Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# An Efficient Synthesis of Heptaaryldipyrromethenes from Tetraarylcyclopentadienones and Ammonium Acetate and Their Extension to Corresponding BODIPYs

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# Content

## 1. $^{1}$H NMR and $^{13}$C NMR spectra for **1b-1n**

**Figure S1** The $^{1}$H NMR spectra of **1b**.

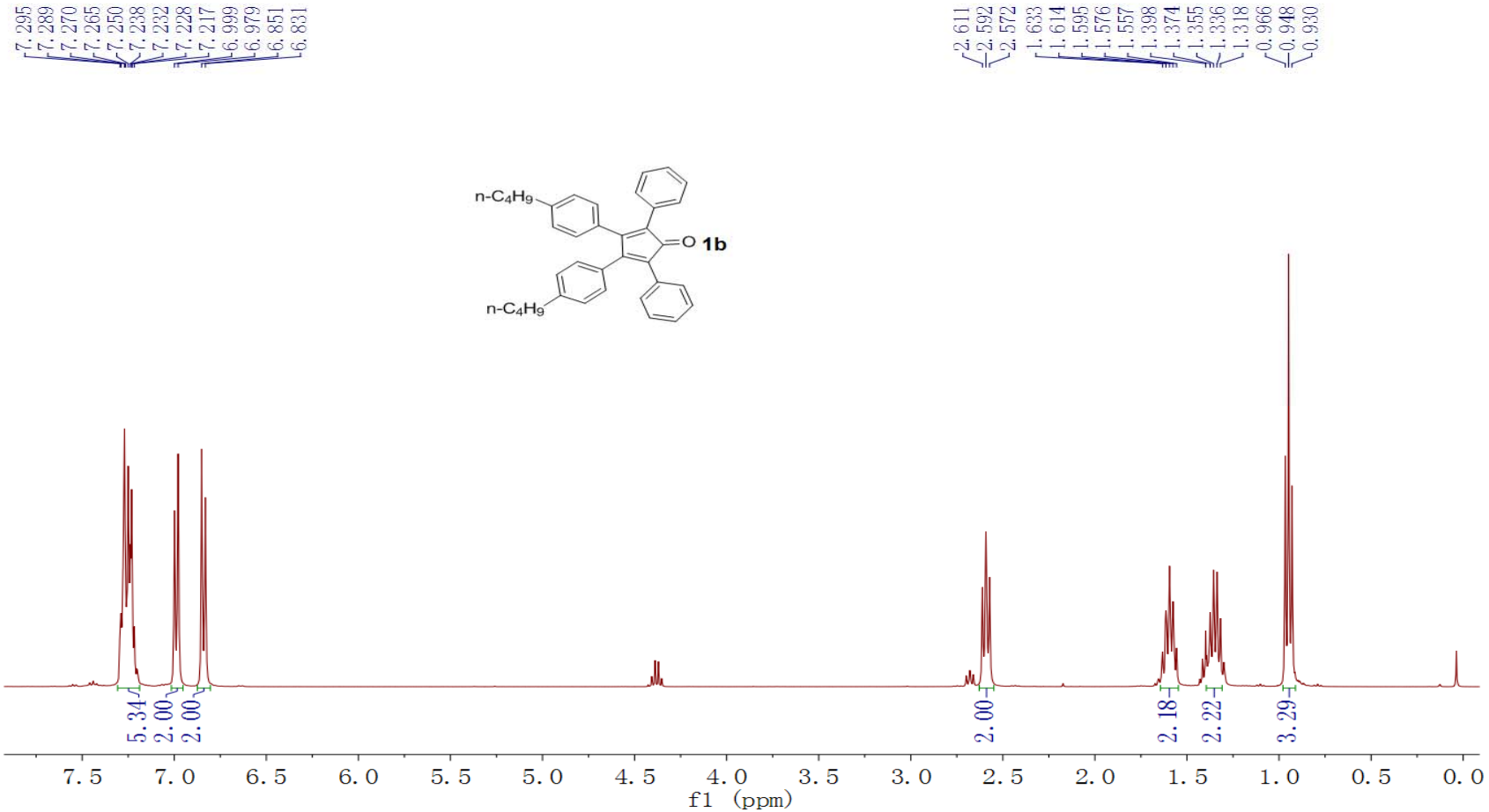


**Figure S2** The $^{13}C$ NMR spectra of **1b**.

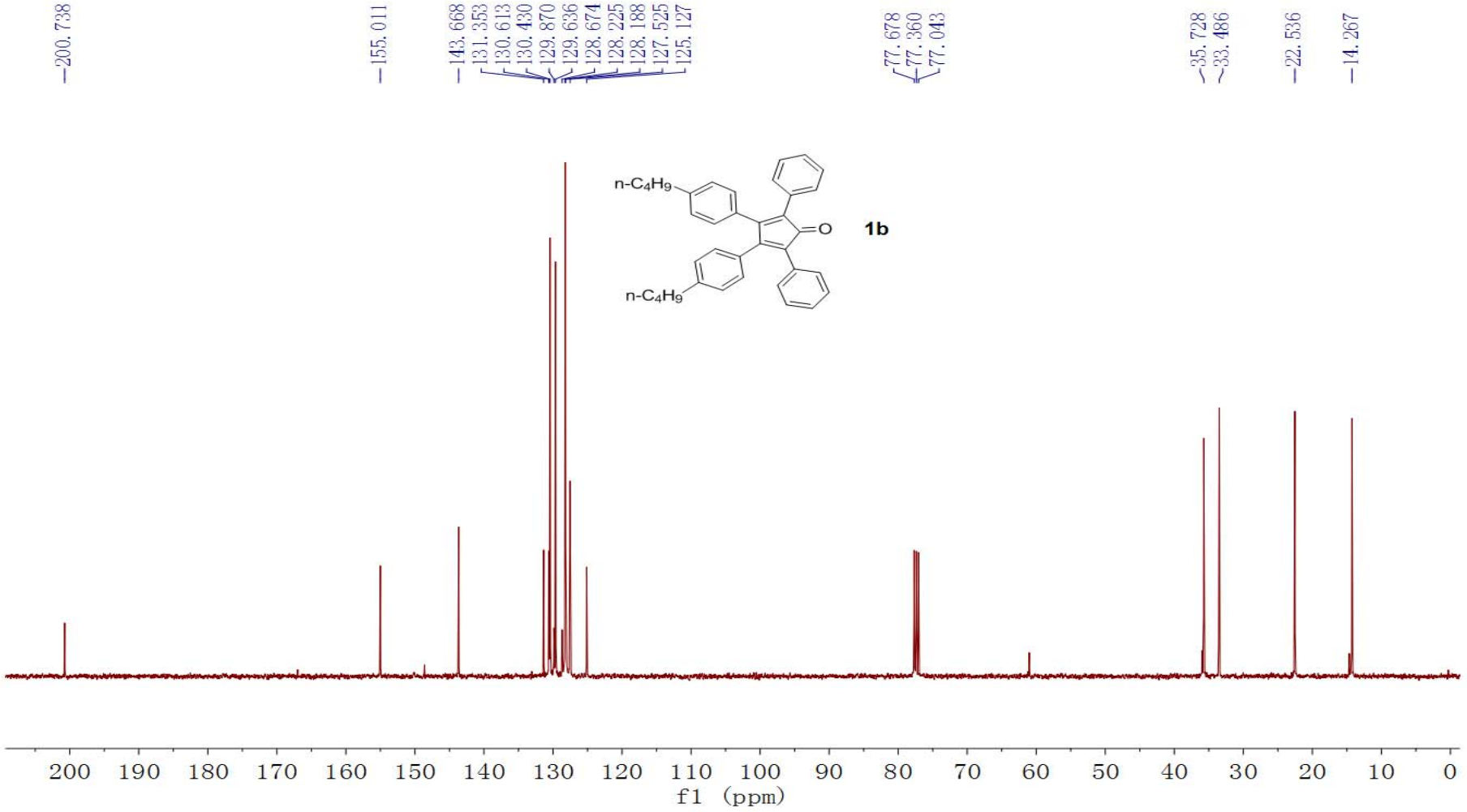


**Figure S3** The $^{1}$H NMR spectra of **1c**.

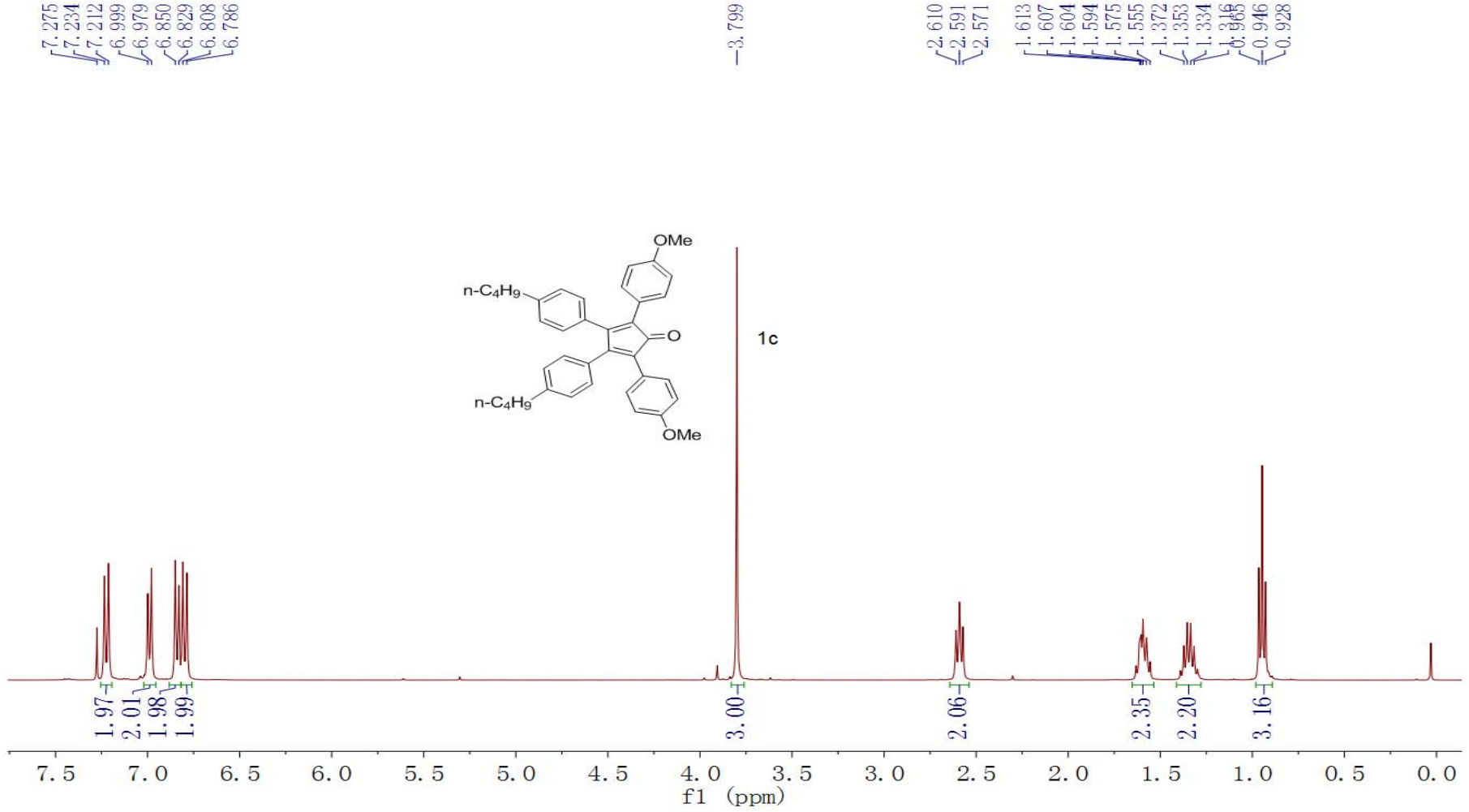


**Figure S4** The $^{13}C$ NMR spectra of **1c**.

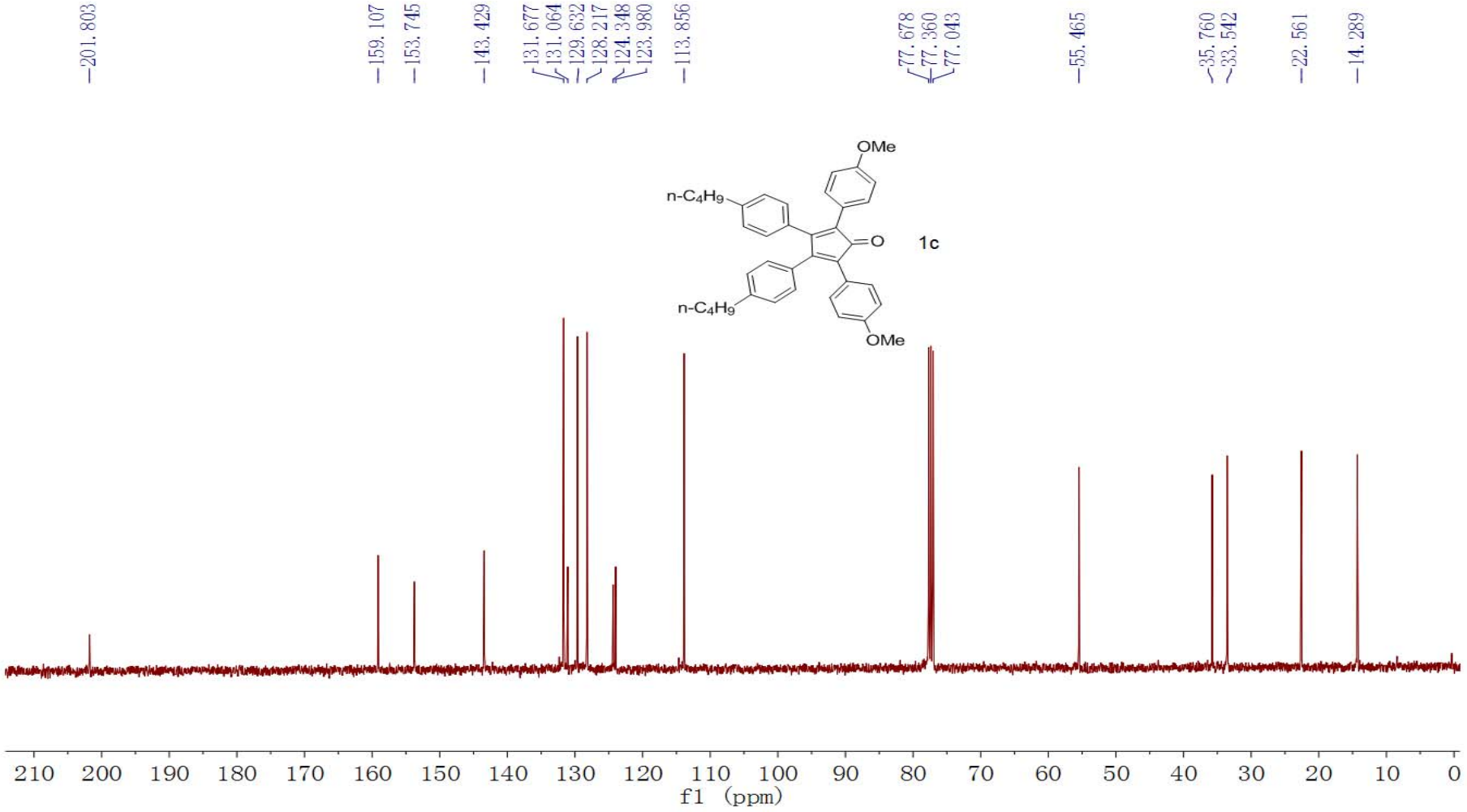


**Figure S5** The $^{1}H$ NMR spectra of **1d**.

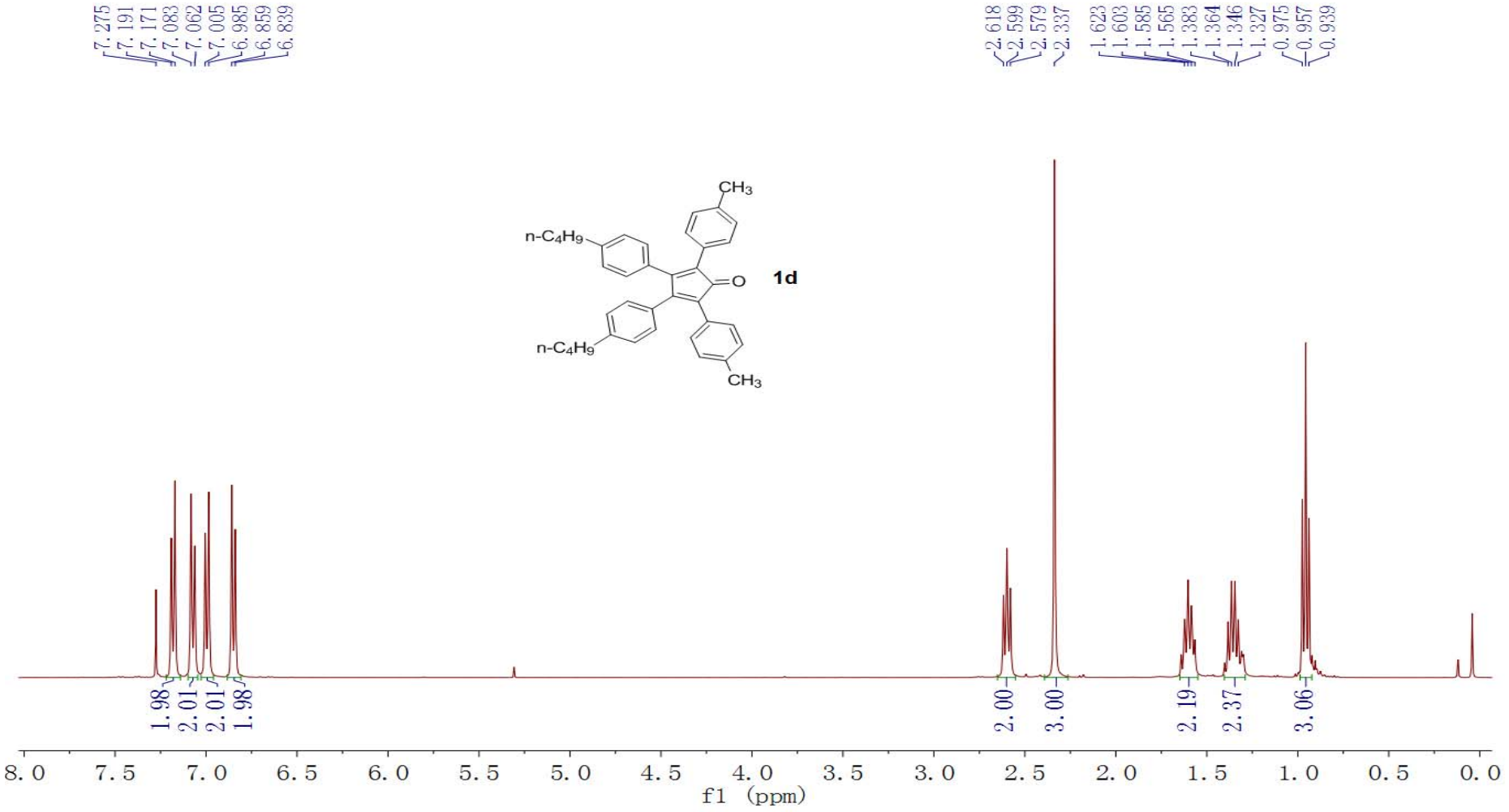


**Figure S6** The $^{13}C$ NMR spectra of **1d**.

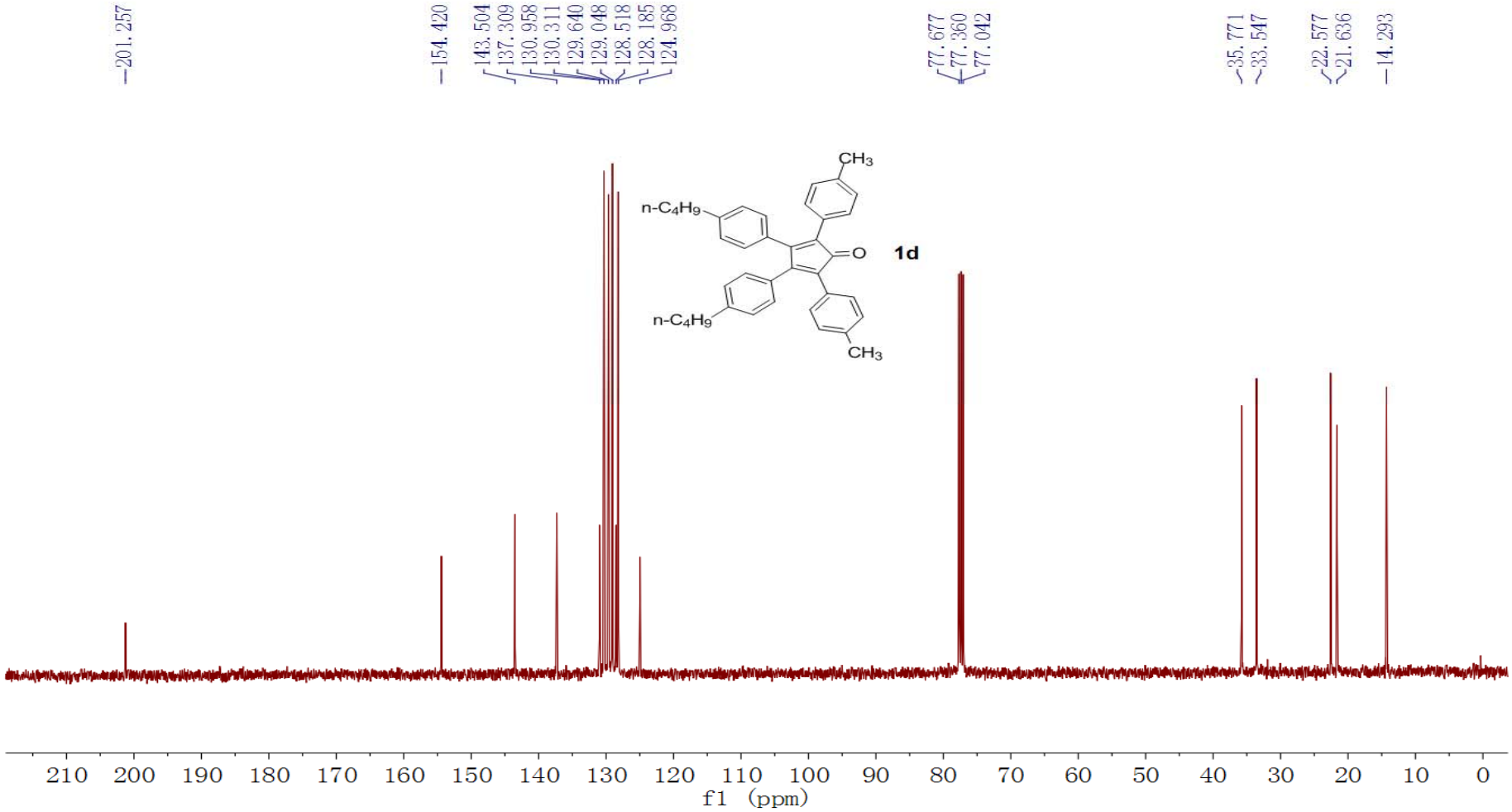


**Figure S7** The $^{1}$H NMR spectra of **1e**.

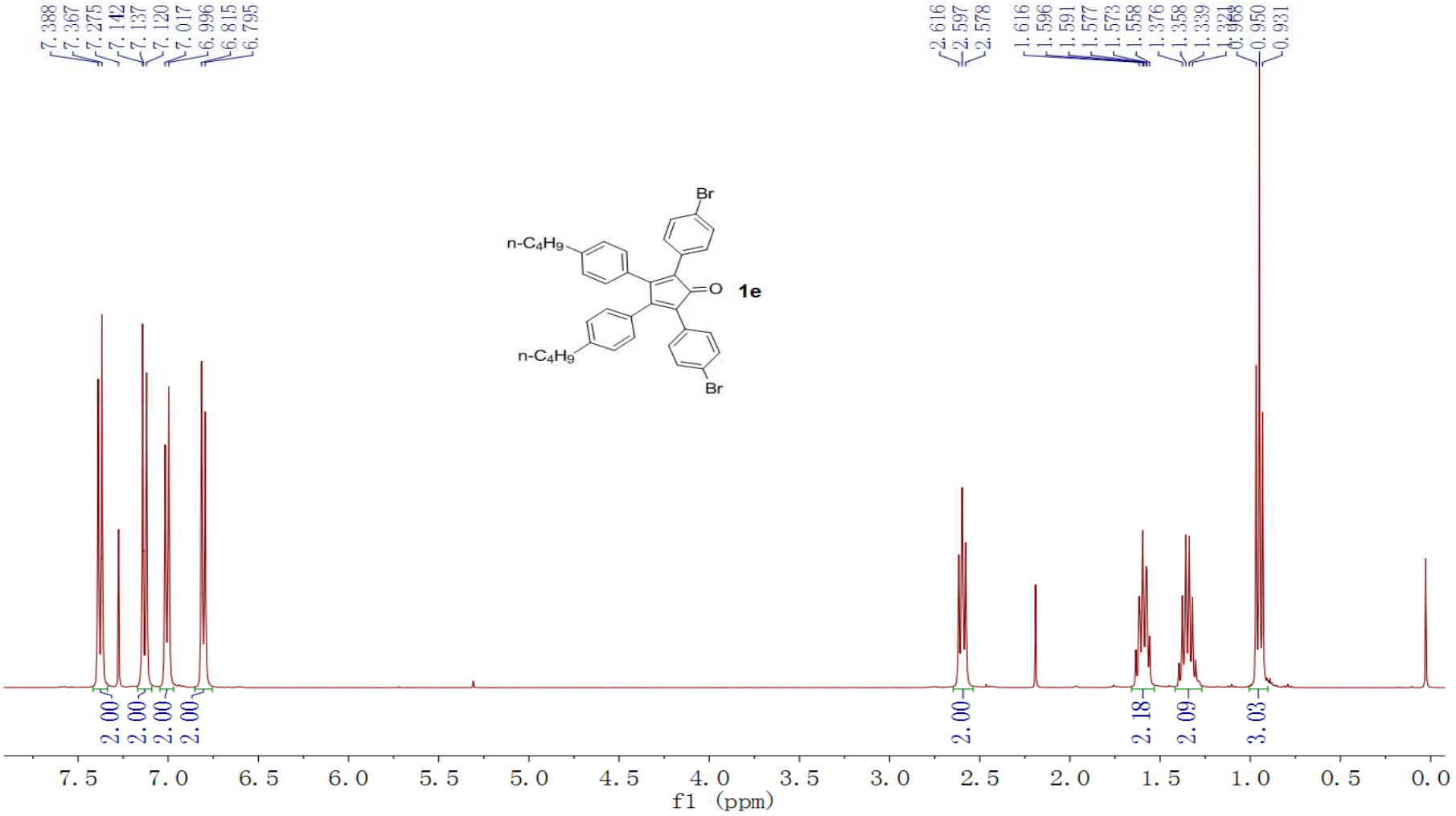


**Figure S8** The $^{13}C$ NMR spectra of **1e**.

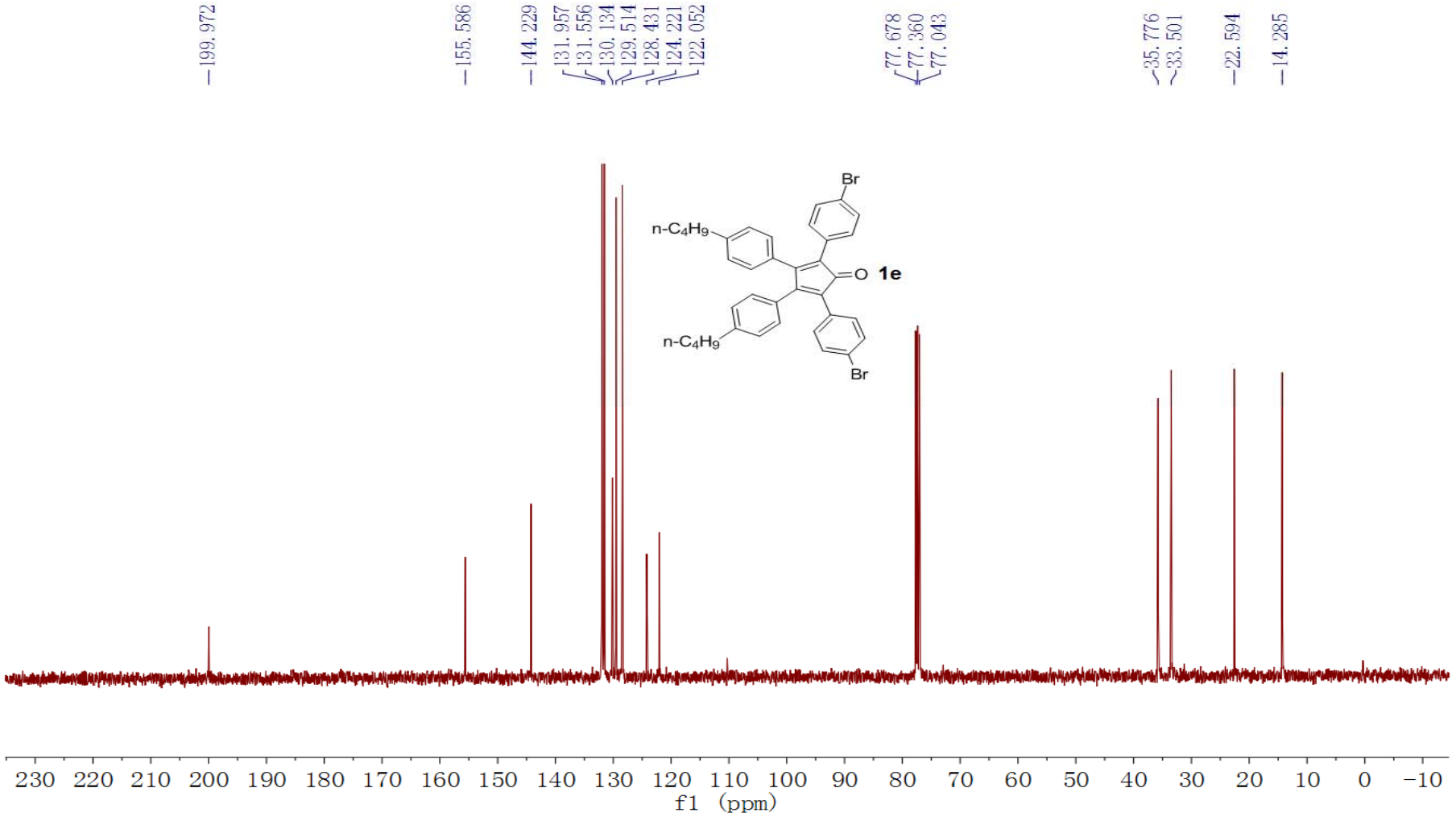


**Figure S9** The $^{1}H$ NMR spectra of **1f**.

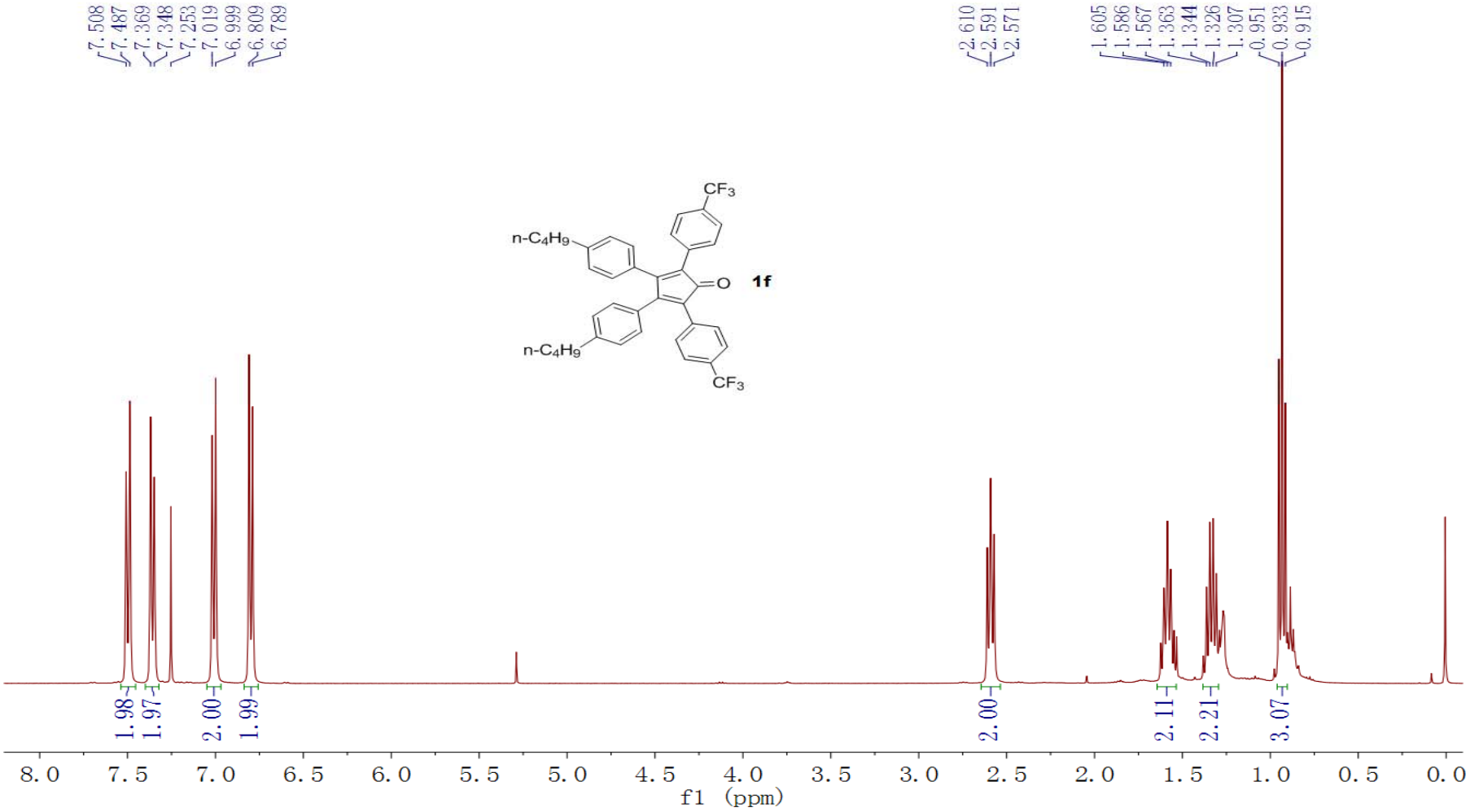


**Figure S10** The $^{13}C$ NMR spectra of **1f**.

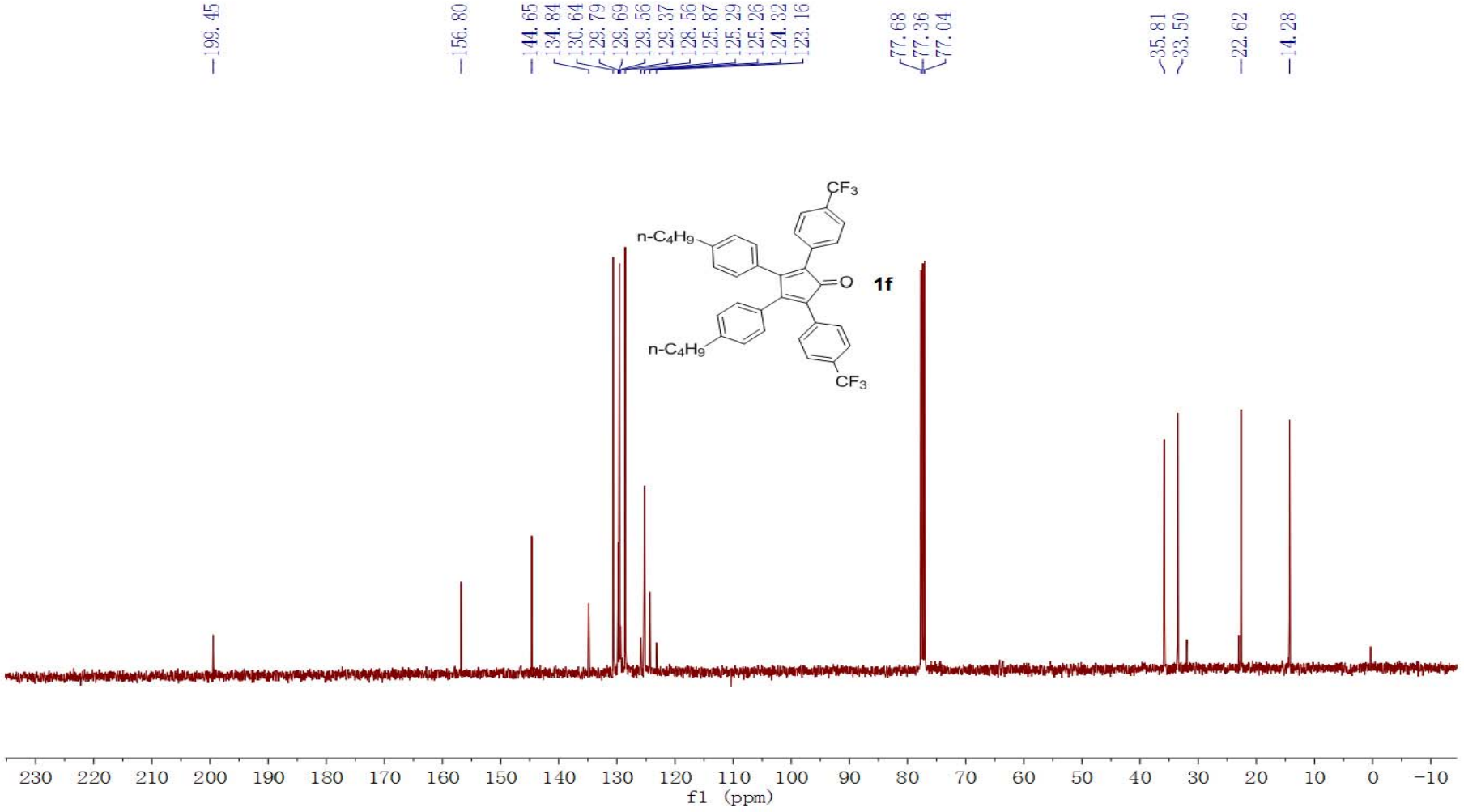


**Figure S11** The $^{1}$H NMR spectra of **1g**.

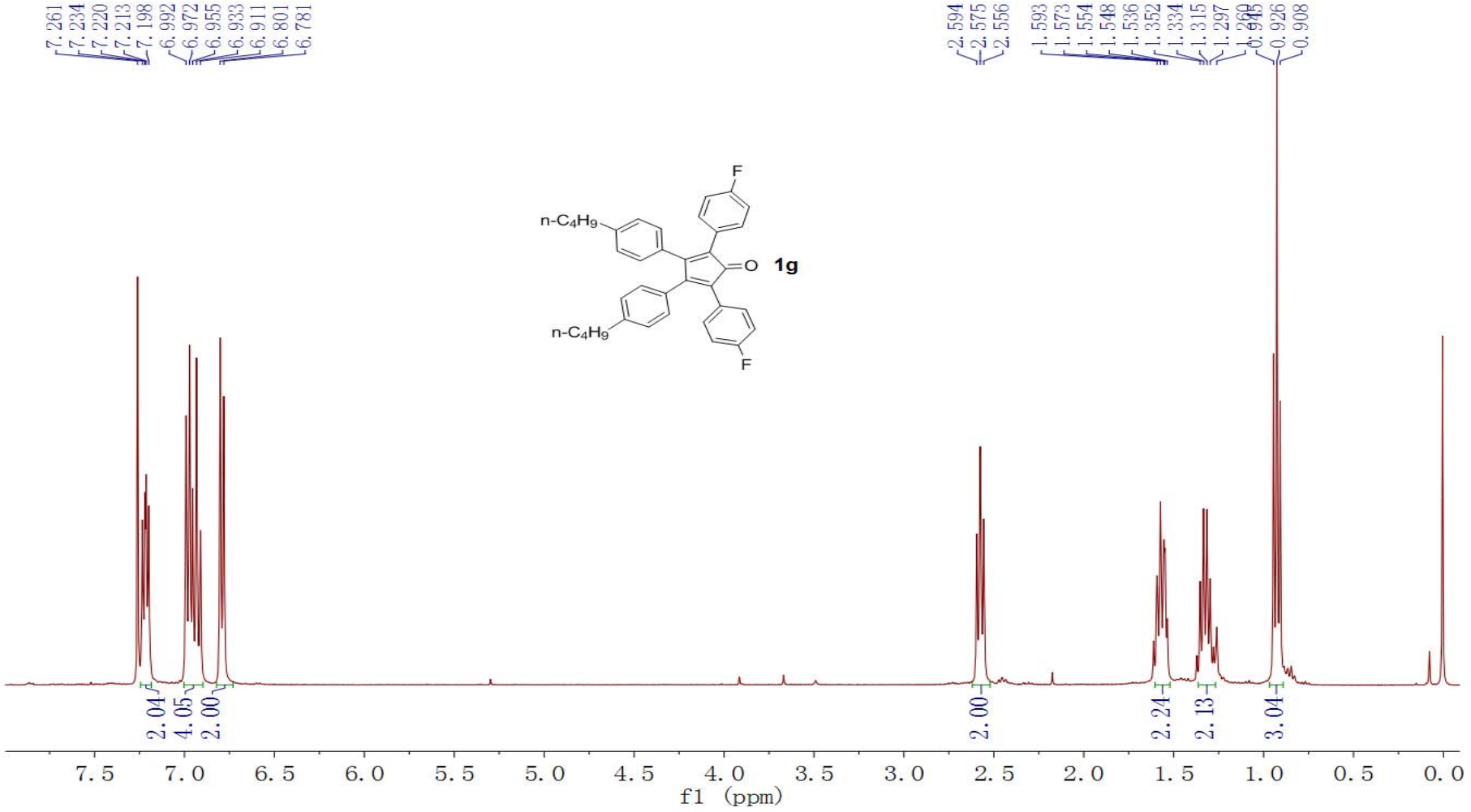


**Figure S12** The $^{13}C$ NMR spectra of **1g**.

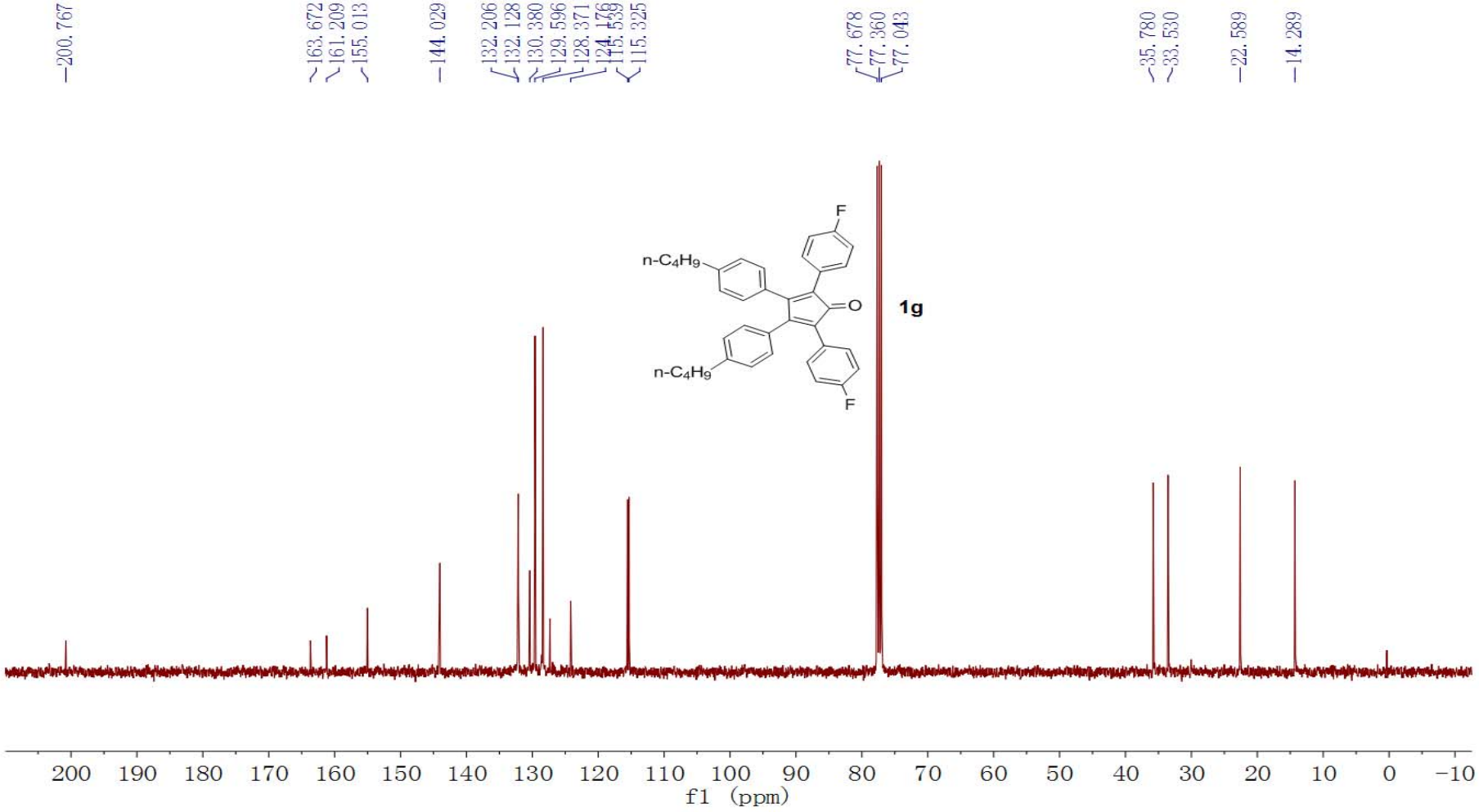


**Figure S13** The $^{1}$H NMR spectra of **1h**.

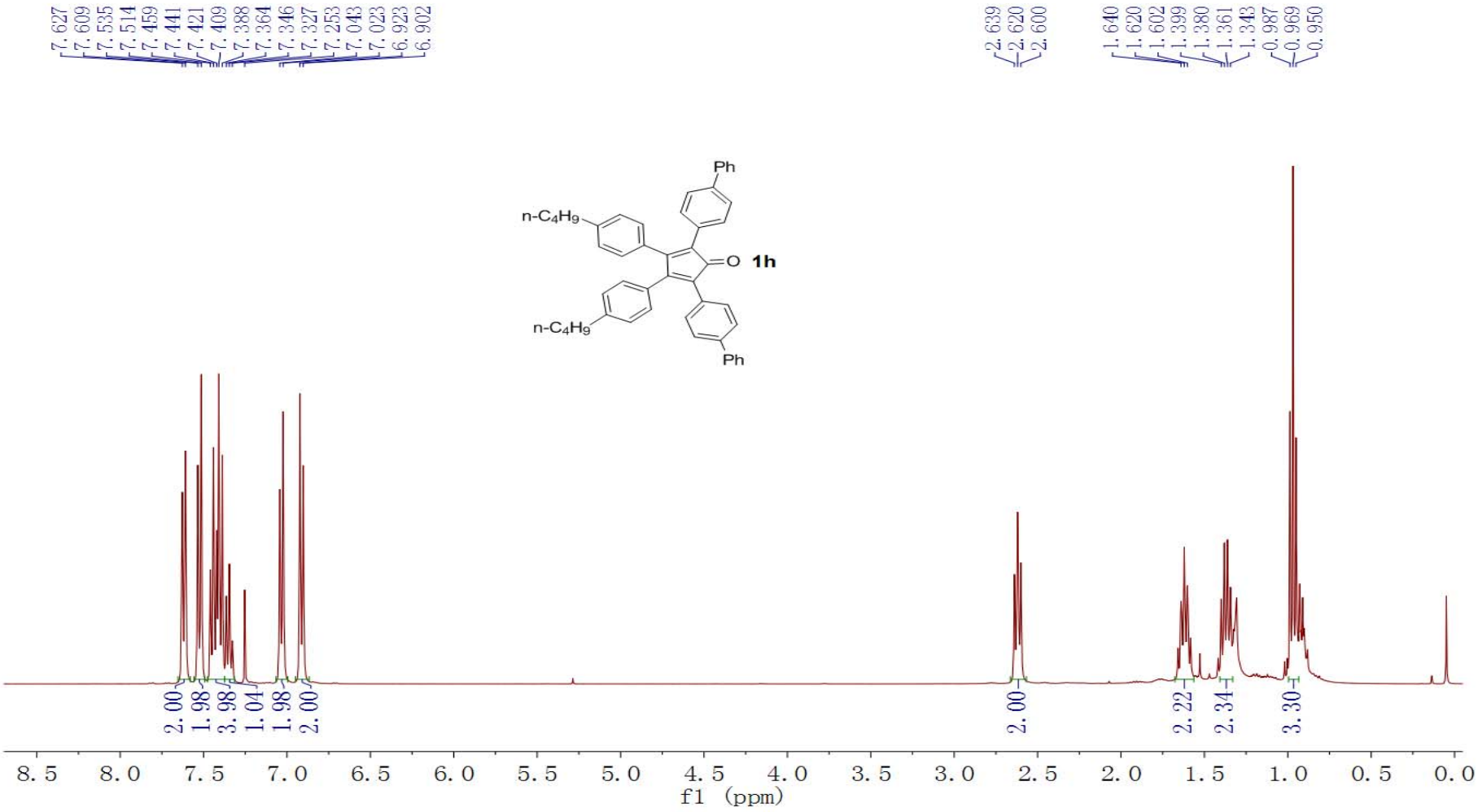


**Figure S14** The $^{13}C$ NMR spectra of **1h**.

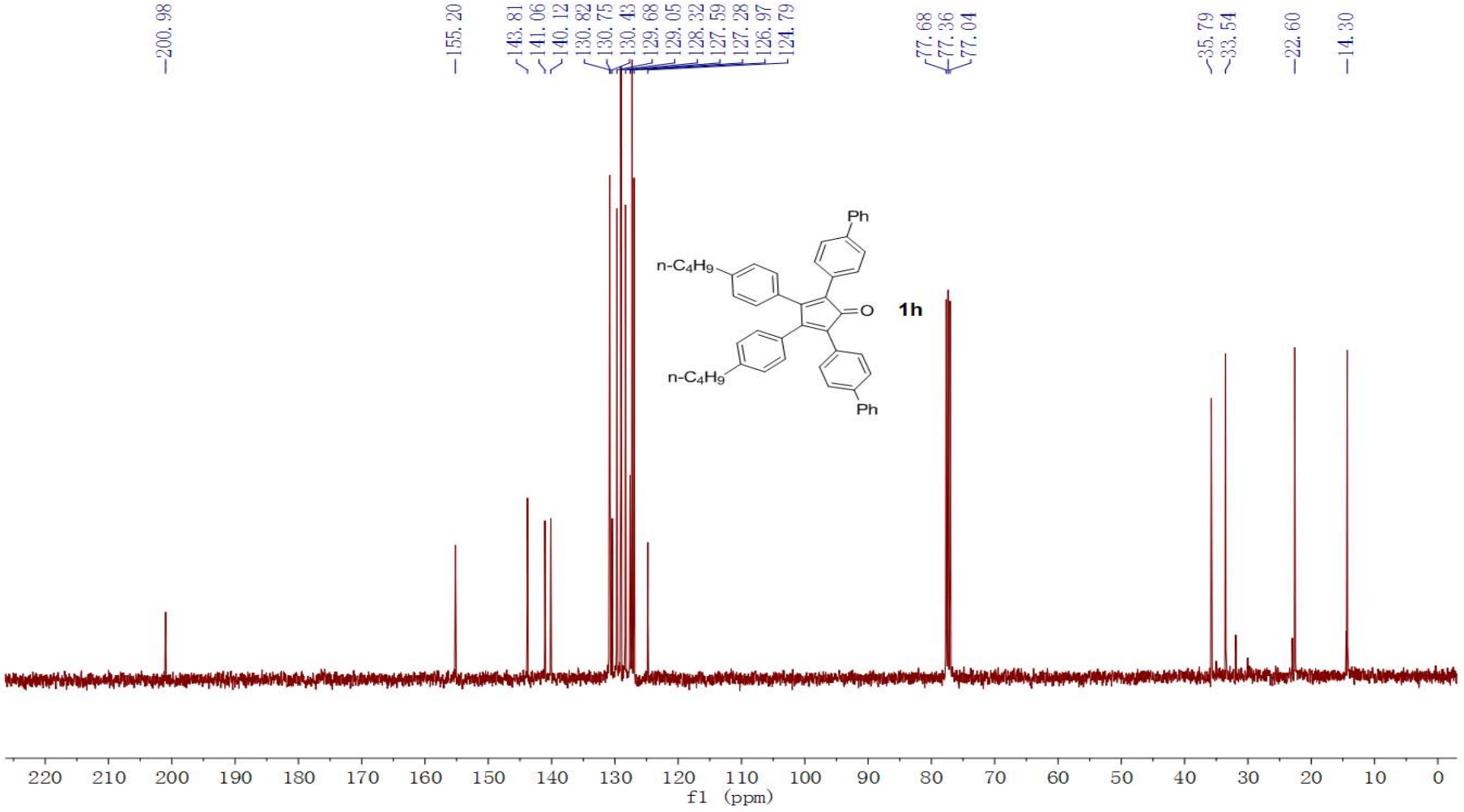


**Figure S15** The $^{1}$H NMR spectra of **1i**.

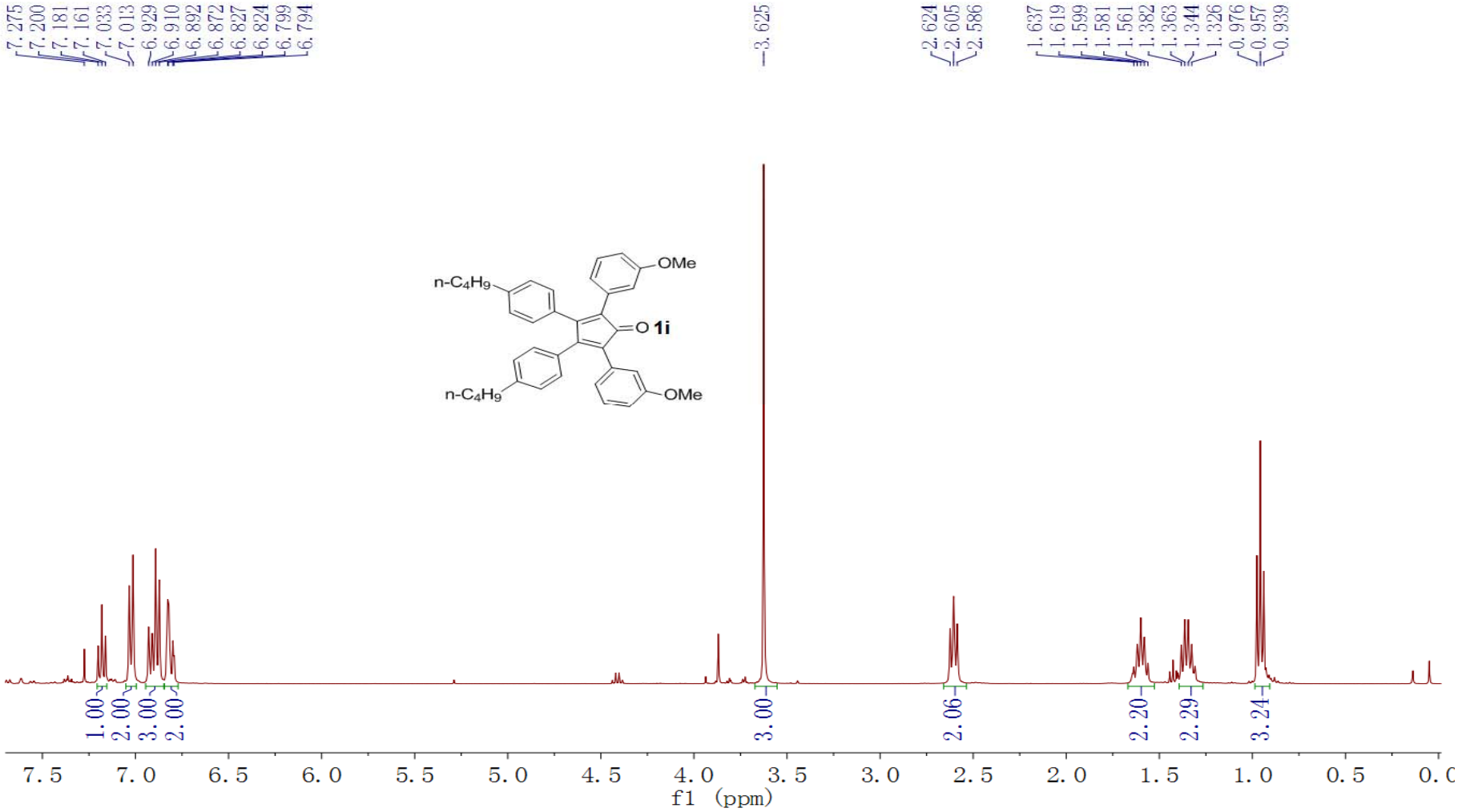


**Figure S16** The $^{13}C$ NMR spectra of **1i**.

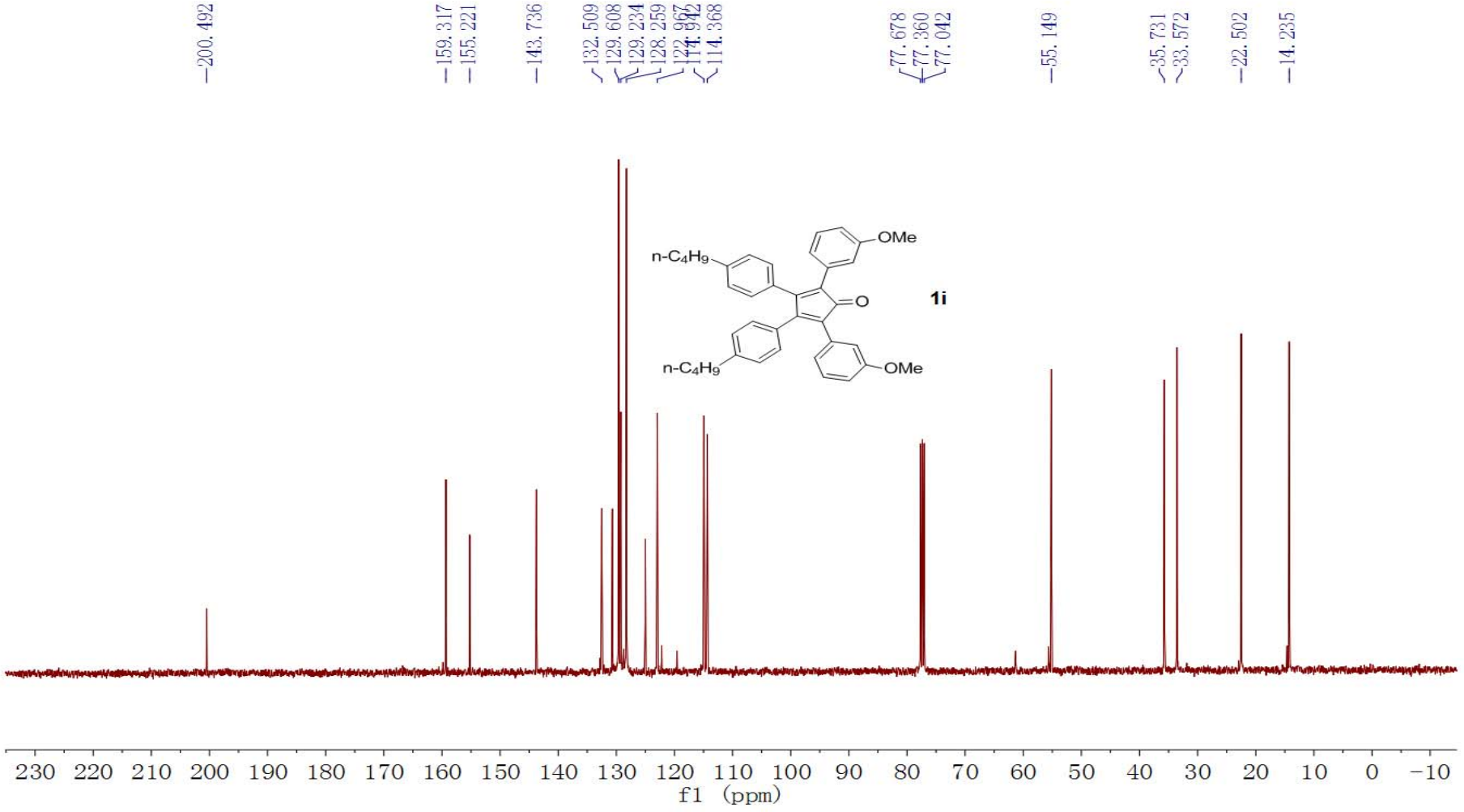


**Figure S17** The $^{1}$H NMR spectra of **1j**.

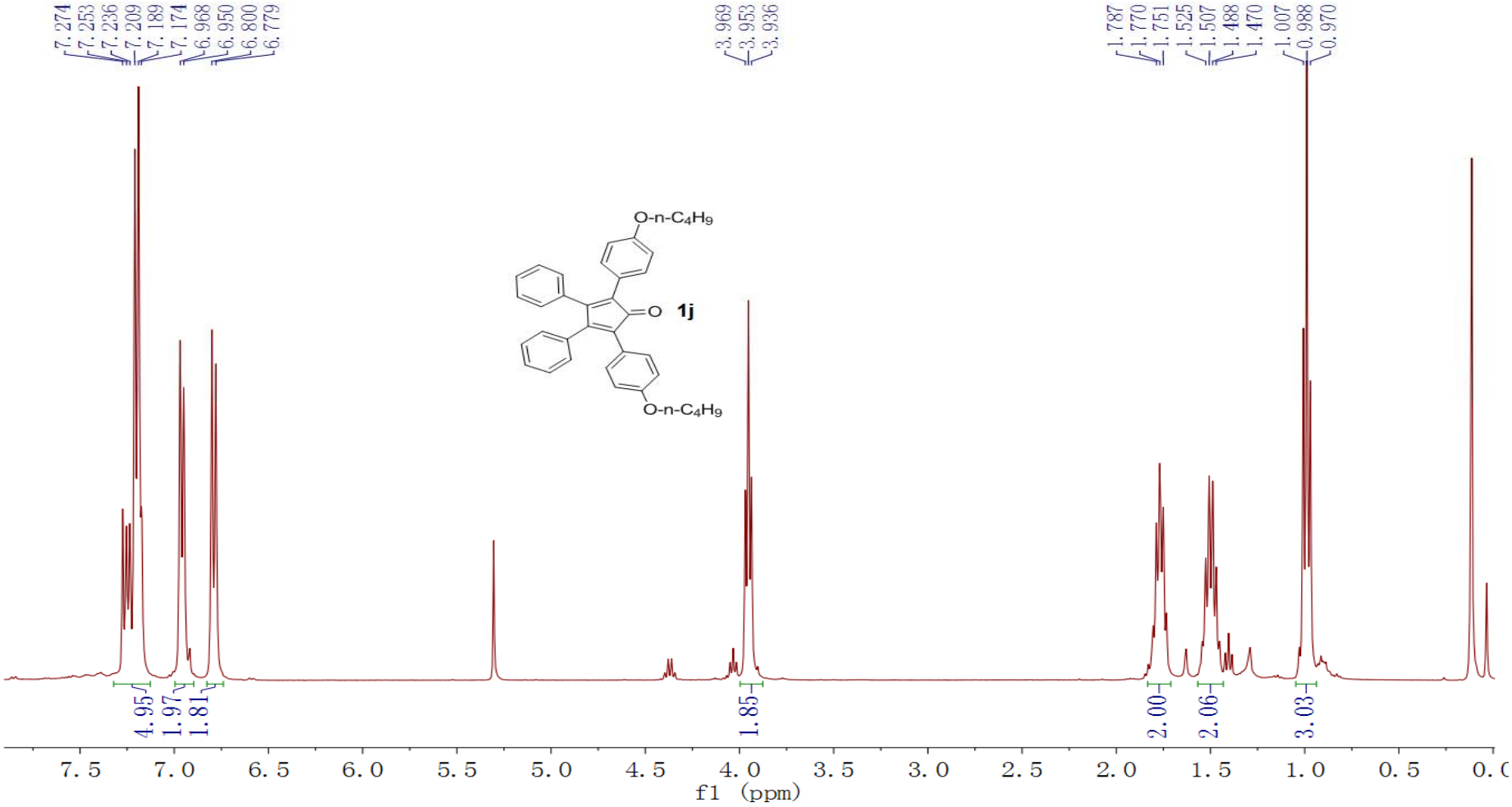


**Figure S18** The $^{13}C$ NMR spectra of **1j**.

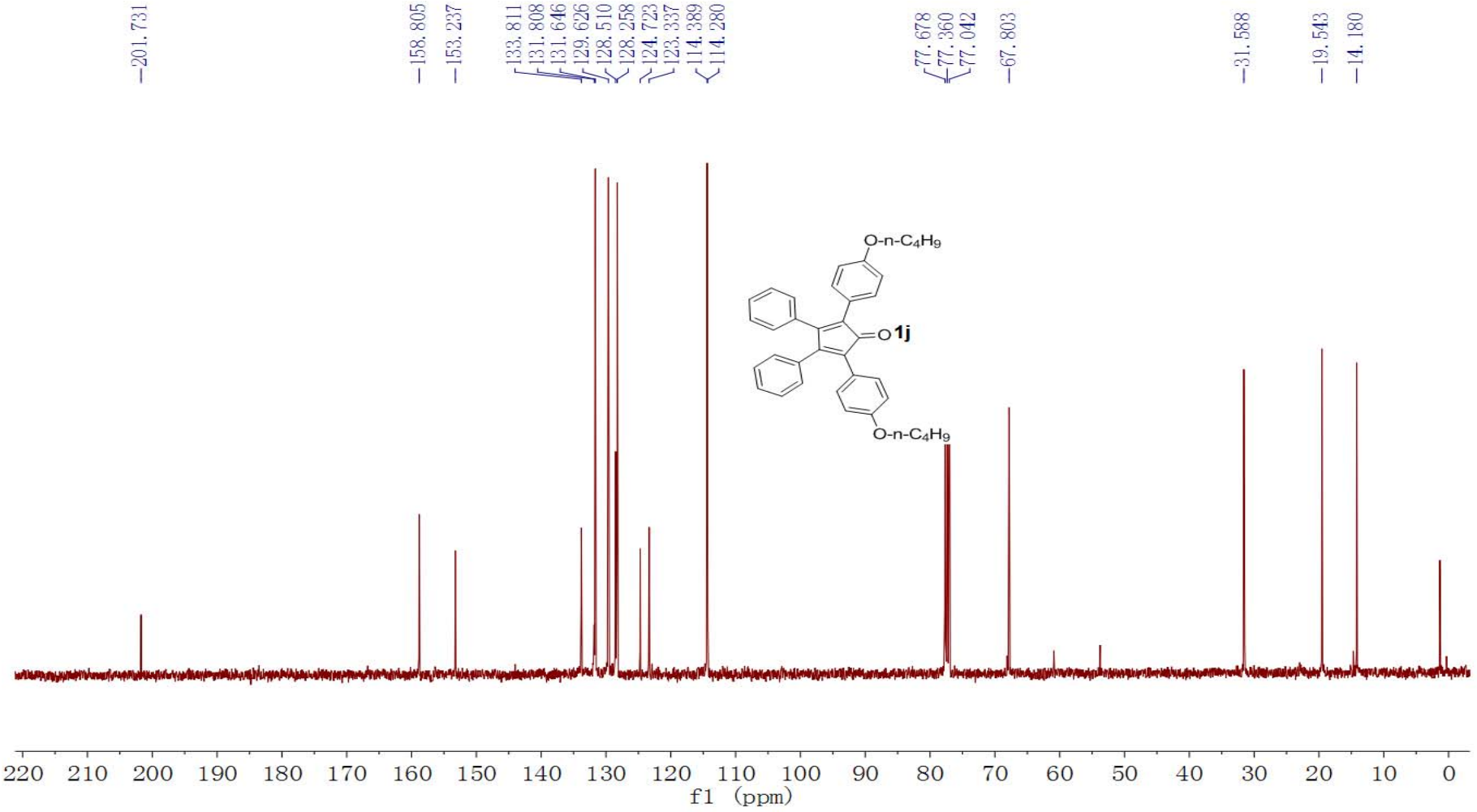


