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# Supporting Information

## Synthesis of a heterogeneous Cu(OAc)$_2$-anchored SBA-15 catalyst and its application in CuAAC reaction

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## 1. General

### *1.1. Reagents and materials*

All chemicals were reagent grade and used without further purification if not being pointed out. De-ionized water was used in all reactions. Proton and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III 500 MHz spectrometer in deuterated solvents with tetramethylsilane (TMS) as internal standard. Melting points (uncorrected) were determined on a BUCHI M-565 apparatus. High resolution mass spectra were recorded in the ESI mode on an Agilent 6210 TOF mass spectrometer. High performance liquid chromatography (HPLC) analyses were performed on Shimadzu LC-20A instrument with UV detector (254 and 230 nm) using an Insertsil ODS-3 column (150 x 4.6 mm (i.d.), 5.0 μ) at room temperature. Flash column chromatography was performed on silica gel (200-300 mesh) with petroleum ether/ethyl acetate as eluent.

### *1.2. Characterization Methods*

The powder X-ray diffraction (XRD) was determined on a Rigaku Ultima IV diffractometer using Cu Kα radiation. The data were collected at low angle from 0.6° to 3° ($2\theta$) with a resolution of 0.02° and a scan rate of 0.5°/min. High resolution transmittance electron microscopic images (HR-TEM) were recorded on a JEOL JEM-2100 transmission electron microscope at 120 KV. Nitrogen adsorption and desorption isotherms were measured using a Thermo Micromeritics ASAP 2021C apparatus at liquid nitrogen temperature. Prior to the measurements, the samples were degassed at 150 °C for 3 h. The data were analyzed using the BJH model and total pore volumes were taken at P/Po = 0.975 single point. The FT-IR spectra of the samples were recorded from 4000 to 500 $cm^{-1}$ on a Nicolet FT-IR 6700 spectrophotometer. Thermo-gravimetric analyses (TGA) were carried out on a NETZSCHTG TGA 209F3A-0139-L instrument. Copper loading of the catalyst was determined using a Varian SPECTR AA-220 atomic absorption spectrophotometer (AAS) with an external standard method. X-ray absorption measurements were acquired in transmission mode at beamline 17C1 at National Synchrotron Radiation Research Center (NSSRC) in Taiwan. A pure Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration. Multiple scans were taken to reduce the noise. Electron paramagnetic resonance (EPR) measurement was performed on a Bruker EMX EPR spectrometer at X-band frequency (9.46 GHz) at room temperature (298K). The acid capacity of the carboxyl functionalized SBA-15 silica (**SBA-15-PTAA**) was determined by the potentiometric titration method on a Mettler Toledo T50 automatic titrator equipped with a Mettler Toledo DGi111-SC combined glass electrode.

## 2. Experimental procedure for synthesis of Cu@SBA-15-PTAA

### *2.1. Synthesis of tert-butyl 2-(3-(trimethoxysilyl)propylthio)acetate silane coupling reagent*

To a solution of 3-mercaptopropyltrimethoxysilane (19.6 g, 0.1 mol) and triethylamine (12.1 g, 0.12 mol) in 250 mL of dried THF, *tert*-butyl 2-bromoacetate (23.4 g, 0.12 mol) was dropwise added within a period of 2.5 h at room temperature and under nitrogen atmosphere. After addition, the mixture was further stirred for another 20 h until the reaction was complete based on GC determination. Then the reaction mixture was filtrated and the filtrate was concentrated under vacuo. Finally, the residual was vacuum distillated with a 15-cm Vigreux column and the fraction at 140-143 ºC/2 mmHg was collected to afford 22.1 g (87%) of desired product as colorless liquid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.67-0.71 (m, 2H), 1.41 (s, 9H), 1.63-1.69 (m, 2H), 2.59 (t, $J$ = 7.3 Hz, 2H), 3.05 (s, 2H), 3.51 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 8.4, 22.4, 27.8, 34.6, 35.3, 50.3, 81.2, 169.6; ESI-HRMS *m*/*z* calcd for $C_{12}H_{26}NaO_5SSi$ $[M+Na]^+$ 333.1162, found 333.1155.

### *2.2. Synthesis of pure siliceous mesoporous SBA-15 silica*

Pure siliceous mesoporous **SBA-15** silica was prepared with Pluronic 123 (Aldrich, average Mw ≅ 5800) as template agent and tetraethoxysilane (TEOS) as silicon source according to the standard procedure (D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120* : 6024-6036). A typical preparative procedure was as follows: 4.0 g of Pluronic 123 was dissolved in 125 g of 1.9 M HCl aqueous solution under room temperature, followed by adding 8.7 g of TEOS. The resulting mixture was stirred at 40 ºC for 20 h and then aged at 100 ºC for additional 24 h under static condition. The formed solid was collected by filtration, washed with ethanol and dried at room temperature overnight. The template was removed from the above as-synthesized material by refluxing in ethanol (400 mL) for 24 h. And then, the resulted **SBA-15** was washed with ethanol and dried at 70 ºC overnight.

### *2.3. Synthesis of carboxyl tert-butyl ester functionalized mesoporous SBA-15 silica (SBA-15-PTAE)*

4.0 g of pure siliceous mesoporous SBA-15 catalyst (**SBA-15**) was refluxed with *tert*-butyl 2-(3-(trimethoxysilyl)propylthio)acetate (4.3 g, 14 mmol) in 250 mL of dried toluene for 24 h. After filtration, the remaining solid was washed thoroughly with toluene and ethanol, and subsequently dried in oven at 80 °C overnight. Finally, 5.2 g of the white powder was obtained and designated as **SBA-15-PTAE**.

### *2.4. Synthesis of carboxyl functionalized mesoporous SBA-15 silica (SBA-15-PTAA)*

5.2 g of **SBA-15-PTAE** was dispersed in 60 ml of toluene, followed by added dropwise with 20 mL of $H_3PO_4$ (85%). And then the resulting suspension was allowed to stir at room temperature for about 6 h. After filtration, the remaining solid was washed with ethanol until neutral, and subsequently dried in an oven at 80 °C overnight. Finally, 4.8 g of the white powder was obtained and designated as **SBA-15-PTAA**.

### *2.5. Synthesis of $Cu(OAc)_2$-anchored mesoporous SBA-15 catalyst (Cu@SBA-15-PTAA)*

1.00 g of **SBA-15-PTAA** was dispersed in 30 mL of de-ionized water containing 0.12 g of $Cu(OAc)_2 \cdot H_2O$ and the resulted suspension was stirred at room temperature for 12 h. The color of the suspension gradually changed from white to blue. The resulted solid was filtered, thoroughly washed with distilled water to remove any free $Cu(OAc)_2$, and then followed with ethanol. After dried in oven at 80 °C overnight, 1.08 g of bluish solid was finally obtained and designated as **Cu@SBA-15-PTAA** catalyst. The loading of Cu(II) ions in **Cu@SBA-15-PTAA** was determined to be 1.29 mmol/g using atomic absorption spectroscopy (AAS) with an external standard method.

## 3. FT-IR analyses

FT-IR method was employed to confirm the preparation procedures and the results were shown in Figure S1. Comparing with parent **SBA-15**, three new adsorption bands (2979.5 $cm^{-1}$, 2935.2 $cm^{-1}$ and

1714.8 cm$^{-1}$) were observed in IR spectrum of **SBA-15-PTAE** (Figure S1(a) and (b)). The newly observed bands clearly indicated the attachment of organic *tert*-butyl ester moiety onto the surface of **SBA-15**. The strong absorbance band at 1714.8 cm$^{-1}$ was attributed to the $\nu$(C=O) stretching vibration of ester group and two weak adjacent absorption bands at 2979.5 cm$^{-1}$ and 2935.2 cm$^{-1}$ were assigned to the $\nu$(C-H) stretching vibration of organic molecule. After ester being hydrolyzed to acid, the C=O stretching frequency of **SBA-15-PTAA** was shifted to a slightly higher wavelength at 1715.6 cm$^{-1}$ (Figure S1(c)). Further incorporating with Cu(OAc)$_2$, this C=O bond stretching frequency of **Cu@SBA-15-PTAA** was shifted to much lower wavelength at 1617.4 cm$^{-1}$ (Figure S1(d)). A new absorption band at 1359.6 cm$^{-1}$ in the IR spectrum of **Cu@SBA-15-PTAA** was assigned to the vibration of the attached acetate anions.

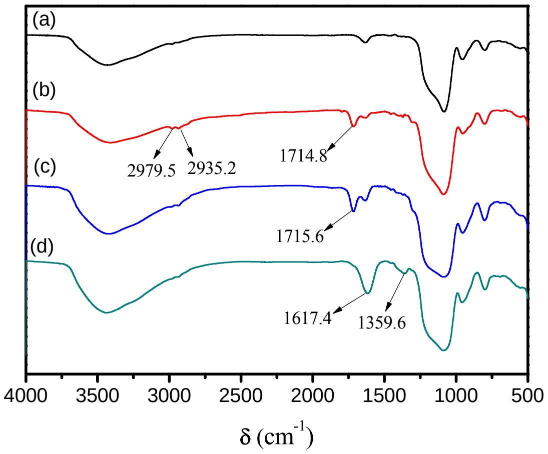


**Figure S1** FT-IR spectra of (a) **SBA-15**, (b) **SBA-15-PTAE**, (c) **SBA-15-PTAA** and (d) **Cu@ SBA-15-PTAA**

## 4. TGA analyses of SBA-15-PTAE and SBA-15-PTAA

The amounts of organic group immobilized on the surfaces of **SBA-15-PTEA** and **SBA-15-PTEA** were measured by thermal gravimetric method. From the TGA and DTG curves of **SBA-15-PTEA** in Figure S2(a), the weight losses below 100 °C and in the range of 100-200 °C were assigned to the water molecules released by the physisorption and the condensation of Si-OH groups bonded to the surface respectively. The weight loss from 200 °C to 700 °C was assigned to the loss of the attached organic group. From this loss mass, a loading of carboxyl *tert*-butyl ester of **SBA-15-PTEA** was calculated to be about 1.27 mmol/g. Similarly, the amount of acid group of **SBA-15-PTAA** was found to be 1.29 mmol/g based on TGA and DTG curves of **SBA-15-PTAA** (Figure S2(b)). These results also indicated that all esters of **SBA-15-PTEA** were converted to corresponding acids after treated with $H_3PO_4$ in toluene.

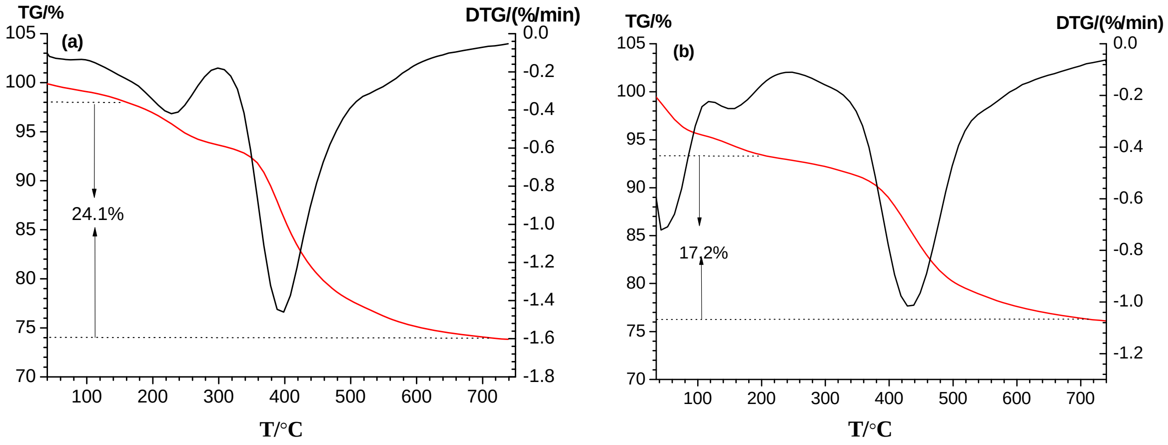


**Figure S2** TGA and DTG curves of (a) **SBA-15-PTAE** and (b) **SBA-15-PTAA**

## 5. Acid capacity determination of SBA-15-PTAA

The amount of acid groups on the surface of **SBA-15-PTAA** was also determined by potentiometric titration method (B. Cinlar and B. H. Shanks, *Appl. Catal. A-Gen.,* **2011**, *396*, 76-84). In a typical experiment, about 0.1 g of **SBA-15-PTAA** was added to 10 mL of 0.1 M aqueous NaCl solution. The resulted suspension was allowed to equilibrate for 48 h and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). With this ion-exchange titration analysis, the amount of COOH on SBA-15 silica surface was determined to be 1.28 mmol/g (Figure S3), which was in good agreement with the result obtained from TGA. In combination with the copper loadings of 1.29 mmol/g in **Cu@SBA-15-PTAA** based on AAS analysis, it showed that the anchoring of $Cu(OAc)_2$ on **SBA-15-PTAA** to form **Cu@SBA-15-PTAA** with a 1:1 complex.

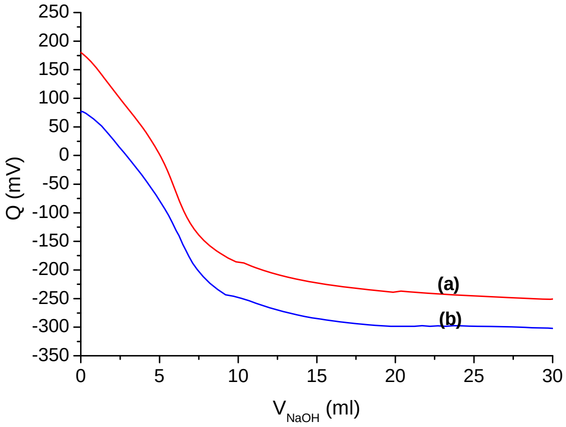


**Figure S3** Potentiometric titration curves of **SBA-15-PTAA** (a) 94 mg and (b) 85 mg

## 6. Nitrogen gas sorption analyses

Figure S4 displayed the $N_2$ adsorption/desorption isotherms and pore size distributions of **SBA-15**, **SBA-15-PTAA** and **Cu@SBA-15-PTAA** at 77 K and the calculating results of surface area, pore volume and pore size were summarized in Table S1. Both the samples showed a typical type IV isotherm with a very large hysteresis loop in the 0.5 to 0.8 $P/P^o$ range. The isotherms accounted for the relatively ordered mesopore and the hysteresis loop was the characteristic for the large tubular pores of SBA-15. As expected, the immobilizations significantly decreased the BET surface area, pore volumes and pore size. For instance, the values of BET surface area, pore volumes and pore size of the **SBA-15** were 678 m$^2$/g, 0.88 cm$^3$/g and 51.9 Å respectively (Entry 1, Table S1). After immobilized with organic carboxylic acid group, these values reduced to 431 m$^2$/g, 0.59 cm$^3$/g and 50.9 Å (Entry 2, Table S1). These values further slightly decreased after subsequently anchoring $Cu(OAc)_2$ (Entry 3, Table S1), suggesting the copper-sites inside the channels of SBA-15 in some extent. Nevertheless, it was noteworthy to point out that the pore size of our prepared **Cu@SBA-15-PTAA** reached to 49.6 Å, which was adequate for most organic molecules to enter in and carry out the reaction.

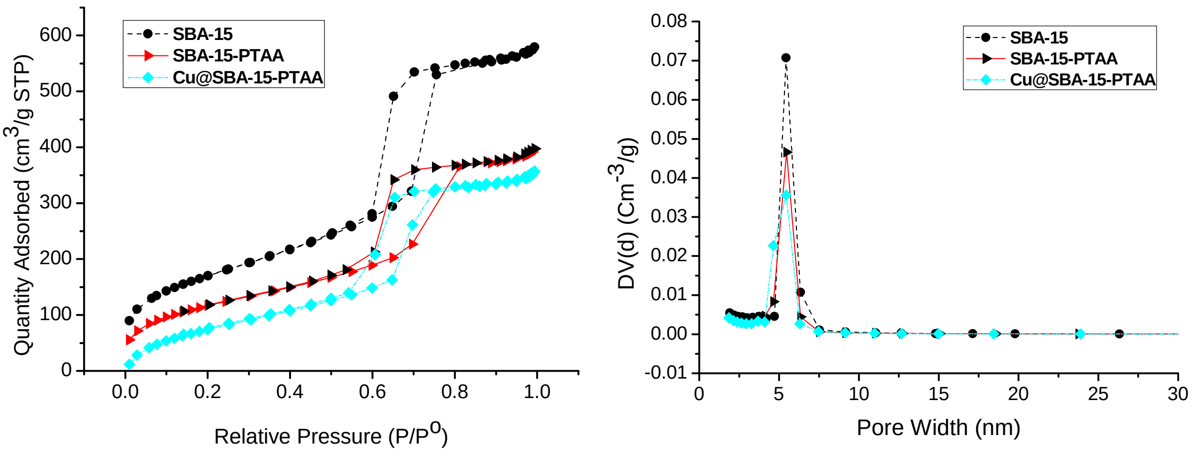


**Figure S4** Nitrogen gas adsorption/desorption isotherms and pore size distributions of **SBA-15**, **SBA-15-PTAA** and **Cu@SBA-15-PTAA**

**Table S1** $N_2$ adsorption/desorption results of **SBA-15**, **SBA-15-PTAA** and **Cu@SBA-15-PTAA**

| Entry | Catalysts | $S_{BET}$ (m$^2$/g) | $V_p$[a] (cm$^3$/g) | $D_p$[b] (Å) |
|---|---|---|---|---|
| 1 | SBA-15 | 621 | 0.88 | 51.9 |
| 2 | SBA-15-PTAA | 431 | 0.59 | 50.9 |
| 3 | Cu@SBA-15-PTAA | 411 | 0.58 | 49.6 |

[a] The pore volume ($V_p$) taken at $P/P_o = 0.97$ single point.

[b] Average pore diameter ($D_p$) from desorption branch applying the BJH model.

## 7. EXAFS fitting results of Cu@SBA-15-PTAA

**Table S2** Summary of EXAFS first shell fitting results [a,b]

| | edge or pre-edge energy (ev) | OS | coordination atom | CN | *d* (Å) |
|---|---|---|---|---|---|
| **Cu@SBA-15-PTAA** | 8977.2 (pre-edge) | +2 | O | 4.0 | 1.96 |

[a] OS: oxidation state; CN: coordination number; *d*: bond distance. [b] R-space spectra and fitting results ($2.408 < k < 12.626$ Å$^{-1}$ and $1.00 < R < 1.84$ Å), EXAFS spectra of **Cu@SBA-15-PTAA**.

