

## *Supporting Information*

### **Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-catalyzed 1,3-dipolar cycloaddition of terminal alkynes to azides leading to 1,5-disubstituted 1,2,3-triazole derivatives: new mechanistic features**

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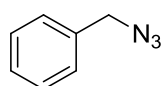
<sup>1</sup>H, <sup>13</sup>C, NMR spectra

## General Information

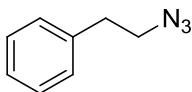
All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene and THF were refluxed and distilled over sodium/ benzophenone ketyl under nitrogen. DMSO, DMF, DCE and CH<sub>3</sub>CN were distilled over calcium hydride. Aryl acetylenes were obtained commercially from Sigma Aldrich or AlfaAesar. Azides were synthesized according to the corresponding literatures. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz using CDCl<sub>3</sub> or benzene-*d*<sub>6</sub> as solvent. Chemical shifts (δ) are reported in ppm downfield of TMS and coupling constants (*J*) are expressed in hertz (Hz). GC-MS were obtained on a Focus GC-ISQ MS instrument. High-resolution mass spectra (HRMS) were recorded using ESI ionization sources.

## Preparation of Azides: (1a-1l)

**General procedure A for synthesis of 1a, 1b, 1c and 1d:**<sup>1,2</sup> To a solution of organic bromide (5 mmol) in water/acetone (1:3, 0.25 M) was added NaN<sub>3</sub> (2.0 equiv) and the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over MgSO<sub>4</sub> and evaporated. The crude material was further dried with molecular sieve.



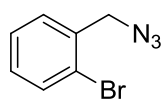
**Benzyl azide<sup>3</sup> (1a).** General procedure A was applied to 15 mmol of benzyl bromide to afford **1a** in a 98% yield as a colorless oil. Spectroscopic data for the title compound were consistent with the literature.



**2-Azidoethyl benzene (1b)**<sup>4</sup>. General procedure A was applied to 5 mmol of (2-bromoethyl)benzene to afford **1b** in a 94% yield as a light yellow oil. Spectroscopic data for the title compound were consistent with the literature.

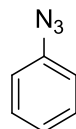


**Azidocyclohexane (1c)**<sup>5</sup>. General procedure A was applied to 5 mmol of bromocyclohexane to afford **1c** in a 74% yield as a colorless oil. Spectroscopic data for the title compound were consistent with the literature.



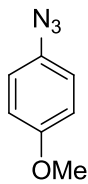
**2-Bromobenzyl azide (1d)**<sup>6</sup>. General procedure A was applied to 5 mmol of 2-bromo-benzyl bromide to afford **1d** in a 93% yield as a yellowish oil. Spectroscopic data for the title compound were consistent with the literature.

**General procedure B** (applied to the preparation of **1e-1k**):<sup>7</sup> aniline 5 mmol was dissolved in CH<sub>3</sub>CN (10 mL) in a 50 mL round-bottomed flask and cooled to 0 °C in an ice bath. To this stirred mixture was added <sup>t</sup>BuONO (7.5 mmol) followed by TMSN<sub>3</sub> (6 mmol) dropwise. The resulting solution was stirred at room temperature for 1 h. The reaction mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography (hexane) to give the product. The crude material was further dried with molecular sieve.

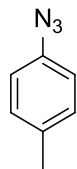


**1-Azidobenzene<sup>7</sup> (1e).** General procedure B was applied to 5 mmol of aniline to afford **1e** in a 90% yield as a pale yellow oil. Spectroscopic data for the title

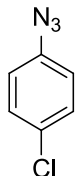
compound were consistent with the literature.



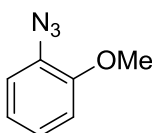
**1-Azido-4-methoxybenzene**<sup>7</sup> (**1f**). General procedure B was applied to 5 mmol of *p*-anisidine to afford **1f** in a 80% yield as a yellow oil. Spectroscopic data for the title compound were consistent with the literature.



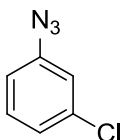
**1-Azido-4-toluene**<sup>8</sup> (**1g**). General procedure B was applied to 5 mmol of *p*-methylaniline to afford **1g** in a 92% yield as a colorless oil. Spectroscopic data for the title compound were consistent with the literature.



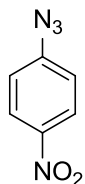
**1-Azido-4-chlorobenzene**<sup>9</sup> (**1h**). General procedure B was applied to 5 mmol of *p*-chloroaniline to afford **1h** in a 80% yield as a yellow oil. Spectroscopic data for the title compound were consistent with the literature.



**1-Azido-2-methoxybenzene**<sup>9</sup> (**1i**). General procedure B was applied to 5 mmol of *o*-methoxy-aniline to afford **1i** in a 90% yield as a yellow oil. Spectroscopic data for the title compound were consistent with the literature.

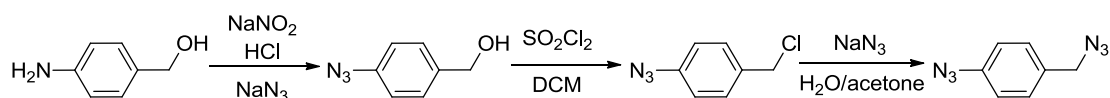


**1-Azido-3-chlorobenzene**<sup>10</sup> (**1j**). General procedure B was applied to 5 mmol of *m*-chloro-aniline to afford **1j** in a 85% yield as a yellow oil. Spectroscopic data for the title compound were consistent with the literature.

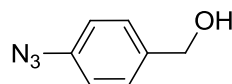


**1-Azido-4-nitrobenzene**<sup>7</sup> (**1k**). General procedure B was applied to 5 mmol of *o*-methoxy-aniline to afford **1k** in a 72% yield as an orange solid. Spectroscopic data for the title compound were consistent with the literature.

#### Procedure C: preparation of 1-Azido-4-(azidomethyl)benzene<sup>11</sup> (**1l**).



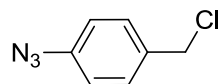
#### Synthesis of (4-azidophenyl)methanol



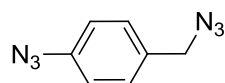
To a solution of NaNO<sub>2</sub> (2.20 g, 33 mmol) in water (30 mL), 4-aminobenzylalcohol (3.20 g, 30 mmol) dissolved in HCl 6N (60 mL) was added dropwise at 0°C. The reaction was stirred at this temperature during 30 minutes before NaN<sub>3</sub> (3.90 g, 60 mmol) dissolved in water (60 mL) was added dropwise. The reaction was followed by TLC and quenched after 2h. After extraction with ether (×3), the organic phase was washed with a NaHCO<sub>3</sub> saturated aqueous solution then with

brine before being dried over MgSO<sub>4</sub>. The evaporation of the solvent in vacuo furnished a crude material, which was purified by flash chromatography on silica gel providing the azide as a yellow solid in 90% yield (4.02 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 7.33 (2H, d, *J* = 8.4 Hz), 7.00 (2H, d, *J* = 8.4 Hz), 4.64 (2H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 139.6, 137.8, 128.8, 119.4, 64.9; Spectroscopic data for the title compound were consistent with the literature.

#### Synthesis of 1-azido-4-(chloromethyl)benzene



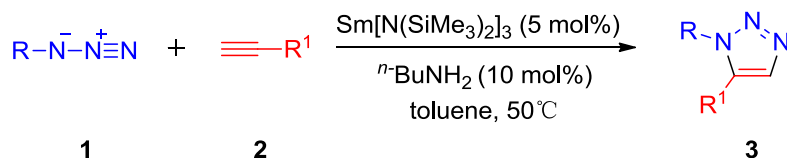
To a solution of (4-azidophenyl)methanol (2.98 g, 20 mmol) in DCM (20 mL), SO<sub>2</sub>Cl<sub>2</sub> (2.9 mL, 40 mmol) was added dropwise at 0°C. The reaction was then stirred at room temperature overnight. After completion of the reaction, as indicated by TLC, the mixture was quenched with water in ice bath, the solution was extracted with ether (×3), the organic phase was washed with a Na<sub>2</sub>CO<sub>3</sub> saturated aqueous solution then with brine before being dried over MgSO<sub>4</sub>. The evaporation of the solvent in vacuo furnished a crude material, which was purified by flash chromatography on silica gel providing the azide as a yellow solid in 90% yield (4.02 g). Spectroscopic data for the title compound were consistent with the literature.



#### Synthesis of 1-Azido-4-(azidomethyl)benzene (11)

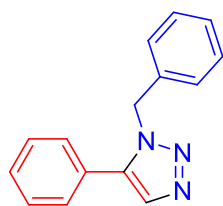
Procedure A was applied to 15 mmol of 1-azido-4-(chloromethyl)benzene to afford **11** in a 92% yield as a yellow oil. Spectroscopic data for the title compound were consistent with the literature.

## General procedure for the synthesis of 1,5-disubstituted-1*H*-1,2,3-triazole



To a mixture of Sm[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (12.6 mg, 0.02 mmol) and <sup>n</sup>BuNH<sub>2</sub> (4.0 μL, 0.04 mmol) in toluene (2.0 mL) were added alkyne **2** (0.44 mmol) and azide **1** (0.4 mmol) at room temperature under N<sub>2</sub> atmosphere. The reaction mixture was heated with stirring at 50 °C. After completion of the reaction as monitored by GC-MS, the reaction was quenched with water (2 mL), the solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, and dried over sodium sulfate. Evaporation of the solvents followed by purification by flash column chromatography on silica gel provides the desired product **3**. The unreacted alkyne and trace impurity were first eluted out with hexane, followed by 1/1 hexane/ether. The pure

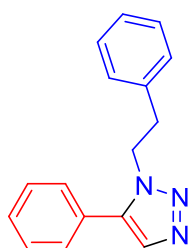
1,5-disubstituted 1,2,3-triazole product was then obtained by elution with ether or ethyl acetate.



**1-benzyl-5-phenyl-1H-1,2,3-triazole (3aa)**<sup>12</sup>:

Yellow solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 5.55 (s, 2H), 7.06 – 7.09 (m, 2H), 7.24 – 7.30 (m, 5H), 7.39 – 7.45 (m, 3H), 7.74 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 51.85, 126.93, 127.22, 128.22, 128.92, 129.08, 129.64, 133.26, 133.34, 135.66, 138.26.

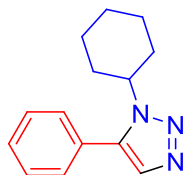
Spectroscopic data for **3aa** were consistent with previously reported data for this compound.