**Figure S19** The $^{1}$H NMR spectra of **1k**.

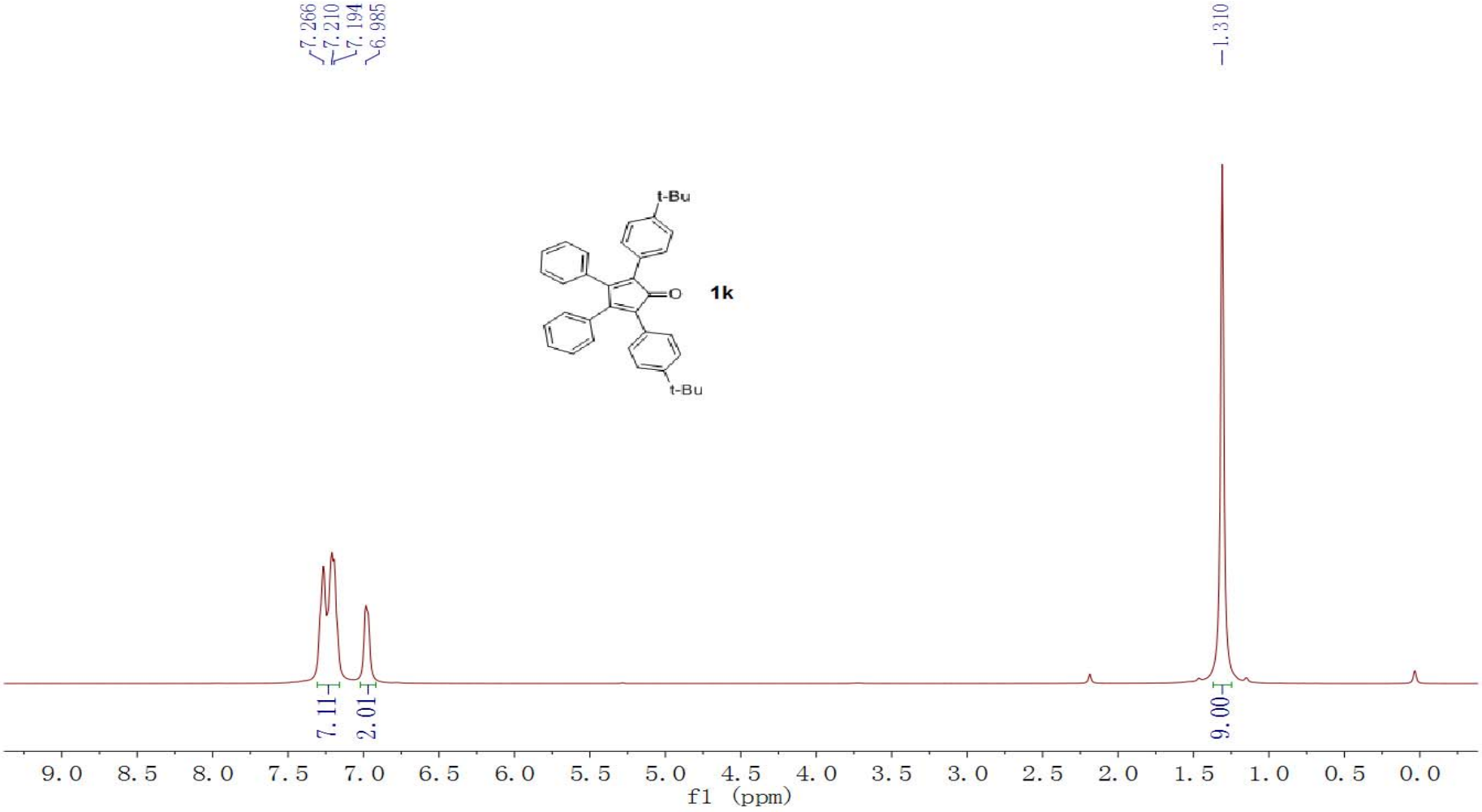


**Figure S20** The $^{13}C$ NMR spectra of **1k**.

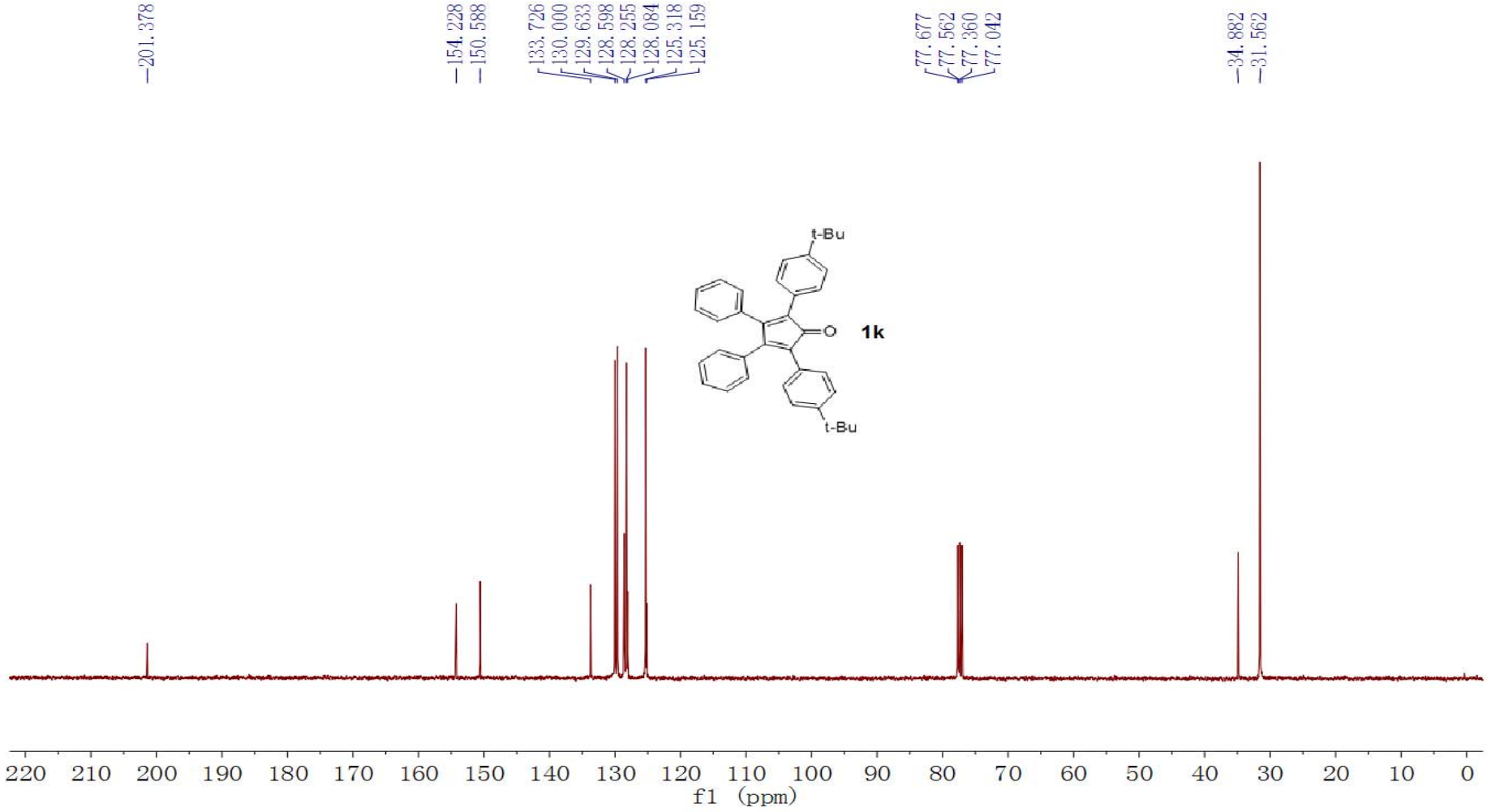


**Figure S21** The $^{1}$H NMR spectra of **1l**.

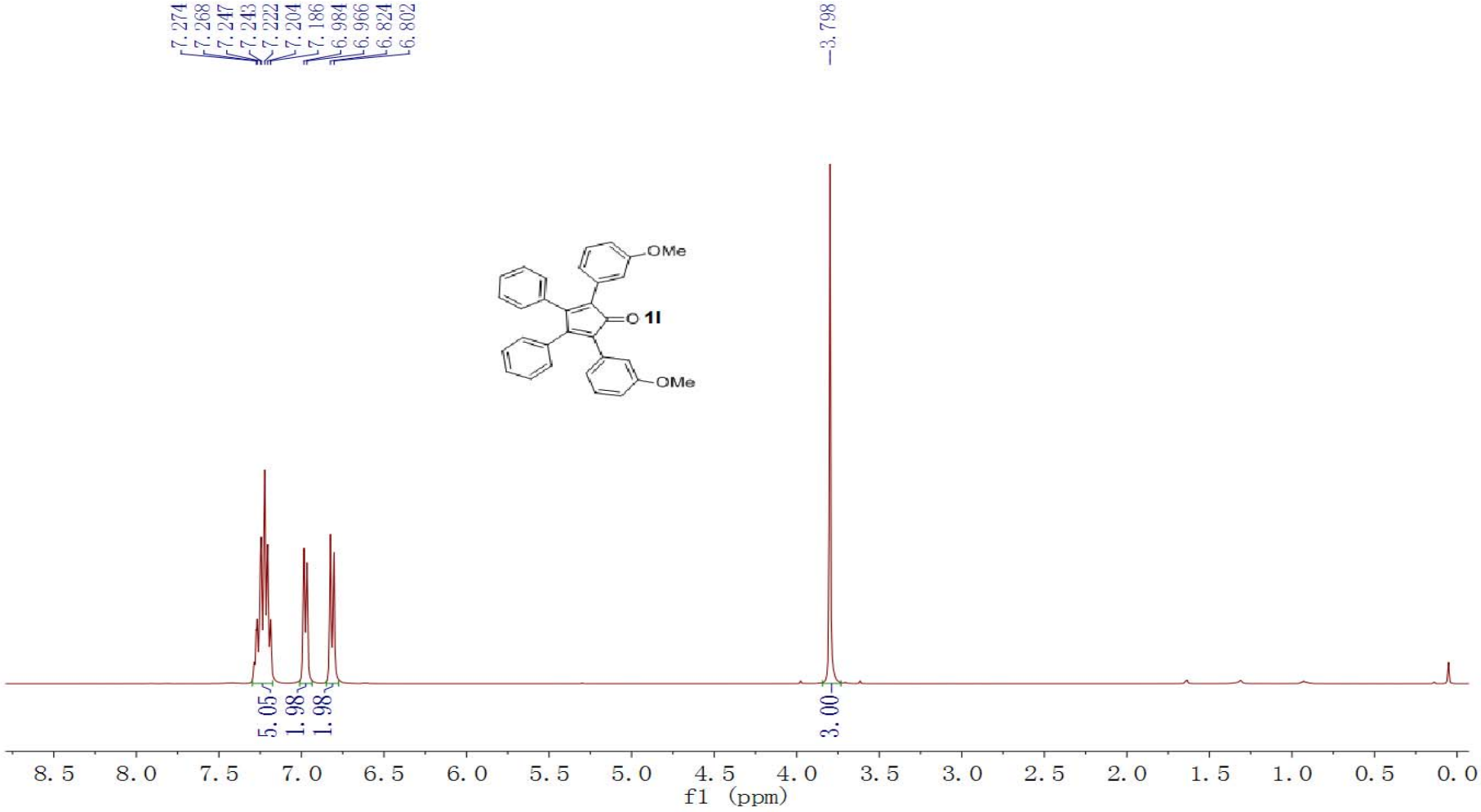


**Figure S22** The $^{13}C$ NMR spectra of **1l**.

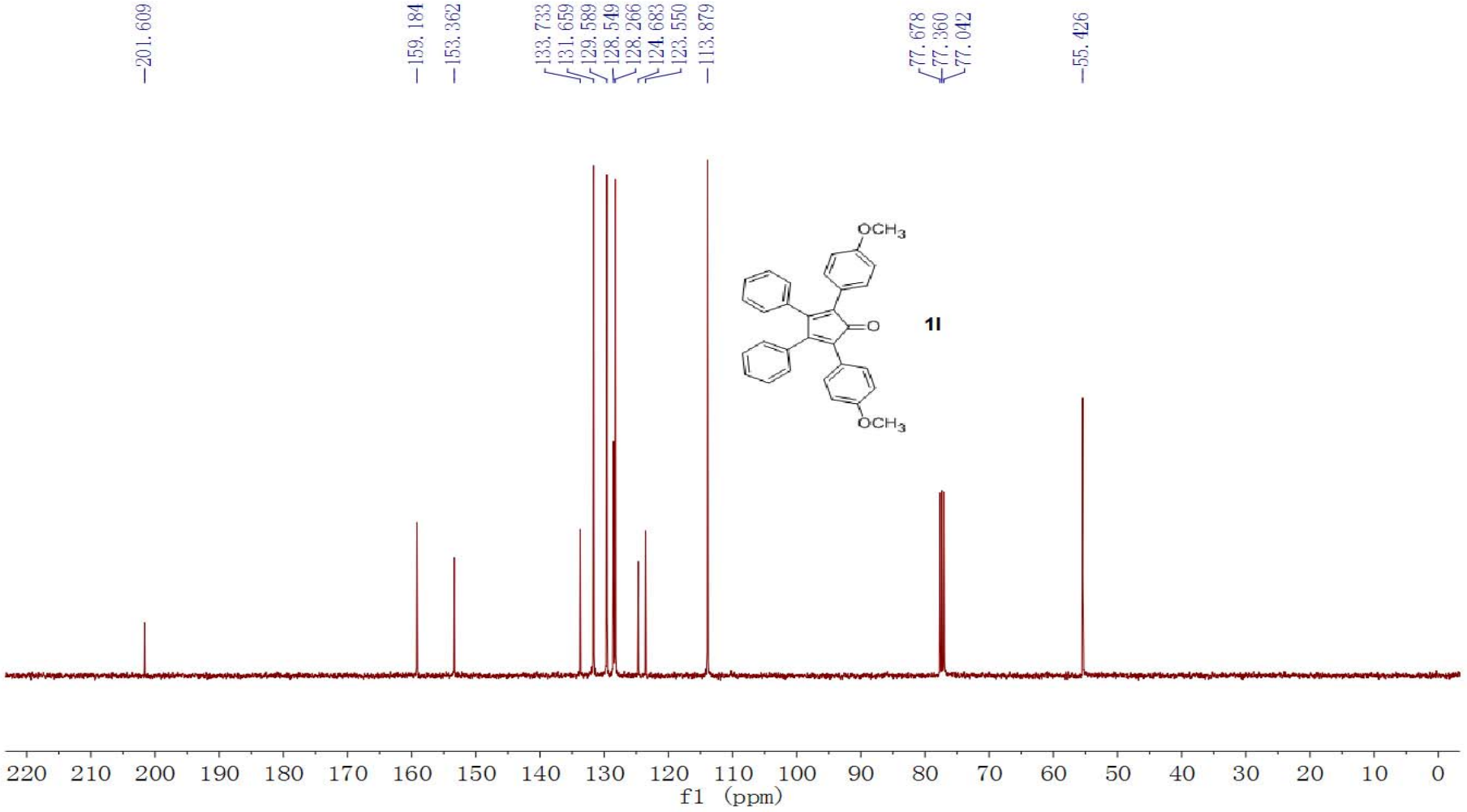


**Figure S23** The $^{1}$H NMR spectra of **1m**.

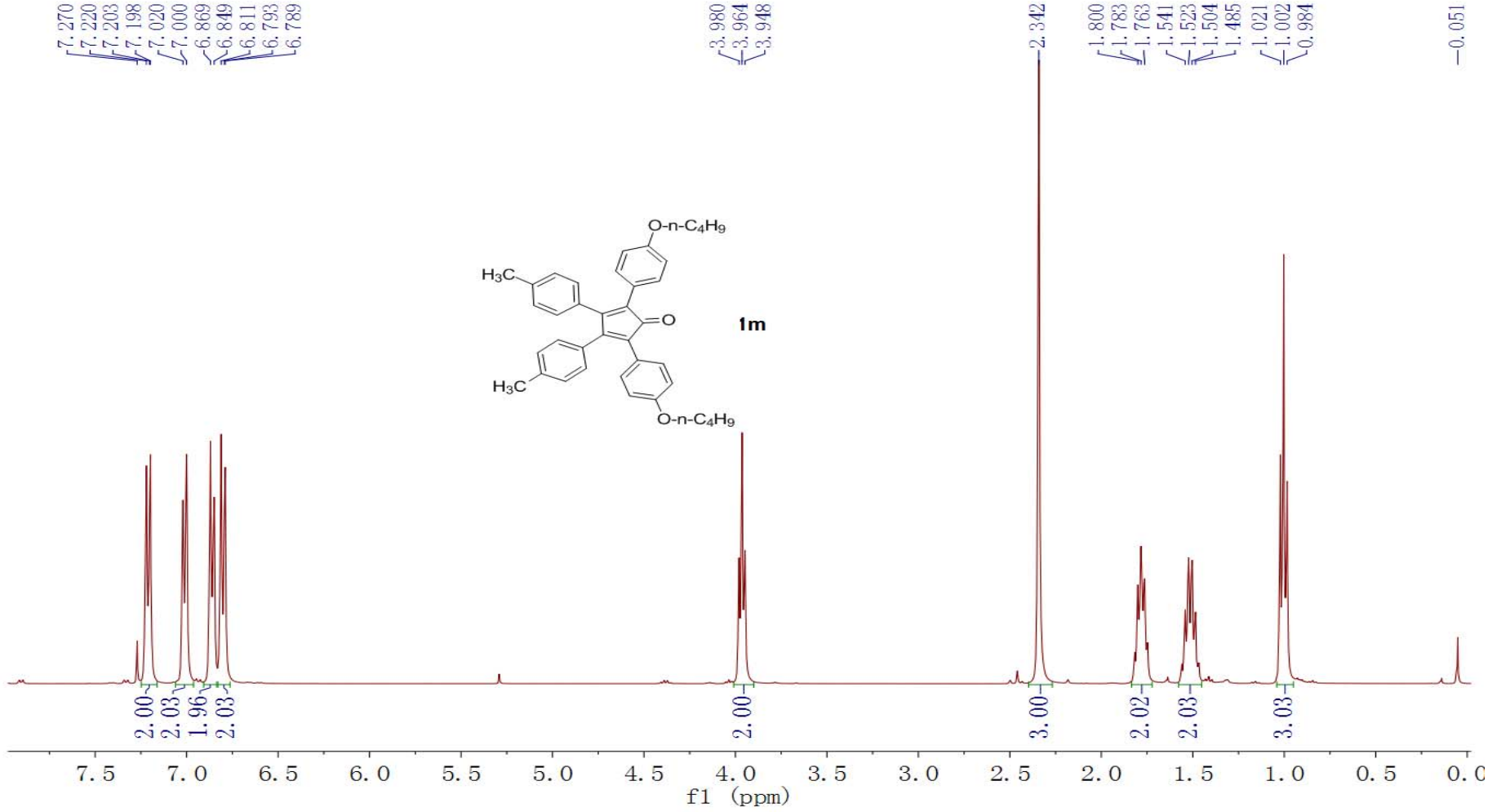


**Figure S24** The $^{13}C$ NMR spectra of **1m**.

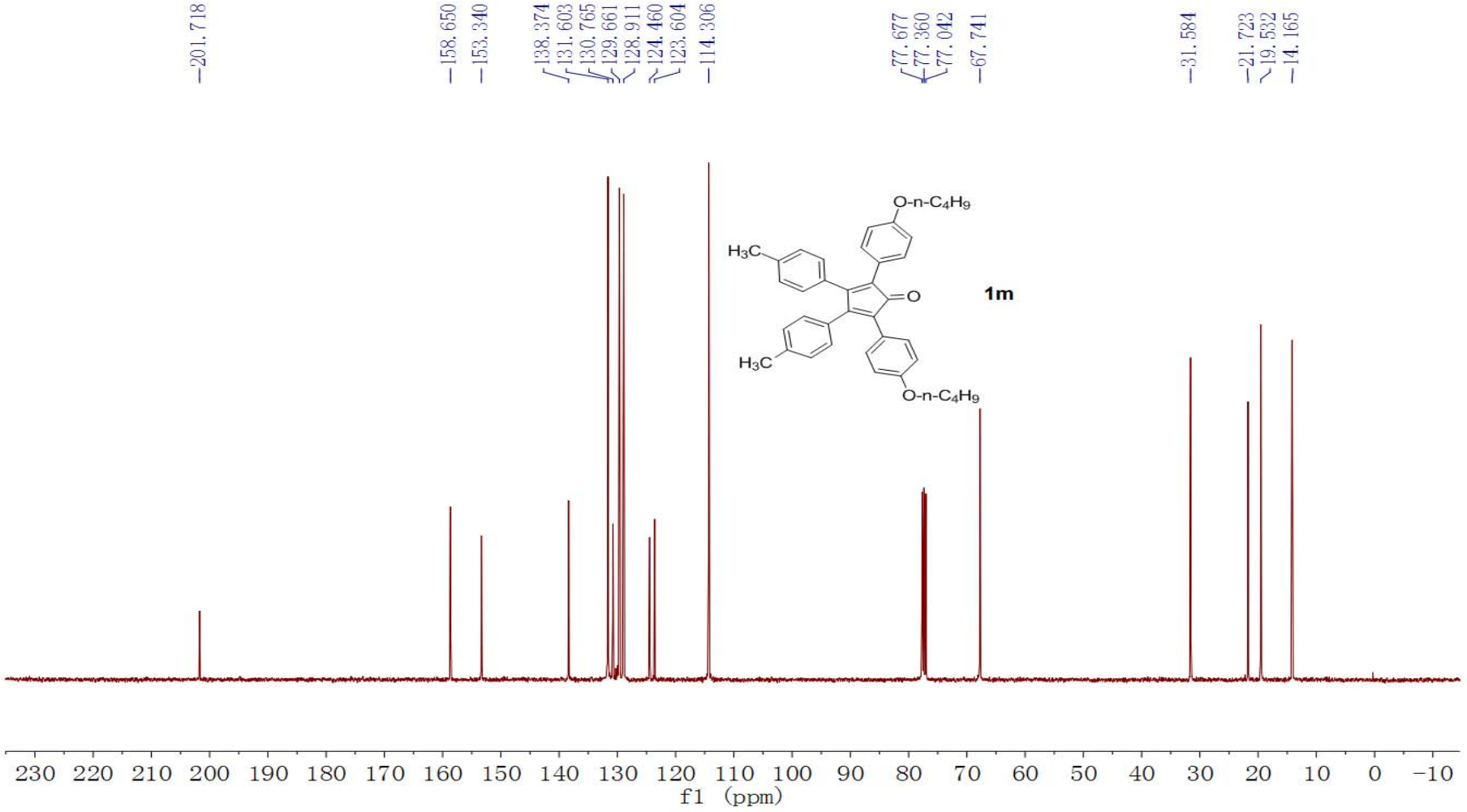


**Figure S25** The $^{1}H$ NMR spectra of **1n**.

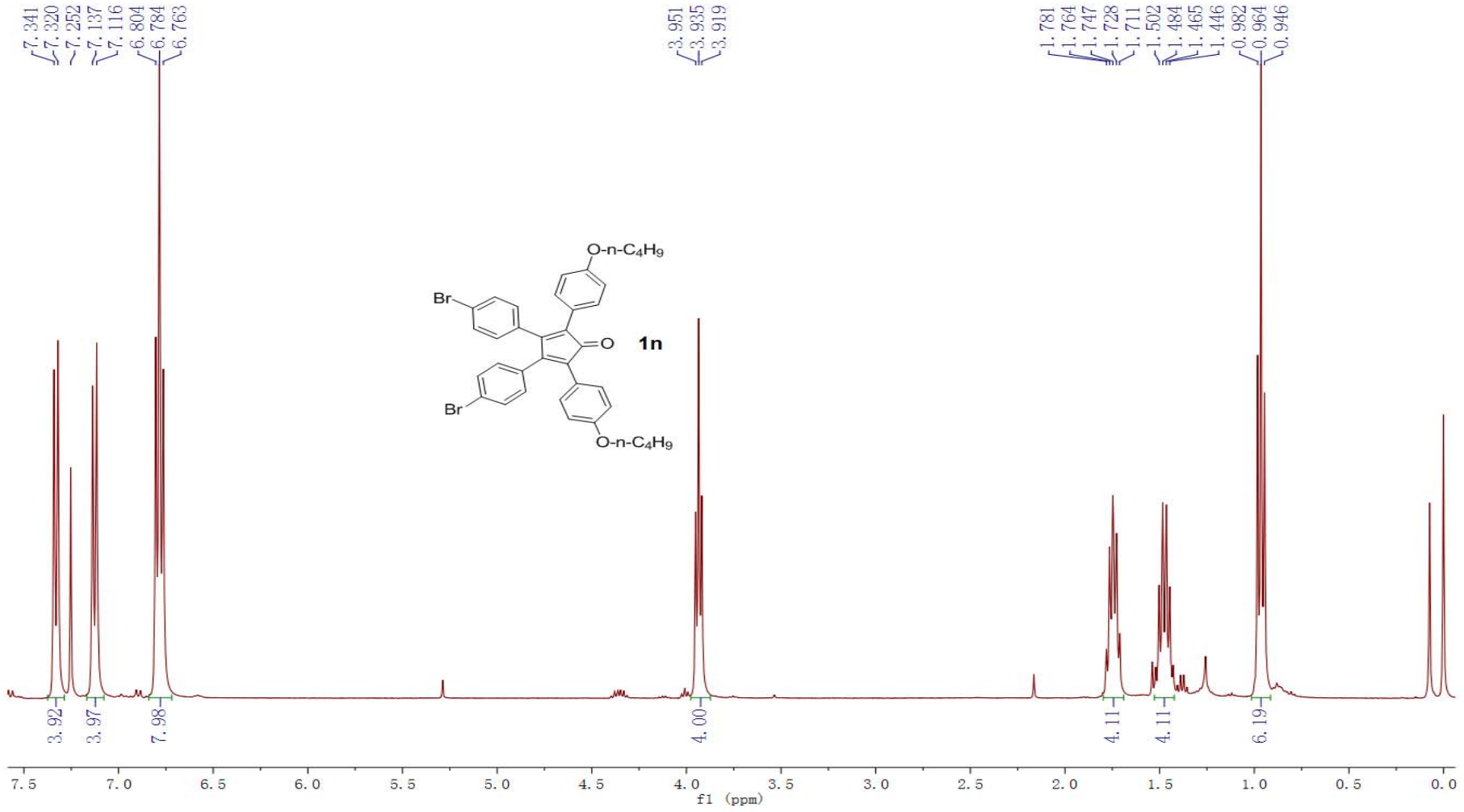
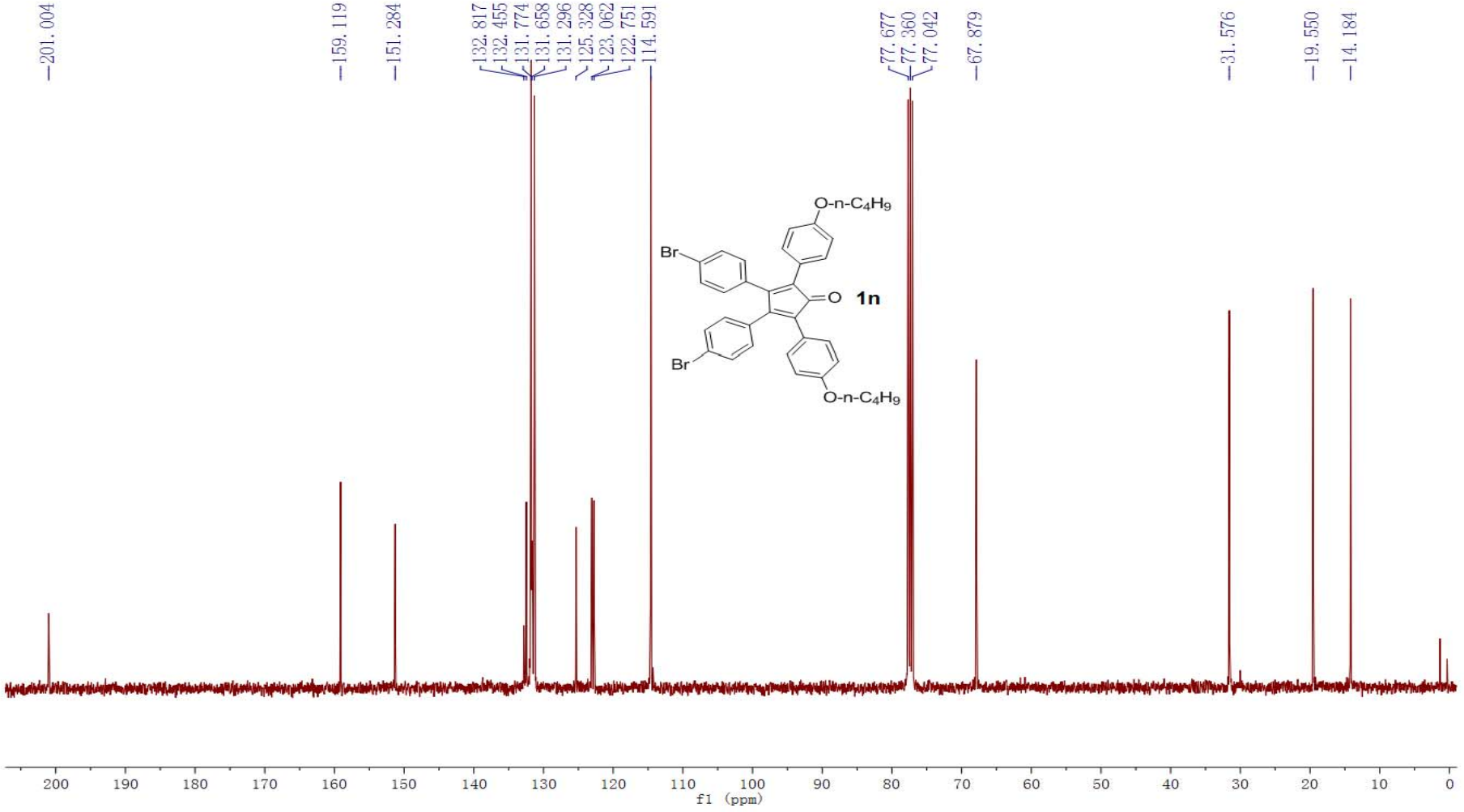


**Figure S26** The $^{13}C$ NMR spectra of **1n**.



**2. Table S1**. The optimization of reaction conditions for the formation of **2b**

| Entry | Ammonium salts | **1b**/$NH_4^+$ (mol ratio) | Solvent/Temp | Time/h | Yield %[a] |
|---|---|---|---|---|---|
| 1 | $NH_4Cl$ | 1/8 | AcOH/ reflux | 24 | 21 |
| 2 | | 1/12 | AcOH/ reflux | 24 | 34 |
| 3 | | 1/16 | AcOH/ reflux | 24 | 53 |
| 4 | | 1/20 | AcOH/ reflux | 24 | 57 |
| 5 | | 1/24 | AcOH/ reflux | 24 | 62 |
| 6 | | 1/30 | AcOH/ reflux | 24 | 64 |
| 7 | $HCOONH_4$ | 1/30 | AcOH/ reflux | 24 | 0 |
| 8 | $NH_4OAc$ | 1/8 | AcOH/ reflux | 24 | 25 |
| 9 | | 1/12 | AcOH/ reflux | 24 | 47 |
| 10 | | 1/16 | AcOH/ reflux | 24 | 63 |
| 11 | | 1/20 | AcOH/ reflux | 24 | 73 |
| 12 | | 1/24 | AcOH/ reflux | 24 | 73 |
| 13 | | 1/30 | AcOH/ reflux | 24 | 72 |
| 14 | | 1/30 | AcOH/ 50 $^oC$ | 24 | 7 |
| 15 | | 1/20 | $Ac_2O$/reflux | 24 | 11 |
| 16 | | 1/20 | Toluene/reflux | 24 | 55 |
| 17 | | 1/20 | AcOH/ reflux | 4 | 15 |
| 18 | | 1/20 | AcOH/ reflux | 8 | 37 |
| 19 | | 1/20 | AcOH/ reflux | 12 | 53 |
| 20 | | 1/20 | AcOH/ reflux | 16 | 68 |
| 21 | | 1/20 | AcOH/ reflux | 20 | 73 |

[a] Yield refers to isolated yield.

Optimal condition: **1b** (1 mmol), $NH_4OAc$ (20 mmol), and AcOH (2 ml) were mixed and refluxed for 20 hours.

