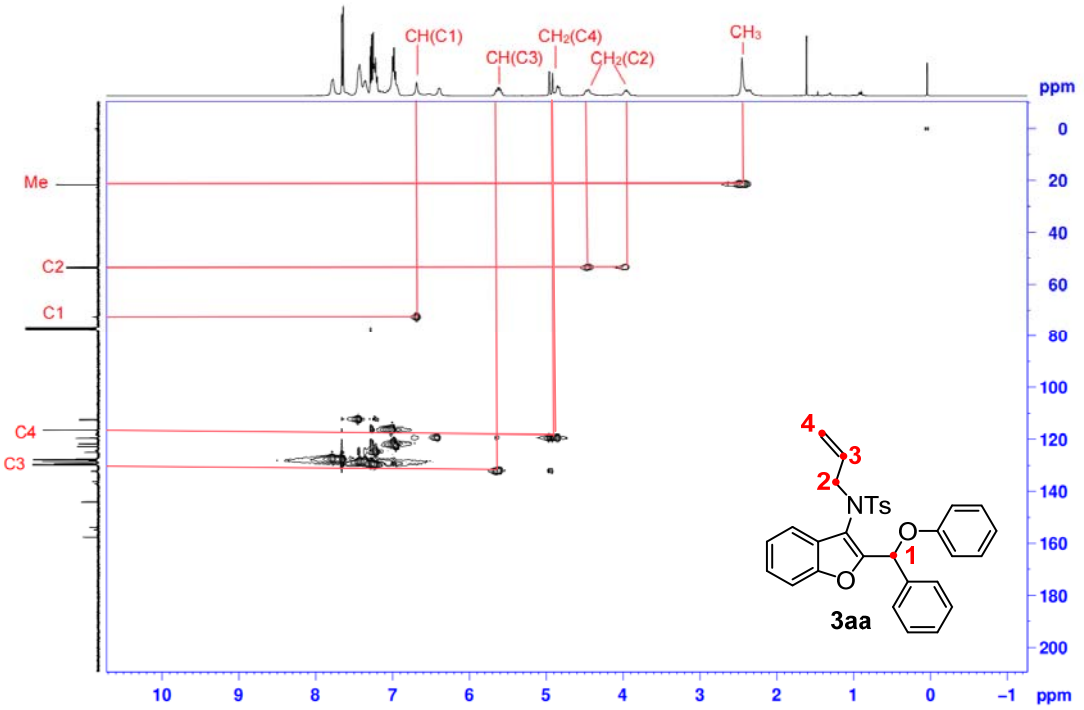
| | |
|---|---|
| $\rho_{calc}$g/cm$^3$ | 1.303 |
| $\mu$/mm$^{-1}$ | 0.162 |
| F(000) | 536.0 |
| Crystal size/mm$^3$ | 0.24 × 0.22 × 0.18 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 3.552 to 65.768 |
| Index ranges | $-14 \leq h \leq 15$, $-16 \leq k \leq 17$, $-17 \leq l \leq 18$ |
| Reflections collected | 19778 |
| Independent reflections | 8711 [$R_{int}$ = 0.0395, $R_{sigma}$ = 0.0626] |
| Data/restraints/parameters | 8711/0/336 |
| Goodness-of-fit on F$^2$ | 1.042 |
| Final R indexes [I>=2$\sigma$ (I)] | $R_1$ = 0.0761, $wR_2$ = 0.1830 |
| Final R indexes [all data] | $R_1$ = 0.1322, $wR_2$ = 0.2166 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.73/-0.52 |

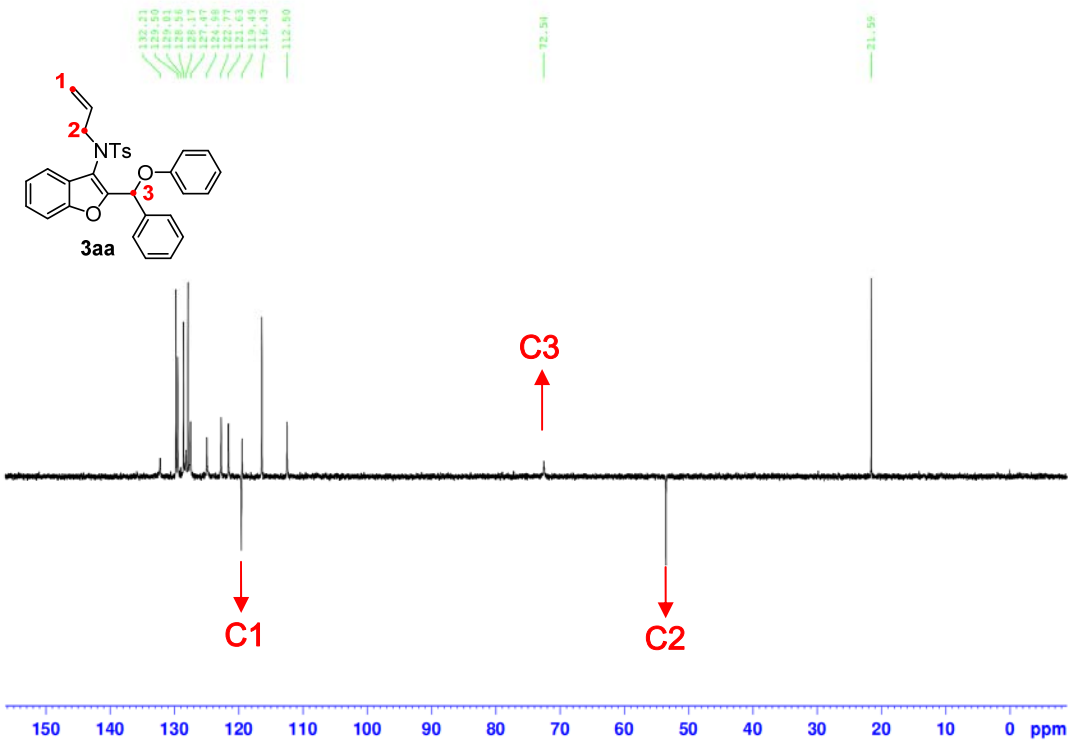
## 3. References


(1) a) H. Chen, X. Jia, Y. Yu, Q. Qian and H. Gong, *Angew. Chem. Int. Ed.*, 2017, **56**, 13103-13106. b) R. Trivedi and J. A. Tunge, *Org. Lett.*, 2009, **11**, 5650-5652.

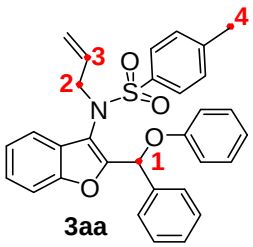
(2) R.-J. Yan, B.-X. Liu, B.-X. Xiao, W. Du, Y.-C. Chen, *Org. Lett.* 2020, **22**, 4240-4244.

## 4. $^{1}$H-$^{13}$C HSQC and DEPT-135 of 3aa



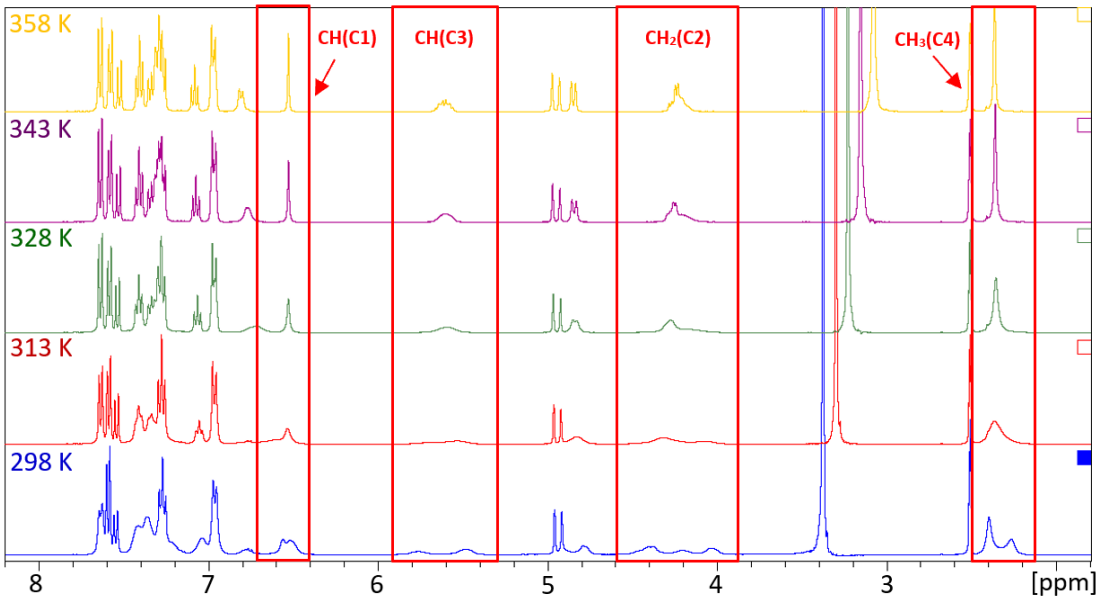



## 5. Variable Temperature $^{1}$H NMR Spectra of 3aa



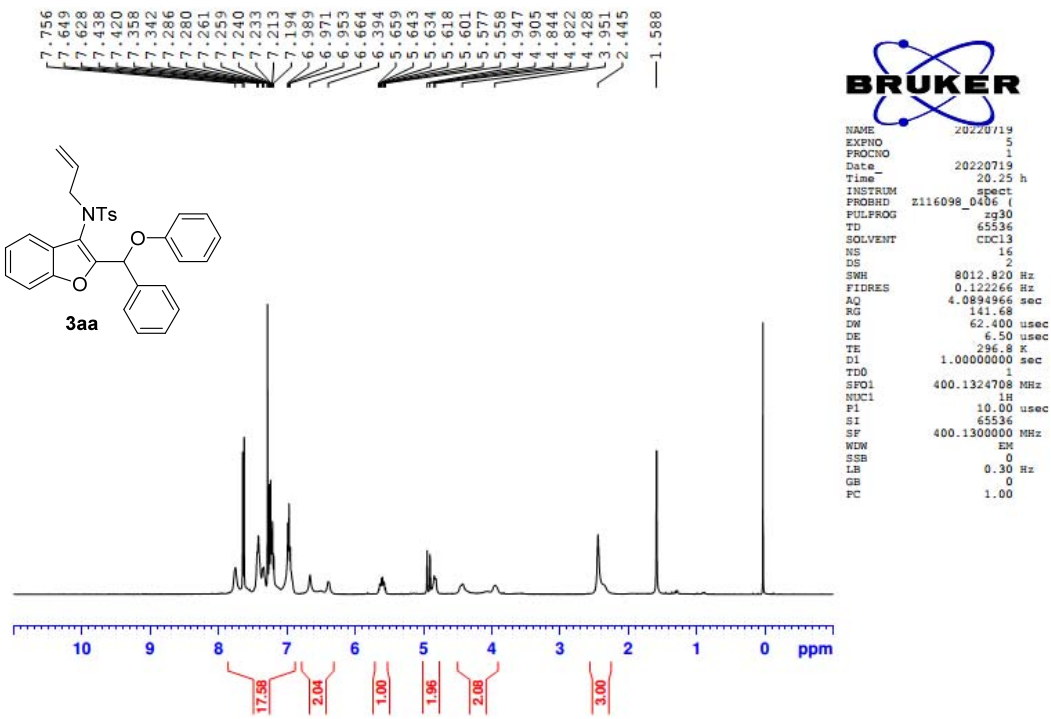

**3aa**

Solvent: DMSO-*d6*

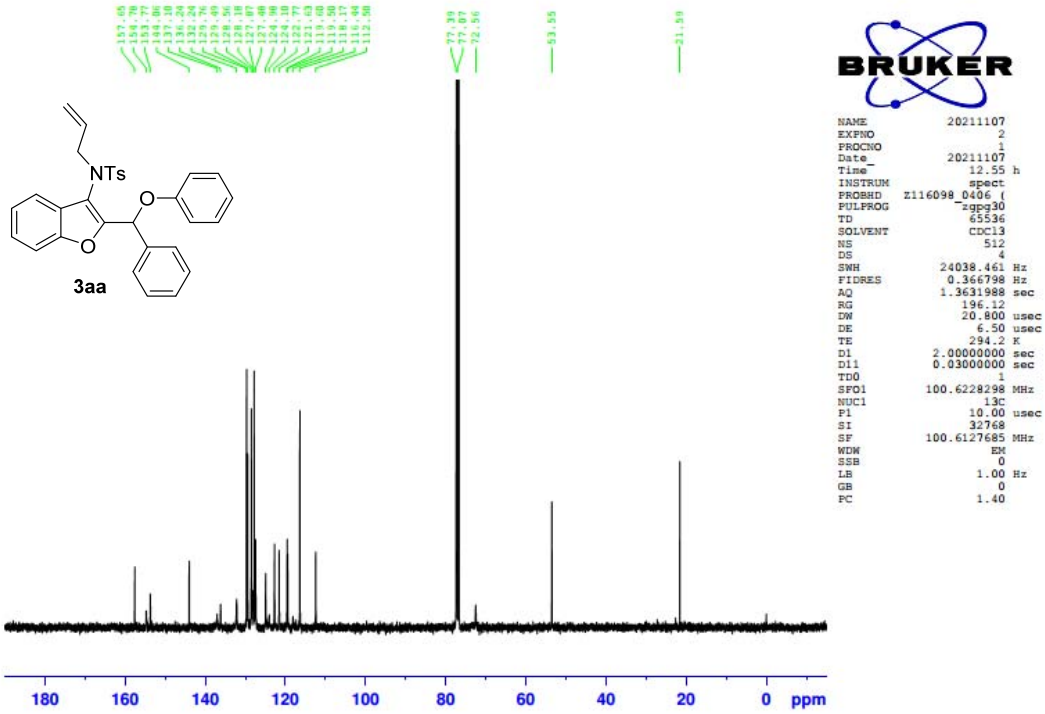


## 6. NMR Spectra of Products 3-5

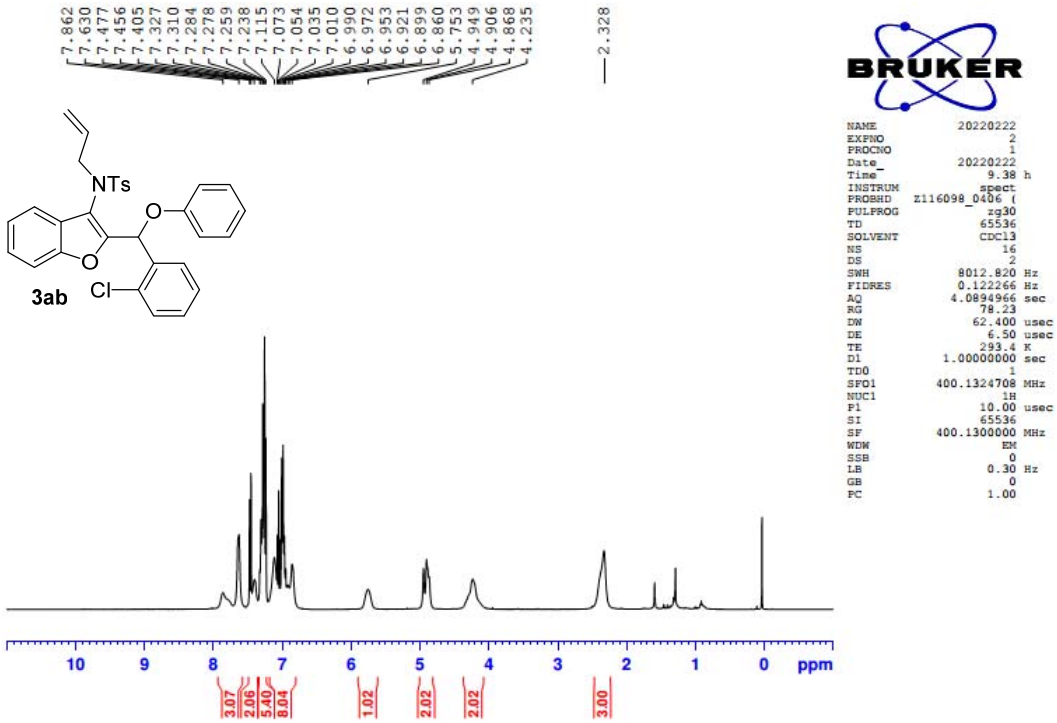
***N*-allyl-4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3aa):**



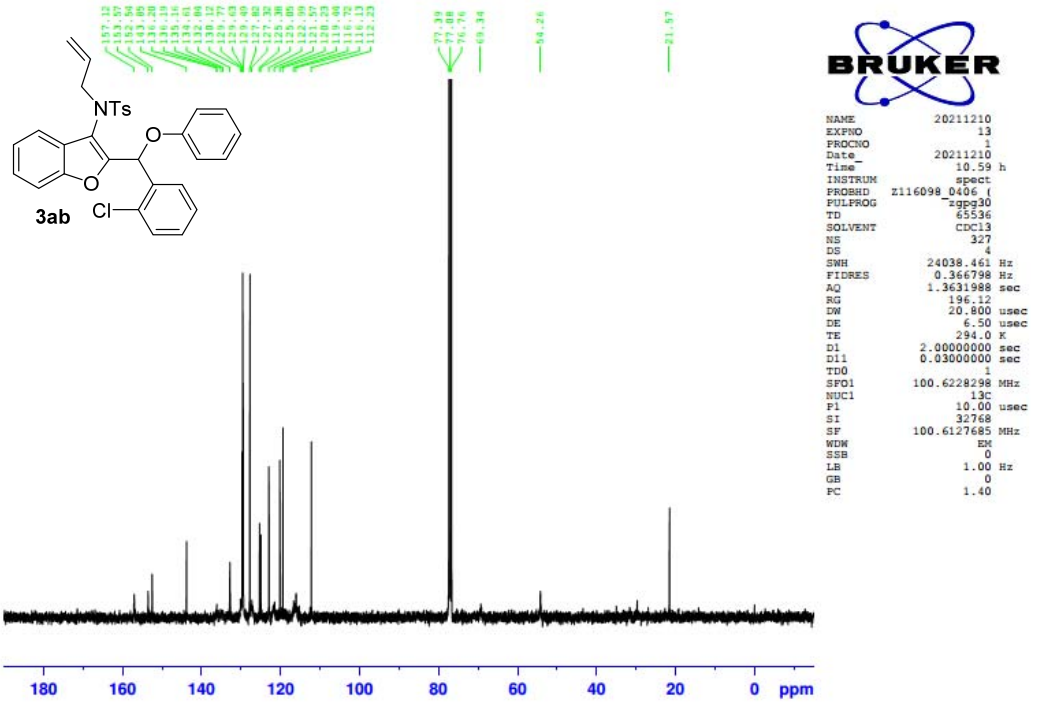

***N*-allyl-4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3aa):**



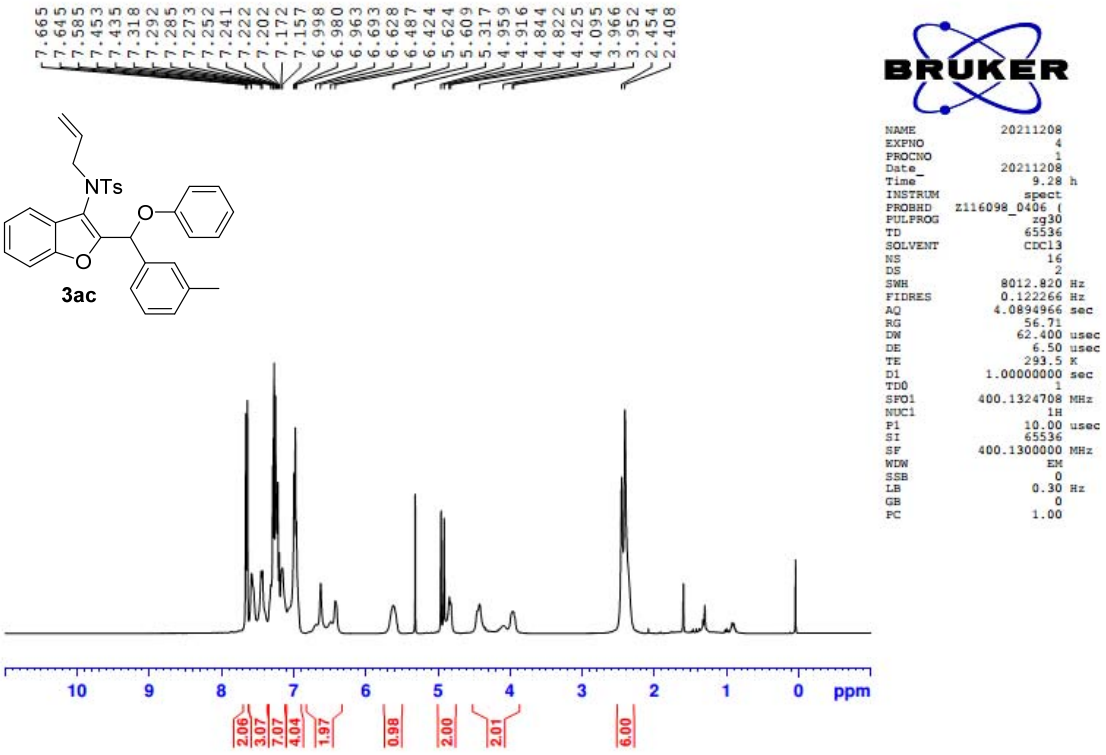
***N*-allyl-*N*-(2-((2-chlorophenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ab):**



