

## Supporting Information

### [3+2] Cycloaddition of Azides with Arynes Formed via C-H Deprotonation of Aryl Sulfonium Salts

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### Contents

1. General Experimental.....	S2
2. General procedure for the synthesis of substrates.....	S2
2.1 General procedure for the synthesis of azides.....	S2
2.2 General procedure for the synthesis of aryl sulfonium salts.....	S3
3. General Procedure for the [3+2] Cycloaddition.....	S5
4. Characterization and procedure of the products.....	S5
5. Transformation of products.....	S23
5.1 Gram reaction.....	S23
5.2 Procedure for the synthesis of 4t.....	S24
5.3 Procedure for the synthesis of 5al.....	S24
5.4 Procedure for the synthesis of 6al.....	S25
5.5 Procedure for the synthesis of 7al.....	S26
5.6 Procedure for the synthesis of 8al.....	S27
6. Reference.....	S28
7. NMR spectra of products.....	S29

## 1. General Experimental.

**Reagents and solvents:** Unless otherwise noted, the chemicals were commercially available from Sigma-Aldrich, TCI, BLD or Alfa Aesar and were used without further purification. PhCF<sub>3</sub> bought from TCI, >98.0%(GC). The reaction does not require the glovebox.

**Purification:** The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). Gradient flash chromatography was conducted eluting with PE/EA, PE refers to pentane and EA refers to ethyl acetate, they were listed as volume/volume ratios.

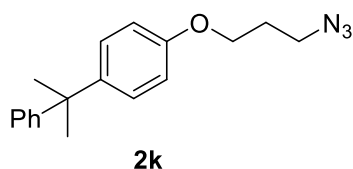
**Data collection:** GC-yields were calculated using hexadecane as internal standard. GC analysis was performed on an Agilent HP-7890A instrument with FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. High resolution mass spectra (HRMS) were recorded on Agilent 6210. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for CDCl<sub>3</sub> were 7.26 ppm (<sup>1</sup>H NMR) and 77.00 ppm (<sup>13</sup>C NMR). All measurements were carried out at room temperature unless otherwise stated.

## 2. General procedure for the synthesis of substrates.

### 2.1 General procedure for the synthesis of azides.<sup>[1]</sup>



A solution of bromide (1 equiv.) and NaN<sub>3</sub> (1.5 eq.) in DMF (0.2M) was heated at 80°C overnight. The reaction mixture was cooled, diluted with EtOAc, washed with H<sub>2</sub>O and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum, the crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product.

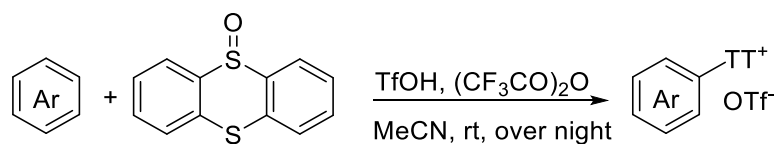


#### 1-(3-azidopropoxy)-4-(2-phenylpropan-2-yl)benzene (2k)

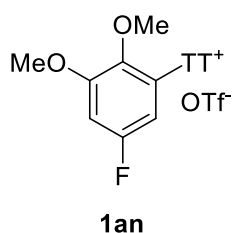
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.25 (m, 4H), 7.22 – 7.12 (m, 3H), 6.90 – 6.78 (m, 2H), 4.05 (t, *J* = 5.9 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.69 (s, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 156.5, 150.8, 143.2, 127.9, 127.8, 126.7, 125.5, 113.8, 64.4, 48.3, 42.3, 30.9, 28.8.

## 2.2 General procedure for the synthesis of aryl sulfonium salts.<sup>[2]</sup>



Aryl thianthrenium triflates were prepared by known literature procedure. Thianthrene S-oxide (1 equiv.), simple arene (1 equiv.) and acetonitrile (0.25M) were added to an appropriately sized vial, equipped with a magnetic stir bar. Trifluoromethanesulfonic acid (1.5 equiv.) was added in one portion, followed by one portion of trifluoroacetic anhydride (3 equiv.). The vial was capped and stirred vigorously at room temperature for 12 hours. Methanol was then added until the reactions dark color dissipated. The mixture was then concentrated under reduced pressure to afford an oily residue. This residue was then triturated with diethyl ether until precipitation ceased. The precipitate was isolated by vacuum filtration and washed by slurry filtration with diethyl ether (3 × 10 mL). After drying under air for 15 minutes the aryl thianthrenium triflate was obtained in pure form.



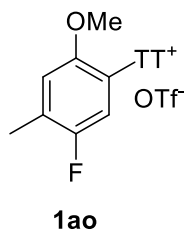
### Aryl Sulfonium Salts 1an

<sup>1</sup>H NMR (300 MHz, DMSO) δ 8.30 (dt, *J* = 8.1, 1.3 Hz, 2H), 8.14 – 8.04 (m, 2H), 7.96 – 7.62 (m, 4H), 7.37 (d, *J* = 12.3 Hz, 1H), 6.47 (d, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.57 (s, 3H).

<sup>13</sup>C NMR (75 MHz, DMSO) δ 156.0 (d, *J* = 245.3 Hz), 155.8 (d, *J* = 10.3 Hz), 146.3, 135.3, 134.9, 134.3, 130.6, 130.3, 119.6, 112.0, 103.3 (d, *J* = 25.8 Hz), 99.7 (d, *J* = 15.4 Hz), 57.4, 56.8.

<sup>19</sup>F NMR (282 MHz, DMSO) δ -77.74.

HRMS (ESI-TOF): *m/z* calcd. for C<sub>20</sub>H<sub>16</sub>FO<sub>2</sub>S<sub>2</sub><sup>+</sup> [M]<sup>+</sup> 371.0571, found 371.0575.



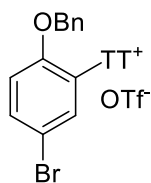
### Aryl Sulfonium Salts 1ao

<sup>1</sup>H NMR (300 MHz, DMSO) δ 8.45 – 8.36 (m, 2H), 8.12 – 8.03 (m, 2H), 7.95 – 7.73 (m, 4H), 7.35 (dd, *J* = 6.0, 0.8 Hz, 1H), 6.43 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.26 (d, *J* = 1.5 Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  154.7 (d,  $J = 239.9$  Hz), 153.9 (d,  $J = 1.6$  Hz), 136.5, 136.0, 135.0, 133.7 (d,  $J = 18.8$  Hz), 130.9, 129.9, 118.0, 117.4 (d,  $J = 4.3$  Hz), 115.5 (d,  $J = 28.7$  Hz), 108.2 (d,  $J = 8.3$  Hz), 57.9, 15.1 (d,  $J = 2.7$  Hz).

$^{19}\text{F}$  NMR (282 MHz, DMSO)  $\delta$  -77.74.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{FOS}_2^+$   $[\text{M}]^+$  355.0622, found 355.0621.



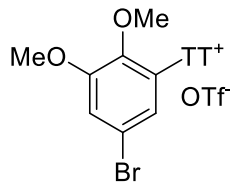
**1ap**

### Aryl Sulfonium Salts 1ap

$^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  8.17 – 8.05 (m, 4H), 7.95 – 7.83 (m, 3H), 7.69 (ddd,  $J = 8.1, 7.4, 1.3$  Hz, 2H), 7.52 – 7.44 (m, 3H), 7.41 – 7.33 (m, 3H), 6.63 (d,  $J = 2.3$  Hz, 1H), 5.34 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  156.2, 138.5, 136.7, 136.3, 135.1, 135.0, 131.1, 130.9, 129.9, 129.4, 129.2, 117.7, 112.7, 112.0, 72.2.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{18}\text{BrOS}_2^+$   $[\text{M}]^+$  476.9977, found 476.9970.



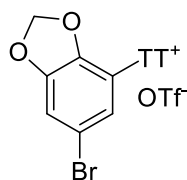
**1aq**

### Aryl Sulfonium Salts 1aq

$^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  8.50 – 8.38 (m, 2H), 8.16 – 8.07 (m, 2H), 7.97 – 7.75 (m, 4H), 7.54 (s, 1H), 6.47 (d,  $J = 0.4$  Hz, 1H), 3.85 (s, 3H), 3.52 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  154.3, 149.0, 136.2, 135.9, 135.1, 130.9, 130.1, 119.3, 118.6, 116.5, 113.8, 113.8, 57.3, 56.4.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{BrO}_2\text{S}_2^+$   $[\text{M}]^+$  430.9770, found 430.9763.



**1ar**

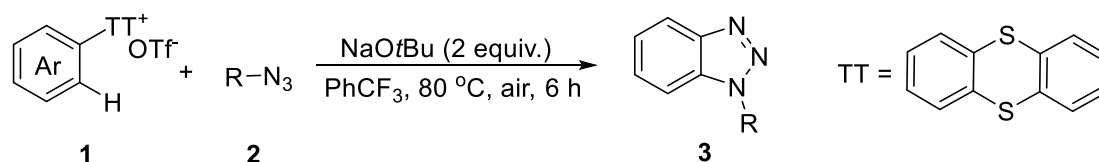
### Aryl Sulfonium Salts 1ar

$^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  8.48 (dd,  $J$  = 8.0, 1.4 Hz, 2H), 8.11 (dd,  $J$  = 7.9, 1.4 Hz, 2H), 7.91 (td,  $J$  = 7.7, 1.5 Hz, 2H), 7.80 (td,  $J$  = 7.7, 1.4 Hz, 2H), 7.65 (s, 1H), 6.59 (s, 1H), 6.20 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  153.5, 148.9, 136.6, 136.0, 135.1, 131.2, 130.0, 119.1, 117.9, 115.6, 115.5, 110.6, 104.6.

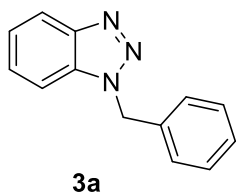
HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{12}\text{BrO}_2\text{S}_2^+ [\text{M}]^+$  414.9457, found 414.9448.

### 3. General Procedure for the [3+2] Cycloaddition.



A 5 mL snap vial equipped with a magnetic stir bar was charged with aryl sulfonium salts (0.3 mmol, 1.5 equiv.), NaOtBu (0.4 mmol, 2.0 equiv.), PhCF<sub>3</sub> (2 mL) and substrate azides (0.2 mmol, 1.0 equiv.) were added via syringe. The reaction mixture was stirred (500 rpm) at 80 °C for 6 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product.

### 4. Characterization and procedure of the products

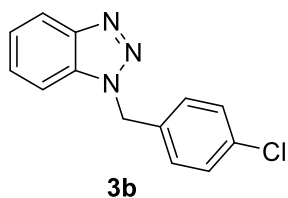


#### 1-benzyl-1H-benzo[d][1,2,3] triazole (3a)<sup>[3]</sup>

Chromatography Pentane/EA = 10:1 (v/v), 34.6 mg (83%).

$^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (dt,  $J$  = 7.7, 1.3 Hz, 1H), 7.38 – 7.13 (m, 8H), 5.76 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  146.2, 134.7, 132.7, 128.9, 128.4, 127.5, 127.4, 123.9, 120.0, 109.7, 52.2.

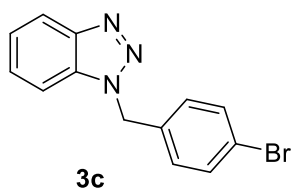


**1-(4-chlorobenzyl)-1H-benzo[d][1,2,3] triazole (3b)<sup>[3]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 28.8 mg (59%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.05 – 7.94 (m, 1H), 7.38 – 7.18 (m, 5H), 7.15 – 7.09 (m, 2H), 5.72 (s, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.2, 134.4, 133.2, 132.6, 129.2, 128.9, 127.6, 124.0, 120.1, 109.4, 51.4.

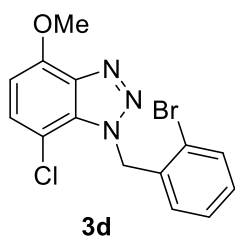


**1-(4-bromobenzyl)-1H-benzo[d][1,2,3] triazole (3c)<sup>[4]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 32.9 mg (57%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.12 – 8.02 (m, 1H), 7.52 – 7.26 (m, 5H), 7.19 – 7.07 (m, 2H), 5.79 (s, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.2, 133.7, 132.6, 132.1, 129.2, 127.6, 124.0, 122.5, 120.1, 109.4, 51.5.



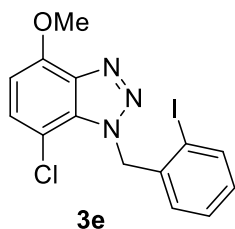
**1-(2-bromobenzyl)-7-chloro-4-methoxy-1H-benzo[d][1,2,3] triazole (3d)**

Chromatography Pentane/EA = 10:1 (v/v), 64.8 mg (92%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.55 (m, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.21 – 7.06 (m, 2H), 6.64 (d, *J* = 8.3 Hz, 1H), 6.39 – 6.29 (m, 1H), 6.19 (s, 2H), 4.11 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.7, 139.2, 135.7, 132.8, 131.5, 129.2, 129.0, 127.7, 127.1, 121.3, 106.9, 104.4, 56.4, 52.6.

HRMS (ESI-TOF): *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>BrClN<sub>3</sub>ONa<sup>+</sup> [*M*+Na<sup>+</sup>] 373.9666, found 373.9670.



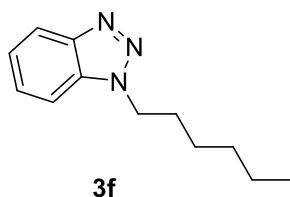
**7-chloro-1-(2-iodobenzyl)-4-methoxy-1H-benzo[d][1,2,3] triazole (3e)**

Chromatography Pentane/EA = 10:1 (v/v), 71.8 mg (90%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.28 (d,  $J = 8.3$  Hz, 1H), 7.14 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.02 – 6.91 (m, 1H), 6.63 (d,  $J = 8.3$  Hz, 1H), 6.29 – 6.19 (m, 1H), 6.09 (s, 2H), 4.10 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 139.5, 139.3, 138.7, 131.5, 129.4, 129.1, 128.6, 126.6, 107.0, 104.5, 96.1, 57.4, 56.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{11}\text{ClIN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 421.9527, found 421.9533.

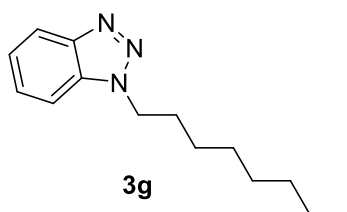


**1-hexyl-1H-benzo[d][1,2,3] triazole (3f)<sup>[5]</sup>**

Chromatography Pentane/EA = 20:1 (v/v), 30.5 mg (75%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.56 – 7.43 (m, 2H), 7.41 – 7.32 (m, 1H), 4.63 (t,  $J = 7.2$  Hz, 2H), 2.08 – 1.92 (m, 2H), 1.43 – 1.18 (m, 6H), 1.00 – 0.79 (m, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 132.9, 127.1, 123.7, 120.0, 109.3, 48.2, 31.2, 29.6, 26.4, 22.4, 13.9.

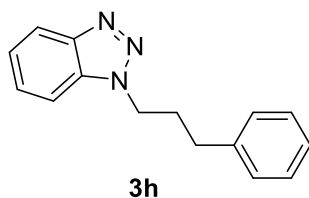


**1-octyl-1H-benzo[d][1,2,3] triazole (3g)<sup>[6]</sup>**

Chromatography Pentane/EA = 20:1 (v/v), 36.0 mg (78%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.56 – 7.43 (m, 2H), 7.36 (ddd,  $J = 8.1, 6.5, 1.4$  Hz, 1H), 4.63 (t,  $J = 7.2$  Hz, 2H), 2.08 – 1.92 (m, 2H), 1.42 – 1.14 (m, 10H), 0.93 – 0.79 (m, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 132.9, 127.1, 123.7, 120.0, 109.3, 48.2, 31.7, 29.7, 29.0, 29.0, 26.7, 22.5, 14.0.

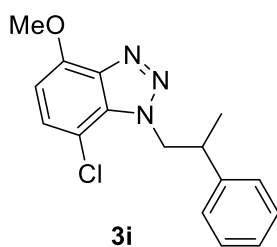


**1-(3-phenylpropyl)-1H-benzo[d][1,2,3] triazole (3h) <sup>17</sup>**

Chromatography Pentane/EA = 20:1 (v/v), 35.1 mg (74%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.99 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.45–7.31 (m, 2H), 7.34–7.23 (m, 1H), 7.27–7.15 (m, 2H), 7.19–7.04 (m, 3H), 4.55 (t, *J* = 7.0 Hz, 2H), 2.67–2.54 (m, 2H), 2.37–2.21 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.9, 140.2, 132.9, 128.5, 128.4, 127.2, 126.3, 123.8, 120.0, 109.2, 47.3, 32.6, 30.9.



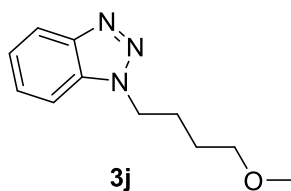
**7-chloro-4-methoxy-1-(2-phenylpropyl)-1H-benzo[d][1,2,3]triazole (3i)**

Chromatography Pentane/EA = 10:1 (v/v), 47.4 mg (79%), 13:1 *rr*.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.26–6.89 (m, 6H), 6.45 (d, *J* = 8.3 Hz, 1H), 5.78–5.61 (m, 1H), 3.97 (s, 3H), 3.45 (dd, *J* = 13.6, 7.5 Hz, 1H), 3.16 (dd, *J* = 13.6, 7.3 Hz, 1H), 1.67 (d, *J* = 6.7 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.5, 138.9, 137.3, 131.0, 129.1, 128.6, 128.3, 126.6, 106.7, 103.6, 57.1, 56.3, 43.5, 21.0.

HRMS (ESI-TOF): *m/z* calcd. for C<sub>16</sub>H<sub>16</sub>ClN<sub>3</sub>ONa<sup>+</sup> [*M*+Na<sup>+</sup>] 324.0874, found 324.0879.



**1-(4-methoxybutyl)-1H-benzo[d][1,2,3] triazole (3j)**

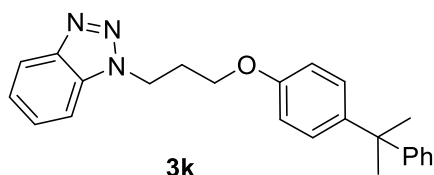
Chromatography Pentane/EA = 5:1 (v/v), 34.0 mg (83%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.04 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.58–7.41 (m, 2H), 7.35 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 4.66 (t, *J* = 7.1 Hz, 2H), 3.38 (t, *J* = 6.1 Hz, 2H), 3.29 (s, 3H), 2.09 (tt, *J* = 7.4, 6.6 Hz, 2H), 1.70–1.53 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.8, 132.9, 127.2, 123.8, 119.9, 109.3, 71.7, 58.5, 48.0, 26.7, 26.6.



HRMS (ESI-TOF):  $m/z$  calcd. for  $C_{11}H_{15}N_3ONa^+$  [ $M+Na^+$ ] 228.1107, found 228.1110.

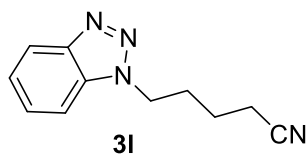


### 1-(3-(4-(2-phenylpropan-2-yl) phenoxy) propyl)-1H-benzo[d][1,2,3] triazole (**3k**)

Chromatography Pentane/EA = 8:1 (v/v), 50.4 mg (65%).

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.97 (dt,  $J$  = 8.2, 1.1 Hz, 1H), 7.50–7.40 (m, 1H), 7.37–7.30 (m, 1H), 7.29–7.23 (m, 1H), 7.21–7.00 (m, 7H), 6.75–6.62 (m, 2H), 4.76 (t,  $J$  = 6.8 Hz, 2H), 3.85 (t,  $J$  = 5.7 Hz, 2H), 2.46–2.27 (m, 2H), 1.57 (s, 6H).

$^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  156.2, 150.8, 145.7, 143.3, 133.2, 127.9, 127.8, 127.3, 126.6, 125.5, 123.9, 119.9, 113.8, 109.3, 64.0, 44.7, 42.2, 30.8, 29.6.



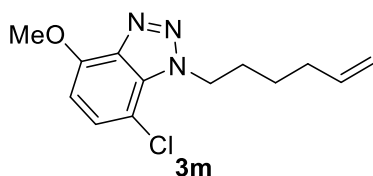
### 5-(1H-benzo[d][1,2,3] triazol-1-yl) pentanenitrile (**3l**)

Chromatography Pentane/EA = 3:1 (v/v), 21.4 mg (53%).

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.06 (dt,  $J$  = 8.3, 1.0 Hz, 1H), 7.58–7.42 (m, 2H), 7.42–7.33 (m, 1H), 4.70 (t,  $J$  = 6.7 Hz, 2H), 2.40 (t,  $J$  = 7.0 Hz, 2H), 2.27–2.11 (m, 2H), 1.77–1.61 (m, 2H).

$^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  145.9, 132.7, 127.5, 124.0, 120.1, 118.9, 109.0, 46.9, 28.3, 22.4, 16.6.

HRMS (ESI-TOF):  $m/z$  calcd. for  $C_{11}H_{12}N_4Na^+$  [ $M+Na^+$ ] 223.0954, found 223.0954.



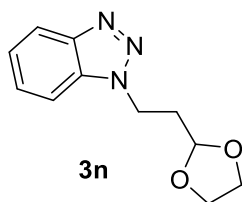
### 7-chloro-1-(hex-5-en-1-yl)-4-methoxy-1H-benzo[d][1,2,3] triazole (**3m**)

Chromatography Pentane/EA = 15:1 (v/v), 46.3 mg (87%), 17:1 *rr*.

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.29 (d,  $J$  = 8.3 Hz, 1H), 6.58 (d,  $J$  = 8.3 Hz, 1H), 5.84–5.65 (m, 1H), 5.05–4.74 (m, 4H), 4.06 (s, 3H), 2.17–1.91 (m, 4H), 1.46 (tt,  $J$  = 9.9, 6.5 Hz, 2H).

$^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  150.7, 139.2, 137.9, 131.2, 128.5, 115.0, 106.8, 103.8, 56.3, 49.3, 33.0, 30.7, 25.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $C_{13}H_{16}ClN_3ONa^+$  [ $M+Na^+$ ] 288.0874, found 288.0879.



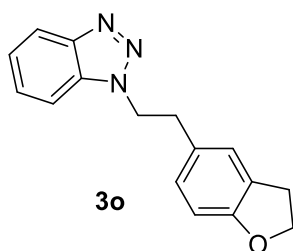
**1-(2-(1,3-dioxolan-2-yl)ethyl)-1H-benzo[d][1,2,3] triazole (3n)**

Chromatography Pentane/EA = 5:1 (v/v), 32.9 mg (75%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06–7.97 (m, 1H), 7.59–7.51 (m, 1H), 7.50–7.42 (m, 1H), 7.38–7.30 (m, 1H), 4.90 (t,  $J$  = 4.3 Hz, 1H), 4.81–4.73 (m, 2H), 4.04–3.75 (m, 4H), 2.42–2.33 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 132.9, 127.2, 123.8, 120.0, 109.3, 101.5, 65.0, 43.0, 33.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_2\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 242.0900, found 242.0905.



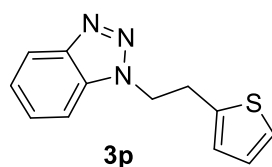
**1-(2-(2,3-dihydrobenzofuran-5-yl)ethyl)-1H-benzo[d][1,2,3] triazole (3o)**

Chromatography Pentane/EA = 5:1 (v/v), 41.9 mg (79%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00–7.89 (m, 1H), 7.49–7.07 (m, 3H), 6.86–6.70 (m, 2H), 6.64–6.53 (m, 1H), 4.76–4.65 (m, 2H), 4.42 (t,  $J$  = 8.7 Hz, 2H), 3.19–3.07 (m, 2H), 2.98 (t,  $J$  = 8.7 Hz, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 145.7, 133.0, 129.1, 128.1, 127.4, 127.0, 125.2, 123.7, 119.8, 109.3, 109.2, 71.1, 50.0, 35.7, 29.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 288.1107, found 288.1111.



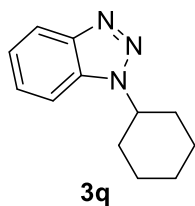
**1-(2-(thiophen-2-yl)ethyl)-1H-benzo[d][1,2,3] triazole (3p)**

Chromatography Pentane/EA = 8:1 (v/v), 33.7 mg (74%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dt,  $J$  = 8.2, 1.1 Hz, 1H), 7.39–7.10 (m, 4H), 6.83–6.73 (m, 2H), 4.77 (t,  $J$  = 7.2 Hz, 2H), 3.27 (t,  $J$  = 7.2 Hz, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 137.4, 133.0, 127.7, 127.2, 126.2, 123.7, 122.2, 119.8, 109.0, 48.9, 30.6.

HRMS (ESI-TOF):  $m/z$  calcd. for  $C_{12}H_{11}N_3SNa^+$   $[M+Na^+]$  252.0566, found 252.0572.

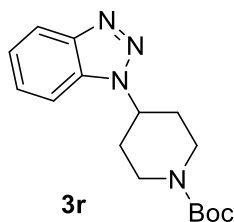


### 1-cyclohexyl-1H-benzo[d] [1,2,3] triazole (**3q**)<sup>181</sup>

Chromatography Pentane/EA = 20:1 (v/v), 27.3 mg (68%).

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.05 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.57 (dt,  $J = 8.4, 1.0$  Hz, 1H), 7.49–7.41 (m, 1H), 7.34 (ddd,  $J = 8.1, 6.9, 1.1$  Hz, 1H), 4.76–4.55 (m, 1H), 2.27–2.06 (m, 4H), 2.05–1.92 (m, 2H), 1.88–1.73 (m, 1H), 1.62–1.21 (m, 3H).

$^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  146.0, 132.2, 126.7, 123.7, 120.0, 109.7, 59.0, 32.5, 25.5, 25.2.



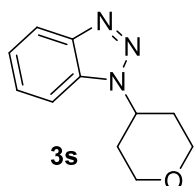
### tert-butyl 4-(1H-benzo[d] [1,2,3] triazol-1-yl) piperidine-1-carboxylate (**3r**)

Chromatography Pentane/EA = 8:1 (v/v), 43.2 mg (71%).

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.55 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.50–7.41 (m, 1H), 7.39–7.30 (m, 1H), 4.88–4.76 (m, 1H), 4.28 (dd,  $J = 24.7, 9.5$  Hz, 2H), 3.01 (t,  $J = 12.7$  Hz, 2H), 2.42–2.22 (m, 2H), 2.20–2.09 (m, 2H), 1.48 (s, 9H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  154.5, 146.0, 132.1, 129.4, 123.9, 120.1, 109.4, 80.0, 56.9, 31.4, 28.3.

HRMS (ESI-TOF):  $m/z$  calcd. for  $C_{16}H_{22}N_4O_2Na^+$   $[M+Na^+]$  325.1635, found 325.1633.



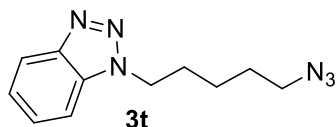
### 1-(tetrahydro-2H-pyran-4-yl)-1H-benzo[d] [1,2,3] triazole (**3s**)

Chromatography Pentane/EA = 5:1 (v/v), 30.1 mg (74%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.59 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.51 – 7.43 (m, 1H), 7.41 – 7.32 (m, 1H), 4.92 (tt,  $J = 11.6, 4.3$  Hz, 1H), 4.24 – 4.14 (m, 2H), 3.70 – 3.59 (m, 2H), 2.58 – 2.43 (m, 2H), 2.18 – 2.07 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 132.0, 127.1, 123.9, 120.2, 109.5, 66.9, 56.0, 32.2.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 204.1137, found 204.1138.



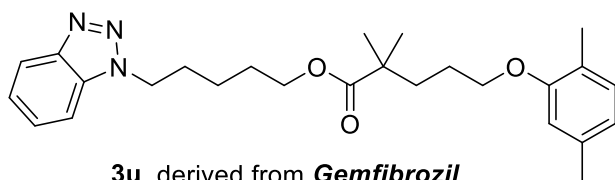
### 1-(5-azidopentyl)-1H-benzo[d][1,2,3] triazole (**3t**)

Chromatography Pentane/EA = 5:1 (v/v), 27.7 mg (60%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.57 – 7.44 (m, 2H), 7.37 (ddd,  $J = 8.4, 6.0, 1.9$  Hz, 1H), 4.65 (t,  $J = 7.0$  Hz, 2H), 3.25 (t,  $J = 6.8$  Hz, 2H), 2.14 – 1.98 (m, 2H), 1.71 – 1.56 (m, 2H), 1.50 – 1.35 (m, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 132.9, 127.3, 123.9, 120.1, 109.1, 51.1, 47.9, 29.2, 28.3, 23.9.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_6\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 253.1172, found 253.1175.



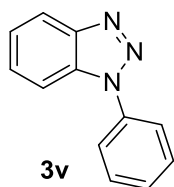
### 5-(1H-benzo[d][1,2,3] triazol-1-yl) pentyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**3u**)

Chromatography Pentane/EA = 5:1 (v/v), 51.0 mg (58%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (dt,  $J = 8.3, 1.1$  Hz, 1H), 7.56 – 7.45 (m, 2H), 7.43 – 7.34 (m, 1H), 7.01 (d,  $J = 7.4$  Hz, 1H), 6.71 – 6.60 (m, 2H), 4.65 (t,  $J = 7.0$  Hz, 2H), 4.06 (t,  $J = 6.5$  Hz, 2H), 3.99 – 3.85 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 2.15 – 1.99 (m, 2H), 1.82 – 1.62 (m, 6H), 1.51 – 1.33 (m, 2H), 1.19 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 156.8, 145.8, 136.4, 132.8, 130.2, 127.2, 123.8, 123.4, 119.9, 111.9, 109.1, 67.8, 63.7, 47.8, 42.0, 36.9, 29.1, 28.0, 25.1, 25.0, 23.1, 21.3, 15.7.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{35}\text{N}_3\text{O}_3\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 460.2570, found 460.2564.

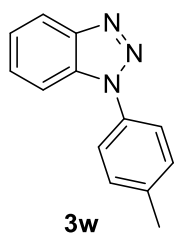


**1-phenyl-1H-benzo[d][1,2,3]triazole (3v)** <sup>[9]</sup>

Chromatography Pentane/EA = 10:1 (v/v), 27.4 mg (70%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.14 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.83 – 7.69 (m, 3H), 7.64 – 7.37 (m, 5H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.4, 136.9, 132.2, 129.8, 128.6, 128.2, 124.3, 122.8, 120.2, 110.3.

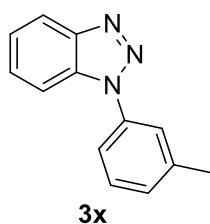


**1-(p-tolyl)-1H-benzo[d][1,2,3]triazole (3w)** <sup>[10]</sup>

Chromatography Pentane/EA = 10:1 (v/v), 29.0 mg (69%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.65 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 2.39 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.8, 139.5, 134.0, 132.5, 130.5, 128.6, 125.3, 123.0, 119.5, 110.7, 21.2.

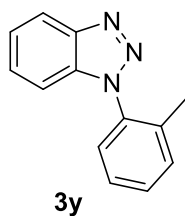


**1-(m-tolyl)-1H-benzo[d][1,2,3]triazole (3x)** <sup>[11]</sup>

Chromatography Pentane/EA = 10:1 (v/v), 27.1 mg (65%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.58 – 7.30 (m, 7H), 2.13 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.6, 135.3, 135.2, 133.9, 131.6, 130.0, 128.0, 127.0, 126.9, 124.1, 120.0, 110.1, 17.8.

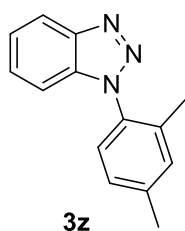


**1-(*o*-tolyl)-1*H*-benzo[*d*][1,2,3]triazole (3y) <sup>[11]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 25.9 mg (62%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.14 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.74 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.59 – 7.39 (m, 4H), 7.35 – 7.28 (m, 1H), 2.49 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.4, 140.1, 136.8, 132.3, 129.5, 129.4, 128.1, 124.3, 123.5, 120.2, 119.8, 110.4, 21.4.

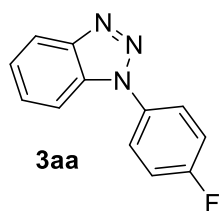


**1-(2,4-dimethylphenyl)-1*H*-benzo[*d*][1,2,3]triazole (3z) <sup>[12]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 32.0 mg (72%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.15 (m, 5H), 7.12 (s, 1H), 2.32 (s, 3H), 1.99 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.9, 134.9, 131.9, 131.3, 130.7, 127.9, 127.4, 124.0, 119.9, 110.2, 20.7, 17.2.



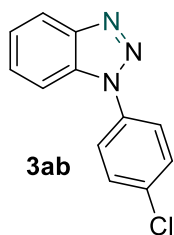
**1-(4-fluorophenyl)-1*H*-benzo[*d*][1,2,3]triazole (3aa) <sup>[11]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 27.3 mg (64%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.68 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.48 – 7.39 (m, 1H), 7.36 – 7.27 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.3 (d, *J* = 249.1 Hz), 146.4, 133.1 (d, *J* = 3.2 Hz), 132.3, 128.4, 124.8 (d, *J* = 8.6 Hz), 124.4, 120.3, 116.8 (d, *J* = 23.1 Hz), 110.0.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.91 – -112.06 (m, 1F).

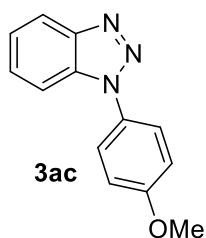


**1-(4-chlorophenyl)-1H-benzo[d][1,2,3]triazole (3ab) <sup>[11]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 38.0 mg (83%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J$  = 8.4 Hz, 1H), 7.79 – 7.65 (m, 3H), 7.63 – 7.49 (m, 3H), 7.49 – 7.37 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 135.4, 134.3, 132.0, 130.0, 128.5, 124.5, 123.8, 120.4, 110.0.

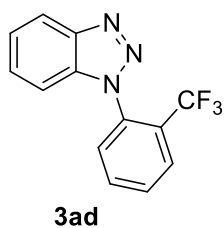


**1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (3ac) <sup>[13]</sup>**

Chromatography Pentane/EA = 5:1 (v/v), 31.5 mg (70%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (dt,  $J$  = 8.3, 1.0 Hz, 1H), 7.70 – 7.59 (m, 3H), 7.54 – 7.47 (m, 1H), 7.45 – 7.37 (m, 1H), 7.15 – 7.04 (m, 2H), 3.89 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 146.2, 132.6, 129.9, 128.0, 124.5, 124.2, 120.1, 114.9, 110.2, 55.6.



**1-(2-(trifluoromethyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ad)**

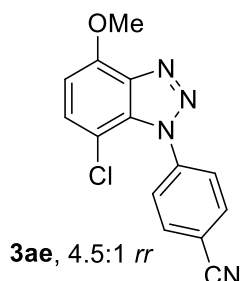
Chromatography Pentane/EA = 10:1 (v/v), 31.5 mg (60%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (dt,  $J$  = 8.2, 1.0 Hz, 1H), 8.01 – 7.88 (m, 1H), 7.88 – 7.69 (m, 2H), 7.57 – 7.37 (m, 3H), 7.34 – 7.28 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 134.9, 133.7 (q,  $J = 1.5$  Hz), 133.1, 130.7, 129.8, 128.4, 128.2 (q,  $J = 31.4$  Hz), 127.8 (q,  $J = 4.8$  Hz), 124.3, 122.6 (q,  $J = 272.2$  Hz), 120.0, 109.8.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -59.90 (s, 3F).

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_8\text{F}_3\text{N}_3\text{H}^+$  [ $\text{M}+\text{H}^+$ ] 264.0749, found 264.0751.



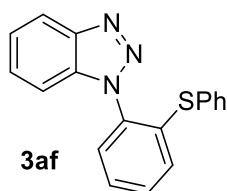
#### 4-(7-chloro-4-methoxy-1H-benzo[d][1,2,3]triazol-1-yl)benzonitrile (3ae)

Chromatography Pentane/EA = 3:1 (v/v), 41.2 mg (73%), 4.5:1 *rr*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91–7.78 (m, 2.79H), 7.76–7.70 (m, 1.88H), 7.42 (d,  $J = 8.4$  Hz, 0.96H), 7.36 (d,  $J = 8.3$  Hz, 0.23H), 6.85 (d,  $J = 8.3$  Hz, 0.24H), 6.74 (d,  $J = 8.4$  Hz, 0.99H), 4.13 (s, 3H), 3.88 (s, 0.67H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 144.5, 139.4, 139.1, 132.6, 132.6, 131.3, 130.5, 127.9, 126.1, 124.9, 117.7, 113.58, 108.2, 106.8, 105.1, 56.7, 56.1.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_9\text{ClN}_4\text{OH}^+$  [ $\text{M}+\text{H}^+$ ] 285.0543, found 285.0541.



#### 1-(2-(phenylthio)phenyl)-1H-benzo[d][1,2,3]triazole (3af)

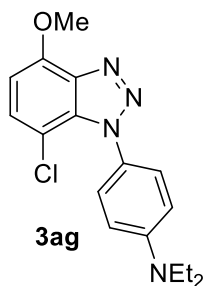
Chromatography Pentane/EA = 6:1 (v/v), 40.6 mg (67%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16–8.09 (m, 1H), 7.54–7.45 (m, 2H), 7.44–7.38 (m, 4H), 7.37–7.32 (m, 1H), 7.23 (s, 5H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 136.0, 134.9, 133.6, 132.9, 132.5, 131.5, 130.4, 129.3, 128.3, 128.0, 127.9, 127.4, 124.1, 120.0, 110.4.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{SNa}^+$  [ $\text{M}+\text{Na}^+$ ] 326.0722, found 326.0730.





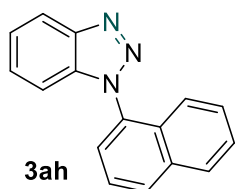
**4-(7-chloro-4-methoxy-1H-benzo[d][1,2,3]triazol-1-yl)-N,N-diethylaniline (3ag)**

Chromatography Pentane/EA = 5:1 (v/v), 13.0 mg (20%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J$  = 8.3 Hz, 3H), 6.68 (dd,  $J$  = 26.0, 8.4 Hz, 3H), 4.12 (s, 3H), 3.43 (q,  $J$  = 7.1 Hz, 4H), 1.22 (t,  $J$  = 7.1 Hz, 6H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 148.6, 138.8, 135.3, 132.0, 129.0, 128.4, 110.6, 107.7, 104.0, 56.5, 44.5, 12.4.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{19}\text{ClN}_4\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 353.1139, found 353.1139.

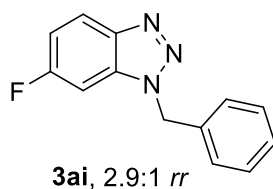


**1-(naphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (3ah) <sup>[14]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 38.5 mg (79%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29–8.15 (m, 1H), 8.14–8.02 (m, 1H), 8.00 (dt,  $J$  = 8.3, 1.1 Hz, 1H), 7.71–7.64 (m, 2H), 7.63–7.54 (m, 1H), 7.52–7.39 (m, 4H), 7.34–7.28 (m, 1H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 134.7, 134.4, 132.5, 130.4, 129.1, 128.3, 128.1, 127.6, 127.0, 125.2, 124.6, 124.3, 122.6, 120.1, 110.3.



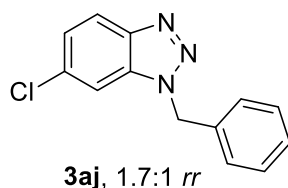
**1-benzyl-6-fluoro-1H-benzo[d][1,2,3]triazole (3ai) <sup>[15]</sup>**

Chromatography Pentane/EA = 10:1 (v/v), 32.1 mg (71%), 2.9:1 *rr*.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98–7.88 (m, 0.41H), 7.64–7.54 (m, 0.94H), 7.32–7.16 (m, 7.98H), 7.13–6.97 (m, 1.51H), 6.94–6.84 (m, 0.45H), 5.75 (s, 2H), 5.71 (s, 0.85H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (d,  $J = 246.8$  Hz), 159.6 (d,  $J = 241.6$  Hz), 146.5 (d,  $J = 12.1$  Hz), 143.1, 134.3, 134.2, 129.7, 129.1, 129.0, 128.6, 127.5, 127.5, 121.5 (d,  $J = 11.0$  Hz), 117.4 (d,  $J = 27.9$  Hz), 113.9 (d,  $J = 27.0$  Hz), 110.7 (d,  $J = 10.2$  Hz), 104.5 (d,  $J = 24.3$  Hz), 95.5 (d,  $J = 27.9$  Hz), 52.6, 52.3.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.29 – -113.77 (m, 1F), -117.71 – -117.97 (m; 1F).

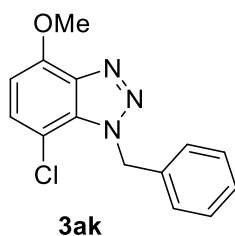


### 1-benzyl-6-chloro-1H-benzo[d][1,2,3]triazole (**3aj**)<sup>[15]</sup>

Chromatography Pentane/EA = 10:1 (v/v), 33.4 mg (69%), 1.7:1 *rr*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.80 (m, 1.67H), 7.57 – 6.99 (m, 11.7H), 5.75 (s, 2H), 5.72 (s, 1.2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 144.8, 134.2, 134.2, 133.8, 133.3, 131.4, 129.9, 129.8, 129.1, 129.1, 128.6, 128.3, 127.5, 125.2, 124.4, 120.9, 119.4, 110.7, 109.5, 52.5, 52.3.



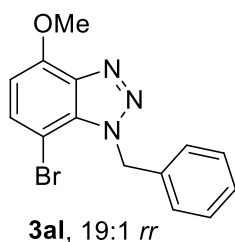
### 1-benzyl-7-chloro-4-methoxy-1H-benzo[d][1,2,3]triazole (**3ak**)

Chromatography Pentane/EA = 10:1 (v/v), 48.2 mg (88%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.08 (m, 6H), 6.51 (d,  $J = 8.3$  Hz, 1H), 6.03 (s, 2H), 4.00 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 139.3, 136.1, 131.3, 128.9, 128.7, 128.1, 127.1, 106.9, 104.1, 56.4, 52.4.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 296.0561, found 296.0568.



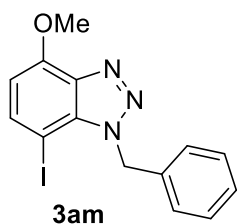
### 1-benzyl-7-bromo-4-methoxy-1H-benzo[d][1,2,3]triazole (**3al**)

Chromatography Pentane/EA = 8:1 (v/v), 60.8 mg (96%), 19:1 *rr*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (dd,  $J = 8.3, 0.4$  Hz, 1H), 7.42 – 7.13 (m, 5H), 6.57 (d,  $J = 8.3$  Hz, 1H), 6.17 (s, 2H), 4.09 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 139.1, 136.2, 132.4, 132.3, 128.6, 127.9, 126.9, 104.8, 92.4, 56.4, 52.0.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{12}\text{BrN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 340.0056, found 340.0065.



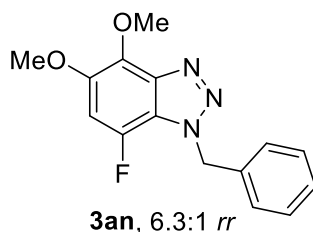
### 1-benzyl-7-bromo-4-methoxy-1H-benzo[d][1,2,3]triazole (3am)

Chromatography Pentane/EA = 8:1 (v/v), 34.5 mg (47%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.30 (m, 3H), 7.29 – 7.19 (m, 3H), 7.06 (d,  $J = 8.9$  Hz, 1H), 5.81 (s, 2H), 3.94 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 149.1, 134.3, 129.0, 128.5, 128.3, 127.5, 114.6, 110.2, 74.2, 57.9, 52.8.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{12}\text{IN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 387.9917, found 387.9926.



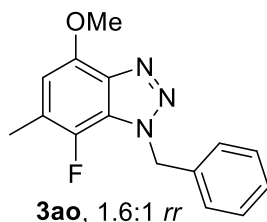
### 1-benzyl-7-fluoro-4,5-dimethoxy-1H-benzo[d][1,2,3]triazole (3an)

Chromatography Pentane/EA = 5:1 (v/v), 50.8 mg (88%), 6.3:1 *rr*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.18 (m, 5H), 6.84 (d,  $J = 11.2$  Hz, 1H), 5.77 (s, 2H), 4.34 (s, 3H), 3.80 (s, 3H).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -126.78 (d,  $J = 11.2$  Hz, 0.16F), -136.63 (d,  $J = 11.1$  Hz, 1F).

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{14}\text{FN}_3\text{O}_2\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 310.0962, found 310.0962.



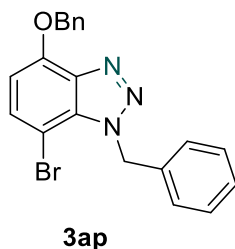
**1-benzyl-7-fluoro-4-methoxy-6-methyl-1H-benzo[d][1,2,3]triazole (3ao)**

Chromatography Pentane/EA = 10:1 (v/v), 51.0 mg (94%), 1.6:1 *rr*.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28–7.11 (m, 7.8H), 6.39 (d,  $J = 4.7$  Hz, 0.6H), 6.28 (d,  $J = 4.7$  Hz, 0.96H), 5.84 (s, 1.21H), 5.76 (s, 1.99H), 3.93 (s, 3H), 3.79 (s, 1.85H), 2.24 (m, 4.88H).

$^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -140.02 (s, 0.59F), -145.08 – -146.79 (m, 1F).

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{14}\text{FN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 294.1013, found 294.1015.



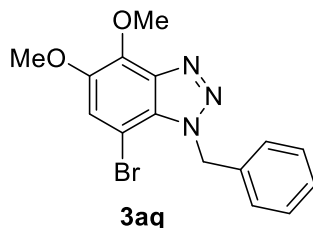
**1-benzyl-4-(benzyloxy)-7-bromo-1H-benzo[d][1,2,3]triazole (3ap)**

Chromatography Pentane/EA = 8:1 (v/v), 66.4 mg (84%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.34 (m, 2H), 7.30–6.94 (m, 9H), 6.49 (d,  $J = 8.3$  Hz, 1H), 6.04 (s, 2H), 5.33 (s, 2H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 139.3, 136.1, 136.0, 132.5, 132.2, 128.6, 128.5, 128.1, 127.9, 127.4, 126.9, 106.9, 92.6, 71.3, 52.0.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{BrN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 416.0369, found 416.0373.



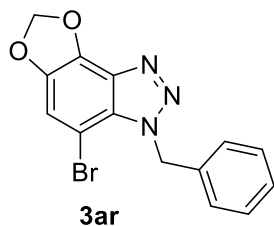
**1-benzyl-7-bromo-4,5-dimethoxy-1H-benzo[d][1,2,3]triazole (3aq)**

Chromatography Pentane/EA = 5:1 (v/v), 39.3 mg (57%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29–7.17 (m, 4H), 7.14–7.07 (m, 2H), 6.04 (s, 2H), 4.45 (s, 3H), 3.83 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 140.6, 139.6, 136.2, 128.7, 128.6, 128.0, 127.0, 121.6, 91.6, 61.7, 58.5, 52.0.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{14}\text{BrN}_3\text{O}_2\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 370.0161, found 370.0162.



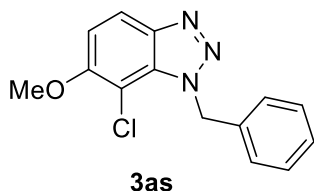
### 3-benzyl-4-bromo-3H-[1,3]dioxolo[4',5':3,4]benzo[1,2-d][1,2,3]triazole (3ar)

Chromatography Pentane/EA = 5:1 (v/v), 43.5 mg (66%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.15 (m, 4H), 7.12 – 7.00 (m, 2H), 6.11 (s, 2H), 6.05 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 136.1, 136.1, 133.5, 129.2, 128.7, 128.0, 126.9, 115.0, 103.3, 91.5, 52.3.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{O}_2\text{Na}^+$  [ $\text{M}+\text{Na}^+$ ] 353.9848, found 353.9852.



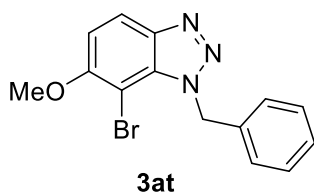
### 1-benzyl-7-chloro-6-methoxy-1H-benzo[d][1,2,3]triazole (3as)

Chromatography Pentane/EA = 8:1 (v/v), 33.4 mg (61%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.21 (m, 3H), 7.20 – 7.14 (m, 2H), 7.12 – 7.04 (m, 2H), 5.73 (s, 2H), 3.86 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 145.1, 134.3, 129.3, 129.0, 128.6, 127.5, 115.9, 111.3, 108.2, 57.9, 52.6.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{ONa}^+$  [ $\text{M}+\text{Na}^+$ ] 296.0561, found 296.0562.



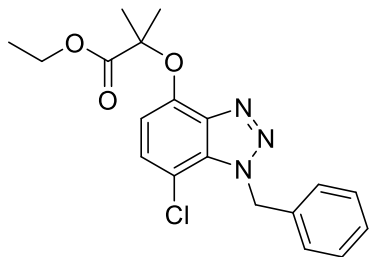
### 1-benzyl-7-bromo-6-methoxy-1H-benzo[d][1,2,3]triazole (3at)

Chromatography Pentane/EA = 8:1 (v/v), 39.6 mg (62%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.30 (m, 3H), 7.29 – 7.20 (m, 3H), 7.16 – 7.09 (m, 1H), 5.82 (s, 2H), 3.95 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 146.4, 134.3, 129.0, 129.0, 128.5, 127.5, 115.6, 109.1, 100.1, 57.9, 52.7.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{12}\text{BrN}_3\text{ONa}^+$   $[\text{M}+\text{Na}^+]$  340.0056, found 340.0054.



**3au**, derived from **Clofibrate**

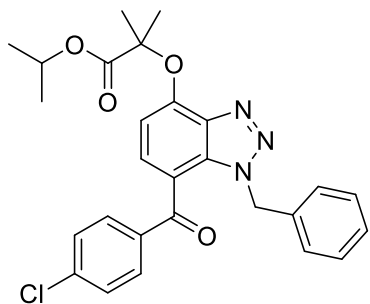
**ethyl 2-((1-benzyl-7-chloro-1H-benzo[d][1,2,3]triazol-4-yl)oxy)-2-methylpropanoate (3au)**

Chromatography Pentane/EA = 6:1 (v/v), 27.8 mg (37%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.09 (m, 6H), 6.43 (d,  $J = 8.4$  Hz, 1H), 6.04 (s, 2H), 4.16 (q,  $J = 7.1$  Hz, 2H), 1.70 (s, 6H), 1.13 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 146.7, 140.6, 136.1, 131.4, 128.7, 128.4, 128.1, 127.1, 109.8, 107.7, 80.7, 61.6, 52.5, 25.3, 14.0.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{20}\text{ClN}_3\text{O}_3\text{Na}^+$   $[\text{M}+\text{Na}^+]$  396.1085, found 396.1088.



**3av**, derived from **Fenofibrate**

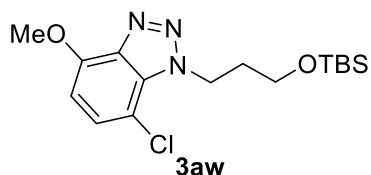
**isopropyl 2-((1-benzyl-7-(4-chlorobenzoyl)-1H-benzo[d][1,2,3]triazol-4-yl)oxy)-2-methylpropanoate (3av)**

Chromatography Pentane/EA = 5:1 (v/v), 33.8 mg (34%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.32 (m, 2H), 7.30 – 7.16 (m, 3H), 7.00 – 6.81 (m, 3H), 6.78 – 6.65 (m, 2H), 6.37 (d,  $J = 8.2$  Hz, 1H), 5.99 (s, 2H), 5.01 (p,  $J = 6.3$  Hz, 1H), 1.76 (s, 6H), 1.09 (d,  $J = 6.3$  Hz, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  192.0, 172.5, 151.5, 139.2, 135.7, 135.0, 132.1, 131.4, 129.4, 128.5, 128.4, 127.7, 127.6, 116.3, 106.6, 81.1, 69.4, 53.9, 25.4, 21.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{26}\text{ClN}_3\text{O}_4\text{Na}^+$   $[\text{M}+\text{Na}^+]$  514.1504, found 514.1507.



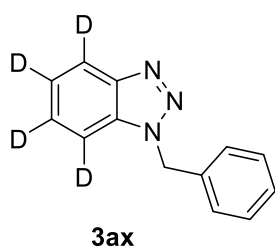
### 1-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-7-chloro-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**3aw**)

Chromatography Pentane/EA = 10:1 (v/v), 58.3 mg (82%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J$  = 8.3 Hz, 1H), 6.54 (d,  $J$  = 8.3 Hz, 1H), 5.04 – 4.94 (m, 2H), 4.03 (s, 3H), 3.67 (t,  $J$  = 5.9 Hz, 2H), 2.24 – 2.06 (m, 2H), 0.84 (s, 9H), 0.00 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 139.2, 131.3, 128.5, 106.9, 103.8, 59.8, 56.4, 46.8, 34.2, 25.8, 18.2, -5.5.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{26}\text{ClN}_3\text{O}_2\text{SiNa}^+$  [ $\text{M}+\text{Na}^+$ ] 378.1375, found 378.1376.



### 1-benzyl-1*H*-benzo[*d*][1,2,3]triazole-4,5,6,7- $\text{d}_4$ (**3ax**)

Chromatography Pentane/EA = 10:1 (v/v), 32.7 mg (77%).

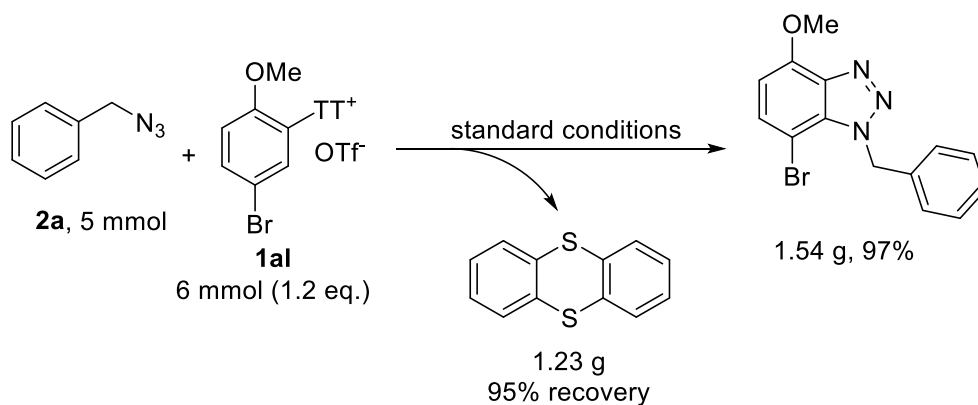
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.13 (m, 5H), 5.75 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2, 134.7, 132.7, 128.9, 128.4, 127.5, 127.2, 123.7 – 123.1 (m), 119.8, 109.6, 52.2.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_7\text{D}_4\text{N}_3\text{H}^+$  [ $\text{M}+\text{H}^+$ ] 214.1282, found 214.1287.

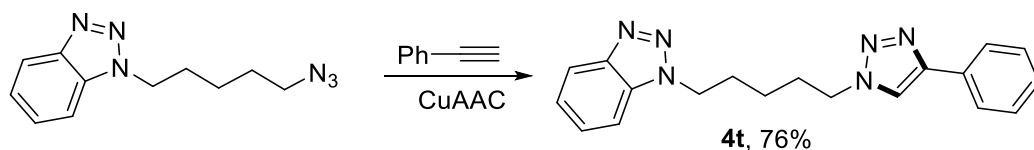
## 5. Transformation of products.

### 5.1 Gram reaction.

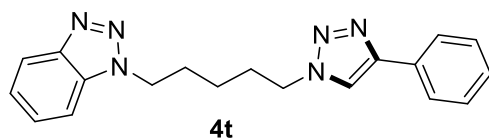


To a 200 mL of Schlenk tube were added aryl sulfonium salt **1a** (6 mmol, 1.2 equiv.), NaOtBu (10 mmol, 2.0 equiv.). PhCF<sub>3</sub> (50 mL) and azide **2a** (5 mmol, 1.0 equiv) were added via syringe. The reaction mixture was stirred at 80 °C for 6 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **3a** (1.54 g, 97%).

5.2 Procedure for the synthesis of **4t**.



A 5 mL snap vial equipped with a magnetic stir bar was charged with CuI (20 mol%), **3t** (1.0 equiv) and evacuated under high vacuum and backfilled with N<sub>2</sub>. THF (0.2 M) and Phenylacetylene (2.0 equiv) were added via syringe. The reaction mixture was stirred (500 rpm) at 60 °C for 4 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **4t**.



#### 1-(5-(4-phenyl-1H-1,2,3-triazol-1-yl)pentyl)-1H-benzo[d][1,2,3]triazole (**4t**)<sup>16f</sup>

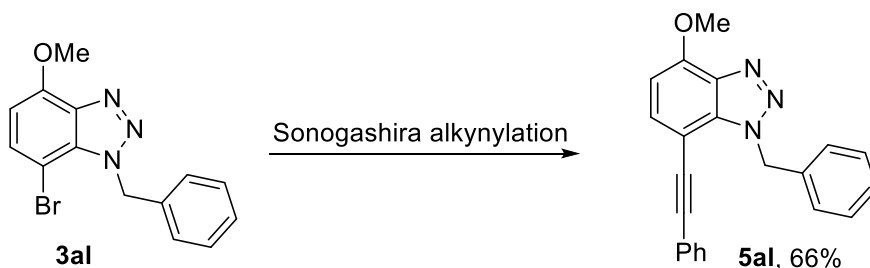
Chromatography Pentane/EA = 2:1 (v/v), 25.4 mg (76%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.03 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.91 – 7.77 (m, 2H), 7.69 (s, 1H), 7.53 – 7.23 (m, 6H), 4.61 (t, *J* = 7.0 Hz, 2H), 4.34 (t, *J* = 7.0 Hz, 2H), 2.13 – 1.89 (m, 4H), 1.57 – 1.31 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.7, 145.9, 132.8, 130.4, 128.8, 128.1, 127.3, 125.6, 123.9, 120.0, 119.5, 109.1, 49.9, 47.6, 29.5, 28.8, 23.5.