**3.** $^{1}$H NMR and $^{13}$C NMR spectra of **2a-2m**

**Figure S27**. $^{1}$H NMR spectra of **2a.**

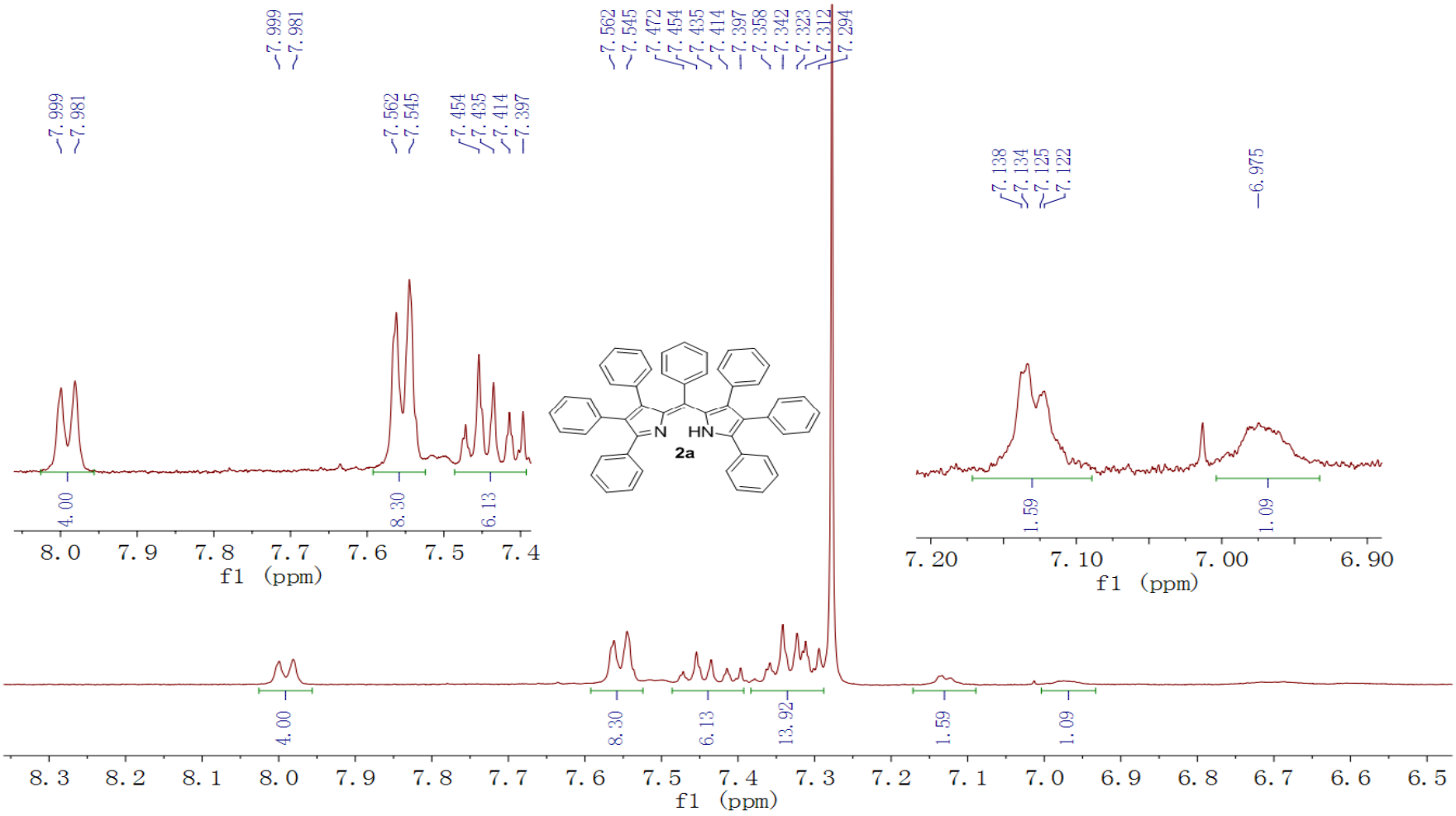


**Figure S28**. The $^{1}$H NMR spectra of **2b.**

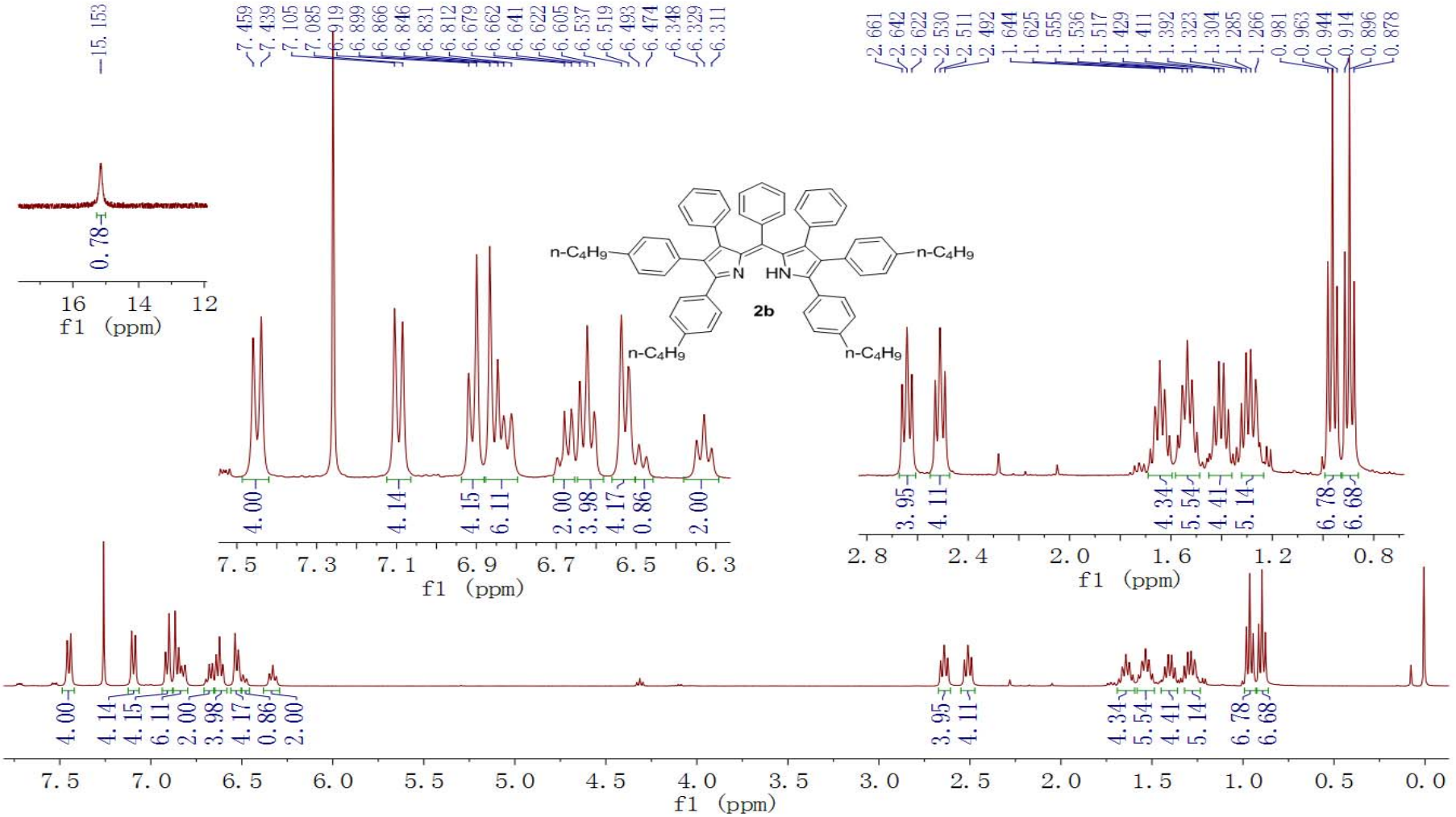


**Figure S29**. The $^{13}C$ NMR spectra of **2b.**

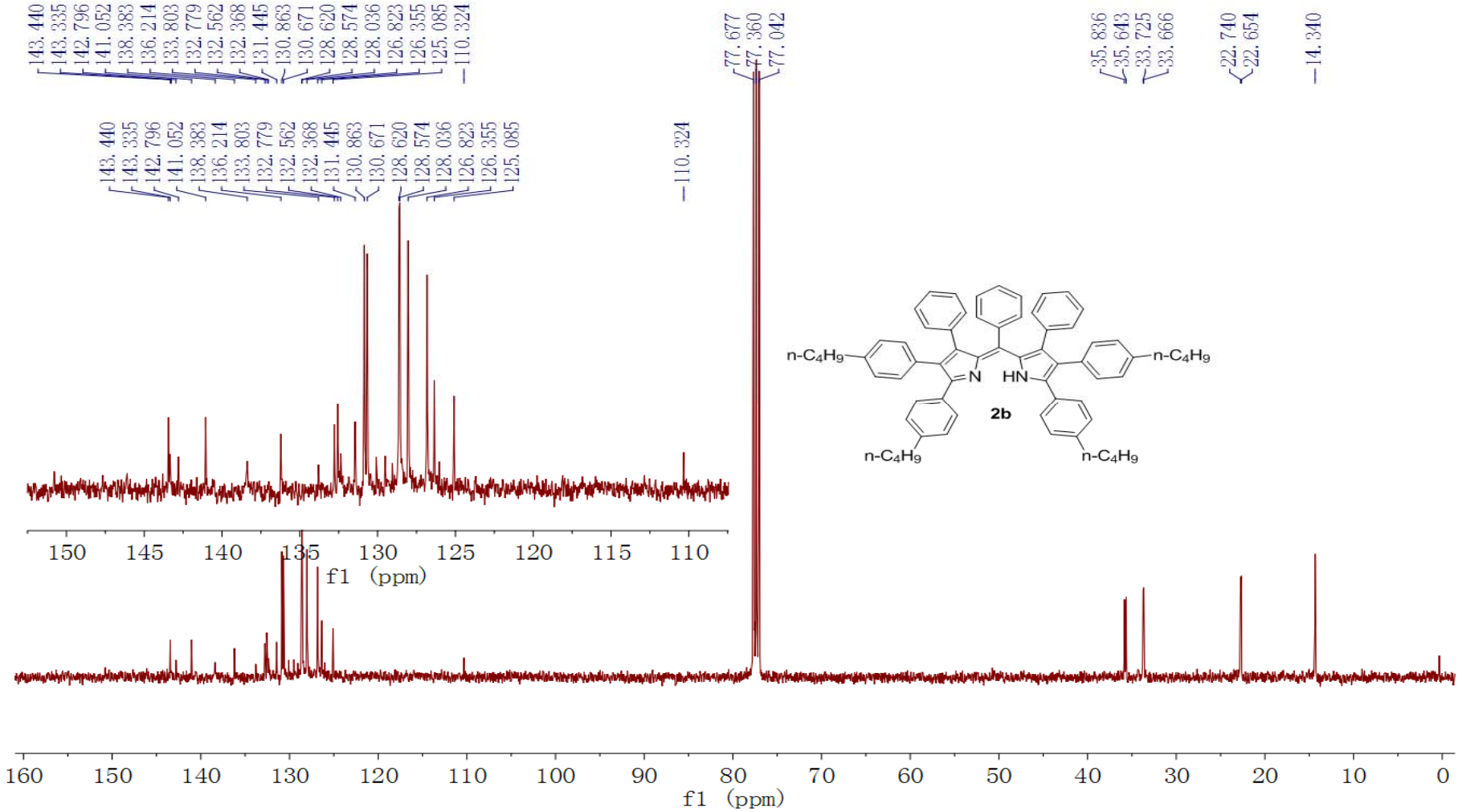


**Figure S30**. The $^{1}$H NMR spectra of **2c.**

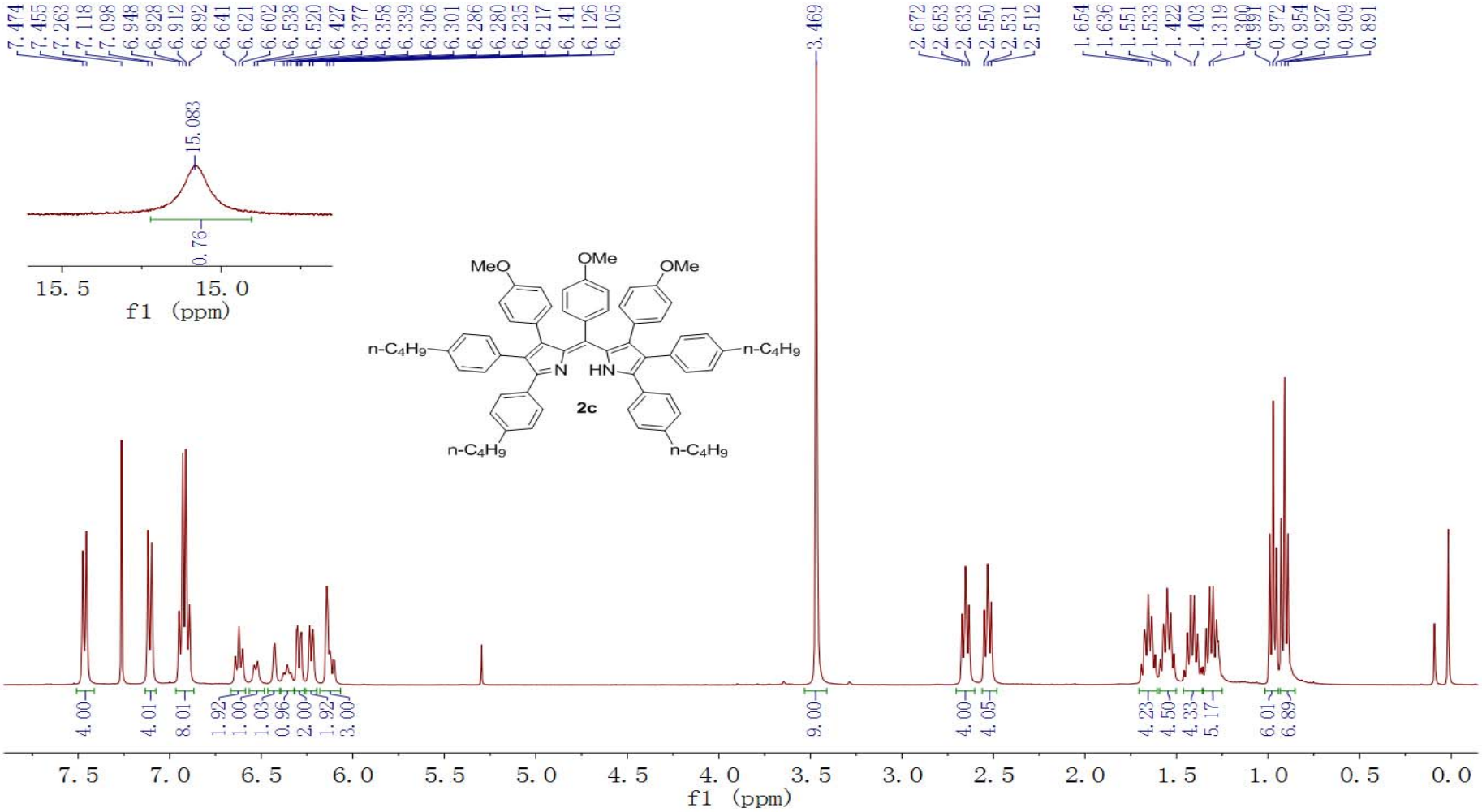


**Figure S31**. The $^{13}C$ NMR spectra of **2c.**

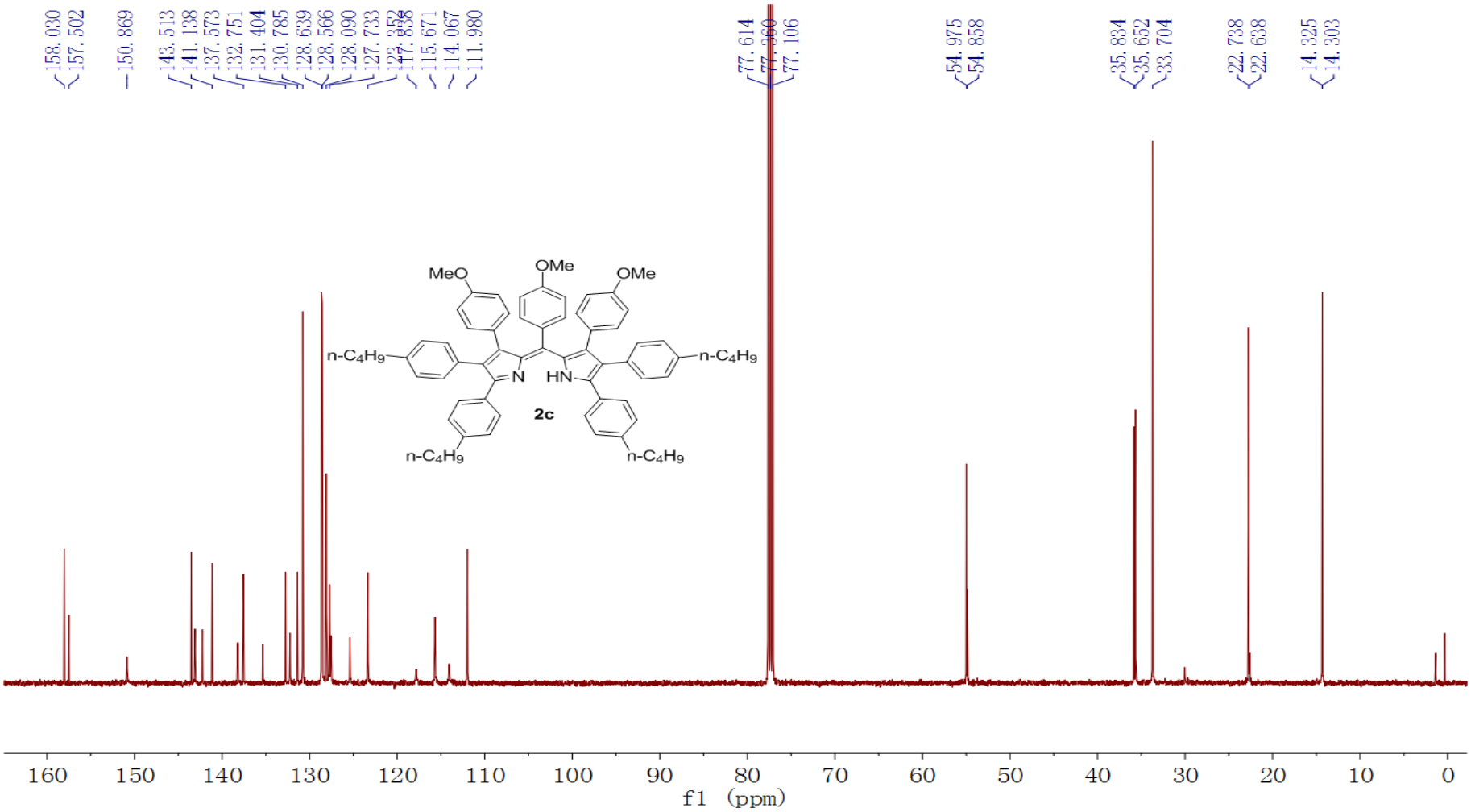


**Figure S32**. The $^{1}$H NMR spectra of **2d.**

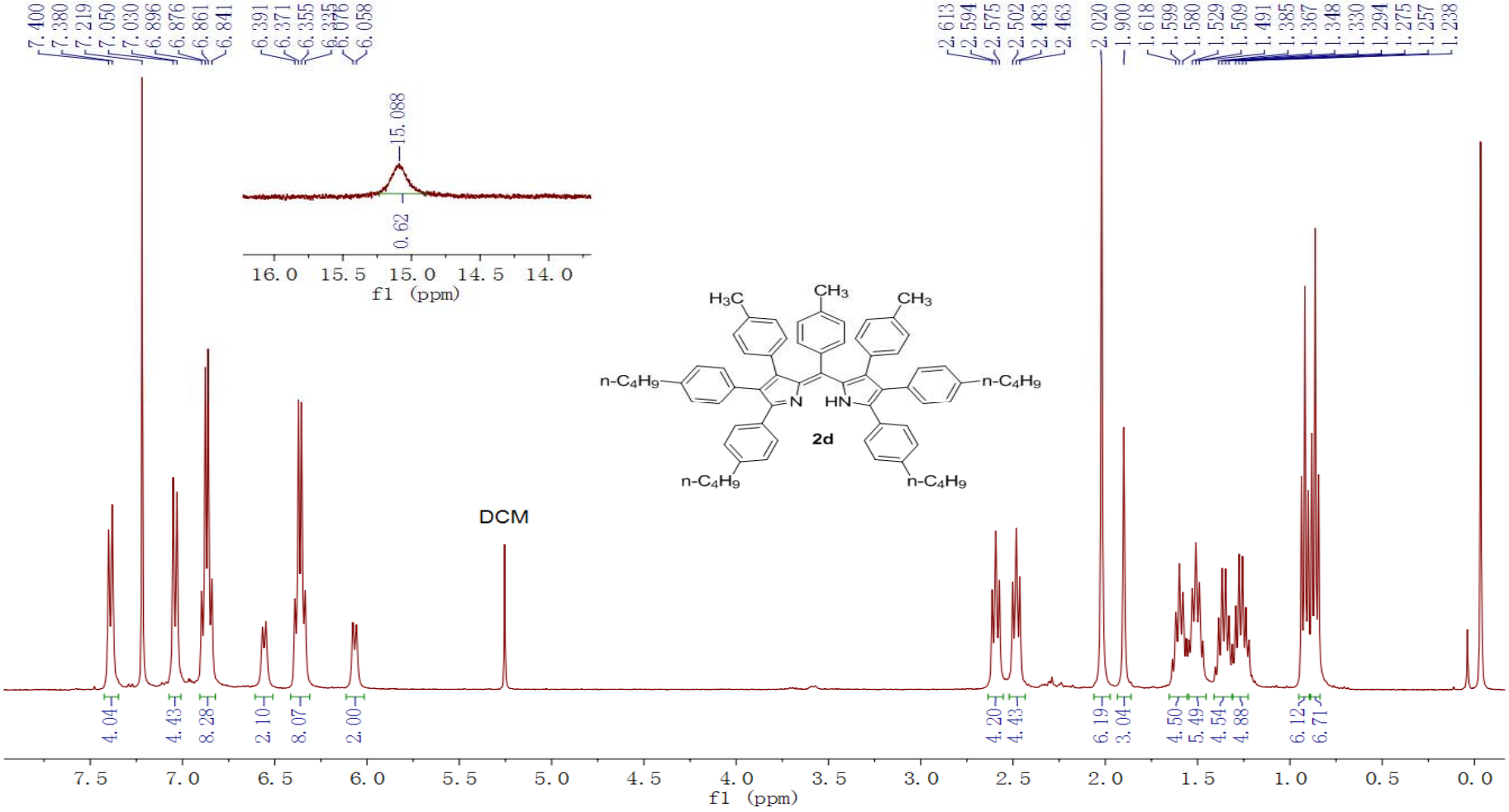


**Figure S33**. The $^{13}C$ NMR spectra of **2d.**

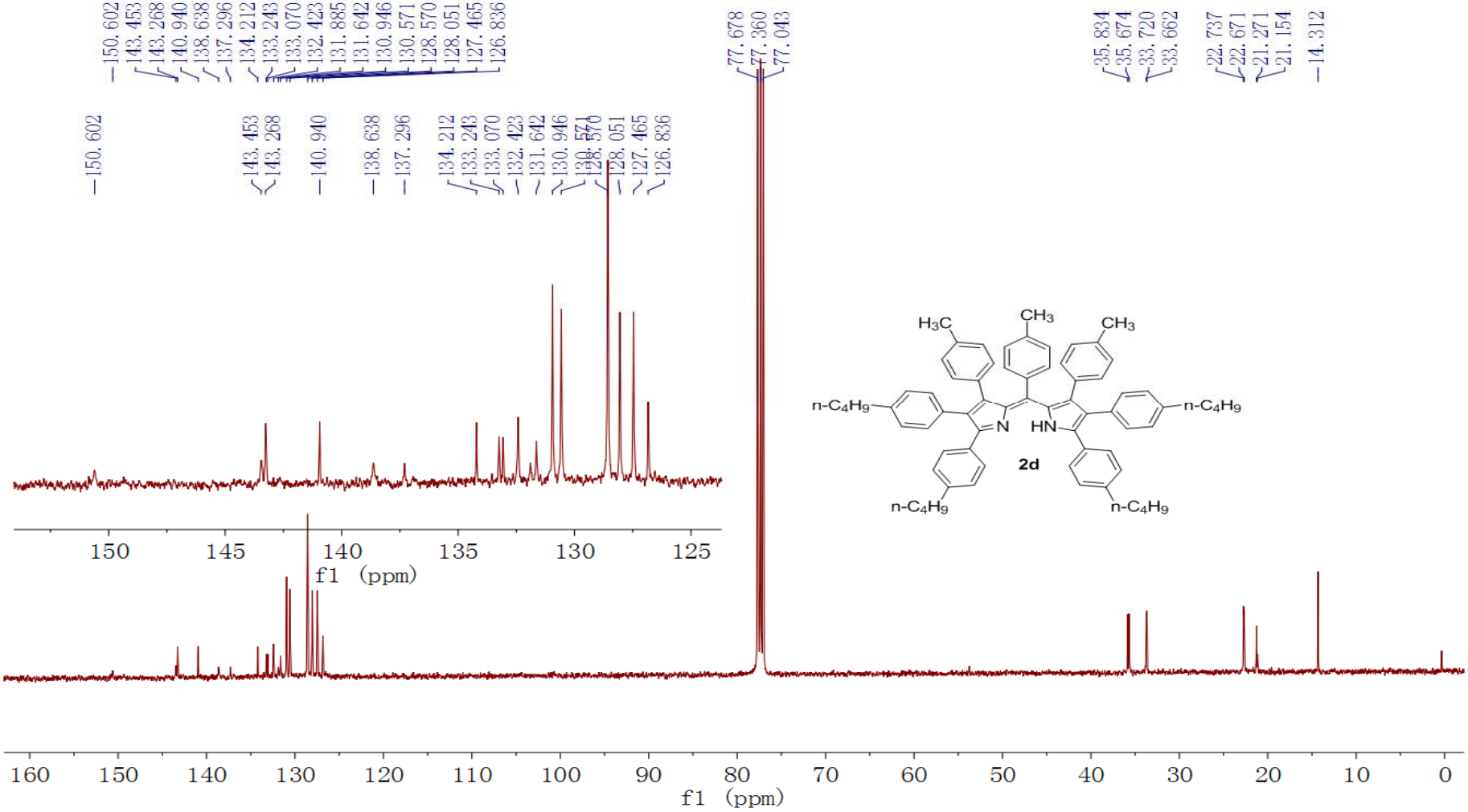


**Figure S34**. The $^{1}$H NMR spectra of **2e.**

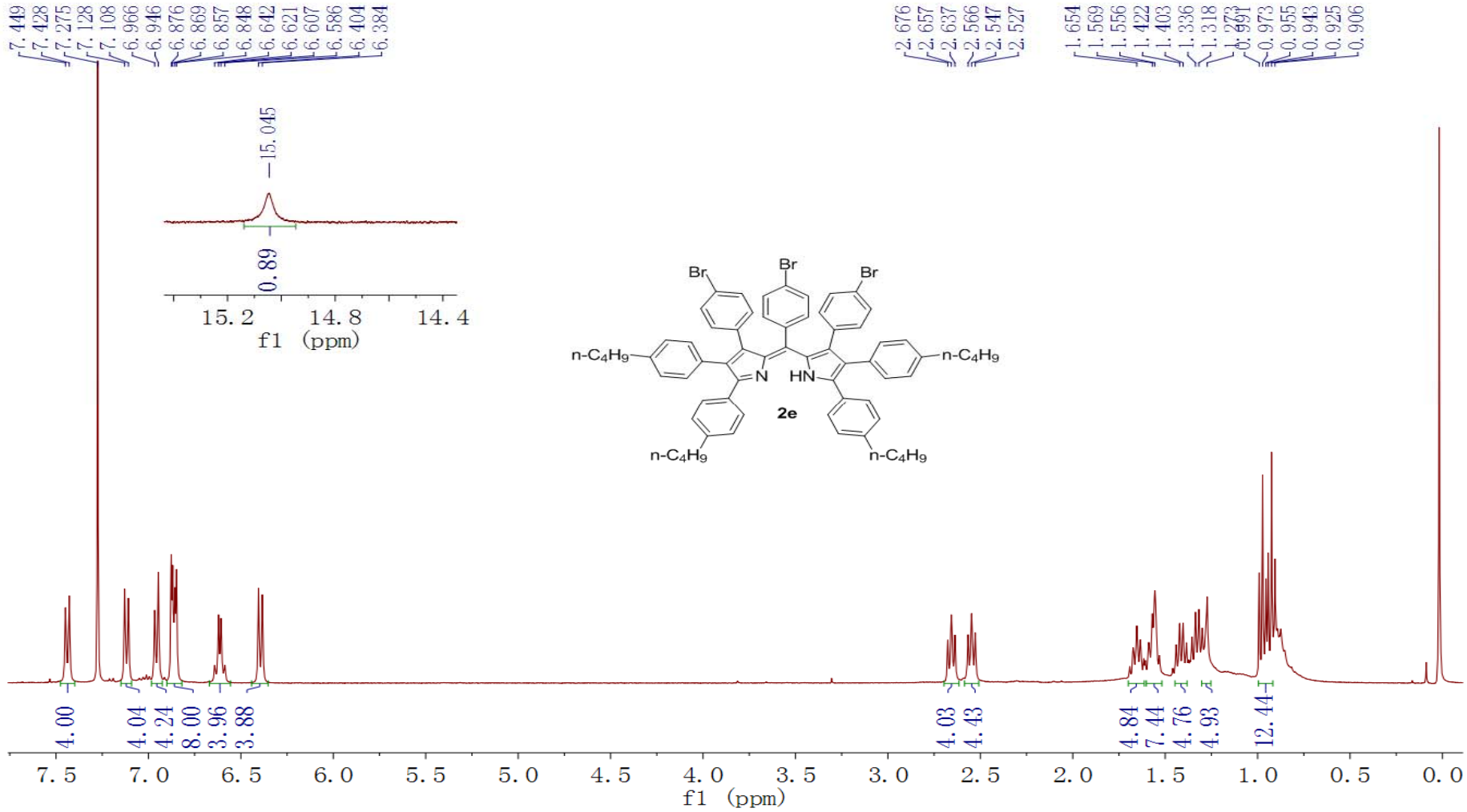


**Figure S35**. The $^{13}C$ NMR spectra of **2e.**

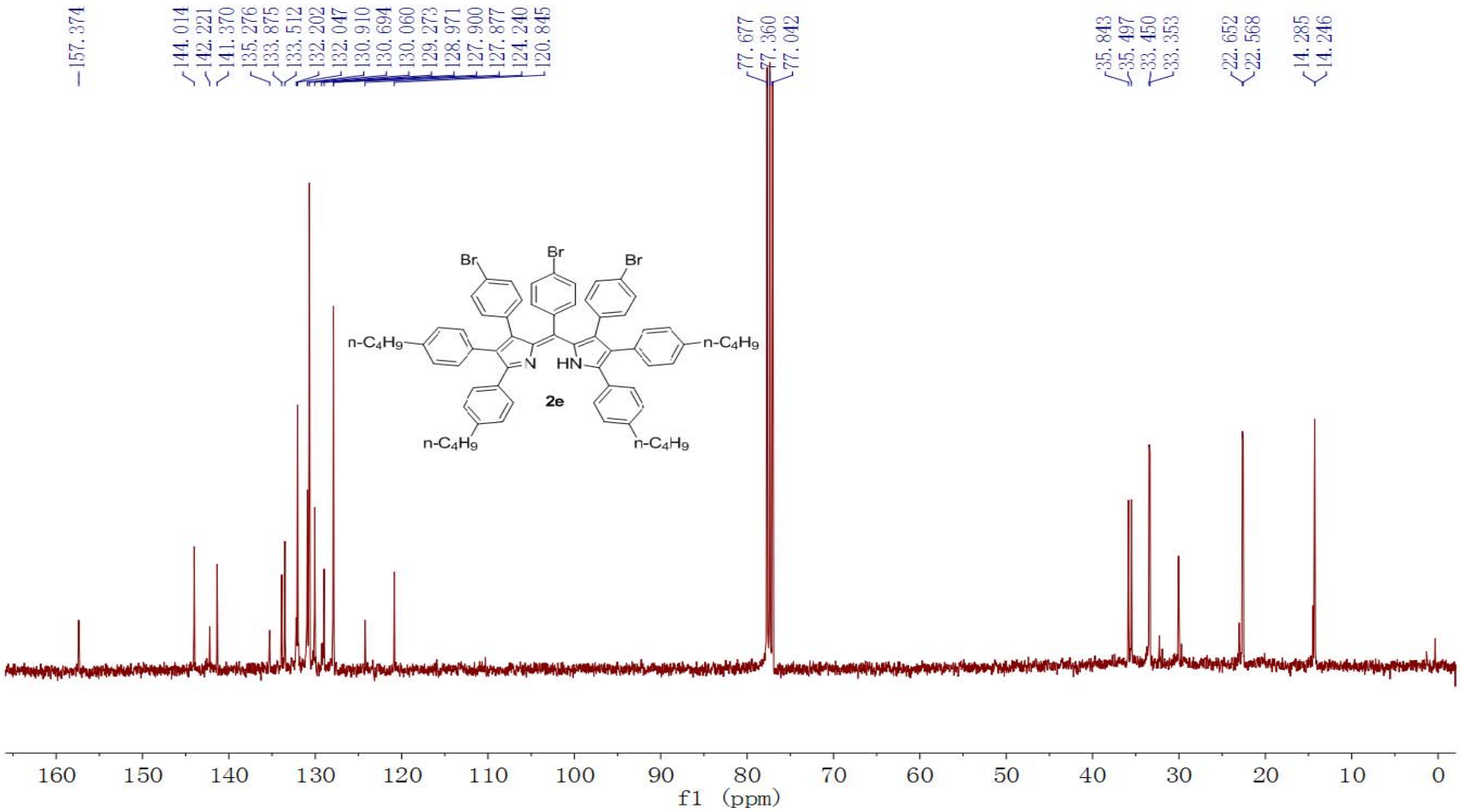


**Figure S36**. The $^{1}$H NMR spectra of **2f.**

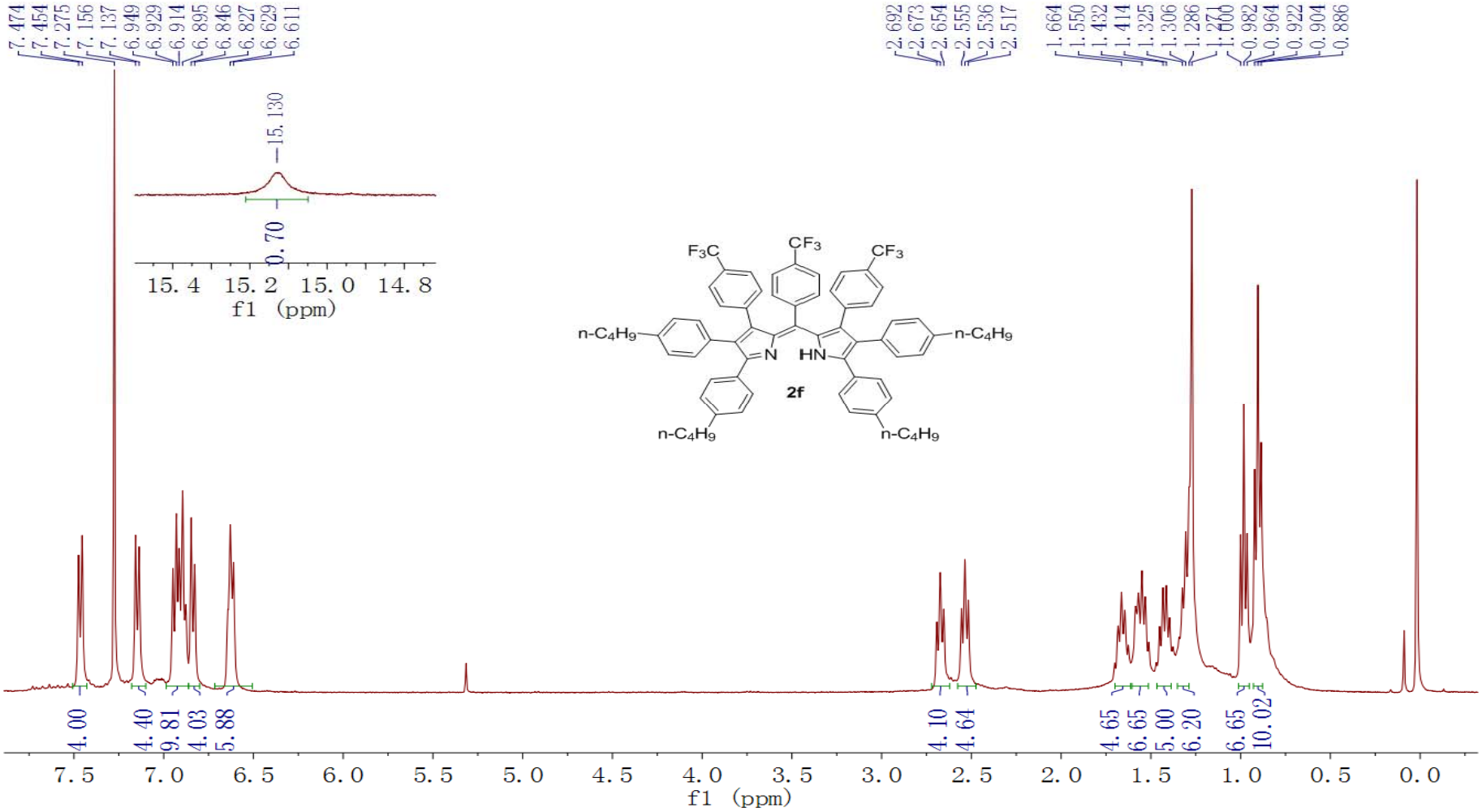


**Figure S37**. The $^{13}C$ NMR spectra of **2f.**

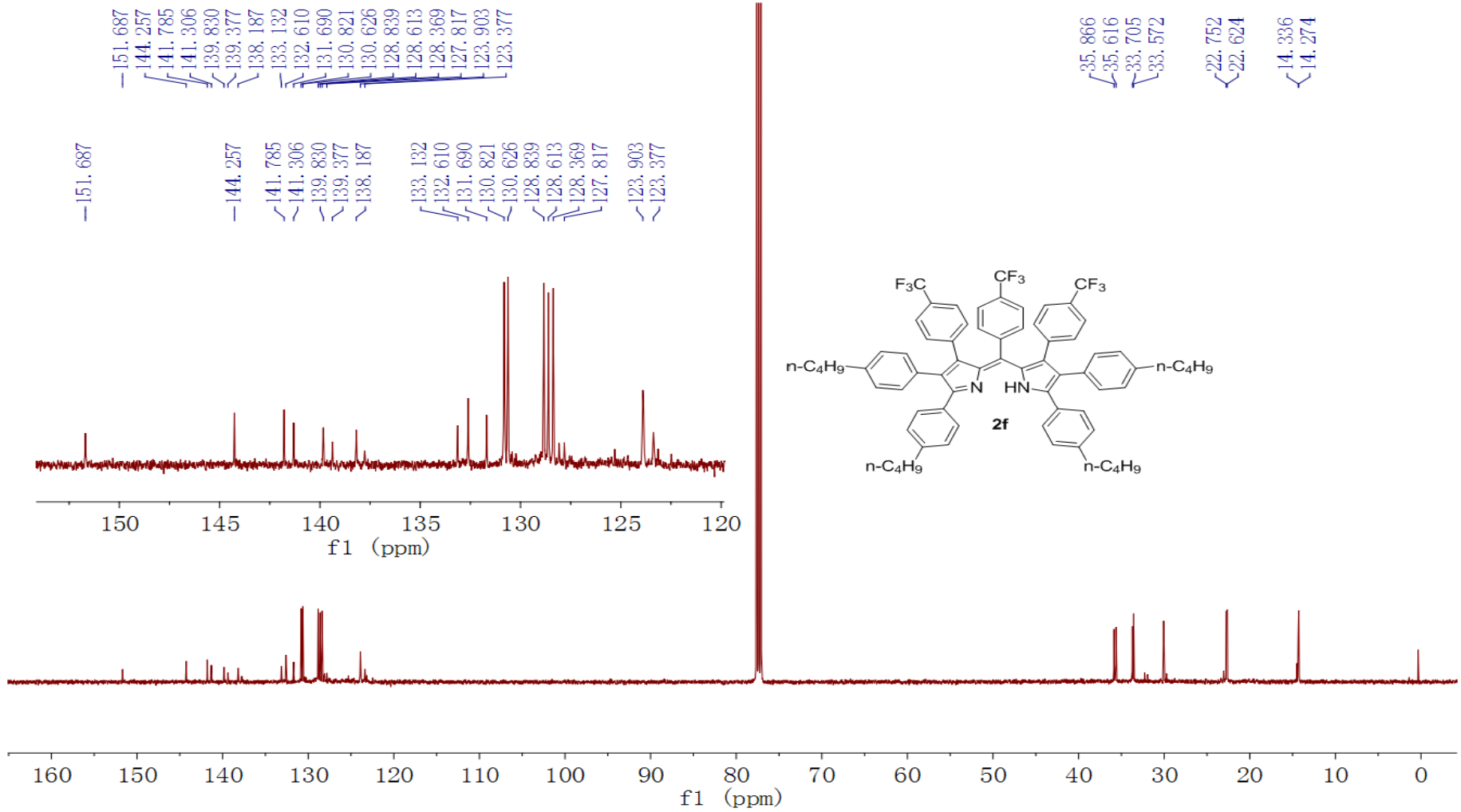