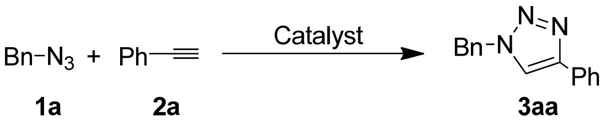
## 8. General procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles from organic azides and terminal alkynes under the catalysis of Cu@SBA-15-PTAA in water

To a 10 mL tube, were successively charged with azides (1.0 mmol), alkylnes (1.1 mmol), **Cu@SBA-15-PTAA** (16.0 mg, 2 mol%) and de-ionized water (2 mL), followed by sealed with a screw cap. The suspension mixtures were stirred at 50 °C for several hours until the reactions were completed based on HPLC analysis. The generated products were extracted with ethyl acetate (3 mL x 4), while the catalyst **Cu@SBA-15-PTAA** remained in aqueous phase, which could be directly reused in the next run. The organic extractions were combined, dried with anhydrous $Na_2SO_4$ and concentrated under vacuo. Finally, the resulting residues were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate), affording the desired 1,4-disubstituted 1,2,3-triazoles.

## 9. Optimization of the reaction conditions

With **Cu@SBA-15-PTAA-**catalyzed cycloaddition reaction of benzyl azide **1a** (1 mmol) and phenyl alkyne **2a** (1.1 mmol) to form 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **3aa** as a model reaction, a wide range of reaction parameters including the amount of catalyst, solvent, reaction temperature were optimized and the results were summarized in Table S3. Blank experiment indicated that in absence of catalyst nearly no reaction occurred between **1a** and **2a** after stirred in water at 50 °C for 12 h (Entry 1, Table S3). However, in the presence of 1 mol% of **Cu@SBA-15-PTAA** and under the same reaction conditions, the corresponding 1,4-disubstituted cycloaddition product **3aa** was obtained as a single regioisomer in 80% yield based on HPLC analyses (Entry 2, Table S3). After increasing the catalyst loading to 2 mol%, completed reaction was observed after 8 h of reaction time and a 98% isolated yield of **3aa** was achieved (Entry 3, Table S3). The catalyst **Cu@SBA-15-PTAA** also showed its catalytic ability on this cycloaddition reaction at room temperature (25 °C), despite that the reaction rate was much slower than that at 50 °C (Entry 4, Table S3). Furthermore, it was found that much lower yields (12-58%) were resulted when the reaction was performed in MeOH, EtOH, MeCN, Toluene and THF and nearly no reaction occurred in DCM (Entries 5-10, Table S3). In order to confirm the true catalytic species for this reaction, several control experiments were also performed. We found that $Cu(OAc)_2$ exhibited definitely catalytic activity on the cycloaddition reaction of **1a** and **1b** in water, which was in accordance with the previous reports (K. R. Reddy, K. Rajgopal and M. L. Kantam, *Synlett,* **2006**, 957-959). However, its catalytic ability was far inferior to **Cu@SBA-15-PTAA**, and only 20% of cyclization product was afforded with the same catalyst loading (2 mol%) and under the same reaction conditions (Entry 11, Table S3). Whereas the naked **SBA-15-PTAA** has no activity on the reaction (Entries 12 and 13, Table S3). Based on these experimental results, it can conclude that the grafted Cu(II) cations were the actual catalytic species for this cycloaddition reaction and the structure of **Cu@SBA-15-PTAA** played a crucial role on its catalysis activity.

**Table S3** Optimizing the reaction condition for 1,3-dipolar cycloaddition of benzyl azide and phenyl alkyne under the catalysis of **Cu@SBA-15-PTAA** [a]



| Entry | Catalyst (x mol% Cu) | T (°C) | Solvent | Time (h) | Yield [b] (%) |
|---|---|---|---|---|---|
| 1 | - | 50 | $H_2O$ | 12 | Trace |
| 2 | Cu@ SBA-15-PTAA (1) | 50 | $H_2O$ | 12 | 80 |
| 3 | Cu@ SBA-15-PTAA (2) | 50 | $H_2O$ | 8 | >99 (98) |
| 4 | Cu@ SBA-15-PTAA (2) | 25 | $H_2O$ | 8 | 32 |
| 5 | Cu@ SBA-15-PTAA (2) | 50 | MeOH | 8 | 42 |
| 6 | Cu@ SBA-15-PTAA (2) | 50 | EtOH | 8 | 58 |
| 7 | Cu@ SBA-15-PTAA (2) | 50 | MeCN | 8 | 12 |
| 8 | Cu@ SBA-15-PTAA (2) | 50 | Toluene | 8 | 14 |
| 9 | Cu@ SBA-15-PTAA (2) | 50 | THF | 8 | 28 |
| 10 | Cu@ SBA-15-PTAA (2) | 50 | DCE | 8 | Trace |
| 11 | $Cu(OAc)_2$ (2) | 50 | $H_2O$ | 8 | 20 |
| 12 | SBA-15-PTAA (16 mg) | 50 | $H_2O$ | 8 | Trace |
| 13 | $Cu(OAc)_2$ (2) + SBA-15-PTAA (16 mg) | 50 | $H_2O$ | 8 | 26 |

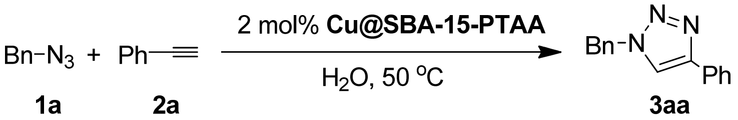
[a] Reaction conditions: benzyl azide **1a** (1.0 mmol, 0.140 g), phenyl alkyne **2a** (1.1 mmol, 0.115 g), catalyst, solvent (2 mL), in a 10 mL sealed tube.

[b] HPLC yields, the datum in parentheses was isolated yield.

## 10. Recyclability test

The reusability of the **Cu@SBA-15-PTAA** catalyst was also studied and the cycloaddition reaction of benzyl azide **1a** and phenyl alkyne **2a** to form 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **3aa** under the identified reaction conditions (with 2 mol% **Cu@SBA-15-PTAA** as catalyst, at 50 °C and in water) was employed as the tested reaction. After completed the first run (8 h) using the fresh catalyst, product **3aa** was extracted with ethyl acetate. Then, to the residual catalyst-containing aqueous suspension phase, was added fresh benzyl azide and phenyl alkyne. As the results illustrated in Table S4, the catalyst did not lose any activity for three cycles. A reduced catalytic activity was observed in subsequent cycles, however, complete reaction still could be achieved at the fourth cycle and 80% yield for the five cycles after prolonging the reaction time to 12 h. In this regard, the catalyst **Cu@SBA-15-PTAA** could be reused for at least 5 times.

**Table S4** Reusability of **Cu@SBA-15-PTAA** catalyst for 1,3-dipolar cycloaddition of benzyl azide and phenyl alkyne [a]



| Cycle(n) | Time | Yield (%) [b] |
|---|---|---|
| Fresh | 8 | >99 |
| 1 | 8 | >99 |
| 2 | 8 | >99 |
| 3 | 8 | 98 |
| 4 | 8 (12) | 88 (>99) |
| 5 | 8 (12) | 70 (80) |

[a] Reaction conditions: benzyl azide **1a** (1.0 mmol, 0.140 g), phenyl alkyne **2a** (1.1 mmol, 0.115 g), **Cu@SBA-15-PTAA** (2 mol% Cu), $H_2O$ (2 mL), at 50 °C, in a 10 mL sealed tube.

[b] HPLC yields.

## 11. Characterization of the reused catalyst

### *11.1. XRD analysis*

Figure S5 showed the XRD patterns of fresh Cu@SBA-15-PTAA and resued Cu@SBA-15-PTAA after the third cycle. There was no obvious difference between these two samples, which indicated that the structure of the catalyst remained unchanged after catalytic reaction.

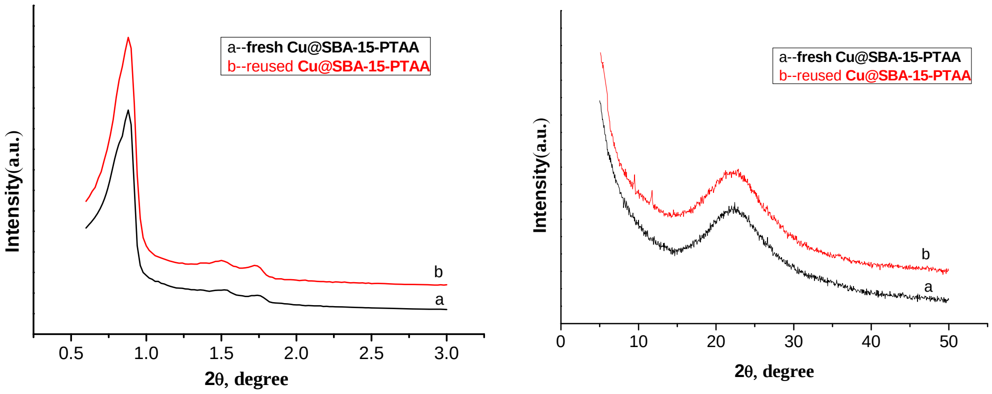


**Figure S5** Small- and wide-angle powder XRD patterns of (a) **fresh Cu@SBA-15-PTAA** and (b) **resued Cu@SBA-15-PTAA** after the third cycle

### *11.2. EPR analysis*

The reused **Cu@SBA-15-PTAA** after the third cycle was also performed with EPR analysis. Its EPR spectrum in Figure S6 indicated that the Cu of the catalyst remained in the +2 oxidation state after catalytic reaction.

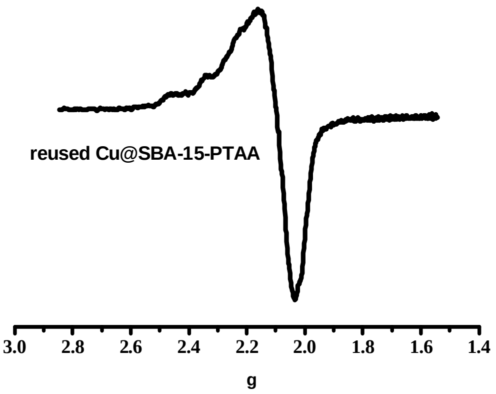


**Figure S6.** EPR spectrum of **resued Cu@SBA-15-PTAA** after the third cycle

## 12. Leaching experiments

### *12.1. Hot filtration test*

Benzyl azide **1a** and phenyl alkyne **2a** were firstly stirred in water at 50 °C for 4 h under the catalysis of **Cu@SBA-15-PTAA** (2 mol%). In this step, it was realized that about 77% of **1a** reacted with **2a** to form corresponding 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **3aa**. Then the reaction mixture was filtered to remove the catalyst. In this step, the formed product **3aa** was removed together because of its insolubility in water. The resulting filtrate again continued to be stirred by itself at 50 °C for another 4 h. It was found that only a very small amount of **3aa** (less than 3%) was formed based on HPLC analysis.

### *12.2. Measurements of Cu leaching in aqueous phase after catalytic reaction and the Cu content of the reused Cu@SBA-15-PTAA*

After the reaction of benzyl azide **1a** and phenyl alkyne **2a** was finished, the formed product was extracted with ethyl acetate, followed by filtrating to remove the catalyst. Then the filtrate was diluted with 5 wt% of Cu nitric acid and performed the atomic absorption spectrometry measurement. Nearly no copper species were detected in this solution. To confirm the Cu leaching of the catalyst, the Cu content of the resued **Cu@SBA-15-PTAA** with different cycles were further measured. Prior to the measurements by atomic absorption spectrometry, the reused catalysts were digested in 65 wt % of nitric acid for 24 h. The results in Table S5 showed that the Cu leaching from the catalyst was ignorable even after the third cycle (within the experimental error). However, a slight leaching was observed in subsequent cycles. Nevertheless, it was still be active at the fifth cycle (see Table S4). Above experimental results signified that **Cu@SBA-15-PTAA** was very stable during the course of the reaction and Cu(II) was tightly grafted on the **SBA-15-PTAA** support.

**Table S5** Cu content of **Cu@SBA-15-PTAA** with different cycles [a]

| Cycle (n) | Cu (mmol/g) |
|---|---|
| Fresh | 1.29 |
| 1 | 1.26 |
| 2 | 1.27 |
| 3 | 1.28 |
| 4 | 1.07 |
| 5 | 0.94 |

[a] Measured by atomic absorption spectrometry with standard curve method.

## 13. Mechanism studies

### *13.1. Kinetic experimental*

Figure S7 exhibited the kinetic curves of the reaction times *vs*. the HPLC yields of **3aa** for the cycloaddition reaction of benzyl azide **1a** and phenyl alkyne **2a** under the identified reaction conditions (with 2 mol% **Cu@SBA-15-PTAA** as catalyst, at 50 °C and in water). The results showed that no obviously induction period was observed for the reaction.

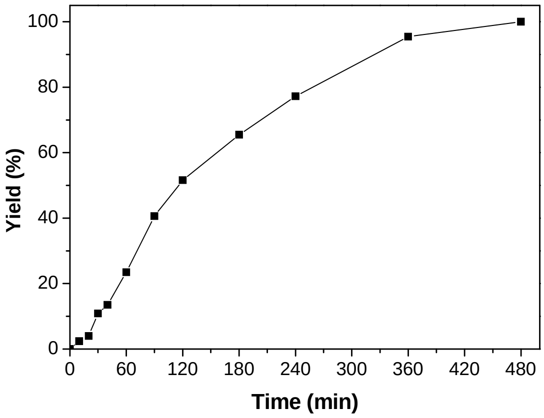
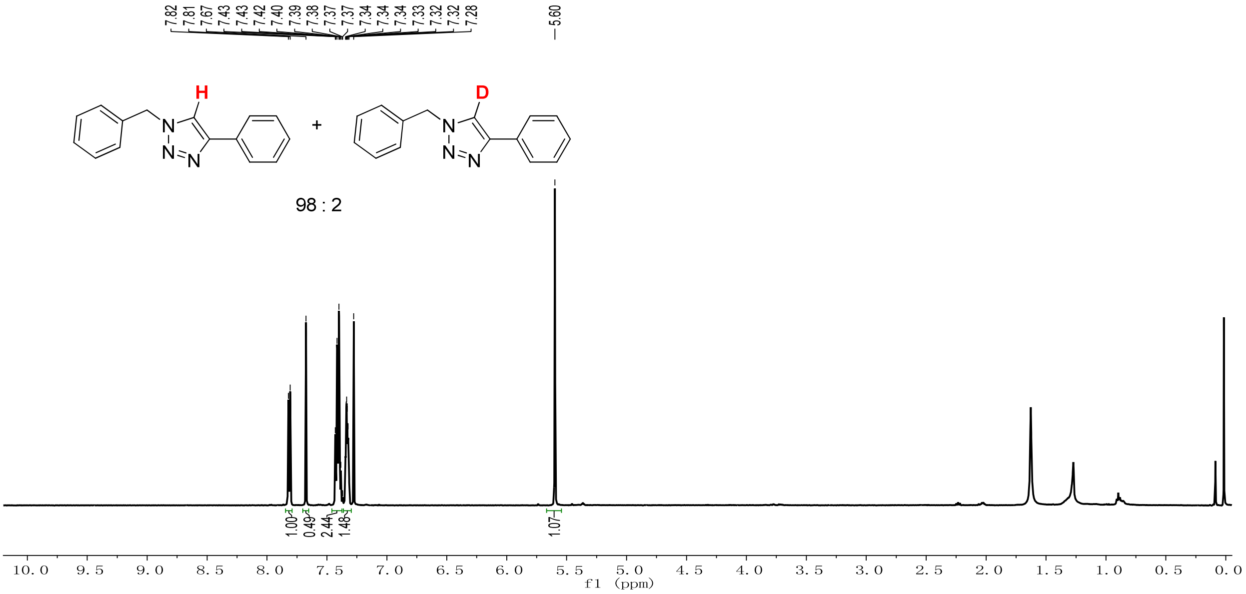


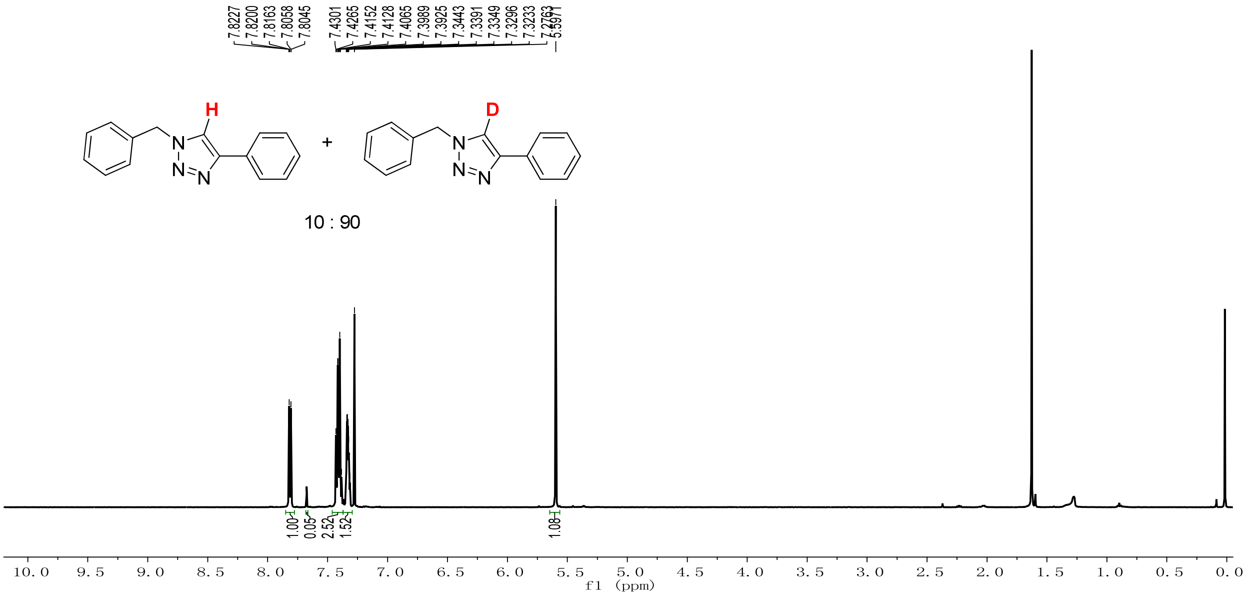
**Figure S7** Kinetic profile of **Cu@SBA-15-PTAA-**catalyzed CuAAC reaction in water. Reaction conditions: benzyl azide **1a** (1.0 mmol, 0.140 g), phenyl alkyne **2a** (1.1 mmol, 0.115 g),

**Cu@SBA-15-PTAA** (2 mol% Cu), $H_2O$ (2 mL), at 50°C, in a 10 mL sealed tube.

### *13.2. The Proton NMR spectrum of 1,2,3-triazole product of the reaction of benzyl azide and 1-deuterium-substituted phenyl alkyne in $H_2O$*



### *13.3. The Proton NMR spectrum of 1,2,3-triazole product of the reaction of benzyl azide and phenyl alkyn in $D_2O$*



## 14. Characterization data for 1,4-disubstituted 1,2,3-triazoles

### 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (3aa, CAS No: 108717-96-0)

Yield: 98%; White solid, m.p.:127.5 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* =7.2 Hz, 2H), 7.68 (s, 1H), 7.43-7.38 (m, 5H), 7.34-7.31 (m, 3H), 5.58 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 148.2, 134.7, 130.5, 129.2, 128.79, 128.77, 128.2, 128.0, 125.7, 119.5, 54.2.

