Electronic supplementary information:

Efficient synthesis of tetrazole hemiaminal silyl ethers *via* three-component hemiaminal silylation

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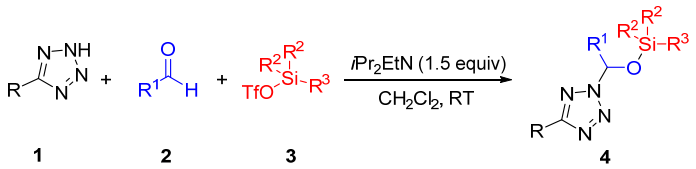
Contents

1. General information

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quaternary, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). CH_2Cl_2 was distilled over calcium hydride prior to use. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. 5-Substituted tetrazoles **1b**,[1] **1e**,[2] **1f**,[3] **1g**,[4] and **1k**[3] are known compounds, and are prepared according to the reported procedures. 5-Substituted tetrazoles **1h**[3] and **1i**[3] are prepared according to the reported procedures. 5-Substituted tetrazole **1a** was purchased from Shaoyuan Technology (Shanghai) Co., Ltd.; 5-Substituted tetrazole **1c**, **1d**, **1j**, and **1l** were purchased from Energy Chemical (Shanghai) Co., Ltd.; 5-Substituted tetrazole **1m** was purchased from TCI (Shanghai) Co., Ltd.

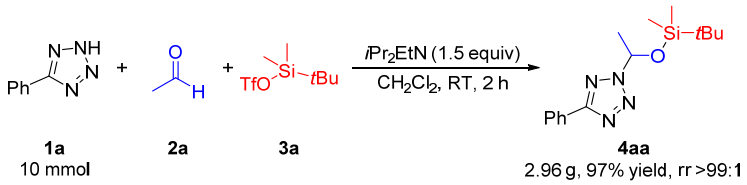
2. General procedure for the synthesis of 2,5-disubstituted tetrazole hemiaminal silyl ethers



In a test tube, 5-phenyl tetrazole **1** (0.2 mmol) was added in CH_2Cl_2 (2 mL) at RT. Subsequently, *i*Pr_2EtN (0.3 mmol, 1.5 equiv) was added. Then, acetaldehyde **2** (0.28 mmol, 1.4 equiv) was added to the solution when 5-phenyl tetrazole **1** was completely dissolved. After that, *tert*-butyldimethylsilyl trifluoromethanesulfonate **3** (0.3 mmol, 1.5 equiv) was added and the reaction mixture was stirred at RT for 2-3 h. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column

chromatography on silica gel (eluent: petroleum ether/ethylacetate = 10/1) to afford the pure product **4**.

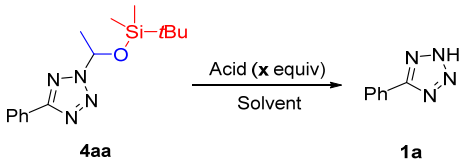
3. Gram-scale synthesis of 2,5-disubstituted tetrazole 4aa



1a 10 mmol | **2a** | **3a** | **4aa** 2.96 g, 97% yield, rr >99:1

In a round flask, 5-phenyl tetrazole **1a** (1.46 g, 10 mmol) was added in CH_2Cl_2 (100 mL) at RT. *i*Pr_2EtN (2.6 mL, 15 mmol, 1.5 equiv) was added subsequently. Then, acetaldehyde **2a** (0.78 mL, 14 mmol, 1.4 equiv) was added to the solution after **1a** is completely dissolved. After that, *tert*-butyldimethylsilyl trifluoromethanesulfonate **3a** (3.5 mL, 15 mmol, 1.5 equiv) were added and the mixture was stirred at RT for 2 h. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column chromatography on silica gel (eluent: petroleum ether/ethylacetate = 10/1) to afford the product **4aa** (2.9550 g, 97% yield) as a colorless oil.

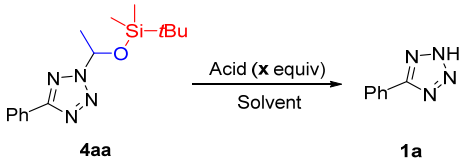
4. The release of 5-phenyl tetrazole 1a from 2,5-disubstituted tetrazole hemiaminal silyl ether 4aa



4aa **1a**

In a test tube, 2-(1-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-phenyl-2*H*-tetrazole **4aa** (61 mg, 0.2 mmol) was added in solvent (2 mL). Then, acid (x equiv) was added and the mixture was stirred at RT. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column chromatography on silica gel (eluent: petroleum ether/ethylacetate = 1/1) to give the desired product **1a** as a white solid.

Table S1. 2,5-disubstituted tetrazole hemiaminal silyl ether 4aa at acid atmosphere

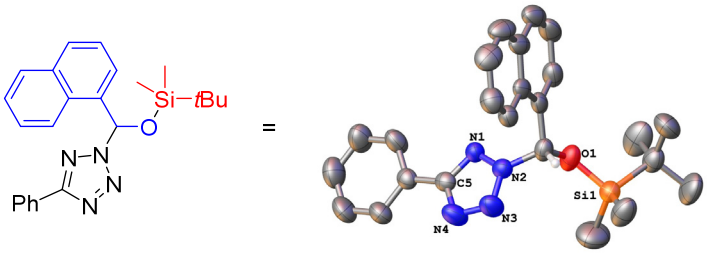


4aa **1a**

Entry	Acid[a]	Solvent	x	t (h)	Yield (%)[b]
1	CH_3COOH	THF	1	8	NR
2	CH_3COOH	CH_3OH	1	8	NR
3	CF_3COOH	CH_3OH	1	8	NR
4	HCl	CH_3OH	1	1	99
5	HCl	H_2O	1	8	NR
6	HCl	CH_3OH:H_2O = 1:3	1	12	5
7	HCl	CH_3OH:H_2O = 1:1	1	12	36
8	HCl	CH_3OH:H_2O = 3:1	1	12	85
9	HCl	CH_3OH	0.1	2	99
10	HCl	CH_3OH	0.05	2	99
11[c]	HCl	CH_3OH	0.01	12	90

[a] Unless otherwise noted, acids were analytical reagent. [b] Isolated yield based on **4aa**. [c] The hydrochloric acid (1.7 μL) used is diluted with 1 mL of analytical reagent hydrochloric acid into 9 mL of distilled water.

5. The X-ray data for tetrazoles 4an and 5aa.



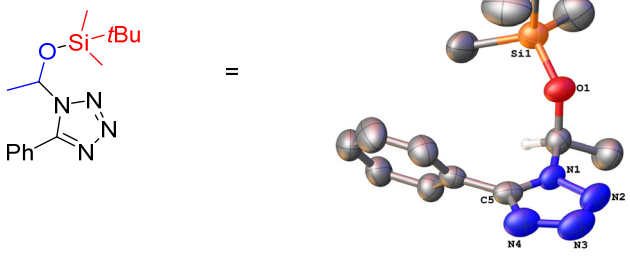
4an **4an**

The tetrazole **4an** was recrystallized by petroleum/ether (10/1).

CCDC 1835497 (**4an**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S2 Crystal data and structure refinement for 4an.

Identification code	cx-20180320
Empirical formula	$C_{24}H_{28}N_4OSi$
Formula weight	416.59
Temperature/K	292.64(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	11.4816(8)
b/Å	12.2451(6)
c/Å	16.6439(9)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2340.0(2)
Z	4
$\rho_{calc}g/cm^3$	1.182
μ/mm^{-1}	0.122
F(000)	888.0
Crystal size/mm^3	0.35 × 0.27 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.902 to 49.958
Index ranges	-13 ≤ h ≤ 10, -14 ≤ k ≤ 10, -19 ≤ l ≤ 13
Reflections collected	6796
Independent reflections	3019 [R_{int} = 0.0216, R_{sigma} = 0.0312]
Data/restraints/parameters	3019/1/276
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0538, wR_2 = 0.0911
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.17
Flack parameter	0.08(7)



5aa **5aa**

The tetrazole **5aa** was recrystallized by petroleum/ether (1/1).

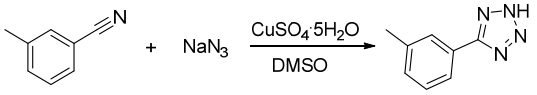
CCDC 1835498 (**5aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S3 Crystal data and structure refinement of 5aa.

Identification code	cyg-20180315
Empirical formula	$C_{15}H_{24}N_4OSi$
Formula weight	304.47
Temperature/K	293.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.5430(8)
b/Å	10.2385(13)
c/Å	14.1084(19)
α/°	71.826(12)
β/°	83.376(10)
γ/°	78.570(10)
Volume/Å3	878.7(2)
Z	2
ρcalcg/cm3	1.151
μ/mm 1	0.138
F(000)	328.0
Crystal size/mm3	0.5 × 0.28 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.896 to 50
Index ranges	-7 ⩽ h ⩽ 7, -11 ⩽ k ⩽ 12, -16 ⩽ l ⩽ 16
Reflections collected	6596
Independent reflections	3077 [Rint = 0.0377, Rsigma = 0.0627]
Data/restraints/parameters	3077/0/196
Goodness-of-fit on F2	1.049
Final R indexes [I>=2σ (I)]	R1 = 0.0675, wR2 = 0.1548
Final R indexes [all data]	R1 = 0.0993, wR2 = 0.1727
Largest diff. peak/hole / e Å-3	0.32/-0.22

6. Synthesis, analytical and spectral characterization data of 5-substituted tetrazoles

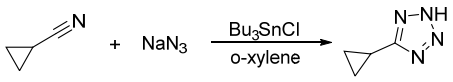
Synthesis of 5-substituted tetrazole **1b**[1]



1b

To a mixture of nitrile (2 mmol) and NaN_3 (2 mmol) in DMSO (6 mL), $CuSO_4{\cdot}5H_2O$ (2 mol%) was added and the mixture was stirred at 140 °C. After completion of the reaction, the mixture was treated with EtOAc and 4 M HCl and stirred vigorously. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic portion was washed with saturated sodium thiosulfate solution and H_2O and subsequently concentrated. The residue was purified by column chromatography (silica gel; hexane-EtOAc) to afford the pure 5-substituted tetrazole **1b**.

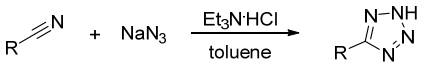
Synthesis of 5-substituted tetrazole **1e**[2]



1e

To a mixture of nitrile (2 mmol) and NaN_3 (5 mmol) in *o*-xylene (20 mL), Bu_3SnCl (5 mmol) was added and the mixture was stirred at reflux for 6 h. Then the reaction mixture was cooled to RT and a solution of NaOH in water was added. After stirring for 1 h at RT, the aqueous layer was diluted with water, cooled to 5-10 ºC and acidified to pH = 2 with 6 N HCl. Finally, the product **1e** was extracted into EtOAc (3×10 mL) and distilled completely. The residue was purified by column chromatography (silica gel; hexane-EtOAc) to afford the pure 5-substituted tetrazole **1e**.

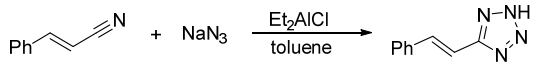
Synthesis of 5-substituted tetrazoles: **1f**,[3] **1h**, **1i** and **1k**[3]



To a mixture of nitrile (2 mmol) and NaN_3 (2.5 mmol) in toluene (10 mL), $Et_3N{\cdot}HCl$ (6 mmol) was added and the mixture was stirred at 110 °C for 18-24 h. After cooling to RT, the mixture was treated with water. To the aqueous layer, 4 M HCl was added dropwise until pH was acidic. After

filtration, the solid was purified by column chromatography (silica gel; hexane-EtOAc) to afford pure 5-substituted tetrazoles.

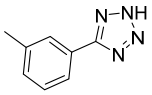
Synthesis of 5-substituted tetrazole **1g**[4]



1g

An oven-dried flask was charged with NaN_3 (3 mmol) and , Et_2AlCl (3 mmol, 0.9 M in toluene) in toluene at 0 °C under nitrogen and stirred for 15 min. The mixture was then warmed to room temperature and stirred for 4 h. Then, nitrile (2 mmol) was added at room temperature in two portions. The mixture was gradually heated to 55 °C and stirred for 18 h. Then, the reaction mixture was cooled to 0 °C and added to a solution of NaOH. The pH value was adjusted to 1.5 with 6 M HCl. The solution was extracted with ethyl acetate to afford the crude product, which was purified by column chromatography (silica gel; hexane-EtOAc) to afford pure 5-substituted tetrazole **1g**.

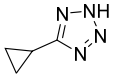
5-(*m*-Tolyl)-2*H*-tetrazole (1b)[1]



White solid.

^{1}H NMR (400 MHz, CD_3OD, δ): 7.85 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H).

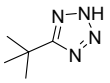
5-Cyclopropyl-2*H*-tetrazole (1e)[2]



White solid.

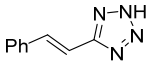
^{1}H NMR (400 MHz, CD_3OD, δ): 2.18-2.25 (m, 1H), 1.20-1.25 (m, 2H), 1.04-1.08 (m, 2H).

5-(*tert*-Butyl)-2*H*-tetrazole (1f)[3]



White solid. **^{1}H NMR** (400 MHz, CD_3OD, δ): 1.45 (s, 9H)

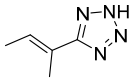
(*E*)-5-Styryl-2*H*-tetrazole (1g)[4]



Brown solid.

^{1}H NMR (400 MHz, CD_3OD, δ): 7.65-7.68 (m, 1H), 7.62-7.65 (m, 2H), 7.36-7.45 (m, 3H), 7.21 (d, J = 8.4 Hz, 1H).

(*E*)-5-(But-2-en-2-yl)-2*H*-tetrazole (1h)



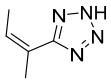
White solid, mp: 144.1-145.6 °C.

^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 6.61 (qq, J = 7.2, 1.6 Hz, 1H), 2.05-2.06 (m, 3H), 1.82-1.85 (m, 3H).

^{13}C NMR (150 MHz, CD_3OD, δ): 132.8, 122.1, 14.0, 13.6.

HRMS: $[M + Na]^+$ calcd. for $C_5H_8N_4Na$, 147.0641; found, 147.0639.

(*Z*)-5-(But-2-en-2-yl)-2*H*-tetrazole (1i)



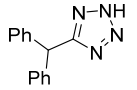
White solid, mp: 88.2-89.3 °C.

^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 6.07 (qq, J = 7.2, 1.6 Hz, 1H), 2.09-2.11 (m, 3H), 1.96 (dq, J = 7.2, 1.6 Hz, 3H).

^{13}C NMR (150 MHz, CD_3OD, δ): 134.2, 121.0, 22.1, 15.7.

HRMS: $[M + Na]^+$ calcd. for $C_5H_8N_4Na$, 147.0641; found, 147.0640.

5-Benzhydryl-2*H*-tetrazole (1k)[3]



White solid.

^{1}H NMR (400 MHz, CD_3OD, δ): 7.35-7.38 (m, 1H), 7.34-7.35 (m, 2H), 7.32-7.33 (m, 1H), 7.28-7.31 (m, 1H), 7.26-7.28 (m, 1H), 7.23-7.24 (m, 2H), 7.18-7.22 (m, 2H), 5.91 (s, 1H).

References:

1 B. Akhlaghinia and S. Rezazadeh, *J. Braz. Chem. Soc.*, 2012, **23**, 2197.

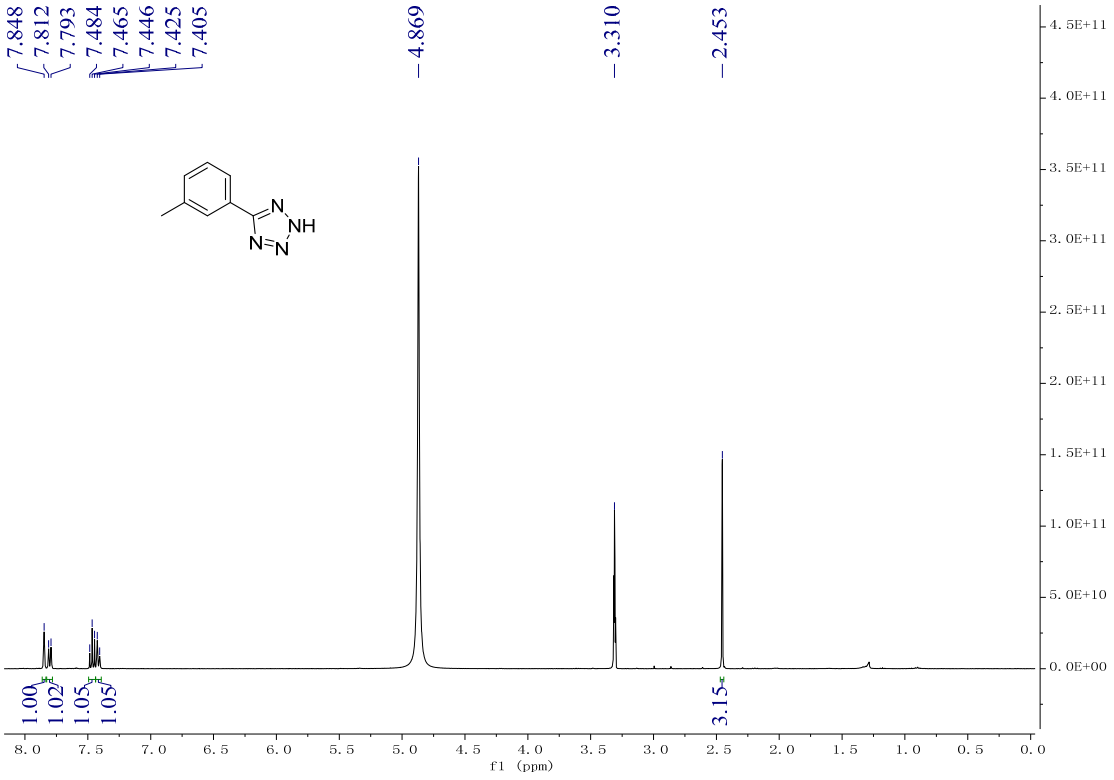
2 A. Sampath, V. Prabhakar Reddy, A. Kalyan Chakravarthy and P. Pratap Reddy, *Asian J. Chem.*, 2013, **25**, 393.

3 C. Behloul, K. Bouchelouche, Y. Hadji, S. Benseghir, D. Guijarro, C. Nájera and M. Yus, *Synthesis-Stuttgart*, 2016, **48**, 2455.

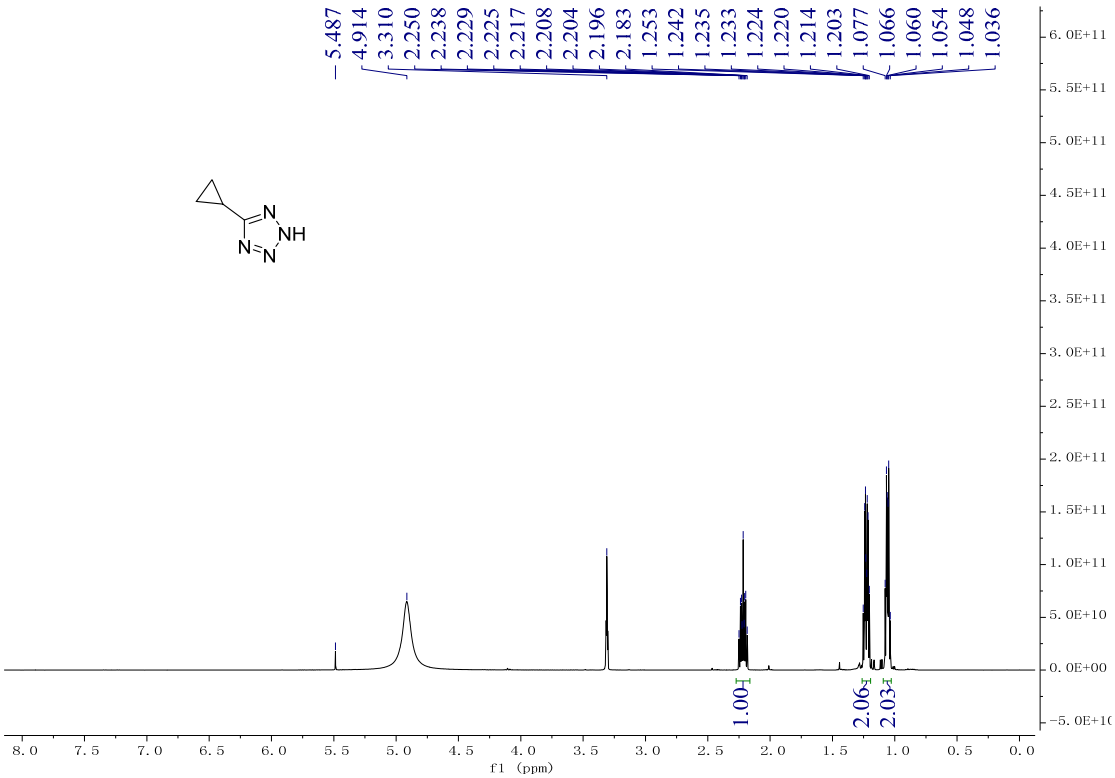
4 V. Aureggi and G. Sedelmeier, *Angew. Chem. Int. Ed.*, 2007, **46**, 8440.

