SUPPORTING INFORMATION

A One-Step Base-Free Synthesis of N-Arylamides via Modified Pivaloyl Mixed Anhydrides Mediated Amide couplings

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1. General Methods.

All reactions were carried out under an air atmosphere. All solvents were purifified and dried according to the standard methods prior to use. All commercial reagents were used without additional purifification. Flash chromatography was carried out with silica gel (200−300 mesh). Melting points were determined without correction on a digital melting-point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded with 400 MHz, 500 MHz and 101 MHz spectrometers in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard, respectively. High-resolution mass spectra (HRMS) were recorded using an ion trap with a positive-ion electrospray ionization (ESI^+) source.

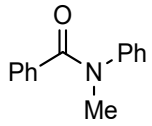
2. General Procedure for the Synthesis of Products.

An 8 mL tube was charged with carboxylic acids **1** (0.55 mmol), *N*-Arylamines **2** (0.5 mmol), Pivalic Anhydride (0.65 mmol) and toluene (1.5 mL). After stirred at the corresponding temperature under an air atmosphere for 4 h, the reaction mixture was extracted with NaOH (2 M, 3 × 15 mL), HCl (2 M, 3 × 15 mL) and then the organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the products **3**.

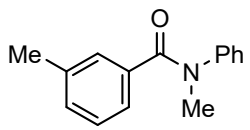
3. Gram Scale Reaction.

A 100 mL round-bottom flask was charged with 2-Methyl-2-propenoic acid (0.9470 g, 11 mmol), *N*-methylaniline (1.0716 g, 10 mmol), pivalic anhydride (2.4213 g, 13 mmol) and toluene (30 mL). After stirred at 50 ℃ under an air atmosphere for 6 h, the reaction mixture was extracted with NaOH (2 M, 3 × 30 mL), HCl (2 M, 3 × 30 mL) and then the organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and recrystallized in ethyl acetate and petroleum ether to give the product **3ta** (1.46 g, 82%).

4. Characterization of products.

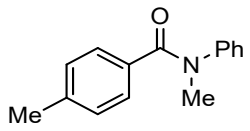


***N*-methylbenzanilide (3aa).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3aa** as a yellow liquid (97.4 mg, 92%); R_f = 0.38 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, J = 9.1 Hz, 2H), 7.25-7.18 (m, 3H), 7.18-7.09 (m, 3H), 7.03 (d, J = 7.5 Hz, 2H), 3.50 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[1]

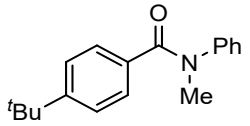


***N*-methyl-3-methyl-*N*-phenylbenzamide (3ba).** The reaction of **1b** (74.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ba** as a white solid (93.2 mg, 83%);

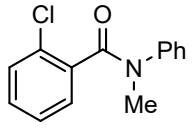
melting point: 65-67 °C; R_f = 0.29 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25-7.18 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 3H), 7.00 (d, *J* = 4.2 Hz, 2H), 3.49 (s, 3H), 2.22 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[1]



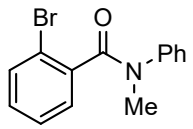
***N*-methyl-4-methyl-*N*-phenylbenzamide (3ca).** The reaction of **1c** (74.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ca** as a white solid (80.9 mg, 72%); melting point: 66-67 °C; R_f = 0.29 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 7.7, 17.2 Hz, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 3.49 (s, 3H), 2.25 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[1]



4-tert-butyl-*N*-methyl-*N*-phenylbenzamide (3da). The reaction of **1d** (98.0 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3da** as a white solid (111.3 mg, 83%); melting point: 115-117 °C; R_f = 0.42 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.21 (m, 4H), 7.19-7.12 (m, 3H), 7.08-7.03 (m, 2H), 3.49 (s, 3H), 1.23 (s, 9H). ^{1}H NMR is consistent with the literature precedent.[2]

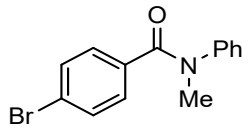


2-chloro-*N*-methyl-*N*-phenylbenzamide (3ea). The reaction of **1e** (86.1 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ea** as a lightyellow solid (88.5 mg, 72%); melting point: 89-91 °C; R_f = 0.24 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21-7.15 (m, 3H), 7.15-7.02 (m, 6H), 3.51 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]

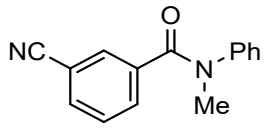


2-bromo-*N*-methyl-*N*-phenylbenzamide (3fa). The reaction of **1f** (110.6 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3fa** as a yellow viscous liquid (94.3 mg,

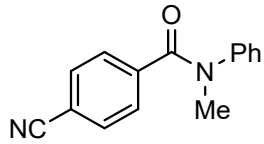
65%); R_f = 0.21 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.24-7.06 (m, 7H), 7.05-6.98 (m, 1H), 3.51 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[4]



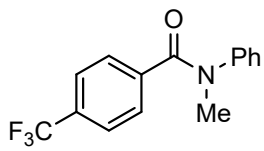
4-bromo-*N*-methyl-*N*-phenylbenzamide (3ga). The reaction of **1g** (110.6 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ga** as a lightyellow viscous liquid (124.0 mg, 85%); R_f = 0.32 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.21 (m, 4H), 7.20-7.14 (m, 3H), 7.02 (d, *J* = 7.7 Hz, 2H), 3.49 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[2]



3-cyano-*N*-methyl-*N*-phenylbenzamide (3ha). The reaction of **1h** (80.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ha** as a white solid (83.3 mg, 71%); melting point: 95-97 °C; R_f = 0.16 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.51 (m, 2H), 7.33-7.23 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.51 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[5]

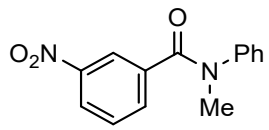


Cyano-*N*-methyl-*N*-phenylbenzamide (3ia). The reaction of **1i** (80.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ia** as a white solid (90.9 mg, 77%); melting point: 123-124 °C; R_f = 0.16 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.0 Hz, 2H), 3.51 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[6]

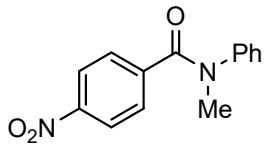


***N*-methyl-*N*-phenyl-4-(trifluoromethyl) benzamide (3ja).** The reaction of **1j** (104.6 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ja** as a lightyellow solid

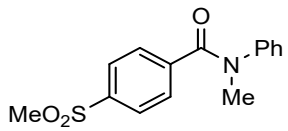
(122.7 mg, 88%); melting point: 109-112 °C; R_f = 0.37 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7 .47-7.37 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.52 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[5]



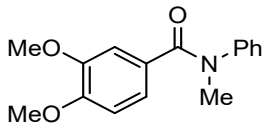
***N*-methyl-3-nitro-*N*-phenylbenzamide (3ka).** The reaction of **1k** (91.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ka** as a light green solid (119.8 mg, 94%); melting point: 136-139 °C; R_f = 0.21 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.31-7.23 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.53 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[7]



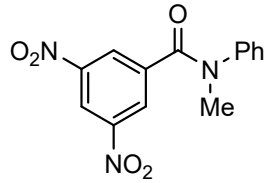
***N*-methyl-4-nitro-*N*-phenylbenzamide (3la).** The reaction of **1l** (91.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3la** as a white solid (114.4 mg, 89%); melting point: 135-137 °C; R_f = 0.22 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.22 (dd, *J* = 7.8, 18.0 Hz, 3H), 7.03 (d, *J* = 7.0 Hz, 2H), 3.53 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]



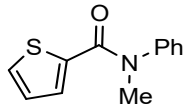
***N*-methyl-4-(methylsulfonyl)-*N*-phenylbenzamide (3ma).** The reaction of **1m** (110.1 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ma** as a light yellow solid (94.2 mg, 65%); melting point: 105-109 °C; R_f = 0.11 (petroleum ether/ethyl acetate 2: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 7.6, 18.4 Hz, 3H), 7.03 (d, *J* = 7.5 Hz, 2H), 3.52 (s, 3H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 143.8, 141.5, 141.0, 129.6, 129.5, 127.4, 127.0, 127.0, 44.4, 38.4. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}NO_3S^+$ $(M+H)^+$ 290.0845, found 290.0842.



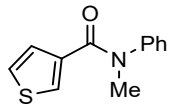
3,4-dimethoxy-*N*-methyl-*N*-phenylbenzamide (3na). The reaction of **1n** (100.2 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3na** as a colorless transparent liquid (99.1 mg, 73%); R_f = 0.25 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.09-7.03 (m, 2H), 6.93 (dd, J = 2.0, 8.4 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.64 (s, 3H), 3.50 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[8]



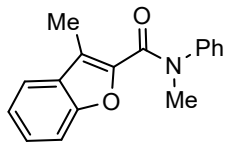
***N*-methyl-3,5-dinitro-*N*-phenylbenzamide (3oa).** The reaction of **1o** (116.7 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3oa** as a light yellow solid (118.6 mg, 79%); melting point: 178-180 °C; R_f = 0.48 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.45 (d, J = 2.1 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.26 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 3.57 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]



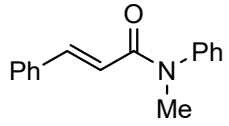
***N*-methyl-*N*-phenyl-2-thiophenecarboxamide (3pa).** The reaction of **1p** (70.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3pa** as a white crystals (90.1 mg, 83%); melting point: 107-108 °C; R_f = 0.32 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.34 (m, 3H), 7.33-7.21 (m, 3H), 6.81-6.75 (m, 1H), 6.72 (dd, J = 1.2, 3.8 Hz, 1H), 3.45 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[6]



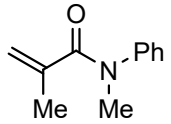
***N*-methyl-*N*-phenyl-3-thiophenecarboxamide (3qa).** The reaction of **1q** (70.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3qa** as a yellow viscous liquid (95.9 mg, 88%); R_f = 0.26 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36-7.29 (m, 2H), 7.29-7.23 (m, 1H), 7.20 (d, J = 1.3 Hz, 1H), 7.16-7.09 (m, 2H), 7.02 (dd, J = 3.0, 5.1 Hz, 1H), 6.87 (dd, J = 1.3, 5.1 Hz, 1H), 3.46 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[8]



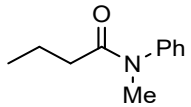
***N*,3-dimethyl-*N*-phenyl-2-benzofurancarboxamide (3ra).** The reaction of **1r** (96.9 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ra** as a white crystals (120.7 mg, 91%); melting point: 149-150 °C; R_f = 0.45 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 6.8 Hz, 1H), 7.31-7.24 (m, 3H), 7.24-7.18 (m, 2H), 7.18-7.13 (m, 2H), 7.08 (d, J = 8.4 Hz, 1H), 3.51 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8, 153.5, 144.3, 144.1, 129.1, 128.9, 126.7, 126.3, 126.1, 122.7, 121.6, 120.4, 111.4, 38.2, 9.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NO_2^+$ $(M+H)^+$ 266.1176, found 266.1181.



***N*-methyl-*N*,3-diphenyl-2-propenamide (3sa).** The reaction of **1s** (81.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3sa** as a yellow viscous liquid (114.0 mg, 96%); R_f = 0.50 (petroleum ether/ethyl acetate 2: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 15.6 Hz, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.32-7.21 (m, 7H), 6.37 (d, J = 15.5 Hz, 1H), 3.42 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[1]

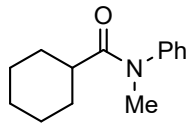


***N*,2-dimethyl-*N*-phenyl-2-propenamide (3ta).** The reaction of **1t** (0.9470 g, 11 mmol) and **2a** (1.0716 g, 10 mmol) gives **3ta** as a lightyellow crystals (1.4554 g, 82%); R_f = 0.36 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.31 (m, 2H), 7.28-7.22 (m, 1H), 7.17-7.11 (m, 2H), 5.07-4.95 (m, 2H), 3.35 (s, 3H), 1.76 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[9]

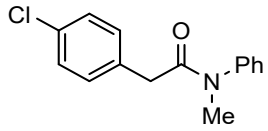


***N*-methyl-*N*-phenylbutanamide (3ua).** The reaction of **1u** (48.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ua** as a yellow liquid (62.5 mg, 71%); R_f = 0.29 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.22-7.13 (m, 2H), 3.27 (s, 3H), 2.05 (t, J = 7.6

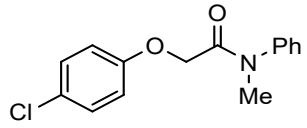
Hz, 2H), 1.60 (p, J = 7.5 Hz, 2H), 0.82 (t, J = 7.4 Hz, 3H). ^{1}H NMR is consistent with the literature precedent.[1]



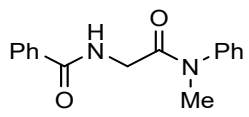
***N*-methyl-*N*-phenyl-cyclohexanecarboxamide (3va).** The reaction of **1v** (70.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3va** as a yellow viscous liquid (86.7 mg, 80%); R_f = 0.42(petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 3.24 (s, 3H), 2.18 (t, J = 11.4 Hz, 1H), 1.73-1.46 (m, 7H), 1.17 (t, J = 12.9 Hz, 1H), 0.95 (q, J = 12.9 Hz, 2H). ^{1}H NMR is consistent with the literature precedent.[8]



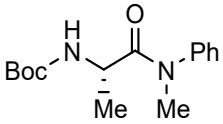
4-chloro-*N*-methyl-*N*-phenyl-benzeneacetamide (3wa). The reaction of **1w** (93.8 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3wa** as a yellow liquid (98.1 mg, 76%); R_f = 0.32 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46-7.32 (m, 3H), 7.20 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 6.8 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 3.42 (s, 2H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 143.8, 133.9, 132.5, 130.5, 129.8, 128.4, 128.1, 127.6, 40.3, 37.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}ClNO^+$ $(M+H)^+$ 260.0837, found 260.0840.



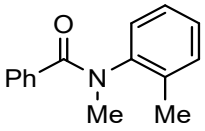
2-(4-chlorophenoxy)-*N*-methyl-*N*-phenyl-acetamide (3xa). The reaction of **1x** (102.6 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3xa** as a lightyellow viscous liquid (122.5 mg, 89%); R_f = 0.43 (petroleum ether/ethyl acetate 2: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, J = 7.3, 17.7 Hz, 3H), 7.24 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 4.38 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 156.7, 142.2, 130.2, 129.3, 128.6, 127.0, 126.3, 116.1, 66.5, 37.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}ClNO_2^+$ $(M+H)^+$ 276.0786, found 276.0787.



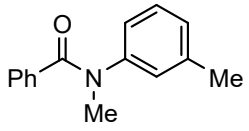
***N*-[2-(methylphenylamino)-2-oxoethyl]-benzamide (3ya).** The reaction of **1y** (98.5 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3ya** as a colorless transparent liquid (71.4 mg, 53%); R_f = 0.2 (petroleum ether/ethyl acetate 2: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.54-7.36 (m, 6H), 7.30-7.21 (m, 3H), 3.94 (d, *J* = 4.2 Hz, 2H), 3.33 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[10]



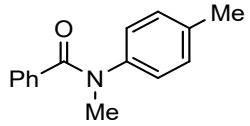
1,1-Dimethylethyl-(2*S*)-2-[(methylphenylamino)carbonyl]-1-pyrrolidinecarboxylate (3za). The reaction of **1z** (107.6 mg, 0.55 mmol) and **2a** (53.6 mg, 0.5 mmol) gives **3za** as a yellow viscous liquid (90.0 mg, 59%); R_f = 0.06 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.35 (d, *J* = 7.9 Hz, 1H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.28 (s, 3H), 1.41 (s, 9H), 1.10 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 155.0, 142.8, 130.0, 128.3, 127.5, 46.8, 37.9, 28.4, 27.2, 19.0. HRMS (ESI) *m/z* calcd for $C_{15}H_{23}N_2O_3^+$ $(M+H)^+$ 279.1703, found 279.1705.



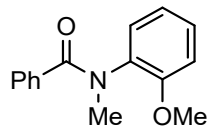
***N*-methyl-*N*-(2-methylphenyl)-benzamide (3ab).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2b** (60.6 mg, 0.5 mmol) gives **3ab** as a white solid (61.9 mg, 55%); melting point: 73-75 °C; R_f= 0.27 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.25 (m, 3H), 7.24-7.17 (m, 1H), 7.16-7.00 (m, 6H), 3.39 (s, 3H), 2.21 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[11]



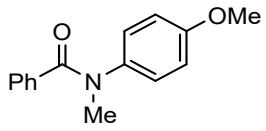
***N*-methyl-*N*-(3-methylphenyl)-benzamide (3ac).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2c** (60.6 mg, 0.5 mmol) gives **3ac** as a yellow viscous liquid (103.3 mg, 92%); R_f = 0.22 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.27 (m, 2H), 7.26-7.19 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.48 (s, 3H), 2.24 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[12]



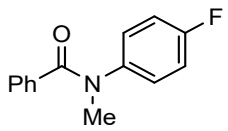
***N*-methyl-*N*-(4-methylphenyl)-benzamide (3ad).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2d** (60.6 mg, 0.5 mmol) gives **3ad** as a white solid (96.7 mg, 86%); melting point: 80-82 °C; R_f = 0.39 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.28 (m, 2H), 7.23 (d, J = 7.4 Hz, 1H), 7.17 (t, J = 7.2 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 3.47 (s, 3H), 2.27 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]



***N*-(2-methoxyphenyl)-*N*-methyl-benzamide (3ae).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2e** (68.6 mg, 0.5 mmol) gives **3ae** as a white solid (78.1 mg, 65%); melting point: 127-130 °C; R_f = 0.19 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, J = 7.6 Hz, 2H), 7.15 (dd, J = 8.9, 18.4 Hz, 4H), 7.02 (d, J = 7.7 Hz, 1H), 6.85-6.71 (m, 2H), 3.72 (s, 3H), 3.36 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]

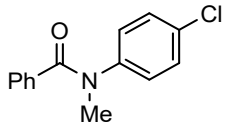


***N*-(4-methoxyphenyl)-*N*-methyl-benzamide (3af).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2f** (68.6 mg, 0.5 mmol) gives **3af** as a white crystal (107.3 mg, 89%); melting point: 84-86 °C; R_f = 0.22 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, J = 6.6 Hz, 2H), 7.19 (dd, J = 7.3, 17.5 Hz, 3H), 6.95 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 3.45 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]

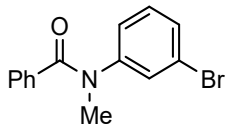


***N*-(4-fluorophenyl)-*N*-methyl-benzamide (3ag).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2g** (62.6 mg, 0.5 mmol) gives **3ag** as a lightyellow viscous liquid (105.5 mg, 92%); R_f = 0.23 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.22 (m, 3H), 7.18 (t, J = 7.3 Hz, 2H), 7.01 (dd, J = 4.8, 8.7 Hz,

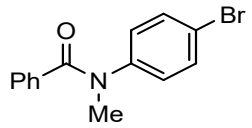
2H), 6.91 (t, J = 8.5 Hz, 2H), 3.47 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[12]



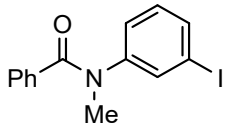
***N*-(4-chlorophenyl)-*N*-methyl-benzamide (3ah).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2h** (70.8 mg, 0.5 mmol) gives **3ah** as a white solid (111.1 mg, 90%); melting point: 73-74 °C; R_f = 0.33 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.24 (m, 3H), 7.20 (dd, J = 5.9, 8.1 Hz, 4H), 6.97 (d, J = 8.7 Hz, 2H), 3.47 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]



***N*-(3-bromophenyl)-*N*-methyl-benzamide (3ai).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2i** (93.0 mg, 0.5 mmol) gives **3ai** as a yellow viscous liquid (113.6 mg, 78%); R_f = 0.19 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.24 (m, 5H), 7.24-7.16 (m, 2H), 7.06 (t, J = 8.2 Hz, 1H), 6.95-6.88 (m, 1H), 3.48 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[13]

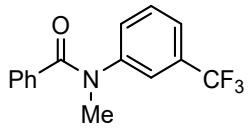


***N*-(4-bromophenyl)-*N*-methyl-benzamide (3aj).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2j** (93.0 mg, 0.5 mmol) gives **3aj** as a white solid (124.8 mg, 86%); melting point: 84-86 °C; R_f = 0.30 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.32 (m, 2H), 7.31-7.24 (m, 3H), 7.24-7.16 (m, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.47 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[3]

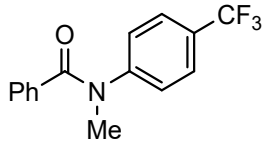


***N*-(3-iodinephenyl)-*N*-methyl-benzamide (3ak).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2k** (116.5 mg, 0.5 mmol) gives **3ak** as a yellow liquid (131.5 mg, 74%); R_f = 0.38 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 6.9 Hz, 2H), 7.35-7.24 (m, 3H), 7.20 (t, J = 7.4 Hz, 2H), 6.99-6.86 (m, 2H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 146.1, 135.6, 135.5, 135.4,

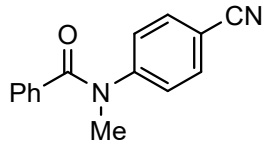
130.5, 130.0, 128.7, 128.0, 126.4, 93.8, 38.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}INO^+$ $(M+H)^+$ 338.0036, found 338.0034.



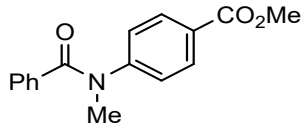
***N*-methyl-*N*-[3-(trifluoromethyl)-phenyl]-benzamide (3al).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2l** (87.6 mg, 0.5 mmol) gives **3al** as a yellow liquid (87.5 mg, 63%); R_f = 0.27 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, J = 7.9 Hz, 1H), 7.37-7.31 (m, 2H), 7.31-7.24 (m, 3H), 7.20 (dd, J = 2.1, 6.2 Hz, 3H), 3.53 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[14]



***N*-methyl-*N*-[4-(trifluoromethyl)-phenyl]-benzamide (3am).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2m** (87.6 mg, 0.5 mmol) gives **3am** as a yellow viscous liquid (43.8 mg, 31%); R_f = 0.23 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.4 Hz, 2H), 7.34-7.27 (m, 3H), 7.21 (t, J = 7.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 3.52 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[14]

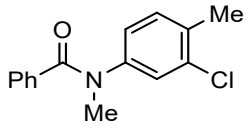


***N*-(4-cyanophenyl)-*N*-methyl-benzamide (3an).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2n** (66.1 mg, 0.5 mmol) gives **3an** as a yellow crystal (35.7 mg, 30%); R_f = 0.15 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, J = 8.6 Hz, 2H), 7.35-7.28 (m, 3H), 7.23 (t, J = 7.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 3.53 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[15]

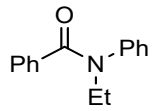


***N*-methyl-4-(benzoyl methylamino) benzoate (3ao)**. The reaction of **1a** (67.2 mg, 0.55 mmol) and **2o** (82.6 g, 0.5 mmol) gives **3ao** as a white viscous liquid (73.7 mg, 55%); R_f = 0.26 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (500 MHz,

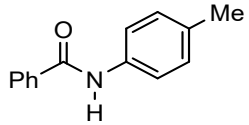
Chloroform-*d*) δ 7.89 (d, J = 8.6 Hz, 2H), 7.33-7.24 (m, 3H), 7.18 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 166.3, 149.0, 135.5, 130.6, 130.1, 128.8, 128.0, 127.8, 126.4, 52.2, 38.1. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}NO_3^+$ $(M+H)^+$ 270.1125, found 270.1123.



***N*-(4-methyl-3-chlorophenyl)-*N*-methyl-benzamide (3ap).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2p** (77.8 mg, 0.5 mmol) gives **3ap** as a yellow liquid (111.8 mg, 86%); R_f = 0.33 (petroleum ether/ethyl acetate 10: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.28 (m, 2H), 7.27 (d, J = 2.5 Hz, 1H), 7.19 (t, J = 8.1 Hz, 2H), 7.11 (d, J = 2.3 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.78 (dd, J = 2.3, 8.1 Hz, 1H), 3.46 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 143.6, 135.6, 134.5, 134.4, 131.1, 129.8, 128.6, 127.9, 127.1, 125.3, 38.5, 27.1, 21.1. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}ClNO^+$ $(M+H)^+$ 260.0837, found 260.0843.



***N*-ethylbenzanilide (3aq).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2q** (60.6 mg, 0.5 mmol) gives **3aq** as a yellow viscous liquid (69.8 mg, 62%); R_f = 0.44 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.25 (m, 2H), 7.25-7.18 (m, 3H), 7.14 (td, J = 1.9, 7.3 Hz, 3H), 7.07-6.98 (m, 2H), 3.99 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{1}H NMR is consistent with the literature precedent.[6]



***N*-(4-methylphenyl)-benzamide (3ar).** The reaction of **1a** (67.2 mg, 0.55 mmol) and **2r** (53.6 mg, 0.5 mmol) gives **3ar** as a lightyellow liquid (69.2 mg, 66%); R_f = 0.42 (petroleum ether/ethyl acetate 5: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92-7.79 (m, 3H), 7.57-7.50 (m, 3H), 7.47 (t, J = 7.3 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H). ^{1}H NMR is consistent with the literature precedent.[1]

5. References.

[1] Z. Li, C. Guo, J. Chen, Y. Yao and Y. Luo, *Appl Organometal Chem.*, 2020, **34**, e5517-e5525.