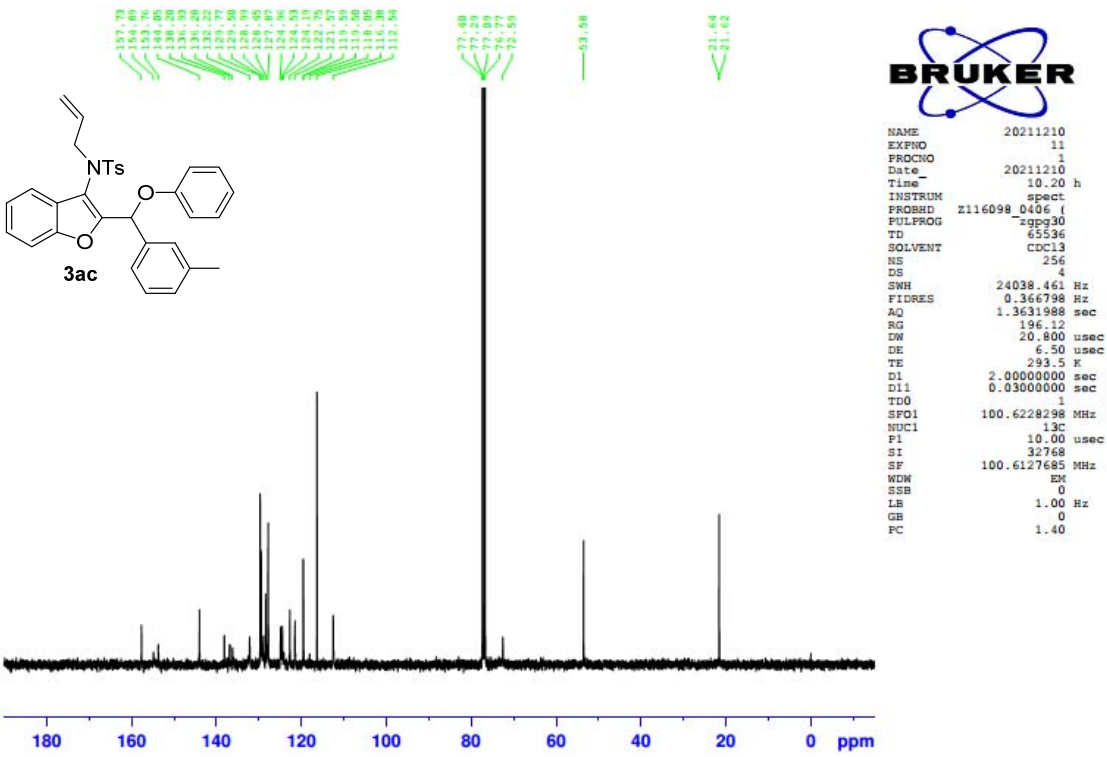

***N*-allyl-*N*-(2-((2-chlorophenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ab):**



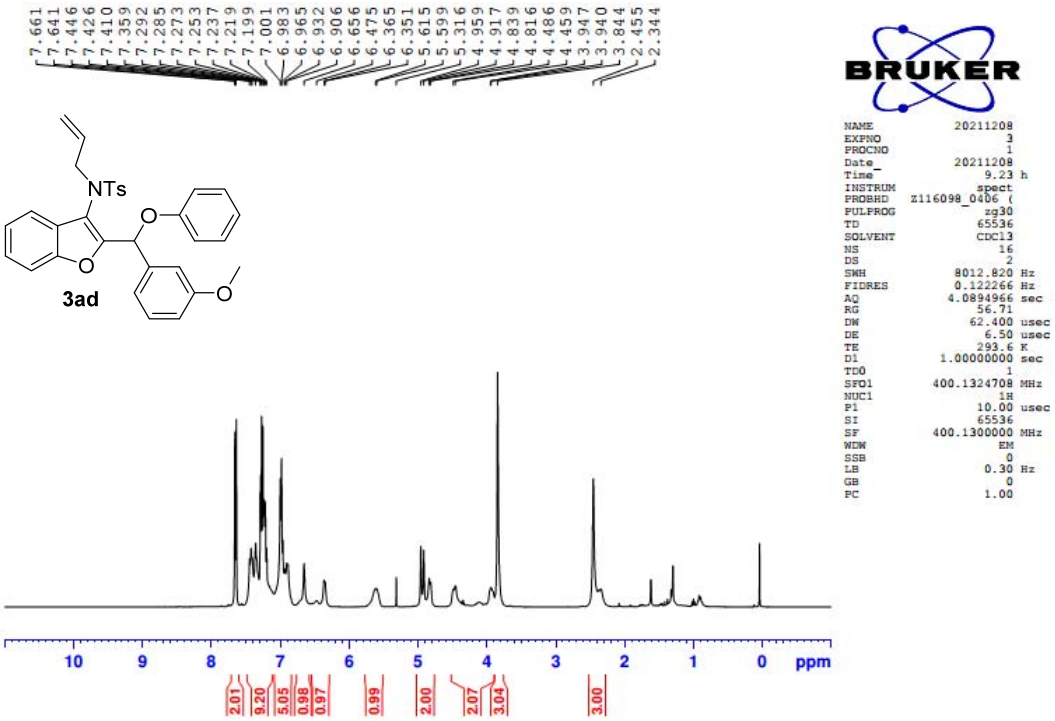
***N*-allyl-4-methyl-*N*-(2-(phenoxy(m-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ac):**



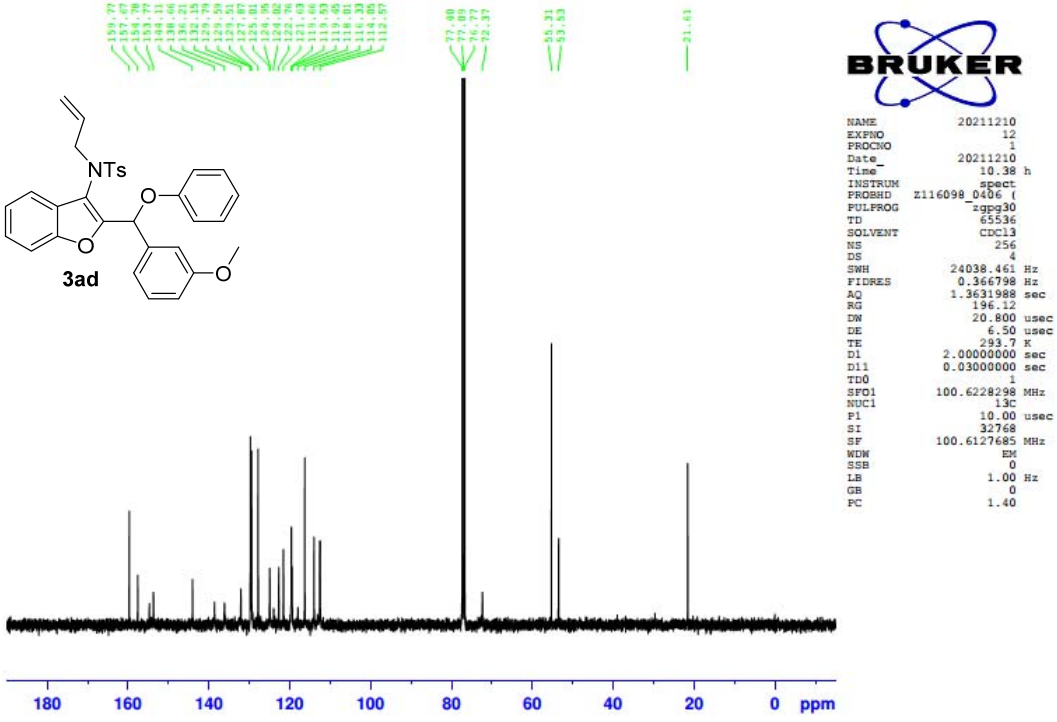

***N*-allyl-4-methyl-*N*-(2-(phenoxy(m-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ac):**



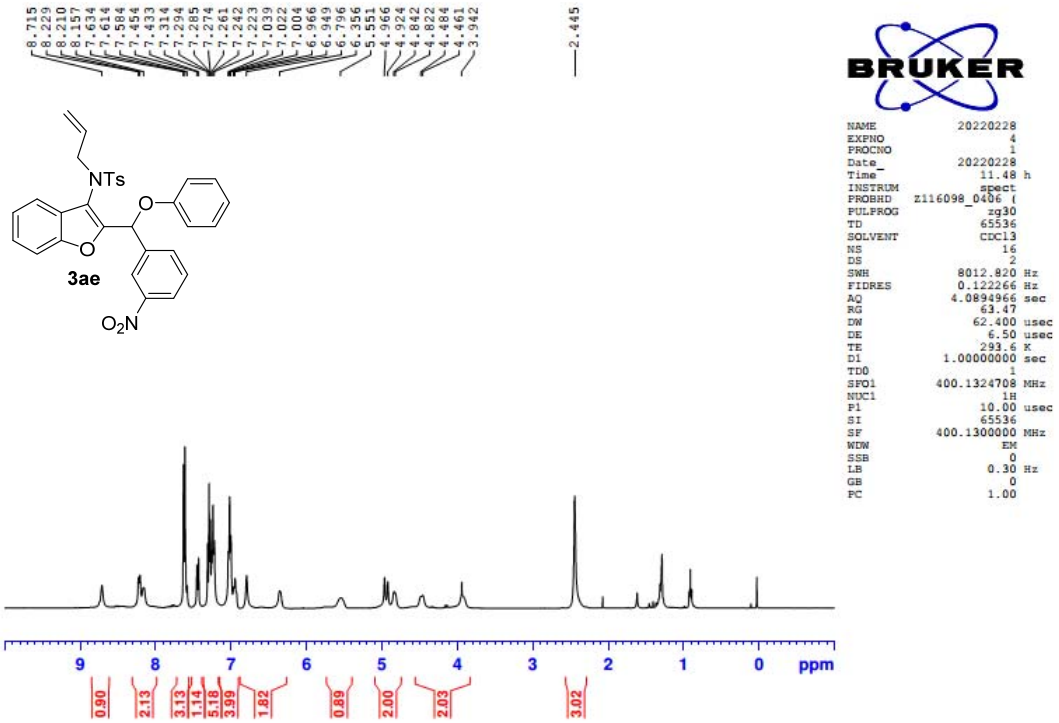
***N*-allyl-*N*-(2-((3-methoxyphenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ad):**



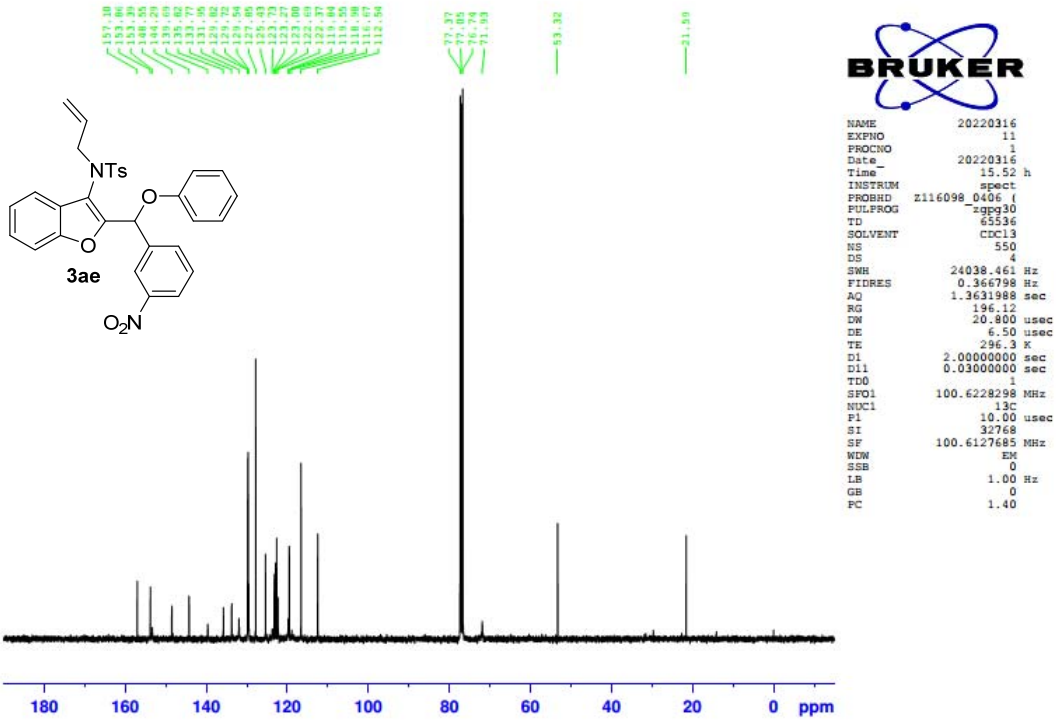

***N*-allyl-*N*-(2-((3-methoxyphenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ad):**



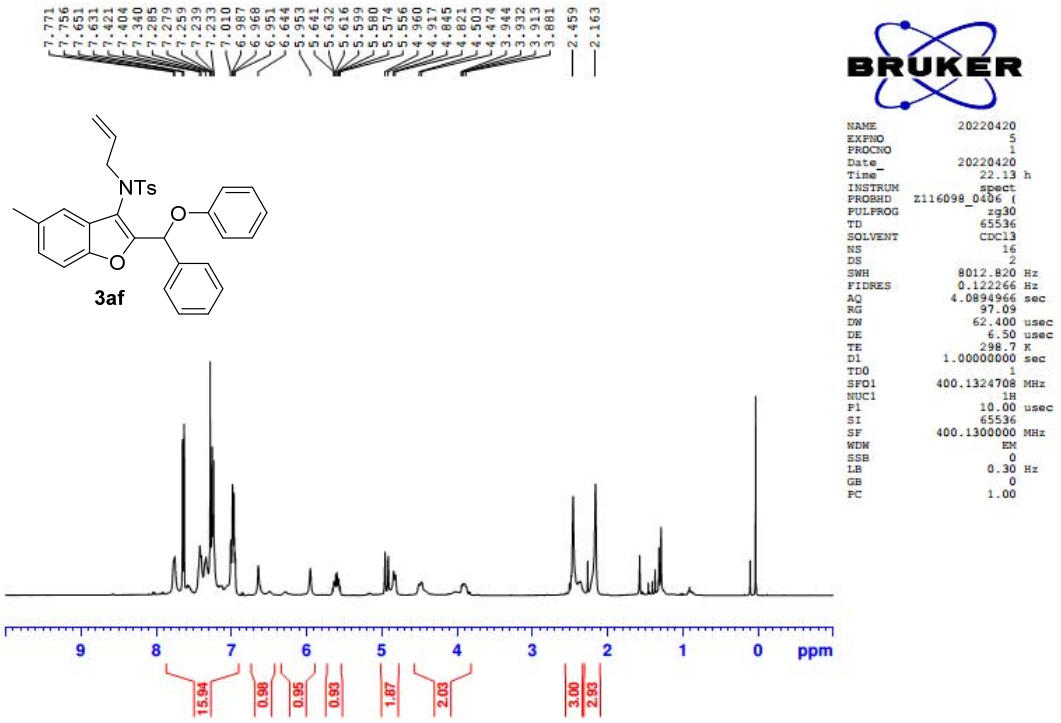
***N*-allyl-4-methyl-*N*-(2-((3-nitrophenyl)(phenoxy)methyl)benzofuran-3-yl)benzenesulfonamide (3ae):**