**1-phenethyl-5-phenyl-1H-1,2,3-triazole (3ba)**<sup>12</sup>:

Off-white solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 3.19 (t, *J* = 7.4 Hz, 2H), 4.54 (t, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 3.4 Hz, 2H), 7.08 (d, *J* = 6.8 Hz, 2H), 7.21 (d, *J* = 5.6 Hz, 3H), 7.41 (dd, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 5.6 Hz, 3H), 7.63 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 36.71, 49.54, 127.10, 128.84, 128.87, 128.95, 128.99, 129.07, 129.50, 133.04, 137.26, 138.35.

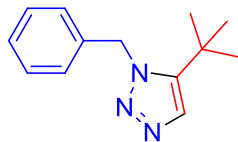
Spectroscopic data for **3ba** were consistent with previously reported data for this compound.



**1-cyclohexyl-5-phenyl-1H-1,2,3-triazole (3ca)**<sup>13</sup>:

Yellow solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 1.23-1.36 (m, 3H), 1.67-1.74 (m, 1H), 1.86-1.95 (m, 2H), 1.97-2.04 (m, 2H), 2.10-2.17 (m, 2H), 4.20 (tt, *J*<sub>1</sub> = 12 Hz, *J*<sub>2</sub> = 3.9Hz, 1H), 7.32-7.37 (m, 2H), 7.46-7.53 (m, 3H), 7.66 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 24.9, 25.4, 33.5, 57.8, 127.4, 128.9, 129.0, 129.3, 132.6, 137.0.

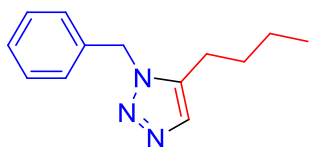
Spectroscopic data for **3ca** were consistent with previously reported data for this compound.



**1-benzyl-5-(tert-butyl)-1H-1,2,3-triazole**<sup>12</sup> (**3ab**)

Yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 1.28 (s, 9H), 5.70 (s, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.26 - 7.32 (m, 3H), 7.47 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 29.90, 30.36, 52.88, 126.46, 127.92, 128.82, 131.64, 136.29, 145.64.

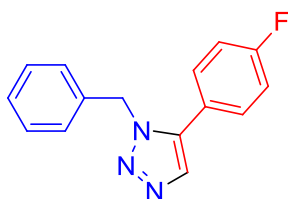
Spectroscopic data for **3ab** were consistent with previously reported data for this compound.



**1-benzyl-5-butyl-1H-1,2,3-triazole<sup>12</sup> (3ac)**

Yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 0.85 (t, *J* = 7.2 Hz, 3H), 1.27 – 1.34 (m, 2H), 1.46 – 1.53 (m, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 5.49 (s, 2H), 7.14 (d, *J* = 6.4 Hz, 2H), 7.31 – 7.33 (m, 3H), 7.47 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 13.74, 22.28, 22.94, 30.02, 51.73, 127.22, 128.38, 129.06, 132.68, 135.22, 137.58.

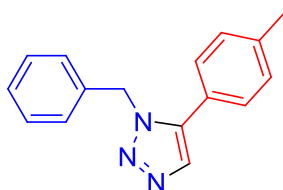
Spectroscopic data for **3ac** were consistent with previously reported data for this compound.



**1-benzyl-5-(p-fluorophenyl)-1H-1,2,3-triazole<sup>14</sup> (3ad)**

Yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 5.52 (s, 2H), 7.05 – 7.12 (m, 4H), 7.19 – 7.23 (m, 2H), 7.28 – 7.29 (m, 3H); 7.71 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 52.05, 116.34 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.8 Hz), 123.14 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.5 Hz), 127.28, 128.46, 129.09, 131.10 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.3 Hz), 133.61, 135.54, 137.37, 163.54 (d, <sup>1</sup>*J*<sub>CF</sub> = 249.3 Hz).

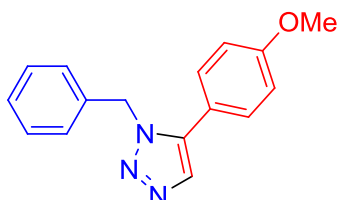
Spectroscopic data for **3ad** were consistent with previously reported data for this compound.



**1-benzyl-5-(p-tolyl)-1H-1,2,3-triazole<sup>15</sup> (3ae)**

Colourless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 2.39 (s, 3H), 5.53 (s, 2H), 7.09 (d, *J* = 5.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.29 (m, 3H), 7.71 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 21.51, 51.88, 124.06, 127.32, 128.29, 128.94, 129.00, 129.84, 133.33, 135.83, 138.42, 139.84.

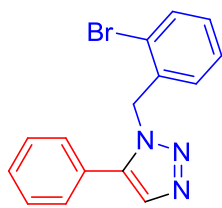
Spectroscopic data for **3ae** were consistent with previously reported data for this compound.



**1-benzyl-5-(p-methoxyphenyl)-1H-1,2,3-triazole<sup>16</sup> (3af)**

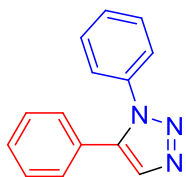
White solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.84 (s, 3H), 5.52 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 6.5 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.29 (m, 3H), 7.69 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 51.82, 55.55, 114.58, 119.11, 127.27, 128.28, 129.00, 130.40, 133.22, 135.83, 138.17, 160.67.

Spectroscopic data for **3af** were consistent with previously reported data for this compound.



**1-(*o*-bromobenzyl)-5-phenyl-1*H*-1,2,3-triazole (3da):**

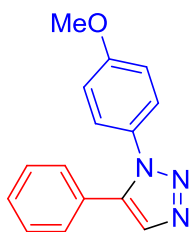
Yellow solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  5.64 (s, 2H), 6.76 (d,  $J = 7.6$  Hz, 1H), 7.13 – 7.17 (m, 1H), 7.21 – 7.26 (m, 3H), 7.40 – 7.41 (m, 3H), 7.55 (d,  $J = 7.9$  Hz, 1H), 7.81 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  51.69, 121.96, 126.44, 127.96, 128.27, 128.44, 129.12, 129.59, 132.84, 133.13, 135.02, 138.58. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{13}\text{BrN}_3$  ( $\text{M}+\text{H}$ ) 314.0293, found 314.0301.



**1,5-diphenyl-1*H*-1,2,3-triazole<sup>17</sup> (3ea)**

Off-white solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.20 - 7.23 (m, 2H), 7.30 - 7.44 (m, 8H), 7.85 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  125.15, 126.67, 128.56, 128.74, 129.15, 129.28, 133.39, 136.55, 137.64.

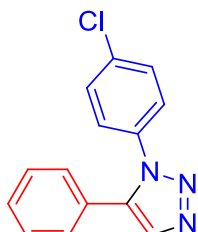
Spectroscopic data for **3ea** were consistent with previously reported data for this compound.



**1-(*p*-methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole<sup>18</sup> (3fa)**

Light brown solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.83 (s, 3H), 6.91 - 6.94 (m, 2H), 7.21 - 7.28 (m, 4H), 7.32 - 7.36 (m, 3H), 7.84 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  55.74, 114.67, 126.77, 127.01, 128.71, 129.01, 129.31, 129.75, 133.34, 137.89, 160.24.

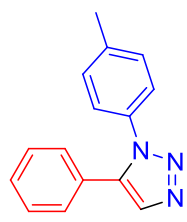
Spectroscopic data for **3fa** were consistent with previously reported data for this compound.



**1-(*p*-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole<sup>18</sup> (3ha)**

Light brown solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.22 - 7.24 (m, 2H), 7.30 - 7.32 (m, 2H), 7.37 - 7.41 (m, 5H), 7.85 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  126.39, 126.49, 128.69, 129.09, 129.54, 129.67, 133.60, 135.13, 135.20, 137.81.

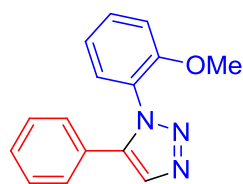
Spectroscopic data for **3ha** were consistent with previously reported data for this compound.



**1-(*p*-tolyl)-5-phenyl-1*H*-1,2,3-triazole<sup>18</sup> (3ga)**

Light brown solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 2.39 (s, 3H), 7.20 - 7.24 (m, 6H), 7.33 - 7.35 (m, 3H), 7.84 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 21.27, 125.08, 126.90, 128.62, 128.90, 129.23, 130.01, 133.34, 134.20, 137.74, 139.45.

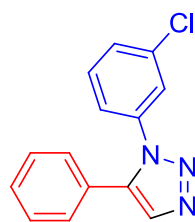
Spectroscopic data for **3ga** were consistent with previously reported data for this compound.



**1-(*o*-methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole<sup>17</sup> (3ia)**

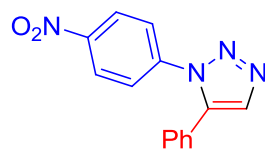
Yellow powder, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 3.46 (s, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.20 - 7.22 (m, 2H), 7.26 - 7.31 (m, 3H), 7.43 - 7.47 (m, 2H), 7.88 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz): δ 55.56, 112.52, 121.10, 125.84, 127.52, 127.53, 128.47, 128.69, 129.00, 131.55, 132.21, 139.43, 153.81.

Spectroscopic data for **3ia** were consistent with previously reported data for this compound.



**1-(*m*-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole (3ja)**

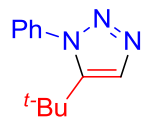
Yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.18-7.20 (m, 1H), 7.22 - 7.24 (m, 2H), 7.31 - 7.42 (m, 5H), 7.46 (s, 1H), 7.85 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 123.36, 125.49, 126.42, 128.73, 129.16, 129.54, 129.69, 130.46, 133.67, 135.20, 137.63, 137.95. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub> (M+H) 256.0642, found 256.0649.



**1-(*p*-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole<sup>17</sup> (3ka)**

Yellow powder, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.24 - 7.26 (m, 2H), 7.40 - 7.60 (m, 3H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.89 (s, 1H), 8.30 (d, *J* = 8.7 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 124.93, 125.31, 126.01, 128.73, 129.30, 129.94, 134.19, 138.01, 141.32, 147.51.

Spectroscopic data for **3ka** were consistent with previously reported data for this compound.

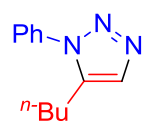


**1-phenyl-5-(*tert*-butyl)-1*H*-1,2,3-triazole<sup>19</sup> (3eb)**



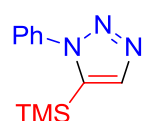
Yellowish oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz):  $\delta$  1.23 (s, 9H), 7.40 (m, 2H), 7.54 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  30.41, 31.01, 128.30, 129.16, 130.39, 131.09, 138.43, 147.50.