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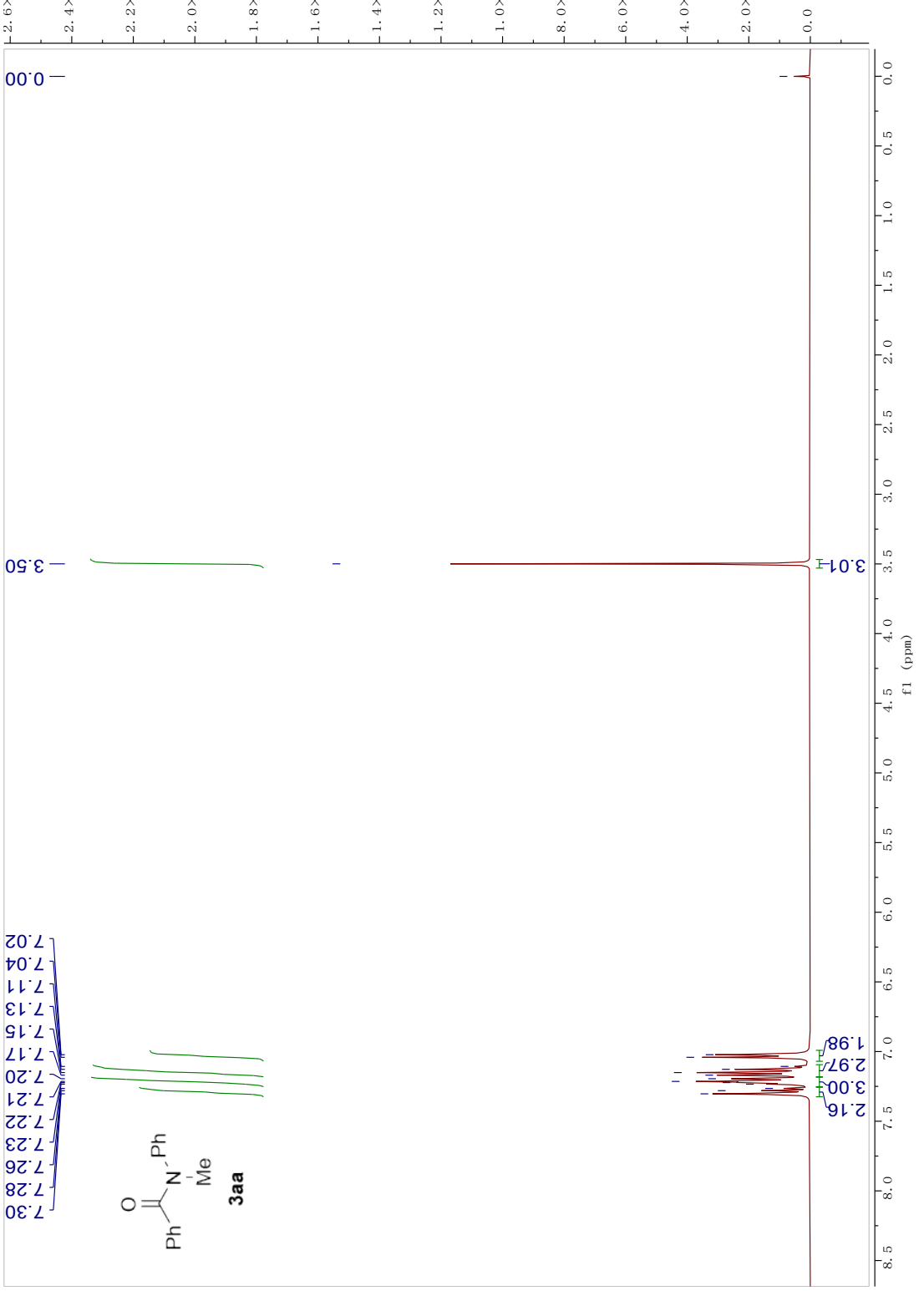
6. NMR spectra of the products.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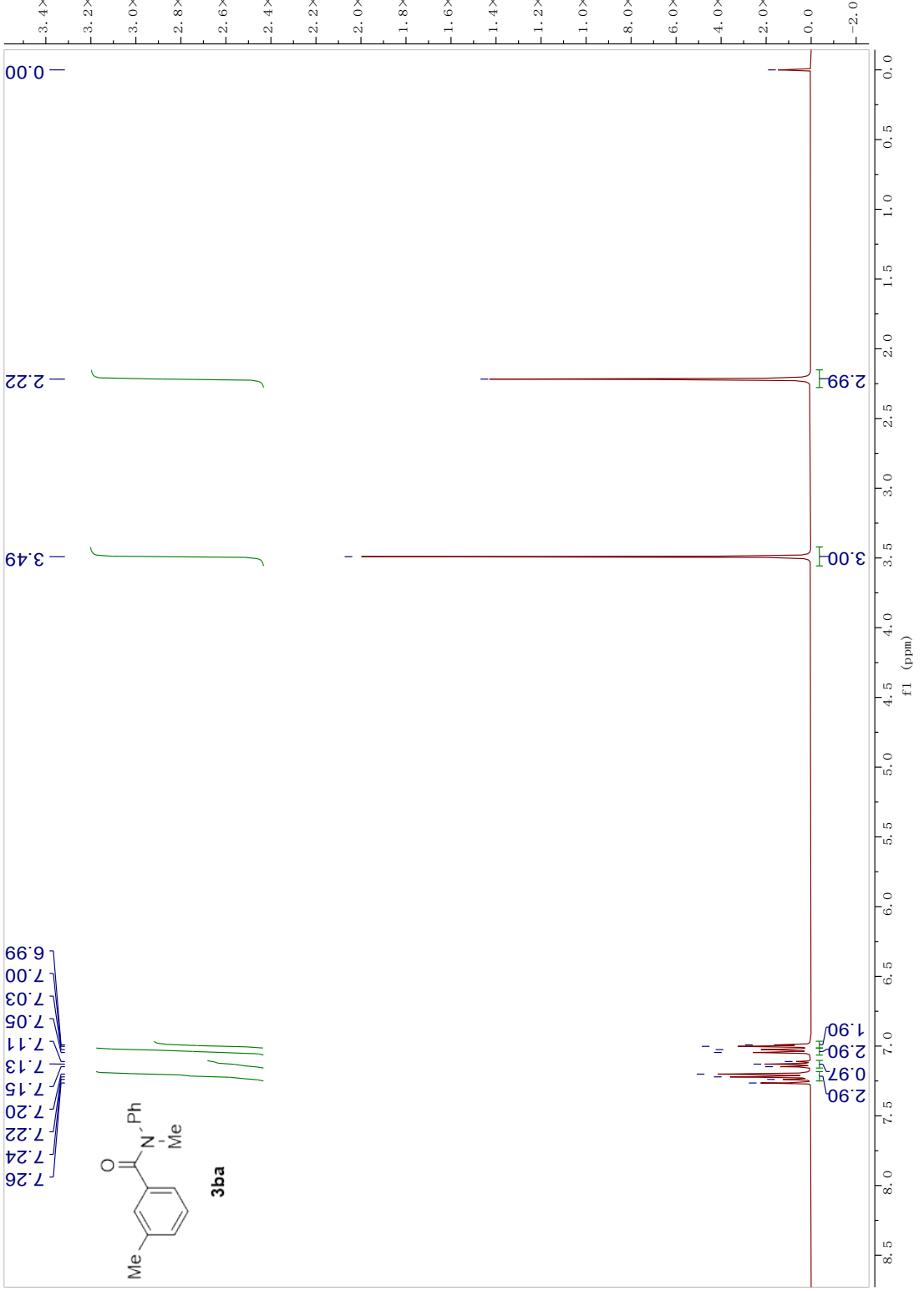
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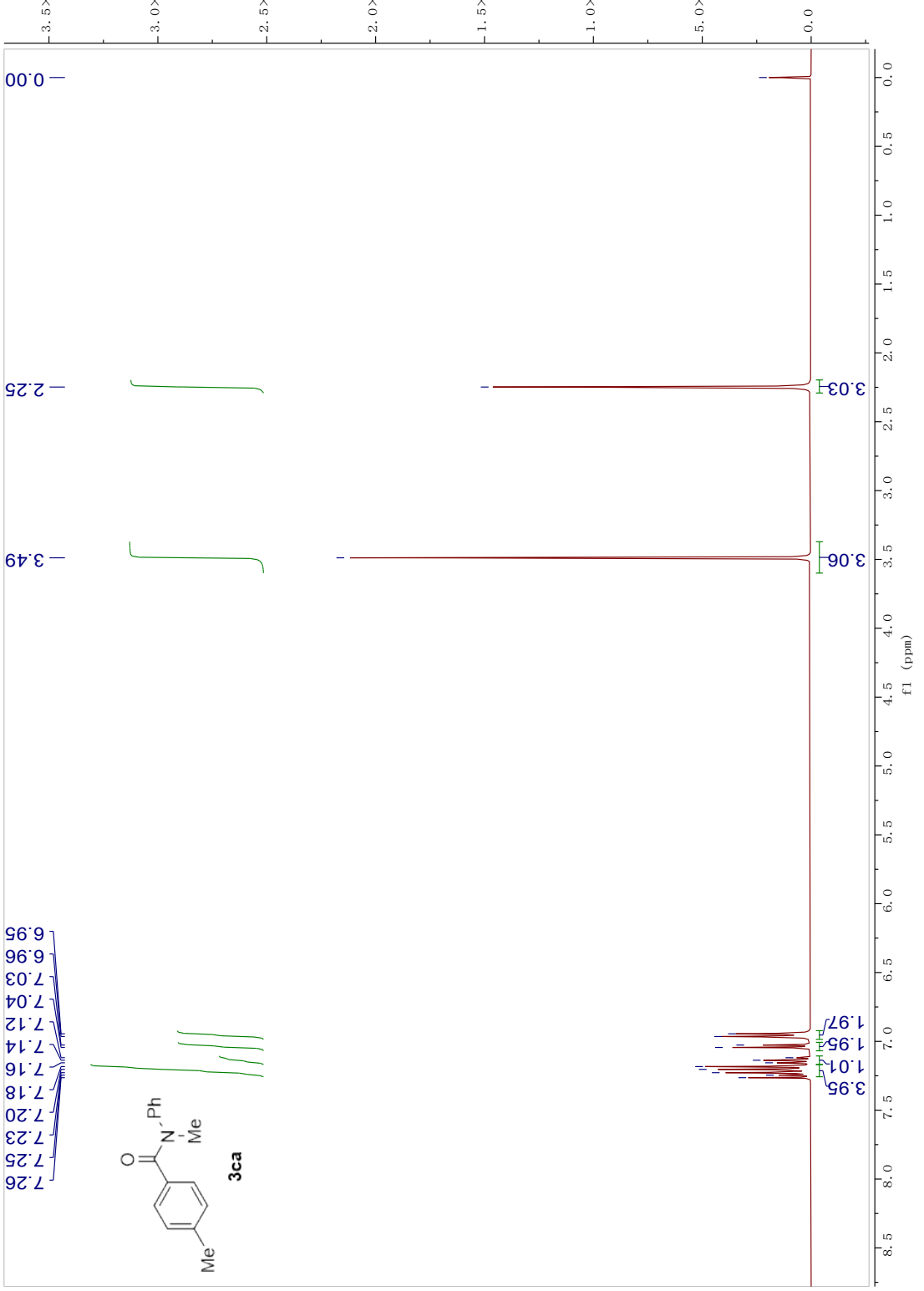
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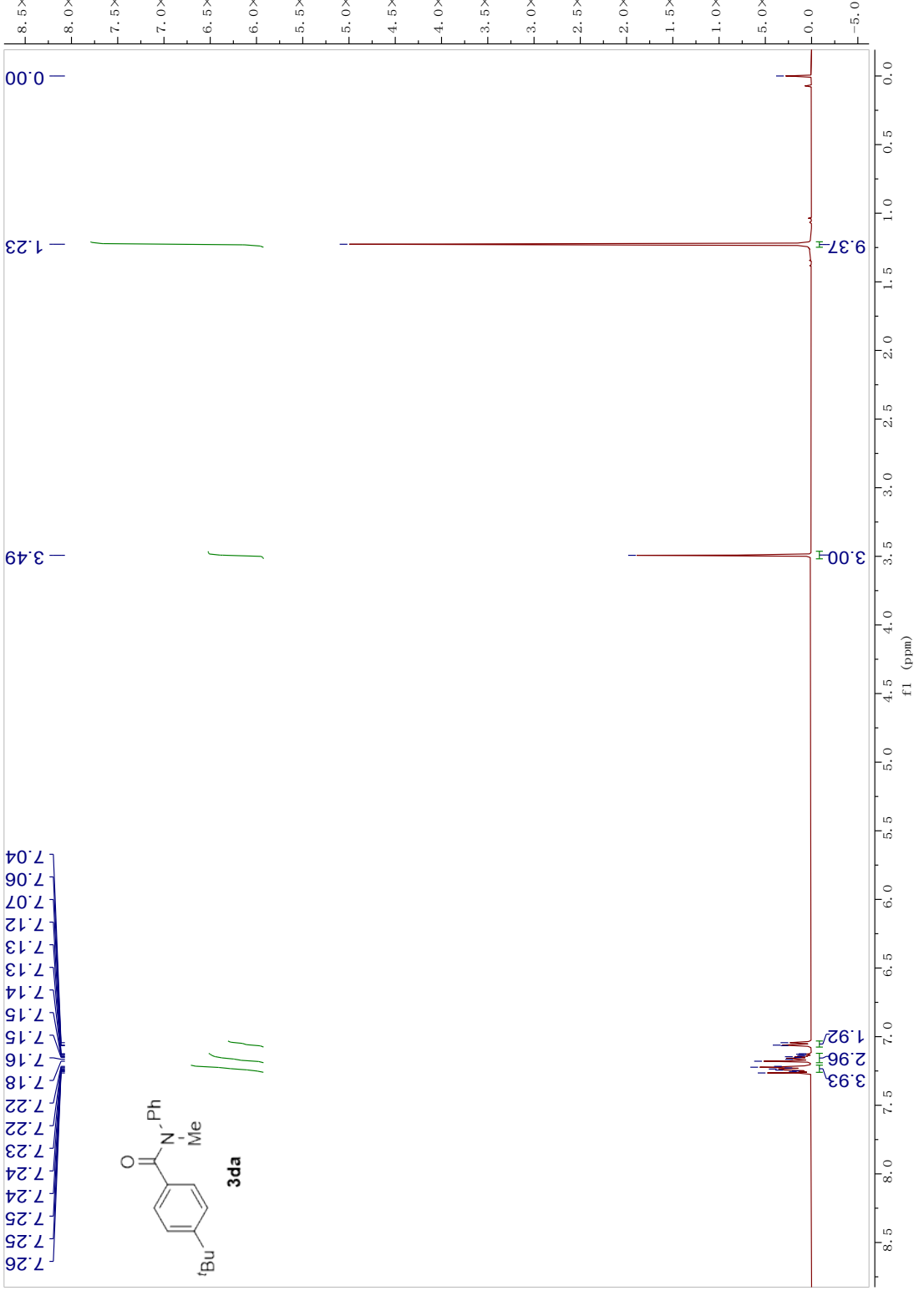
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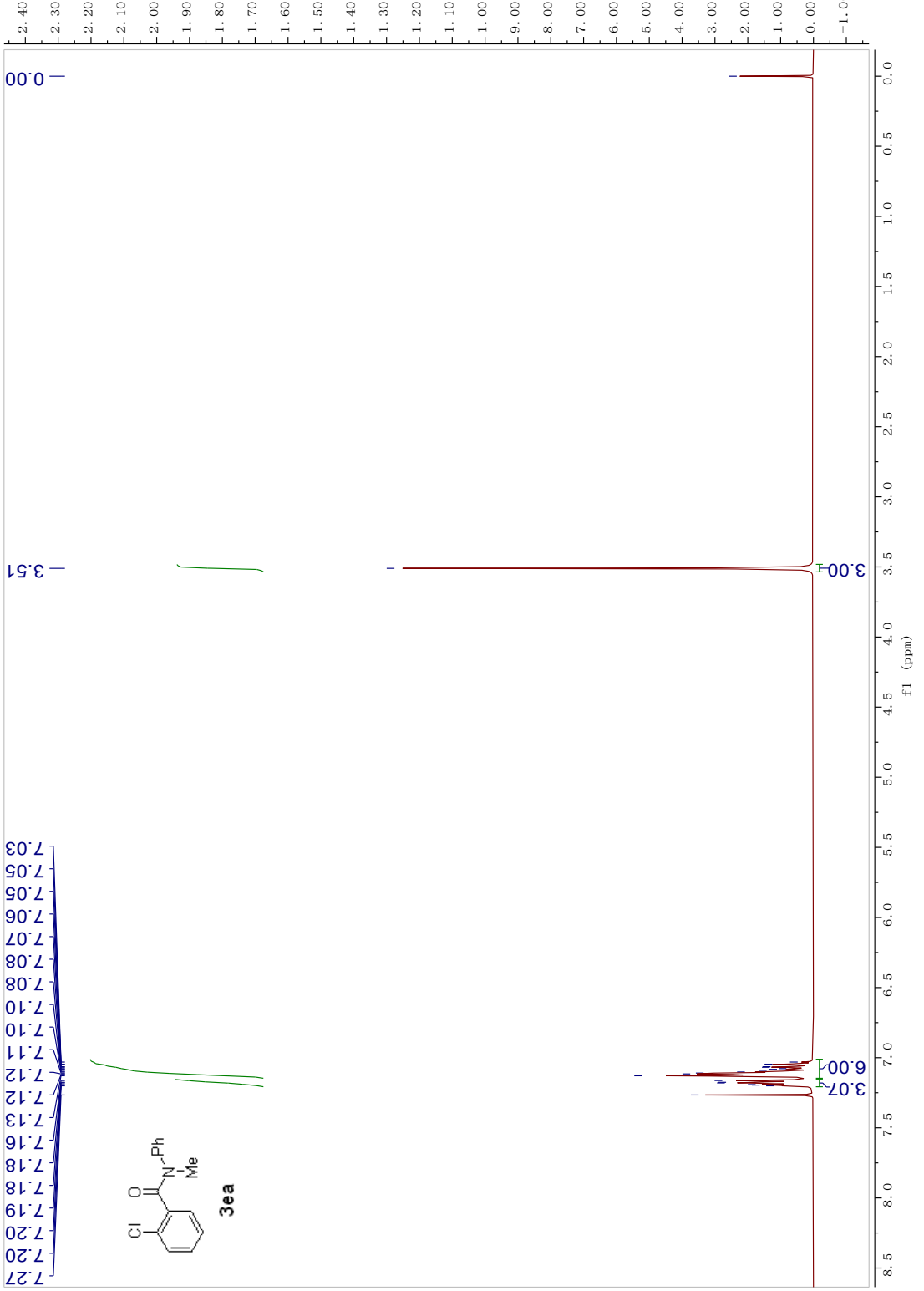
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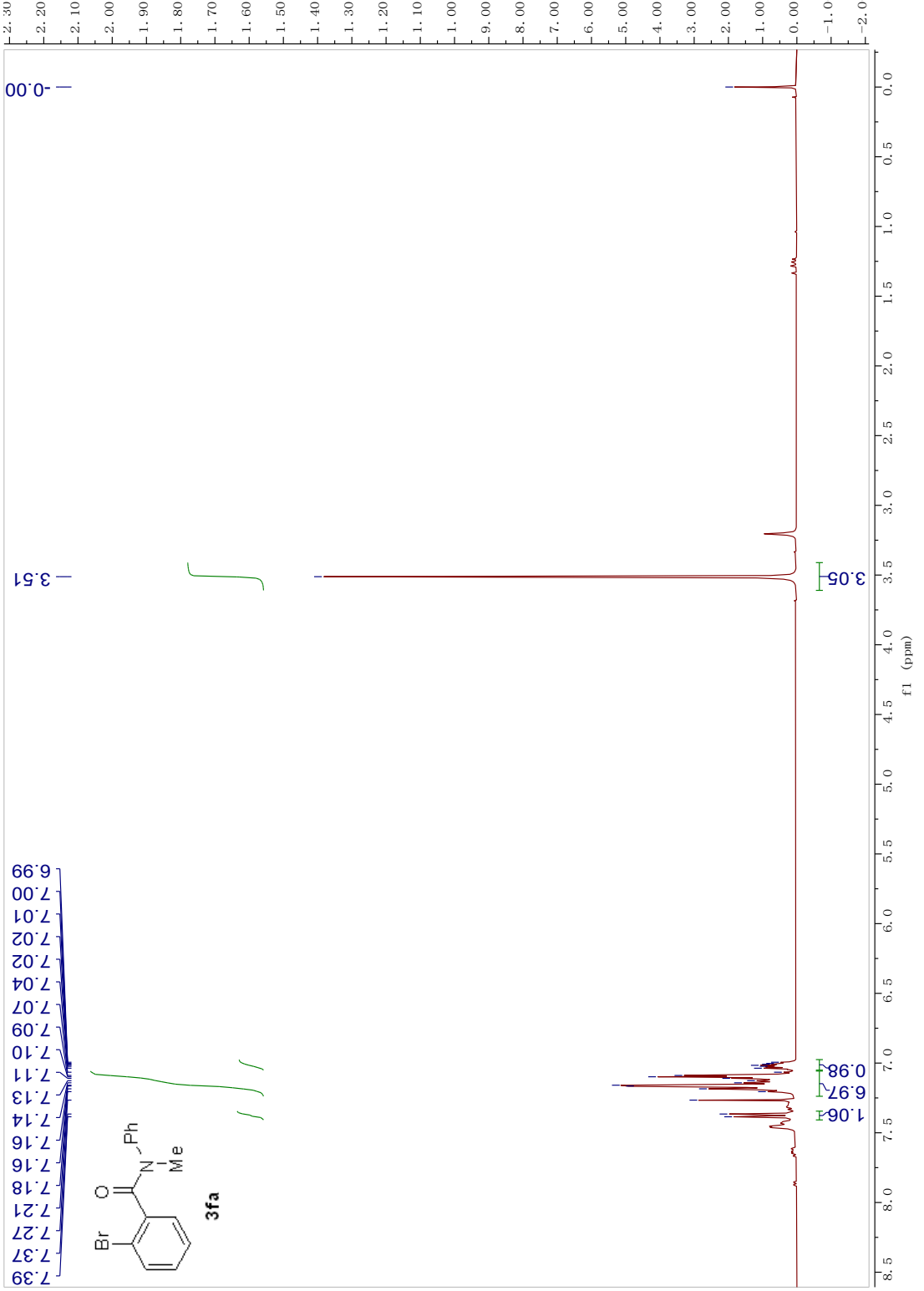
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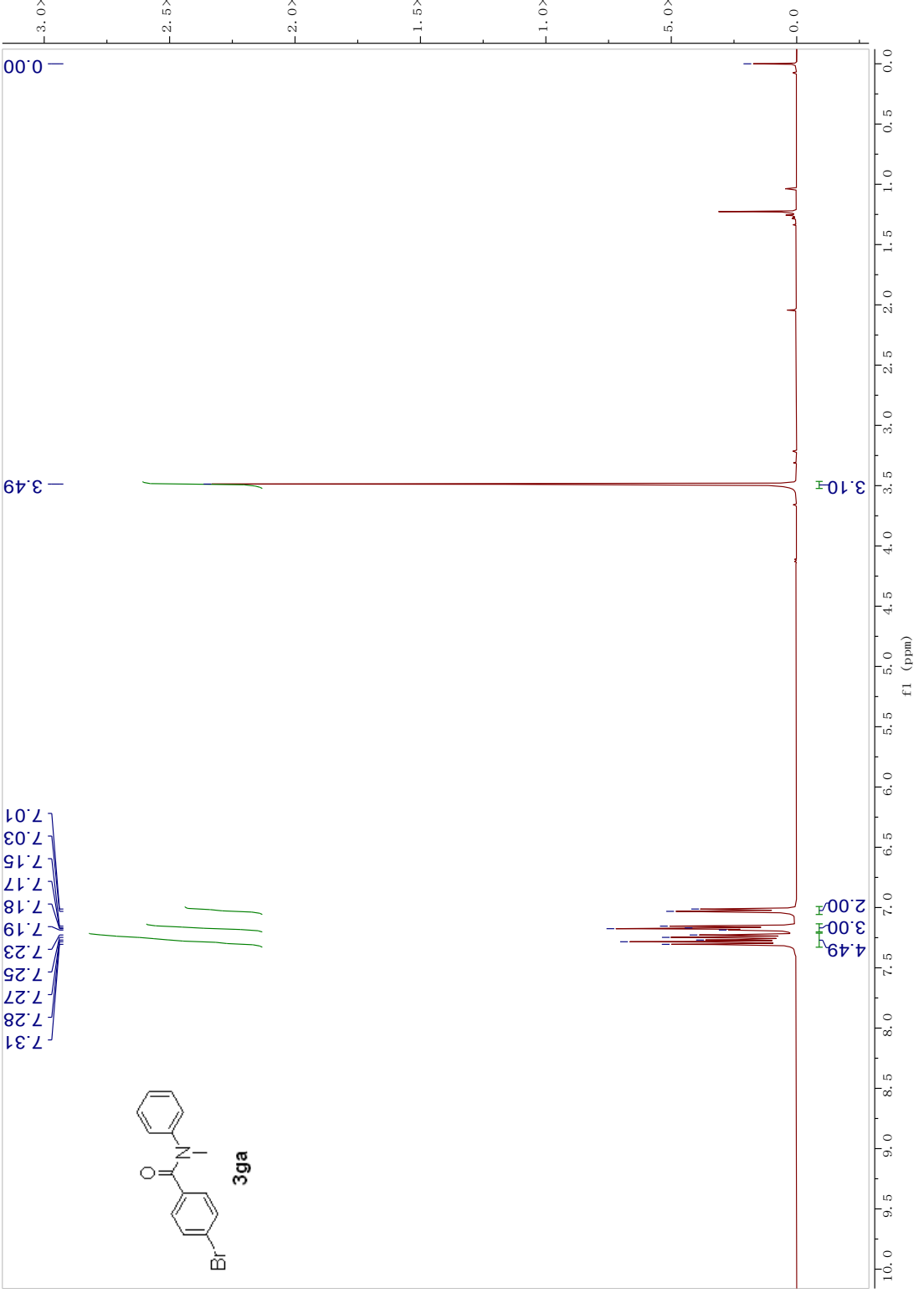
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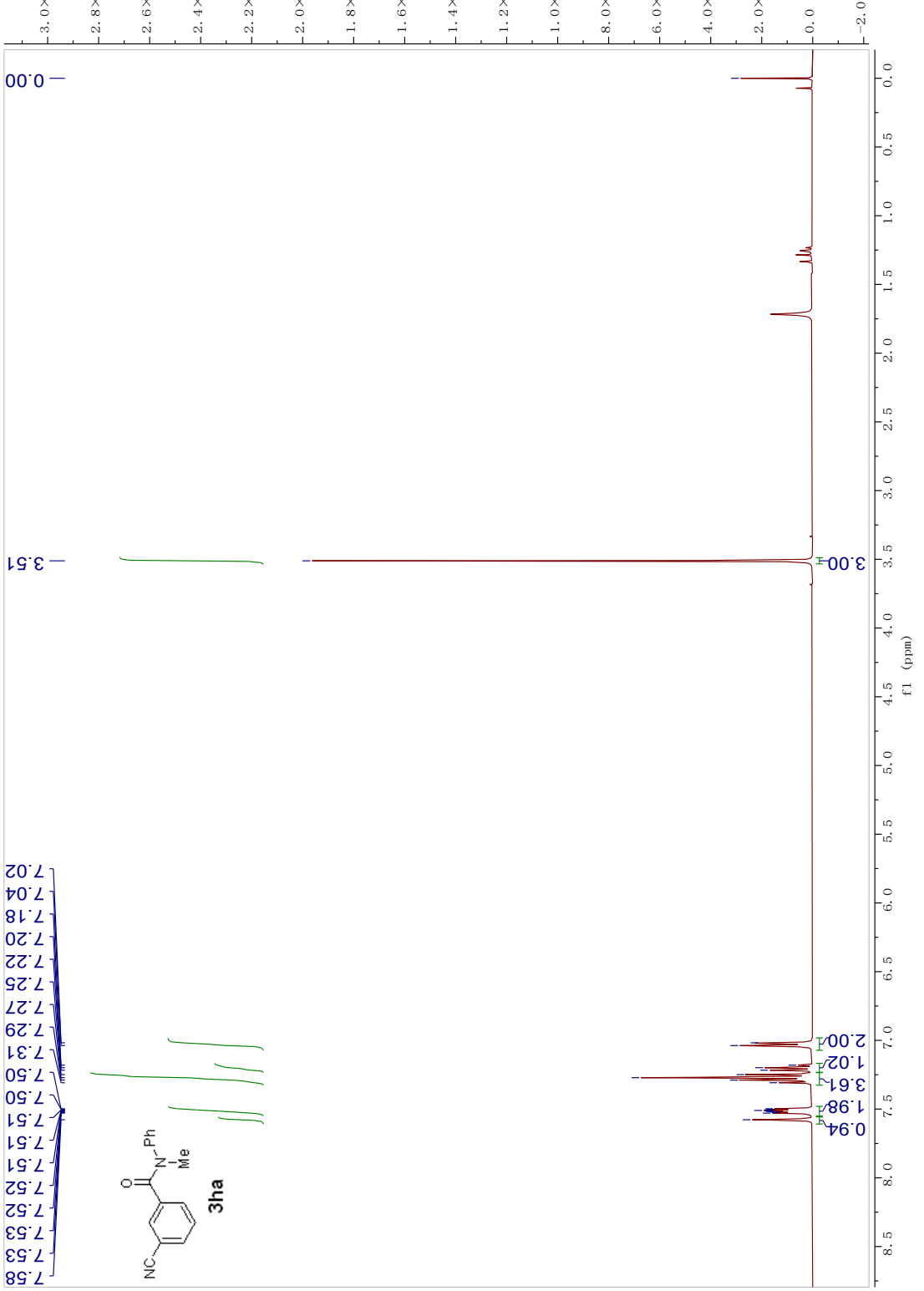