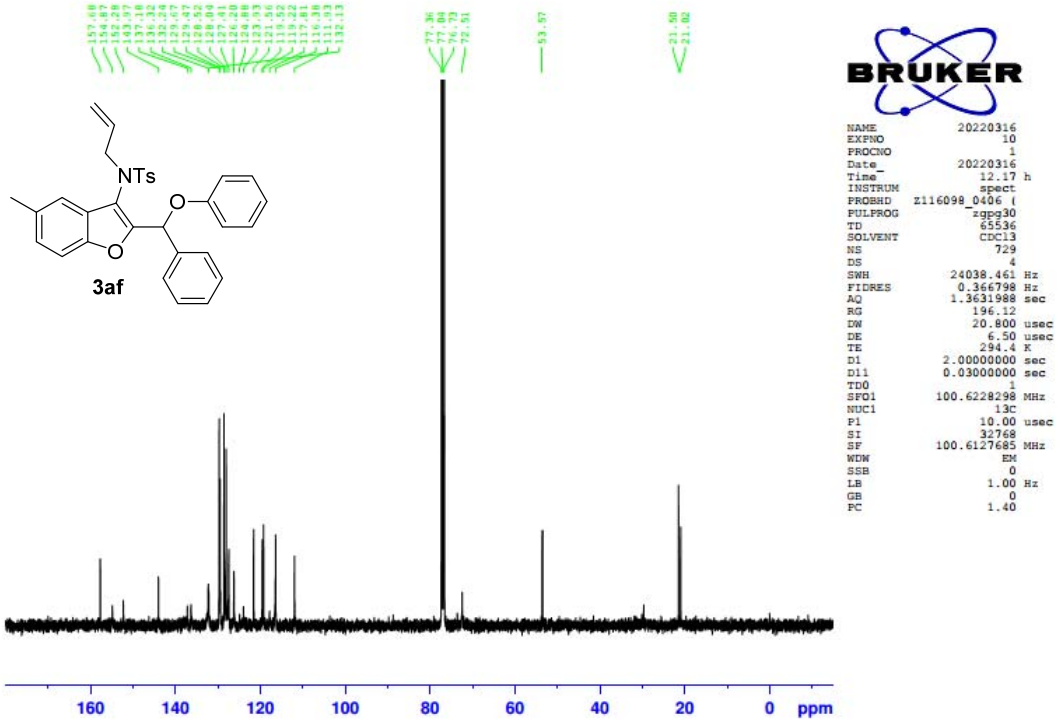

***N*-allyl-4-methyl-*N*-(2-((3-nitrophenyl)(phenoxy)methyl)benzofuran-3-yl)benzenesulfonamide (3ae):**



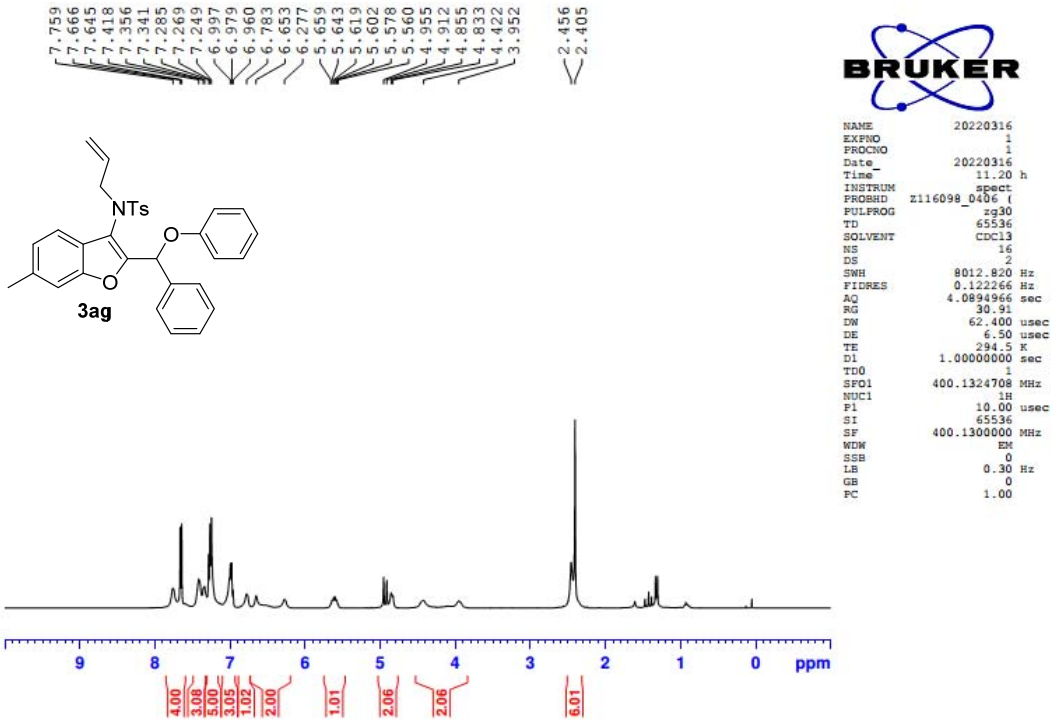
***N*-allyl-4-methyl-*N*-(5-methyl-2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3af):**



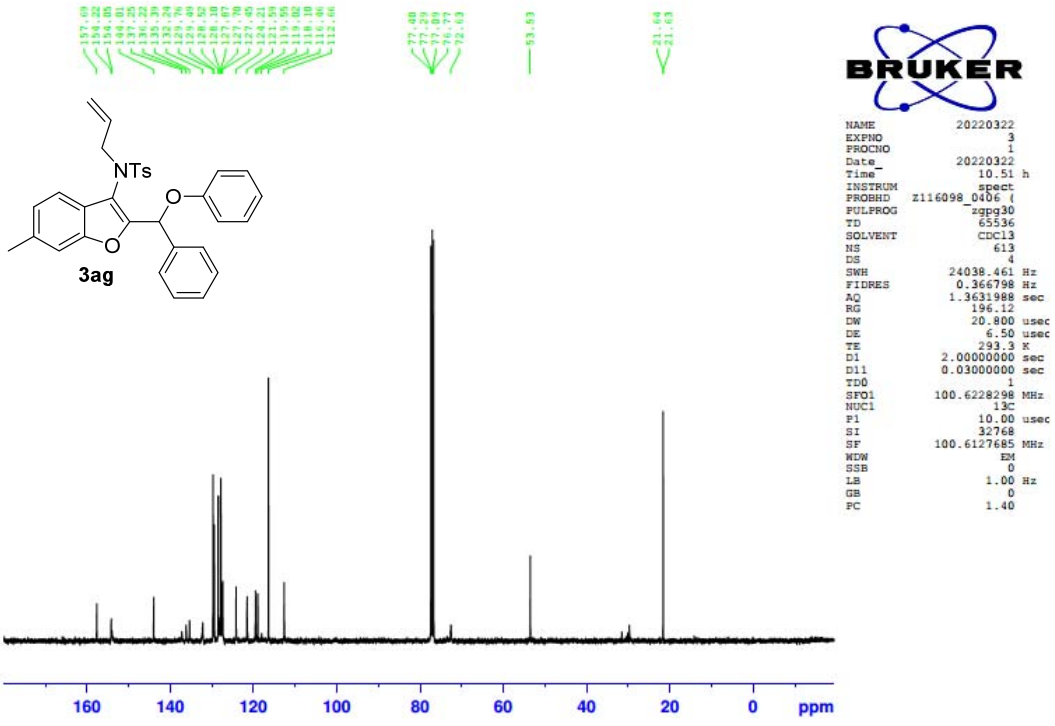

***N*-allyl-4-methyl-*N*-(5-methyl-2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3af):**



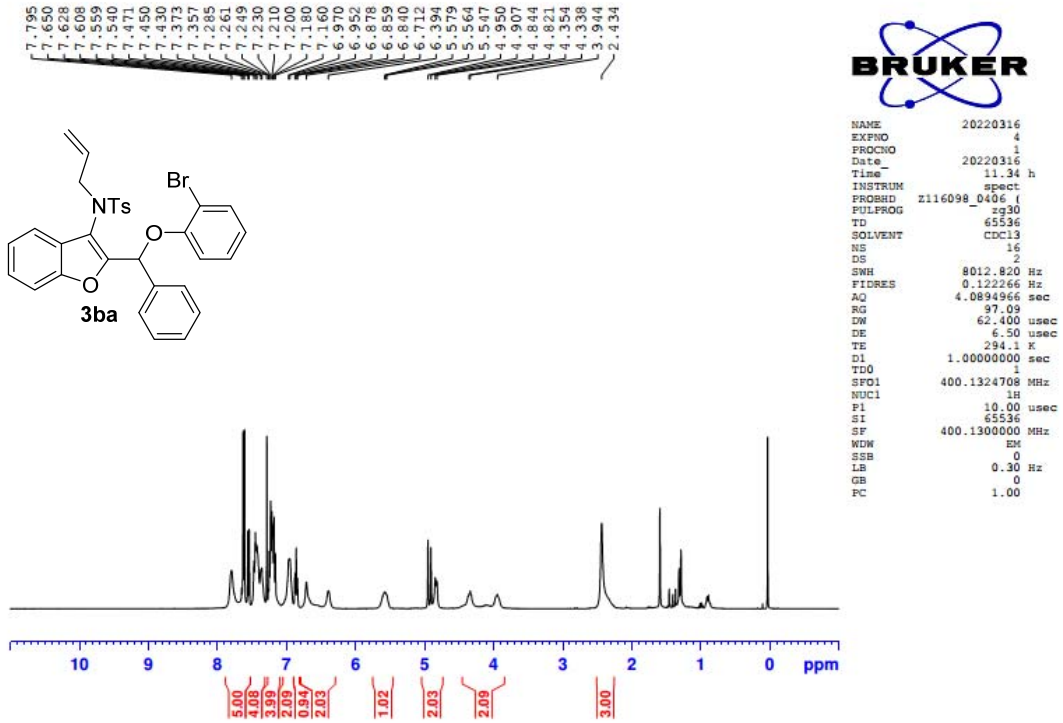
***N*-allyl-4-methyl-*N*-(6-methyl-2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ag):**



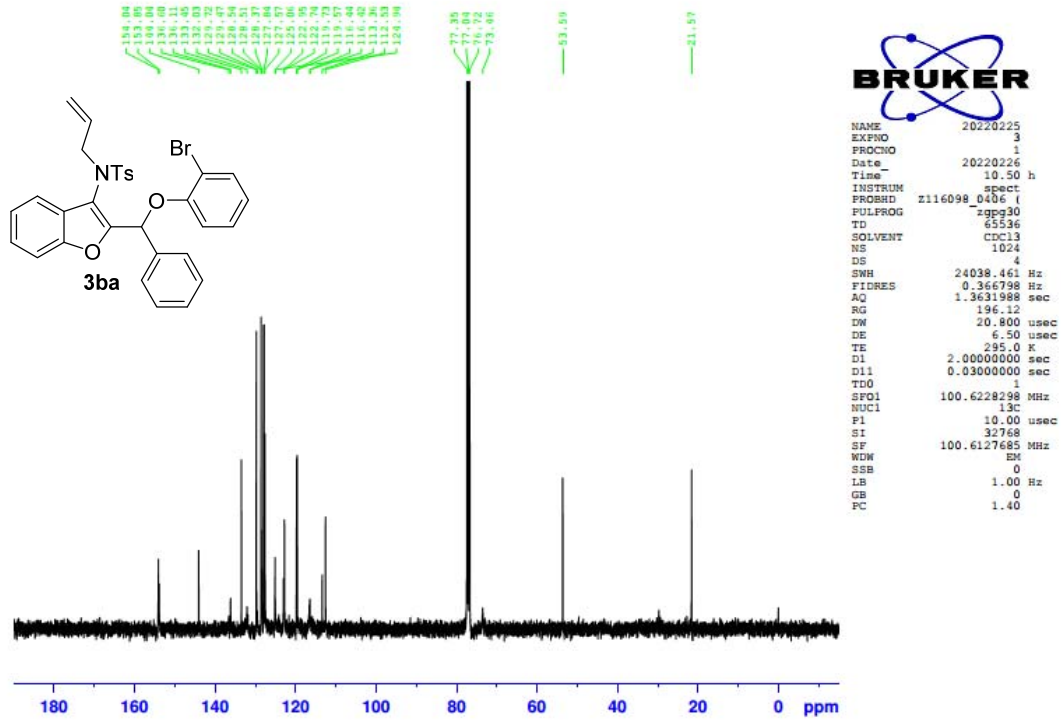

***N*-allyl-4-methyl-*N*-(6-methyl-2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ag):**



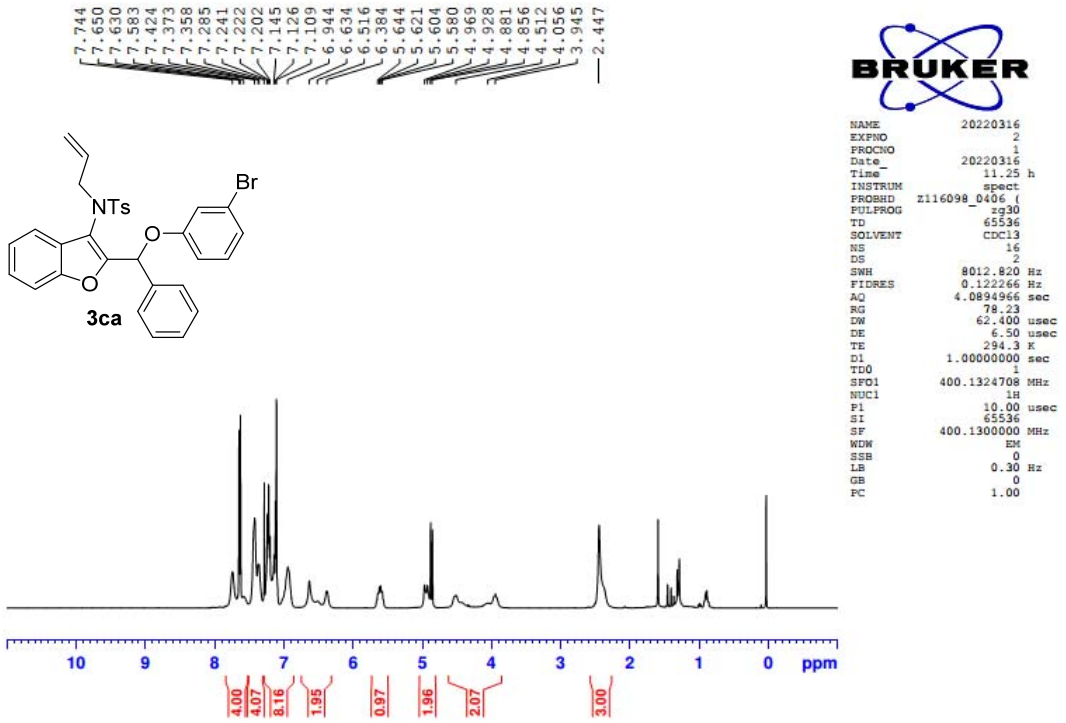
***N*-allyl-*N*-(2-((2-bromophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ba):**



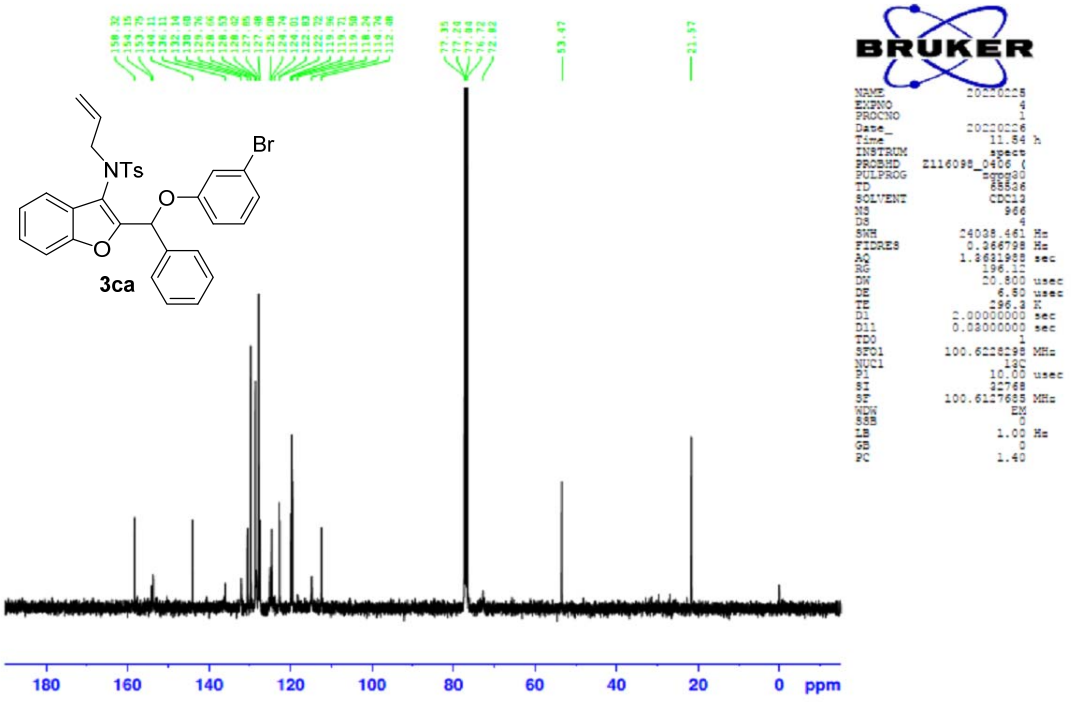

***N*-allyl-*N*-(2-((2-bromophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ba):**



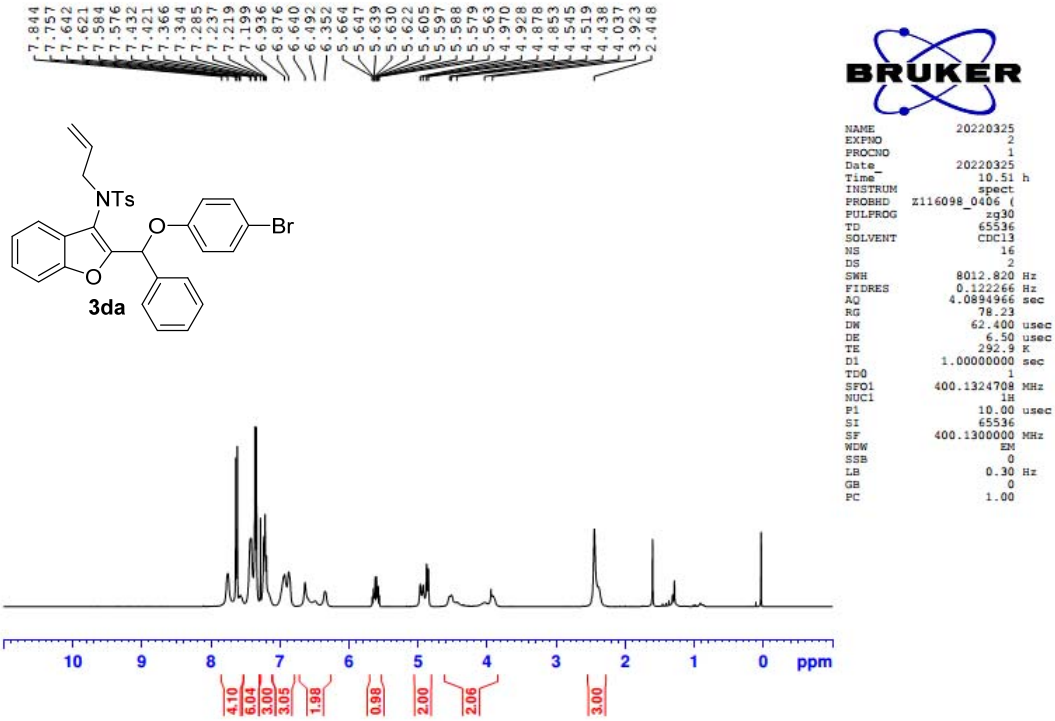
***N*-allyl-*N*-(2-((3-bromophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ca):**




