Nickel-catalyzed oxidative thiolation of α-amino carbonyl compounds with thiols

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1. General Comments

All the materials and solvents were purchased from commercial suppliers and used without additional purification. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400M at ambient temperature with $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) as the solvent. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass analyses of the products were performed on a Bruker Esquire 6000 (ESI-ION Trap) mass spectrometer.

2. Experimental Section

2.1 Preparation of α-Amino carbonyl compounds

To a 250 mL Round-bottomed flask were added $NaHCO_3$ (0.84g, 10 mmol) and α-bromoacetophenone derivative (10 mmol). DMSO (100 mL) was then added, and the mixture was stirred at room temperature. Arylamine (12 mmol, 1.2 equiv) was added slowly to the reaction mixture and stirred for 4 hours. After that time, water (20 mL) was added, and the solution was extracted with ethyl acetate (3 x 20 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The filtrates were concentrated under reduced pressure and the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, V/V) to afford the desired product **1a-l**.[1-2]

1m was commercially avaible and used without further purification.

1n,[3] **1o**,[4] **1p**,[5] **1q**,[6] **1r**[7] and **1s**[8] were prepared according to the literatures.

2.2 General procedure for the Ni-catalyzed oxidative thiolation of α-amino carbonyl compounds 1 with thiols 2

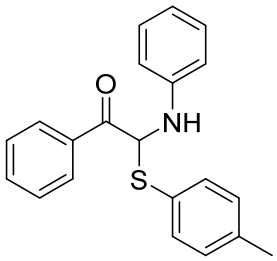
To a 25 mL Schlenk tube were added α-amino carbonyl compound **1** (0.5 mmol), thiol **2** (2.5 mmol, 5.0 equiv), $NiCl_2 \cdot 6H_2O$ (10 mol%), acetonitrile (5 mL) and TBHP (1.5 equiv, 70% in water). The tube was then charged with air and stirred at 80 ^oC for 12 hours. After the reaction was finished, water (10 mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum to give a residue that was purified by column chromatography (silica gel, PE-EtOAc).

2.3 General procedure for the control experiments

Control experiments A, B, D and E were conducted on 0.5 mmol scale with a similar procedure of Section 2.2.

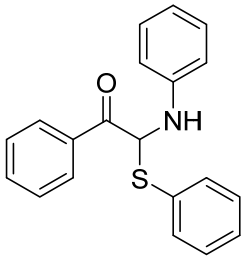
Control experiment C was conducted as follows: To a 25 mL Schlenk tube were added 1-phenyl-2-(phenylamino)ethenone **1a** (2 mmol), $NiCl_2 \cdot 6H_2O$ (10 mol%), acetonitrile (15 mL) and TBHP (1.5 equiv, 70% in water). The tube was then charged with air and stirred at 80 ^oC for 12 hours. After the reaction was finished, water (15 mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum to give a residue that was purified by column chromatography (silica gel, PE-EtOAc). The imine compound **4** was finally obtained in 54% (226 mg) yield as a

yellow solid.[9] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.42 (d, J = 7.7 Hz, 2H), 7.93 – 7.60 (m, 3H), 7.51 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.4, 158.9, 136.7, 134.7, 133.1, 131.5, 129.3, 128.6, 125.3, 119.9, 77.3, 77.0, 76.8, 29.7.



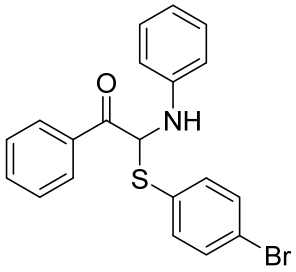
1-Phenyl-2-(phenylamino)-2-(p-tolylthio)ethan-1-one (3aa)

The indicated compound was obtained in 94% yield (156 mg) as a yellow solid: mp 120-122℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.89 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.25 (dd, J = 8.4, 7.5 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 6.91–6.74 (m, 5H), 6.20 (d, J = 9.5 Hz, 1H), 5.03 (d, J = 9.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 143.1, 139.9, 137.4, 134.5, 133.6, 129.8, 129.5, 128.9, 128.7, 125.0, 119.3, 115.0, 63.0, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{19}NNaOS$, 356.1080; found, 356.1074.



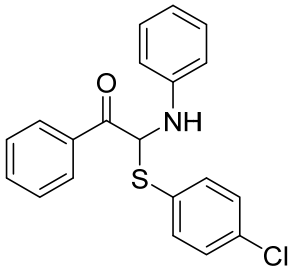
1-Phenyl-2-(phenylamino)-2-(phenylthio)ethan-1-one (3ab)

The indicated compound was obtained in 90% yield (144 mg) as a yellow solid: mp 123-125℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.40–7.29 (m, 3H), 7.24 (dd, J = 13.4, 5.6 Hz, 3H), 7.04 (d, J = 7.1 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.31 (d, J = 9.5 Hz, 1H), 5.13 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 142.9, 137.4, 134.4, 133.7, 129.6, 129.5, 128.9, 128.8, 128.7, 128.6, 119.3, 115.0, 63.0. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{17}NNaOS$: 342.0923; found: 342.0920.



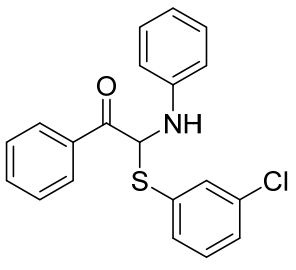
2-((4-Bromophenyl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3ac)

The indicated compound was obtained in 76% yield (151 mg) as a yellow solid: mp 119-122℃;^{1}H NMR (400 MHz,$CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37–7.23 (m, 4H), 6.94–6.72 (m, 5H), 6.24 (d, J = 9.3 Hz, 1H), 5.06 (d, J = 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 142.6, 138.9, 134.1, 133.9, 132.3, 132.1, 129.6, 129.5, 129.0, 128.7, 127.7, 124.6, 119.5, 114.9, 63.0. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{16}BrNNaOS$: 420.0028; found: 420.0024.



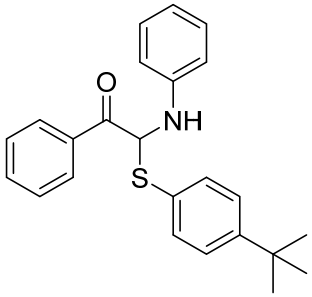
2-((4-Chlorophenyl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3ad)

The indicated compound was obtained in 80% yield (141 mg) as a yellow solid: mp 130-135℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.48–7.38 (m, 1H), 7.33 (t, J = 7.9 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.97–6.88 (m, 4H), 6.31 (d, J = 9.3 Hz, 1H), 5.13 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 142.6, 138.7, 136.2, 134.1, 133.8, 129.6, 129.1, 129.0, 128.7, 127.1, 119.5, 114.9, 63.1. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{16}ClNNaOS$: 376.0533; found: 376.0533.



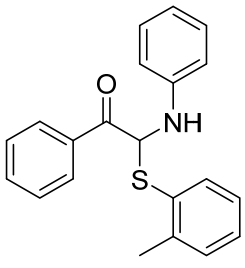
2-((3-Chlorophenyl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3ae)

The indicated compound was obtained in 61% yield (108 mg) as a yellow solid, mp 108-109 ℃; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.37–7.28 (m, 3H), 7.16 (t, J = 7.9 Hz, 1H), 7.01 (s, 1H), 6.92 (t, J = 9.2 Hz, 4H), 6.34 (d, J = 9.4 Hz, 1H), 5.18 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 142.6, 136.9, 135.4, 134.3, 134.2, 133.9, 130.8, 130.6, 129.8, 129.6, 129.0, 128.7, 119.7, 115.1, 63.3. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{16}ClNNaOS$: 376.0533; found: 376.0535.



2-((4-(*tert*-Butyl)phenyl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3af)

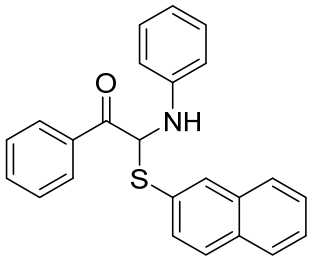
The indicated compound was obtained in 78% yield (146 mg) as a yellow solid: mp 132-135℃; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.3, 1.1 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 8.4, 7.4 Hz, 2H), 7.16–7.12 (m, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.81 (dd, J = 12.9, 7.4 Hz, 3H), 6.18 (d, J = 9.6 Hz, 1H), 5.04 (d, J = 9.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 152.8, 143.1, 137.2, 134.6, 133.6, 129.5, 128.9, 158.7, 125.9, 125.0, 119.2, 115.0, 63.0, 34.8, 31.3. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{25}NNaOS$: 398.1549; found:398.1549.



1-Phenyl-2-(phenylamino)-2-(*o*-tolylthio)ethan-1-one (3ag)

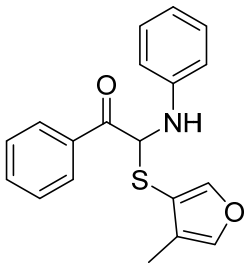
The indicated compound was obtained in 72% yield (120 mg) as a yellow solid: mp 120-122℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.62 (t, J = 6.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.22 (s, 1H), 7.14 (d, J

= 7.5 Hz, 1H), 7.03 (d, *J* = 4.3 Hz, 2H), 6.89 (dd, *J* = 14.7, 7.5 Hz, 3H), 6.32 (d, *J* = 9.4 Hz, 1H), 5.15 (d, *J* = 9.4 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 144.3, 143.1, 138.4, 134.1, 133.6, 130.5, 129.6, 129.5, 128.9, 128.8, 128.4, 125.9, 119.3, 114.8, 62.9, 21.0. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{19}NNaOS$: 356.1080; found: 356.1082.



