Electronic Supplementary Material

Iron-catalysed Tandem Cross-dehydrogenative Coupling (CDC) of Terminal Allylic C(sp3) to Styrene and Benzoannulation in the Synthesis of Polysubstituted Naphthalenes

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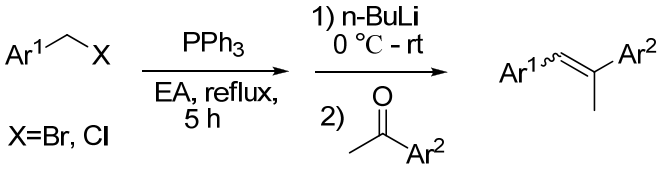
General Remarks

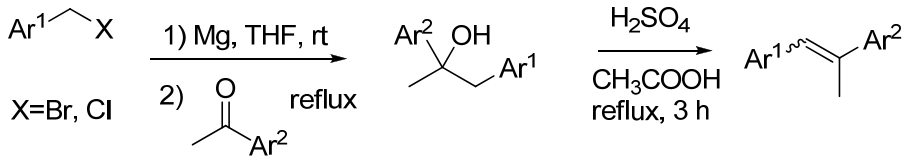
^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal residual chloroform signal at 7.26 ppm as a standard. The data were reported as (s = single, d = double, t = triple, q = quart, m = multiple, brs = broad single, coupling constant(s) in Hz, integration). Proton decoupled ^{13}C NMR spectra were recorded on a Bruker DPX 400 at 100 MHz spectrometer in chloroform-d_3. Chemical shifts were reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

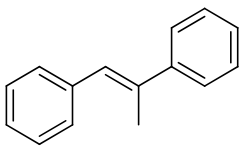
General procedure for 1,2-diarylprop-1-enes 1

Most of the substrates were prepared through Wittig reactions[1], in which the phosphonium salts were obtained by treating the corresponding bromides or chlorides with triphenylphosphine in dry ethyl acetate under reflux for 5 h. The pure *E* isomers were obtained by recrystallization from ethanol.



The remaining substrates were prepared by acetic acid/sulfuric acid dehydration [2] of the propanols, which were obtained *via* a Grignard synthesis.[3] The pure *E* isomers were obtained by recrystallization from ethanol.





(*E*)-1,2-Diphenylprop-1-ene (1a) [4]

Prepared *via* a Wittig reaction, white solid, yield: 42%, Mp: 81 – 82 °C (lit. [4] Mp: 81 – 82 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 2H), 7.42 – 7.20 (m, 8H), 6.84 (s, 1H), 2.28 (d, J = 1.1 Hz, 3H).

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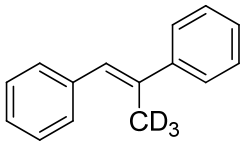
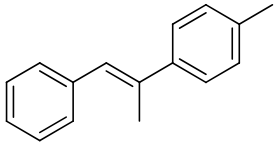


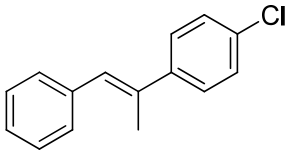
1a-D3

Prepared *via* a Wittig reaction, white solid, yield: 45%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.20 (m, 8H), 6.84 (s, 1H), 2.28 (s, 0.4 H).



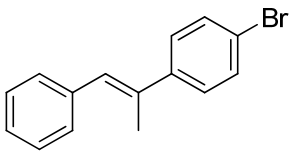
(*E*)-2-(4-Methylphenyl)-1-phenylprop-1-ene (1b) [5]

Prepared *via* a Grignard reaction, white solid, yield: 57%, Mp: 68 – 69 °C (lit. [6] Mp: 67 – 69 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.35 (m, 4H), 7.27 – 7.22 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 1.0 Hz, 1H), 2.38 (s, 3H), 2.28 (d, *J* = 1.3 Hz, 3H).



(*E*)-2-(4-Chlorophenyl)-1-phenylprop-1-ene (1c)

Prepared *via* a Grignard reaction, white solid, yield: 58%, Mp: 75 – 76 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.30 (m, 6H), 7.29 – 7.22 (m, 1H), 6.82 (s, 1H), 2.25 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.1, 136.3, 133.0, 129.2, 128.5, 128.3, 128.2, 127.3, 126.7, 17.4. IR ν 3023, 2976, 2917, 1487, 1445, 1400, 1091, 1006, 820, 747, 701, 681, 514 cm^{-1}. HRMS (EI): Calcd for $C_{15}H_{13}Cl$: 228.0706 , $[M]^+$, found: 228.0707



(*E*)-2-(4-Bromophenyl)-1-phenylprop-1-ene (1d)

Prepared *via* a Grignard reaction, white solid, yield: 55%, Mp: 87 – 89 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.44 – 7.35 (m, 6H), 7.32 – 7.25 (m, 1H), 6.85 (s, 1H), 2.28 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.0, 136.3, 131.4, 129.2, 128.3, 128.2, 127.7, 126.7, 121.1, 17.4. IR ν 3024, 2948, 2919, 1486, 1444, 1397, 1074, 1003, 818, 743, 699, 514 cm^{-1}. HRMS (EI): Calcd for $C_{15}H_{13}Br$: 272.0201, $[M]^+$, found: 272.0203

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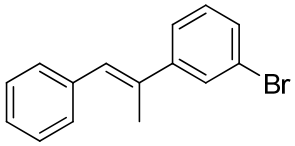
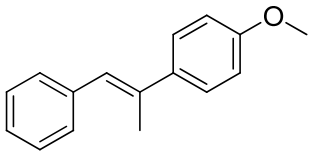


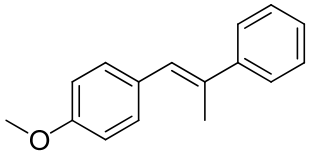
(*E*)-2-(3-Bromophenyl)-1-phenylprop-1-ene (1e)

Prepared *via* a Grignard reaction, white solid, yield: 52%, Mp: 64 – 66 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.46 – 7.31 (m, 6H), 7.28 – 7.19 (m, 2H), 6.82 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 137.9, 136.1, 130.1, 129.9, 129.2, 128.8, 128.3, 126.8, 124.7, 122.6, 17.4. IR ν 3089, 2923, 2854, 1552, 1480, 1439, 1405, 1065, 970, 872, 789, 748, 705, 519 cm^{-1}. HRMS (EI): Calcd for $C_{15}H_{13}Br$: 272.0201, $[M]^+$, found: 272.0202.



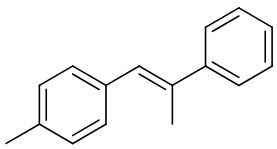
(*E*)-2-(4-Methoxyphenyl)-1-phenylprop-1-ene (1f)

Prepared *via* a Grignard reaction, white solid, yield: 34%, Mp: 101 – 102 °C (lit. [6] Mp: 93 – 94 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.40 – 7.32 (m, 4H), 7.26 – 7.19 (m, 1H), 6.94 – 6.88 (m, 2H), 6.78 (d, J = 1.1 Hz, 1H), 3.83 (s, 3H), 2.26 (d, J = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 138.6, 136.8, 136.4, 129.2, 128.2, 127.1, 126.3, 126.3, 113.7, 55.4, 17.5. IR ν 3016, 2952, 2913, 1603, 1511, 1442, 1255, 1027, 834, 820, 720, 697, 513 cm^{-1}. HRMS (EI): Calcd for $C_{16}H_{16}O$: 224.1201 , $[M]^+$, found: 224.1202



(*E*)-1-(4-Methoxylphenyl)-2-phenylprop-1-ene (1g)

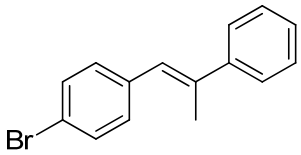
Prepared *via* a Wittig reaction, white solid, yield: 36%, Mp: 86 – 87 °C (lit. [7] Mp: 83 – 84 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 2H), 7.47 – 7.34 (m, 3H), 7.02 – 6.97 (m, 4H), 6.87 (s, 1H), 3.90 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 144.3, 136.0 , 131.0, 130.5, 128.4, 127.4, 127.0, 126.0, 113.7, 55.3, 17.6. IR ν 3028, 2952, 2921, 1598, 1570, 1507, 1441, 1242, 117, 1027, 831, 766, 700, 546 cm^{-1}. HRMS (EI): Calcd for $C_{16}H_{16}O$: 224.1201 , $[M]^+$, found: 224.1203



(*E*)-1-(4-Methylphenyl)-2-phenylprop-1-ene (1h) [8]

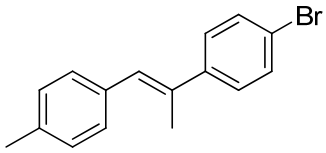
Prepared *via* a Wittig reaction, white solid, yield: 41%, Mp: 51 – 52 °C (lit. [9] Mp: 48 – 49 °C), ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 – 7.24 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 2.38 (s, 3H), 2.29 (d, J = 1.3 Hz, 3H).



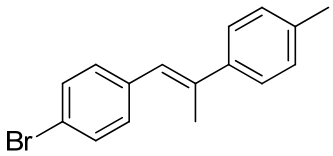
(*E*)-1-(4-Bromophenyl)-2-phenylprop-1-ene (1i) [10]

Prepared *via* a Wittig reaction, white solid, yield: 44%, Mp: 86 – 88 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 1H), 7.24 (d, J = 8.4 Hz, 2H), 6.76 (s, 1H), 2.27 (d, J = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 138.3, 137.3, 131.4, 130.8, 128.4, 127.5, 126.5, 126.0, 120.4, 17.6.



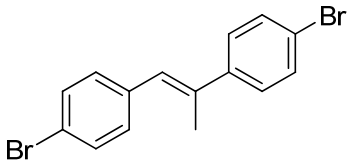
(*E*)-1-(4-Methylphenyl)-2-(4-bromophenyl)prop-1-ene (1j)

Prepared *via* a Wittig reaction, white solid, yield: 39%, Mp: 118 – 119 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.43 – 7.37 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 2.40 (s, 3H), 2.27 (d, J = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 136.5, 135.6, 135.1, 131.4, 129.1, 129.0, 128.2, 127.6, 120.9, 21.3, 17.4. IR ν 3022, 2942, 2920, 2851, 1510, 1489, 1441, 1070, 1009, 887, 825, 522 cm^{-1}. HRMS (EI): Calcd for $C_{16}H_{15}Br$: 286.0357, $[M]^+$, found: 286.0358.



(*E*)-1-(4-Bromophenyl)-2-(4-methylphenyl)prop-1-ene (1k)

Prepared *via* a Wittig reaction, white solid, yield: 41%, Mp: 114 – 115 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.24 – 7.15 (m, 4H), 6.72 (s, 1H), 2.37 (s, 3H), 2.23 (d, J = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.1, 137.4, 137.2, 131.3, 130.8, 129.1, 125.8, 125.7, 120.2, 21.1, 17.5. IR ν 3020, 2951, 2933, 2851, 1510, 1488, 1443, 1375, 1082, 1007, 882, 823, 552, 510 cm^{-1}. HRMS (EI): Calcd for $C_{16}H_{15}Br$: 286.0357, $[M]^+$, found: 286.0361.



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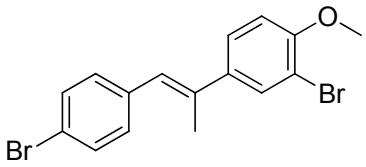
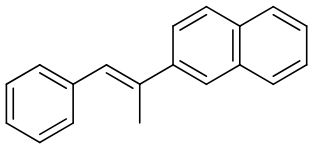
(*E*)-1,2-Di-(4-bromophenyl)prop-1-ene (1l)

Prepared *via* a Wittig reaction, white solid, yield: 44%, Mp: 136 – 137 °C (lit. [11] Mp: 136 – 137 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H), 7.40 – 7.34 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.73 (s, 1H), 2.23 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.1, 136.9, 131.5, 131.4, 130.7, 127.6, 127.0, 121.3, 120.6, 17.4. IR ν 2981, 2948, 2918, 1484, 1400, 1073, 1004, 829, 517 cm^{-1}. HRMS (EI): Calcd for $C_{15}H_{13}Br_2$: 349.9306 , $[M]^+$, found: 349.9305



(*E*)- 2-(3-Bromo-4-methoxyphenyl) - 1-(4-bromophenyl)prop-1-ene (1m)

Prepared *via* a Wittig reaction, white solid, yield: 40%, Mp: 114 – 116 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.67 (s, 1H), 3.90 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 137.4, 137.0, 136.4, 131.3, 130.9, 130.8, 126.0, 120.4, 111.7, 111.6, 56.4, 17.4. IR ν 3015, 2975, 2941, 1589, 1498, 1286, 1261, 1052, 871, 809, 682, 525 cm^{-1}. HRMS (EI): Calcd for $C_{16}H_{14}OBr_2$: 379.9411, $[M]^+$, found: 379.9409.

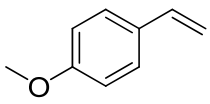


(*E*)-2-Naphthyl-1-phenylprop-1-ene (1n)

Prepared *via* a Wittig reaction, white solid, yield: 34%, Mp: 141 – 142 °C (lit. [12] Mp: 144 – 145 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91 – 7.82 (m, 3H), 7.74 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.54 – 7.38 (m, 6H), 7.32 – 7.26 (m, 1H), 7.03 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 137.3, 133.6, 132.8, 129.3, 128.3, 128.3, 128.2, 127.9, 127.6, 126.6, 126.3, 125.8, 124.8, 124.5, 17.6. IR ν 3054, 3026, 2960, 2917, 1594, 1487, 1443, 1385, 1071, 856, 815, 714, 697, 515 cm^{-1}. HRMS (EI): Calcd for $C_{19}H_{16}$: 244.1252 , $[M]^+$, found: 244.1253

Procedure for the synthesis of styrenes 5

The styrenes **5** were obtained *via* a Wittig reaction. [13]



4-Methoxylstyrene (5b) [14]

Colorless oil, yield: 84%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 6.92 – 6.87 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.16 (d, *J* = 10.9 Hz, 1H), 3.84 (s, 3H).

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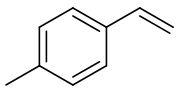
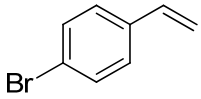


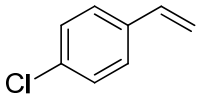
4-Methylstyrene (5c) [15]

Colorless oil, yield: 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 2.35 (s, 3H).



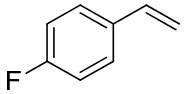
4-Bromostyrene (5d) [16]

Colorless oil, yield: 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.29 – 7.23 (m, 2H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 11.0 Hz, 1H).



4-Chlorostyrene (5e) [17]

Colorless oil, yield: 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H).



4-Fluorostyrene (5f) [18]

Colorless oil, yield: 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.05 – 6.95 (m, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H).

Procedure for cyclopantene derivative 3

To a 10 mL of round bottomed-flask containing (*E*)-1,2-diphenylprop-1-ene **1a** (58 mg, 0.3 mmol) in 2 mL of anhydrous CH_3NO_2 was added $FeCl_3$ in anhydrous CH_3NO_2 (0.3 mL, 0.1 M), DDQ (82 mg, 0.36 mmol) at room temperature. The resulting mixture was heated to 50 °C and stirred for 12 hrs. After the reaction was completed as judged by TLC, the mixture was cooled to room temperature and directly purified by column chromatography on silica gel (eluent: petroleum ether) to give product **3**.

The isotopic labeling experiment was also carried out according to above-mentioned procedure to obtain **3-D5** from **1a-D3**.

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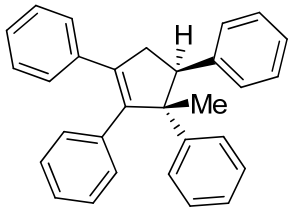
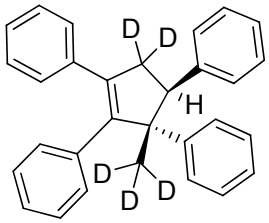


3-Methyl-1,2,3,4-tetraphenylcyclopent-1-ene (3)

Colorless oil, yield: 41%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.13 (m, 9H), 7.11 – 7.00 (m, 5H), 6.88 – 6.82 (m, 2H), 3.88 (t, *J* = 7.9 Hz, 1H), 3.41 (dd, *J* = 16.0, 7.9 Hz, 1H), 3.21 (dd, *J* = 16.0, 7.9 Hz, 1H), 1.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 145.3, 141.6, 138.0, 137.7, 137.4, 129.8, 128.4, 128.4, 128.1, 128.0, 128.0, 127.8, 127.5, 126.9, 126.6, 126.5, 126.0, 60.2, 57.1, 39.8, 19.7. IR ν 3062, 3021, 2951, 2937, 2851, 1600, 1497, 1442, 1369, 1071, 1030, 907, 753, 730, 701, 548 cm^{-1}. HRMS (EI): Calcd for $C_{30}H_{26}$: 386.2035, $[M]^+$, found: 386.2039.



3-Methyl-1,2,3,4-tetraphenylcyclopent-1-ene (3-D5)

Colorless oil, yield: 40%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.13 (m, 9H), 7.11 – 7.00 (m, 5H), 6.88 – 6.82 (m, 2H), 3.86 (s, 1H), 3.40 (d, *J* = 7.9 Hz, 0.13 H), 3.20 (d, *J* = 7.9 Hz, 0.13 H), 1.06 (s, 0.4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 145.3, 141.6, 138.0, 137.7, 137.4, 129.8, 128.4, 128.4, 128.1, 128.0, 128.0, 127.8, 127.5, 126.9, 126.6, 126.5, 126.0, 60.0, 56.8, 39.1 (m), 19.2 (m). IR ν 3061, 3019, 2950, 2935, 2850, 1600, 1490, 1442, 1369, 1071, 1030, 907, 753, 730, 701 cm^{-1}. HRMS (EI): Calcd for $C_{30}D_5H_{21}$: 391.2348, $[M]^+$, found: 391.2338.

The proposed reaction mechanism for the formation of 3.

Instead of forming the desired product **2**, allylic carbocation **A** couples with another equivalent of compound **1a** *via* electrophilic addition to form carbocation **C**, which was then undergoes an electrophilic cyclisation and subsequent deprotonation to form product **3** (as shown in Figure 1). According to this hypothetical reaction pathway, the reaction can be considered as an iron-catalyzed CDC reaction of a monoactivated allylic C-H bond with an alkene. Also we reasoned that carbocation **A** could tautomerize quickly to form more stable allylic carbocation **B**. However, this was not evidenced as coupled product **4** from path c was not detected, perhaps due to steric interactions between cation **B** and **1a**. If this is true, we reasoned, a less hindered simple alkene such as styrene might favor the path c.

Electronic Supplementary Material

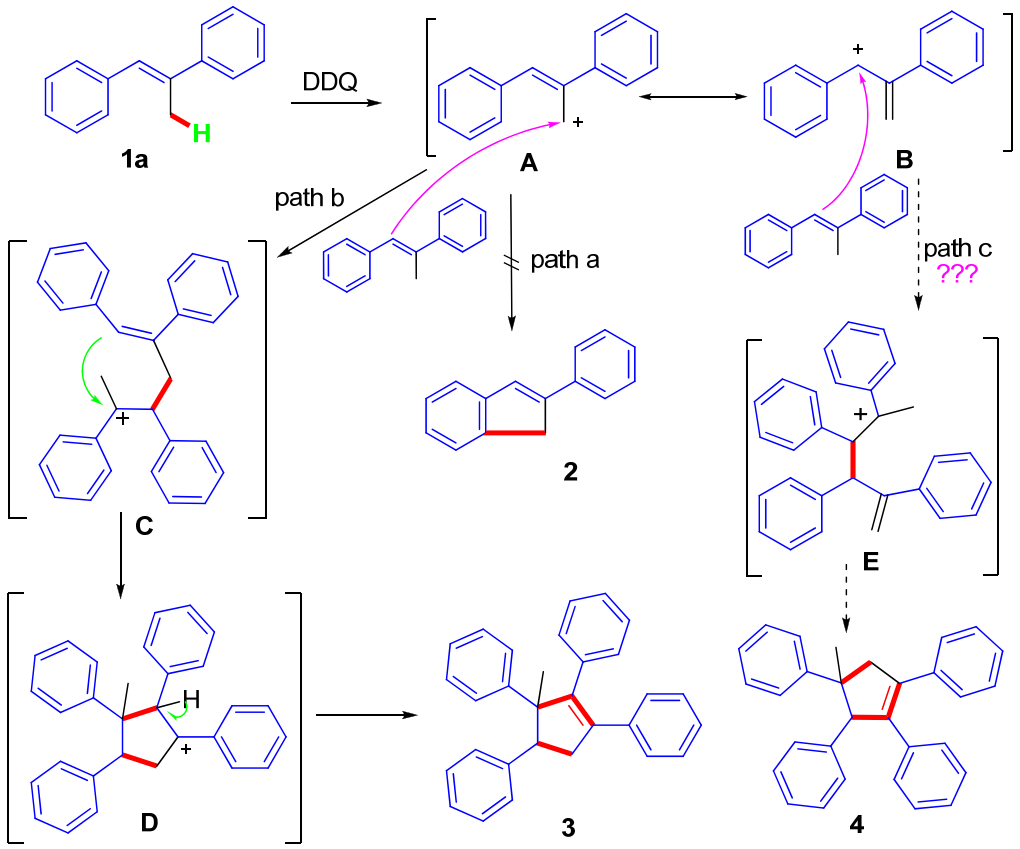


Figure 1. A hypothetical reaction pathway for the formation of **3**.

General procedure for the reaction of (*E*)-1,2-diphenylprop-1-ene 1a and styrene 5a under N_2.

Anhydrous CH_3NO_2 (2 mL) and styrene **5a** (0.051 mL, 0.45 mmol) were added to a dry 10 mL Schlenk tube containing (*E*)-1,2-diphenylprop-1-ene **1a** (58 mg, 0.3 mmol) and the catalyst (0.06 mmol) under a nitrogen atmosphere. DDQ (136 mg, 0.6 mmol) was then added in one portion whilst stirring at room temperature. The resulting mixture was then stirred until the reaction was completed as judged by TLC, the mixture was directly purified by column chromatography on silica gel (eluent: petroleum ether) to give the target product 1-methyl-2,4-diphenylnaphthalene **6aa**.

The optimization of CDC reaction condition for the synthesis of naphthalene 6aa, please see Table 1 and Table 2 for details:

Table 1 : Investigation of the catalyst and their loading.

substrate/styrene / DDQ	Lewis acid	Solvent	Temperature	Time	Yield% [a]
1 / 1.5 / 2	--	CH_3NO_2	r. t.	15 h	N.R [b]
1 / 1.5 / 2	$ZnCl_2$ (20 %)	CH_3NO_2	r. t.	15 h	20 % [b]

1 / 1.5 / 2	$InCl_3$ (20 %)	CH_3NO_2	r. t.	15 h	48 % [b]
1 / 1.5 / 2	$Cu(OTf)_2$ (20 %)	CH_3NO_2	r. t.	15 h	46 % [b]
1 / 1.5 / 2	$FeCl_2$ (20 %)	CH_3NO_2	r. t.	3 h	65 % [b]
1 / 1.5 / 2	$FeCl_3$ (20 %)	CH_3NO_2	r. t.	3 h	68 % [b]
1 / 1.5 / 2	$FeCl_3$ (20 %)	CH_3NO_2	r. t.	3 h	75 % [c]
1 / 2 / 2.5	$FeCl_3$ (20 %)	CH_3NO_2	r. t.	3 h	79 % [c]
1 / 2 / 3	$FeCl_3$ (20 %)	CH_3NO_2	r. t.	3 h	72 % [c]
1 / 2 / 2.5	$FeCl_3$ (2 %)	CH_3NO_2	r. t.	15 h	44 % [c]
1 / 2 / 2.5	$FeCl_3$ (5 %)	CH_3NO_2	r. t.	15 h	67 % [c]
1 / 2 /2.5	$FeCl_3$ (10 %)	CH_3NO_2	r. t.	3 h	79 % [c]
1 / 2 /2.5	$FeCl_3$ (40 %)	CH_3NO_2	r. t.	2h	77 % [c]

a. Isolated yield.

b. The reaction was carried out under N_2.

c. The reaction was carried out under air atmosphere

Table 2. Screening of solvents and reaction temperature.

substrate/styrene / DDQ	Lewis acid	Solvent	Temperature	Time	Yield % [a. b]
1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3NO_2	r. t. (25 ^oC)	3 h	79 %
1 / 2 / 2.5	$FeCl_3$ (10 %)	DCE	r. t.	15 h	49 %
1 / 2 / 2.5	$FeCl_3$ (10 %)	Toluene	r. t.	15 h	36 %
1 / 2 / 2.5	$FeCl_3$ (10 %)	$CHCl_3$	r. t.	15 h	N.R
1 / 2 / 2.5	$FeCl_3$ (10 %)	THF	r. t.	15 h	N.R
1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3CN	r. t.	15 h	N.R
1 / 2 /2.5	$FeCl_3$ (10 %)	CH_2Cl_2	r. t.	15 h	N.R

1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3NO_2	0 °C	15 h	25 %
1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3NO_2	50 °C	2 h	80 %
1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3NO_2	50 °C	2 h	76 %[c]
1 / 2 / 2.5	$FeCl_3$ (10 %)	CH_3NO_2	50 °C	2 h	69 %[d]

a. The reaction was carried out under air atmosphere.

