Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Mesoporous graphitic carbon nitride as a heterogeneous catalyst for photoinduced copper(I)-catalyzed azide-alkyne cycloaddition

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EXPERIMENTAL

Materials

Benzyl bromide (Aldrich, 98%), phenylacetylene (Aldrich, 98%), 9-anthracenemethanol (Aldrich, 97%), ethyl 2-bromopropionate (Aldrich, 99%), 3-bromo-2-methylpropene (Aldrich, 97%), 1-bromooctane (Fluka, 98%), aniline (Aldrich, 99.5%), 4-fluoroaniline (Aldrich, 99%), 4-nitro aniline (Fluka, 98%), 2-ethynylpyridine (Aldrich, 98%), 3-ethynylthiophene (Aldrich, 96%), propargyl acrylate (Aldrich, 98%), propargyl alcohol (Aldrich, 99%), propargylamine (Aldrich, 98%), sodium azide (NaN_3, Panreac, 99%), and copper(II) chloride ($Cu^{II}Cl_2$, Acros Organics, 99%) were used as received without any further purification. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was purified by passing through basic alumina (Al_2O_3) prior to use. All solvents were purchased from Merck and used as received. Sodium nitrite ($NaNO_2$, Carlo Erba), magnesium sulfate ($MgSO_4$, Alfa Aesar, 99.5%), sodium bicarbonate ($NaHCO_3$, Aldrich, ≥99.7%), cyanamide (Aldrich, 99%), ammonium hydrogen difluoridewere (NH_4HF_2, Wako Chemicals, 95%), and SiO_2 particles in water (Ludox HS-40, Aldrich, 40 wt% suspension in H_2O) were used as received.

Instrumentation

^1H NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard at 500 MHz on a Agilent VNMRS 500 spectrometer at room temperature (125 MHz for ^{13}C NMR).

Fourier transform infrared (FTIR) spectra were recorded on PerkinElmer FTIR Spectrum One spectrometer with an ATR accessory (ZnSe, PikeMiracle accessory) and cadmium telluride (MCT) detector.

Photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified PerkinElmer Diamond DSC equipped with a Polilight PL400 Forensic Plus light source between 350 and 500 nm. A uniform UV light intensity was delivered across the DSC cell to the sample and reference pans. The measurements were carried out in an isothermal mode at 25 °C.

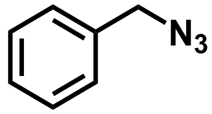
Preparation of Mesoporous Graphitic Carbon Nitride (mpg-C_3N_4)[1]

A unity mass ratio of silica to cyanamide was used to synthesize mpg-C_3N_4. Cyanamide (20 g, 0.475 mol) was dissolved in a 40 wt% dispersion of 12 nm SiO_2 particles in water (50 g) with stirring at 353 K for about 3 h to evaporate the water. The resulting white powder was then heated at a rate of 2.3 K min^{-1} over 4 h to reach a temperature of 823 K, and then held at this temperature for an additional 4 h. The resulting brown-yellow powder was stirred in 200 mL of 4 M NH_4HF_2 for 2 h, followed by filtration and washing with 100 mL of H_2O and 50 mL of ethanol. This washing cycle was repeated to completely remove the silica template. The powder was then stirred in 200 mL of H_2O for 2 h, then filtered and washed with H_2O and ethanol. Finally, the powders were dried at 393 K overnight. The yield of mpg-C_3N_4 was about 40%, based on carbon content.

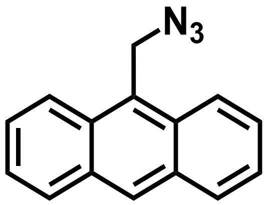
General Procedures for the Preparation of Azide Components

General procedure A:[2]

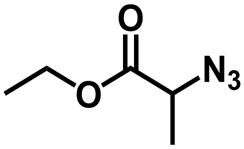
To a solution of the corresponding bromide compound (15 mmol, 1.0 eq) in 200 mL of DMSO was added sodium azide in excess (1.5 eq). The solution was stirred for at least 2 h at room temperature. Water (200 mL) was added to the mixture and after cooling down to room temperature, the aqueous solution was extracted with diethyl ether (3 × 100 mL). The organic layers were merged and washed with water (2 × 100 mL) and brine (100 mL). After drying over $MgSO_4$, the ether was removed under reduced pressure to yield azides **1a-b and 1f-h.**



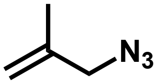
Benzyl azide (1a). From benzyl bromide. Yellow oil. Yield 96%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.43-7.34 (m, 5H), 4.36 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.4, 128.8, 128.3, 128.2, 54.8.



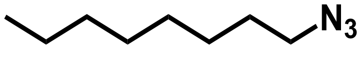
9-(Azidomethyl)anthracene (1b). From 9-(bromomethyl)anthracene. Yellow solid. Yield 95%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.52 (s, 1H), 8.31 (d, 2H), 8.07 (d, 2H), 7.63-7.59 (m, 2H), 7.54-7.51 (m, 2H), 5.35 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 131.4, 130.7, 129.3, 128.7, 129.0, 126.8, 125.8, 125.2, 123.5, 46.4.



Ethyl 2-azidopropanoate (1f). From ethyl 2-bromopropionate. Colorless oil. Yield 97%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 4.24 (q, 2H), 3.91 (q, 1H), 1.46 (d, 3H), 1.30 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 170.9, 128.3, 61.7, 57.3, 16.7, 14.1.



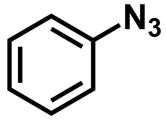
3-Azido-2-methylpropene (1g). From 3-bromo-2-methylpropene. Yellow oil. Yield 86%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 4.98 (s, 1H), 4.86 (s, 1H), 3.48 (s, 1H), 1.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 140.7, 116.2, 57.3, 22.3.



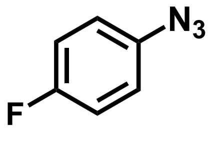
1-Azidooctane (1h). From 1-bromooctane. Pale yellow oil. Yield 93%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.26 (t, 2 H), 1.68-1.20 (m, 12H), 0.89 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 51.5, 31.7, 29.1, 28.8, 26.7, 22.6, 15.2, 14.0.

General procedure B:[3]

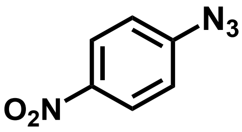
The corresponding aniline derivative (15 mmol, 1 eq.) was added to 80 mL of hydrochloric acid (17%) at room temperature followed by drop wise addition of ethanol to obtain a clear solution. The solution was cooled to 0 °C and $NaNO_2$ (1.5 eq.) was added in small portions. After stirring at 0 °C for 30 minutes, NaN_3 (1.5 eq.) was slowly added and the mixture was stirred for further 2 h at room temperature. The reaction mixture was extracted with diethyl ether (3 × 100 mL) and the combined organic fractions were washed with saturated $NaHCO_3$ solution (3 × 50 mL) and with brine (50 mL). After drying over $MgSO_4$, the ether was removed under reduced pressure to obtain azides **1c-e**.



Phenyl azide (1c). From aniline. Yellow oil. Yield 93%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H), 77.17-7.14 (m, 1H), 7.07-7.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 129.7, 124.8, 119.0.



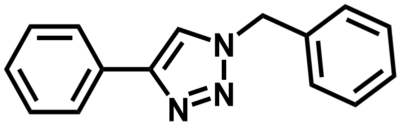
1-Azido-4-fluorobenzene (1d). From 4-fluoroaniline. Orange oil. Yield 91%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.08-7.03 (m, 2H), 7.01-6.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 158.9, 135.8, 120.2, 116.7, 116.5.



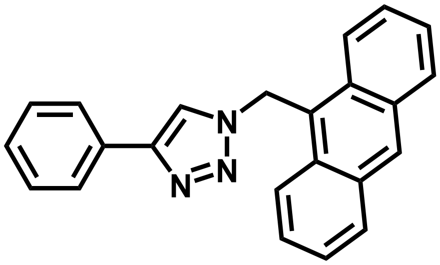
1-Azido-4-nitrobenzene (1e). From 4-nitro aniline. Orange solid. Yield 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26-8.23 (m, 2H), 7.16-7.13 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 144.6, 125.6, 119.4.

General Procedure for the Preparation of 1,4-Disubstituted Triazoles

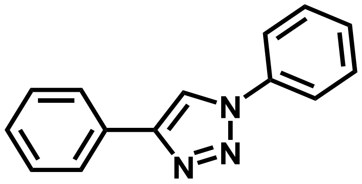
In a Pyrex tube $Cu^{II}Cl_2$ (6.75 mg, 0.05 mmol) and PMDETA (10.5 μL, 0.10 mmol) were dissolved in 3 mL of MeCN. To the mixture were added 1 mmol azide, 1 mmol alkyne, and 20 mg of mpg-C_3N_4. The mixture was then irradiated in a Rayonet photoreactor equipped with 18 lamps (Philips 8 W BLB, λ_{max}> 350 nm) with the light intensity of 25 mW cm^{-2} at room temperature. After irradiation, mpg-C_3N_4 was separated and the resultant was purified by a short column chromatography.



