Supporting Information for

Catalyst-free inverse-electron-demand aza-Diels-Alder reaction of 4,4-dicyano-2-methylenebut-3-enoates and 1,3,5-triazinanes: access to polysubstituted tetrahydropyridines

Dezhi Yang,*[a,b] Meng Zhu,[a,b,†] Taimin Wang,[b,†] Yixuan He,[b] Lang Xie,[a,b] Jiayong Zhang,*[b] and Bin Cheng*[a,b]

[a.] *School of Pharmacy, Zunyi Medical University, Zunyi 563000, China. E-mail:lpydz@163.com*

[b.] *Institute of Marine Biomedicine/Postdoctoral Innovation Practice Base, Shenzhen Polytechnic, Shenzhen 518055, China.E-mail: zhangjiayong@mail.nankai.edu.cn; chengbin@szpt.edu.cn*

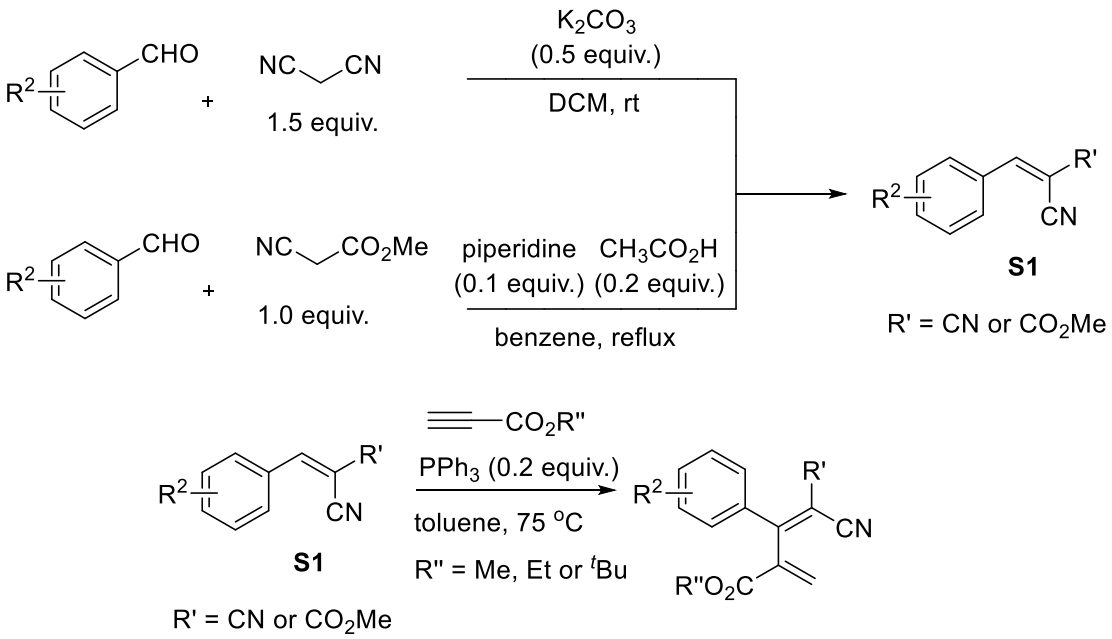
† These authors contributed equally to this work.

Table of Contents

1. General Information

Unless otherwise specified, all reactions were conducted under anhydrous conditions. All solvents were distilled and dried according to the standard procedures. All chemicals or reagents which are commercially available were used without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (GF-254) using UV-light (254 and 365 nm). Column chromatography was performed by using silica gel (200-300 mesh) as stationary phase eluting with petroleum ether (60–90 ℃) and ethyl acetate. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$ on a JEOL 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) and tetramethylsilane (TMS) was used as the internal standard. HRMS spectra were acquired in the ESI mode by using the mass analyzer of TOF. Melting points were determined on a micro melting point apparatus.

2. General Procedures for Synthesis of 1,3-Dienes 1 and 4



The substrate 1,3-dienes **1**[1,2] and **4**[3] were prepared according to the literature.

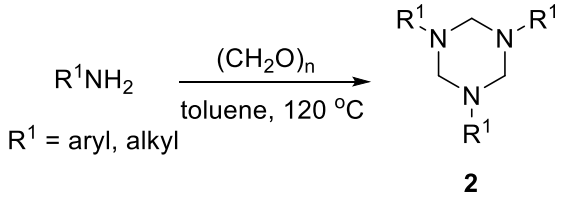
Synthetic procedure for R' = CN. To a solution of aldehyde (1 mmol, 1.0 equiv) and nitrile (1.5 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) was added K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv). The mixture was stirred at room temperature and monitored by TLC until the aldehyde was consumed completely. Then the resulting solution was washed with H_2O, and extracted with CH_2Cl_2. The combined organic layers were washed with brine and

dried over Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure to give a residue, which was purified by silica gel flash column chromatography using petroleum ether/ethyl acetate (5:1) as the eluent to afford **S1**.

Synthetic procedure for R' = CO_2Me. To a solution of aldehyde (10 mmol, 1.0 equiv), methyl cyanoacetate (10 mmol, 1.0 equiv), and piperidine (85 mg, 1.0 mmol) in benzene (20 mL) was added glacial acetic acid (120 mg, 2.0 mmol), and the mixture was headed at refluxing until the starting materials were consumed as indicated by TLC analysis. After being cooled down to room temperature, the reaction mixture was diluted with Sat $NaHCO_3$ and extracted with EtOAc. The combined organic phases were dried with anhydrous Na_2SO_4. The mixture was filtered and the filtrate was concentrated under reduced pressure to give a residue, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) to afford alkene **S1**.

To a solution of **S1** (2.0 mmol) and PPh_3 (105 mg, 0.2 equiv) in toluene (20 mL) at 75 ℃ was added slowly a solution of propiolate (2.4 mmol, 1.2 equiv) in toluene (20 mL) within 3 h. Once the addition was finished, the reaction mixture was cooled down to room temperature. The solvent was evaporated to give a residue, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate (15:1) as the eluent to give the corresponding 1,3-diene substrate.

3. General Procedures for Synthesis of 1,3,5-triazinanes 2

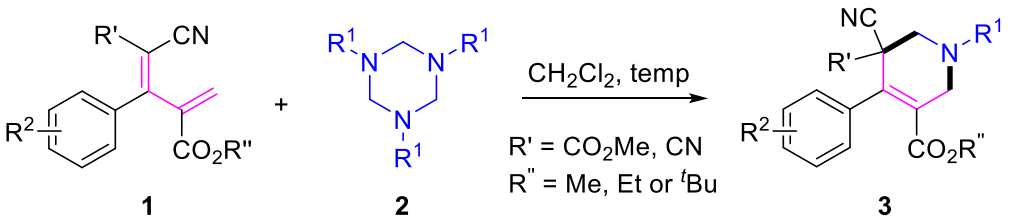


2

The substrate **2** was prepared according to the literature.[4]

To a solution of paraformaldehyde (1 mmol) in toluene (75 mL) was added amine (1 mmol), and then the mixture was stirred and refluxed at 120 °C for 2 h. The mixture was cooled, filtered, and washed three times with cold toluene. The product was dried at 60 °C without further purification to give the corresponding 1,3,5-triazinane.

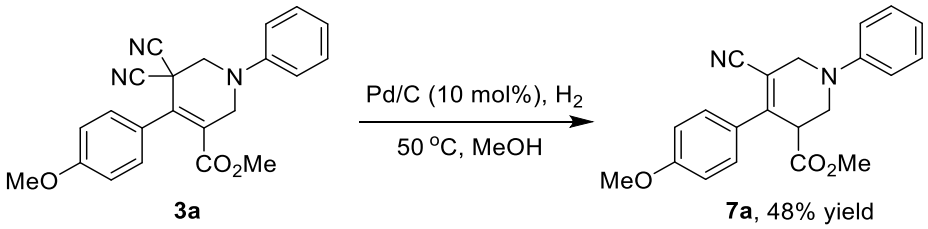
4. General Procedures for the aza-Diels-Alder reaction between electron-deficient 1,3-dienes and 1,3,5-triazinanes



To a solution of **1** (0.2 mmol, 1.0 equiv) in dry DCM (2 mL) was added **2** (0.16 mmol, 0.8 equiv), and the mixture was stirred at room temperature for 40 min unless otherwise noted. Heating at 50 °C for 3 h (**3j**) or for 6 h (**5a** and **5b**) was adopted instead. After completion of the annulation reaction monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired product **3**.

The synthesis of **5a** and **5b** in Scheme 3 follows the same procedure as **3** and the starting material of **4** (0.2 mmol) was adopted.

5. Further transformation of 3a



To a solution of **3a** (95 mg, 0.25 mmol) in methanol (5 mL) was added Pd/C (15 mg, 10 mol%). Then the reaction mixture was added HCl (0.3 mL, 0.01 M) and charged with H_2. The reaction mixture was heated at 50 °C for 17 h. Until **3a** was consumed completely according to the results as monitored by TLC, the reaction mixture was filtered through a plug of celite and washed with CH_2Cl_2. The filtrate was added saturated $NaHCO_3$ solution and adjusted to be neutral. The filtrate was extracted with CH_2Cl_2. Then the resulting solution was dried over Na_2SO_4. After filtration, the solvent

was evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent to afford **7a** (43 mg, 48% yield) as a yellow solid.

6. References

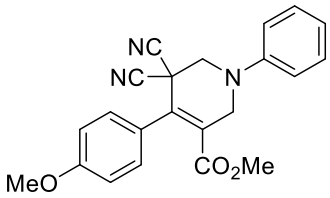
1. F. Lan, C. Zhou, X. Huang, B. An and X. Zhang, *Green Chem*., 2022, **24**, 2391–2396.

2. X. Jiang, D. Fu, X. Shi, S. Wang and R. Wang, *Chem. Commun*., 2011, **47**, 8289–8291.

3. S.-S. Zhang, D.-C. Wang, M.-S. Xie, G.-R. Qu and H.-M. Guo, *Org. Lett*., 2018, **20**, 8026–8029.

4. E. M. Nour-Eddine, Q. Yuan, F. Huang, *J. Appl. Polym. Sci.*, 2012, **125**, 1773–1781.

7. Characterization Data of New Compounds



3a

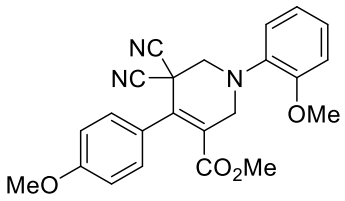
Methyl 5,5-dicyano-4-(4-methoxyphenyl)-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3a)

Compound **3a** (58 mg, 78% yield, R_f = 0.7 (PE/DCM = 1:1.5)) was isolated as a yellow solid, m.p. 115–116 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.11–7.01 (m, 3H), 6.97 (d, J = 8.7 Hz, 2H), 4.15 (s, 2H), 4.06 (s, 2H), 3.85 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.6, 148.0, 134.0, 133.7, 129.8, 129.8, 127.2, 122.5, 117.4, 114.3, 113.1, 56.4, 55.4, 52.6, 49.1, 39.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_3$ 374.1499, found 374.1499.



3b

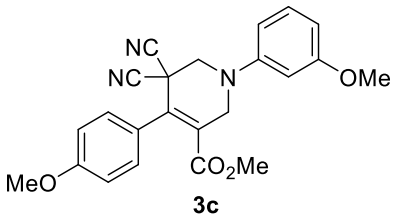
Methyl 5,5-dicyano-1-(2-methoxyphenyl)-4-(4-methoxyphenyl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3b)

Compound **3b** (60 mg, 74% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow solid, m.p. 98–99 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.14 (td, J = 7.8, 1.6 Hz, 1H), 7.07 (dd, J = 8.0, 1.5 Hz, 1H), 6.99–6.92 (m, 4H), 4.09 (s, 2H), 3.95 (s, 2H), 3.94 (s, 3H), 3.85 (s, 3H), 3.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 160.5, 153.2, 136.9, 134.3, 133.6, 129.9, 127.4, 125.4, 121.2, 120.7, 114.2, 113.3, 112.0, 55.9, 55.6, 55.4, 52.4, 49.9, 39.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_4$ 404.1605, found 404.1607.



3c

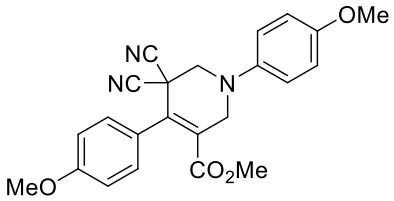
Methyl 5,5-dicyano-1-(3-methoxyphenyl)-4-(4-methoxyphenyl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3c)

Compound **3c** (48 mg, 60% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 98–99 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.27–7.24 (m, 1H), 6.99–6.94 (m, 2H), 6.69–6.64 (m, 1H), 6.61–6.56 (m, 2H), 4.14 (s, 2H), 4.05 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 161.0, 160.6, 149.3, 134.0, 133.6, 130.6, 129.8, 127.1, 114.3, 113.0, 109.7, 107.2, 103.9, 56.2, 55.5, 55.4, 52.6, 49.0, 39.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_4$ 404.1605, found 404.1606.



3d

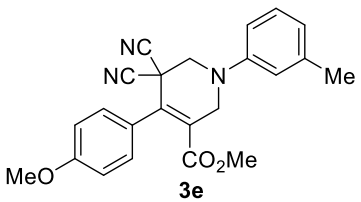
Methyl 5,5-dicyano-1,4-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3d)

Compound **3d** (55 mg, 68% yield, R_f = 0.6 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 99–100 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.08–7.02 (m, 2H), 6.99–6.94 (m, 2H), 6.93–6.88 (m, 2H), 4.05 (s, 2H), 3.92 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.5, 155.9, 142.0, 134.0, 133.7, 129.8, 127.2, 120.2, 115. 0, 114.3, 113.2, 57.6, 55.7, 55.4, 52.5, 50.4, 39.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_4$ 404.1605, found 404.1606.



3e

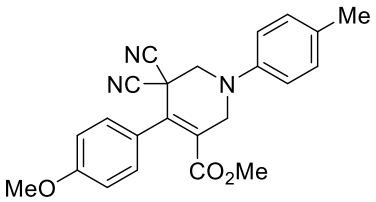
Methyl 5,5-dicyano-4-(4-methoxyphenyl)-1-(m-tolyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3e)

Compound **3e** (48 mg, 62% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 122–123 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.7 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.92–6.82 (m, 3H), 4.14 (s, 2H), 4.04 (s, 2H), 3.85 (s, 3H), 3.55 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.6, 148.0, 139.7, 133.9, 133.8, 129.8, 129.6, 127.2, 123.4, 118.2, 114.4, 114.3, 113.1, 56.4, 55.4, 52.5, 49.2, 39.4, 21.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_3$ 388.1656, found 388.1656.



3f

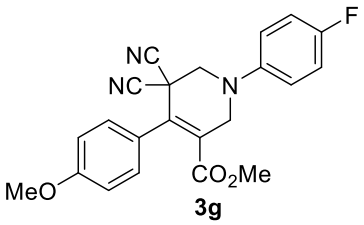
Methyl 5,5-dicyano-4-(4-methoxyphenyl)-1-(*p*-tolyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (**3f**)

Compound **3f** (60 mg, 77% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 125–126 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.00–6.95 (m, 4H), 4.11 (s, 2H), 4.00 (s, 2H), 3.85 (s, 3H), 3.55 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.5, 145.8, 133.9, 133.8, 132.3, 130.3, 129.8, 127.2, 117.8, 114.2, 113.1, 56.8, 55.4, 52.5, 49.5, 39.4, 20.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_3$ 388.1656, found 388.1656.



3g

Methyl 5,5-dicyano-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3g)

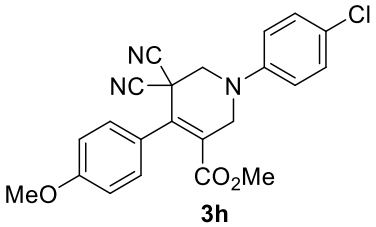
Compound **3g** (50 mg, 64% yield, R_f = 0.6 (PE/DCM = 1:1)) was isolated as a yellow solid; m.p. 130–131 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 4.9 Hz, 4H), 6.96 (d, J = 8.5 Hz, 2H), 4.09 (s, 2H), 3.98 (s, 2H), 3.85 (s, 3H), 3.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.6, 158.8 (d, J = 243.8 Hz), 144.4 (d, J = 2.3 Hz), 133.9, 133.6, 129.8, 127.1, 119.7 (d, J = 8.0 Hz), 116.4 (d, J = 22.8 Hz), 114.3, 113.0, 57.1, 55.4, 52.6, 49.9, 39.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ –120.2.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}FN_3O_3$ 392.1405, found 392.1405.



3h

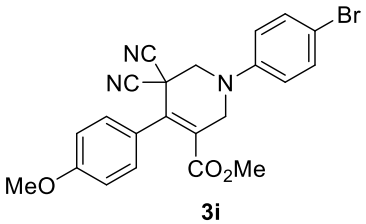
Methyl 1-(4-chlorophenyl)-5,5-dicyano-4-(4-methoxyphenyl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3h)

Compound **3h** (54 mg, 66% yield, R_f = 0.5 (PE/DCM = 1:1)) was isolated as a yellow solid; m.p. 132–133 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 4H), 7.00 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 8.72 Hz, 2H), 4.12 (s, 2H), 4.03 (s, 2H), 3.85 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.6, 146.5, 134.1, 133.4, 129.7 (d, J = 1.4 Hz), 127.6, 127.0, 118.6, 114.3, 112.9, 56.2, 55.4, 52.6, 49.0, 39.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}ClN_3O_3$ 408.1109, found 408.1110.



3i

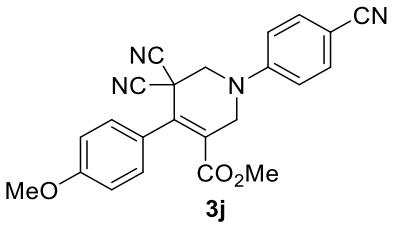
Methyl 1-(4-bromophenyl)-5,5-dicyano-4-(4-methoxyphenyl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3i)

Compound **3i** (51 mg, 56% yield, R_f = 0.6 (PE/DCM = 1:3)) was isolated as a yellow solid; m.p. 135–136 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.33–7.27 (m, 2H), 7.01–6.90 (m, 4H), 4.12 (s, 2H), 4.03 (s, 2H), 3.85 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.6, 147.0, 134.1, 133.3, 132.7, 129.7, 127.0, 118.9, 115.0, 114.3, 112.9, 56.1, 55.4, 52.6, 48.9, 39.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}BrN_3O_3$ 452.0604, found 452.0606.



3j

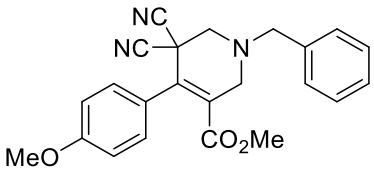
Methyl 5,5-dicyano-1-(4-cyanophenyl)-4-(4-methoxyphenyl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3j)

Compound **3j** (34 mg, 43% yield, R_f = 0.6 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 150–151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 4.27 (s, 2H), 4.21 (s, 2H), 3.85 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 160.8, 150.5, 134.6, 134.1, 132.5, 129.7, 126.7, 119.2, 115.5, 114.4, 112.5, 104.1, 55.4, 54.0, 52.8, 47.6, 38.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{19}N_4O_3$ 399.1452, found 399.1453.



3k

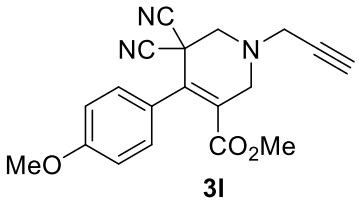
Methyl 1-benzyl-5,5-dicyano-4-(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3k)

Compound **3k** (39 mg, 50% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 5H), 7.30–7.26 (m, 2H), 6.96–6.91 (m, 2H), 3.84 (s, 2H), 3.83 (s, 3H), 3.53 (s, 2H), 3.49 (s, 3H), 3.26 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 160.4, 135.8, 134.0, 133.3, 129.8, 129.1, 128.9, 128.3, 127.2, 114.2, 113.3, 60.8, 56.6, 55.4, 52.7, 52.4, 39.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_3$ 388.1656, found 388.1654.



3l

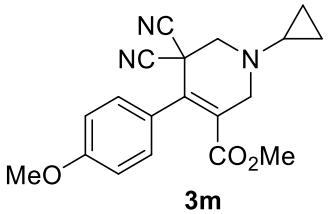
Methyl 5,5-dicyano-4-(4-methoxyphenyl)-1-(prop-2-yn-1-yl)-1,2,5,6-tetrahydro-pyridine-3-carboxylate (3l)

Compound **3l** (27 mg, 40% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 105–106 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 6.95–6.89 (m, 2H), 3.82 (s, 3H), 3.65 (d, J = 2.4 Hz, 2H), 3.60 (s, 2H), 3.49 (s, 3H), 3.35 (s, 2H), 2.37 (t, J = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.5, 133.9, 133.0, 129.9, 127.0, 114.2, 113.3, 76.1, 75.4, 56.4, 55.4, 52.4, 50.8, 45.5, 39.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}N_3O_3$ 336.1343, found 336.1342.



3m

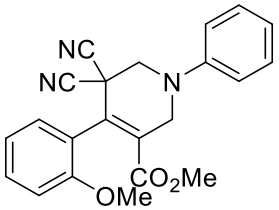
Methyl 5,5-dicyano-1-cyclopropyl-4-(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3m)

Compound **3m** (34 mg, 50% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.63 (s, 2H), 3.51 (s, 3H), 3.47 (s, 2H), 2.07–1.99 (m, 1H), 0.67–0.58 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 160.4, 134.3, 133.0, 129.8, 127.4, 114.2, 113.4, 58.0, 55.4, 52.4, 52.3, 39.3, 36.5, 6.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{20}N_3O_3$ 338.1499, found 338.1499.



3n

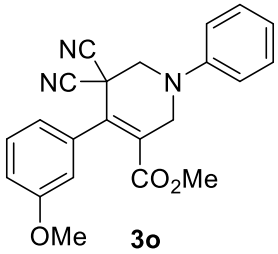
Methyl 5,5-dicyano-4-(2-methoxyphenyl)-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3n)

Compound **3n** (40 mg, 54% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 103–104 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 1H), 7.40–7.35 (m, 2H), 7.23 (dd, J = 7.5, 1.7 Hz, 1H), 7.11–7.06 (m, 2H), 7.03 (td, J = 7.5, 1.0 Hz, 2H), 6.99 (d, J = 8.3 Hz, 1H), 4.23 (br s, 2H), 4.07(br s, 2H), 3.85 (s, 3H), 3.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 156.6, 148.1, 133.7, 133.3, 131.3, 129.7, 129.6, 124.3, 122.1, 120.9, 117.0, 113.2, 111.1, 55.8, 55.6, 52.4, 48.8, 39.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_3$ 374.1499, found 374.1499.



3o

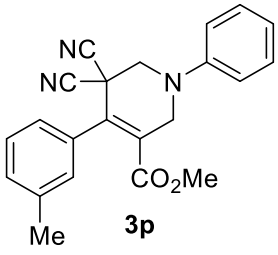
Methyl 5,5-dicyano-4-(3-methoxyphenyl)-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3o)

Compound **3o** (39 mg, 52% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 102–103 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 3H), 7.10–7.02 (m, 3H), 7.01–6.97 (m, 1H), 6.97–6.91 (m, 2H), 4.17 (s, 2H), 4.07 (s, 2H), 3.84 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 159.8, 147.9, 136.2, 134.0, 133.9, 130.0, 129.8, 122.6, 120.7, 117.4, 115.5, 113.7, 113.0, 56.5, 55.5, 52.6, 49.0, 39.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_3$ 374.1499, found 374.1499.



3p

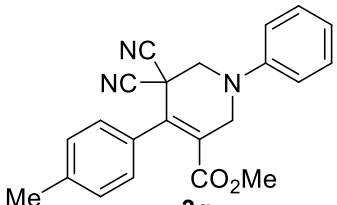
Methyl 5,5-dicyano-1-phenyl-4-(m-tolyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3p)

Compound **3p** (41 mg, 57% yield, R_f = 0.5 (PE/DCM = 1:1)) was isolated as a yellow solid; m.p. 128–129 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.33 (d, J = 7.5 Hz, 1H), 7.30–7.23 (m, 2H), 7.21–7.14 (m, 2H), 7.10–7.02 (m, 2H), 4.17 (s, 2H), 4.07 (s, 2H), 3.53 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.0, 138.6, 135.0, 134.4, 133.6, 130.5, 129.8, 128.7, 128.7, 125.5, 122.5, 117.4, 112.9, 56.5, 52.5, 49.0, 39.2, 21.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_2$ 358.1550, found 358.1550.



3q

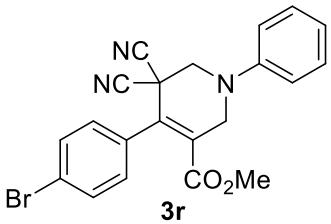
Methyl 5,5-dicyano-1-phenyl-4-(p-tolyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (3q)

Compound **3q** (45 mg, 63% yield, R_f = 0.4 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 130–131 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (m, 2H), 7.29–7.23 (m, 4H), 7.10–7.01 (m, 3H), 4.16 (s, 2H), 4.06 (s, 2H), 3.54 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 148.0, 139.7, 134.4, 133.5, 132.1, 129.8, 129.6, 128.2, 122.5, 117.4, 113.0, 56.3, 52.5, 49.0, 39.3, 21.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_2$ 358.1550, found 358.1550.



3r

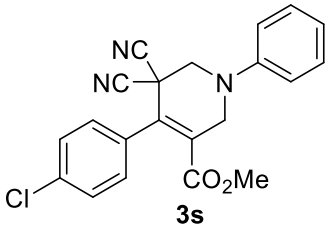
Methyl 4-(4-bromophenyl)-5,5-dicyano-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3r)

Compound **3r** (39 mg, 46% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 136–137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 2H), 7.40–7.34 (m, 2H), 7.27–7.26 (m, 1H), , 7.25–7.23 (m, 1H), 7.10 – 7.03 (m, 3H), 4.17 (s, 2H), 4.07 (s, 2H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 147.9, 134.4, 133.8, 133.5, 132.2, 130.1, 129.9, 124.3, 122.8, 117.5, 112.7, 56.4, 52.7, 49.1, 39.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{17}BrN_3O_2$ 422.0499, found 422.0500.



3s

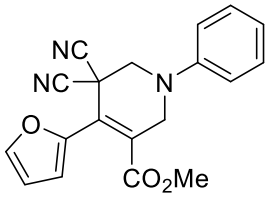
Methyl 4-(4-chlorophenyl)-5,5-dicyano-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3s)

Compound **3s** (39 mg, 52% yield, R_f = 0.7 (PE/EA = 5:1)) was isolated as a yellow solid; mp 133–134 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.41–7.29 (m, 4H), 7.12–7.03 (m, 3H), 4.17 (s, 2H), 4.07 (s, 2H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 147.8, 136.0, 134.5, 133.5, 133. 3, 129.8, 129.2, 122.7, 117.5, 112.7, 56.4, 52.7, 49.1, 39.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}ClN_3O_2$ 378.1004; Found 378.1001.



3t

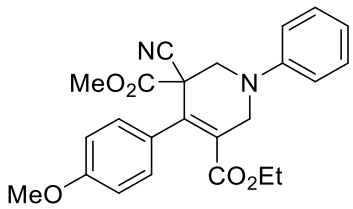
Methyl 5,5-dicyano-4-(furan-2-yl)-1-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (3t)

Compound **3t** (33 mg, 49% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow solid; m.p. 85–86 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.7 Hz, 1H), 7.39–7.33 (m, 2H), 7.08–7.02 (m, 3H), 6.88 (d, *J* = 3.6 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.14 (s, 2H), 4.09 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 147.6, 146.6, 144.5, 132.4, 129.8, 122.8, 121.0, 117.6, 113.3, 112.5, 112.1, 56.9, 53.0, 49.5, 35.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{16}N_3O_3$ 334.1186, found 334.1185.