7. Copies of NMR spectra of the 5-substituted tetrazoles

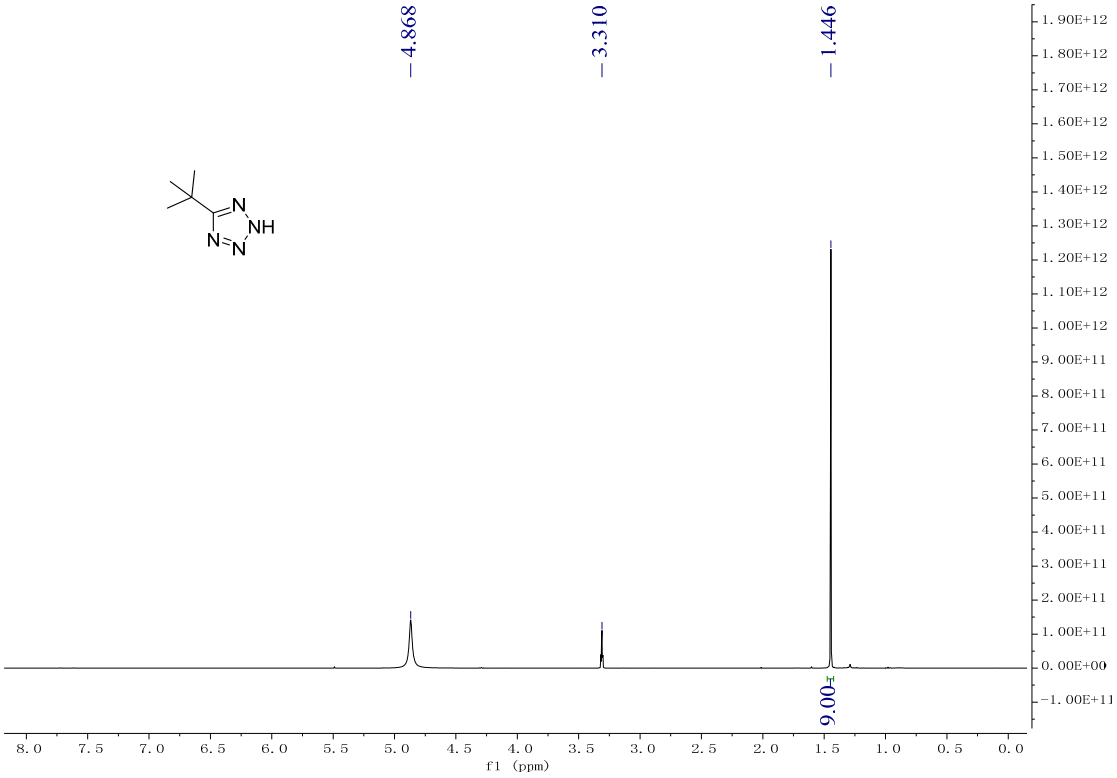
^{1}H-NMR of 1b



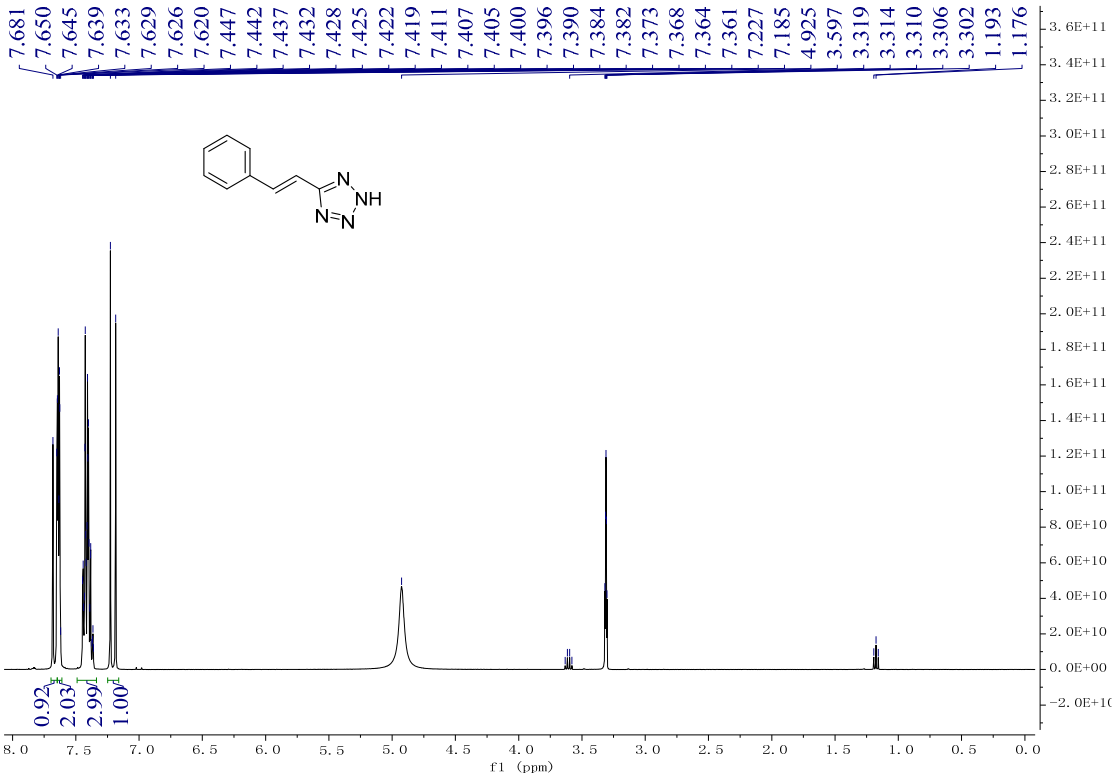
^{1}H-NMR of 1e



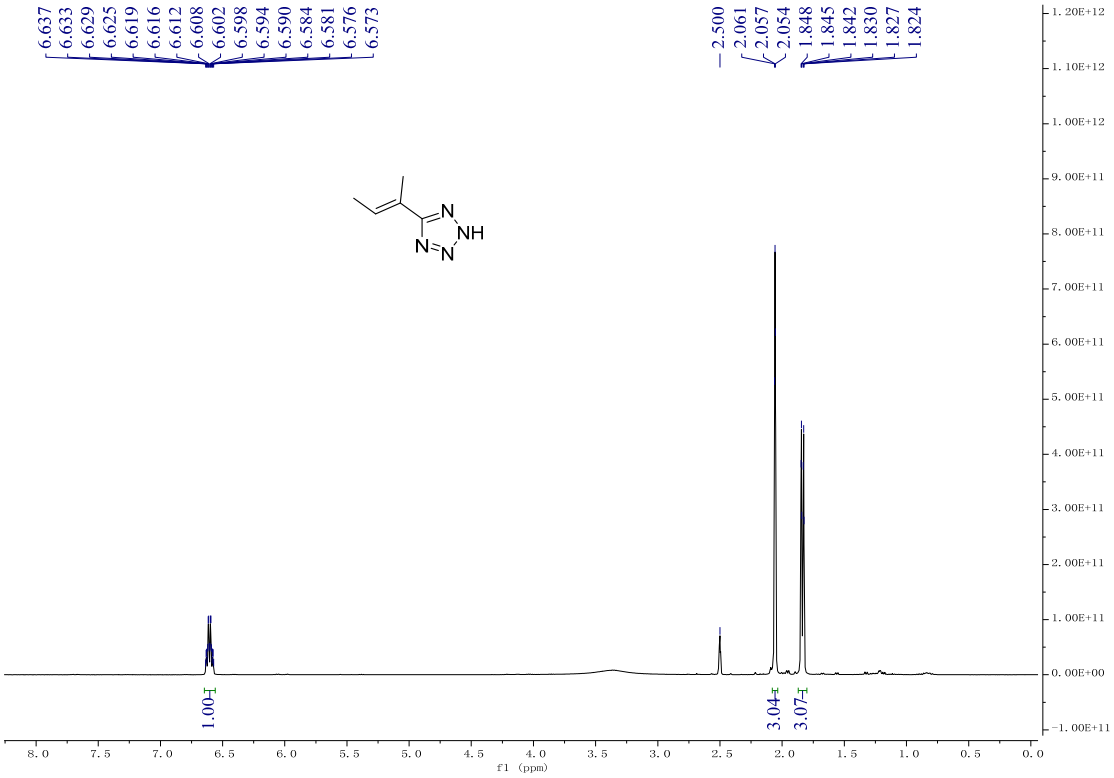
^{1}H-NMR of 1f



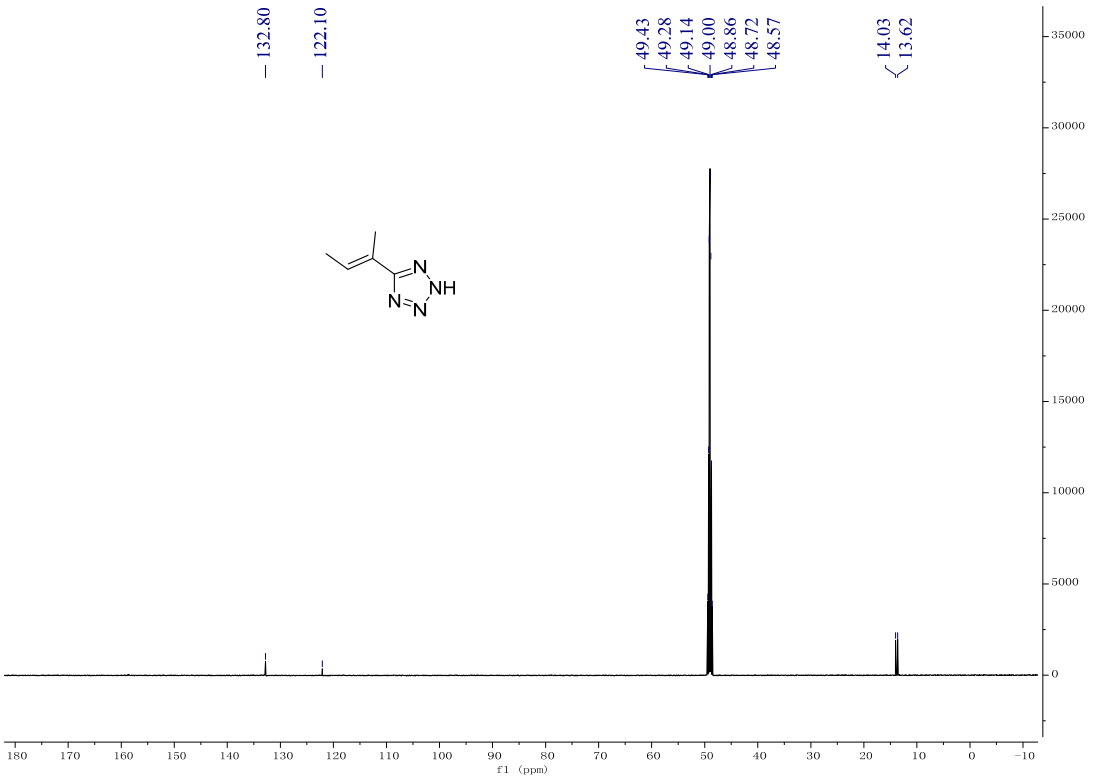
^{1}H-NMR of 1g



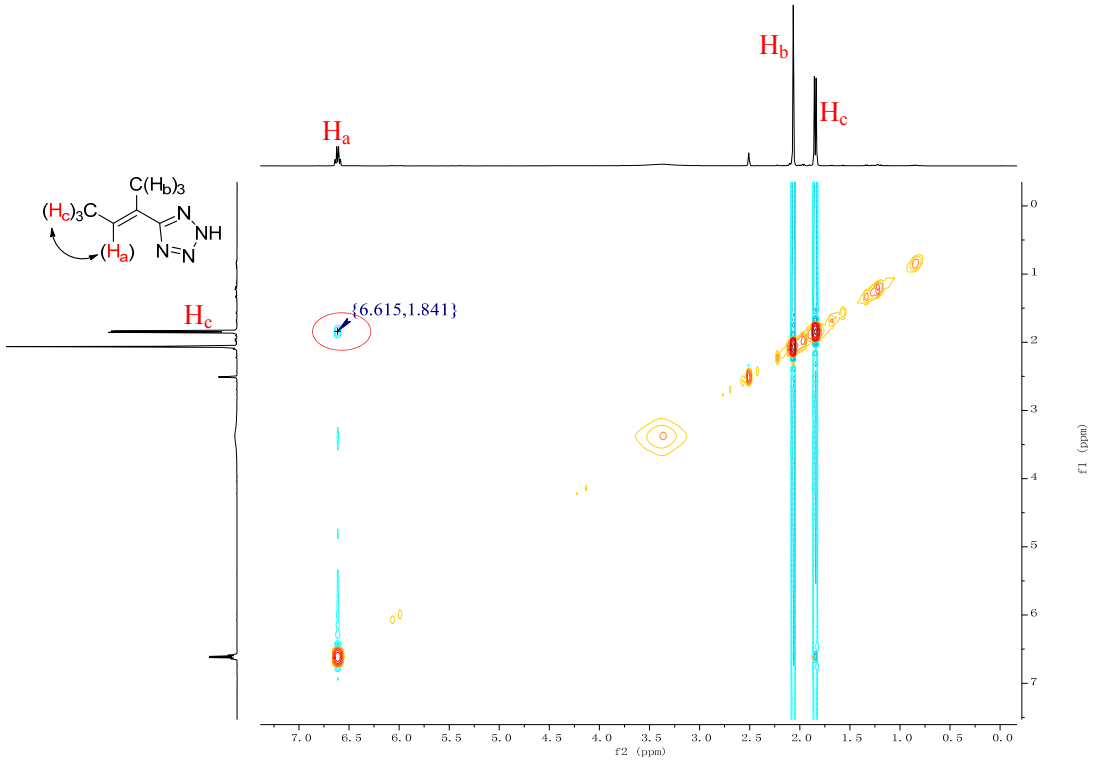
^{1}H-NMR of 1h



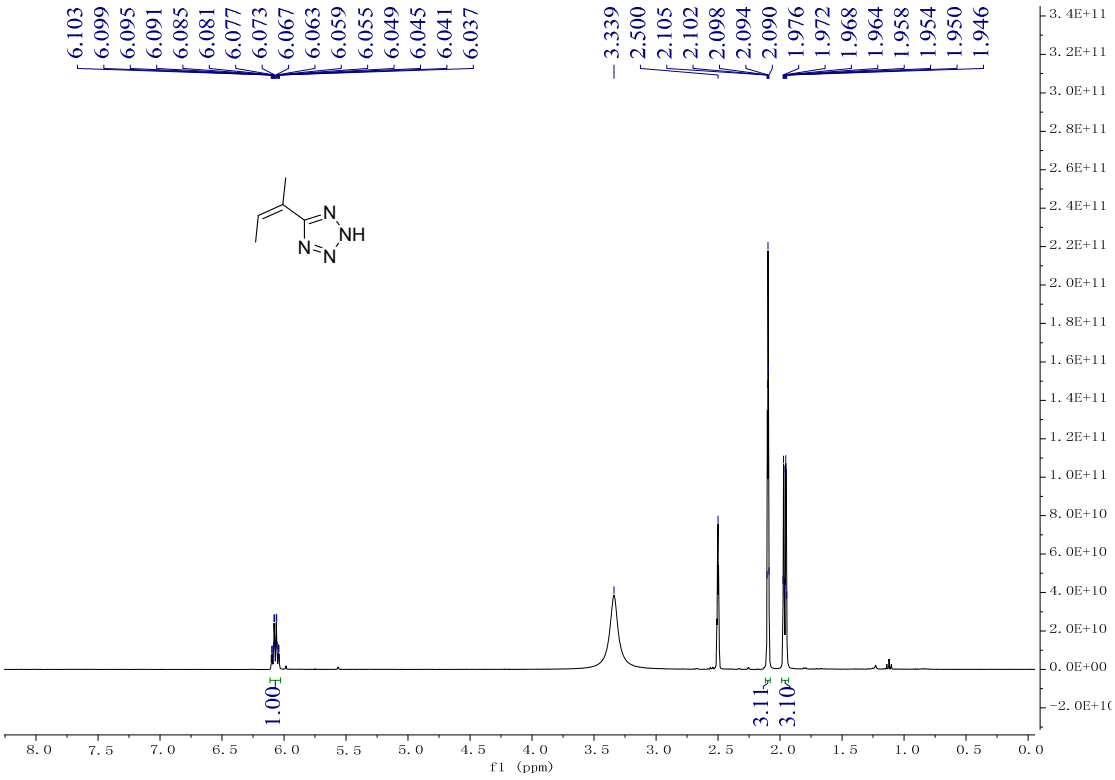
^{13}C-NMR of 1h



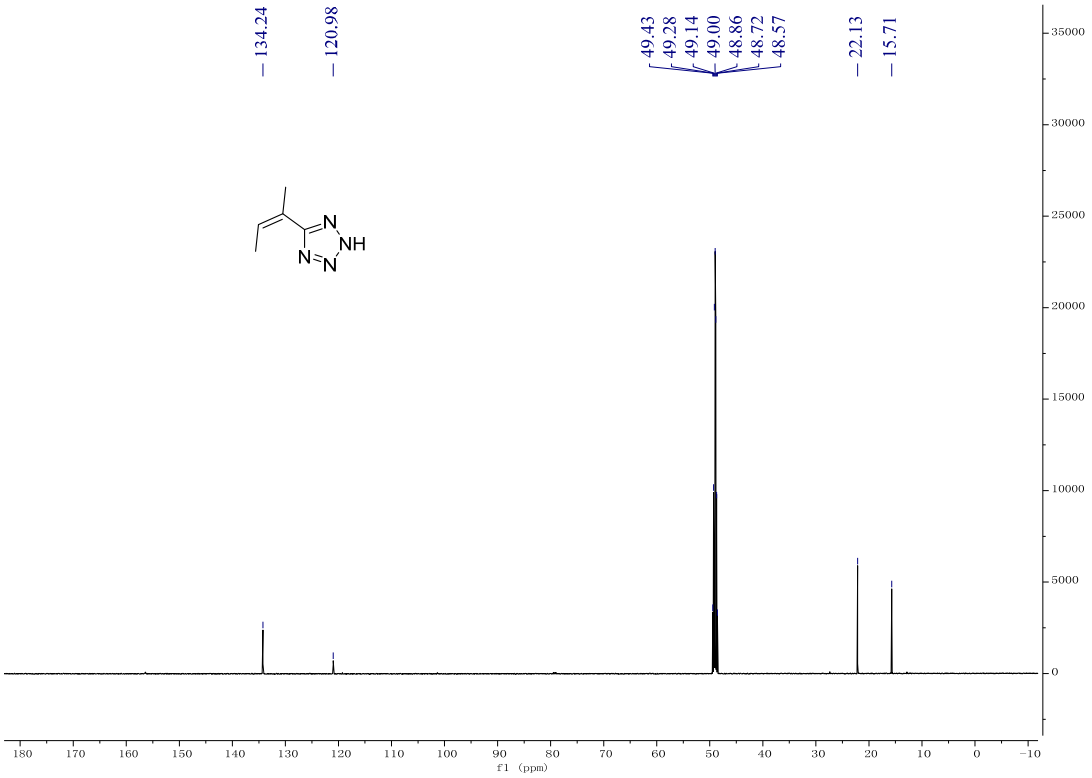
NOESY of 1h



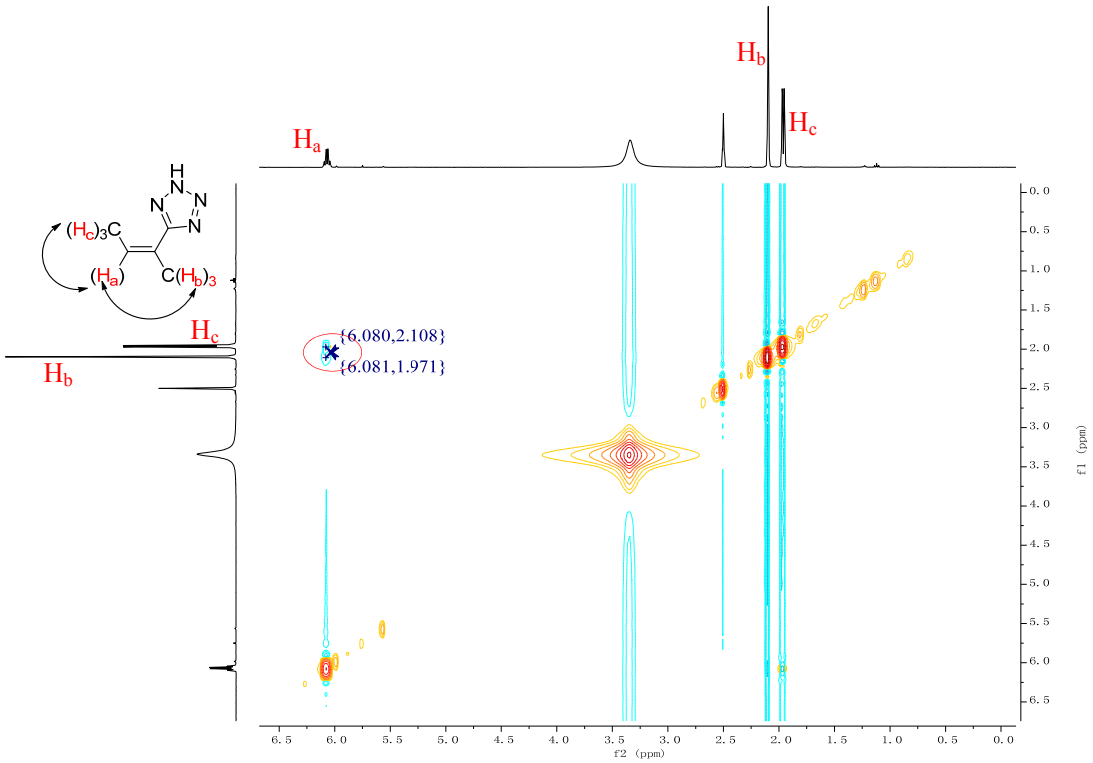
^{1}H-NMR of 1i



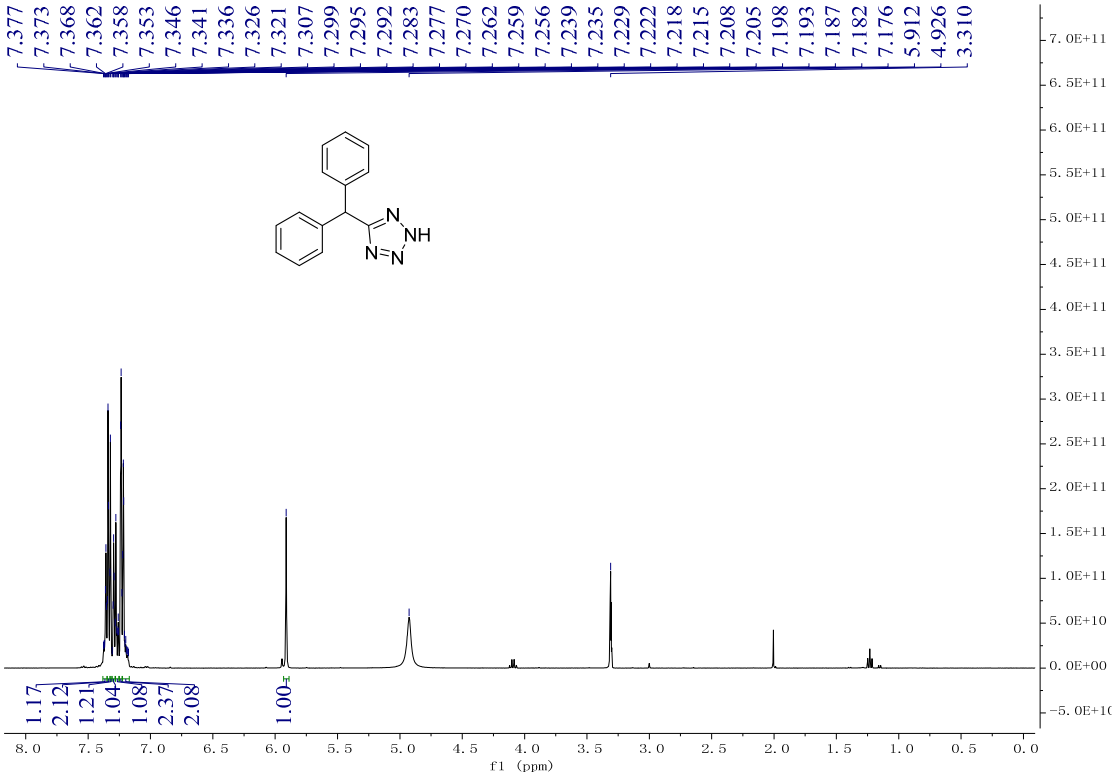
^{13}C-NMR of 1i



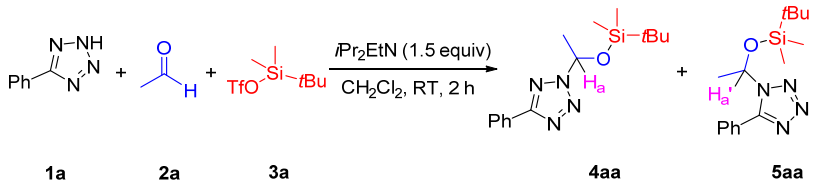
NOESY of 1i



^{1}H-NMR of 1k

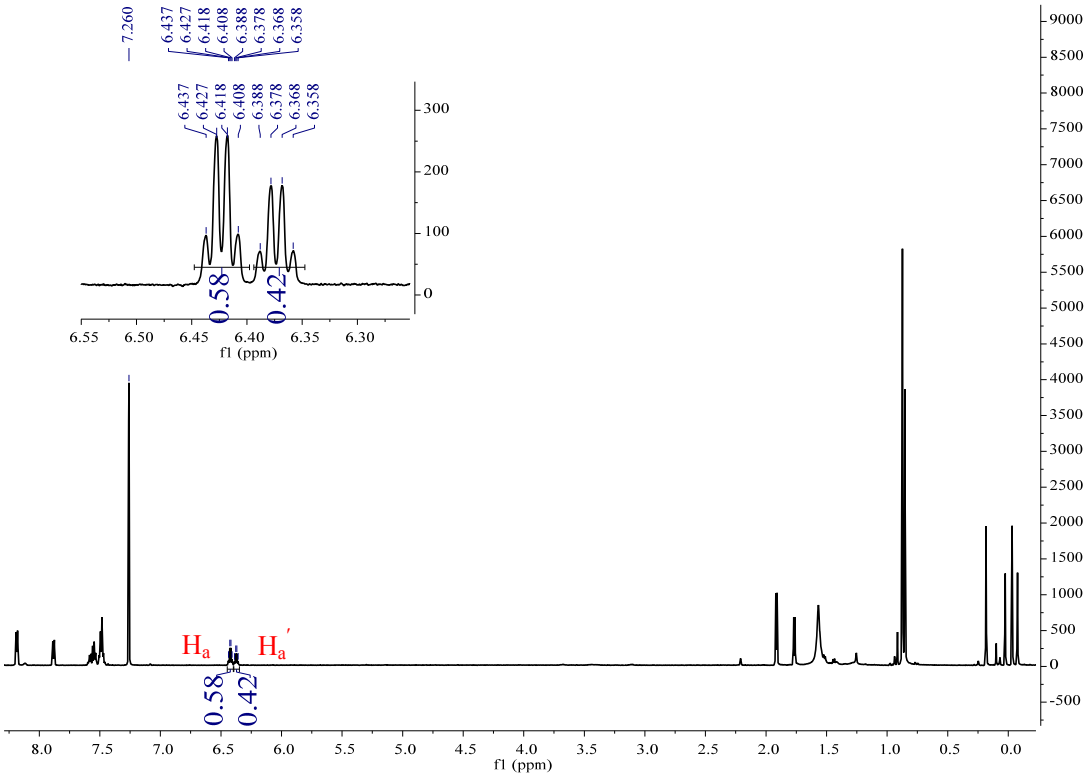

7.377
7.373
7.368
7.362
7.358
7.353
7.346
7.341
7.336
7.326
7.321
7.307
7.299
7.295
7.292
7.283
7.277
7.270
7.262
7.259
7.256
7.239
7.235
7.229
7.222
7.218
7.215
7.208
7.205
7.198
7.193
7.187
7.182
7.176
5.912
4.926
3.310
NH
N
N
1.17
2.12
1.21
1.04
1.08
2.37
2.08
1.00
f1 (ppm)

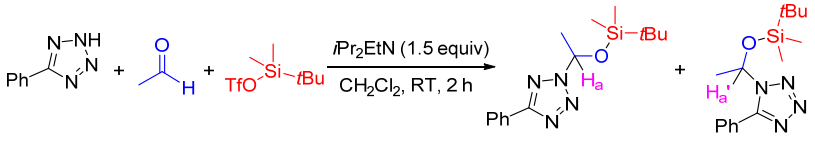
8. ^{1}H NMR spectroscopy of the crude reaction mixtures.



1a **2a** **3a** **4aa** **5aa**

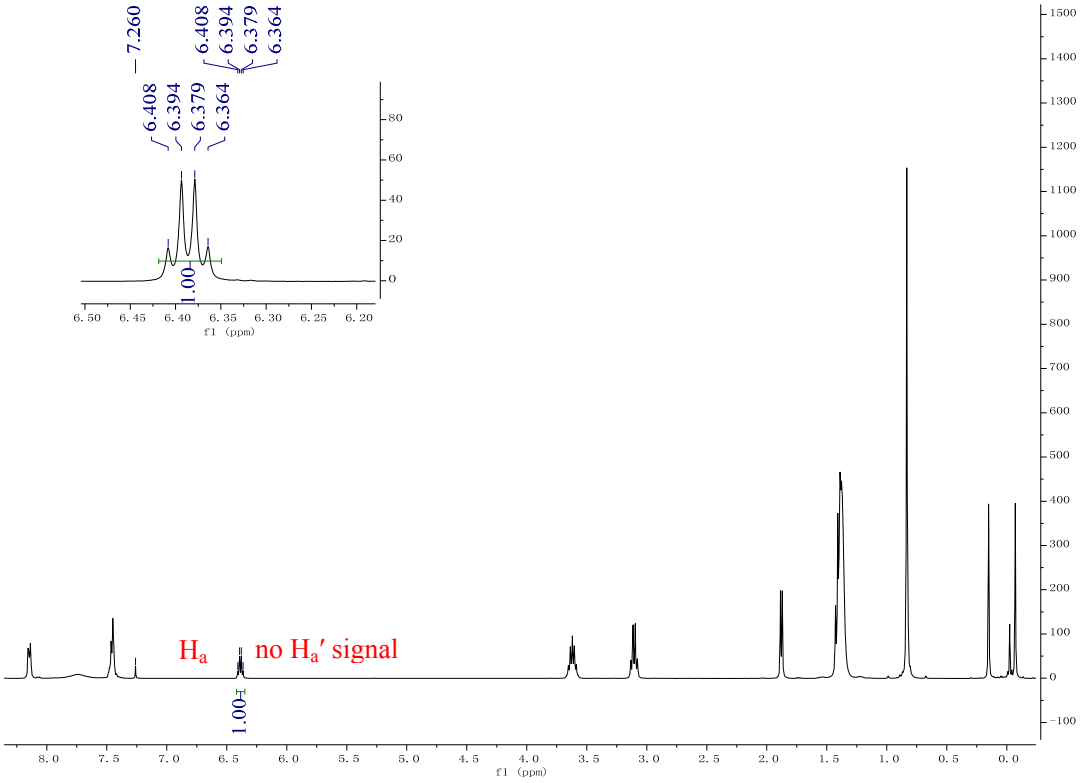
1a:**2a**:**3a** = 1:1.5:1 **4aa**:**5aa** = 58:42

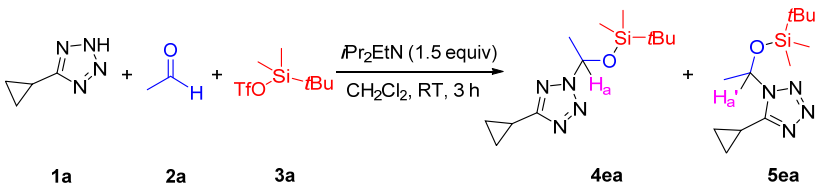




1a **2a** **3a** **4aa** **5aa**

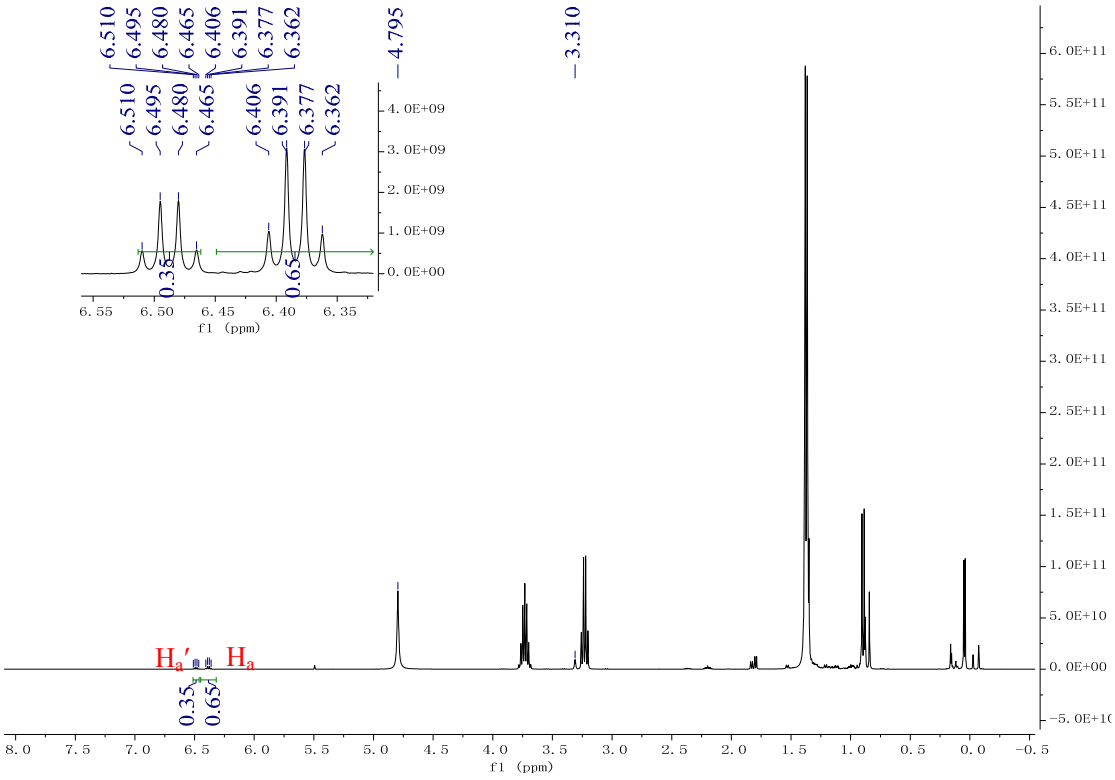
1a:**2a**:**3a** = 1:1.4:1.5 **4aa**:**5aa** >99:1

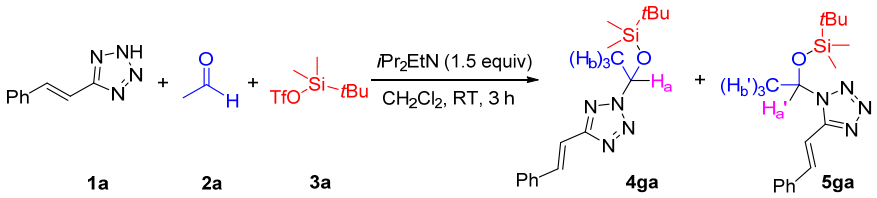




1a **2a** **3a** **4ea** **5ea**

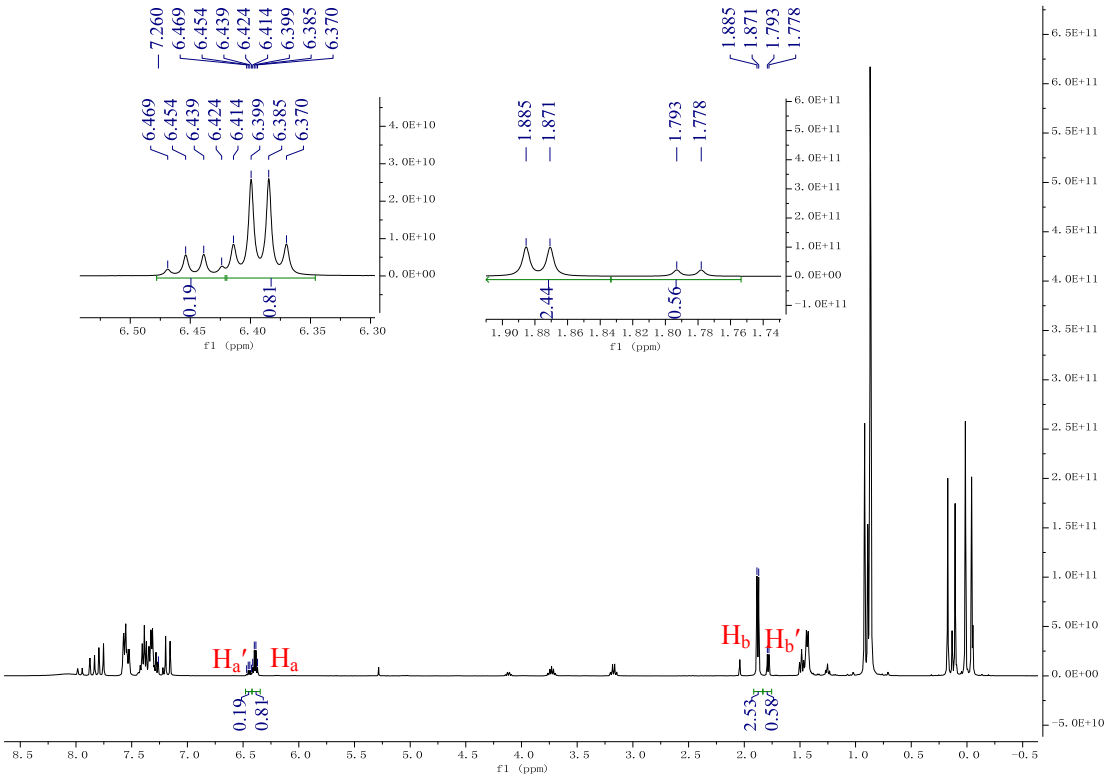
4ea:**5ea** = 65:35

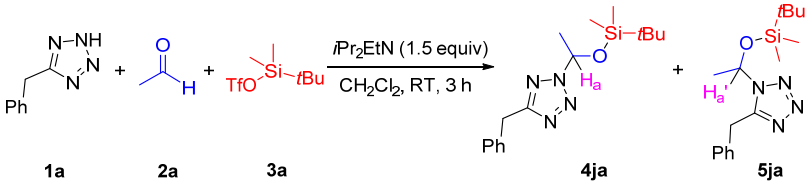




1a 2a 3a

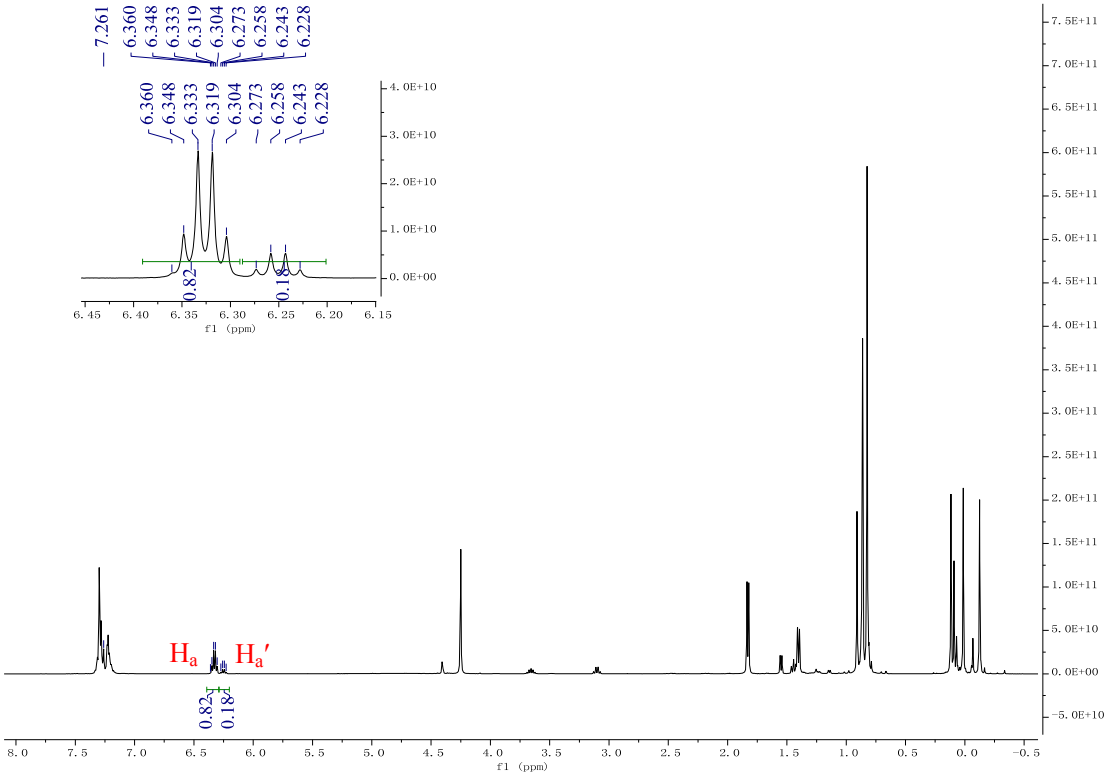
4ga:**5ga** = 81:19

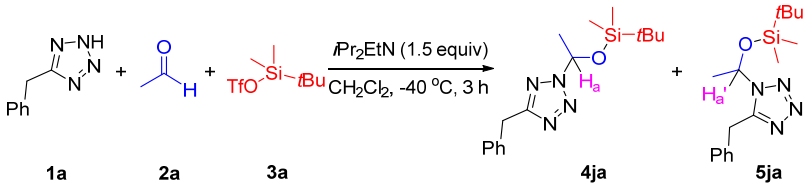




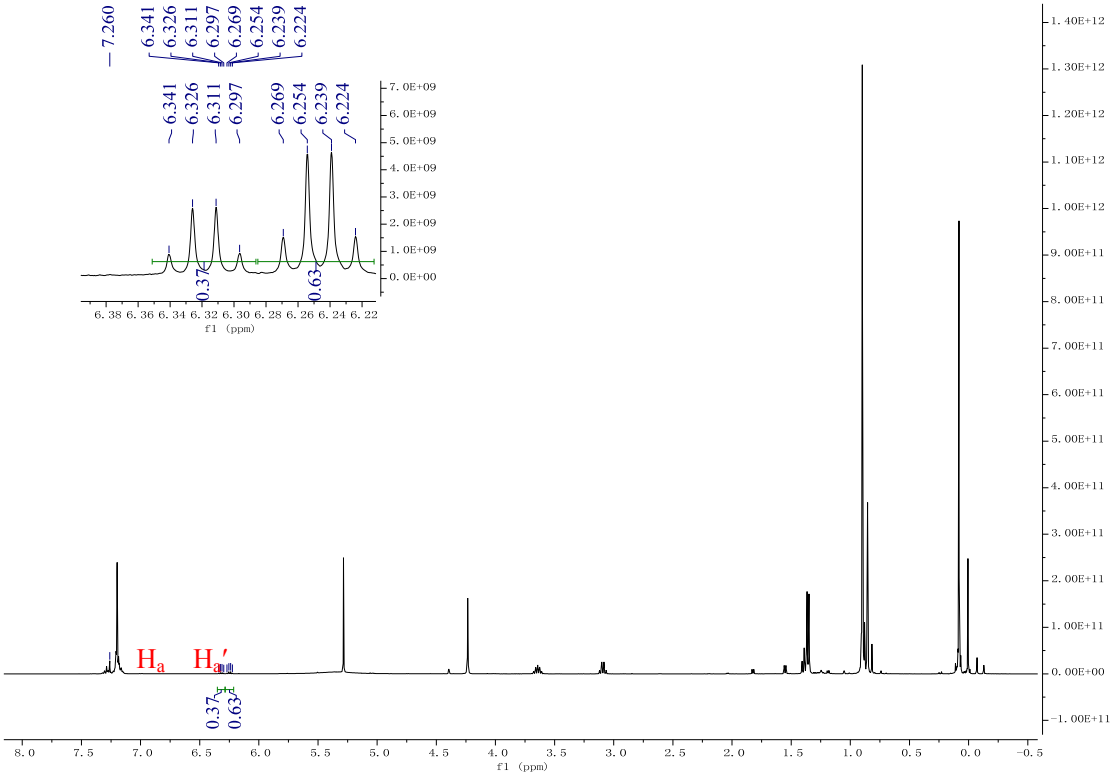
1a **2a** **3a** **4ja** **5ja**

4ja:**5ja** = 82:18



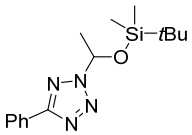

iPr2EtN (1.5 equiv)
CH2Cl2, -40 °C, 3 h
Ph
TfO
tBu
Si
Ha
Ha'
1a
2a
3a
4ja
5ja

4ja:**5ja** = 37:63


7.260
6.341
6.326
6.311
6.297
6.269
6.254
6.239
6.224
0.37
0.63
Ha
Ha'
f1 (ppm)

9. The analytical and spectral characterization data for the 2,5-disubstituted tetrazole hemiaminal silyl ethers

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-phenyl-2*H*-tetrazole (4aa).



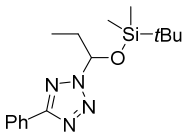
Colorless oil (60.4 mg, 99% yield).

^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.19 (d, J = 7.8 Hz, 2H), 7.45-7.50 (m, 3H), 6.25 (q, J = 6.0 Hz, 1H), 1.91 (d, J = 6.0 Hz, 3H), 0.88 (s, 9H), 0.18 (s, 3H), -0.03 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 83.6, 25.6, 23.3, 18.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{15}H_{24}N_4NaOSi$, 327.1612; found, 327.1620.

2-(1-((*tert*-Butyldimethylsilyl)oxy)propyl)-5-phenyl-2*H*-tetrazole (4ab).



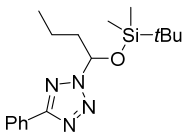
Colorless oil (61.2 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.16 (t, J = 6.4 Hz, 1H), 2.20-2.32 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 88.3, 30.2, 25.6, 18.1, 9.2, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSi$, 341.1768; found, 341.1776.

2-(1-((*tert*-Butyldimethylsilyl)oxy)butyl)-5-phenyl-2*H*-tetrazole (4ac).



Colorless oil (64.3 mg, 97% yield).

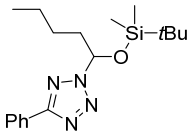
^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.19 (d, J = 7.8 Hz, 2H), 7.45-7.50 (m, 3H), 6.25 (t, J = 6.0 Hz,

1H), 2.23-2.29 (m, 1H), 2.14-2.20 (m, 1H), 1.41-1.52 (m, 1H), 1.24-1.33 (m, 1H), 0.97 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.10 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 86.8, 38.9, 25.6, 18.1, 13.6, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{17}H_{28}N_4NaOSi$, 355.1925; found, 355.1919.

2-(1-((*tert*-Butyldimethylsilyl)oxy)pentyl)-5-phenyl-2*H*-tetrazole (4ad).



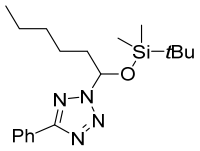
Colorless oil (64.5 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.47-7.52 (m, 3H), 6.23 (t, J = 6.4 Hz, 1H), 2.15-2.31 (m, 2H), 1.33-1.42 (m, 3H), 1.19-1.26 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.10 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 87.1, 36.6, 26.8, 25.6, 22.2, 18.1, 14.0, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{18}H_{30}N_4NaOSi$, 369.2081; found, 369.2090.

2-(1-((*tert*-Butyldimethylsilyl)oxy)hexyl)-5-phenyl-2*H*-tetrazole (4ae).



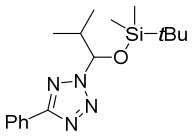
Colorless oil (65.5 mg, 91% yield).

^{1}H NMR (600 MHz, CD_3OD, δ): 8.10-8.13 (m, 2H), 7.48-7.53 (m, 3H), 6.33 (t, J = 6.0 Hz, 1H), 2.23-2.29 (m, 1H), 2.15-2.21 (m, 1H), 1.43-1.50 (m, 1H), 1.30-1.38 (m, 4H), 1.22-1.29 (m, 1H), 0.89 (t, J = 7.2 Hz, 3H), 0.85 (s, 9H), 0.18 (s, 3H), -0.10 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 87.1, 36.6, 31.2, 25.6, 24.3, 22.5, 18.1, 14.0, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{19}H_{32}N_4NaOSi$, 383.2238; found, 383.2247.

2-(1-((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-5-phenyl-2*H*-tetrazole (4af).



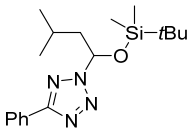
Colorless oil (61.5 mg, 93% yield).

^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.19-8.20 (m, 2H), 7.46-7.52 (m, 3H), 5.87 (d, J = 8.4 Hz, 1H), 2.54-2.60 (m, 1H), 1.14 (d, J = 6.6 Hz, 3H), 0.86 (s, 9H), 0.76 (d, J = 6.6 Hz, 3H), 0.13 (s, 3H), -0.16 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 92.0, 35.0, 25.6, 18.2, 18.1, 17.6, -5.3, -5.4.

HRMS: $[M + Na]^+$ calcd. for $C_{17}H_{28}N_4NaOSi$, 355.1925; found, 355.1920.

2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-methylbutyl)-5-phenyl-2*H*-tetrazole (4ag).



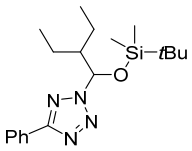
Colorless oil (63.7 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.33 (t, J = 7.2 Hz, 1H), 2.19-2.26 (m, 1H), 1.99-2.05 (m, 1H), 1.60-1.71 (m, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.14 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 85.7, 45.5, 25.6, 24.2, 22.9, 22.0, 18.1, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{18}H_{30}N_4NaOSi$, 369.2081; found, 369.2081.