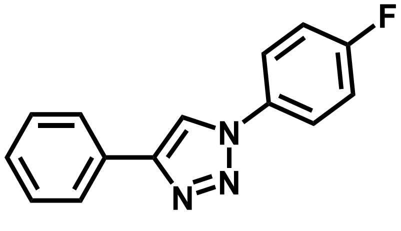
4-Benzyl-1-phenyl-1*H*-1,2,3-triazole (3a). White solid. Yield 98%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, 2H), 7.67 (s, 1H), 7.42-7.27 (m, 8H), 5.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.2, 134.7, 130.6, 129.1, 128.8, 128.7, 128.2, 128.1, 125.7, 119.4, 54.2.



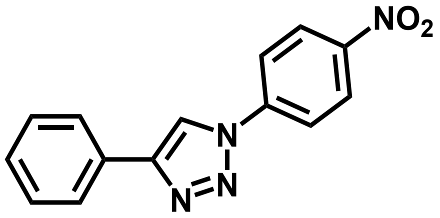
1-(Anthracen-9-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole (3b). Yellow solid. Yield 99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.36 (d, 2H), 8.11 (d, 2H), 7.65-7.21 (m, 11H), 6.58 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.8, 134.1, 131.4, 130.8, 130.7, 130.4, 129.9, 129.5, 129.3, 128.9, 128.61, 127.9, 127.2, 126.8, 125.57, 125.5, 125.2, 124.7, 123.7, 123.5, 123.0, 119.0, 46.6.



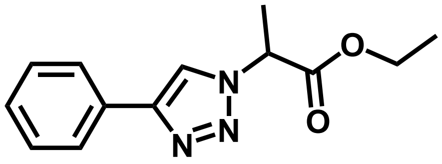
1,4-Diphenyl-1*H*-1,2,3-triazole (3c). Pale yellow oil. Yield 96%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.94 (d, 2H), 7.81 (d, 2H), 7.58-7.34 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 137.0, 132.5, 130.3, 129.8, 128.9, 128.4, 125.9, 120.54, 117.56.



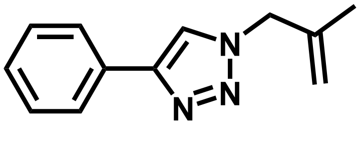
1-(4-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole (3d). Pale yellow solid. Yield 99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.93-7.91 (d, 2H), 7.80-7.76 (d, 2H), 7.55-7.47 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1, 157.5, 132.5, 129.2, 128.9, 125.9, 122.5, 128.4, 125.8, 122.5, 121.8, 116.9.



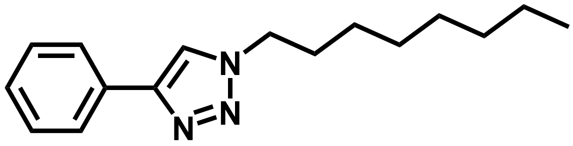
1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (3e). Brownish solid. Yield 99%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.43(s, 1H), 8.26-8.24 (m, 3H), 8.13-8.07 (m, 2H), 7.15 (m, 2H), 6.64 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 155.1, 152.3, 149.5, 146.8, 144.5, 132.5, 126.3, 125.6, 124.9, 124.0, 119.4, 113.4.



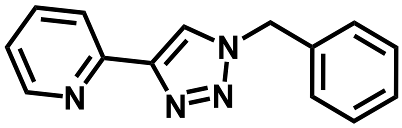
Ethyl 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propanoate (3f). White solid. Yield 97%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.98 (s, 1H), 7.86 (d, 2H), 7.44-7.41 (t, 2H), 7.35-7.31 (t, 1H), 5.50 (d, 1H), 4.26-4.21 (m, 2H), 1.88 (d, 3H), 1.29-1.26 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 169.3, 147.8, 130.4, 128.9, 128.2, 125.8, 119.0, 116.4, 62.4, 58.4, 18.4, 14.0.



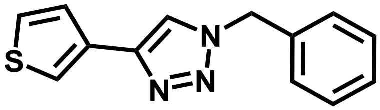
1-(2-methylallyl)-4-phenyl-1*H*-1,2,3-triazole (3g). Pale yellow solid. Yield 92%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.21 (s, 1H), 7.58-7.33 (m, 5H), 5.1 (s, 2H), 4.98 (s, 2H) 1.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 148.1, 139.4, 130.6, 128.8, 128.4, 128.1, 125.7, 120.5, 119.4, 115.5, 56.4, 19.7.



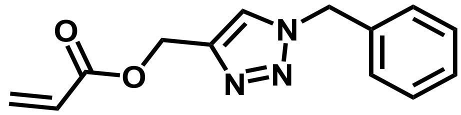
1-Octyl-4-phenyl-1*H*-1,2,3-triazole (3h). White solid. Yield 95%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (d, 2H), 7.75 (s, 1H), 7.45-7.32 (m, 3H), 4.40 (t, 2H), 1.96 (m, 2H), 1.36-1.27 (m, 10H), 0.89 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 147.8, 137.7, 128.8, 128.0, 127.7, 119.3, 50.4, 31.7, 30.3, 28.9, 26.5, 22.6, 14.0.



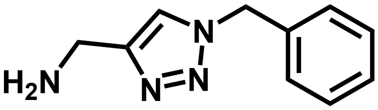
2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (3i). Yellow solid. Yield 79%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.53 (d, 1H), 8.20 (d, 1H), 8.05 (s, 1H), 7.78-7.75 (m, 1H), 7.40-7.33 (m, 5H), 7.22-7.19 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.2, 149.3, 148.7, 136.9, 134.3, 129.2, 128.8, 128.3, 122.8, 121.9, 120.2, 54.4.



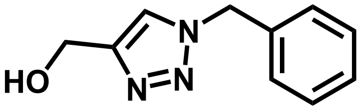
1-Benzyl-4-(thiophen-3-yl)-1*H*-1,2,3-triazole (3j). White solid. Yield 88%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 (m, 1H), 7.56 (s, 1H), 7.43-7.35 (m, 5H), 7.30 (m, 2H), 5.57 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 144.4, 134.6, 131.8, 129.1, 128.8, 128.0, 126.3, 125.8, 121.1, 119.3, 54.2.



(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl acrylate (3k). Pale yellow oil. Yield 99%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.54 (s, 1H), 7.39-7.27 (m, 5H), 6.44-6.40 (m, 1H), 6.14-6.09 (m, 1H), 5.97-5.94 (m, 1H), 5.53 (s, 2H), 5.28 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.1, 143.2, 134.24, 131.4, 129.1, 128.8, 128.1, 127.9, 126.6, 57.7, 54.2.



(1-Benzyl-1H-1,2,3-triazol-4-yl)methanamine (3l). White solid. Yield 87%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.30 (s, 1H), 7.51-7.26 (m, 5H), 5.55 (s, 2H), 4.78 (s, 2H), 1.38 (t, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.0, 143.4, 128.7, 128.2, 116.5, 54.7, 43.5.



(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methanol (3m). White solid. Yield 68%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (s, 1H), 7.47-7.44 (d, 2H), 7.42-7.27 (m, 3H), 5.60 (s, 2H), 5.30 (s, 1H), 4.78 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 140.1, 134.7, 129.4, 128.4, 128.1, 121.4, 56.7, 51.7.

Photocalorimetric Studies:

To a mixture of $Cu^{II}Cl_2$/PMDETA (0.025 mmol, 0.05 equiv) in 0.5 mL of acetonitrile were added benzyl azide **1a** (0.5 mmol, 1 eq), phenylacetylene **2a** (0.5 mmol, 1 eq) and mpg-C_3N_4 (10 mg). Approximately 15-20 mg of the solution was transferred into a photoDSC pan and irradiate in an isothermal mode at 25 °C. The thermograms (Figure S1) were drawn after baseline corrections. The real time conversions were calculated according to eq S1:

$$Yield\ (\%) = (\Delta H_t / \Delta H_0) \times 100 \quad \text{(eq S1)},$$

where, ΔH_t is the total heat change till time t and ΔH_0 is the theoretical energy (14.9 kcal/mol).[4]