***N*-allyl-*N*-(2-((3-bromophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ca):**



***N*-allyl-*N*-(2-((4-bromophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3da):**

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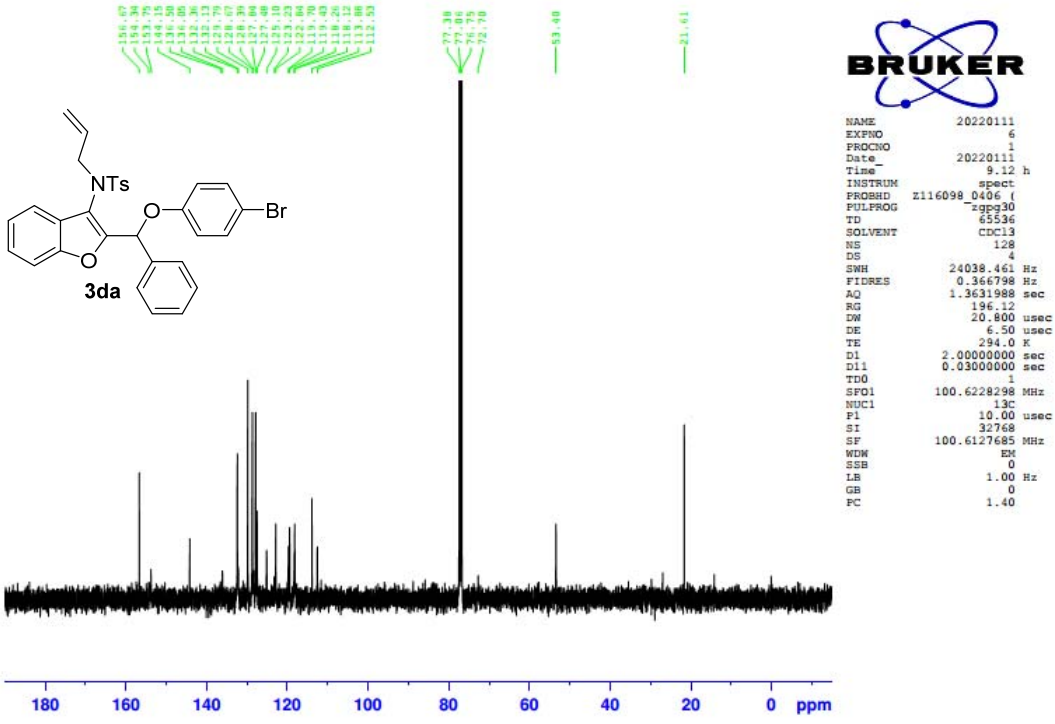
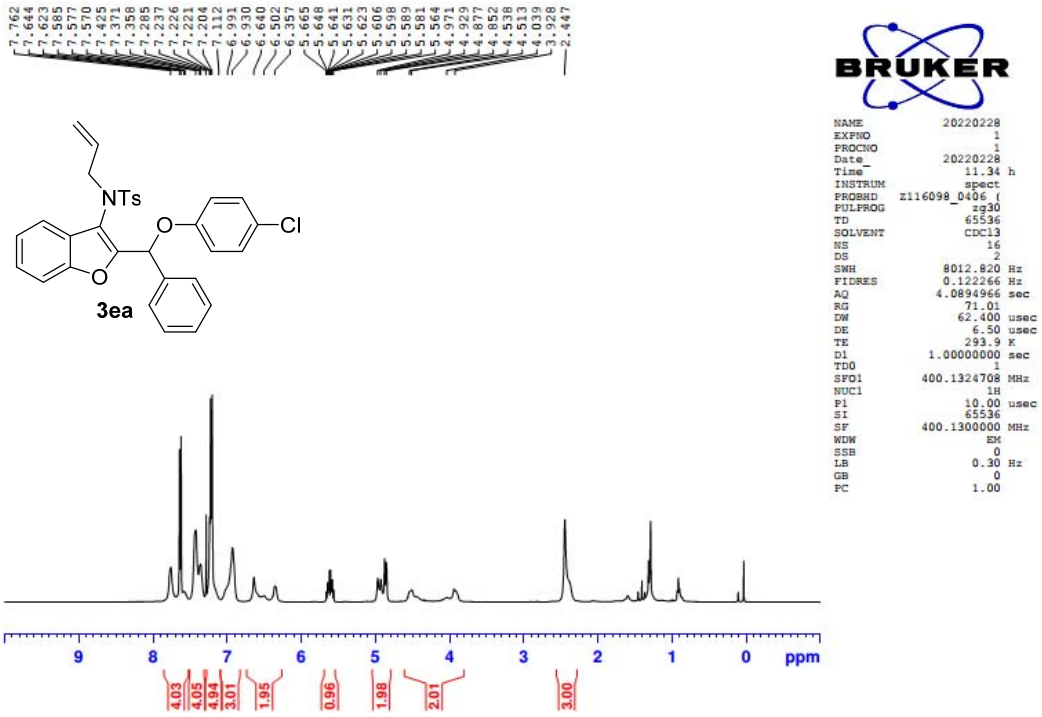
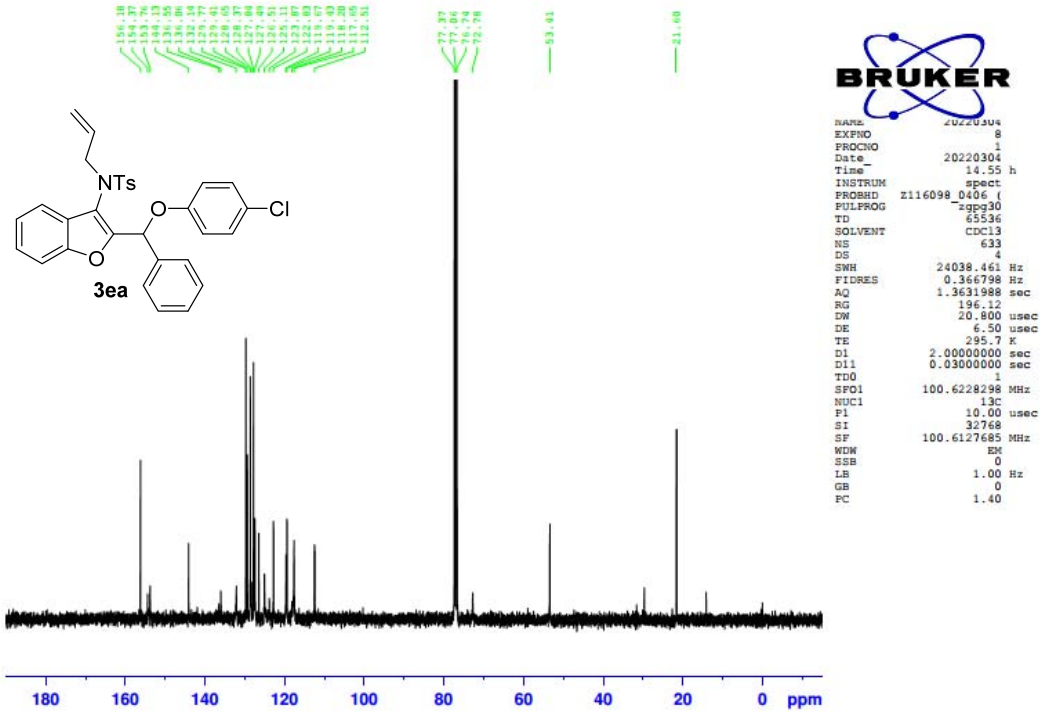


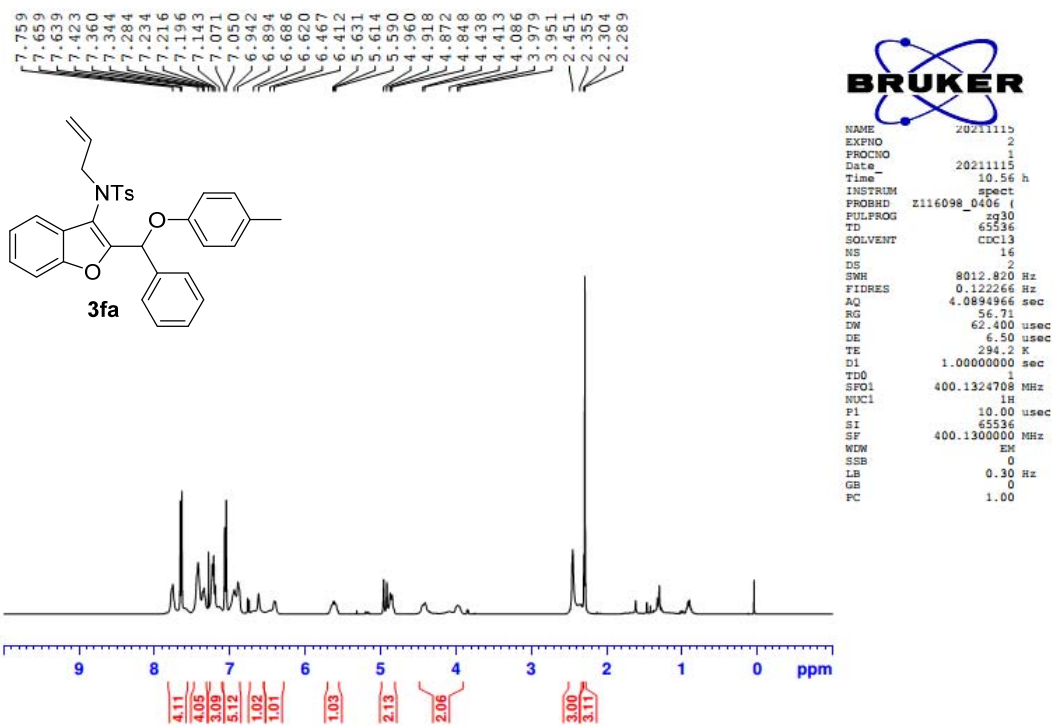
***N*-allyl-*N*-(2-((4-chlorophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ea):**



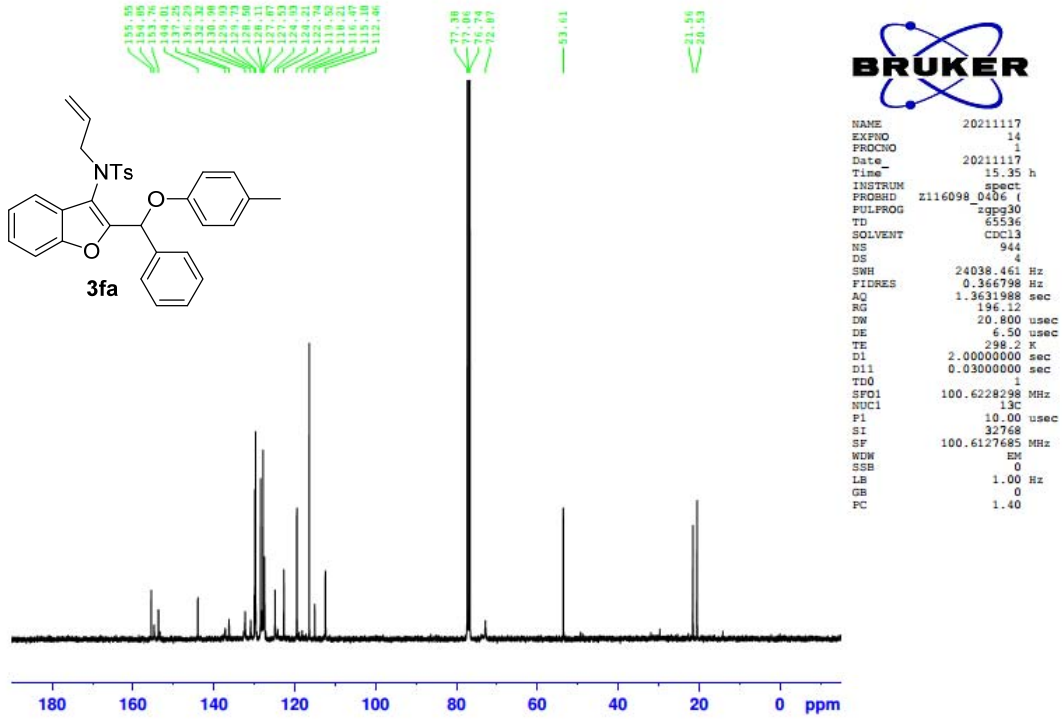

***N*-allyl-*N*-(2-((4-chlorophenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ea):**



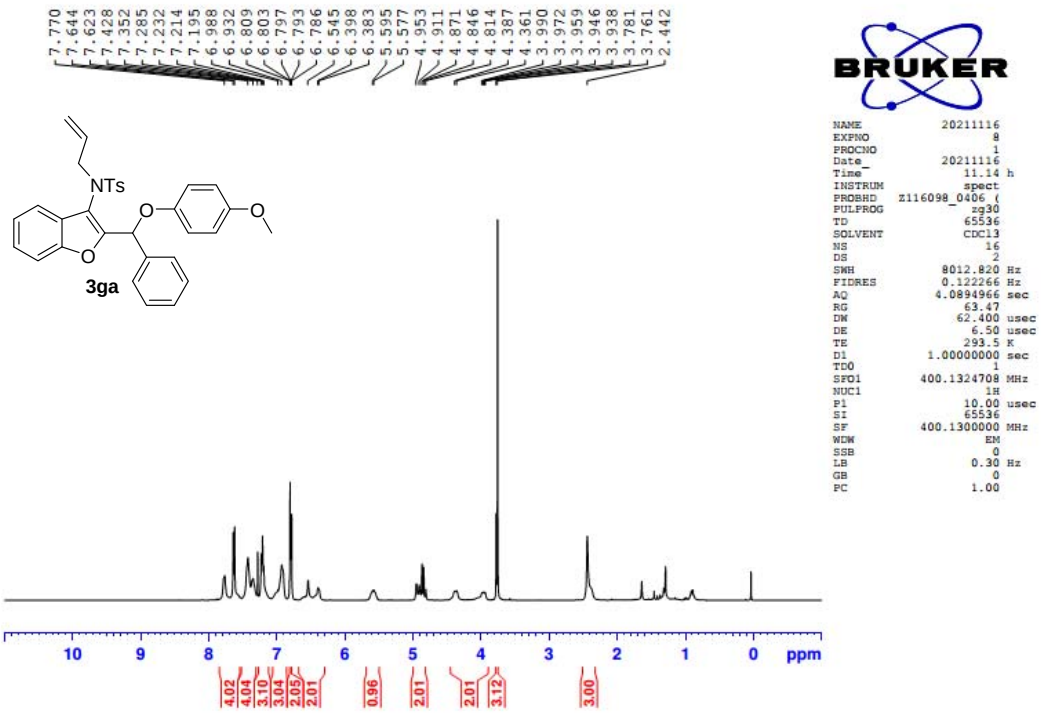
***N*-allyl-4-methyl-*N*-(2-(phenyl(p-tolyloxy)methyl)benzofuran-3-yl)benzenesulfonamide (3fa):**



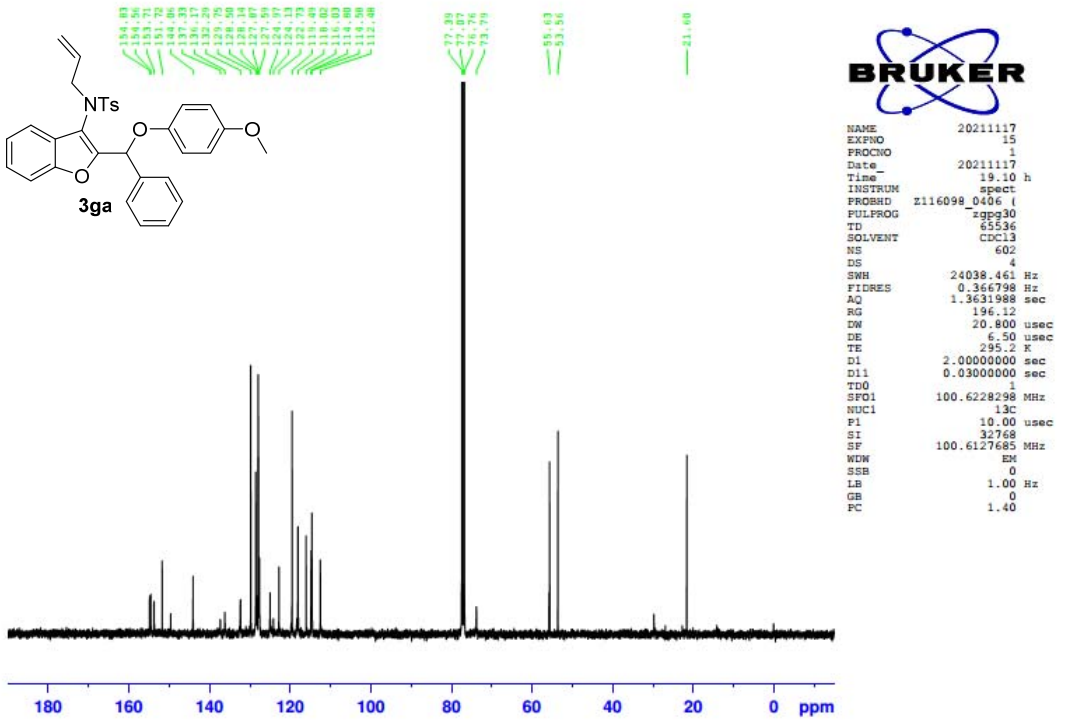

***N*-allyl-4-methyl-*N*-(2-(phenyl(p-tolyloxy)methyl)benzofuran-3-yl)benzenesulfonamide (3fa):**



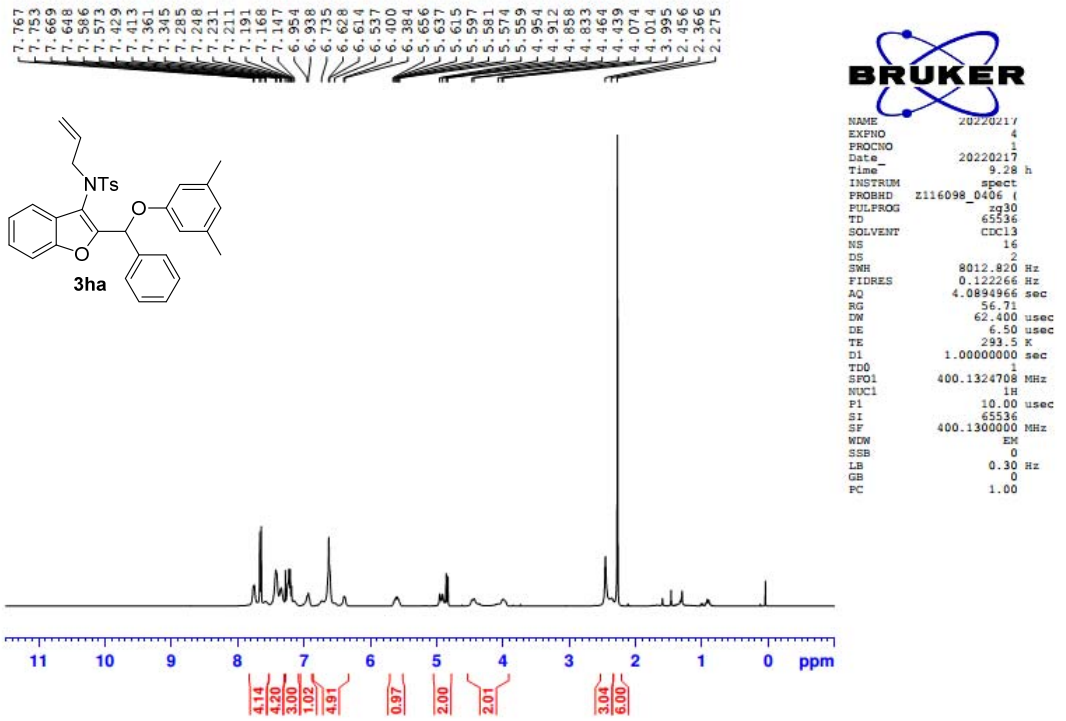
***N*-allyl-*N*-(2-((4-methoxyphenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ga):**