Spectroscopic data for **3eb** were consistent with previously reported data for this compound.



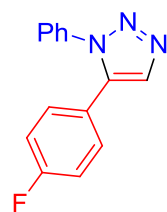
**1-phenyl-5-butyl-1H-1,2,3-triazole (3ec)**

Yellowish oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz):  $\delta$  0.87 (t,  $J = 8.0$  Hz, 3H), 1.33 (sext,  $J = 8.0$  Hz, 2H), 1.58 (quin,  $J = 8.0$  Hz, 2H), 2.66 (t,  $J = 8.0$  Hz, 2H), 7.44 (d,  $J = 7.2$  Hz, 2H), 7.51 - 7.54 (m, 3H), 7.59 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  13.74, 22.27, 23.48, 30.48, 125.41, 129.59, 129.61, 132.45, 136.60, 138.36. HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_3$  (M+H) 202.1344, found 202.1349.



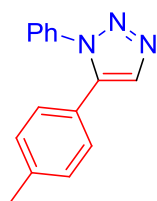
**1-phenyl-5-(trimethylsilyl)-1H-1,2,3-triazole (3eg)**

Yellowish oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz):  $\delta$  0.16 (s, 9H), 7.42 - 7.44 (m, 2H), 7.52 - 7.54 (m, 3H), 7.80 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  -0.72, 126.19, 129.36, 130.01, 136.84, 138.89, 141.60. HRMS (ESI) calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}_3\text{Si}$  (M+H) 218.1113, found 218.1117.



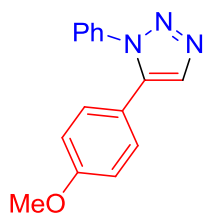
**1-phenyl-5-(p-fluorophenyl)-1H-1,2,3-triazole (3ed)**

Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.05 (t,  $J = 8.2$  Hz, 2H), 7.20 - 7.23 (m, 2H), 7.33 - 7.36 (m, 2H), 7.44 - 7.46 (m, 3H), 7.84 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  116.27 (d,  $^2J_{\text{CF}} = 21.8$  Hz), 123.01 (d,  $^4J_{\text{CF}} = 3.5$  Hz), 125.35, 129.54, 129.62, 130.71 (d,  $^3J_{\text{CF}} = 8.4$  Hz), 133.48, 136.76 (d,  $^1J_{\text{CF}} = 43.7$  Hz). HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{11}\text{FN}_3$  (M+H) 240.0937, found 240.0942.



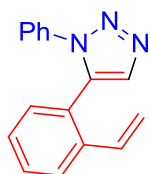
**1-phenyl-5-(p-tolyl)-1H-1,2,3-triazole (3ee)**

Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.34 (s, 3H), 7.11 (d,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 2H), 7.35 - 7.37 (m, 2H), 7.42 - 7.44 (m, 3H), 7.83 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  21.42, 123.87, 125.33, 128.57, 129.29, 129.46, 129.69, 133.31, 136.82, 137.93, 139.50. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_3$  (M+H) 236.1188, found 236.1195.



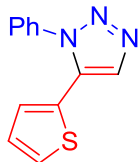
**1-phenyl-5-(*p*-methoxyphenyl)-1*H*-1,2,3-triazole (3ef)**

Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.79 (s, 3H), 6.85 (d,  $J = 7.8$  Hz, 2H), 7.14 (d,  $J = 7.8$  Hz, 2H), 7.35 – 7.37 (m, 2H), 7.42 – 7.44 (m, 3H), 7.8 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  55.41, 114.45, 118.97, 125.32, 129.27, 129.46, 130.04, 133.03, 136.82, 137.71, 160.37. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$  ( $\text{M}+\text{H}$ ) 252.1137, found 252.1143.



**1-phenyl-5-(*o*-vinylphenyl)-1*H*-1,2,3-triazole (3eh)**

Yellowish oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  5.14 (d,  $J = 11.0$  Hz, 1H), 5.55 (d,  $J = 17.4$  Hz, 1H), 6.46 (dd,  $J = 11.0$  and 17.4 Hz, 1H), 7.13 (d,  $J = 7.7$  Hz, 1H), 7.24 – 7.34 (m, 6H), 7.39 – 7.42 (m, 1H), 7.59 (d,  $J = 8$  Hz, 1H), 7.79 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  117.13, 124.44, 125.67, 126.16, 128.05, 128.99, 129.37, 130.12, 130.91, 133.80, 135.19, 136.21, 136.74, 137.65. HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_3$  ( $\text{M}+\text{H}$ ) 248.1188, found 248.1196.



**1-phenyl-5-(2-thienyl)-1*H*-1,2,3-triazole (3ei)**

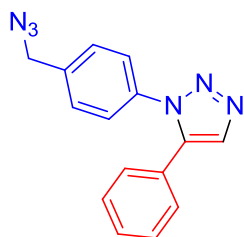
Brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  6.93 (d,  $J = 3.5$  Hz, 1H), 6.98 – 7.00 (m, 1H), 7.35 (d,  $J = 5.0$  Hz, 1H), 7.42 – 7.44 (m, 2H), 7.48 – 7.55 (m, 3H), 7.90 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  126.26, 127.21, 127.89, 127.94, 128.30, 129.63, 130.15, 132.66, 133.11, 136.40; HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{S}$  ( $\text{M}+\text{H}$ ) 228.0595, found 228.0601.



**1-phenyl-5-(2-pyridyl)-1*H*-1,2,3-triazole<sup>18</sup> (3ej)**

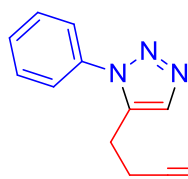
Brown oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.22 (d,  $J = 7.8$  Hz, 1H), 7.26 (dd,  $J = 7.2$  Hz and 5.1 Hz, 1H), 7.41 – 7.47 (m, 5H), 7.66 (dd,  $J = 7.2$  Hz and 7.8 Hz, 1H), 8.12 (s, 1H), 8.59 (d,  $J = 5.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  123.55, 123.77, 125.56, 129.47, 129.58, 134.65, 136.86, 137.09, 137.41, 146.76, 150.30.

Spectroscopic data for **3ej** were consistent with previously reported data for this compound.



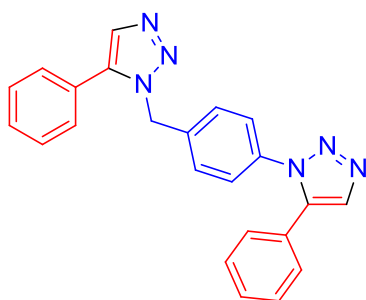
**1-(*p*-(azidomethyl)phenyl)-5-phenyl-1*H*-1,2,3-triazole (3la)**

Yellow powder;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.43 (s, 2H), 7.22 - 7.23 (m, 2H), 7.36 - 7.39 (m, 7H), 7.86 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  54.18, 125.66, 126.76, 128.78, 129.12, 129.15, 129.53, 133.68, 136.56, 136.85, 137.93; HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_6$  (M+H) 277.1202, found 277.1209.



**1-phenyl-5-(but-3-yn-1-yl)-1*H*-1,2,3-triazole (3ek)**

Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.00 (s, 1H), 2.48 (t,  $J = 7.2$  Hz, 2H), 2.92 (t,  $J = 7.2$  Hz, 2H), 7.44 - 7.46 (m, 2H), 7.54 - 7.56 (m, 3H), 7.73 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  18.00, 23.20, 70.33, 81.94, 125.59, 129.81, 129.92, 132.88, 136.34, 136.43. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{11}\text{FN}_3$  (M+H) 198.1031, found 198.1037.



**5-phenyl-1-(4-(5-phenyl-1*H*-1,2,3-triazol-1-yl)benzyl)-1*H*-1,2,3-triazole (4la)**

Yellow powder;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  5.62 (s, 2H), 7.11 - 7.14 (d,  $J = 12$  Hz, 2H), 7.18 - 7.20 (d,  $J = 8$  Hz, 2H), 7.24 - 7.26 (d,  $J = 8$  Hz, 2H), 7.28 - 7.31 (d,  $J = 12$  Hz, 2H), 7.33 - 7.38 (m, 3H), 7.39 - 7.46 (m, 3H), 7.75 (s, 1H), 7.83 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  51.18, 125.50, 126.47, 126.58, 128.12, 128.59, 128.78, 128.95, 129.09, 129.42, 129.75, 133.40, 133.49, 136.31, 136.71, 137.75, 138.25; HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_6$  (M+H) 277.1202, found 379.1671.

**Synthesis of  $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-Cl})(\text{THF})_2]_2$ :**<sup>20</sup>  $\text{YCl}_3$  (1.95 g, 10.0 mmol) and 20 mL of tetrahydrofuran were added to a Schlenk flask in the glove-box. The suspension was heated at 80 °C for 10 h. Then a 10 mL tetrahydrofuran solution of  $\text{KN}(\text{SiMe}_3)_2$  (20 mL, 1M in THF) was added. The reaction was continued to stir overnight at 80 °C. Removing the solvent gave a white powder, which was extracted with toluene. The clear solution was concentrated and crystallized at -30 °C to afford  $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-Cl})(\text{THF})_2]_2$  as a colorless solid. Yield: 3.05 g (59 % based on  $\text{YCl}_3$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400MHz):  $\delta$  0.44 (s, 72 H), 1.26 (br, 8 H), 3.84 (br, 8 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,

100MHz):  $\delta$  5.3, 24.9, 70.5. Spectroscopic data for  $[\text{Y}(\mu\text{-Cl})\{\text{N}(\text{SiMe}_3)_2(\text{THF})\}_2]$  were consistent with previously reported data for this compound.

**Synthesis of lithium phenylacetylide:**<sup>21</sup> *n*-BuLi (1 mmol, 1.6 M in hexane) was added dropwise at  $-78$  °C to a solution of phenylacetylene (1 mmol) in THF (5 mL), and the mixture was stirred at  $-78$  °C for 0.5 h. The reaction mixture was allowed to warm to room temperature, and was concentrated in vacuum to give lithium phenylacetylide in quantitative yield as a white powder. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz):  $\delta$  6.99-7.30 (m, 5H); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 75 MHz):  $\delta$  115.71, 125.54, 128.26, 129.11, 131.73, 135.14. Spectroscopic data for lithium phenylacetylide were consistent with previously reported data for this compound.

