Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2016

Electronic Supplementary Information

Manuscript ID NJ-ART-09-2015-002681

New organometallic Schiff-base copper complexes as efficient "click" reaction precatalysts

Xiang Liu, Néstor Novoa, Carolina Manzur, David Carrillo and Jean-René Hamon

Contents

1

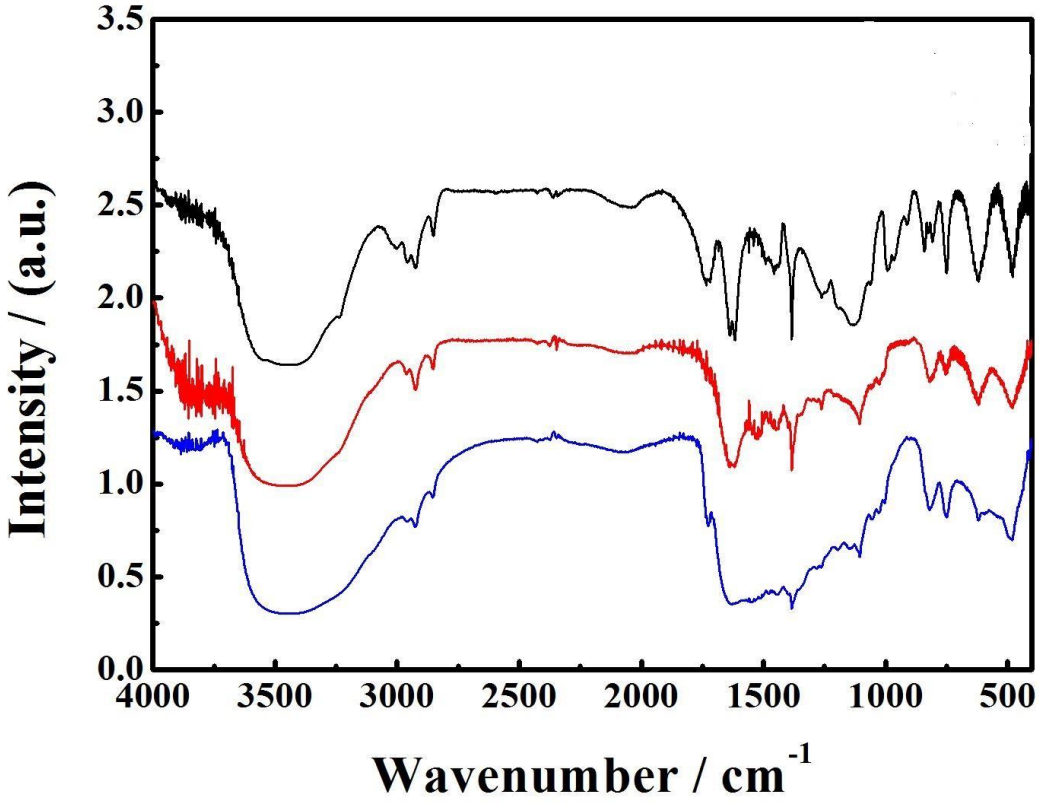


Fig. S1 Solid-state FT-IR spectrum of the heterobimetallic Schiff base complex **2** (black), free PMMA matrix (red), and metallopolymer **3** (blue)

2

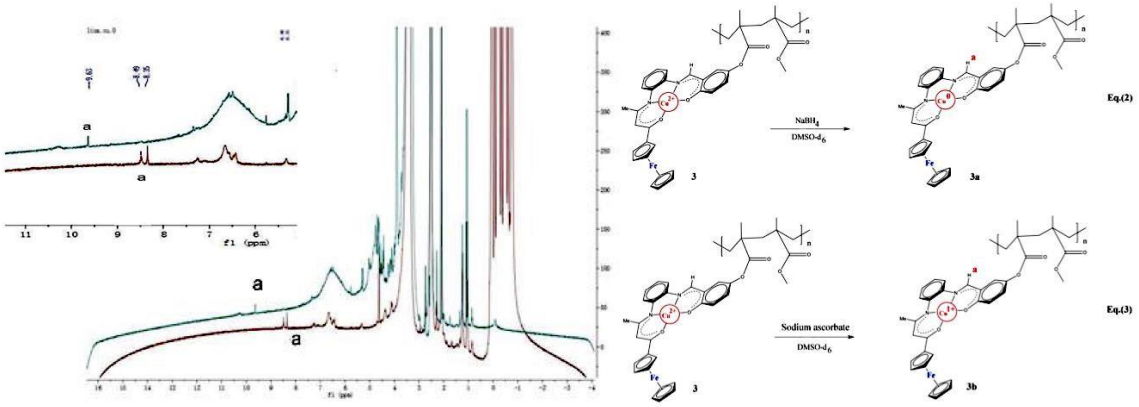


Fig. S2 ^{1}H-NMR spectrum of the complexes **3a** and **3b**: The **red spectrum** was obtained following reaction between 0.5 mg complex **3** and 2 equiv. $NaBH_4$ in DMSO-d_6. The free metalloligand is obtained as indicated by the presence of signals of H^a at 8.35 and 8.49 ppm. This free ligand is seemingly obtained upon decoordination from Cu(0) after reaction of **3** with $NaBH_4$ The fate of copper nanoparticles formed in this reaction was not researched further, but their stabilization by such a Schiff-base ligands may be later investigated. The **green spectrum** was obtained following reaction between 0.5 mg complex **3** and 2 equiv. sodium ascorbate in DMSO-d_6. It shows a diamagnetic complex that is obtained with a new imine signal at 9.63 ppm consistent with the generation of a Cu^I complex. It appears to be very different from the **red spectrum** obtained with $NaBH_4$, in accord with the single electron reduction of **3** upon reaction with sodium ascorbate.

3. Figs. S3-S6 TEM and ^{1}H-NMR spectra showing the absence of Cu species in solution

The residual copper in solution that would eventually result from the reaction between the PMMA-anchored catalyst **3** (10.5 mg, 2 mol%) and sodium ascorbate (20 mol%) has been checked after the 3rd catalytic recycling as follows:

The system was purged three times with N_2 and ethynylbenzene (0.50 mmol), (azidomethyl)benzene (0.50 mmol) and 2 mL of degassed ethanol were successively added by syringe. The resulting mixture was stirred for 24 h at rt under N_2. After 3 recycling, complex **3** was filtered through a paper filter. The organic solution (B) was divided into two parts. One part was used for and TEM (Scheme 2) . The other part was concentrated *in vacuo*, and the residue was checked by ^{1}H-NMR.

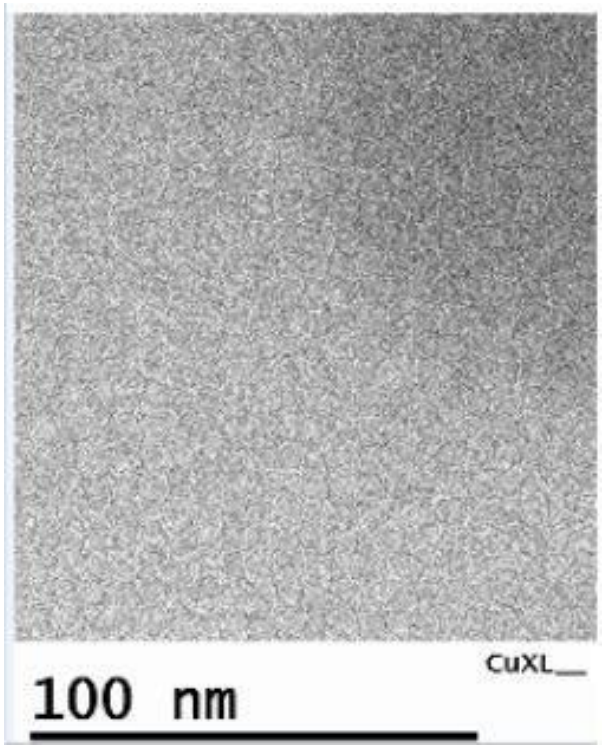


Fig. S3

Fig. S3 Transmission electron microscopy (TEM) picture of the organic solution (B) showing that there is no nanoparticles in solution (B), consistent with reduction of Cu^{2+} from PMMA-anchored catalyst **3** to Cu^{+} by sodium ascorbate.

4

The Fig. **S4**, **S5** and **S6** (^{1}H-NMR spectra of the click reaction product, triazole) together show the absence of copper salt in solution. Taken together with the TEM picture that shows the absence of nanoparticules in this solution, this is proof for the absence of leached copper from **3** during catalysis. The details of the NMR samples in **Figs**. **S4**, **S5** and **S6** follow:

Fig. S4 : After the click reaction, the complex 3 was removed by filtration on filter paper; then the solvent was removed *in vacuo*, and the ^{1}H NMR spectrum of 10 mg of the residue in $CDCl_3$ that was recorded is shown.

.

Fig. S5 : After the click reaction, complex **3** was removed by filter paper; then the solvent was removed *in vacuo*, and a 2% mmol sodium ascorbate was added to 10 mg of the residue in $CDCl_3$. The signal of H^a (triazole) is located at 7.60 ppm (as shown in the **Fig.S4**). This signal is the same as in the purified product **4a** without change.

Fig. S6 : After the click reaction, complex **3** was removed by filtration on filter paper, then the solvent was removed *in vacuo*, and 20% mmol $CuSO_4$ and 40% sodium ascorbate were added to 10 mg of the residue. The ^{1}H NMR spectrum in $CDCl_3$ is shown. 20 % of the signal of H^a (triazole) is shifted from 7.60 ppm to 7.99 ppm. This shift is known to be due to the coordination of triazole to Cu^I. Since this shift is not observed in **Fig. S5**, this means that there is no Cu^{2+} in the solution resulting from the click reaction catalyzed by complex **3**.

5

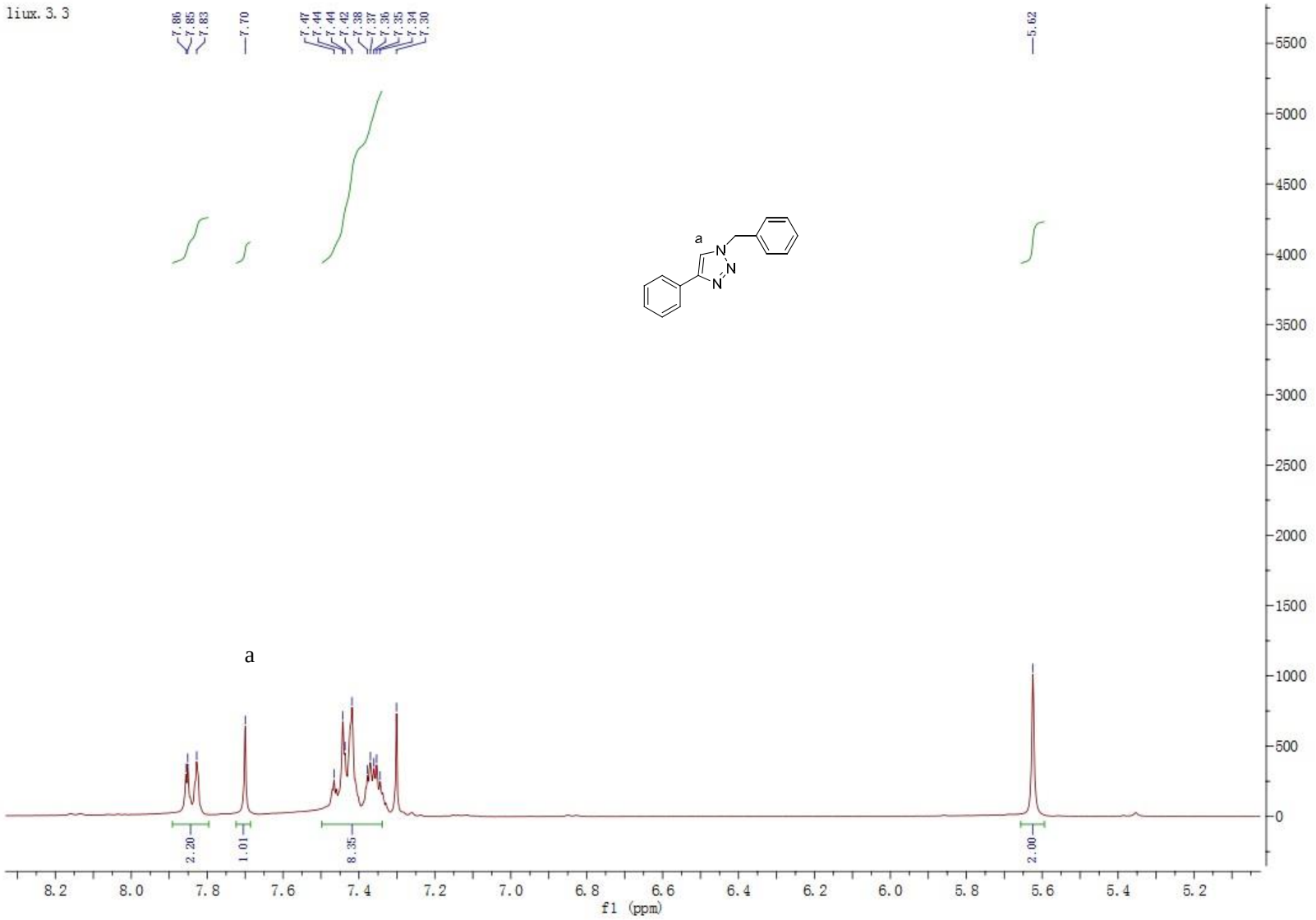


Fig. S4 After the click reaction, the complex **3** was removed by filtration on filter paper; then the solvent was removed *in vacuo*, and the ^{1}H NMR spectrum of 10 mg of the residue in $CDCl_3$ that was recorded is shown.