### 1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3ab, CAS No: 116557-81-4)

Yield: 98%; White solid, m.p.: 137.1 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.8 Hz, 2H), 7.59 (s, 1H), 7.42-7.38 (m, 3H), 7.33-7.31 (m, 2H), 6.94 ((d, *J* = 8.8 Hz, 2H), 5.57 (s, 2H), 3.84 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 159.6, 148.1, 134.8, 129.1, 128.7, 128.1, 127.0, 123.3, 118.7, 114.2, 55.3, 54.2.

### 1-Benzyl-4-(biphenyl-4-yl)-1*H*-1,2,3-triazole (3ac, CAS No: 1188337-88-3)

Yield: 99%; White solid, m.p.: 224.1 °C; $^{1}$H NMR (500 MHz, DMSO): δ = 8.72 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43-7.34 (m, 6H), 5.67 (s, 2H); $^{13}$C NMR (125 MHz, DMSO): δ = 146.3, 139.55, 139.46, 136.0, 129.8, 128.97, 128.82, 128.2, 127.9, 127.6, 127.1, 126.5, 125.7, 121.7, 53.1.

### 1-Benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole (3ad, CAS No: 1009089-48-8)

Yield: 93%; White solid, m.p.: 148.6 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.69 (s, 1H), 7.67 (d, *J* = 2.8 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.43-7.39 (m, 3H), 7.34-7.32 (m, 2H), 5.59 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 147.2, 134.5, 131.9, 129.5, 129.2, 128.9, 128.1, 127.2, 122.0, 119.6, 54.3.

### 1-Benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (3ae, CAS No: 104951-45-3)

Yield: 94%; Yellow solid, m.p.: 164.4 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 9.0Hz, 2H), 7.98 (d, *J* = 8.8Hz, 2H), 7.81 (s, 1H), 7.45-7.41 (m, 3H), 7.36-7.34 (m, 2H), 5.63 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 147.4, 146.1, 136.8, 134.2, 129.3, 129.1, 128.2, 126.2, 124.3, 120.9, 54.5.

**1-Benzyl-4-(3-aminophenyl)-1*H*-1,2,3-triazole (3af, CAS No: 1151920-00-1)**

Yield: 96%; Yellow solid, m.p.: 149.5 °C; $^{1}$H NMR (500 MHz, DMSO): δ = 8.47 (s, 1H), 7.40-7.33 (m, 5H), 7.11 (s, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.62 (s, 2H), 5.17 (s, 2H); $^{13}$C NMR (125 MHz, DMSO): δ = 149.0, 147.3, 136.1, 131.1, 129.3, 128.7, 128.1, 127.9, 121.1, 113.6, 113.0, 110.4, 52.9.

**1-Benzyl-4-(4-ethynylphenyl)-1*H*-1,2,3-triazole (3ag, CAS No: 1248568-43-5)**

Yield: 94%; White solid, m.p.: 161.0 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.54 (d, *J* = 4.9 Hz, 2H), 7.43-7.39 (m, 3H), 7.34-7.32 (m, 2H), 5.60 (s, 2H), 3.13 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 147.5, 134.5, 132.6, 130.9, 129.2, 128.9, 128.1, 125.5, 121.8, 119.8, 83.5, 77.9, 54.3.

**1-Benzyl-4-butyl-1*H*-1,2,3-triazole (3ah, CAS No: 871689-95-1)**

Yield: 92%; White solid, m.p.: 60.4 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 3H), 7.27-7.25 (m, 2H), 7.19 (s, 1H), 5.50 (s, 2H), 2.70 (t, *J* = 7.6 Hz 2H), 1.63 (quint, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 148.9, 135.0, 129.0, 128.6, 127.9, 120.4, 53.9, 31.5, 25.4, 22.3, 13.8; GC-MS (EI): m/z 215 ($M^+$), 130 (100).

**1-Benzyl-4-cyclopropyl-1*H*-1,2,3-triazole (4ai, CAS No: 1151920-05-6)**

Yield: 97%; White solid, m.p.: 57.9 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.34 (m, 3H), 7.27-7.25 (m, 2H), 7.15 (s, 1H), 5.47 (s, 2H), 1.95-1.90 (m, 1H), 0.95-0.91 (m, 2H), 0.84-0.81 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 150.7, 134.9, 129.0, 128.6, 128.0, 119.5, 54.0, 7.7, 6.7.

**2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (3aj, CAS No: 116557-80-3)**

Yield: 98%; White solid, m.p.: 79.5 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.34 (m, 4H), 7.28-7.27 (m, 2H), 5.49 (s, 2H), 1.61 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 156.0, 134.6, 129.1, 128.7, 128.1, 119.0, 68.5, 54.1, 30.4.

***N*-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)aniline (3ak, CAS No: 958986-30-6)**

Yield: 91%; White solid, m.p.: 104.7 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.34 (m, 4H), 7.26-7.24 (m, 2H), 7.19 (t, $J$ = 7.9 Hz, 2H), 6.75 (t, $J$ = 7.3 Hz, 1H), 6.66 (d, $J$ = 7.9 Hz, 2H), 5.50 (s, 2H), 4.44 (s, 2H), 4.21 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 147.6, 146.7, 134.7, 129.3, 129.1, 128.7, 128.0, 121.5, 118.0, 113.2, 54.1, 40.0.

**1-Benzyl-4-(*p*-tolylthiomethyl)-1*H*-1,2,3-triazole (3al, CAS No: 1643792-66-8)**

Yield: 96%; White solid, m.p.: 82.7 °C, $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.35 (m, 3H), 7.21-7.19 (m, 5H), 7.04 (d, $J$ = 8.0 Hz, 2H), 5.47 (s, 2H), 4.17 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 145.5, 136.8, 134.7, 131.5, 130.7, 129.7, 129.1, 128.7, 127.9, 122.0, 54.1, 29.8, 21.0.

**1-Benzyl-4-(benzyloxymethyl)-1*H*-1,2,3-triazole (3am, CAS No: 1049744-08-2)**

Yield: 96%; White solid, m.p.: 56.4 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.47 (s, 1H), 7.41-7.37 (m, 3H), 7.35-7.34 (m, 4H), 7.32-7.28 (m, 3H), 5.53 (s, 2H), 4.67 (s, 2H), 4.60 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 145.7, 137.8, 134.6, 129.1, 128.8, 128.4, 128.2, 127.9, 127.8, 122.4, 72.6, 63.7, 54.2.

**Ethyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (3an, CAS No: 126800-24-6)**

Yield: 97%; White solid, m.p.: 88.4 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.37-7.33 (m, 3H), 7.28-7.25 (m, 2H), 5.56 (s, 2H), 4.35 (q, $J$ = 7.2 Hz, 2H), 1.34 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 160.5, 140.4, 133.7, 129.1, 128.9, 128.1, 127.3, 61.1, 54.2, 14.1.

**3-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (3ao, CAS No: 1034194-35-8)**

Yield: 96%; White solid, m.p.: 101.1 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 1.8 Hz, 1H), 8.57 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.19 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.76 (s, 1H), 7.44-7.39 (m, 3H), 7.38-7.33 (m, 3H), 5.61 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 149.3, 147.1, 145.2, 134.4, 133.0, 129.3, 129.0, 128.1, 126.7, 123.7, 119.8, 54.4.

**2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (3ap, CAS No: 862675-34-1)**

Yield: 94%; White solid, m.p.: 116.6 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 5.2 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.06 (s, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42-7.37 (m, 3H), 7.35-7.33 (m, 2H), 7.24-7.21 (m, 1H), 5.60 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 150.3, 149.4, 148.8, 136.9, 134.3, 129.2, 128.9, 128.3, 122.9, 121.9, 120.3, 54.4.

**1-Benzyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (3aq, CAS No: 876744-92-2)**

Yield: 97%; White solid, m.p.: 125.4 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.60 (s, 1H), 7.41-7.37 (m, 3H), 7.35 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.32-7.30 (m, 2H), 7.28-7.27 (m, 1H), 7.06-7.04.(m, 1H), 5.55 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ= 143.2, 134.5, 132.8, 129.1, 128.8, 128.0, 127.5, 125.0, 124.1, 119.0, 54.2.

**1,4-Diphenyl-1*H*-1,2,3-triazole (3ba, CAS No: 13148-78-2)**

Yield: 96%; White solid, m.p.: 185.6 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.94-7.93 (m, 2H), 7.83-7.81 (m, 2H), 7.59-7.56 (m, 2H), 7.50-7.47 (m, 3H), 7.41-7.38 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 148.4, 137.1, 130.3, 129.8, 128.9, 128.8, 128.4, 125.9, 120.6, 117.6; GC-MS (EI): m/z 221 ($M^+$), 193 (100).

**4-Butyl-1-phenyl-1*H*-1,2,3-triazole (3bh, CAS No: 151451-82-0)**

Yield: 93%; White solid, m.p.: 69.9 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.73-7.72 (m, 3H), 7.53-7.50(m, 2H), 7.43-7.40 (m, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 1.73 (quint, *J* = 7.5 Hz, 2H), 1.44 (sext, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ= 149.2, 137.3, 129.7, 128.4, 120.4, 118.8, 31.5, 25.4, 22.4, 13.9.

**2-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (3bj, CAS No: 856863-40-6)**

Yield: 95%; White solid, m.p.: 97.9 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.72-7.70 (m, 2H), 7.52-7.48 (m, 2H), 7.44-7.41 (m, 1H), 3.11 (s, 1H), 1.71 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 156.4, 137.1, 129.7, 128.6, 120.5, 117.6, 68.6, 30.5.

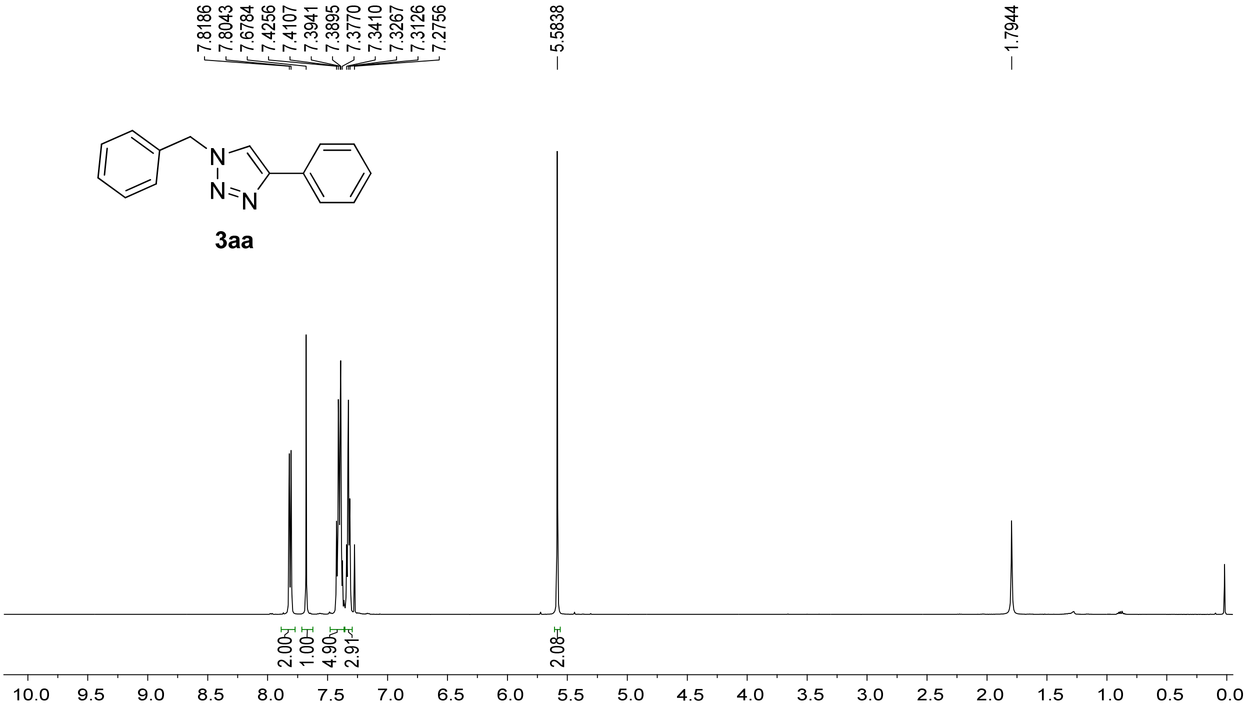
**N-((1-Phenyl-1*H*-1,2,3-triazol-4-yl)methyl)aniline (3bk, CAS No: 867030-69-1)**

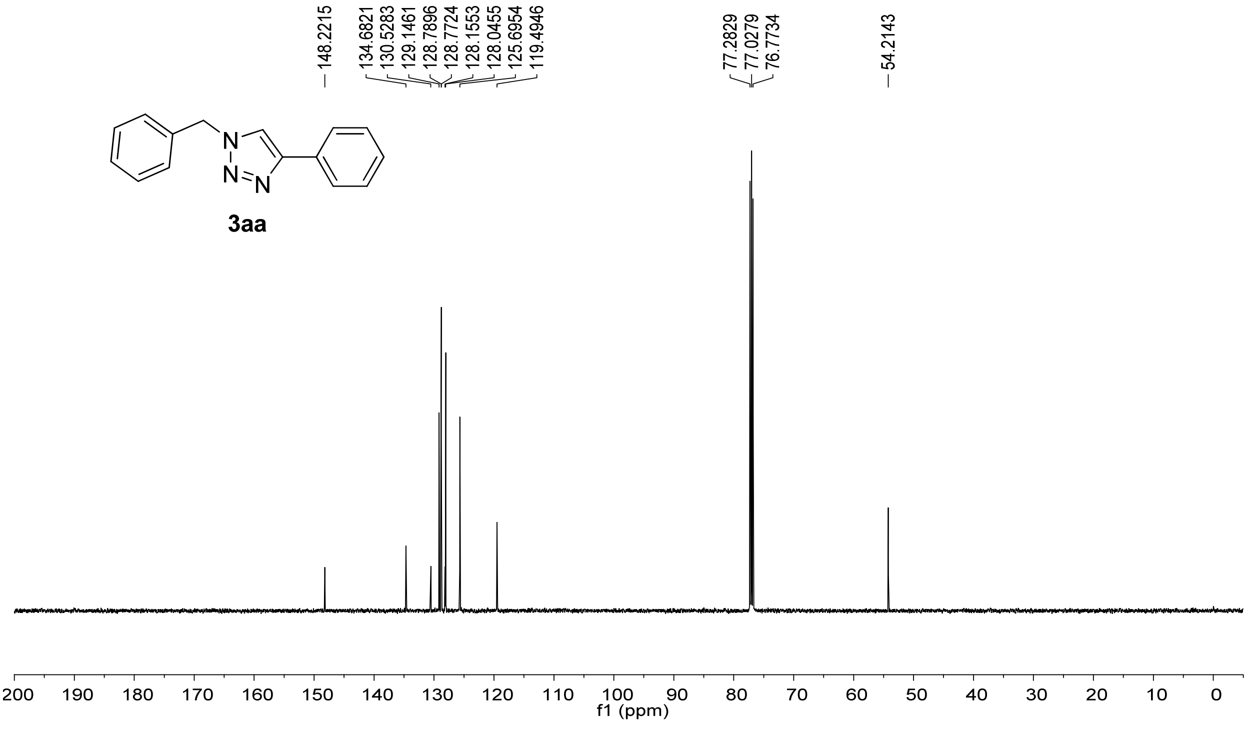
Yield: 94%; White solid, m.p.: 146.6 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.72-7.70 (m, 2H), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 1H), 7.24-7.20 (m, 2H), 6.77 (t, *J* = 7.3Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 4.57 (s, 2H), 4.32 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 147.5, 147.1, 137.0, 129.7, 129.3, 128.7, 120.5, 119.8, 118.2, 113.2, 40.0.

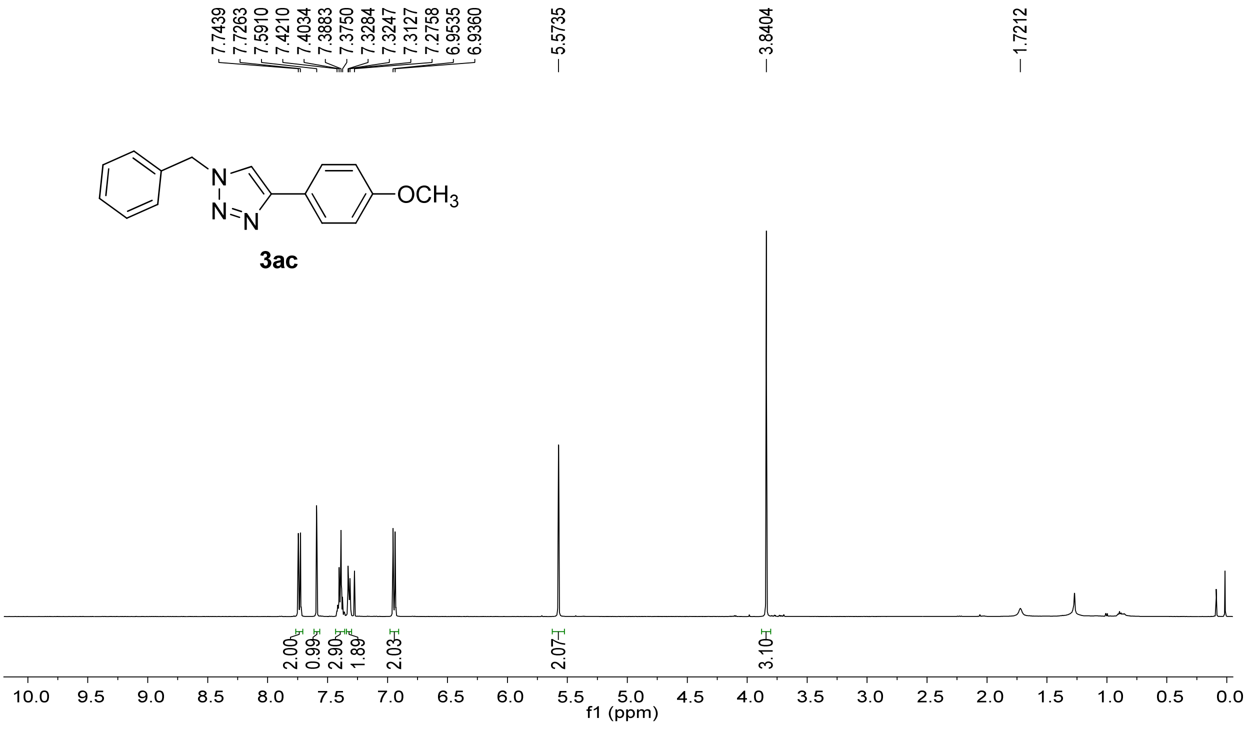
**4-(Benzyloxymethyl)-1-phenyl-1*H*-1,2,3-triazole (3bm, CAS No: 400083-26-3)**

Yield: 96%; Yellow liquid; 1H NMR (500 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.75-7.73 (m, 2H), 7.55-7.52 (m, 2H), 7.47-7.44 (m, 1H), 7.42-7.36 (m, 4H), 7.34-7.30 (m, 1H), 4.79 (s, 2H), 4.68 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 146.0, 137.7, 137.1, 129.7, 128.8, 128.5, 128.0, 127.9, 120.8, 120.6, 72.7, 63.7.