**Reaction of yttrium phenylacetylide with phenyl azide:**  $[\text{Y}(\mu\text{-Cl})\{\text{N}(\text{SiMe}_3)_2(\text{THF})\}_2]$  (103 mg, 0.2 mmol) was dissolved in 4 mL THF and then added dropwise to a THF solution of lithium phenylacetylide (0.2 mL, 1M in THF) at  $-78$  °C. The reaction mixture was allowed to warm to room temperature. After stirring for 1h, the reaction mixture was concentrated in vacuum and the residue was washed with hexane ( $3 \times 10$  mL) to afford yellow solid. To a toluene extract of the residue was added phenyl azide (**1e**) (24 mg, 0.2 mmol). The reaction mixture was stirred at 50 °C for 24 h. After completion of the reaction as indicated by GC-MS, the mixture was worked up according to the standard process to afford the 1,2,3-triazole **3ea**. Yield: 21 mg (48 % based on azide **1e**).

**Synthesis of 1-benzyl-4-methyl-5-phenyl-1*H*-1,2,3-triazole (5):** To a mixture of  $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3$  (126 mg, 0.2 mmol) and phenylacetylene (**2a**) (20 mg, 0.2 mmol) in 10 mL toluene was added benzyl azide (**1a**) (26 mg, 0.2 mmol). After stirring for 24 h at 50 °C, toluene was removed under reduced pressure. DMF (2 mL) and MeI (0.4 mmol) were added to the residue solid under a N<sub>2</sub> atmosphere. The mixture was heated at 80 °C for 24 h and then was cooled to room temperature. The reaction mixture was worked up by the method mentioned above. The product **5** was obtained as an yellow oil. Yield: 11 mg (23 % based on the benzyl azide). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.34 (s, 3H), 5.45 (s, 2H), 7.03-7.07 (m, 2H), 7.15-7.20 (m, 2H), 7.25-7.30 (m, 3H), 7.44-7.46 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  11.09, 52.50, 127.73, 128.51, 129.10, 129.31, 129.72, 129.90, 135.14, 135.90, 142.11. Spectroscopic data for **5** were consistent with previously reported data for this compound.<sup>22</sup>

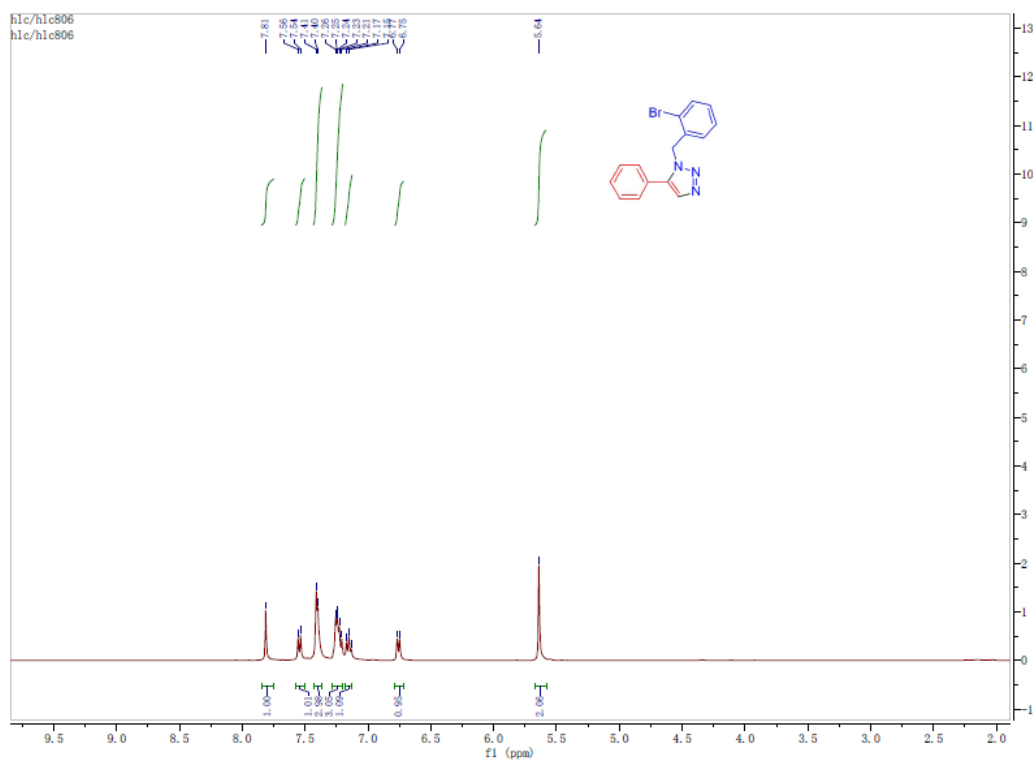
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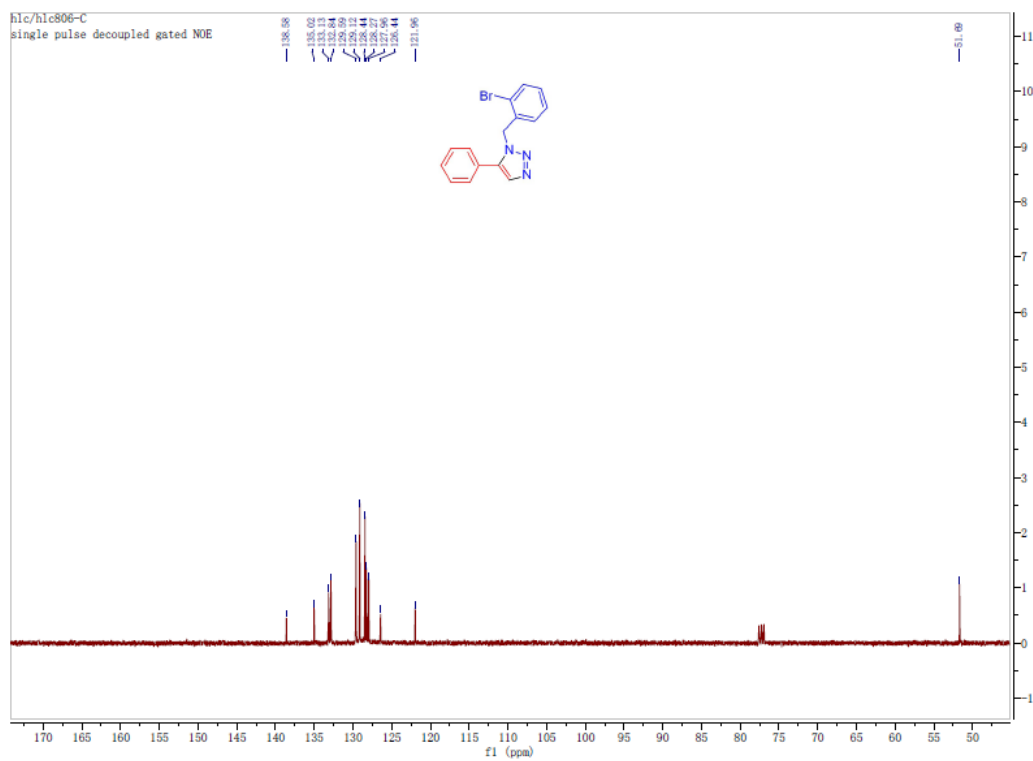
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## Selected NMR spectra of 1, 5-disubstituted triazoles.

The  $^1\text{H}$  NMR spectrum of **3da** in  $\text{CDCl}_3$ .

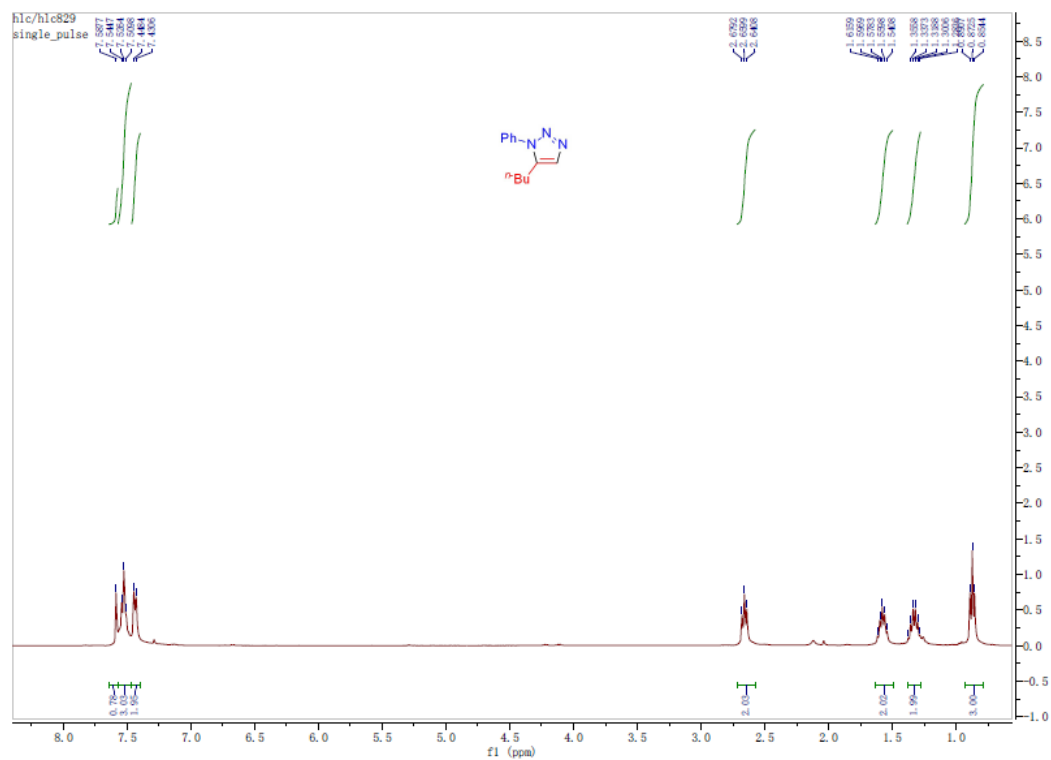


The  $^{13}\text{C}$  NMR spectrum of **3da** in  $\text{CDCl}_3$ .