6

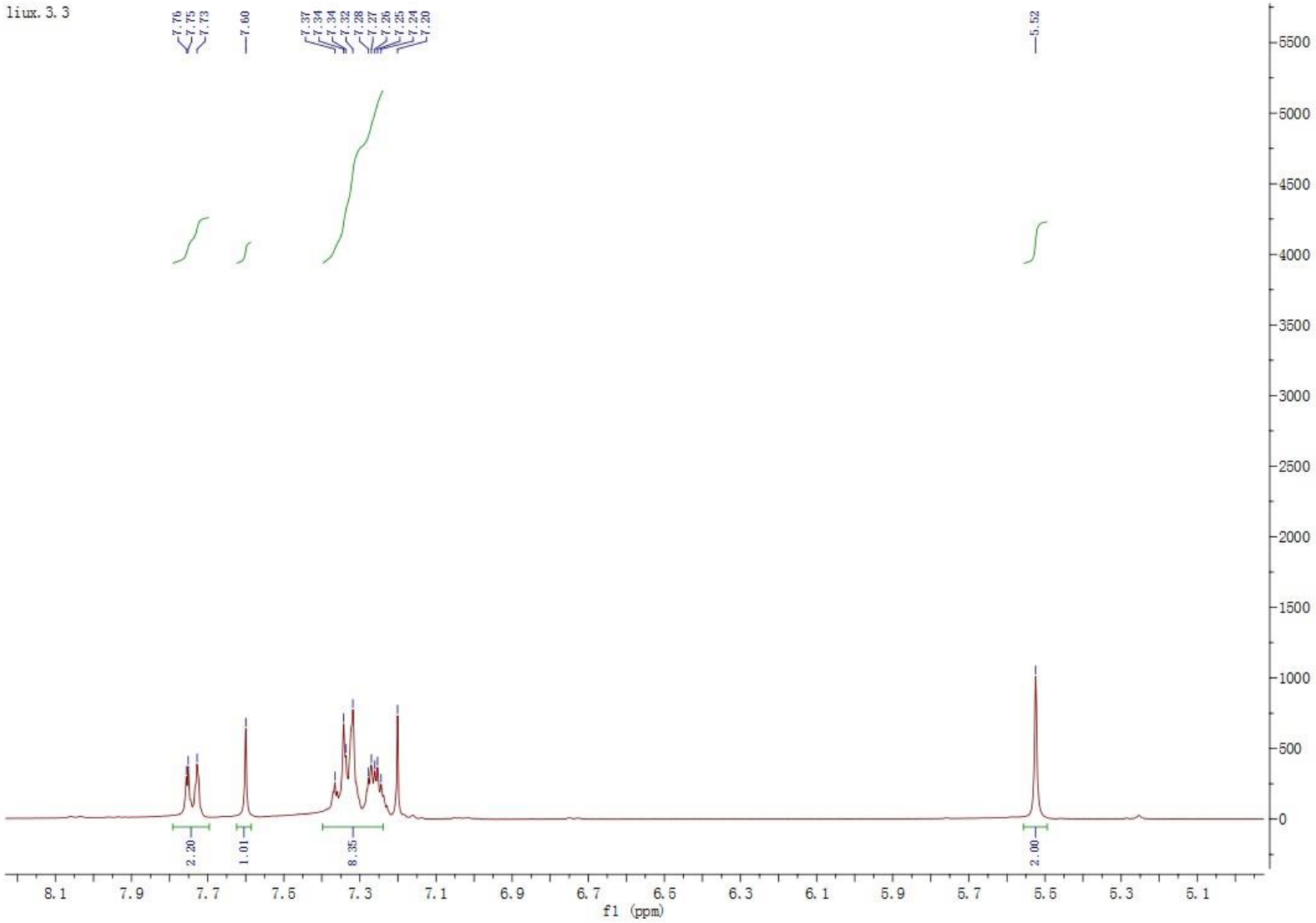


Fig. S5 After the click reaction, complex **3** was removed by filter paper; then the solvent was removed *in vacuo*, and a 2% mmol sodium ascorbate was added to 10 mg of the residue in $CDCl_3$.

7

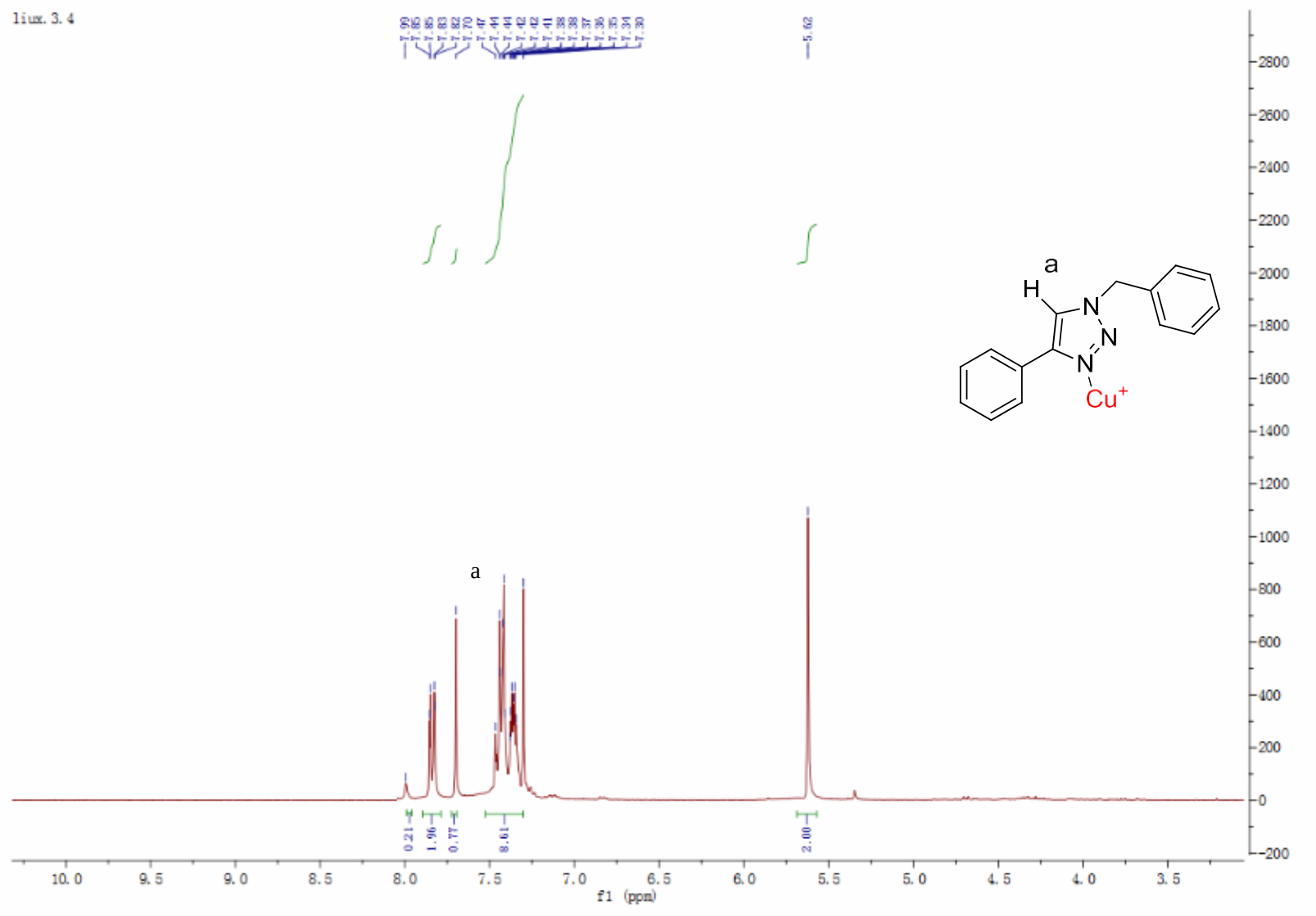
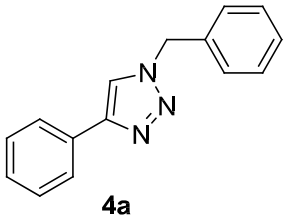


Fig. S6 After the click reaction, complex **3** was removed by filtration on paper filter, then the solvent was removed in vacuo, and 20% mmol $CuSO_4$ and 40% sodium ascorbate were added to 10 mg of the residue. The ^1H NMR spectrum in $CDCl_3$ is shown.

8

4. Spectral data of the 1,4-disubstituted 1,2,3-triazoles 4a-m

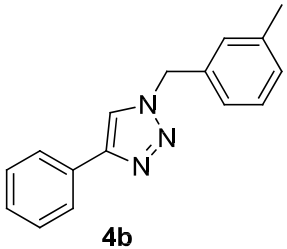
4.1. 1-benzyl-4-phenyl-1H-1,2,3-triazole (4a)



4a

C_6H_5-C≡CH (51 mg), $C_6H_5CH_2N_3$ (66.5 mg), complex **2** (0.5 mg); white solid, yield: 108 mg, 92.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75-7.73 (d, J = 6Hz, 2H), 7.60 (s, 1H), 7.32-7.23 (m, 4H), 7.20 (s, 4H), 5.52 (s, 2H).

4.2. 1-(3-methylbenzyl)-4-phenyl-1H-1,2,3-triazole (4b)

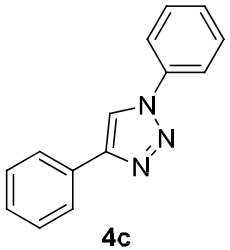


4b

C_6H_5-C≡CH (51 mg), 3-Me$C_6H_4CH_2N_3$ (80 mg), complex **2** (0.5 mg); white solid, yield: 116 mg, 88.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83-7.80 (d, J = 6 Hz, 2H), 7.72(s, 1H), 7.48-7.16 (m, 7H), 5.62 (s, 2H), 2.44 (s, 3H).

9

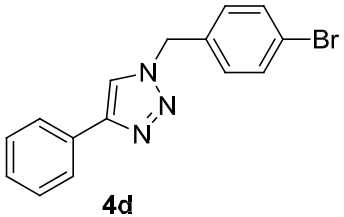
4.3. 1,4-diphenyl-1H-1,2,3-triazole (4c)



4c

C_6H_5-C≡CH (51 mg), $C_6H_5N_3$ (60 mg), complex **2** (0.5 mg); white solid, yield: 97 mg, 88.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.13 (s, 1H), 7.86-7.84 (d, J = 6 Hz, 2H), 7.75-7.72 (d, J = 9 Hz, 2H), 7.49-7.31 (m, 6H).

4.4. 1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (4d)

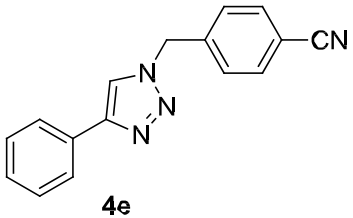


4d

C_6H_5-C≡CH (51 mg), 4-Br$C_6H_4CH_2N_3$ (105 mg), complex **2** (0.5 mg); white solid, yield: 146 mg, 93.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.84-7.79 (m, 2H), 7.67 (s, 1H), 7.46-7.27 (m, 7H), 5.59 (s, 2H).

10

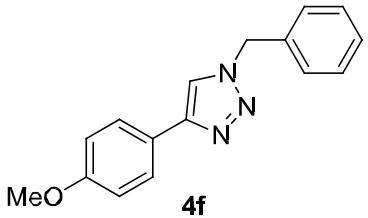
4.5. 4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (4e)



4e

C_6H_5-C≡CH (51 mg), 4-$CNC_6H_4CH_2N_3$ (79 mg), complex **2** (0.5 mg); white solid, yield: 107 mg, 82.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77-7.64 (m, 2H), 7.64-7.59 (m, 3H), 7.40-7.19 (m, 5H), 5.59 (s, 2H).

4.6. 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (4f)

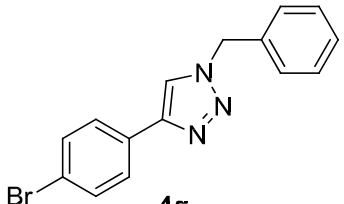


4f

4-$MeOC_6H_4$-C≡CH (66 mg), $C_6H_5CH_2N_3$ (66.5 mg), complex **2** (0.5 mg); white solid, yield: 116 mg, 87.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.74 (d, J = 6 Hz, 2H), 7.60 (s, 1H), 7.42-7.39 (t, J = 4.5 Hz, 3H), 7.34-7.33 (m, 2H), 7.28 (s, 4H), 6.97-6.95 (d, J = 6 Hz, 2H), 5.59 (s, 2H), 3.85 (s, 3H).

11

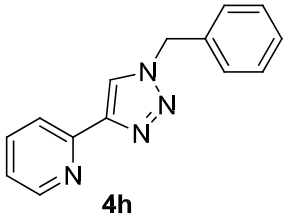
4.7. 1-benzyl-4-(4-bromophenyl)-1H-1,2,3-triazole (4g)



4g

4-BrC_6H_4-C≡CH (90 mg), $C_6H_5CH_2N_3$ (66.5 mg), complex **2** (0.5 mg); white solid, yield: 146 mg, 93.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71-7.69 (d, J = 6 Hz, 2H), 7.56-7.54 (d, J = 6 Hz, 2H), 7.43-7.41 (d, J = 6 Hz, 2H), 7.45-7.33 (m, 2H), 7.28 (s, 2H), 5.60 (s, 2H).