2-(1-((*tert*-Butyldimethylsilyl)oxy)-2-ethylbutyl)-5-phenyl-2*H*-tetrazole (4ah).



Colorless oil (66.3 mg, 92% yield).

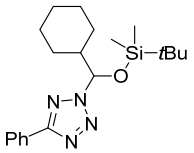
^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.10 (d, J = 8.0 Hz, 1H),

2.22-2.30 (m, 1H), 1.54-1.74 (m, 2H), 1.10-1.17 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.81 (t, *J* = 7.6 Hz, 3H), 0.14 (s, 3H), -0.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 89.3, 46.4, 25.6, 20.6, 20.4, 18.1, 10.7, 10.1, -5.3, -5.5.

HRMS: $[M + Na]^+$ calcd. for $C_{19}H_{32}N_4NaOSi$, 383.2238; found, 383.2239.

2-(((*tert*-Butyldimethylsilyl)oxy)(cyclohexyl)methyl)-5-phenyl-2*H*-tetrazole (4ai).



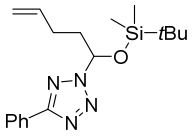
Colorless oil (61.0 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.19-8.21 (m, 2H), 7.45-7.52 (m, 3H), 5.90 (d, *J* = 8.4 Hz, 1H), 2.23-2.33 (m, 1H), 5.90 (d, *J* = 8.4 Hz, 1H), 2.13 (d, *J* = 12.8 Hz, 1H), 1.80-1.84 (m, 1H), 1.61-1.71 (m, 2H), 1.24-1.36 (m, 1H), 1.08-1.20 (m, 3H),0.93-1.06 (m, 2H), 0.85 (s, 9H), 0.12 (s, 3H), -0.16 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 91.2, 43.8, 28.7, 27.8, 26.2, 25.62, 25.56, 25.4, 18.1, -5.27, -5.34.

HRMS: $[M + Na]^+$ calcd. for $C_{20}H_{32}N_4NaOSi$, 395.2238; found, 395.2241.

2-(1-((*tert*-Butyldimethylsilyl)oxy)pent-4-en-1-yl)-5-phenyl-2*H*-tetrazole (4aj).



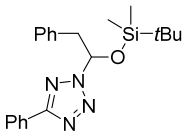
Colorless oil (62.4 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.26 (t, *J* = 6.4 Hz, 1H), 5.76-5.86 (m, 1H), 5.02-5.08 (m, 2H), 2.25-2.44 (m, 2H), 2.04-2.23 (m, 2H), 0.86 (s, 9H), 0.16 (s, 3H), -0.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 136.5, 130.5, 129.0, 127.6, 127.1, 116.2, 86.3, 35.9, 28.8, 25.6, 18.1, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{18}H_{28}N_4NaOSi$, 367.1925; found, 367.1917.

2-(((*tert*-Butyldimethylsilyl)oxy)(phenyl)methyl)-5-phenyl-2*H*-tetrazole (4ak).



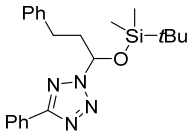
Colorless oil (54.6 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23-8.26 (m, 2H), 7.50-7.57 (m, 3H), 7.28-7.35 (m, 5H), 6.42 (dd, J = 7.6 , 5.6 Hz, 1H), 3.49-3.63 (m, 2H), 0.81 (s, 9H), -0.03 (s, 3H), -0.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 135.2, 130.5, 129.9, 129.0, 128.7, 127.6, 127.4, 127.1, 87.7, 43.5, 25.5, 18.0, -5.3, -5.6.

HRMS: $[M + Na]^+$ calcd. for $C_{21}H_{28}N_4NaOSi$, 403.1925; found, 403.1915.

2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-phenylpropyl)-5-phenyl-2*H*-tetrazole (4al).



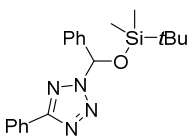
Colorless oil (67.1 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.19-8.22 (m, 2H), 7.46-7.53 (m, 3H), 7.29-7.33 (m, 2H), 7.19-7.23 (m, 3H), 6.26 (t, J = 6.0 Hz, 1H), 2.65-2.81 (m, 2H), 2.51-2.64 (m, 2H), 0.88 (s, 9H), 0.16 (s, 3H), -0.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.2, 140.2, 130.5, 129.0, 128.7, 128.5, 127.6, 127.1, 126.5, 86.2, 38.4, 30.9, 25.6, 18.1, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{22}H_{30}N_4NaOSi$, 417.2081; found, 417.2090.

2-(((*tert*-Butyldimethylsilyl)oxy)(phenyl)methyl)-5-phenyl-2*H*-tetrazole (4am).



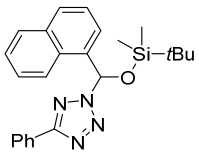
White solid (52.2 mg, 71% yield). mp: 53.8-54.5 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.15-8.17 (m, 2H), 7.58-7.60 (m, 2H), 7.44-7.49 (m, 3H), 7.39-7.44 (m, 3H), 7.36 (s, 1H), 0.95 (s, 9H), 0.23 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.4, 137.5, 130.4, 129.5, 128.9, 128.7, 127.5, 127.1, 126.3, 87.1, 25.6, 18.2, -5.2, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{20}H_{26}N_4NaOSi$, 389.1768; found, 389.1770.

2-(((*tert*-Butyldimethylsilyl)oxy)(naphthalen-1-yl)methyl)-5-phenyl-2*H*-tetrazole (4an).



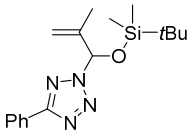
White solid (40.1 mg, 48% yield). mp: 140.1-140.9 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.27 (d, J = 7.2 Hz, 1H), 8.08-8.10 (m, 2H), 7.98 (s, 1H), 7.93-7.95 (m, 2H), 7.88-7.89 (m, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.45-7.47 (m, 2H), 7.42-7.44 (m, 3H), 0.95 (s, 9H), 0.29 (s, 3H),0.06 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.4, 133.8, 132.0, 130.5, 130.4, 129.9, 129.2, 128.9, 127.5, 127.2, 127.1, 126.0, 125.5, 122.2, 84.6, 25.7, 18.3, -5.0, -5.2.

HRMS: $[M + Na]^+$ calcd. for $C_{24}H_{28}N_4NaOSi$, 439.1925; found, 439.1929.

2-(1-((*tert*-Butyldimethylsilyl)oxy)-2-methylallyl)-5-phenyl-2*H*-tetrazole (4ao).



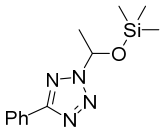
Colorless oil (40.1 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.51 (m, 3H), 6.60 (s, 1H), 5.51 (s, 1H), 5.20-5.24 (m, 1H), 1.76 (s, 3H), 0.90 (s, 9H), 0.20 (s, 3H), -0.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.2, 140.7, 130.4, 129.0, 127.6, 127.2, 115.9, 88.3, 25.6, 18.2, 17.5, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{17}H_{26}N_4NaOSi$, 353.1768; found, 353.1773.

2-(1-((Trimethylsilyl)oxy)ethyl)-5-phenyl-2*H*-tetrazole (4ap).



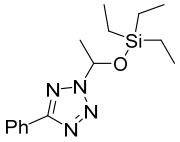
Colorless oil (20.8 mg, 40% yield).

^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.46-7.54 (m, 3H), 6.43 (q, J = 6.0 Hz, 1H), 1.91 (d, J = 6.0 Hz, 3H), 0.12 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.5, 129.0, 127.7, 127.1, 83.2, 23.4, -0.3.

HRMS: $[M + Na]^+$ calcd. for $C_{12}H_{18}N_4NaOSi$, 285.1142; found, 285.1151.

2-(1-((Triethylsilyl)oxy)ethyl)-5-phenyl-2*H*-tetrazole (4aq).



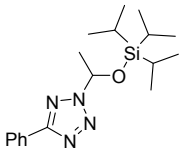
Colorless oil (43.5 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18-8.20 (m, 2H), 7.46-7.52 (m, 3H), 6.44 (q, J = 6.0 Hz, 1H), 1.91 (d, J = 6.0 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.56-0.67 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 88.3, 23.5, 6.5, 4.4.

HRMS: $[M + Na]^+$ calcd. for $C_{15}H_{24}N_4NaOSi$, 327.1612; found, 327.1612.

2-(1-((Triisopropylsilyl)oxy)ethyl)-5-phenyl-2*H*-tetrazole (4ar).



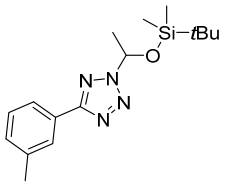
Colorless oil (63.8 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.17-8.20 (m, 2H), 7.44-7.52 (m, 3H), 6.55 (q, J = 6.0 Hz, 1H), 1.92 (d, J = 5.6 Hz, 3H), 1.09-1.17 (m, 3H), 1.05(d, J = 7.2 Hz, 9H), 0.98(d, J = 7.2 Hz, 9H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 83.6, 23.8, 17.9, 17.7, 12.1.

HRMS: $[M + Na]^+$ calcd. for $C_{18}H_{30}N_4NaOSi$, 369.2081; found, 369.2071.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(*m*-tolyl)-2*H*-tetrazole (4ba) .



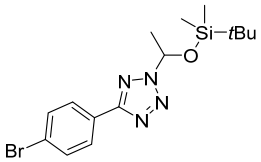
Colorless oil (62.5 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.02 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.42 (q, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 1.91 (d, *J* = 5.6 Hz, 3H), 0.87 (s, 9H), 0.18 (s, 3H), -0.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 165.1, 138.7, 131.2, 128.9, 127.6, 127.5, 124.2, 83.5, 25.6, 23.3, 21.5, 18.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSi$, 341.1768; found, 347.1765.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(4-bromophenyl)-2*H*-tetrazole (4ca).



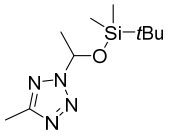
Colorless oil (48.9 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 8.05-8.07 (m, 2H), 7.61-7.63 (m, 2H), 6.41 (q, *J* = 6.0 Hz, 1H), 1.90 (d, *J* = 5.6 Hz, 3H), 0.86 (s, 9H), 0.18 (s, 3H), -0.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, *δ*): 164.2, 132.3, 128.6, 126.7, 124.5, 83.7, 25.6, 23.3, 18.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{15}H_{23}BrN_4NaOSi$, 405.0717; found, 405.0720.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-methyl-2*H*-tetrazole (4da).



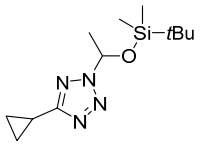
Colorless oil (13.2 mg, 27% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.33 (q, *J* = 6.0 Hz, 1H), 2.55 (s, 3H), 1.82 (d, *J* = 6.0 Hz, 3H), 0.85 (s, 9H), 0.15 (s, 3H), -0.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 83.1, 25.6, 23.3, 18.1, 11.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{10}H_{22}N_4NaOSi$, 265.1455; found, 265.1445.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-cyclopropyl-2*H*-tetrazole (4ea).



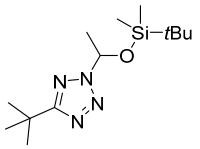
Colorless oil (18.8 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.28 (q, *J* = 6.0 Hz, 1H), 2.15-2.24 (m, 1H), 1.80 (d, *J* = 5.6 Hz, 3H), 1.06-1.08 (m, 4H), 0.84 (s, 9H), 0.13 (s, 3H), -0.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 168.7, 83.1, 25.6, 23.2, 18.1, 8.71, 8.65, 6.8, -5.1, -5.4.

HRMS: $[M + Na]^+$ calcd. for $C_{12}H_{24}N_4NaOSi$, 291.1612; found, 291.1612.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(*tert*-butyl)-2*H*-tetrazole (4fa).



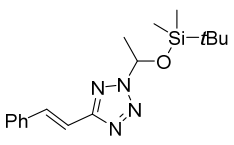
Colorless solid (16.5 mg, 29% yield). mp: 157.8-158.9 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.31 (q, *J* = 6.0 Hz, 1H), 1.84 (d, *J* = 6.0 Hz, 3H), 1.43 (s, 9H), 0.83 (s, 9H), 0.12 (s, 3H), -0.11 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 174.3, 83.1, 31.7, 29.7, 25.6, 23.1, 18.0, -5.2, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{13}H_{28}N_4NaOSi$, 307.1925; found, 307.1917.

(*E*)-2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-styryl-2*H*-tetrazole (4ga).



Colorless oil (45.6 mg, 69% yield).

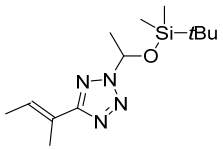
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, *J* = 16.8 Hz, 1H), 7.55-7.58 (m, 2H), 7.31-7.42 (m, 3H), 7.17 (d, *J* = 16.8 Hz, 1H), 6.39 (q, *J* = 6.0 Hz, 1H), 1.88 (d, *J* = 6.0 Hz, 3H), 0.87 (s, 9H), 0.17 (s,

3H), -0.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 164.2, 136.6, 135.9, 129.2, 129.0, 127.3, 113.7, 83.4, 25.6, 23.4, 18.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{17}H_{26}N_4NaOSi$, 353.1768; found, 353.1764.

(*E*)-2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(but-2-en-2-yl)-2*H*-tetrazole (4ha).



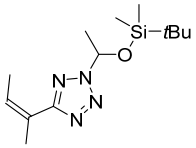
Colorless oil (50.1 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.83 (qq, *J* = 7.2, 1.6 Hz, 1H), 6.32 (q, *J* = 6.0 Hz, 1H), 2.11-2.12 (m, 3H), 1.83-1.87 (m, 6H), 0.85 (s, 9H), 0.14 (s, 3H), -0.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 167.1, 128.7, 123.9, 83.2, 25.6, 23.2, 18.1, 13.9, 13.5, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{13}H_{26}N_4NaOSi$, 305.1768; found, 305.1767.

(*Z*)- 2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(but-2-en-2-yl)-2*H*-tetrazole (4ia).



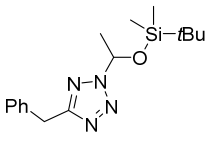
Colorless oil (51.2 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.36 (q, *J* = 6.0 Hz, 1H), 5.97 (qq, *J* = 7.2, 1.6 Hz, 1H), 2.17-2.18 (m, 3H), 2.07 (dq, *J* = 7.2, 1.6 Hz, 3H), 1.86 (d, *J* = 5.6 Hz, 3H), 0.85 (s, 9H), 0.14 (s, 3H), -0.07 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.4, 130.8, 123.1, 83.3, 25.6, 23.2, 22.2, 18.1, 15.8, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{13}H_{26}N_4NaOSi$, 305.1768; found, 305.1769.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-benzyl-2*H*-tetrazole (4ja).



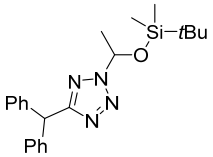
Colorless oil (19.6 mg, 31% yield).

^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.28-7.32 (m, 4H), 7.21-7.24(m, 1H), 6.33(q, J = 6.0 Hz, 1H), 4.26 (s, 2H), 1.83 (d, J = 5.4 Hz, 3H), 0.83 (s, 9H), 0.12 (s, 3H), -0.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 165.5, 136.9, 128.9, 128.7, 126.9, 83.3, 32.0, 25.5, 23.2, 18.0, -5.1, -5.4.

HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSi$, 341.1768; found, 341.1772.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-benzhydryl-2*H*-tetrazole (4ka).



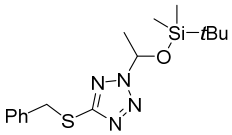
Colorless oil (43.4 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34-7.35 (m, 2H), 7.31-7.32 (m, 3H), 7.27-7.30 (m, 3H), 7.21-7.25 (m, 2H), 6.35 (q, J = 6.0 Hz, 1H), 5.84 (s, 1H), 1.85 (d, J = 6.0 Hz, 3H), 0.83 (s, 9H), 0.12 (s, 3H), -0.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 167.8, 140.92, 140.91, 128.89, 128.87, 128.65, 128.64, 127.09, 127.07, 83.5, 48.8, 25.5, 23.2, 18.0, -5.1, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{22}H_{30}N_4NaOSi$, 417.2081; found, 417.2079.

2-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(benzylthio)-2*H*-tetrazole (4la).



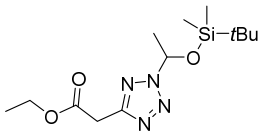
Colorless oil (39.3 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38-7.41 (m, 2H), 7.22-7.31 (m, 3H), 6.30 (q, J = 6.0 Hz, 1H), 4.43 (s, 2H), 1.82 (d, J = 6.0 Hz, 3H), 0.85 (s, 9H), 0.13 (s, 3H), -0.10 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 163.7, 136.8, 129.2, 128.7, 127.7, 83.7, 36.7, 25.6, 23.2, 18.0, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSSi$, 373.1489; found, 373.1491.

Ethyl 2-(2-(1-((*tert*-butyldimethylsilyl)oxy)ethyl)-2*H*-tetrazol-5-yl)acetate (4ma).



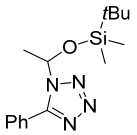
Colorless oil (23.3 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.36 (q, *J* = 6.0 Hz, 1H), 4.19 (q, *J* = 6.0 Hz, 2H), 3.98 (s, 2H), 1.85 (d, *J* = 5.6 Hz, 3H), 1.25 (t, *J* = 6.8 Hz, 3H), 1.91 (d, *J* = 6.0 Hz, 3H), 0.85 (s, 9H), 0.15 (s, 3H), -0.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 168.4, 160.1, 83.6, 61.7, 32.1, 25.6, 23.3, 18.0, 14.2, -5.1, -5.4.

HRMS: $[M + Na]^+$ calcd. for $C_{13}H_{26}N_4NaO_3Si$, 337.1666; found, 337.1660.

1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-phenyl-1*H*-tetrazole (5aa).



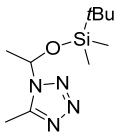
White solid. mp: 75.0-75.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$, *δ*): 7.86-7.88 (m, 2H), 7.52-7.59 (m, 3H), 6.36 (q, *J* = 6.0 Hz, 1H), 1.76 (d, *J* = 6.0 Hz, 3H), 0.84 (s, 9H), 0.01 (s, 3H), -0.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, *δ*): 153.9.0, 131.4, 129.6, 129.1, 124.7, 80.4, 25.5, 23.2, 17.9, -4.8, -5.1.

HRMS: $[M + Na]^+$ calcd. for $C_{15}H_{24}N_4NaOSi$, 327.1612; found, 327.1621.

1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-methyl-1*H*-tetrazole (5da).



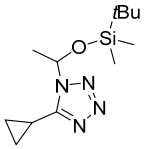
Colorless oil (12.2 mg, 25% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.33 (q, *J* = 6.0 Hz, 1H), 2.67 (s, 3H), 1.73 (d, *J* = 6.0 Hz, 3H), 0.86 (s, 9H), 0.11 (s, 3H), -0.07 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 150.8, 80.8, 25.6, 23.9, 18.0, 10.0, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{10}H_{22}N_4NaOSi$, 265.1455; found, 265.1451.

1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-cyclopropyl-1*H*-tetrazole (5ea).



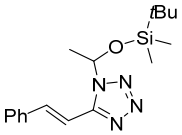
Colorless oil (10.1 mg, 19% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.36 (q, *J* = 6.0 Hz, 1H), 2.23-2.29 (m, 1H), 1.80 (d, *J* = 6.0 Hz, 3H), 1.38-1.42 (m, 1H), 1.15-1.25 (m, 3H), 0.87 (s, 9H), 0.11 (s, 3H), -0.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.7, 80.7, 25.6, 24.1, 17.9, 10.3, 9.3, 5.1, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{12}H_{24}N_4NaOSi$, 291.1612; found, 291.1614.

(*E*)-1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-styryl-1*H*-tetrazole (5ga).



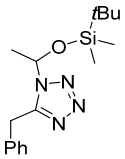
Colorless oil (8.0 mg, 12% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95 (d, *J* = 16.4 Hz, 1H), 7.55-7.58 (m, 2H), 7.37-7.45 (m, 3H), 7.23 (d, *J* = 16.4 Hz, 1H), 6.44 (q, *J* = 6.0 Hz, 1H), 1.78 (d, *J* = 6.0 Hz, 3H), 0.89 (s, 9H), 0.13 (s, 3H), -0.06 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 151.9, 140.1, 135.2, 130.1, 129.2, 127.7, 108.8, 81.4, 25.6, 24.8, 18.0, -5.0, -5.3.

HRMS: $[M + Na]^+$ calcd. for $C_{17}H_{26}N_4NaOSi$, 353.1768; found, 353.1756.

1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-benzyl-1*H*-tetrazole (5ja).



White solid (30.5 mg, 48% yield). mp: 95.2-95.8 °C.

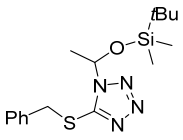
^{1}H NMR (600 MHz, $CDCl_3$, *δ*): 7.31-7.33 (m, 2H), 7.25-7.28(m, 1H), 7.22-7.23 (m, 2H), 6.25(q,

J = 6.0 Hz, 1H), 4.41 (dd, *J* = 21.0, 16.2 Hz, 2H), 1.54 (d, *J* = 6.0 Hz, 3H), 0.86 (s, 9H), 0.07 (s, 3H), -0.07 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, *δ*): 152.8, 134.5, 129.1, 128.8, 127.6, 81.0, 30.0, 25.6, 24.2, 18.0, -4.9, -5.2.

HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSi$, 341.1768; found, 341.1766.

1-(1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-(benzylthio)-1*H*-tetrazole (5la).



Colorless oil (19.6 mg, 28% yield).

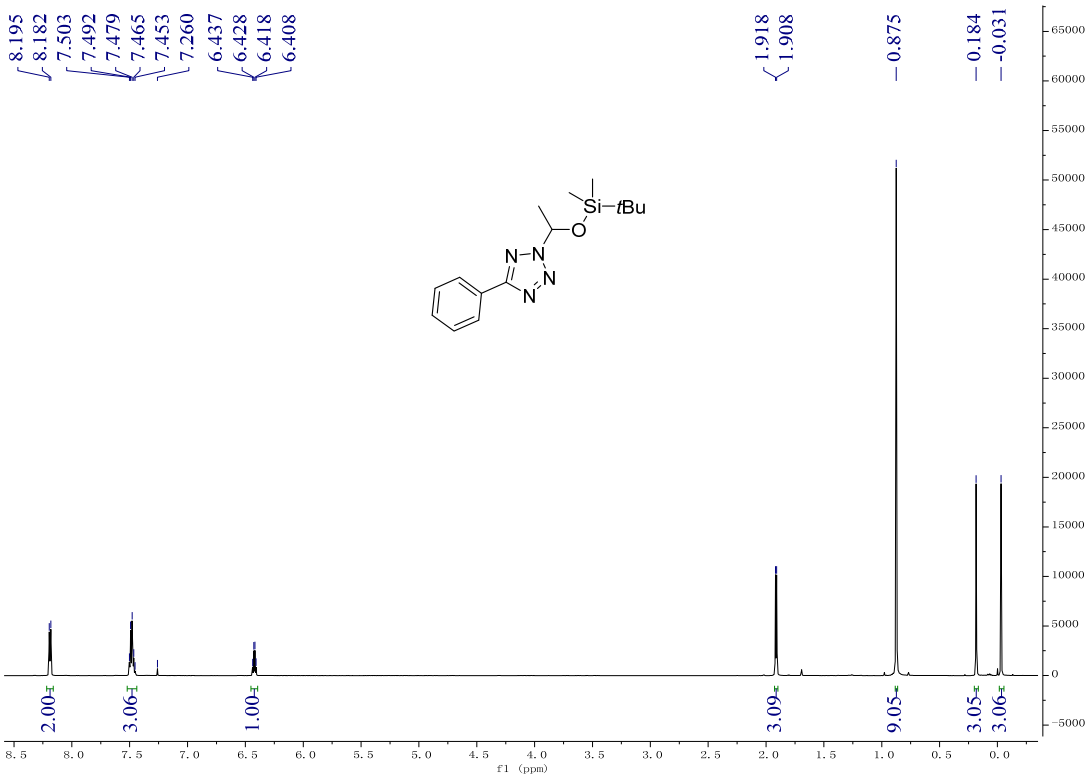
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39-7.42 (m, 2H), 7.27-7.34 (m, 3H), 6.14 (q, *J* = 6.0 Hz, 1H), 4.58 (s, 2H), 1.67 (d, *J* = 6.0 Hz, 3H), 0.84 (s, 9H), 0.06 (s, 3H), -0.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 152.5, 135.9, 129.3, 128.9, 128.1, 80.6, 37.4, 25.6, 23.2, 18.0, -5.0, -5.2.

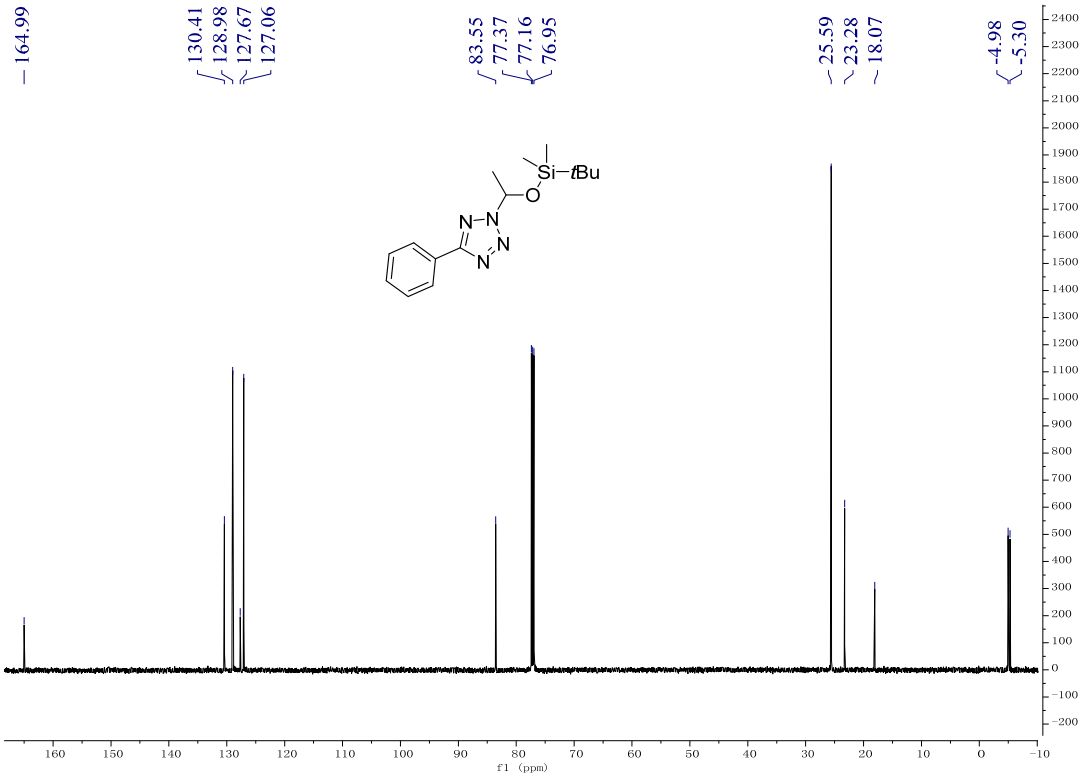
HRMS: $[M + Na]^+$ calcd. for $C_{16}H_{26}N_4NaOSSi$, 373.1489; found, 373.1487.