**Figure S38**. The $^{1}$H NMR spectra of **2g.**

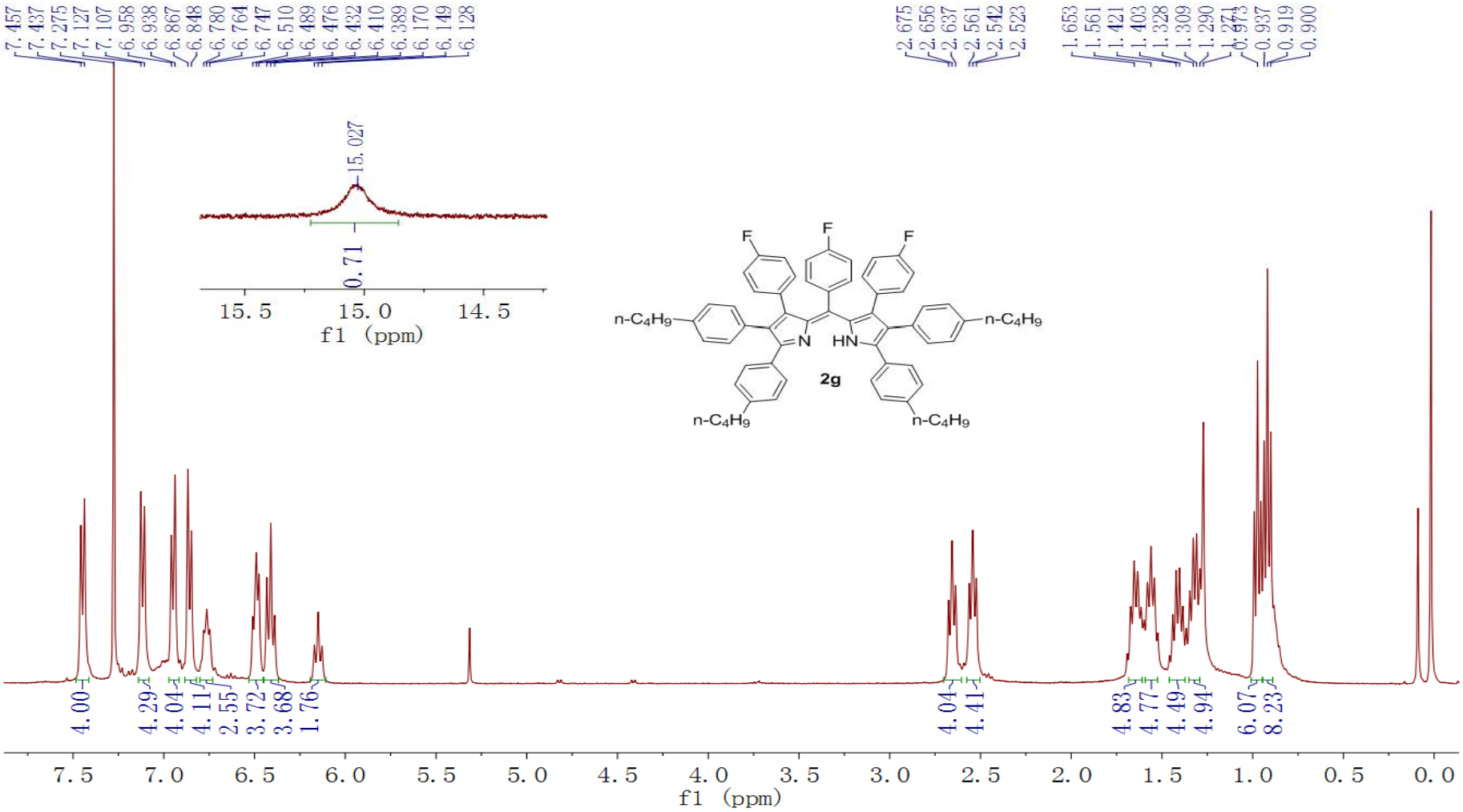


**Figure S39**. The $^{13}C$ NMR spectra of **2g.**

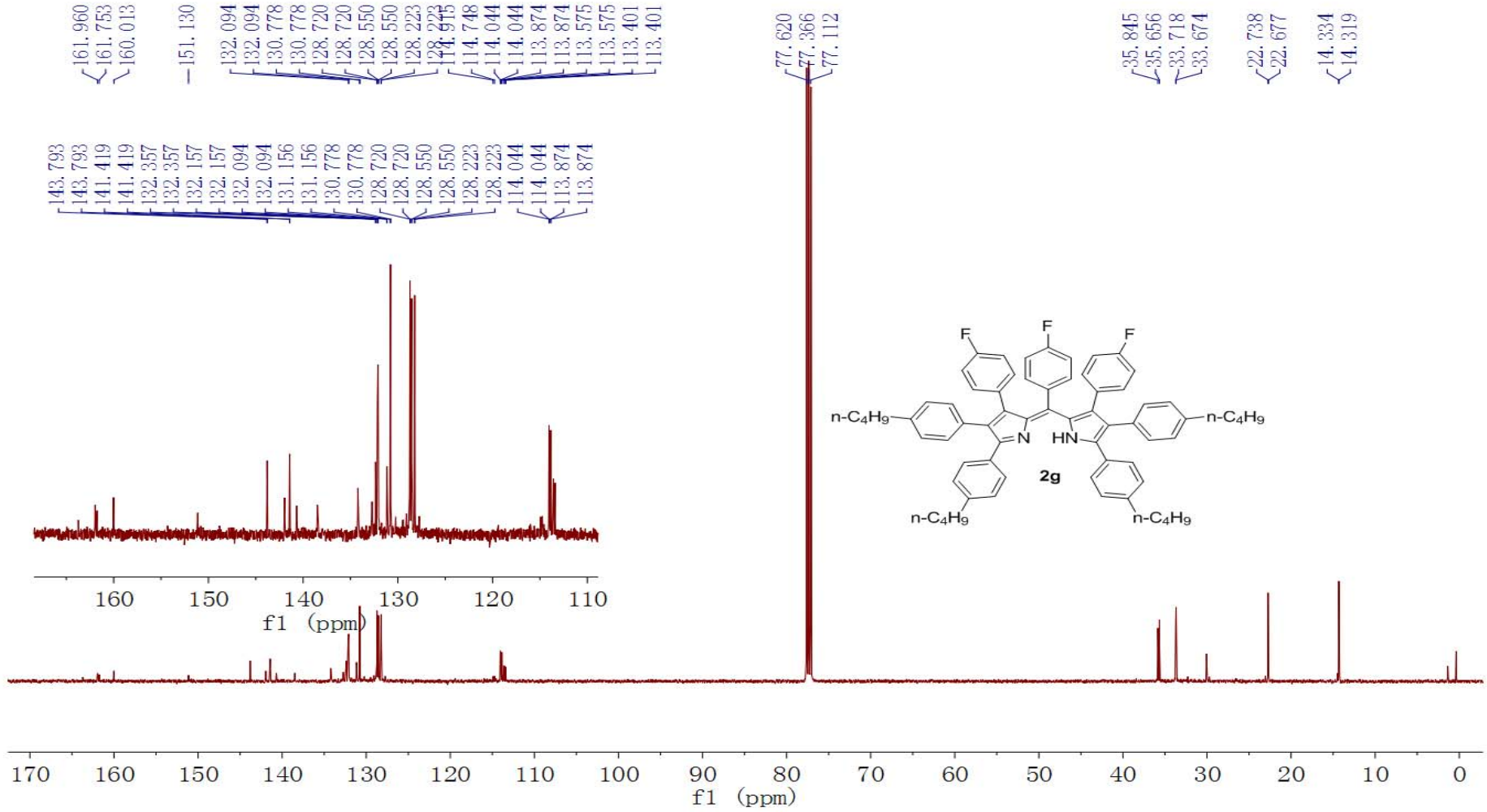


**Figure S40**. The $^{1}$H NMR spectra of **2h.**

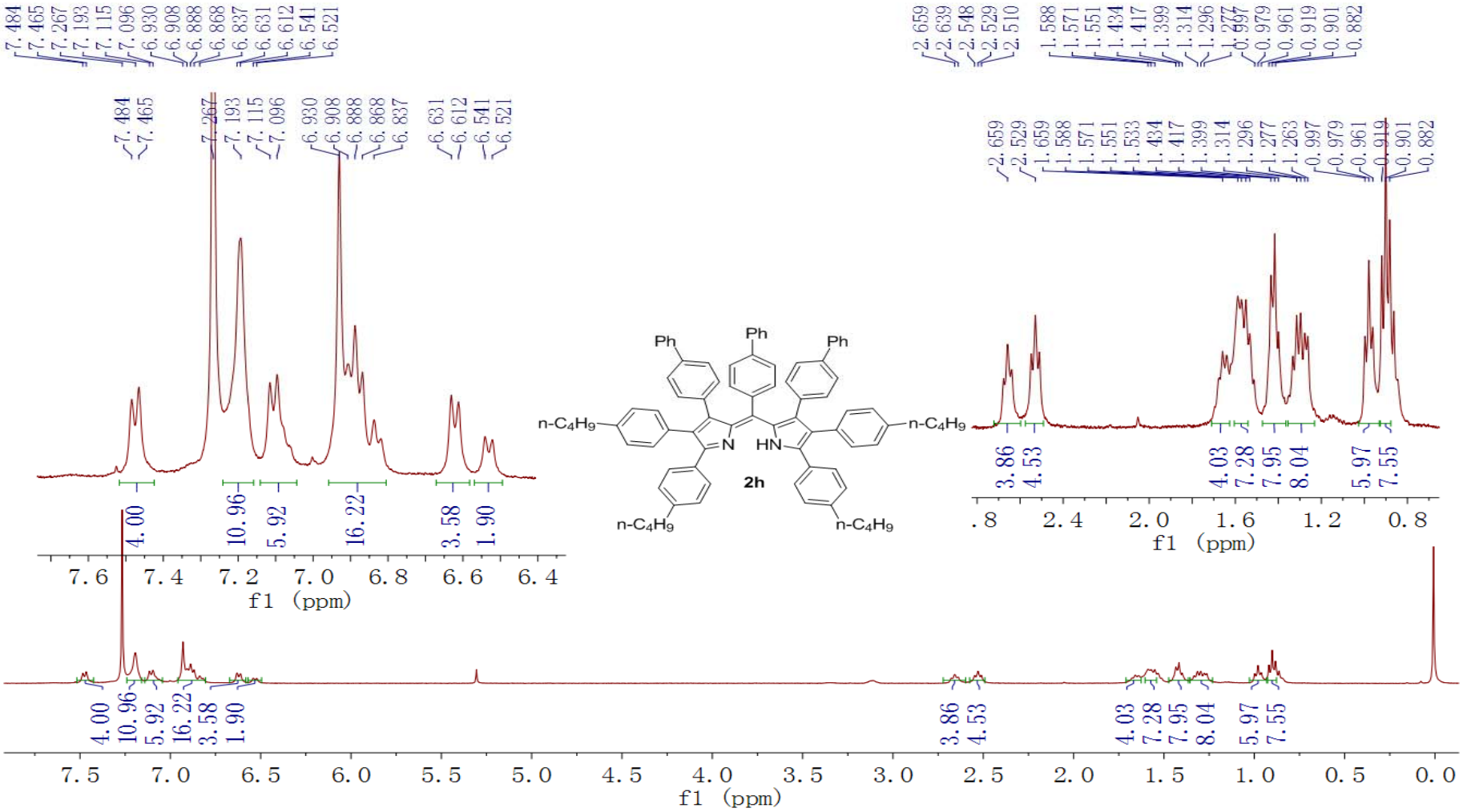


**Figure S41**. The $^{13}$C NMR spectra of **2h.**

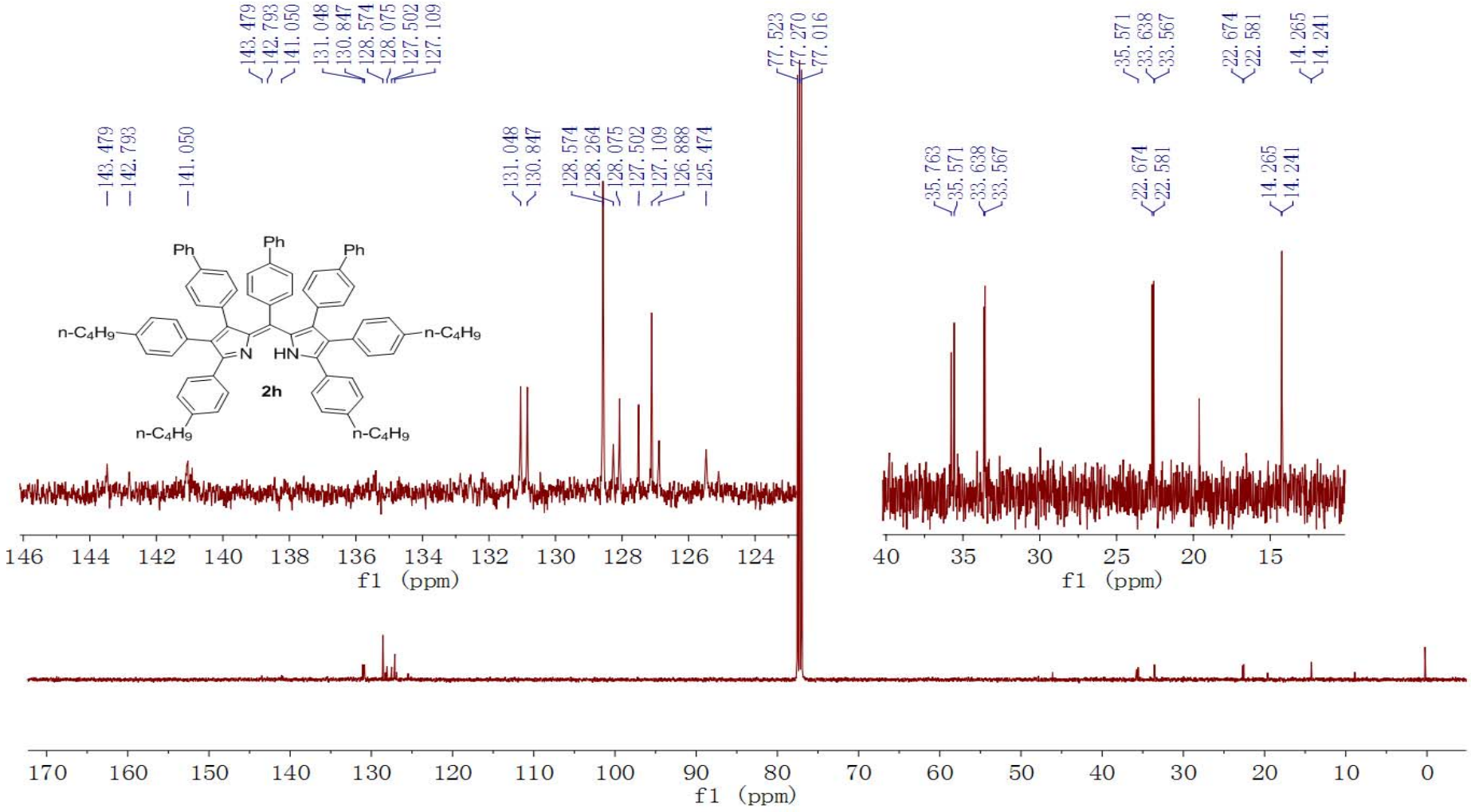


**Figure S42**. The $^{1}$H NMR spectra of **2i.**

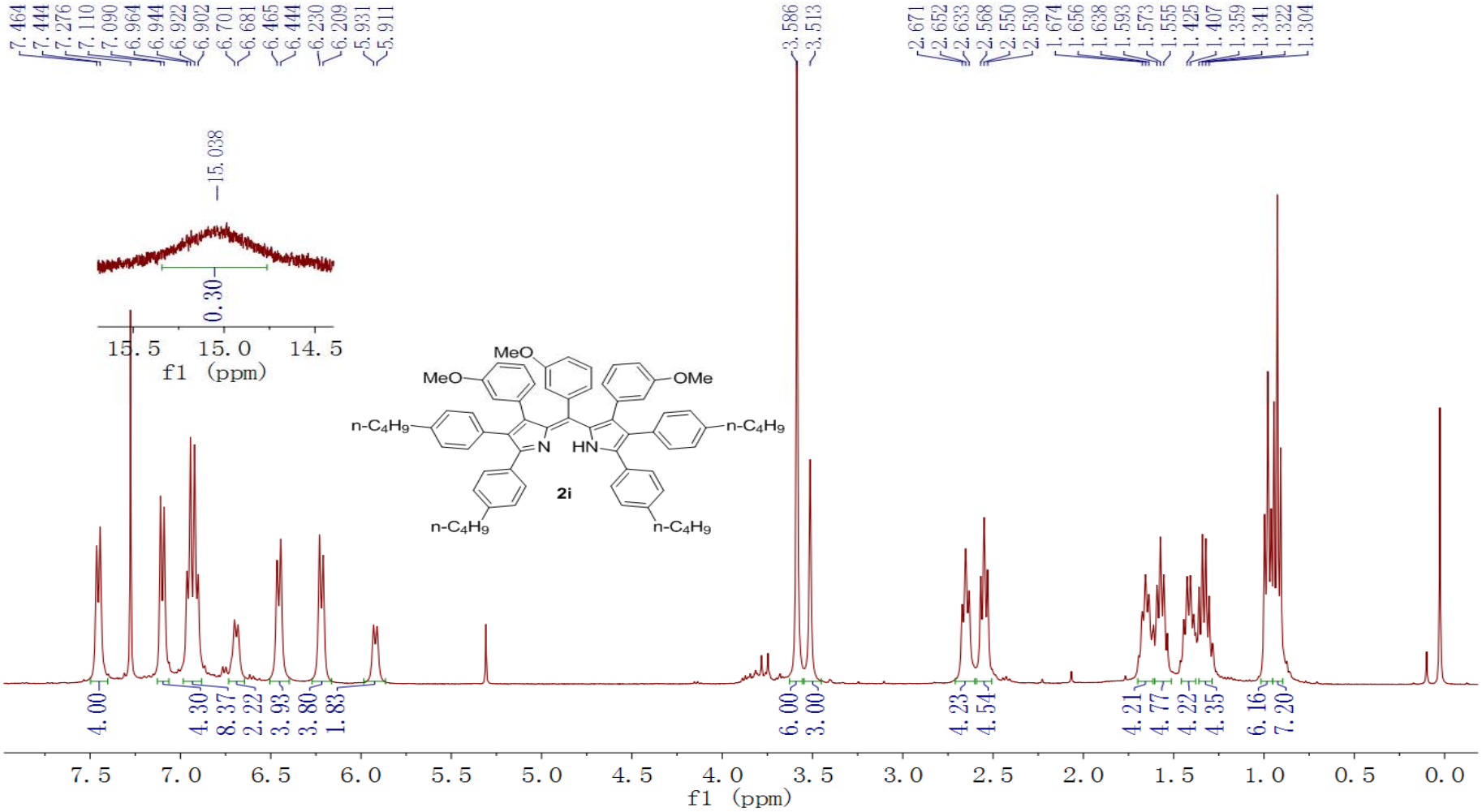


**Figure S43**. The $^{1}$H NMR spectra of **2j.**

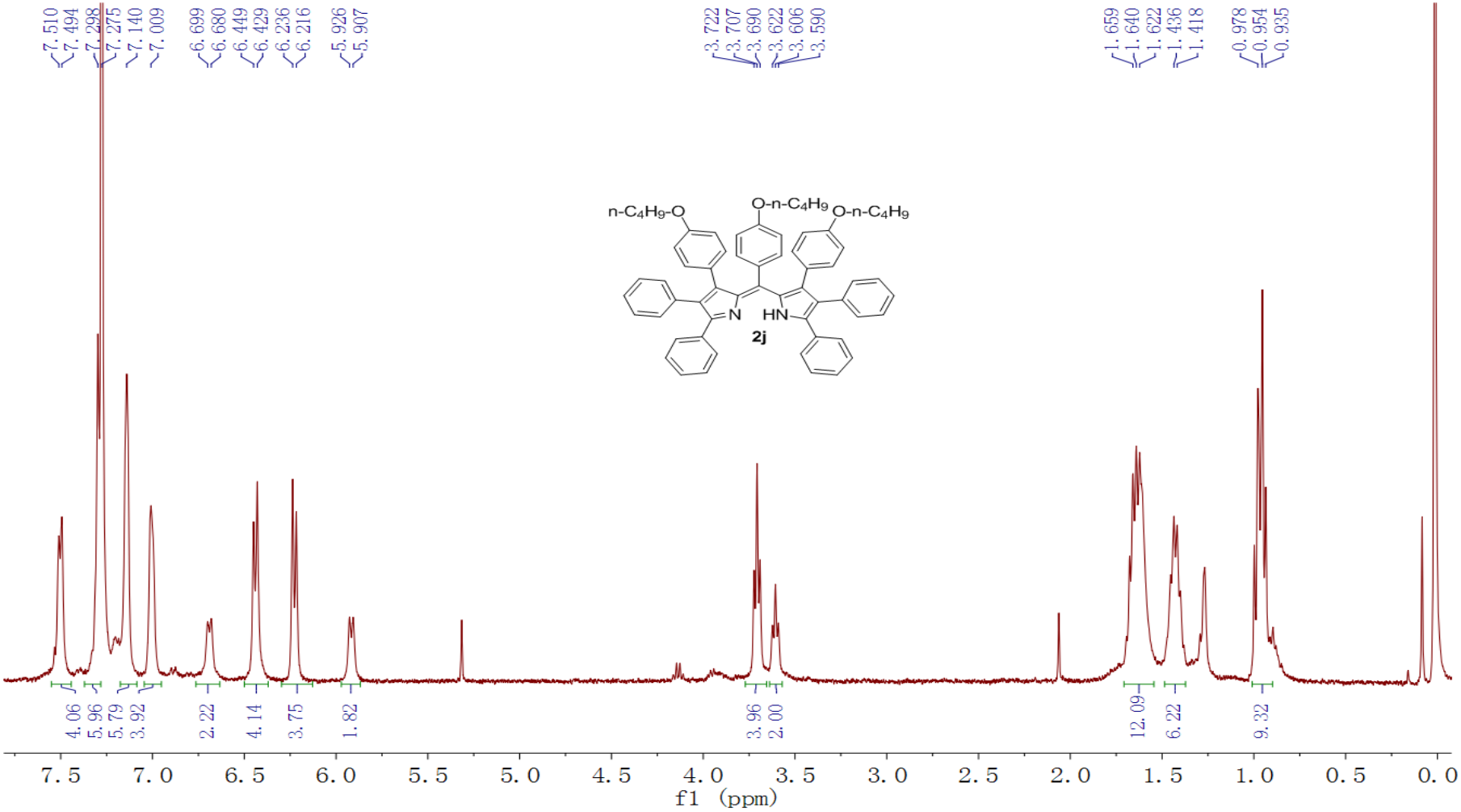


**Figure S44**. The $^{13}C$ NMR spectra of **2j.**

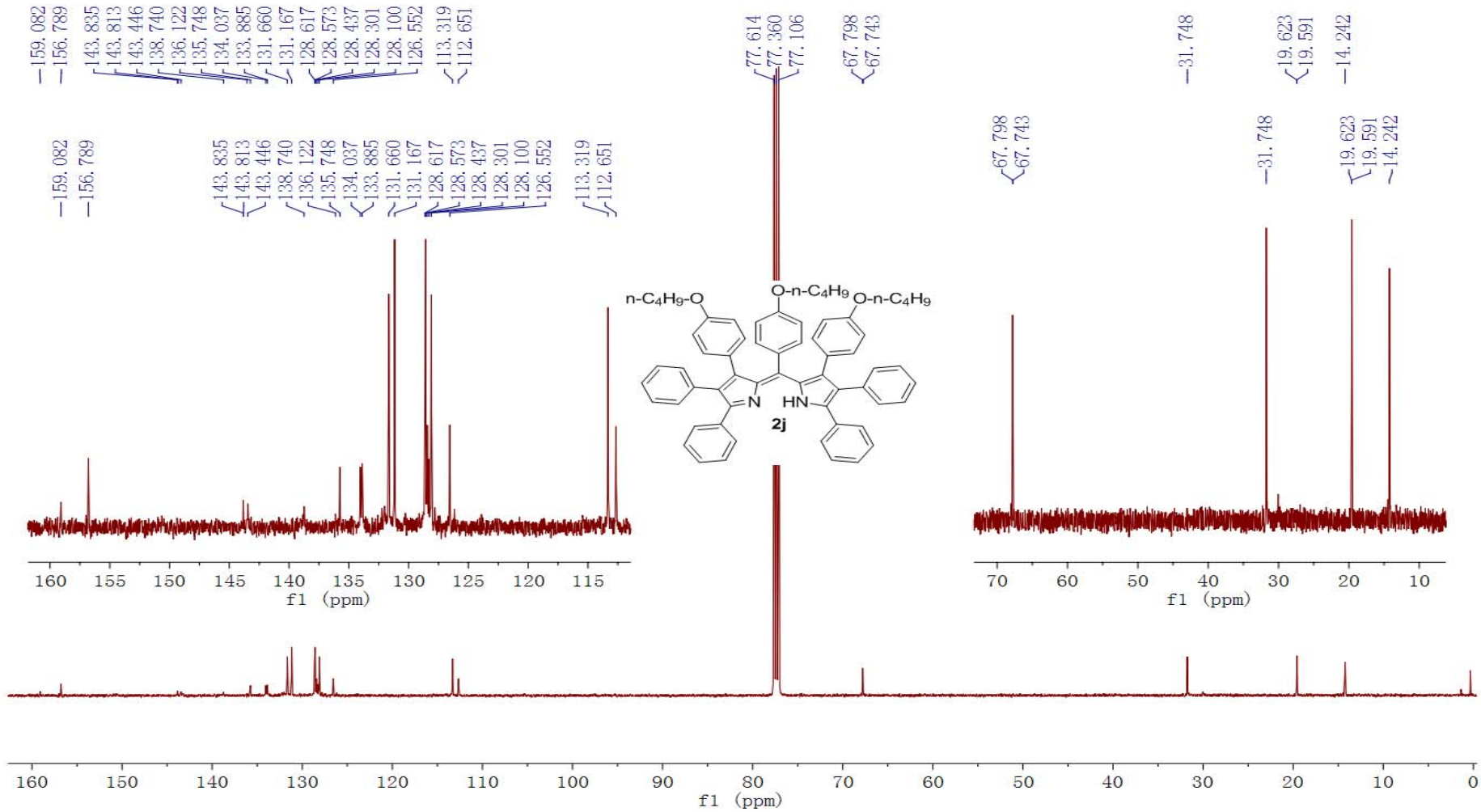


**Figure S45**. The $^{1}$H NMR spectra of **2k.**

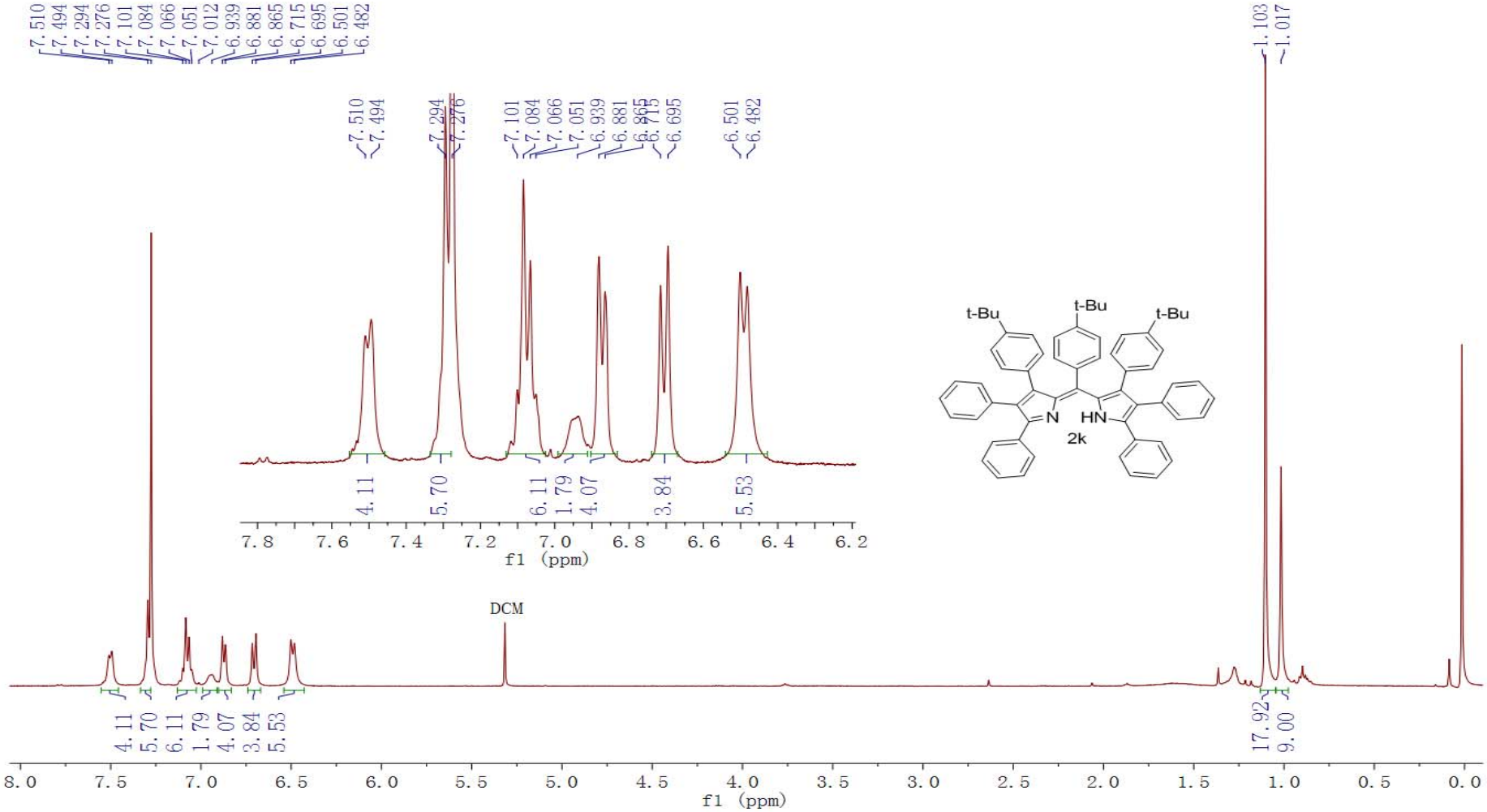


**Figure S46**. The $^{13}C$ NMR spectra of **2k.**

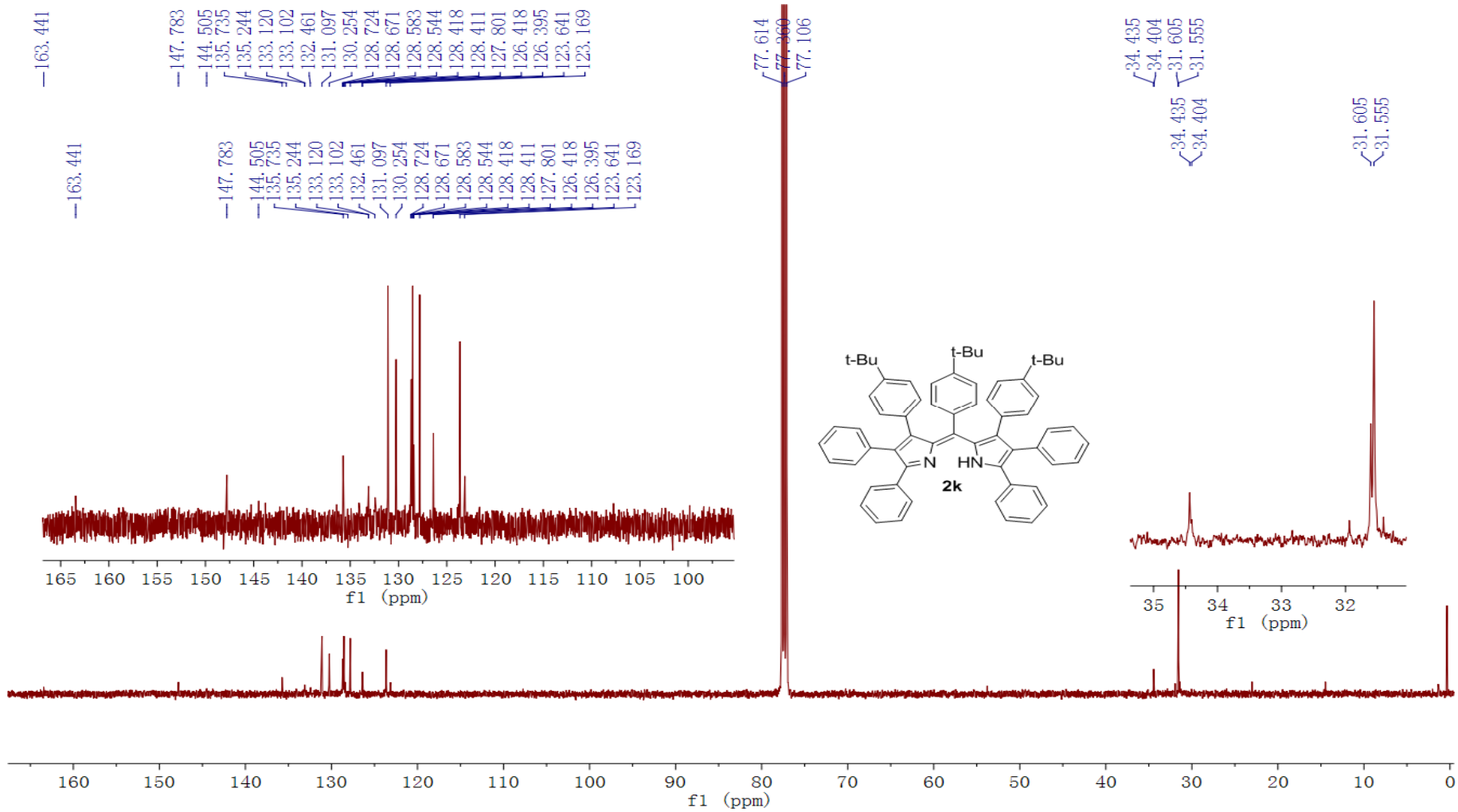


**Figure S47**. The $^{1}$H NMR spectra of **2l.**

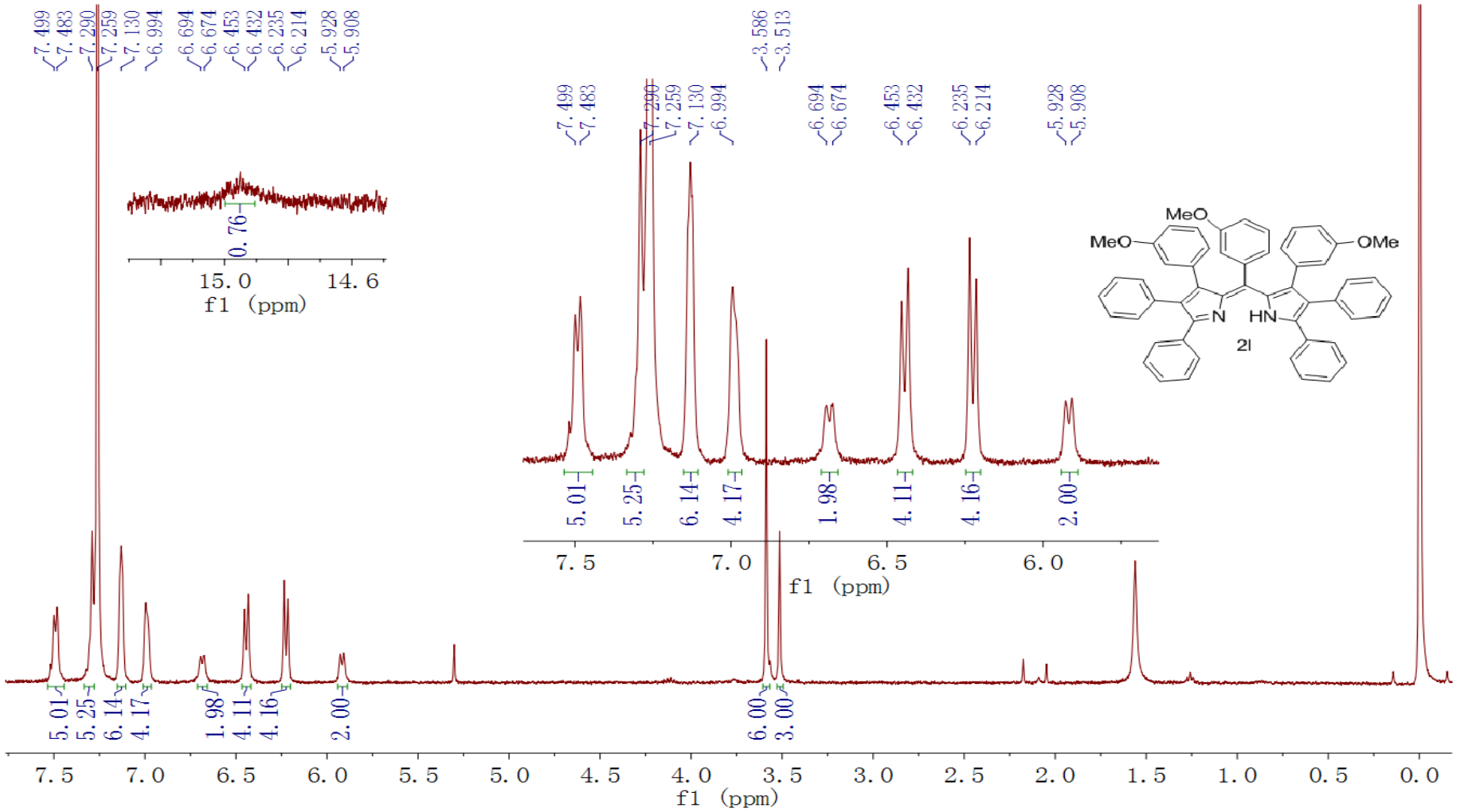


**Figure S48**. The $^{1}$H NMR spectra of **2m.**

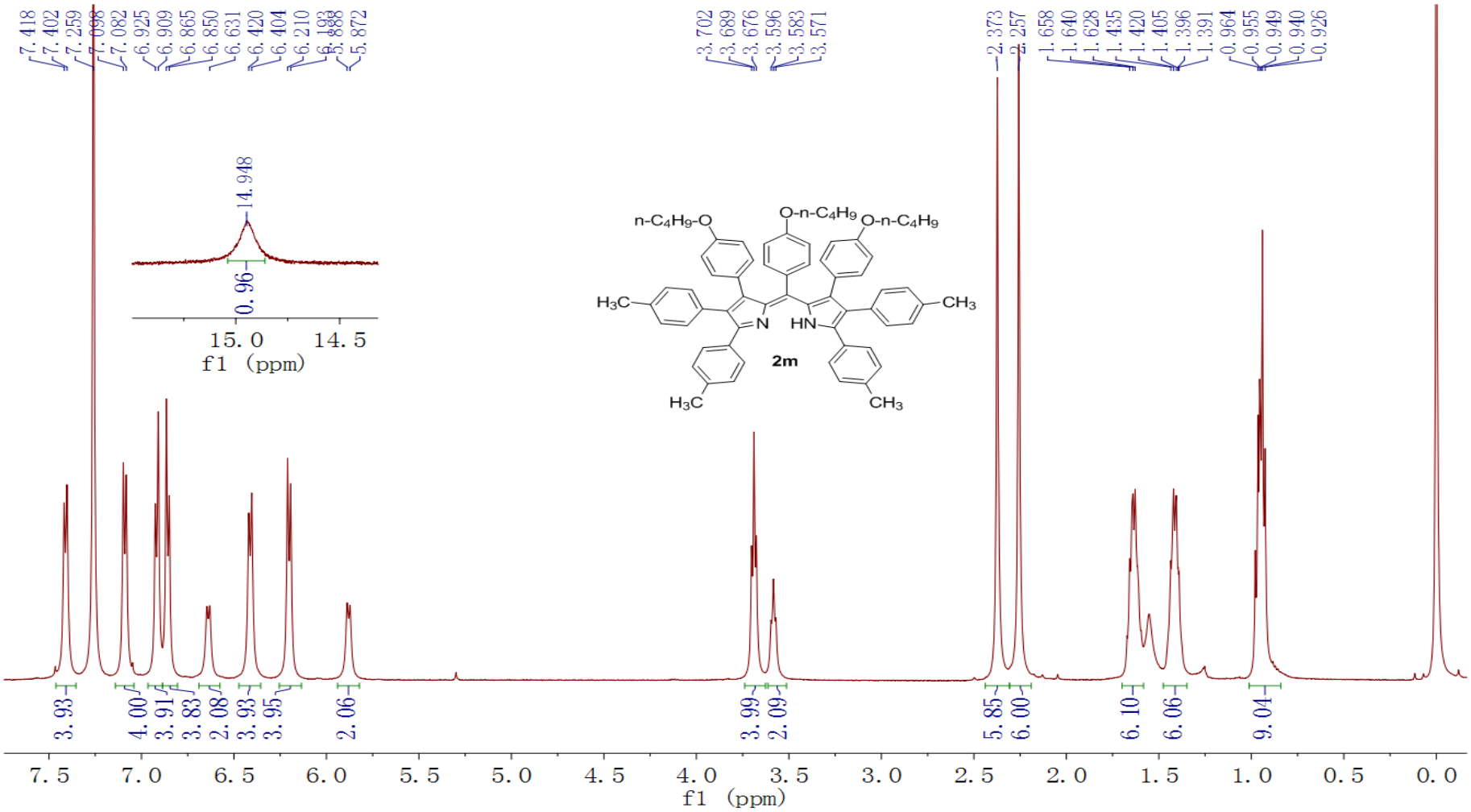
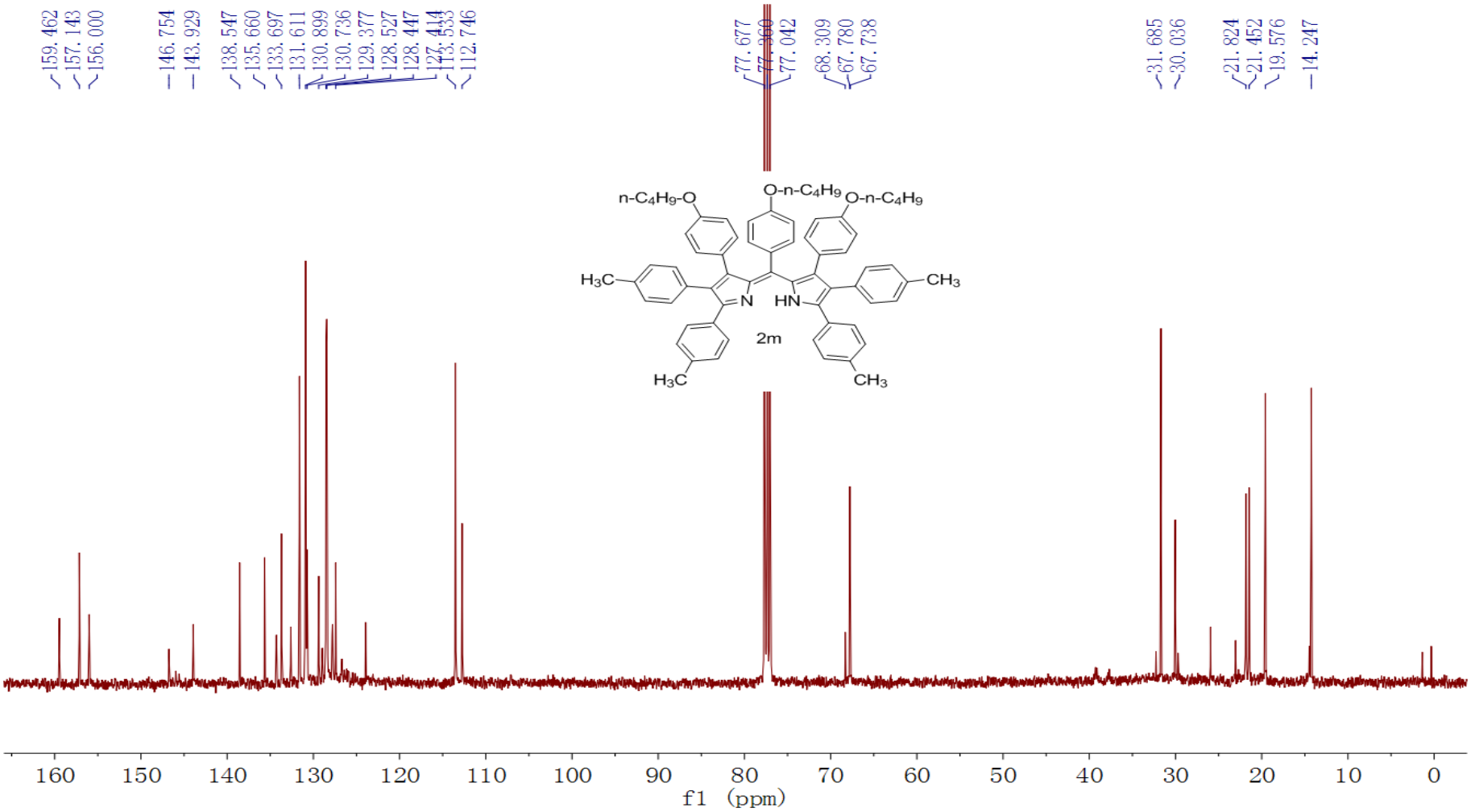