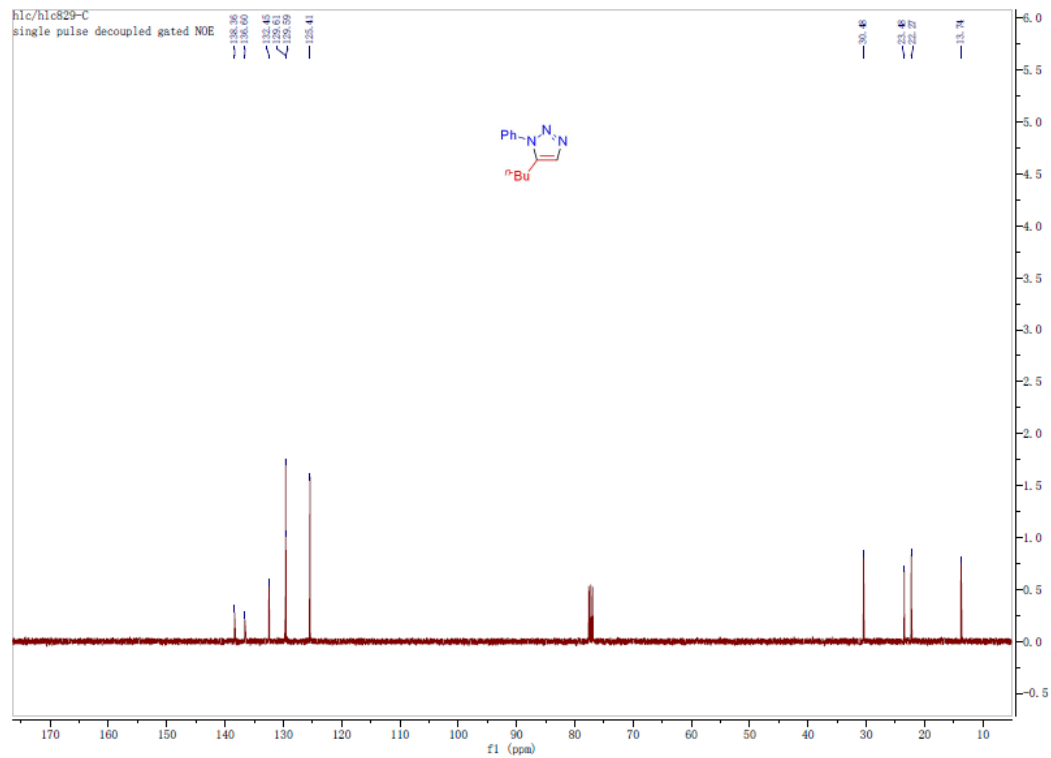




The  $^1\text{H}$  NMR spectrum of **3ec** in  $\text{CDCl}_3$ .

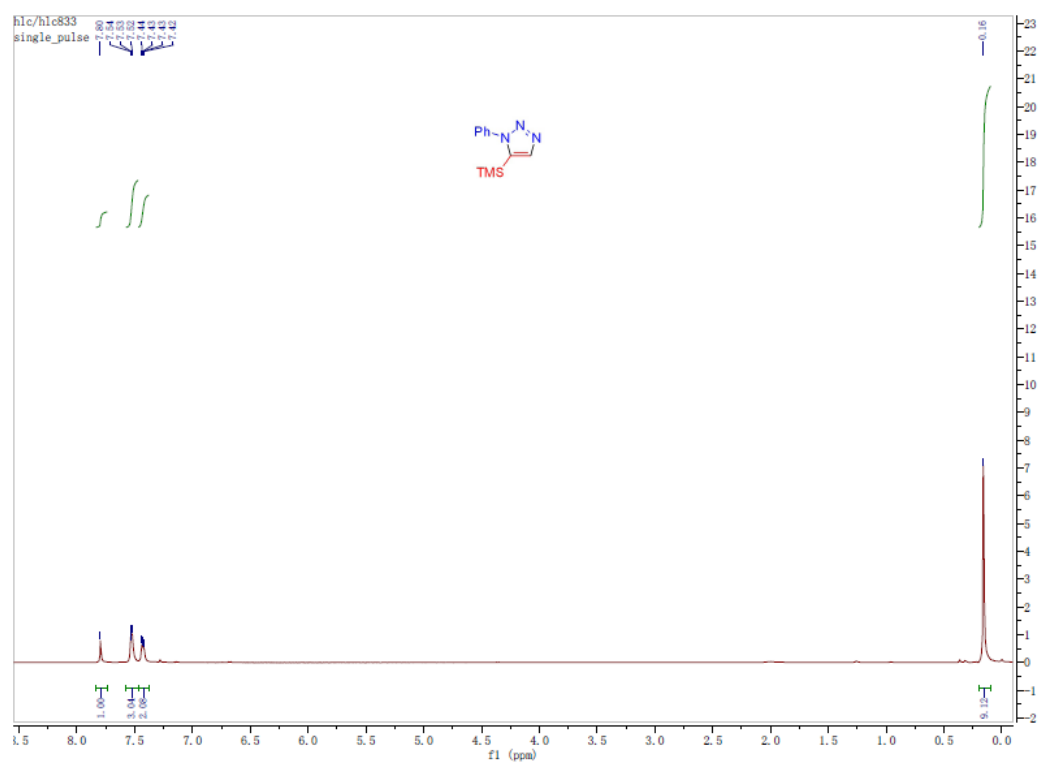


The  $^{13}\text{C}$  NMR spectrum of **3ec** in  $\text{CDCl}_3$ .

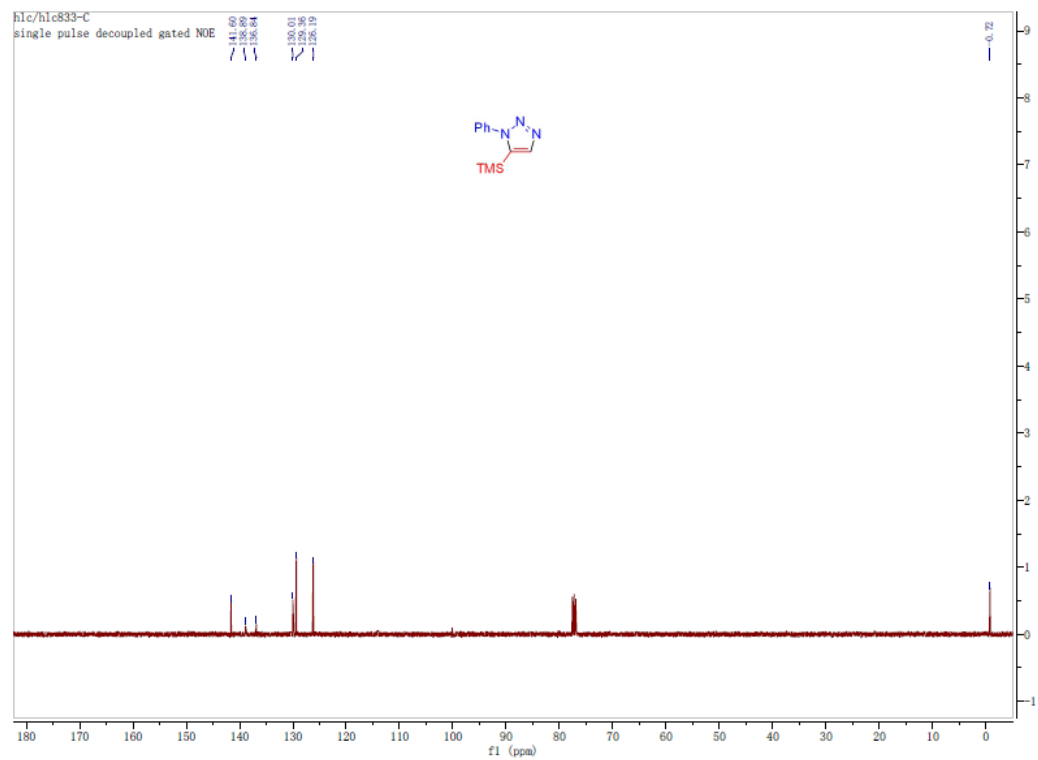




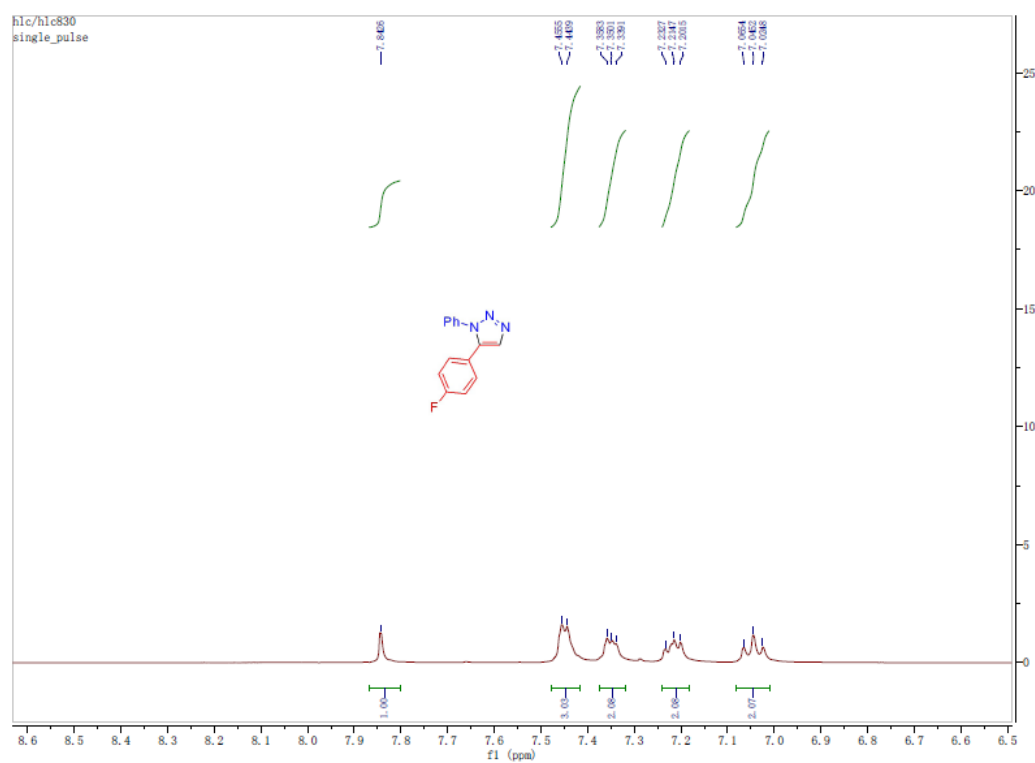
The  $^1\text{H}$  NMR spectrum of **3eg** in  $\text{CDCl}_3$ .