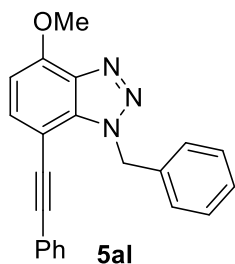
HRMS (ESI-TOF): *m/z* calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>6</sub>Na<sup>+</sup> [*M*+Na<sup>+</sup>] 355.1642, found 355.1650.

5.3 Procedure for the synthesis of **5a**.



A 5 mL snap vial equipped with a magnetic stir bar was charged with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3 mol%), CuI (2 mol%), **3a** (0.2 mmol, 1.0 equiv) and evacuated under high vacuum and backfilled with N<sub>2</sub>. Et<sub>3</sub>N (2 mL) and Phenylacetylene (1.1 equiv) were added via syringe. The reaction mixture was stirred (500 rpm) at 60 °C for 12 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **5a**.





**1-benzyl-4-methoxy-7-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (5al)<sup>[17]</sup>**

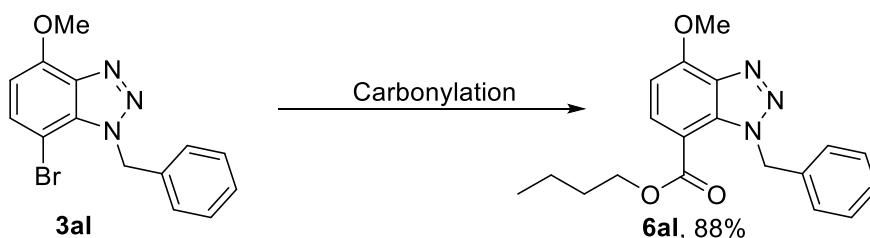
Chromatography Pentane/EA = 6:1 (v/v), 44.7 mg (66%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.28 – 6.98 (m, 8H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.14 (s, 2H), 4.03 (s, 3H).

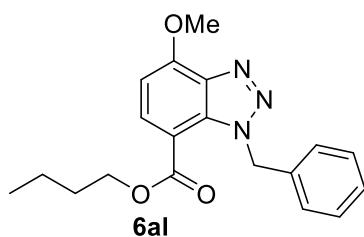
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 152.3, 138.1, 136.1, 133.9, 133.6, 131.2, 128.7, 128.6, 128.5, 128.0, 127.3, 122.6, 103.9, 98.2, 93.5, 84.6, 56.4, 51.7.

HRMS (ESI-TOF): *m/z* calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>ONa<sup>+</sup> [*M*+Na<sup>+</sup>] 362.1264, found 362.1260.

5.4 Procedure for the synthesis of 6al.



A 4 mL snap vial equipped with a magnetic stir bar was charged with Pd(OAc)<sub>2</sub> (1.5 mol%), *n*BuPAd<sub>2</sub> (4.5 mmol%), **3al** (0.2 mmol, 1 equiv) and closed with a rubber-based septum. The vial was evacuated and backfilled with argon. *n*BuOH (1 mL) and TMEDA (0.75 equiv) were added via syringe. The vial was then connected to a atmosphere with a cannula and transferred into a 300 mL autoclave, under argon counterflow. The closed autoclave was flushed three times with nitrogen (~ 5 bar), three times with CO (~ 5 bar), and 6 bar of carbon monoxide (measured by pressure meter) was charged. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction mixture was stirred (500 rpm) at 120 °C for 12 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **6al**.



**butyl 1-benzyl-4-methoxy-1H-benzo[d][1,2,3]triazole-7-carboxylate (6al)<sup>[18]</sup>**

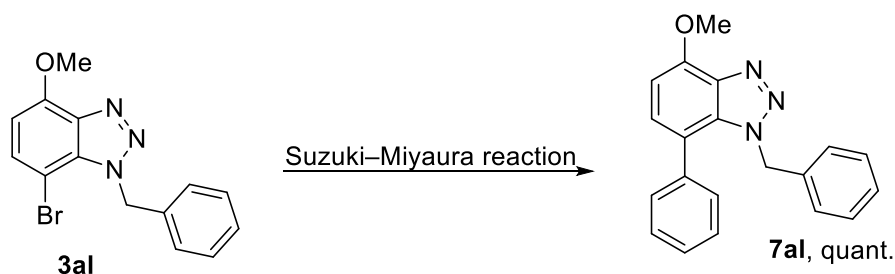
Chromatography Pentane/EA = 5:1 (v/v), 59.9 mg (88%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.3$  Hz, 1H), 7.32 – 7.13 (m, 3H), 7.11 – 6.94 (m, 2H), 6.67 (d,  $J = 8.4$  Hz, 1H), 6.39 (s, 2H), 4.26 (t,  $J = 6.6$  Hz, 2H), 4.14 (s, 3H), 1.75 – 1.59 (m, 2H), 1.41 – 1.35 (m, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H).

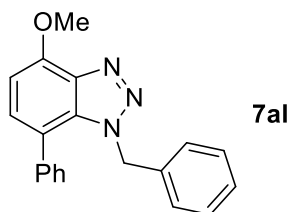
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 155.4, 139.2, 136.5, 133.3, 132.8, 128.3, 127.5, 127.0, 108.7, 102.7, 64.9, 56.5, 54.2, 30.6, 19.1, 13.6.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_3\text{Na}^+$  [ $\text{M} + \text{Na}^+$ ] 362.1475, found 362.1475.

5.5 Procedure for the synthesis of 7al.



A 5 mL snap vial equipped with a magnetic stir bar was charged with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (5 mol%),  $\text{PhB}(\text{OH})_2$  (1.2 equiv),  $\text{K}_3\text{PO}_4$  (2.5 equiv), **3al** (0.2 mmol, 1.0 equiv) and evacuated under high vacuum and backfilled with  $\text{N}_2$ . dioxane (1 ml) and  $\text{H}_2\text{O}$  (0.1 ml) were added via syringe. The reaction mixture was stirred (500 rpm) at  $100^\circ\text{C}$  for 16 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **7al**.



#### 1-benzyl-4-methoxy-7-phenyl-1H-benzo[d][1,2,3]triazole (**7al**)<sup>[19]</sup>

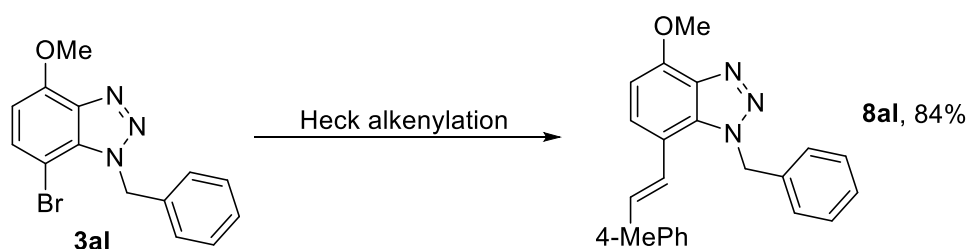
Chromatography Pentane/EA = 6:1 (v/v), 64.4 mg (quant.).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.13 (m, 3H), 7.10 – 6.88 (m, 6H), 6.60 (d,  $J = 7.9$  Hz, 1H), 6.41 – 6.30 (m, 2H), 5.48 (s, 2H), 4.02 (s, 3H).

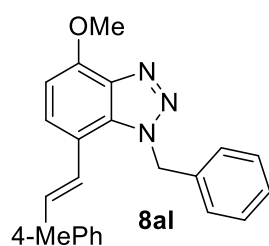
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 138.6, 137.2, 135.4, 132.1, 129.8, 129.7, 128.1, 128.1, 127.7, 127.4, 126.5, 118.7, 103.1, 56.1, 52.7.

HRMS (ESI-TOF):  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}\text{Na}^+$  [ $\text{M} + \text{Na}^+$ ] 338.1264, found 338.1270.

## 5.6 Procedure for the synthesis of 8al.



A 5 mL snap vial equipped with a magnetic stir bar was charged with Pd(OAc)<sub>2</sub> (3 mol%), K<sub>3</sub>PO<sub>4</sub> (1.4 equiv), **3al** (0.2 mmol, 1.0 equiv) and evacuated under high vacuum and backfilled with N<sub>2</sub>. DMAc (0.5 ml) and styrene (1.2 equiv) were added via syringe. The reaction mixture was stirred (500 rpm) at 140 °C for 12 h. After reaction, cooling to room temperature. The crude product was purified by silica gel chromatography (pentane/EA) to afford the corresponding product **8al**.



### (*E*)-1-benzyl-4-methoxy-7-(4-methylstyryl)-1H-benzo[*d*][1,2,3]triazole (**8al**)<sup>[20]</sup>

Chromatography Pentane/EA = 6:1 (v/v), 59.5 mg (84%).

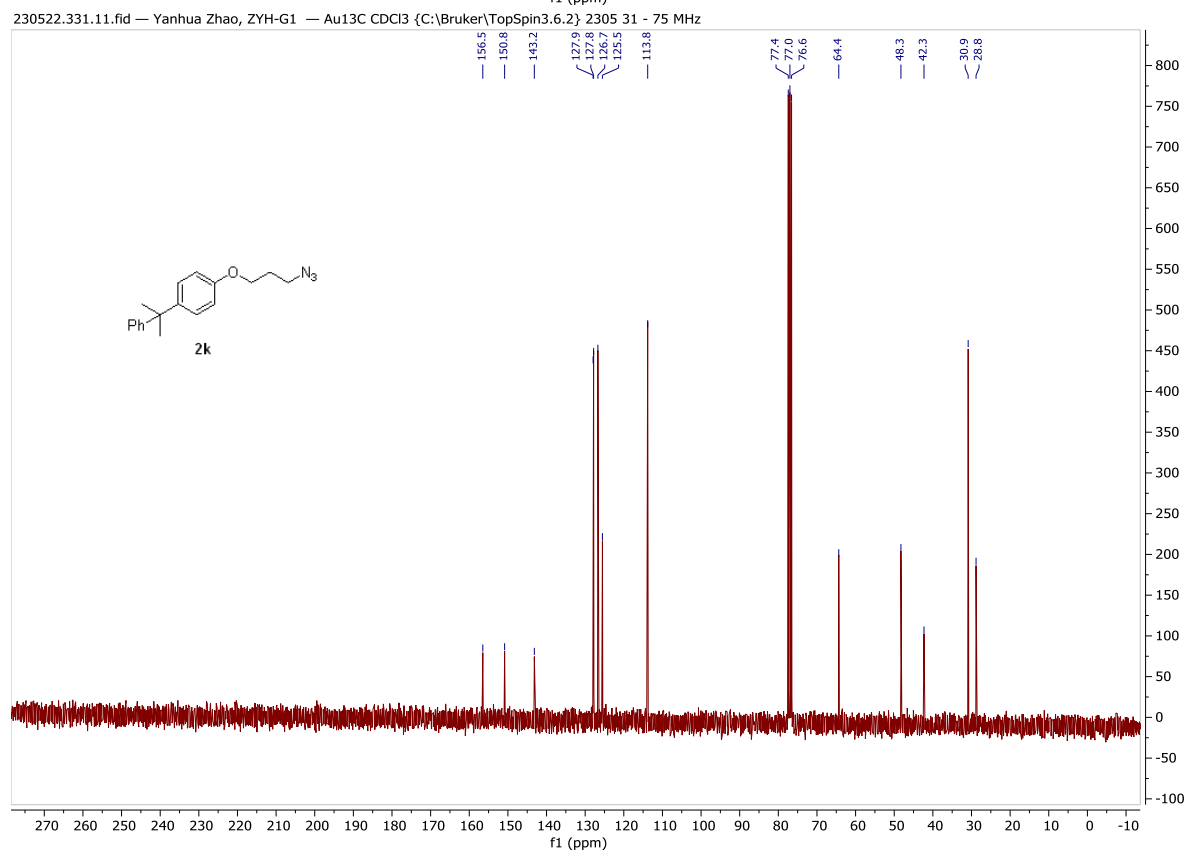
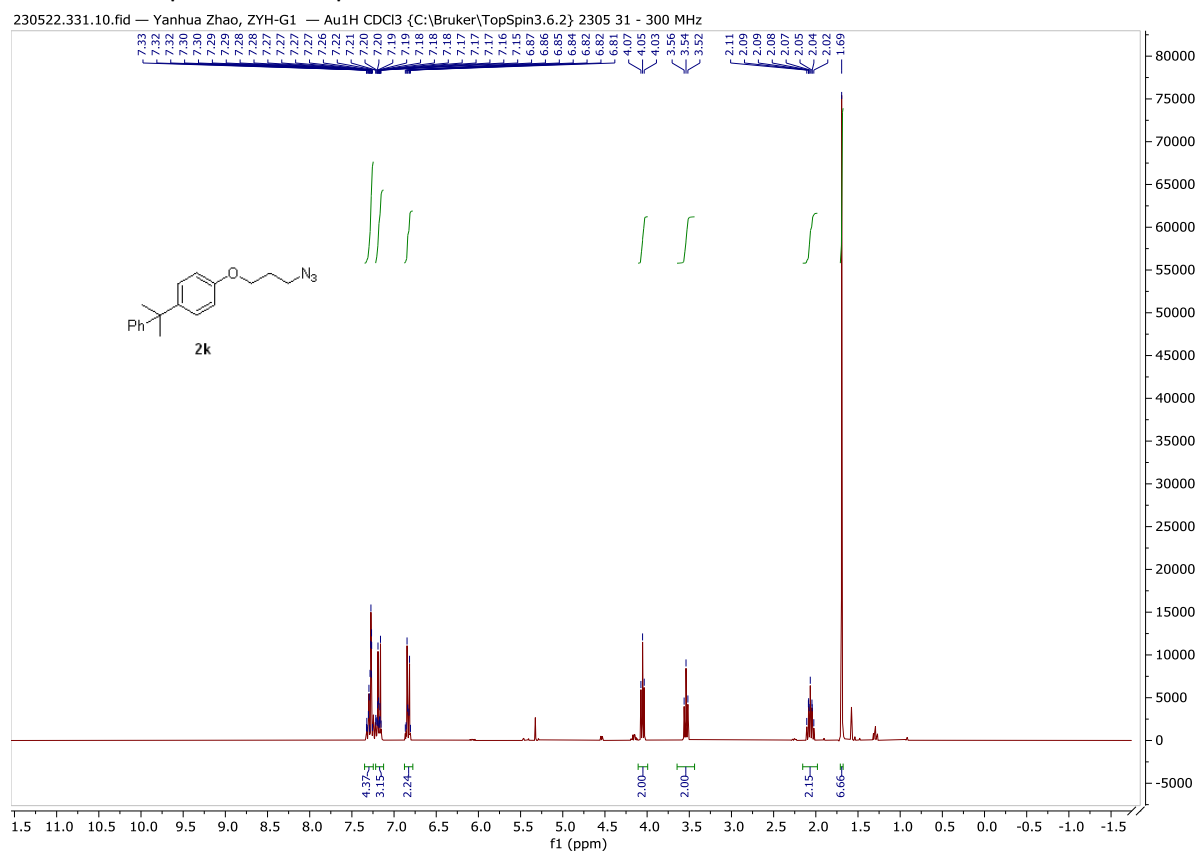
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.45 (dt, *J* = 8.1, 0.7 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.20 – 7.06 (m, 7H), 6.82 (d, *J* = 15.9 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.02 (s, 2H), 4.12 (s, 3H), 2.37 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.1, 138.6, 137.7, 136.3, 134.1, 132.7, 130.9, 129.4, 129.0, 128.1, 126.3, 126.2, 125.9, 121.6, 115.5, 103.9, 56.2, 53.2, 21.2.

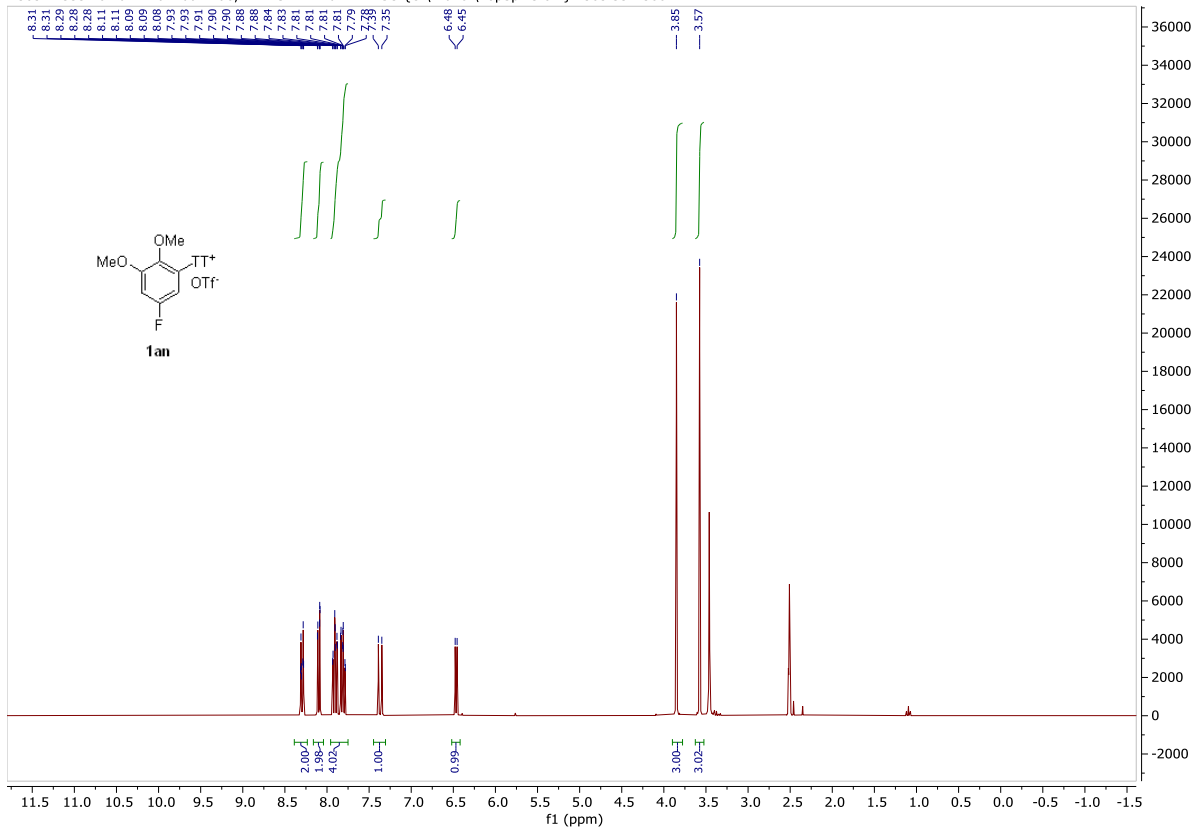
## 6. Reference

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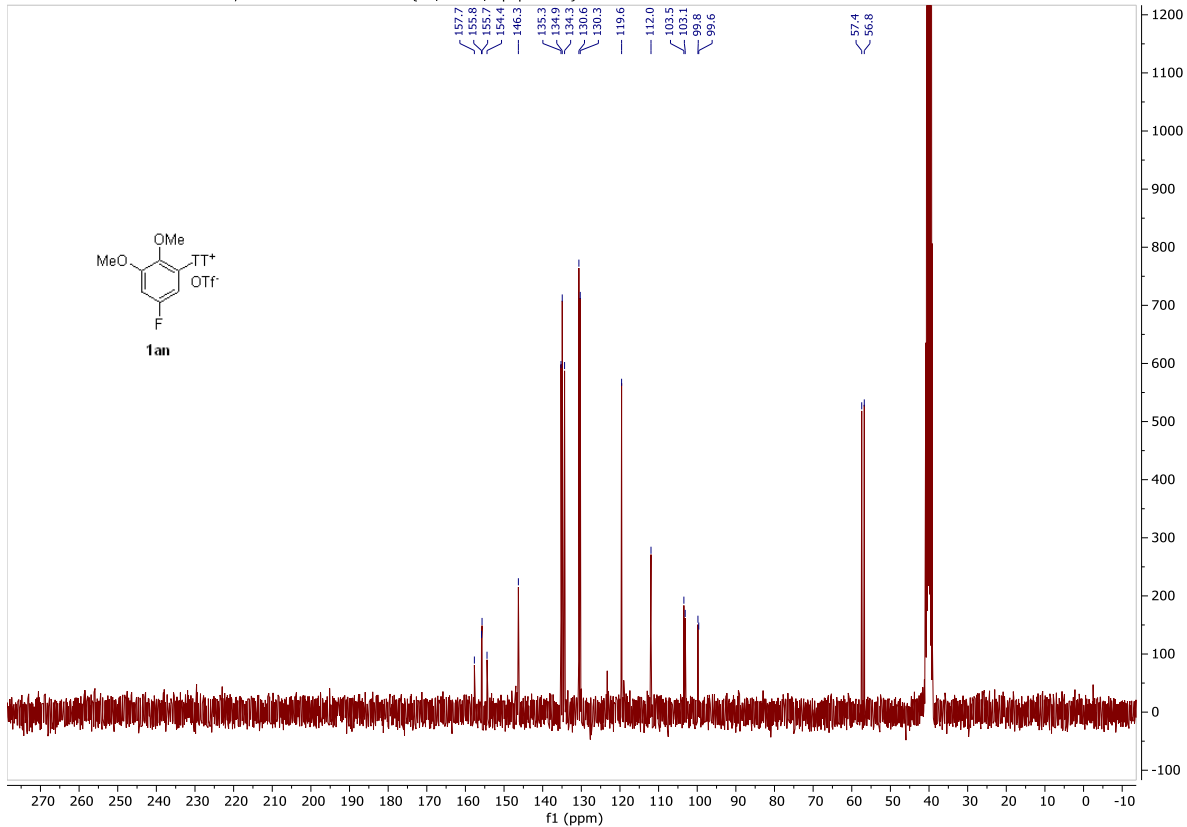
## 7. NMR spectra of products

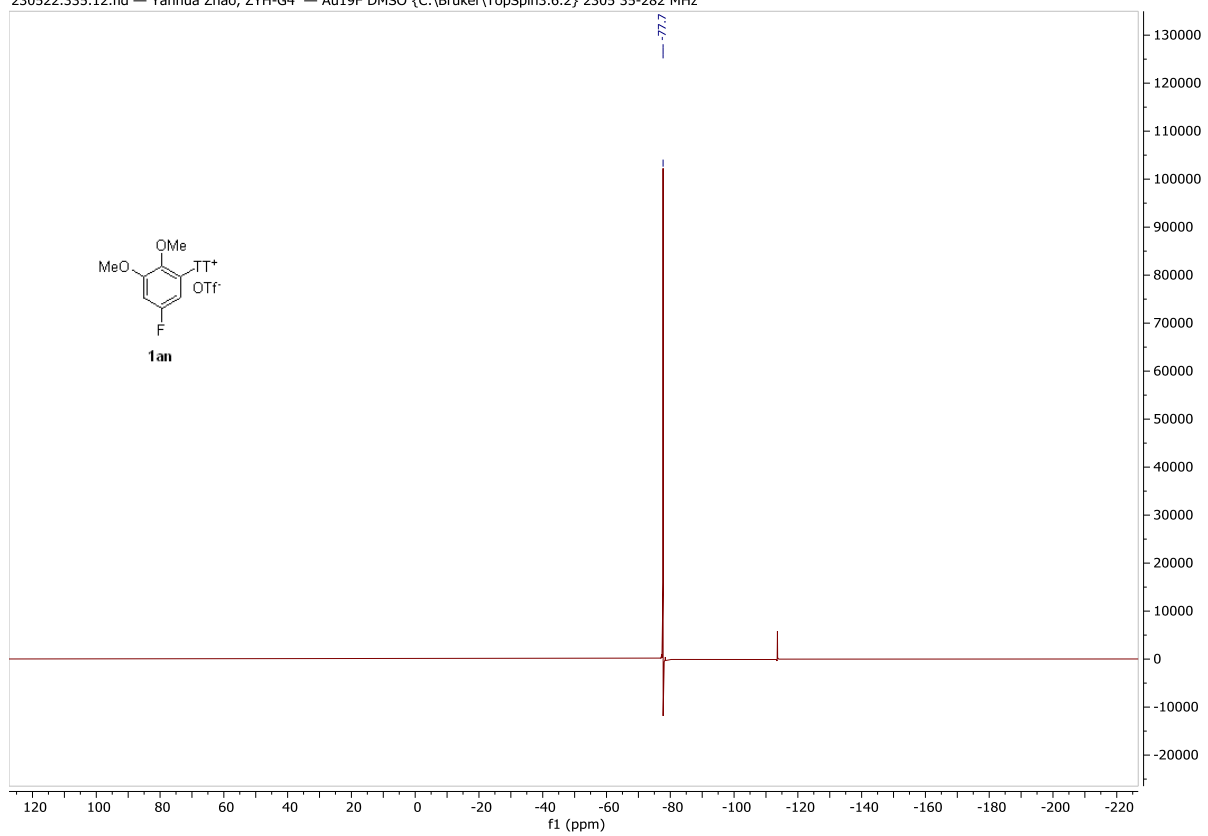


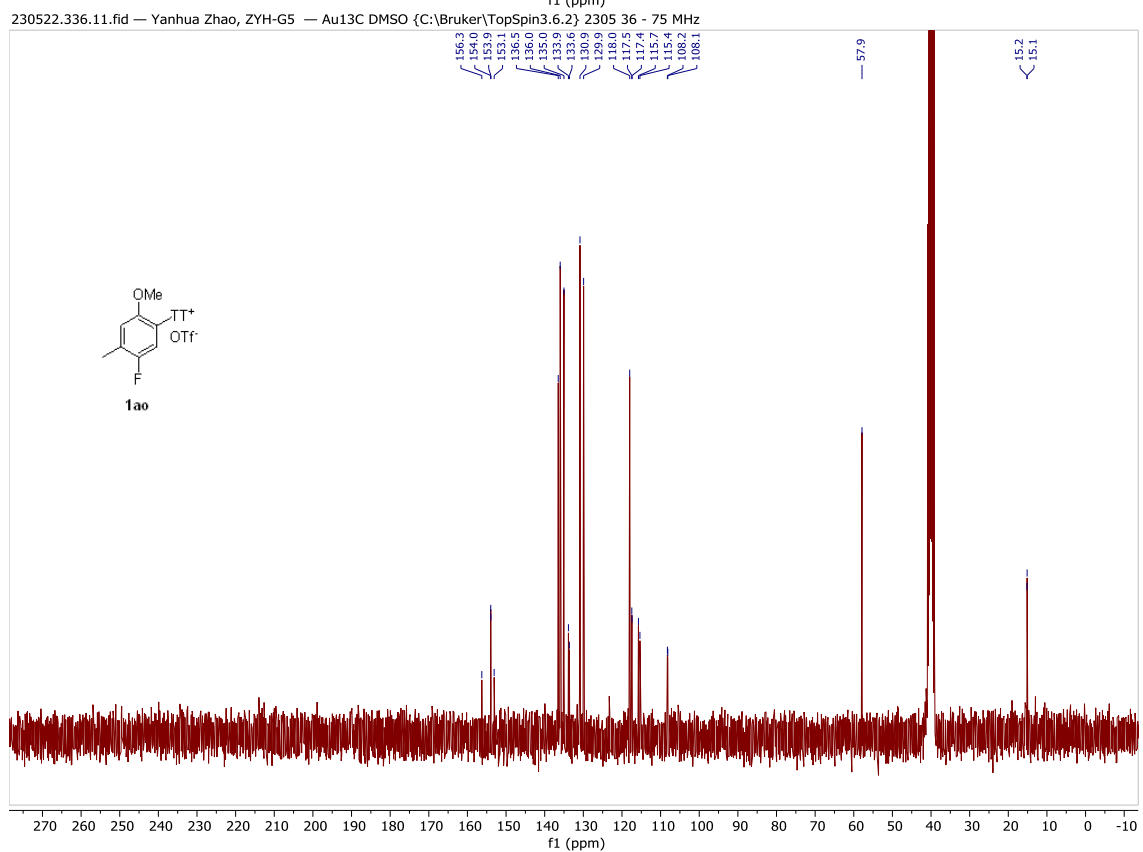
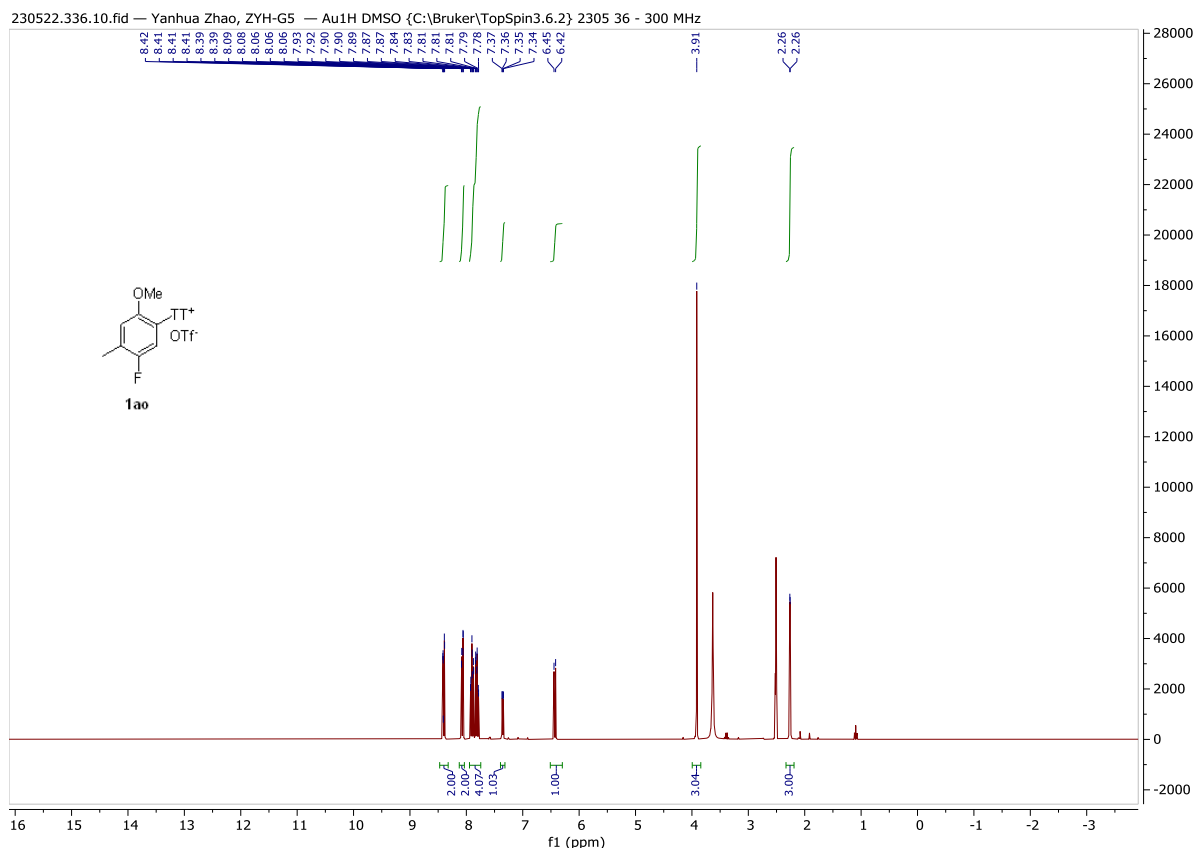
230522.335.10.fid — Yanhua Zhao, ZYH-G4 — Au1H DMSO {C:\Bruker\TopSpin3.6.2} 2305 35 - 300 MHz



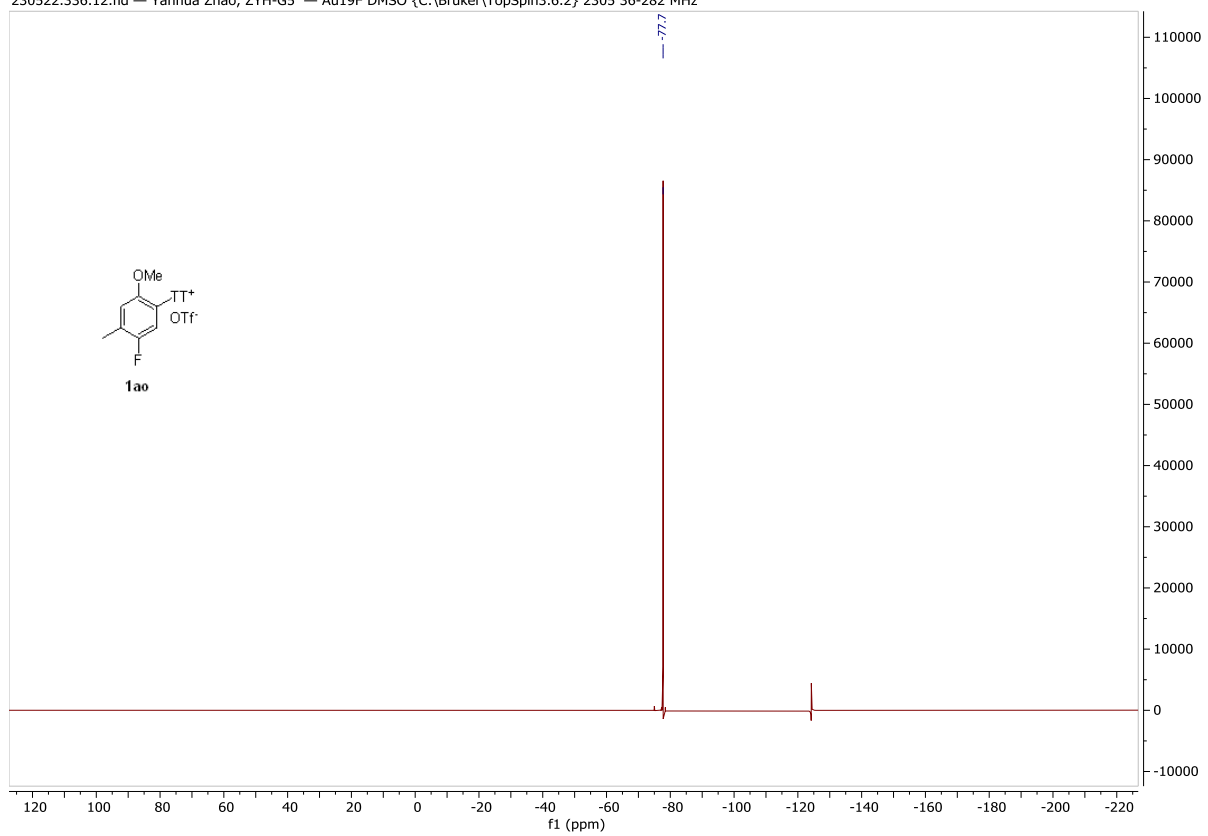
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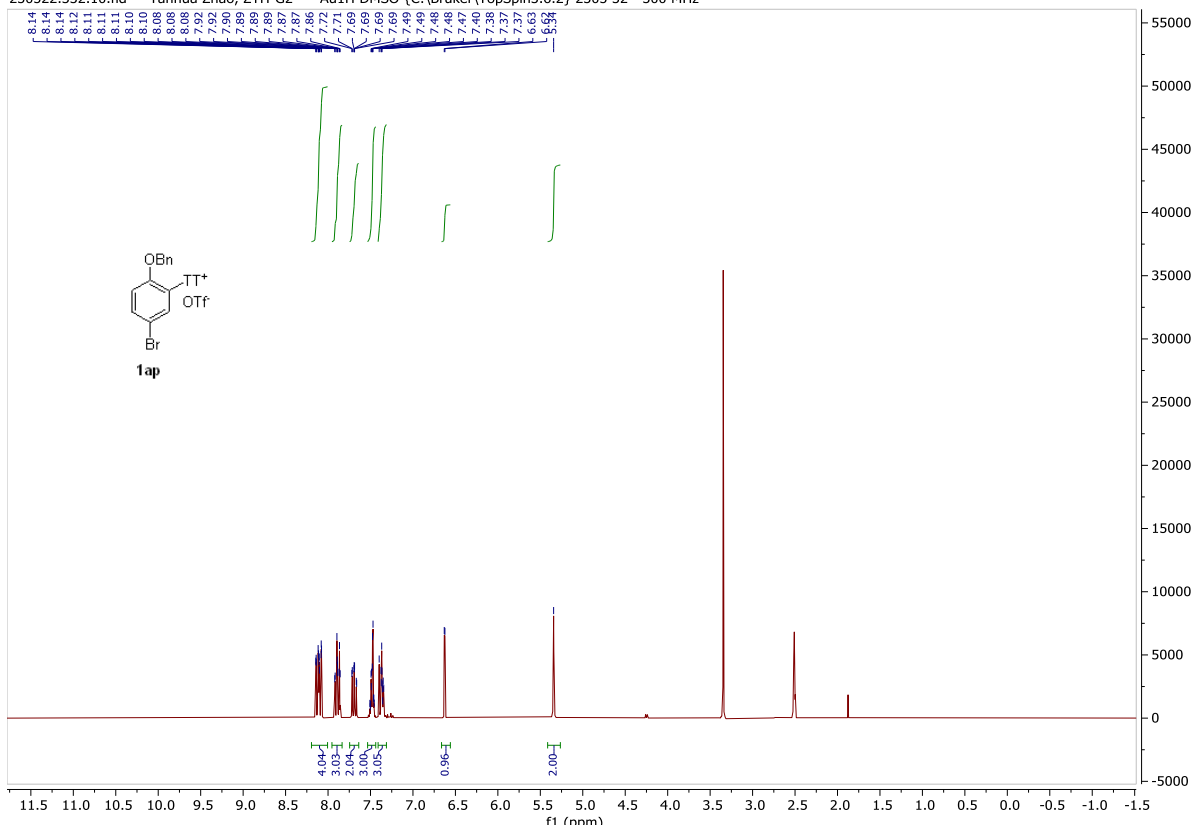




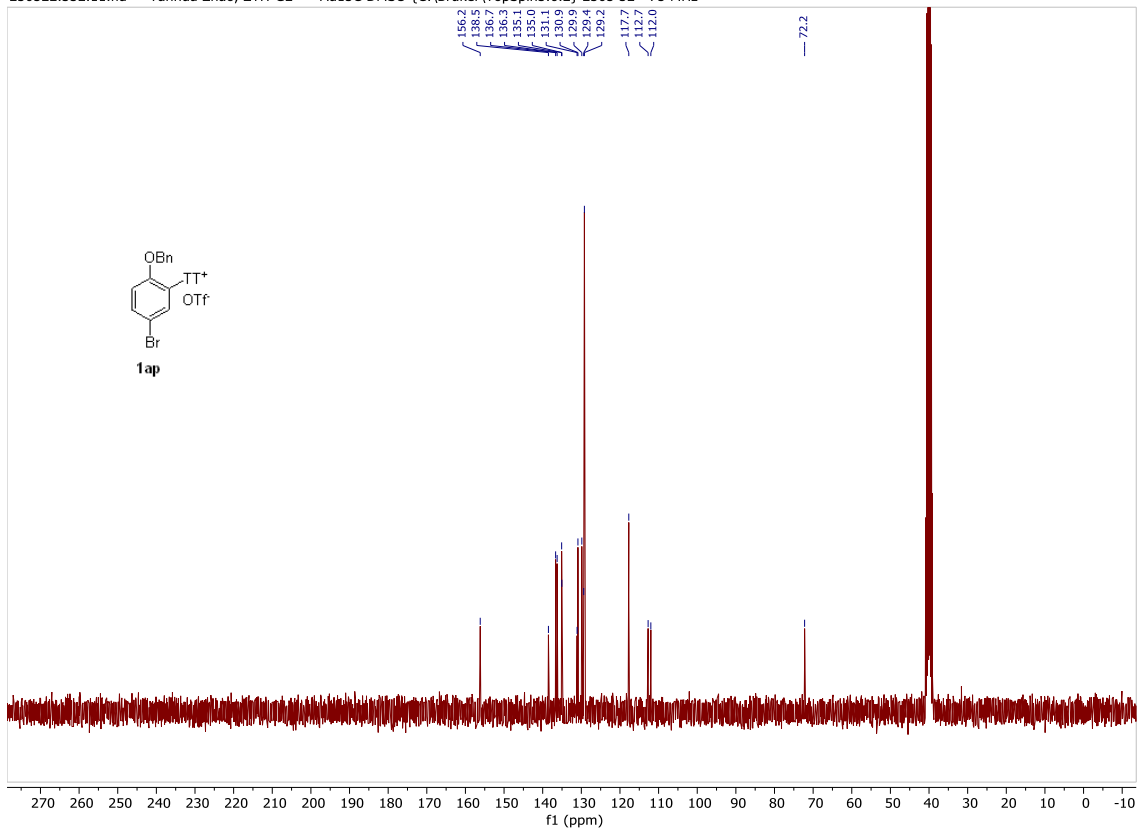




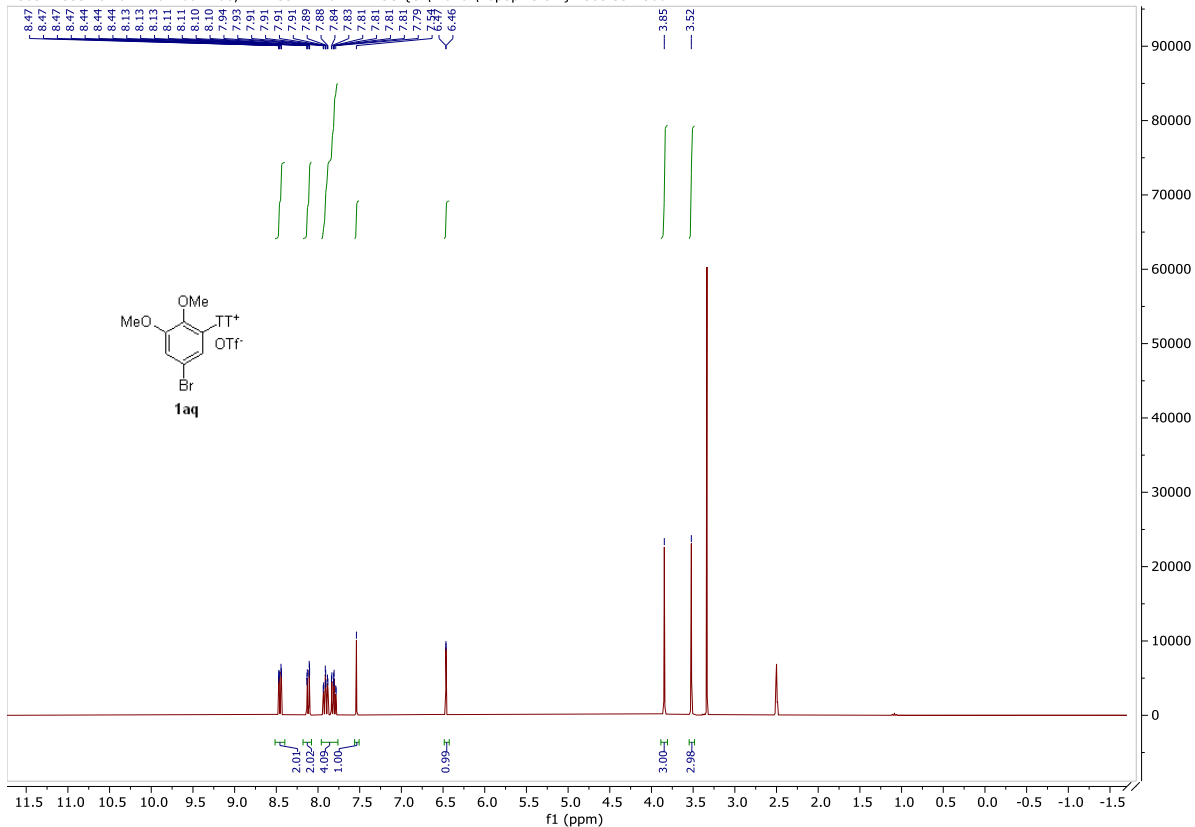
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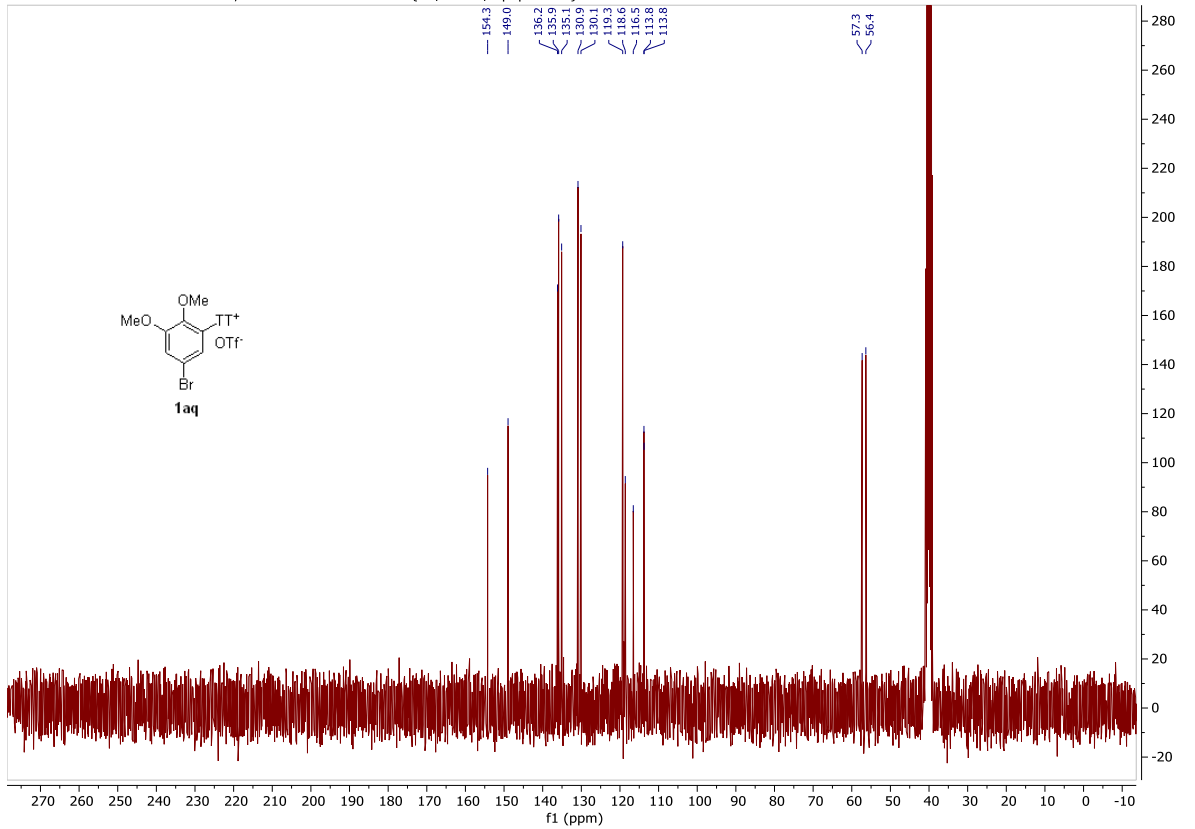
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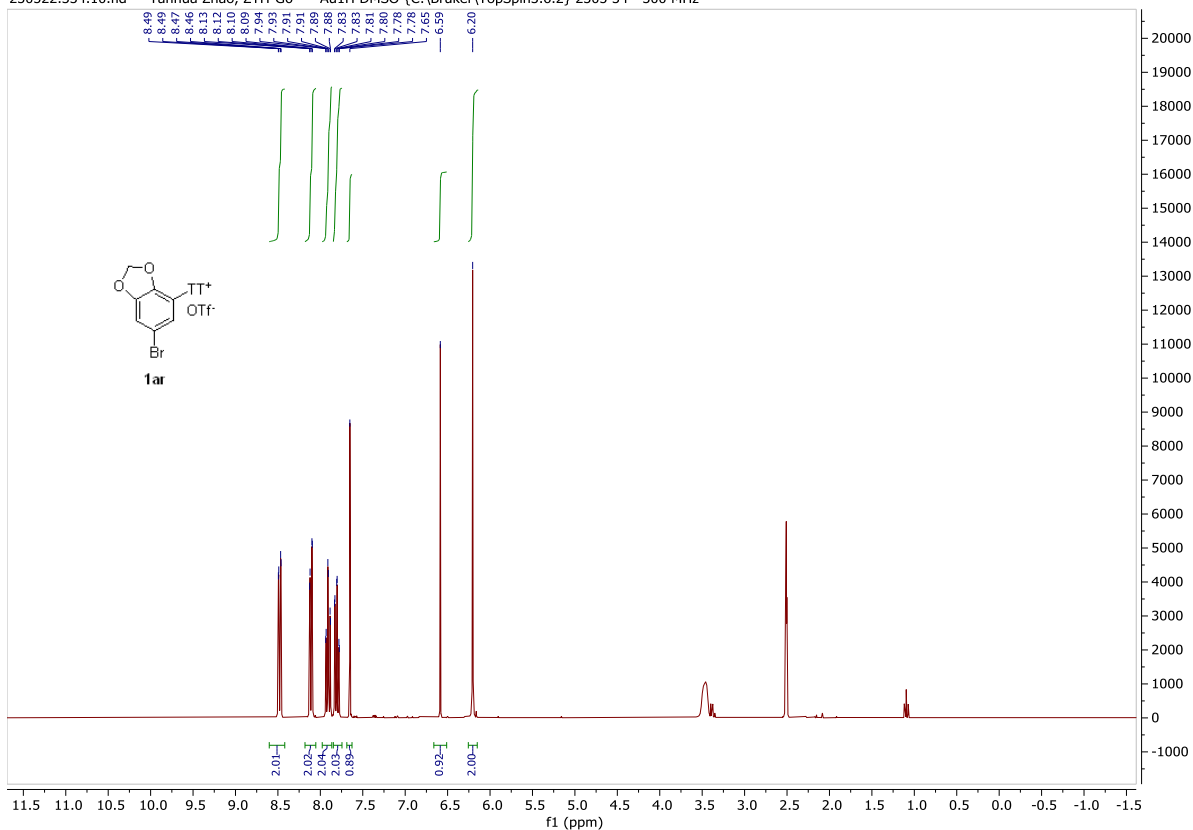
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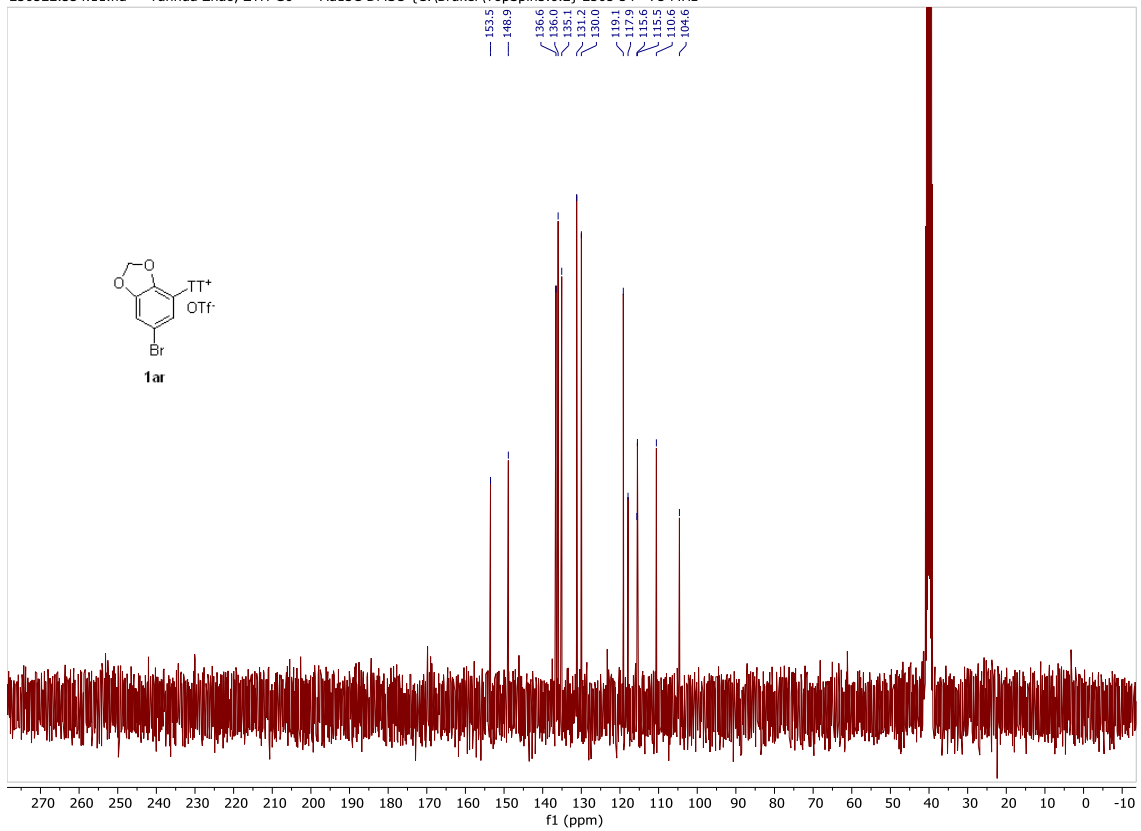
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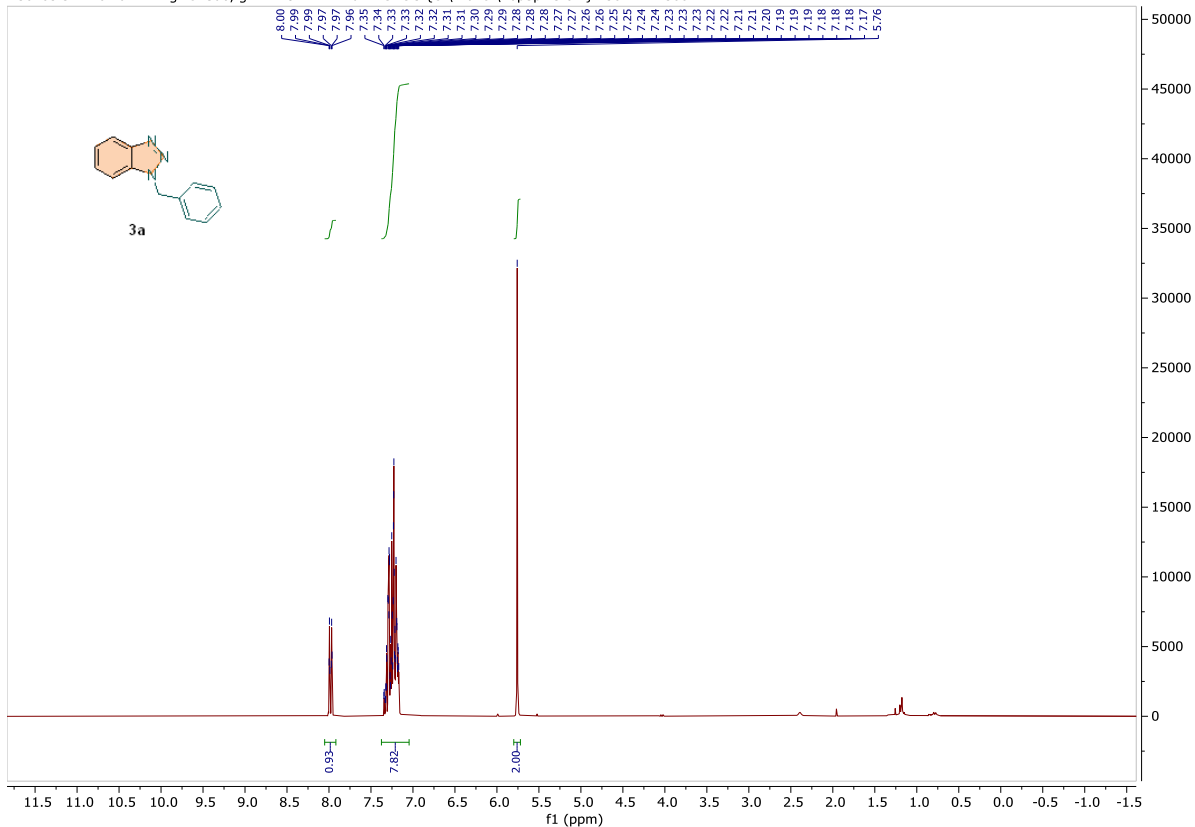
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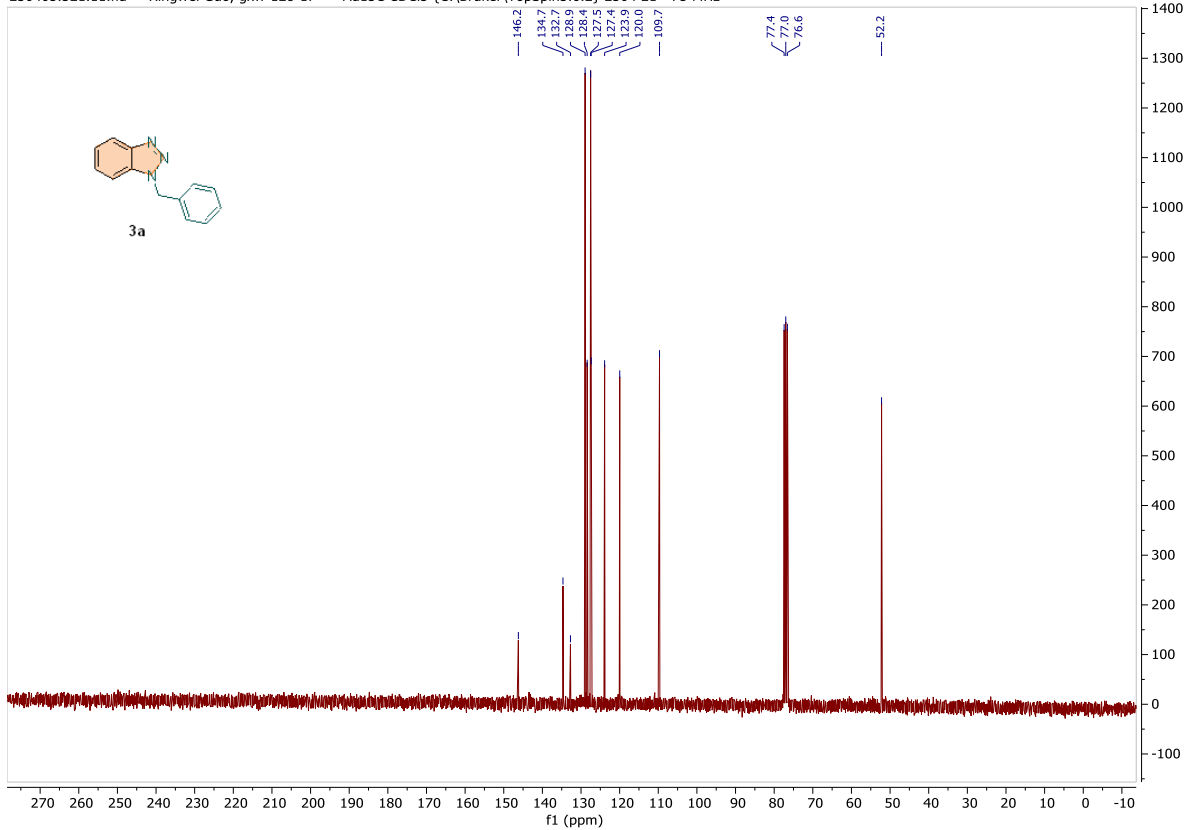
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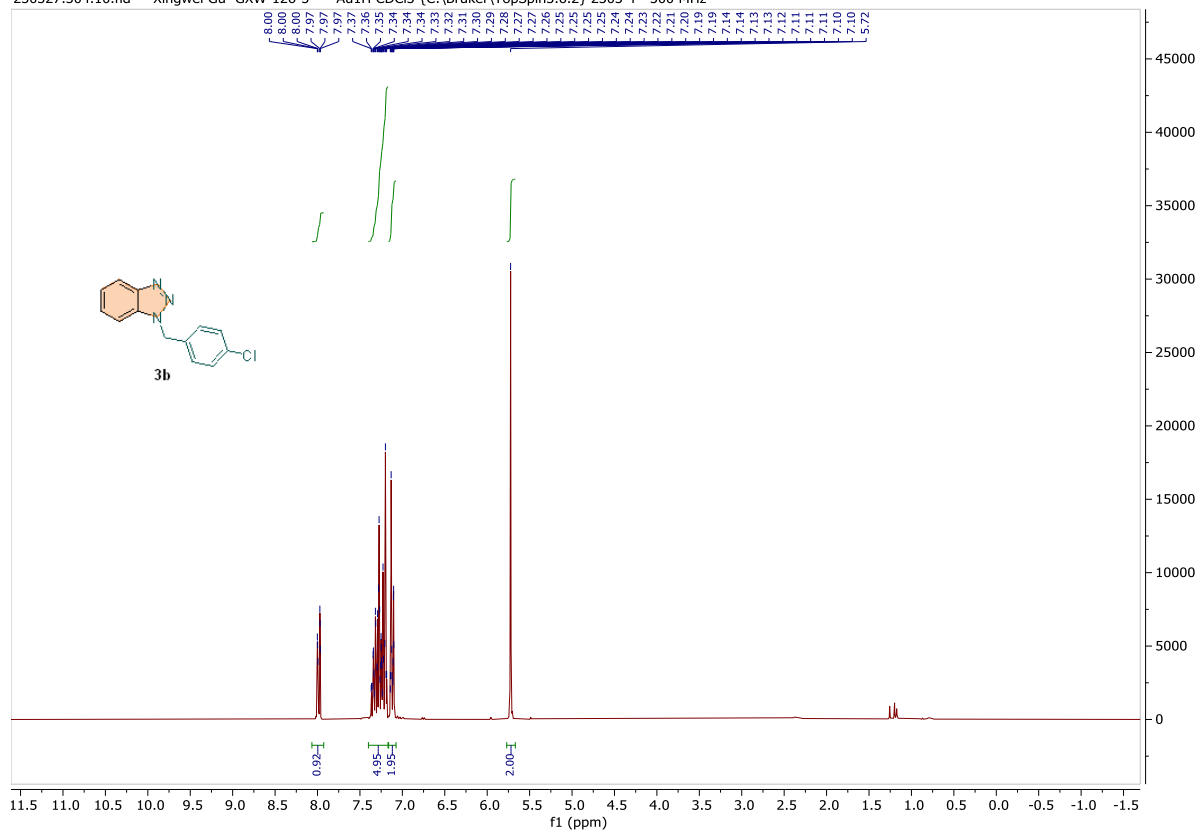
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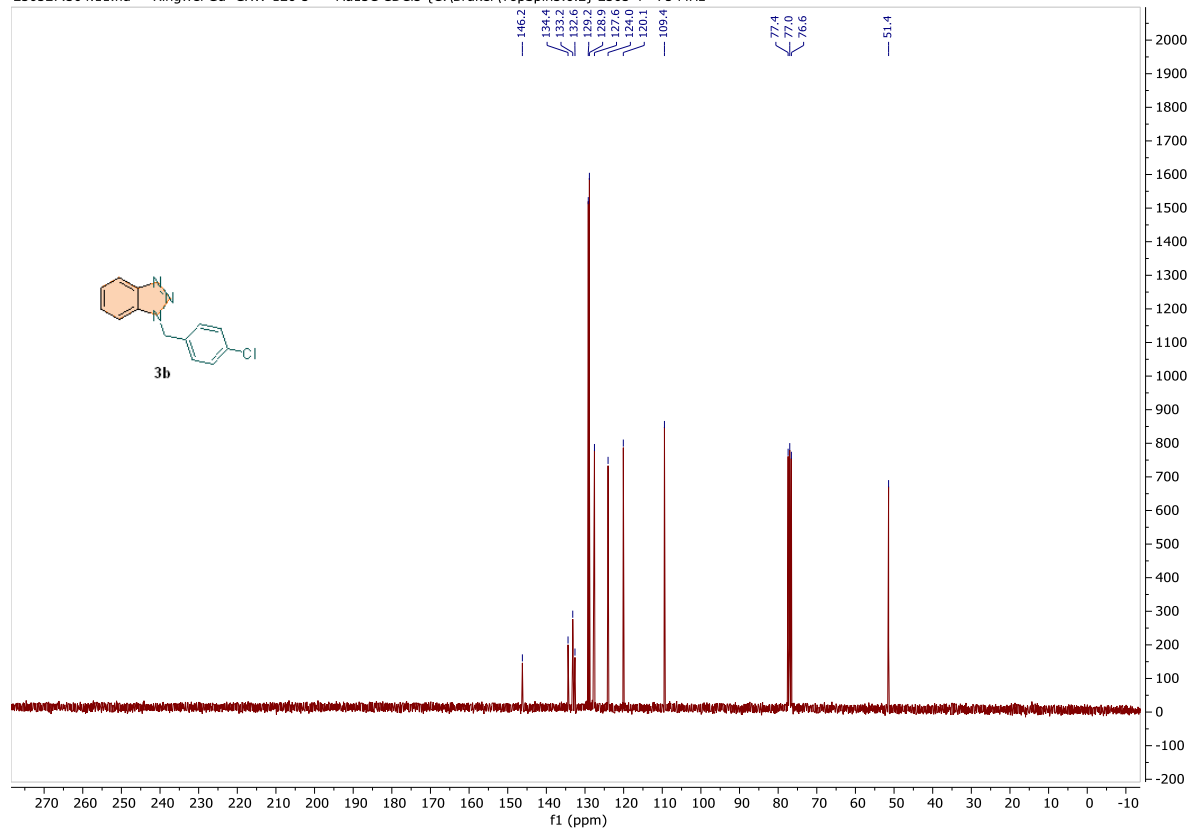
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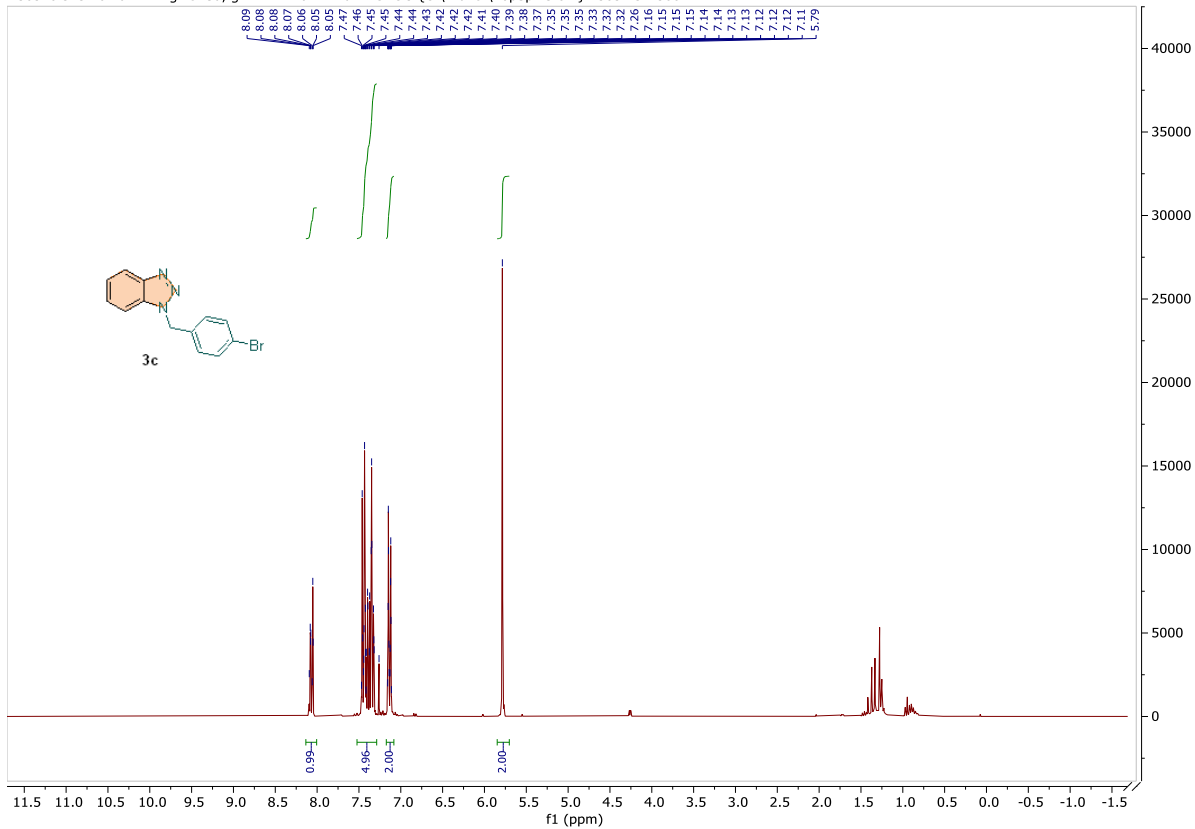
230327.304.10.fid — Xingwei Gu GXW-126-5 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 300 MHz