**Figure S49**. The $^{1}$H NMR spectra of **2m.**



## 4. GC-MS for eliminated aromatic aldehydes

**Figure S50**. The GC-MS for eliminated benzaldehyde in the preparation of **2a.**

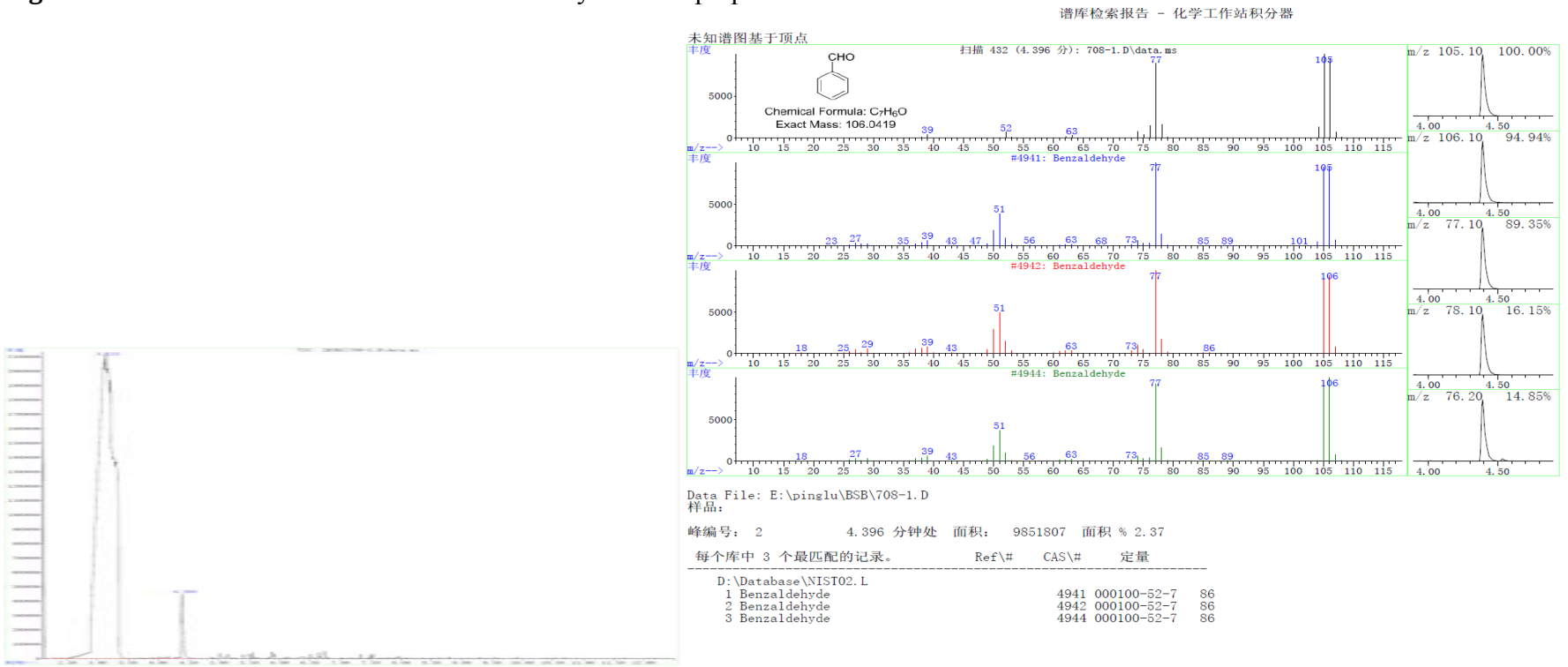
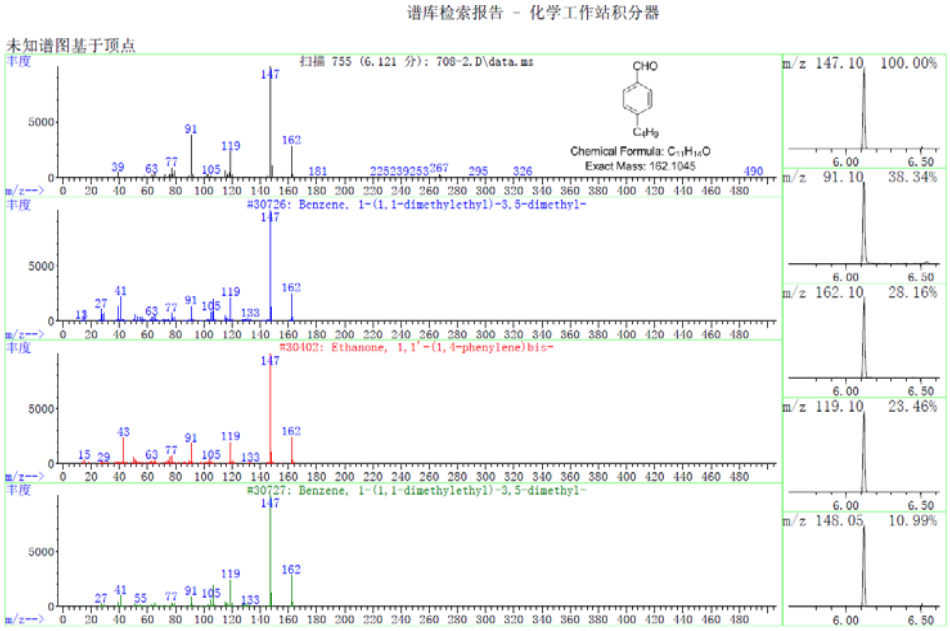


**Figure S51**. The GC-MS for eliminated 4-butylbenzaldehyde in the preparation of **2b**




Data File: E:\PINGLU\Snapshot\BSB\708-2.D
样品:

峰编号: 3 6.121 分钟处 面积: 3458085 面积 % 0.72

| 每个库中 3 个最匹配的记录。 | Ref\# | CAS\# | 定量 |
|---|---|---|---|
| D:\Database\NIST02.L | | | |
| 1 Benzene, 1-(1,1-dimethylethyl)-3... | 30726 | 000098-19-1 | 86 |
| 2 Ethanone, 1,1'-(1,4-phenylene)bis- | 30402 | 001009-61-6 | 86 |
| 3 Benzene, 1-(1,1-dimethylethyl)-3... | 30727 | 000098-19-1 | 80 |