5a

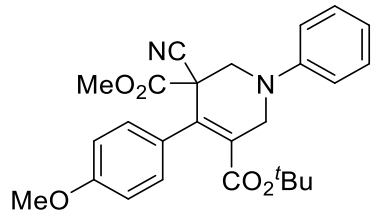
5-Ethyl 3-methyl 3-cyano-4-(4-methoxyphenyl)-1-phenyl-1,2,3,6-tetrahydropyridine-3,5-dicarboxylate (5a)

Compound **5a** (62 mg, 74% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.22 (dt, *J* = 9.6, 2.8 Hz, 2H), 7.04–6.99 (m, 2H), 6.99–6.93 (m, 1H), 6.87 (dt, *J* = 9.6, 2.8 Hz, 2H), 4.14 (d, *J* = 6.3 Hz, 2H), 4.06 (d, *J* = 12.6 Hz, 1H), 4.00–3.93 (m, 3H), 3.81 (s, 3H), 3.64 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 159.8, 148.6, 136.8, 132.7, 129.9, 129.5, 128.8, 121.2, 116.7, 116.5, 113.6, 61.2, 55.4, 55.3, 53.9, 51.6, 48.9, 13.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_5$ 421.1758, found 421.1763.



5b

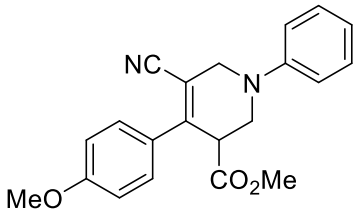
5-(*tert*-Butyl) 3-methyl 3-cyano-4-(4-methoxyphenyl)-1-phenyl-1,2,3,6-tetrahydropyridine-3,5-dicarboxylate (5b)

Compound **5b** (56 mg, 62% yield, R_f = 0.5 (PE/EA = 5:1)) was isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.22 (dt, *J* = 9.6, 3.2 Hz, 2H), 7.04–6.99 (m, 2H), 6.97–6.92 (m, 1H), 6.88 (dt, *J* = 9.6, 2.8 Hz, 2H), 4.10 (d, *J* = 3.9 Hz, 2H), 4.06 (d, *J* = 12.7 Hz, 1H), 3.94 (d, *J* = 12.6 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 159.8, 148.8, 135.1, 134.2, 130.2, 129.6, 129.0, 121.1, 117.0, 116.5, 113.6, 82.4, 55.5, 55.4, 53.9, 51.6, 48.9, 27.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_5$ 449.2071, found 449.2076.



10a

Methyl 5-cyano-4-(4-methoxyphenyl)-1-phenyl-1,2,3,6-tetrahydropyridine-3-carboxylate (10a)

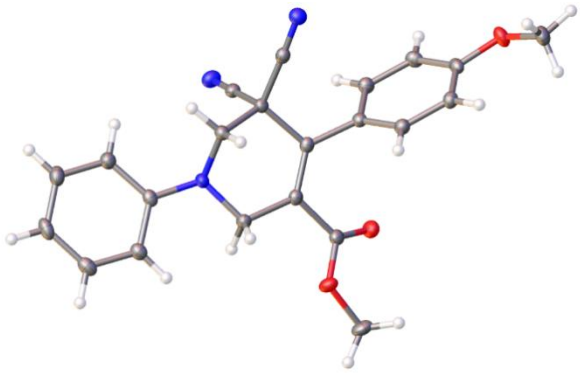
Compound **10a** (43 mg, 48% yield, R_f = 0.8 (DCM/EA = 2.5:1)) was isolated as a yellow solid; m.p. 84–85 ℃.

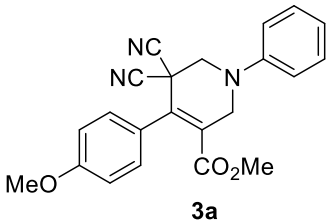
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, J = 9.6, 3.0 Hz, 2H), 7.35–7.28 (m, 2H), 6.99–6.89 (m, 5H), 4.21–4.12 (m, 2H), 3.89 (dd, J = 16.8, 2.2 Hz, 1H), 3.86–3.80 (m, 4H), 3.58 (s, 3H), 3.44 (dd, J = 12.8, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 160.7, 150.7, 148.9, 129.9, 129.6, 129.1, 120.7, 117.9, 116.0, 114.3, 108.4, 55.5, 52.7, 49.9, 47.2.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_3$ 349.1547; Found 349.1544.

8. X-ray Crystallographic Structure and Data of 3a and 10a





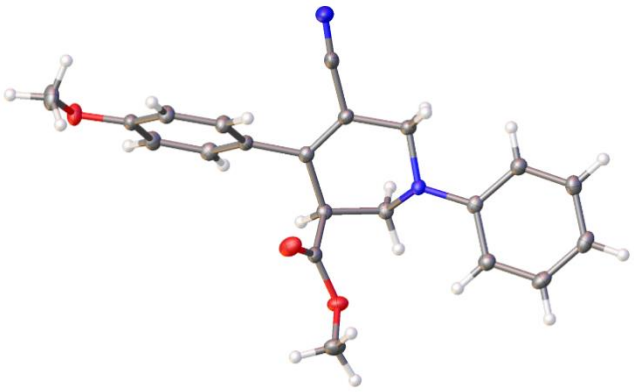
3a

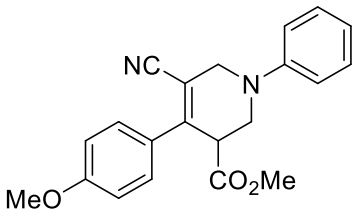
(CCDC 2252186)

Table S1. Crystal data and structure refinement for compound **3a**

Identification code	**3a**
Empirical formula	$C_{22}H_{19}N_3O_3$
Formula weight	373.40
Temperature/K	100.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.5755(4)
b/Å	9.8662(5)
c/Å	11.7817(6)
α/°	94.9180(10)
β/°	108.5270(10)
γ/°	90.4850(10)
Volume/Å^3	941.01(8)
Z	2
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	0.463
F(000)	392.0
Crystal size/mm^3	0.22 × 0.18 × 0.16
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	6.914 to 114.198
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	21965
Independent reflections	3838 [R_{int} = 0.0756, R_{sigma} = 0.0726]
Data/restraints/parameters	3838/0/256

Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0337, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.0727, wR_2 = 0.1024
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.21





10a

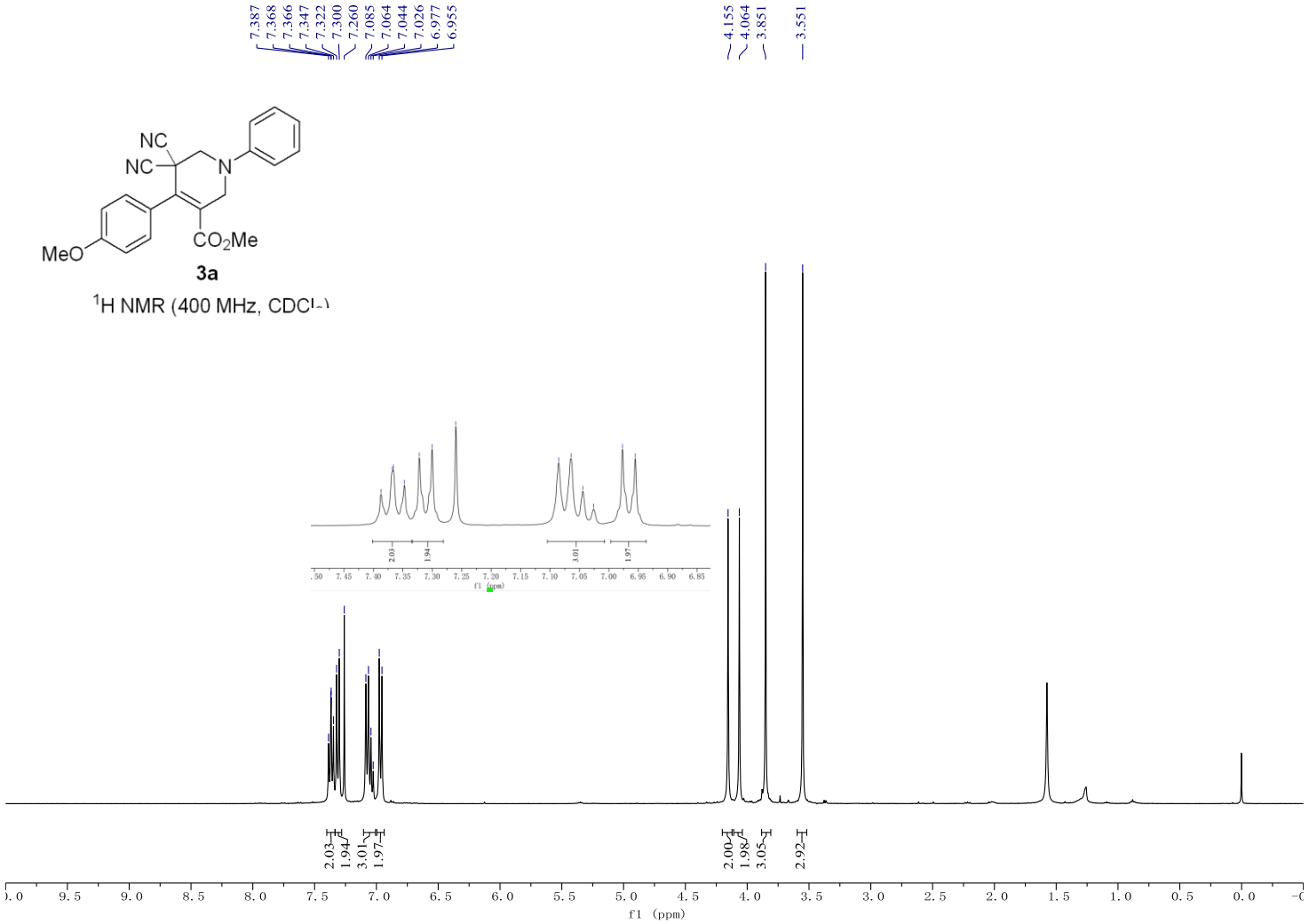
(CCDC 2252187)

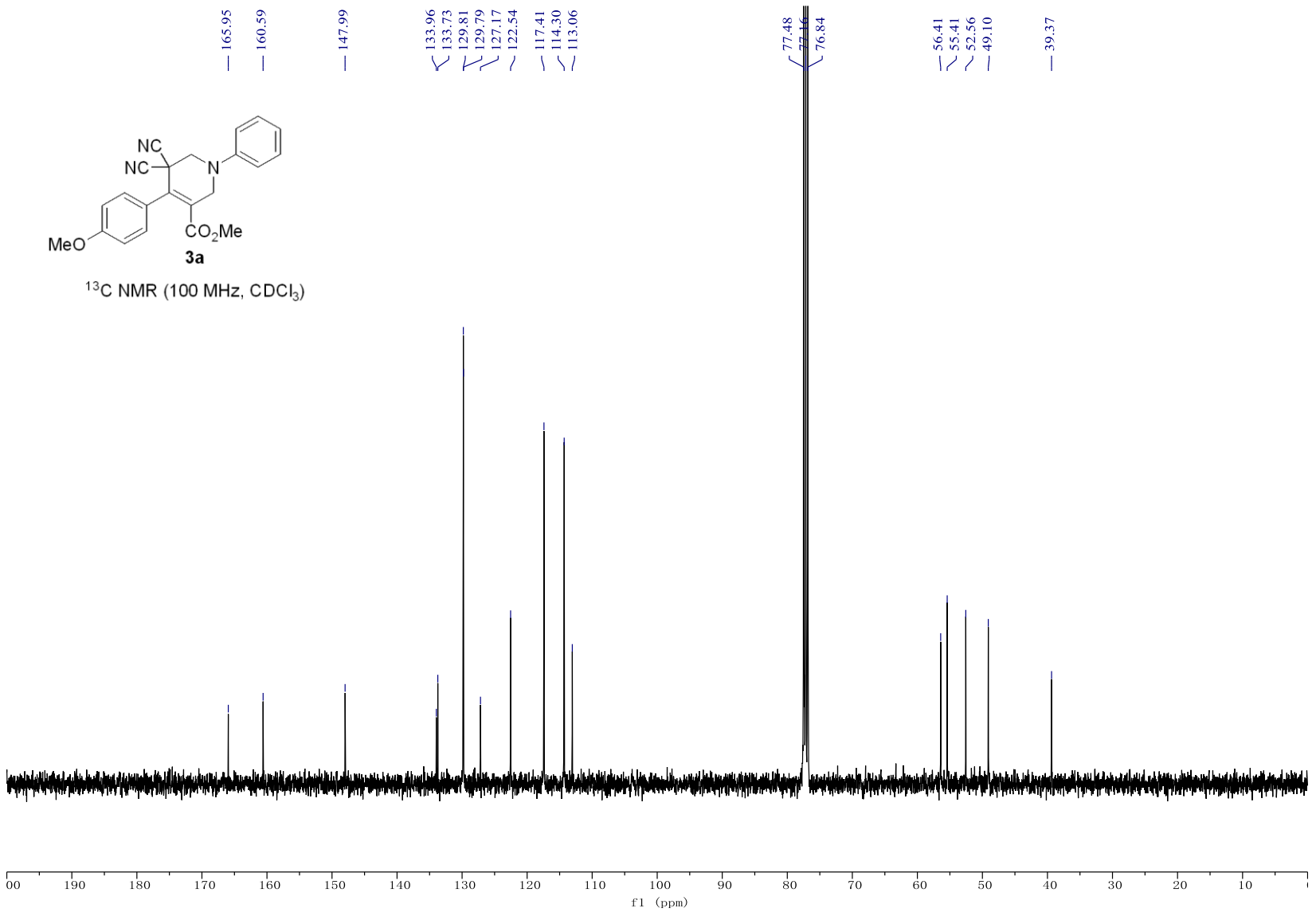
Table S2. Crystal data and structure refinement for compound **10a**

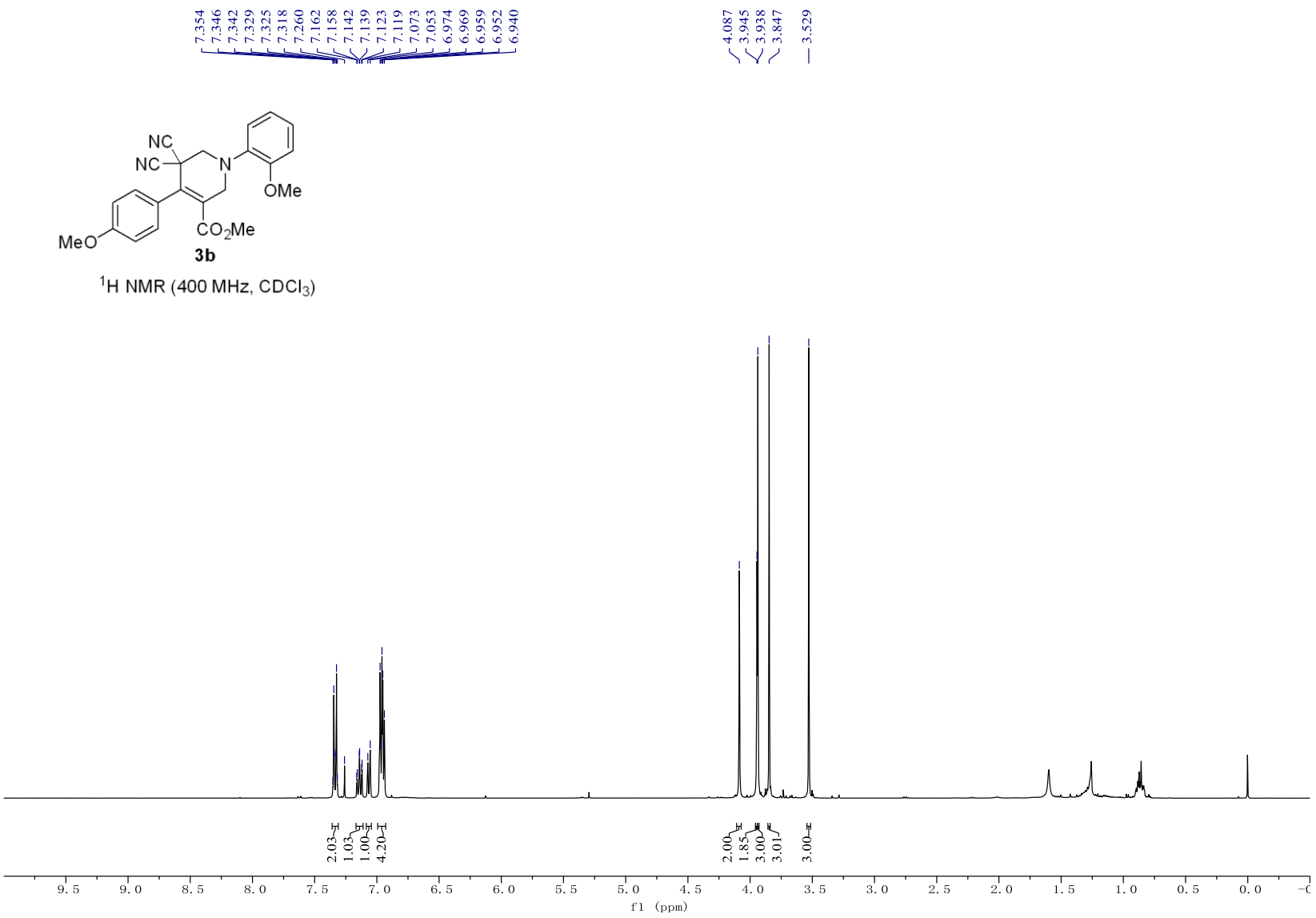
Identification code	**10a**
Empirical formula	$C_{21}H_{20}N_2O_3$
Formula weight	348.39
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	Cc
a/Å	9.7031(7)
b/Å	10.4099(7)
c/Å	17.7960(10)
α/°	90
β/°	95.421(2)
γ/°	90
Volume/$Å^3$	1789.5(2)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.087
F(000)	736.0
Crystal size/mm^3	0.35 × 0.31 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.754 to 54.982

Index ranges	$-12 \leq h \leq 12, -13 \leq k \leq 13, -22 \leq l \leq 23$
Reflections collected	21287
Independent reflections	4095 [R_{int} = 0.0397, R_{sigma} = 0.0280]
Data/restraints/parameters	4095/2/238
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0286, wR_2 = 0.0728
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0740
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.15
Flack parameter	-0.4(2)

9. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of New Compounds

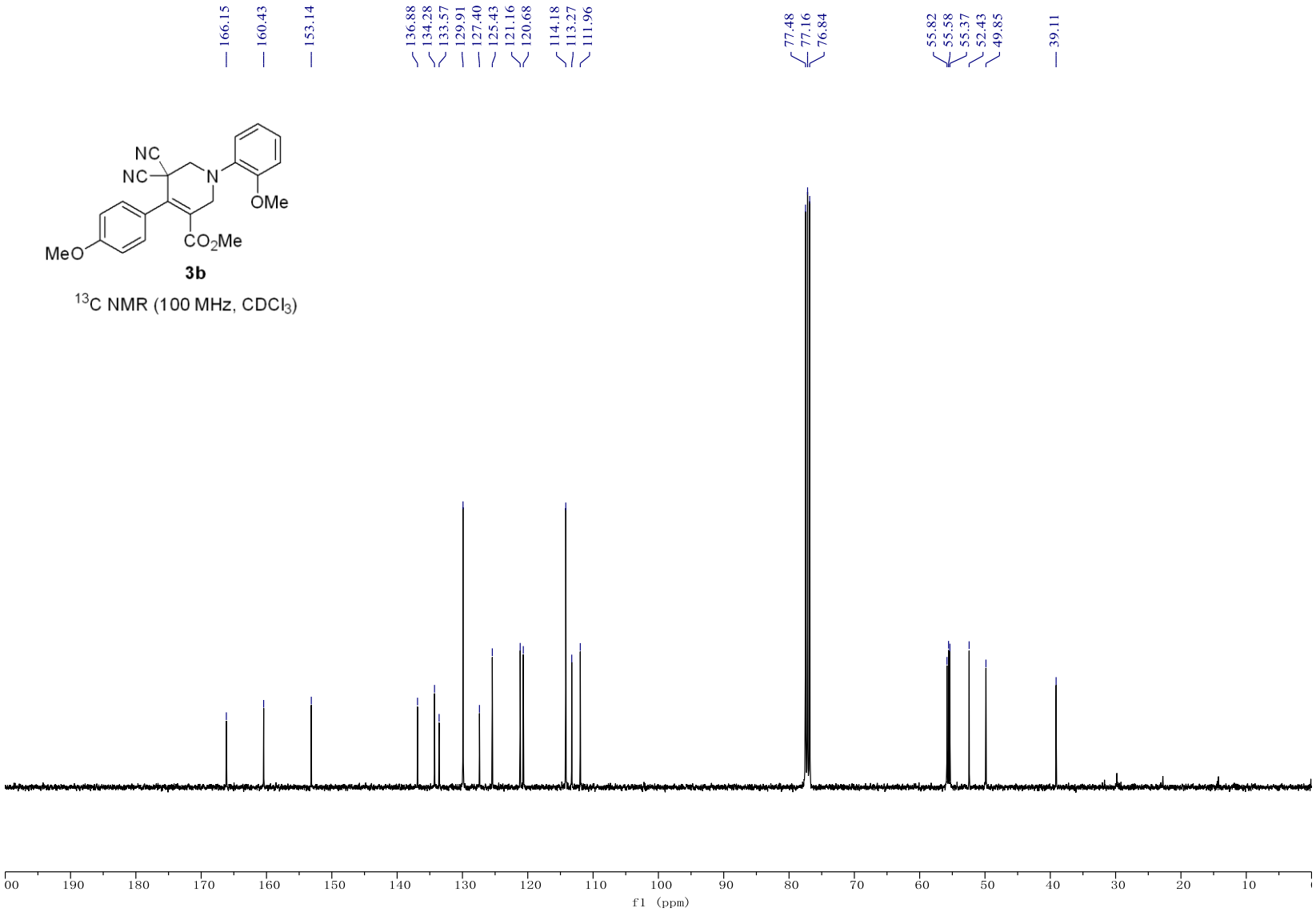


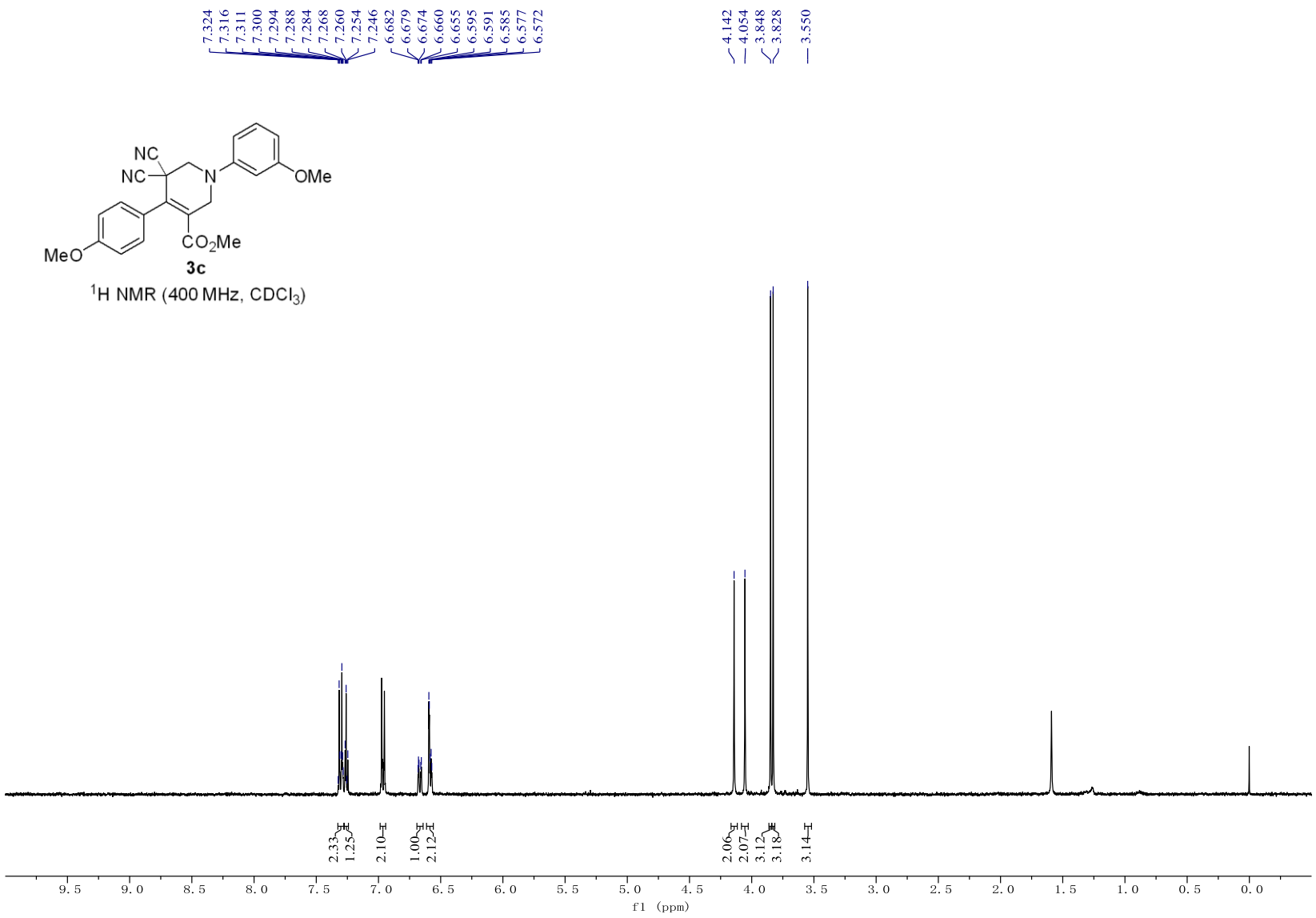

165.95
160.59
147.99
133.96
133.73
129.81
129.79
127.17
122.54
117.41
114.30
113.06
77.48
77.16
76.84
56.41
55.41
52.56
49.10
39.37
NC
NC
N
MeO
CO2Me
3a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