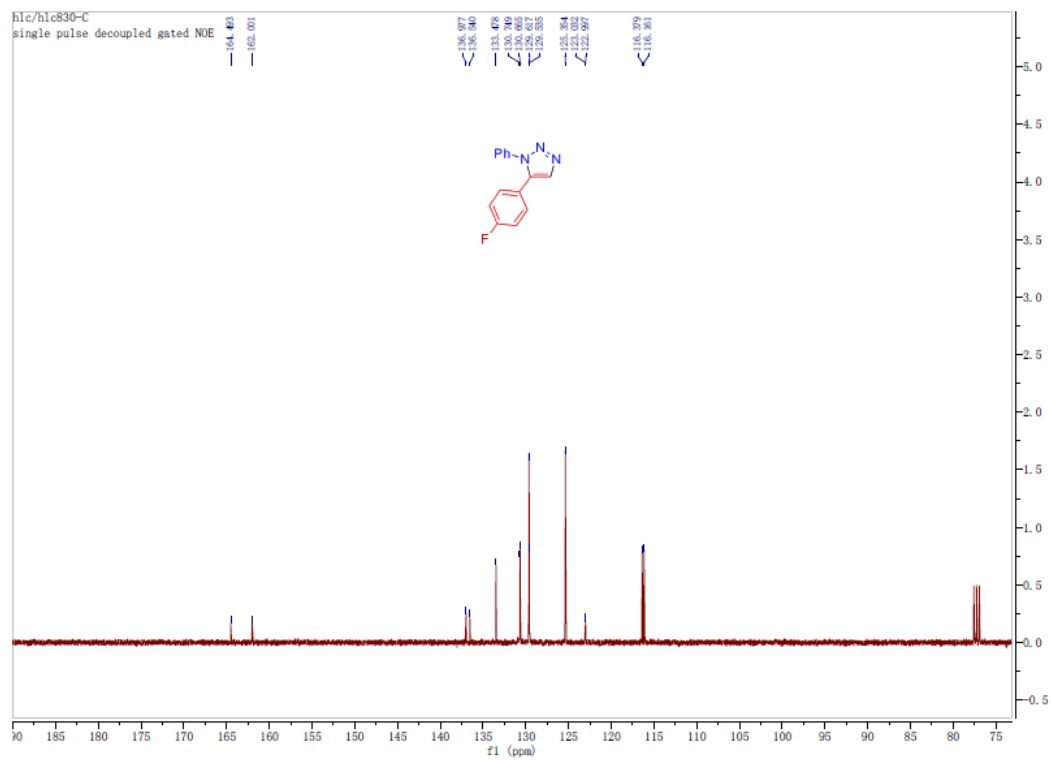
The  $^{13}\text{C}$  NMR spectrum of **3eg** in  $\text{CDCl}_3$ .



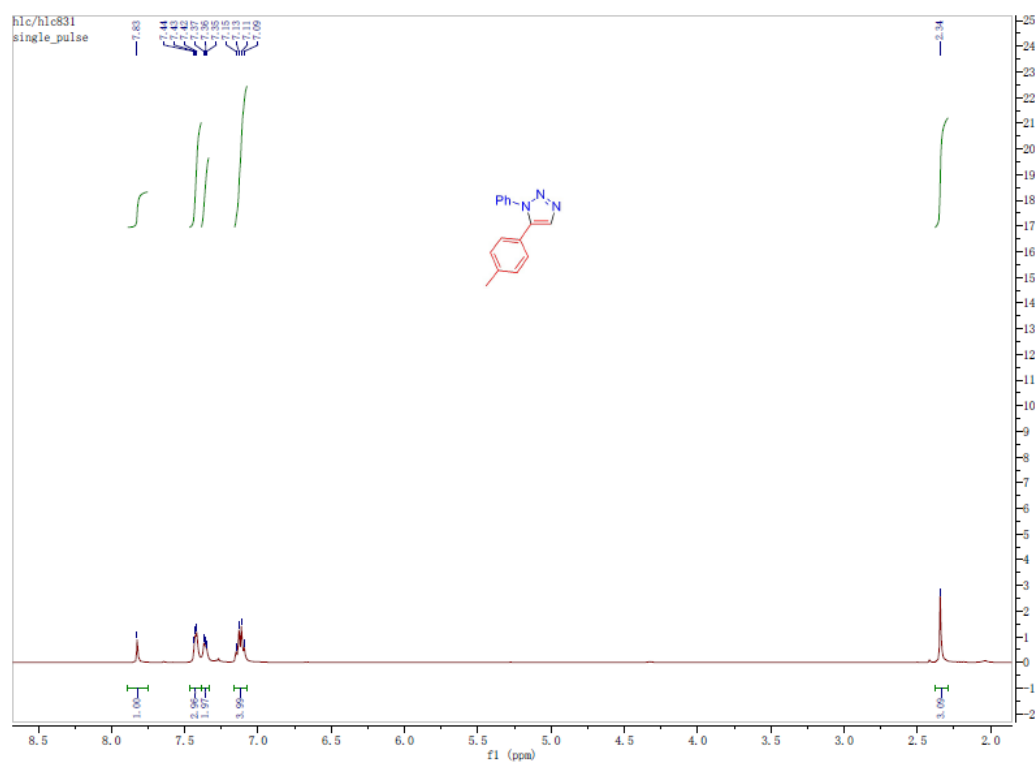
The  $^1\text{H}$  NMR spectrum of **3ed** in  $\text{CDCl}_3$ .



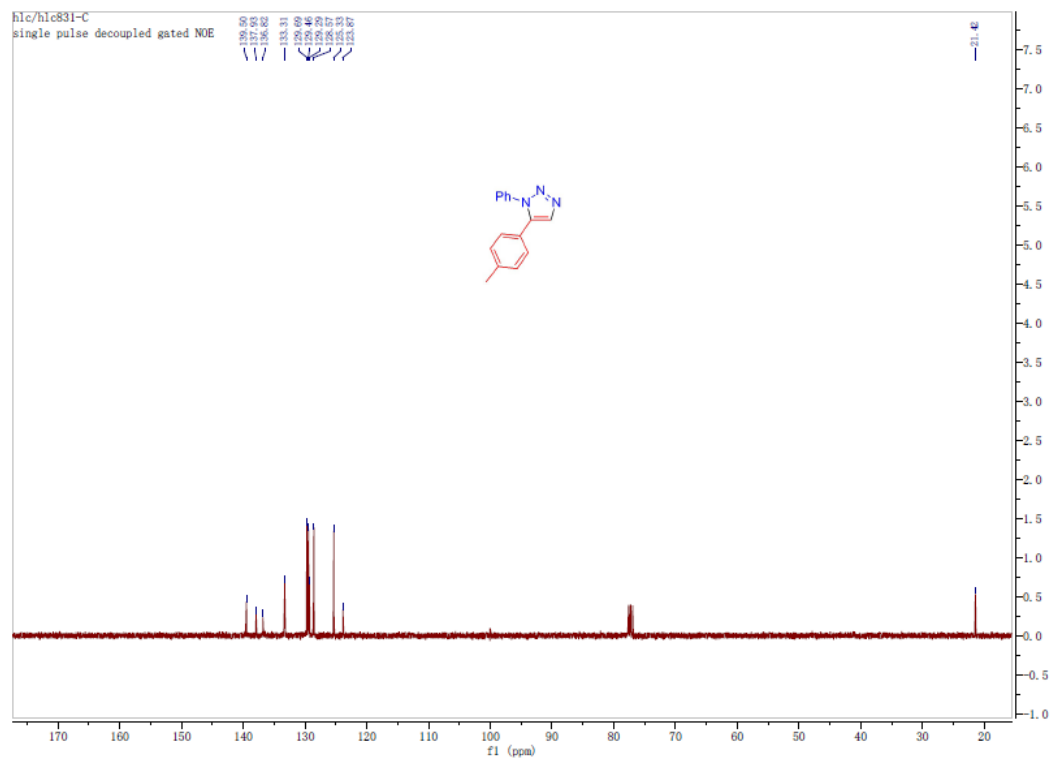
The  $^{13}\text{C}$  NMR spectrum of **3ed** in  $\text{CDCl}_3$ .



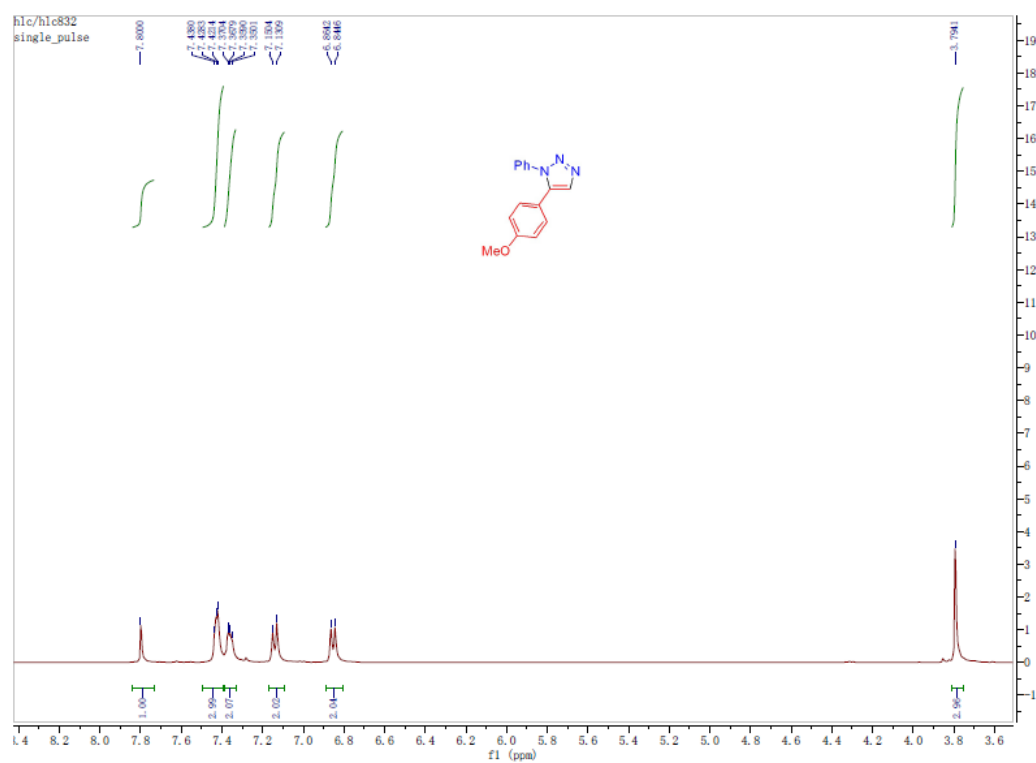
The  $^1\text{H}$  NMR spectrum of **3ee** in  $\text{CDCl}_3$ .