10. Copies of NMR spectra of the adducts

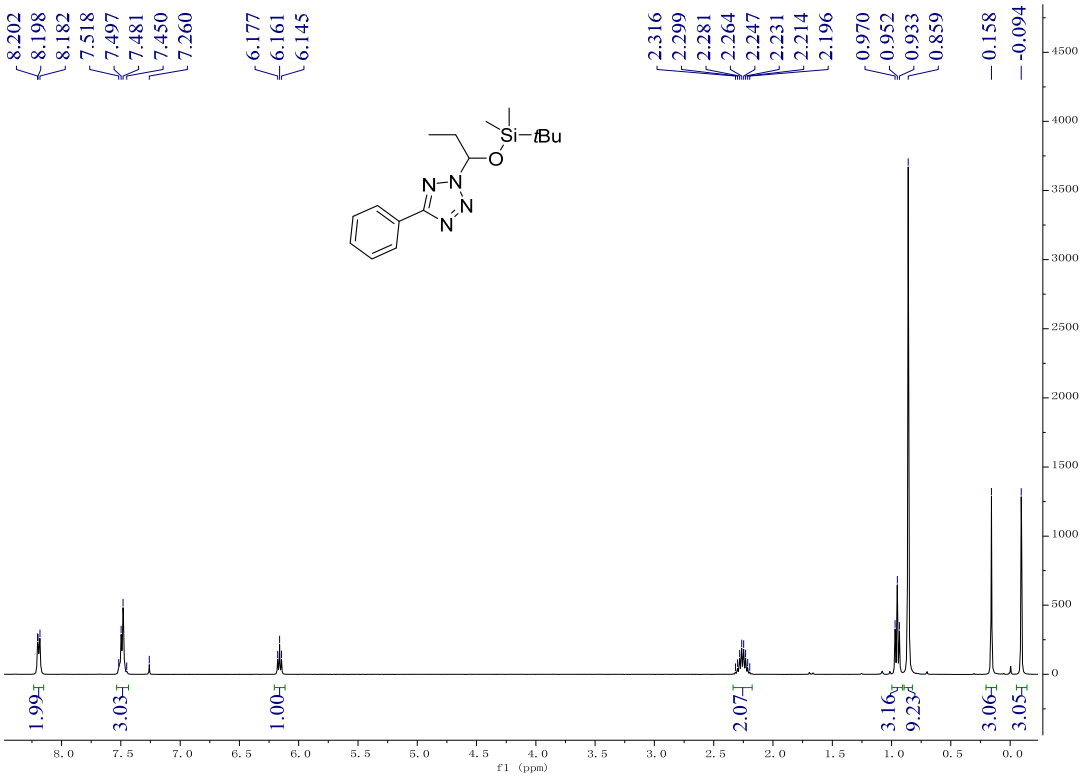
^{1}H-NMR of 4aa



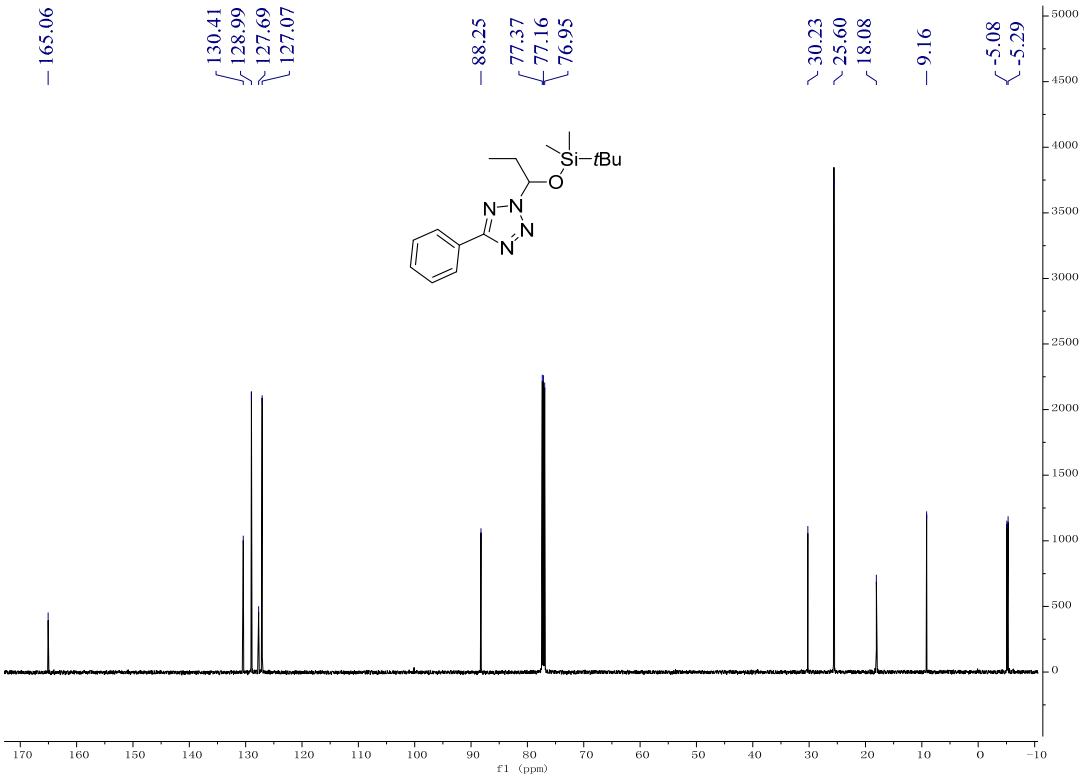
^{13}C-NMR of 4aa



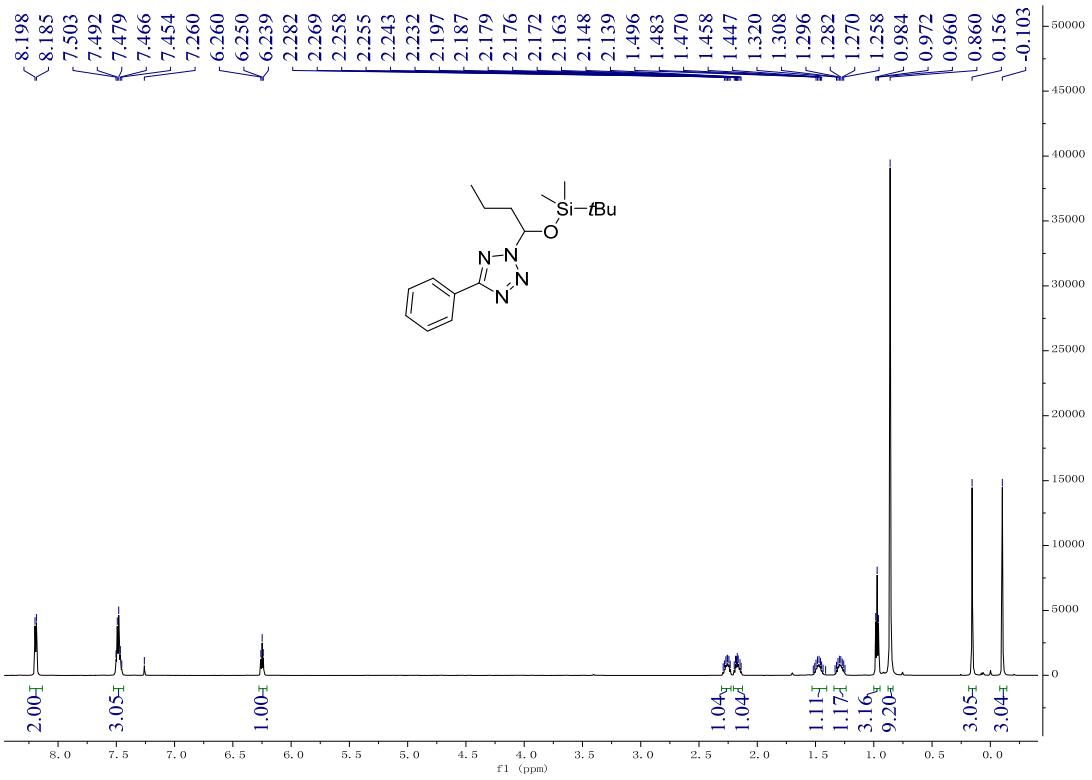
^{1}H-NMR of 4ab



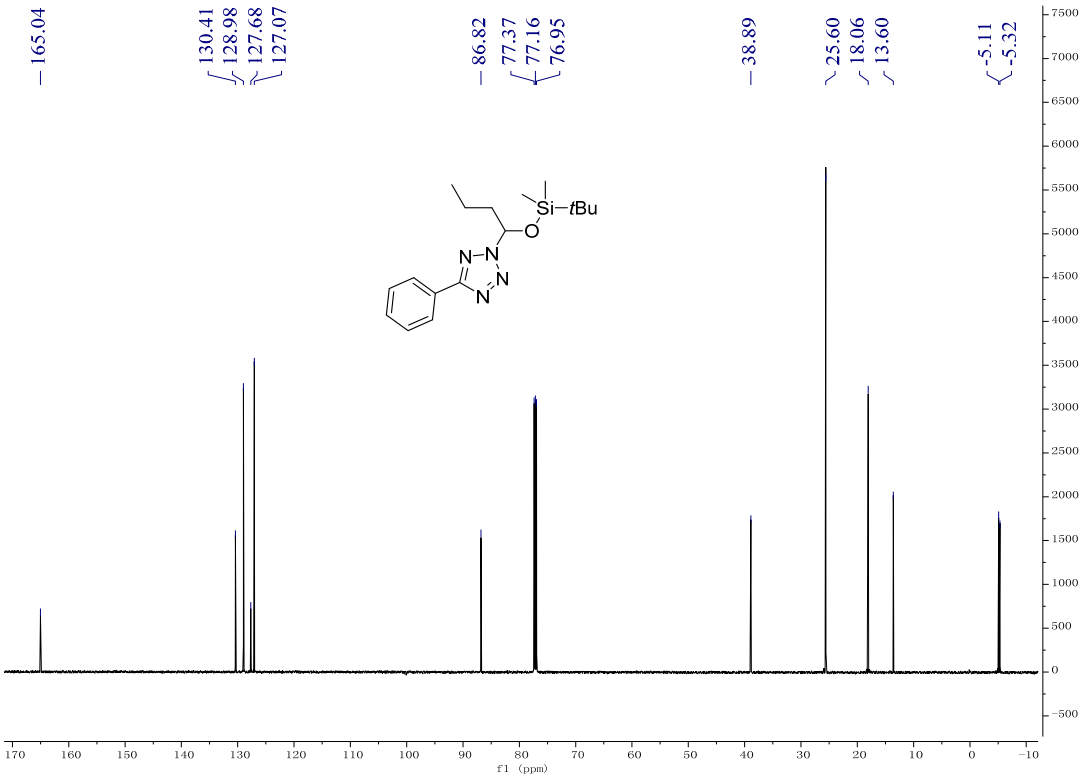
^{13}C-NMR of 4ab



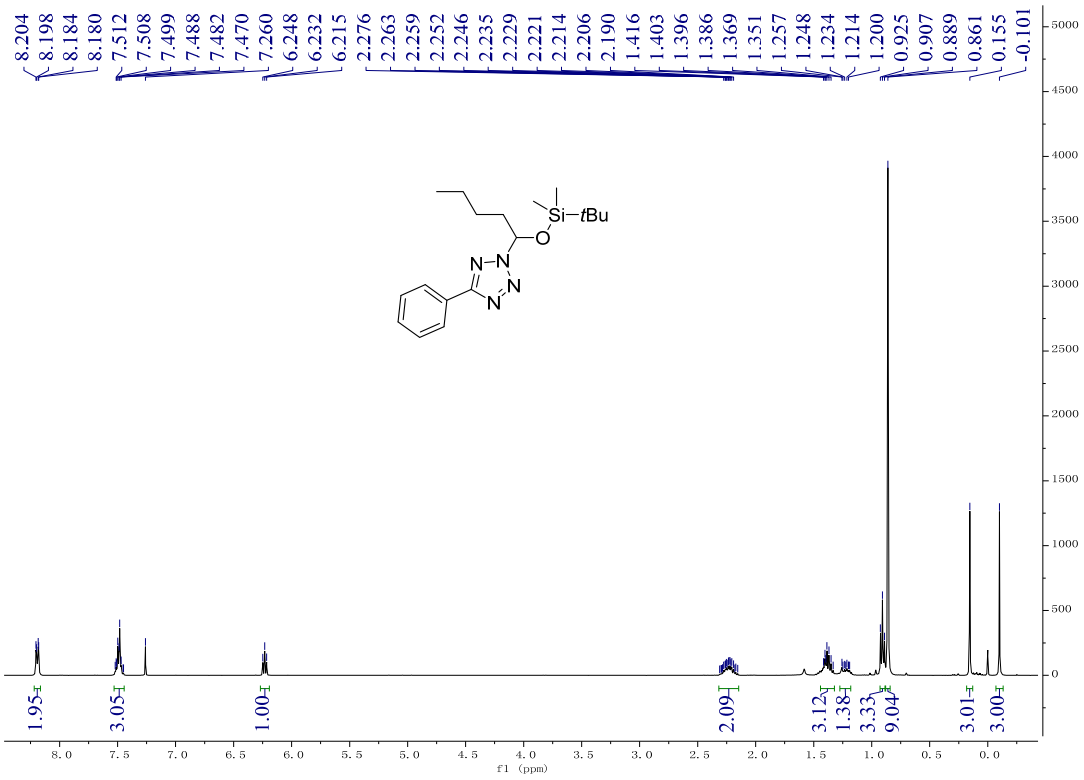
^{1}H-NMR of 4ac



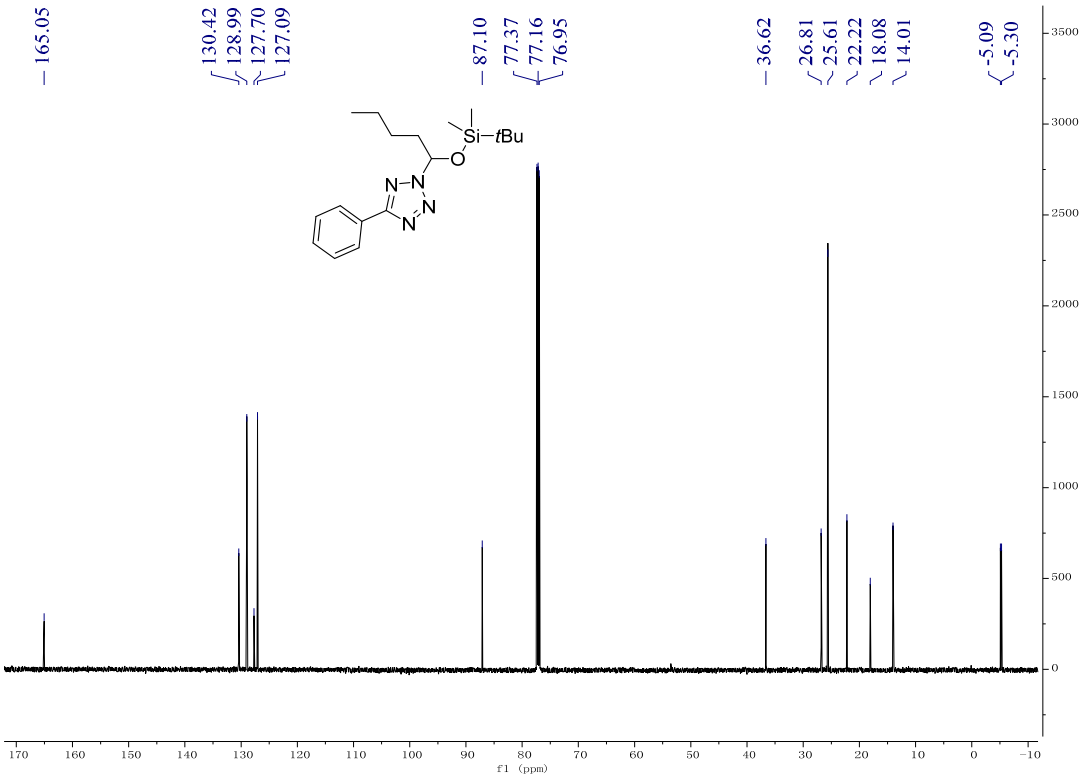
^{13}C-NMR of 4ac



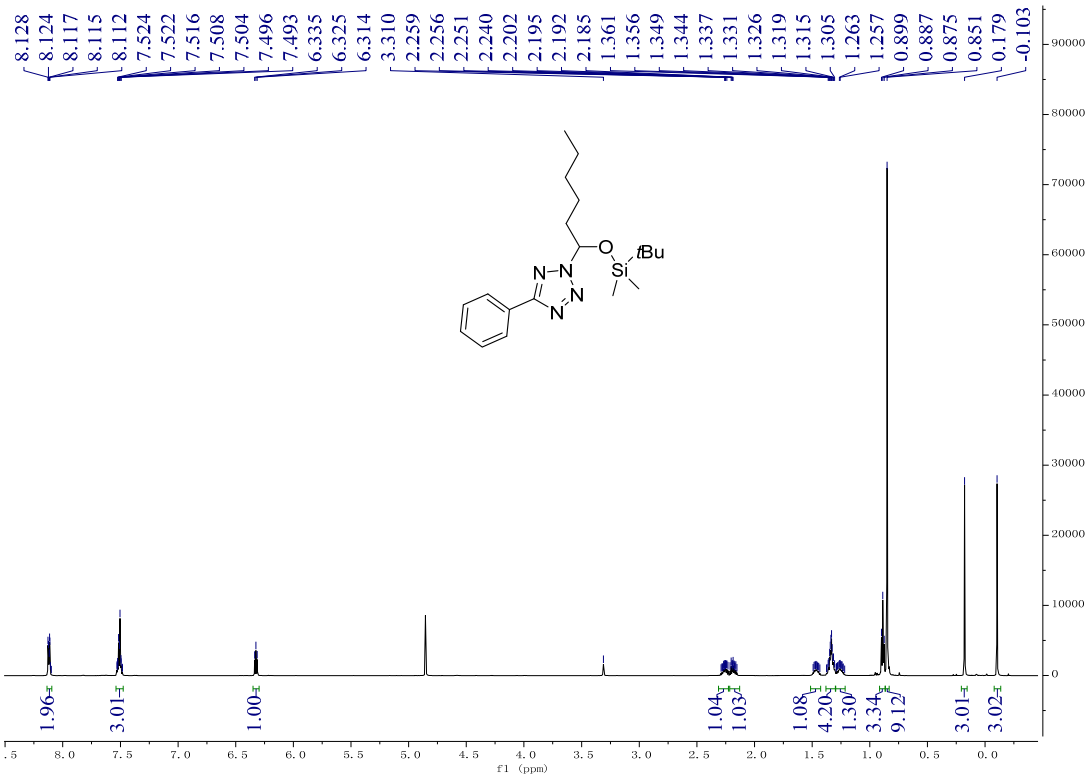
^{1}H-NMR of 4ad



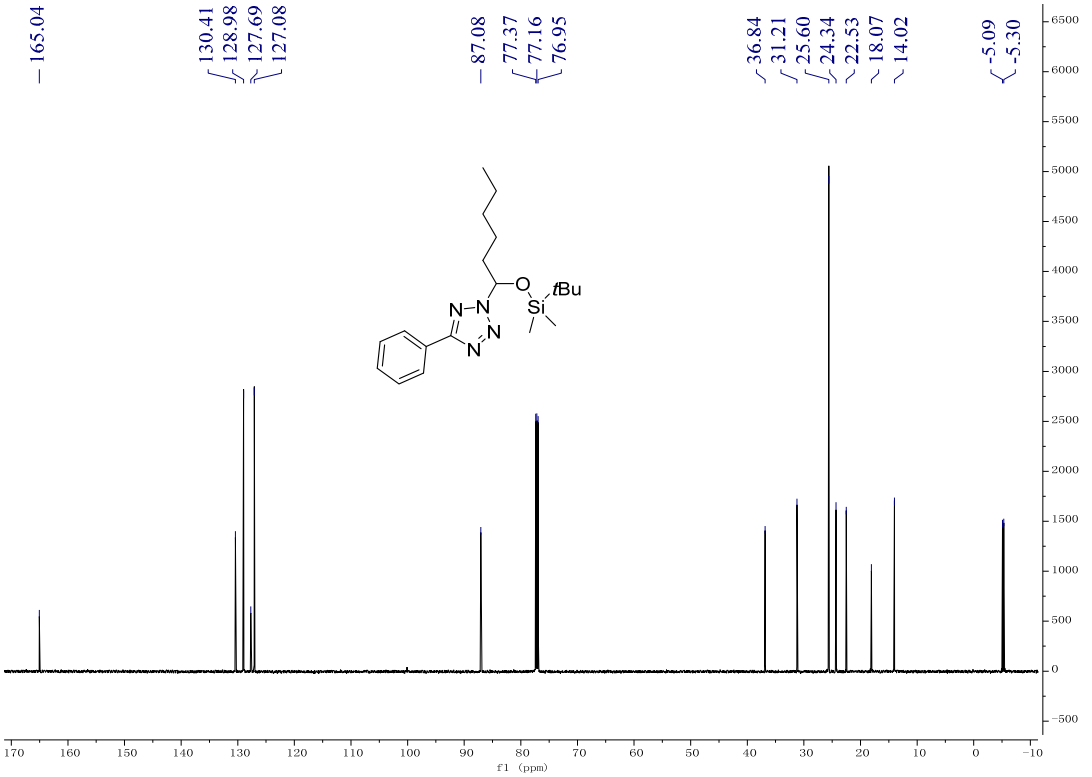
^{13}C-NMR of 4ad



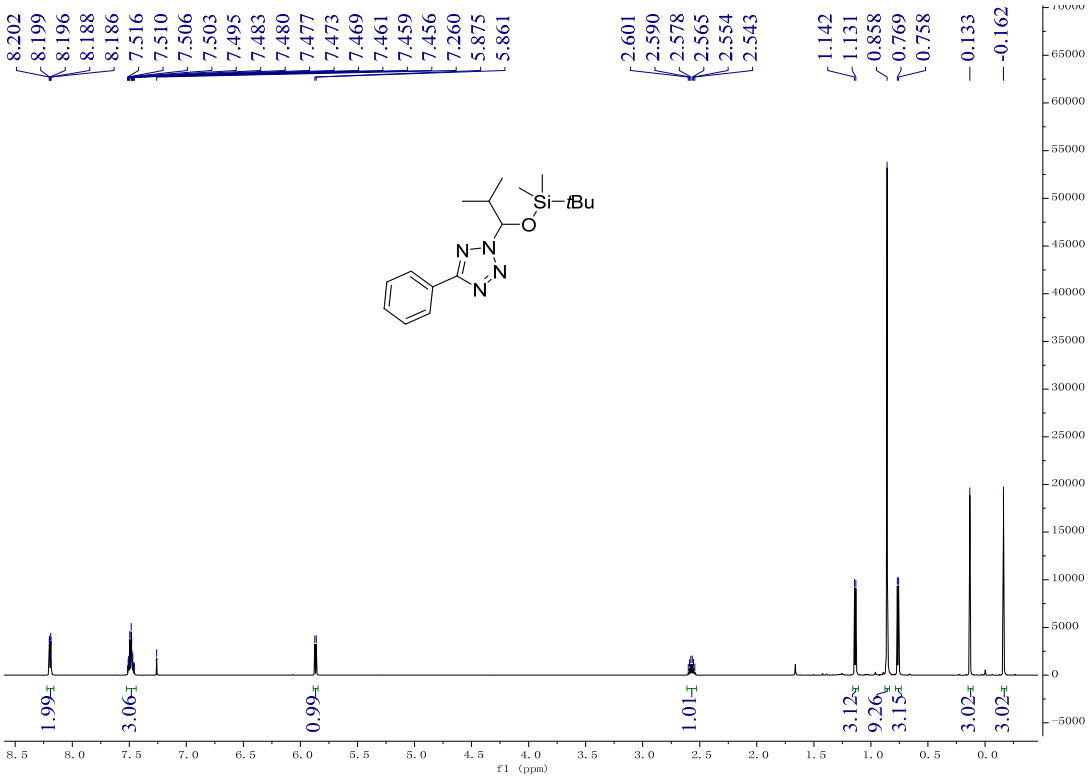
^{1}H-NMR of 4ae



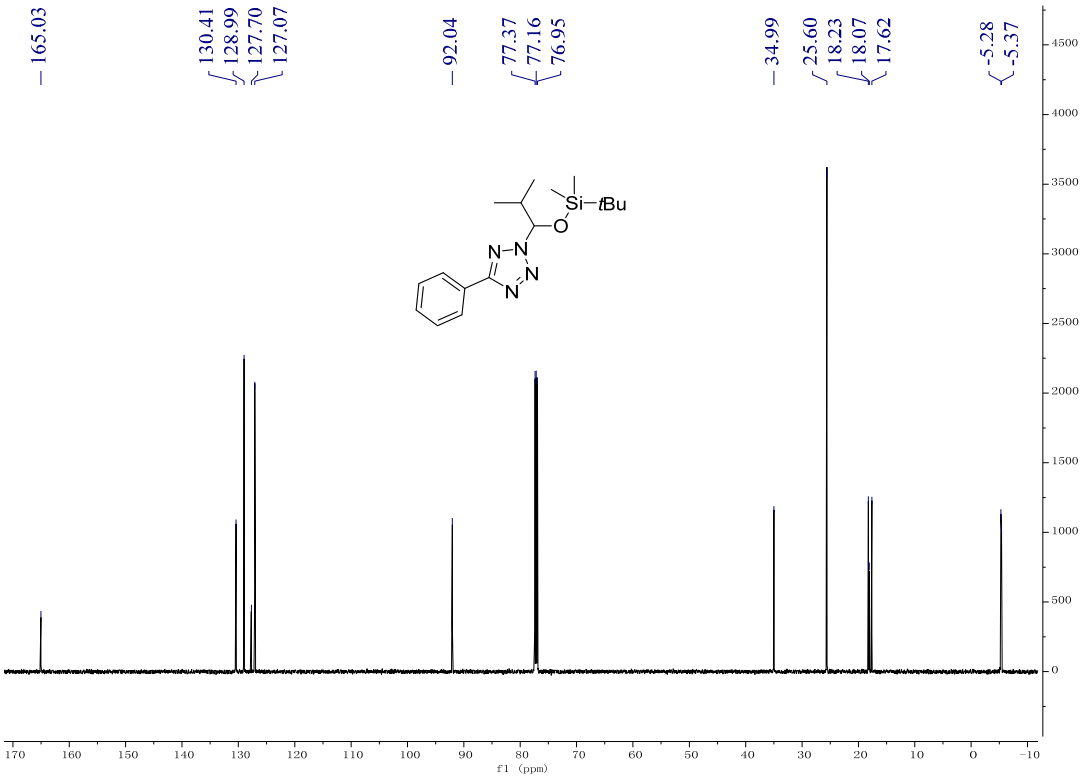
^{13}C-NMR of 4ae



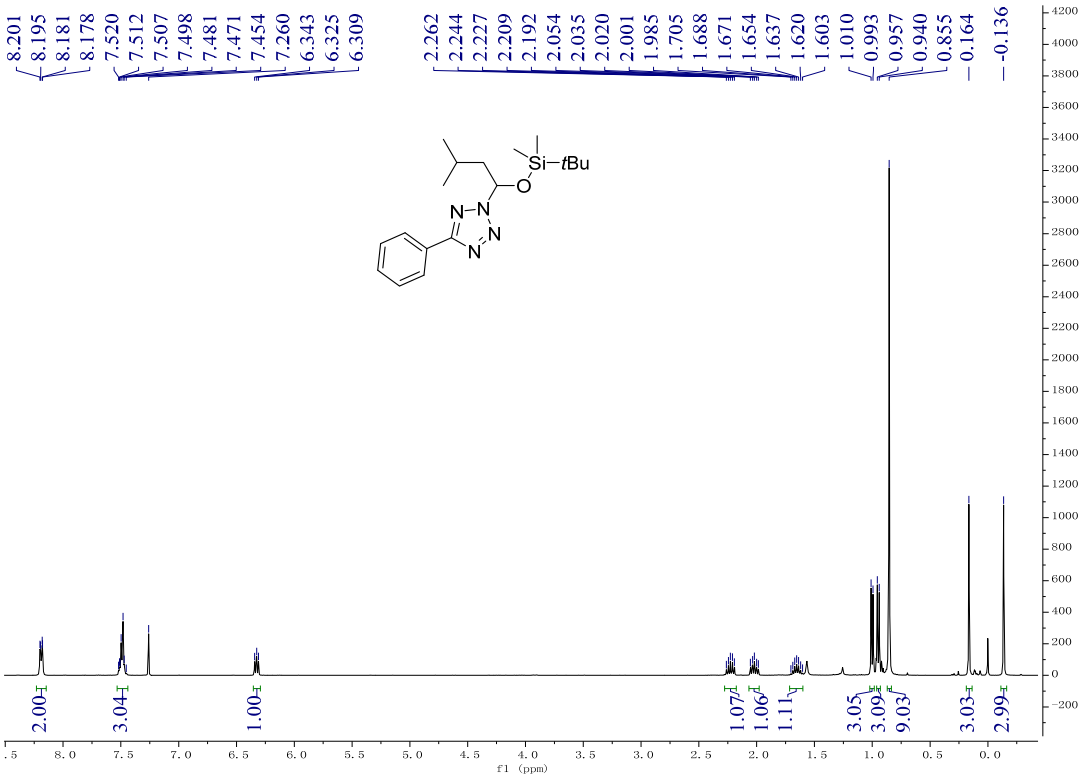
^{1}H-NMR of 4af



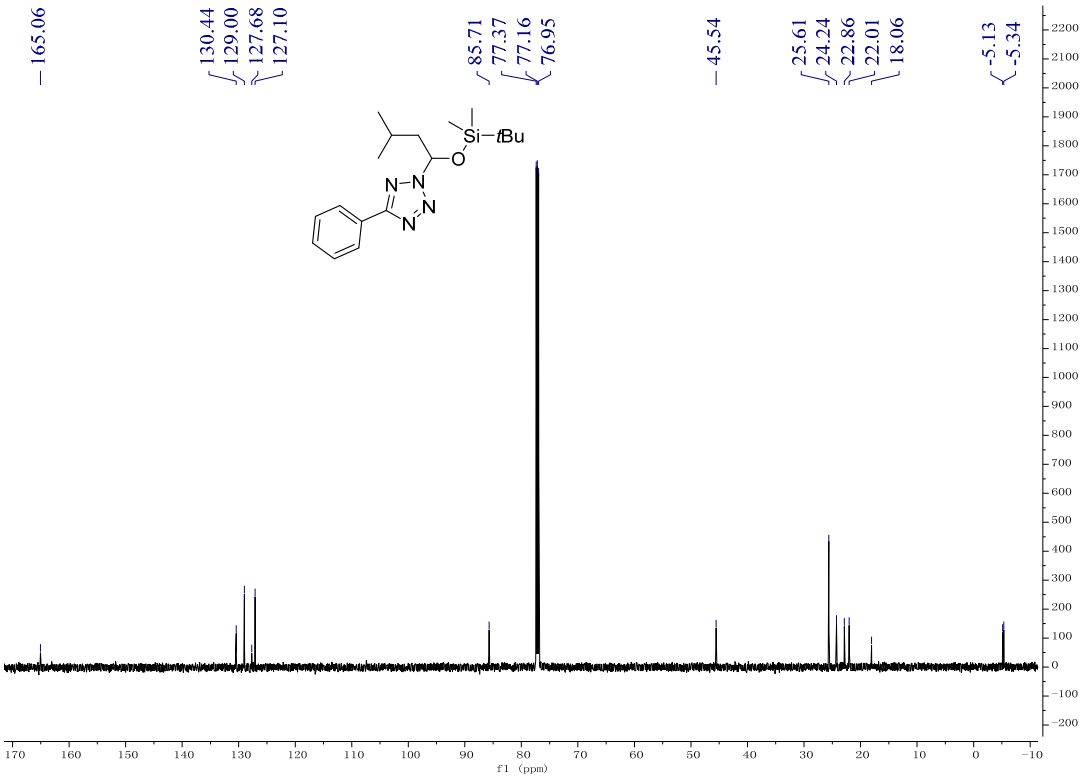
^{13}C-NMR of 4af



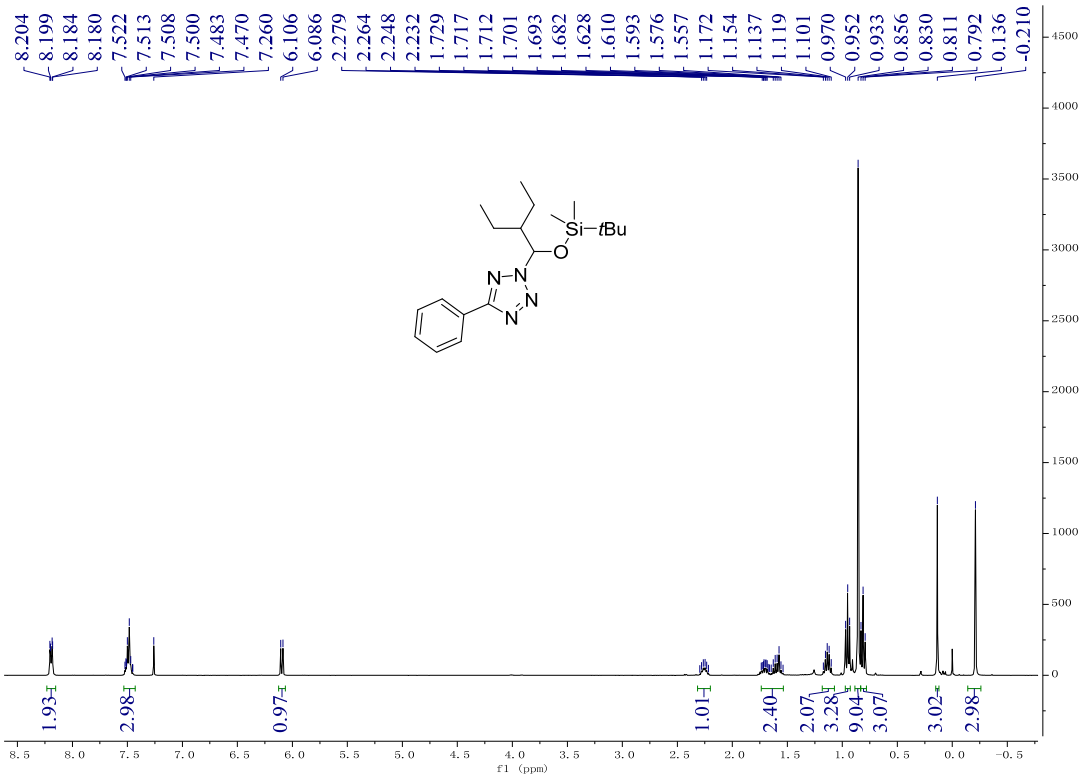
^{1}H-NMR of 4ag



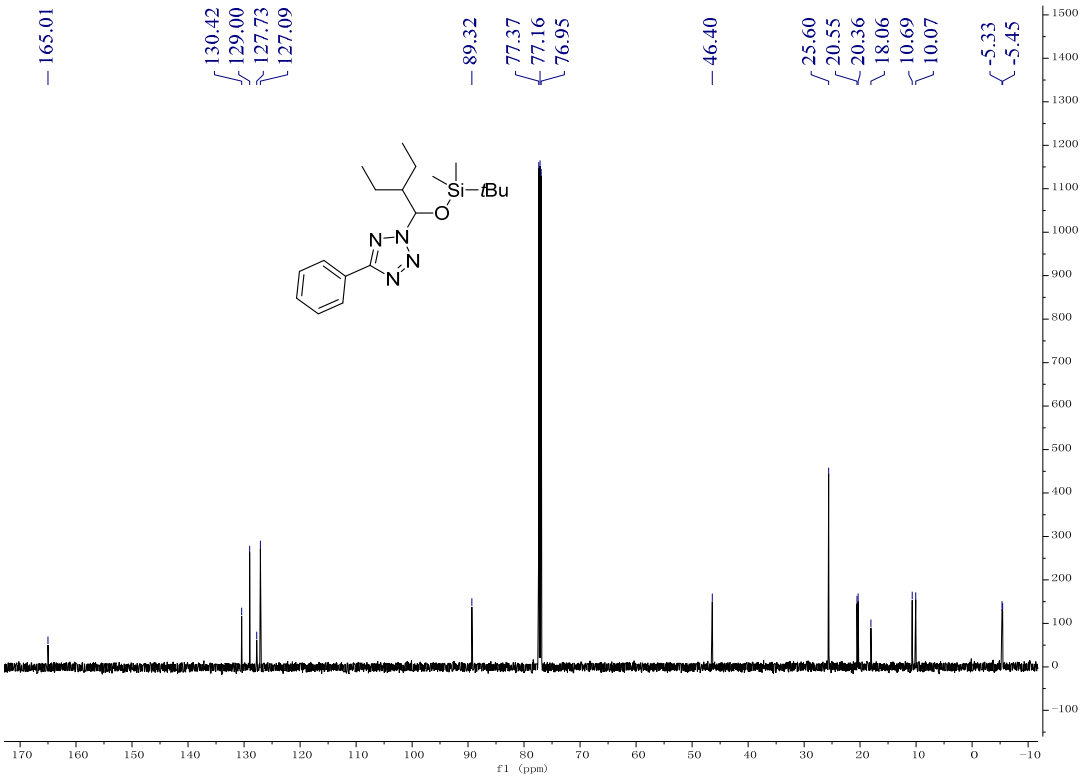
^{13}C-NMR of 4ag



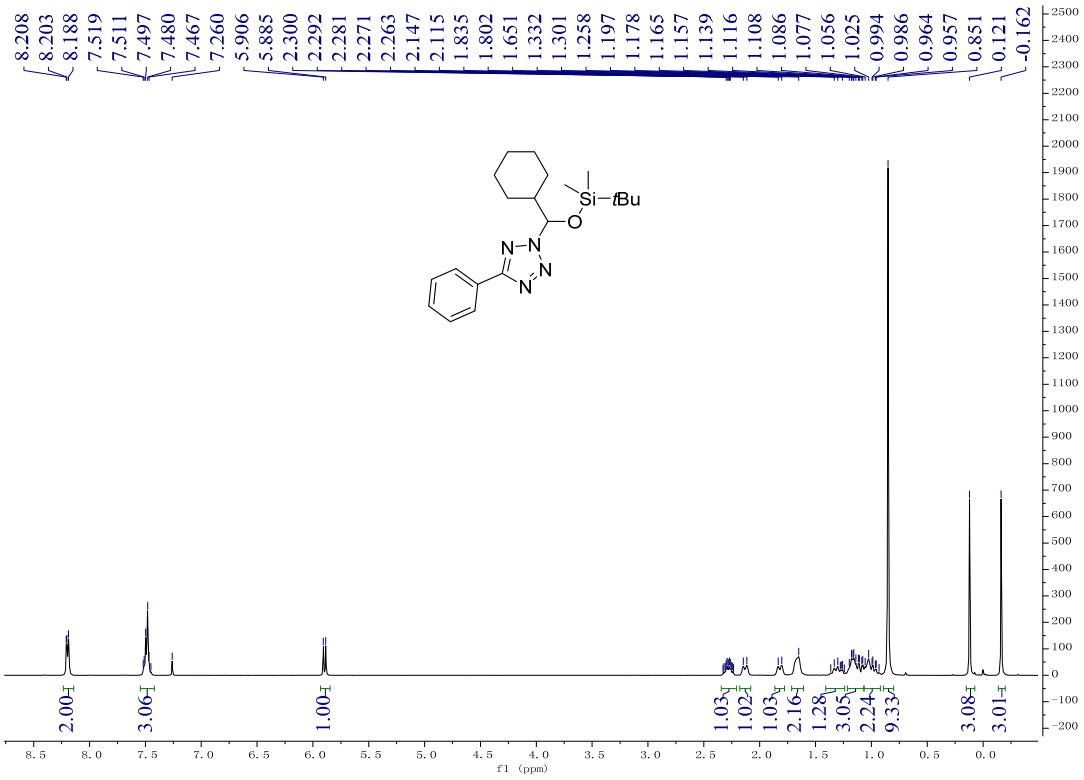
^{1}H-NMR of 4ah



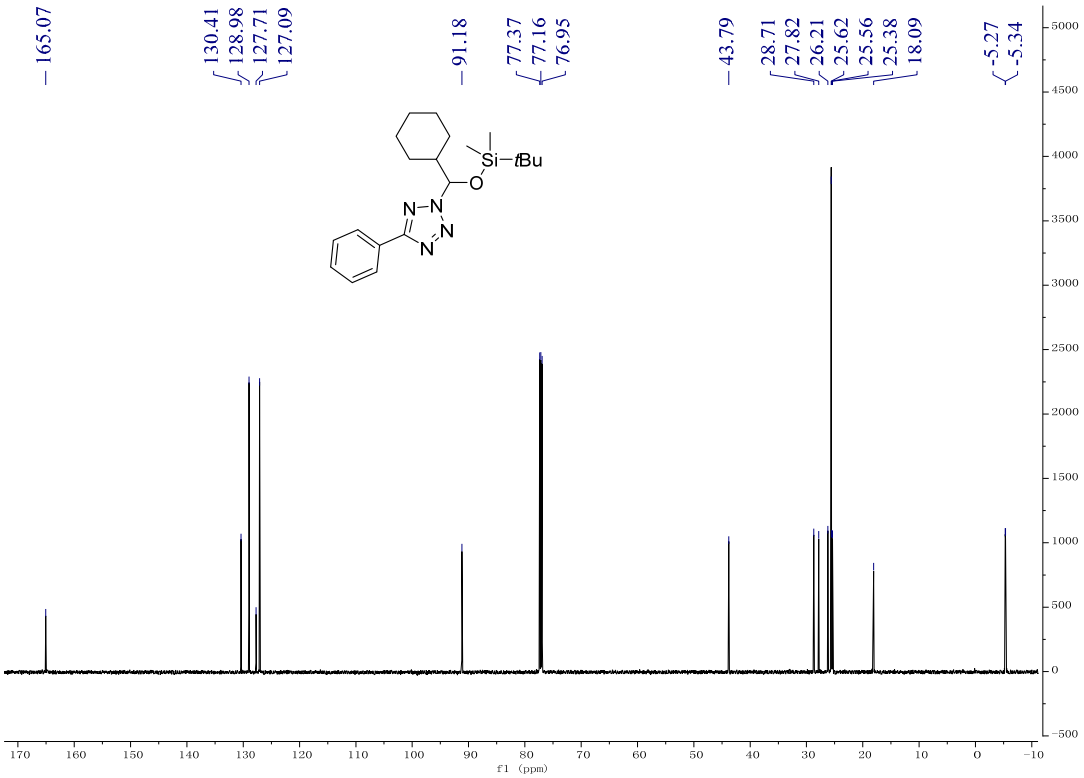
^{13}C-NMR of 4ah



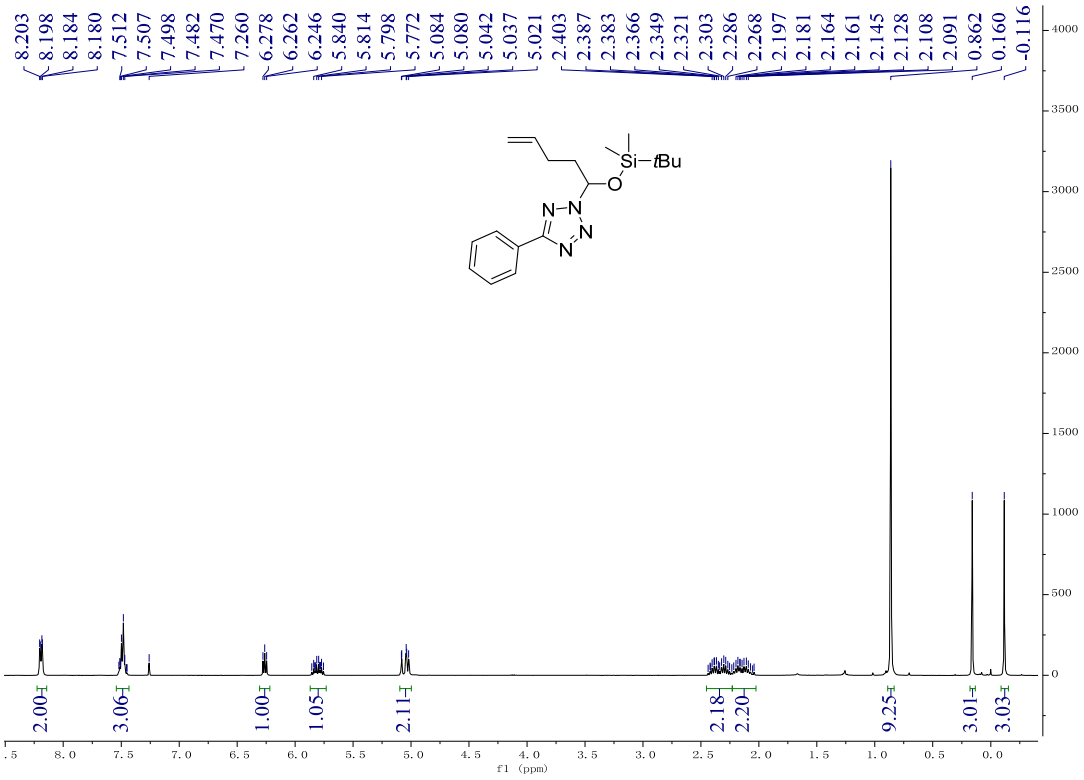
^{1}H-NMR of 4ai



^{13}C-NMR of 4ai



^{1}H-NMR of 4aj



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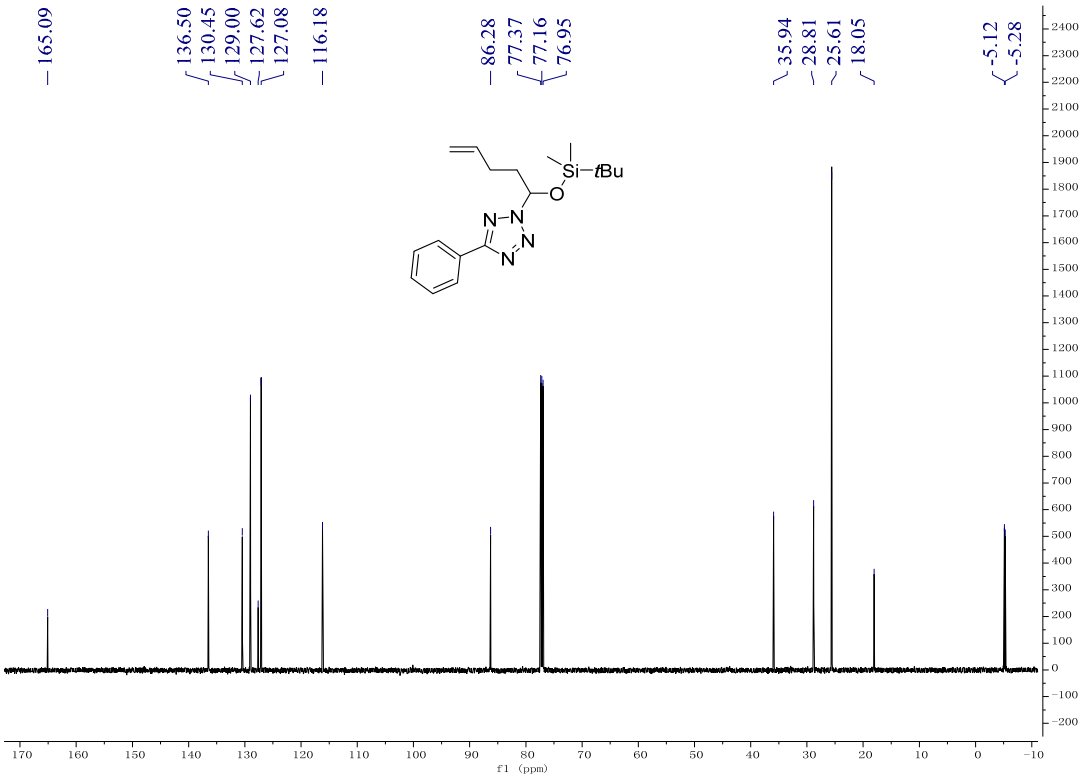
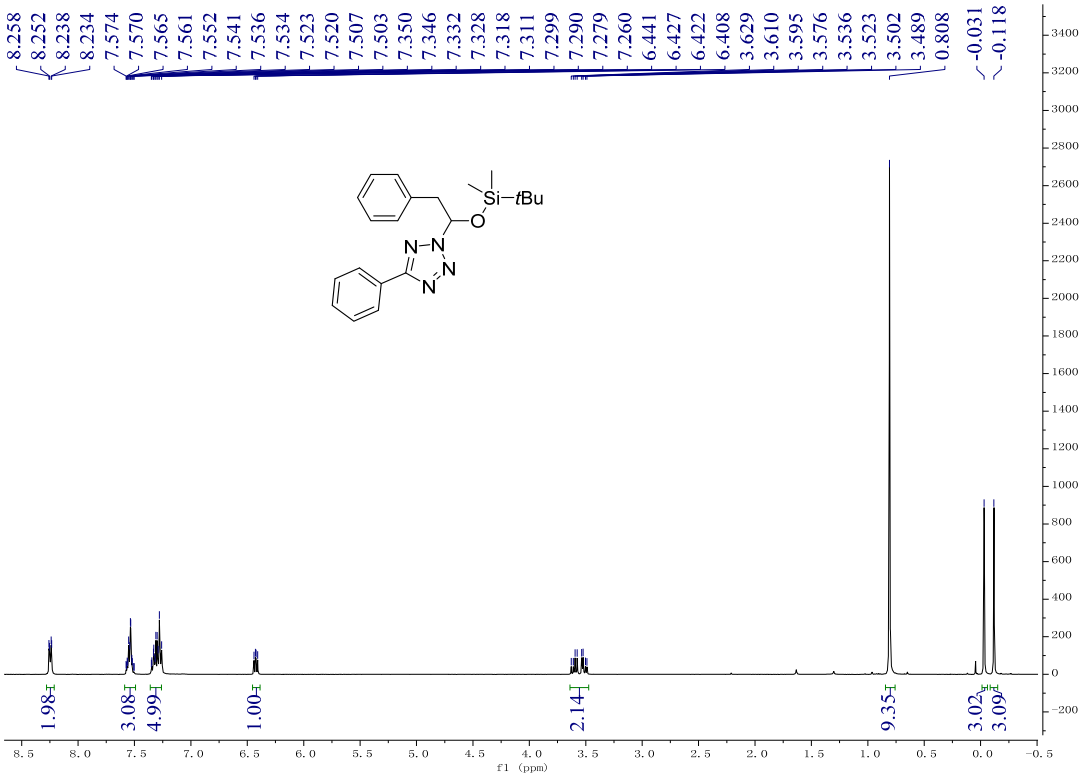
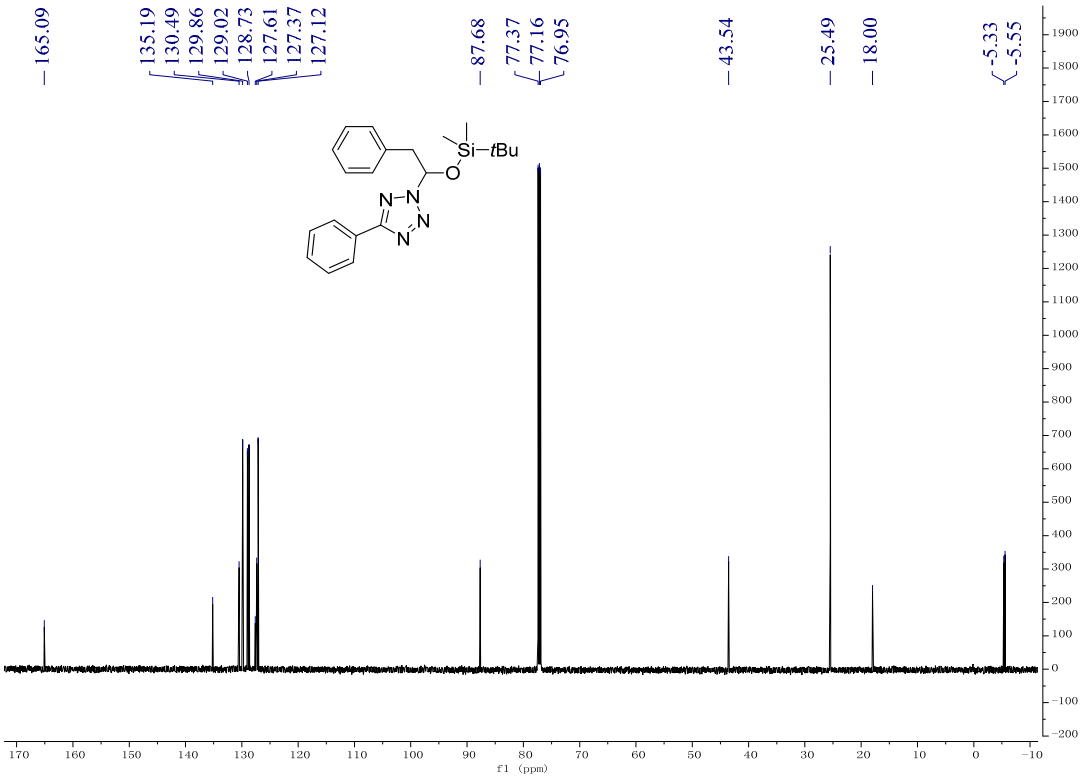