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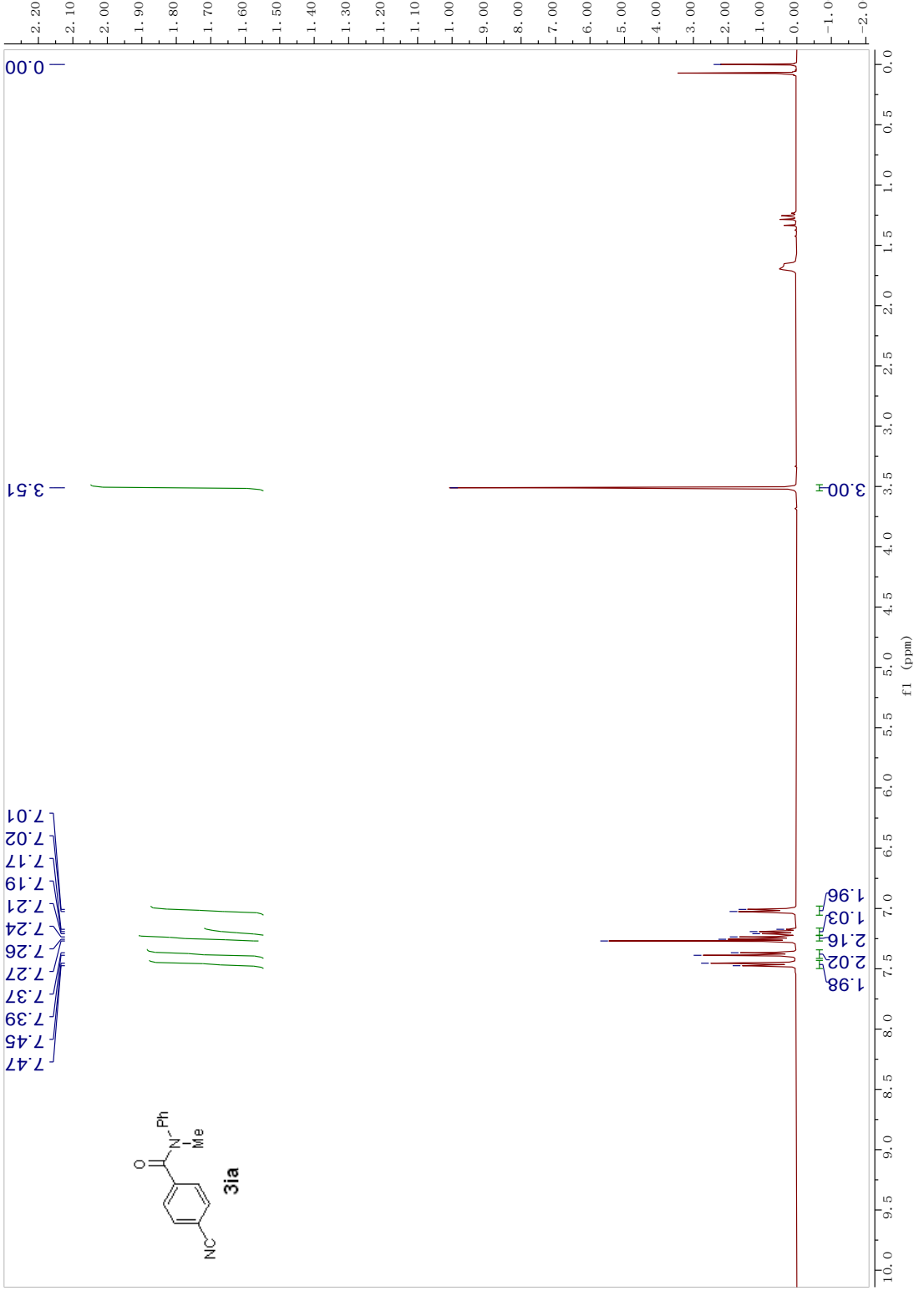
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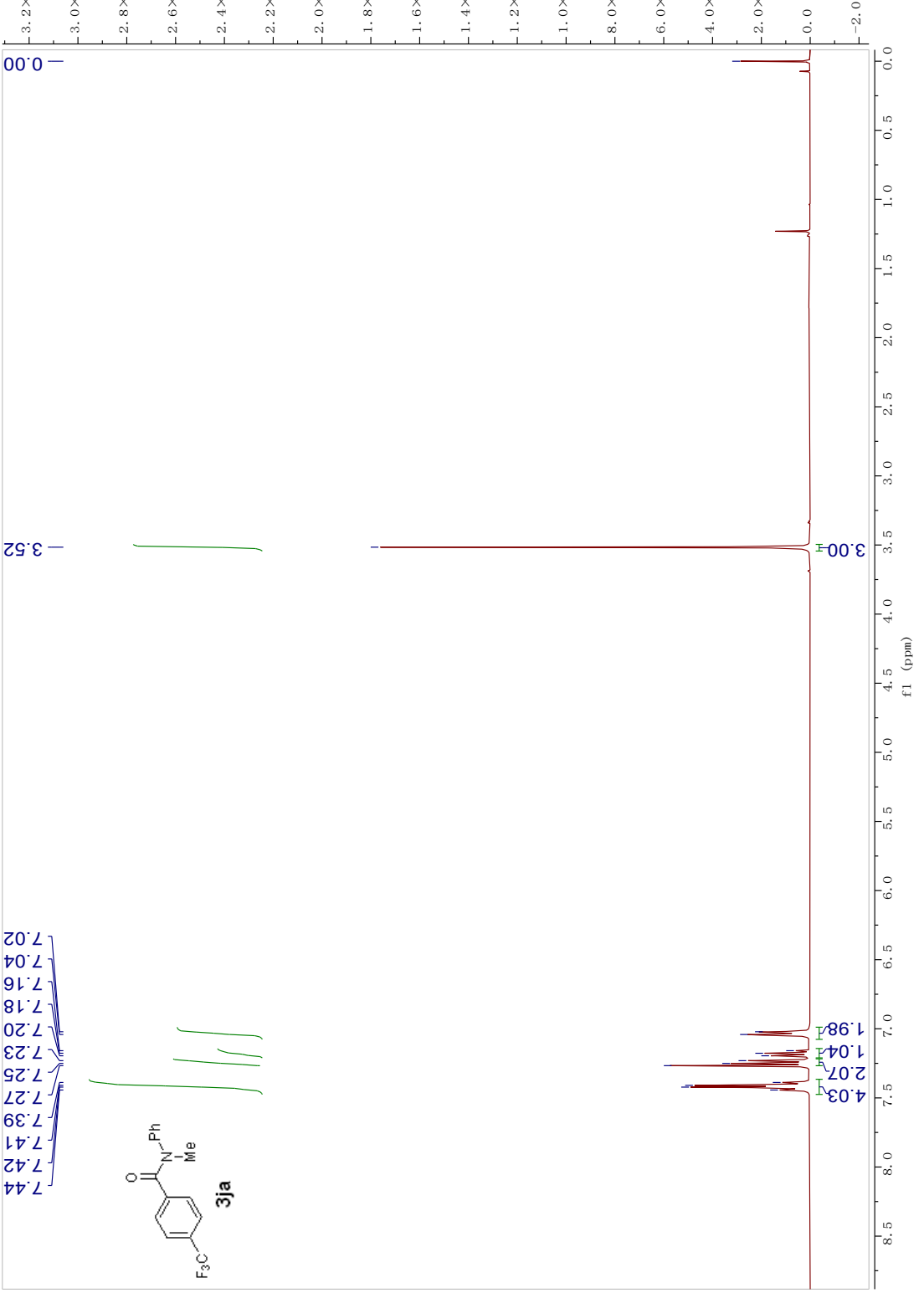
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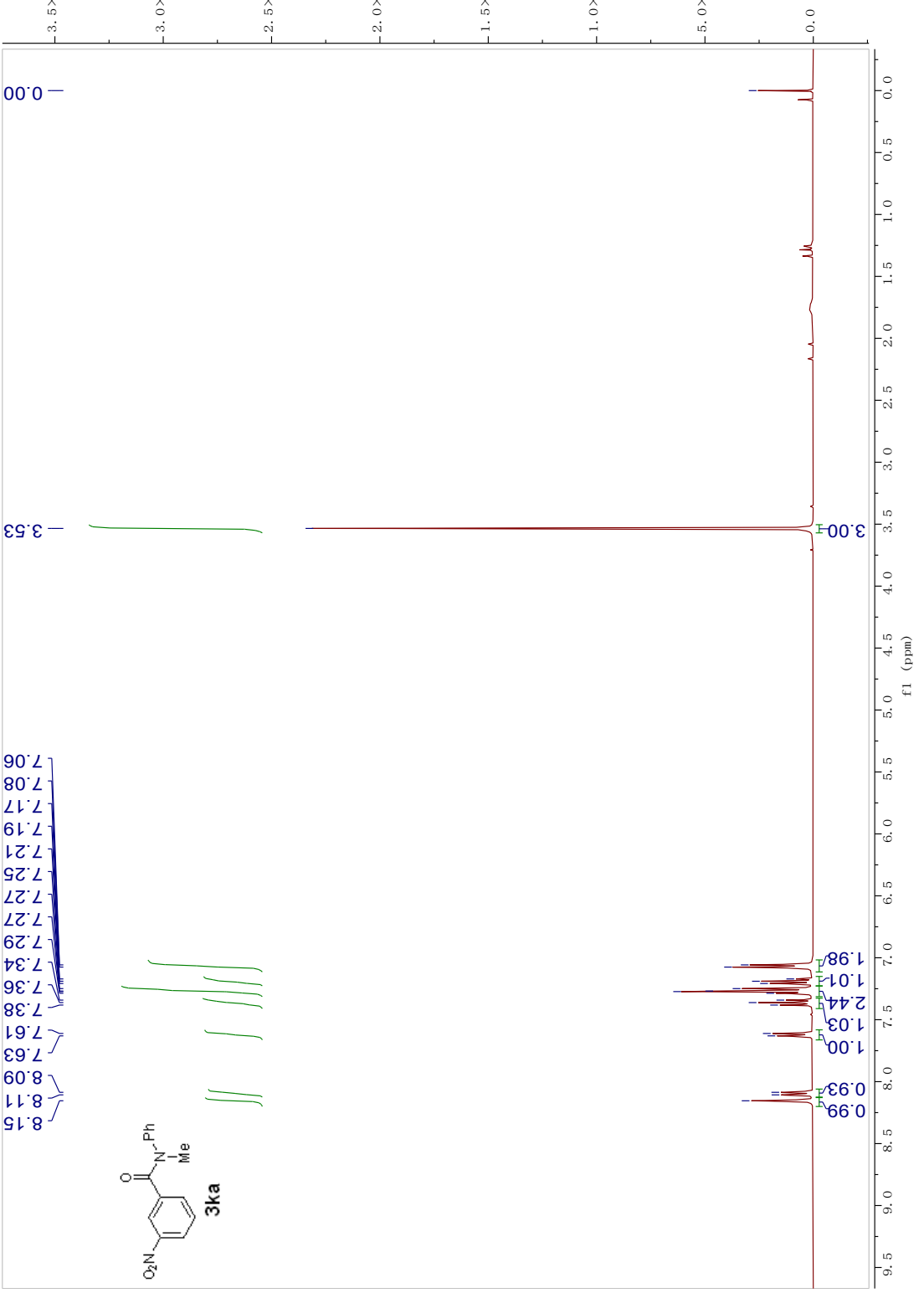
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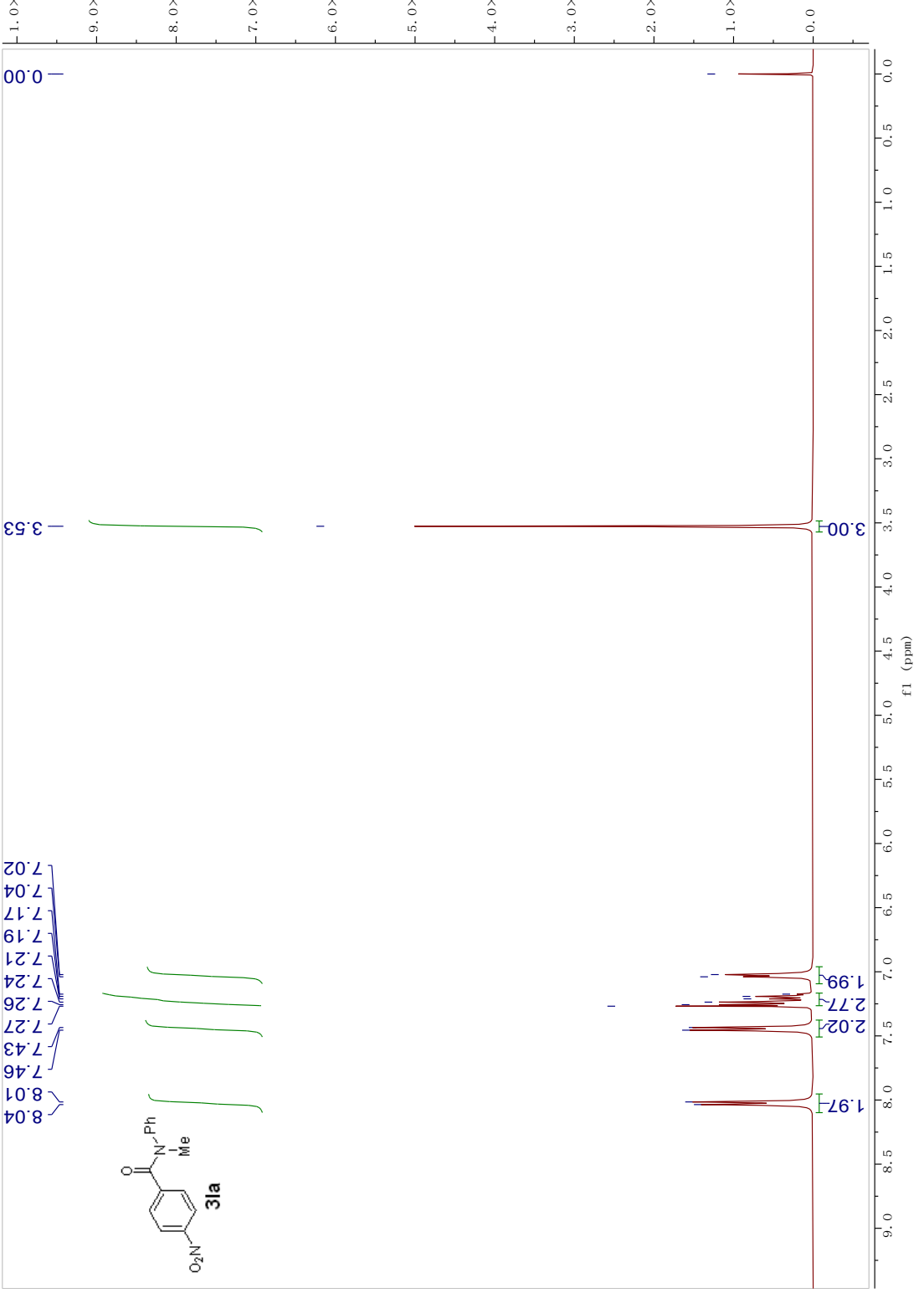
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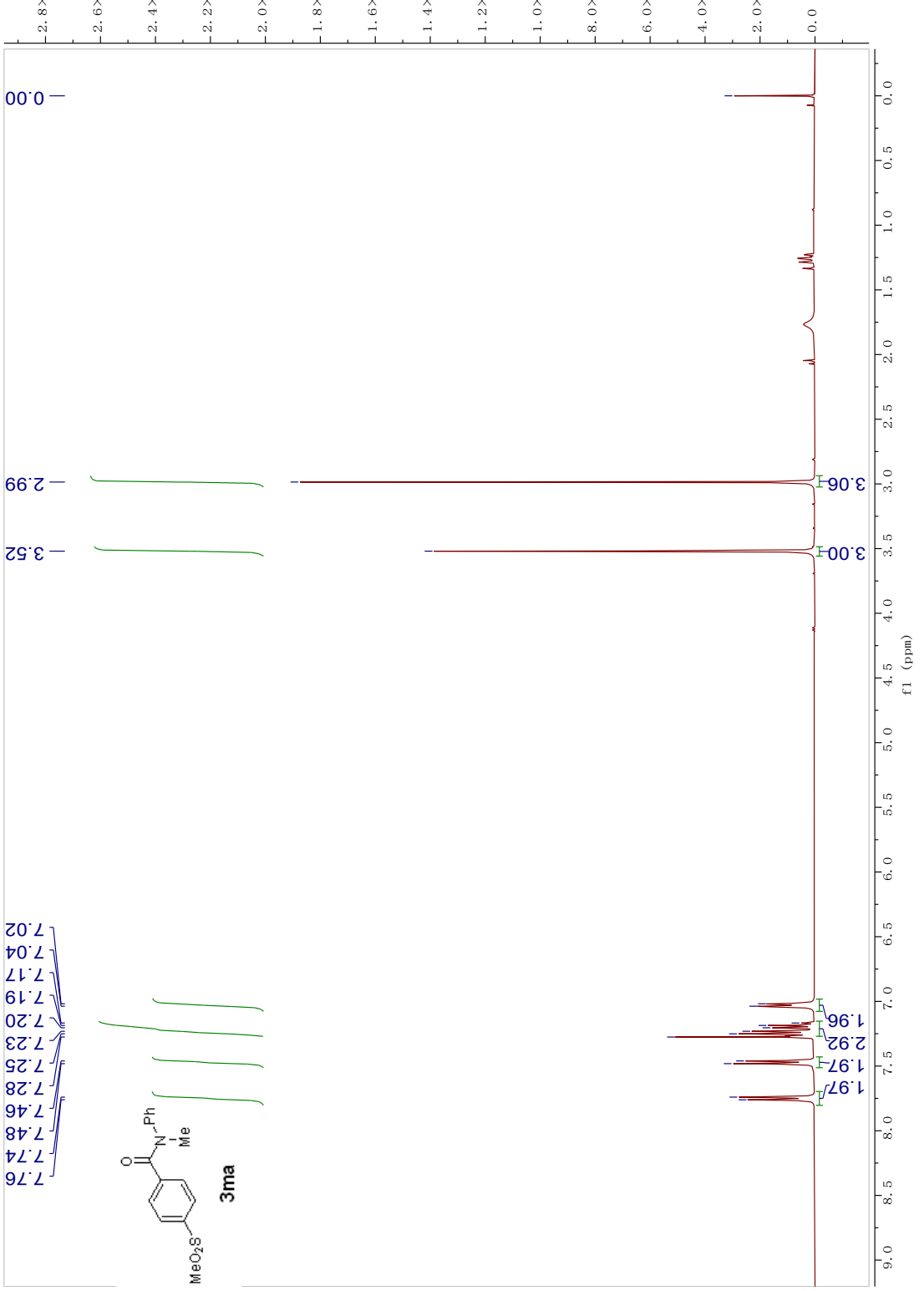
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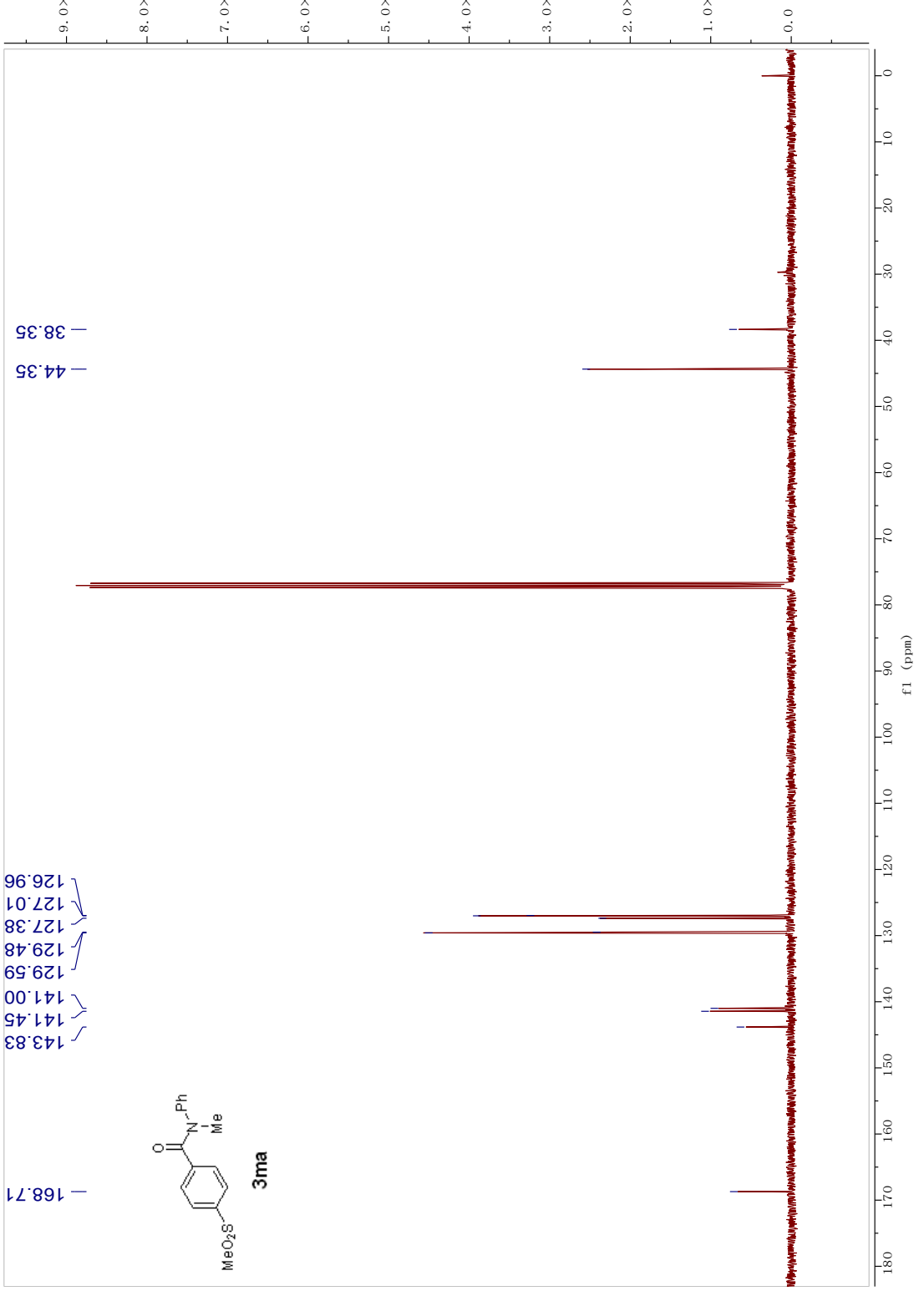
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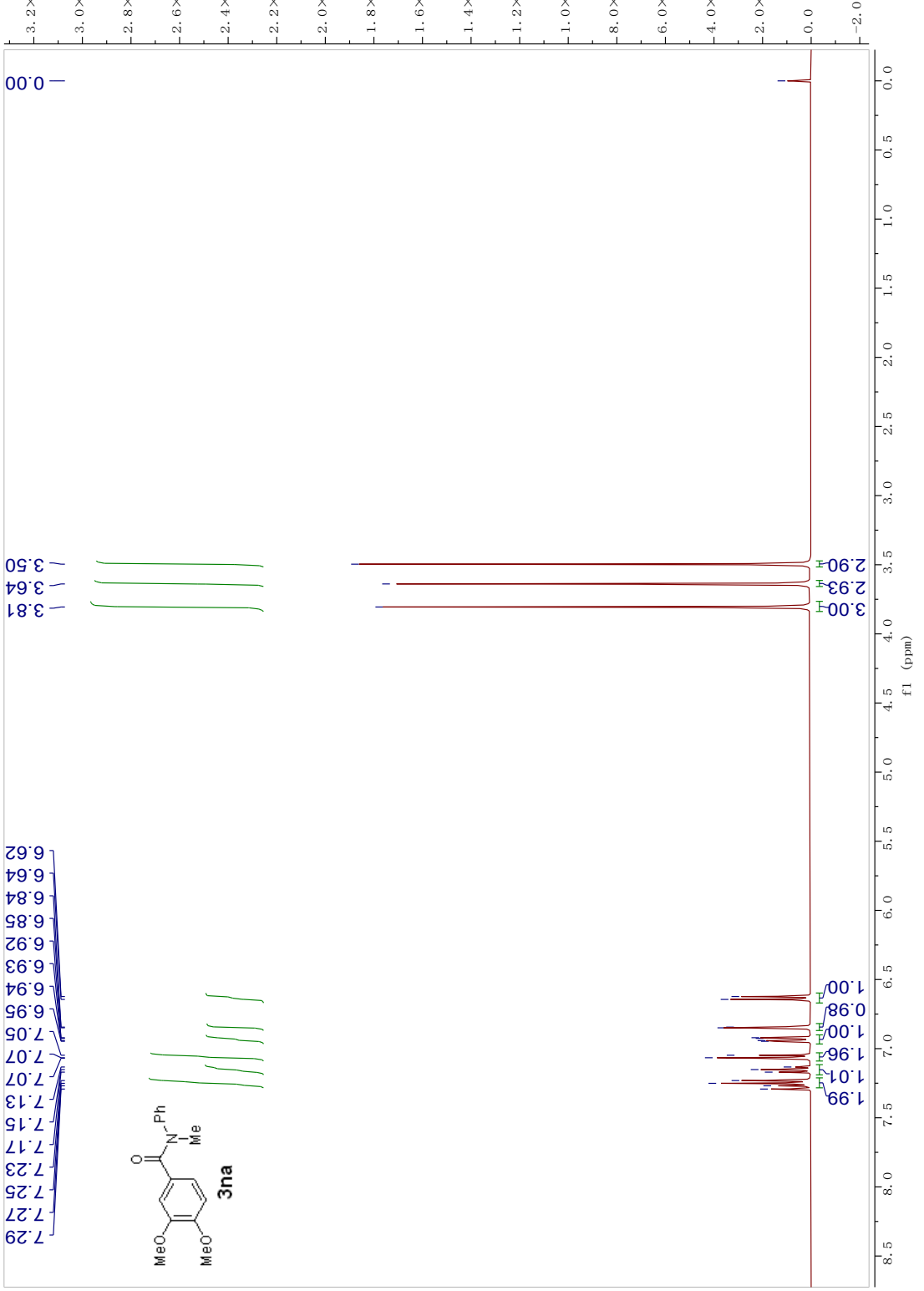
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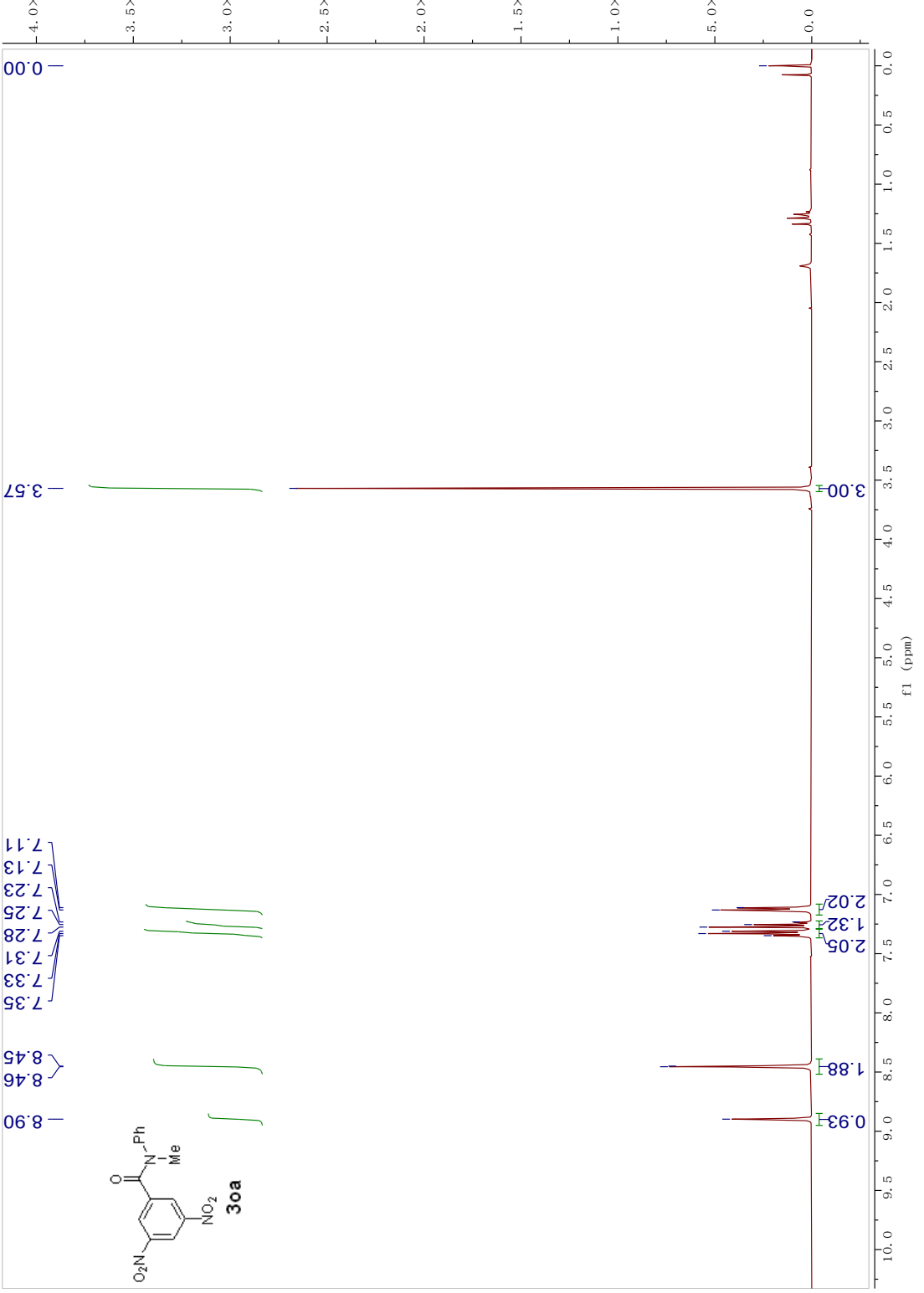
