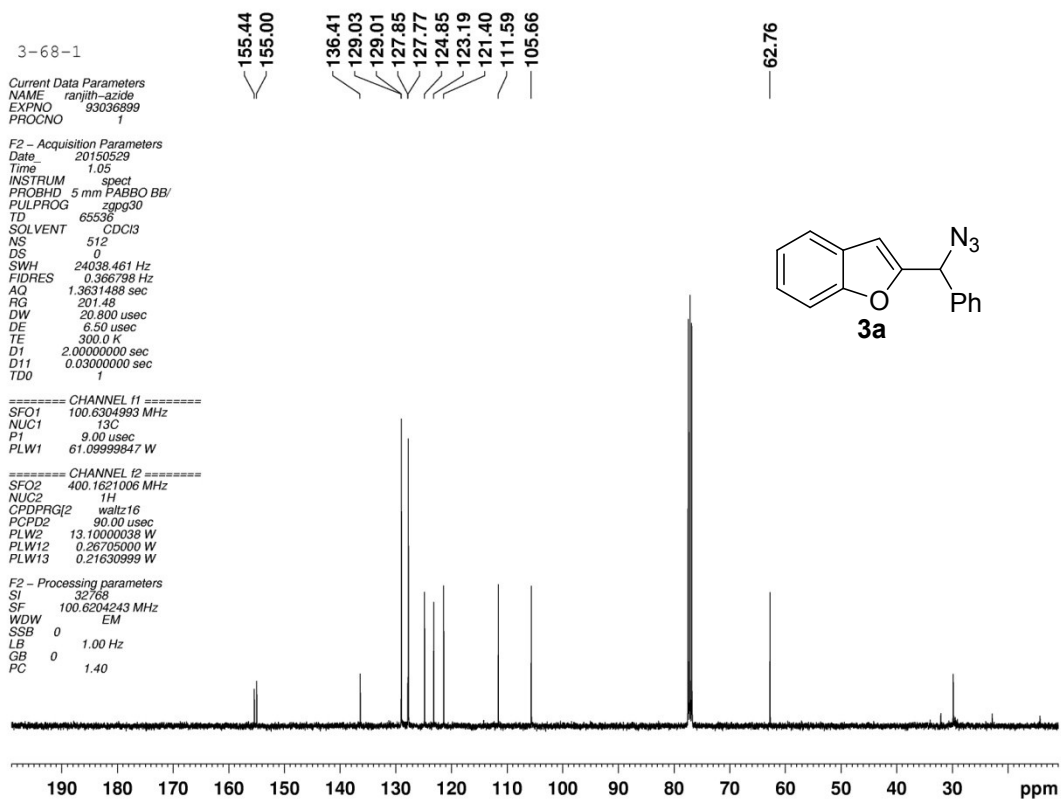
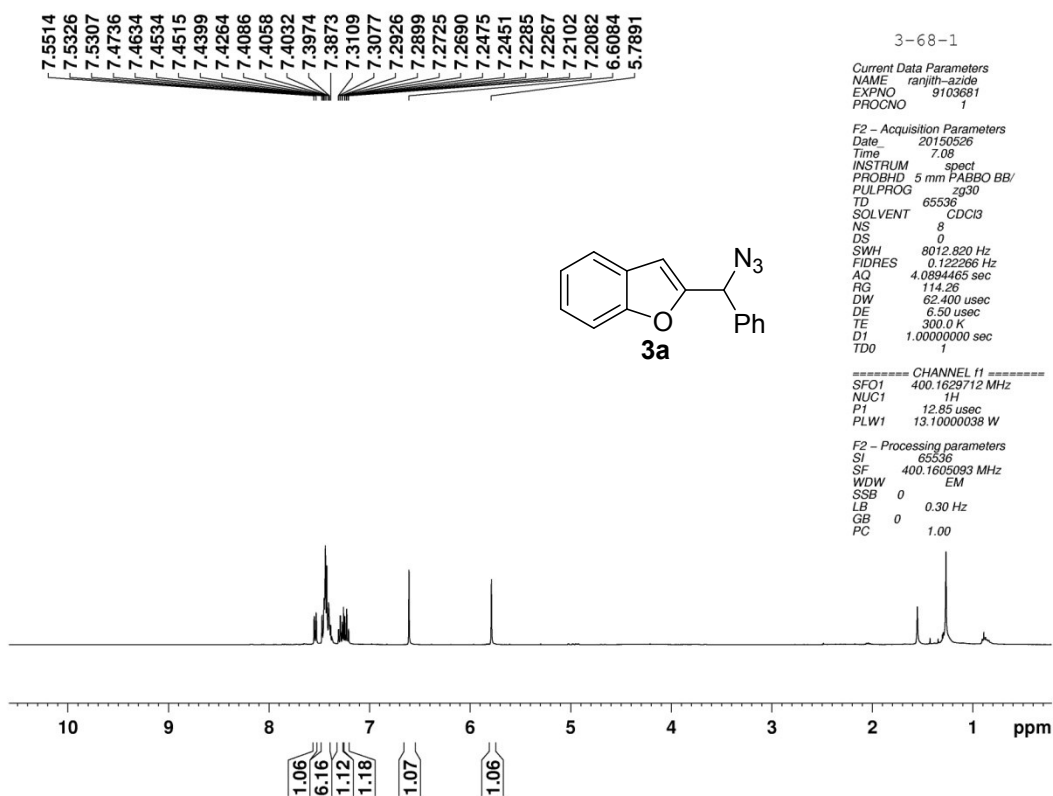


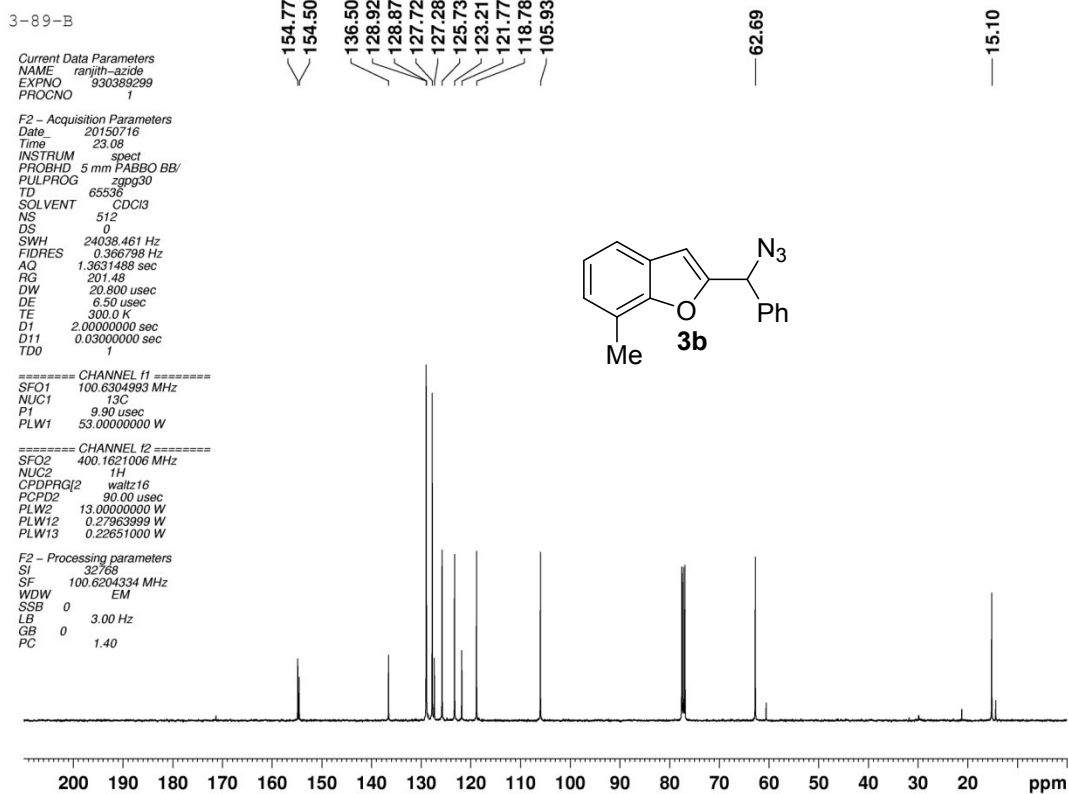
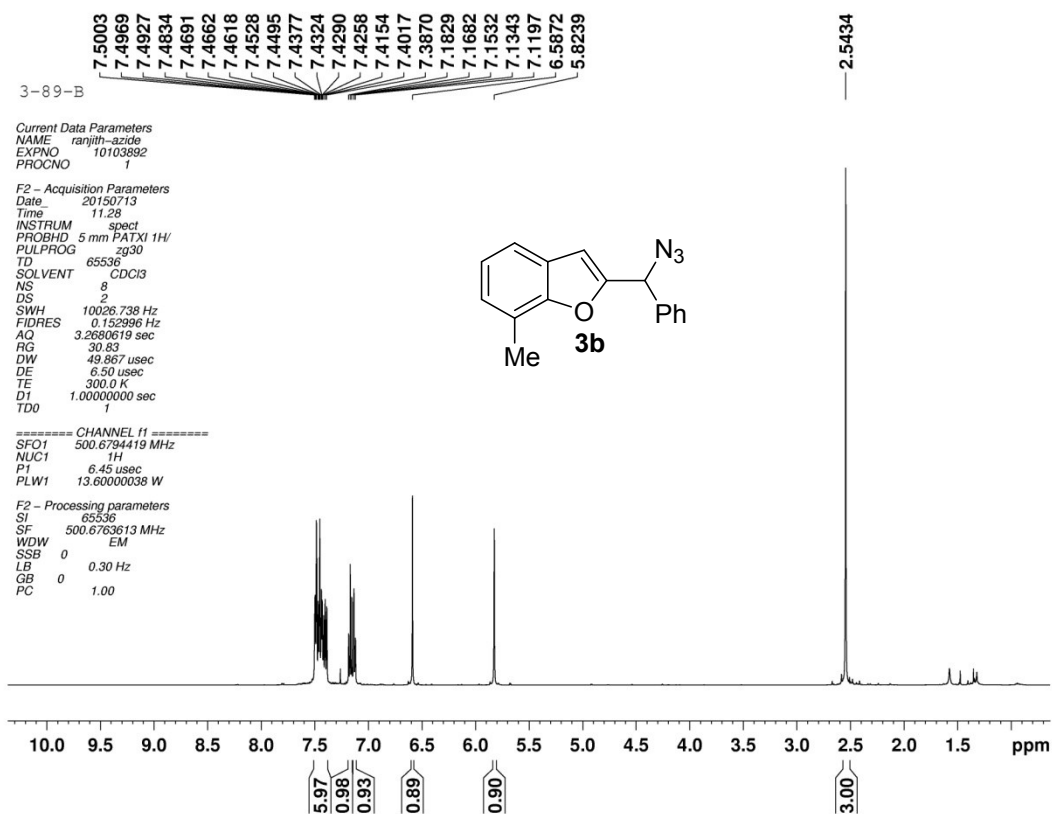
## Synthesis of benzofuranyl and indolyl methyl azides by tandem silver-catalyzed cyclization and azidation

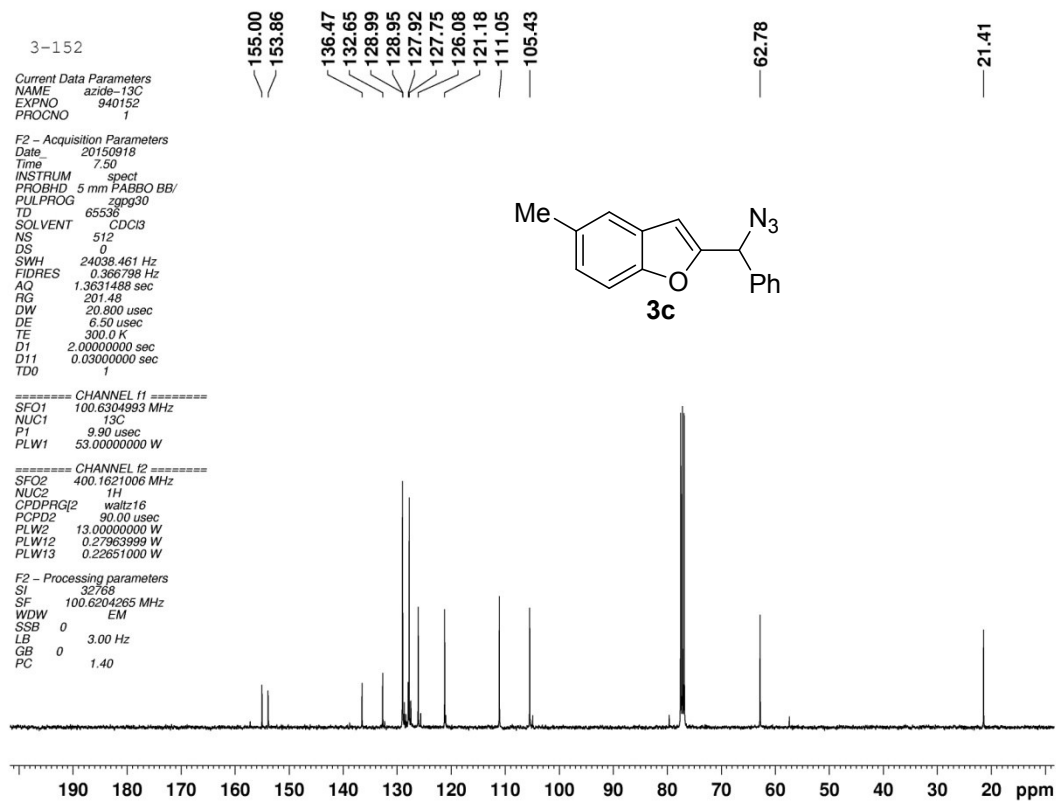
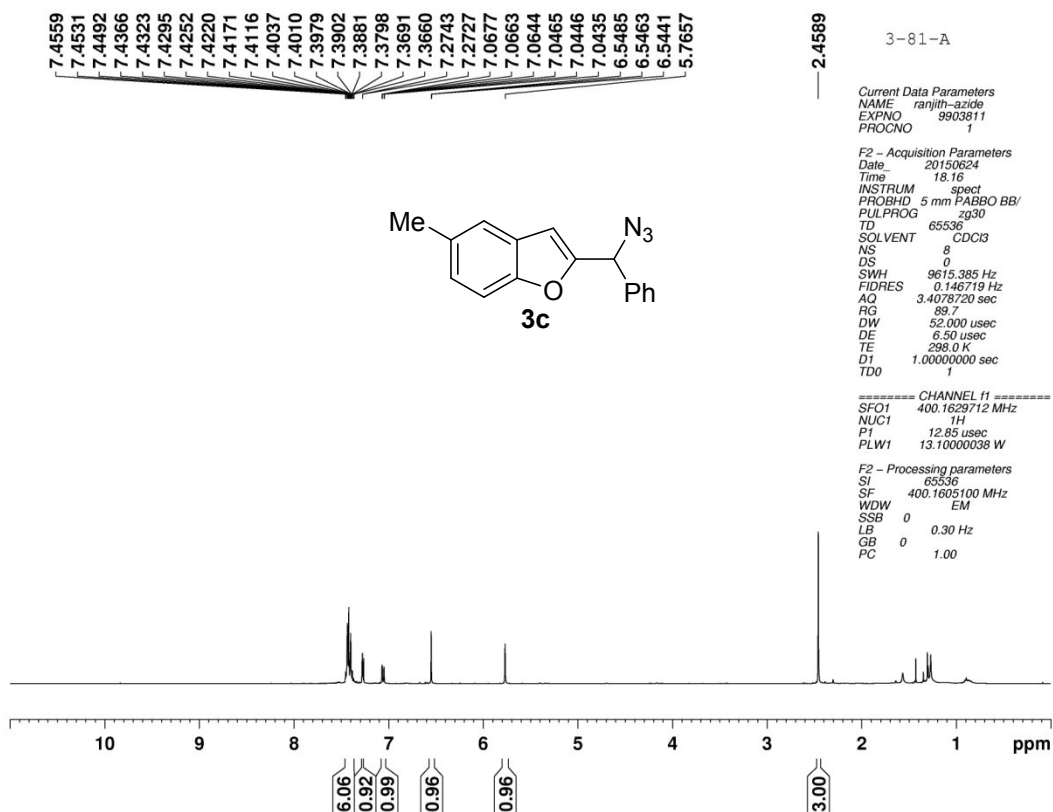
Gadi Ranjith Kumar,<sup>a,b</sup>Yalla Kiran Kumar,<sup>a</sup>Ruchir Kant<sup>c</sup> and Maddi Sridhar Reddy<sup>a,b</sup>

*<sup>a</sup>Medicinal & Process Chemistry Division, CSIR-Central Drug Research Institute, BS-10/1, Sector 10, Jankipuram extension, Sitapur Road, Lucknow 226031, India. <sup>b</sup>Academy of Scientific and Innovative Research, New Delhi 110001, India. <sup>c</sup>Molecular & Structural Biology Division, CSIR-CDRI, Lucknow 226031, India. Email: msreddy@gmail.com*

|                                                             |         |
|-------------------------------------------------------------|---------|
| Copy of <sup>1</sup> H and <sup>13</sup> C NMR Spectra..... | S02-S51 |
| X-ray crystallography information.....                      | S52-S55 |









3-133-B

Current Data Parameters  
 NAME ranjith-azide  
 EXPNO 9201332  
 PROCNO 1

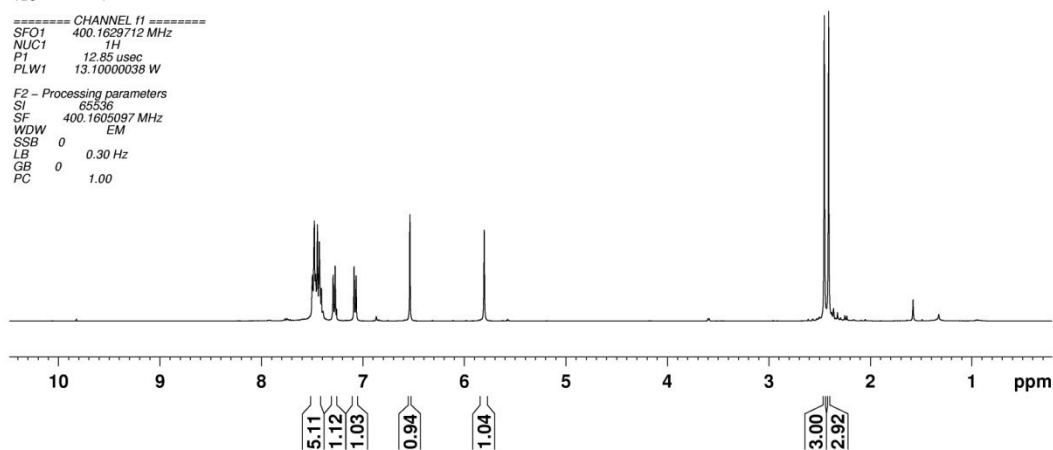
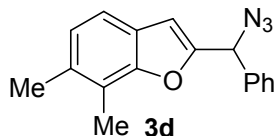
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 Time 18.01  
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 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 31.99  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 12.85 usec  
 PLW1 13.10000038 W

F2 - Processing parameters  
 SI 65536  
 SF 400.1605097 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.4989  
7.4799  
7.4710  
7.4663  
7.4607  
7.4502  
7.4314  
7.4272  
7.2947  
7.2751  
7.0883  
7.0686  
6.5381  
5.8059

2.4543  
2.4121



3-133-B

Current Data Parameters  
 NAME azide-13C  
 EXPNO 9101332  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20150826  
 Time 12.54  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 512  
 DS 0  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 201.48  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 300.2 K  
 D11 2.00000000 sec  
 D1 0.03000000 sec  
 TDO 1

===== CHANNEL f1 =====  
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 P1 9.00 usec  
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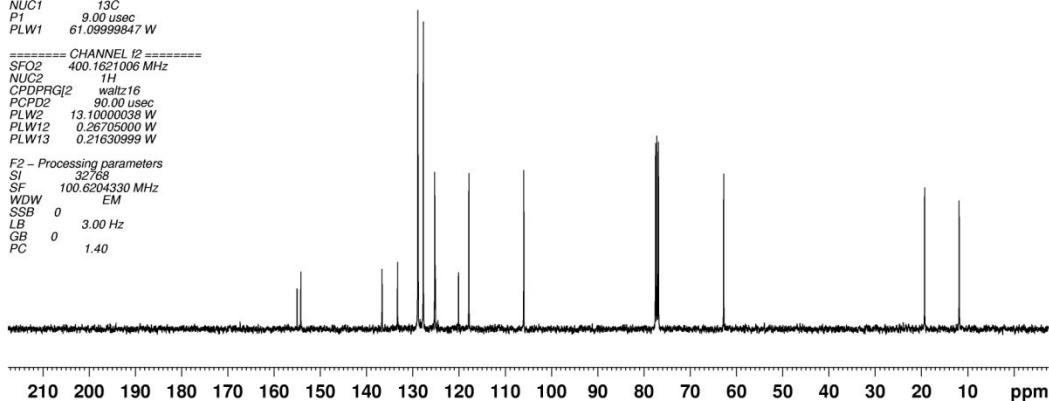
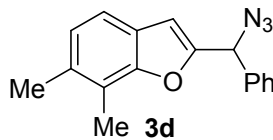
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 NUC2 1H  
 CPDPRG2 waltz16  
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 PLW2 13.10000038 W  
 PLW12 0.26705000 W  
 PLW13 0.21630999 W

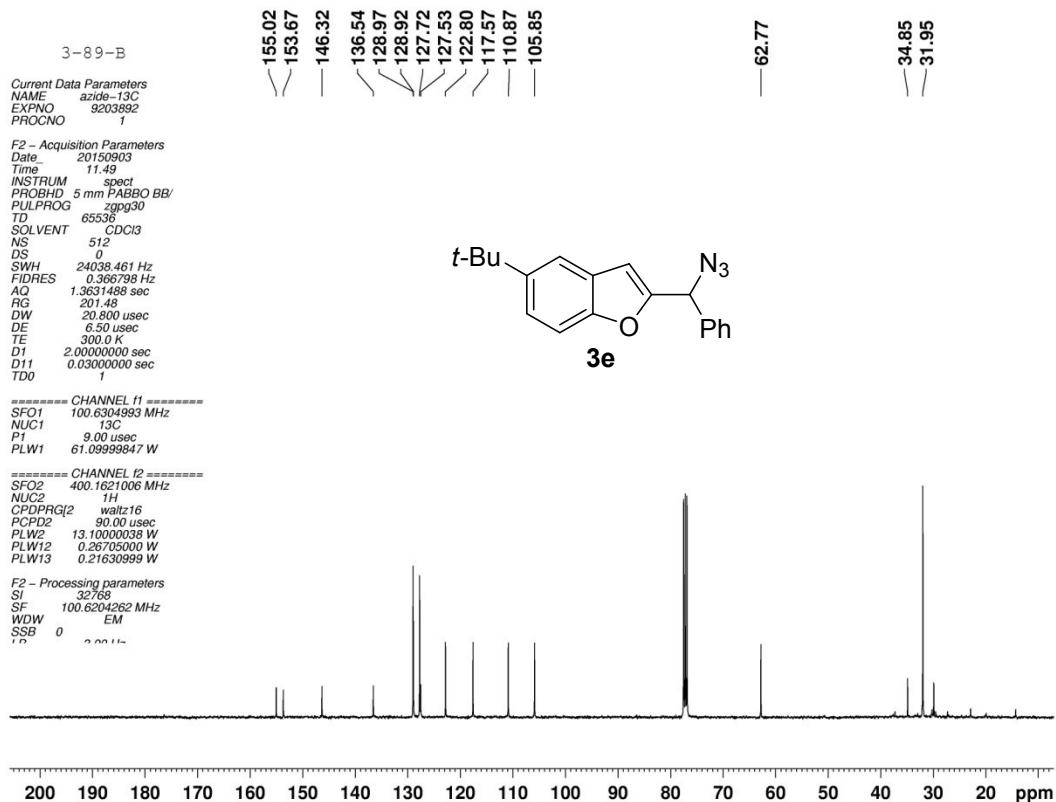
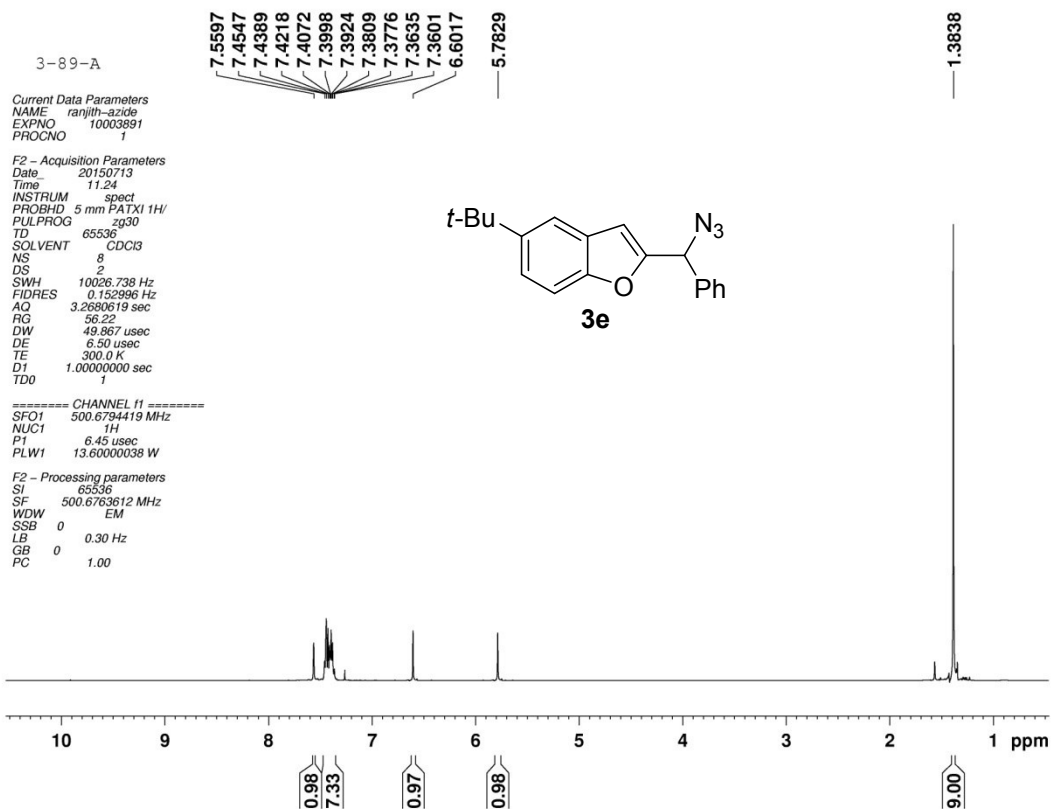
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 SF 100.6204330 MHz  
 WDW EM  
 SSB 0  
 LB 3.00 Hz  
 GB 0  
 PC 1.40

155.01  
154.20  
136.62  
133.28  
128.88  
128.80  
127.71  
125.23  
125.10  
120.09  
117.85  
105.98

62.74

19.29  
11.81





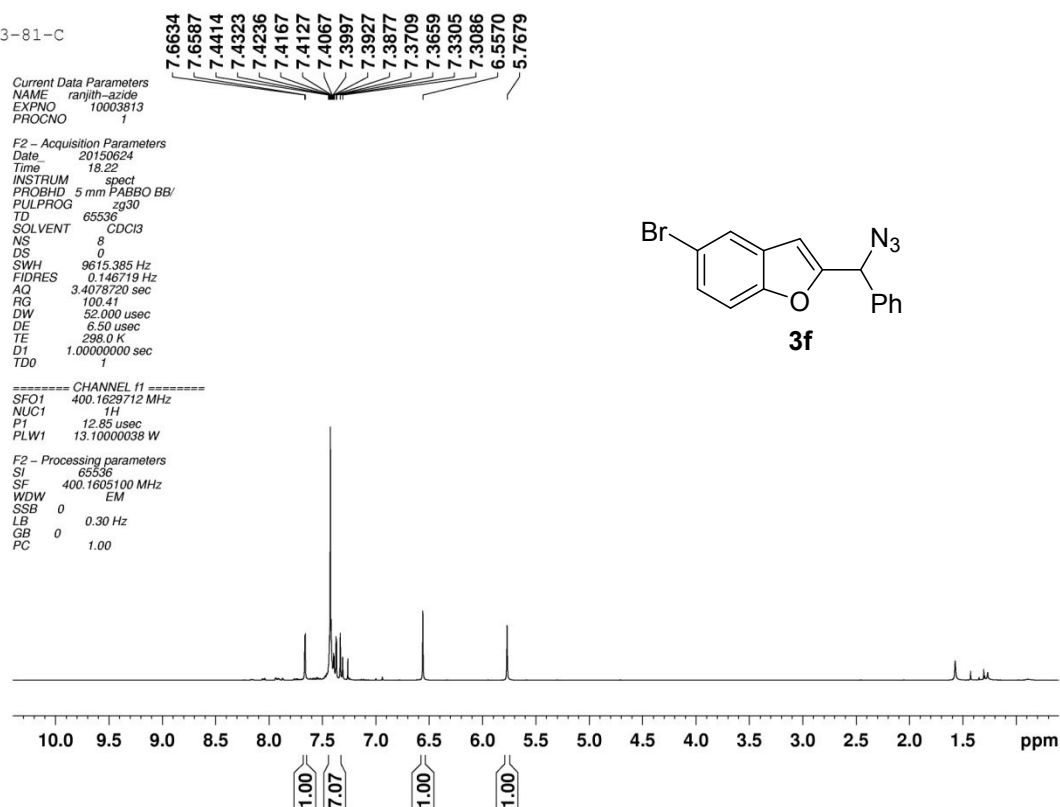
3-81-C

Current Data Parameters  
 NAME ranjith-azide  
 EXPNO 10003813  
 PROCNO 1

F2 - Acquisition Parameters  
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 Time 18.25  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 100.41  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 12.85 usec  
 PLW1 13.10000038 W

F2 - Processing parameters  
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 SF 400.1605100 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