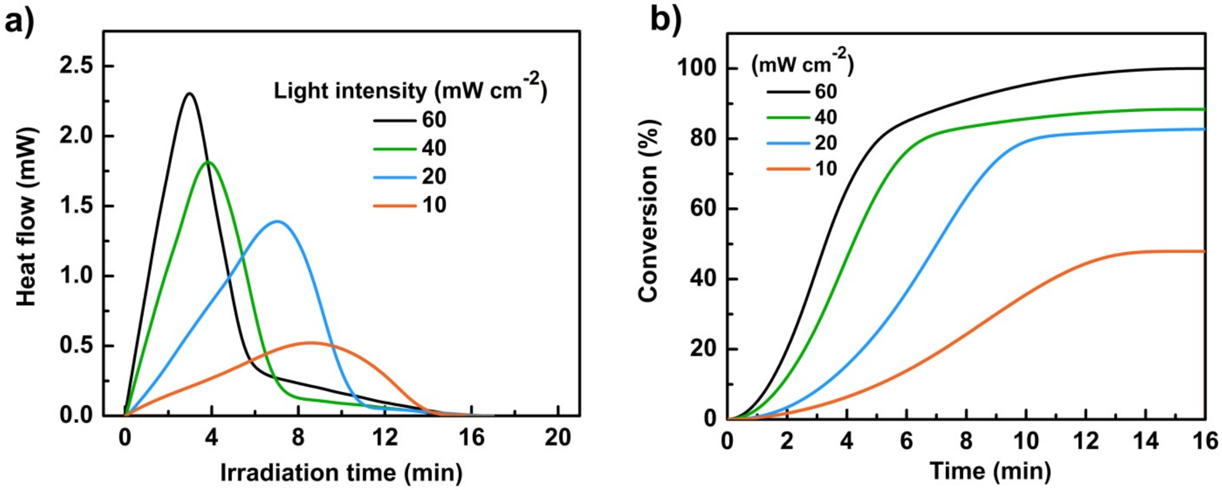


Figure S1. Calorimetric results of photoinduced CuAAC in the presence of mpg-C_3N_4 deploying benzyl azide (**1a**) and phenylacetylene (**2a**) as the model substitutes: a) effect of light intensity on photoclicking process and b) real time conversion in different light intensities

Table S1. Effect of different solvents on the photoinduced CuAAC using mpg-C_3N_4 [a]

Entry	Solvent [b]	Yield (%) [c]
1	MeCN	98
2	CH_2Cl_2	98
3	THF	96
4	DMF	93
5	DMSO	95
6	MeOH	83
7	BuOH	49
8	H_2O	20

[a] A mixture of benzyl azide (**1a**) and phenylacetylene (**2a**) in the presence of mpg-C_3N_4 and $Cu^{II}Cl_2$/PMDETA was irradiated for 45 min, [b] MeCN: acetonitrile, CH_2Cl_2: dichloromethane, THF: tetrahydrofuran, DMF: dimethylformamide, DMSO: dimethyl sulfoxide, MeOH: methanol, BuOH: butanol, H_2O: water, [c] Isolated yields.

Reusability of the photocatalyst mpg-C_3N_4 was examined in the model reaction employing benzyl azide (**1a**) and phenylacetylene (**2a**) according to the general procedure described above for the click experiments. After each step, mpg-C_3N_4 was separated and loaded for the next use applying fresh Cu(II).

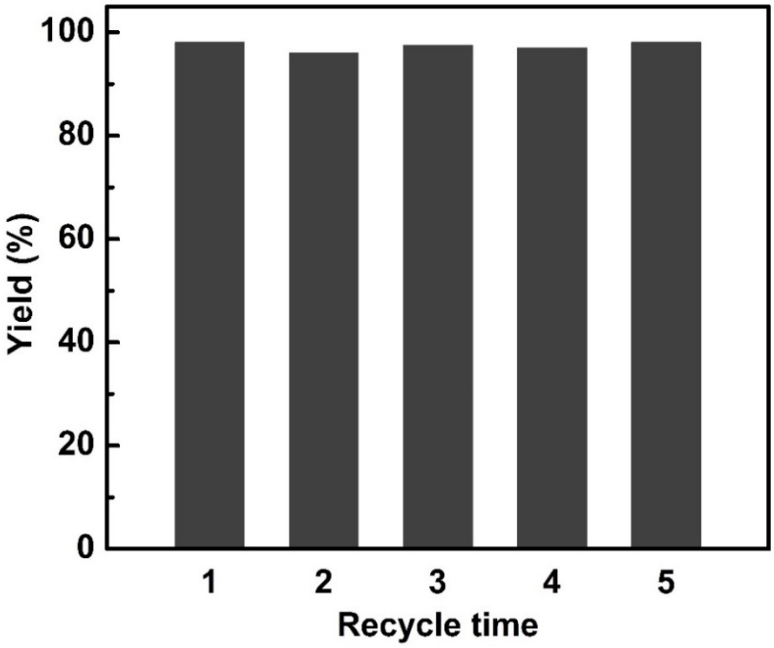


Figure S2. Repeated use of mpg-C_3N_4 in photoclicking benzyl azide (**1a**) and phenylacetylene (**2a**) under the same experimental conditions as that of the model reaction.

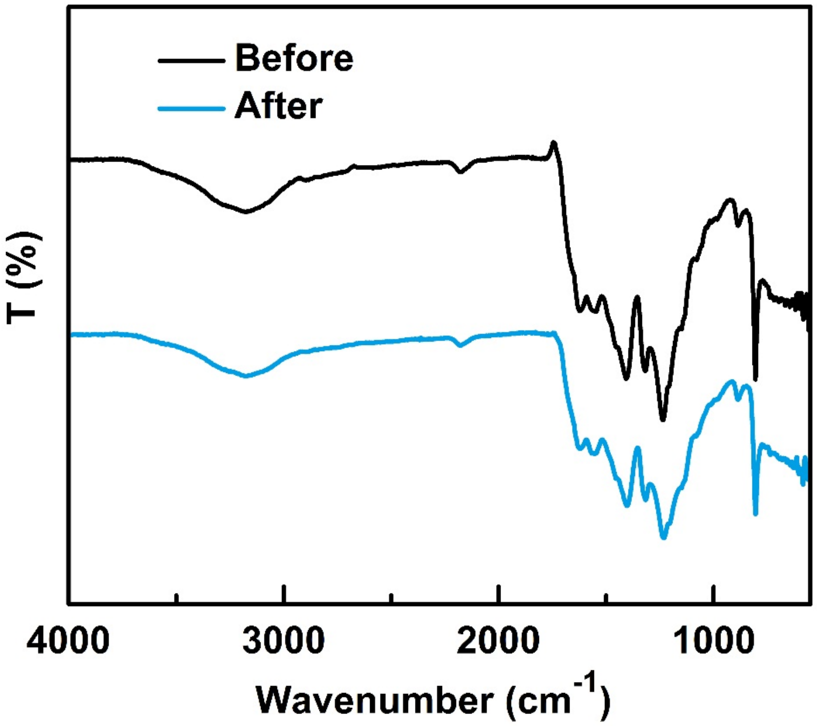
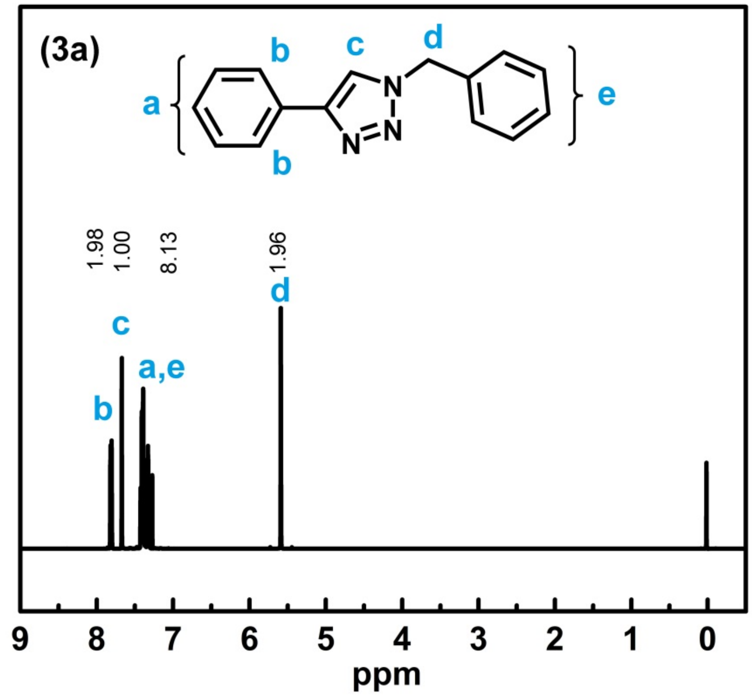


Figure S3. FTIR spectra of mpg-C_3N_4 before and after using in photoclicking process.

