Supplementary Information of

Probing the Intermolecular Interactions of Aromatic Amides Containing *N*-heterocycles and Triptycene

*Nongyi Cheng, Qifan Yan, Shuai Liu, Dahui Zhao**

Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Email: dhzhao@pku.edu.cn

General Methods. Chemicals were used as received unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded on Mercury plus 300 (300 MHz), Bruker Avance 400 (400 MHz), or Bruker-500 MHz Avance III (500 MHz). Chemical shifts in ^{1}H and ^{13}C NMR spectra were reported in parts per million (ppm) with internal references of TMS (0 ppm) and DMSO-d_6 (2.50 ppm) for ^{1}H and DMSO-d_6 (40.45 ppm) for ^{13}C spectra. ESI mass spectra were recorded on a Bruker APEX IV mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Melting points were measured with a SGW-X4 melting point apparatus equipped with a microscopy and a JM628 digital thermometer. Thermal gravity analyses (TGA) were carried out on a TA Instrument SDT Q600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter under nitrogen atmosphere.

X-ray Crystallography.

Single crystals of **1** and **2** were obtained by vapor diffusion of methanol into a

solution of **1** or **2** in DMF. Single crystals of **2a**, **1b**, **2c**, and **3** were obtained by slowly evaporating solutions of corresponding molecules in 1,4-dioxane, chloroform, chloroform, and methanol, respectively. Other solvents including THF, ethyl acetate, ethanol, dichloromethane, acetonitrile and acetone were also tried via either solvent evaporation or diffusion method, but did not provide good-quality crystals. Single crystal data were collected on MM007HF Saturn724+ and ST Saturn724+.

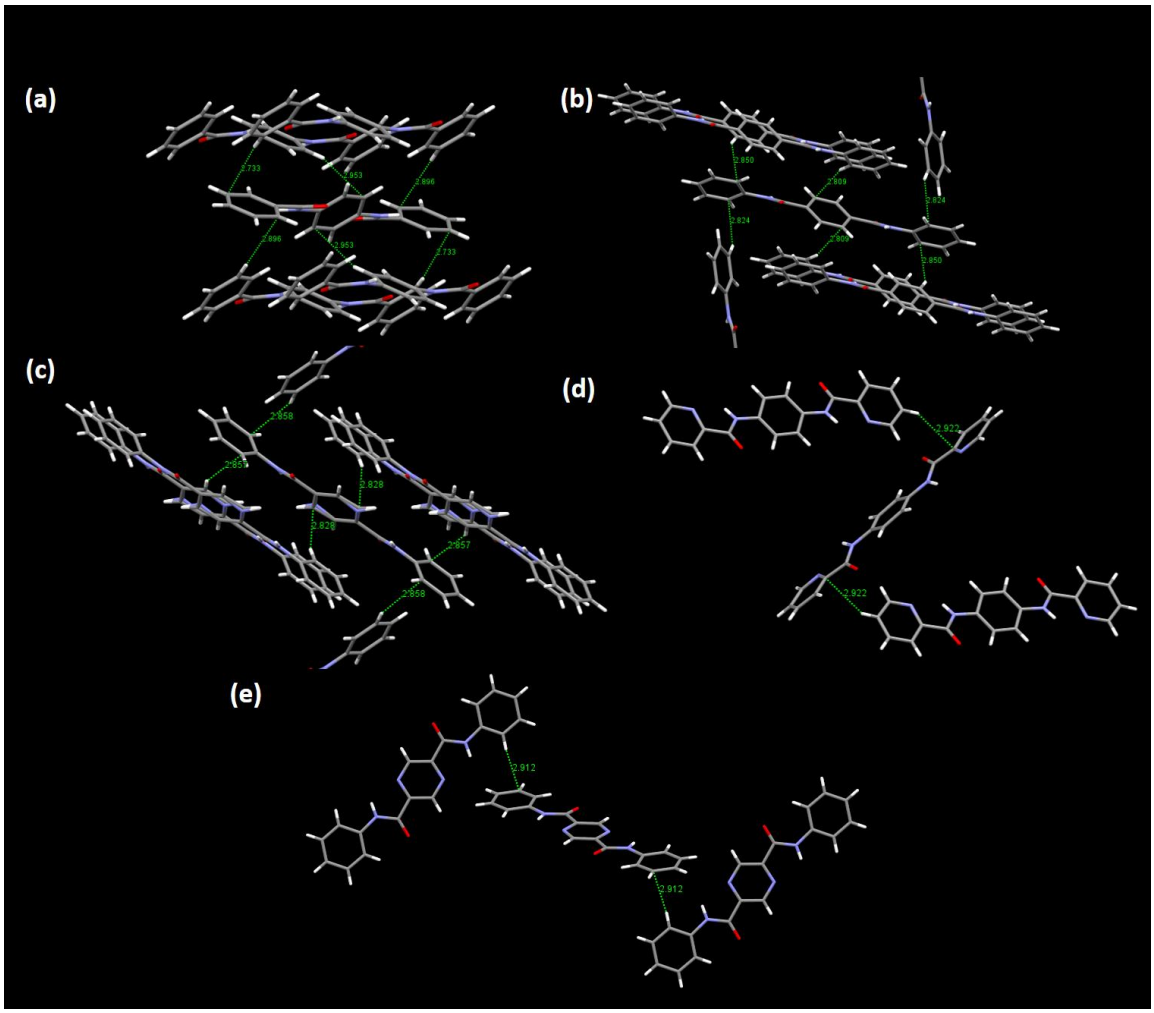


Fig. S1 CH-π contacts[1] in crystal structures of **1** (a)**, 2** (b)**, 2a** (c)**, 1b** (d) and **2c** (e) (gray: C; blue: N; red: O; white: H).

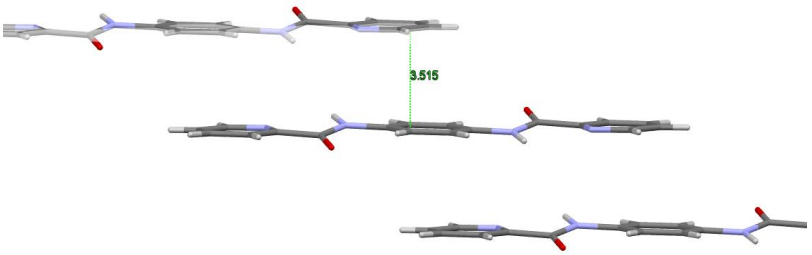


Fig. S2 Face-to-face aromatic stacking among **1b** in the crystal (gray: C; blue: N; red: O; white: H)

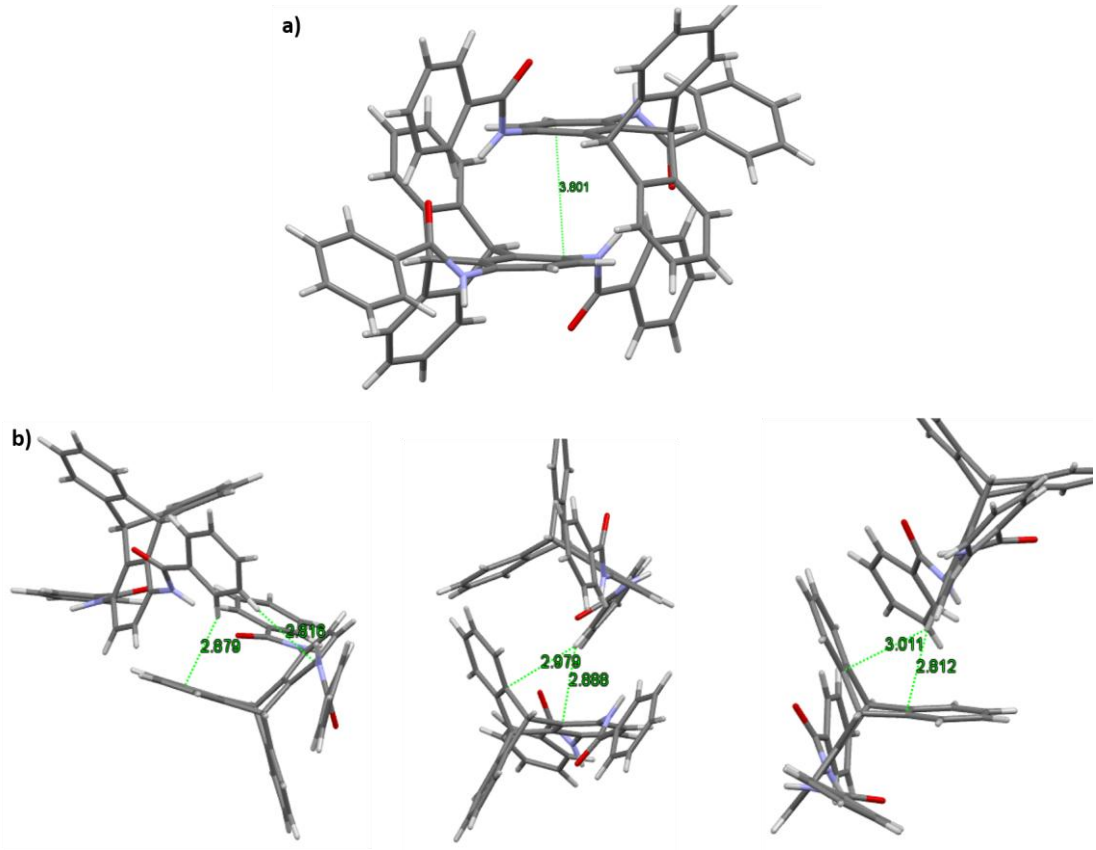


Fig. S3 Aromatic stacking (a) and CH-π (b) interactions among **3** in the crystal (gray: C; blue: N; red: O; white: H).