2-(Naphthalen-2-ylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3ah)

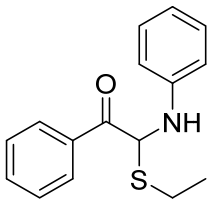
The indicated compound was obtained in 52% yield (96 mg) as a yellow solid: mp 66-68℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.66–7.60 (m, 2H), 7.56–7.50 (m, 3H), 7.50–7.43 (m, 2H), 7.38–7.32 (m, 2H), 7.09 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.95–6.88 (m, 3H), 6.36 (d, *J* = 9.6 Hz, 1H), 5.14 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 143.0, 137.9, 134.5, 133.7, 133.5, 133.5, 133.4, 129.5, 129.0, 128.8, 128.3, 128.0, 127.8, 127.2, 126.4, 125.9, 119.5, 115.1, 63.2. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{19}NNaOS$, 392.1080; found, 392.1074.



2-((2-Methylfuran-3-yl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3ai)

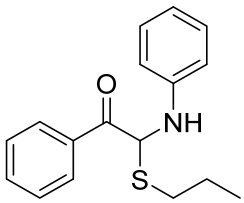
The indicated compound was obtained in 67% yield (108 mg) as a yellow solid: mp 112-113℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.21 (d, *J* = 1.9 Hz, 1H), 6.91–6.81 (m, 3H), 6.12 (d, *J* = 9.5 Hz, 1H), 5.92 (d, *J* = 1.9 Hz, 1H), 5.15 (d, *J* = 9.5 Hz, 1H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 159.5, 143.0, 140.5, 134.1, 133.7, 129.4, 128.9, 128.8 (d, *J* = 13.9 Hz), 119.2, 116.2, 114.7, 104.1, 62.0, 11.6. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{17}NNaO_2S$, 346.0872; found,

346.0867.



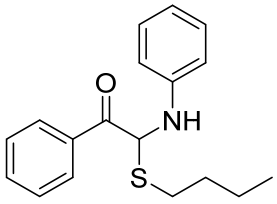
2-(Ethylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3aj)[10]

The indicated compound was obtained in 92% yield (125 mg) as a yellow solid: mp 64.4-66.8℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.01 (m, 2H), 7.59 (ddd, J = 8.6, 4.6, 1.2 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.26 (dt, J = 14.4, 7.2 Hz, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 6.03 (d, J = 8.0 Hz, 1H), 5.34 (d, J = 7.9 Hz, 1H), 2.40–2.27 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 143.5, 134.1, 133.8, 129.4, 128.9, 128.7, 119.0, 114.5, 59.1, 21.2, 14.1.



1-Phenyl-2-(phenylamino)-2-(propylthio)ethan-1-one (3ak)[10]

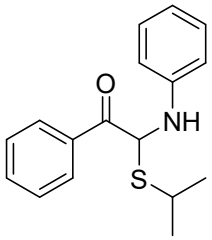
The indicated compound was obtained in 90% yield (128 mg) as a yellow solid: mp 68.8-72.1℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 6.03 (d, J = 8.0 Hz, 1H), 5.34 (d, J = 7.9 Hz, 1H), 2.28 (td, J = 7.4, 1.4 Hz, 2H), 1.43–1.31 (m, 2H), 0.78 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 143.5, 134.1, 133.6, 129.3, 128.8, 128.7, 118.9, 114.5, 59.0, 29.0, 22.5, 13.7.



2-(Butylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3al)[10]

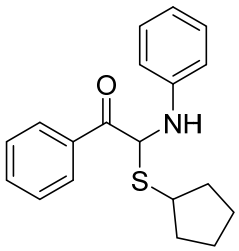
The indicated compound was obtained in 89% yield (133 mg) as a white solid: mp 65-66.9℃; ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 6.88 (d, J = 7.7 Hz, 2H), 6.83 (t,

J = 7.1 Hz, 1H), 6.03 (d, *J* = 7.9 Hz, 1H), 5.33 (d, *J* = 7.7 Hz, 1H), 2.30 (d, *J* = 3.7 Hz, 2H), 1.33 (dt, *J* = 14.5, 7.1 Hz, 2H), 1.20 (dd, *J* = 14.5, 7.2 Hz, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 143.6, 134.2, 133.7, 129.4, 128.8, 128.7, 119.0, 114.5, 59.0, 31.0, 26.7, 22.2, 13.6.



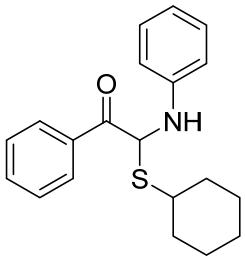
2-(Isopropylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3am)[10]

The indicated compound was obtained in 91% yield (130 mg) as a white solid: mp 94.4-97.8℃; ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.04 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.62–7.57 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.29–7.23 (m, 2H), 6.88 (dd, *J* = 7.7, 1.0 Hz, 2H), 6.85–6.79 (m, 1H), 6.04 (d, *J* = 7.9 Hz, 1H), 5.34 (d, *J* = 7.9 Hz, 1H), 2.89 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.09 (dd, *J* = 6.9, 1.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 143.8, 134.3, 133.7, 129.4, 128.9, 128.8, 118.9, 114.4, 59.9, 33.2, 25.2, 24.5.



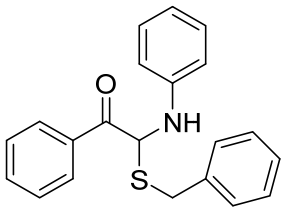
2-(Cyclopentylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3an)

The indicated compound was obtained in 82% yield (128 mg) as a yellow solid: mp 92-93℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.06 (d, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 8.0 Hz, 1H), 2.94 (p, *J* = 7.7 Hz, 1H), 1.87 (dd, *J* = 12.2, 7.0 Hz, 2H), 1.58–1.49 (m, 2H), 1.47–1.37 (m, 2H), 1.31–1.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 143.8, 134.3, 133.6, 129.3, 128.8, 128.8, 118.7, 114.4, 60.0, 40.7, 35.1, 34.0, 24.9, 24.7. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{21}NNaOS$: 334.1236; found: 334.1228.



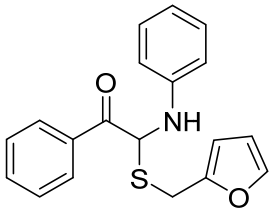
2-(Cyclohexylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3ao)[10]

The indicated compound was obtained in 87% yield (141 mg) as a yellow solid: mp 140.2-144.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.25 (dd, J = 8.4, 7.5 Hz, 2H), 6.88 (d, J = 7.6 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 6.02 (d, J = 7.9 Hz, 1H), 5.35 (d, J = 7.9 Hz, 1H), 2.76–2.55 (m, 1H), 1.7–1.42 (m, 5H), 1.27–1.06 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 143.8, 134.3, 133.6, 129.3, 128.8, 128.7, 118.8, 114.5, 59.7, 41.0, 35.2, 34.6, 26.3, 25.5.



2-(Benzylthio)-1-phenyl-2-(phenylamino)ethan-1-one (3ap)[11]

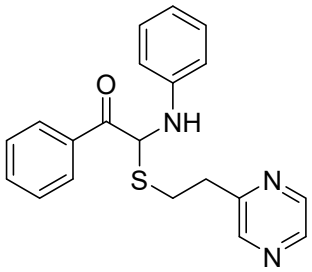
The indicated compound was obtained in 89% yield (148 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.30–7.21 (m, 2H), 7.10 (m, 5H), 6.83 (t, J = 8.5 Hz, 3H), 6.07 (d, J = 7.9 Hz, 1H), 5.29 (d, J = 7.0 Hz, 1H), 3.58-3.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 143.4, 136.9, 134.1, 133.8, 129.4, 129.2, 128.9, 128.8, 128.5, 127.1, 119.2, 114.7, 59.9, 32.1.



2-((Furan-2-ylmethyl)thio)-1-phenyl-2-(phenylamino)ethan-1-one (3aq)

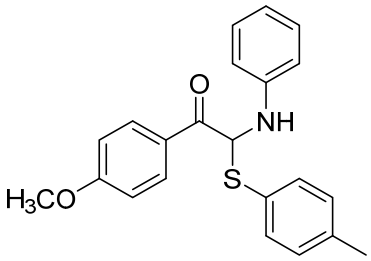
The indicated compound was obtained in 76% yield (123 mg) as a yellow solid: mp 124-125°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 2H), 7.63–7.57 (m,1H),

7.49 (t, *J* = 7.7 Hz, 2H), 7.28–7.19 (m, 3H), 6.88–6.78 (m, 3H), 6.20 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.12 (d, *J* = 8.3 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 5.32 (d, *J* = 8.2 Hz, 1H), 3.66–3.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 190.1, 150.7, 143.4, 142.1, 134.1, 133.8, 129.4, 128.9, 128.8, 119.3, 114.6, 110.6, 108.0, 59.7, 24.6. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{17}NNaO_2S$, 346.0872; found, 346.0864.



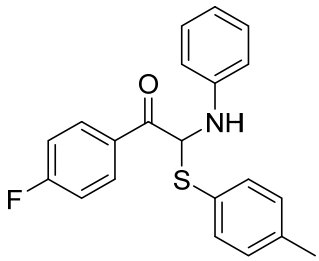
1-Phenyl-2-(phenylamino)-2-((2-(pyrazin-2-yl)ethyl)thio)ethan-1-one (3ar)

The indicated compound was obtained in 70% yield (122 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.30 (d, *J* = 22.6 Hz, 2H), 8.10 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 2H), 6.84 (dd, *J* = 12.8, 7.6 Hz, 3H), 6.04 (d, *J* = 7.8 Hz, 1H), 5.42 (d, *J* = 7.6 Hz, 1H), 2.85–2.79 (m, 2H), 2.79–2.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 189.8, 155.3, 144.8, 144.1, 143.2, 142.5, 133.9, 133.8, 129.5, 128.9, 128.8, 119.2, 114.5, 59.1, 34.9, 26.2. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{19}N_3NaOS$, 372.1141; found, 372.1129.