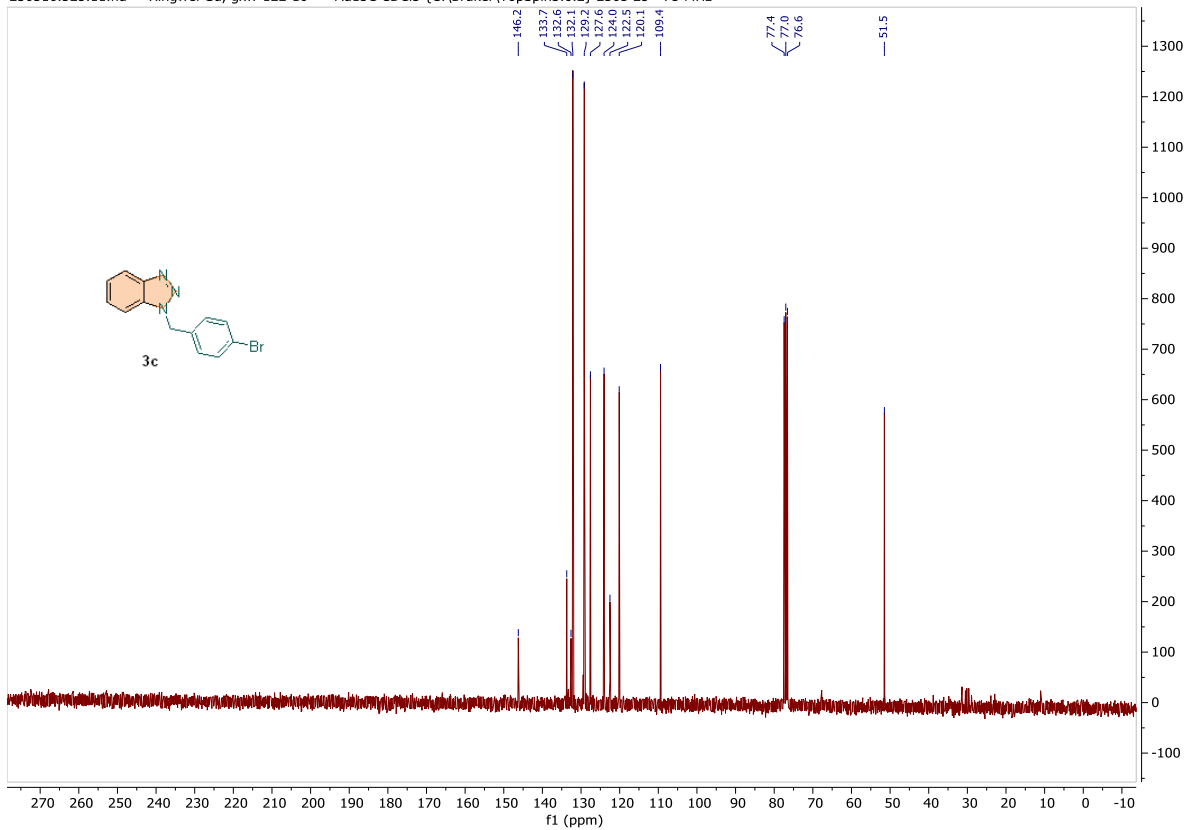
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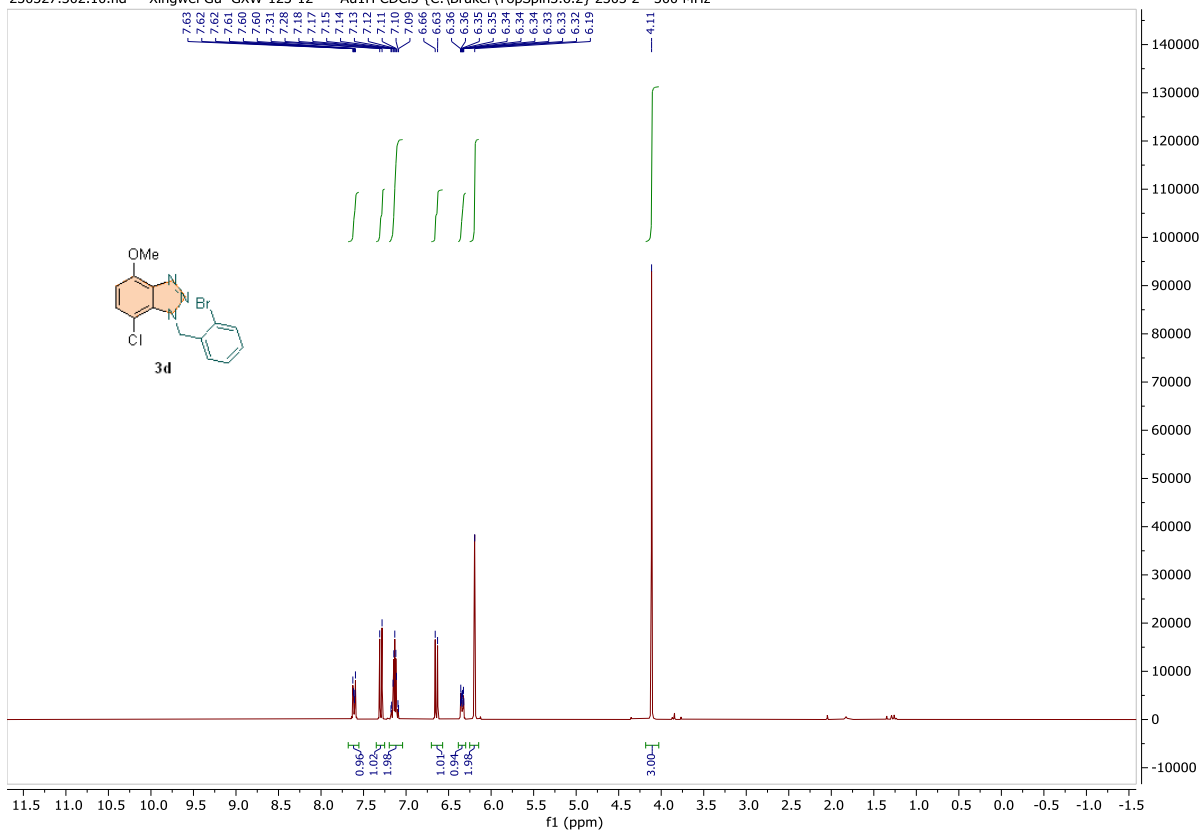
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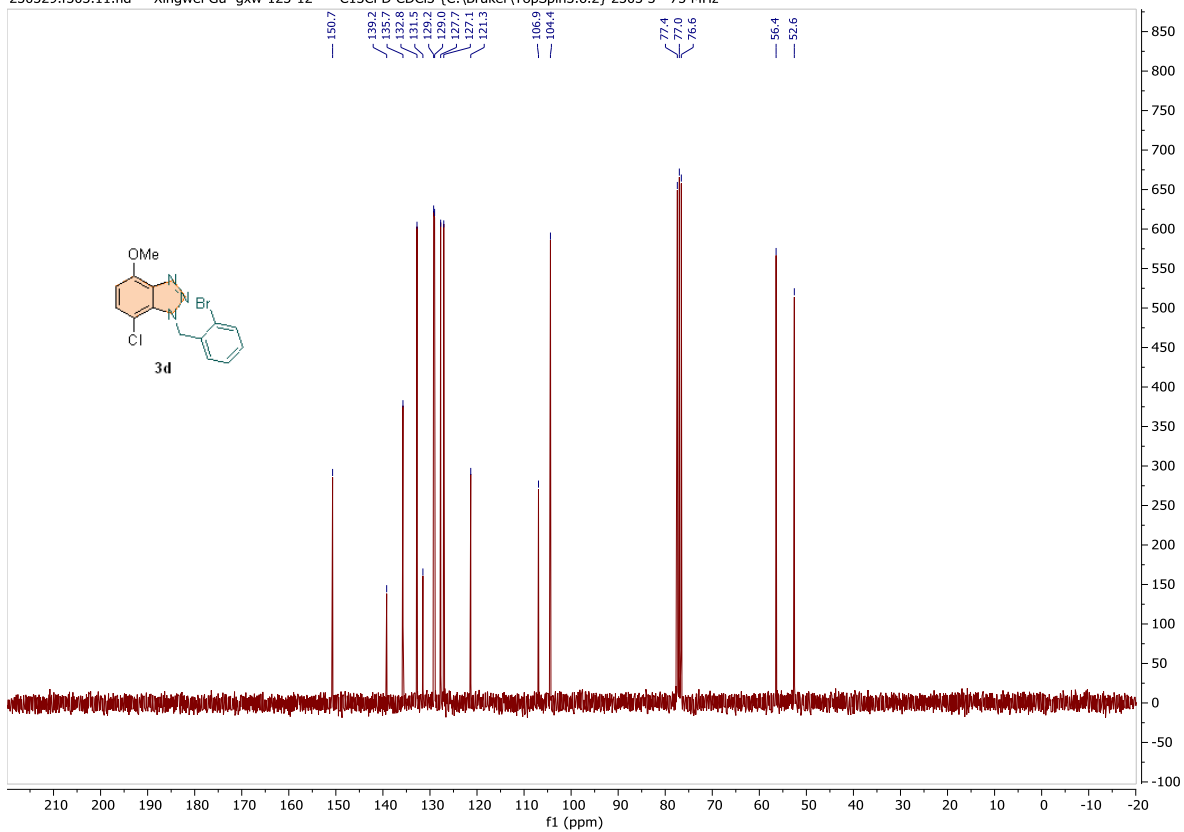
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230327.302.10.fid — Xingwei Gu GXW-123-12 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 2 - 300 MHz

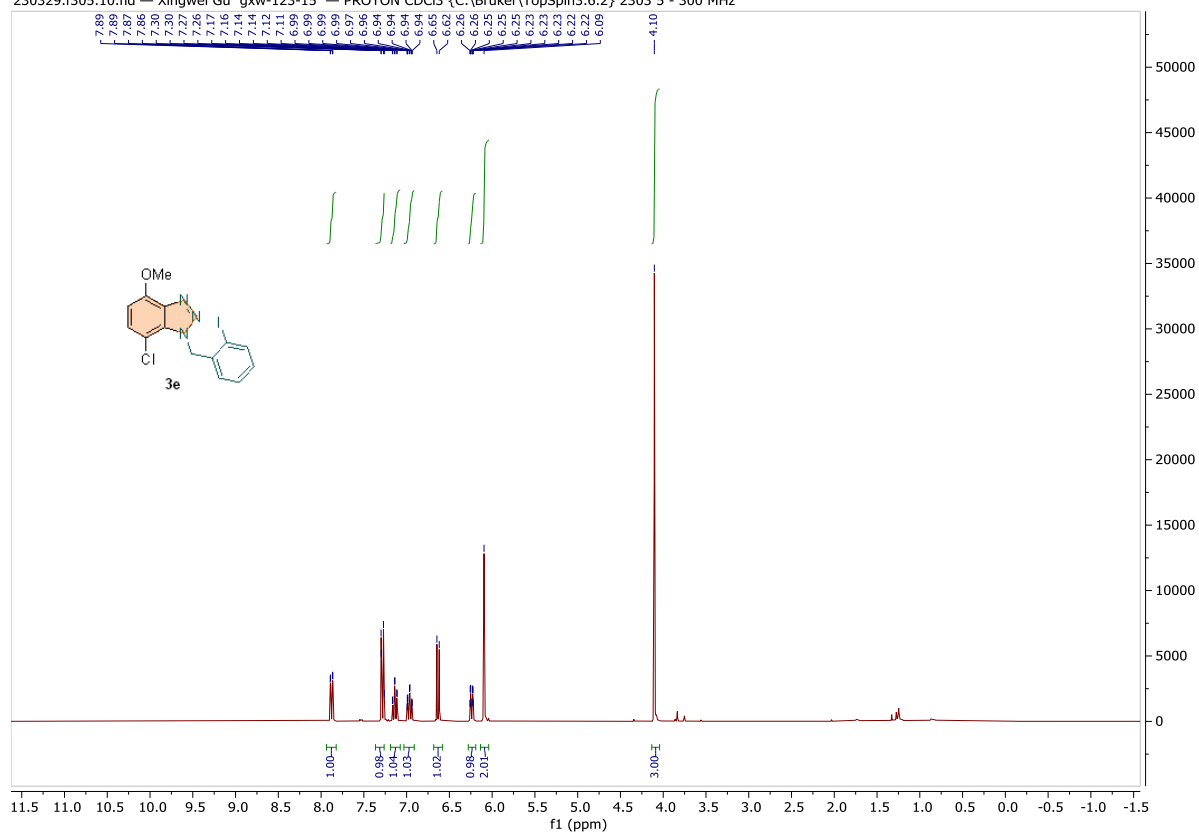


230329.f303.11.fid — Xingwei Gu gxw-123-12 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 3 - 75 MHz

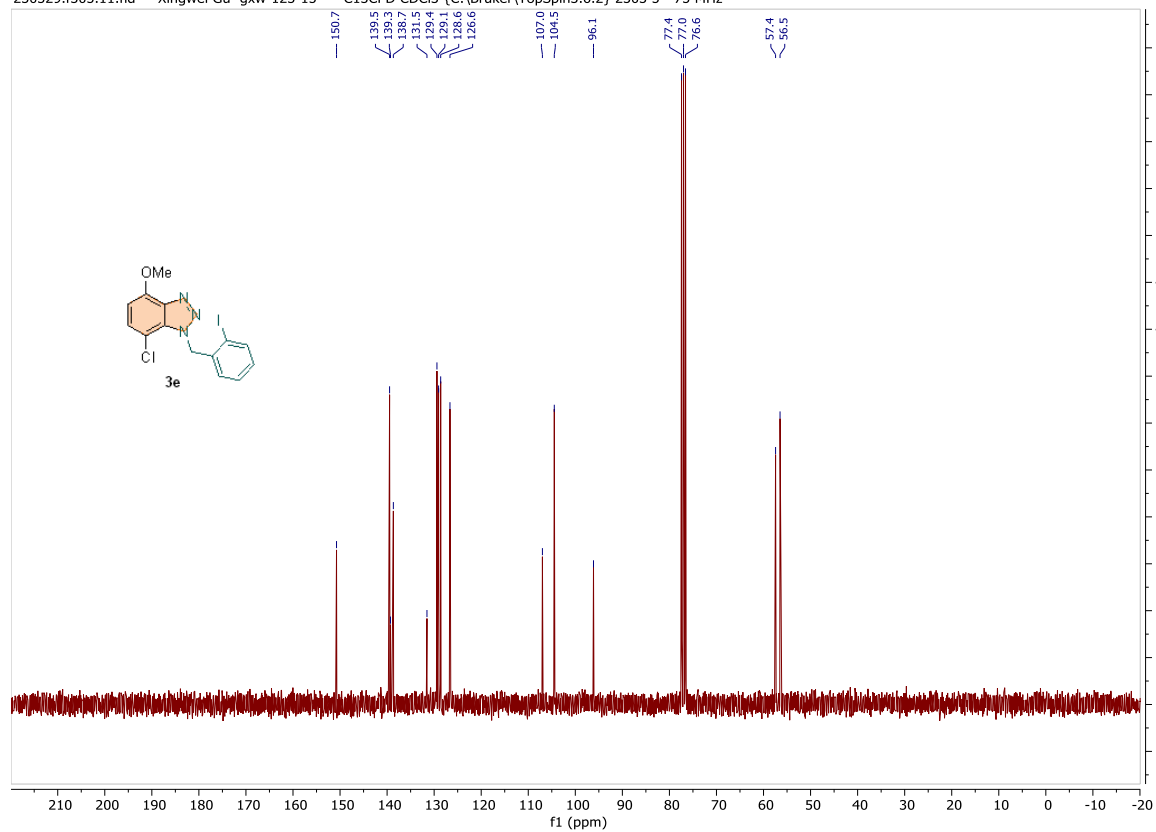


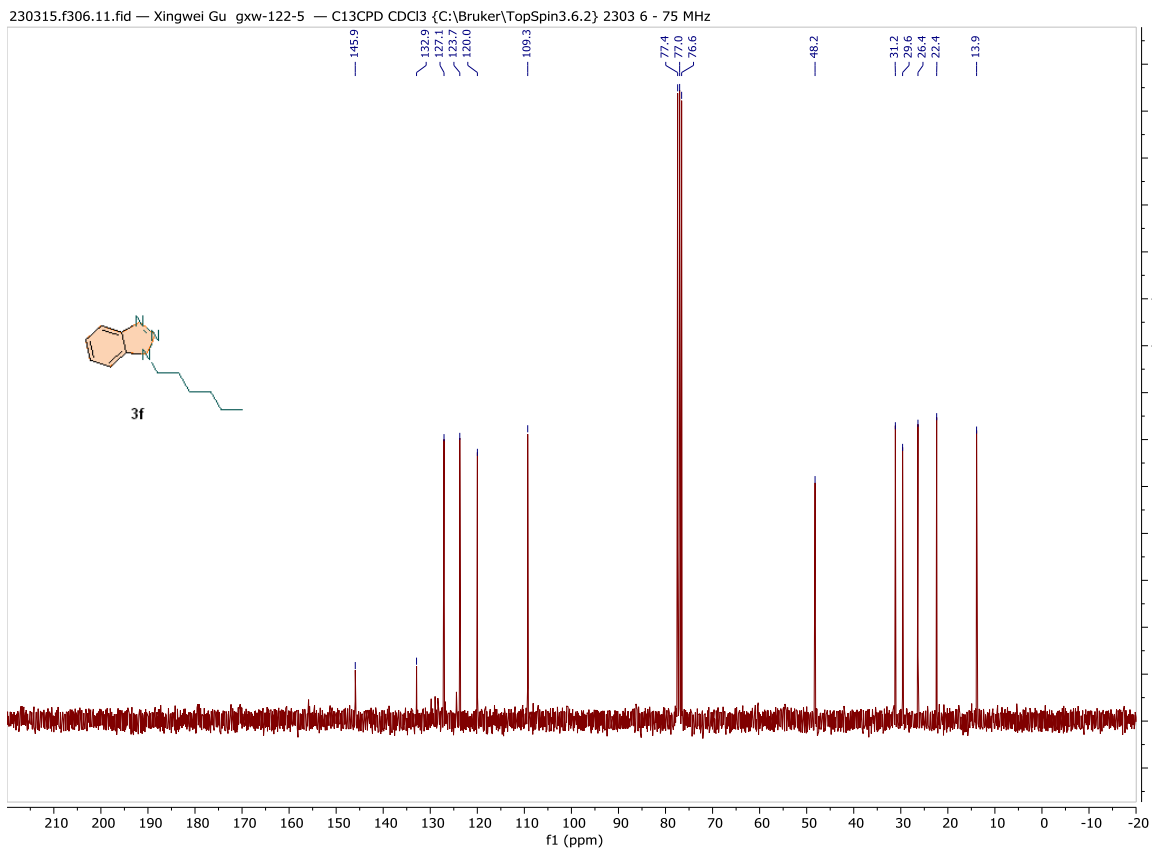
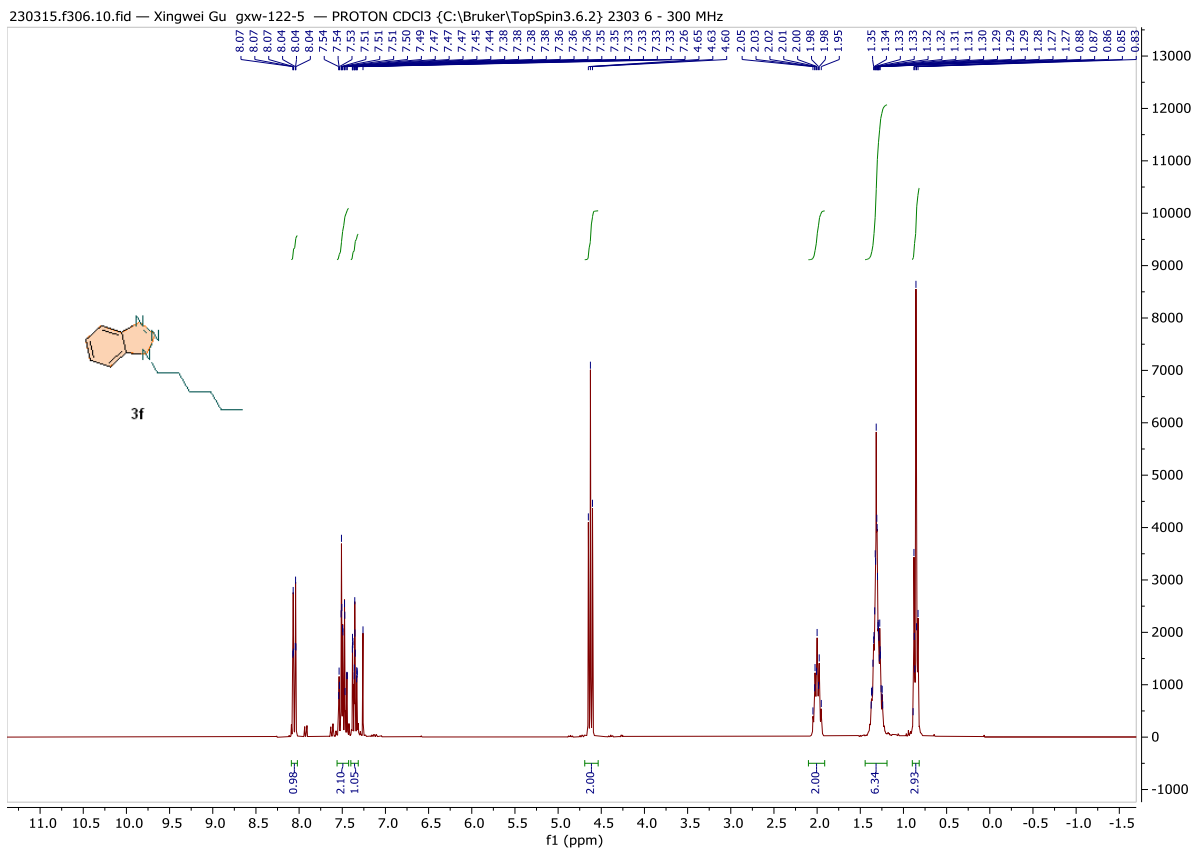


230329.f305.10.fid — Xingwei Gu gxw-123-15 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 5 - 300 MHz

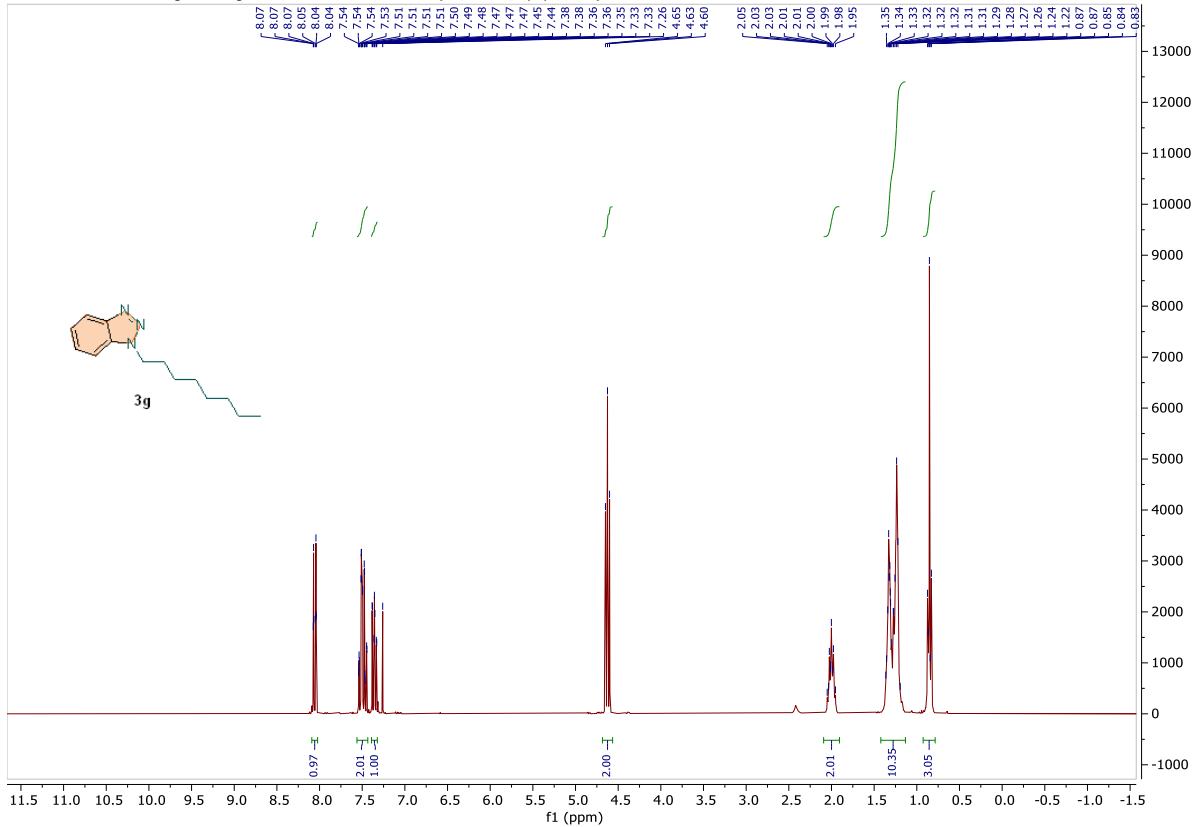


230329.f305.11.fid — Xingwei Gu gxw-123-15 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 5 - 75 MHz

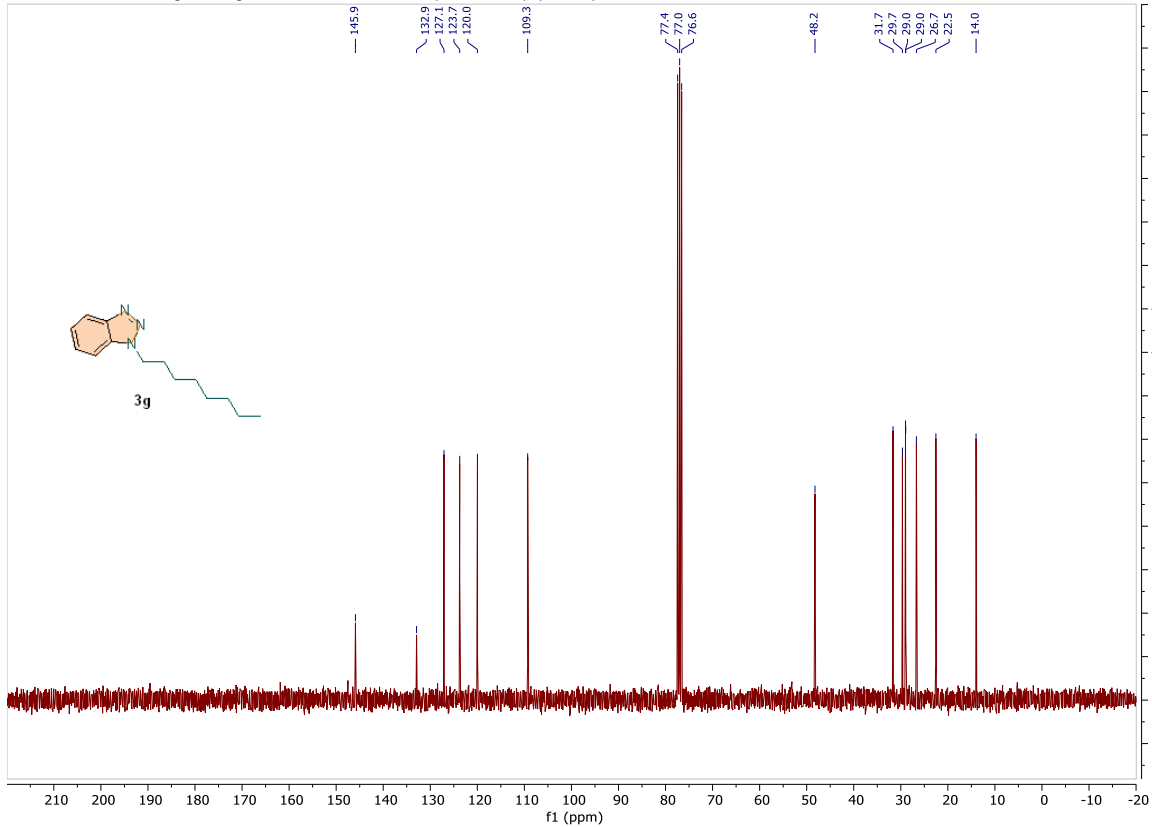


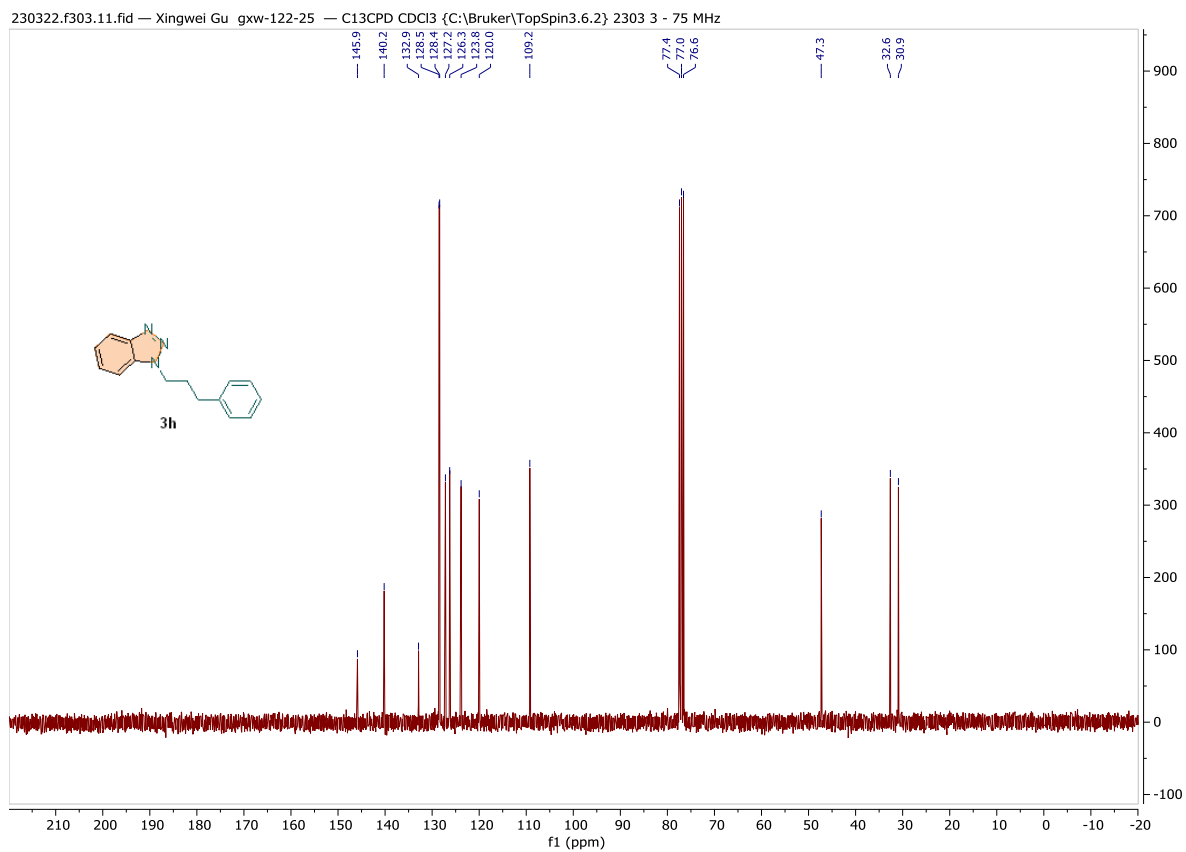
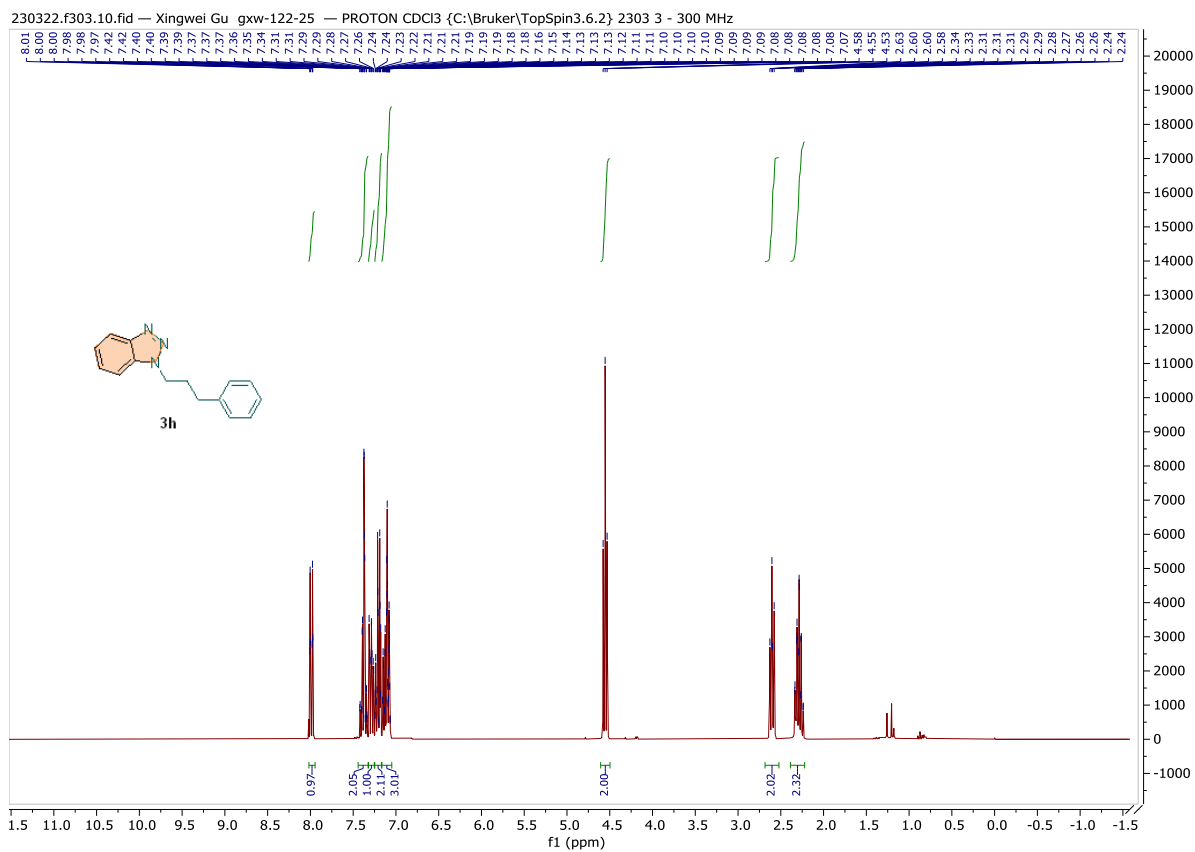


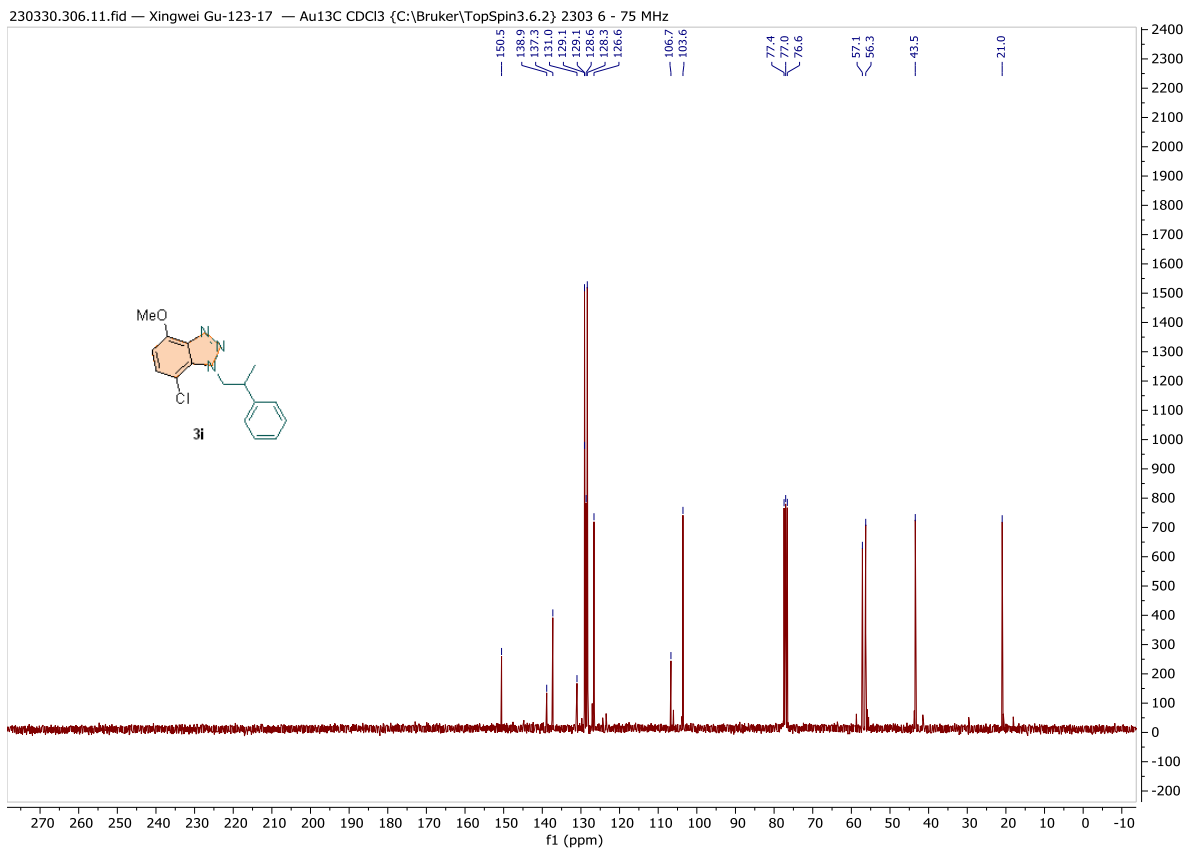
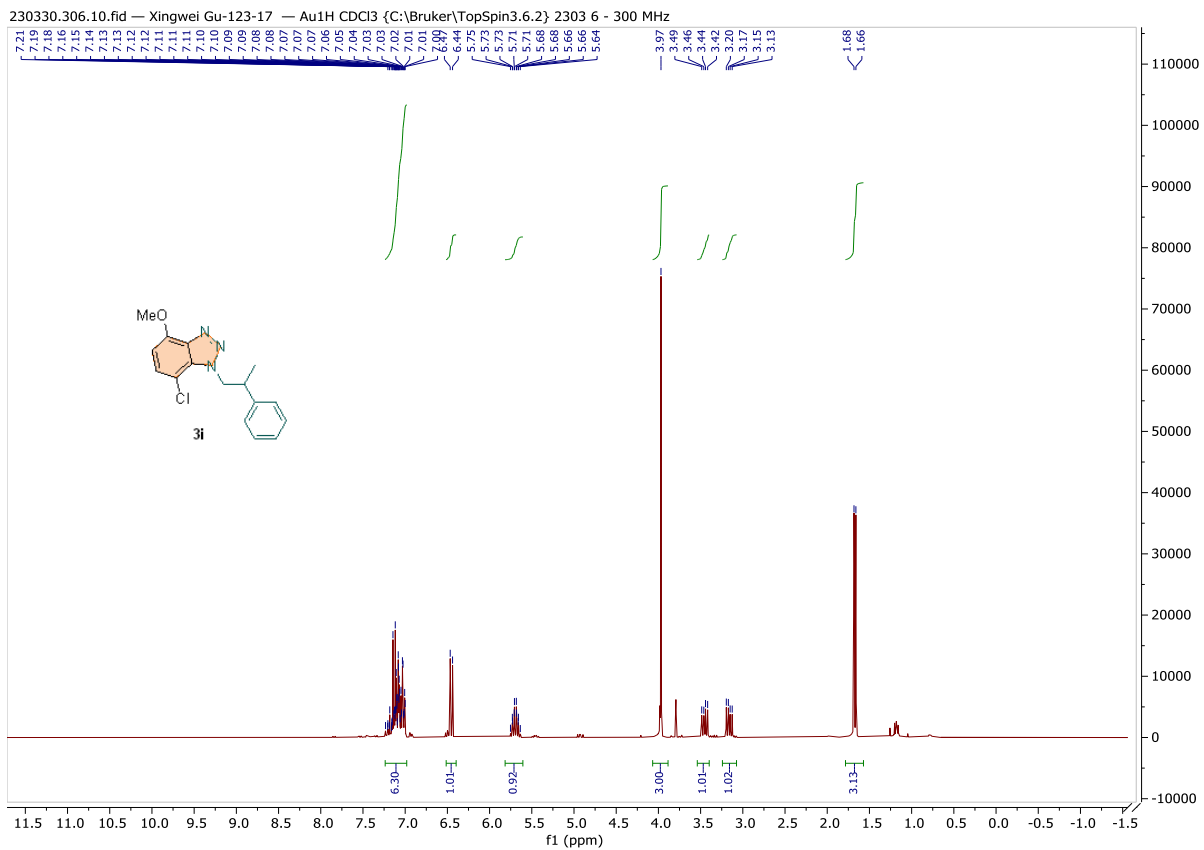
230315.f307.10.fid — Xingwei Gu gxw-122-6 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 7 - 300 MHz

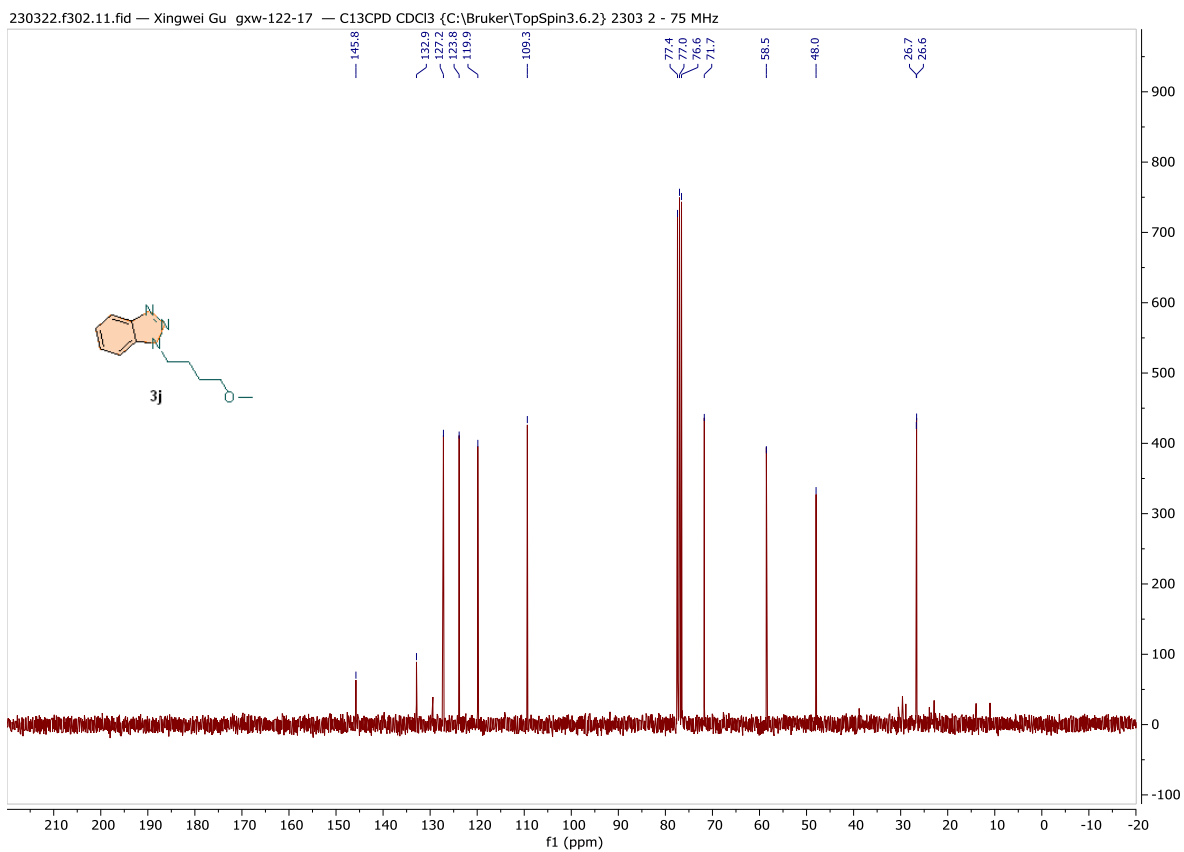
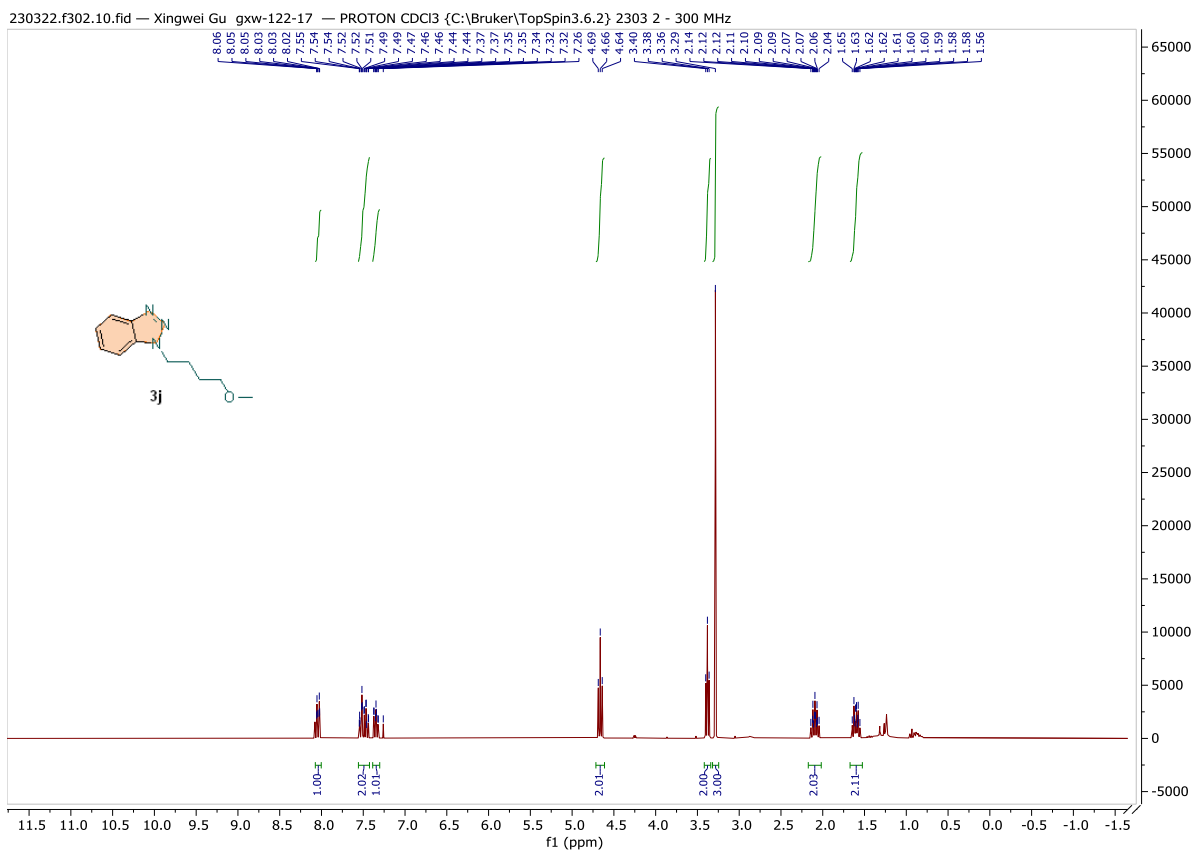