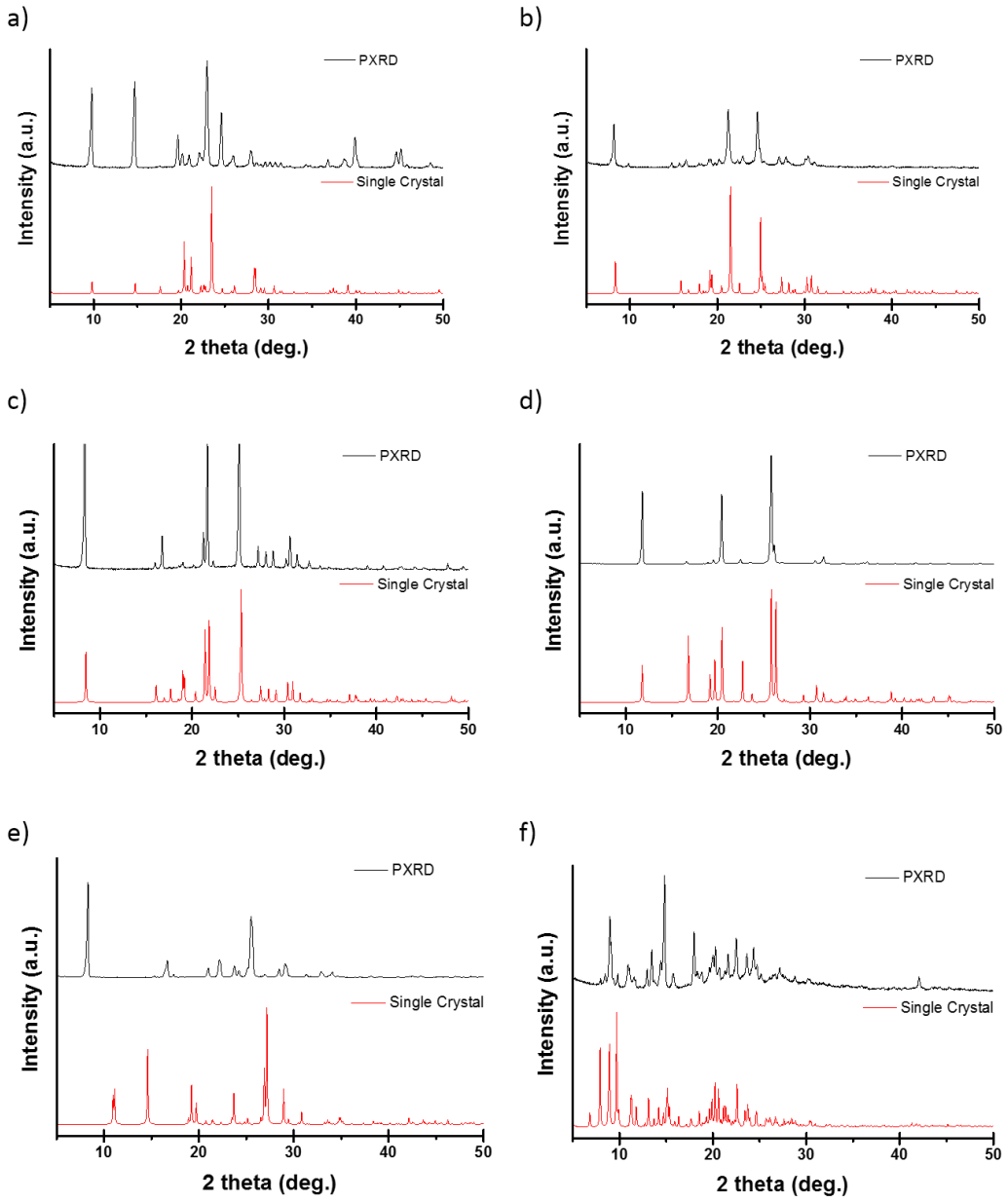


Fig. S4 Powder XRD patterns of **1** (a), **2** (b), **2a** (c), **1b** (d), **2c** (e) and **3** (f) in comparison with those simulated from single crystals.

Syntheses of *tert*-butyl substituted analogues of 1, 2, 2a and 2c.

***N,N'*-(1,4-phenylene)bis(4-(*tert*-butyl)benzamide)** (analogue of **1**) A synthesis procedure similar to that of **1** was adopted. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.05 (s, 2H), 7.84 (d, 4H, J = 8.4 Hz), 7.62 (s, 4H), 7.47 (d, 4H, J = 8.4 Hz), 1.35 (s, 18 H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 165.2, 154.2, 134.9, 132.2, 127.4, 125.0,

120.5, 34.6, 30.9.

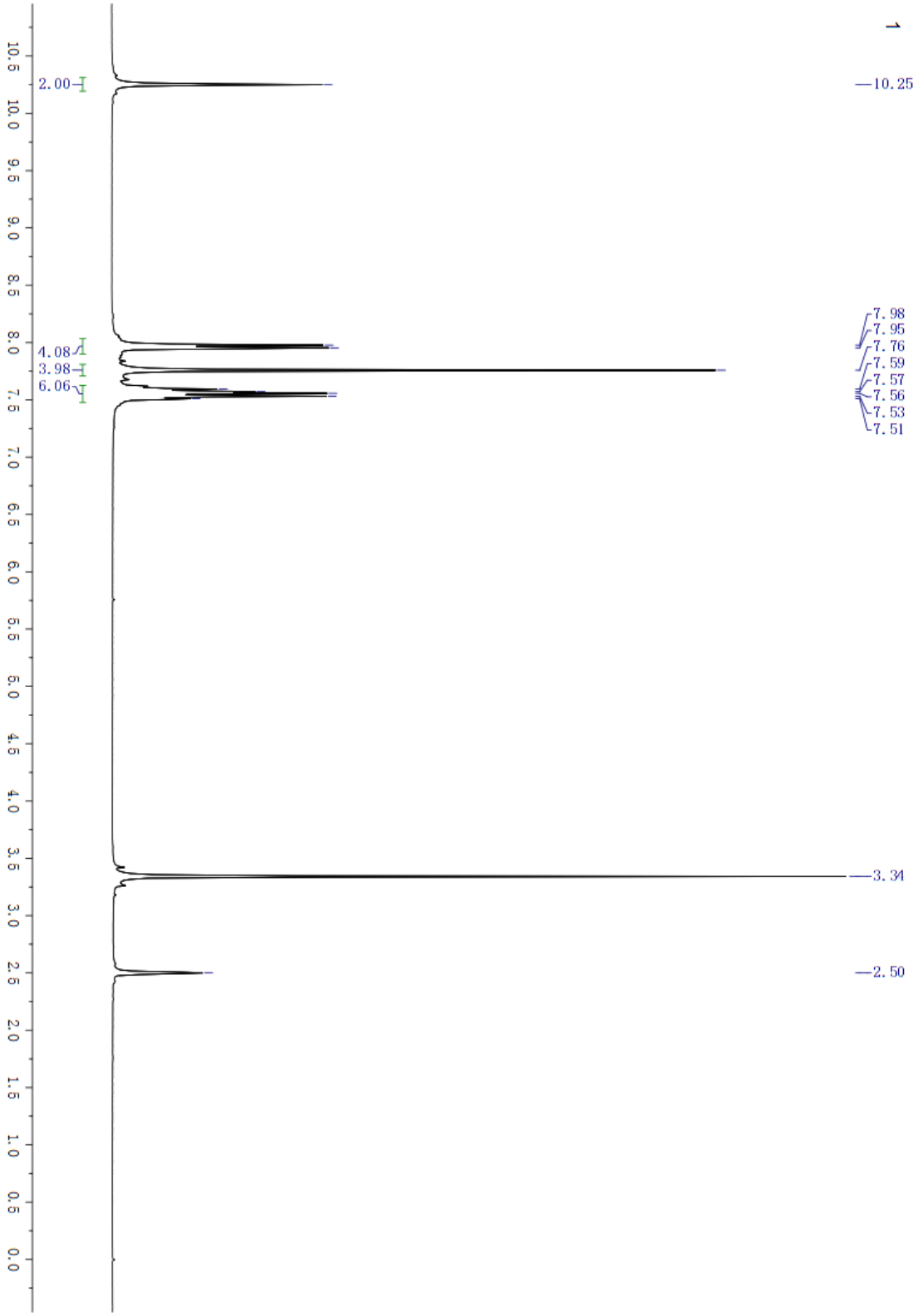
***N,N'*-bis(4-(*tert*-butyl)phenyl)terephthalamide** (analogue of **2**)[2] A synthesis procedure similar to that of **2** was adopted. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.97 (s, 2H), 7.92 (s, 4H), 7.59 (d, 4H, J = 8.7 Hz), 7.40 (d, 4H, J = 8.4 Hz), 1.33 (s, 18 H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 164.5, 146.2, 137.3, 136.3, 127.6, 125.2, 120.2, 34.0, 31.1.

***N,N'*-bis(4-(tert-butyl)phenyl)pyridine-2,5-dicarboxamide** (analogue of **2a**) A synthesis procedure similar to that of **2a** was adopted. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.92 (s, 1H), 9.07 (s, 1H), 8.32-8.35 (m, 2H), 8.05 (s, 1H), 7.70 (d, 2H, J = 8.7 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.43 (d, 2H, J = 3.0 Hz), 7.40 (d, 2H, J = 3.0 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 163.1, 161.6, 151.8, 147.7, 146.6, 146.5, 137.2, 136.1, 135.6, 132.9, 125.32, 125.28, 121.9, 120.2, 34.1, 31.2.