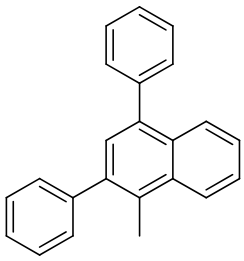
b. Isolated yield.

c. 4 mL of CH_3NO_2 was used.

d. 10 mL of CH_3NO_2 was used.

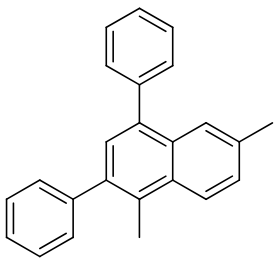
Typical procedure for polysubstituted naphthalene derivatives 6

To a 10 mL of round bottomed-flask containing (*E*)-1,2-diphenylprop-1-ene **1a** (58 mg, 0.3 mmol) in anhydrous CH_3NO_2 (2 mL) was added $FeCl_3$ in anhydrous CH_3NO_2 (0.3 mL, 0.1 M) and styrene **5a** (0.069 mL, 0.6 mmol) successively under air atmosphere. DDQ (170 mg, 0.75 mmol) was added in one portion to the stirred solution at room temperature. The resulting mixture was then heated to 50 °C. After the reaction was completed as judged by TLC, the mixture was then cooled to room temperature and purified by column chromatography on silica gel (eluent: petroleum ether) to give the target product 1-methyl-2,4- diphenylnaphthalene **6aa** .



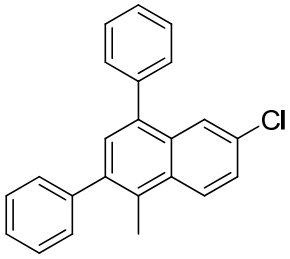
1-Methyl-2,4-diphenylnaphthalene (6aa)

White solid, yield: 80%, Mp: 104 – 106 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.35 (m, 13H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.8, 138.7, 138.2, 133.3, 130.9, 130.4, 130.3, 129.9, 129.4, 128.3, 128.2, 127.2, 126.9, 126.7, 126.2, 125.6, 124.9, 16.5. IR ν 3054, 3023, 2920, 1588, 1507, 1438, 1028, 1001, 761, 700, 606, 507 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{18}$: 294.1409 , $[M]^+$, found: 294.1411.



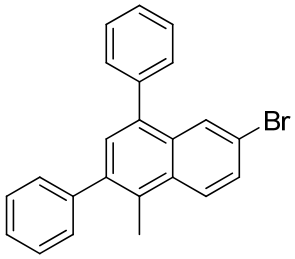
1,6-Dimethyl-2,4-diphenylnaphthalene (6ba)

White solid, yield: 66%, Mp: 137 – 138 °C (lit. [19] Mp: 140 – 141 °C), ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.14 (d, *J* = 8.64 Hz, 1H), 7.81 (s, 1H), 7.62 – 7.38(m, 12H), 2.72 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.9, 136.7, 136.4, 134.1, 130.4, 130.0, 129.2, 129.1, 128.8, 128.4, 127.2, 127.1, 127.0, 125.9, 125.6, 124.4, 123.7, 20.7, 15.3. IR ν 3053, 3025, 2913, 2856, 1590, 1492, 1439, 1073, 1027, 892, 778, 703, 604, 543 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{20}$: 308.1565, $[M]^+$, found: 308.1564.



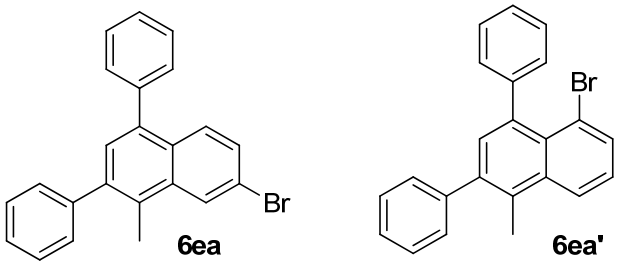
6-Chloro-1-methyl-2,4-diphenylnaphthalene (6ca)

White solid, yield: 70%, Mp: 113 – 115 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.1 Hz, 1H), 7.98 (m, 1H), 7.57 – 7.39 (m, 12H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.1, 139.1, 137.5, 131.9, 131.8, 131.7, 130.5, 130.2, 129.8, 128.5, 128.2, 127.5, 127.1, 126.9, 126.7, 125.4, 16.5. IR ν 3052, 2945, 2851, 1589, 1490, 1441, 1370, 1100, 942, 893, 861, 762, 702, 607 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Cl$: 328.1019, $[M]^+$, found: 328.1026.



6-Bromo-1-methyl-2,4-diphenylnaphthalene (6da)

White solid, yield: 61%, Mp: 119 – 121 °C, ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.08 (d, *J* = 2.04 Hz, 1H), 8.02 (d, *J* = 9.06 Hz, 1H), 7.63 (dd, *J* = 9.06, 2.08 Hz, 1H), 7.51—7.34 (m, 11H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.0, 139.1, 137.4, 132.3, 131.9, 130.5, 130.4, 130.1, 129.7, 129.4, 128.6, 128.5, 128.2, 127.5, 127.0, 126.8, 120.1, 16.4. IR ν 3063, 3021, 2951, 2845, 1587, 1490, 1442, 1375, 1087, 896, 851, 760, 703, 615 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Br$: 372.0514, $[M]^+$, found: 372.0518.

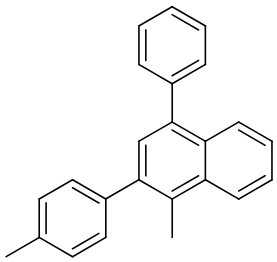


7-Bromo-1-methyl-2,4-diphenylnaphthalene (6ea)

Colorless oil, yield: 28%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.57 – 7.36 (m, 12H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.1, 139.8, 138.2, 134.7, 130.1, 129.8, 129.7, 129.6, 129.4, 128.8, 128.5, 128.4, 128.2, 127.4, 127.3, 127.1, 120.6, 16.4. IR ν 3055, 3025, 2922, 2864, 1600, 1498, 1443, 1002, 702, 532 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Br$: 372.0514, $[M]^+$, found: 372.0515.

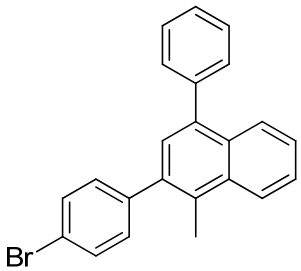
5-Bromo-1-methyl-2,4-diphenylnaphthalene (6ea')

Colorless oil, yield: 28%, ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.32 (d, *J* = 1.95 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.51 (dd, *J* = 9.0, 1.95 Hz, 1H), 7.49 – 7.35 (m, 11H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.2, 139.8, 138.2, 134.7, 130.2, 129.8, 129.7, 129.6, 129.5, 128.8, 128.5, 128.4, 128.2, 127.4, 127.3, 127.1, 120.7, 16.4. IR ν 3065, 3029, 2959, 2871, 1598, 1497, 1441, 1400, 1070, 910, 861, 820, 750, 702, 603 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Br$: 372.0514, $[M]^+$, found: 372.0520.



1-Methyl-2-(4-methylphenyl) -4-phenylnaphthalene (6ha)

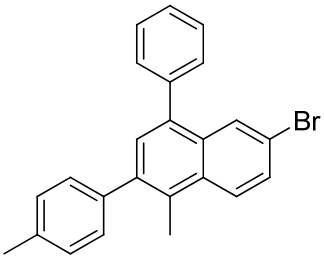
Colorless oil, yield: 70%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.39 (m, 7H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.70 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.6, 138.6, 138.1, 136.5, 133.3, 130.8, 130.3, 130.3, 129.8, 129.5, 128.8, 128.2, 127.2, 126.6, 126.1, 125.5, 124.9, 21.2, 16.5. IR ν 3021, 2951, 2849, 1593, 1507, 1443, 1371, 1109, 991, 895, 820, 765, 699, 609, 507 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{20}$: 308.1565, $[M]^+$, found: 308.1573.



2-(4-Bromophenyl)-1-methyl-4-phenylnaphthalene (6ia)

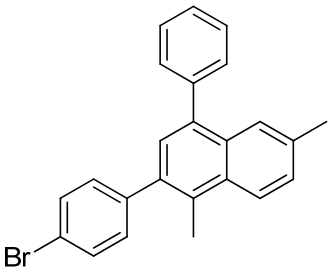
Colorless oil, yield: 63%, ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.19(d, *J* = 8.45 Hz, 1H), 7.99 (d, *J* = 8.27 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.55 – 7.41 (m, 6H), 7.35 (s, 1H), 7.34 – 7.29 (m, 2H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.6, 138.4, 137.4, 133.3, 131.6, 131.3, 131.1, 130.4, 130.2, 128.9, 128.3, 127.3, 126.7, 126.3, 125.8, 124.9, 121.1, 16.4. IR ν 3062, 3021, 2943, 2850, 1590, 1483, 1440, 1372, 1065, 1010, 987, 822, 766, 704, 609, 503 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Br$: 372.0514, $[M]^+$, found: 372.0515.

Electronic Supplementary Material



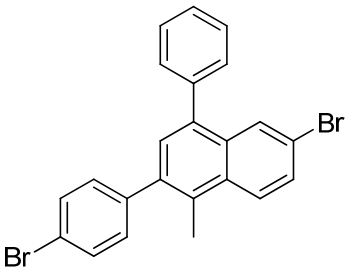
6-Bromo-1-methyl-2-(4-methylphenyl) -4-phenylnaphthalene (6ja)

White solid, yield: 67%, Mp: 128 – 130 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 1H), 8.06 (d, *J* = 9.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.57 – 7.43 (m, 6H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.68 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.2, 139.1, 137.4, 136.8, 132.3, 132.0, 130.6, 130.5, 130.2, 129.7, 129.4, 128.9, 128.6, 128.5, 127.5, 126.8, 120.1, 21.3, 16.5. IR ν 3027, 2934, 2859, 1590, 1515, 1480, 1436, 1379, 1090, 850, 822, 771, 702, 617 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{19}Br$: 386.0670, $[M]^+$, found: 386.0674.



2-(4-Bromophenyl)-1,2-dimethyl-4-phenylnaphthalene (6ka)

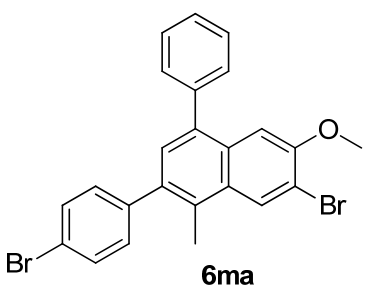
White solid, yield: 62%, Mp: 125 – 127 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 1H), 7.78 (s, 1H), 7.63 – 7.44 (m, 8H), 7.36 – 7.30 (m, 3H), 2.67 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 140.8, 137.8, 136.5, 135.5, 131.6, 131.5, 131.3, 131.2, 130.3, 129.1, 128.5, 128.3, 127.2, 125.6, 124.8, 121.0, 21.8, 16.4. IR ν 3063, 2931, 2857, 1589, 1491, 1439, 1385, 1070, 1007, 825, 760, 700, 610 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{19}Br$: 386.0670, $[M]^+$, found: 386.0669.



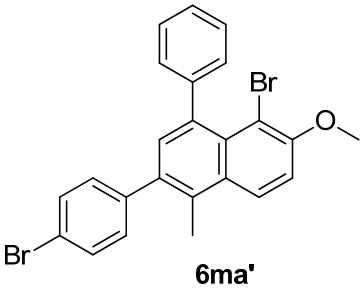
6-Bromo-2-(4-bromophenyl)-1-methyl-4-phenylnaphthalene (6la)

White solid, yield: 62% (based on recovery of SM), Mp: 155 – 157 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.65 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 – 7.41 (m, 5H), 7.34 (s, 1H), 7.31 – 7.26 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.8, 137.8, 137.6, 132.4, 131.8, 131.4, 131.4, 130.6, 130.1, 129.9, 129.6, 128.7, 128.5, 127.6, 126.8, 121.3, 120.4, 16.4. IR ν 3051, 2920, 2875, 1589, 1482, 1389, 1082, 1018, 856, 825, 771, 708, 512 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{16}Br_2$: 449.9619, $[M]^+$, found:

449.9617.



6ma



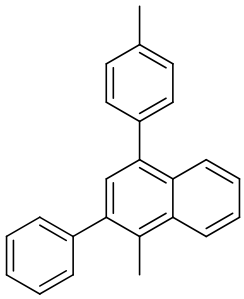
6ma'

7-Bromo-2-(4-bromophenyl)-6-methoxy-1-methyl-4-phenylnaphthalene (6ma)

Colorless oil, yield: 22%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.48 (m, 4H), 7.31 – 7.28 (m, 5H), 3.83 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 141.0, 140.4, 137.2, 136.3, 131.5, 131.4, 131.3, 129.9, 129.8, 129.7, 129.6, 129.5, 128.6, 127.5, 121.2, 113.9, 105.7, 56.1, 16.5. IR ν 3075, 3057, 2962, 2923, 2855, 1593, 1485, 1456, 1424, 1264, 1041, 828, 666 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{18}OBr_2$: 479.9724, $[M]^+$, found: 479.9723.

5-Bromo-2-(4-bromophenyl)-6-methoxy-1-methyl-4-phenylnaphthalene (6ma')

Colorless oil, yield: 21%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.31 (m, 7H), 7.29 – 7.23 (m, 2H), 4.02 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 143.6, 140.7, 137.8, 135.6, 133.8, 131.5, 131.3, 130.9, 130.8, 130.7, 129.9, 127.6, 126.6, 126.2, 121.2, 113.2, 107.9, 57.1, 17.0. IR ν 3057, 2957, 2921, 2851, 1600, 1525, 1459, 1274, 1078, 1055, 804, 771, 725, 699 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{18}OBr_2$: 479.9724, $[M]^+$, found: 479.9726.



1-Methyl-4-(4-methylphenyl)-2-phenylnaphthalene (6ac)

Colorless oil, yield: 33%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.50 – 7.36 (m, 9H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.67 (s,3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.7, 138.1, 137.8, 136.8, 133.3, 131.0, 130.1, 129.9, 129.3, 129.0, 128.1, 126.8, 126.7, 126.1, 125.5, 124.8, 21.3, 16.4. IR ν 3022, 2920, 2879, 1593, 1500, 1449, 1375, 1040, 900, 827, 754, 703, 609, 511 cm^{-1}. HRMS (EI): Calcd for $C_{24}H_{20}$: 308.1565, $[M]^+$, found: 308.1572.

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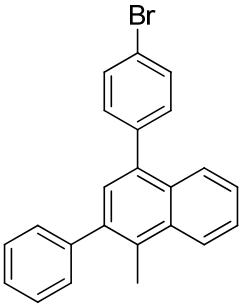
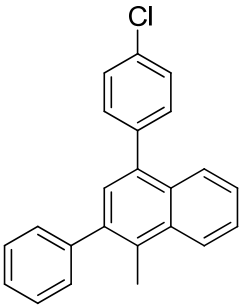


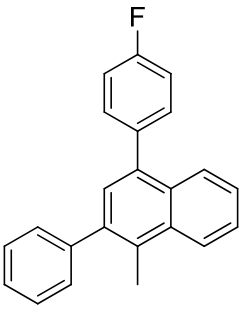
4-(4-Bromophenyl)-1-methyl-2-phenylnaphthalene (6ad)

White solid, yield: 70%, Mp: 86 – 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.53 – 7.37 (m, 9H), 2.70 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.7, 138.7, 136.8, 133.4, 131.9, 131.5, 130.9, 130.7, 129.9, 129.3, 128.2, 127.0, 126.3, 126.3, 125.8, 125.0, 121.4, 16.5. IR ν 3065, 2920, 2895, 1596, 1485, 1439, 1376, 1071, 1009, 903, 827, 745, 709, 596 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Br$: 372.0514, $[M]^+$, found: 372.0512.



4-(4-Chlorophenyl)-1-methyl-2-phenylnaphthalene (6ae)

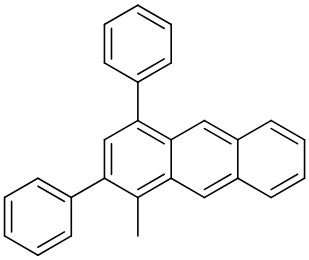
Colorless oil, yield: 74%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.54 – 7.39 (m, 10H), 7.38 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.2, 138.7, 136.8, 133.3, 133.2, 131.5, 130.8, 130.7, 129.8, 129.3, 128.5, 128.2, 127.0, 126.3, 125.8, 125.0, 16.5. IR ν 3050, 2965, 2875, 1589, 1478, 1434, 1369, 1089, 1019, 900, 839, 756, 710, 603 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}Cl$: 328.1019, $[M]^+$, found: 328.1016.



4-(4-Fluorophenyl)-1-methyl-2-phenylnaphthalene (6af)

Colorless oil, yield: 71%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.50 – 7.35 (m, 8H), 7.34 (s, 1H), 7.19 – 7.11 (m, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.0, 142.4, 138.7, 137.0, 136.7, 136.6, 133.3, 131.8,

131.7, 130.9, 130.6, 129.8, 129.4, 128.1, 126.9, 126.4, 126.2, 125.7, 124.9, 115.3, 115.1, 16.5. IR ν 3089, 2905, 2849, 1605, 1525, 1450, 1381, 1223, 1159, 989, 900, 841, 760, 704, 600, 536 cm^{-1}. HRMS (EI): Calcd for $C_{23}H_{17}F$: 312.1314, $[M]^+$, found: 312.1318.



1-Methyl-2,4-diphenylanthracene (6na)

White solid, yield: 30%, Mp: 125 – 127 °C, ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.2 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.37 (m, 12H)，7.15 – 7.09 (m, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.2, 139.5, 138.0, 132.9, 132.7, 132.5, 131.0, 130.6, 129.8, 129.2, 128.9, 128.8, 128.2, 128.1, 127.9, 127.8, 126.9, 126.9, 125.9, 124.7, 123.4, 17.2. IR ν 3061, 2941, 2845, 1600, 1490, 1435, 1410, 1080, 1003, 881, 812, 741, 700, 613 cm^{-1}. HRMS (EI): Calcd for $C_{27}H_{20}$: 344.1565, $[M]^+$, found: 344.1567.

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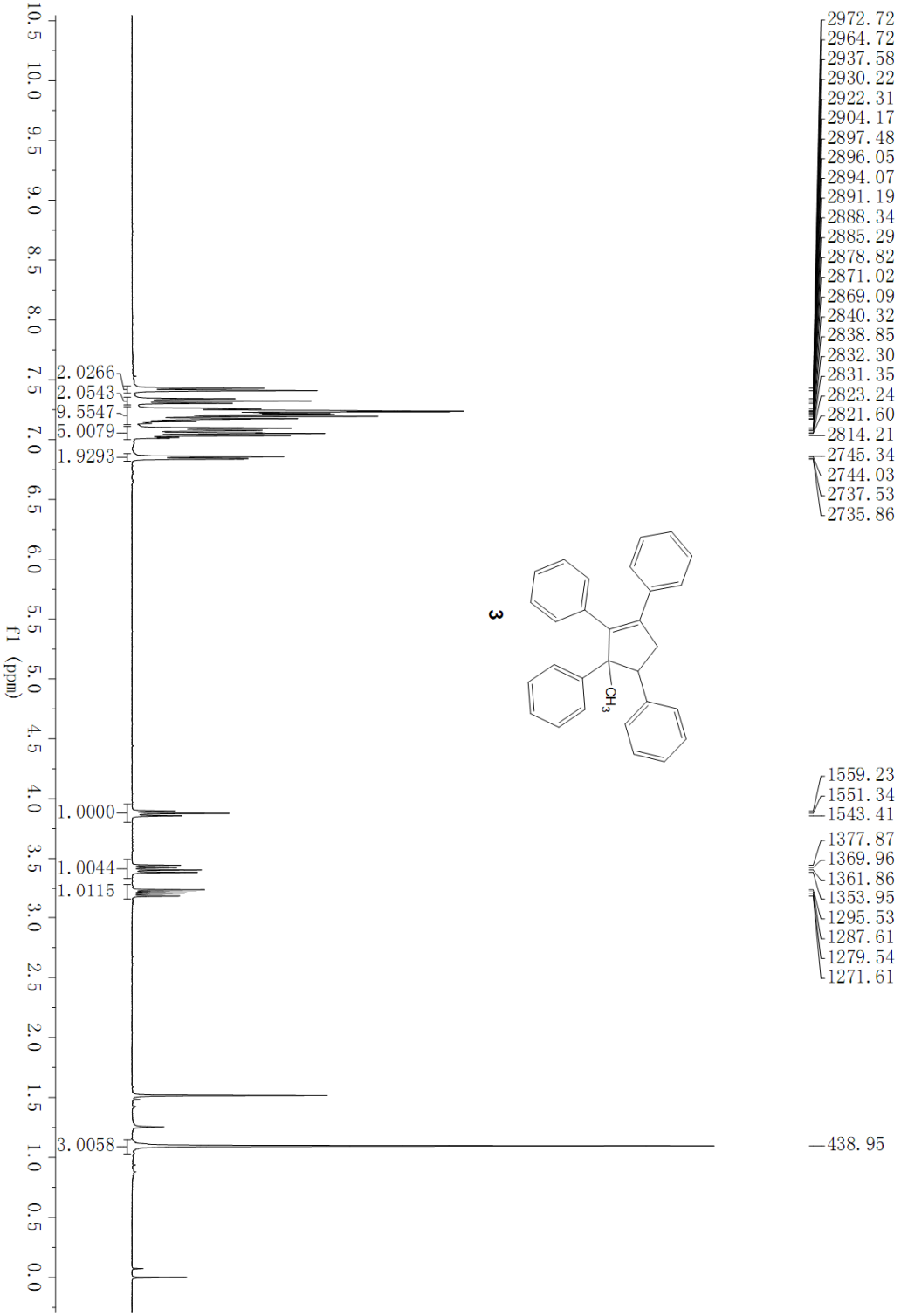