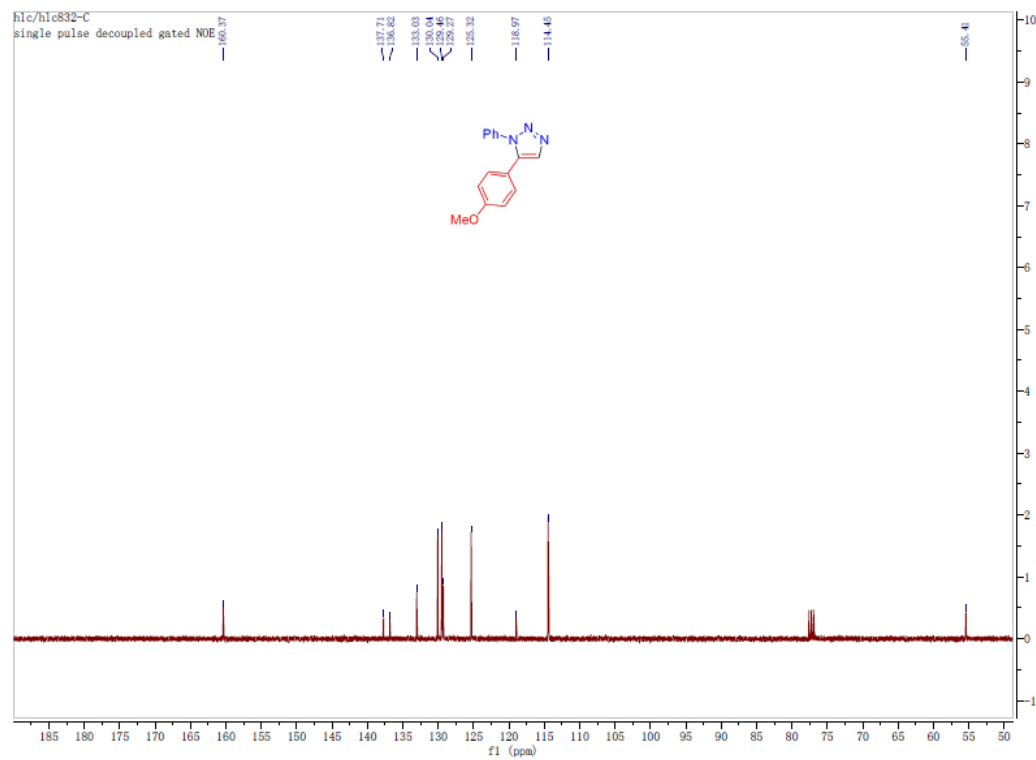
The  $^{13}\text{C}$  NMR spectrum of **3ee** in  $\text{CDCl}_3$ .



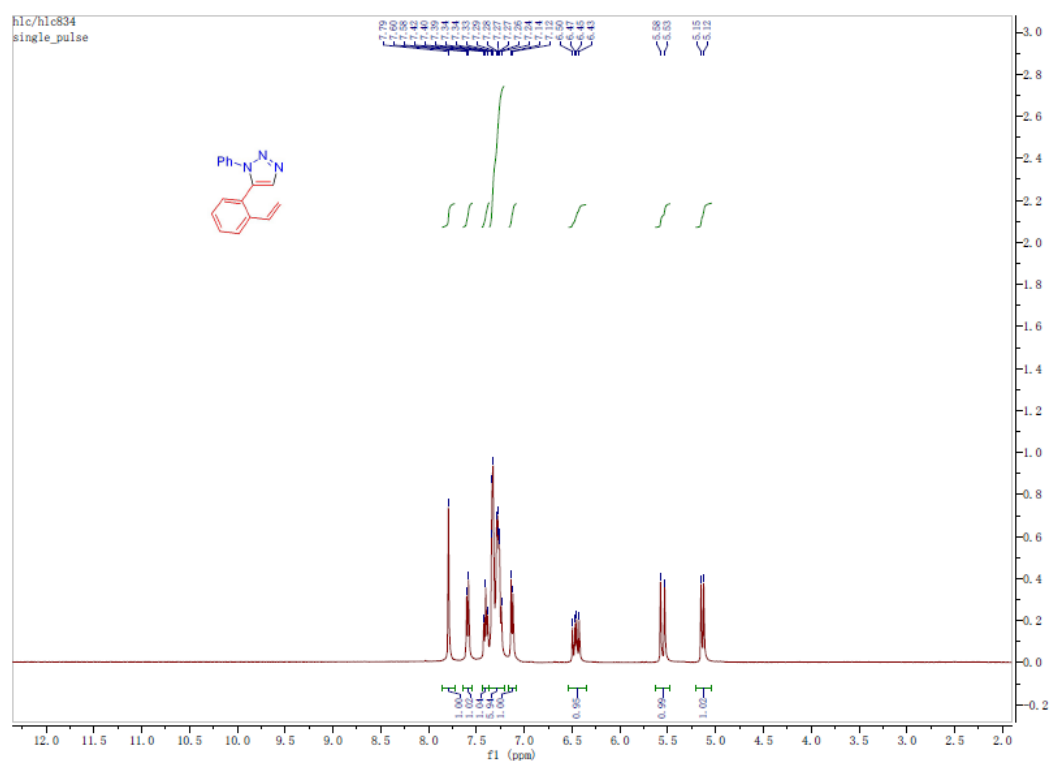
The  $^1\text{H}$  NMR spectrum of **3ef** in  $\text{CDCl}_3$ .



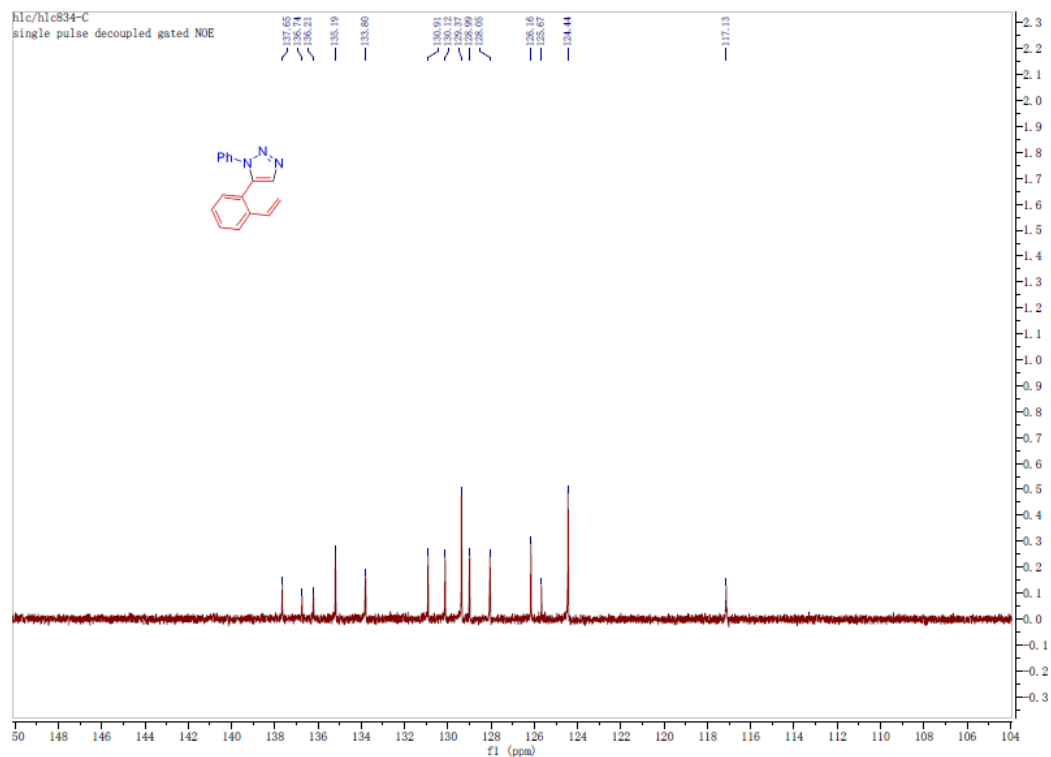
The  $^{13}\text{C}$  NMR spectrum of **3ef** in  $\text{CDCl}_3$ .



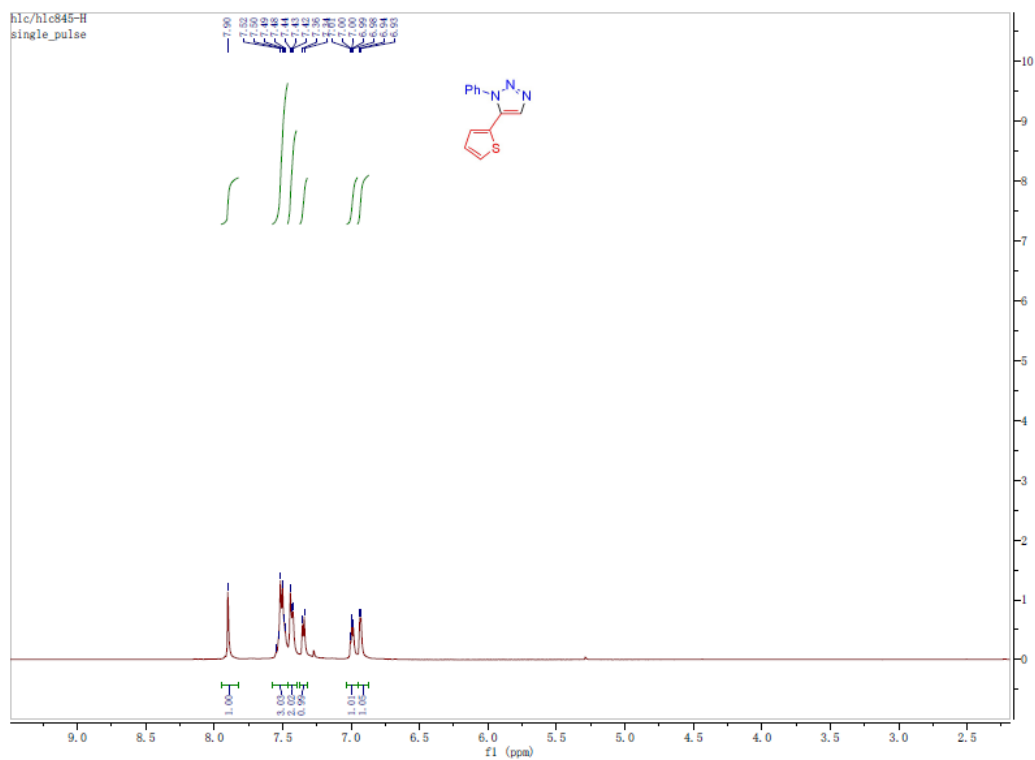
The  $^1\text{H}$  NMR spectrum of **3eh** in  $\text{CDCl}_3$ .