**5.** $^{1}$H NMR and 13C NMR spectra of **3a-3p**

**Figure S52**. The $^{1}$H NMR spectra of **3a.**

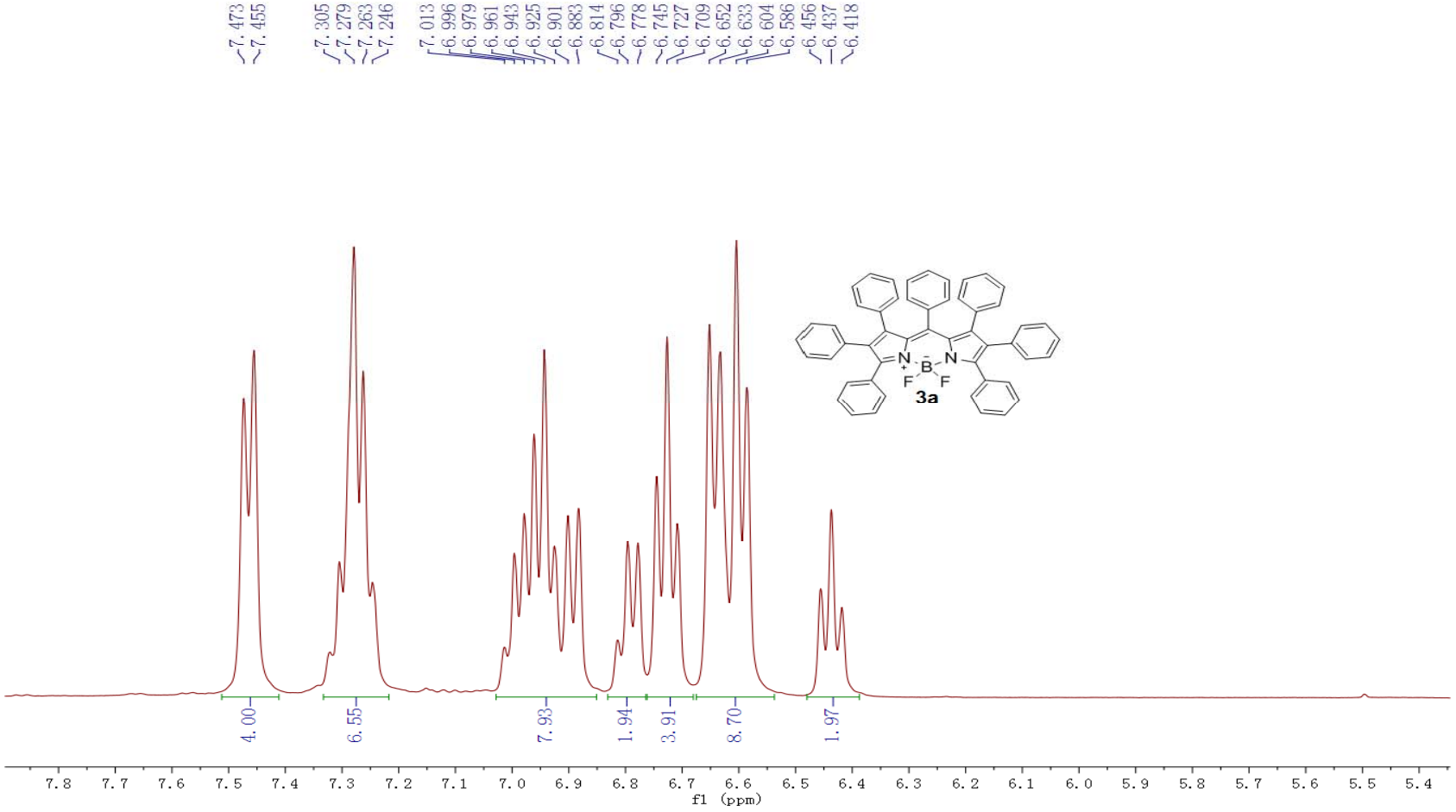


**Figure S53**. The $^{13}$C NMR spectra of **3a.**

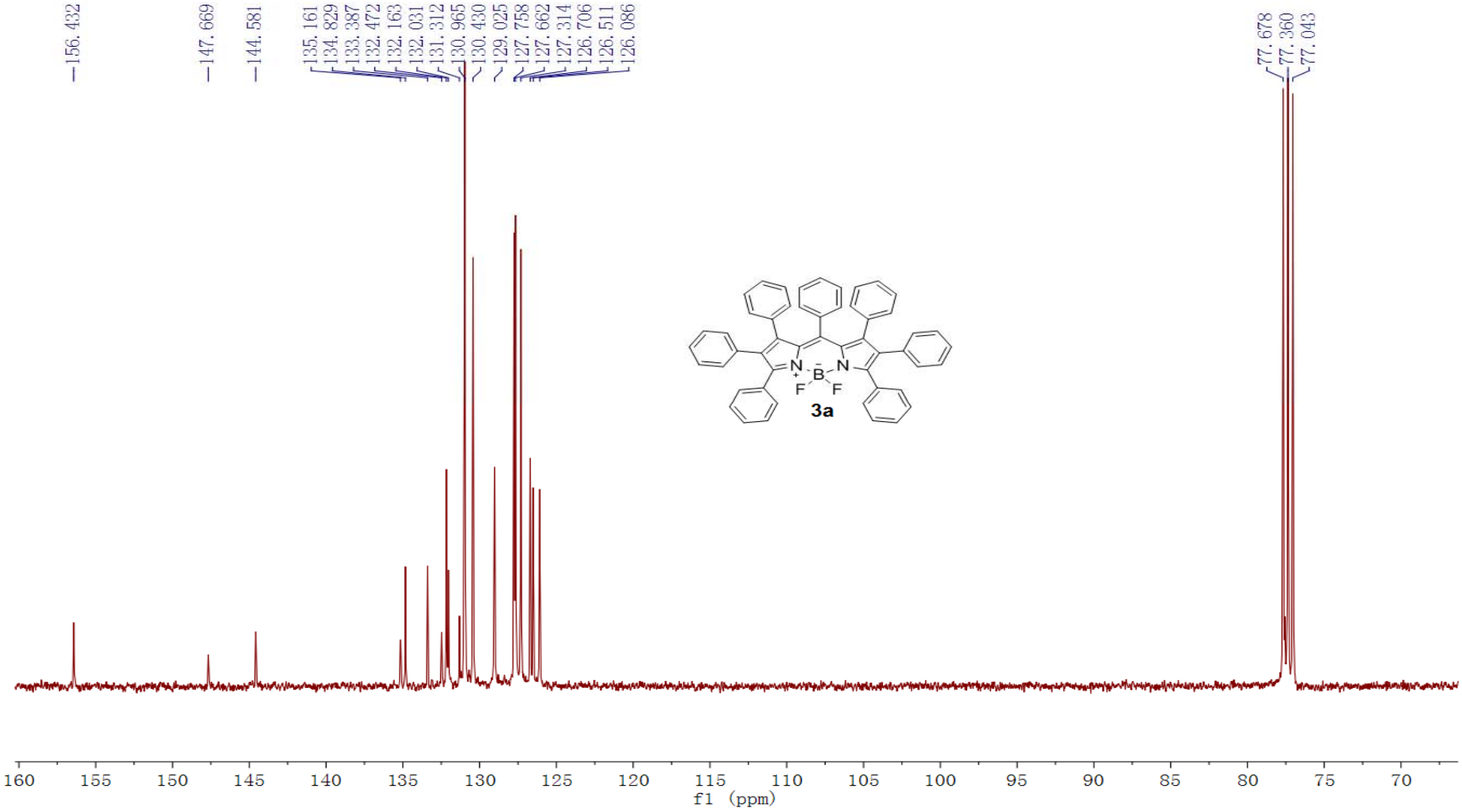


**Figure S54**. The $^{1}$H NMR spectra of **3b.**

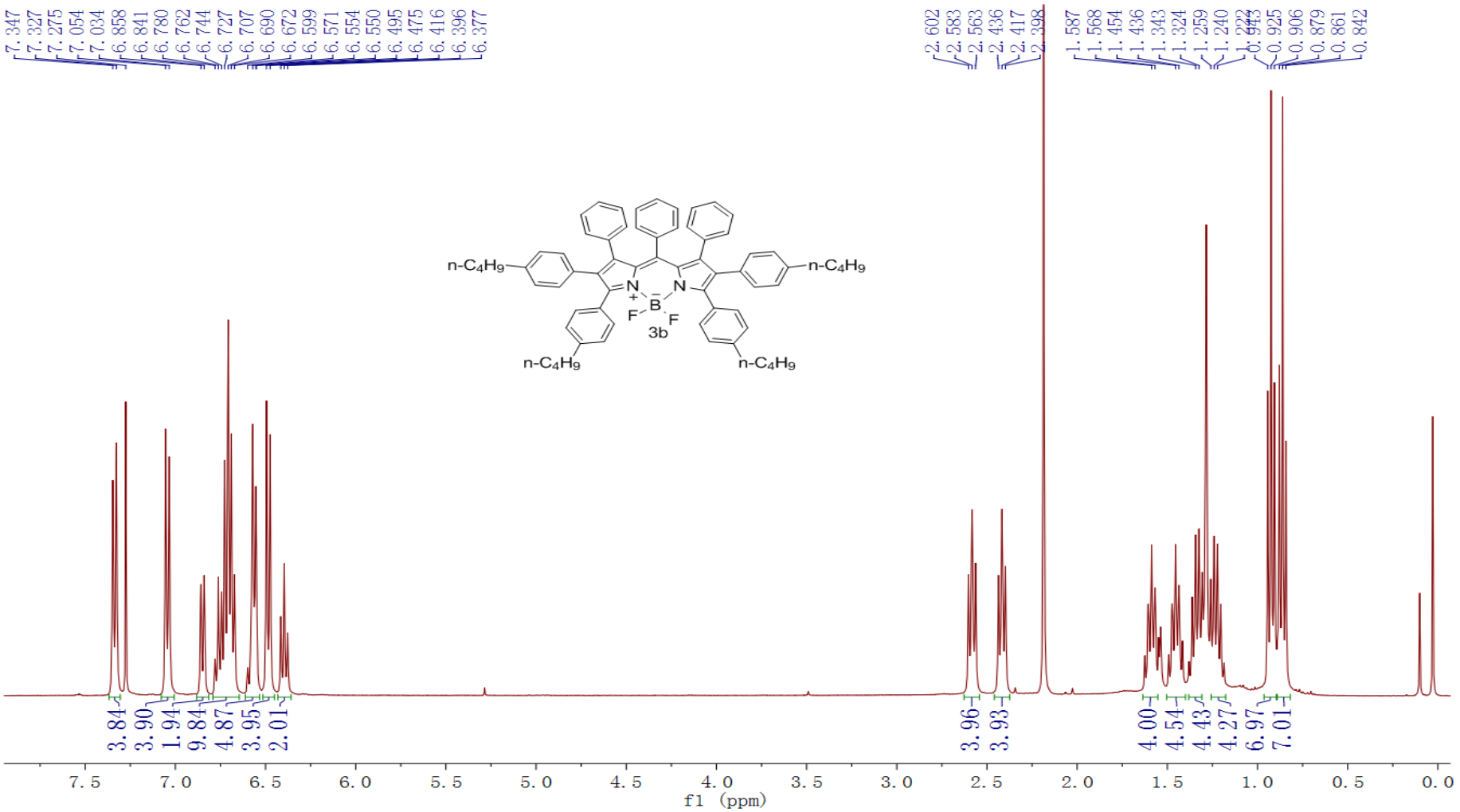


**Figure S55**. The $^{13}C$ NMR spectra of **3b.**

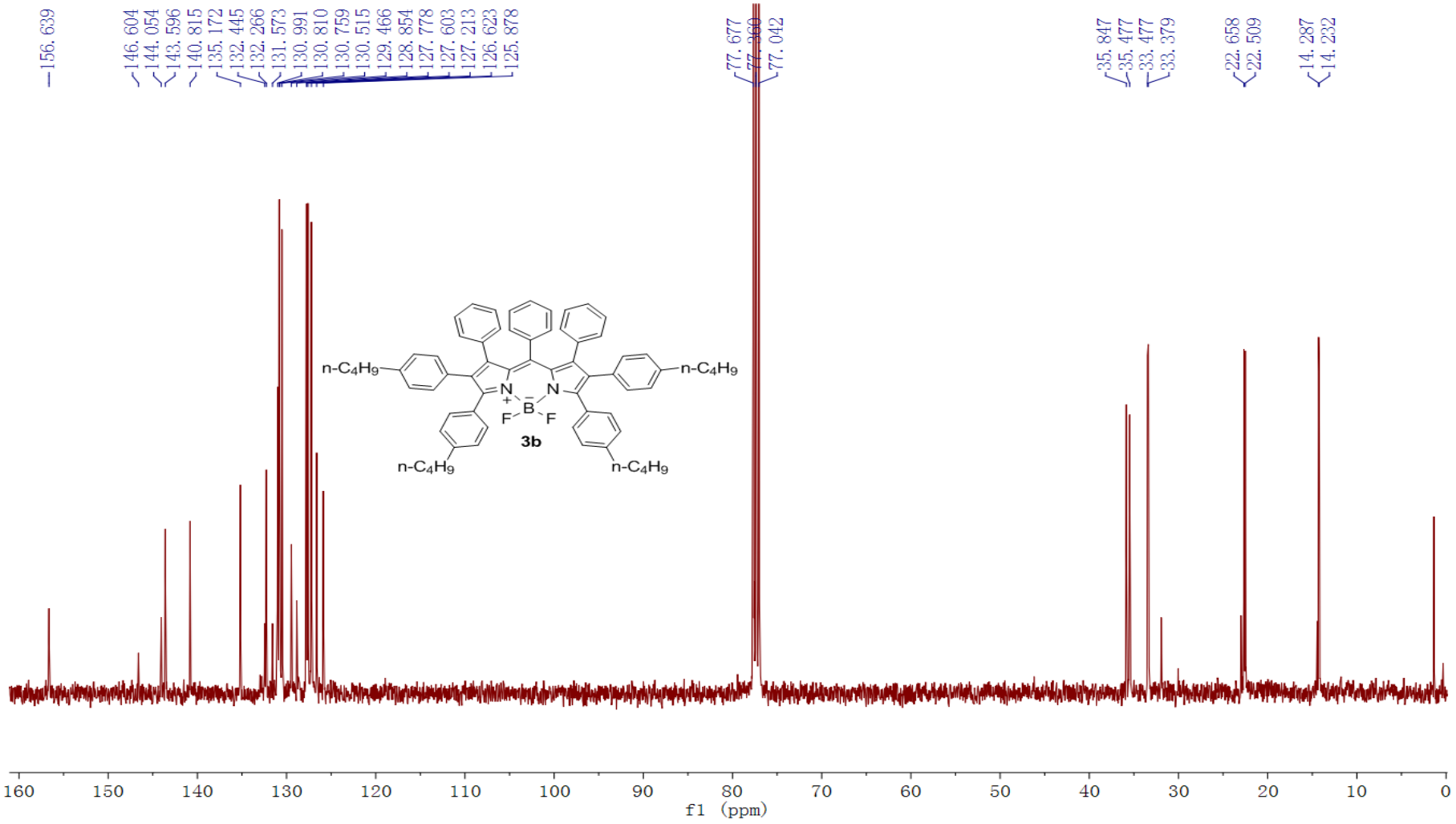


**Figure S56**. The $^{1}$H NMR spectra of **3c.**

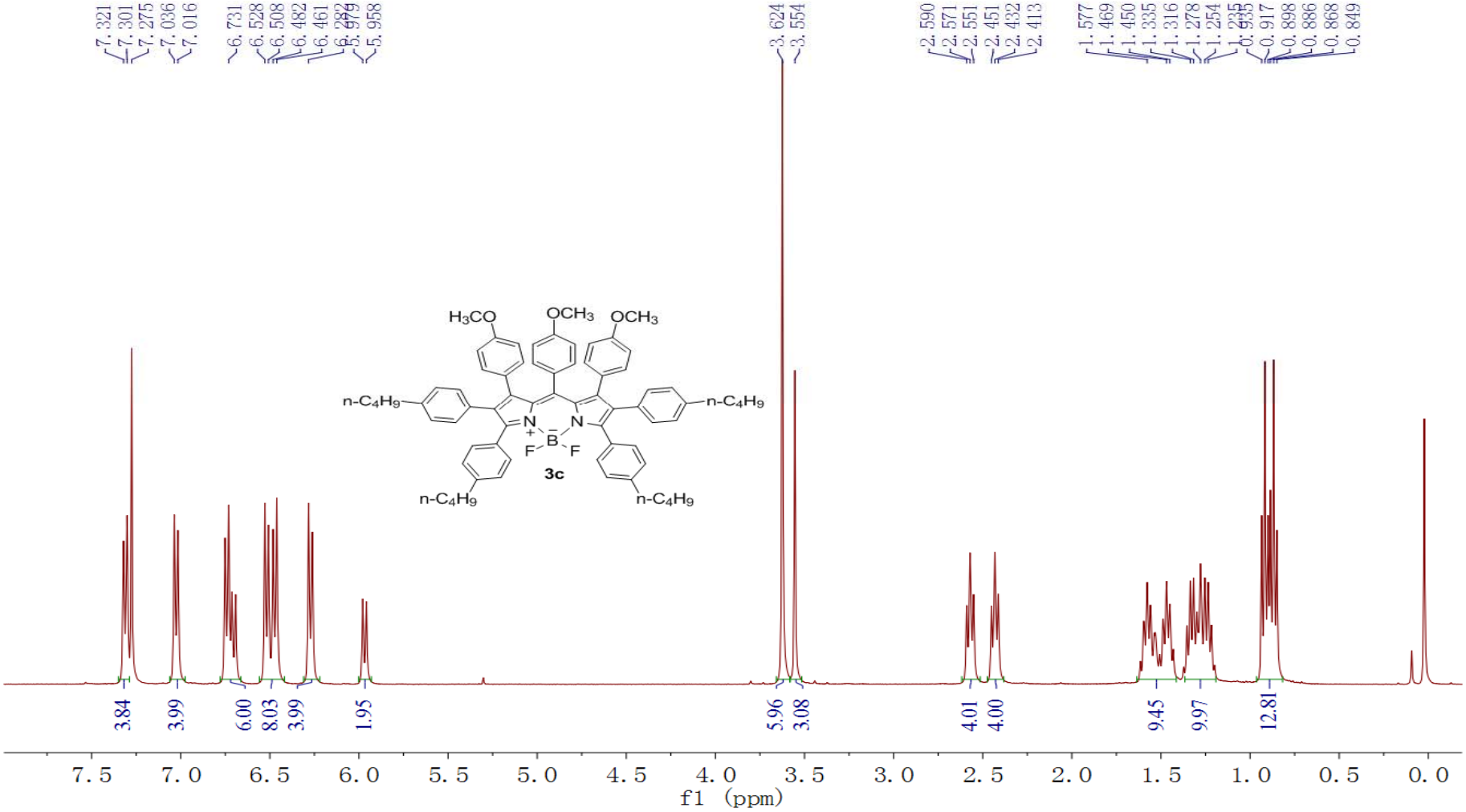


**Figure S57** The $^{13}C$ NMR spectra of **3c.**

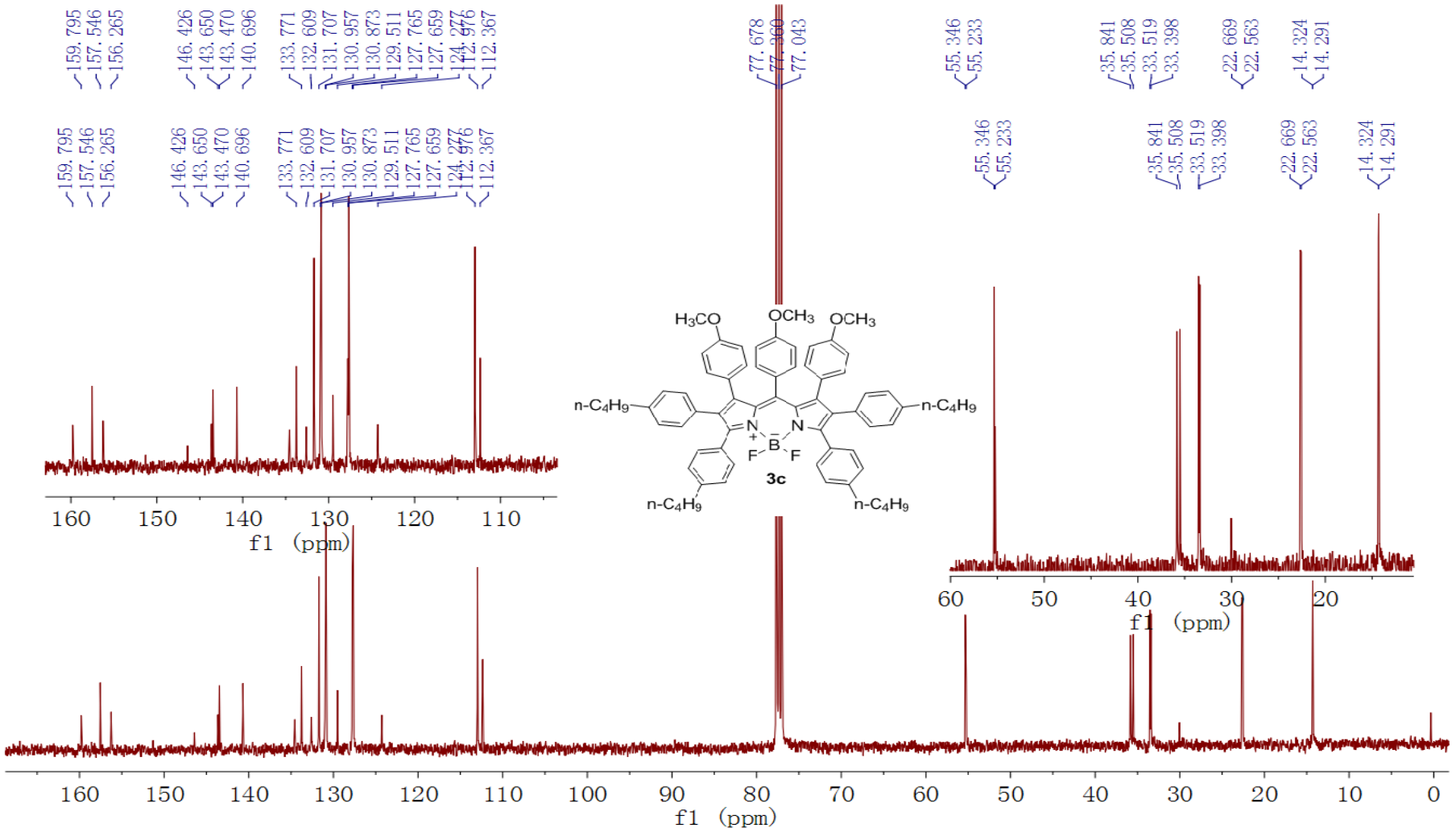


**Figure S58**. The $^{1}$H NMR spectra of **3d.**

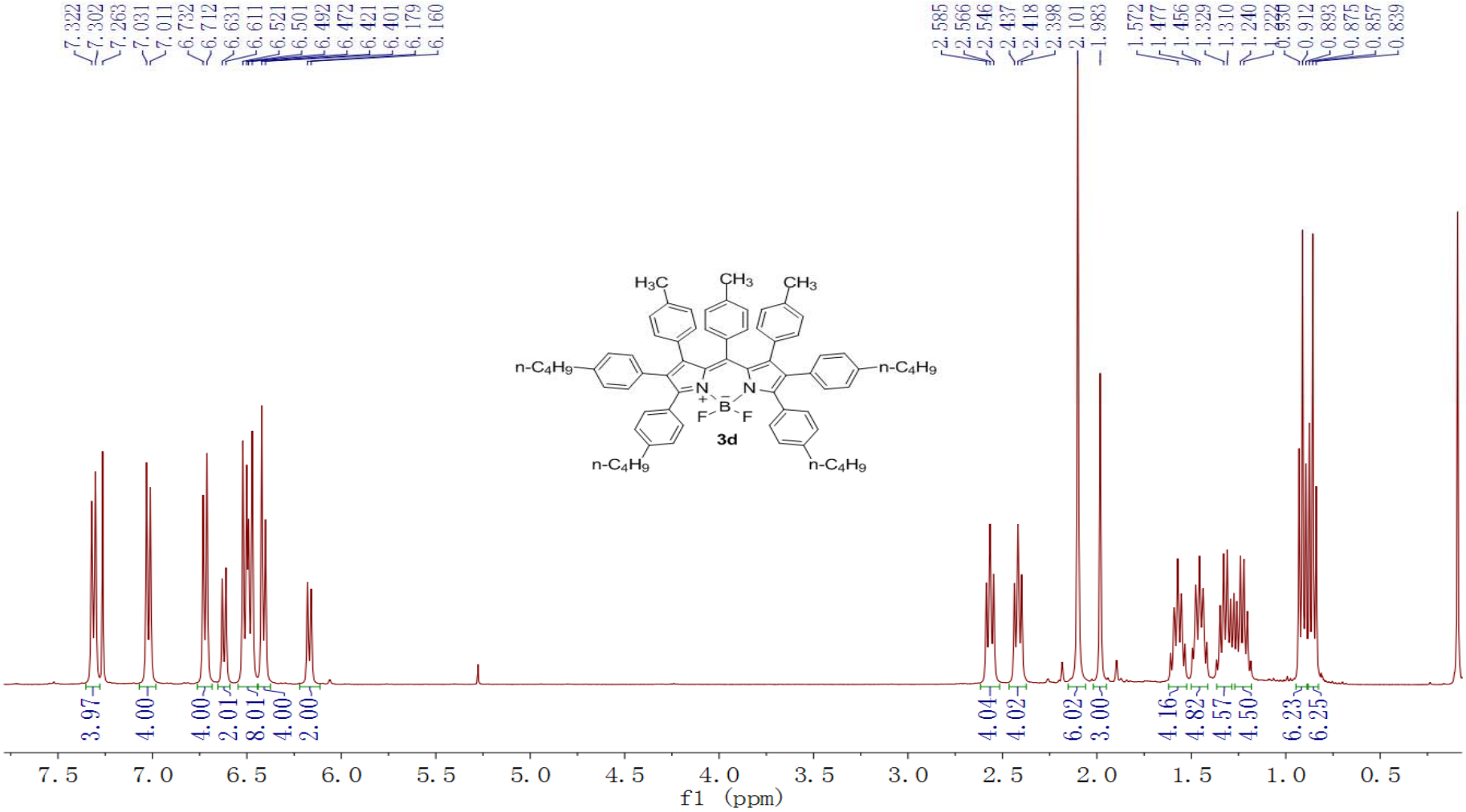


**Figure S59**. The $^{13}C$ NMR spectra of **3d.**

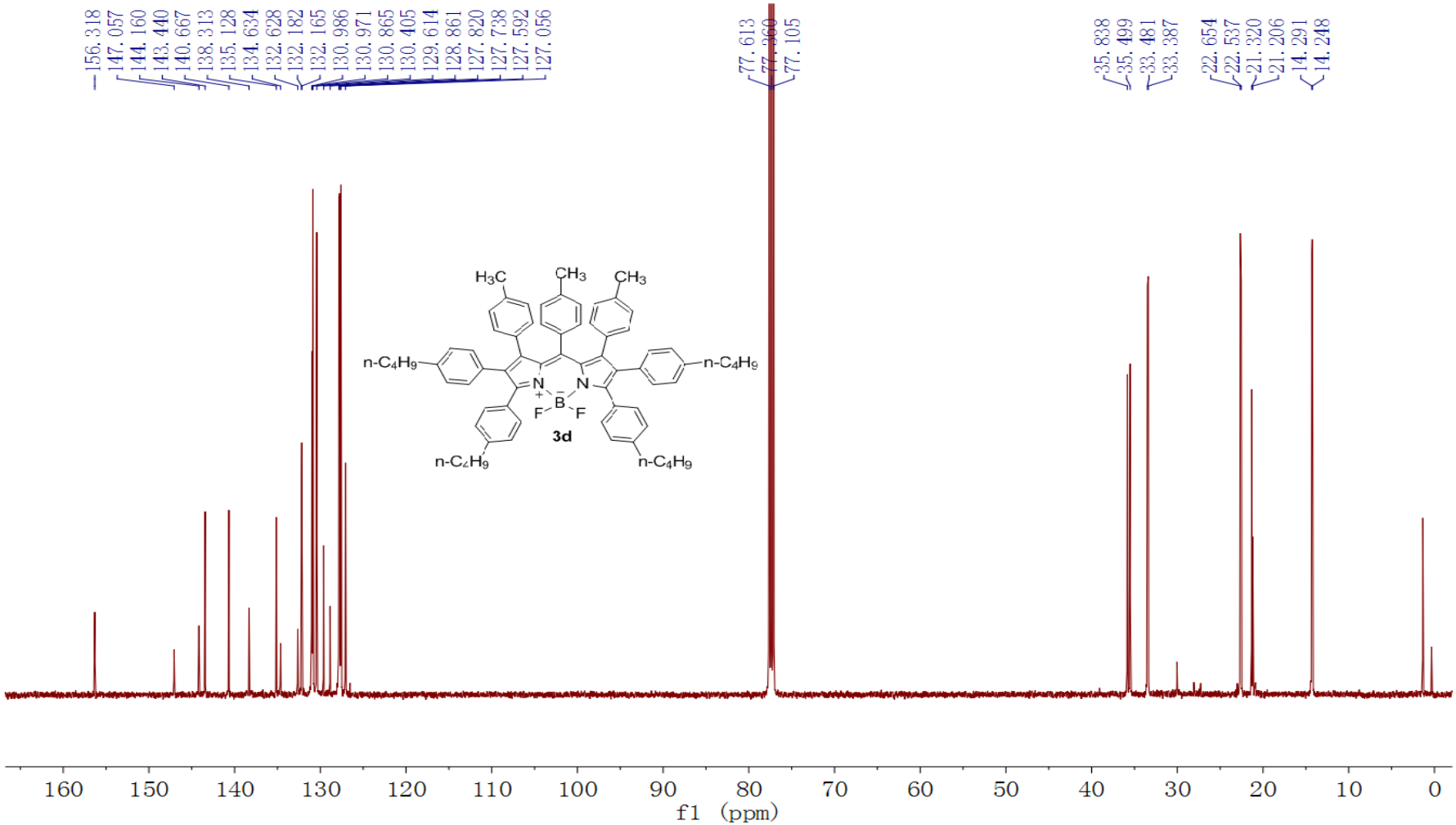


**Figure S60**. The $^{1}$H NMR spectra of **3e.**

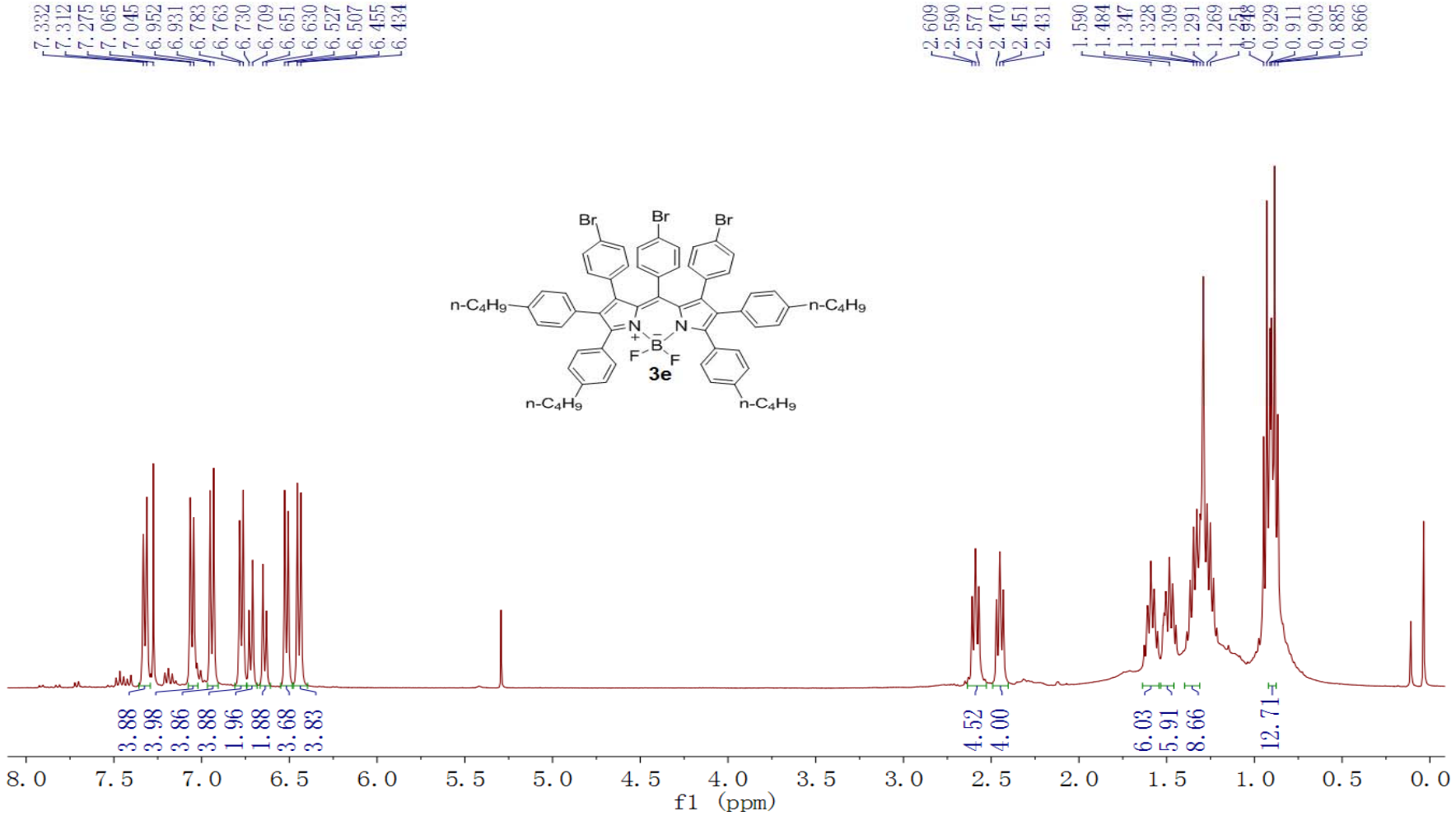


**Figure S61**. The $^{1}$H NMR spectra of **3f.**

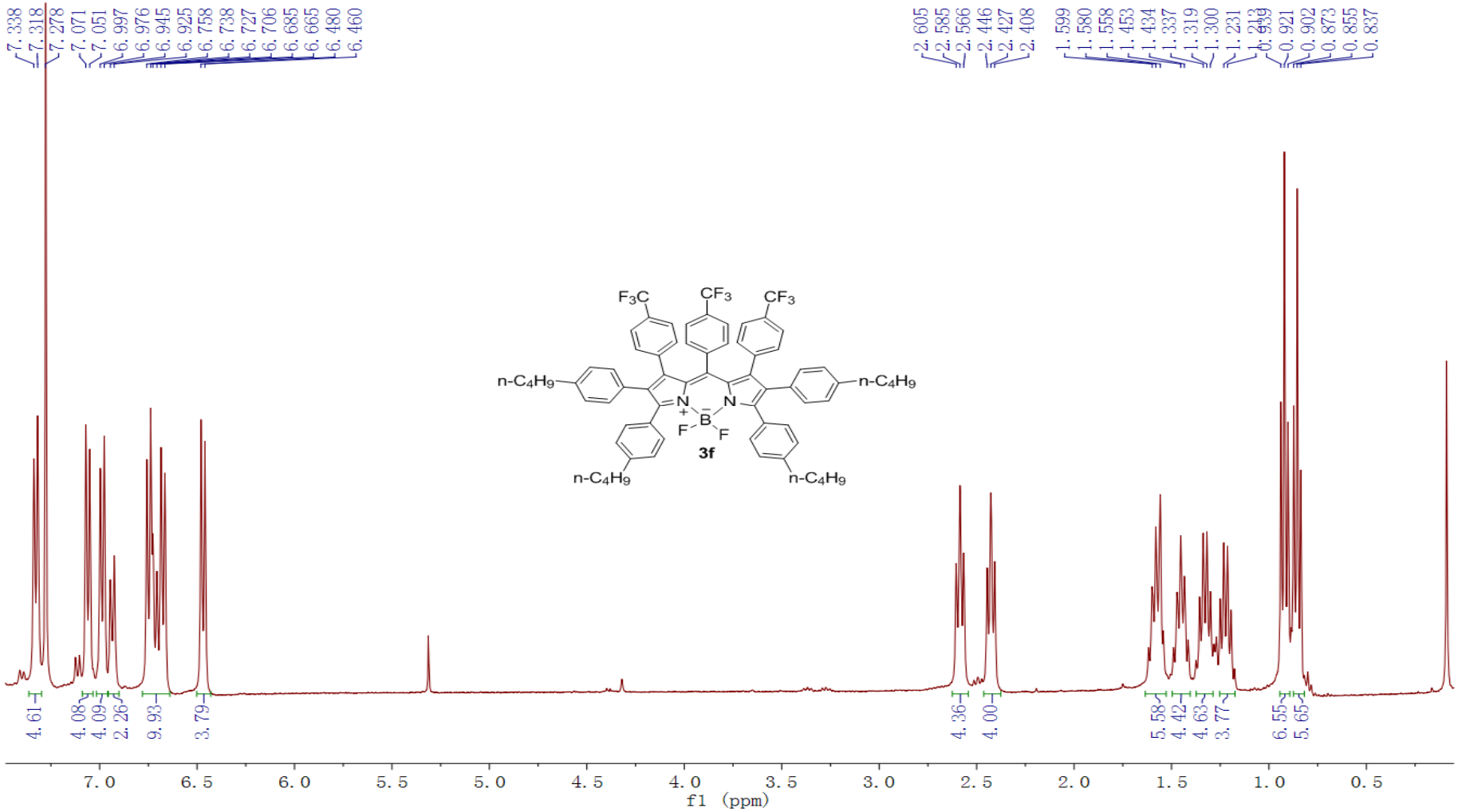


**Figure S62**. The $^{1}$H NMR spectra of **3g.**

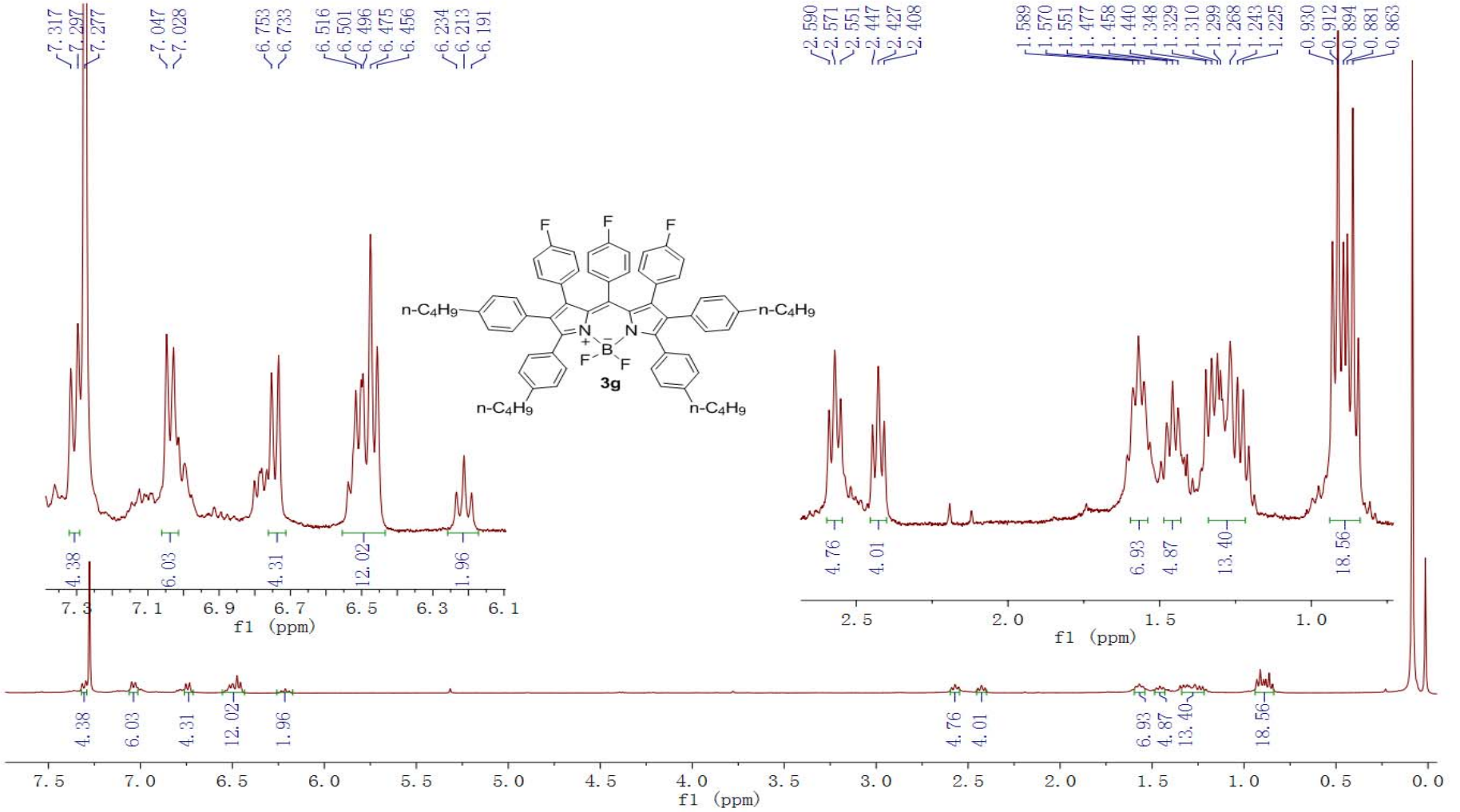


**Figure S63**. The $^{1}$H NMR spectra of **3h.**

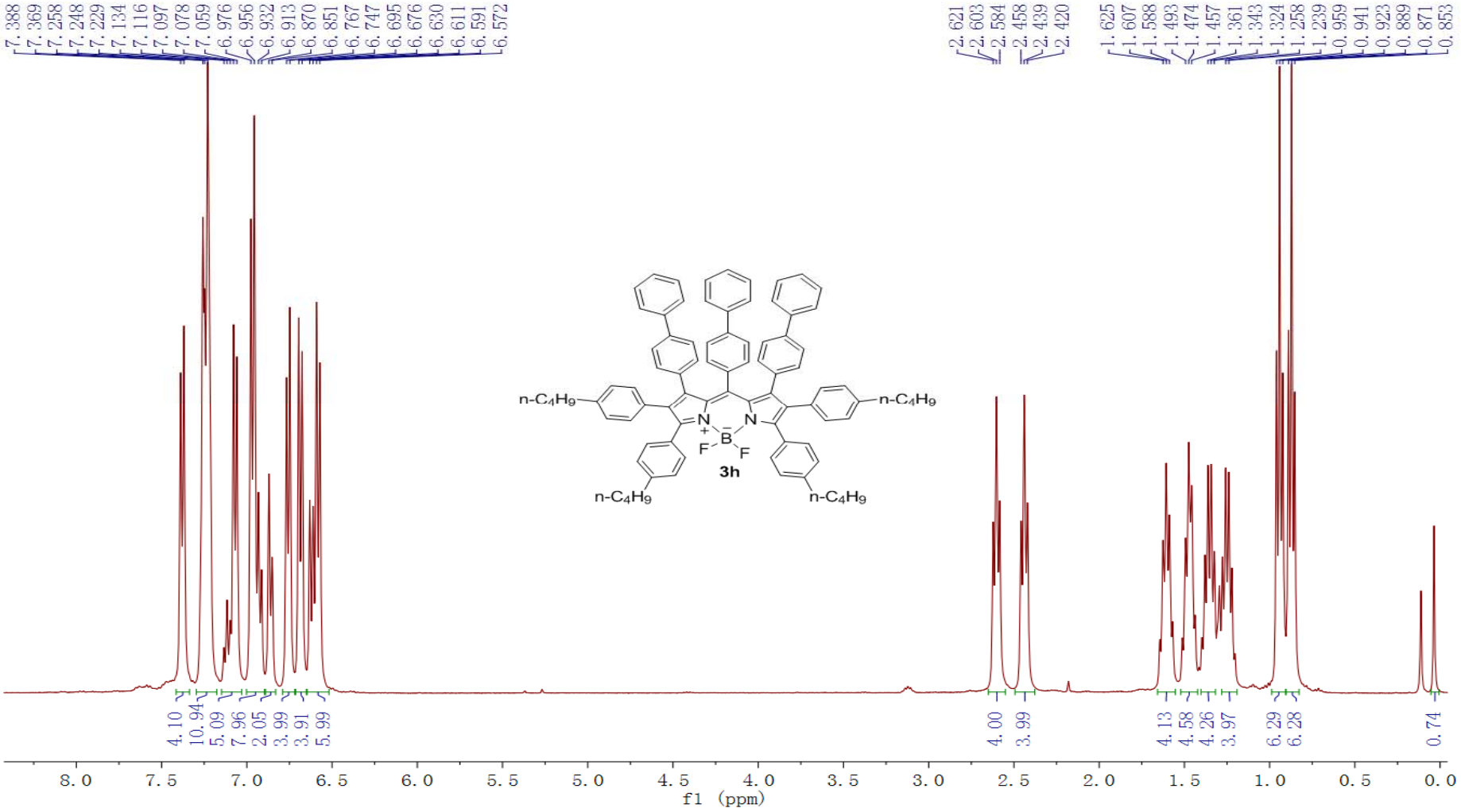


**Figure S64.** The $^{13}$C NMR spectra of **3h.**

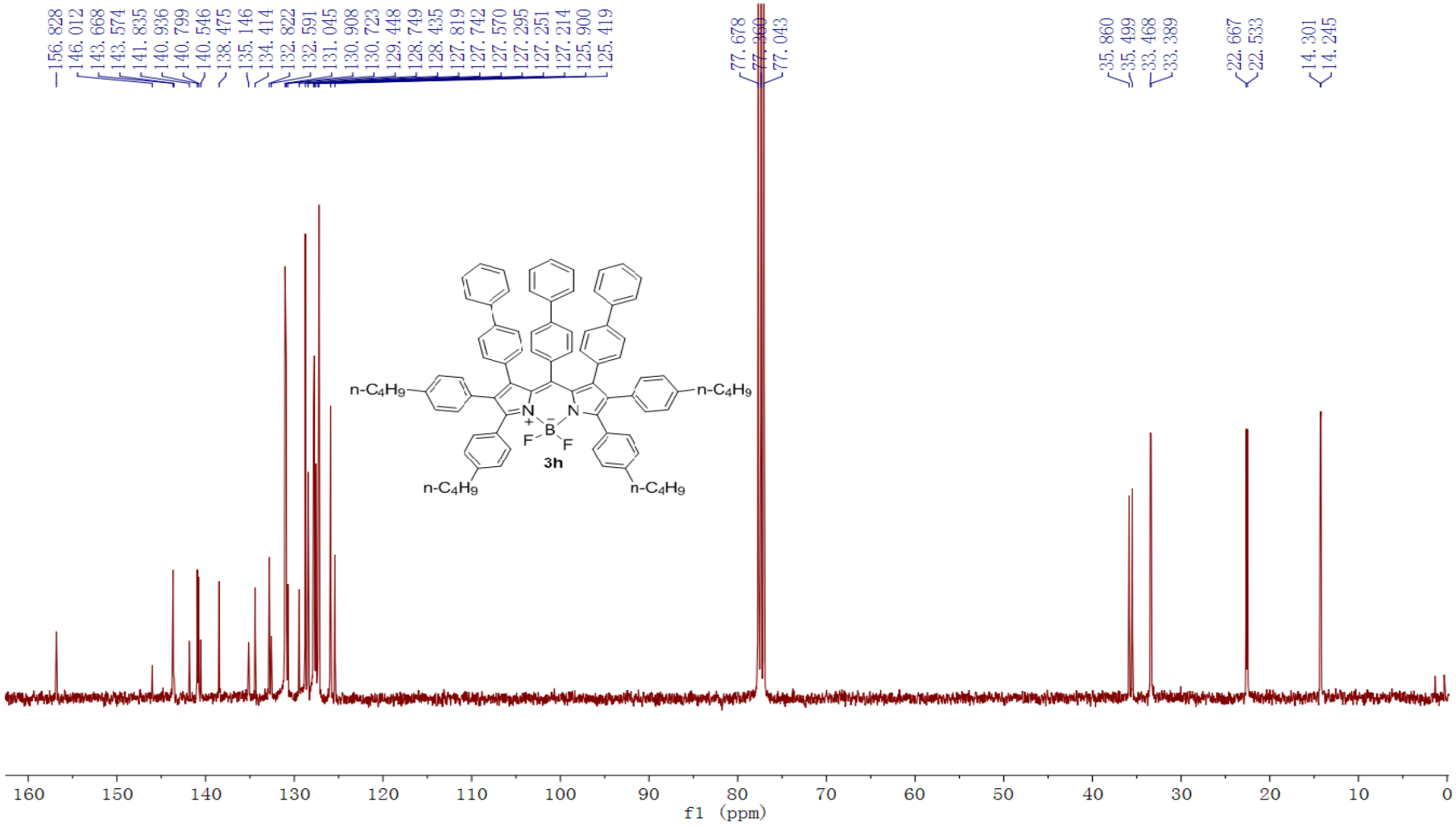