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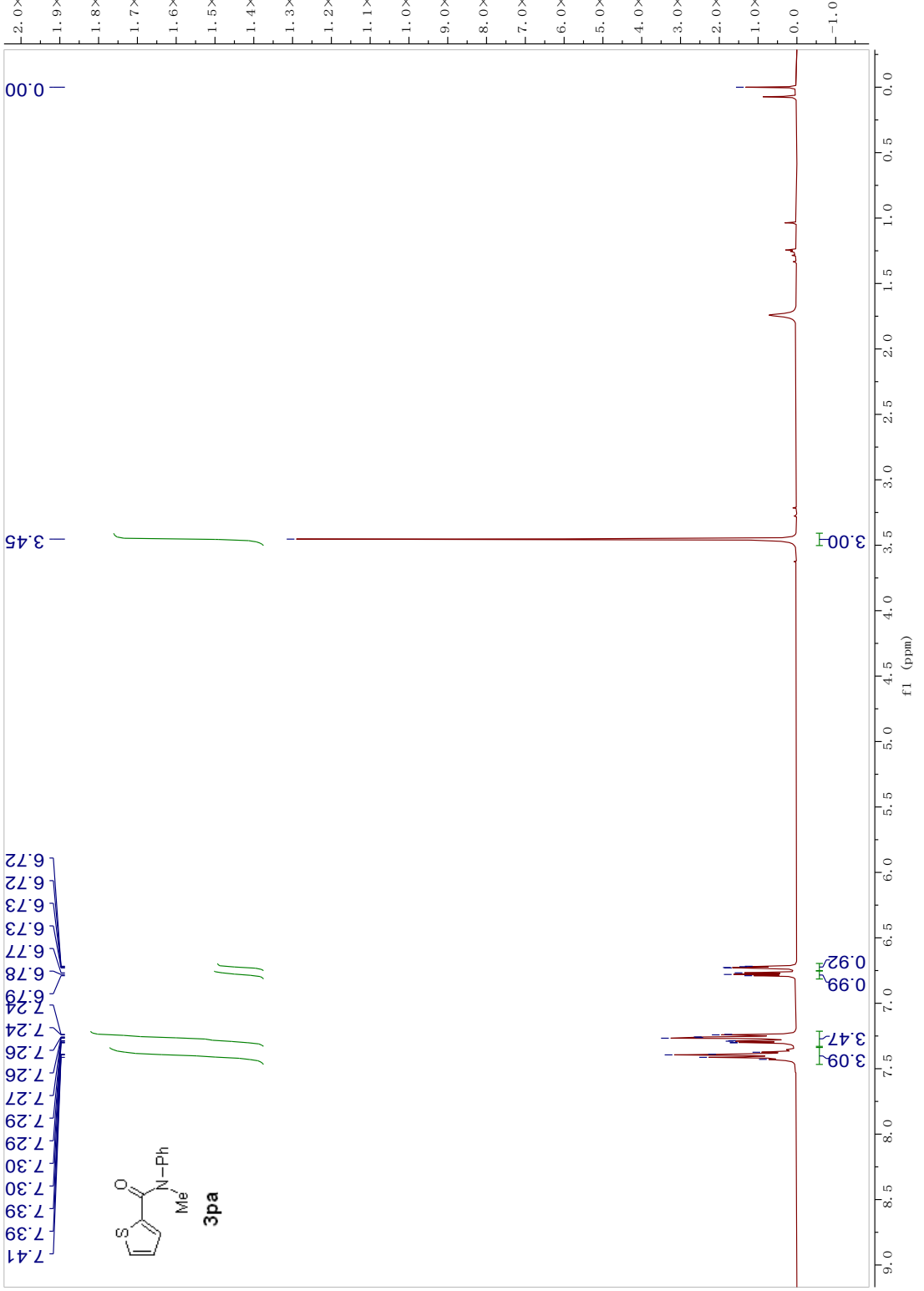
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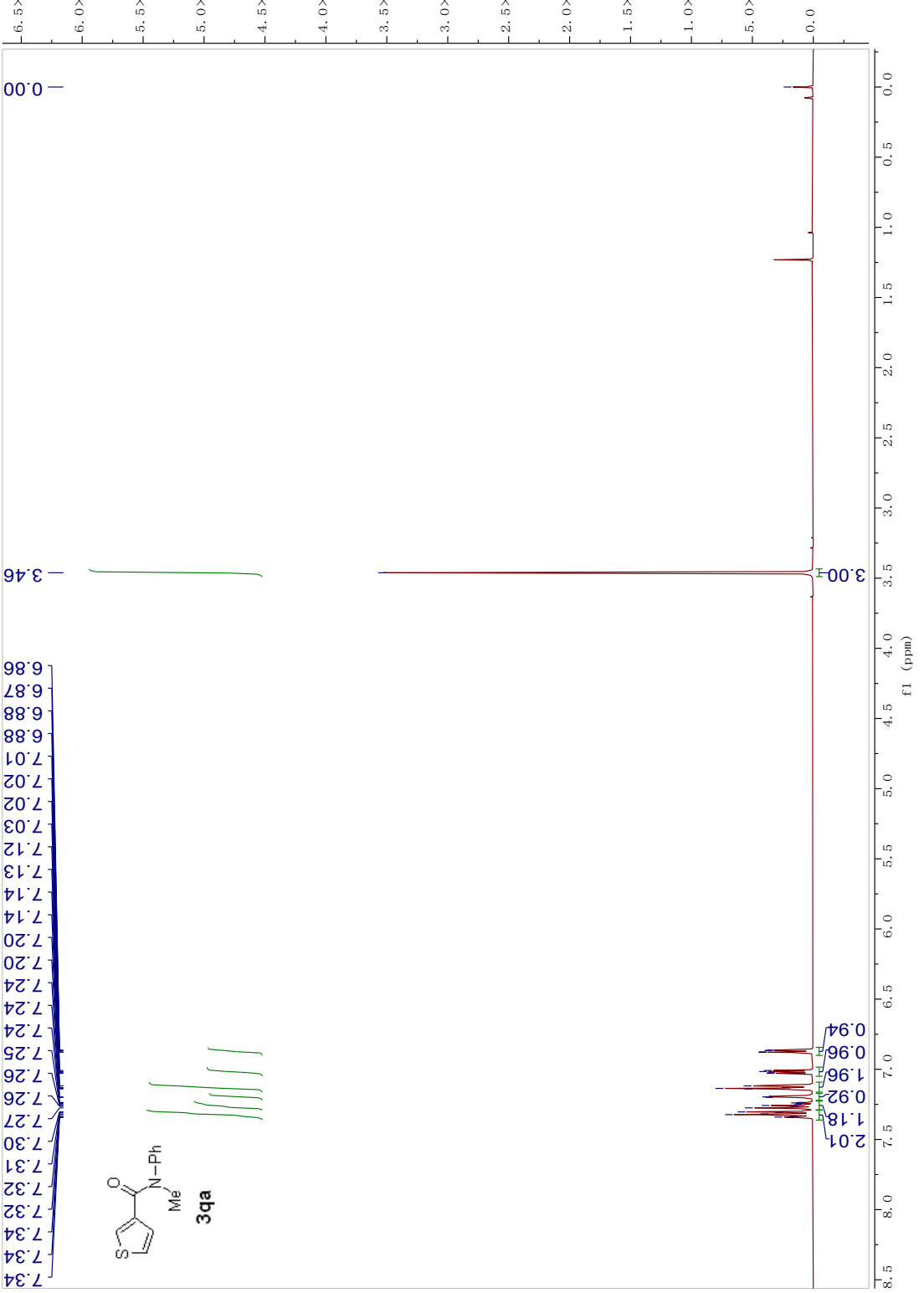
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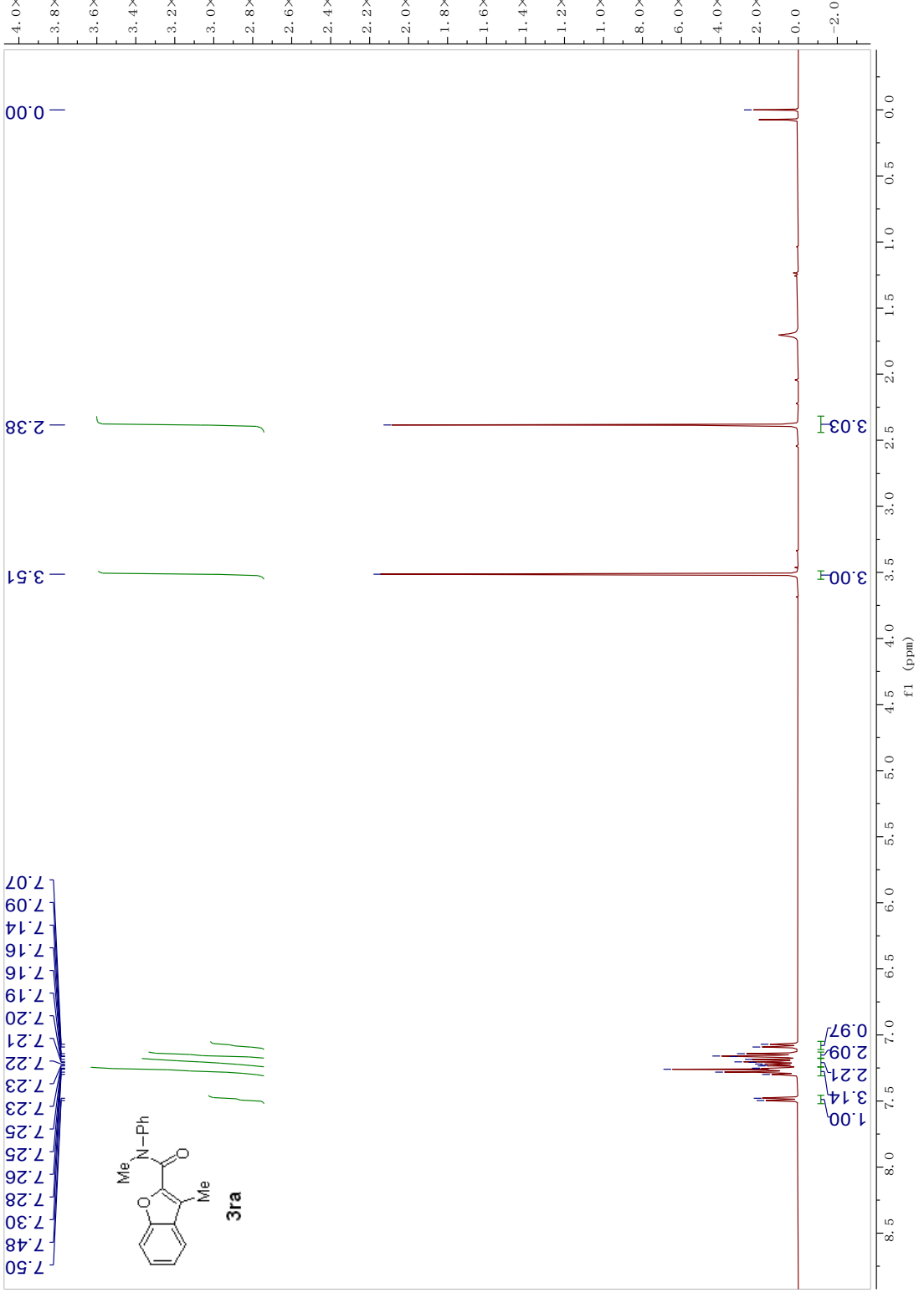
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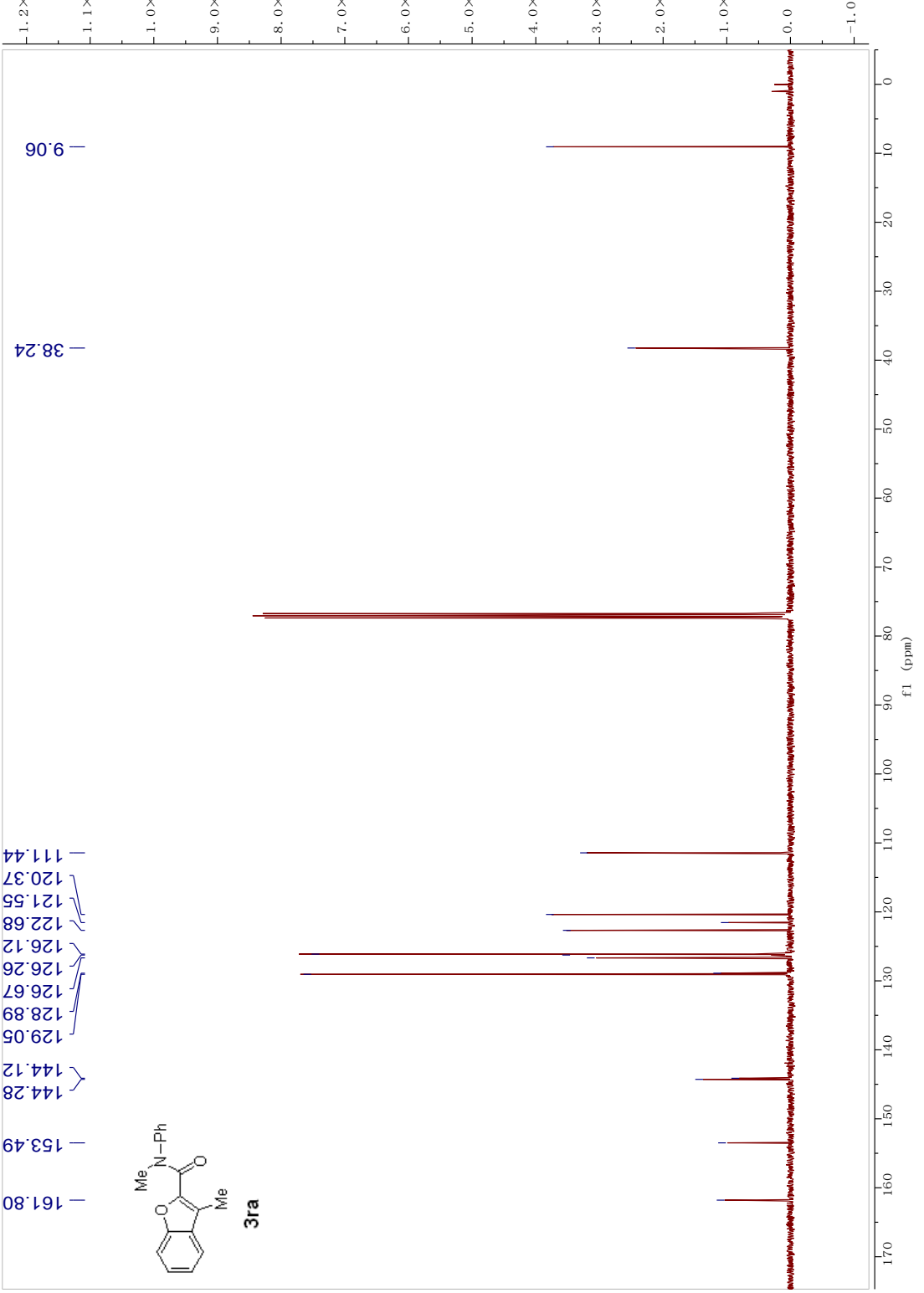
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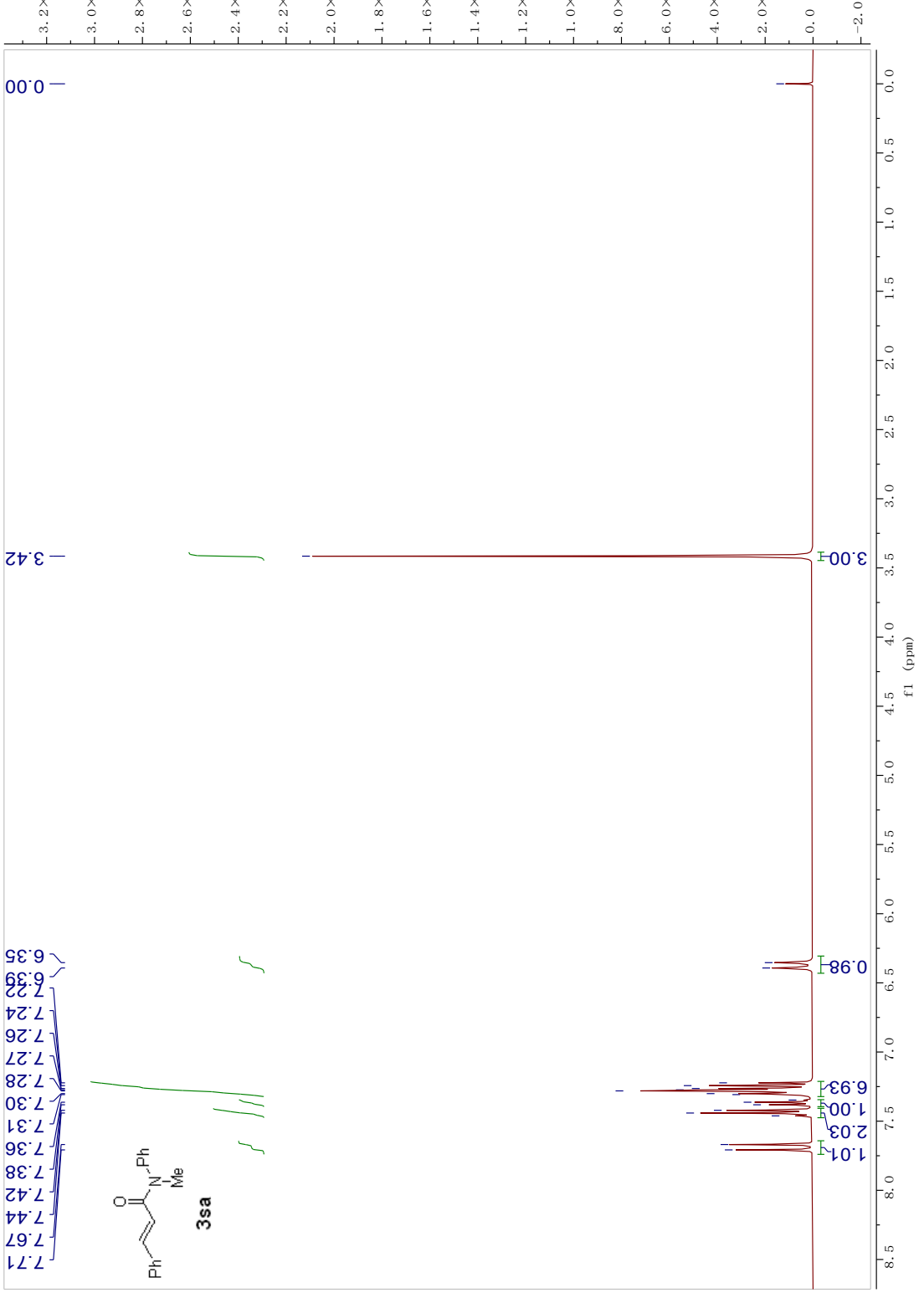
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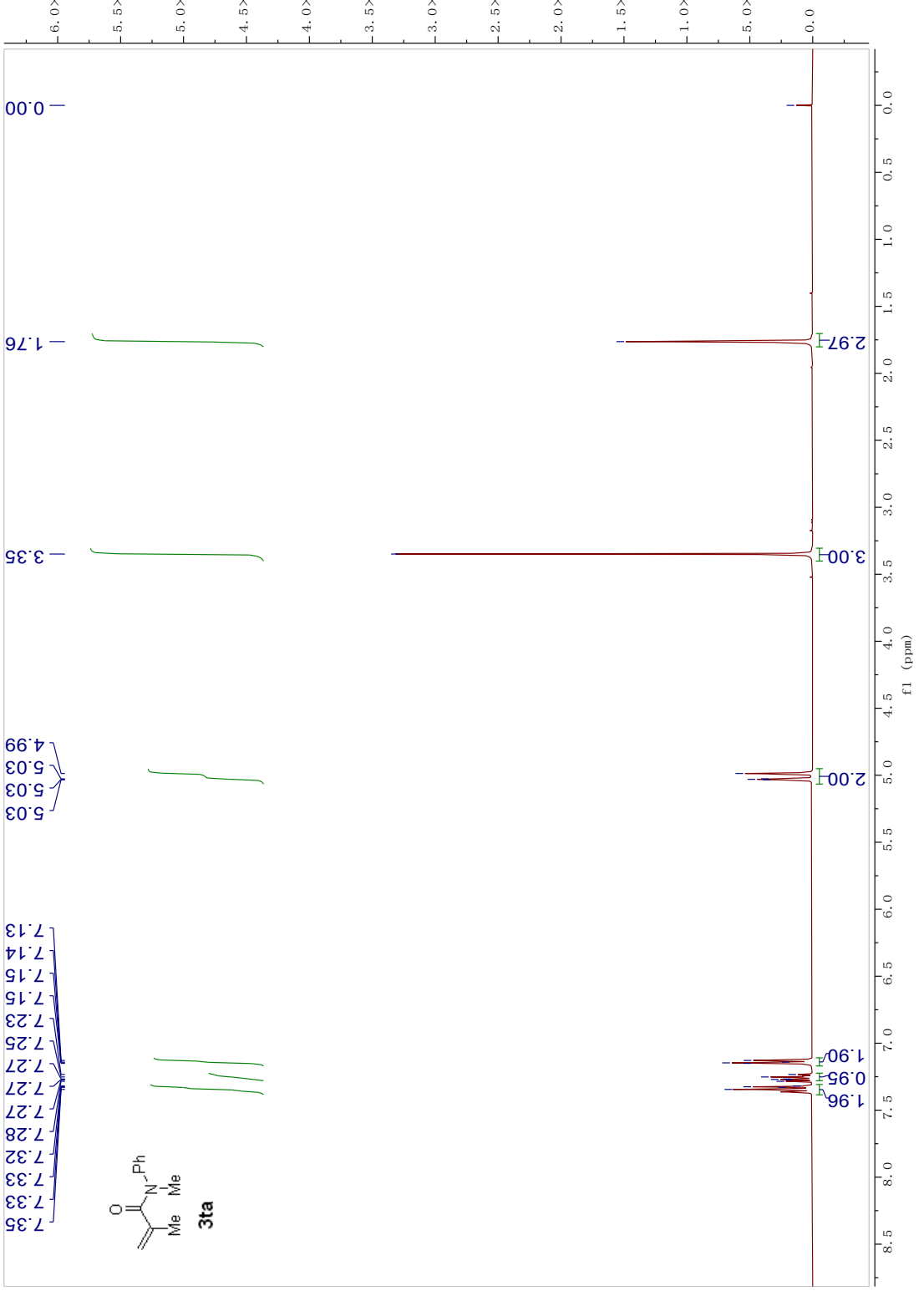
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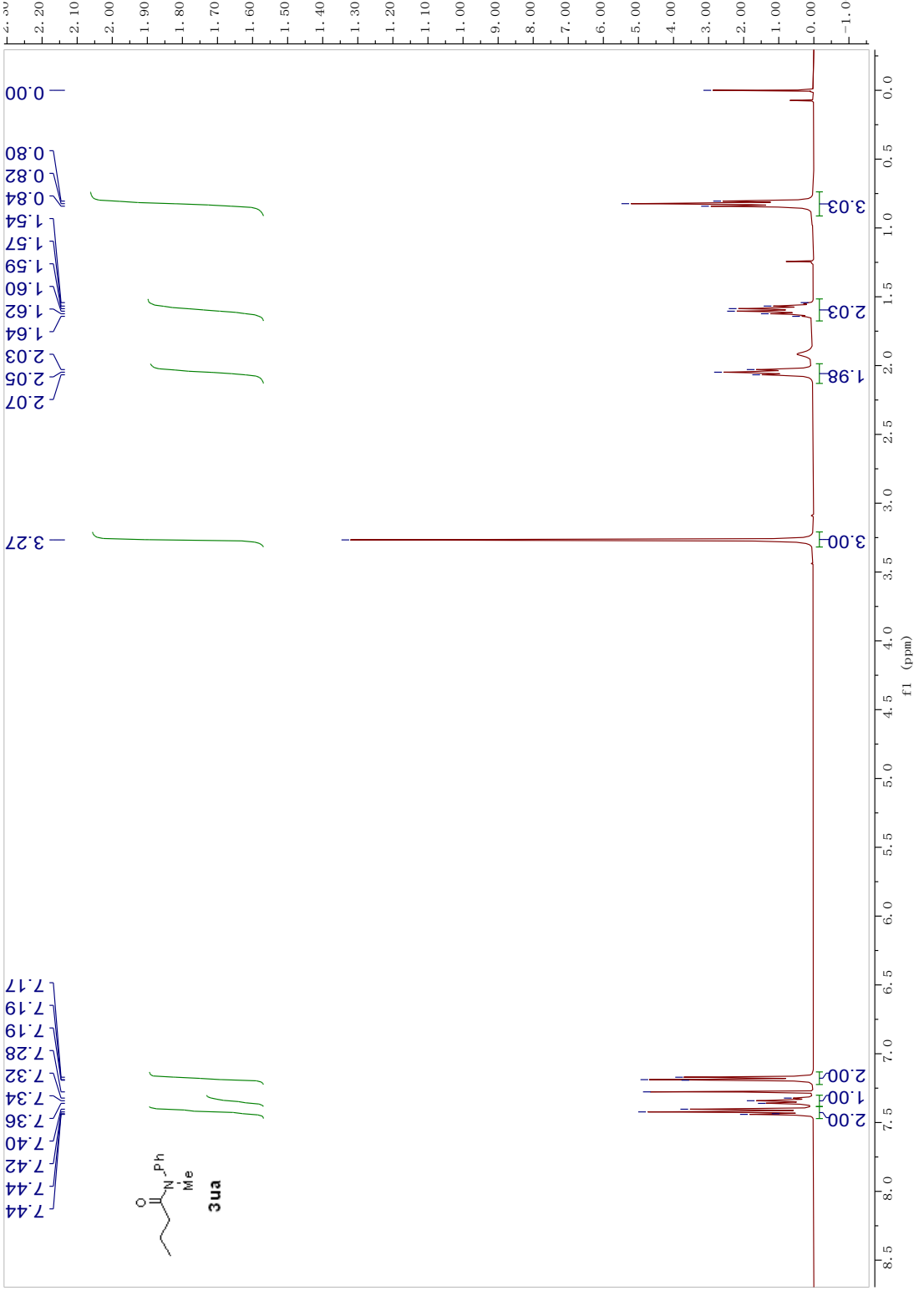