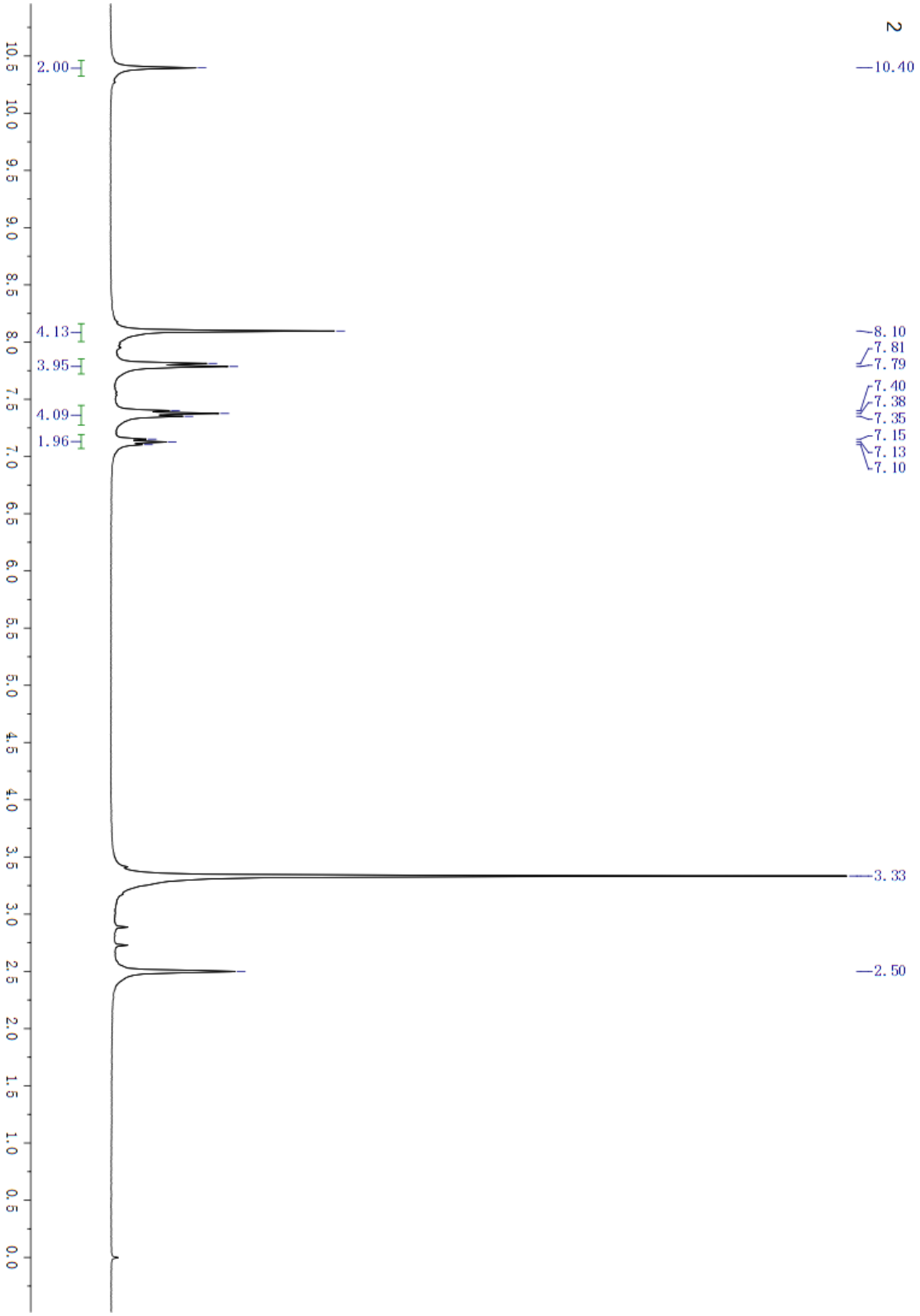
***N,N'*-bis(4-(tert-butyl)phenyl)pyrazine-2,5-dicarboxamide** (analogue of **2c**)[3] A synthesis procedure similar to that of **2c** was adopted. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.68 (s, 2H), 9.49 (s, 2H), 7.72 (d, 4H, J = 8.4 Hz), 7.44 (d, 4H, J = 9.0 Hz), 1.35 (s, 18H).