**Figure S65**. The $^{1}$H NMR spectra of **3i.**

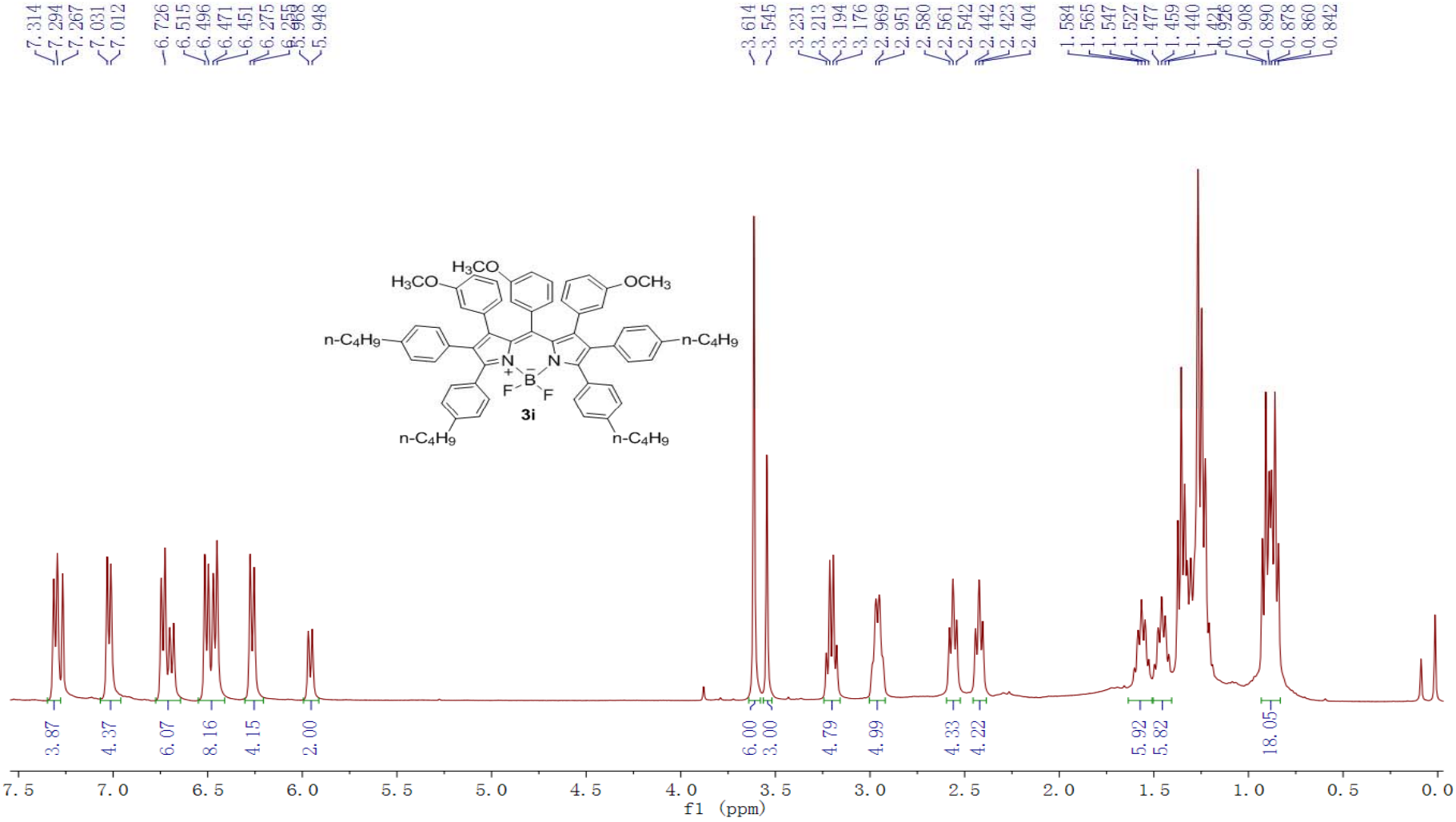


**Figure S66**. The $^{13}$C NMR spectra of **3i.**

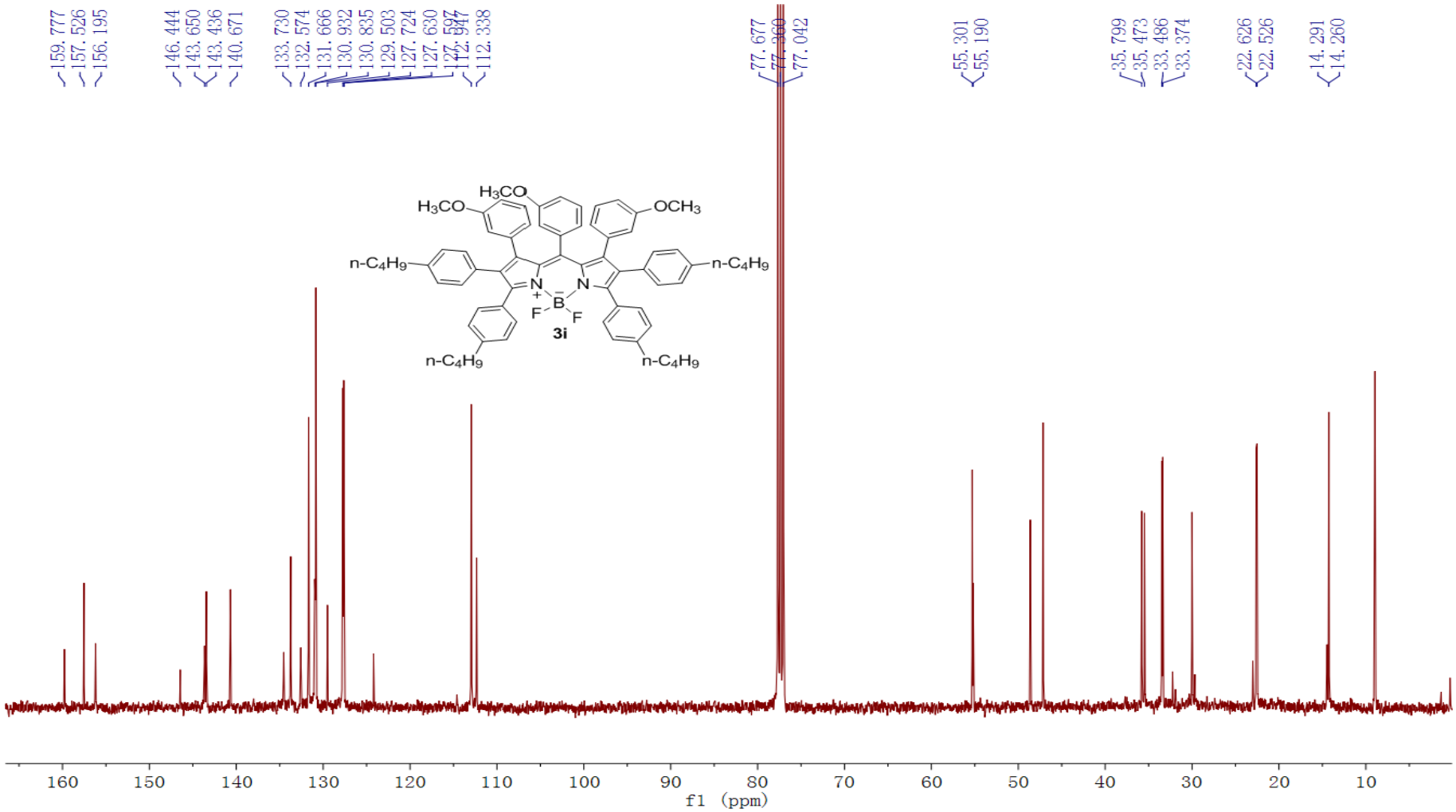


**Figure S67**. The $^{1}$H NMR spectra of **3j.**

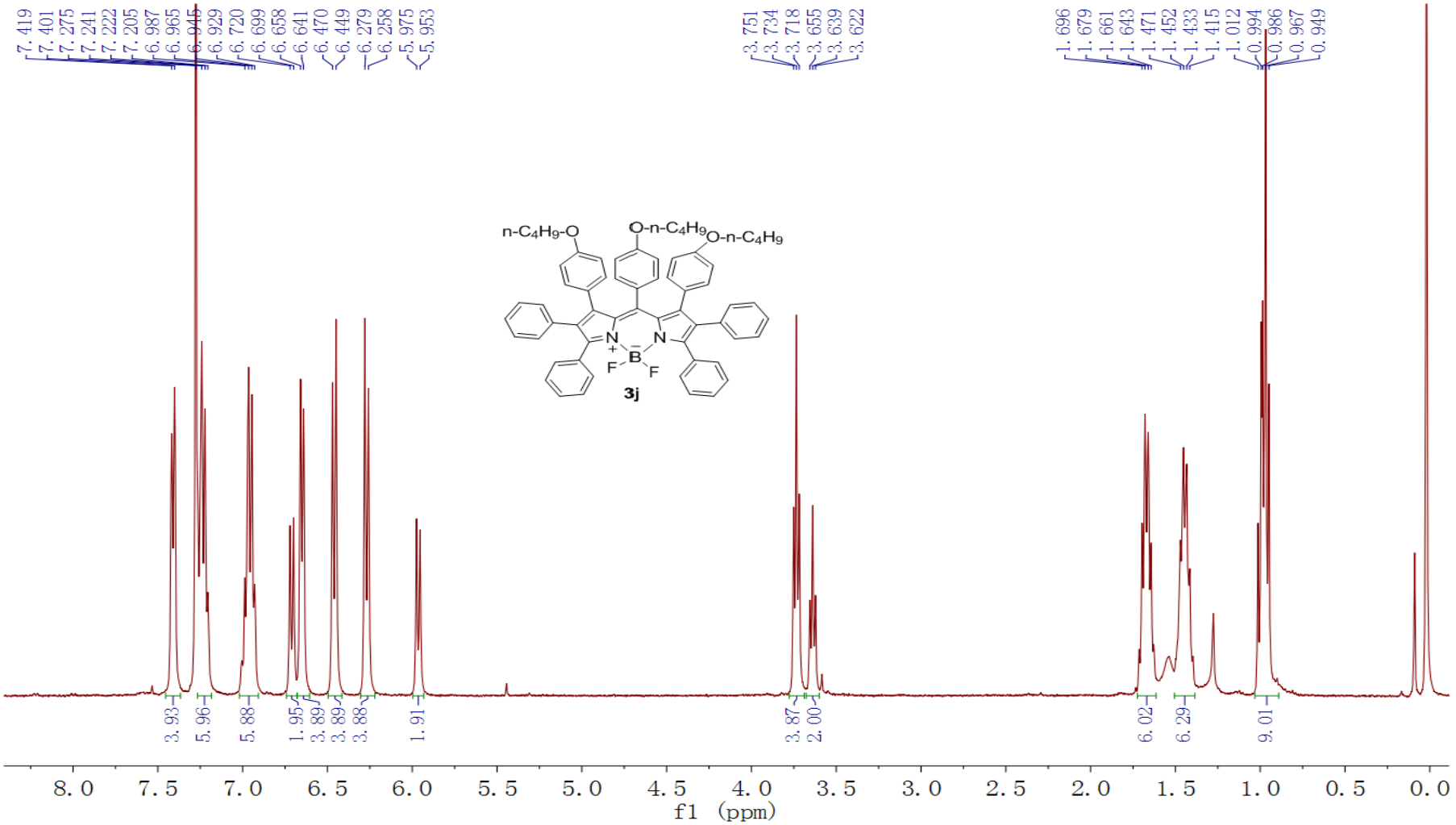


**Figure S68**. The $^{13}$C NMR spectra of **3j.**

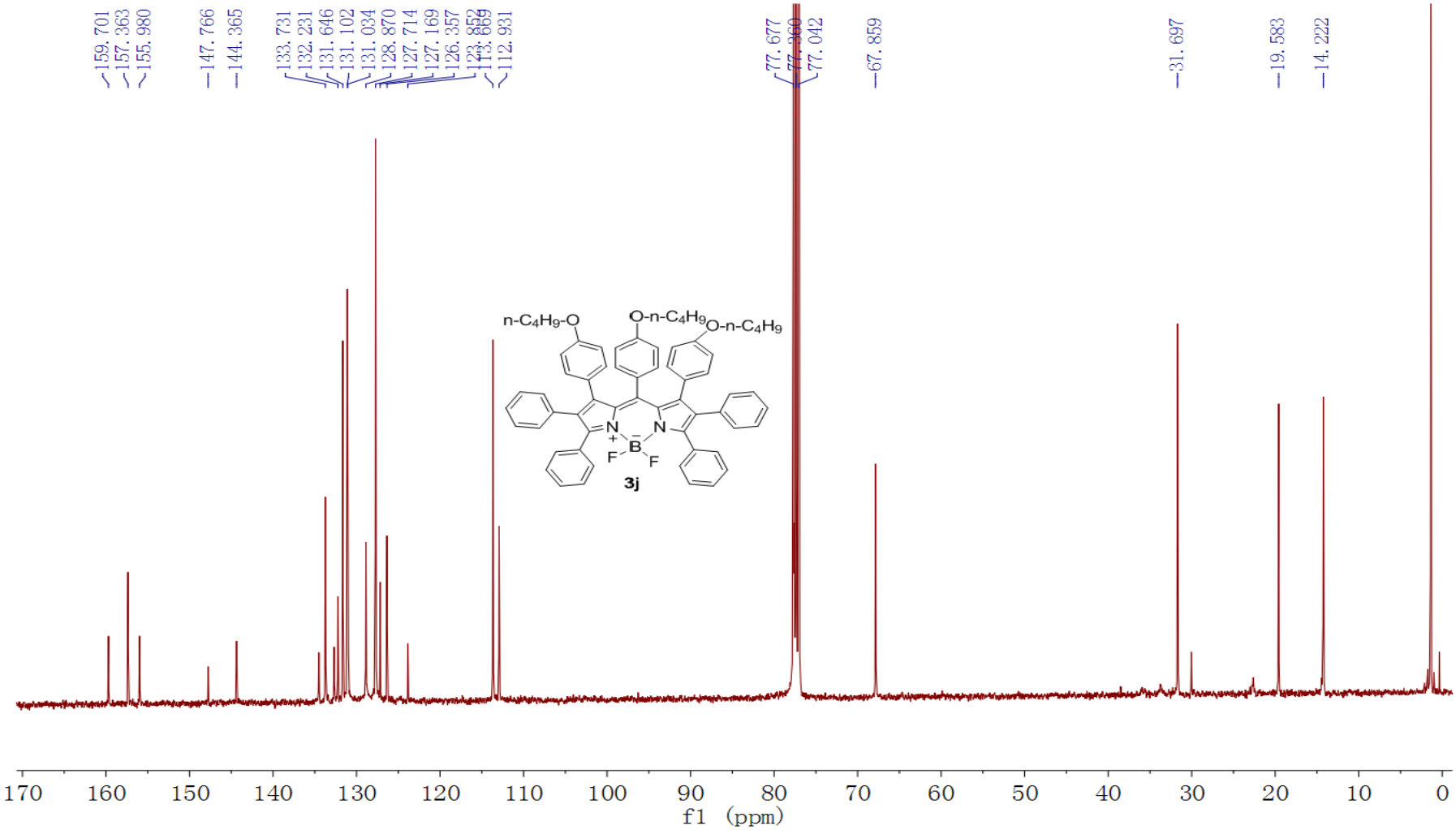


**Figure S69**. The $^{1}$H NMR spectra of **3k.**

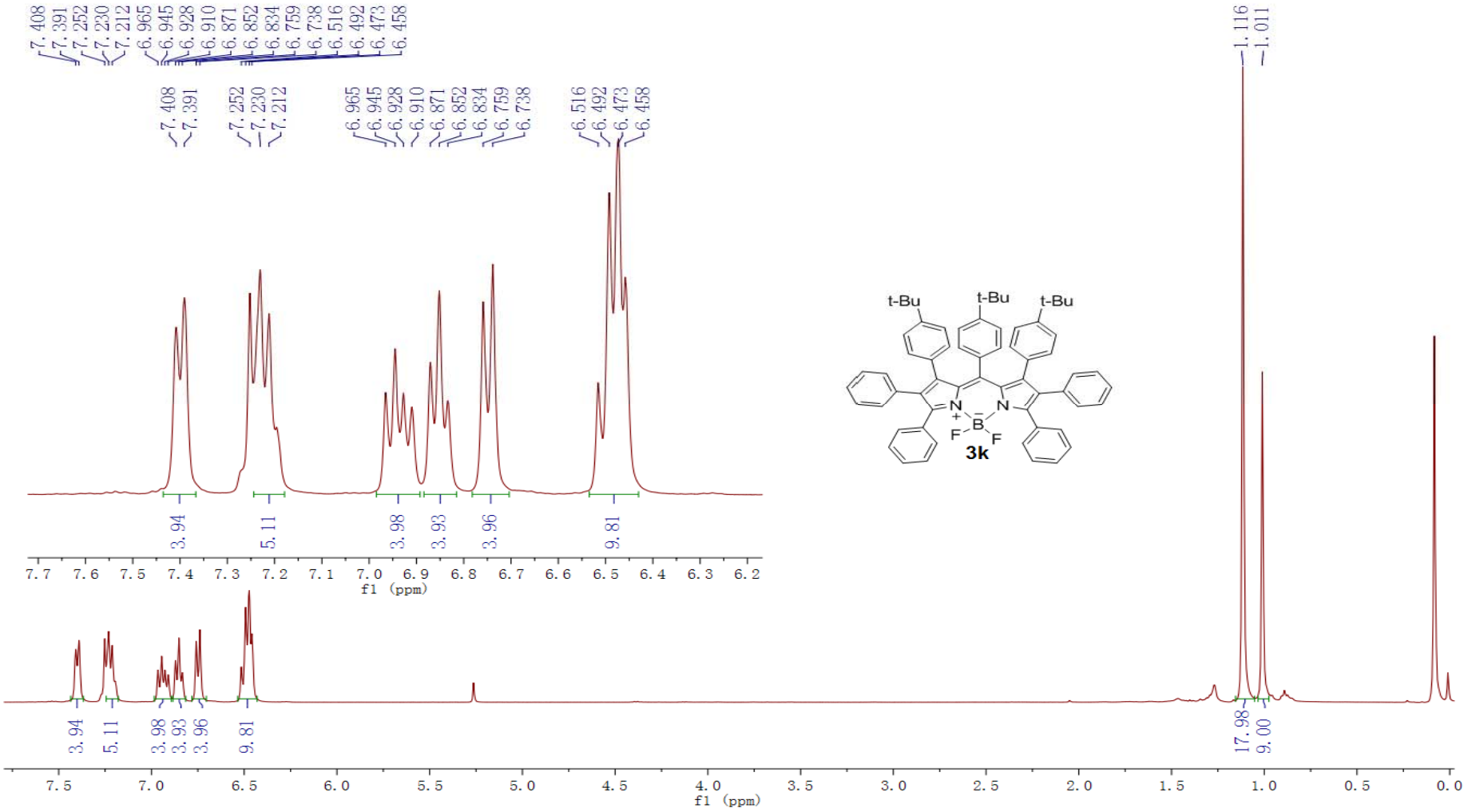


**Figure S70**. The $^{13}C$ NMR spectra of **3k.**

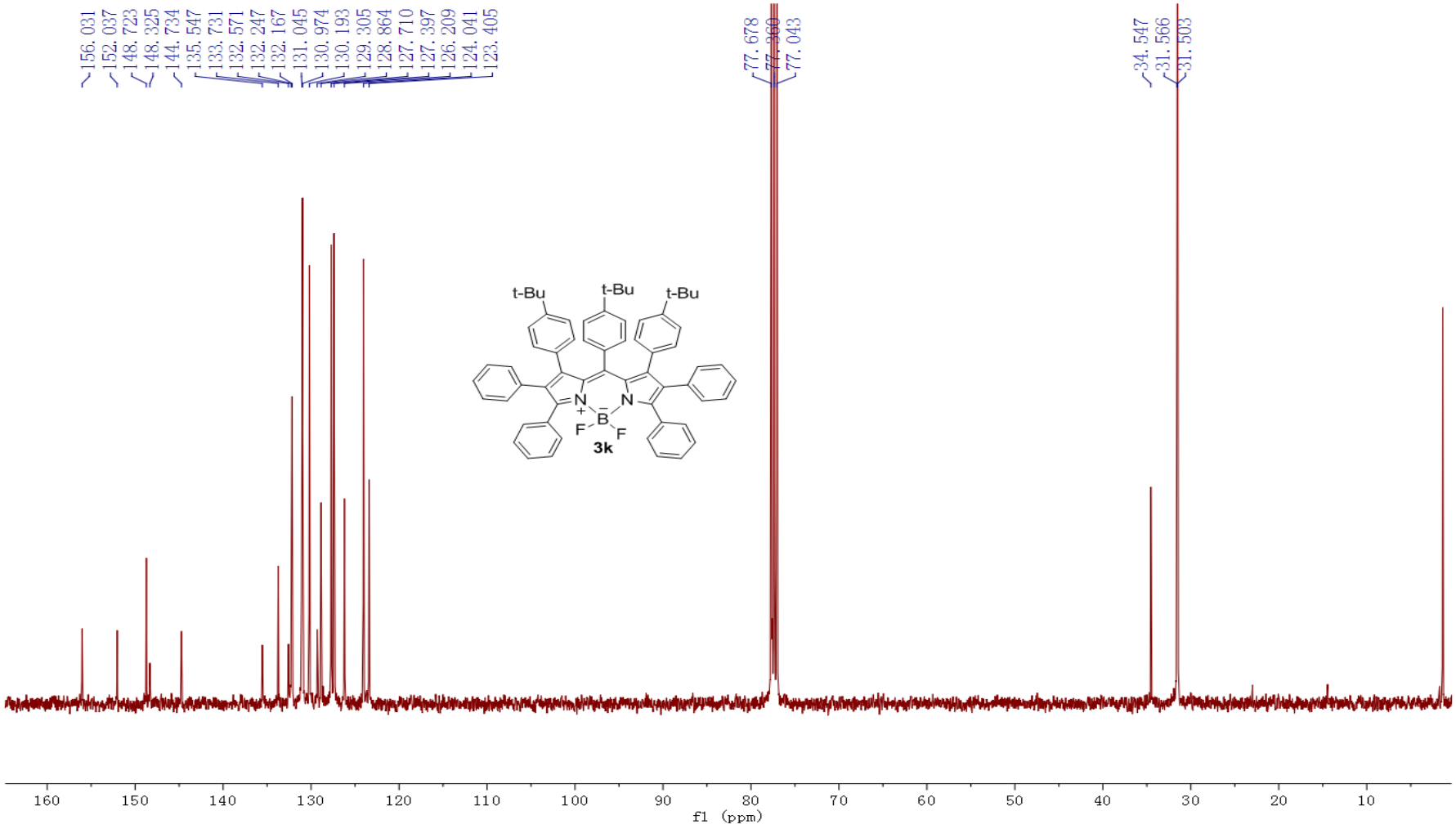


**Figure S71**. The $^{1}$H NMR spectra of **3l.**

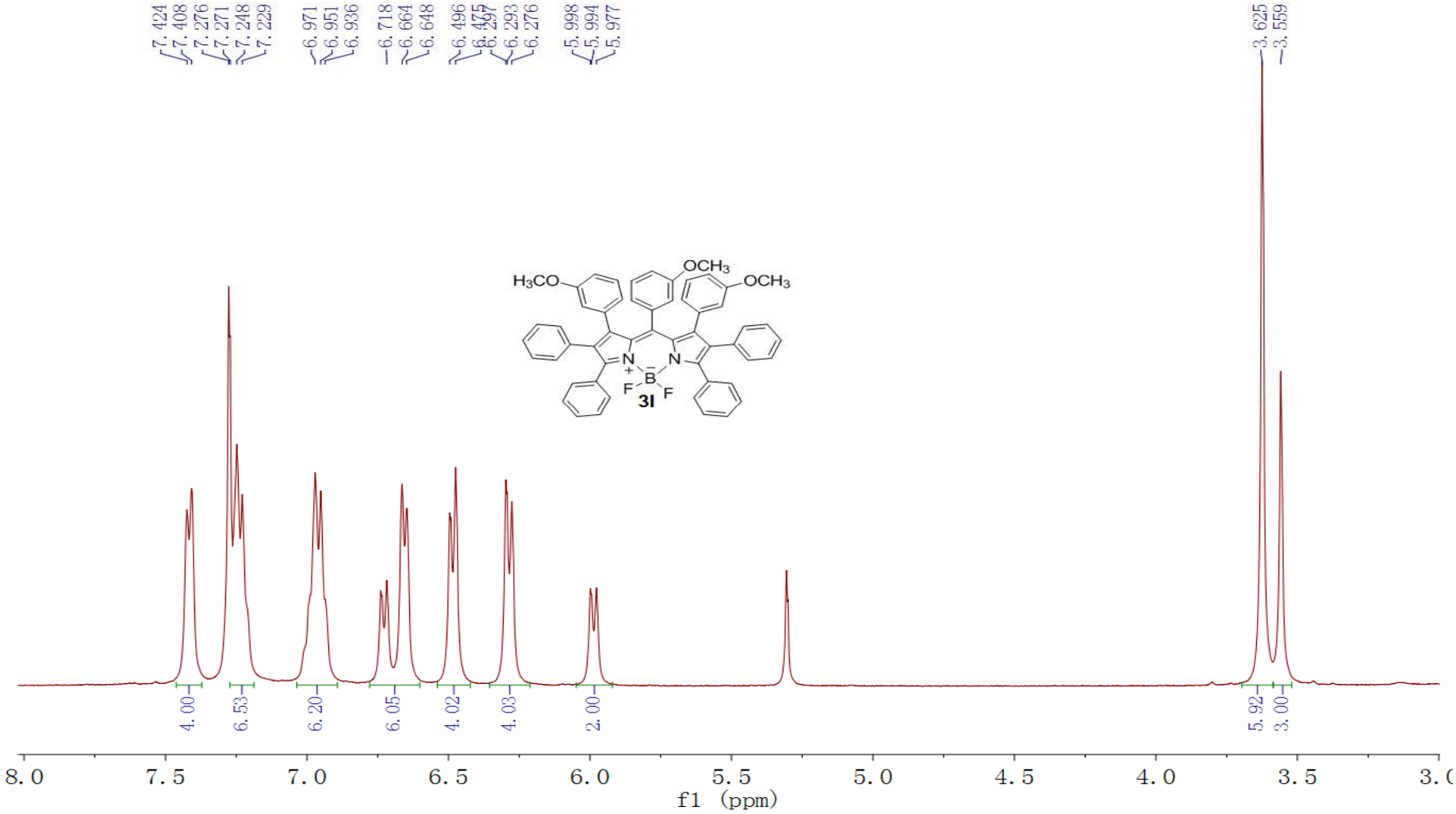


**Figure S72**. The $^{1}$H NMR spectra of **3l.**

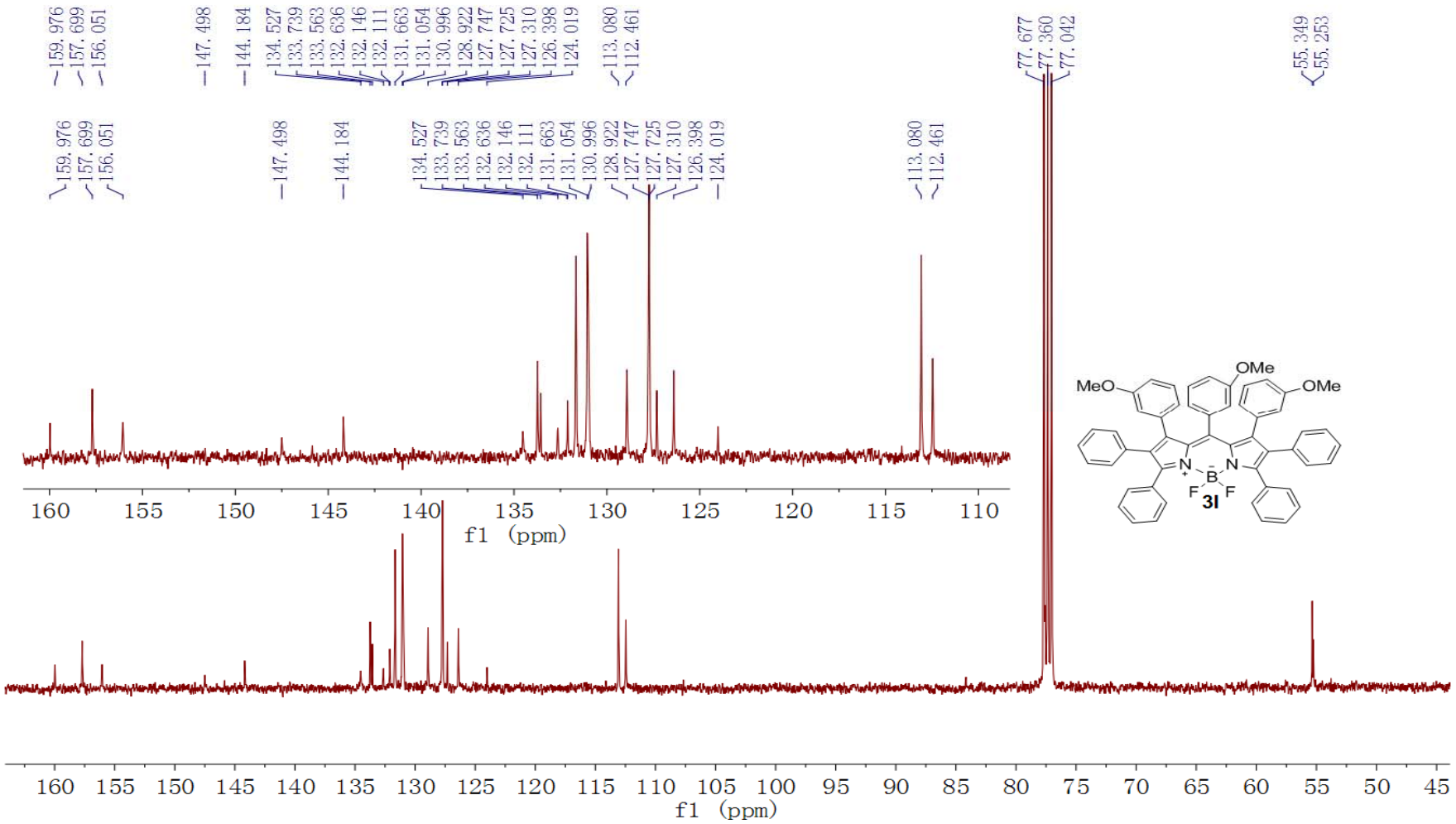


**Figure S73**. The $^{1}$H NMR spectra of **3m.**

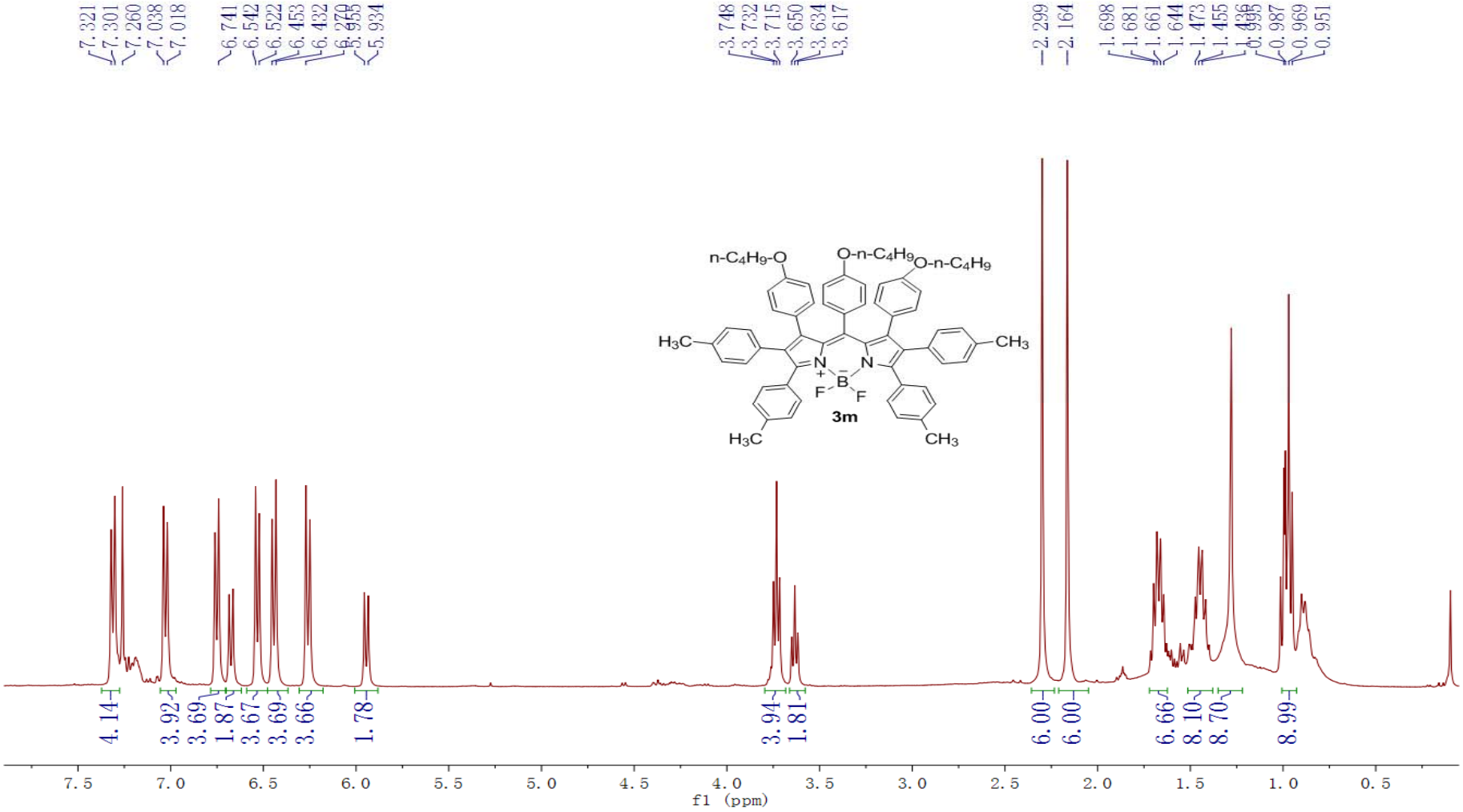


**Figure S74**. The $^{13}C$ NMR spectra of **3m.**

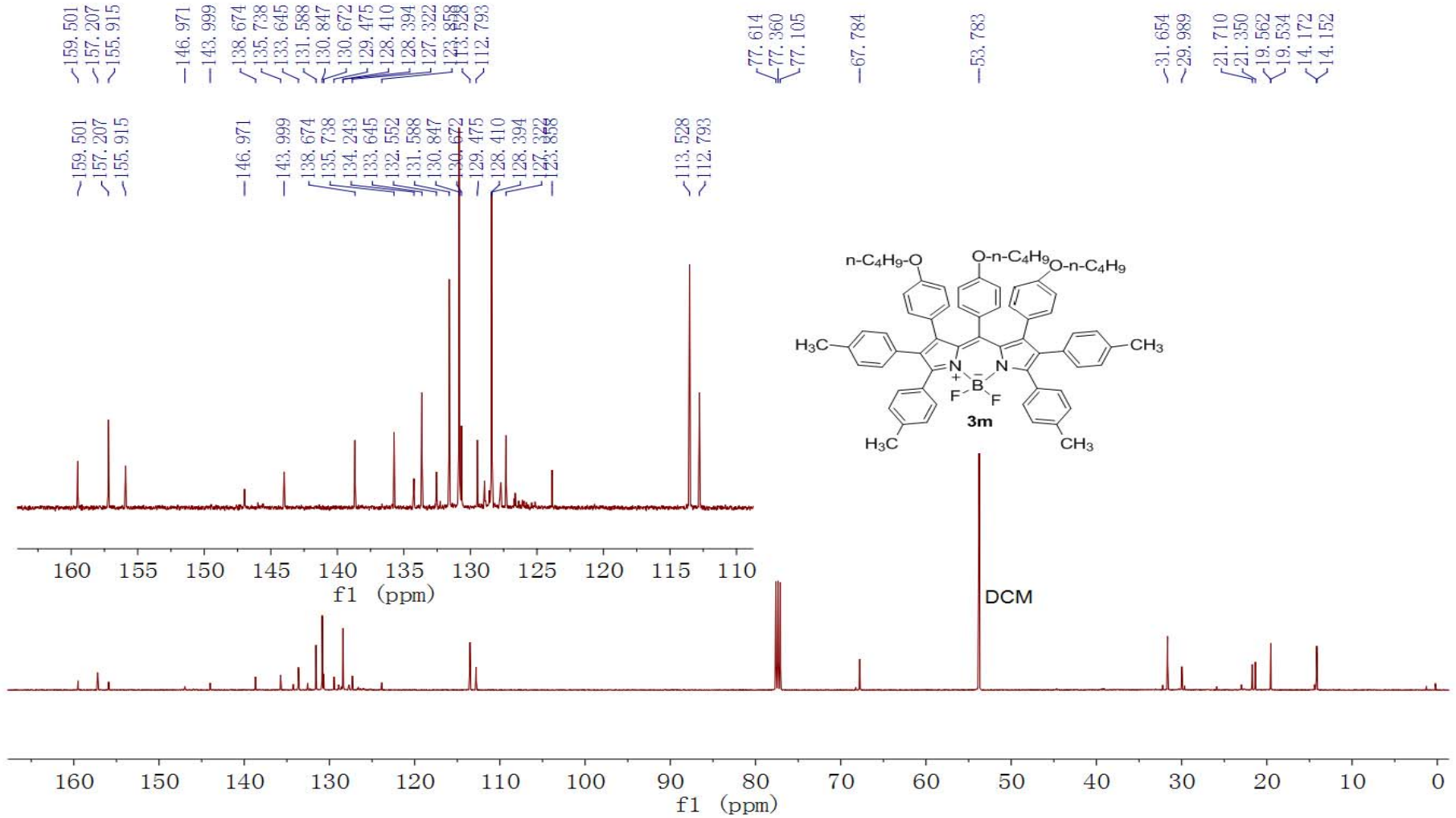


**Figure S75**. The $^{1}$H NMR spectra of **3n.**

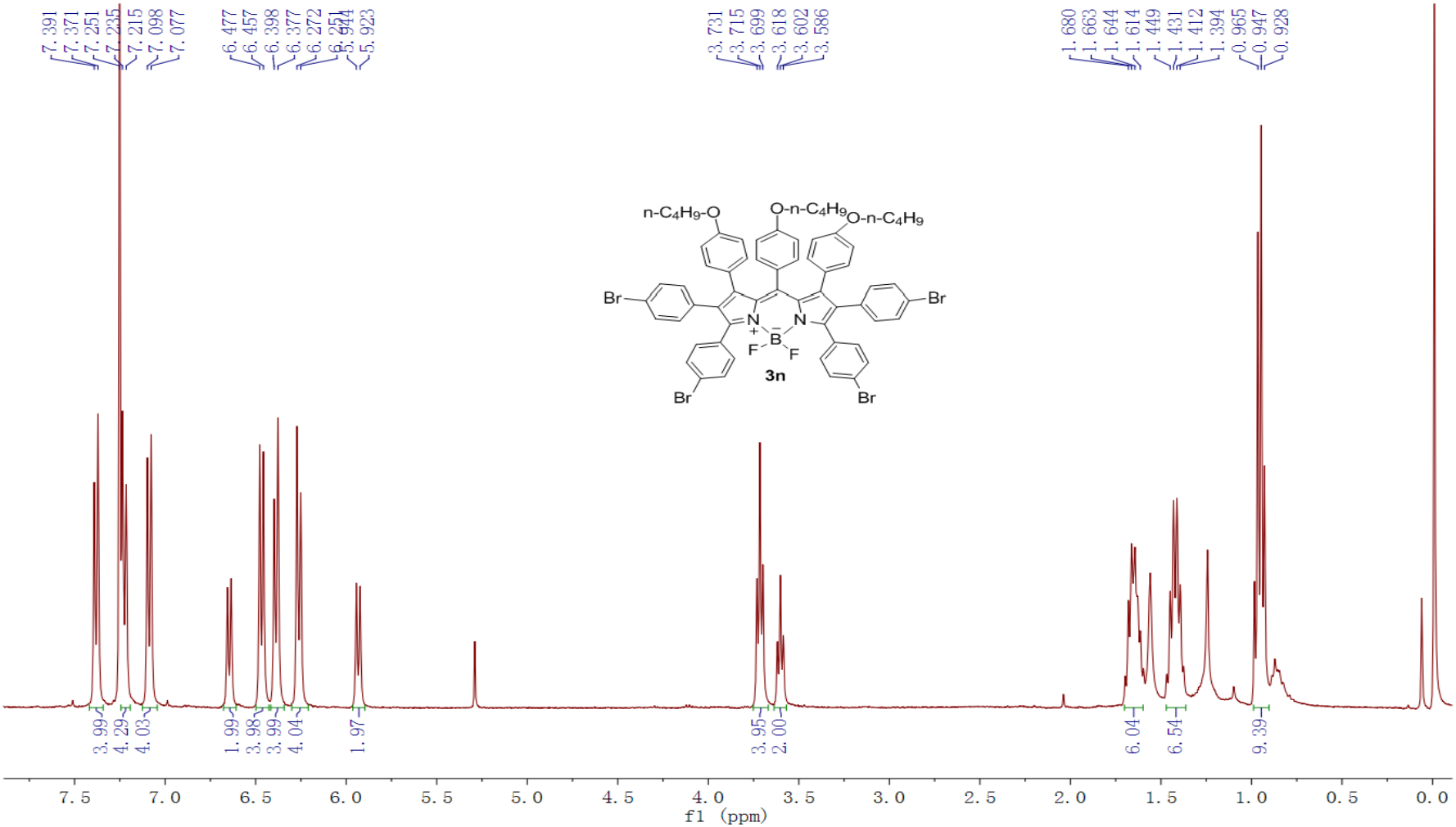


**Figure S76**. The $^{13}C$ NMR spectra of **3n.**

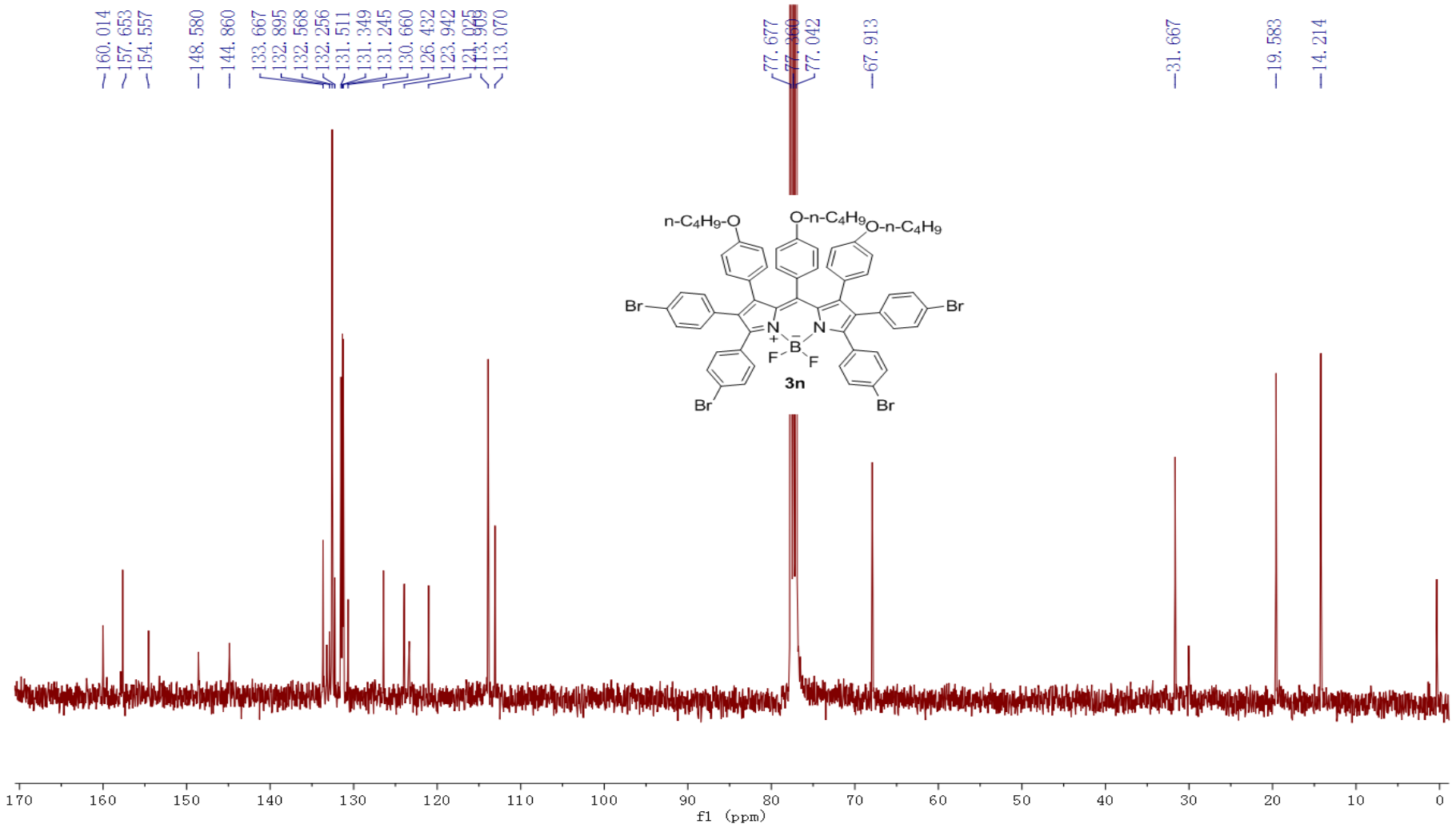


**Figure S77**. The $^{1}$H NMR spectra of **3o.**

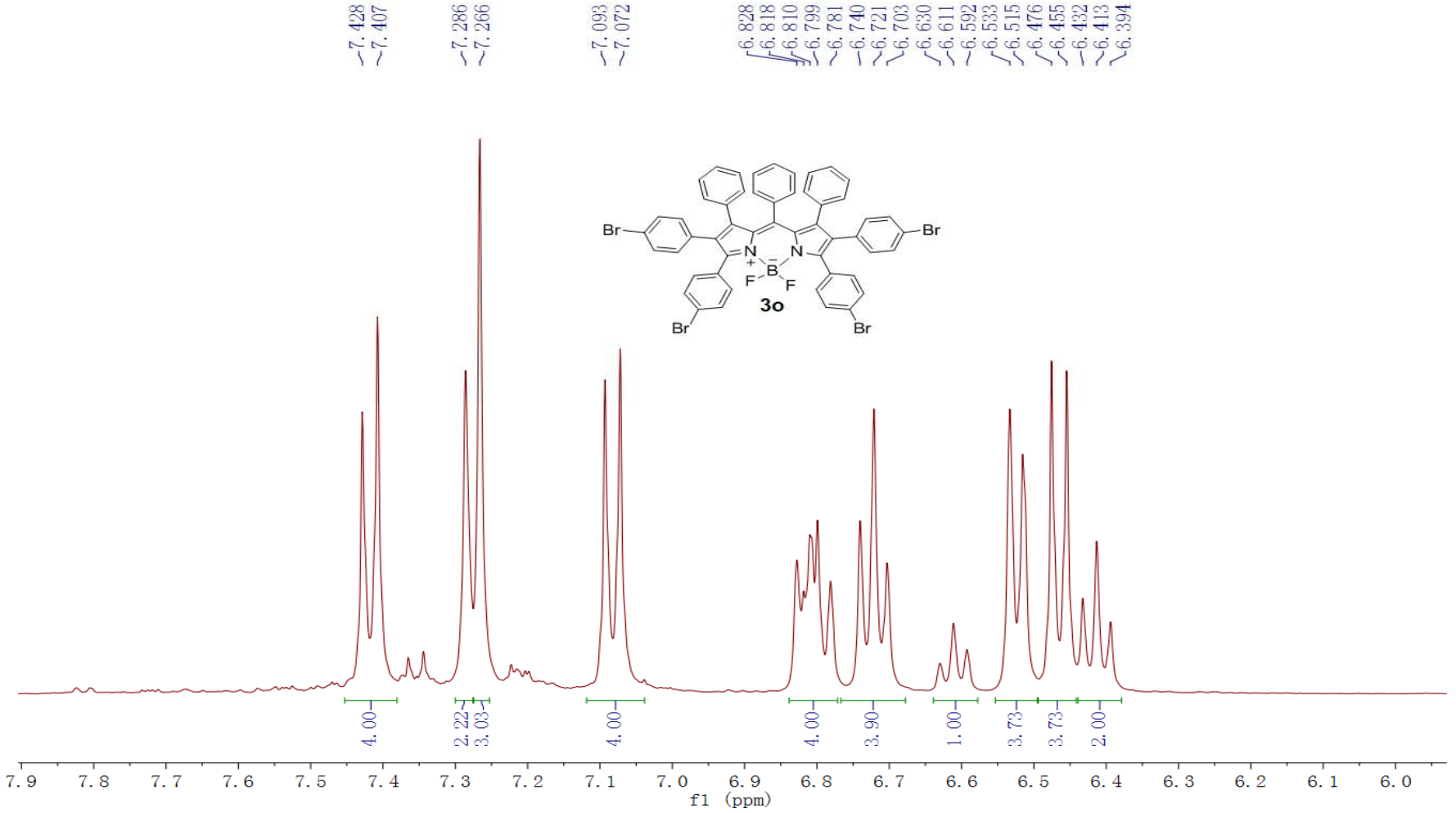
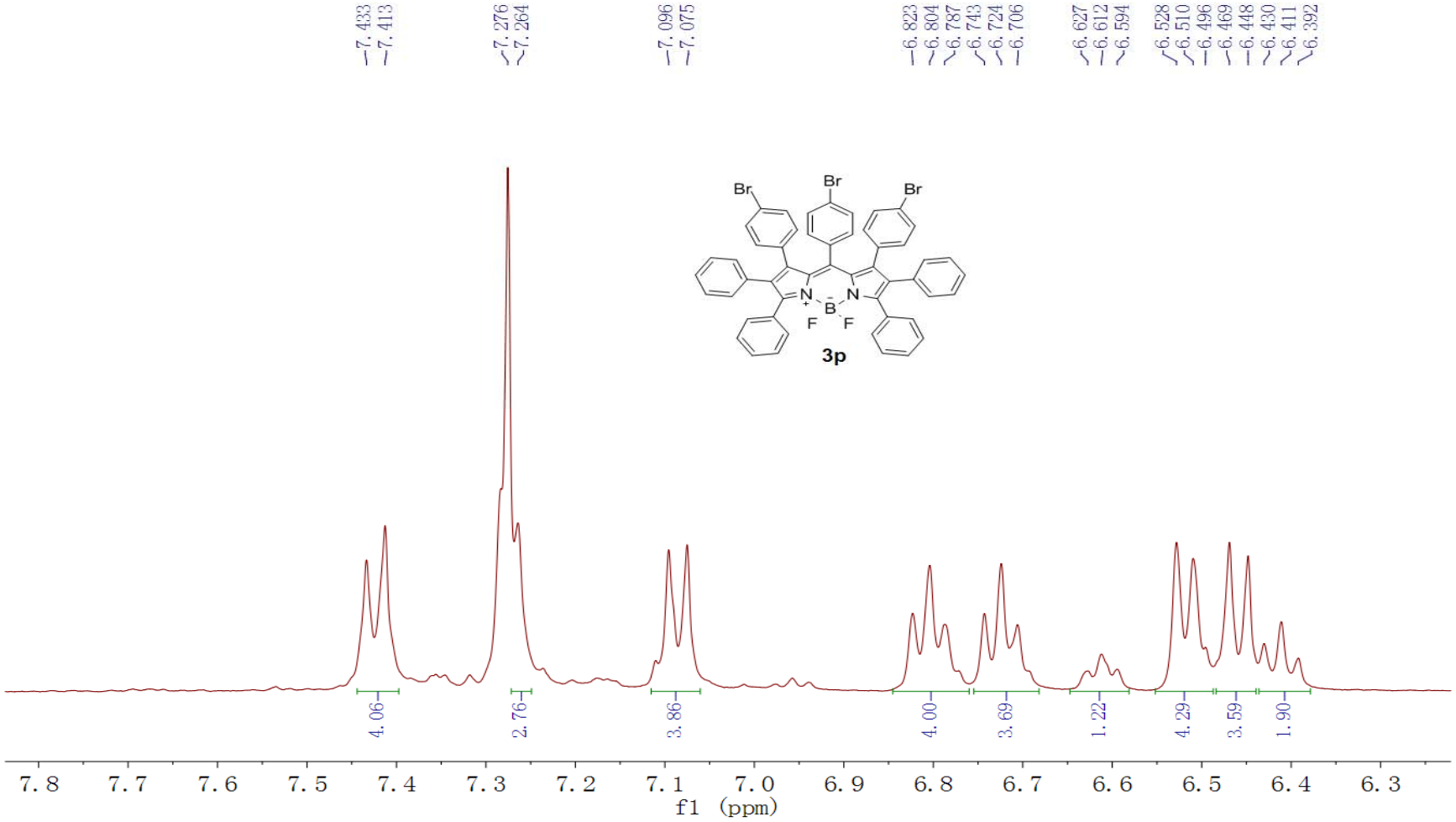