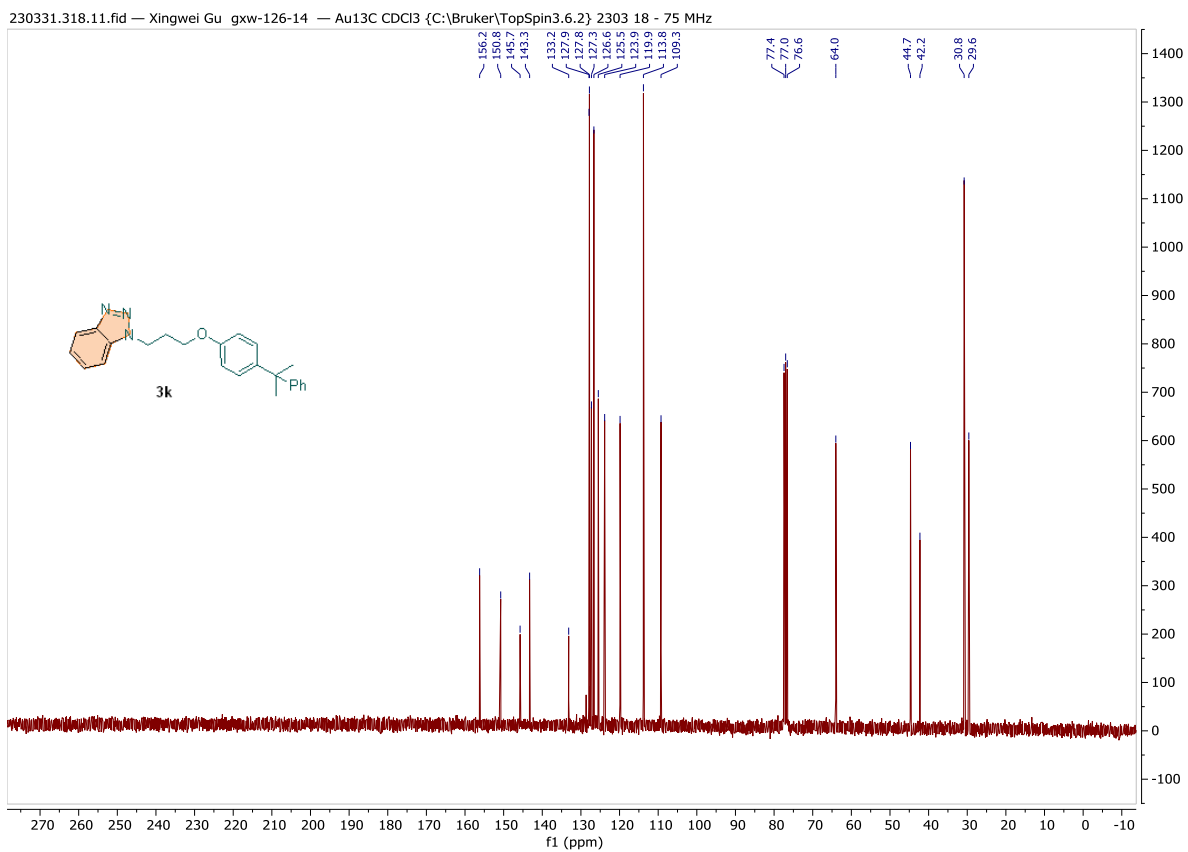
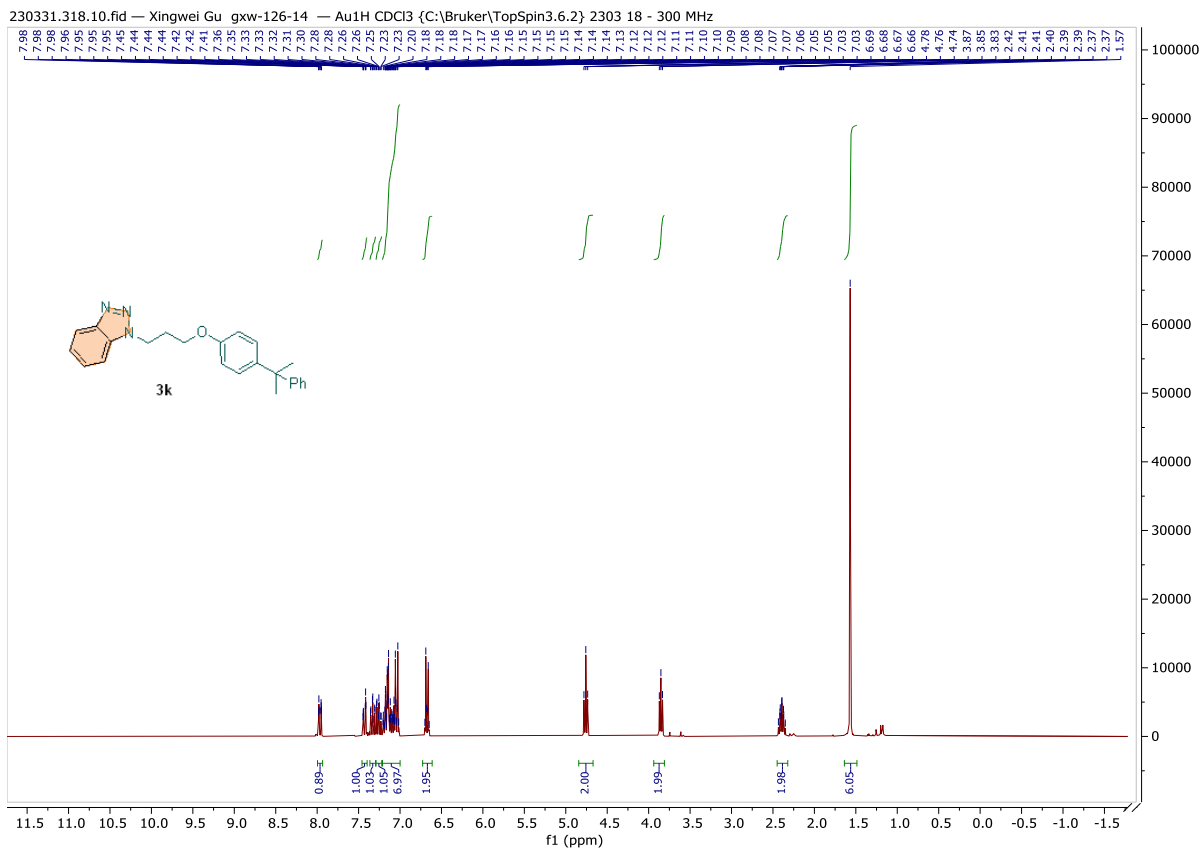
230315.f307.11.fid — Xingwei Gu gxw-122-6 — C13CPD CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 7 - 75 MHz

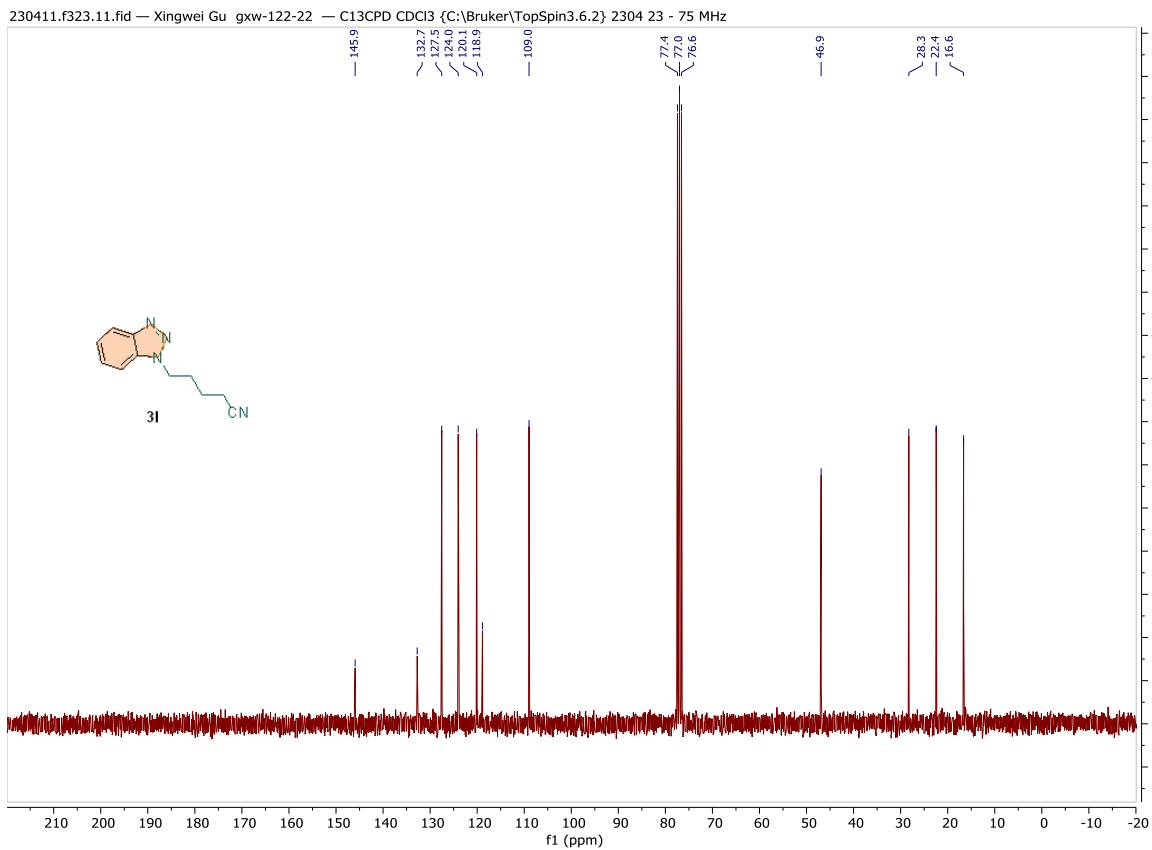
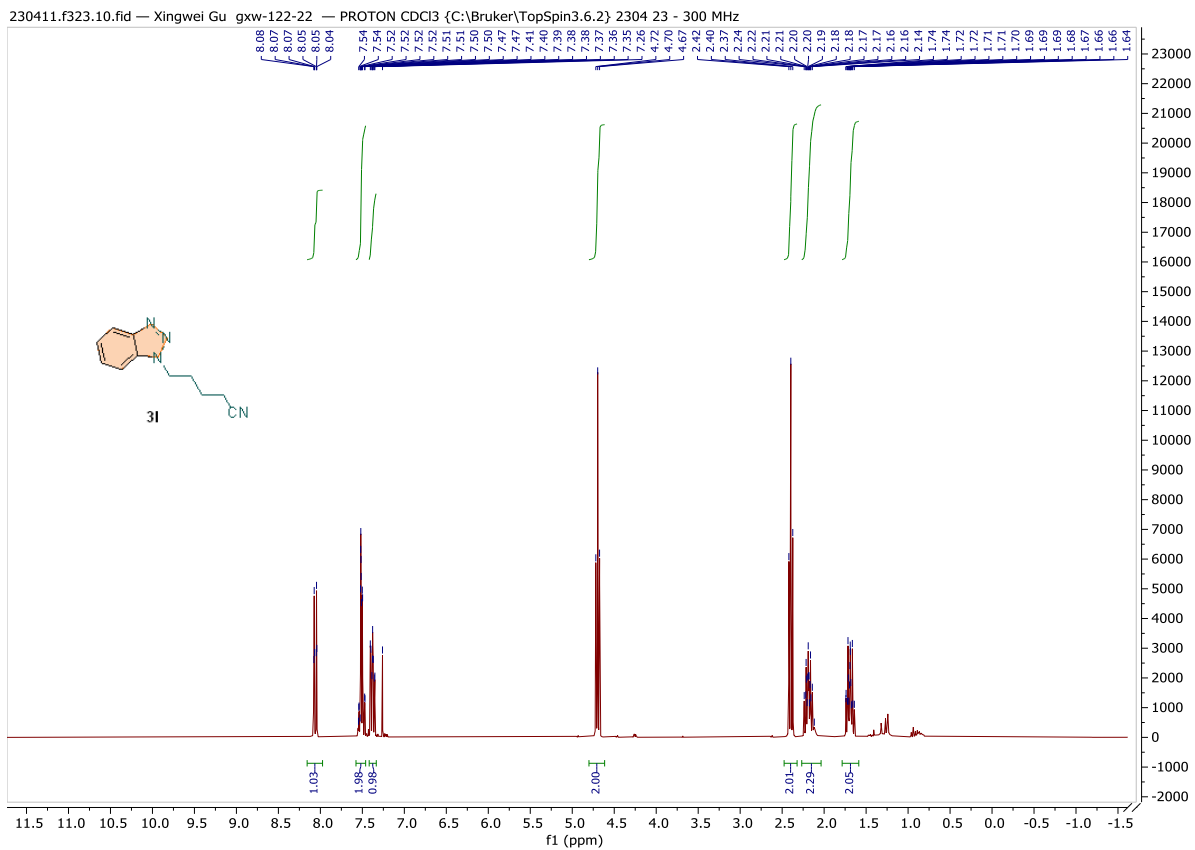




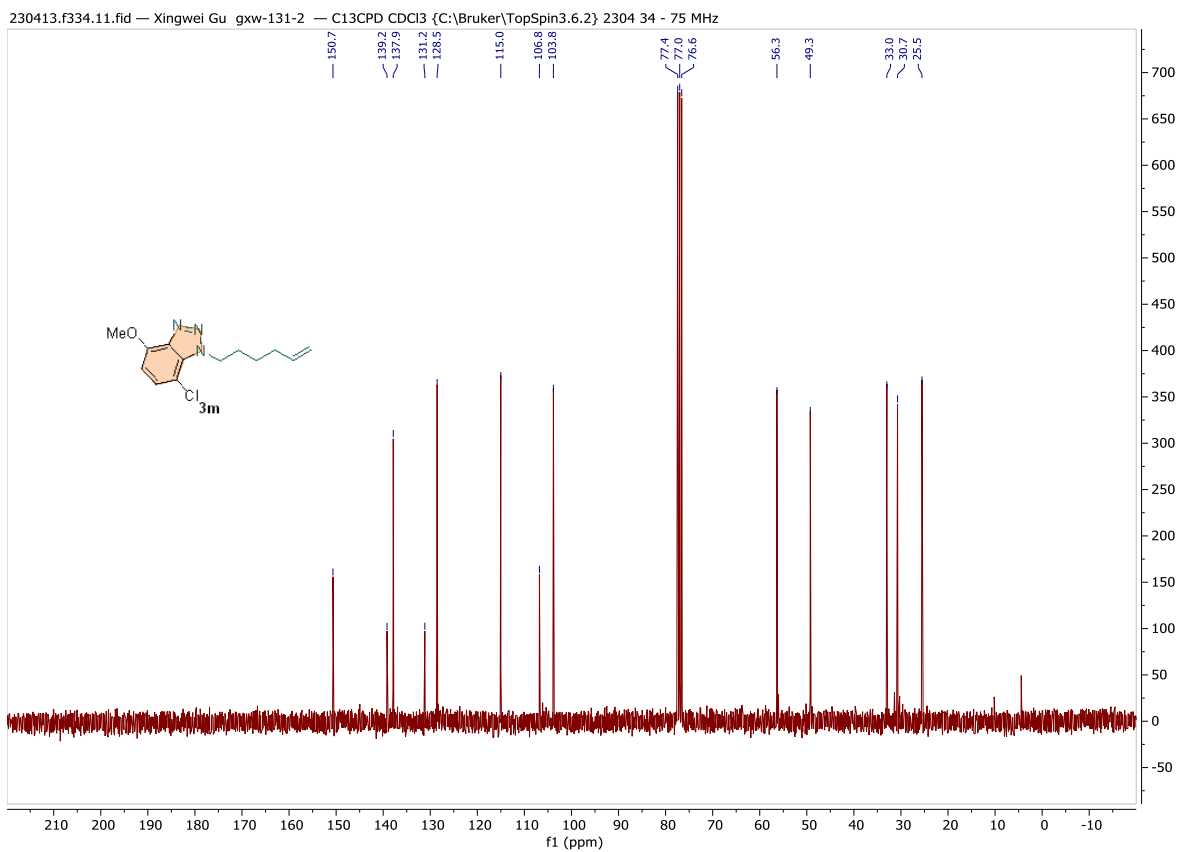
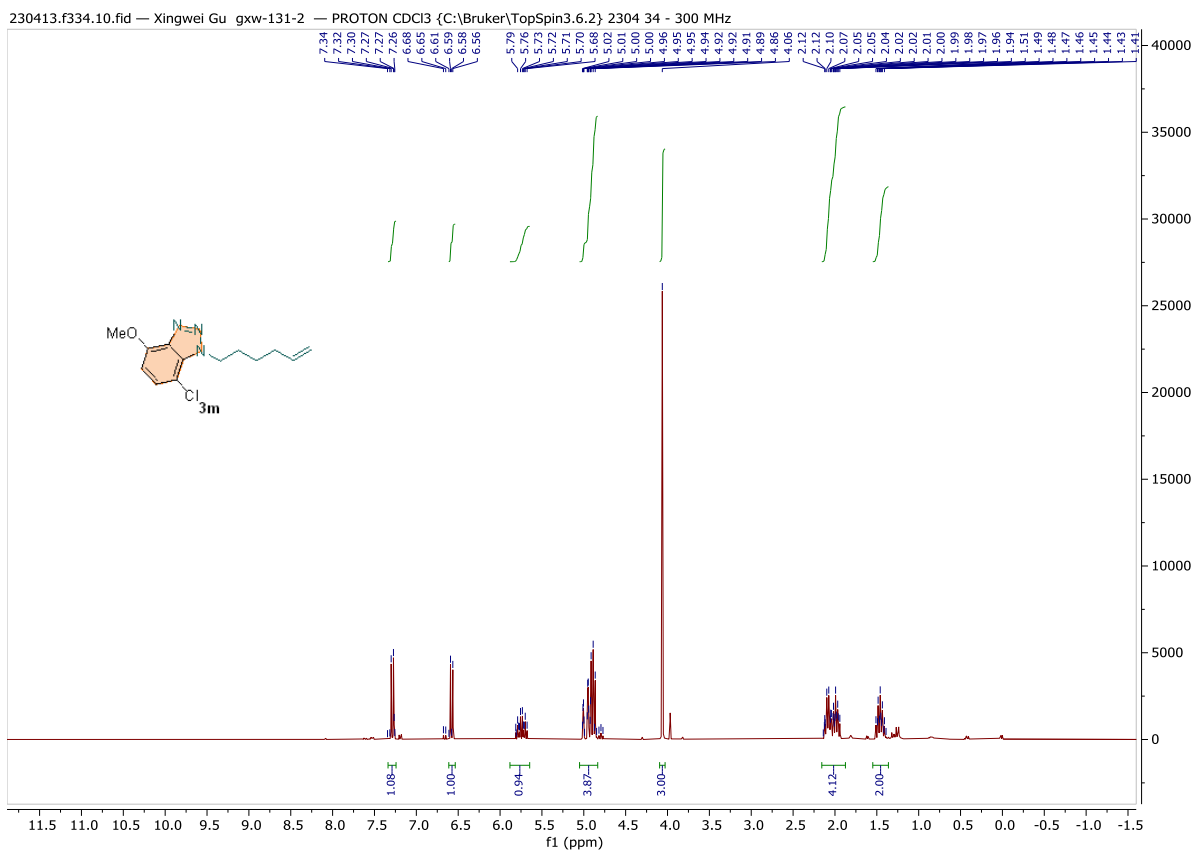


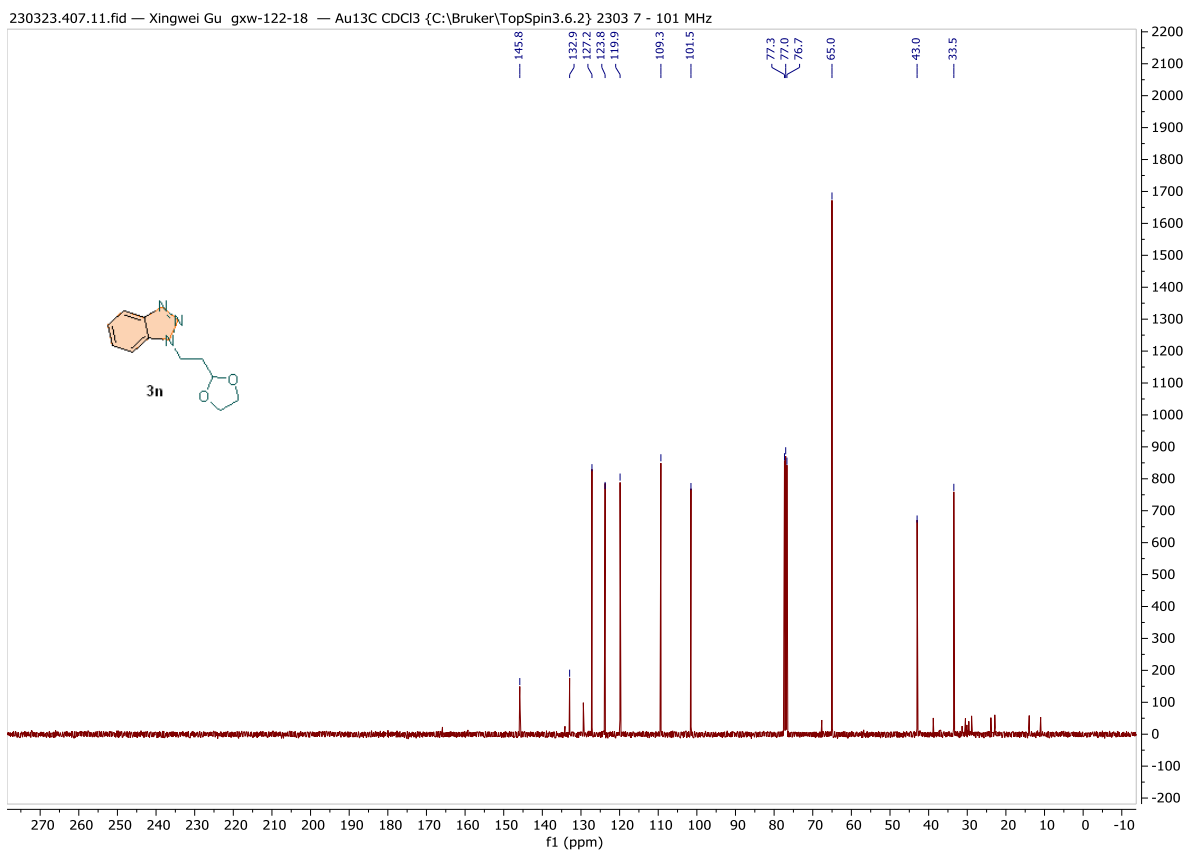
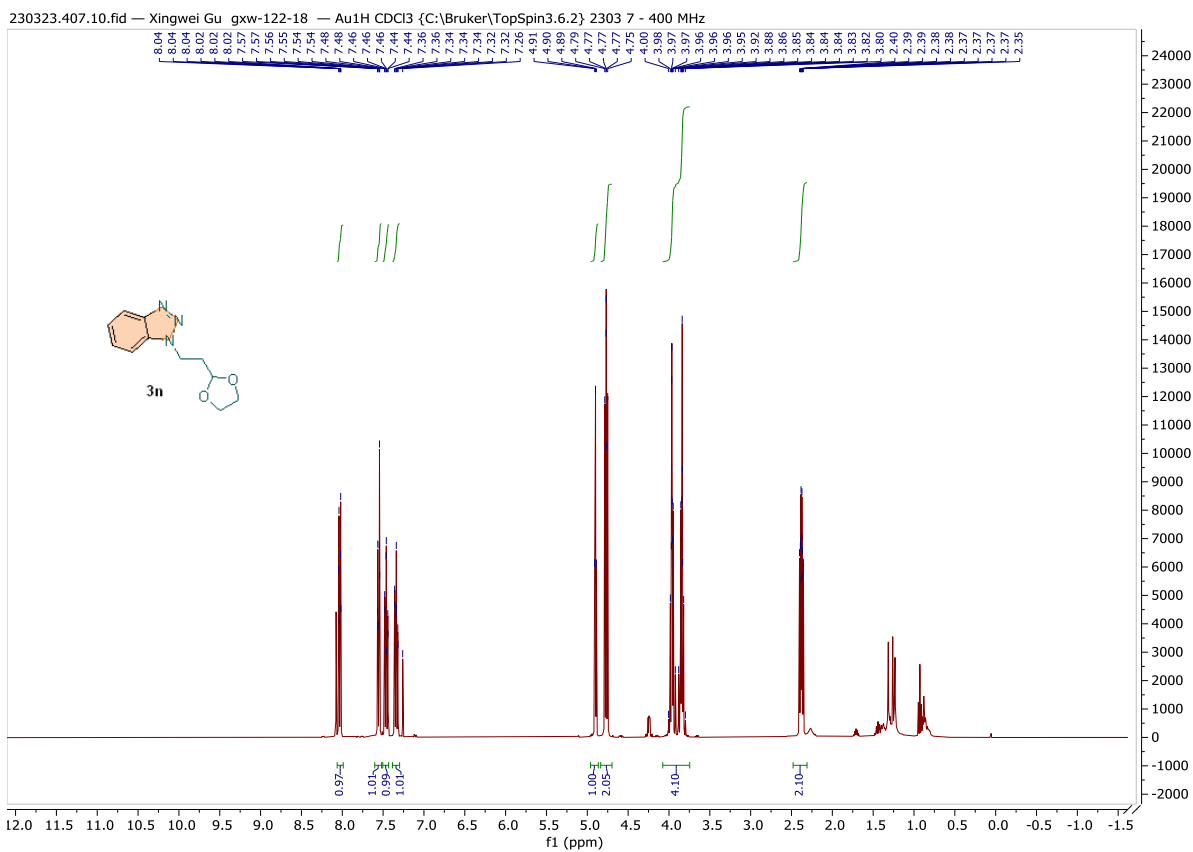


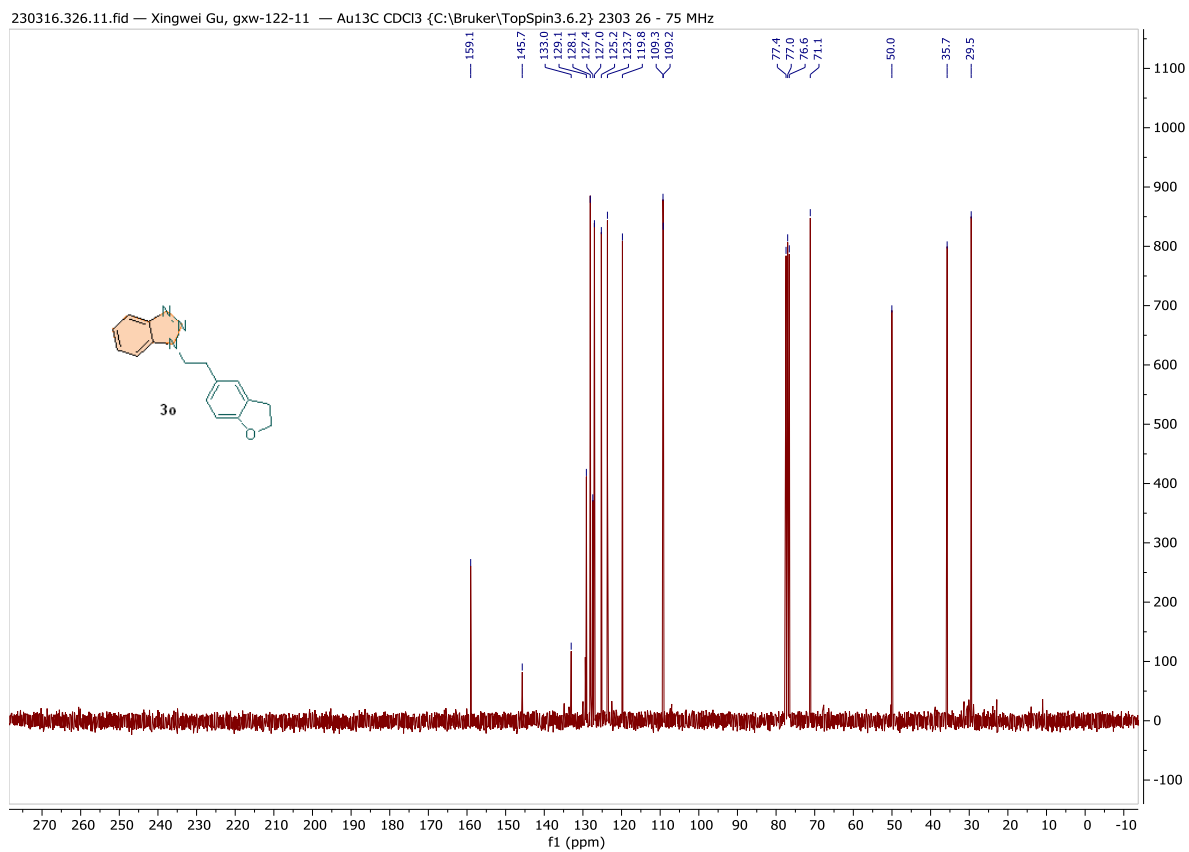
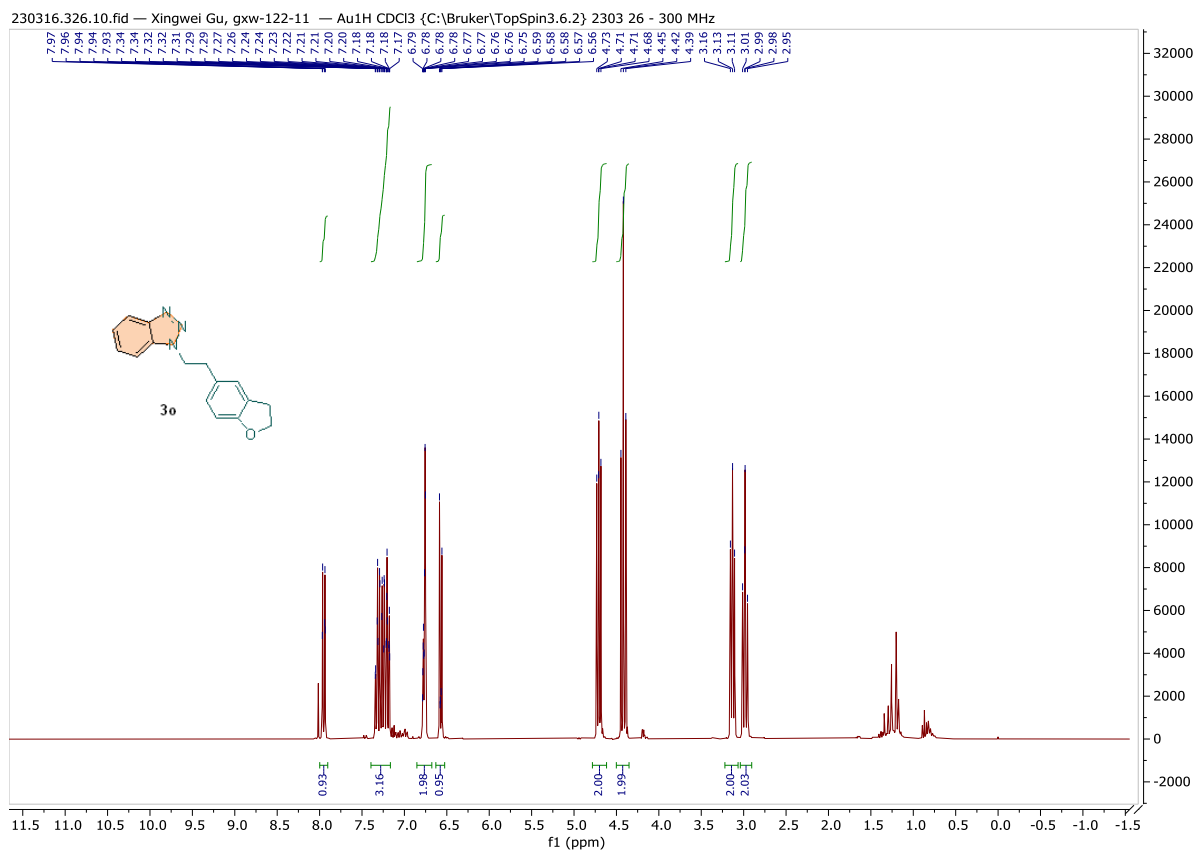




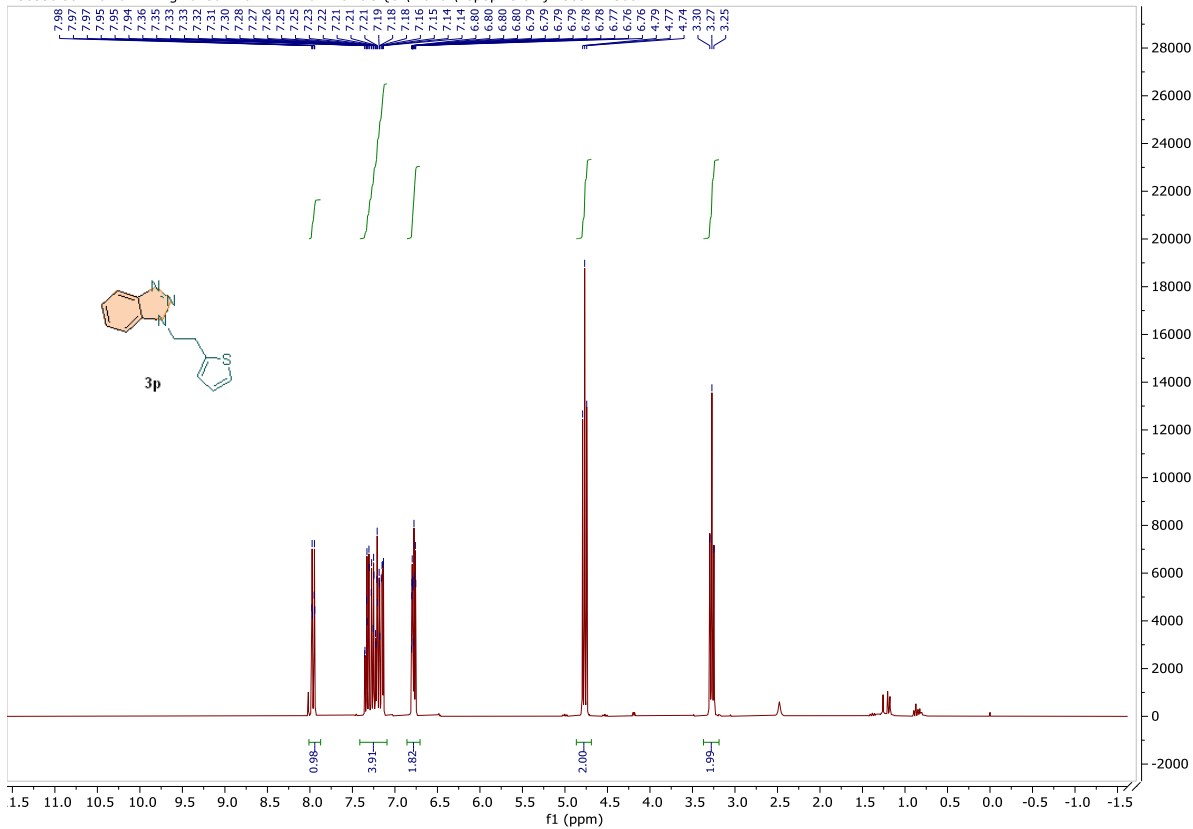




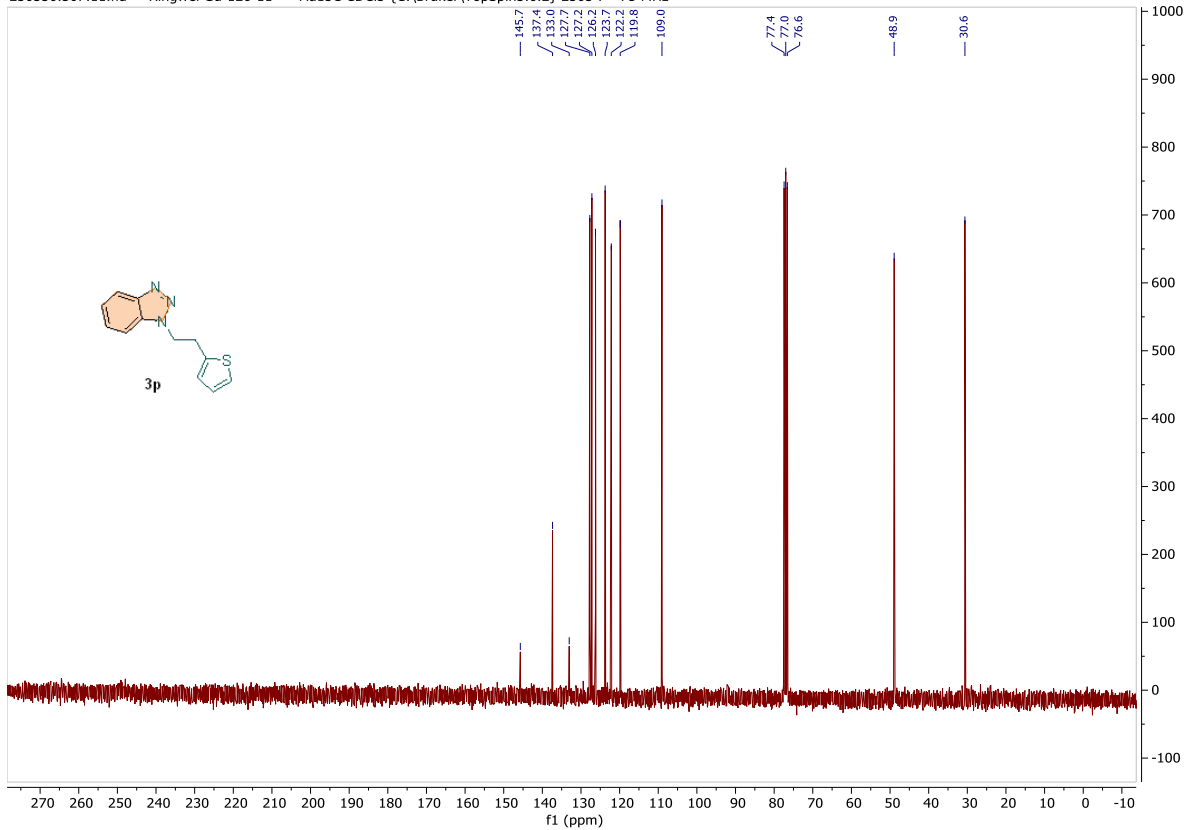


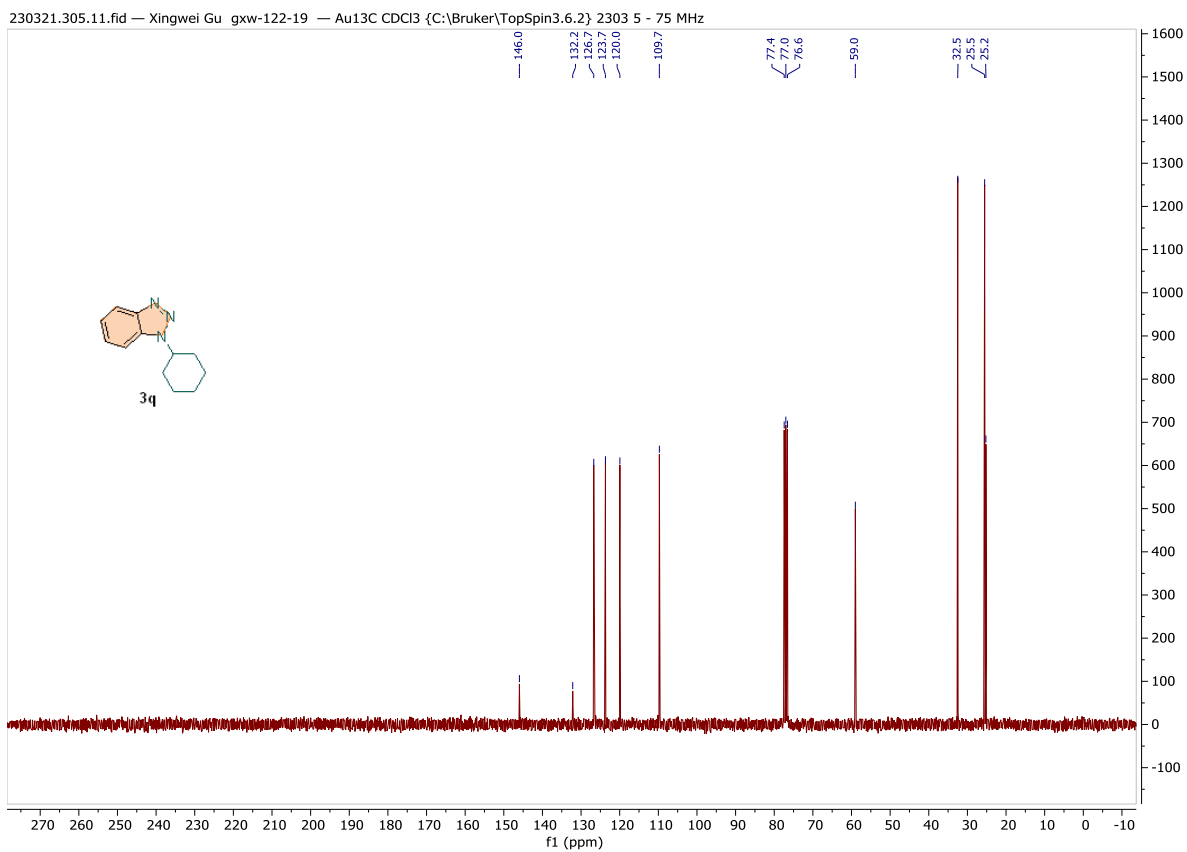
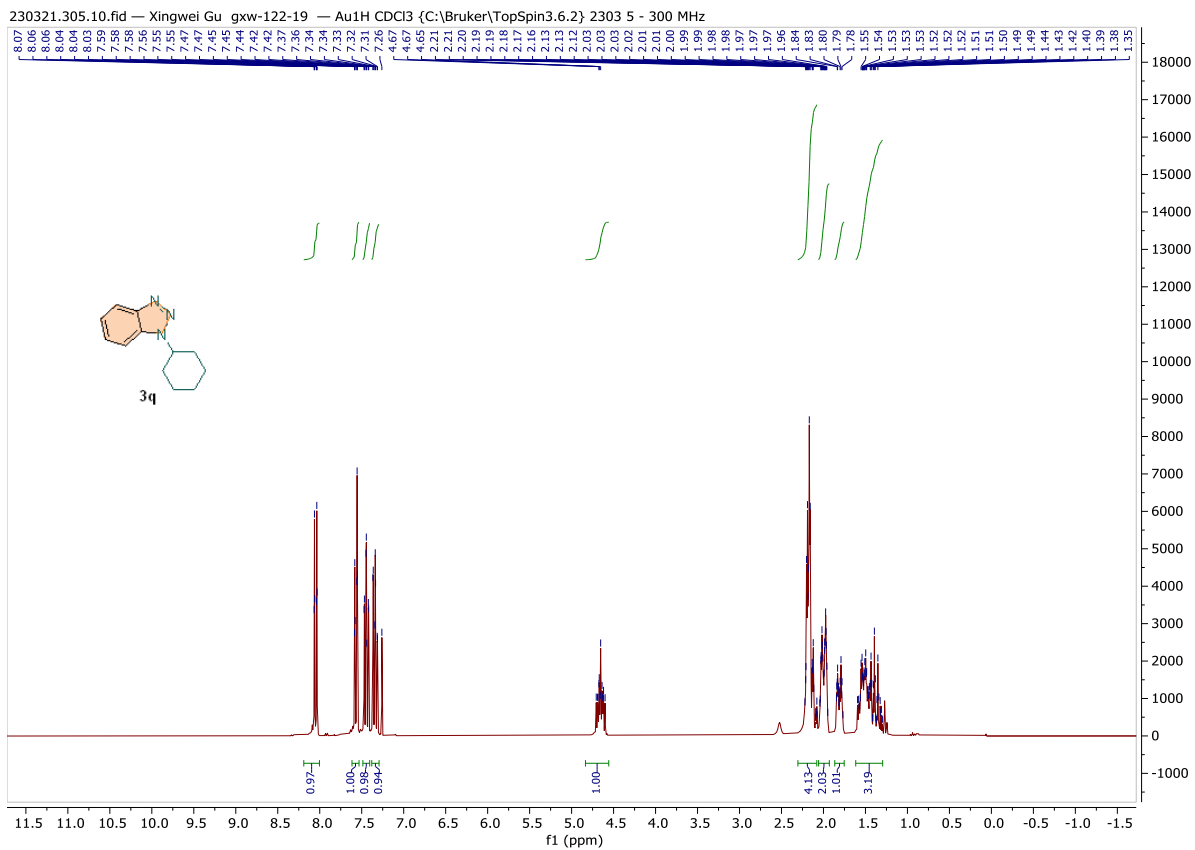


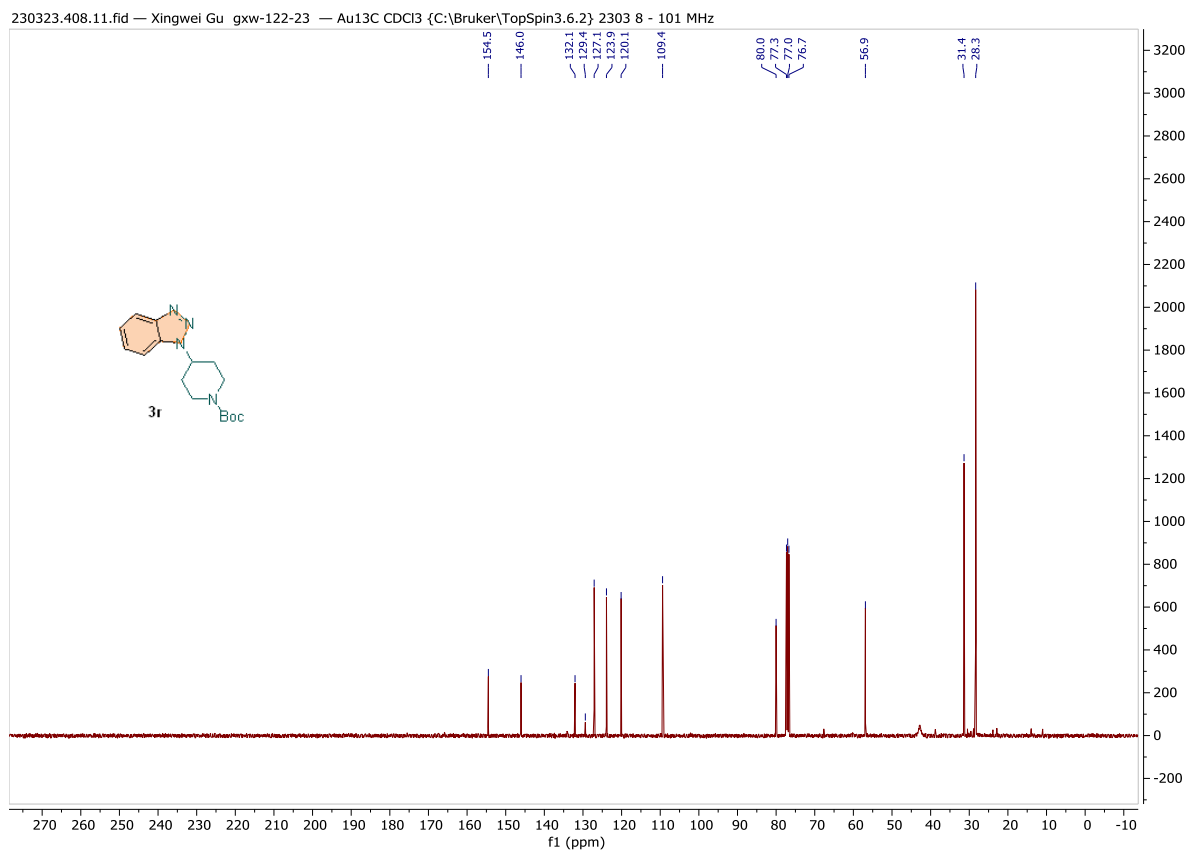
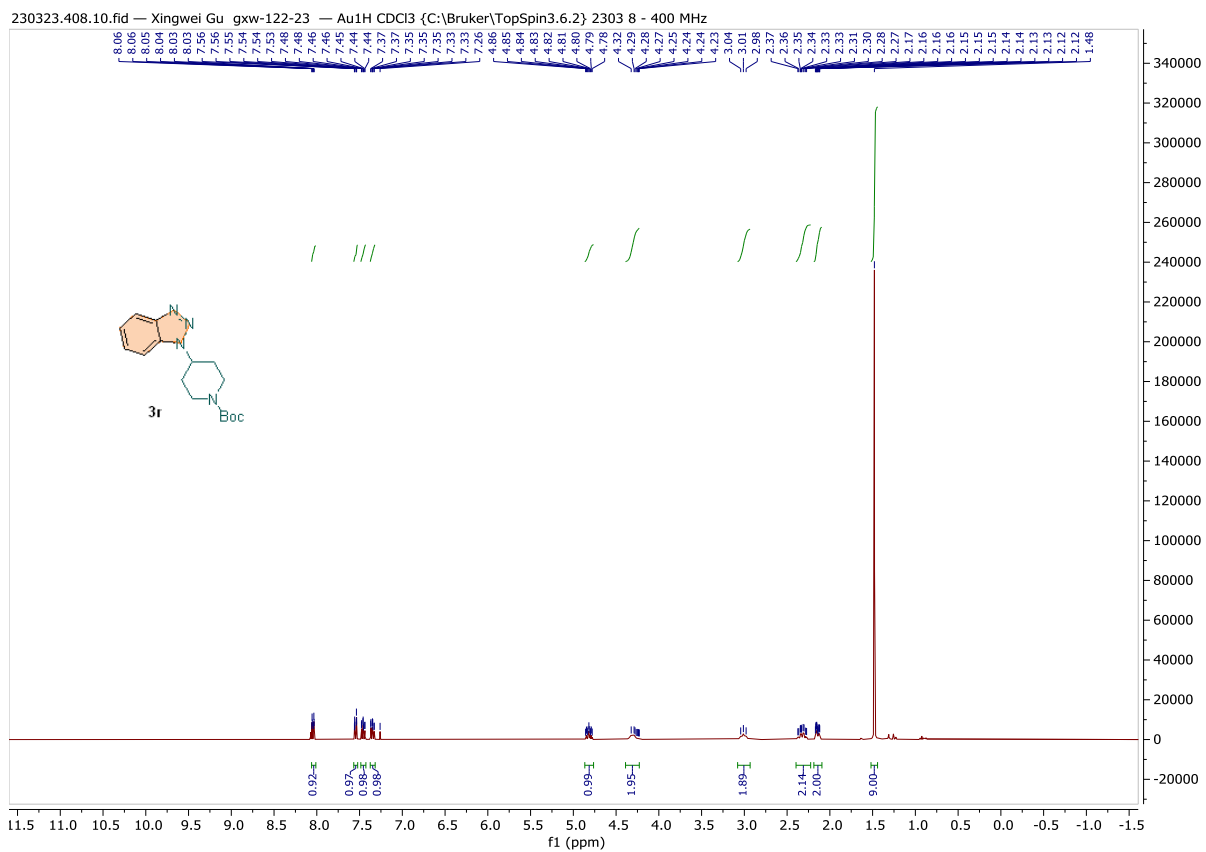
230330.307.10.fid — Xingwei Gu-126-11 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 7 - 300 MHz

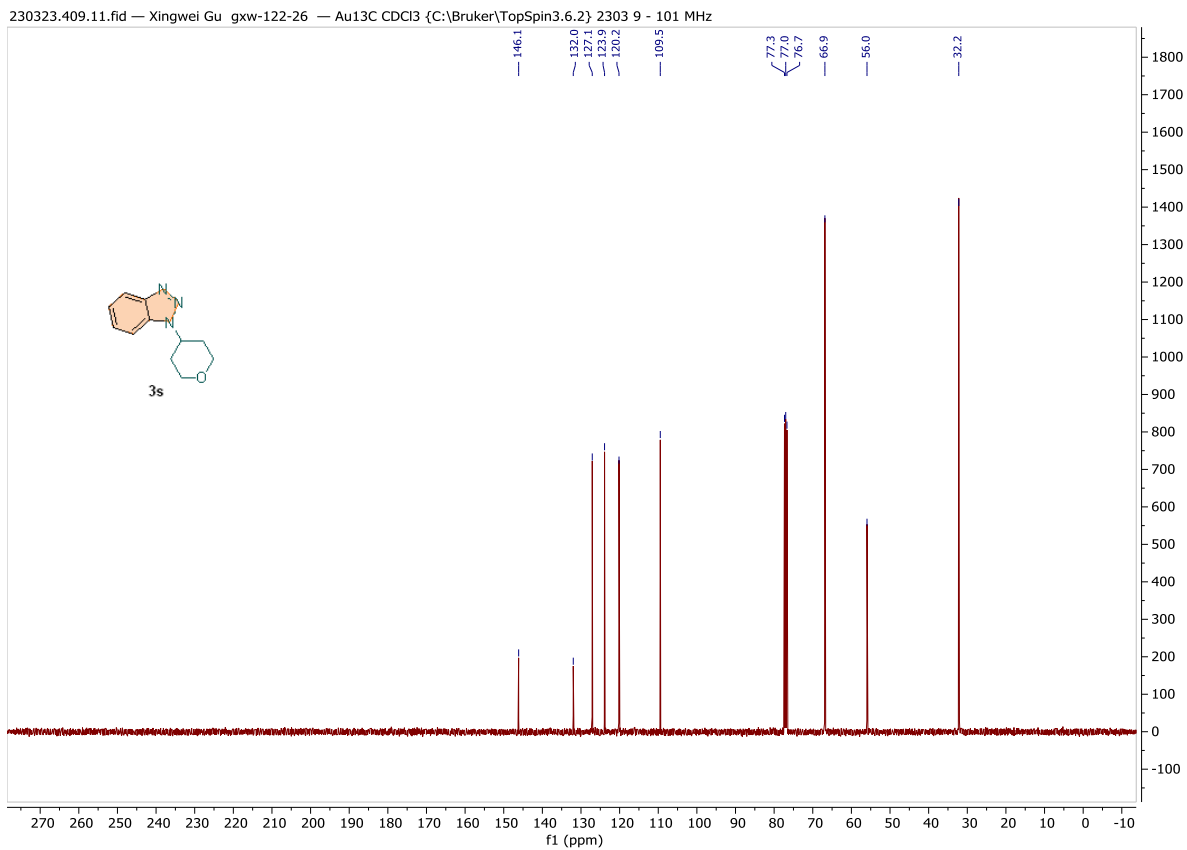
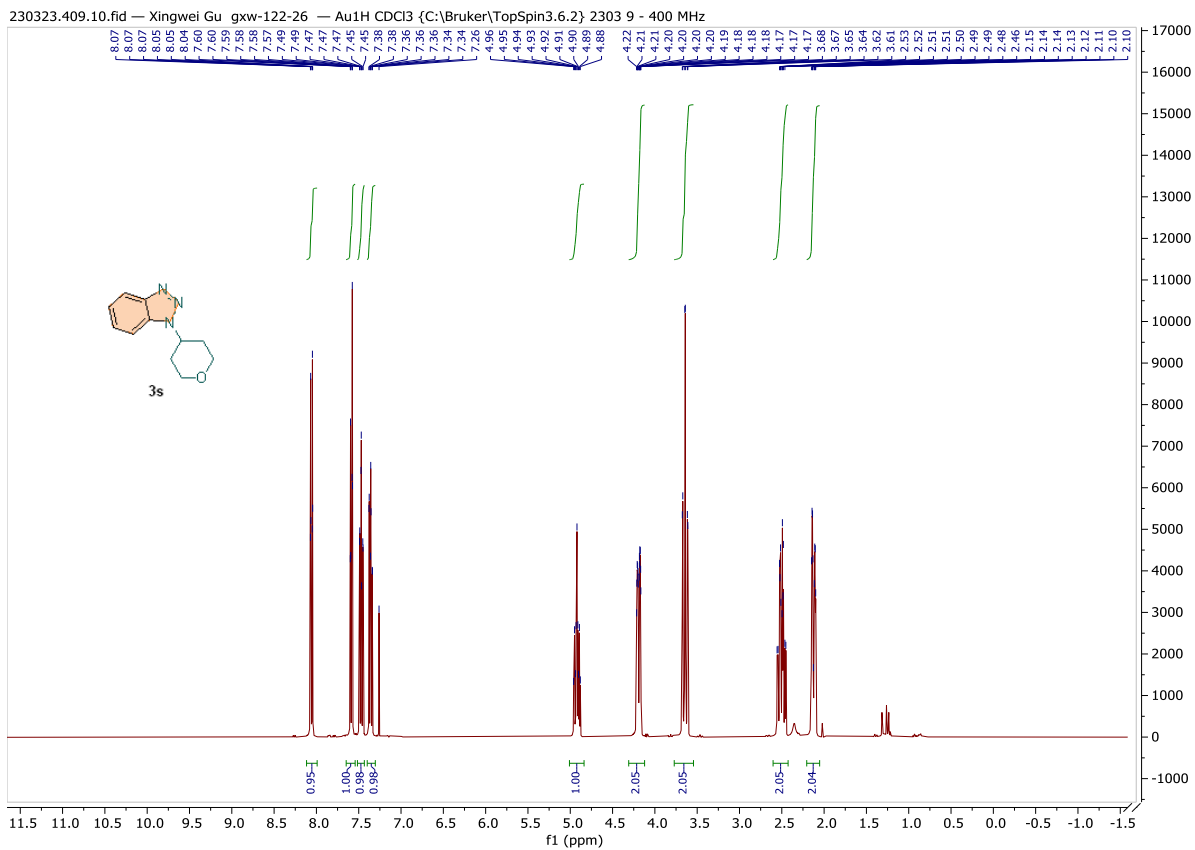