3-81-c

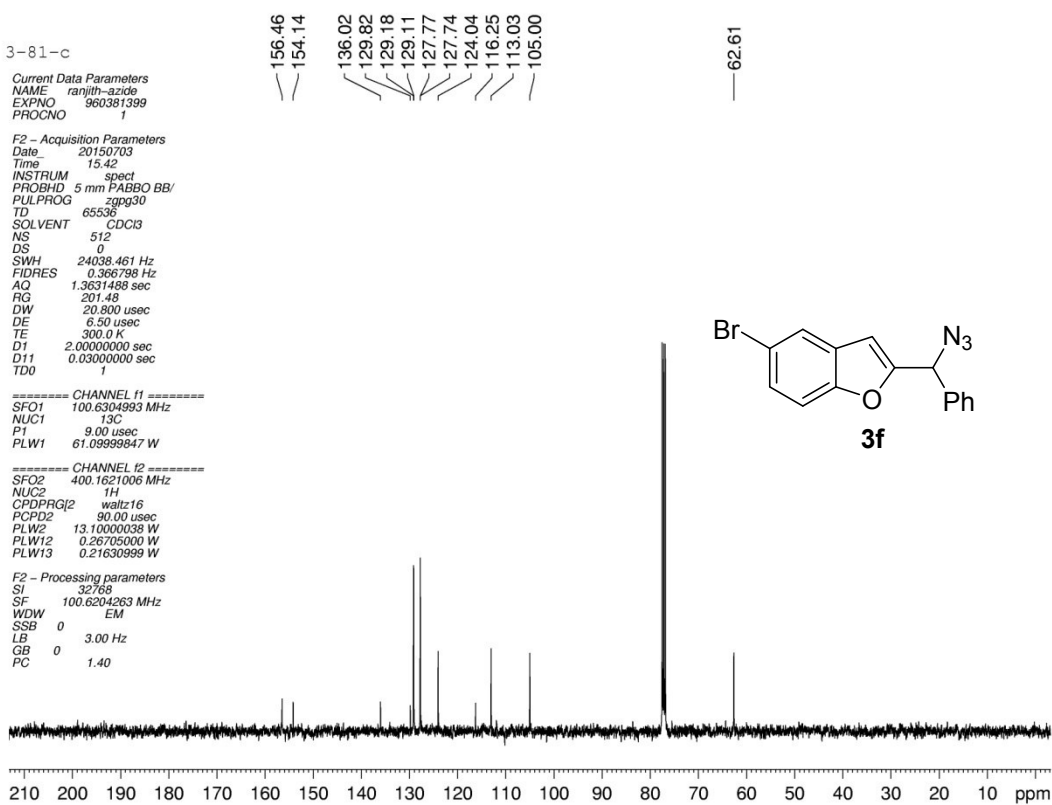
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 EXPNO 960381389  
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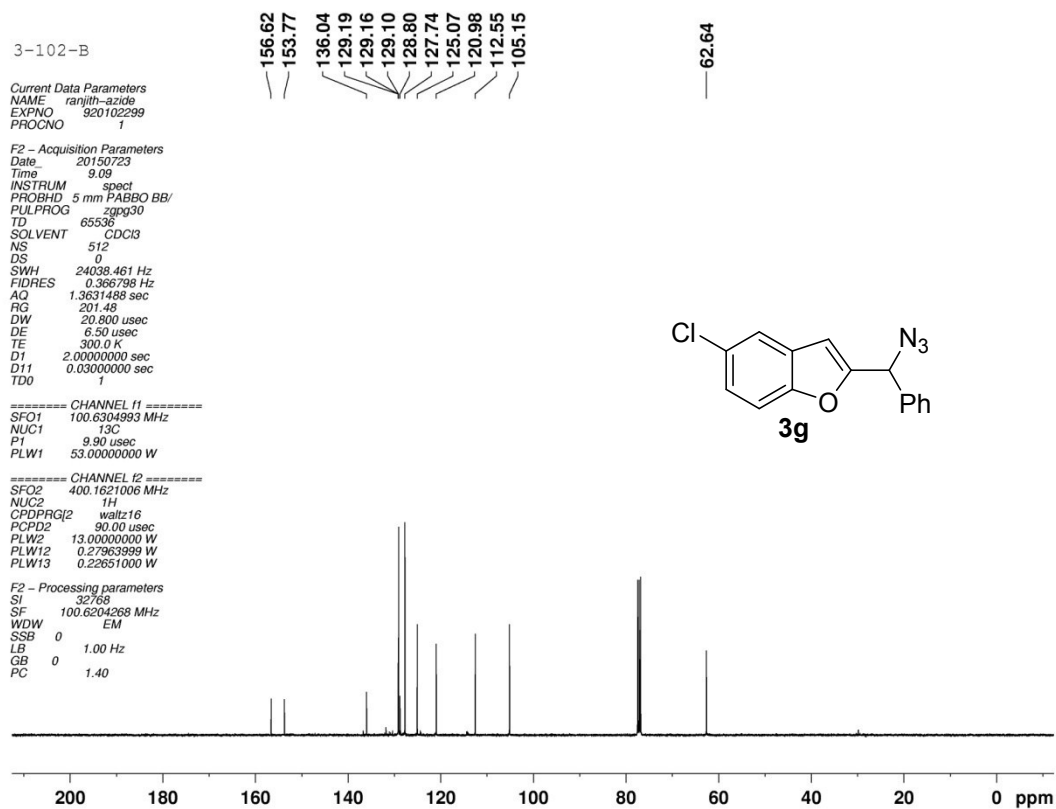
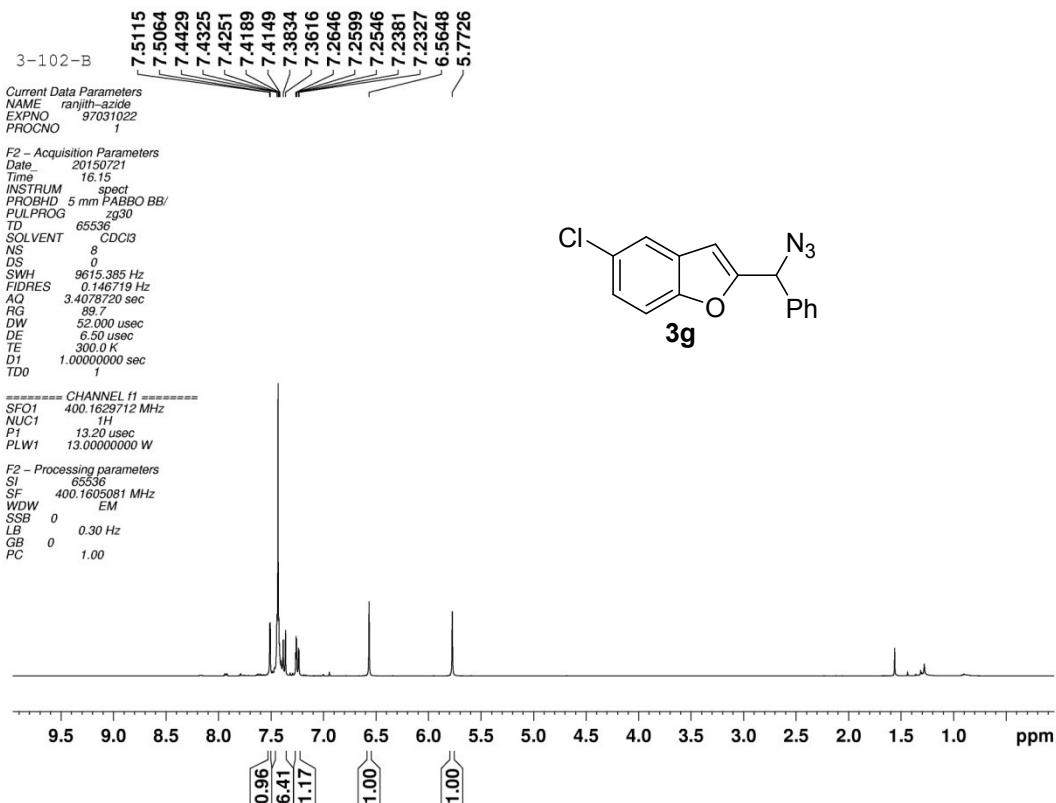
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 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 512  
 DS 0  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 201.48  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

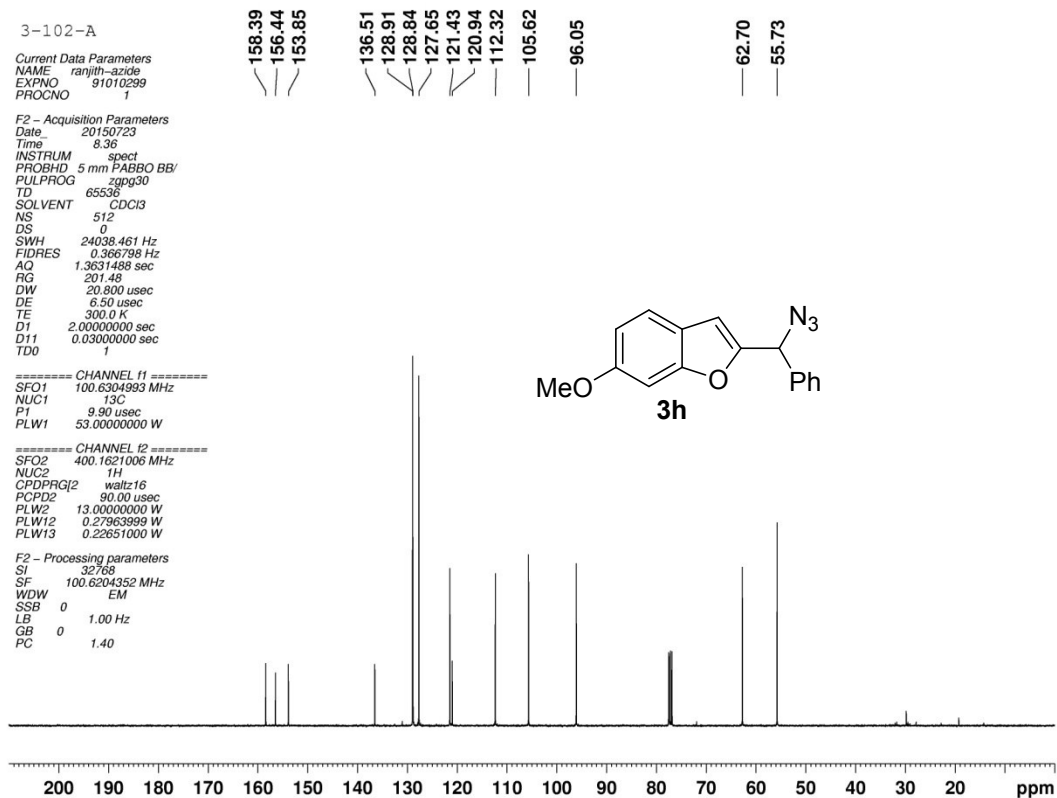
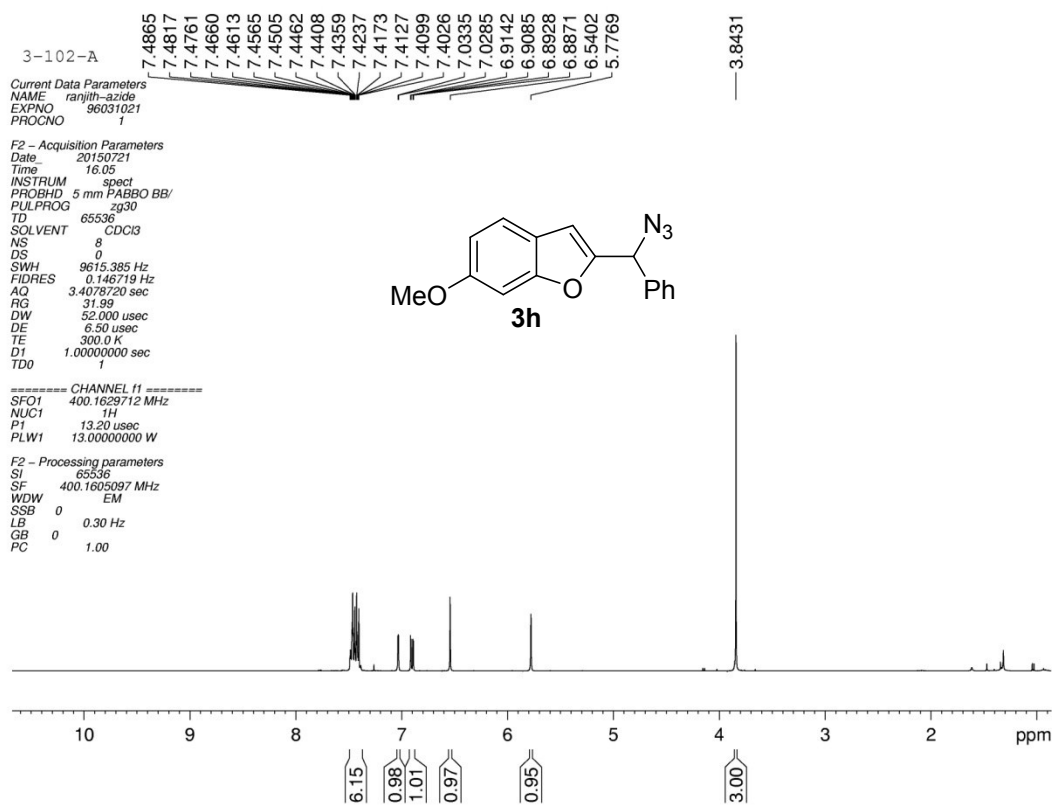
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 SFO1 100.6304993 MHz  
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 P1 9.00 usec  
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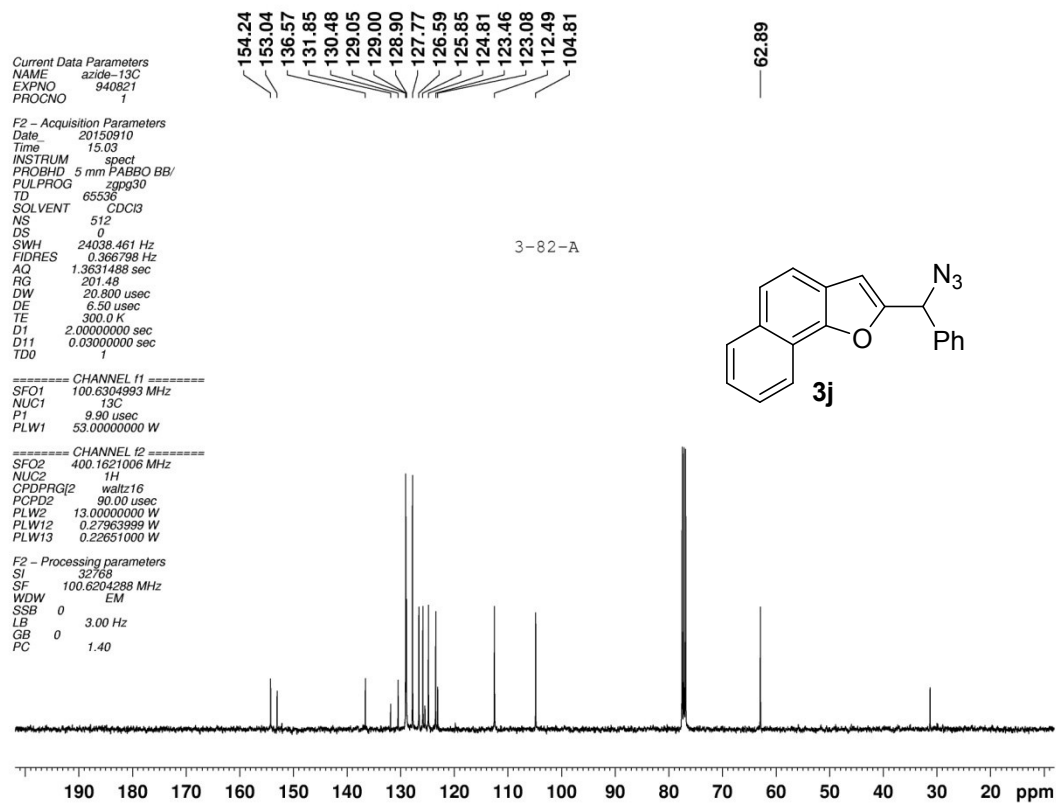
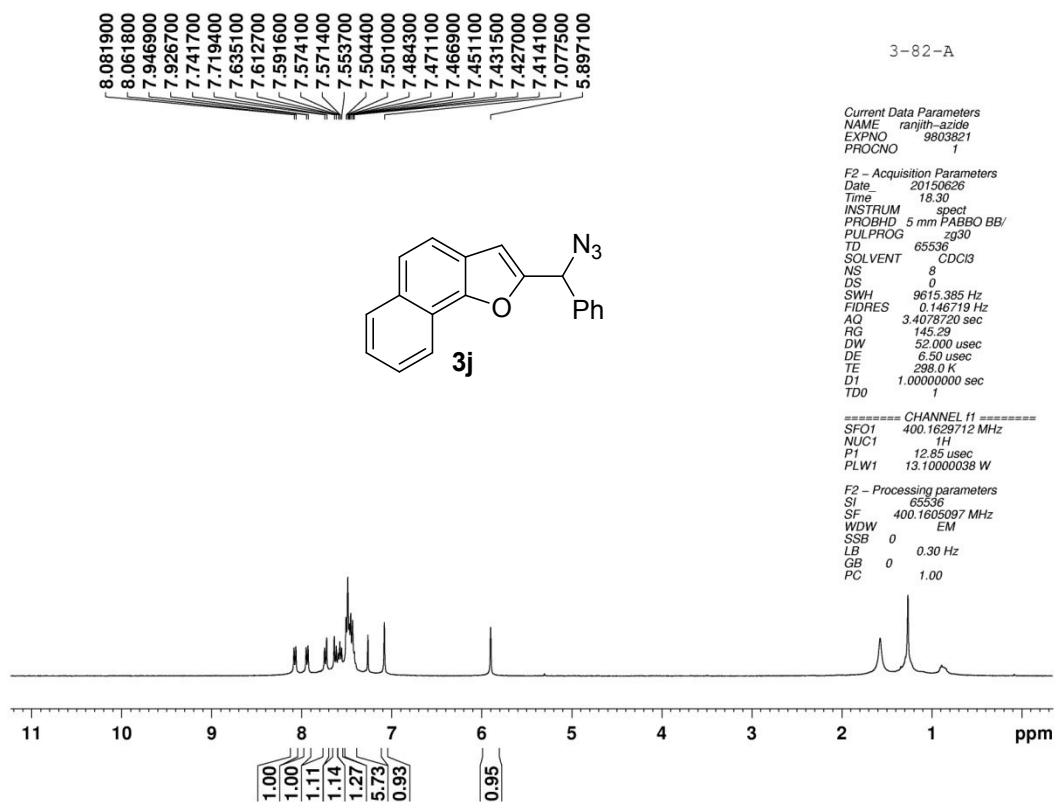
===== CHANNEL f2 =====  
 SFO2 400.1621006 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 90.00 usec  
 PLW2 13.10000038 W  
 PLW12 0.26705000 W  
 PLW13 0.21630999 W

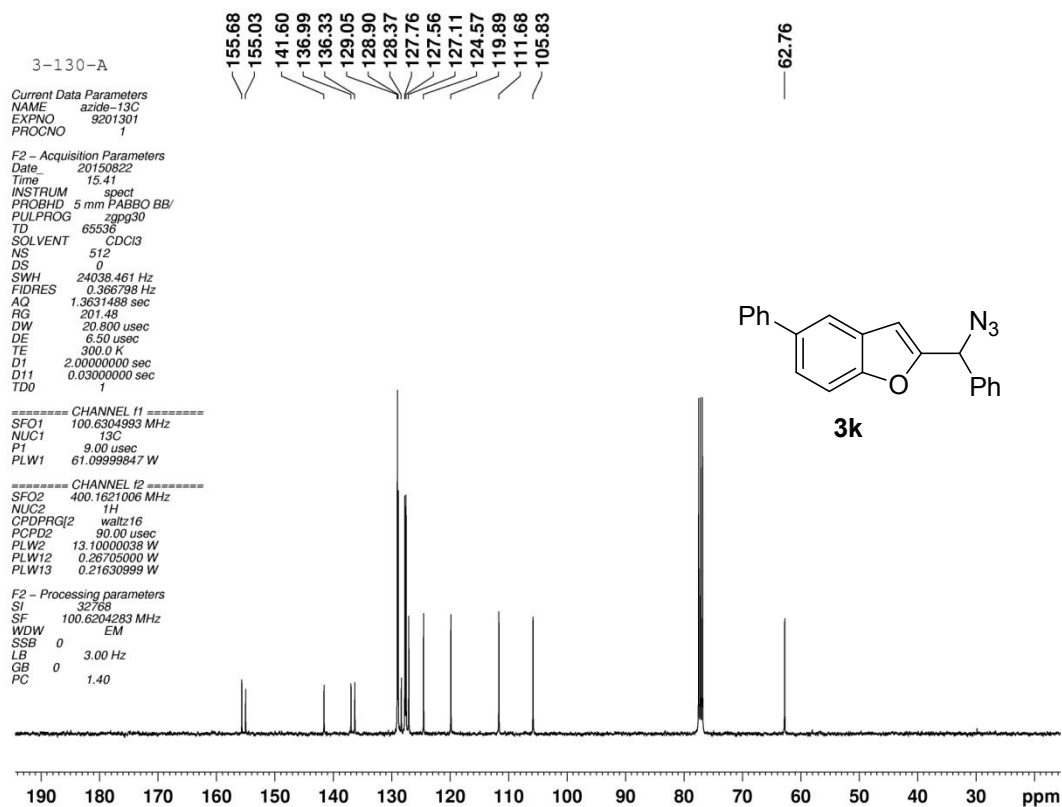
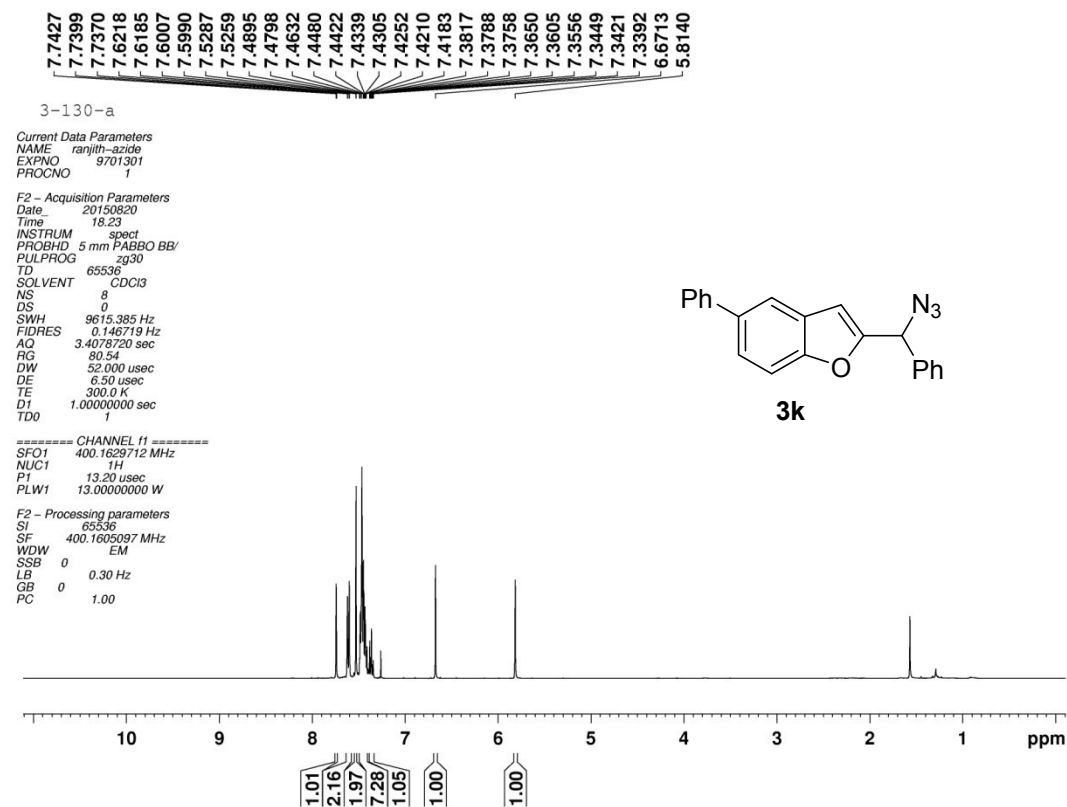
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 GB 0  
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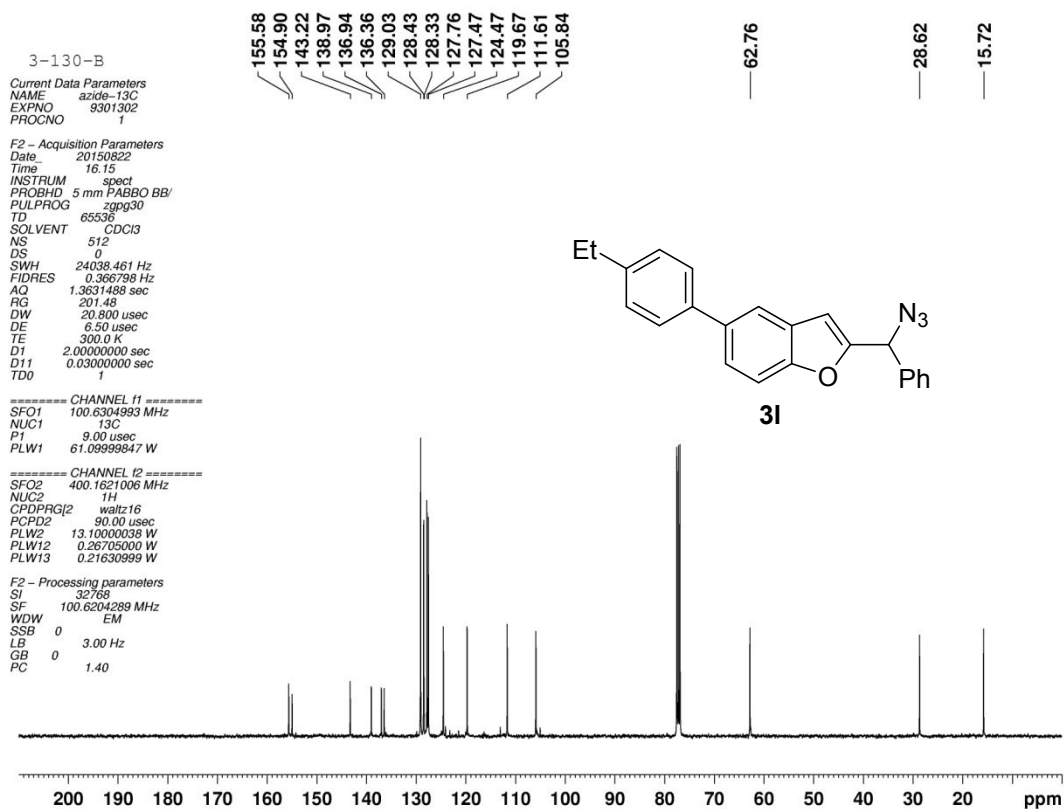
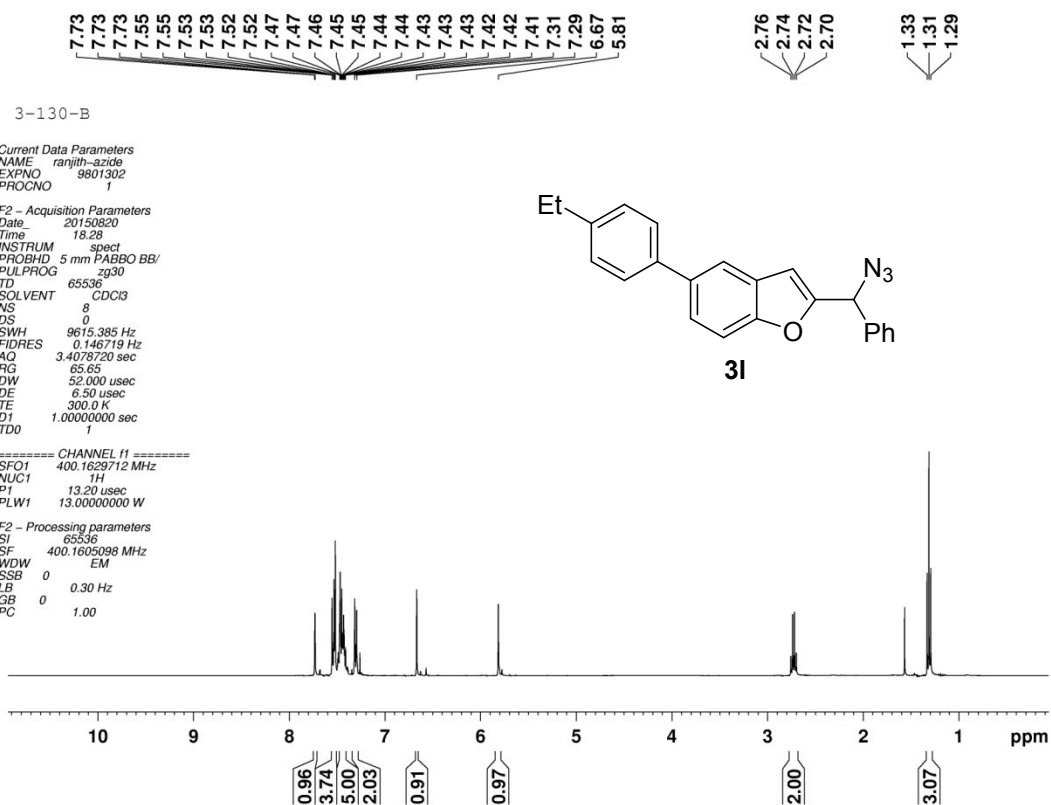




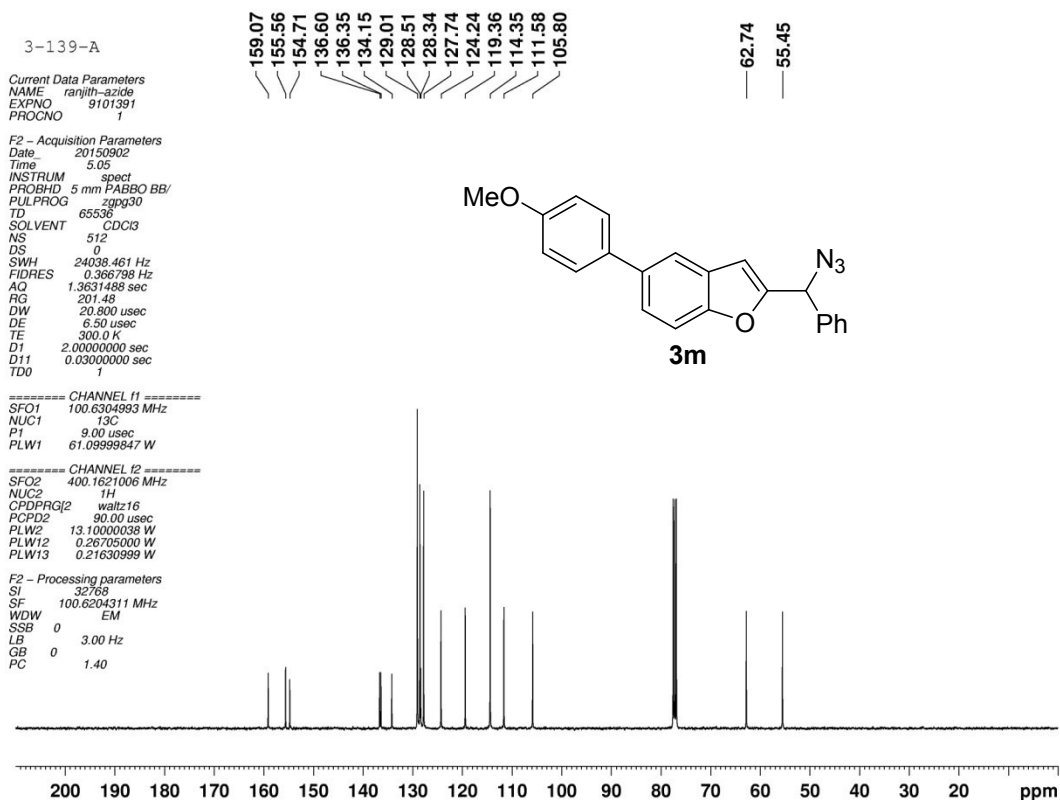
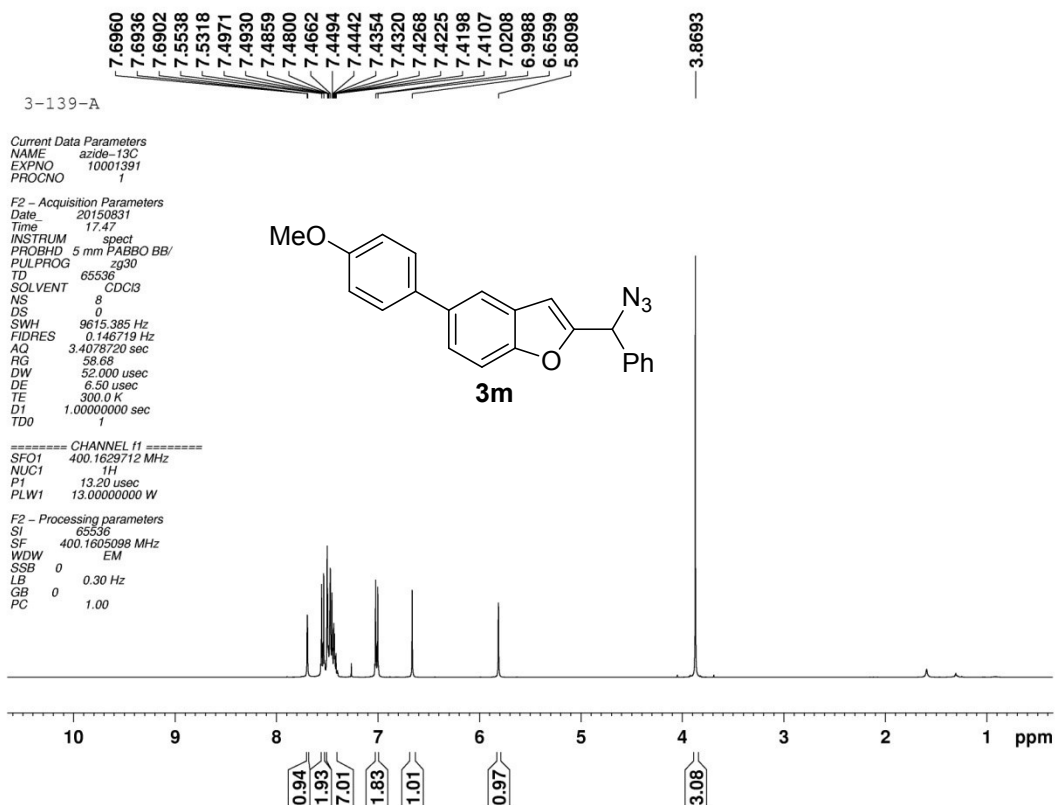