Copies of ^{1}H NMR spectra

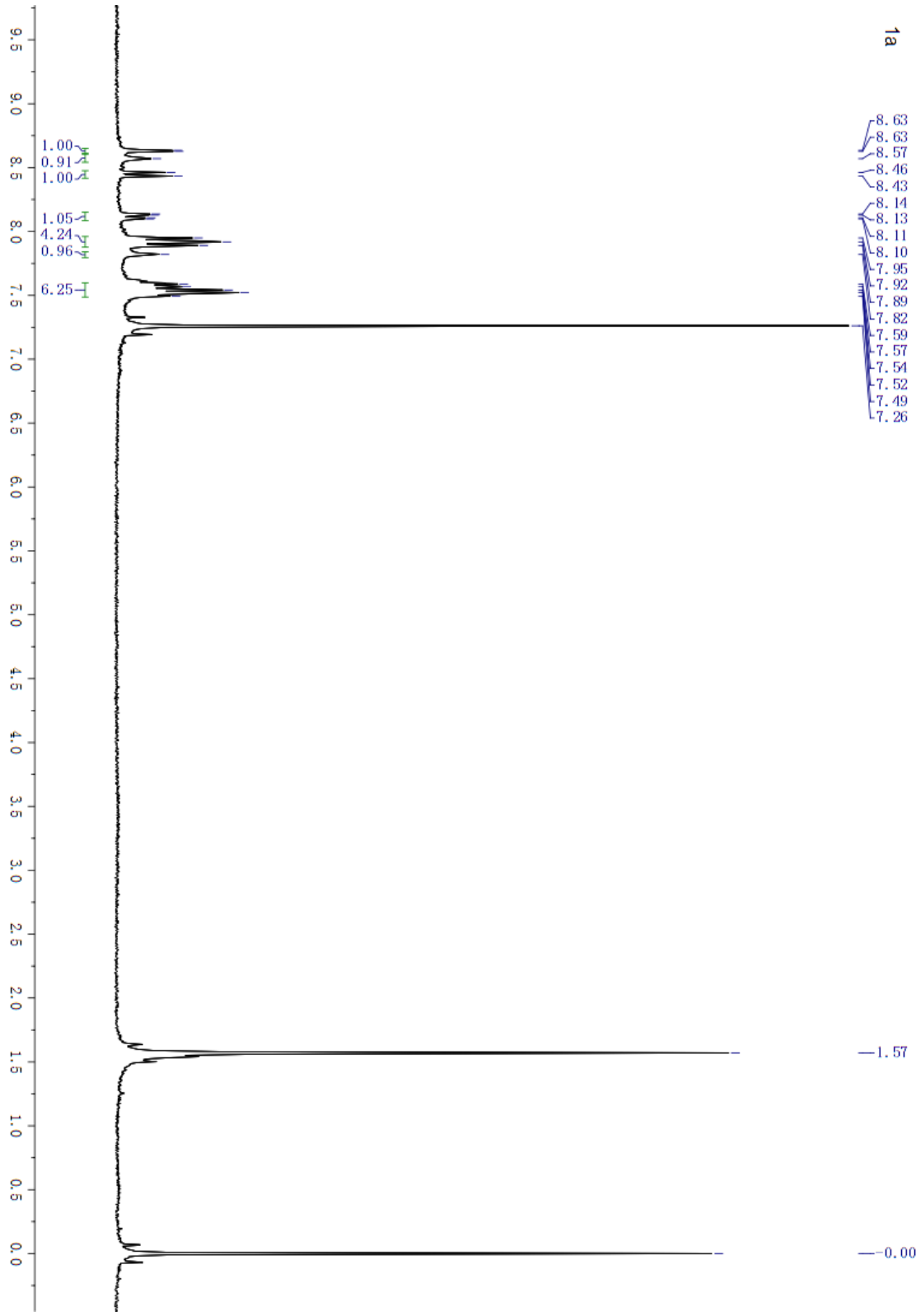
Compound **1**



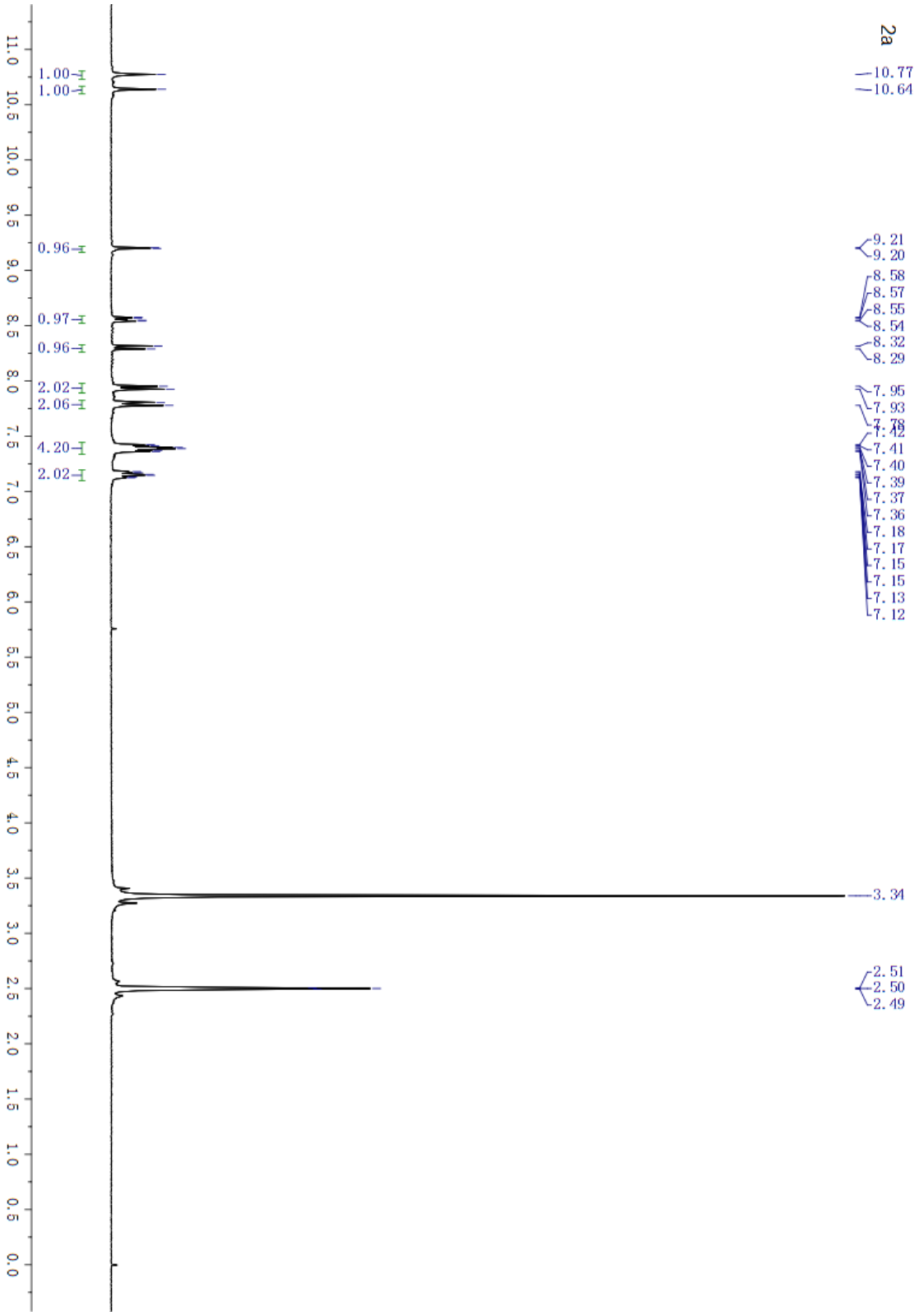
Compound **2**


2
10.40
8.10
7.81
7.79
7.40
7.38
7.35
7.15
7.13
7.10
3.33
2.50
2.00
4.13
3.95
4.09
1.96

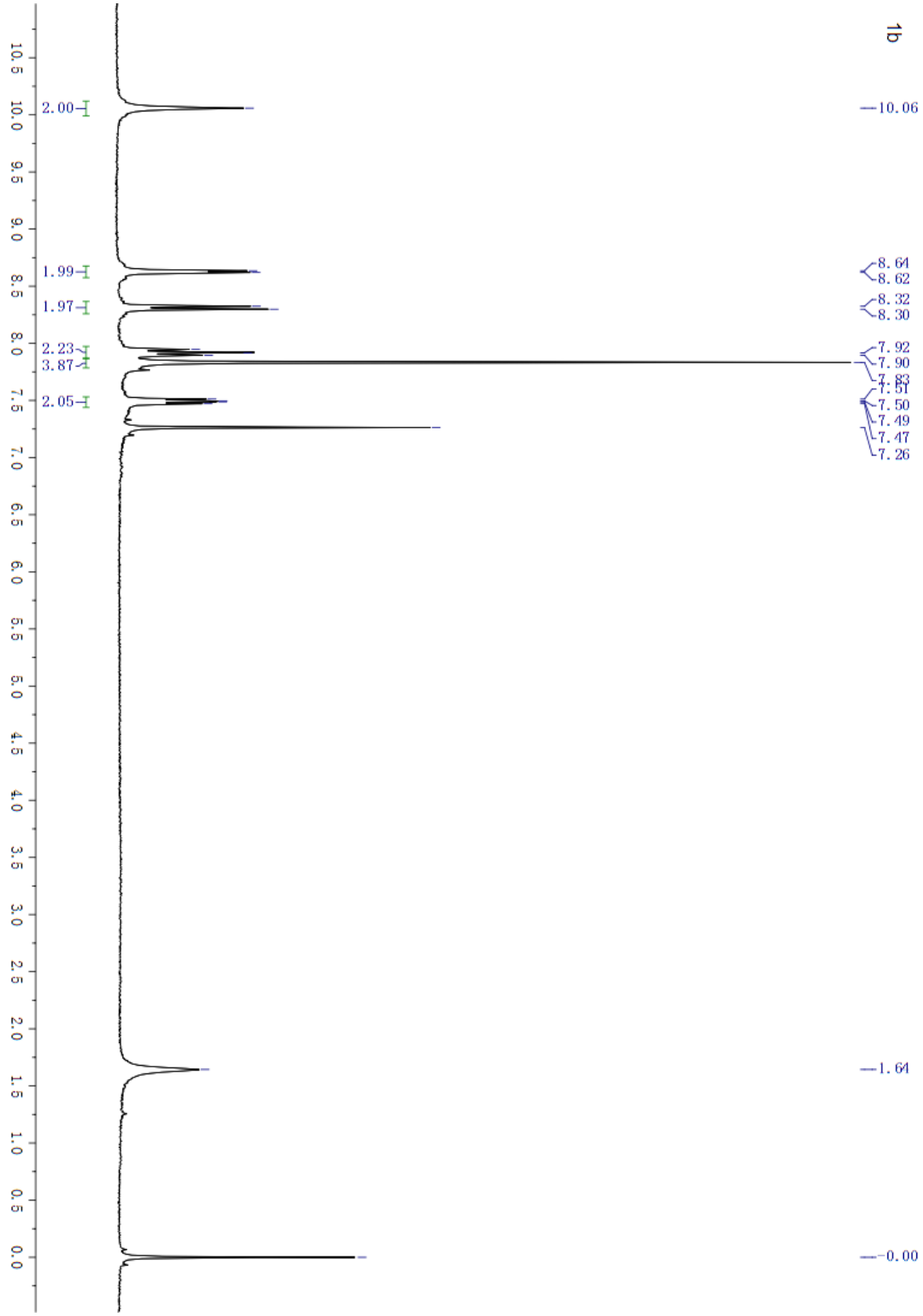
Compound **1a**


1a
8.63
8.63
8.57
8.46
8.43
8.14
8.13
8.11
8.10
7.95
7.92
7.89
7.82
7.59
7.57
7.54
7.52
7.49
7.26
1.00
0.91
1.00
1.05
4.24
0.96
6.25
1.57
0.00