4.8. 2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (4h)

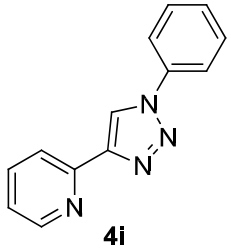


4h

2-NC_5H_4-C≡CH (52 mg), $C_6H_5CH_2N_3$ (66.5 mg), complex **2** (0.5 mg); white solid, yield: 108 mg, 91.3%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.15-8.14 (d, J = 3 Hz, 2H), 7.74 (s, 1H), 7.30-7.27 (m, 4H), 7.19-7.14 (m, 2H), 5.51 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.7, 148.8, 137.8, 137.2, 134.5, 129.4, 129.0, 128.7, 128.5, 126.3, 120.7, 54.6.

4.9. -(1-phenyl-1H-1,2,3-triazol-4-yl)pyridine (4i)

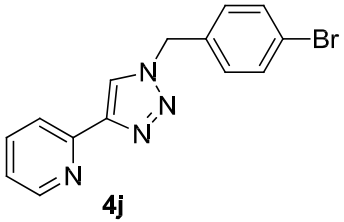
12



4i

2-NC_5H_4-C≡CH (52 mg), $C_6H_5N_3$ (60 mg), complex **2** (0.5 mg); white solid (yield: 100 mg, 90.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.85 (s, 1H), 8.66 (s, 1H), 8.33-8.31 (d, J = 6 Hz, 1H), 7.91 -7.82 (m, 3H), 7.56-7.46 (m, 2H), 7.33 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.5, 148.7, 147.9, 138.3, 137.1, 130.1, 129.2, 123.5, 121.1, 120.9, 120.7.

4.10. 2-(1-(4-bromobenzyl)-1H-1,2,3-triazol-4-yl)pyridine (4j)

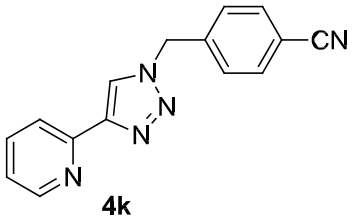


4j

2-NC_5H_4-C≡CH (52 mg), 4-$BrC_6H_4CH_2N_3$ (105 mg), complex **2** (0.5 mg); white solid, yield: 145 mg, 92.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.48-8.47 (d, J = 3 Hz, 1H), 8.12-8.10 (d, J = 6 Hz, 1H), 7.99 (s, 1H), 7.74-7.71 (t, J = 4.5 Hz, 1H), 7.45-7.43 (d, J = 6 Hz, 2H), 7.19-7.12 (m, 4H), 5.47 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 149.6, 149.1, 137.2, 134.1, 133.5, 132.6, 130.1, 123.3, 122.1, 120.5, 53.9.

13

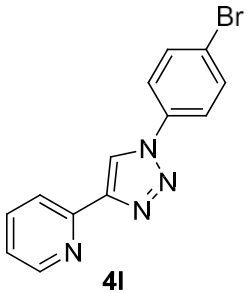
4.11. 4-((4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (4k)



4k

2-NC_5H_4-C≡CH (52 mg), 4-$CNC_6H_4CH_2N_3$ (79 mg), complex **2** (0.5 mg); white solid, yield: 109 mg, 83.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.46-8.43 (d, J = 6 Hz, 1H), 8.13-8.06 (m, 2H), 7.75-7.73 (t, J = 3 Hz, 1H), 7.62-7.59 (d, J = 9 Hz, 2H), 7.35-7.32 (d, J = 9 Hz, 2H), 7.20-7.16 (m, 1H), 5.59 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ149.1, 149.6, 149.3, 139.8, 137.3, 133.1, 128.8, 123.4, 122.4, 120.5, 118.3, 113.1, 53.8.

4.12. 2-(1-(4-bromophenyl)-1H-1,2,3-triazol-4-yl)pyridine (4l)



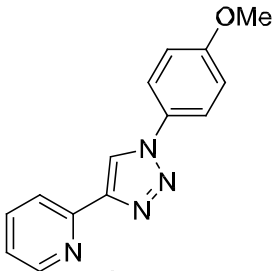
4l

2-NC_5H_4-C≡CH (52 mg), 4-$BrC_6H_4N_3$ (98 mg), complex **2** (0.5 mg); white solid, yield: 136 mg, 90.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.64-8.63 (d, J = 3 Hz, 1H), 8.30-8.28 (d, J = 6 Hz, 1H), 7.75-7.68 (m, 1H), 7.67-7.35 (m, 4H), 7.30-7.28 (m, 1H). ^{13}C NMR

14

(75 MHz, $CDCl_3$): δ149.7, 149.3, 148.9, 137.6, 136.1, 133.2, 123.5, 122.7, 122.0, 120.8, 120.2.

4.13. 2-(1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine (4m)



4m

2-NC_5H_4-C≡CH (52 mg), 4-$MeOC_6H_4N_3$ (75 mg), complex **2** (0.5 mg); white solid, yield: 111 mg, 88.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.55-8.53(d, J = 6 Hz, 1H), 8.46 (s, 1H), 8.19-8.16 (d, J = 9 Hz, 1H), 7.77-7.74(t, J = 4.5 Hz, 1H), 7.64-7.61 (d, J = 9 Hz, 2H), 7.21-7.17 (m, 1H), 6.98-6.95 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ160.1, 150.2, 149.8, 148.9, 137.2, 130.6, 123.2, 122.2, 120.6, 120.3, 115.0, 55.8.