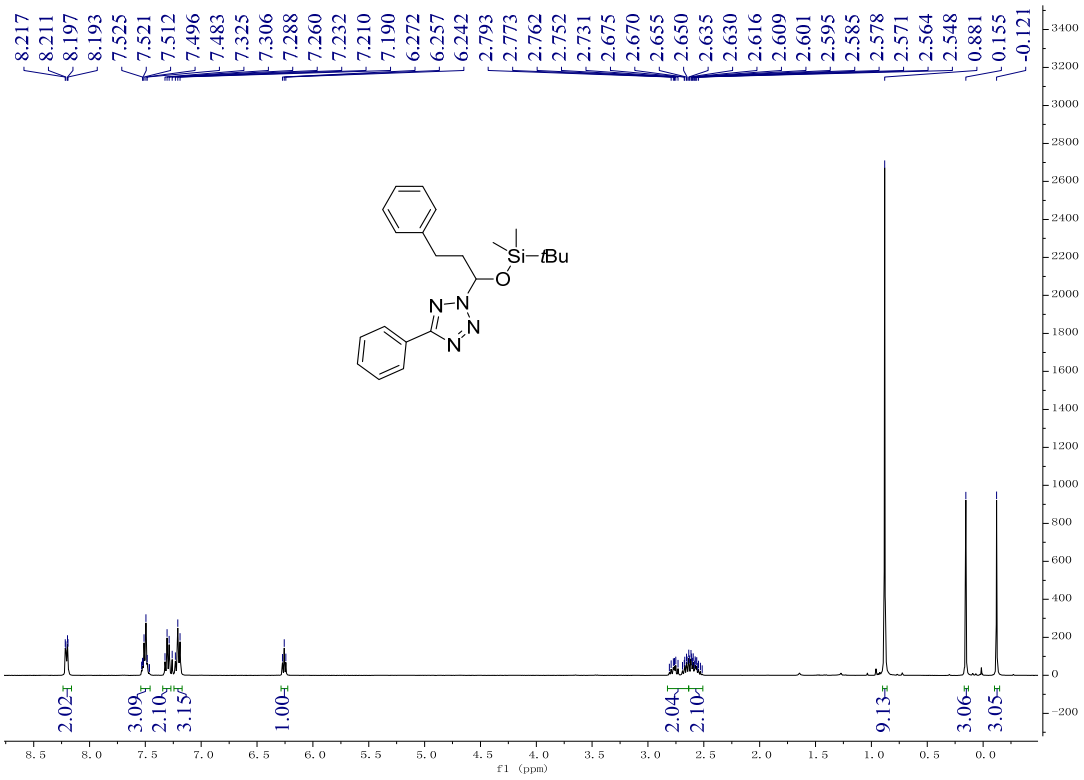
^{1}H-NMR of 4ak



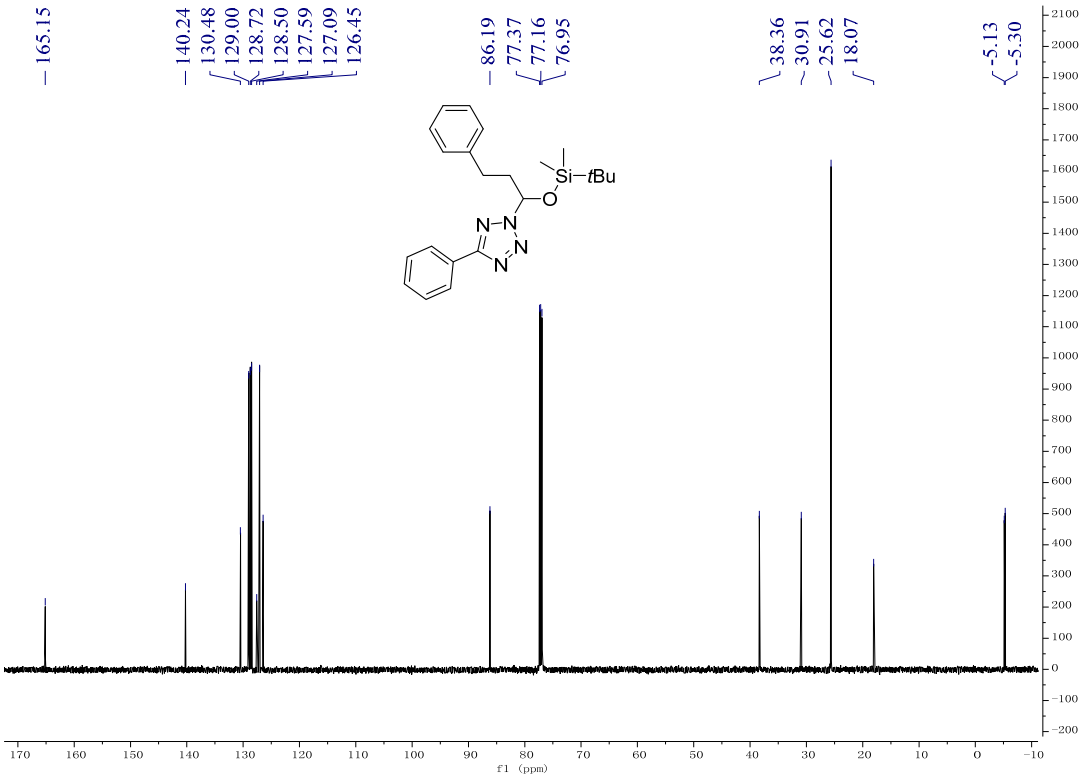
^{13}C-NMR of 4ak



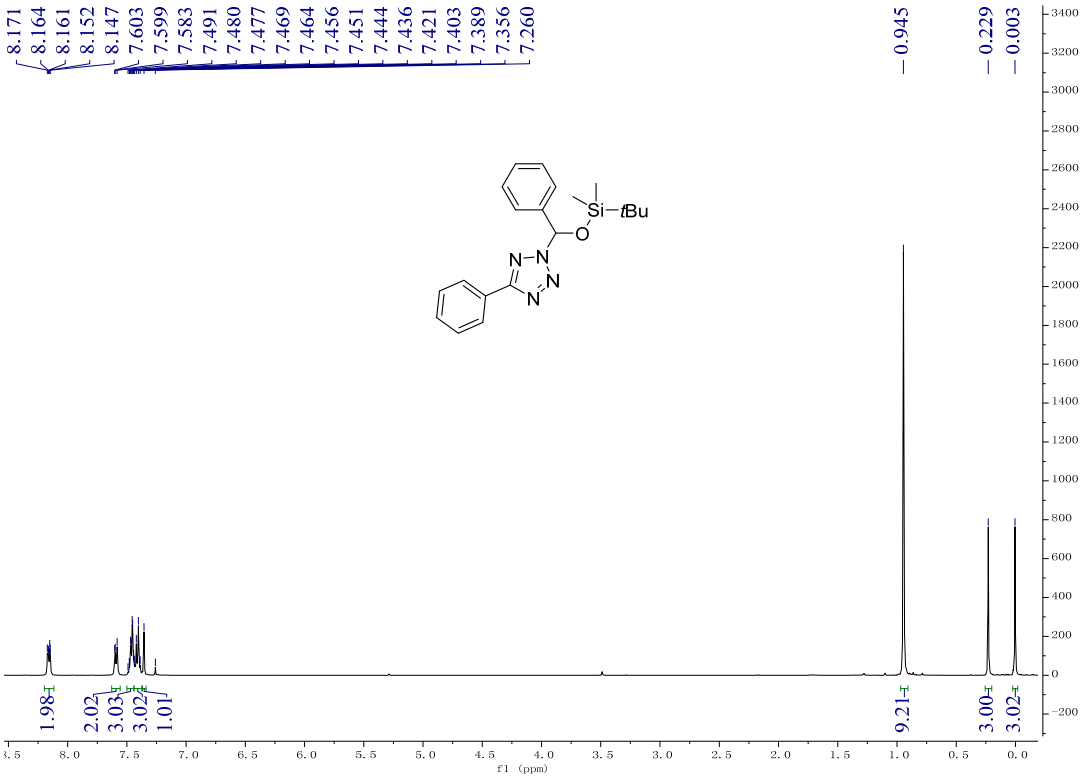
^{1}H-NMR of 4al



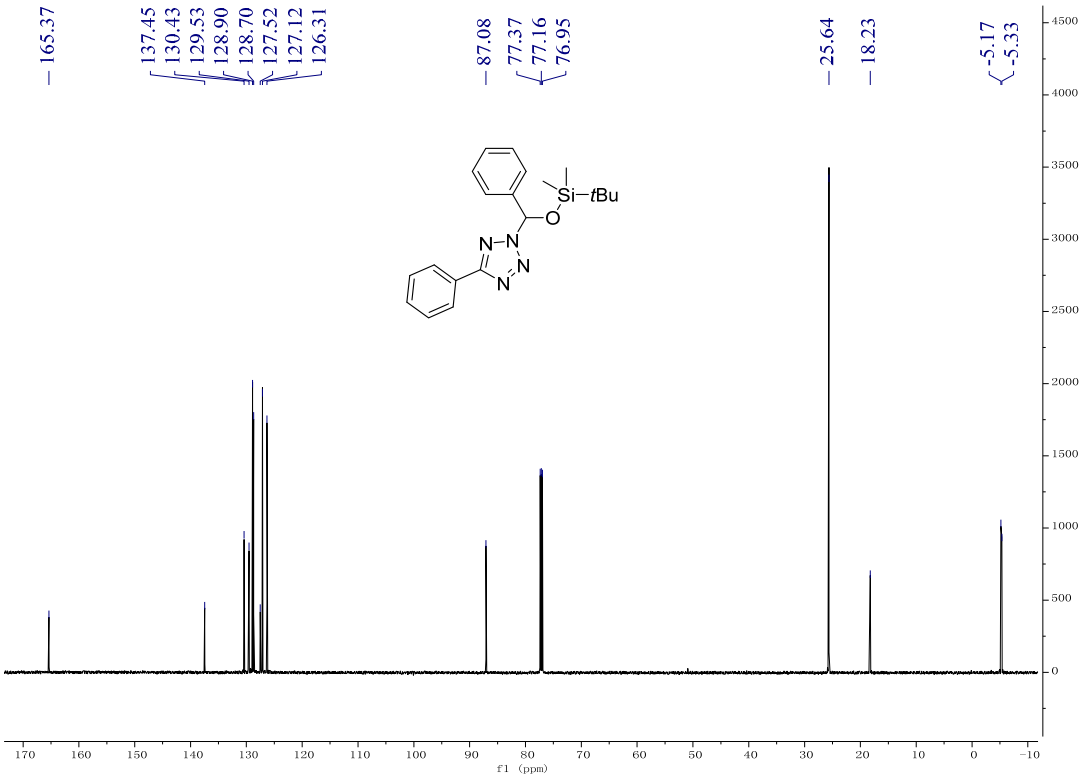
^{13}C-NMR of 4al



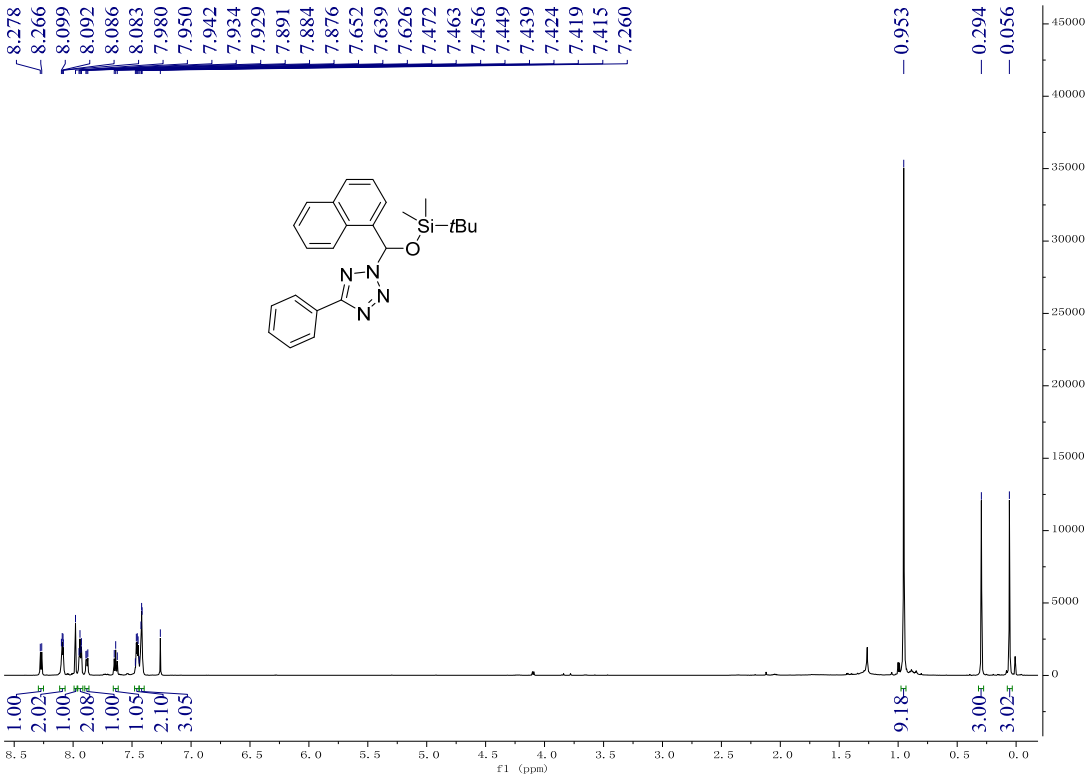
^{1}H-NMR of 4am



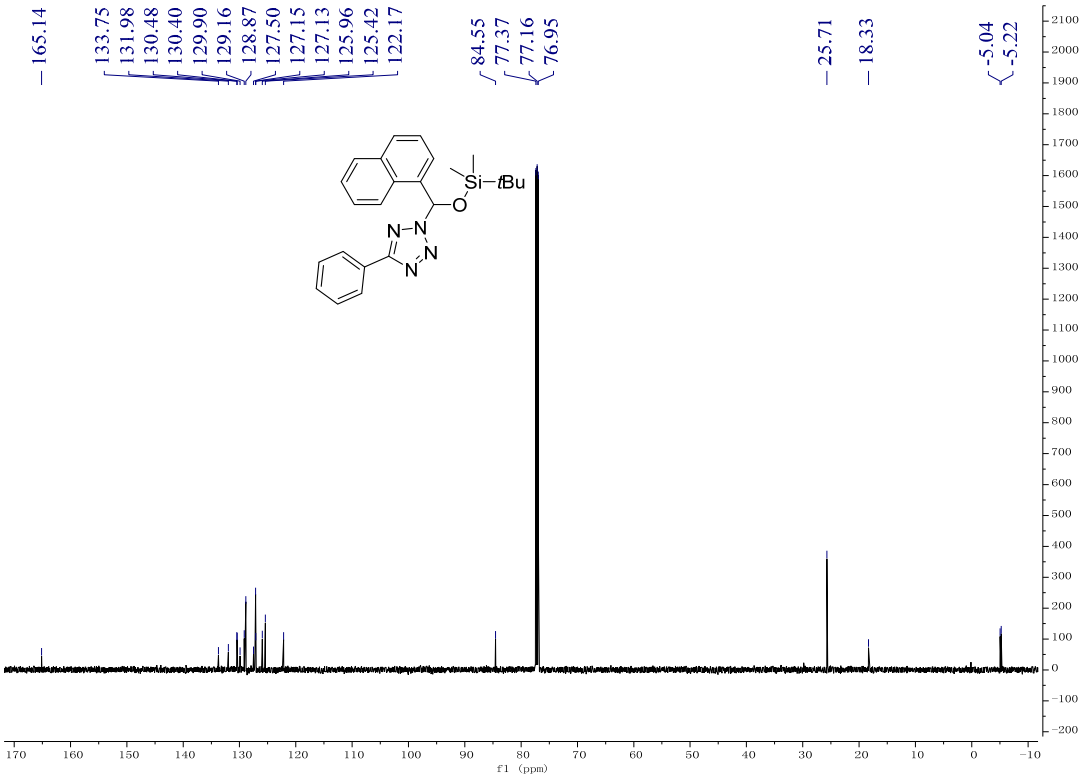
^{13}C-NMR of 4am



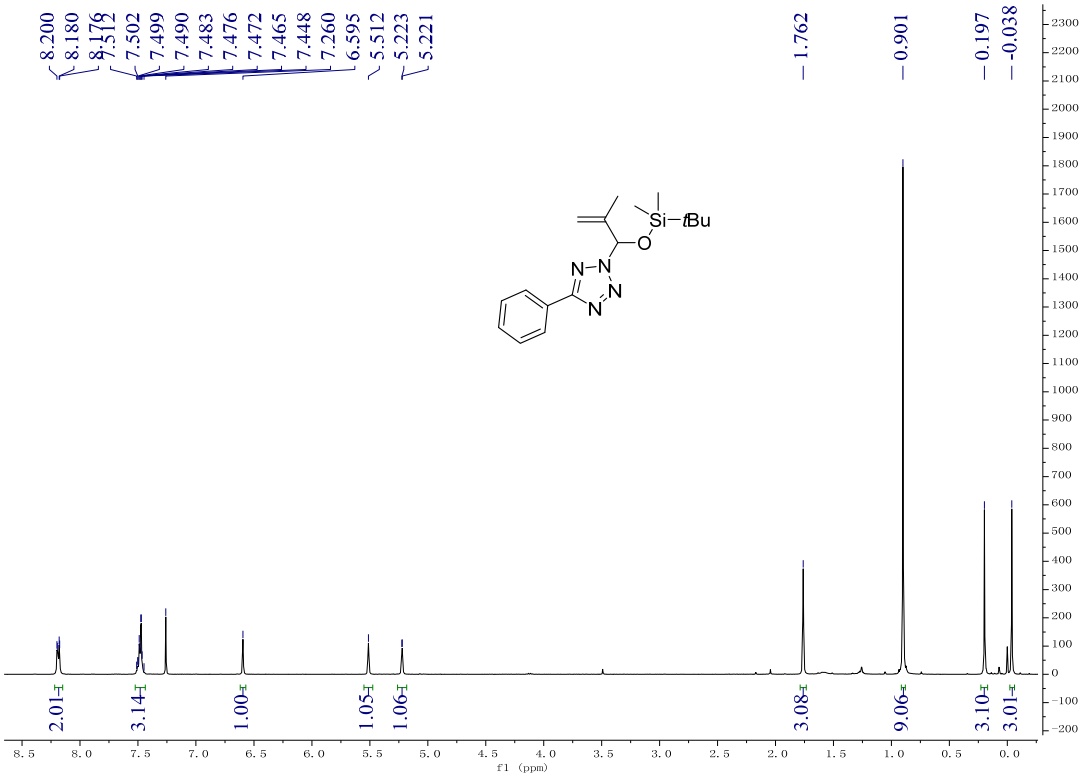
^{1}H-NMR of 4an



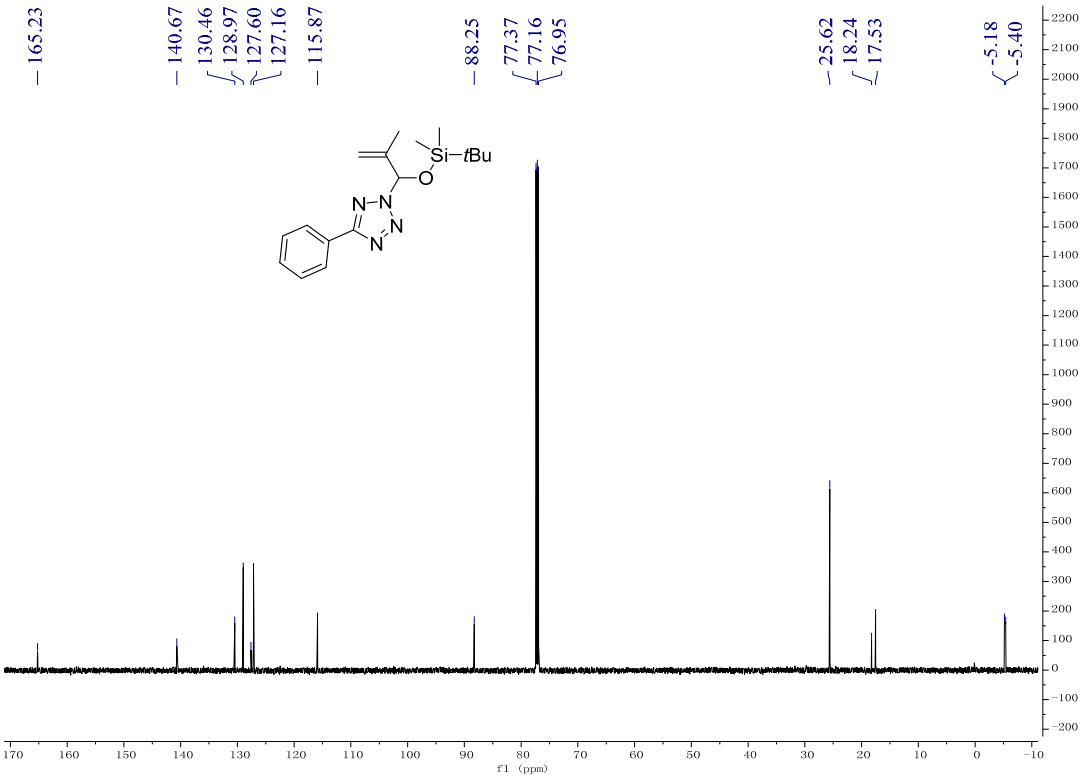
^{13}C-NMR of 4an



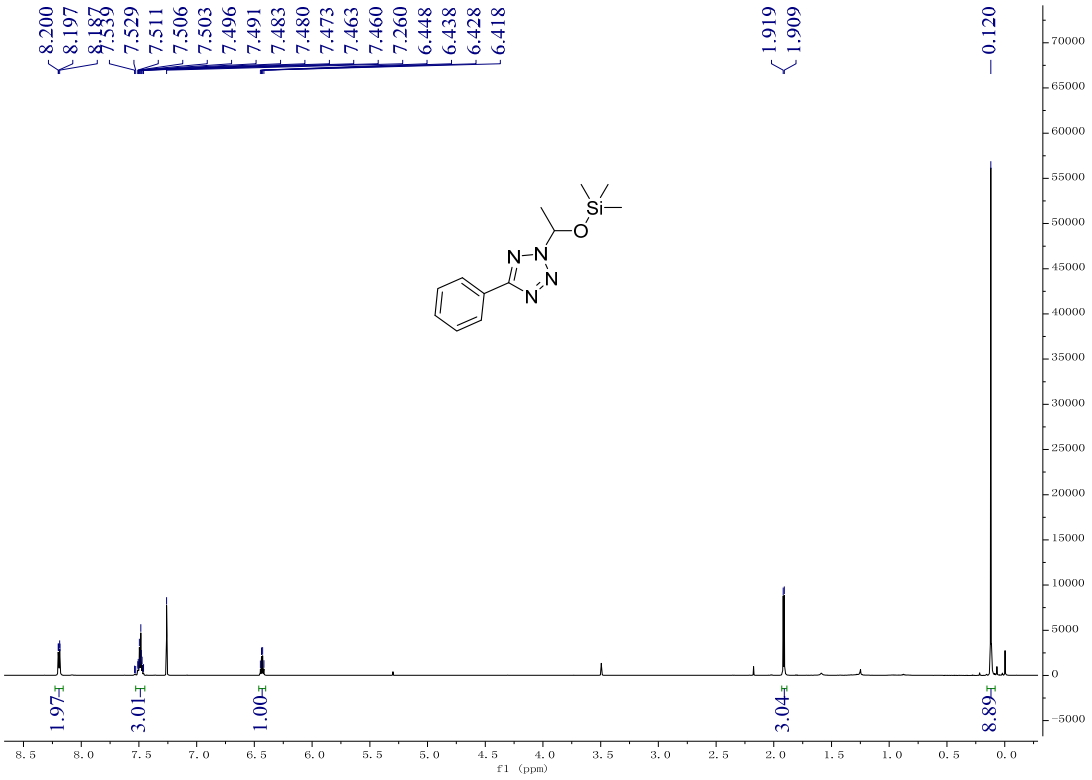
^{1}H-NMR of 4ao



^{13}C-NMR of 4ao



^{1}H-NMR of 4ap



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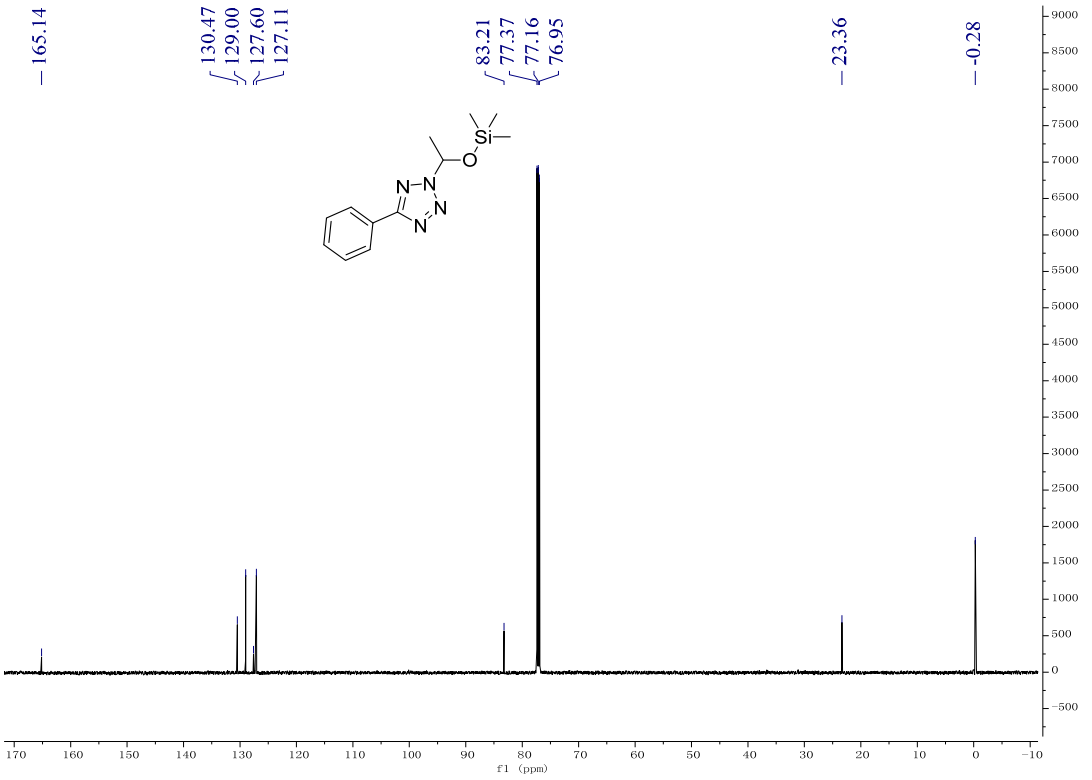
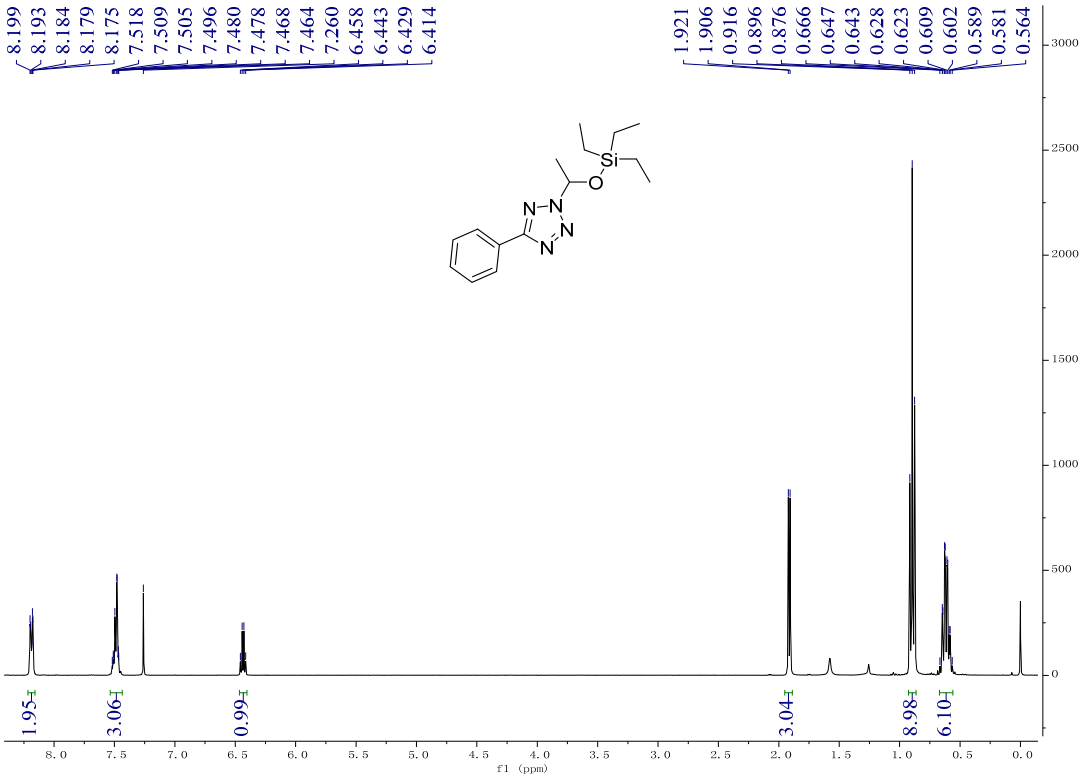
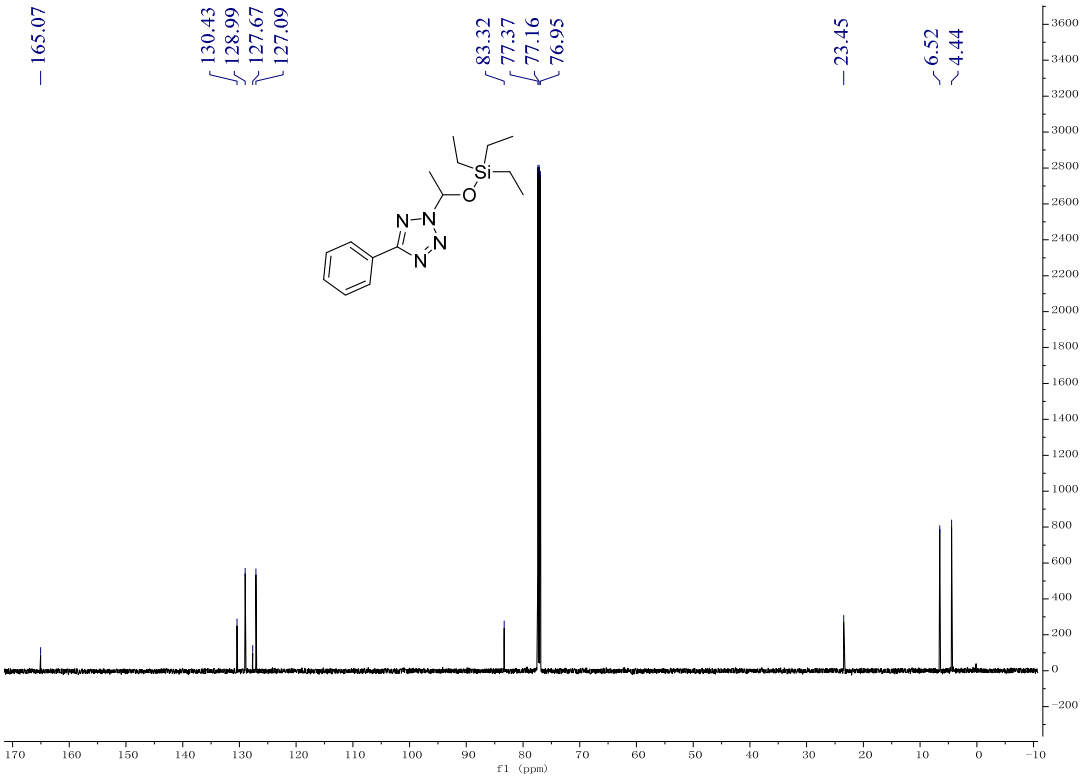