^{1}H NMR AND ^{13}C NMR SPECTRA


(3a)
a
b
c
d
e
N
N
N
1.98
1.00
8.13
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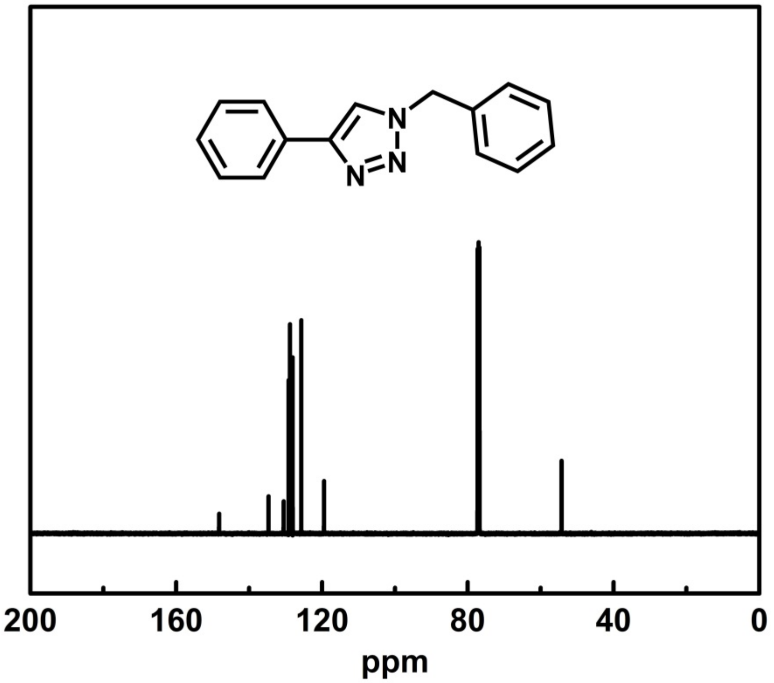
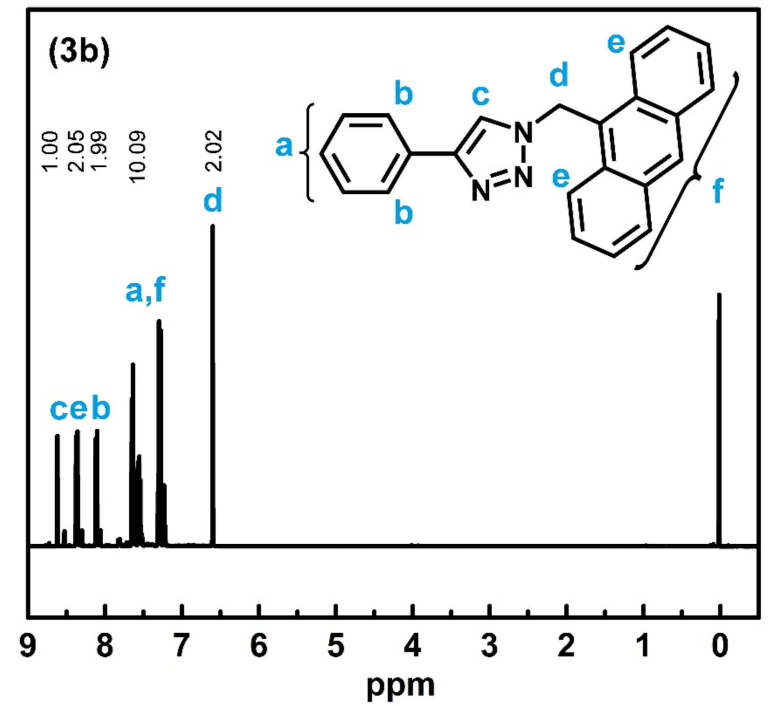
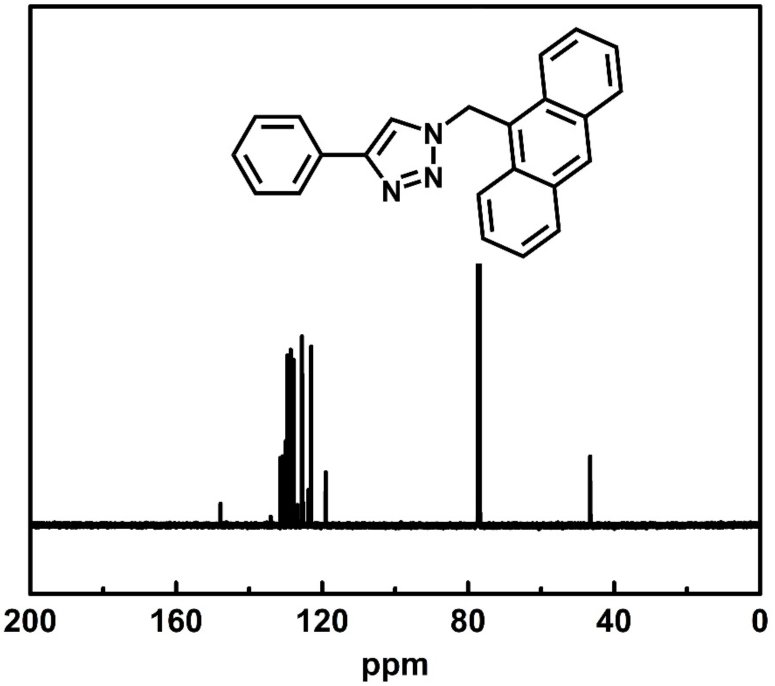
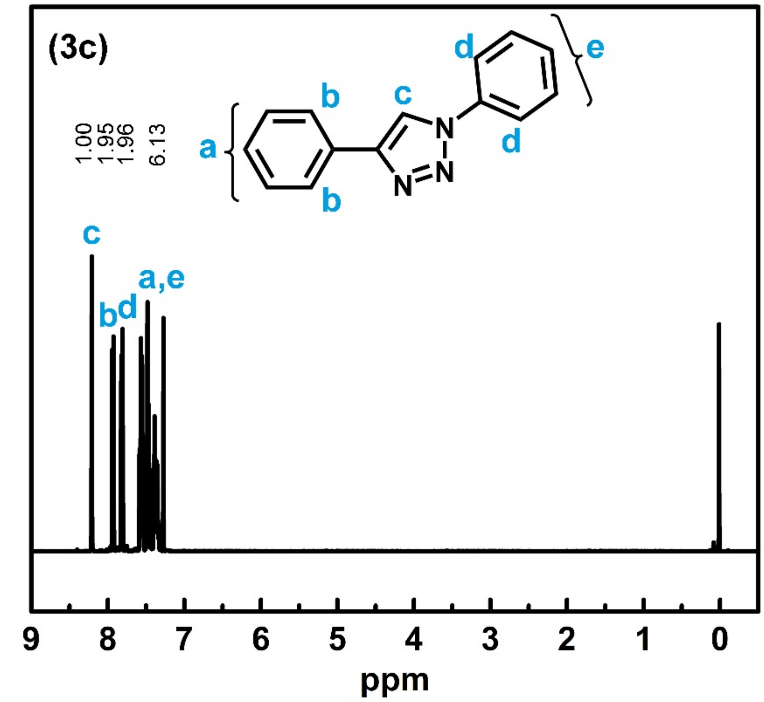
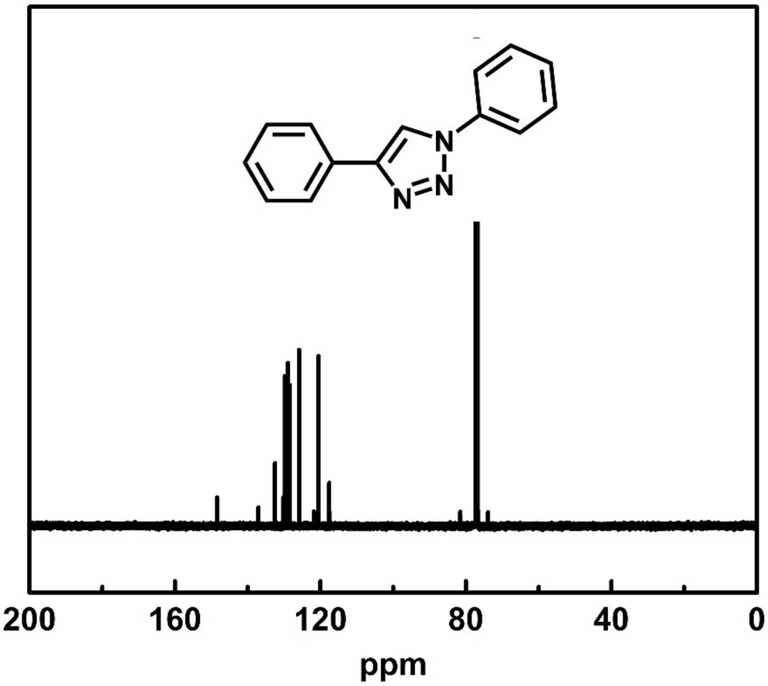
0
ppm

