Electronic supplementary information

A novel magnetic nanoparticle as an efficient and recyclable heterogeneous catalyst for suzuki cross-coupling reaction

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1. General Remarks

All the solvents used in this experiment are commercially available for analysis. In the absence of special instructions, it means that there is no need for any treatment or purification before use. Sodium dichromate, nitric acid, sulfuric acid and tetraethyl orthosilicate (TEOS) were all purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd., acenaphthene, diglycolamine, cuprous iodide and propyl triethoxysilane isocyanate were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., N-bromosuccinamide (NBS), tetraphenylphosphine palladium, 2-aminomethylthiophene, cetyltrimethylammonium bromide (CTAB), palladium chloride, inorganic base. Organic base and silica gel used for column chromatography (300-400 mesh) were purchased from Shanghai Titan Technology Co., Ltd. Halogenated aromatic hydrocarbons and their derivatives, phenylboronic acid and their derivatives used in Suzuki-Miyaura coupling reaction were purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd.

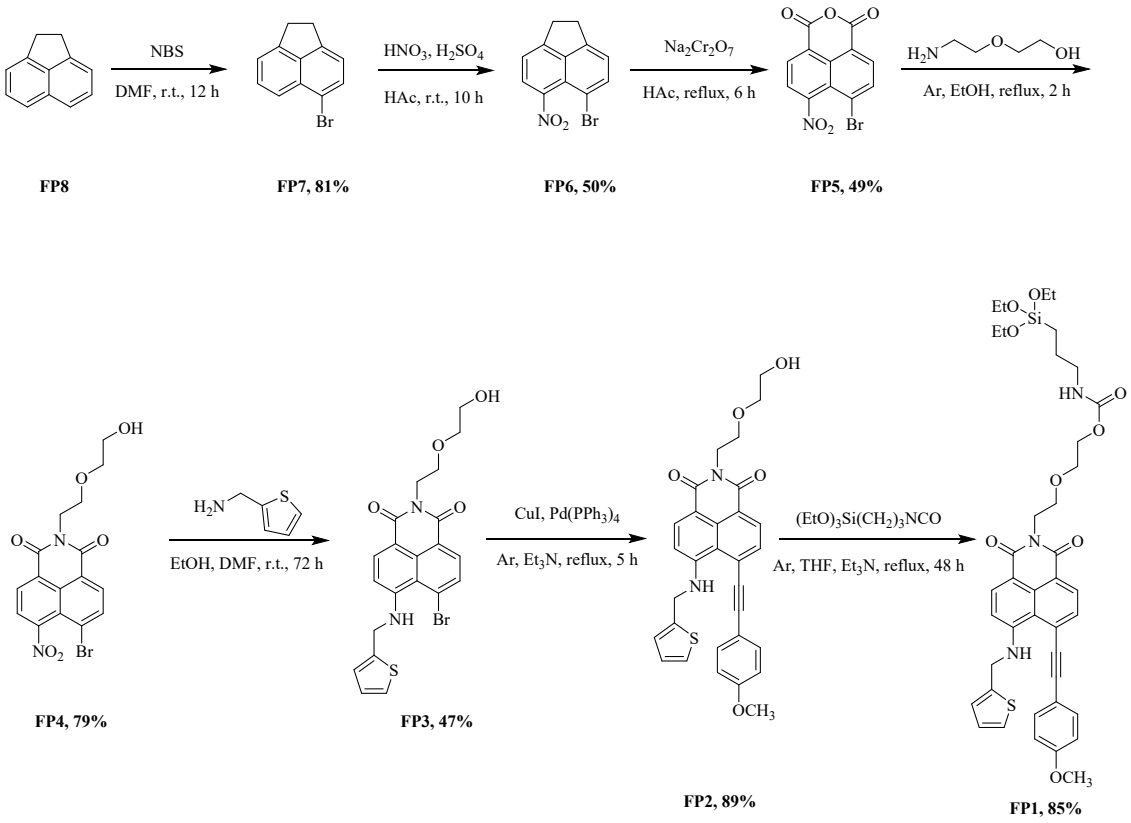
The nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) for the structural analysis of the compounds were collected by Bruker- AVANCE III 400 MHz nuclear magnetic resonance (TMS internal standard), the high-resolution mass spectrometry was provided by mass spectrometer Wates XEVO G2 TOF (ESI source, and the mass spectra of Suzuki-Miyaura coupling products were collected from gas chromatography-mass spectrometry (GC-MS). The infrared spectrum was measured by Thermo Fisher-Nicolet 6700. The palladium content was measured by plasma emission spectrometer Agilent ICP-OES 725. The elemental analysis of the sample was obtained by German Elementar Vario EL III element analyzer, the morphology images were obtained by transmission electron microscope JEOL JEM 2100 F, the element valence on the surface of the sample was characterized by X-ray photoelectron spectroscopy Thermo Fisher 6700 Xi, and the crystal structure of the sample was measured by X-ray diffractometer Bruker D8 Advance. The hysteresis loop of the sample is obtained by vibrating sample magnetometer Lake Shore 7404.

2. Synthesis of Fe_3O_4@FSM@Pd

Synthesis and characterization of Palladium Ion fluorescence probe FP1

The synthesis route of palladium ion fluorescence probe[1] is obtained from raw material acenaphthene FP8 through seven-step reactions. The key intermediate N-(2-(2-hydroxyethoxy) ethyl)-4-bromo-5-nitro-1-naphthalimide FP4 was prepared by bromination, nitration, oxidation of sodium dichromate and

reaction with diglycolamine. Then it was modified with 2-aminomethylthiophene and p-alkynyl anisole to prepare the palladium ion fluorescence probe FP2. Finally, FP2 was modified by propyl triethoxysilane isocyanate to prepare FP1, which bind to the silane on the surface of magnetic nanomaterials. The intermediates and products were characterized by ^{1}H-NMR, ^{13}C-NMR and some of them were characterized by mass spectrometry.



Scheme S1. The synthesis route of palladium ion fluorescence probe FP1.

Synthesis of Fe_3O_4@SiO_2

To a stirred solution of $FeCl_3 \cdot 6H_2O$ (2 g, 7.4 mmol) in 35mL ethylene glycol was added anhydrous sodium acetate (2 g, 24.4 mmol). The mixture was stirred at room temperature for 0.5 h and 200 °C for 8 h. The supernatant was removed by centrifugation, washed with ethanol for three times, and dried in an infrared oven to obtain nanometer ferric oxide (nano Fe_3O_4). Next, to a stirred solution of cetyltrimethyl ammonium bromide (CTAB, 1.5 g, 3.8 mmol) in 10 mL water was added the above nano Fe_3O_4 (200 mg). The mixture was mechanically stirred at 60 °C for 0.5 h. To a mechanically stirred mixture were slowly added 2M NaOH aqueous solution (60 mL) and tetraethyl orthosilicate (TEOS, 2

mL) at 70 °C for 3 h. The solid crude product was magnetically separated, and was washed with ethanol for three times, and then dried in an infrared oven to give magnetic nanomaterials (Fe_3O_4@ SiO_2).

Synthesis of Fe_3O_4@FSM

A mixture of Silanization probe FP1 (10 mg, 0.01 mmol) and dried and activated Fe_3O_4@SiO_2 (particle size about 100 nm) in anhydrous ethanol (20 mL) was stirred at and refluxed for 72 h under argon. After stopping the reaction, the solid crude product was magnetically separated, and washed with ethanol until the supernatant was no fluorescence, and then dried in an infrared oven to give the black solid (Fe_3O_4@FSM).

Synthesis of Fe_3O_4@FSM@Pd

To a stirred aqueous solution of 10 M palladium chloride ($PdCl_2$, 100 mL) was added Fe_3O_4@FSM (2 g). The mixture was stirred at room temperature for 3 h. The solid crude product was magnetically separated, and washed with water for three times, and then drying in infrared oven to give the black solid (Fe_3O_4@FSM@Pd).

3. Characterization of Fe_3O_4@FSM@Pd

FT-IR characterization

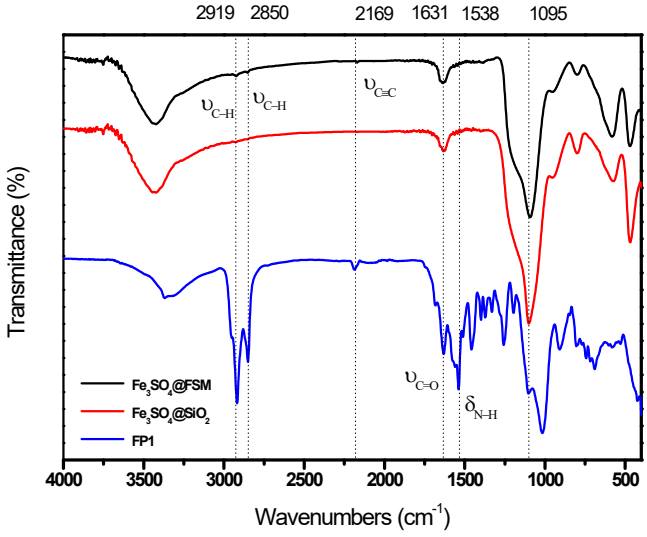
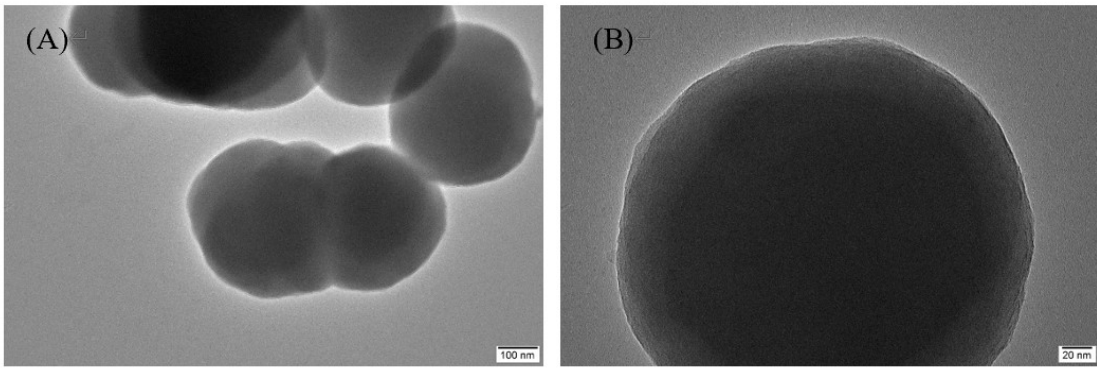


Fig. S1. The FT-IR spectra of FP1, Fe_3O_4@SiO_2 and Fe_3O_4@FSM.



TEM characterization

Fig. S2. The TEM images of Fe_3O_4@FSM.

DLS characterization

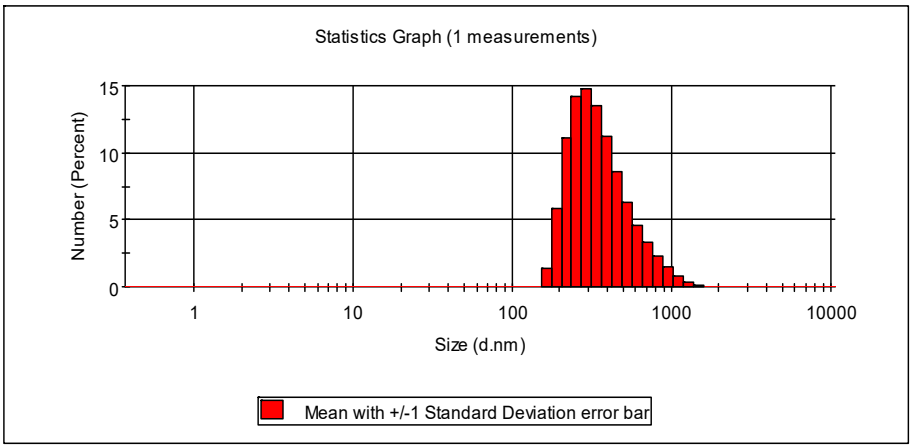


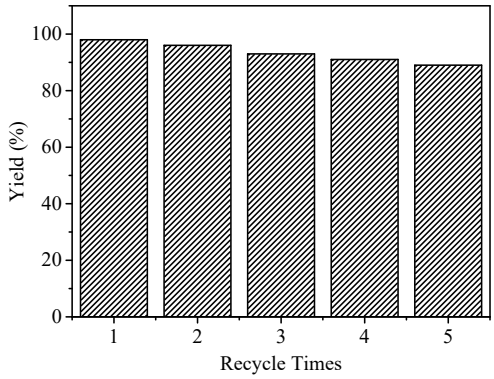
Fig. S3. The DLS image of Fe_3O_4@FSM.

4. General Procedure for Suzuki-Miyaura Cross-Coupling Catalyzed by Fe_3O_4@FSM@Pd

Halogenated aromatic hydrocarbons (1.0 mmol), phenylboronic acid or their derivatives (1.5 mmol), catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%), *N, N*-diisopropylamine ($(i\text{-}Pr)_2NH$, 0.35 mL, 2.5mmol) were mixed in pure water (2 mL). The mixture was stirred at 100 °C for 30 min under air. The catalyst was separated and recovered from the reaction solution by external magnetic field. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid. The products were confirmed by ^{1}H-NMR and ^{13}C-NMR.

5. Study on the conditions of catalytic activity of different heterocyclic substrates

Halogenated aromatic hydrocarbons (1.0 mmol), Heteroarylboronic acid (1.5 mmol), catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%), *N, N*-diisopropylamine ((i-Pr)$_2$NH, 0.35 mL, 2.5mmol) were mixed in pure water (2 mL). The mixture was stirred at 100 ^oC for 30 min under air. The catalyst was separated and recovered from the reaction solution by external magnetic field. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid. The products were confirmed by ^{1}H-NMR and ^{13}C-NMR.



6. Catalyst Recycling and Reuse

Fig. S4. Recyclability of Fe_3O_4@FSM@Pd.

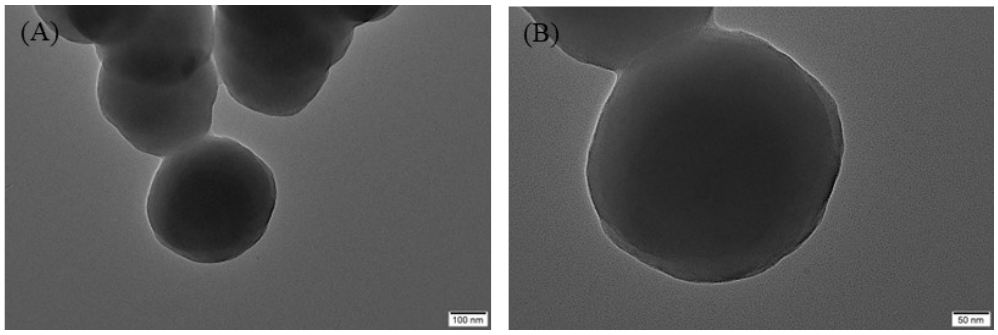


Fig. S5. The TEM images of the recycled Fe_3O_4@FSM@Pd.

Table S1 Elemental analysis results of unused Fe_3O_4@FSM@Pd and recycled Fe_3O_4@FSM@Pd.

Sample	N (%)	C (%)	H (%)	S (%)
Fe_3O_4@FSM@Pd [a]	0.78	3.80	1.35	0.16
Fe_3O_4@FSM@Pd [b]	0.62	3.42	1.34	0.17

[a] unused Fe_3O_4@FSM@Pd. [b] The catalyst Fe_3O_4@FSM@Pd was reused 5 time.

4-bromoanisole (125 μL, 1.0 mmol), phenylboric acid (183 mg, 1.5 mmol), catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%), *N, N*-diisopropylamine ((i-Pr)$_2$NH, 0.35 mL, 2.5 mmol) were mixed in pure water (2 mL). The mixture was stirred at 100 °C for 30 min under air. The catalyst was separated and recovered from the reaction solution by external magnetic field. The catalyst was separated and recovered from the reaction solution by external magnetic field. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid. Wash the catalyst with water and ethanol at the end of each reaction, and then use it for the next time after drying in the infrared oven. The catalyst can be reused for 5 times without a significant loss of activity. The product was confirmed by ^{1}H-NMR, ^{13}C-NMR and gas chromatography-mass spectrometry (GC-MS).

7. Maitlis' filtration test

Firstly, 4-bromoanisole (125 μL, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%), *N, N*- diisopropylamine ((i-Pr)$_2$NH, 0.35 mL, 2.5 mmol), were mixed in pure water (2mL). The mixture was stirred at 100 °C for 10 min under air. The catalyst was separated from the reaction solution by an external magnetic field, and then the reaction solution was stirred at 100 °C for 1 h under air. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid.

Secondly, the catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%) and *N, N*-diisopropylamine ((i-Pr)$_2$NH, 0.35 mL, 2.5 mmol) were mixed in pure water (2 mL). The mixture was stirred at 100 °C for 30 min under air. The catalyst was separated from the reaction solution by an external magnetic field, and then 4-bromoanisole (125 μL, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) were added to the filtrate. The mixture was stirred at 100 °C for 30 min under air. The crude product was diluted with

dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid.

8. Kinetic experiment of catalytic reaction

The three mixtures of 4-bromoanisole (125 μL, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), N, N-diisopropylamine ($(i\text{-}Pr)_2NH$, 0.35 mL, 2.5 mmol) in pure water (2 mL) were added with different amounts of catalyst Fe_3O_4@FSM@Pd (5 mg, 0.1 mol%; 10 mg, 0.2 mol%, 25 mg, 0.5 mol%, respectively). The three mixtures were stirred at 100 ^oC for 5 min, 10 min, 15 min, 20 min, 25 min and 30 min respectively under air. The catalyst was separated and recovered from the reaction solution by external magnetic field. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid. The product was confirmed by ^1H-NMR and ^{13}C-NMR.

9. Phase trajectory test

Phenylboronic acid (366 mg, 3.0 mmol), catalyst Fe_3O_4@FSM@Pd (10 mg, 0.2 mol%) or palladium acetate ($Pd(OAc)_2$, 0.2 mg, 0.2 mol%) and N, N-diisopropylamine ($(i\text{-}Pr)_2NH$, 0.7 mL,5.0 mmol) were mixed in pure water (4 mL). To a stirred of mixtures were added bromobenzene (0.15 mL, 1.0 mmol) and 4-bromoacetophenone (199 mg, 1.0 mmol) at 100 ^oC for different times under air. The catalyst was separated and recovered from the reaction solution by an external magnetic field. The crude product was diluted with dichloromethane, washed with water, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 100/1, v/v) to give products as the white powdery solid. The phase trajectory curves of the two catalysts were compared with the isolated yields of the two products.

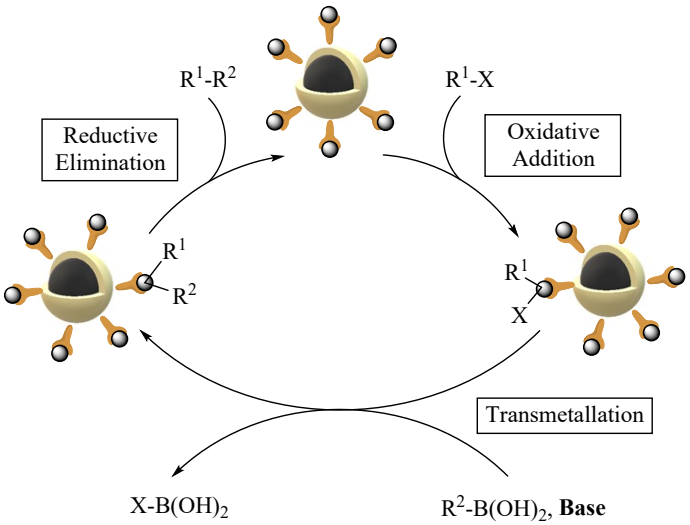
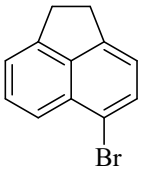


Fig. S6. The proposed mechanism for Fe_3O_4@FSM@Pd in Suzuki reaction.

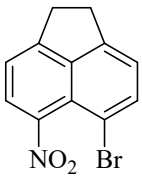
10. Spectroscopic data of fluorescence probe

FP**7:**



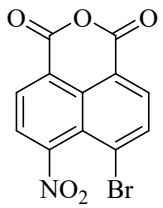
Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 1H), δ 7.61 (d, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 1H) , 7.08 (t, *J* = 7.6 Hz, 1H), 3.38-3.34 (m, 2H), 3.29-3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.27, 145.98, 140.29, 130.90, 129.08, 121.77, 120.20, 120.07, 116.80, 30.65, 29.94.

FP**6:**



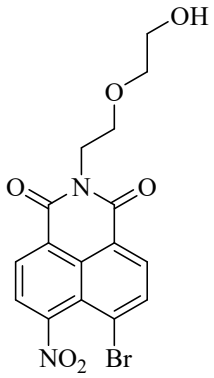
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 3.46-3.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.41, 146.49,144.74, 141.22, 136.25, 125.36, 122.23, 121.39, 118.83, 111.58, 30.61, 30.16.

FP**5:**



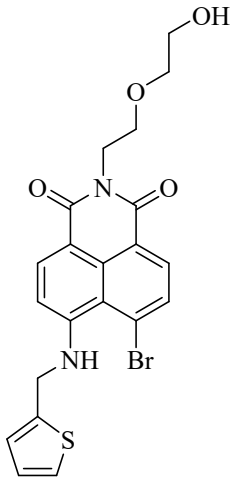
Reddish brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (d, J = 7.6 Hz, 1H), 8.48-8.8.42 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.23, 159.62, 160.98, 136.91, 133.65, 132.92, 132.64, 125.11, 123.92, 123.88, 120.57, 120.43

FP**4:**



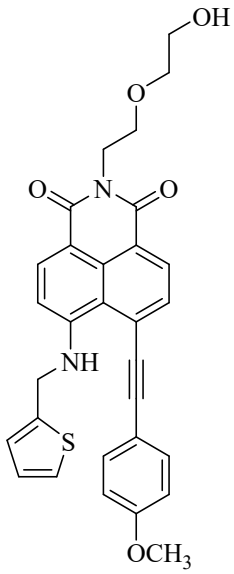
Brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63 (d, J = 8.0 Hz, 1H), 8.44-8.36 (m, 3H), 4.53 (m, 1H), 4.23 (t, J = 6.4 Hz, 2H), 3.67 (t, J = 6.4 Hz, 2H), 3.47 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.98, 162.27, 150.61, 136.66, 132.38, 131.53, 130.39, 126.14, 124.87, 122.96, 120.24, 72.60, 67.11, 60.64.

FP**3:**



Brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.22 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.05 (t, J = 5.6 Hz, 1H), 8.90 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 5.2 Hz, 1H) , 7.23 (d, J = 4.4 Hz, 1H) , 7.04 (t, J = 4.0 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 4.85 (d, J = 5.6 Hz, 2H), 4.58 (s, 1H), 4.16 (t, J = 6.4 Hz, 2H) , 3.61 (t, J = 6.4 Hz, 2H) , 3.46 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.58, 162.95, 149.99, 141.08, 134.45, 132.54, 132.01, 131.42, 127.57, 126.74, 126.04, 125.07, 122.02, 117.81, 109.63, 107.41, 72.55, 67.37, 60.65, 42.66, 39.02 .

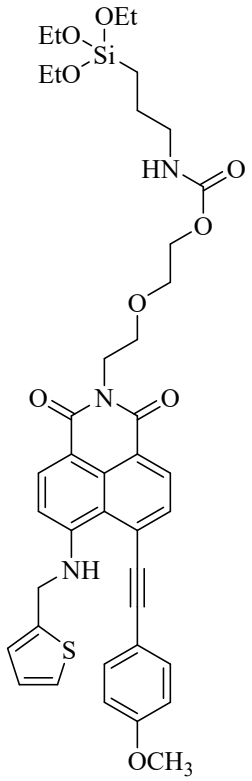
FP2:



Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39-8.35 (m, 2H), 8.32 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 4.4 Hz, 1H), 7.31 (d, J = 2.8 Hz, 1H) , 7.16 (d, J = 8.8 Hz, 2H) , 7.08-7.06 (m, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 4.86 (d, J = 4.4 Hz, 2H), 4.58 (t, J = 6.0 Hz, 1H), 4.19

(t, *J* = 6.4 Hz, 2H) , 3.82 (s, 3H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.47 (d, *J* = 2.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.57, 164.23, 160.63, 150.33, 138.95, 134.94, 133.06, 131.96, 130.86, 130.25, 127.24, 126.06, 124.08, 122.06, 118.48, 114.24, 113.17, 110.17, 105.26, 101.19, 88.24, 72.28, 68.66, 61.91, 55.43, 43.11, 39.37 .

FP1:



Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.48 (m, 3H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.98 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.81-6.78 (m, 3H), 5.02(s, 1H), 4.75 (d, *J* = 4.4 Hz, 2H), 4.42 (t, *J* = 6.4 Hz, 2H), 4.18(t, *J* = 4.4 Hz, 2H), 3.85-3.80 (m, 11H), 3.74-3.72 (t, *J* = 4.4 Hz, 2H), 3.14(q, *J* = 6.4 Hz, 2H), 1.25-1.19 (m, 9 H), 0.87(q, *J* = 6.4 Hz, 2H), 0.62(q, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.31, 162.96, 161.54, 159.61, 155.39, 149.30, 138.00, 133.80, 132.03, 130.98, 129.91, 129.16, 126.20, 125.00, 123.01, 121.22, 117.61, 113.22, 112.17, 109.31, 104.22, 100.09, 87.19, 68.13, 66.96, 63.13, 57.44, 57.42, 54.39, 54.37, 42.44, 42.10, 37.82, 35.47, 30.41, 28.68, 22.27, 17.41, 17.27, 6.57. MS (HR-ESI) *m/z*, calcd. For [$C_{40}H_{47}N_3O_9SSi$ + Na^+] 796.2694, found 796.2691.