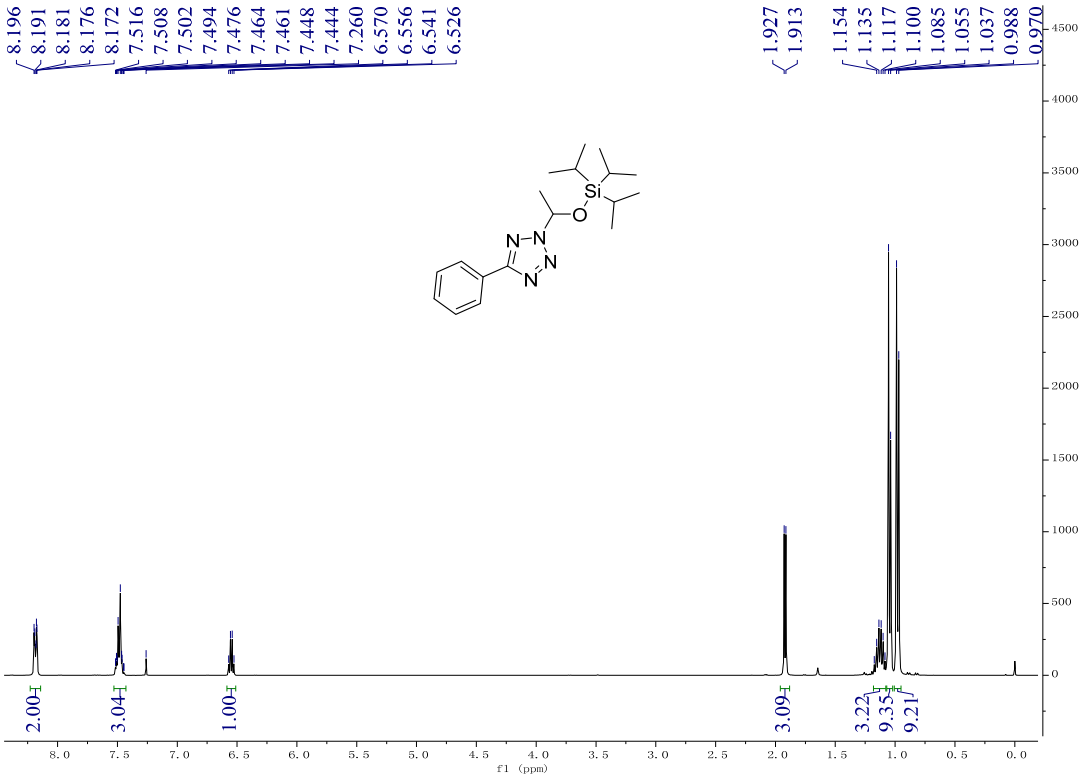
^{1}H-NMR of 4aq



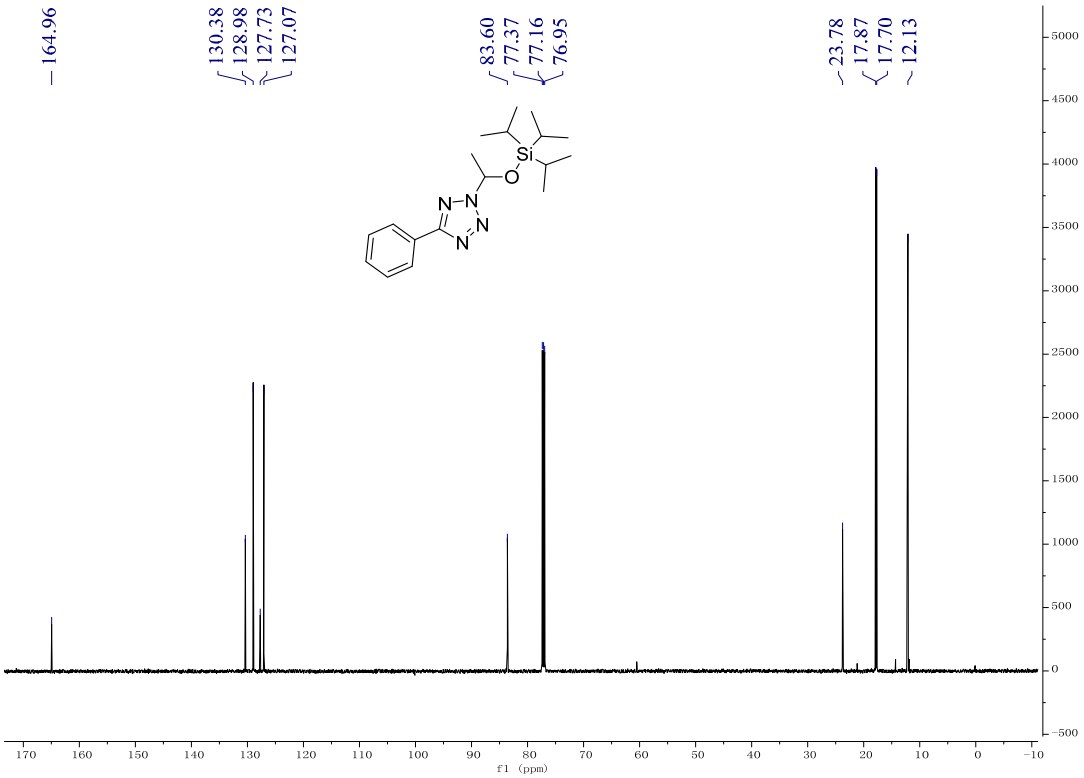
^{13}C-NMR of 4aq



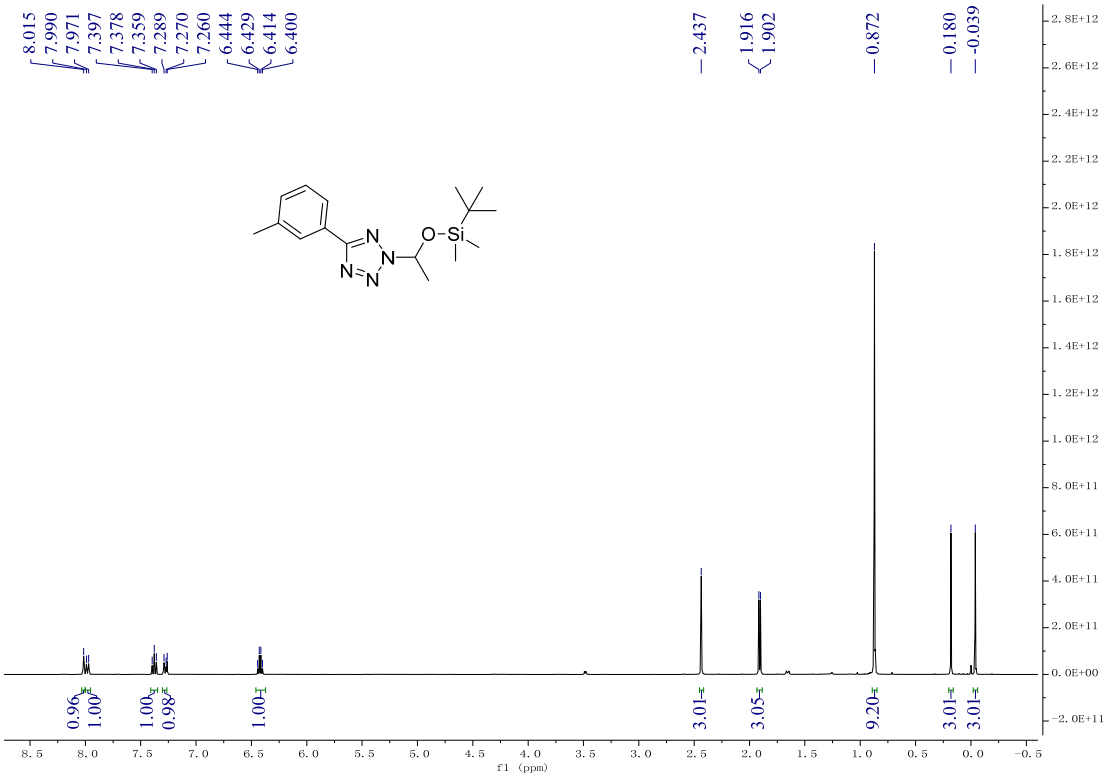
^{1}H-NMR of 4ar



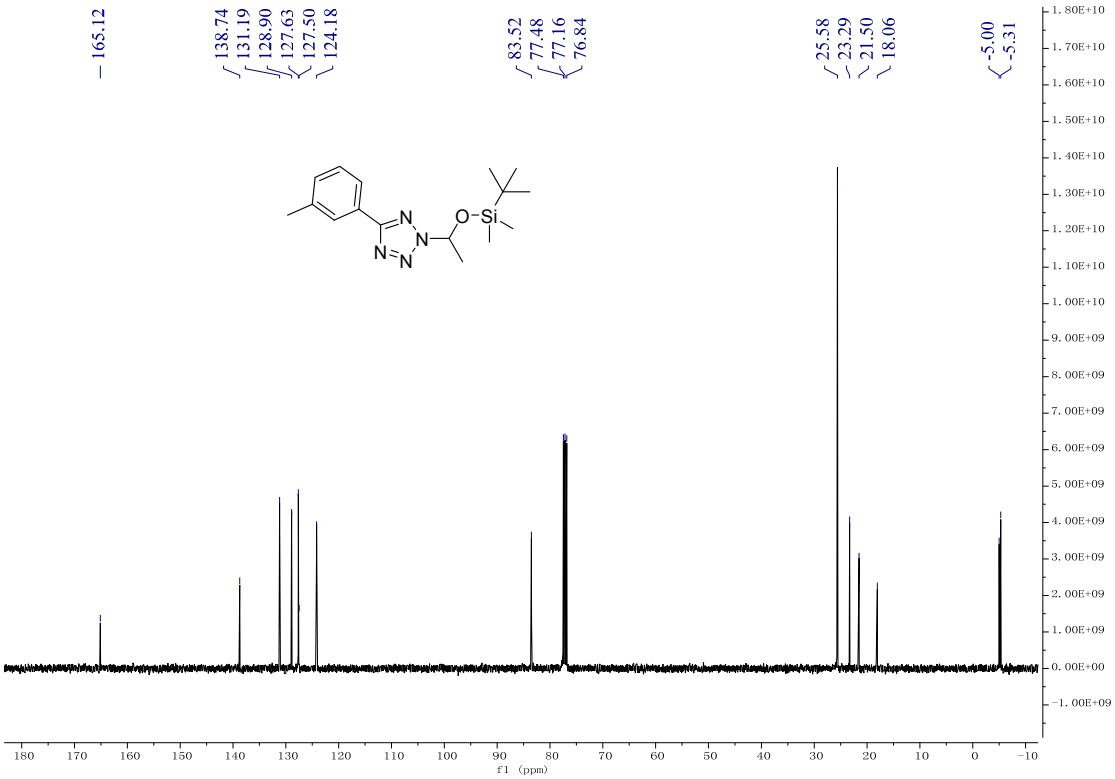
^{13}C-NMR of 4ar



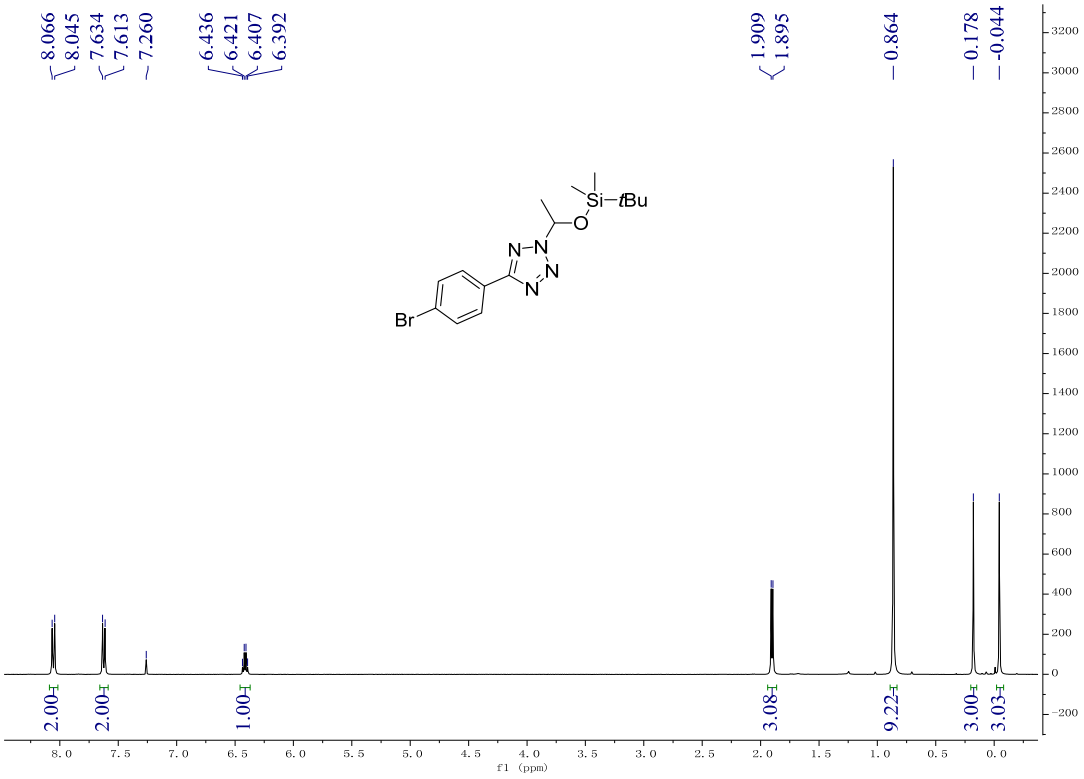
^{1}H-NMR of 4ba



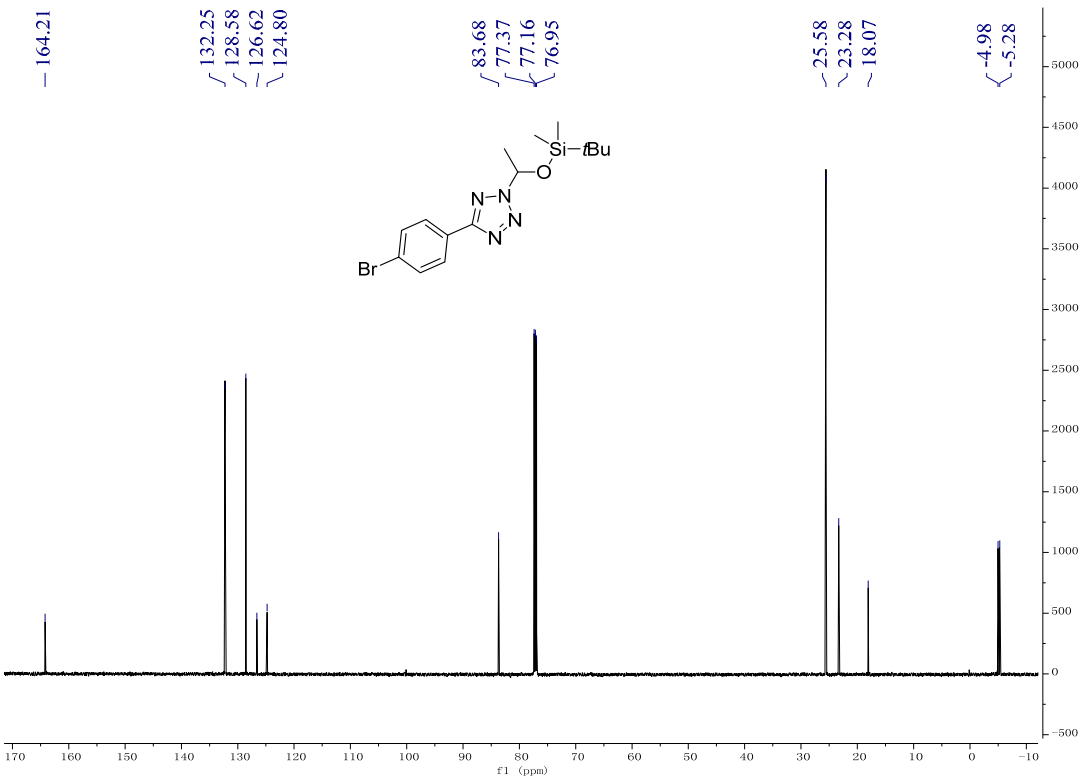
^{13}C-NMR of 4ba



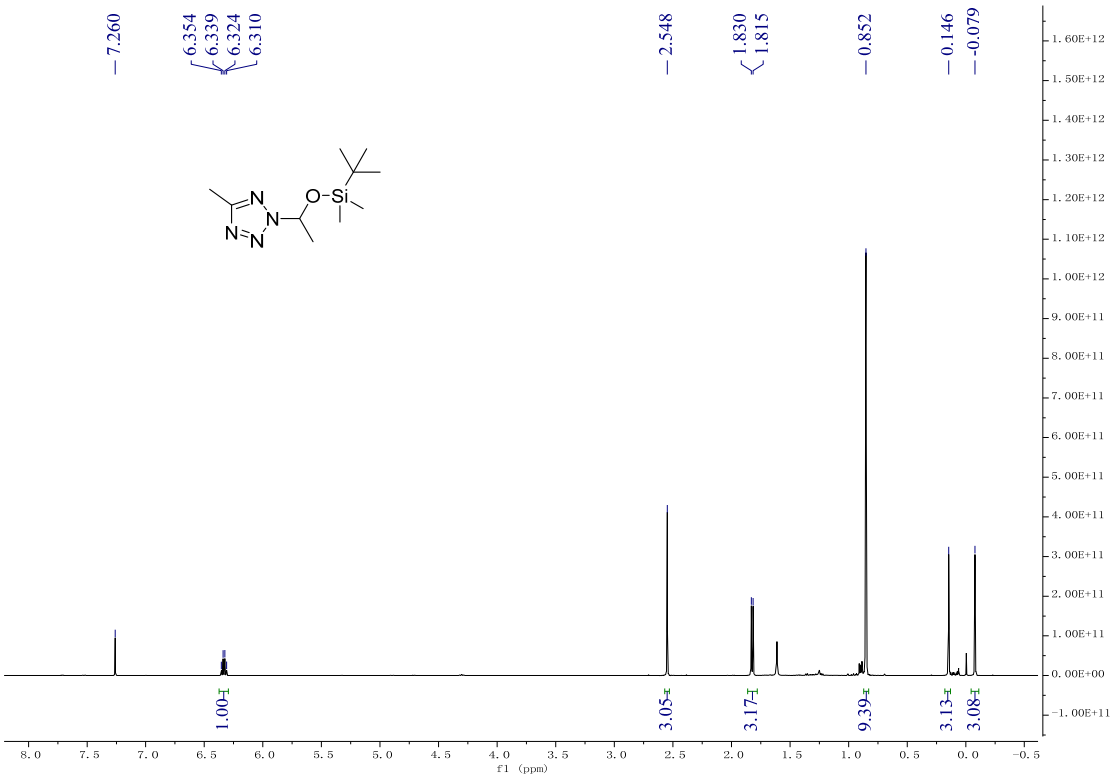
^{1}H-NMR of 4ca



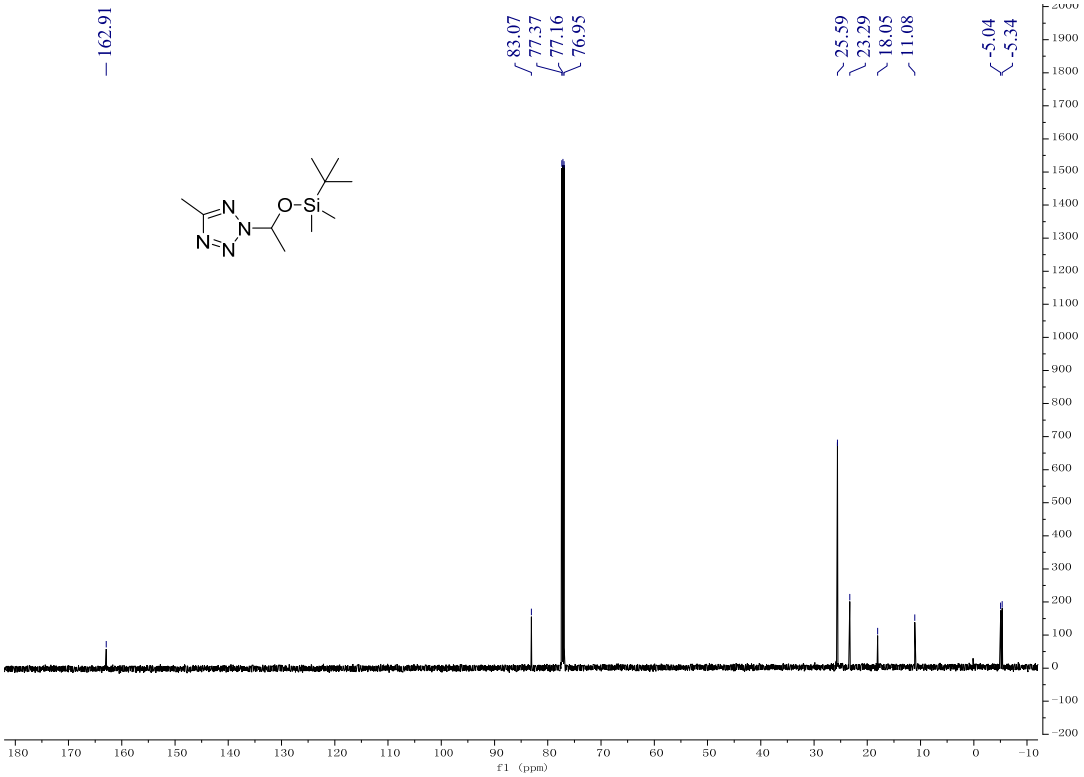
^{13}C-NMR of 4ca



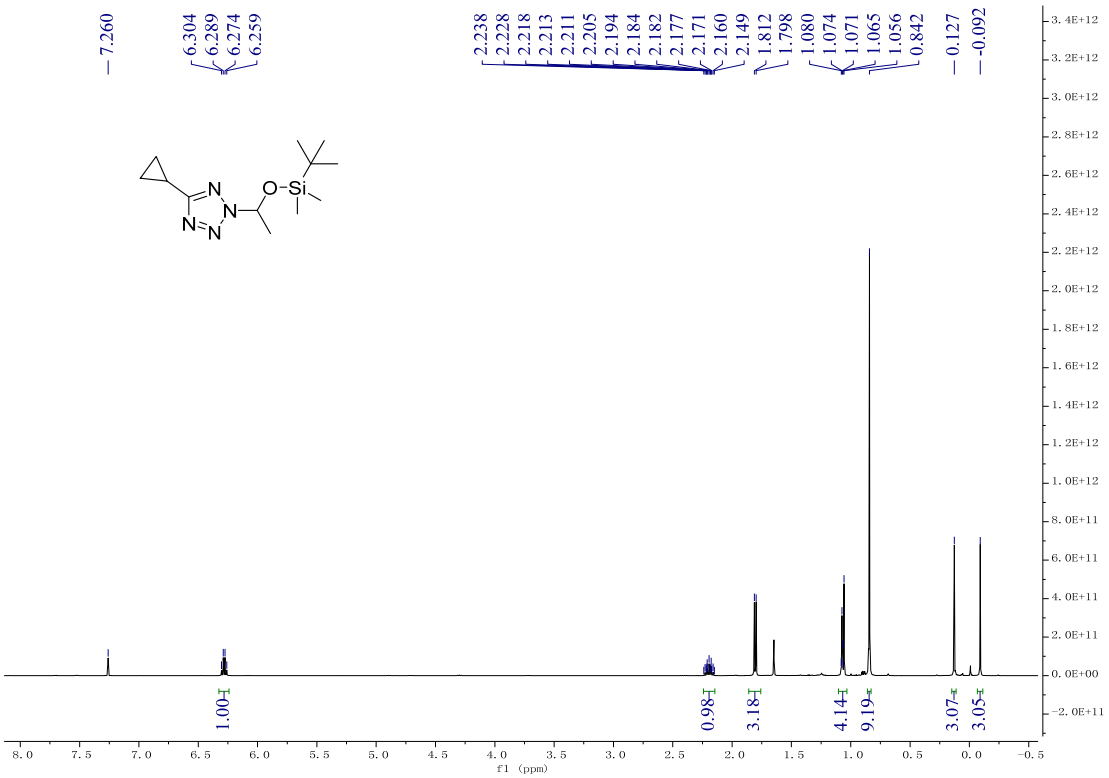
^{1}H-NMR of 4da



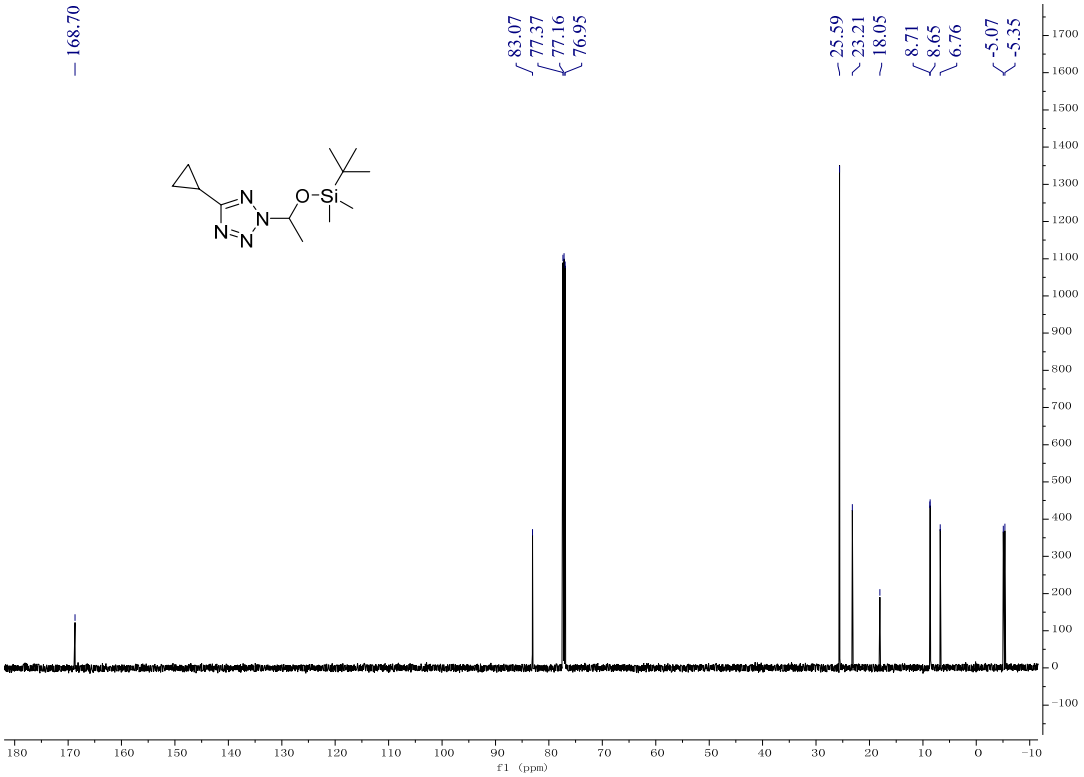
^{13}C-NMR of 4da



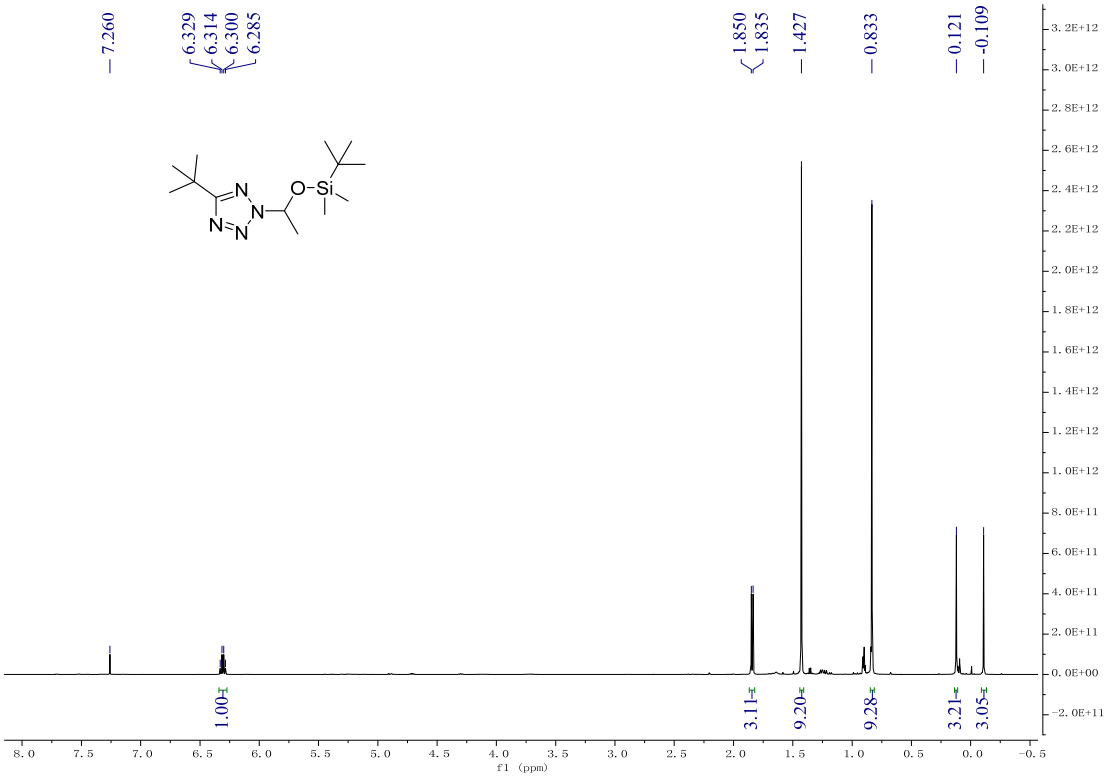
^{1}H-NMR of 4ea



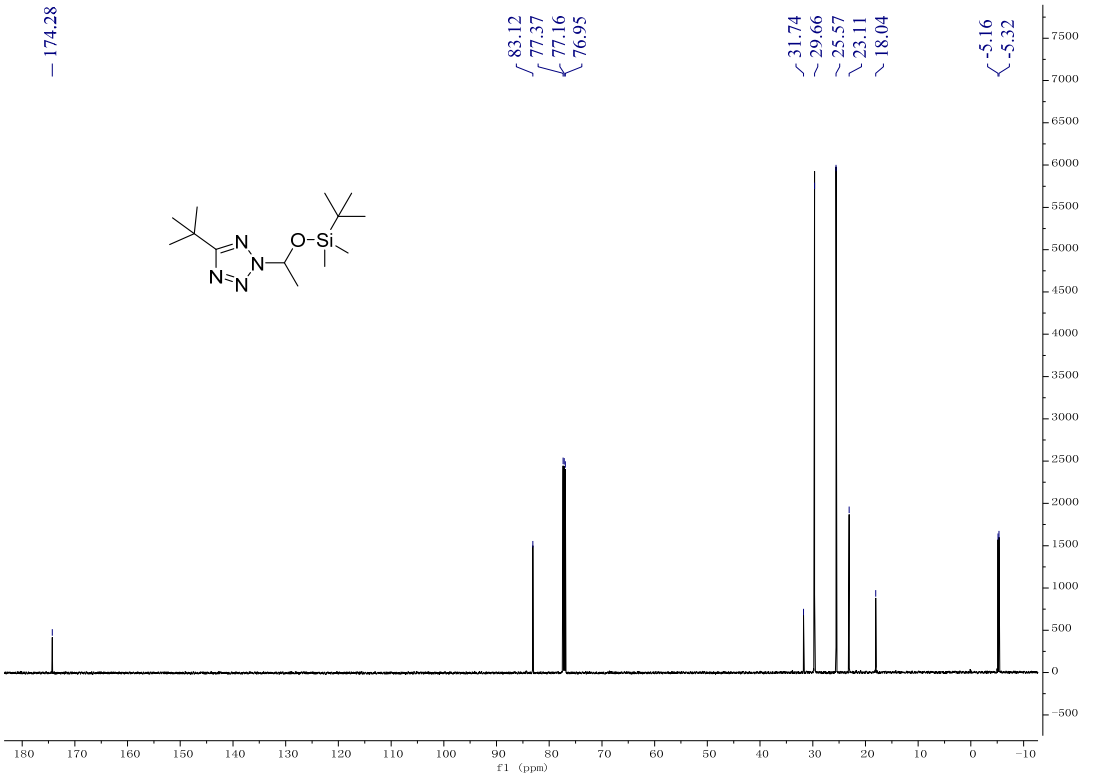
^{13}C-NMR of 4ea



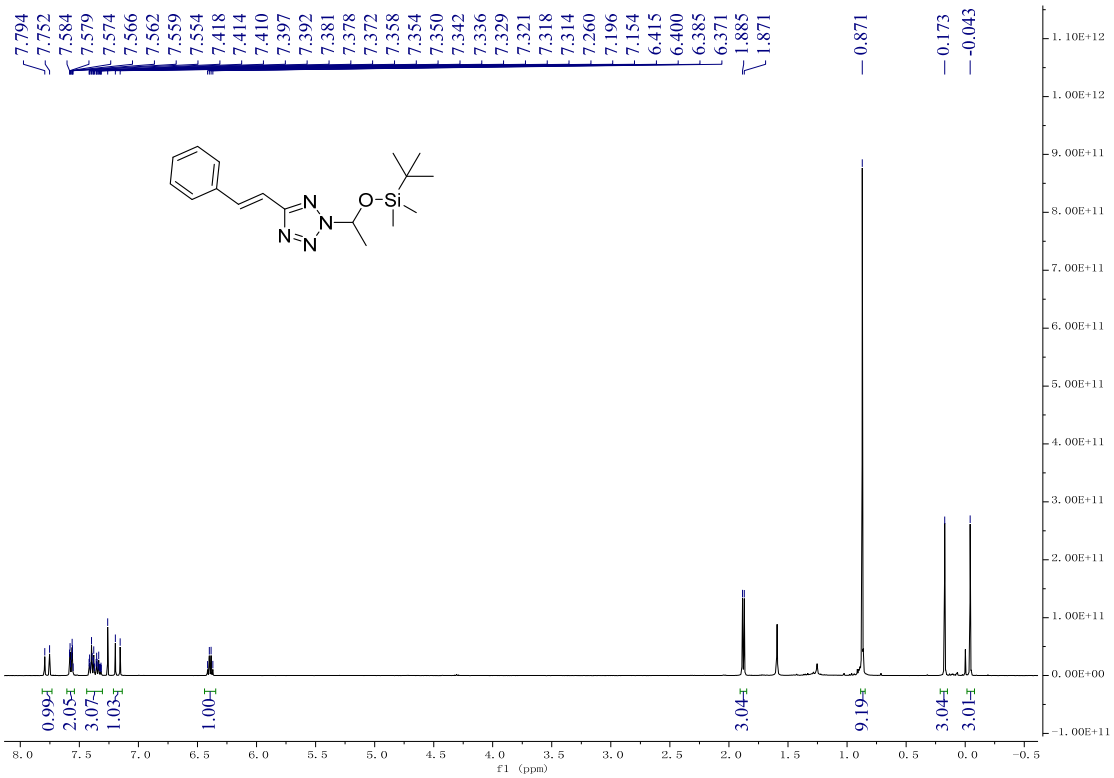
^{1}H-NMR of 4fa



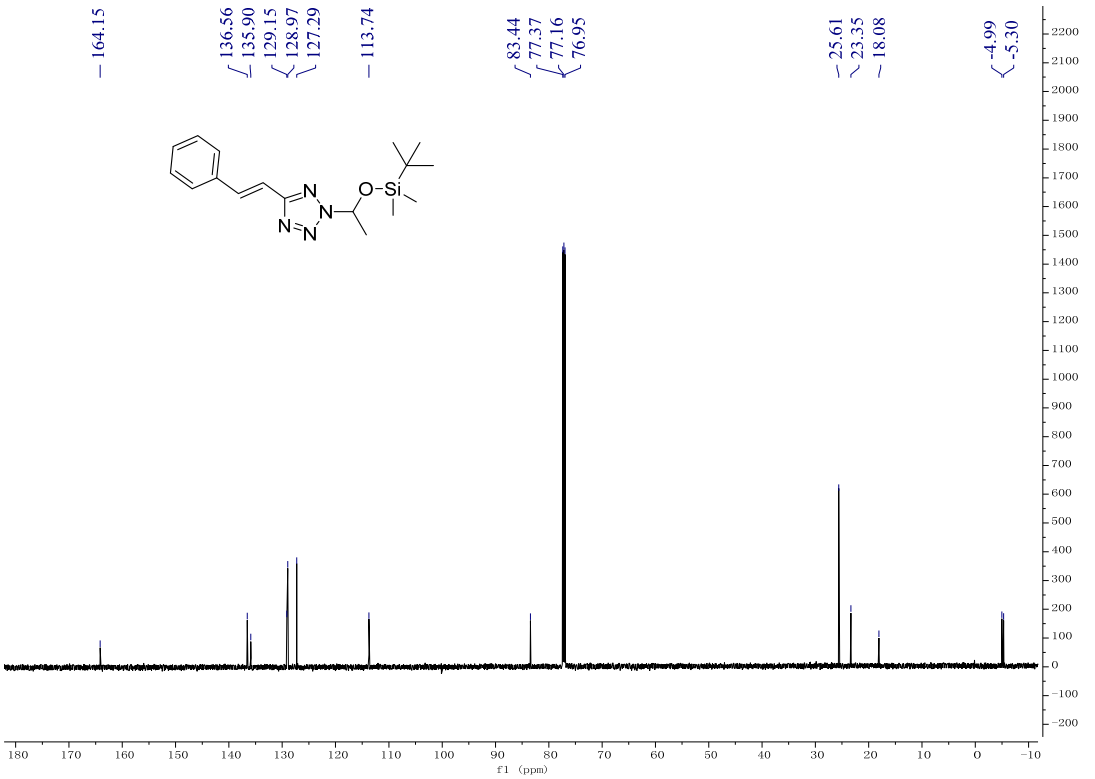