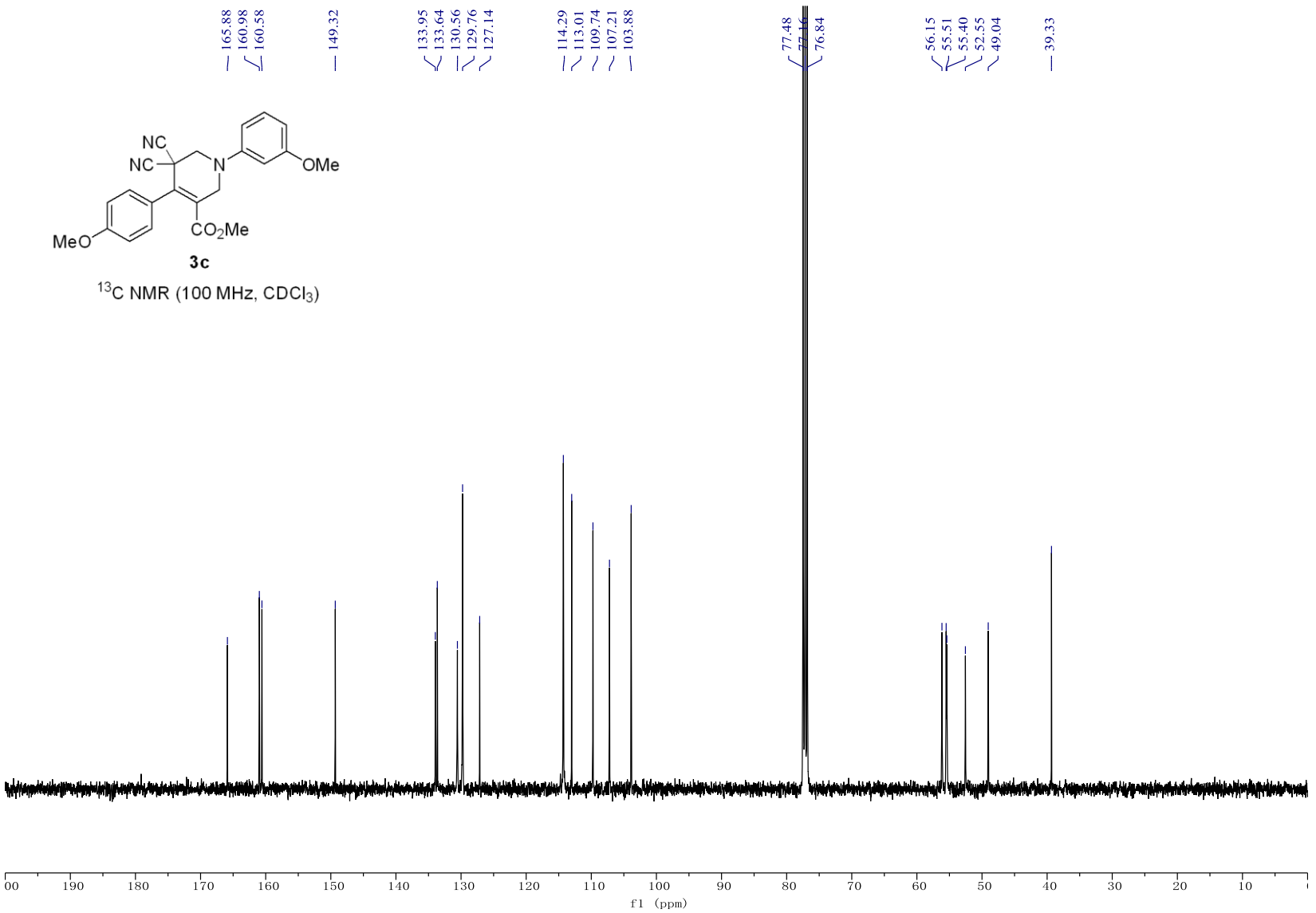


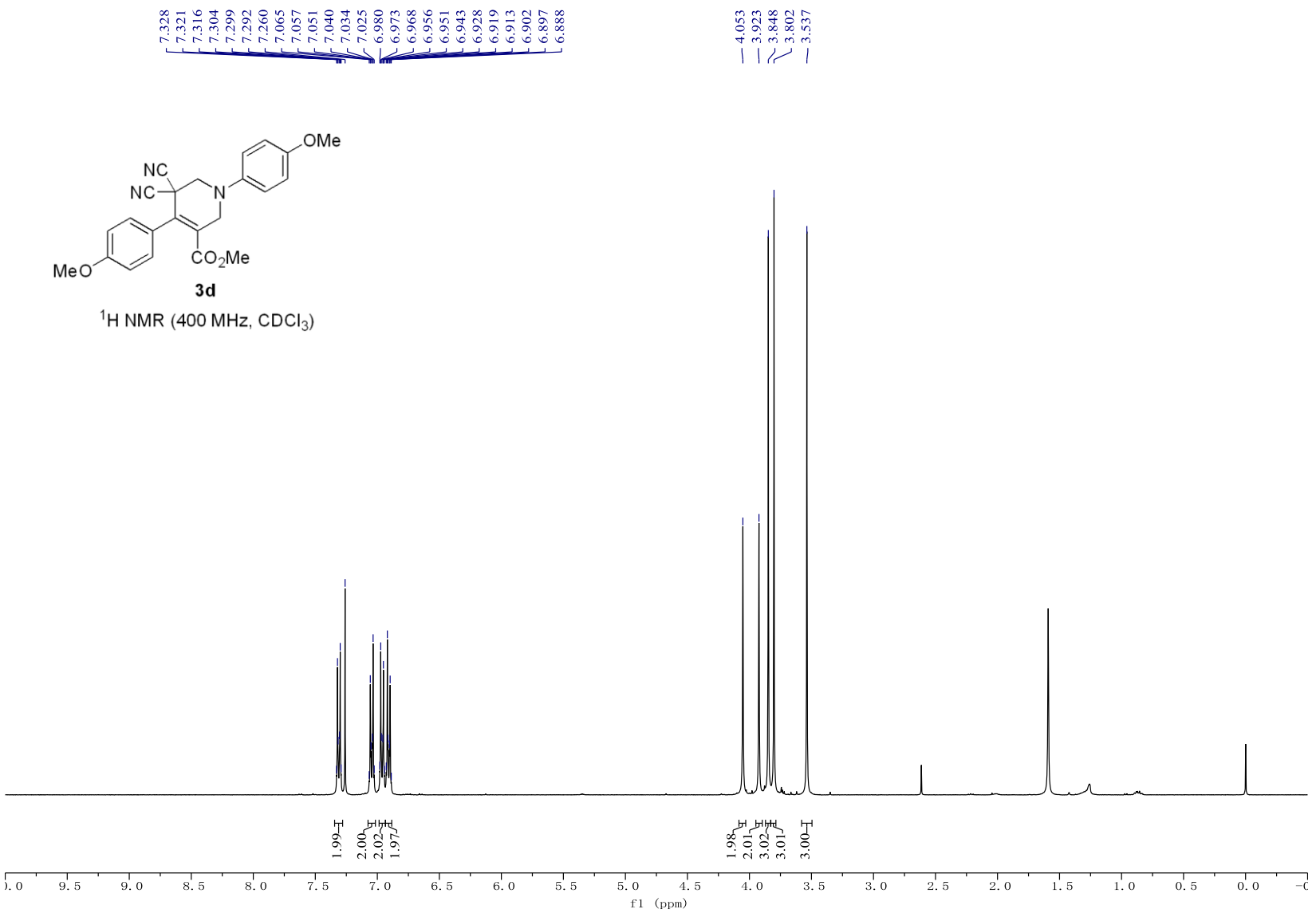
3b

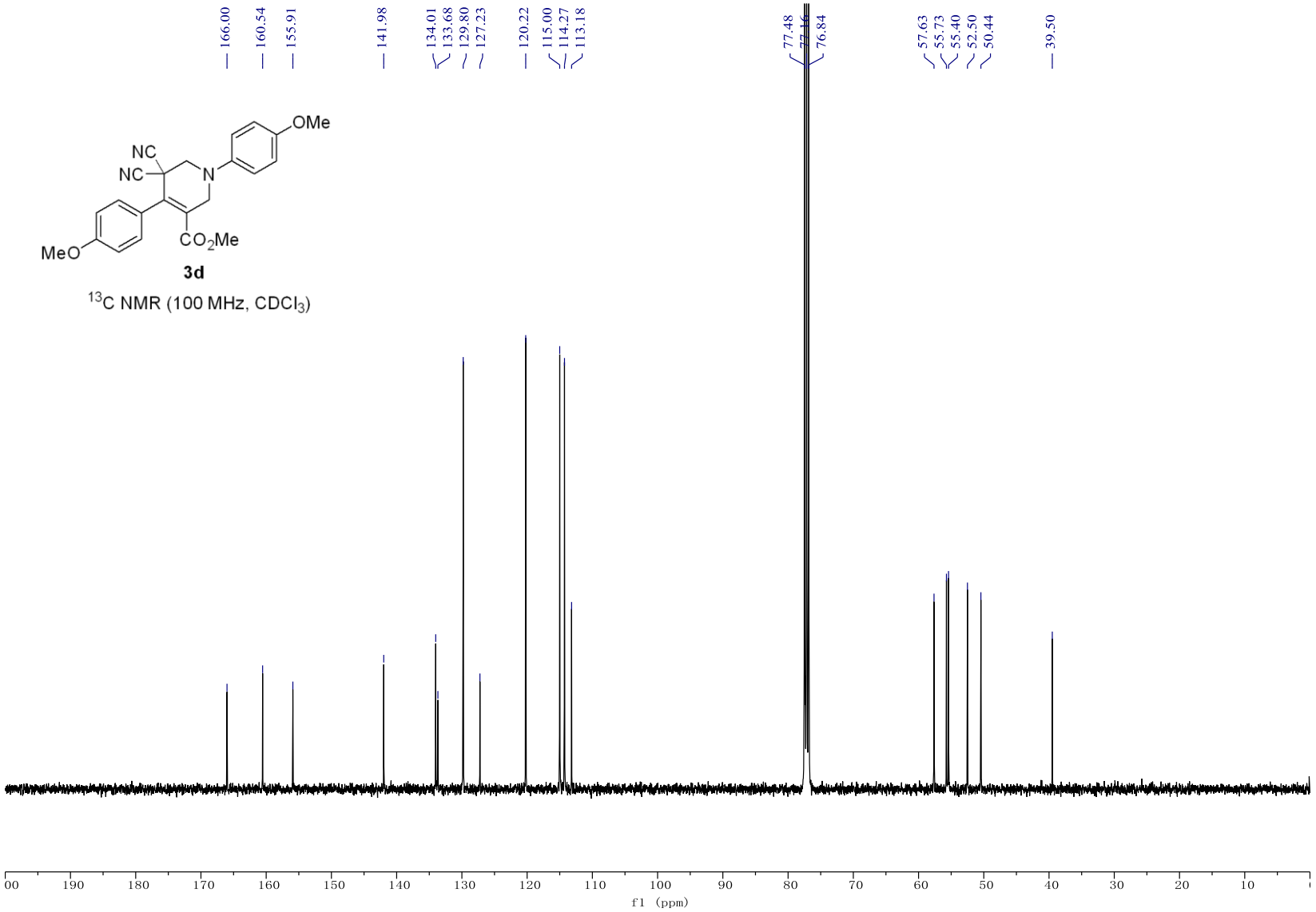
^{1}H NMR (400 MHz, $CDCl_3$)

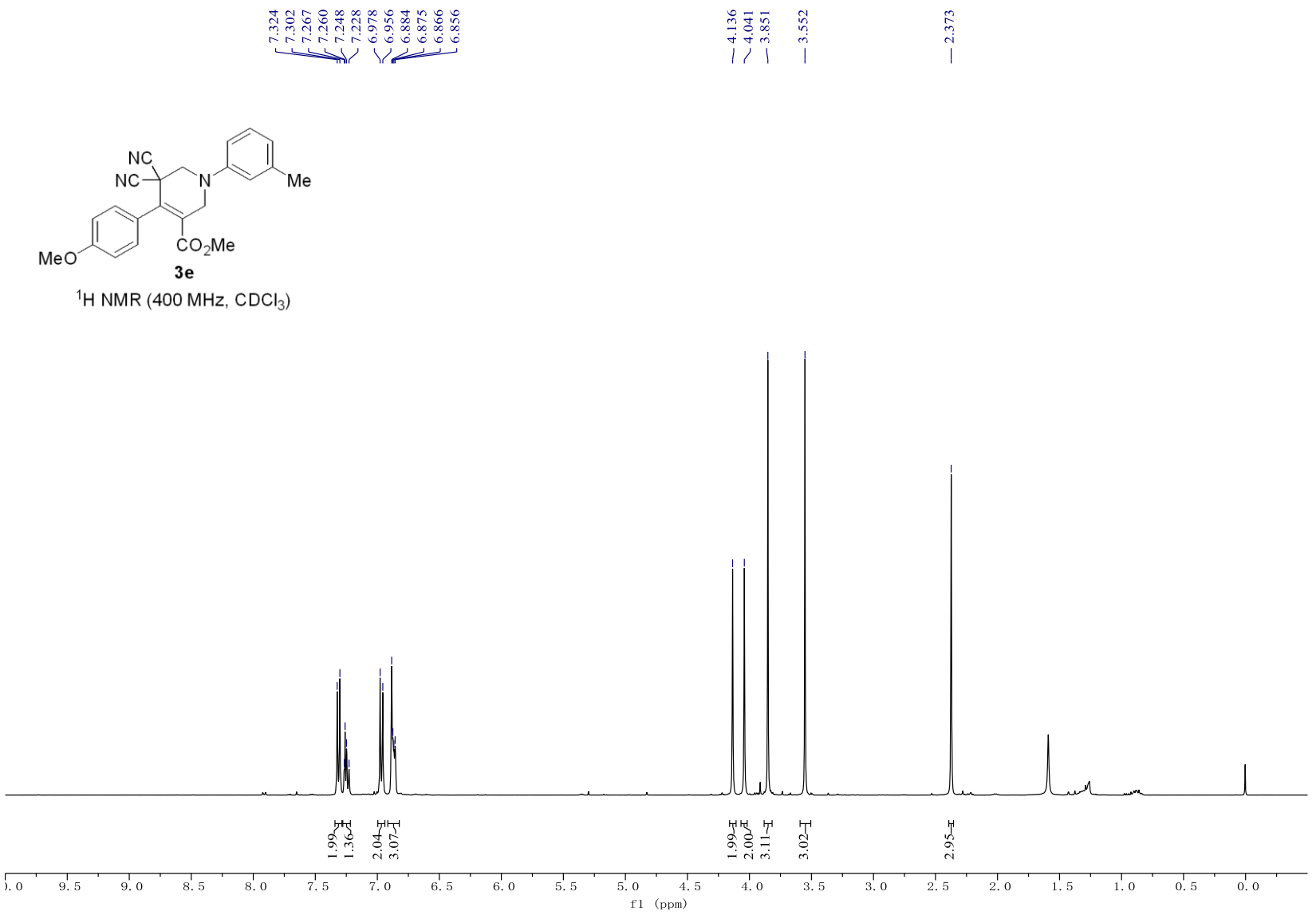

166.15
160.43
153.14
136.88
134.28
133.57
129.91
127.40
125.43
121.16
120.68
114.18
113.27
111.96
77.48
77.16
76.84
55.82
55.58
55.37
52.43
49.85
39.11
NC
NC
N
OMe
MeO
CO2Me
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

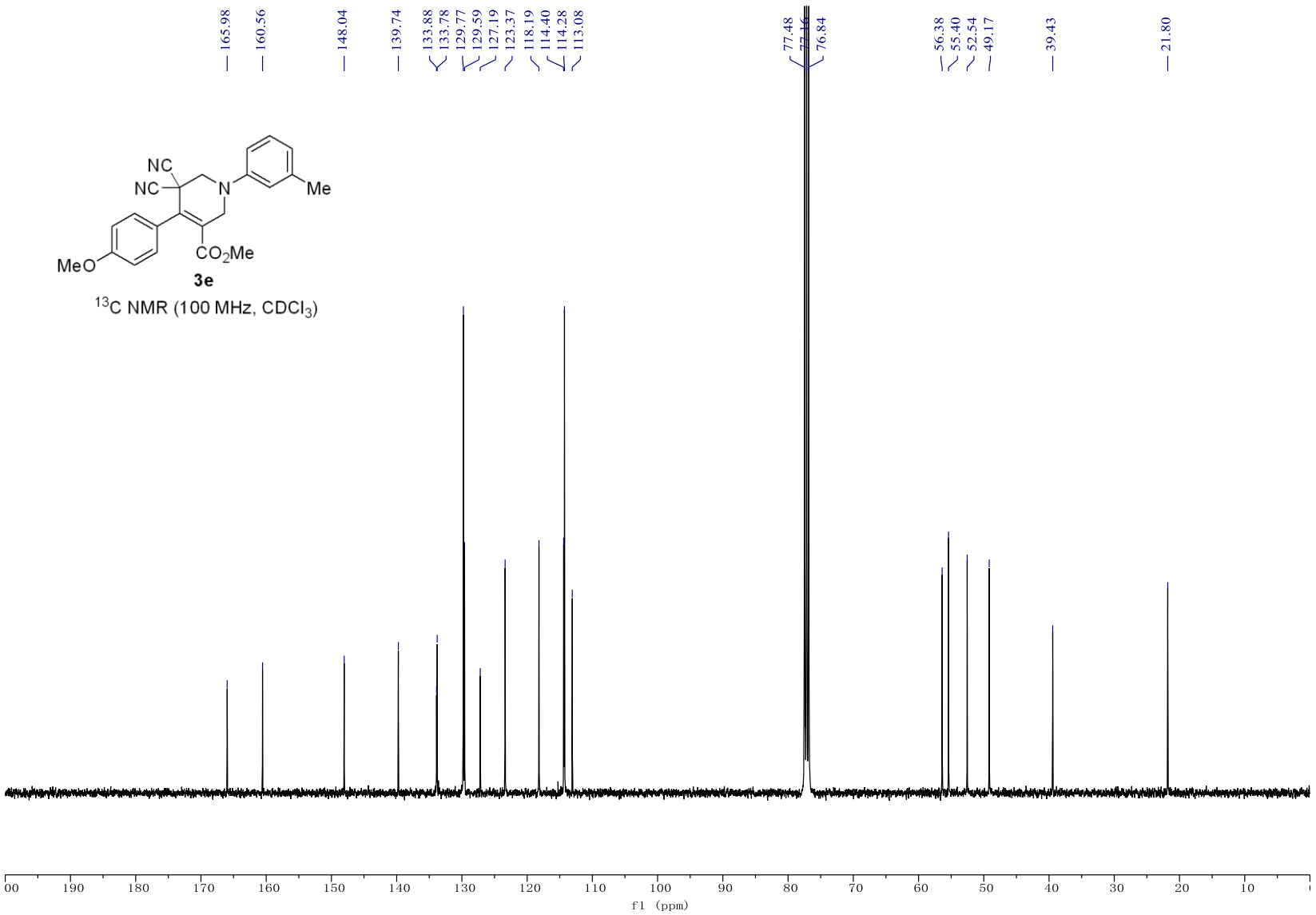

7.324
7.316
7.311
7.300
7.294
7.288
7.284
7.268
7.260
7.254
7.246
6.682
6.679
6.674
6.660
6.655
6.595
6.591
6.585
6.577
6.572
4.142
4.054
3.848
3.828
3.550
NC
NC
N
OMe
MeO
CO2Me
3c
1H NMR (400 MHz, CDCl3)
2.33
1.25
2.10
1.00
2.12
2.06
2.07
3.12
3.18
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

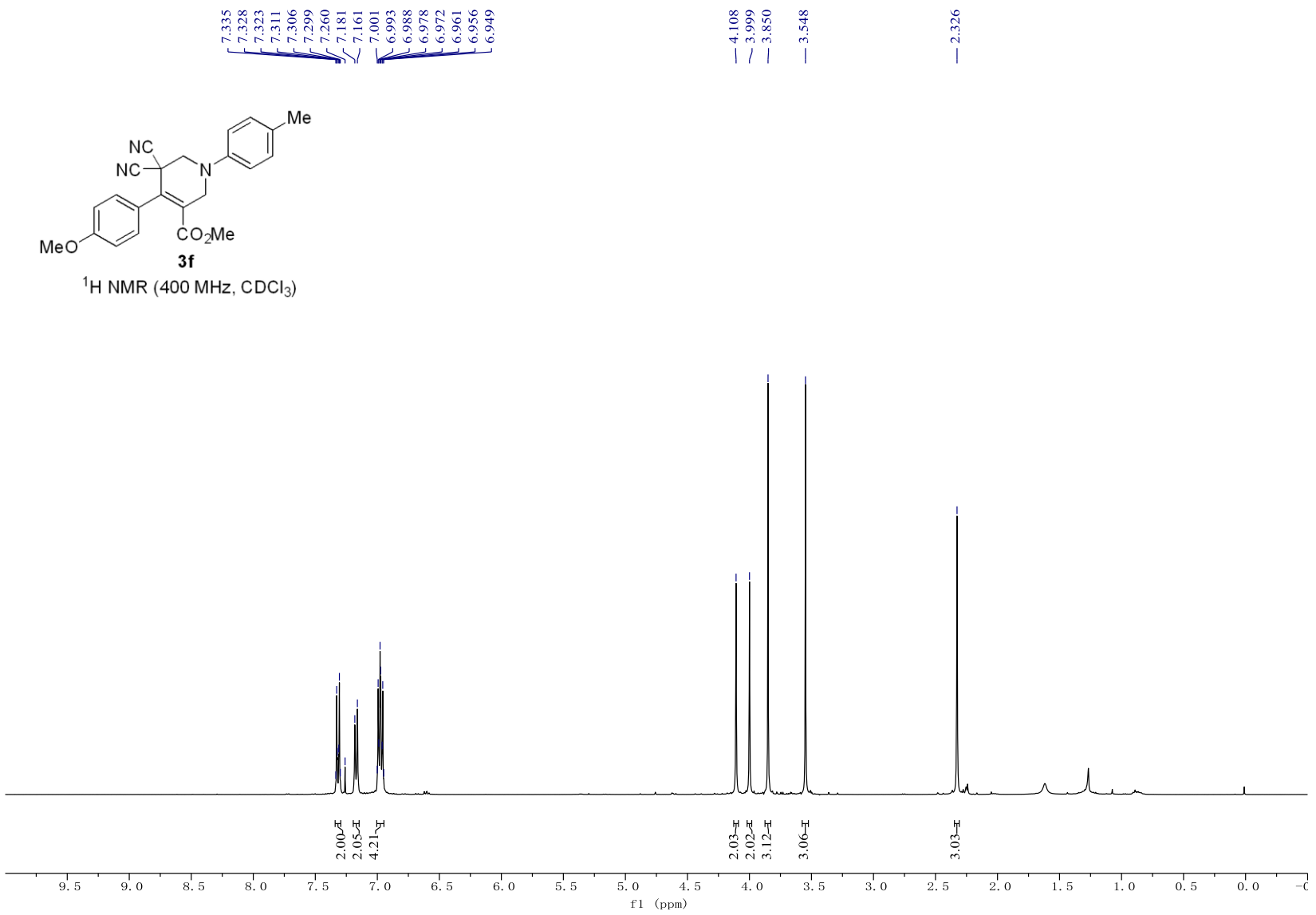

165.88
160.98
160.58
149.32
133.95
133.64
130.56
129.76
127.14
114.29
113.01
109.74
107.21
103.88
77.48
77.16
76.84
56.15
55.51
55.40
52.55
49.04
39.33
NC
NC
N
OMe
MeO
CO2Me
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

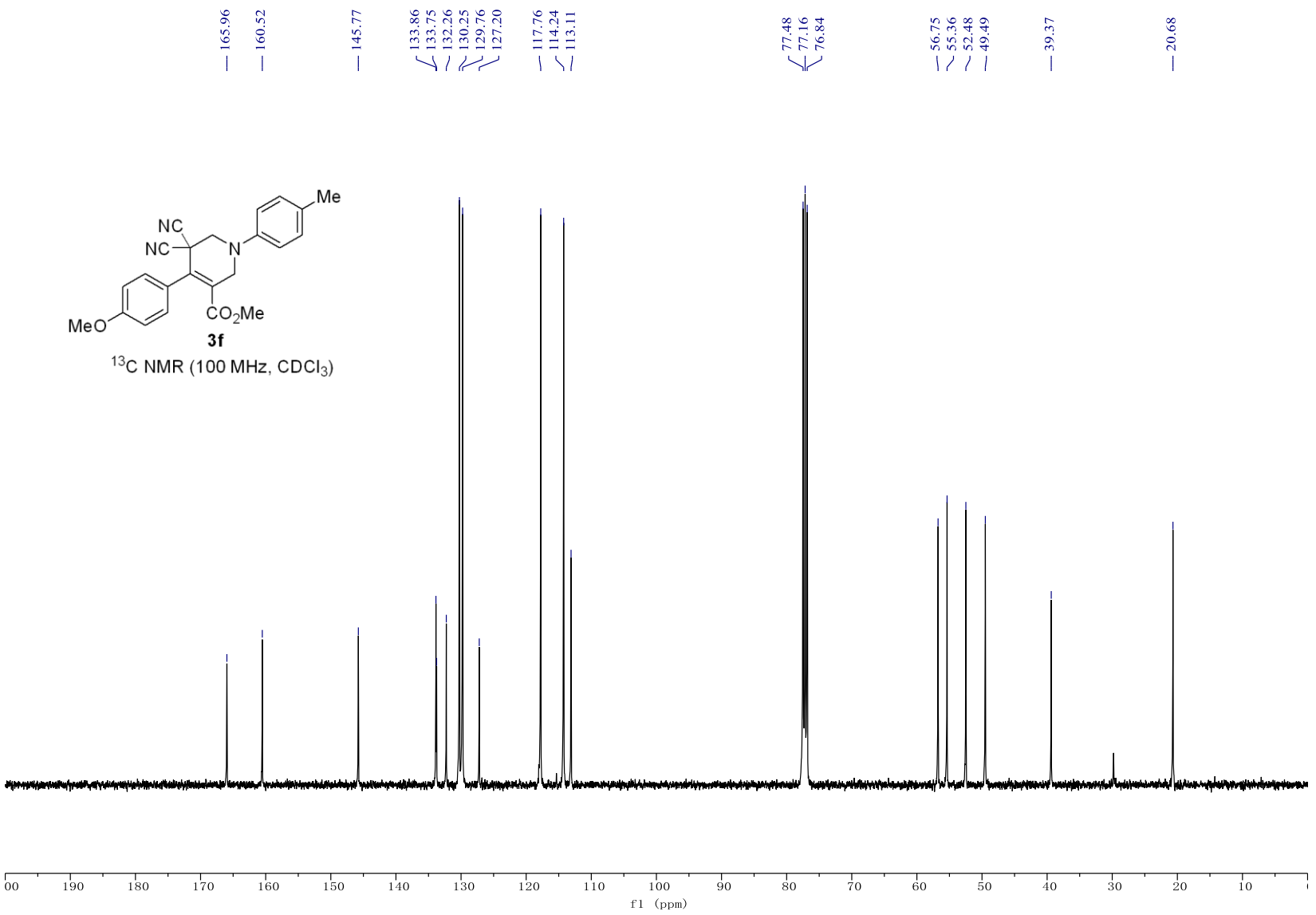

7.328
7.321
7.316
7.304
7.299
7.292
7.260
7.065
7.057
7.051
7.040
7.034
7.025
6.980
6.973
6.968
6.956
6.951
6.943
6.928
6.919
6.913
6.902
6.897
6.888
4.053
3.923
3.848
3.802
3.537
OMe
NC
NC
N
MeO
CO2Me
3d
1H NMR (400 MHz, CDCl3)
1.99
2.00
2.02
1.97
1.98
2.01
3.02
3.01
3.00
f1 (ppm)