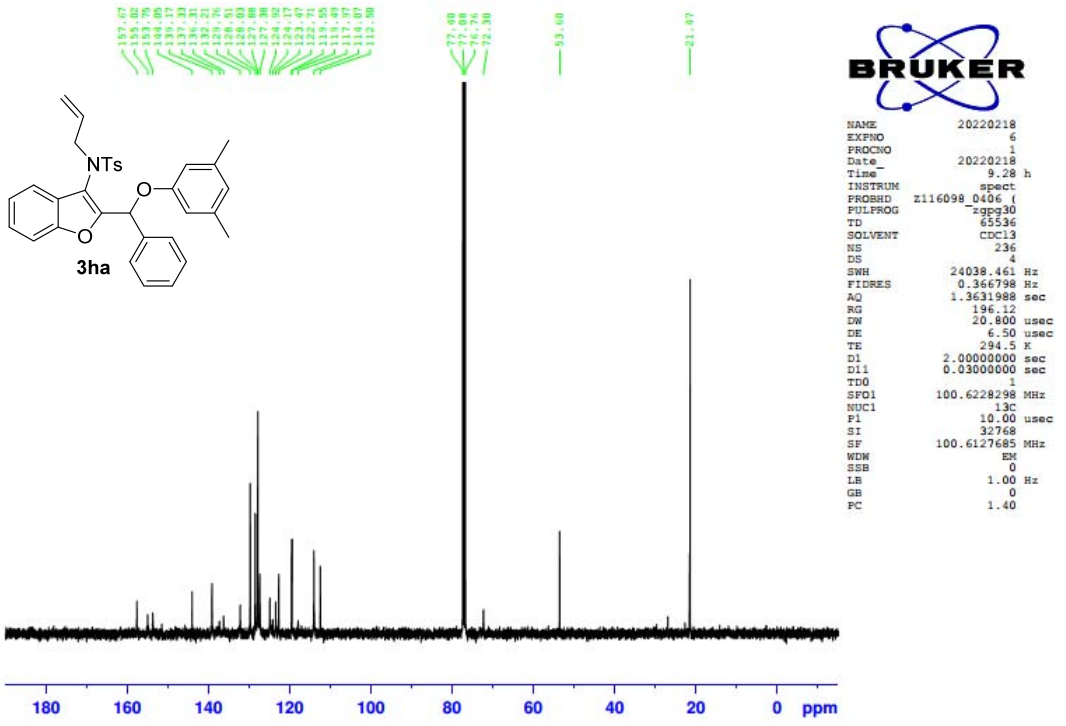

***N*-allyl-*N*-(2-((4-methoxyphenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ga):**



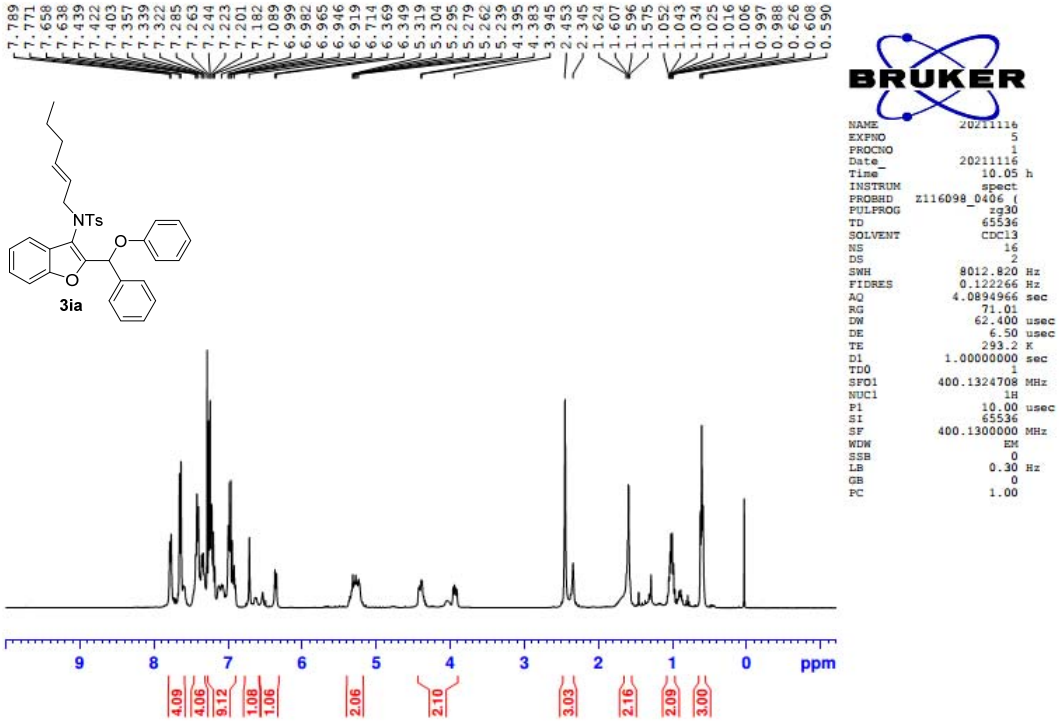
***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzene-sulfonamide (3ha):**



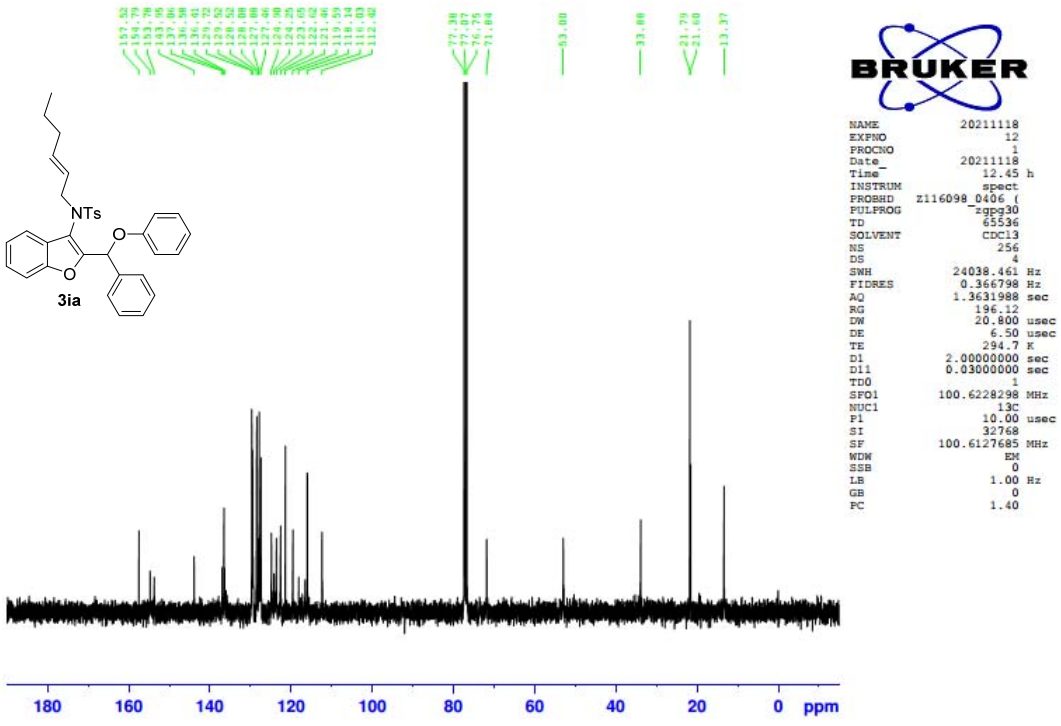

***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzene-sulfonamide (3ha):**



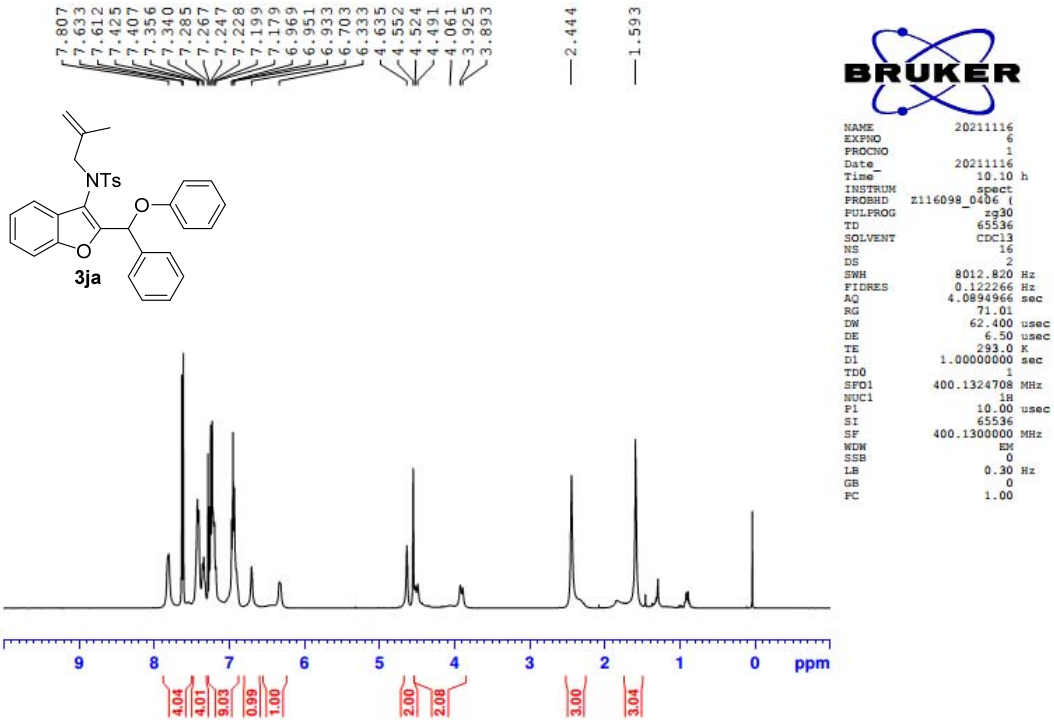
***(E)*-*N*-(hex-2-en-1-yl)-4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ia):**




***(E)*-*N*-(hex-2-en-1-yl)-4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ia):**



**4-methyl-*N*-(2-methylallyl)-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ja):**

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DE                 6.50 usec
TE                293.0 K
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TD0                    1
SFO1           400.1324708 MHz
NUC1                  1H
P1                10.00 usec
SI                 65536
SF             400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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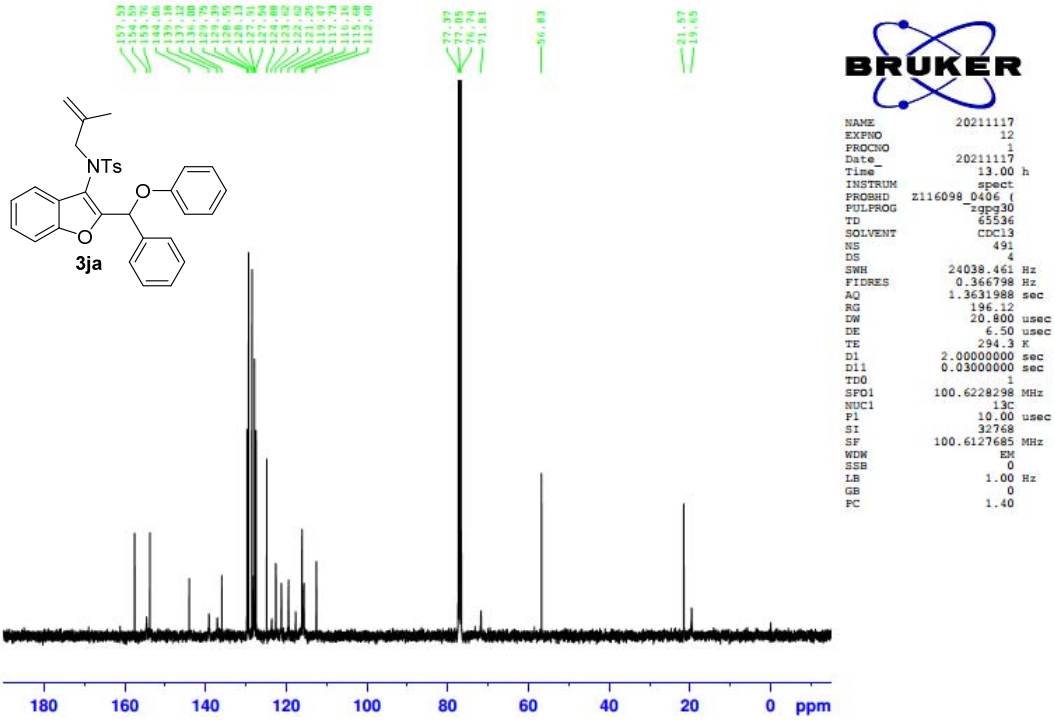
**4-methyl-*N*-(2-methylallyl)-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ja):**

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DE                 6.50 usec
TE                294.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           100.6228298 MHz
NUC1                  13C
P1                10.00 usec
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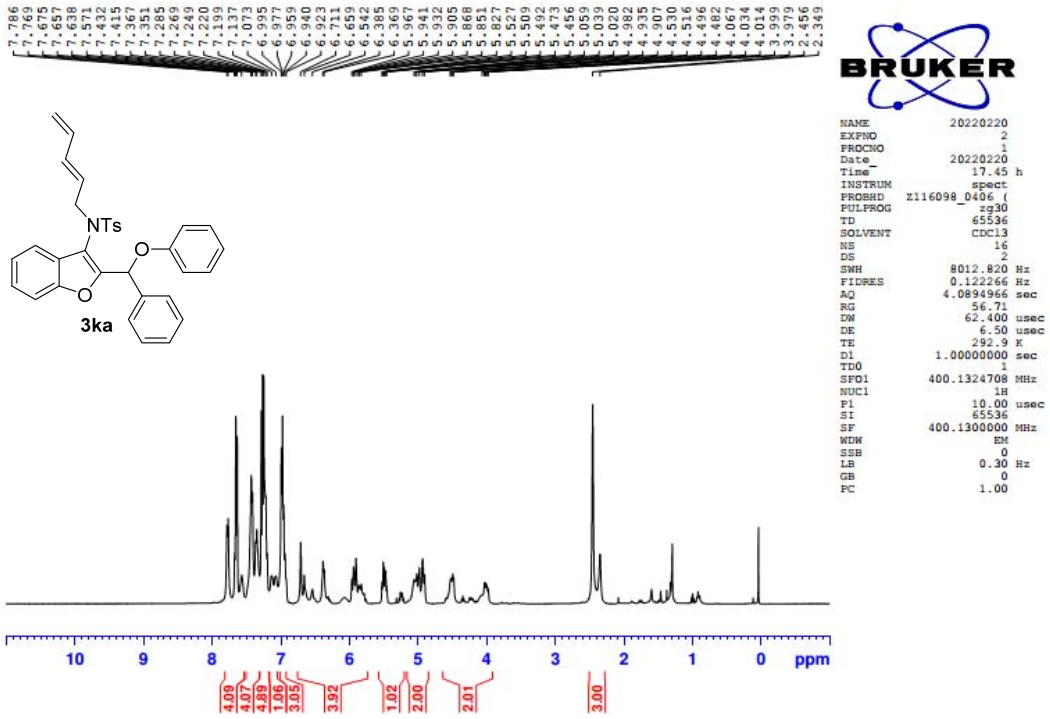
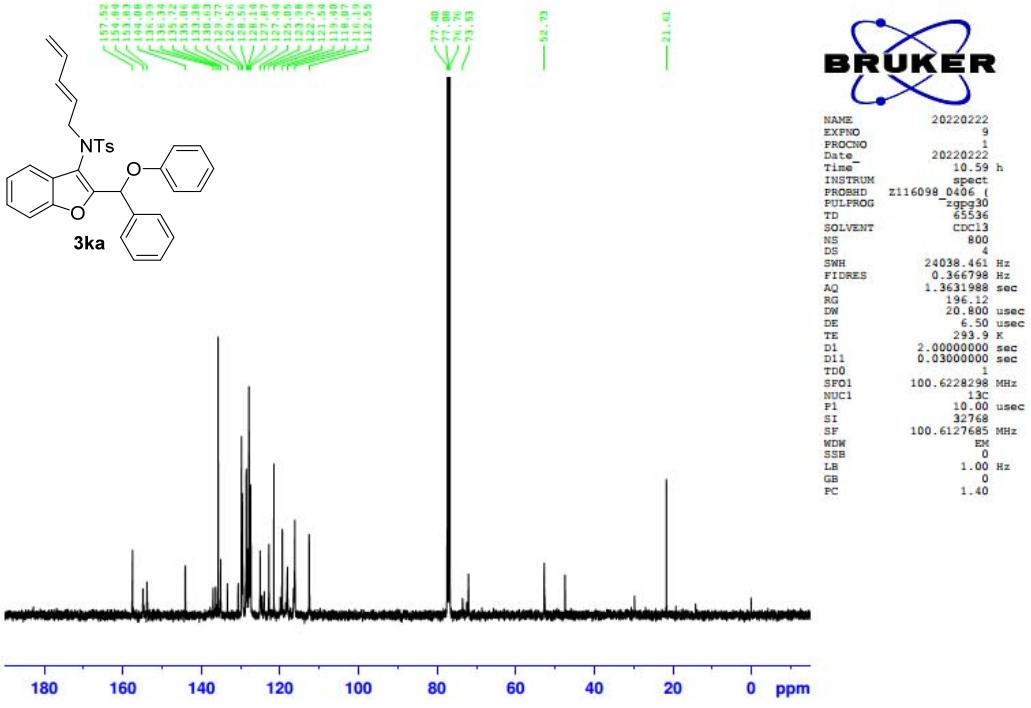
SF             100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