11. ^{1}H NMR and ^{13}C NMR spectra of fluorescence probe

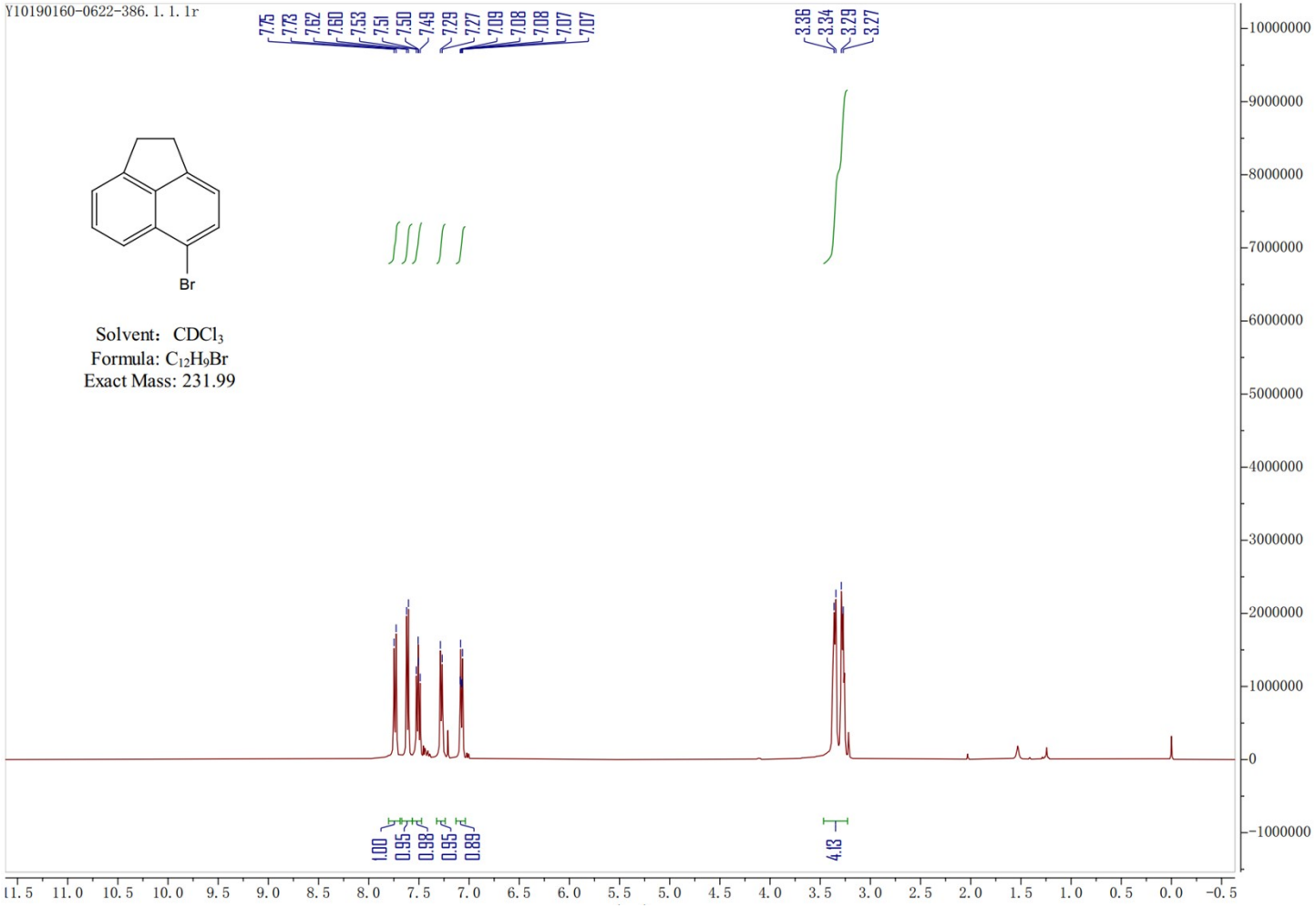


Fig. S7. The ^{1}H NMR spectrum of FP7

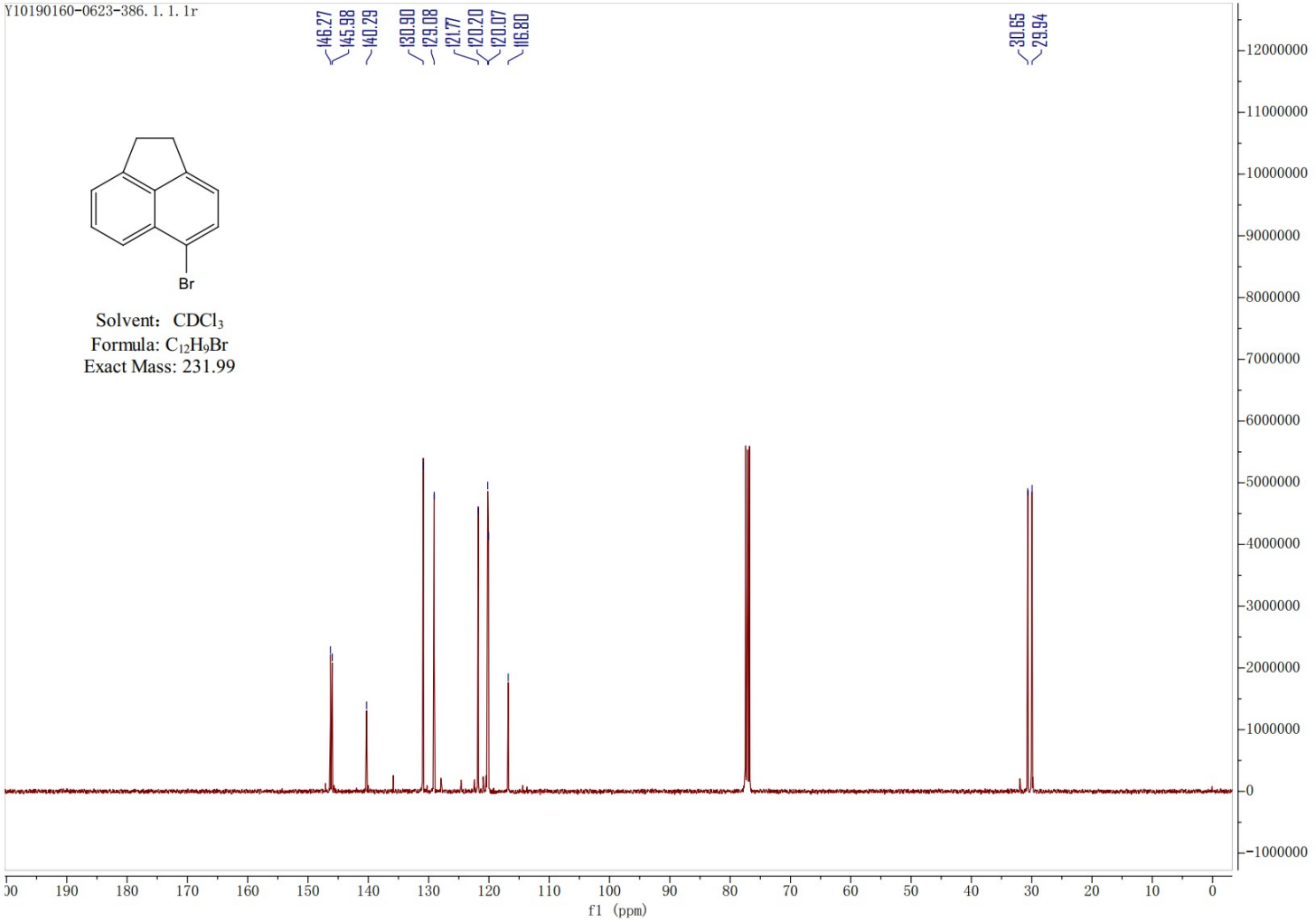


Fig. S8. The ^{13}C NMR spectrum of FP7

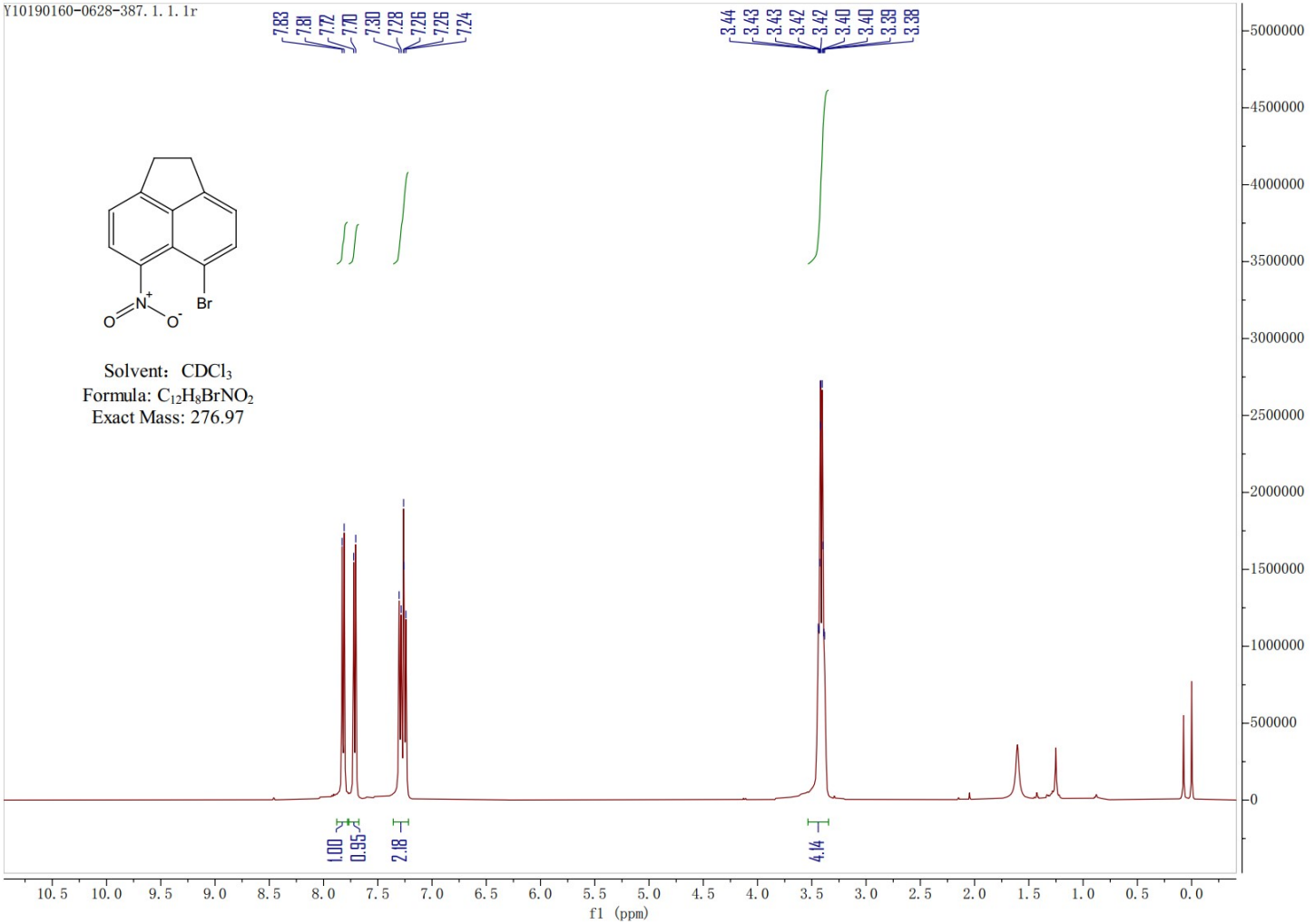


Fig. S9. The ^{1}H NMR spectrum of FP6

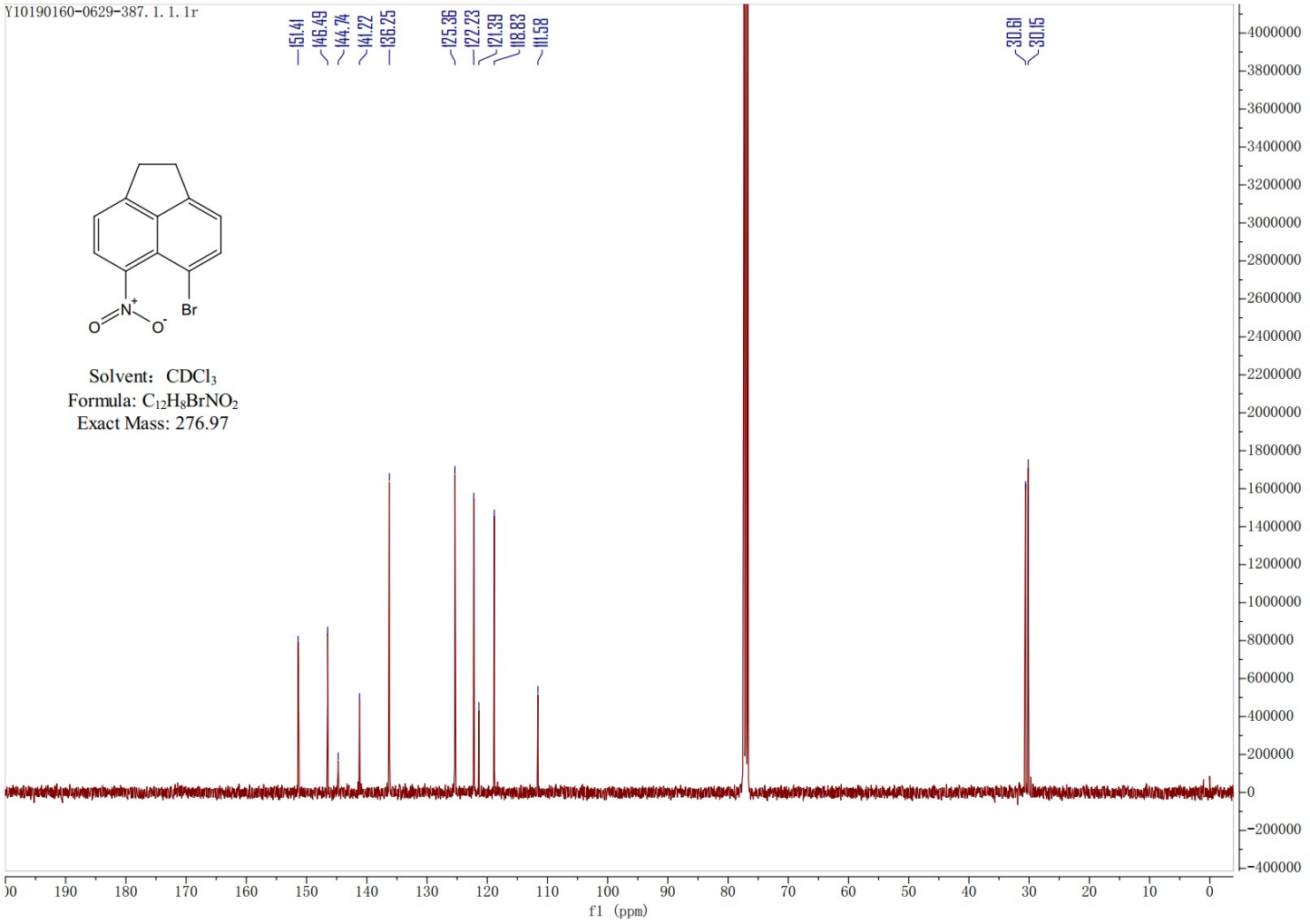


Fig. S10. The ^{13}C NMR spectrum of FP6

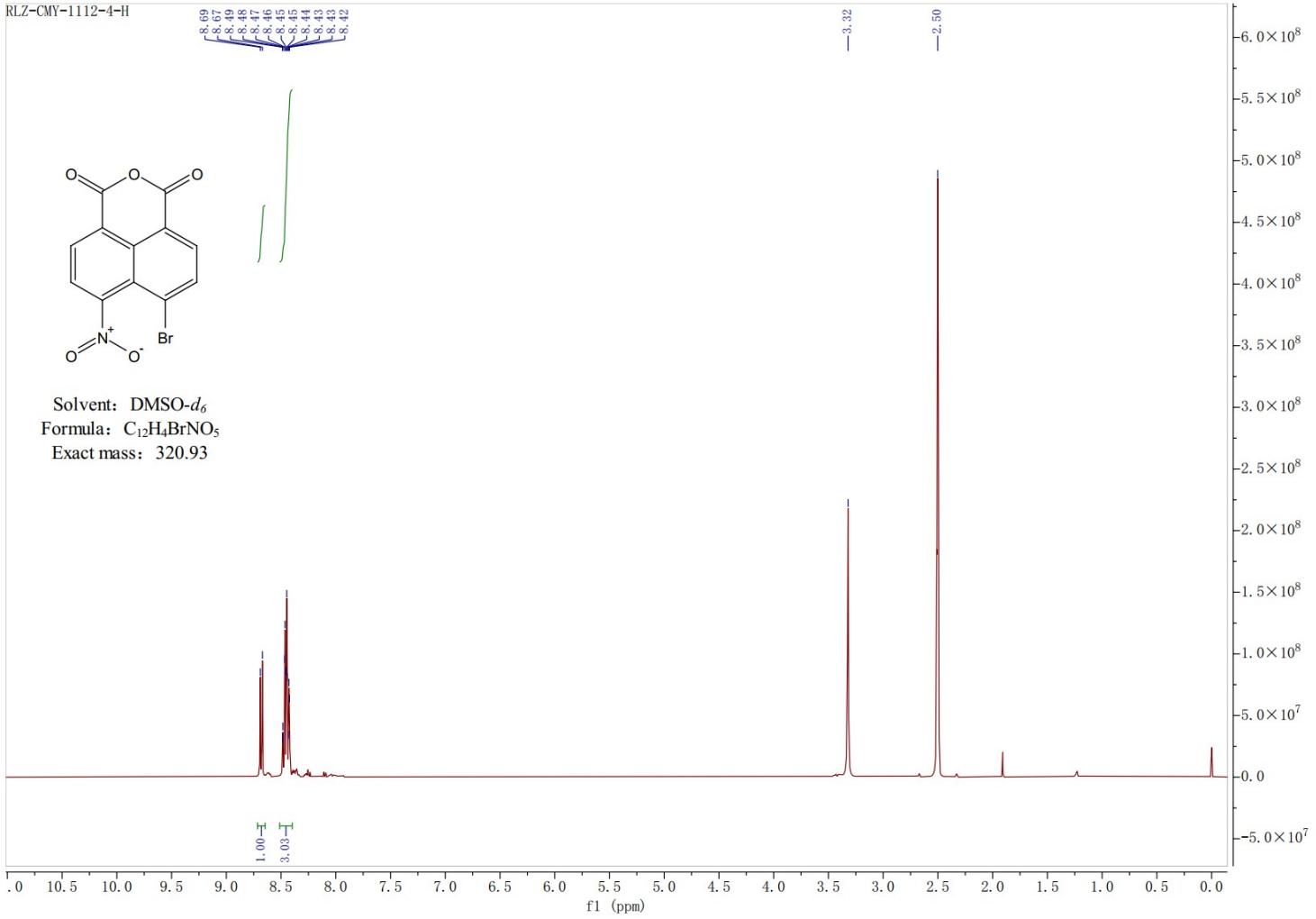


Fig. S11. The ^{1}H NMR spectrum of FP5

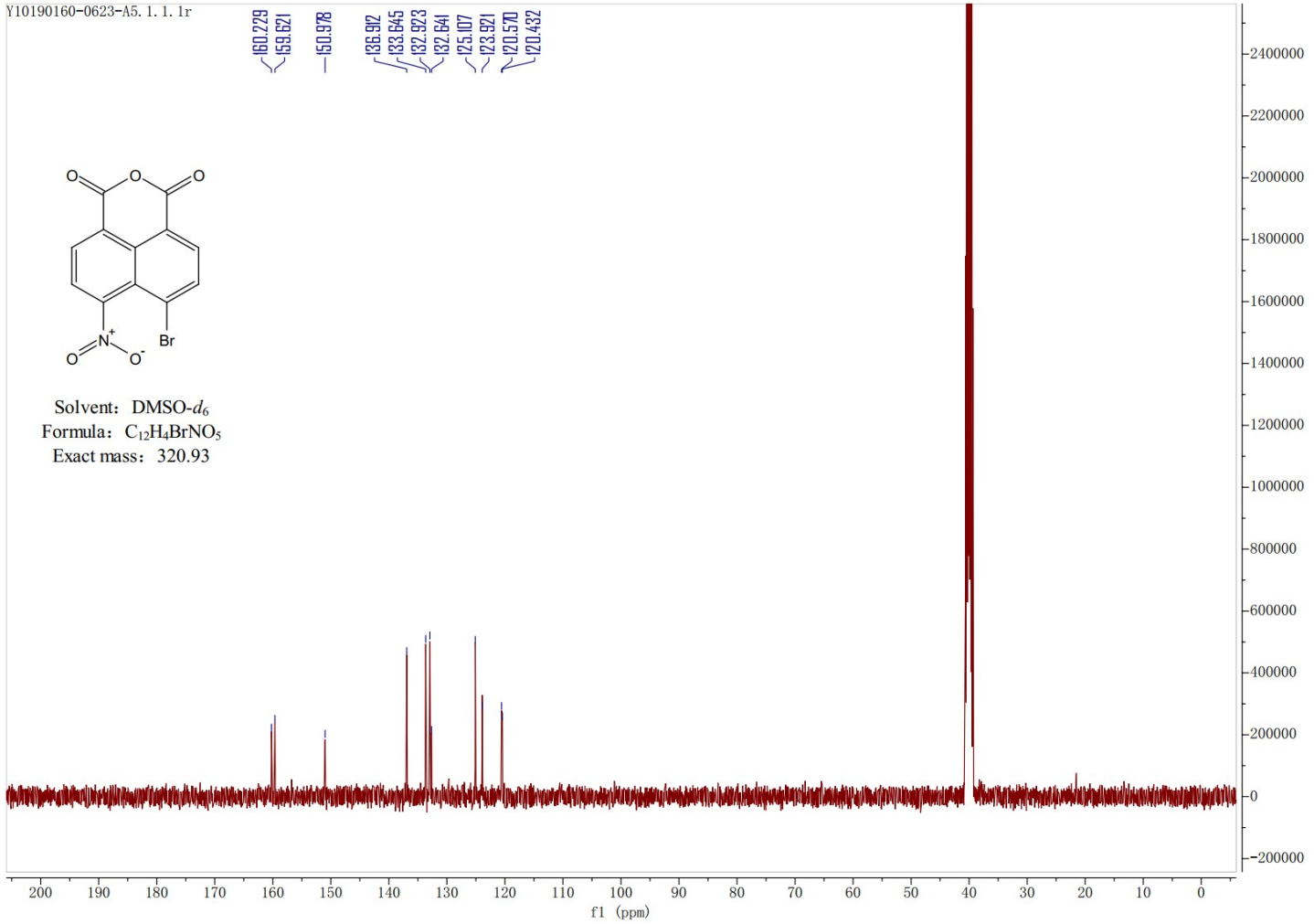


Fig. S12. The ^{13}C NMR spectrum of FP5

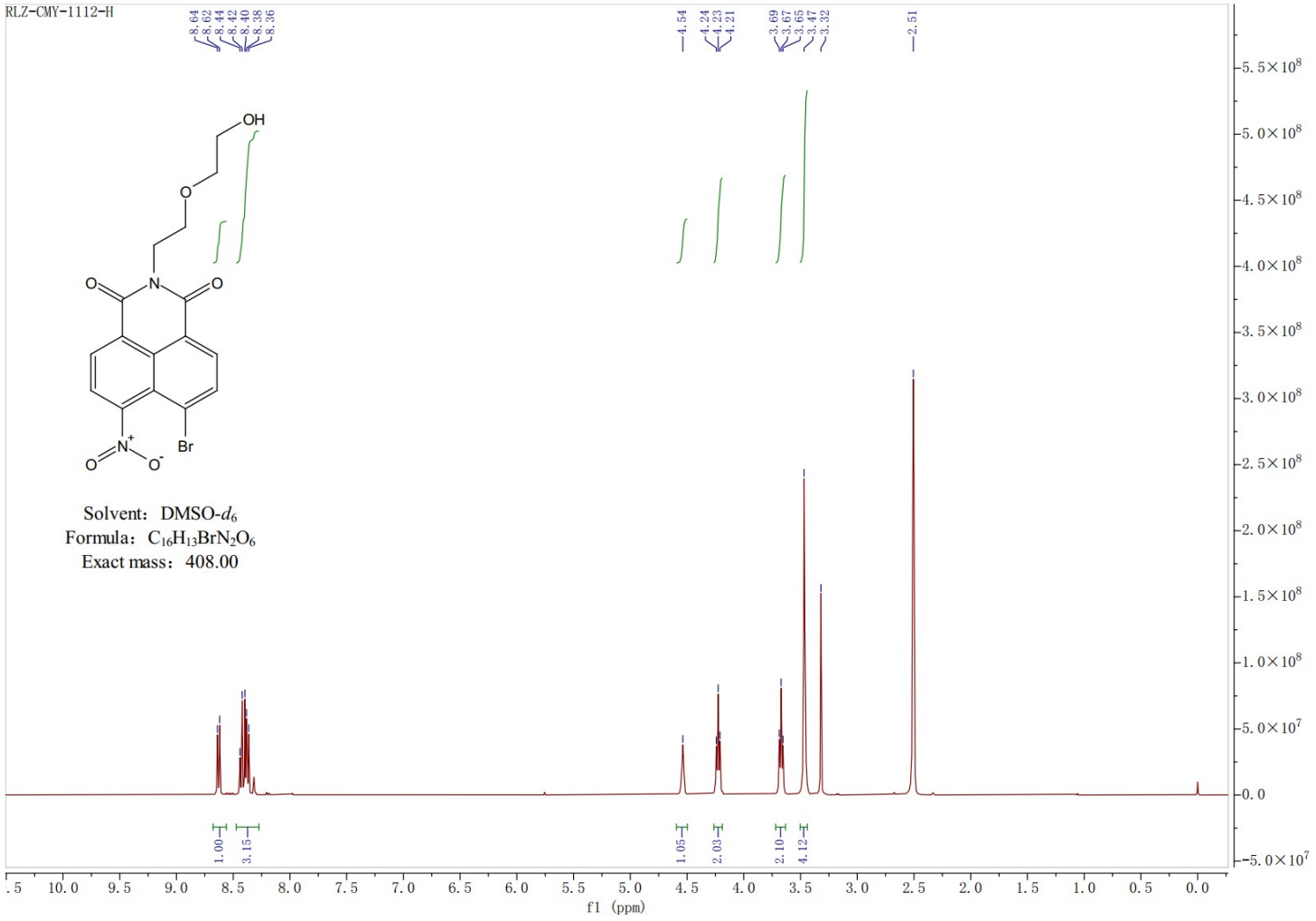


Fig. S13. The ^{1}H NMR spectrum of FP4

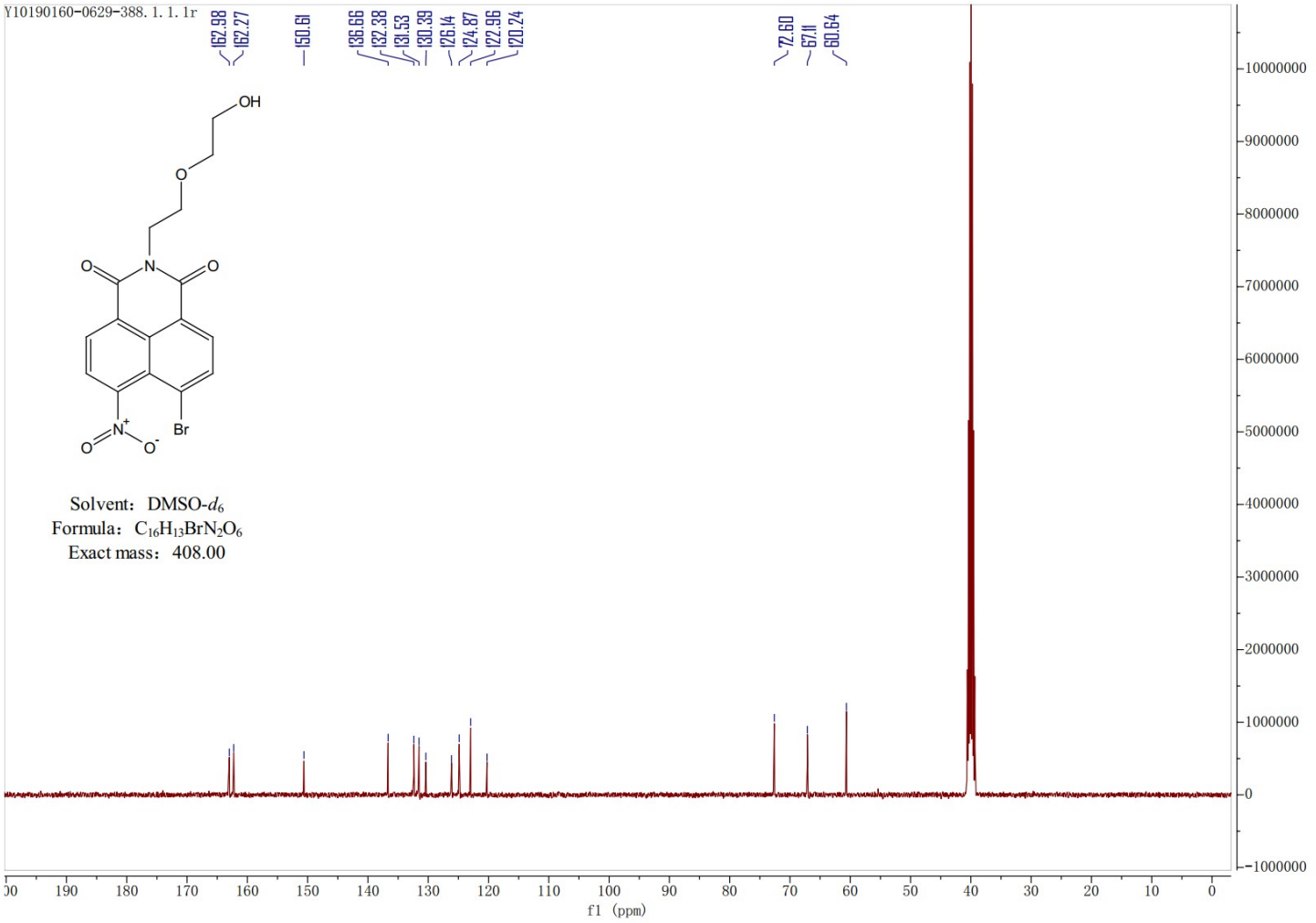


Fig. S14. The ^{13}C NMR spectrum of FP4.

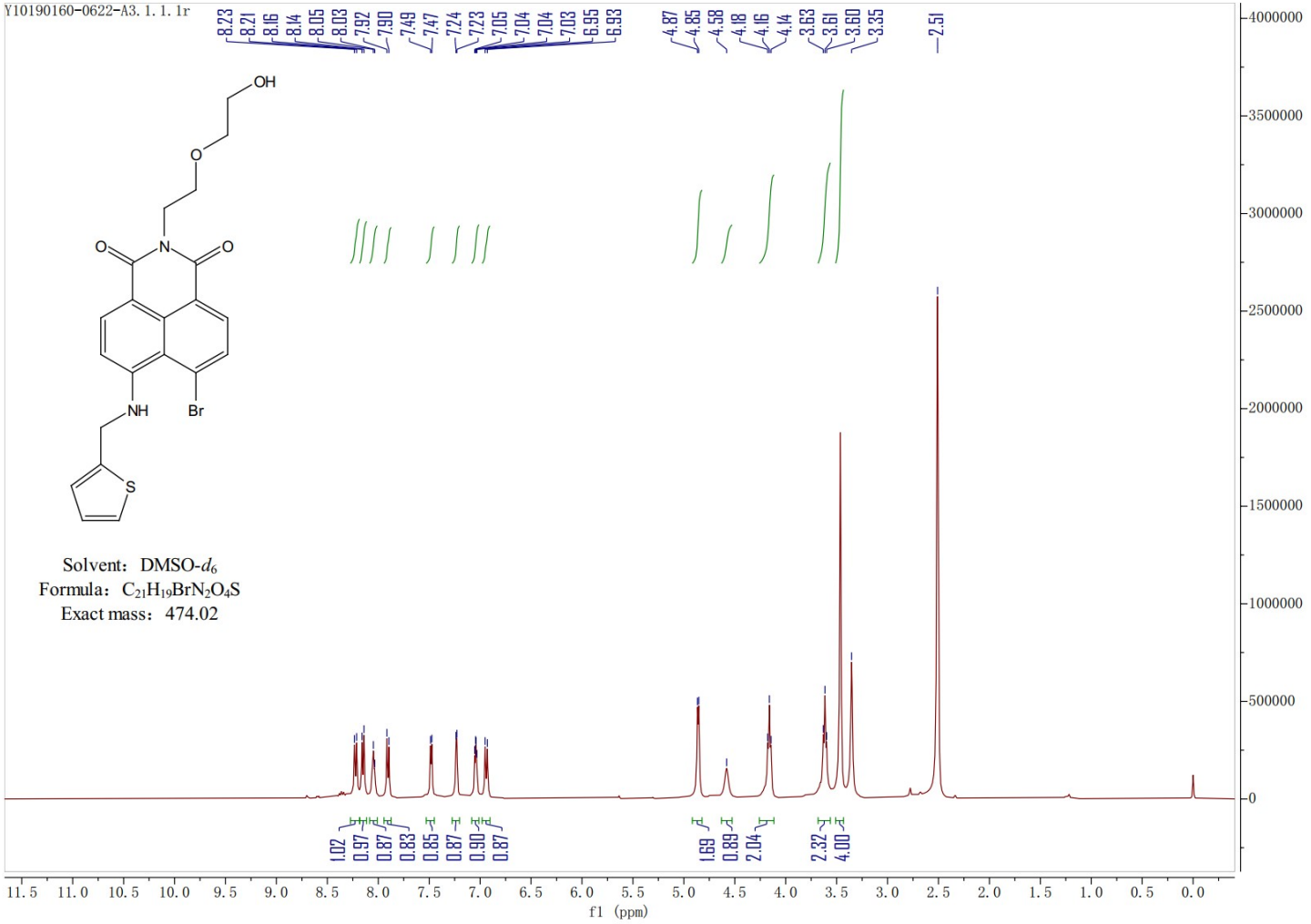


Fig. S15. The ^{1}H NMR spectrum of FP3

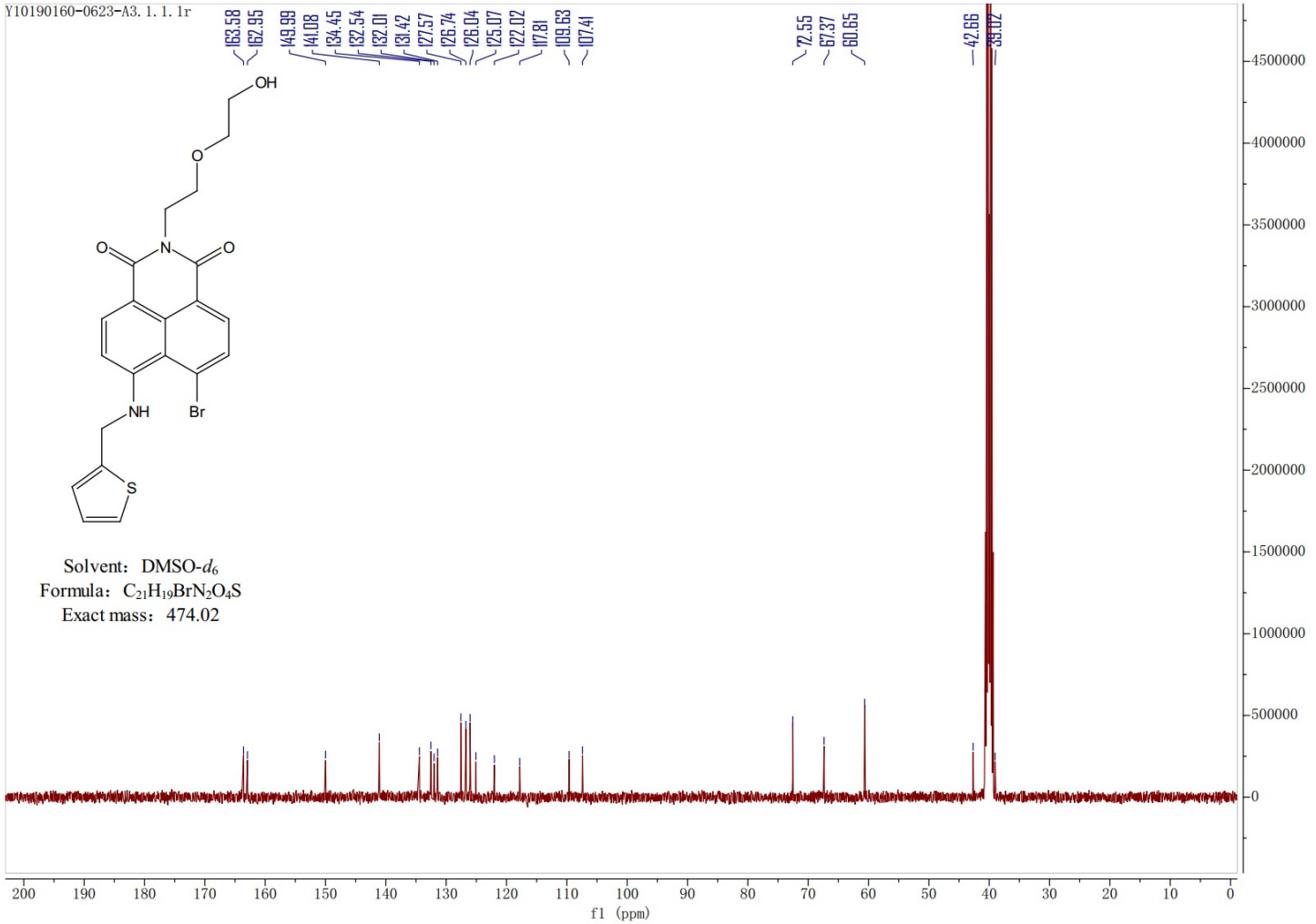


Fig. S16. The ^{13}C NMR spectrum of FP3.

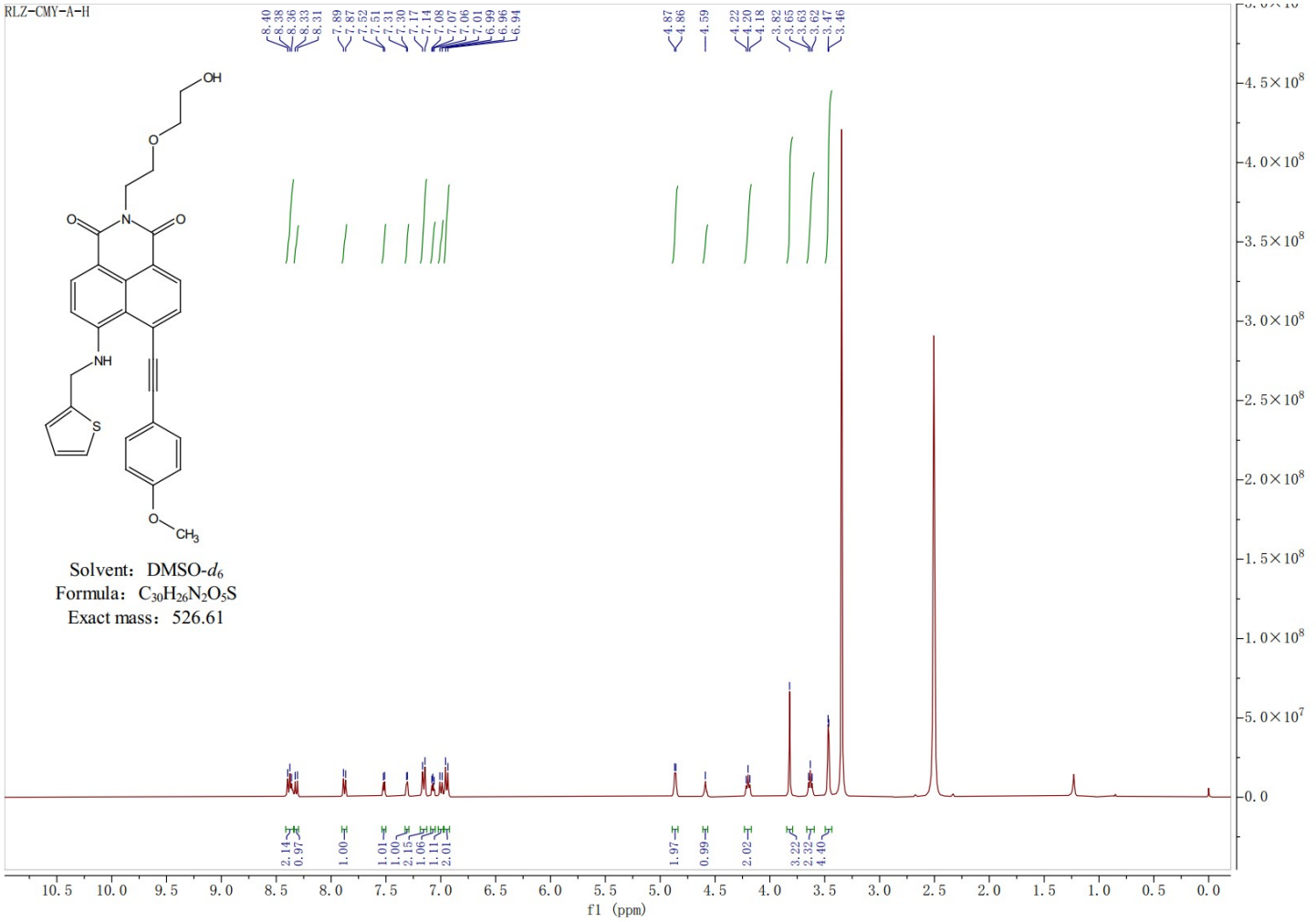


Fig. S17. The ^{1}H NMR spectrum of FP2

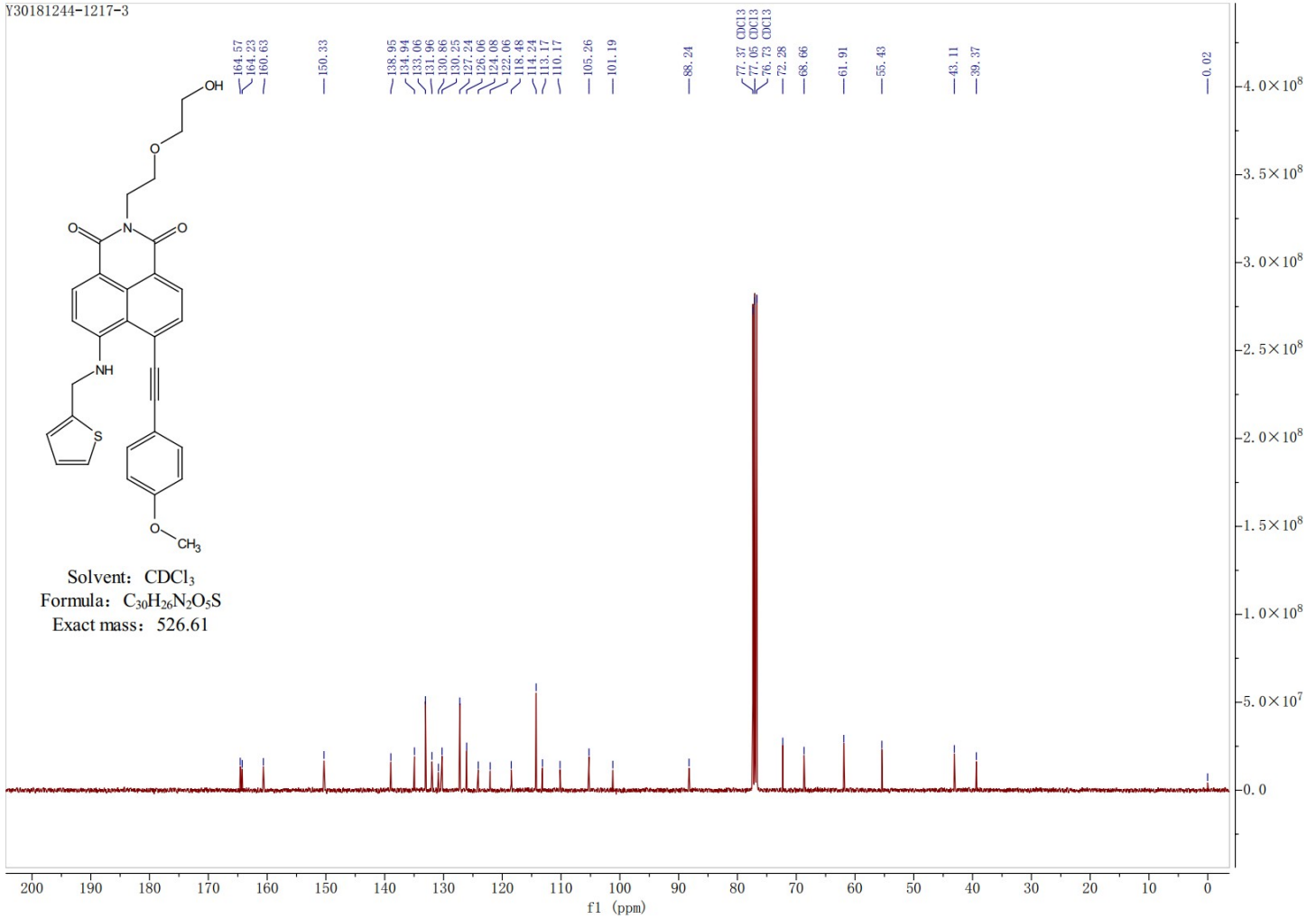


Fig. S18. The ^{13}C NMR spectrum of FP2.

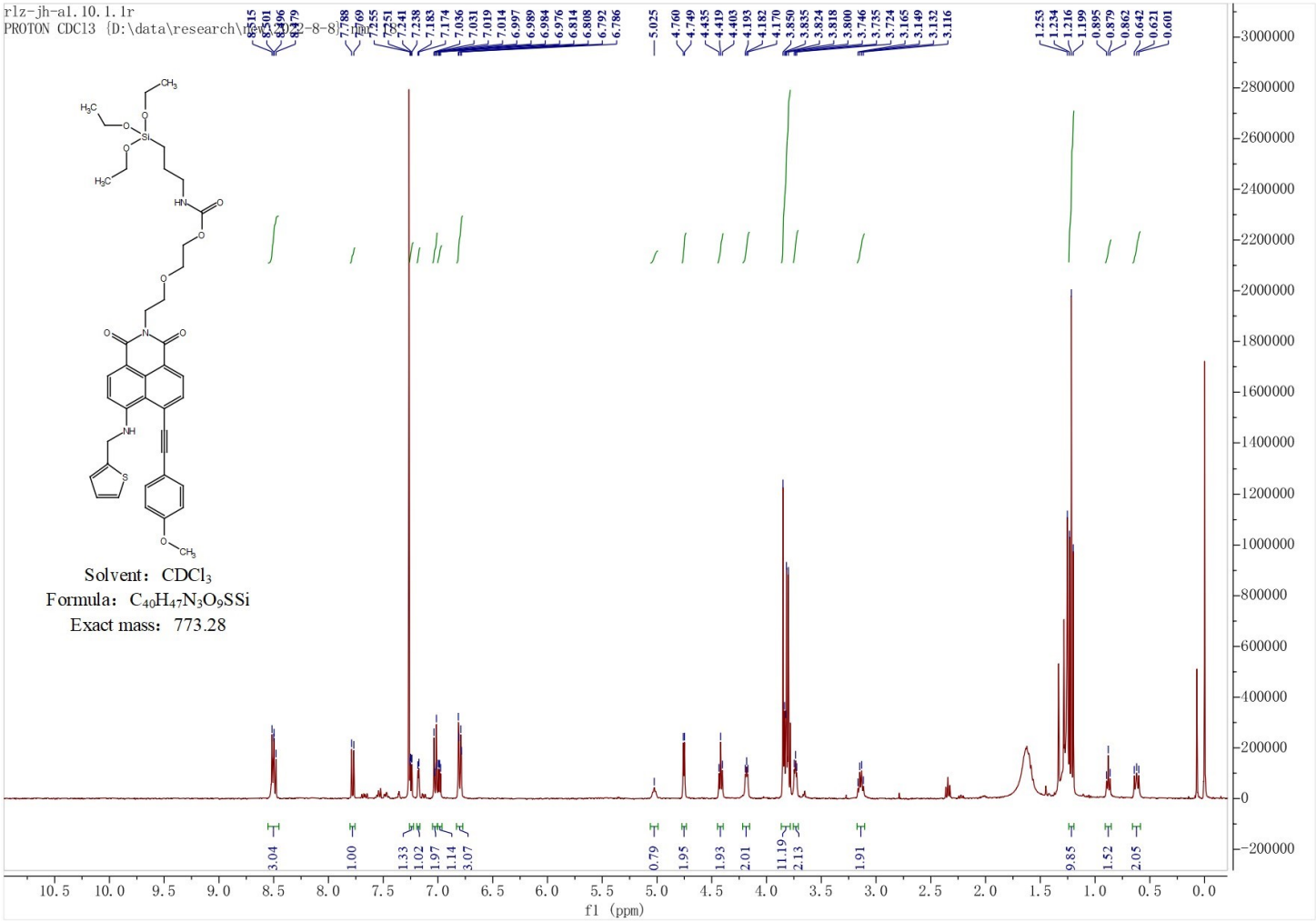


Fig. S19. The ^{1}H NMR spectrum of FP1

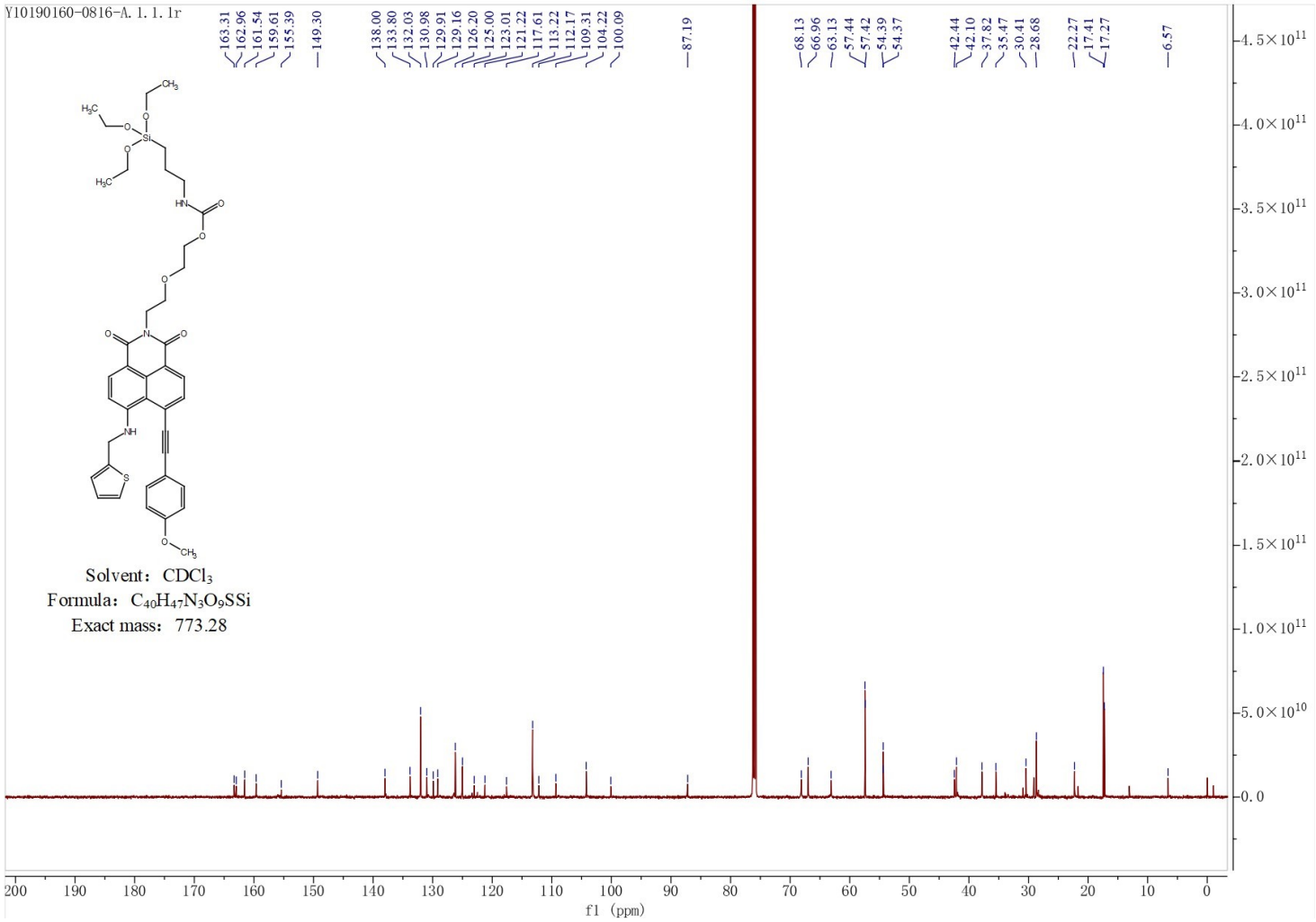


Fig. S20. The ^{13}C NMR spectrum of FP1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
302 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-40 H: 0-47 N: 0-3 O: 0-9 S: 0-1 Si: 0-1 Na: 0-1

WP-ZHU
ZWP-CMY-A1 312 (3.597) Cm (307:312)

1: TOF MS ES+
4.20e+003

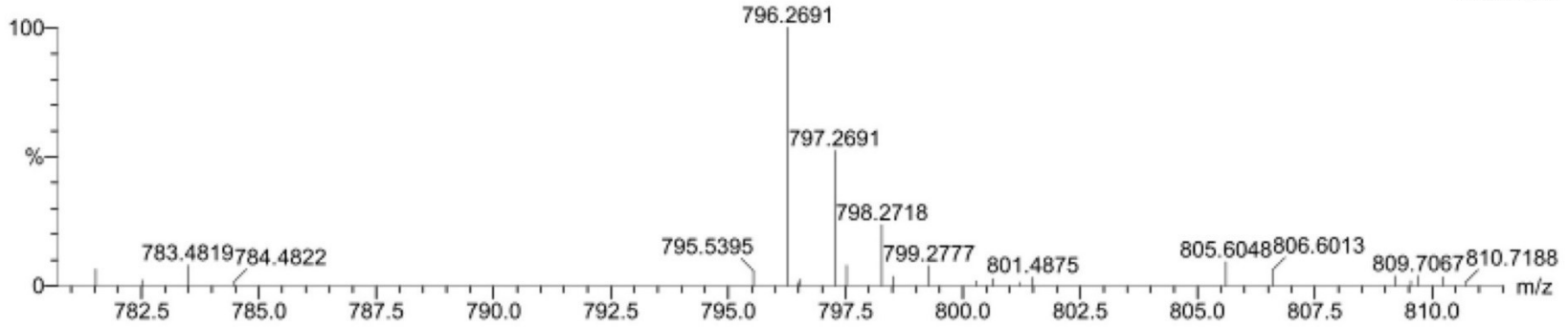
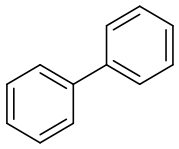


Fig. S21. The HRMS spectrum of FP1

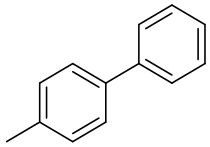
12. Spectroscopic data of coupling products

X1-3: Diphenyl



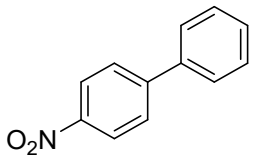
Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6):δ 7.72 - 7.62 (m, 4H), 7.47 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.68, 129.41, 127.90, 127.17.