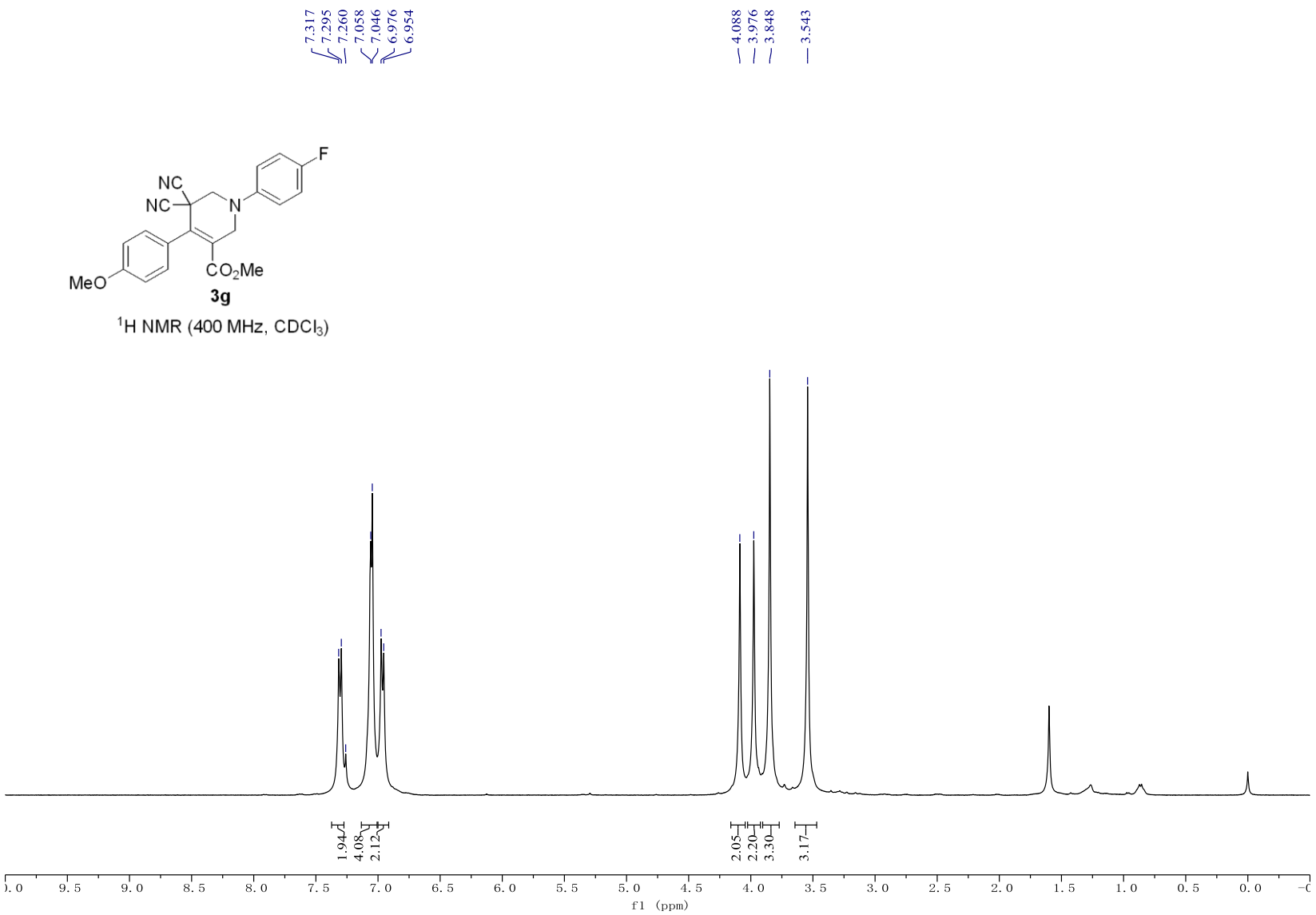

166.00
160.54
155.91
141.98
134.01
133.68
129.80
127.23
120.22
115.00
114.27
113.18
77.48
77.16
76.84
57.63
55.73
55.40
52.50
50.44
39.50
OMe
NC
NC
N
MeO
CO2Me
3d
13C NMR (100 MHz, CDCl3)
f1 (ppm)

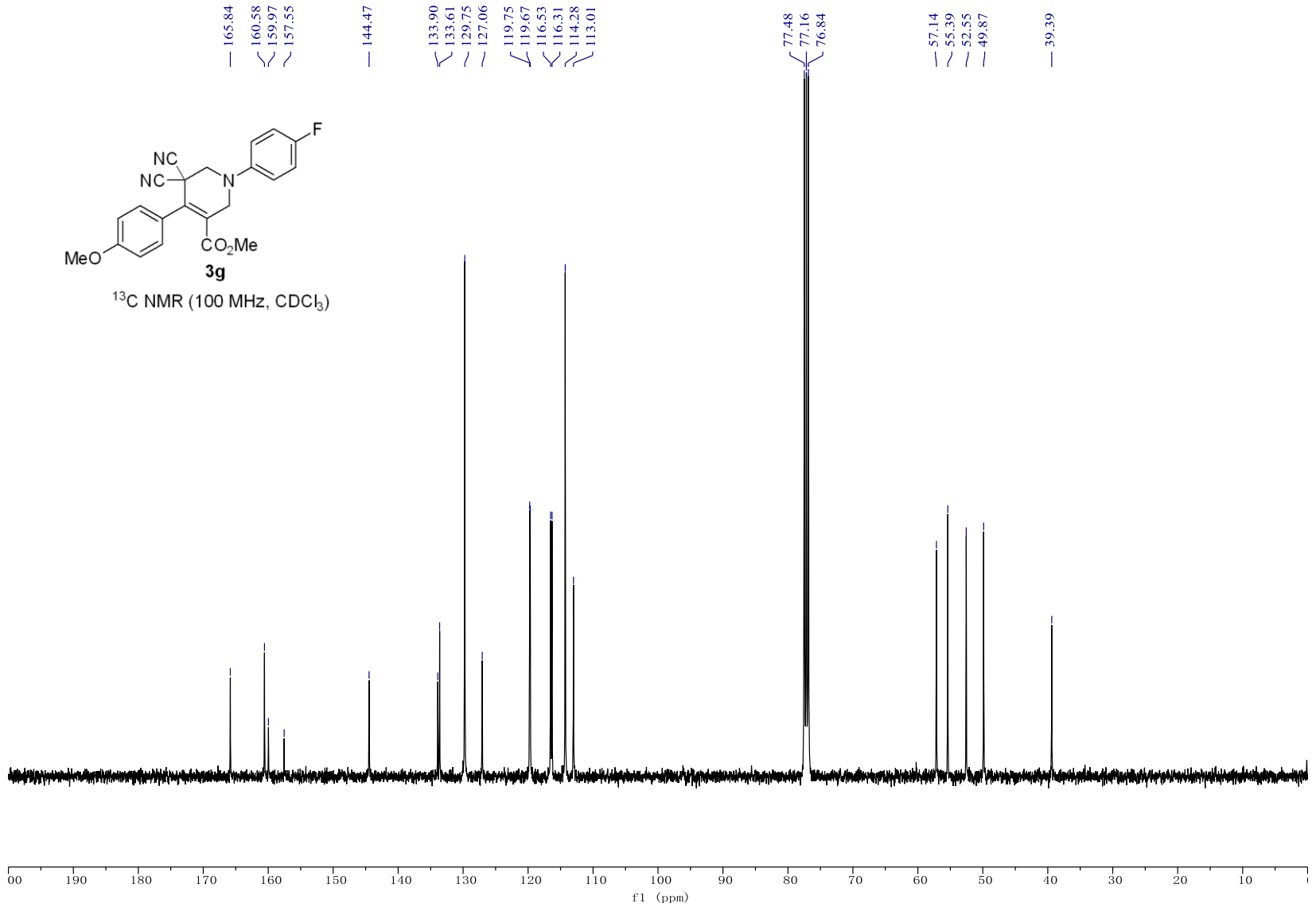

7.324
7.302
7.267
7.260
7.248
7.228
6.978
6.956
6.884
6.875
6.866
6.856
4.136
4.041
3.851
3.552
2.373
NC
NC
N
Me
MeO
CO2Me
3e
1H NMR (400 MHz, CDCl3)
1.99
1.36
2.04
3.07
1.99
2.00
3.11
3.02
2.95
f1 (ppm)

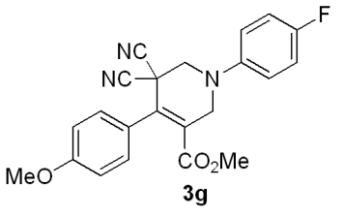

165.98
160.56
148.04
139.74
133.88
133.78
129.77
129.59
127.19
123.37
118.19
114.40
114.28
113.08
77.48
77.16
76.84
56.38
55.40
52.54
49.17
39.43
21.80
NC
NC
N
Me
MeO
CO2Me
3e
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.335
7.328
7.323
7.311
7.306
7.299
7.260
7.181
7.161
7.001
6.993
6.988
6.978
6.972
6.961
6.956
6.949
4.108
3.999
3.850
3.548
2.326
Me
NC
NC
N
CO2Me
MeO
3f
1H NMR (400 MHz, CDCl3)
2.00
2.05
4.21
2.03
2.02
3.12
3.06
3.03
f1 (ppm)


165.96
160.52
145.77
133.86
133.75
132.26
130.25
129.76
127.20
117.76
114.24
113.11
77.48
77.16
76.84
56.75
55.36
52.48
49.49
39.37
20.68
Me
NC
NC
N
CO2Me
MeO
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)

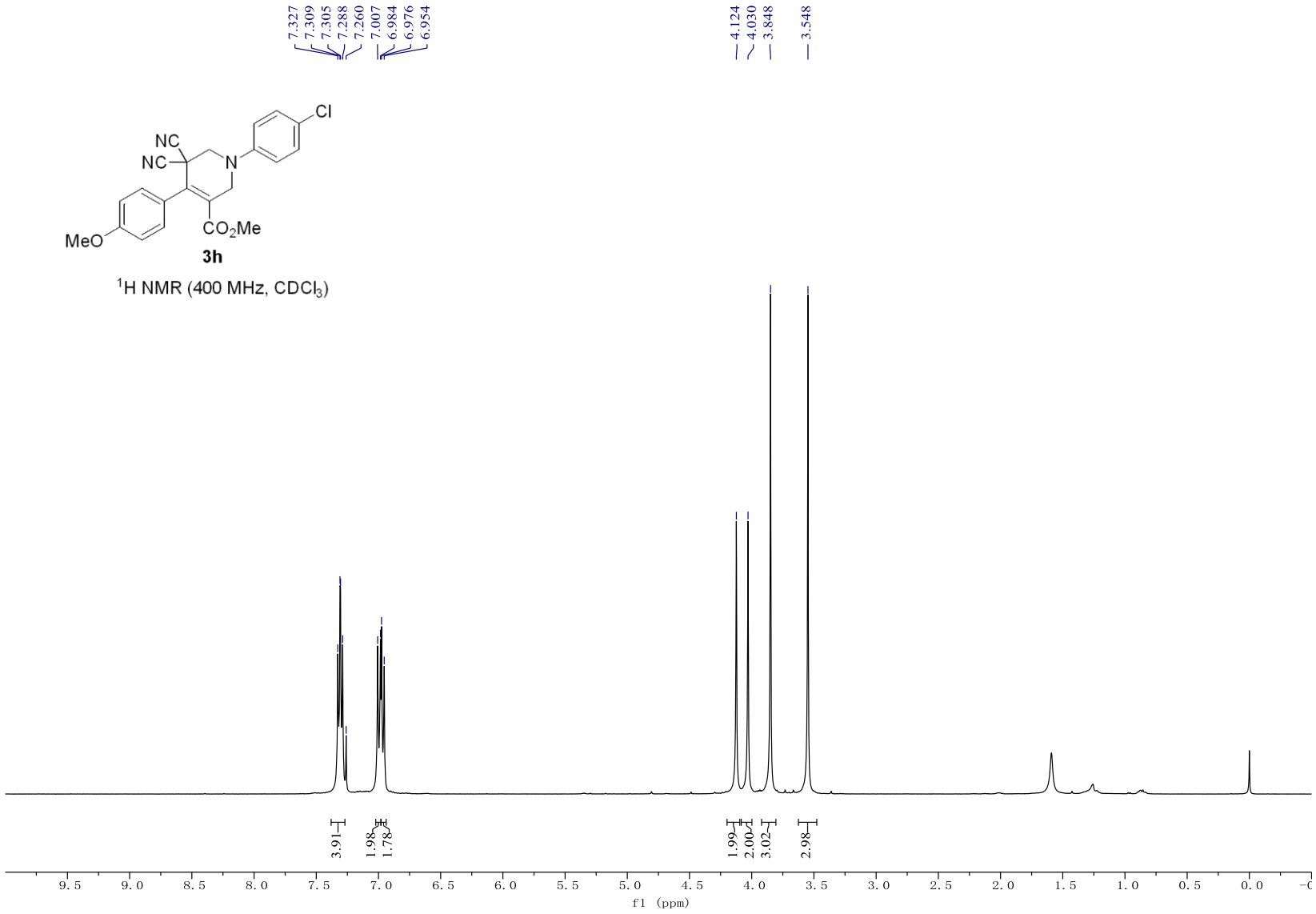

7.317
7.295
7.260
7.058
7.046
6.976
6.954
4.088
3.976
3.848
3.543
F
NC
NC
N
MeO
CO2Me
3g
1H NMR (400 MHz, CDCl3)
1.94
4.08
2.12
2.05
2.20
3.30
3.17
f1 (ppm)

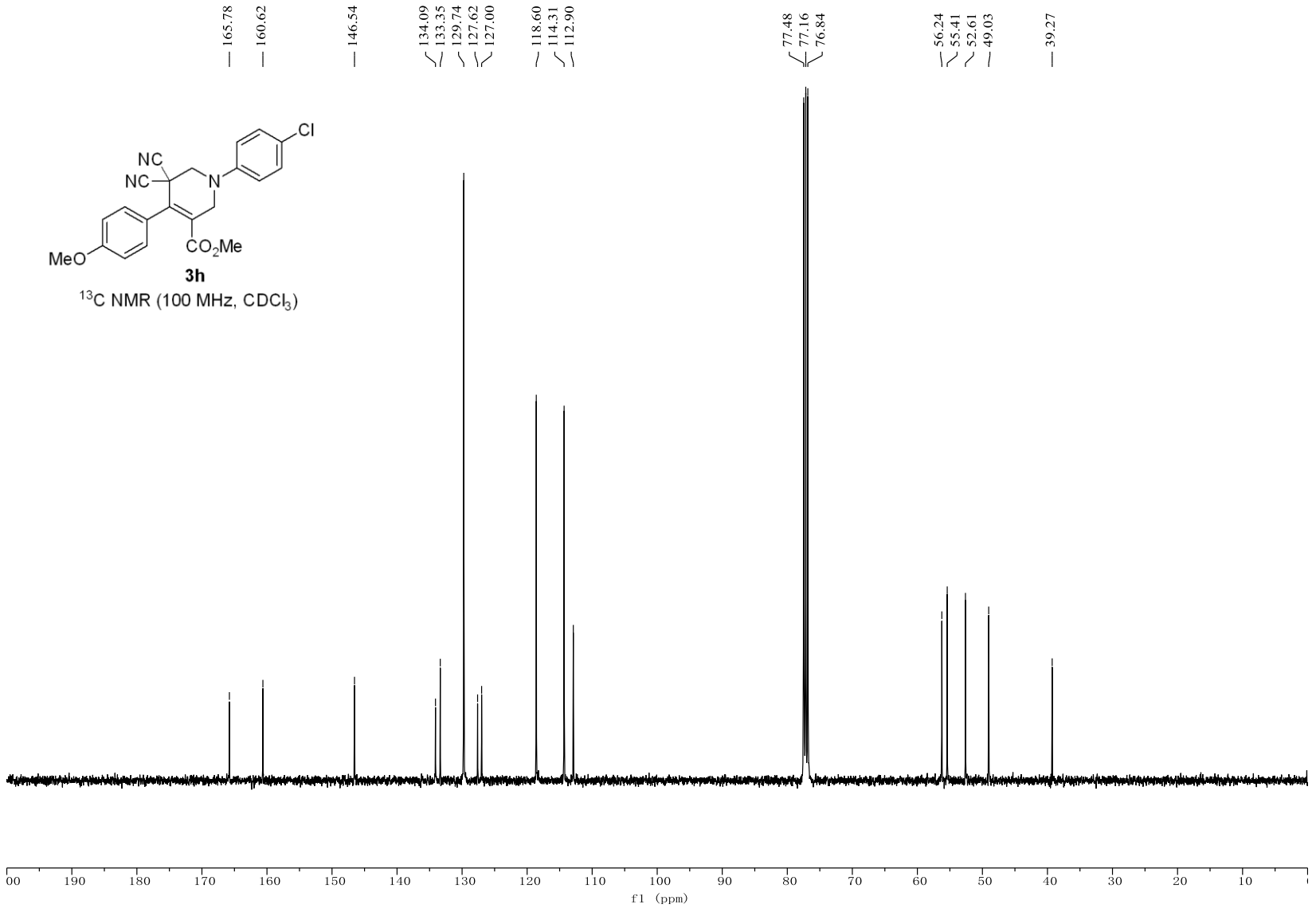

165.84
160.58
159.97
157.55
144.47
133.90
133.61
129.75
127.06
119.75
119.67
116.53
116.31
114.28
113.01
77.48
77.16
76.84
57.14
55.39
52.55
49.87
39.39
F
NC
NC
N
MeO
CO2Me
3g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

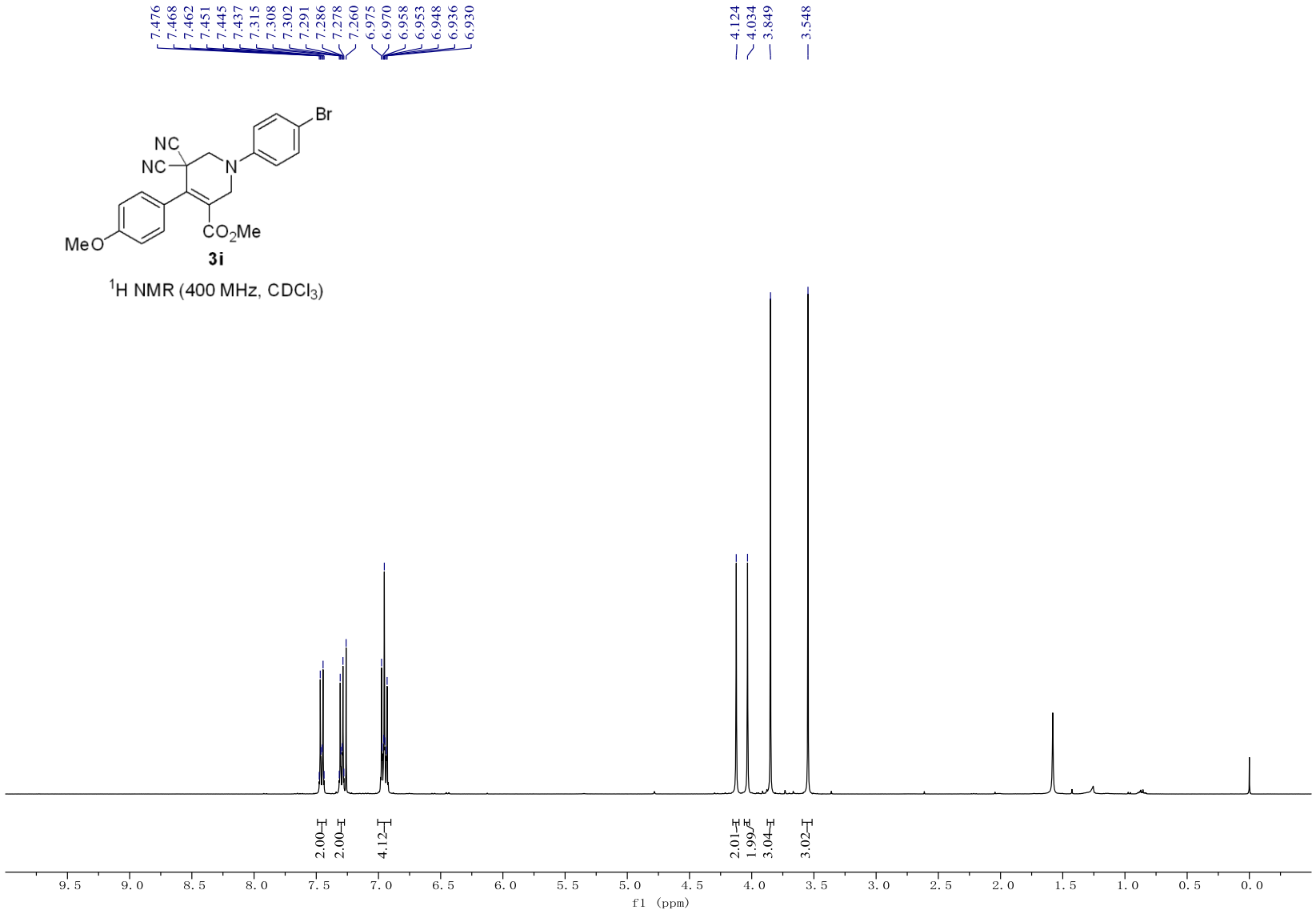


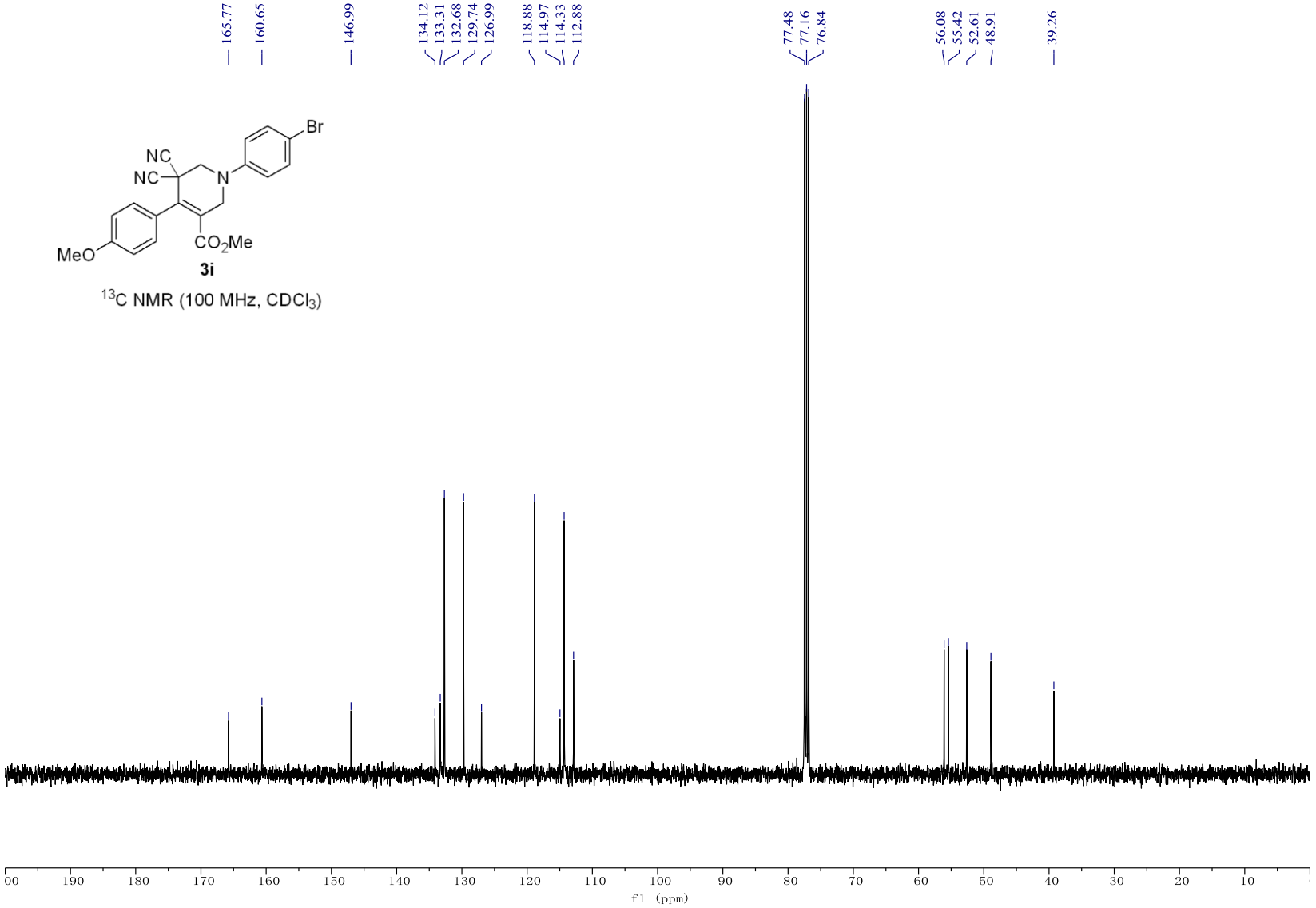
3g

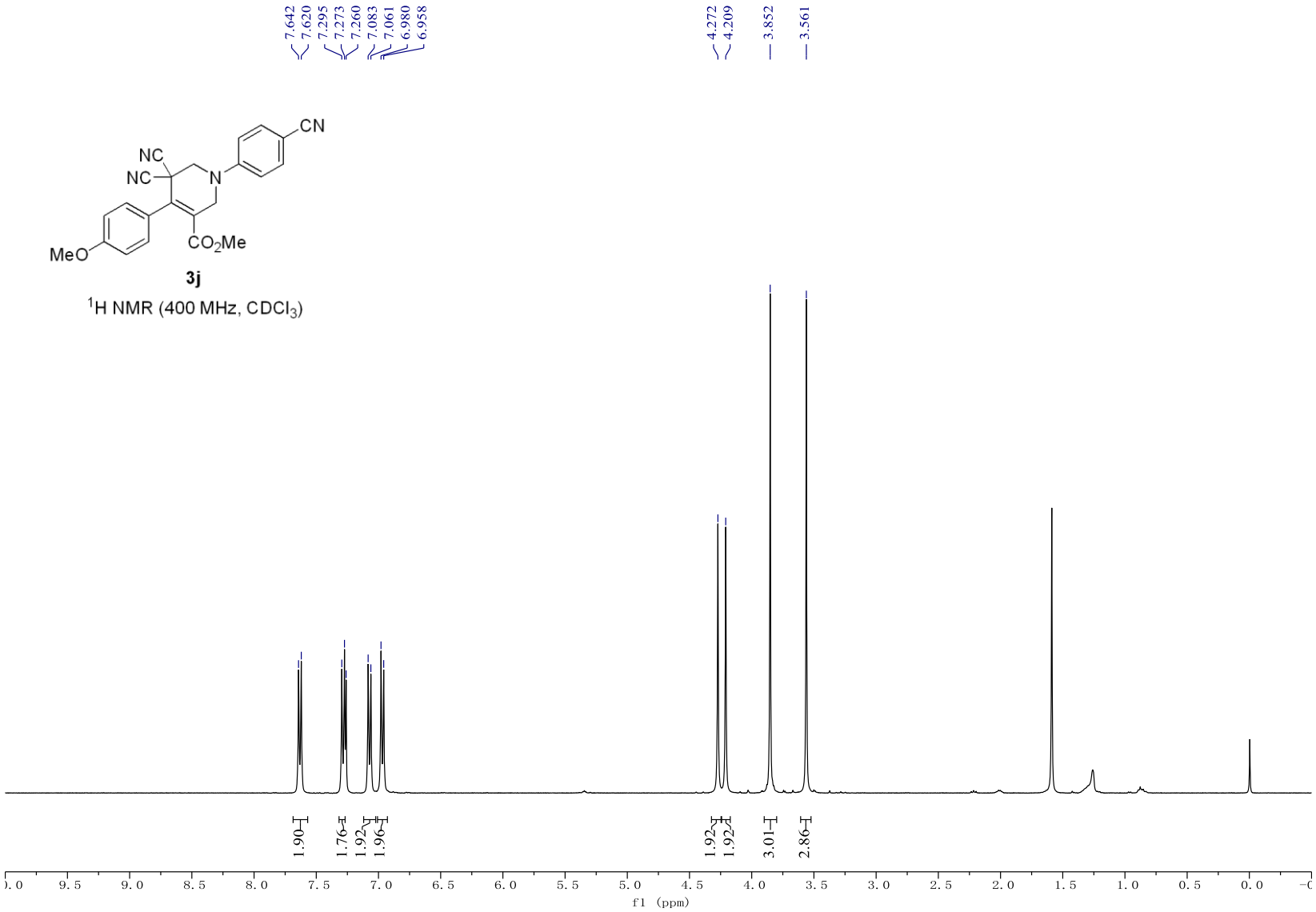
^{19}F NMR (376 MHz, $CDCl_3$)