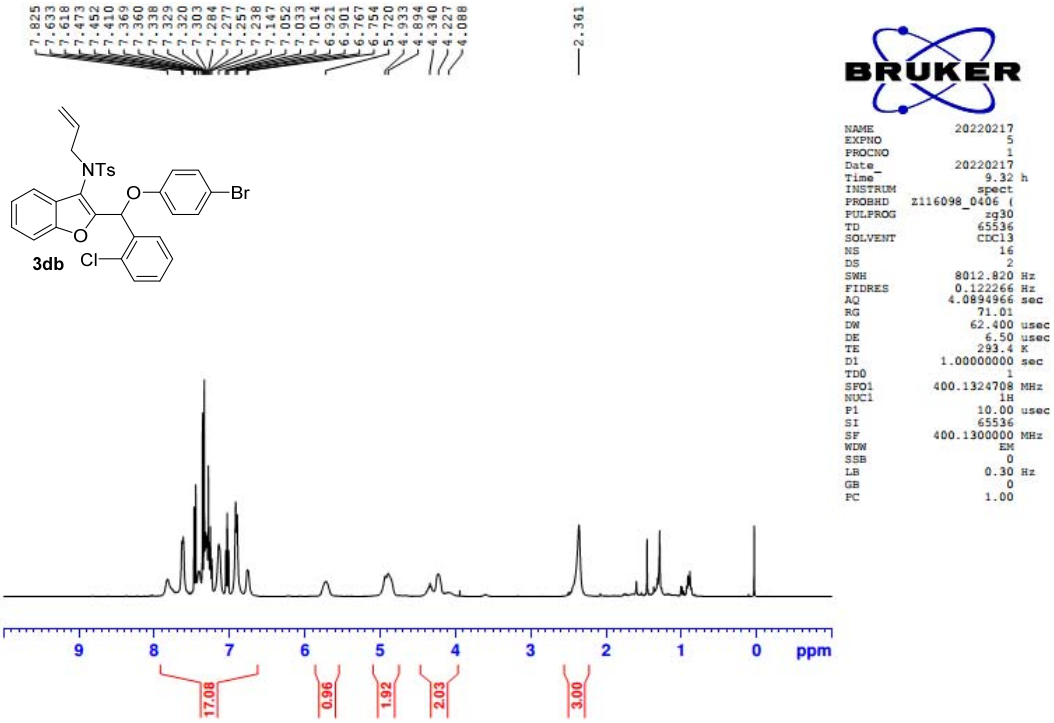
***(E)*-4-methyl-*N*-(penta-2,4-dien-1-yl)-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzene sulfonamide (3ka):**



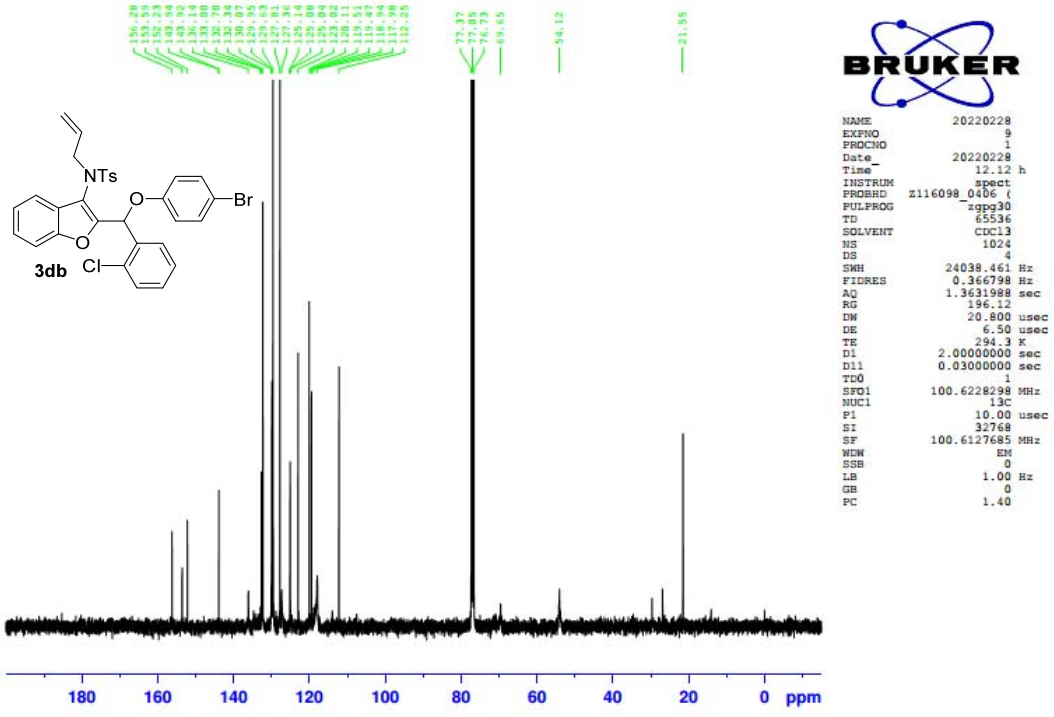

***(E)*-4-methyl-*N*-(penta-2,4-dien-1-yl)-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)benzene sulfonamide (3ka):**



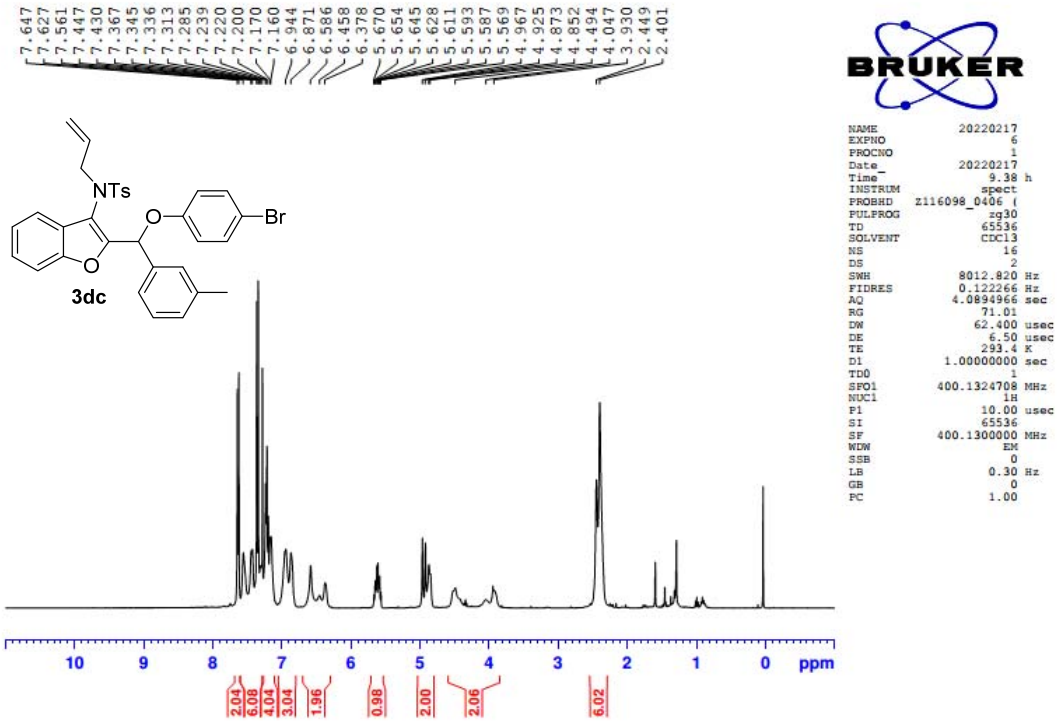
***N*-allyl-*N*-(2-((4-bromophenoxy)(2-chlorophenyl)methyl)benzofuran-3-yl)-4-methylbenzenesul fonamide (3db):**



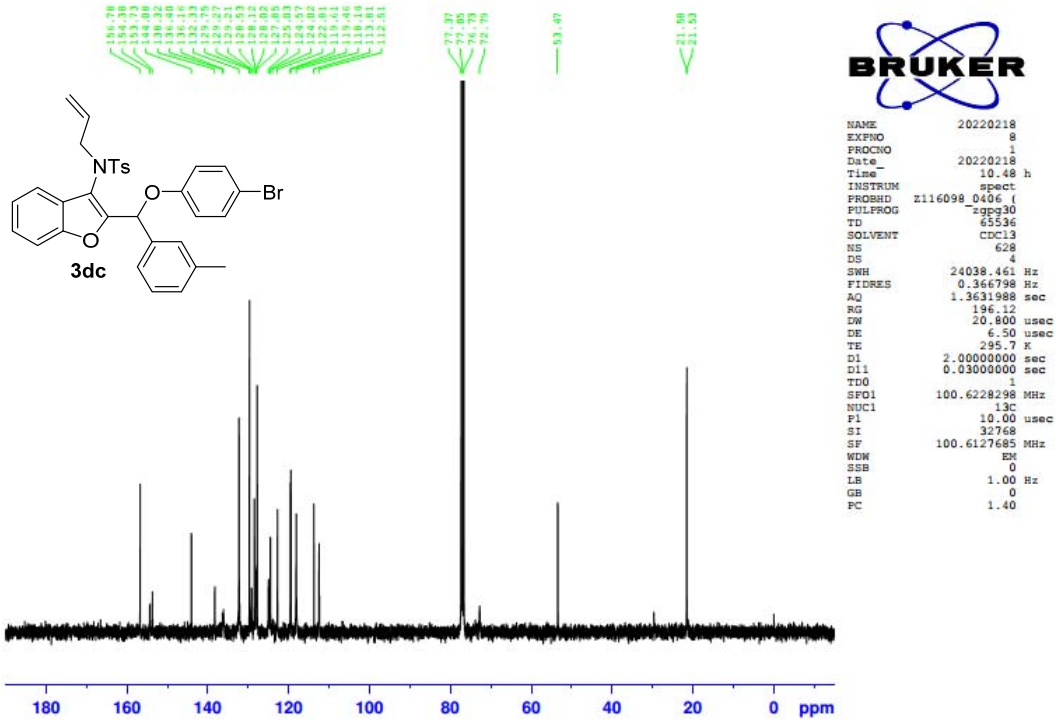

***N*-allyl-*N*-(2-((4-bromophenoxy)(2-chlorophenyl)methyl)benzofuran-3-yl)-4-methylbenzenesul fonamide (3db):**



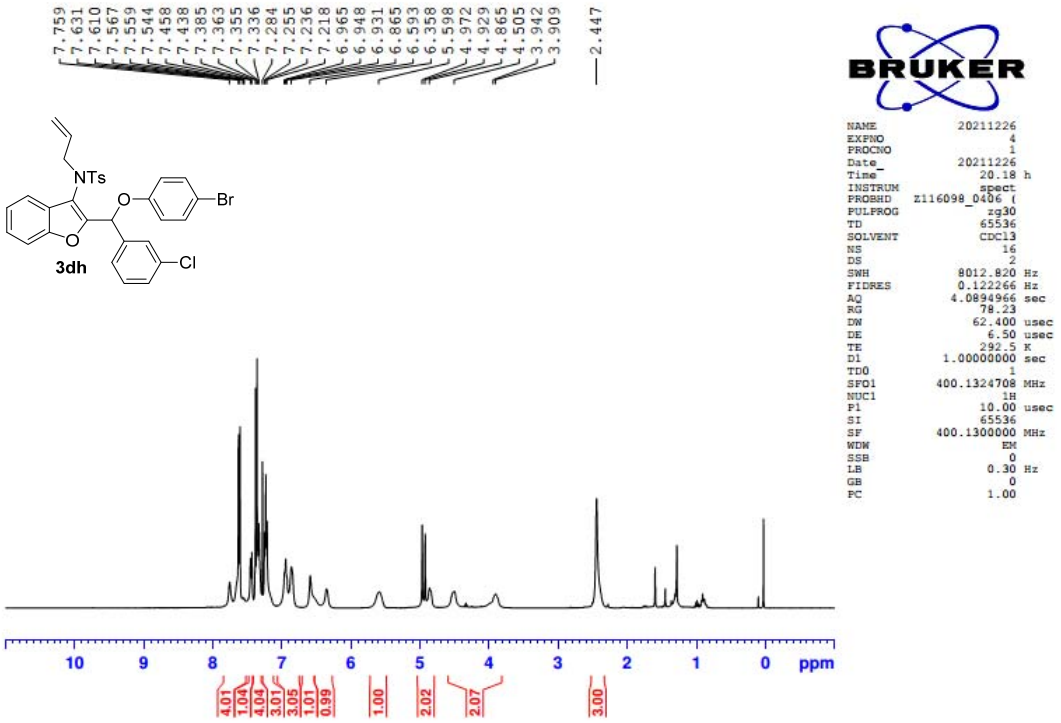
***N*-allyl-*N*-(2-((4-bromophenoxy)(m-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3dc):**



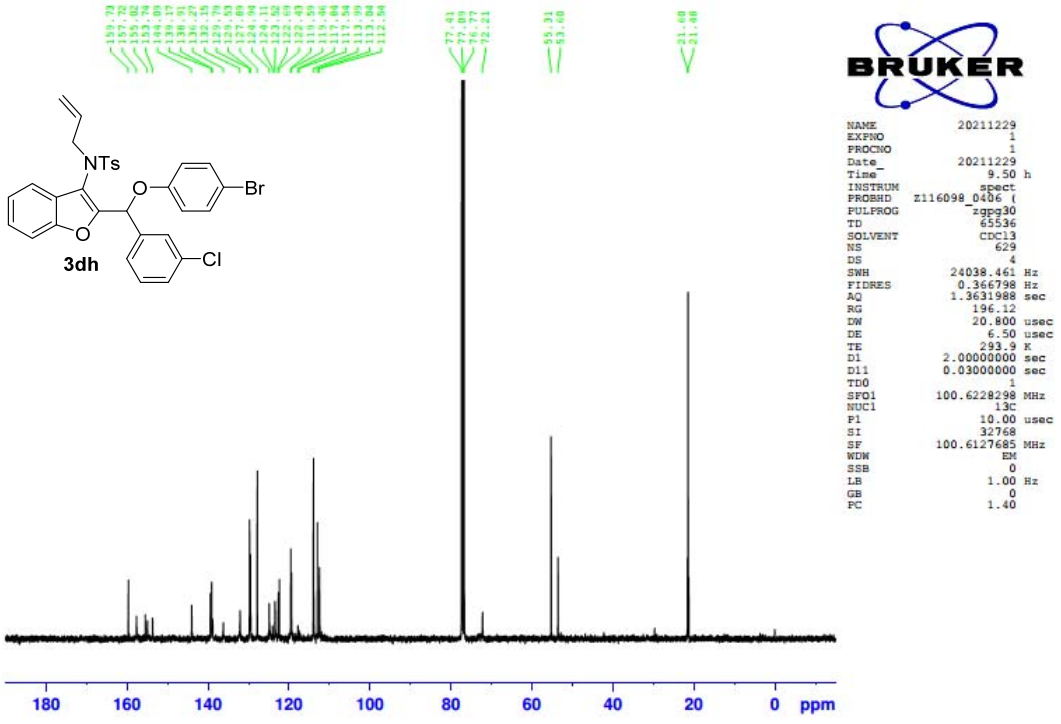

***N*-allyl-*N*-(2-((4-bromophenoxy)(m-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3dc):**



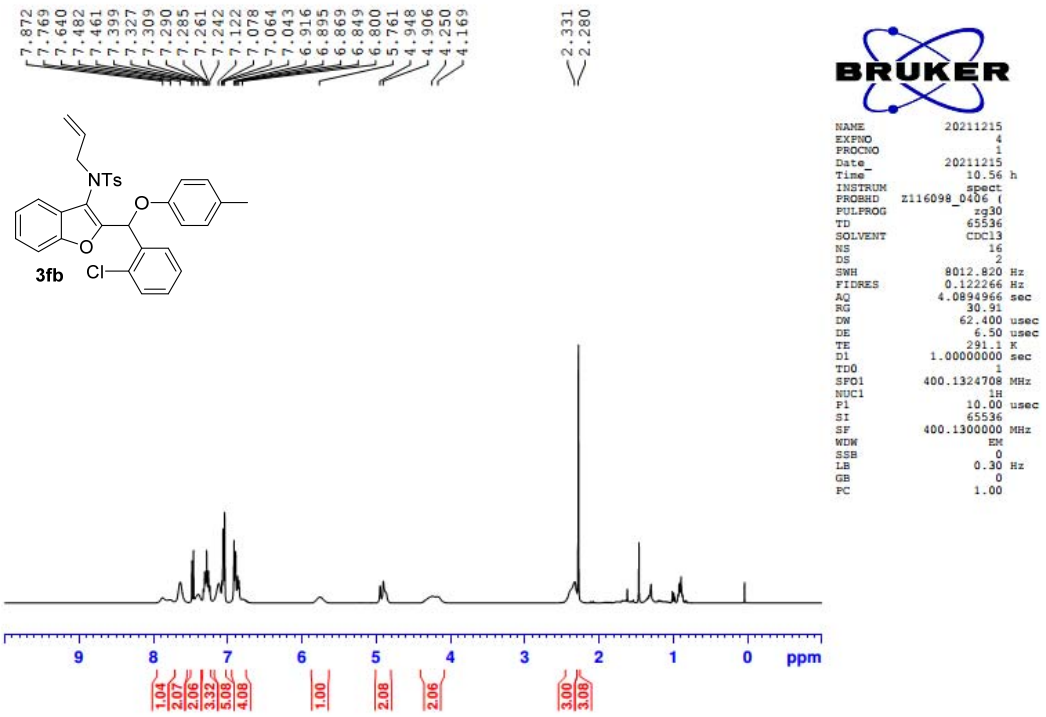
***N*-allyl-*N*-(2-((4-bromophenoxy)(3-chlorophenyl)methyl)benzofuran-3-yl)-4-methylbenzene sulfonamide (3dh):**