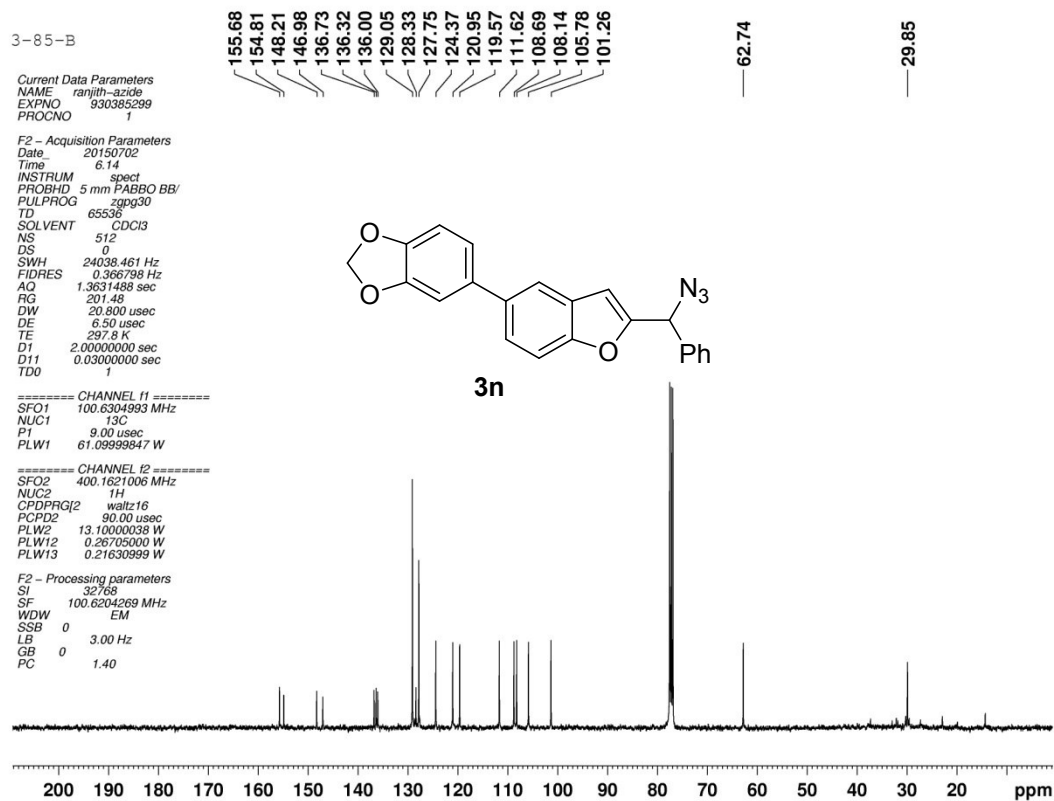
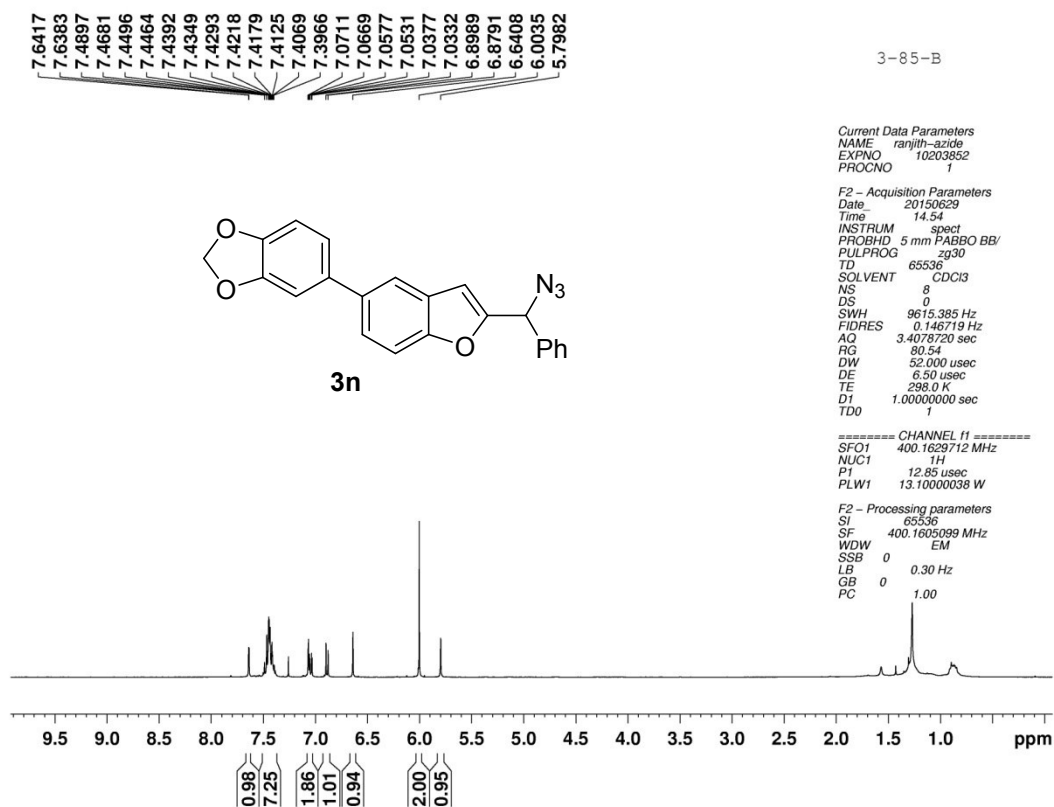


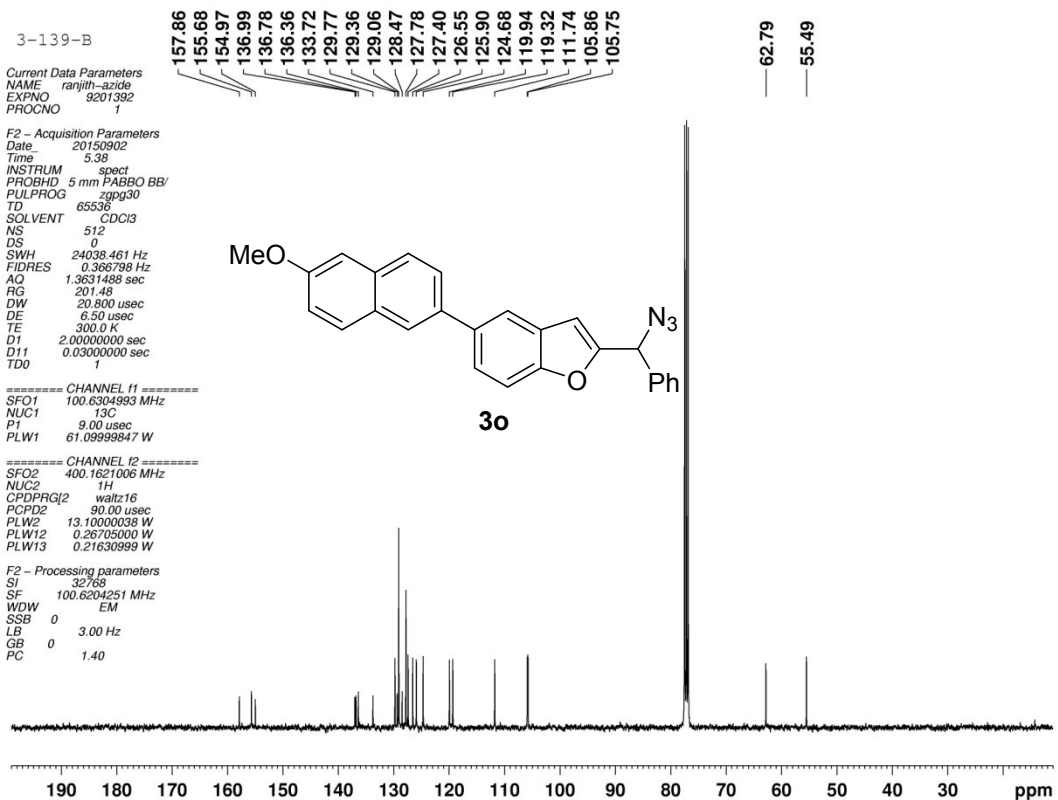
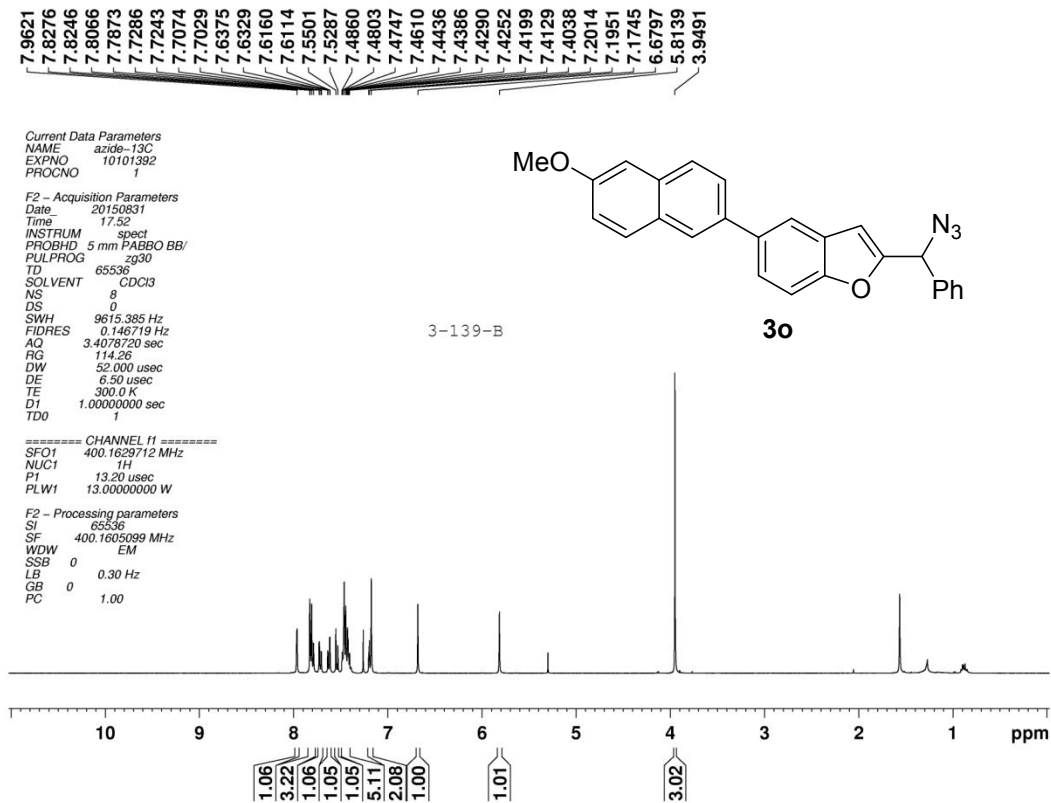


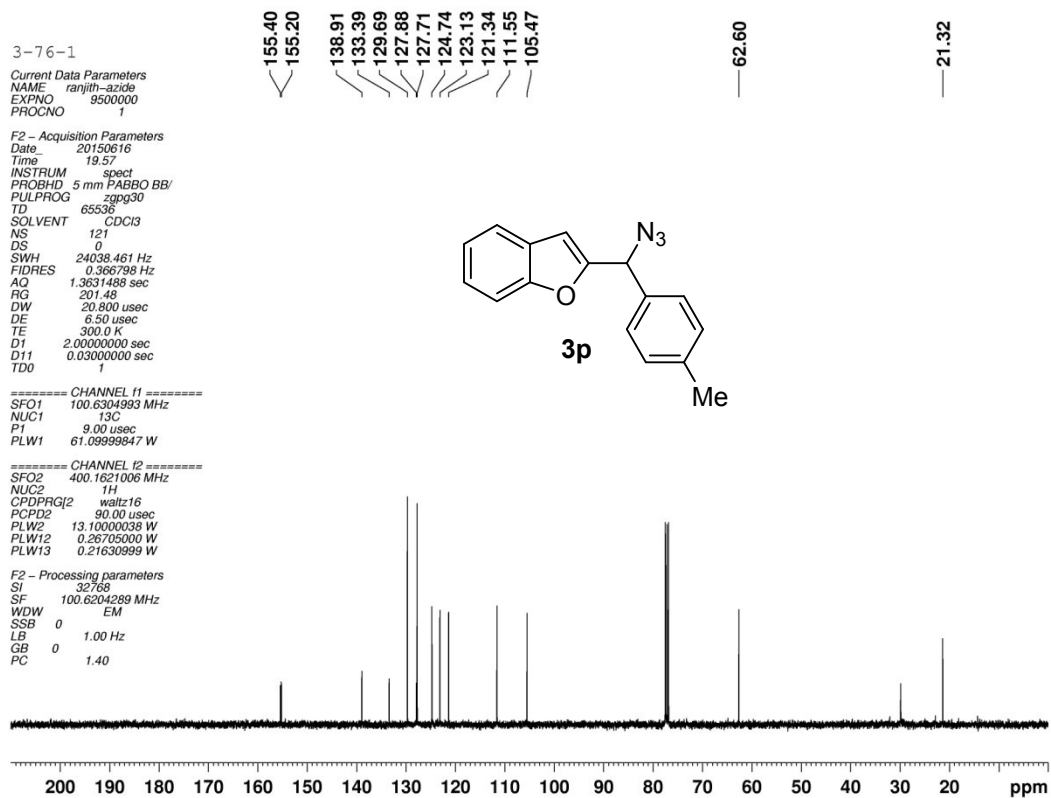
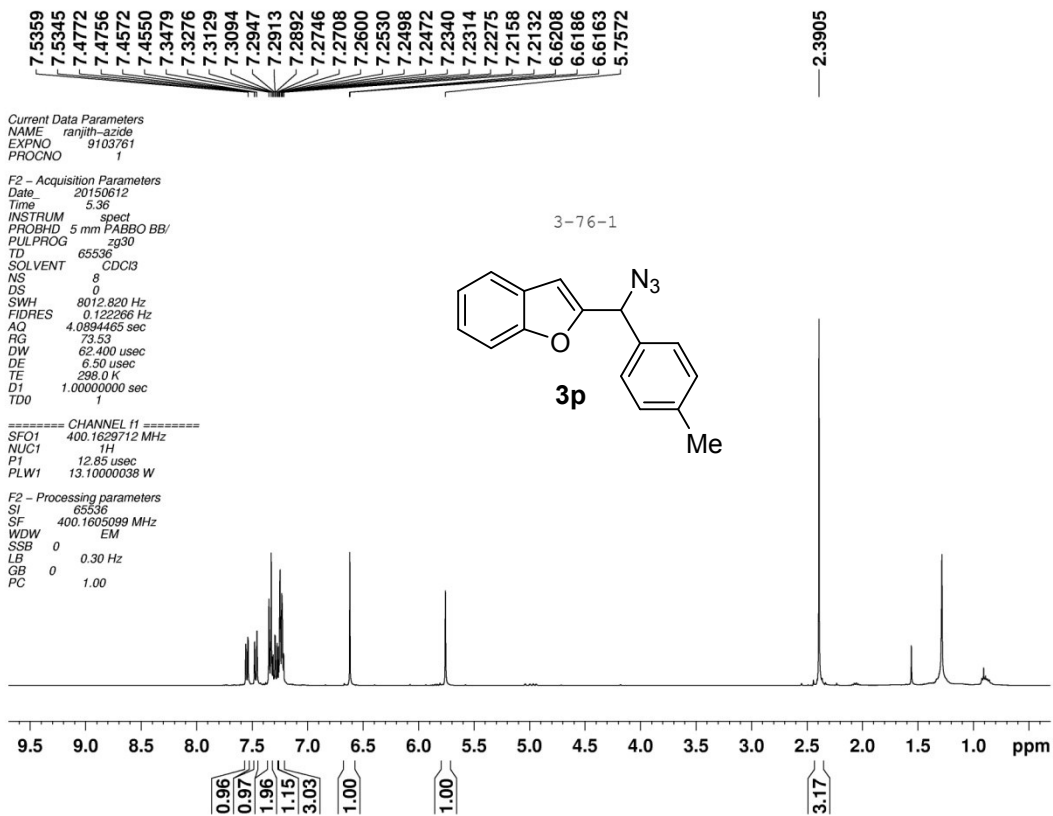


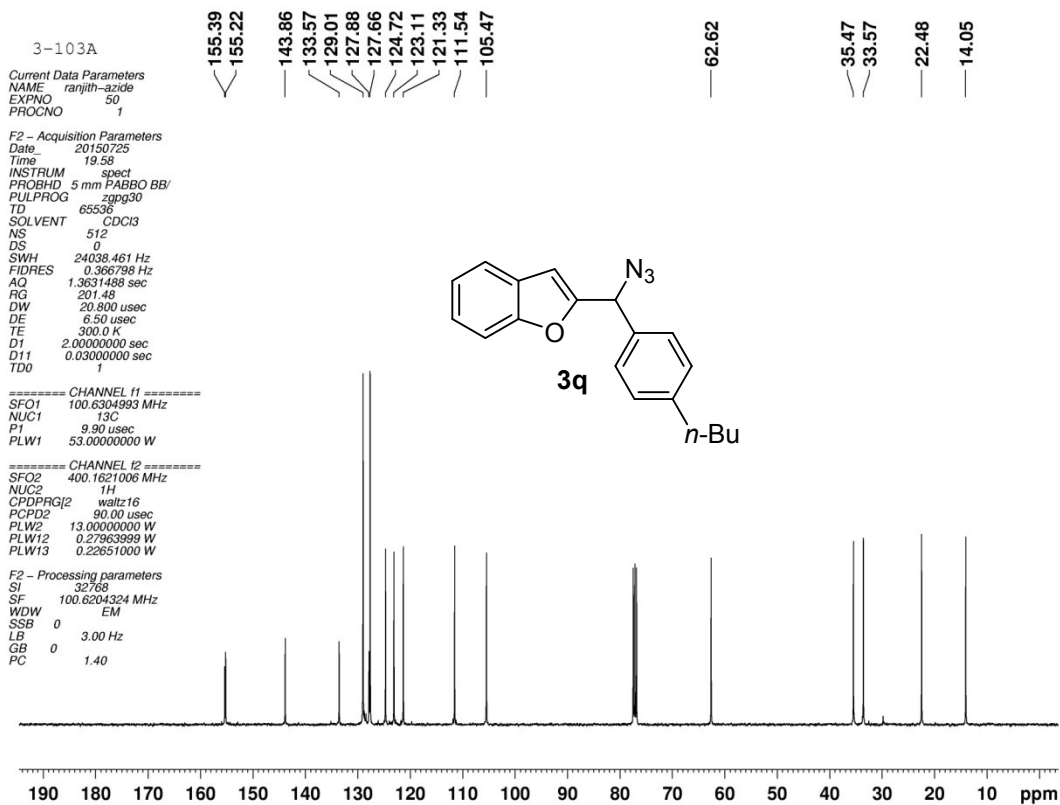
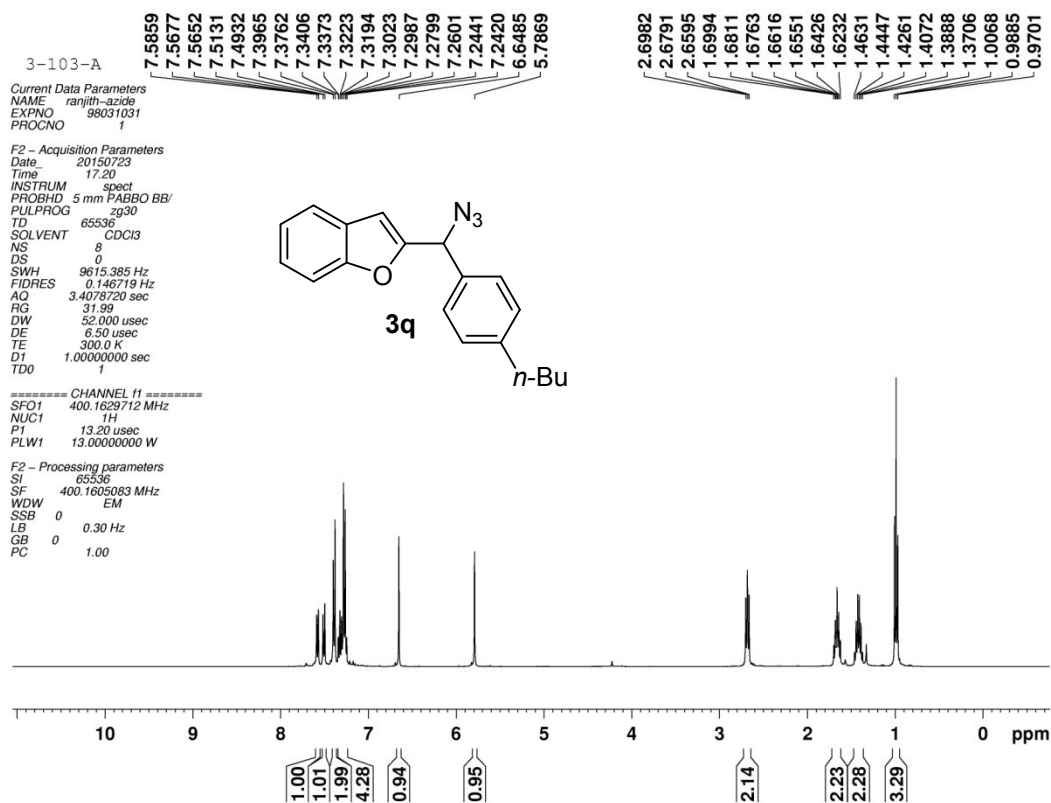


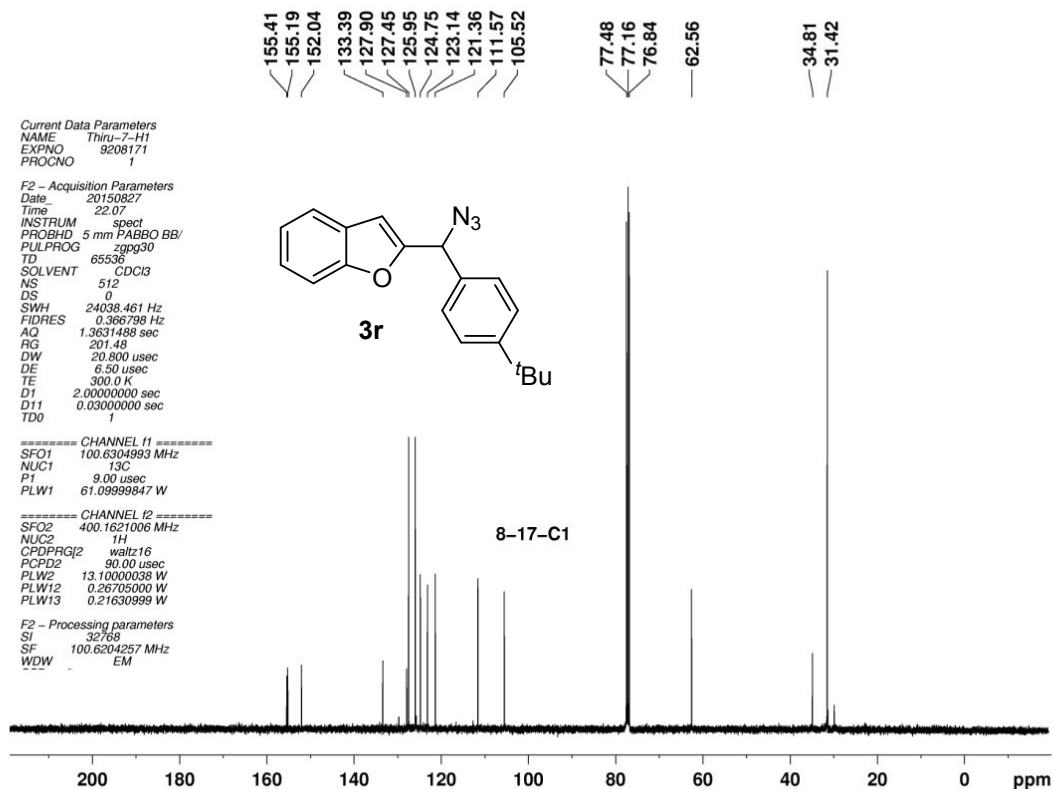
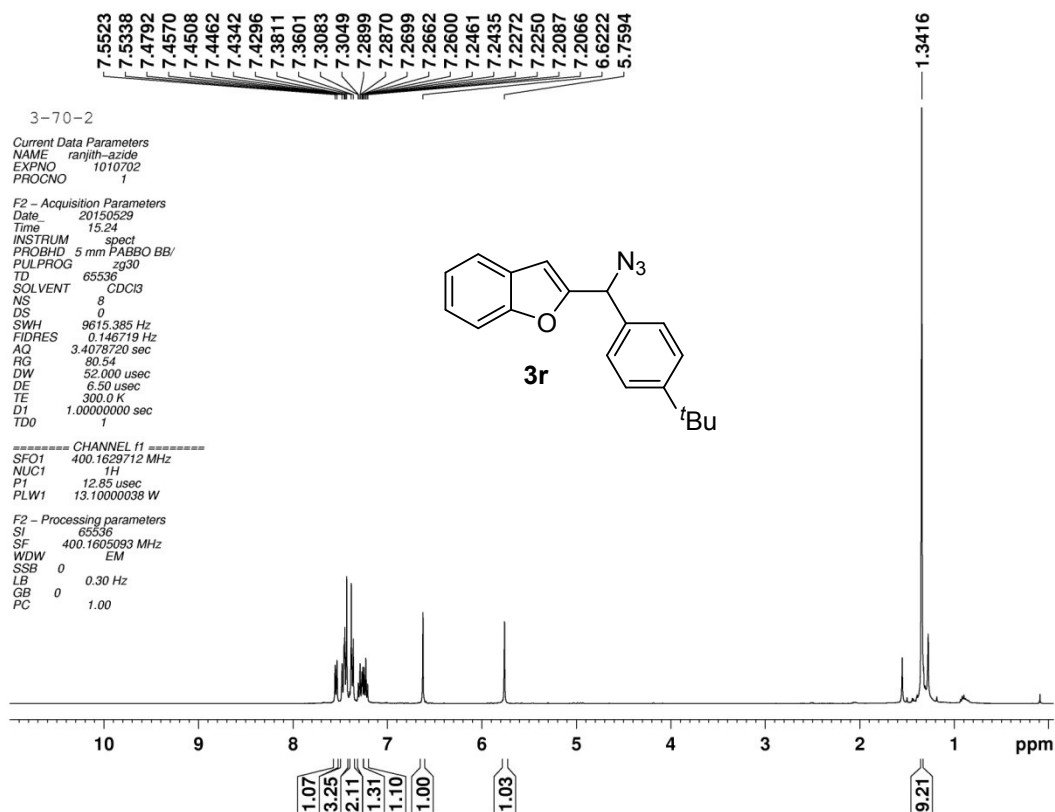


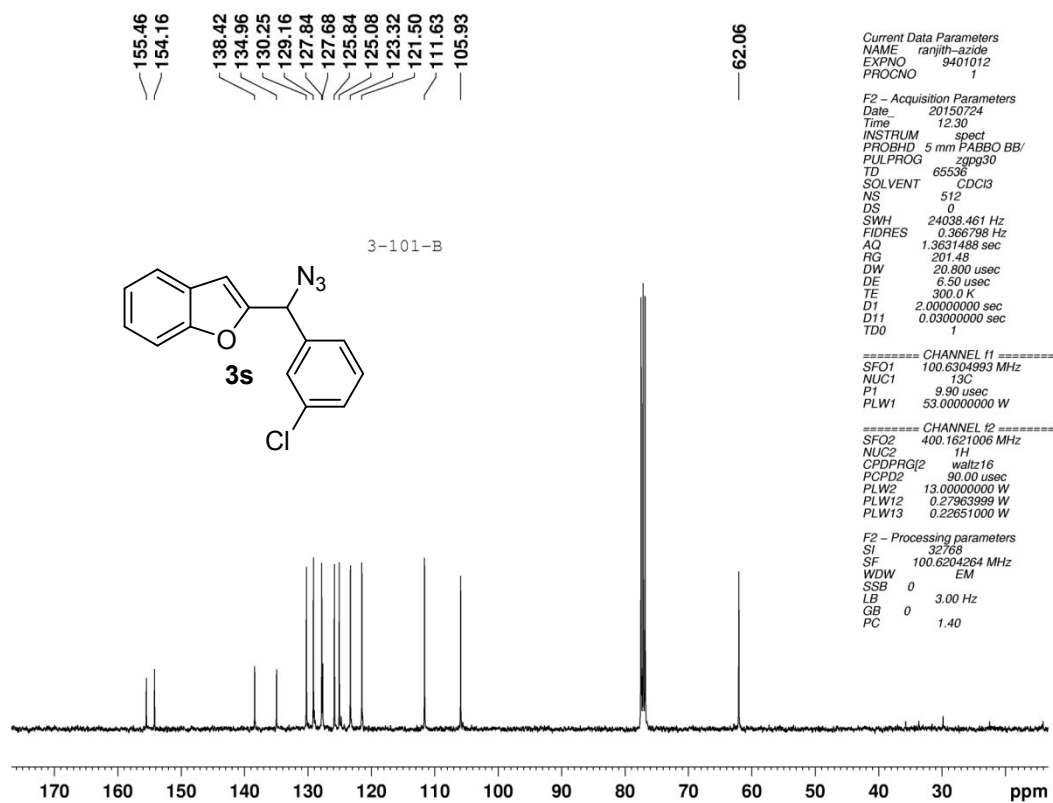
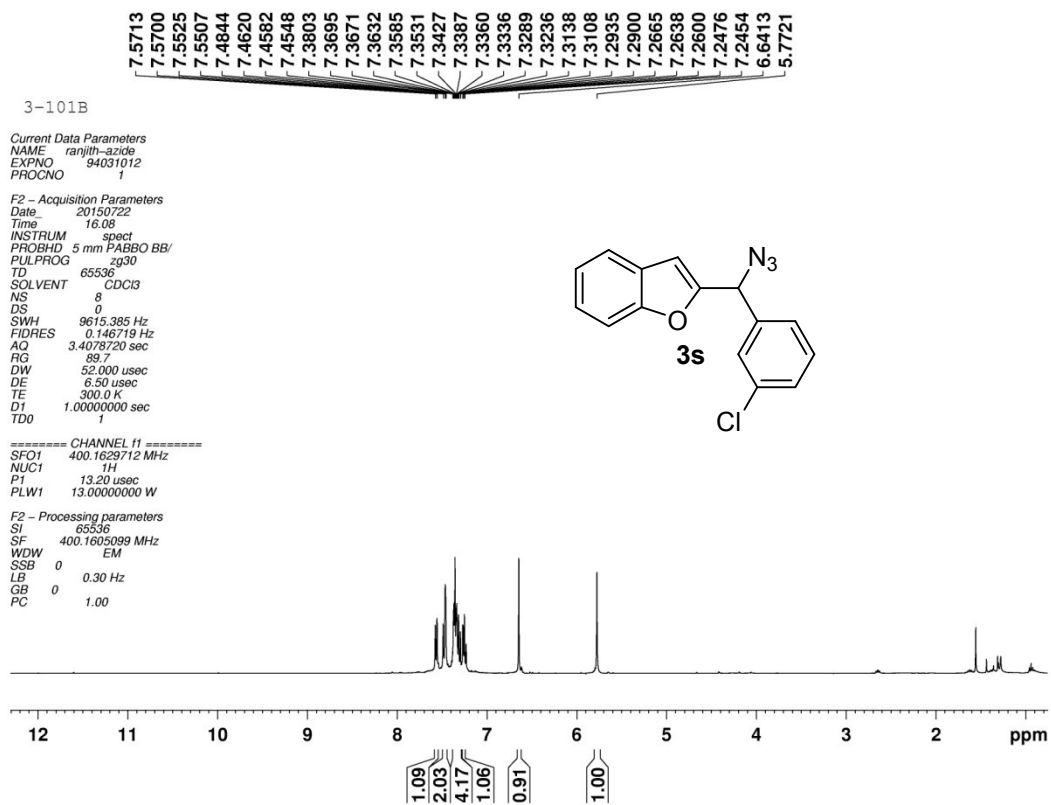


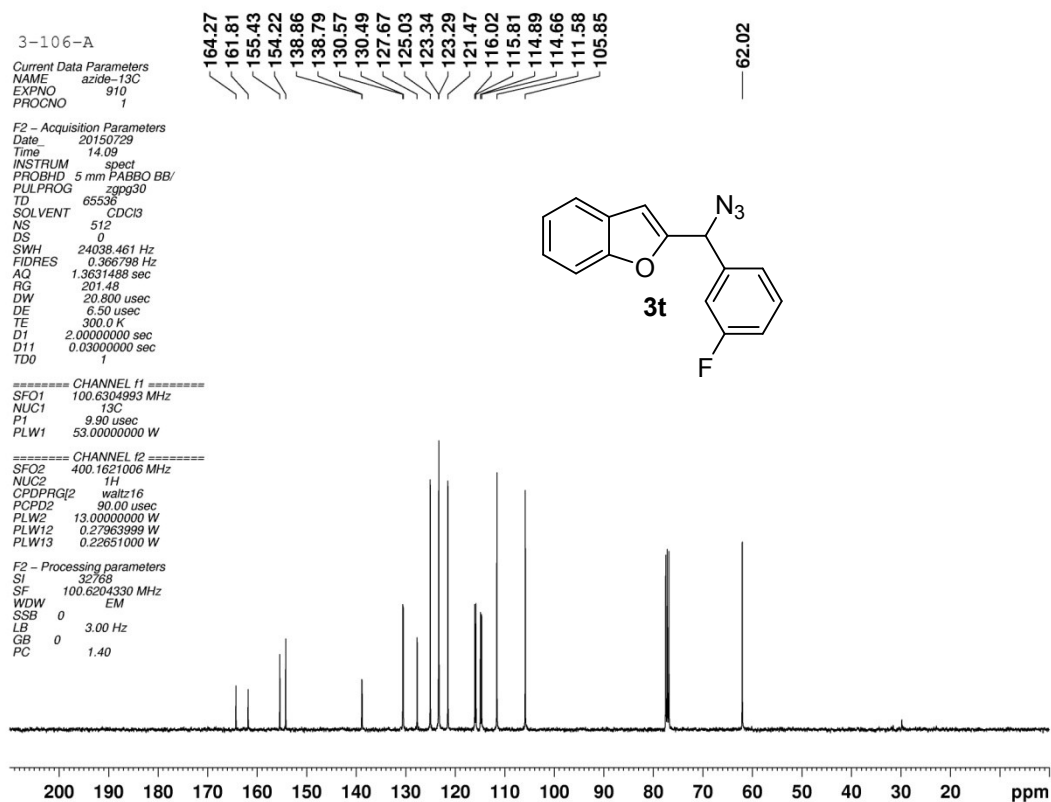
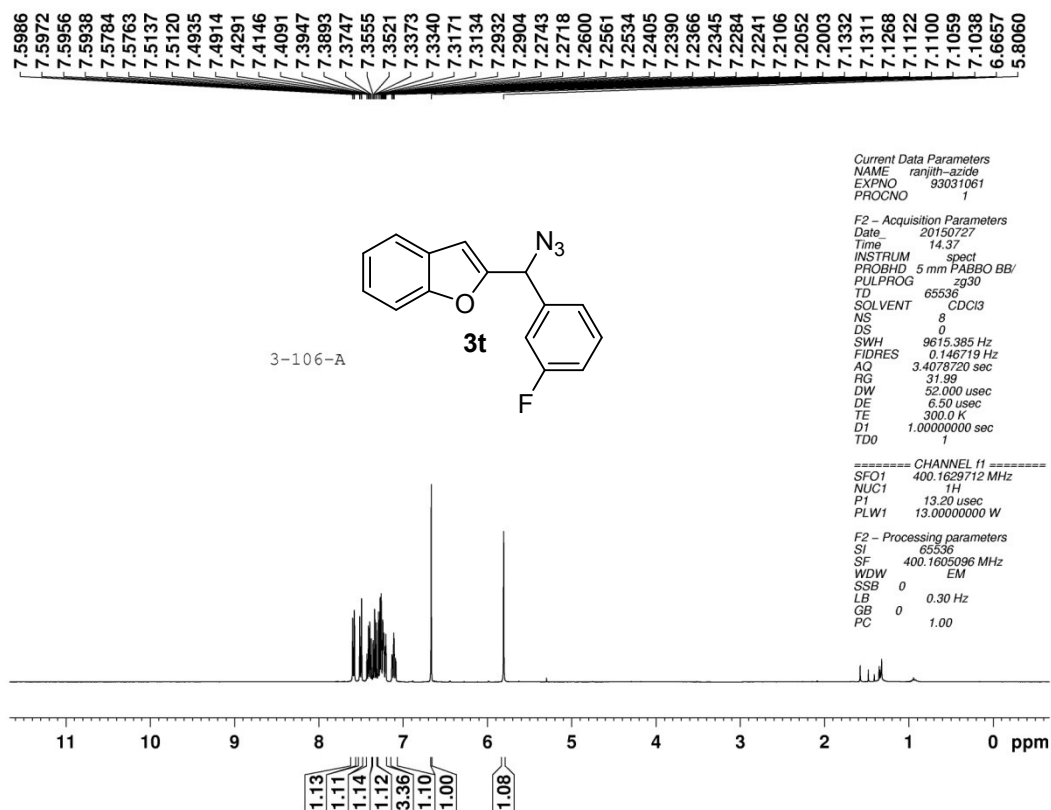




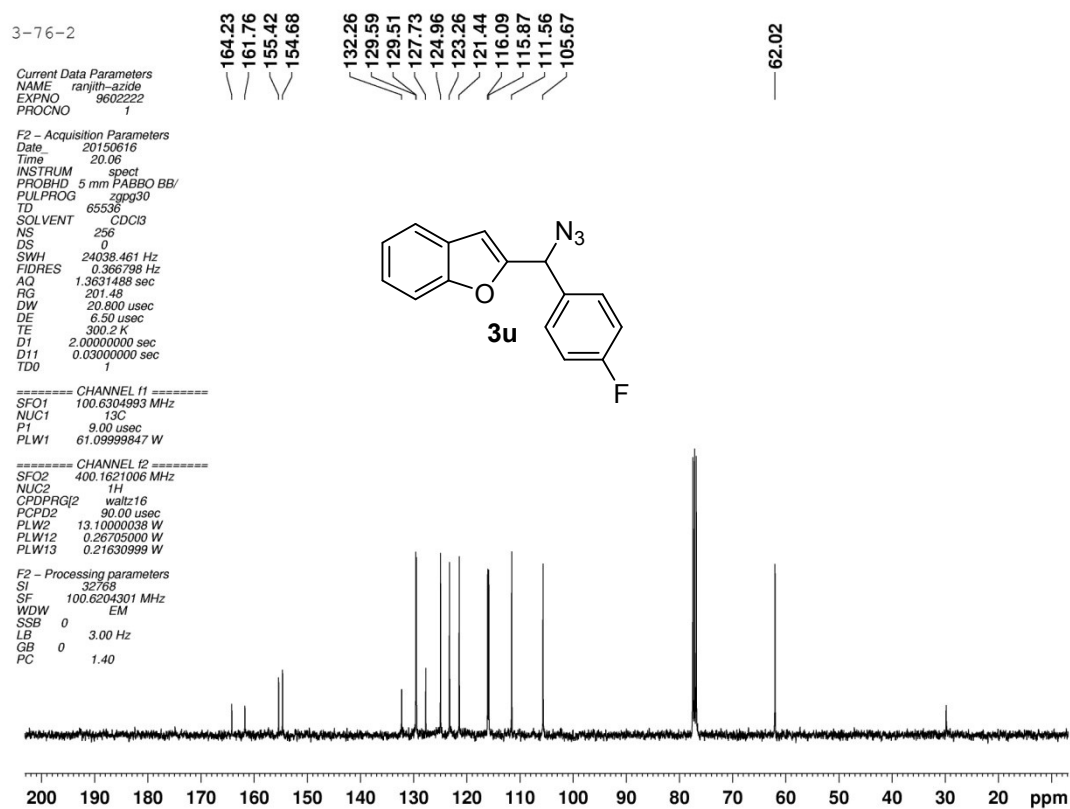
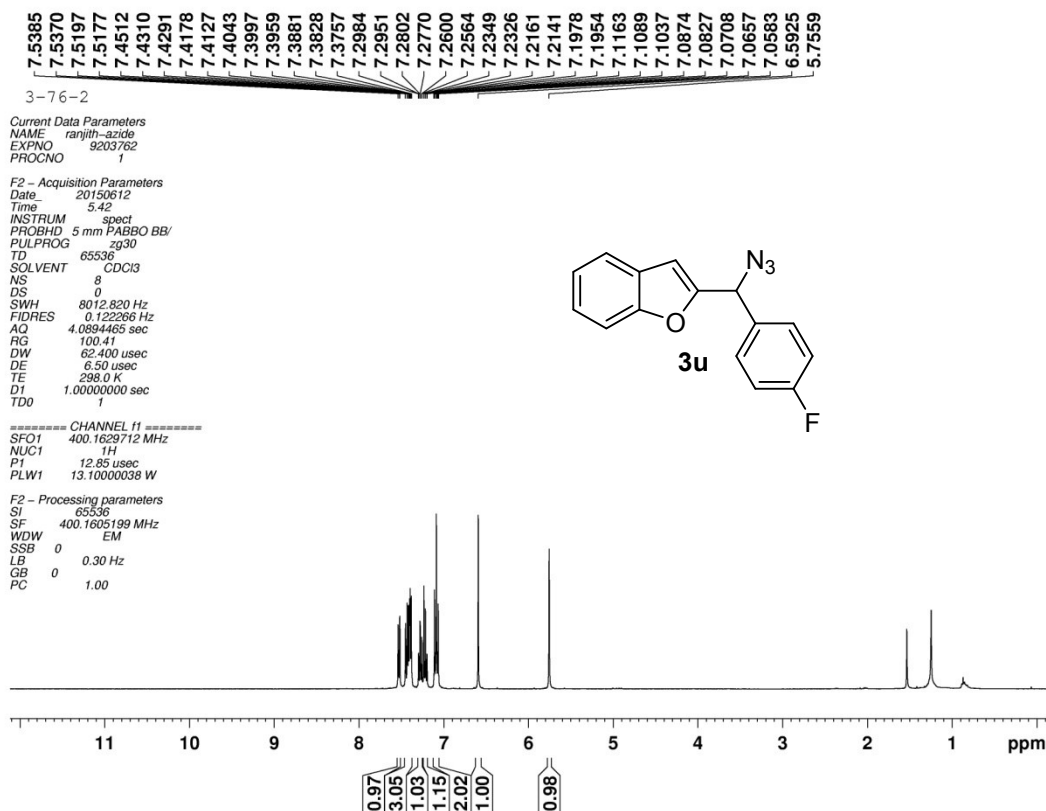


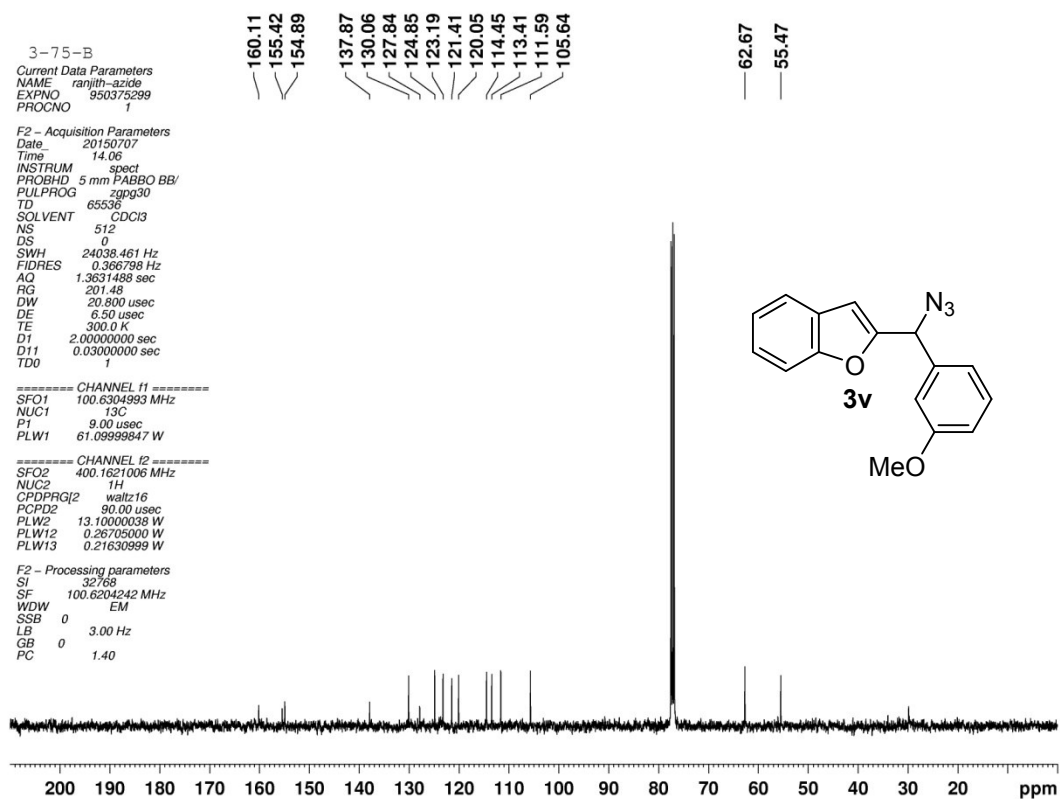
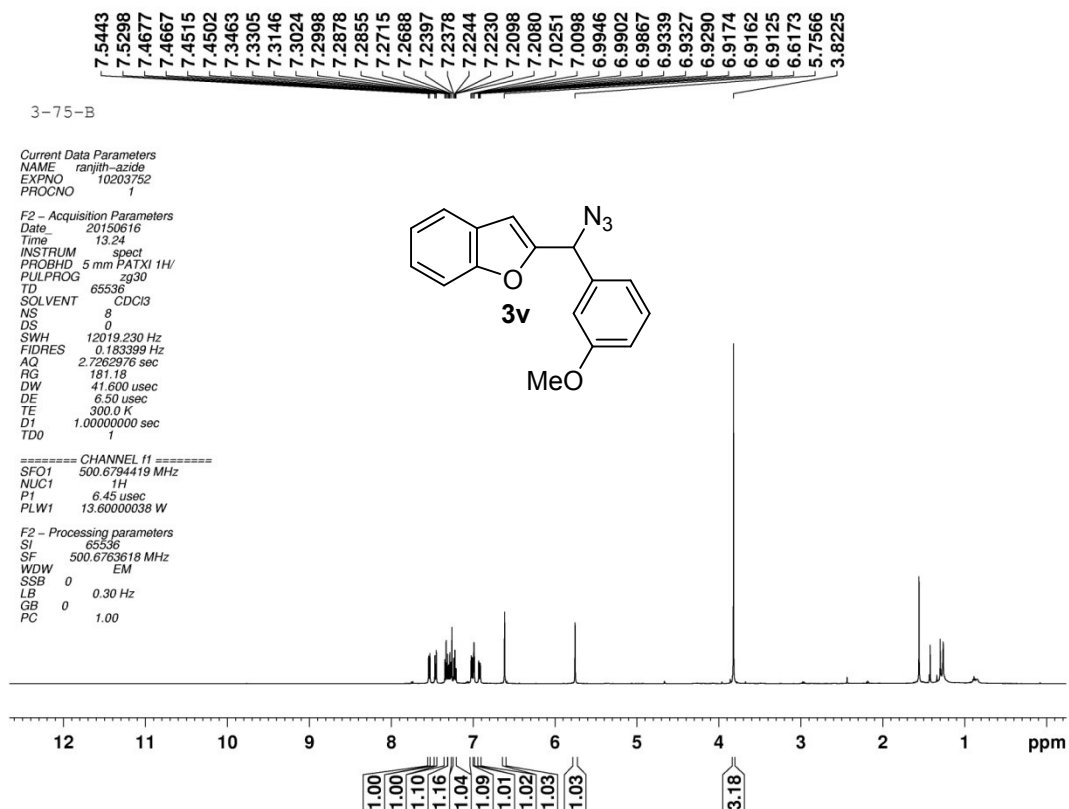


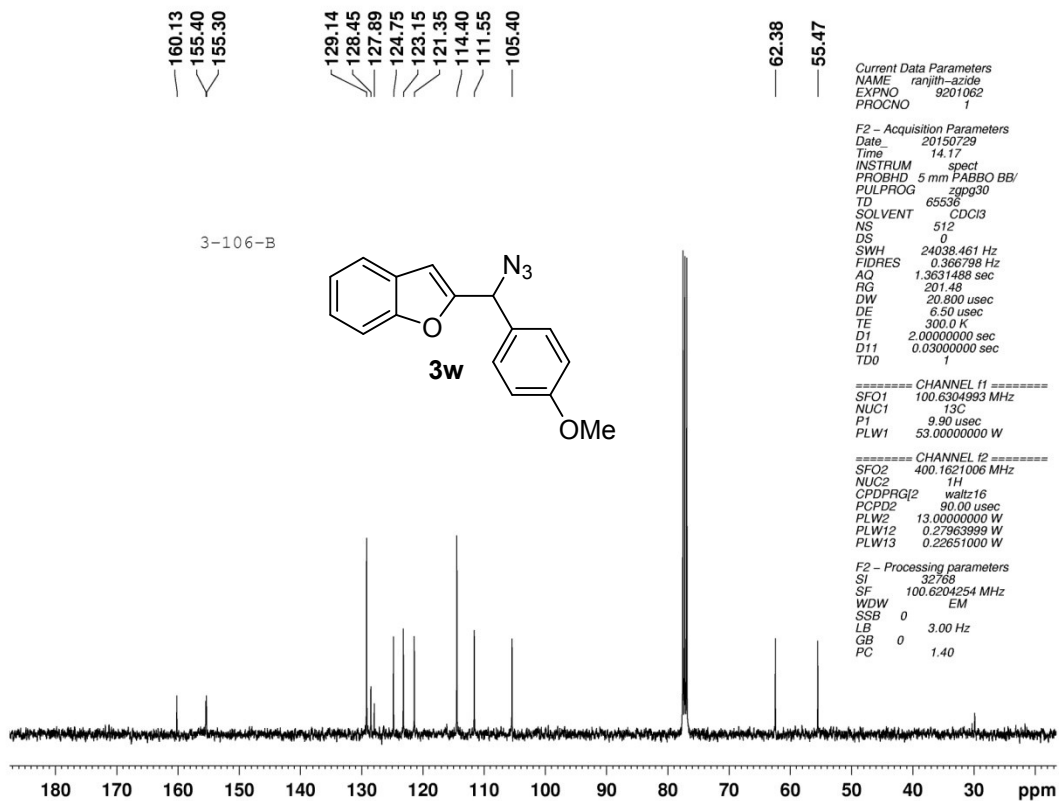
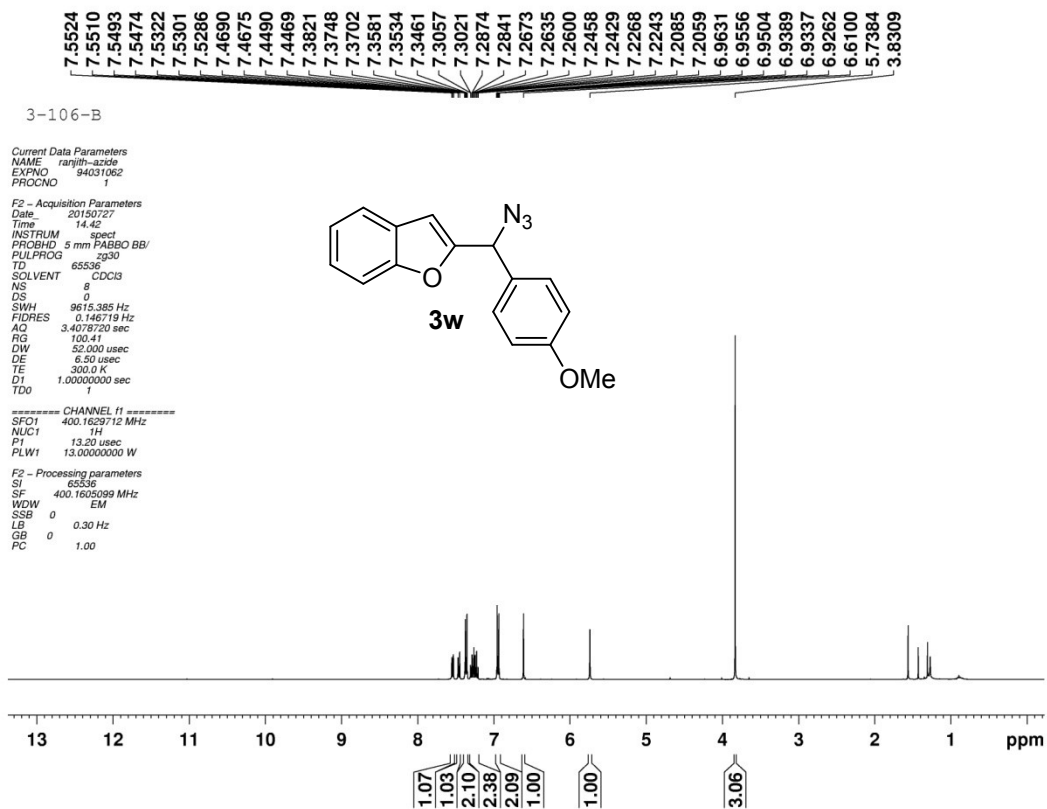


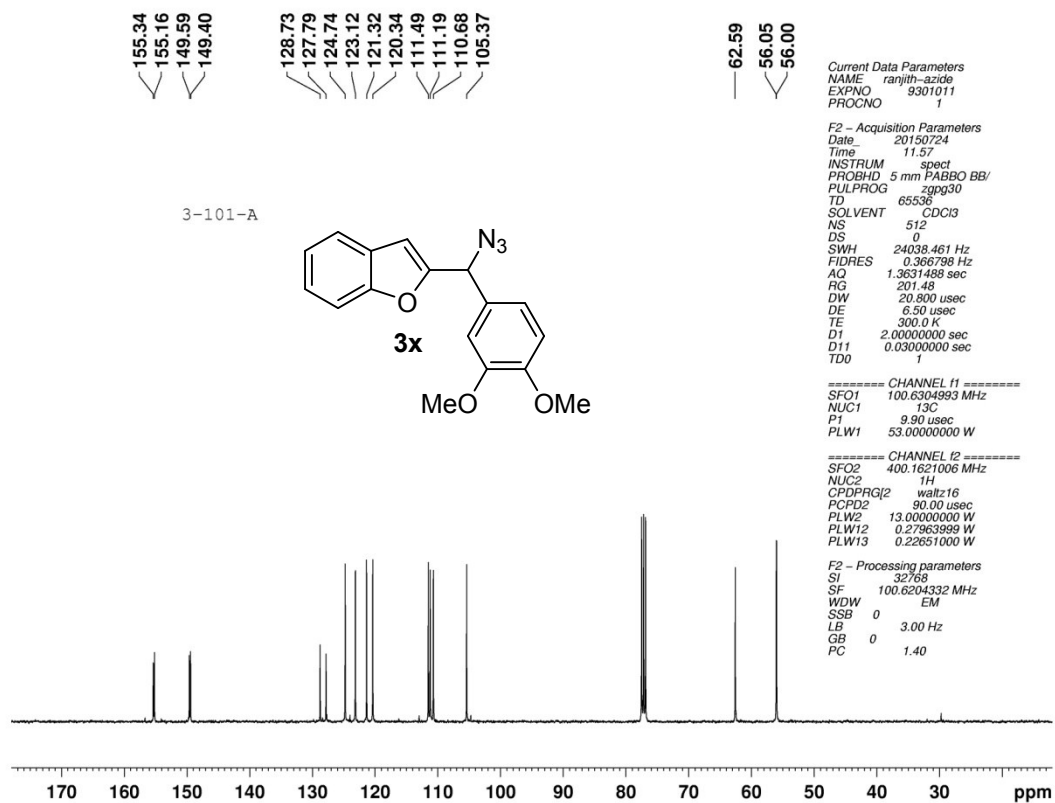
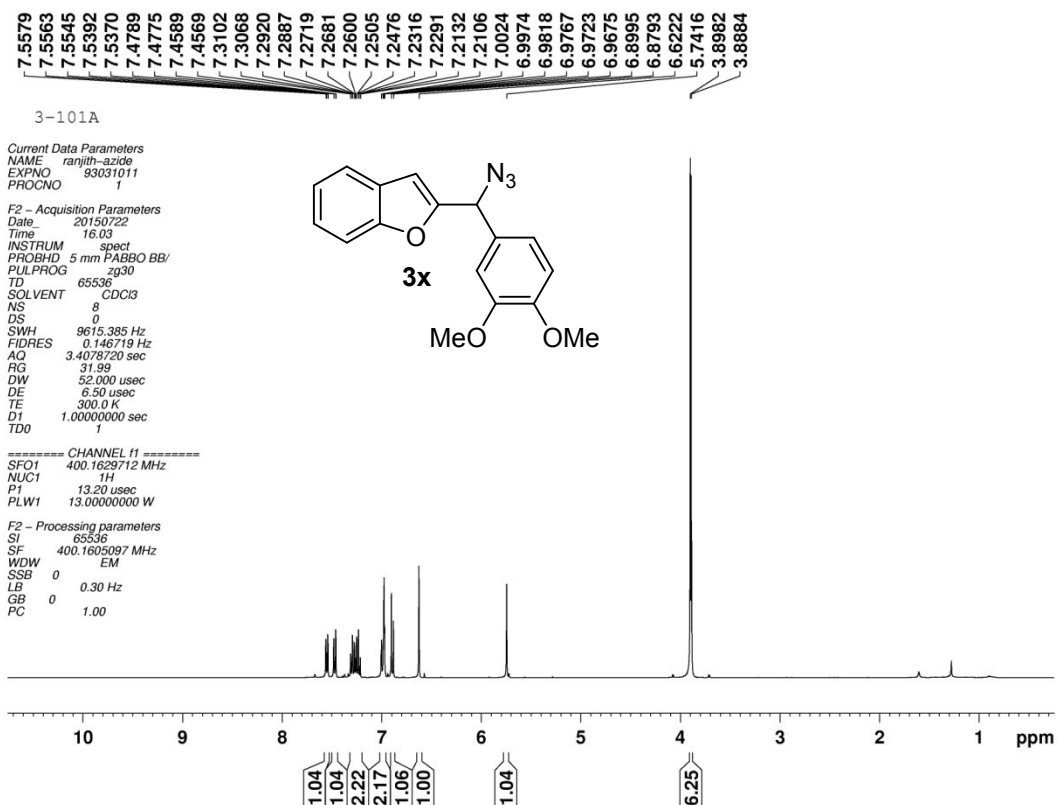


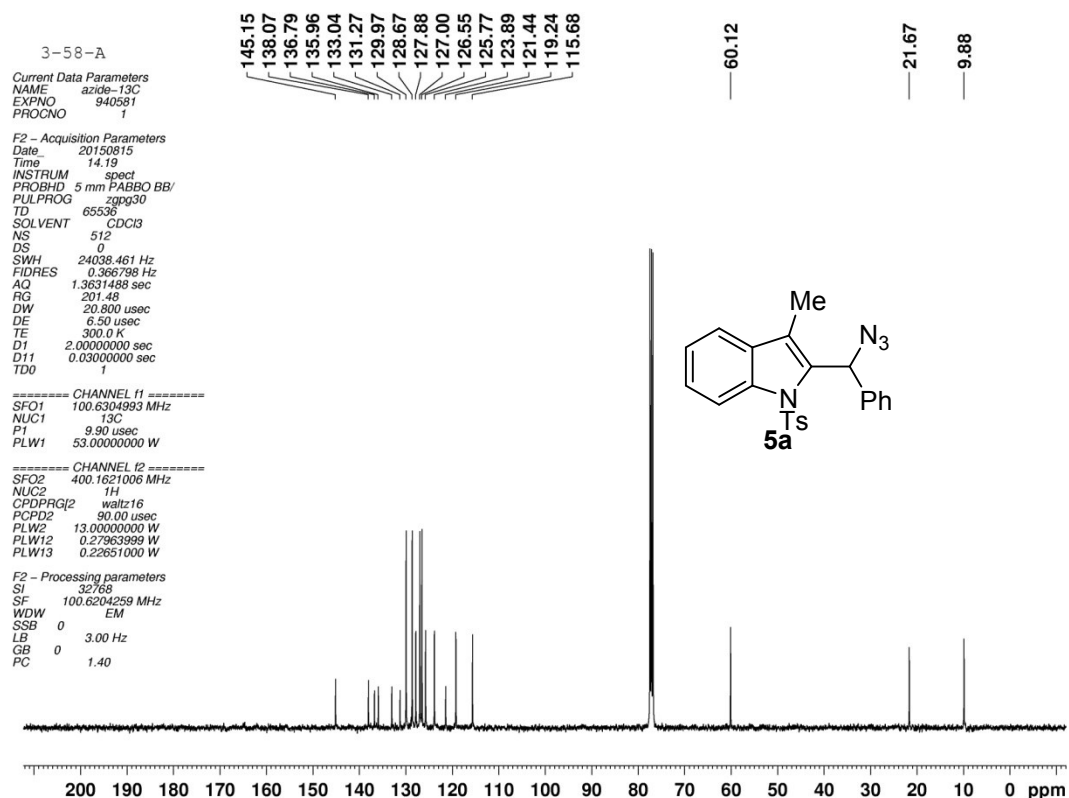
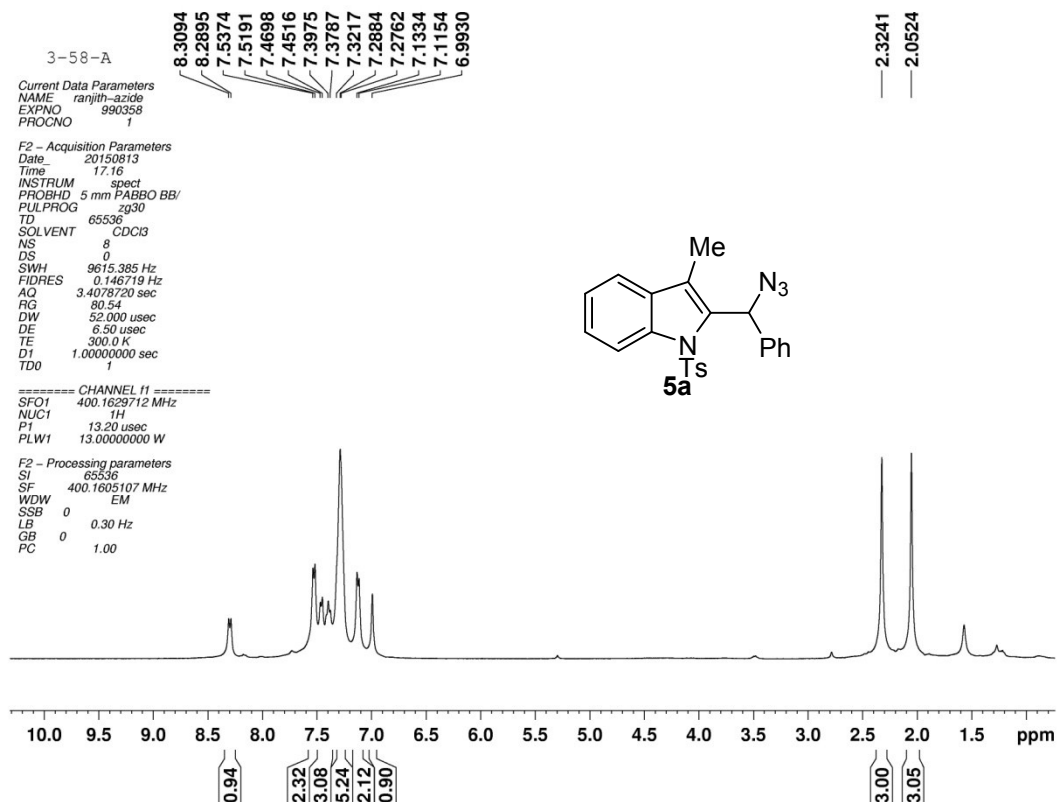


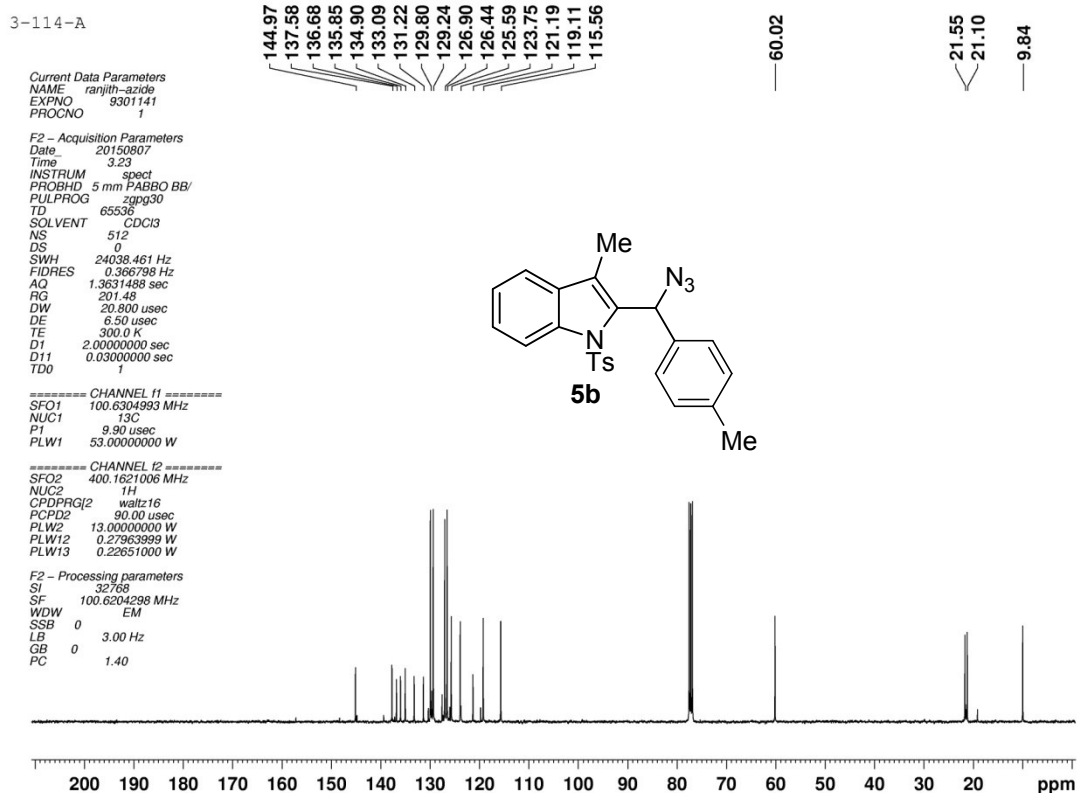
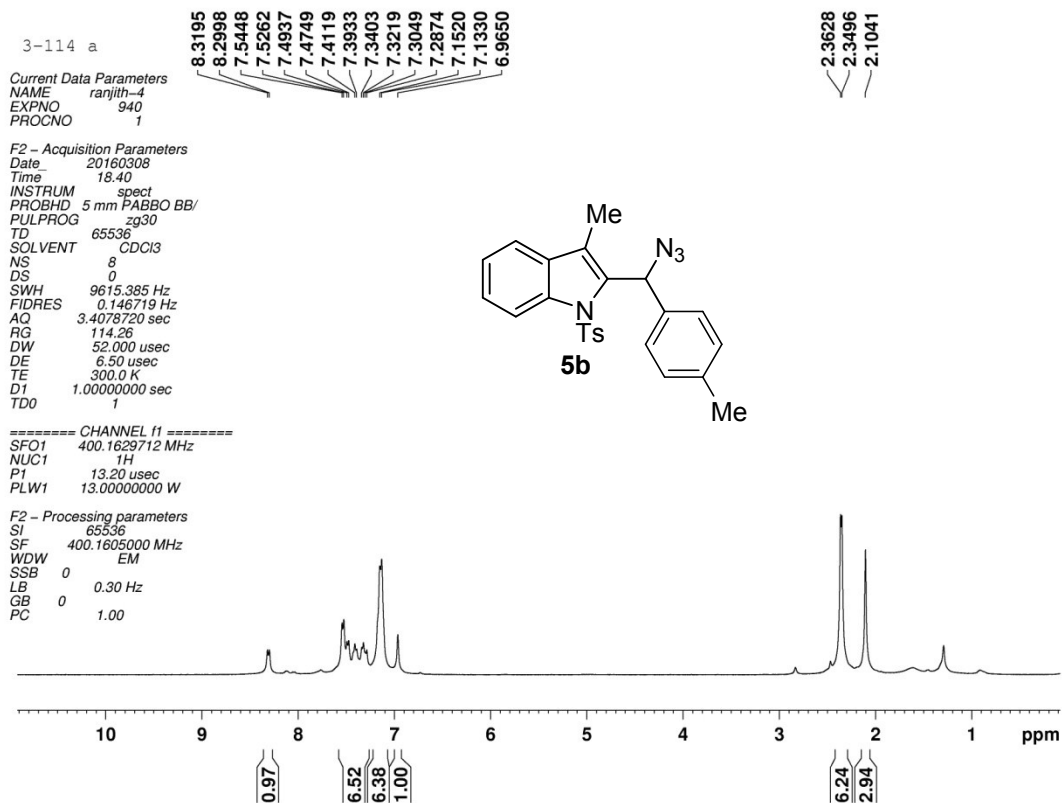


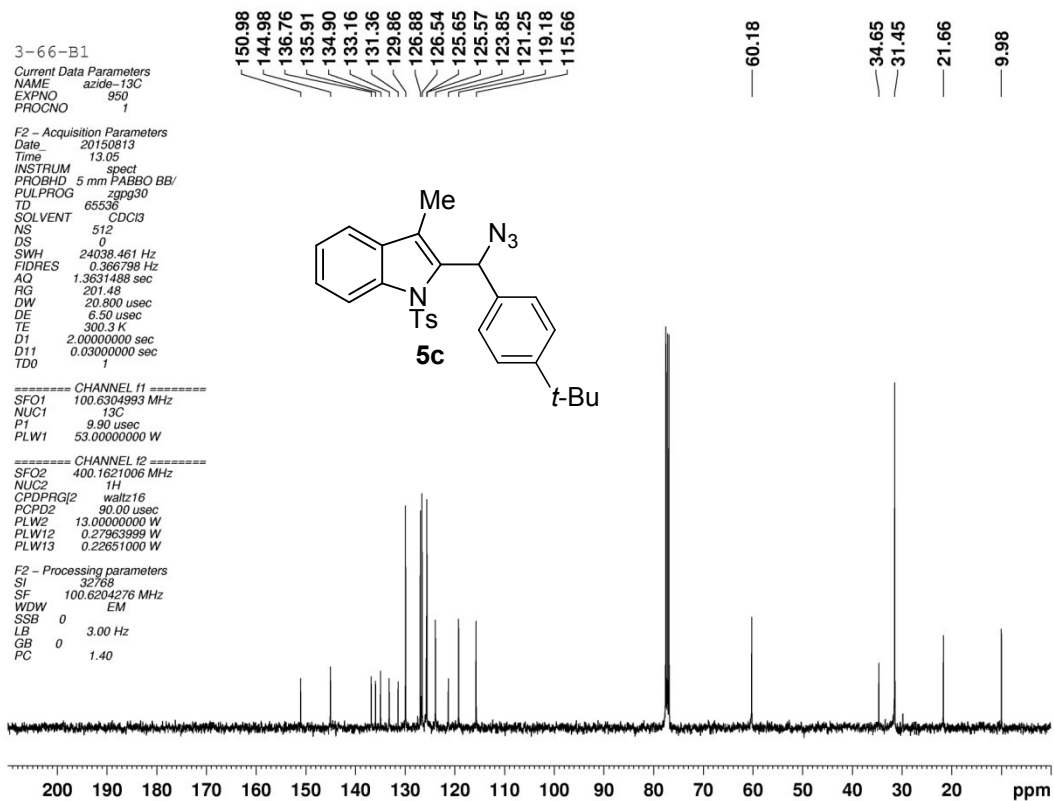
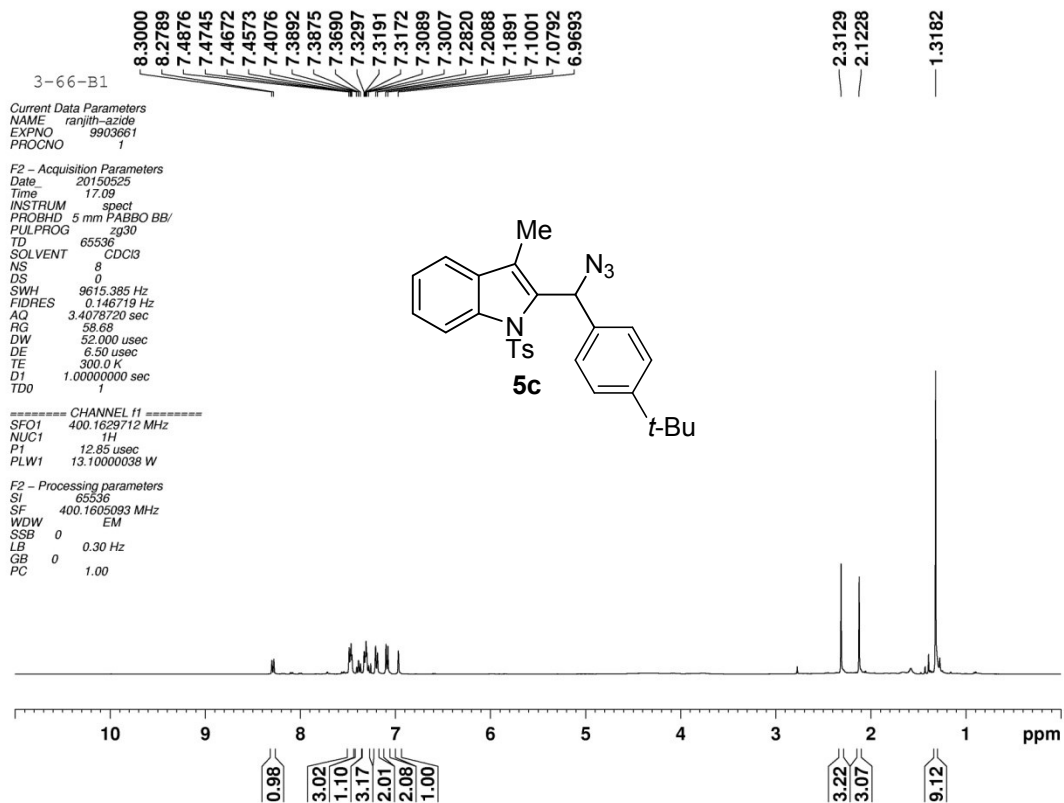


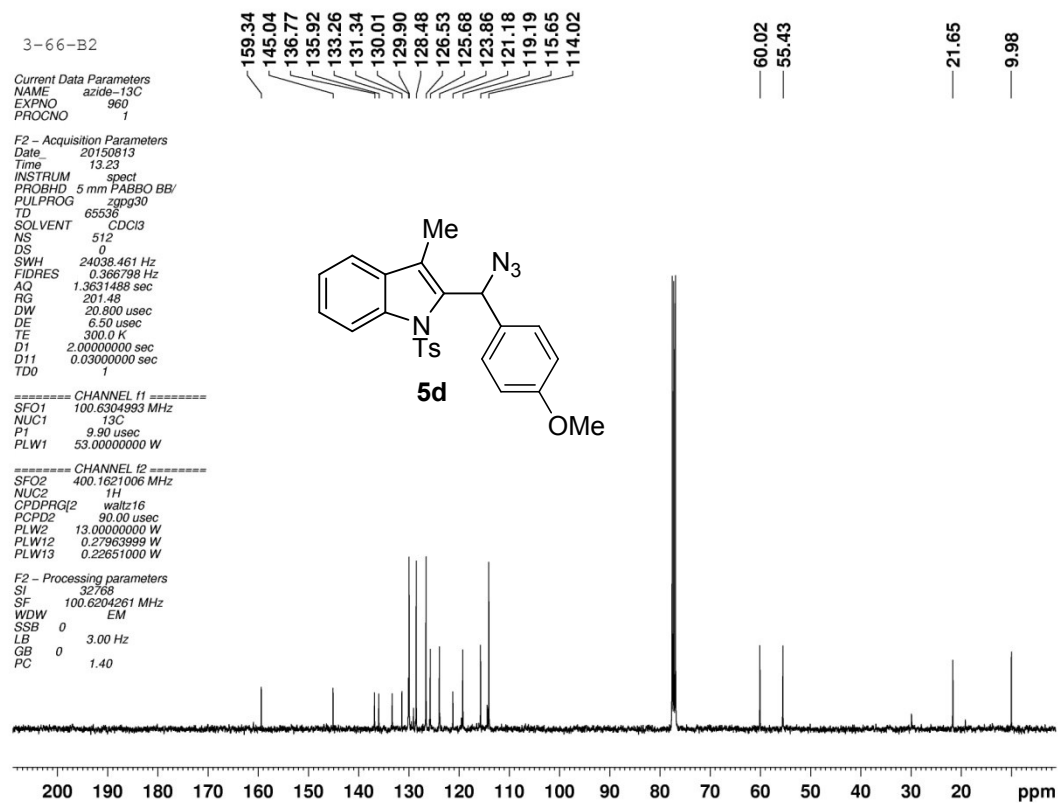
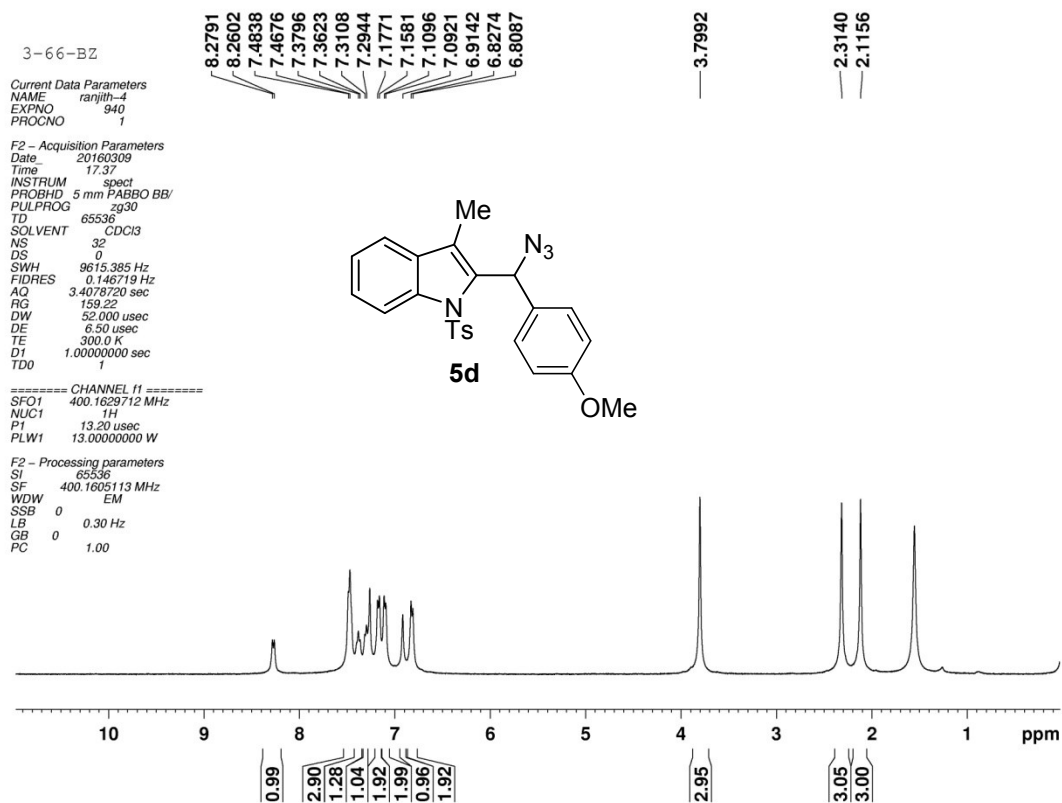




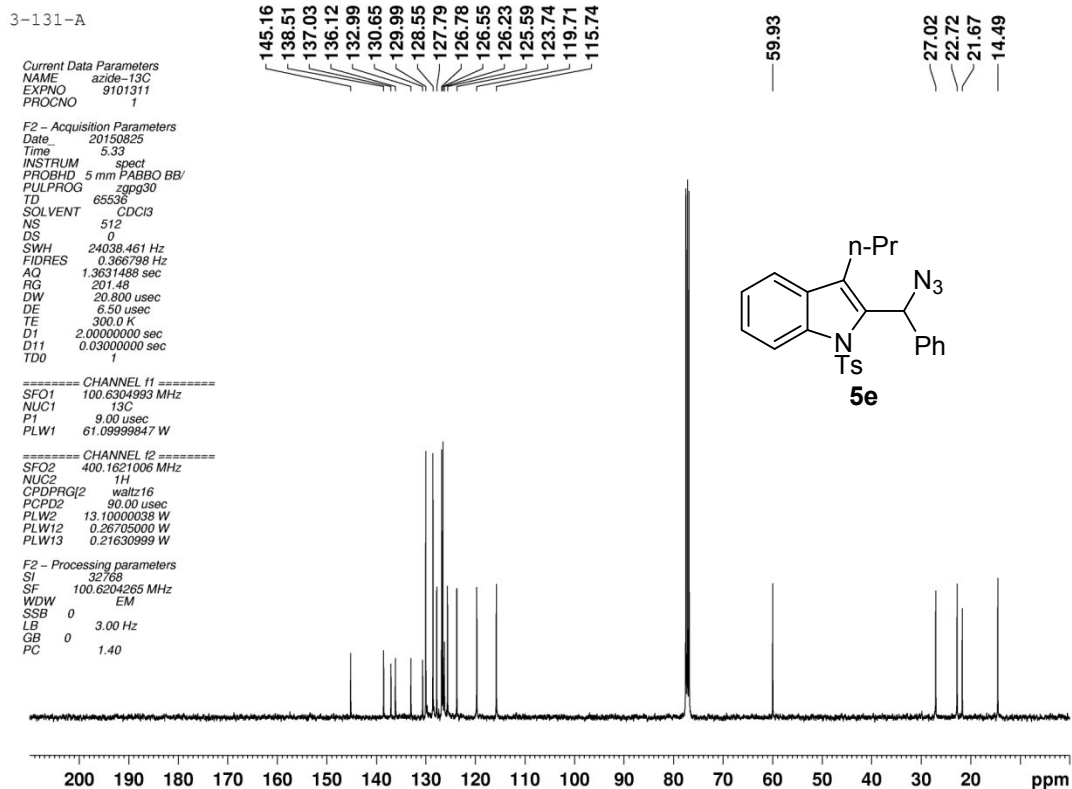
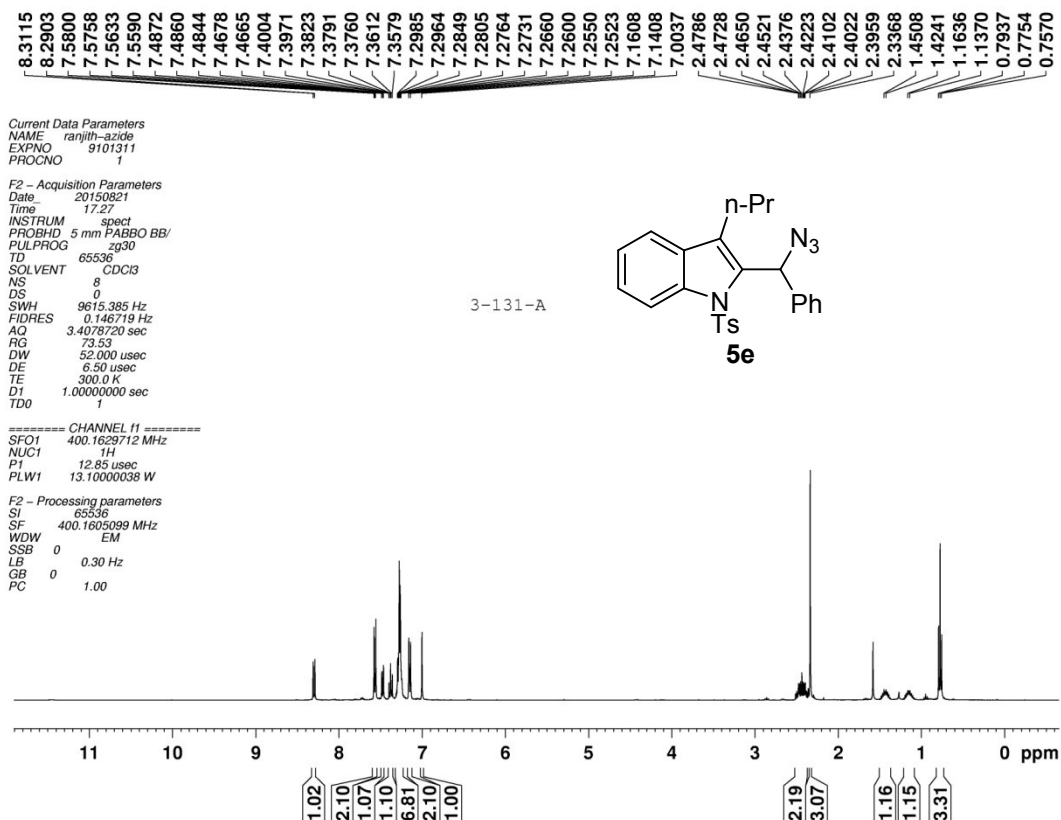


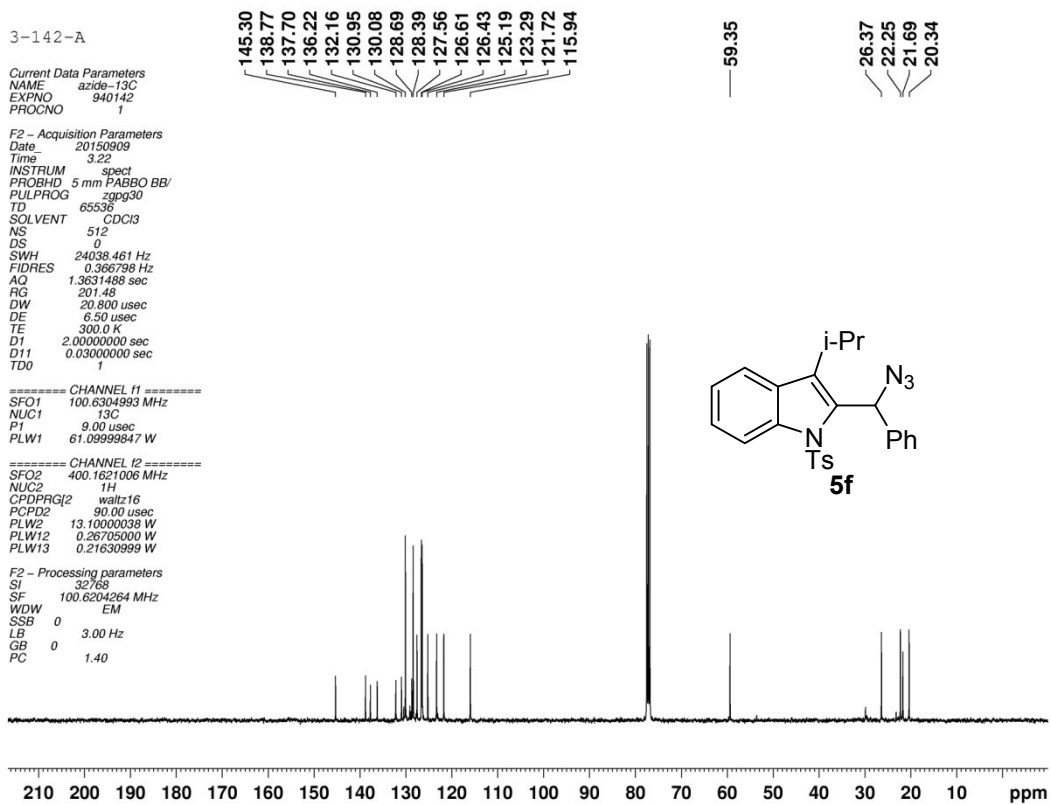
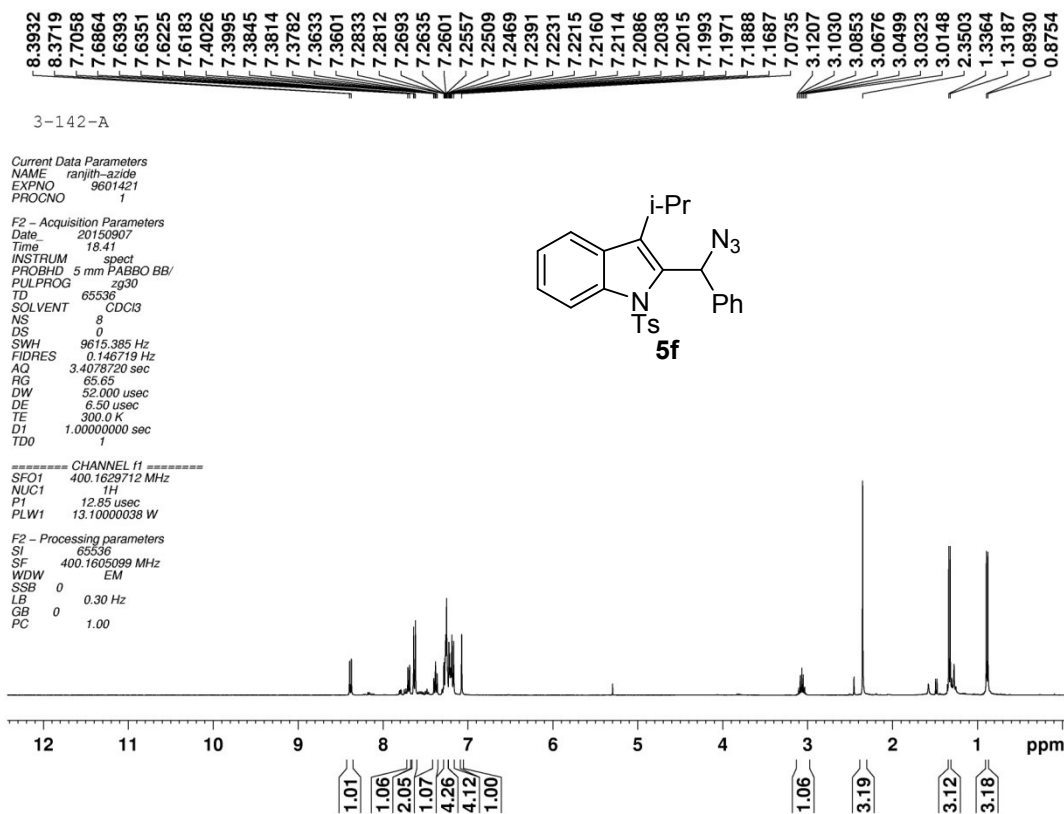


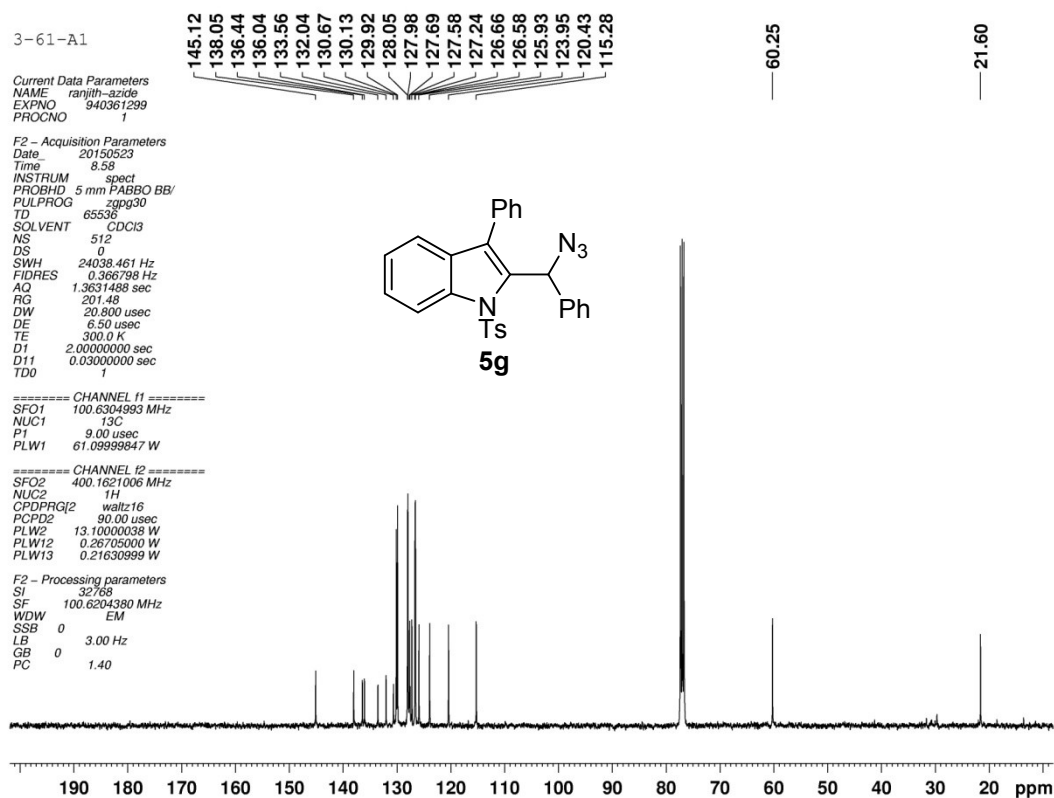
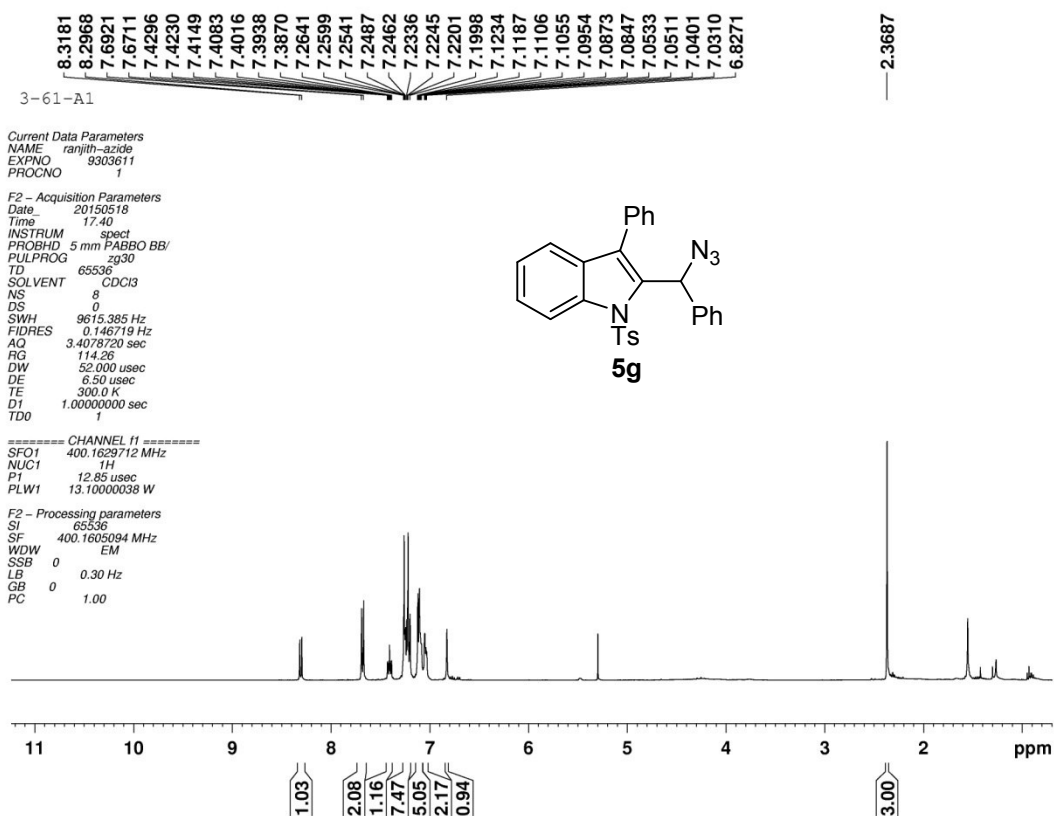


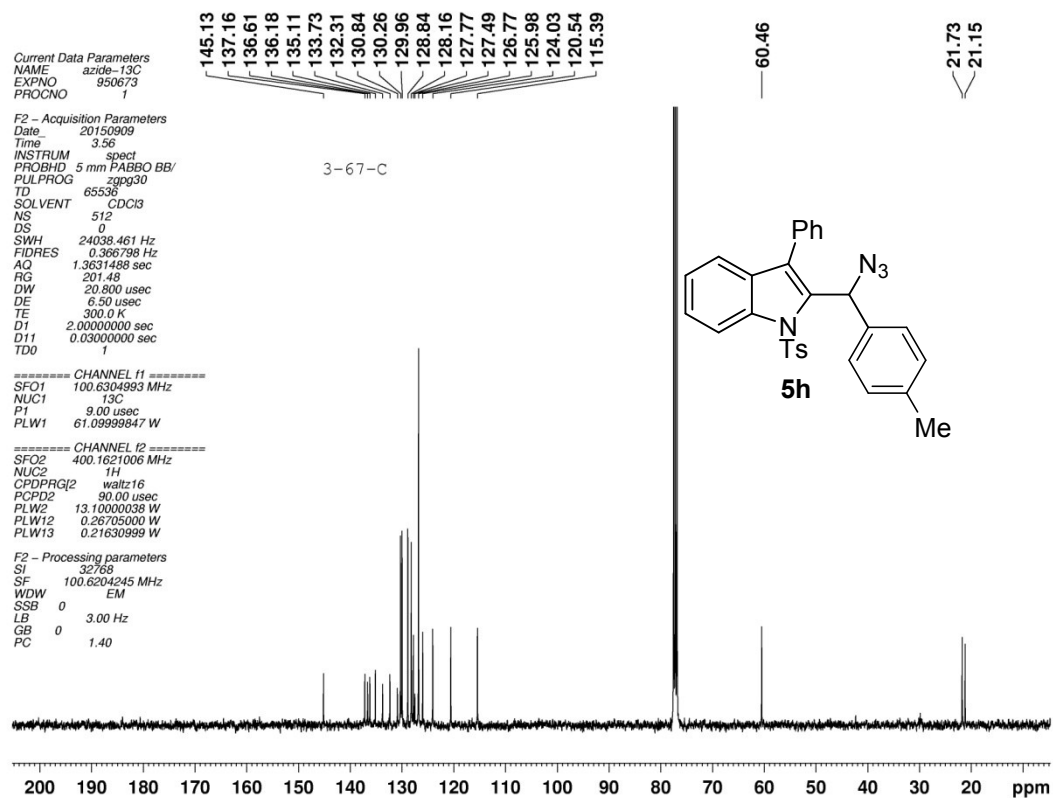
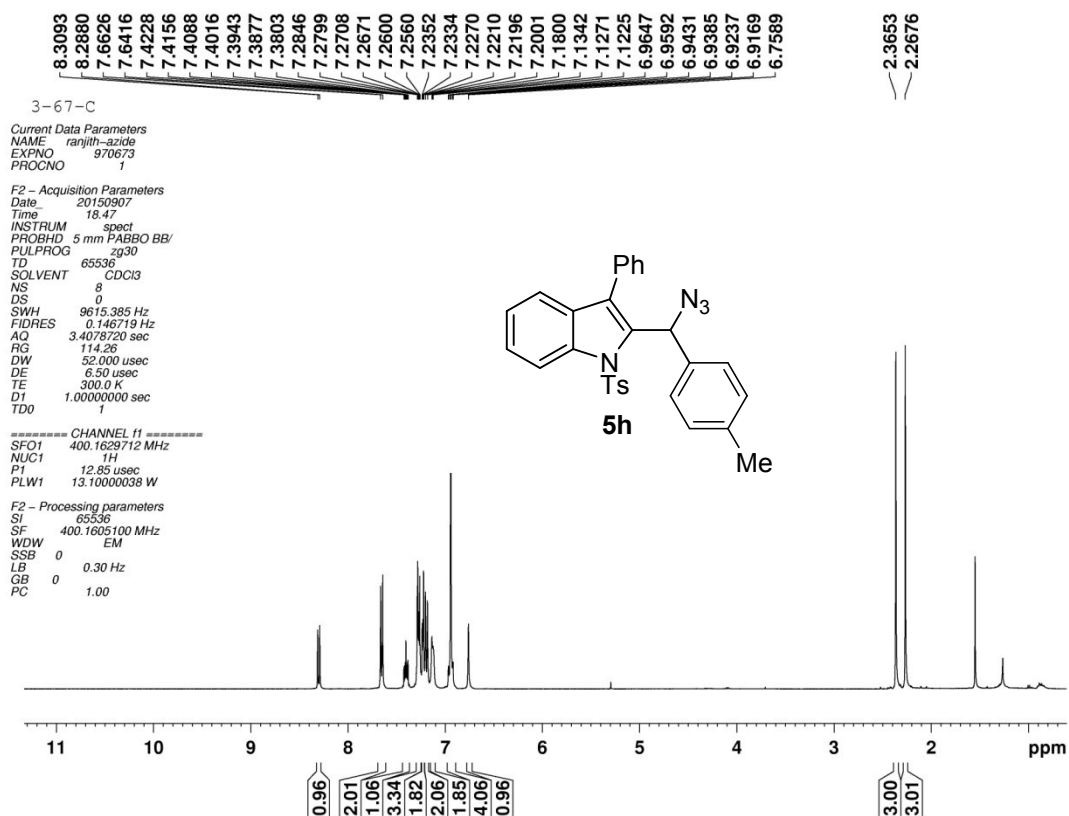