X4-6: 4-Phenyltoluene



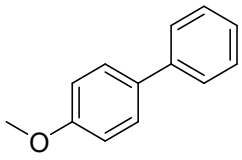
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.63 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.62, 137.81, 137.14, 129.98, 129.32, 127.55, 126.97, 126.90, 21.12.

X7-9: 4-Nitrobiphenyl



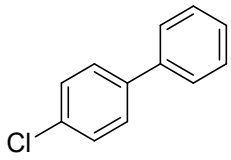
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 6.9 Hz, 2H), 7.50 (dd, J = 15.4, 6.9 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.30, 147.13, 147.09, 138.29, 133.31, 129.83, 129.70, 129.53, 128.32, 127.74, 125.83, 124.55.

X10-12, B1: 4-Methoxybiphenyl



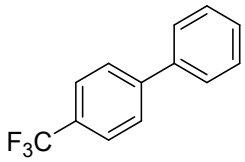
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.69 - 7.53 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.37, 140.32, 133.01, 129.33, 128.22, 127.17, 126.64, 114.83, 55.62.

X13: 4-Chlorobiphenyl



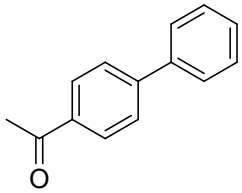
Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.75 - 7.61 (m, 4H), 7.56 - 7.43 (m, 4H), 7.39 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.46, 139.30, 132.81, 129.50, 129.40, 129.35, 128.93, 128.28, 127.17, 127.12.

X14: 4-(Trifluoromethyl)-biphenyl



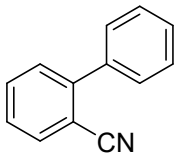
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.97, 145.00, 139.38, 136.12, 129.57, 129.38, 128.86, 127.47, 127.35, 27.24.

X15: 4-Acetylbiphenyl



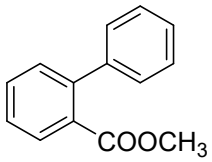
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.06 - 8.01 (m, 2H), 7.71 - 7.67 (m, 2H), 7.63 (dt, J = 3.1, 1.9 Hz, 2H), 7.50 - 7.45 (m, 2H), 7.43 - 7.38 (m, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): 197.96, 145.00, 139.39, 136.12, 129.57, 129.38, 128.85, 127.47, 127.34.

X16: 2-Cyanobiphenyl



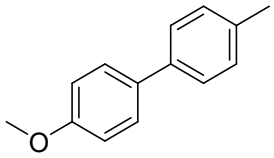
Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96 (d, J = 7.8 Hz, 1H), 7.80 (td, J = 7.8, 1.1 Hz, 1H), 7.69 - 7.46 (m, 7H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.02, 138.32, 134.31, 134.00, 130.60, 129.19, 128.67, 119.03, 110.67.

X17: Methyl biphenyl-2-carboxylate



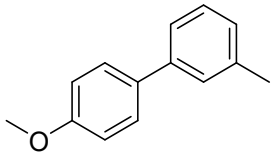
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.74 (dd, J = 7.7, 1.0 Hz, 1H), 7.63 (td, J = 7.6, 1.3 Hz, 1H), 7.50 (td, J = 7.6, 1.1 Hz, 1H), 7.43 (t, J = 7.9 Hz, 3H), 7.40 - 7.35 (m, 1H), 7.32 - 7.27 (m, 2H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.44, 141.03, 136.24, 133.37, 130.72, 128.69, 94.68, 52.96.

B2-3: 4-Methoxy-4'-Methylbiphenyl



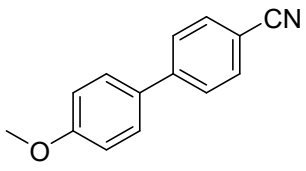
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 - 7.38 (m, 4H), 7.23 (m, 2H), 7.00 (m, 2H), 3.78 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.13, 137.45, 136.34, 134.95, 132.96, 129.92, 129.00, 127.94, 126.47, 114.78, 83.93, 55.62, 25.15, 21.09.

B4: 4-Methoxy-3'-Methylbiphenyl



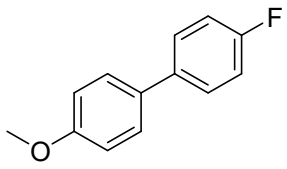
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 - 7.55 (m, 2H), 7.44 - 7.37 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.05 - 6.98 (m, 2H), 3.79 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.29, 140.27, 138.41, 133.11, 129.22, 128.20, 127.82, 127.32, 123.77, 114.77, 55.62, 21.61.

B5: 4-Methoxy-[1,1'-biphenyl]-4'-carbonitrile



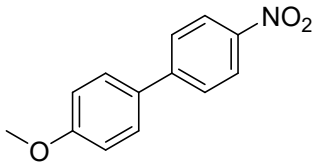
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86 (q, J = 8.5 Hz, 4H), 7.72 (t, J = 5.8 Hz, 2H), 7.12 - 7.03 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.39, 144.73, 133.26, 130.88, 128.80, 127.33, 119.49, 115.09, 109.60, 55.76.

B6: 4-Fluoro-4'-methoxybiphenyl



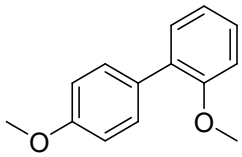
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 - 7.61 (m, 2H), 7.61 - 7.55 (m, 2H), 7.30 - 7.21 (m, 2H), 7.05 - 6.99 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.12, 160.70, 159.33, 136.83, 136.80, 132.01, 128.57, 128.49, 128.20, 116.15, 115.94, 114.84, 55.63.

B7: 4-Methoxy-4'-nitrobiphenyl



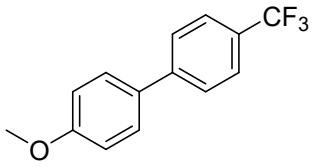
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.33 - 8.22 (m, 2H), 7.98 - 7.88 (m, 2H), 7.82 - 7.71 (m, 2H), 7.09 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.67, 146.76, 146.48, 130.41, 129.05, 127.48, 124.57, 115.17, 55.79.

B8: 1-methoxy-2-(4-methoxyphenyl)benzene



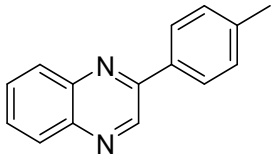
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.41 (d, J = 8.4 Hz, 2H), 7.35 - 7.22 (m, 2H), 7.10 (t, J = 10.9 Hz, 1H), 6.99 (dd, J = 17.9, 7.8 Hz, 3H), 3.77 (d, J = 12.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.71, 156.55, 130.86, 130.80, 130.62, 129.96, 128.78, 121.21, 113.92, 112.16, 55.89, 55.54.

B9: 1-methoxy-4-[4-(trifluoromethyl)phenyl]benzene



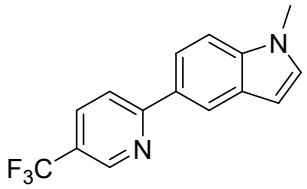
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.15, 131.26, 128.68, 127.25, 126.17, 126.13, 115.02, 55.70.

A1: 2-(4-methylphenyl)quinoxaline



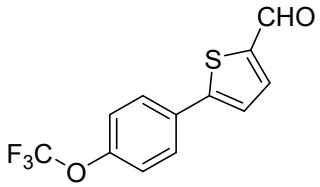
Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.57 (s, 1H), 8.26 (d, J = 8.2 Hz, 2H), 8.17 - 8.07 (m, 2H), 7.86 (dtd, J = 14.8, 6.9, 1.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.41, 144.10, 141.91, 141.44, 140.81, 133.75, 131.04, 130.22, 130.14, 129.59, 129.31, 127.83, 21.45.

A2: 1-methyl-5-[5-(trifluoromethyl)-2-pyridinyl]-indole



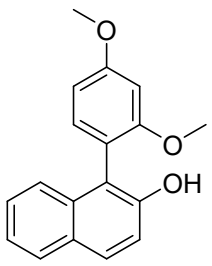
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99 (s, 1H), 8.43 (s, 1H), 8.19 (d, J = 1.4 Hz, 2H), 8.02 (dd, J = 8.7, 1.5 Hz, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 3.1 Hz, 1H), 6.57 (d, J = 2.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.72, 146.50, 146.46, 138.04, 134.76, 134.72, 131.46, 128.85, 128.81, 125.99, 123.29, 122.98, 122.66, 120.88, 120.36, 120.01, 110.62, 102.08, 33.10.

A3: 5-[4-(trifluoromethoxy)phenyl]-2-thiophenecarboxaldehyde



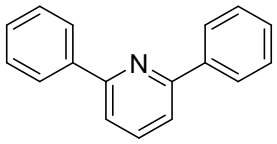
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.94 (s, 1H), 8.07 (d, J = 3.9 Hz, 1H), 7.94 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 3.9 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 184.65, 151.09, 149.34, 143.10, 139.62, 132.22, 128.72, 126.63, 122.31.

A4: 1-(2,4-dimethoxyphenyl)-2-naphthalenol



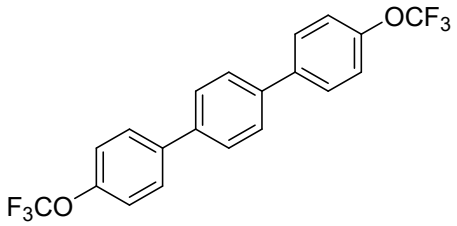
White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.18 (s, 1H), 7.80 - 7.75 (m, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.29 - 7.19 (m, 3H), 7.16 (dd, J = 7.9, 1.0 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.70 (d, J = 2.3 Hz, 1H), 6.63 (dd, J = 8.3, 2.4 Hz, 1H), 3.84 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6):δ 160.51, 158.87, 152.78, 134.57, 133.04, 128.66, 128.27, 128.19, 126.23, 124.79, 122.64, 118.83, 118.36, 117.64, 105.37, 99.15, 55.67.

M1: 2,6-diphenylpyridine



White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 - 8.18 (m, 4H), 8.02 - 7.91 (m, 3H), 7.55 (t, J = 7.4 Hz, 4H), 7.51 - 7.43 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.11, 139.16, 138.82, 129.64, 129.27, 127.10, 119.32.

M2: 4,4''-bis(trifluoromethoxy)-1,1':4',1''-terphenyl



White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86 (d, J = 7.9 Hz, 4H), 7.81 (s, 4H), 7.48 (d, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.43, 139.26, 138.59, 129.02, 127.92, 122.00.