**Figure S78**. The $^{1}$H NMR spectra of **3p.**



**6.** $^{1}$H NMR and $^{13}$C NMR spectra of **4-5**

**Figure S79**. The $^{1}$H NMR spectra of **4a.**

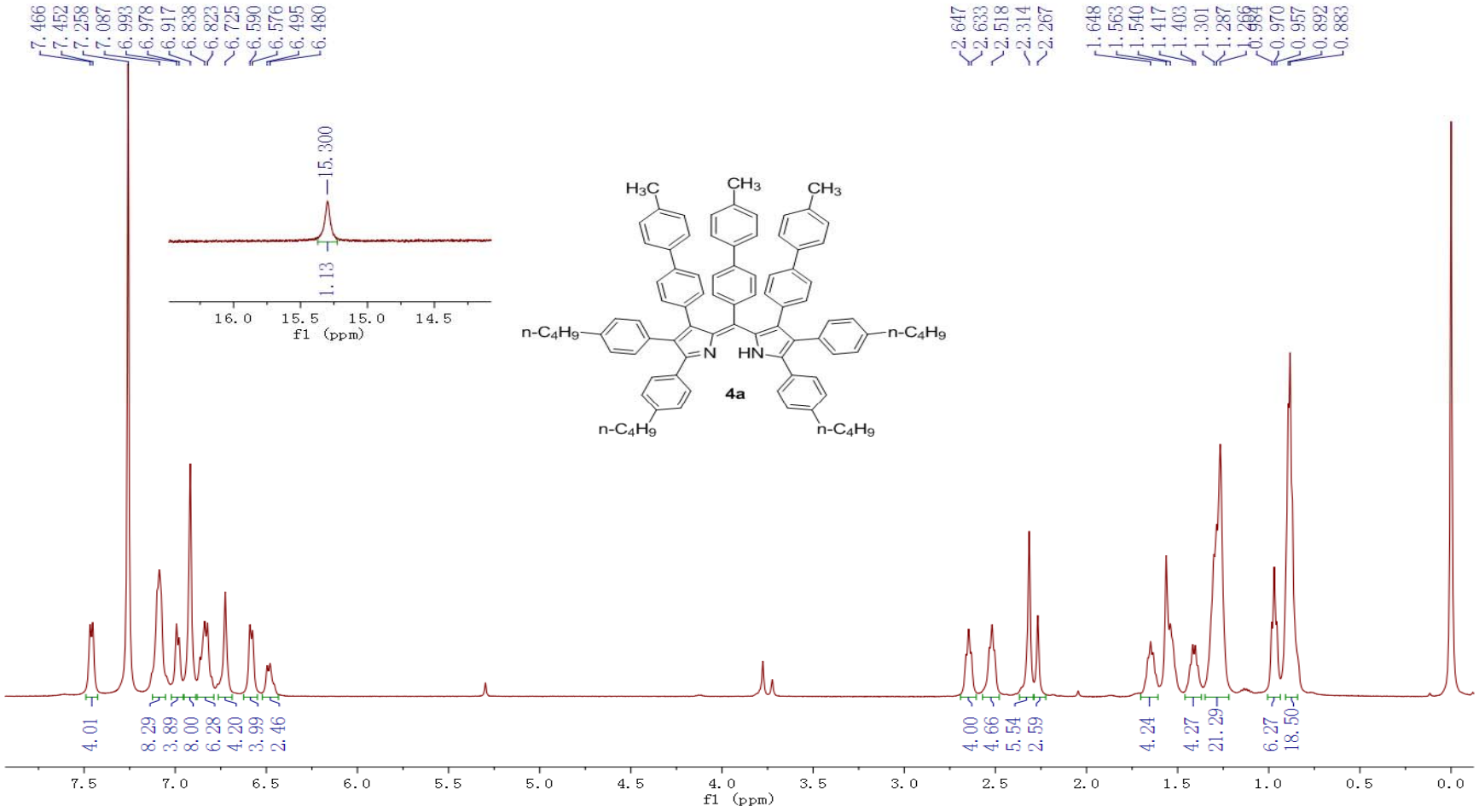


**Figure S80**. The $^{13}C$ NMR spectra of **4a.**

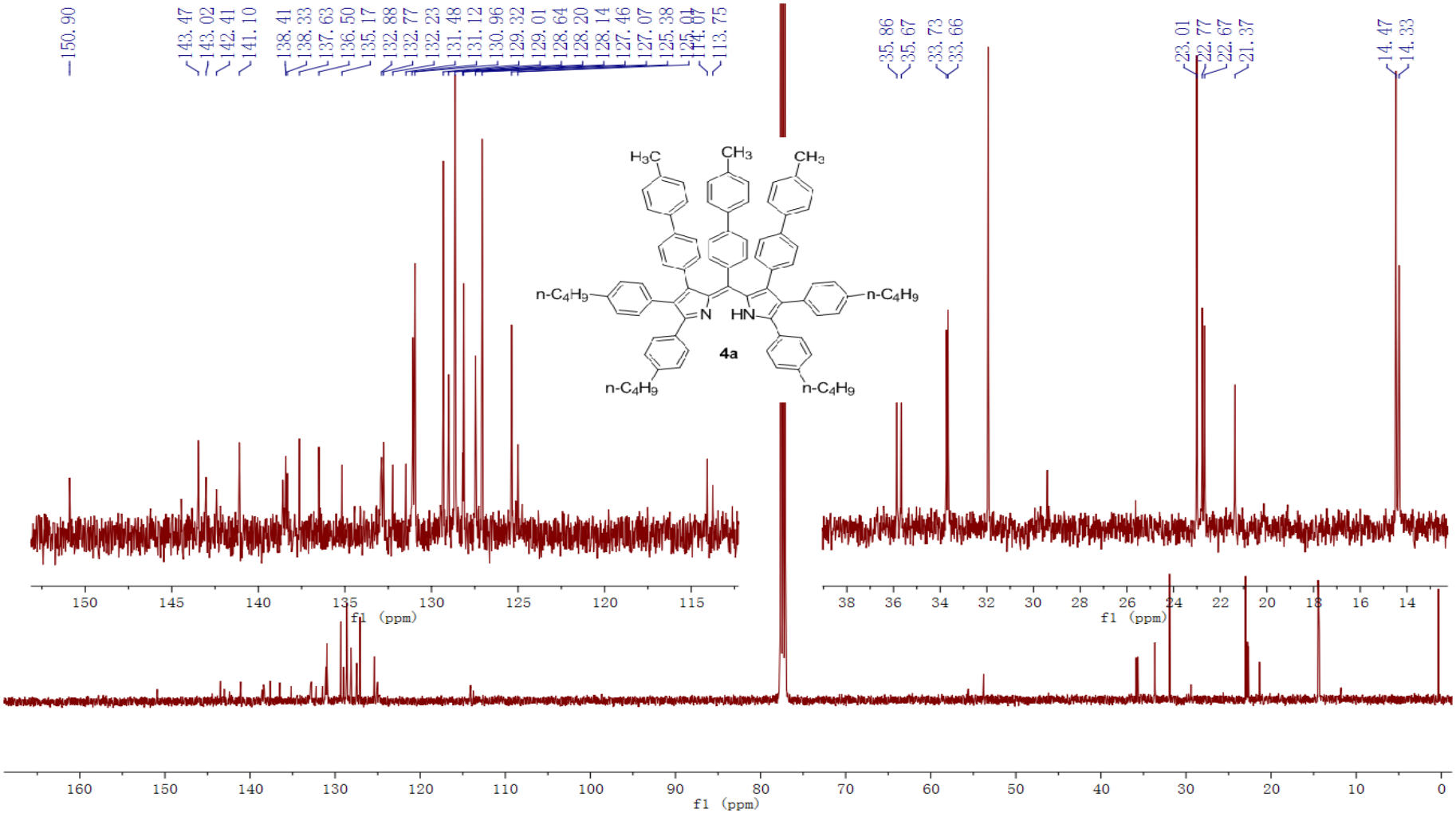


**Figure S81**. The $^{1}$H NMR spectra of **4b.**

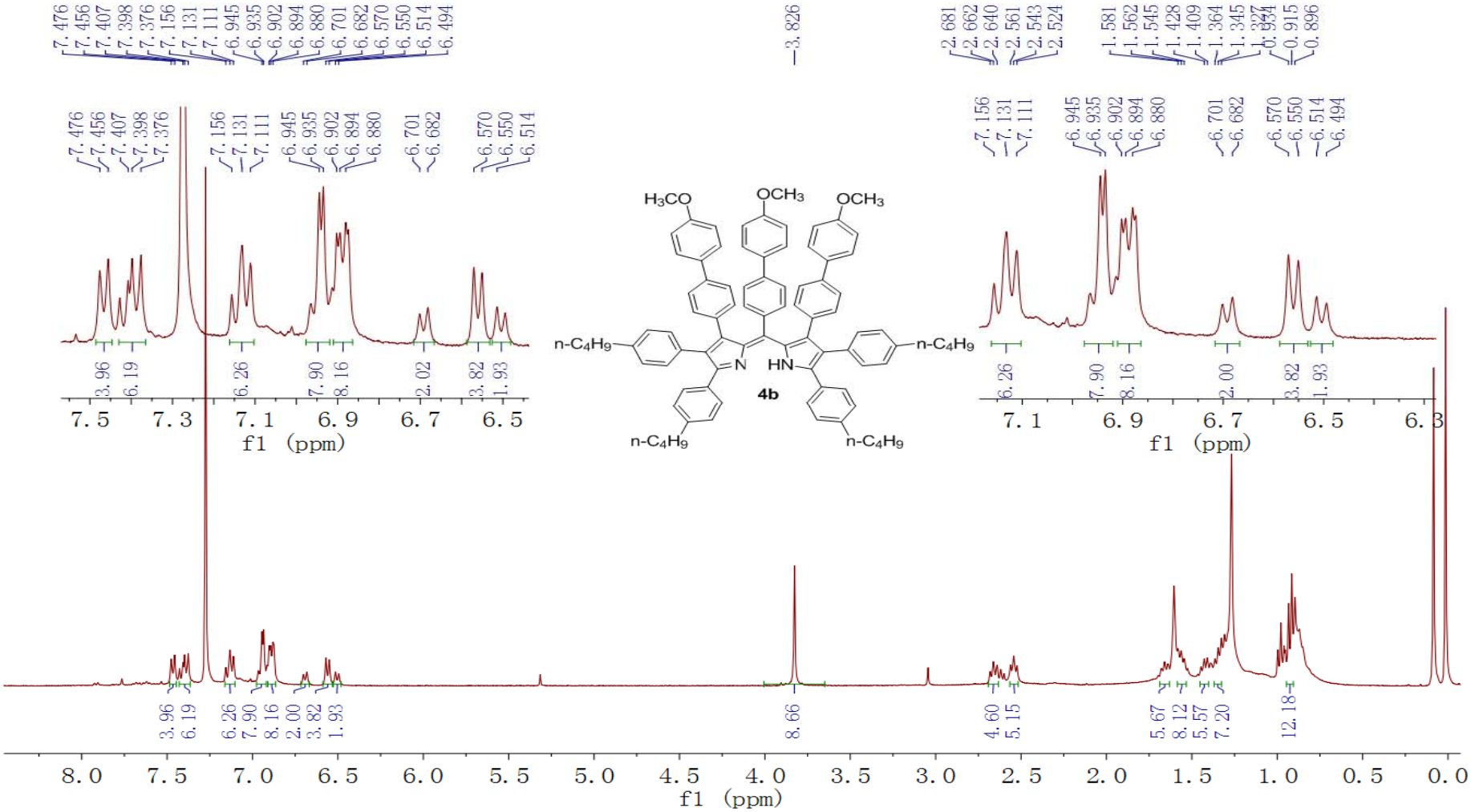


**Figure S82**. The $^{1}$H NMR spectra of **4c.**

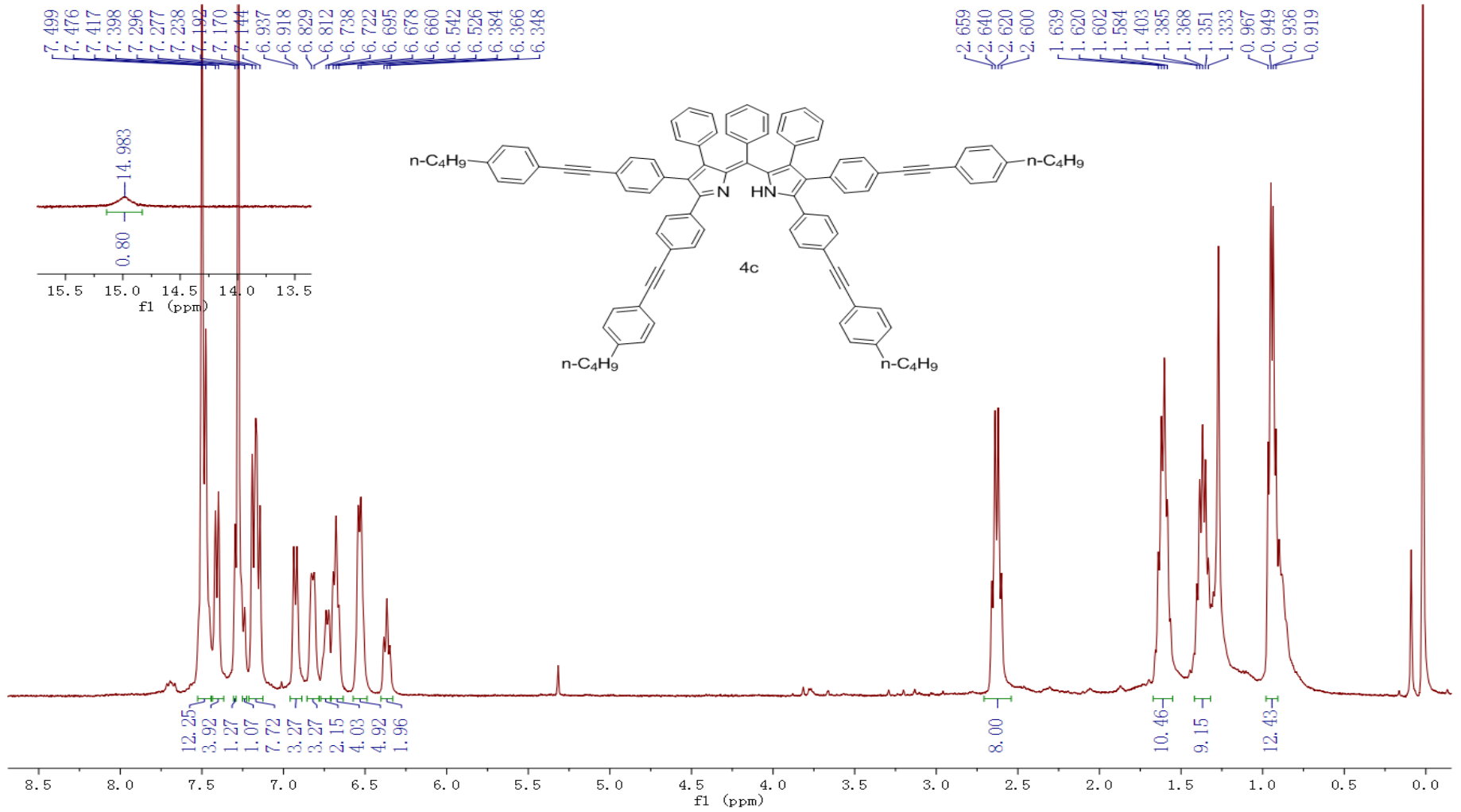


**Figure S83**. The $^{13}C$ NMR spectra of **4c.**

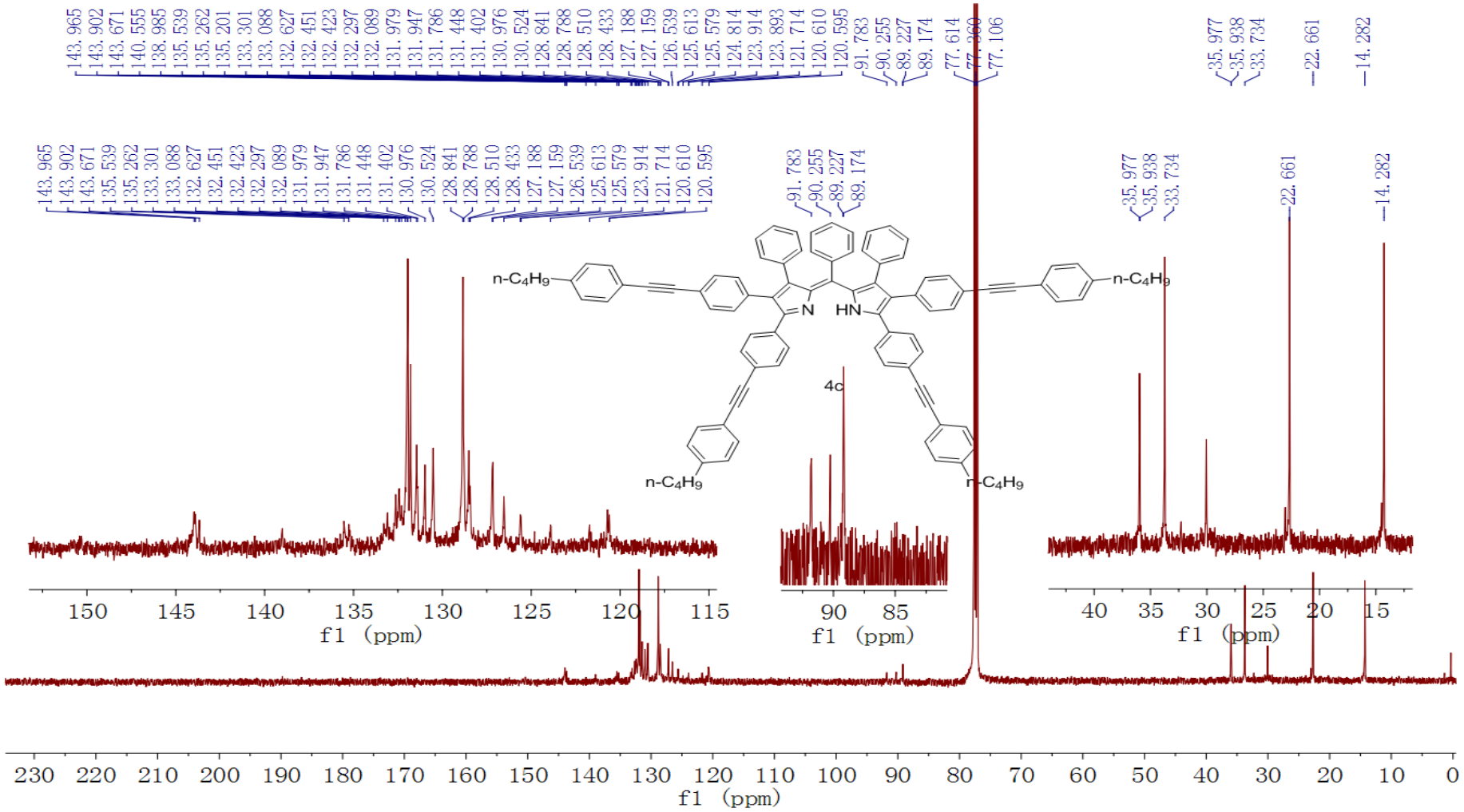


**Figure S84**. The $^{1}$H NMR spectra of **4d.**

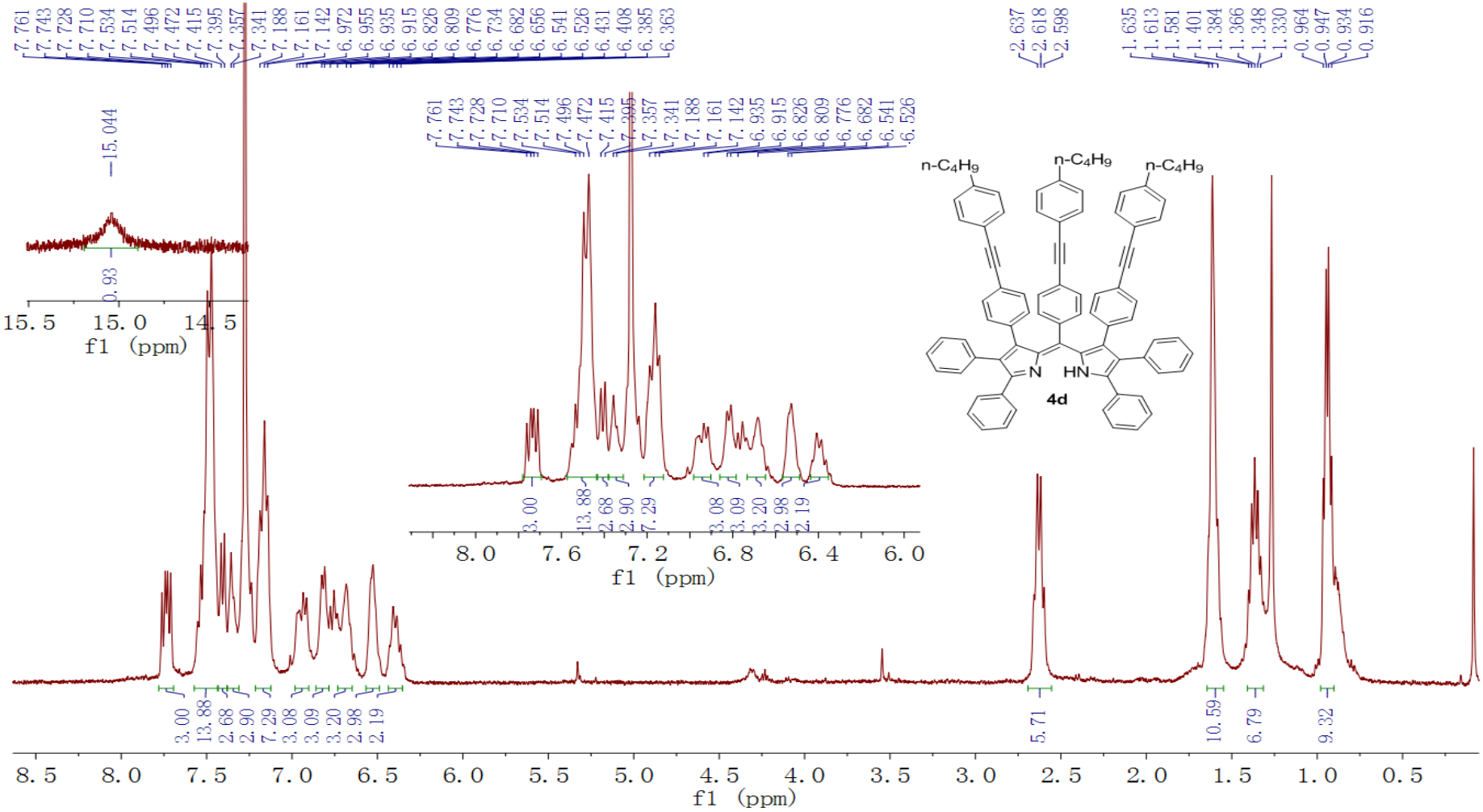


**Figure S85**. The $^{1}$H NMR spectra of **5a.**

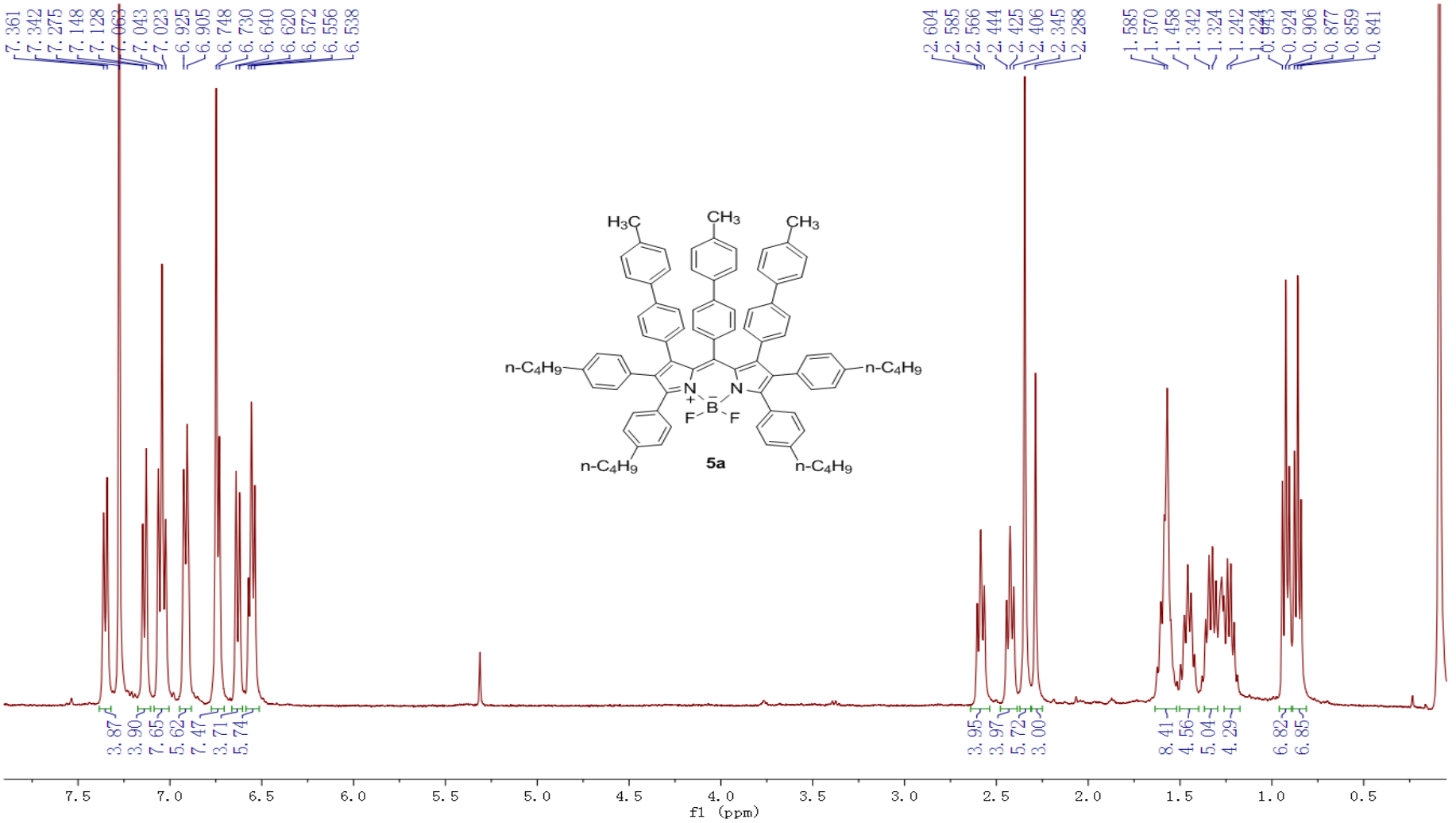


**Figure S86**. The $^{13}C$ NMR spectra of **5a.**

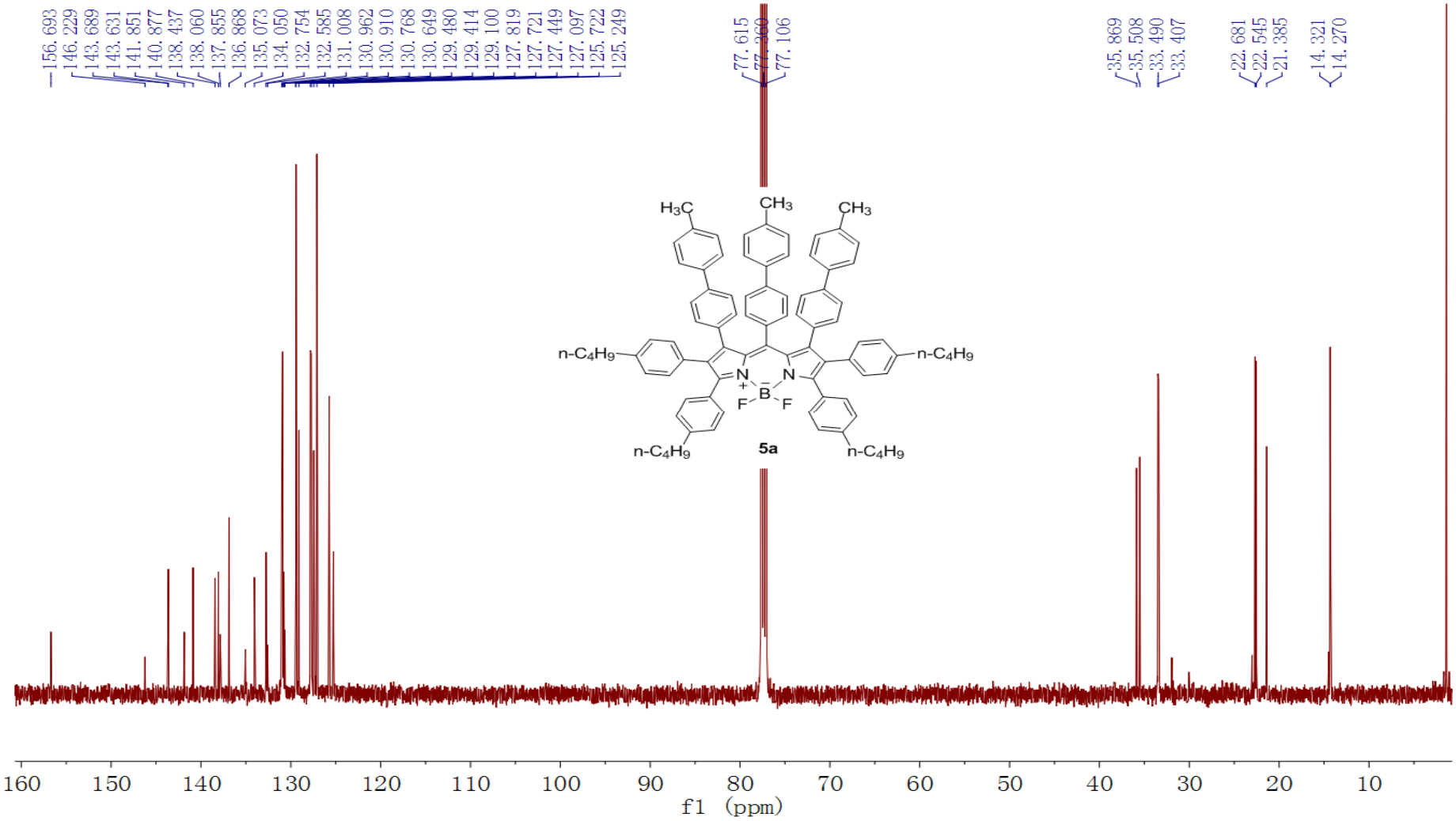


**Figure S87**. The $^{1}$H NMR spectra of **5b.**

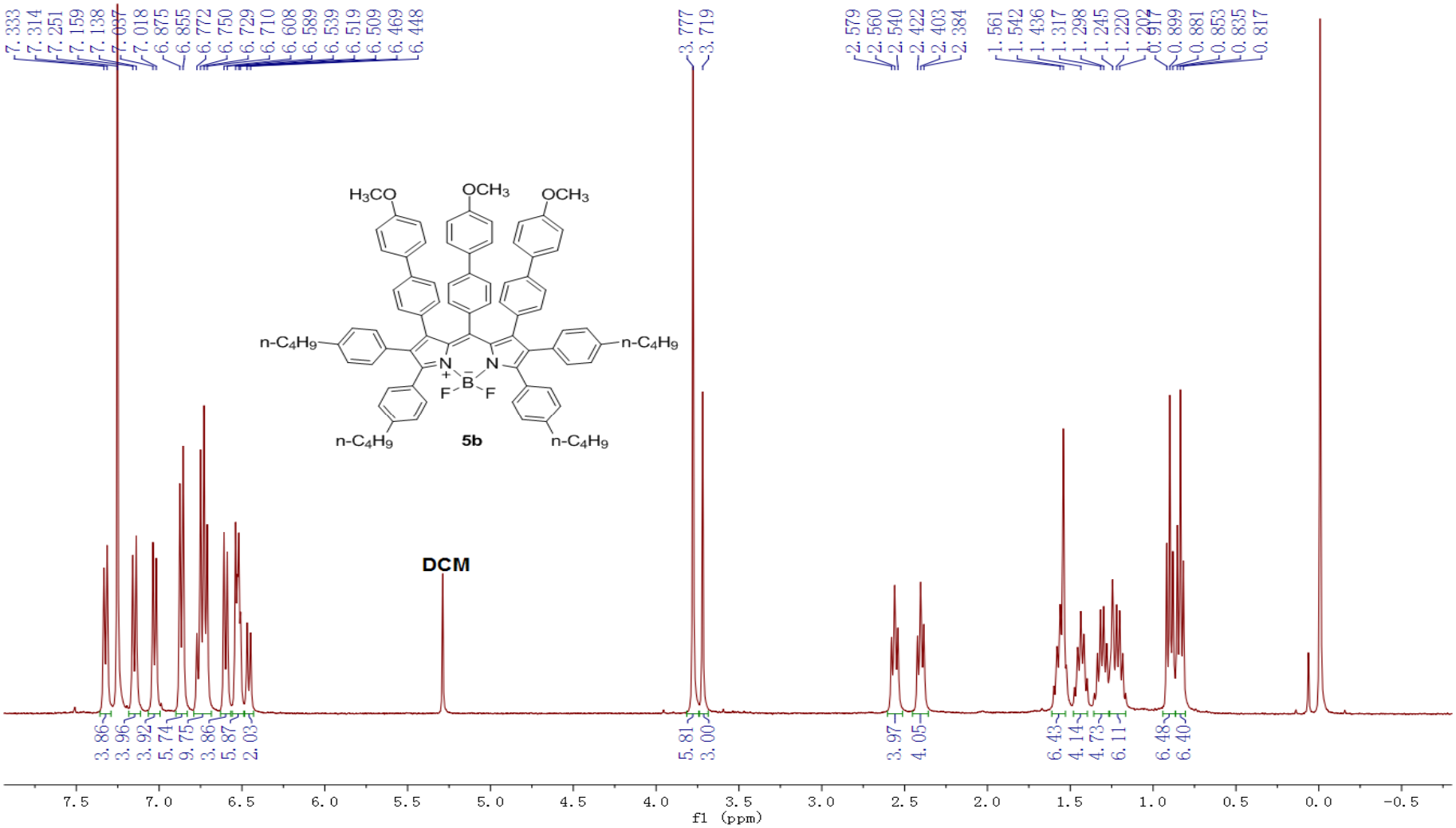


**Figure S88**. The $^{13}C$ NMR spectra of **5b.**

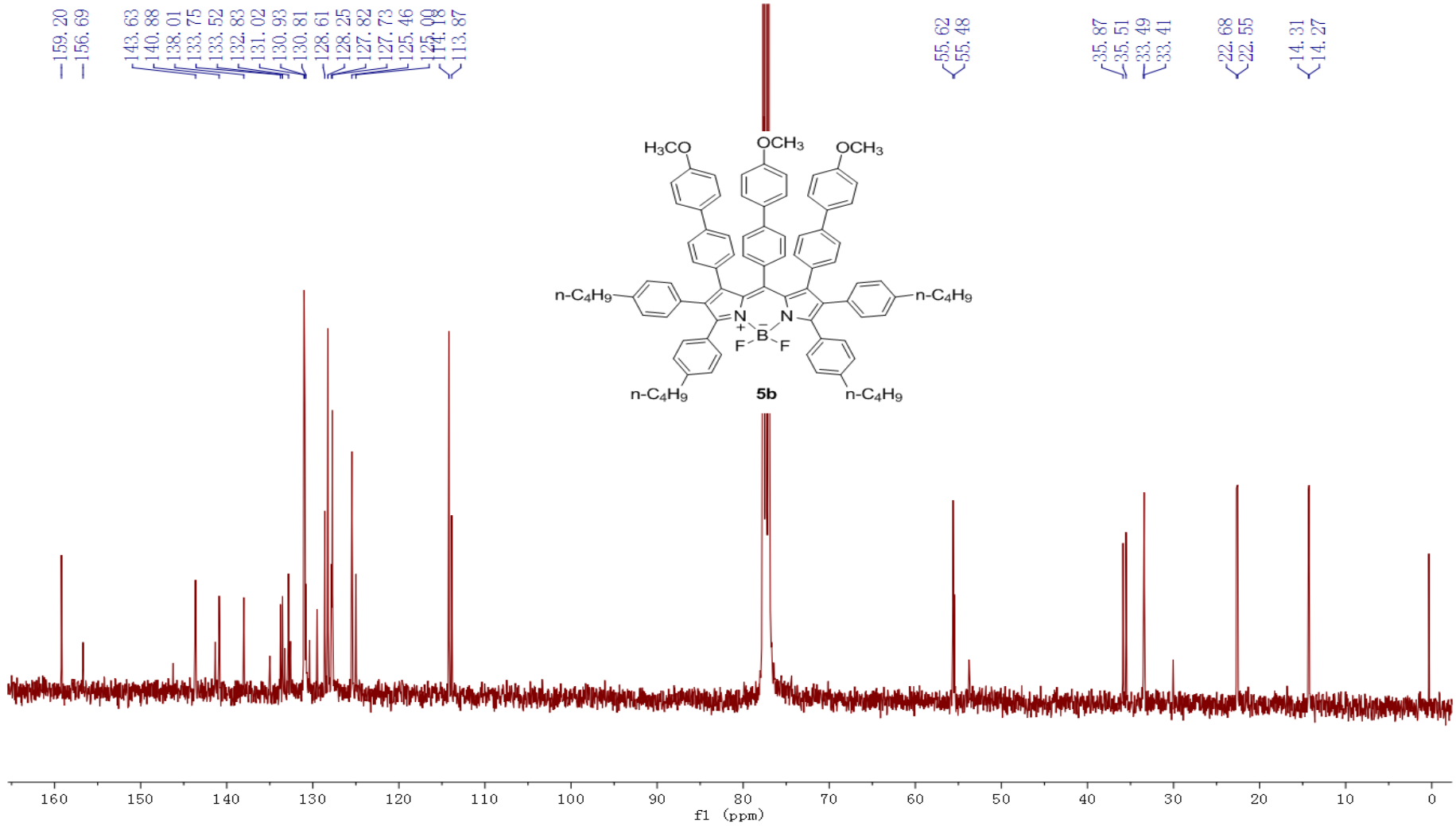


**Figure S89**. The $^{1}$H NMR spectra of **5c.**

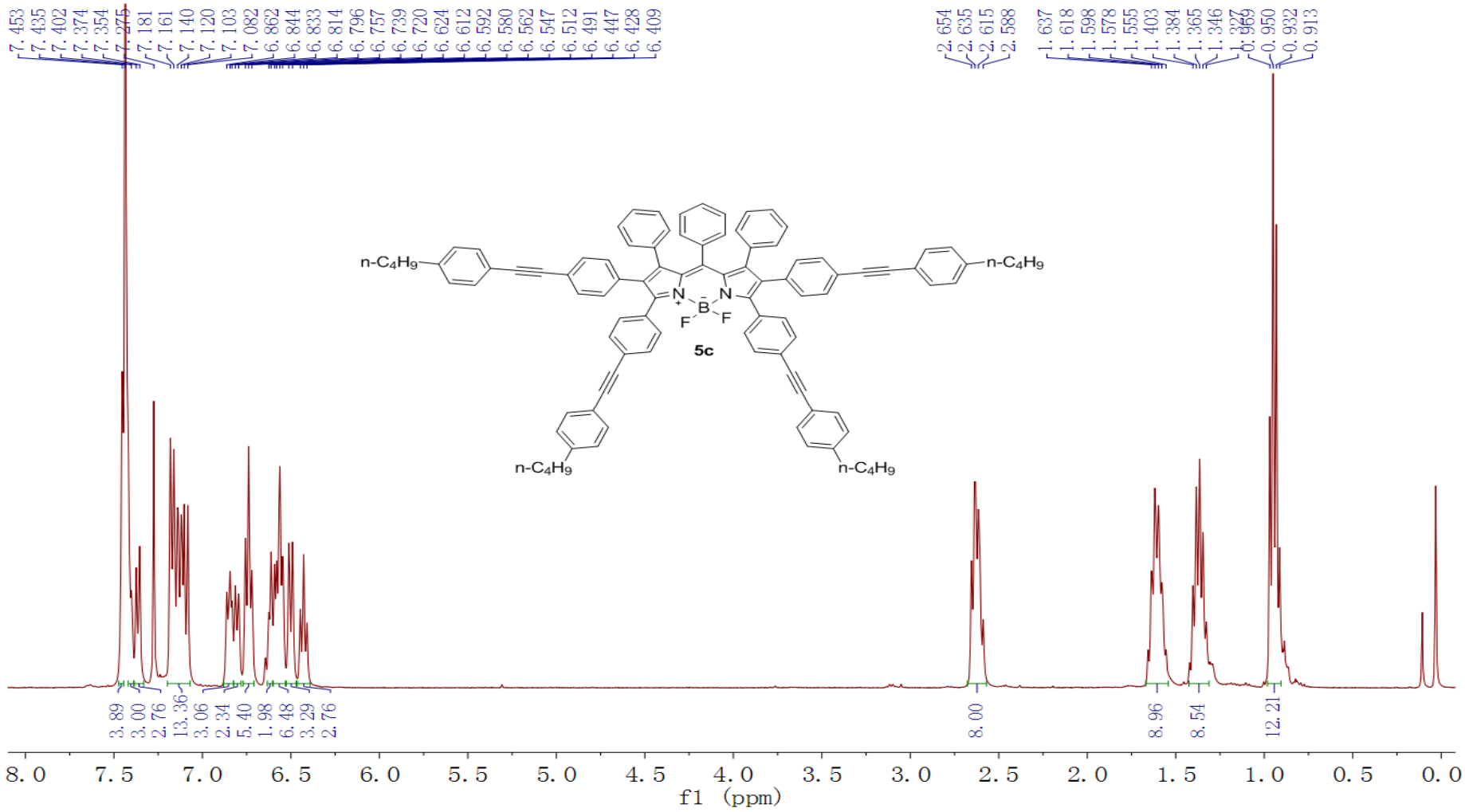
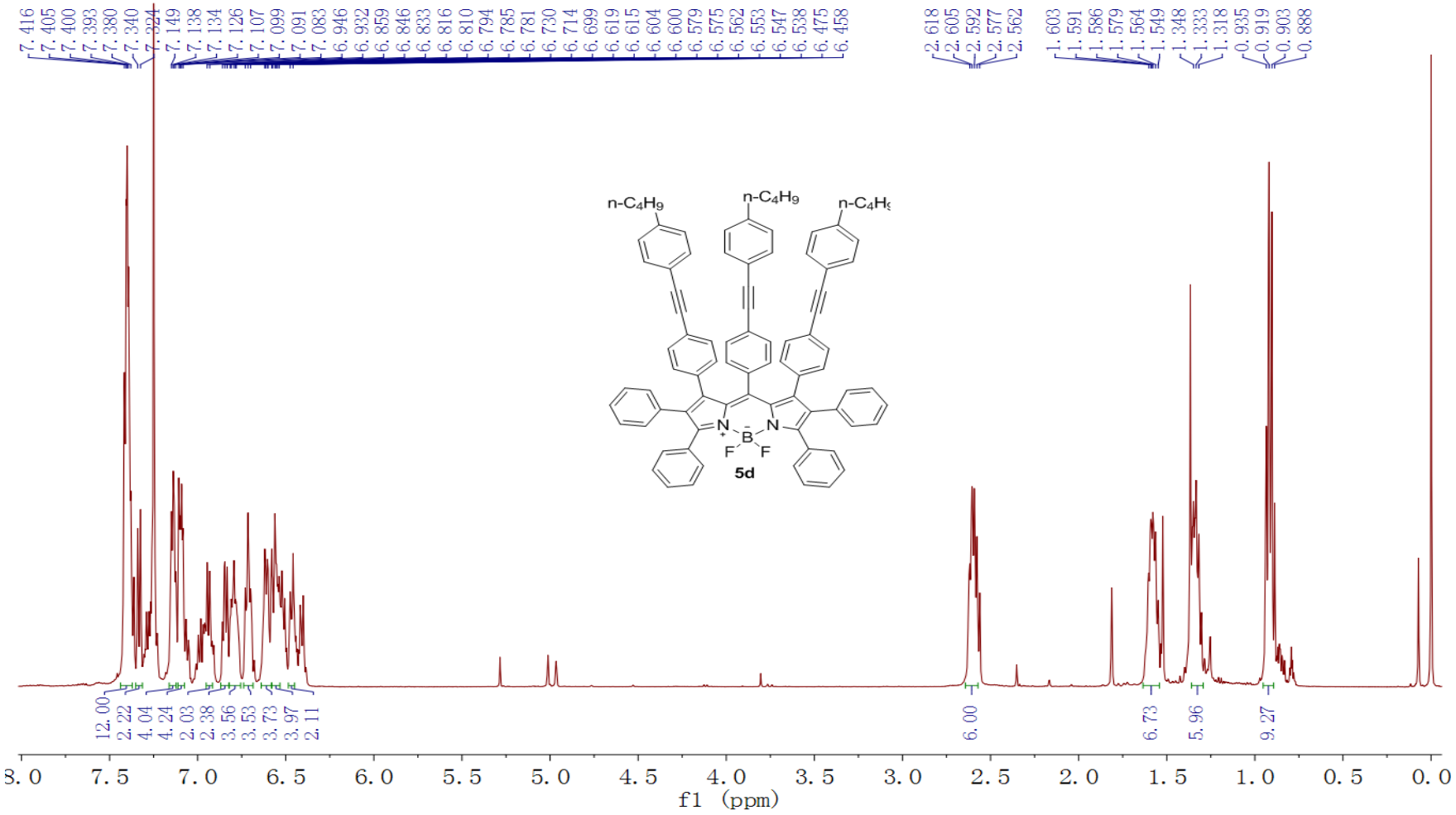


**Figure S90**. The $^{1}$H NMR spectra of **5d.**



# 7. UV and FL of heptaaryldipyrromethenes and BODIPYs

**Table S2.** The photophysical properties of heptaaryldipyrromethenes and BODIPYs

| | Absorption | | | Absorption | | Emission | | |
|---|---|---|---|---|---|---|---|---|
| Entry | λmax /nm | ε(L/mol.cm) | Entry | λmax /nm | ε(L/mol.cm) | ex/nm | λmax /nm | $\Phi_F$[a] |
| **2a** | 542 | 5600 | **3a** | 570 | 55800 | 577 | 604 | 0.30 |
| **2b** | 540 | 4310 | **3b** | 582 | 74200 | 590 | 626 | 0.15 |
| **2c** | 560 | 9150 | **3c** | 581 | 75000 | 589 | 619 | 0.21 |
| **2d** | 560 | 8390 | **3d** | 579 | 62400 | 585 | 618 | 0.22 |
| **2e** | 564 | 10600 | **3e** | 591 | 8300 | 590 | 635 | 0.26 |
| **2f** | 565 | 12900 | **3f** | 596 | 18800 | 600 | 640 | 0.17 |
| **2g** | 559 | 10900 | **3g** | 588 | 15000 | 594 | 627 | 0.2 |
| **2h** | 564 | 7320 | **3h** | 586 | 42700 | 596 | 627 | 0.26 |
| **2i** | 558 | 2130 | **3i** | 580 | 115000 | 591 | 620 | 0.21 |
| **2j** | 547 | 8740 | **3j** | 568 | 18900 | 567 | 600 | 0.11 |
| **2k** | 540 | 6100 | **3k** | 571 | 44200 | 571 | 605 | 0.07 |
| **2l** | 542 | 5800 | **3l** | 568 | 45200 | 573 | 601 | 0.18 |
| **2m** | 555 | 12650 | **3m** | 577 | 42900 | 584 | 614 | 0.21 |
| **2n** | 550 | 6890 | **3n** | 572 | 16200 | 584 | 606 | 0.02 |
| **4a** | 563 | 8750 | **5a** | 586 | 36540 | 589 | 624 | 0.23 |
| **4b** | 564 | 6890 | **5b** | 587 | 39630 | 591 | 625 | 0.25 |
| **4c** | 580 | 8148 | **5c** | 590 | 48940 | 586 | 632 | 0.15 |
| **4d** | 564 | 11640 | **5d** | 585 | 36210 | 583 | 625 | 0.11 |

a The relative quantum yield is measured based on Rhodamine 6G as external standard.

Rhodamine 6G was dissolved in freshly distilled EtOH and diluted to $1\times10^{-5}$ mol/L. Heptaaryldipyrromethenes (**2a-2n** and **4a-4d**) and corresponding BODIPYs (**3a-3n and 5a-5d)** were dissolved in freshly distilled DCM and diluted to $1\times10^{-5}$ mol/L for absorption and emission measurement.

## 8. Absorbance of 2c-2i, 2l response to acidity

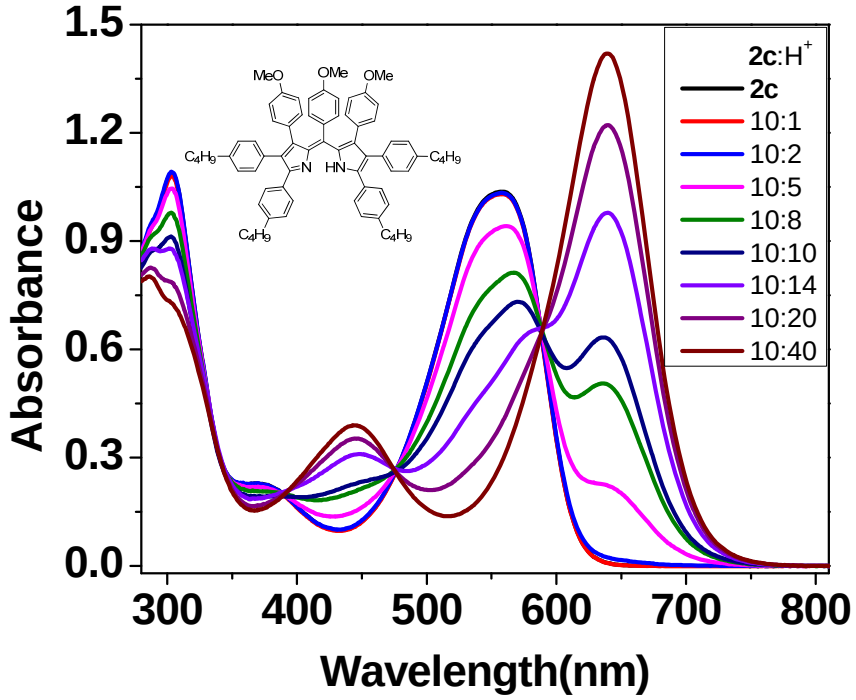



**Figure S91.** The UV absorption spectra of **2c** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

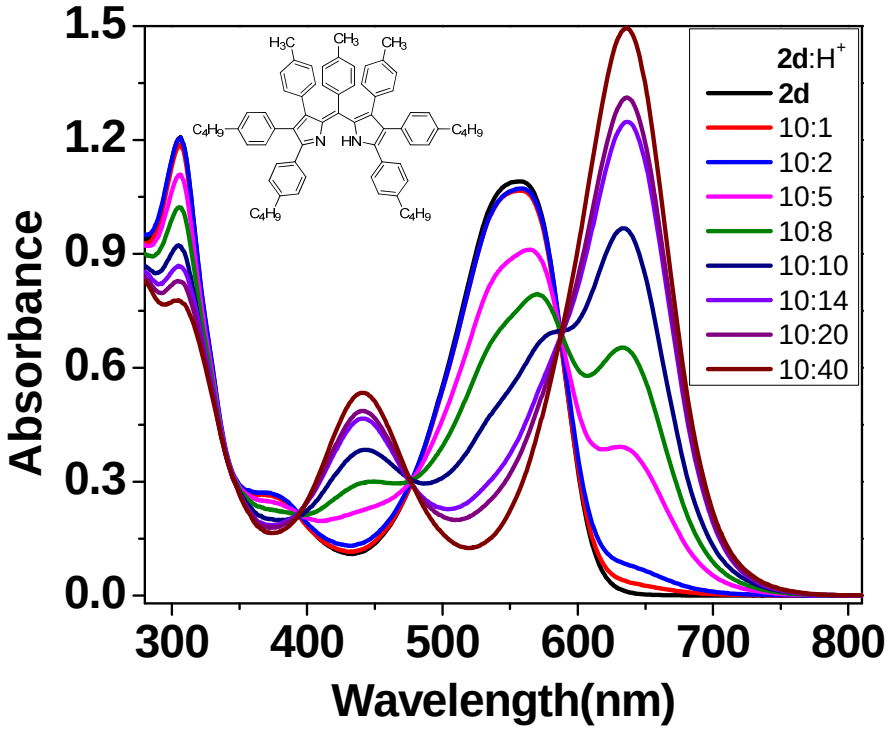



**Figure S92.** The UV absorption spectra of **2d** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

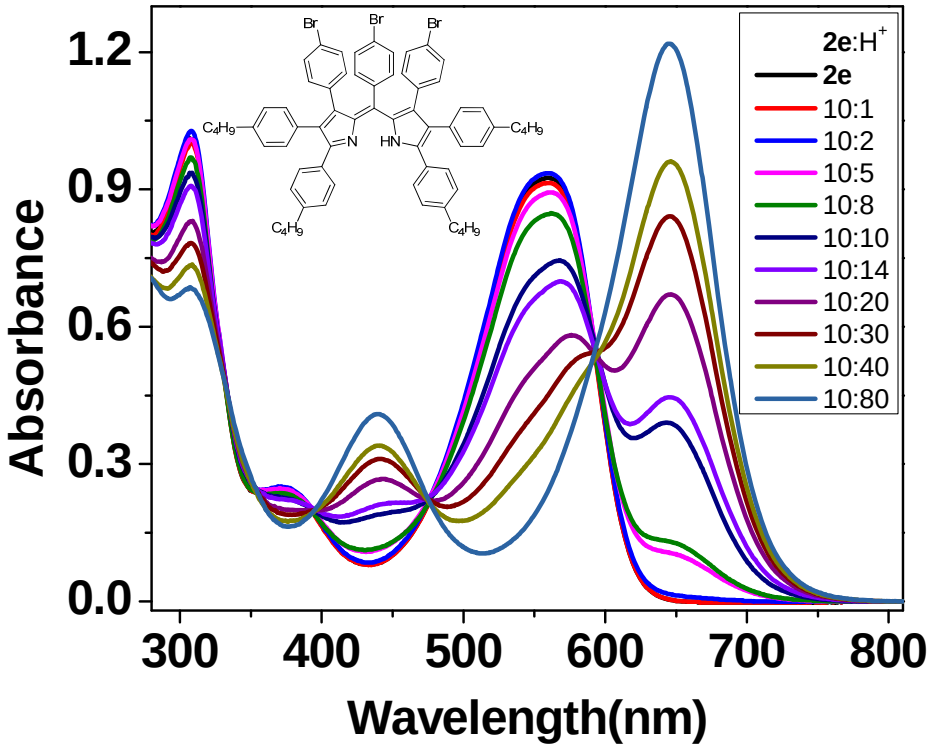



**Figure S93.** The UV absorption spectra of **2e** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

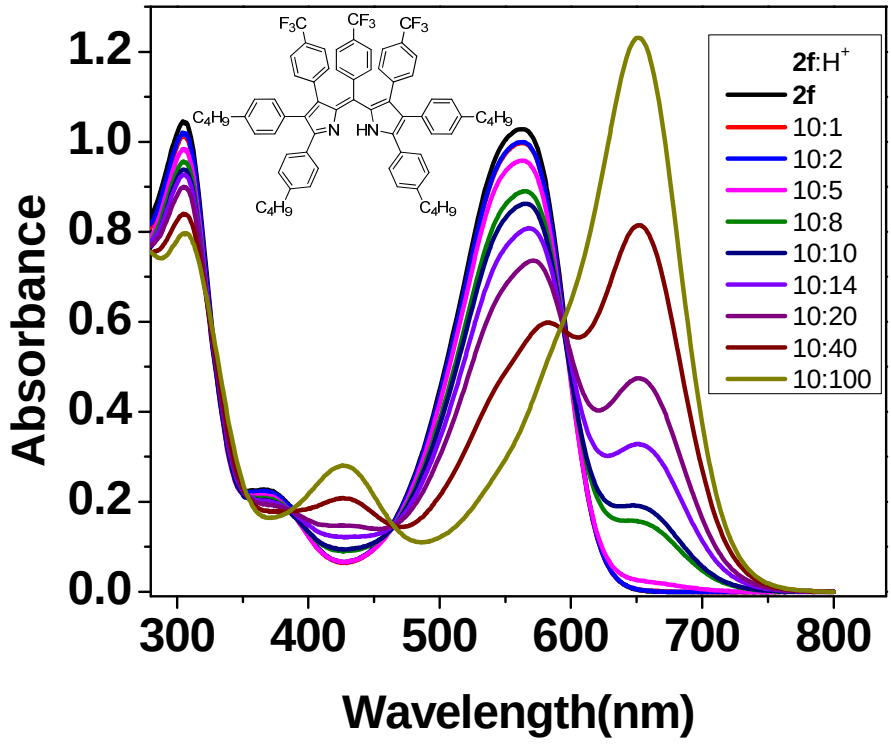



**Figure S94.** The UV absorption spectra of **2f** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

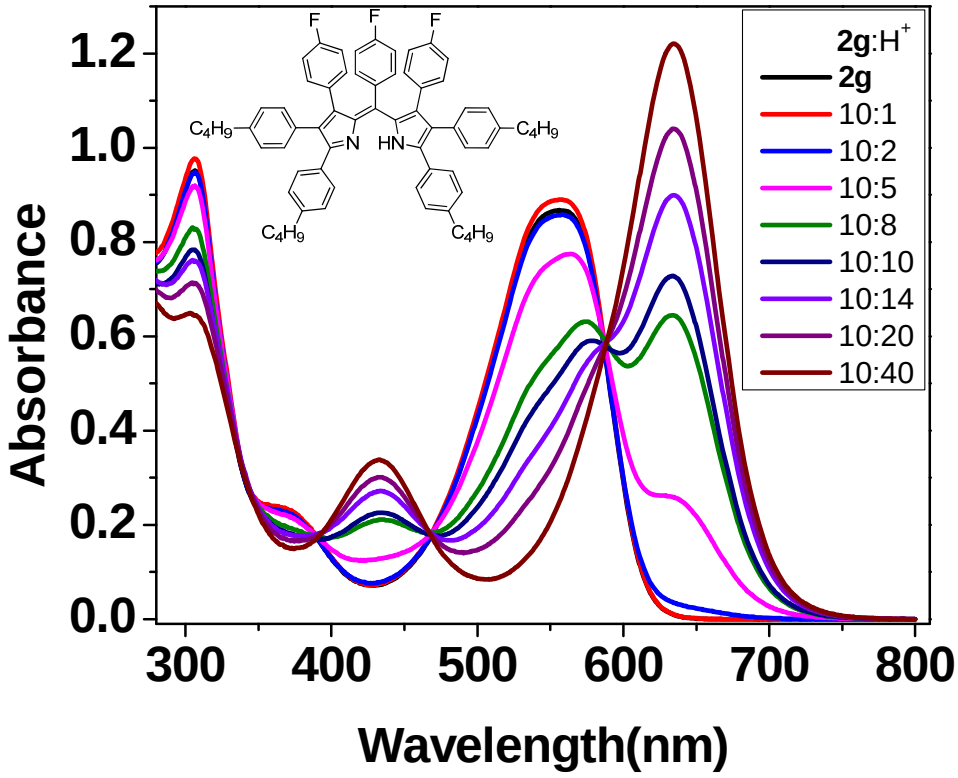



**Figure S95.** The UV absorption spectra of **2g** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

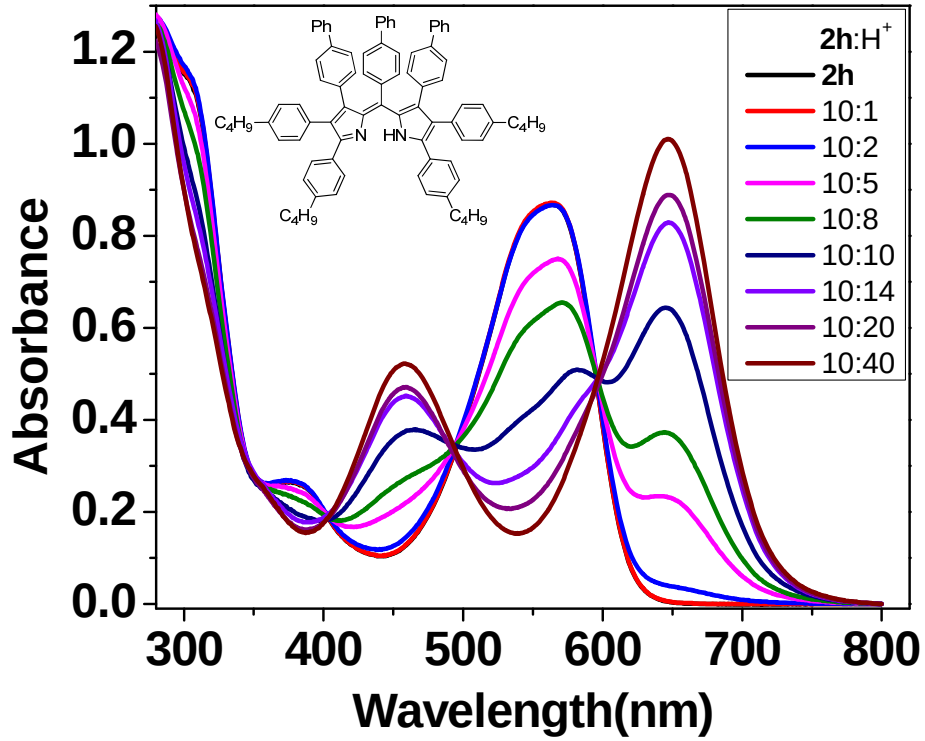



**Figure S96.** The UV absorption spectra of **2h** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

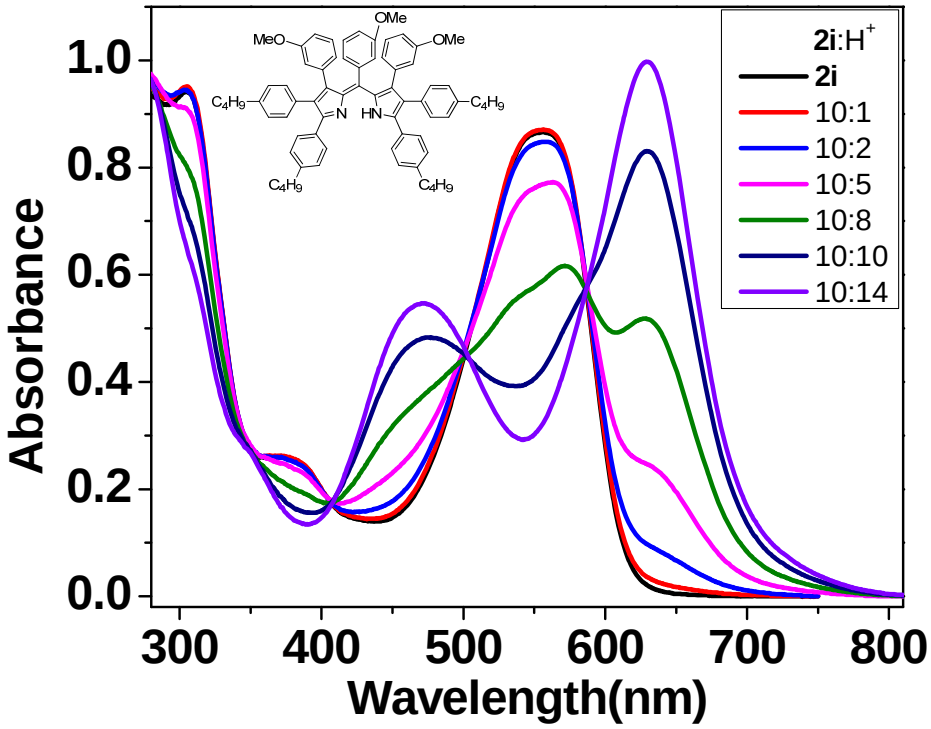



**Figure S97.** The UV absorption spectra of **2i** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).

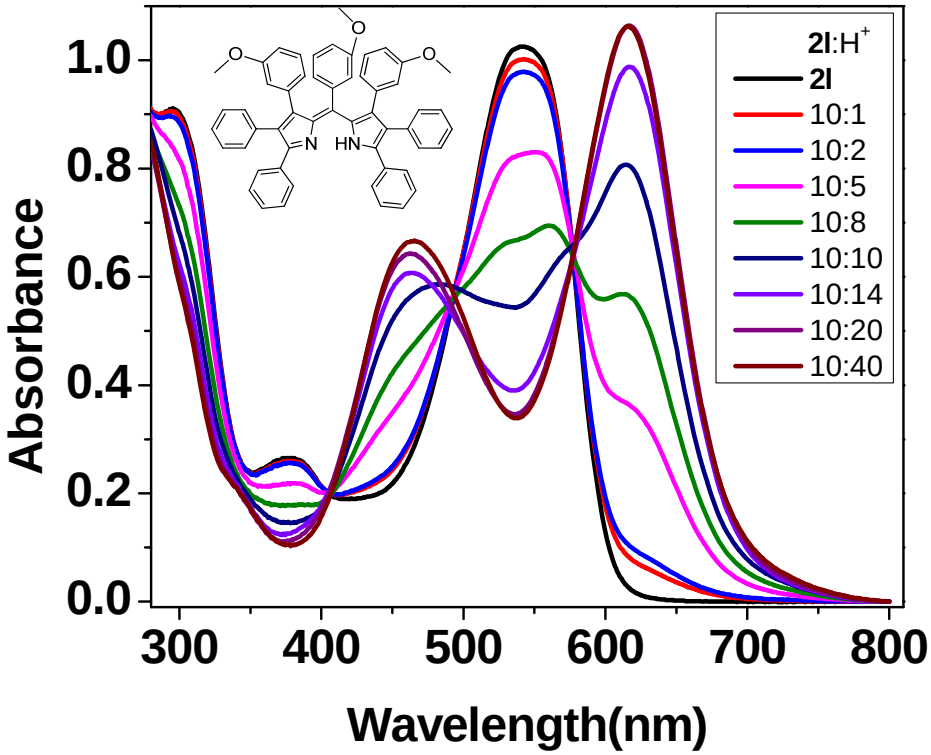



**Figure S98.** The UV absorption spectra of **2l** (the black line) and its response to increased $H^+$ (the colored lines) in THF solution ($10^{-5}$ M).