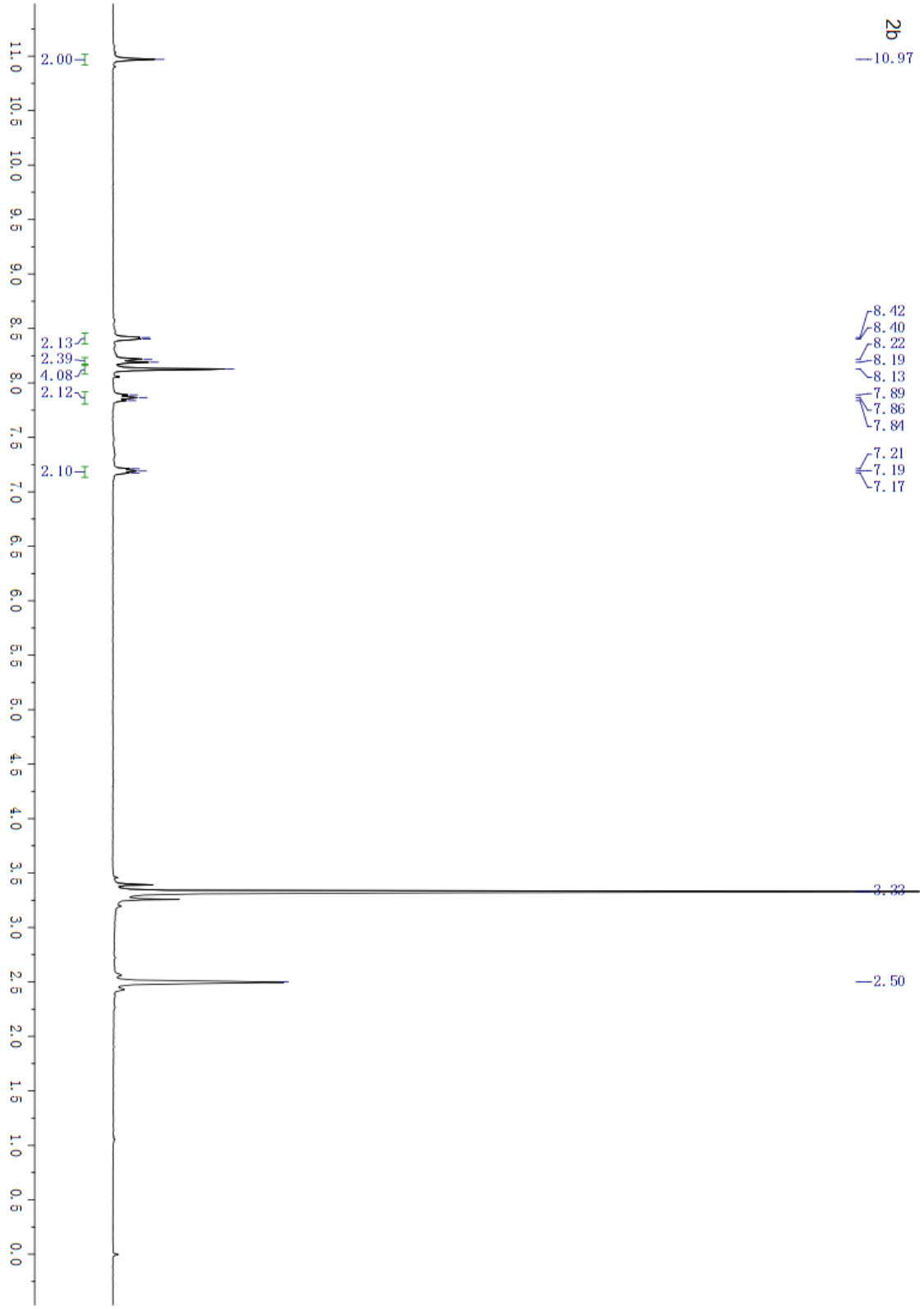
Compound **2a**


2a
1.00
1.00
0.96
0.97
0.96
2.02
2.06
4.20
2.02
10.77
10.64
9.21
9.20
8.58
8.57
8.55
8.54
8.32
8.29
7.95
7.93
7.78
7.42
7.41
7.40
7.39
7.37
7.36
7.18
7.17
7.15
7.15
7.13
7.12
3.34
2.51
2.50
2.49

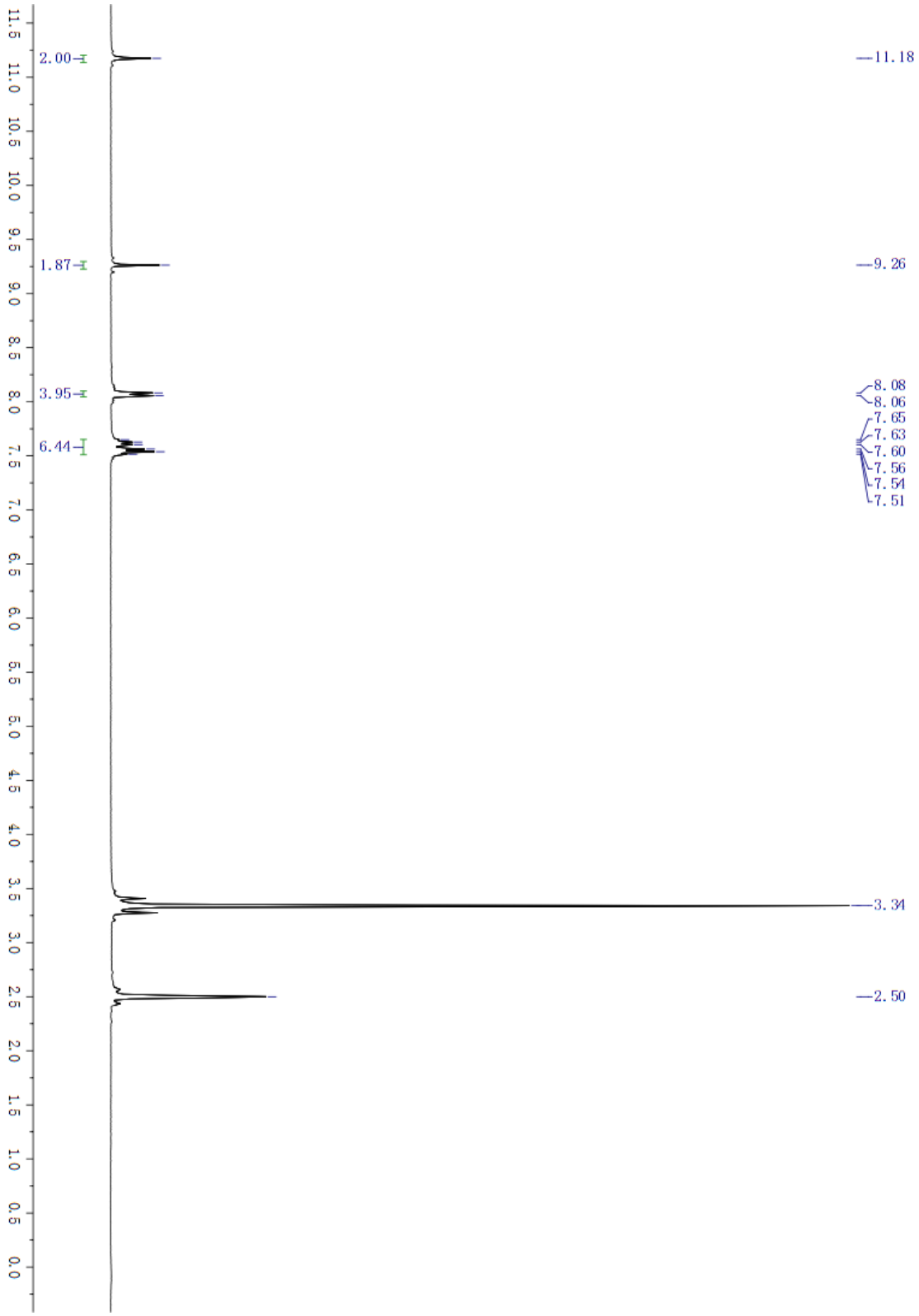
Compound **1b**


1b
10.06
8.64
8.62
8.32
8.30
7.92
7.90
7.83
7.51
7.50
7.49
7.47
7.26
1.64
0.00
2.00
1.99
1.97
2.23
3.87
2.05

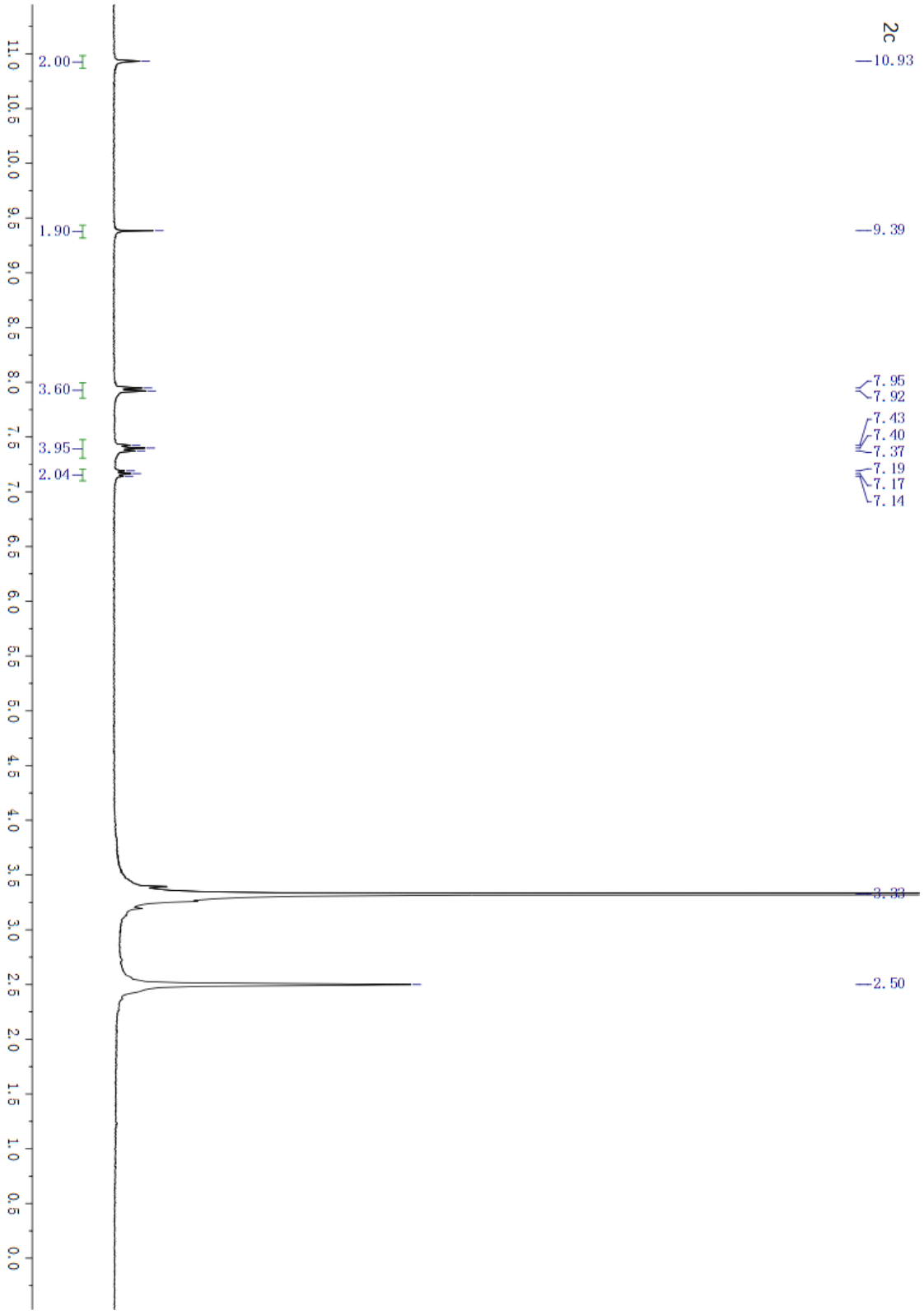
Compound **2b**


2b
10.97
8.42
8.40
8.22
8.19
8.13
7.89
7.86
7.84
7.21
7.19
7.17
3.33
2.50
2.00
2.13
2.39
4.08
2.12
2.10