13. ^{1}H NMR and ^{13}C NMR spectra of coupling products

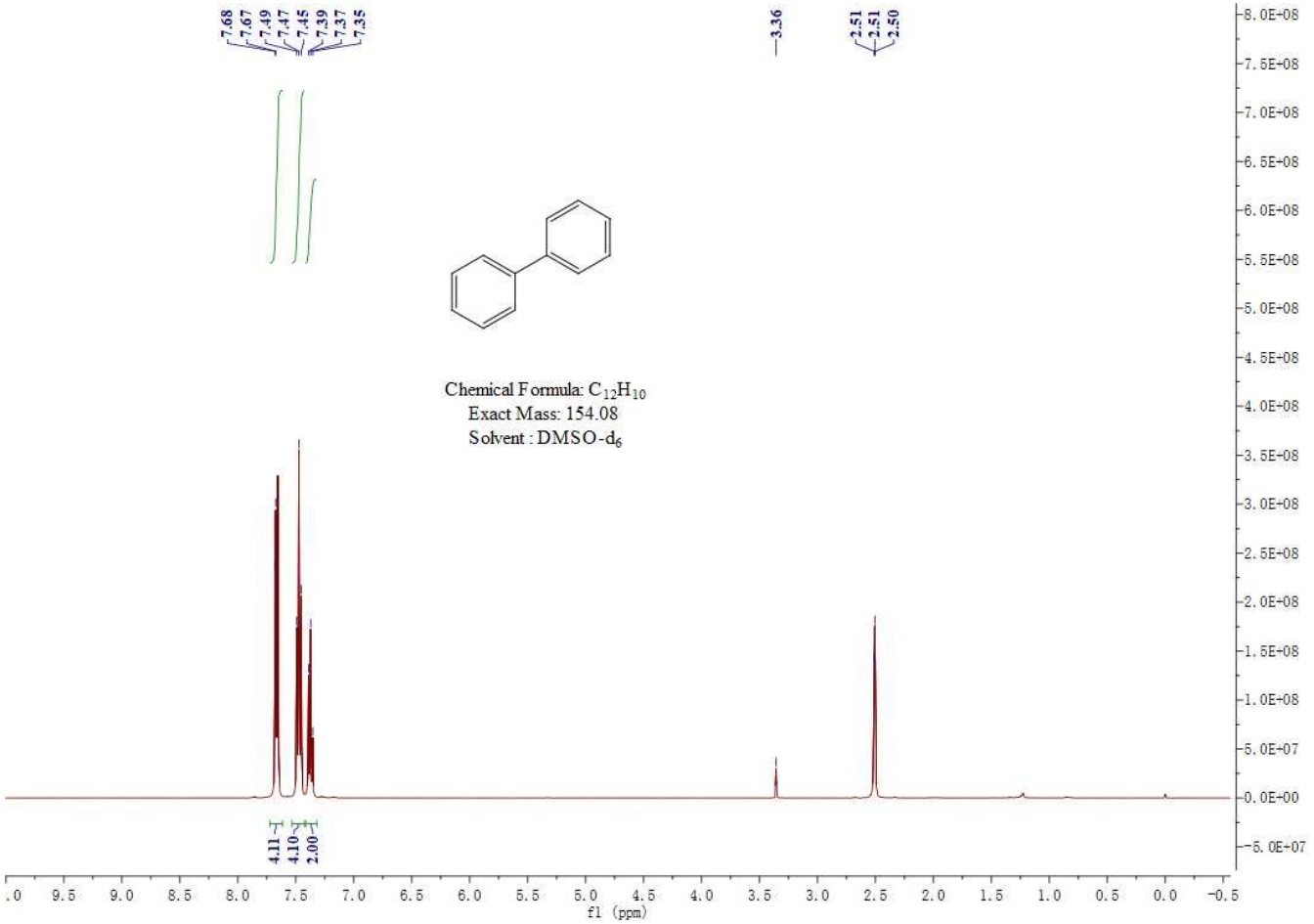


Fig. S22. The ^{1}H NMR spectrum of X1-3

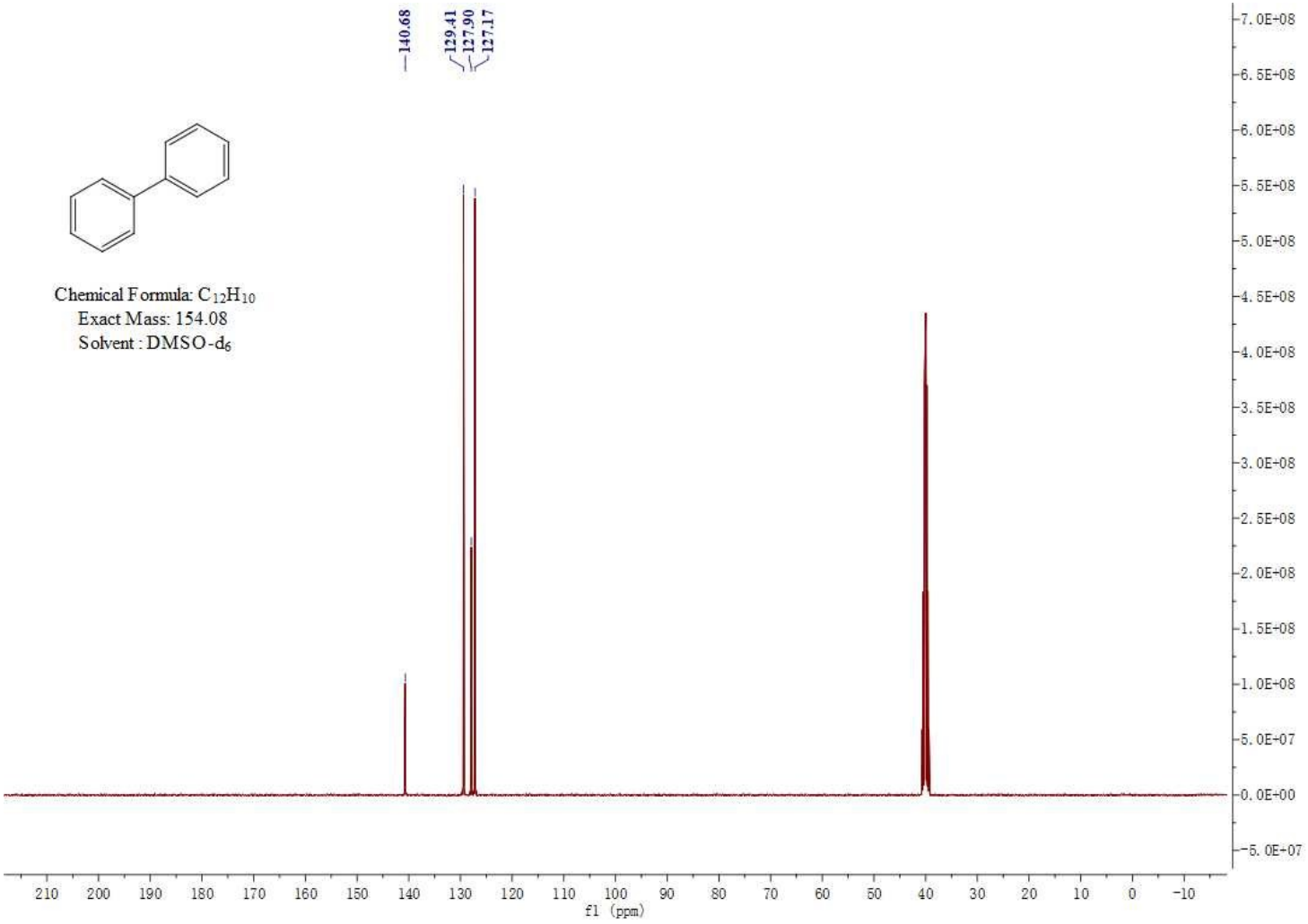


Fig. S23. The ^{13}C NMR spectrum of X1-3

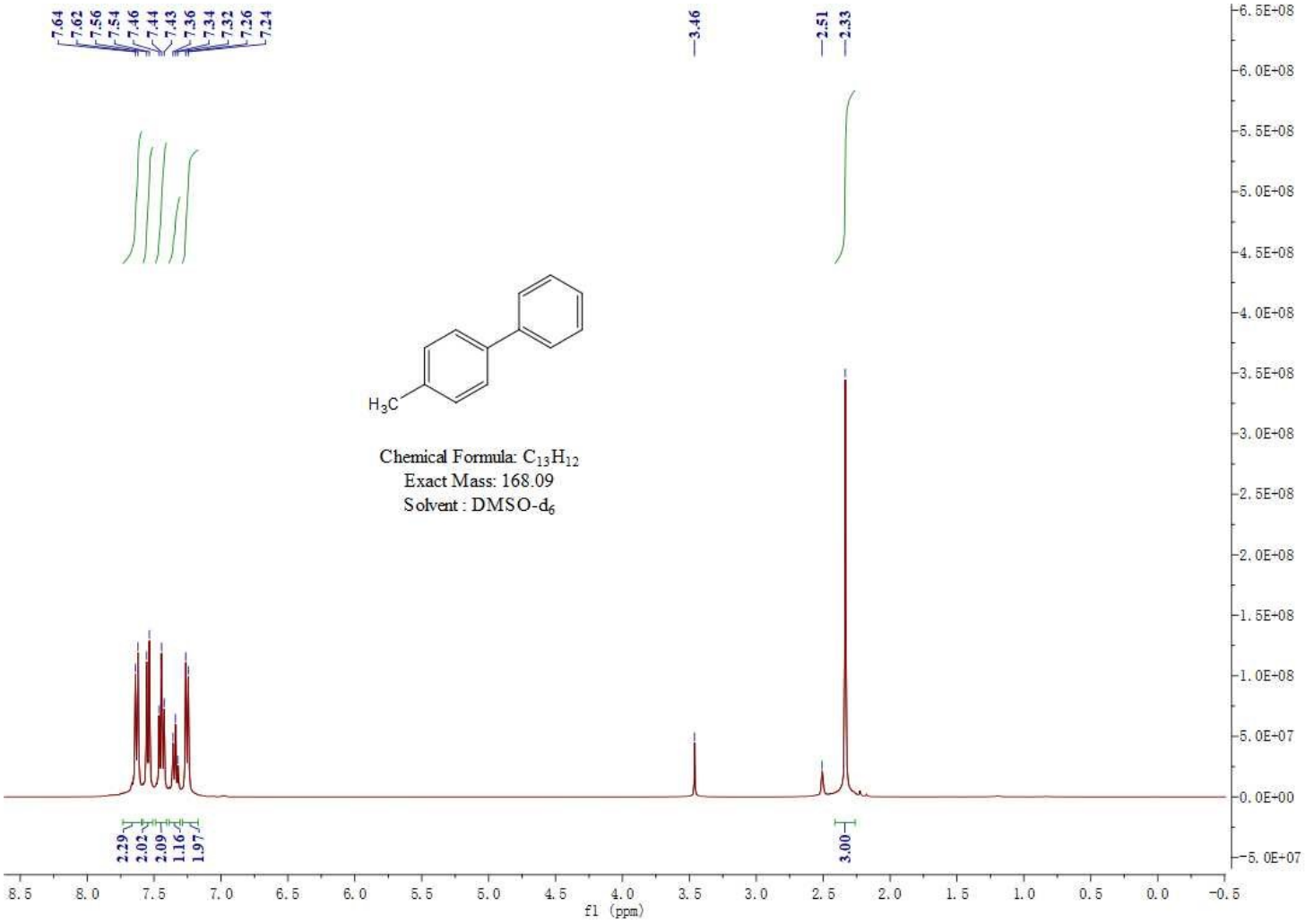


Fig. S24. The ^{1}H NMR spectrum of X4-6

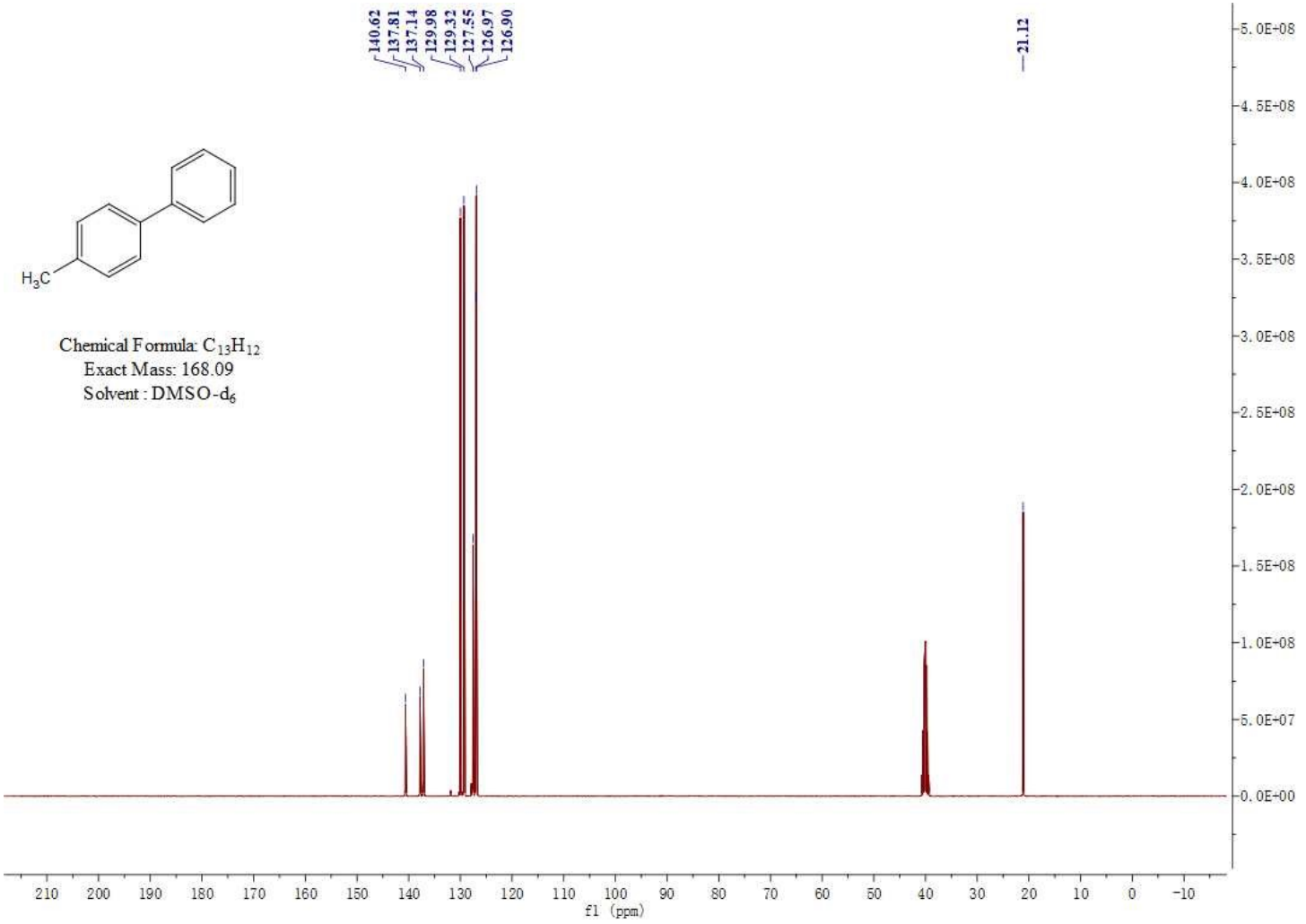


Fig. S25. The ^{13}C NMR spectrum of X4-6

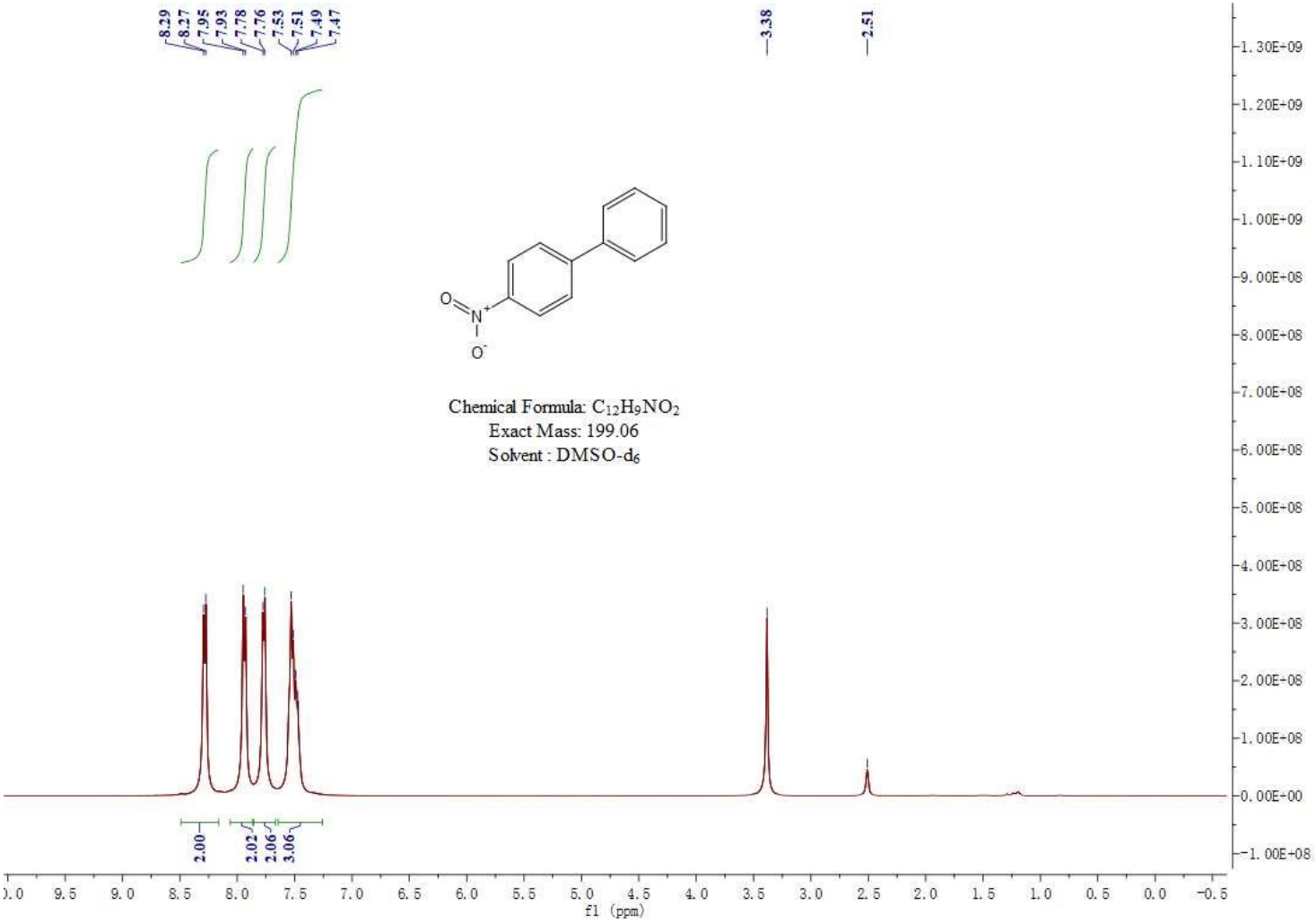


Fig. S26 The ^{1}H NMR spectrum of X7-9

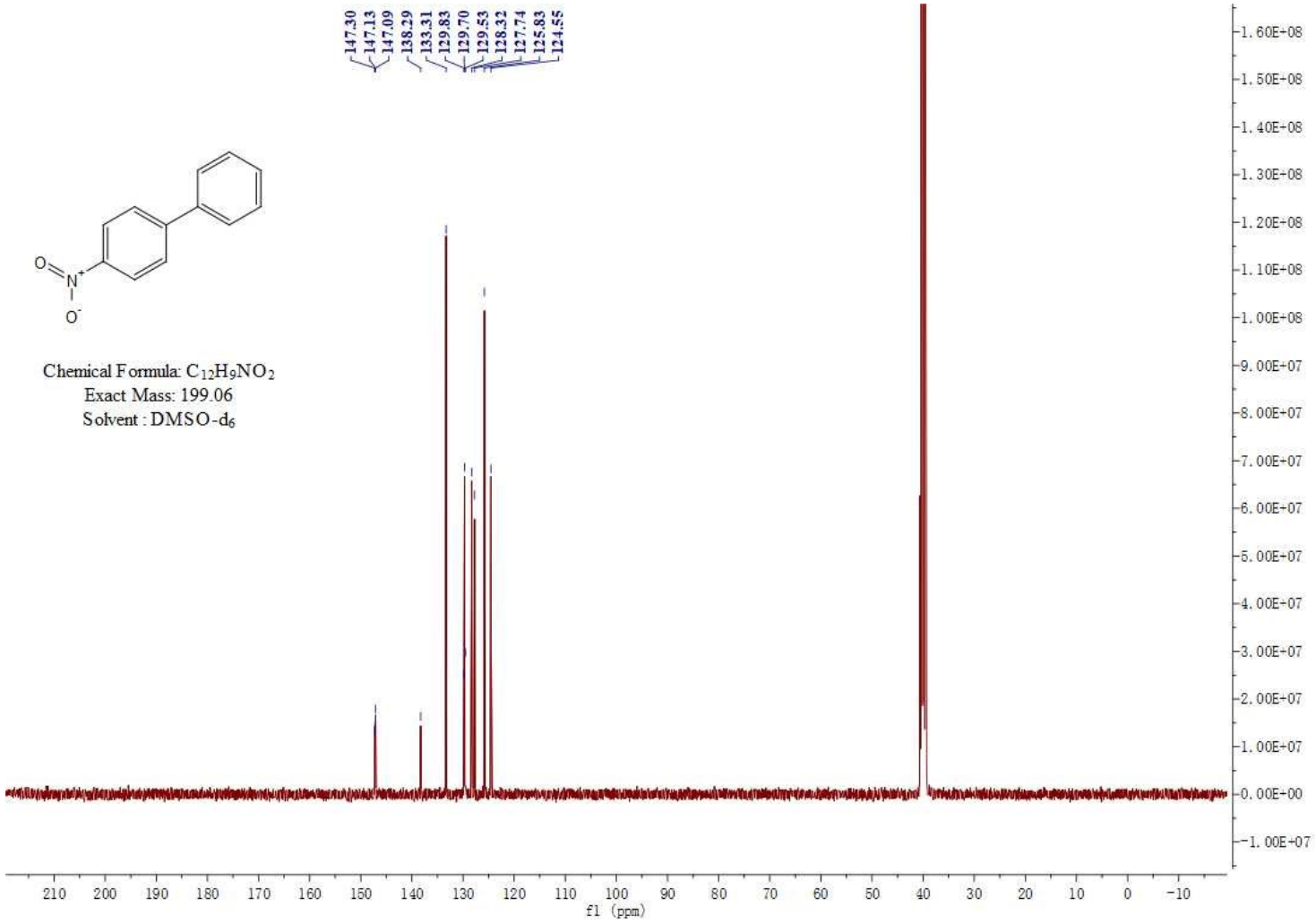


Fig. S27. The ^{13}C NMR spectrum of X7-9

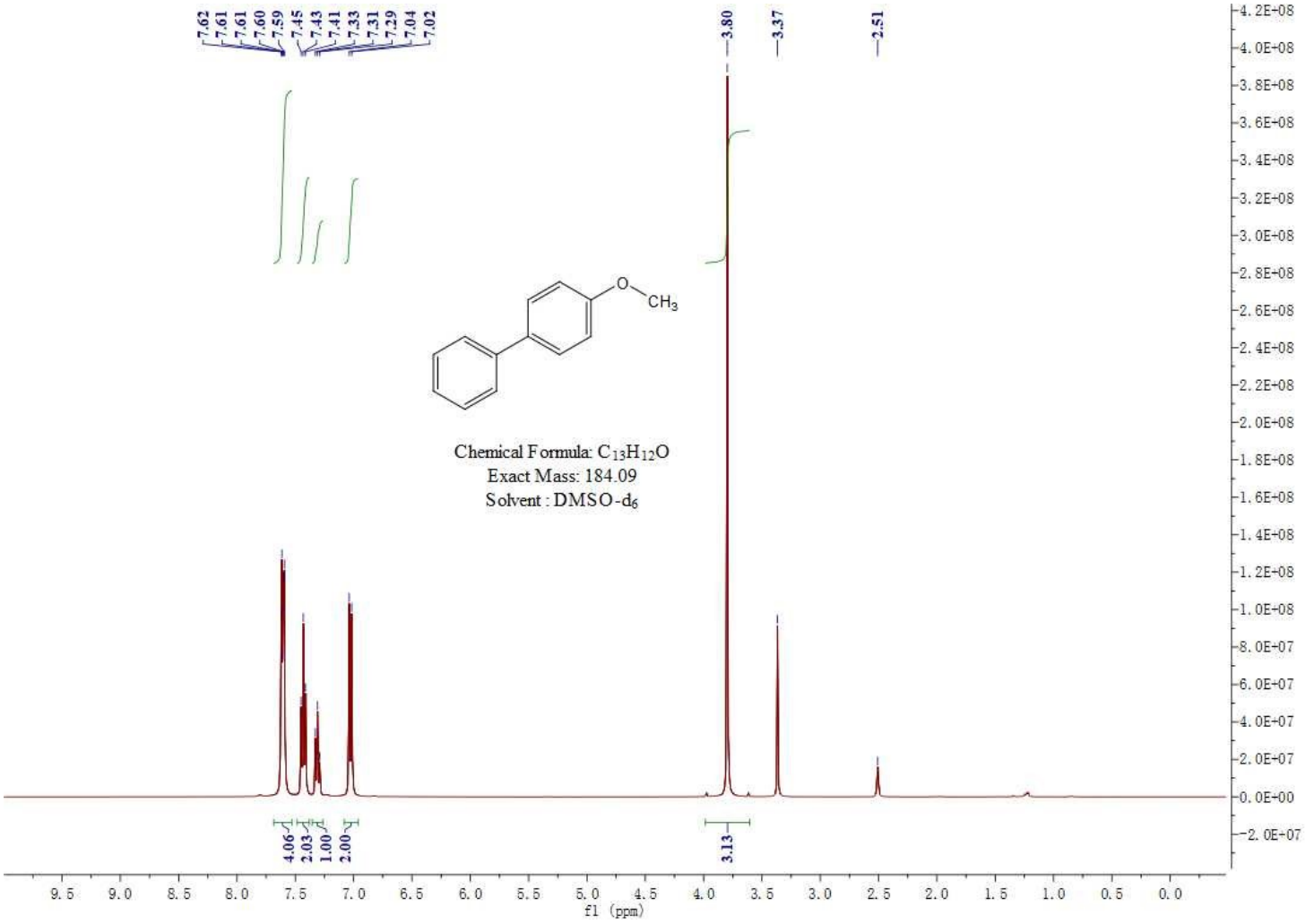


Fig. S28. The ^{1}H NMR spectrum of X10-12; B1

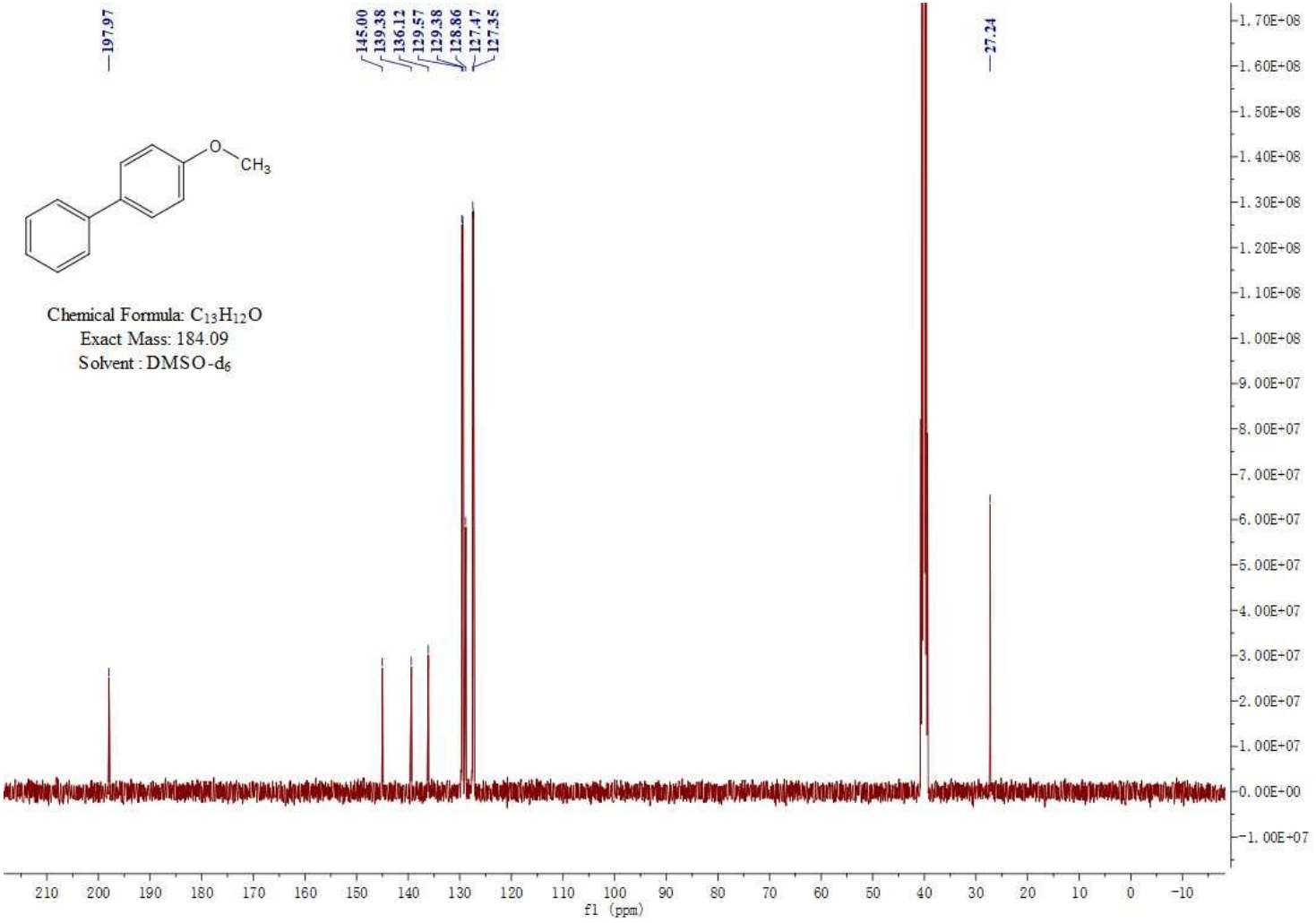


Fig. S29. The ^{13}C NMR spectrum of X10-12; B1

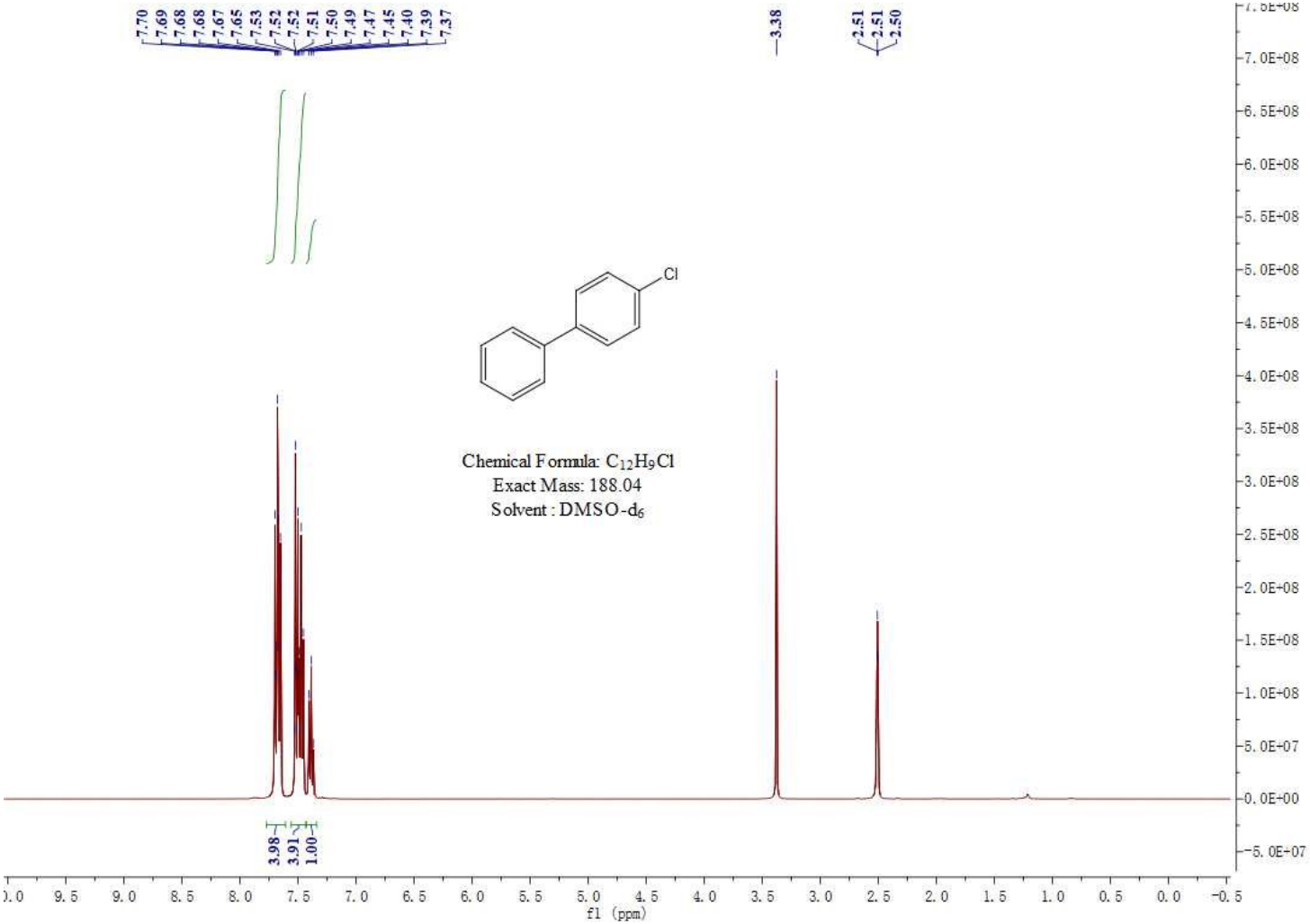


Fig. S30. The ^{1}H NMR spectrum of X13

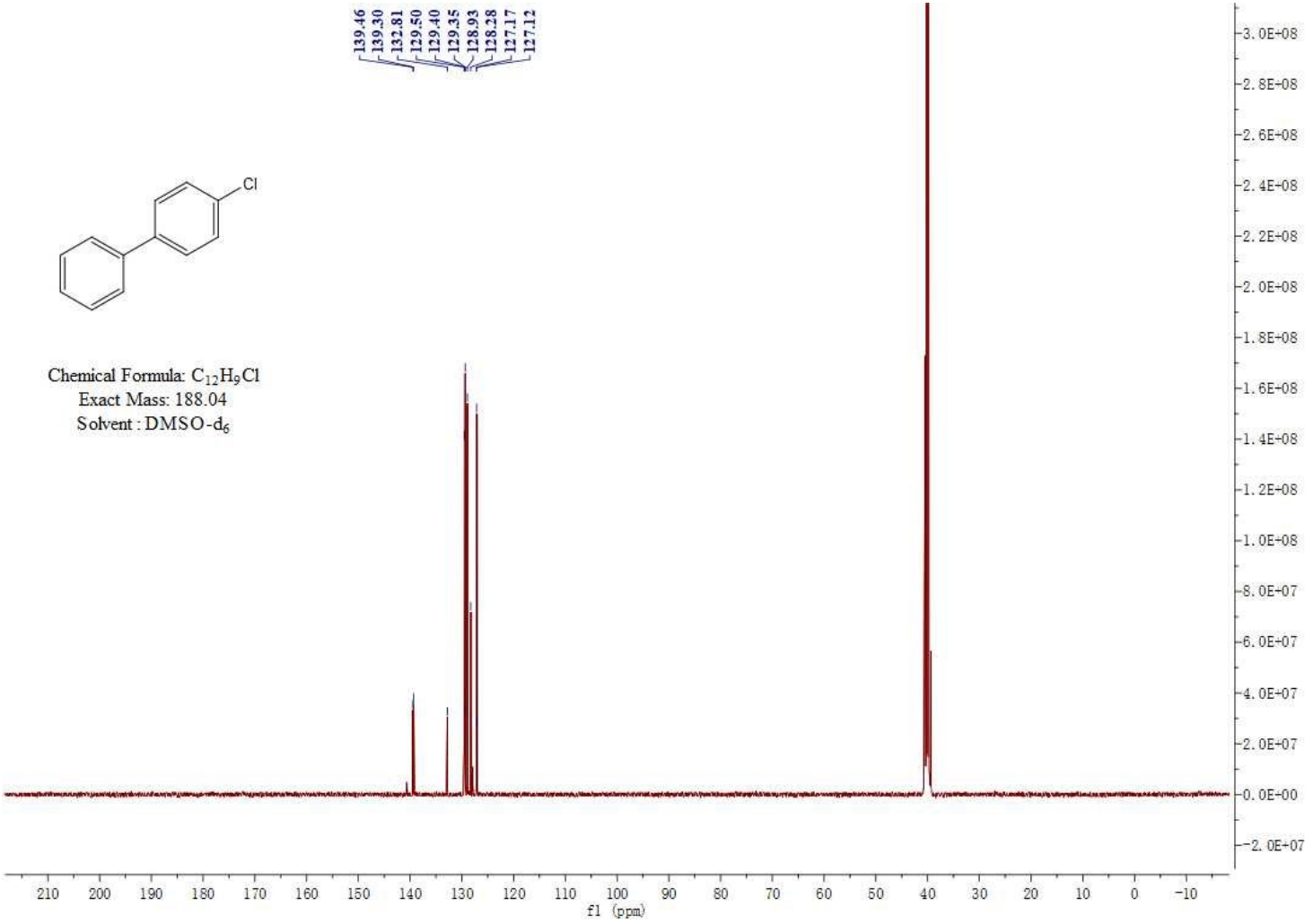


Fig. S31. The ^{13}C NMR spectrum of X13

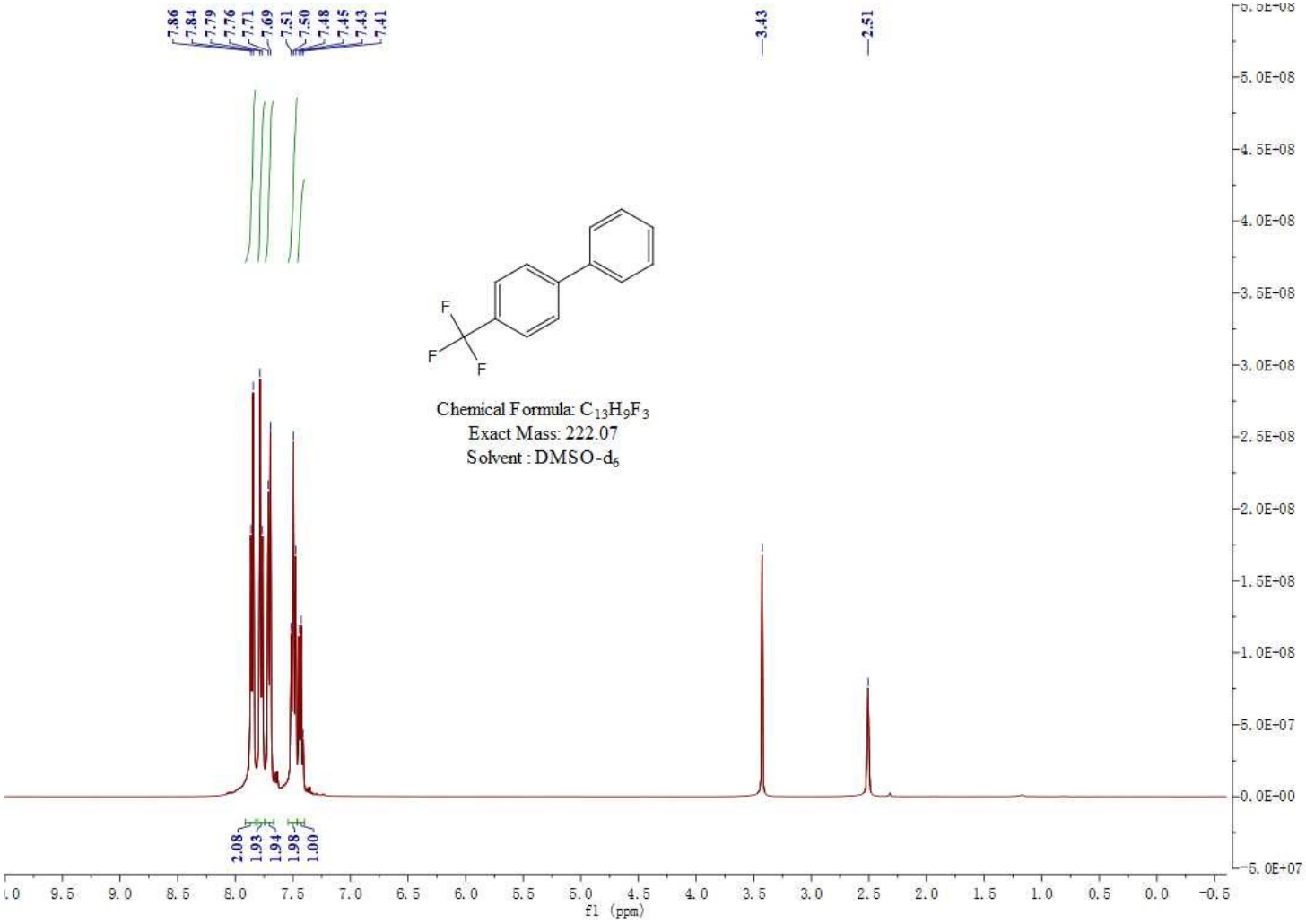


Fig. S32. The ^{1}H NMR spectrum of X14

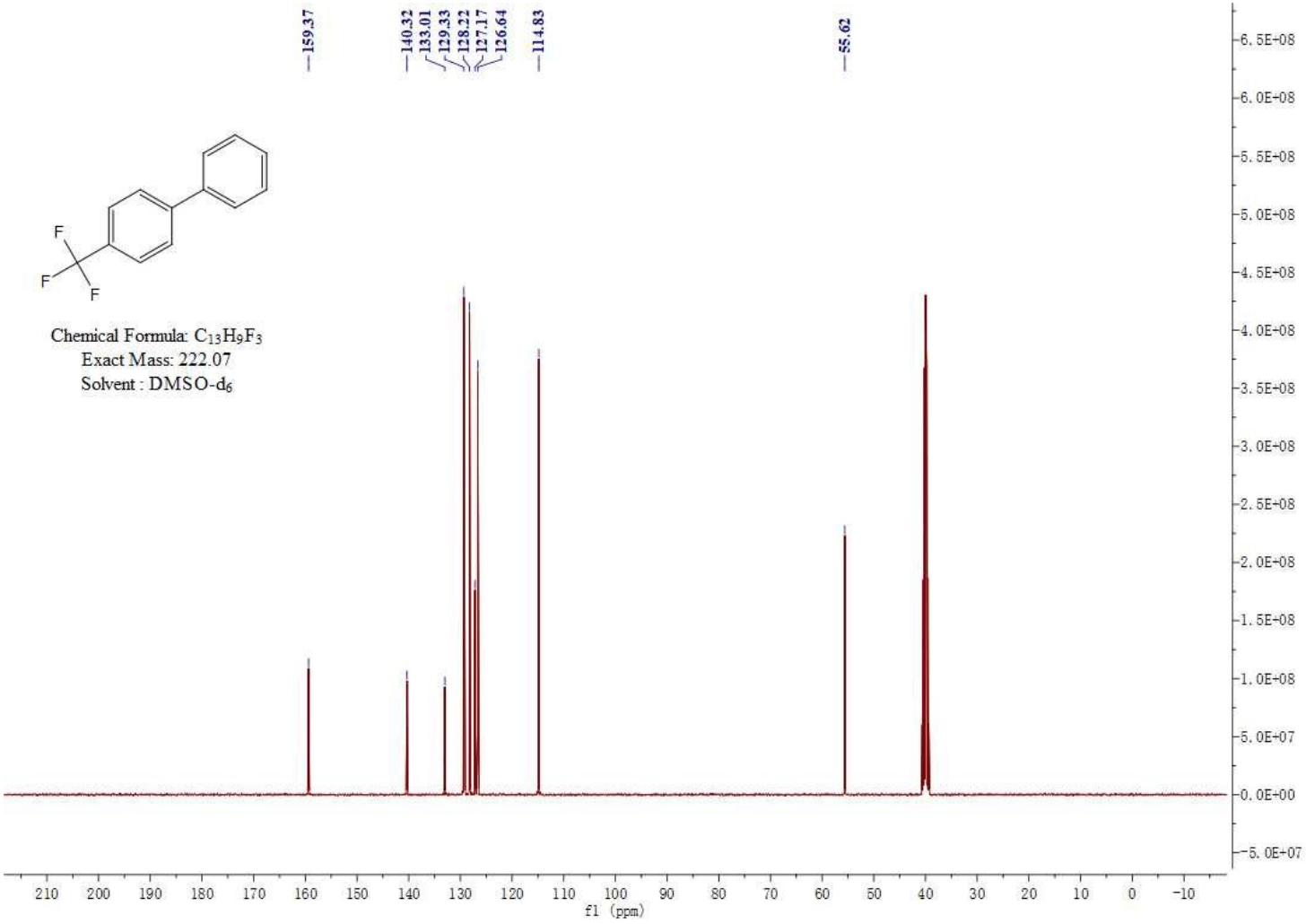


Fig. S33. The ^{13}C NMR spectrum of X14

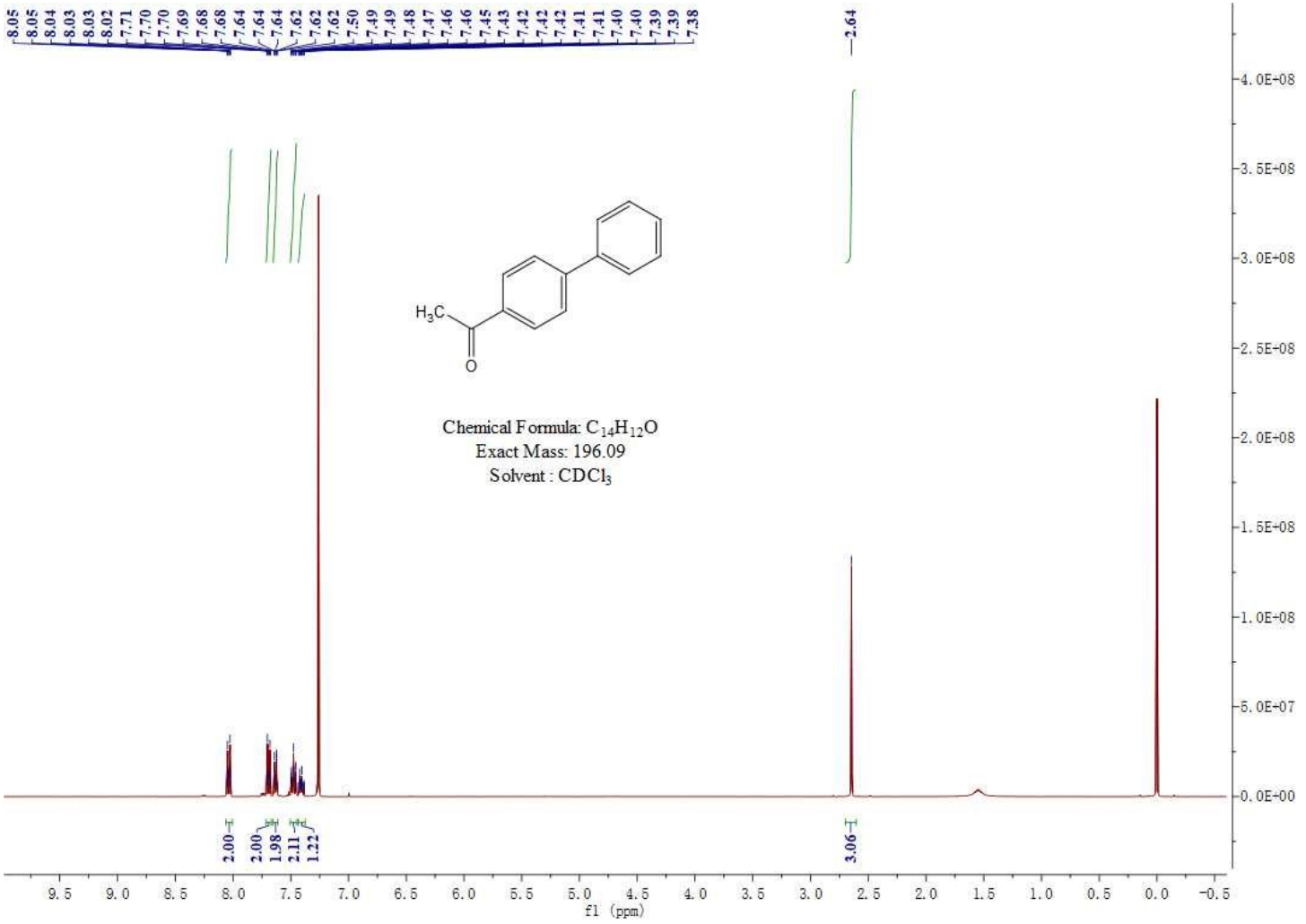


Fig. S34. The ^{1}H NMR spectrum of X15

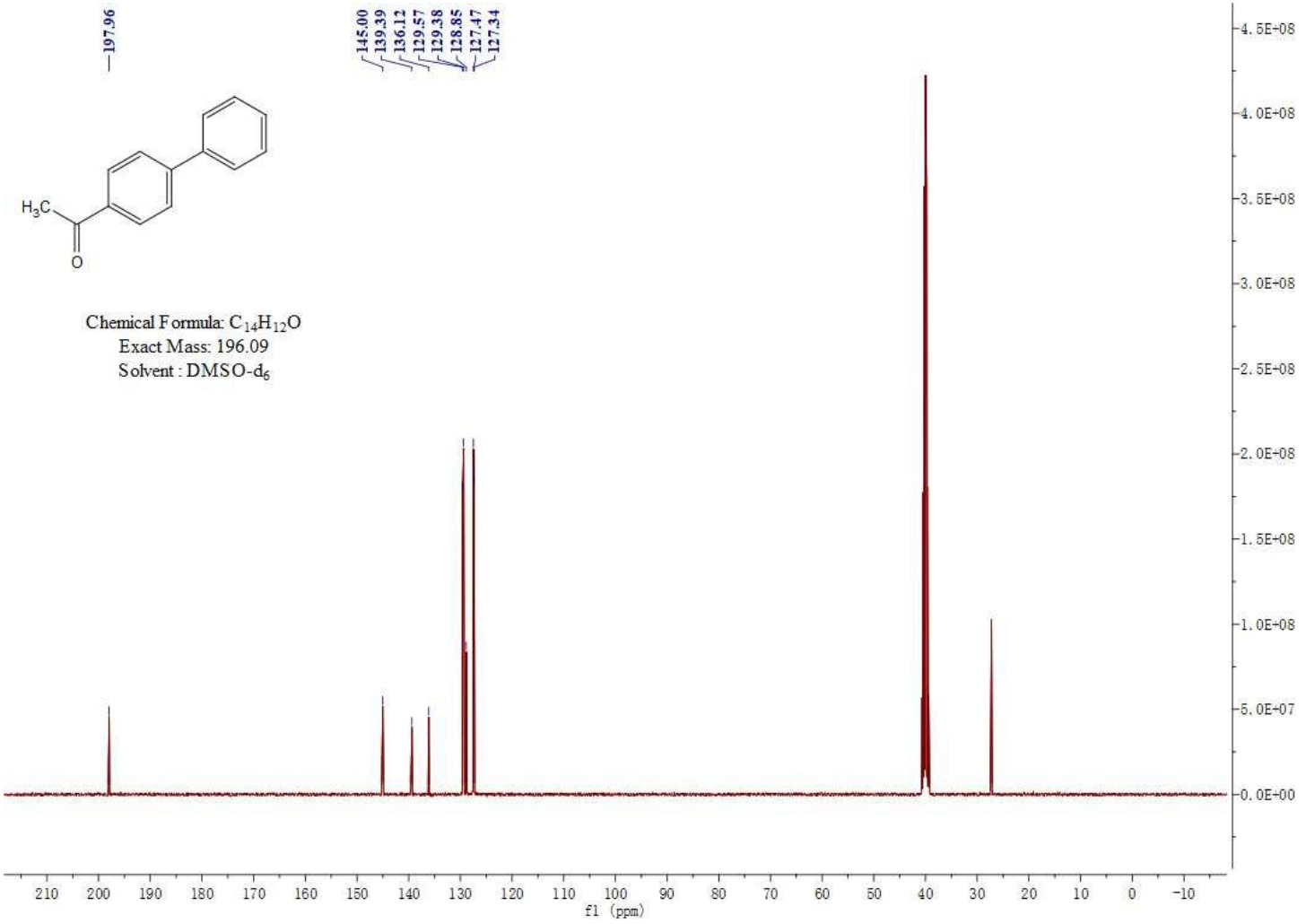


Fig. S35. The ^{13}C NMR spectrum of X15

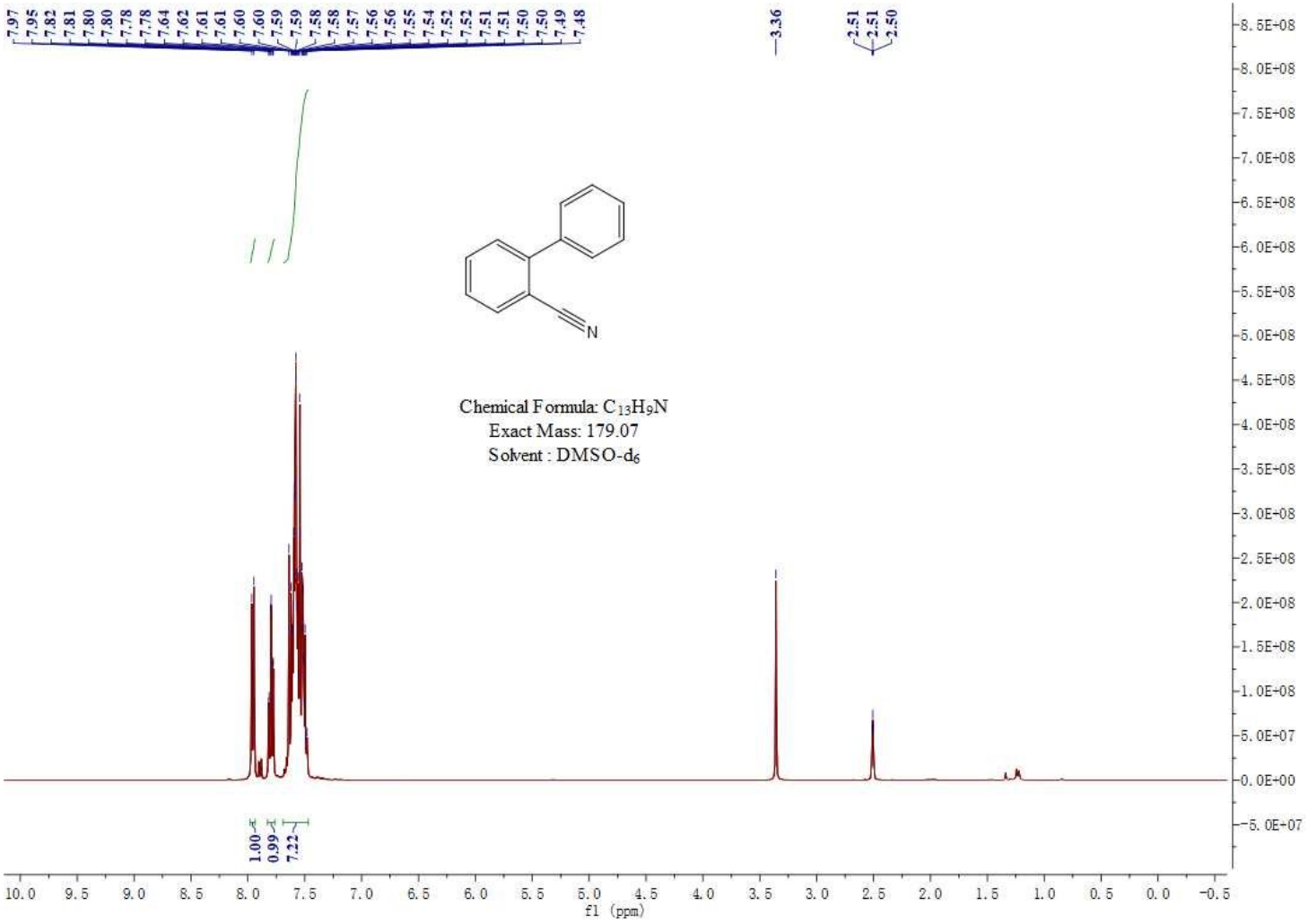


Fig. S36. The ^{1}H NMR spectrum of X16

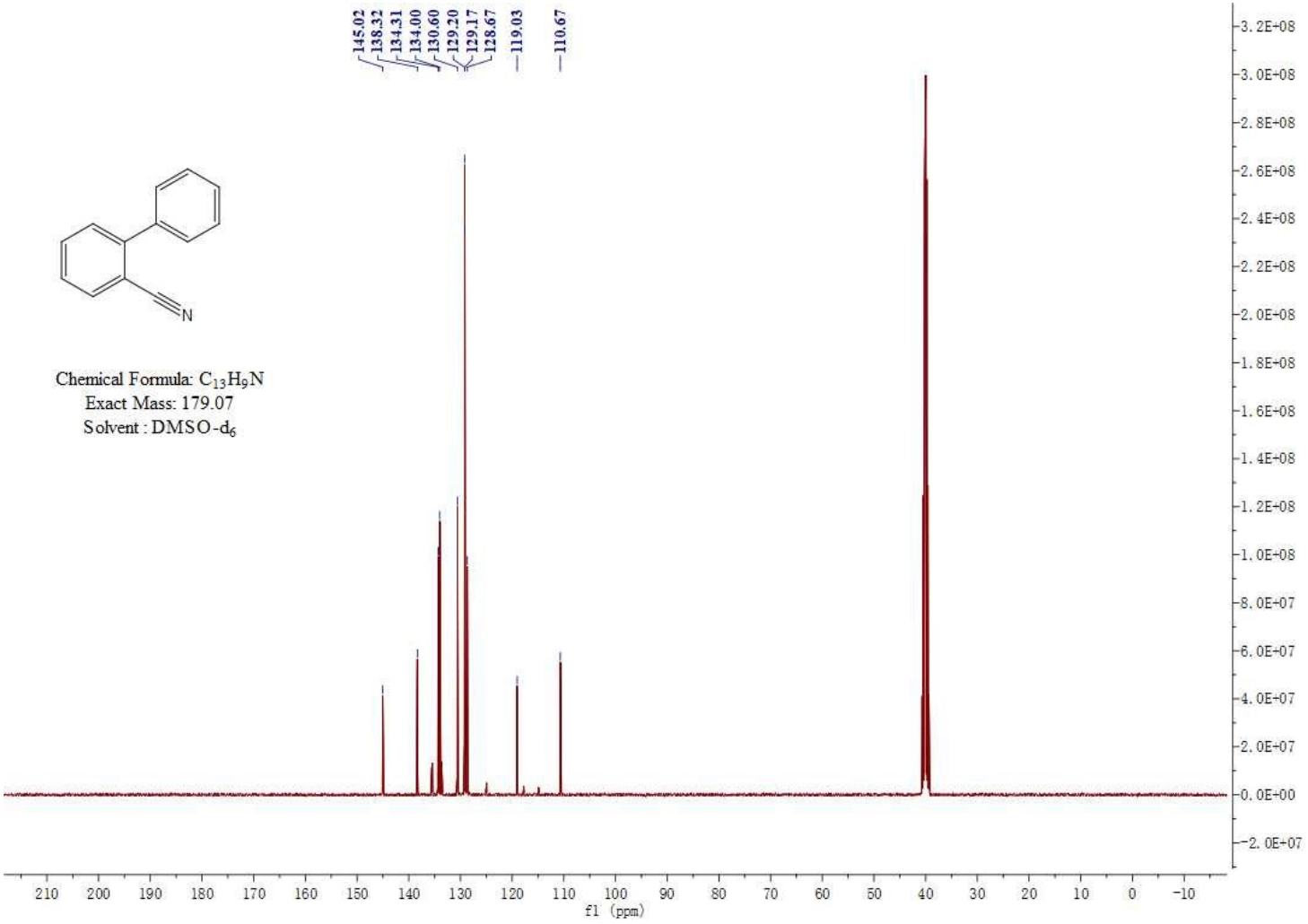


Fig. S37. The ^{13}C NMR spectrum of X16

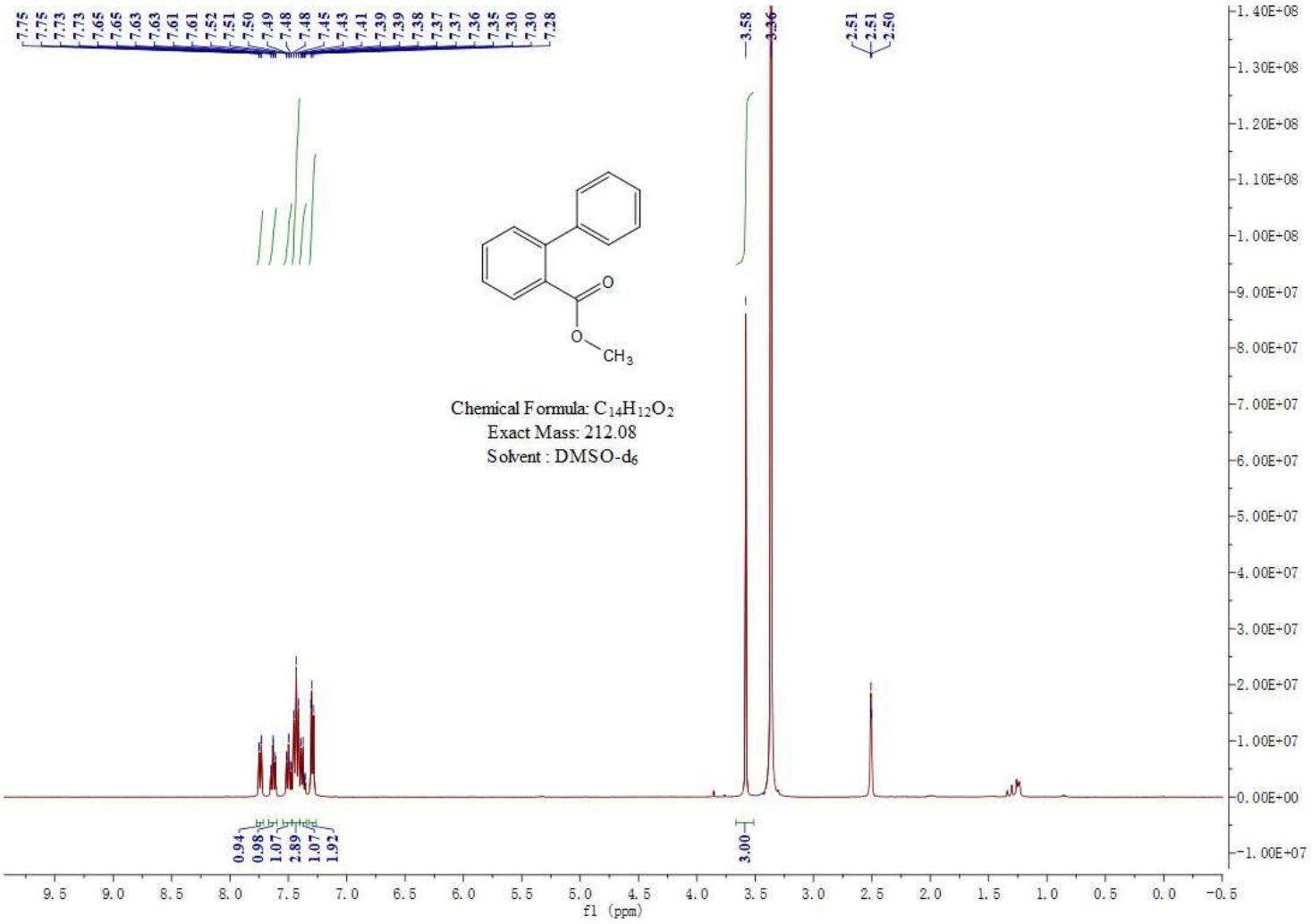


Fig. S38. The ^{1}H NMR spectrum of X17

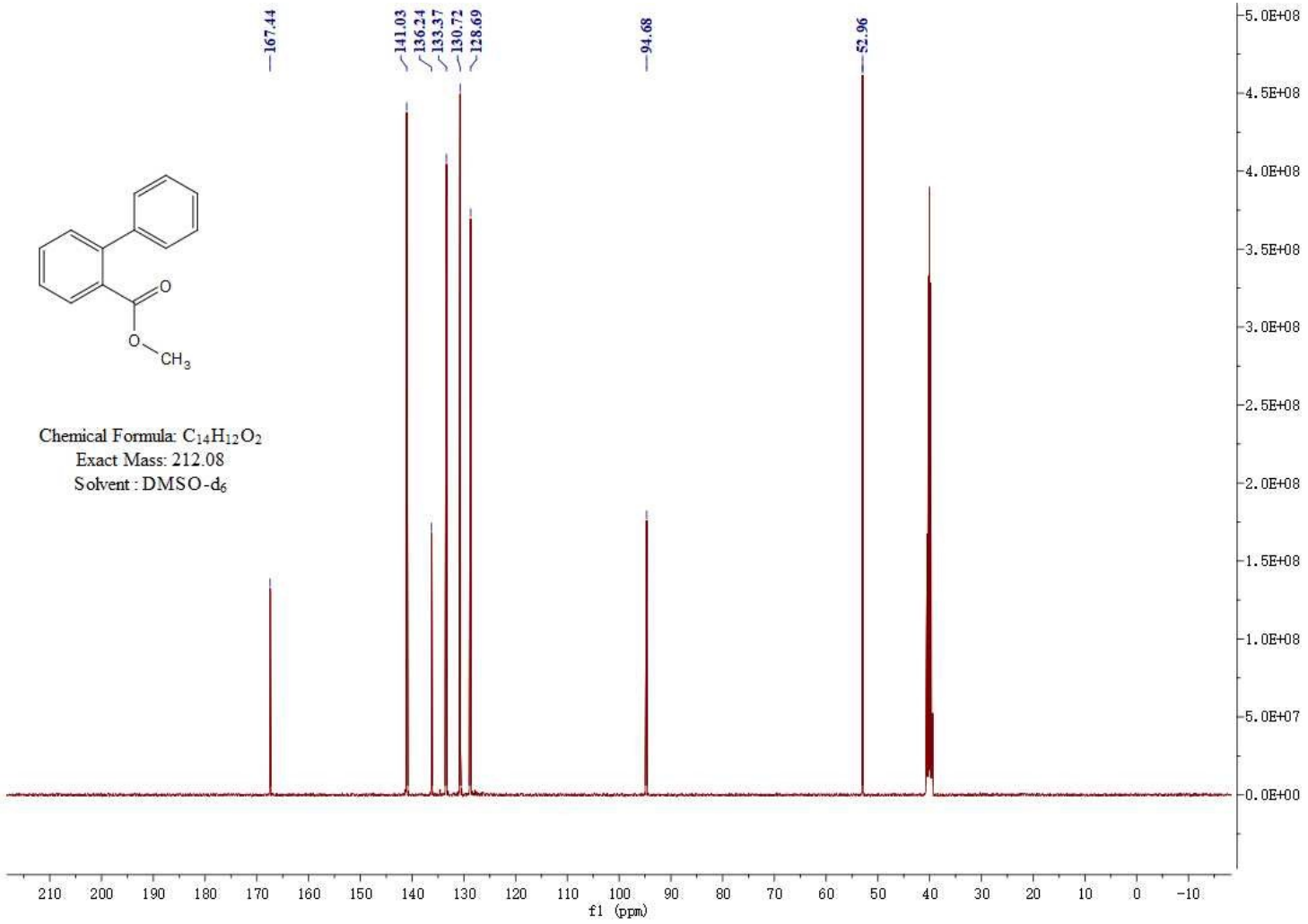


Fig. S39. The ^{13}C NMR spectrum of X17

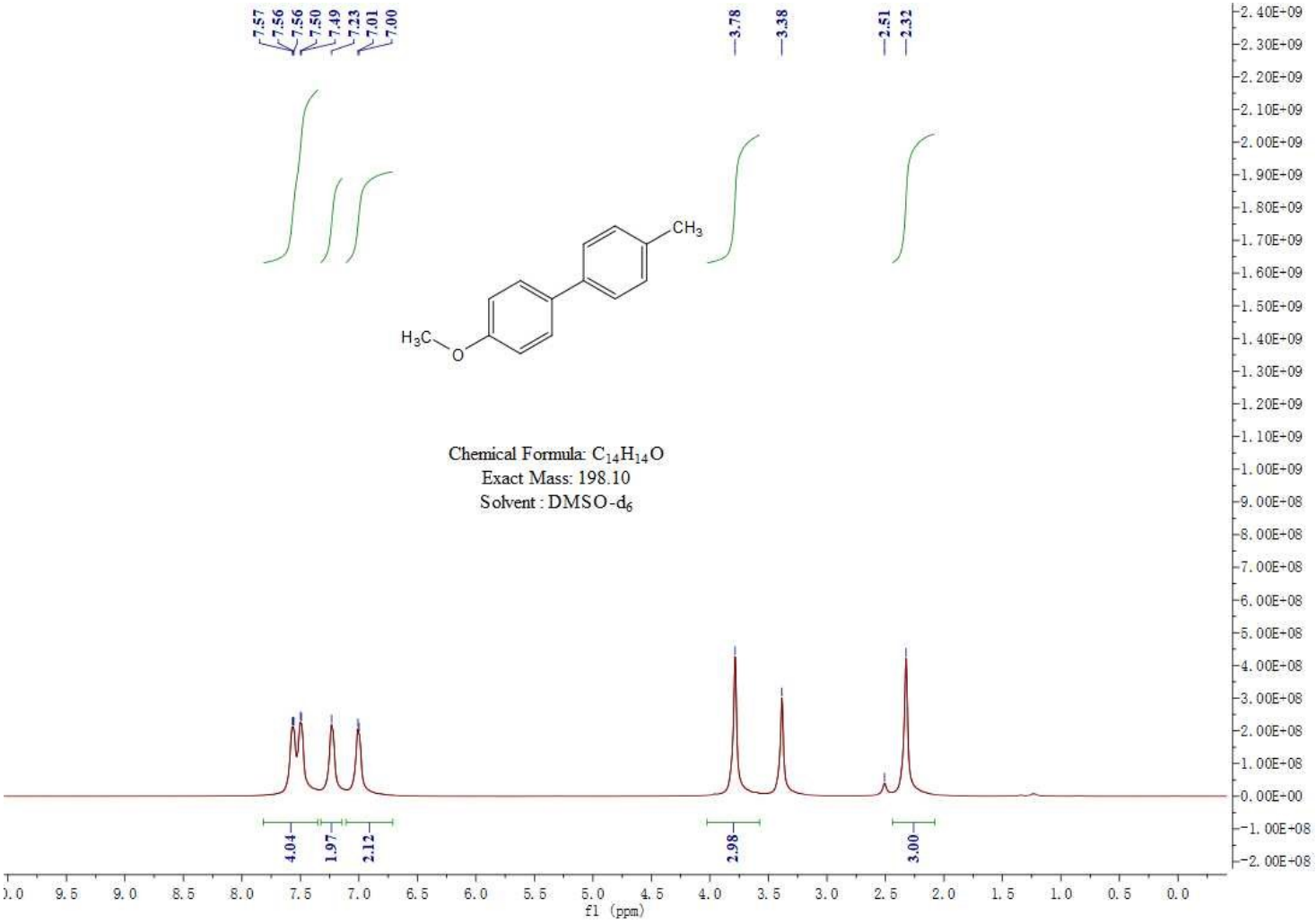


Fig. S40. The ^{1}H NMR spectrum of B2-3