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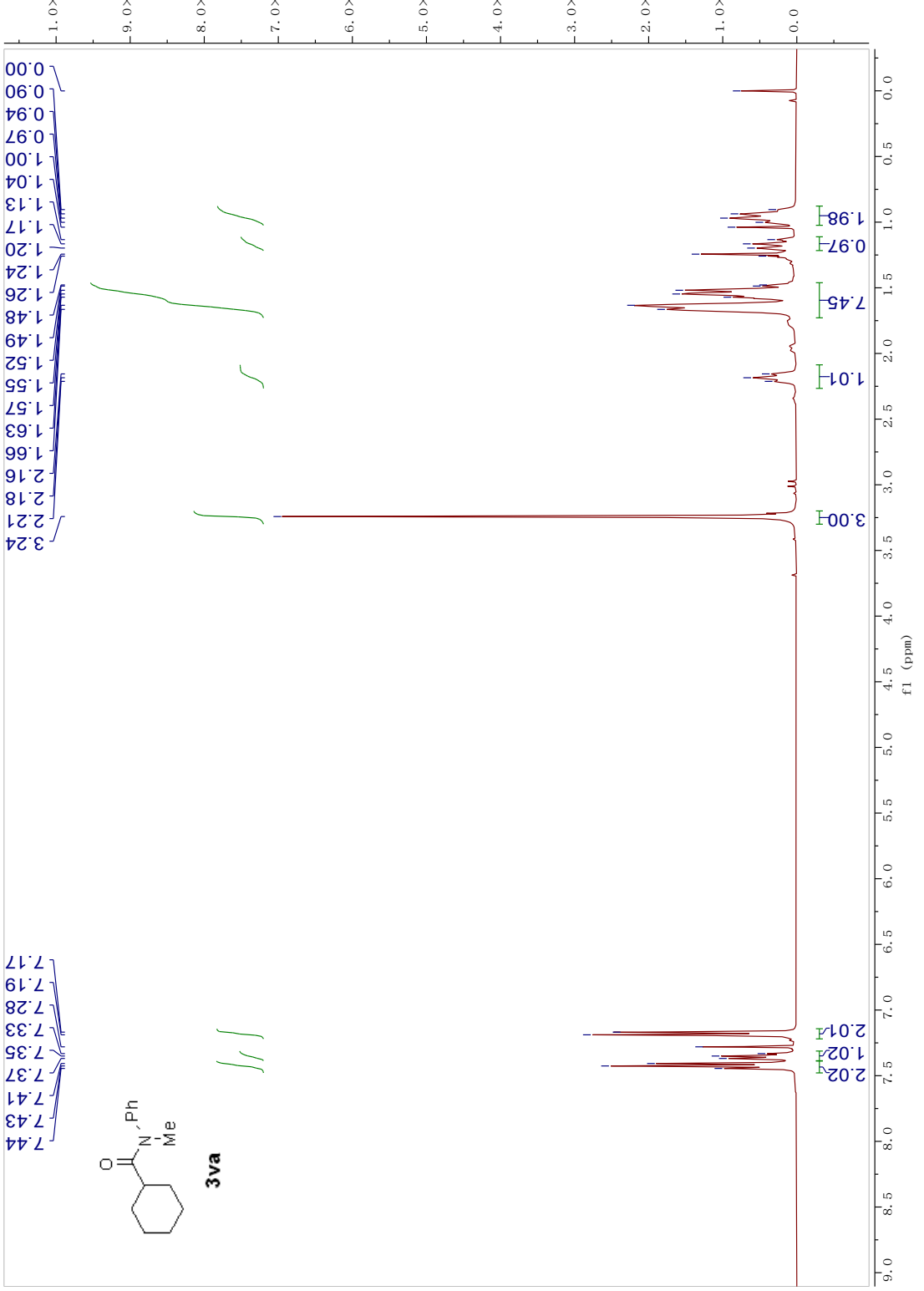
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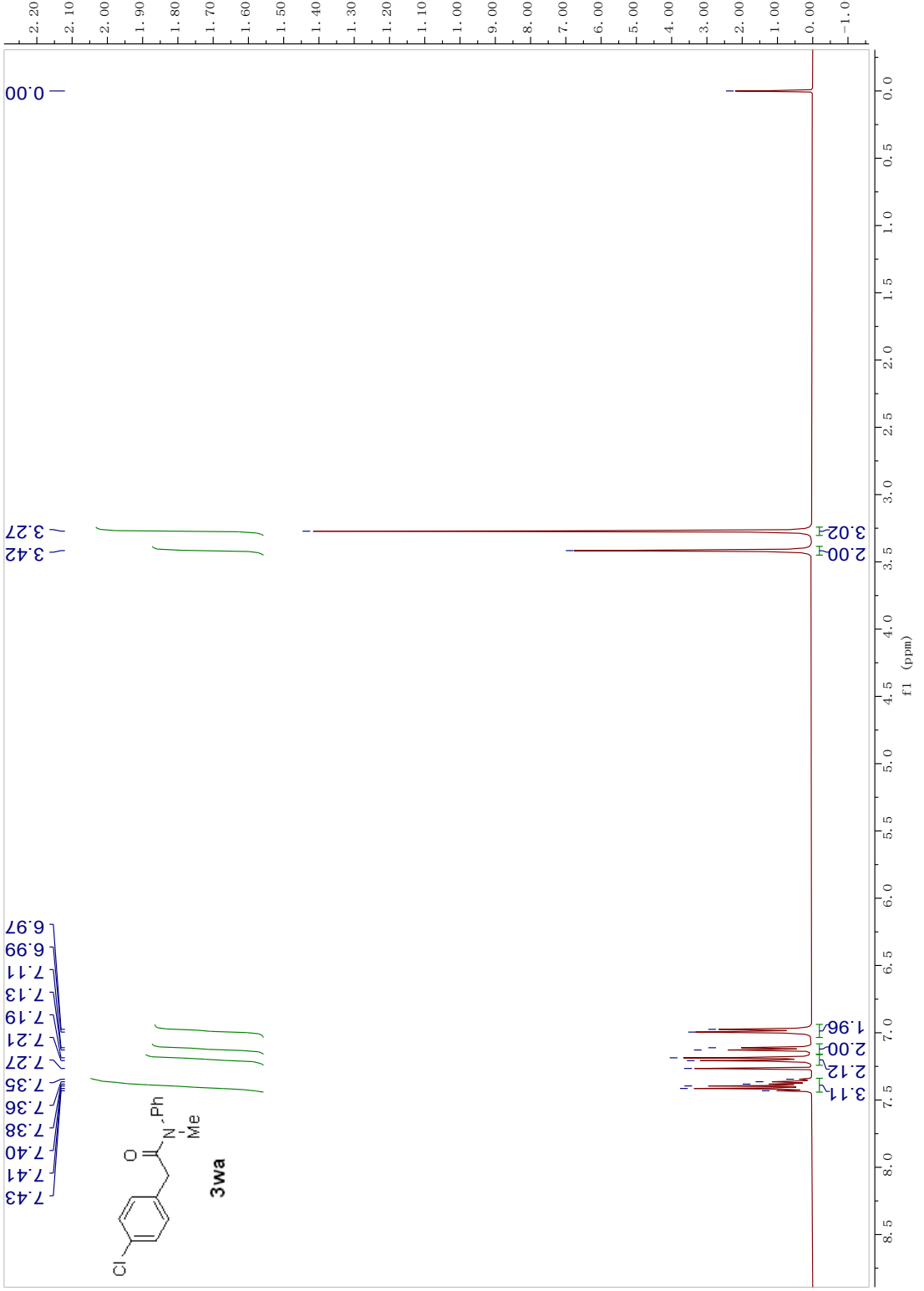
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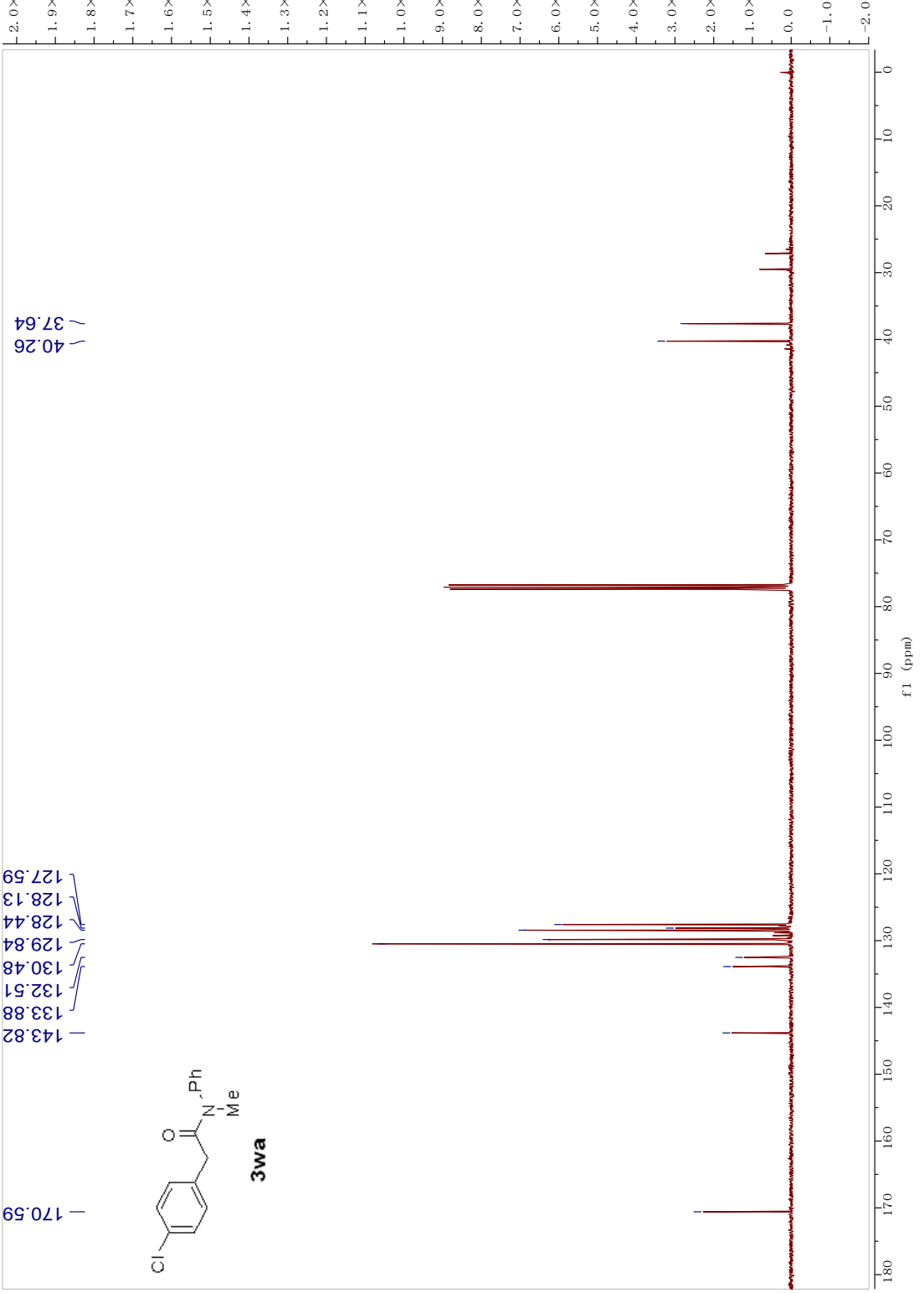
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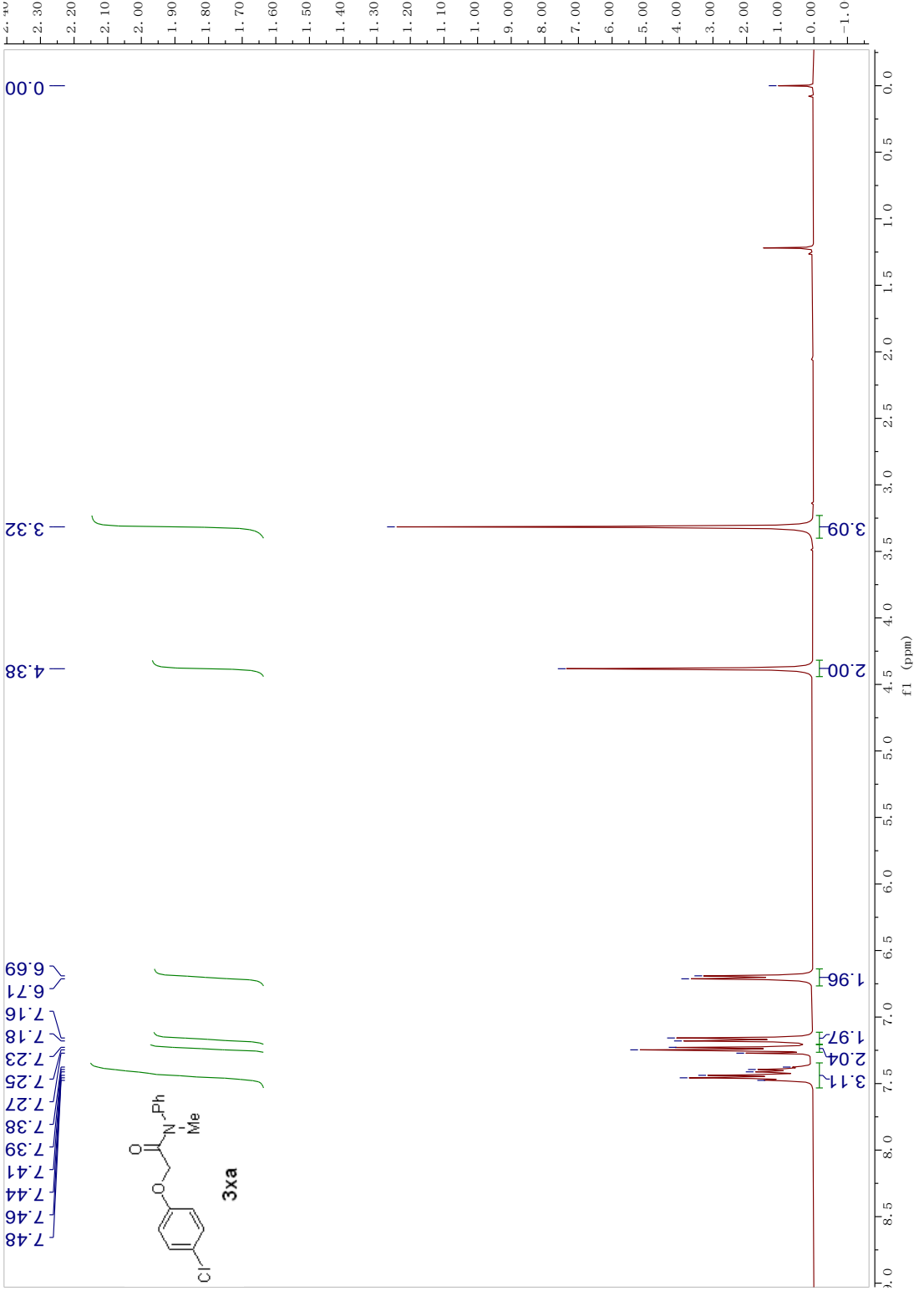
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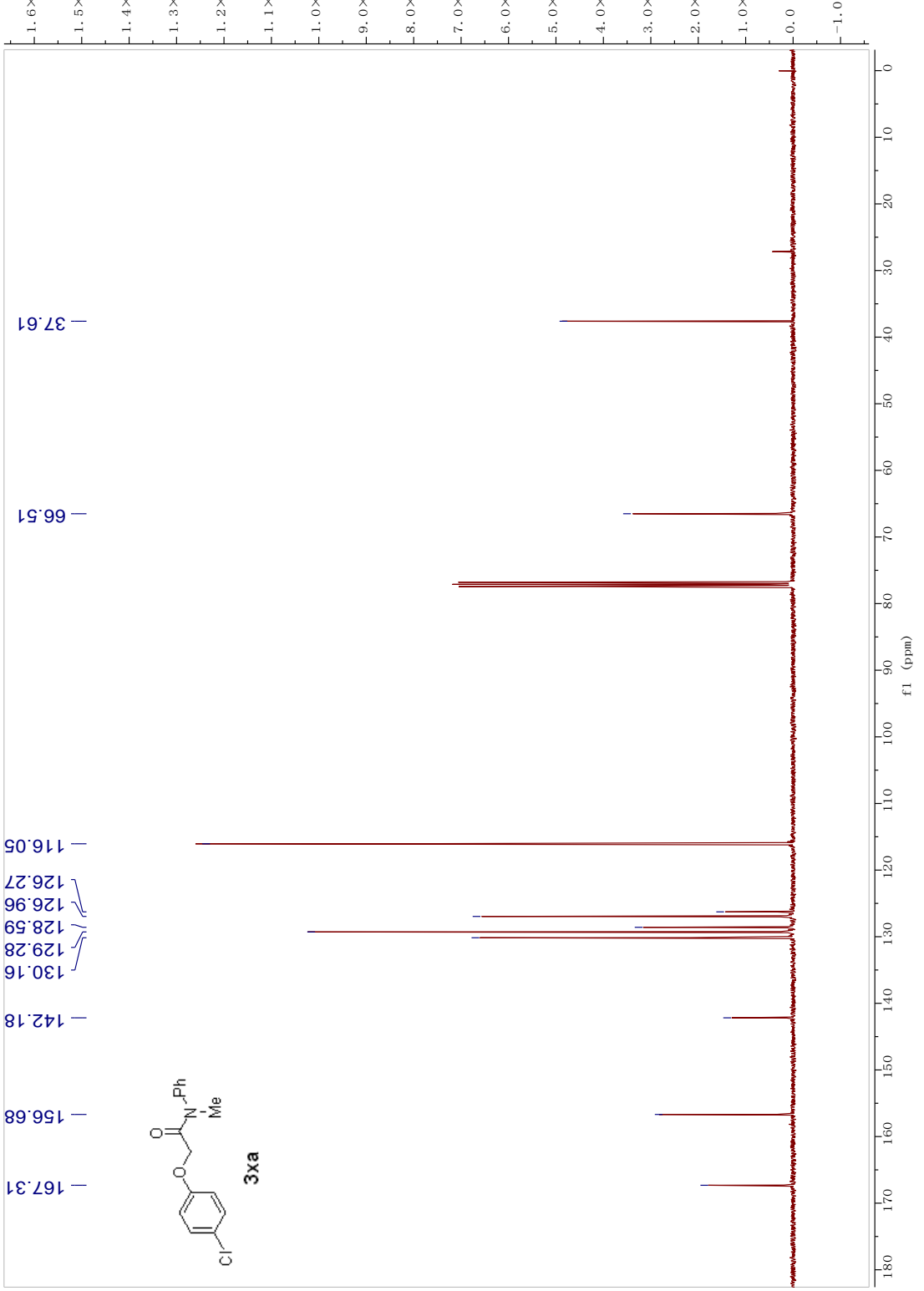
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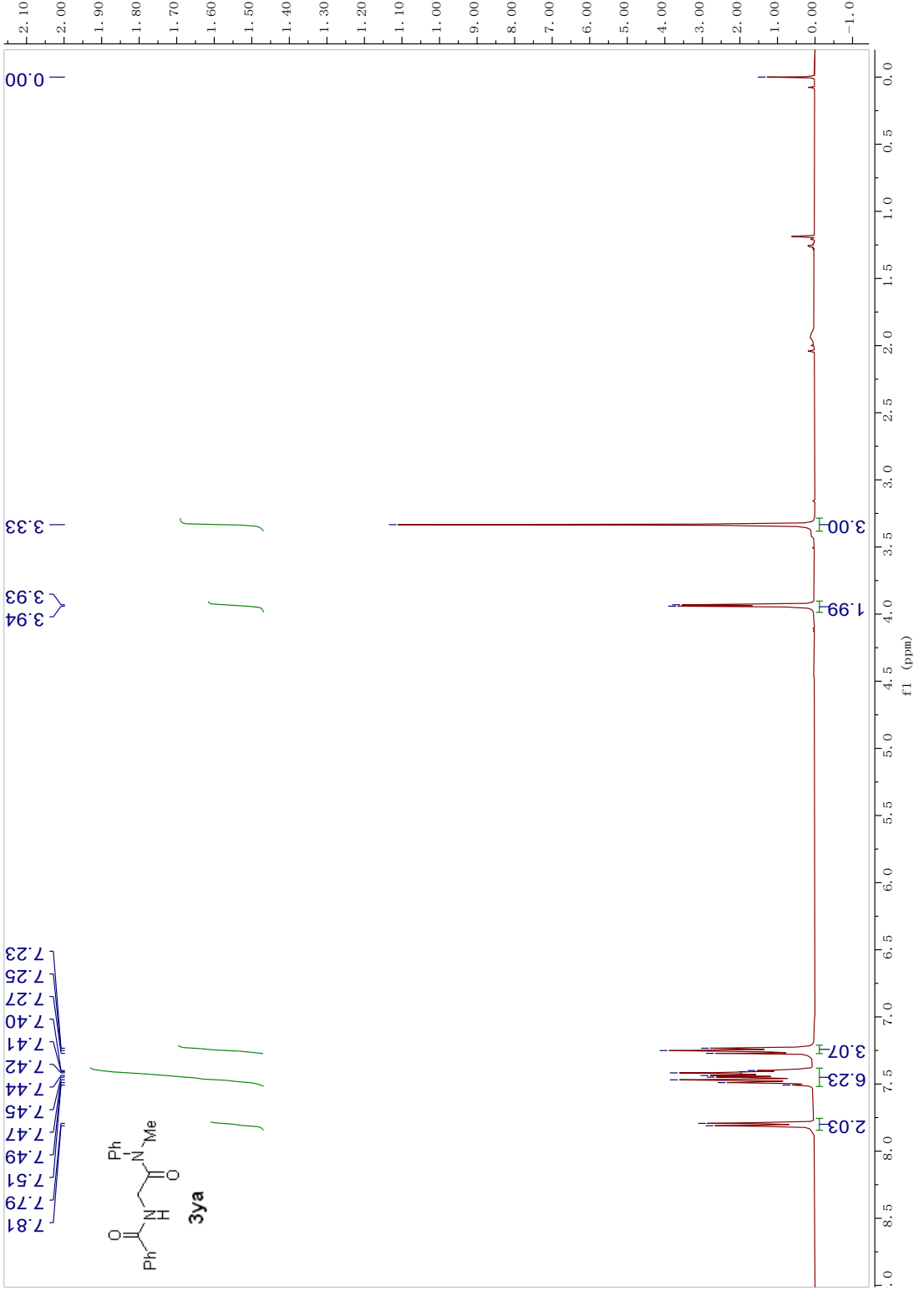
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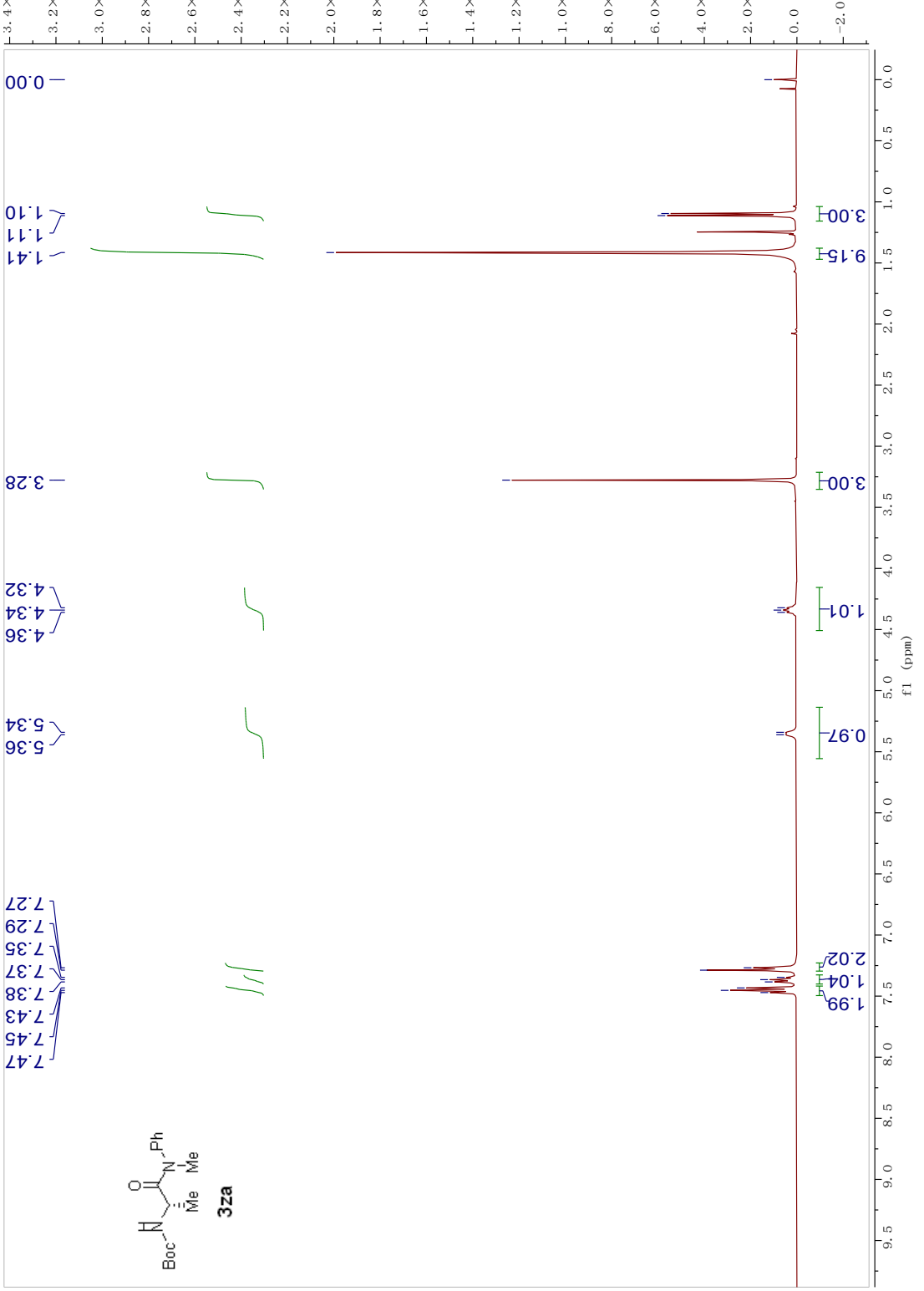
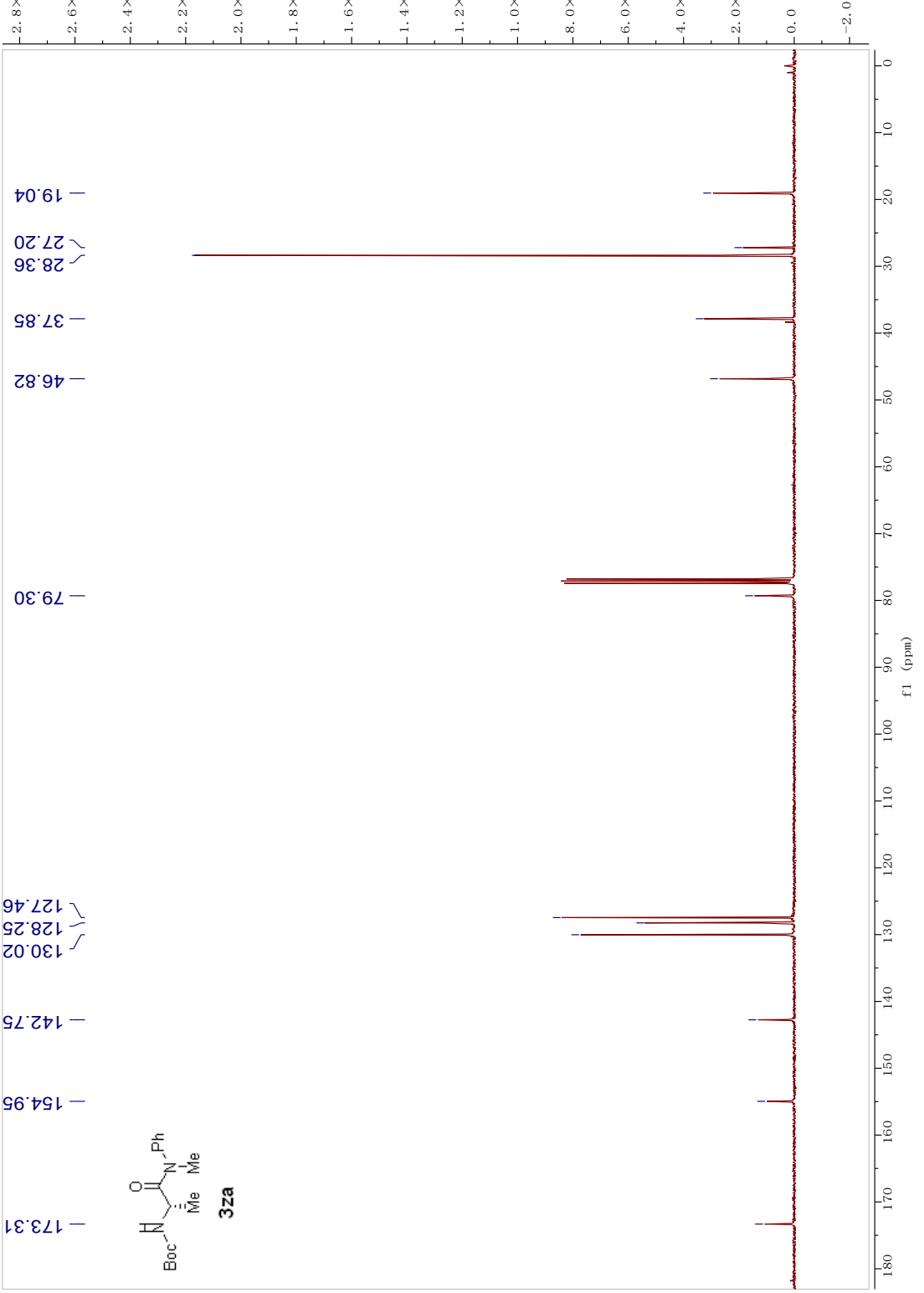
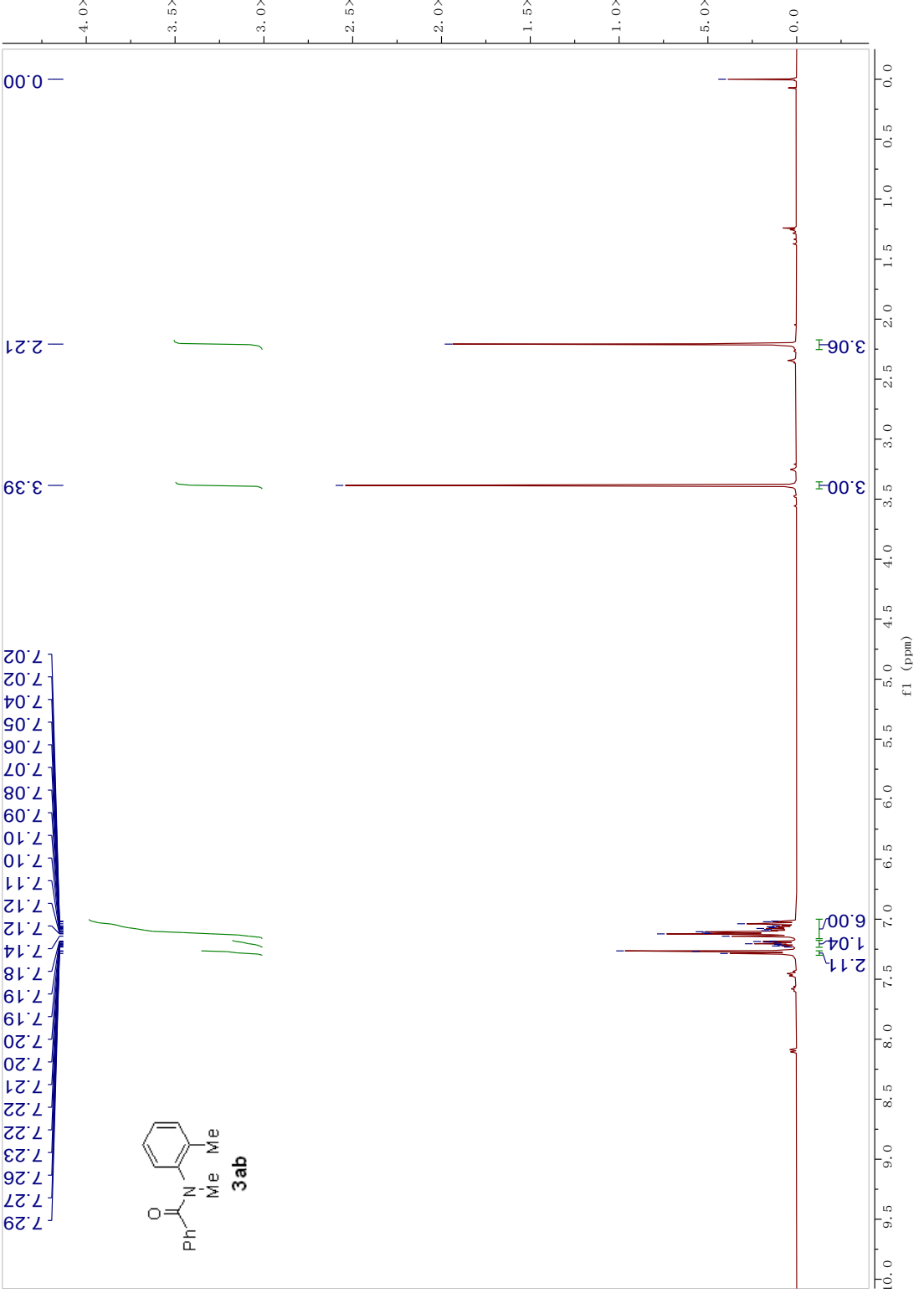
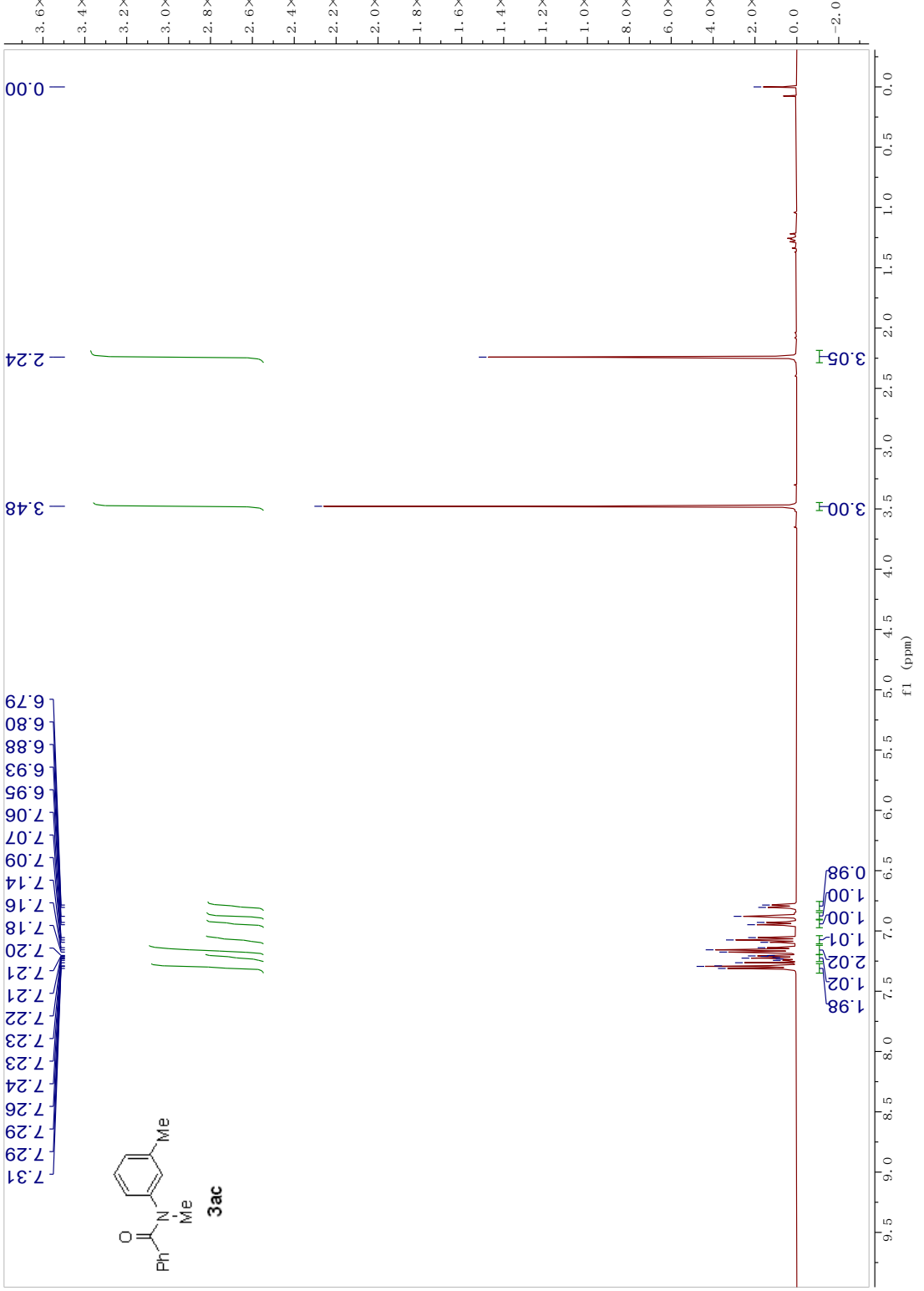
f1 (ppm)