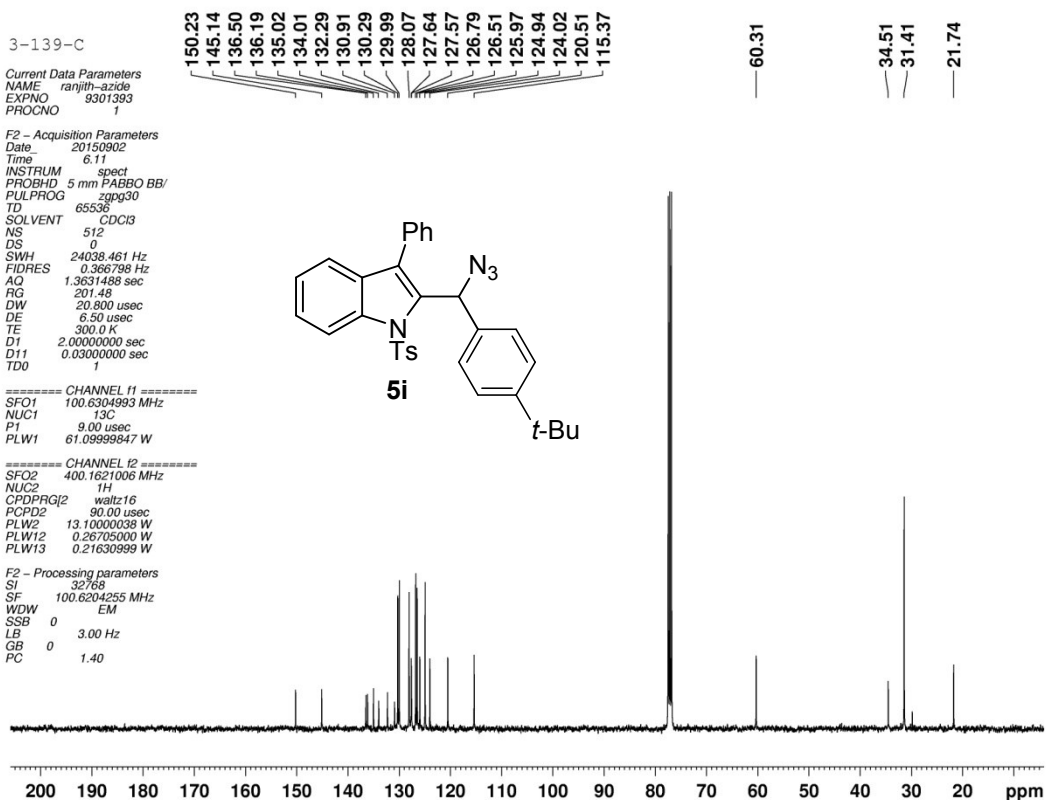
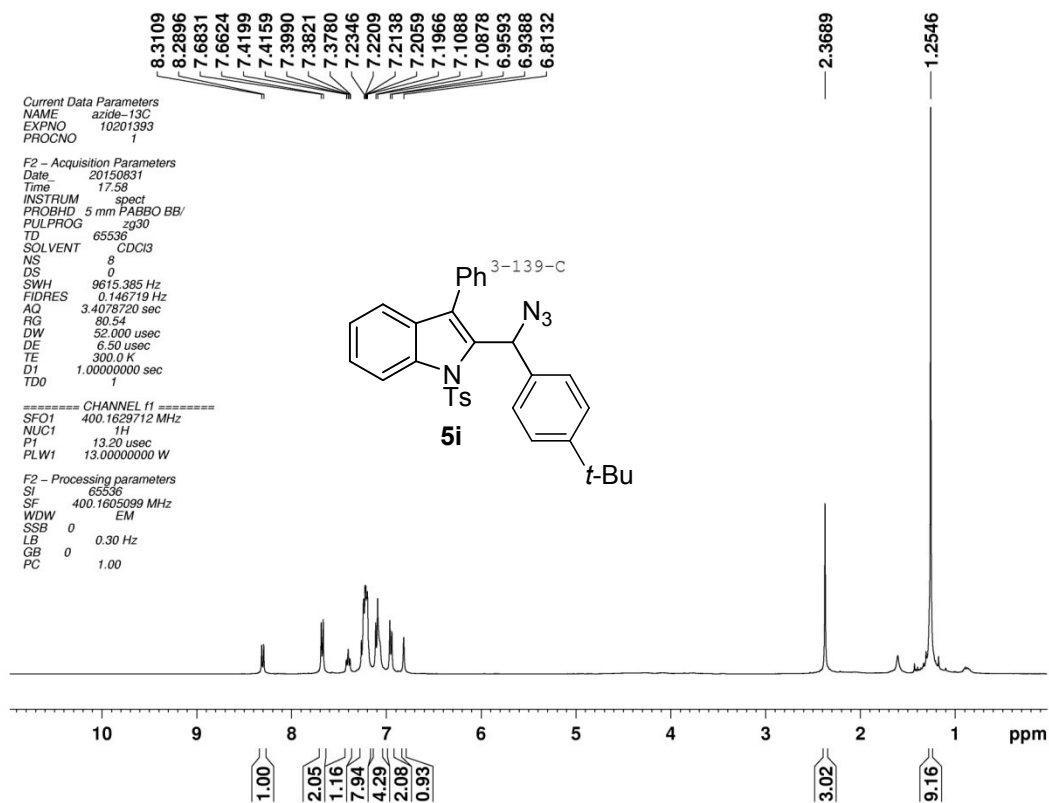


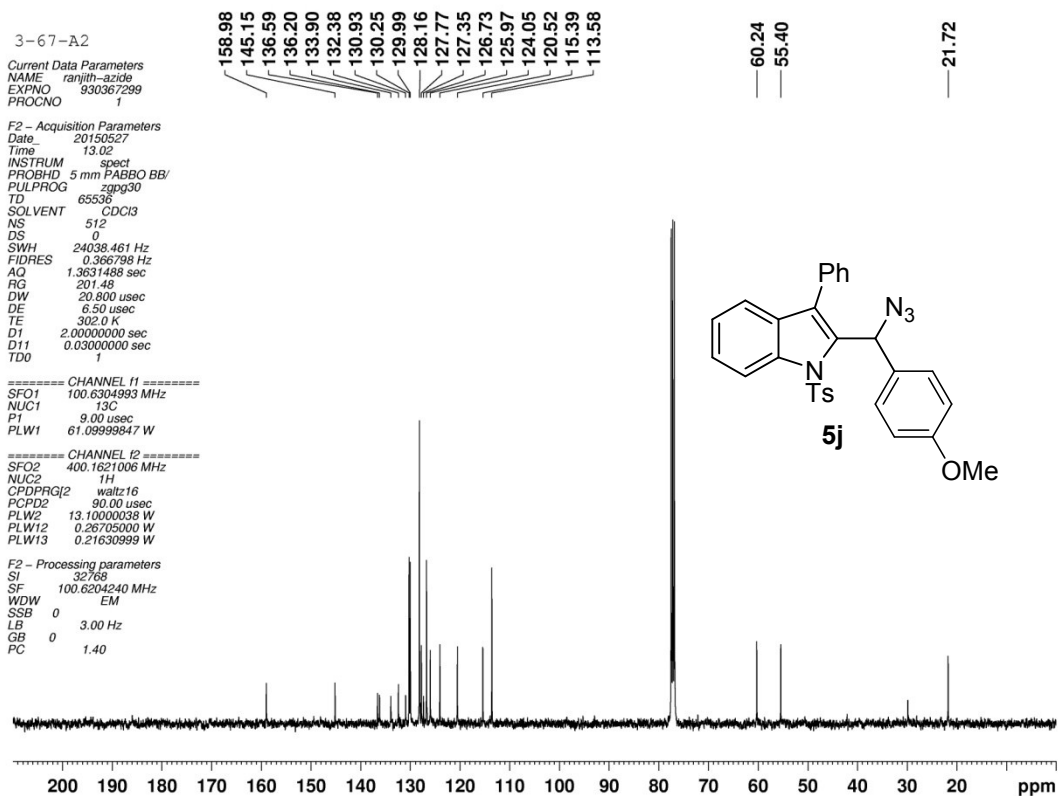
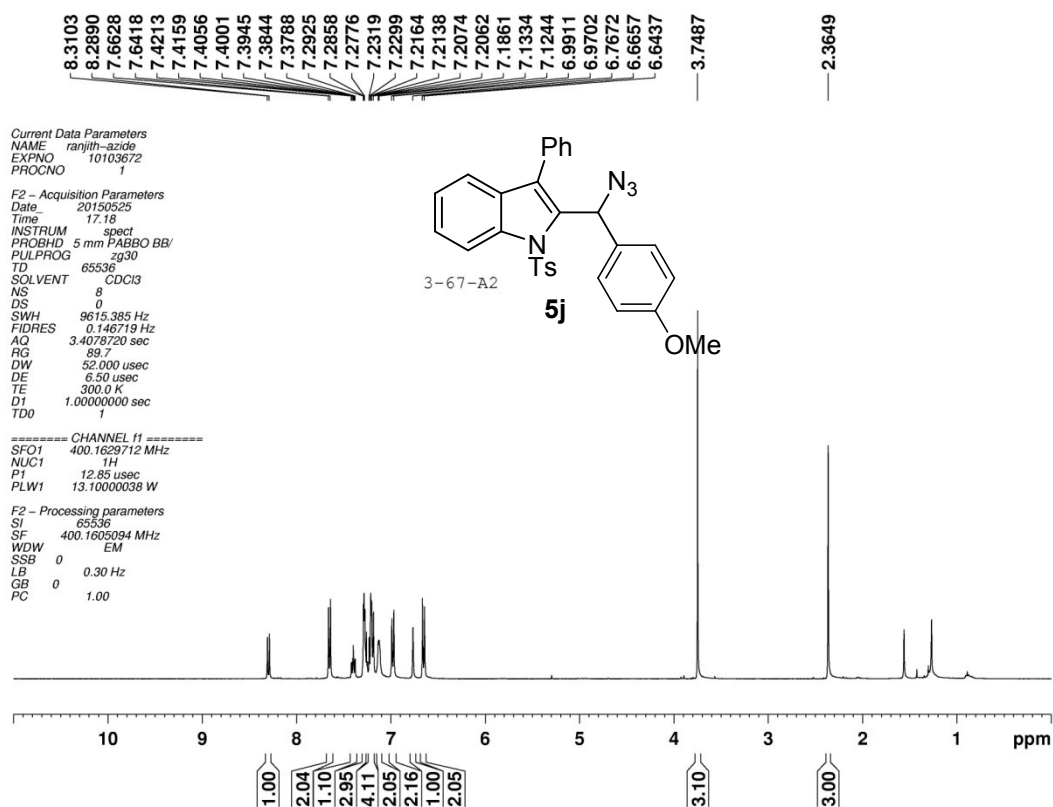


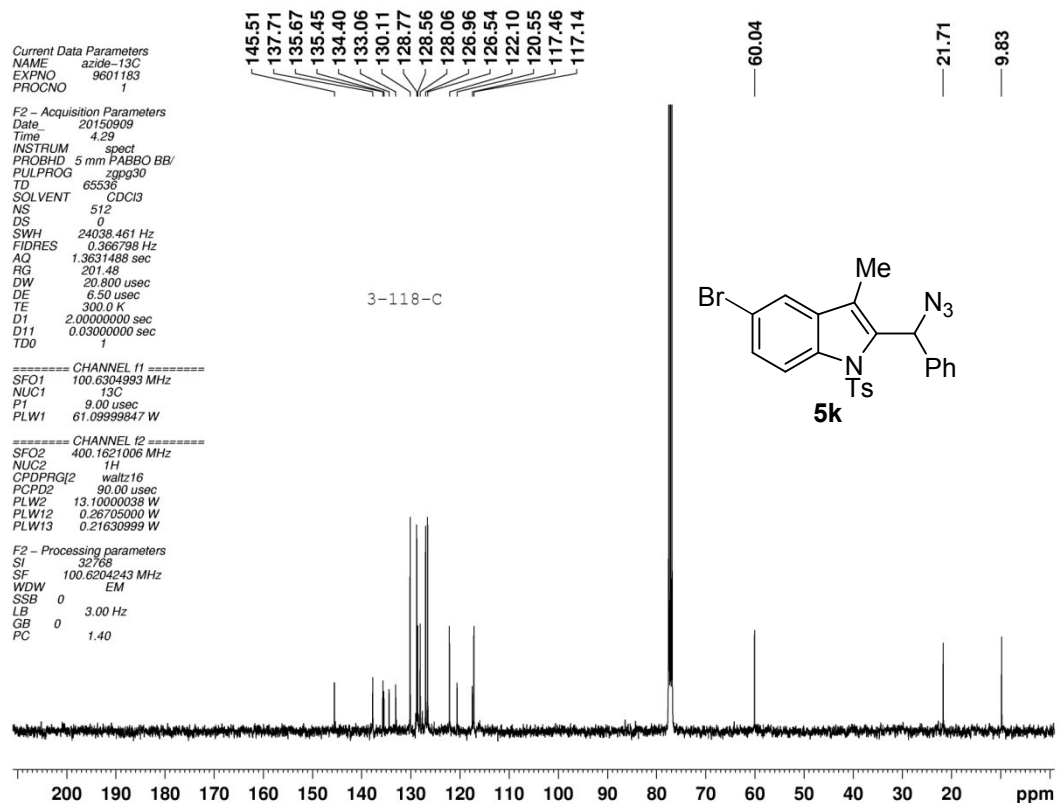
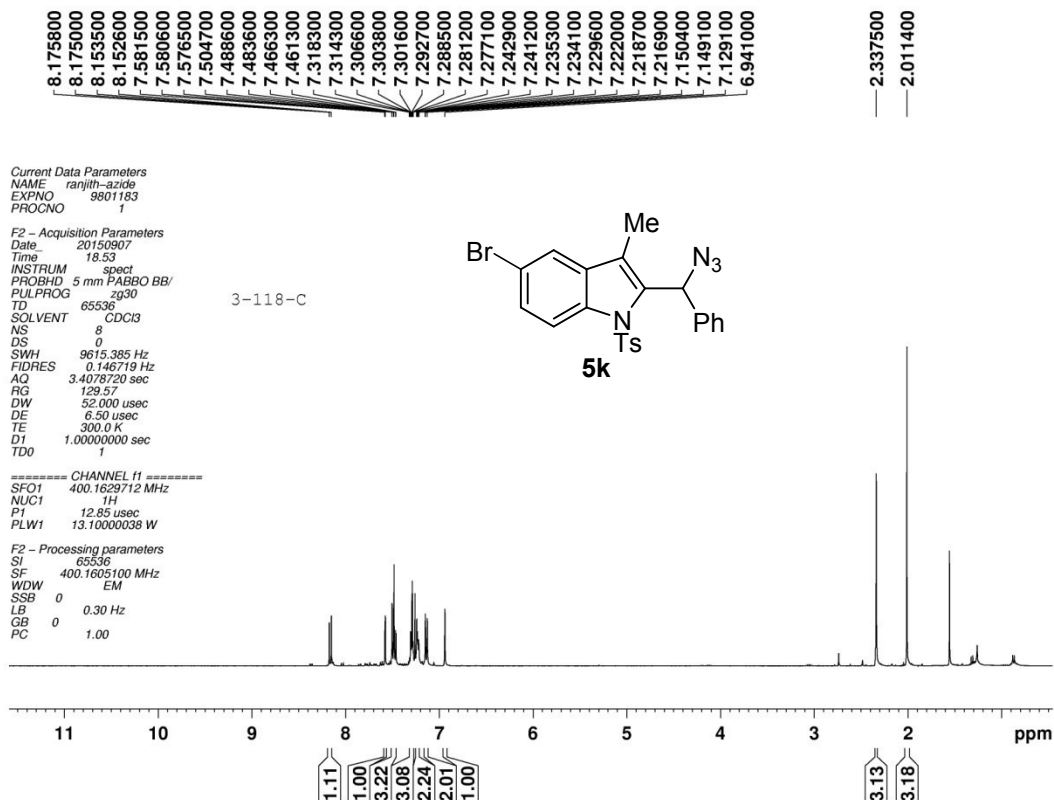


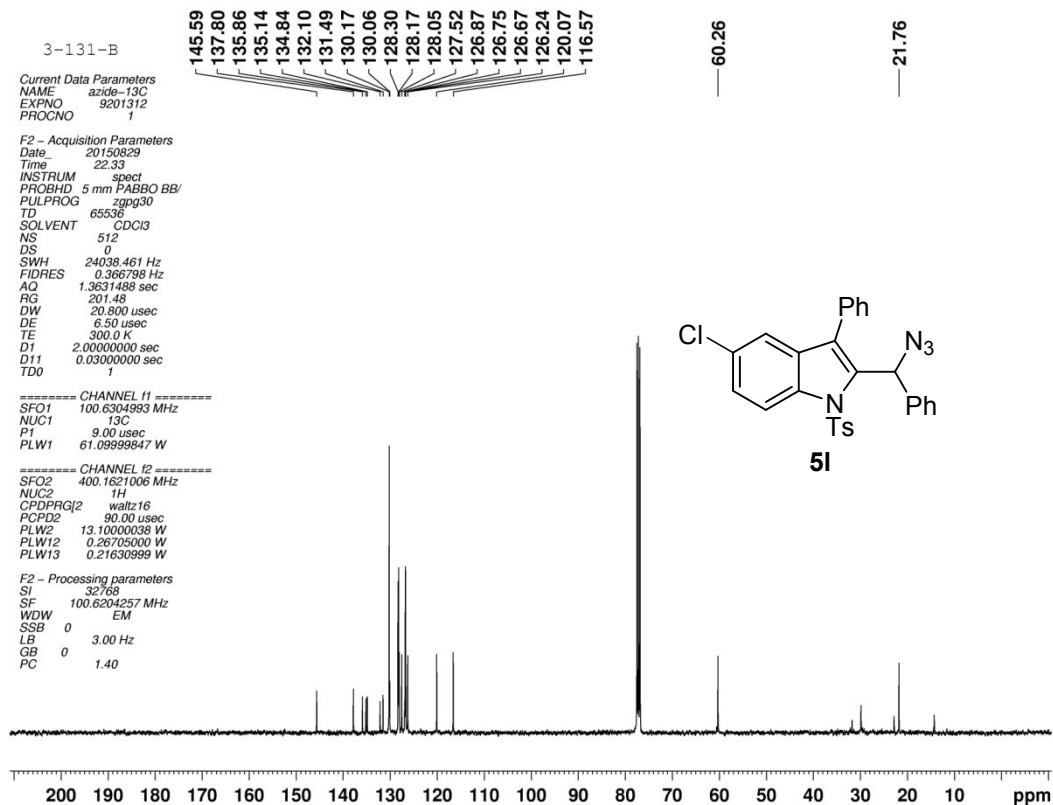
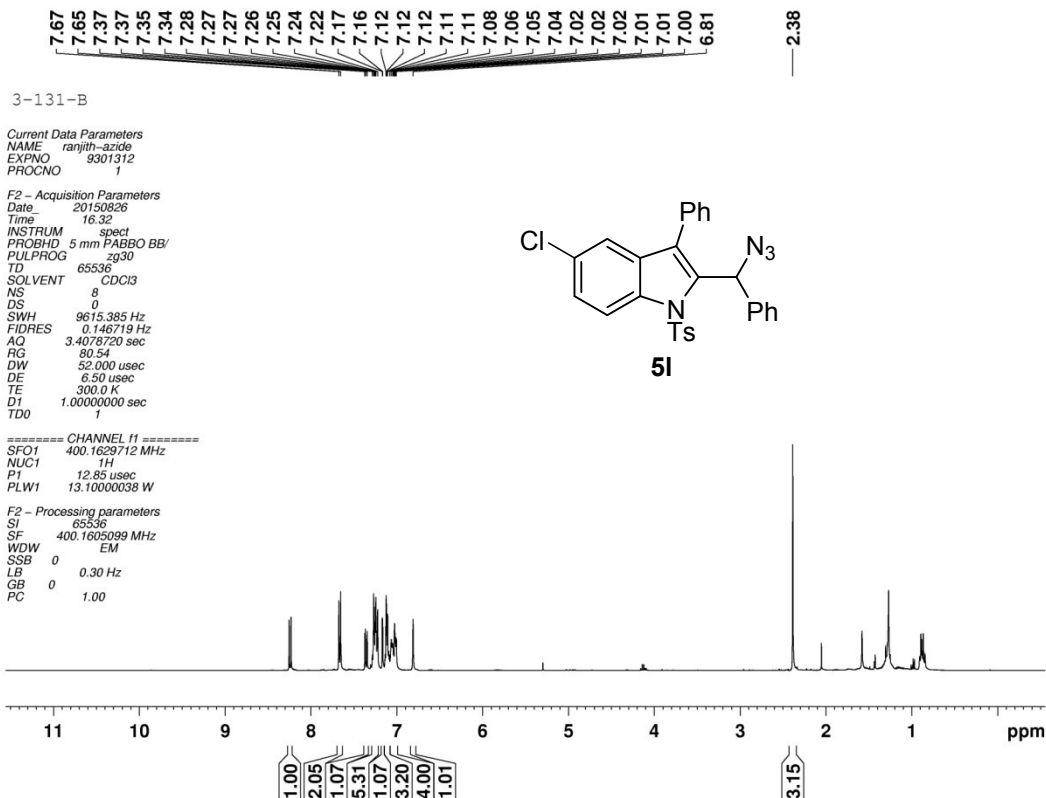




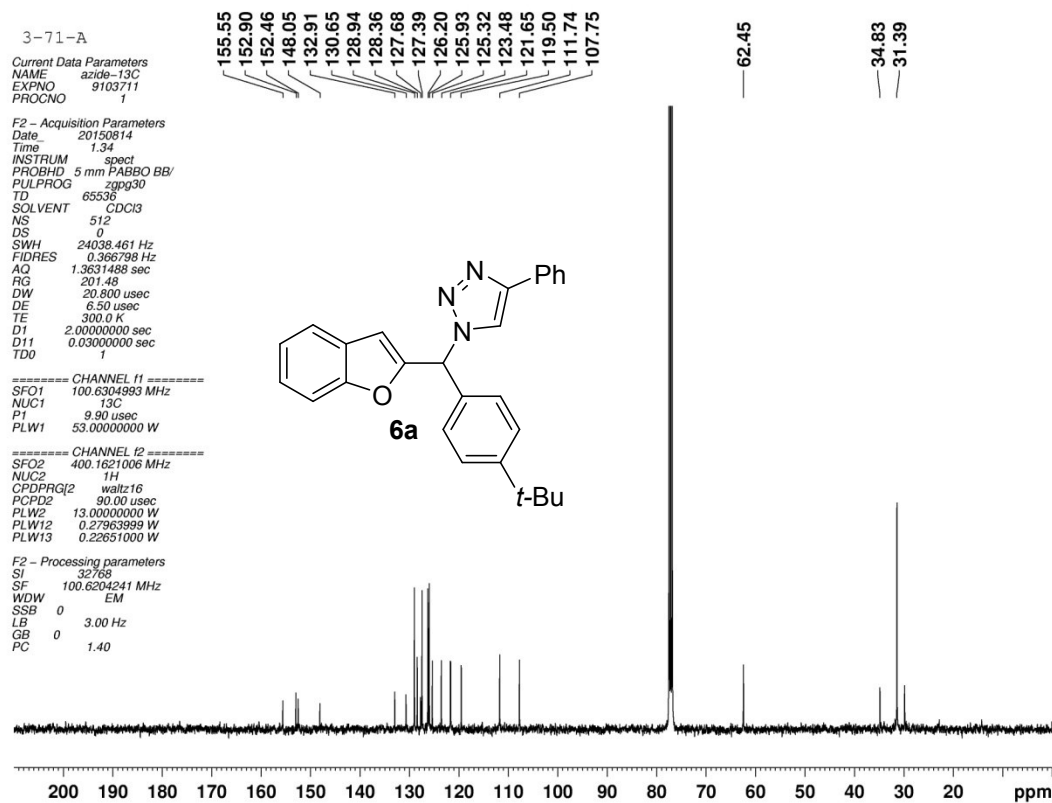
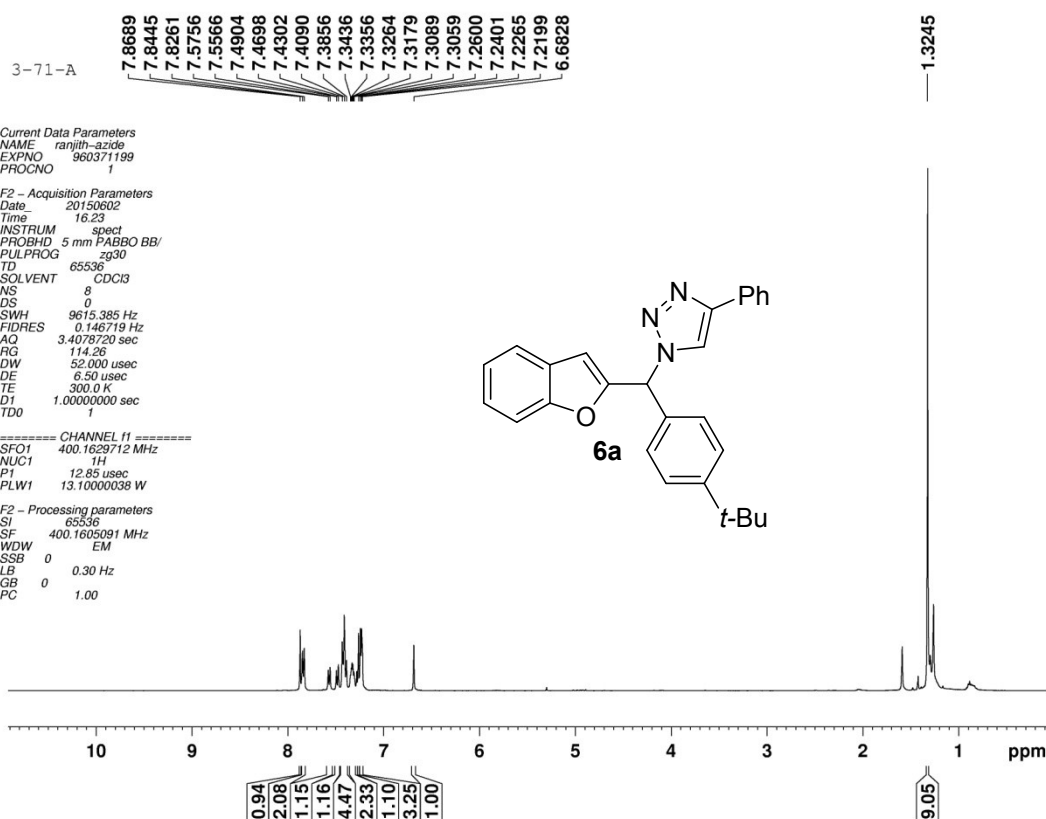


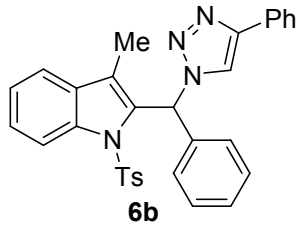
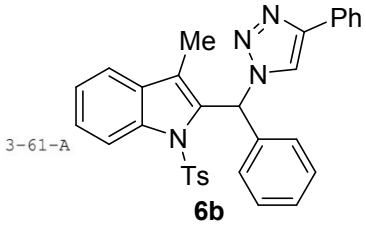


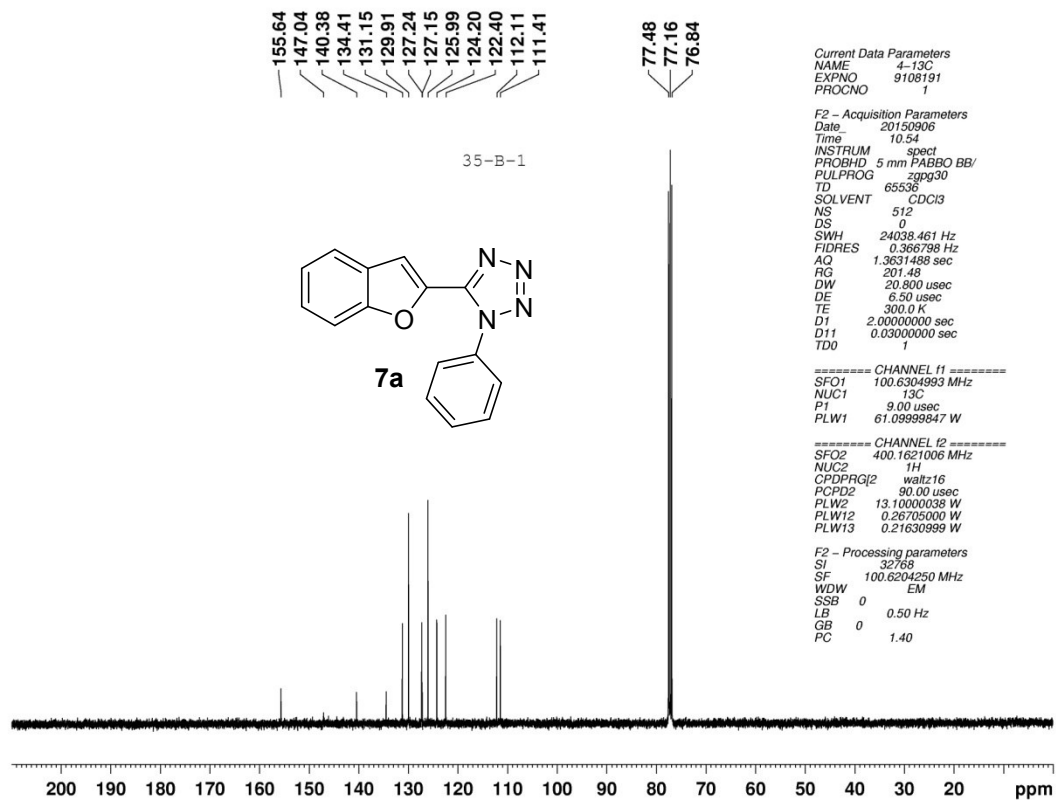
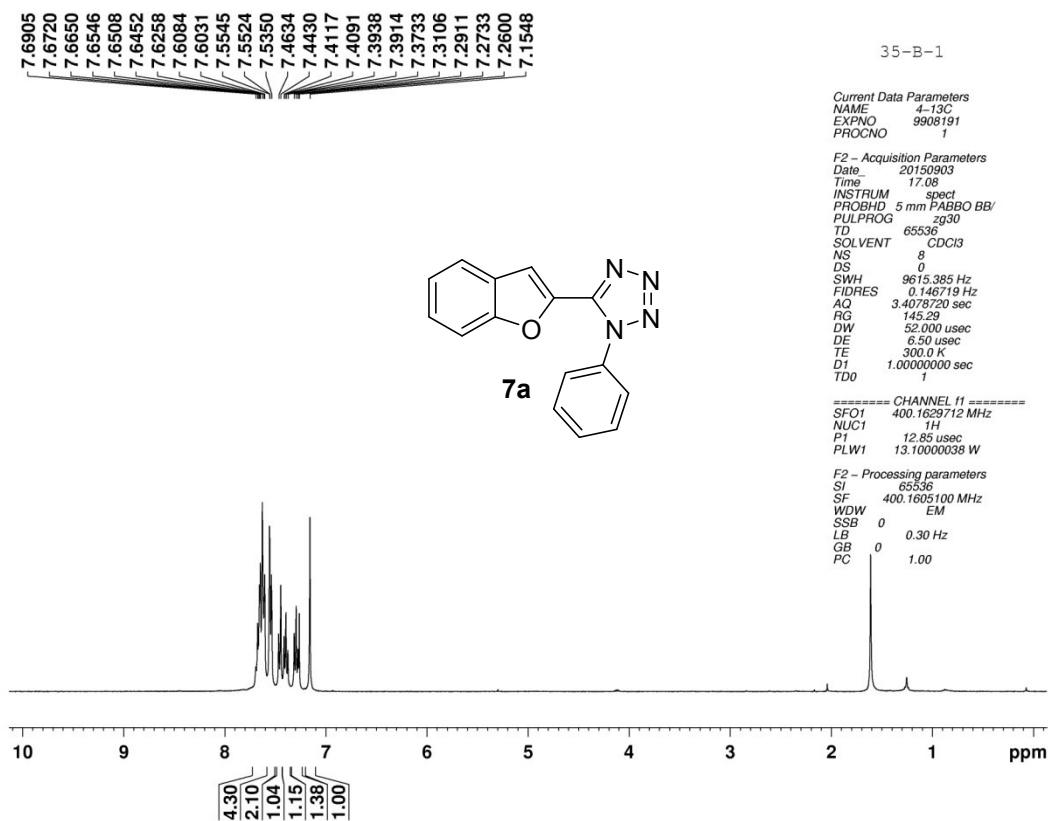














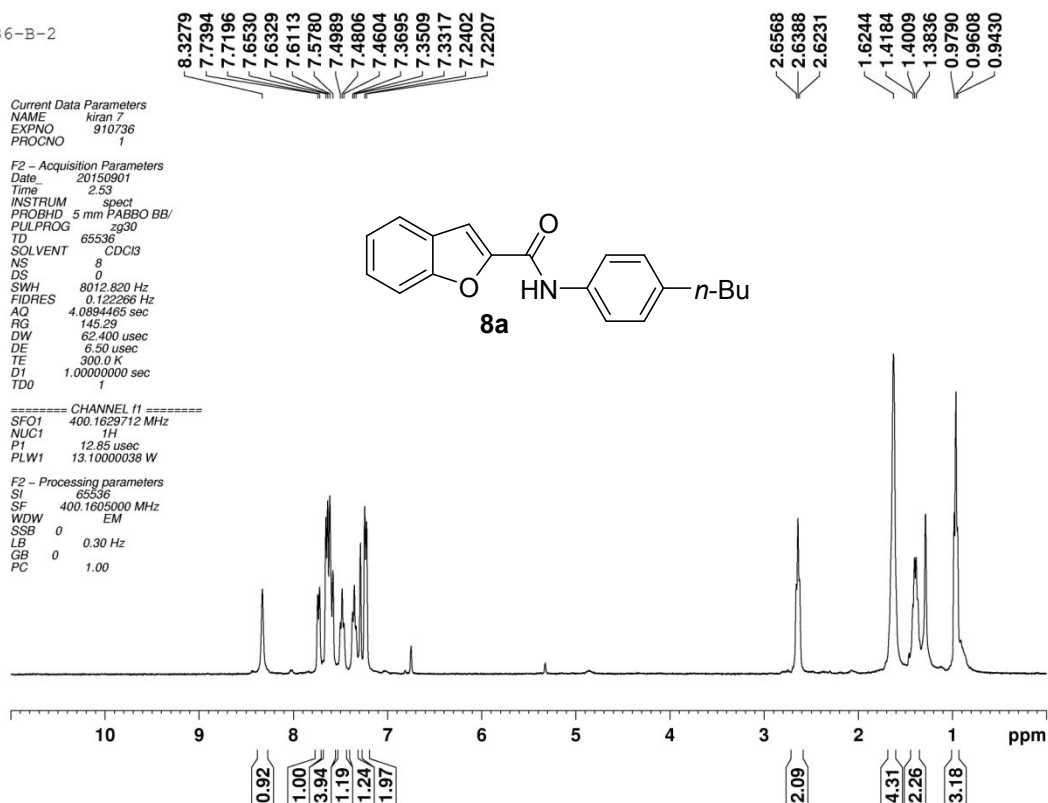
36-B-2

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EXPNO 910736  
PROCNO 1

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PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 8012.820 Hz  
FIDRES 0.122206 Hz  
AQ 4.0894465 sec  
RG 145.29  
DW 62.400 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

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NUC1 1H  
P1 12.85 usec  
PLW1 13.10000038 W

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PC 1.00



36-B-2

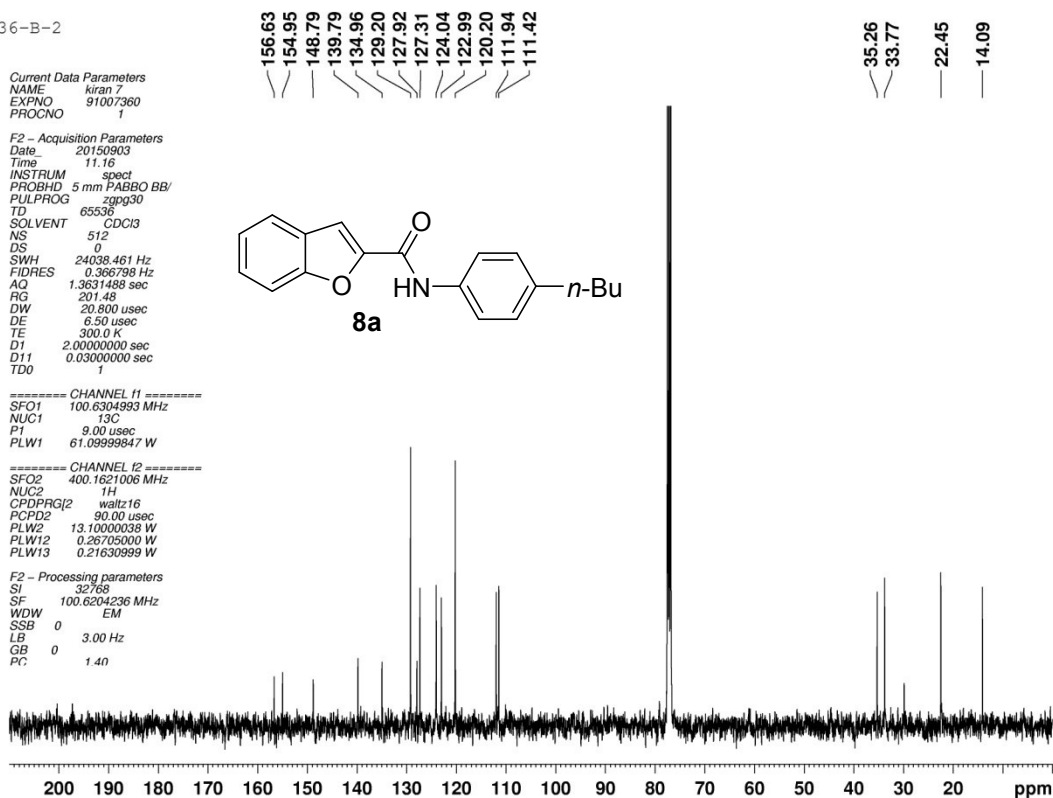
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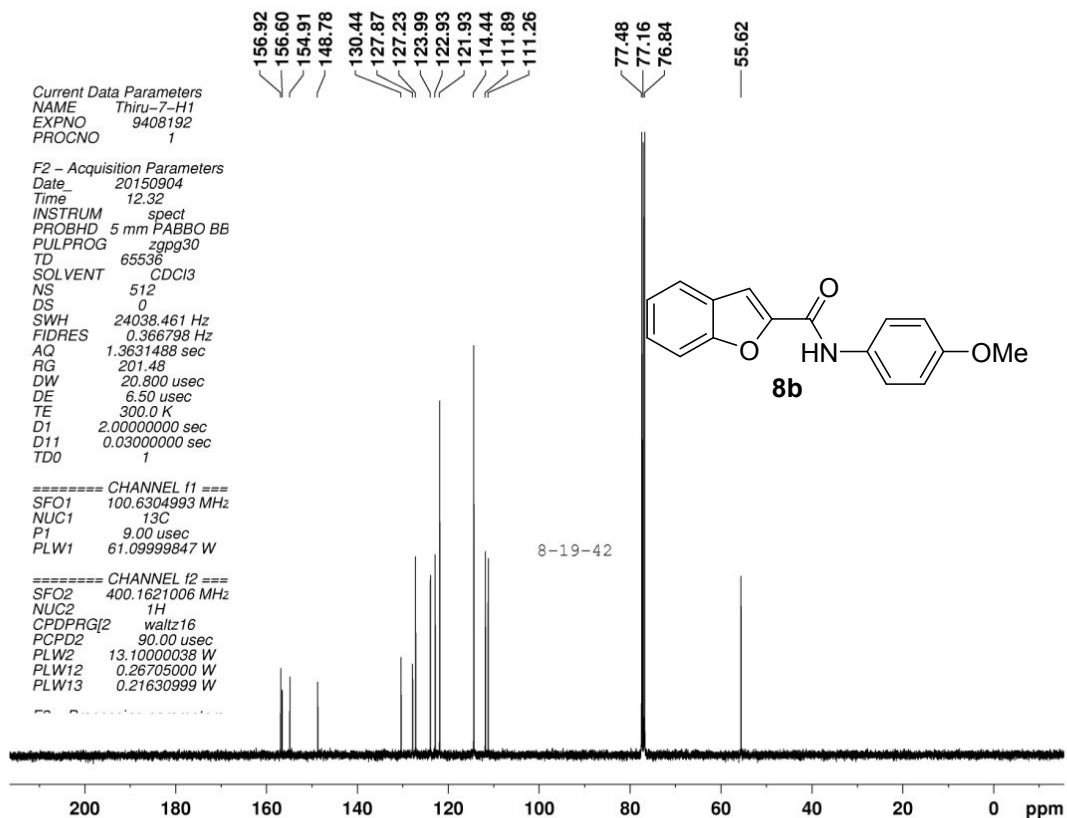
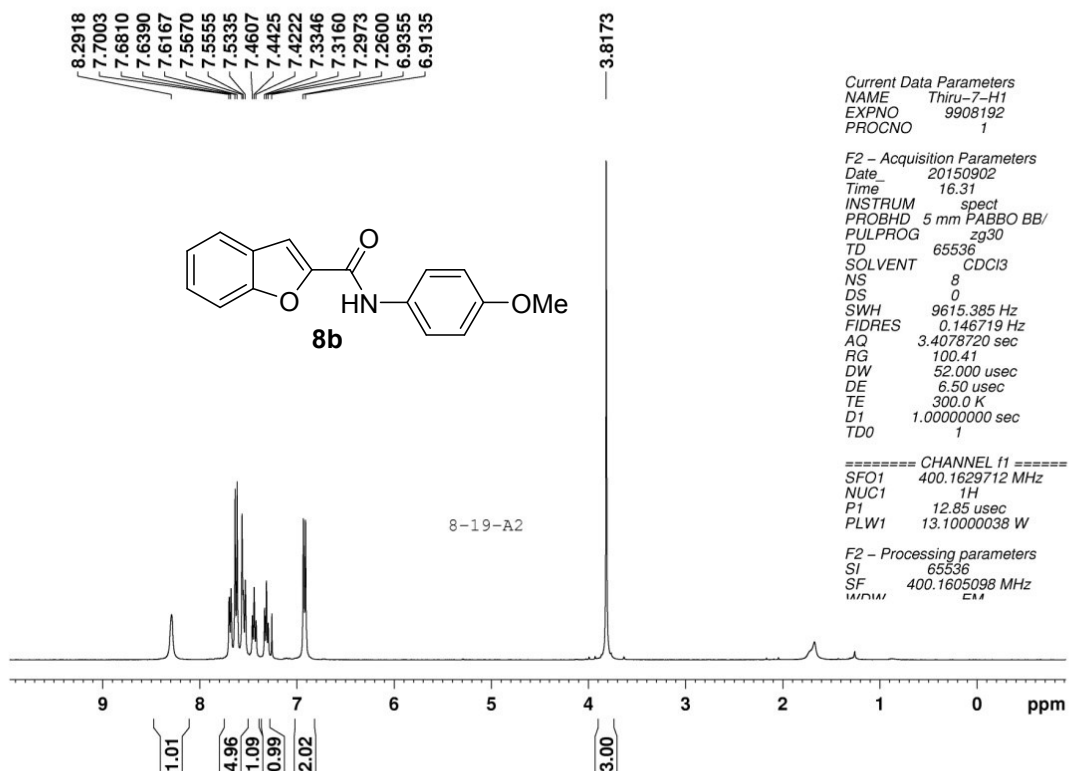
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SOLVENT CDCl3  
NS 512  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366788 Hz  
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D11 0.03000000 sec  
TD0 1

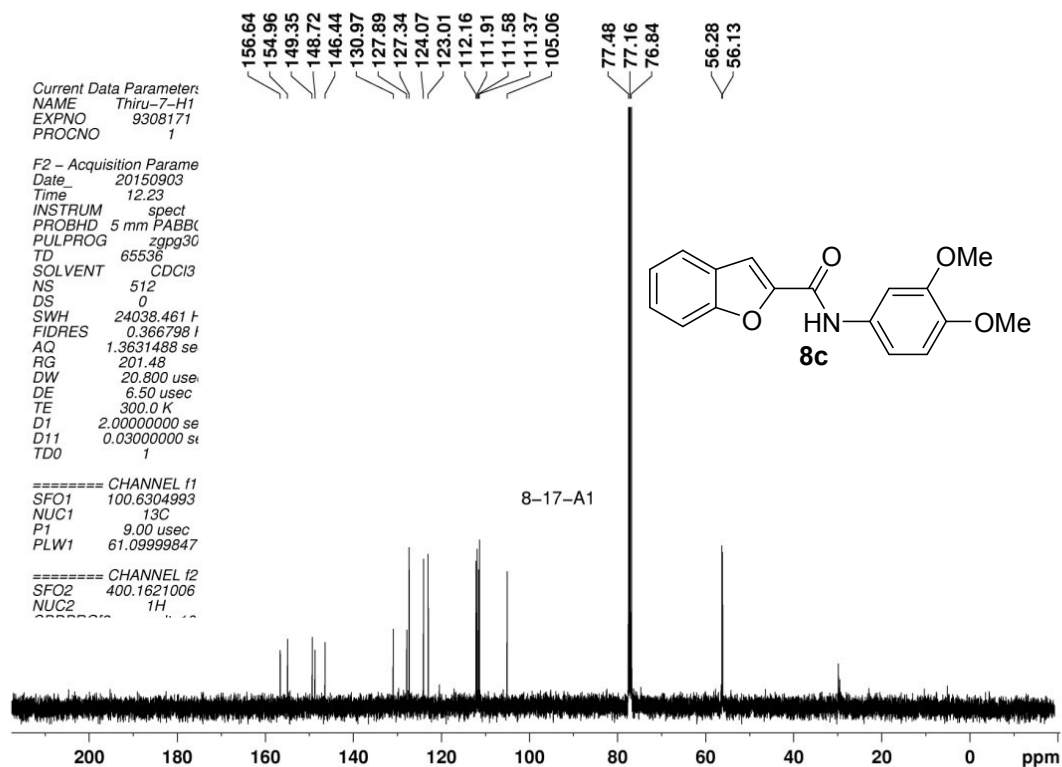
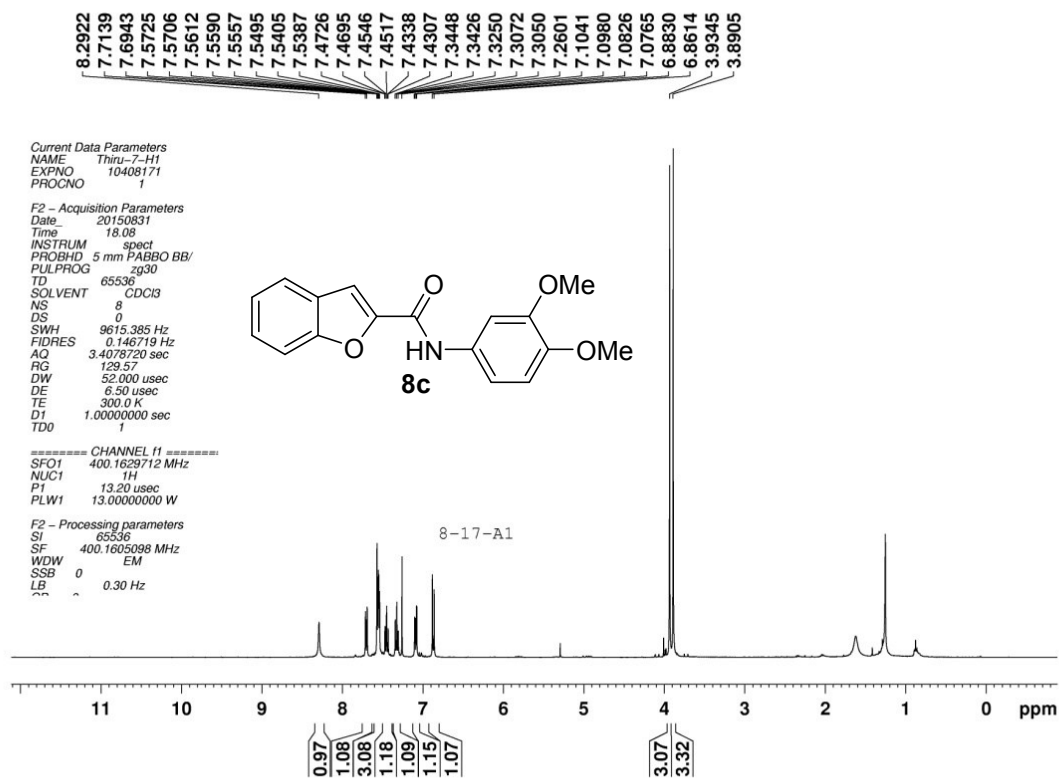
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NUC1 13C  
P1 9.00 usec  
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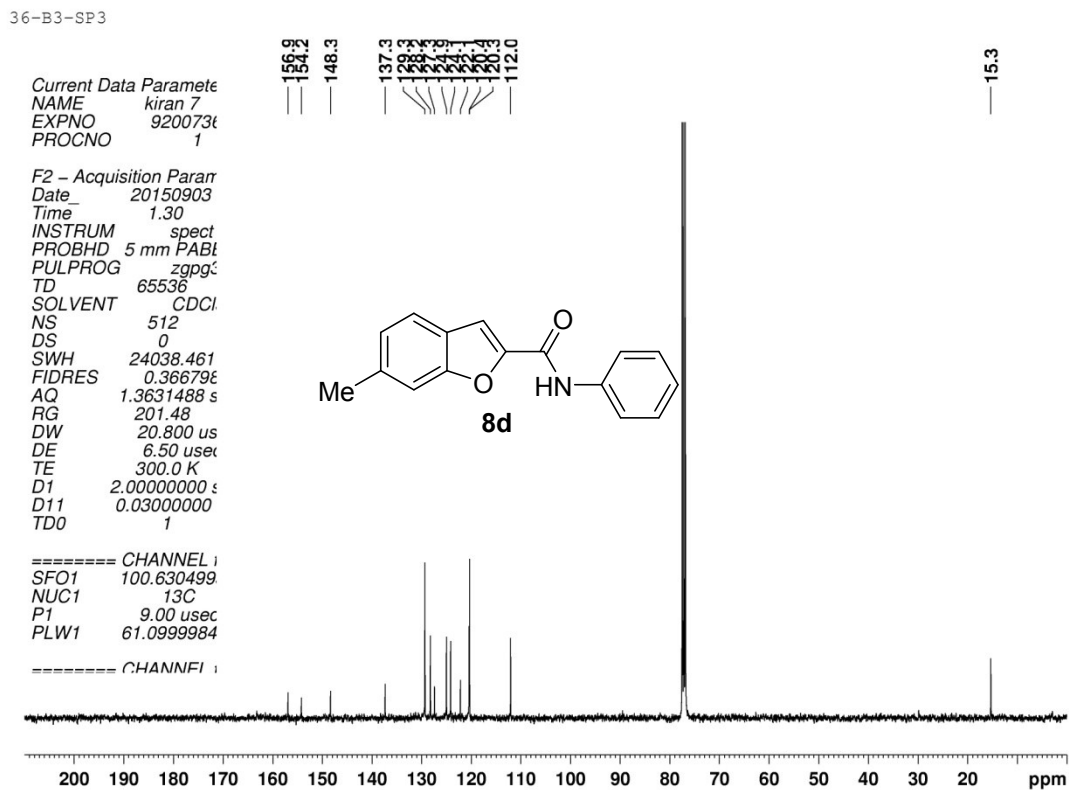
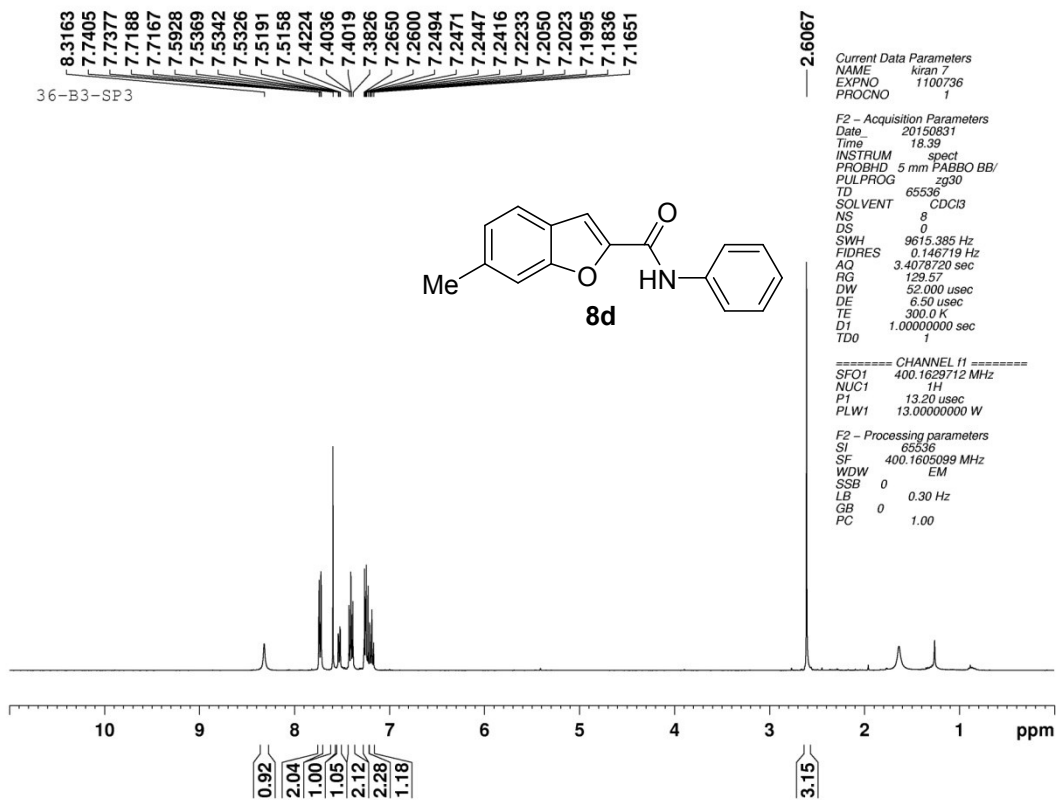
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NUC2 1H  
CPDPRG2 waltz16  
PCPD2 90.00 usec  
PLW2 13.10000038 W  
PLW12 0.26705000 W  
PLW13 0.21630999 W

F2 - Processing parameters  
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WDW EM  
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LB 3.00 Hz  
GB 0  
PC 1.40

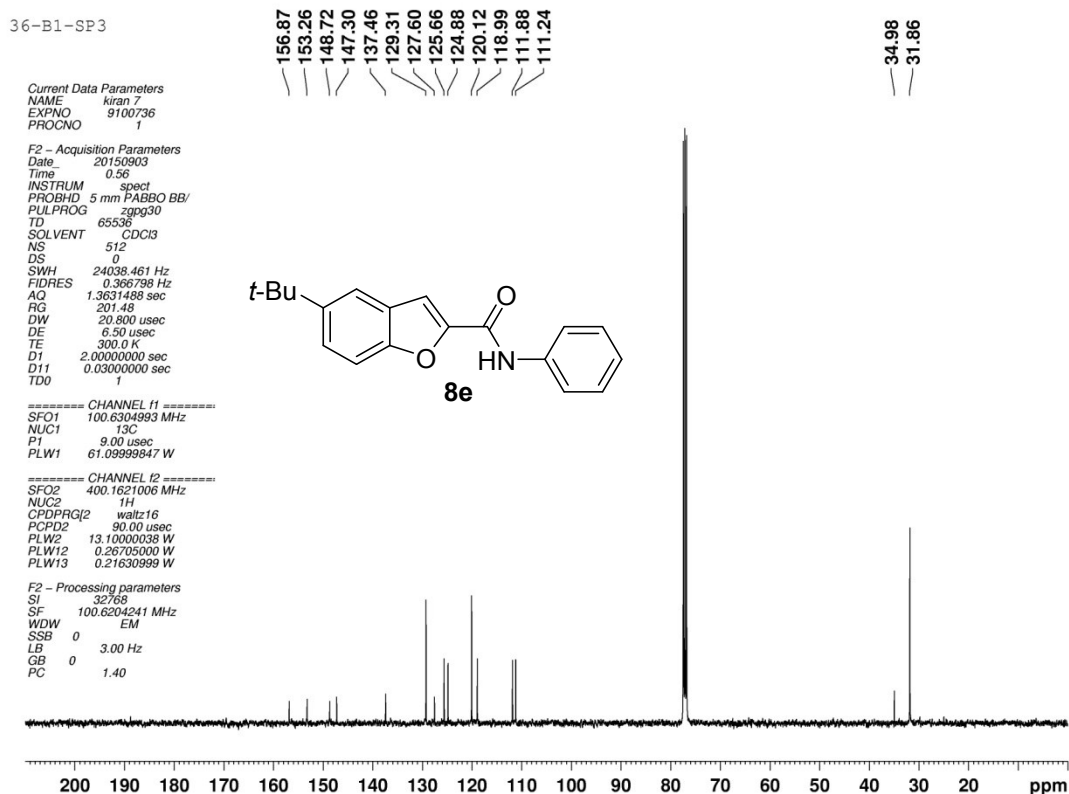
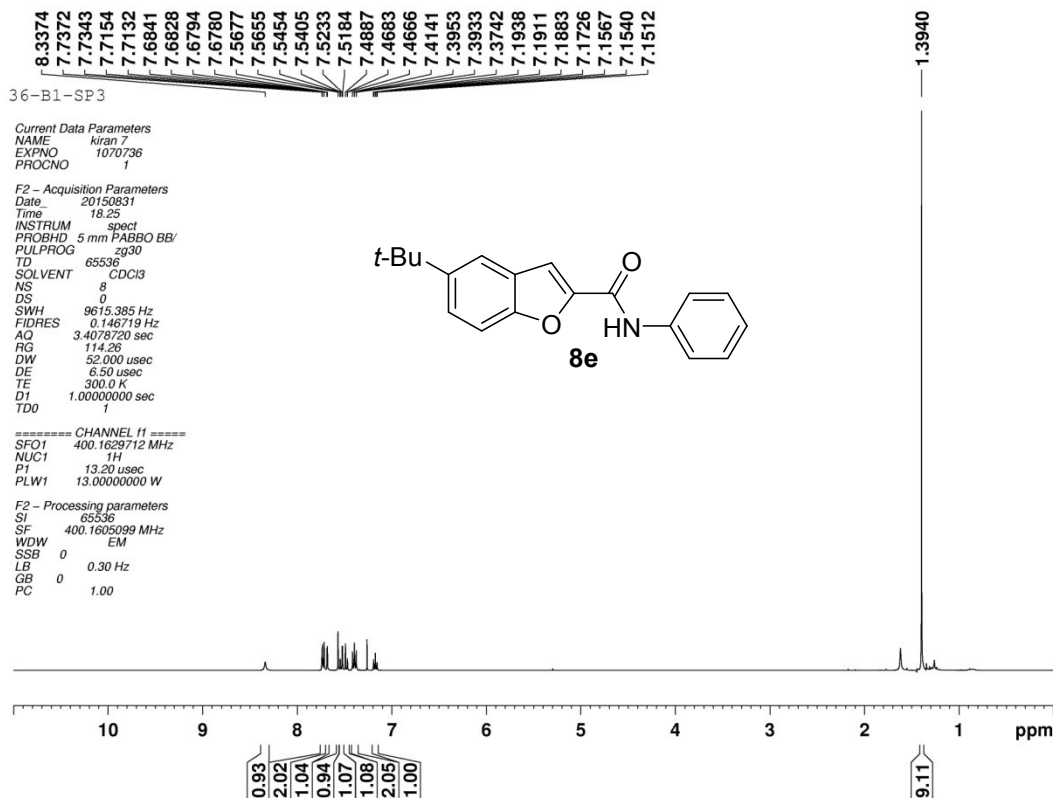


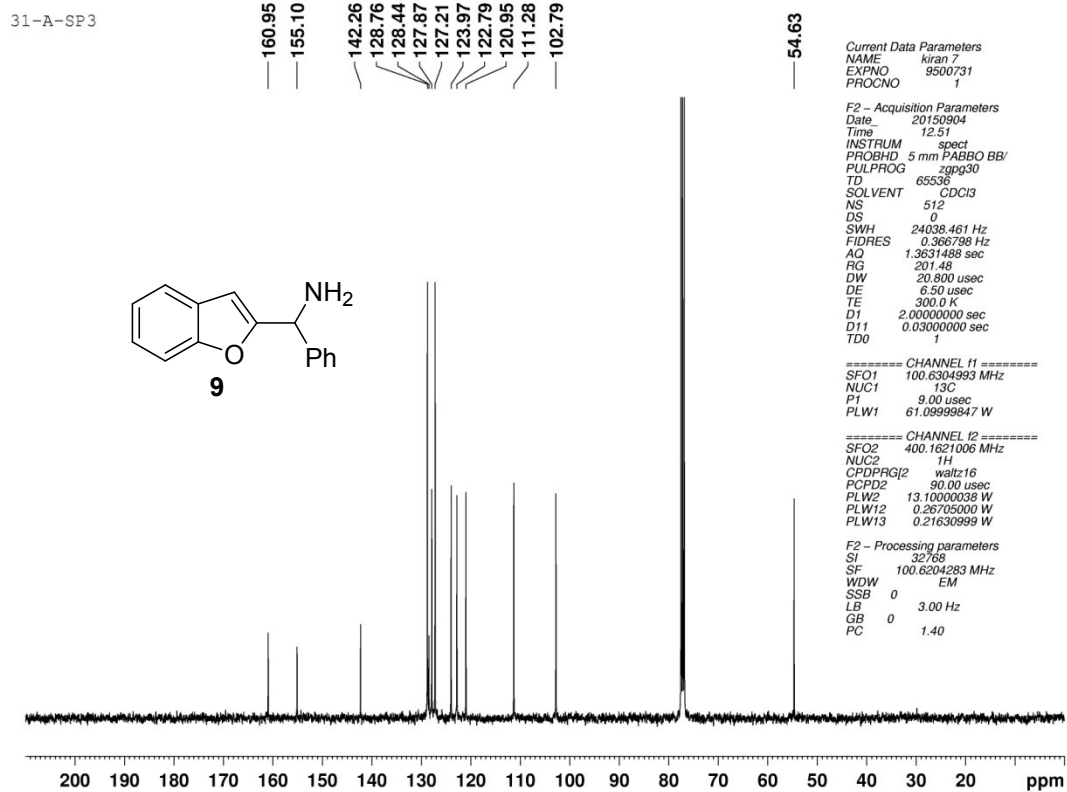
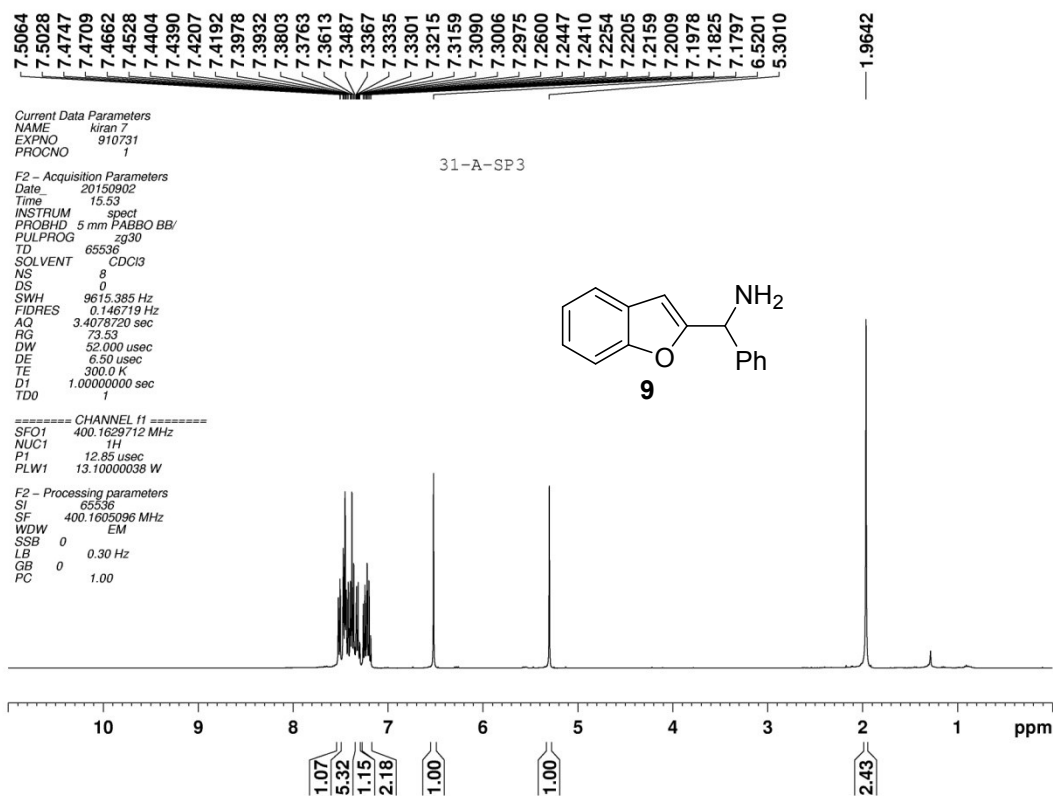