^{13}C-NMR of 4fa



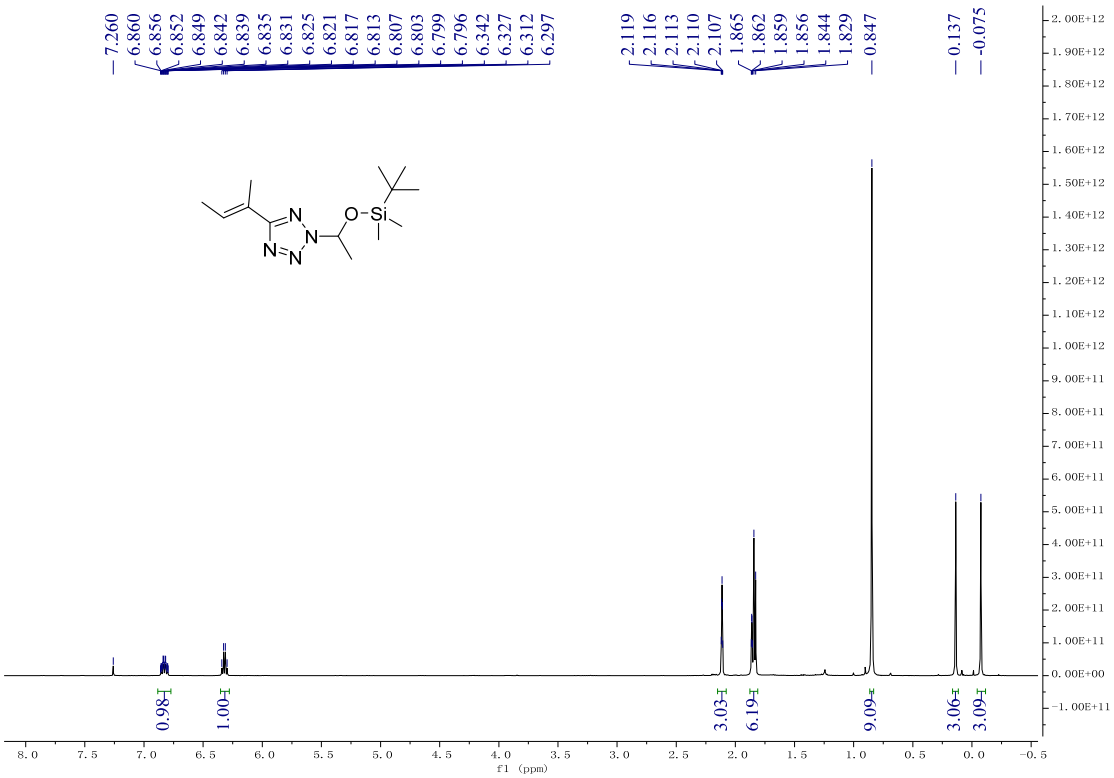
^{1}H-NMR of 4ga



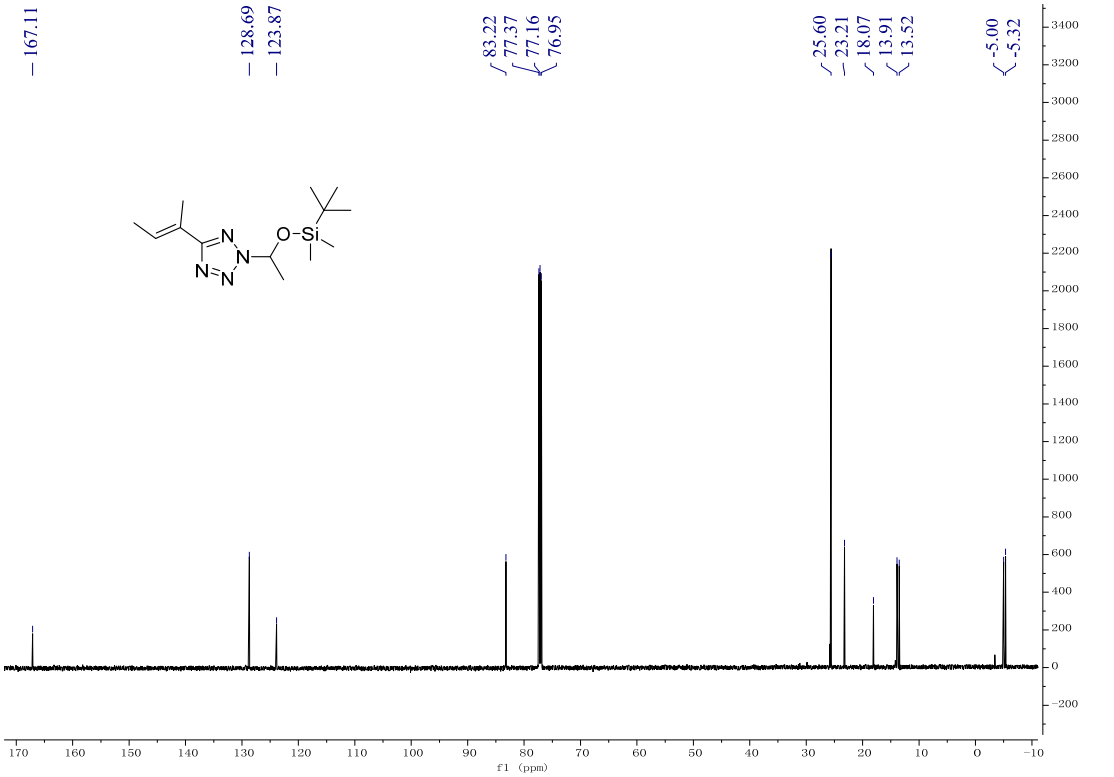
^{13}C-NMR of 4ga



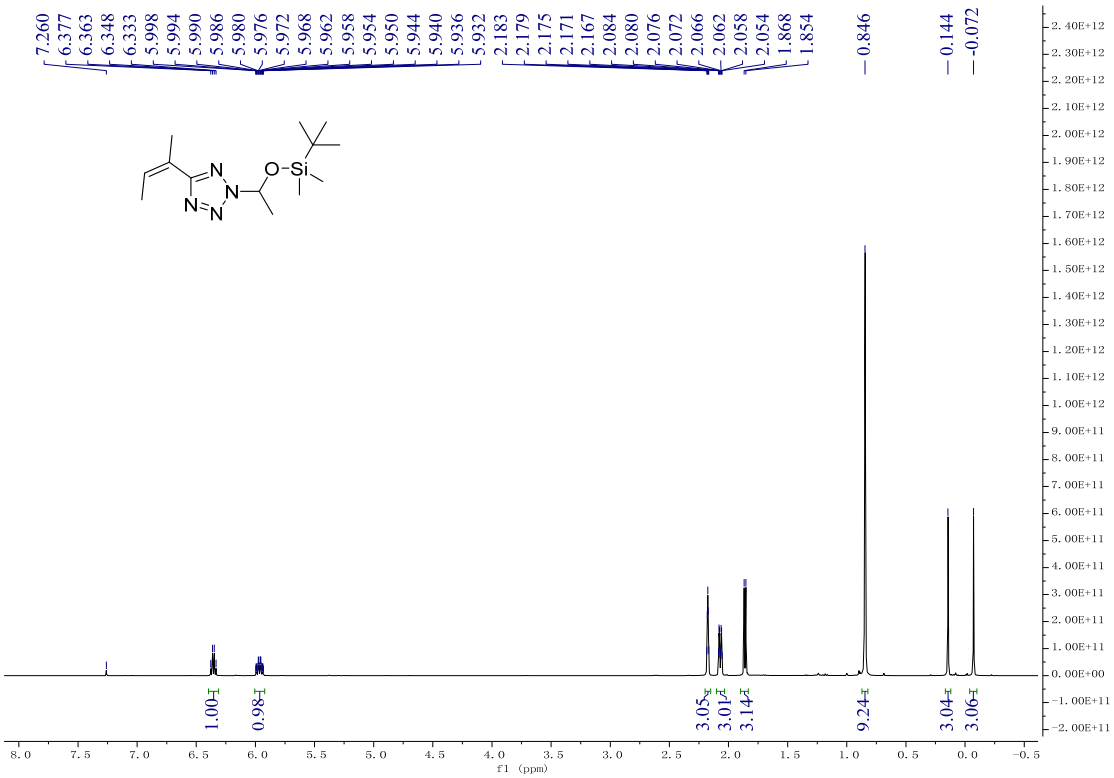
^{1}H-NMR of 4ha



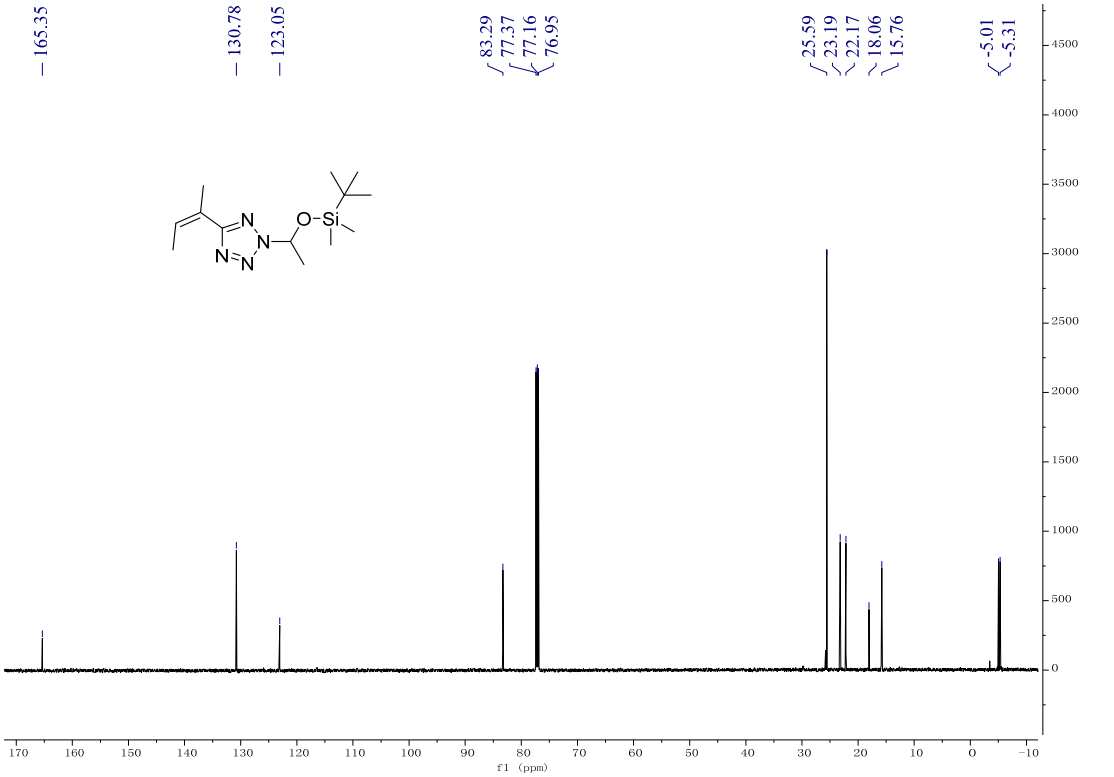
^{13}C-NMR of 4ha



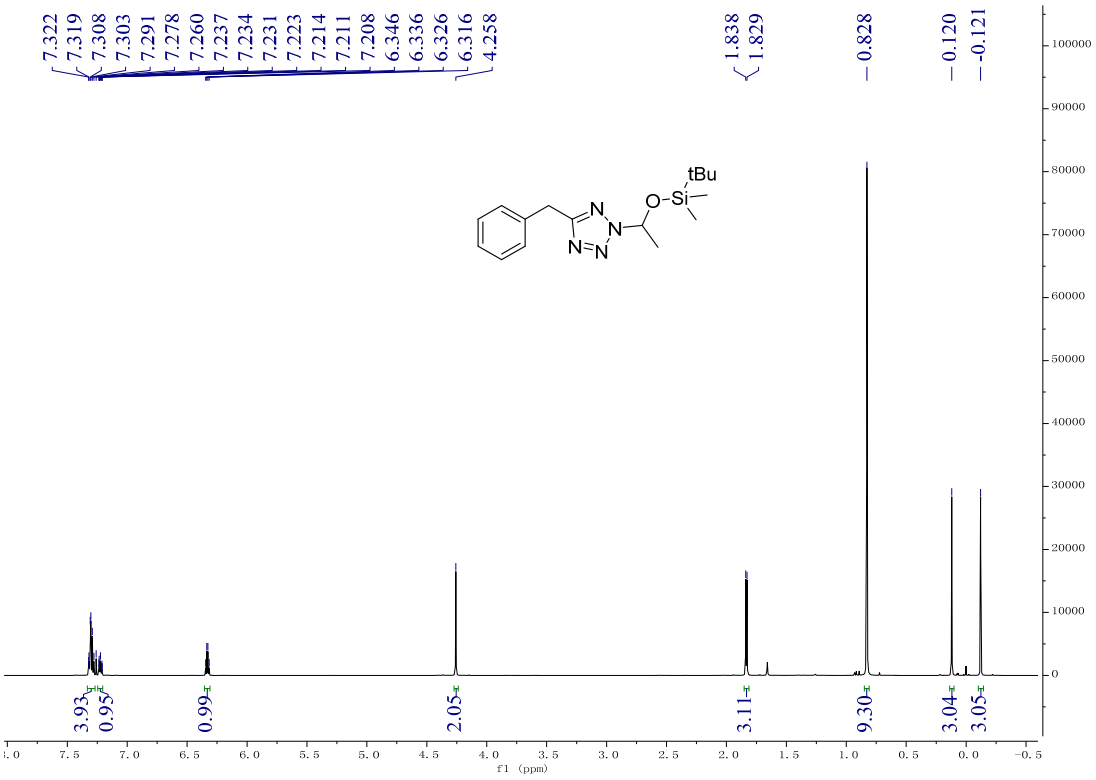
^{1}H-NMR of 4ia



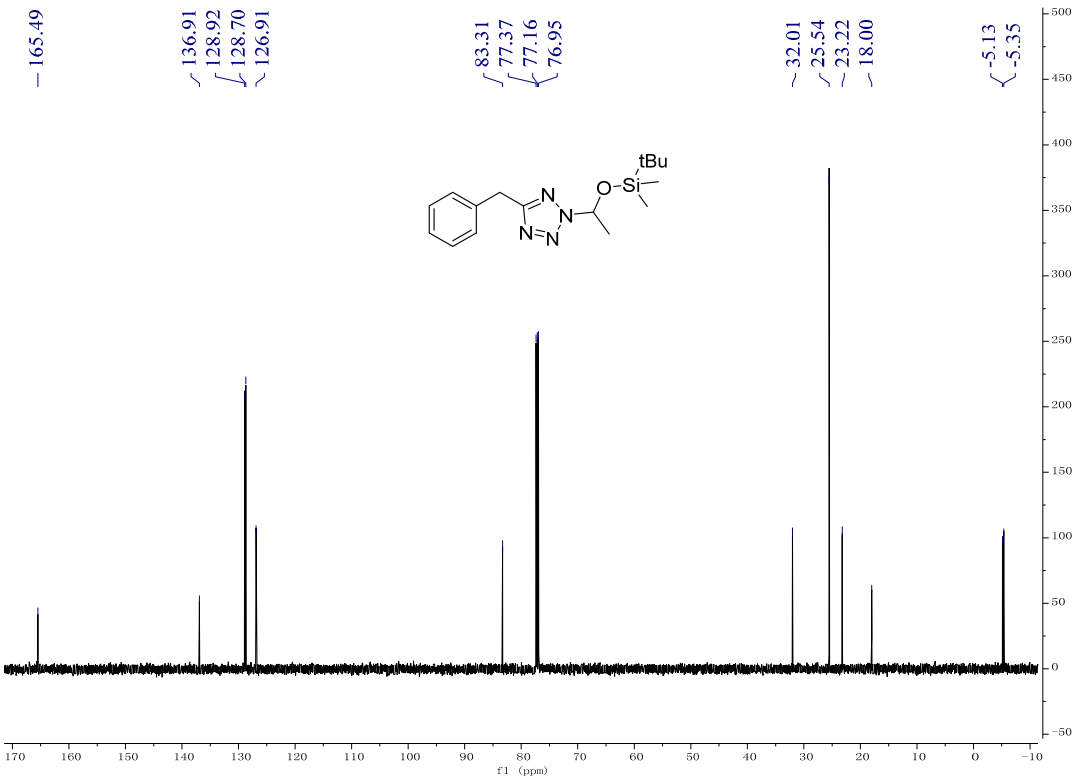
^{13}C-NMR of 4ia



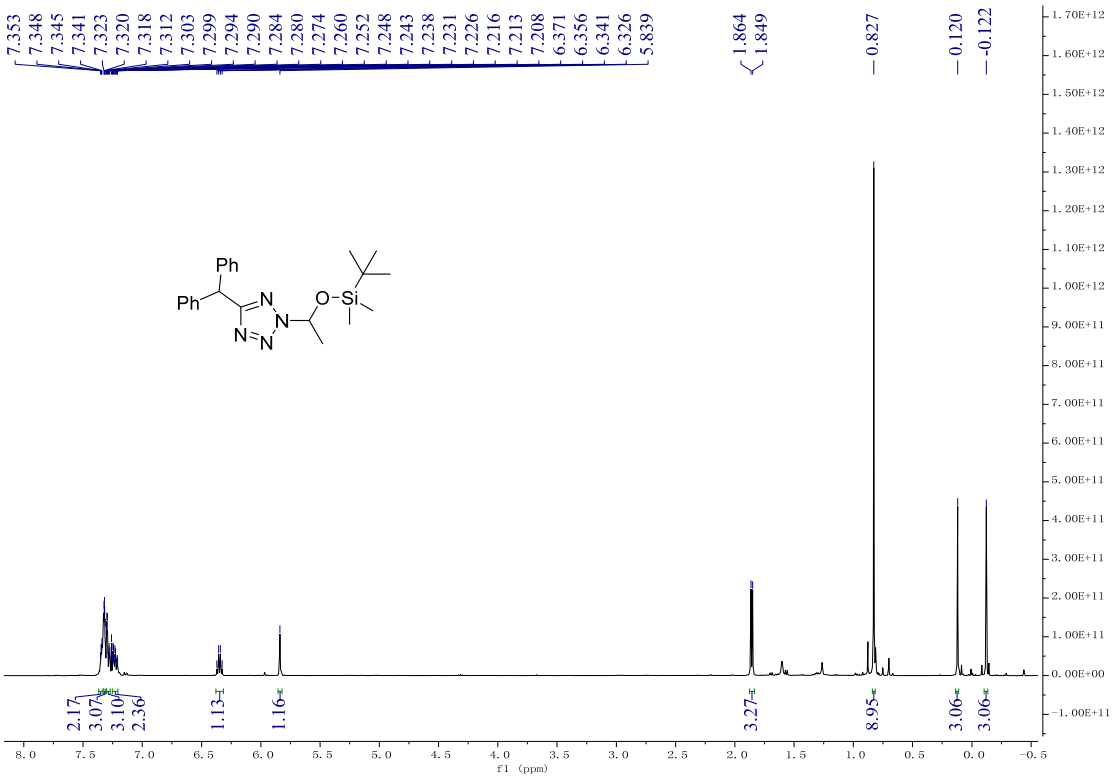
^{1}H-NMR of 4ja



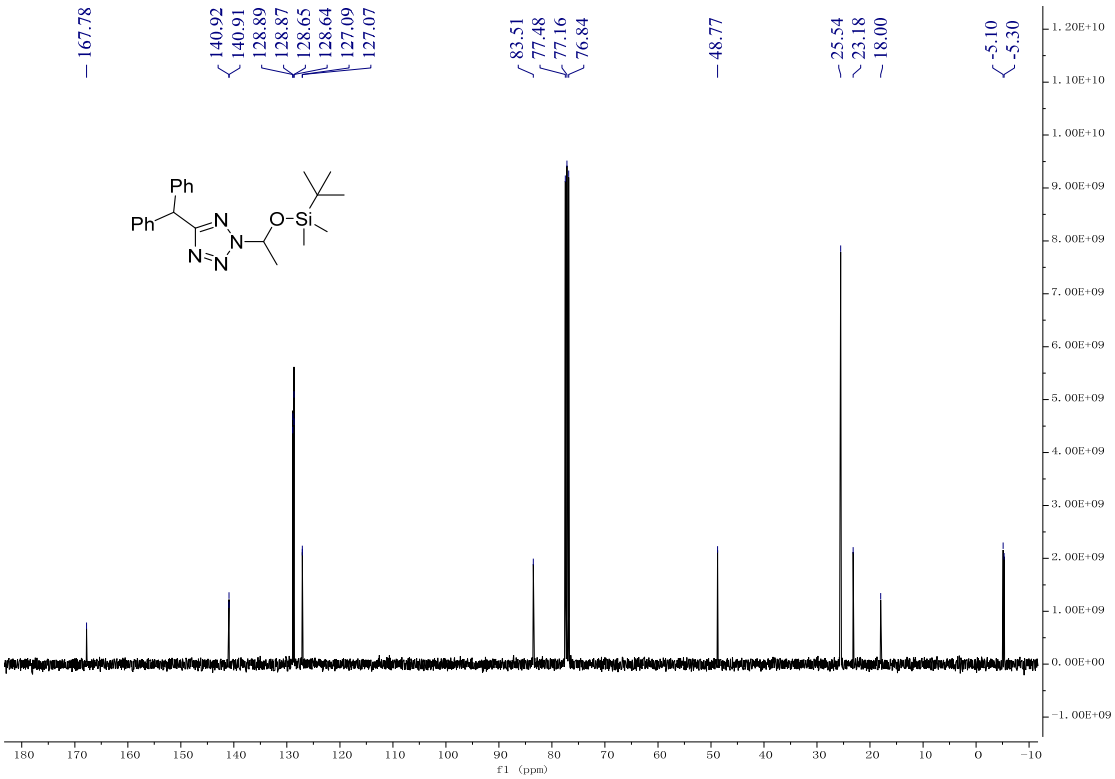
^{13}C-NMR of 4ja



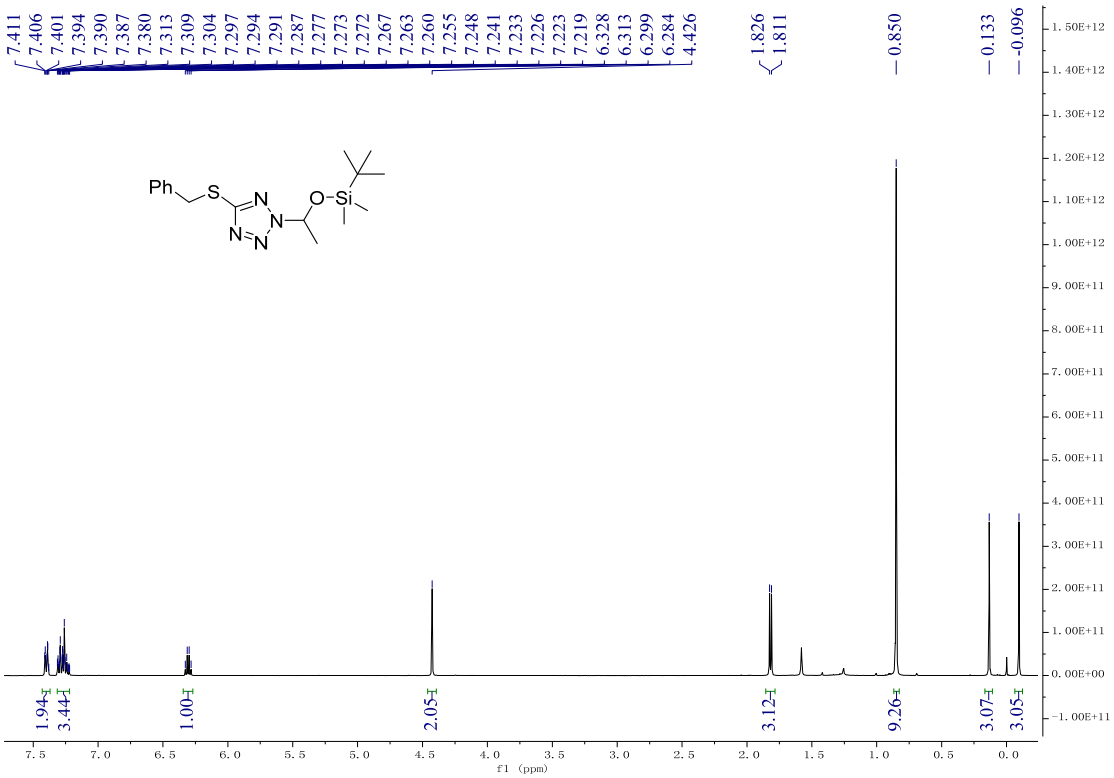
^{1}H-NMR of 4ka



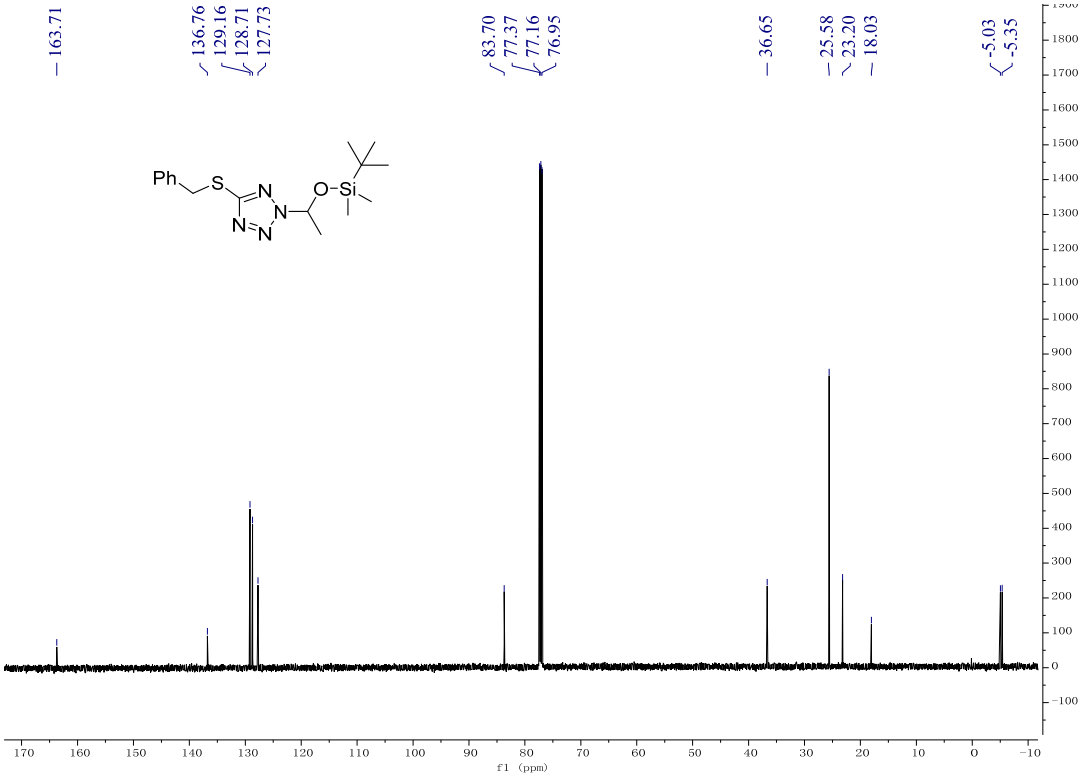
^{13}C-NMR of 4ka



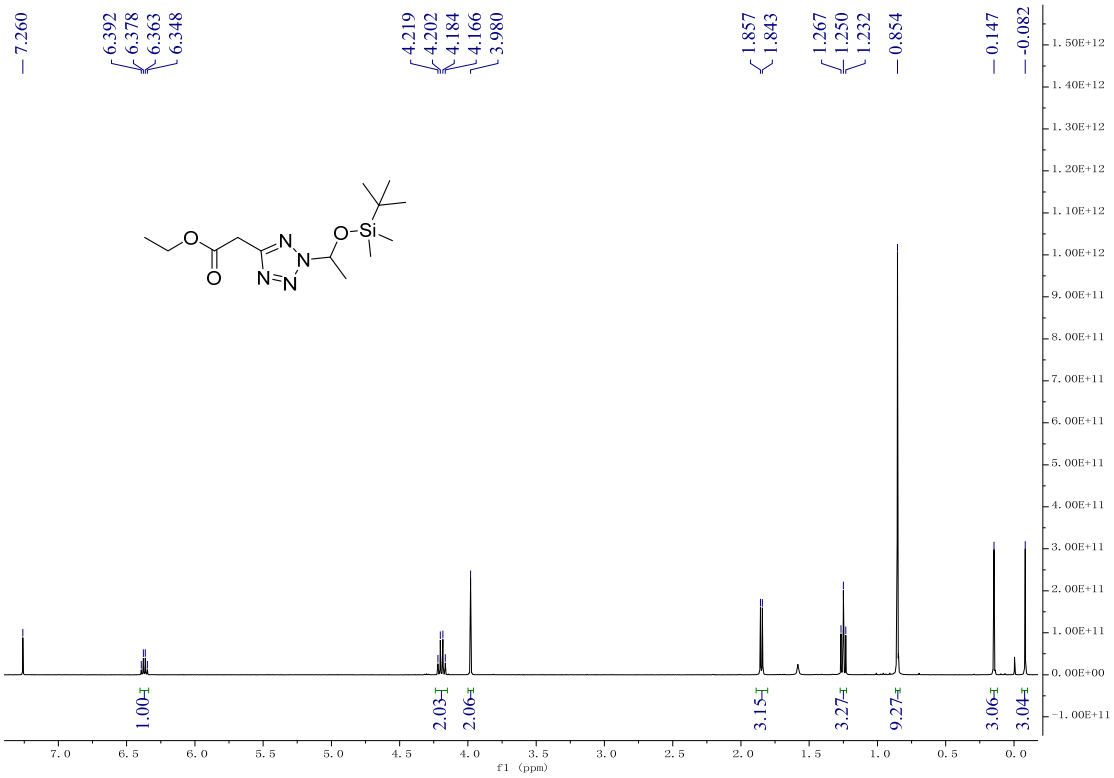
^{1}H-NMR of 4la



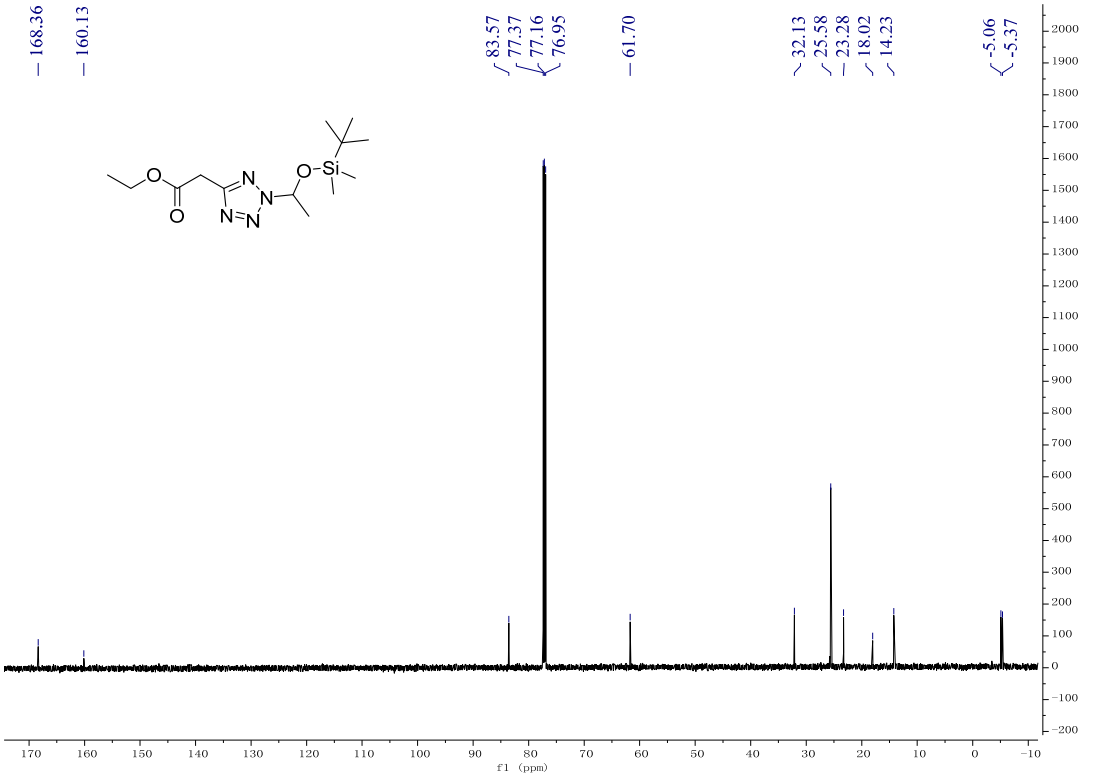
^{13}C-NMR of 4la



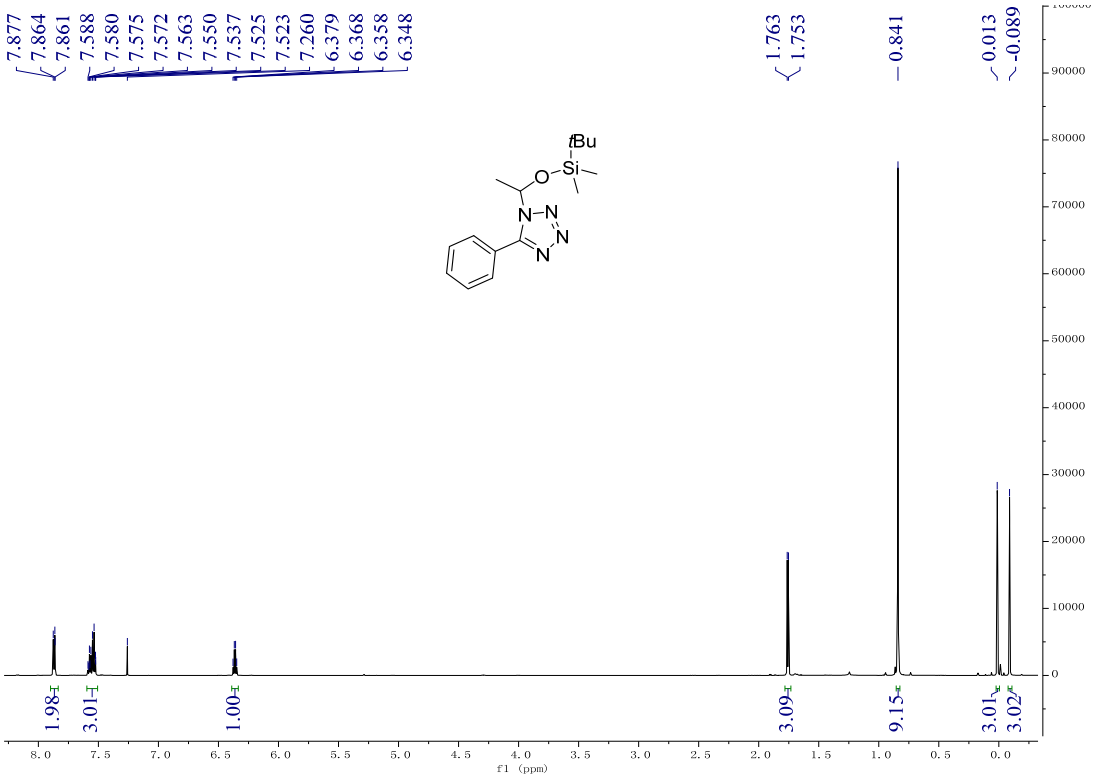