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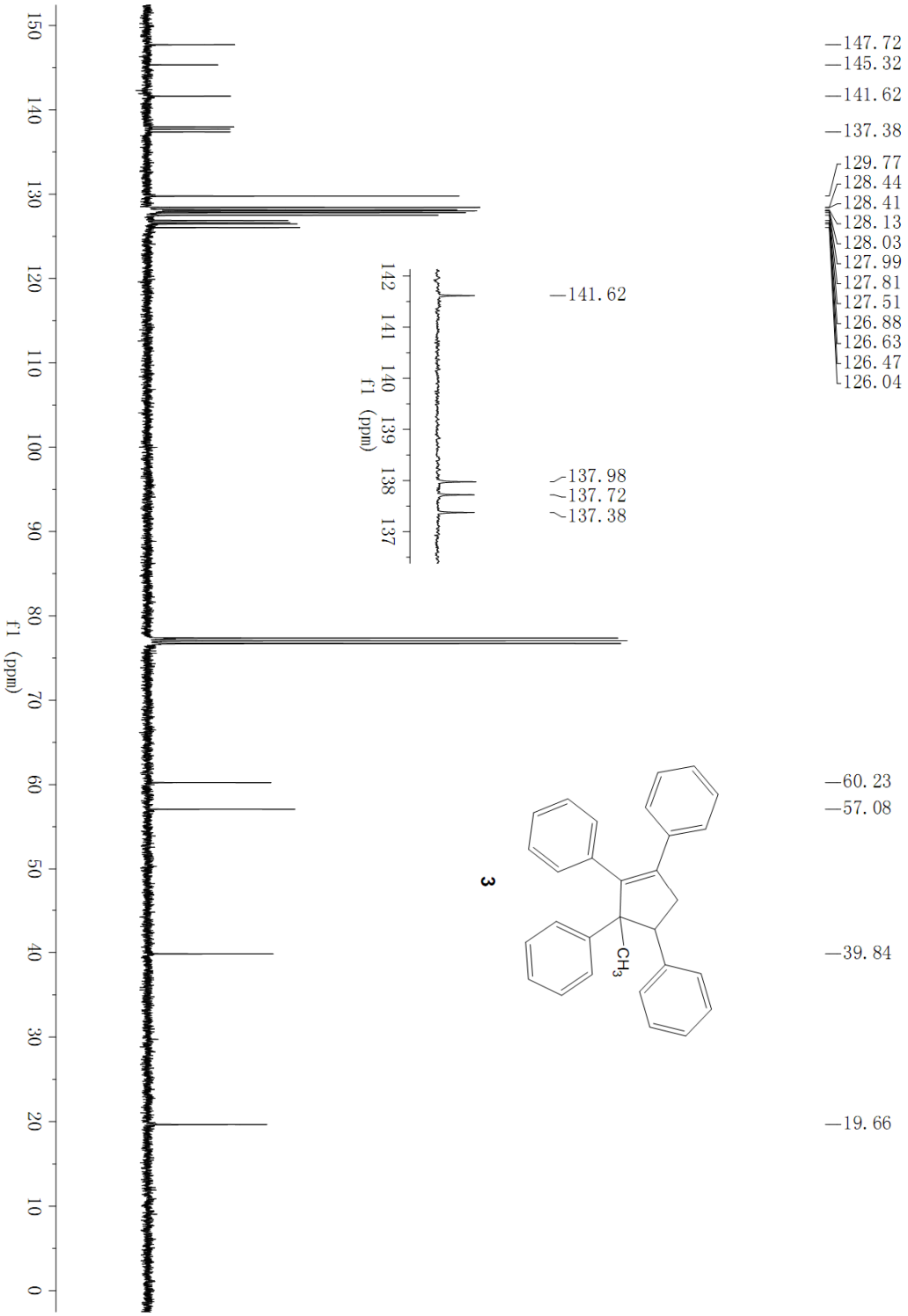

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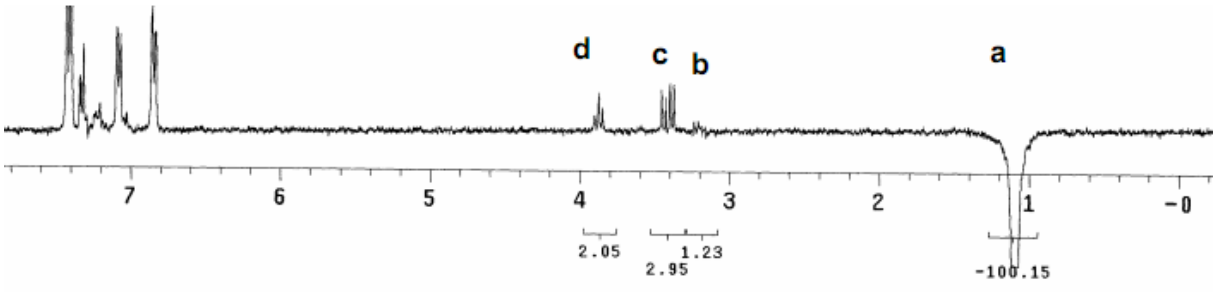

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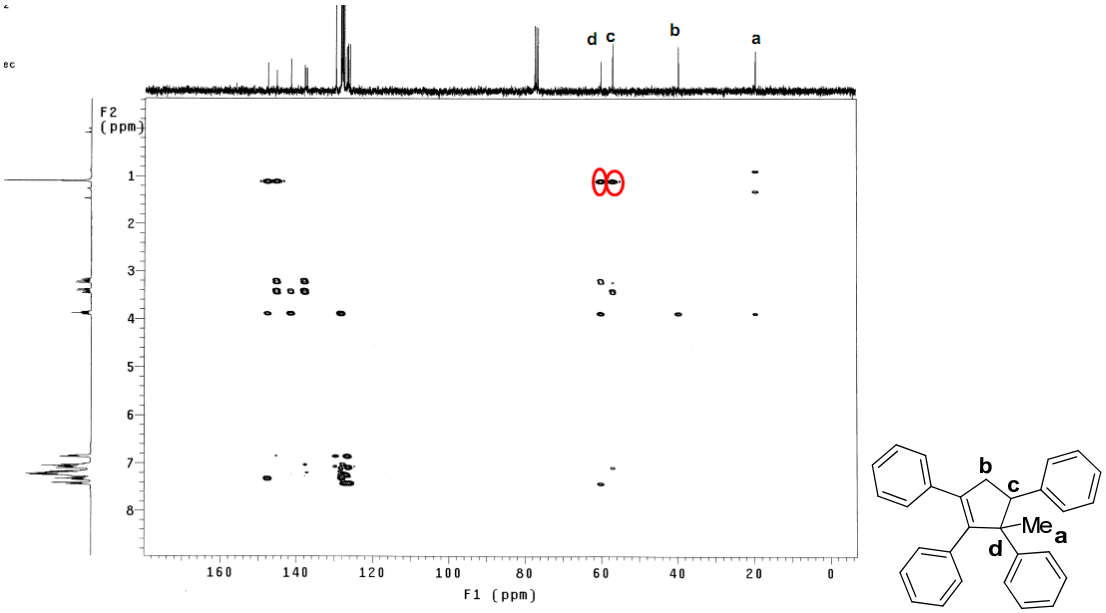

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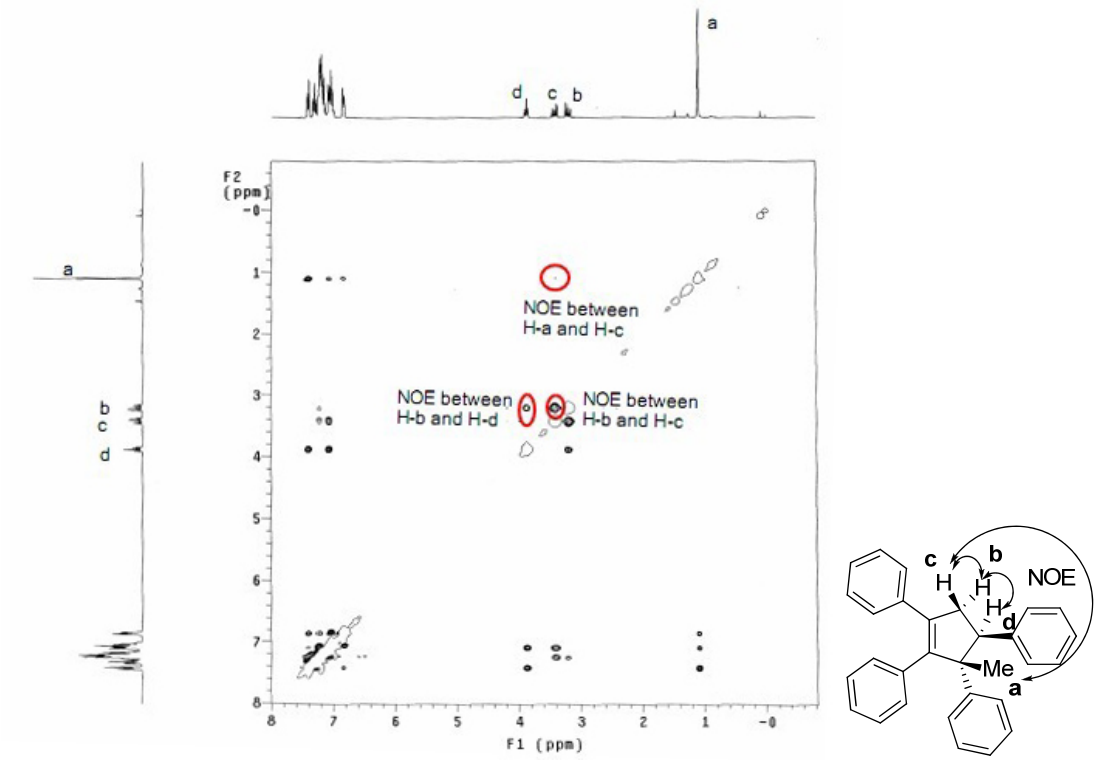

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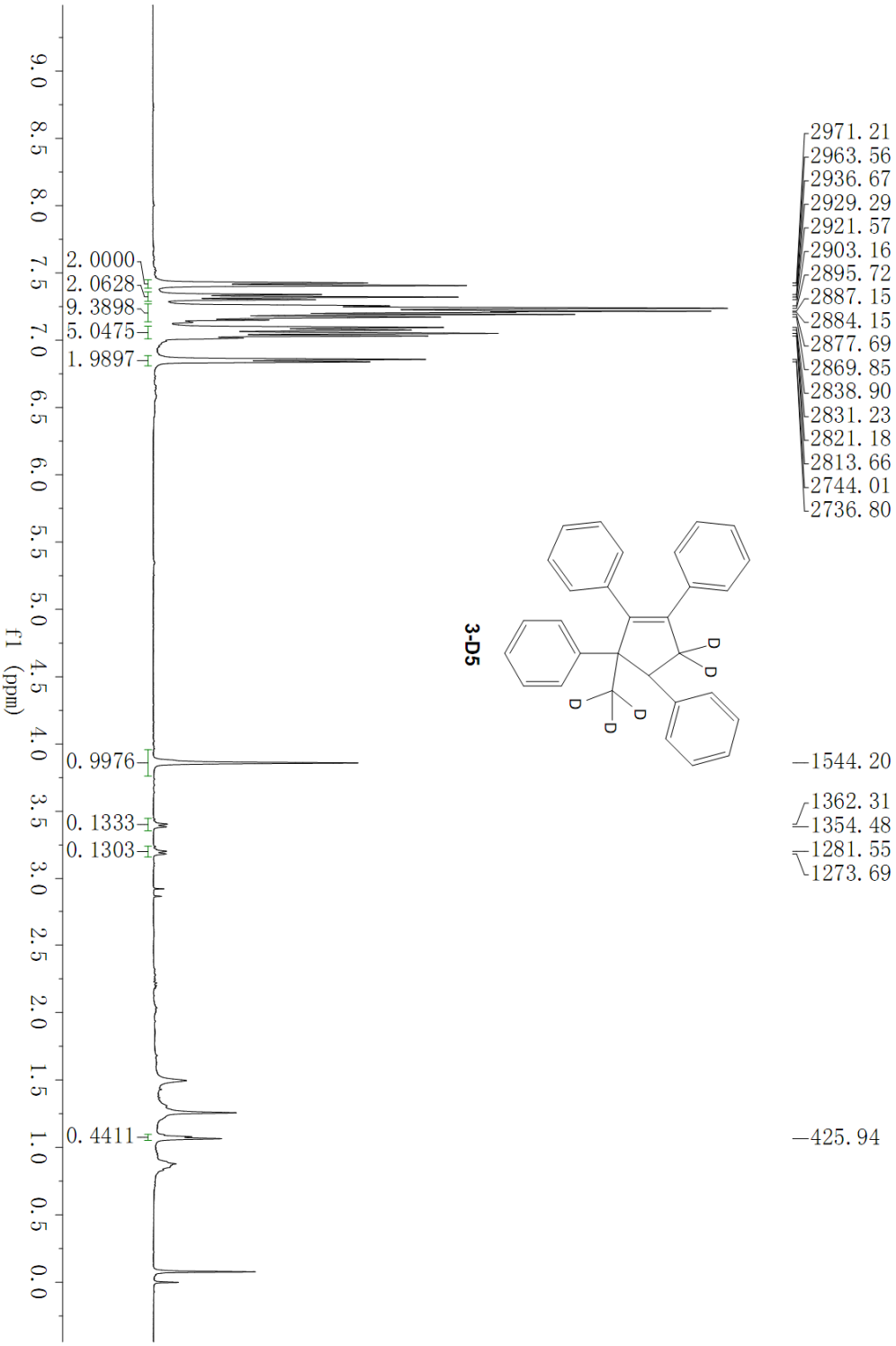

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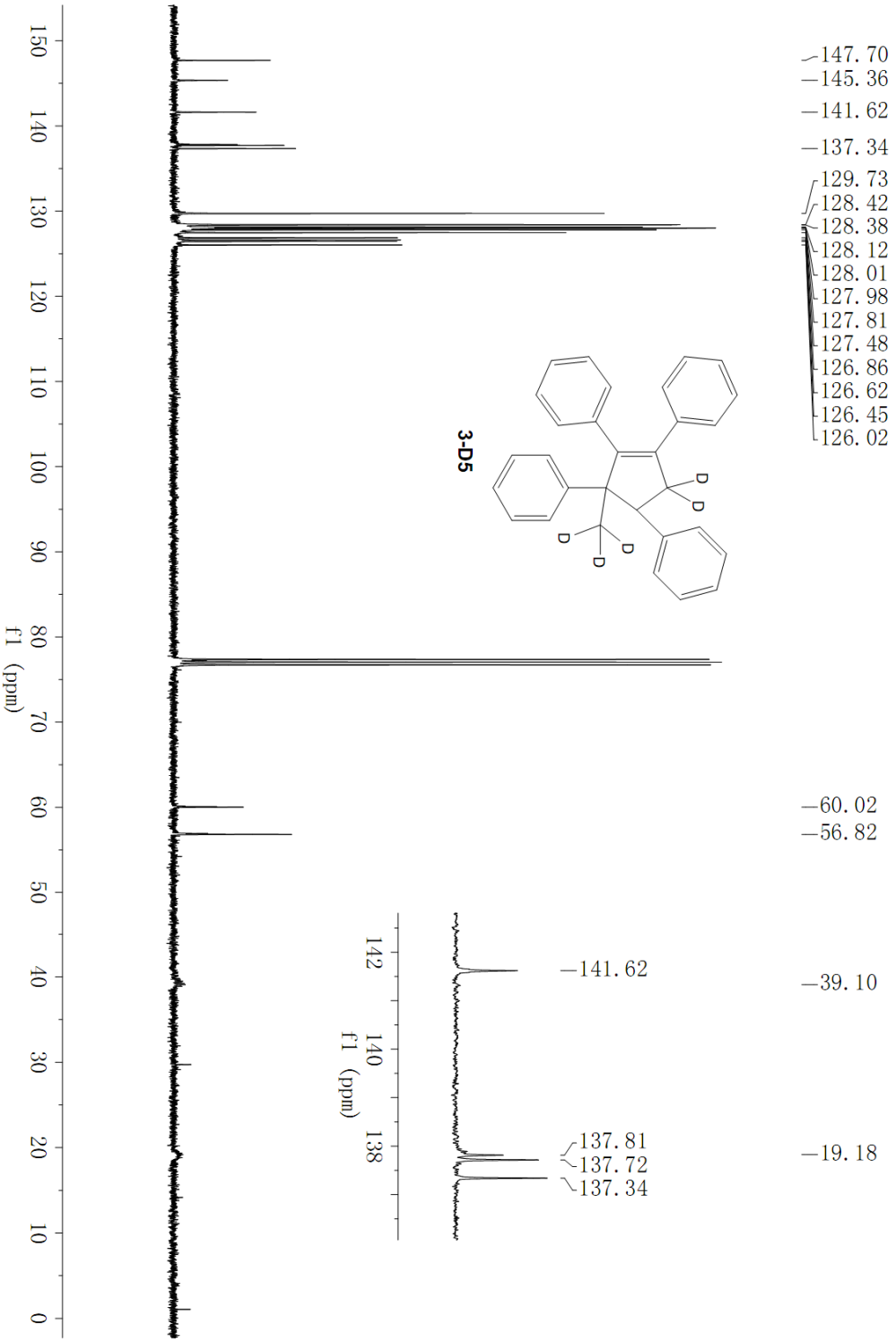