7.327
7.309
7.305
7.288
7.260
7.007
6.984
6.976
6.954
4.124
4.030
3.848
3.548
NC
NC
N
Cl
MeO
CO2Me
3h
1H NMR (400 MHz, CDCl3)
3.91
1.98
1.78
1.99
2.00
3.02
2.98
f1 (ppm)


165.78
160.62
146.54
134.09
133.35
129.74
127.62
127.00
118.60
114.31
112.90
77.48
77.16
76.84
56.24
55.41
52.61
49.03
39.27
NC
NC
N
Cl
MeO
CO2Me
3h
13C NMR (100 MHz, CDCl3)
f1 (ppm)

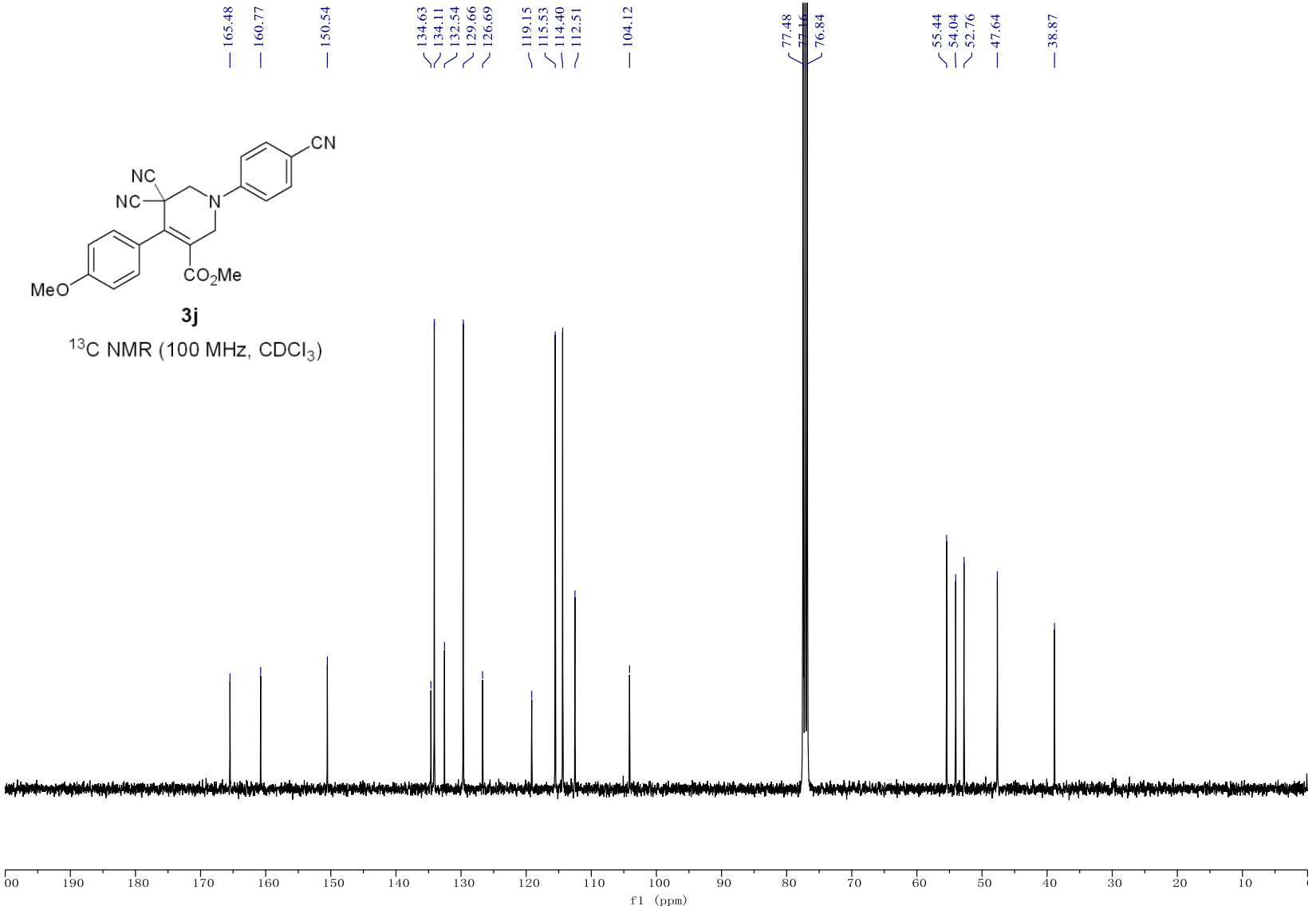

7.476
7.468
7.462
7.451
7.445
7.437
7.315
7.308
7.302
7.291
7.286
7.278
7.260
6.975
6.970
6.958
6.953
6.948
6.936
6.930
4.124
4.034
3.849
3.548
Br
NC
NC
N
MeO
CO2Me
3i
1H NMR (400 MHz, CDCl3)
2.00
2.00
4.12
2.01
1.99
3.04
3.02
f1 (ppm)

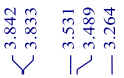

165.77
160.65
146.99
134.12
133.31
132.68
129.74
126.99
118.88
114.97
114.33
112.88
77.48
77.16
76.84
56.08
55.42
52.61
48.91
39.26
Br
NC
NC
N
MeO
CO2Me
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)

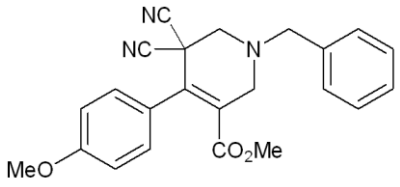


3j

^{1}H NMR (400 MHz, $CDCl_3$)

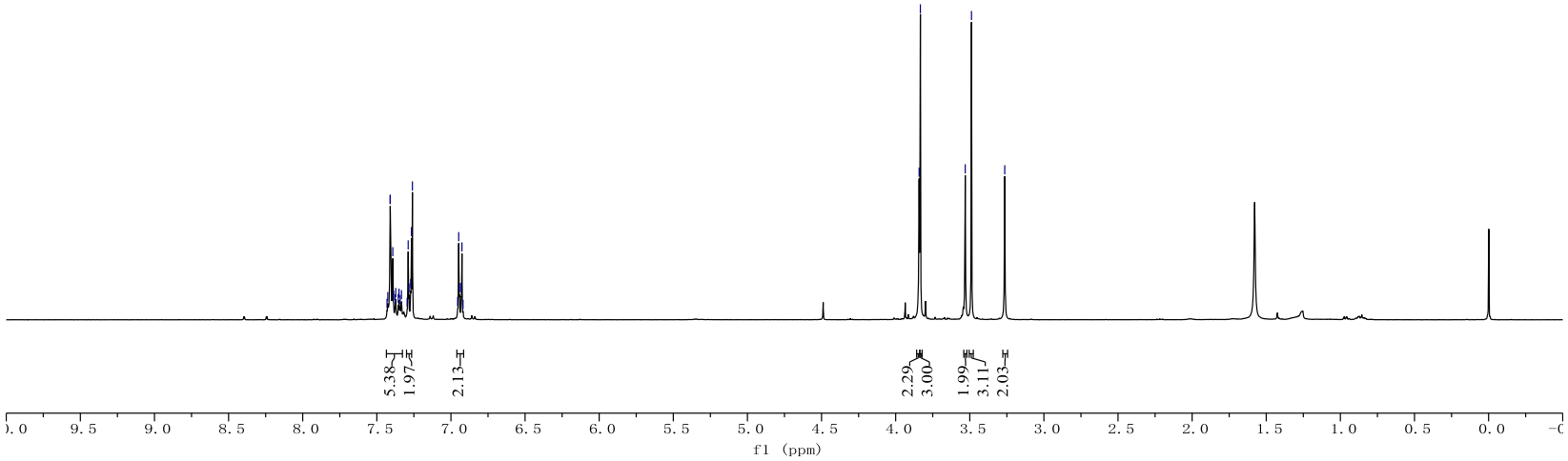

165.48
160.77
150.54
134.63
134.11
132.54
129.66
126.69
119.15
115.53
114.40
112.51
104.12
77.48
77.16
76.84
55.44
54.04
52.76
47.64
38.87
CN
NC
NC
N
MeO
CO2Me
3j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

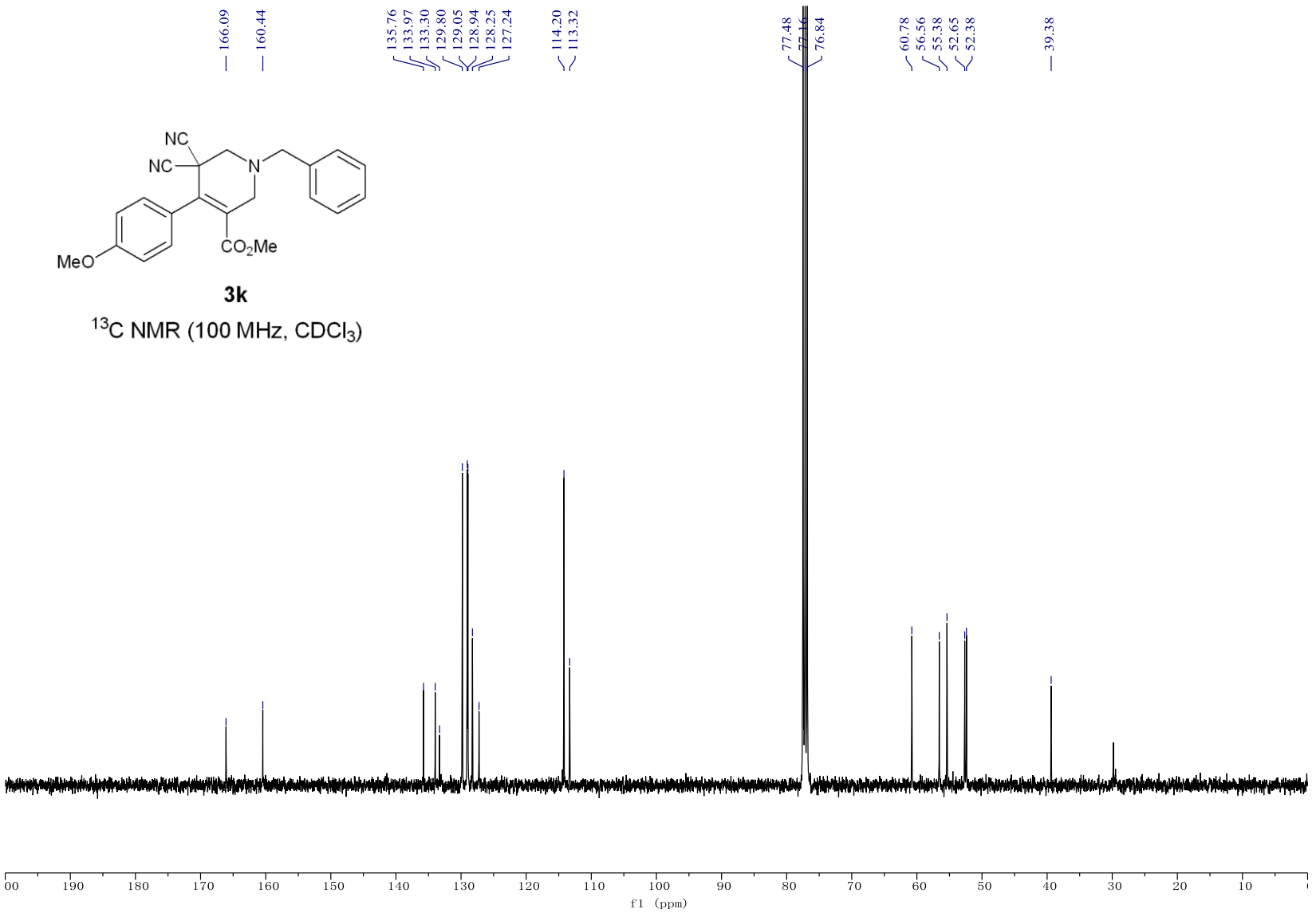




3k

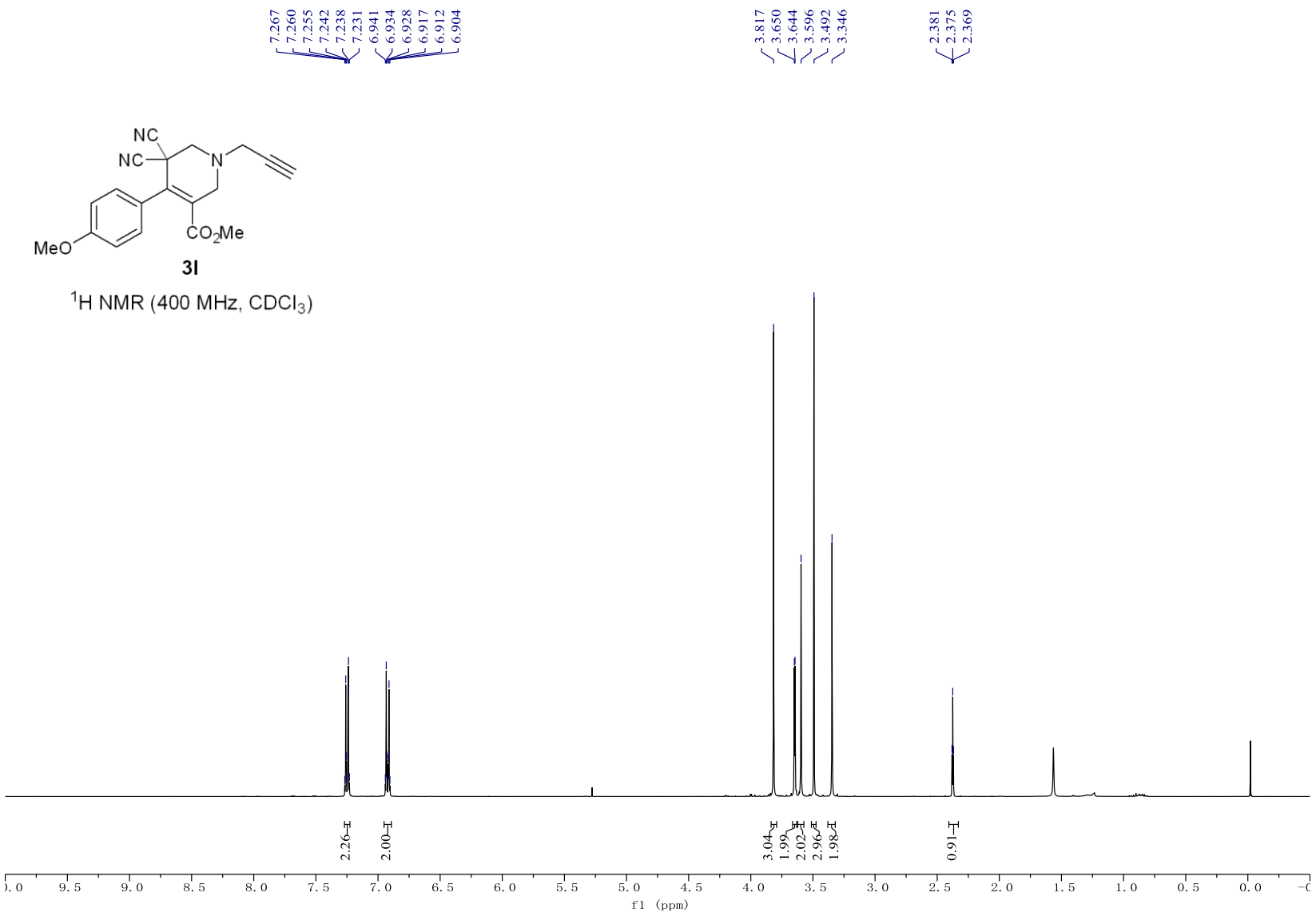
^{1}H NMR (400 MHz, $CDCl_3$)

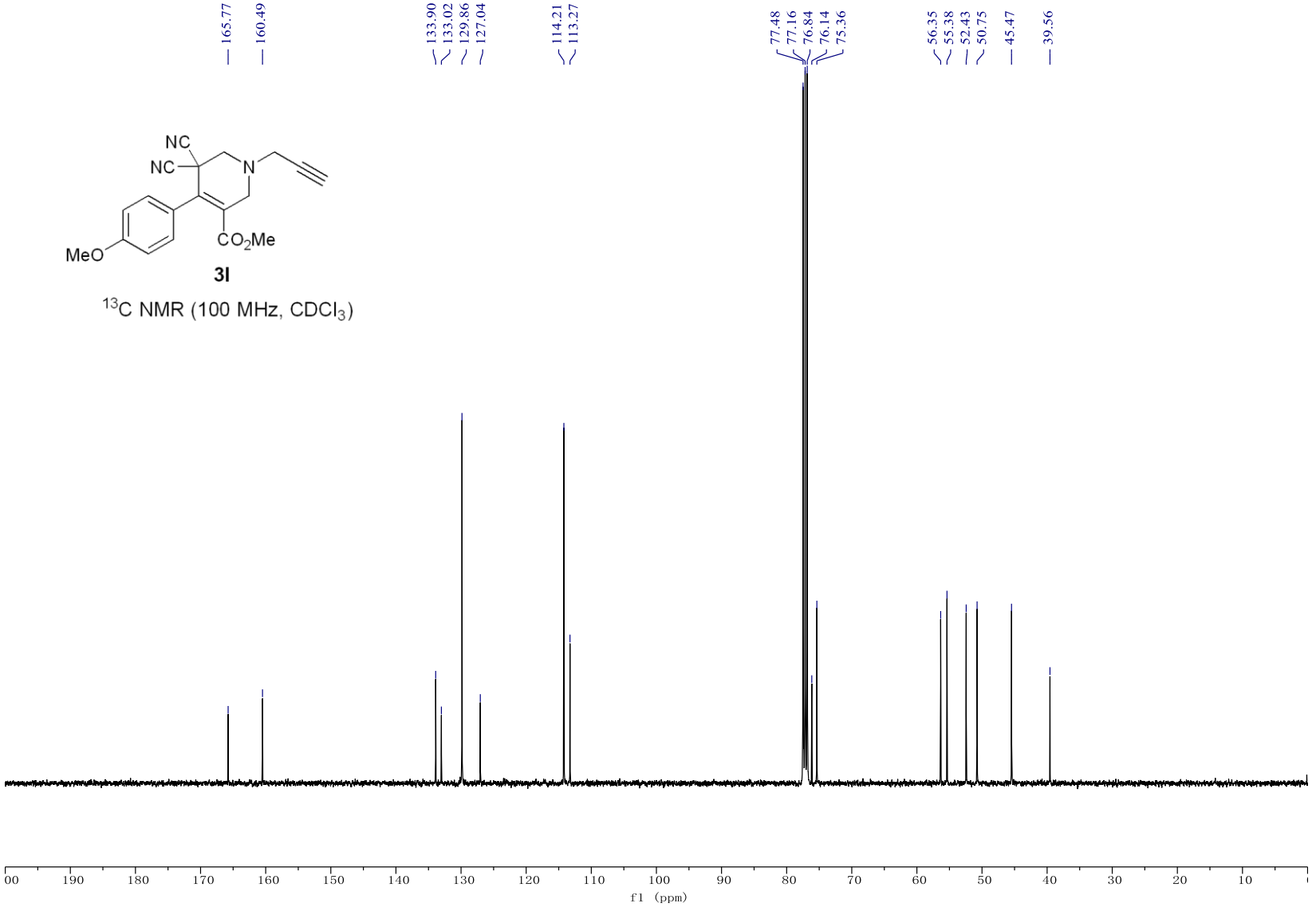




3k

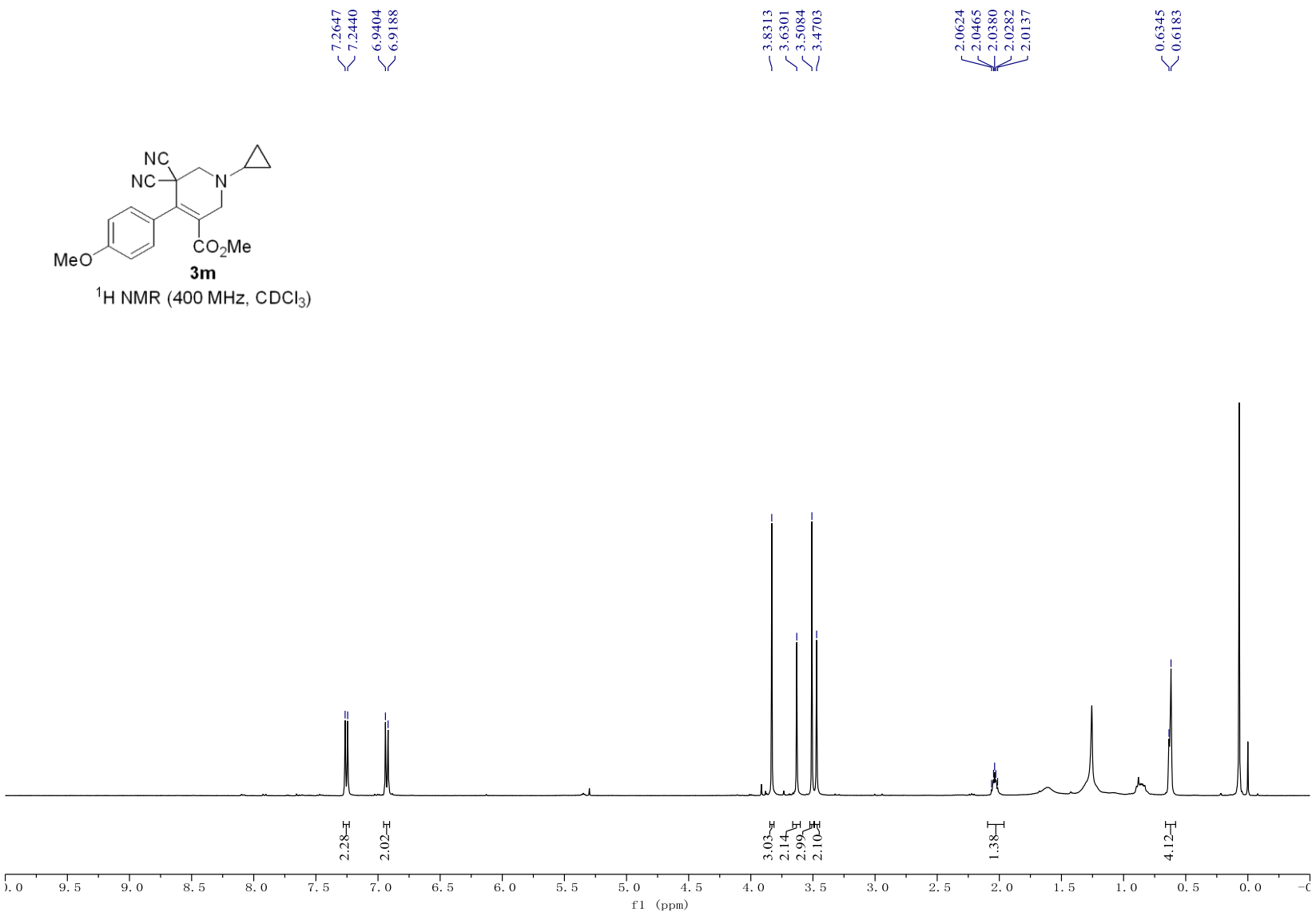
^{13}C NMR (100 MHz, $CDCl_3$)


7.267
7.260
7.255
7.242
7.238
7.231
6.941
6.934
6.928
6.917
6.912
6.904
3.817
3.650
3.644
3.596
3.492
3.346
2.381
2.375
2.369
NC
NC
N
MeO
CO2Me
3I
1H NMR (400 MHz, CDCl3)
2.26
2.00
3.04
1.99
2.02
2.96
1.98
0.91
f1 (ppm)