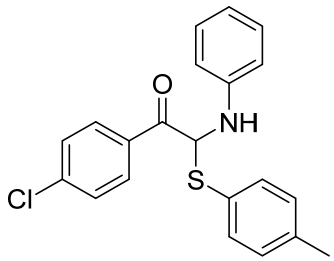
1-(4-Methoxyphenyl)-2-(phenylamino)-2-(*p*-tolylthio)ethan-1-one (3ba)

The indicated compound was obtained in 94% yield (171 mg) as a white solid: mp 112-115°C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 8.9 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.01 (dd, *J* = 10.9, 8.5 Hz, 4H), 6.97–6.73 (m, 5H), 6.21 (d, *J* = 9.4 Hz, 1H), 5.13 (d, *J* = 9.4 Hz, 1H), 3.91 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 187.4, 163.9, 143.1, 139.8, 137.4, 131.0, 129.7, 129.4, 127.0, 125.1, 119.1, 115.0, 114.1, 62.6, 55.7, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{21}NNaO_2S$: 386.1185; found: 386.1184.



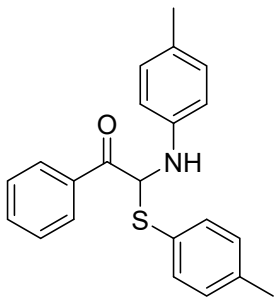
1-(4-Fluorophenyl)-2-(phenylamino)-2-(*p*-tolylthio)ethan-1-one (3ca)

The indicated compound was obtained in 86% yield (151 mg) as a white solid: mp 125-127℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.7, 5.4 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 8.5 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 7.8 Hz, 5H), 6.22 (d, J = 9.5 Hz, 1H), 5.08 (d, J = 9.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 167.3, 164.7, 142.9, 140.0, 137.3, 131.4 (d, J = 9.4 Hz), 130.7 (d, J = 3.2 Hz), 129.8, 129.5, 124.8, 119.3, 116.2, 116.0, 115.0, 62.9, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{18}FNNaOS$: 374.0985; found: 374.0989.



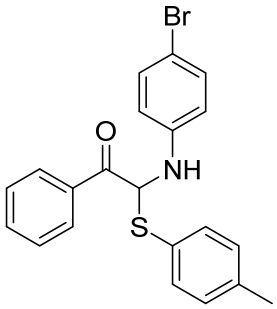
1-(4-Chlorophenyl)-2-(phenylamino)-2-(*p*-tolylthio)ethan-1-one (3da)

The indicated compound was obtained in 90% yield (165 mg) as a yellow solid: mp 108-111℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.6 Hz, 5H), 6.21 (d, J = 9.4 Hz, 1H), 5.07 (d, J = 9.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 142.9, 140.0 (d, J = 5.6 Hz), 137.3, 132.8, 130.1, 129.8, 129.5, 129.2, 124.7, 119.4, 115.0, 63.0, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{18}ClNNaOS$: 390.0690; found: 390.0688.



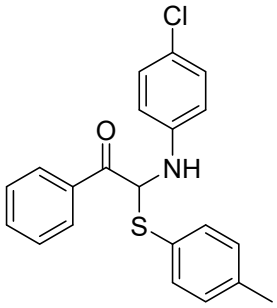
1-Phenyl-2-(*p*-tolylamino)-2-(*p*-tolylthio)ethan-1-one (3ea)

The indicated compound was obtained in 82% yield (142 mg) as a white solid: mp 116-119°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.26 (d, J = 9.7 Hz, 1H), 4.99 (d, J = 9.7 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 140.6, 139.8, 137.4, 134.6, 133.5, 130.0, 129.7, 128.9, 128.7, 128.5, 125.0, 115.1, 63.40, 21.5, 20.7. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. For $C_{22}H_{21}NNaOS$, 370.1236; found, 370.1236.



2-((4-Bromophenyl)amino)-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3fa)

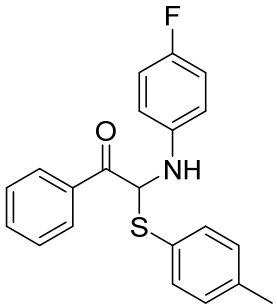
The indicated compound was obtained in 93% yield (191 mg) as a yellow solid: mp 141-143°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.1 Hz, 2H), 7.64 (ddd, J = 8.6, 4.7, 1.3 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 6.17 (d, J = 9.4 Hz, 1H), 5.12 (d, J = 9.3 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 141.7, 140.1, 137.5, 134.3, 133.8, 129.8, 129.5, 129.1 (d, J = 56.9 Hz), 124.6, 124.0, 116.2, 116.1, 62.7, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{18}BrNNaOS$: 434.0185; found: 434.0179.



2-((4-Chlorophenyl)amino)-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3ga)

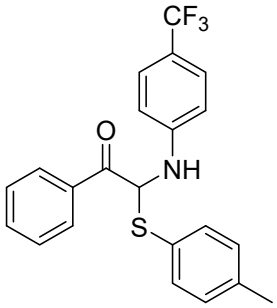
The indicated compound was obtained in 91% yield (167 mg) as a yellow solid: mp 139-142°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.4

Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.17 (d, *J* = 9.4 Hz, 1H), 5.12 (d, *J* = 9.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 141.7, 140.0, 137.3, 134.2, 133.6, 129.7, 129.3, 128.8 (d, *J* = 18.6 Hz), 124.6, 123.9, 116.1, 62.7, 21.4. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{18}ClNNaOS$: 390.0690; found: 390.0688.



2-((4-Fluorophenyl)amino)-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3ha)

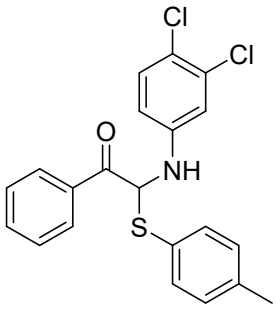
The indicated compound was obtained in 84% yield (147 mg) as a yellow solid: mp 134-136°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.08–6.98 (m, 4H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.85–6.78 (m, 2H), 6.19 (d, *J* = 9.3 Hz, 1H), 5.02 (d, *J* = 9.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 157.9, 155.6, 139.9, 139.3 (d, *J* = 2.0 Hz), 137.3, 134.3, 133.6, 129.7, 128.8, 128.6, 124.7, 116.1, 115.9, 115.8, 115.7, 63.3, 21.4. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{18}FNNaOS$: 374.0985; found: 374.0984.



1-Phenyl-2-(*p*-tolylthio)-2-((4-(trifluoromethyl)phenyl)amino)ethan-1-one (3ia)

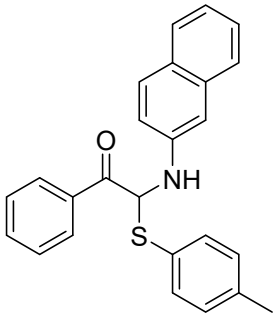
The indicated compound was obtained in 89% yield (178 mg) as a white solid: mp 146-148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.67–7.61 (m, 1H), 7.58–7.51 (m, 4H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.91 (dd, *J* = 13.6, 8.3 Hz, 4H), 6.21 (d, *J* = 8.9 Hz, 1H), 5.41 (d, *J* = 8.9 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 145.9, 140.3, 137.3, 134.1, 133.9, 129.9, 129.7, 129.0, 128.8, 126.8 (d, *J* = 14.0 Hz), 126.3, 124.3, 123.6, 121.0, 120.7, 120.3, 114.4, 113.6, 61.9, 21.5.

HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{18}F_3NNaOS$: 424.0953; found: 424.0956.



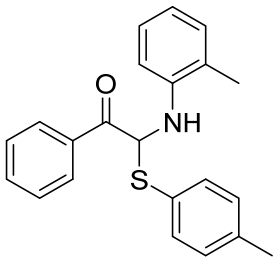
2-((3,4-Dichlorophenyl)amino)-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3ja)

The indicated compound was obtained in 90% yield (180 mg) as a yellow solid: mp 162-164℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.3, 1.2 Hz, 2H), 7.67–7.61 (m, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 2.7 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 6.70 (dd, J = 8.7, 2.7 Hz, 1H), 6.11 (d, J = 9.1 Hz, 1H), 5.19 (d, J = 9.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 142.8, 140.3, 137.3, 134.0, 133.9, 133.1, 130.9, 129.9, 129.0, 128.8, 124.3, 121.9, 116.1, 114.7, 62.3, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{17}Cl_2NNaOS$: 424.0300; found: 424.0304.



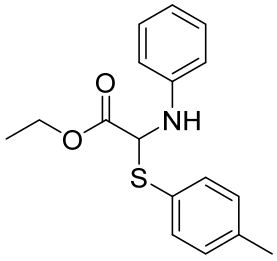
2-(Naphthalen-2-ylamino)-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3ka)

The indicated compound was obtained in 85% yield (163 mg) as a yellow solid: mp 132-134℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.4 Hz, 2H), 7.86–7.69 (m, 3H), 7.63 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.34–7.24 (m, 2H), 7.01 (d, J = 7.4 Hz, 3H), 6.90 (d, J = 7.9 Hz, 2H), 6.36 (d, J = 9.3 Hz, 1H), 5.26 (d, J = 7.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 140.7, 140.0, 137.5, 135.0, 134.5, 133.7, 129.8, 129.4, 129.0, 128.8, 128.4, 127.9, 126.7, 126.6, 124.9, 123.0, 118.6, 108.3, 62.9, 21.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{21}NNaOS$: 406.1236; found: 406.1236.



1-Phenyl-2-(*o*-tolylamino)-2-(*p*-tolylthio)ethan-1-one (3la)

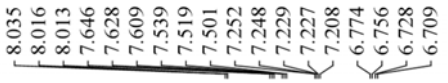
The indicated compound was obtained in 71% yield (123 mg) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 6.87–6.77 (m, 3H), 6.30 (d, J = 9.4 Hz, 1H), 5.00 (d, J = 9.4 Hz, 1H), 2.30 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 140.9, 139.9, 137.4, 134.5, 133.6, 130.5, 129.7, 129.0, 128.8 (d, J = 98.0 Hz), 127.2, 124.9, 123.5, 118.8, 112.8, 62.5, 21.4, 17.3. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{21}NNaOS$: 370.1236; found: 370.1240.