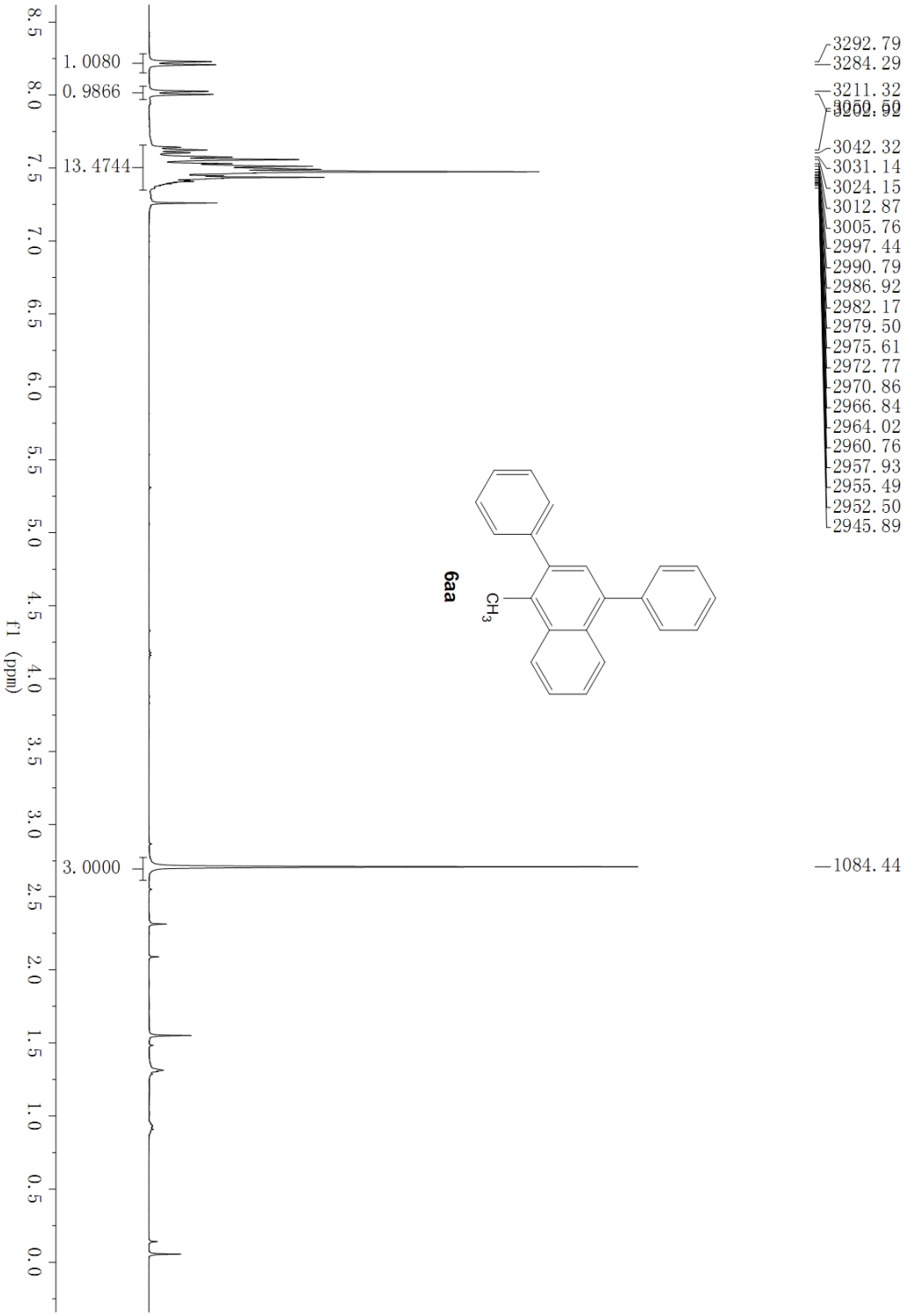

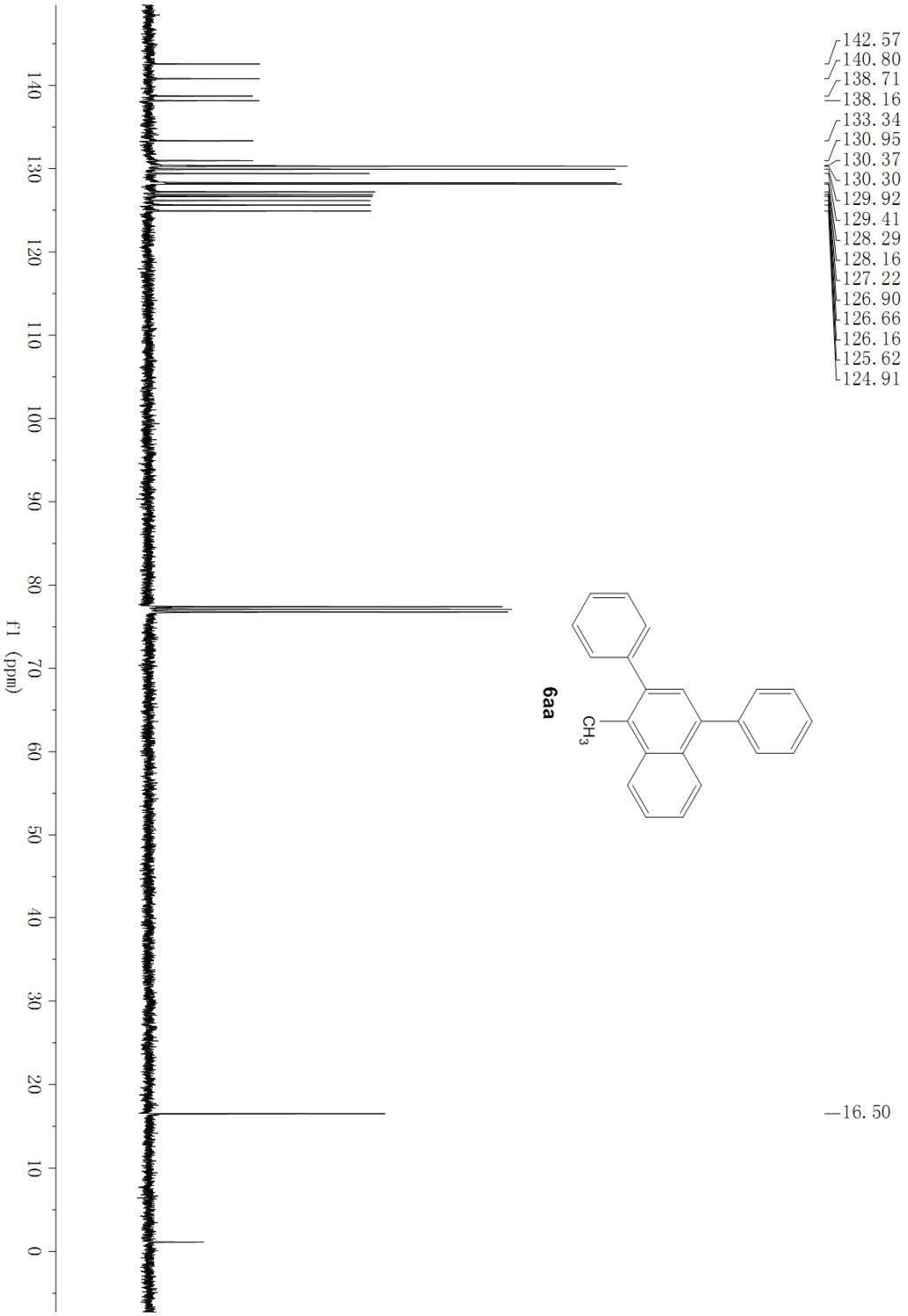

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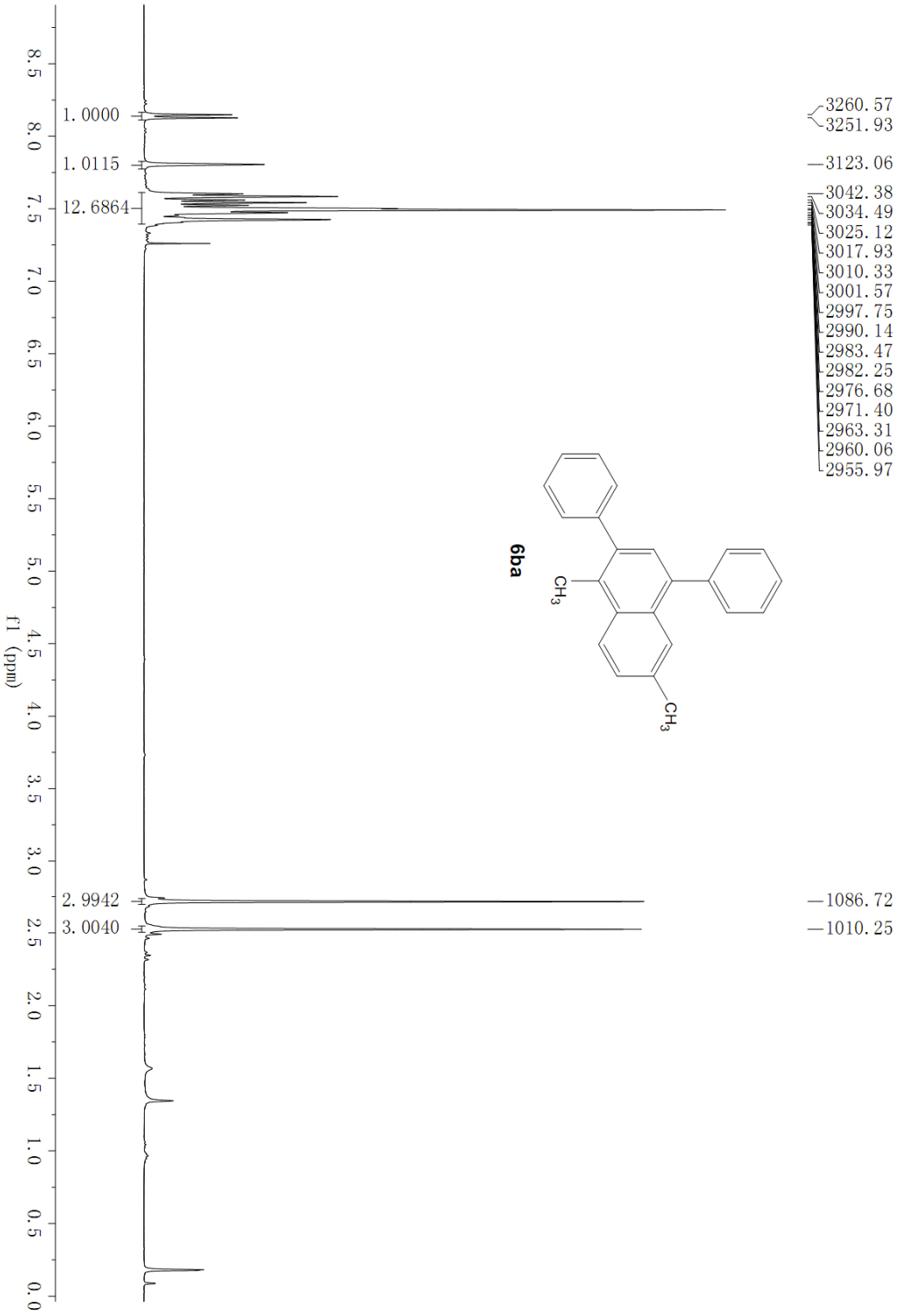

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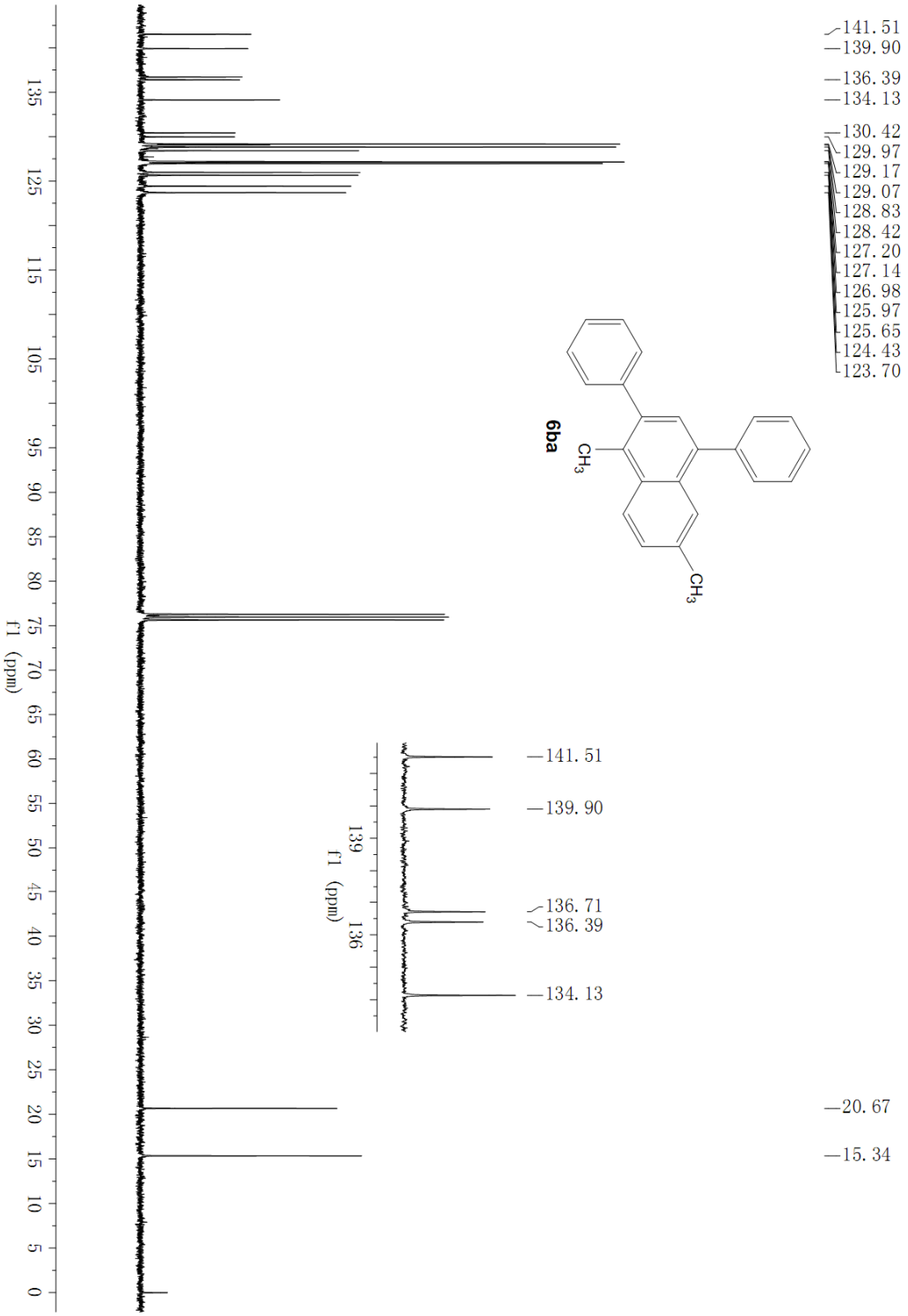

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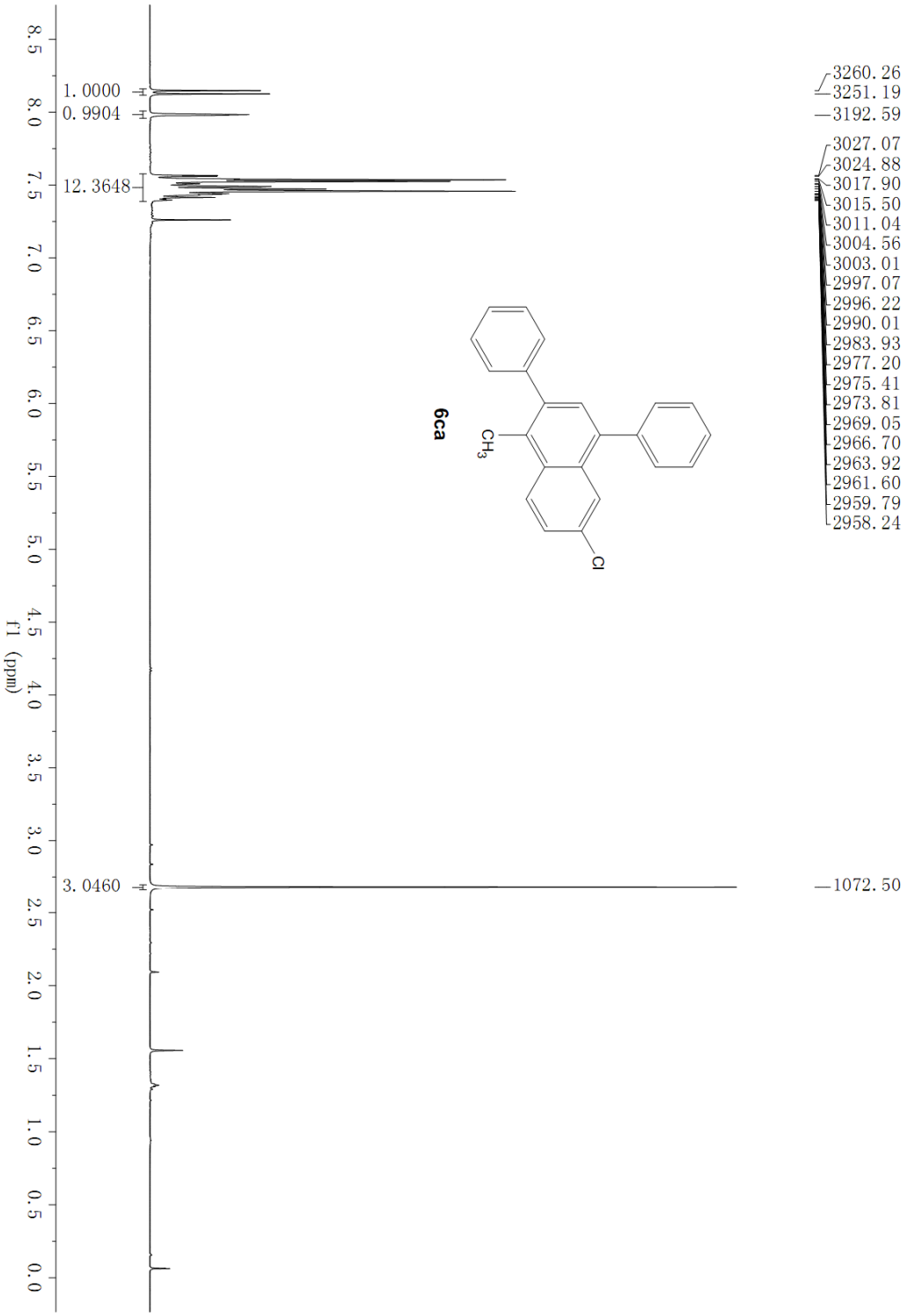

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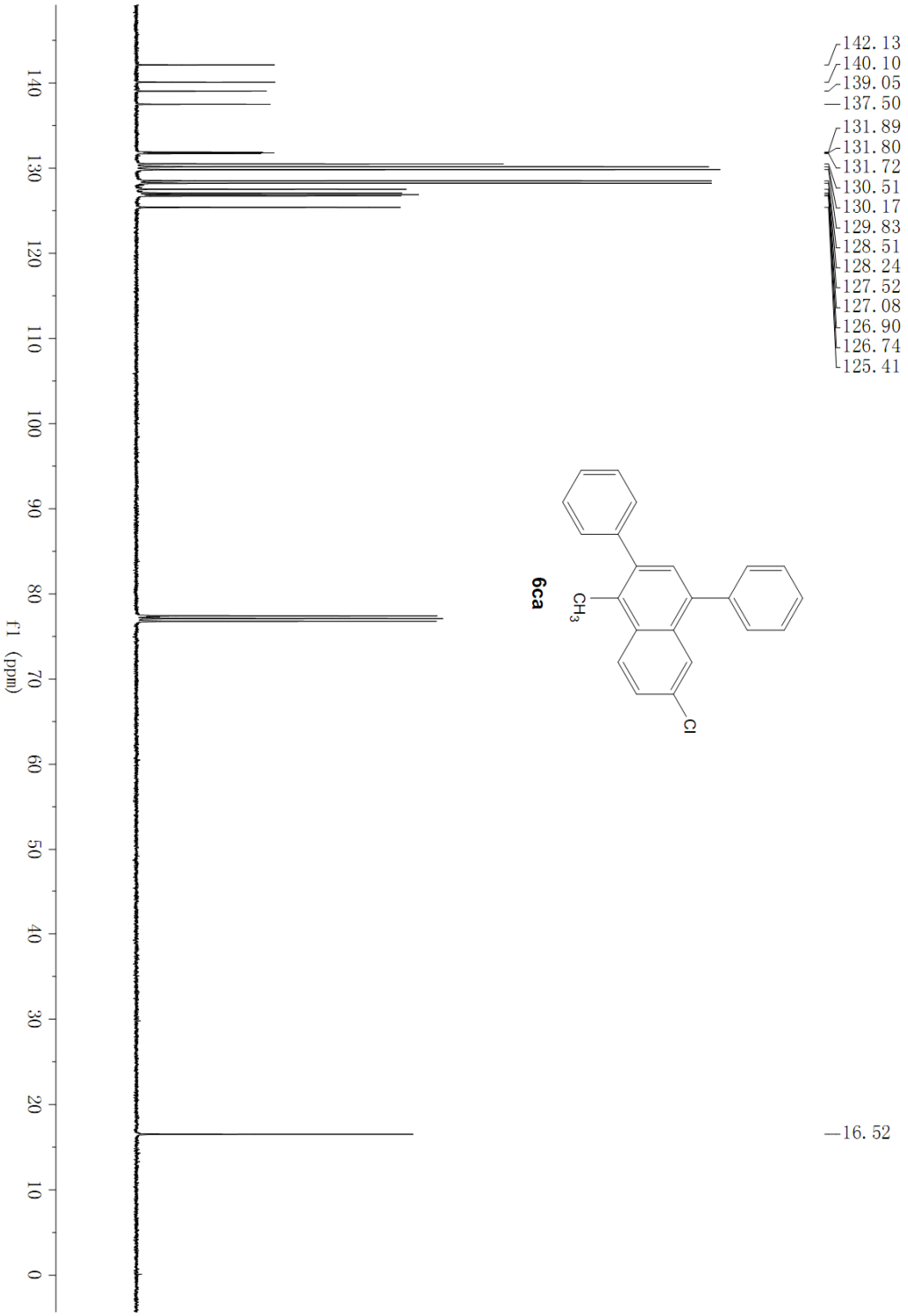

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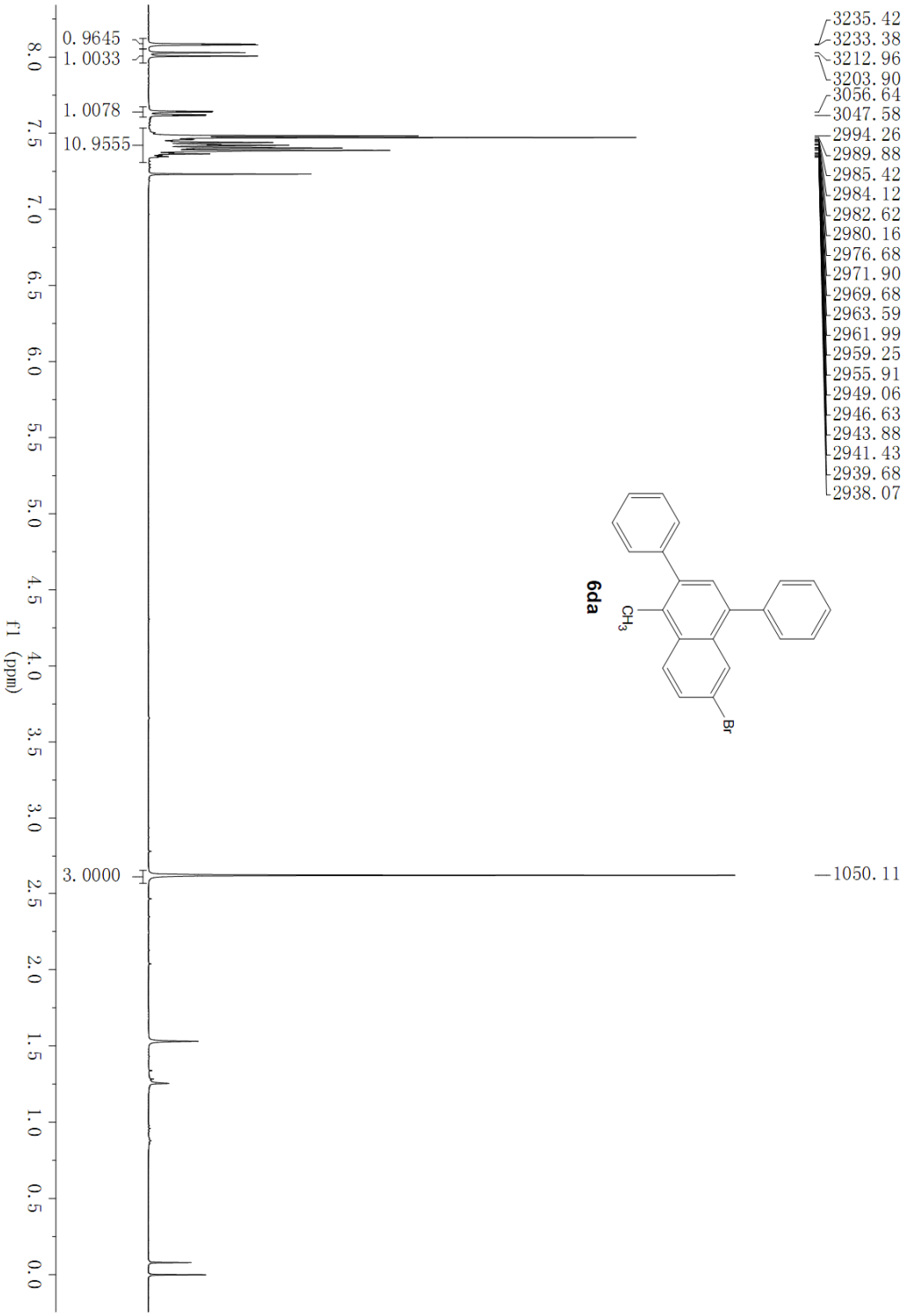

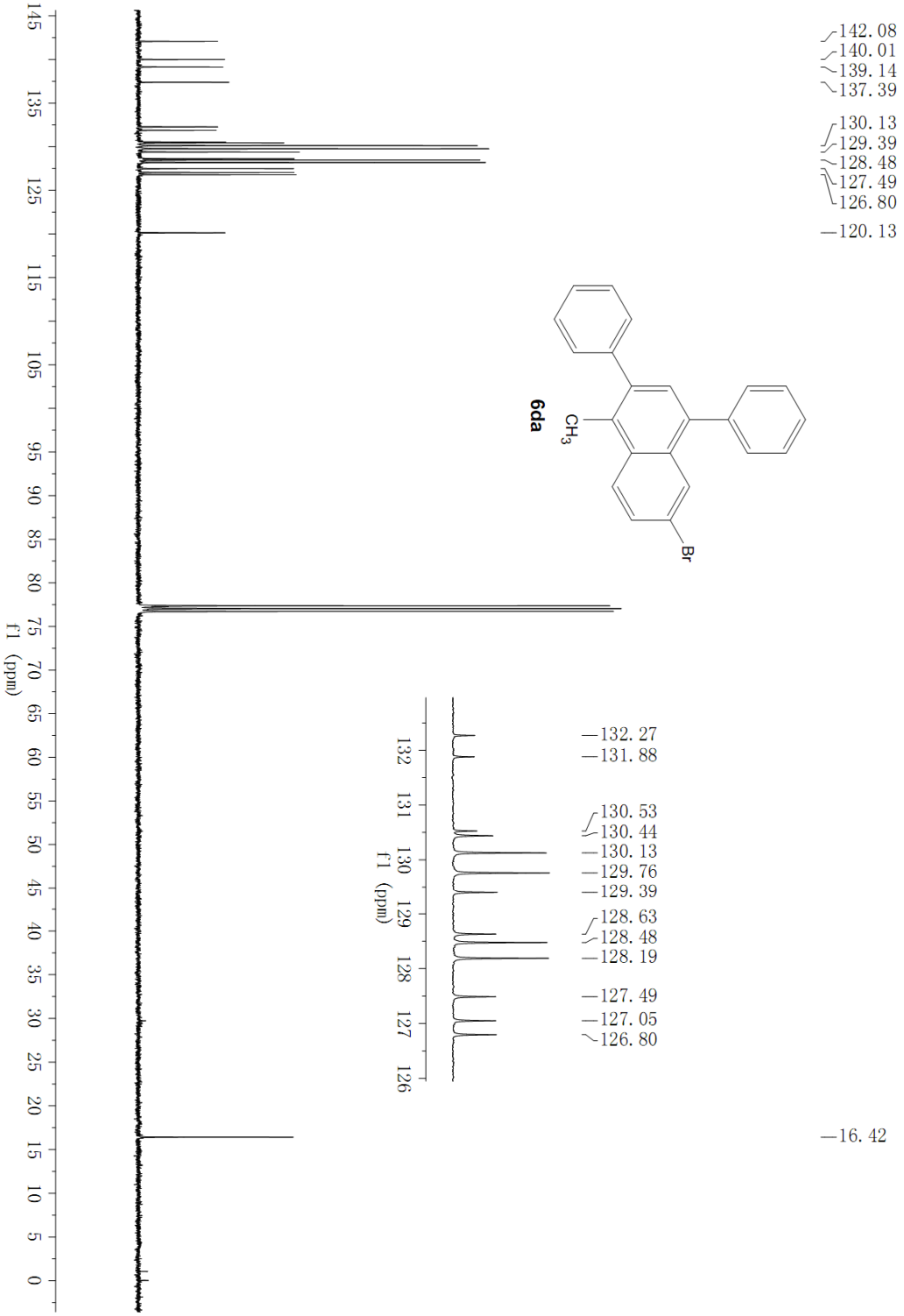

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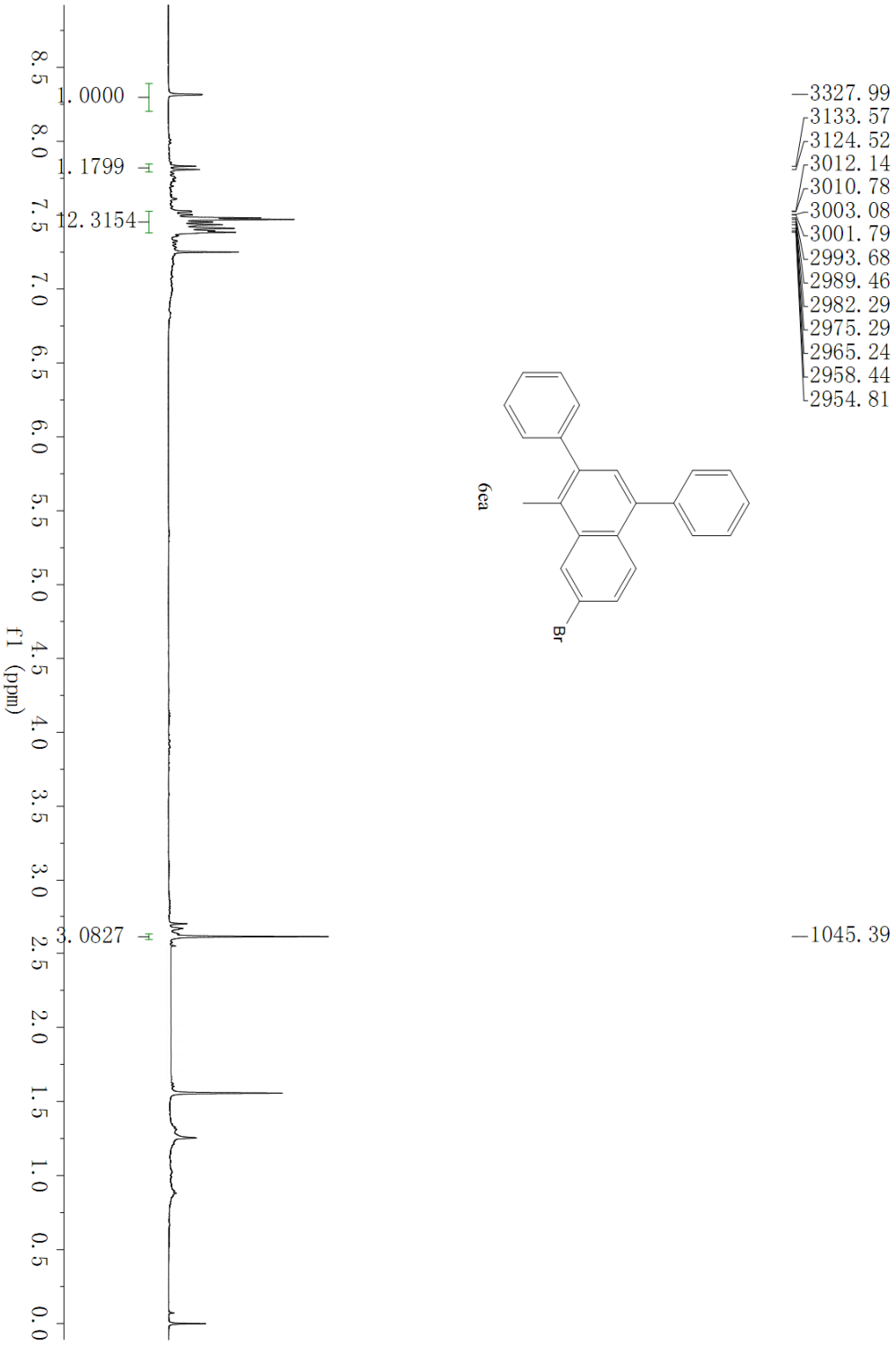