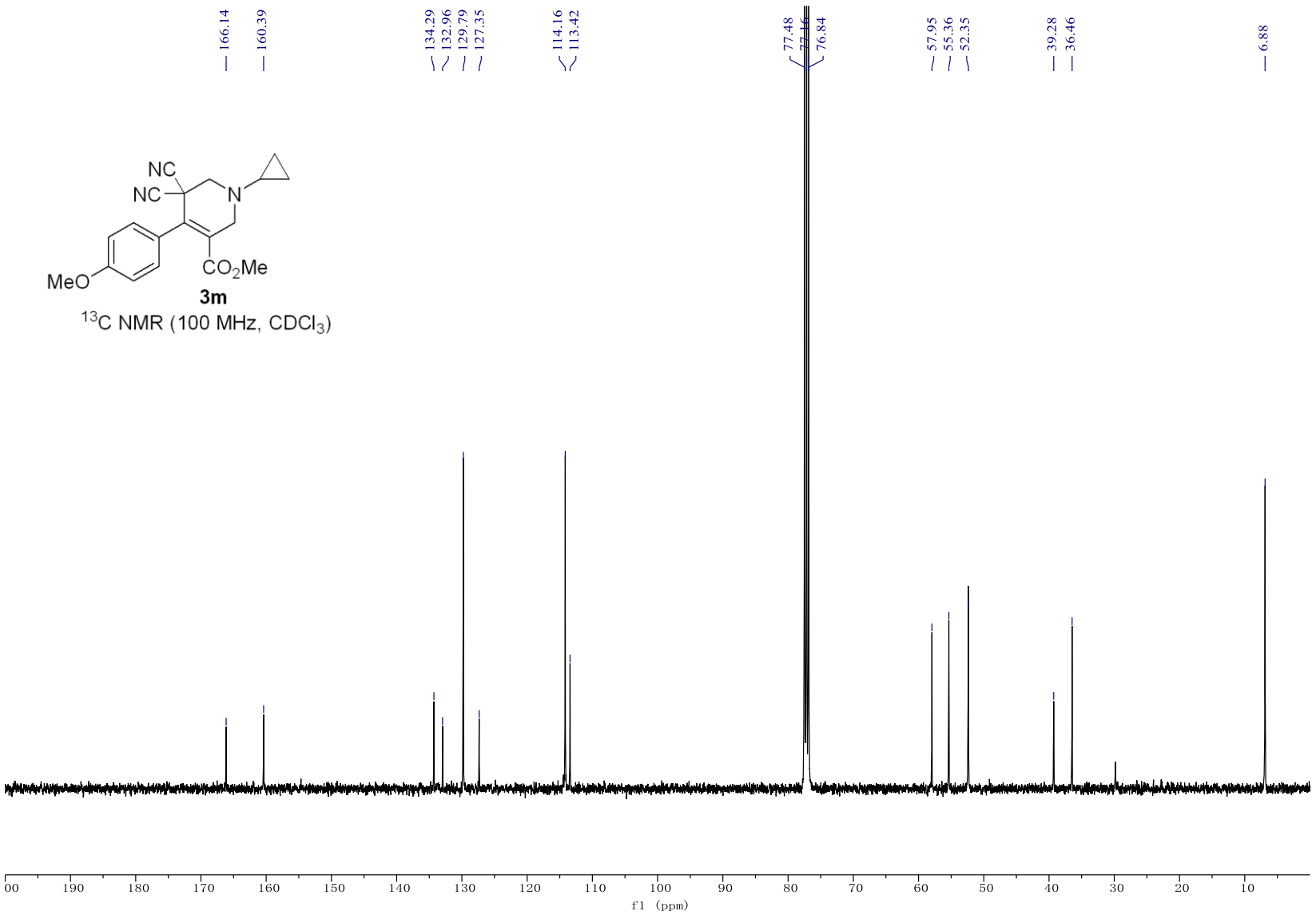
3l

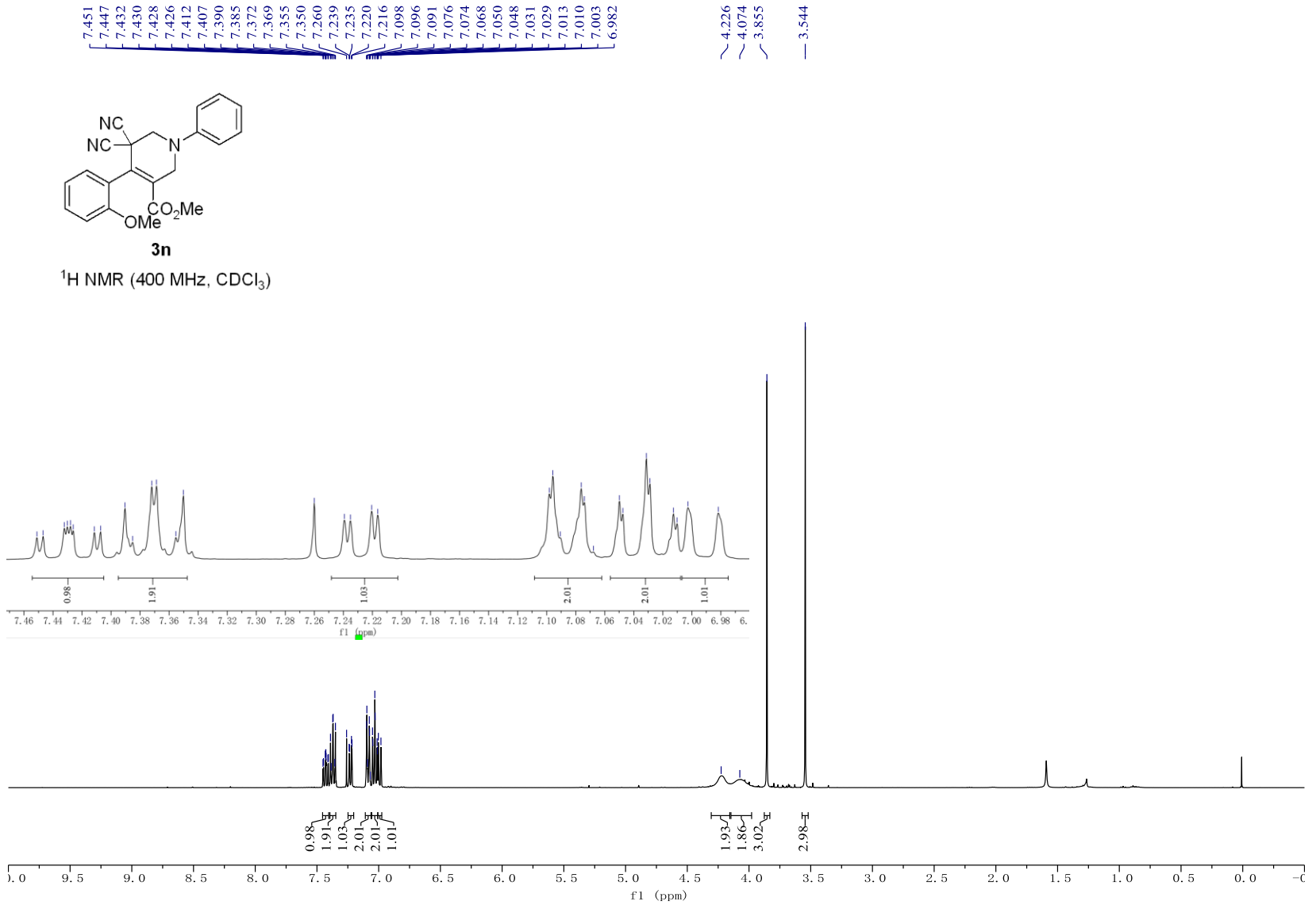
^{13}C NMR (100 MHz, $CDCl_3$)



3m

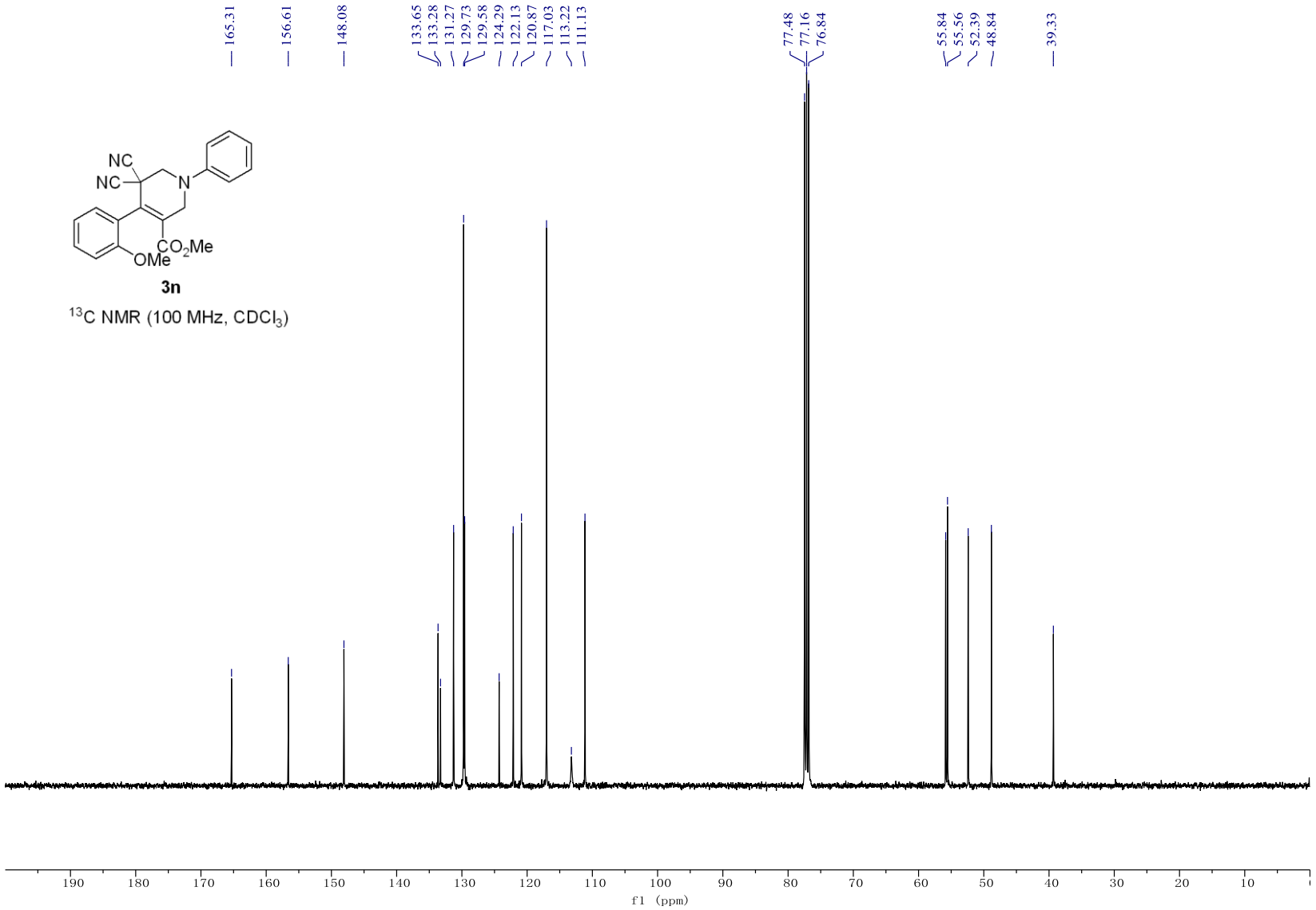
^{1}H NMR (400 MHz, $CDCl_3$)

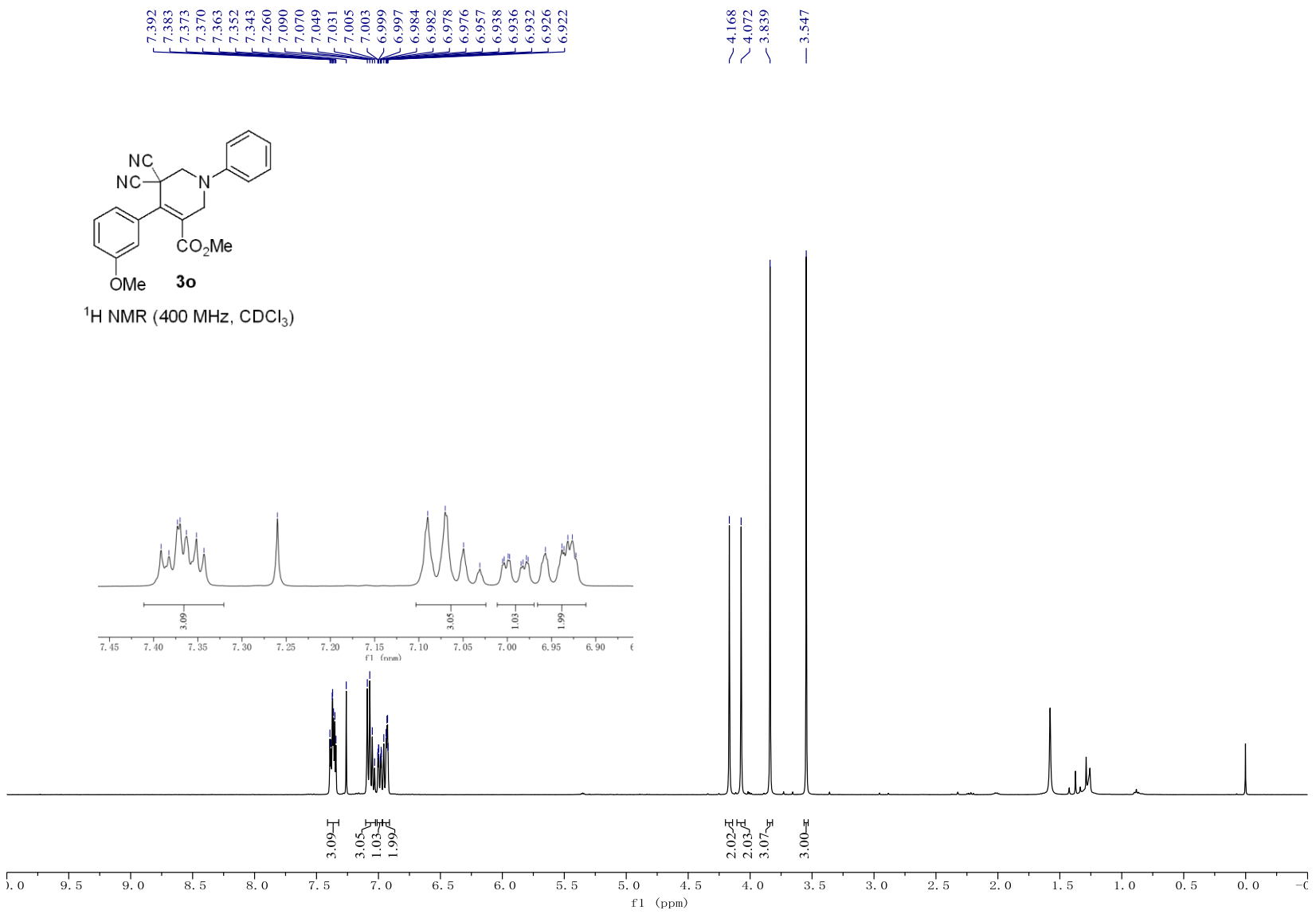

166.14
160.39
134.29
132.96
129.79
127.35
114.16
113.42
77.48
77.16
76.84
57.95
55.36
52.35
39.28
36.46
6.88
NC
NC
N
MeO
CO2Me
3m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

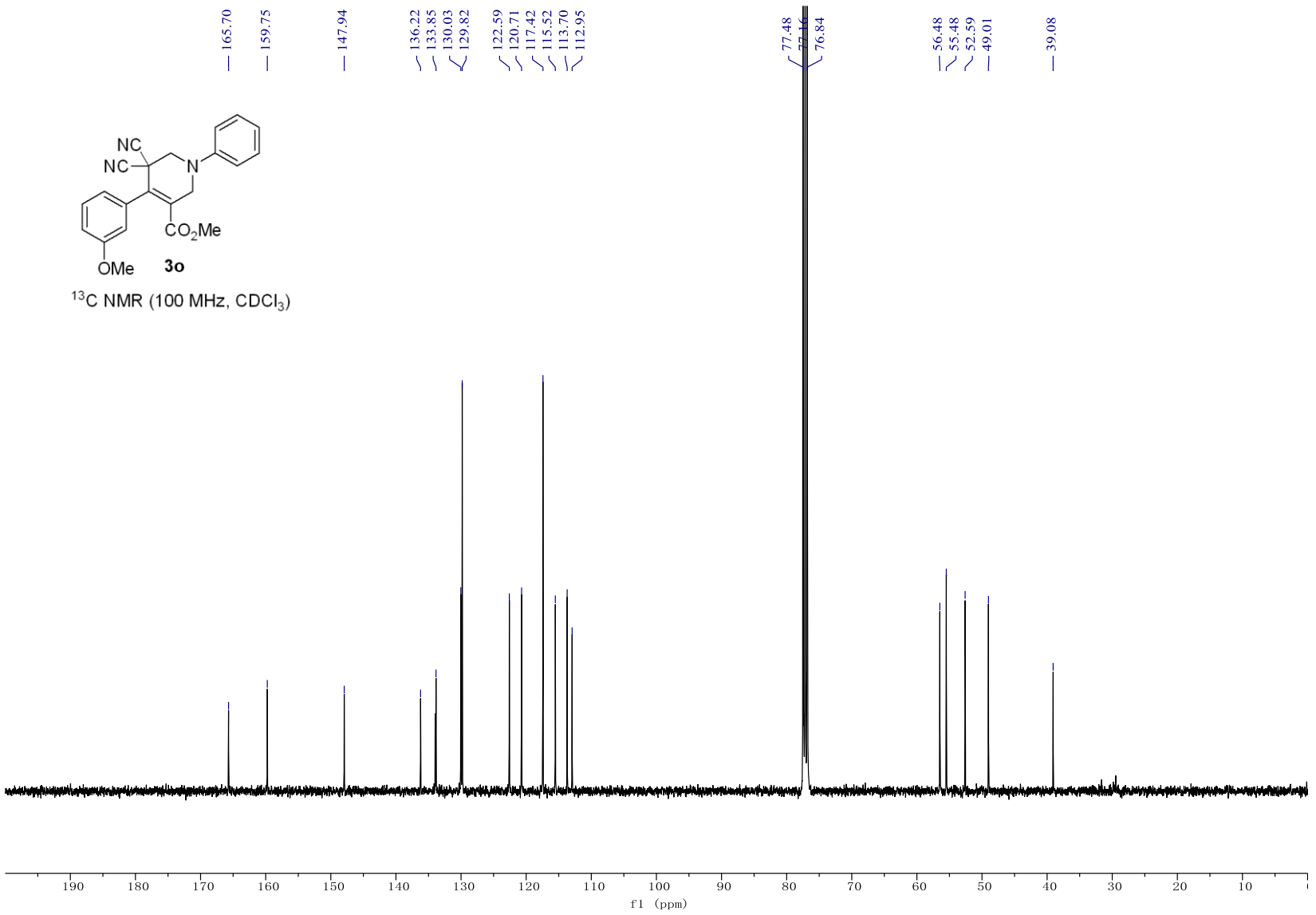


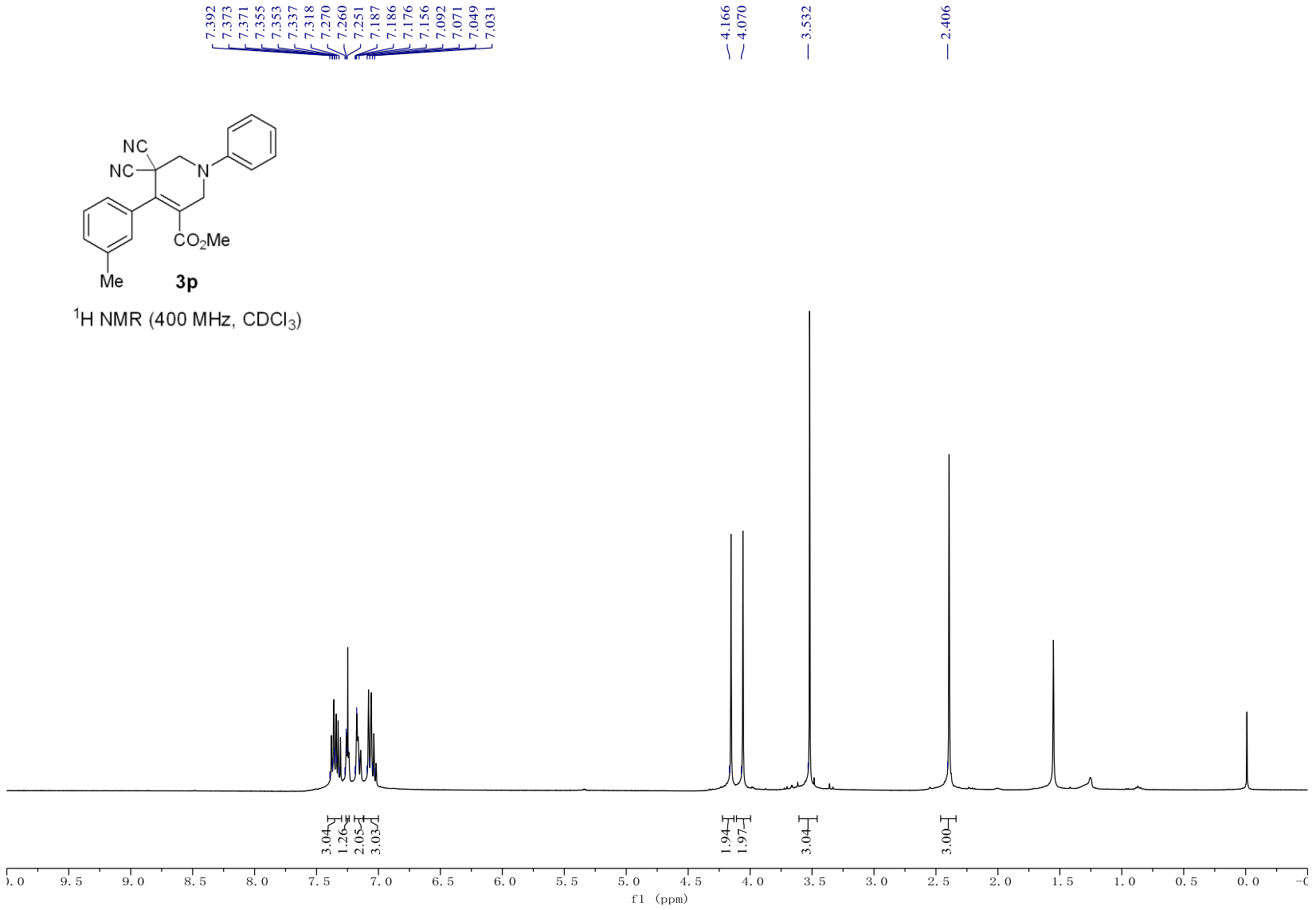
3n

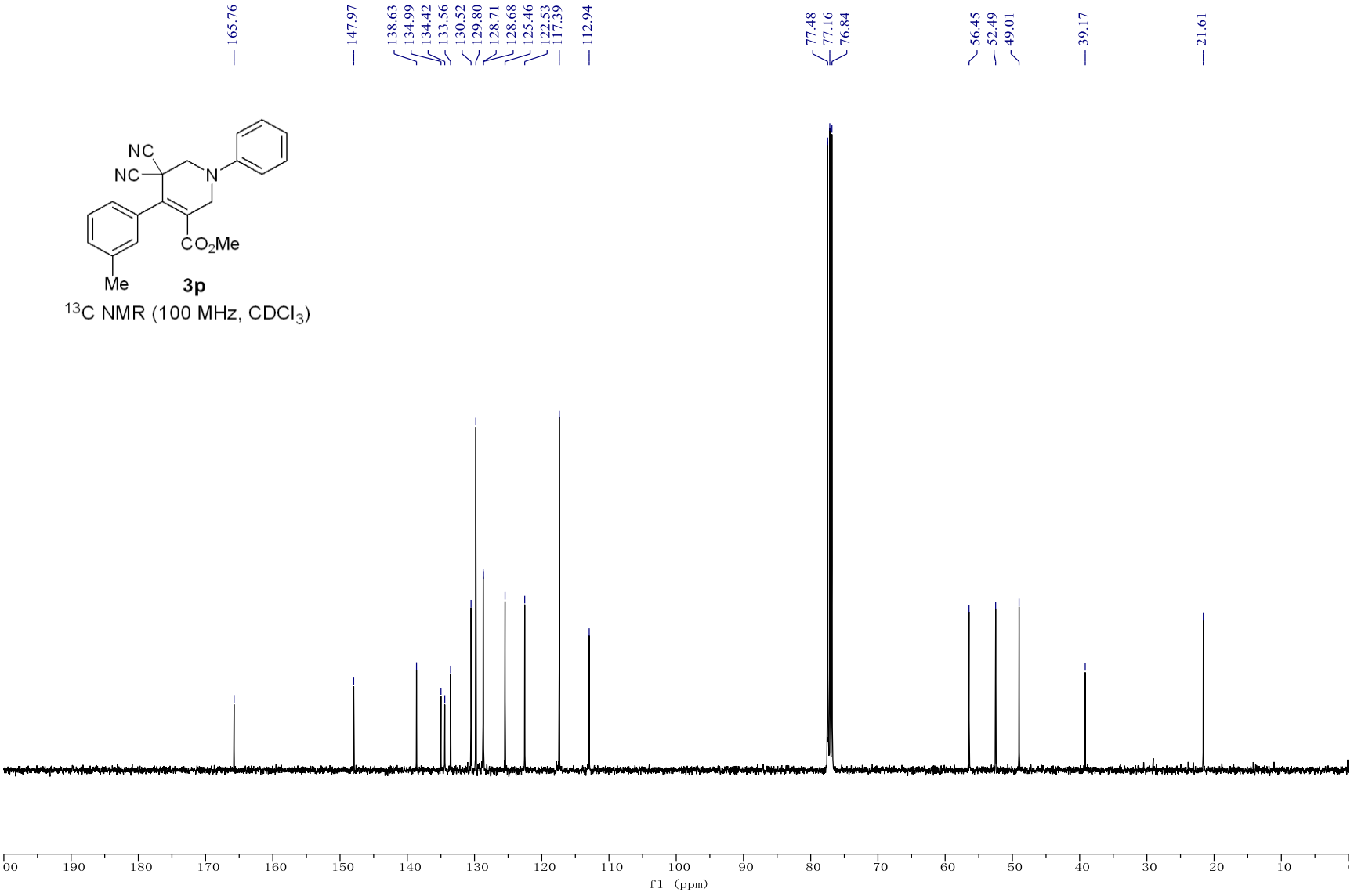
^{1}H NMR (400 MHz, $CDCl_3$)

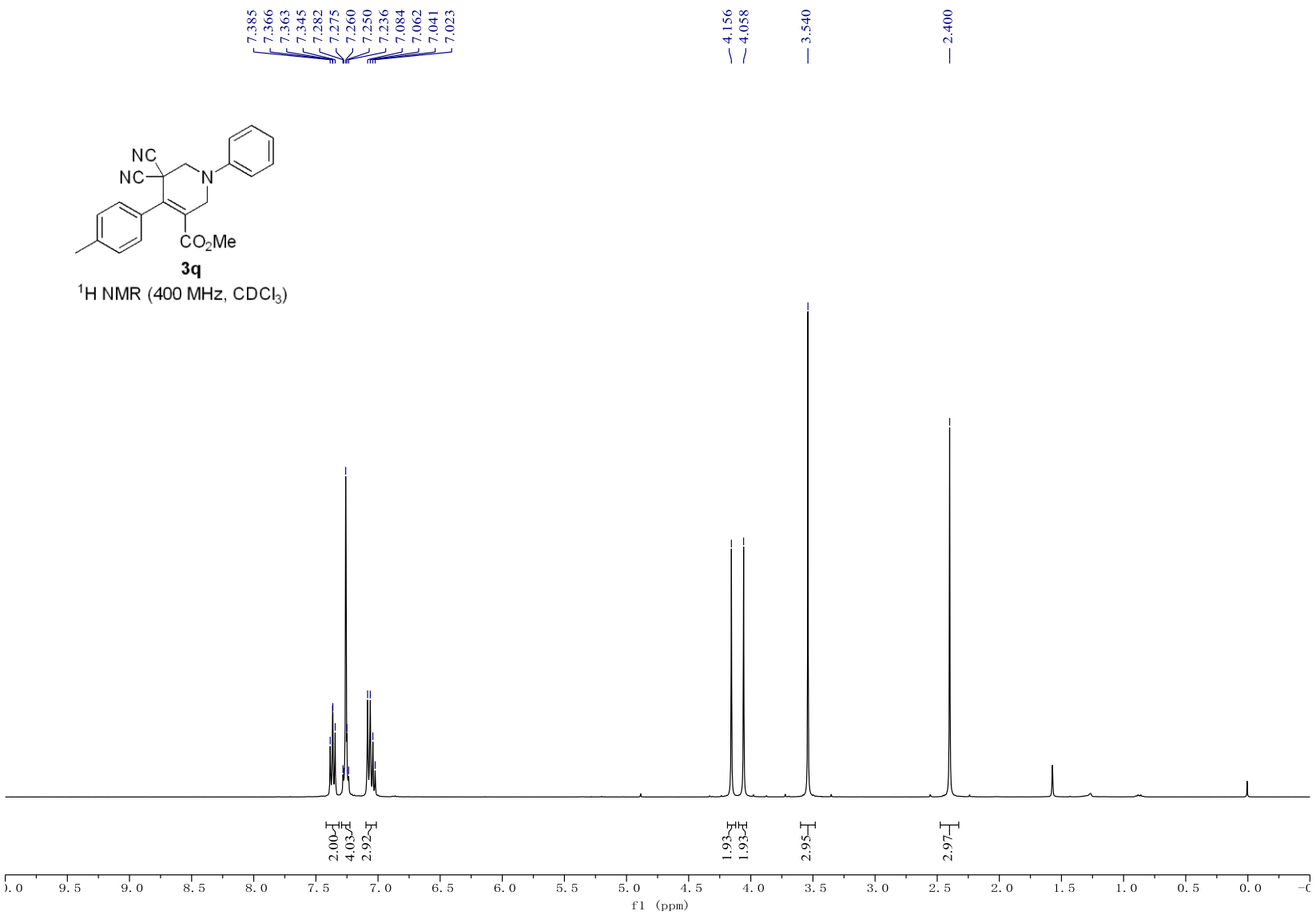

165.31
156.61
148.08
133.65
133.28
131.27
129.73
129.58
124.29
122.13
120.87
117.03
113.22
111.13
77.48
77.16
76.84
55.84
55.56
52.39
48.84
39.33
NC
NC
N
CO2Me
OMe
3n
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