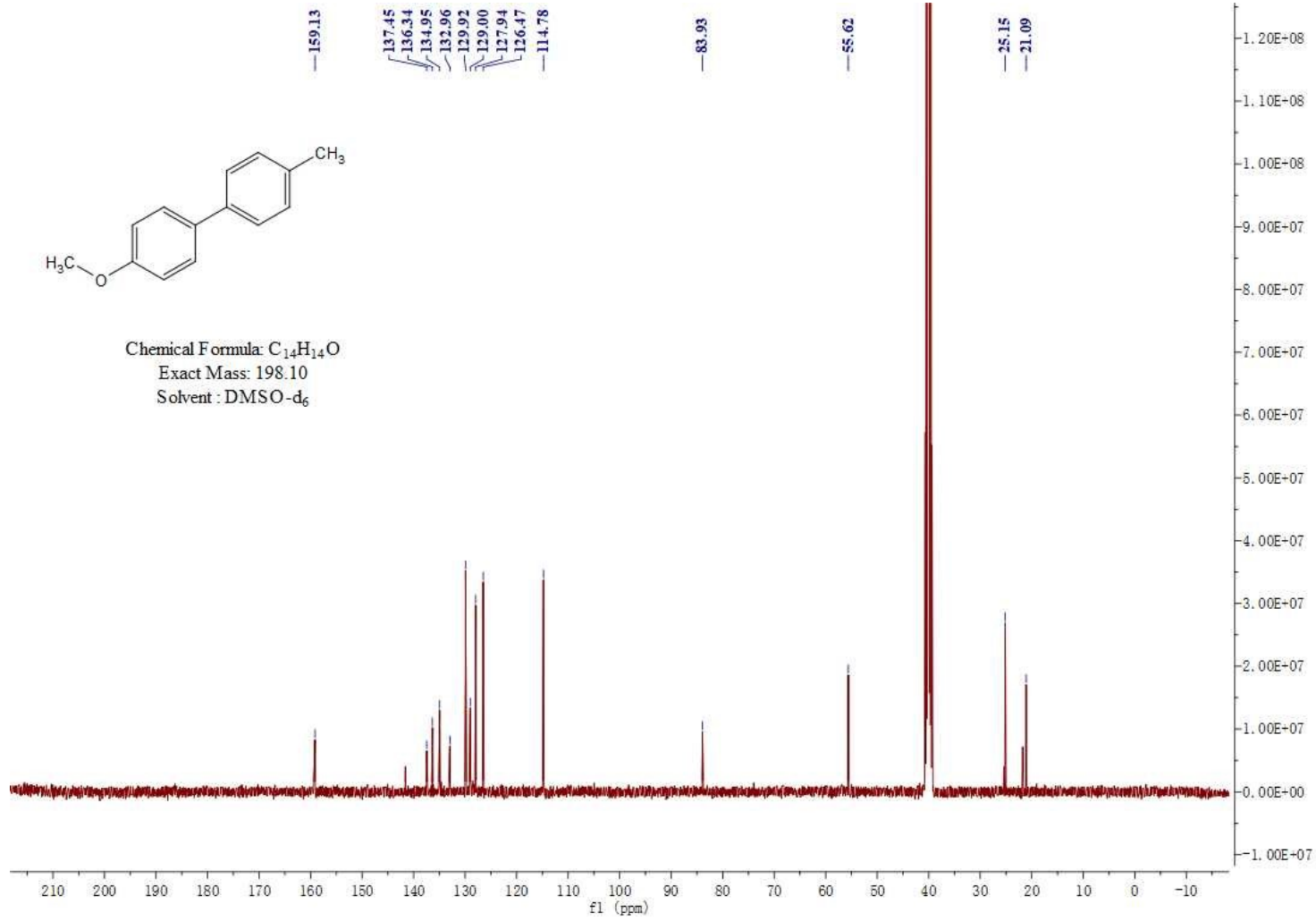


Fig. S41. The ^{13}C NMR spectrum of B2-3

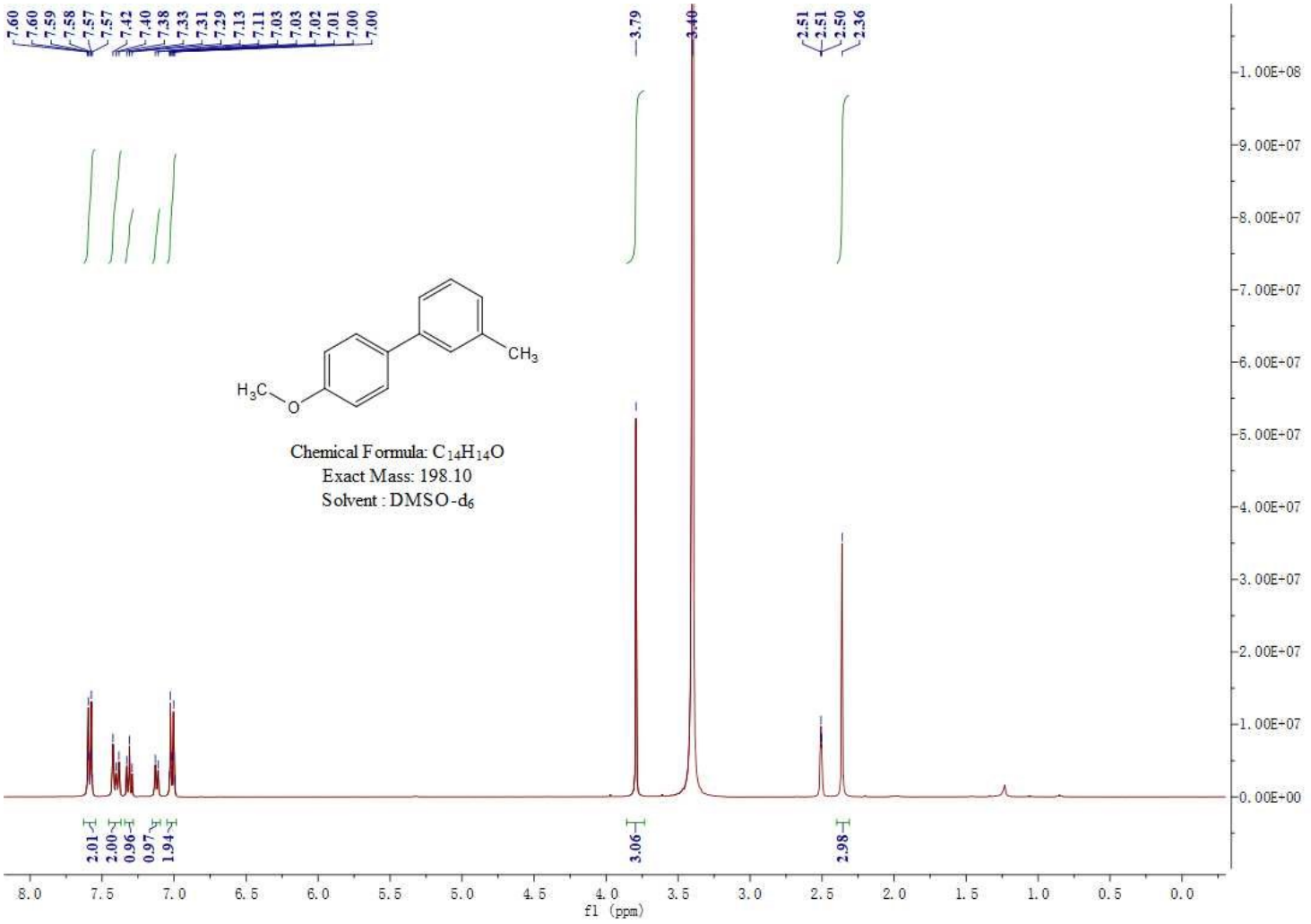


Fig. S42. The ^{1}H NMR spectrum of B4

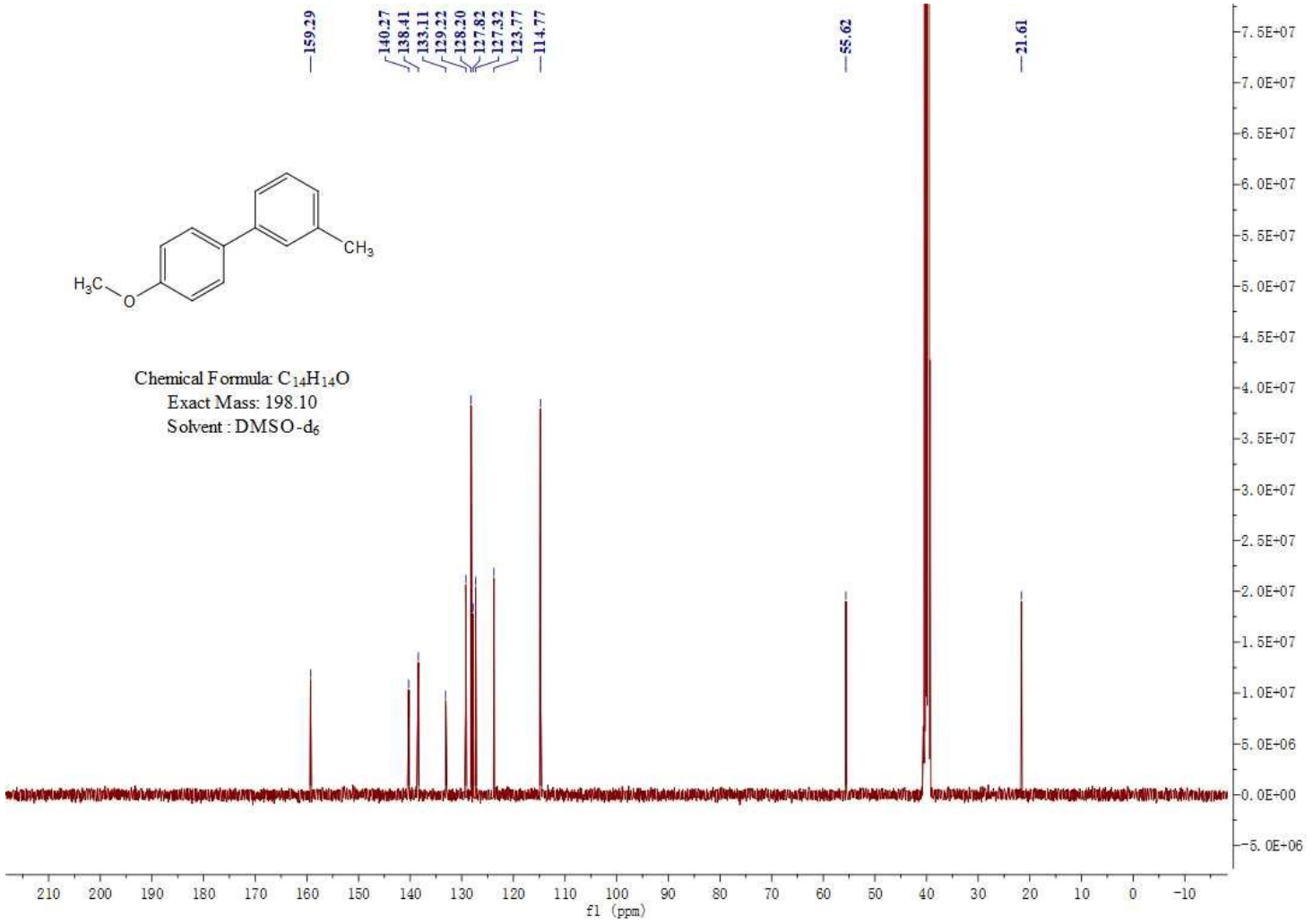


Fig. S43. The ^{13}C NMR spectrum of B4

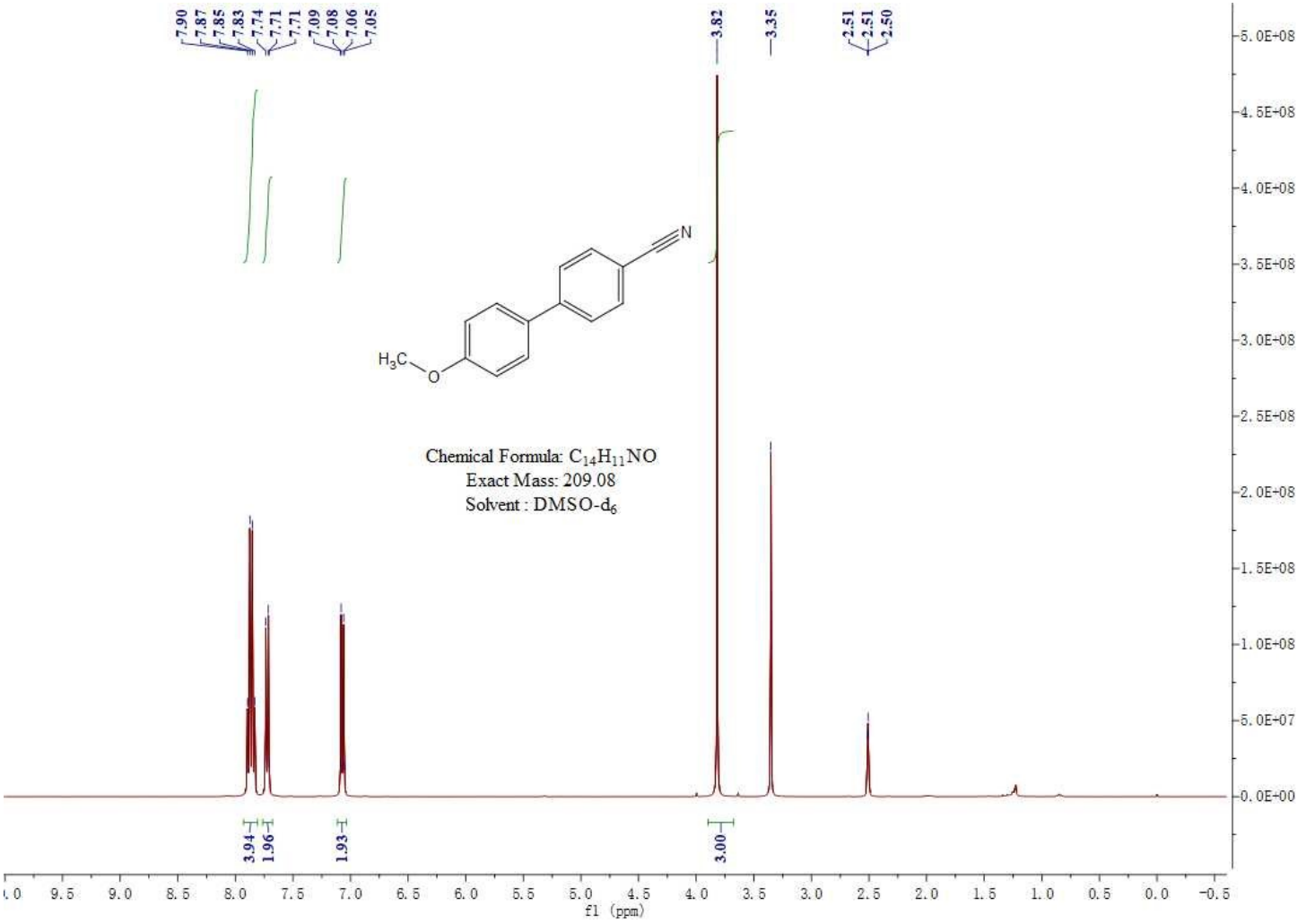


Fig. S44. The ^{1}H NMR spectrum of B5

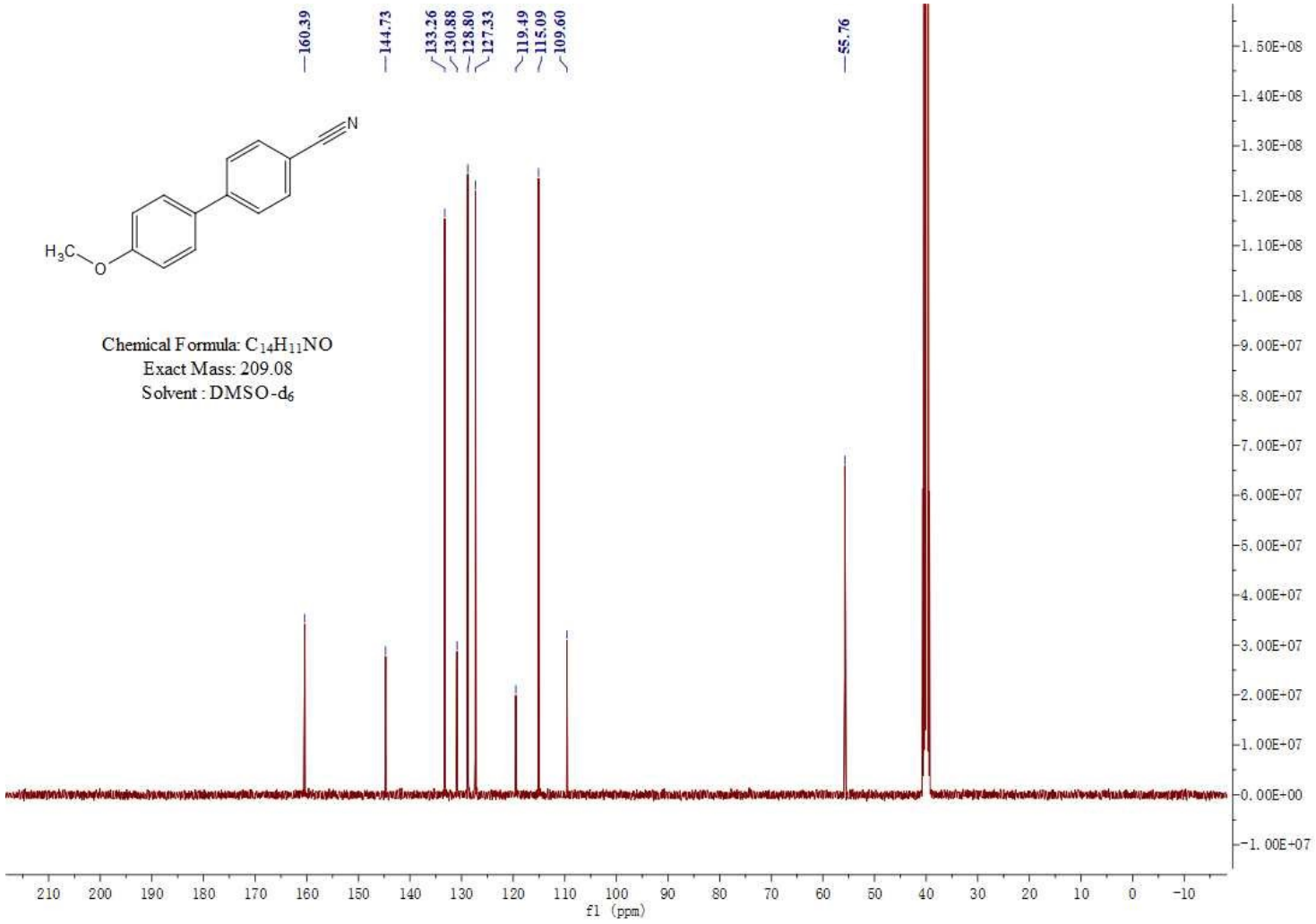


Fig. S45. The ^{13}C NMR spectrum of B5

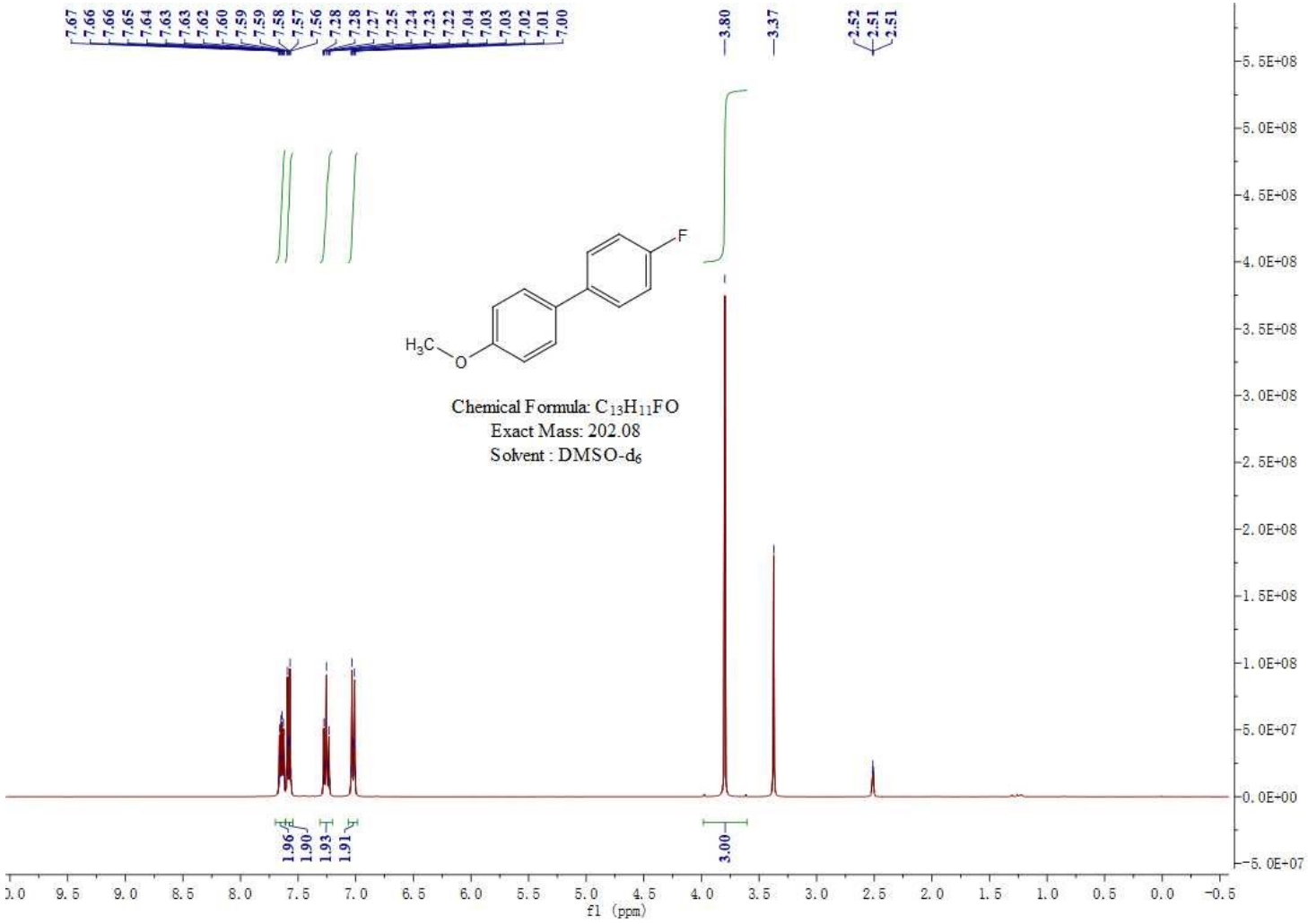


Fig. S46. The ^{1}H NMR spectrum of B6

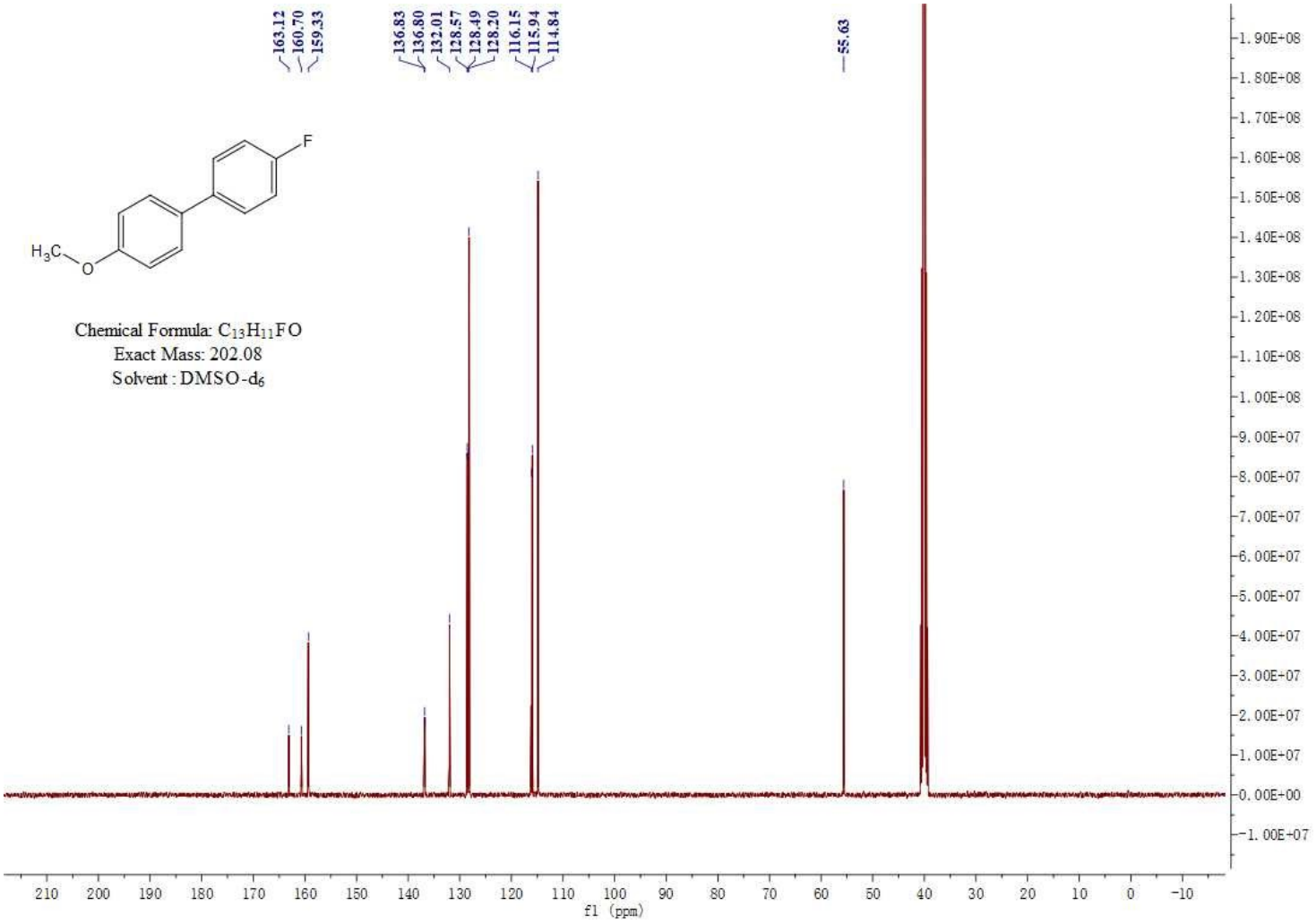


Fig. S47. The ^{13}C NMR spectrum of B6

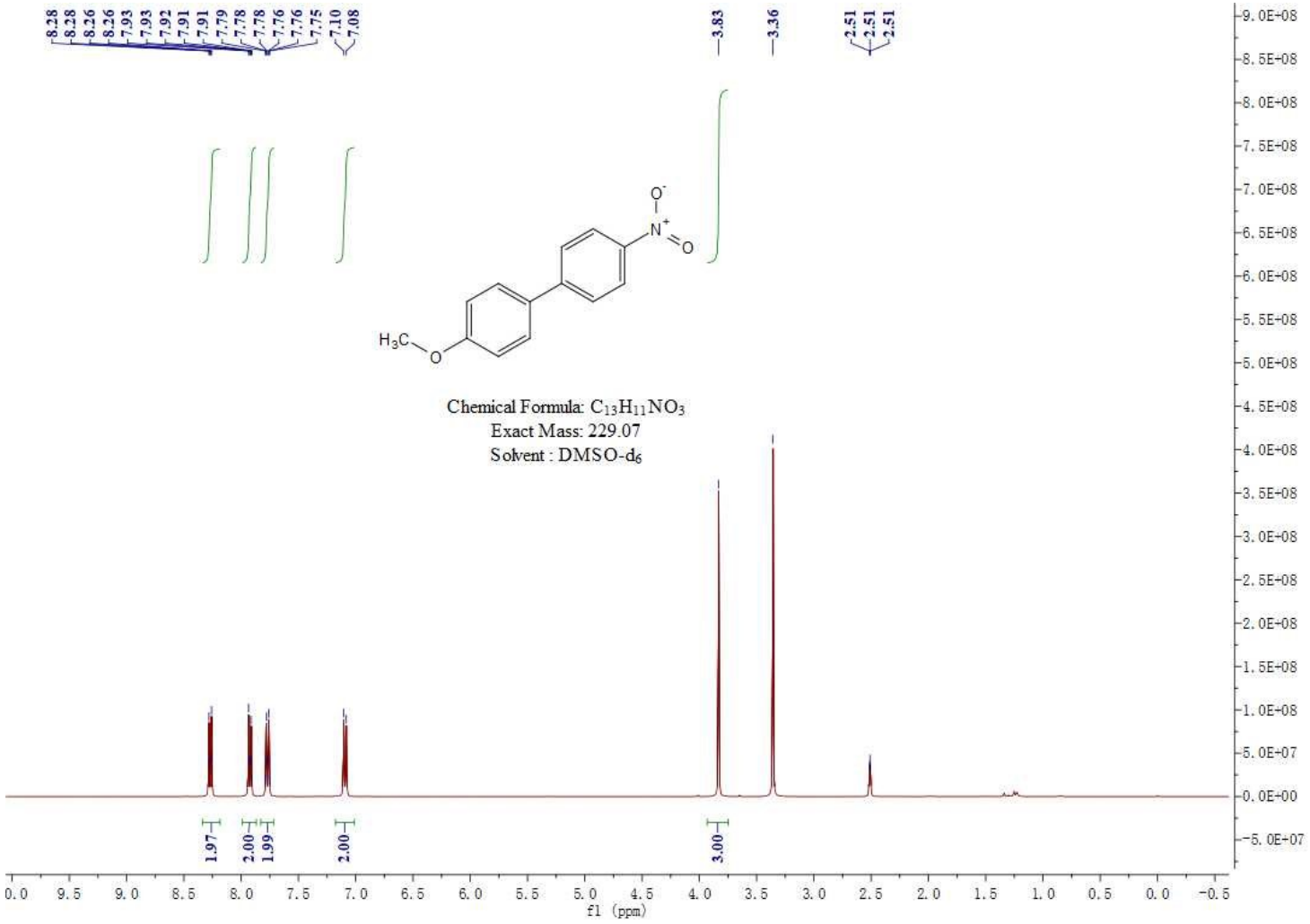


Fig. S48. The ^{1}H NMR spectrum of B7

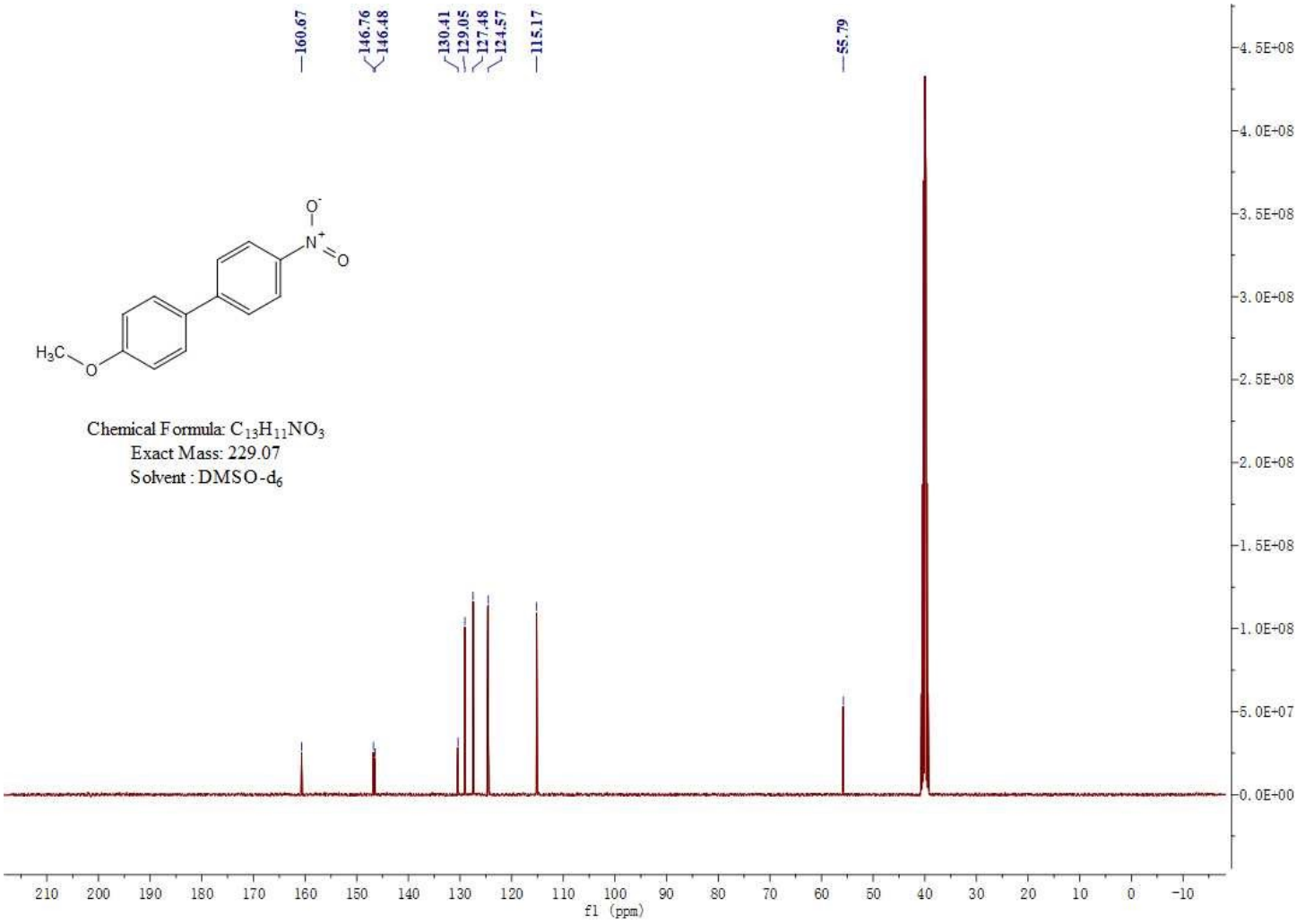


Fig. S49. The ^{13}C NMR spectrum of B7

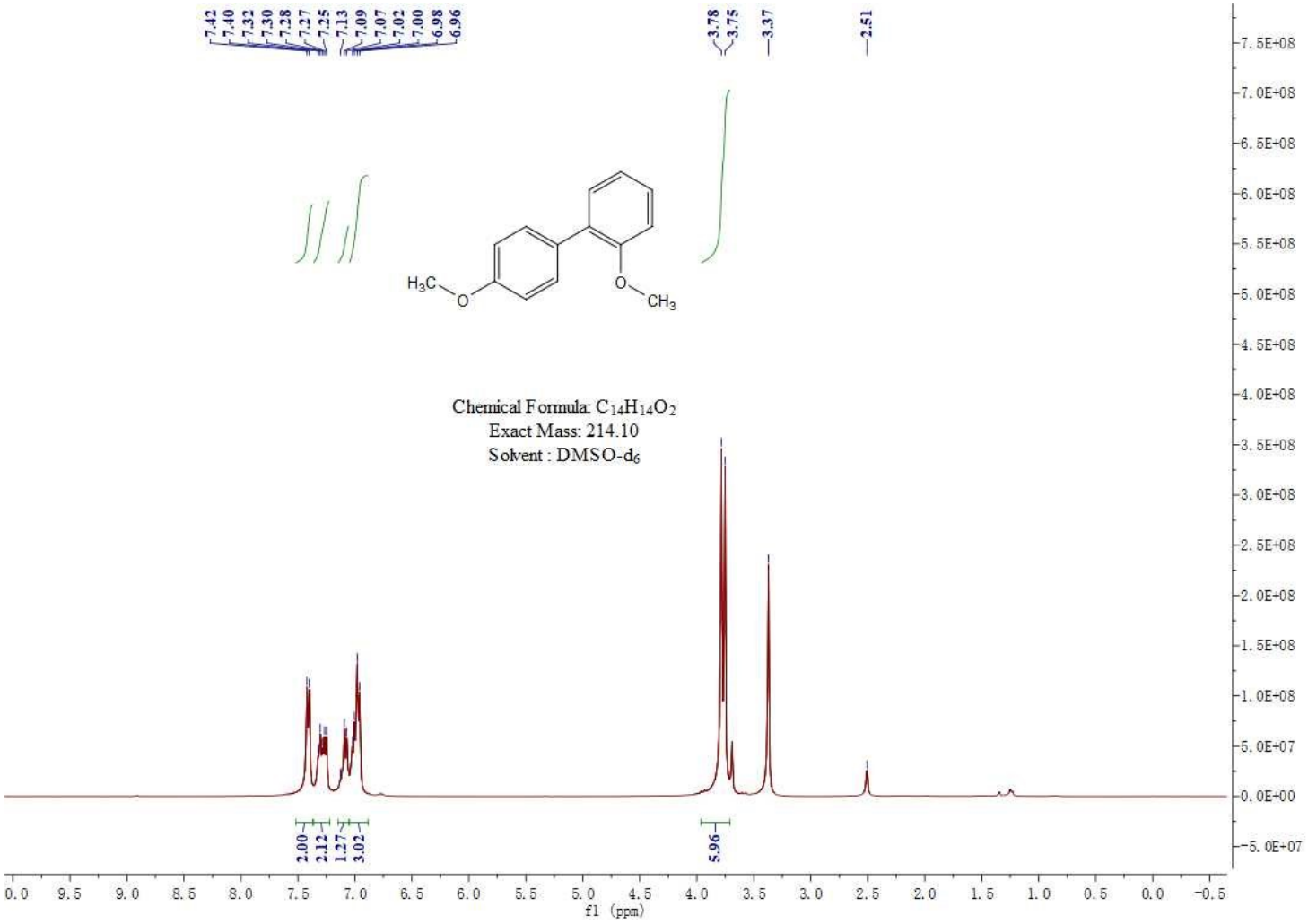


Fig. S50. The ^{1}H NMR spectrum of B8

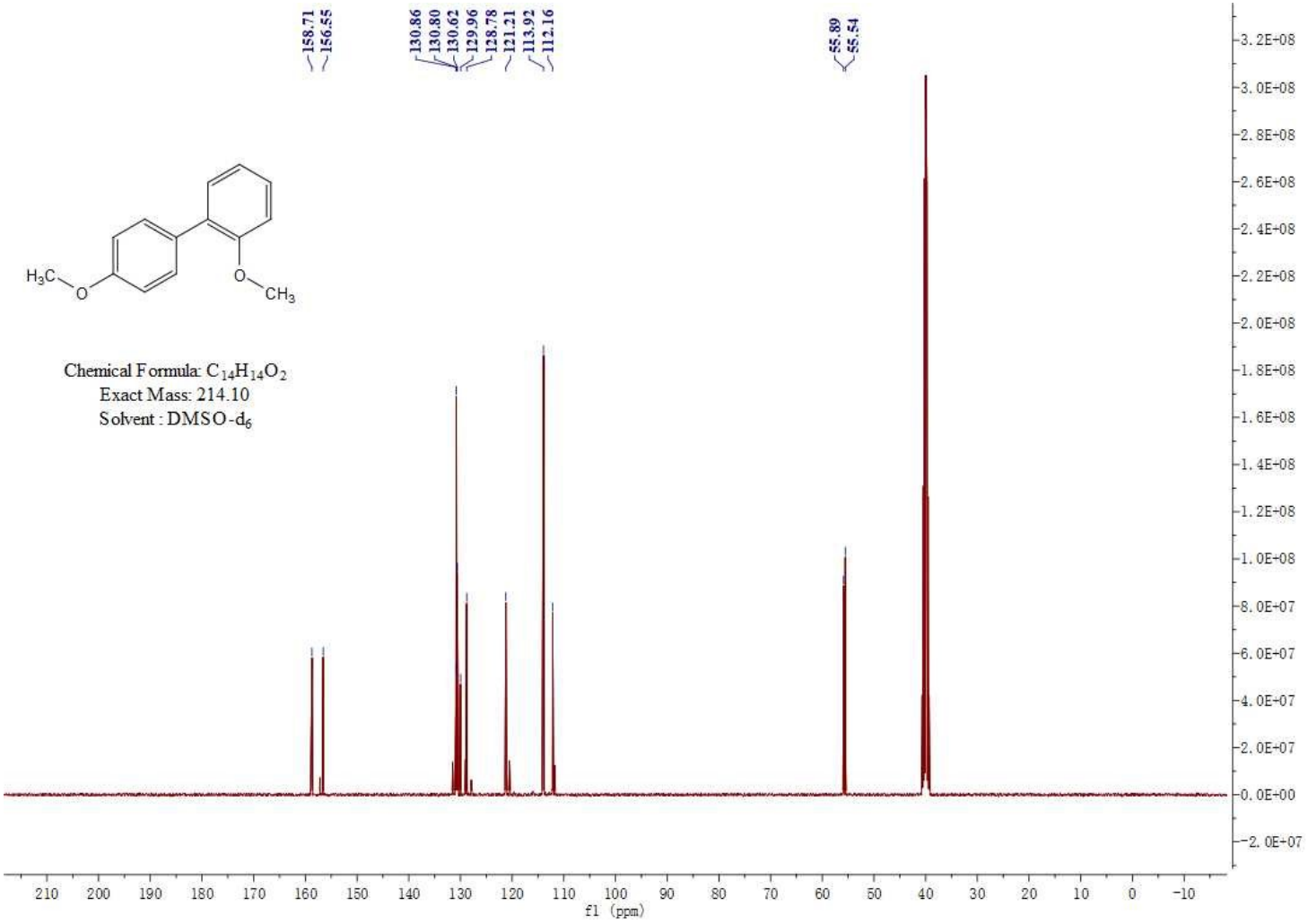


Fig. S51. The ^{13}C NMR spectrum of B8

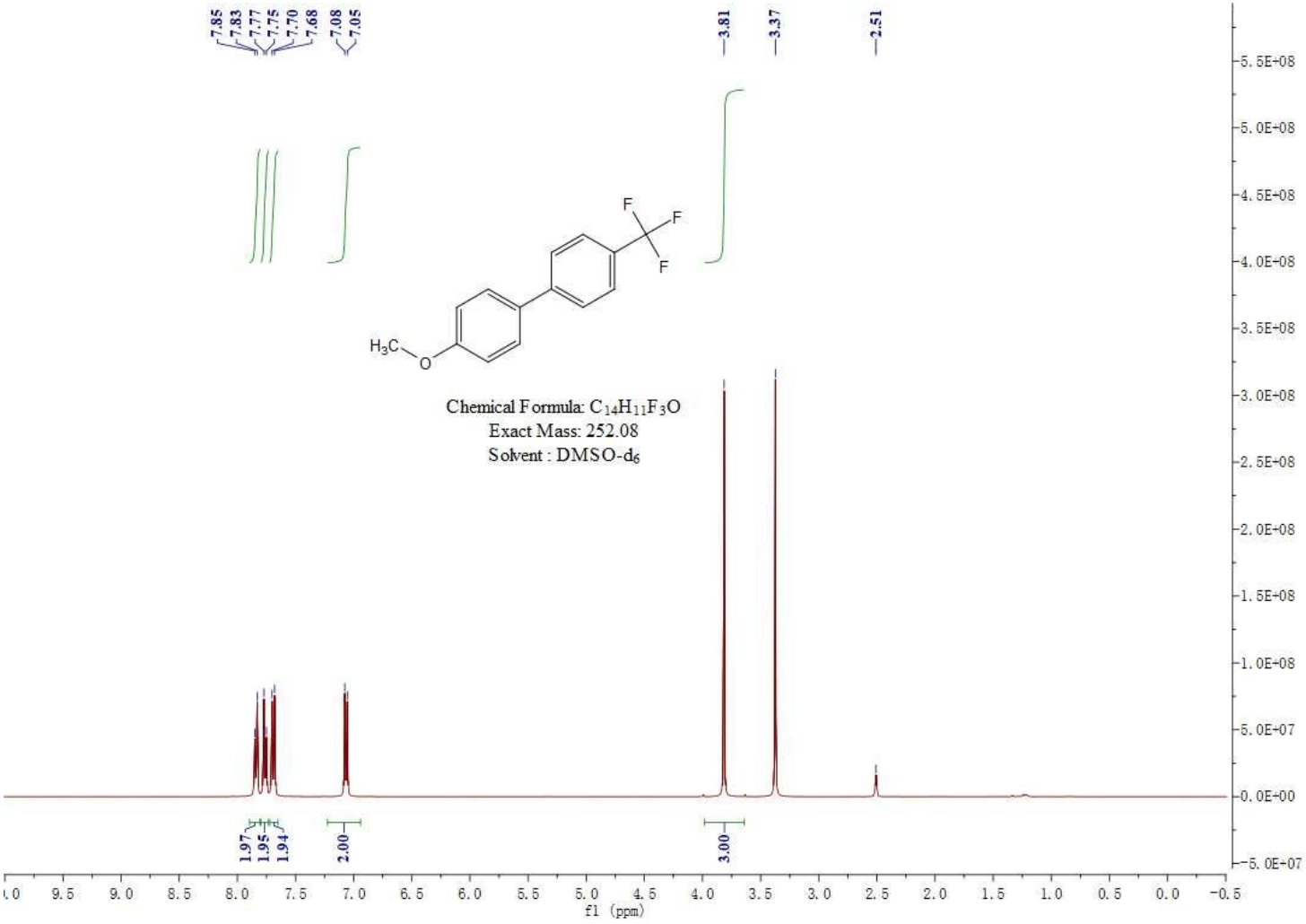


Fig. S52. The ^{1}H NMR spectrum of B9

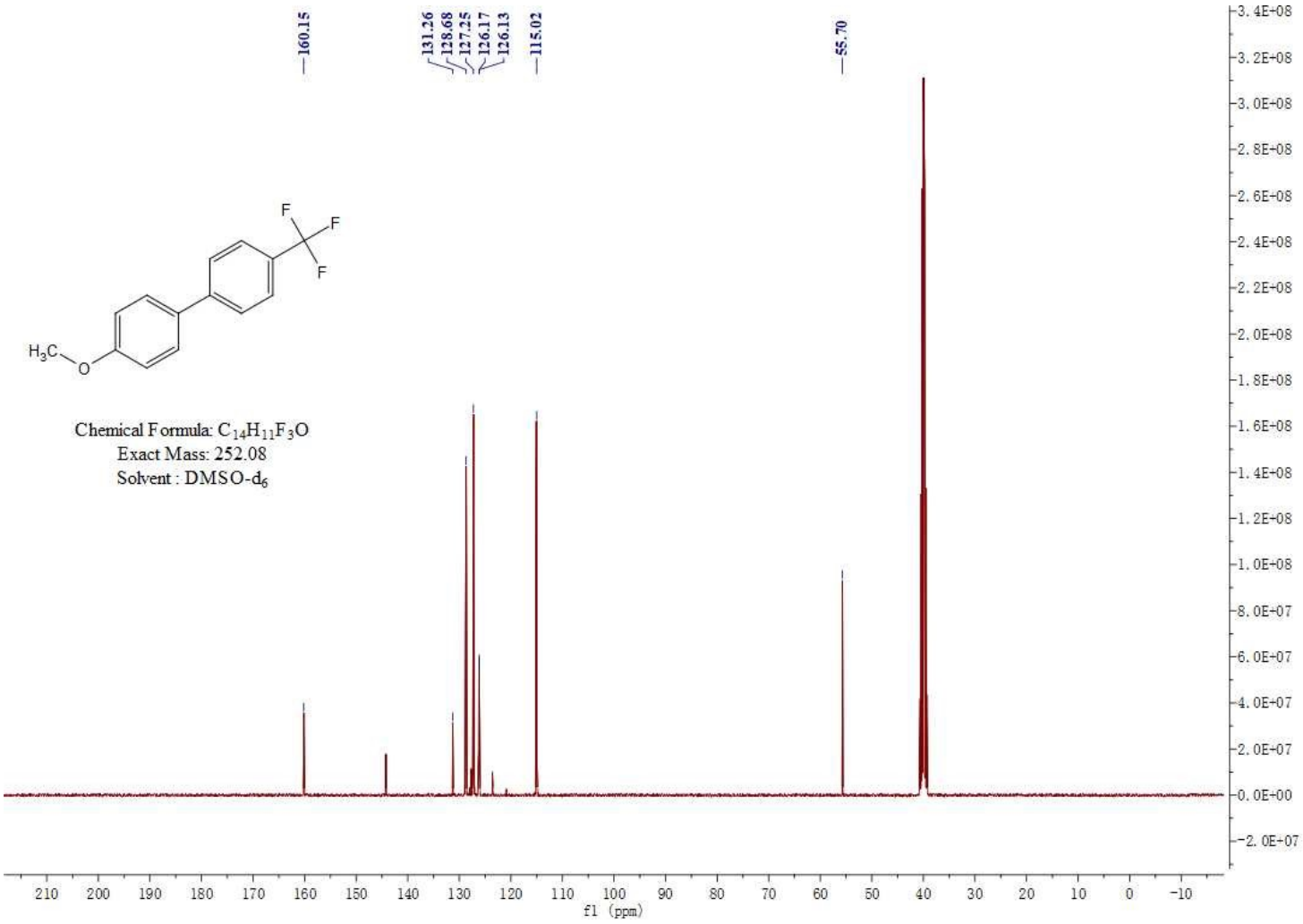


Fig S53. The ^{13}C NMR spectrum of B9

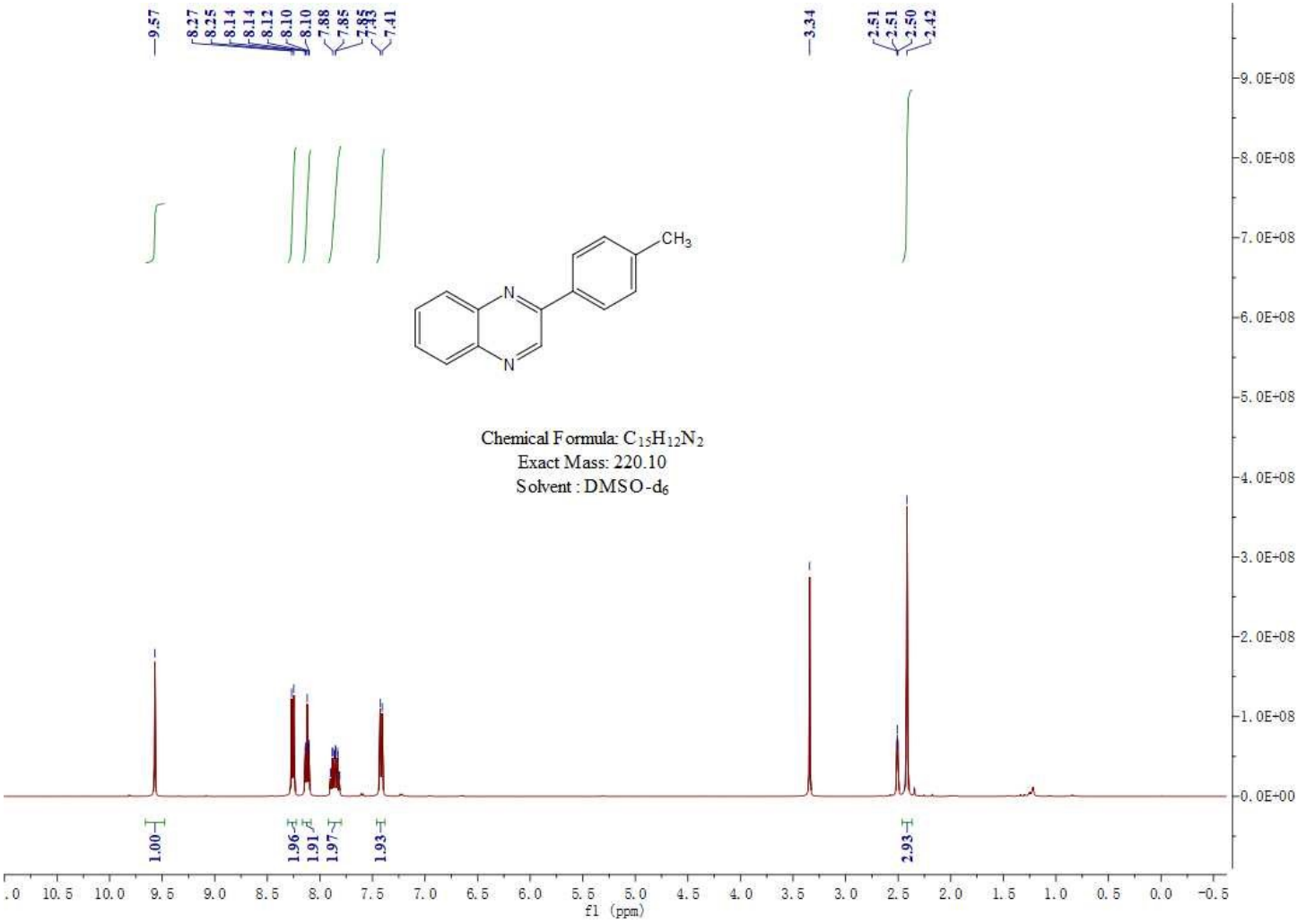


Fig. S54. The ^{1}H NMR spectrum of A1

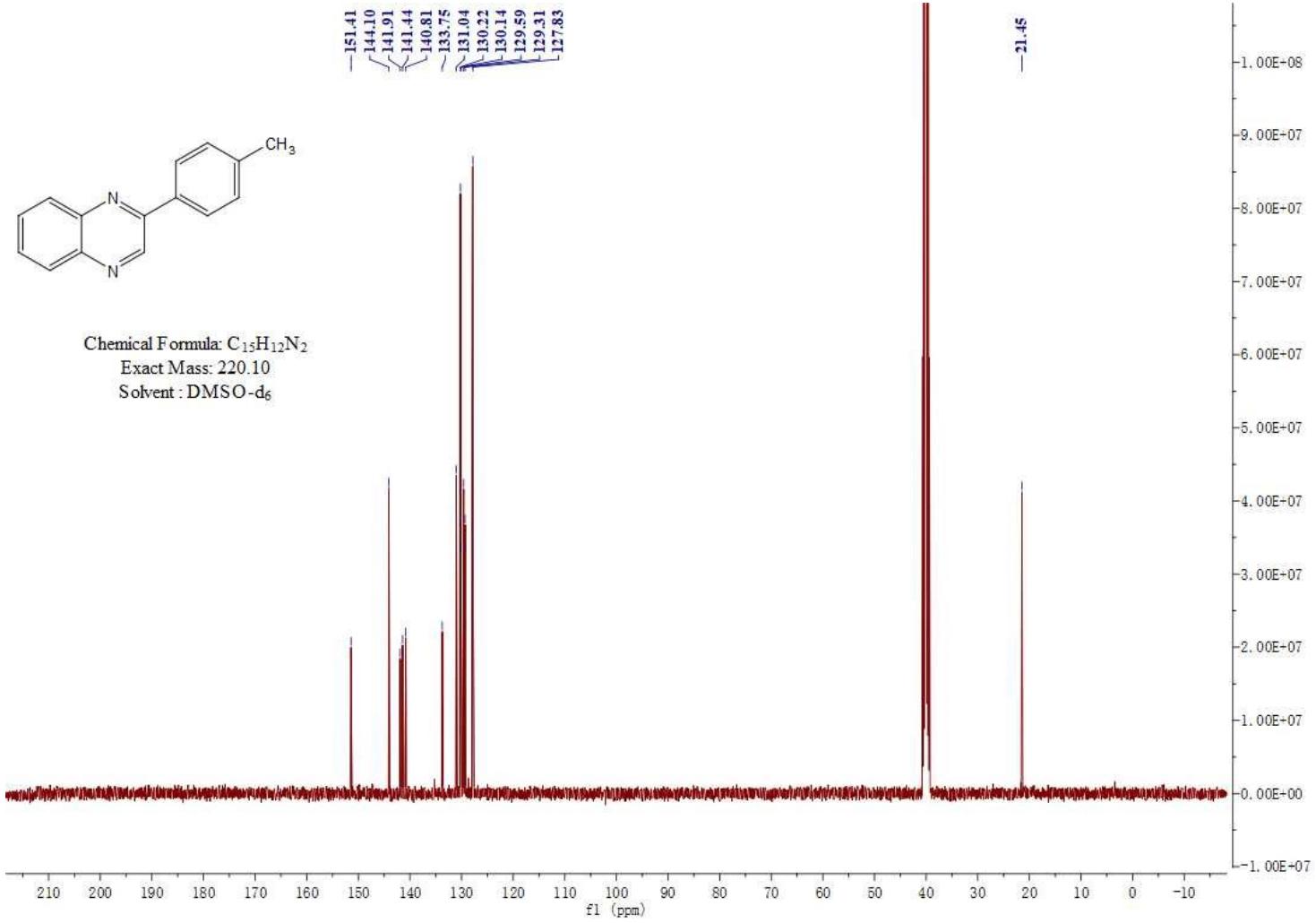


Fig. S55. The ^{13}C NMR spectrum of A1

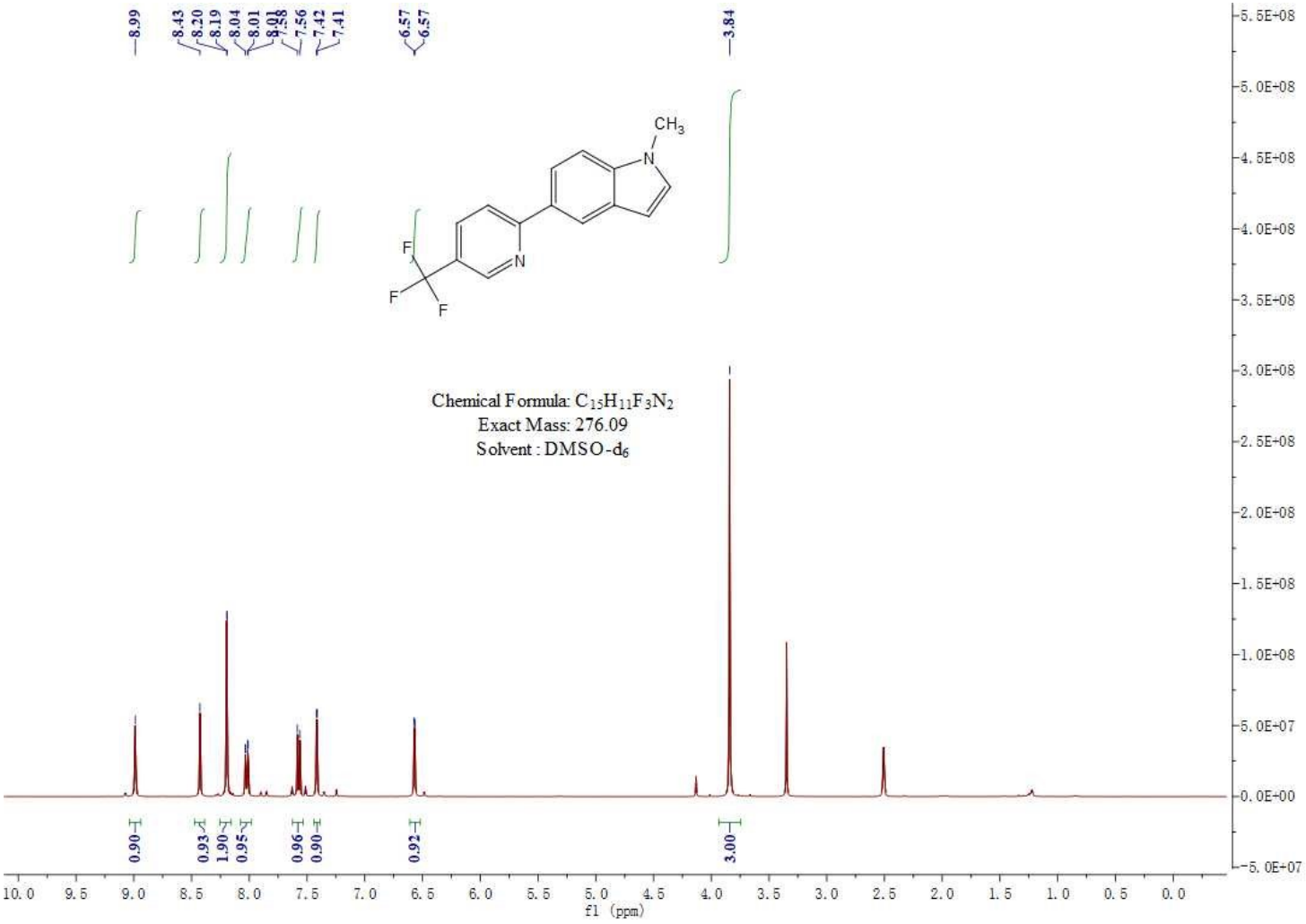


Fig. S56. The ^{1}H NMR spectrum of A2

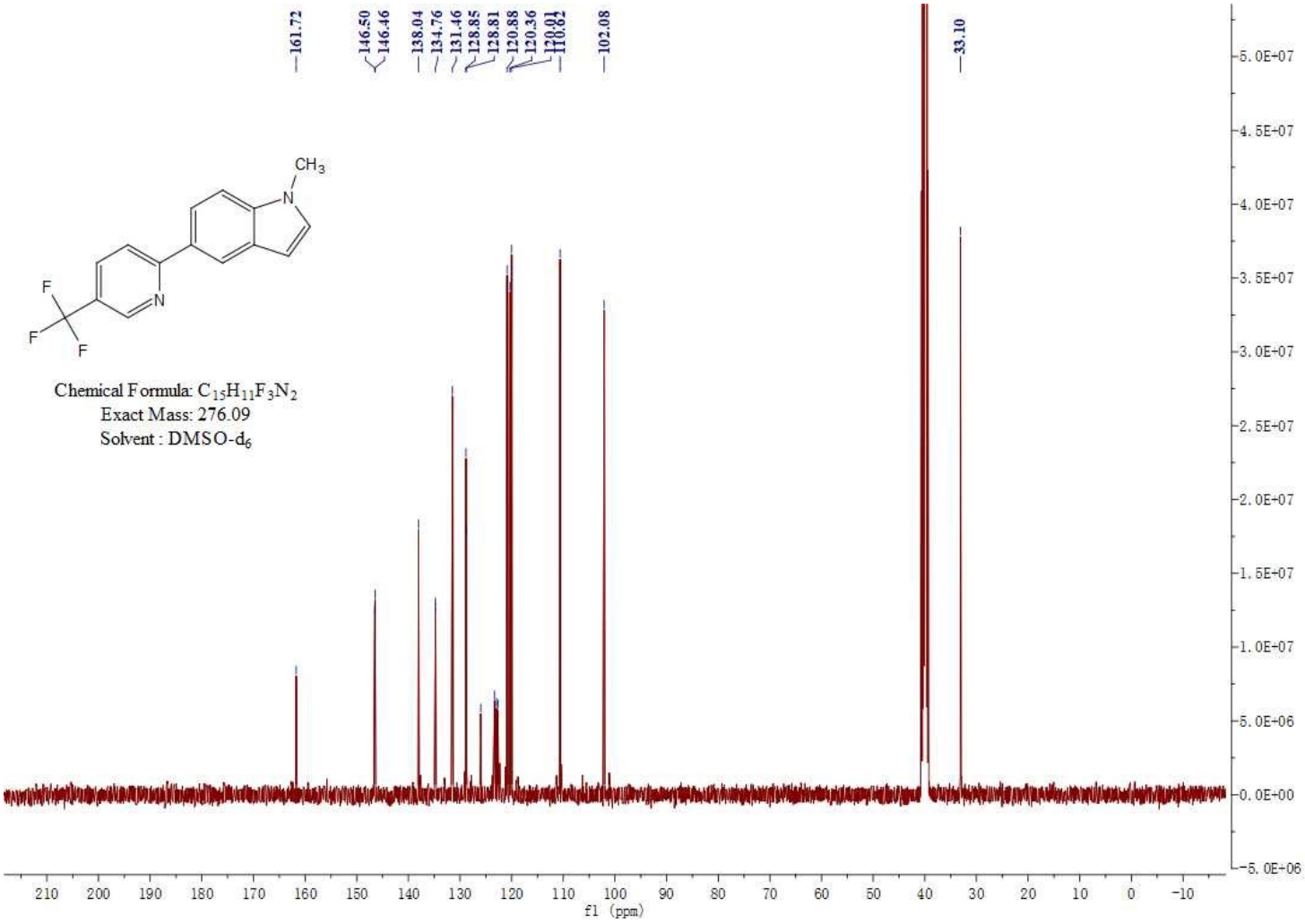


Fig. S57. The ^{13}C NMR spectrum of A2

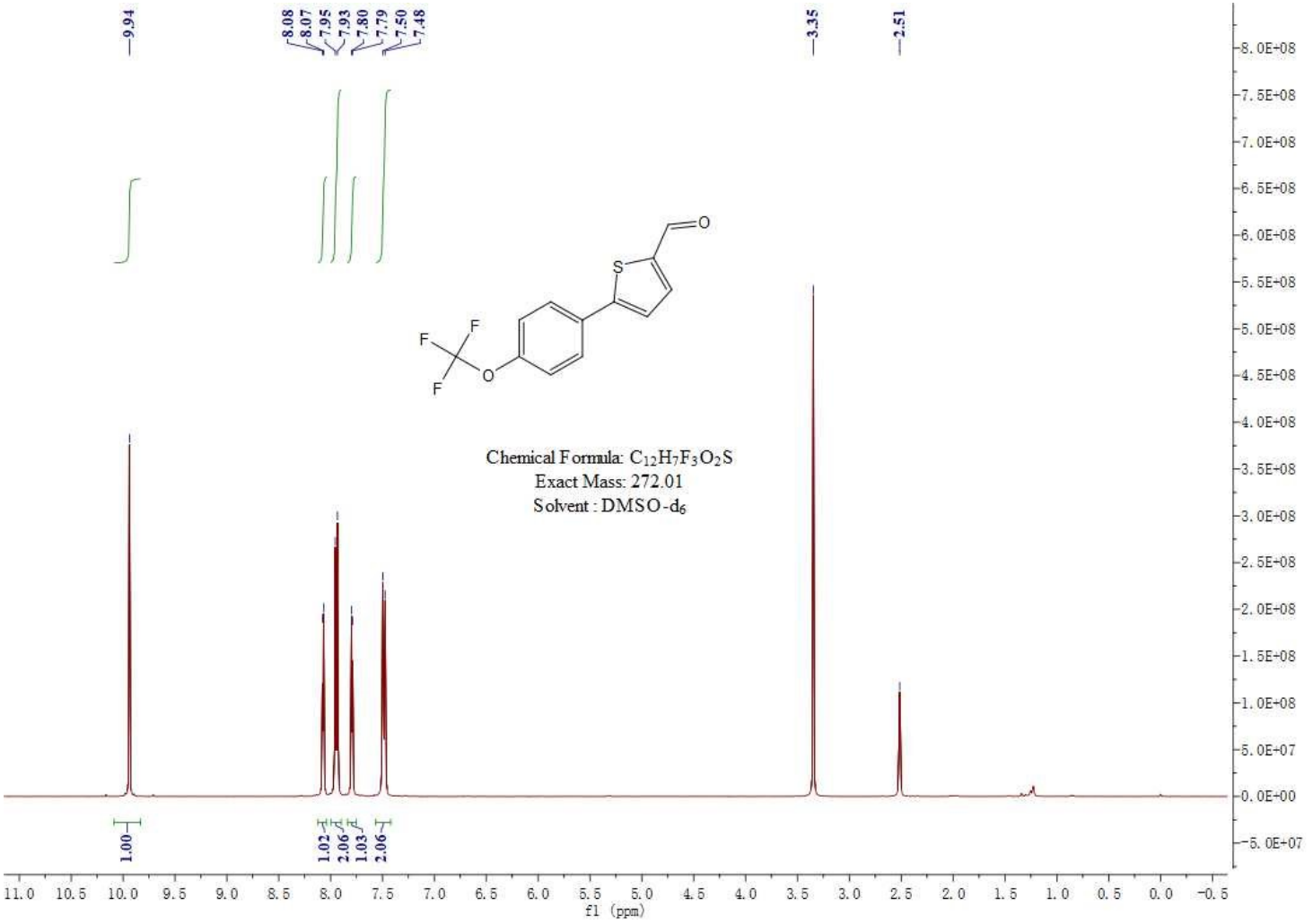


Fig. S58. The ^{1}H NMR spectrum of A3

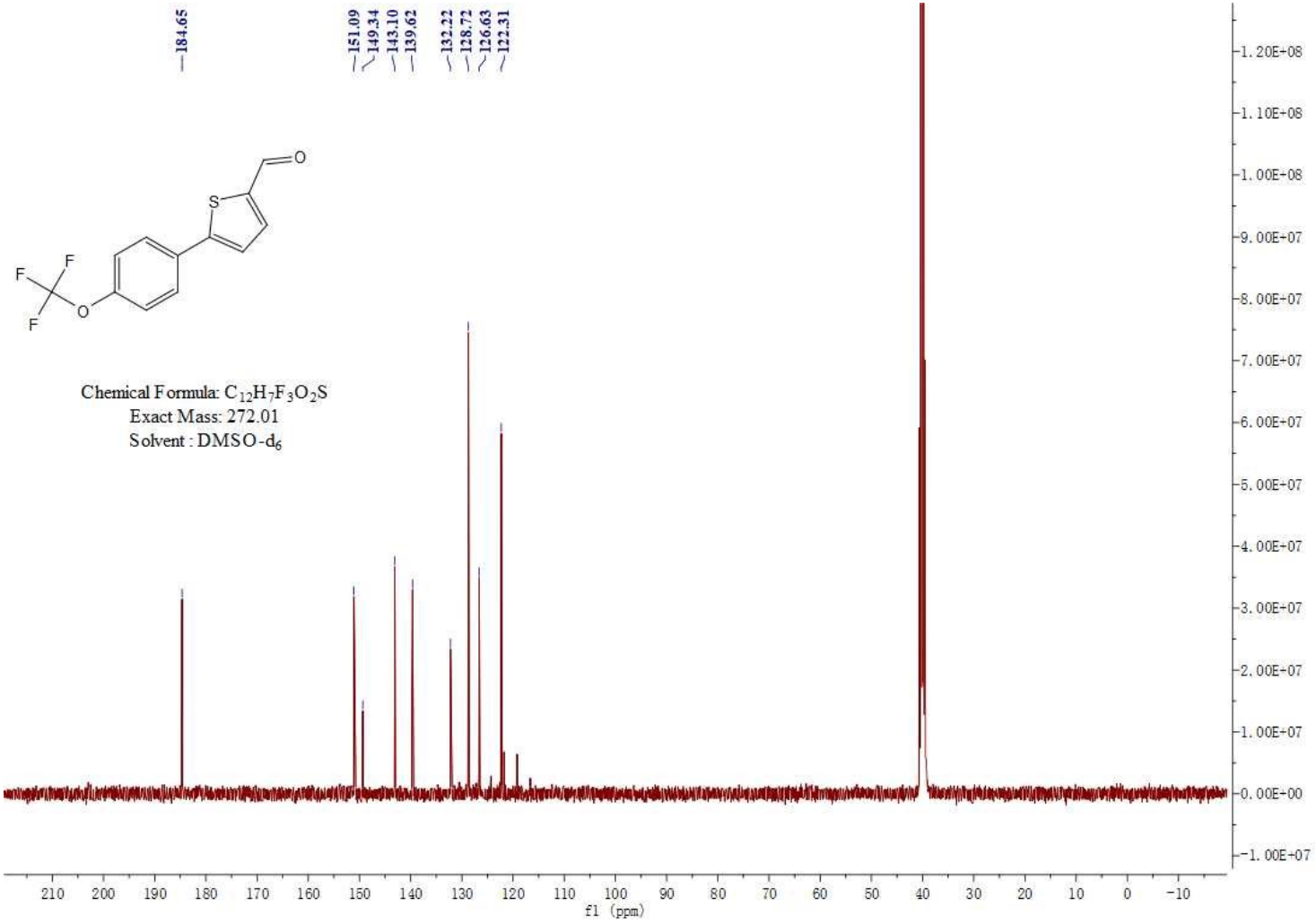


Fig. S59. The ^{13}C NMR spectrum of A3

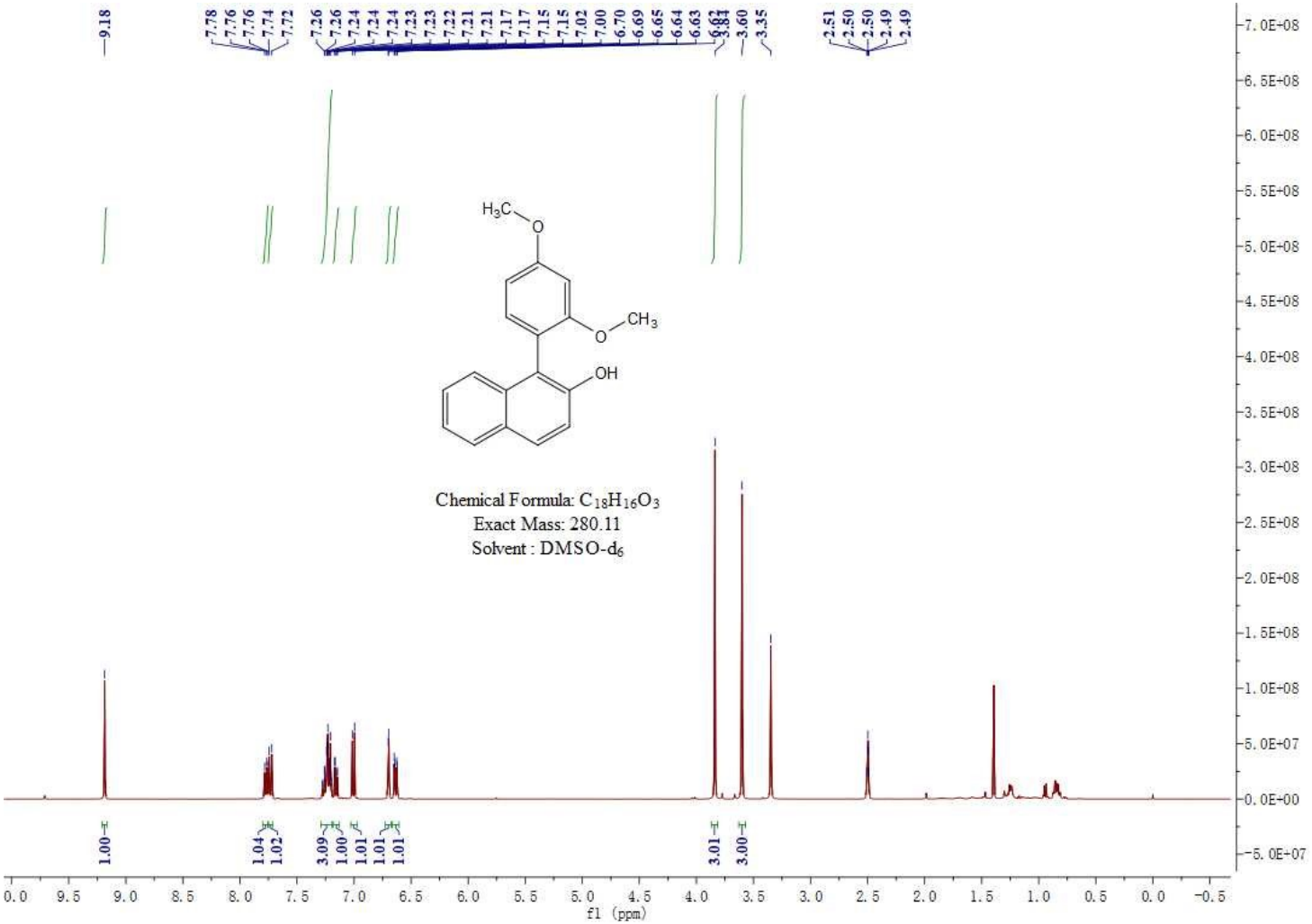


Fig. S60. The ^{1}H NMR spectrum of A4