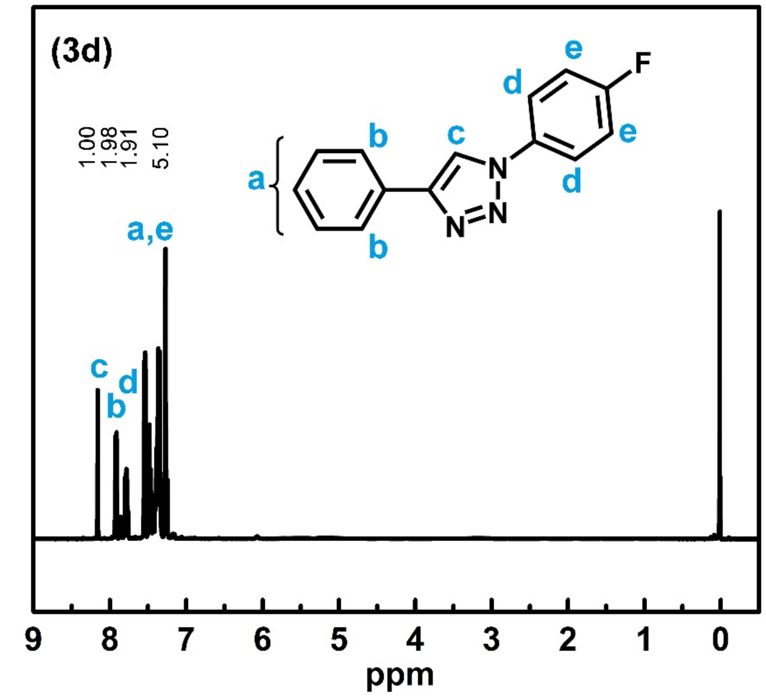

N
N
N
200
160
120
80
40
0
ppm

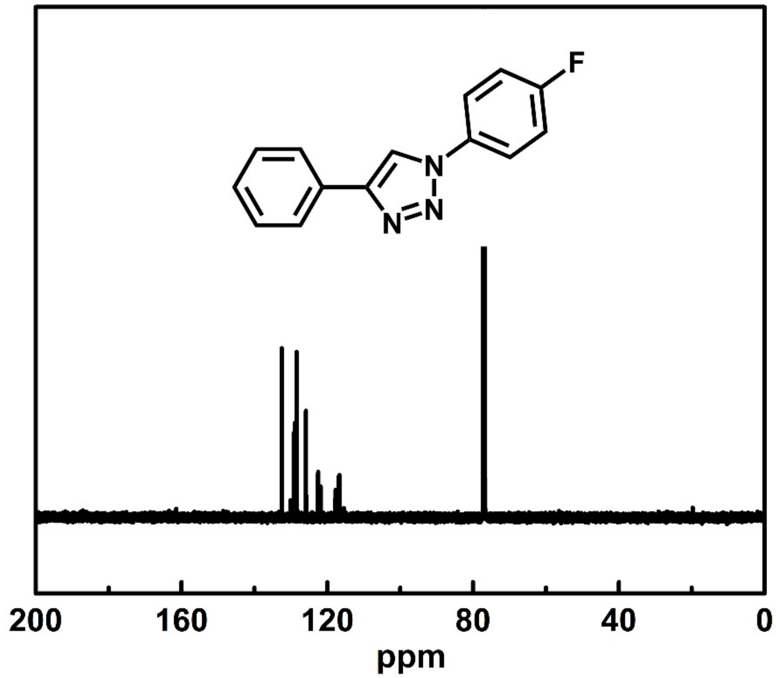

(3b)
1.00
2.05
1.99
10.09
2.02
d
a,f
ceb
a
b
b
c
d
e
e
f
N
N
N
9
8
7
6
5
4
3
2
1
0
ppm

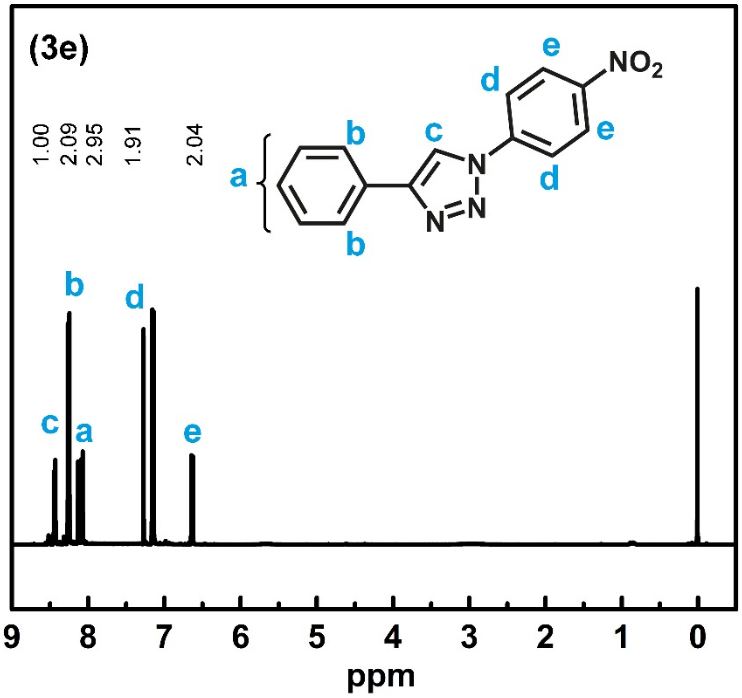

N
N
N
200
160
120
80
40
0
ppm

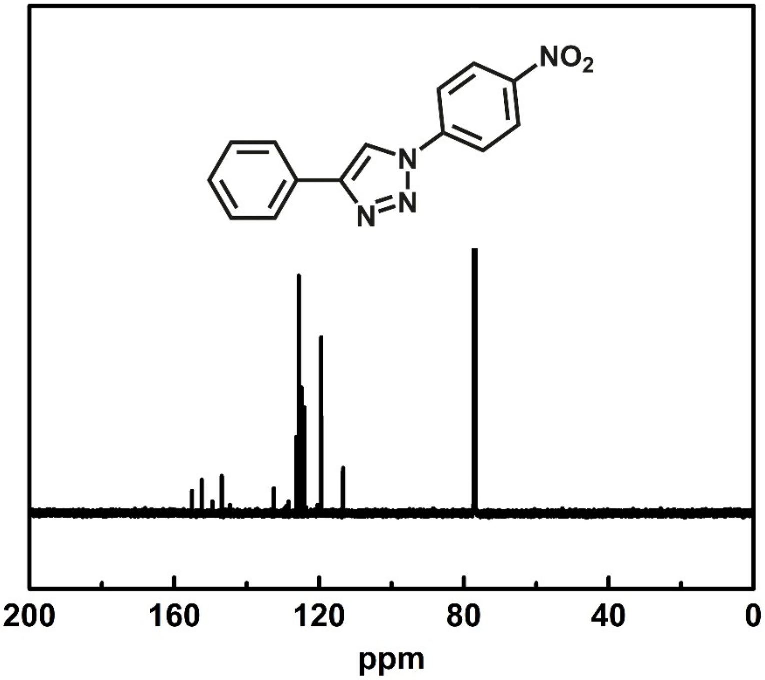

(3c)
a
b
b
c
d
d
e
N
N
N
1.00
1.95
1.96
6.13
c
b
d
a,e
9
8
7
6
5
4
3
2
1
0
ppm

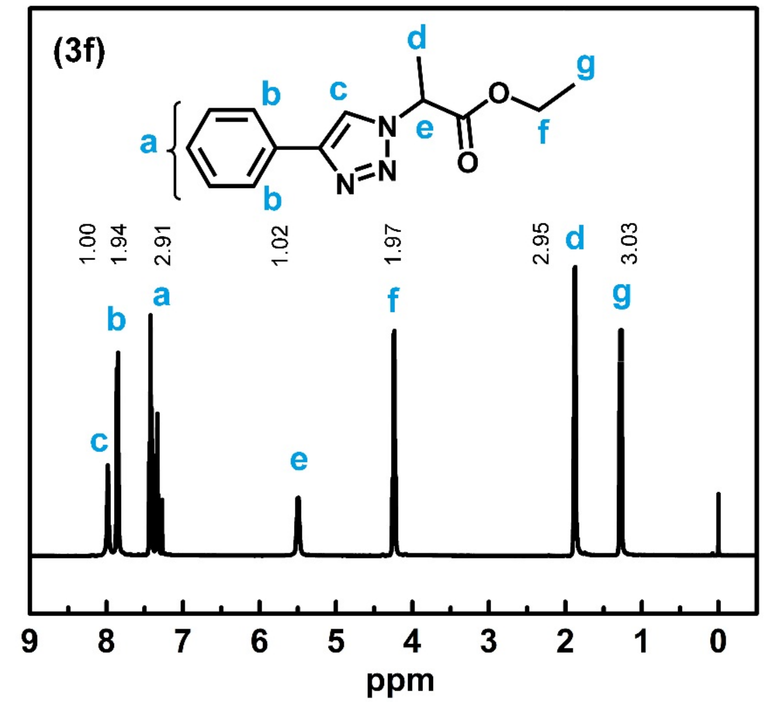

N
N
N
200
160
120
80
40
0
ppm

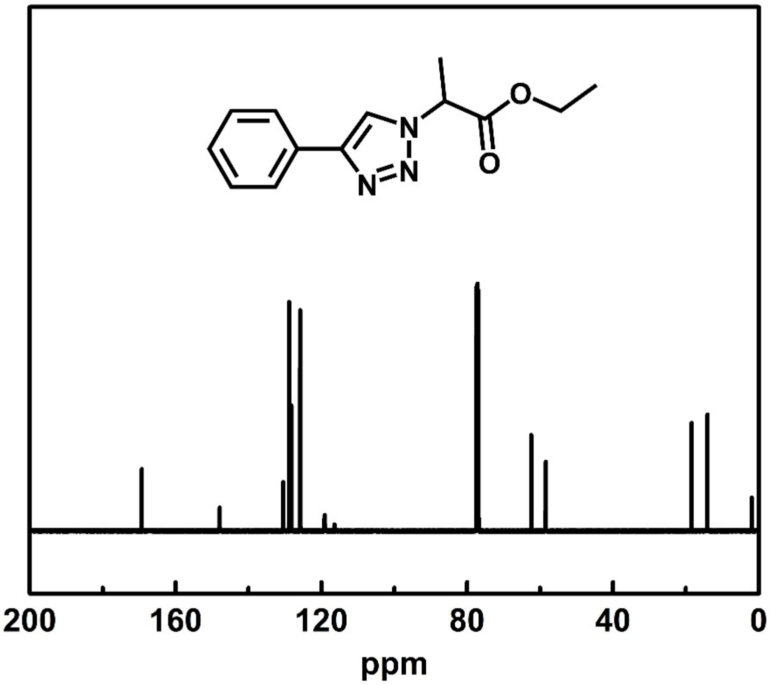

(3d)
1.00
1.98
1.91
5.10
a,e
c
d
b
a
b
b
c
N
N
N
d
d
e
e
F
9
8
7
6
5
4
3
2
1
0
ppm