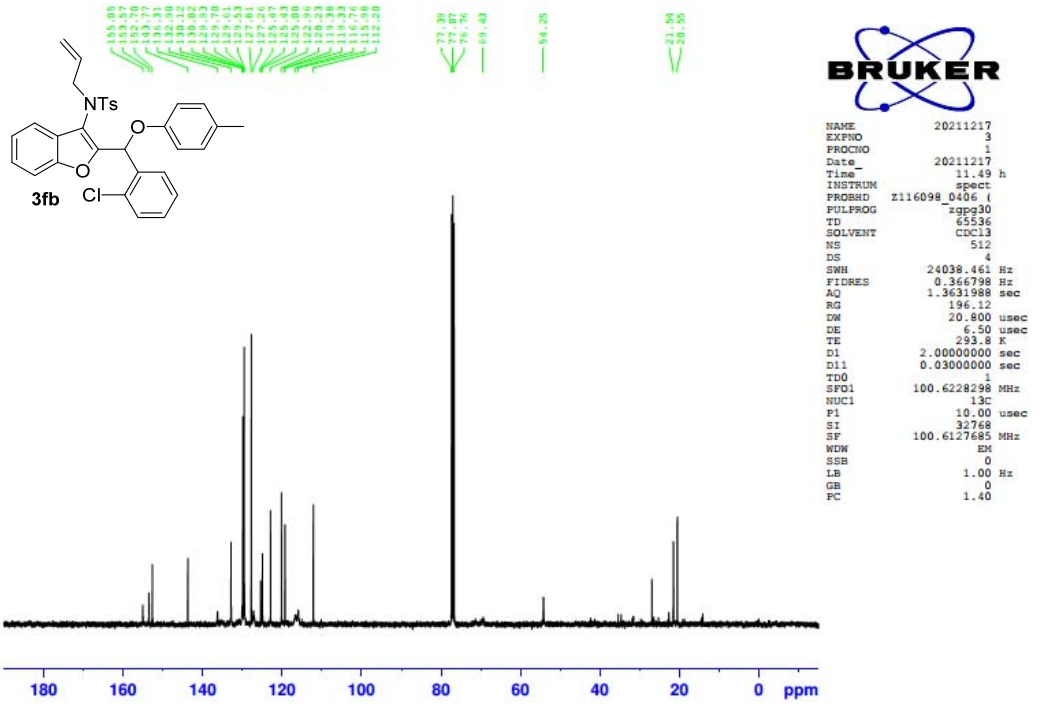

***N*-allyl-*N*-(2-((4-bromophenoxy)(3-chlorophenyl)methyl)benzofuran-3-yl)-4-methylbenzene sulfonamide (3dh):**



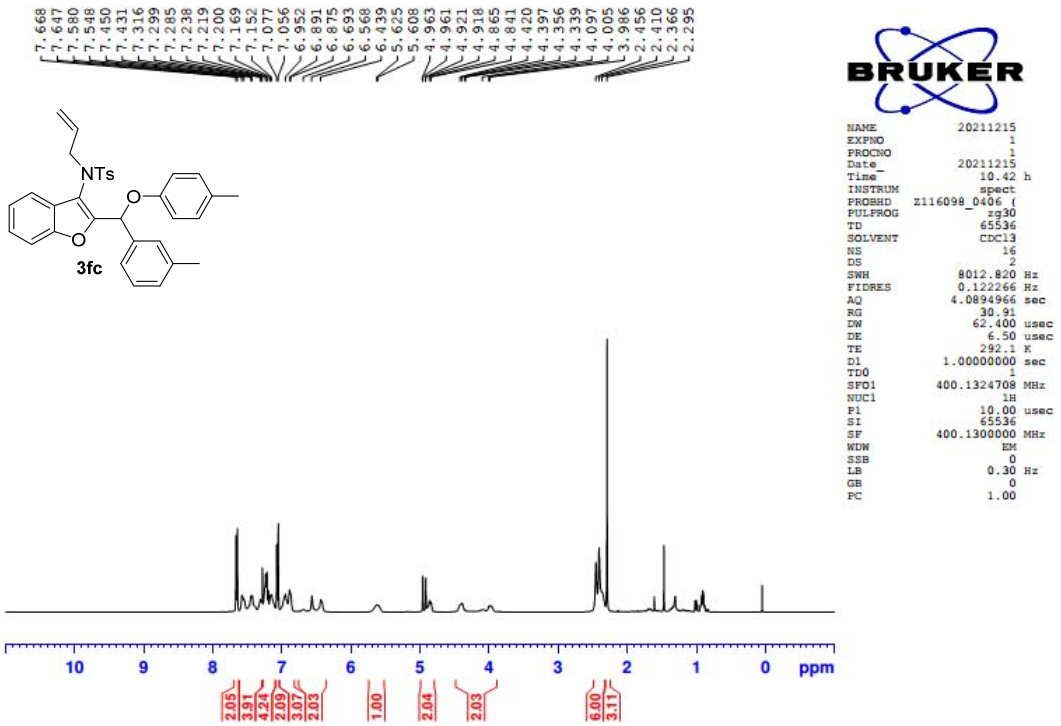
***N*-allyl-*N*-(2-((2-chlorophenyl)(p-tolyloxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfon amide (3fb):**



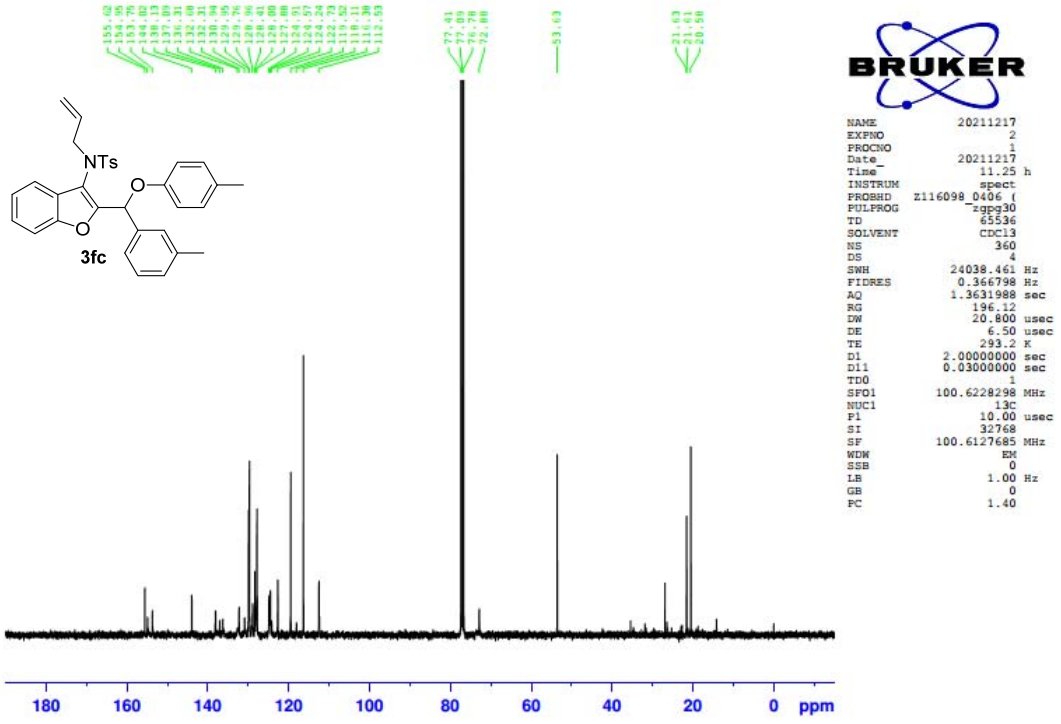

***N*-allyl-*N*-(2-((2-chlorophenyl)(p-tolyloxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfon amide (3fb):**



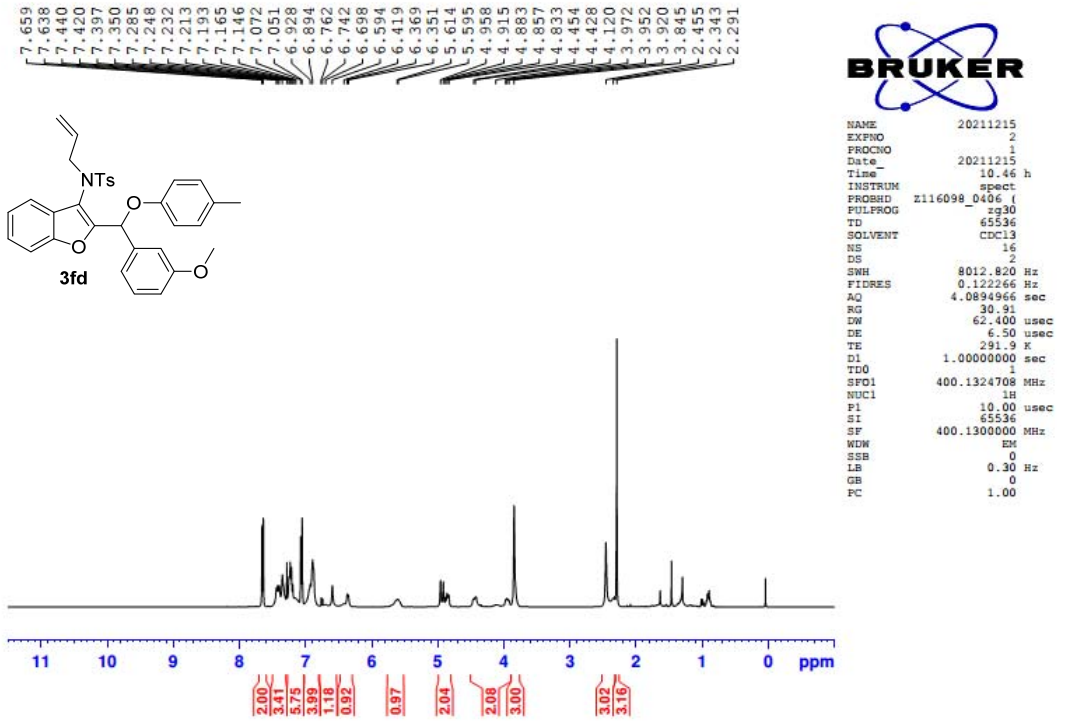
***N*-allyl-4-methyl-*N*-(2-(m-tolyl(p-tolyloxy)methyl)benzofuran-3-yl)benzenesulfonamide (3fc):**



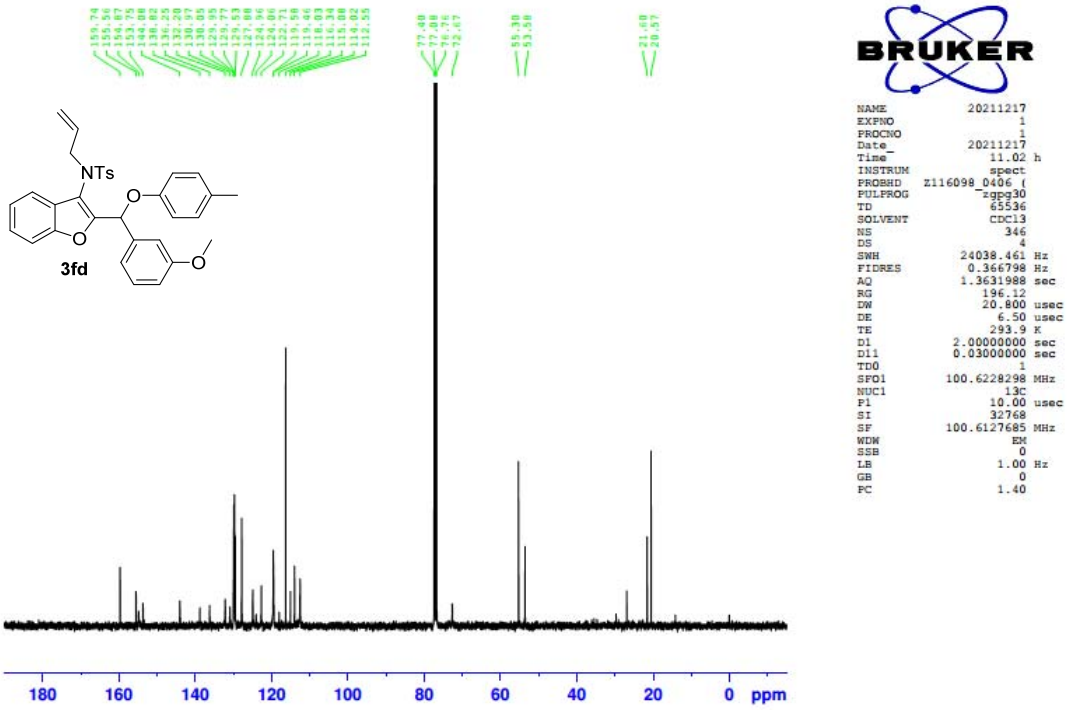

***N*-allyl-4-methyl-*N*-(2-(m-tolyl(p-tolyloxy)methyl)benzofuran-3-yl)benzenesulfonamide (3fc):**



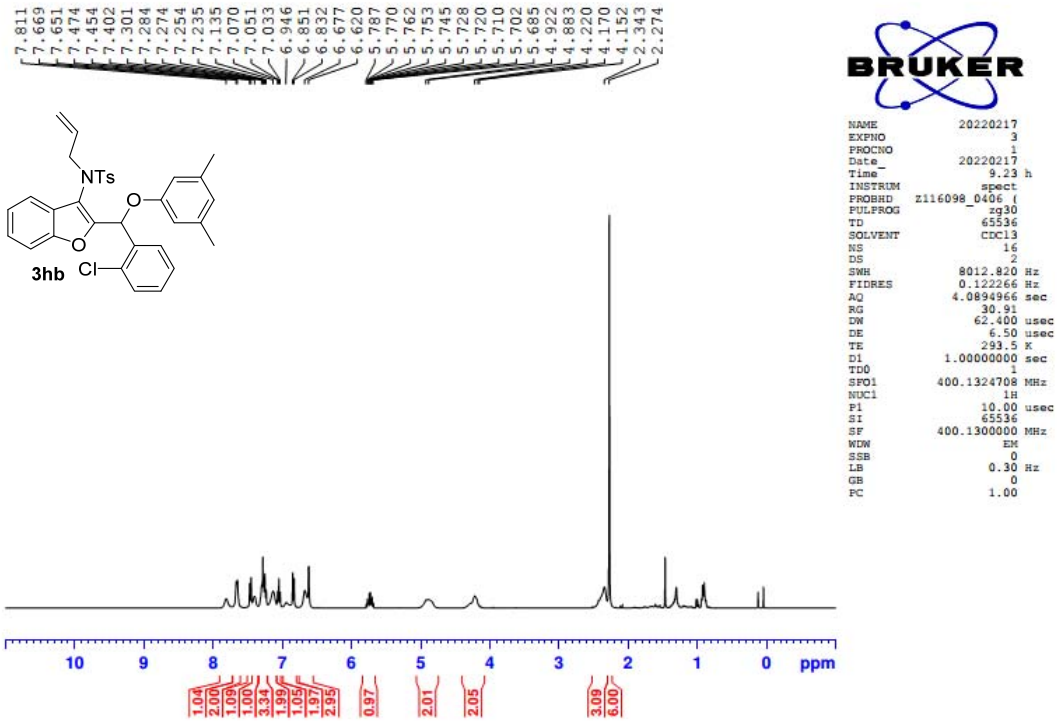
***N*-allyl-*N*-(2-((3-methoxyphenyl)(p-tolyloxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfona mide (3fd):**



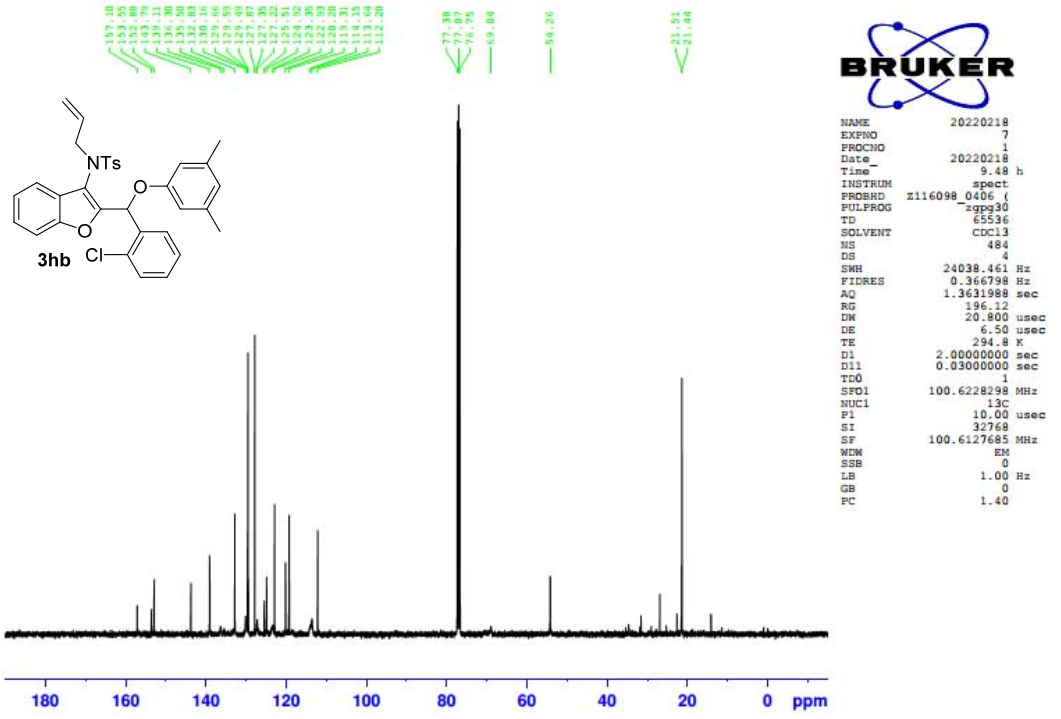

***N*-allyl-*N*-(2-((3-methoxyphenyl)(p-tolyloxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfona mide (3fd):**



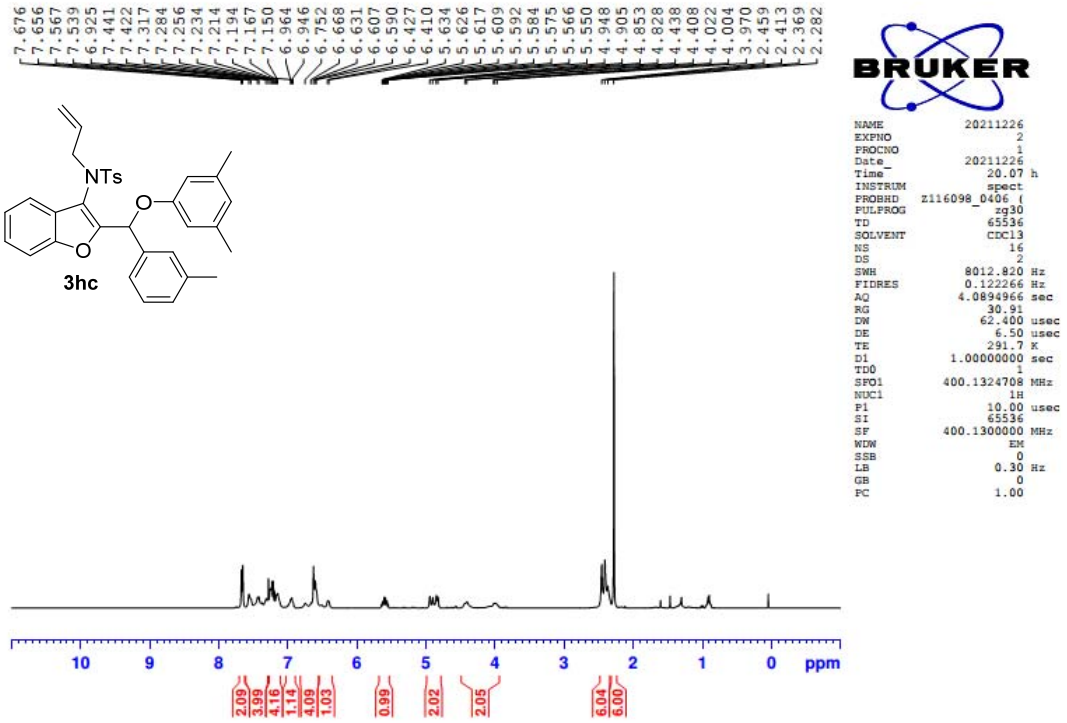
***N*-allyl-*N*-(2-((2-chlorophenyl)(3,5-dimethylphenoxy)methyl)benzofuran-3-yl)-4-methylbenzene sulfonamide (3hb):**