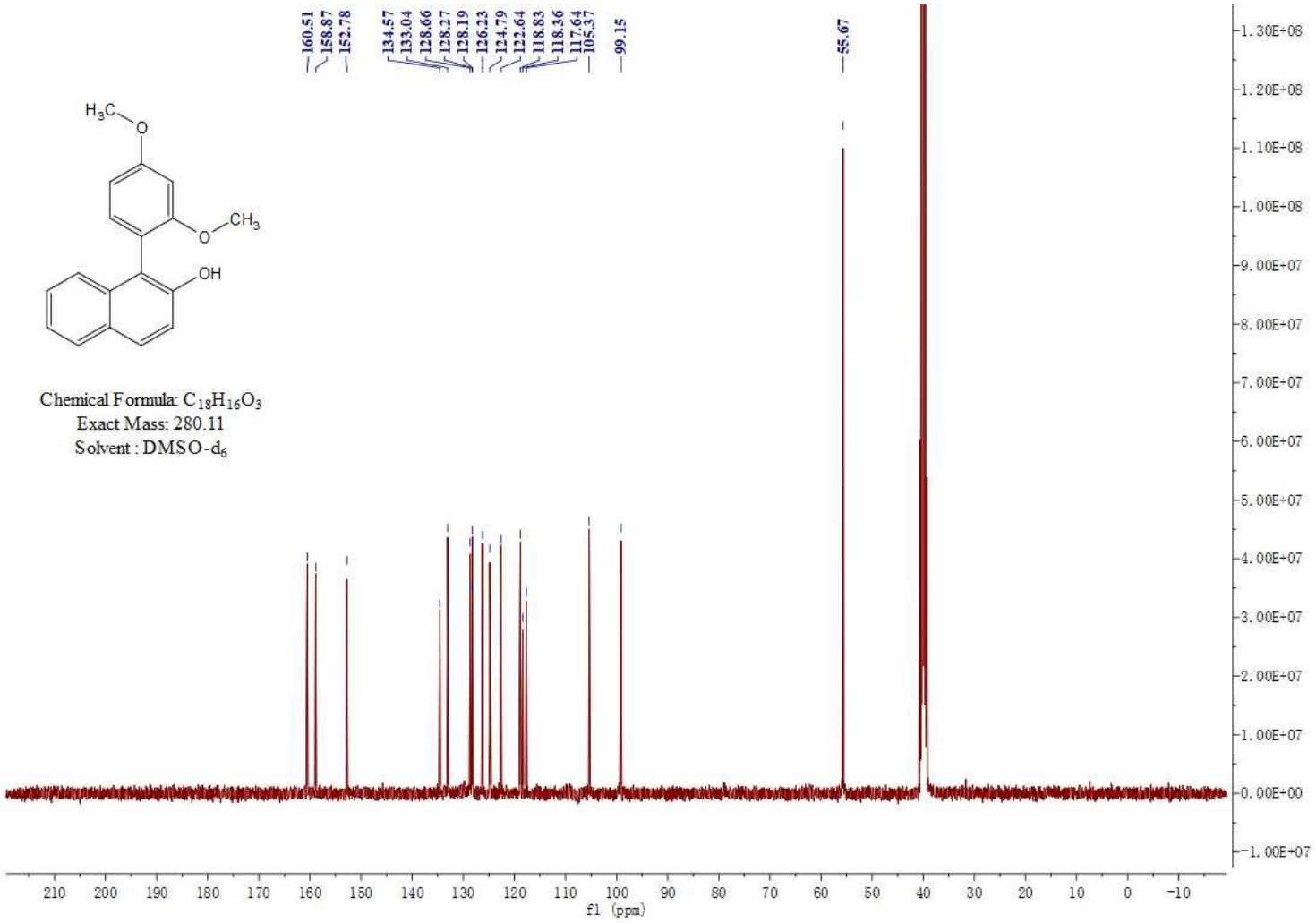


Fig. S61. The ^{13}C NMR spectrum of A4

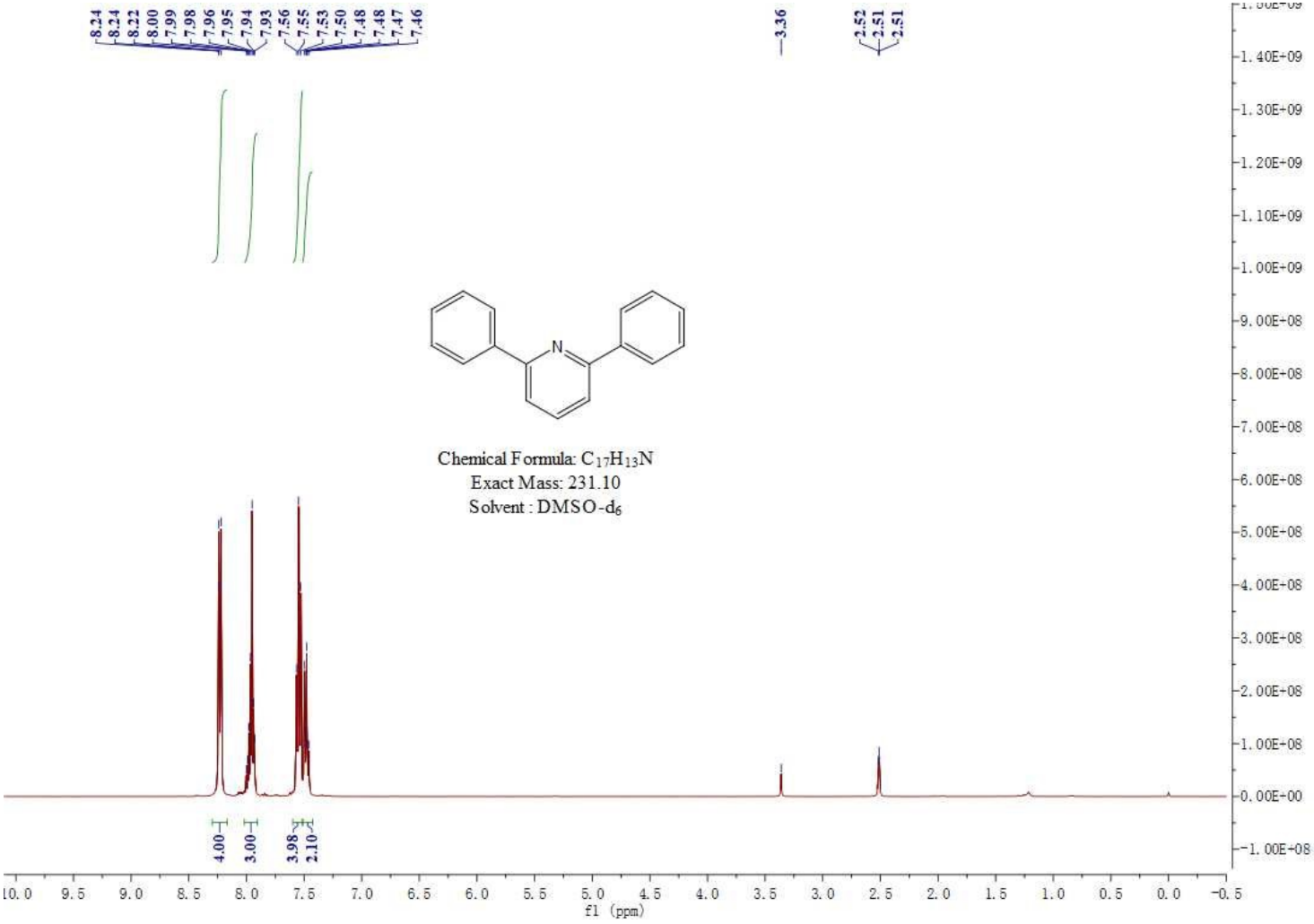


Fig. S62. The ^{1}H NMR spectrum of M1

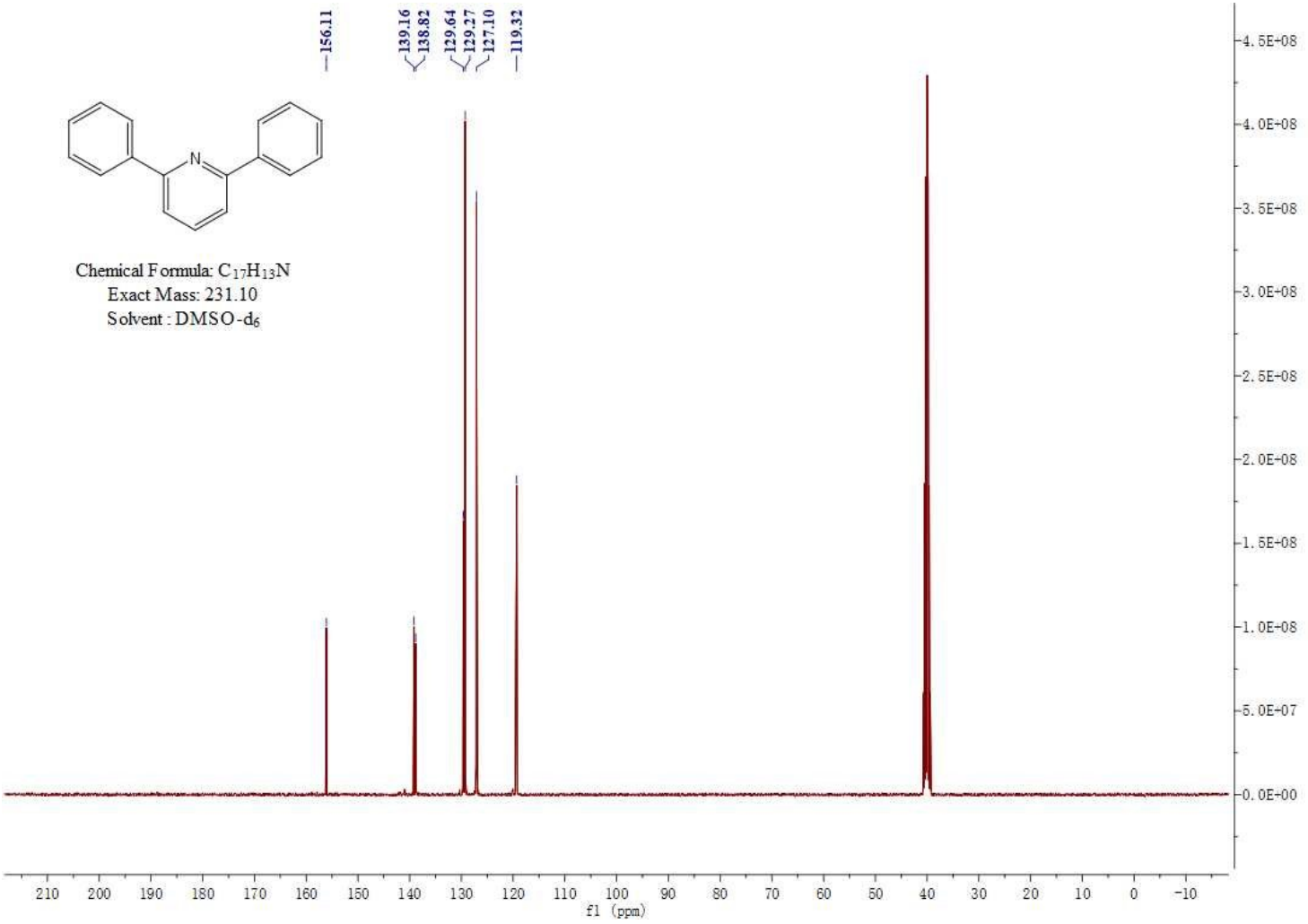


Fig. S63. The ^{13}C NMR spectrum of M1

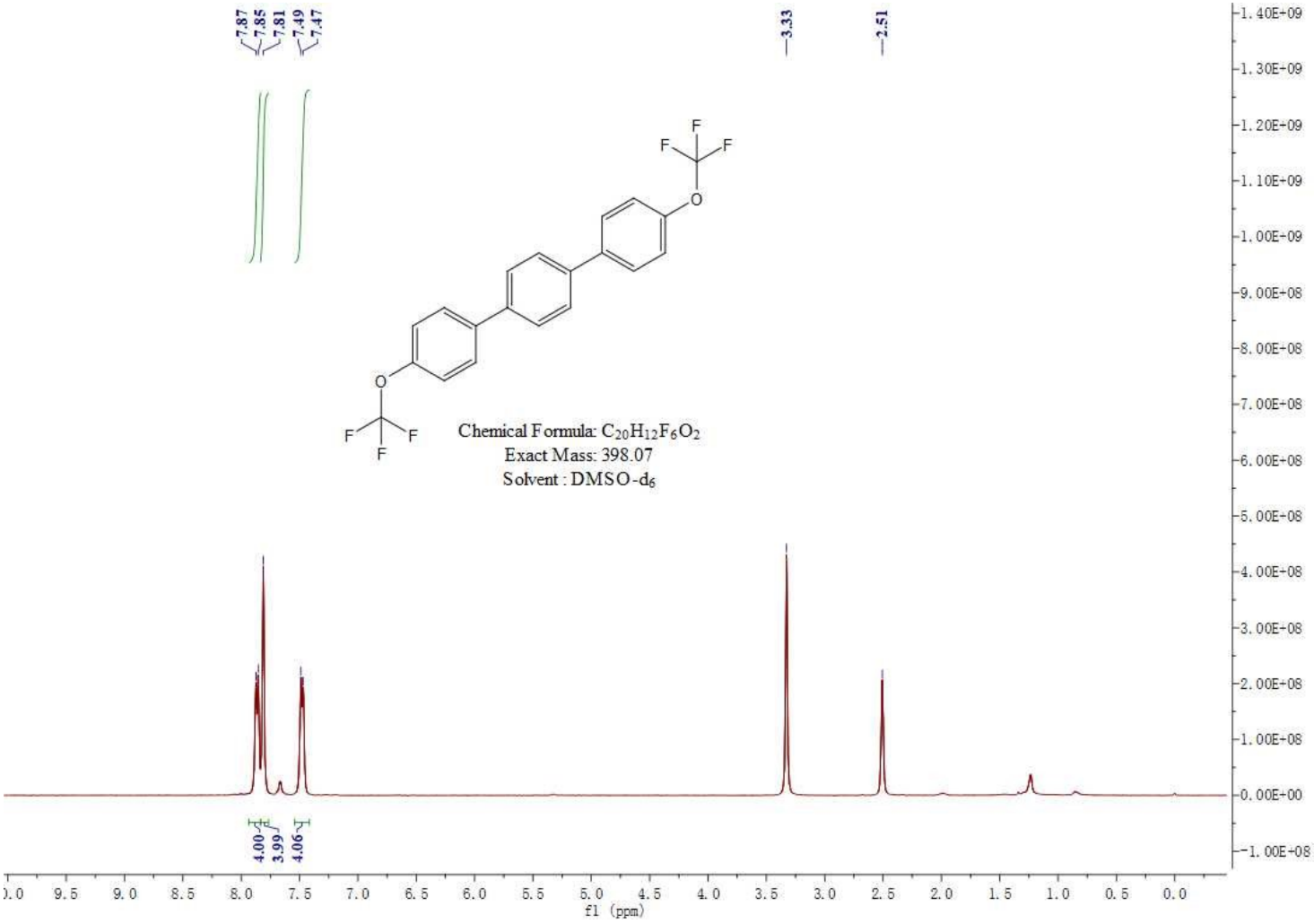


Fig. S64. The ^{1}H NMR spectrum of M2

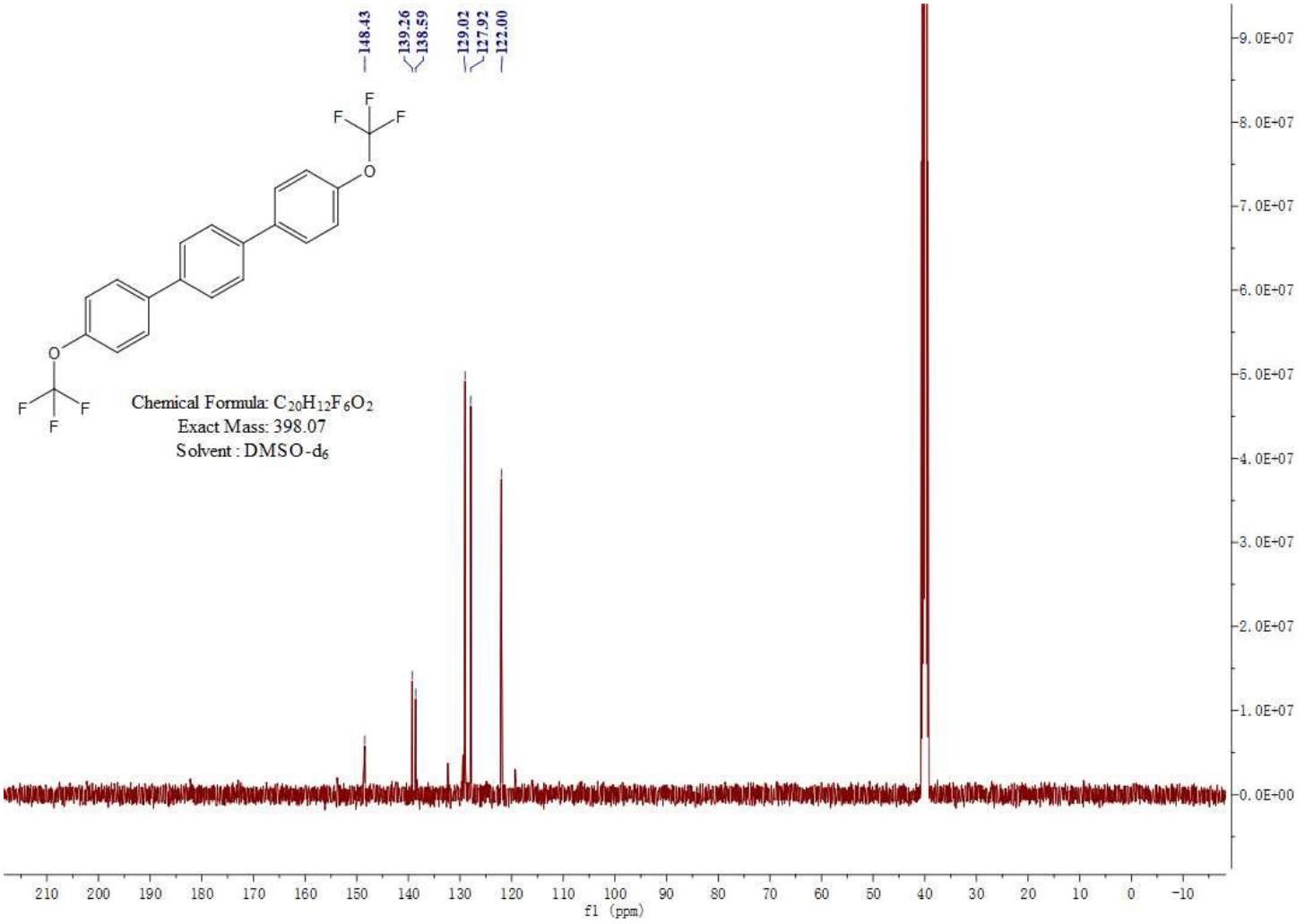
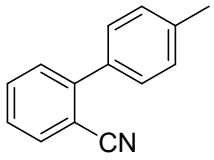


Fig. S65. The ^{13}C NMR spectrum of M2

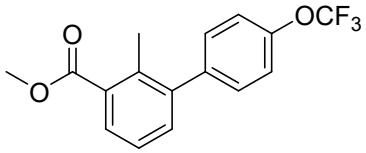
14. Spectroscopic data of API intermediates

API intermediates 1: 4'-Methyl-2-cyanobiphenyl



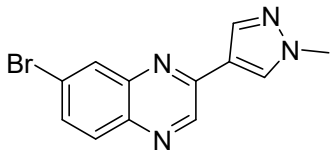
White solid. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.94 (dd, J = 7.7, 0.7 Hz, 1H), 7.78 (td, J = 7.8, 1.2 Hz, 1H), 7.57 (ddd, J = 9.6, 8.6, 4.4 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 3.35 (s, 2H), 2.39 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 145.02, 138.73, 135.45, 134.28, 133.92, 130.45, 129.77, 129.01, 128.39, 119.12, 110.57, 21.23. MS (HR-ESI) *m/z*, calcd. For [$C_{14}H_{11}N + Na^+$] 216.0784, found 216.0790.

API intermediates 2: Methyl 2-methyl-4'-(trifluoromethoxy)[1,1'-biphenyl]-3-carboxylate



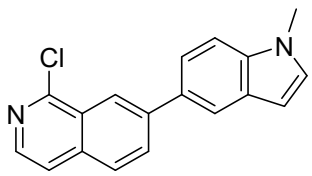
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 7.5, 1.3 Hz, 1H), 7.36 - 7.30 (m, 2H), 7.27 (dd, J = 7.4, 2.5 Hz, 3H), 3.92 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.49, 148.07, 142.17, 140.50, 136.15, 135.69, 133.49, 132.05, 131.66, 129.51, 126.31, 121.33, 52.61, 18.45. MS (HR-ESI) *m/z*, calcd. For [$C_{16}H_{13}F_3O_3 + H^+$] 311.0890, found 311.0894.

API intermediates 3: 7-Bromo-2-(1-methyl-1H-pyrazol-4-yl)quinoxaline