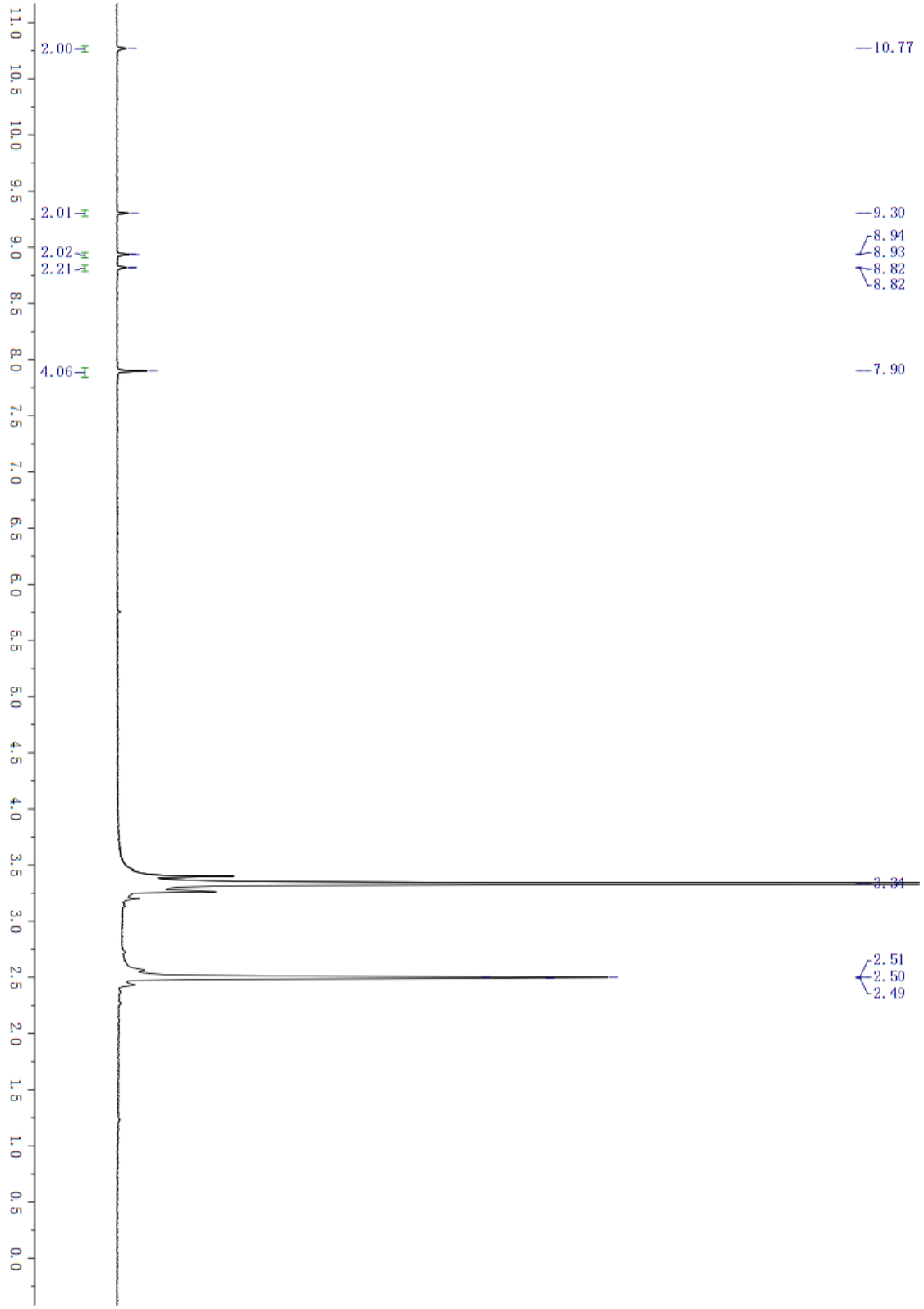
Compound **1c**



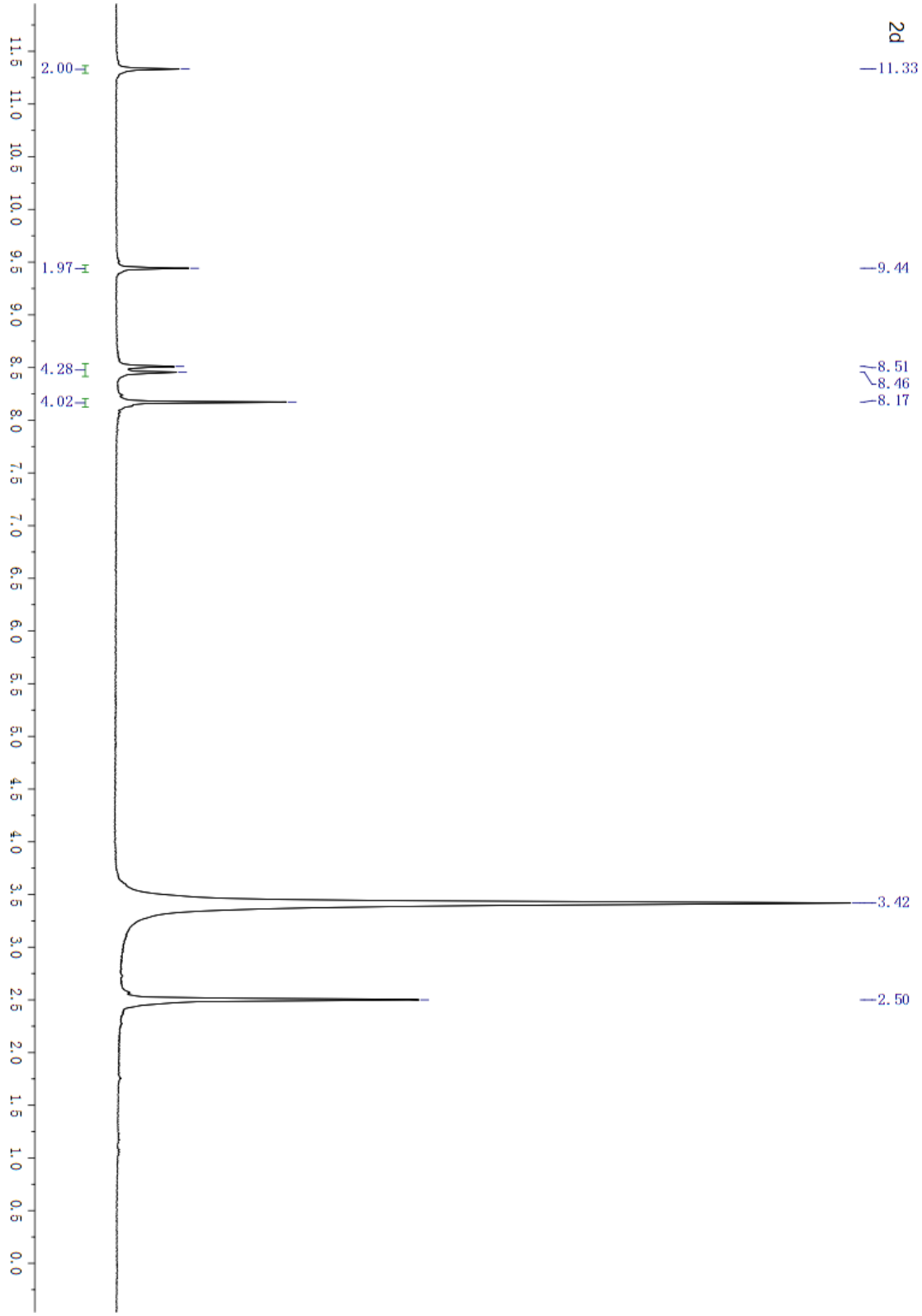
Compound **2c**


2c
2.00
1.90
3.60
3.95
2.04
10.93
9.39
7.95
7.92
7.43
7.40
7.37
7.19
7.17
7.14
3.33
2.50