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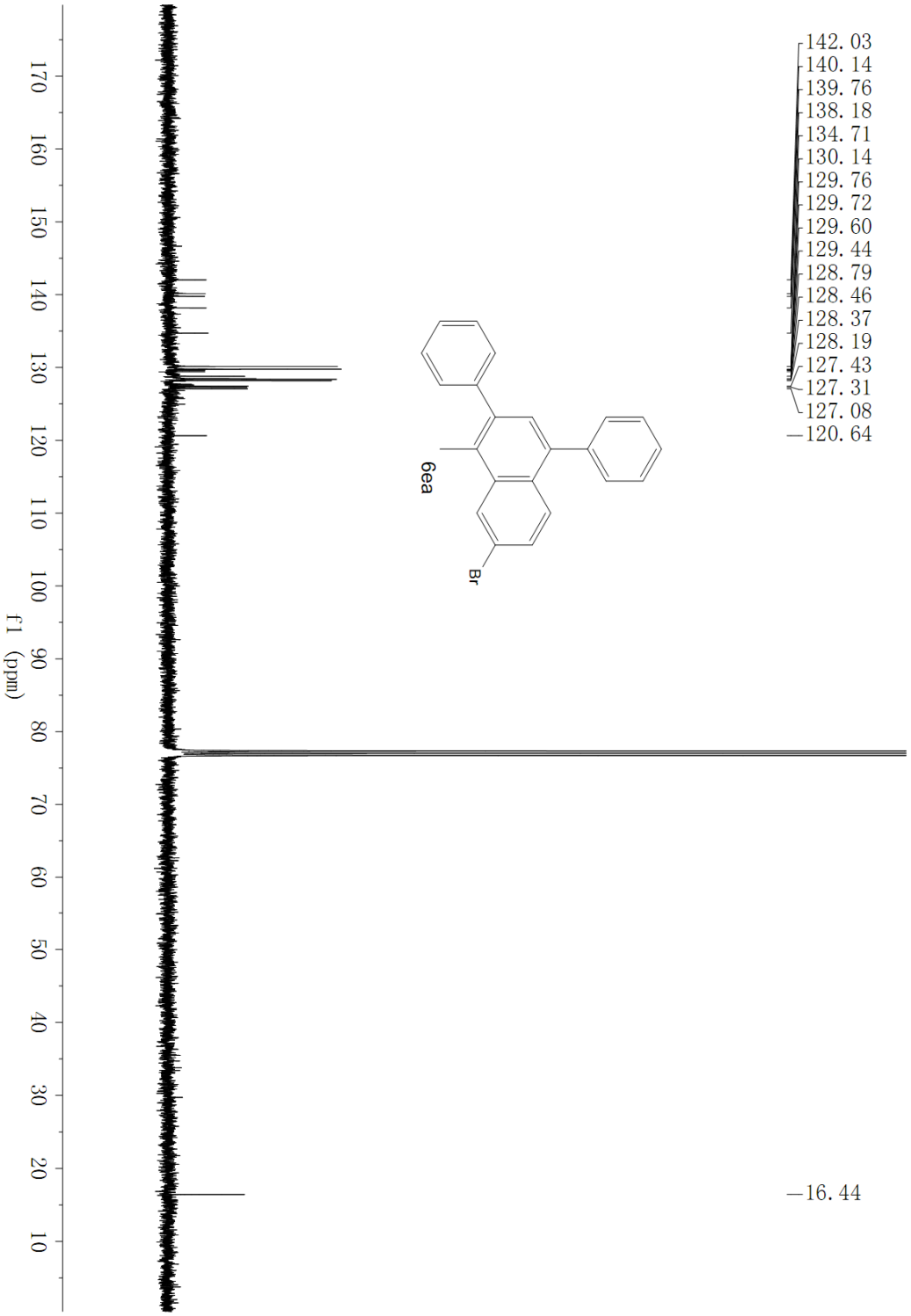

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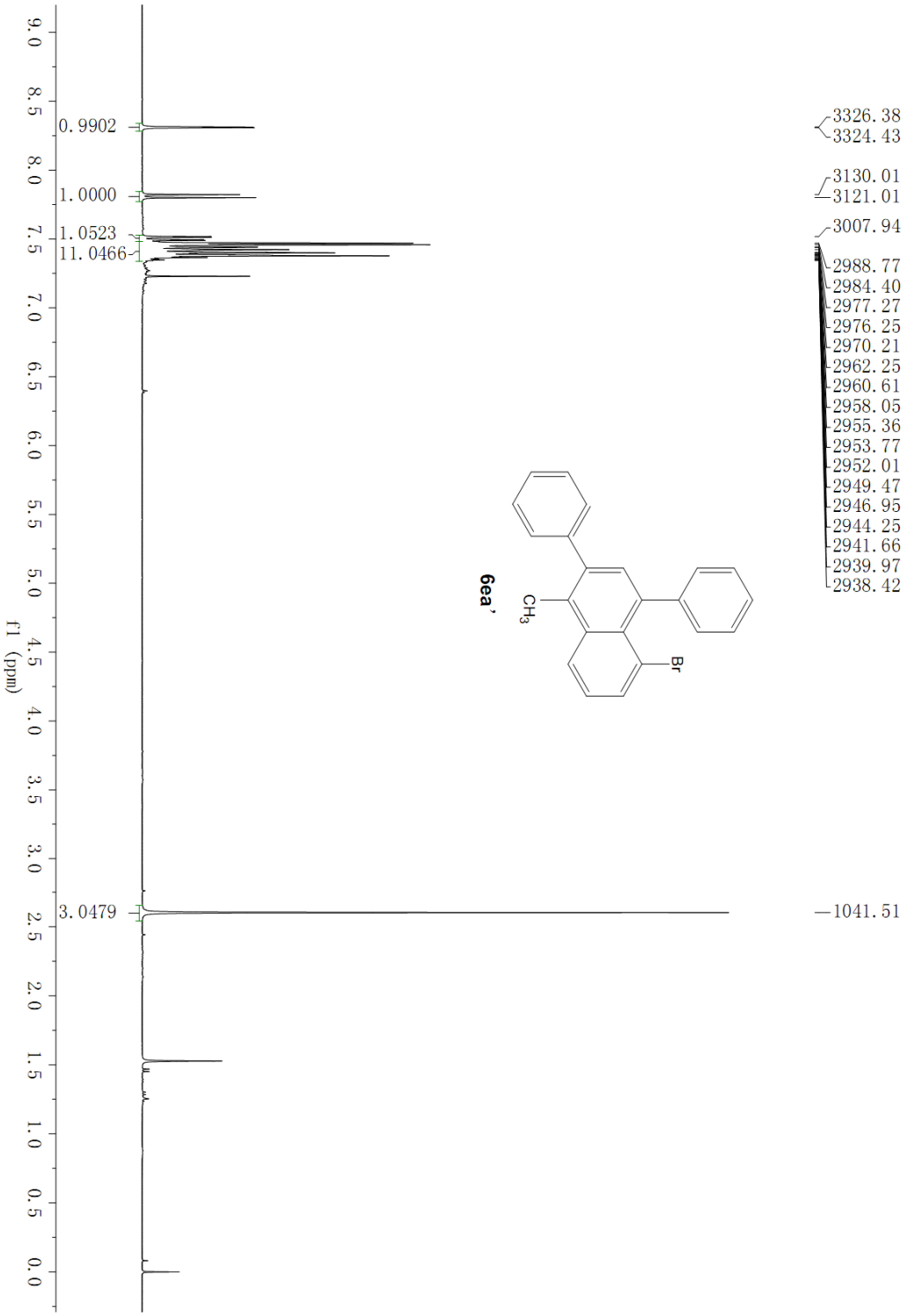

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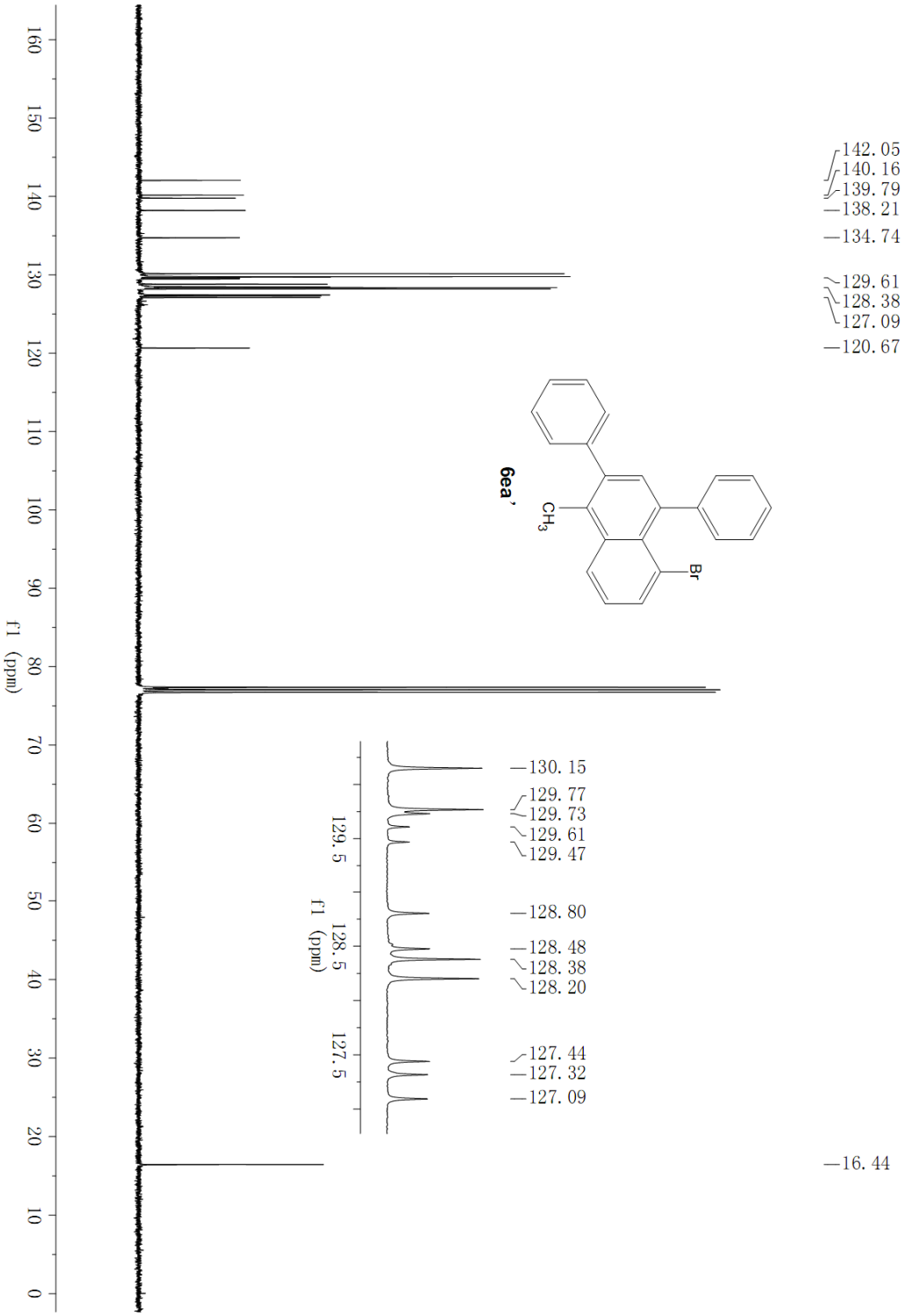

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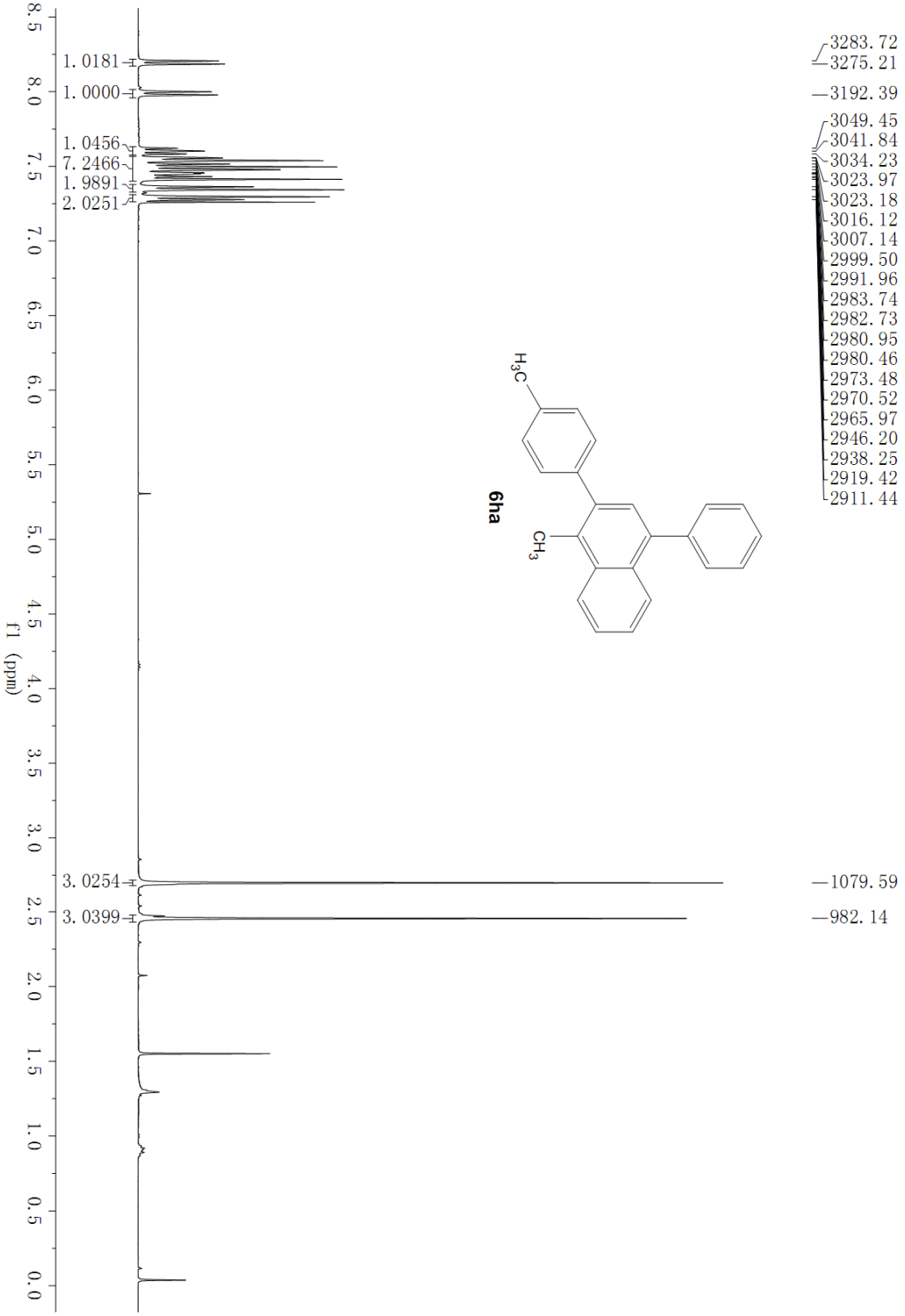

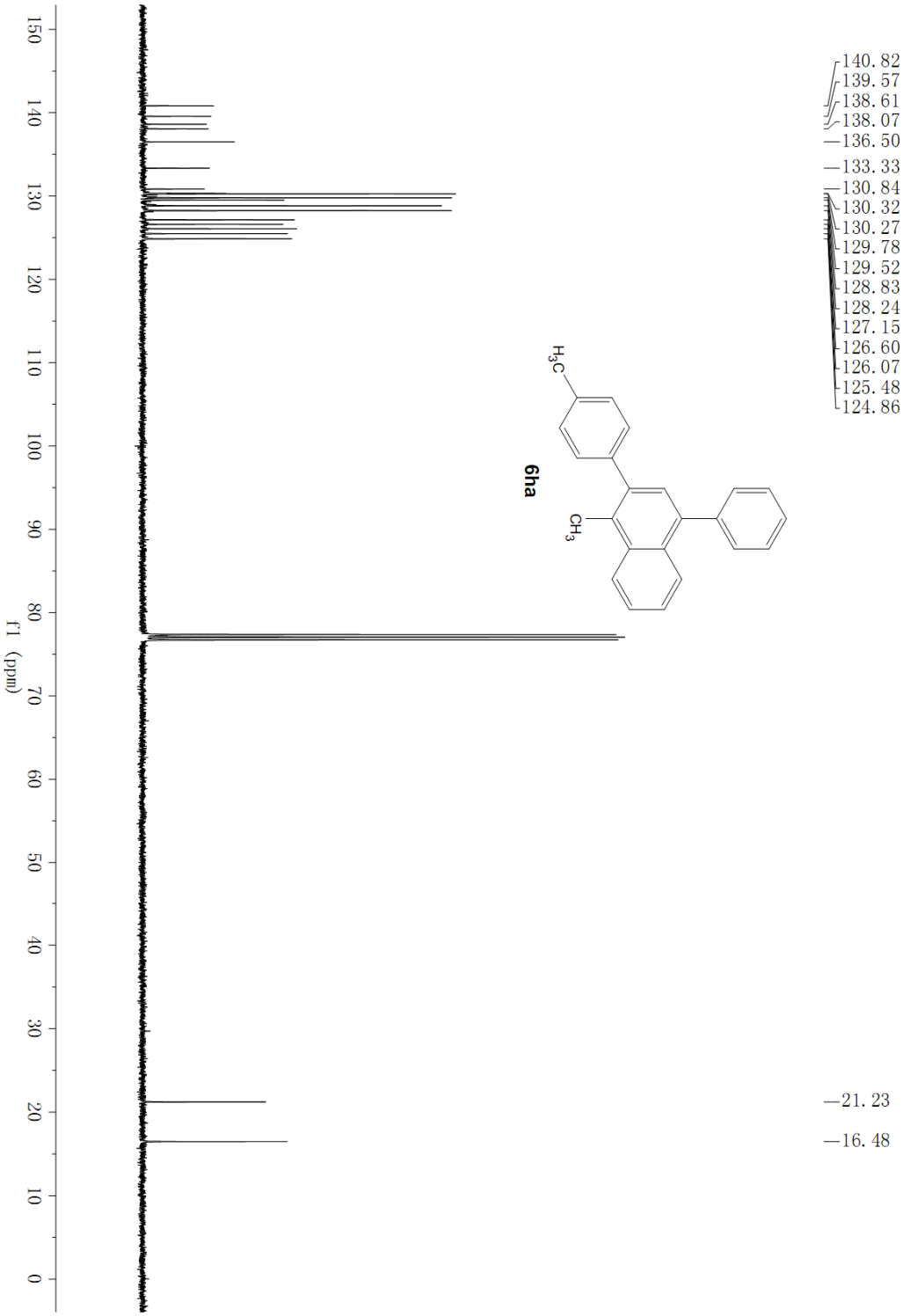

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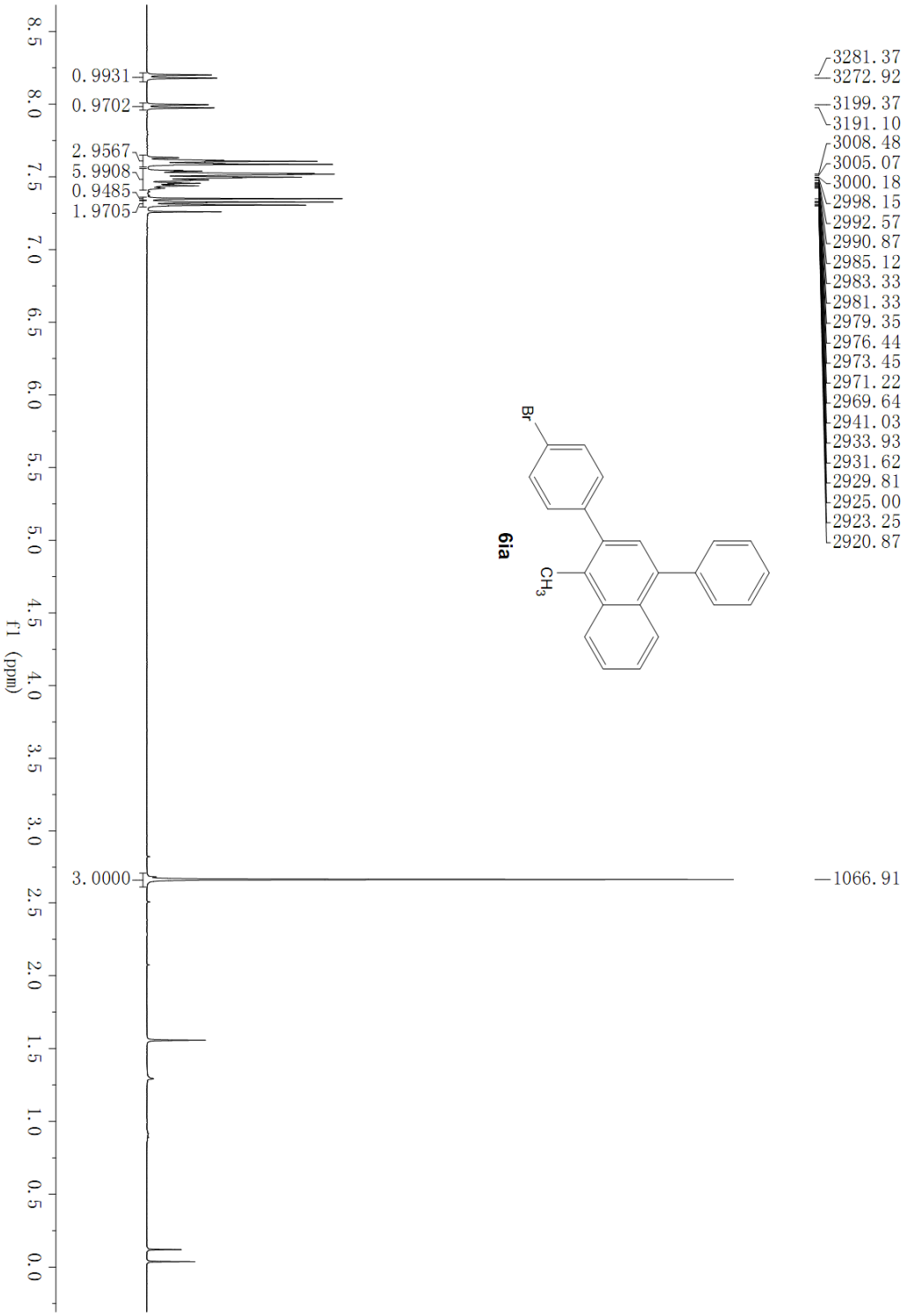