15

5. ^{1}H and ^{13}C NMR spectrum of the 1,4-disubstituted 1,2,3-triazoles 4a-m

16

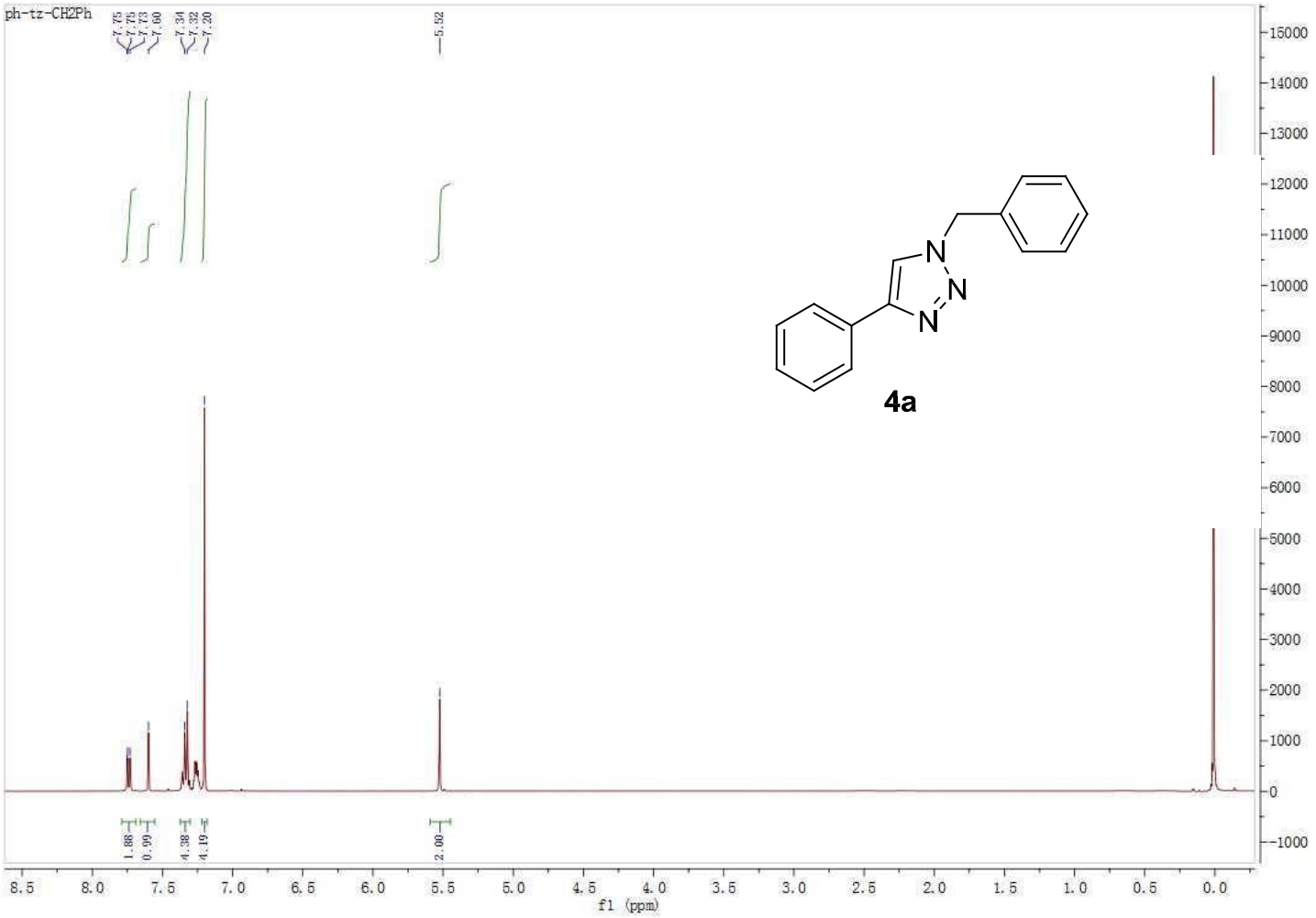


Fig. S7. 300 MHz ^{1}H NMR spectra of **4a** recorded in $CDCl_3$ at 298 K

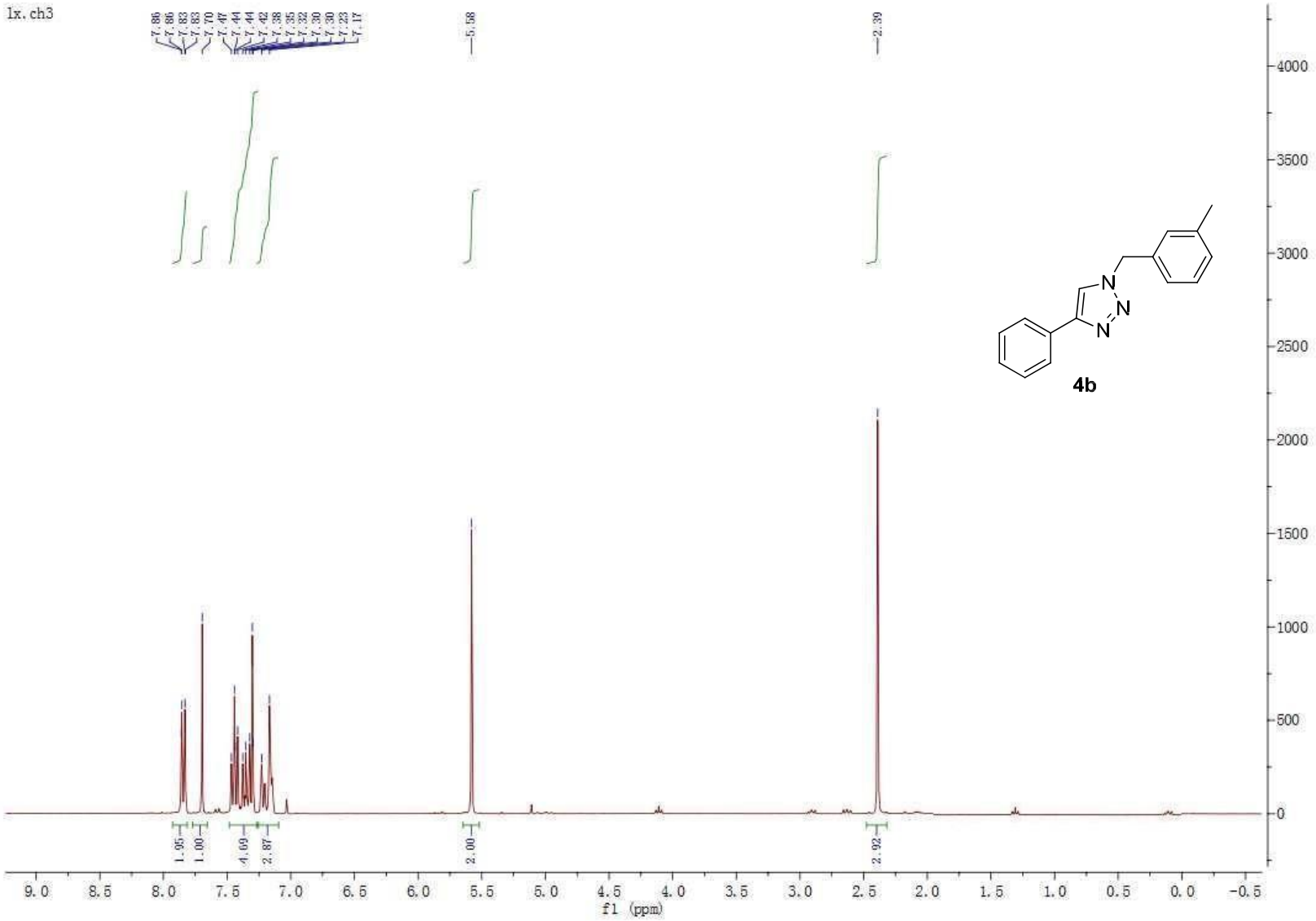


Fig. S8. 300 MHz ^{1}H NMR spectra of **4b** recorded in $CDCl_3$ at 298 K

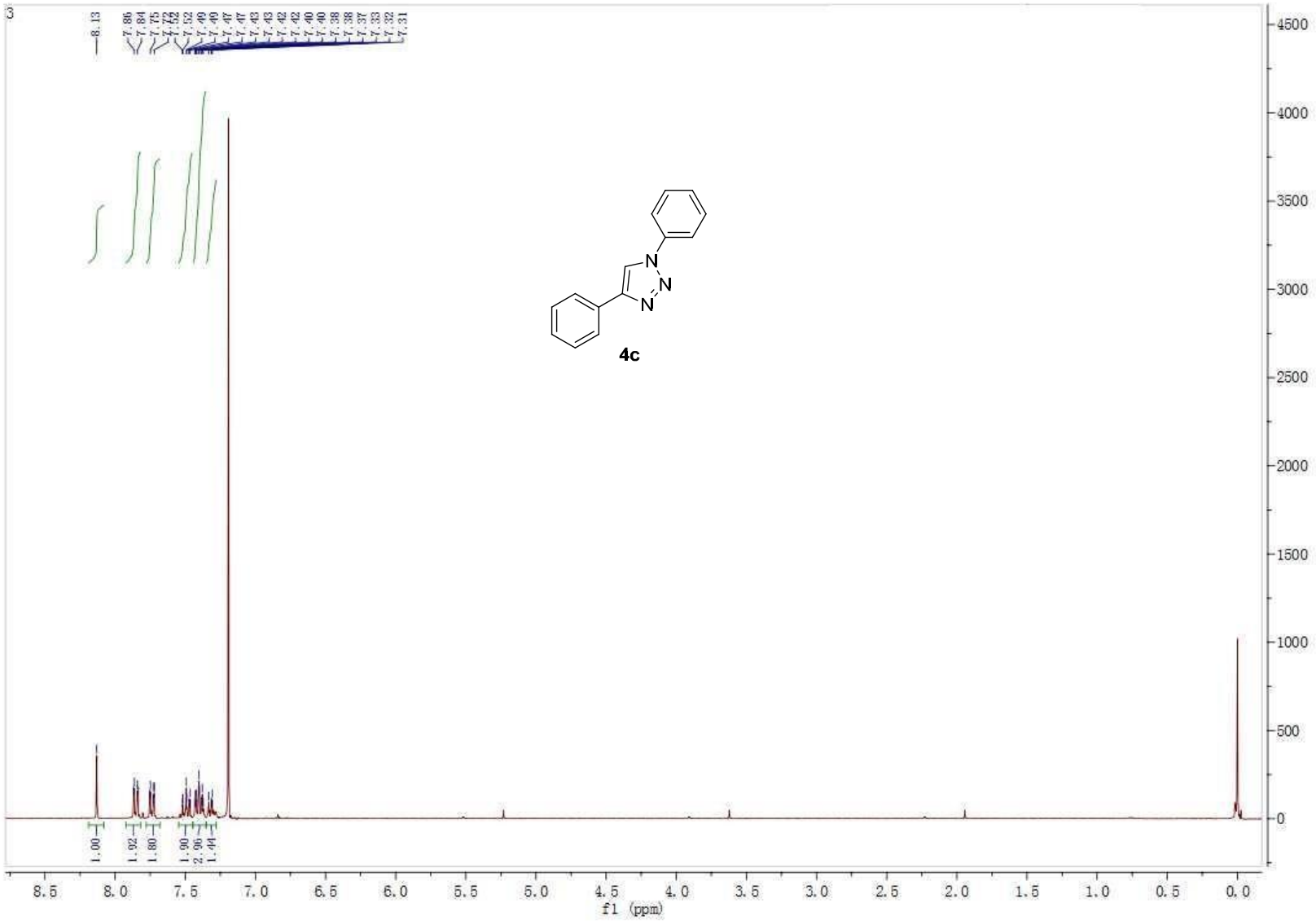


Fig. S9. 300 MHz ^{1}H NMR spectra of **4c** recorded in $CDCl_3$ at 298 K

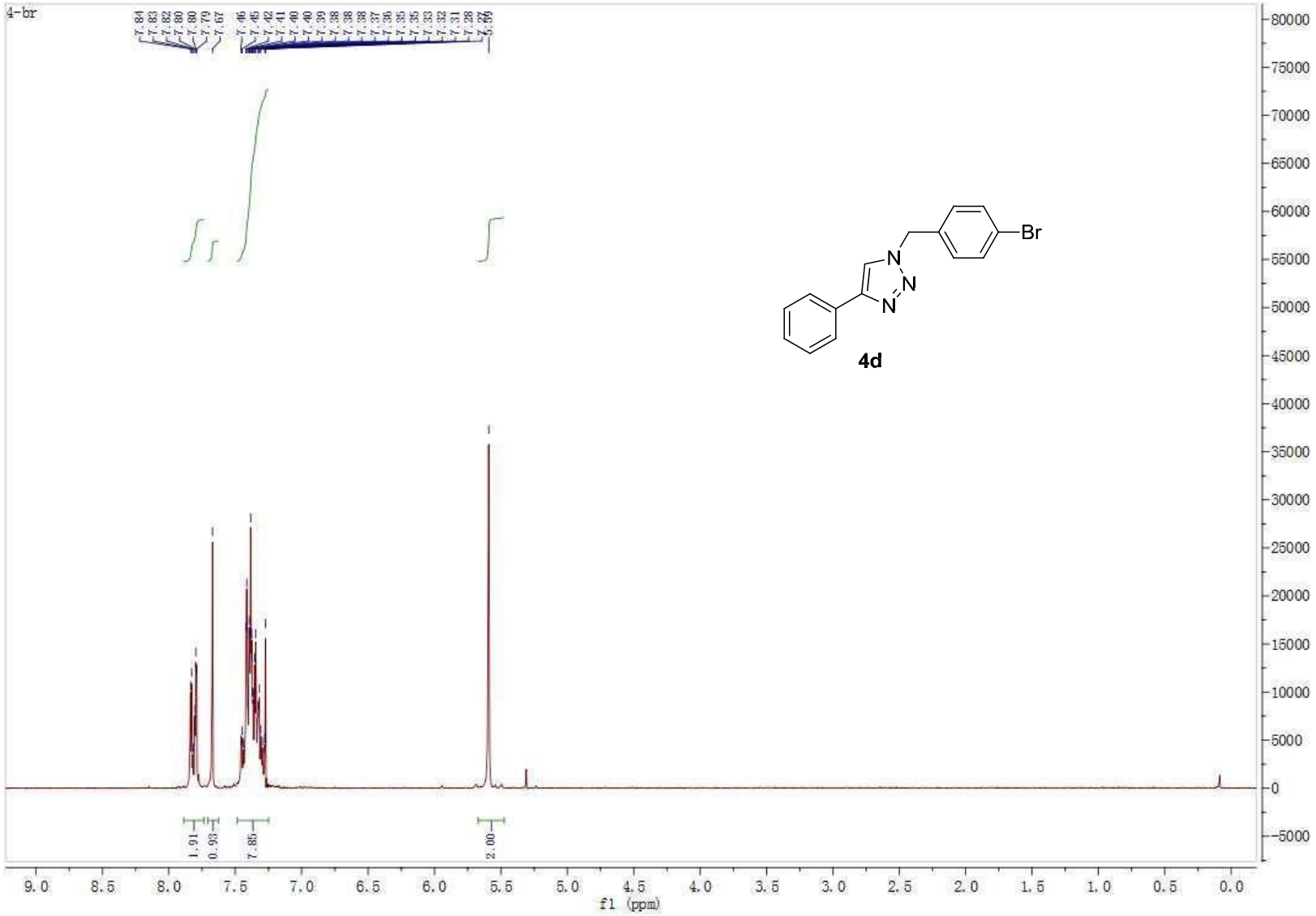