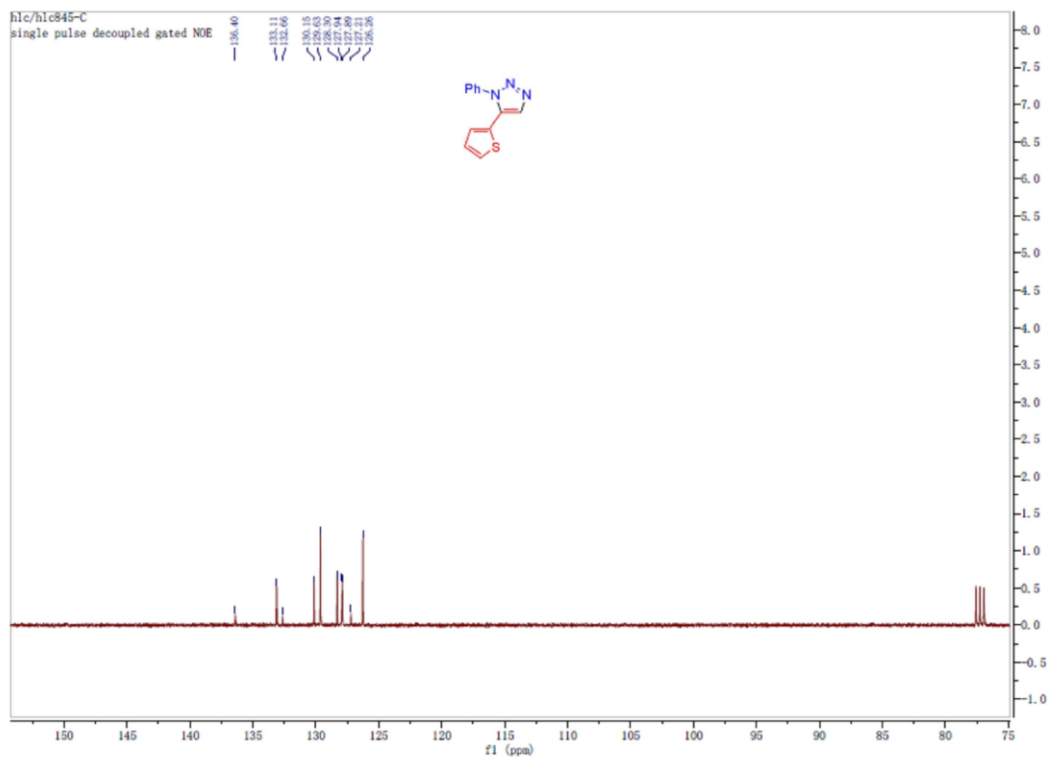
The  $^{13}\text{C}$  NMR spectrum of **3eh** in  $\text{CDCl}_3$ .



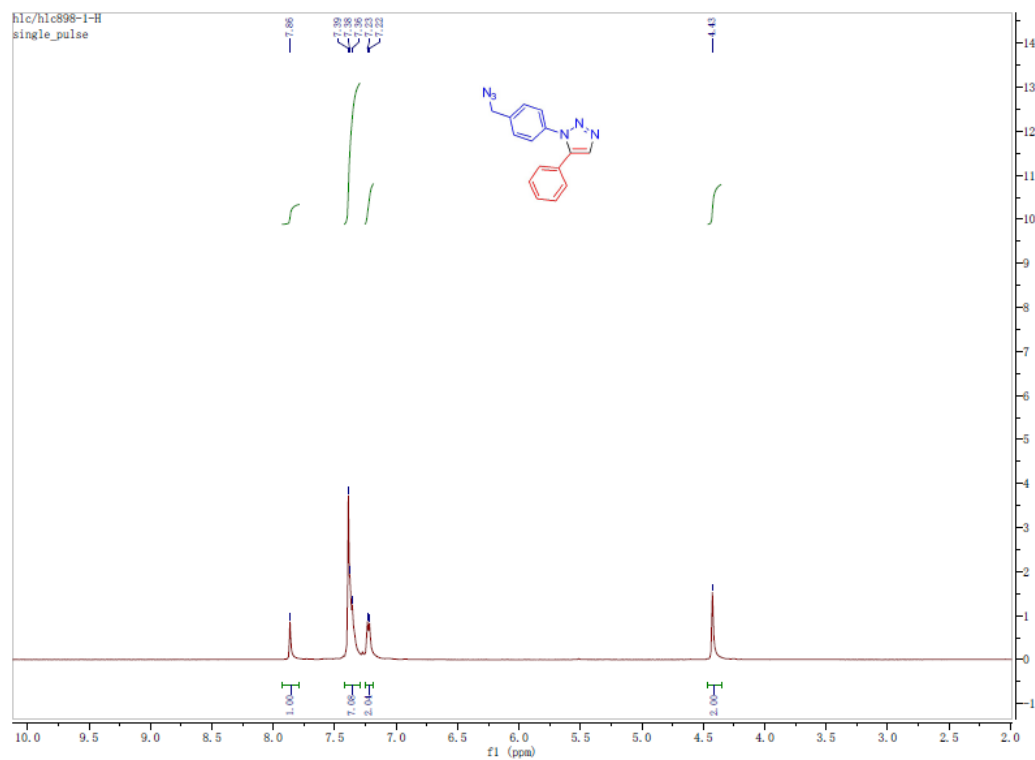
The  $^1\text{H}$  NMR spectrum of **3ei** in  $\text{CDCl}_3$ .



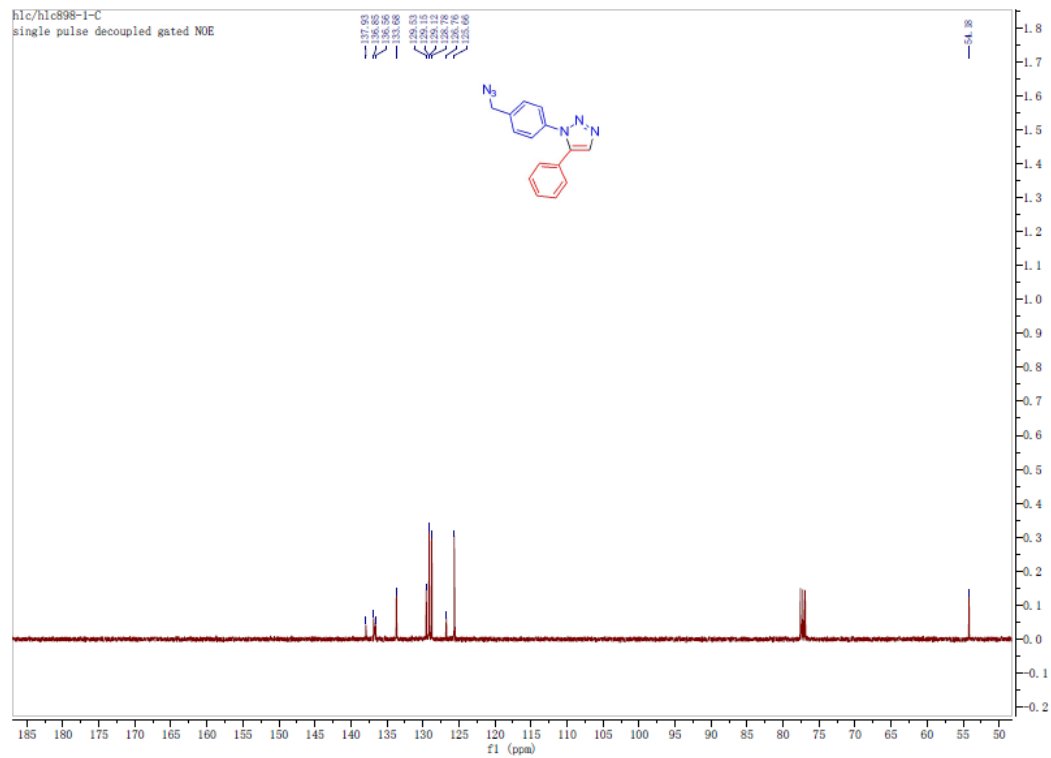
The  $^{13}\text{C}$  NMR spectrum of **3ei** in  $\text{CDCl}_3$ .



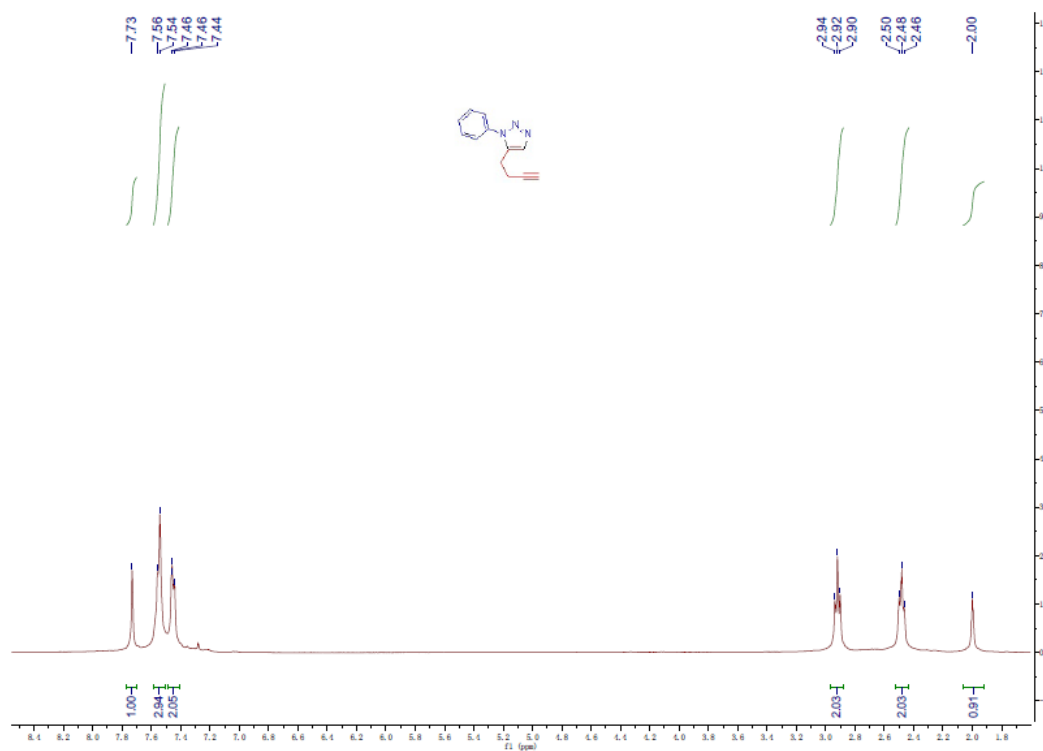
The  $^1\text{H}$  NMR spectrum of **3la** in  $\text{CDCl}_3$ .



The  $^{13}\text{C}$  NMR spectrum of **3la** in  $\text{CDCl}_3$ .



The  $^1\text{H}$  NMR spectrum of **3ek** in  $\text{CDCl}_3$ .



The  $^{13}\text{C}$  NMR spectrum of **3ek** in  $\text{CDCl}_3$ .