White solid. ^{1}H-NMR (400 MHz, DMSO- d_6): δ 9.32 (s, 1H), 8.63 (s, 1H), 8.29 (s, 1H), 8.17 (d, J = 2.1 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.86 (dd, J = 8.8, 2.2 Hz, 1H), 3.97 (s, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): δ 148.44 (s), 144.91 (s), 142.89 (s), 139.64 (s), 138.73 (s), 132.17 (s), 131.86 (s), 131.23 (s), 130.75 (s), 123.79 (s), 120.18 (s), 25.42 (s), 25.07 (s). MS (HR-ESI) *m/z*, calcd. For [$C_{12}H_9BrN_4 + H^+$] 289.0083, found 289.0087.

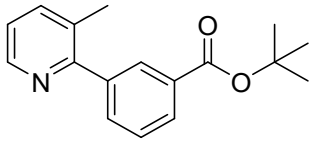
API intermediates 4: 1-chloro-7-(1-methyl-1H-indol-5-yl)- isoquinoline



White solid. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.43 (s, 1H), 8.33 - 8.23 (m, 2H), 8.15 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 1.0 Hz, 1H), 7.92 (d, J = 5.5 Hz, 1H), 7.63 (dt, J = 16.8, 5.1 Hz, 2H), 7.42 (d,

J = 3.0 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 150.57, 142.94, 141.47, 136.93, 136.56, 131.76, 131.28, 130.43, 129.25, 128.50, 127.05, 122.17, 121.60, 121.10, 119.78, 111.00, 101.61, 33.10. MS (HR-ESI) *m/z*, calcd. For [$C_{18}H_{13}ClN_2$ + H^+] 293.0840, found 293.0874.

API intermediates 5: *tert*-Butyl 3-(3-methylpyridin-2-yl)benzoate



White solid. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.52 (dd, *J* = 4.6, 1.1 Hz, 1H), 8.05 (t, *J* = 1.6 Hz, 1H), 7.99 - 7.93 (m, 1H), 7.82 (dd, *J* = 6.5, 1.2 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.33 (s, 3H), 1.56 (s, 9H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.26, 157.13, 147.48, 141.02, 139.29, 133.72, 131.75, 131.09, 129.98, 128.90, 128.79, 123.19, 81.36, 28.23, 20.06. MS (HR-ESI) *m/z*, calcd. For [$C_{17}H_{19}NO_2$ + H^+] 270.1489, found 270.1495.