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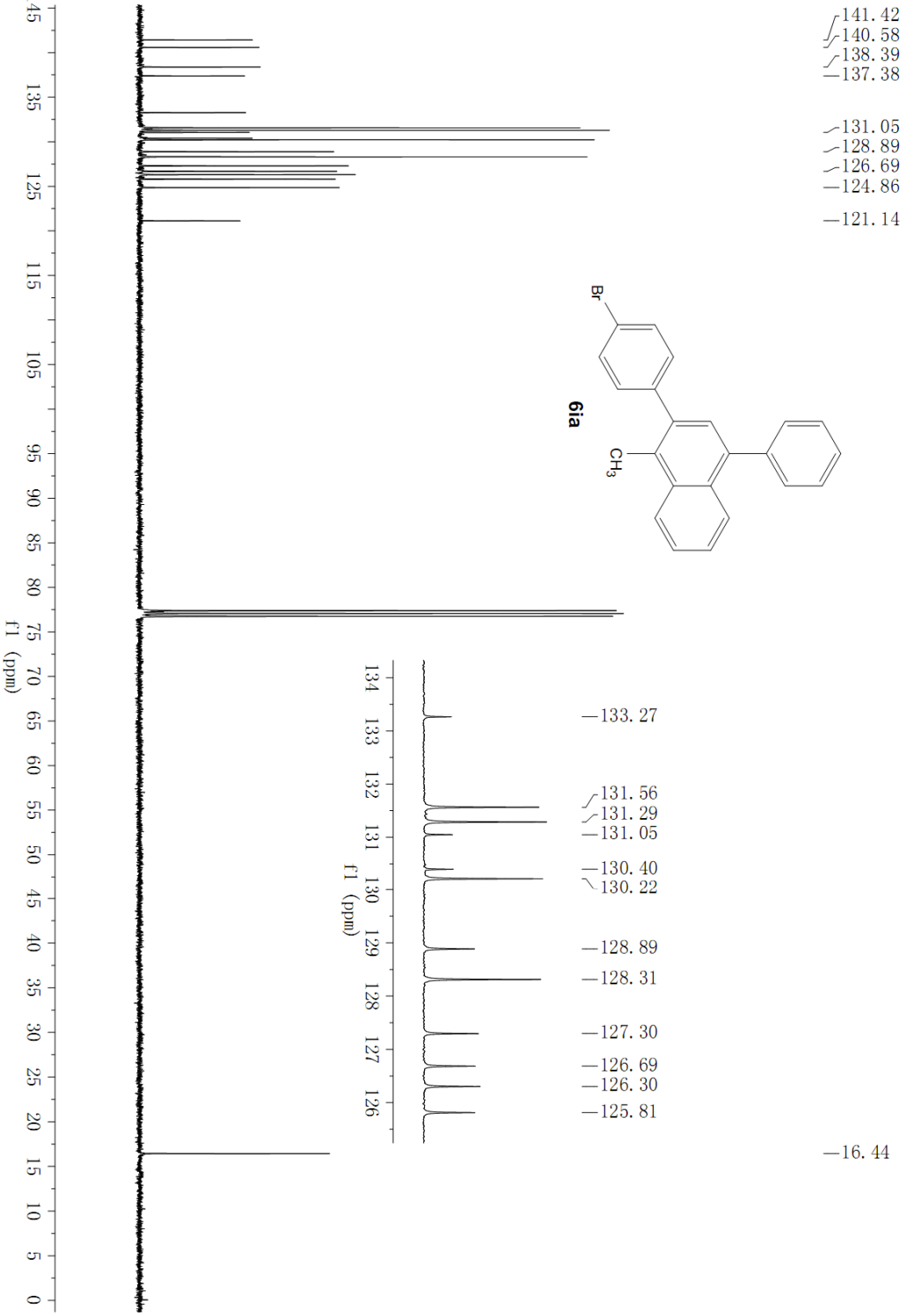

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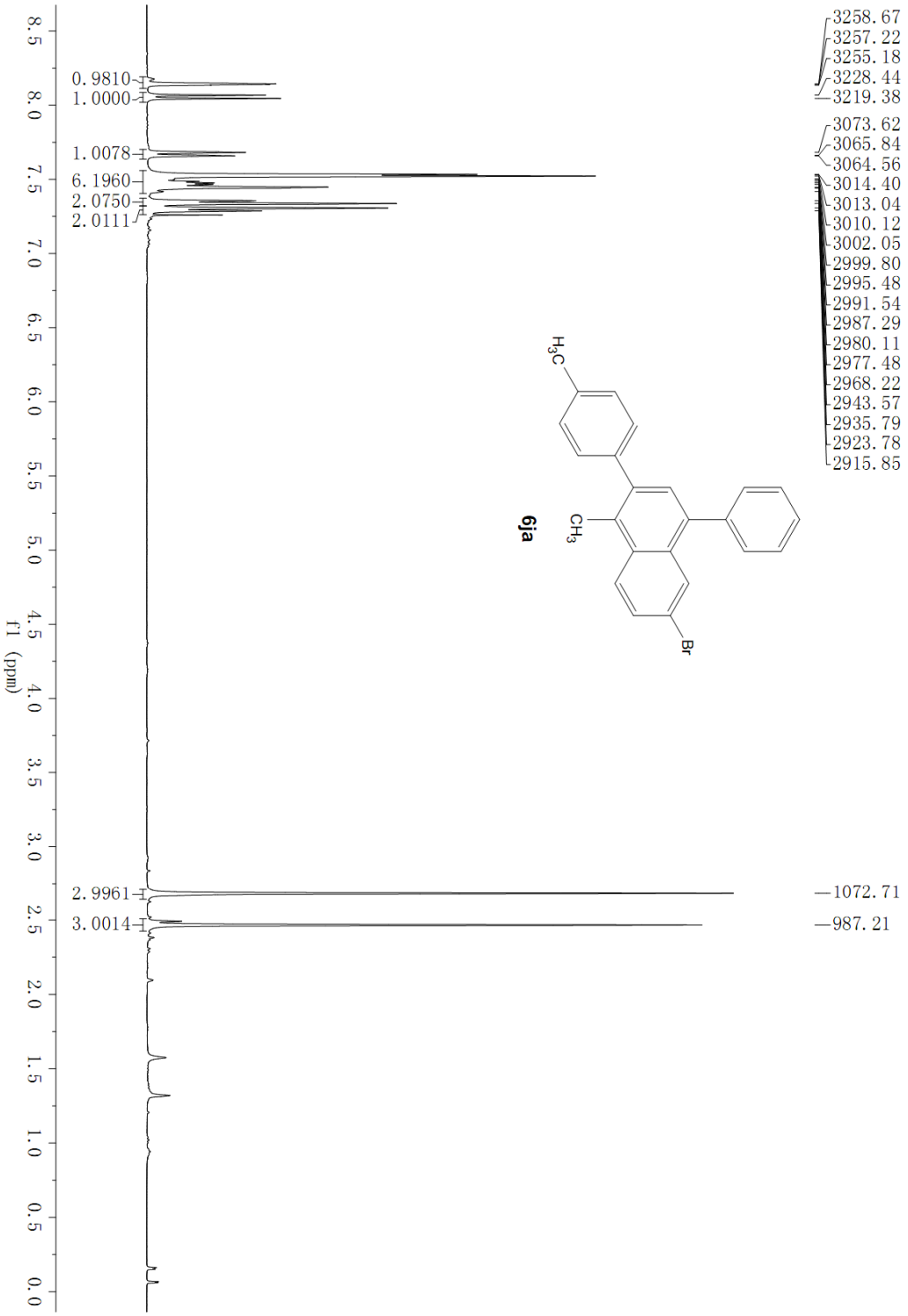

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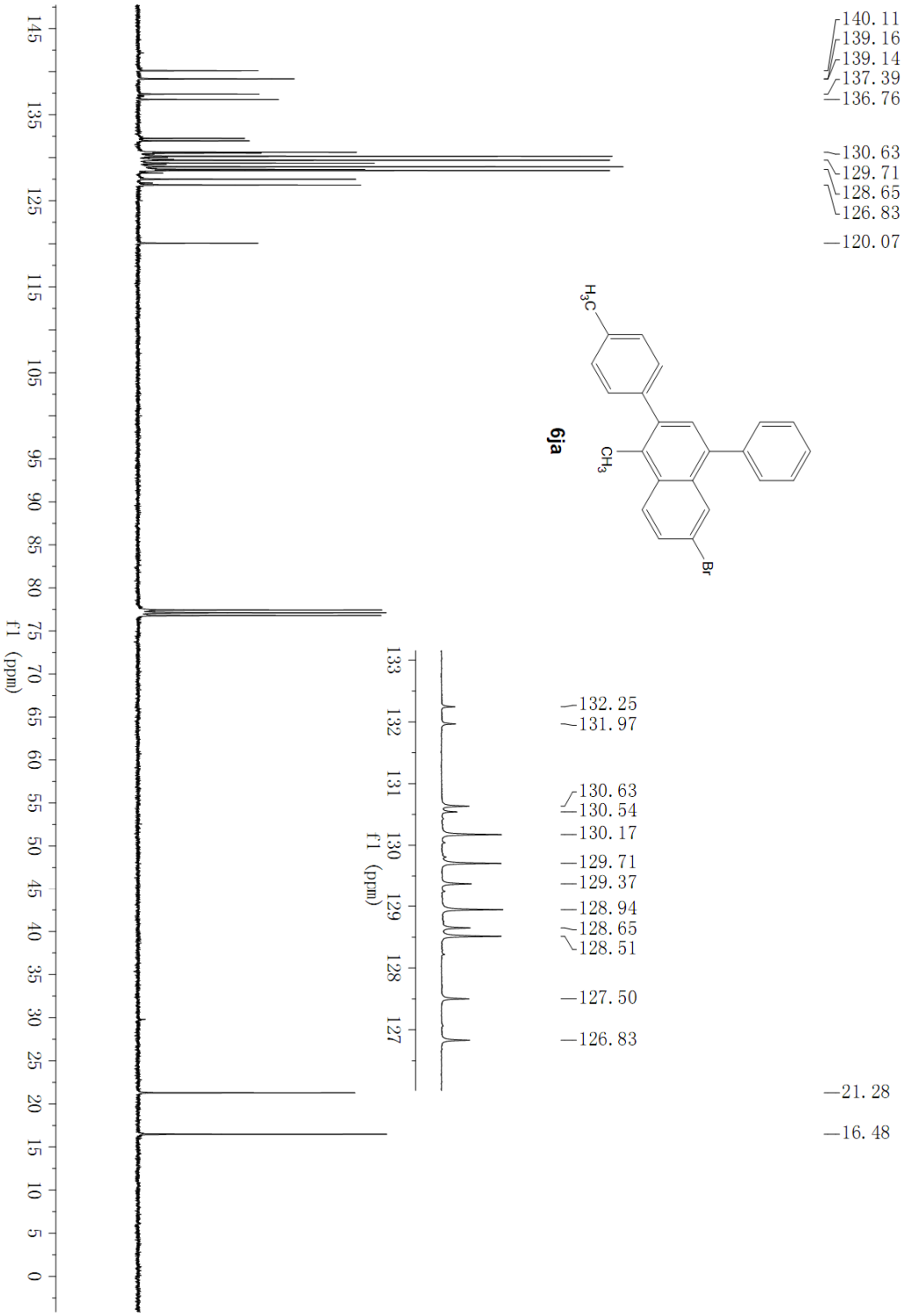

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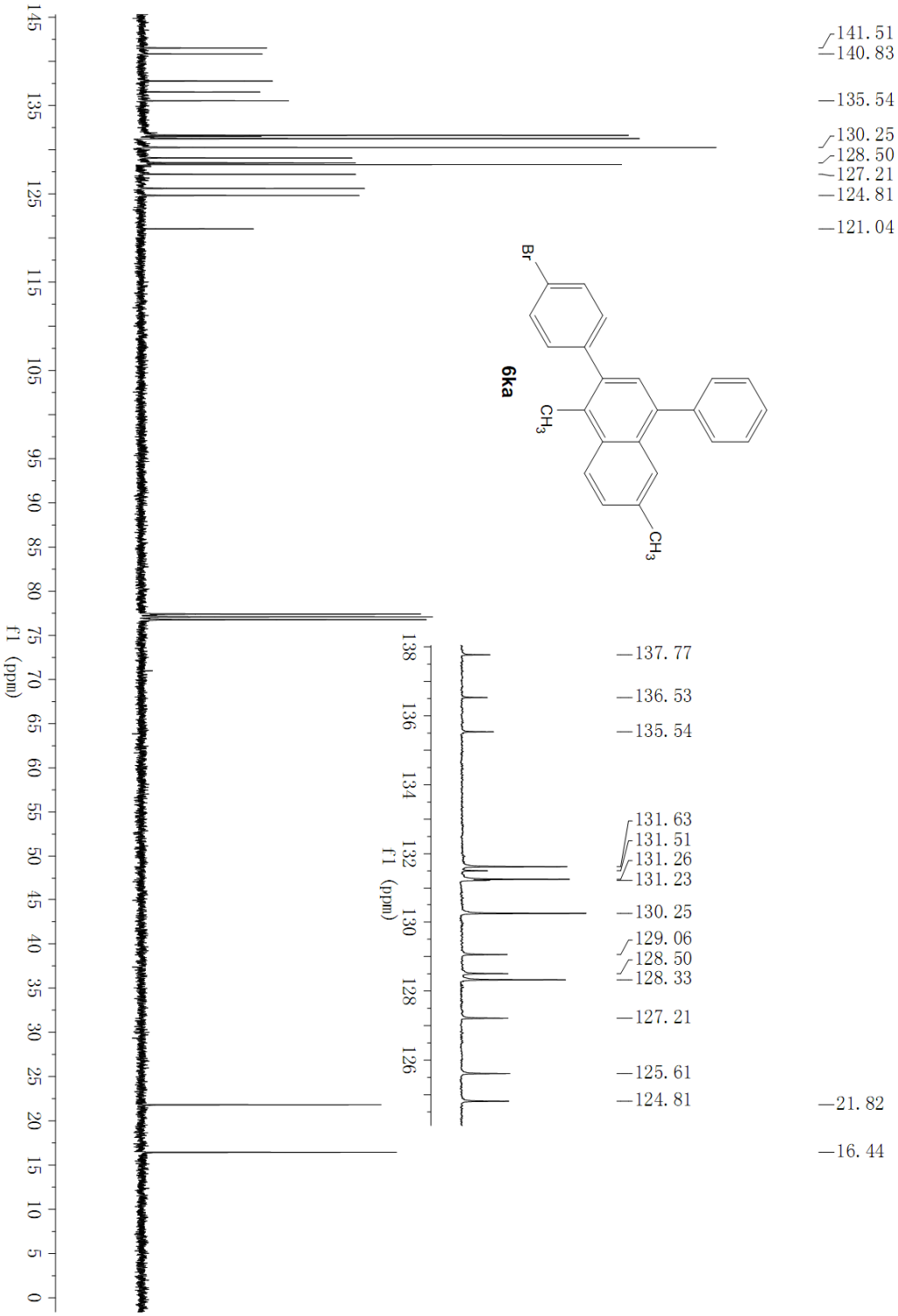

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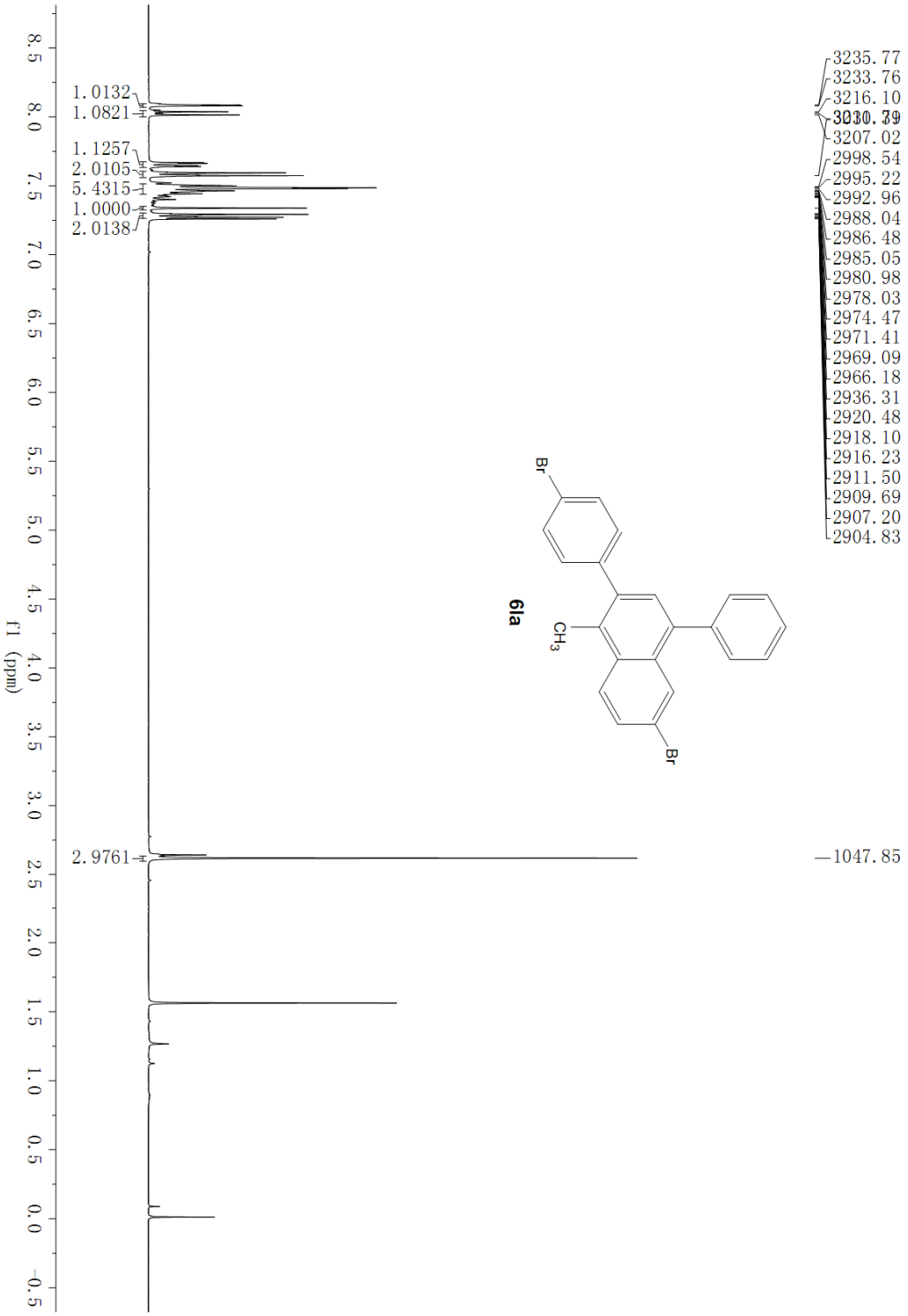

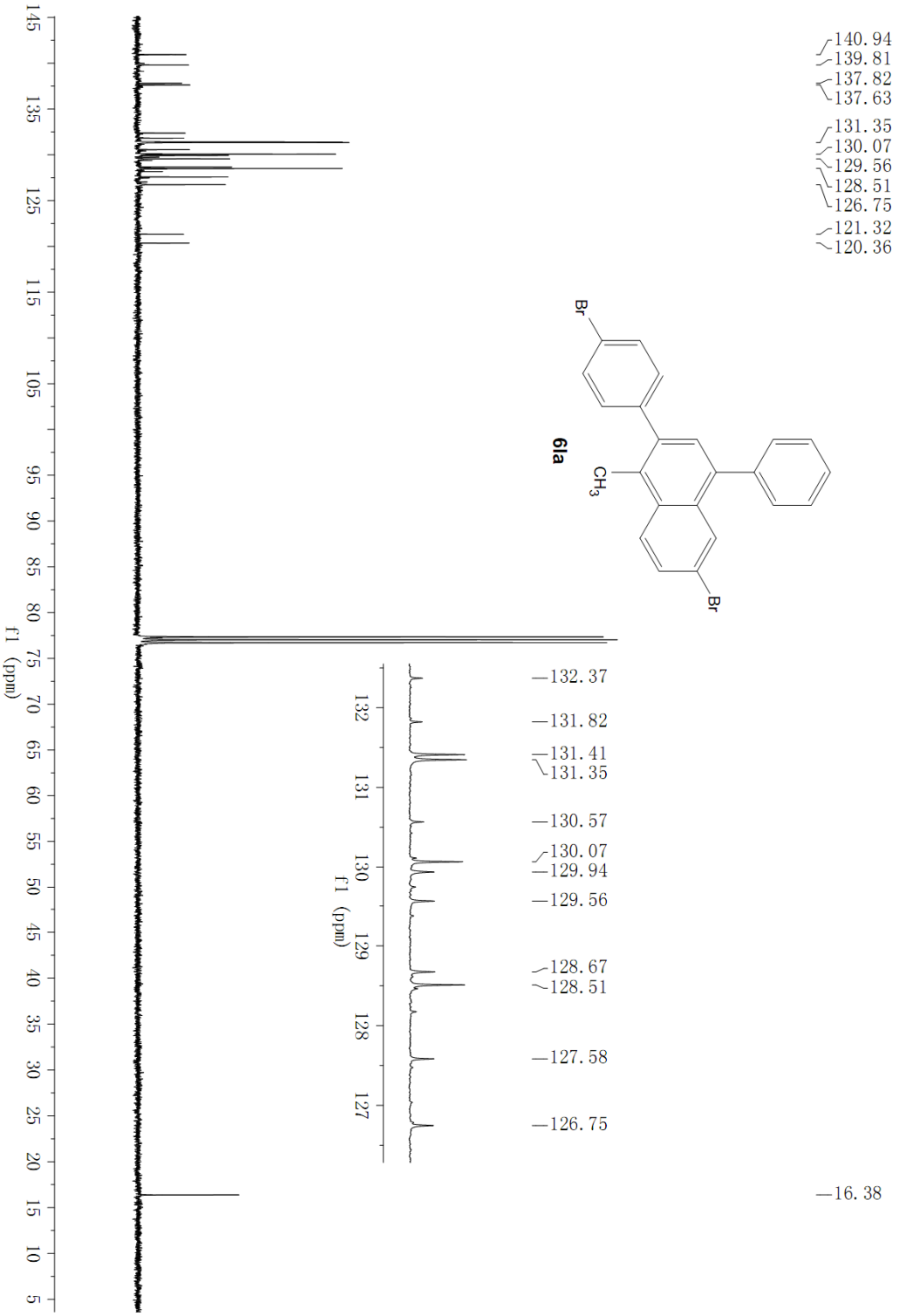

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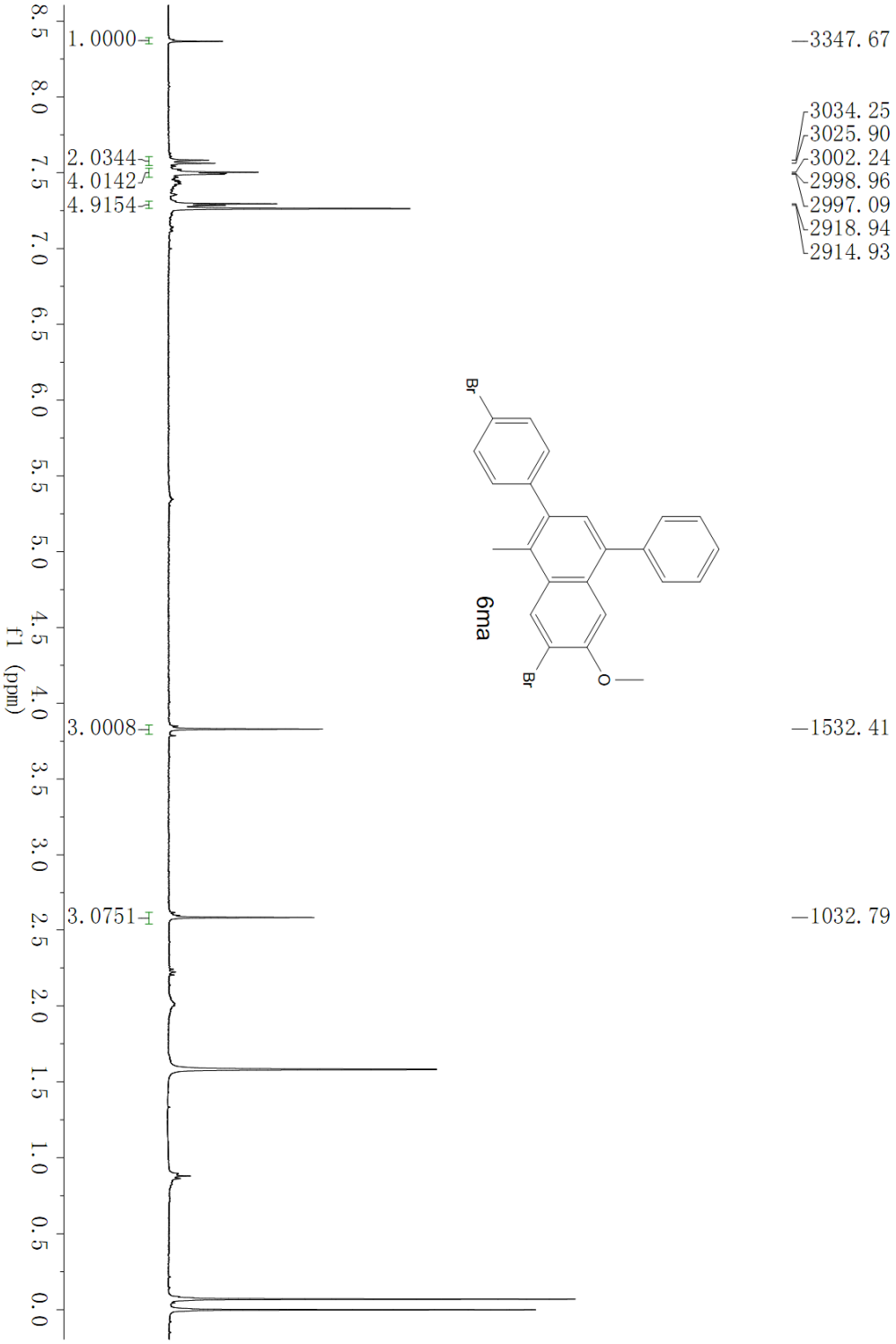