## 15. Proton NMR and $^{13}$C NMR Spectra for 1,4-disubstituted 1,2,3-triazoles



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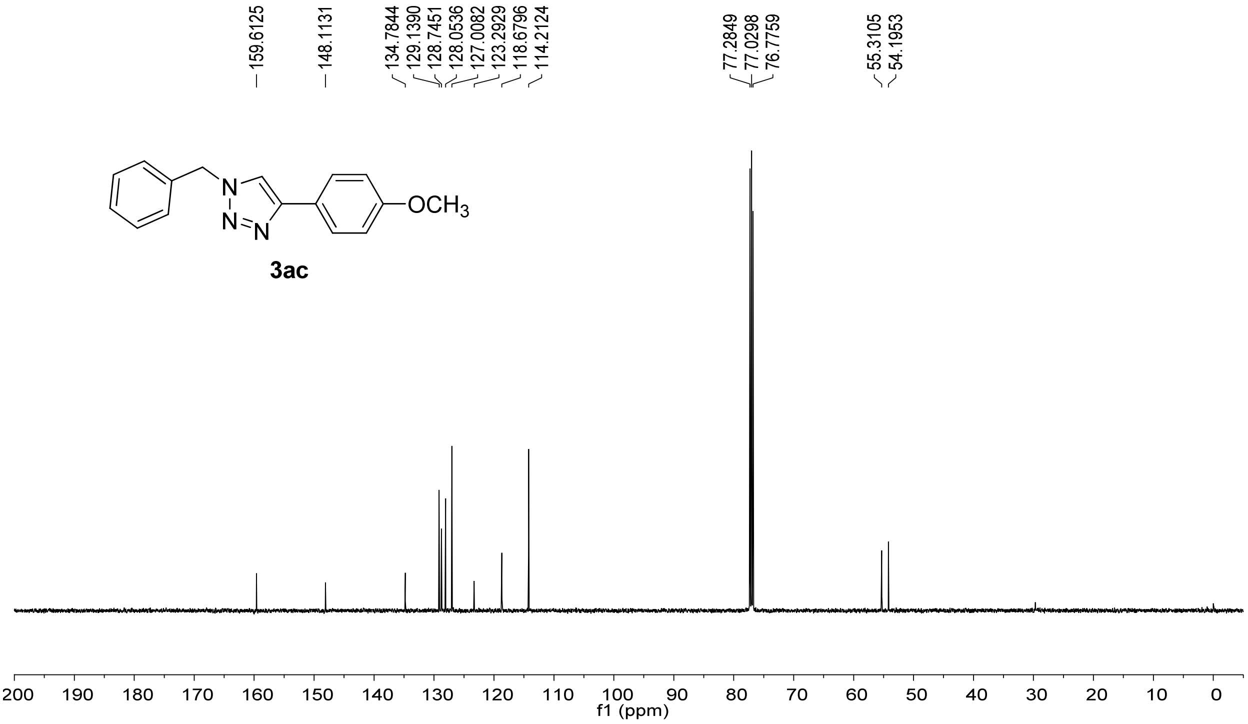
6.9360
5.5735
3.8404
1.7212
N
N
N
OCH$_3$
3ac
2.00
0.99
2.90
1.89
2.03
2.07
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0298
76.7759
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N
N
OCH$_3$
3ac
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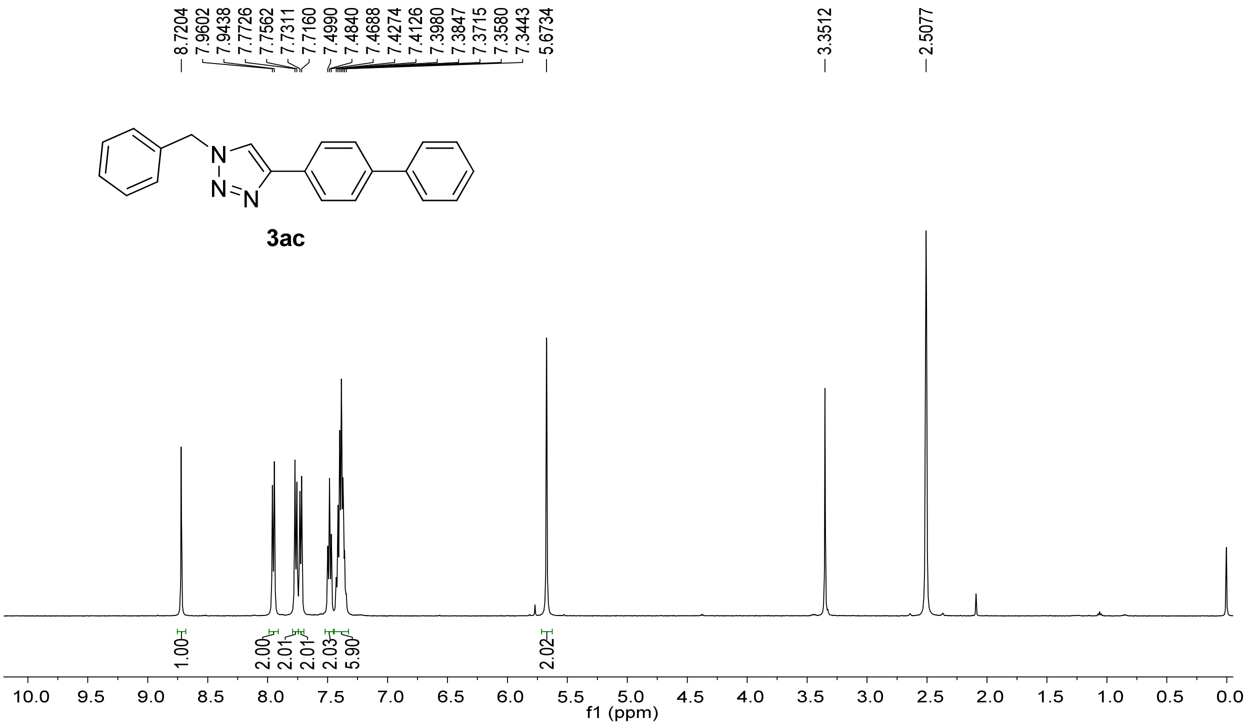
f1 (ppm)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2.5077
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N
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2.00
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2.01
2.03
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2.02
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
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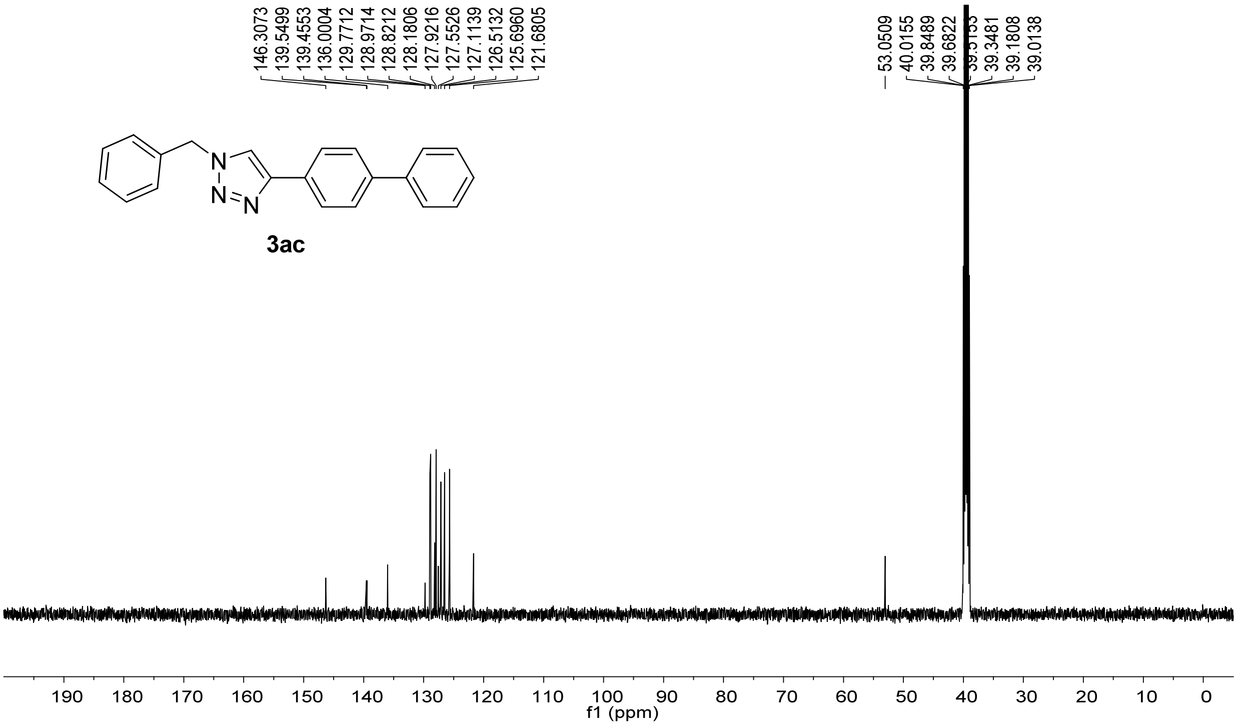
0.5
0.0
f1 (ppm)

**3ac**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39.6822
39.3481
39.1808
39.0138
N
N
N
190
180
170
160
150
140
130
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110
100
90
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70
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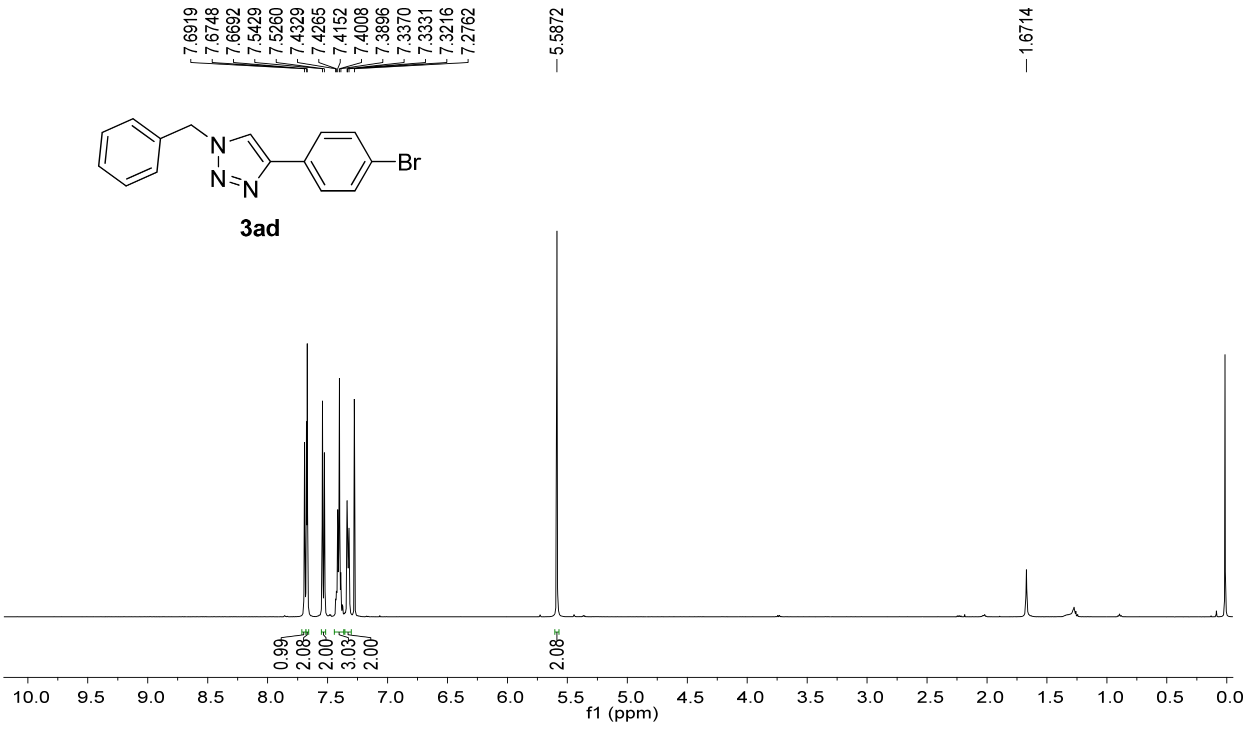
50
40
30
20
10
0
f1 (ppm)

**3ac**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7.3331
7.3216
7.2762
5.5872
1.6714
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N
N
Br
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2.00
3.03
2.00
2.08
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9.0
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7.0
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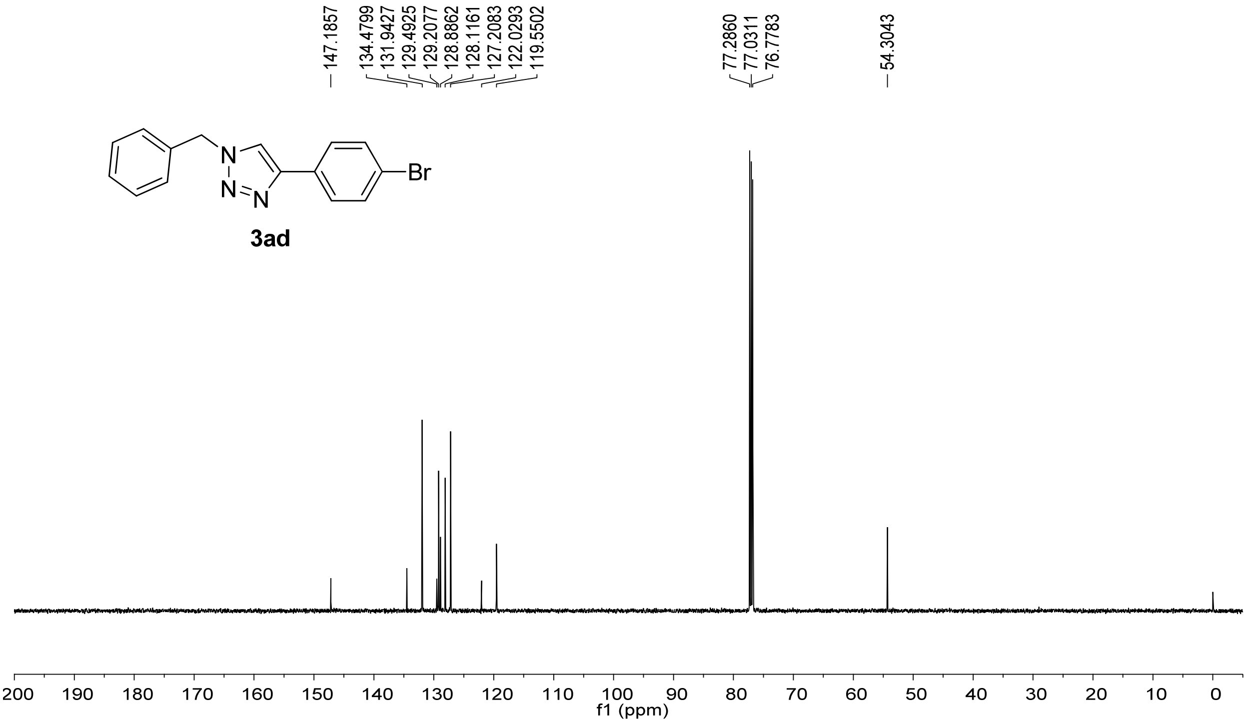
0.5
0.0
f1 (ppm)

**3ad**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77.0311
76.7783
54.3043
N
N
N
Br
200
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180
170
160
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140
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110
100
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70
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30
20
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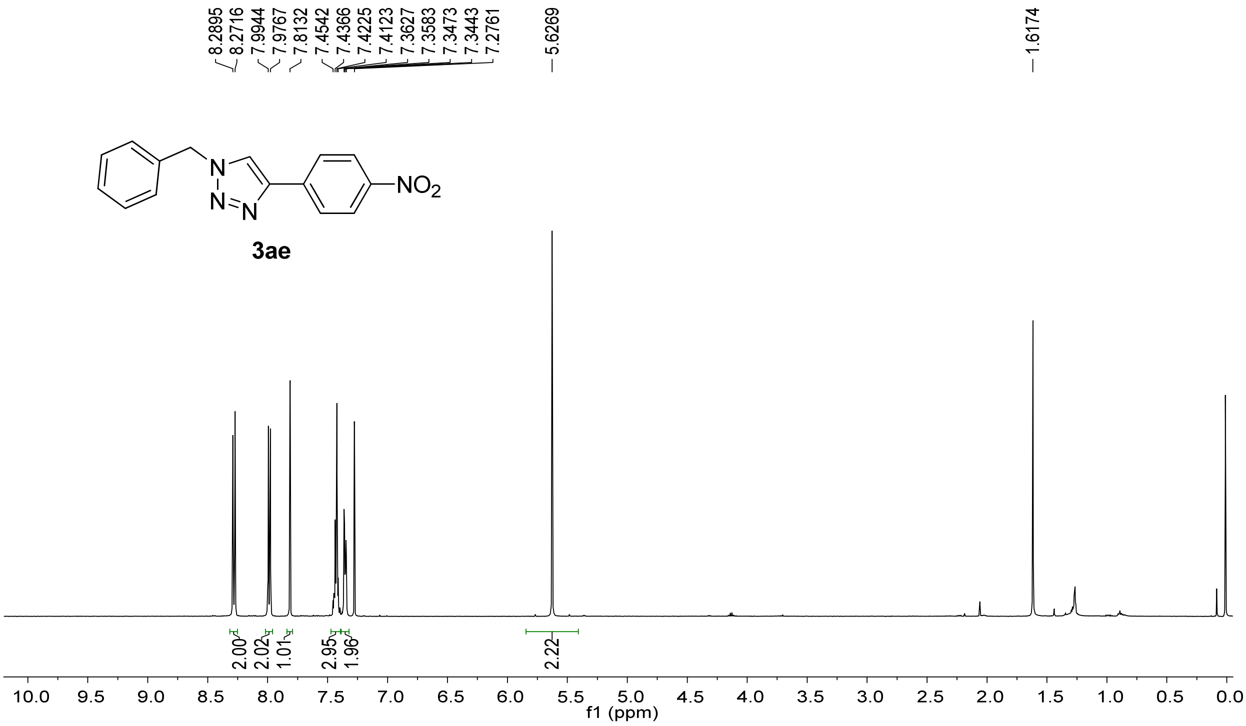
f1 (ppm)