Fig. S10. 300 MHz ^{1}H NMR spectra of **4d** recorded in $CDCl_3$ at 298 K

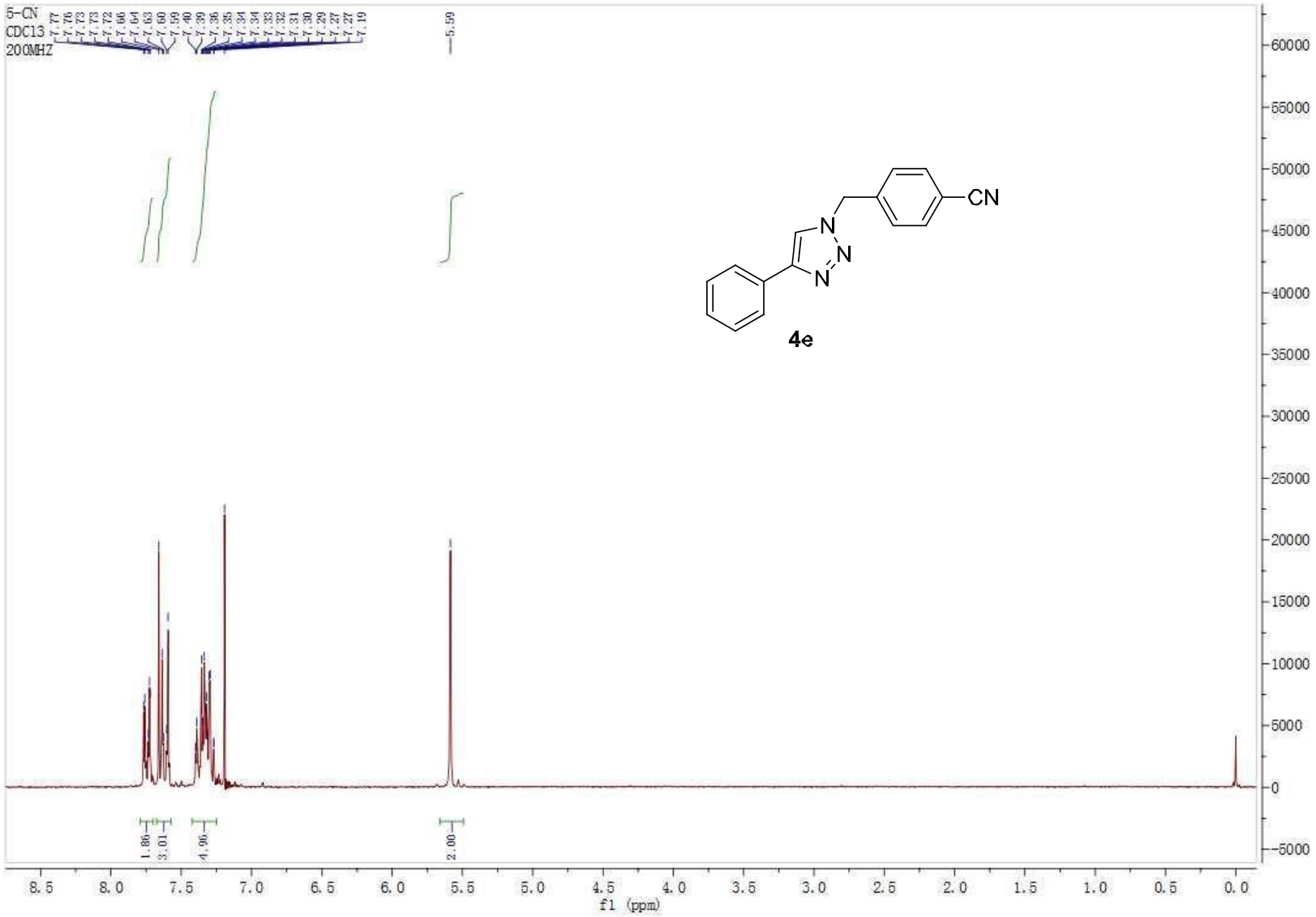


Fig. S11. 300 MHz ^{1}H NMR spectra of **4e** recorded in $CDCl_3$ at 298 K

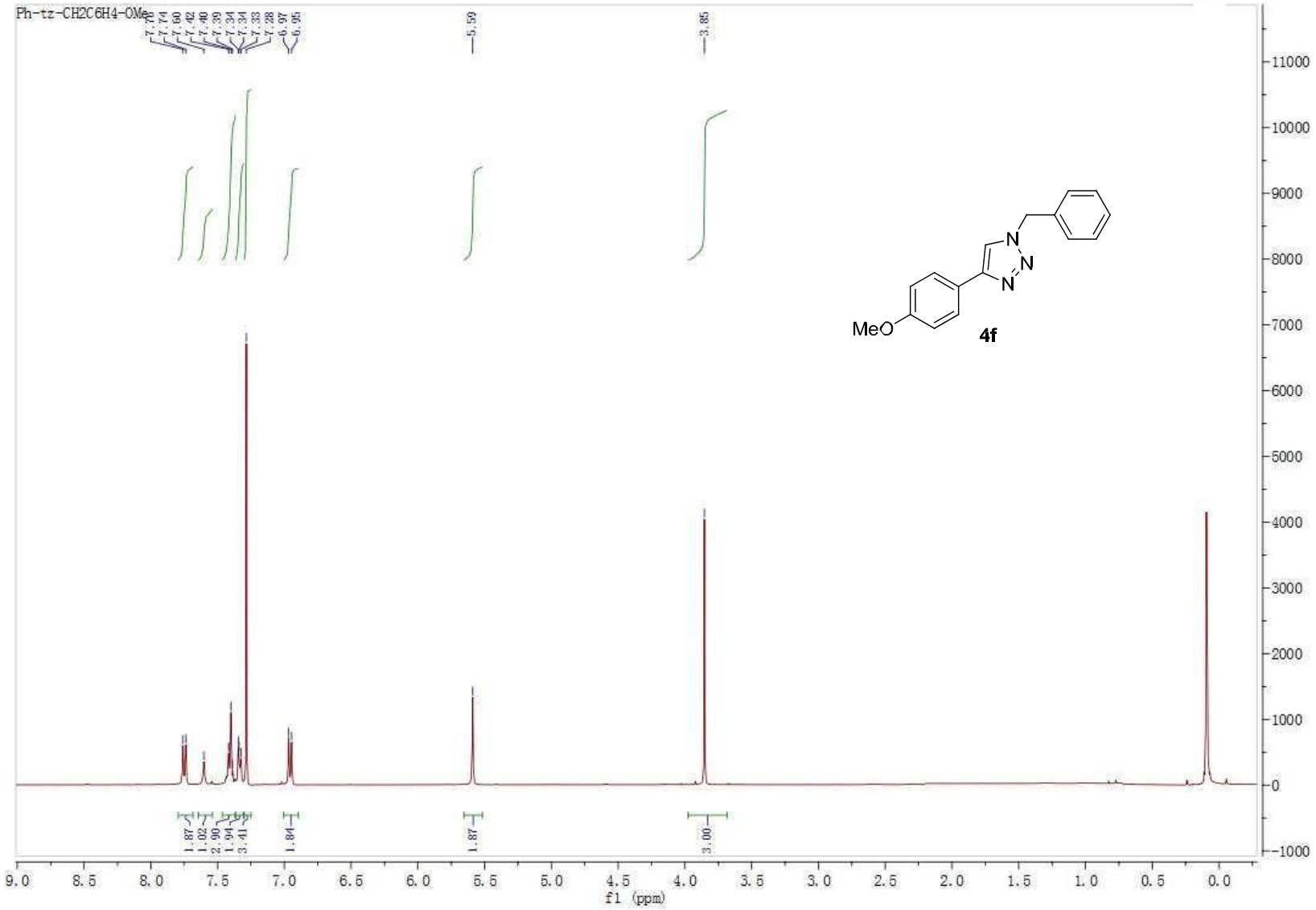


Fig. S12. 300 MHz ^{1}H NMR spectra of **4f** recorded in $CDCl_3$ at 298 K

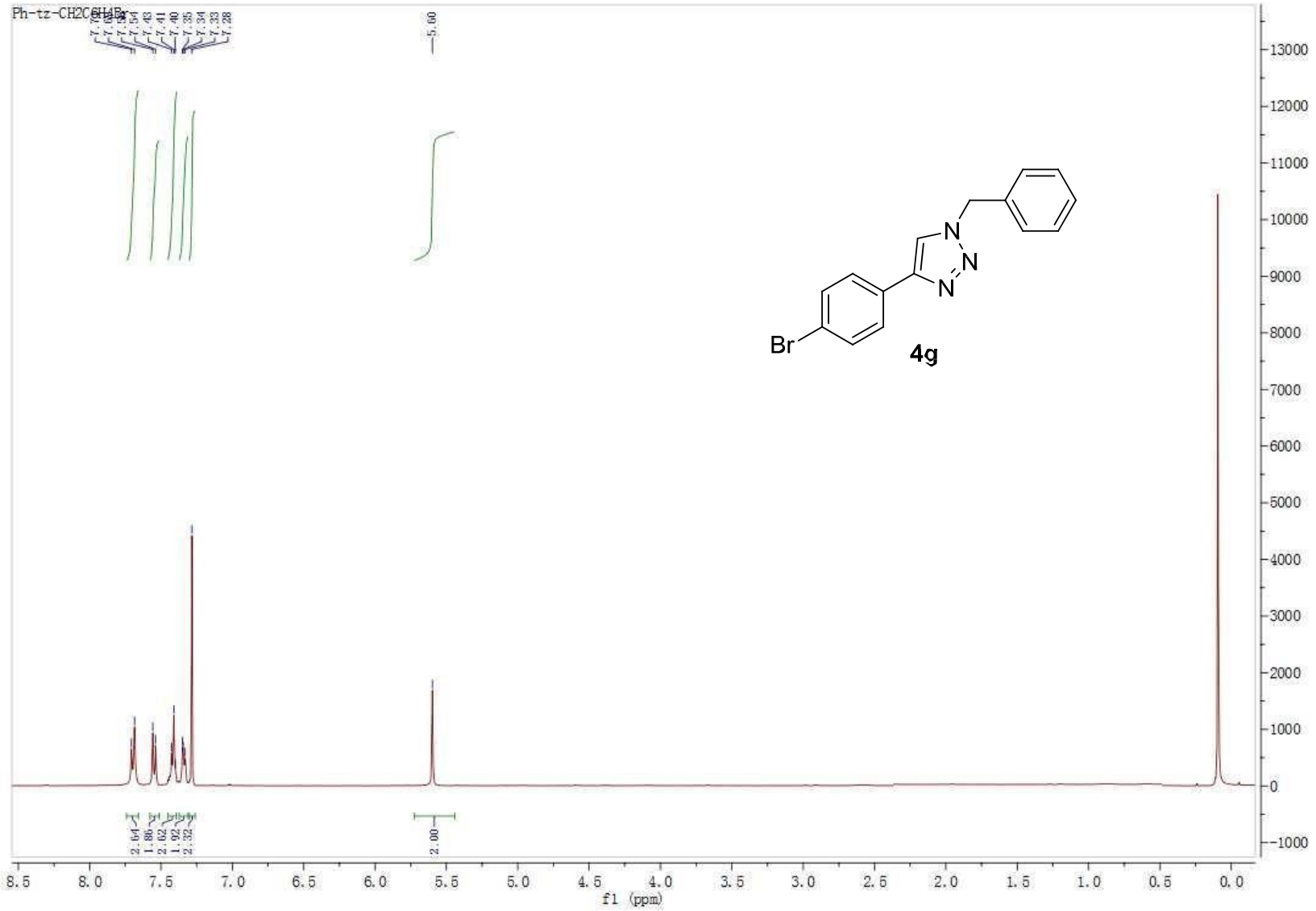


Fig. S13 300 MHz ^{1}H NMR spectra of **4g** recorded in $CDCl_3$ at 298 K

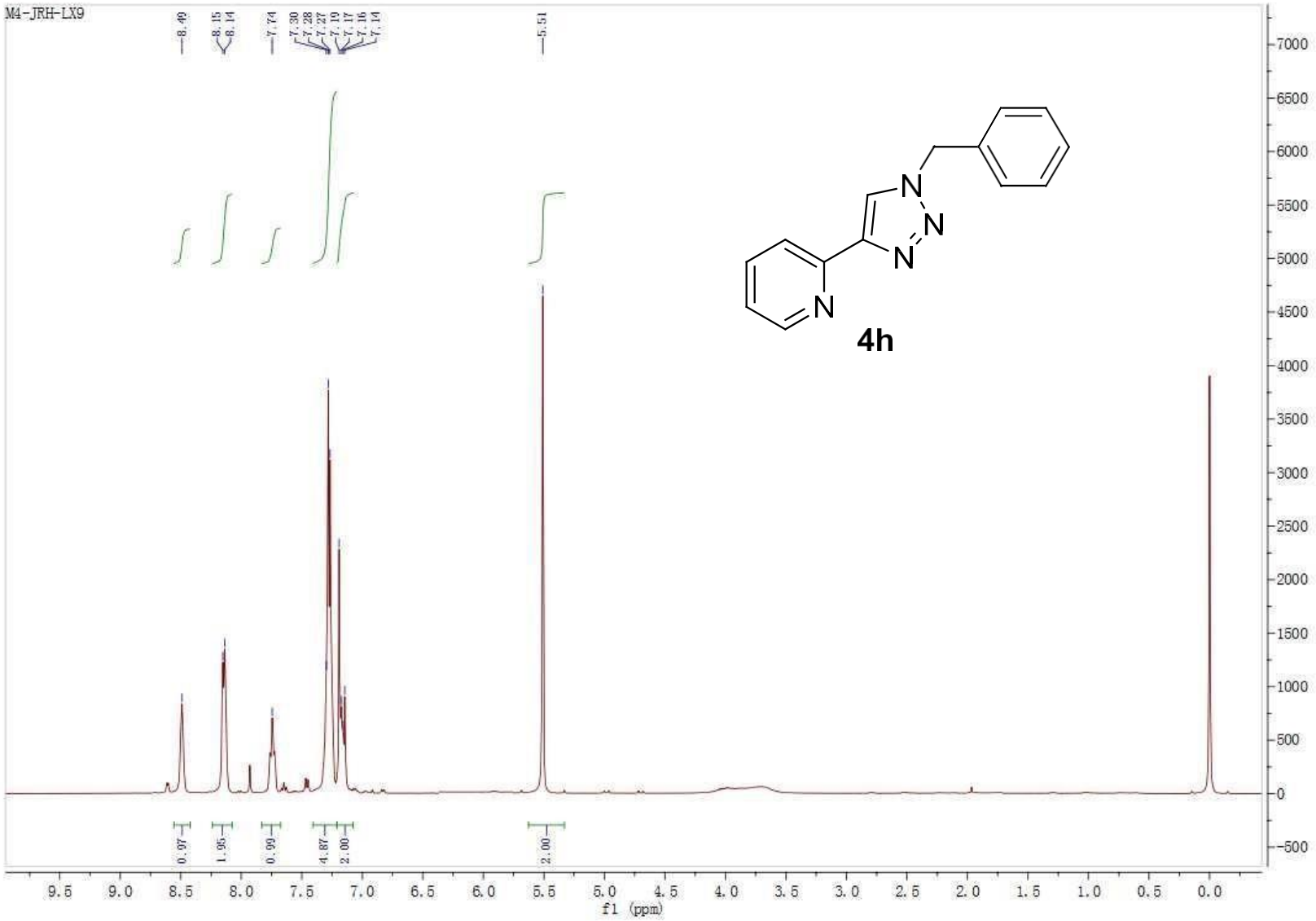