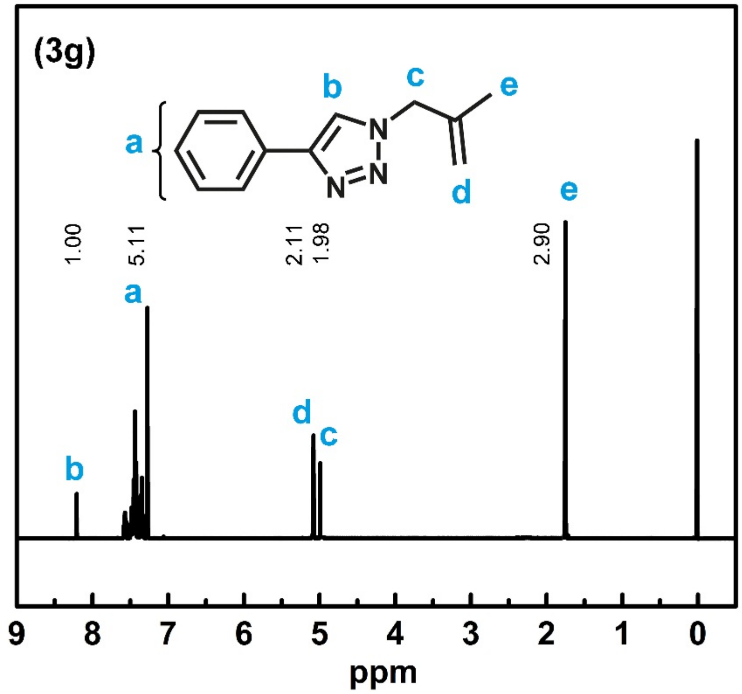

F
N
N
N
200
160
120
80
40
0
ppm

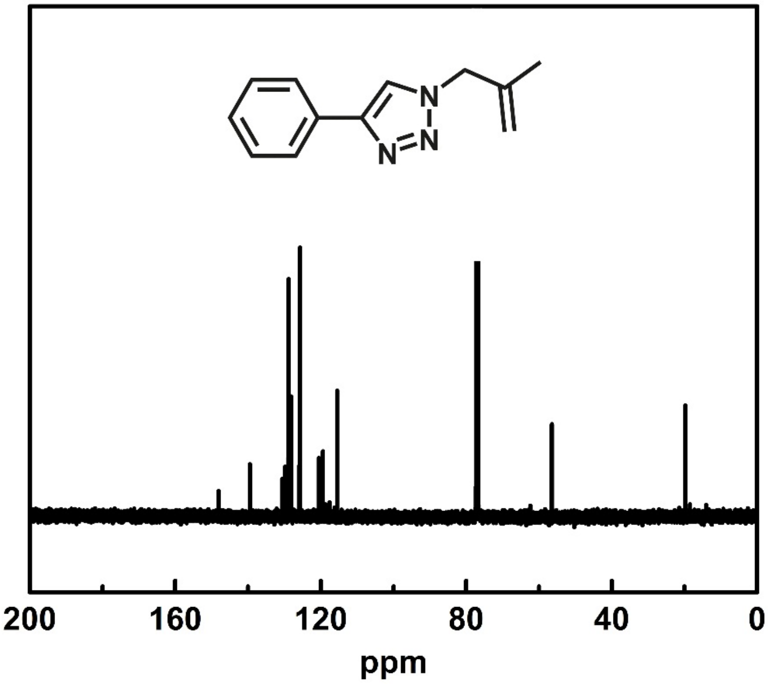

(3e)
1.00
2.09
2.95
1.91
2.04
a
b
b
c
d
d
e
e
NO2
N
N
N
b
d
c
a
e
9
8
7
6
5
4
3
2
1
0
ppm

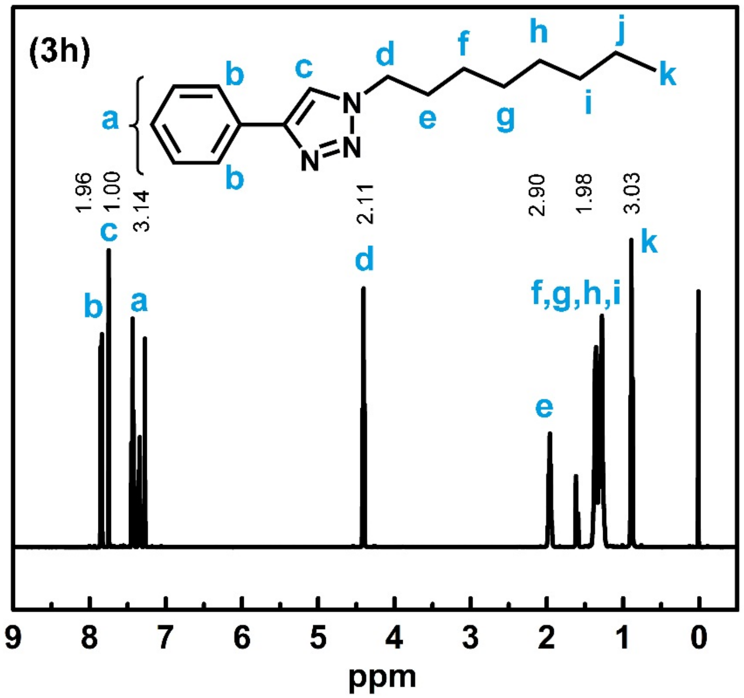

NO2
N
N
N
200
160
120
80
40
0
ppm

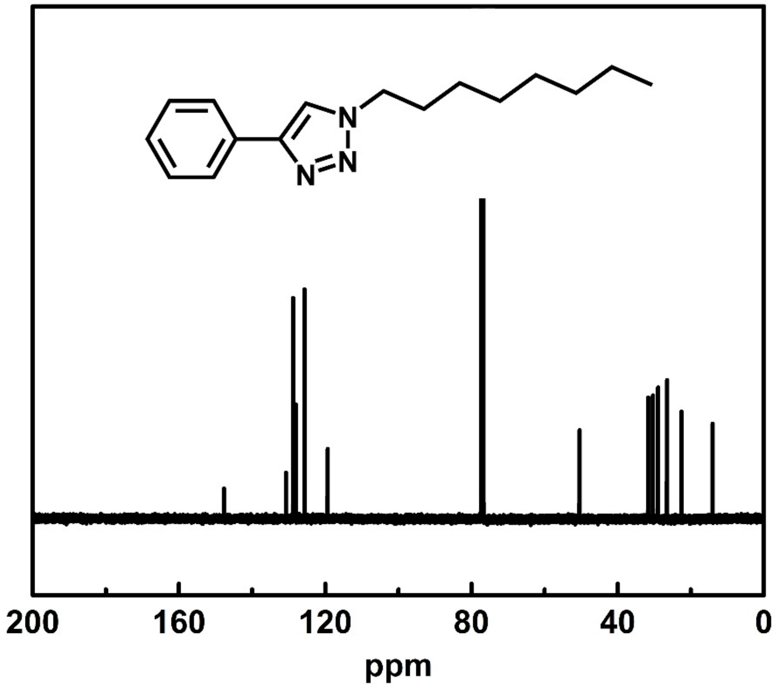

(3f)
a
b
b
c
d
e
f
g
N
N
N
O
O
1.00
1.94
2.91
1.02
1.97
2.95
3.03
c
b
a
e
f
d
g
9
8
7
6
5
4
3
2
1
0
ppm