15. ^{1}H NMR ,^{13}C NMR and HRMS spectra of API intermediates

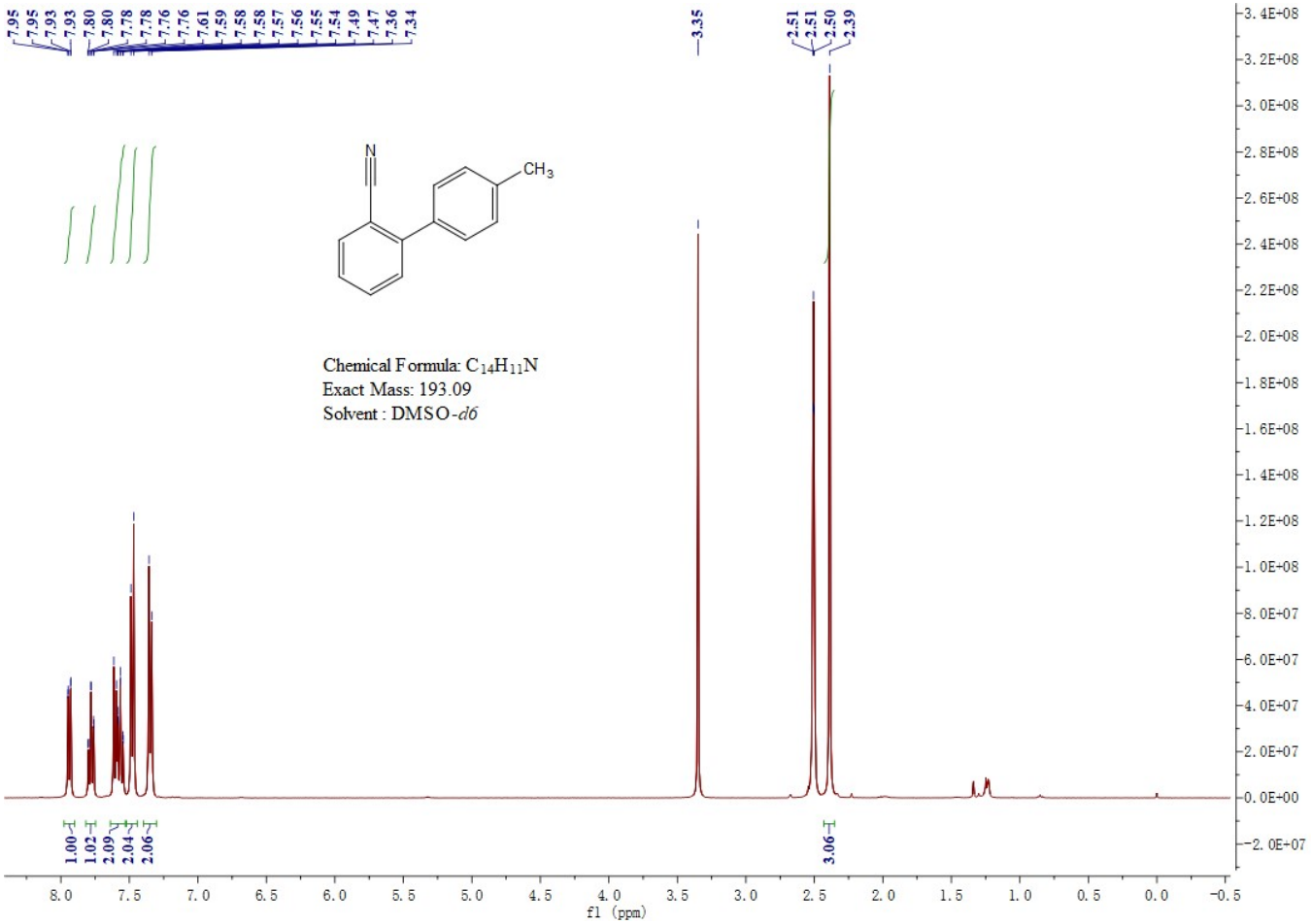


Fig. S66. The ^{1}H NMR spectrum of intermediate 1

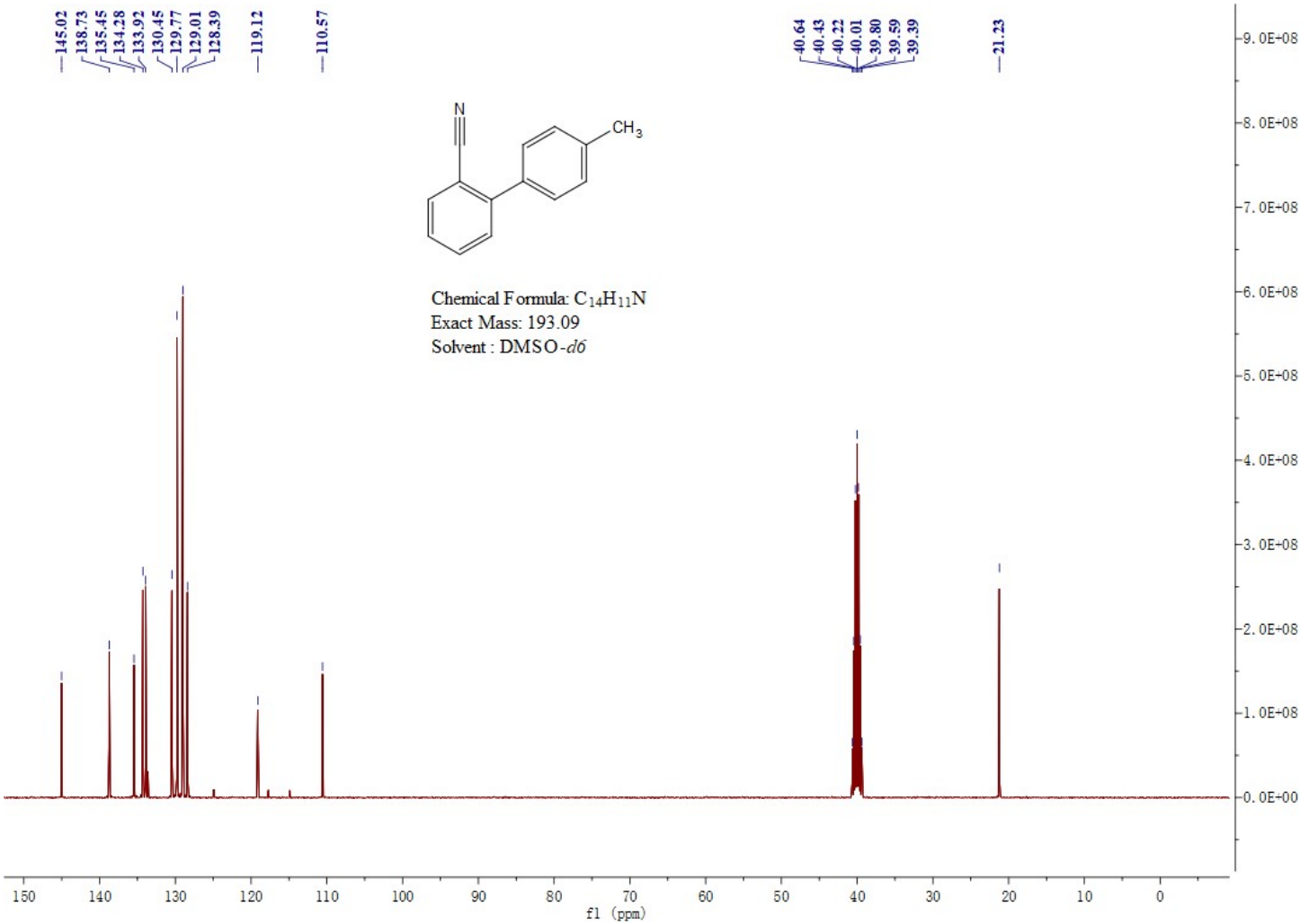


Fig. S67. The ^{13}C NMR spectrum of intermediate 1

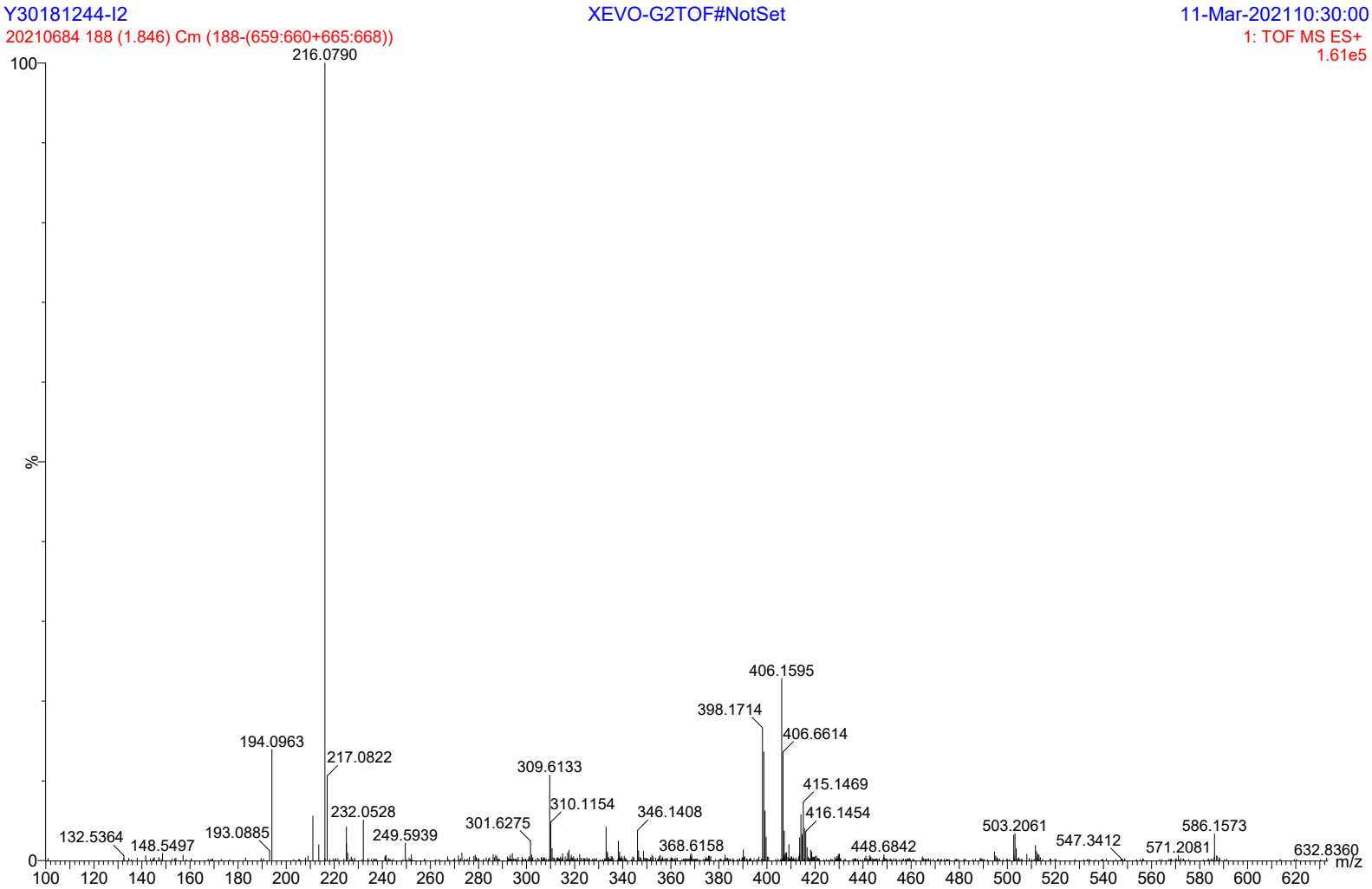


Fig. S68. The HRMS spectrum of intermediate 1

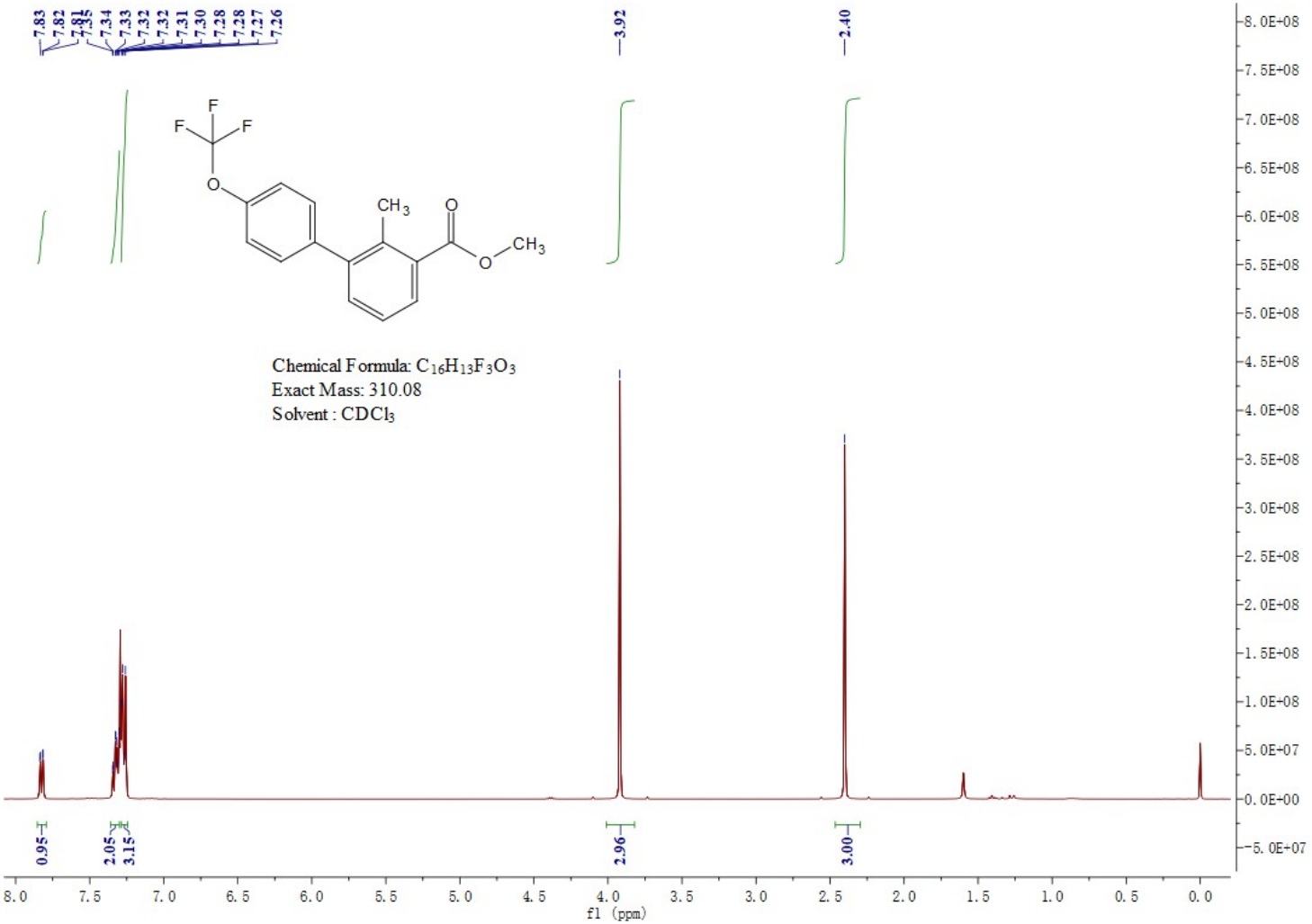


Fig. S69. The ^{1}H NMR spectrum of intermediate 2

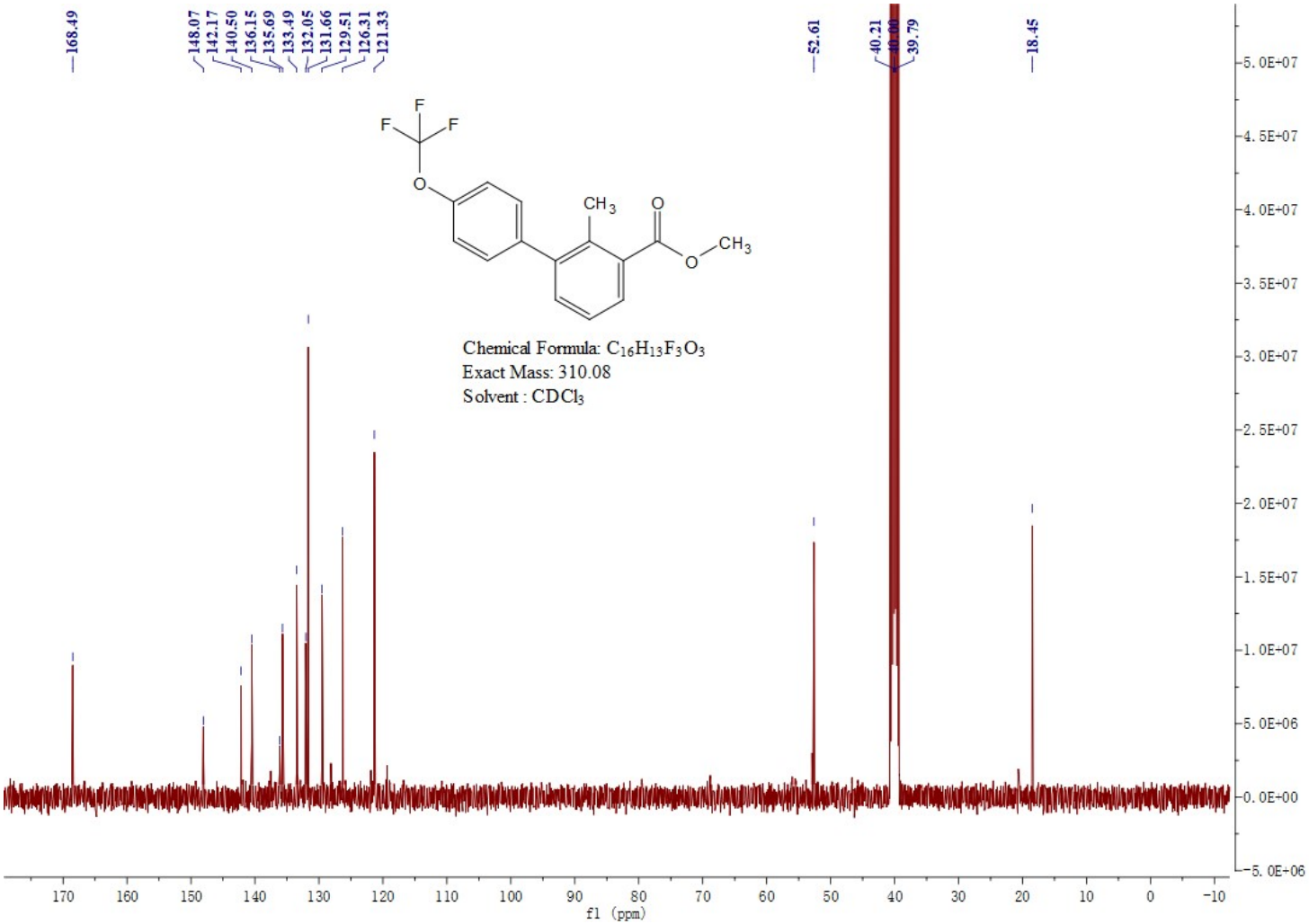


Fig. S70. The ^{13}C NMR spectrum of intermediate 2

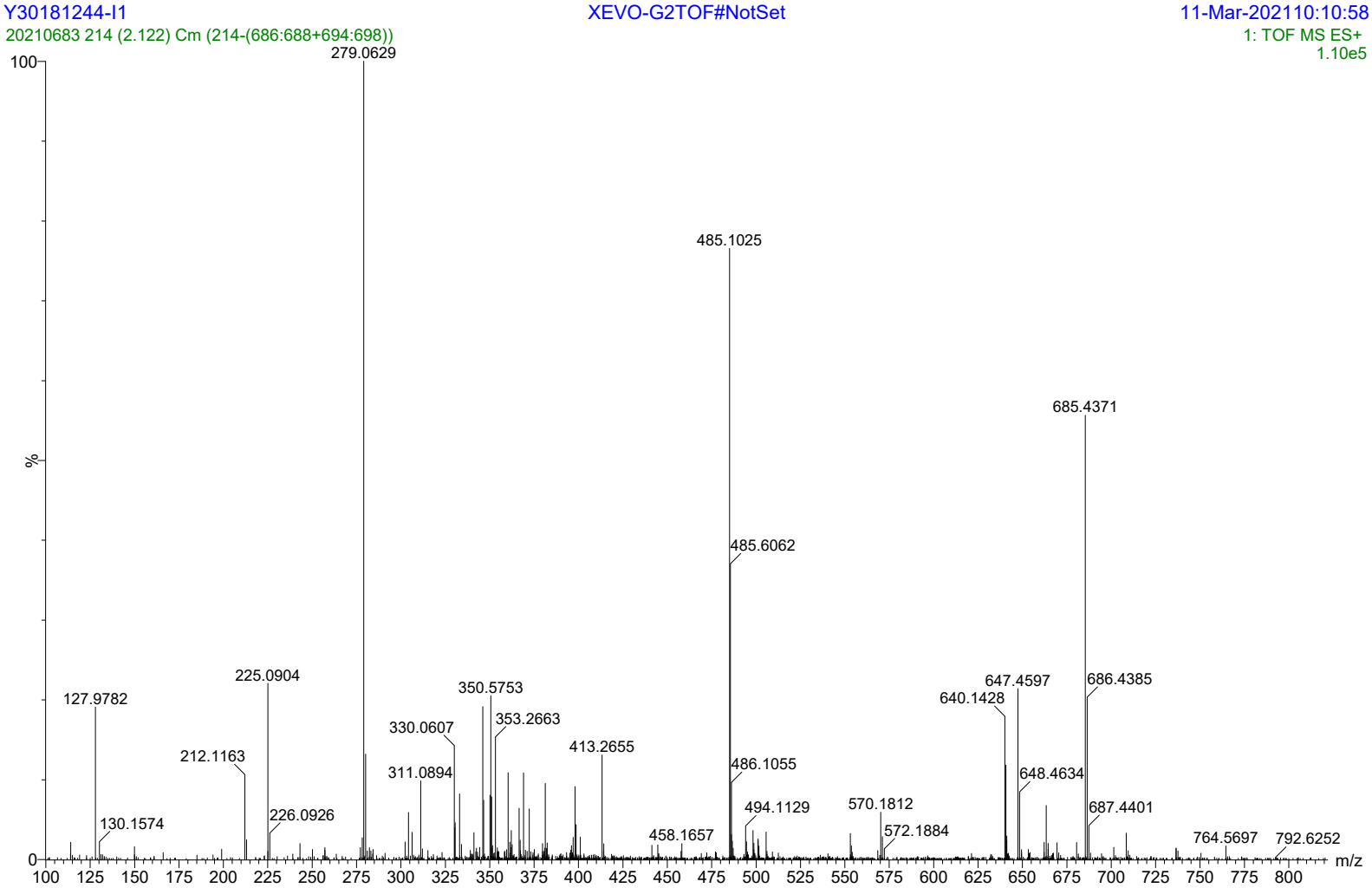


Fig. S71. The HRMS spectrum of intermediate 2

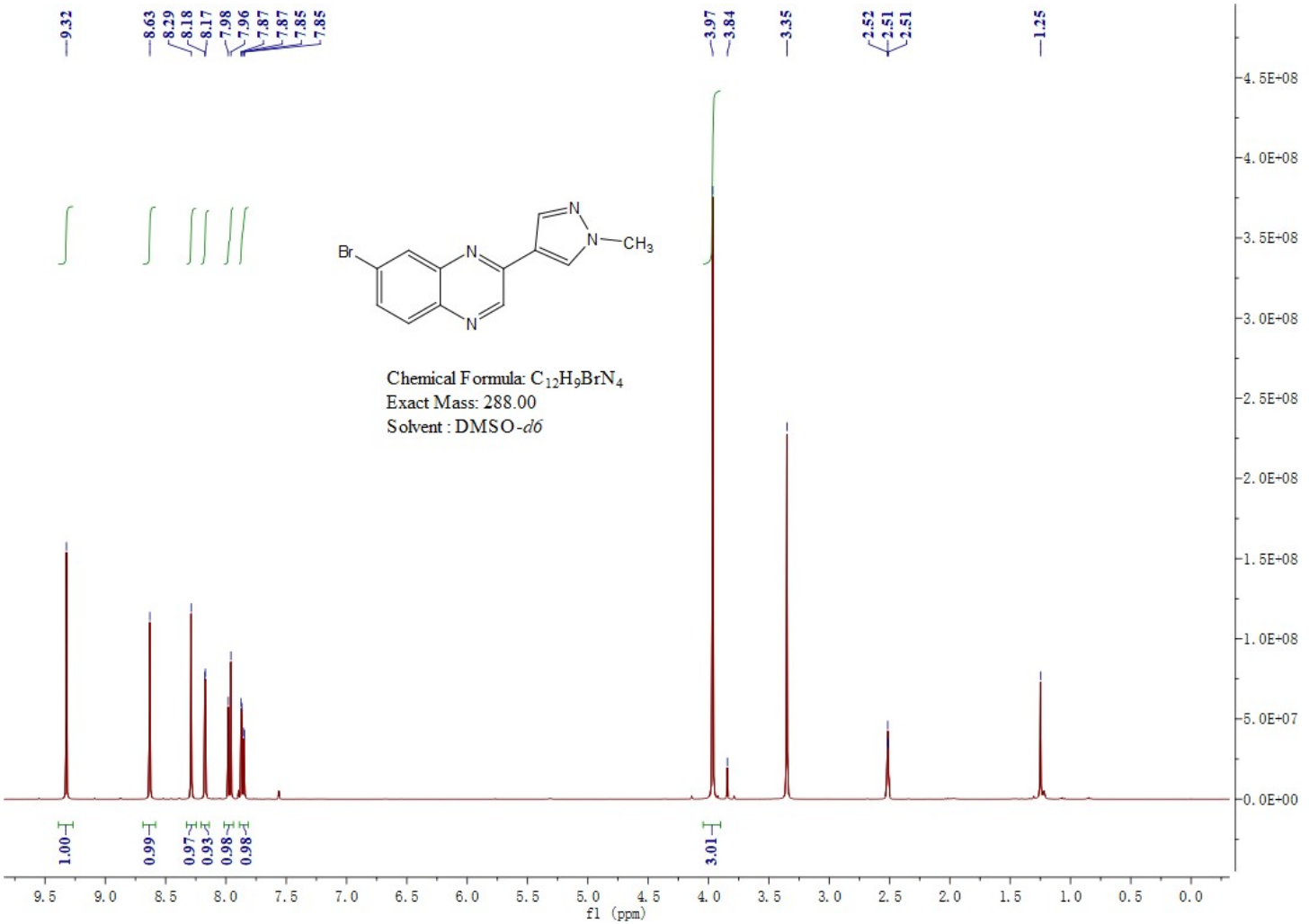


Fig. S72. The ^{1}H NMR spectrum of intermediate 3

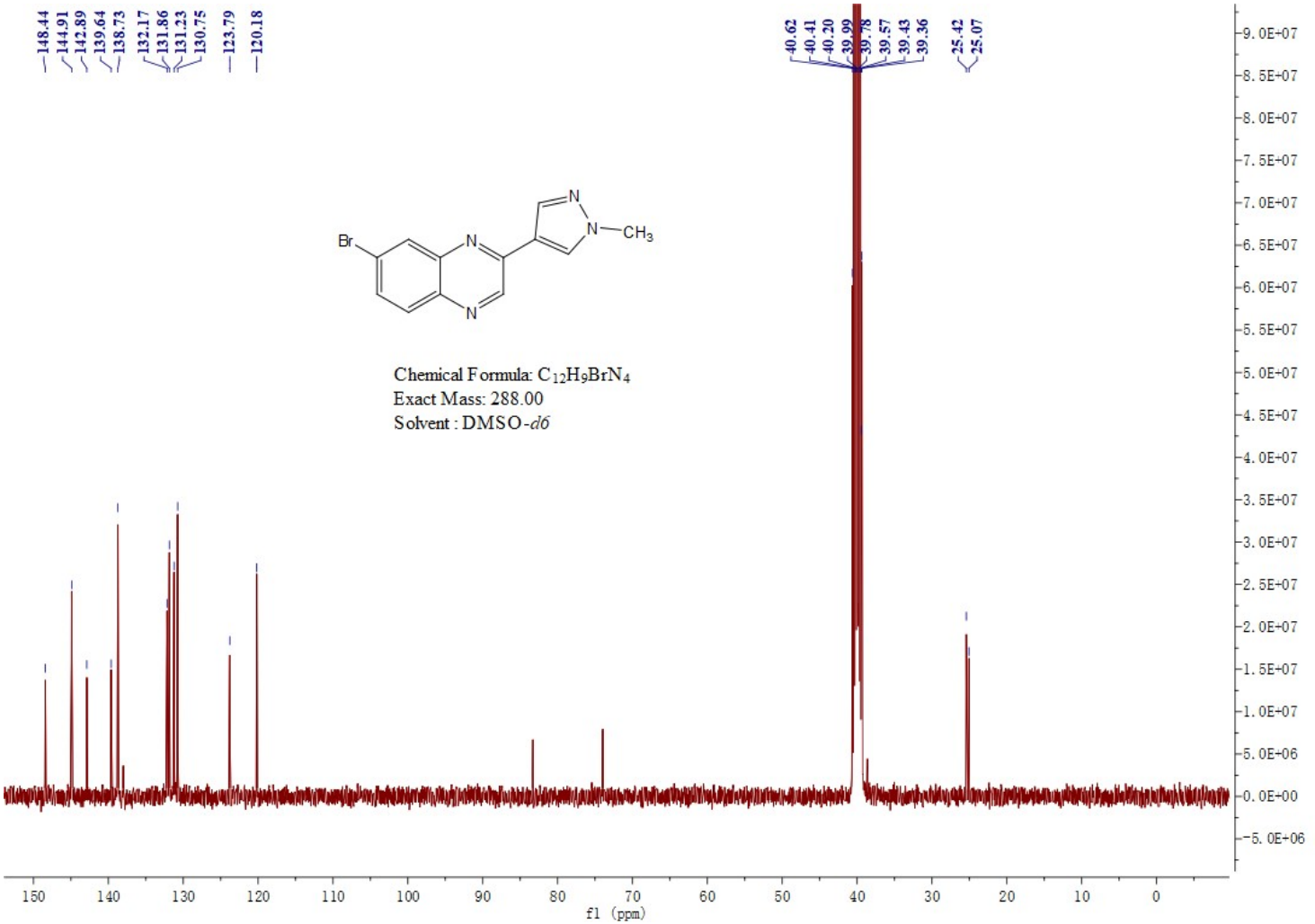


Fig. S73. The ^{13}C NMR spectrum of intermediate 3

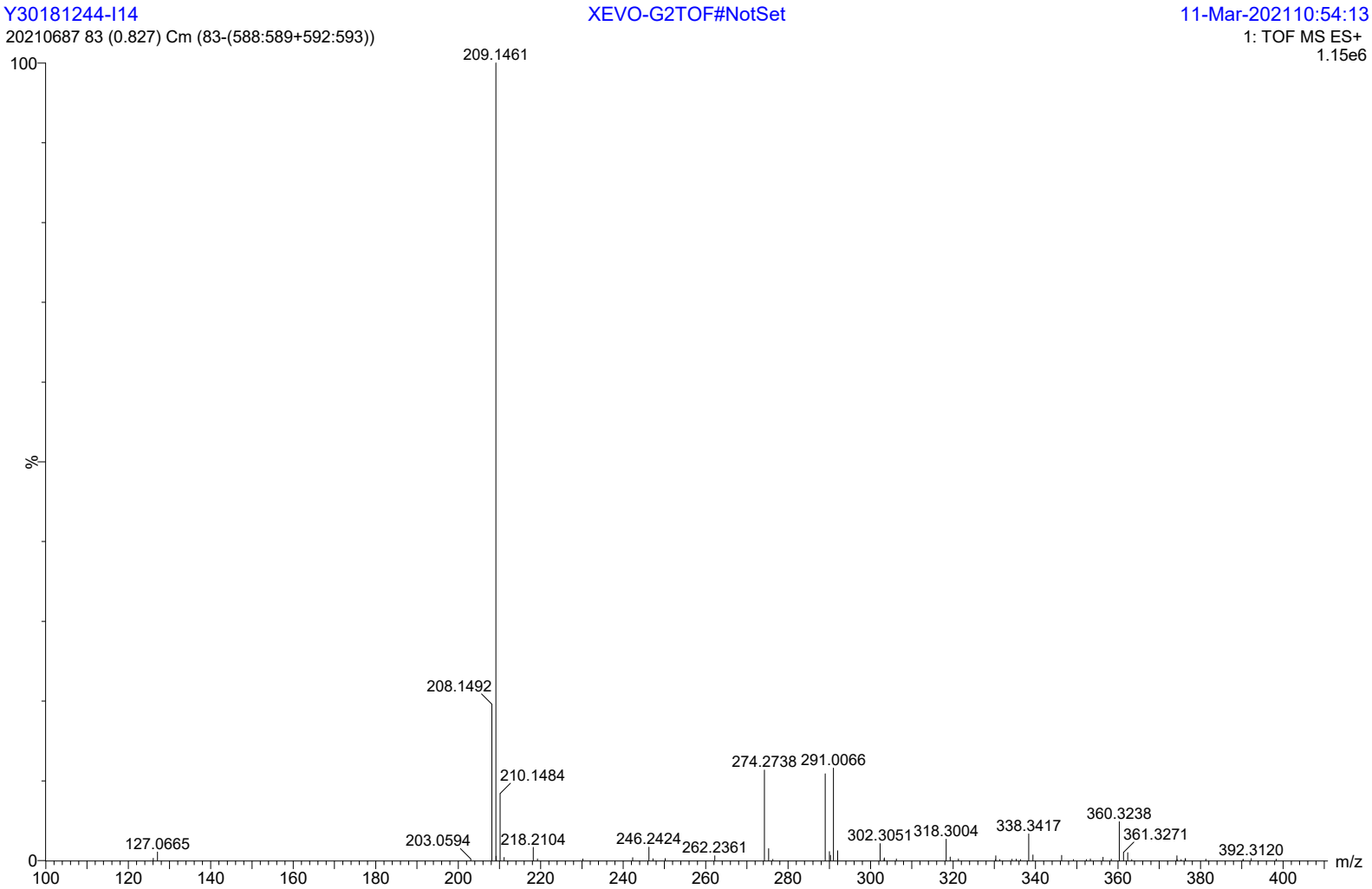


Fig. S74. The HRMS spectrum of intermediate 3

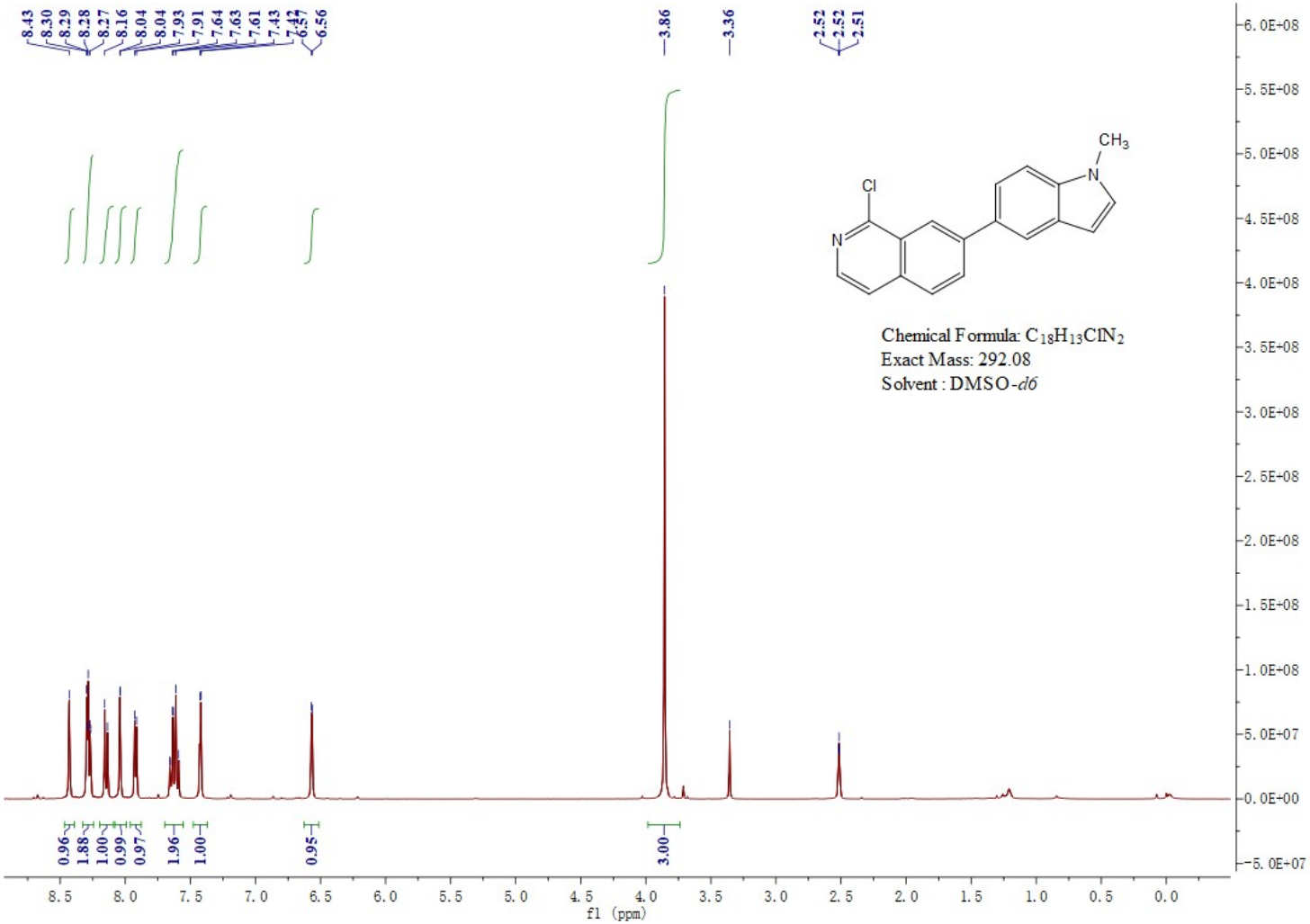


Fig. S75. The ^{1}H NMR spectrum of intermediate 4

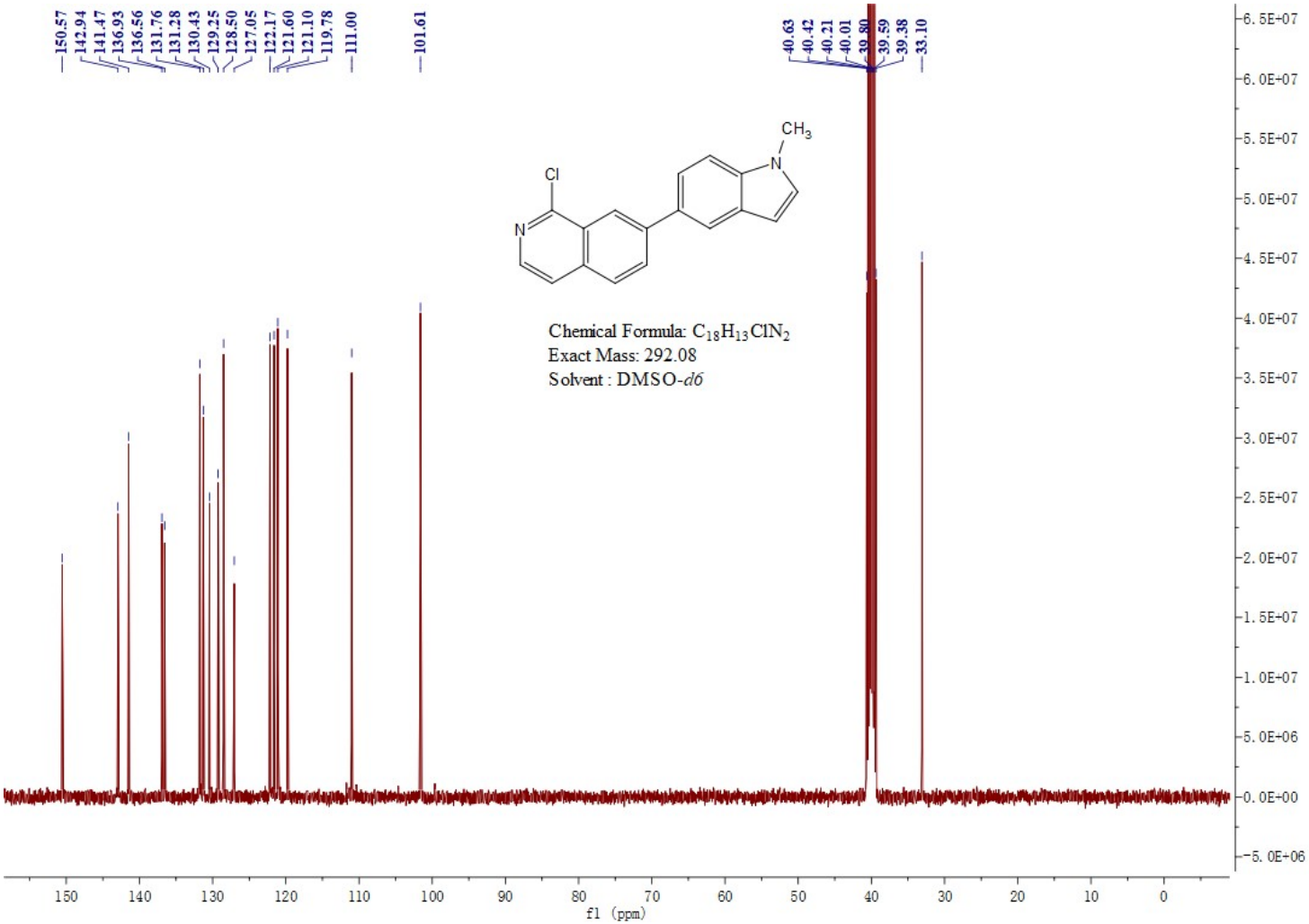


Fig. S76. The ^{13}C NMR spectrum of intermediate 4

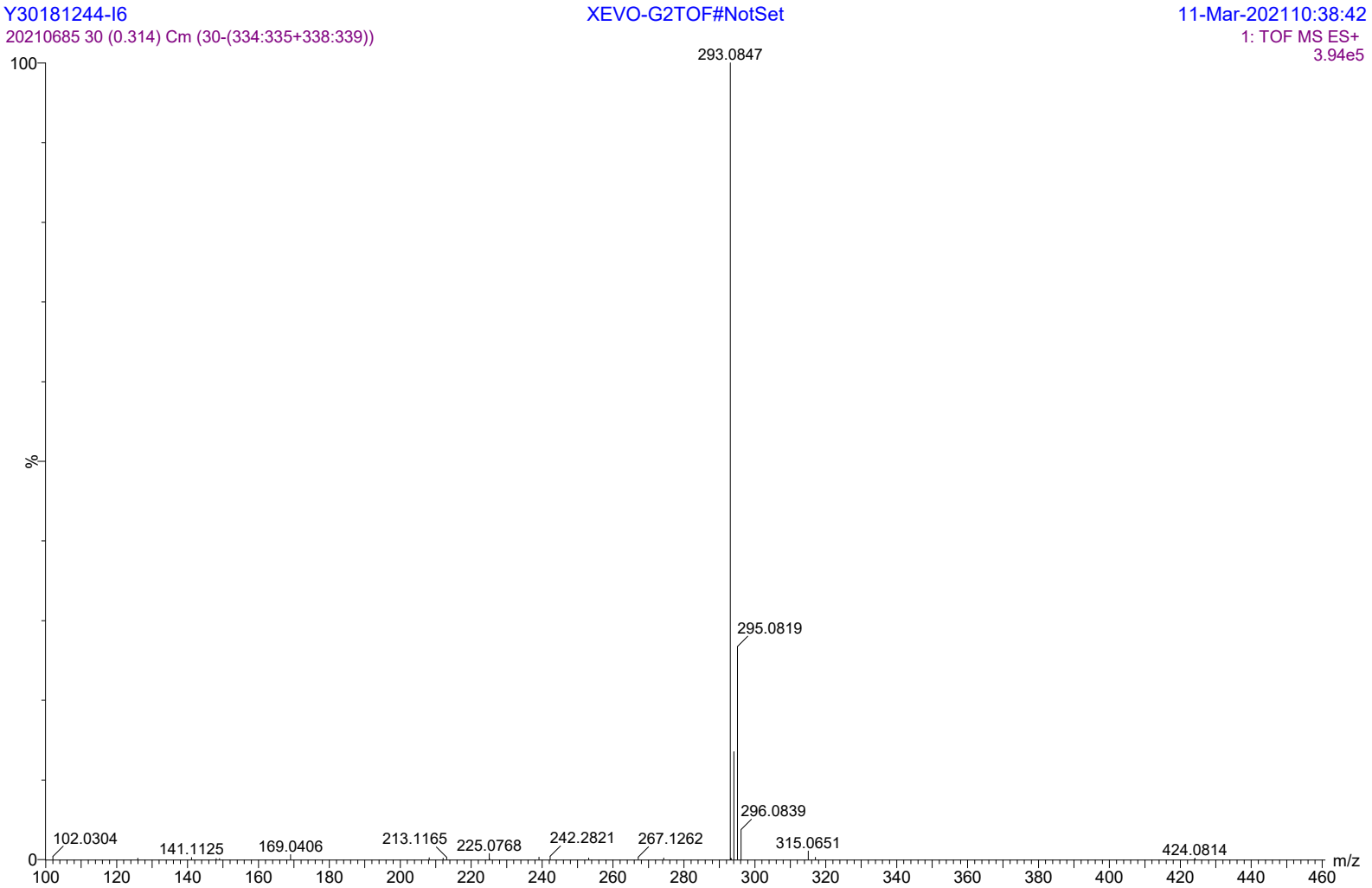


Fig. S77. The HRMS spectrum of intermediate 4

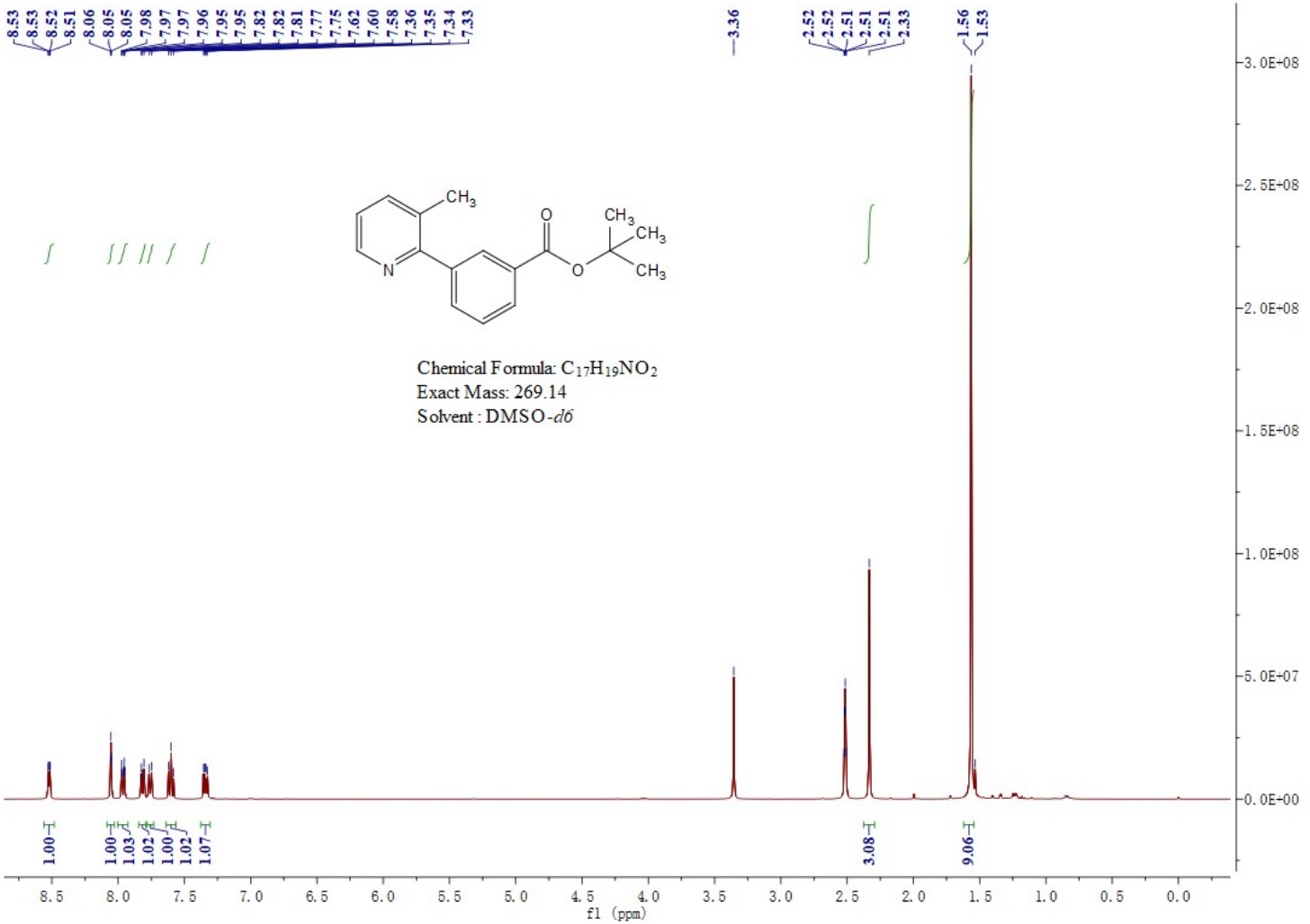


Fig. S78. The ^{1}H NMR spectrum of intermediate 5

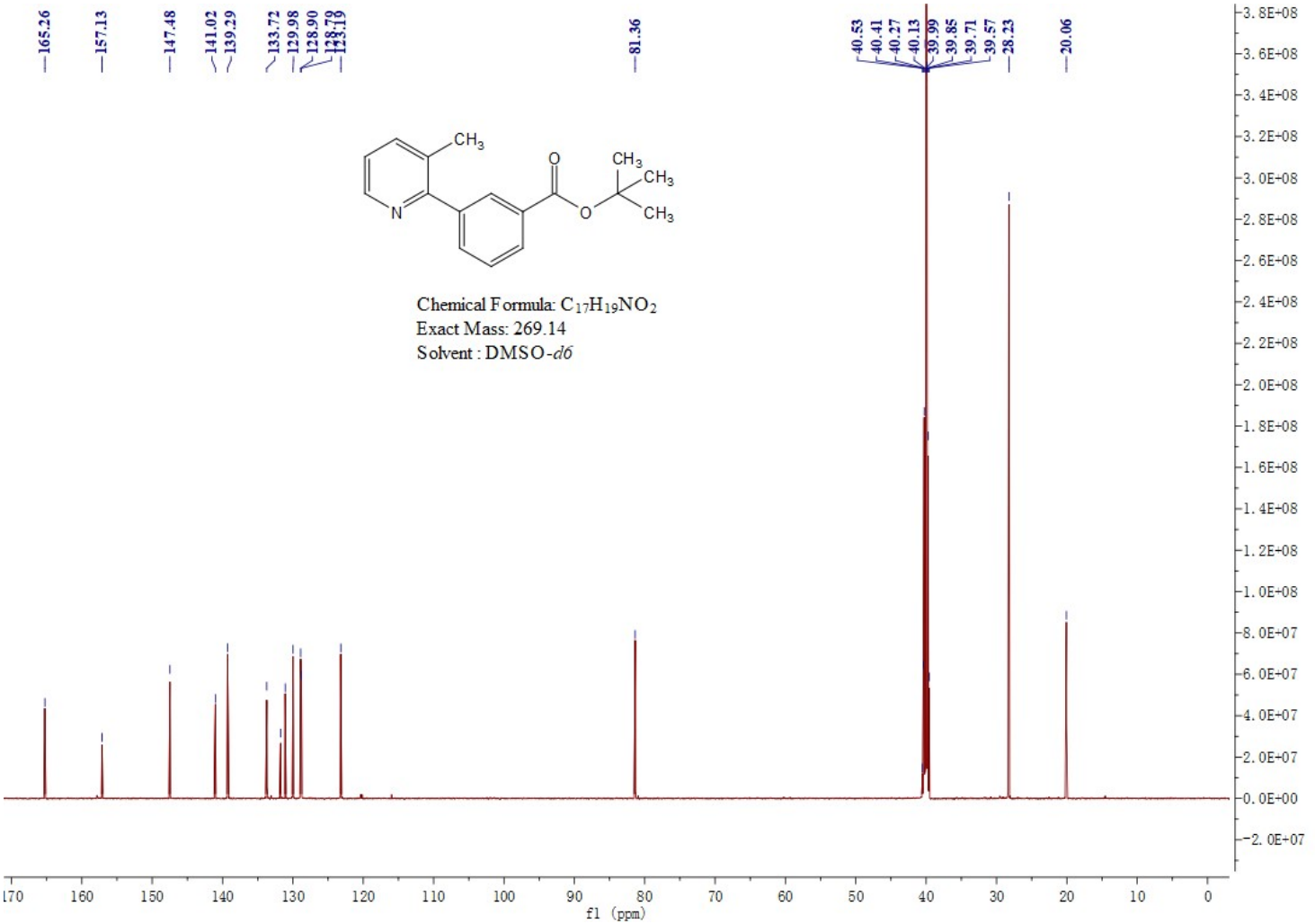


Fig. S79. The ^{13}C NMR spectrum of intermediate 5

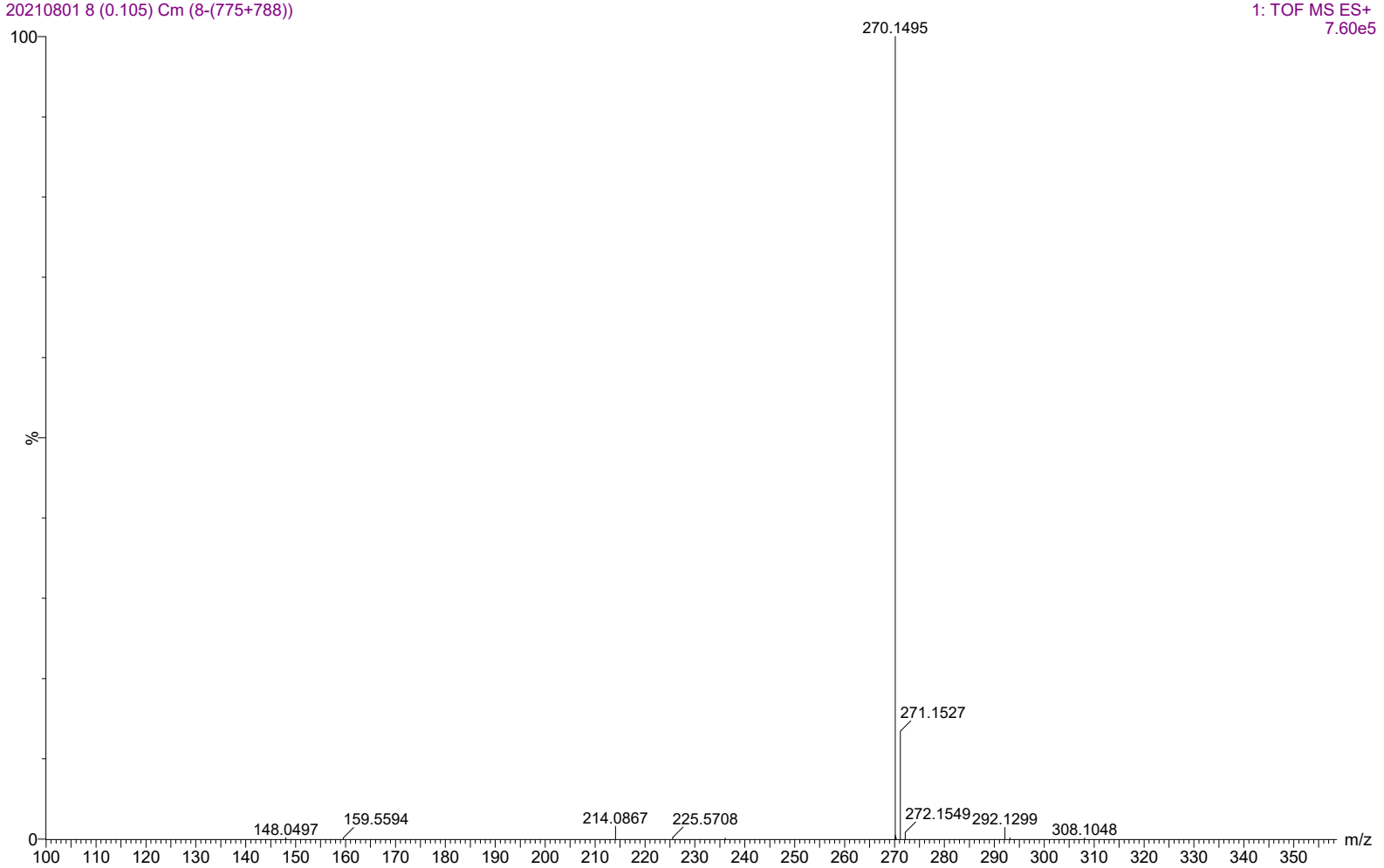


Fig. S80. The HRMS spectrum of intermediate 5

16. Comparison of the results obtained from Fe_3O_4@FSM@Pd and those reported with other Pd catalyst

Table S2. Performance comparison of different catalysts

Catalyst	Reaction temperature (°C)	Solvent	Base	Base usage	Reaction time (h)	Catalyst usage (mol %)	Yield (%)	TON	TOF (h^{-1})	Reference
$Pd(PPh_3)_4$	120	DMF	K_2CO_3	2	18	0.2	88	440	24.4	[2]
$Pd(OAc)_2$	40	DMF	Cs_2CO_3	3	16	3	90	30	1.9	[3]
FP1@Pd	100	H_2O	$(i\text{-}Pr)_2NH$	2.5	1.5	1	95	95	63.3	This work
Pd/ C	Room temperature	Me_2CHOH/ H_2O=1/1, v/v	Na_3PO_4	2.5	8	2.6	97	37.3	4.7	[4]
Fe_3O_4/SiO_2@PDA/ Pd	40	EtOH/ H_2O	K_2CO_3	2	3	0.1	96	960	320	[5]
γ-Fe_2O_3-acetamidine-Pd	100	DMF	Et_3N	2	2	0.12	81	675	337.5	[6]
Fe_3O_4/P(GMA-AA-MMA)-Schiff base-Pd	80	DMF/ H_2O	K_2CO_3	2	1	0.1	97	970	970	[7]
Pd@FSM	100	H_2O	K_2CO_3	2	8	0.05	97	1940	242.5	[8]
Fe_3O_4@FSM@Pd	100	H_2O	$(i\text{-}Pr)_2NH$	2.5	0.5	0.1	98	980	1960	This work
Fe_3O_4@FSM@Pd[a]	100	H_2O	$(i\text{-}Pr)_2NH$	2.5	0.5	0.1	98	980	1960	This work

[a] The catalyst Fe_3O_4@FSM@Pd was exposed to air for 6 months.

17. References

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