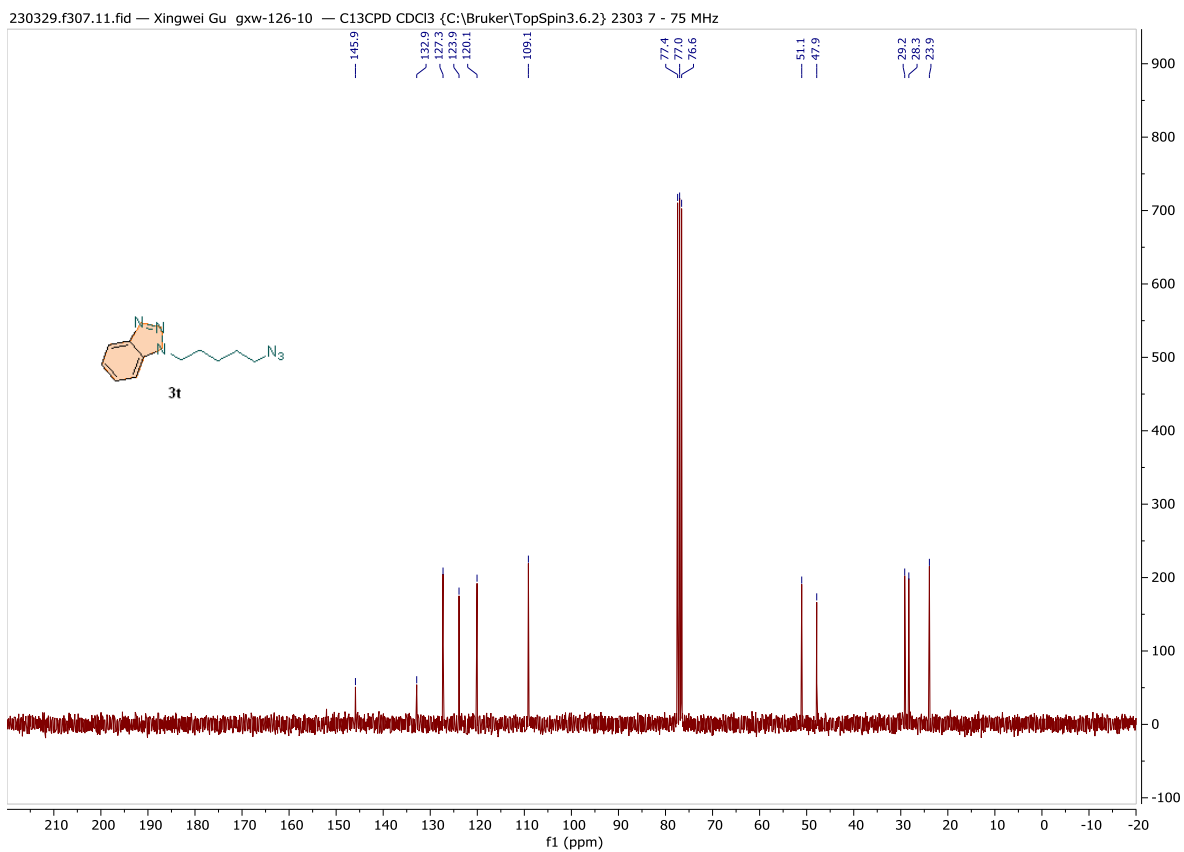
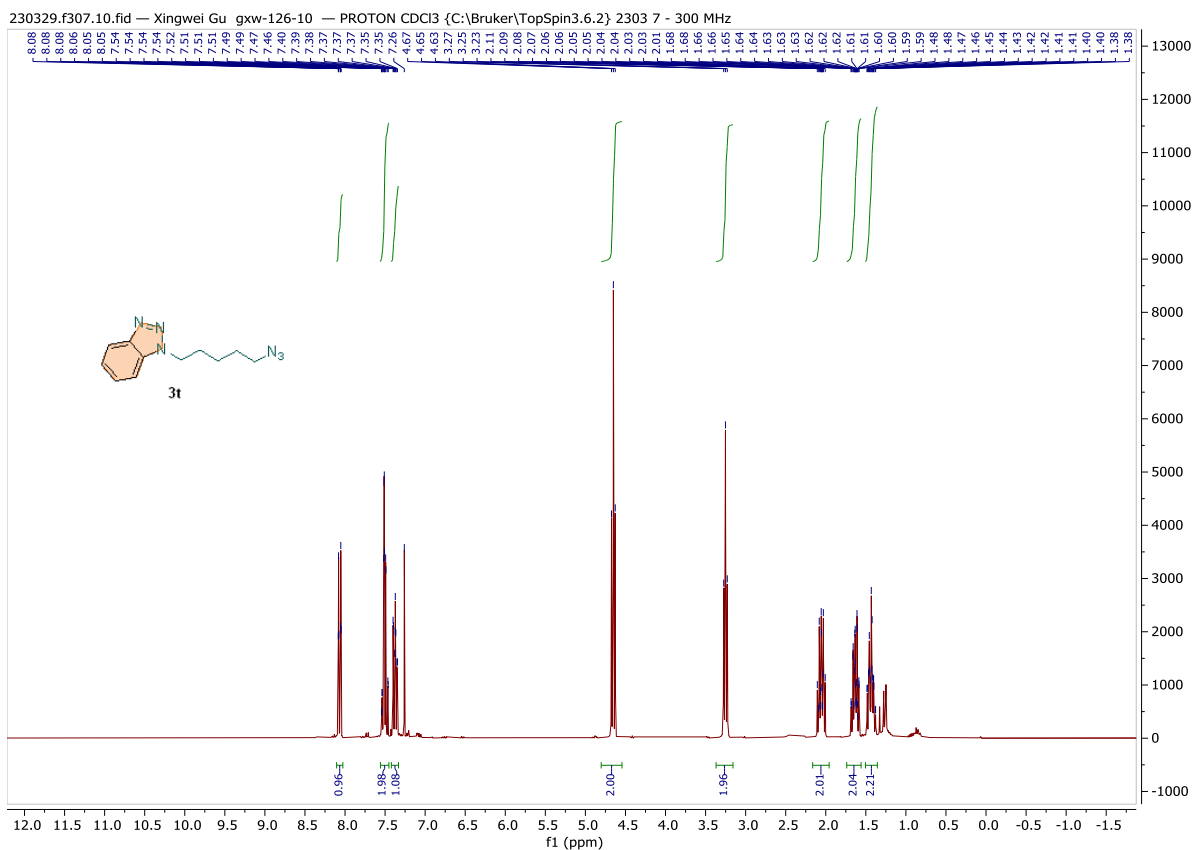
230330.307.11.fid — Xingwei Gu-126-11 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 7 - 75 MHz



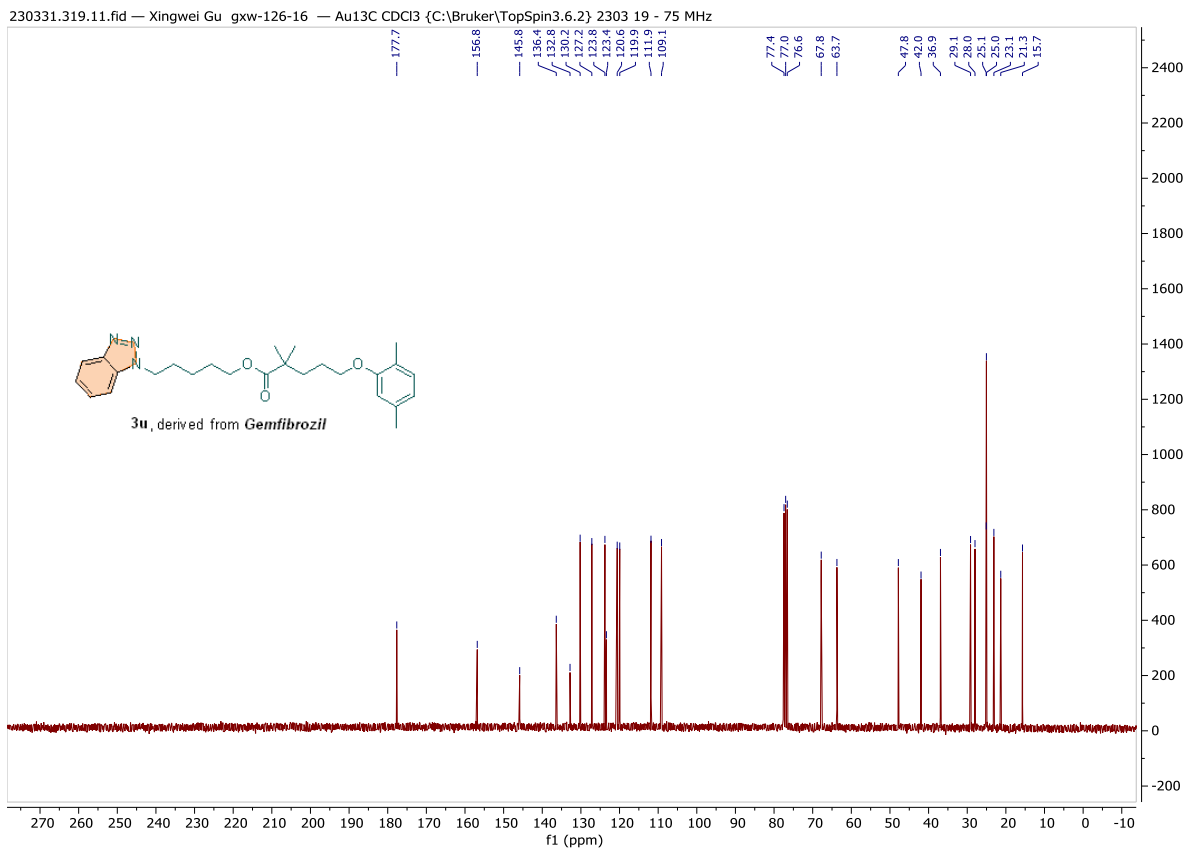
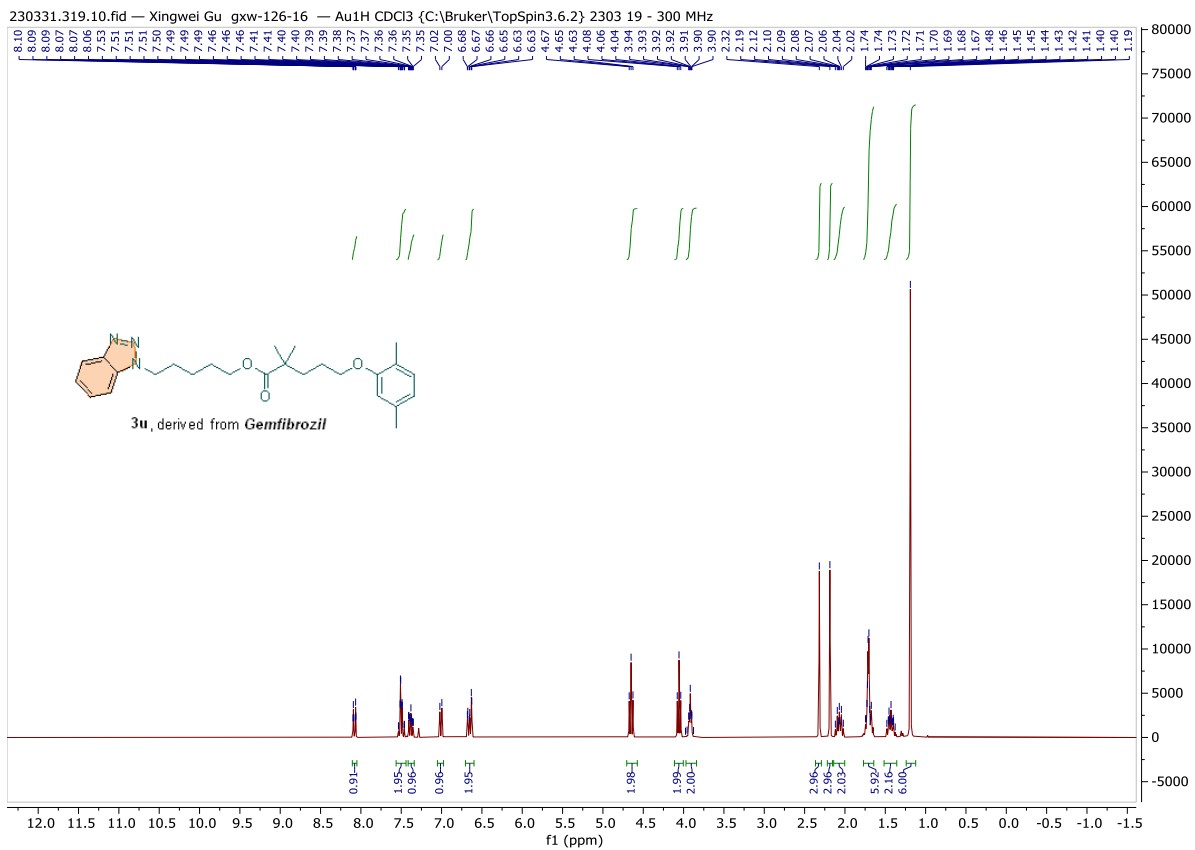




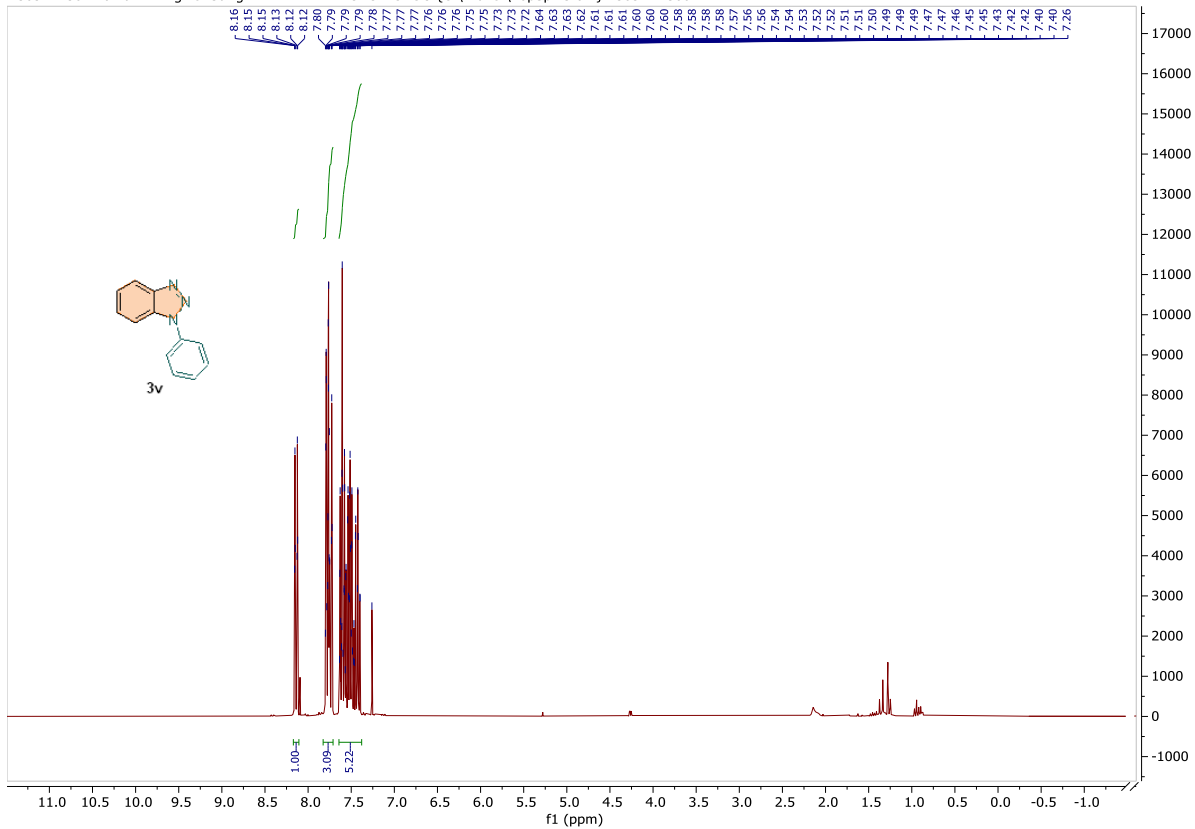




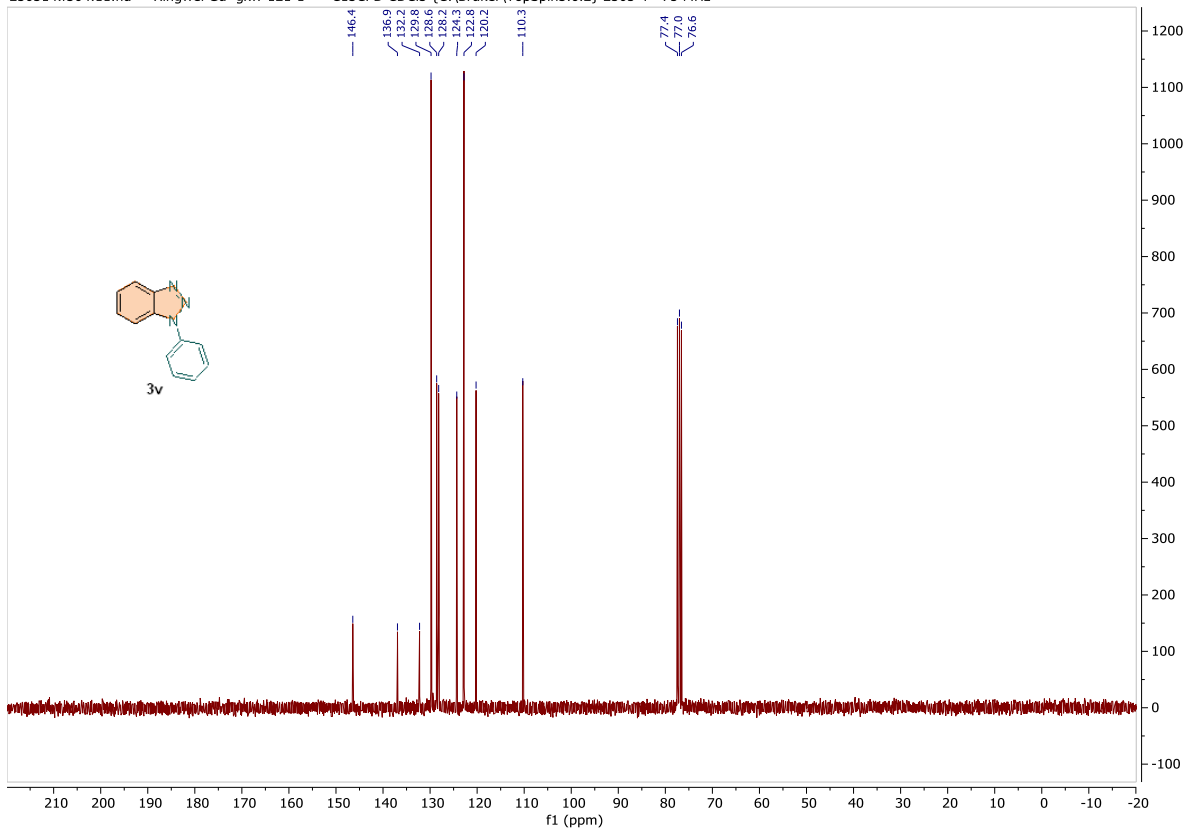




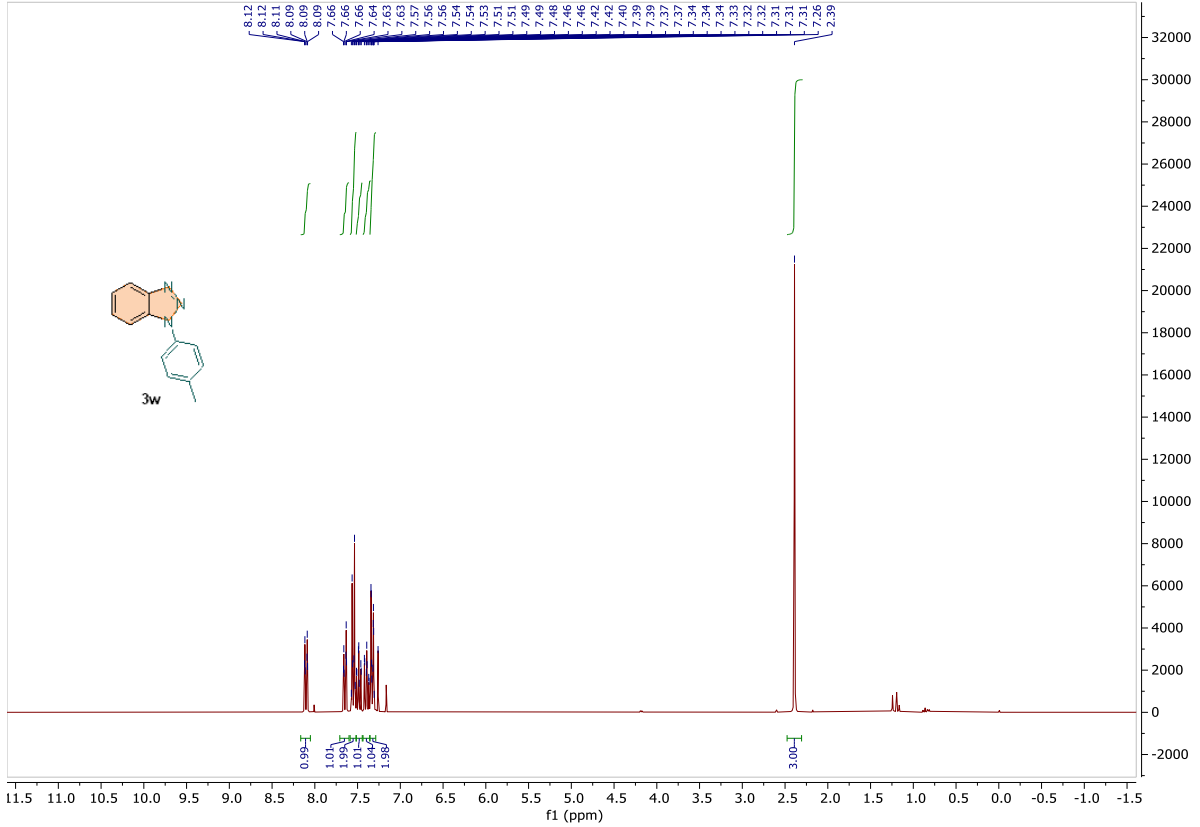
230314.f304.10.fid — Xingwei Gu gxw-121-1 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 300 MHz



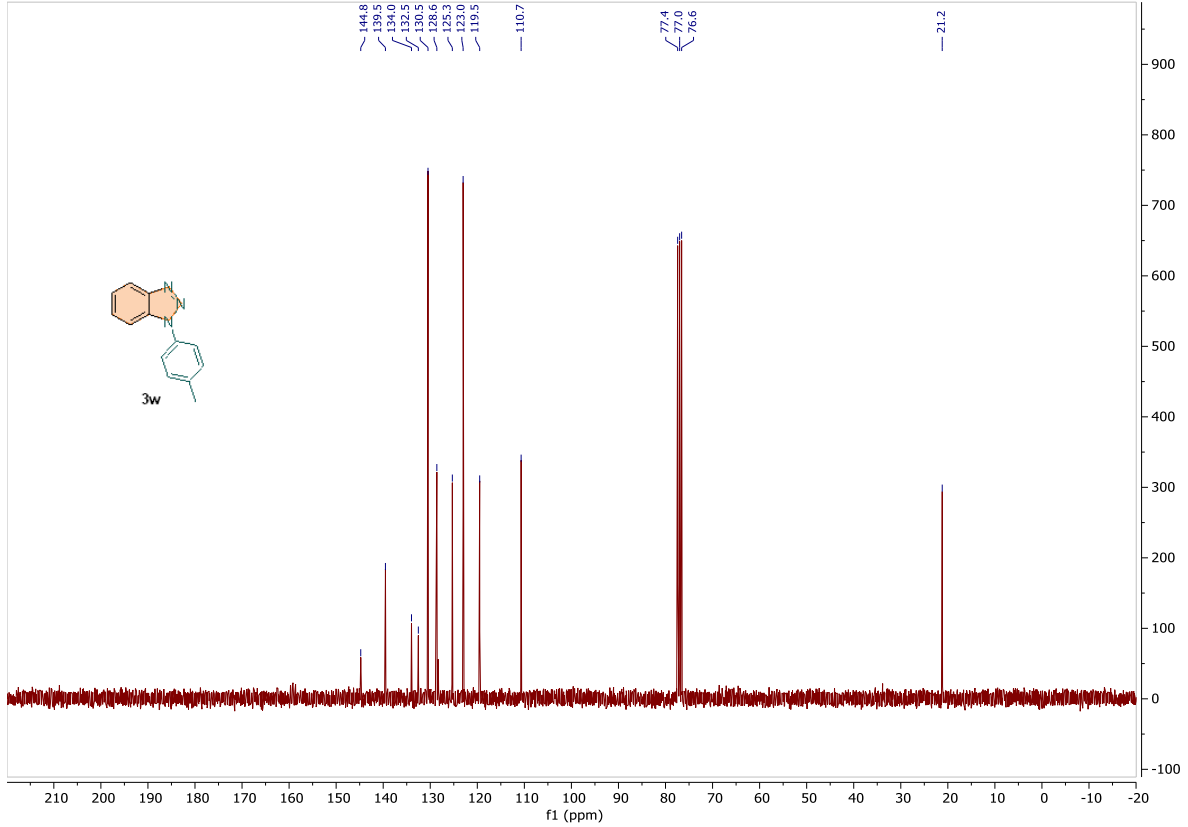
230314.f304.11.fid — Xingwei Gu gxw-121-1 — C13CPD CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 75 MHz



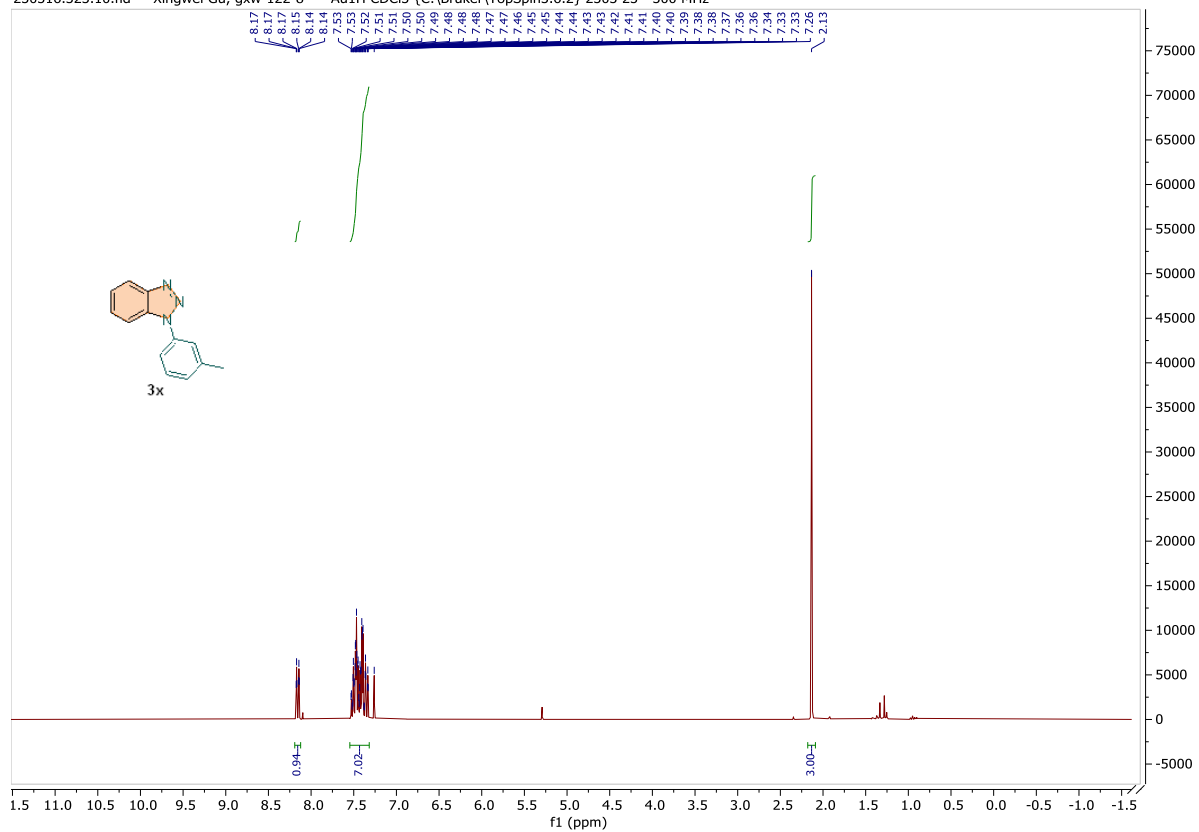
230316.f303.10.fid — Xingwei Gu gxw-122-7 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 3 - 300 MHz



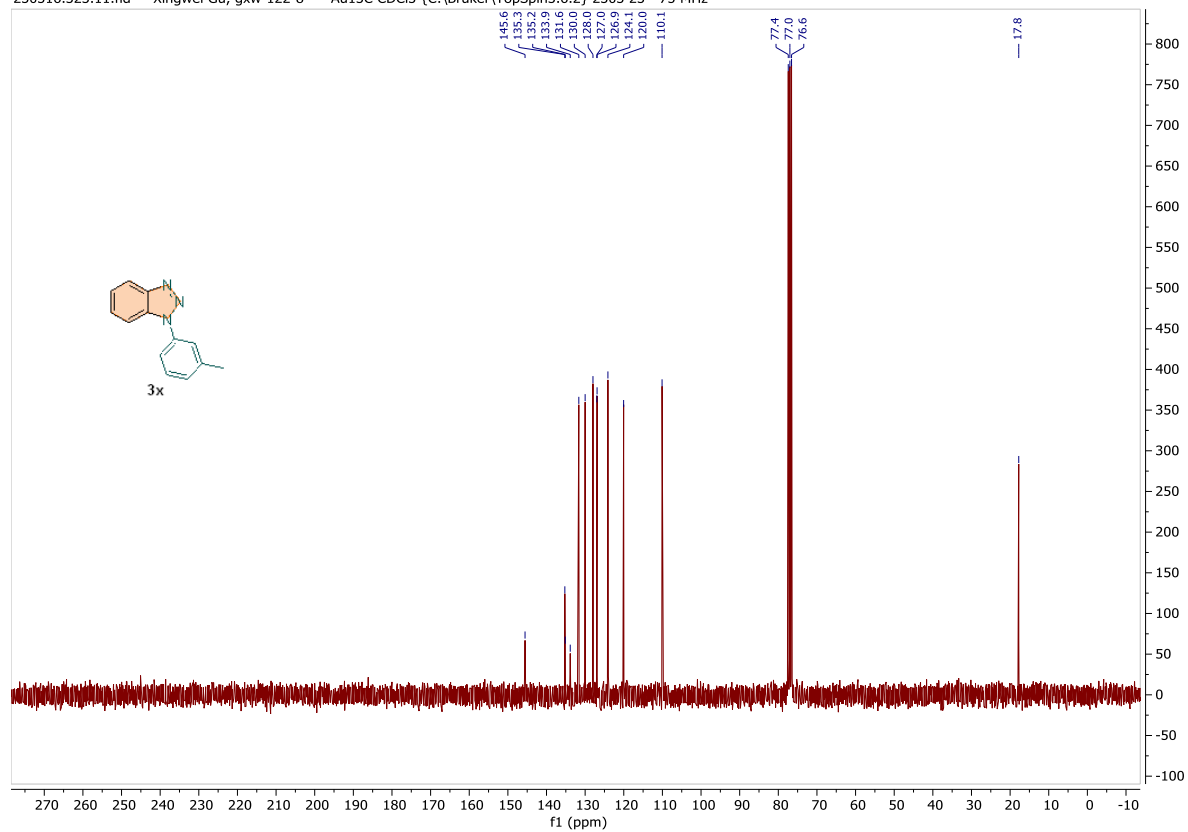
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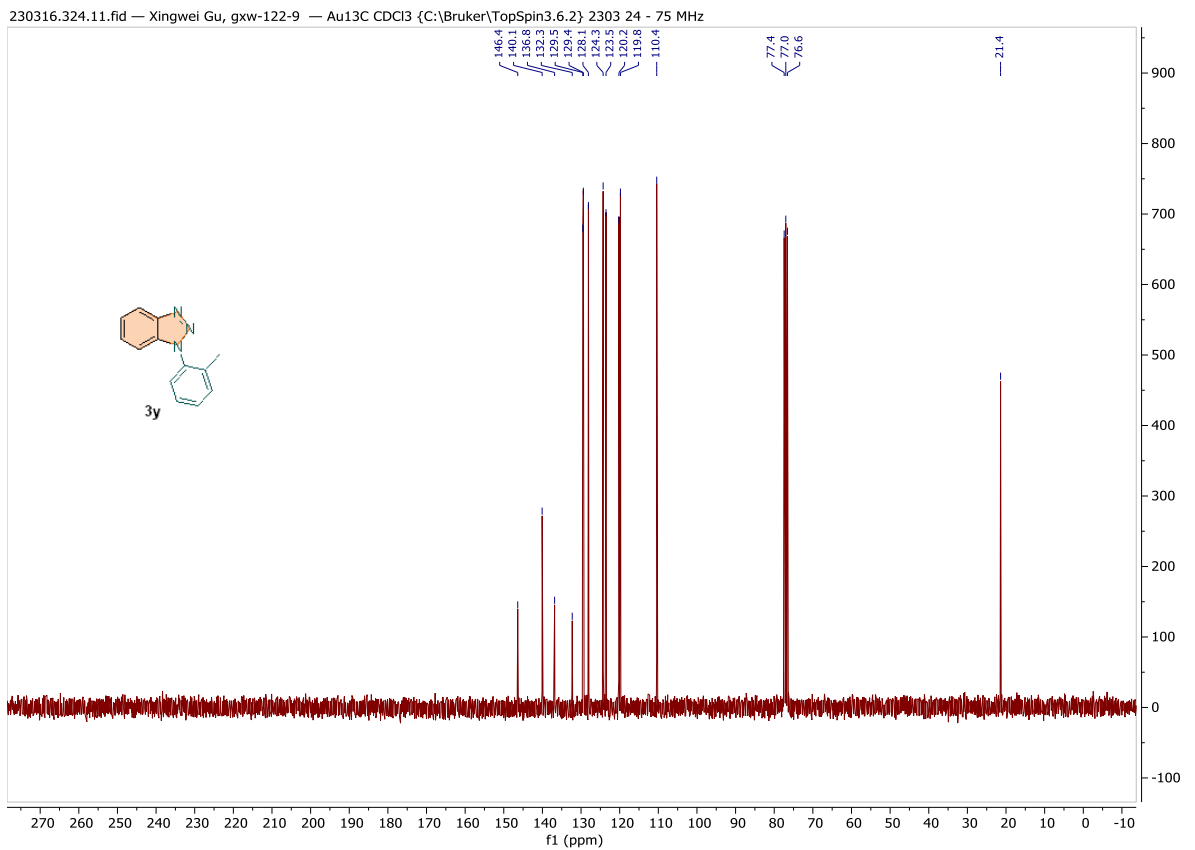
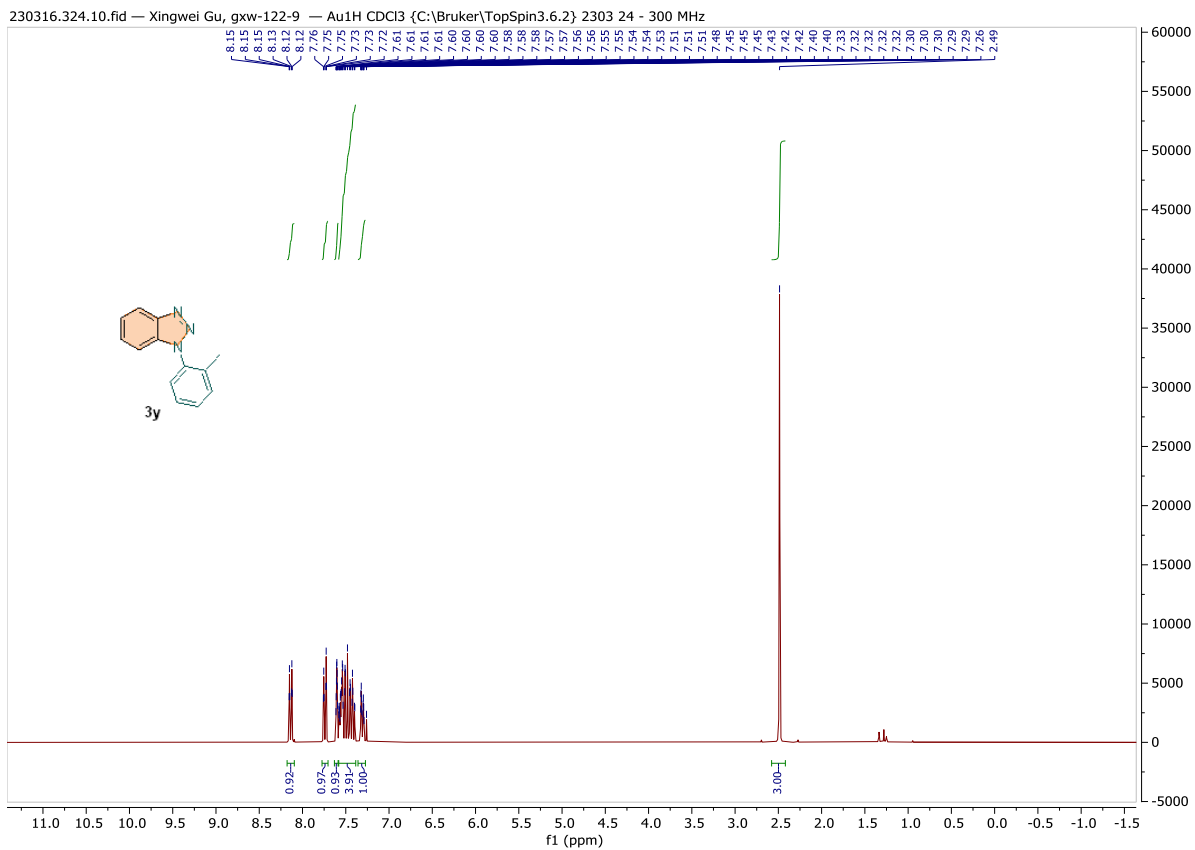


230316.323.10.fid — Xingwei Gu, gxw-122-8 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 23 - 300 MHz

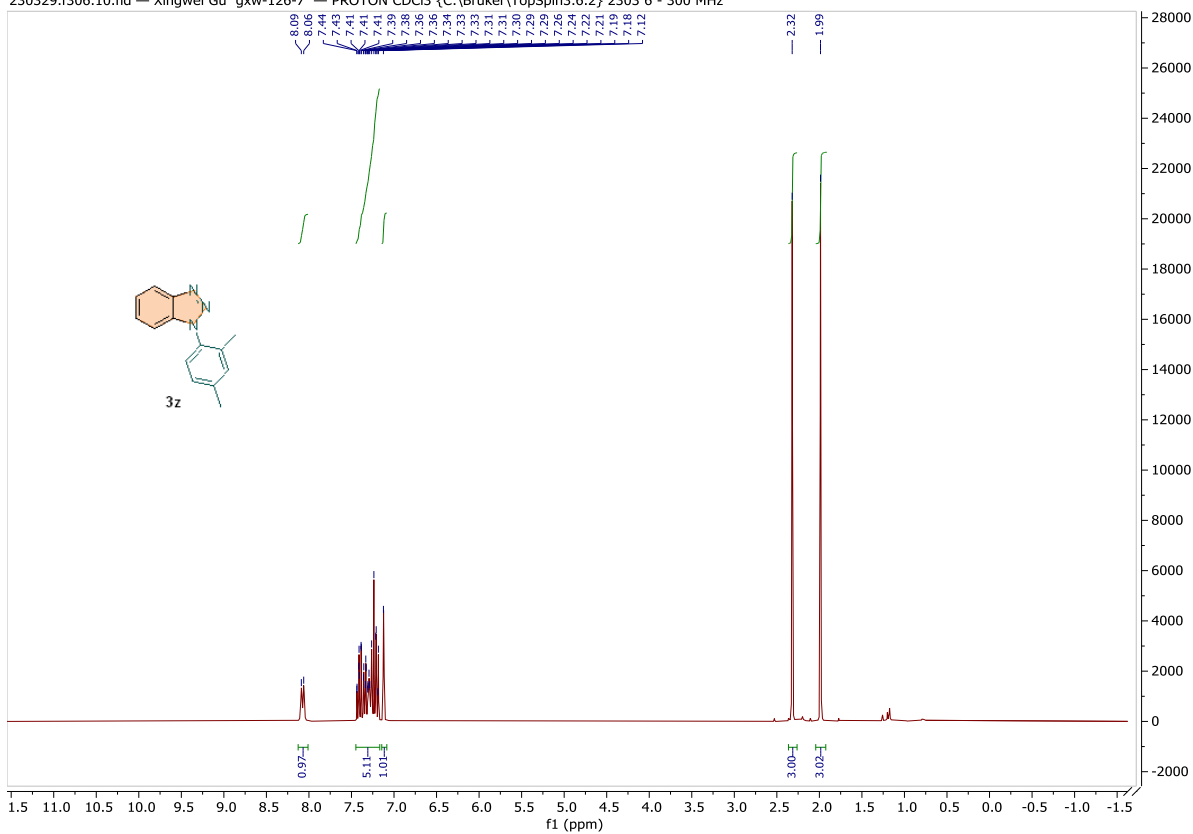


230316.323.11.fid — Xingwei Gu, gxw-122-8 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 23 - 75 MHz

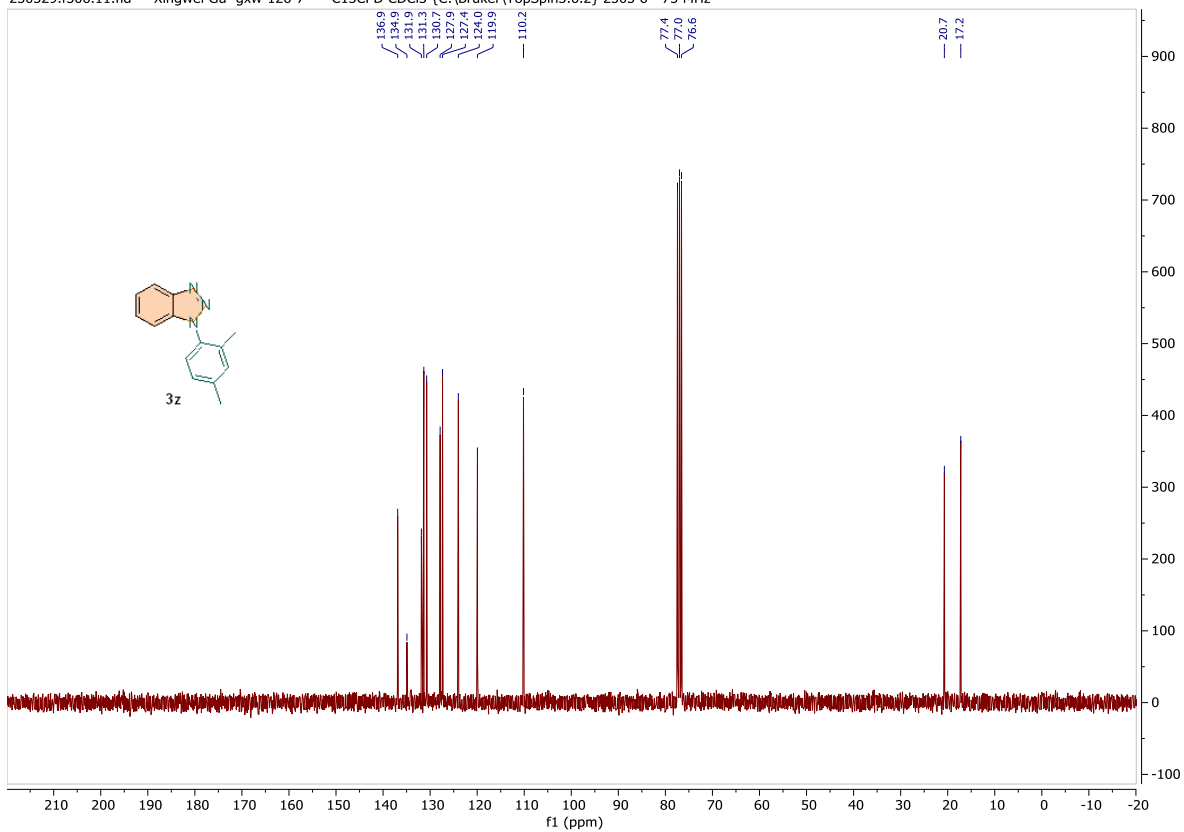




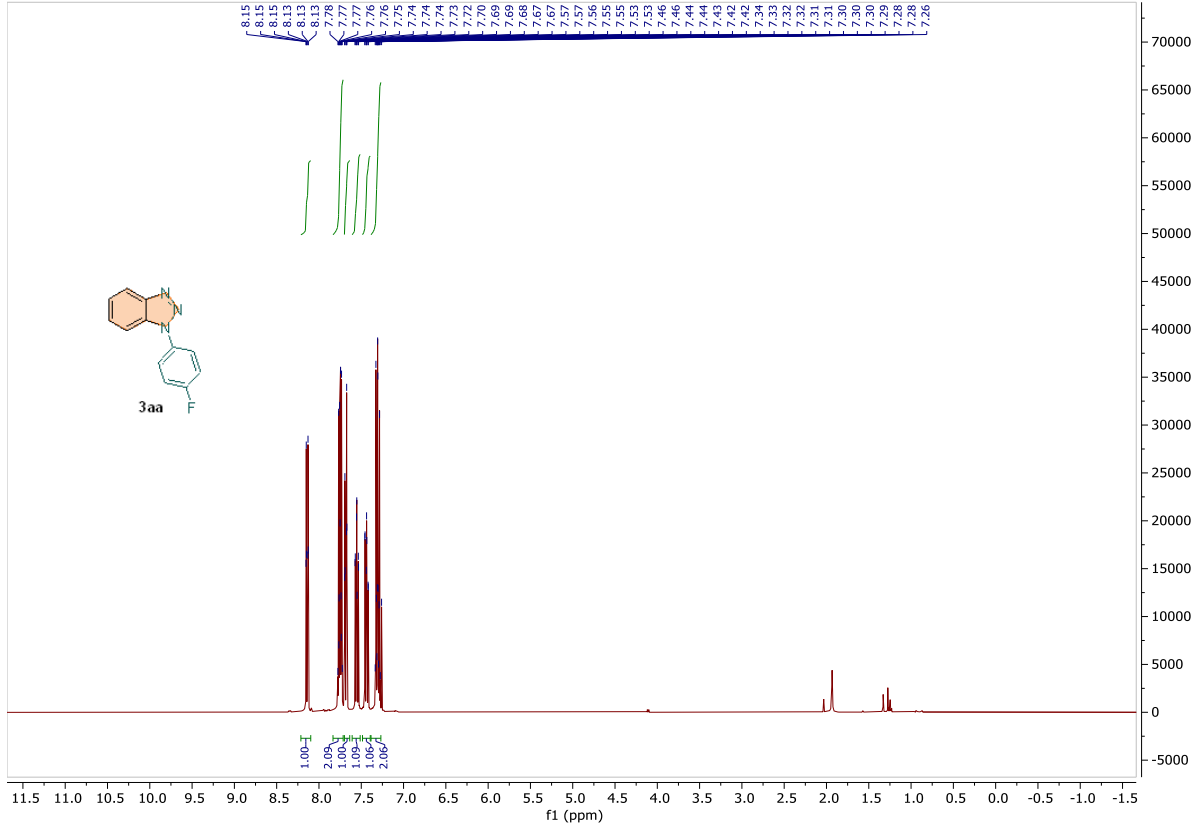
230329.f306.10.fid — Xingwei Gu gwx-126-7 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 6 - 300 MHz



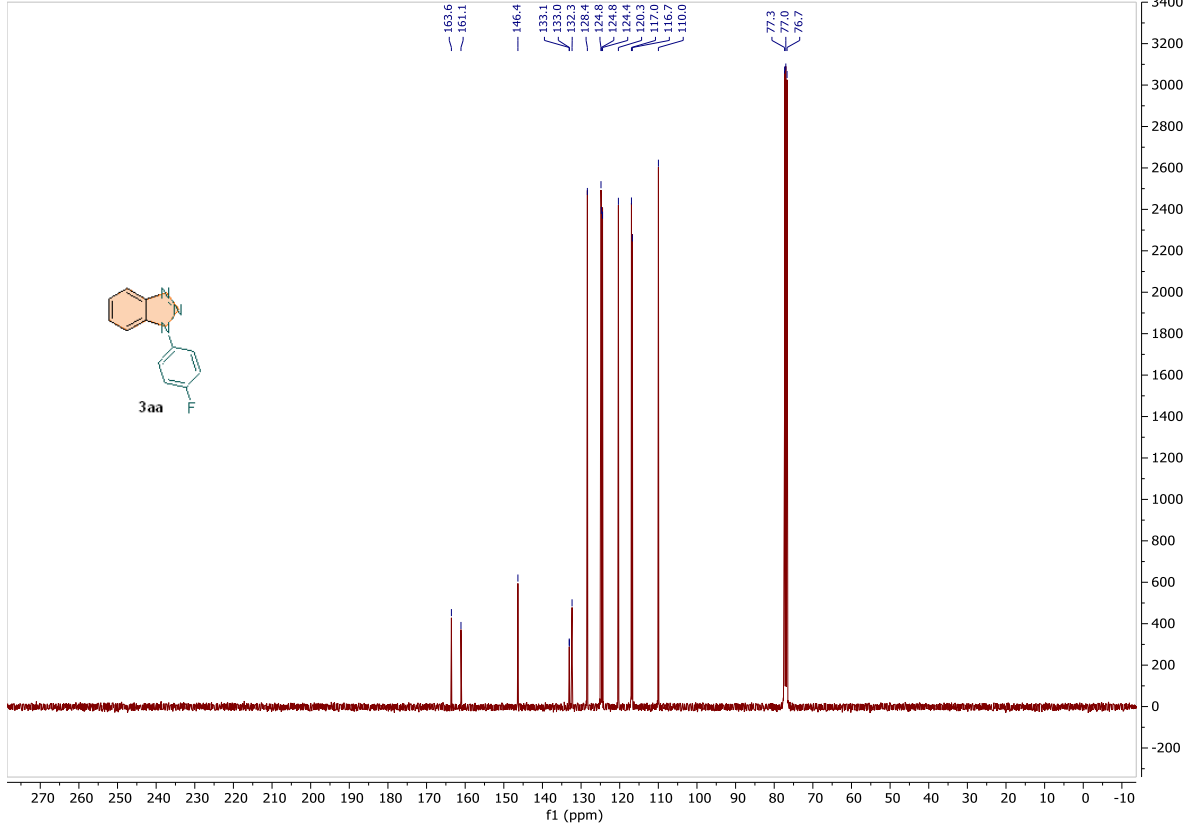
230329.f306.11.fid — Xingwei Gu gwx-126-7 — C13CPD CDCI3 {C:\Bruker\TopSpin3.6.2} 2303 6 - 75 MHz

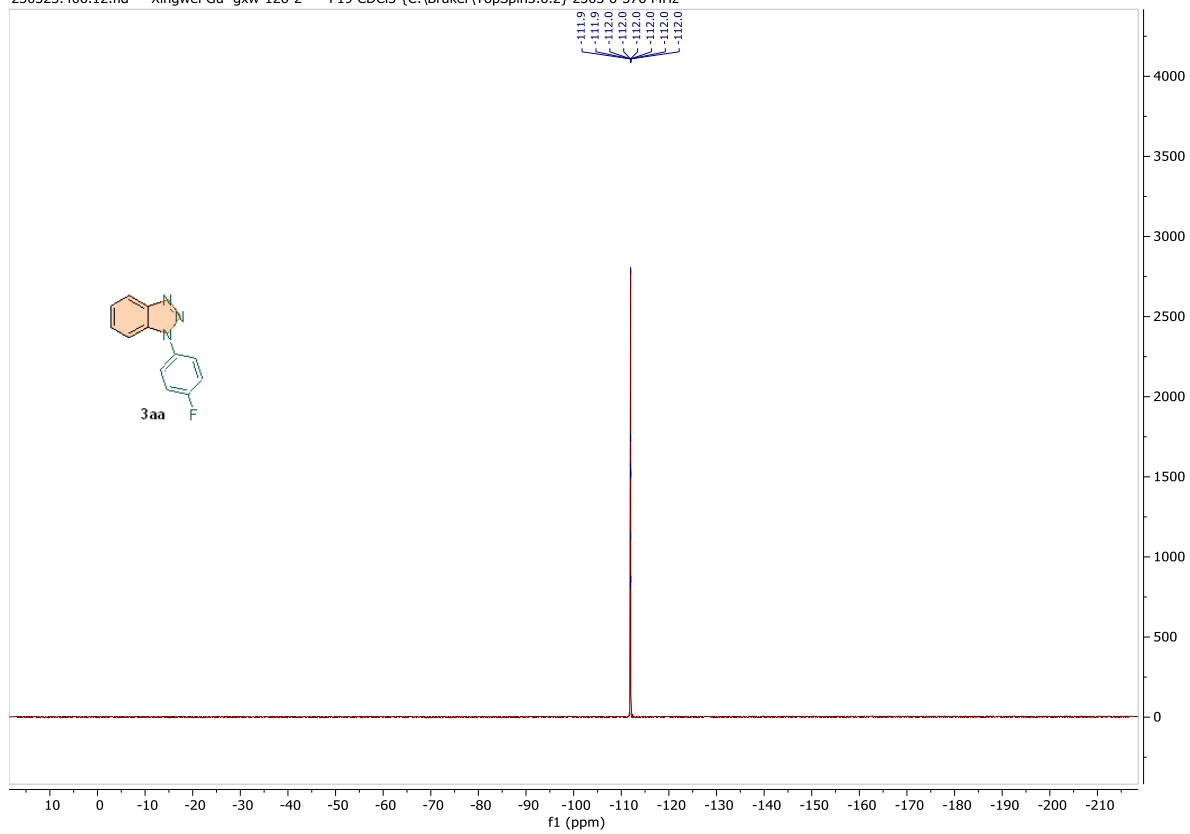


230323.406.10.fid — Xingwei Gu gxw-126-2 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 6 - 400 MHz



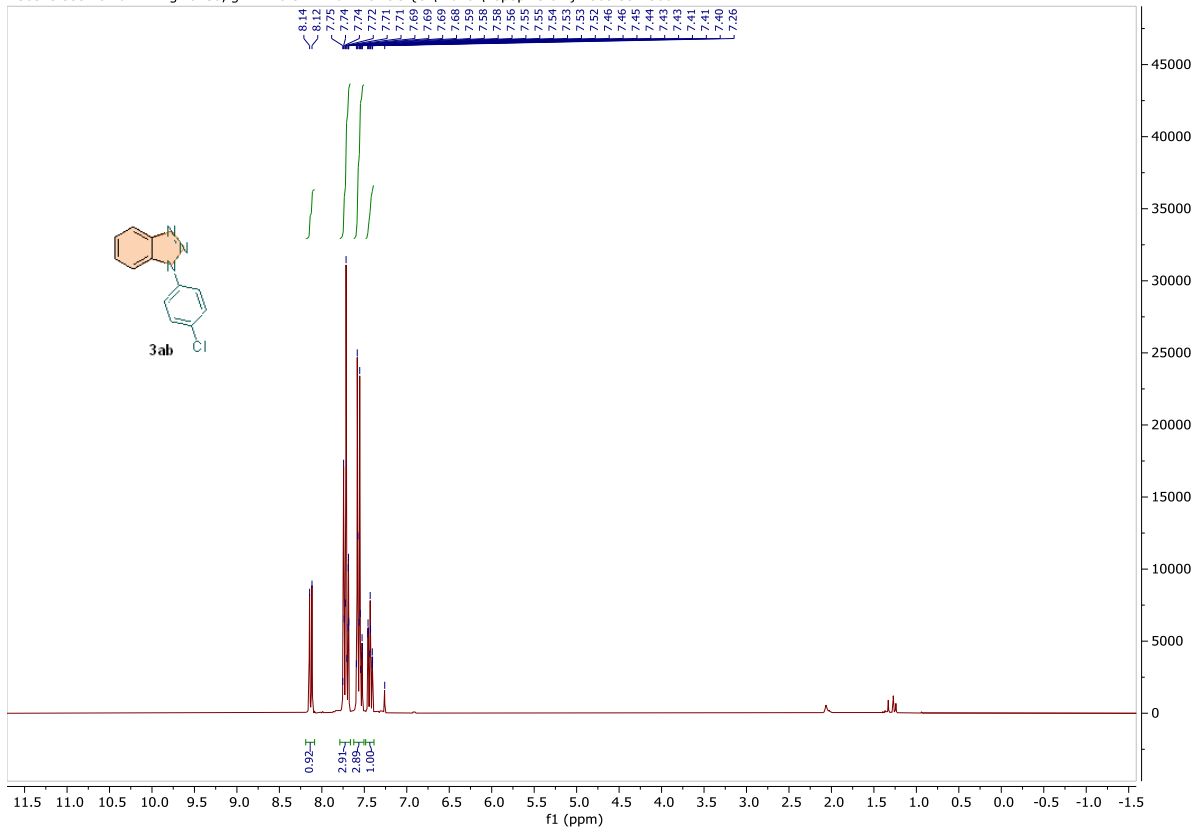
230323.406.11.fid — Xingwei Gu gxw-126-2 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 6 - 101 MHz