Fig. S14 300 MHz ^{1}H NMR spectra of **4h** recorded in $CDCl_3$ at 298 K

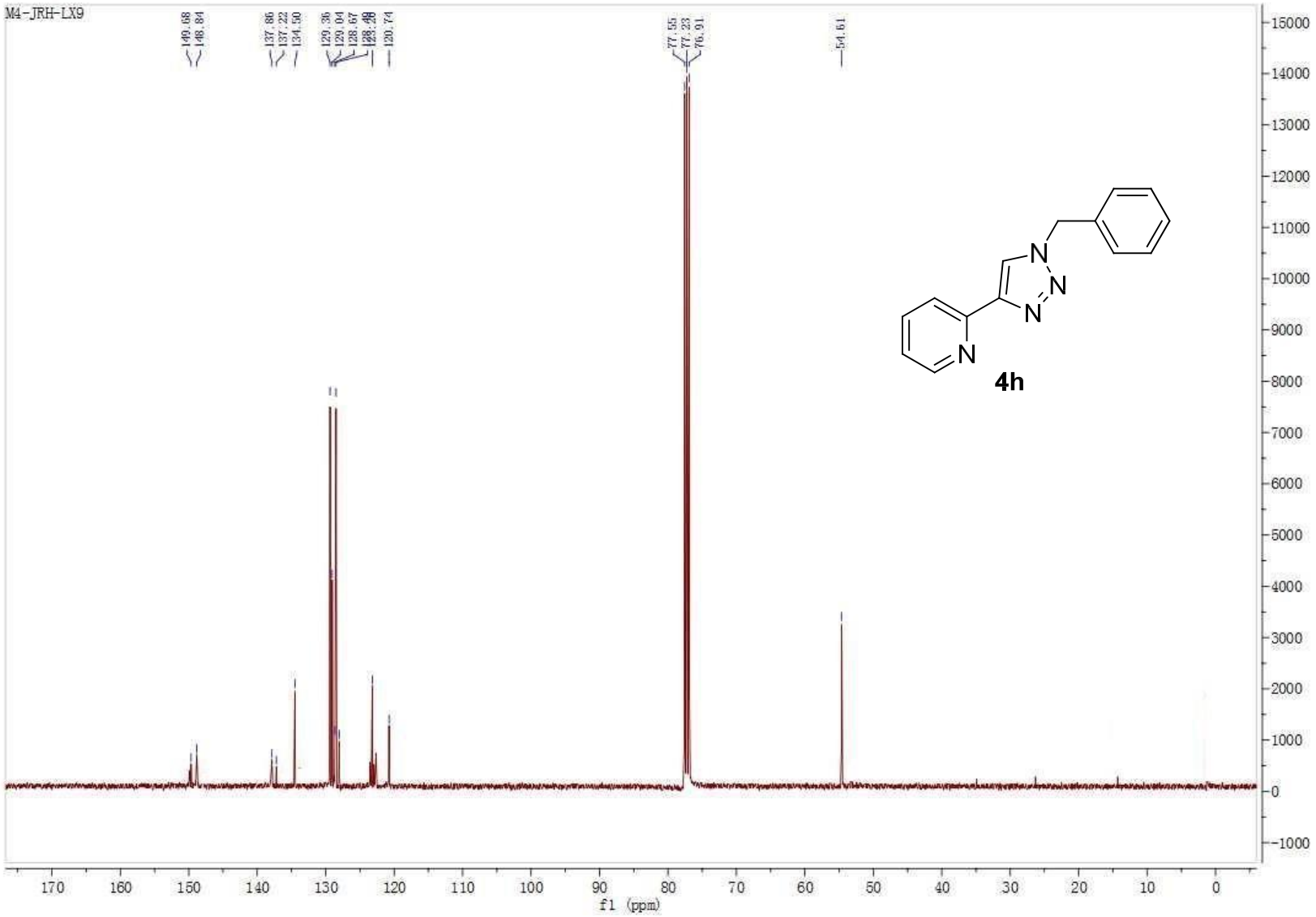


Fig. S15. 75 MHz ^{13}C NMR spectra of **4h** recorded in $CDCl_3$ at 298 K

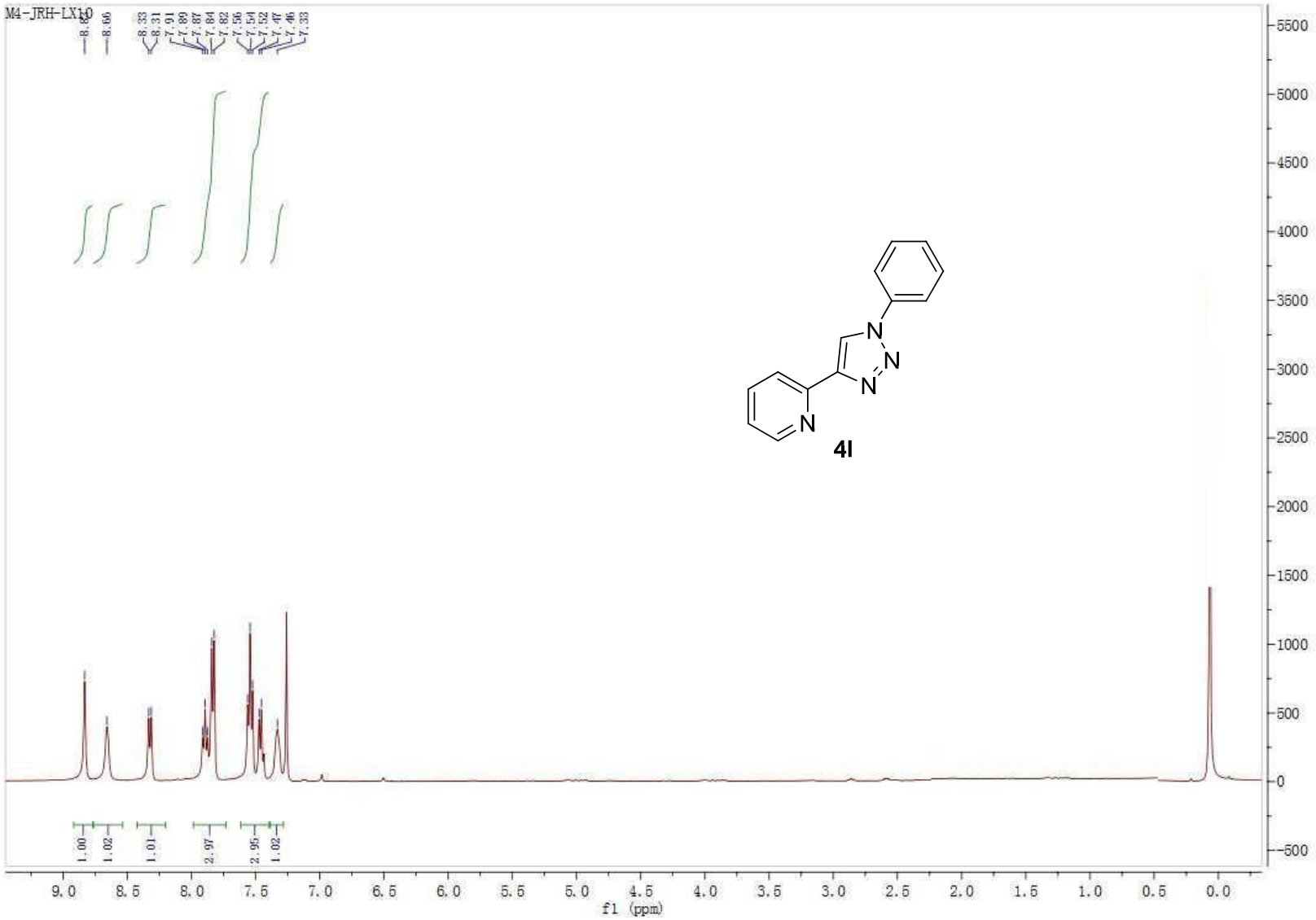


Fig. S16 300 MHz ^{1}H NMR spectra of **4i** recorded in $CDCl_3$ at 298 K

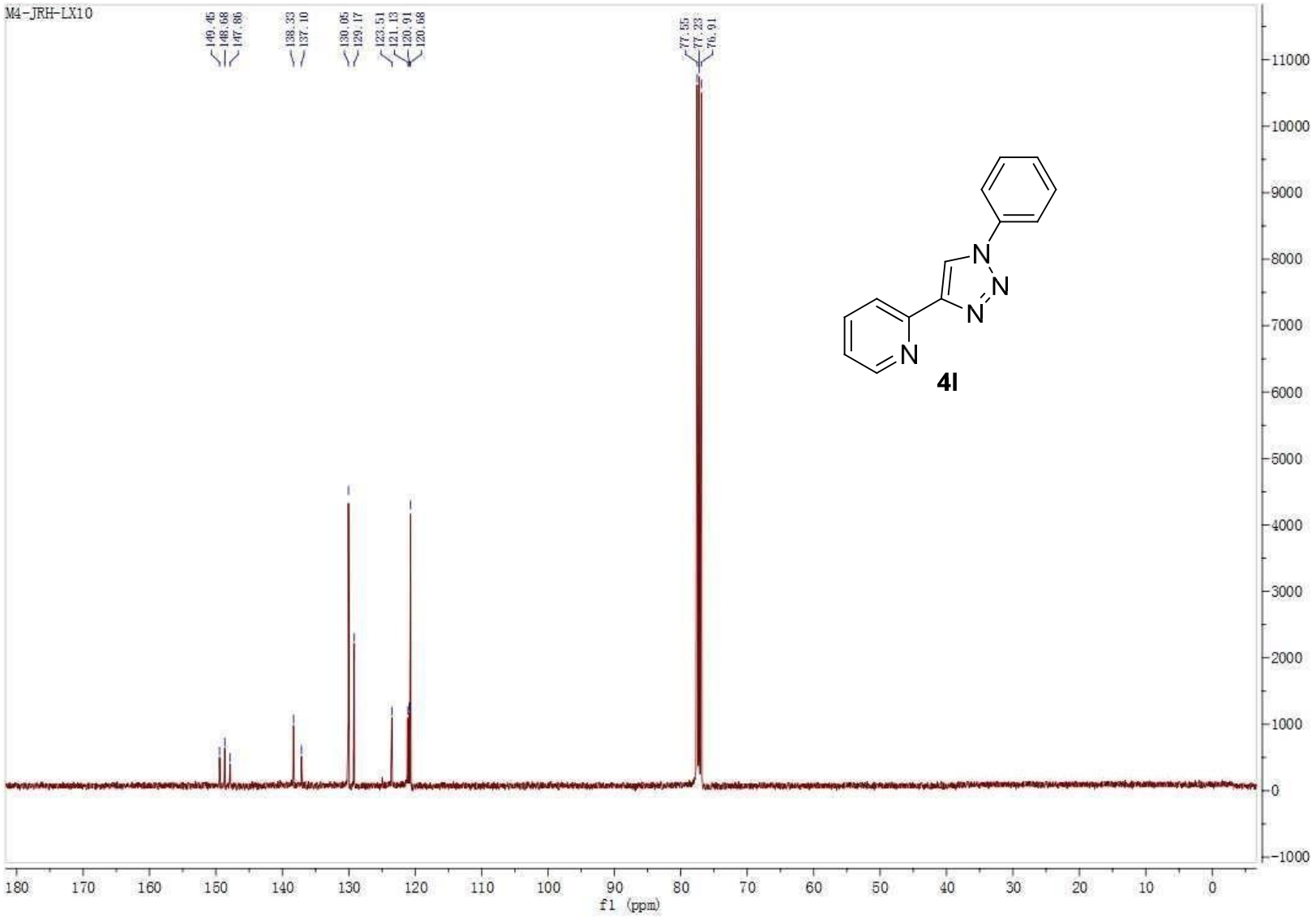


Fig. S17 75 MHz ^{13}C NMR spectra of **4i** recorded in $CDCl_3$ at 298 K

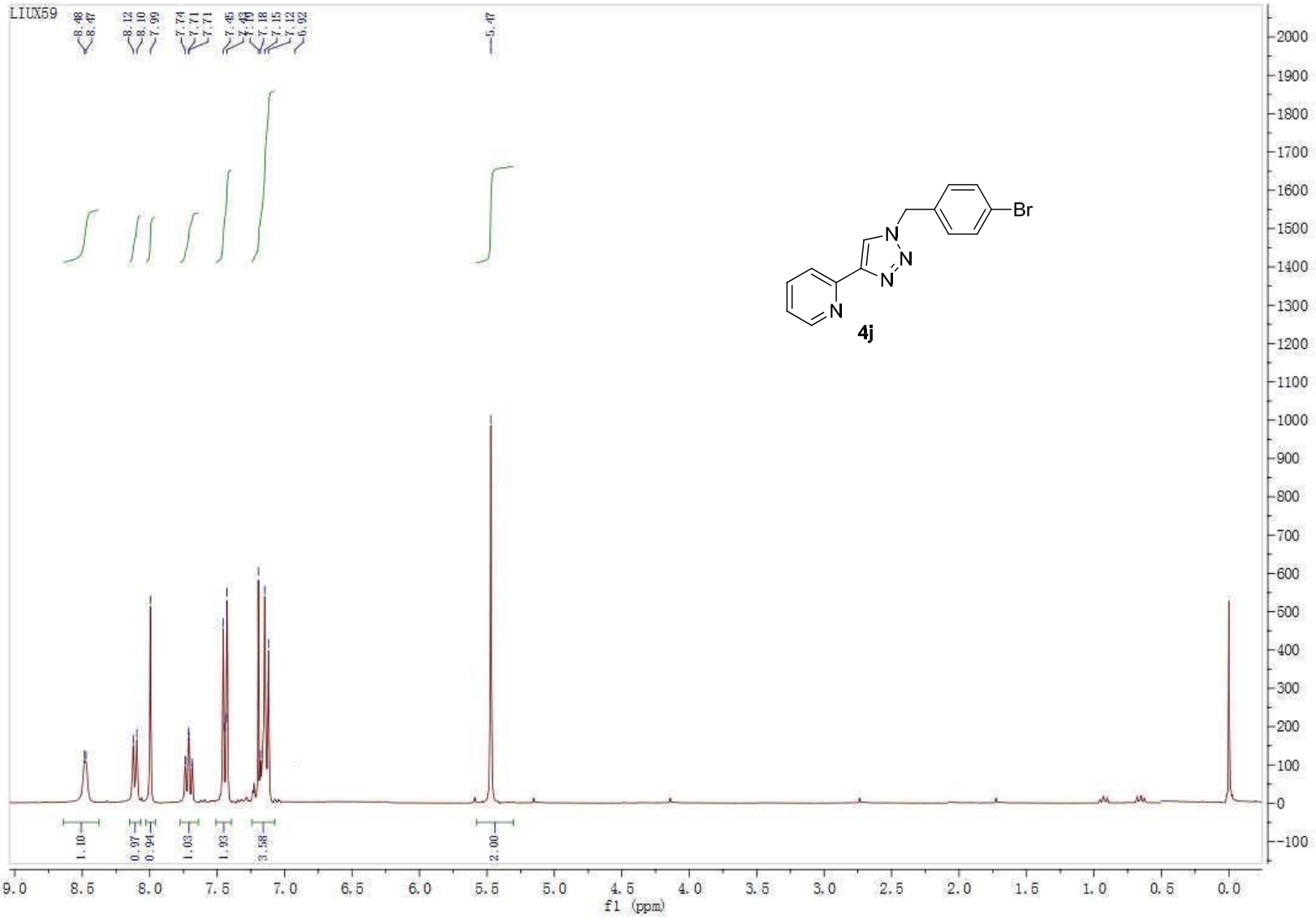


Fig. S18 300 MHz ^{1}H NMR spectra of **4j** recorded in $CDCl_3$ at 298 K