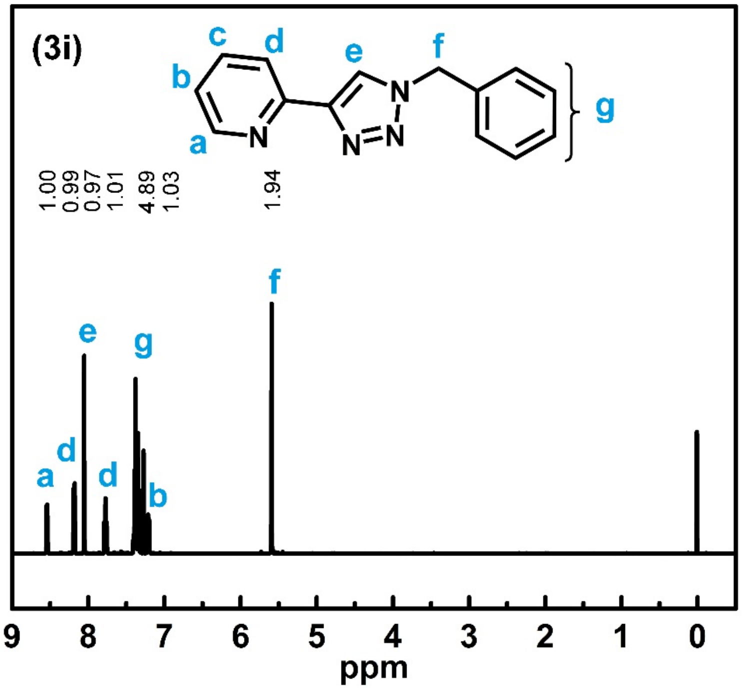

N
N
N
O
O
200
160
120
80
40
0
ppm


(3g)
a
b
c
d
e
N
N
N
1.00
5.11
2.11
1.98
2.90
9
8
7
6
5
4
3
2
1
0
ppm

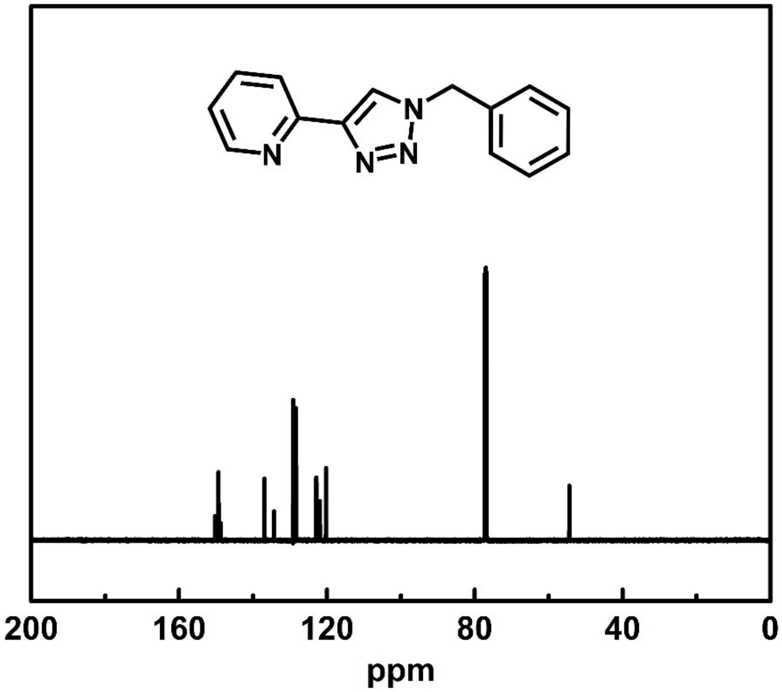

N
N
N
200
160
120
80
40
0
ppm


(3h)
a
b
b
c
d
e
f
g
h
i
j
k
N
N
N
1.96
1.00
3.14
2.11
2.90
1.98
3.03
b
c
a
d
e
f,g,h,i
k
9
8
7
6
5
4
3
2
1
0
ppm

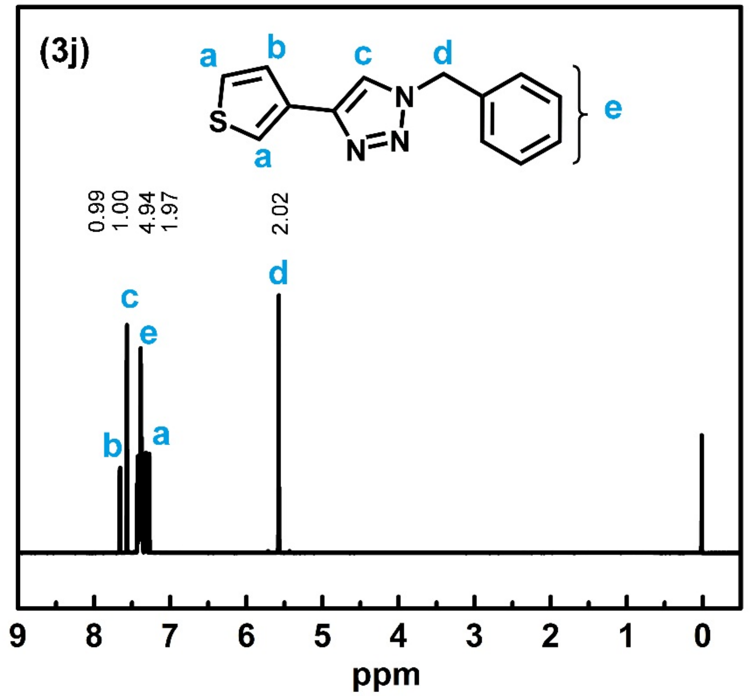

N
N
N
200
160
120
80
40
0
ppm

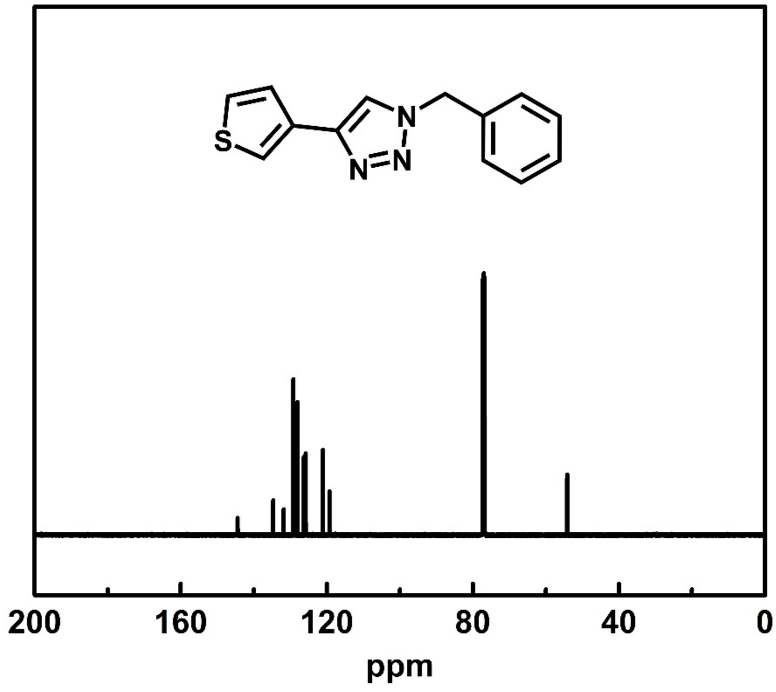


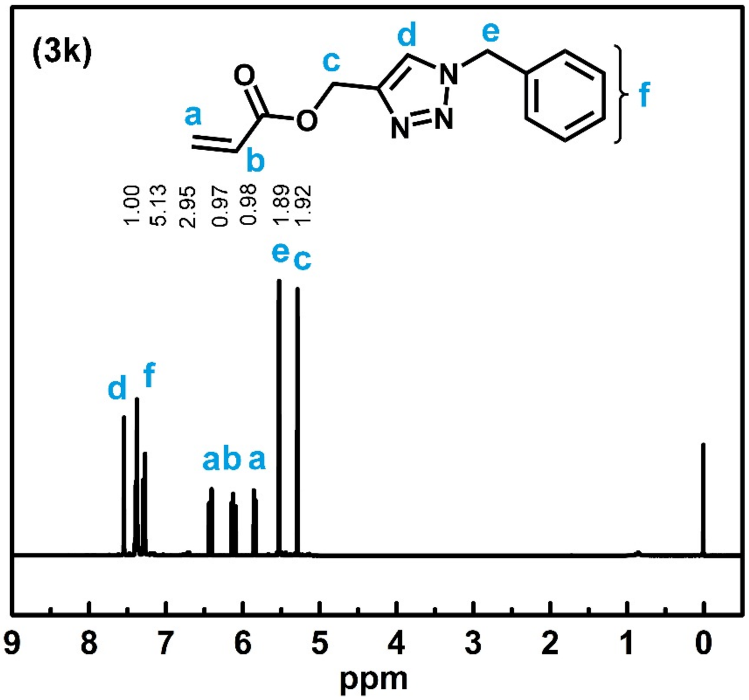
(3i)
a
b
c
d
e
f
g
N
N
N
N
1.00
0.99
0.97
1.01
4.89
1.03
1.94
f
e
g
d
a
d
b
9
8
7
6
5
4
3
2
1
0
ppm