3za
Boc
Me
Me
Ph
7.47
7.45
7.43
7.38
7.37
7.35
7.29
7.27
5.36
5.34
4.36
4.34
4.32
3.28
1.41
1.11
1.10
0.00
1.99
1.04
2.02
0.97
1.01
3.00
9.15
3.00
f1 (ppm)


19.04
27.20
28.36
37.85
46.82
79.30
127.46
128.25
130.02
142.75
154.95
173.31
Boc
Me
Me
Ph
3za
f1 (ppm)


0.00
2.21
3.39
7.02
7.02
7.04
7.05
7.06
7.07
7.08
7.09
7.10
7.10
7.11
7.12
7.12
7.14
7.18
7.19
7.19
7.20
7.20
7.21
7.22
7.22
7.23
7.26
7.27
7.29
3.06
3.00
6.00
1.04
2.11
Ph
O
N
Me
Me
3ab
f1 (ppm)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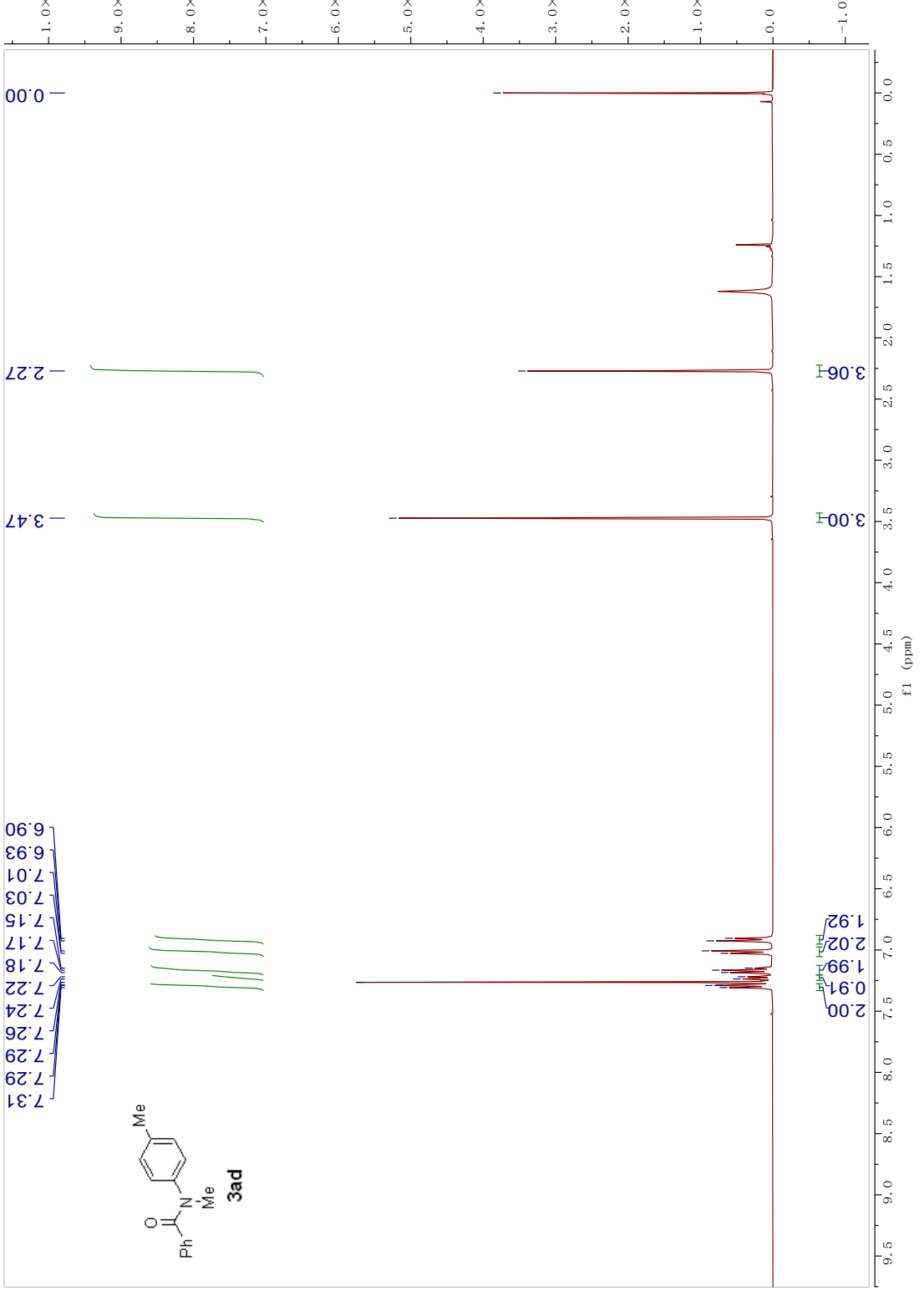
2.24
3.48
3.05
3.00
0.98
1.00
1.00
1.01
2.02
1.02
1.98
6.79
6.80
6.88
6.93
6.95
7.06
7.07
7.09
7.14
7.16
7.18
7.20
7.21
7.21
7.22
7.23
7.23
7.24
7.26
7.29
7.29
7.31
Me
N
Me
O
Ph
3ac
f1 (ppm)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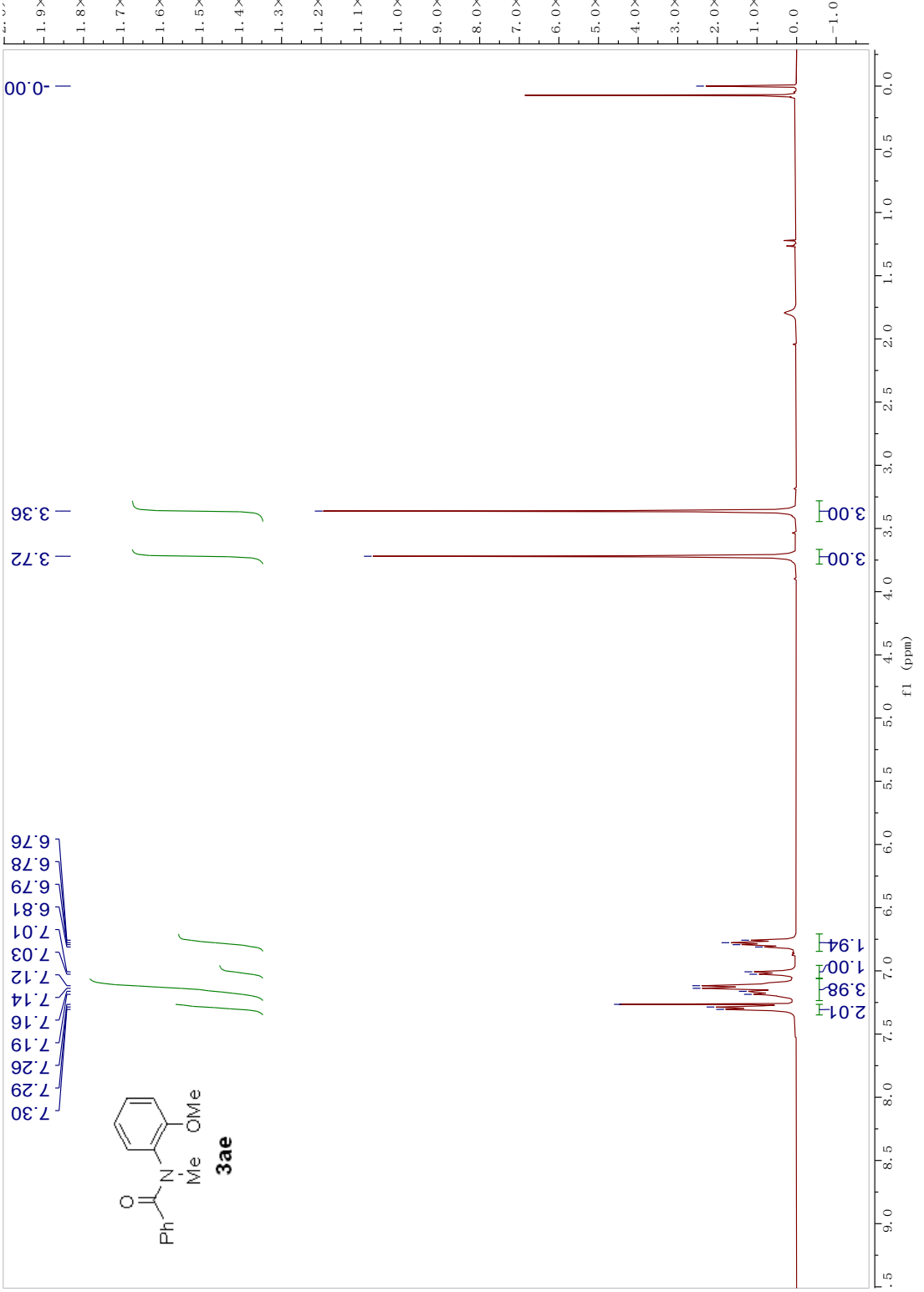
2.27
3.47
7.31
7.29
7.29
7.26
7.24
7.22
7.18
7.17
7.15
7.03
7.01
6.93
6.90
2.00
0.91
1.99
2.02
1.92
3.00
3.06
Me
N
Me
O
Ph
3ad
f1 (ppm)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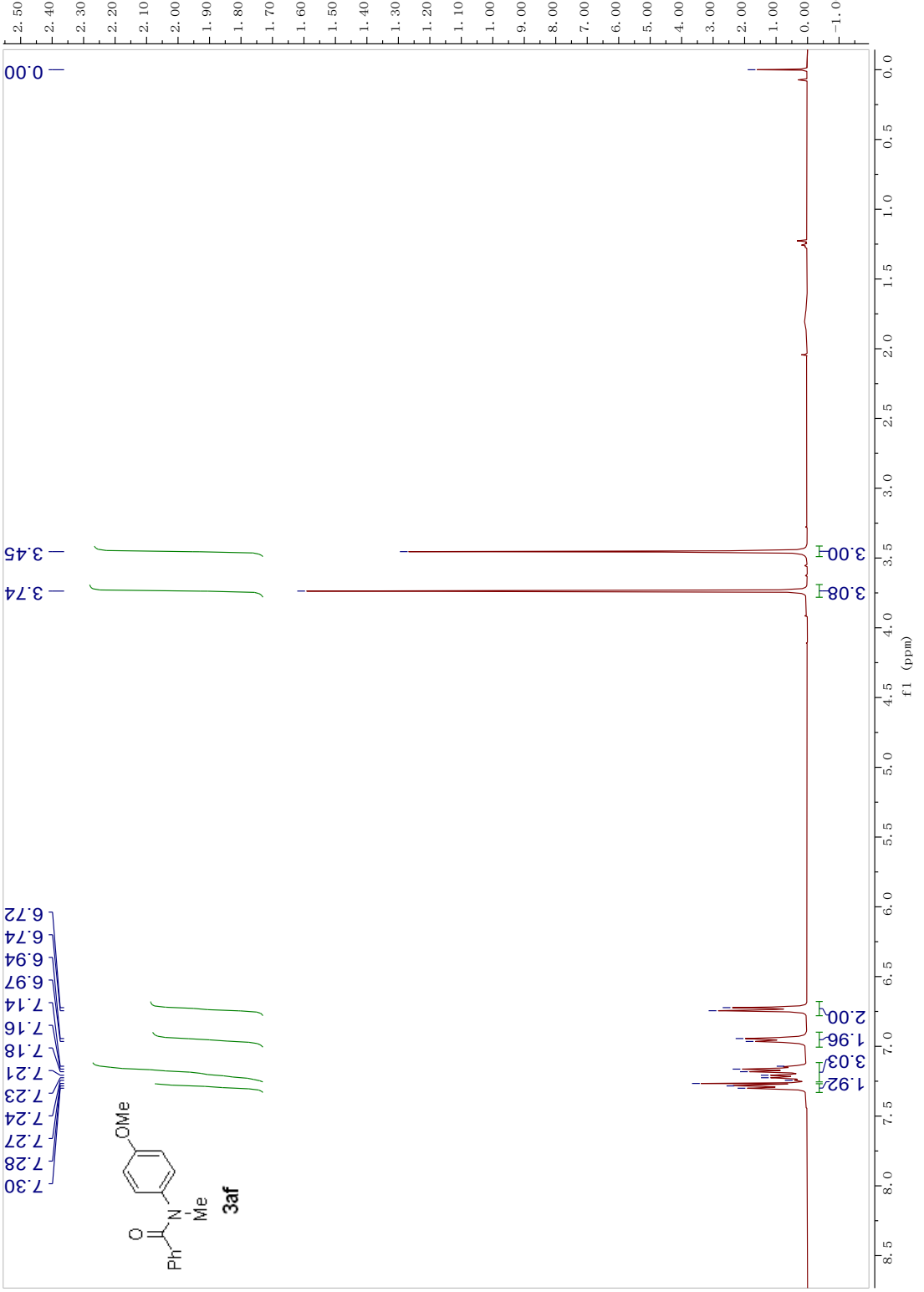
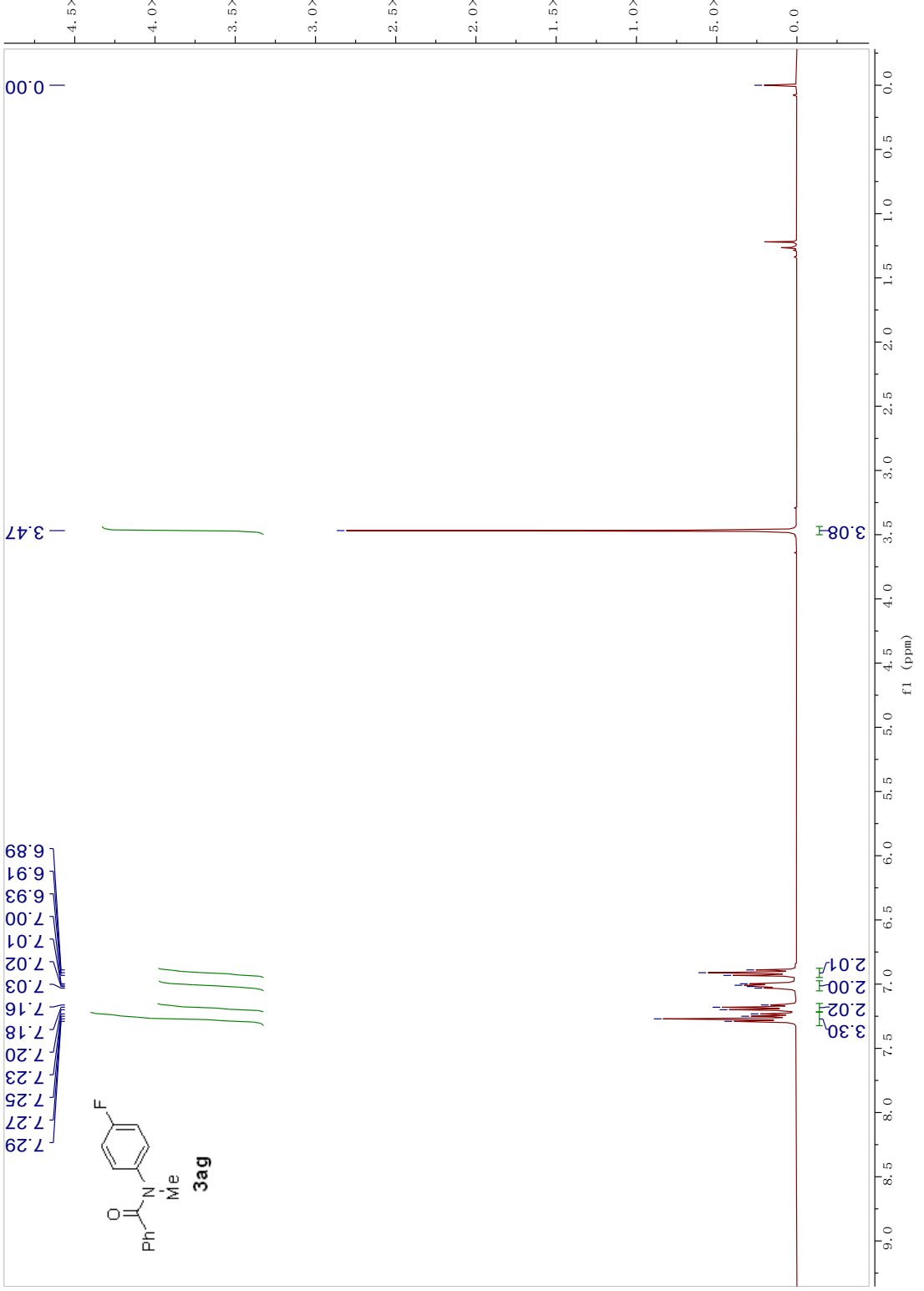
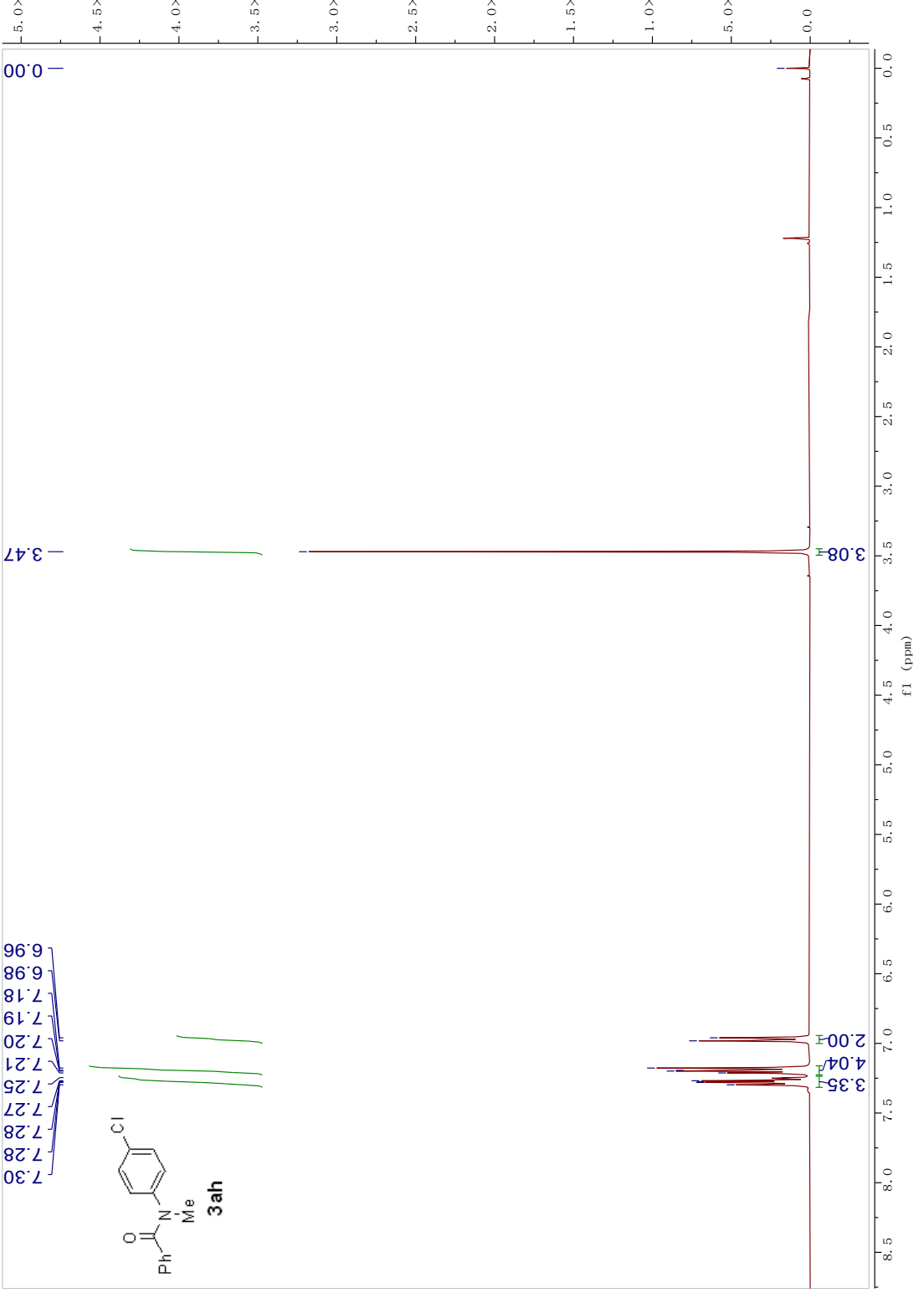
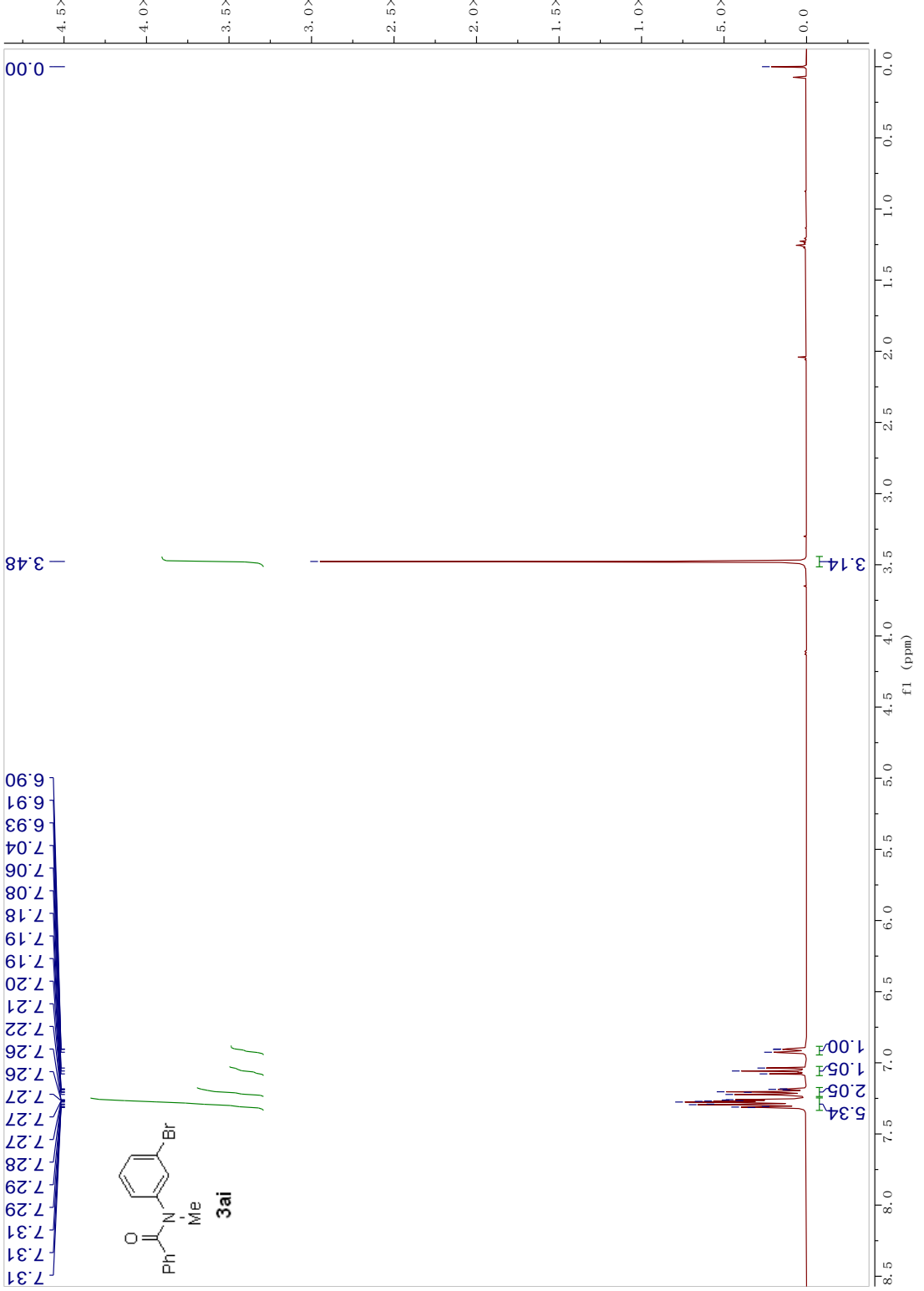
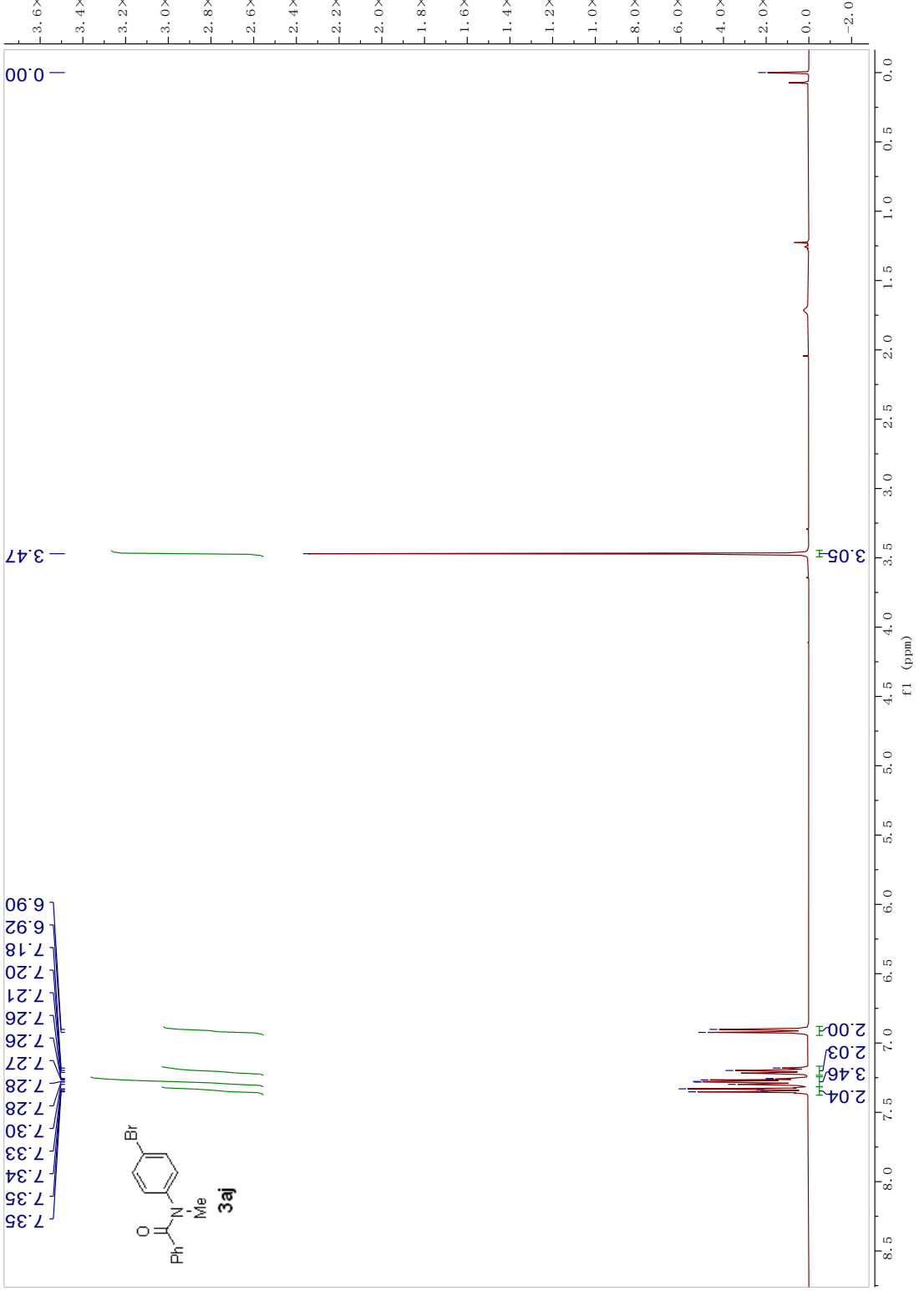
3.36
3.72
7.30
7.29
7.26
7.19
7.16
7.14
7.12
7.03
7.01
6.81
6.79
6.78
6.76
3.00
3.00
1.94
1.00
3.98
2.01
OMe
Me
N
O
Ph
3ae
f1 (ppm)