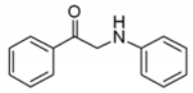


Ethyl 2-(phenylamino)-2-(*p*-tolylthio)acetate (3ma)

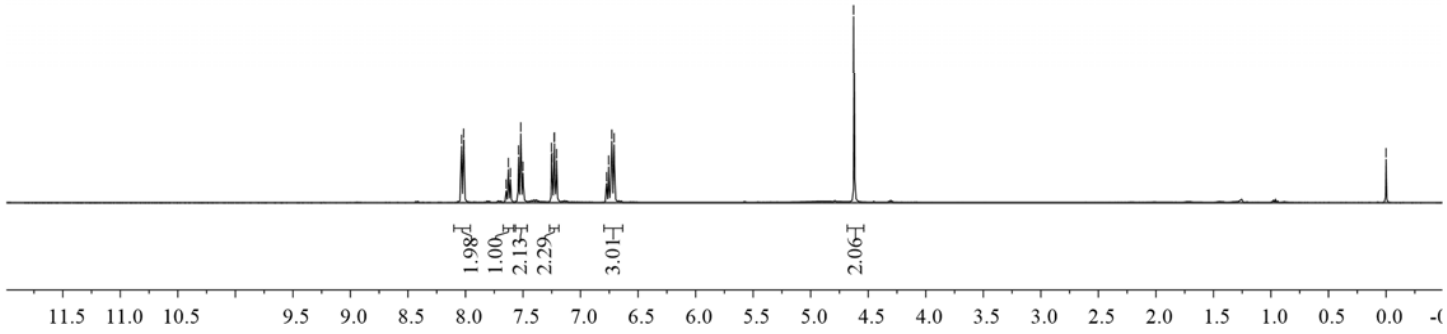
The indicated compound was obtained in 56% yield (84 mg) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 6.73 (dd, J = 8.5, 0.8 Hz, 2H), 5.27 (d, J = 10.2 Hz, 1H), 4.66 (d, J = 10.2 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.0, 139.6, 136.7, 129.7, 129.4, 126.2, 119.4, 114.9, 62.0, 21.4, 14.2. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{19}NNaO_2S$, 324.1029; found, 324.1024.

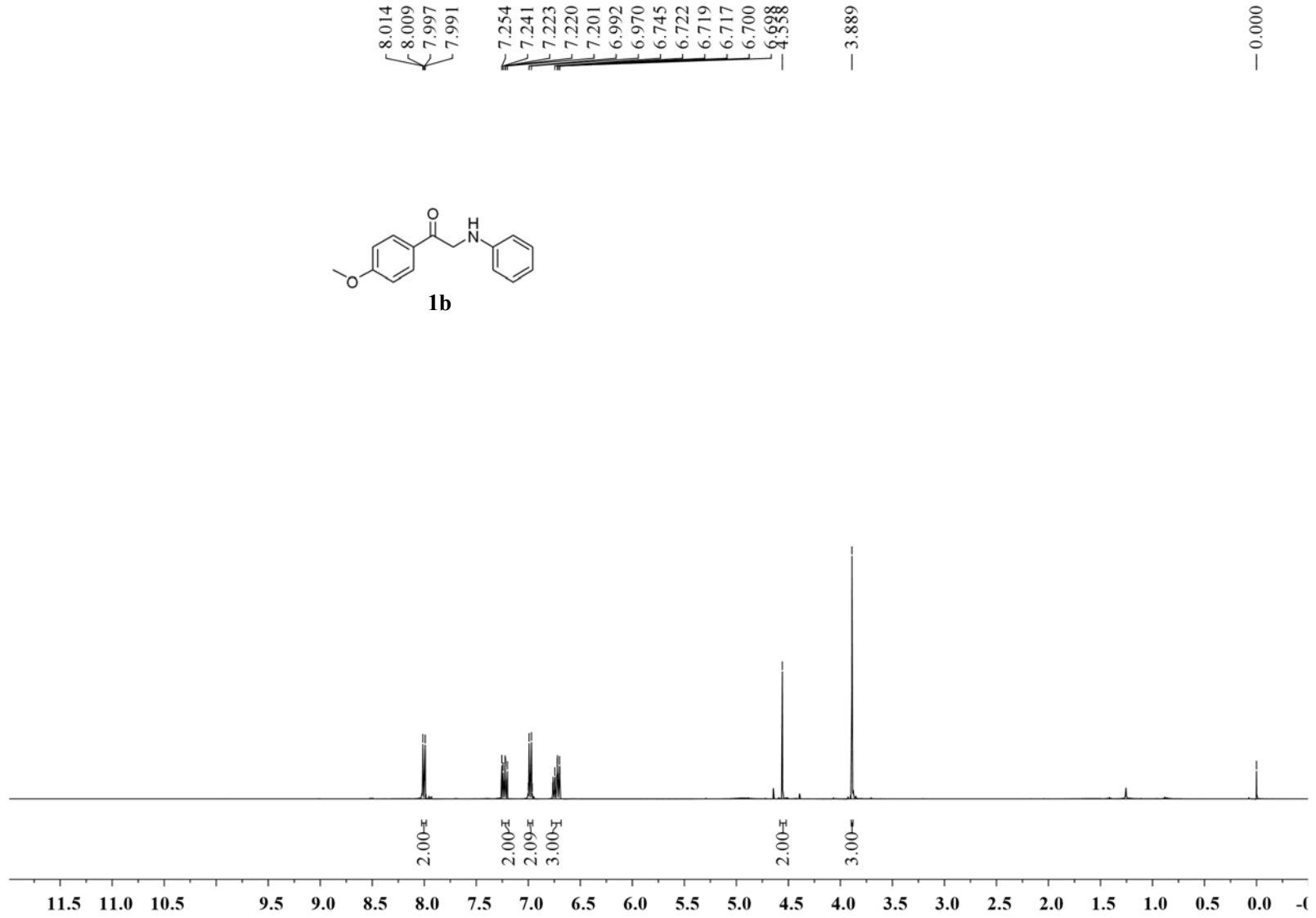
3. Copies of ^{1}H NMR , ^{13}C NMR and HRMS Spectra





1a

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7.220
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6.745
6.722
6.719
6.717
6.700
4.558
3.889
0.000
2.00
2.00
2.09
3.00
2.00
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

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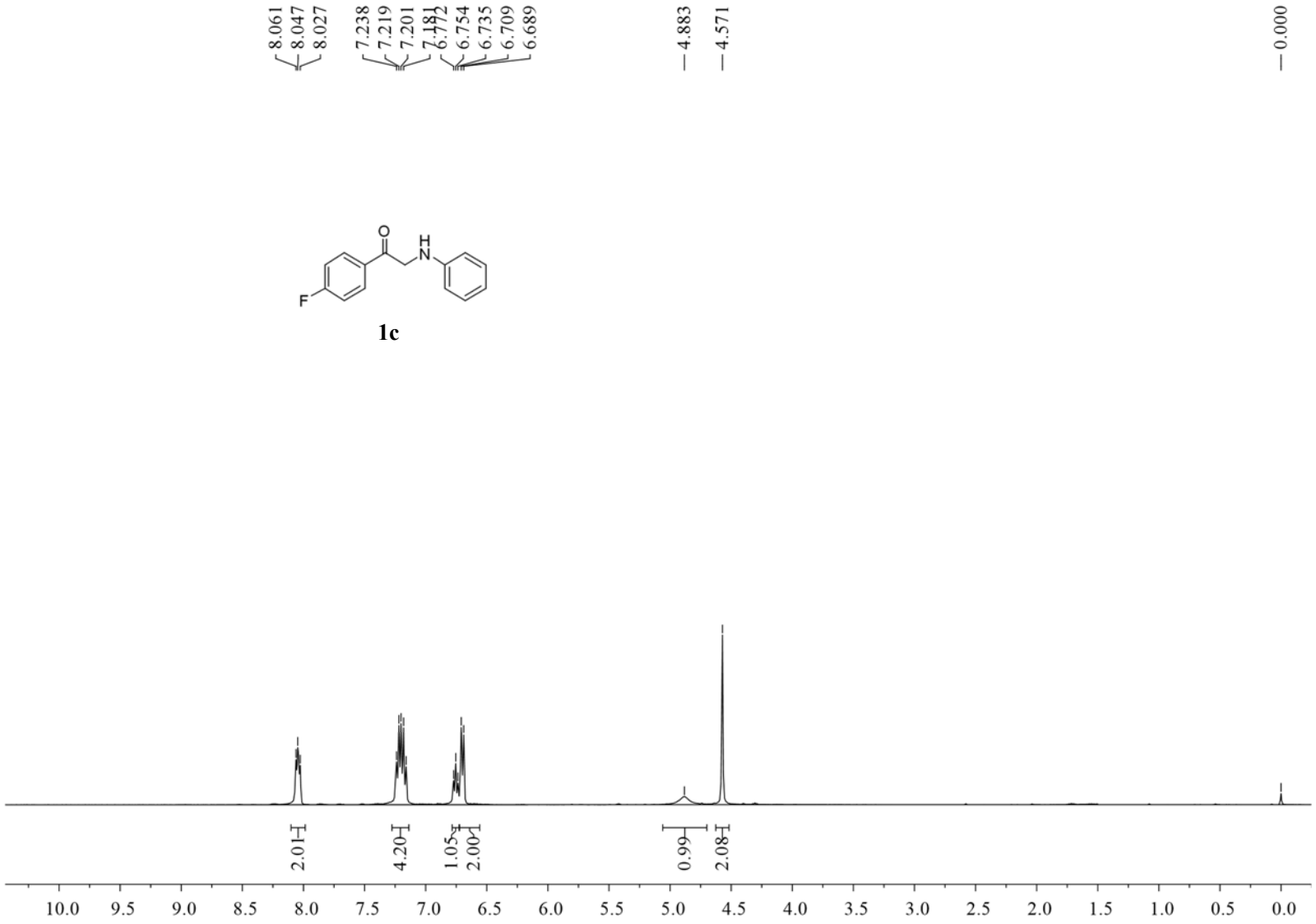
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O
H
N
F
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4.20
1.05
2.00
0.99
2.08
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9.0
8.5
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6.0
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0.5
0.0