^{1}H-NMR of 4ma



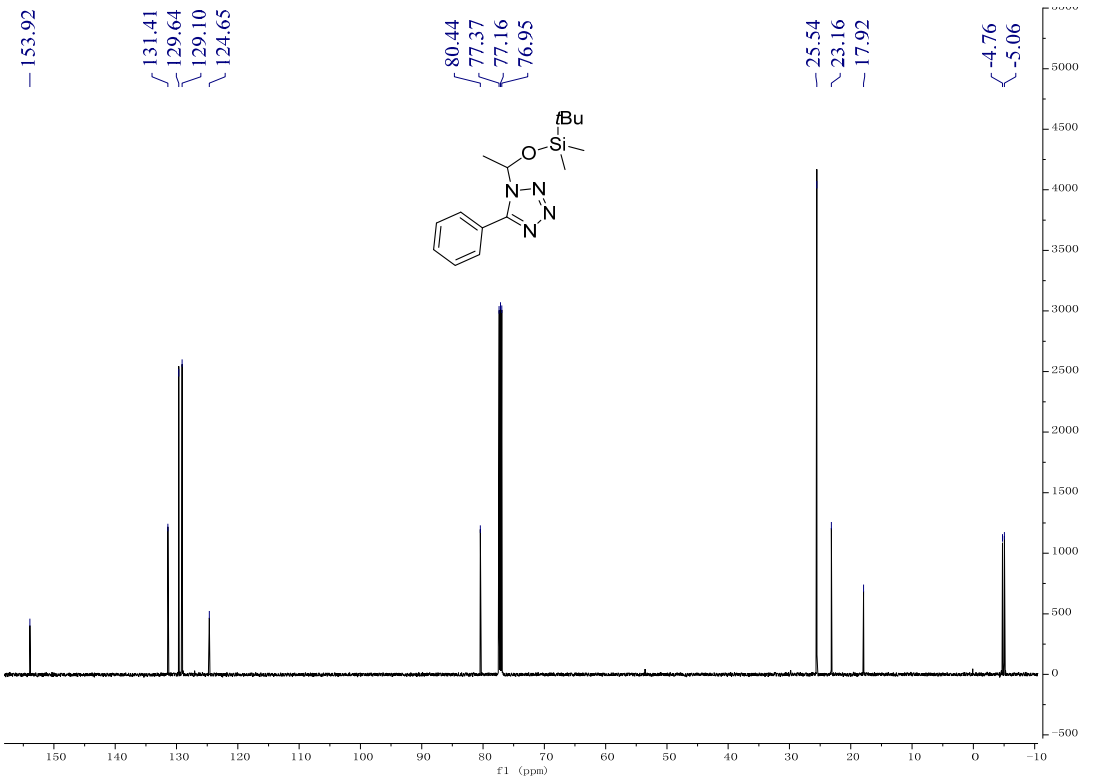
^{13}C-NMR of 4ma



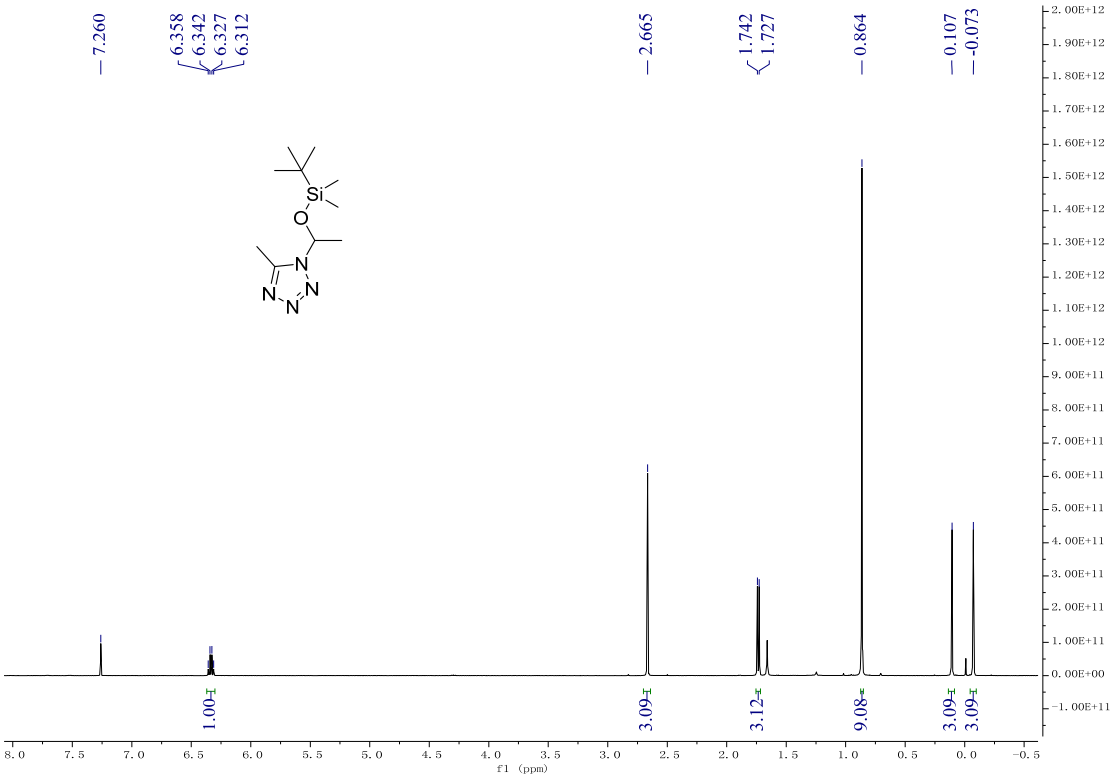
^{1}H-NMR of 5aa



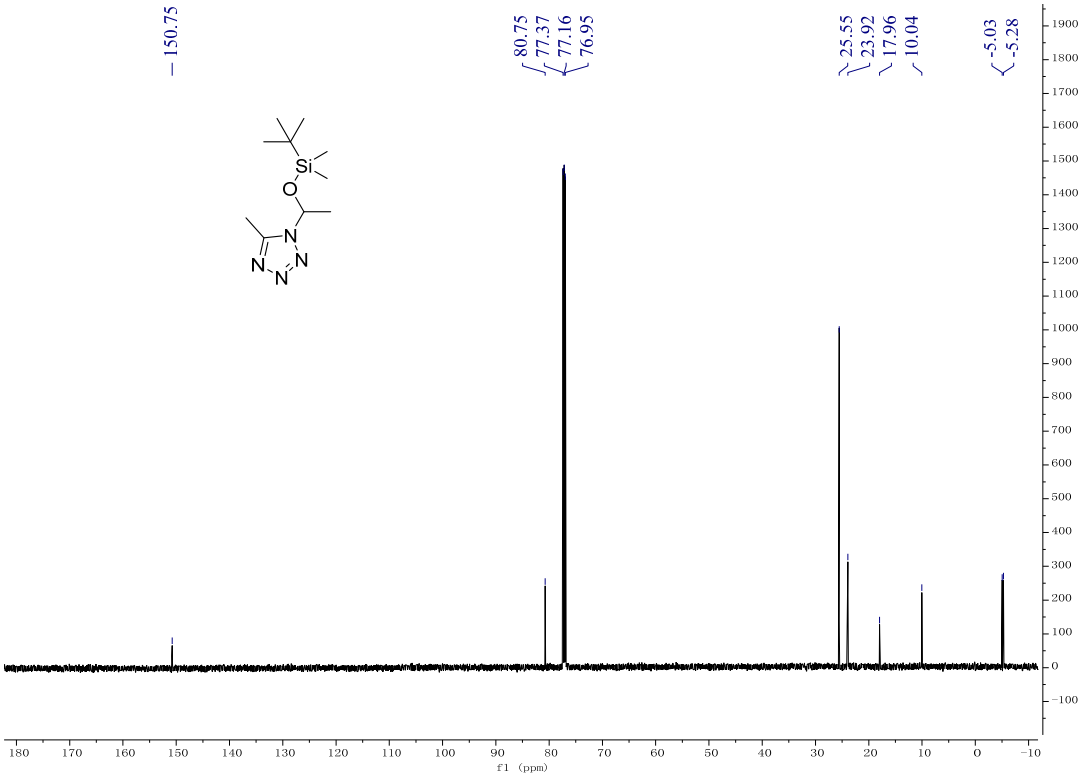
^{13}C-NMR of 5aa



^{1}H-NMR of 5da



^{13}C-NMR of 5da



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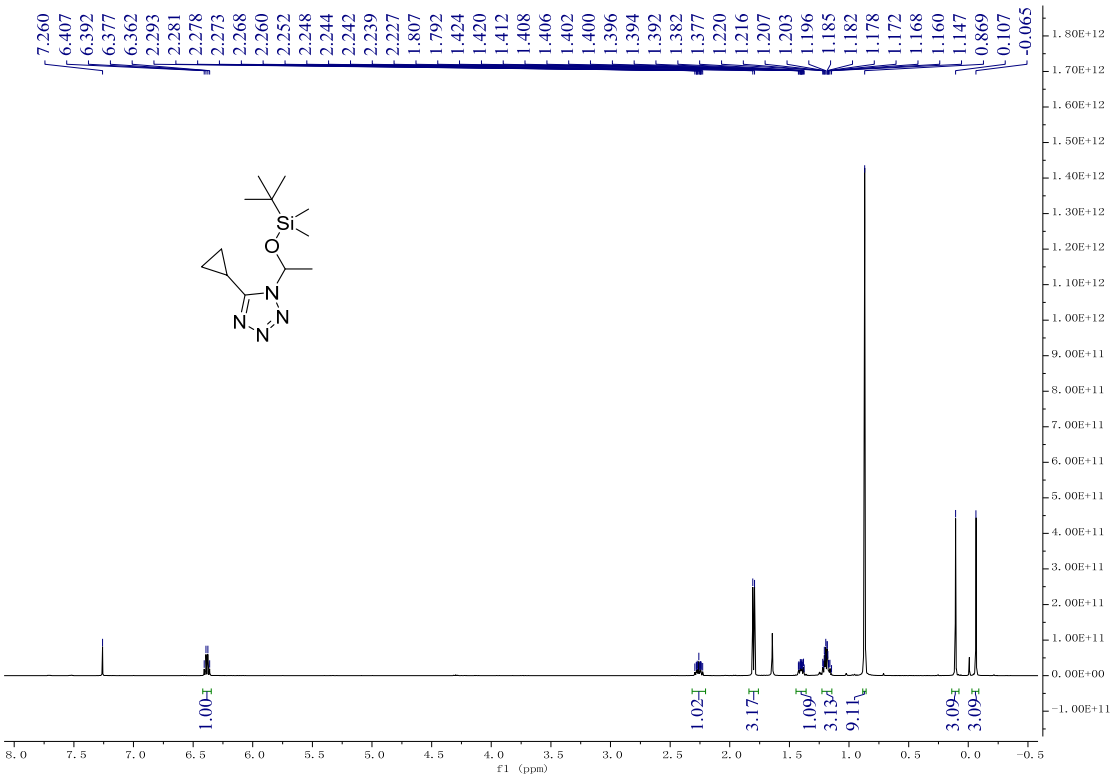

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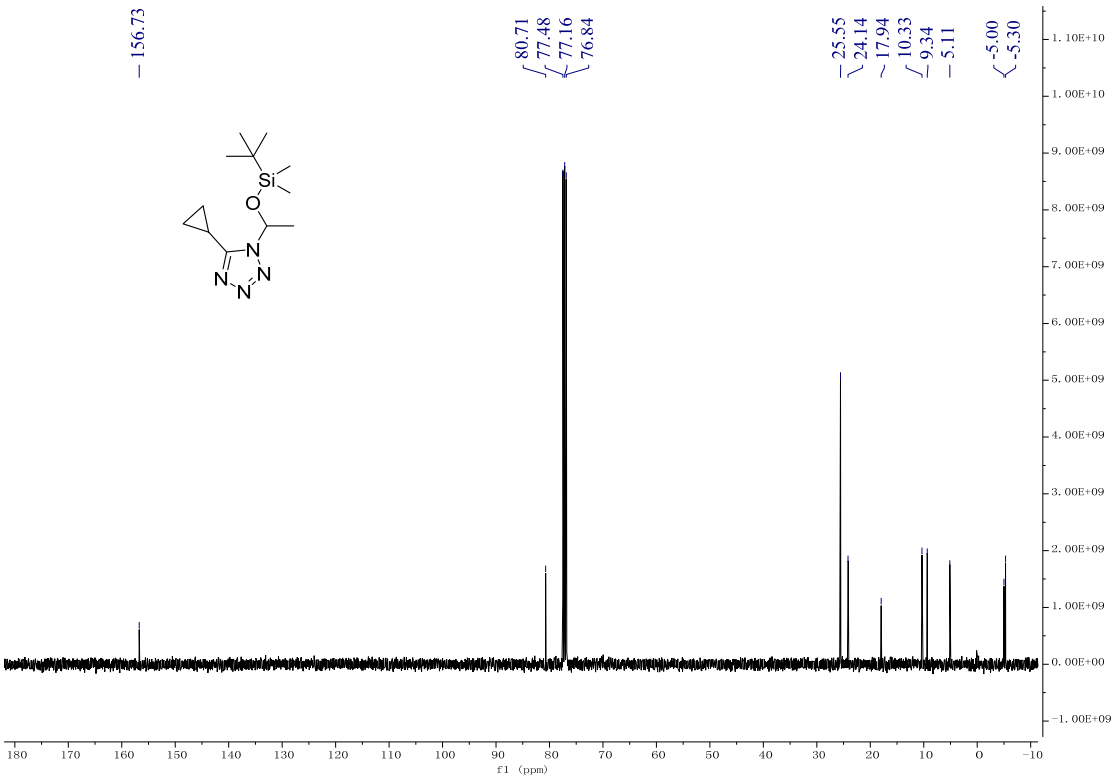
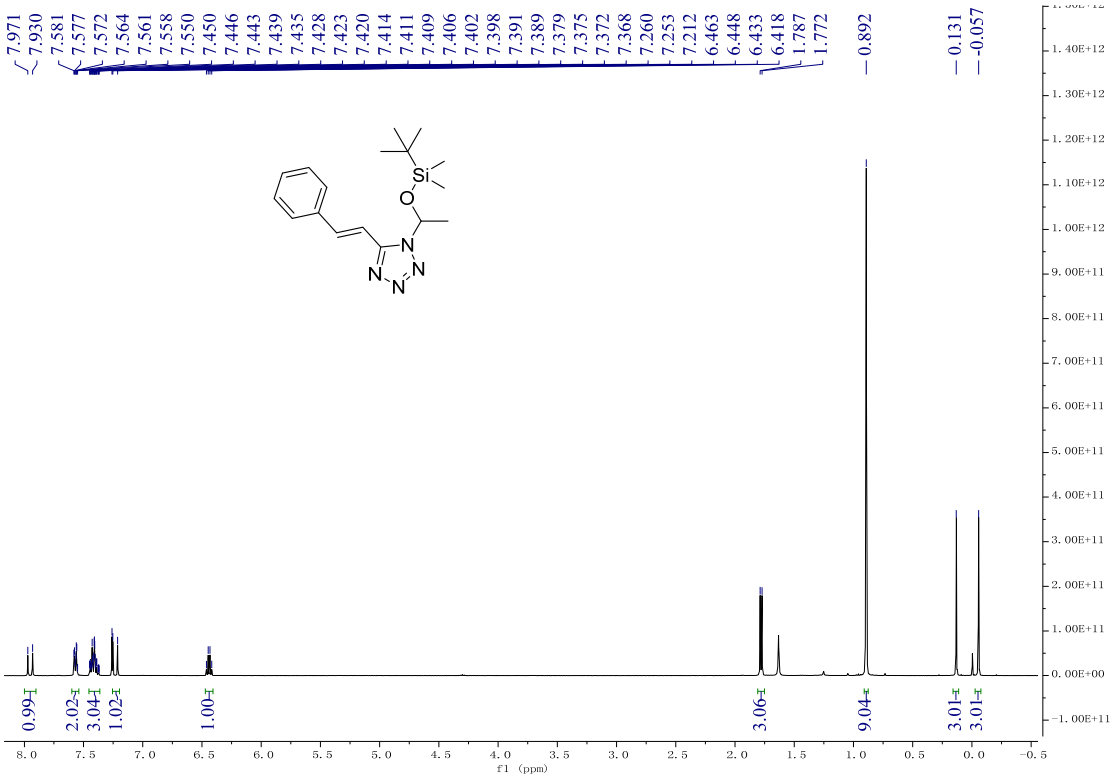


^{1}H-NMR of 5ga



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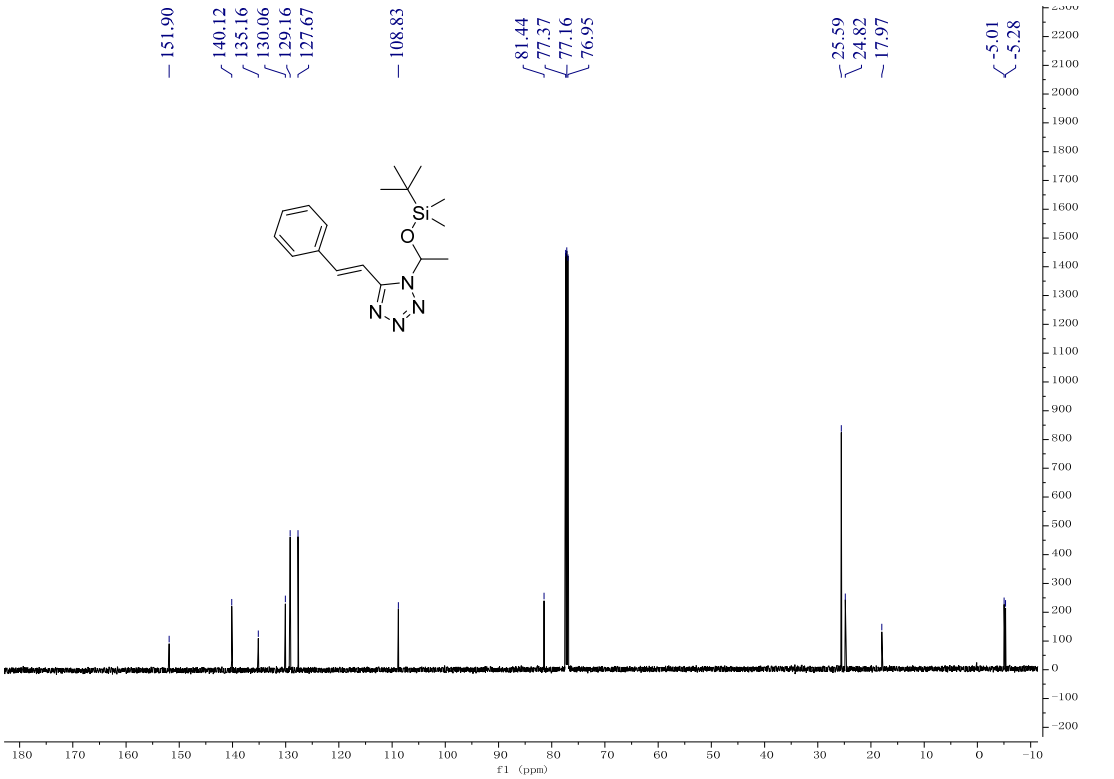
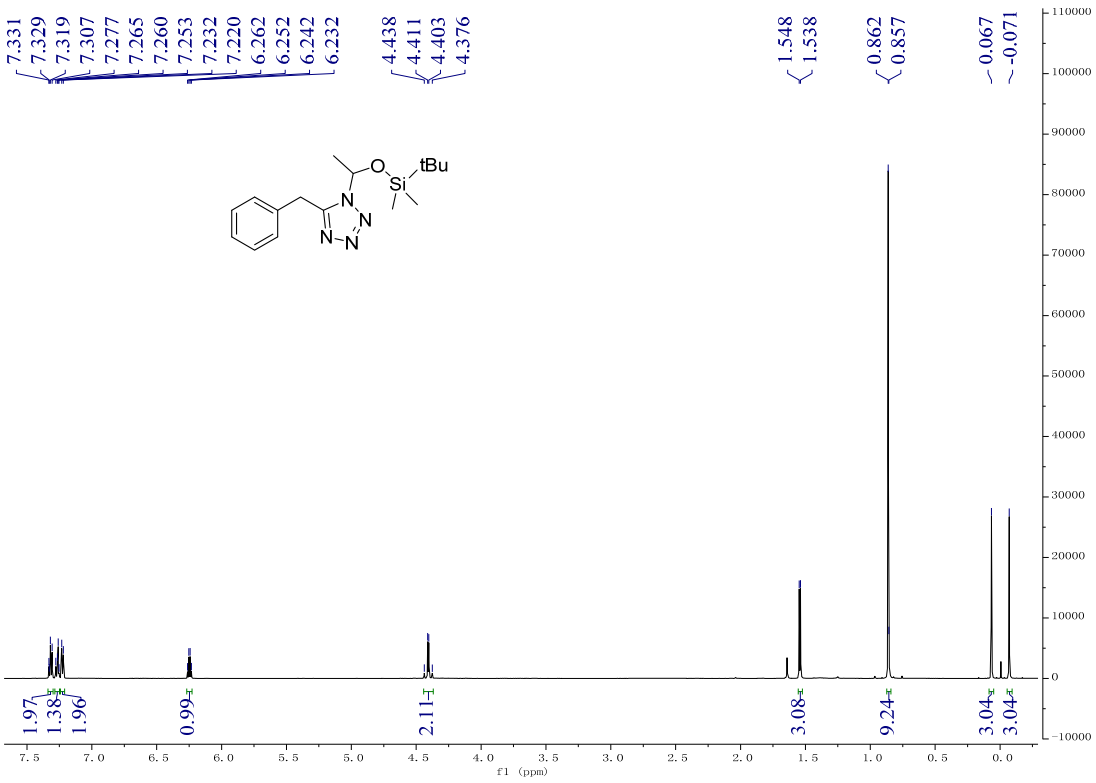


^{1}H-NMR of 5ja



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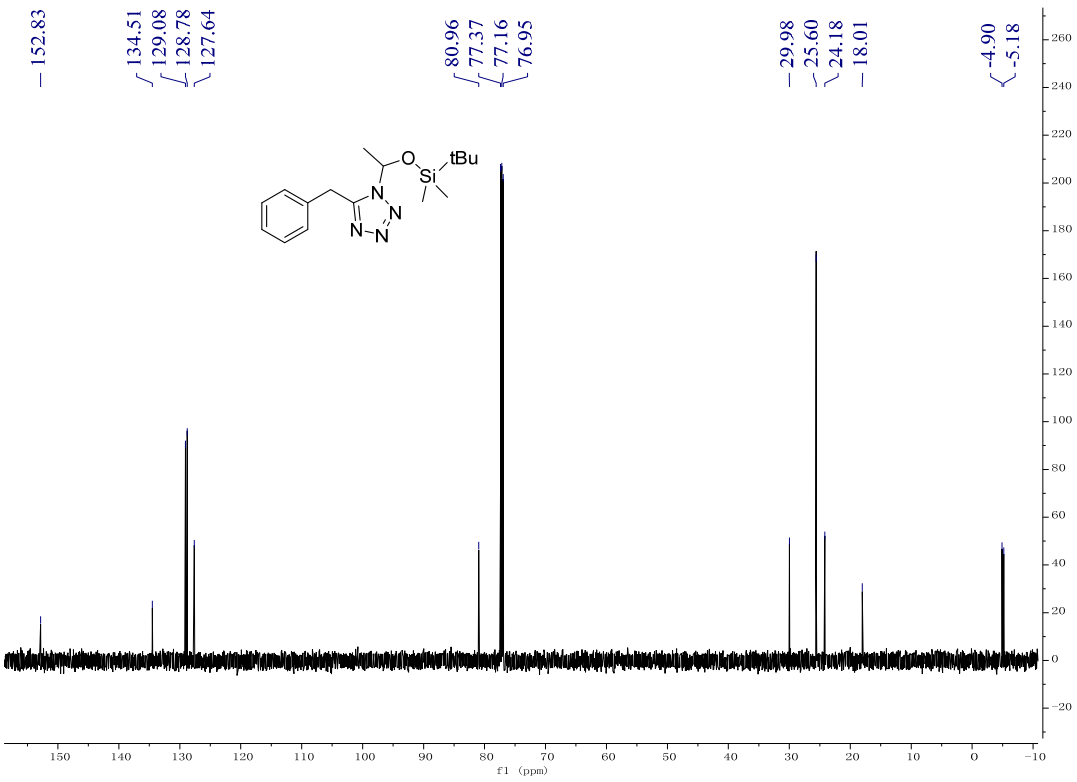
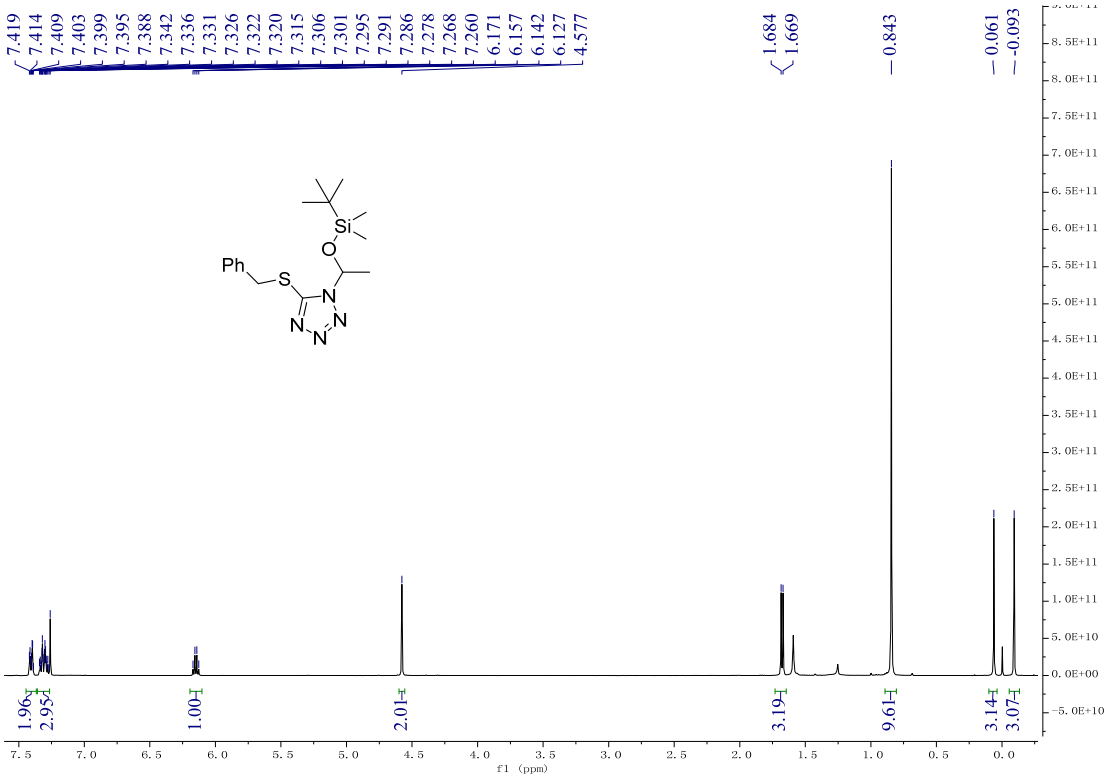


^{1}H-NMR of 5la



^{13}C-NMR of 5la