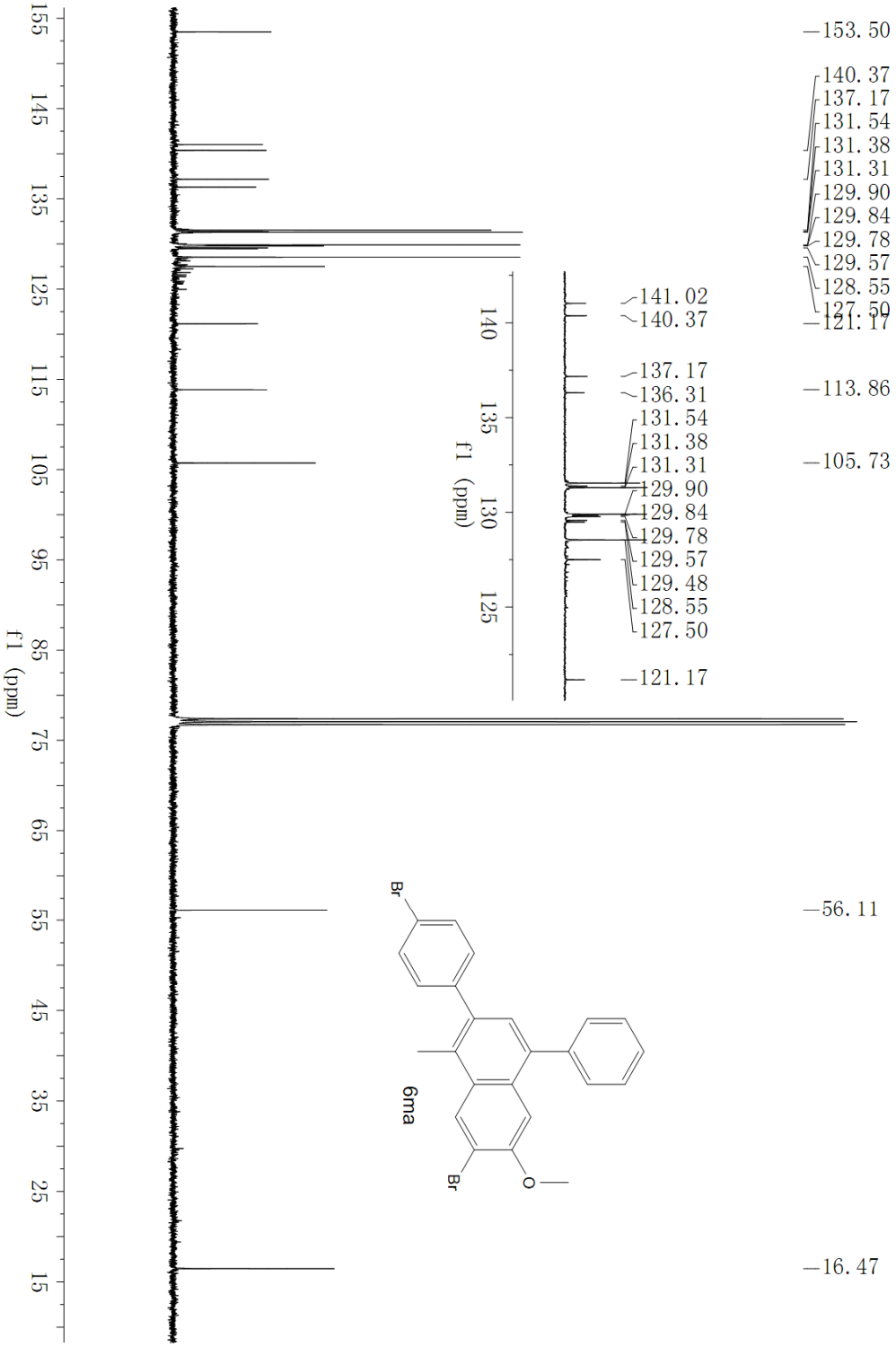

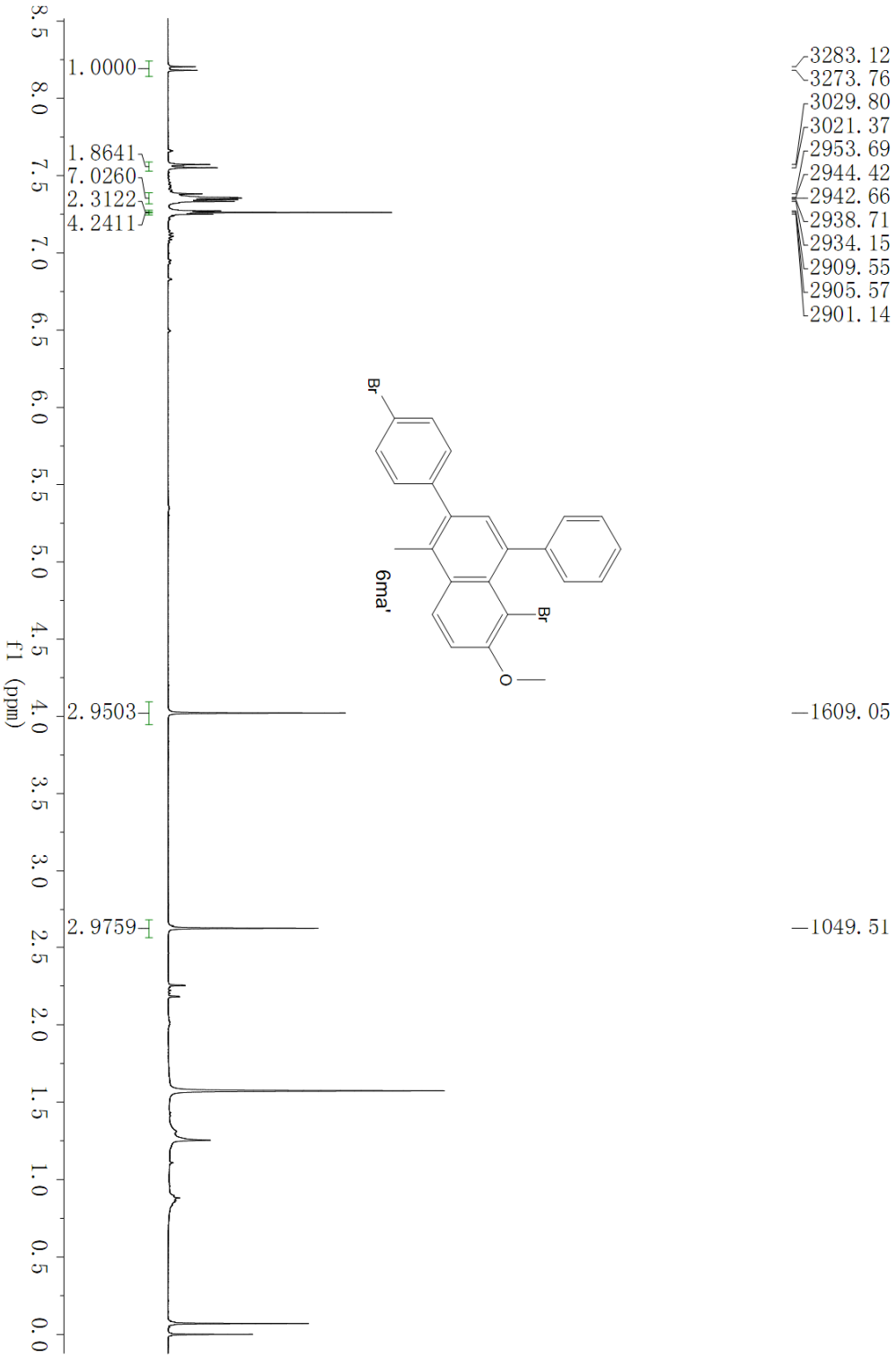

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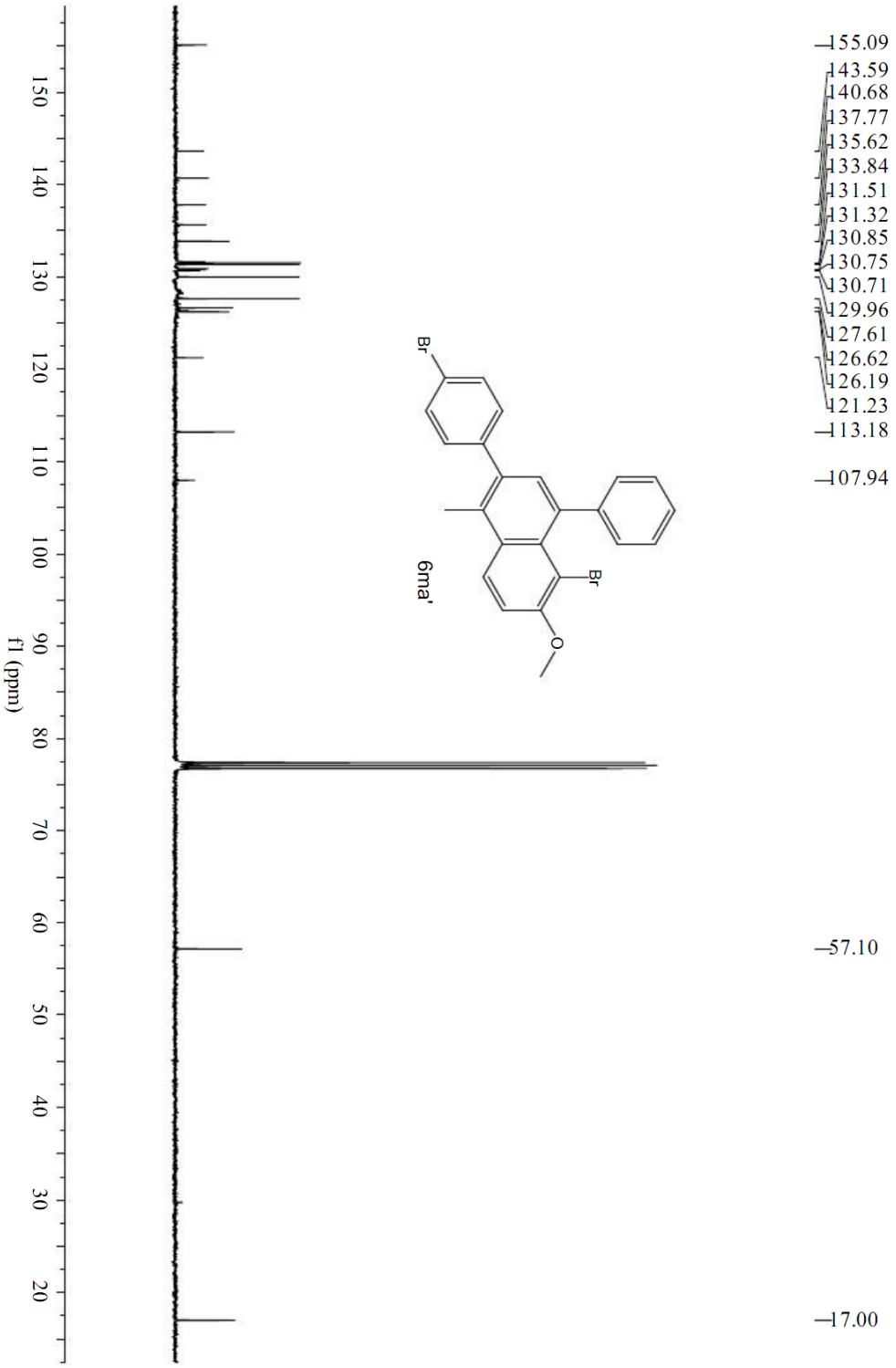

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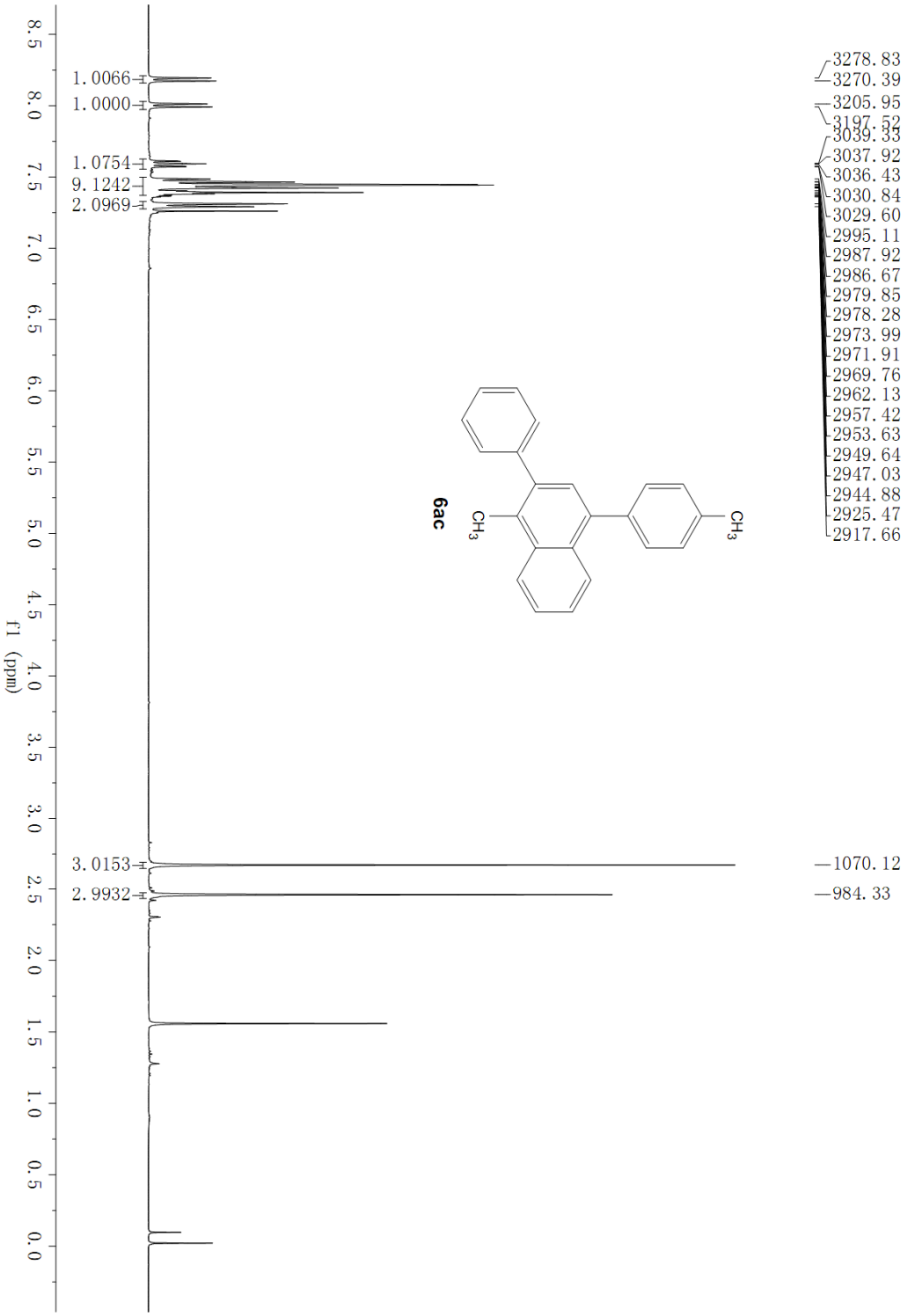

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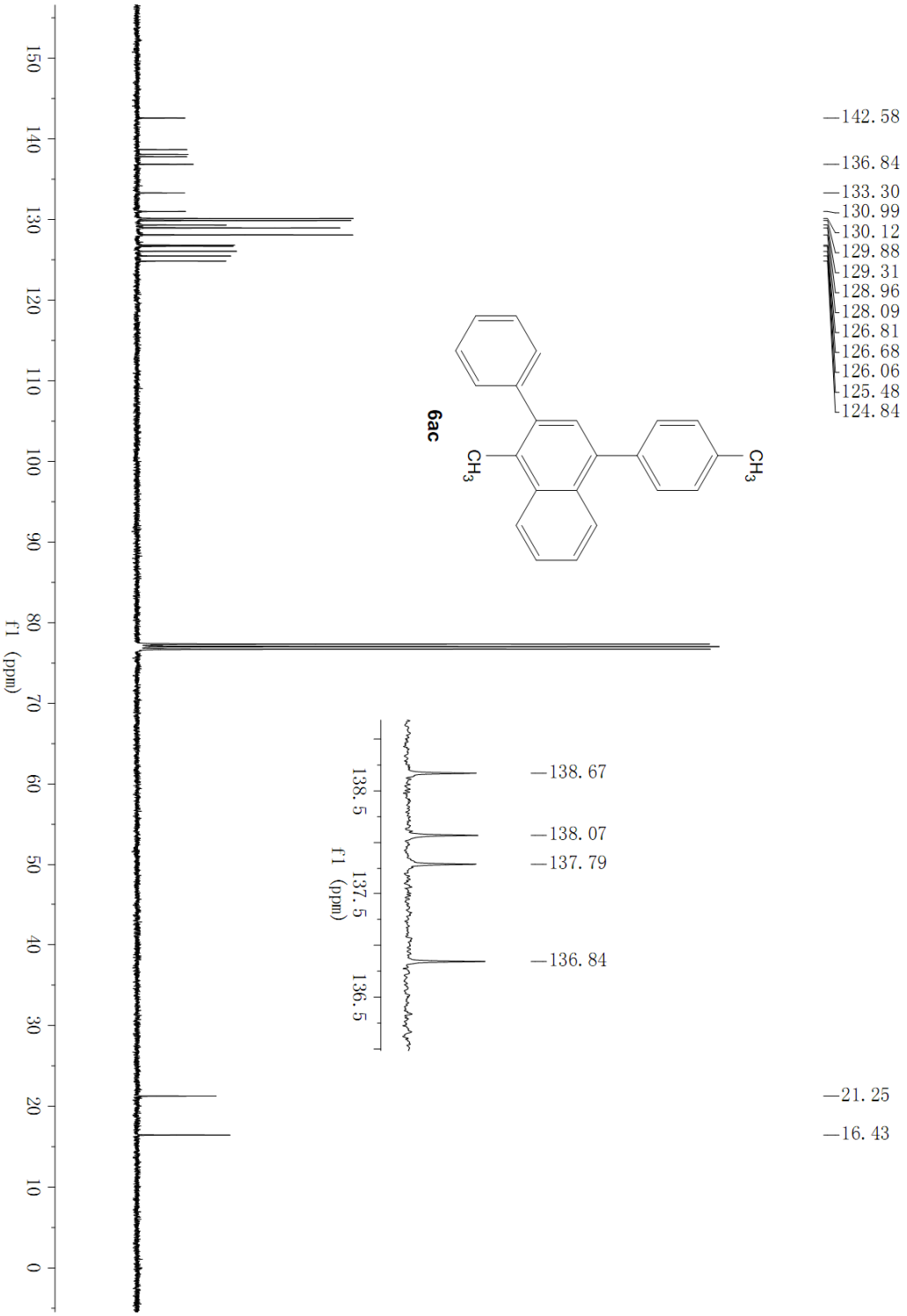

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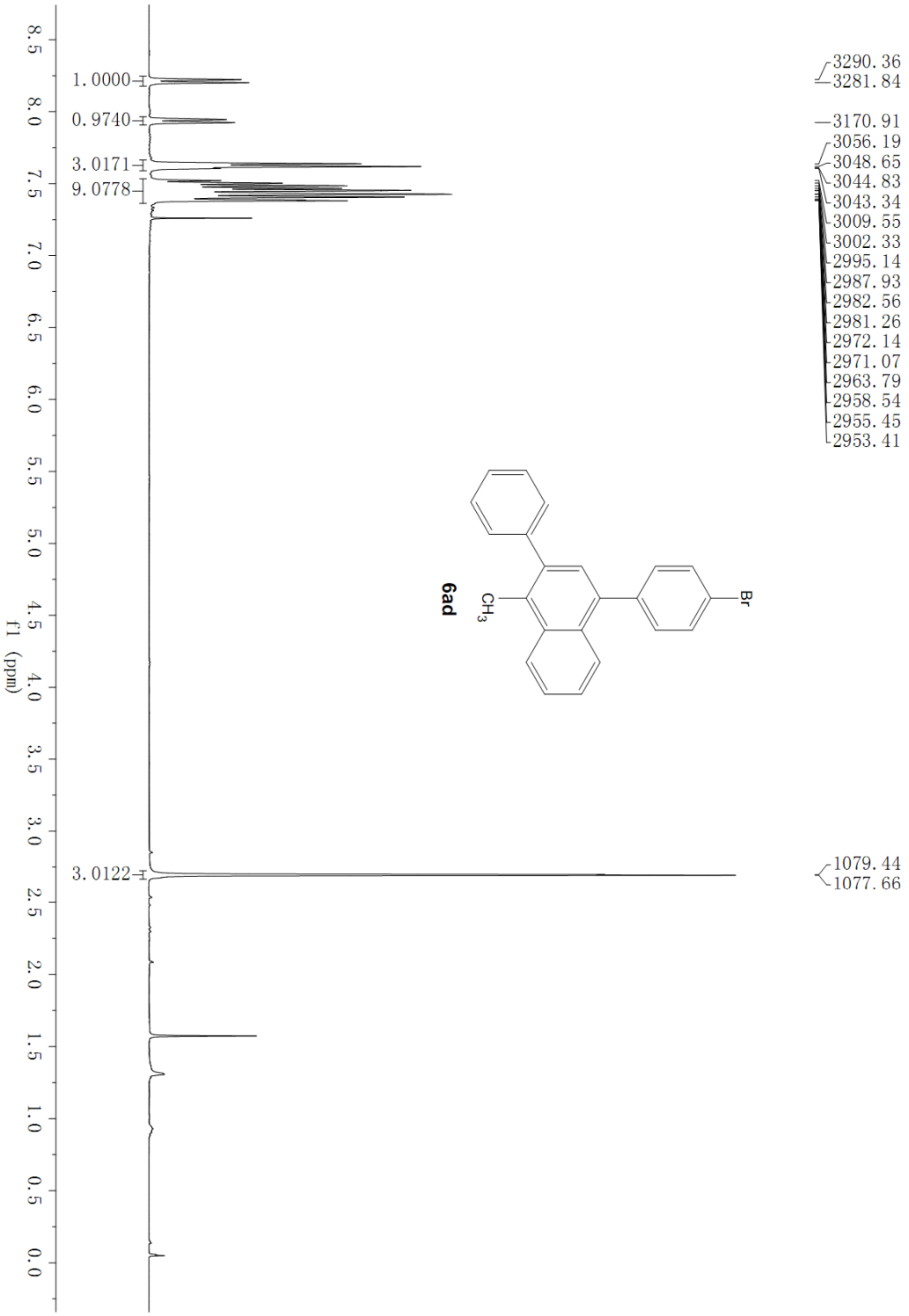