**3ad**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7.2761
5.6269
1.6174
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N
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NO2
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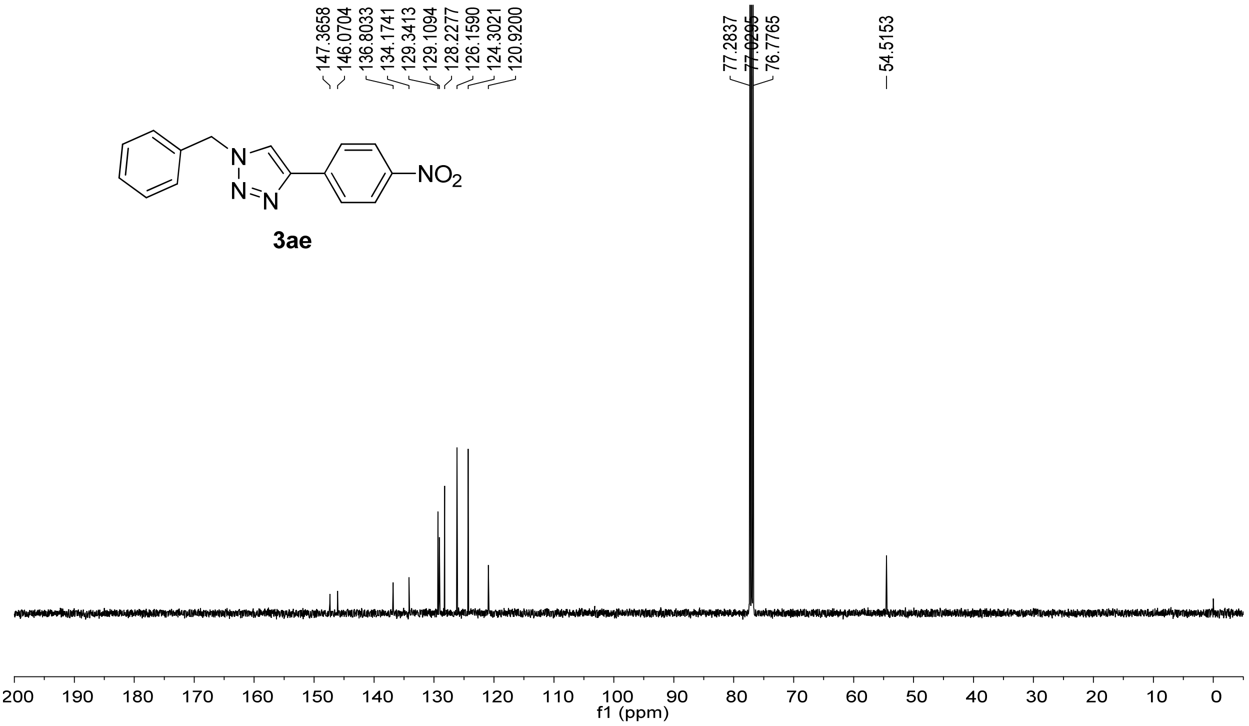
2.00
2.02
1.01
2.95
1.96
2.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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N
N
N
NO2
3ae
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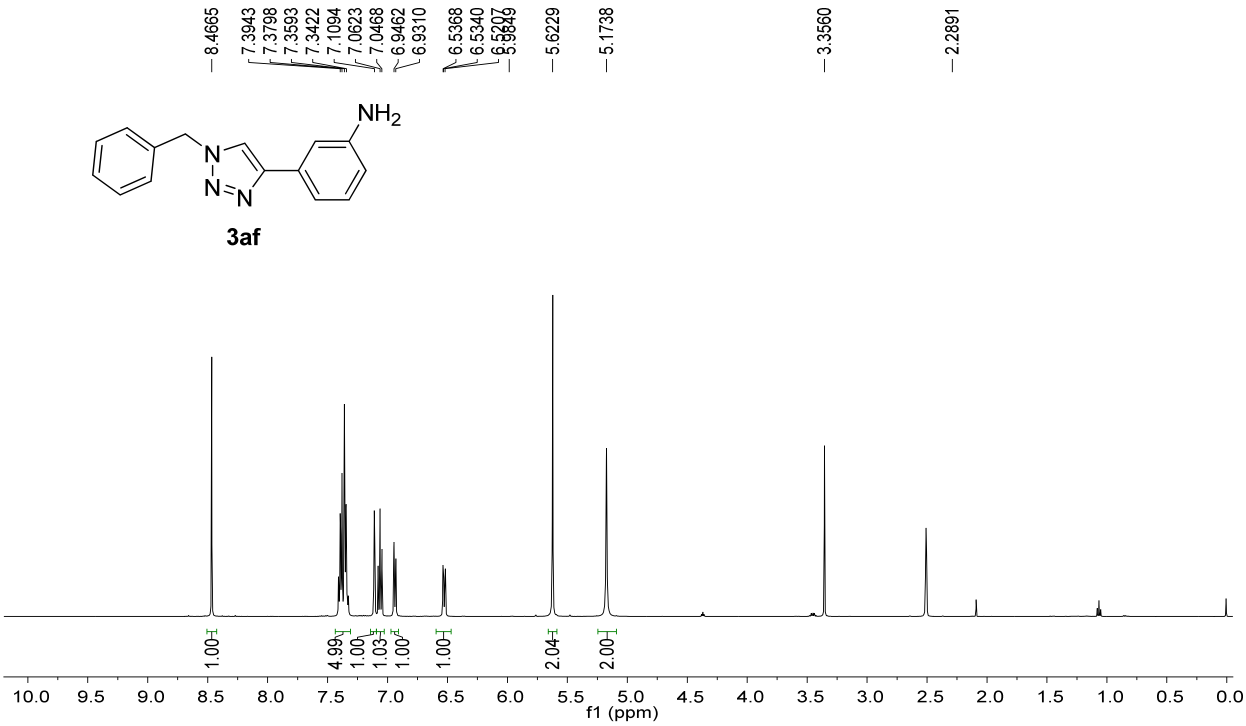
f1 (ppm)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6.5340
6.5207
5.9649
5.6229
5.1738
3.3560
2.2891
NH2
N
N
N
3af
1.00
4.99
1.00
1.03
1.00
1.00
2.04
2.00
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5.5
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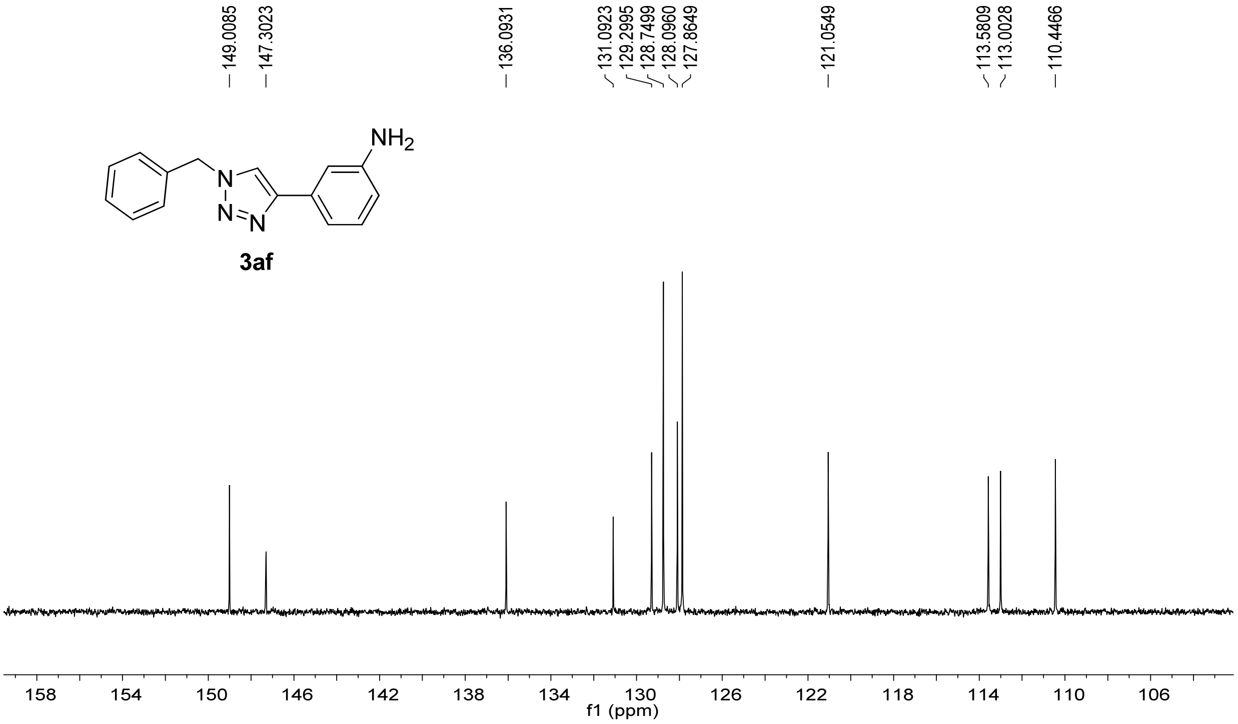
f1 (ppm)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113.0028
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NH2
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142
138
134
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122
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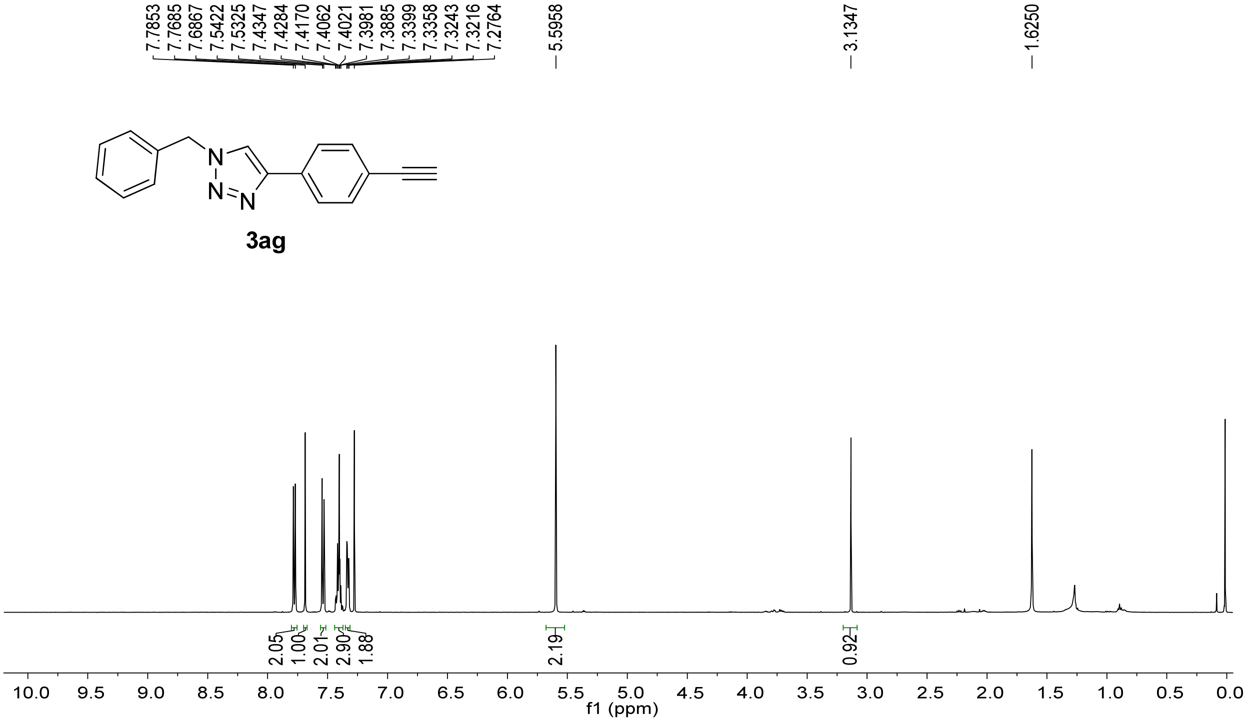
110
106
f1 (ppm)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N
N
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1.00
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8.0
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6.5
6.0
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0.0
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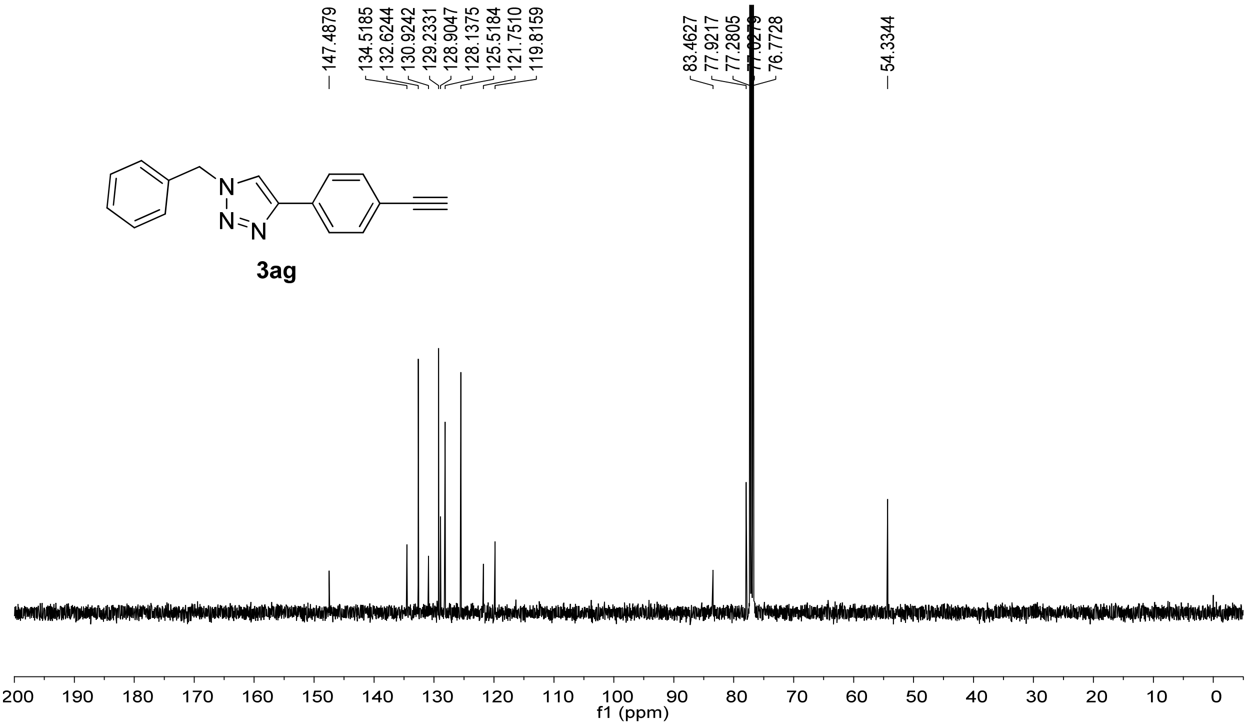
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76.7728
54.3344
N
N
N
3ag
200
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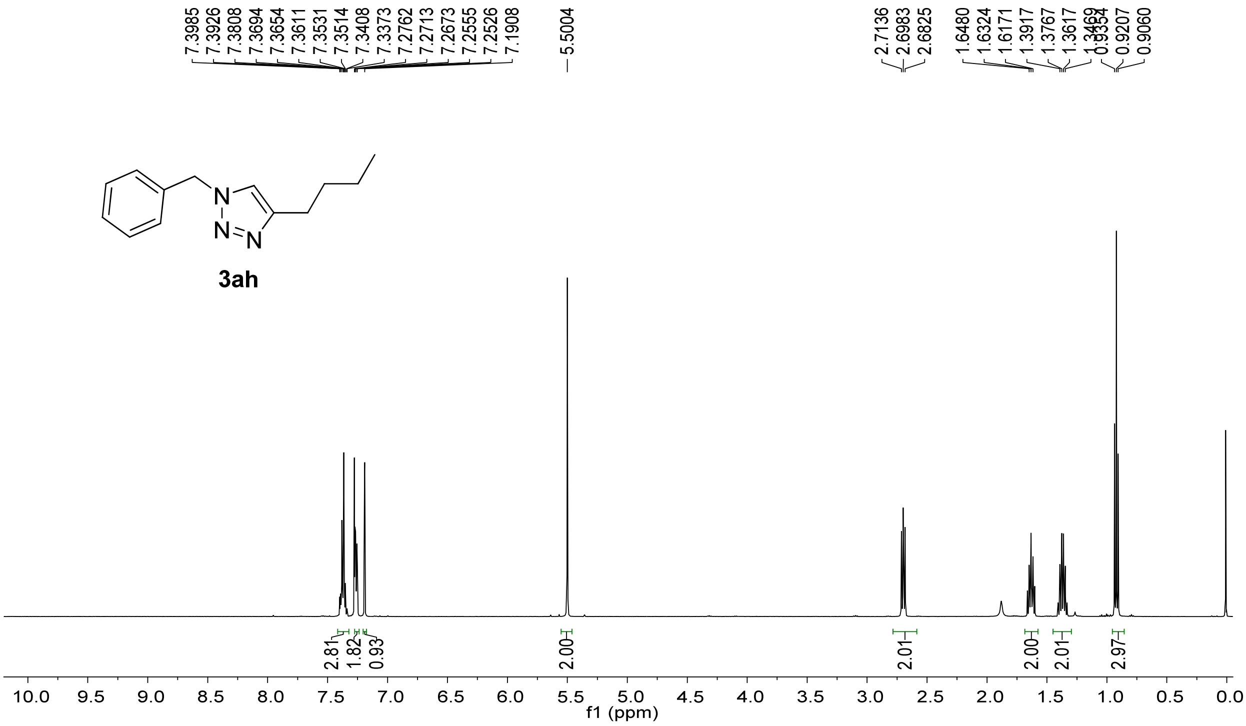
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7.2526
7.1908
5.5004
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2.6825
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1.6324
1.6171
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2.01
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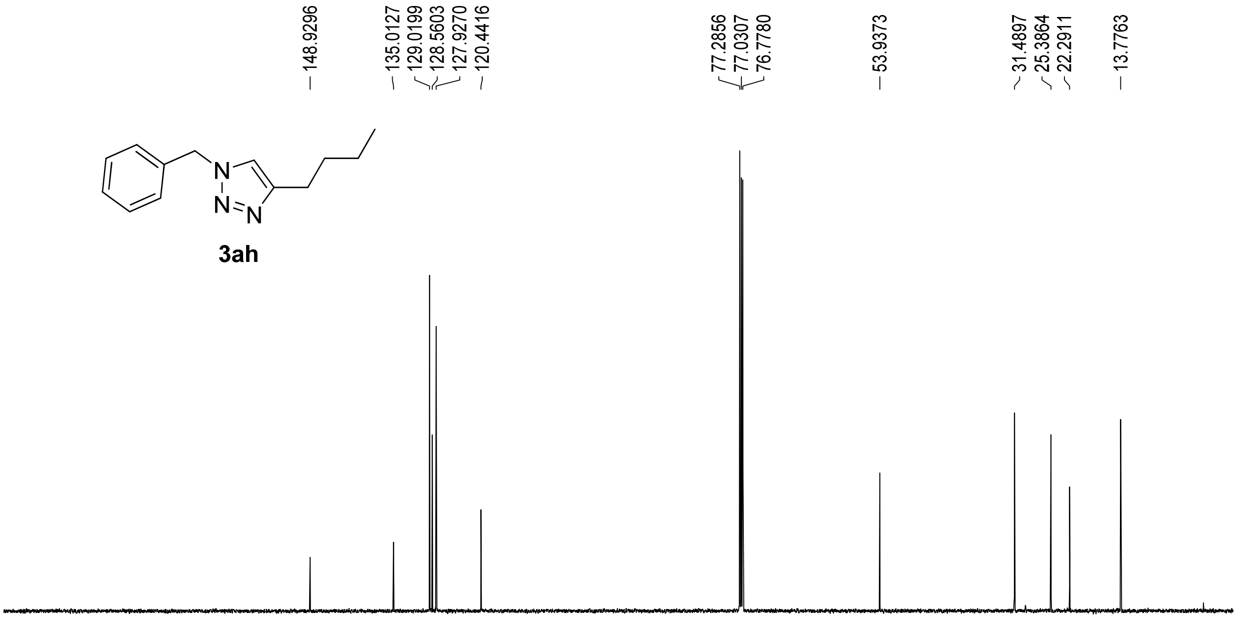
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N
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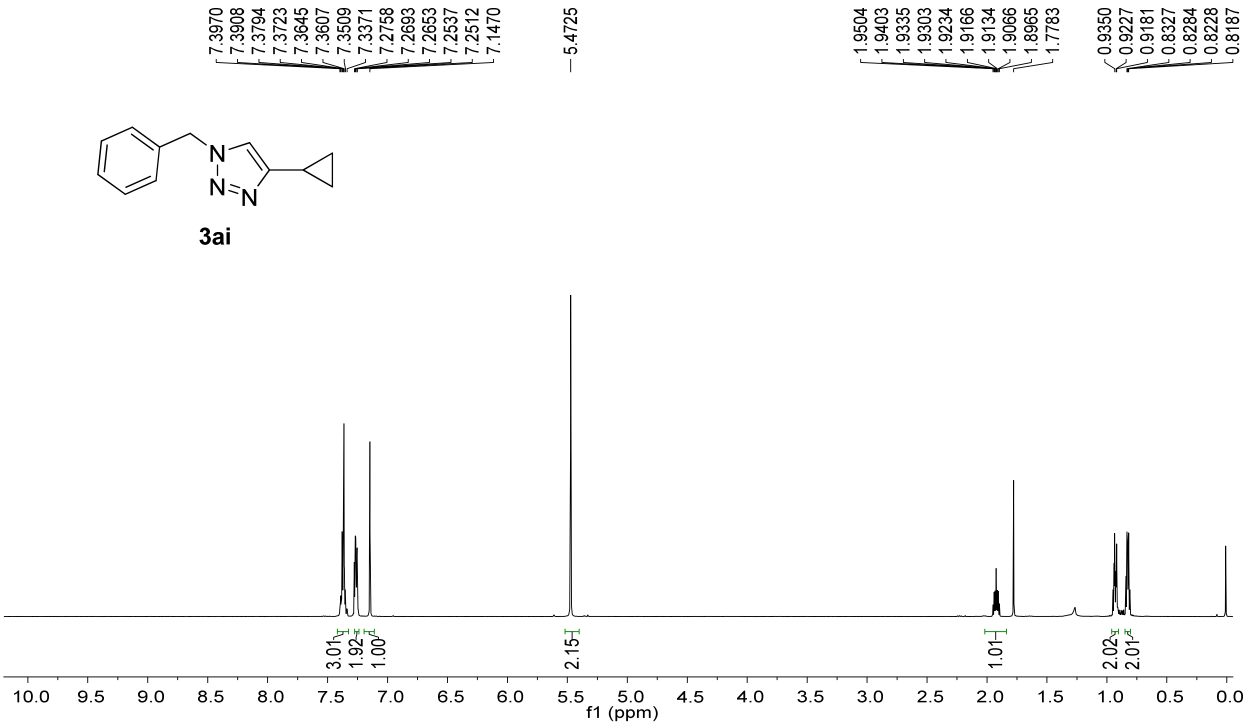
**3ai**