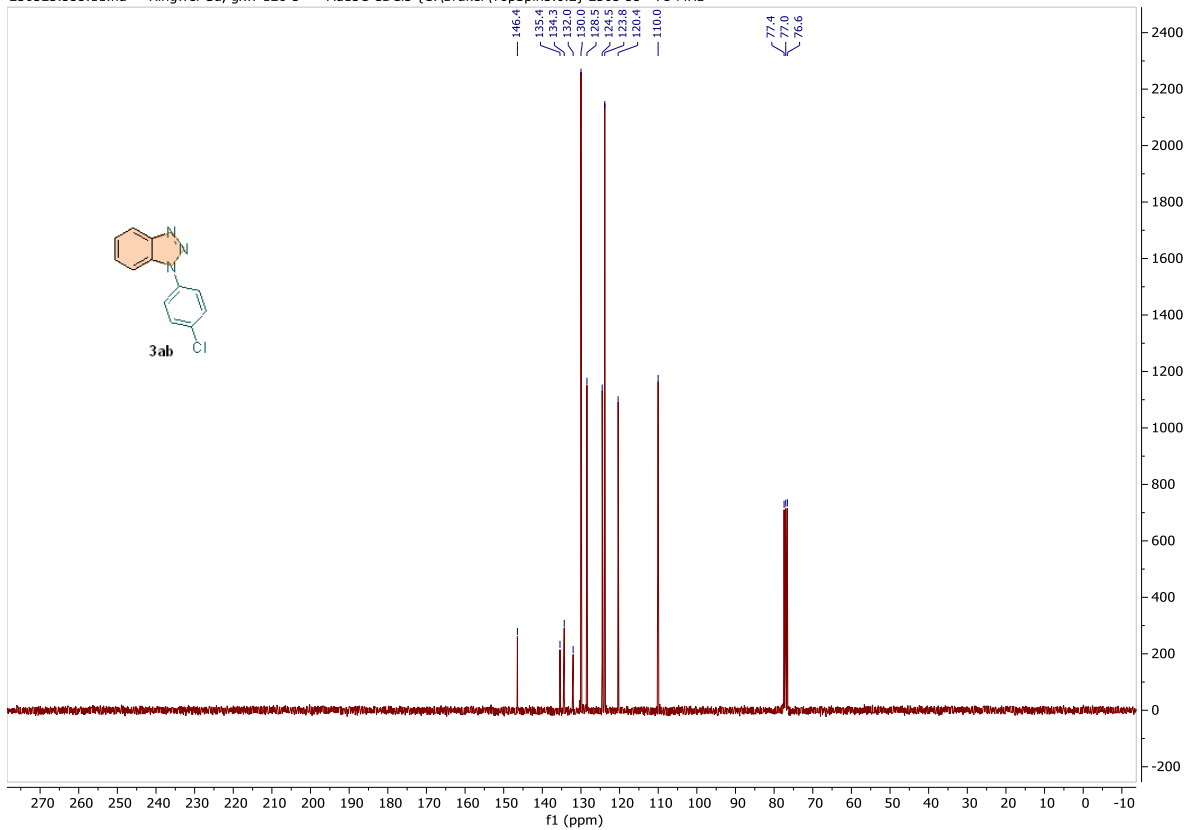


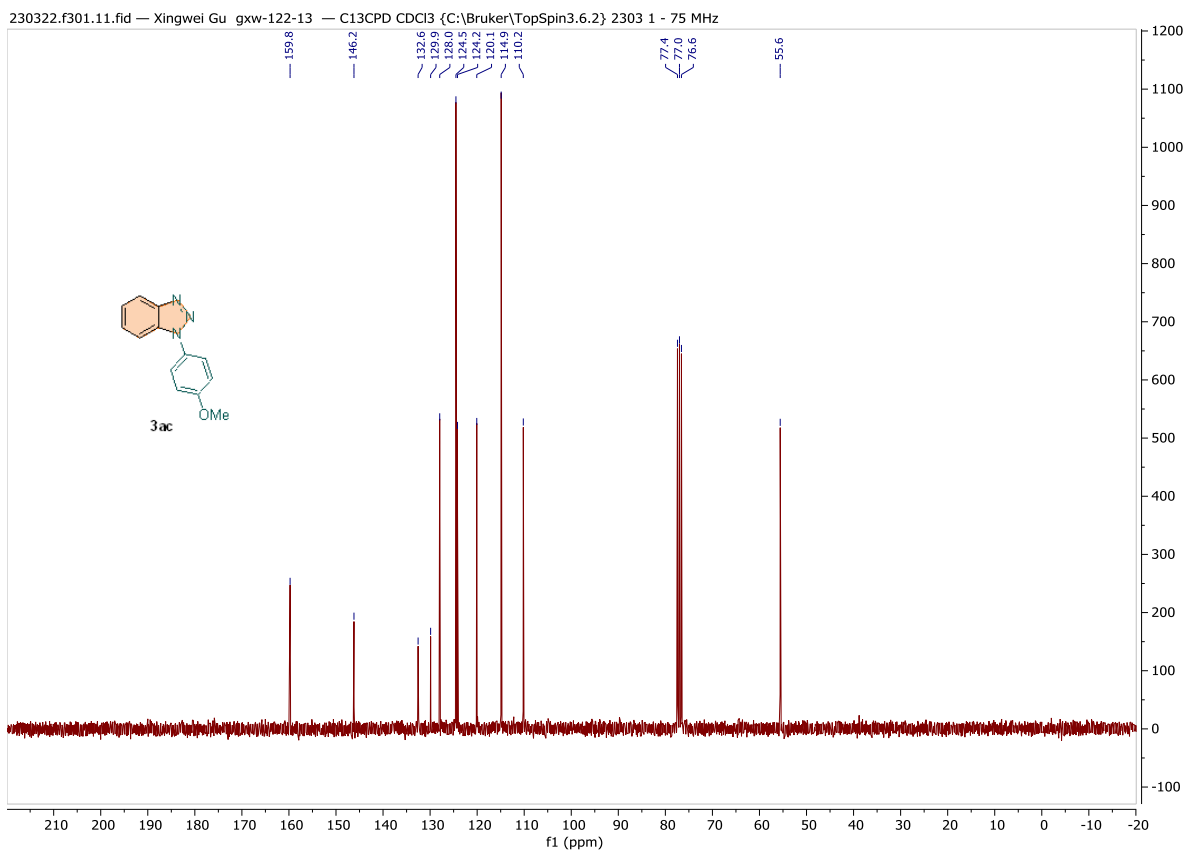
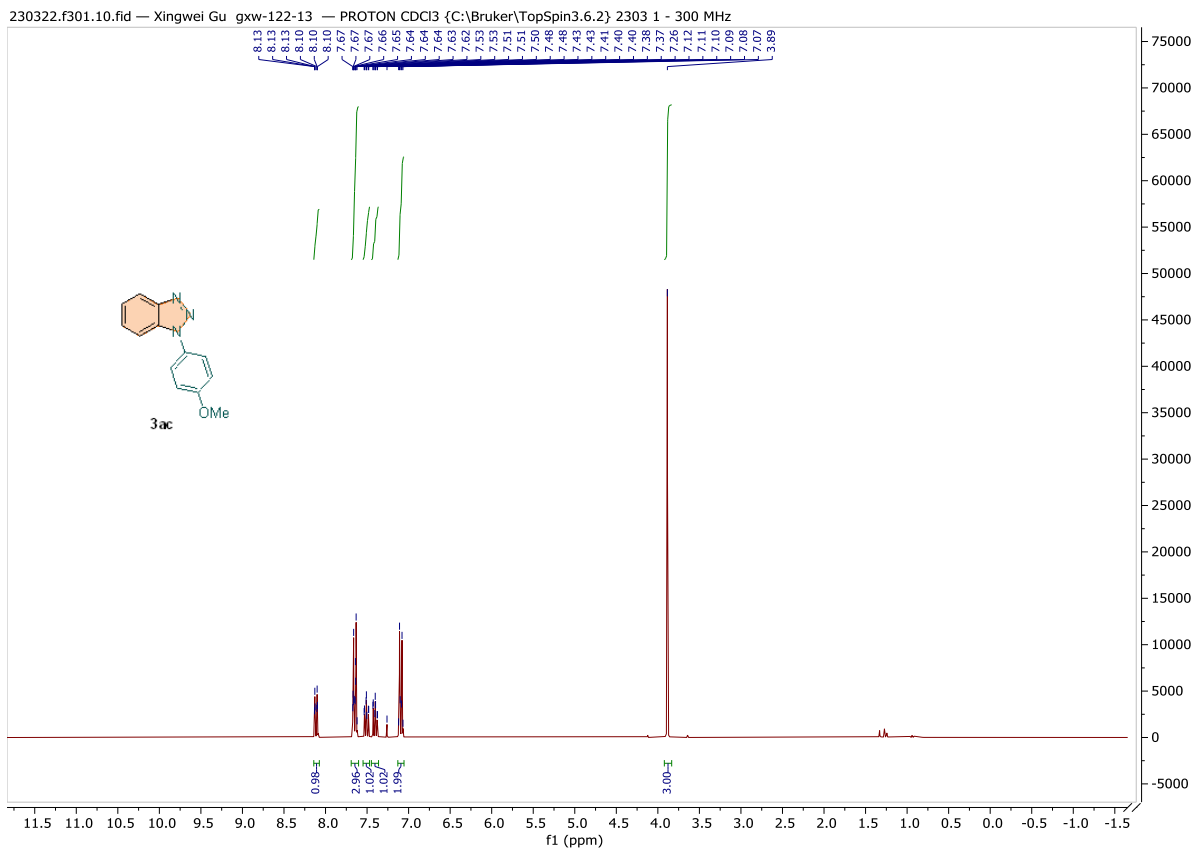


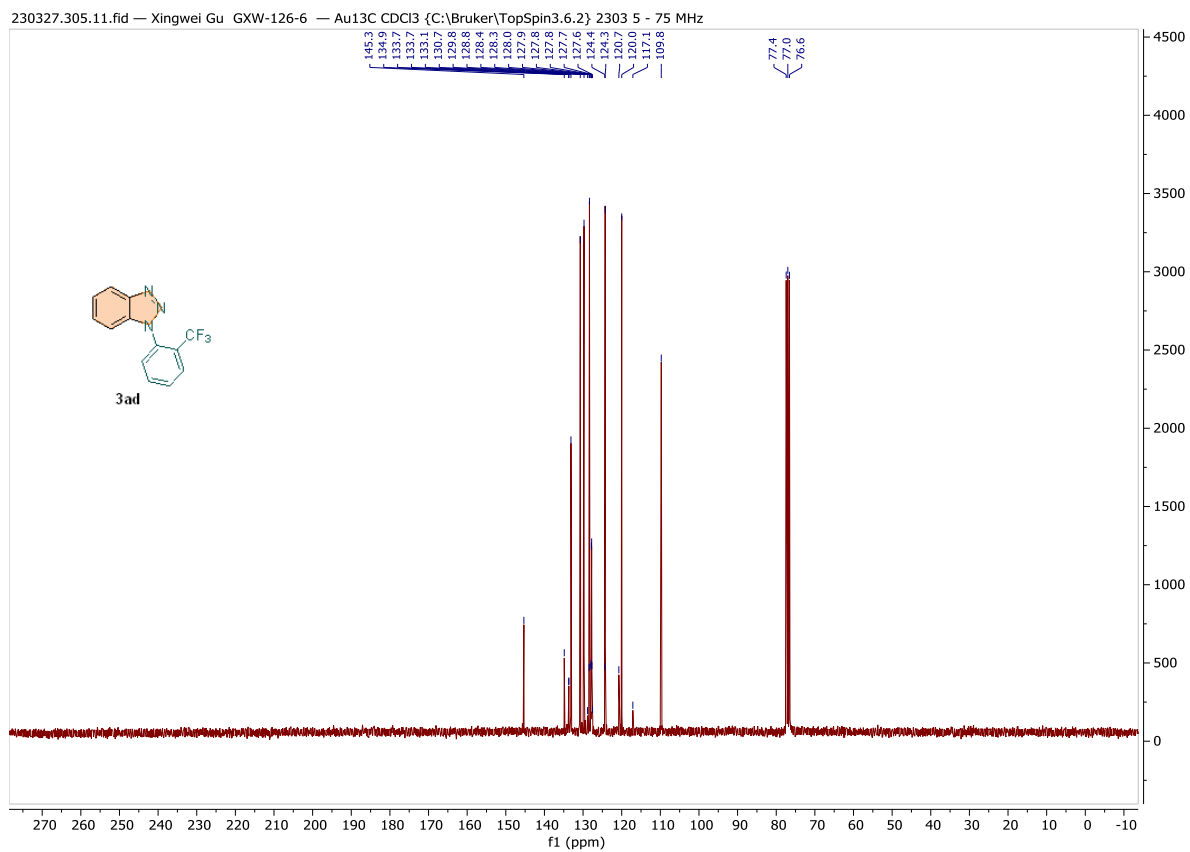
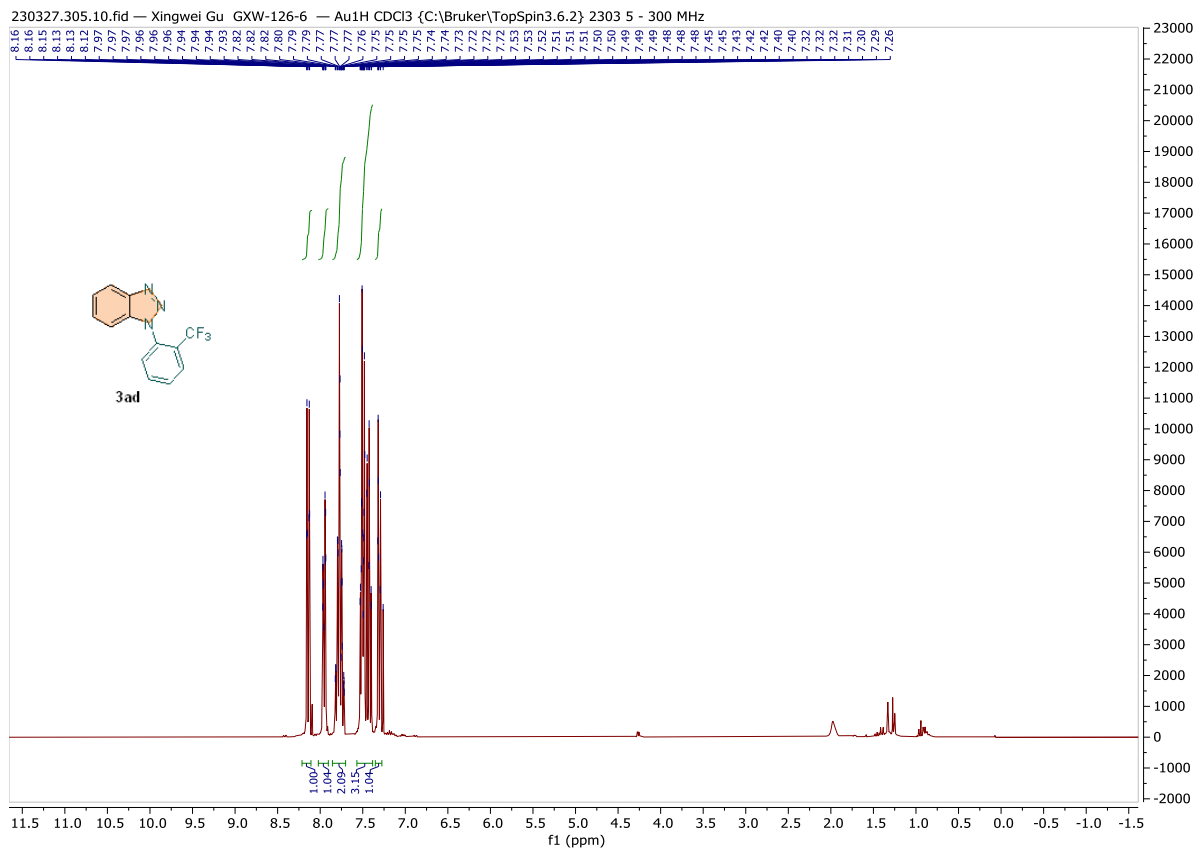
230323.355.10.fid — Xingwei Gu, gxw-126-3 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 55 - 300 MHz

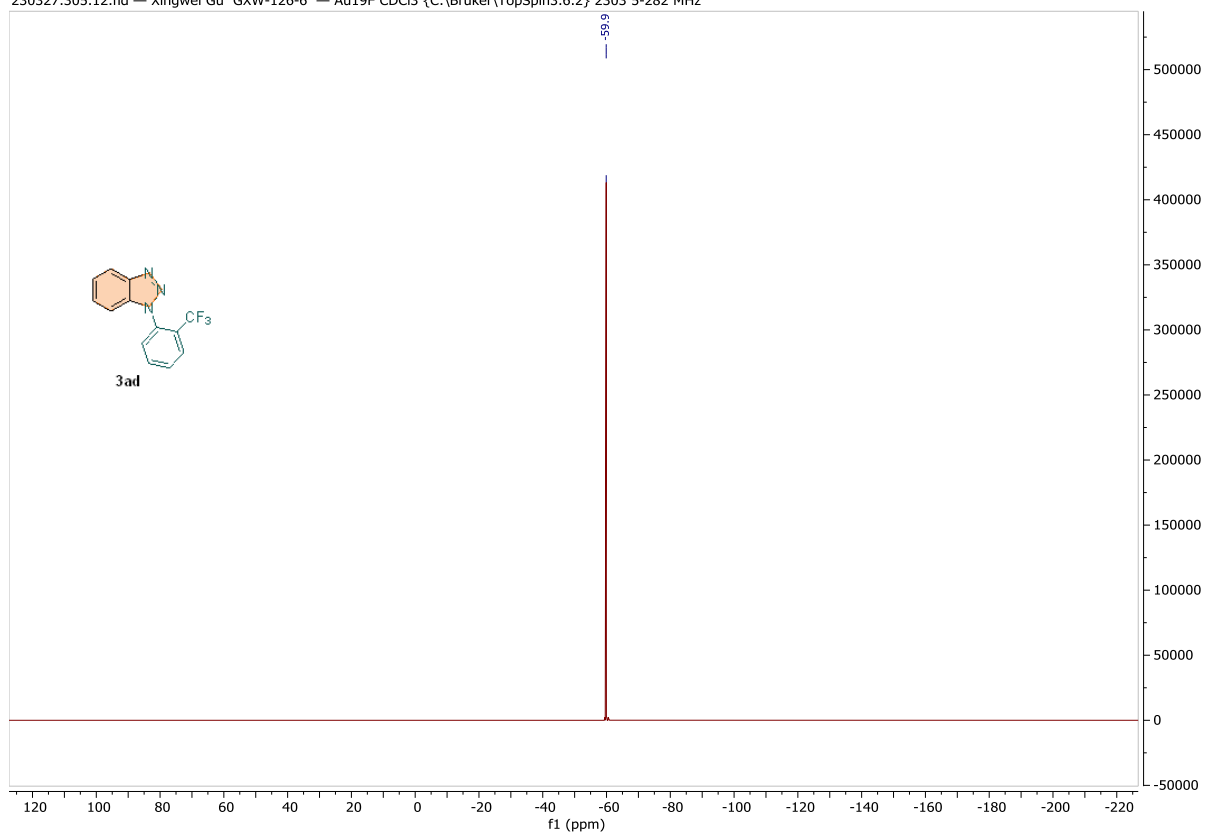


230323.355.11.fid — Xingwei Gu, gxw-126-3 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 55 - 75 MHz

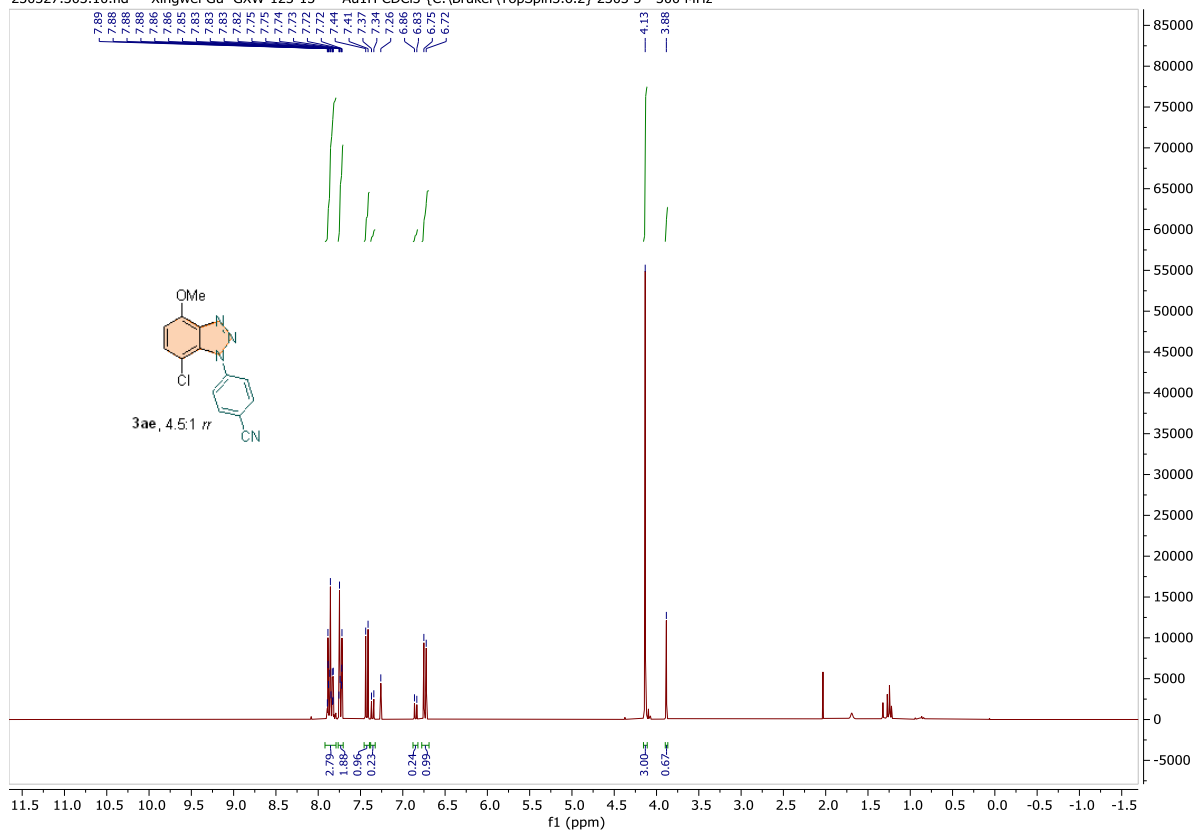




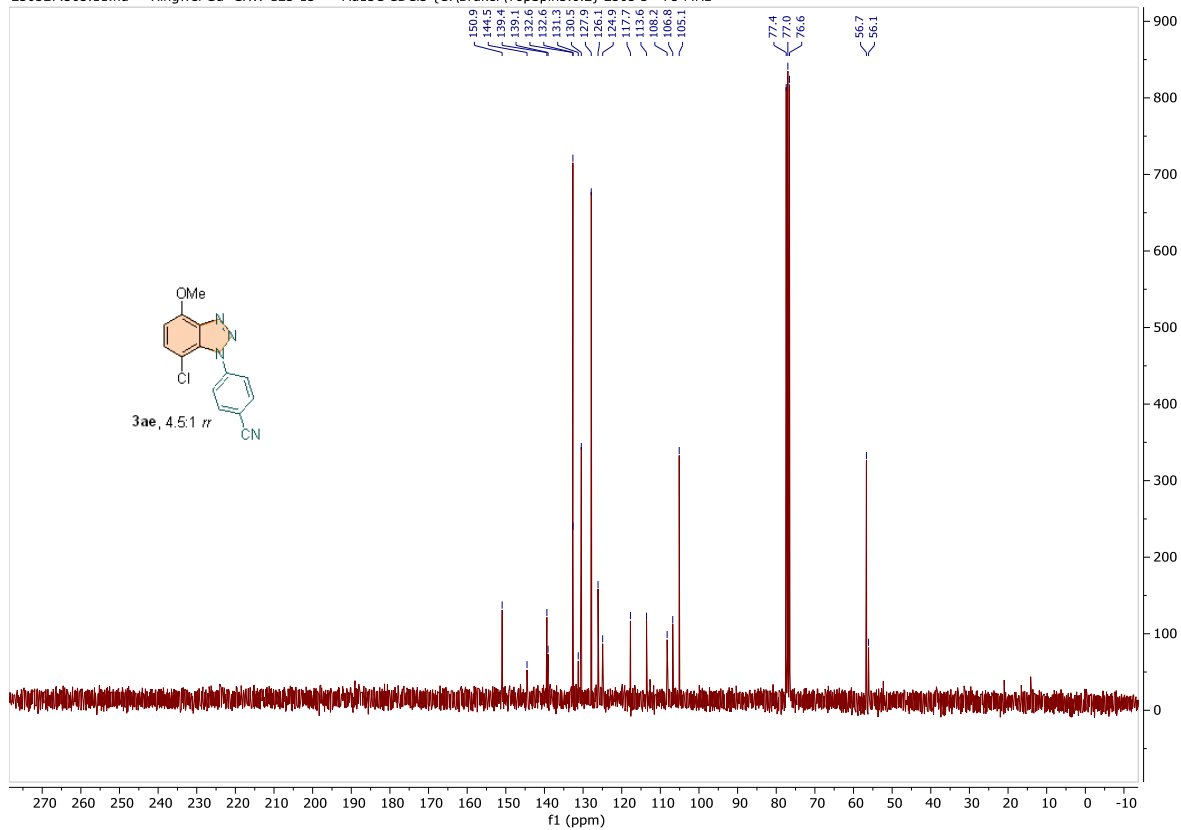


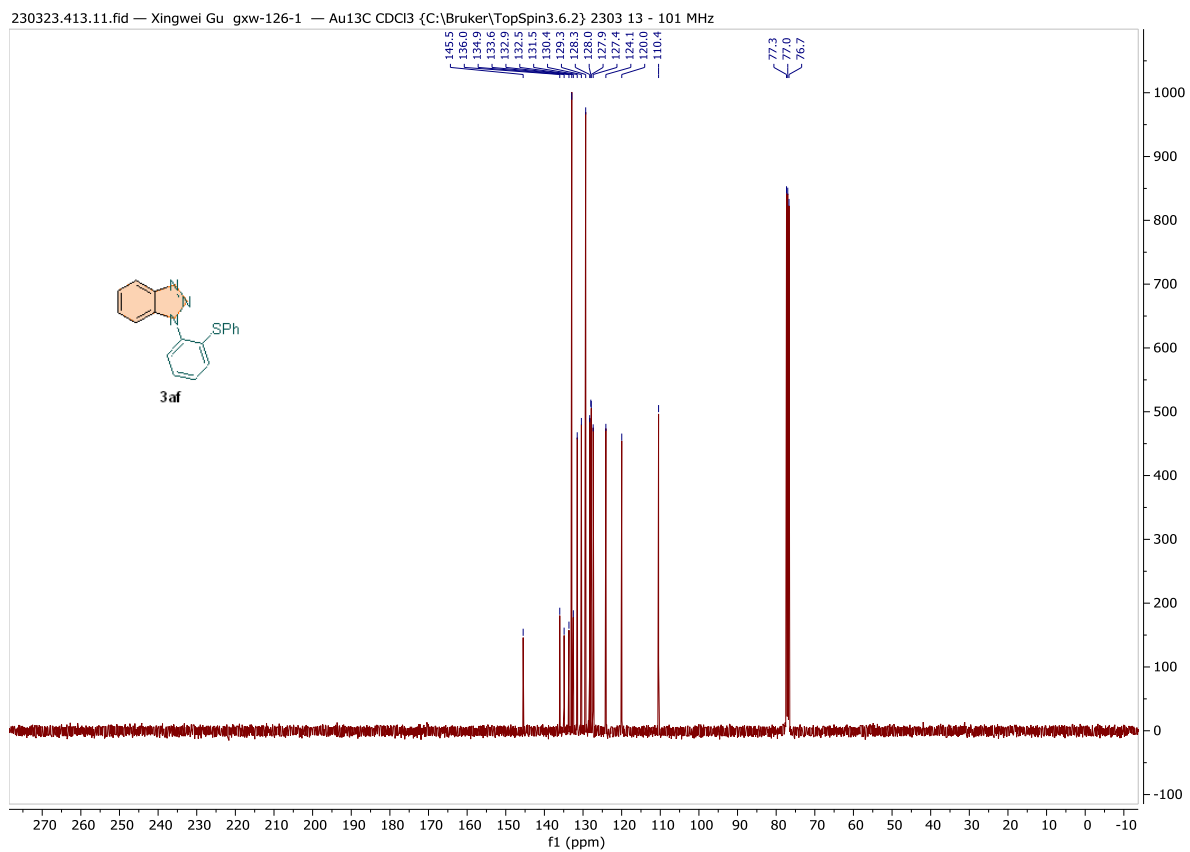
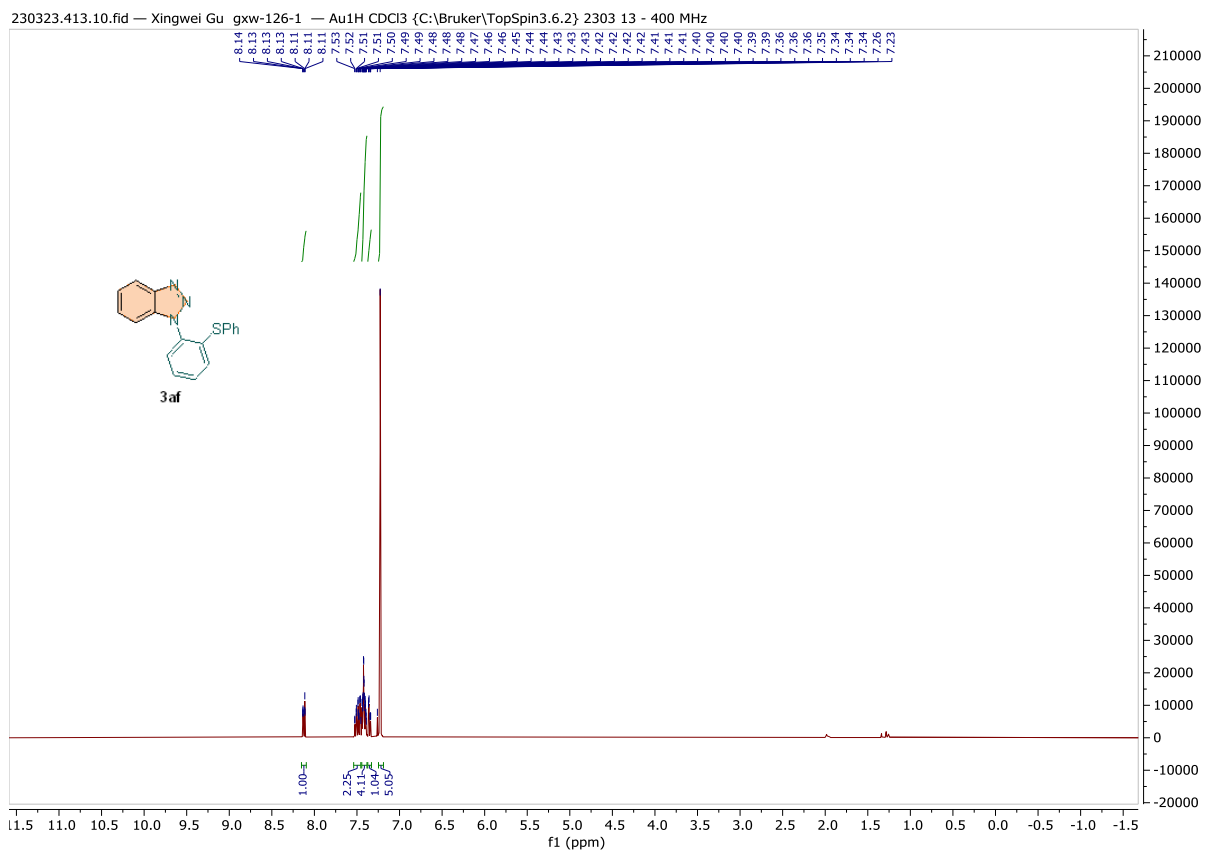


230327.303.10.fid — Xingwei Gu GXW-123-13 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 3 - 300 MHz

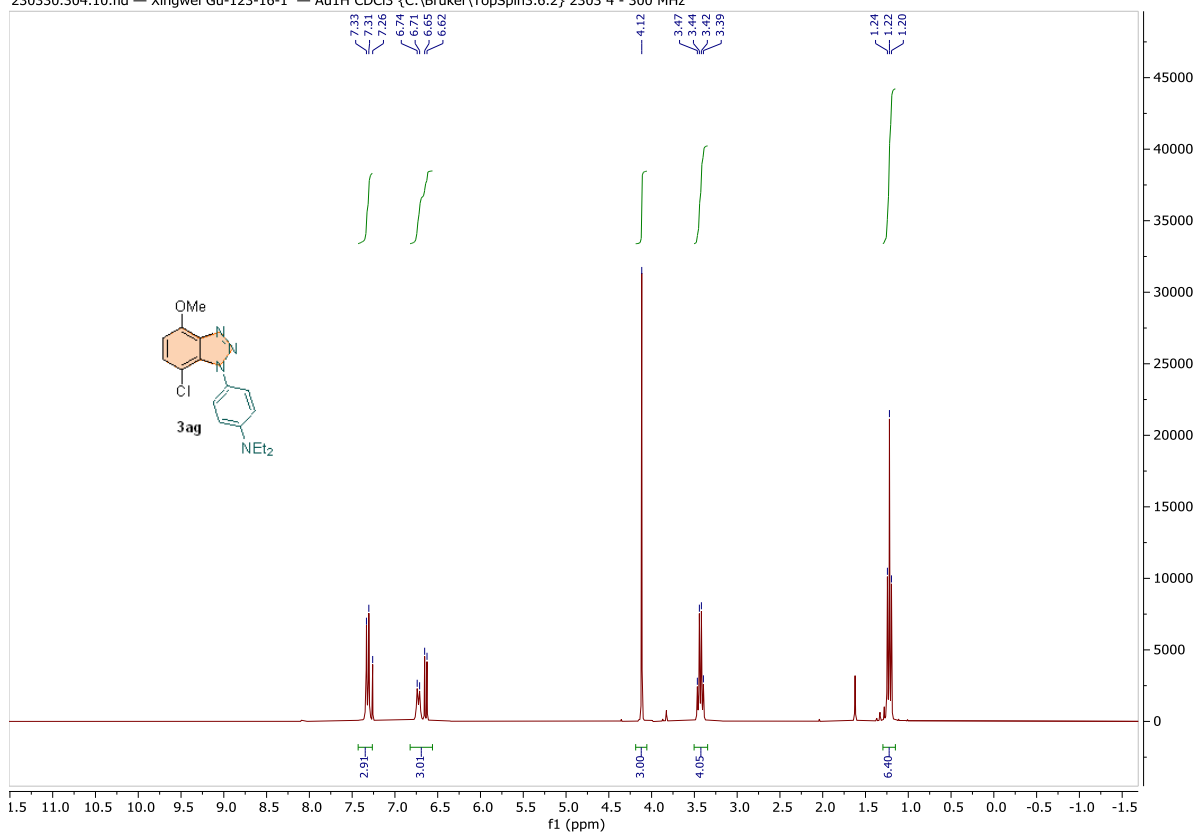


230327.303.11.fid — Xingwei Gu GXW-123-13 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 3 - 75 MHz

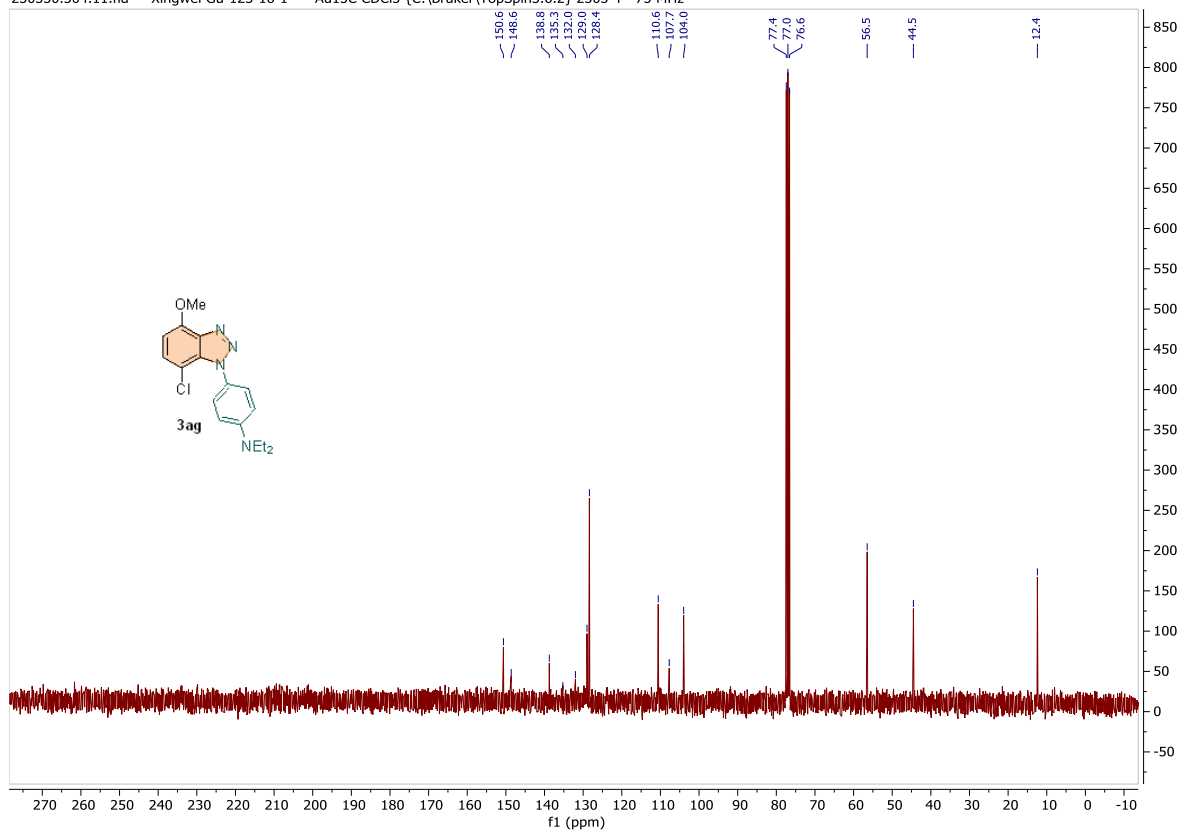


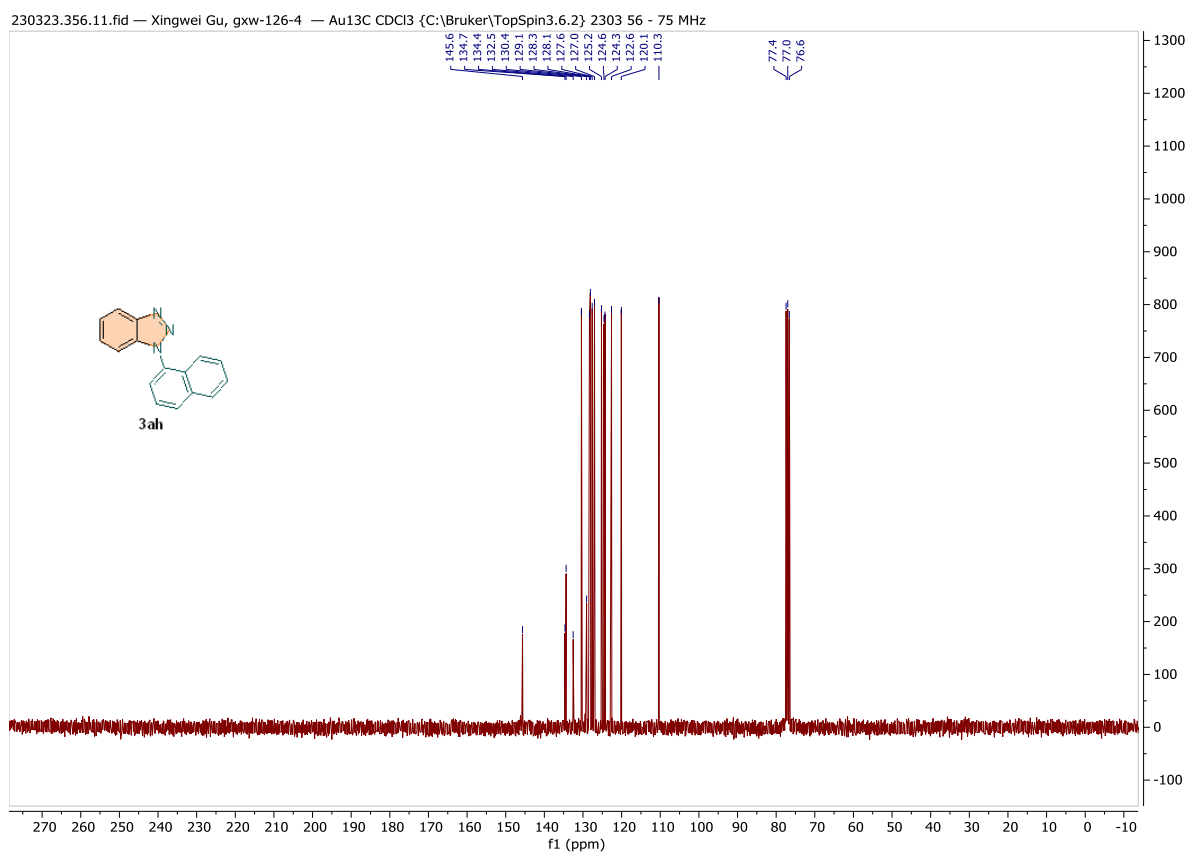
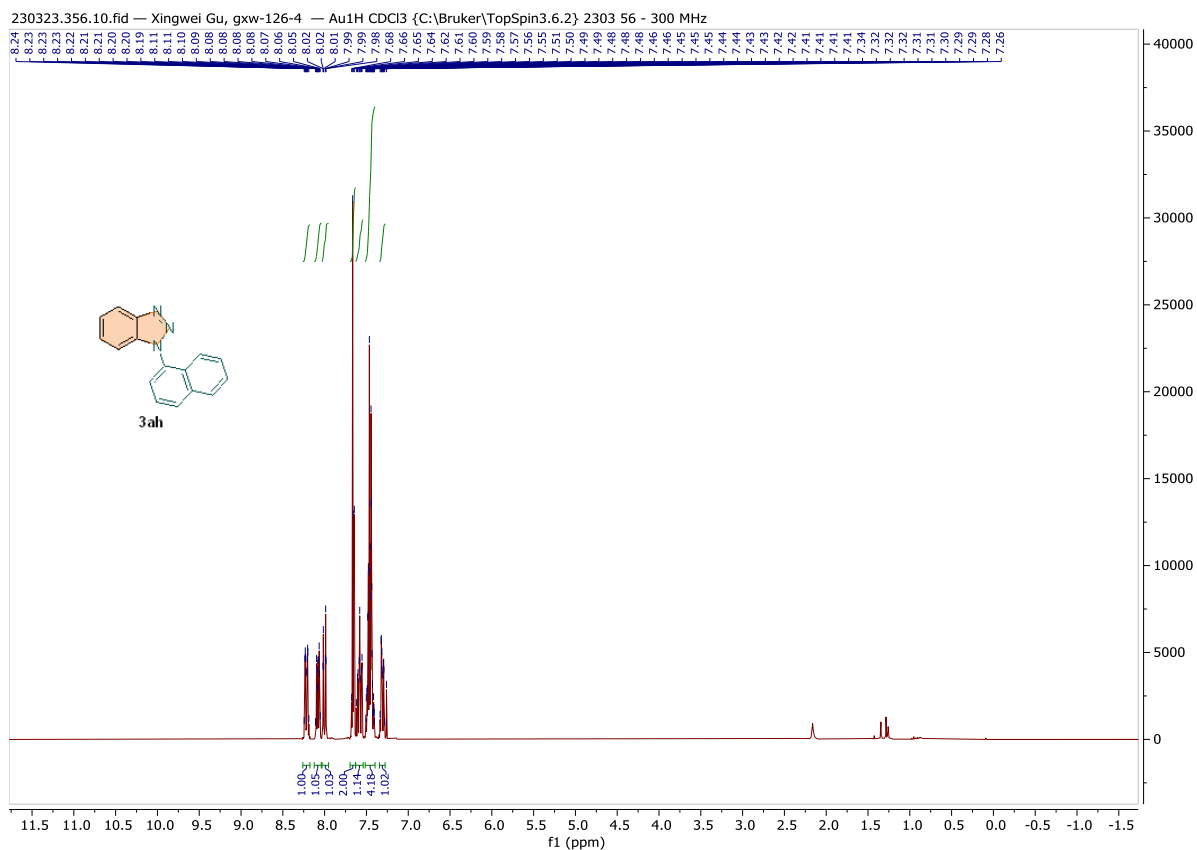


230330.304.10.fid — Xingwei Gu-123-16-1 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 300 MHz



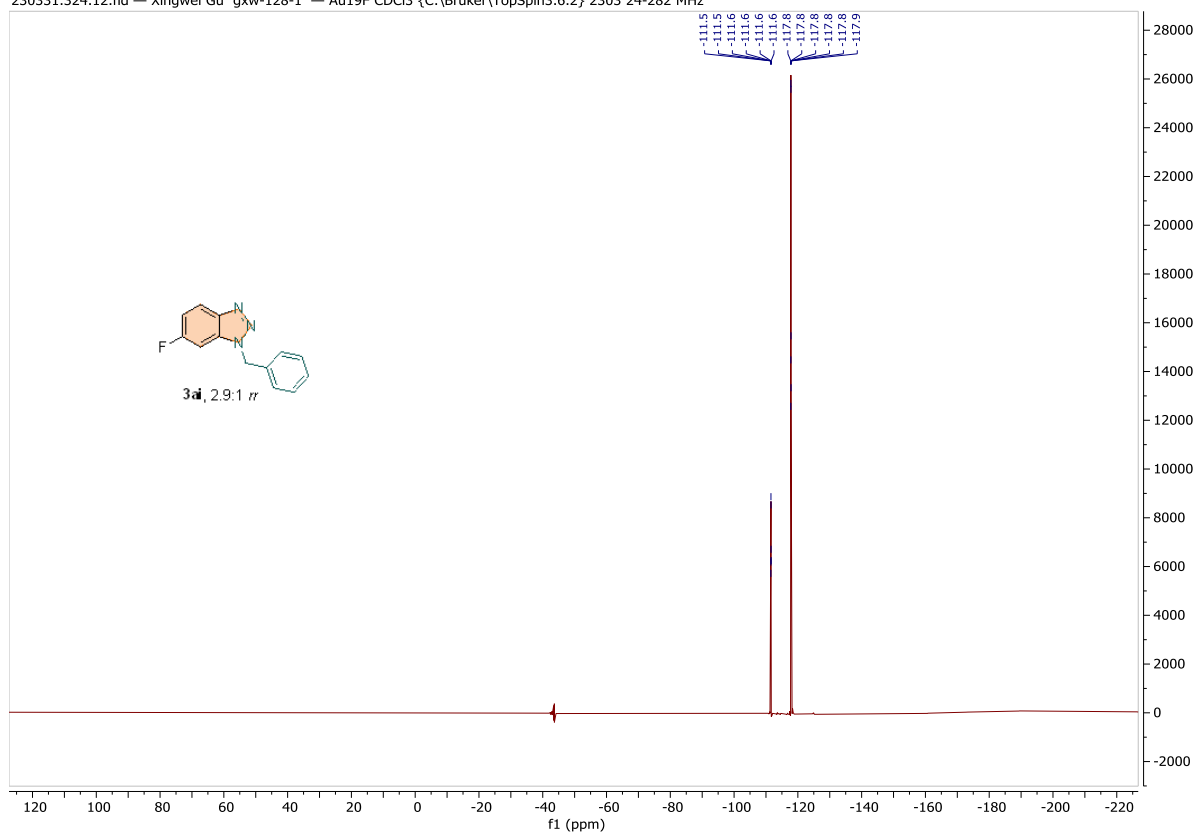
230330.304.11.fid — Xingwei Gu-123-16-1 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 75 MHz



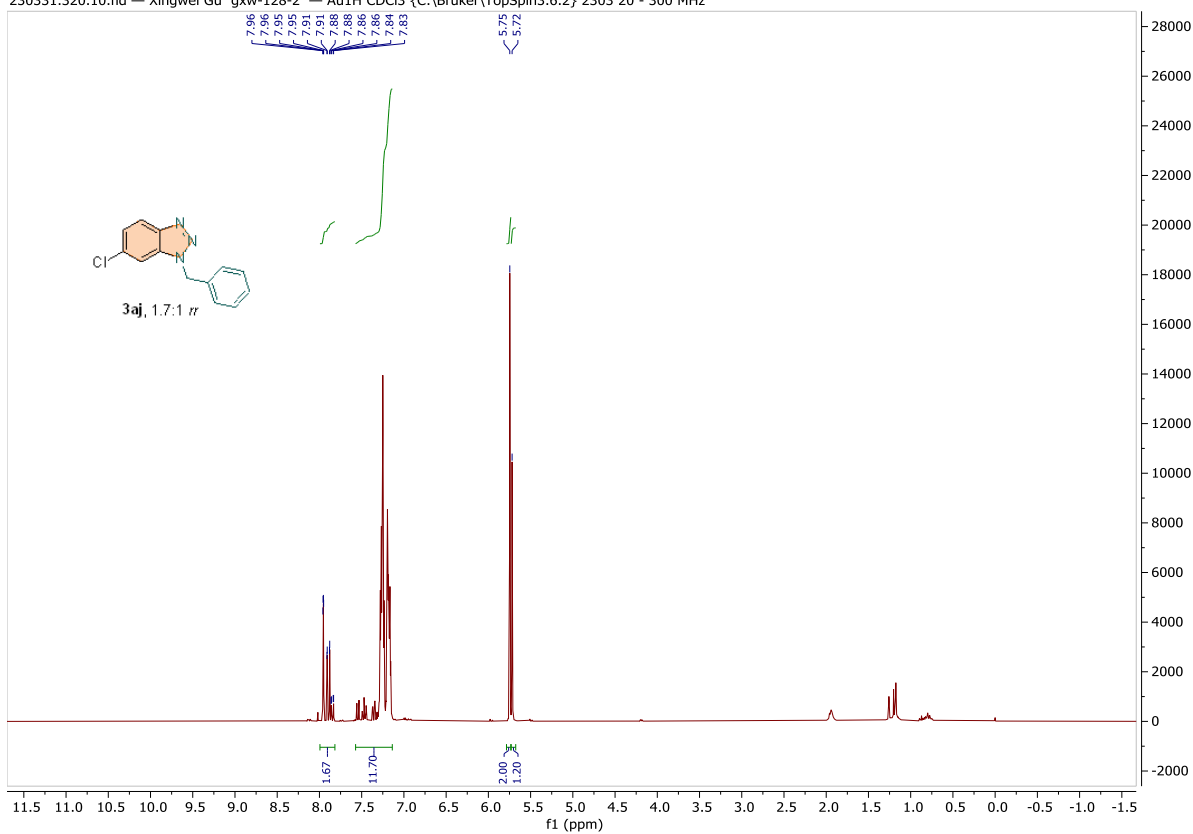




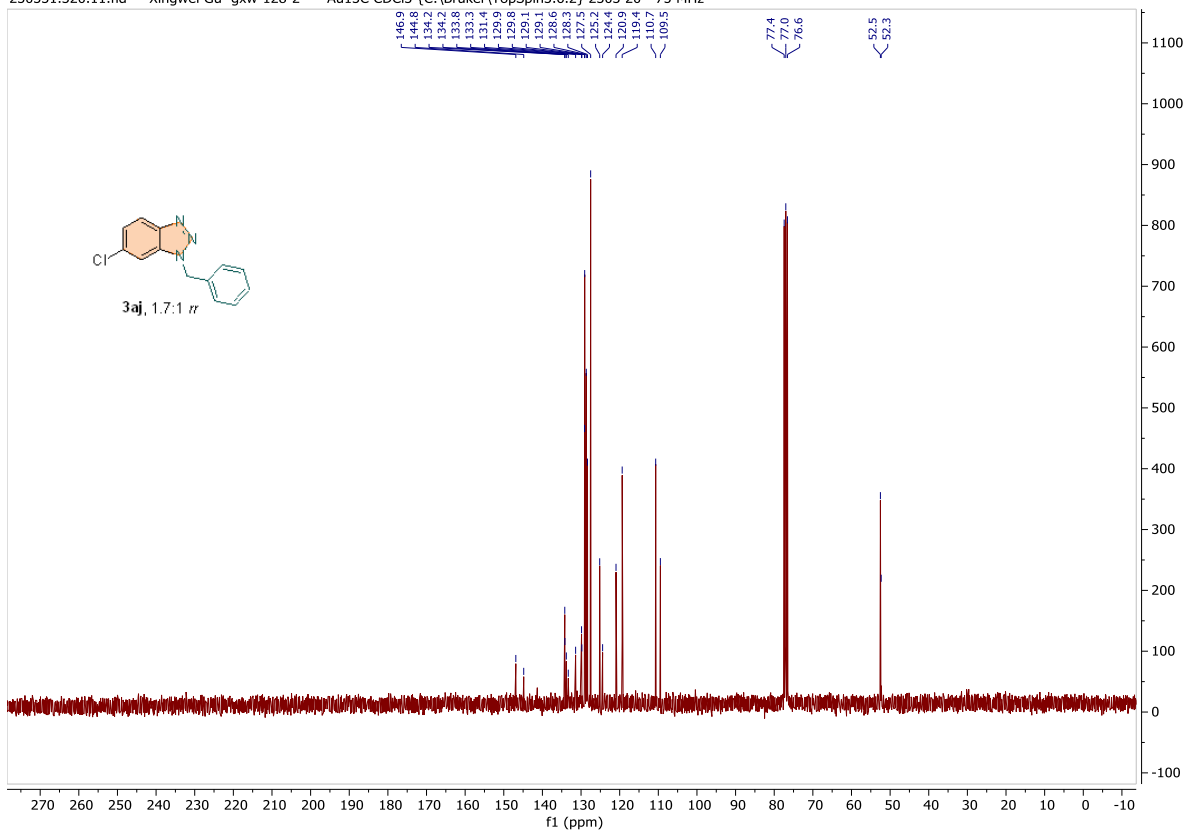




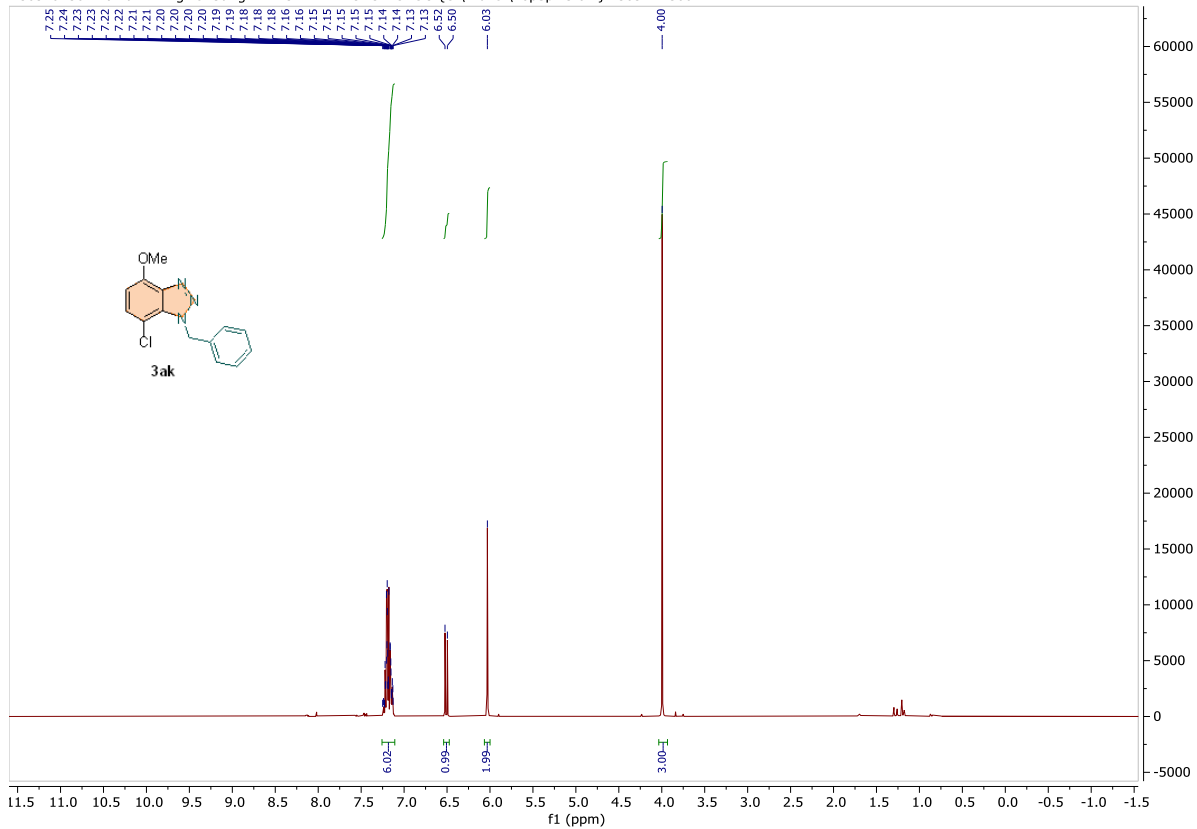
230331.320.10.fid — Xingwei Gu gxw-128-2 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 20 - 300 MHz



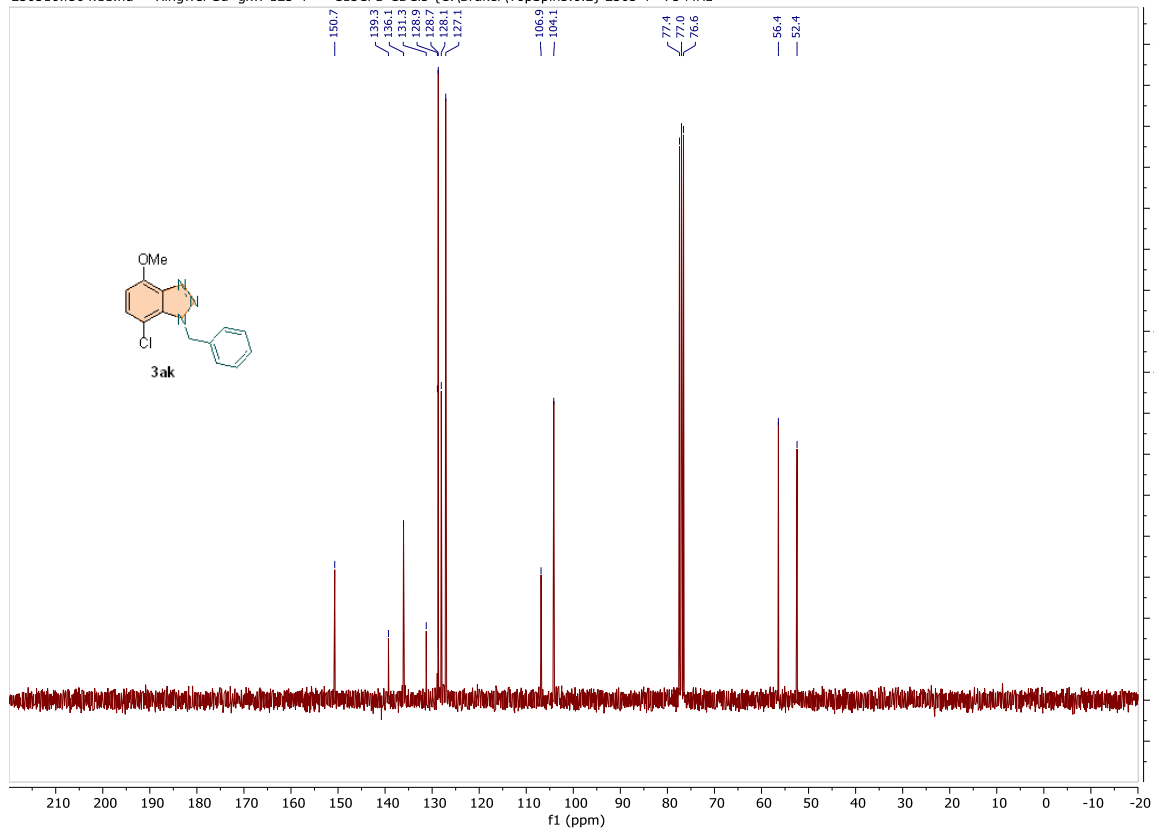
230331.320.11.fid — Xingwei Gu gxw-128-2 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 20 - 75 MHz