1c


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7.506
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7.490
7.259
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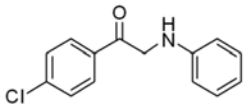
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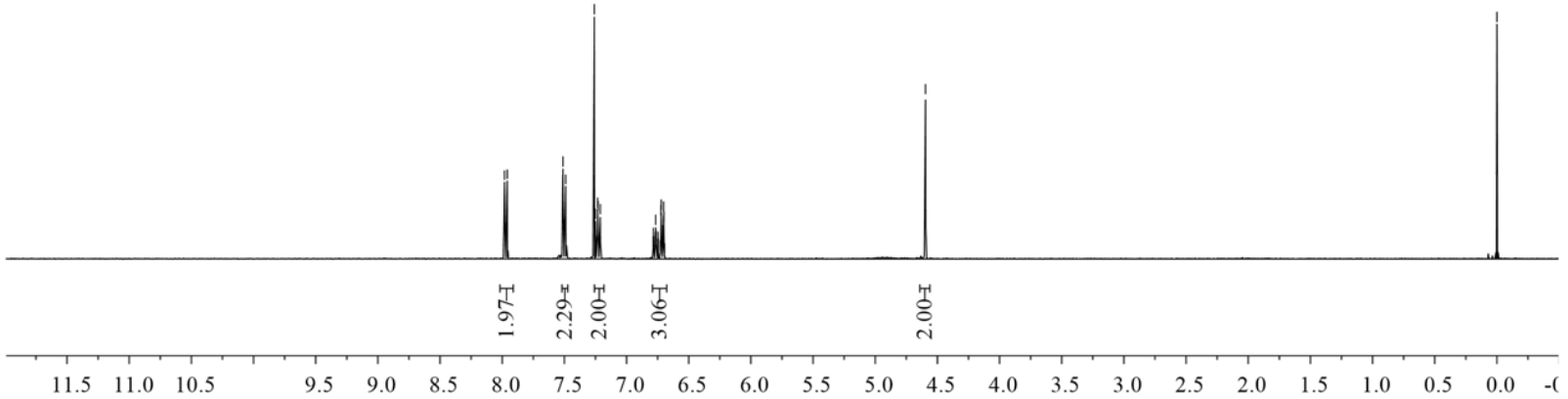
Cl

1d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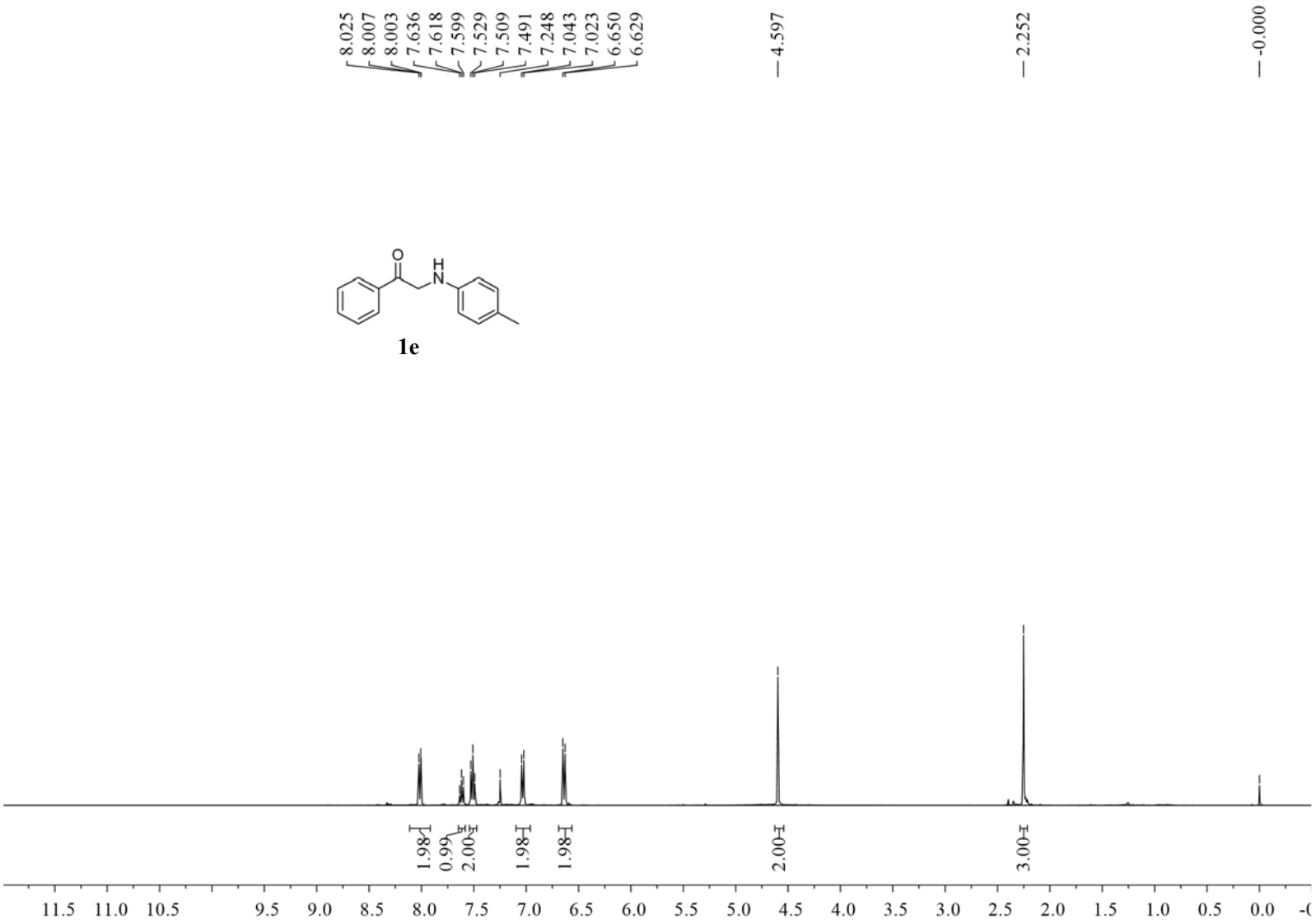
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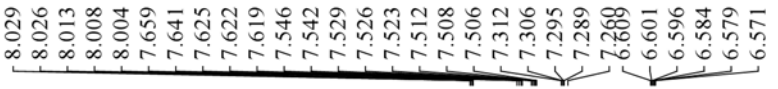
0.99
2.00
1.98
1.98
2.00
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1e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7.523
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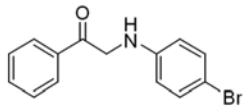
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Br