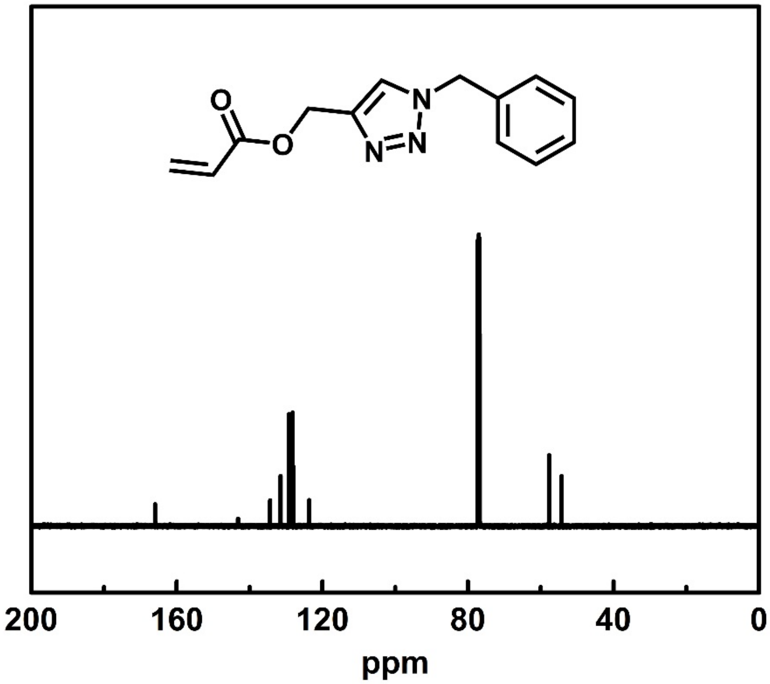


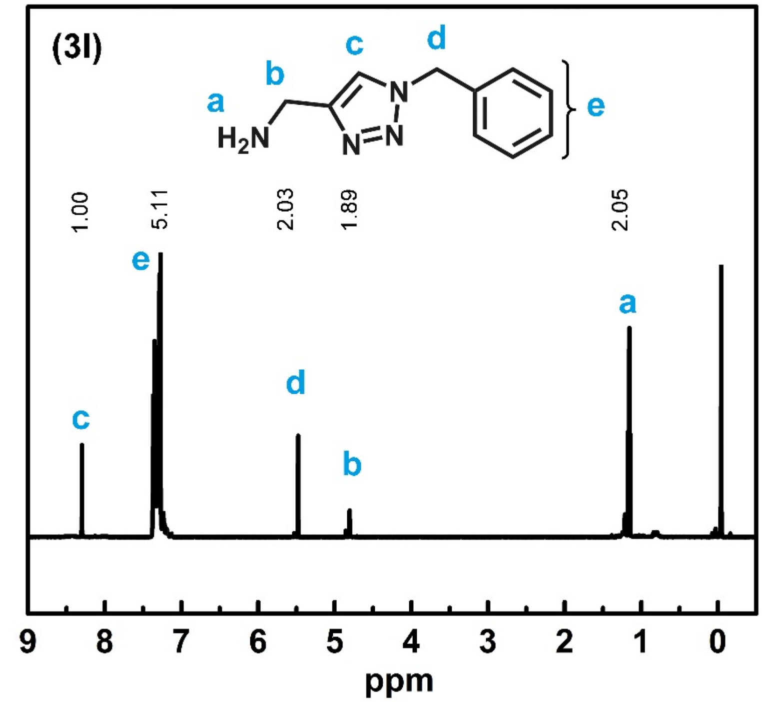
N
N
N
N
200
160
120
80
40
0
ppm

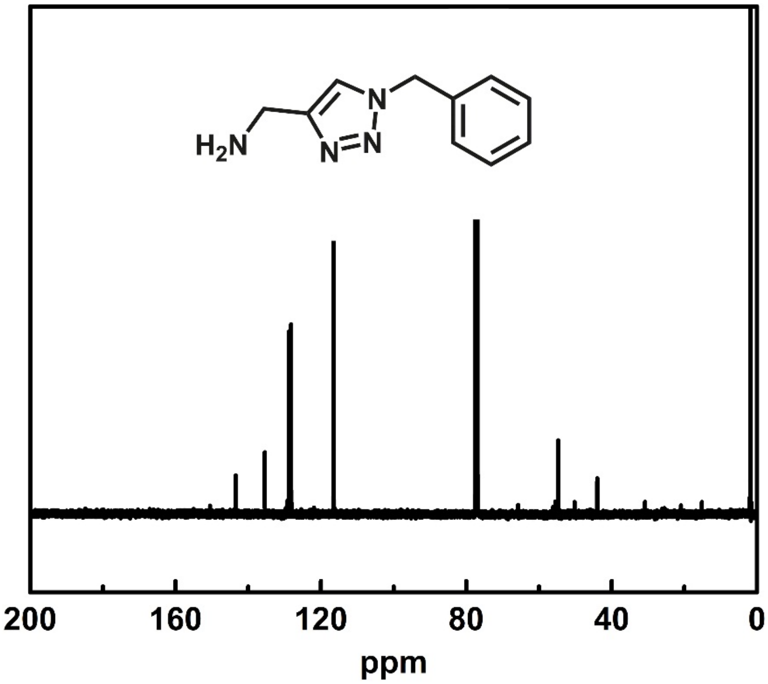

(3j)
a
b
c
d
e
a
S
N
N=N
0.99
1.00
4.94
1.97
2.02
c
e
b
a
d
9
8
7
6
5
4
3
2
1
0
ppm

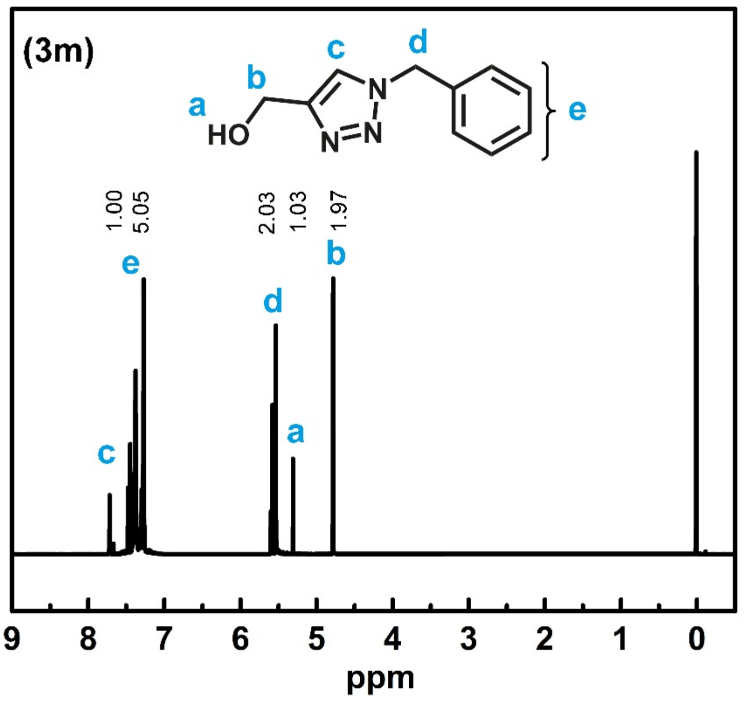

S
N
N=N
200
160
120
80
40
0
ppm

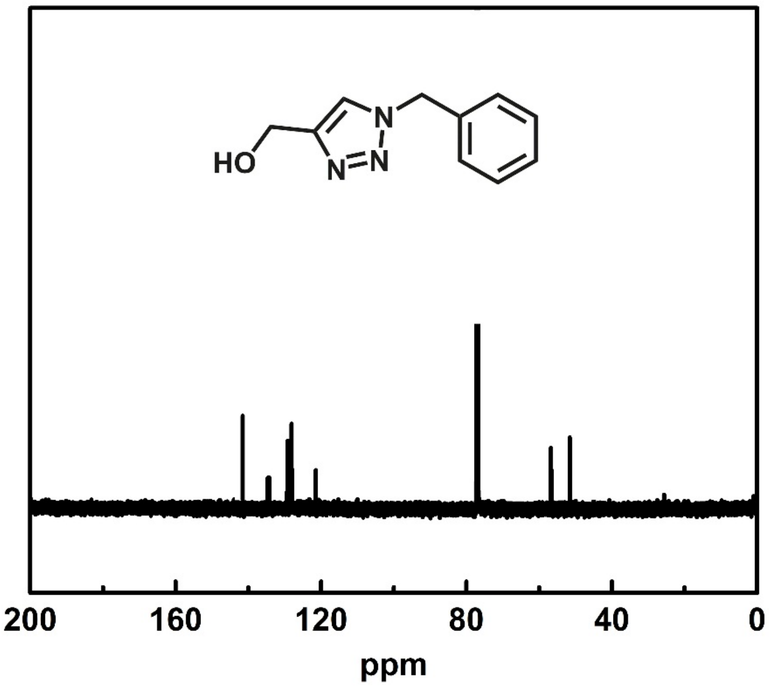

(3k)
a
b
c
d
e
f
O
O
N
N
N
1.00
5.13
2.95
0.97
0.98
1.89
1.92
e
c
d
f
ab
a
9
8
7
6
5
4
3
2
1
0
ppm


O
O
N
N
N
200
160
120
80
40
0
ppm


(3l)
c
d
b
a
H2N
N
N=N
e
1.00
5.11
2.03
1.89
2.05
e
c
d
b
a
9
8
7
6
5
4
3
2
1
0
ppm


H2N
N
N=N
200
160
120
80
40
0
ppm


(3m)
a
b
c
d
e
HO
N
N
N
1.00
5.05
2.03
1.03
1.97
e
d
b
a
c
9
8
7
6
5
4
3
2
1
0
ppm


HO
N
N
N
200
160
120
80
40
0
ppm

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