Supporting Information For:

$Cu(TFA)_2$-Catalyzed Oxidative Tandem Cyclization/1,2-Alkyl Migration of Enamino Amides for Synthesis of Pyrrolin-4-ones

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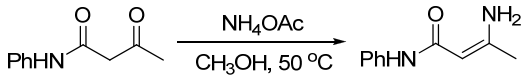
CONTENTS

1. General Information

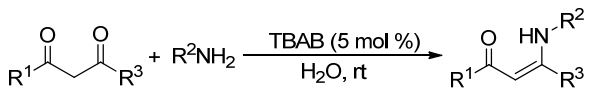
^{1}H and ^{13}C NMR spectra were recorded on Varian instrument (400 MHz) and (100 MHz), The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, a = apparent. Coupling constants, J were reported in Hertz unit (Hz). Preparative TLC was performed on TLC plate, Analytical thin layer chromatography was performed on 10-25um silica gel GF254, visualization was carried out with UV light. Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel (200-300 mesh)). Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

2. Typical Procedure for Preparation of Enamino Amide 1a



The mixture of 3-oxo-*N*-phenylbutanamide (5 mmol), and NH_4OAc (20 mmol) was stirred in methanol (CH_3OH, 15 mL) at 50 °C for 24 hours. After completion of the reaction (detected by TLC), ammonium hydroxide (2 N) was dropwise via addition funnel. Then, the product was filtered, washed with 1:1 MeOH/water and dried. The desired enamino amides **1a** was obtained in 95% isolated yield.

3. Typical Procedure for Preparation of Enamino Amides 1b-1j and 1ea-1es



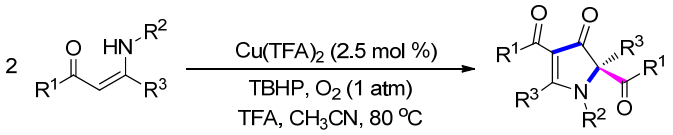
Amine (5 mmol) was added to a suspension of 1,3-dicarbonyl compounds (5 mmol) and TBAB (0.25 mmol) in water (10 mL) at room temperature. The resulting mixture was stirred at room temperature for 12 h, then filtered, washed with water (3 × 30 mL), and dried in vacuo to afford corresponding enamino amides **1b-1j** and **1ea-1es**.

Reference:

(a) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585.

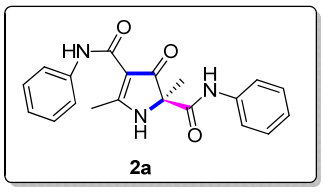
(b) Guan, Z.-H.; Yan, Z.-Y.; Ren, Z.-H.; Liu, X.-Y.; Liang, Y.-M. *Chem. Commun.* **2010**, *46*, 2823.

4. Typical Procedure for Synthesis of Pyrrolin-4-ones

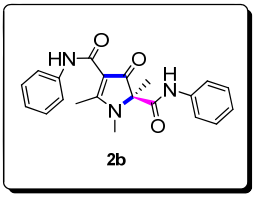


Enamino amides **1** (0.4 mmol), $Cu(TFA)_2$ (2.5 mol %, 2.9 mg), TBHP (0.25 equiv, 13.0 mg), TFA (0.5 equiv, 22.8 mg), and CH_3CN (3 mL) was charged in a 25 mL round bottom flask. Then, the flask was evacuated and back-filled with O_2 (3-times, balloon) and stirred at 80 ^oC. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding pyrrolin-4-ones **2** with hexane/ethyl acetate as the eluent.

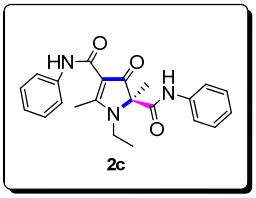
5. Spectroscopic Data for Products



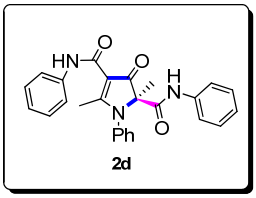
2a: ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.92 (s, 1 H), 9.48 (s, 1 H), 9.14 (s, 1 H), 7.65-7.63 (d, *J* = 8.0 Hz, 2 H), 7.58-7.56 (d, *J* = 8.0 Hz, 2 H), 7.38-7.30 (m, 4 H), 7.20-7.16 (t, *J* = 8.0 Hz, 1 H), 7.09-7.05 (t, *J* = 8.0 Hz, 1 H), 2.75 (s, 3 H), 1.77 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.0, 181.7, 164.8, 161.6, 138.4, 136.5, 129.1, 128.9, 125.4, 123.6, 120.2, 120.0, 70.3, 25.1, 17.5. HRMS Calcd (ESI) m/z for $C_{20}H_{19}N_3NaO_3$: $[M+Na]^+$ 372.1319, found: 372.1323.



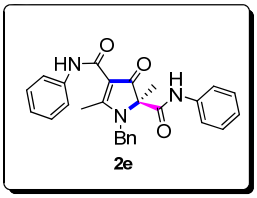
2b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.11 (s, 1 H), 9.28 (s, 1 H), 7.63-7.61 (d, *J* = 8.0 Hz, 2 H), 7.55-7.53 (d, *J* = 8.0 Hz, 2 H), 7.35-7.28 (m, 4 H), 7.15-7.11 (t, *J* = 8.0 Hz, 1 H), 7.07-7.03 (t, *J* = 8.0 Hz, 1 H), 3.44 (s, 3 H), 2.79 (s, 3 H), 1.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.5, 180.8, 163.7, 161.6, 138.5, 136.9, 128.9, 128.7, 124.8, 123.3, 120.0, 119.9, 102.1, 74.0, 31.3, 22.2, 14.4. HRMS Calcd (ESI) m/z for $C_{21}H_{21}N_3NaO_3$: $[M+Na]^+$ 386.1475, found: 386.1464.



2c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.12 (s, 1 H), 9.24 (s, 1 H), 7.63-7.61 (d, *J* = 8.0 Hz, 2 H), 7.55-7.53 (d, *J* = 8.0 Hz, 2 H), 7.33-7.26 (m, 4 H), 7.15-7.11 (t, *J* = 8.0 Hz, 1 H), 7.07-7.03 (t, *J* = 8.0 Hz, 1 H), 4.06-3.89 (m, 2 H), 2.82 (s, 3 H), 1.78 (s, 3 H), 1.37-1.34 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.2, 180.8, 163.6, 161.7, 138.5, 136.9, 128.9, 128.7, 124.8, 123.3, 120.0, 119.9, 102.4, 74.6, 40.1, 22.8, 15.5, 14.8. HRMS Calcd (ESI) m/z for $C_{22}H_{24}N_3O_3$: $[M+H]^+$ 378.1812, found: 378.1799.

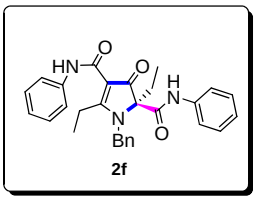


2d: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.16 (s, 1 H), 8.91 (s, 1 H), 7.62-7.60 (d, *J* = 8.0 Hz, 2 H), 7.55-7.53 (d, *J* = 8.0 Hz, 2 H), 7.46-7.45 (d, *J* = 4.0 Hz, 3 H), 7.37-7.36 (m, 2 H), 7.34-7.26 (m, 4 H), 7.14-7.11 (t, *J* = 8.0 Hz, 1 H), 7.08-7.04 (t, *J* = 8.0 Hz, 1 H), 2.56 (s, 3 H), 1.73 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.2, 182.5, 163.2, 161.5, 138.4, 137.0, 135.6, 129.6, 129.5, 129.5, 128.9, 124.8, 123.5, 120.3, 120.0, 103.5, 22.1, 16.4. HRMS Calcd (ESI) m/z for $C_{26}H_{23}N_3NaO_3$: $[M+Na]^+$ 448.1632, found: 448.1640.



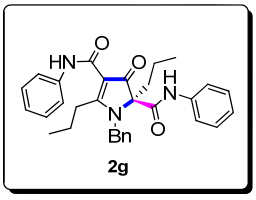
2e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.15 (s, 1 H), 9.22 (s, 1 H), 7.64-7.62 (d, *J* =

8.0 Hz, 2 H), 7.56-7.54 (d, *J* = 8.0 Hz, 2 H), 7.31-7.22 (m, 8 H), 7.16-7.14 (m, *J* = 8.0 Hz, 3 H), 7.08-7.04 (t, *J* = 8.0 Hz, 1 H), 5.31-5.21 (m, 2 H), 2.71 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.5, 182.2, 163.8, 161.5, 138.4, 136.8, 135.9, 126.8, 125.8, 124.8, 123.4, 120.0, 119.9, 102.8, 74.7, 48.7, 22.4, 15.5. HRMS Calcd (ESI) m/z for $C_{27}H_{26}N_3O_3$: $[M+Na]^+$ 440.1969, found: 440.1985.



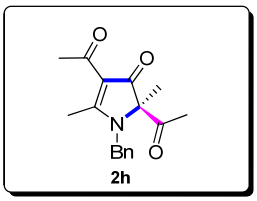
2f

2f: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.28 (s, 1 H), 9.42 (s, 1 H), 7.68-7.66 (d, *J* = 8.0 Hz, 2 H), 7.54-7.52 (d, *J* = 8.0 Hz, 2 H), 7.34-7.30 (m, 9 H), 7.15-7.12 (t, *J* = 8.0 Hz, 1 H), 7.09-7.05 (t, *J* = 8.0 Hz, 1 H), 5.41-5.37 (d, *J* = 16.4 Hz, 1 H), 5.09-5.05 (d, *J* =16.8 Hz, 1 H), 3.22-3.13 (m, 2 H), 2.31-2.26 (m, 2 H), 1.21-1.17 (t, *J* = 8.0 Hz, 3 H), 0.82-0.79 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.6, 188.0, 163.4, 160.9, 138.6, 136.8, 136.1, 129.0, 128.9, 128.8, 127.8, 126.7, 124.8, 123.4, 120.1, 120.0, 103.5, 78.5, 48.7, 30.5, 22.0, 11.8, 7.7. HRMS Calcd (ESI) m/z for $C_{29}H_{29}N_3NaO_3$: $[M+Na]^+$ 490.2101, found: 490.2121.



2g

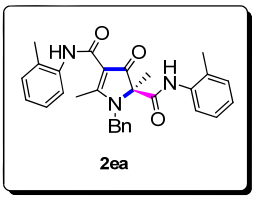
2g: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.28 (s, 1 H), 9.37 (s, 1 H), 7.66-7.64 (d, *J* = 8.0 Hz, 2 H), 7.54-7.52 (d, *J* = 8.0 Hz, 2 H), 7.33-7.29 (m, 9 H), 7.14-7.11 (m, 1 H), 7.07-7.05 (m, 1 H), 5.39-5.35 (d, *J* = 16.0 Hz, 1 H), 5.13-5.09 (d, *J* =16.0 Hz, 1 H), 3.32-3.25 (m, 1 H), 3.00-2.96 (m, 1 H), 2.14-2.10 (m, 2 H), 1.73 (m, 2 H), 1.58-1.54 (m, 2 H), 0.97-0.93 (t, *J* = 8.0 Hz, 3 H), 0.70-0.66 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.6, 186.3, 163.5, 161.0, 138.5, 136.8, 136.0, 128.9, 128.8, 128.8, 127.9, 126.8, 124.8, 123.3, 120.0, 120.0, 103.4, 78.4, 48.8, 38.8, 30.3, 21.5, 16.6, 14.4, 13.4. HRMS Calcd (ESI) m/z for $C_{31}H_{33}N_3NaO_3$: $[M+Na]^+$ 518.2414, found: 518.2420.



2h

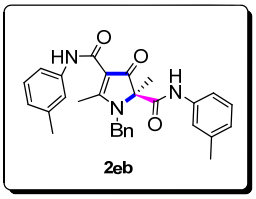
2h: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39-7.32 (m, 3 H), 7.13-7.11 (d, *J* = 8.0 Hz, 2 H), 5.01-4.96 (d, *J* = 20.0 Hz, 1 H), 4.46-4.42 (s, *J* = 16.0 Hz, 1 H), 2.67 (s, 3 H), 2.45 (s, 3 H), 2.24 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 199.6, 193.8, 191,3, 181.9, 135.2, 129.2, 128.2, 126.2, 109.9, 83.3, 48.4, 30.1, 24.9, 18.6, 15.7.

HRMS Calcd (ESI) m/z for $C_{17}H_{19}KNO_3$: $[M+K]^+$ 326.1364, found: 326.1368.



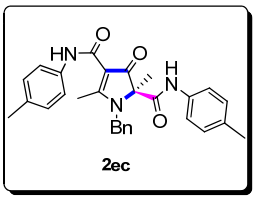
2ea

2ea: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.10 (s, 1 H), 9.26 (s, 1 H), 8.23-8.21 (d, *J* = 8.0 Hz, 1 H), 7.87-7.85 (d, *J* = 8.0 Hz, 1 H), 7.39-7.36 (t, *J* = 8.0 Hz, 2 H), 7.32-7.29 (t, *J* = 8.0 Hz, 1 H), 7.24-7.19 (m, 6 H), 7.10-7.06 (t, 1 H), 7.03-6.99 (t, *J* = 8.0 Hz, 1 H), 5.39-5.26 (m, 2 H), 2.75 (s, 3 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.76 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.1, 182.2, 164.1, 161.5, 136.9, 136.0, 134.9, 130.6, 130.2, 129.0, 128.8, 127.8, 127.4, 126.6, 126.6, 125.9, 125.3, 123.5, 121.9, 121.4, 103.2, 74.6, 48.8, 22.8, 18.1, 17.6, 15.6. HRMS Calcd (ESI) m/z for $C_{29}H_{30}N_3O_3$: $[M+H]^+$ 468.2282, found: 468.2261.



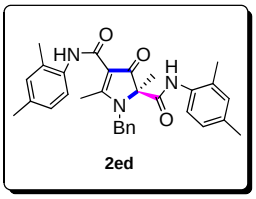
2eb

2eb: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.10 (s, 1 H), 9.16 (s, 1 H), 7.38 (s, 1 H), 7.43-7.35 (m, 6 H), 7.32-7.28 (m, 4 H), 7.24-7.20 (d, *J* = 8.0 Hz, 1 H), 7.17-7.15 (d, *J* = 8.0 Hz, 1 H), 5.35-5.23 (m, 2 H), 2.73 (s, 3 H), 2.34 (s, 6 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.6, 182.2, 163.9, 161.5, 139.0, 138.6, 138.4, 136.7, 135.9, 129.0, 128.8, 128.6, 127.8, 125.8, 125.7, 124.2, 120.6, 120.6, 117.1, 117.0, 102.9, 74.6, 48.8, 22.5, 21.5, 21.4, 15.6. HRMS Calcd (ESI) m/z for $C_{29}H_{29}N_3NaO_3$: $[M+Na]^+$ 490.2101, found: 490.2109.



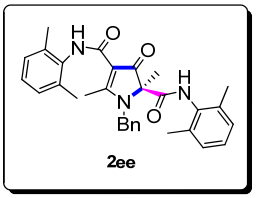
2ec

2ec: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.09 (s, 1 H), 9.15 (s, 1 H), 7.53-7.51 (d, *J* = 8.0 Hz, 2 H), 7.44-7.42 (d, *J* = 8.0 Hz, 2 H), 7.36-7.32 (m, 2 H), 7.30-7.26 (m, 1 H), 7.15-7.10 (m, 6 H), 5.29-5.18 (m, 2 H), 2.70 (s, 3 H), 2.30 (s, 6 H), 1.69 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.6, 182.1, 163.7, 161.4, 135.9, 135.9, 134.5, 134.3, 132.8, 129.4, 129.2, 128.9, 127.7, 125.8, 120.0, 119.9, 102.8, 74.6, 48.7, 22.4, 20.8, 20.8, 15.4. HRMS Calcd (ESI) m/z for $C_{29}H_{30}N_3O_3$: $[M+H]^+$ 468.2282, found: 468.2263.



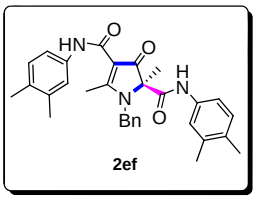
2ed

2ed: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.05 (s, 1 H), 9.17 (s, 1 H), 8.09-8.07 (d, *J* = 8.0 Hz, 1 H), 7.71-7.69 (d, *J* = 8.0 Hz, 1 H), 7.39-7.35 (t, *J* = 8.0 Hz, 2 H), 7.32-7.30 (t, *J* = 8.0 Hz, 1 H), 7.20-7.18 (d, *J* = 8.0 Hz, 2 H), 7.02 (s, 4 H), 5.37-5.24 (m, 2 H), 2.74 (s, 3 H), 2.37 (s, 3 H), 2.29 (s, 9 H), 1.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.1, 182.0, 164.0, 161.5, 136.0, 134.9, 134.2, 132.9, 132.2, 131.2, 130.8, 128.9, 127.7, 127.4, 127.1, 126.9, 125.9, 122.0, 121.4, 103.1, 74.6, 48.7, 22.7, 20.7, 20.7, 18.0, 17.4, 15.4. HRMS Calcd (ESI) m/z for $C_{31}H_{34}N_3O_3$: $[M+H]^+$ 496.2595, found: 496.2586.



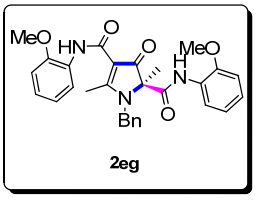
2ee

2ee: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.55 (s, 1 H), 8.74 (s, 1 H), 7.39-7.36 (m, 2 H), 7.32-7.30 (m, 1 H), 7.24-7.19 (m, 2 H), 7.08-7.05 (m, 6 H), 5.26-5.22 (m, 2 H), 2.71 (s, 3 H), 2.28 (s, 6 H), 2.18 (s, 6 H), 1.80 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.9, 182.3, 164.5, 161.7, 136.0, 135.3, 134.9, 134.4, 132.8, 129.0, 128.2, 127.9, 127.7, 127.4, 126.6, 126.0, 102.5, 75.1, 48.9, 22.3, 18.1, 15.3. HRMS Calcd (ESI) m/z for $C_{31}H_{34}N_3O_3$: $[M+H]^+$ 496.2595, found: 496.2601.



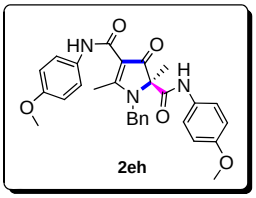
2ef

2ef: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.05 (s, 1 H), 9.10 (s, 1 H), 7.45 (s, 1 H), 7.37-7.27 (m, 6 H), 7.16-7.14 (d, *J* = 8.0 Hz, 2 H), 7.09-7.05 (t, *J* = 8.0 Hz, 2 H), 5.33-5.21 (m, 2 H), 2.72 (s, 3 H), 2.24 (s, 6 H), 2.21 (s, 6 H), 1.69 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.6, 182.0, 163.7, 161.4, 137.2, 136.9, 136.2, 136.0, 134.5, 133.2, 133.2, 131.6, 129.9, 129.7, 129.0, 127.7, 125.8, 121.2, 117.5, 117.4, 102.9, 74.6, 48.7, 22.4, 19.8, 19.8, 19.1, 19.1, 15.5. HRMS Calcd (ESI) m/z for $C_{31}H_{34}N_3O_3$: $[M+H]^+$ 496.2595, found: 496.2603.

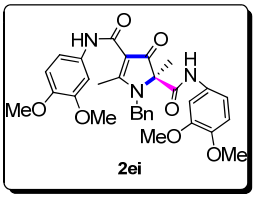


2eg

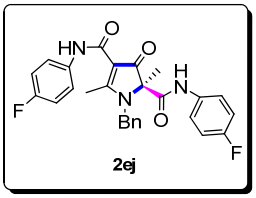
2eg: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.59 (s, 1 H), 9.57 (s, 1 H), 7.50-8.48 (d, *J* = 8.0 Hz, 1 H), 8.21-8.19 (d, *J* = 8.0 Hz, 1 H), 7.37-7.33 (t, *J* = 8.0 Hz, 2 H), 7.28-7.25 (t, *J* = 8.0 Hz, 1 H), 7.17-7.16 (d, *J* = 4.0 Hz, 2 H), 7.09-7.05 (m, 1 H), 7.02-6.99 (m, 1 H), 6.96-6.94 (m, 2 H), 6.90-6.88 (m, 2 H), 5.23 (s, 2 H), 3.96-3.93 (s, 6 H), 2.74 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.4, 181.8, 163.7, 161.7, 148.7, 148.4, 136.0, 128.9, 128.5, 128.4, 127.6, 126.7, 125.8, 124.5, 122.8, 120.7, 120.0, 119.9, 110.3, 110.0, 103.2, 75.0, 55.8, 55.8, 48.6, 22.0, 15.3. HRMS Calcd (ESI) m/z for $C_{29}H_{30}N_3O_5$: $[M+H]^+$ 500.2180, found: 500.2169.



2eh: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.01 (s, 1 H), 9.08 (s, 1 H), 7.55-7.52 (d, *J* = 12.0 Hz, 2 H), 7.45-7.43 (d, *J* = 8.0 Hz, 2 H), 7.38-7.34 (t, *J* = 8.0 Hz, 2 H), 7.32-7.26 (m, 1 H), 7.17-7.15 (d, *J* = 8.0 Hz, 2 H), 6.87-6.86 (d, *J* = 4.0 Hz, 4 H), 5.34-5.22 (m, 2 H), 3.79 (s, 6 H), 2.72 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.7, 182.1, 163.7, 161.5, 156.7, 155.8, 136.0, 131.6, 129.0, 127.8, 125.9, 121.8, 121.7, 114.1, 113.9, 102.8, 74.5, 55.4, 48.7, 22.5, 15.5. HRMS Calcd (ESI) m/z for $C_{29}H_{30}N_3O_5$: $[M+H]^+$ 500.2180, found: 500.2153.

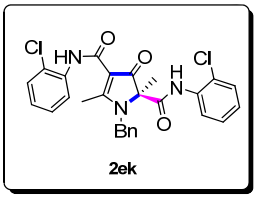


2ei: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.05 (s, 1 H), 9.06 (s, 1 H), 7.41 (s, 1 H), 7.37-7.35 (d, *J* = 8.0 Hz, 1 H), 7.32-7.31 (d, *J* = 4.0 Hz, 1 H), 7.25 (s, 2 H), 7.17-7.15 (d, *J* = 8.0 Hz, 2 H), 7.07-7.05 (d, *J* = 8.0 Hz, 1 H), 7.01-7.00 (d, *J* = 4.0 Hz, 1 H), 6.83-6.81 (d, *J* = 8.0 Hz, 2 H), 5.37-5.24 (m, 2 H), 3.89 (s, 6 H), 3.86 (s, 6 H), 2.74 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.7, 182.1, 163.6, 161.4, 148.9, 148.8, 146.2, 145.1, 135.9, 132.1, 130.3, 129.0, 127.8, 125.8, 112.1, 111.8, 111.2, 111.1, 104.7, 104.6, 102.9, 74.6, 56.0, 55.9, 55.8, 48.7, 29.6, 22.4, 15.5. HRMS Calcd (ESI) m/z for $C_{31}H_{33}N_3NaO_7$: $[M+Na]^+$ 582.2211, found: 582.2223.

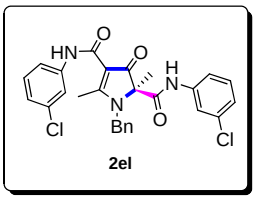


2ej: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.09 (s, 1 H), 9.19 (s, 1 H), 7.60-7.57 (m, 2 H), 7.52-7.49 (m, 2 H), 7.39-7.31 (m, 3 H), 7.17-7.16 (d, *J* = 4.0 Hz, 2 H), 7.05-6.98 (m, 4 H), 5.33-5.23 (m, 2 H), 2.72 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =

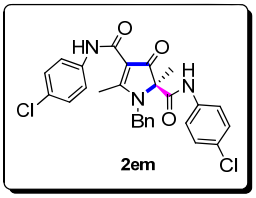
194.6, 182.3, 163.8, 161.4, 160.8, 160.0, 158.3, 157.6, 135.8, 134.5, 134.5, 132.9, 132.8, 129.1, 125.8, 121.8, 121.8, 121.6, 121.5, 115.8, 115.5, 115.5, 115.2, 102.7, 74.6, 48.8, 22.5, 15.5.HRMS Calcd (ESI) m/z for $C_{27}H_{23}F_2NaN_3O_3$: $[M+Na]^+$ 498.1624, found: 498.1632.



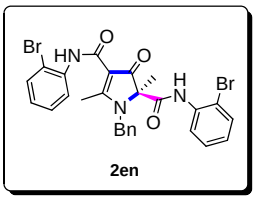
2ek: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.61 (s, 1 H), 9.66 (s, 1 H), 8.50-8.48 (d, *J* = 8.0 Hz, 1 H), 8.18-8.16 (d, *J* = 8.0 Hz, 1 H), 7.40-7.36 (m, 3 H), 7.33-7.31 (m, 2 H), 7.28-7.22 (m, 2 H), 7.20-7.18 (d, *J* = 8.0 Hz, 2 H), 7.10-7.07 (t, *J* = 8.0 Hz, 1 H), 7.01-6.98 (t, *J* = 4.0 Hz, 1 H), 5.28 (s, 2 H), 2.76 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.3, 182.3, 164.3, 161.7, 135.8, 135.8, 133.8, 129.4, 129.1, 127.9, 127.4, 127.2, 125.9, 125.5, 124.5, 123.7, 123.2, 122.0, 121.8, 103.0, 74.9, 48.8, 22.4, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}Cl_2N_3NaO_3$: $[M+Na]^+$ 530.1009, found: 530.0997.



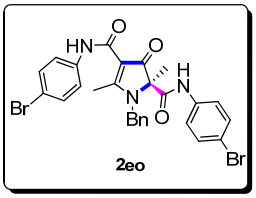
2el: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.15 (s, 1 H), 9.26 (s, 1 H), 7.80 (s, 1 H), 7.69 (s, 1 H), 7.45-7.43 (d, *J* = 8.0 Hz, 1 H), 7.39-7.36 (m, 3 H), 7.33-7.29 (m, 1 H), 7.27-7.20 (m, 2 H), 7.17-7.15 (d, *J* = 8.0 Hz, 2 H), 7.12-7.10 (d, *J* = 8.0 Hz, 1 H), 7.04-7.02 (d, *J* = 8.0 Hz, 1 H), 5.33-5.23 (m, 2 H), 2.72 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.4, 182.5, 163.9, 161.4, 139.7, 137.9, 135.6, 134.7, 134.4, 130.0, 129.7, 129.1, 127.9, 125.9, 124.9, 123.4, 120.1, 119.9, 118.0, 117.8, 102.7, 74.6, 48.9, 22.6, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}Cl_2N_3NaO_3$: $[M+Na]^+$ 530.1029, found: 530.1019.



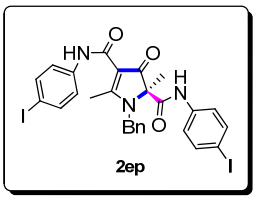
2em: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.13 (s, 1 H), 9.23 (s, 1 H), 7.61-7.59 (d, *J* = 8.0 Hz, 2 H), 7.51-7.49 (d, *J* = 8.0 Hz, 2 H), 7.40-7.36 (m, 2 H), 7.33-7.27 (m, 5 H), 7.18-7.16 (d, *J* = 8.0 Hz, 2 H), 5.36-5.25 (m, 2 H), 2.73 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.5, 182.4, 163.9, 161.4, 137.1, 135.7, 135.4, 129.9, 129.1, 129.0, 128.8, 128.2, 127.9, 125.9, 121.2, 121.1, 102.8, 74.6, 48.9, 22.7, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}Cl_2N_3NaO_3$: $[M+Na]^+$ 530.1033, found: 530.1014.



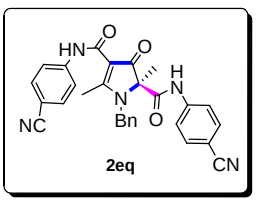
2en: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.52 (s, 1 H), 9.55 (s, 1 H), 8.47-8.45 (d, *J* = 8.0 Hz, 1 H), 8.15-8.13 (d, *J* = 8.0 Hz, 1 H), 7.57-7.55 (d, *J* = 8.0 Hz, 2 H), 7.37-7.35 (m, 2 H), 7.31-7.25 (m, 3 H), 7.19-7.17 (d, *J* = 8.0 Hz, 2 H), 7.02-6.98 (t, *J* = 8.0 Hz, 1 H), 6.94-6.90 (t, *J* = 8.0 Hz, 1 H), 5.26 (s, 2 H), 2.75 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.1, 182.3, 164.3, 161.6, 137.0, 135.8, 134.9, 132.6, 132.4, 129.0, 128.0, 127.8, 127.7, 126.0, 125.8, 124.2, 122.4, 122.3, 114.7, 113.5, 102.8, 74.9, 48.8, 22.2, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}Br_2N_3NaO_3$: $[M+Na]^+$ 617.9998, found: 618.0021.



2eo: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.12 (s, 1 H), 9.22 (s, 1 H), 7.56-7.54 (d, *J* = 8.0 Hz, 2 H), 7.45-7.31 (m, 9 H), 7.17-7.15 (d, *J* = 8.0 Hz, 2 H), 5.35-5.24 (m, 2 H), 2.73 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.5, 182.5, 163.9, 161.4, 137.6, 135.9, 135.7, 132.0, 131.7, 129.1, 127.9, 125.9, 121.5, 121.4, 117.6, 115.8, 102.8, 74.6, 48.9, 22.7, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}Br_2N_3NaO_3$: $[M+Na]^+$ 617.9998, found: 617.9996.

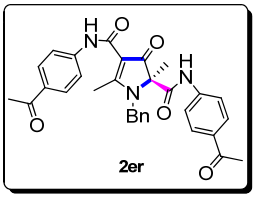


2ep: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.11 (s, 1 H), 9.20 (s, 1 H), 7.64-7.58 (m, 4 H), 7.43-7.42 (d, *J* = 4.0 Hz, 2 H), 7.38-7.31 (m, 5 H), 7.16-7.15 (d, *J* = 4.0 Hz, 2 H), 5.33-5.23 (m, 2 H), 2.71 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.4, 182.4, 163.8, 161.4, 138.3, 137.9, 137.7, 136.6, 135.7, 129.1, 127.9, 125.9, 121.8, 121.7, 102.8, 88.3, 86.3, 74.7, 48.9, 22.6, 15.6. HRMS Calcd (ESI) m/z for $C_{27}H_{23}I_2N_3NaO_3$: $[M+Na]^+$ 713.9721, found: 713.9690.

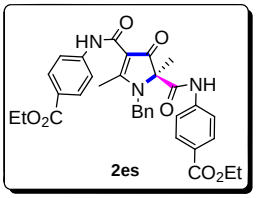


2eq: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.30 (s, 1 H), 9.38 (s, 1 H), 7.72-7.70 (d, *J* =

8.0 Hz, 2 H), 7.66-7.64 (d, *J* = 8.0 Hz, 2 H), 7.60-7.58 (d, *J* = 8.0 Hz, 2 H), 7.55-7.53 (d, *J* = 8.0 Hz, 2 H), 7.37-7.34 (t, *J* = 8.0 Hz, 2 H), 7.31-7.29 (d, *J* = 8.0 Hz, 1 H), 7.16-7.14 (d, *J* = 8.0 Hz, 2 H), 5.26 (s, 2 H), 2.72 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.1, 182.8, 164.0, 161.4, 142.6, 140.7, 135.2, 133.2, 133.0, 129.1, 128.0, 125.8, 119.9, 119.5, 119.1, 118.5, 107.8, 105.8, 102.6, 74.9, 49.0, 22.5, 15.7. HRMS Calcd (ESI) m/z for $C_{29}H_{24}N_5O_3$: $[M+H]^+$ 490.1874, found: 490.1861.

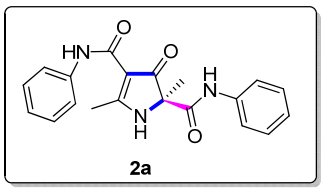


2er: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.35 (s, 1 H), 9.43 (s, 1 H), 7.96-7.92 (m, 4 H), 7.74-7.72 (d, *J* = 8.0 Hz, 2 H), 7.68-7.65 (d, *J* = 12.0 Hz, 2 H), 7.41-7.33 (m, 3 H), 7.20-7.18 (d, *J* = 8.0 Hz, 2 H), 5.31-5.29 (d, *J* = 8.0 Hz, 2 H), 2.75 (s, 3 H), 2.58-2.57 (s, 6 H), 1.76 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 197.0, 196.8, 194.2, 182.6, 163.9, 161.5, 143.0, 141.0, 135.4, 133.3, 132.0, 129.6, 129.6, 129.1, 128.0, 125.8, 119.3, 118.9, 102.7, 74.9, 48.9, 26.4, 26.3, 22.5, 15.7. HRMS Calcd (ESI) m/z for $C_{31}H_{29}N_3NaO_5$: $[M+Na]^+$ 546.1999, found: 546.2019.

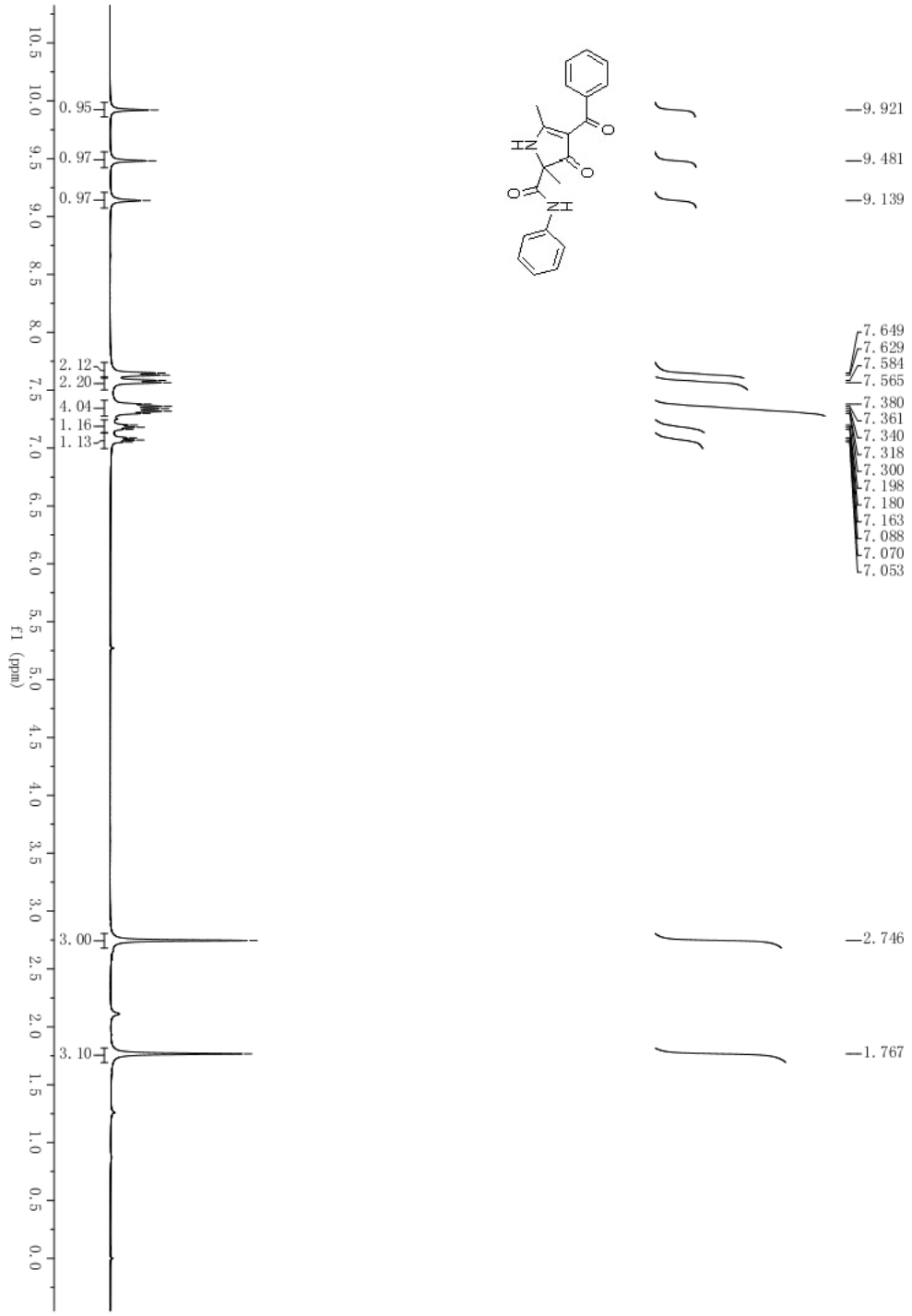


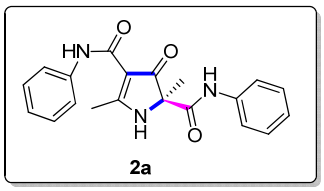
2es: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.33 (s, 1 H), 9.40 (s, 1 H), 8.05-8.00 (t, *J* = 8.0 Hz, 3 H), 7.74-7.42 (d, *J* = 8.0 Hz, 2 H), 7.65-7.63 (d, *J* = 8.0 Hz, 2 H), 7.40-7.37 (m, 2 H), 7.34-7.27 (m, 2 H), 7.19-7.17 (d, *J* = 4.0 Hz, 2 H), 5.37-5.27 (m, 2 H), 4.37-4.35 (m, 4 H), 2.75 (s, 3 H), 1.74 (s, 3 H), 1.41-1.37 (t, *J* = 8.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.3, 182.6, 166.3, 165.9, 164.0, 161.5, 142.7, 140.8, 135.6, 130.7, 130.6, 129.1, 128.0, 126.6, 125.8, 125.0, 119.1, 118.8, 102.8, 74.8, 60.9, 60.7, 48.9, 22.6, 15.7, 14.3, 14.3. HRMS Calcd (ESI) m/z for $C_{33}H_{33}N_3NaO_7$: $[M+Na]^+$ 606.2211, found: 606.2185.

6. Copies of ^{1}H and ^{13}C NMR Spectra

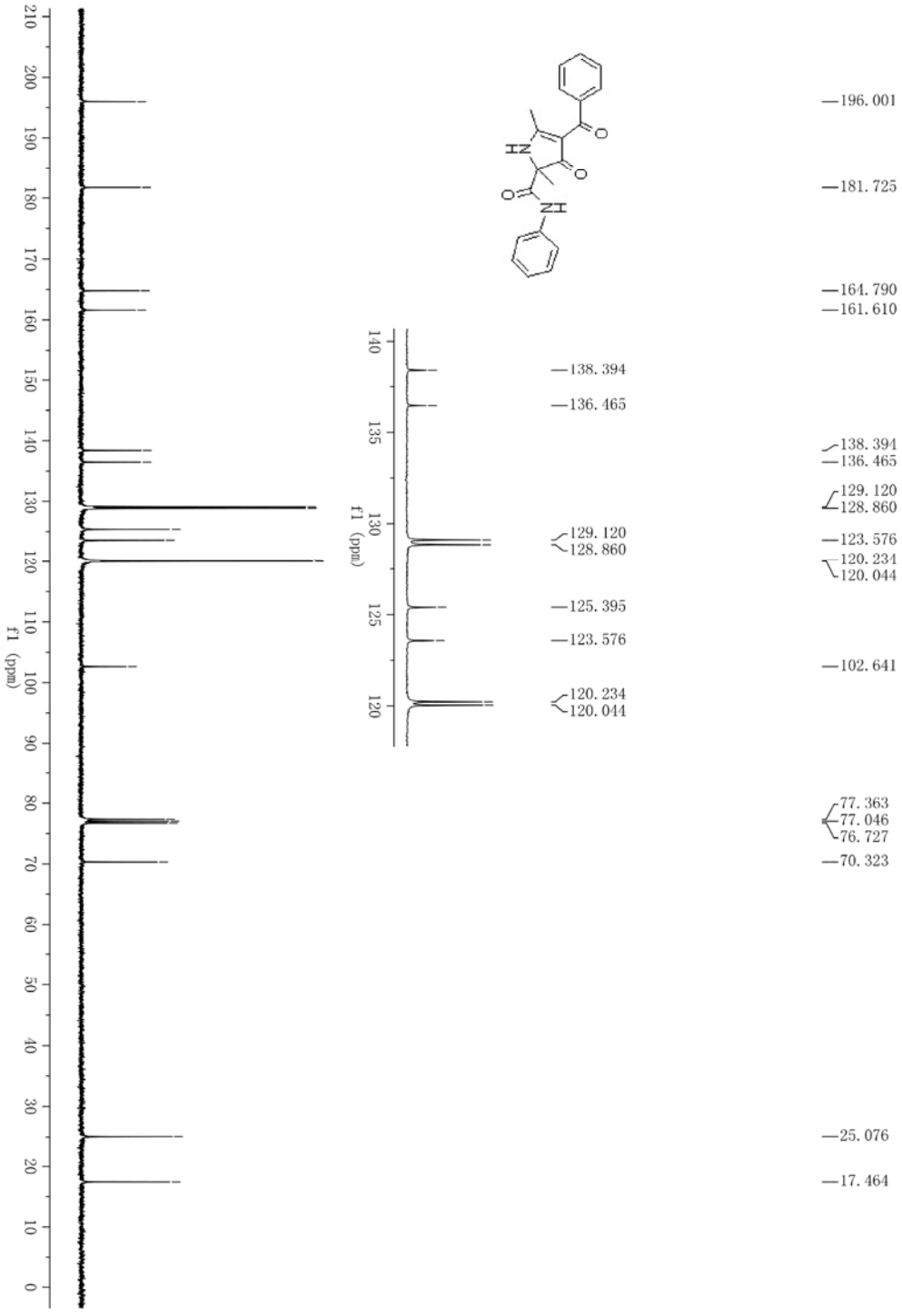


2a




HN
O
O
H
N
N
H
O

2a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f1 (ppm)
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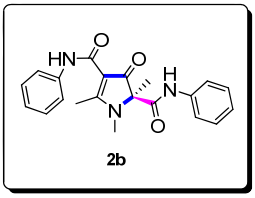
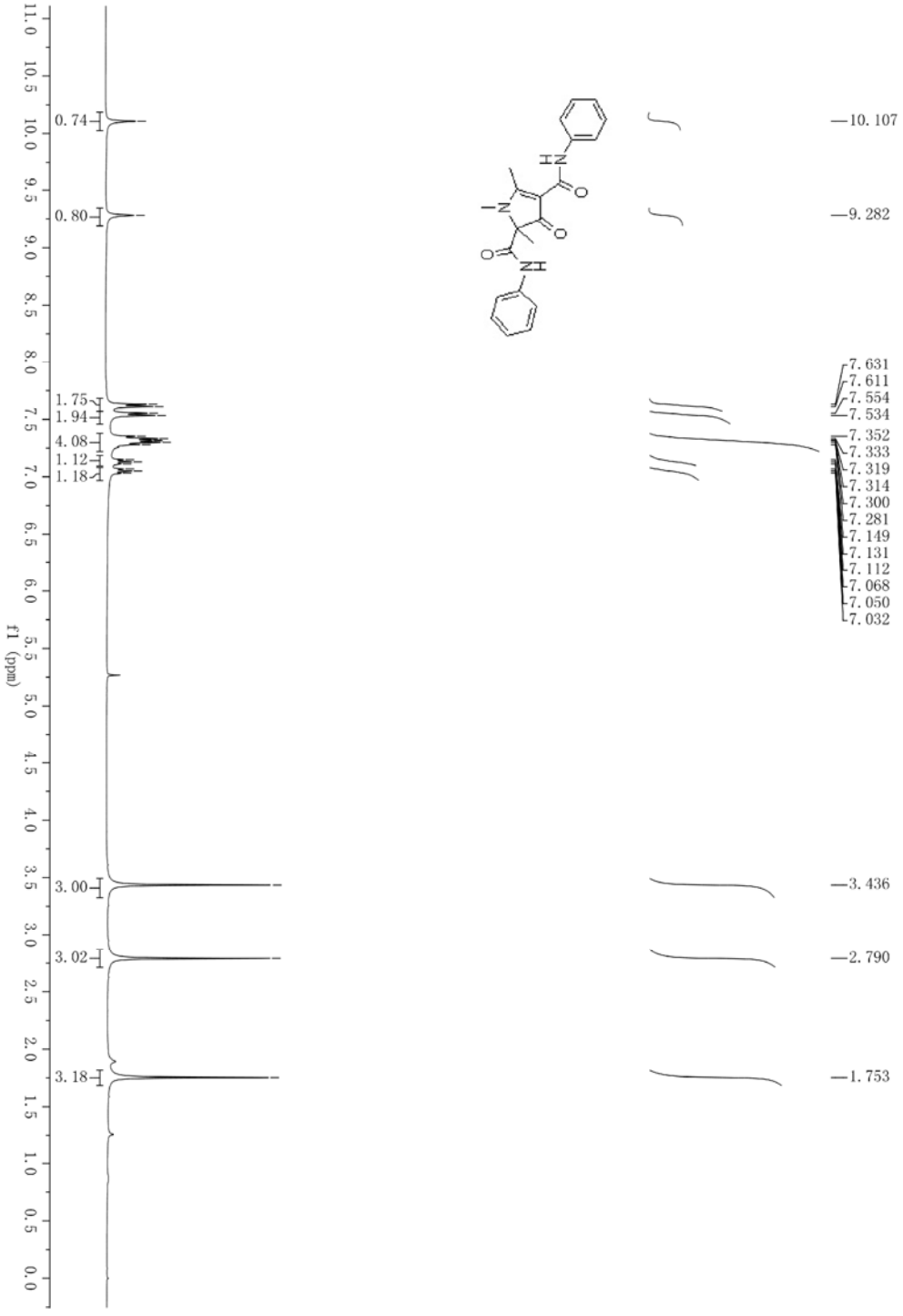
—181.725
—164.790
—161.610
—138.394
—136.465
—129.120
—128.860
—123.576
—125.395
—120.234
—120.044
—102.641
—77.363
—77.046
—76.727
—70.323
—25.076
—17.464


HN
O
O
H
N
N
O
2b


11.0 10.5 10.0 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)
0.74
0.80
1.75
1.94
4.08
1.12
1.18
3.00
3.02
3.18
—10.107
—9.282
7.631
7.611
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7.032
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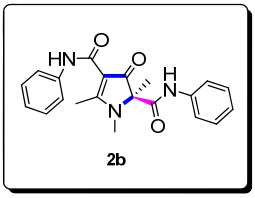
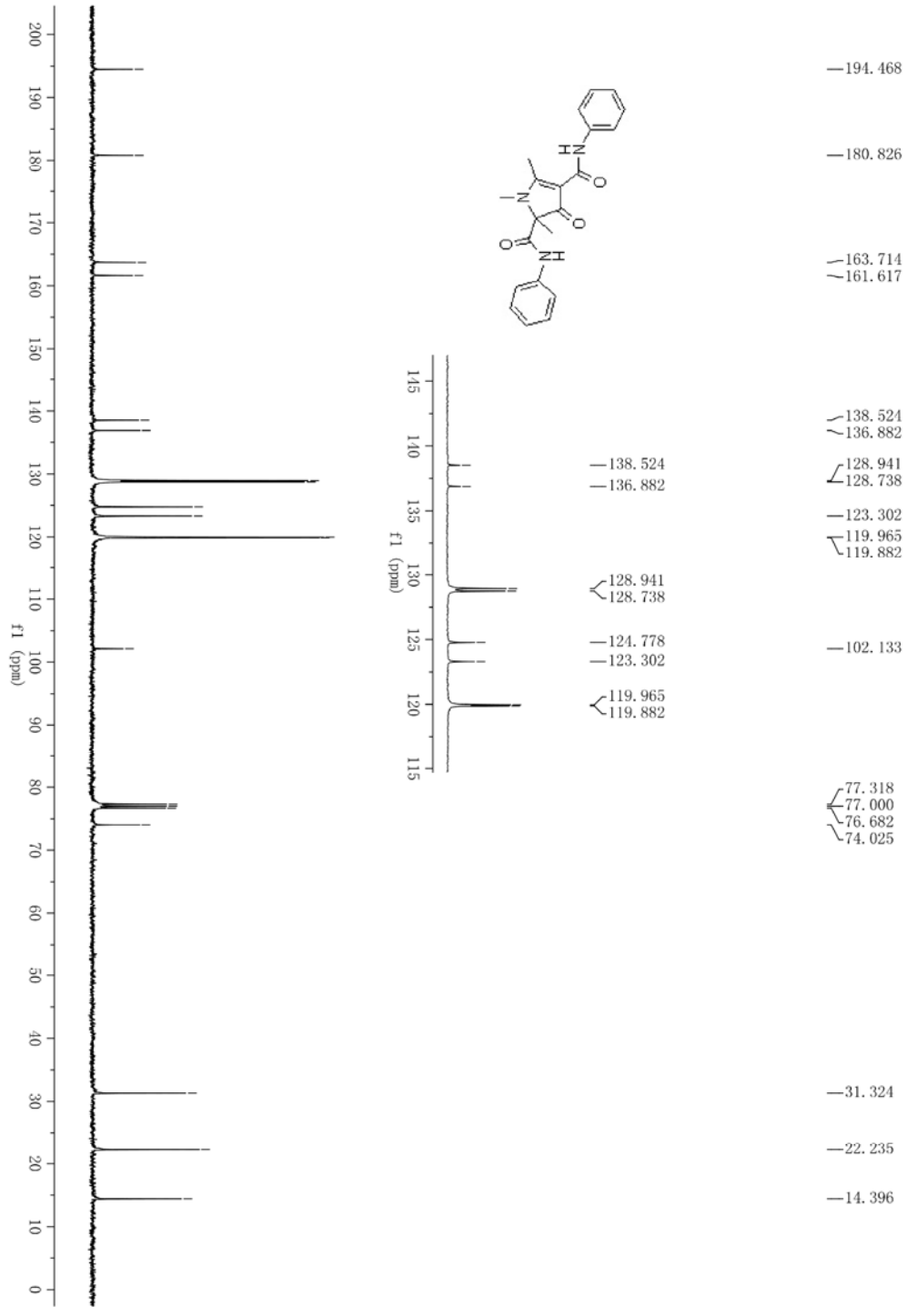
—2.790
—1.753


HN
O
O
H
N
N
O
2b


f1 (ppm)
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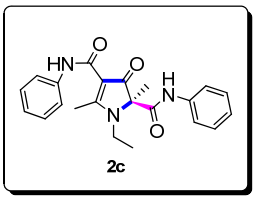
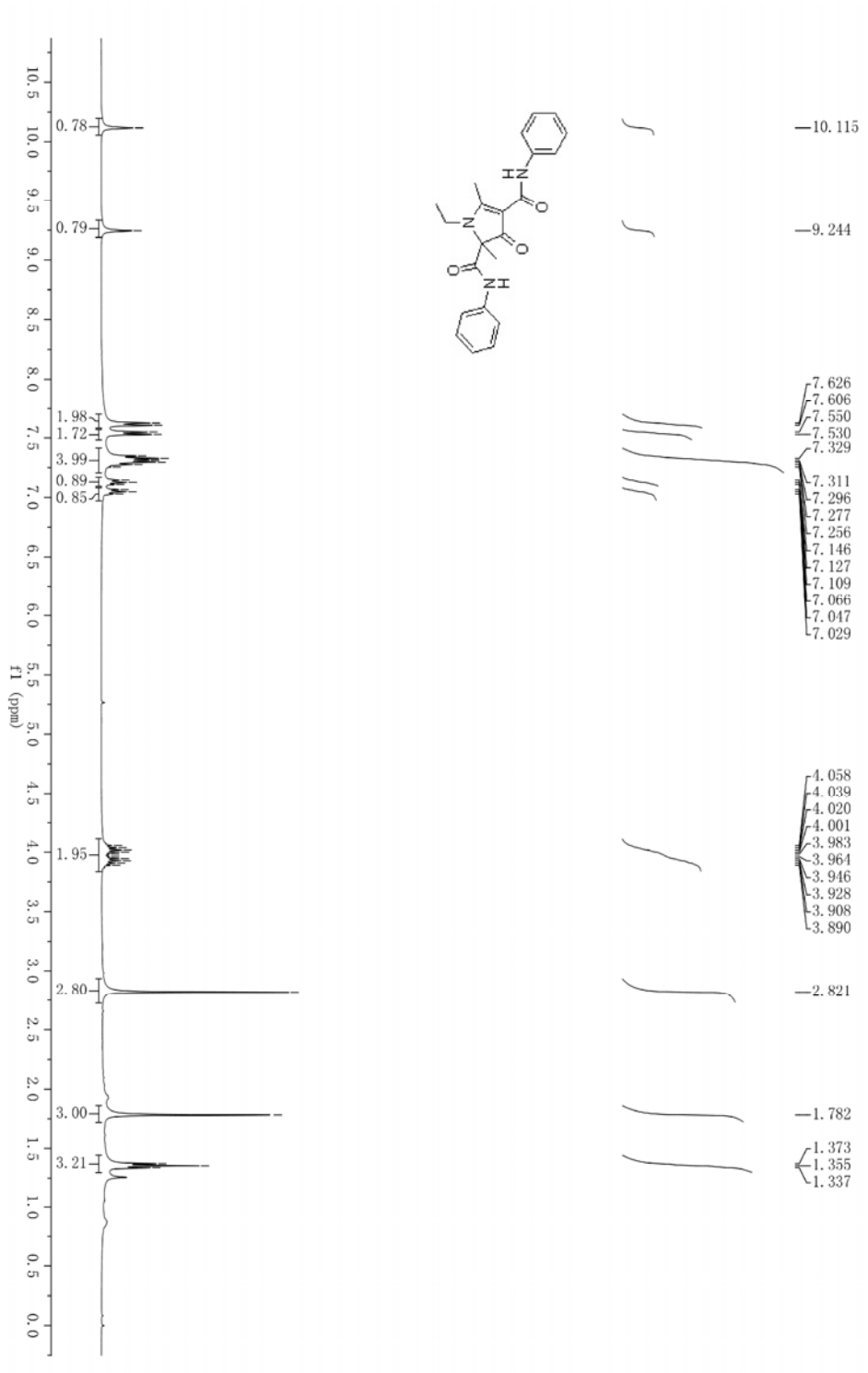
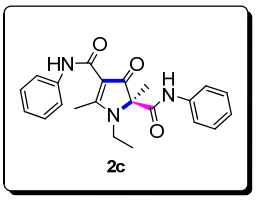
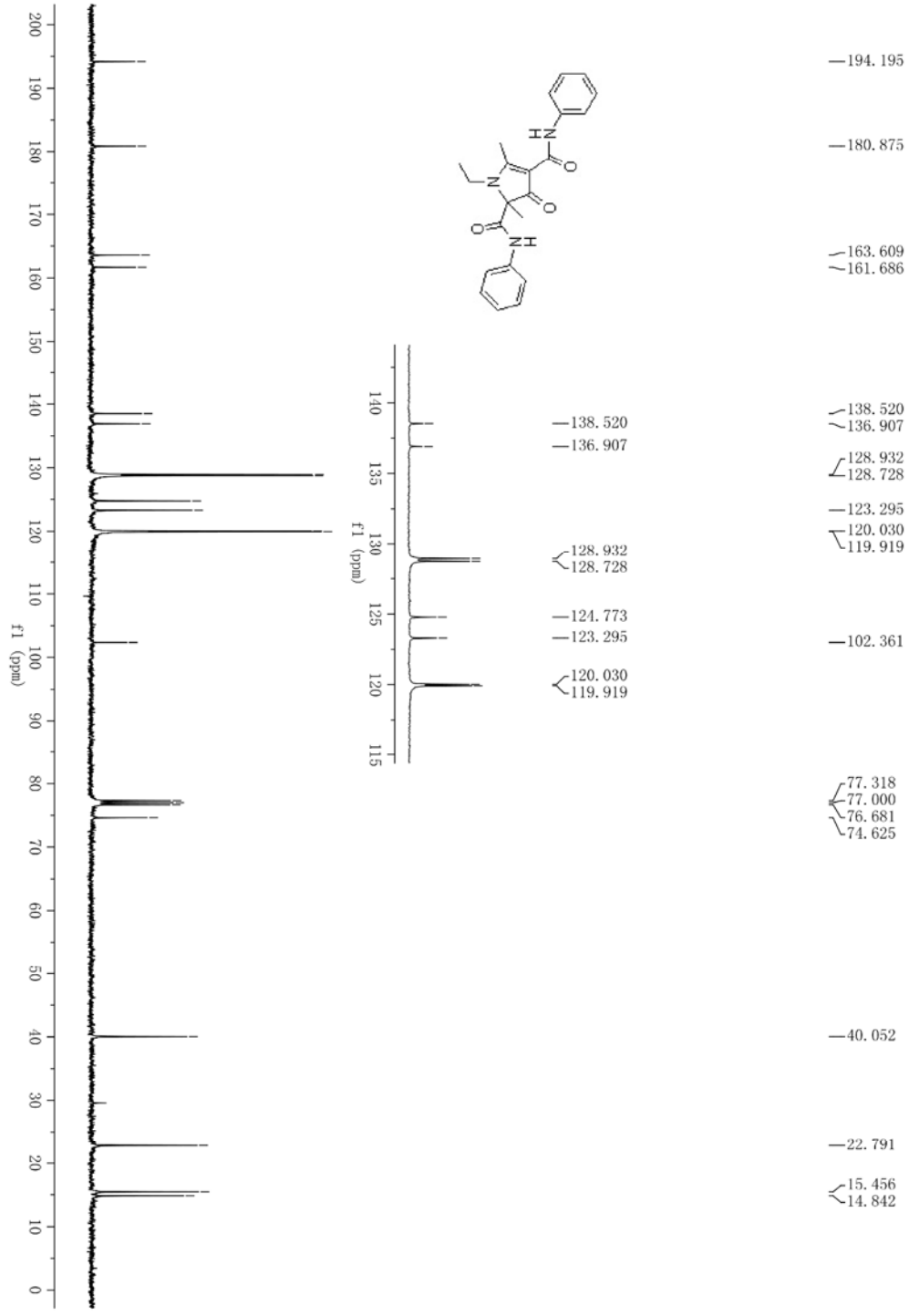
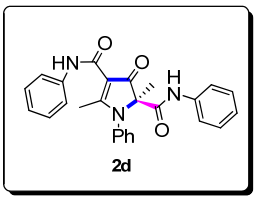
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
—194.468
—180.826
—163.714
—161.617
—138.524
—136.882
—128.941
—128.738
—123.302
—119.965
—119.882
—102.133
—77.318
—77.000
—76.682
—74.025
—31.324
—22.235
—14.396
f1 (ppm)
145
140
135
130
125
120
115
—138.524
—136.882
—128.941
—128.738
—124.778
—123.302
—119.965
—119.882


2c

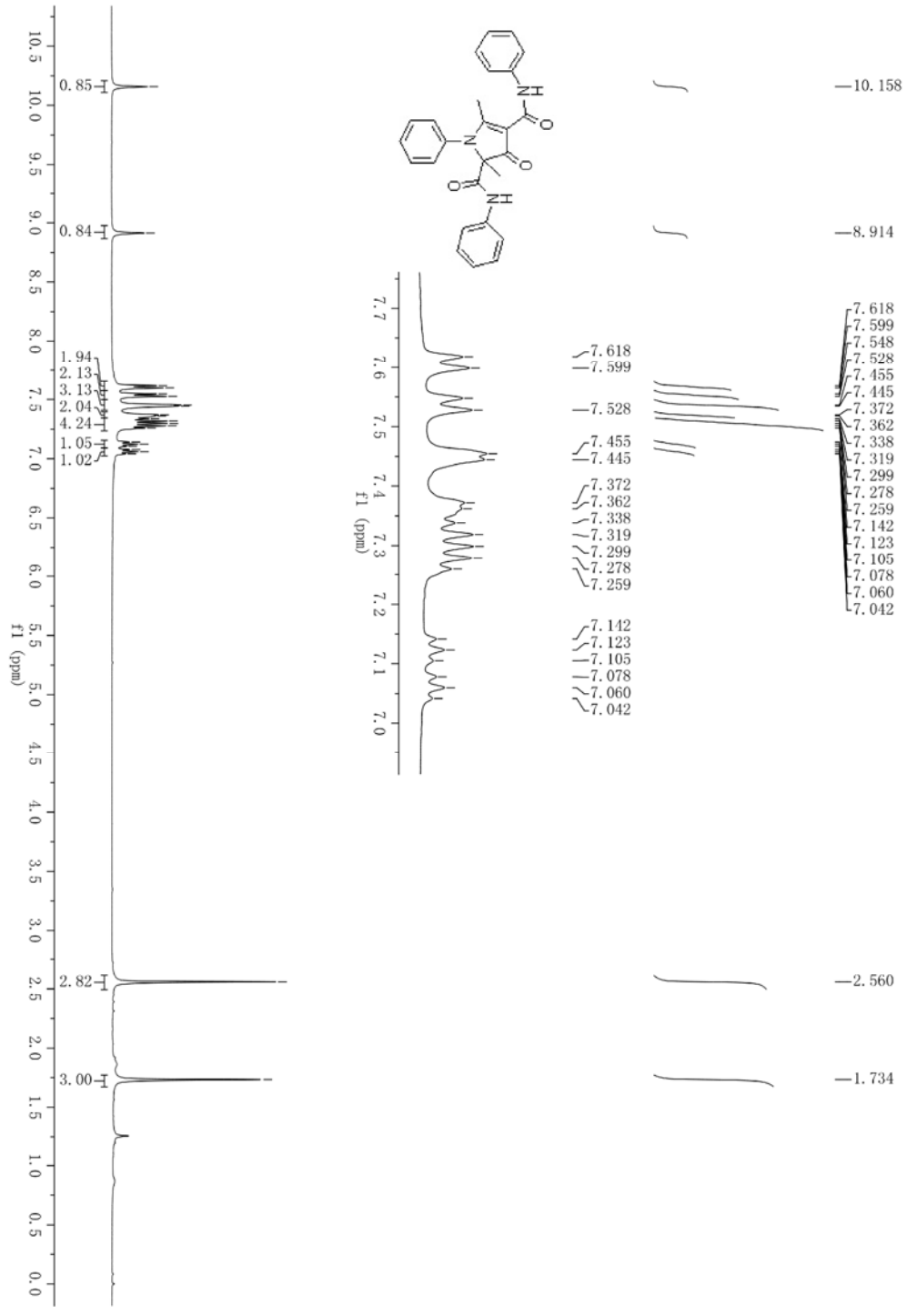

10.115
9.244
7.626
7.606
7.550
7.530
7.329
7.311
7.296
7.277
7.256
7.146
7.127
7.109
7.066
7.047
7.029
4.058
4.039
4.020
4.001
3.983
3.964
3.946
3.928
3.908
3.890
2.821
1.782
1.373
1.355
1.337
0.78
0.79
1.98
1.72
3.99
0.89
0.85
1.95
2.80
3.00
3.21
f1 (ppm)

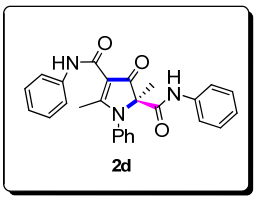

2c


194.195
180.875
163.609
161.686
138.520
136.907
128.932
128.728
123.295
120.030
119.919
102.361
77.318
77.000
76.681
74.625
40.052
22.791
15.456
14.842
f1 (ppm)

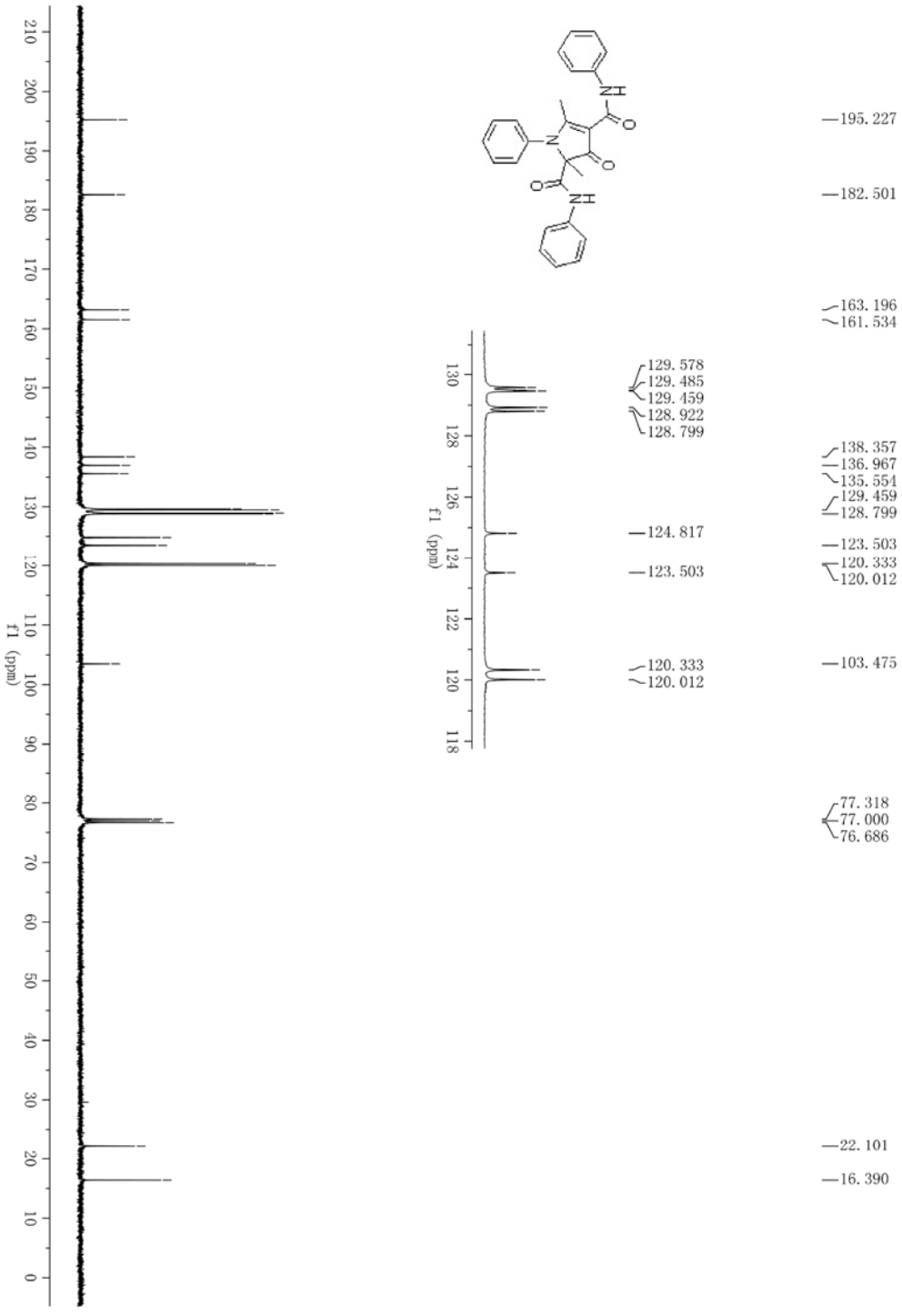

HN
O
O
H
N
N
Ph
O

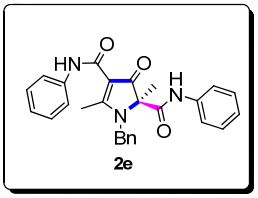
2d

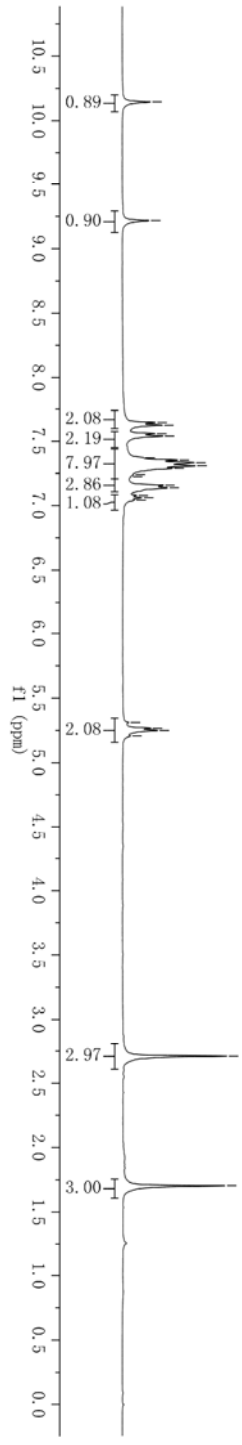

0.85
0.84
1.94
2.13
3.13
2.04
4.24
1.05
1.02
2.82
3.00
f1 (ppm)
7.618
7.599
7.528
7.455
7.445
7.372
7.362
7.338
7.319
7.299
7.278
7.259
7.142
7.123
7.105
7.078
7.060
7.042
10.158
8.914
2.560
1.734

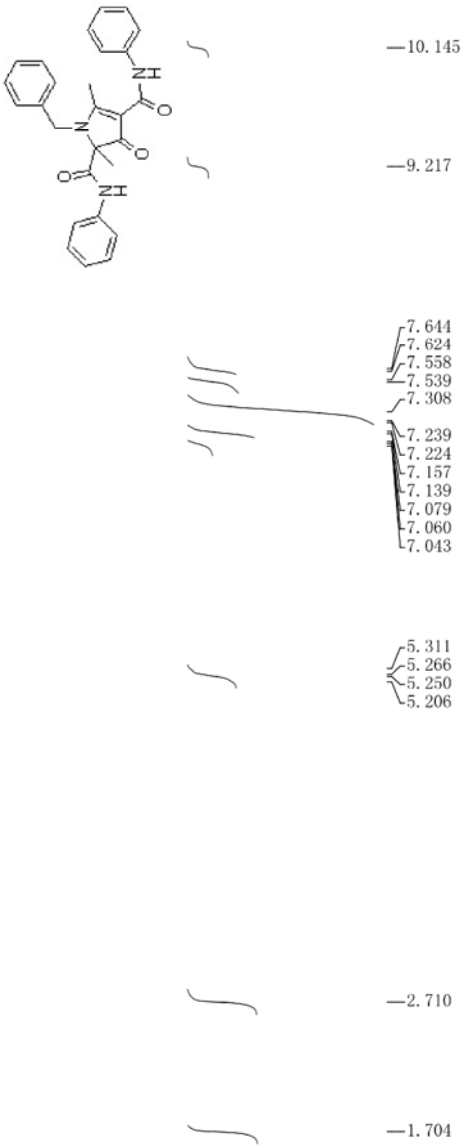

HN
O
O
H
N
N
Ph
O

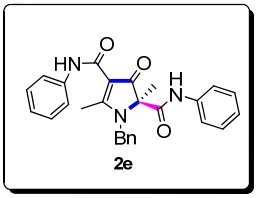
2d

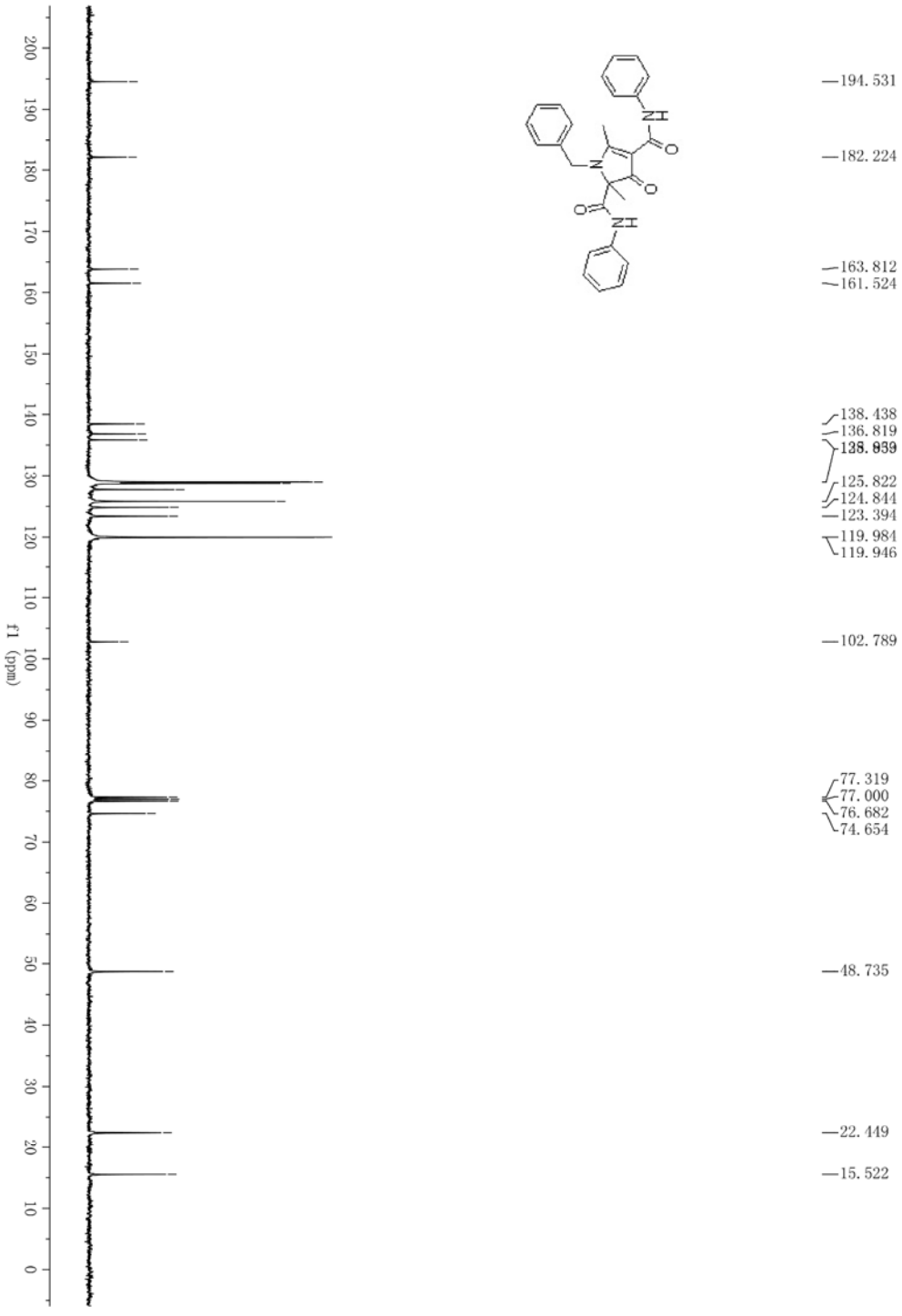

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
NH
O
N
O
NH
130
128
126
124
122
120
118
f1 (ppm)
129.578
129.485
129.459
128.922
128.799
124.817
123.503
120.333
120.012
195.227
182.501
163.196
161.534
138.357
136.967
135.554
129.459
128.799
123.503
120.333
120.012
103.475
77.318
77.000
76.686
22.101
16.390

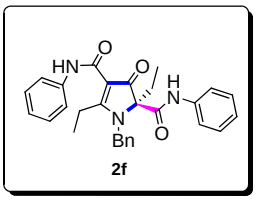

HN
O
O
H
N
N
Bn
O
2e


0.89
0.90
2.08
2.19
7.97
2.86
1.08
2.08
2.97
3.00
f1 (ppm)

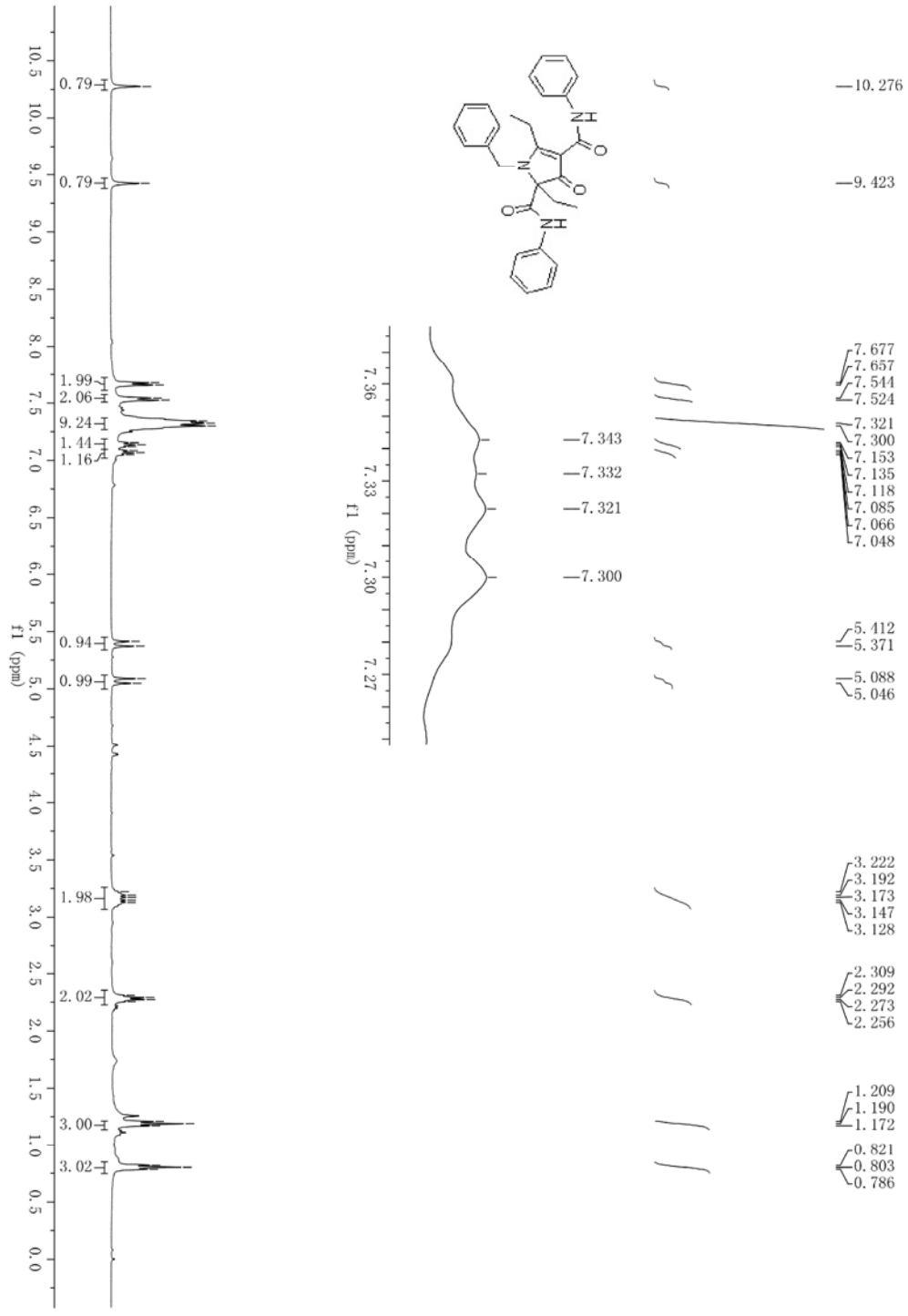

10.145
9.217
7.644
7.624
7.558
7.539
7.308
7.239
7.224
7.157
7.139
7.079
7.060
7.043
5.311
5.266
5.250
5.206
2.710
1.704

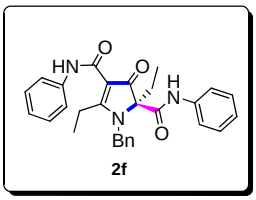

HN
O
O
H
N
N
Bn
O
2e


f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
194.531
182.224
163.812
161.524
138.438
136.819
125.822
124.844
123.394
119.984
119.946
102.789
77.319
77.000
76.682
74.654
48.735
22.449
15.522

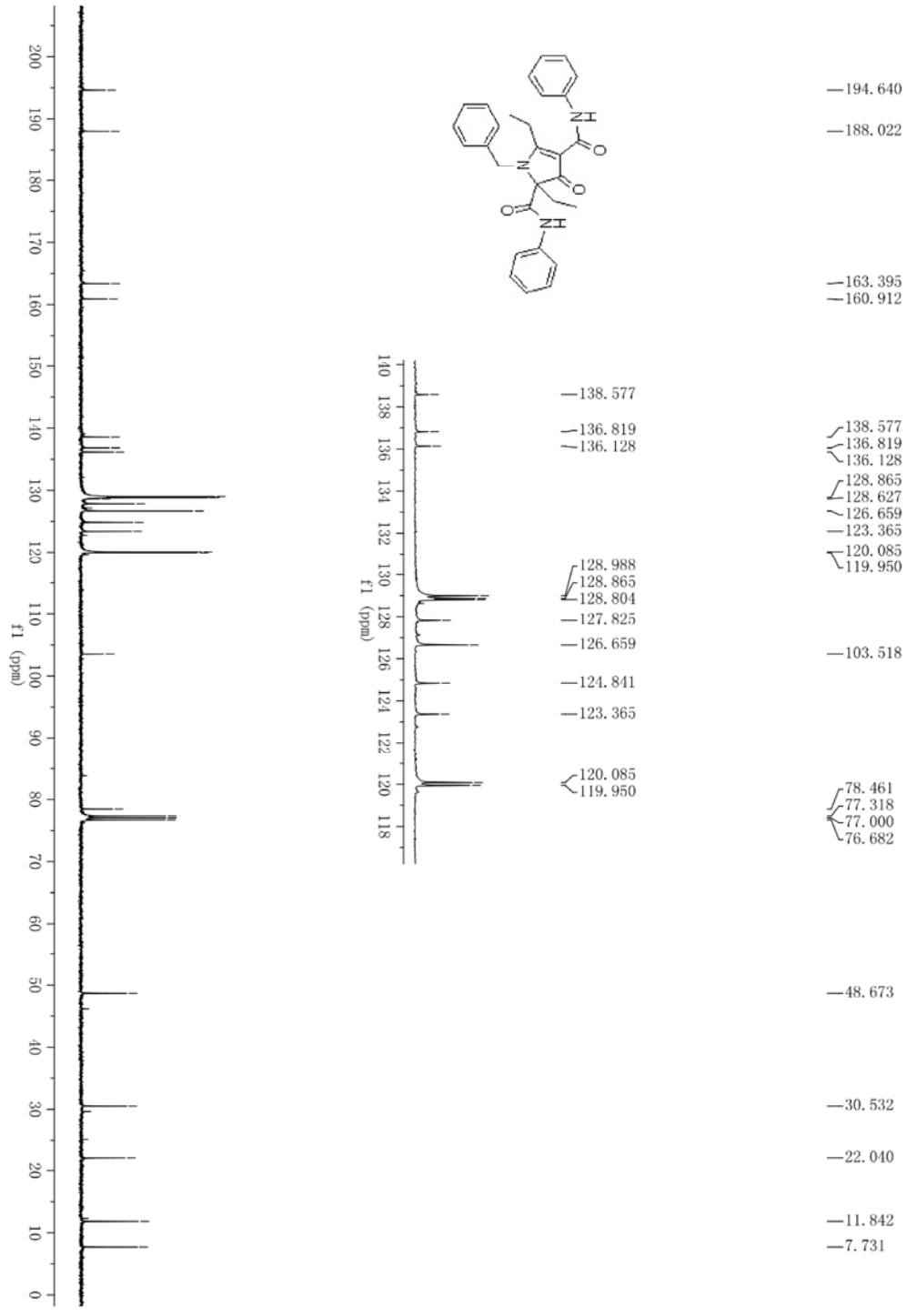

HN
O
O
H
N
N
Bn
O

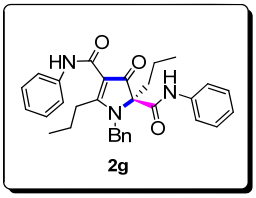
2f


f1 (ppm)
0.79
0.79
1.99
2.06
9.24
1.44
1.16
0.94
0.99
1.98
2.02
3.00
3.02
7.36
7.33
7.30
7.27
7.343
7.332
7.321
7.300
10.276
9.423
7.677
7.657
7.544
7.524
7.321
7.300
7.153
7.135
7.118
7.085
7.066
7.048
5.412
5.371
5.088
5.046
3.222
3.192
3.173
3.147
3.128
2.309
2.292
2.273
2.256
1.209
1.190
1.172
0.821
0.803
0.786

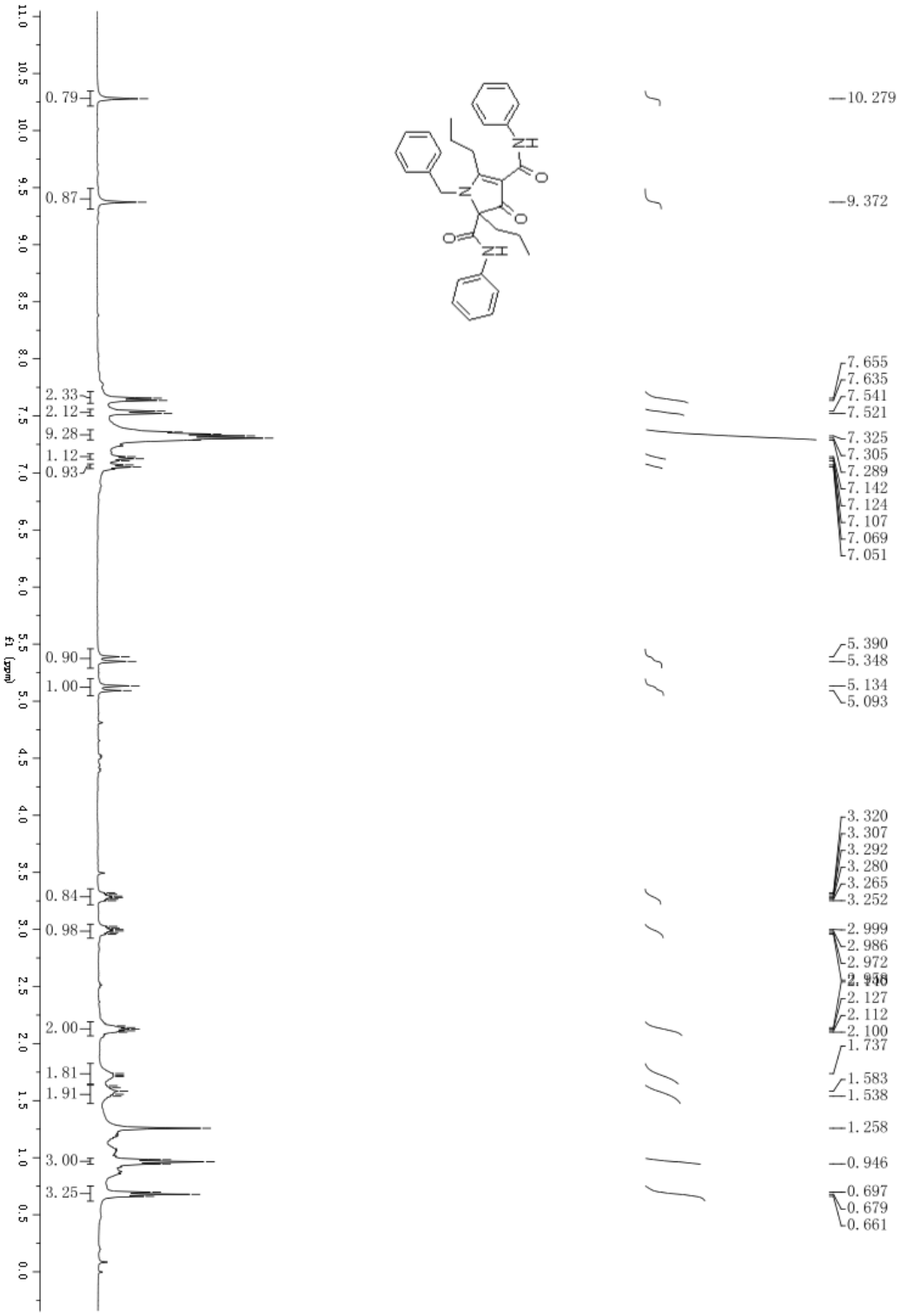

HN
O
O
H
N
N
Bn
O

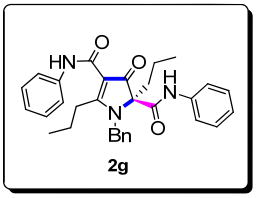
2f


f1 (ppm)
194.640
188.022
163.395
160.912
138.577
136.819
136.128
128.865
128.627
126.659
123.365
120.085
119.950
103.518
78.461
77.318
77.000
76.682
48.673
30.532
22.040
11.842
7.731

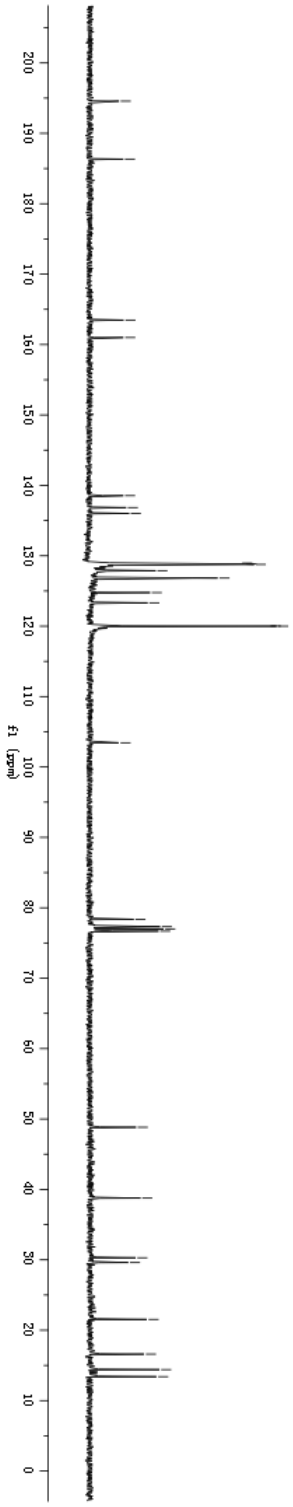

HN
O
O
H
N
N
Bn
O

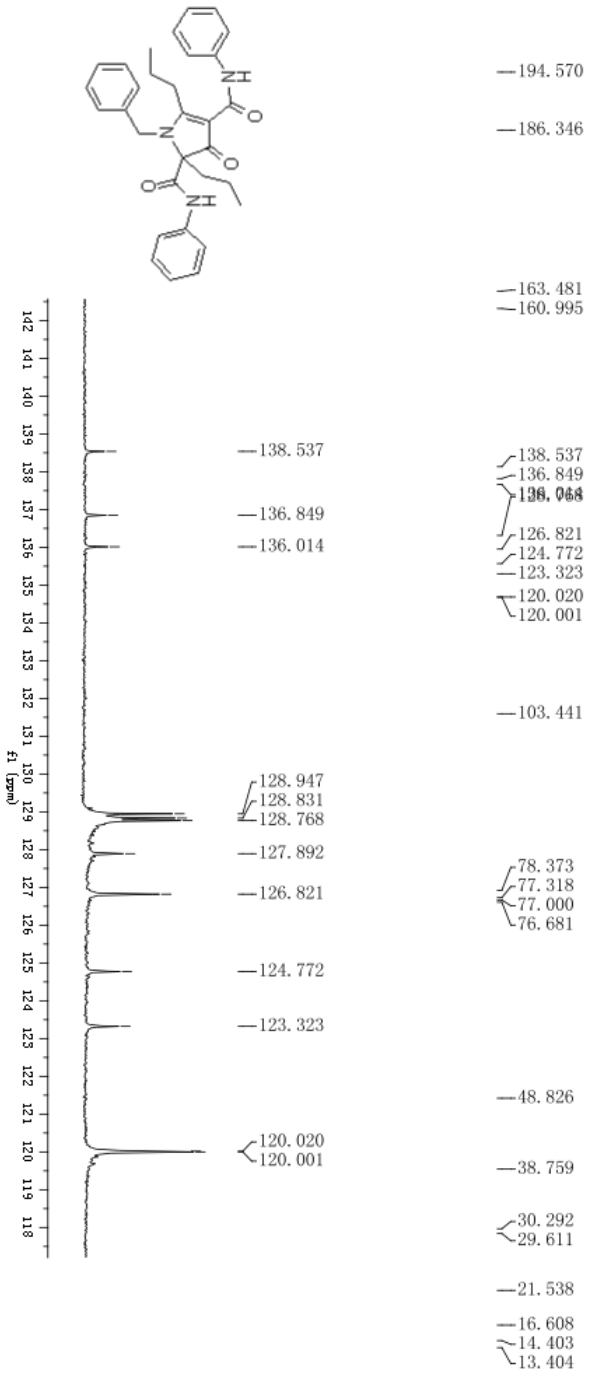
2g

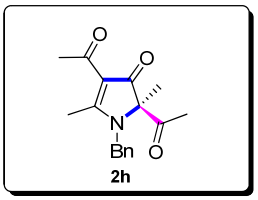

0.79
0.87
2.33
2.12
9.28
1.12
0.93
0.90
1.00
0.84
0.98
2.00
1.81
1.91
3.00
3.25
f1 (ppm)
NH
O
N
O
O
NH
10.279
9.372
7.655
7.635
7.541
7.521
7.325
7.305
7.289
7.142
7.124
7.107
7.069
7.051
5.390
5.348
5.134
5.093
3.320
3.307
3.292
3.280
3.265
3.252
2.999
2.986
2.972
2.127
2.112
2.100
1.737
1.583
1.538
1.258
0.946
0.697
0.679
0.661

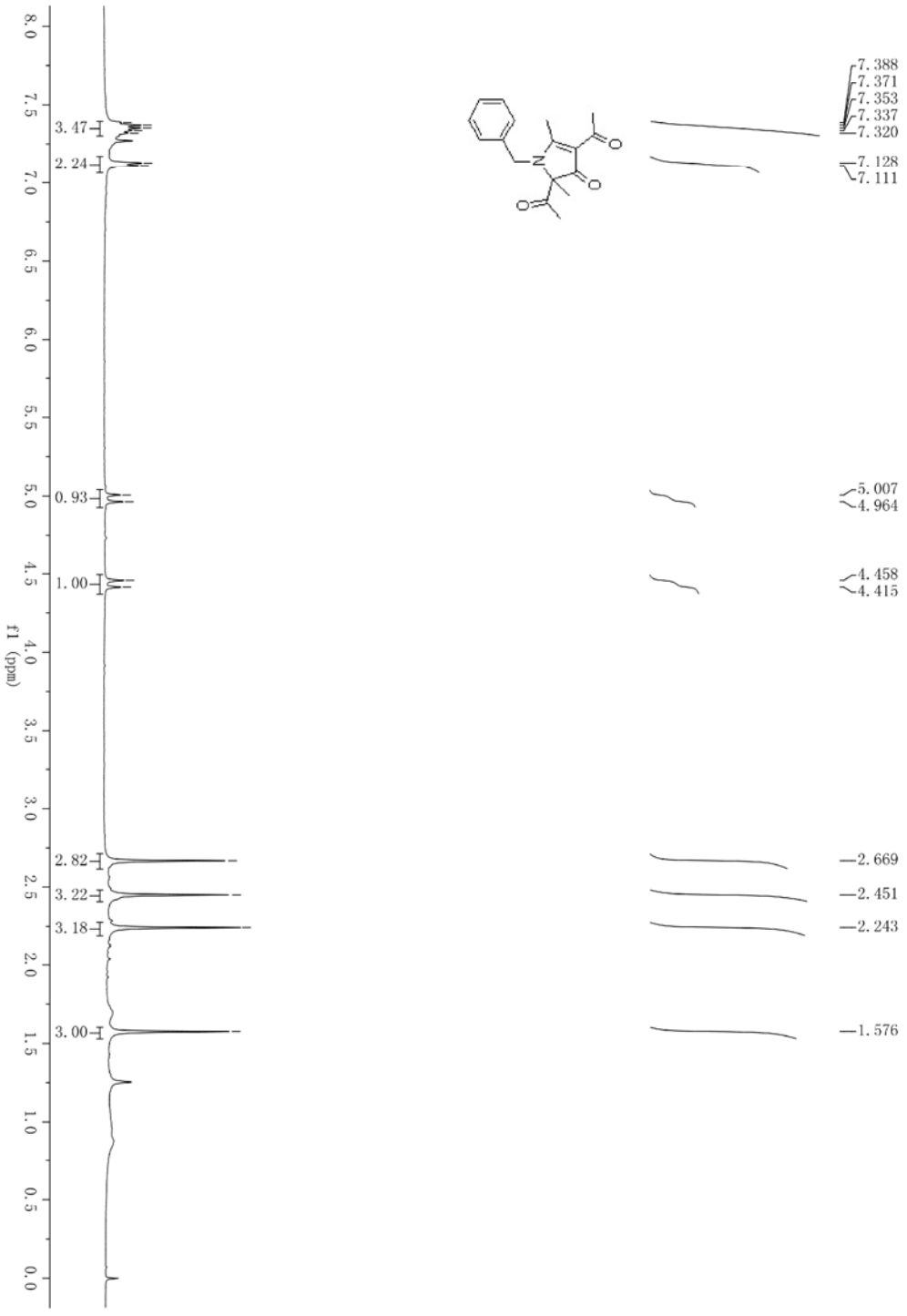

HN
O
O
H
N
N
Bn
O

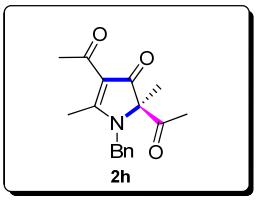
2g

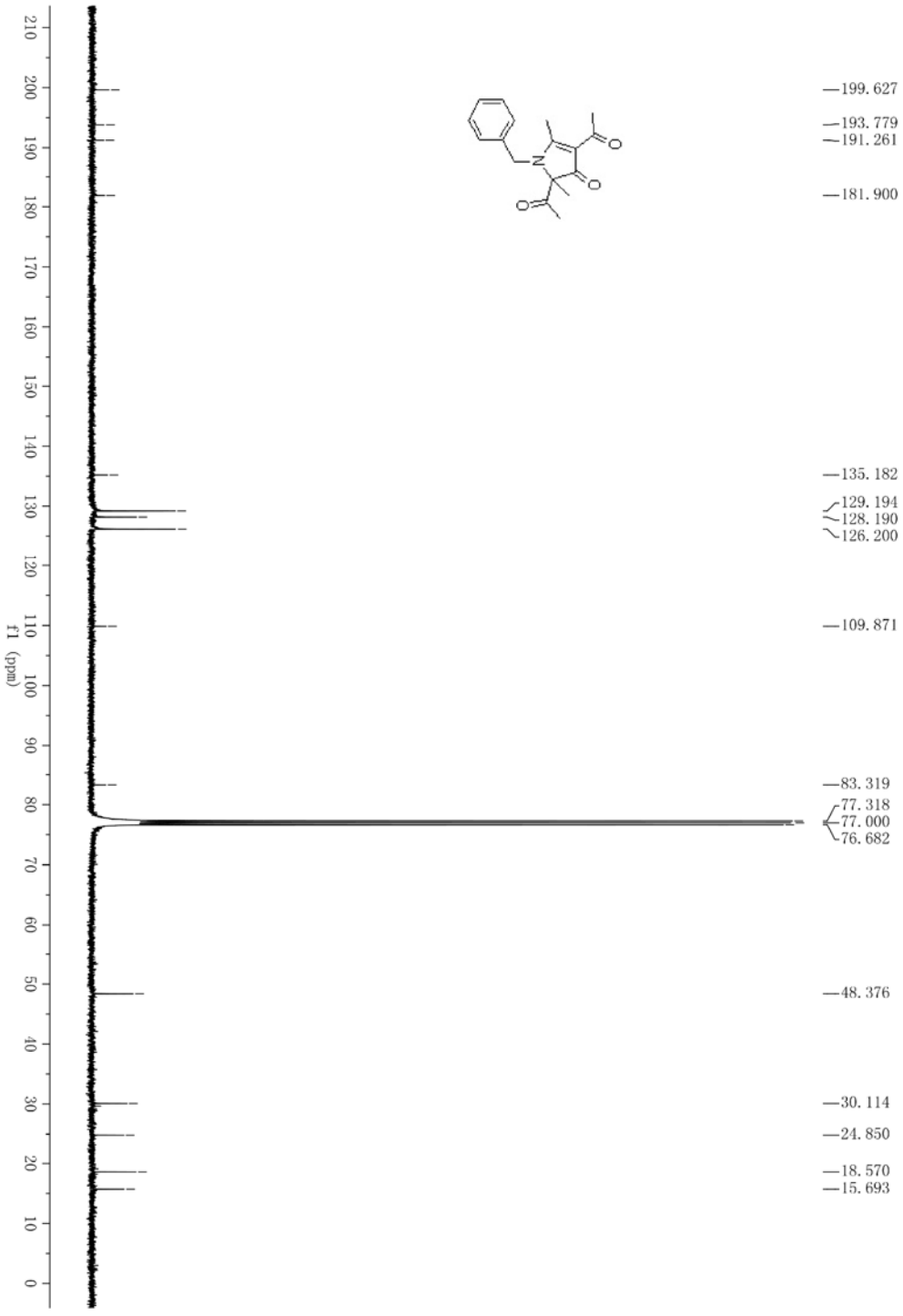

f1 (ppm)

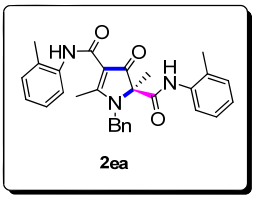

194.570
186.346
163.481
160.995
138.537
136.849
136.014
128.947
128.831
128.768
127.892
126.821
124.772
123.323
120.020
120.001
103.441
78.373
77.318
77.000
76.681
48.826
38.759
30.292
29.611
21.538
16.608
14.403
13.404
f1 (ppm)


O
O
N
Bn
O
2h

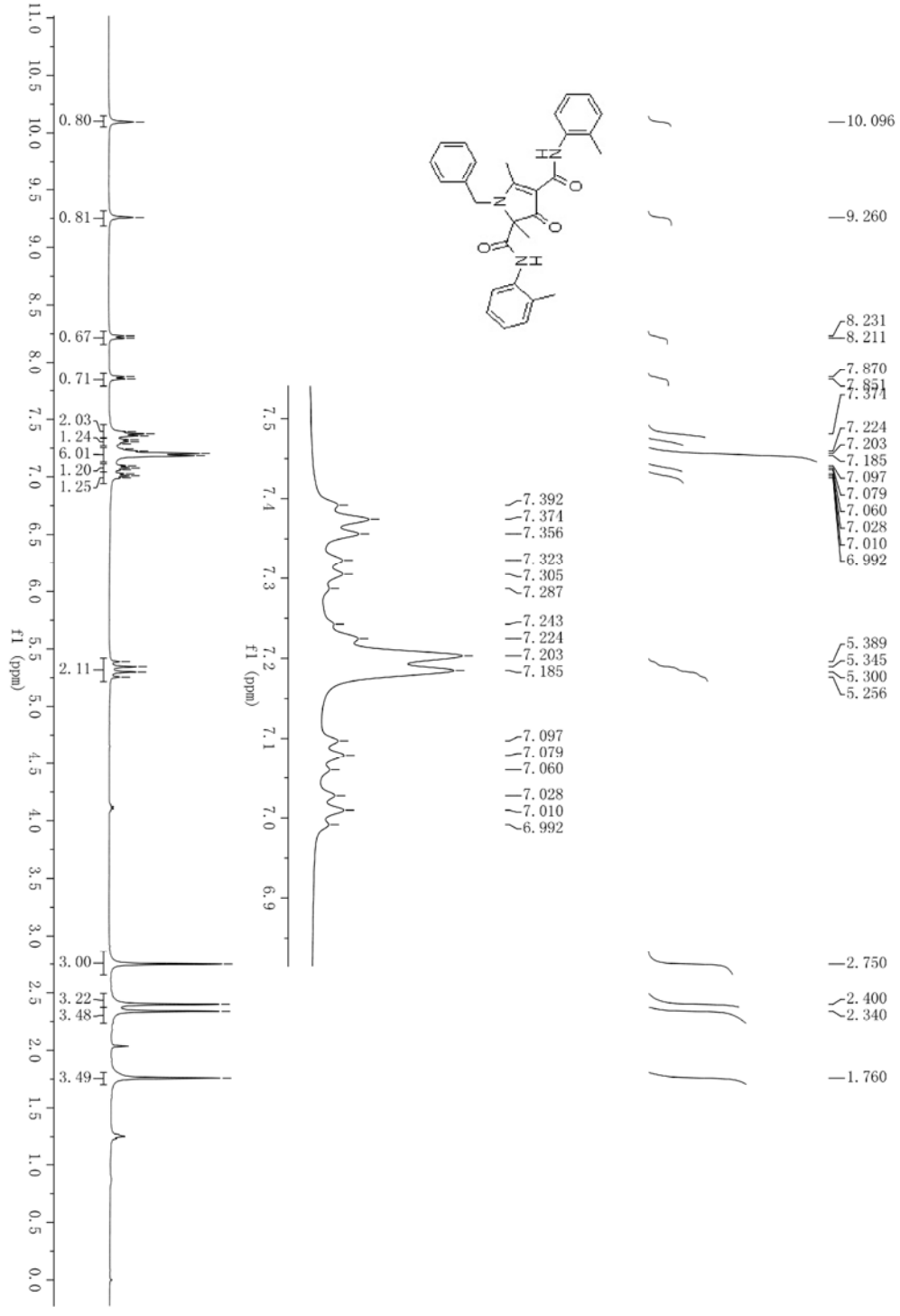

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3.47
2.24
0.93
1.00
2.82
3.22
3.18
3.00
7.388
7.371
7.353
7.337
7.320
7.128
7.111
5.007
4.964
4.458
4.415
2.669
2.451
2.243
1.576

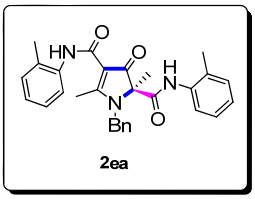

O
O
N
Bn
O
2h


199.627
193.779
191.261
181.900
135.182
129.194
128.190
126.200
109.871
83.319
77.318
77.000
76.682
48.376
30.114
24.850
18.570
15.693
f1 (ppm)

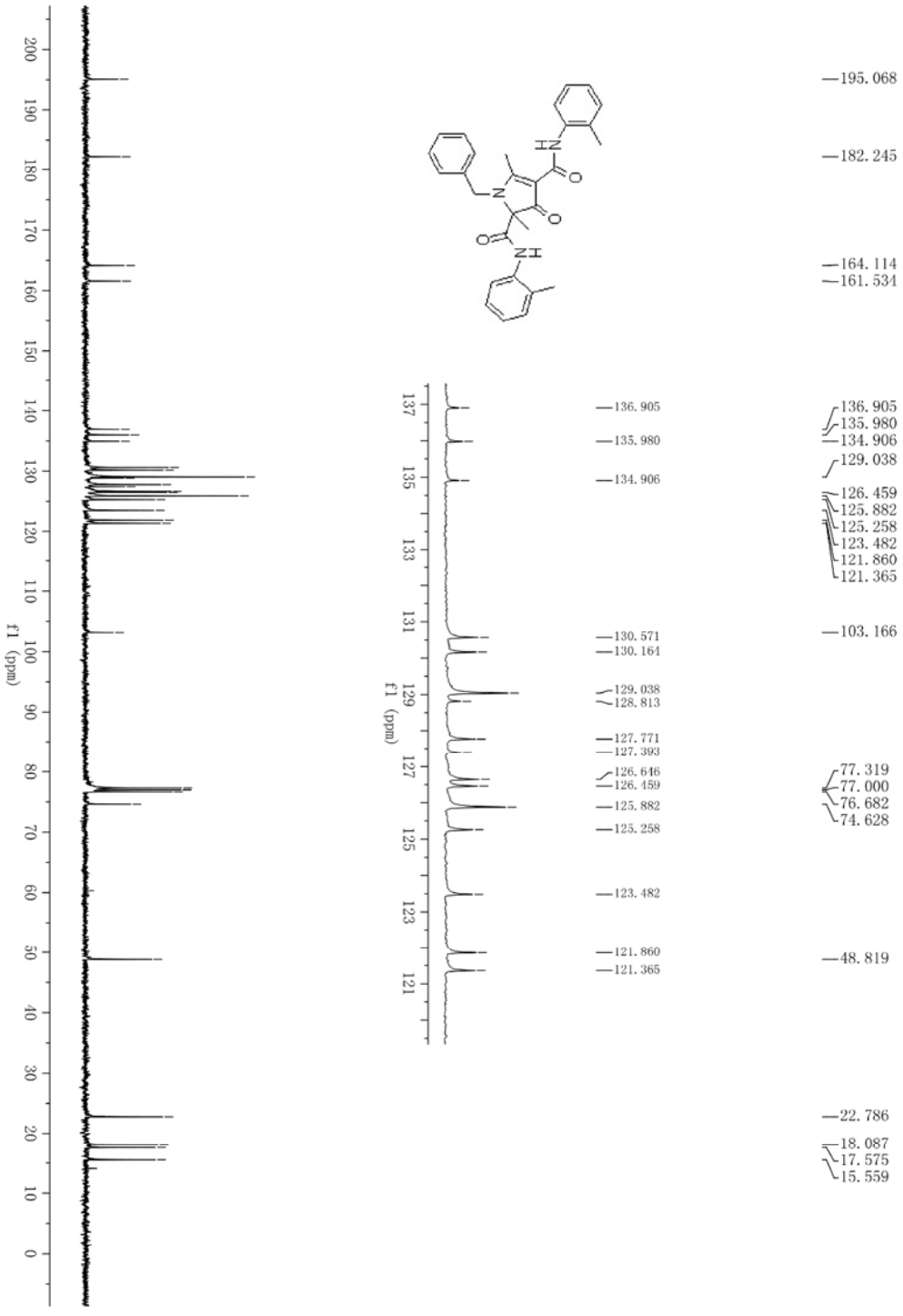

HN
O
O
H
N
N
Bn
O

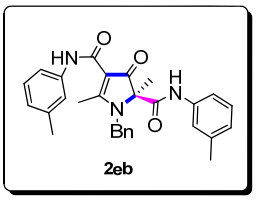
2ea

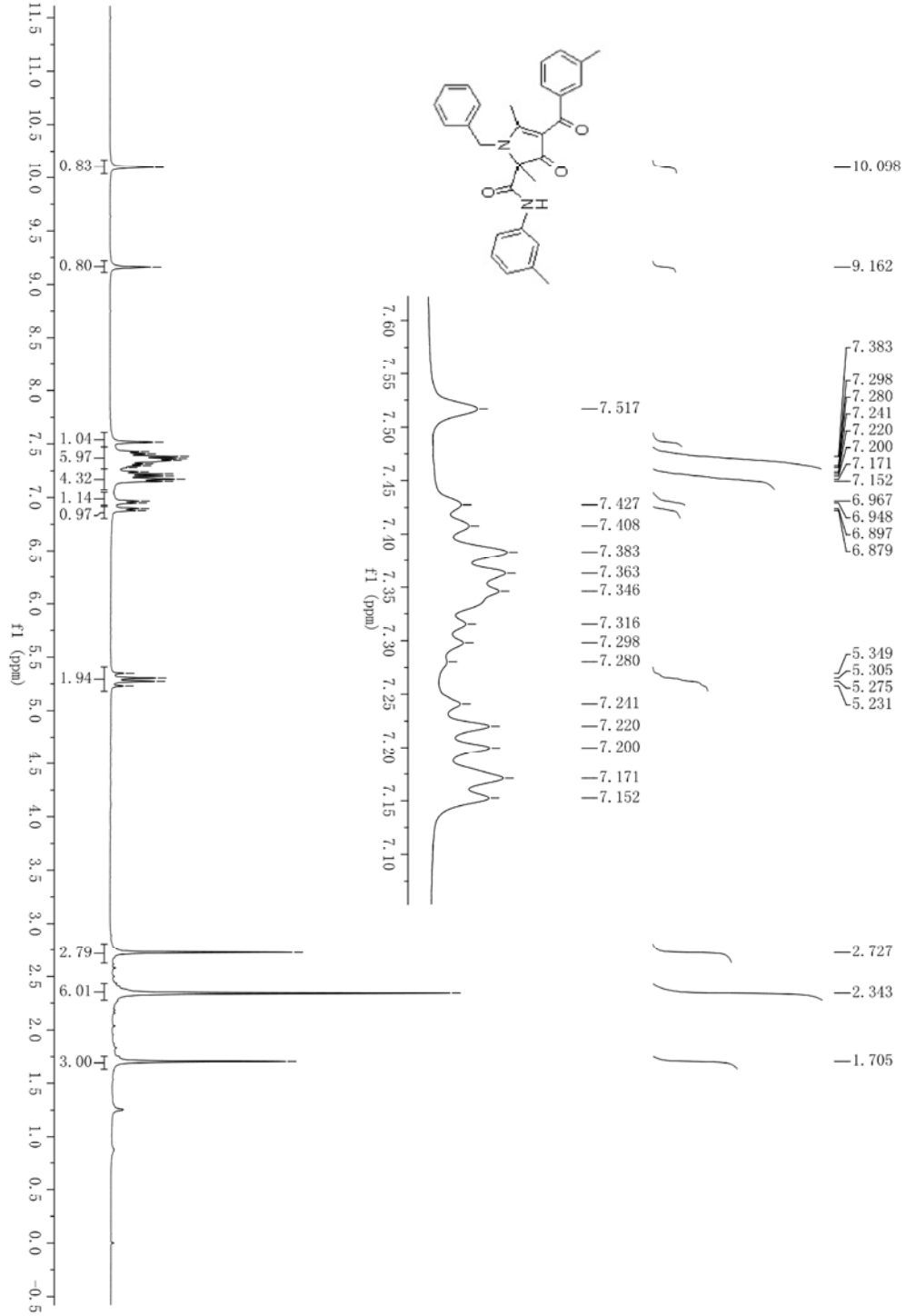

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
0.80
0.81
0.67
0.71
2.03
1.24
6.01
1.20
1.25
2.11
3.00
3.22
3.48
3.49
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
7.392
7.374
7.356
7.323
7.305
7.287
7.243
7.224
7.203
7.185
7.097
7.079
7.060
7.028
7.010
6.992
10.096
9.260
8.231
8.211
7.870
7.851
7.371
7.224
7.203
7.185
7.097
7.079
7.060
7.028
7.010
6.992
5.389
5.345
5.300
5.256
2.750
2.400
2.340
1.760


HN
O
O
N
H
N
Bn
O

2ea


f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
—195.068
—182.245
—164.114
—161.534
—136.905
—135.980
—134.906
—130.571
—130.164
—129.038
—128.813
—127.771
—127.393
—126.646
—126.459
—125.882
—125.258
—123.482
—121.860
—121.365
—103.166
—77.319
—77.000
—76.682
—74.628
—48.819
—22.786
—18.087
—17.575
—15.559


2eb


f1 (ppm)
0.83
0.80
1.04
5.97
4.32
1.14
0.97
1.94
2.79
6.01
3.00
—10.098
—9.162
—7.517
—7.427
—7.408
—7.383
—7.363
—7.346
—7.316
—7.298
—7.280
—7.241
—7.220
—7.200
—7.171
—7.152
7.383
7.298
7.280
7.241
7.220
7.200
7.171
7.152
6.967
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6.897
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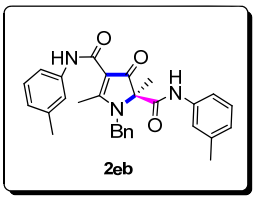
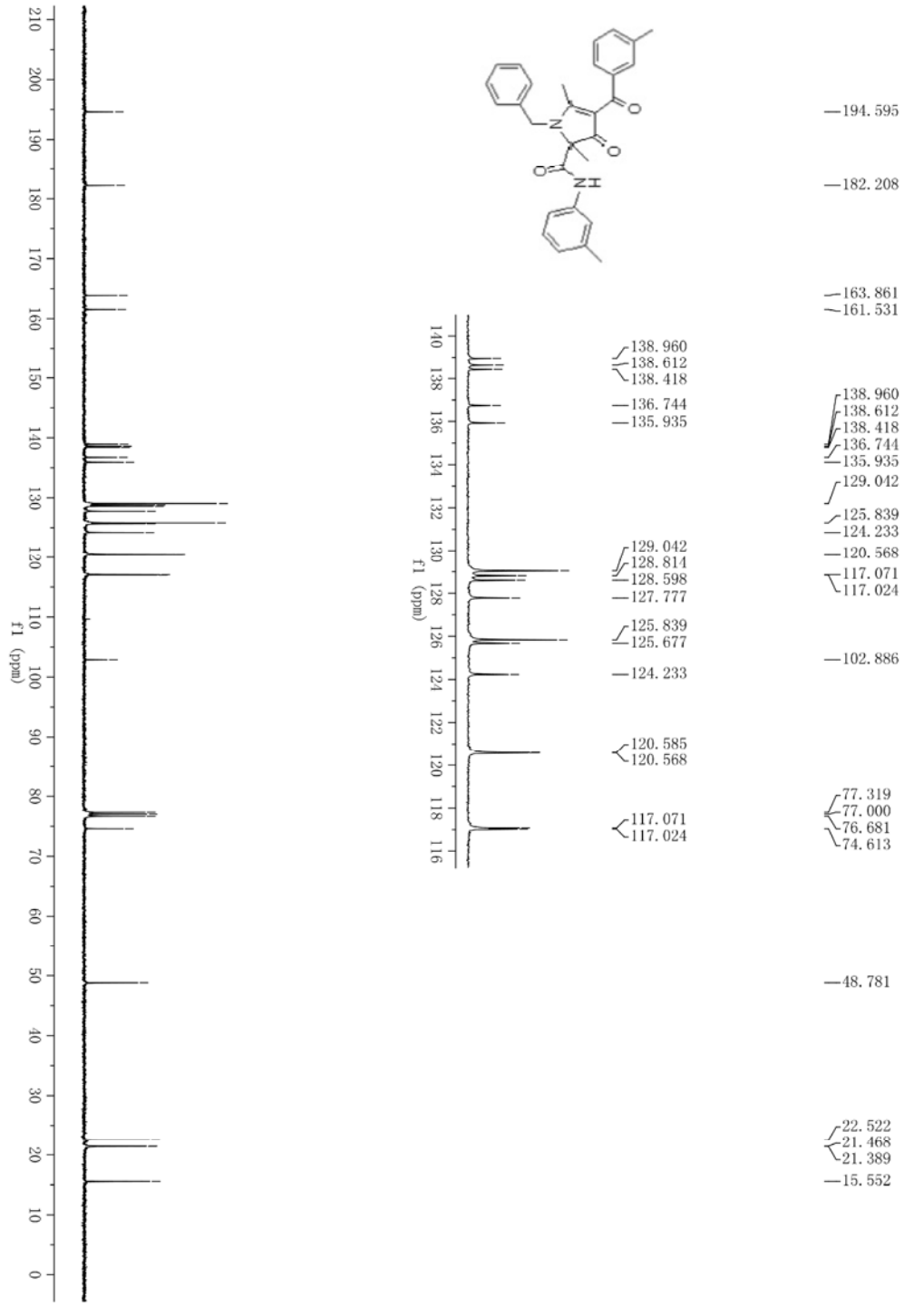
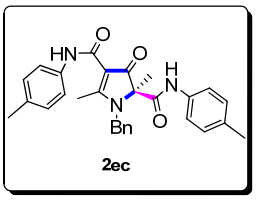
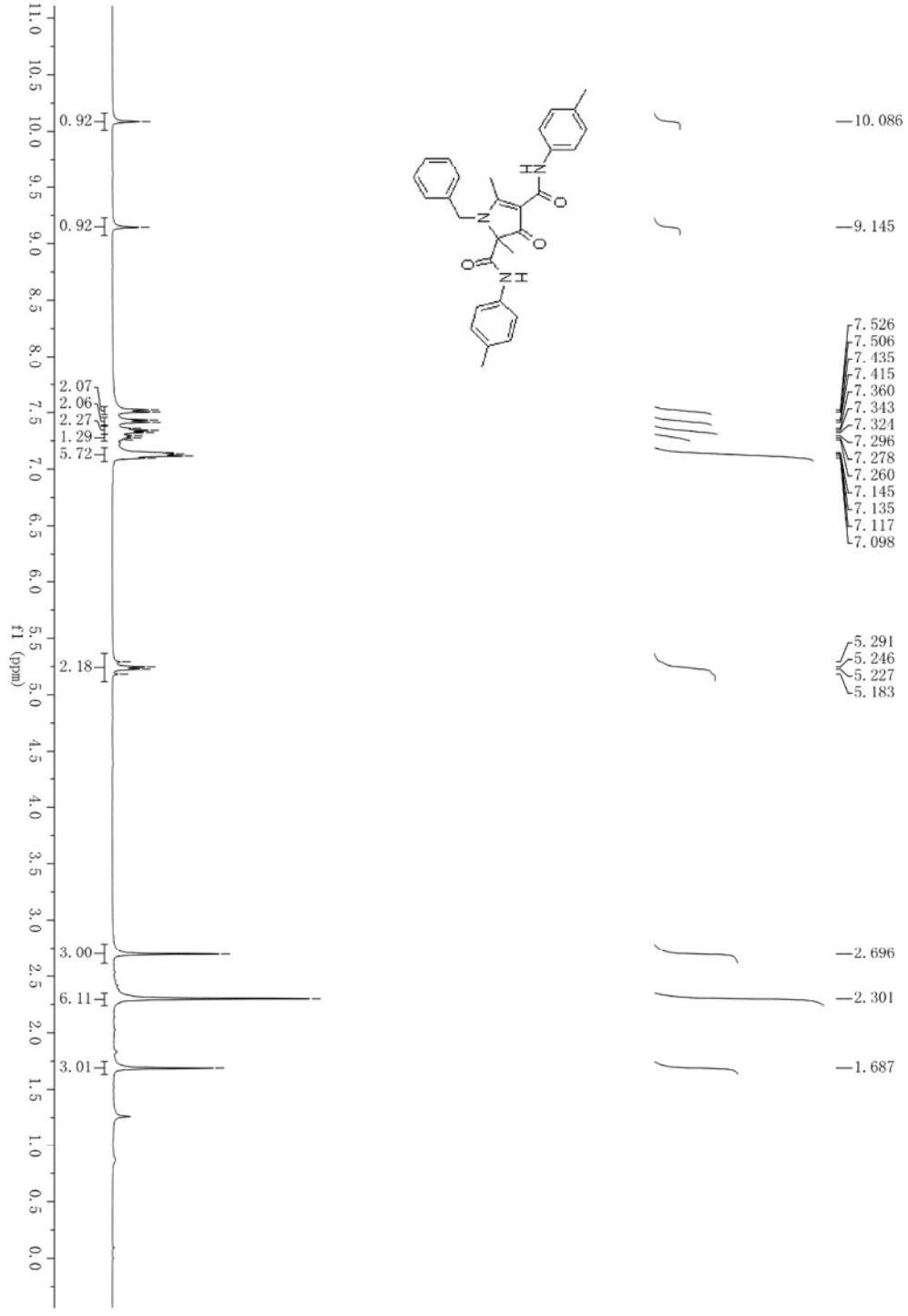
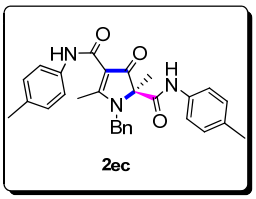
5.275
5.231
—2.727
—2.343
—1.705

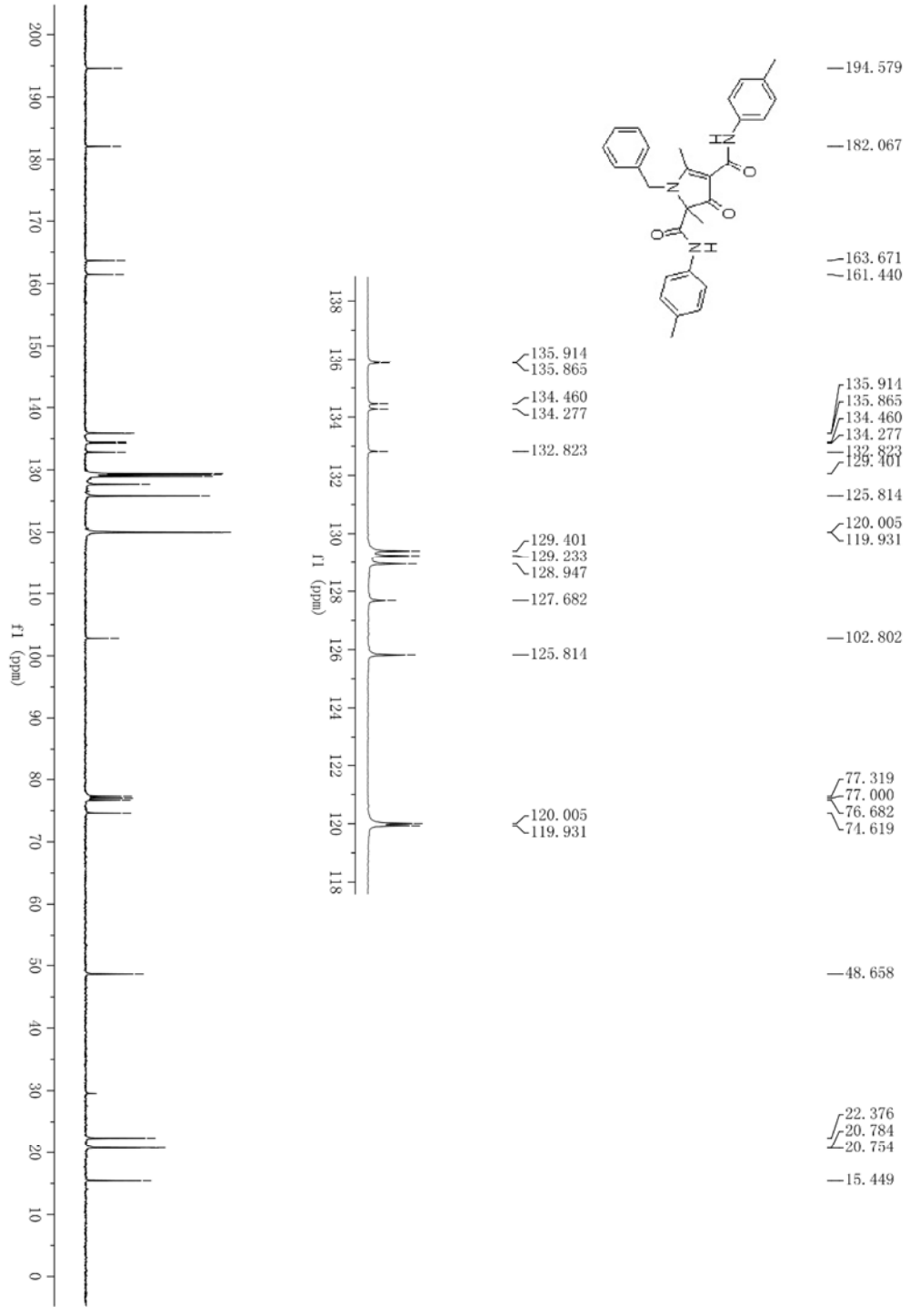

HN
O
O
H
N
N
Bn
O
2eb

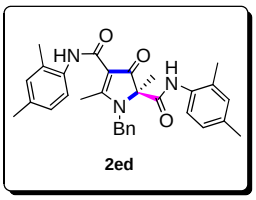

f1 (ppm)
194.595
182.208
163.861
161.531
138.960
138.612
138.418
136.744
135.935
129.042
128.814
128.598
127.777
125.839
125.677
124.233
120.585
120.568
117.071
117.024
102.886
77.319
77.000
76.681
74.613
48.781
22.522
21.468
21.389
15.552


HN
O
O
H
N
N
Bn
O
2ec

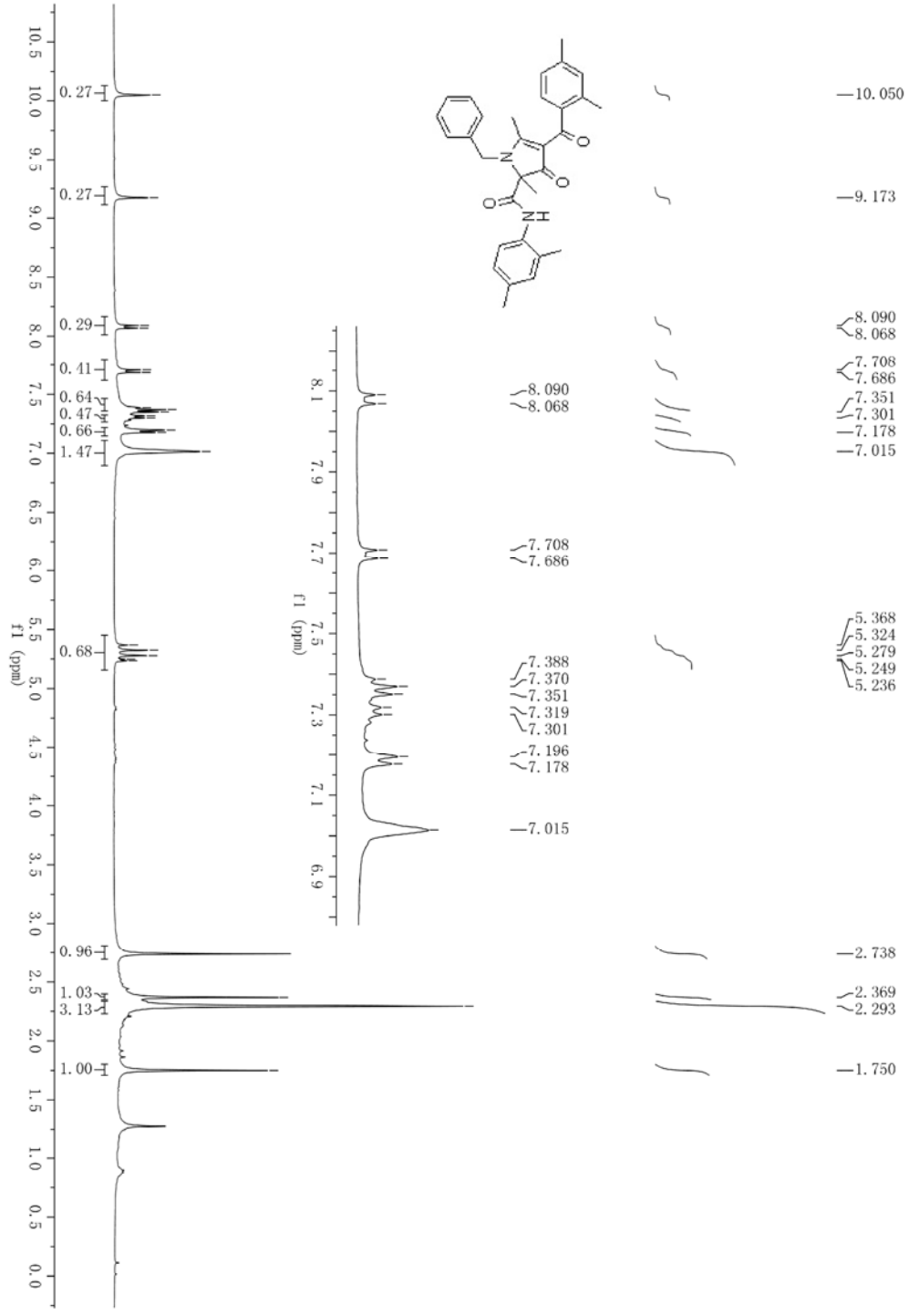

0.92
0.92
2.07
2.06
2.27
1.29
5.72
2.18
3.00
6.11
3.01
f1 (ppm)
—10.086
—9.145
7.526
7.506
7.435
7.415
7.360
7.343
7.324
7.296
7.278
7.260
7.145
7.135
7.117
7.098
5.291
5.246
5.227
5.183
—2.696
—2.301
—1.687

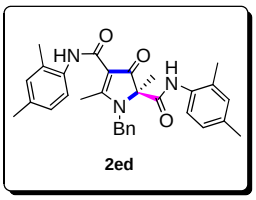

HN
O
O
H
N
N
Bn
O
2ec


f1 (ppm)
f1 (ppm)
194.579
182.067
163.671
161.440
135.914
135.865
134.460
134.277
132.823
129.401
129.233
128.947
127.682
125.814
120.005
119.931
102.802
77.319
77.000
76.682
74.619
48.658
22.376
20.784
20.754
15.449

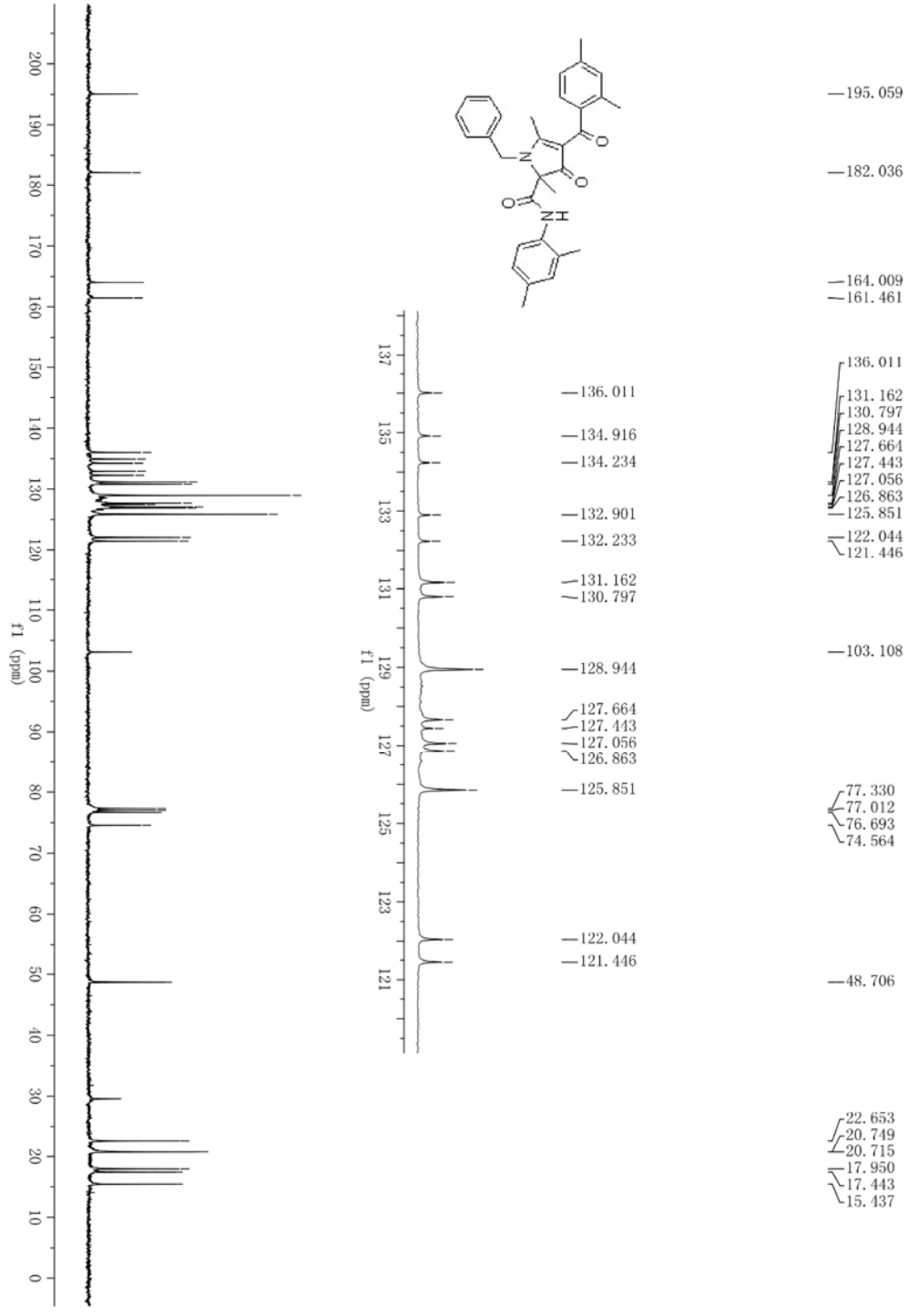

HN
O
O
H
N
N
Bn
O

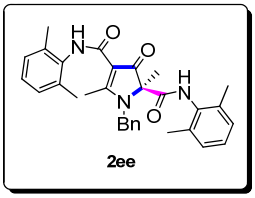
2ed

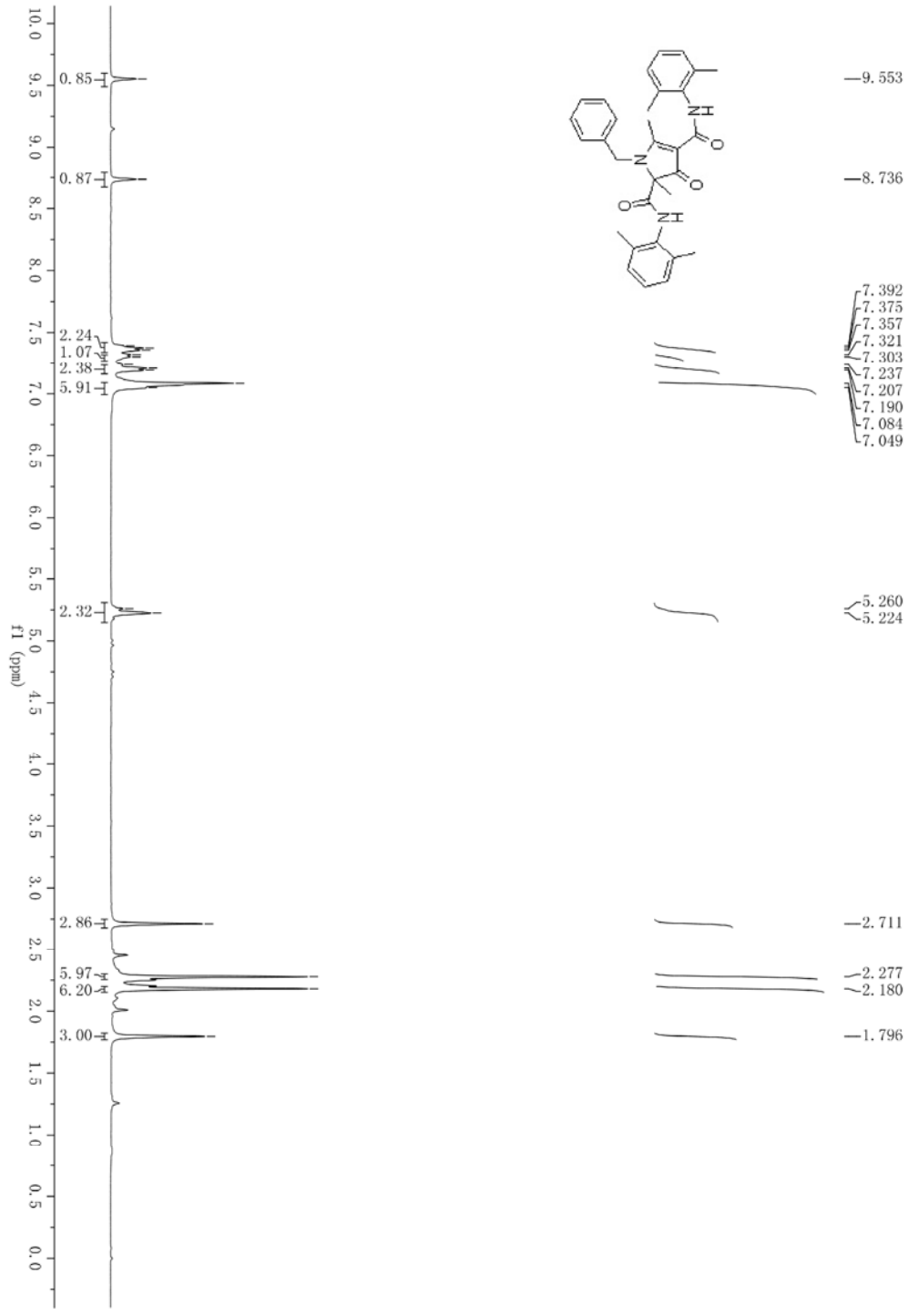

0.27
0.27
0.29
0.41
0.64
0.47
0.66
1.47
0.68
0.96
1.03
3.13
1.00
f1 (ppm)
8.090
8.068
7.708
7.686
7.388
7.370
7.351
7.319
7.301
7.196
7.178
7.015
10.050
9.173
8.090
8.068
7.708
7.686
7.351
7.301
7.178
7.015
5.368
5.324
5.279
5.249
5.236
2.738
2.369
2.293
1.750

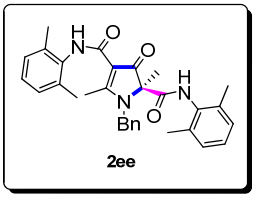

HN
O
O
H
N
N
Bn
O

2ed

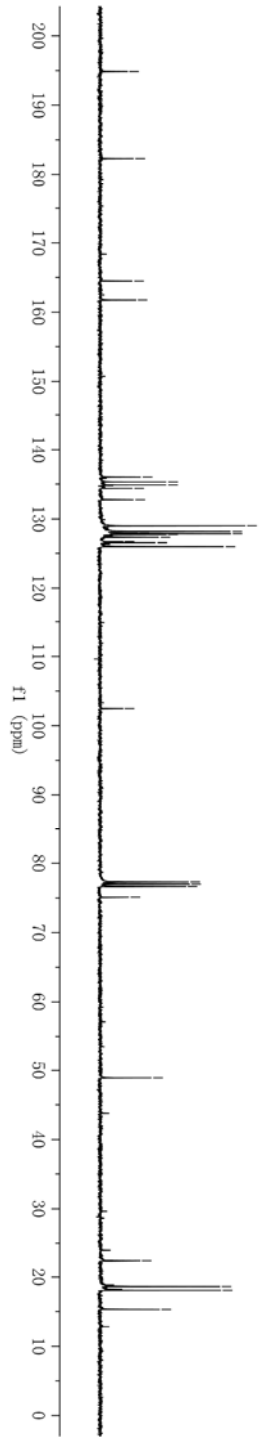

f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
137
135
133
131
129
127
125
123
121
—136.011
—134.916
—134.234
—132.901
—132.233
—131.162
—130.797
—128.944
—127.664
—127.443
—127.056
—126.863
—125.851
—122.044
—121.446
—195.059
—182.036
—164.009
—161.461
—136.011
131.162
130.797
128.944
127.664
127.443
127.056
126.863
125.851
122.044
121.446
—103.108
77.330
77.012
76.693
74.564
—48.706
22.653
20.749
20.715
17.950
17.443
15.437

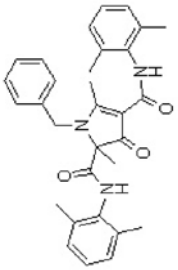

2ee

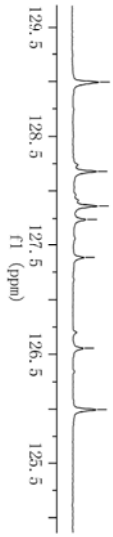

0.85
0.87
2.24
1.07
2.38
5.91
2.32
2.86
5.97
6.20
3.00
f1 (ppm)
9.553
8.736
7.392
7.375
7.357
7.321
7.303
7.237
7.207
7.190
7.084
7.049
5.260
5.224
2.711
2.277
2.180
1.796



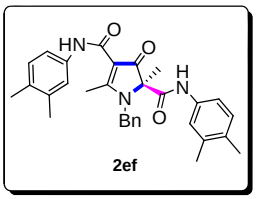
2ee

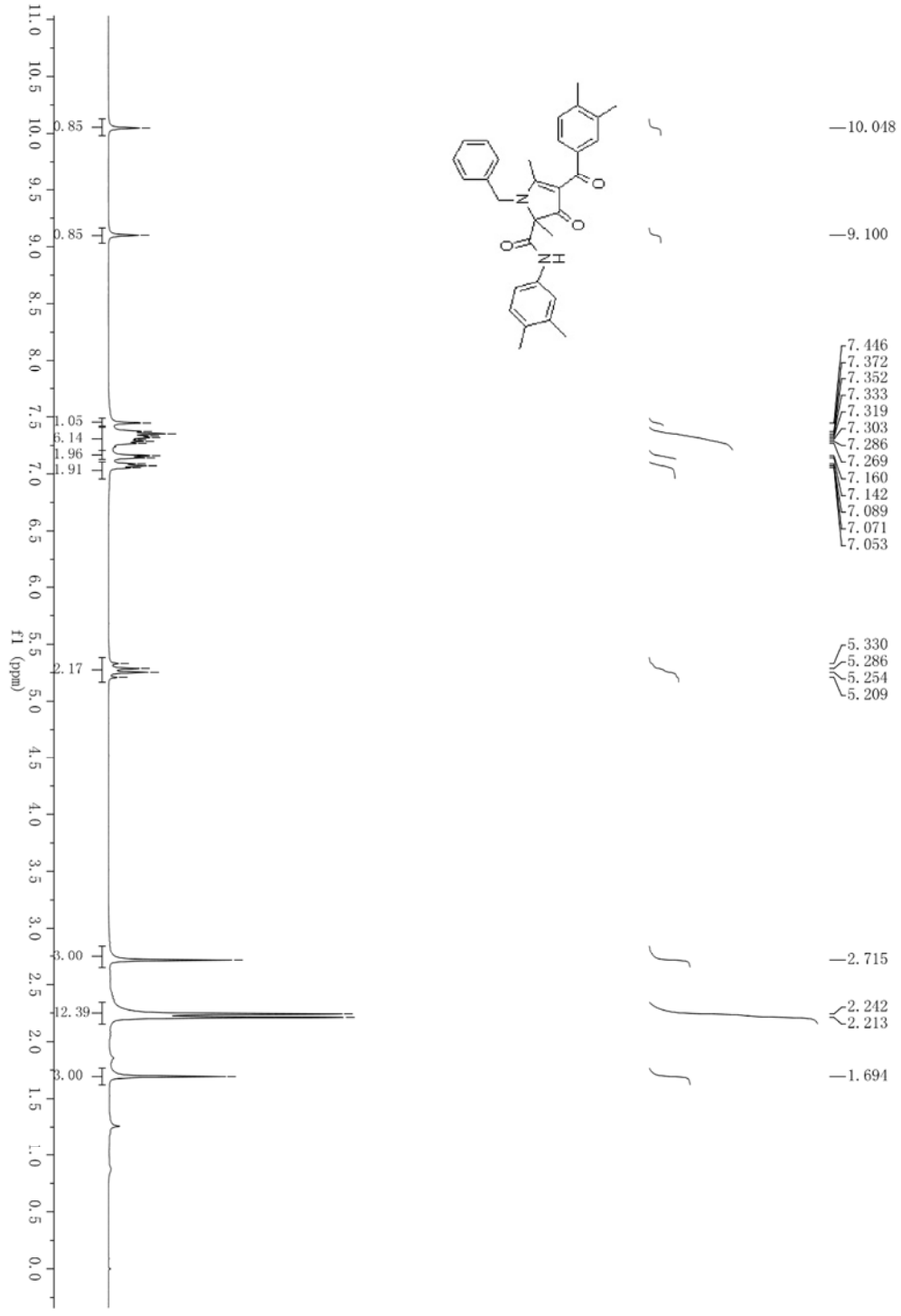


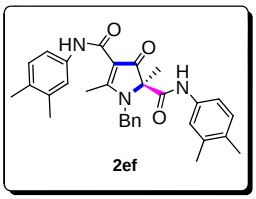


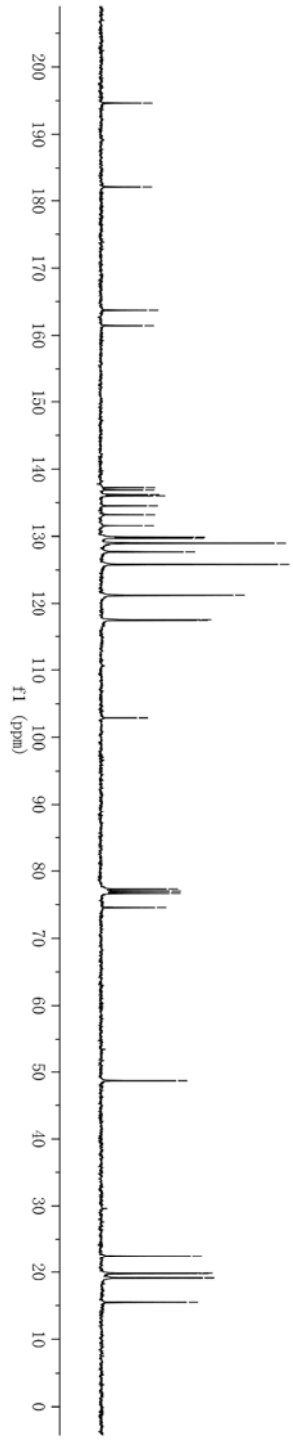


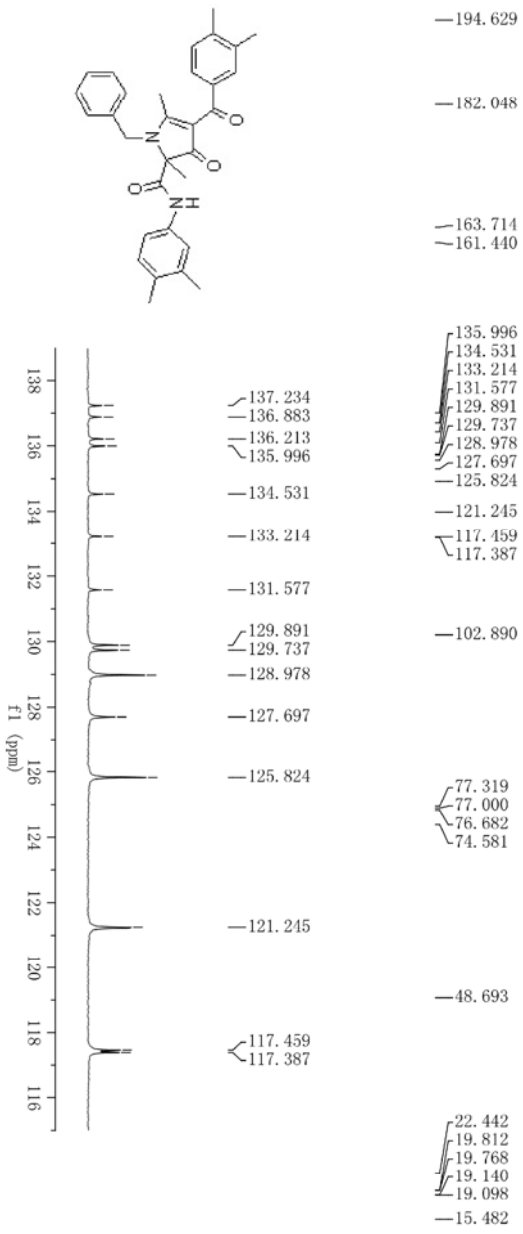
194.871
182.272
164.491
161.745
136.036
135.336
134.892
134.407
132.780
128.995
128.995
128.180
127.865
127.741
127.741
127.385
127.385
126.703
126.556
125.997
126.556
125.997
102.467
77.318
77.000
76.681
75.088
48.897
22.349
18.080
15.339

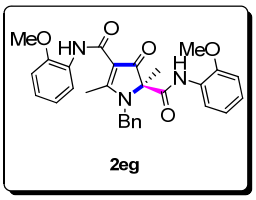

HN
O
O
H
N
N
Bn
O
2ef


f1 (ppm)
0.85
0.85
1.05
5.14
1.96
1.91
2.17
3.00
12.39
3.00
10.048
9.100
7.446
7.372
7.352
7.333
7.319
7.303
7.286
7.269
7.160
7.142
7.089
7.071
7.053
5.330
5.286
5.254
5.209
2.715
2.242
2.213
1.694

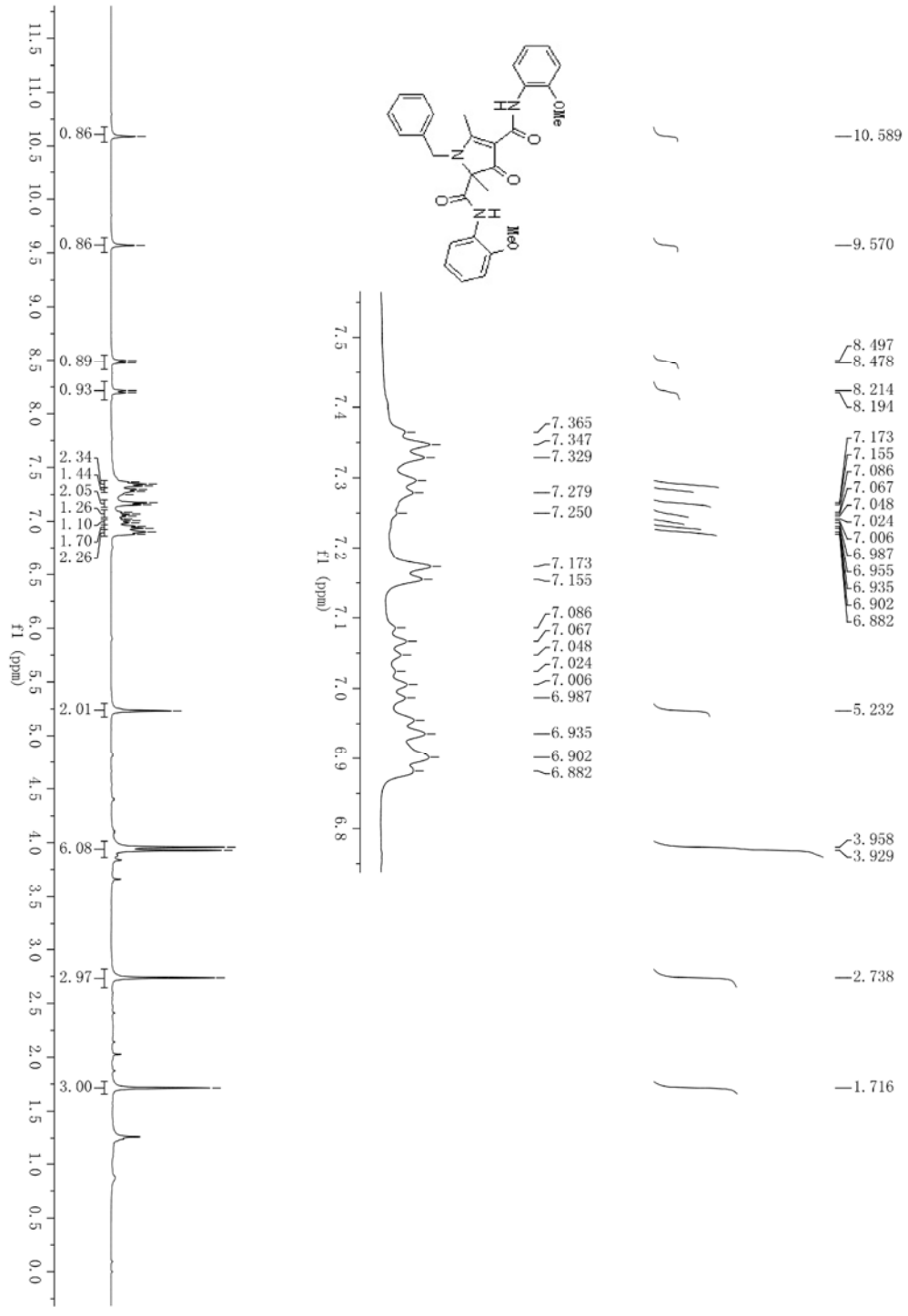

HN
O
O
H
N
N
Bn
O
2ef

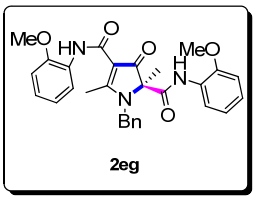

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


194.629
182.048
163.714
161.440
135.996
134.531
133.214
131.577
129.891
129.737
128.978
127.697
125.824
121.245
117.459
117.387
102.890
77.319
77.000
76.682
74.581
48.693
22.442
19.812
19.768
19.140
19.098
15.482
137.234
136.883
136.213
135.996
134.531
133.214
131.577
129.891
129.737
128.978
127.697
125.824
121.245
117.459
117.387
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)

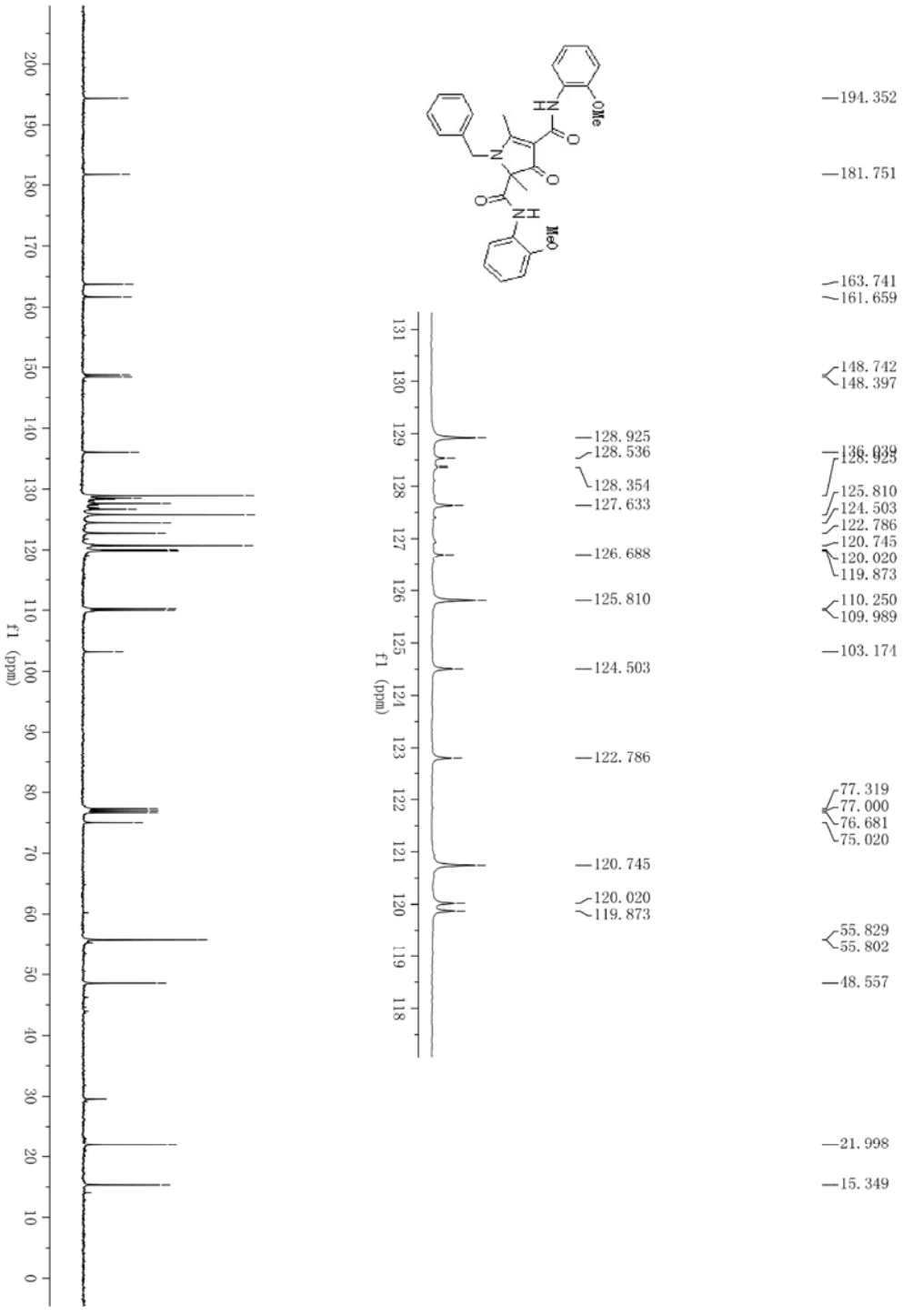

MeO
HN
O
O
MeO
H
N
N
Bn
O

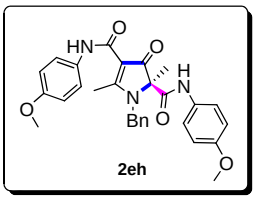
2eg

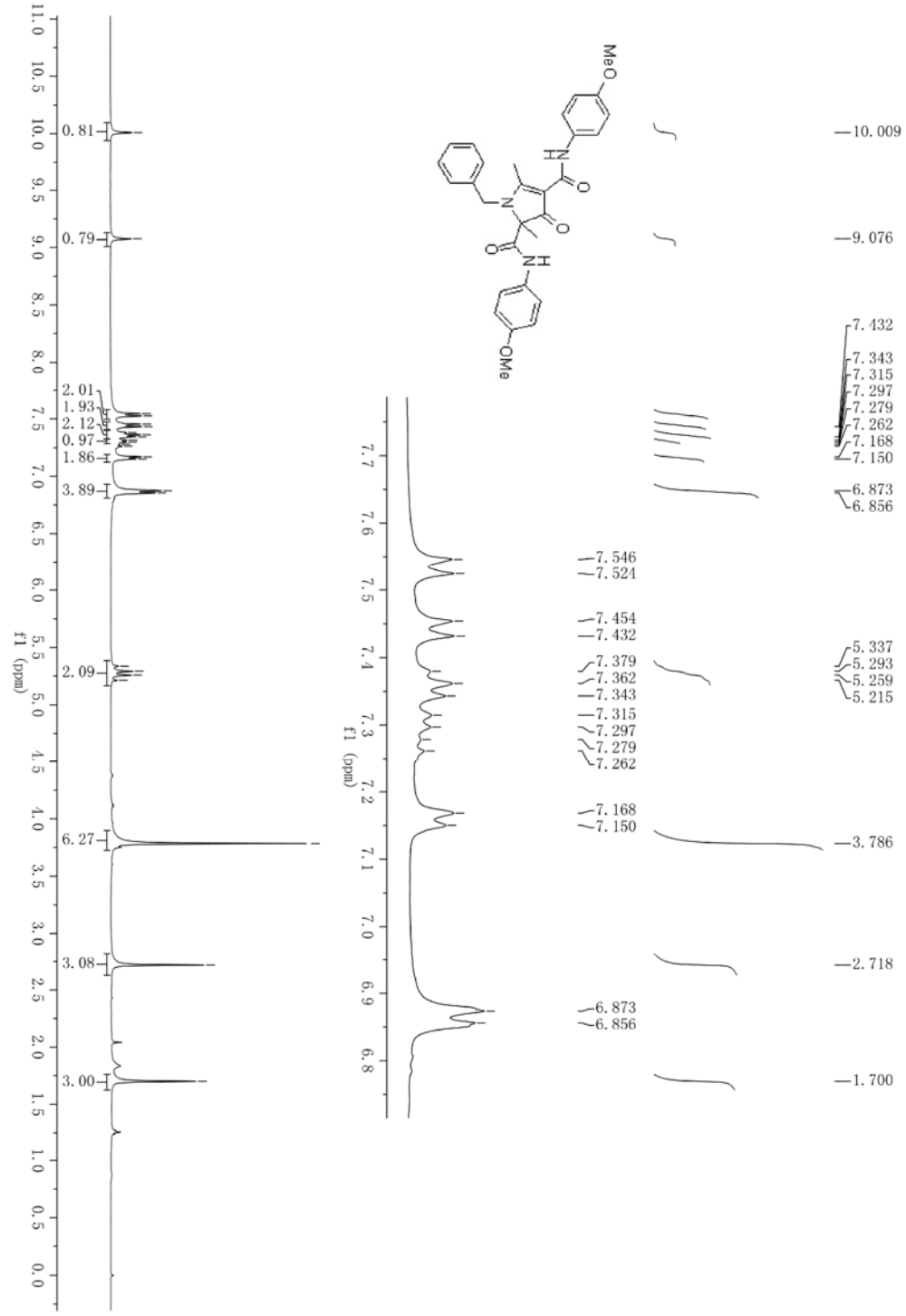

0.86
0.86
0.89
0.93
2.34
1.44
2.05
1.26
1.10
1.70
2.26
2.01
6.08
2.97
3.00
f1 (ppm)
7.365
7.347
7.329
7.279
7.250
7.173
7.155
7.086
7.067
7.048
7.024
7.006
6.987
6.935
6.902
6.882
10.589
9.570
8.497
8.478
8.214
8.194
7.173
7.155
7.086
7.067
7.048
7.024
7.006
6.987
6.955
6.935
6.902
6.882
5.232
3.958
3.929
2.738
1.716

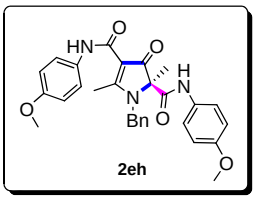

MeO
HN
O
O
MeO
H
N
N
Bn
O

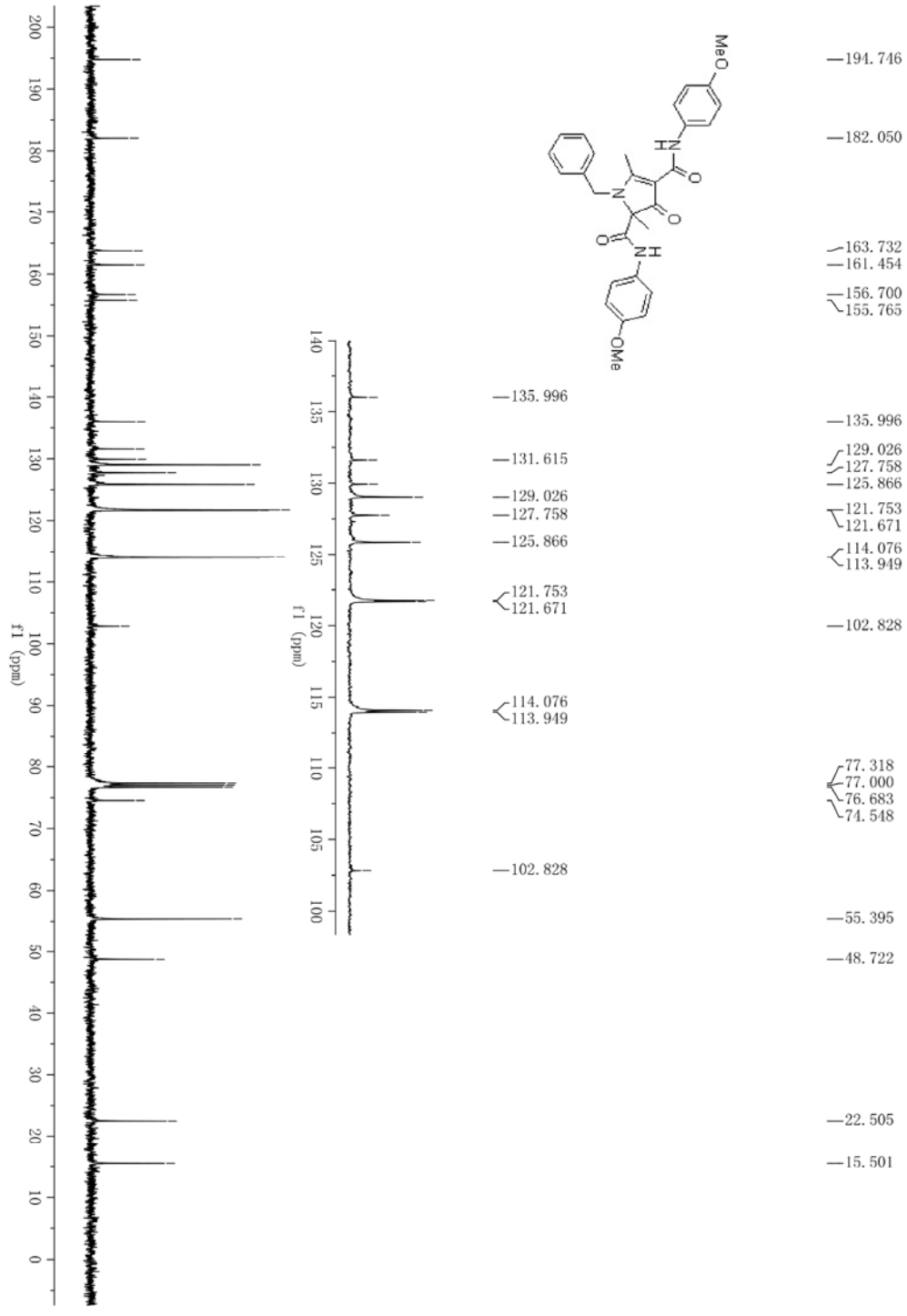
2eg

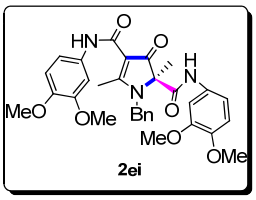

194.352
181.751
163.741
161.659
148.742
148.397
136.039
128.925
128.536
128.354
127.633
126.688
125.810
124.503
122.786
120.745
120.020
119.873
110.250
109.989
103.174
77.319
77.000
76.681
75.020
55.829
55.802
48.557
21.998
15.349
f1 (ppm)

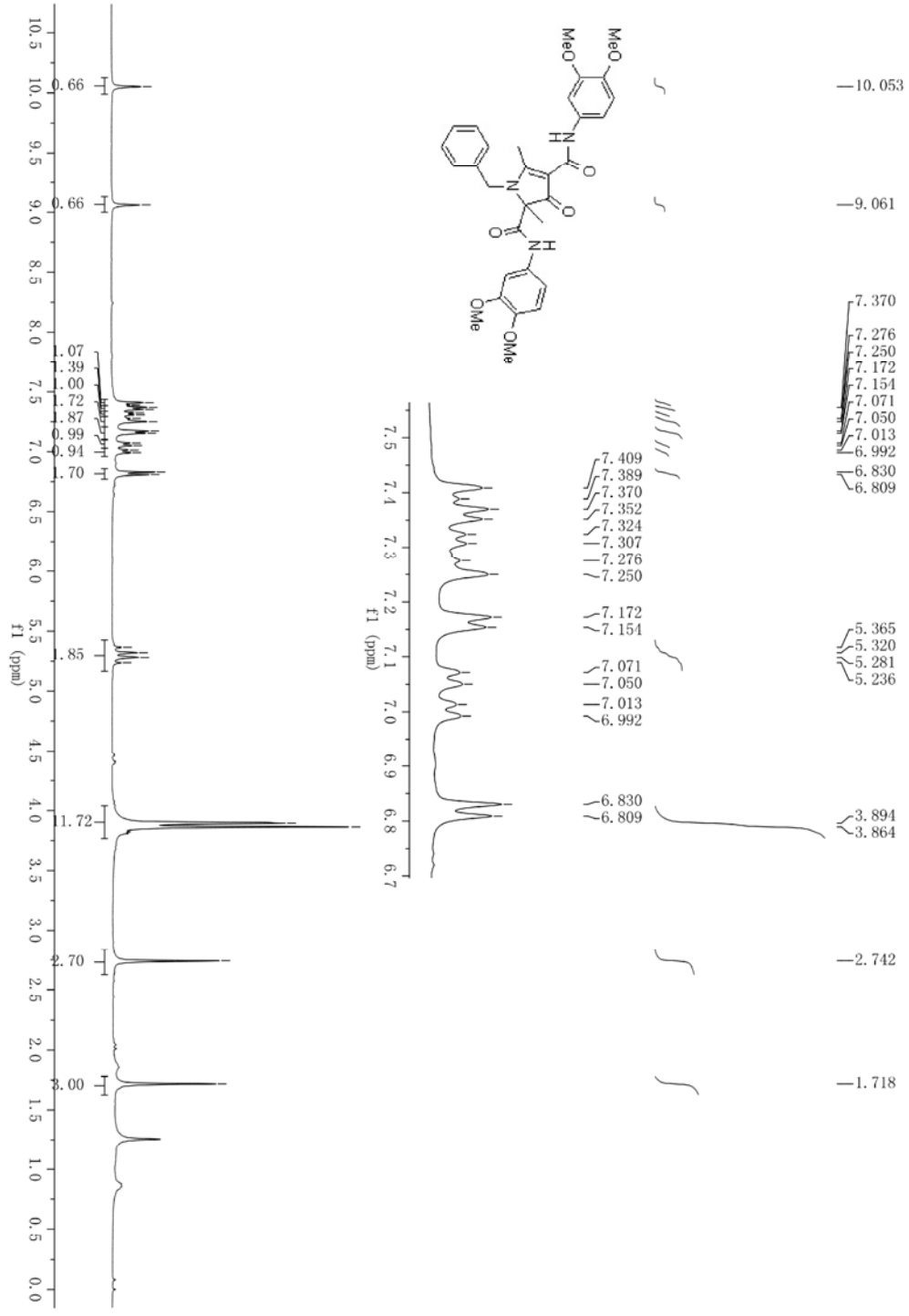

HN
O
O
H
N
N
Bn
O
O
O
2eh

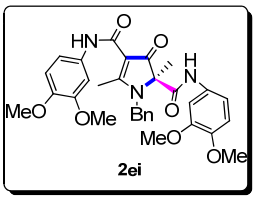

MeO
OMe
f1 (ppm)
0.81
0.79
2.01
1.93
2.12
0.97
1.86
3.89
2.09
6.27
3.08
3.00
10.009
9.076
7.432
7.343
7.315
7.297
7.279
7.262
7.168
7.150
6.873
6.856
7.546
7.524
7.454
7.432
7.379
7.362
7.343
7.315
7.297
7.279
7.262
7.168
7.150
6.873
6.856
5.337
5.293
5.259
5.215
3.786
2.718
1.700

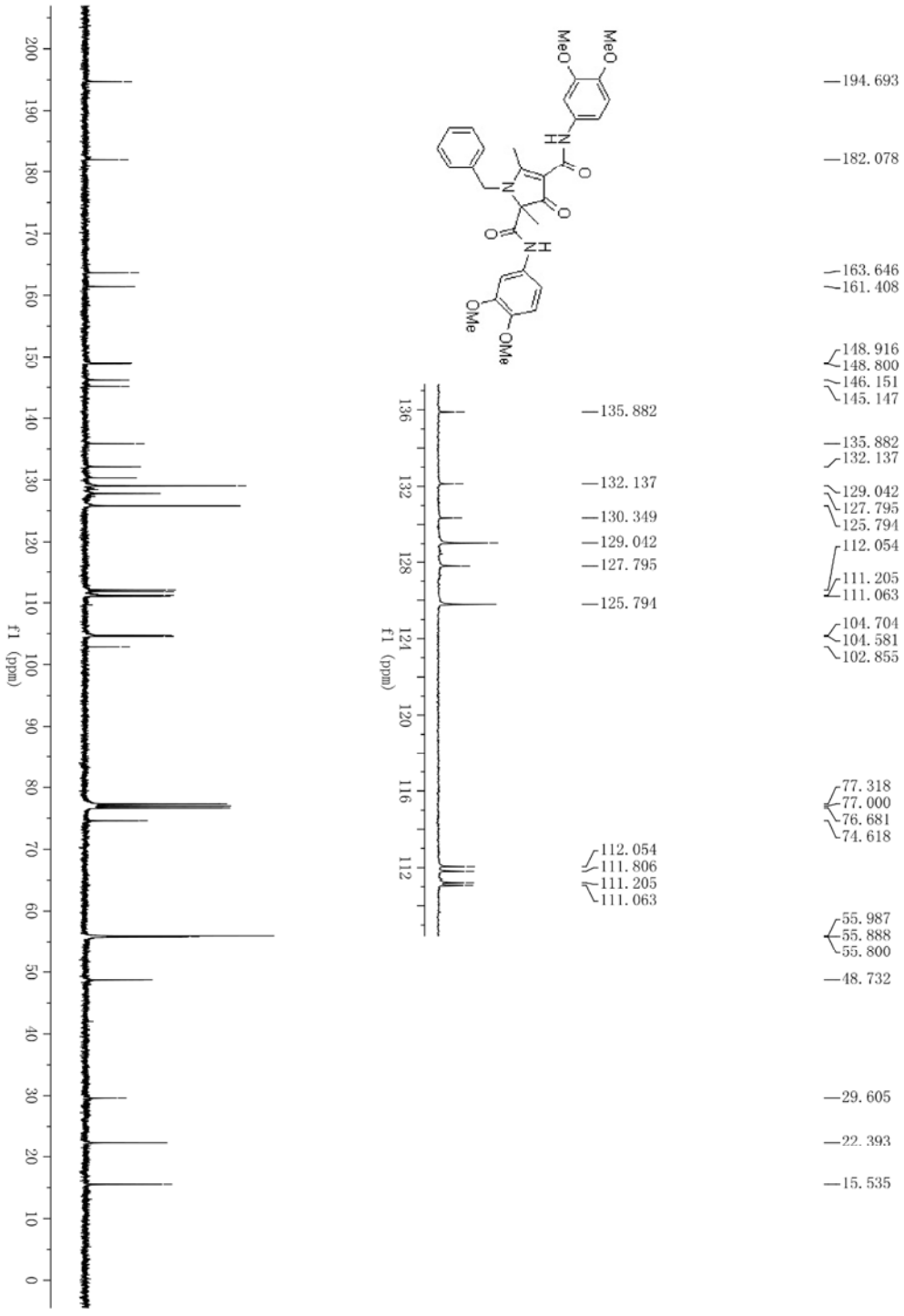

HN
O
O
H
N
N
Bn
O
O
O
2eh

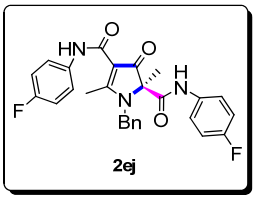

MeO
OMe
194.746
182.050
163.732
161.454
156.700
155.765
135.996
131.615
129.026
127.758
125.866
121.753
121.671
114.076
113.949
102.828
77.318
77.000
76.683
74.548
55.395
48.722
22.505
15.501
f1 (ppm)

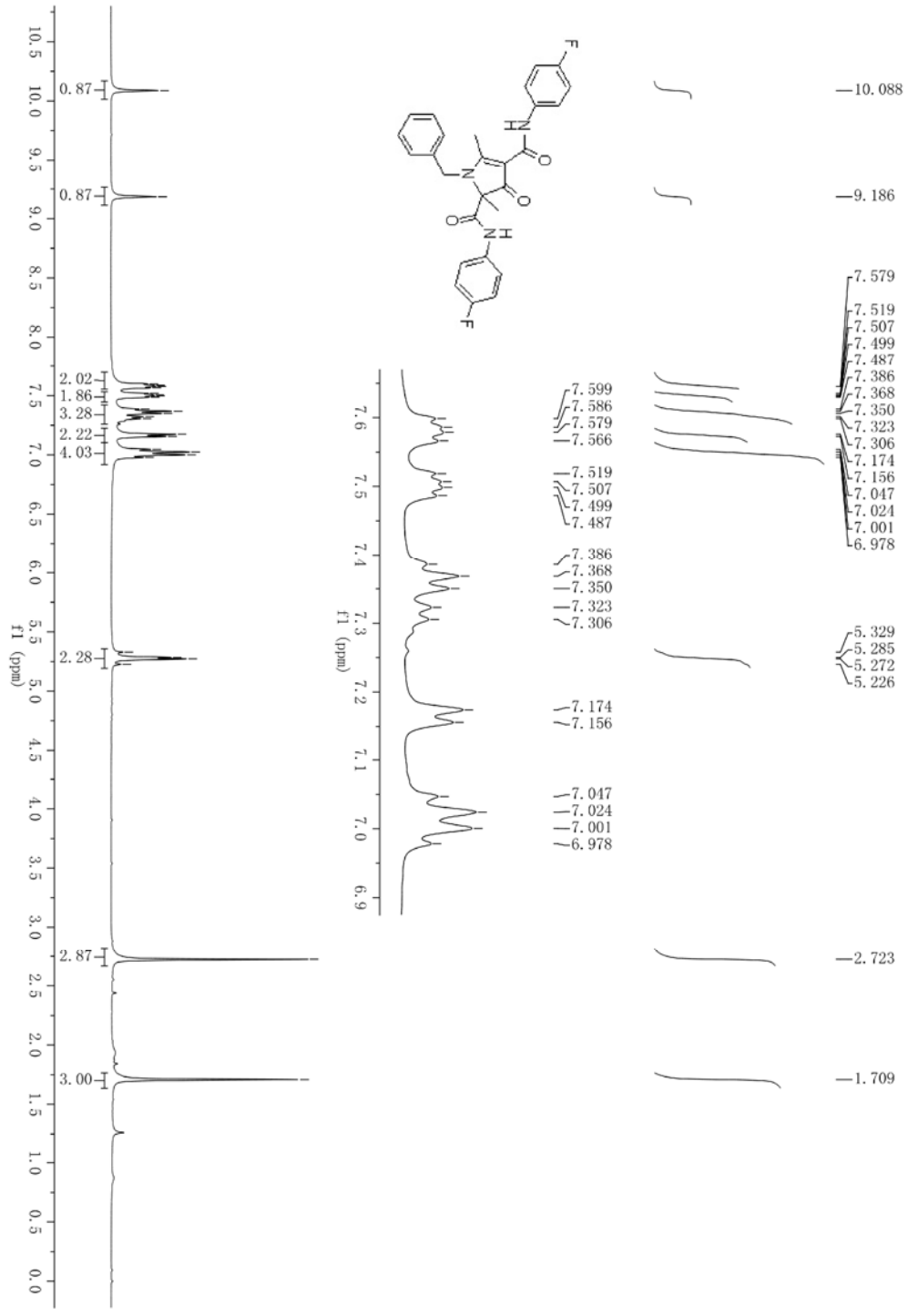

HN
O
O
H
N
N
Bn
O
MeO
OMe
MeO
OMe
2ei

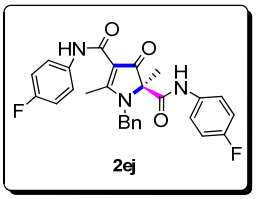

MeO
MeO
OMe
OMe
10.053
9.061
7.370
7.276
7.250
7.172
7.154
7.071
7.050
7.013
6.992
6.830
6.809
5.365
5.320
5.281
5.236
3.894
3.864
2.742
1.718
0.66
0.66
1.07
1.39
1.00
1.72
1.87
0.99
0.94
1.70
1.85
11.72
2.70
3.00
f1 (ppm)

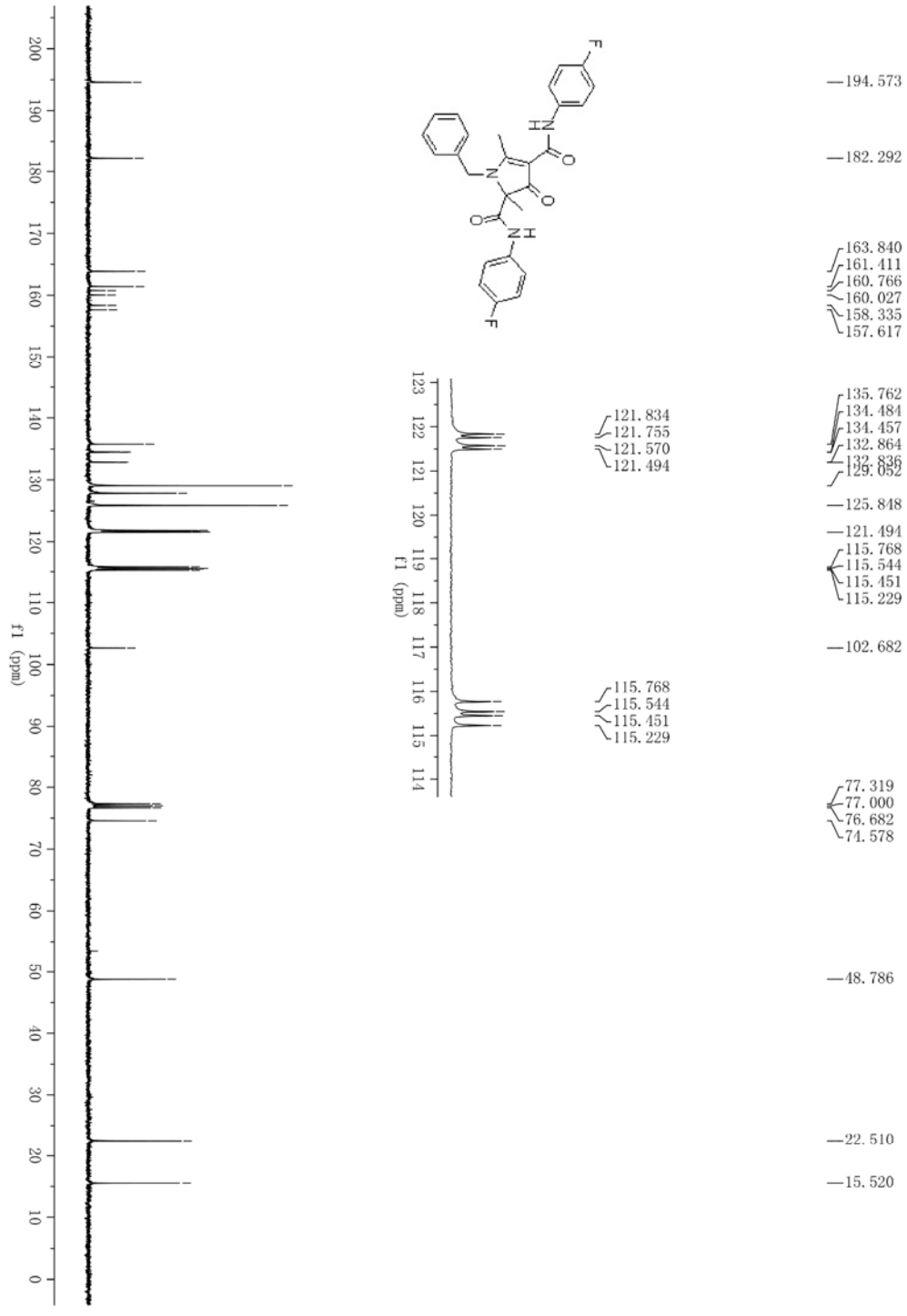

HN
O
O
H
N
N
Bn
O
MeO
OMe
MeO
OMe
2ei

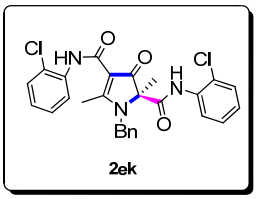

MeO
MeO
OMe
OMe
194.693
182.078
163.646
161.408
148.916
148.800
146.151
145.147
135.882
132.137
129.042
127.795
125.794
112.054
111.205
111.063
104.704
104.581
102.855
77.318
77.000
76.681
74.618
55.987
55.888
55.800
48.732
29.605
22.393
15.535
f1 (ppm)

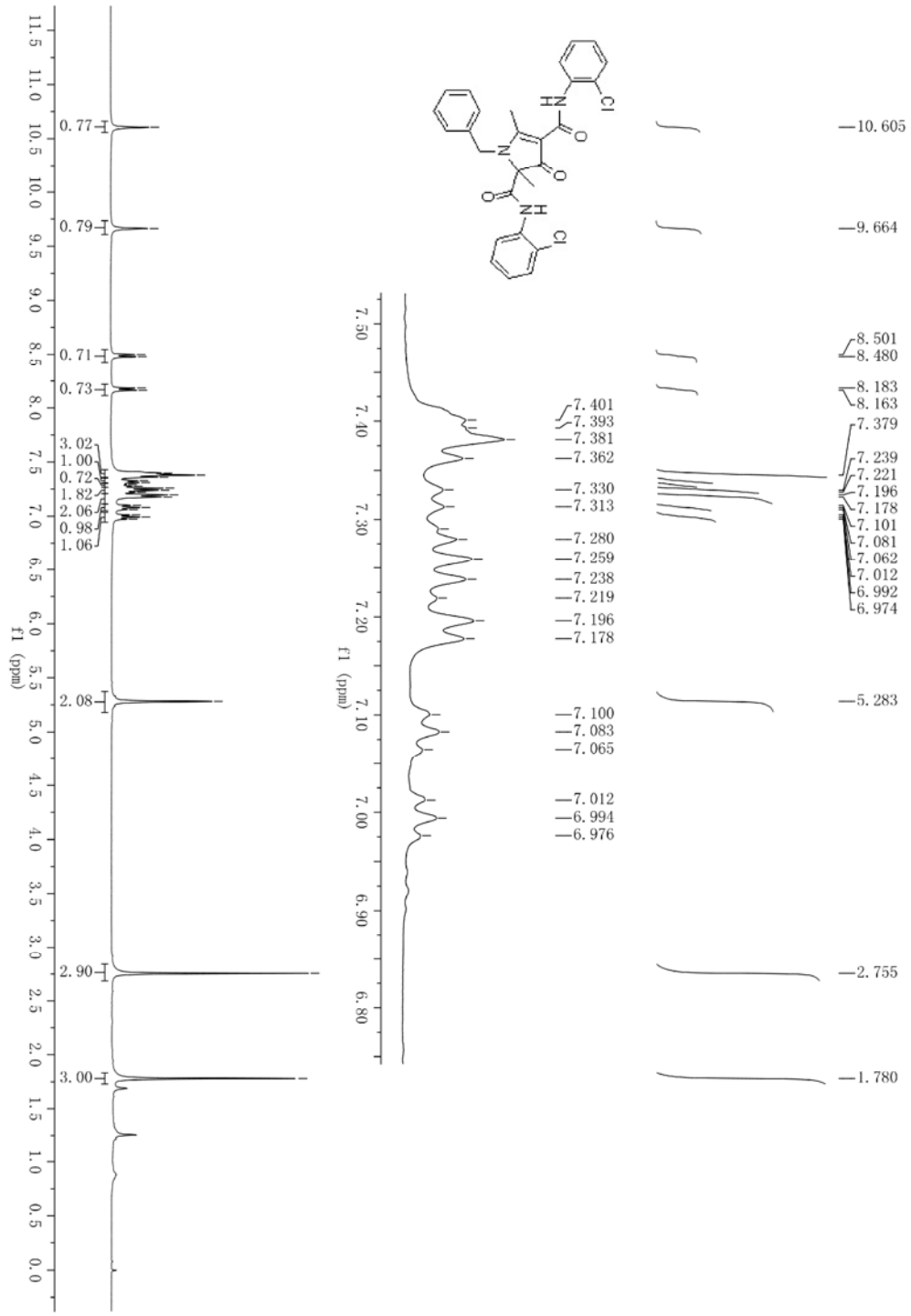

2ej

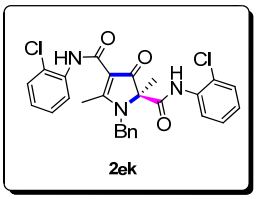

0.87
0.87
2.02
1.86
3.28
2.22
4.03
2.28
2.87
3.00
f1 (ppm)
7.599
7.586
7.579
7.566
7.519
7.507
7.499
7.487
7.386
7.368
7.350
7.323
7.306
7.174
7.156
7.047
7.024
7.001
6.978
10.088
9.186
7.579
7.519
7.507
7.499
7.487
7.386
7.368
7.350
7.323
7.306
7.174
7.156
7.047
7.024
7.001
6.978
5.329
5.285
5.272
5.226
2.723
1.709


HN
O
O
H
N
F
N
Bn
O
F
2ej

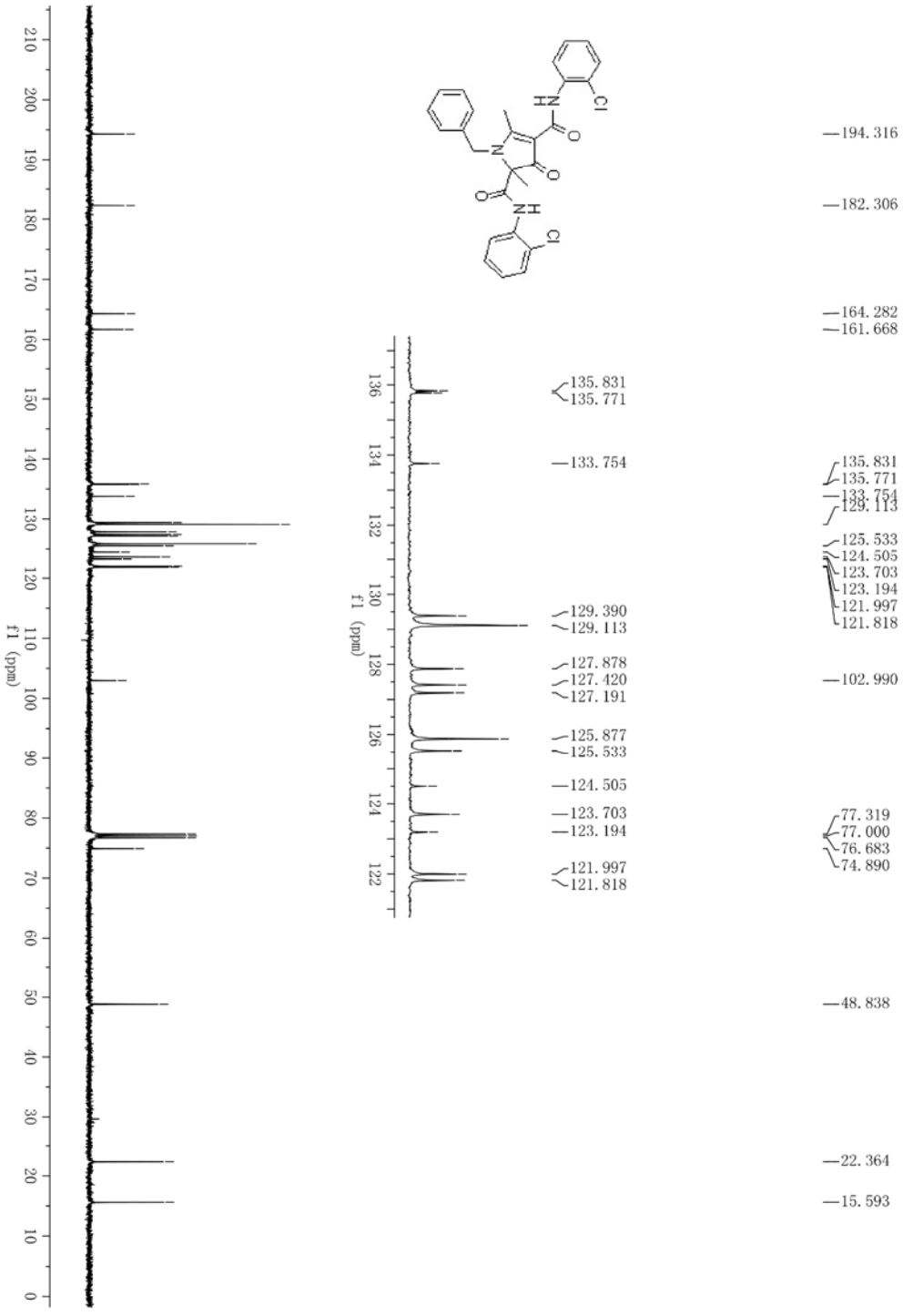

f1 (ppm)
194.573
182.292
163.840
161.411
160.766
160.027
158.335
157.617
135.762
134.484
134.457
132.864
132.836
129.052
125.848
121.494
115.768
115.544
115.451
115.229
102.682
77.319
77.000
76.682
74.578
48.786
22.510
15.520
121.834
121.755
121.570
121.494
115.768
115.544
115.451
115.229

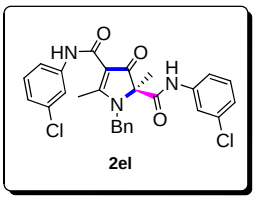

Cl
HN
O
O
H
N
Cl
N
Bn
O
2ek


0.77
0.79
0.71
0.73
3.02
1.00
0.72
1.82
2.06
0.98
1.06
2.08
2.90
3.00
f1 (ppm)
7.401
7.393
7.381
7.362
7.330
7.313
7.280
7.259
7.238
7.219
7.196
7.178
7.100
7.083
7.065
7.012
6.994
6.976
f1 (ppm)
10.605
9.664
8.501
8.480
8.183
8.163
7.379
7.239
7.221
7.196
7.178
7.101
7.081
7.062
7.012
6.992
6.974
5.283
2.755
1.780

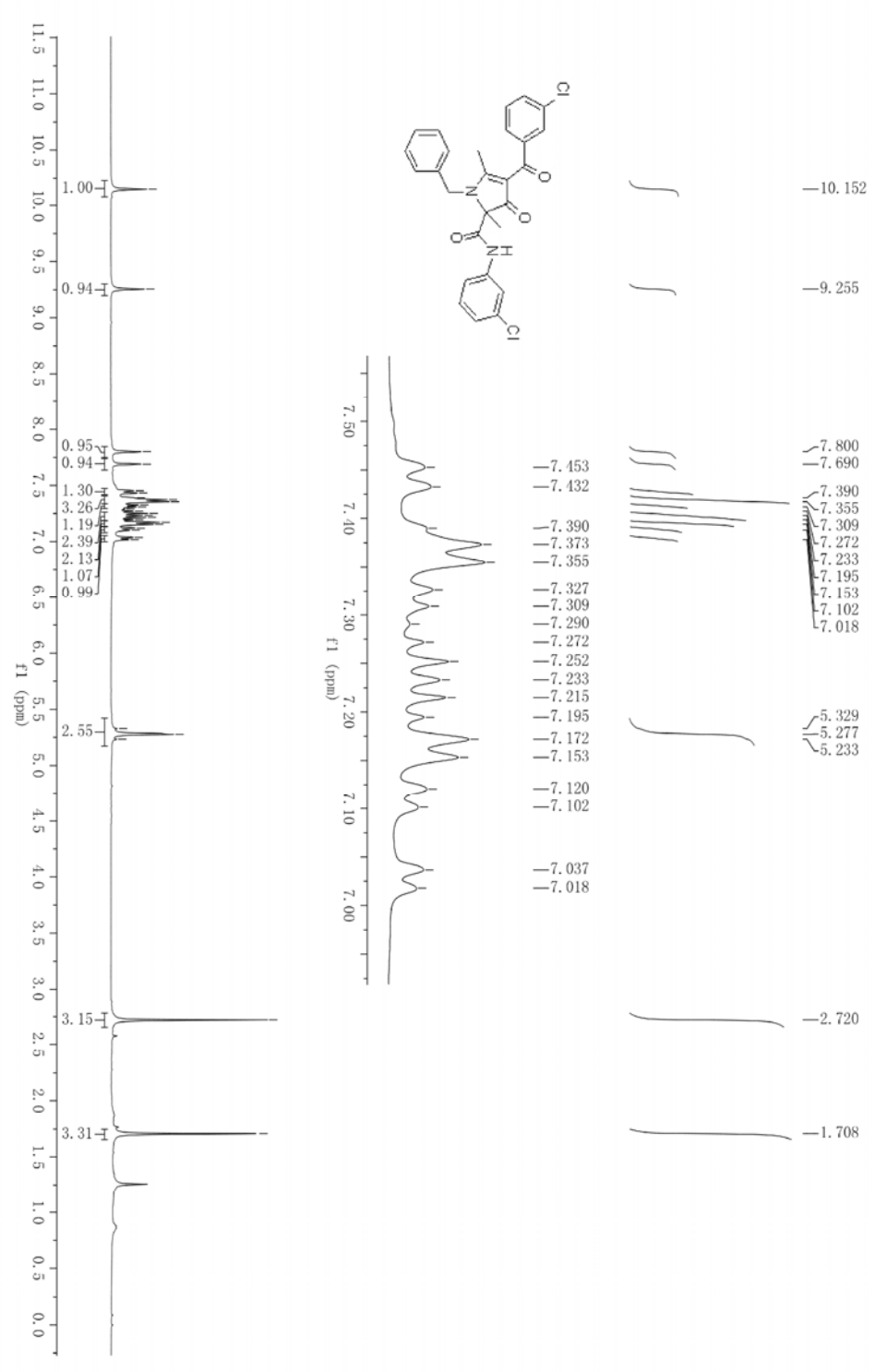

Cl
HN
O
O
H
N
Cl
N
Bn
O

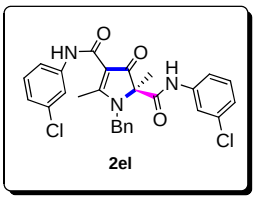
2ek

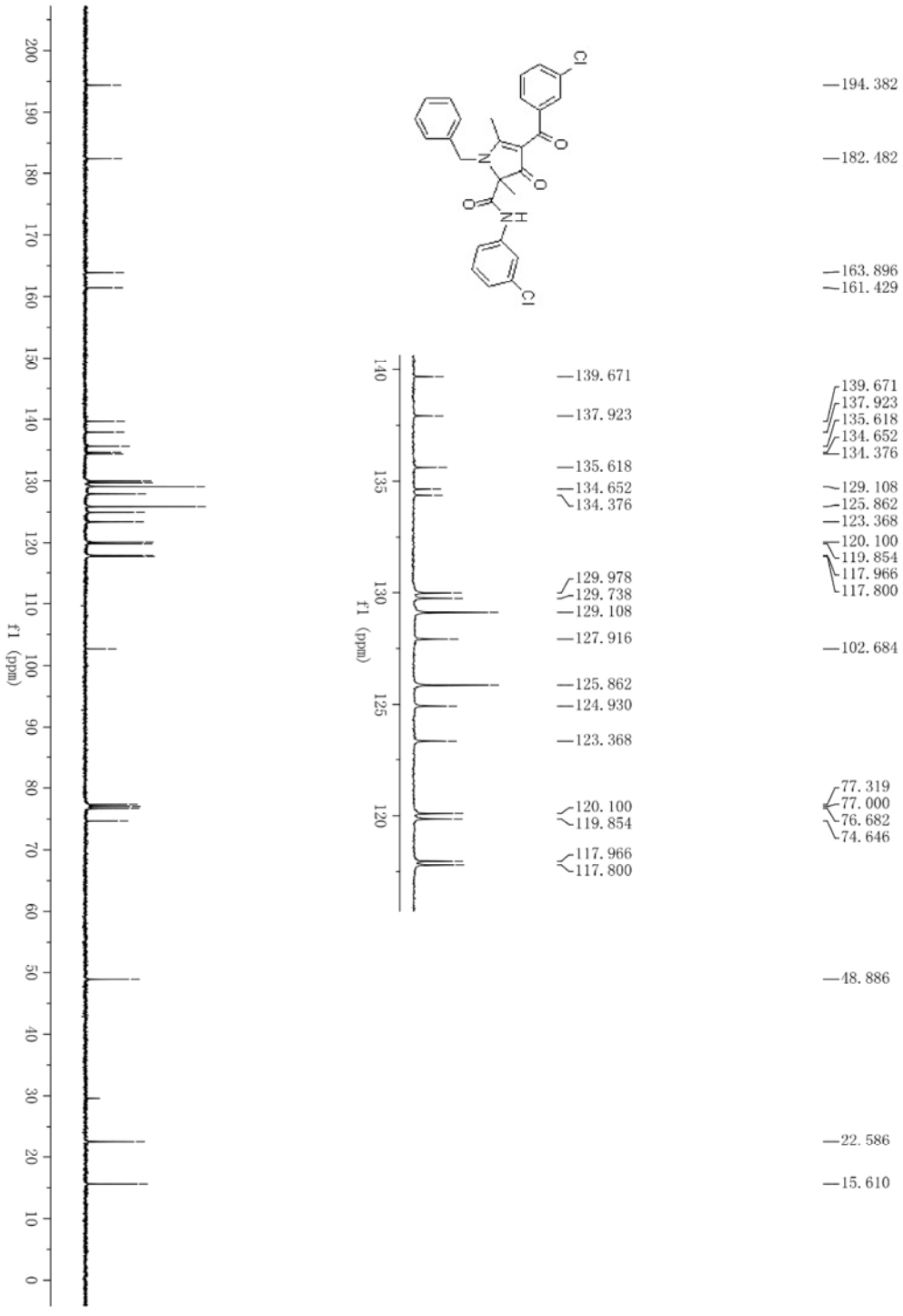

f1 (ppm)
194.316
182.306
164.282
161.668
135.831
135.771
133.754
129.390
129.113
127.878
127.420
127.191
125.877
125.533
124.505
123.703
123.194
121.997
121.818
102.990
77.319
77.000
76.683
74.890
48.838
22.364
15.593

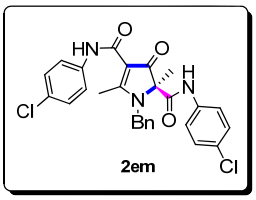

HN
O
O
H
N
N
Bn
O
Cl
Cl

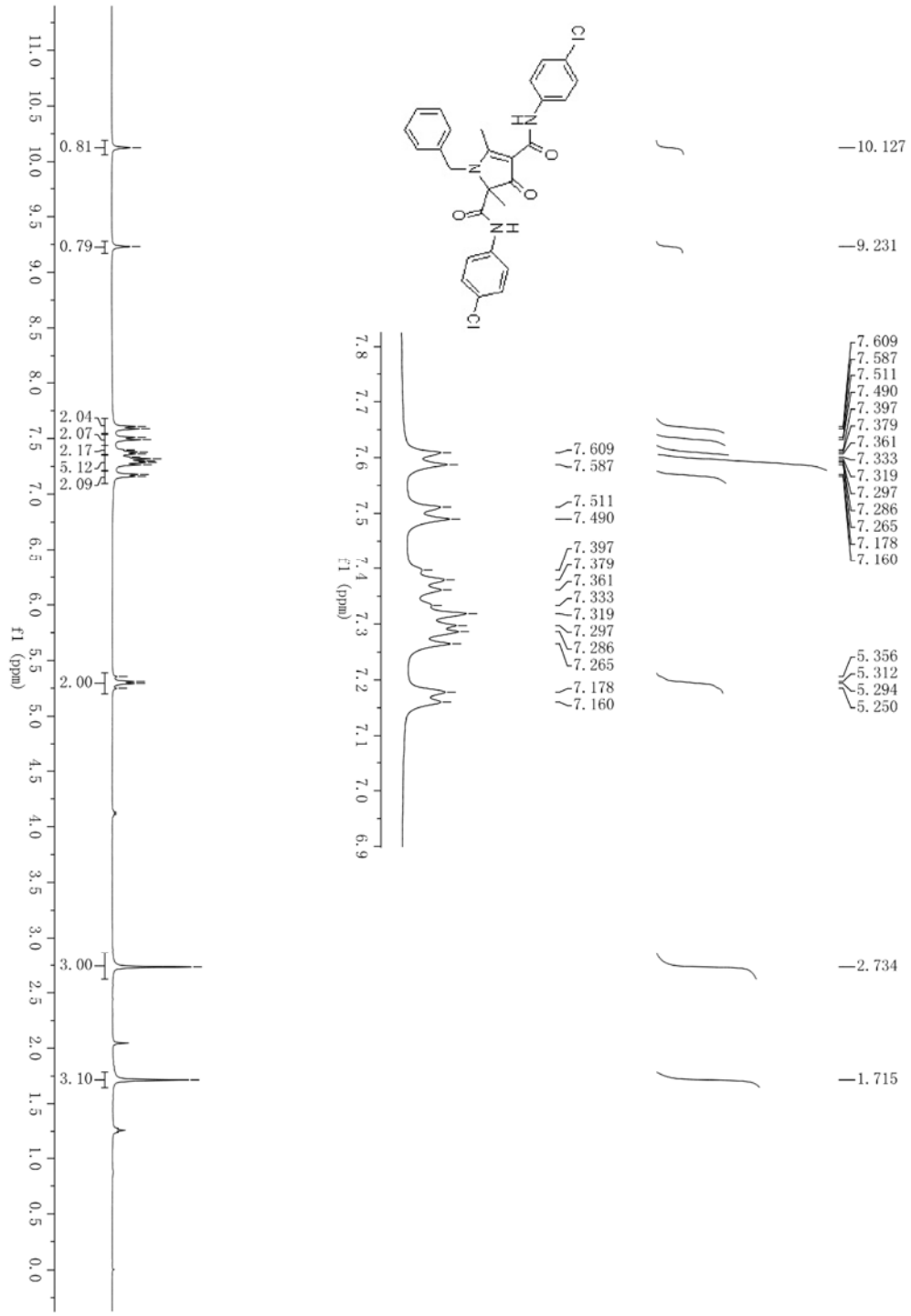
2el

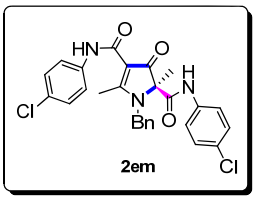

1.00
0.94
0.95
0.94
1.30
3.26
1.19
2.39
2.13
1.07
0.99
2.55
3.15
3.31
f1 (ppm)
7.453
7.432
7.390
7.373
7.355
7.327
7.309
7.290
7.272
7.252
7.233
7.215
7.195
7.172
7.153
7.120
7.102
7.037
7.018
10.152
9.255
7.800
7.690
7.390
7.355
7.309
7.272
7.233
7.195
7.153
7.102
7.018
5.329
5.277
5.233
2.720
1.708

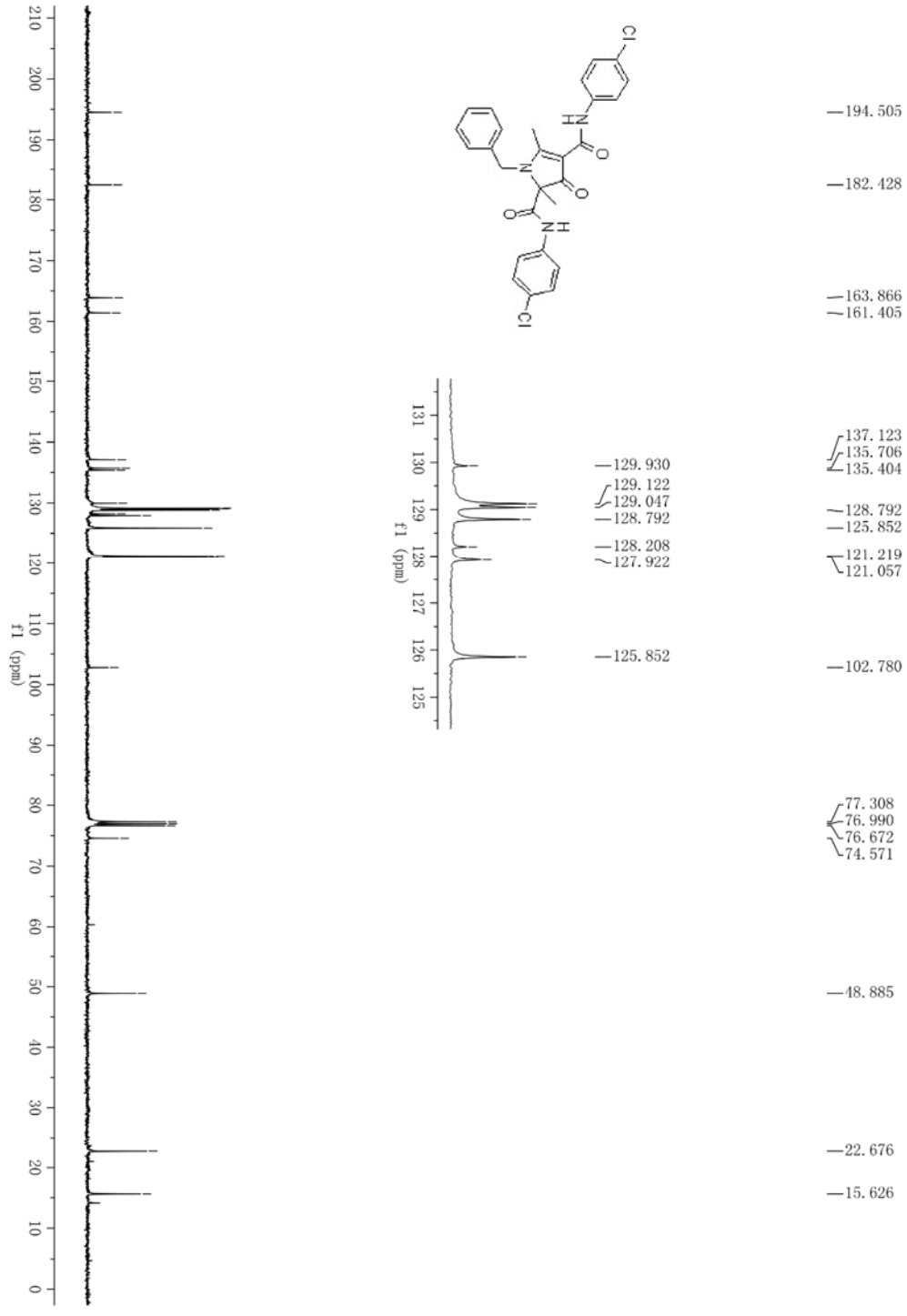

HN
O
O
H
N
N
Bn
O
Cl
Cl
2el

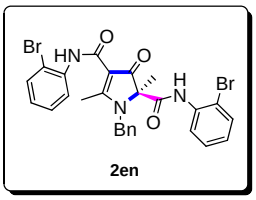

f1 (ppm)
194.382
182.482
163.896
161.429
139.671
137.923
135.618
134.652
134.376
129.978
129.738
129.108
127.916
125.862
124.930
123.368
120.100
119.854
117.966
117.800
102.684
77.319
77.000
76.682
74.646
48.886
22.586
15.610


HN
O
O
H
N
N
Bn
O
Cl
Cl
2em

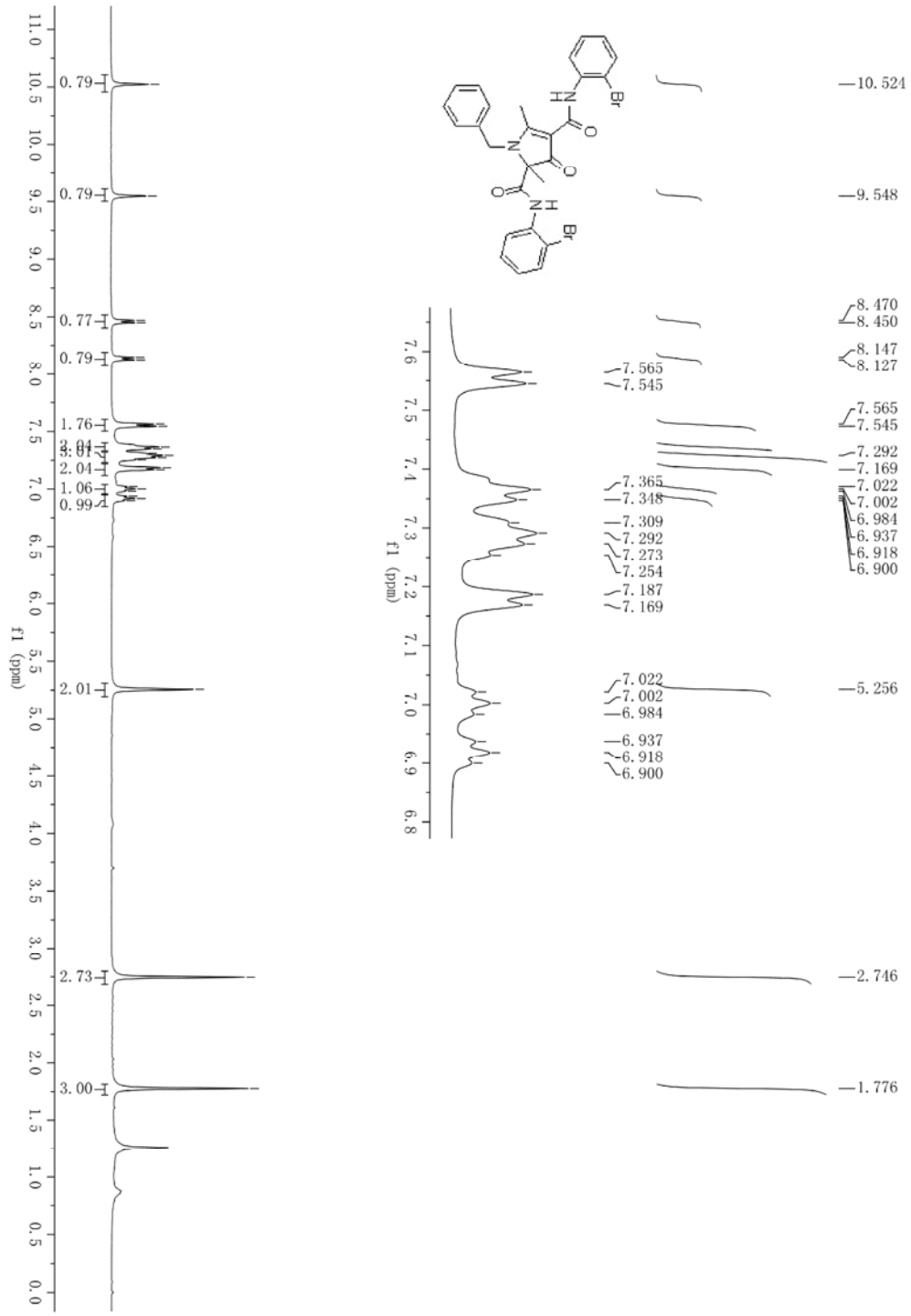

0.81
0.79
2.04
2.07
2.17
5.12
2.09
2.00
3.00
3.10
f1 (ppm)
Cl
HN
O
N
O
NH
Cl
7.609
7.587
7.511
7.490
7.397
7.379
7.361
7.333
7.319
7.297
7.286
7.265
7.178
7.160
10.127
9.231
5.356
5.312
5.294
5.250
2.734
1.715

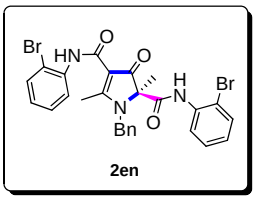

HN
O
O
H
N
N
Bn
O
Cl
Cl
2em


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
131 130 129 128 127 126 125
f1 (ppm)
Cl
N
H
O
O
N
H
Cl
194.505
182.428
163.866
161.405
137.123
135.706
135.404
129.930
129.122
129.047
128.792
128.208
127.922
125.852
128.792
125.852
121.219
121.057
102.780
77.308
76.990
76.672
74.571
48.885
22.676
15.626

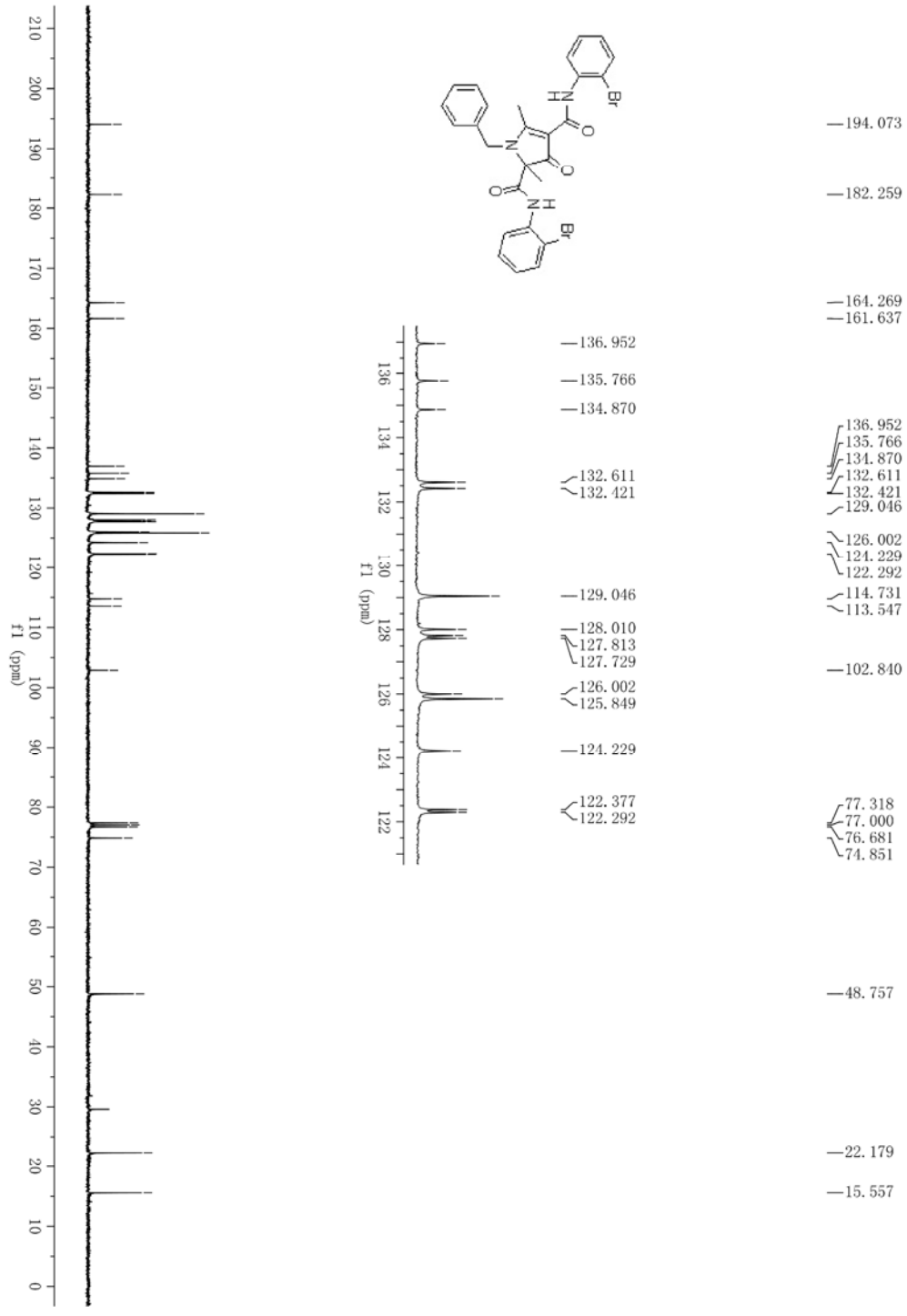

Br
HN
O
O
H
N
Br
N
Bn
O

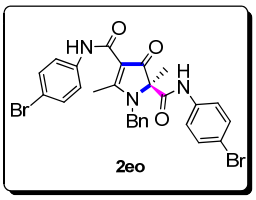
2en

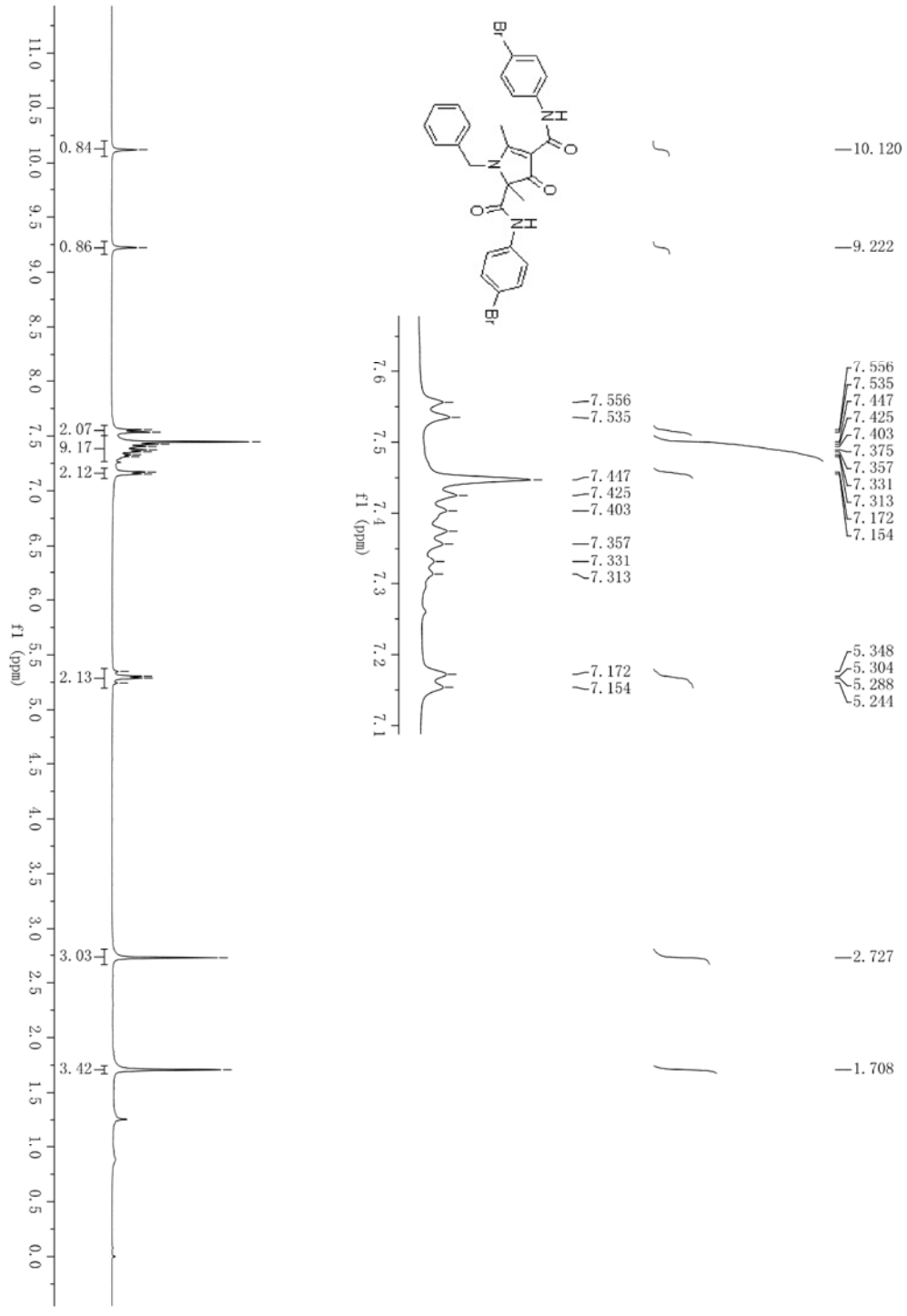

0.79
0.79
0.77
0.79
1.76
3.04
3.01
2.04
1.06
0.99
2.01
2.73
3.00
f1 (ppm)
10.524
9.548
8.470
8.450
8.147
8.127
7.565
7.545
7.292
7.169
7.365
7.348
7.309
7.273
7.254
7.187
7.022
7.002
6.984
6.937
6.918
6.900
5.256
2.746
1.776

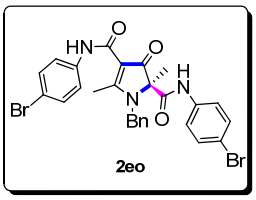

Br
HN
O
O
H
N
Br
N
Bn
O

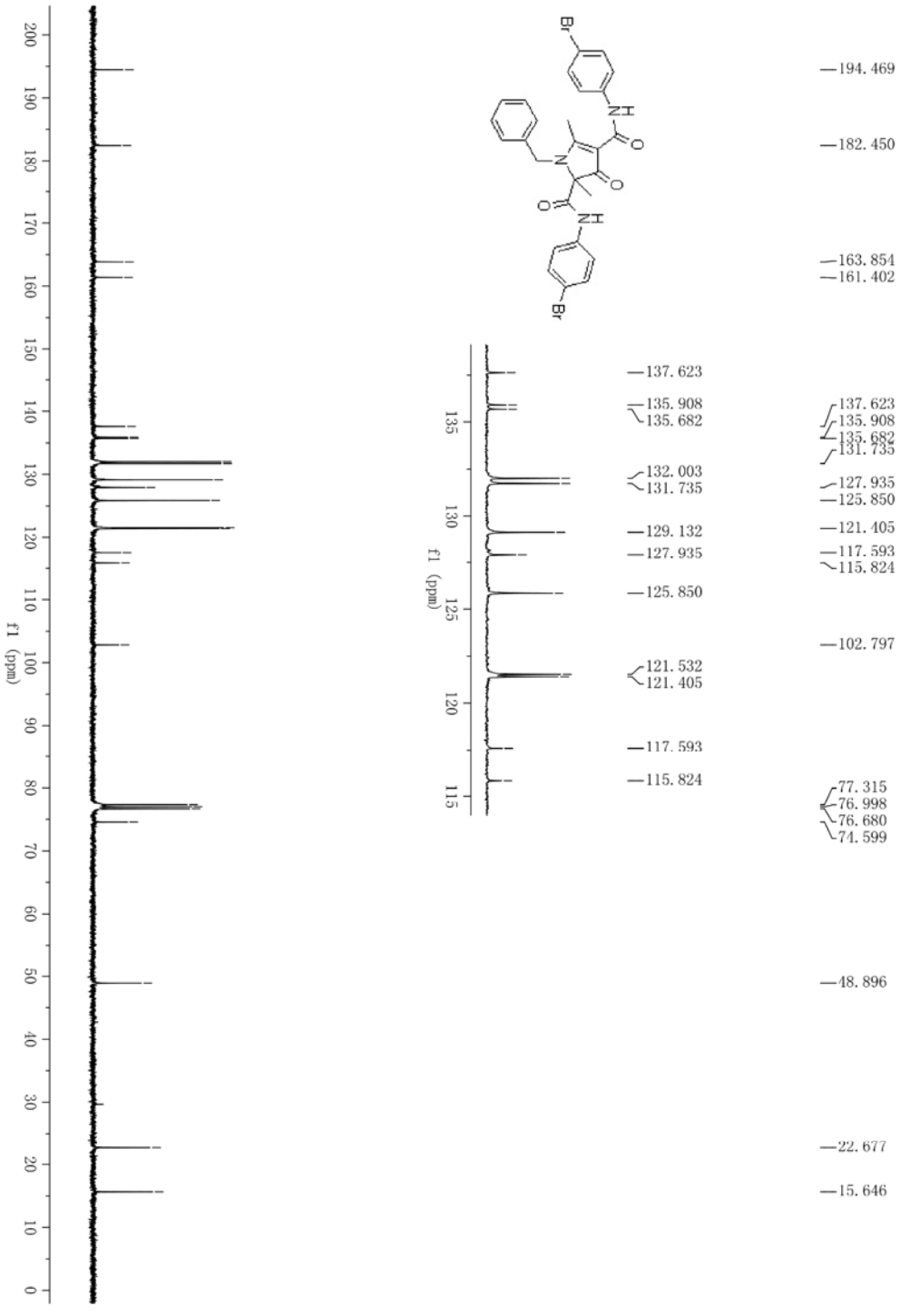
2en

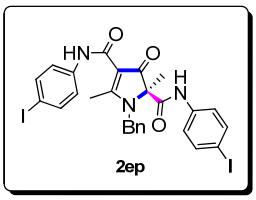

f1 (ppm)
194.073
182.259
164.269
161.637
136.952
135.766
134.870
132.611
132.421
129.046
128.010
127.813
127.729
126.002
125.849
124.229
122.377
122.292
102.840
77.318
77.000
76.681
74.851
48.757
22.179
15.557

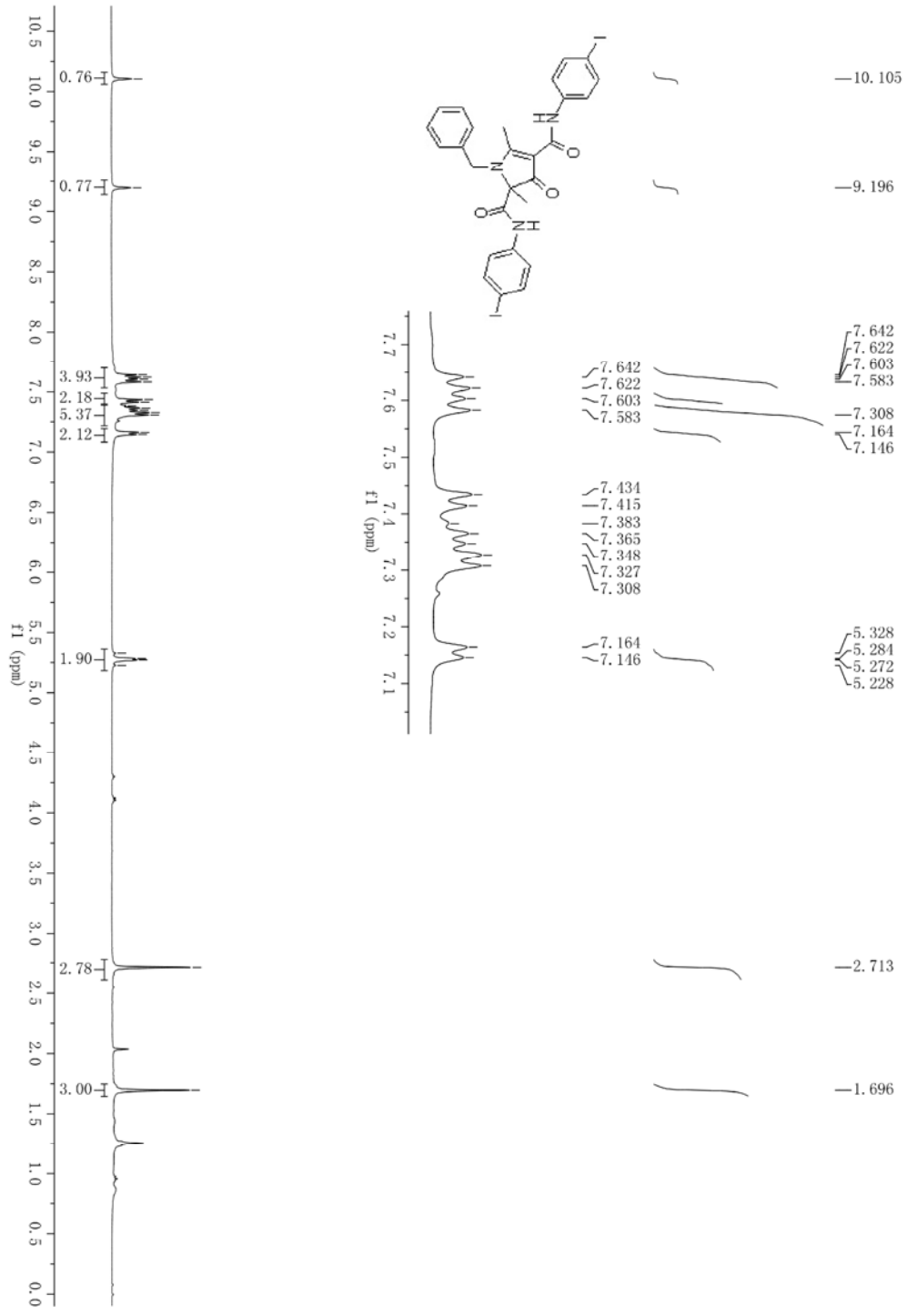

HN
O
O
H
N
Br
N
Bn
O
Br
2eo

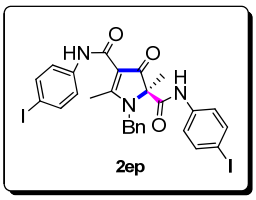

0.84
0.86
2.07
9.17
2.12
2.13
3.03
3.42
f1 (ppm)
—10.120
—9.222
—7.556
—7.535
—7.447
—7.425
—7.403
—7.357
—7.331
—7.313
—7.172
—7.154
—2.727
—1.708
5.348
5.304
5.288
5.244

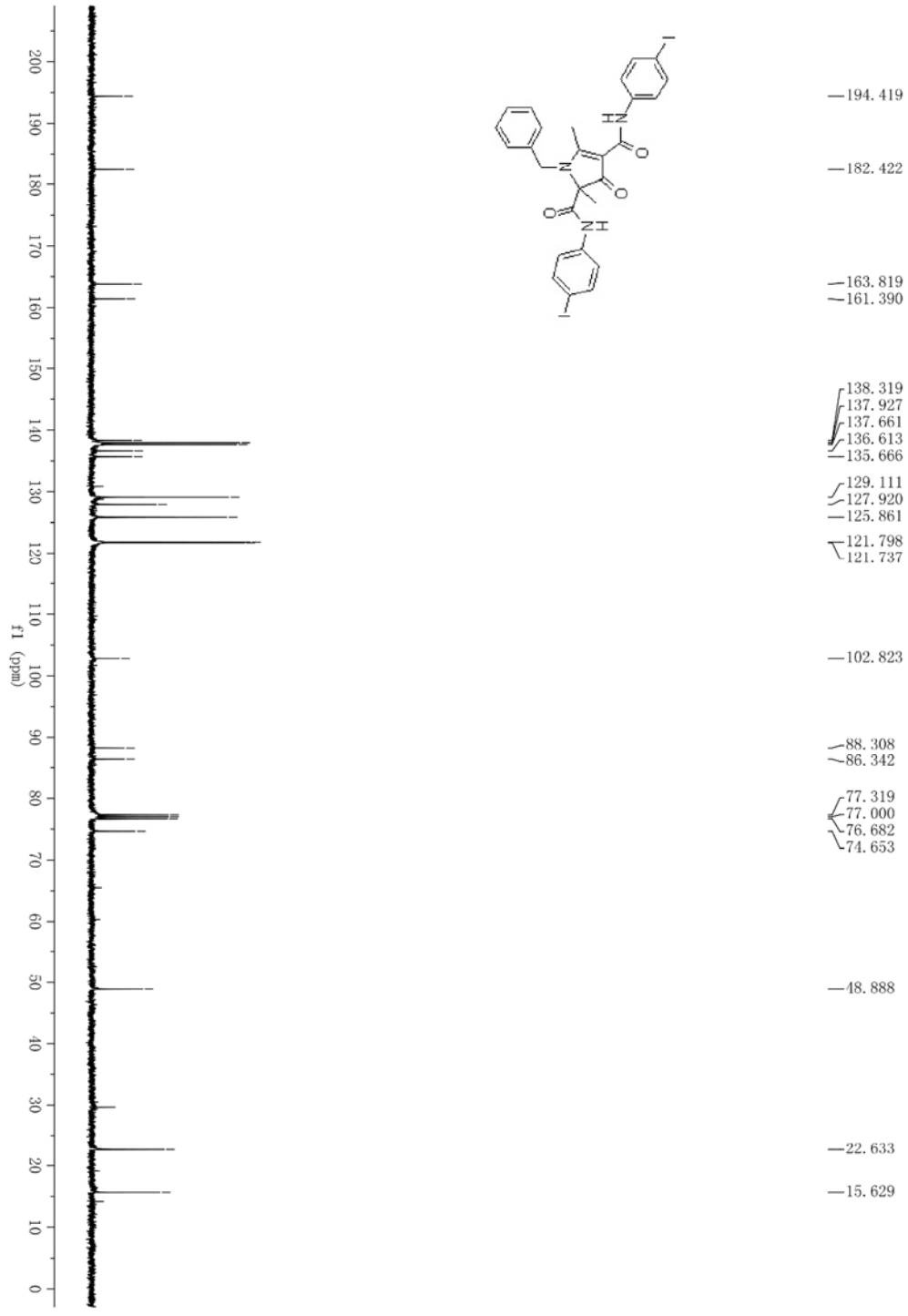

HN
O
O
H
N
Br
N
Bn
O
Br
2eo

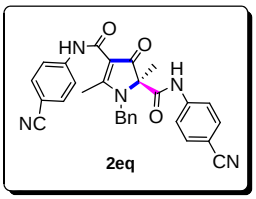

f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Br
NH
O
O
O
NH
Br
194.469
182.450
163.854
161.402
137.623
135.908
135.682
132.003
131.735
129.132
127.935
125.850
121.532
121.405
117.593
115.824
102.797
77.315
76.998
76.680
74.599
48.896
22.677
15.646
135
130
125
120
115
f1 (ppm)

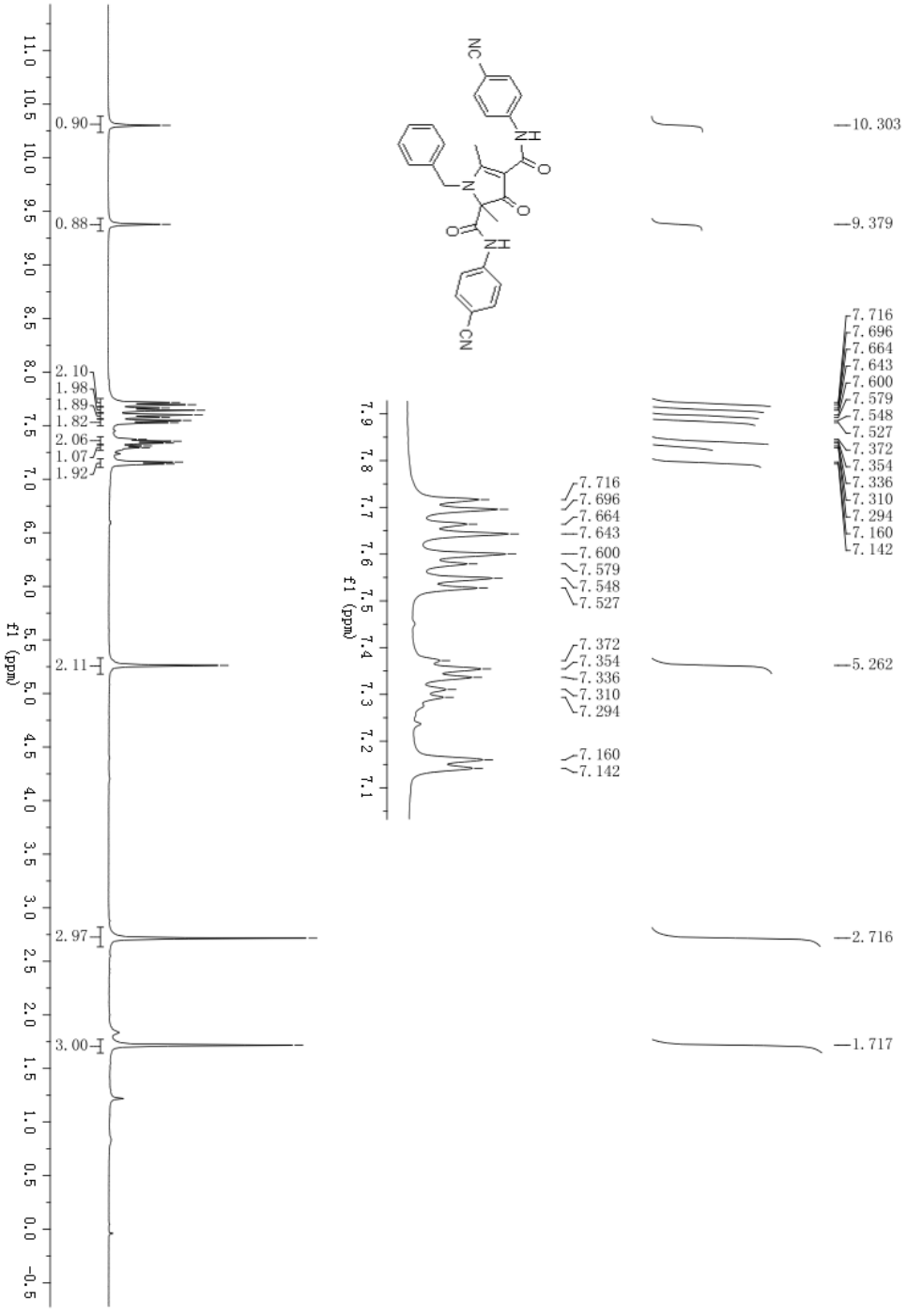

HN
O
O
H
N
N
Bn
O
I
I
2ep

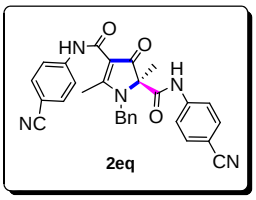

10.105
9.196
7.642
7.622
7.603
7.583
7.308
7.164
7.146
7.434
7.415
7.383
7.365
7.348
7.327
7.308
5.328
5.284
5.272
5.228
2.713
1.696
0.76
0.77
3.93
2.18
5.37
2.12
1.90
2.78
3.00
f1 (ppm)

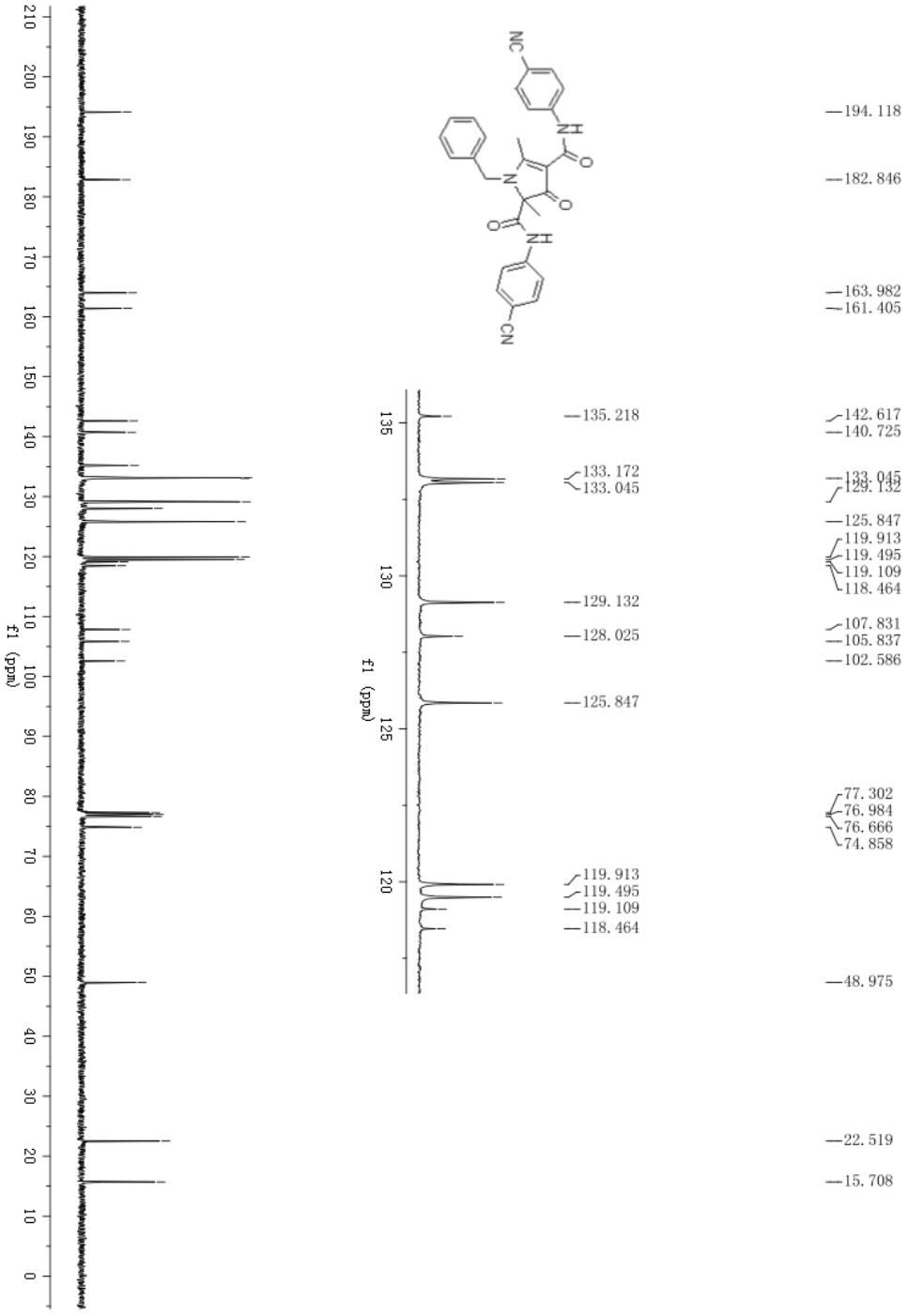

HN
O
O
H
N
N
Bn
O
I
I
2ep

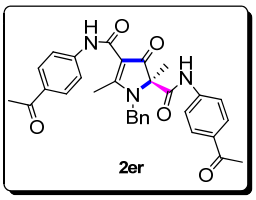

f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
194.419
182.422
163.819
161.390
138.319
137.927
137.661
136.613
135.666
129.111
127.920
125.861
121.798
121.737
102.823
88.308
86.342
77.319
77.000
76.682
74.653
48.888
22.633
15.629

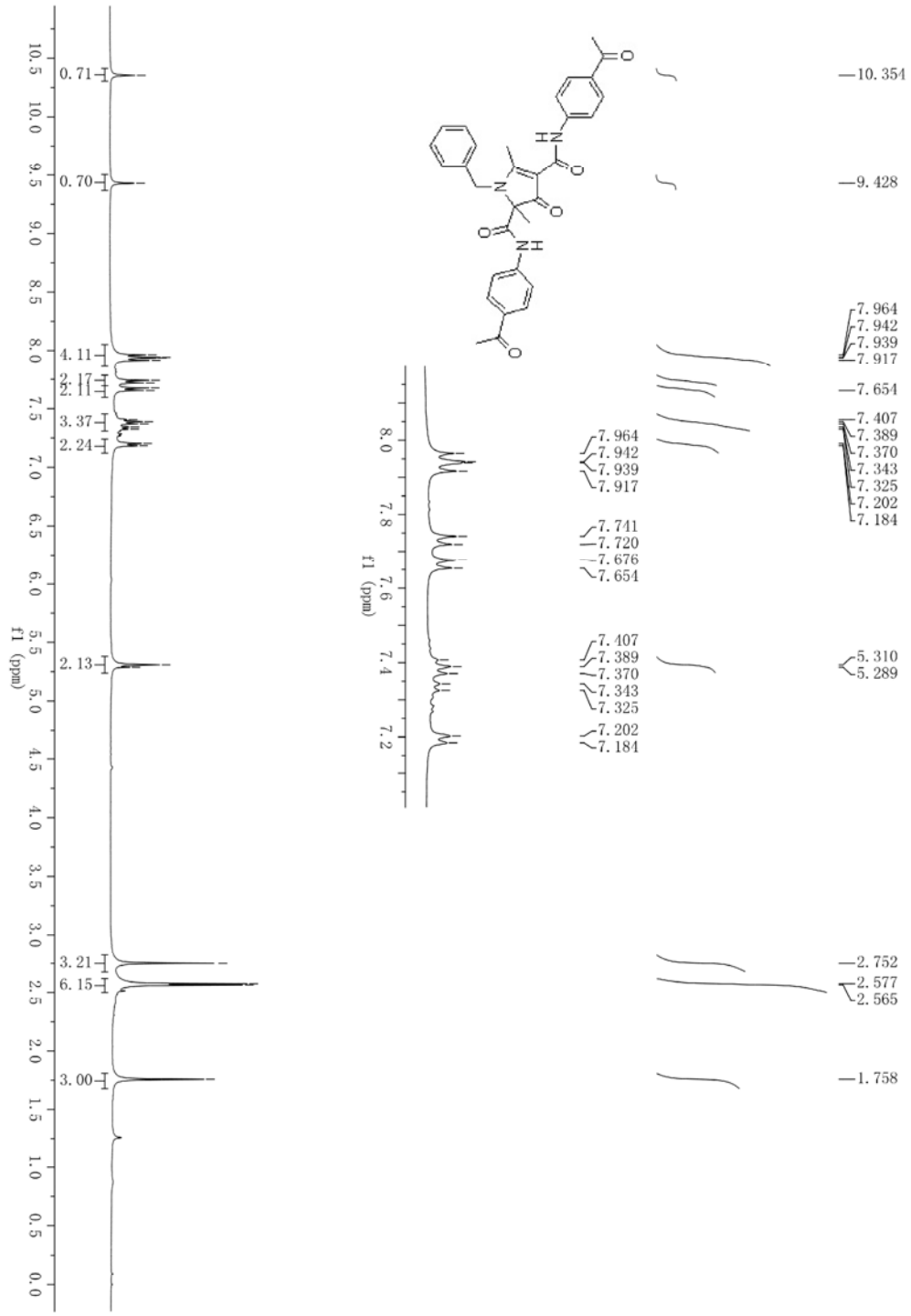

HN
O
O
H
N
N
Bn
O
NC
CN
2eq

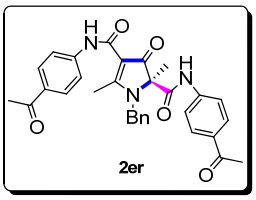

f1 (ppm)
0.90
0.88
2.10
1.98
1.89
1.82
2.06
1.07
1.92
2.11
2.97
3.00
NC
CN
7.716
7.696
7.664
7.643
7.600
7.579
7.548
7.527
7.372
7.354
7.336
7.310
7.294
7.160
7.142
10.303
9.379
5.262
2.716
1.717

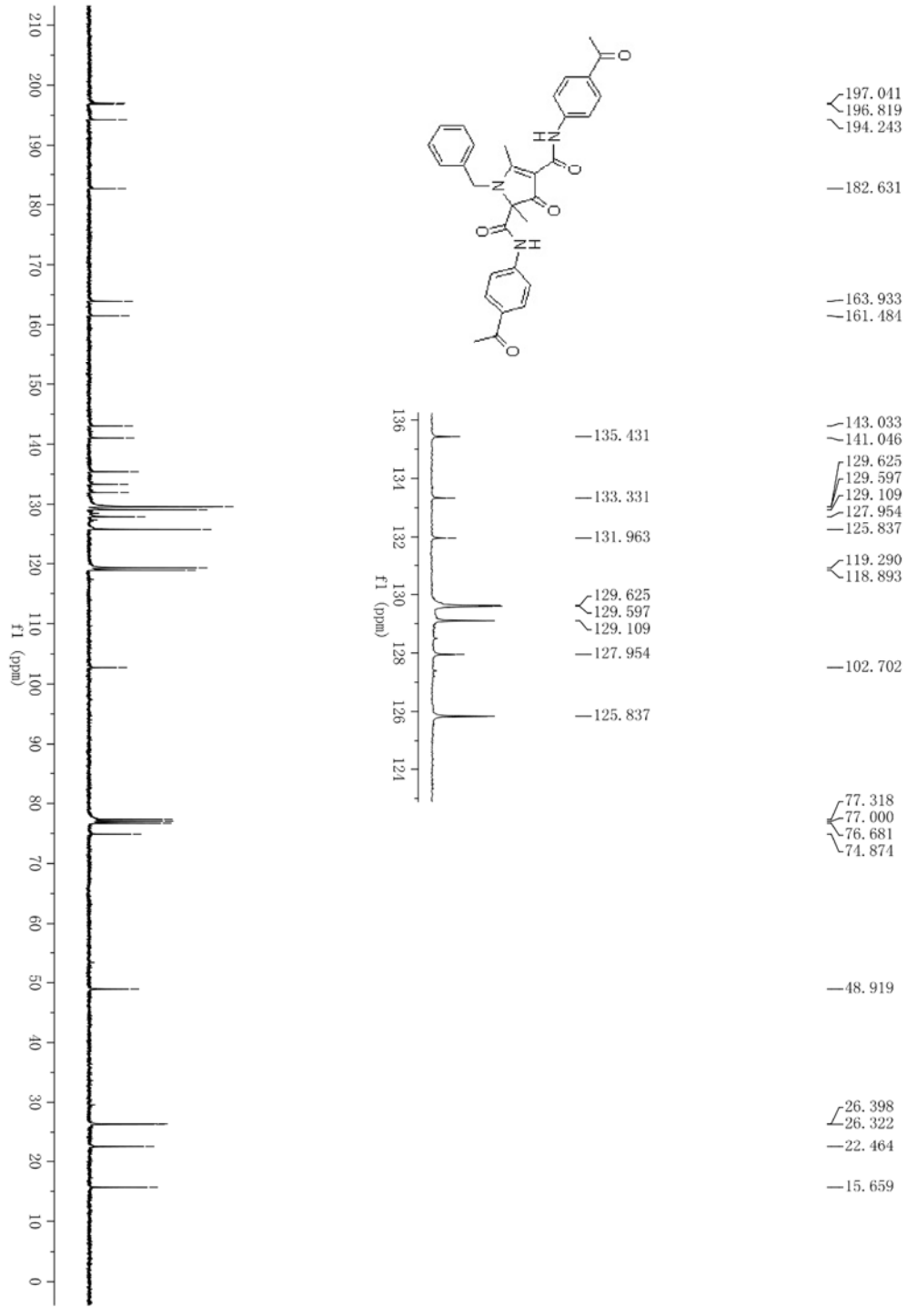

HN
O
O
H
N
N
Bn
O
NC
CN
2eq

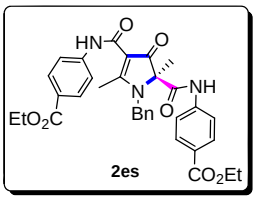

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NC
N
H
O
O
N
O
N
H
CN
135
130
125
120
f1 (ppm)
—135.218
133.172
133.045
—129.132
—128.025
—125.847
119.913
119.495
—119.109
—118.464
—194.118
—182.846
—163.982
—161.405
142.617
—140.725
133.045
129.132
—125.847
119.913
119.495
119.109
118.464
107.831
—105.837
—102.586
77.302
76.984
76.666
74.858
—48.975
—22.519
—15.708

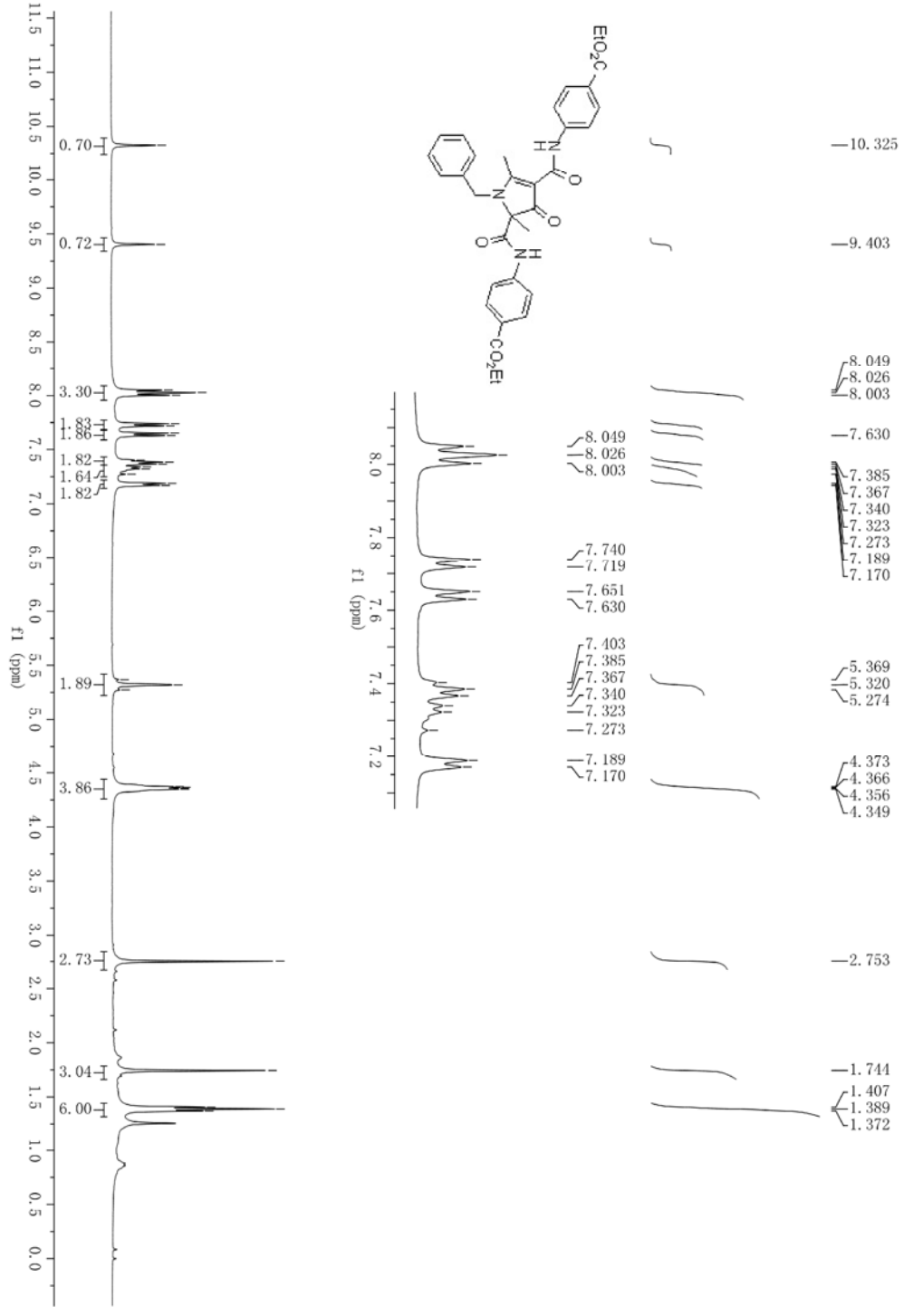

2er

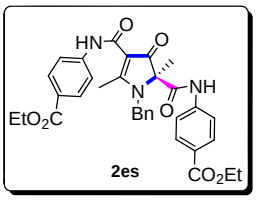

10.354
9.428
7.964
7.942
7.939
7.917
7.654
7.407
7.389
7.370
7.343
7.325
7.202
7.184
5.310
5.289
2.752
2.577
2.565
1.758
0.71
0.70
4.11
2.17
2.11
3.37
2.24
2.13
3.21
6.15
3.00
f1 (ppm)


2er

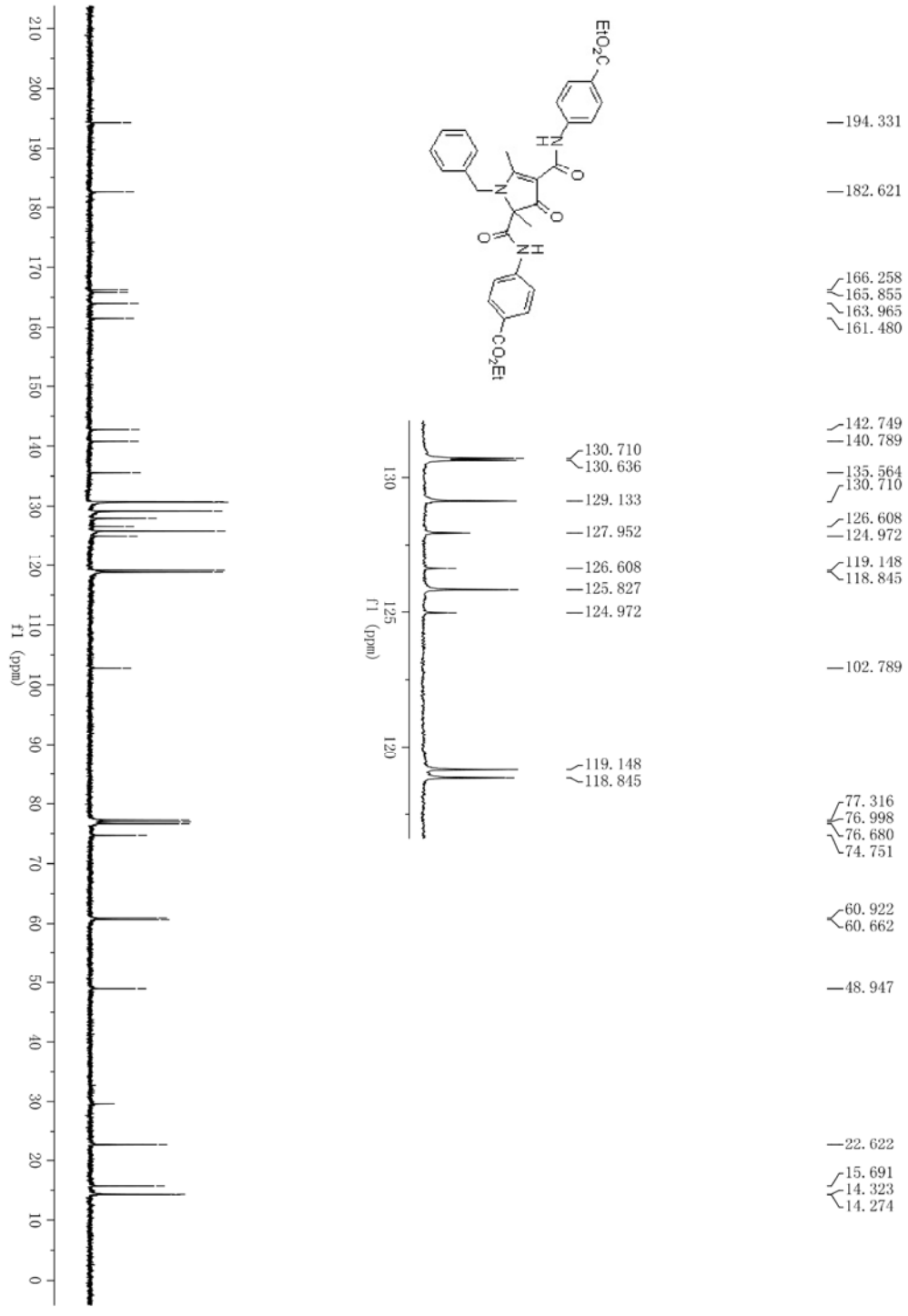

f1 (ppm)
197.041
196.819
194.243
182.631
163.933
161.484
143.033
141.046
129.625
129.597
129.109
127.954
125.837
119.290
118.893
102.702
77.318
77.000
76.681
74.874
48.919
26.398
26.322
22.464
15.659
135.431
133.331
131.963
129.625
129.597
129.109
127.954
125.837


HN
O
O
NH
N
Bn
O
EtO2C
2es
CO2Et


f1 (ppm)
0.70
0.72
3.30
1.83
1.86
1.82
1.64
1.82
1.89
3.86
2.73
3.04
6.00
EtO2C
CO2Et
8.049
8.026
8.003
7.740
7.719
7.651
7.630
7.403
7.385
7.367
7.340
7.323
7.273
7.189
7.170
10.325
9.403
8.049
8.026
8.003
7.630
7.385
7.367
7.340
7.323
7.273
7.189
7.170
5.369
5.320
5.274
4.373
4.366
4.356
4.349
2.753
1.744
1.407
1.389
1.372


HN
O
O
NH
N
Bn
O
EtO2C
CO2Et

2es


f1 (ppm)
EtO2C
CO2Et
194.331
182.621
166.258
165.855
163.965
161.480
142.749
140.789
135.564
130.710
130.636
129.133
127.952
126.608
125.827
124.972
119.148
118.845
102.789
77.316
76.998
76.680
74.751
60.922
60.662
48.947
22.622
15.691
14.323
14.274

7. The X-ray Data and Crystal Structure of 2a