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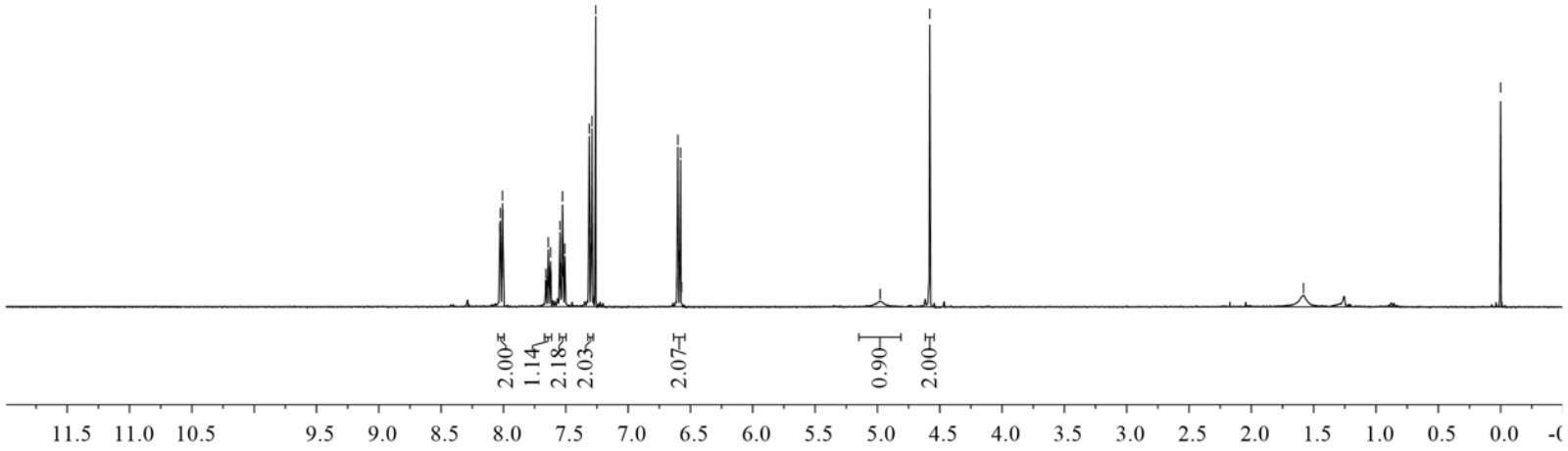
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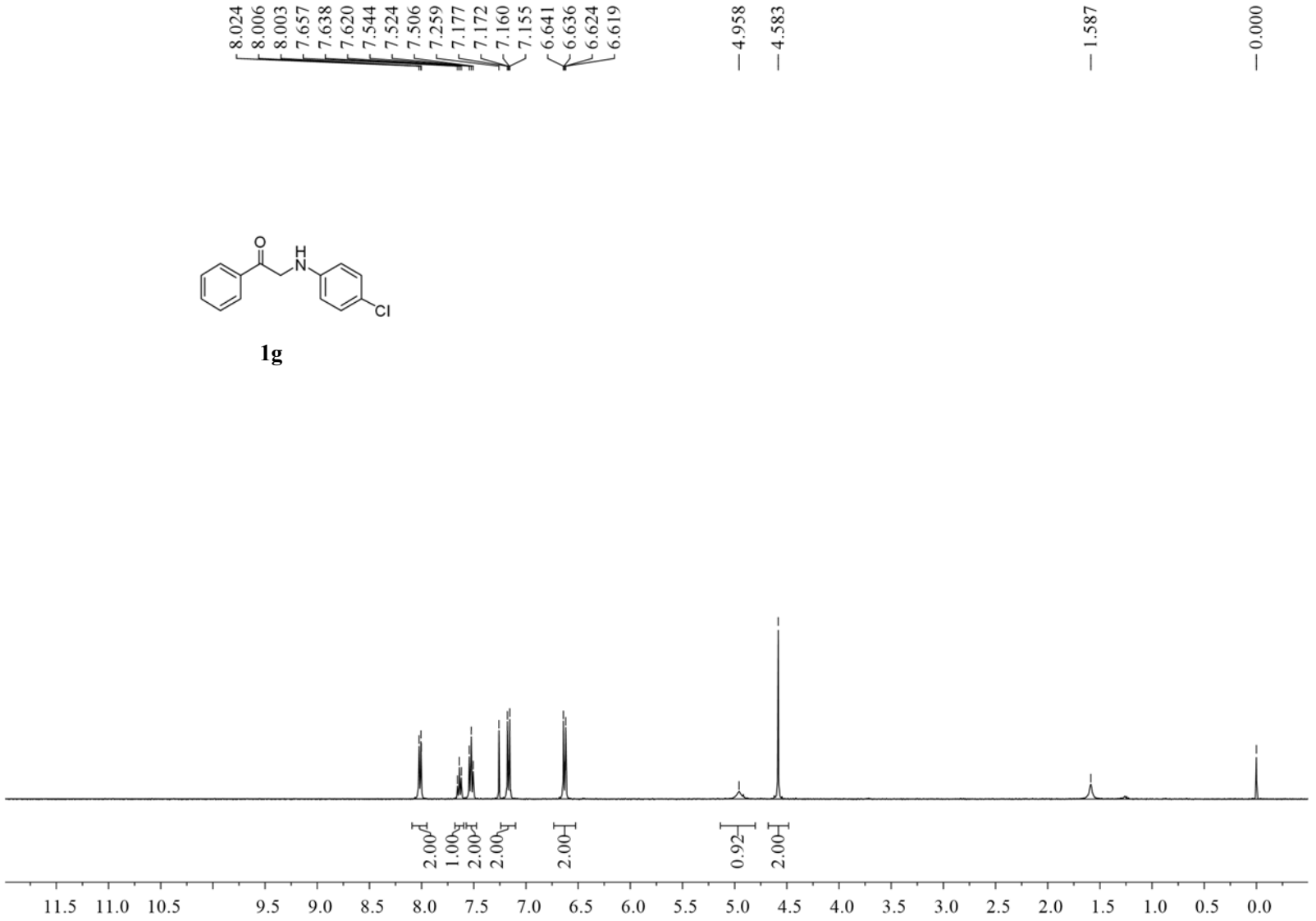
2.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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6.619
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N
Cl
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2.00
0.92
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6.0
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0.0

1g


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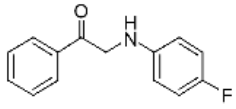
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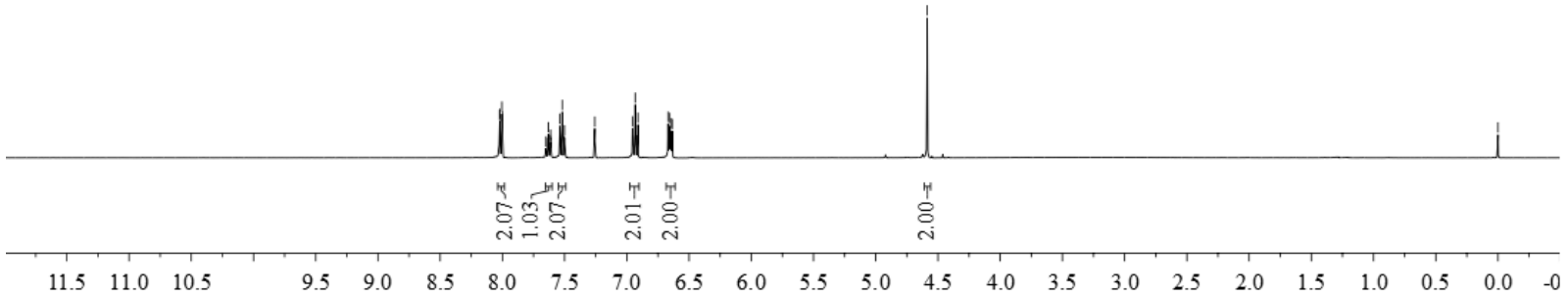
N
F

1h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8.044
8.042
8.029
8.024
8.020
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7.671
7.660
7.655
7.651
7.640
7.637
7.634
7.560
7.556
7.540
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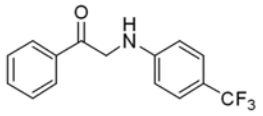
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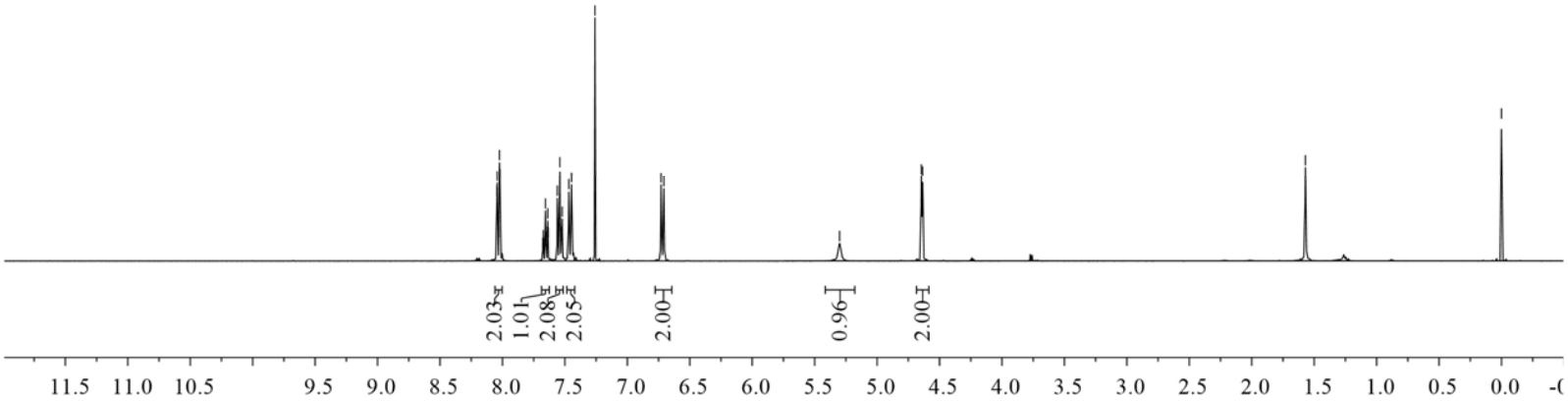
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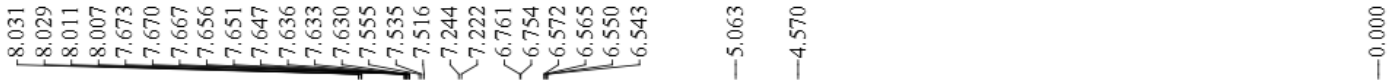
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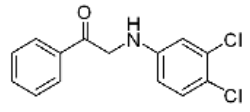
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Cl

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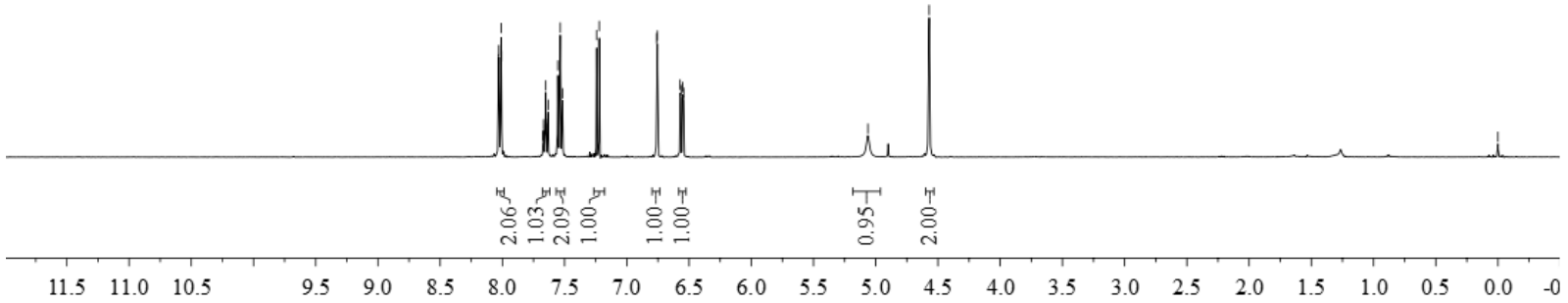
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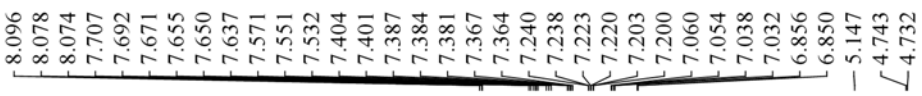
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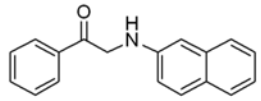