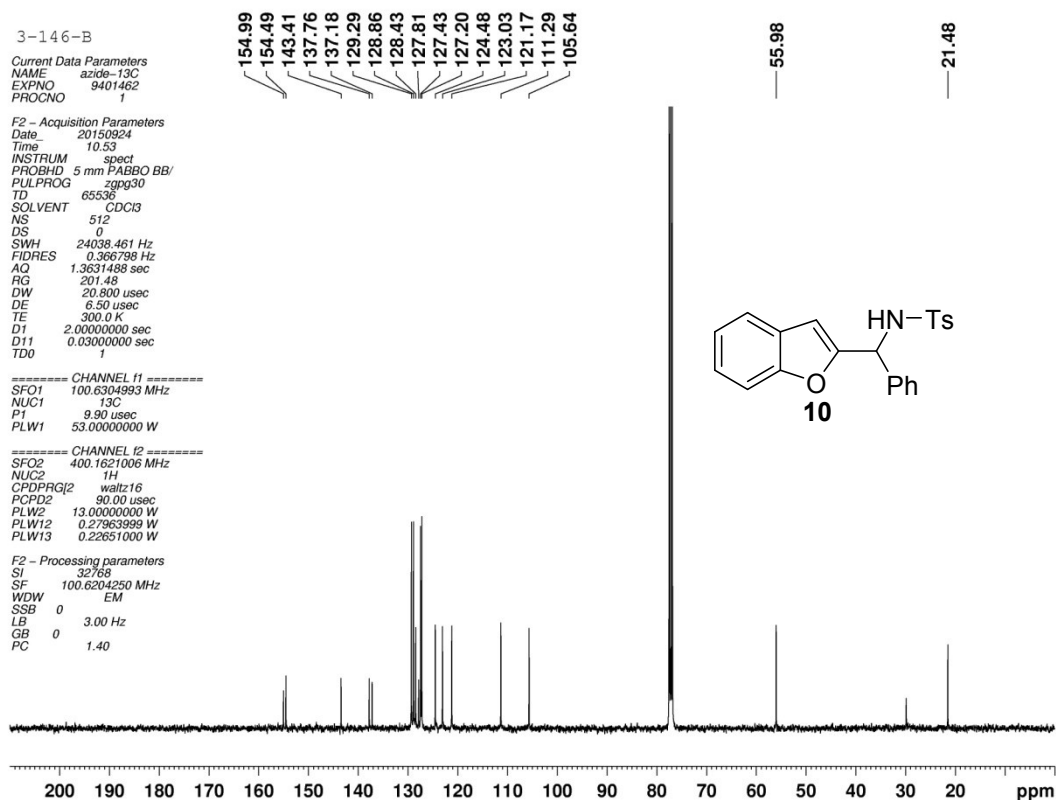
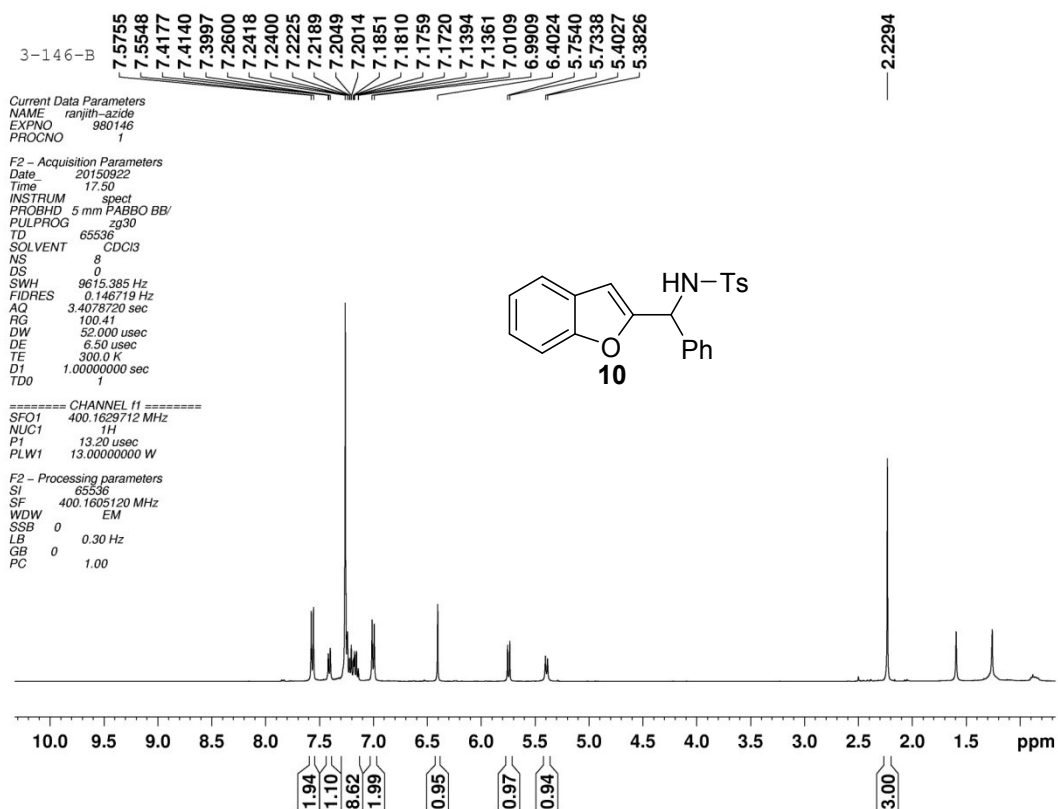


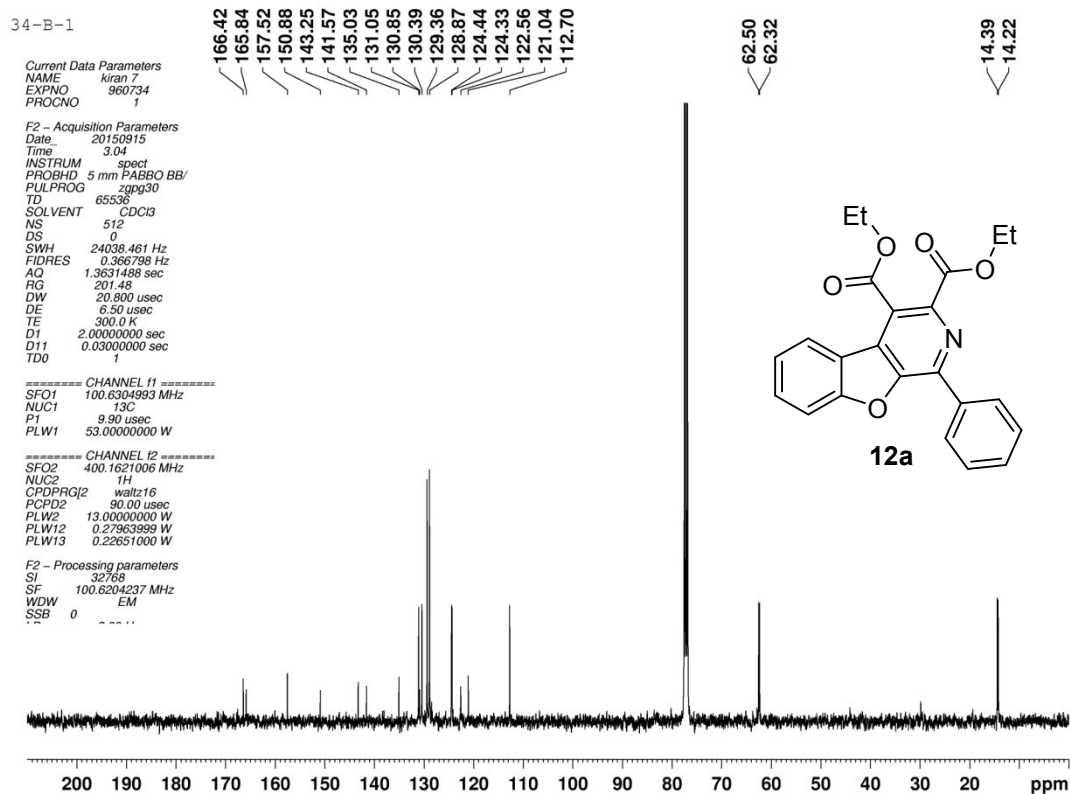
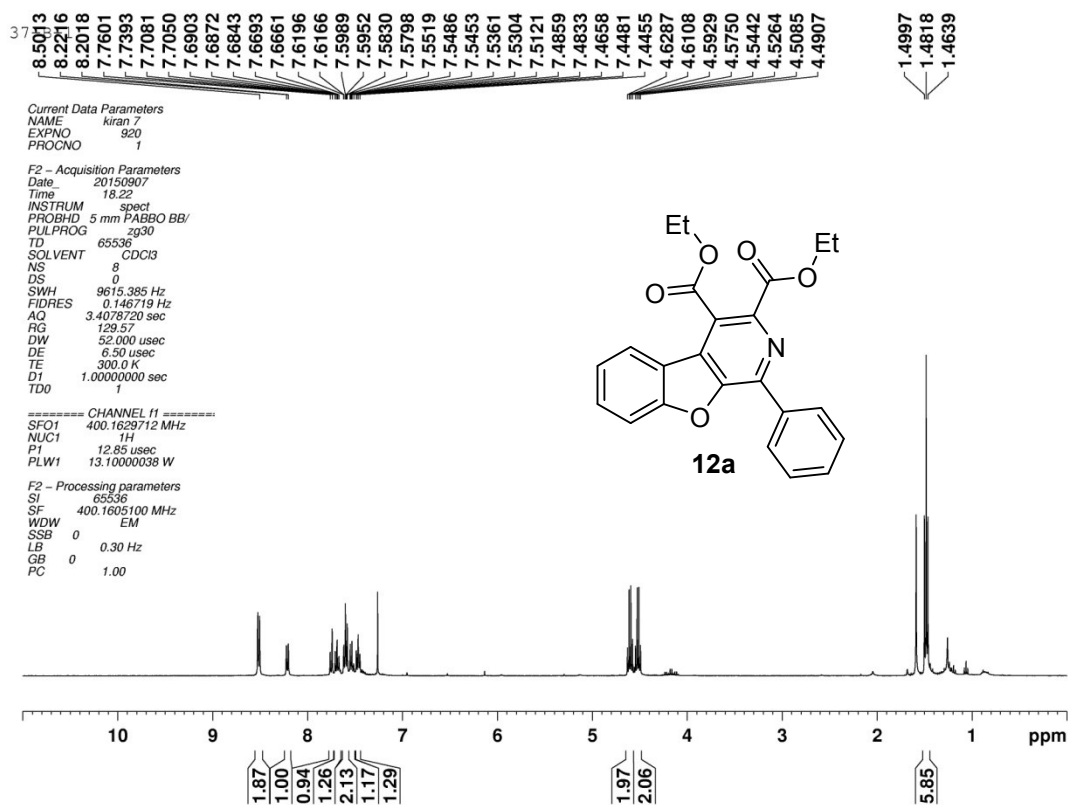


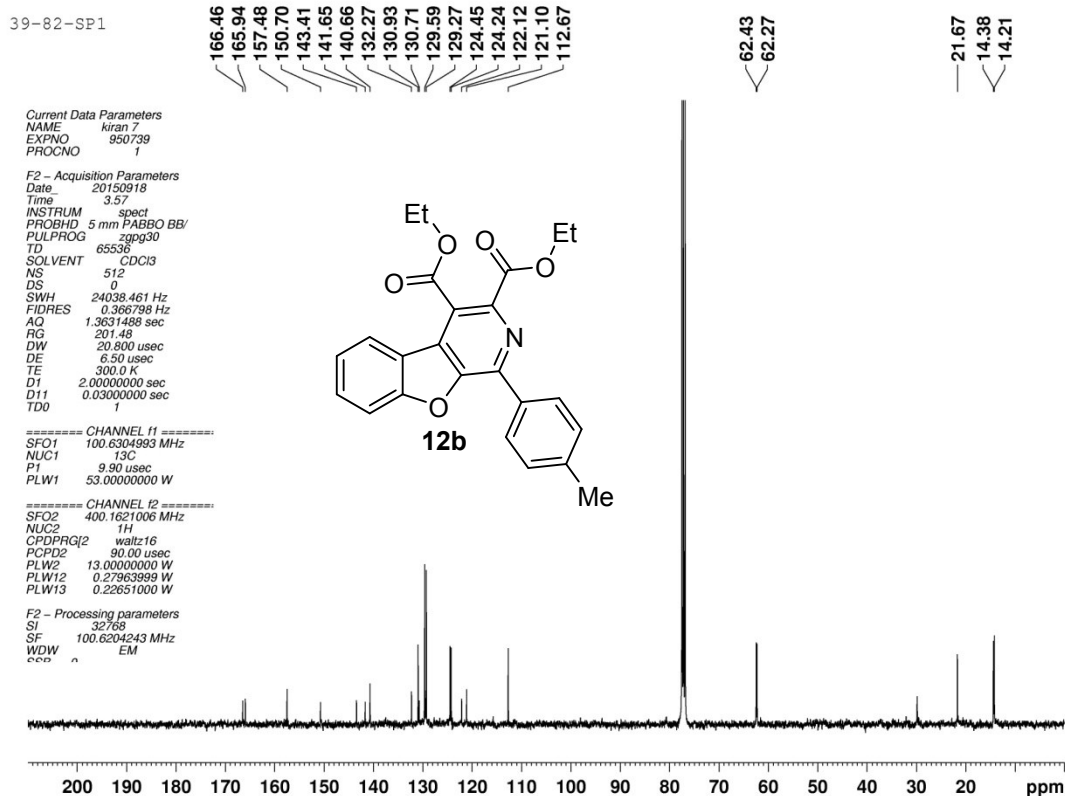
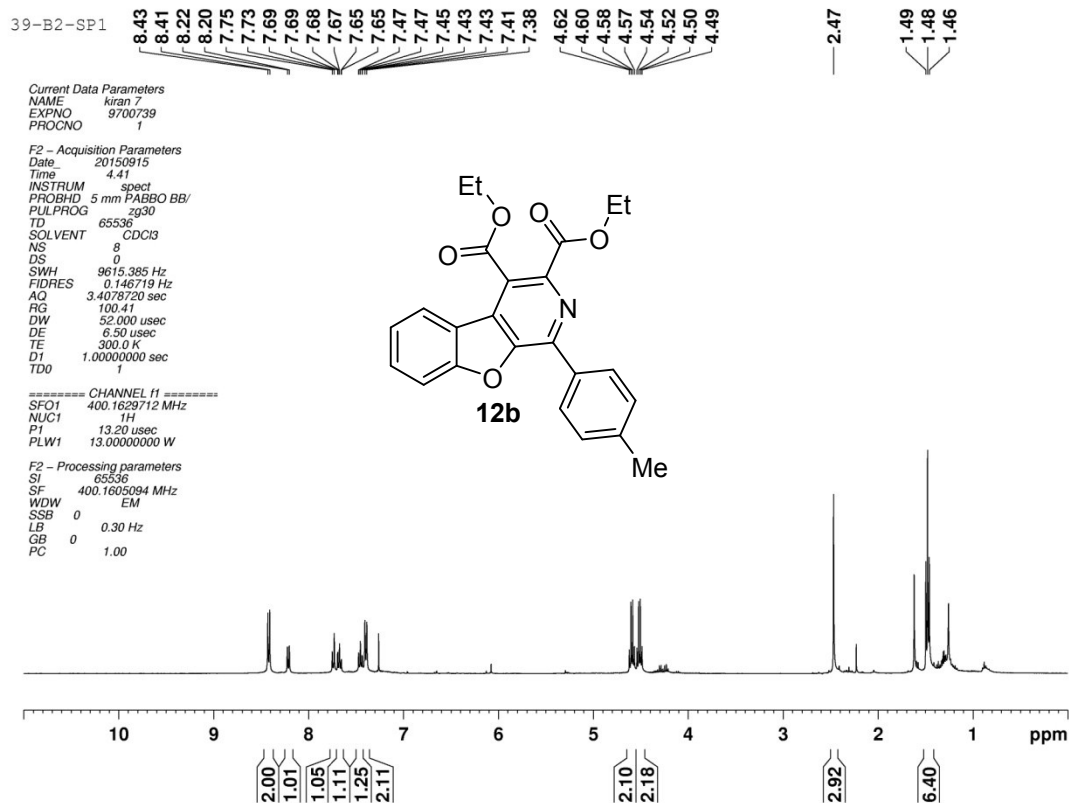


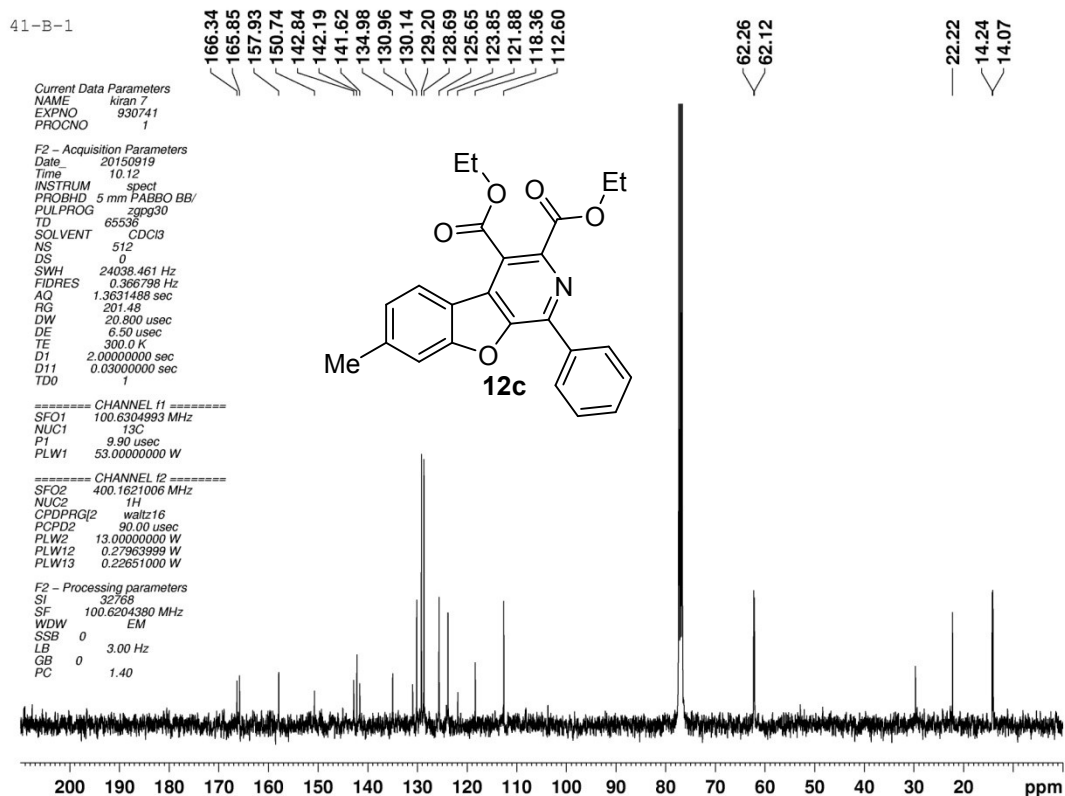
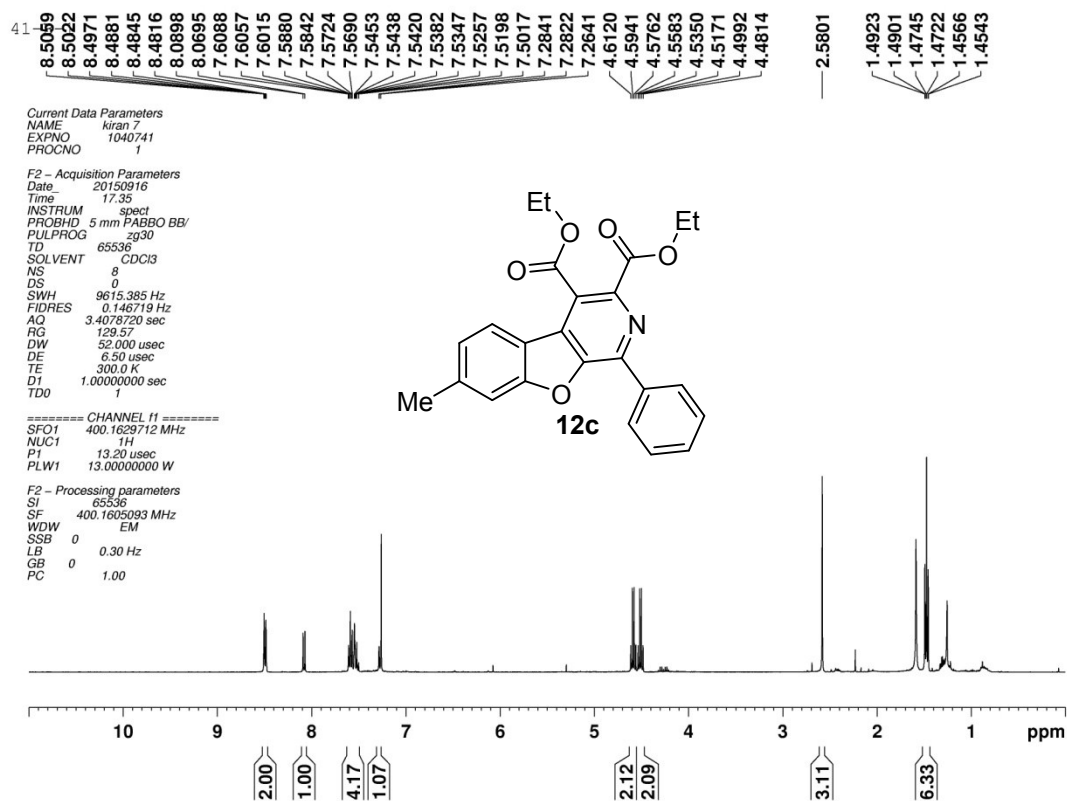


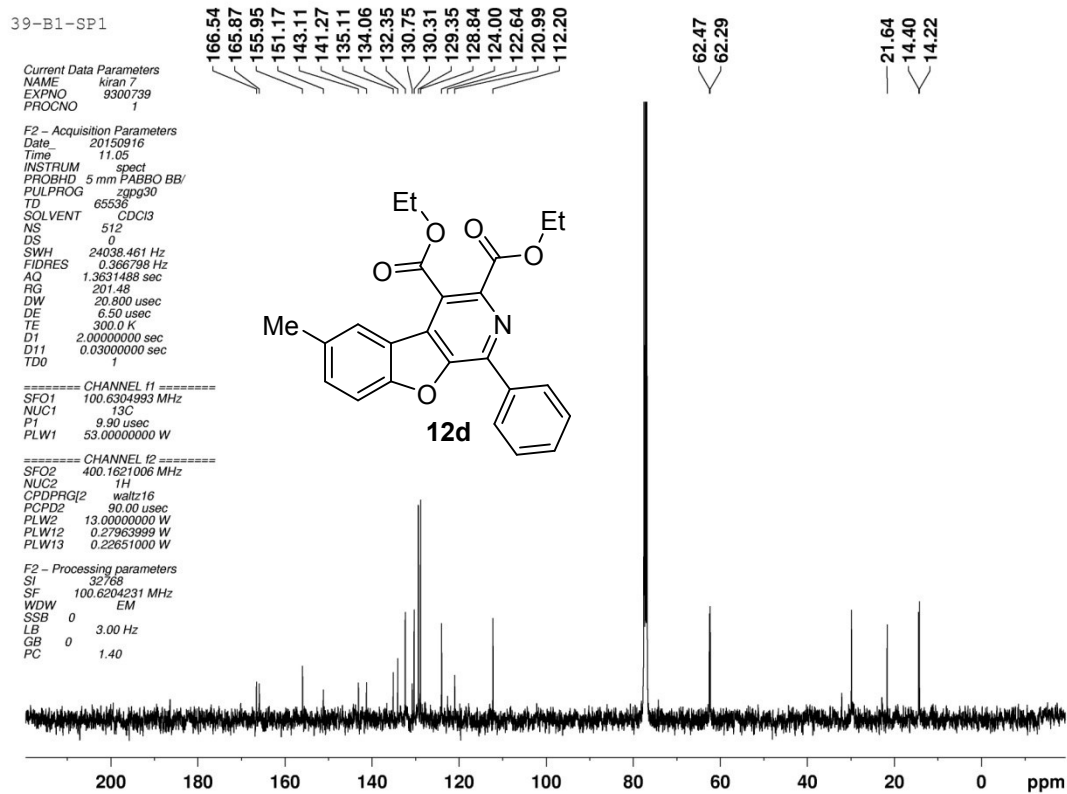
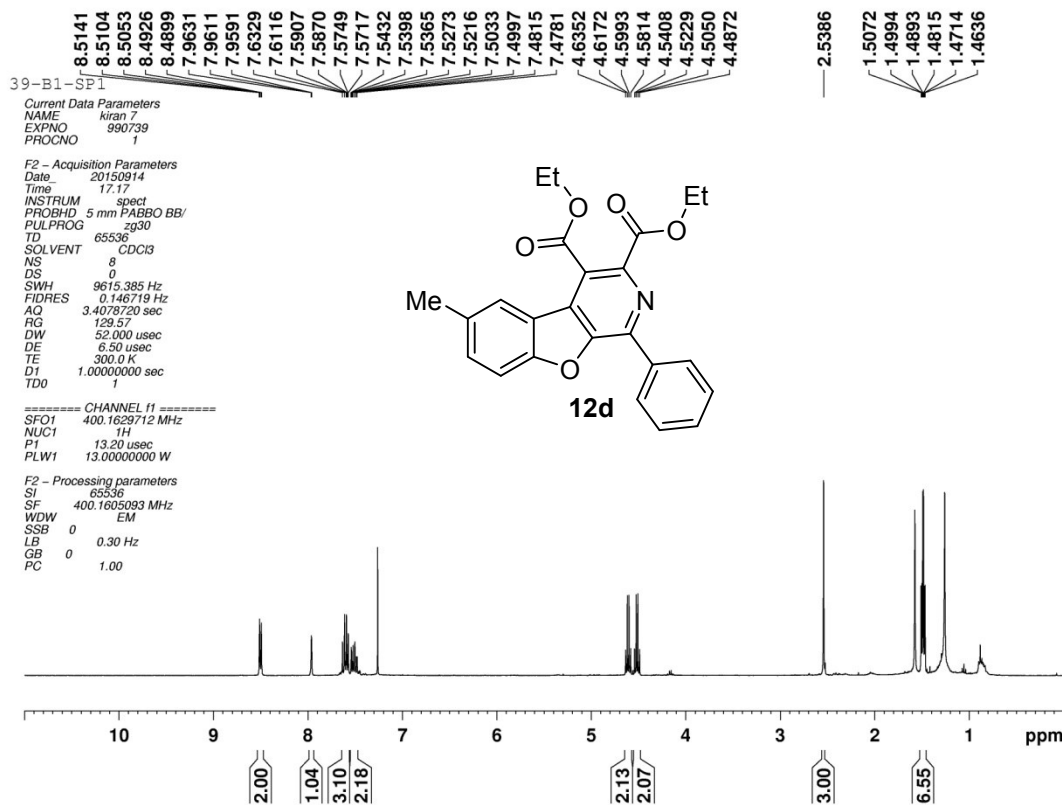




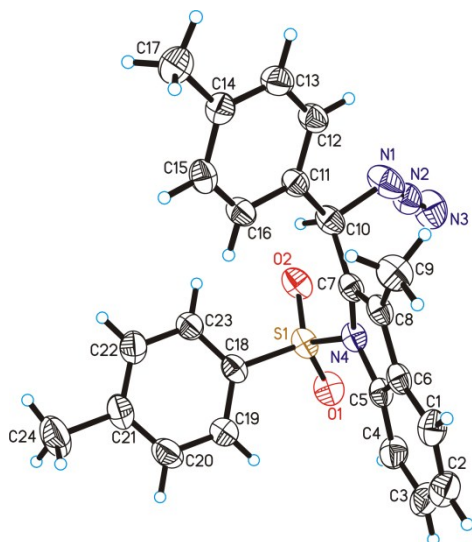








X-ray data of the compound **5b** :



### **5b**

**Figure 1** ORTEP diagram of **5b** drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **5b** determined at 293 K.

**Crystallization:** Crystals of compound **5b** were grown from the solvent chloroform by slow evaporation method.

#### **X-Ray Data Collection and Structure Refinement Details of 5b:**

A good quality single crystal of size 0.34 x 0.32 x 0.20 mm, was selected under a polarizing microscope and was mounted on a glass fibre for data collection. Single crystal X-ray data for compound **5b** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-K $\alpha$  radiation generated from the micro focus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using  $\omega$ -scans of 0.5 $^\circ$  steps at 293(2)K. Cell determination, data collection and data reduction was performed using the Rigaku Crystal Clear-SM Expert 2.1 b24<sup>1</sup> software. Structure solution and refinement were performed by using SHELX-97<sup>2</sup>. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

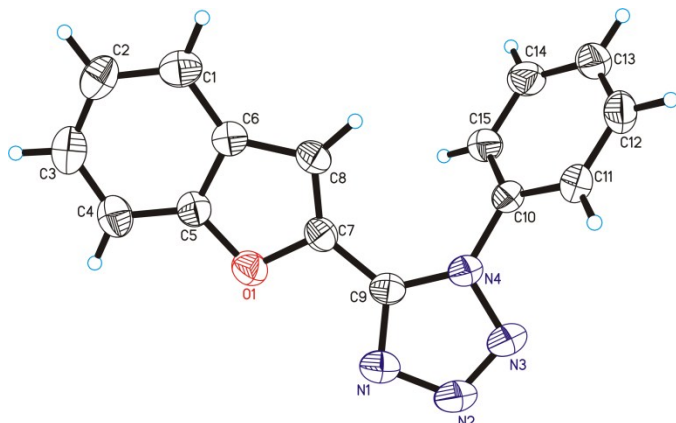


Supplementary:

**Table 1** Crystal data and structure refinement details for 5b.

| Compound                                                        | 5b                                                              |
|-----------------------------------------------------------------|-----------------------------------------------------------------|
| Empirical formula                                               | C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> S |
| Formula weight                                                  | 430.52                                                          |
| Crystal System                                                  | Monoclinic                                                      |
| Space group                                                     | <i>P</i> 21                                                     |
| <i>a</i> (Å)                                                    | 8.431(2)                                                        |
| <i>b</i> (Å)                                                    | 12.486(3)                                                       |
| <i>c</i> (Å)                                                    | 10.251(3)                                                       |
| $\alpha$ (°)                                                    | 90.00                                                           |
| $\beta$ (°)                                                     | 90.558(5)                                                       |
| $\gamma$ (°)                                                    | 90.00                                                           |
| <i>V</i> (Å <sup>3</sup> )                                      | 1079.1(5)                                                       |
| <i>Z</i>                                                        | 2                                                               |
| D <sub>c</sub> (g/cm <sup>3</sup> )                             | 1.325                                                           |
| <i>F</i> <sub>000</sub>                                         | 452                                                             |
| $\mu$ (mm <sup>-1</sup> )                                       | 0.179                                                           |
| $\theta_{\max}$ (°)                                             | 25.36                                                           |
| Total reflections                                               | 7344                                                            |
| Unique reflections                                              | 3637                                                            |
| Reflections [ <i>I</i> > 2σ( <i>I</i> )]                        | 2940                                                            |
| Parameters                                                      | 280                                                             |
| <i>R</i> <sub>int</sub>                                         | 0.0405                                                          |
| Goodness-of-fit                                                 | 0.948                                                           |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] | 0.0410                                                          |
| <i>wR</i> ( <i>F</i> <sup>2</sup> , all data)                   | 0.0957                                                          |
| CCDC No.                                                        | 1433117                                                         |

X-ray data of the compound **7a**:



## 7a

**Figure 2** ORTEP diagram of **7a** drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **7a** determined at 293 K.

**Crystallization:** Crystals of compound **7a** were grown from the solvent di ethyl ether by slow evaporation method.

### X-Ray Data Collection and Structure Refinement Details of **7a**:

A good quality single crystal of size 0.27 x 0.25 x 0.11 mm, was selected under a polarizing microscope and was mounted on a glass fibre for data collection. Single crystal X-ray data for compound **7a** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the mono chromated Mo-K $\alpha$  radiation generated from the micro focus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using  $\omega$ -scans of 0.5 $^\circ$  steps at 293(2)K. Cell determination, data collection and data reduction was performed using the Rigaku Crystal Clear-SM Expert 2.1 b24<sup>1</sup> software. Structure solution and refinement were performed by using SHELX-97<sup>2</sup>. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

1. Crystal Clear 2.1, Rigaku Corporation, Tokyo, Japan
2. Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.

Supplementary:

**Table 2** Crystal data and structure refinement details for 7a.

| Compound                                                        | 7a                                               |
|-----------------------------------------------------------------|--------------------------------------------------|
| Empirical formula                                               | C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> O |
| Formula weight                                                  | 262.27                                           |
| Crystal System                                                  | Orthorhombic                                     |
| Space group                                                     | <i>P c a</i> 21                                  |
| <i>a</i> (Å)                                                    | 13.301(3)                                        |
| <i>b</i> (Å)                                                    | 13.892(4)                                        |
| <i>c</i> (Å)                                                    | 6.7933(16)                                       |
| $\alpha$ (°)                                                    | 90.00                                            |
| $\beta$ (°)                                                     | 90.00                                            |
| $\gamma$ (°)                                                    | 90.00                                            |
| <i>V</i> (Å <sup>3</sup> )                                      | 1255.2(5)                                        |
| <i>Z</i>                                                        | 4                                                |
| D <sub>c</sub> (g/cm <sup>3</sup> )                             | 1.388                                            |
| <i>F</i> <sub>000</sub>                                         | 544                                              |
| $\mu$ (mm <sup>-1</sup> )                                       | 0.092                                            |
| $\theta_{\max}$ (°)                                             | 25.31                                            |
| Total reflections                                               | 7990                                             |
| Unique reflections                                              | 2203                                             |
| Reflections [ <i>I</i> > 2σ( <i>I</i> )]                        | 1726                                             |
| Parameters                                                      | 181                                              |
| <i>R</i> <sub>int</sub>                                         | 0.0508                                           |
| Goodness-of-fit                                                 | 0.918                                            |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] | 0.0363                                           |
| <i>wR</i> ( <i>F</i> <sup>2</sup> , all data)                   | 0.0825                                           |
| CCDC No.                                                        | 1432433                                          |