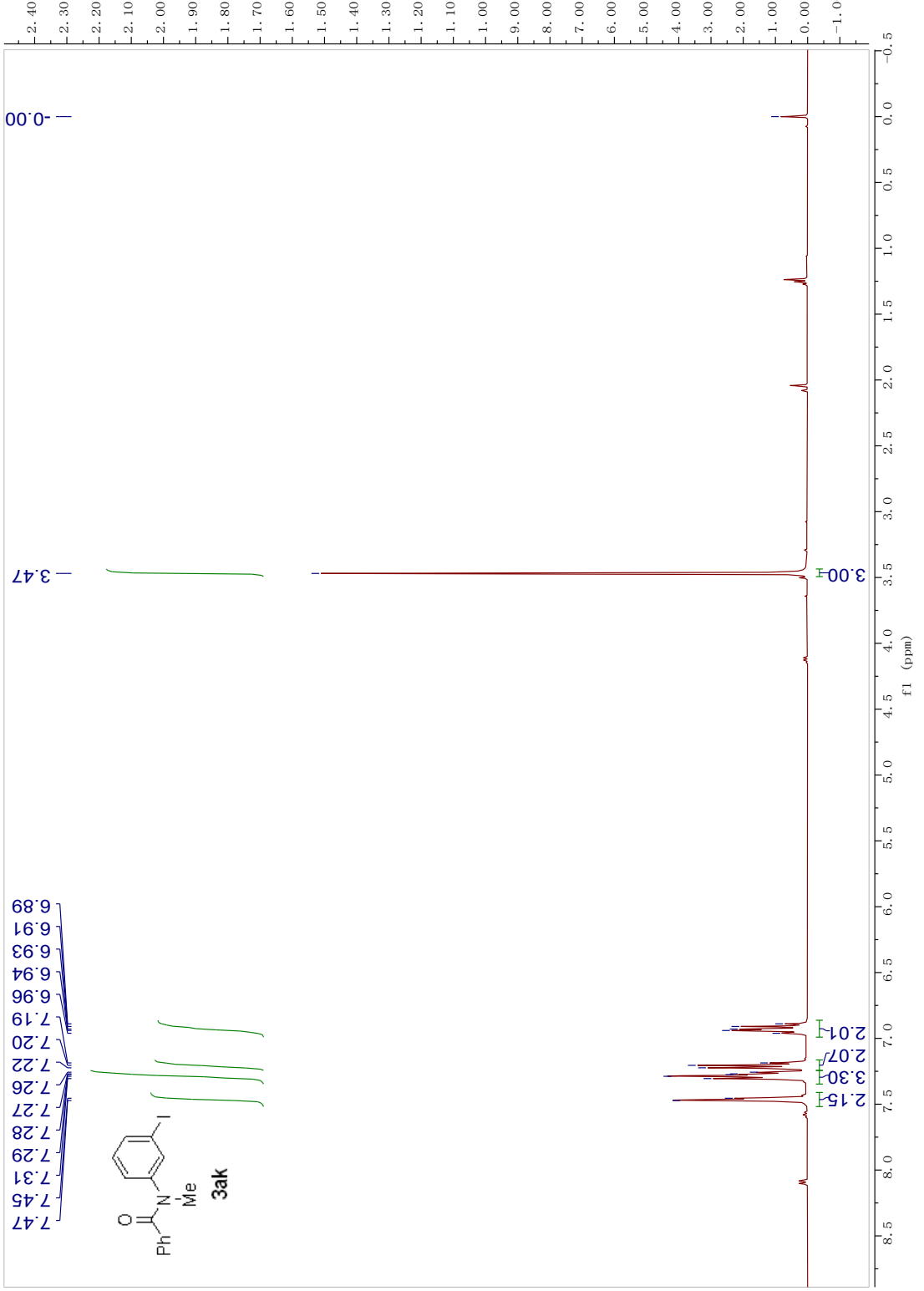

0.00
3.45
3.74
3.00
3.08
2.00
1.96
3.03
1.92
7.30
7.28
7.27
7.24
7.23
7.21
7.18
7.16
7.14
6.97
6.94
6.74
6.72
OMe
N
Me
Ph
O
3af
f1 (ppm)

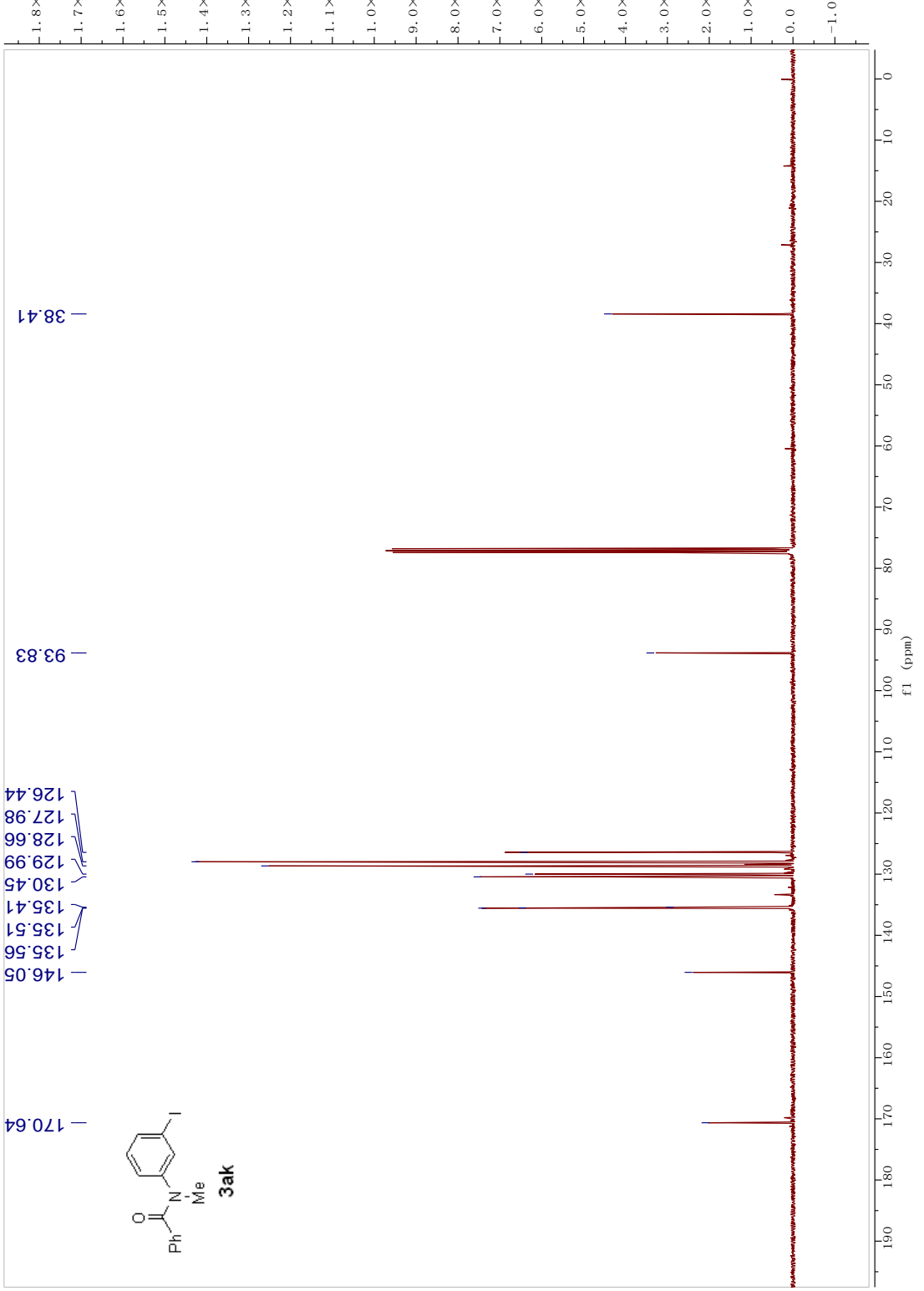

0.00
3.47
3.08
2.01
2.00
2.02
3.30
7.29
7.27
7.25
7.23
7.20
7.18
7.16
7.03
7.02
7.01
7.00
6.93
6.91
6.89
F
O
Ph
N
Me
3ag
f1 (ppm)

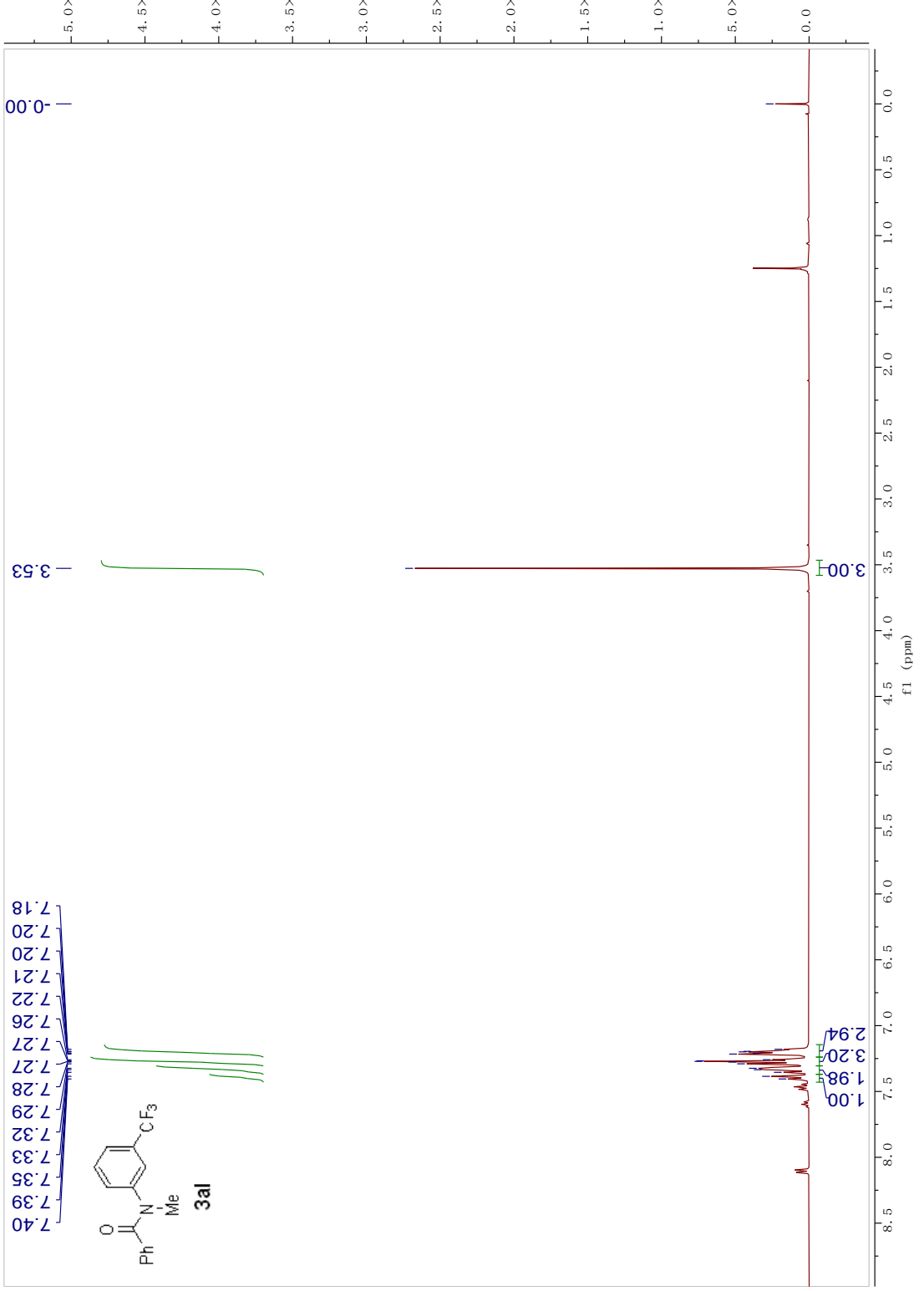

0.00
3.47
3.08
2.00
4.04
3.35
7.30
7.28
7.28
7.27
7.25
7.21
7.20
7.19
7.18
6.98
6.96
Cl
N
Me
O
Ph
3ah
f1 (ppm)

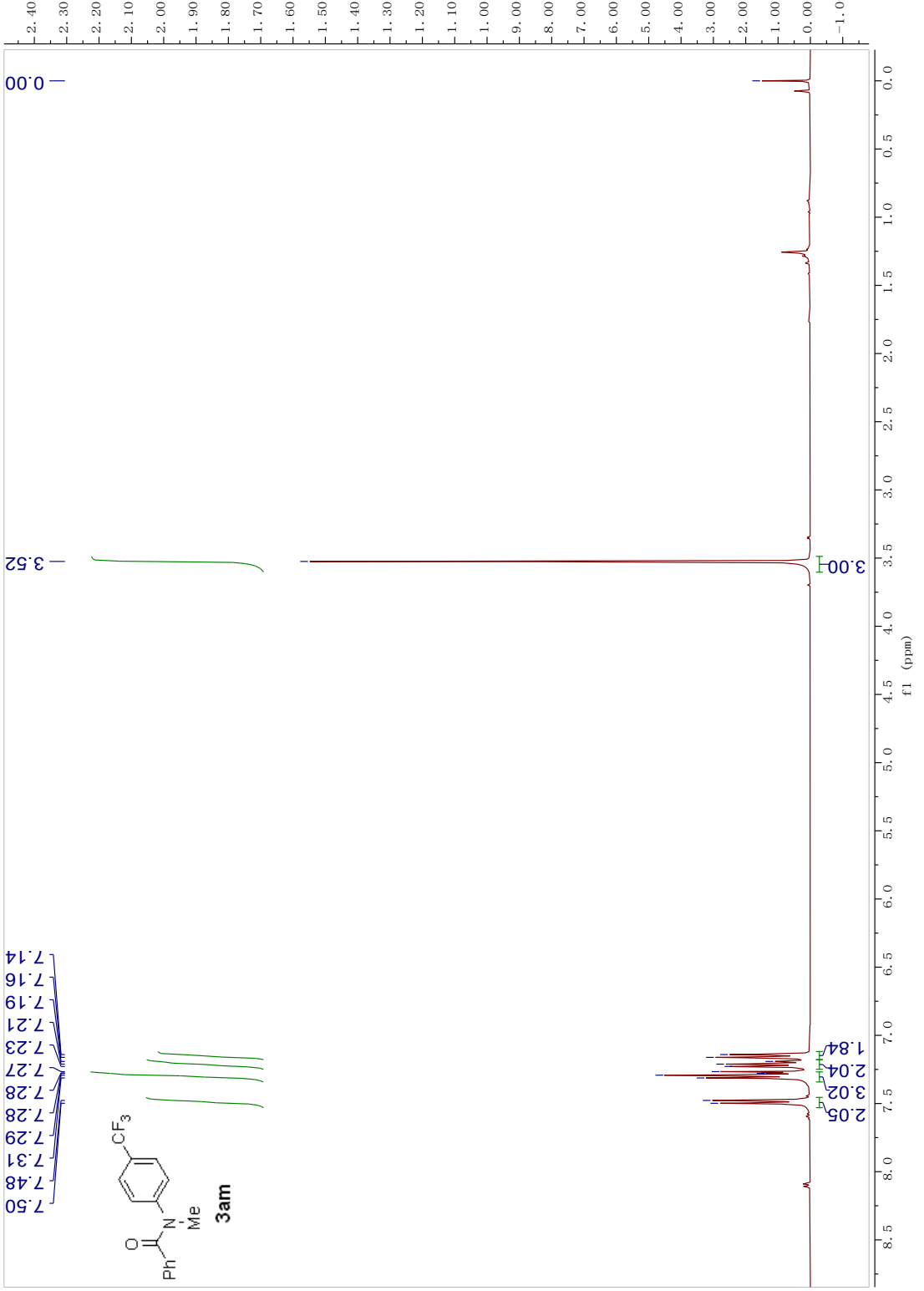

0.00
3.48
3.14
1.00
1.05
2.05
5.34
6.90
6.91
6.93
7.04
7.06
7.08
7.18
7.19
7.19
7.20
7.21
7.22
7.26
7.26
7.27
7.27
7.27
7.28
7.29
7.29
7.31
7.31
7.31
Br
N
Me
Ph
O
3ai
f1 (ppm)