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7.3723
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7.3371
7.2758
7.2693
7.2653
7.2537
7.2512
7.1470
5.4725
1.9504
1.9403
1.9335
1.9303
1.9234
1.9166
1.9134
1.9066
1.8965
1.7783
0.9350
0.9227
0.9181
0.8327
0.8284
0.8228
0.8187
3.01
1.92
1.00
2.15
1.01
2.02
2.01
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9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
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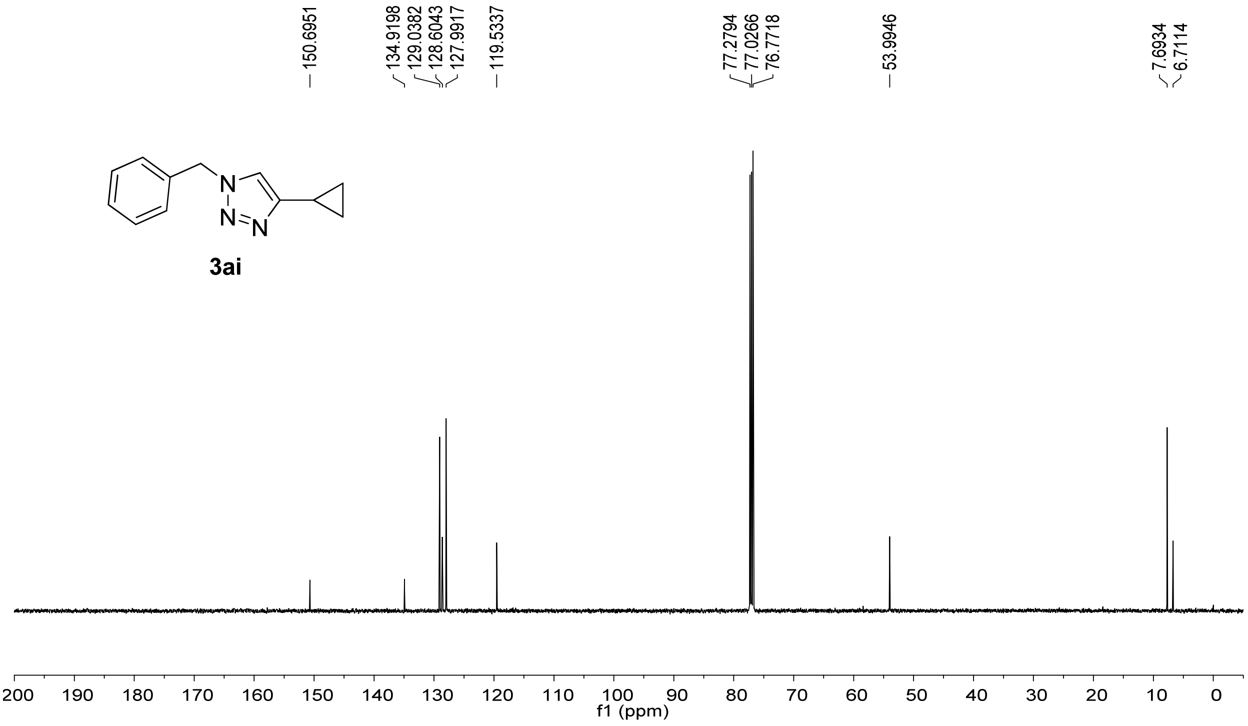
N