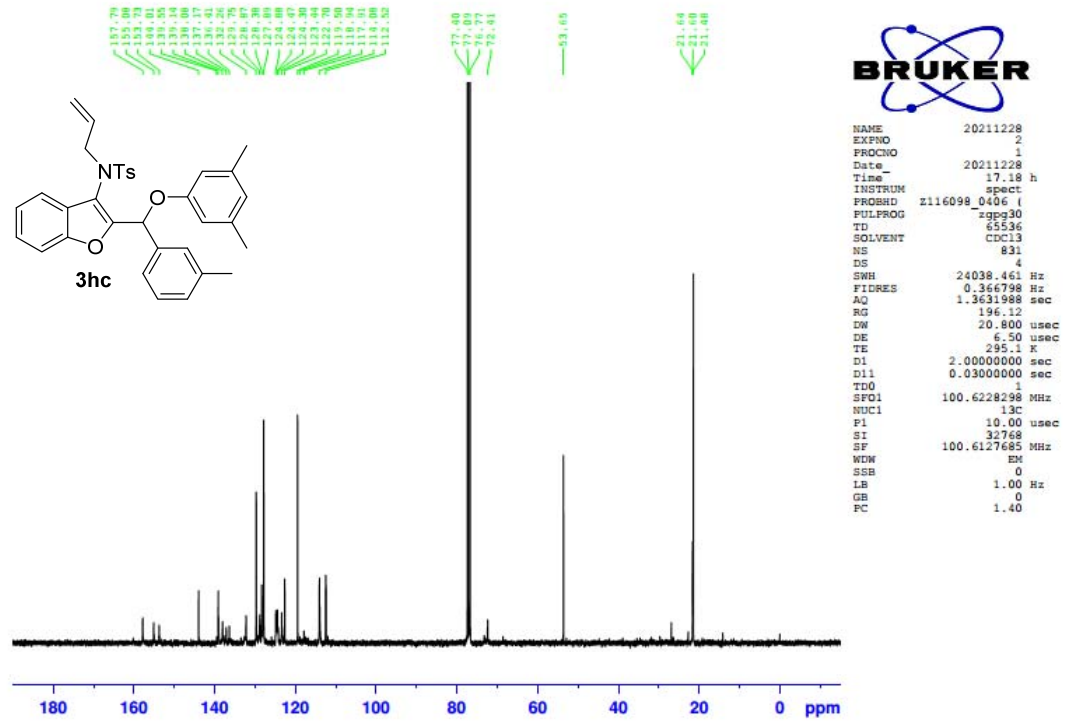

***N*-allyl-*N*-(2-((2-chlorophenyl)(3,5-dimethylphenoxy)methyl)benzofuran-3-yl)-4-methylbenzene sulfonamide (3hb):**



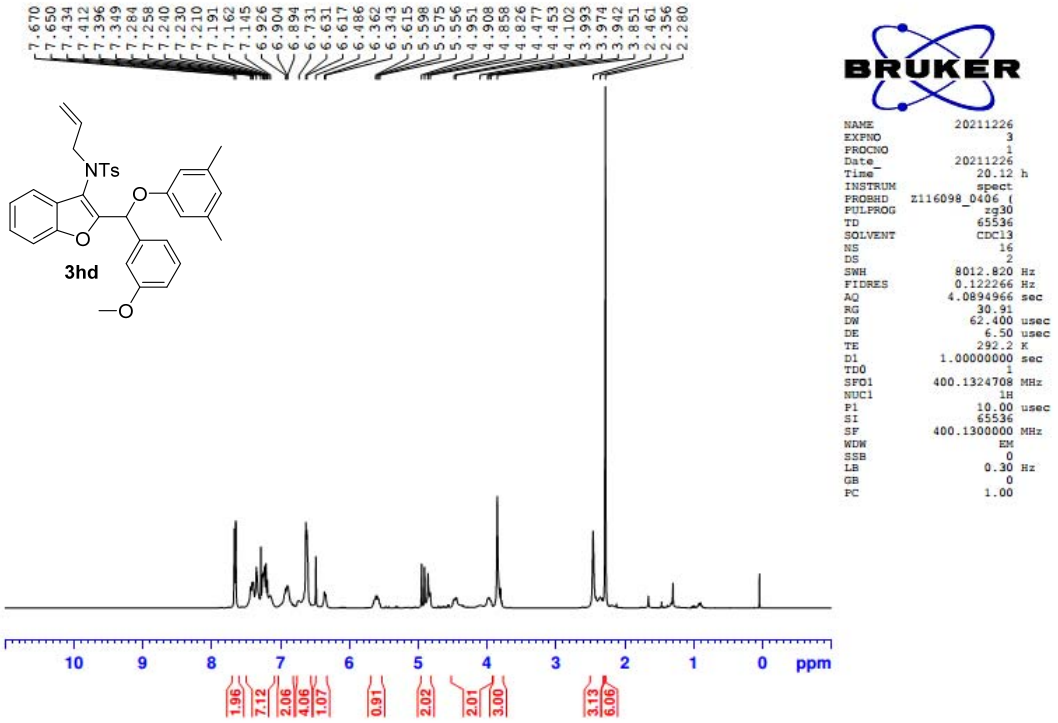
***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(*m*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3hc):**



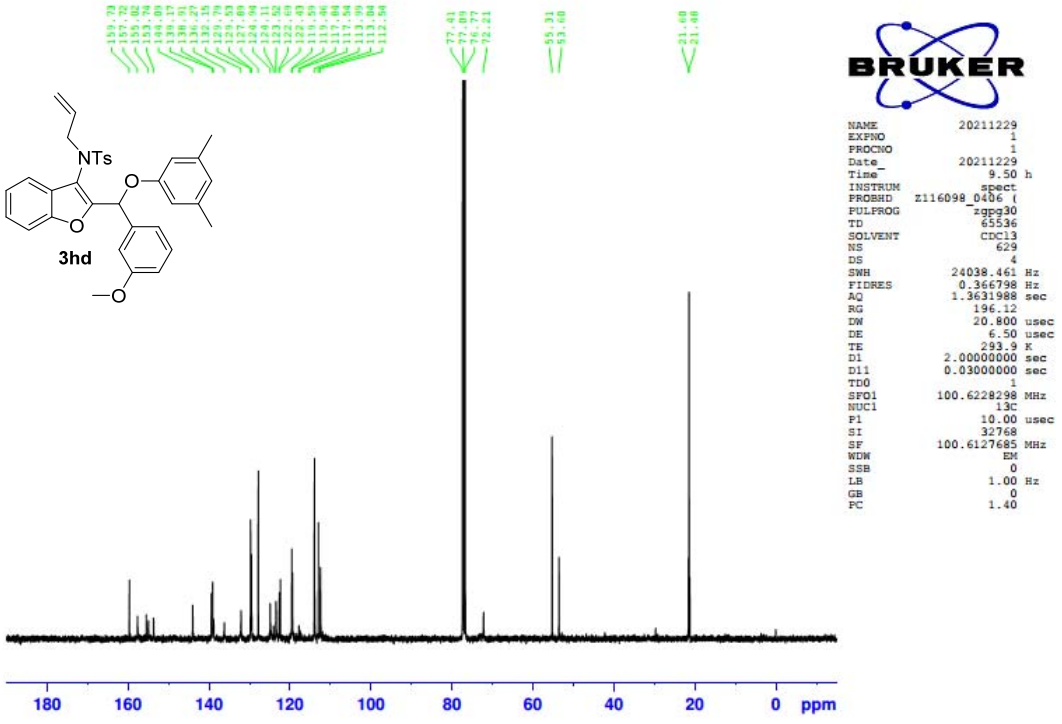

***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(*m*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3hc):**



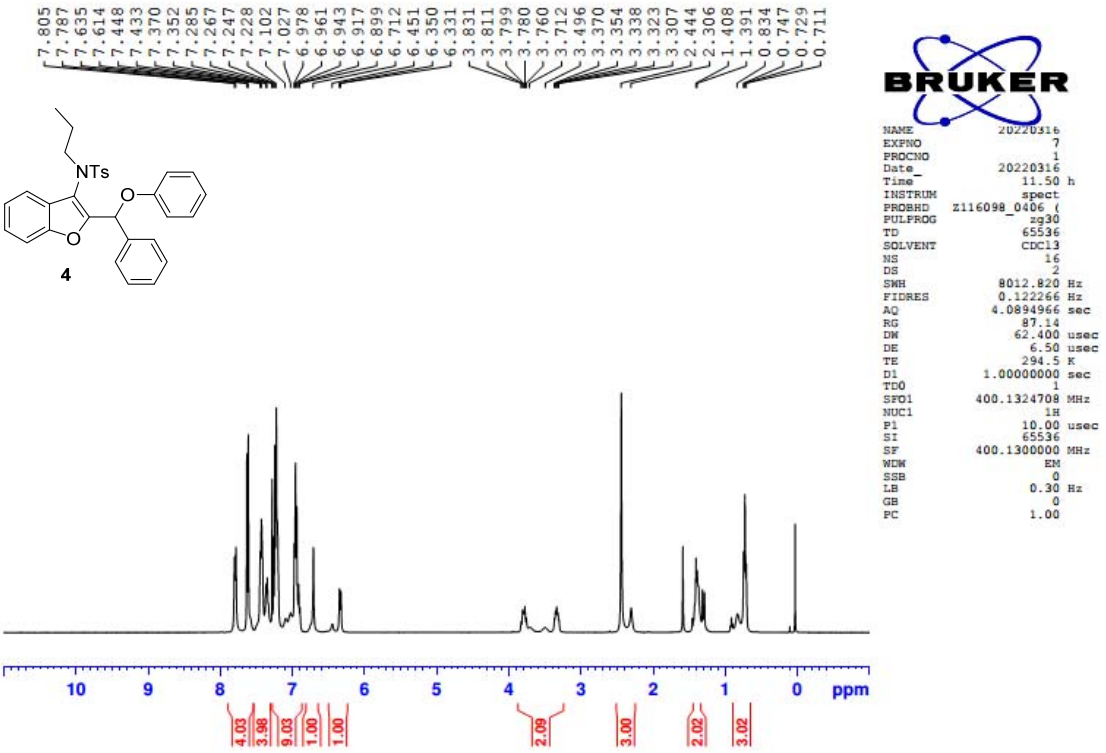
***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(3-methoxyphenyl)methyl)benzofuran-3-yl)-4-methylben zenesulfonamide (3hd):**



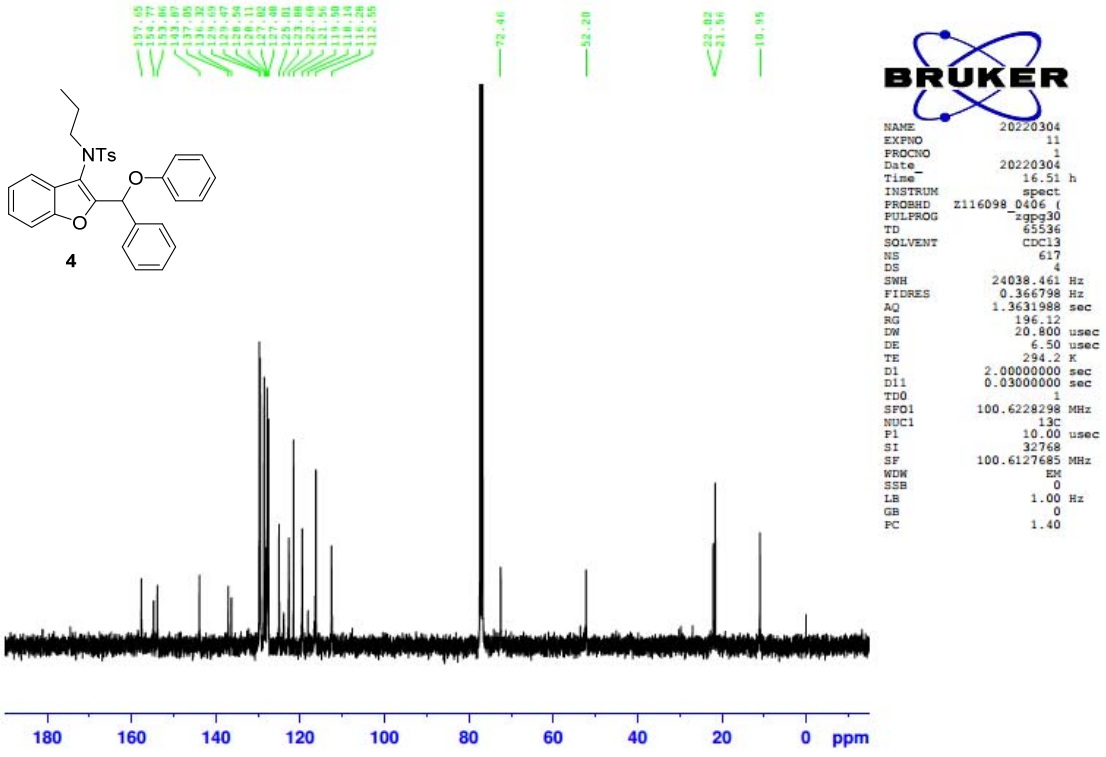

***N*-allyl-*N*-(2-((3,5-dimethylphenoxy)(3-methoxyphenyl)methyl)benzofuran-3-yl)-4-methylben zenesulfonamide (3hd):**



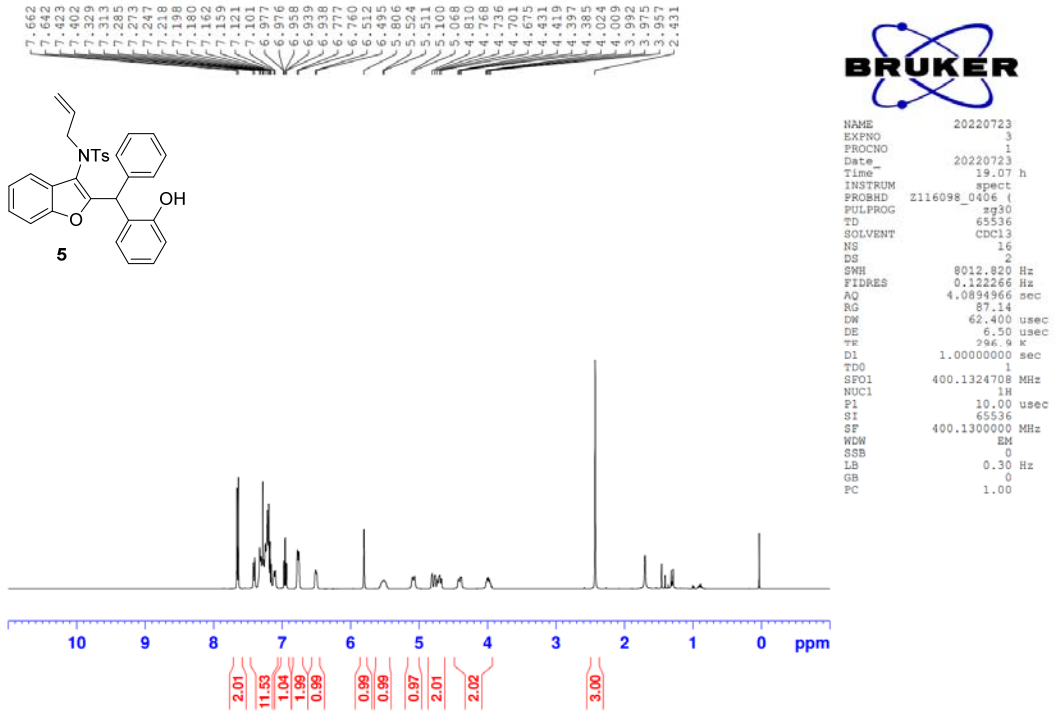
**4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)-*N*-propylbenzenesulfonamide (4)**




**4-methyl-*N*-(2-(phenoxy(phenyl)methyl)benzofuran-3-yl)-*N*-propylbenzenesulfonamide (4)**



***N*-allyl-*N*-(2-((2-hydroxyphenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfona mide (5):**




BRUKER

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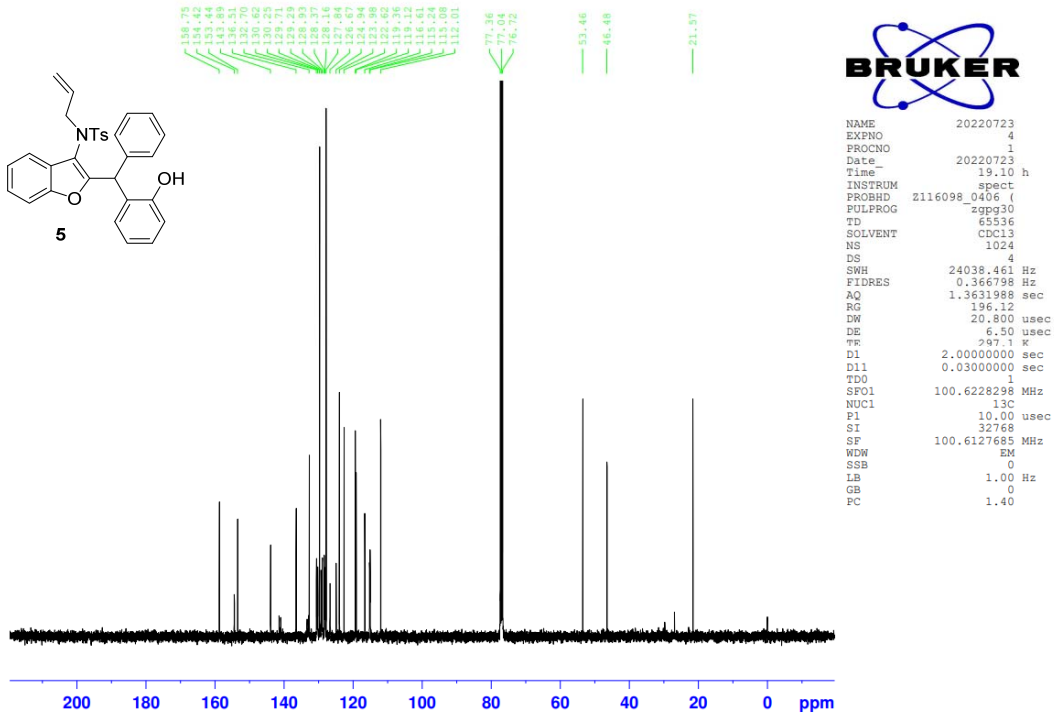
| SWH | 8012.820 Hz |
| FIDRES | 0.122266 Hz |
| AQ | 4.0894966 sec |
| RG | 87.14 |
| DW | 62.400 usec |
| DE | 6.50 usec |
| TE | 296.9 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| SFO1 | 400.1324708 MHz |
| NUC1 | 1H |
| P1 | 10.00 usec |
| SI | 65536 |
| SF | 400.1300000 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

***N*-allyl-*N*-(2-((2-hydroxyphenyl)(phenoxy)methyl)benzofuran-3-yl)-4-methylbenzenesulfona mide (5):**




BRUKER

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| RG | 196.12 |
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| DE | 6.50 usec |
| TE | 297.1 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 100.6228298 MHz |
| NUC1 | 13C |
| P1 | 10.00 usec |
| SI | 32768 |
| SF | 100.6127685 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |