Electronic Supplementary Information

A Recyclable Self-Supported Nanoporous PdCu Heterogeneous Catalyst for Aqueous Suzuki-Miyaura Cross-Coupling

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1. Materials and Methods

All reagents and solvents were purchased from commercial suppliers and used as received, unless otherwise indicated. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 advanced X-ray diffractometer using Cu K_α radiation (λ = 1.5418 Å) at a scan rate of 0.04 °/s. The structure and chemical composition of all samples were characterized on a JEOL JSM-6700F field emission scanning electron microscope (SEM), equipped with an Oxford INCA X-sight energy dispersive X-ray spectrometer. Transmission electron microscopy (TEM) images were obtained with a JEM-2100 high-resolution transmission electron microscope (200 kV). The electron structures of NP PdCu were analyzed with an AXIS SUPRA X-ray photoelectron spectrometer (XPS), using monochromatized Mg K_α X-ray as the excitation source, and choosing C 1s (284.60 eV) as the reference line. All reactions were carried out in oven-dried glassware under air atmosphere, and monitored by thin layer chromatography (TLC) at short time intervals. Reaction products were further purified by silica-gel column chromatography using silica gel (200–300 mesh) if necessary. Nuclear magnetic resonance spectra (NMR) were tested on Bruker AV400 (400 MHz) in deuerated solvent with tetramethylsilane (TMS) as internal standard for ^{1}H NMR and ^{13}C NMR. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. EDS analysis was carried out using EDAX Genesis with HITACHI FE-SEM S4300 operated at an accelerating voltage of 20kV.

2. Fabrication of NP-PdCu Catalyst

$Pd_{15}Cu_5Al_{80}$ alloy foils with the thickness at ~50 μm were fabricated by melting pure Pd, Cu, and Al (>99.9%) in an arc furnace under the protection of argon, followed by spinning as reported in our previous work (C. Xu, Y. Liu, J. Wang, H. Geng and H. Qiu, *J. Power Sources*, 2012, **199**, 124-131.). The alloy foils were etched in 1.0 M NaOH solution for 24 h The as-dealloyed samples were washed by ultrapure

water for several times and dried under the natural atmosphere before utilization.

3. General Procedure for NP-PdCu catalyzed Suzuki-Miyaura Coupling Reaction

To a round-bottom flask with a magnetic stir bars, halogenated benzene (1.0 mmol), aromatic boronic acid (1.2 mmol), EtOH (3.0 ml), H_2O (3.0 mL), Na_2CO_3 (1.5 mmol) and NP-PdCu (6.0 mg) were successively added. The reaction mixture was stirred gently at 80 ℃ for a specified period. The reaction progress was monitored by thin layer chromatography (TLC). After the reaction finished, the reaction mixture was cooled to room temperature. NP-PdCu was easily recovered via centrifugation and washed several times with water and methanol. The catalyst was dried at room temperature for its reuse. Most of EtOH in the reaction solution was evaporated under reduced pressure. Then 15.0 mL of water was added to the reaction mixture, which can be extracted by CH_2Cl_2 (13.0 mL). The organic phase was separated and dried over anhydrous sodium sulfate. After evaporating under reduced pressure, the crude product was obtained, which was further purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 6/1) to give target product. Lastly, the pure product was confirmed with NMR.

4. Gram-scale Production for 2-Cyano-4'-Methylbiphenyl

To a round-bottom flask with a magnetic stir bars, 2-bromobenzonitrile (10 mmol, 1.82 g), 4-methylbenzeneboronic acid (12 mmol, 1.63 g), EtOH (20 ml), H_2O (20 mL), Na_2CO_3 (15 mmol, 1.59 g) and NP-PdCu (60 mg) were successively added. The reaction mixture was stirred gently at 80 ℃ for 6 h. The reaction progress was monitored by thin layer chromatography (TLC). After the reaction finished, the reaction mixture was cooled to room temperature. NP-PdCu was easily recovered via centrifugation and washed several times with water and methanol. The catalyst was dried at room temperature for its reuse. Most of EtOH in the reaction solution was evaporated under reduced pressure. Then 40.0 mL of water was added to the reaction

mixture, which can be extracted by CH_2Cl_2 (30.0 mL). The organic phase was separated and dried over anhydrous sodium sulfate. After evaporating under reduced pressure, the crude product was obtained, which was further purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 6/1) to give target product. Lastly, the pure product was confirmed with NMR.

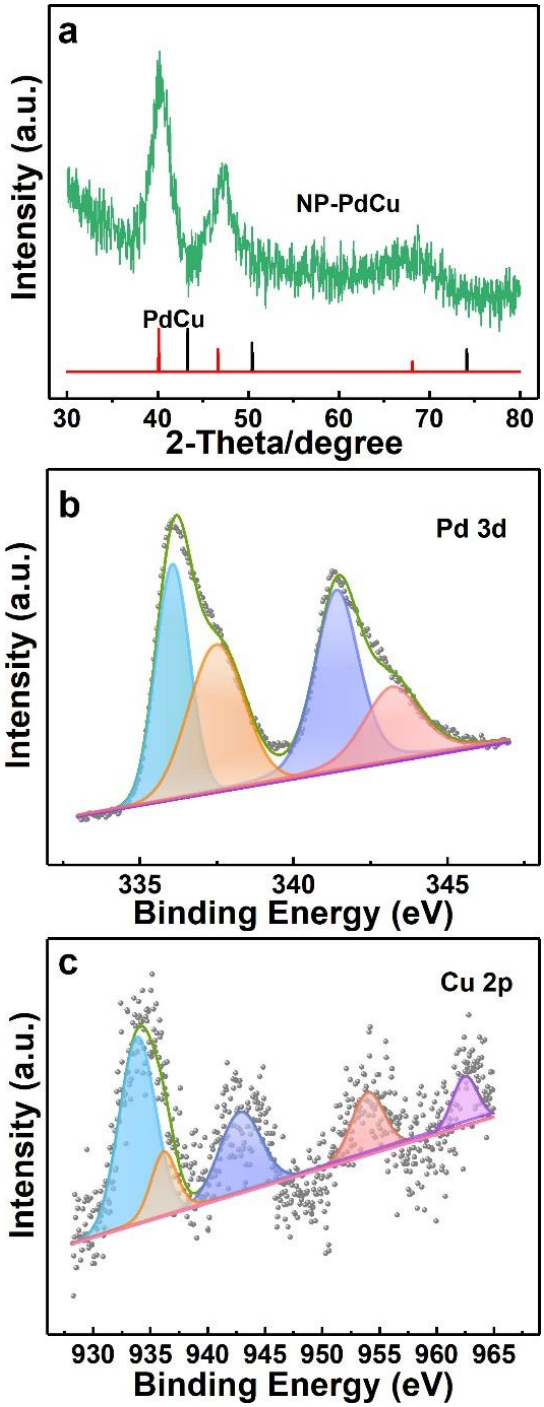


Fig. S1 (a) XRD pattern of NP-PdCu alloy with the standard patterns of pure Pd (JCPDS 65-2867) and Cu (JCPDS 04-0836) attached for comparison, XPS data of NP-PdCu alloy for (b) Pd 3d and (c) Cu 2p core levels.

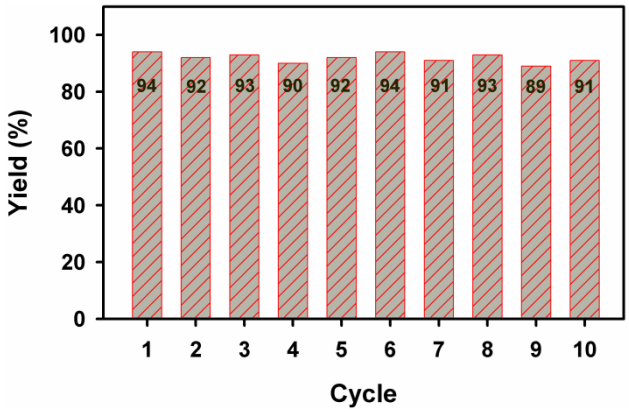
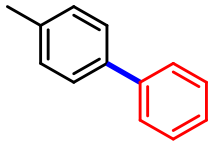


Fig. S2 The recyclability of the NP-PdCu catalyst for the Suzuki-Miyaura cross-coupling between *p*-bromotoluene and phenylboronic acid.

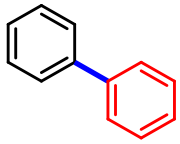
5. Products Analysis

4-methyl-1,1'-biphenyl (3a)



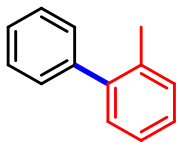
white solid (156.8 mg, 93%). ^{1}H NMR (400 MHz, d-DMSO): δ 7.647-7.628 (m, 2H), 7.558 (d, 2H, J = 8 Hz), 7.451 (t, 2H, J = 8 Hz), 7.342 (t, 1H, J = 7.2 Hz), 7.274 (d, 2H, J = 8 Hz), 2.364 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.19, 138.38, 137.04, 129.50, 128.73, 127.02, 127.00, 21.13.

1,1'-biphenyl (3b)



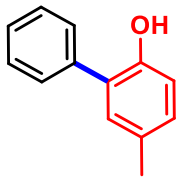
white solid (144.9 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.642-7.641 (m, 4H), 7.496-7.477 (m, 4H), 7.400-7.363 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.26, 128.78, 127.28, 127.19.

2-methyl-1,1'-biphenyl (3c)



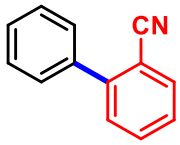
white solid (151.4 mg, 90%). ^{1}H NMR (400 MHz, d-DMSO): δ 7.444 (t, 2H, J = 7.6 Hz), 7.381-7.232 (m, 6H), 7.203-7.182 (m, 1H), 2.227 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.01, 141.98, 135.38, 130.34, 129.84, 129.23, 128.10, 127.28, 126.80, 125.80, 20.51.

5-methyl-[1,1'-biphenyl]-2-ol (3d)



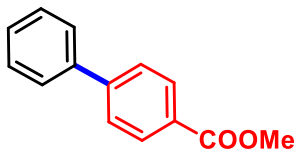
white solid (178.7 mg, 97%). ^{1}H NMR (400 MHz, d-DMSO): δ 9.268 (s, 1H), 7.541-7.518 (m, 2H), 7.404-7.366 (m, 2H), 7.300-7.263 (m, 1H), 7.054 (d, 1H, J = 2 Hz), 6.960 (dd, 1H, J = 2, 8 Hz), 6.836 (d, 1H, J = 8 Hz), 2.242 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.19, 137.30, 130.70, 130.02, 129.64, 129.24, 129.09, 127.86, 127.79, 115.66, 20.52.

[1,1'-biphenyl]-2-carbonitrile (3e)



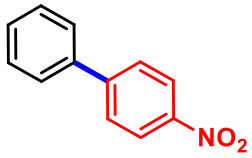
pale yellow grease (166.7 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.800 (dd, 1H, J = 7.6, 8 Hz), 7.678 (td, 1H, J = 1.2, 7.6 Hz), 7.608-7.587 (m, 2H), 7.561-7.454 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.52, 138.16, 133.77, 132.84, 130.11, 128.78, 128.75, 127.57, 118.75, 111.30.

methyl [1,1'-biphenyl]-4-carboxylate (3f)



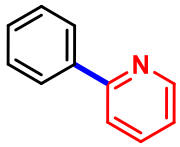
white solid (195.2 mg, 92%). ^{1}H NMR (400 MHz, d-DMSO): δ 8.040 (d, 2H, J = 8.4 Hz), 7.830 (d, 2H, J = 8.4 Hz), 7.740 (d, 2H, J = 7.6 Hz), 7.515 (t, 2H, J = 8 Hz), 7.439 (t, 1H, J = 7.2 Hz), 3.883 (s, 3H). ^{13}C NMR (100 MHz, d-DMSO): δ 166.53, 145.16, 130.28, 130.24, 129.58, 128.89, 127.45, 127.43, 127.40, 52.63.

4-nitro-1,1'-biphenyl (3g)



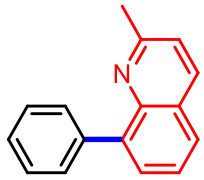
white solid (169.3 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.332 (m, 2H), 7.786-7.759 (m, 2H), 7.669-7.648 (m, 2H), 7.552-7.457 (m, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.66, 147.11, 138.80, 129.17, 128.93, 127.82, 127.40, 124.13.

2-phenylpyridine (3h)



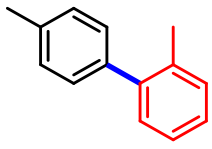
colorless liquid (135.0 mg, 87%), ^{1}H NMR (400 MHz, d-DMSO): δ 8.687-8.674 (m, 1H), 8.109-8.088 (m, 2H), 7.977-7.957 (m, 1H), 7.875 (td, 1H, J = 2, 7.6 Hz), 7.524-7.425 (m, 3H), 7.359 (ddd, 1H, J = 0.8, 5.2, 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.49, 149.71, 139.44, 136.75, 128.97, 128.77, 126.94, 122.11, 120.57.

2-methyl-8-phenylquinoline (3i)



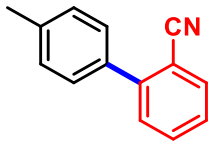
pale yellow grease (142.5 mg, 65%), ^{1}H NMR (400 MHz, d-DMSO): δ 8.298 (d, 1H, J = 8.4 Hz), 7.930 (dd, 1H, J = 0.8, 8 Hz), 7.717-7.671 (m, 3H), 7.595 (t, 1H, J = 7.6 Hz), 7.488-7.371 (m, 4H), 2.592 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.74, 145.47, 139.91, 139.61, 136.22, 131.05, 130.27, 127.75, 127.23, 127.11, 126.95, 125.39, 121.79, 25.76.

2,4'-dimethyl-1,1'-biphenyl (3j)



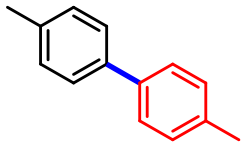
faint yellow liquid (165.8 mg, 91%). ^{1}H NMR (400 MHz, d-DMSO): δ7.287-7.155 (m, 8H), 2.348 (s, 3H), 2.222 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.90, 139.06, 136.40, 135.42, 130.31, 129.88, 129.10, 128.80, 127.09, 125.77, 21.20, 20.54.

4'-methyl-[1,1'-biphenyl]-2-carbonitrile (3k)



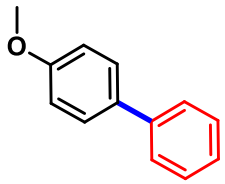
white solid (183.6 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.780 (dd, 1H, J = 0.8, 8 Hz), 7.656 (td, 1H, J = 1.2, 7.6 Hz), 7.543-7.425 (m, 4H), 7.332 (d, 2H, J = 8 Hz), 2.451 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.56, 138.72, 135.29, 133.74, 132.78, 130.00, 129.74, 128.64, 127.29, 118.90, 111.22, 21.28.

4,4'-dimethyl-1,1'-biphenyl (3l)



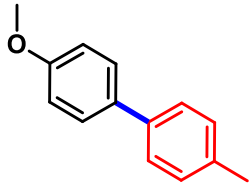
white solid (171.3 mg, 94%). ^{1}H NMR (400 MHz, d-DMSO): δ 7.530 (d, 4H, J = 8 Hz), 7.253 (d, 4H, J = 8 Hz), 2.336 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.30, 136.71, 129.45, 126.83, 21.10.

4-methoxy-1,1'-biphenyl (3m)



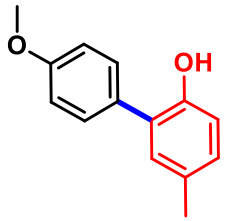
white solid (175.0 mg, 95%). ^{1}H NMR (400 MHz, d-DMSO): δ 7.620-7.598 (m, 4H), 7.435 (t, 2H, J = 8 Hz), 7.311 (t, 1H, J = 7.2 Hz), 7.031 (d, 2H, J = 7.2 Hz), 3.799 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14, 140.84, 133.80, 128.73, 128.17, 126.75, 126.67, 114.21, 55.36.

4-methoxy-4'-methyl-1,1'-biphenyl (3n)



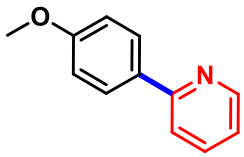
light grey solid (192.3 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.559-7.520 (m, 2H), 7.497-7.470 (m, 2H), 7.257 (d, 2H, J = 8 Hz), 7.015-6.978 (m, 2H), 3.876 (s, 3H), 2.413 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.94, 137.98, 136.36, 133.76, 129.44, 127.97, 126.60, 114.17, 55.36, 21.06.

4'-methoxy-5-methyl-[1,1'-biphenyl]-2-ol (3o)



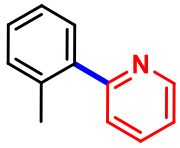
pale yellow solid (210.0 mg, 98%). ^{1}H NMR (400 MHz, d-DMSO): δ 9.204 (s, 1H), 7.484-7.462 (m, 2H), 7.027 (d, 1H, J = 1.6 Hz), 6.960-6.902 (m, 3H), 6.811 (d, 1H, J = 8 Hz), 3.777 (s, 3H), 2.230 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.26, 150.29, 130.72, 130.25, 129.93, 129.42, 129.26, 127.56, 115.50, 114.67, 55.38, 20.52.

2-(4-methoxyphenyl)pyridine (3p)

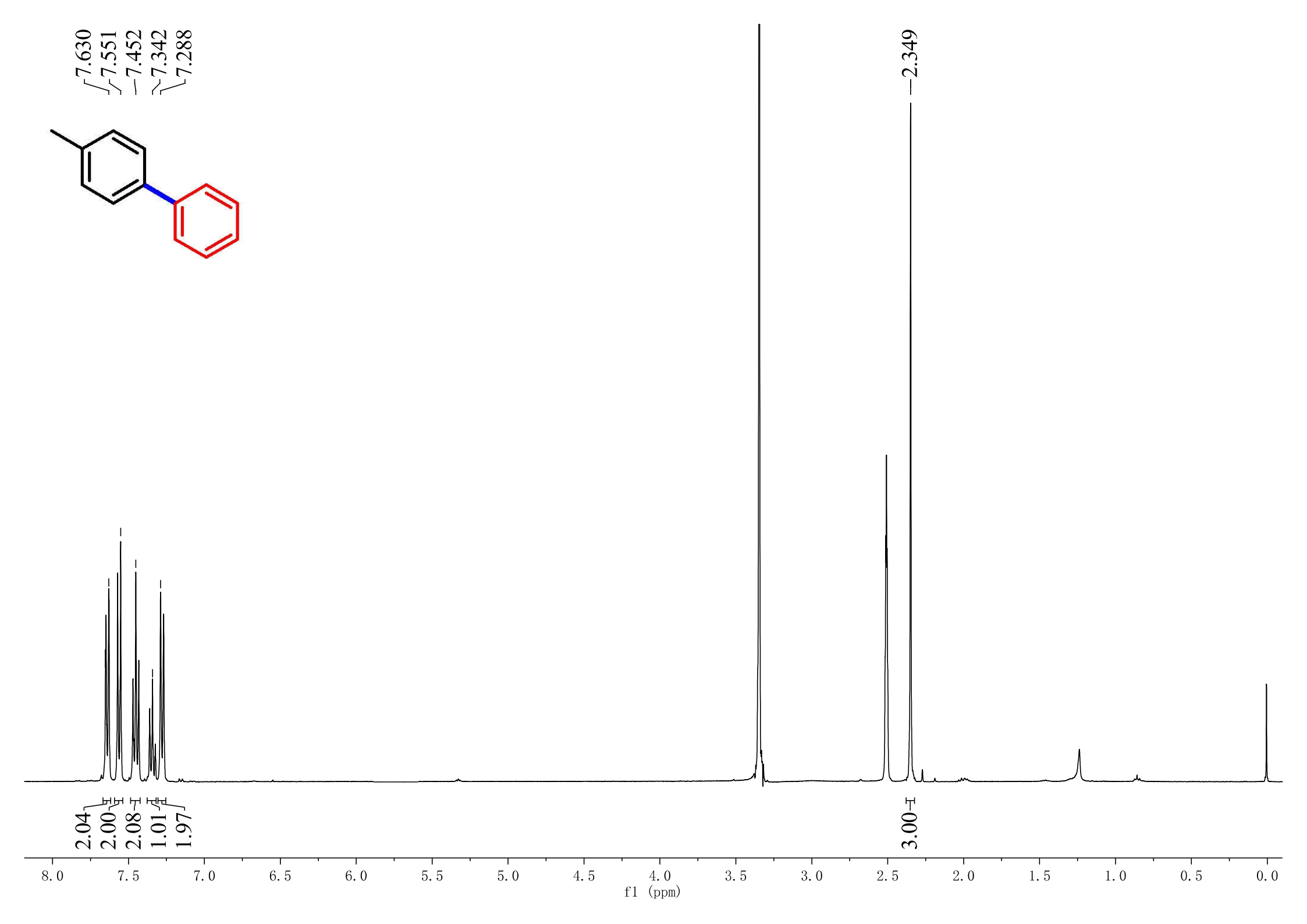


white solid (166.7 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.683-8.670 (m, 1H), 7.975 (dt, 2H, J = 2.8, 8.8 Hz), 7.762-7.682 (m, 2H), 7.199 (ddd, 1H, J = 1.2, 5.4, 6.2 Hz), 7.025 (dt, 2H, J = 2.8, 8.8 Hz), 3.890 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.47, 157.16, 149.53, 136.72, 132.01, 128.19, 121.44, 119.89, 116.10, 114.78, 114.14, 55.37.

2-(*o*-tolyl)pyridine (3q)



white solid (150.6 mg, 89%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.686-8.688 (m, 1H), 7.975 (dt, 2H, J = 3.2, 8.8 Hz), 7.766-7.683 (m, 2H), 7.219-7.185 (m, 1H), 7.026 (dt, 2H, J = 3.2, 8.8 Hz), 3.893 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.46, 157.14, 149.56, 136.66, 132.06, 128.17, 121.41, 119.81, 114.13, 29.72.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6.0
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3.5
3.0
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1.0
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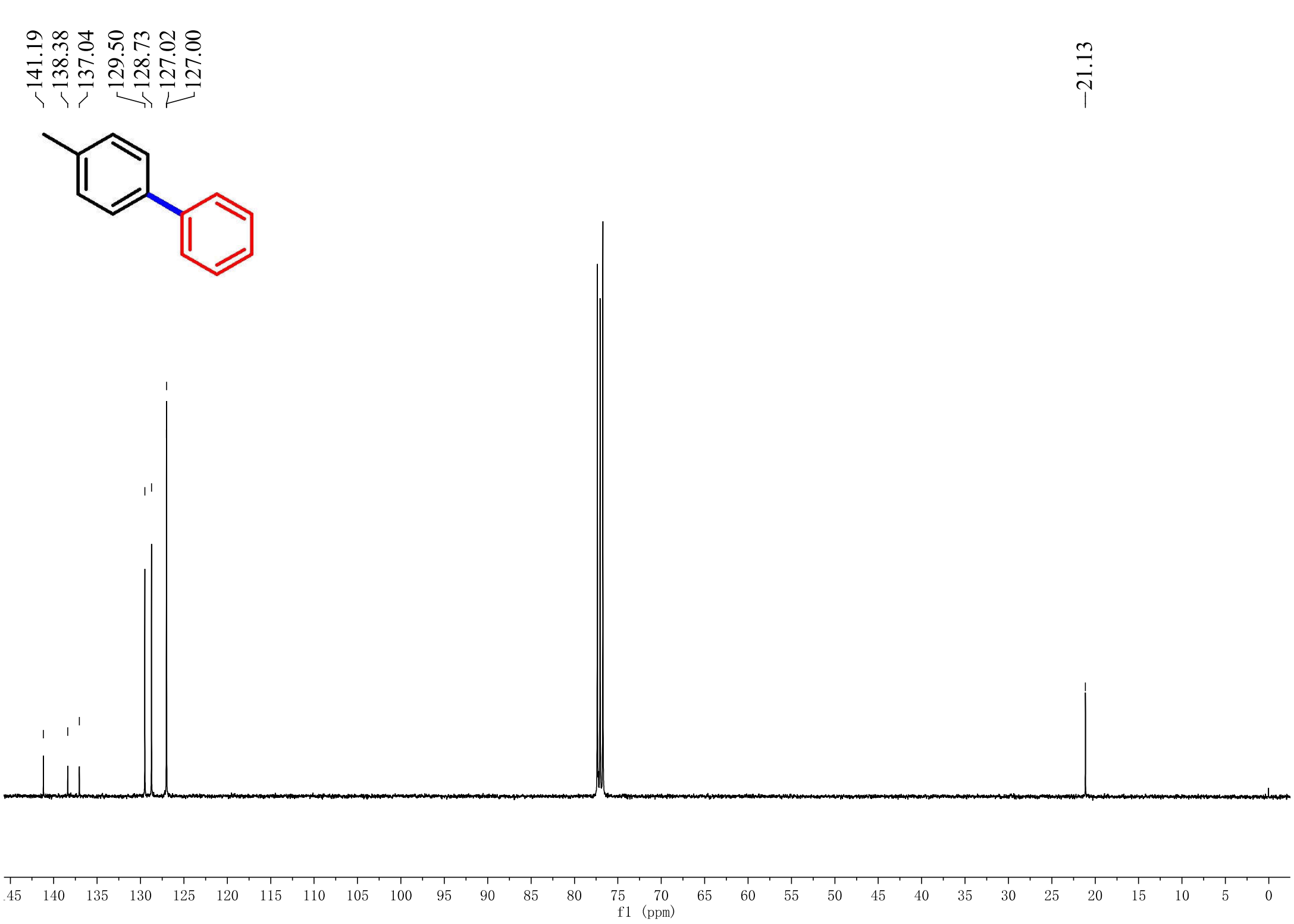
0.0
f1 (ppm)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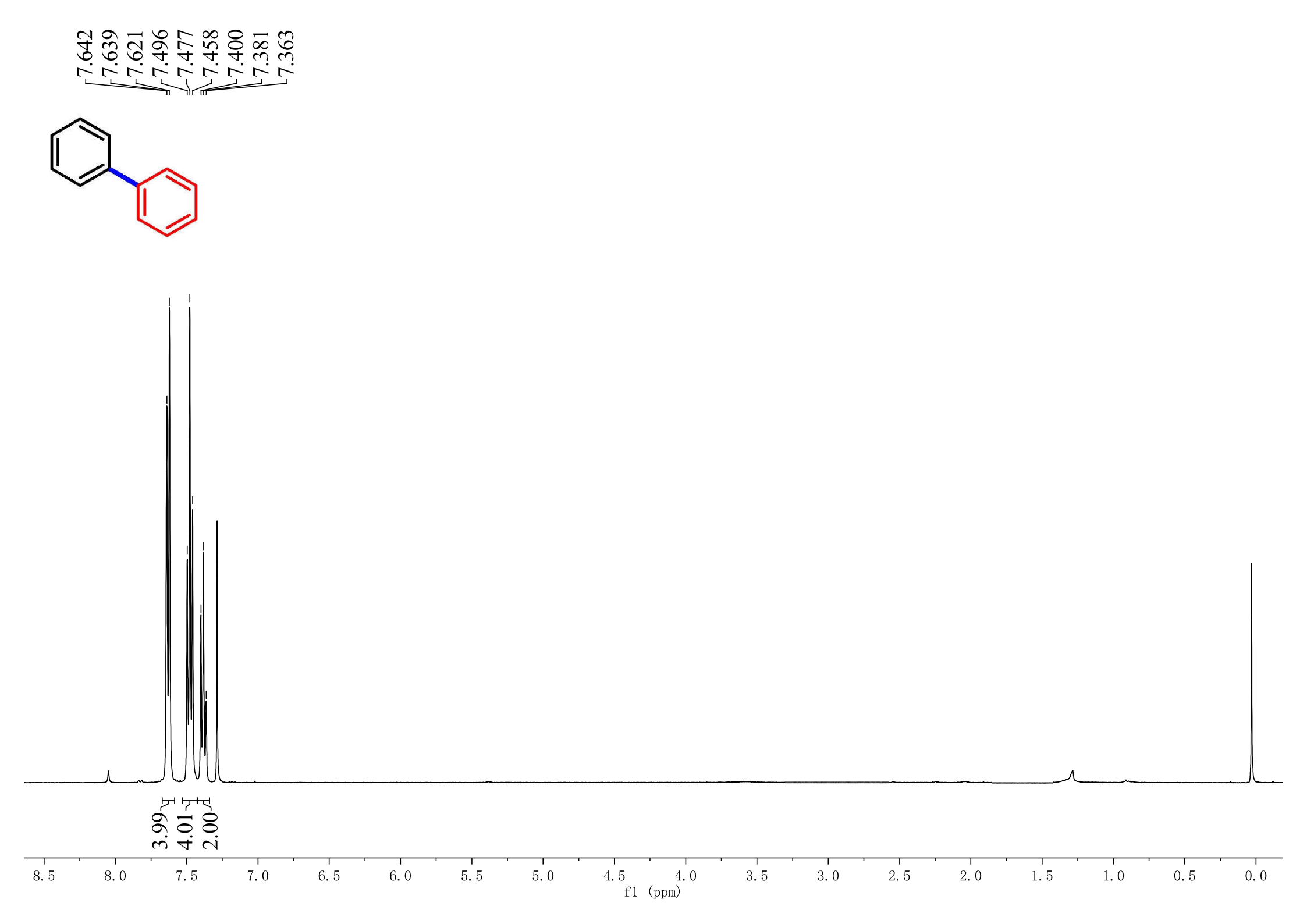
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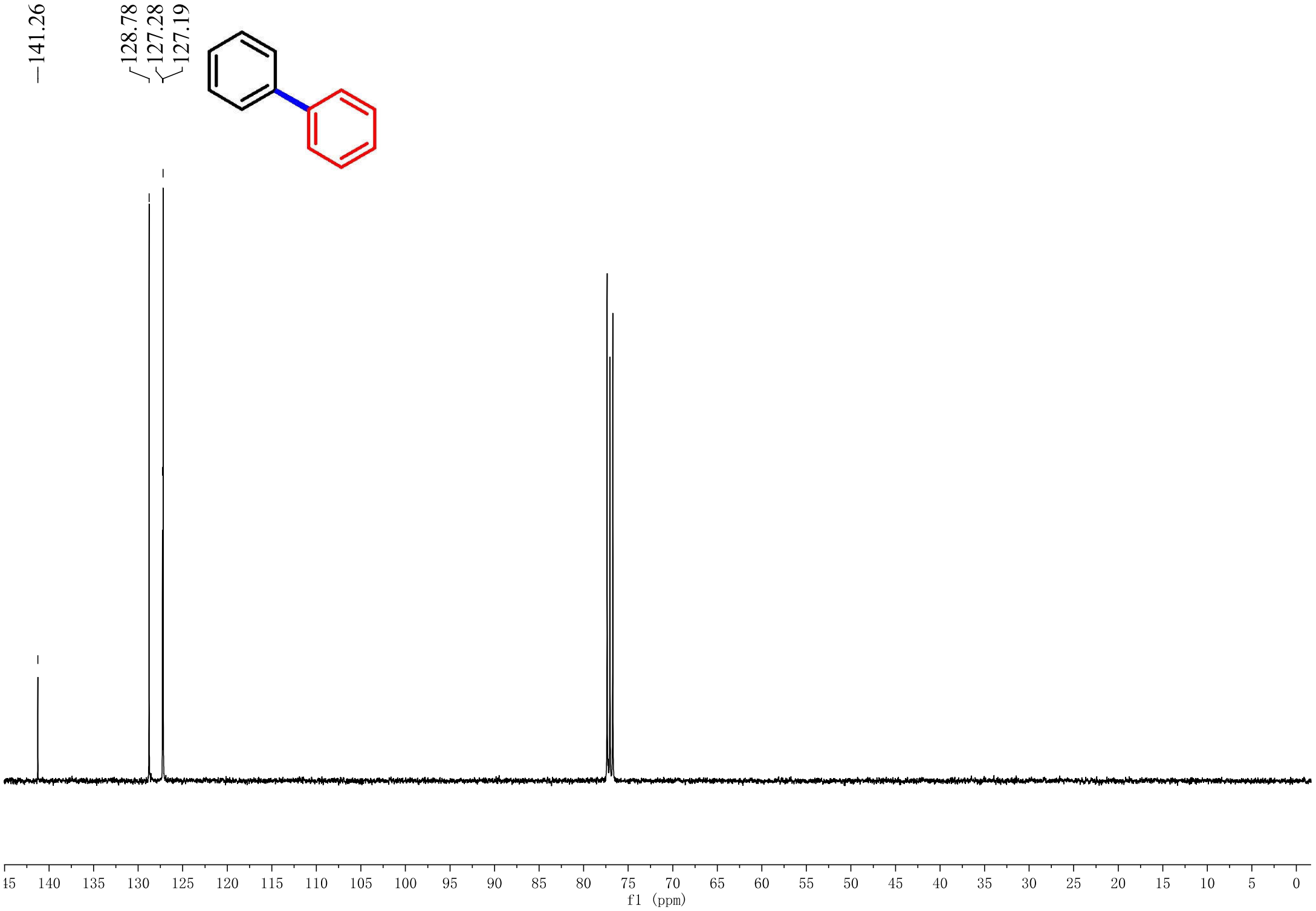
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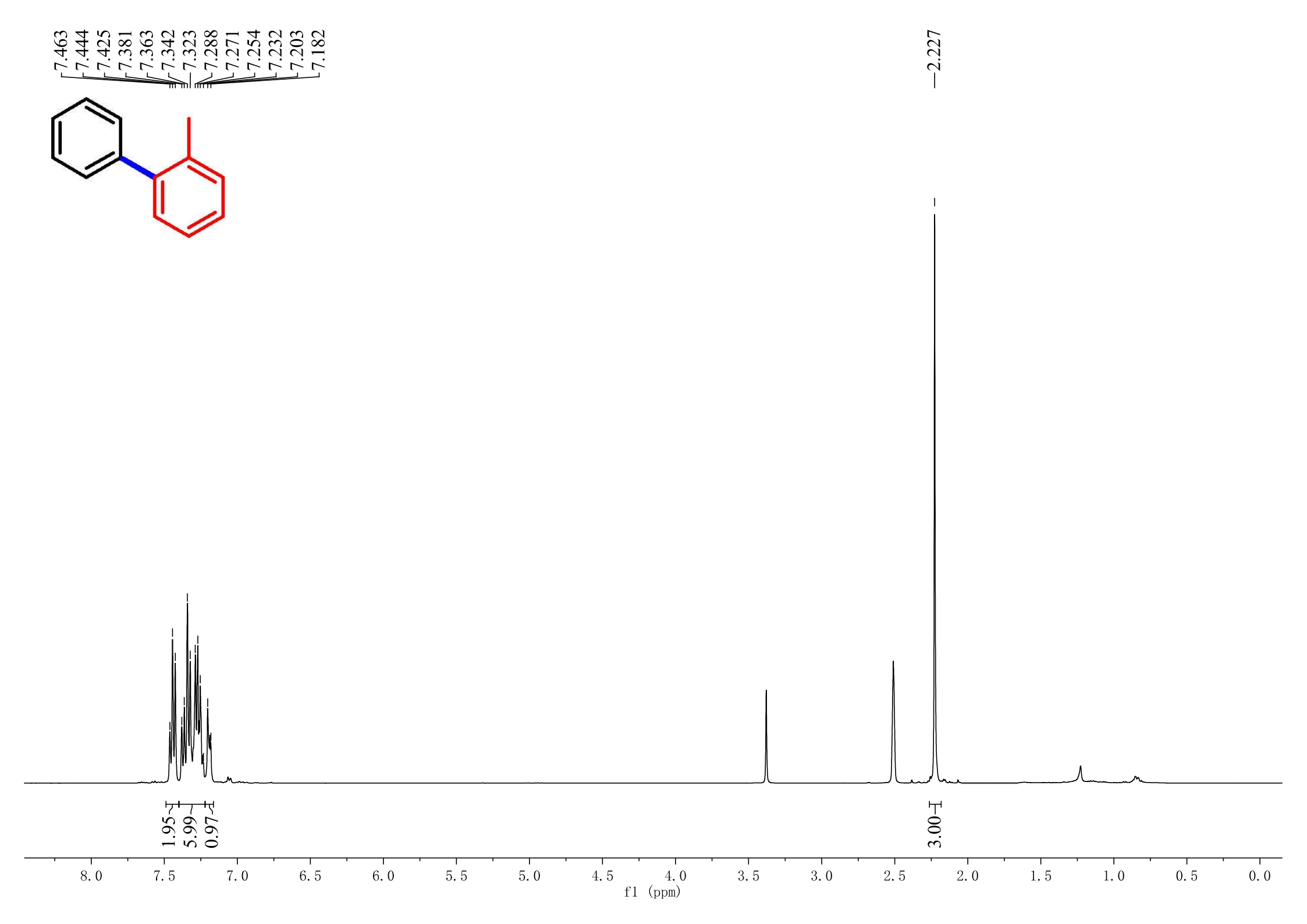
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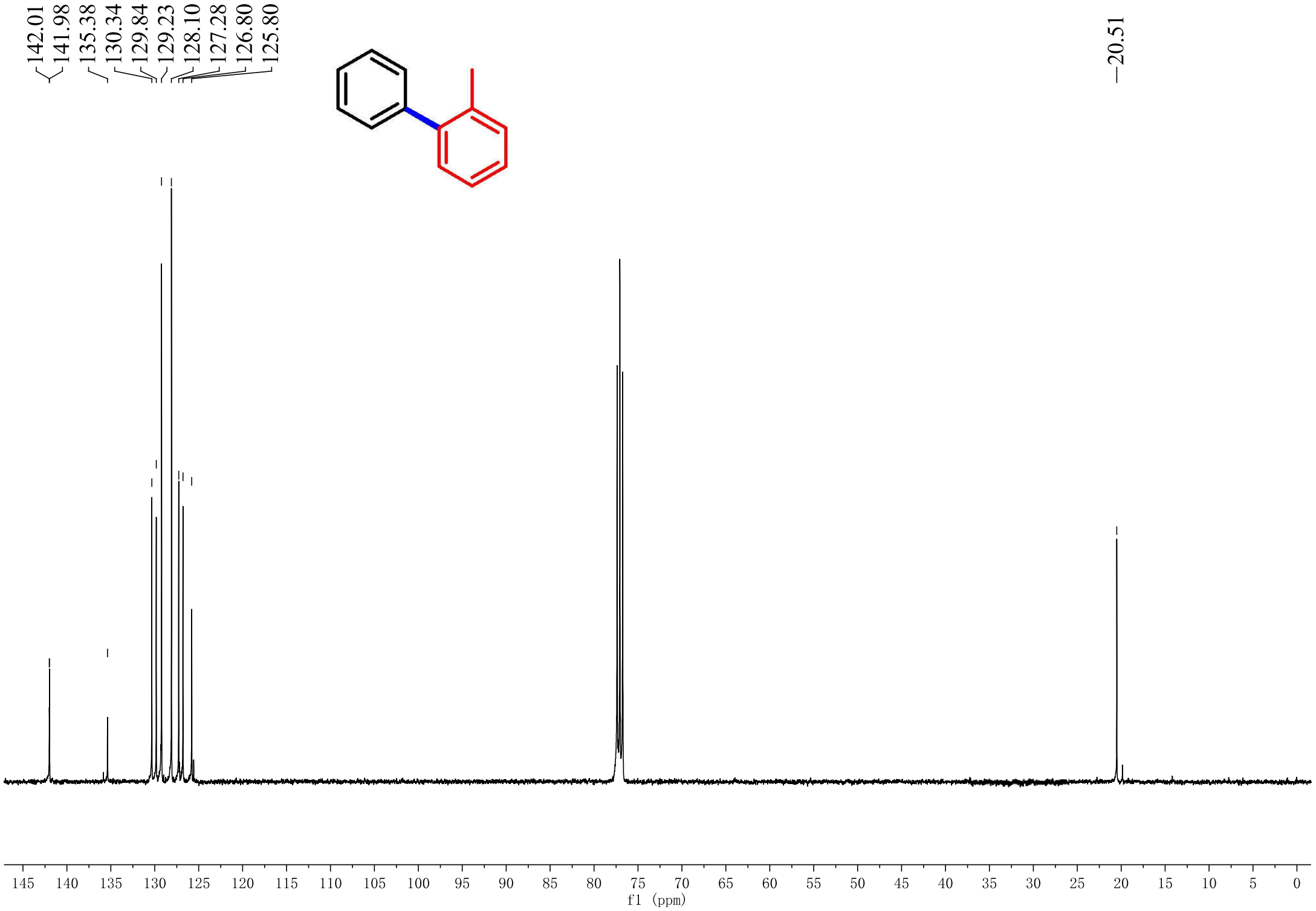
f1 (ppm)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128.10
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125.80
20.51
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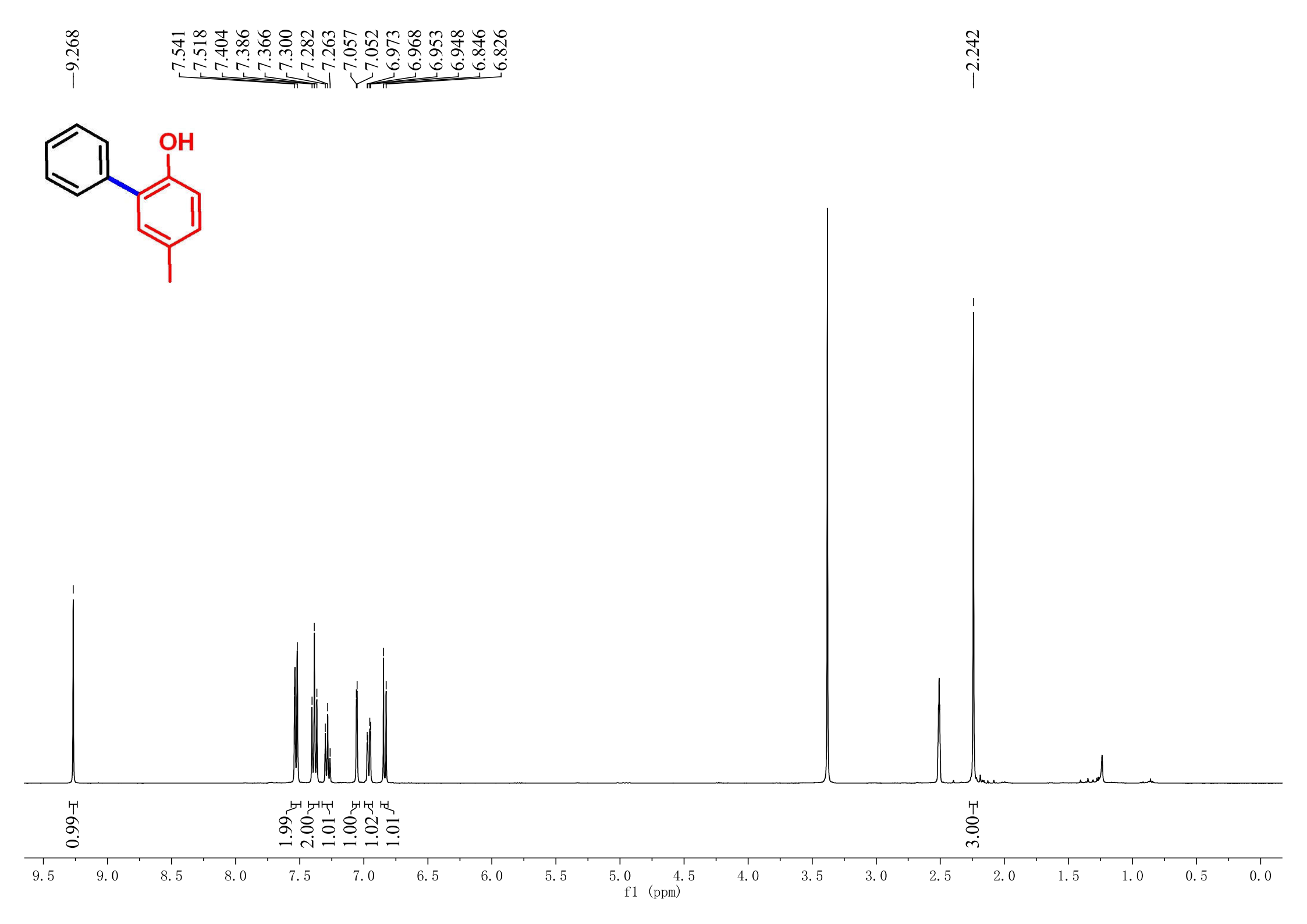
f1 (ppm)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7.282
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6.968
6.953
6.948
6.846
6.826
2.242
OH
0.99
1.99
2.00
1.01
1.00
1.02
1.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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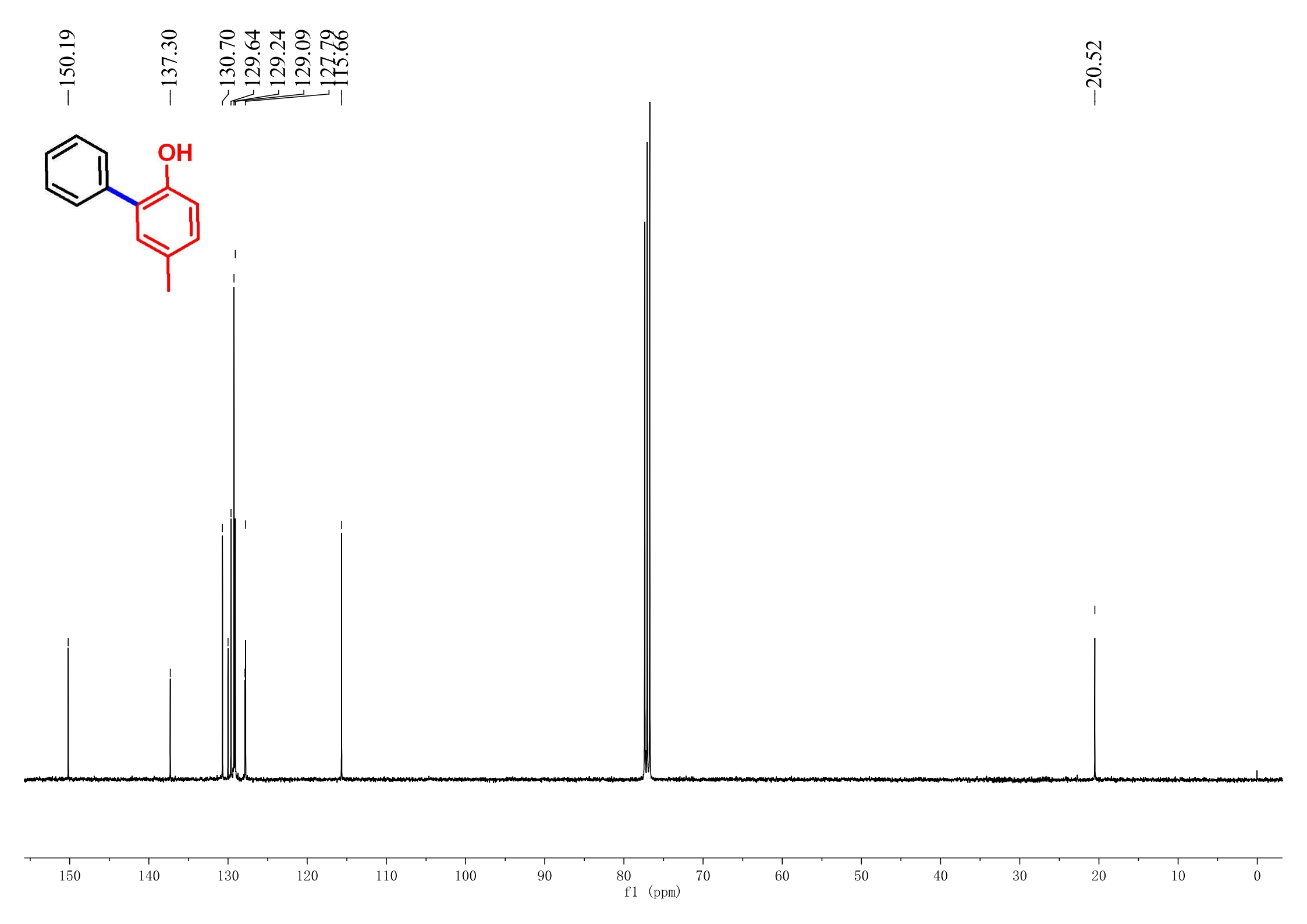
0.0
f1 (ppm)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137.30
130.70
129.64
129.24
129.09
127.79
115.66
20.52
OH
150
140
130
120
110
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90
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70
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50
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30
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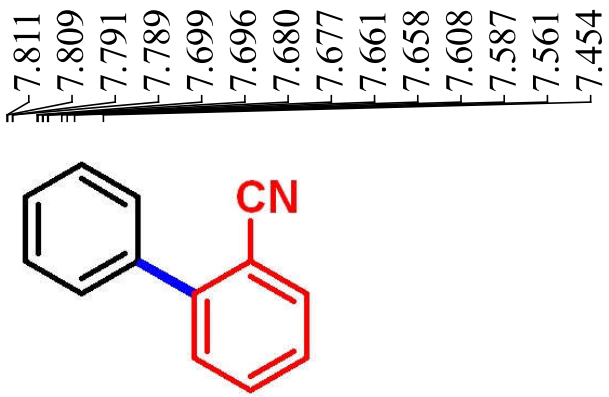
10
0
f1 (ppm)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7.809
7.791
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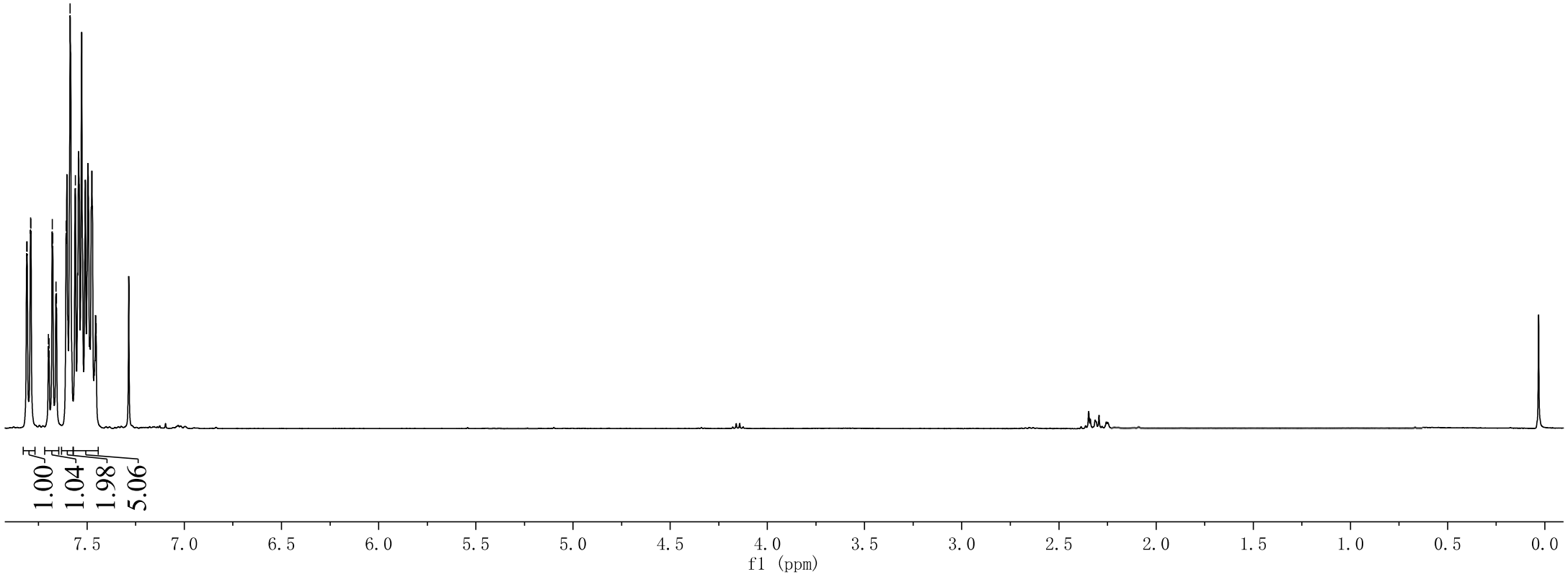
7.677
7.661
7.658
7.608
7.587
7.561
7.454
CN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1.04
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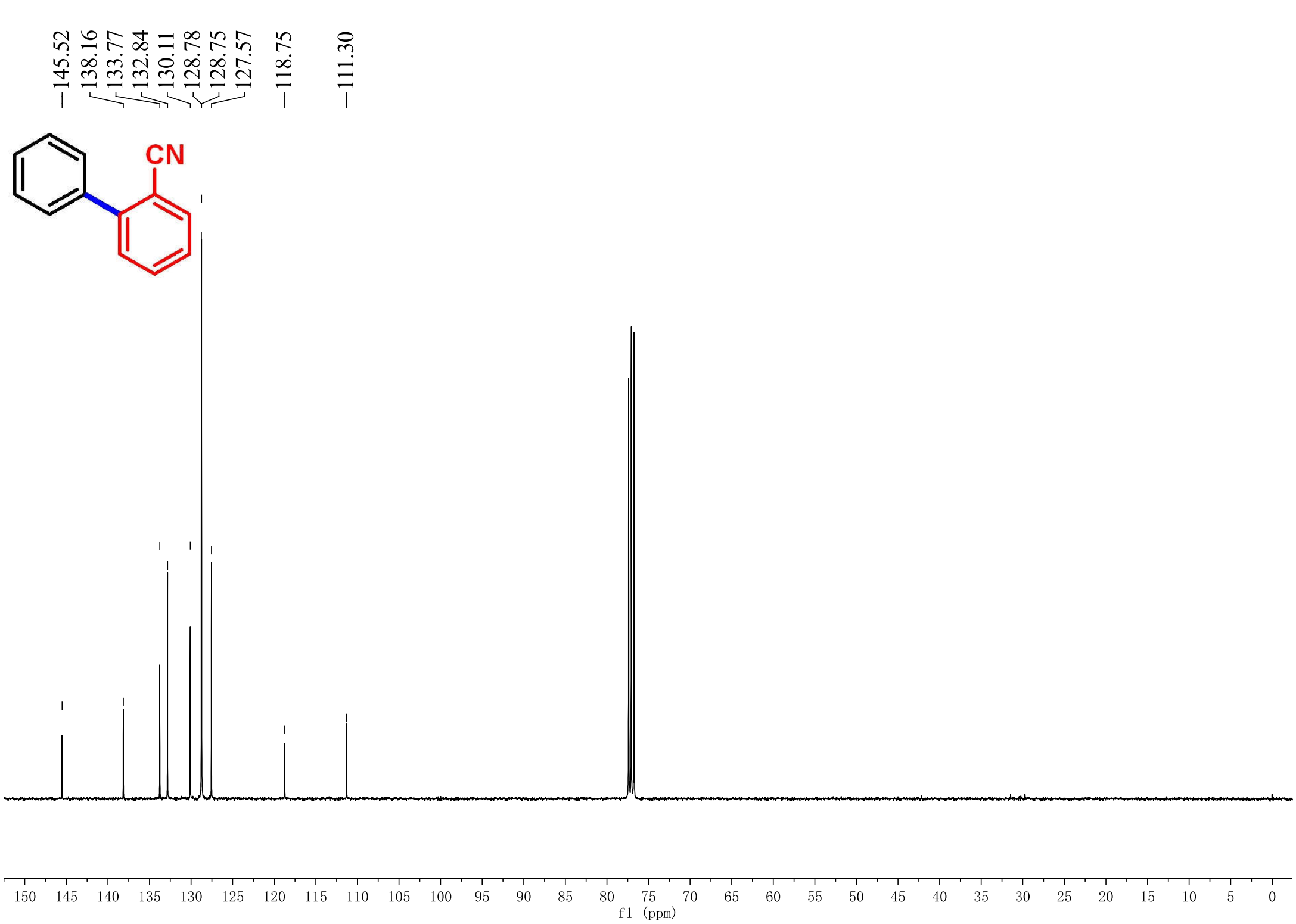
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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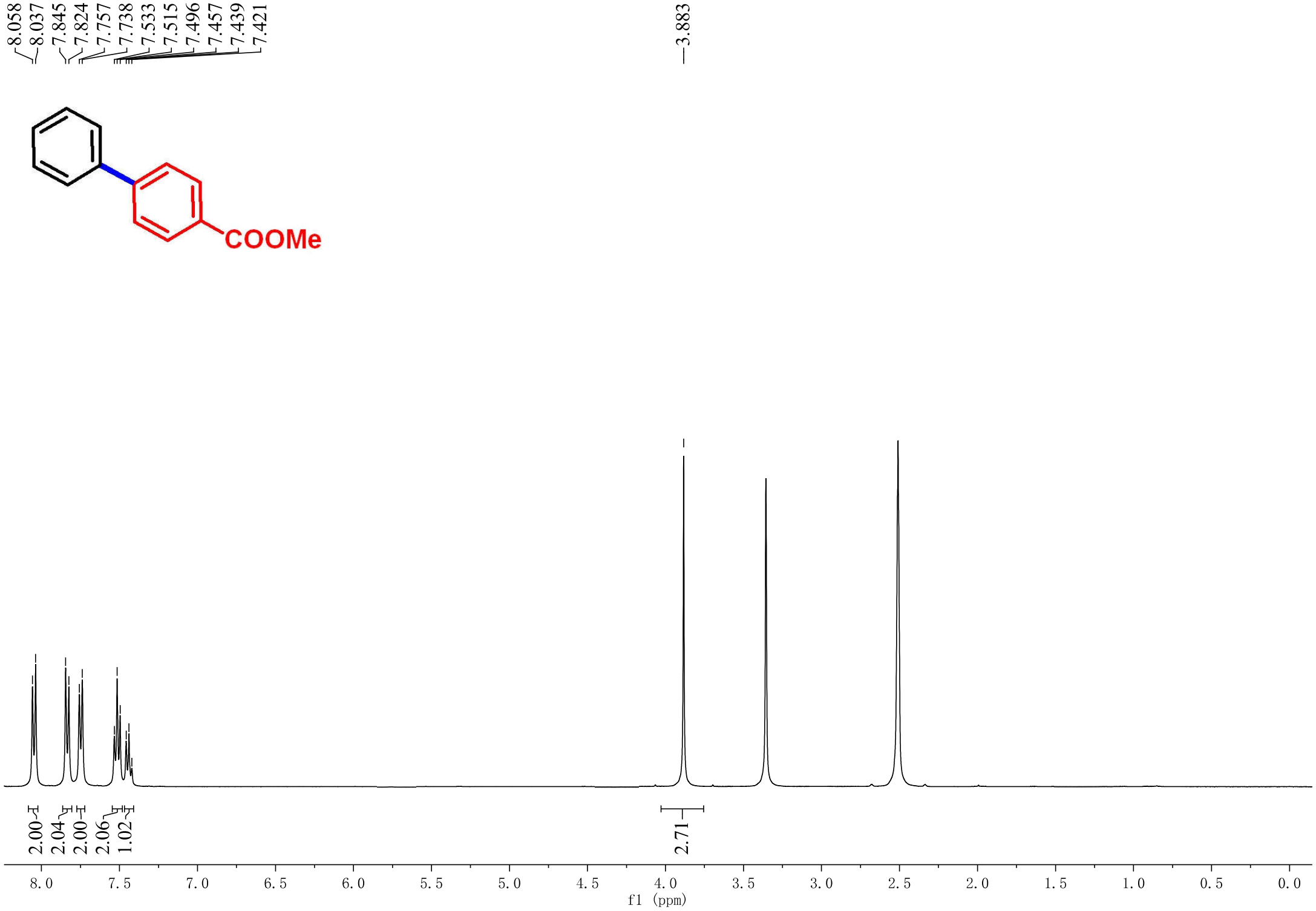
133.77
132.84
130.11
128.78
128.75
127.57
118.75
111.30
CN
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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7.533
7.515
7.496
7.457
7.439
7.421
3.883
COOMe
2.00
2.04
2.00
2.06
1.02
2.71
8.0
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
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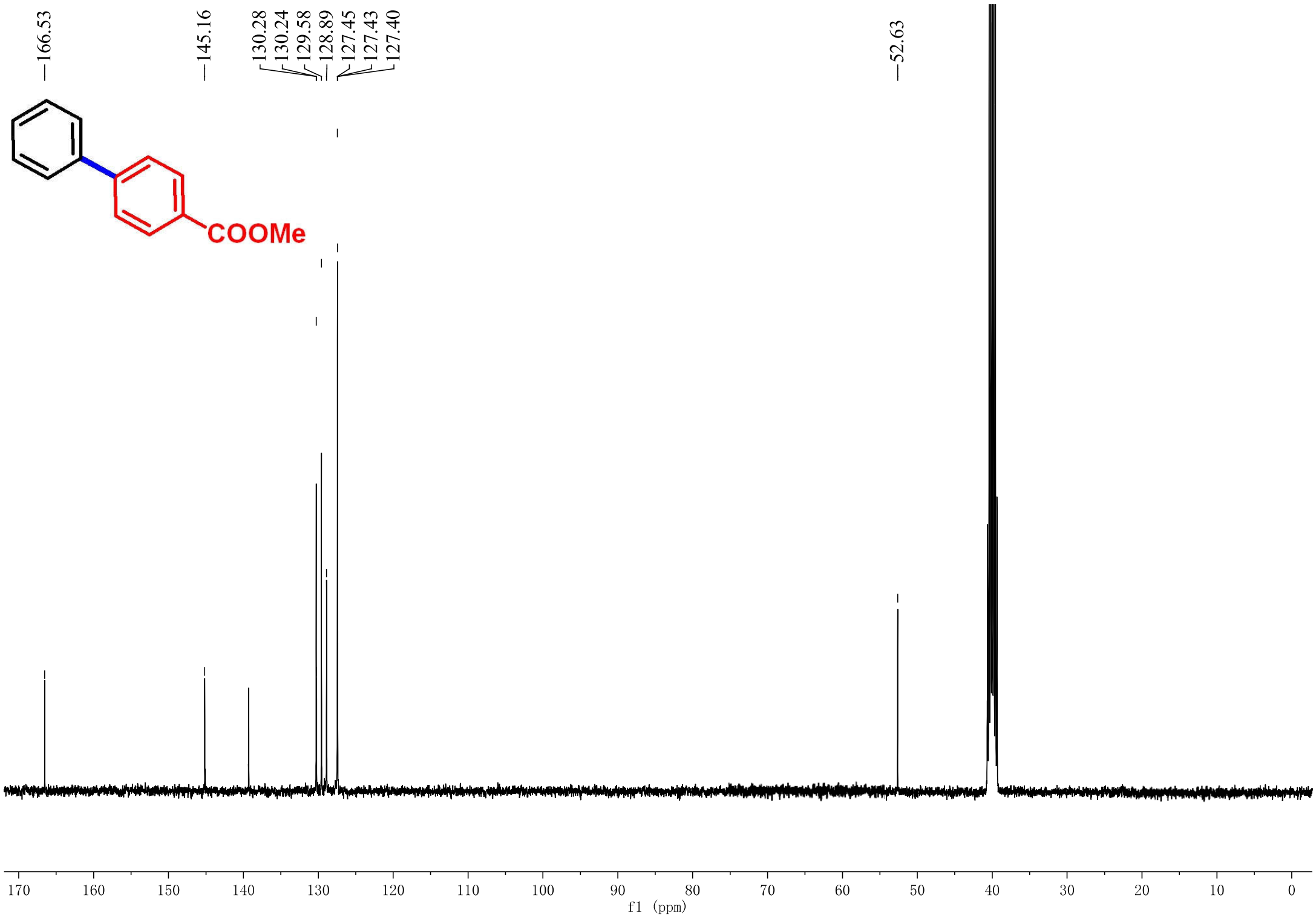
0.0
f1 (ppm)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128.89
127.45
127.43
127.40
52.63
COOMe
170
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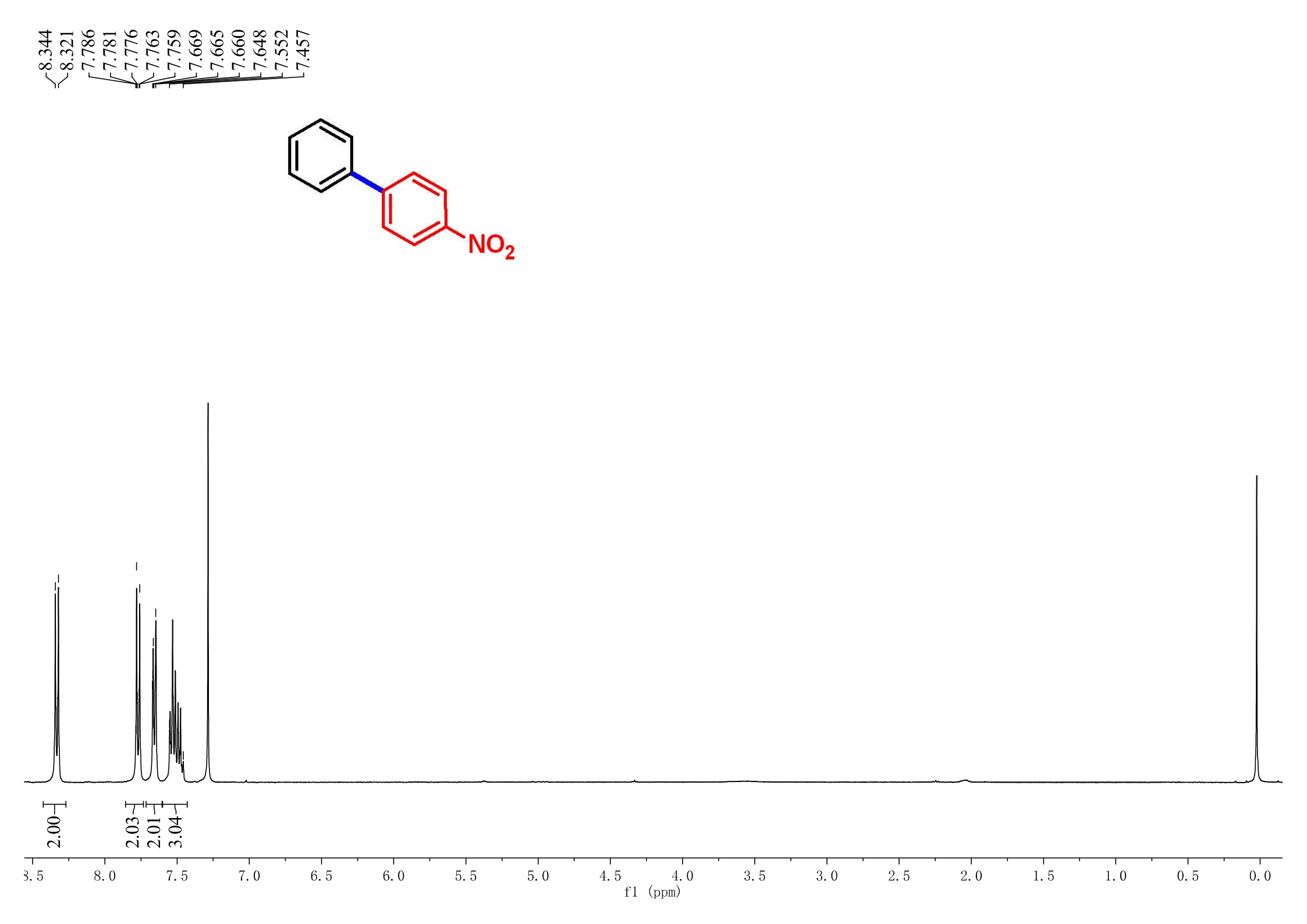
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.321
7.786
7.781
7.776
7.763
7.759
7.669
7.665
7.660
7.648
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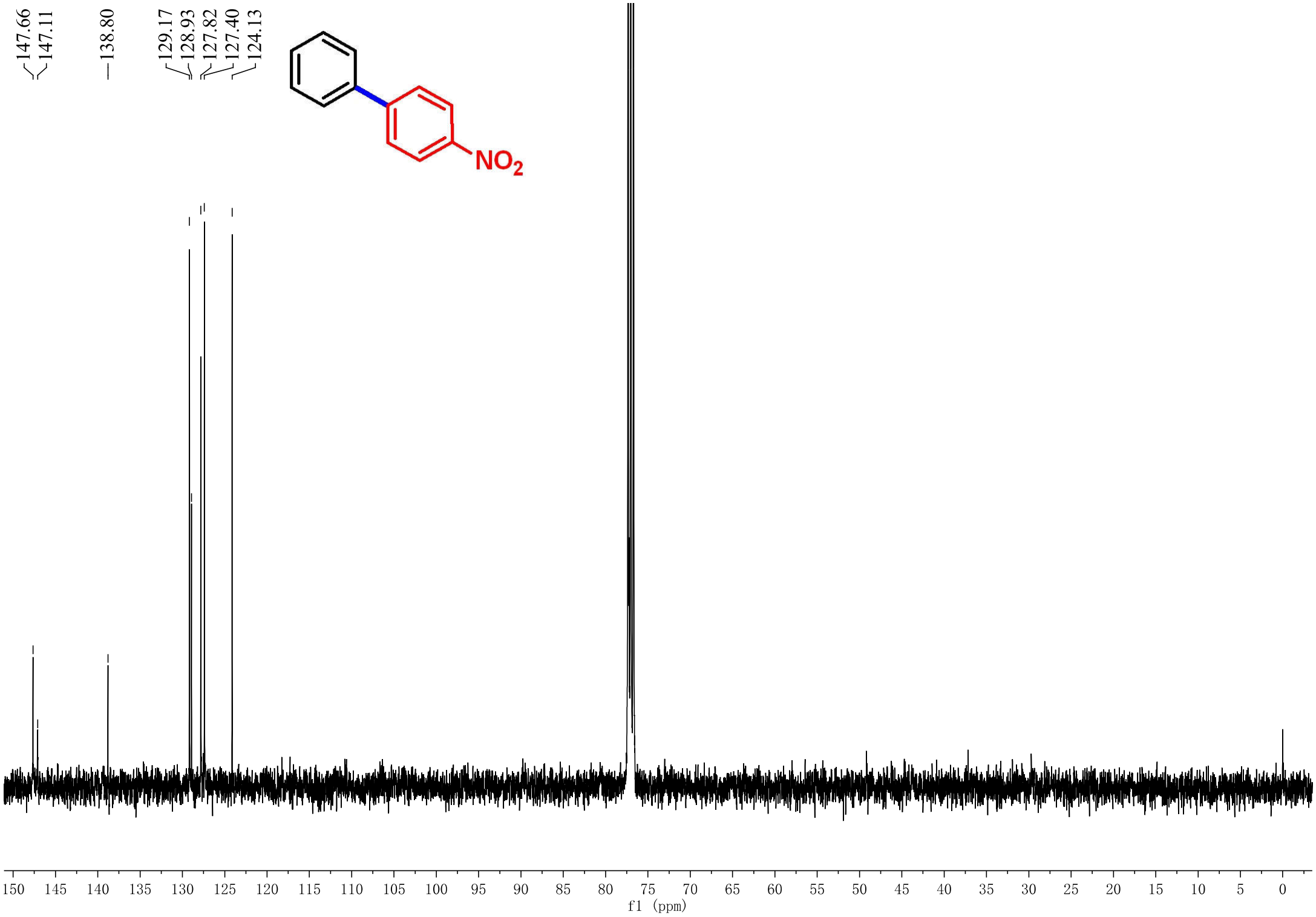
2.00
2.03
2.01
3.04
f1 (ppm)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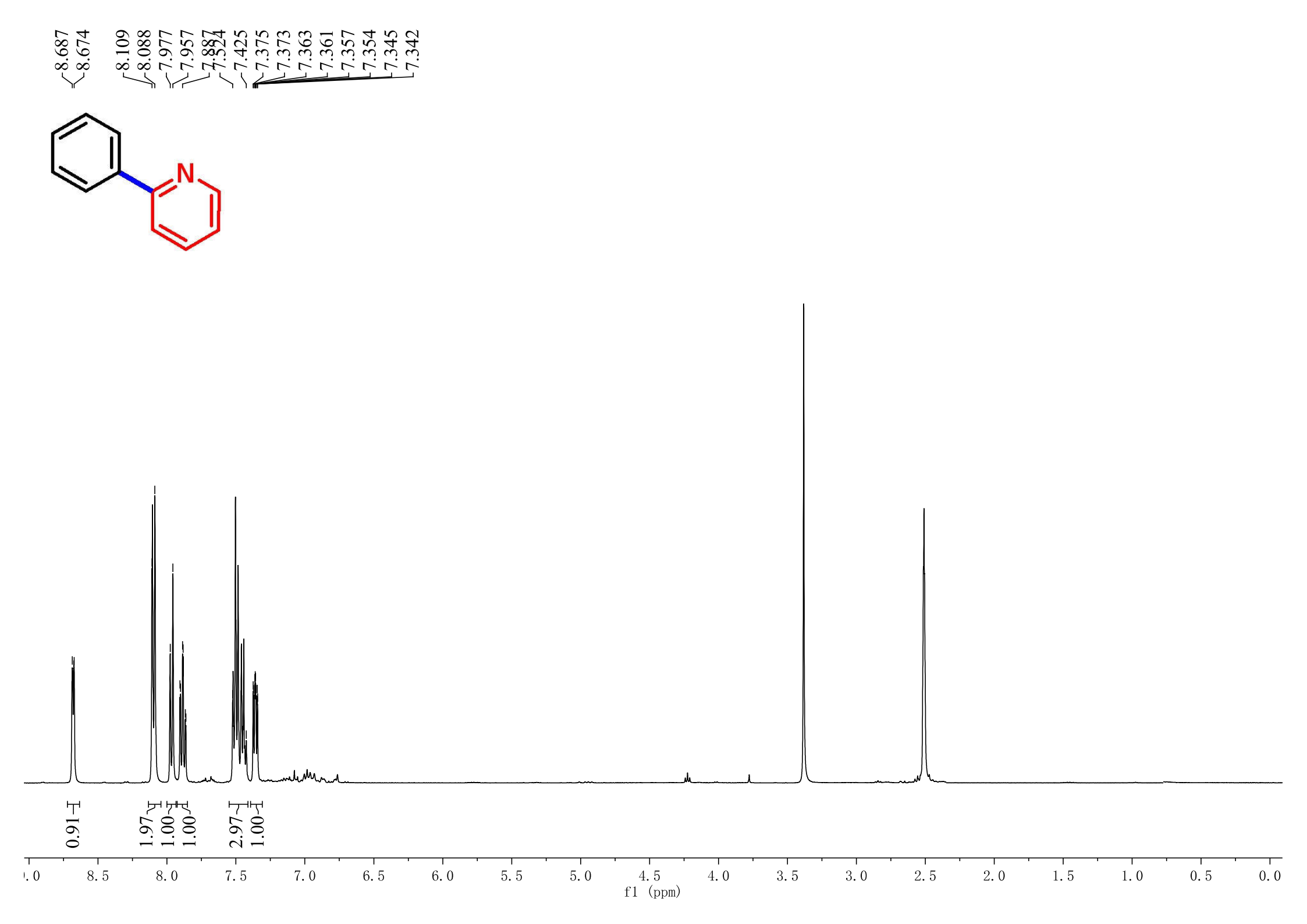
147.11
138.80
129.17
128.93
127.82
127.40
124.13
NO2
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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8.674
8.109
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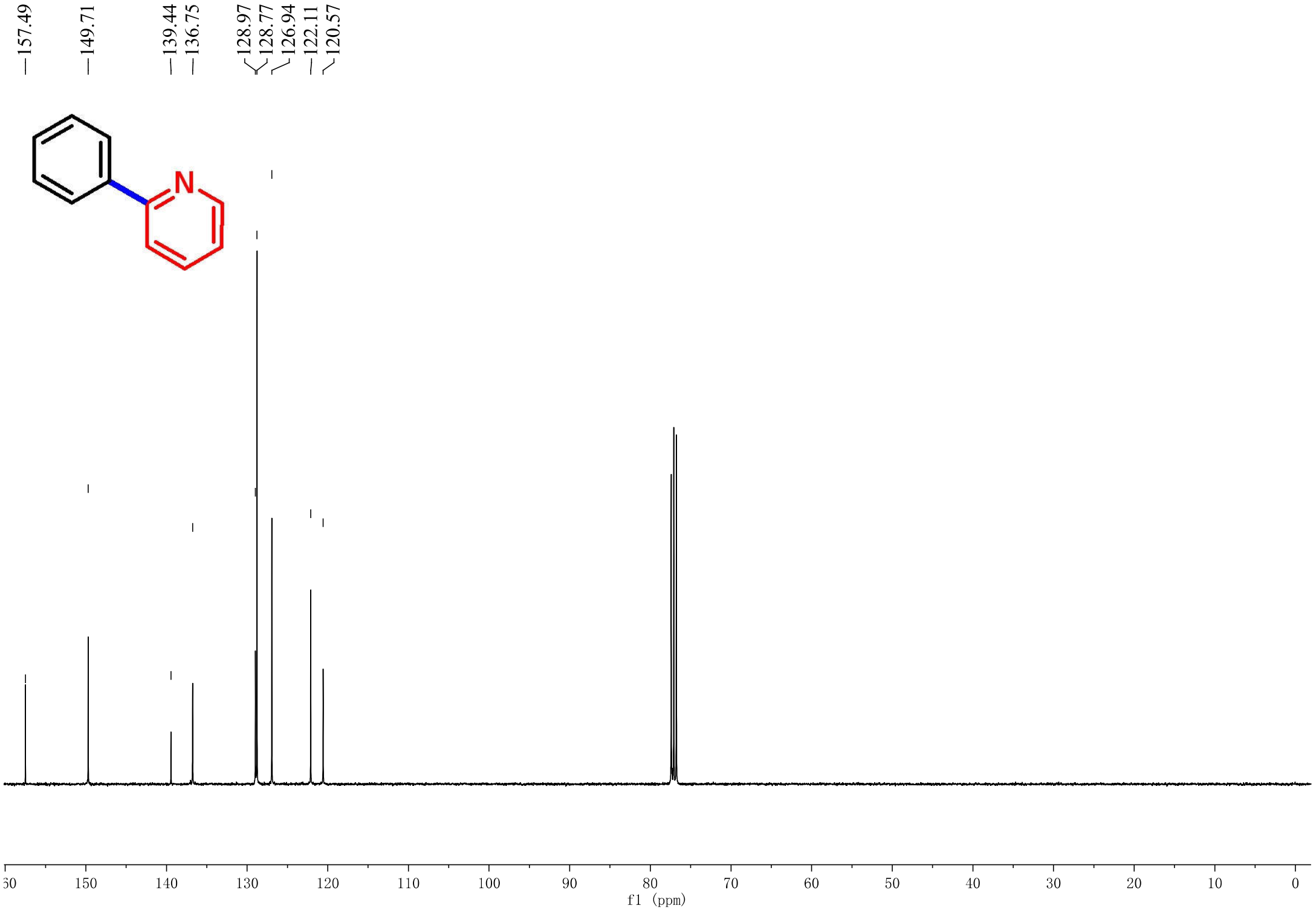
7.957
7.887
7.524
7.425
7.375
7.373
7.363
7.361
7.357
7.354
7.345
7.342
N
0.91
1.97
1.00
1.00
2.97
1.00
f1 (ppm)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139.44
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128.97
128.77
126.94
122.11
120.57
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130
120
110
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90
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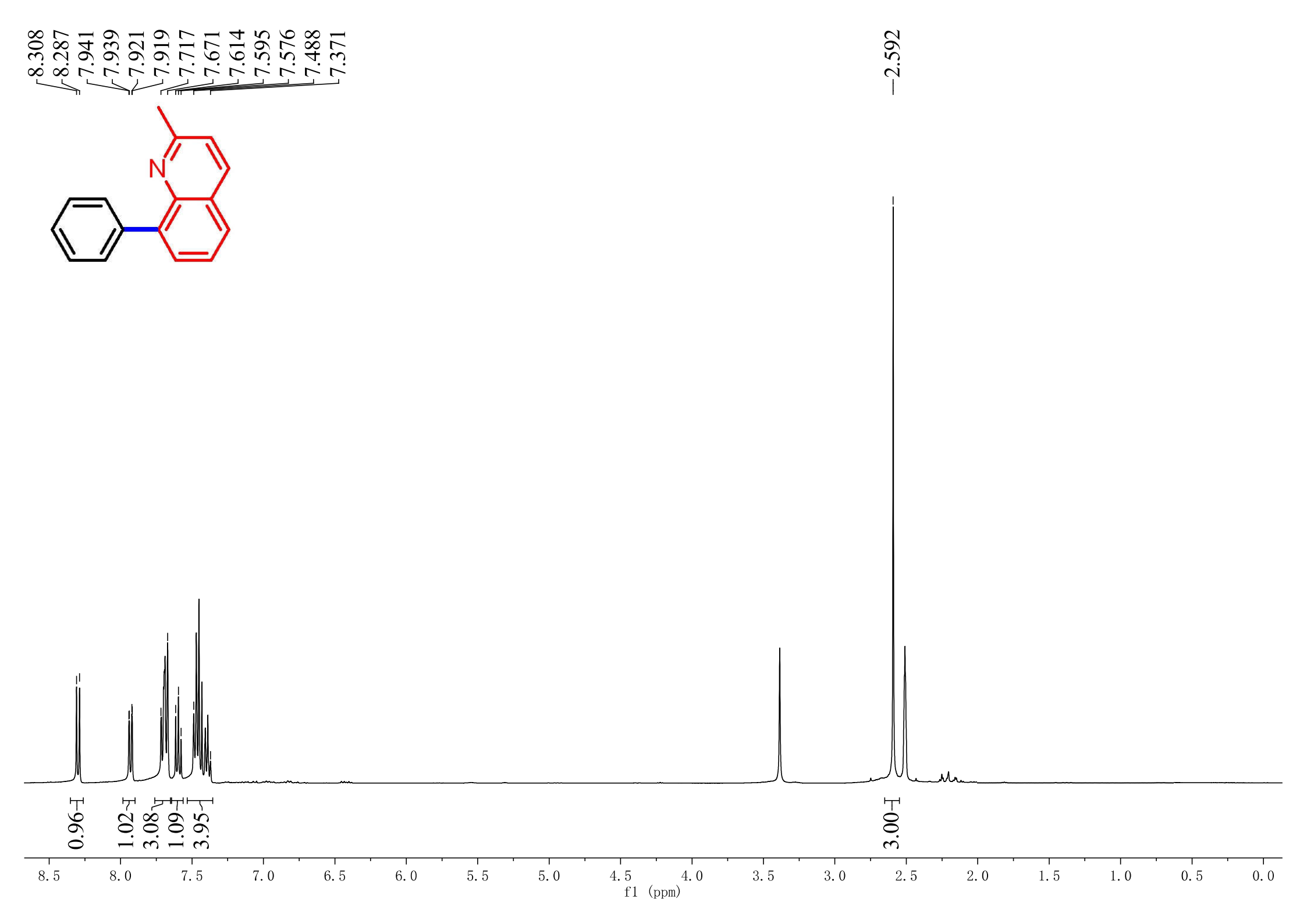
70
60
50
40
30
20
10
0
f1 (ppm)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7.614
7.595
7.576
7.488
7.371
2.592
N
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1.02
3.08
1.09
3.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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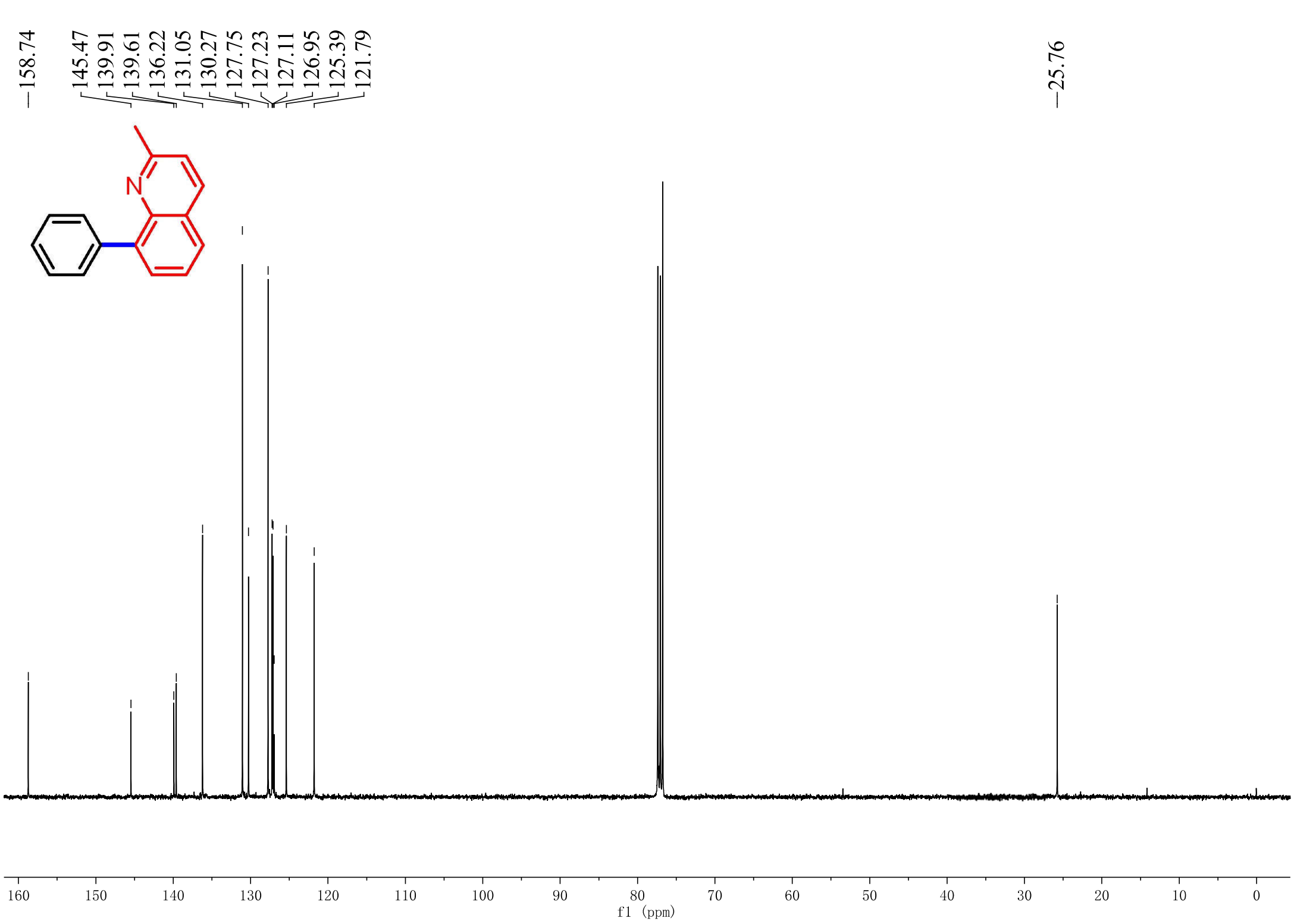
0.0
f1 (ppm)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136.22
131.05
130.27
127.75
127.23
127.11
126.95
125.39
121.79
25.76
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150
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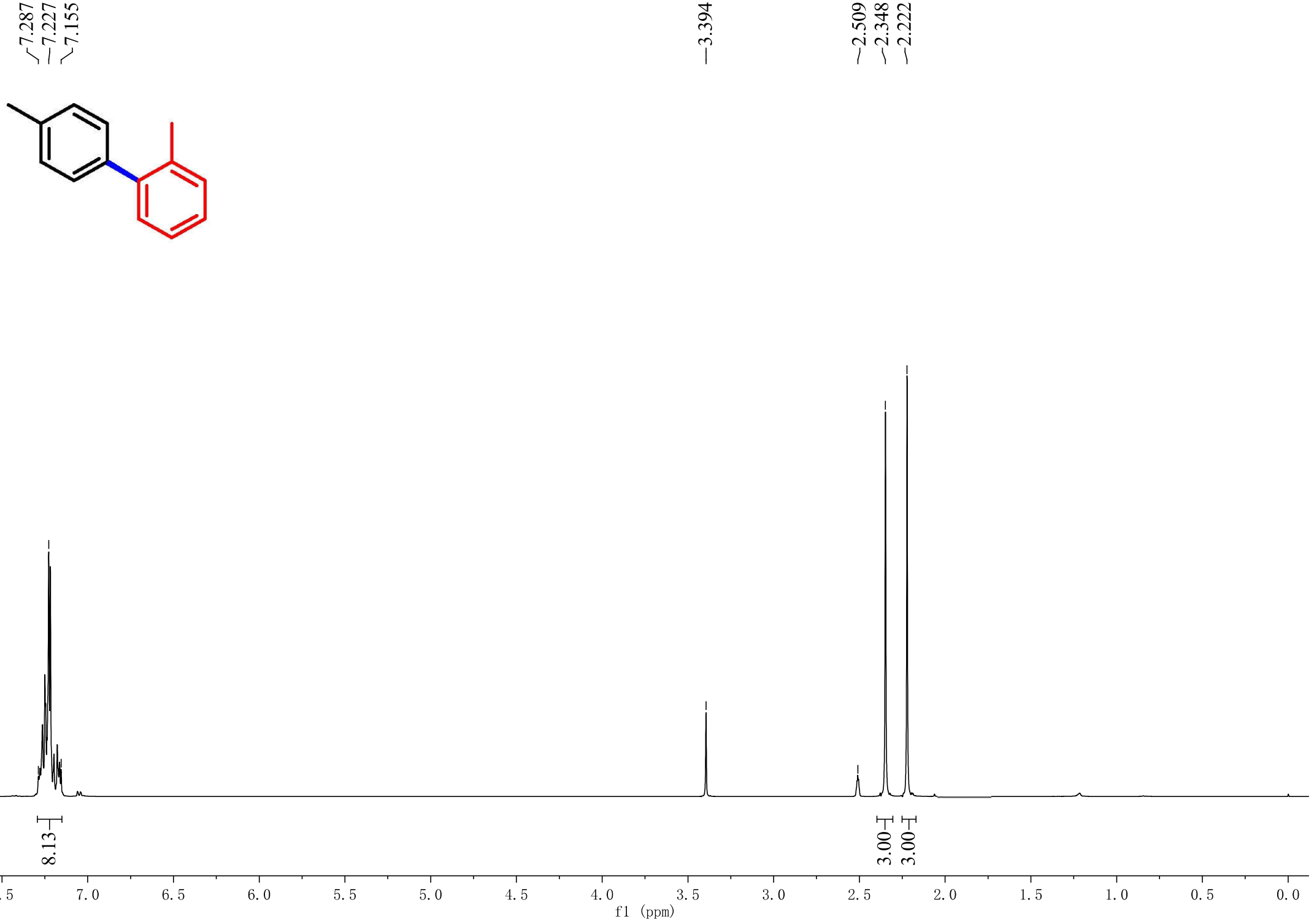
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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2.222
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3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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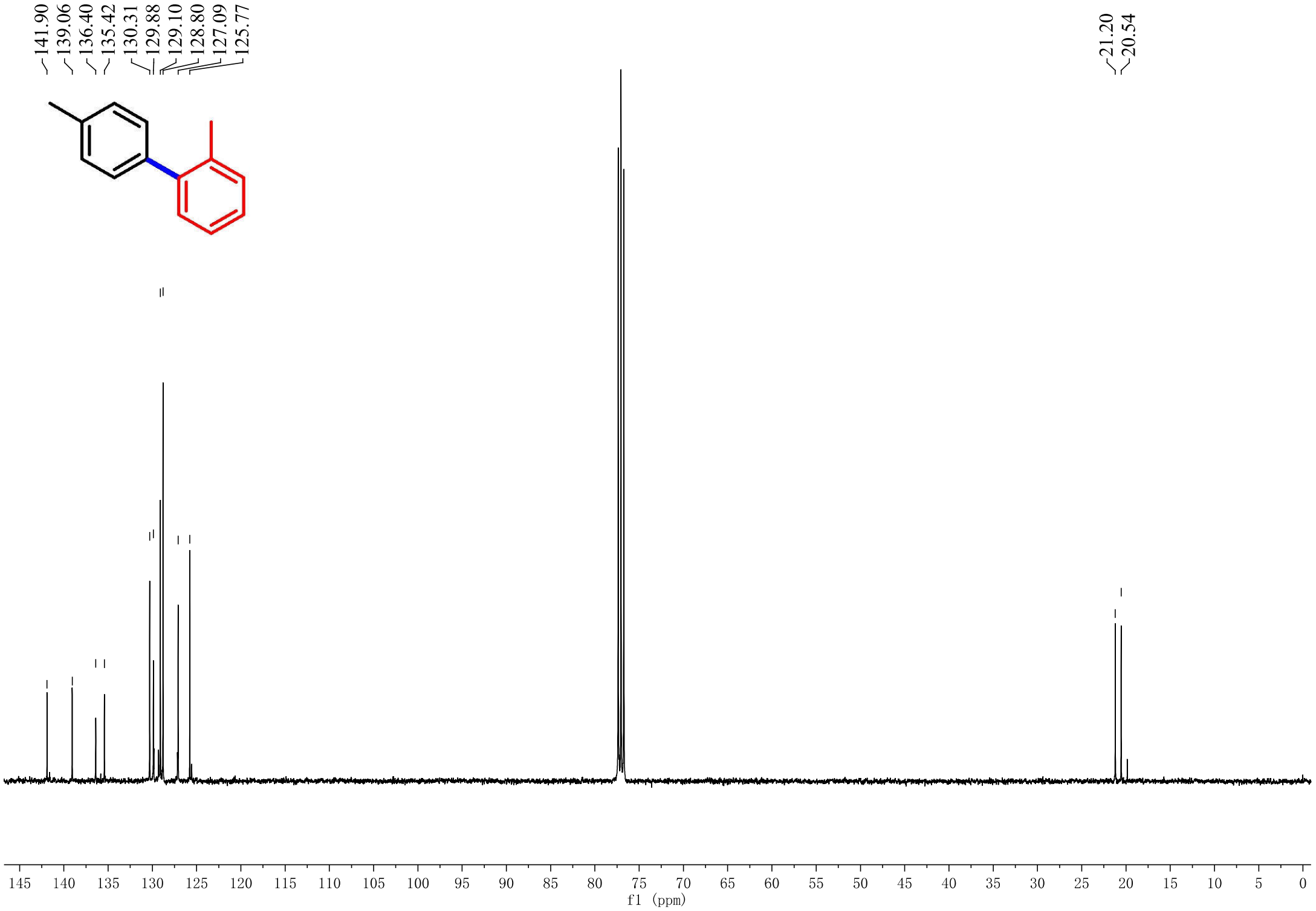
0.0
f1 (ppm)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130.31
129.88
129.10
128.80
127.09
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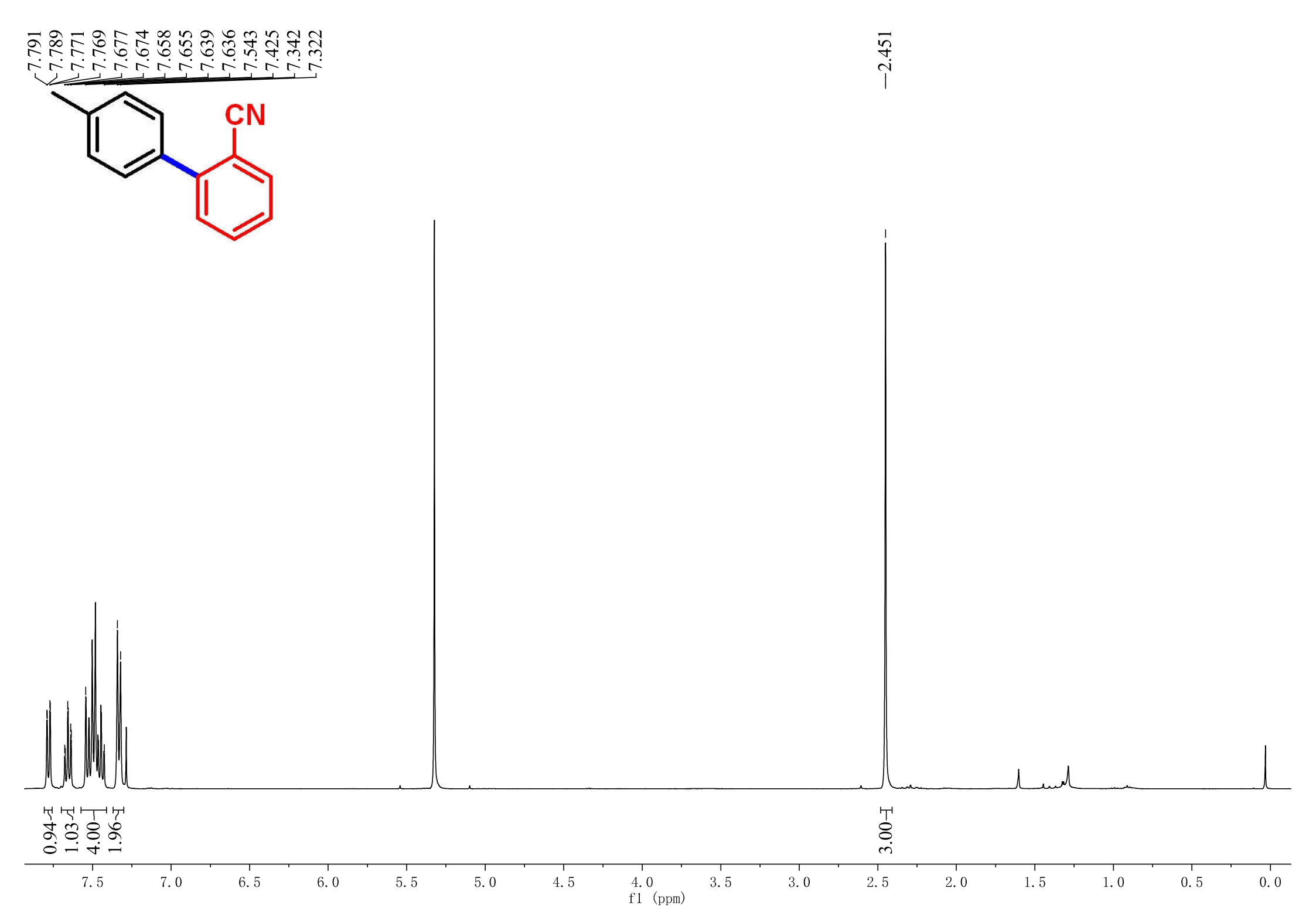
21.20
20.54
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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7.425
7.342
7.322
2.451
CN
0.94
1.03
4.00
1.96
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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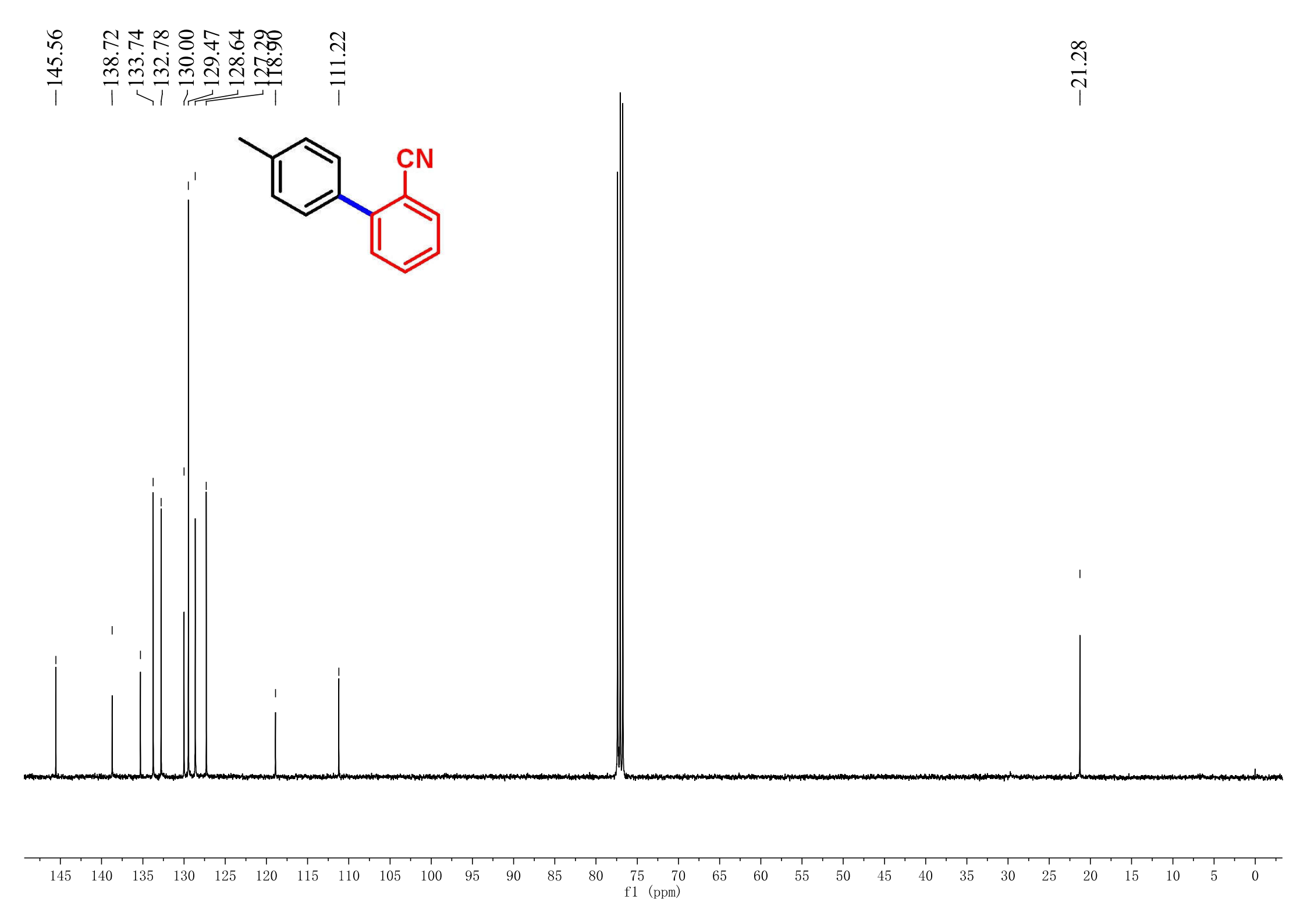
0.0
f1 (ppm)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128.64
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118.90
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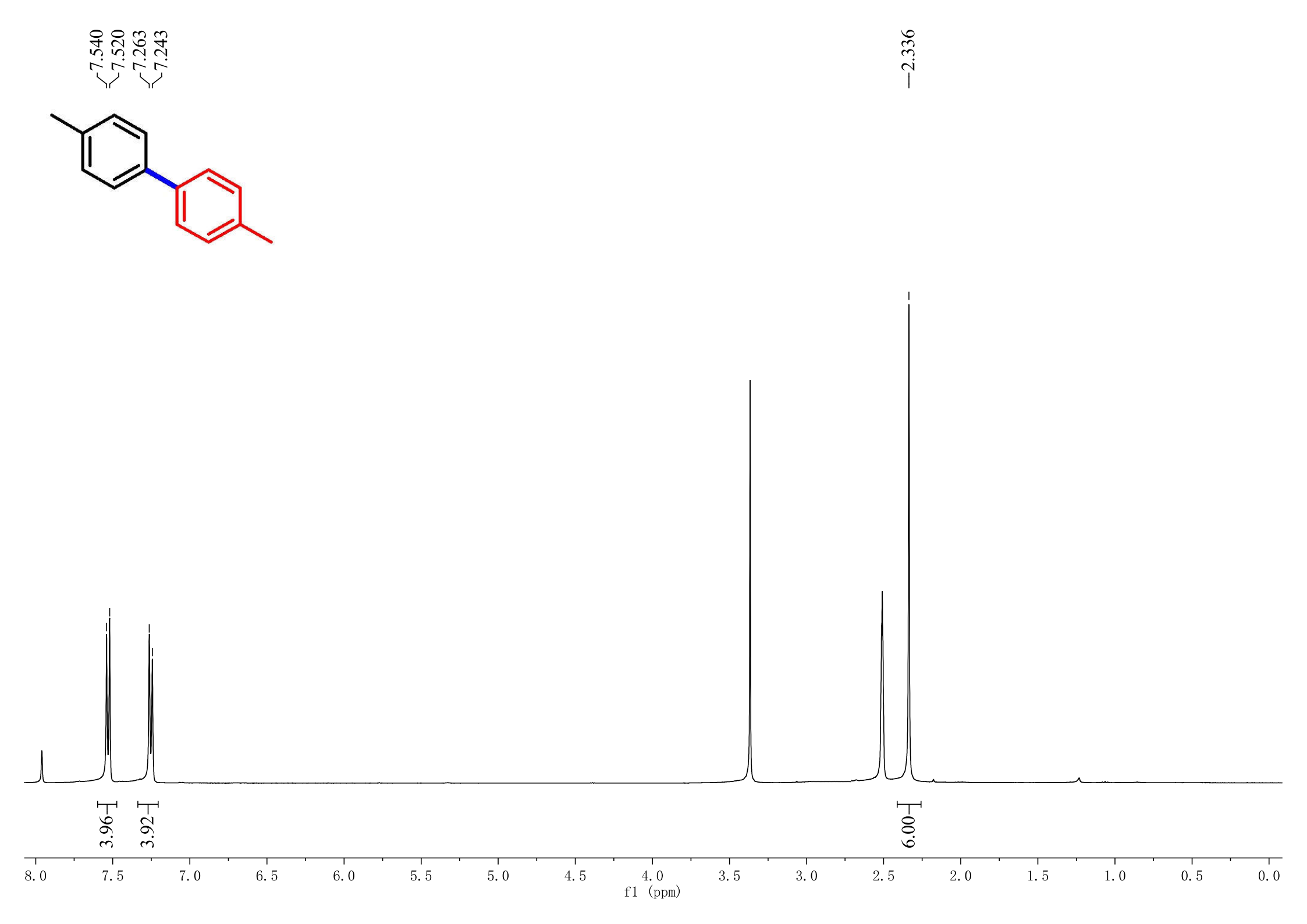
21.28
CN
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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3.92
6.00
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7.0
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6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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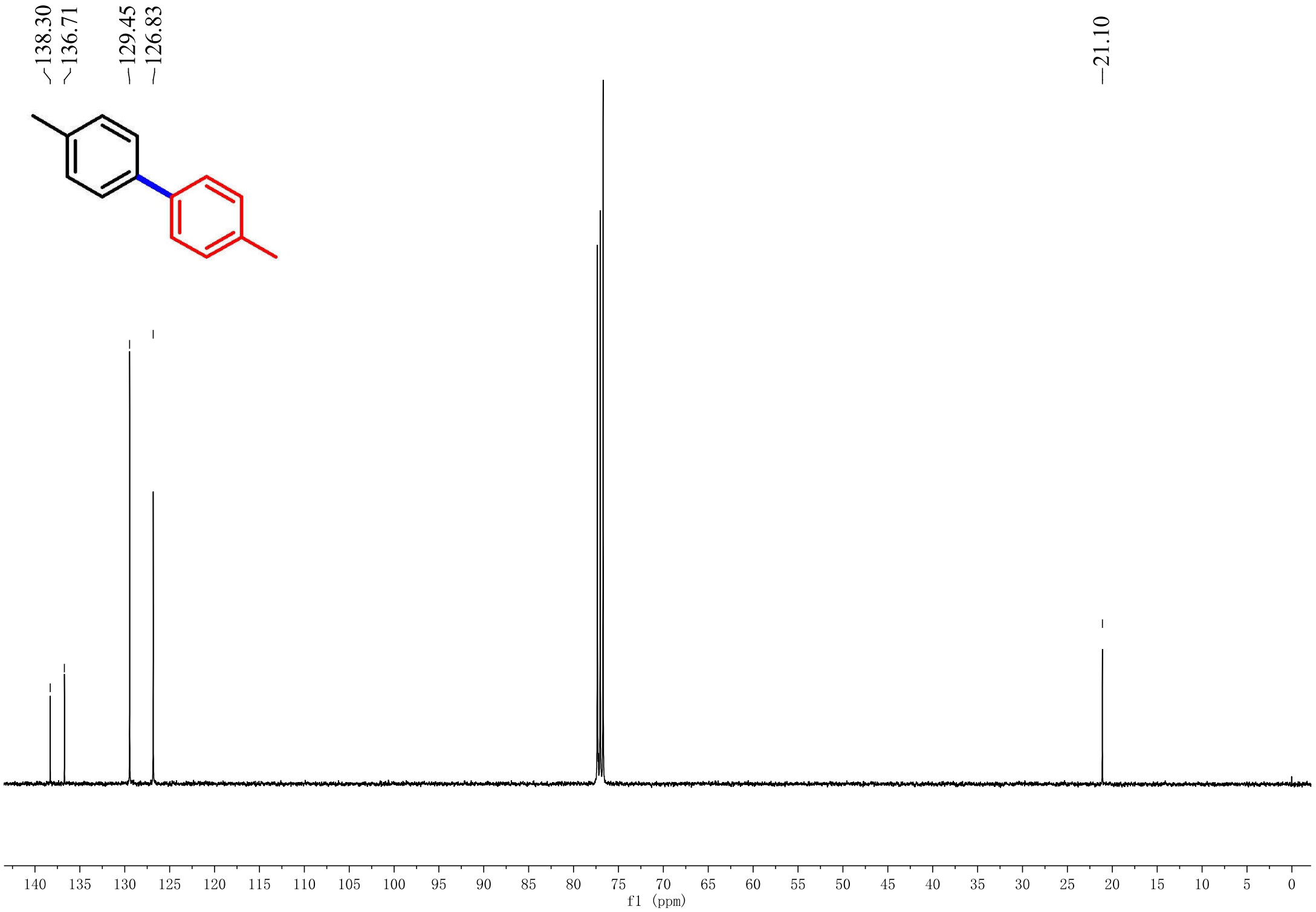
0.0
f1 (ppm)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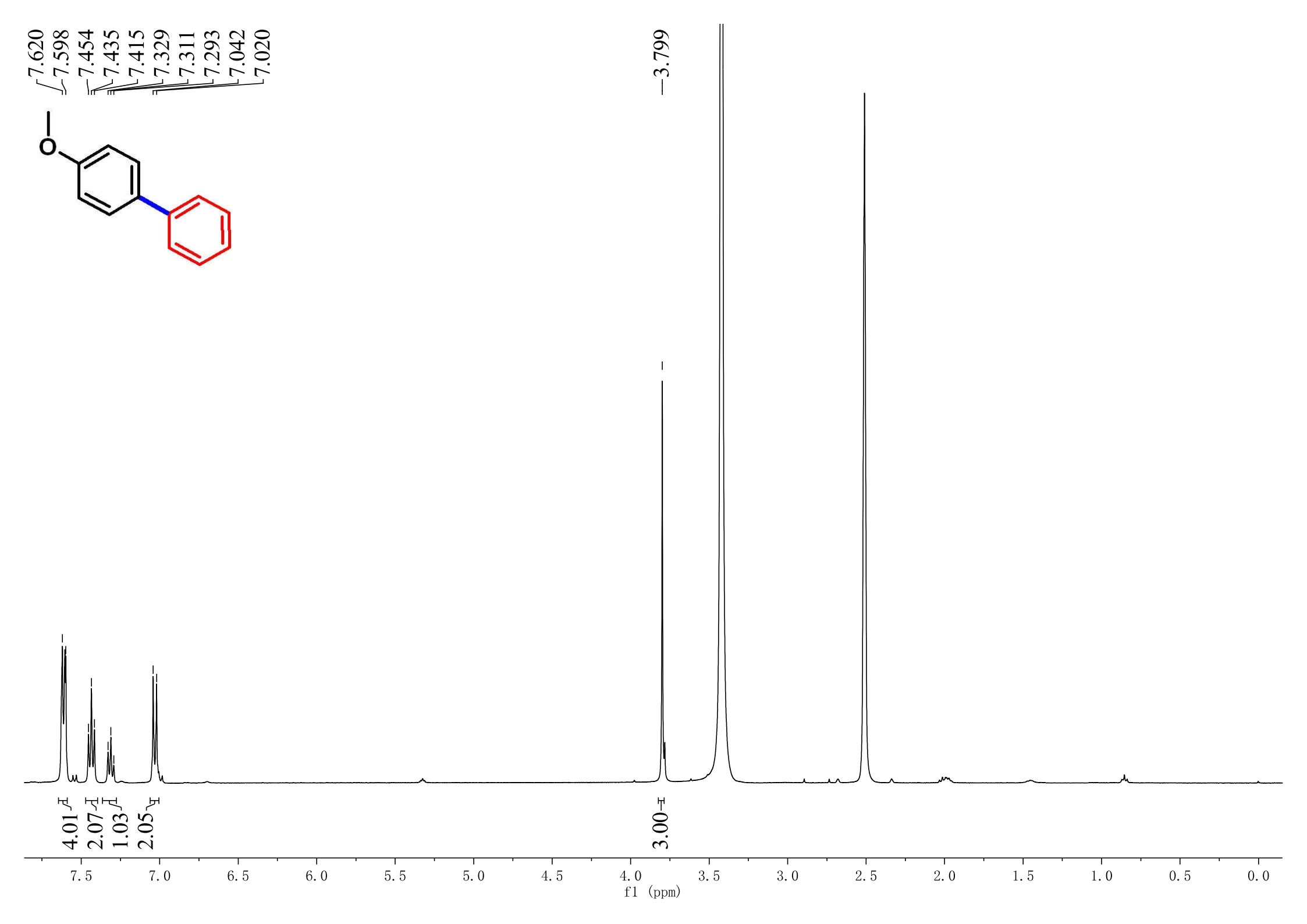
f1 (ppm)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7.020
3.799
O
4.01
2.07
1.03
2.05
3.00
7.5
7.0
6.5
6.0
5.5
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2.5
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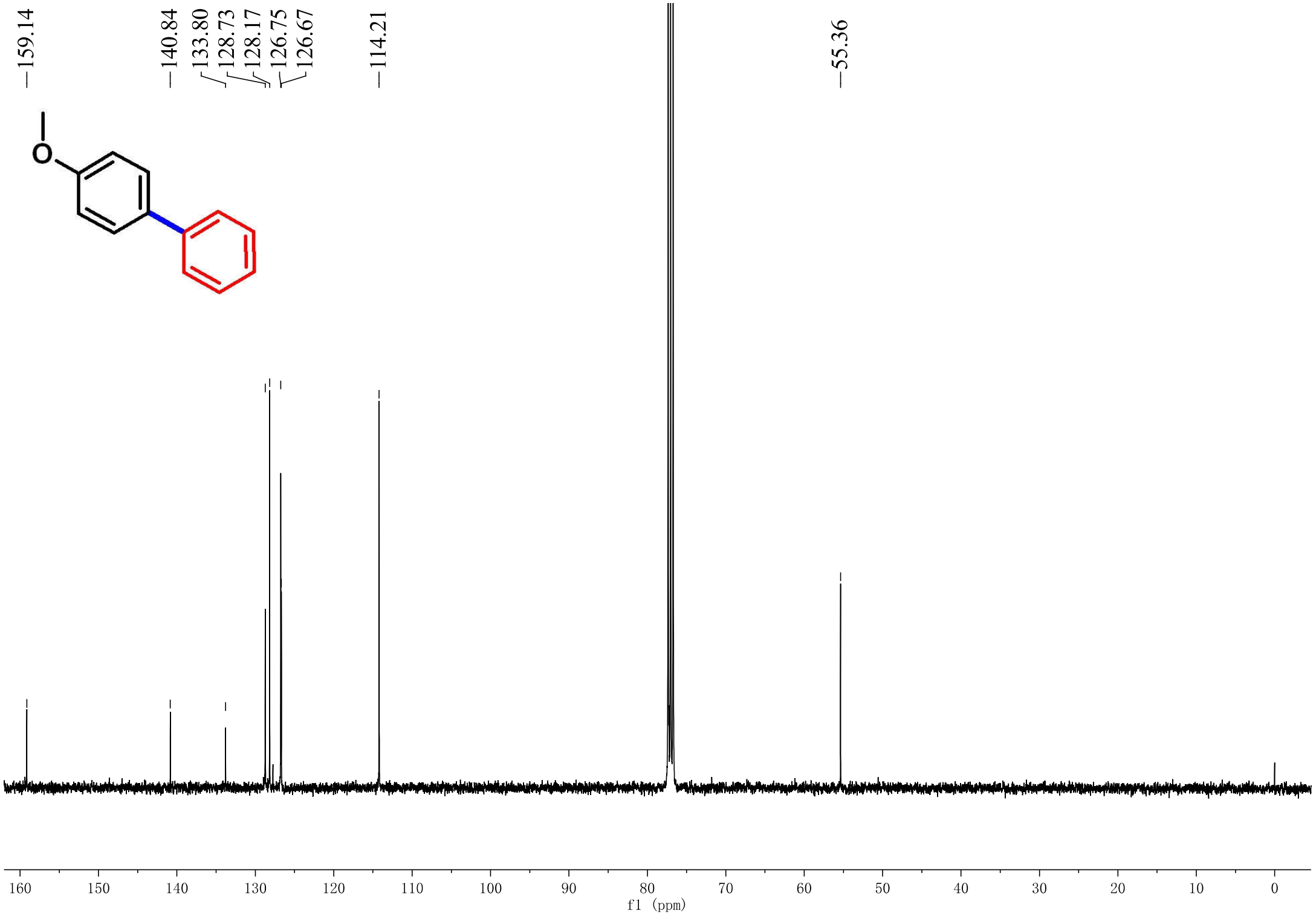
f1 (ppm)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126.75
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114.21
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120
110
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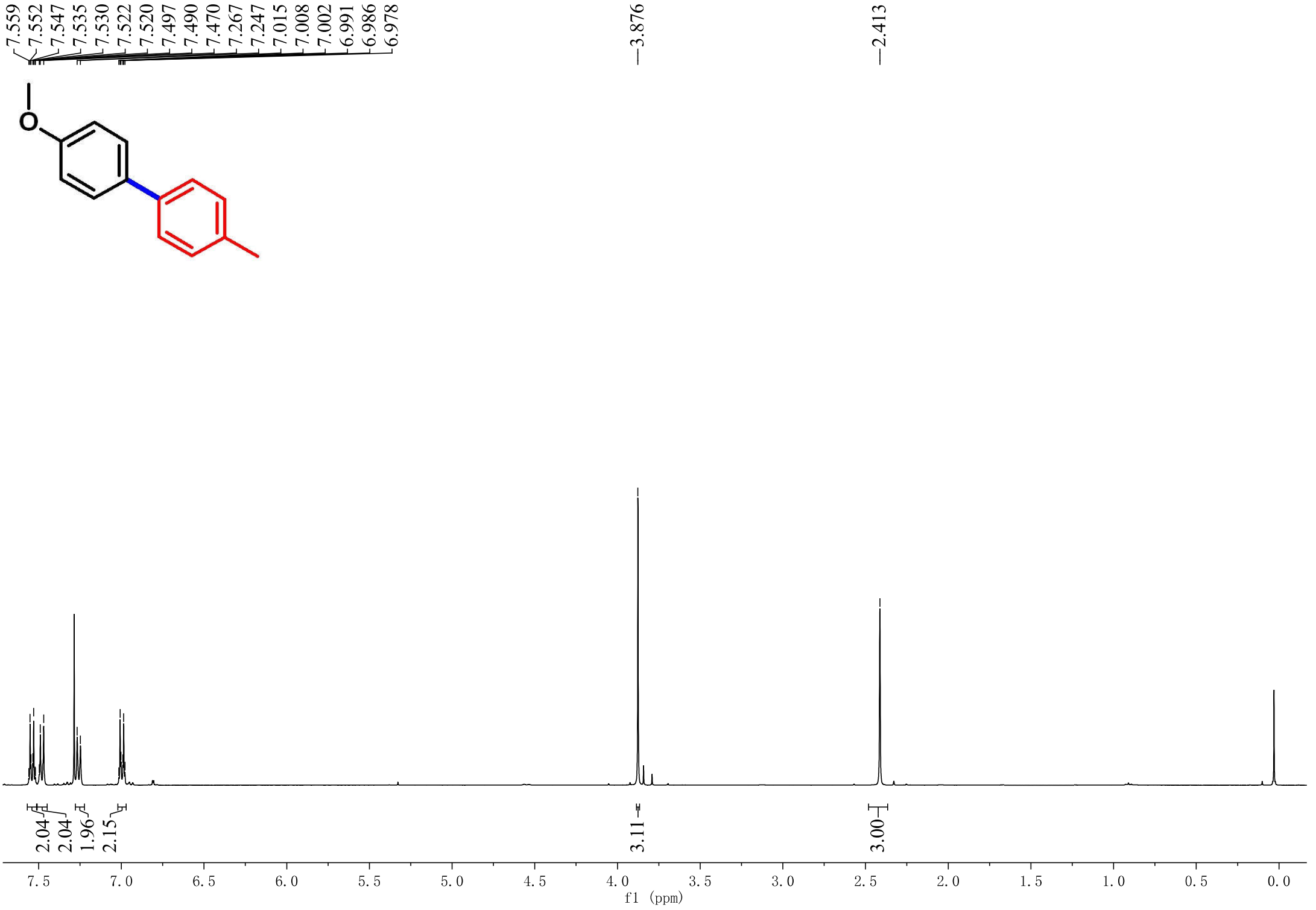
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.267
7.247
7.015
7.008
7.002
6.991
6.986
6.978
3.876
2.413
O
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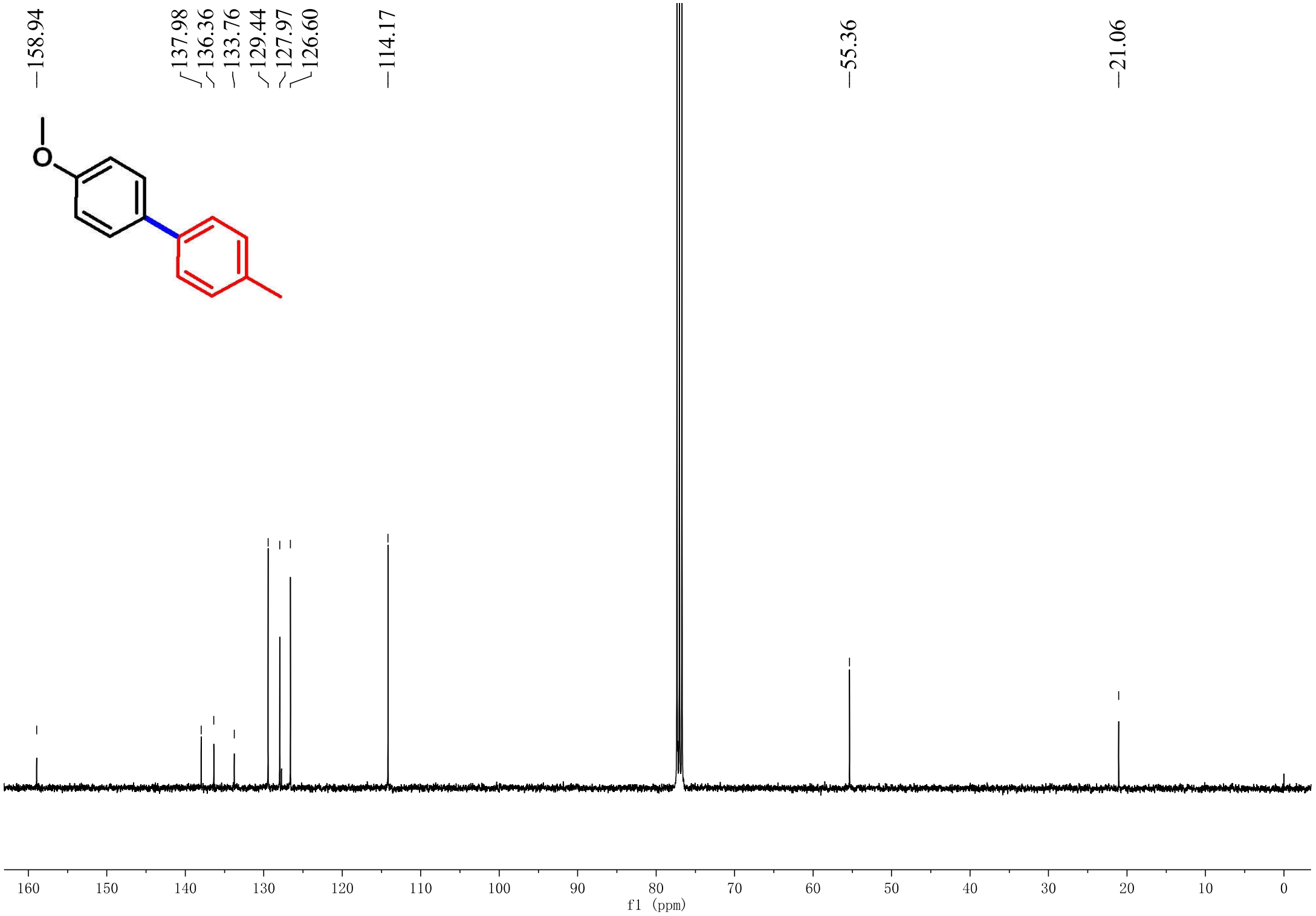
2.04
1.96
2.15
3.11
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130
120
110
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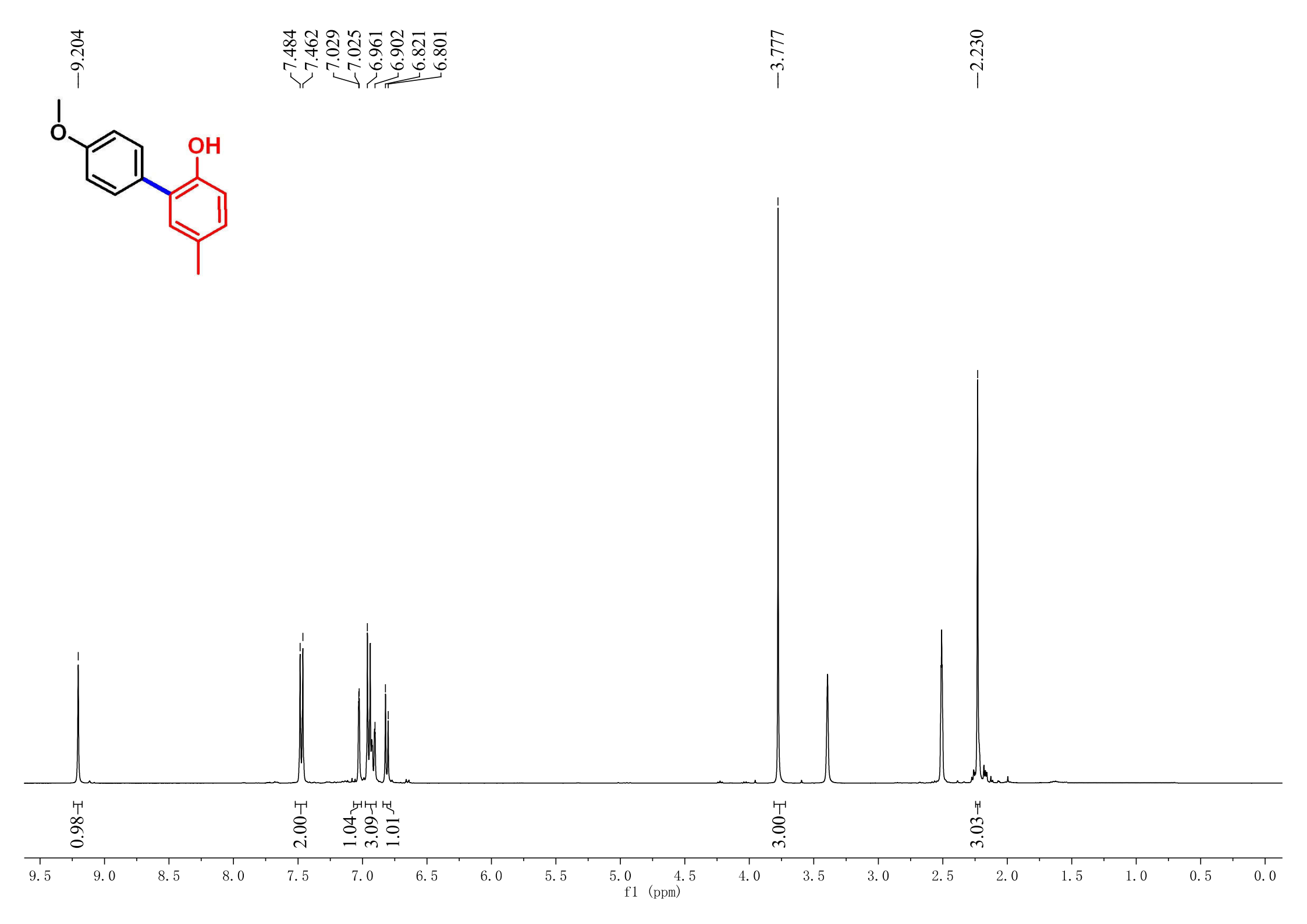
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.821
6.801
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OH
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2.00
1.04
3.09
1.01
3.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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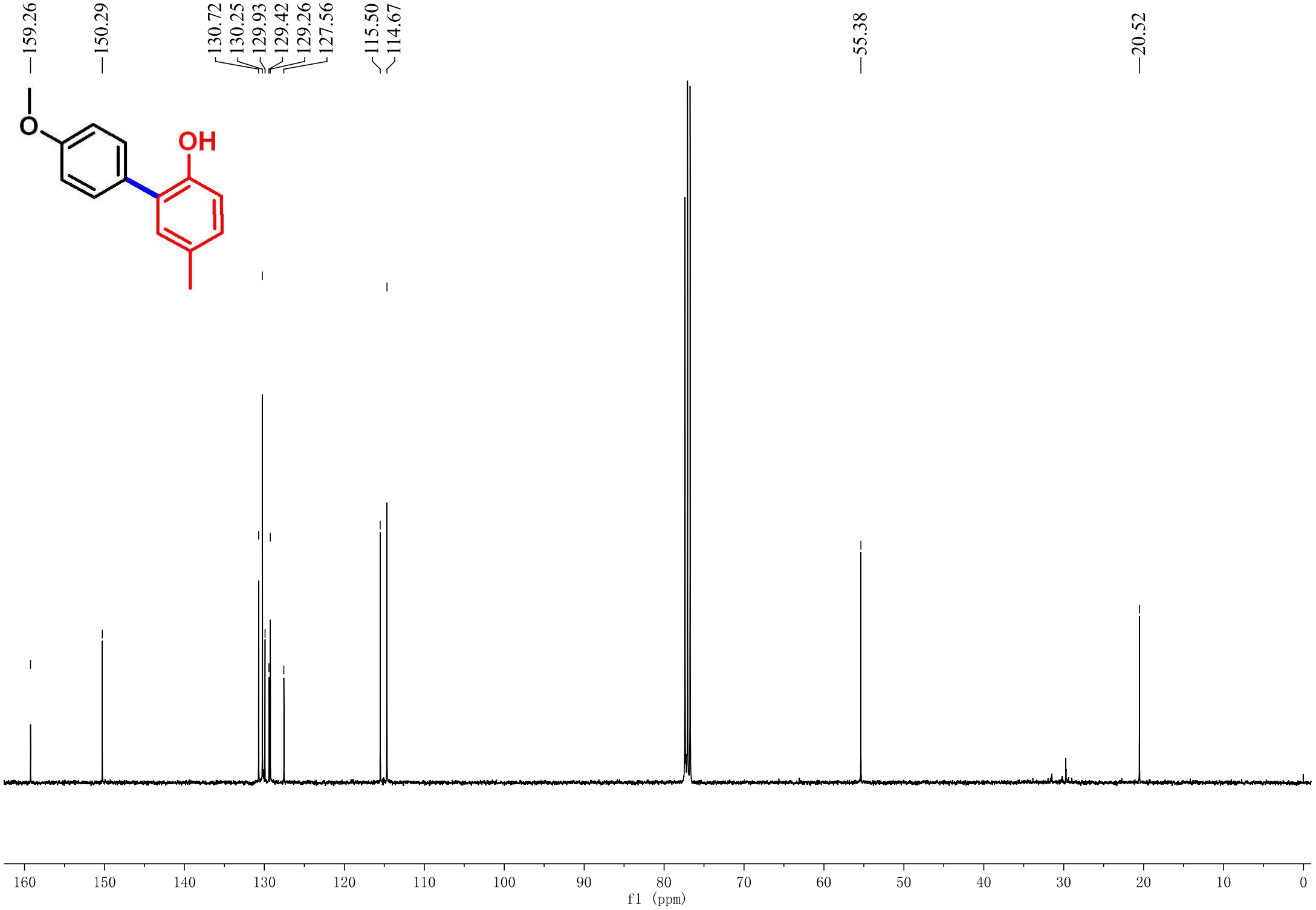
0.0
f1 (ppm)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127.56
115.50
114.67
55.38
20.52
O
OH
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130
120
110
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90
80
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50
40
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10
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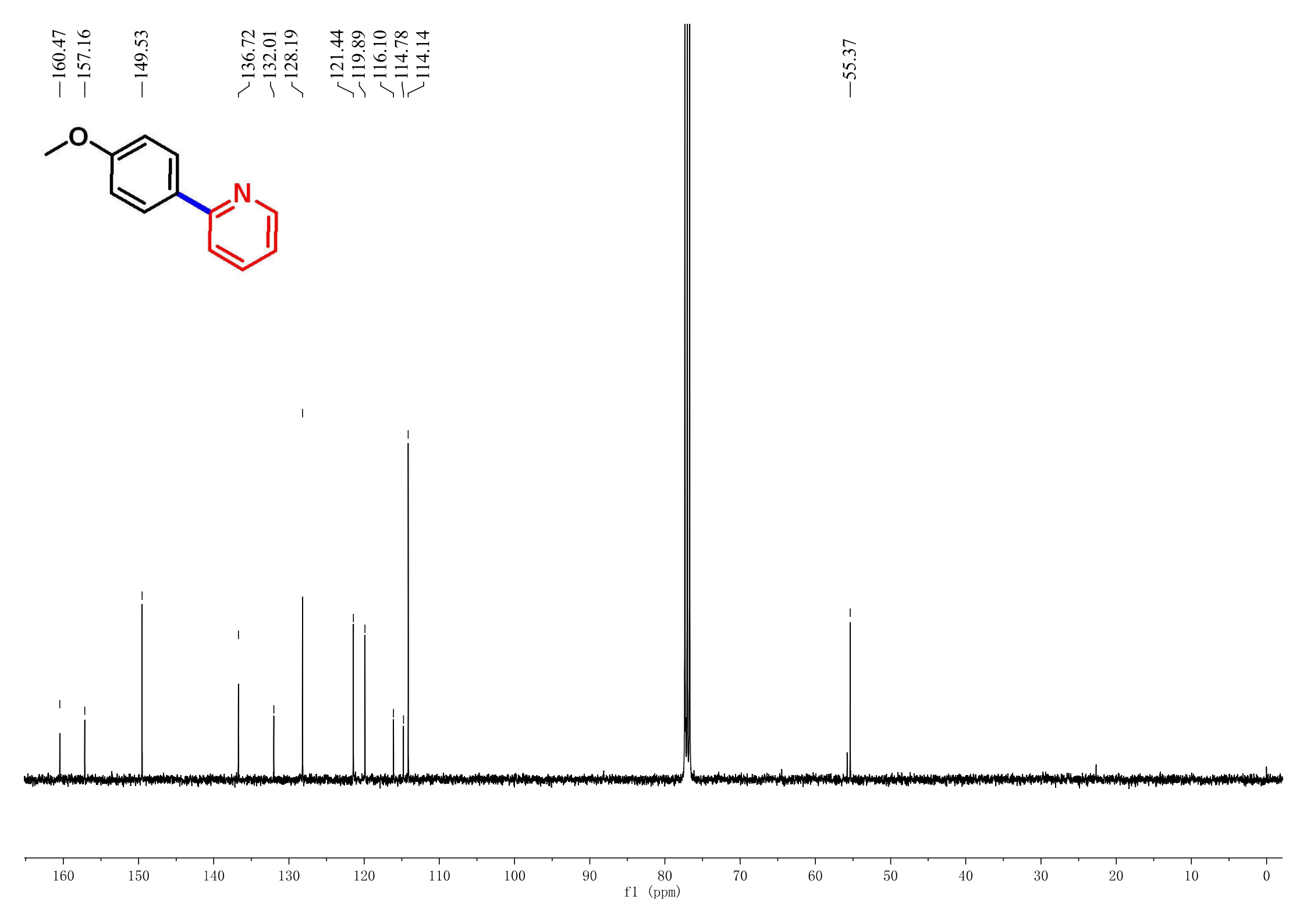
f1 (ppm)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132.01
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119.89
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114.78
114.14
55.37
O
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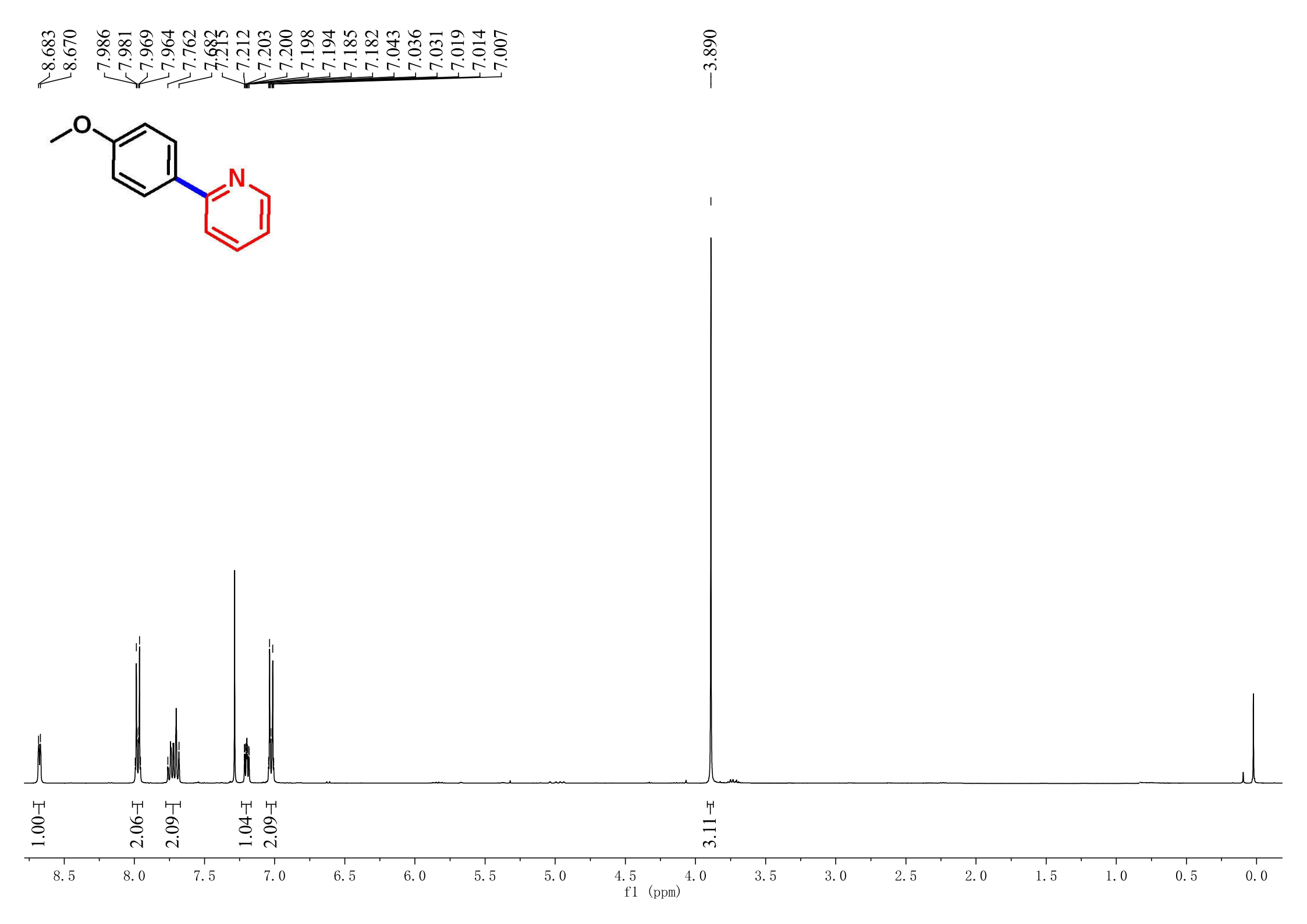
f1 (ppm)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7.194
7.185
7.182
7.043
7.036
7.031
7.019
7.014
7.007
3.890
O
N
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2.06
2.09
1.04
2.09
3.11
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7.0
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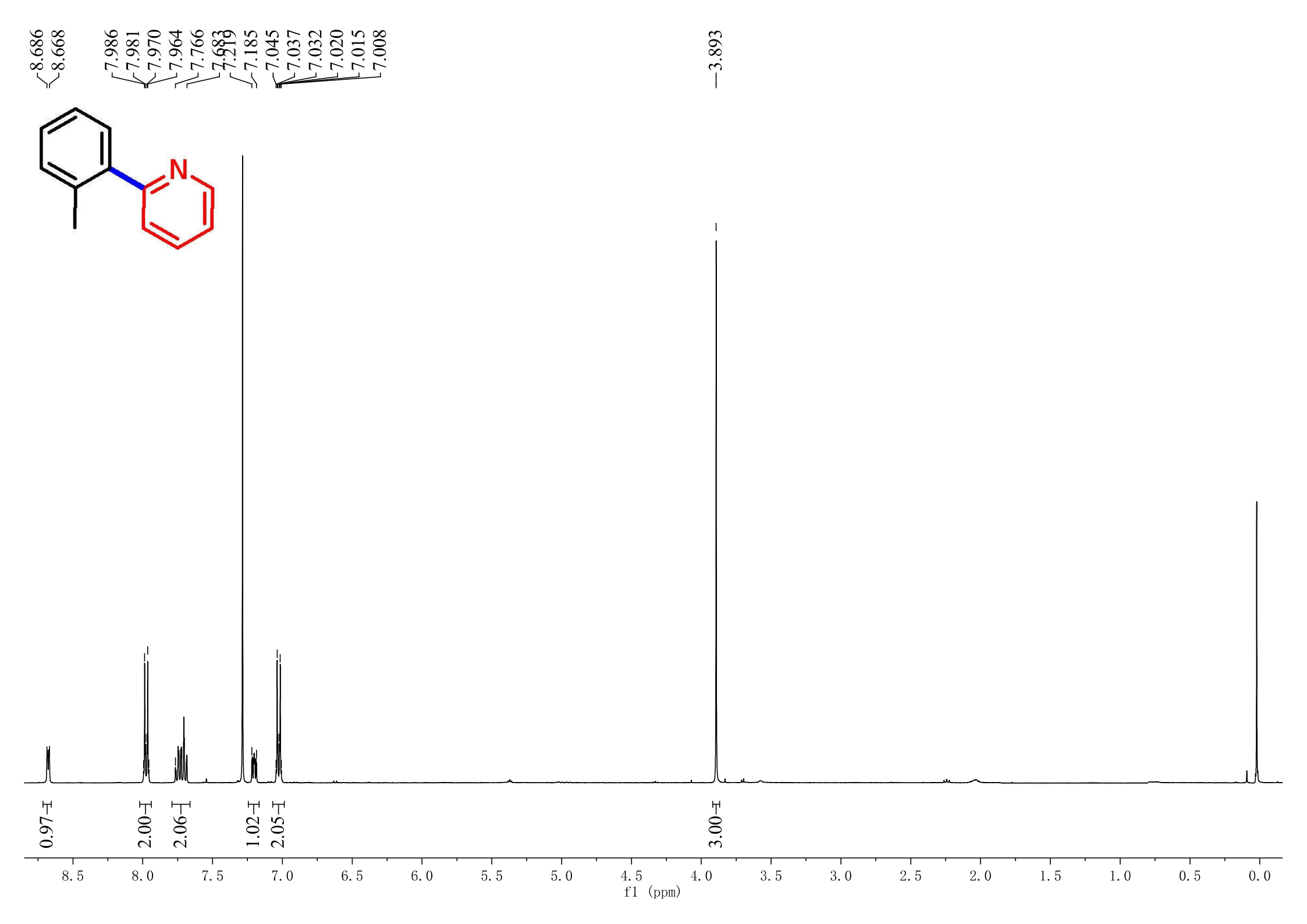
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7.032
7.020
7.015
7.008
3.893
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1.02
2.05
3.00
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7.5
7.0
6.5
6.0
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2.5
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1.0
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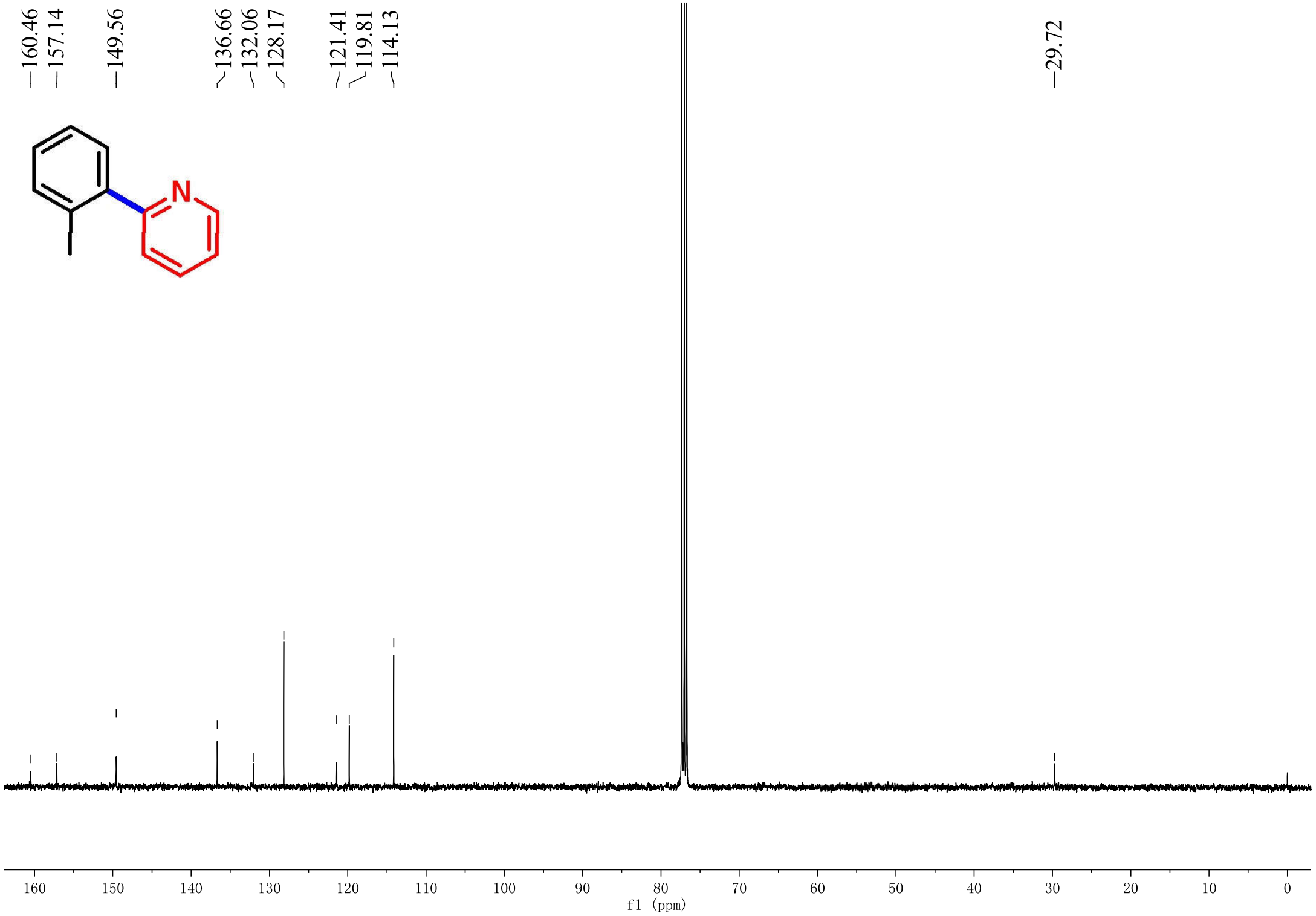
0.0
f1 (ppm)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114.13
29.72
N
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120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)