**3ai**

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7.6934
6.7114
200
190
180
170
160
150
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60
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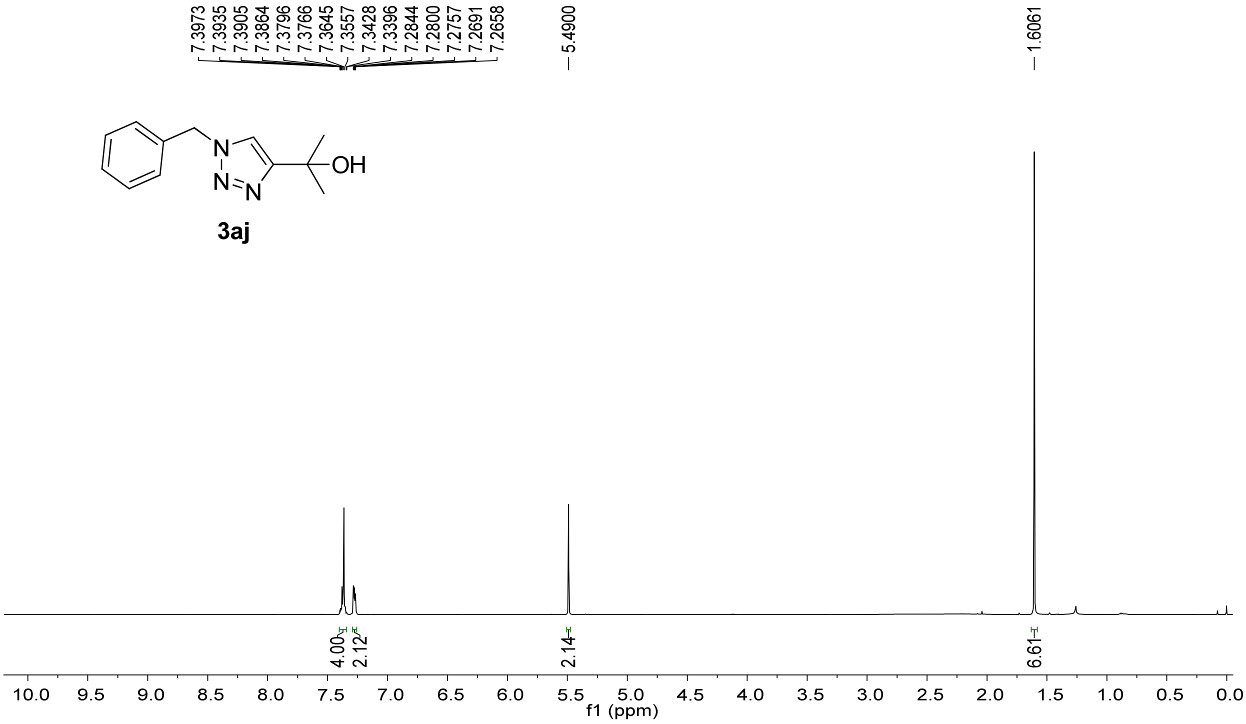
N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7.2691
7.2658
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N
N
OH
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2.12
2.14
6.61
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9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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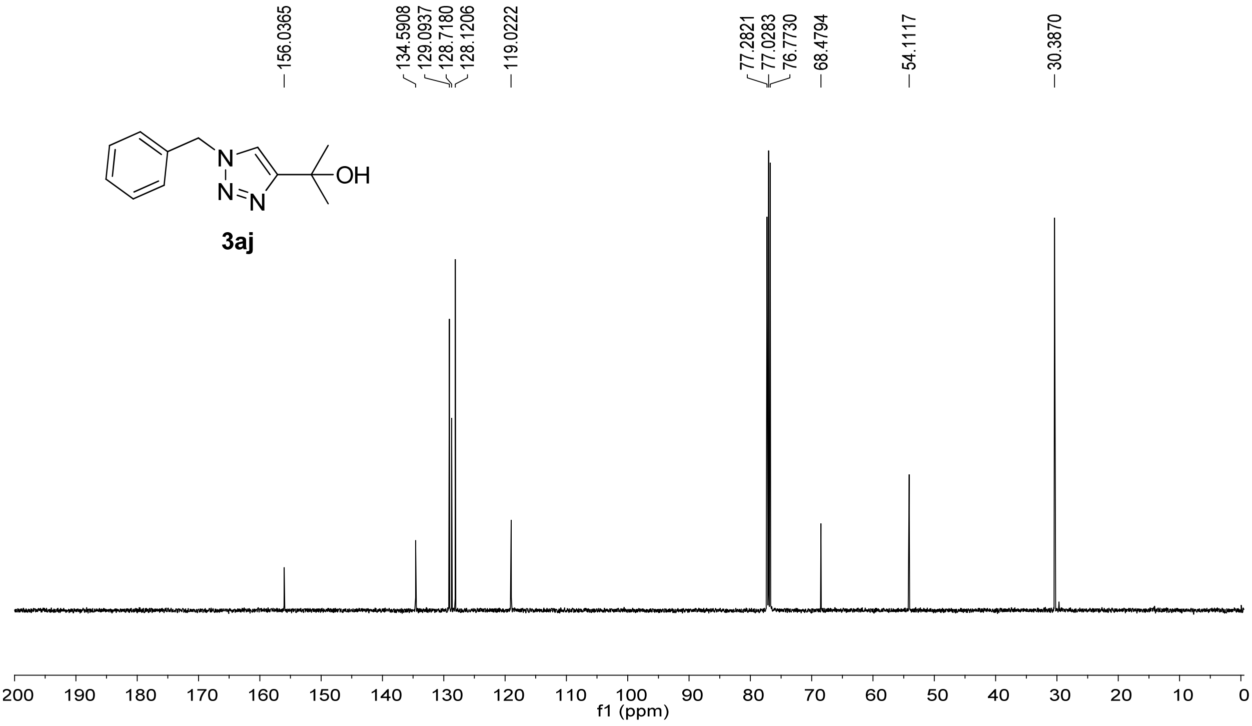
0.0
f1 (ppm)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OH
3aj
200
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180
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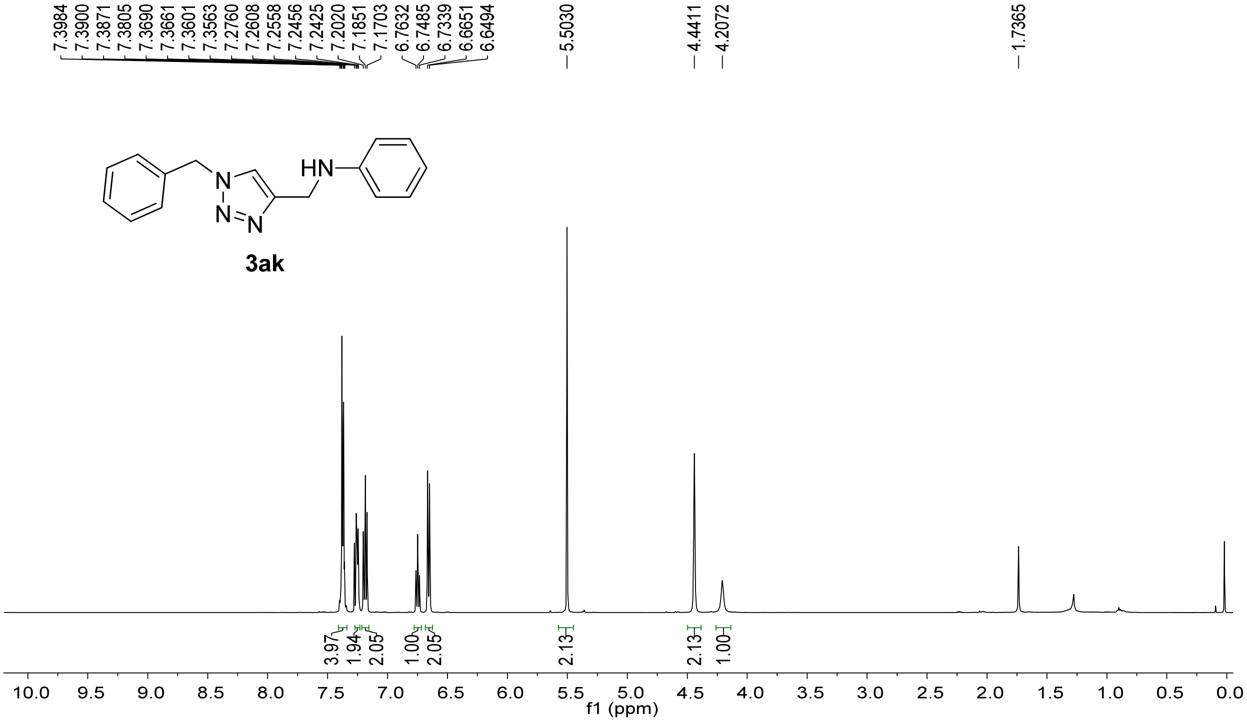
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7.2558
7.2456
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6.6651
6.6494
5.5030
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4.2072
1.7365
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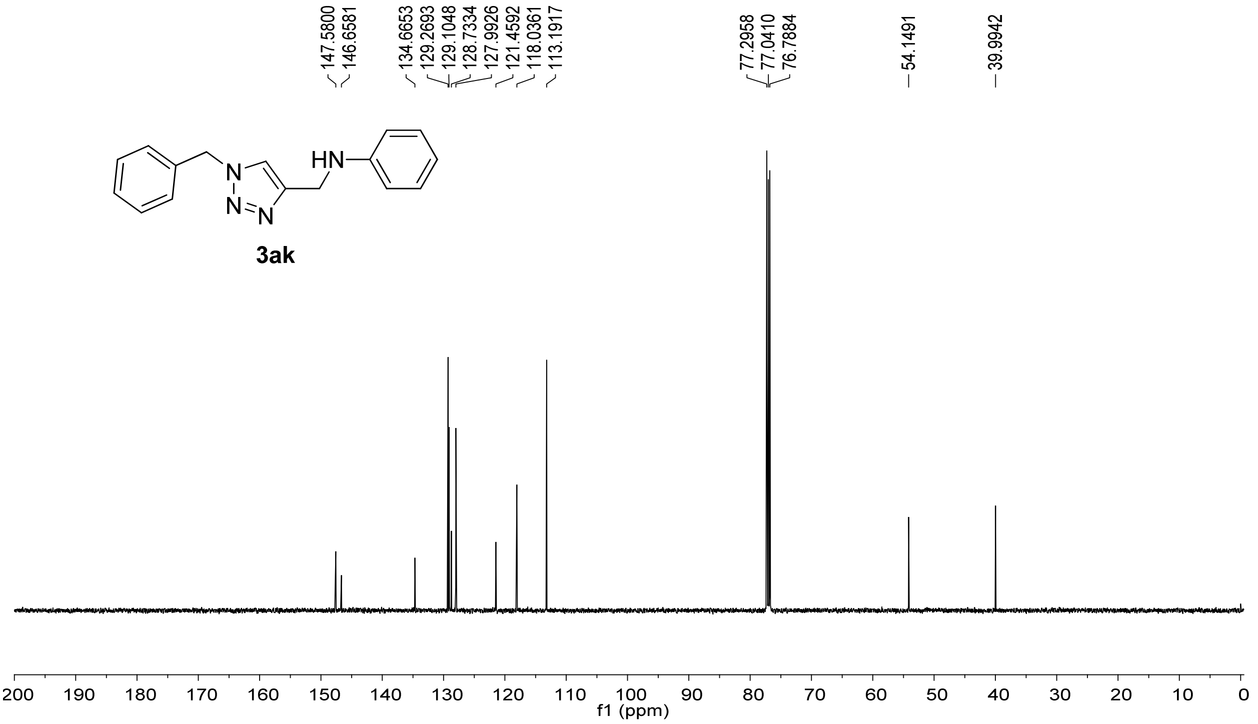
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N
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200
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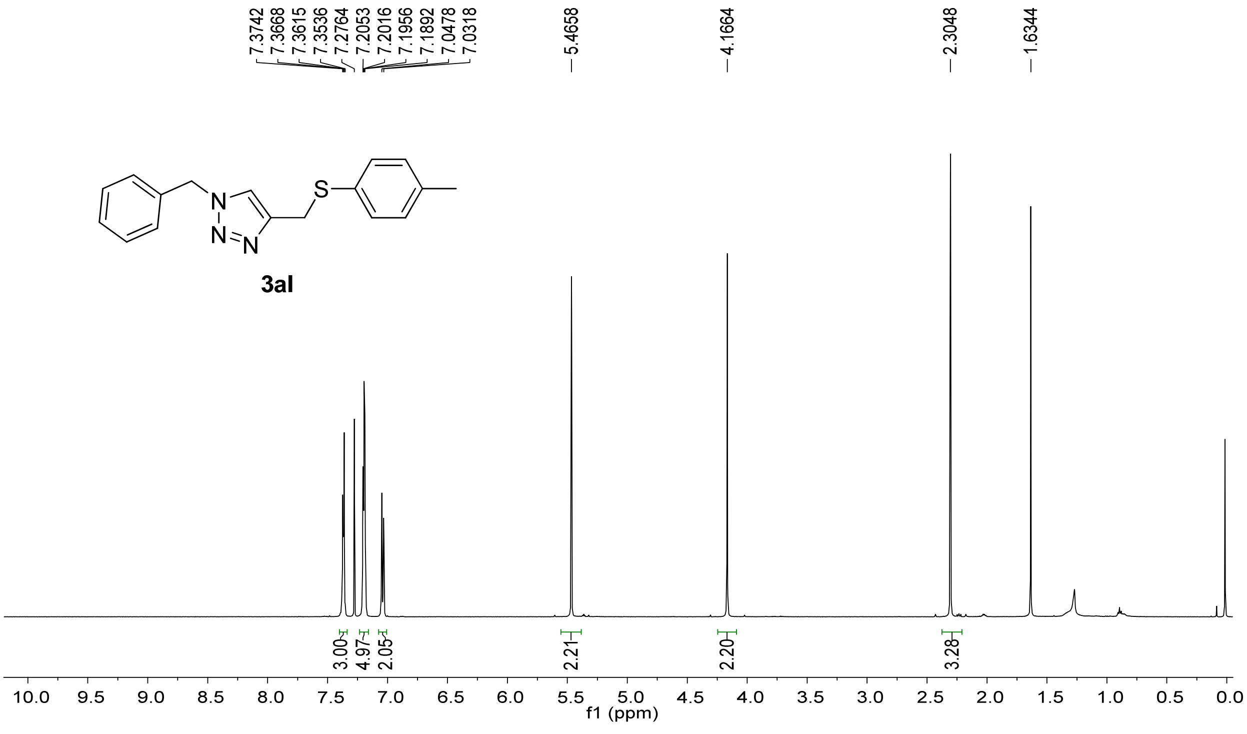
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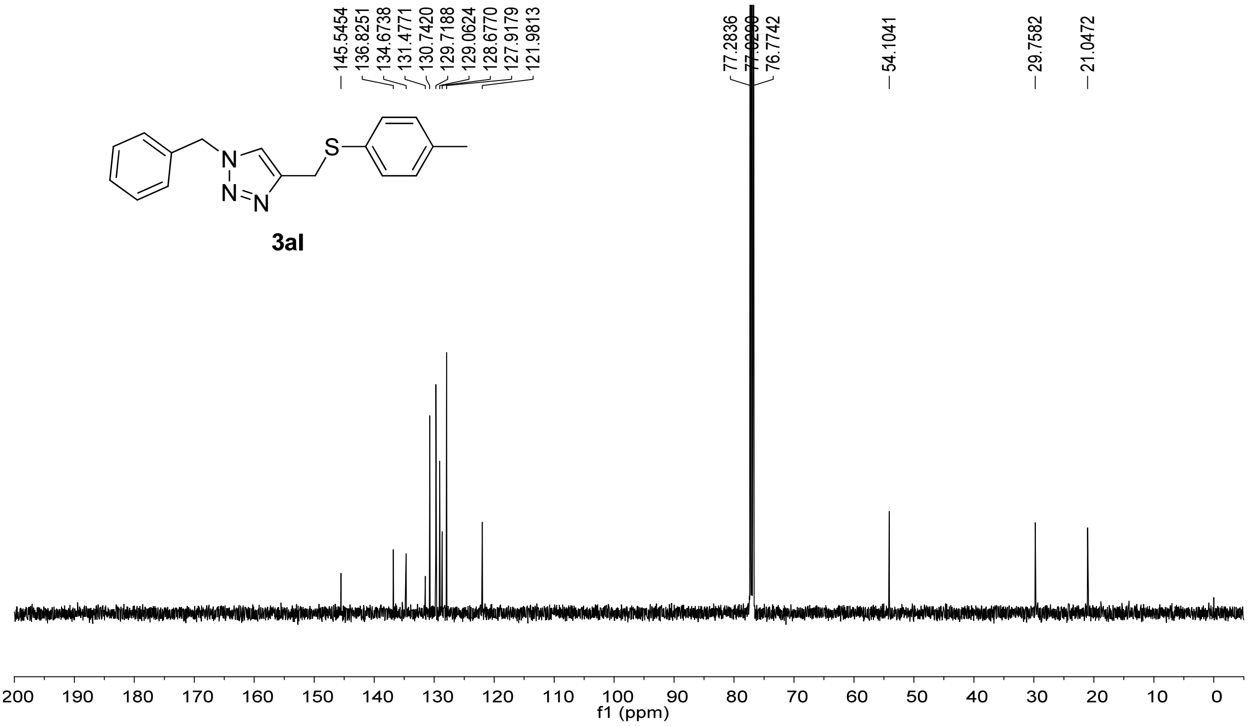
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54.1041
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S
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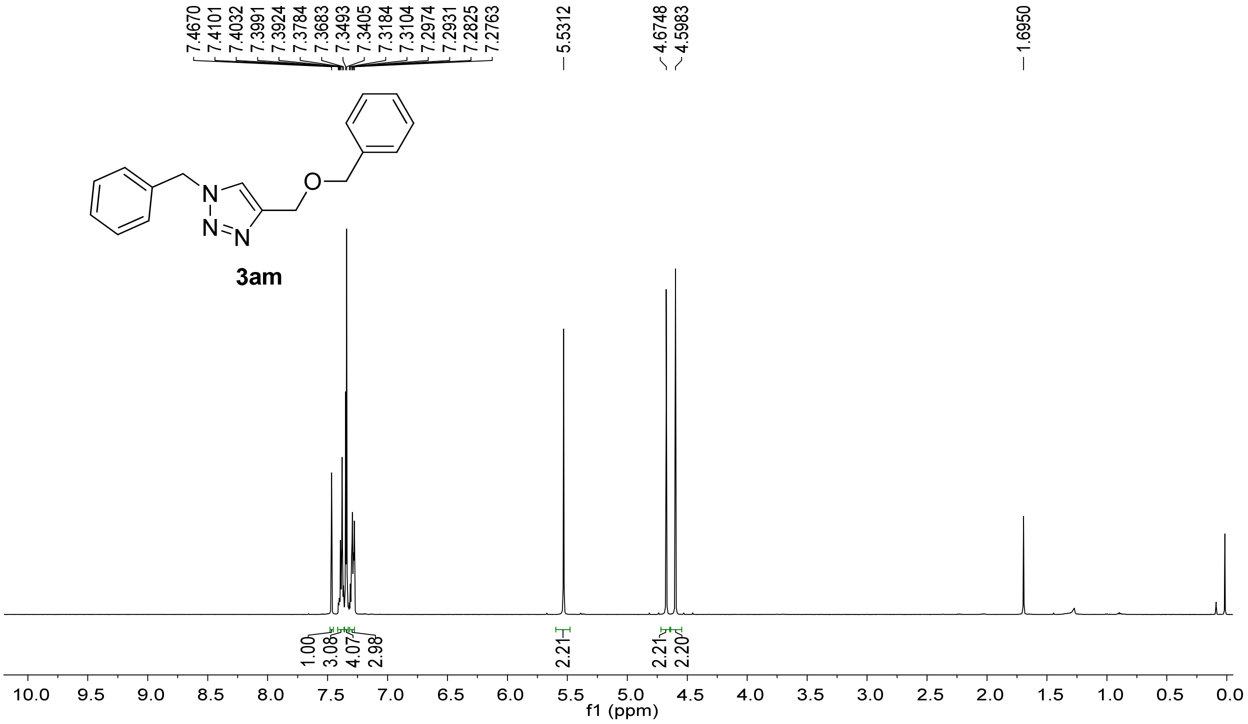
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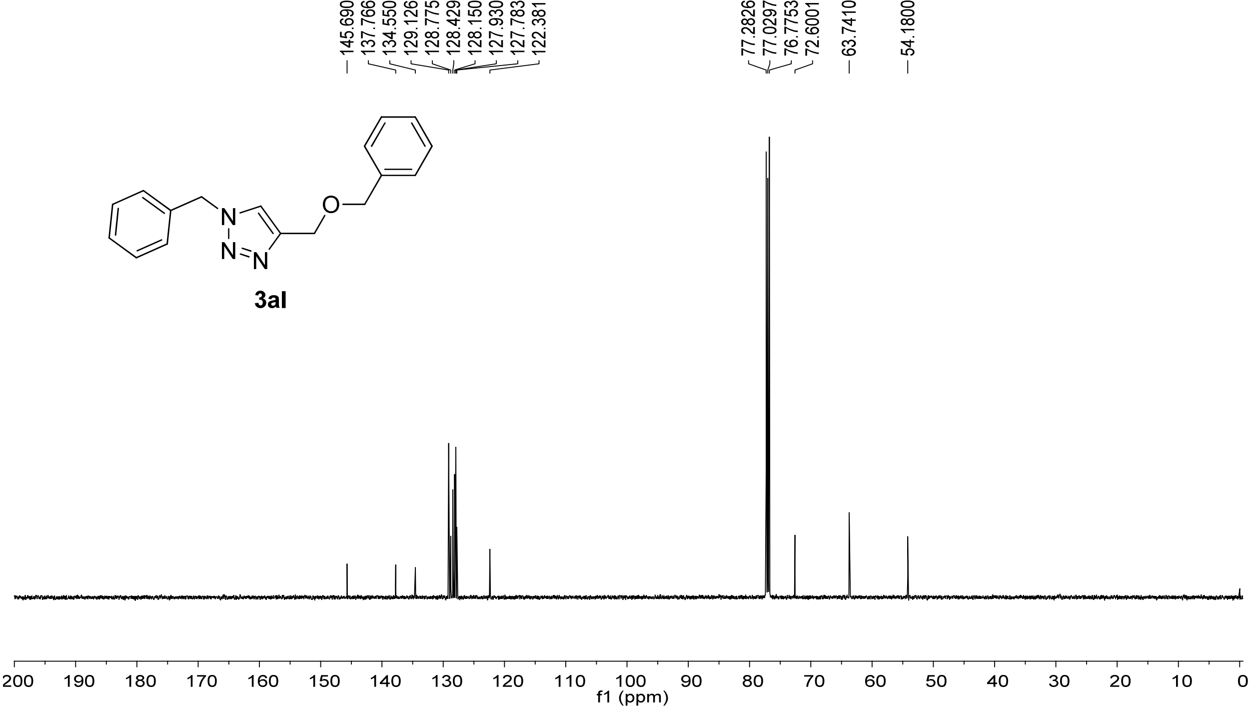
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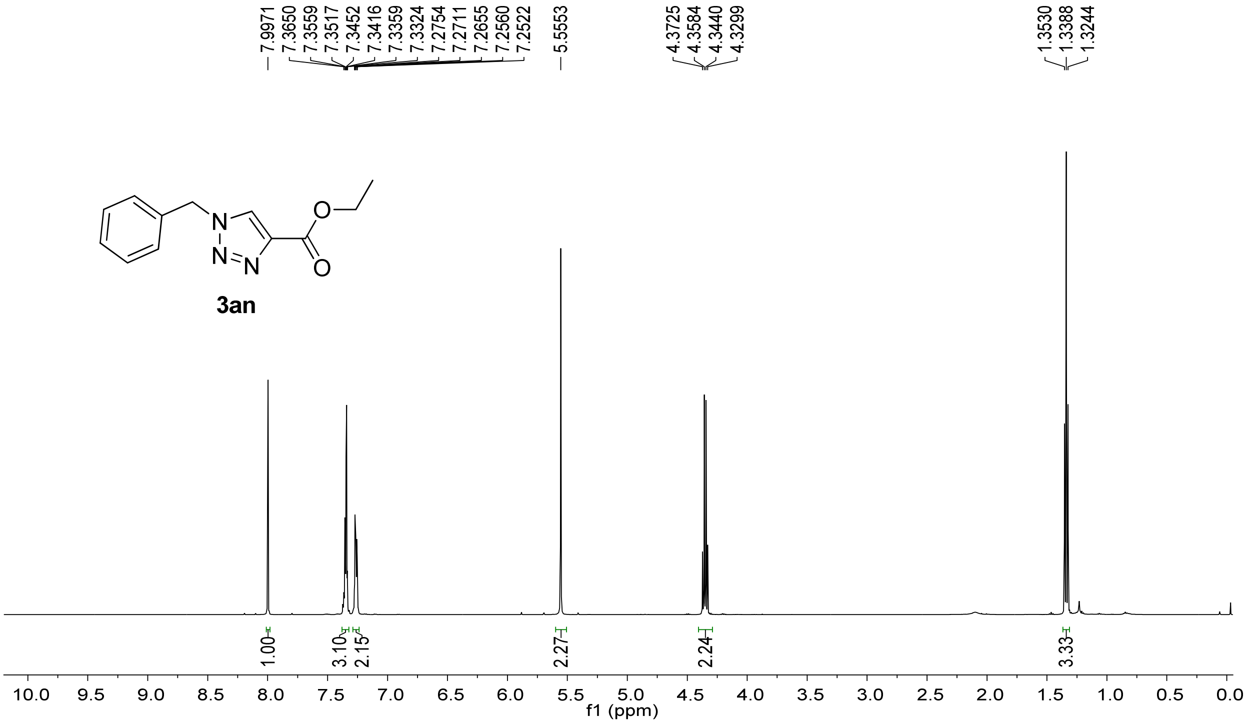

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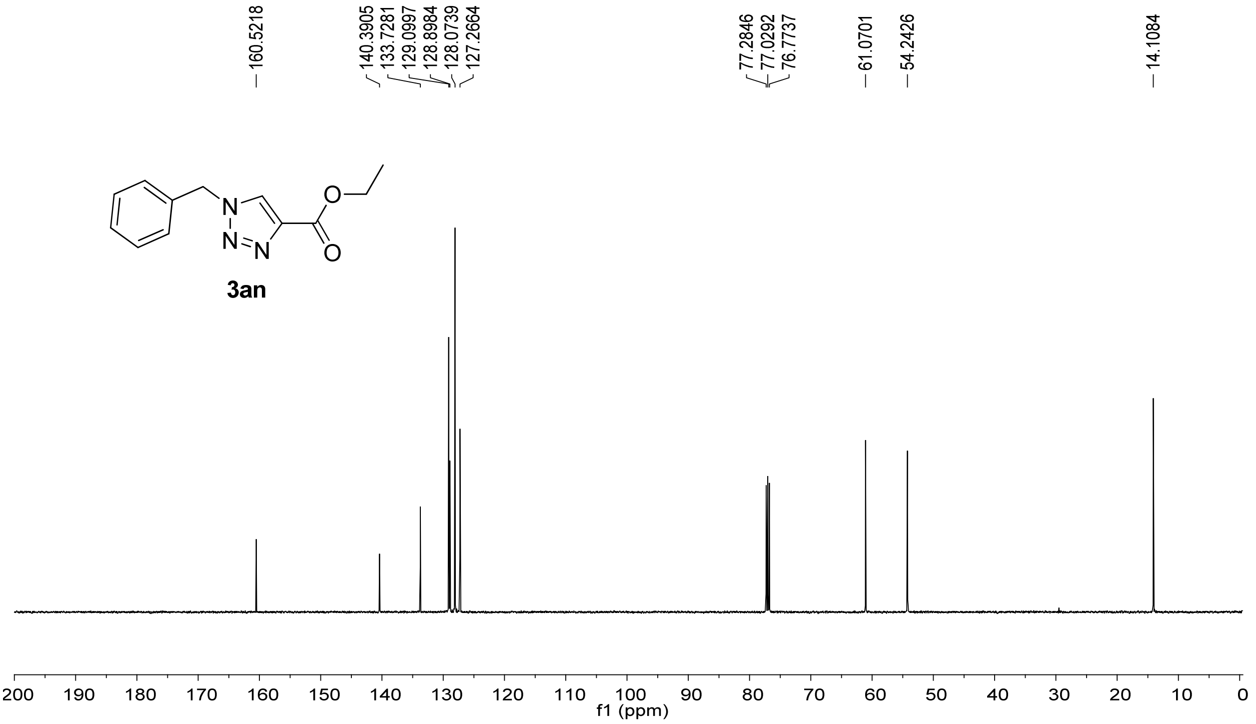