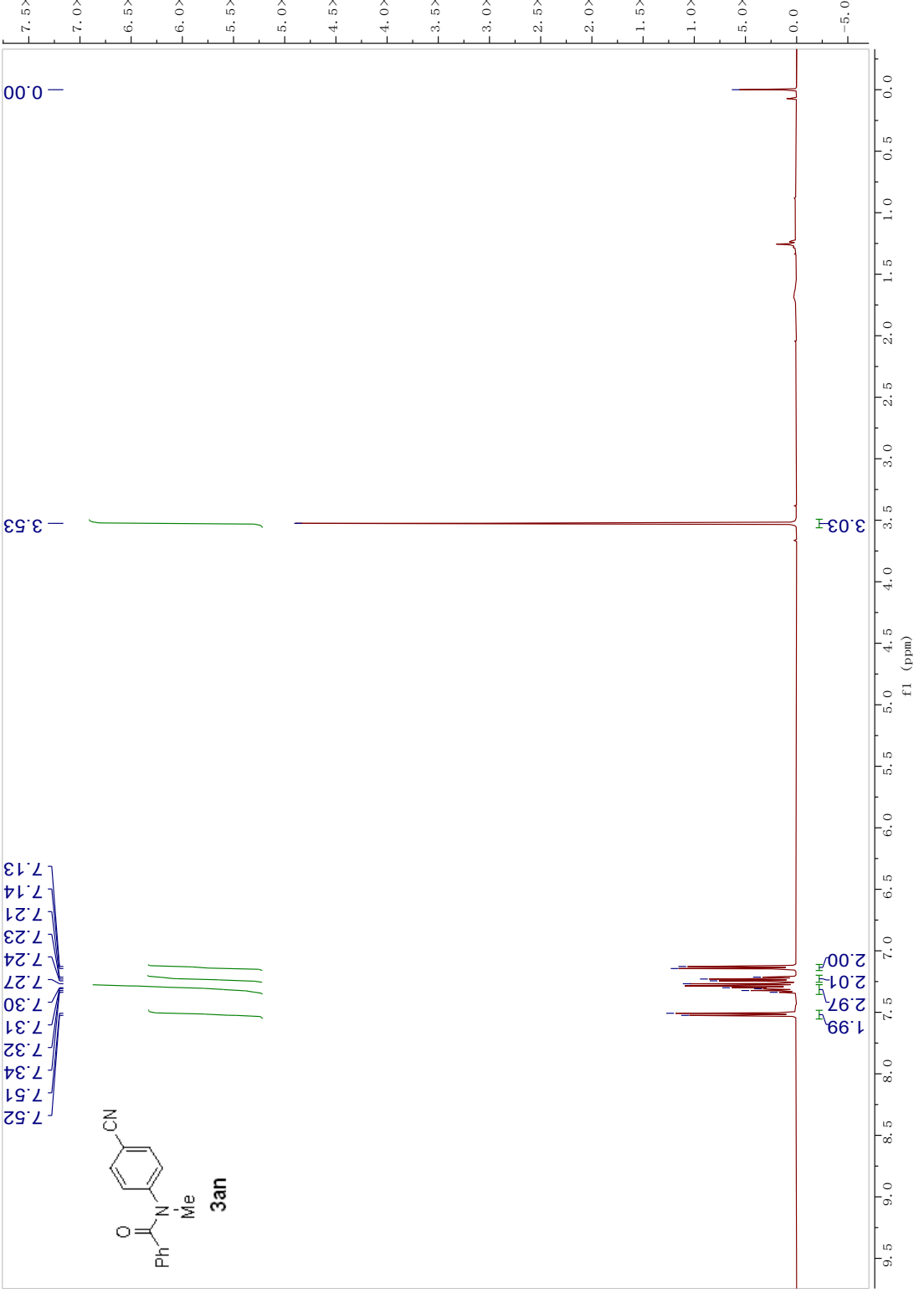

0.00
3.47
3.05
2.00
2.03
3.46
2.04
6.90
6.92
7.18
7.20
7.21
7.26
7.26
7.27
7.28
7.28
7.30
7.33
7.34
7.35
7.35
Br
O
Ph
N
Me
3aj
f1 (ppm)

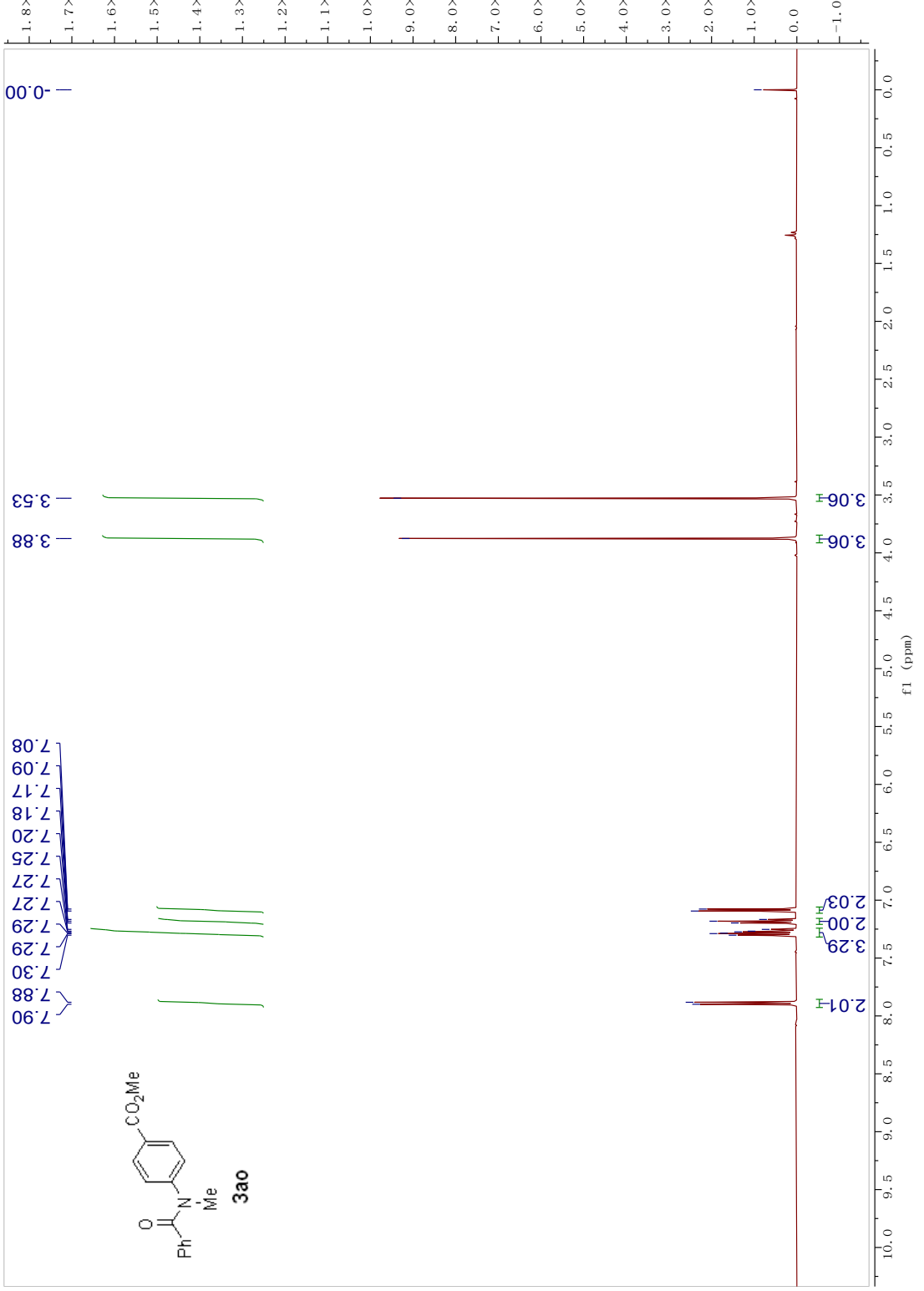

-0.00
3.47
7.47
7.45
7.31
7.29
7.28
7.27
7.26
7.22
7.20
7.19
6.96
6.94
6.93
6.91
6.89
3.00
2.01
2.07
3.30
2.15
f1 (ppm)
3ak

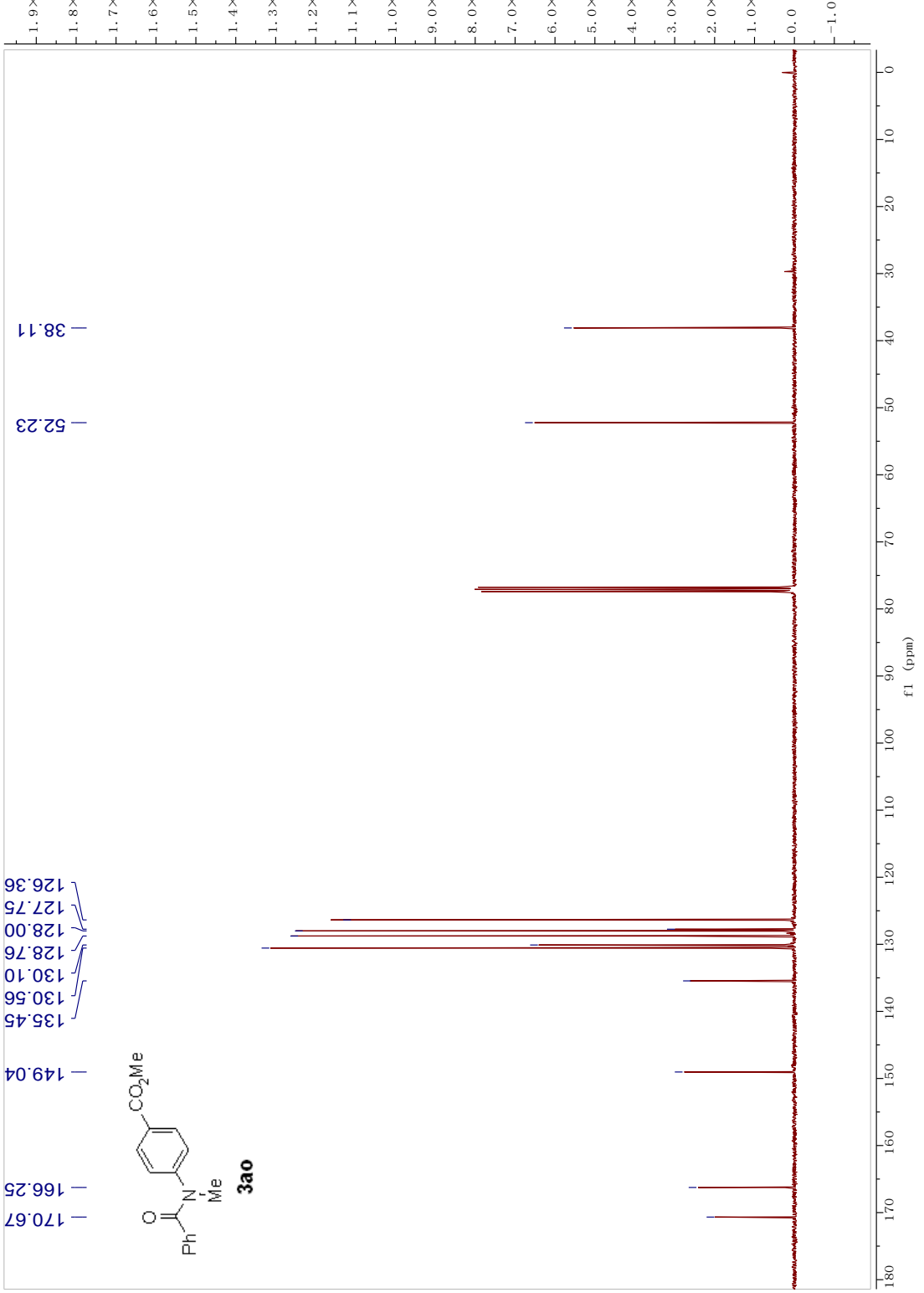

38.41
93.83
126.44
127.98
128.66
129.99
130.45
135.41
135.51
135.56
146.05
170.64
Ph
O
N
Me
I
3ak
f1 (ppm)

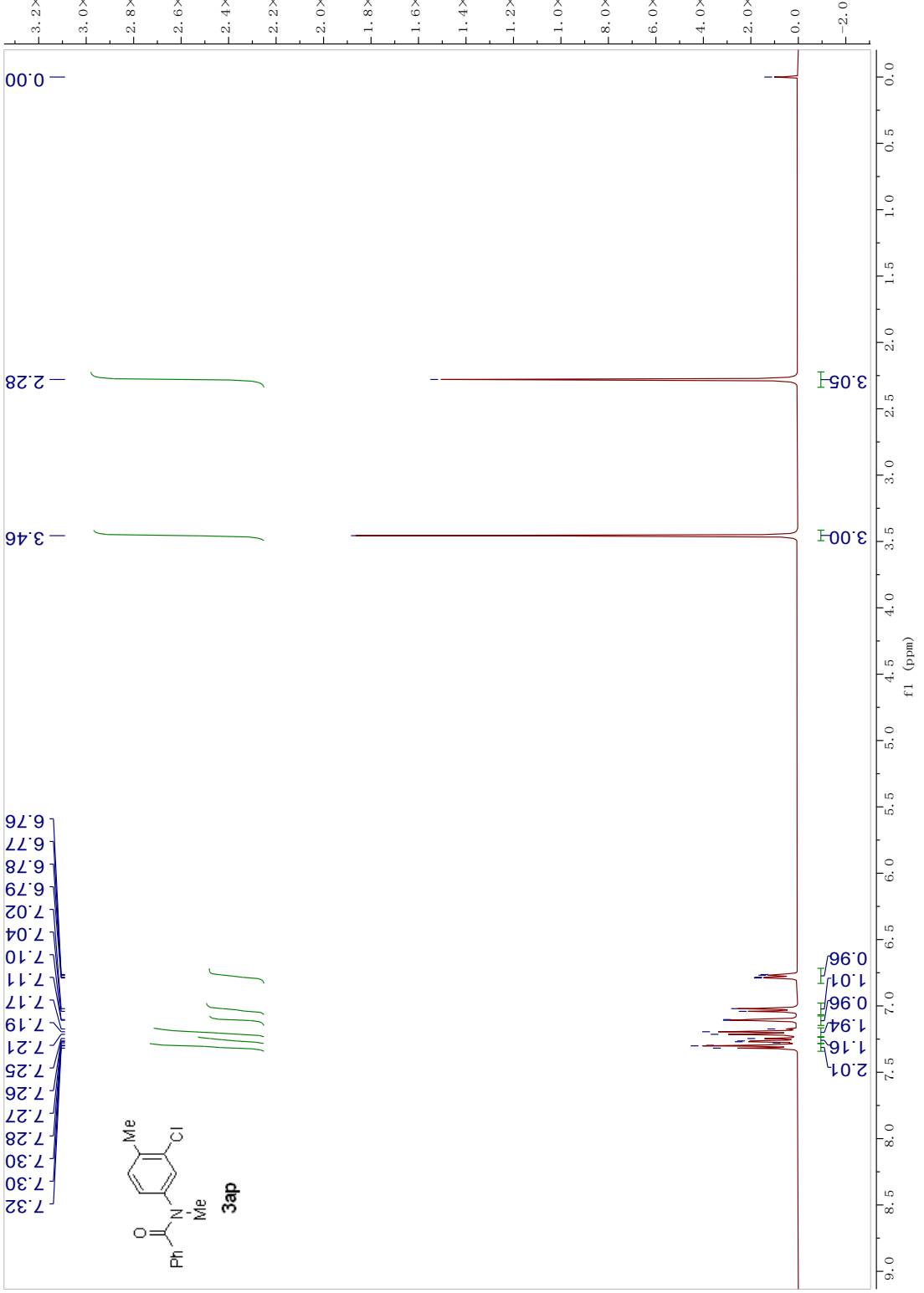

-0.00
3.53
3.00
7.18
7.20
7.20
7.21
7.22
7.26
7.27
7.27
7.28
7.29
7.32
7.33
7.35
7.39
7.40
1.00
1.98
3.20
2.94
f1 (ppm)
Ph
O
N
Me
CF3
3al

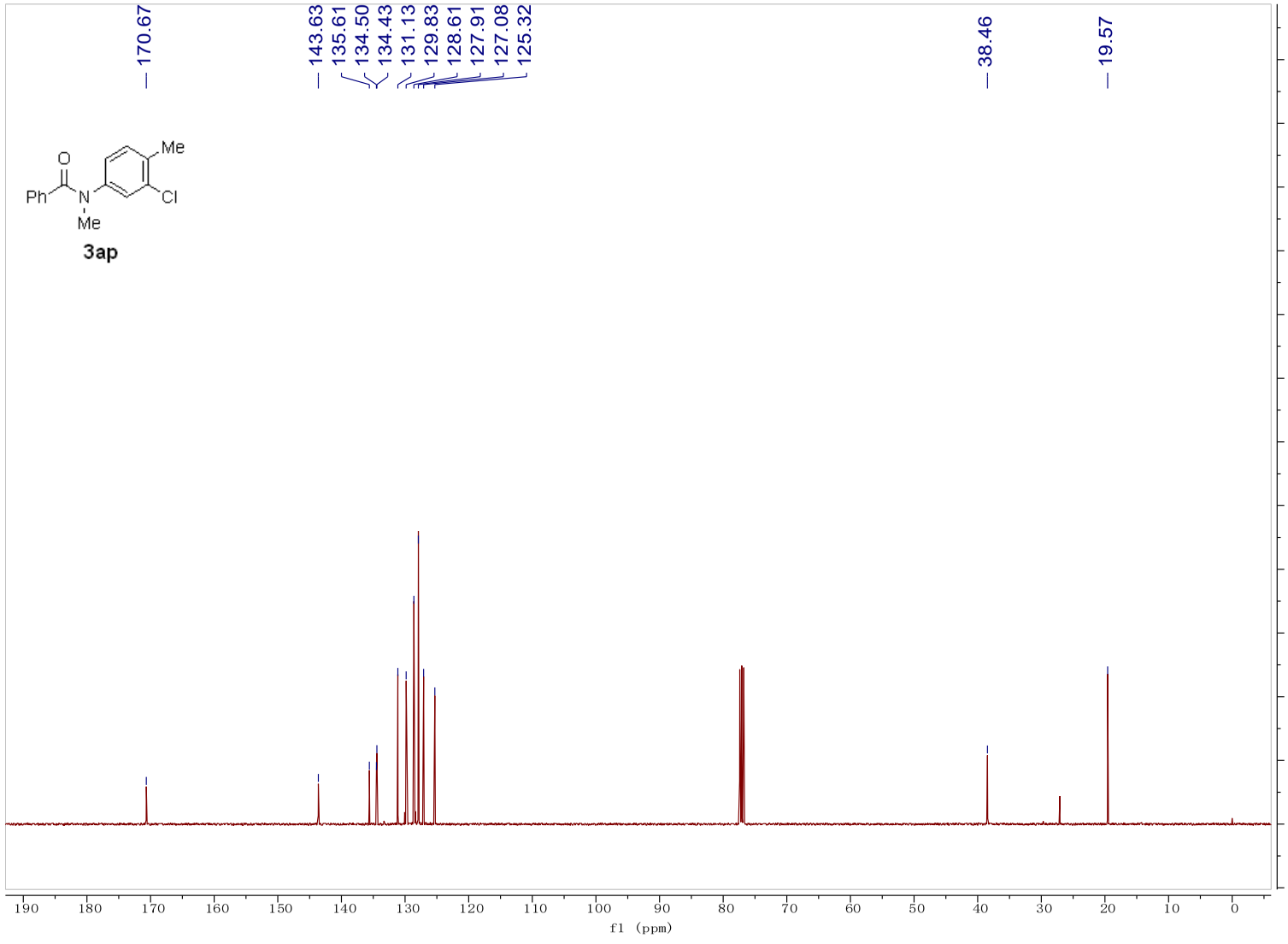

7.50
7.48
7.31
7.29
7.28
7.28
7.27
7.23
7.21
7.19
7.16
7.14
3.52
0.00
3.00
2.05
3.02
2.04
1.84
CF3
O
N
Me
Ph
3am
f1 (ppm)


0.00
3.53
3.03
7.52
7.51
7.34
7.32
7.31
7.30
7.27
7.24
7.23
7.21
7.14
7.13
2.00
2.01
2.97
1.99
CN
N
Me
Ph
O
3an
f1 (ppm)


-0.00
3.53
3.88
7.08
7.09
7.17
7.18
7.20
7.25
7.27
7.27
7.29
7.29
7.30
7.88
7.90
3.06
3.06
2.03
2.00
3.29
2.01
CO2Me
N
Me
O
Ph
3ao
f1 (ppm)


38.11
52.23
126.36
127.75
128.00
128.76
130.10
130.56
135.45
149.04
166.25
170.67
CO2Me
N
Me
Ph
O
3ao
f1 (ppm)


0.00
2.28
3.46
3.05
3.00
0.96
1.01
0.96
1.94
1.16
2.01
7.32
7.30
7.30
7.28
7.27
7.26
7.25
7.21
7.19
7.17
7.11
7.10
7.04
7.02
6.79
6.78
6.77
6.76
Me
Cl
N
Me
O
Ph
3ap
f1 (ppm)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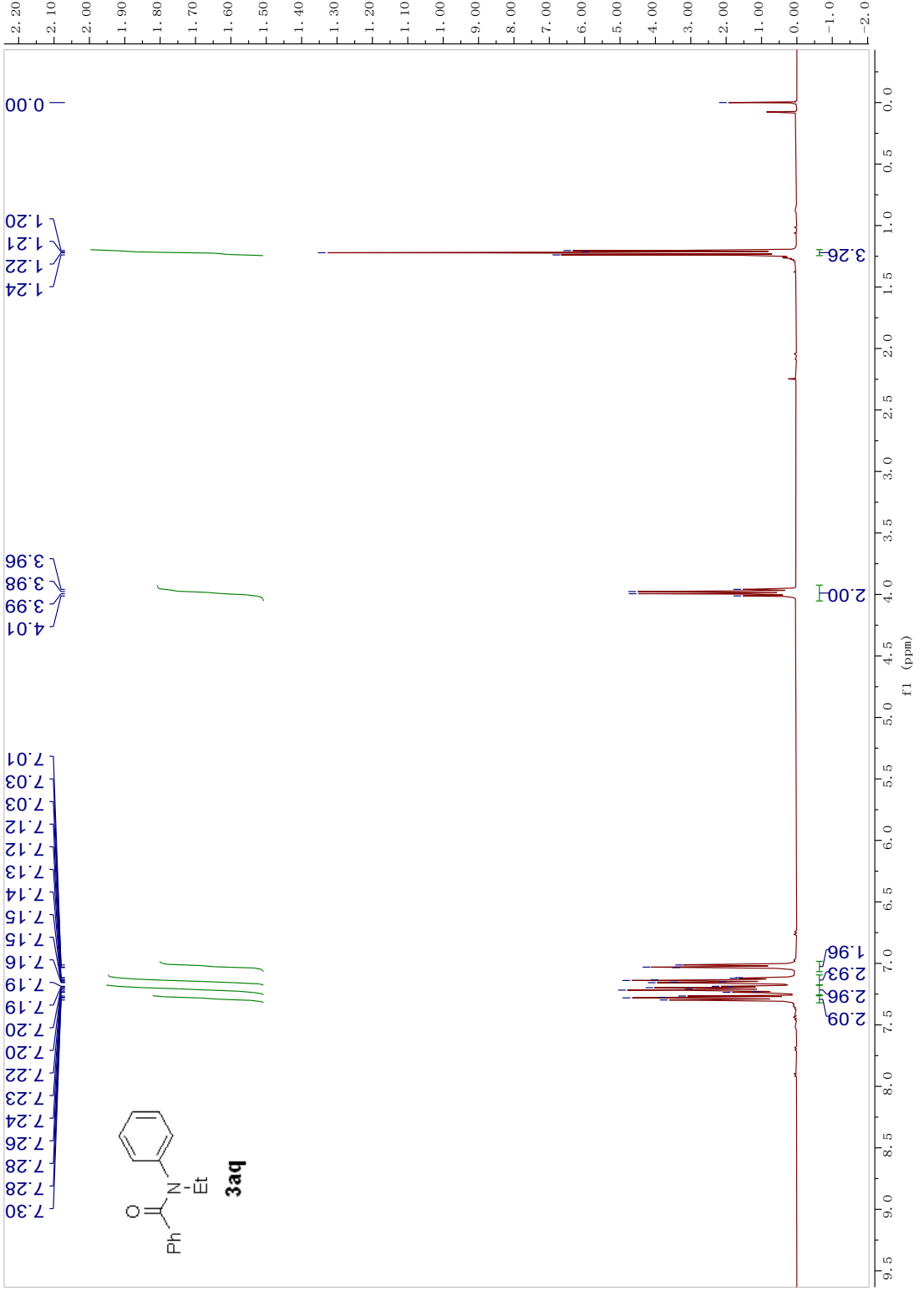
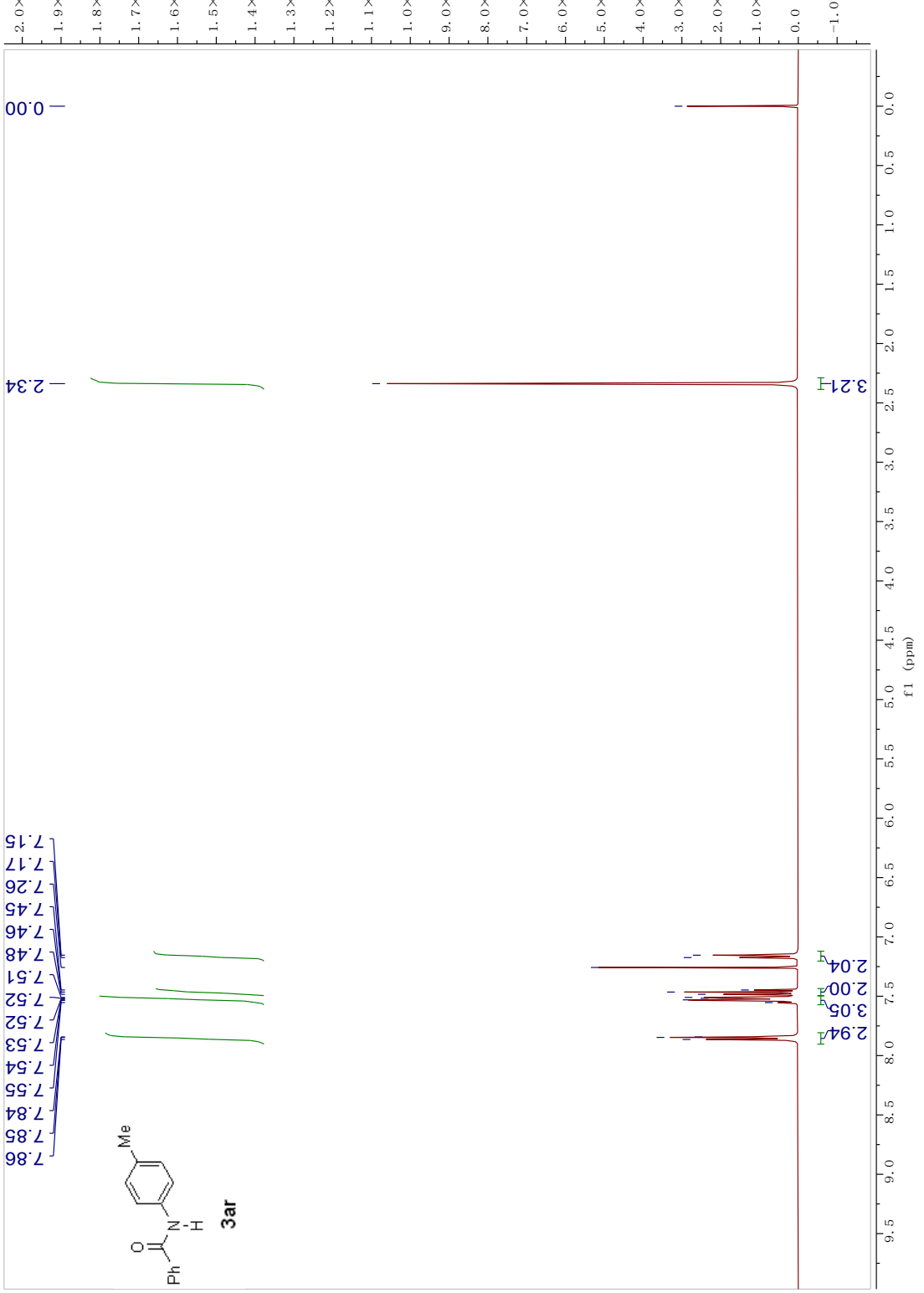
143.63
135.61
134.50
134.43
131.13
129.83
128.61
127.91
127.08
125.32
38.46
19.57
Ph
O
N
Me
Me
Cl
3ap
f1 (ppm)


0.00
1.20
1.21
1.22
1.24
3.26
3.96
3.98
3.99
4.01
2.00
7.01
7.03
7.03
7.12
7.12
7.13
7.14
7.15
7.15
7.16
7.19
7.19
7.20
7.20
7.22
7.23
7.24
7.26
7.28
7.28
7.30
1.96
2.93
2.96
2.09
Ph
O
N
Et
3aq
f1 (ppm)


0.00
2.34
3.21
2.04
2.00
3.05
2.94
7.15
7.17
7.26
7.45
7.46
7.48
7.51
7.52
7.52
7.53
7.54
7.55
7.84
7.85
7.86
Me
N-H
O
Ph
3ar
f1 (ppm)