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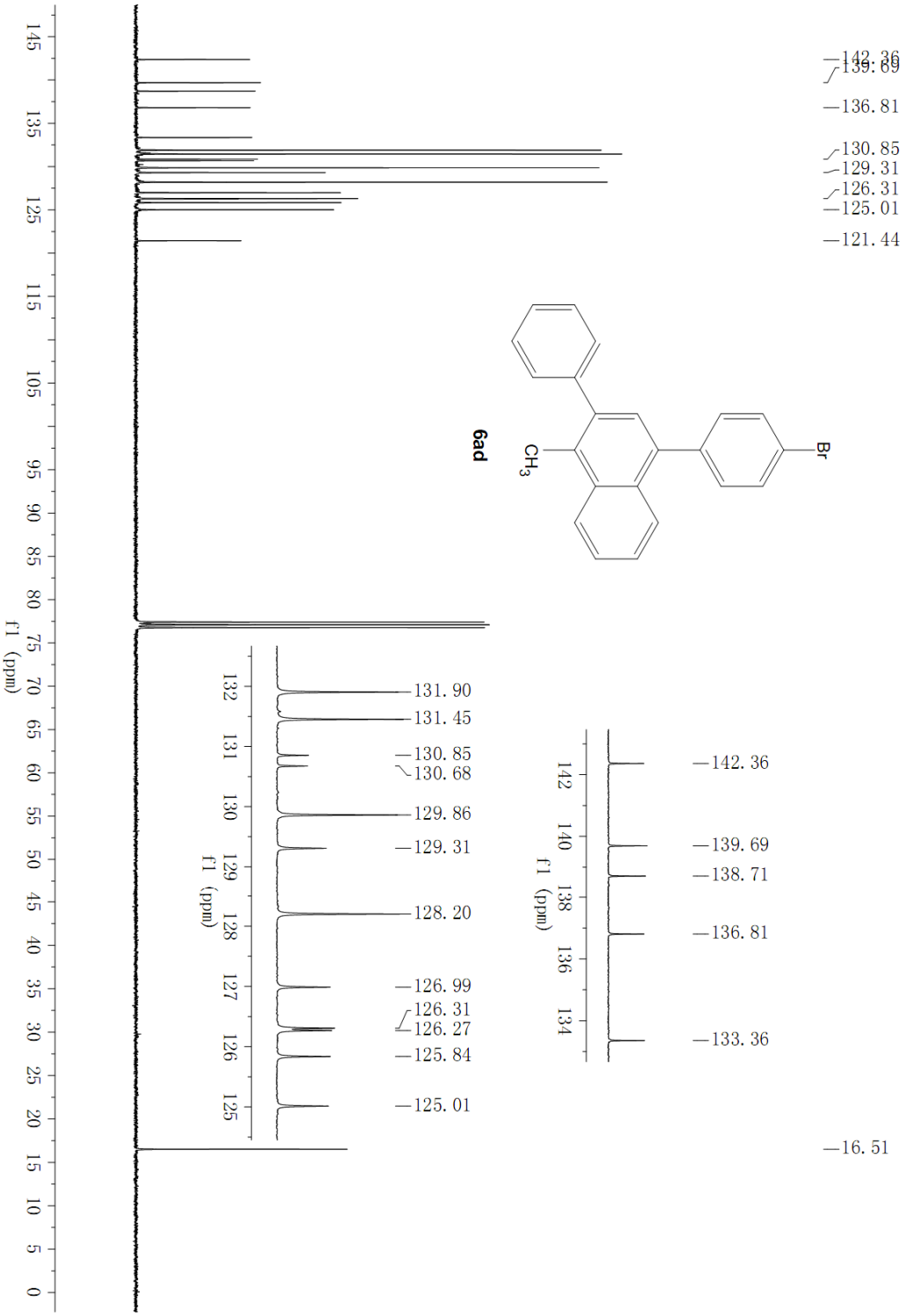

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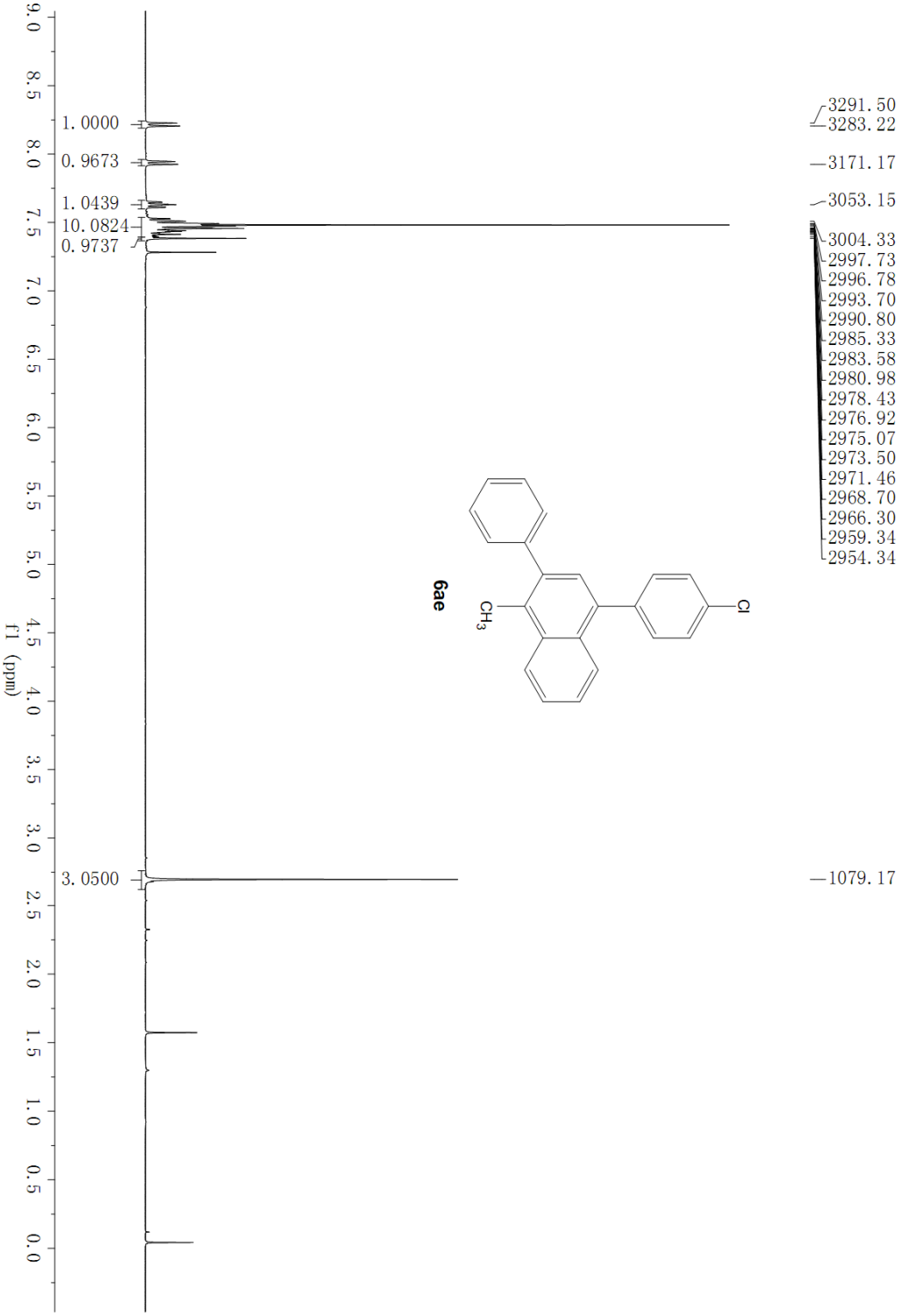

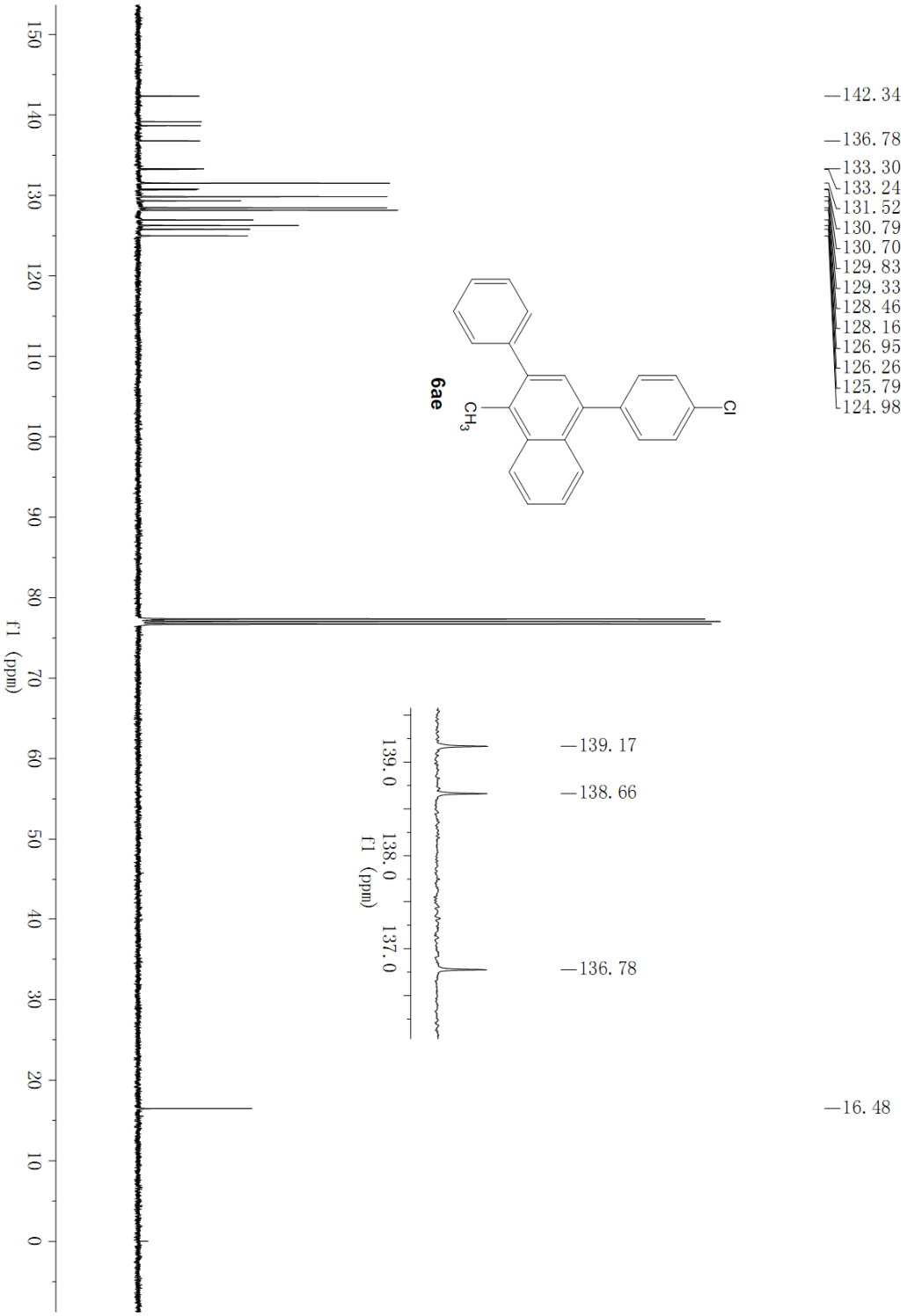

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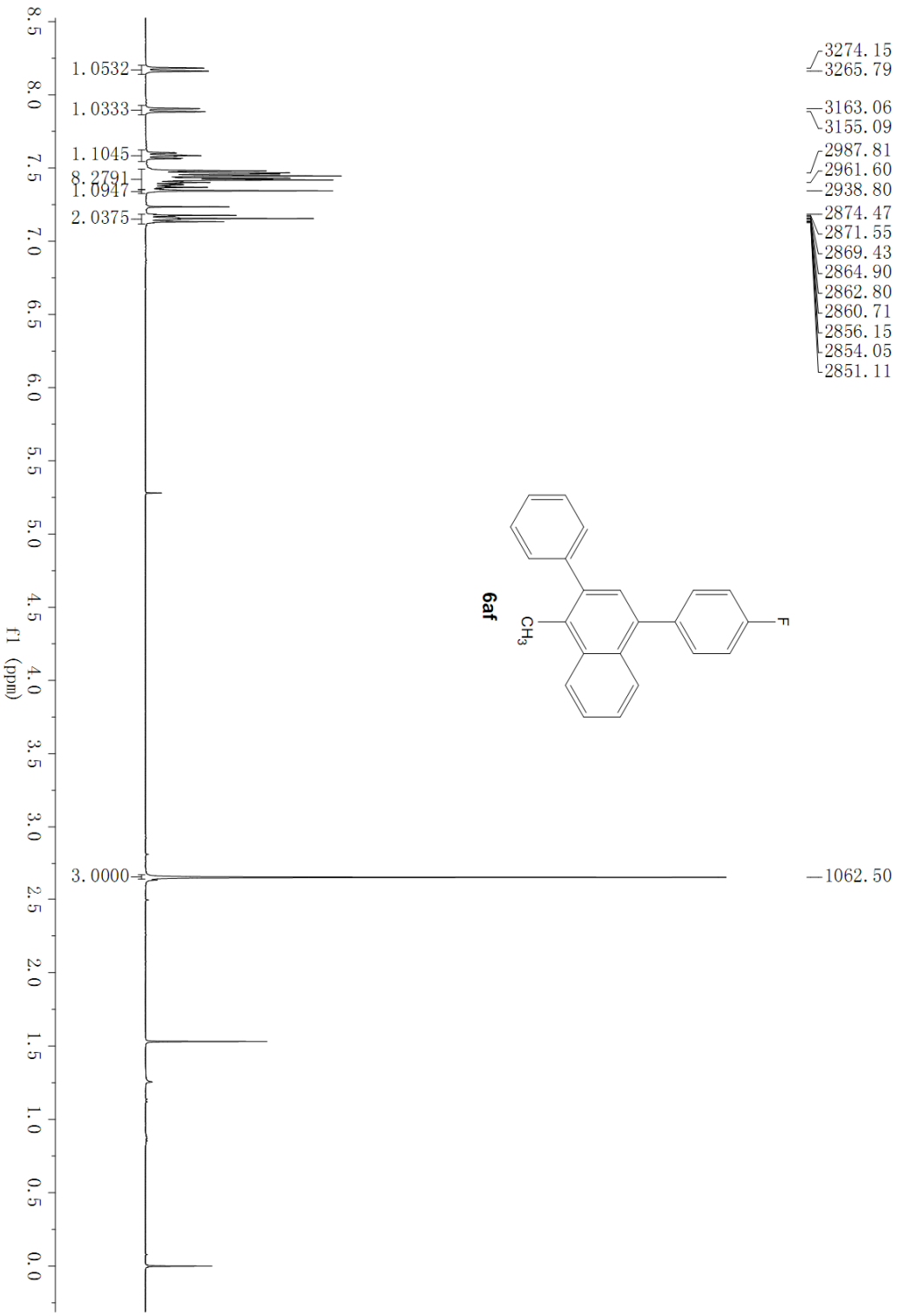

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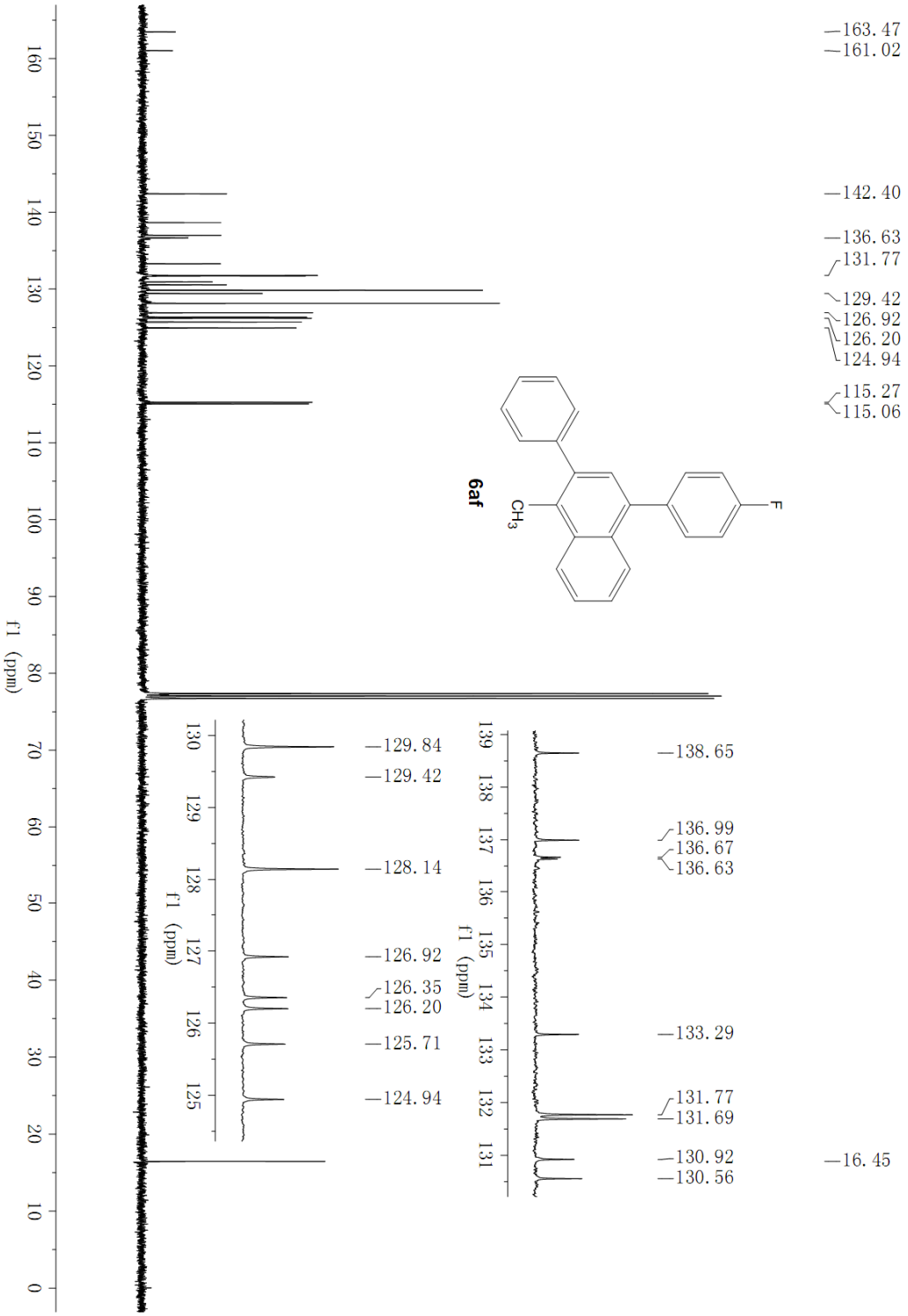

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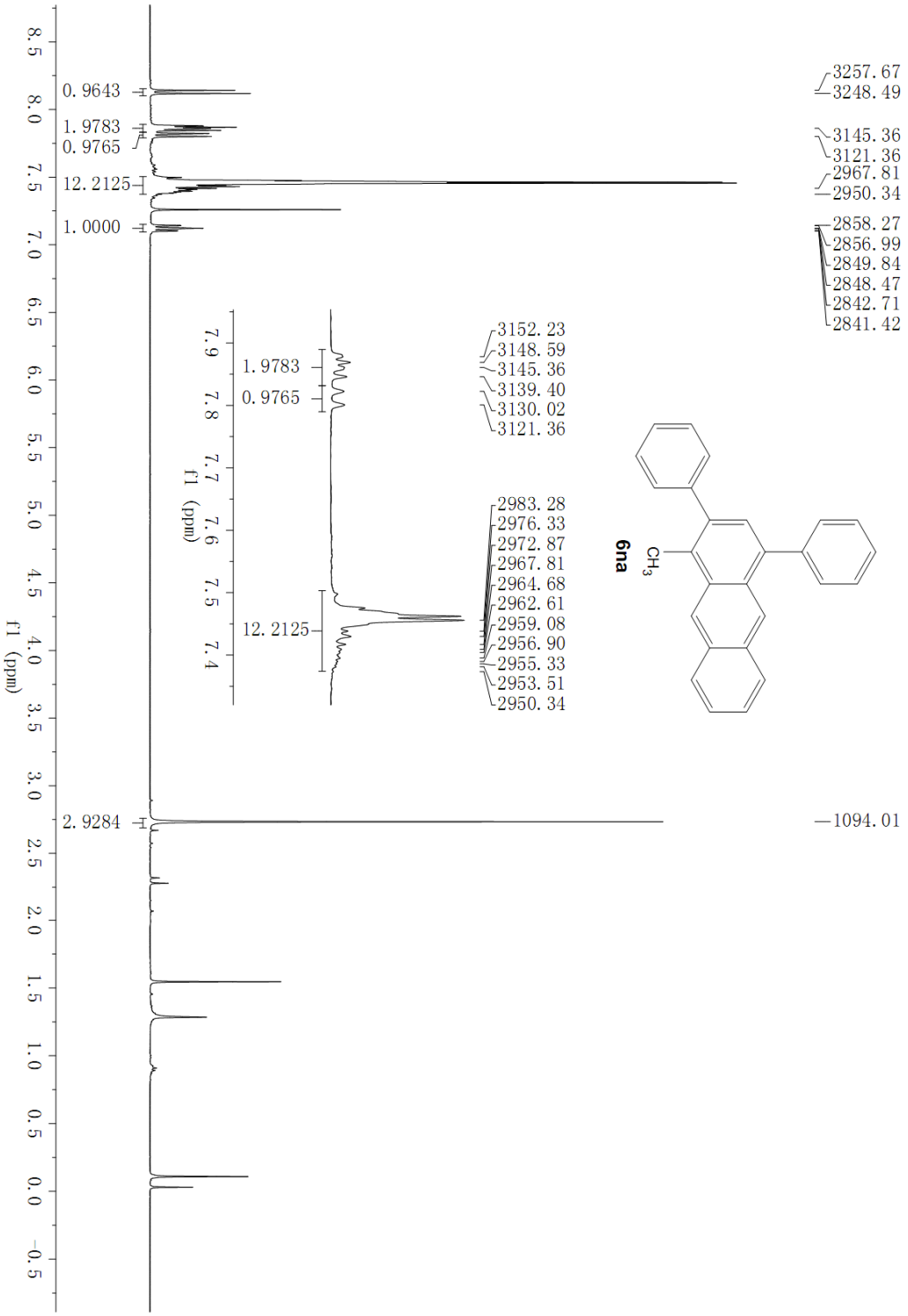

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