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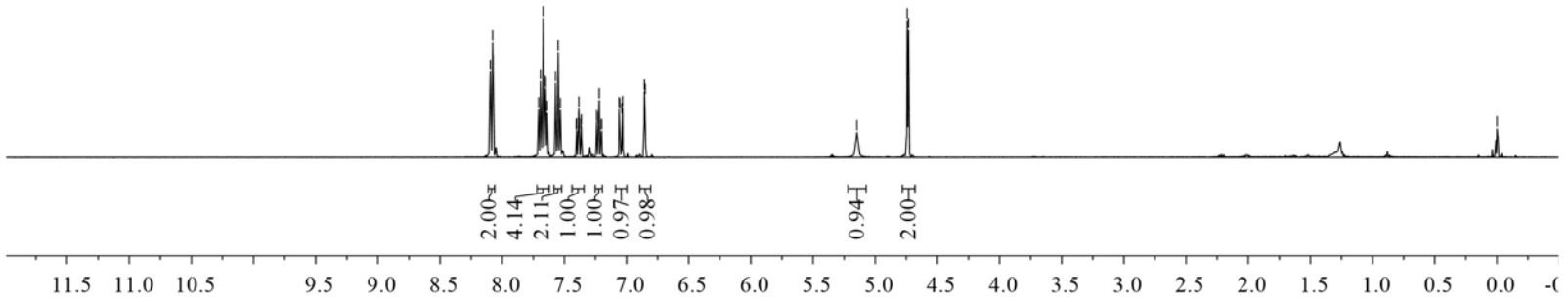
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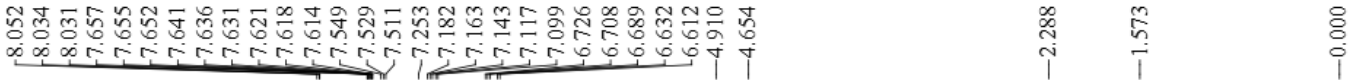
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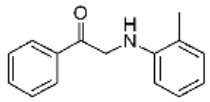