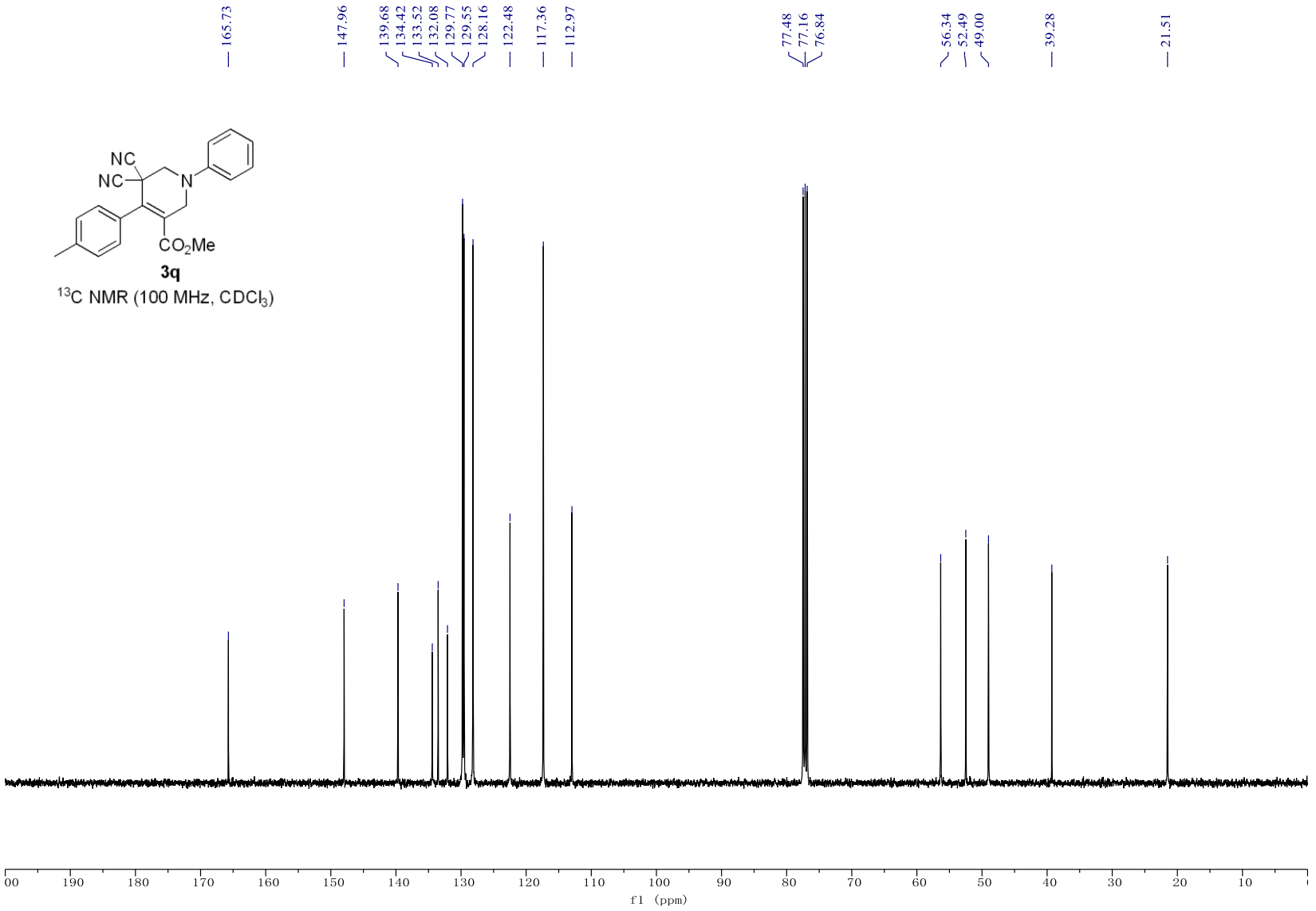

7.392
7.383
7.373
7.370
7.363
7.352
7.343
7.260
7.090
7.070
7.049
7.031
7.005
7.003
6.999
6.997
6.984
6.982
6.978
6.976
6.957
6.938
6.936
6.932
6.926
6.922
4.168
4.072
3.839
3.547
NC
NC
N
CO2Me
OMe
3o
1H NMR (400 MHz, CDCl3)
3.09
3.05
1.03
1.99
2.02
2.03
3.07
3.00
f1 (ppm)

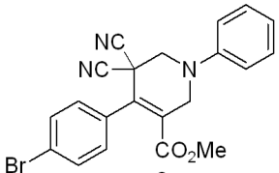

165.70
159.75
147.94
136.22
133.85
130.03
129.82
122.59
120.71
117.42
115.52
113.70
112.95
77.48
77.16
76.84
56.48
55.48
52.59
49.01
39.08
NC
NC
N
CO2Me
OMe
3o
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.392
7.373
7.371
7.355
7.353
7.337
7.318
7.270
7.260
7.251
7.187
7.186
7.176
7.156
7.092
7.071
7.049
7.031
4.166
4.070
3.532
2.406
NC
NC
N
CO2Me
Me
3p
1H NMR (400 MHz, CDCl3)
3.04
1.26
2.05
3.03
1.94
1.97
3.04
3.00
f1 (ppm)


165.76
147.97
138.63
134.99
134.42
133.56
130.52
129.80
128.71
128.68
125.46
122.53
117.39
112.94
77.48
77.16
76.84
56.45
52.49
49.01
39.17
21.61
NC
NC
N
CO2Me
Me
3p
13C NMR (100 MHz, CDCl3)
f1 (ppm)

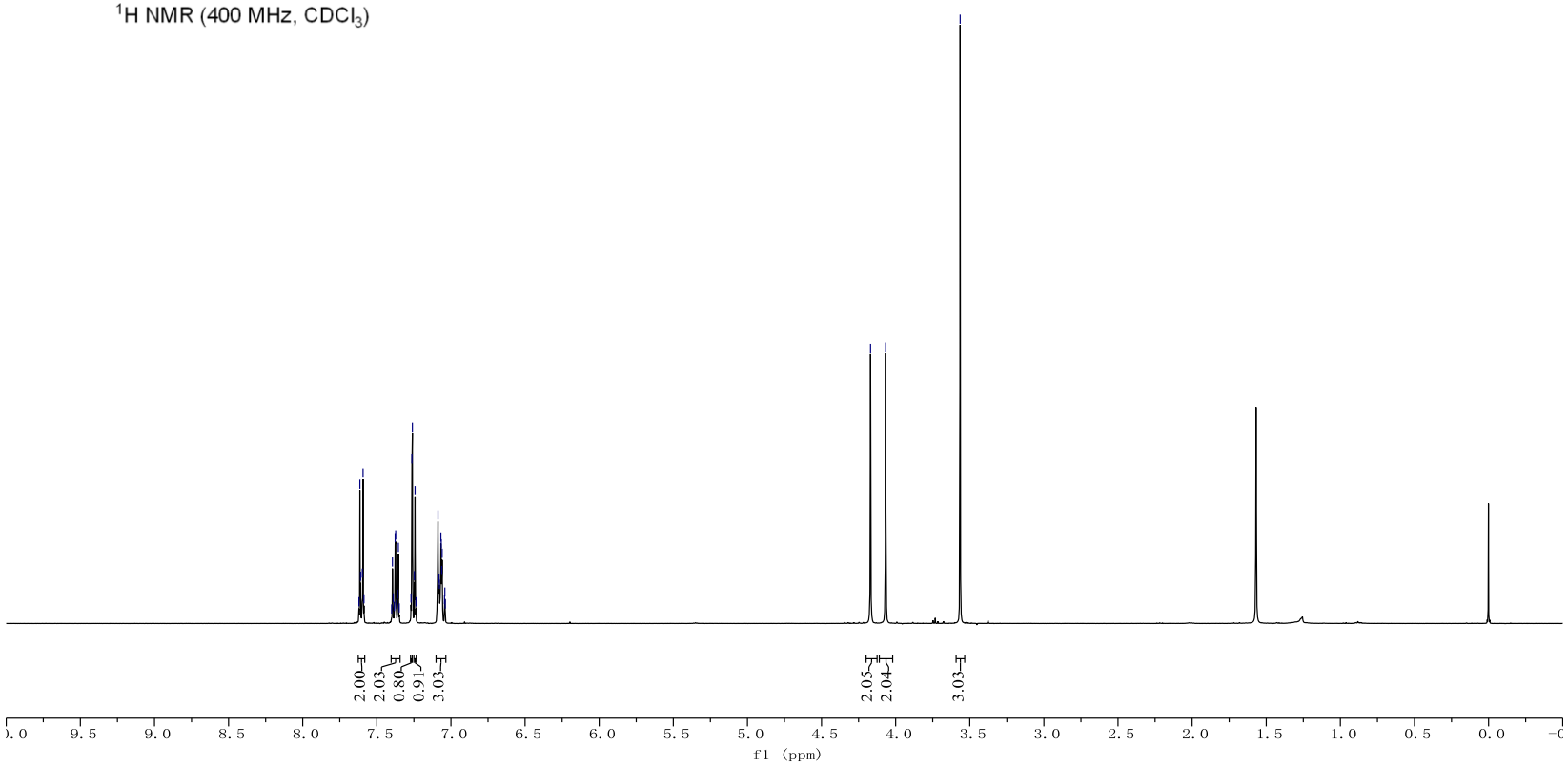

7.385
7.366
7.363
7.345
7.282
7.275
7.260
7.250
7.236
7.084
7.062
7.041
7.023
4.156
4.058
3.540
2.400
NC
NC
N
CO2Me
3q
1H NMR (400 MHz, CDCl3)
2.00
4.03
2.92
1.93
1.93
2.95
2.97
f1 (ppm)

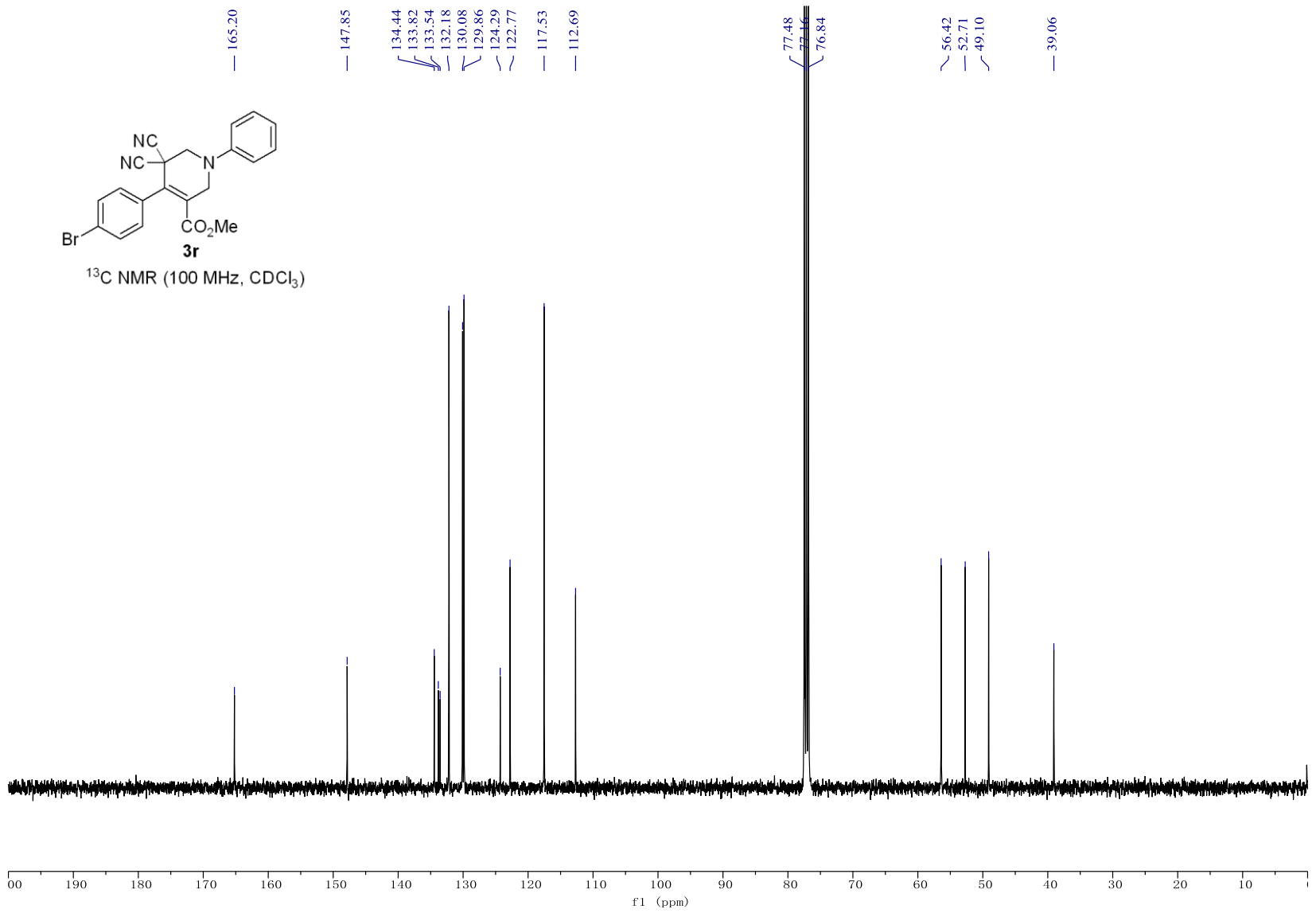

165.73
147.96
139.68
134.42
133.52
132.08
129.77
129.55
128.16
122.48
117.36
112.97
77.48
77.16
76.84
56.34
52.49
49.00
39.28
21.51
NC
NC
N
CO2Me
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)

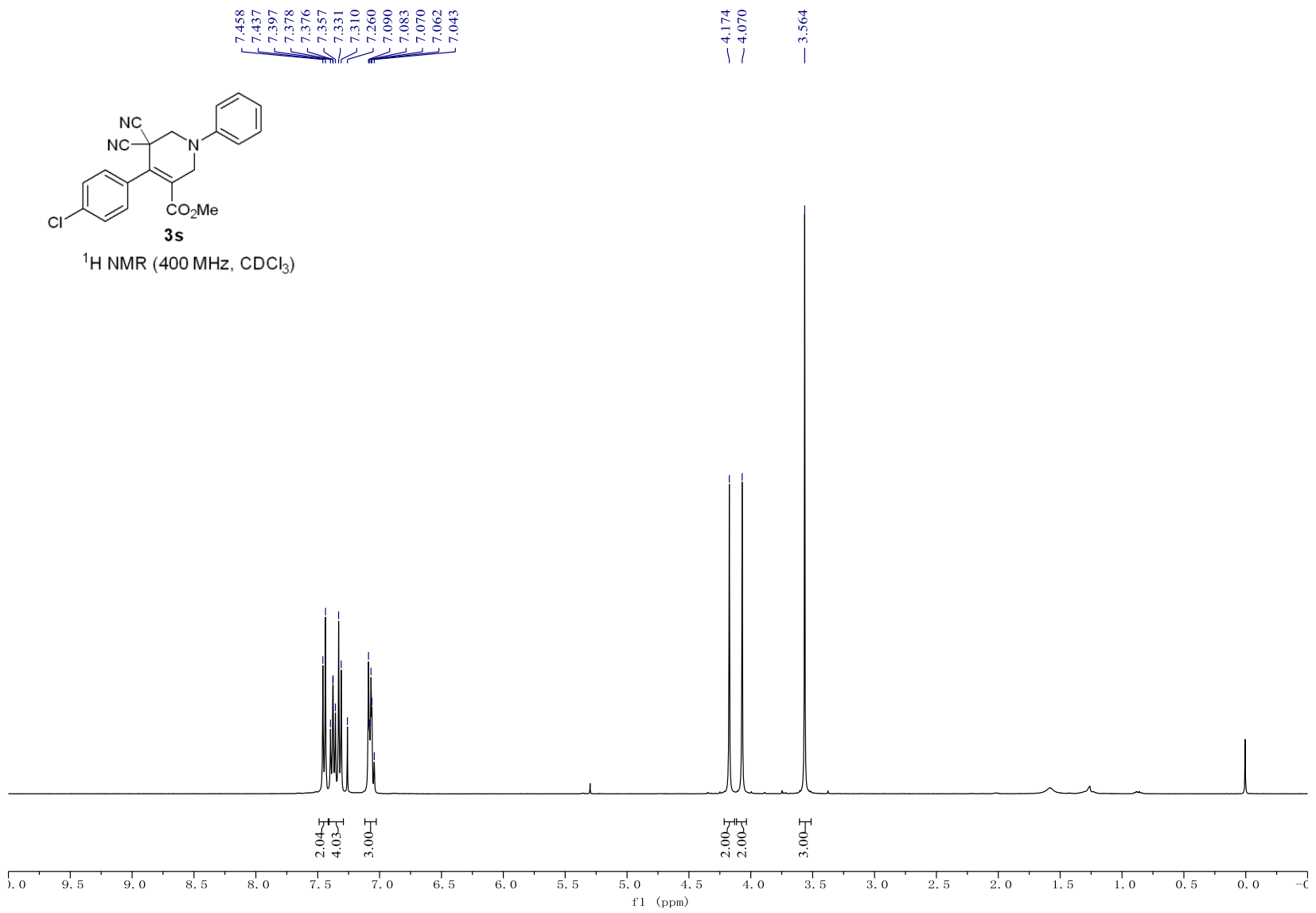


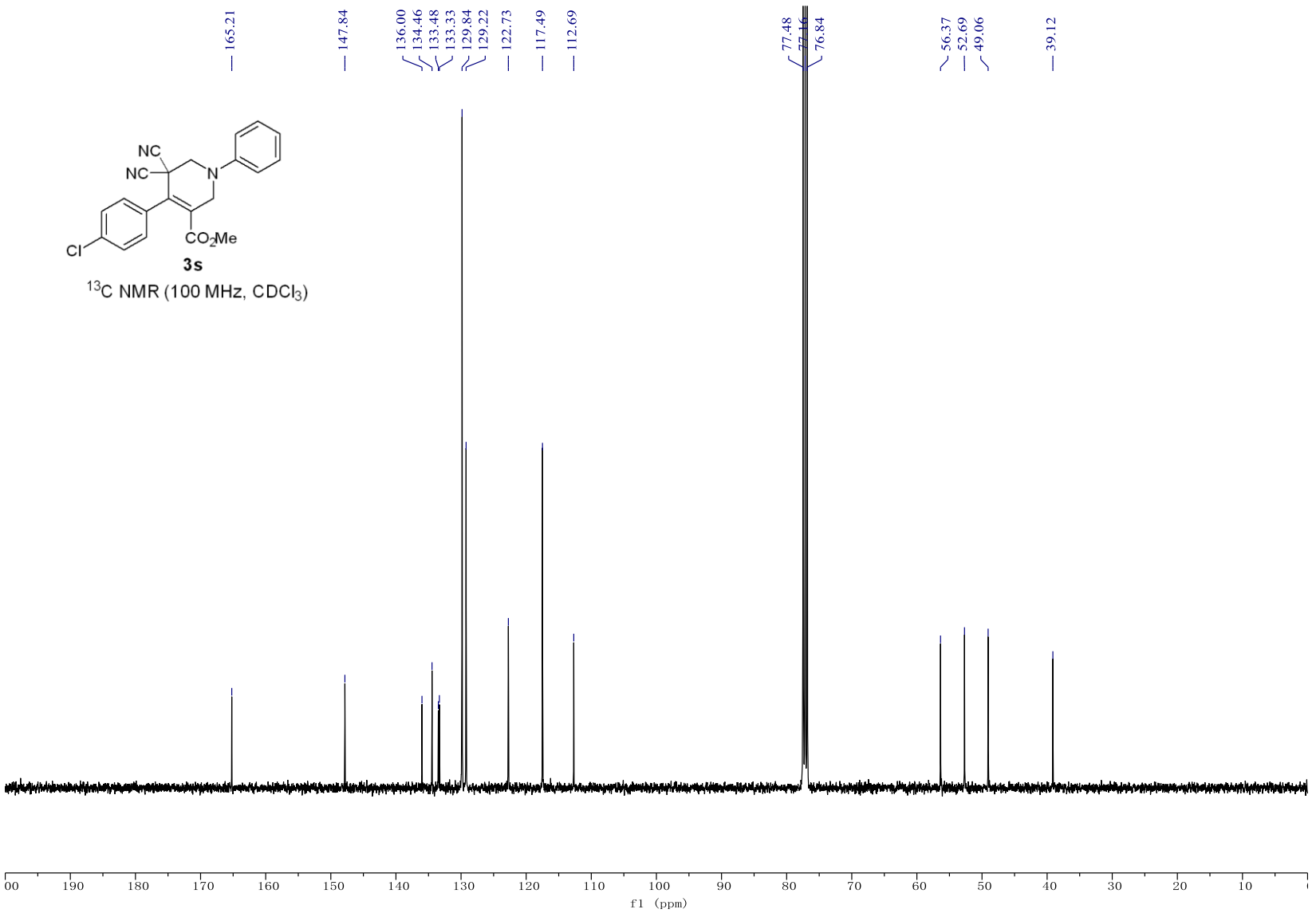
3r

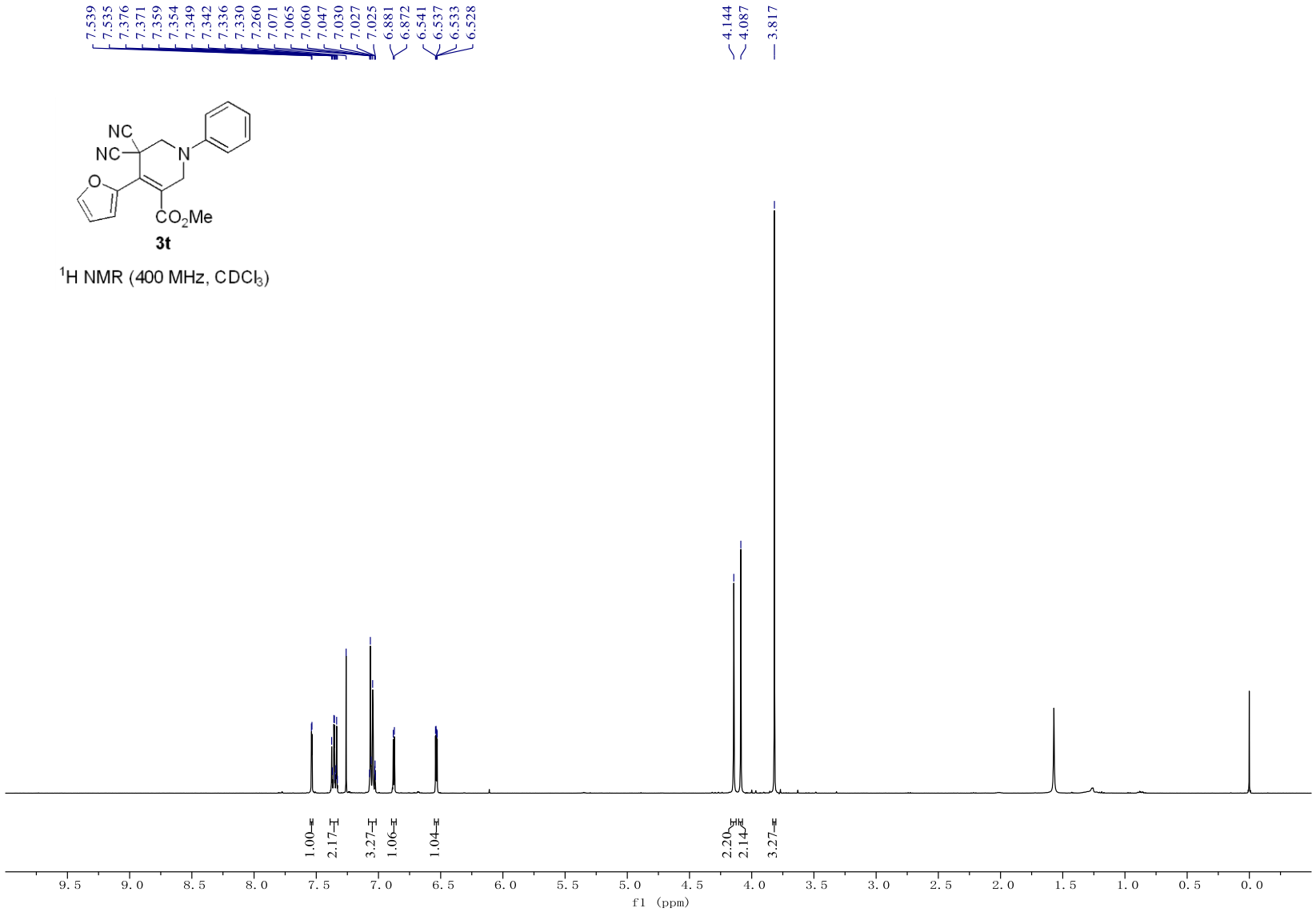
^{1}H NMR (400 MHz, $CDCl_3$)




165.20
147.85
134.44
133.82
133.54
132.18
130.08
129.86
124.29
122.77
117.53
112.69
77.48
77.16
76.84
56.42
52.71
49.10
39.06
NC
NC
N
Br
CO2Me
3r
13C NMR (100 MHz, CDCl3)
f1 (ppm)

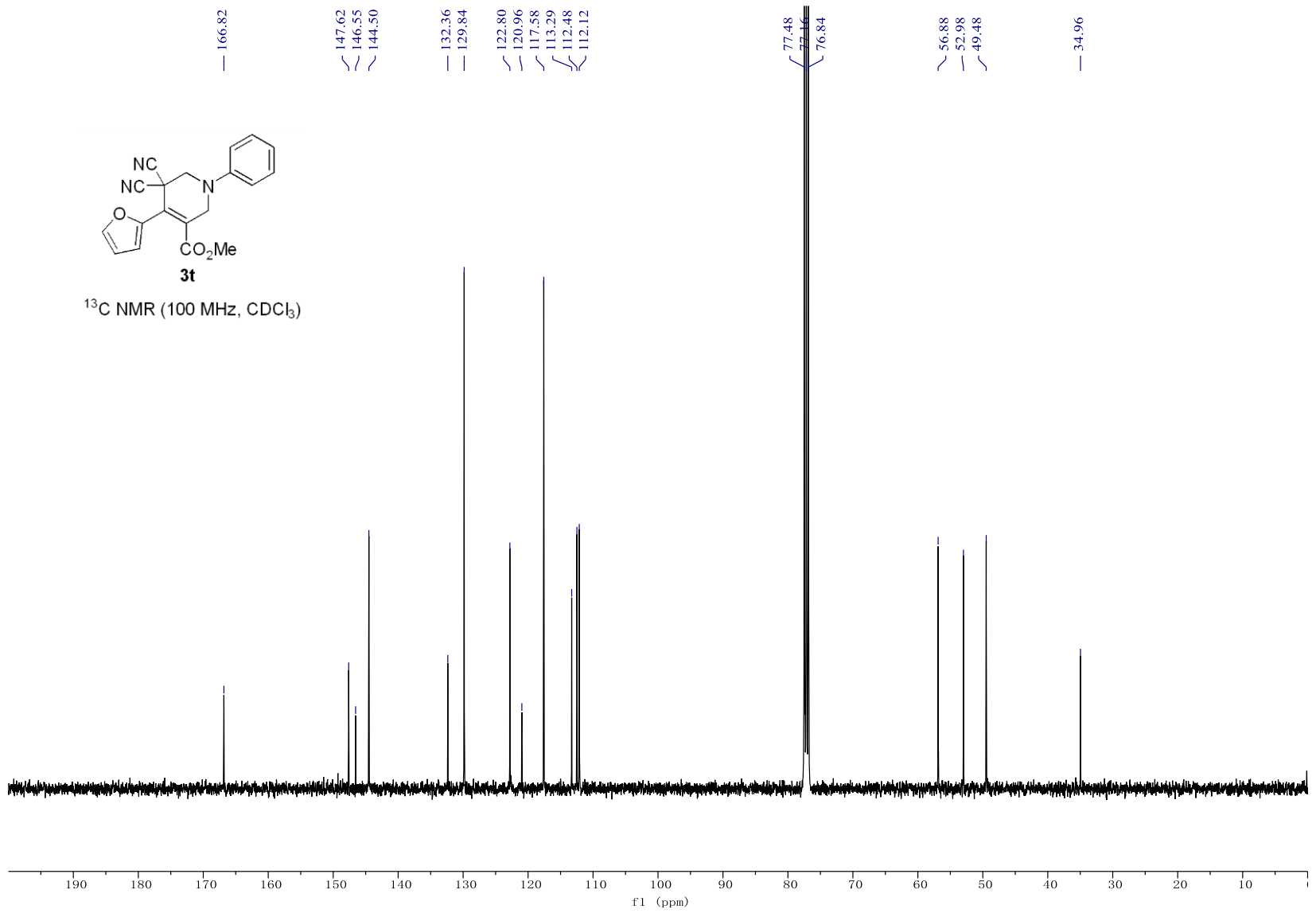

7.458
7.437
7.397
7.378
7.376
7.357
7.331
7.310
7.260
7.090
7.083
7.070
7.062
7.043
4.174
4.070
3.564
NC
NC
N
Cl
CO2Me
3s
1H NMR (400 MHz, CDCl3)
2.04
4.03
3.00
2.00
2.00
3.00
f1 (ppm)