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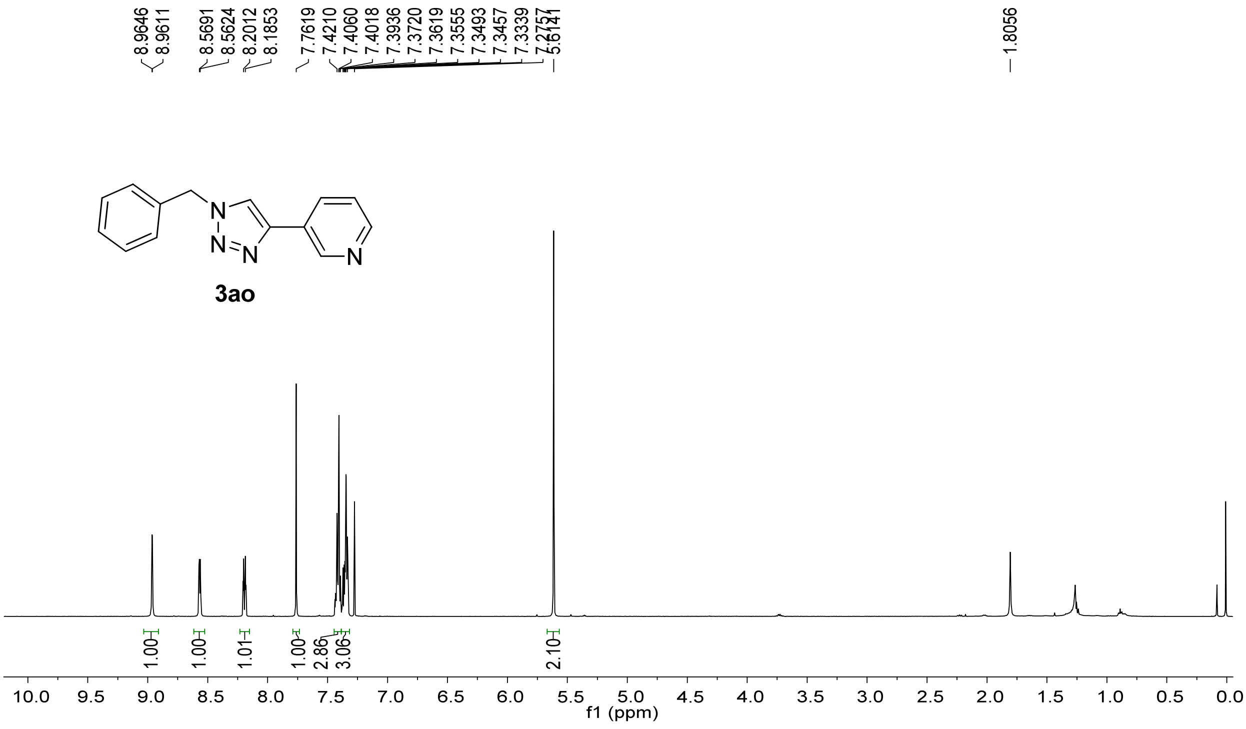
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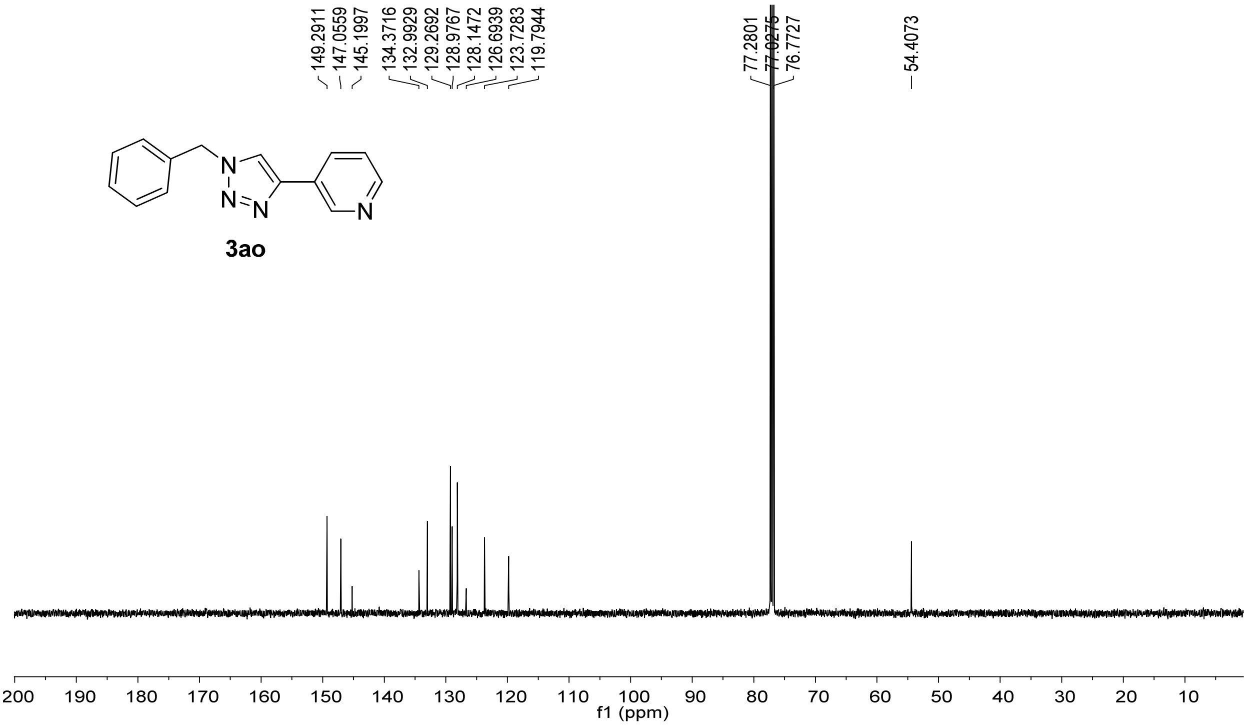
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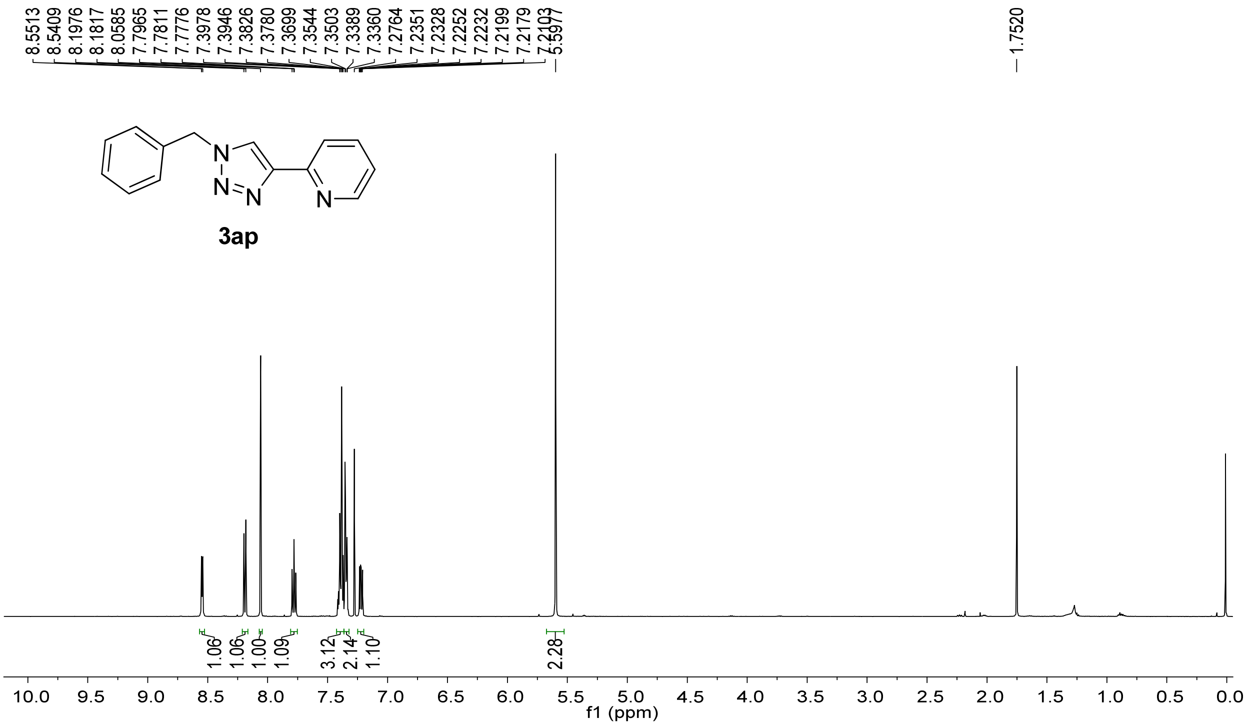
f1 (ppm)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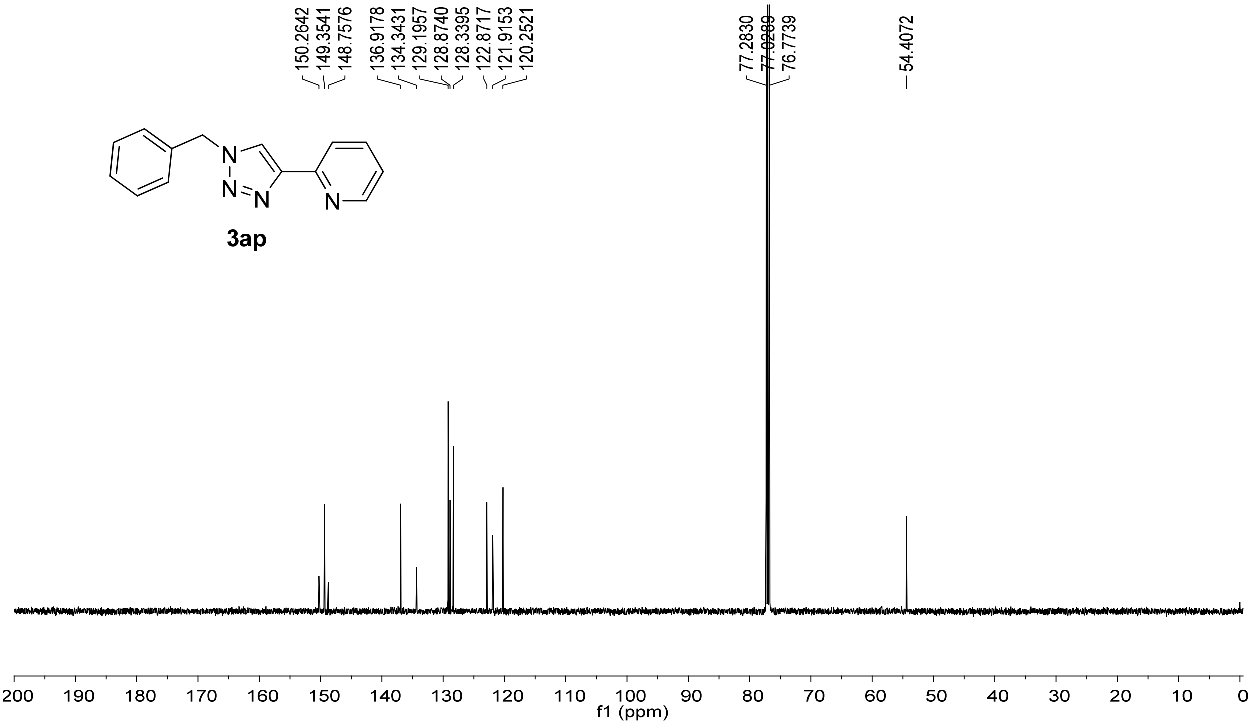
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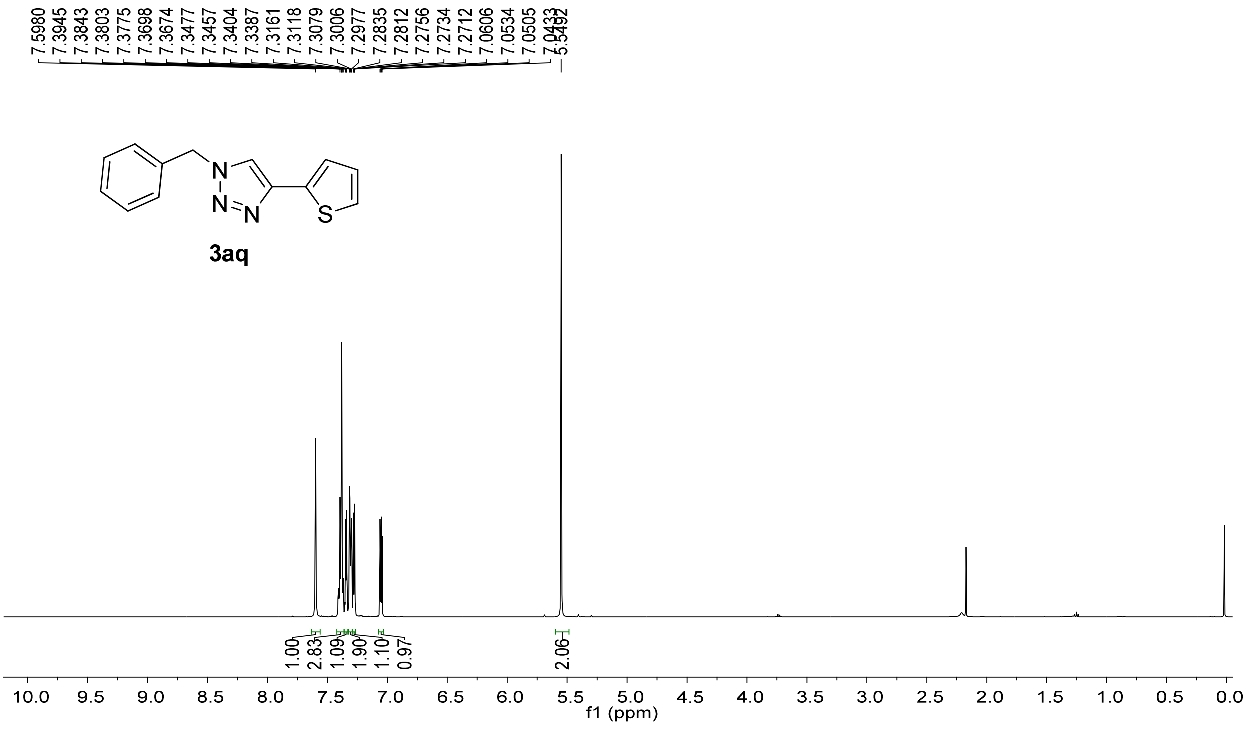
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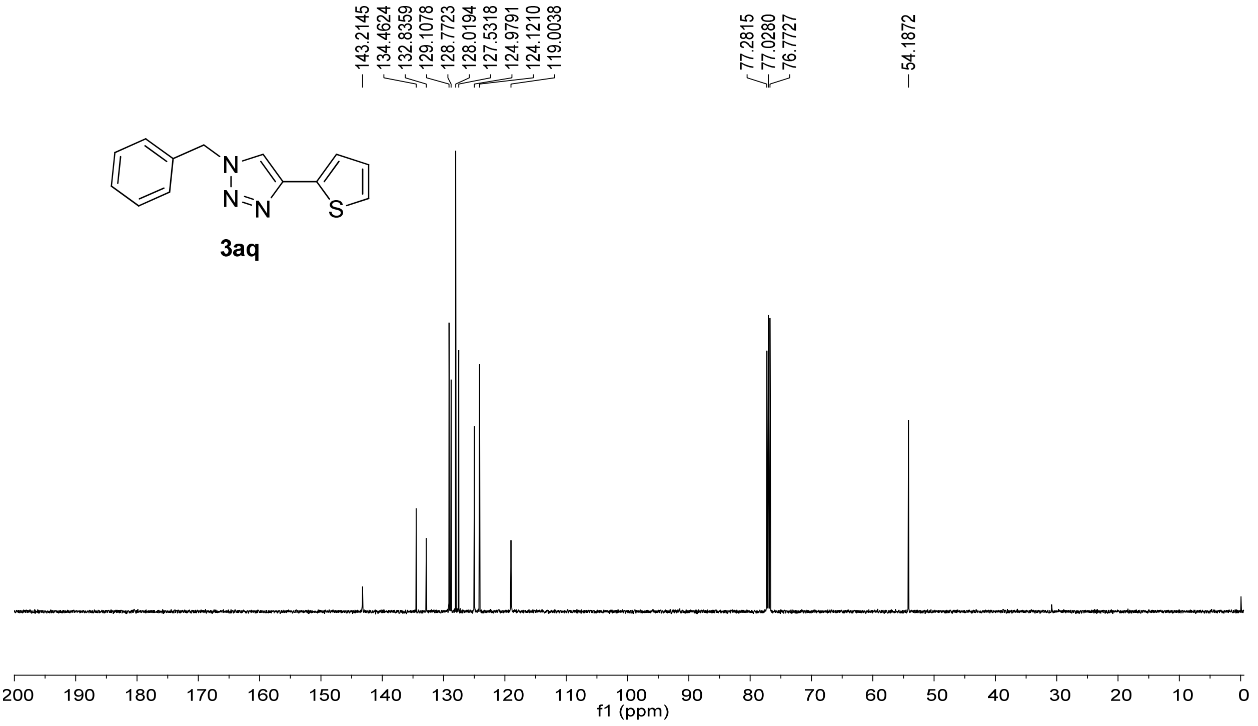
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10
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f1 (ppm)