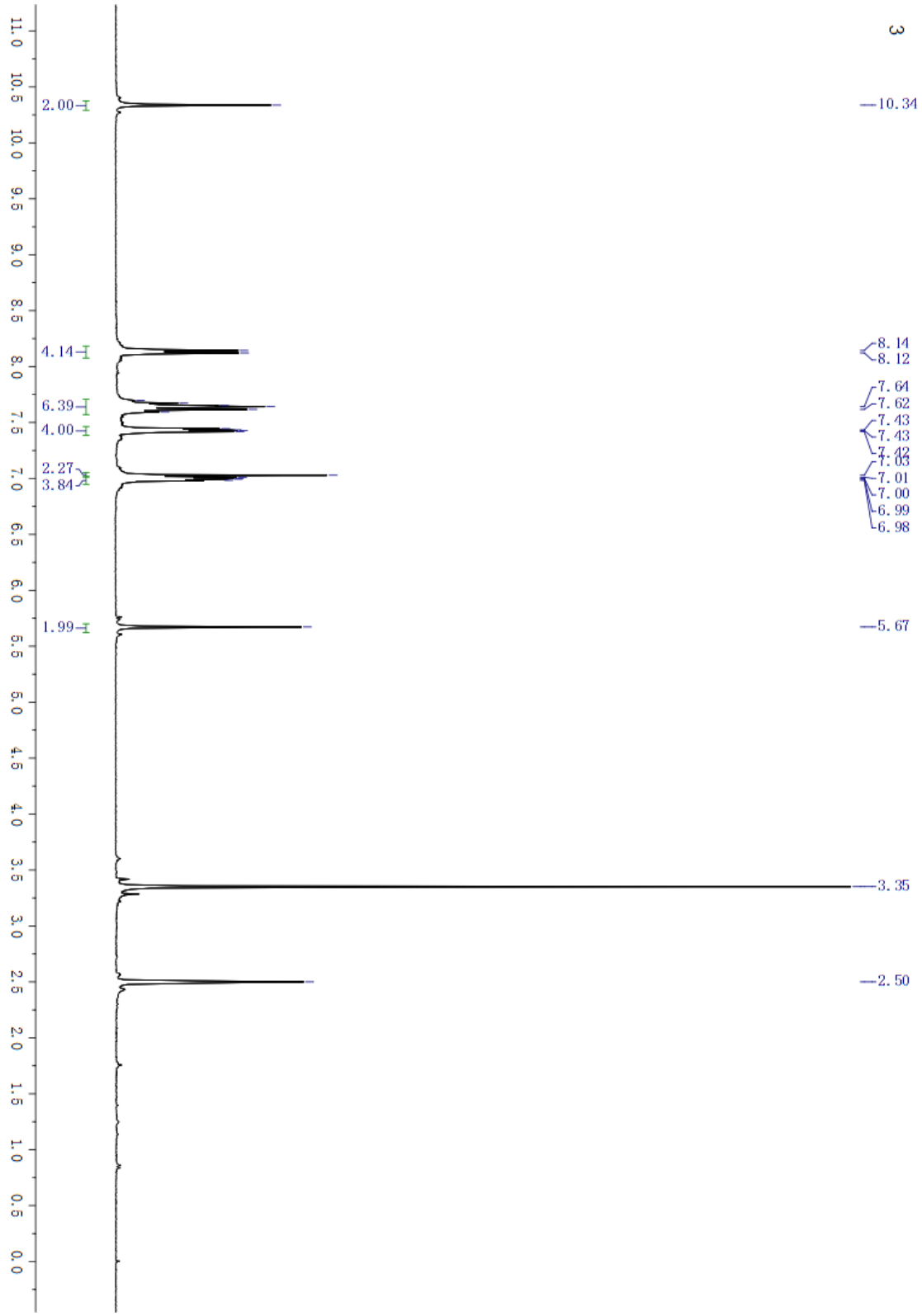
Compound **1d**



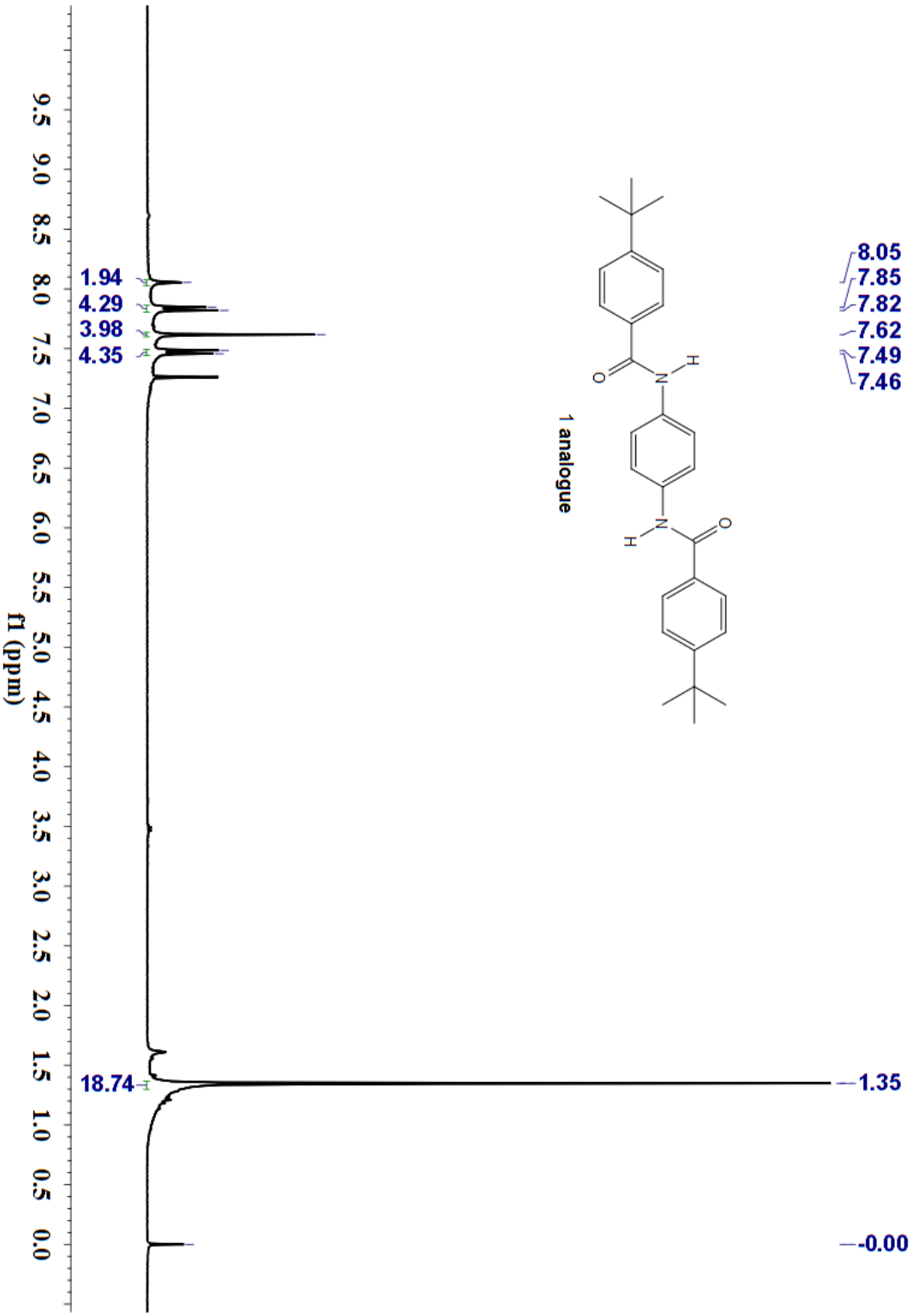
Compound **2d**



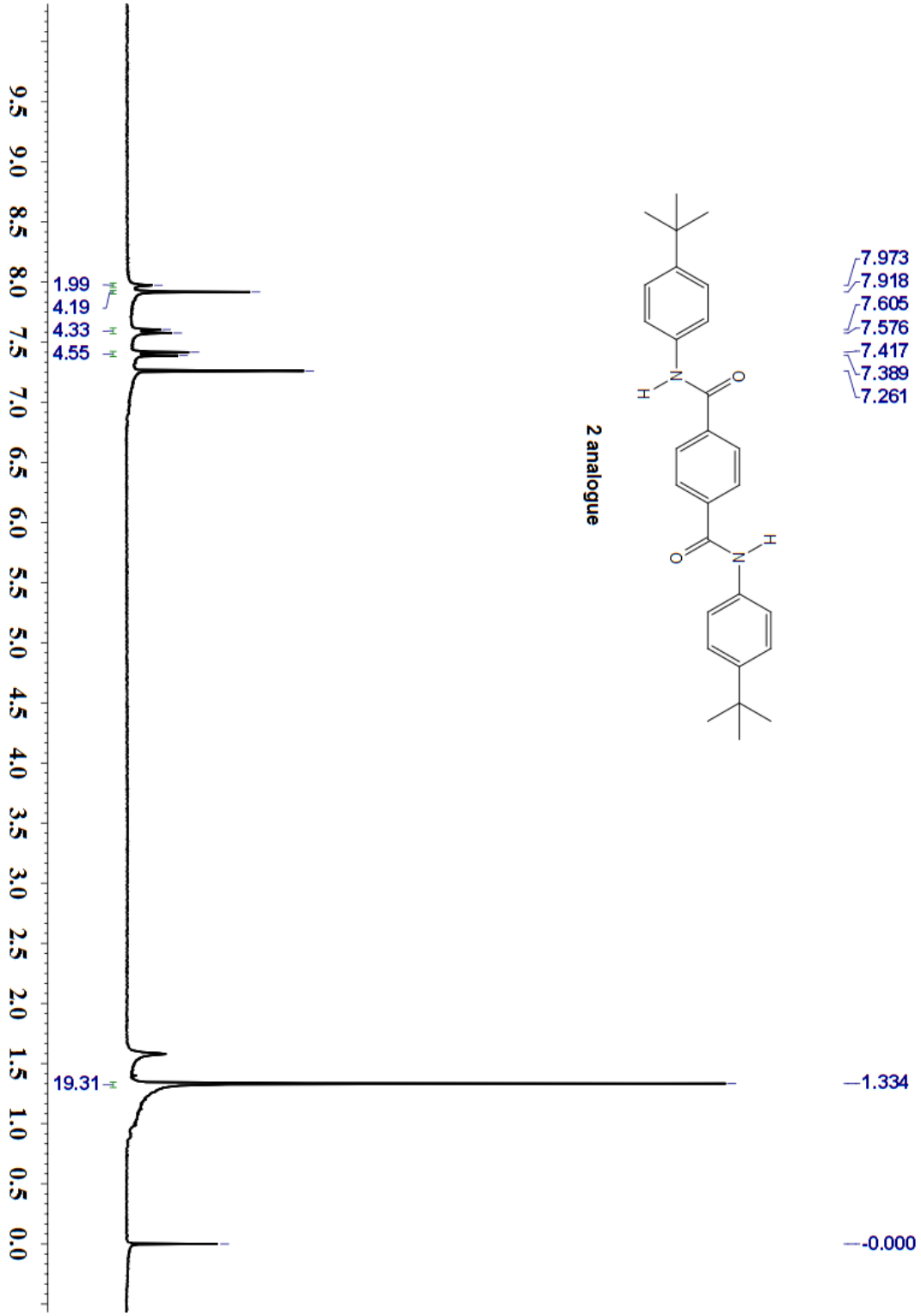
Compound **3**


3
2.00
4.14
6.39
4.00
2.27
3.84
1.99
10.34
8.14
8.12
7.64
7.62
7.43
7.43
7.42
7.03
7.01
7.00
6.99
6.98
5.67
3.35
2.50