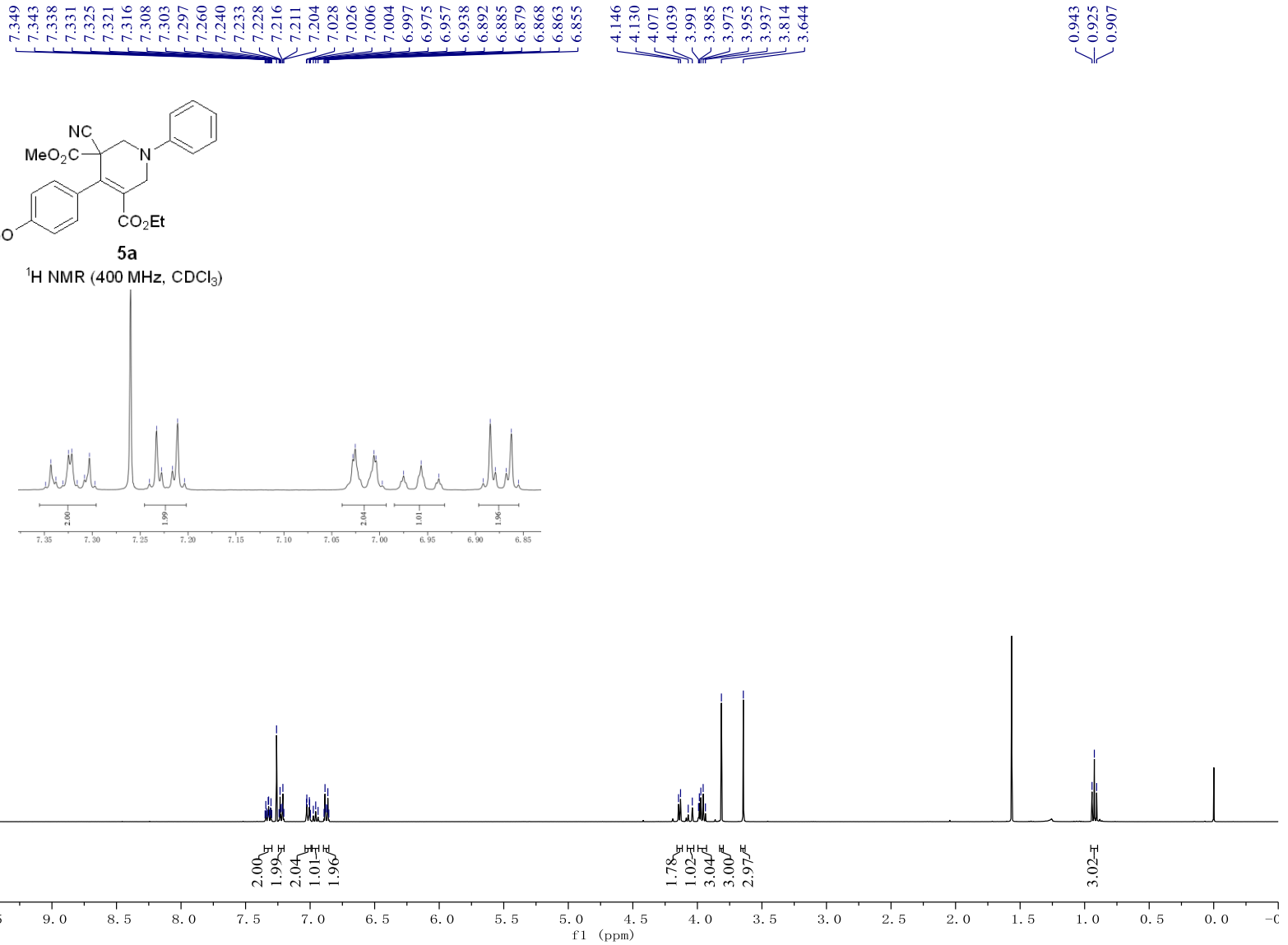

165.21
147.84
136.00
134.46
133.48
133.33
129.84
129.22
122.73
117.49
112.69
77.48
77.16
76.84
56.37
52.69
49.06
39.12
NC
NC
N
Cl
CO2Me
3s
13C NMR (100 MHz, CDCl3)
f1 (ppm)

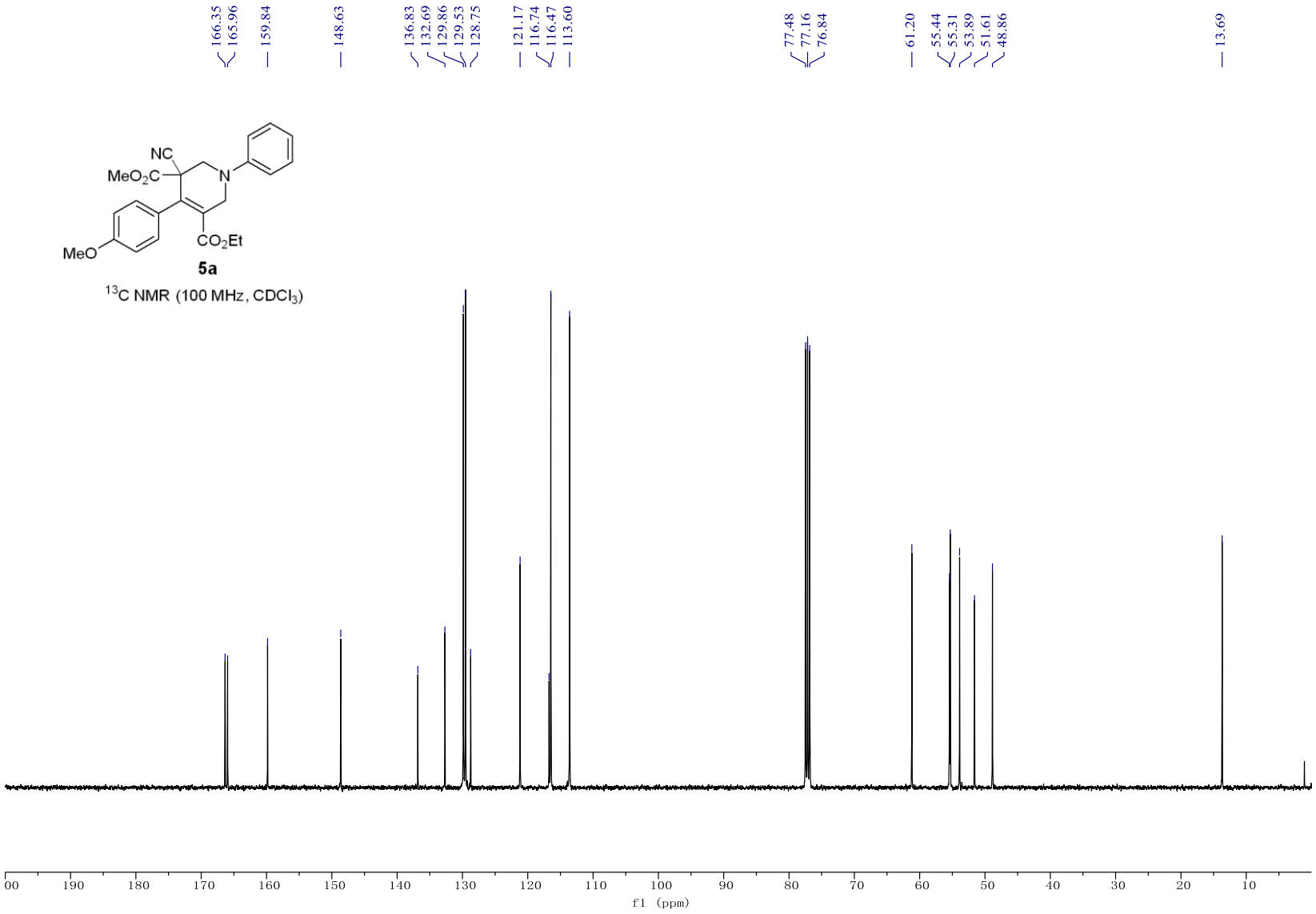


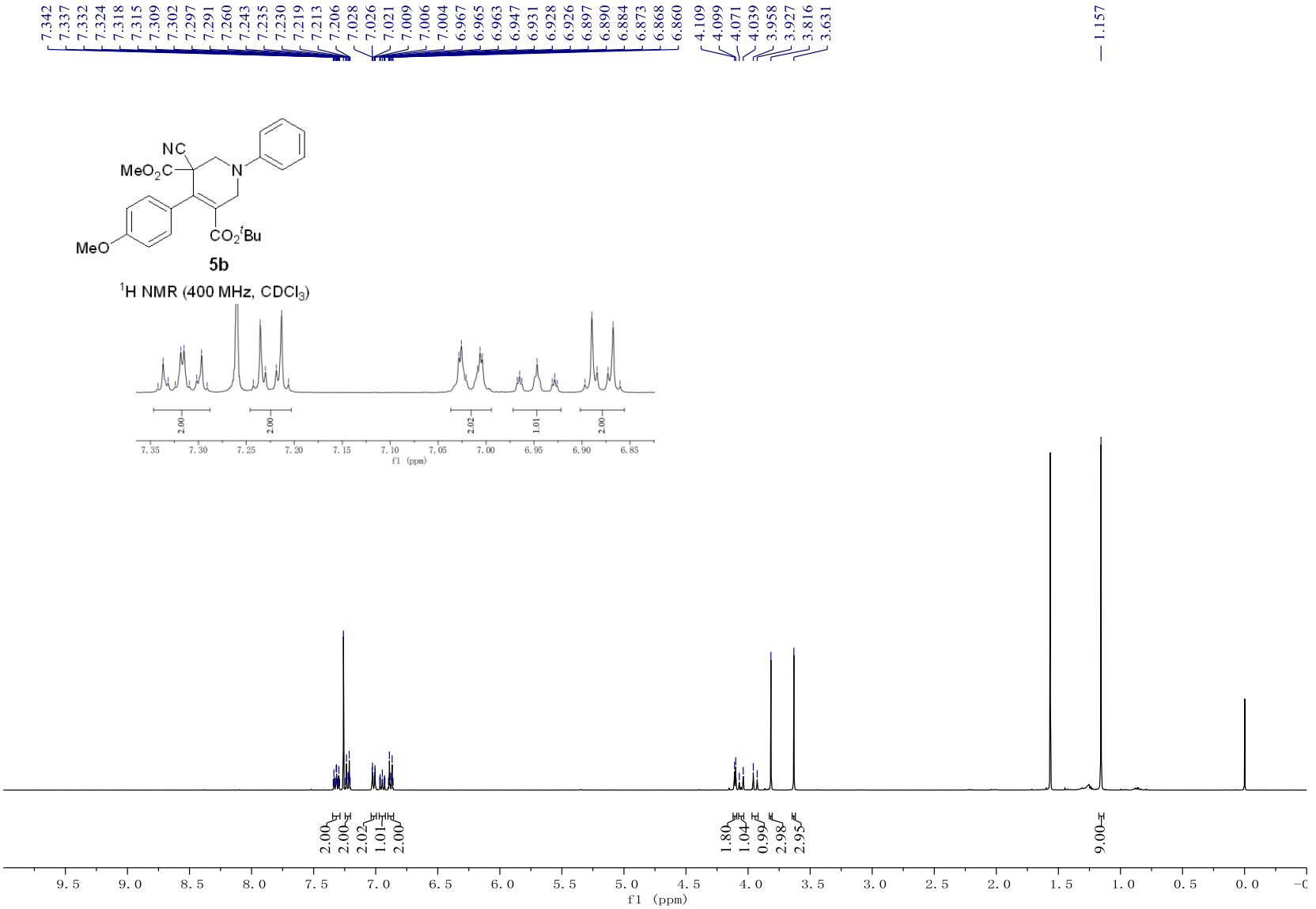
3t

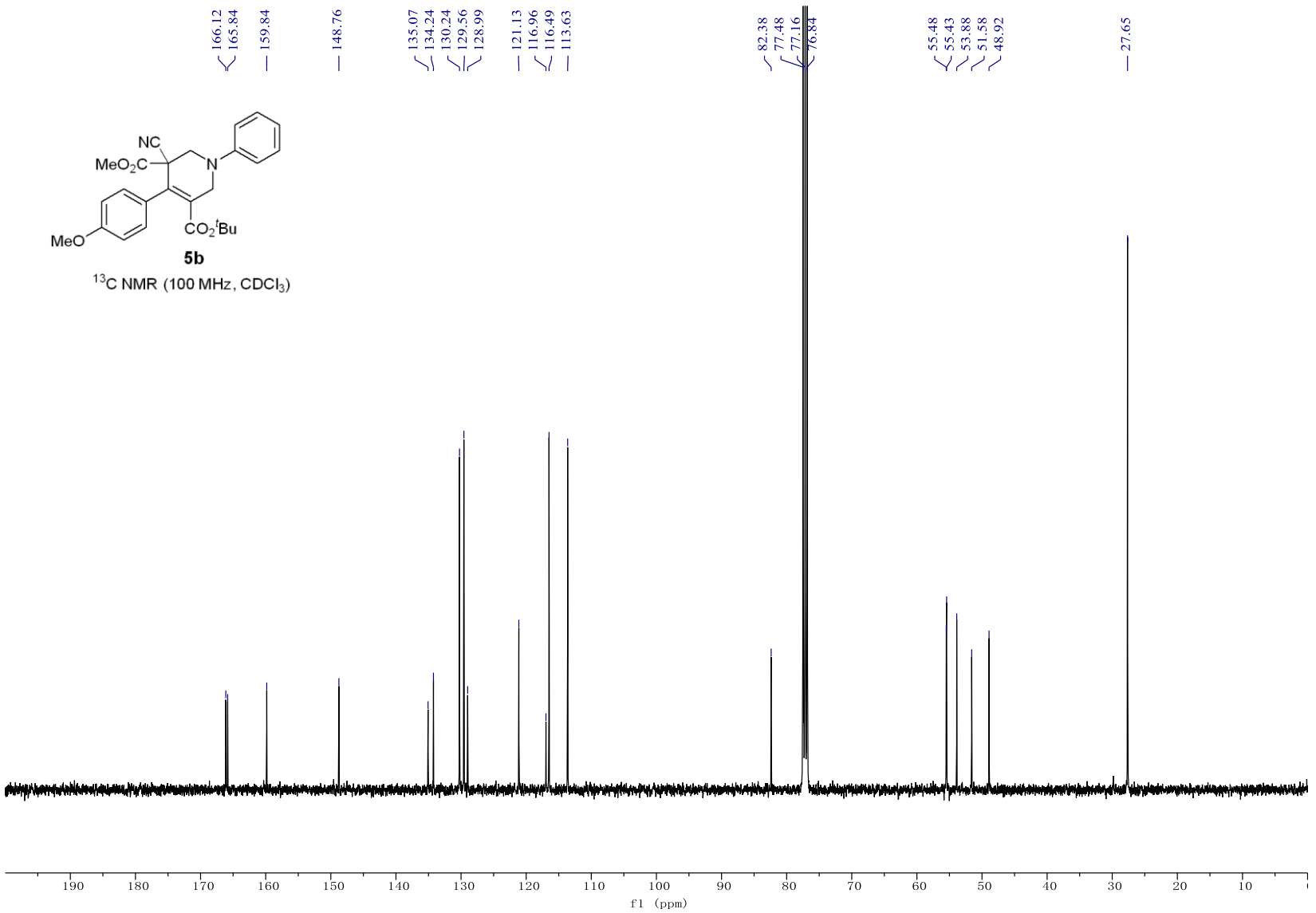
^{1}H NMR (400 MHz, $CDCl_3$)

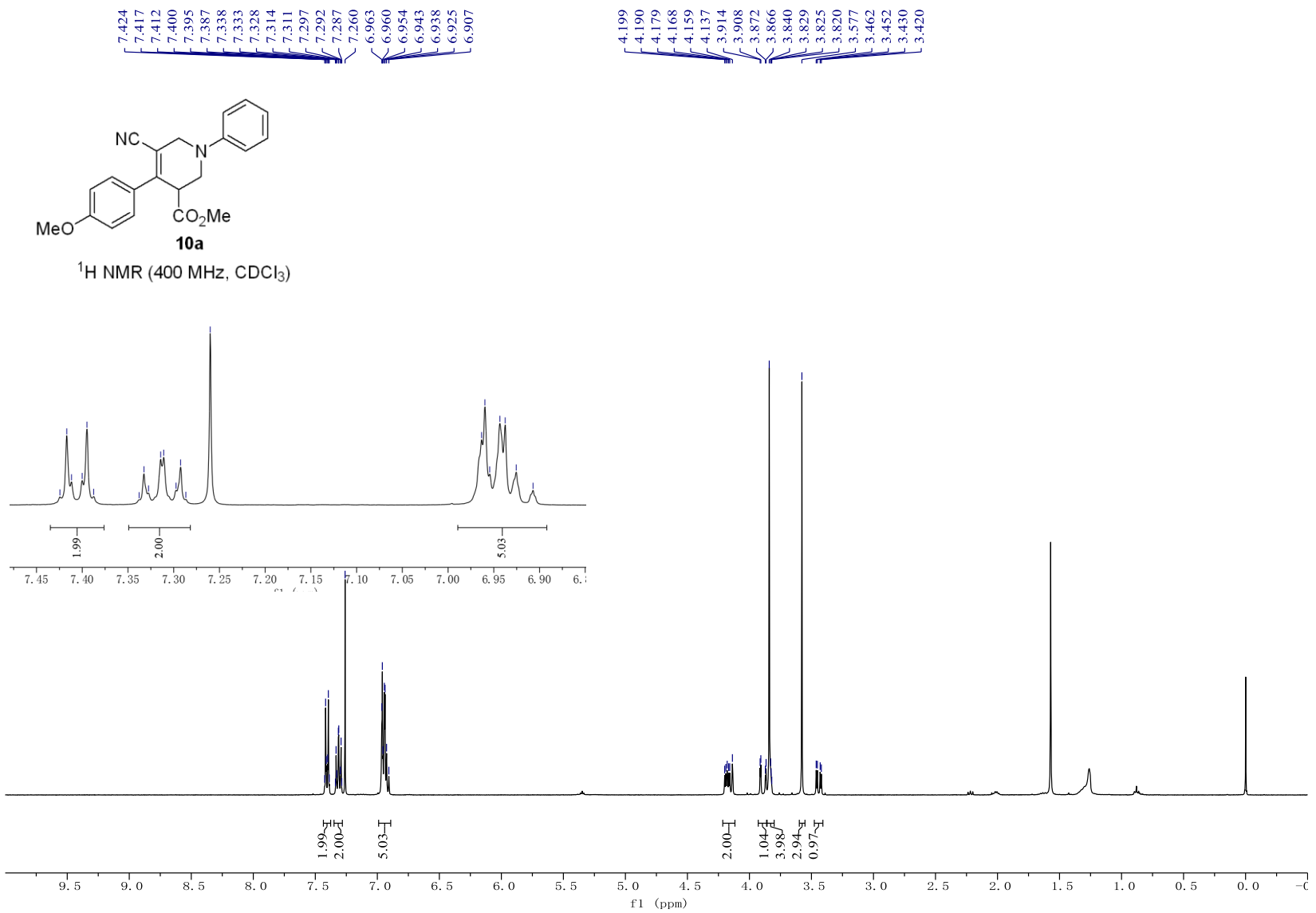

166.82
147.62
146.55
144.50
132.36
129.84
122.80
120.96
117.58
113.29
112.48
112.12
77.48
77.16
76.84
56.88
52.98
49.48
34.96
NC
NC
N
O
CO2Me
3t
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

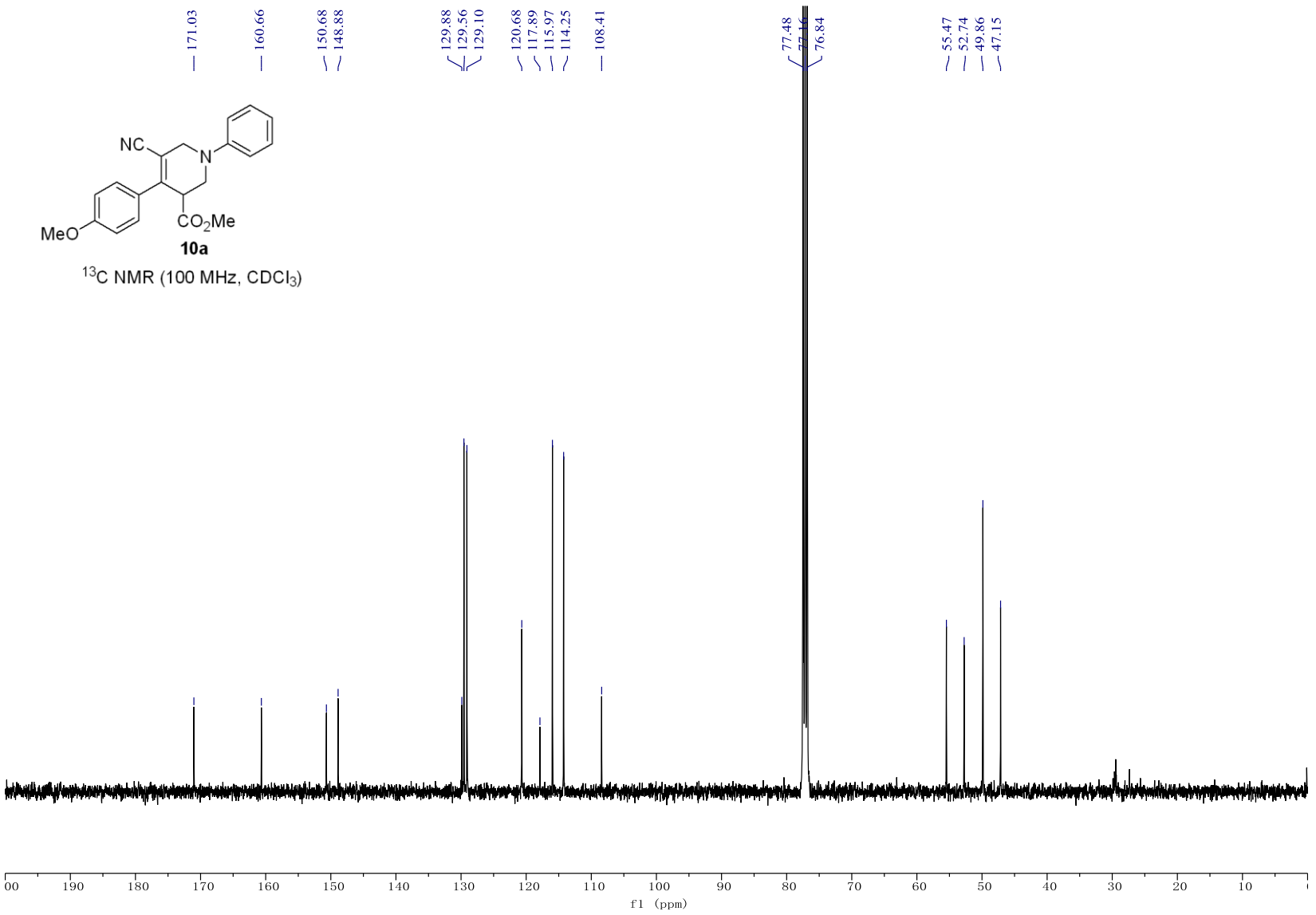

7.349
7.343
7.338
7.331
7.325
7.321
7.316
7.308
7.303
7.297
7.260
7.240
7.233
7.228
7.216
7.211
7.204
7.028
7.026
7.006
7.004
6.997
6.975
6.957
6.938
6.892
6.885
6.879
6.868
6.863
6.855
4.146
4.130
4.071
4.039
3.991
3.985
3.973
3.955
3.937
3.814
3.644
0.943
0.925
0.907
NC
MeO2C
N
CO2Et
MeO
5a
1H NMR (400 MHz, CDCl3)
2.00
1.99
2.04
1.01
1.96
1.78
1.02
3.04
3.00
2.97
3.02
f1 (ppm)


166.35
165.96
159.84
148.63
136.83
132.69
129.86
129.53
128.75
121.17
116.74
116.47
113.60
77.48
77.16
76.84
61.20
55.44
55.31
53.89
51.61
48.86
13.69
NC
MeO2C
N
CO2Et
MeO
5a
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.342
7.337
7.332
7.324
7.318
7.315
7.309
7.302
7.297
7.291
7.260
7.243
7.235
7.230
7.219
7.213
7.206
7.028
7.026
7.021
7.009
7.006
7.004
6.967
6.965
6.963
6.947
6.931
6.928
6.926
6.897
6.890
6.884
6.873
6.868
6.860
4.109
4.099
4.071
4.039
3.958
3.927
3.816
3.631
1.157
NC
MeO2C
N
CO2tBu
MeO
5b
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.02
1.01
2.00
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
f1 (ppm)
2.00
2.00
2.02
1.01
2.00
1.80
1.04
0.99
2.98
2.95
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.12
165.84
159.84
148.76
135.07
134.24
130.24
129.56
128.99
121.13
116.96
116.49
113.63
82.38
77.48
77.16
76.84
55.48
55.43
53.88
51.58
48.92
27.65
NC
MeO2C
N
CO2tBu
MeO
5b
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.424
7.417
7.412
7.400
7.395
7.387
7.338
7.333
7.328
7.314
7.311
7.297
7.292
7.287
7.260
6.963
6.960
6.954
6.943
6.938
6.925
6.907
4.199
4.190
4.179
4.168
4.159
4.137
3.914
3.908
3.872
3.866
3.840
3.829
3.825
3.820
3.577
3.462
3.452
3.430
3.420
NC
N
CO2Me
MeO
10a
1H NMR (400 MHz, CDCl3)
1.99
2.00
5.03
2.00
1.04
3.98
2.94
0.97
f1 (ppm)


171.03
160.66
150.68
148.88
129.88
129.56
129.10
120.68
117.89
115.97
114.25
108.41
77.48
77.16
76.84
55.47
52.74
49.86
47.15
NC
N
MeO
CO2Me
10a
13C NMR (100 MHz, CDCl3)
f1 (ppm)