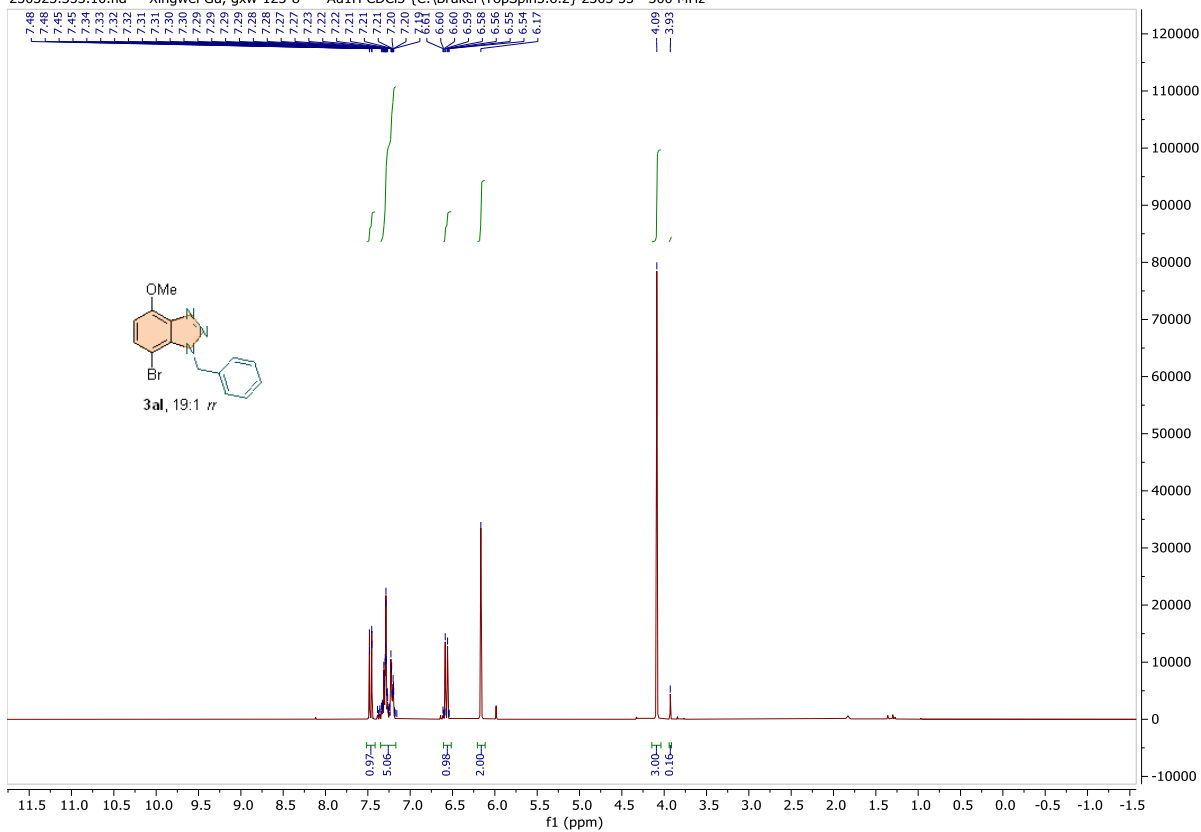
230316.f304.10.fid — Xingwei Gu gxw-123-4 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 300 MHz



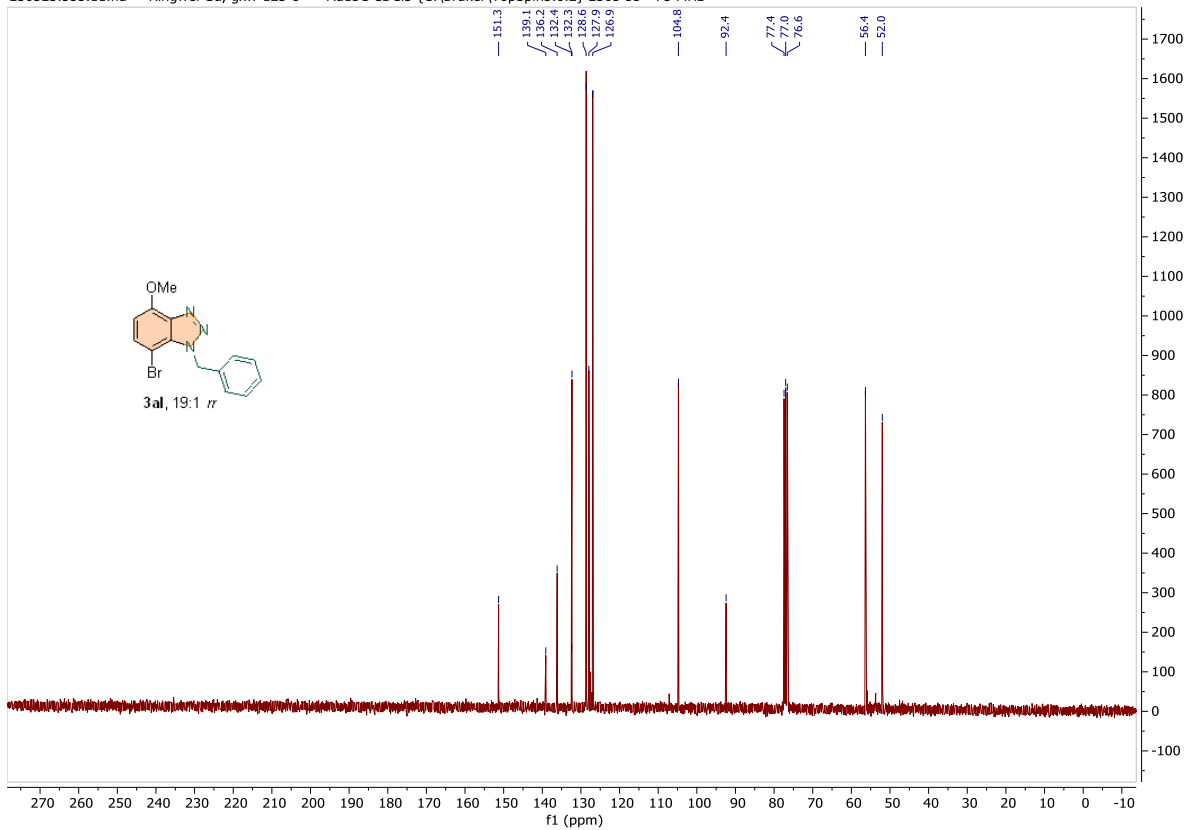
230316.f304.11.fid — Xingwei Gu gxw-123-4 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 4 - 75 MHz



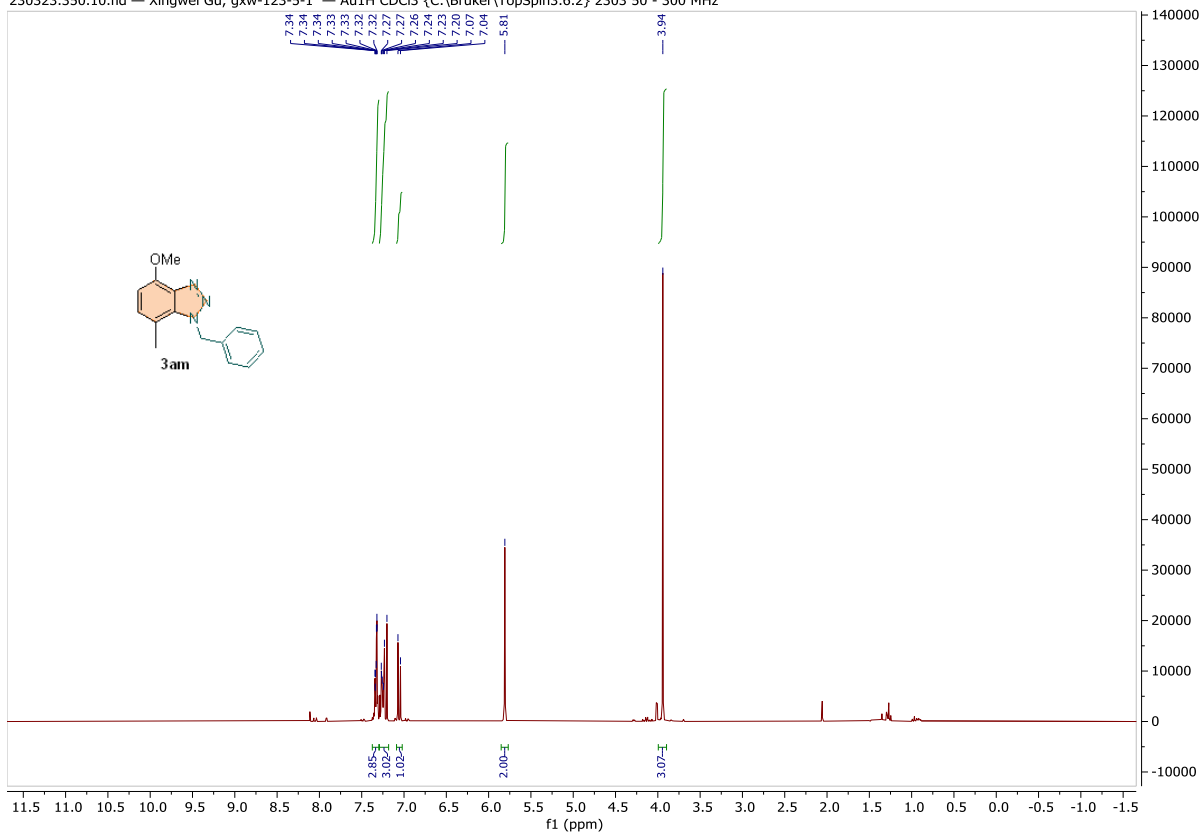
230323.353.10.fid — Xingwei Gu, gxw-123-8 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 53 - 300 MHz



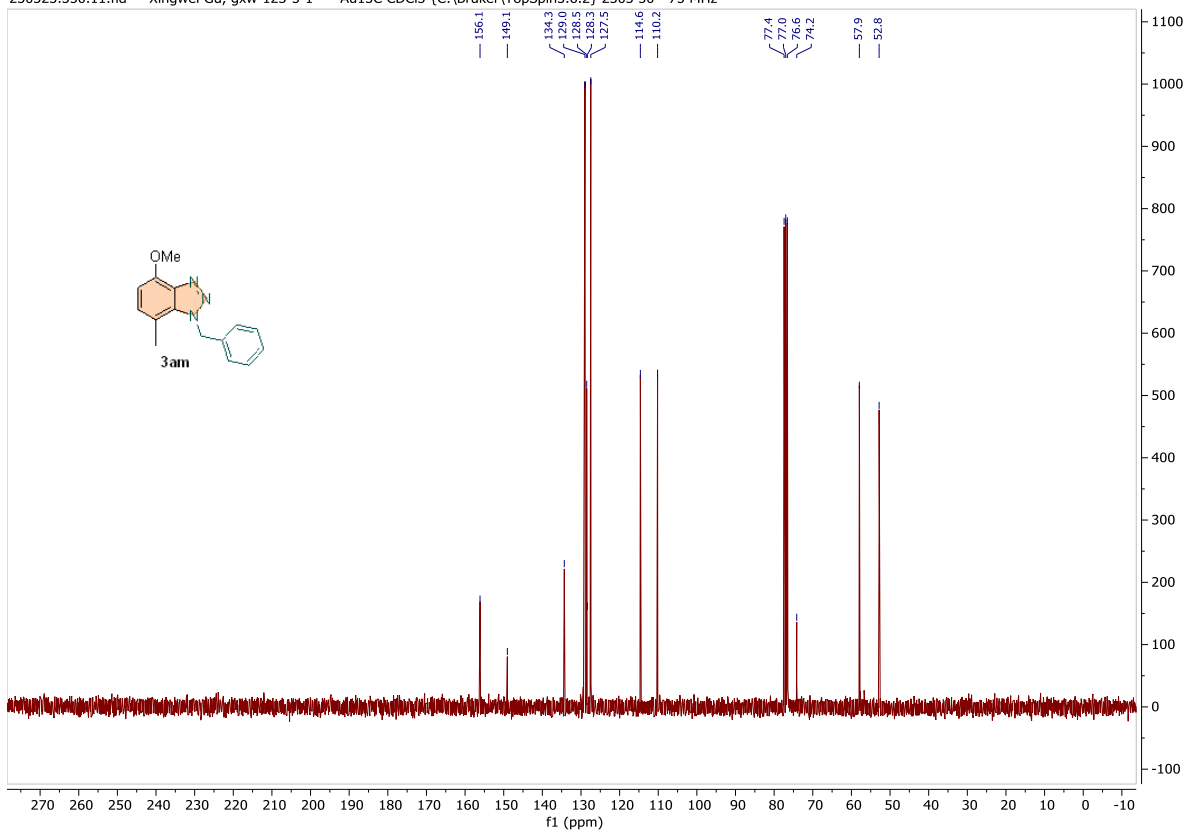
230323.353.11.fid — Xingwei Gu, gxw-123-8 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 53 - 75 MHz



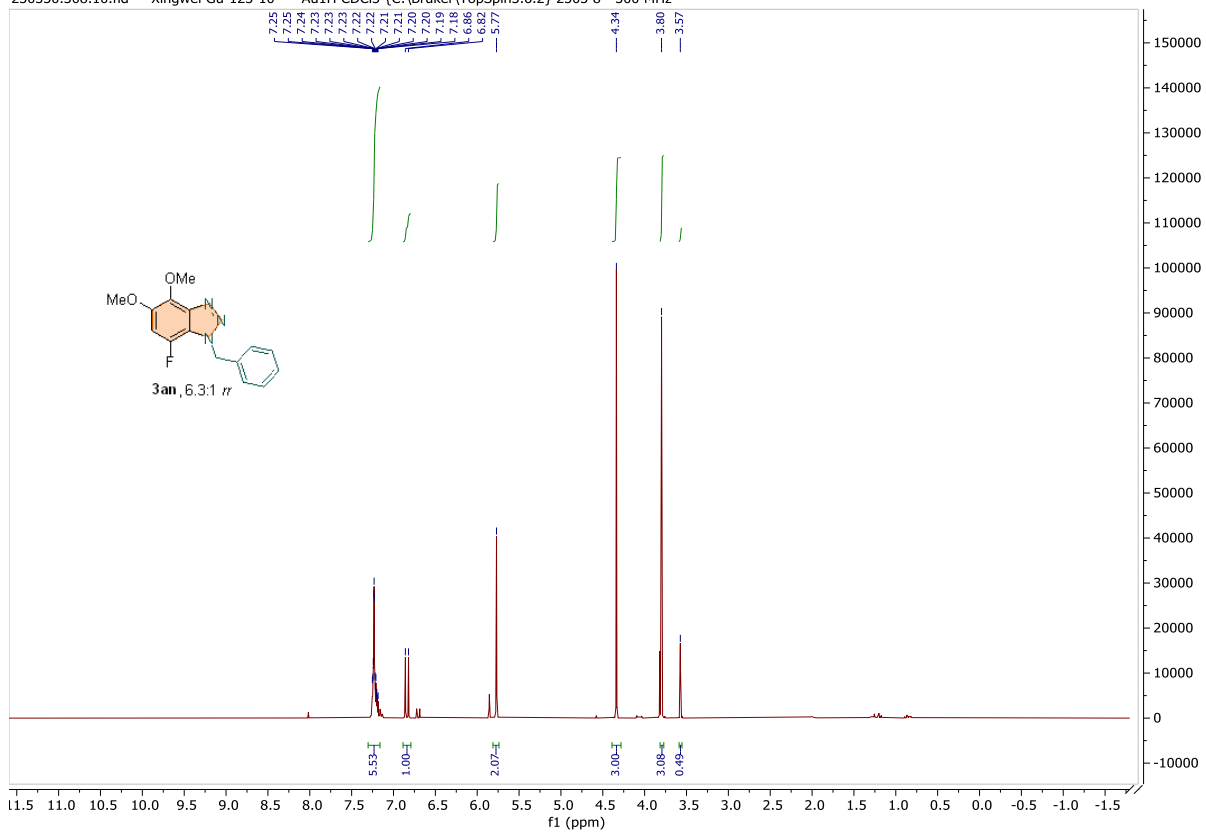
230323.350.10.fid — Xingwei Gu, gxw-123-5-1 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 50 - 300 MHz



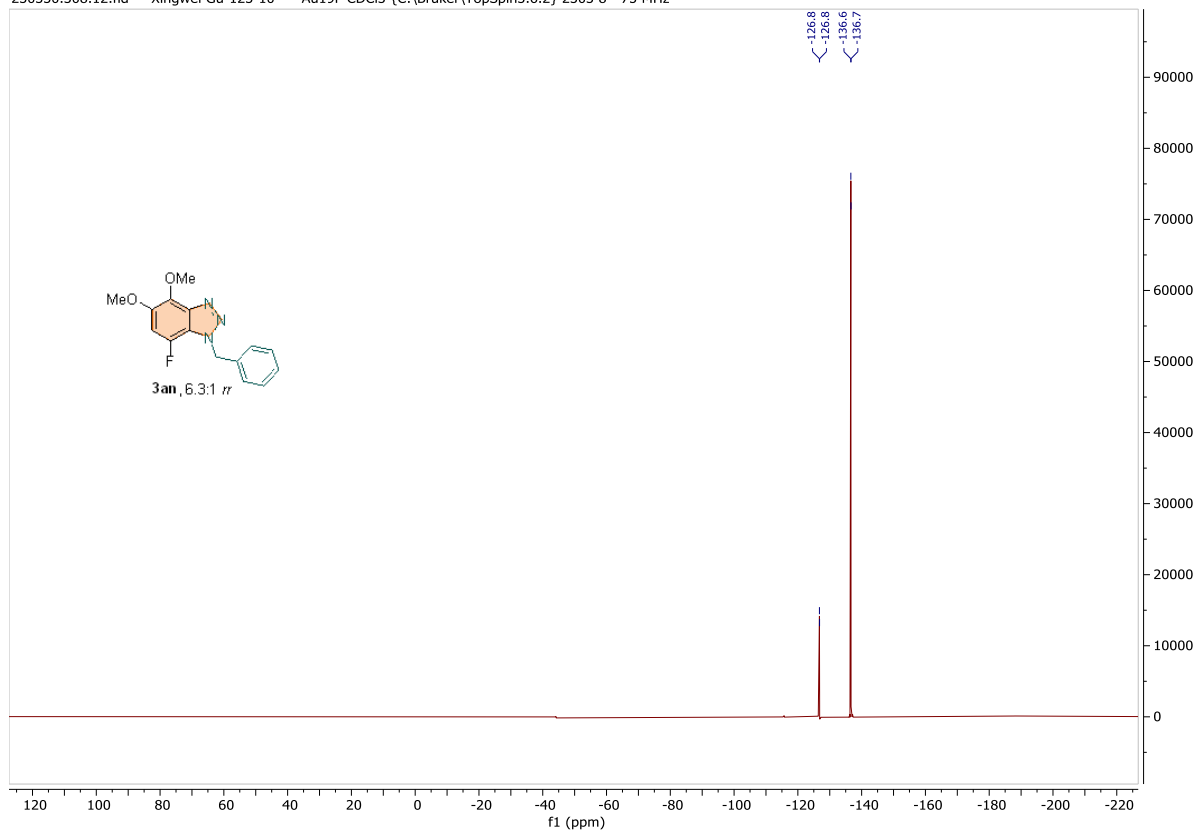
230323.350.11.fid — Xingwei Gu, gxw-123-5-1 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 50 - 75 MHz



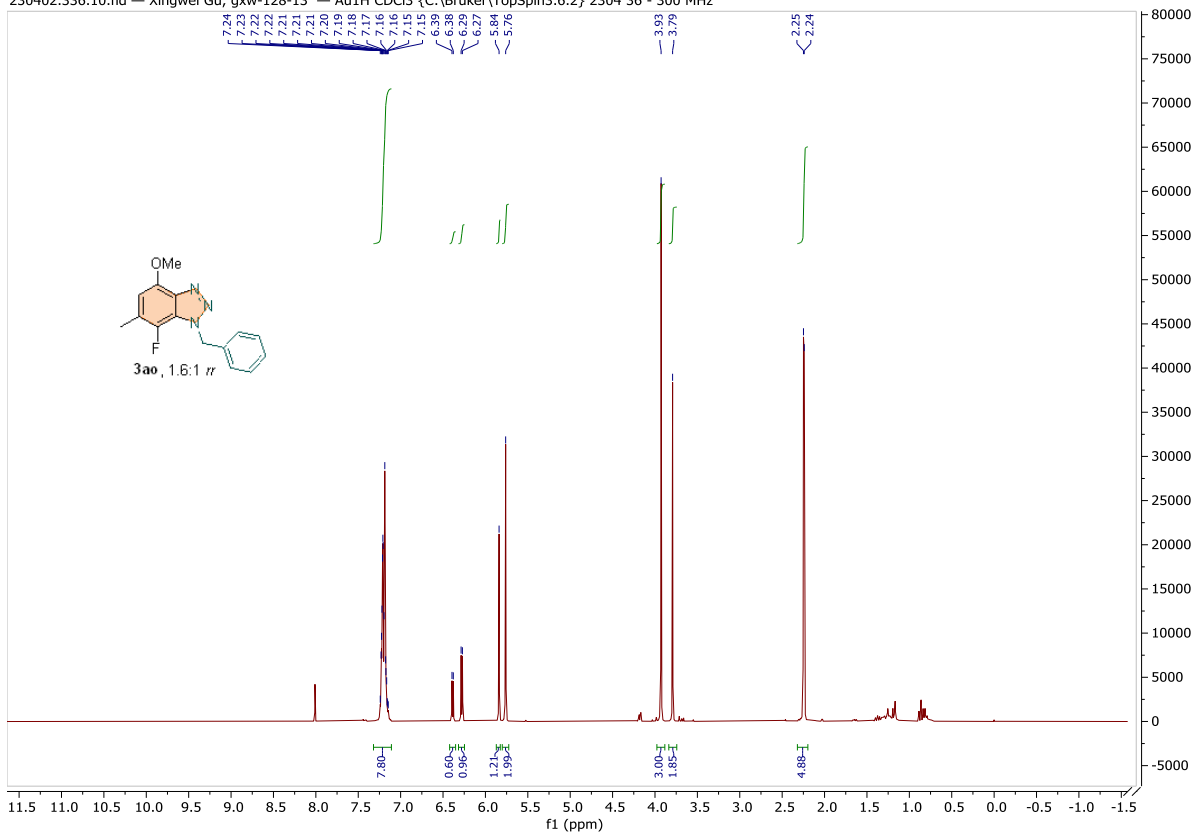
230330.308.10.fid — Xingwei Gu-123-10 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 8 - 300 MHz



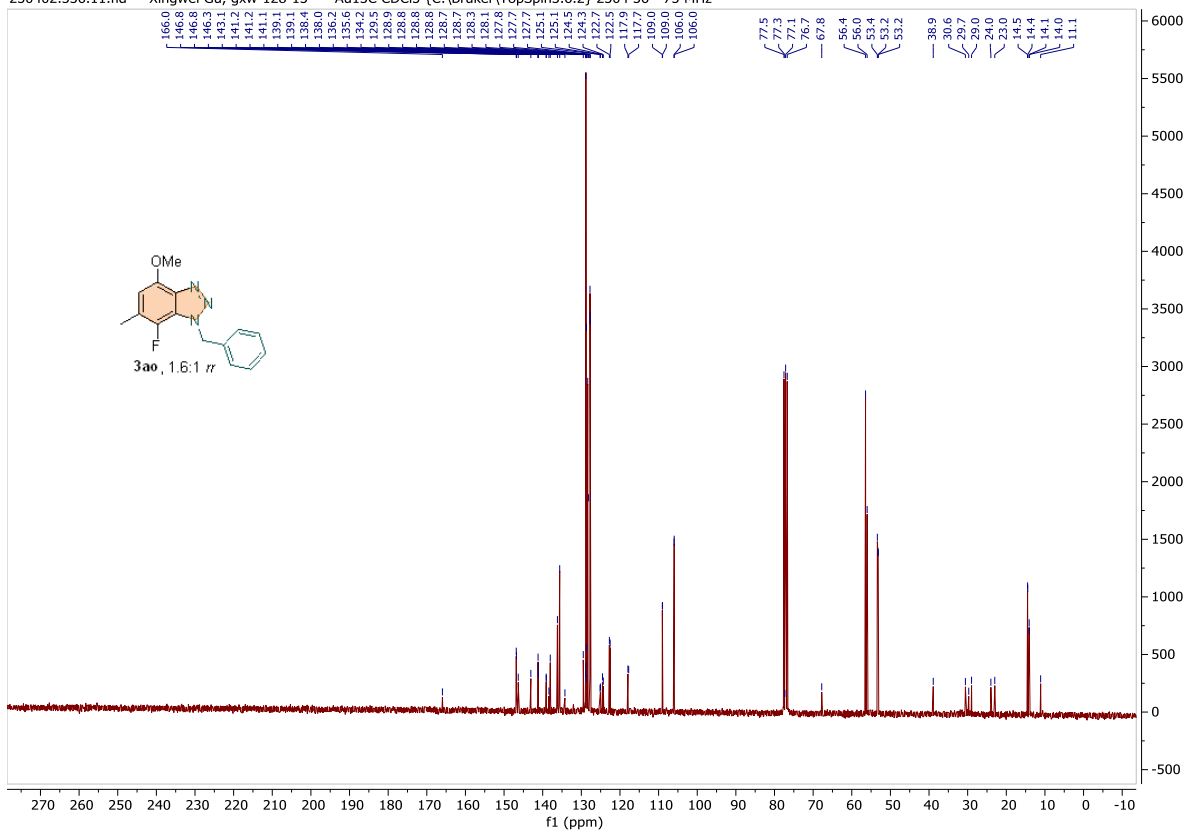
230330.308.12.fid — Xingwei Gu-123-10 — Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 8 - 75 MHz



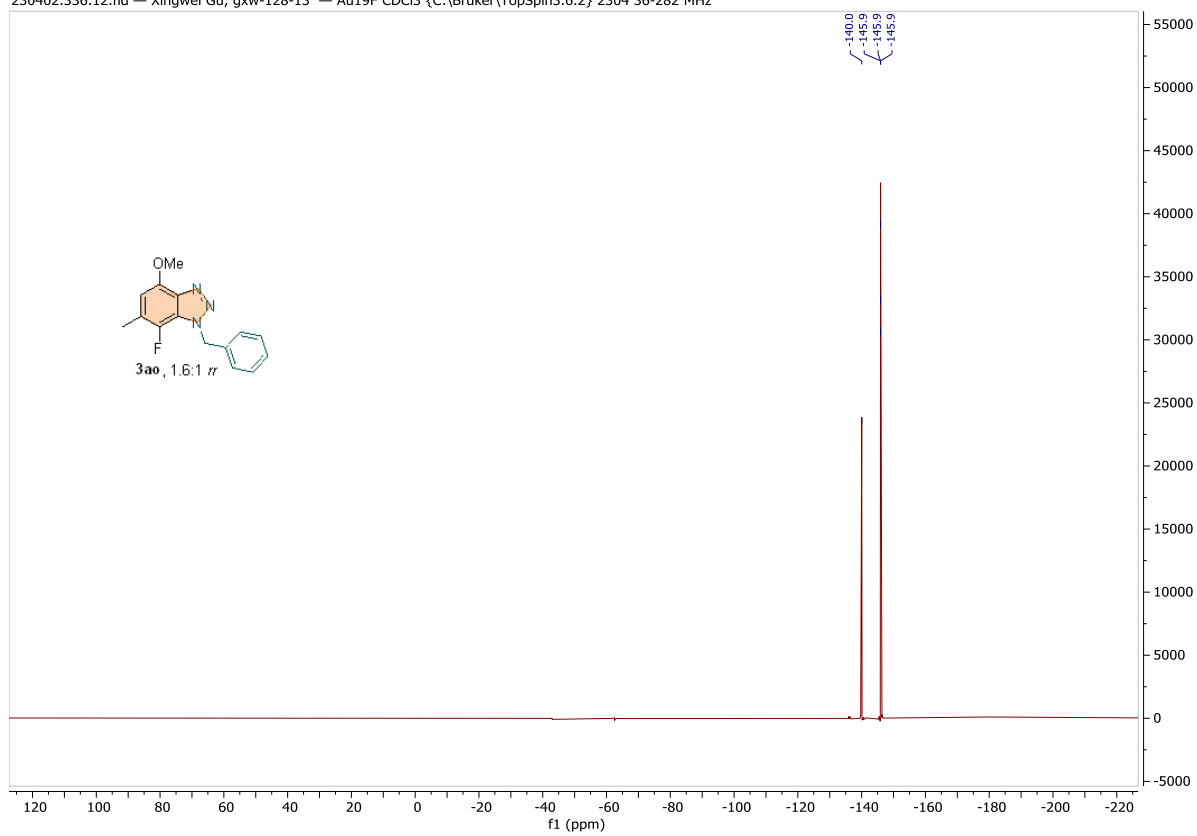
230402.336.10.fid — Xingwei Gu, gxw-128-13 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 36 - 300 MHz



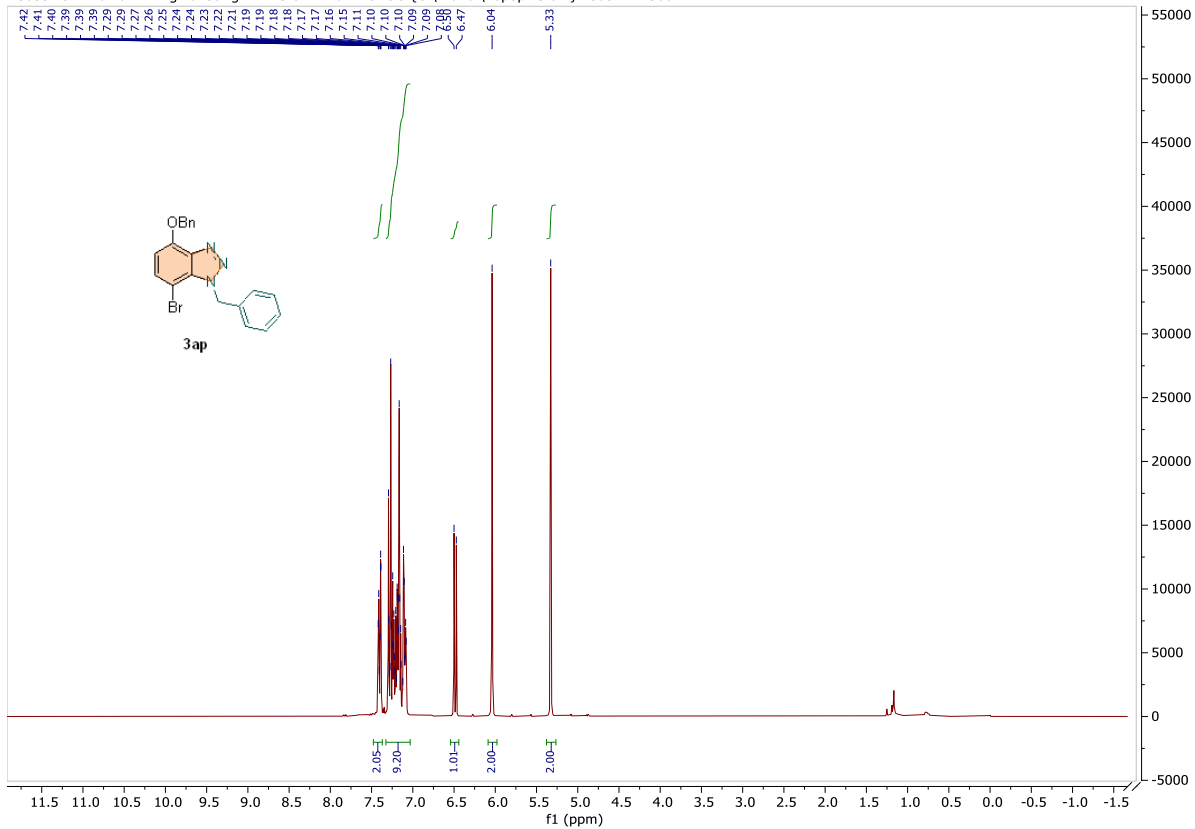
230402.336.11.fid — Xingwei Gu, gxw-128-13 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 36 - 75 MHz



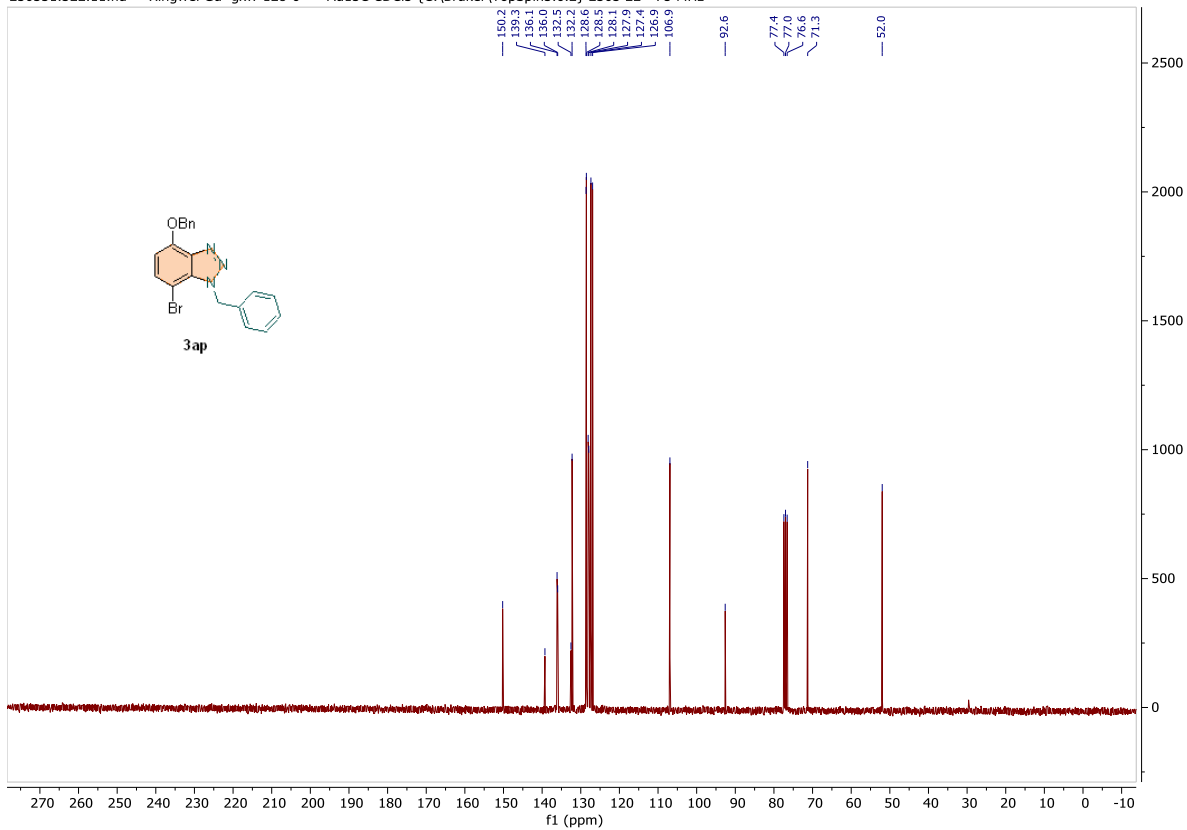




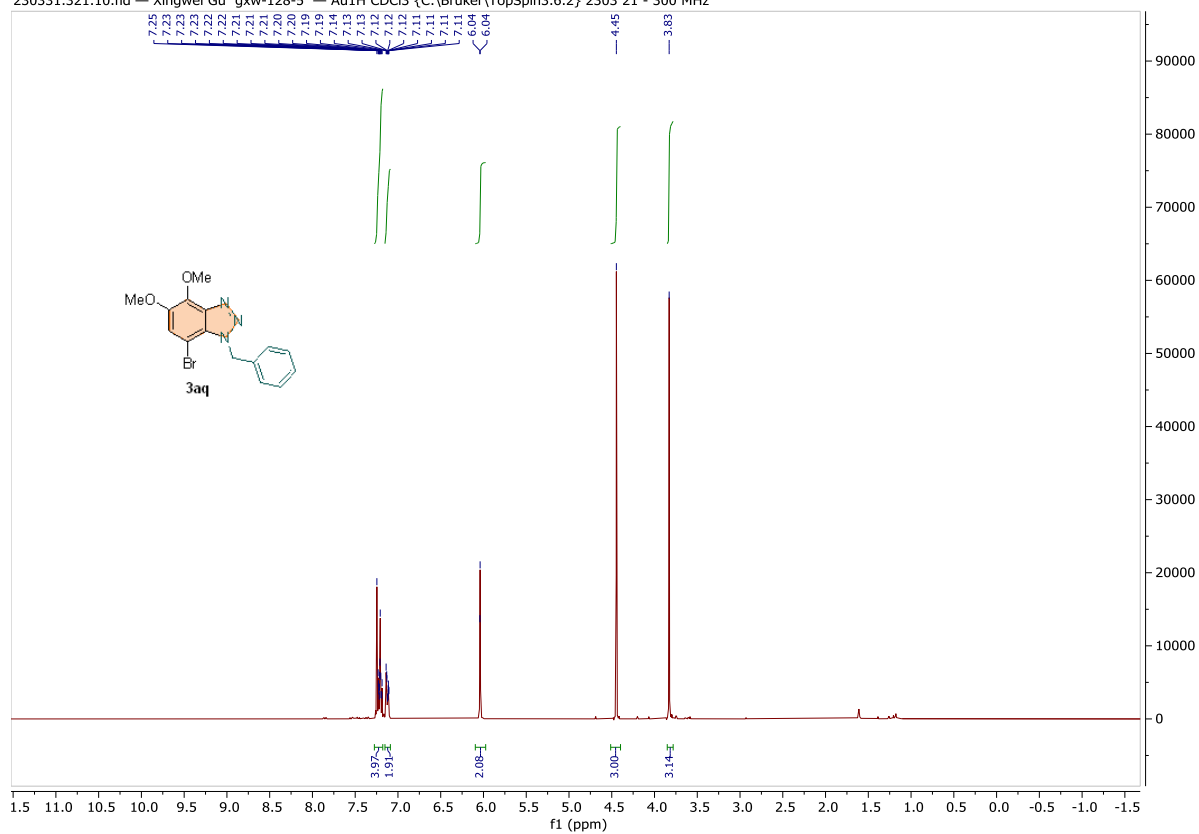
230331.322.10.fid — Xingwei Gu gxw-128-6 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 22 - 300 MHz



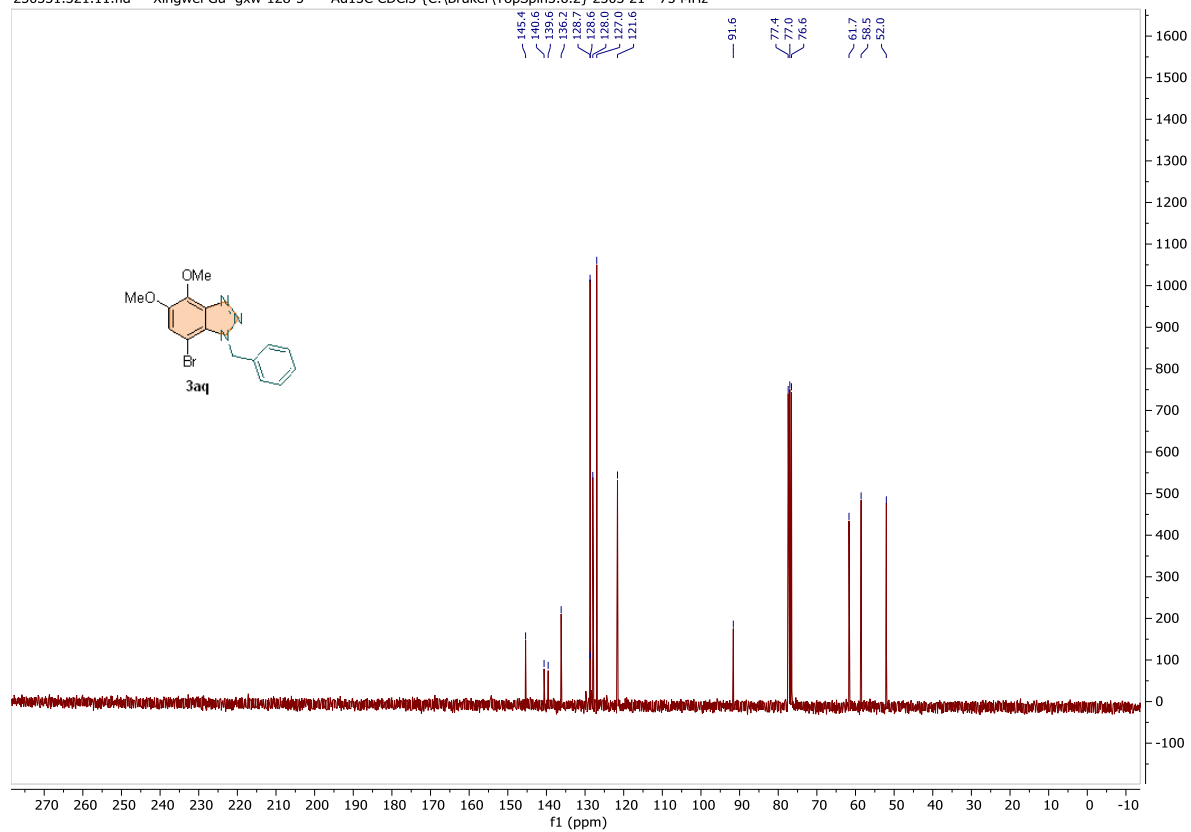
230331.322.11.fid — Xingwei Gu gxw-128-6 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 22 - 75 MHz



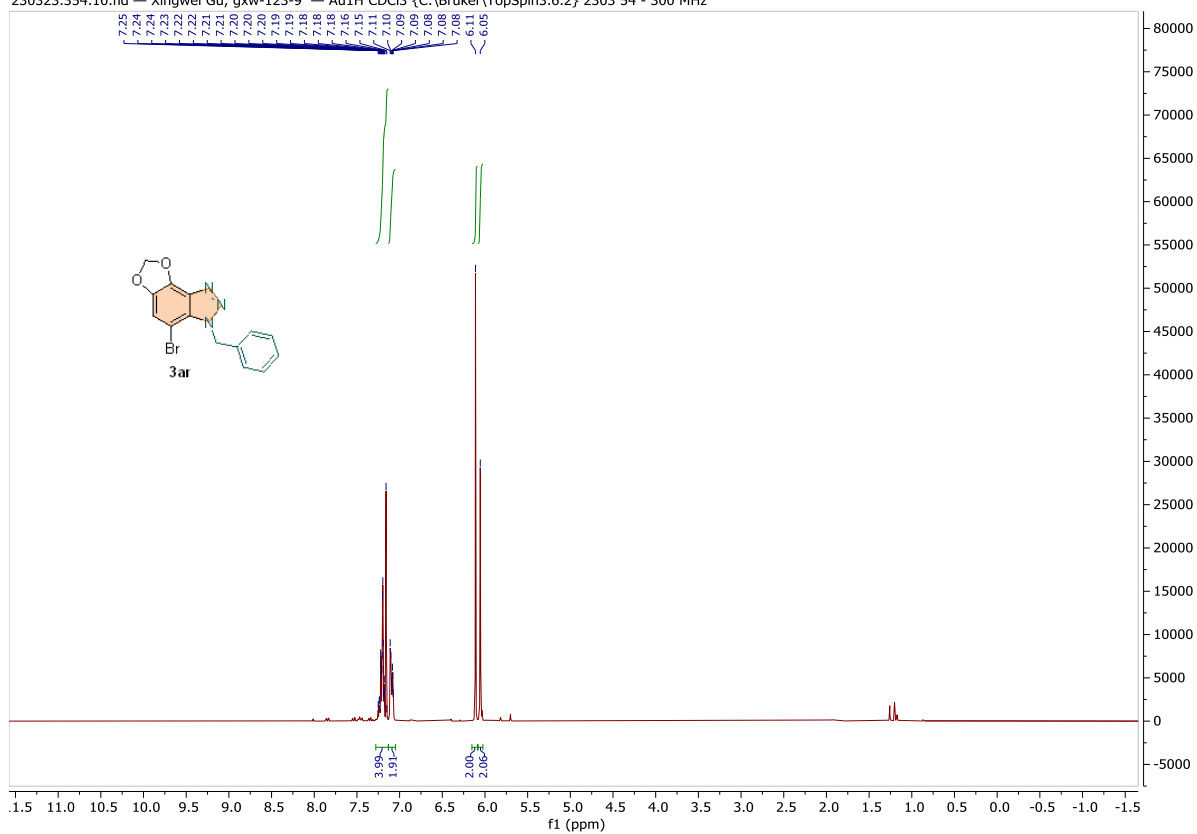
230331.321.10.fid — Xingwei Gu gxw-128-5 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 21 - 300 MHz



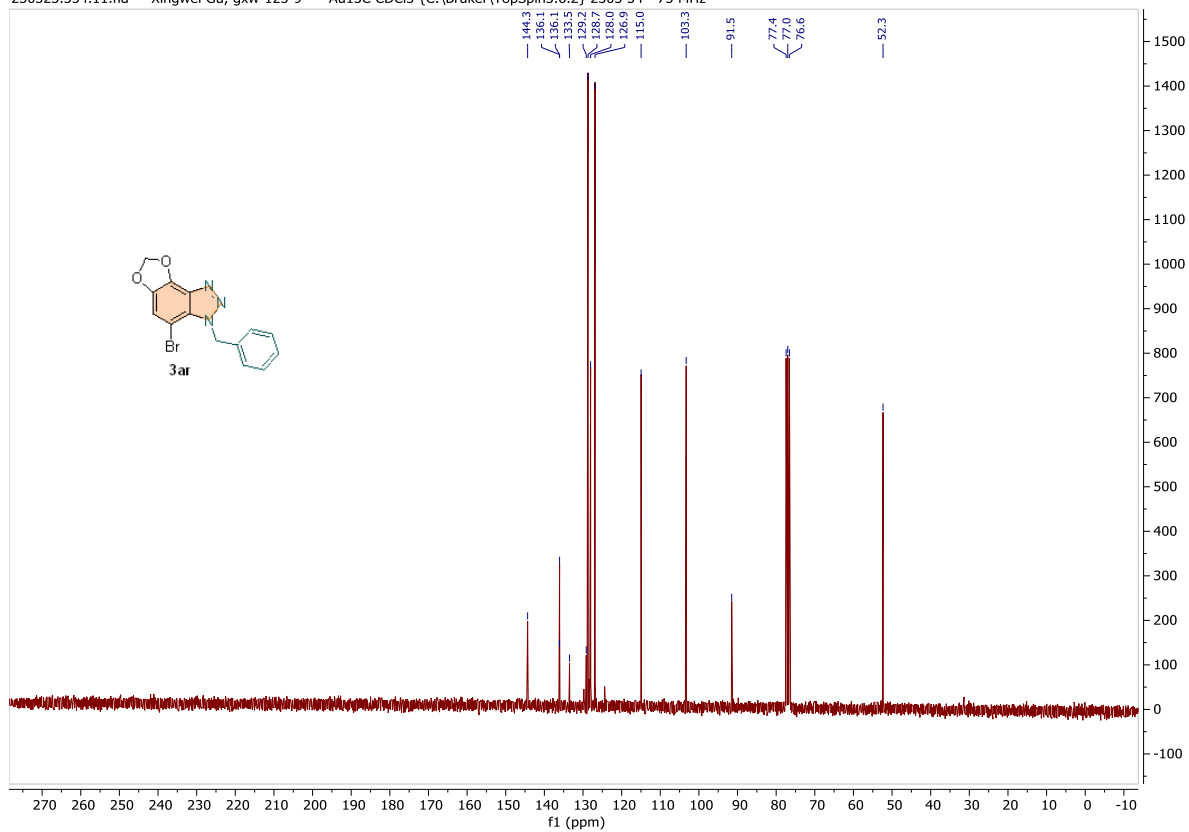
230331.321.11.fid — Xingwei Gu gxw-128-5 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 21 - 75 MHz



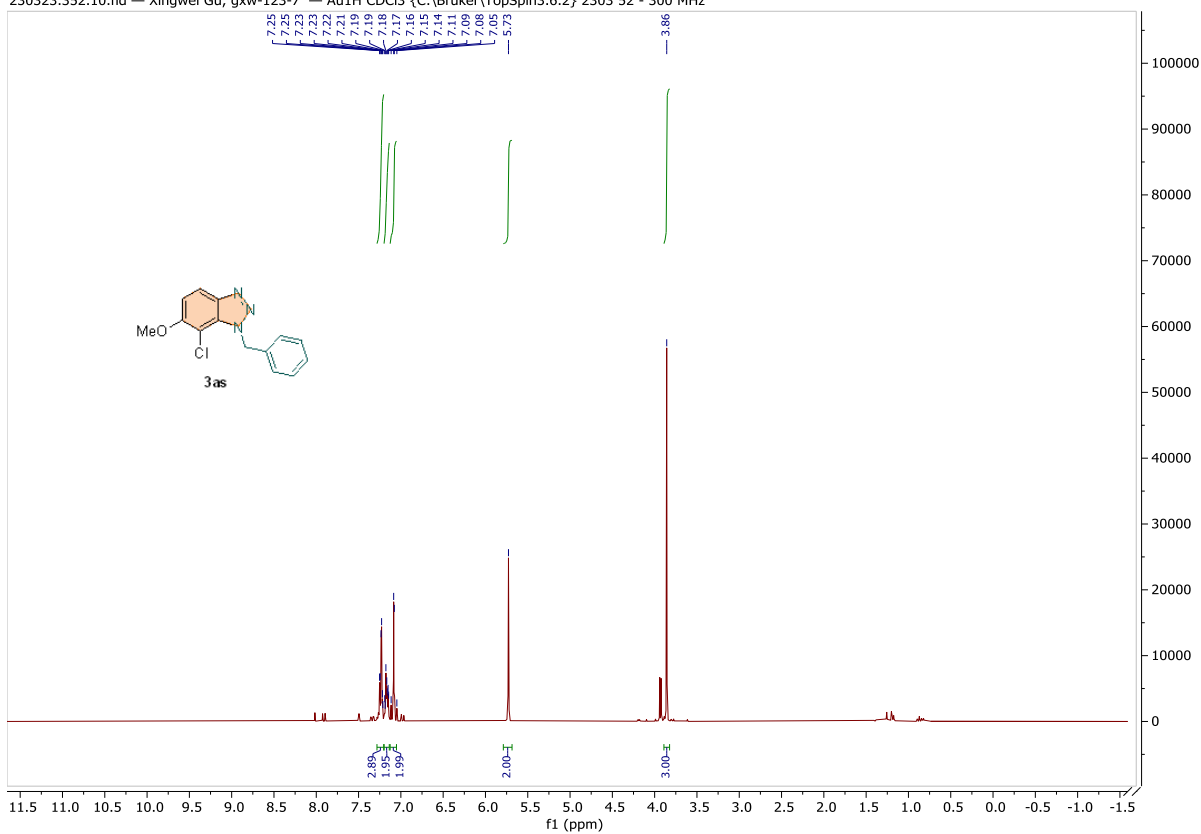
230323.354.10.fid — Xingwei Gu, gxw-123-9 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 54 - 300 MHz



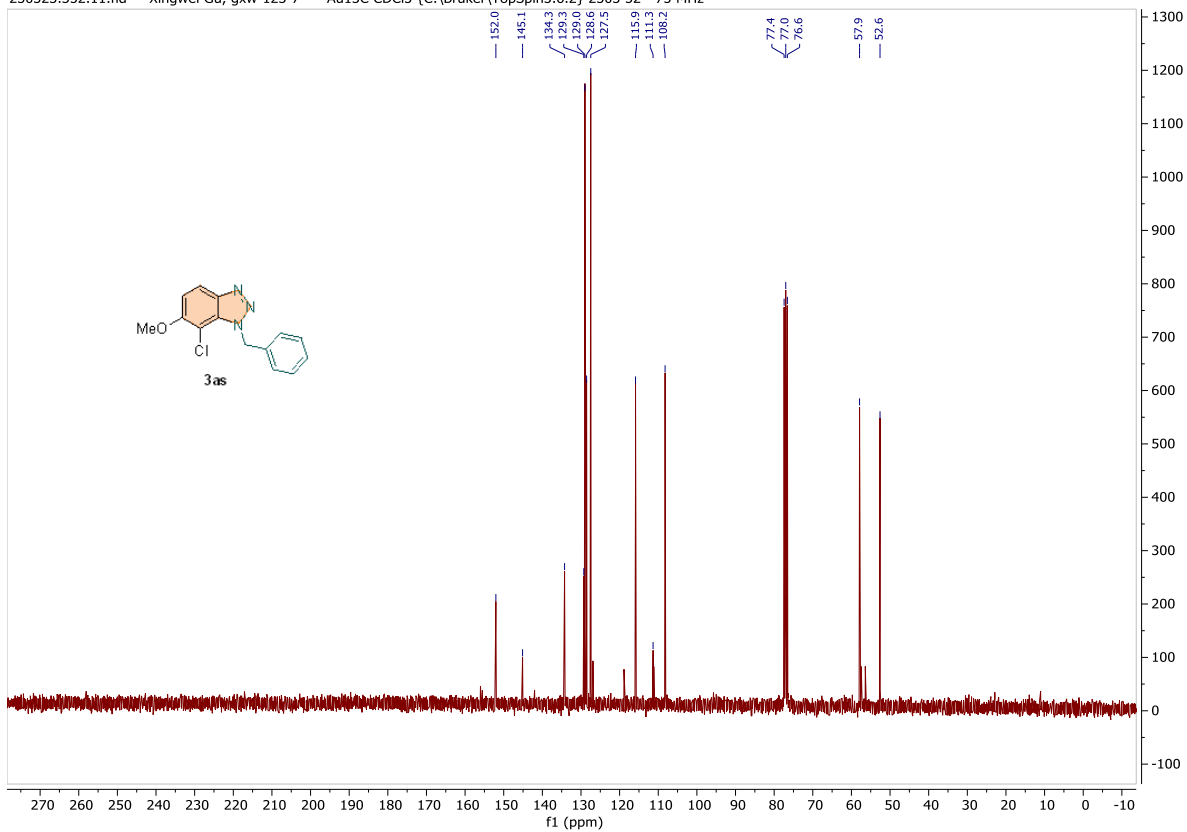
230323.354.11.fid — Xingwei Gu, gxw-123-9 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 54 - 75 MHz



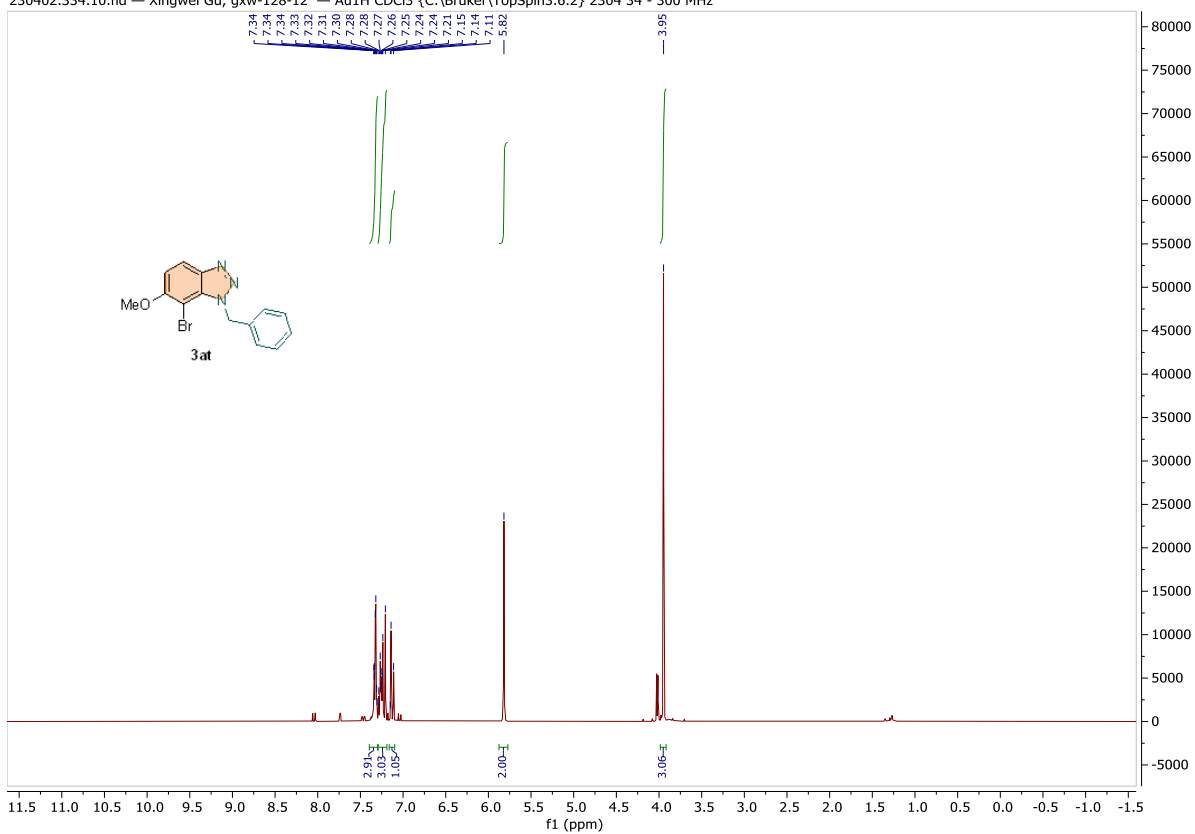
230323.352.10.fid — Xingwei Gu, gxw-123-7 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 52 - 300 MHz