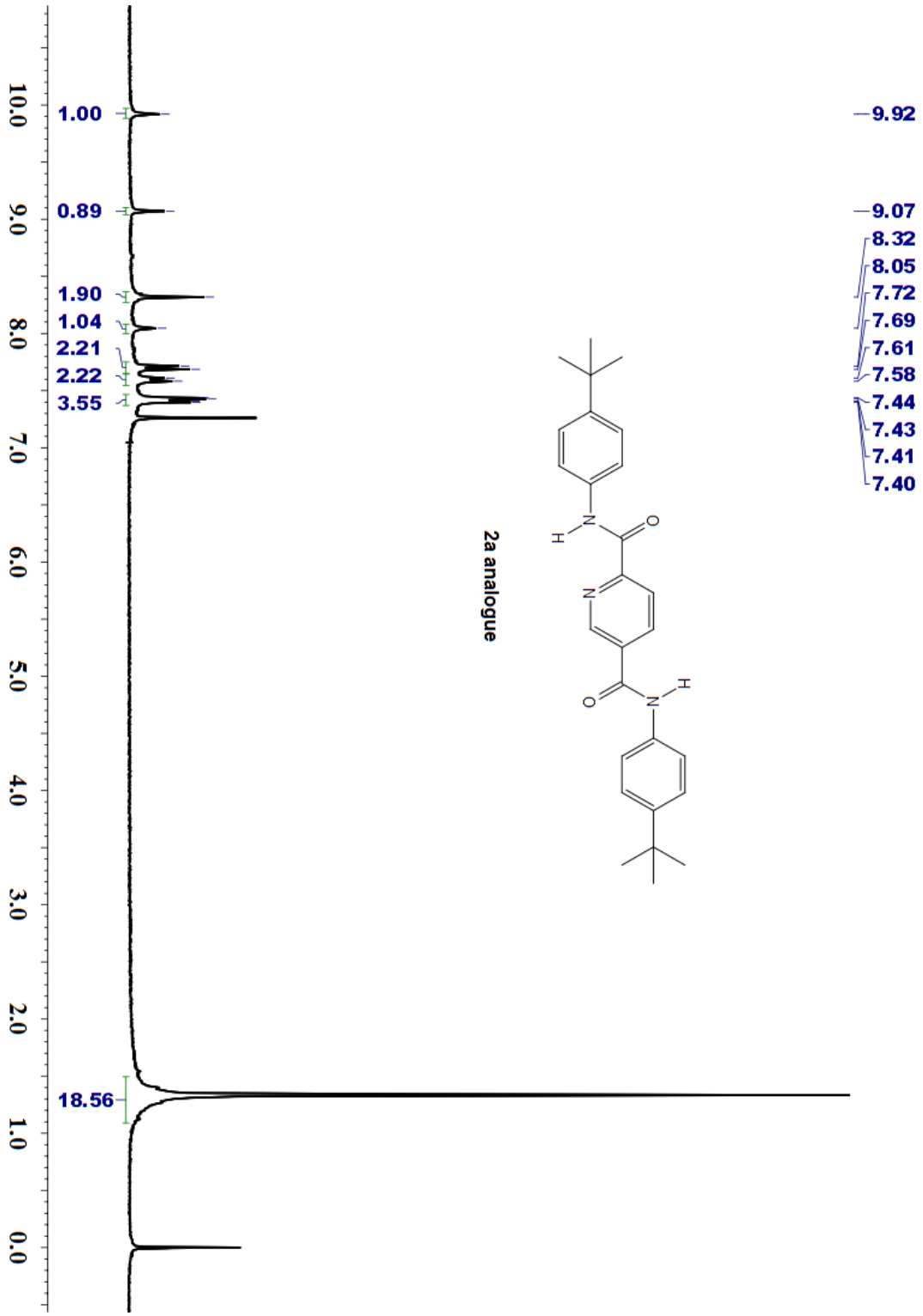
N,*N*'-(1,4-phenylene)bis(4-(*tert*-butyl)benzamide) (analogue of **1**).



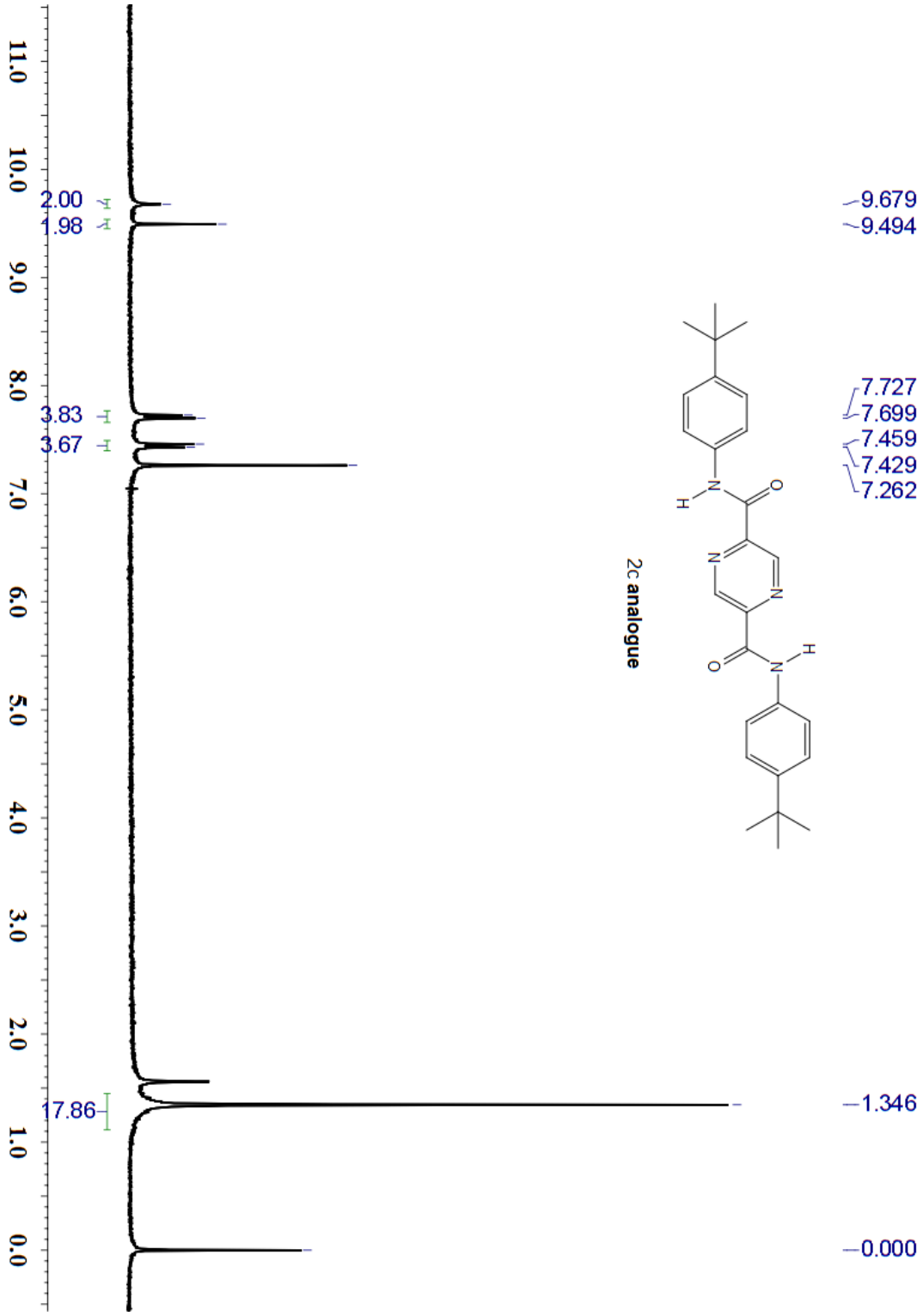
N,*N*'-bis(4-(*tert*-butyl)phenyl)terephthalamide (analogue of **2**)



N,*N*'-bis(4-(tert-butyl)phenyl)pyridine-2,5-dicarboxamide (analogue of **2a**)



N,*N*'-bis(4-(tert-butyl)phenyl)pyrazine-2,5-dicarboxamide (analogue of **2c**).



References

1. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.
2. C. A. Hunter, C. M. R. Low, M. J. Packer, S. E. Spey, J. G. Vinter, M. O. Vysotsky and C. Zonta, *Angew. Chem. Int. Ed.*, 2001, **40**, 2678-2682.
3. ^{13}C NMR data are not available due to the low solubility of the molecule in organic solvents, giving insufficient signal to noise ratio of ^{13}C NMR spectra.