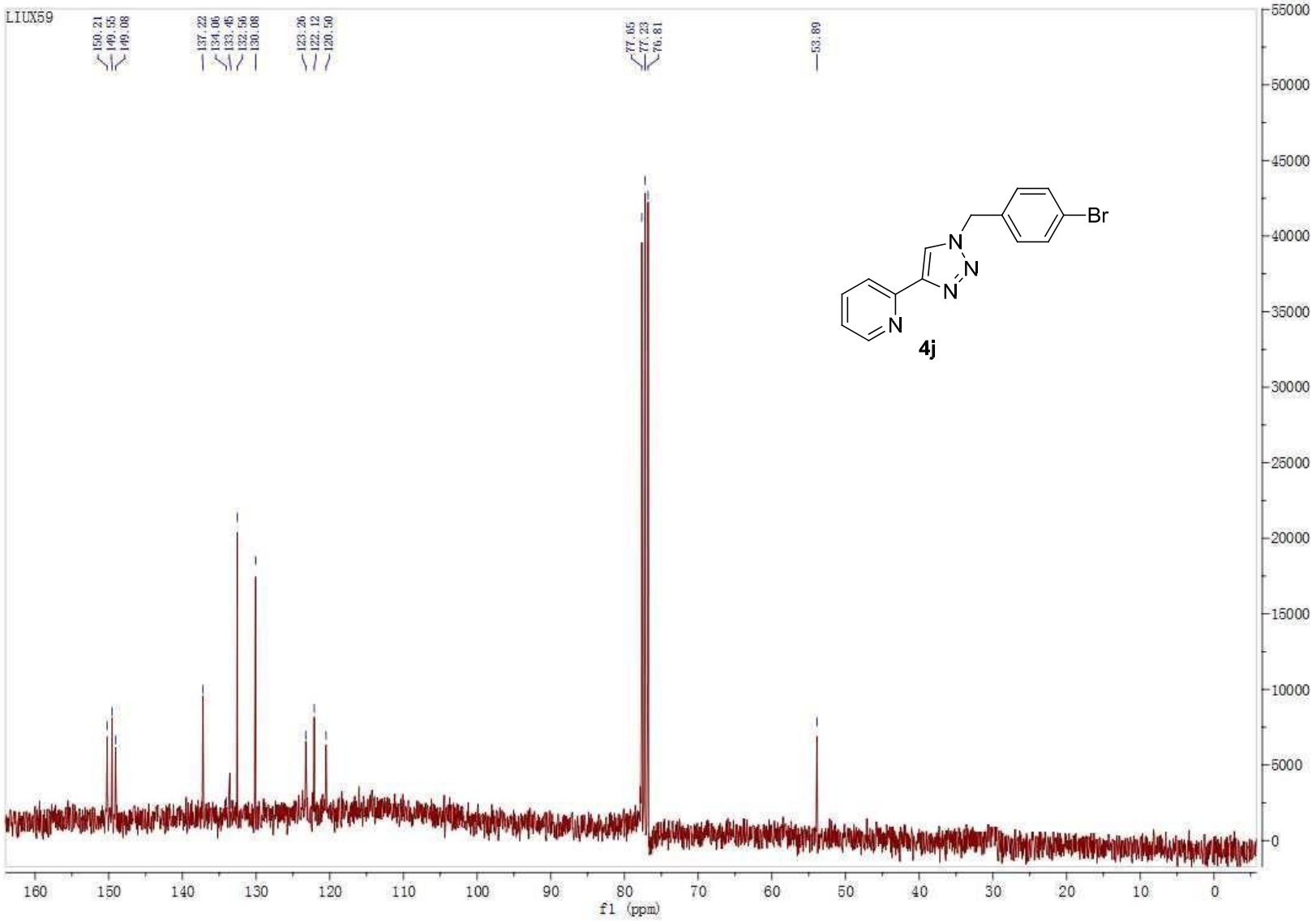


Fig. S19 75 MHz ^{13}C NMR spectra of **4j** recorded in $CDCl_3$ at 298 K

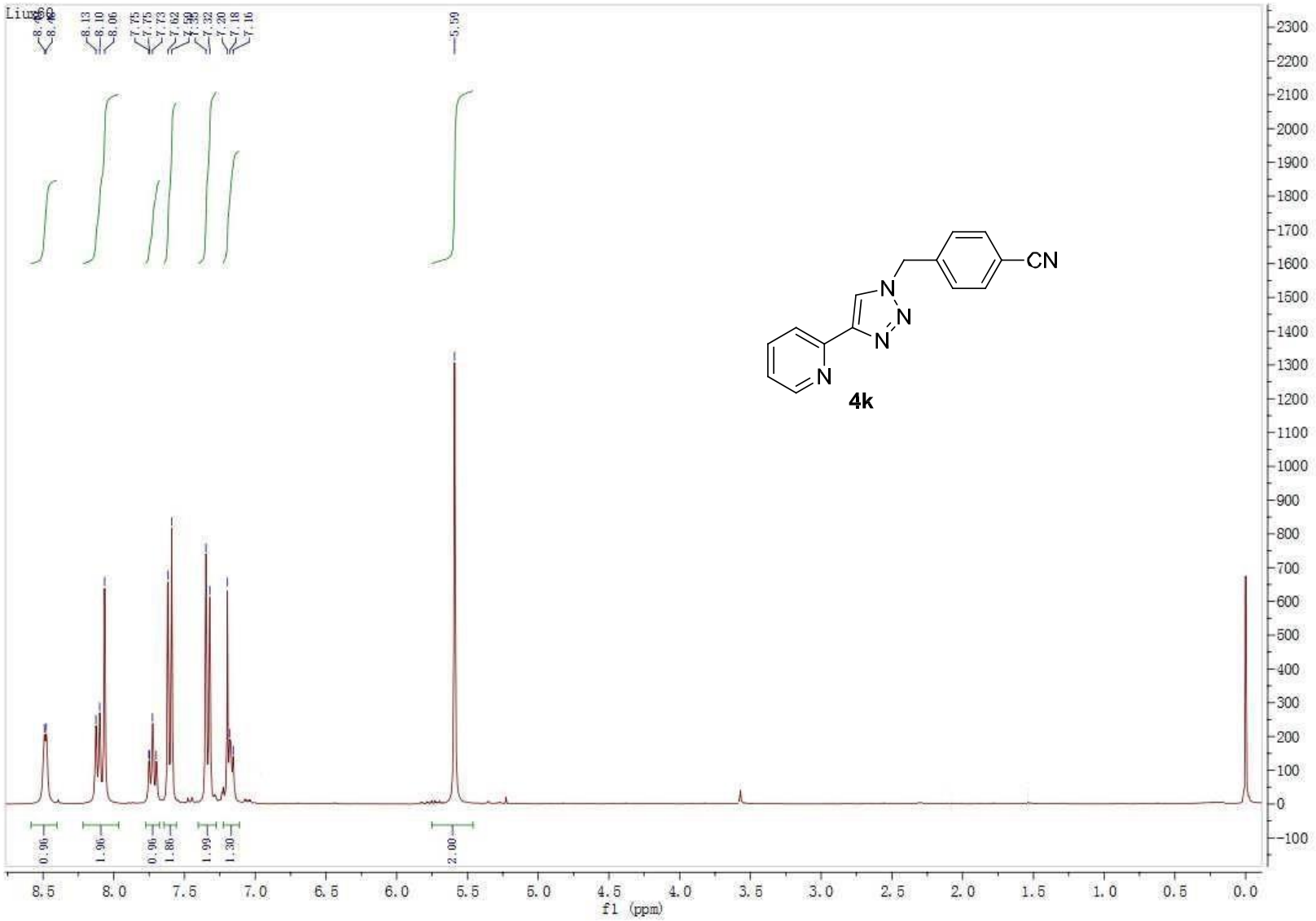


Fig. S20 300 MHz ^{1}H NMR spectra of **4k** recorded in $CDCl_3$ at 298 K

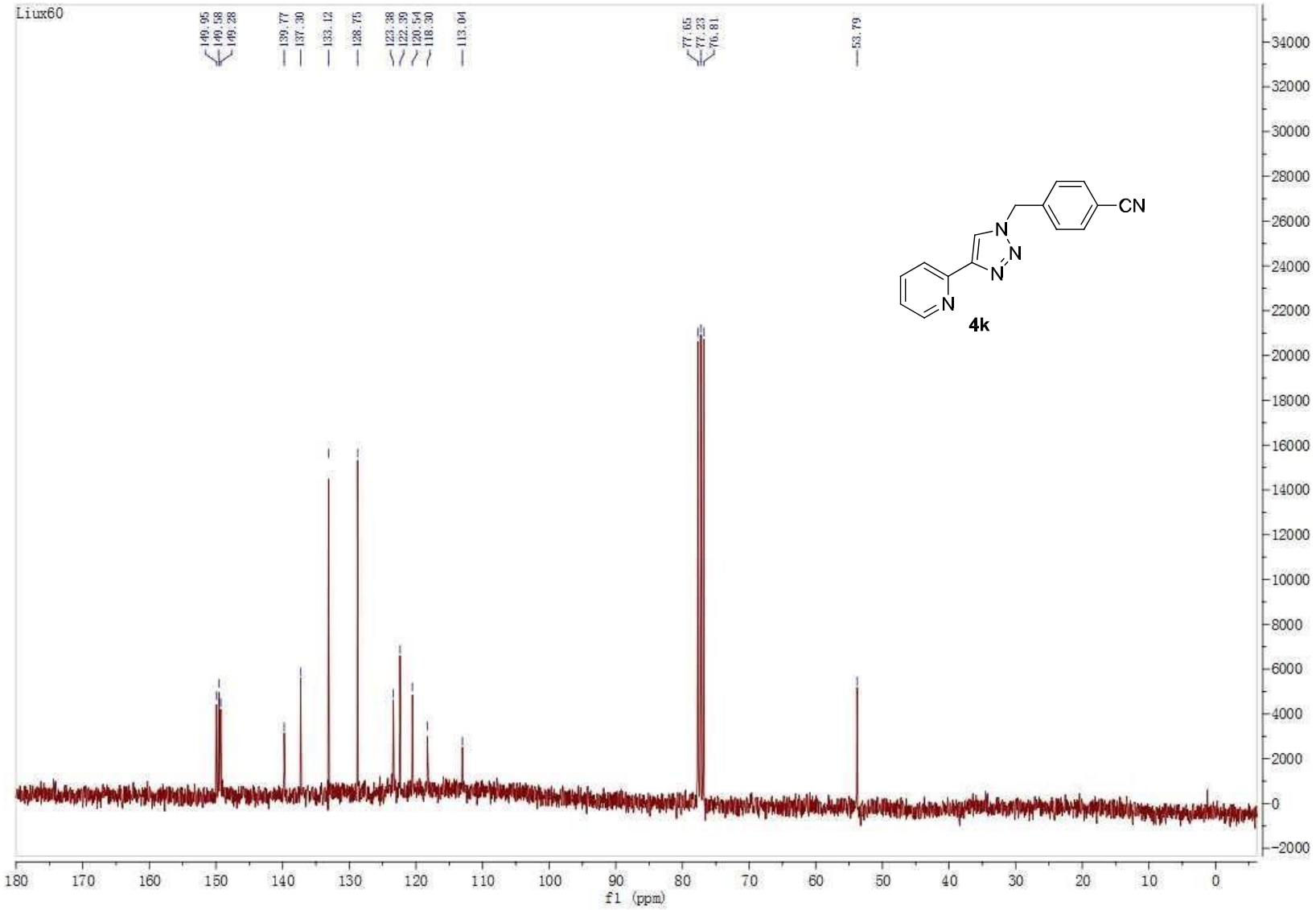


Fig. S21 75 MHz ^{13}C NMR spectra of **4k** recorded in $CDCl_3$ at 298 K

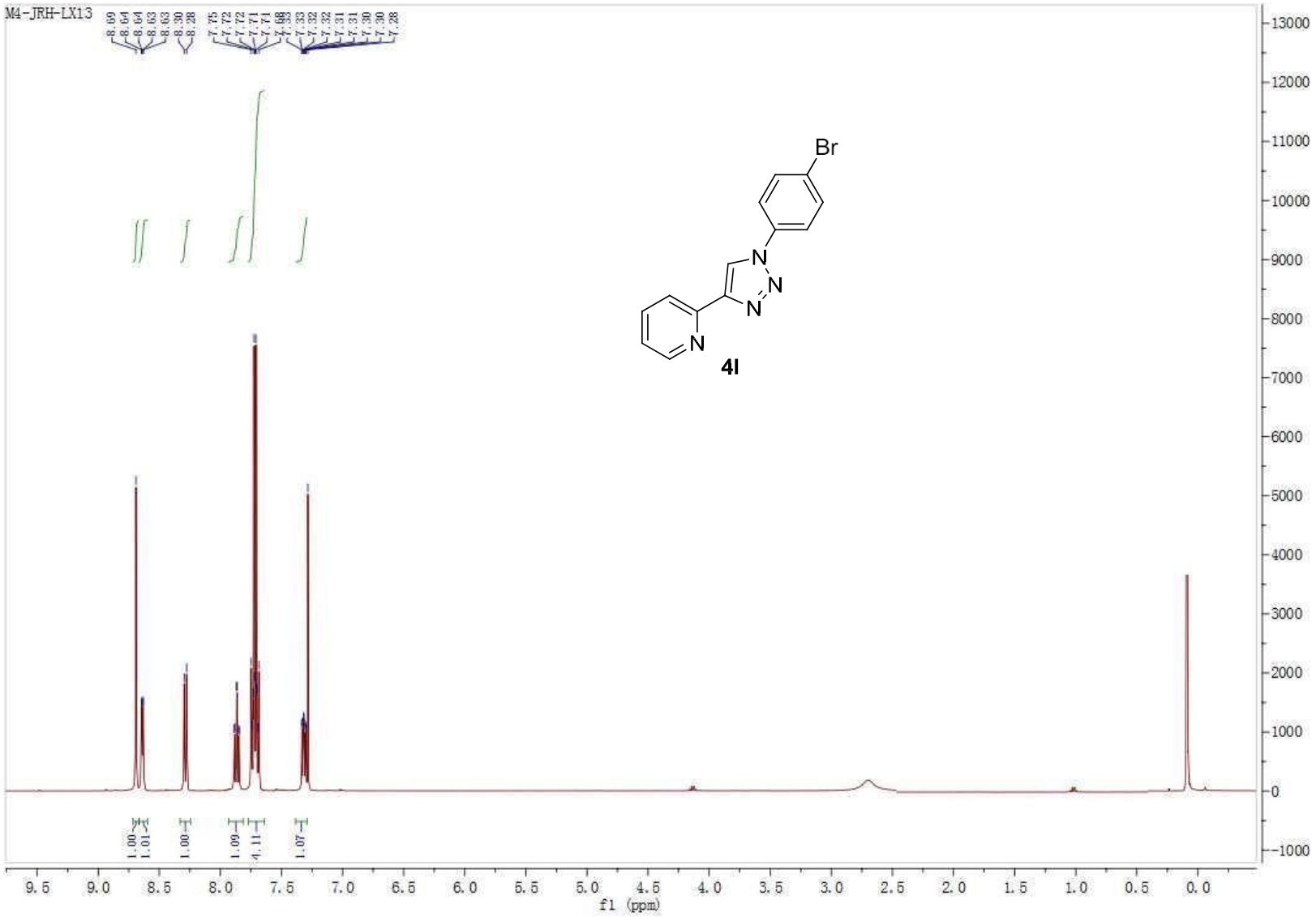


Fig. S22 300 MHz ^{1}H NMR spectra of **4l** recorded in $CDCl_3$ at 298 K

3.

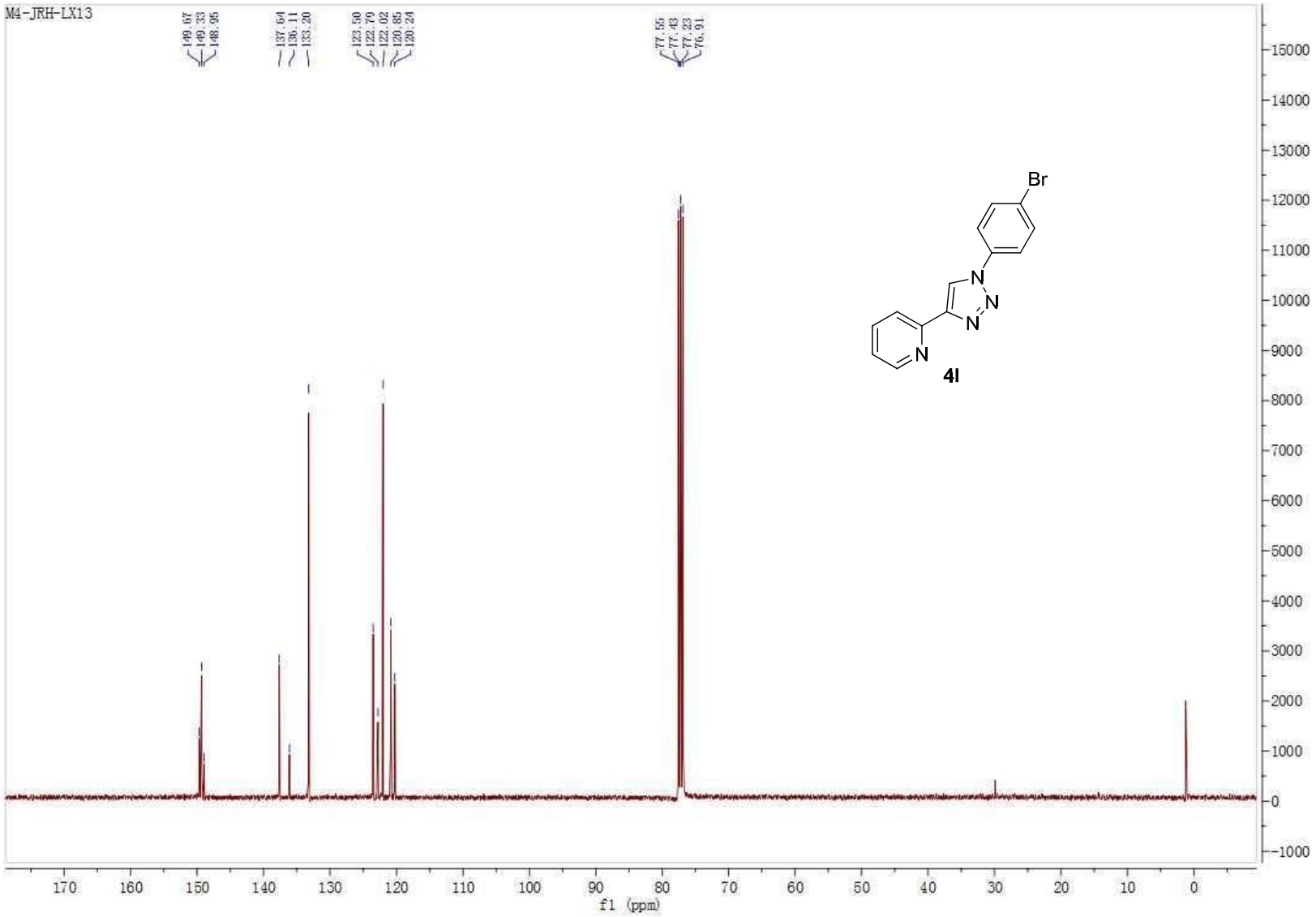


Fig. S23 75 MHz ^{13}C NMR spectra of **4l** recorded in $CDCl_3$ at 298 K

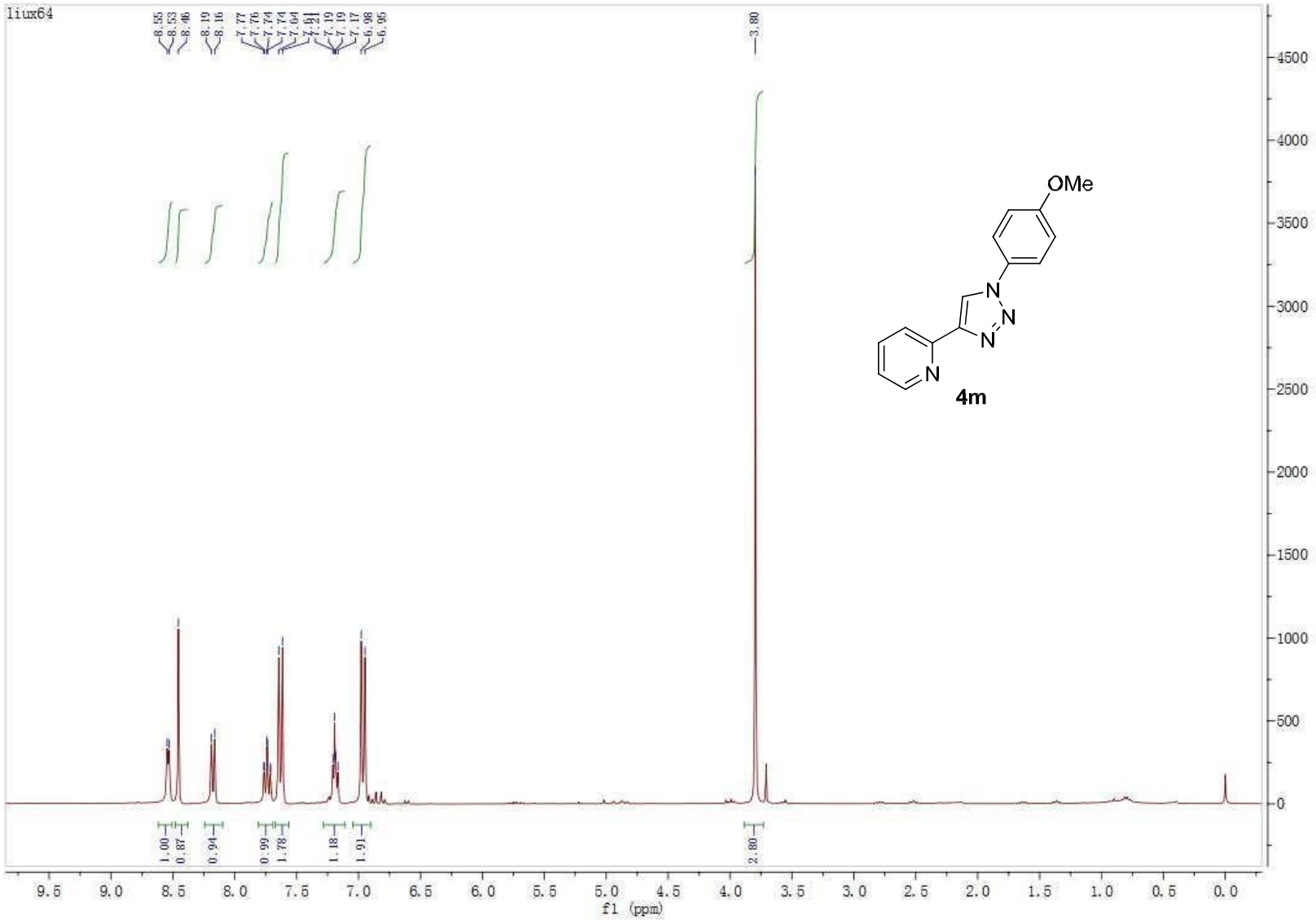


Fig. S24 300 MHz ^{1}H NMR spectra of **4m** recorded in $CDCl_3$ at 298 K

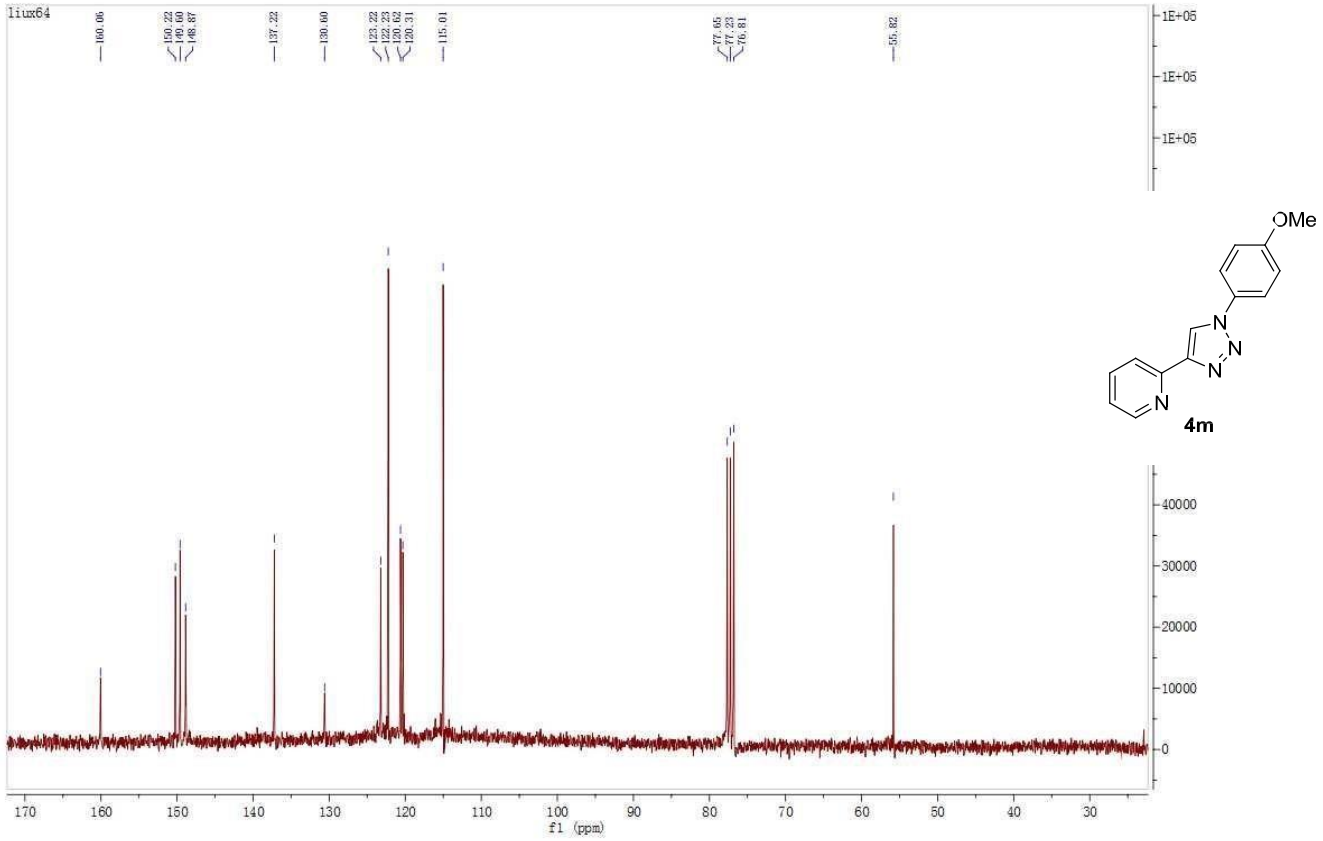


Fig. S25 75 MHz ^{13}C NMR spectra of **4m** recorded in $CDCl_3$ at 298 K

35