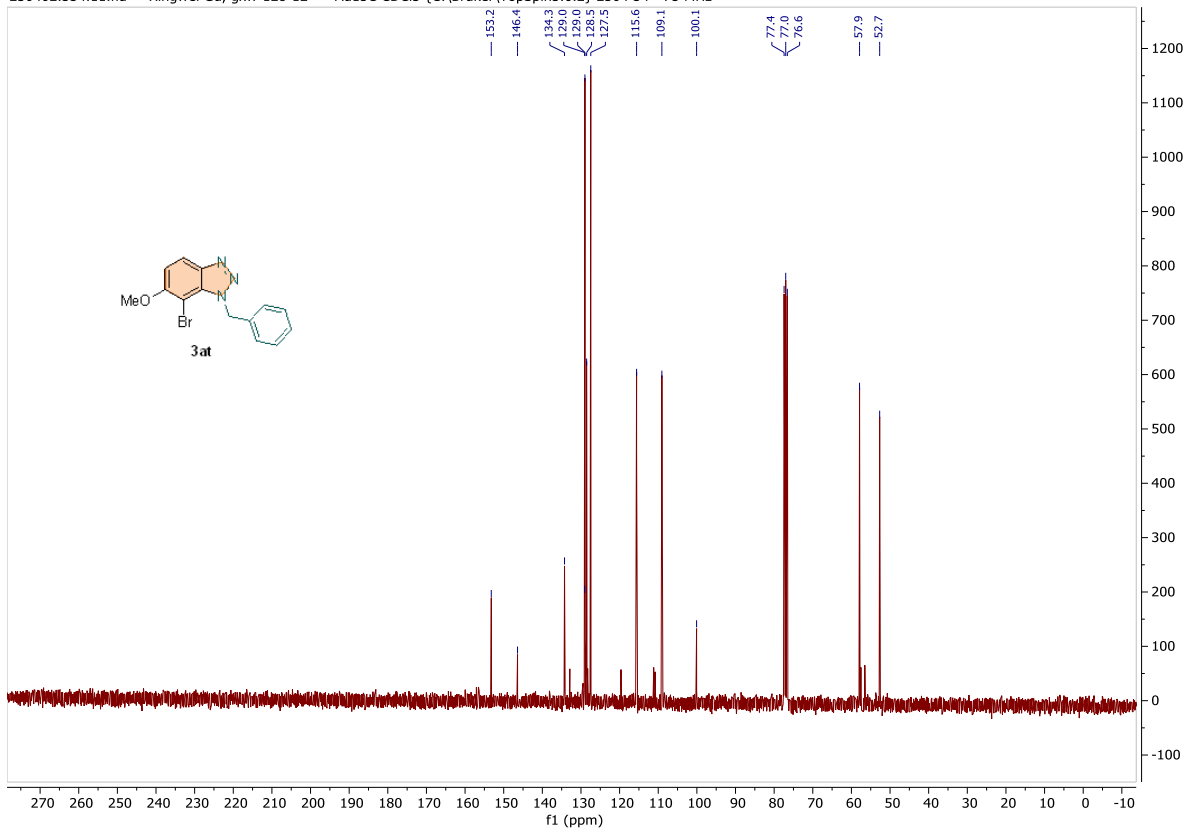
230323.352.11.fid — Xingwei Gu, gxw-123-7 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 52 - 75 MHz



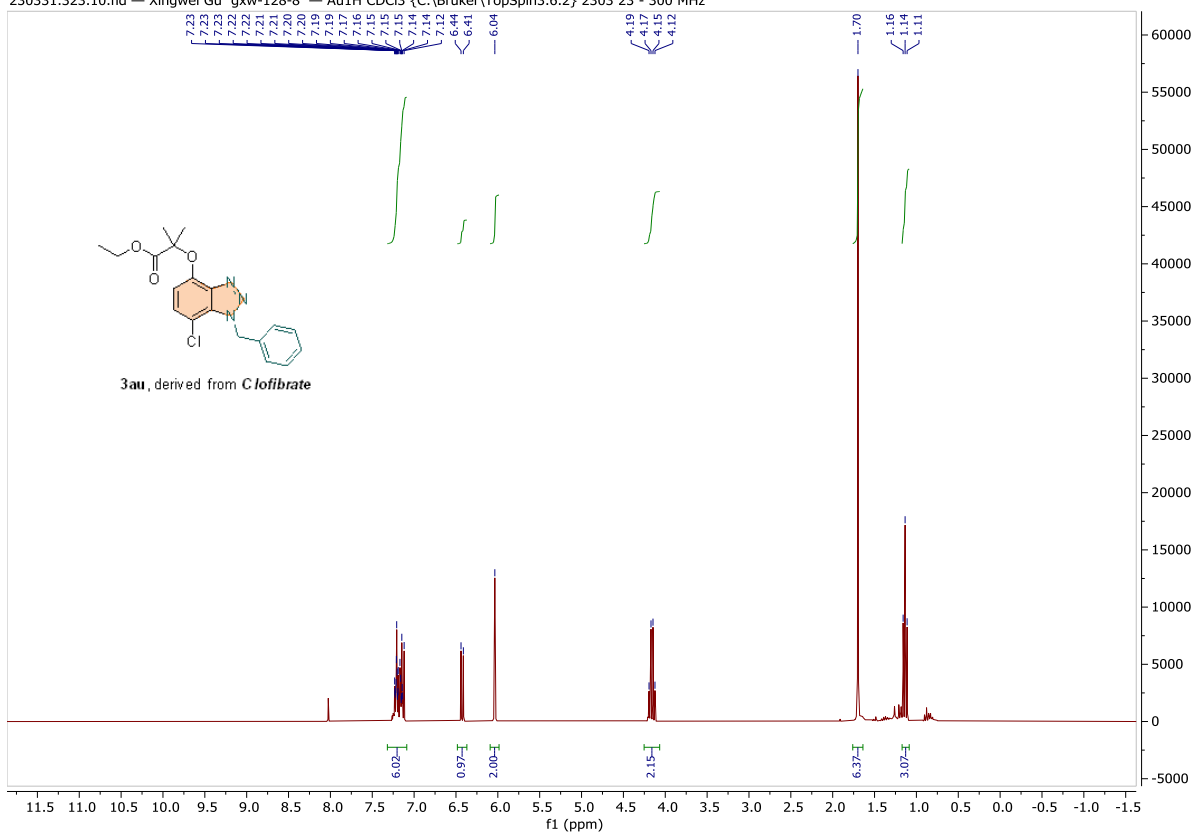
230402.334.10.fid — Xingwei Gu, gxw-128-12 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 34 - 300 MHz



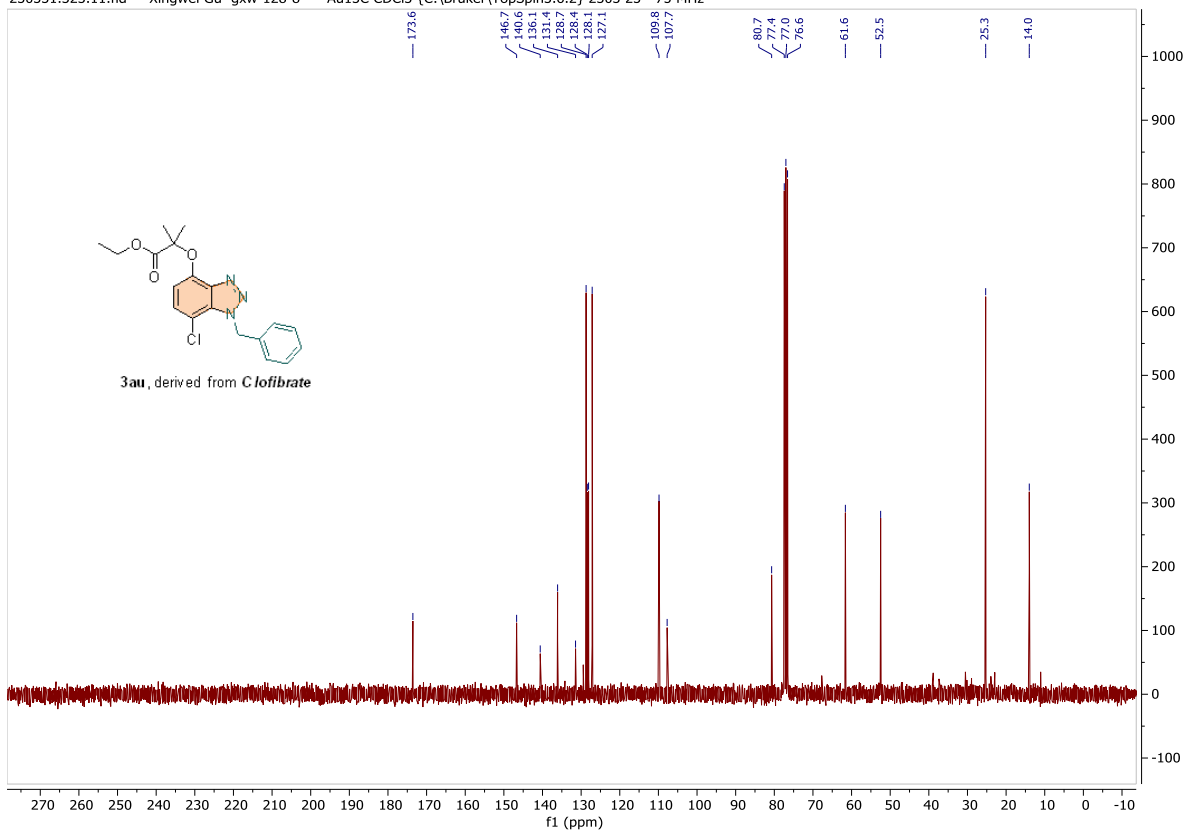
230402.334.11.fid — Xingwei Gu, gxw-128-12 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 34 - 75 MHz



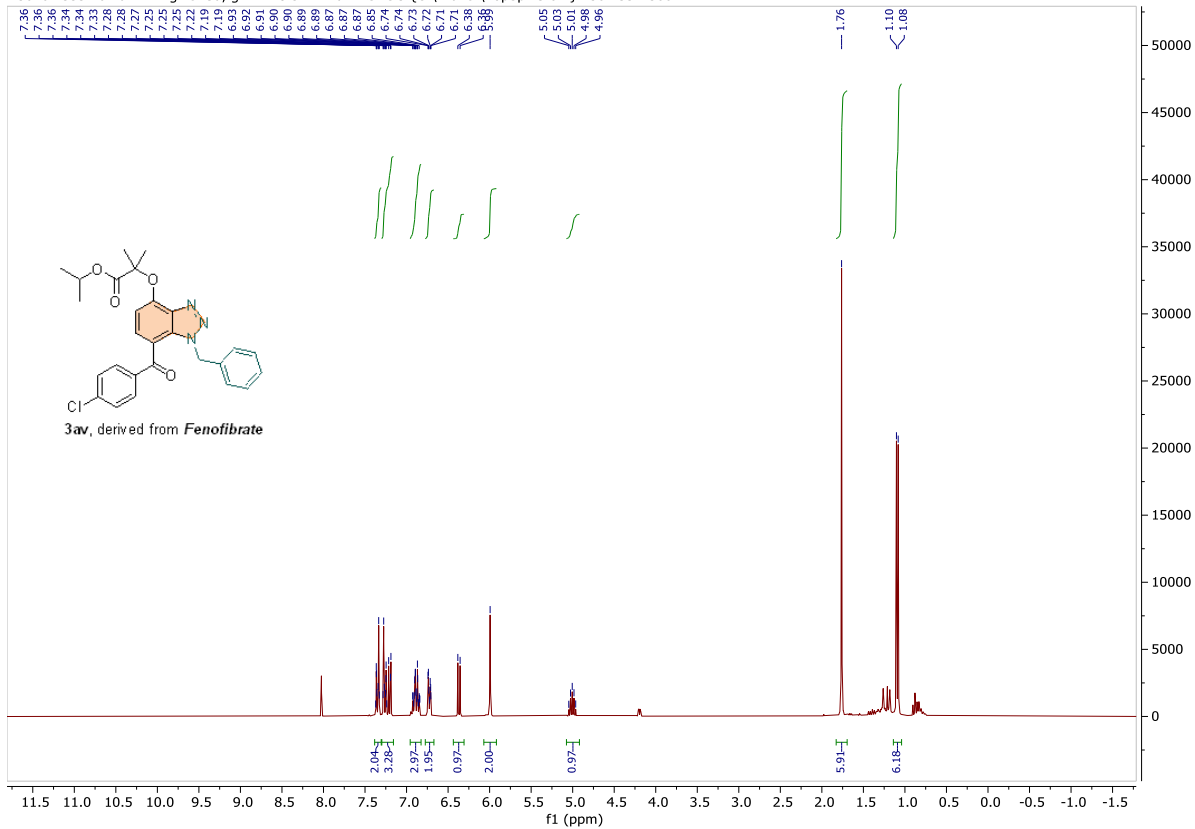
230331.323.10.fid — Xingwei Gu gxw-128-8 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 23 - 300 MHz



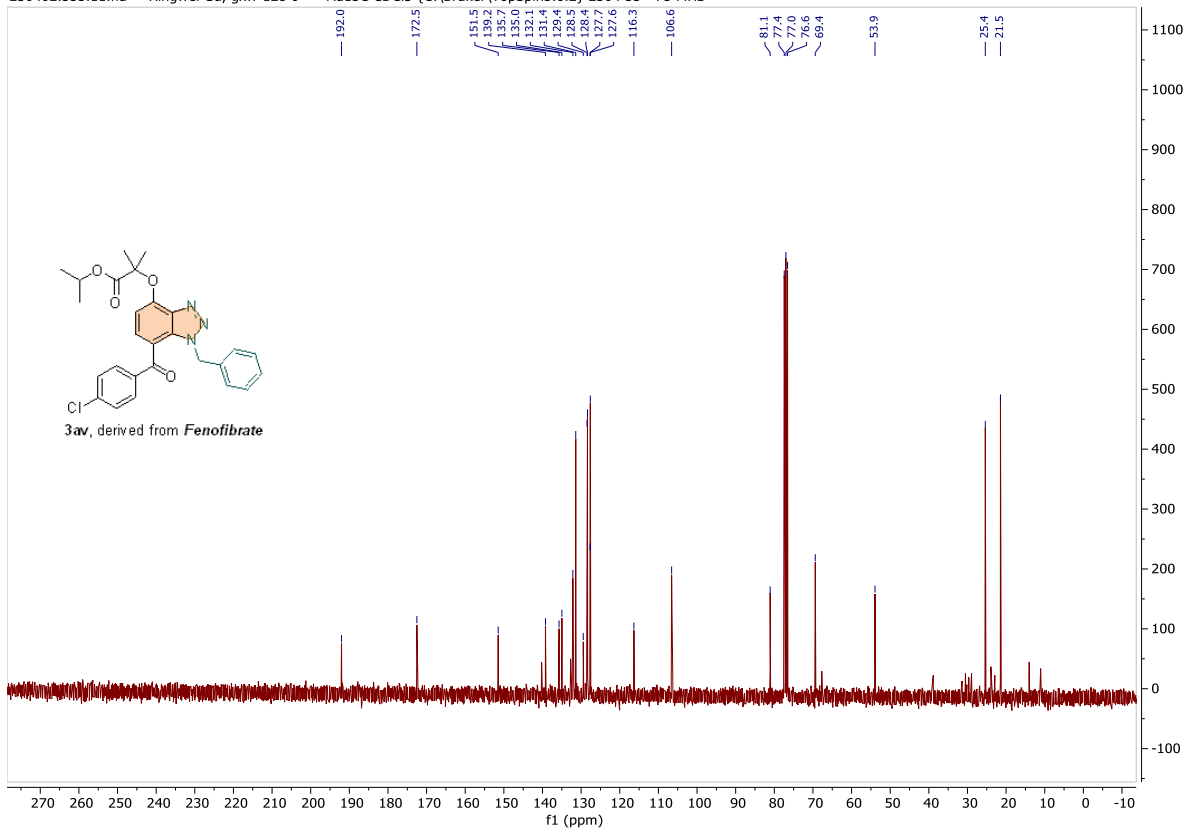
230331.323.11.fid — Xingwei Gu gxw-128-8 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2303 23 - 75 MHz



230402.333.10.fid — Xingwei Gu, gxw-128-9 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 33 - 300 MHz

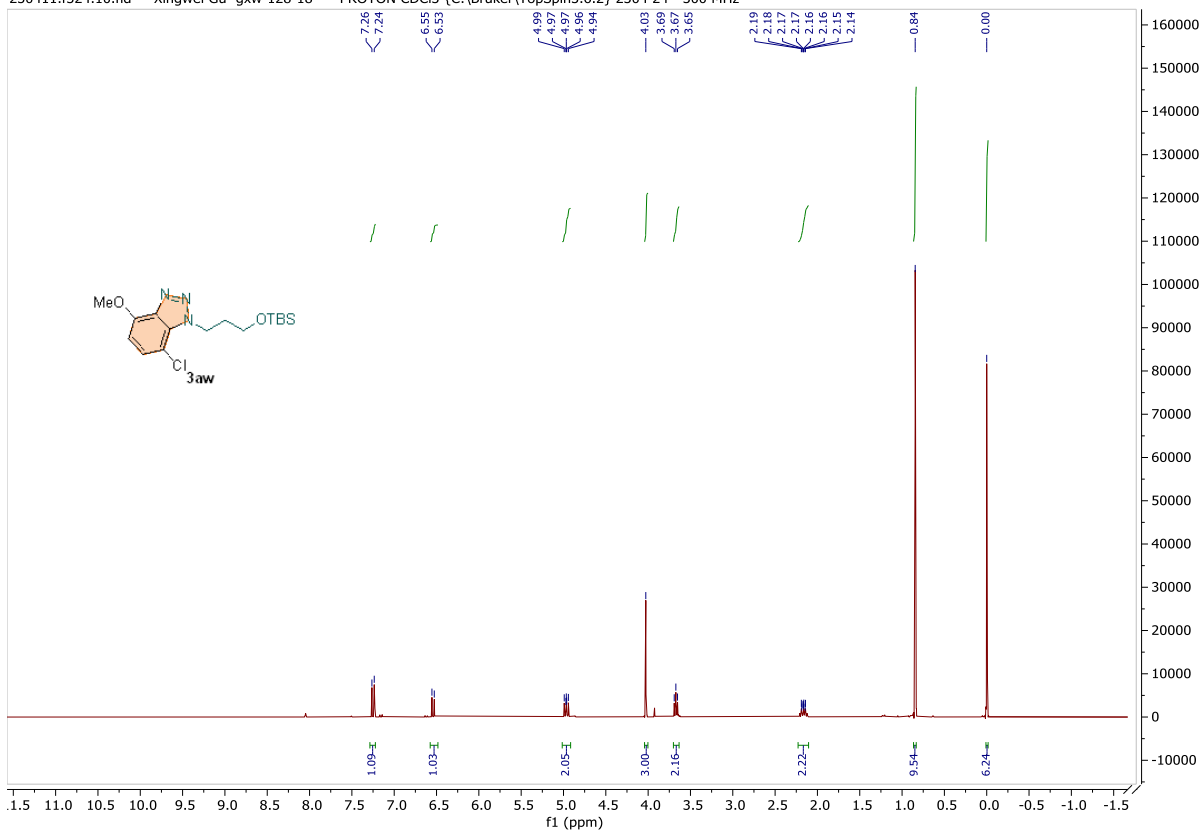


230402.333.11.fid — Xingwei Gu, gxw-128-9 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 33 - 75 MHz

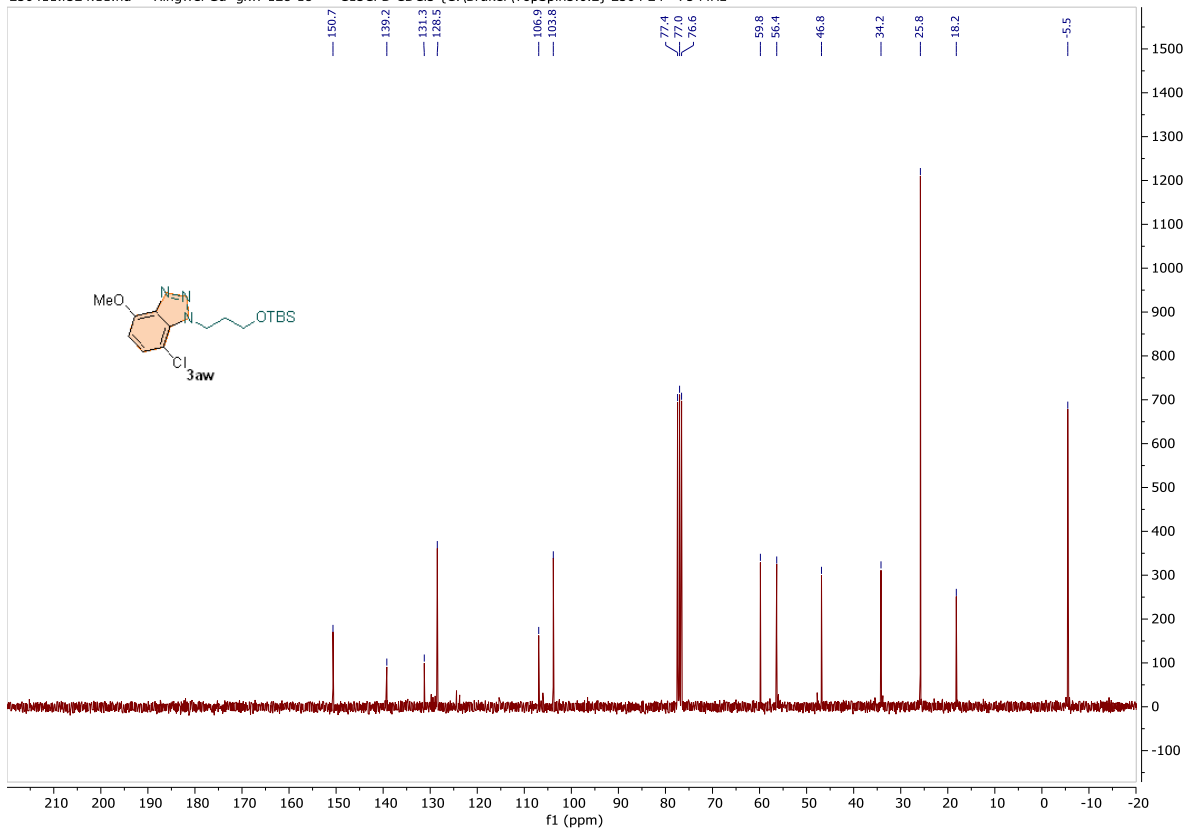




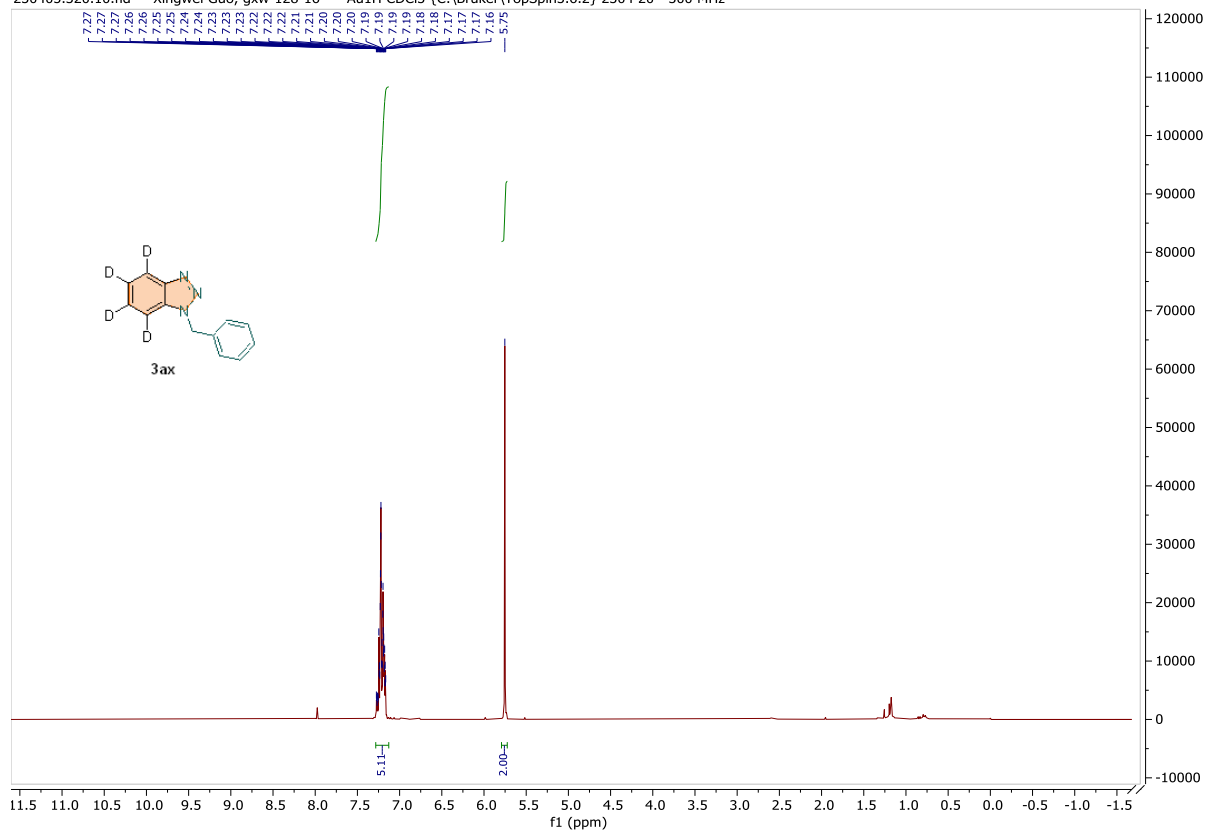
230411.f324.10.fid — Xingwei Gu gxw-128-18 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 24 - 300 MHz



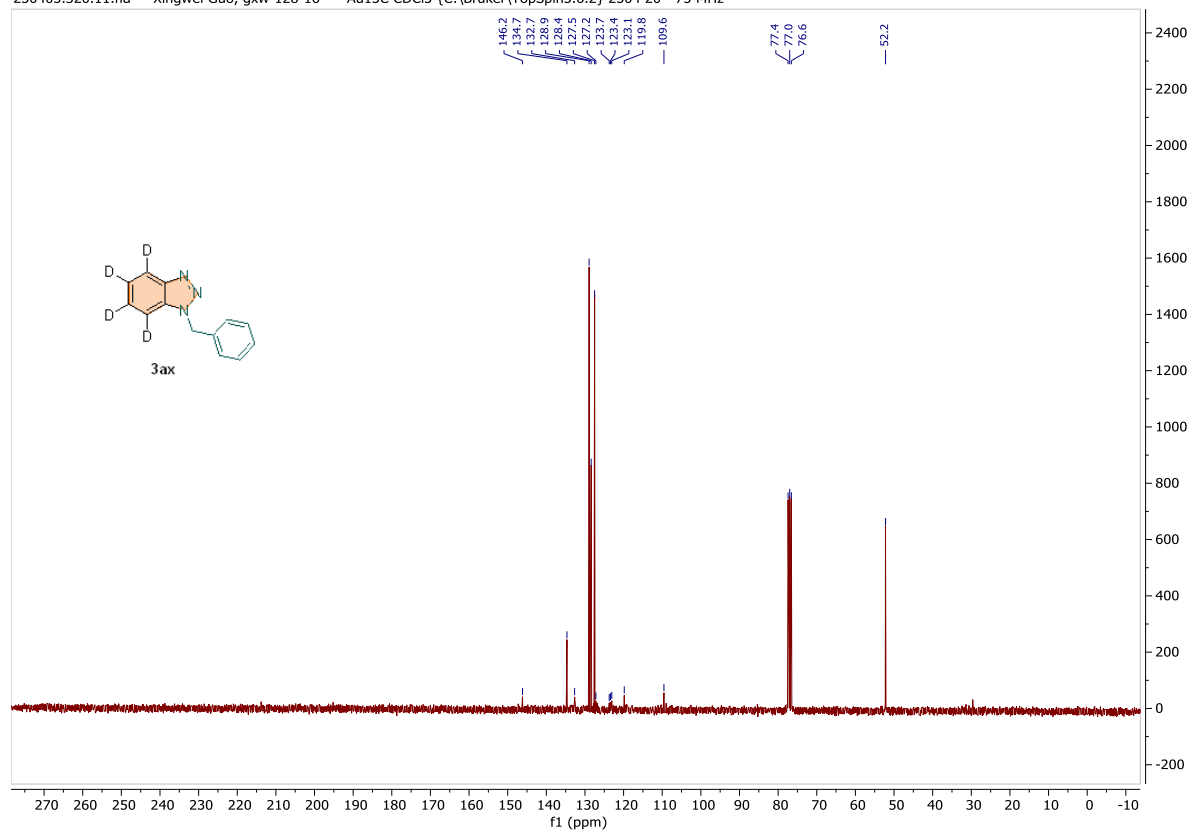
230411.f324.11.fid — Xingwei Gu gxw-128-18 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 24 - 75 MHz

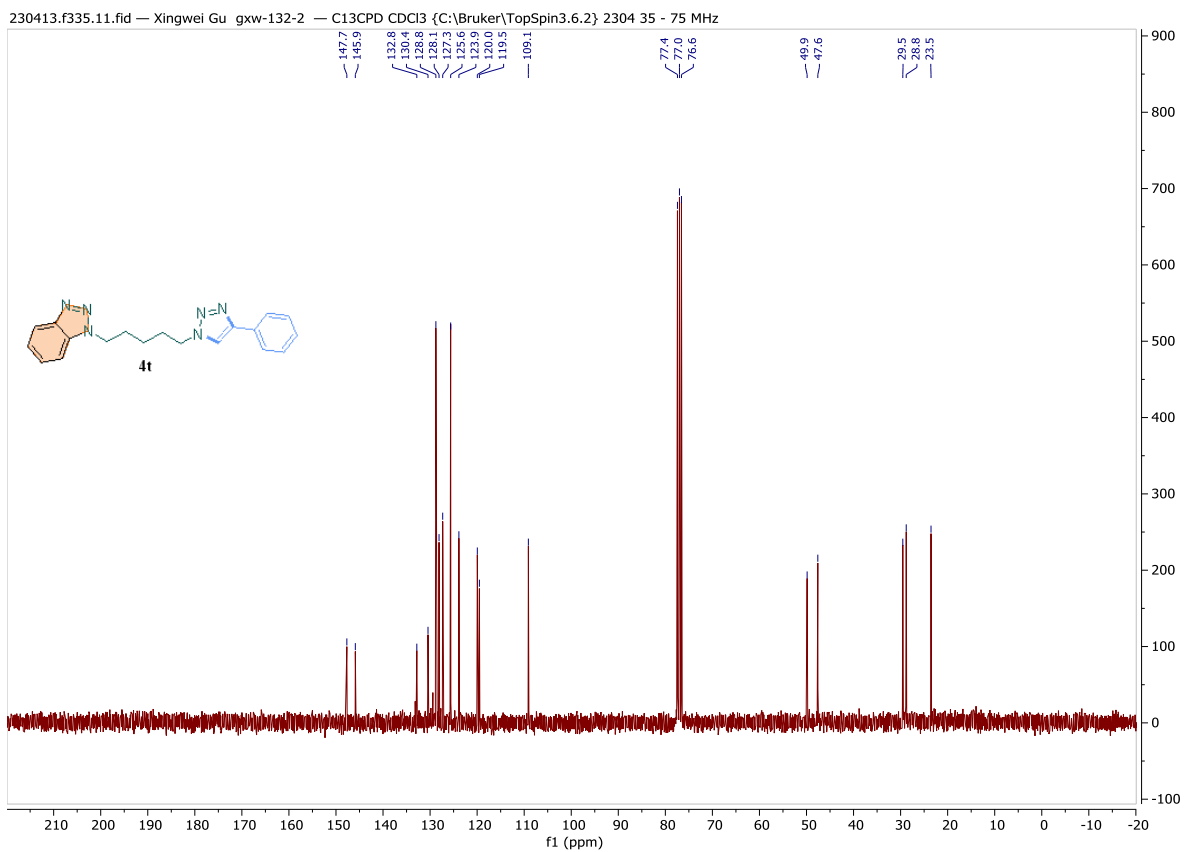
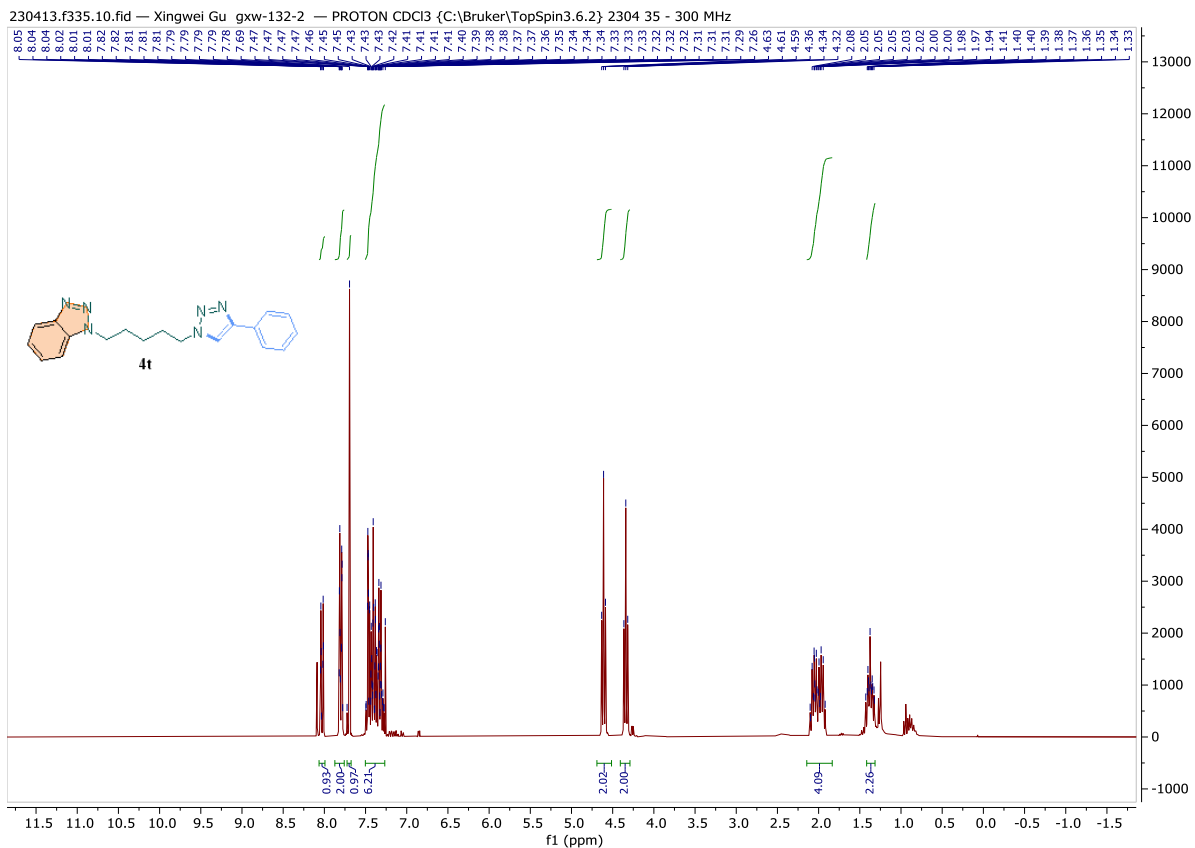


230405.320.10.fid — Xingwei Guo, gxw-128-16 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 20 - 300 MHz

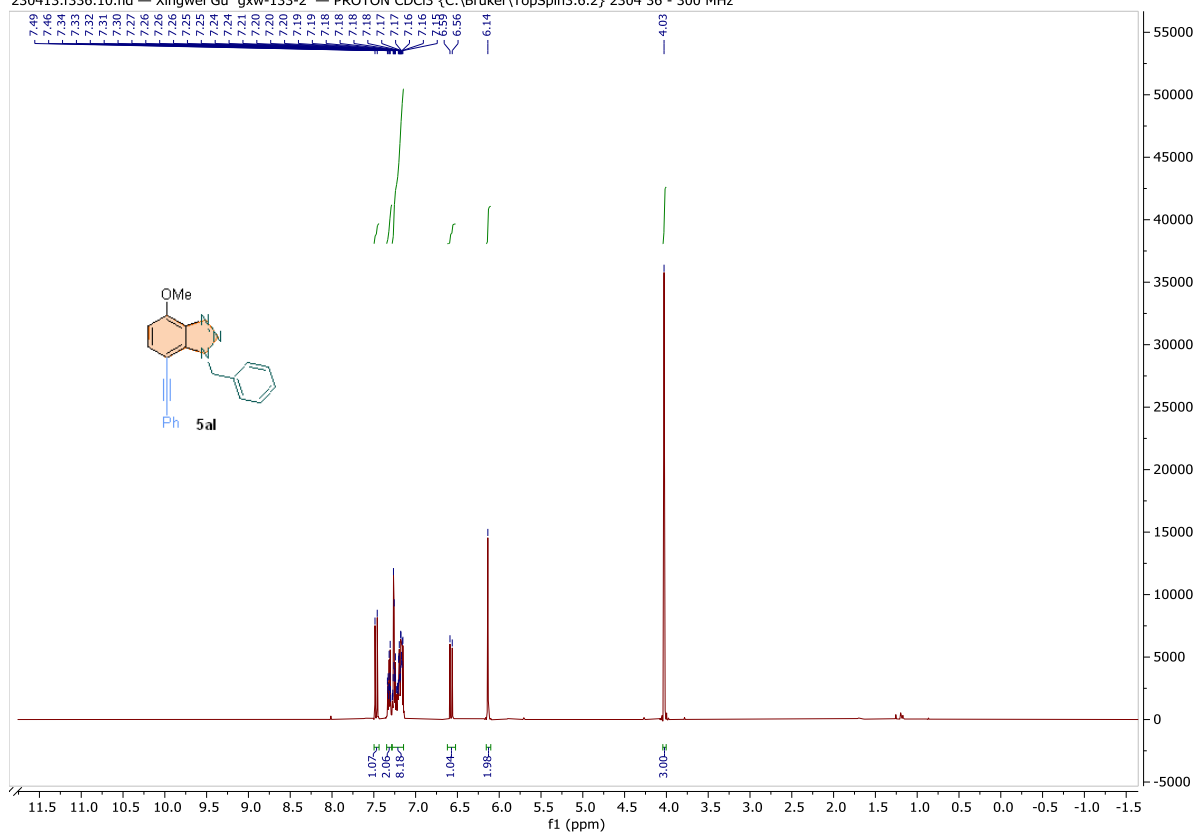


230405.320.11.fid — Xingwei Guo, gxw-128-16 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 20 - 75 MHz

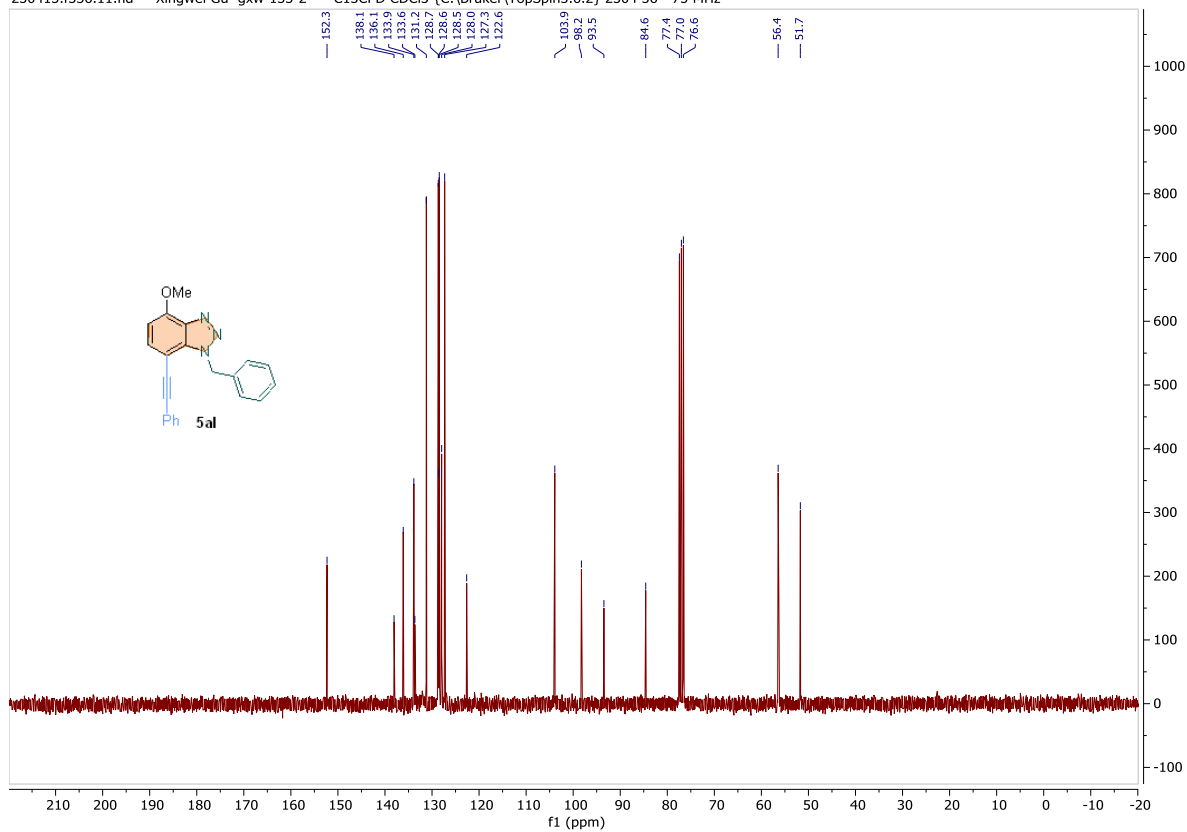


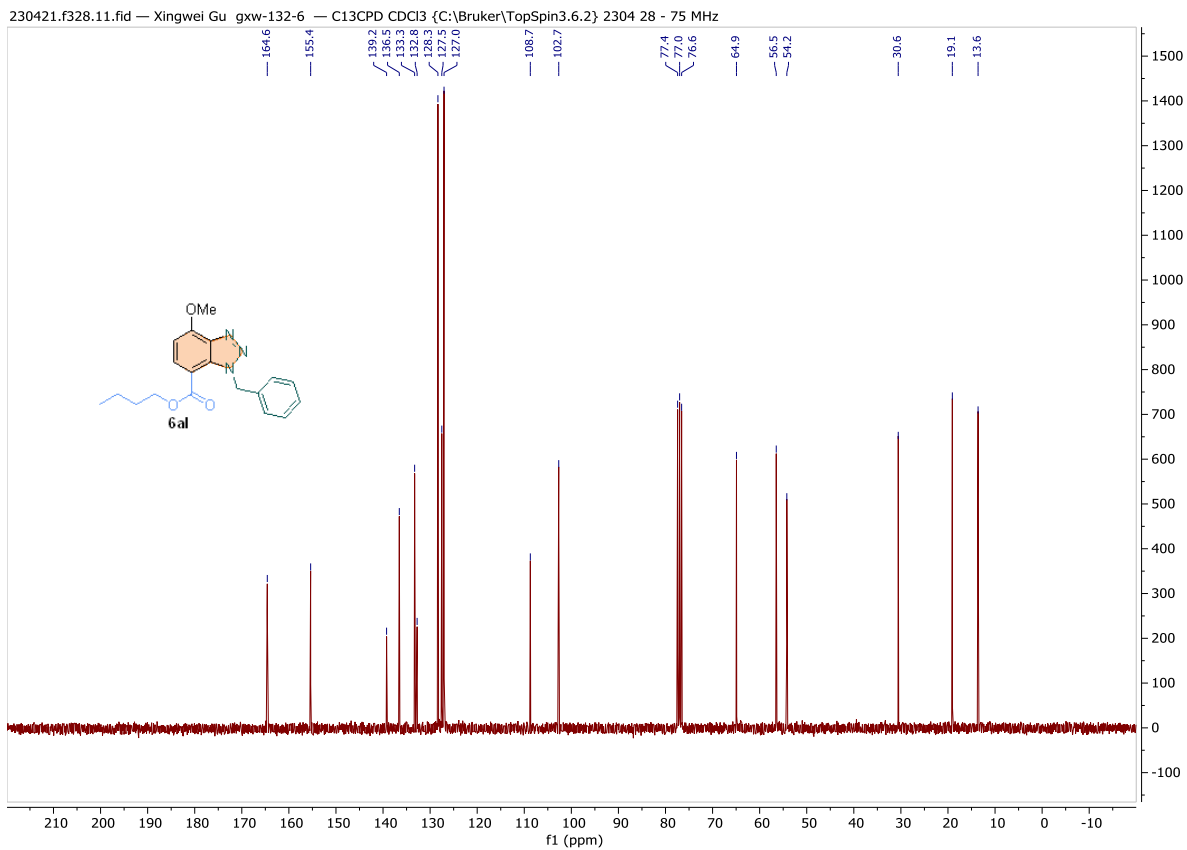
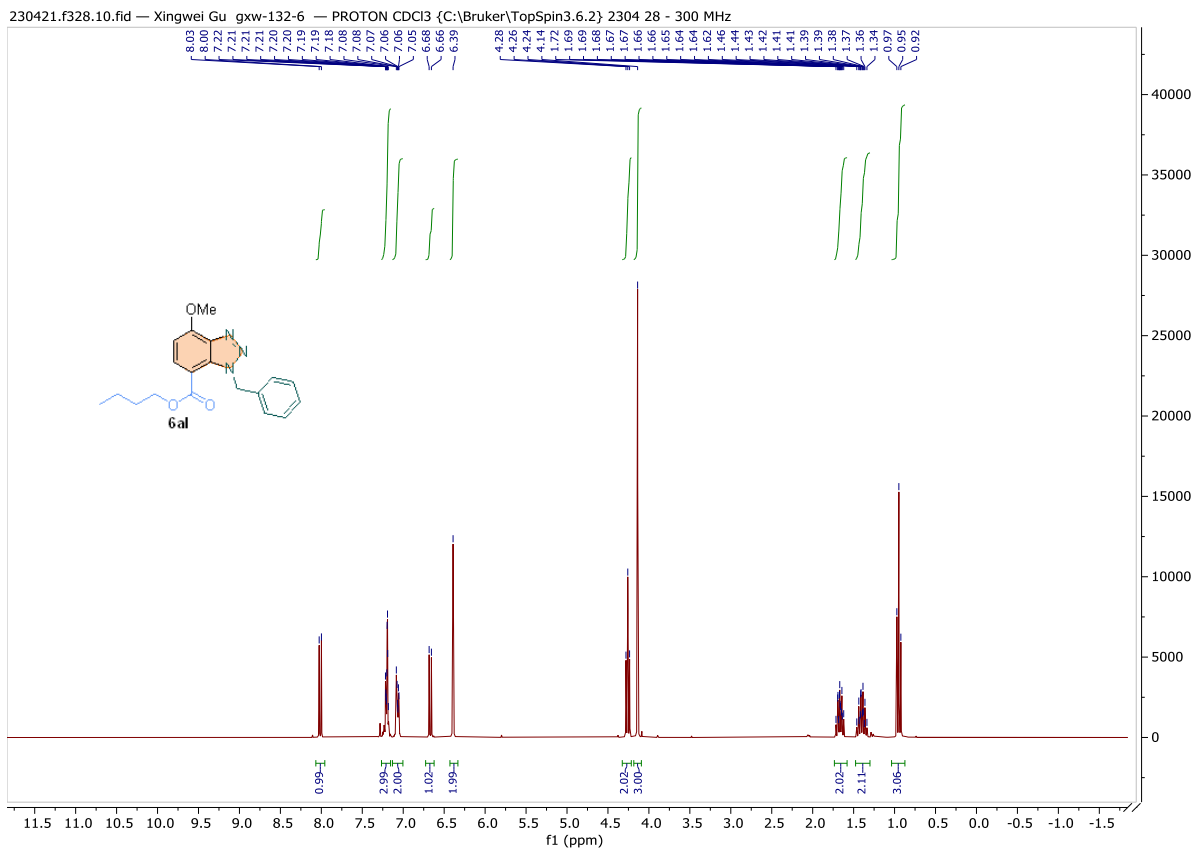


230413.f336.10.fid — Xingwei Gu gxw-133-2 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2304 36 - 300 MHz

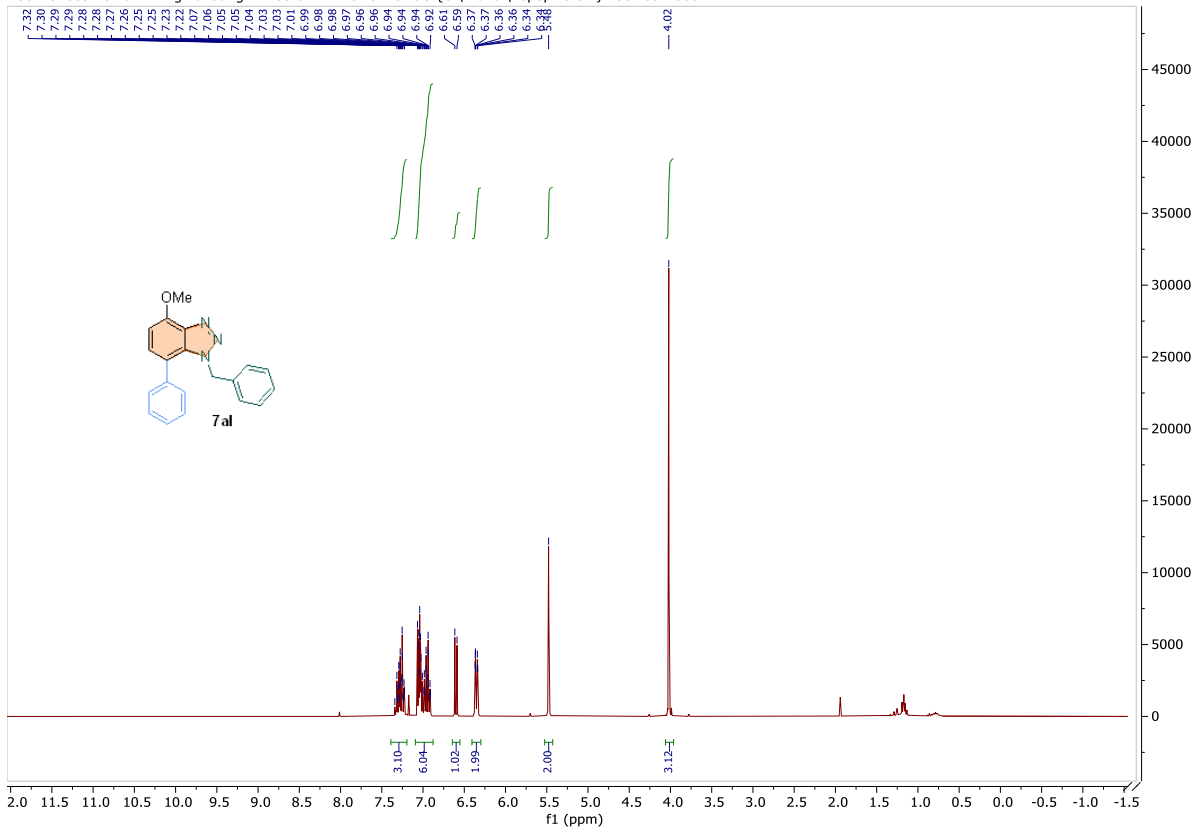


230413.f336.11.fid — Xingwei Gu gxw-133-2 — C13CPD CDCI3 {C:\Bruker\TopSpin3.6.2} 2304 36 - 75 MHz

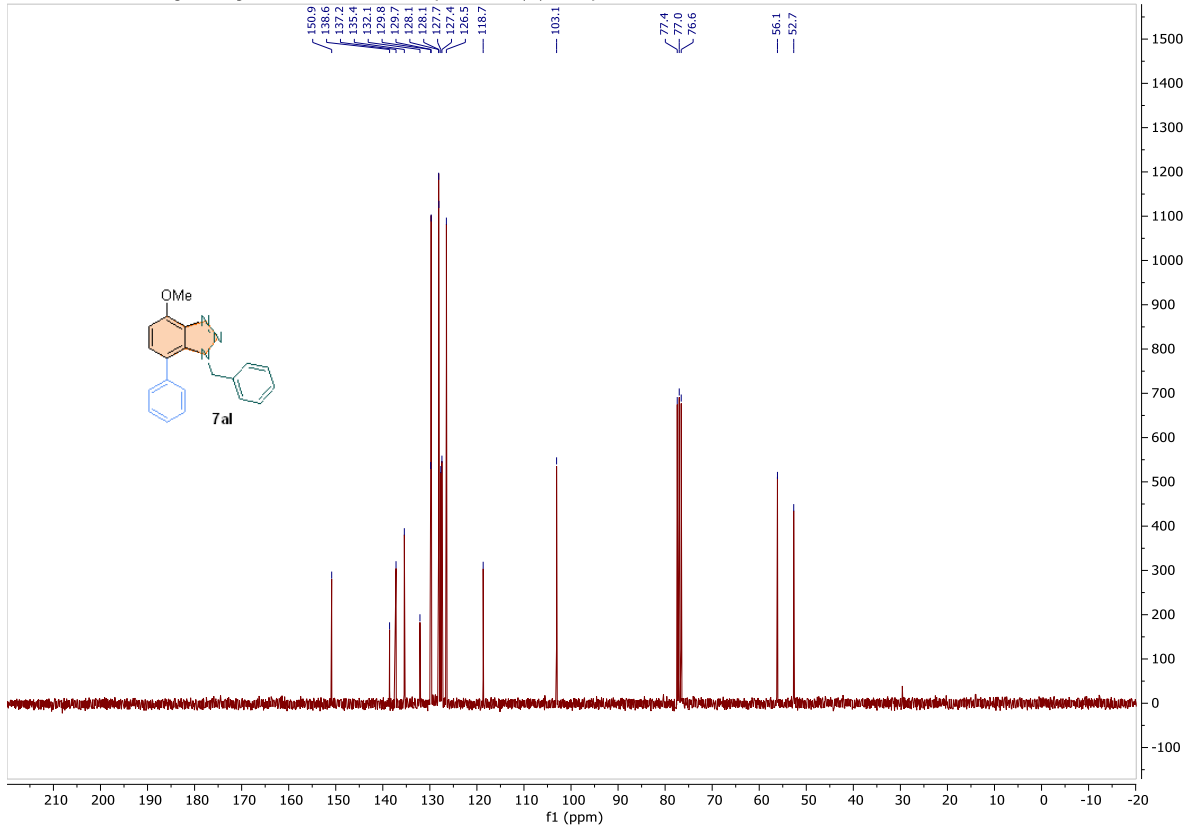




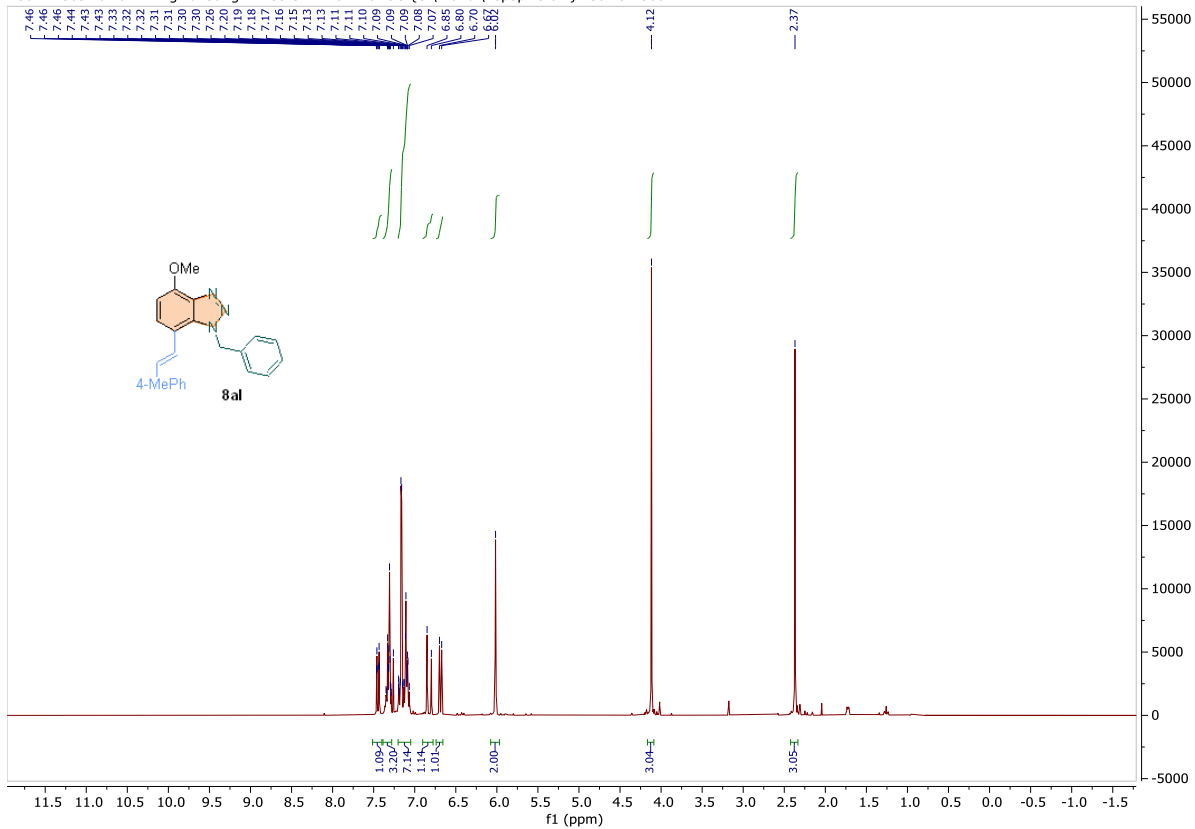
230413.f339.10.fid — Xingwei Gu gxw-133-6 — PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2304 39 - 300 MHz



230413.f339.11.fid — Xingwei Gu gxw-133-6 — C13CPD CDCI3 {C:\Bruker\TopSpin3.6.2} 2304 39 - 75 MHz



230417.305.10.fid — Xingwei Gu gxw-133-5 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 5 - 300 MHz



230417.305.11.fid — Xingwei Gu gxw-133-5 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2304 5 - 75 MHz