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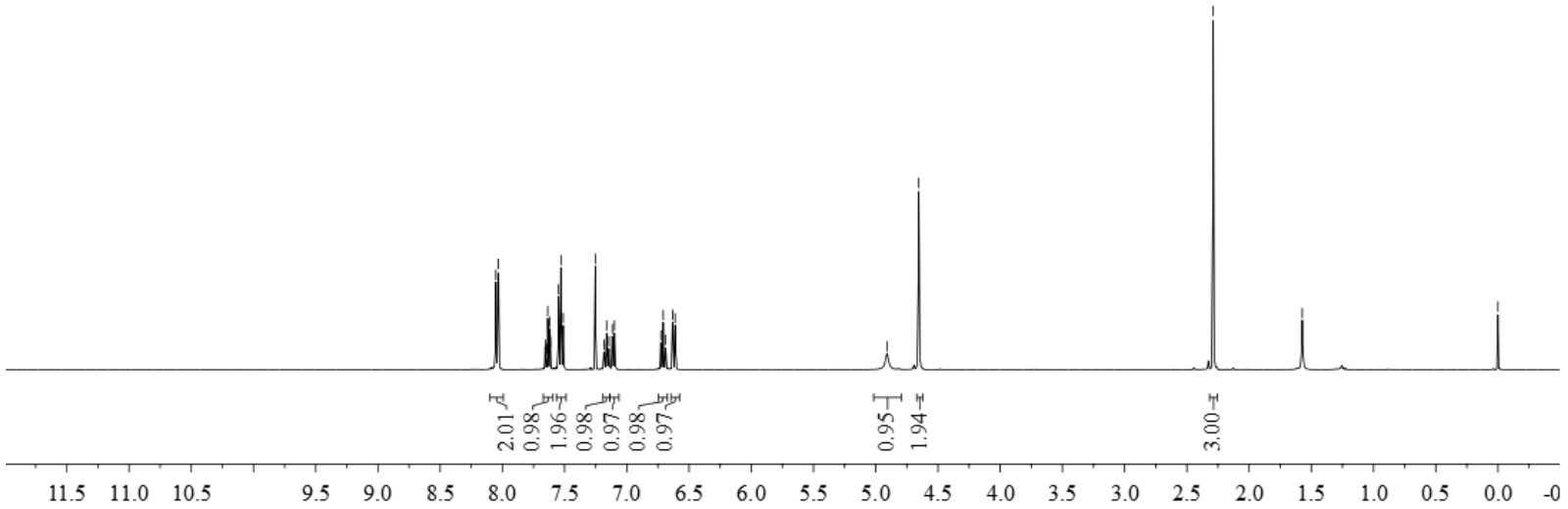
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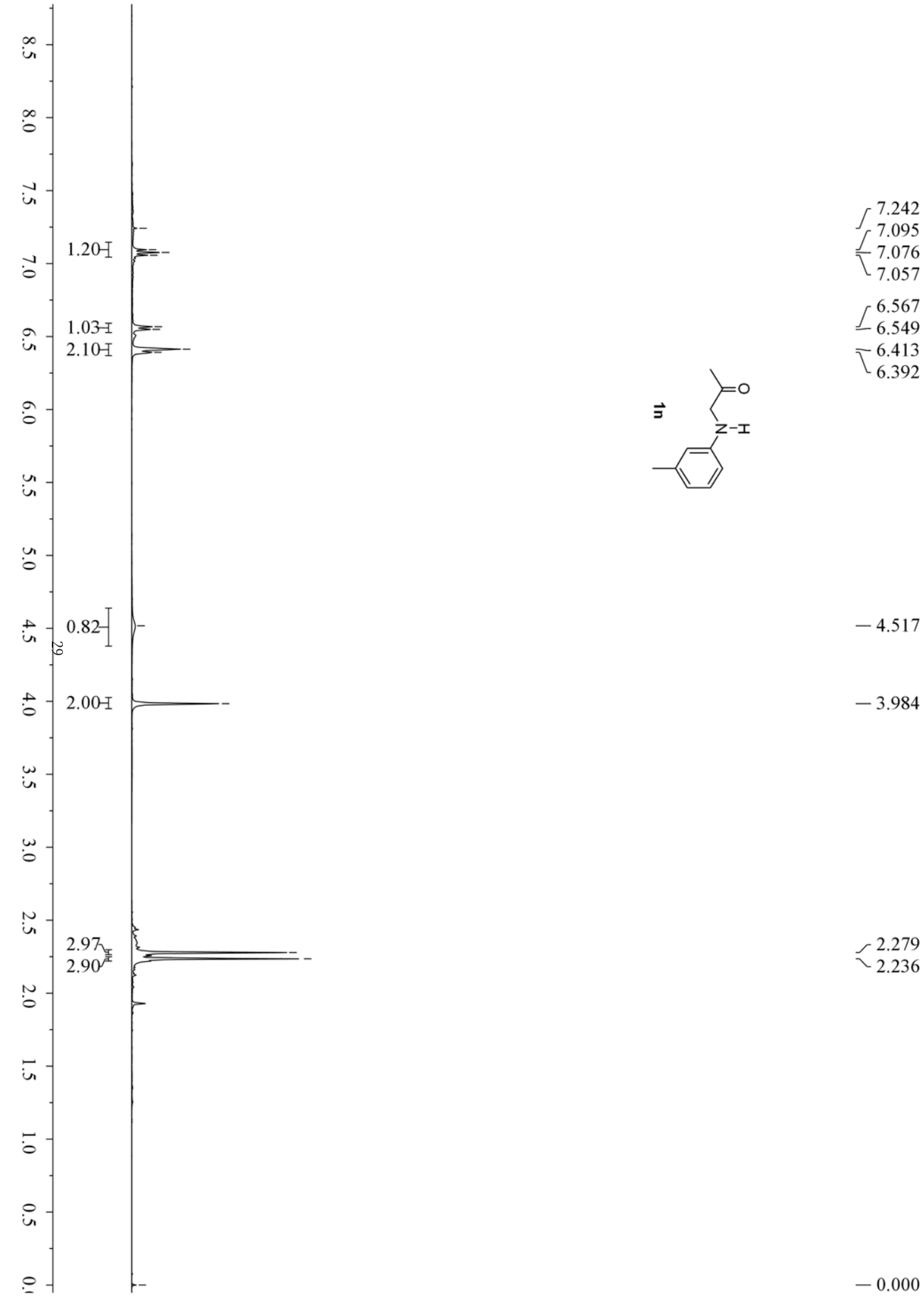
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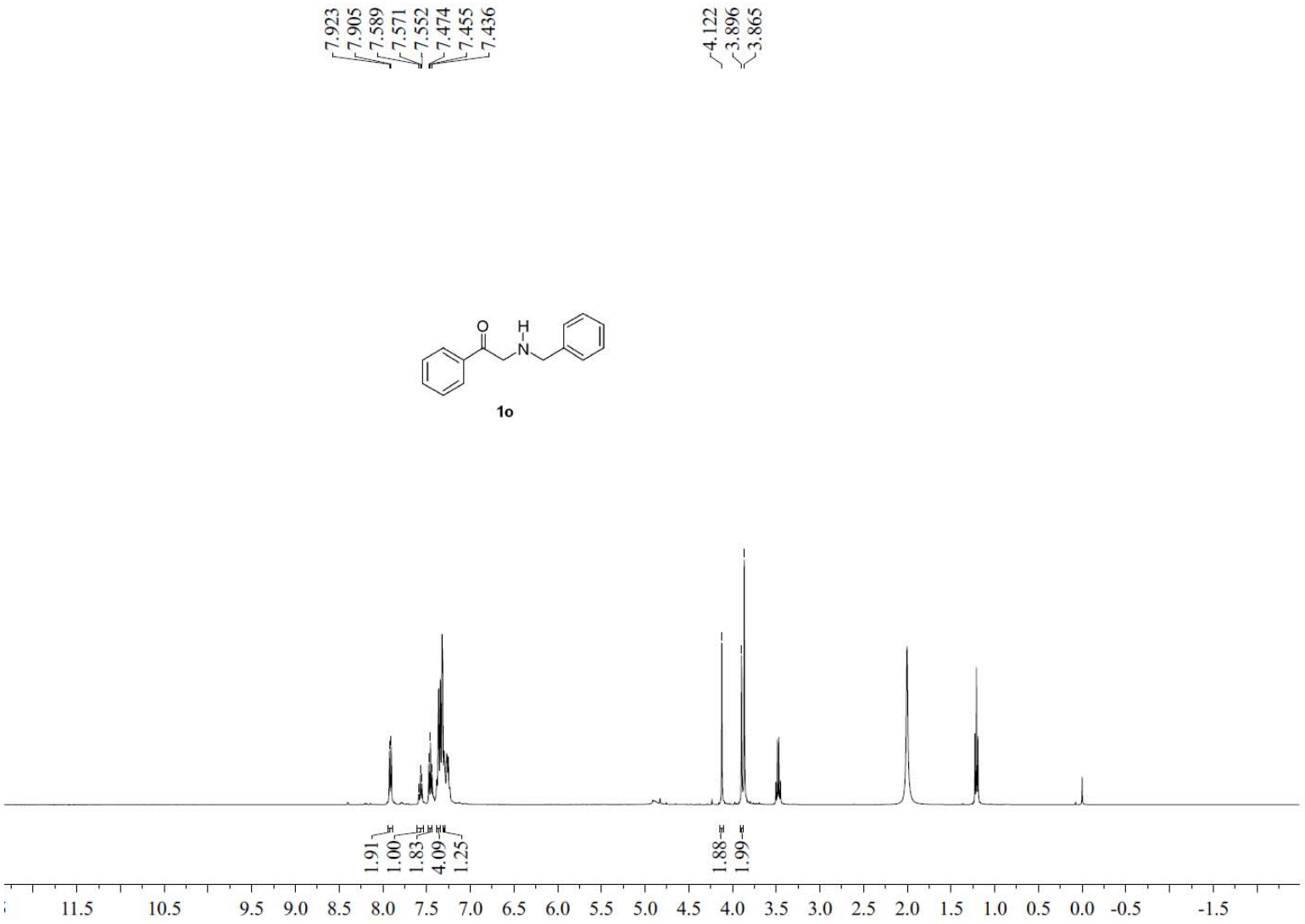
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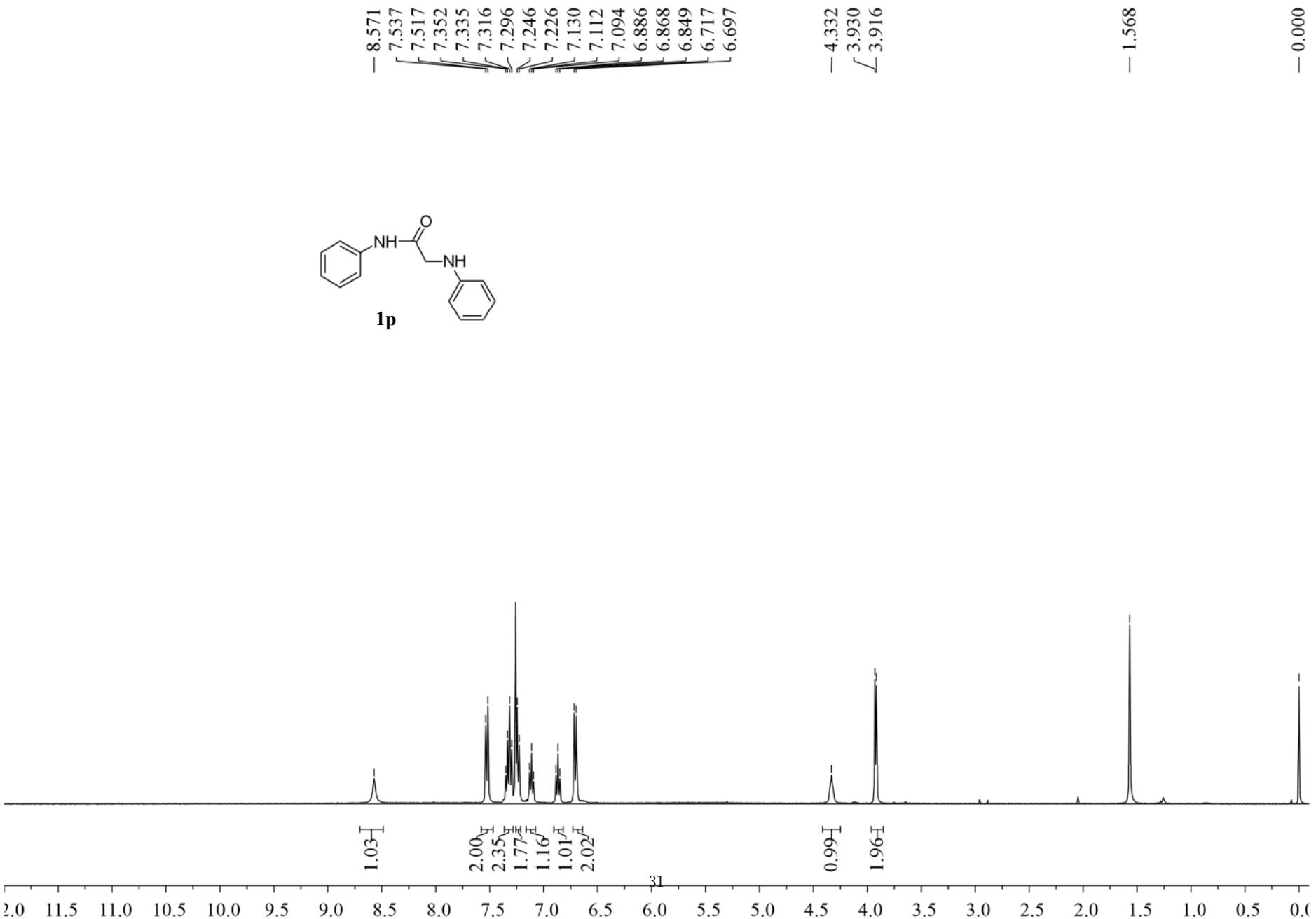
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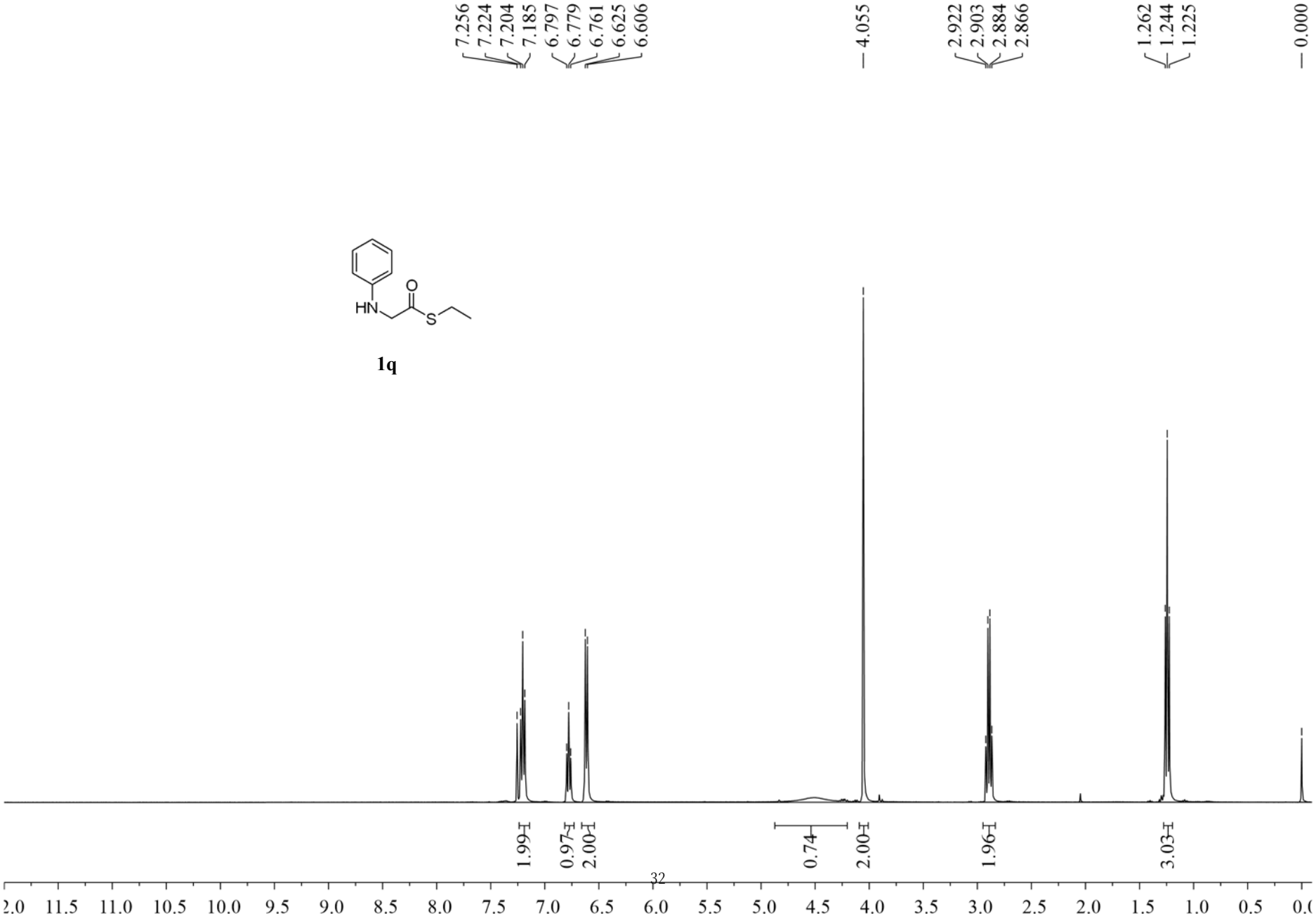
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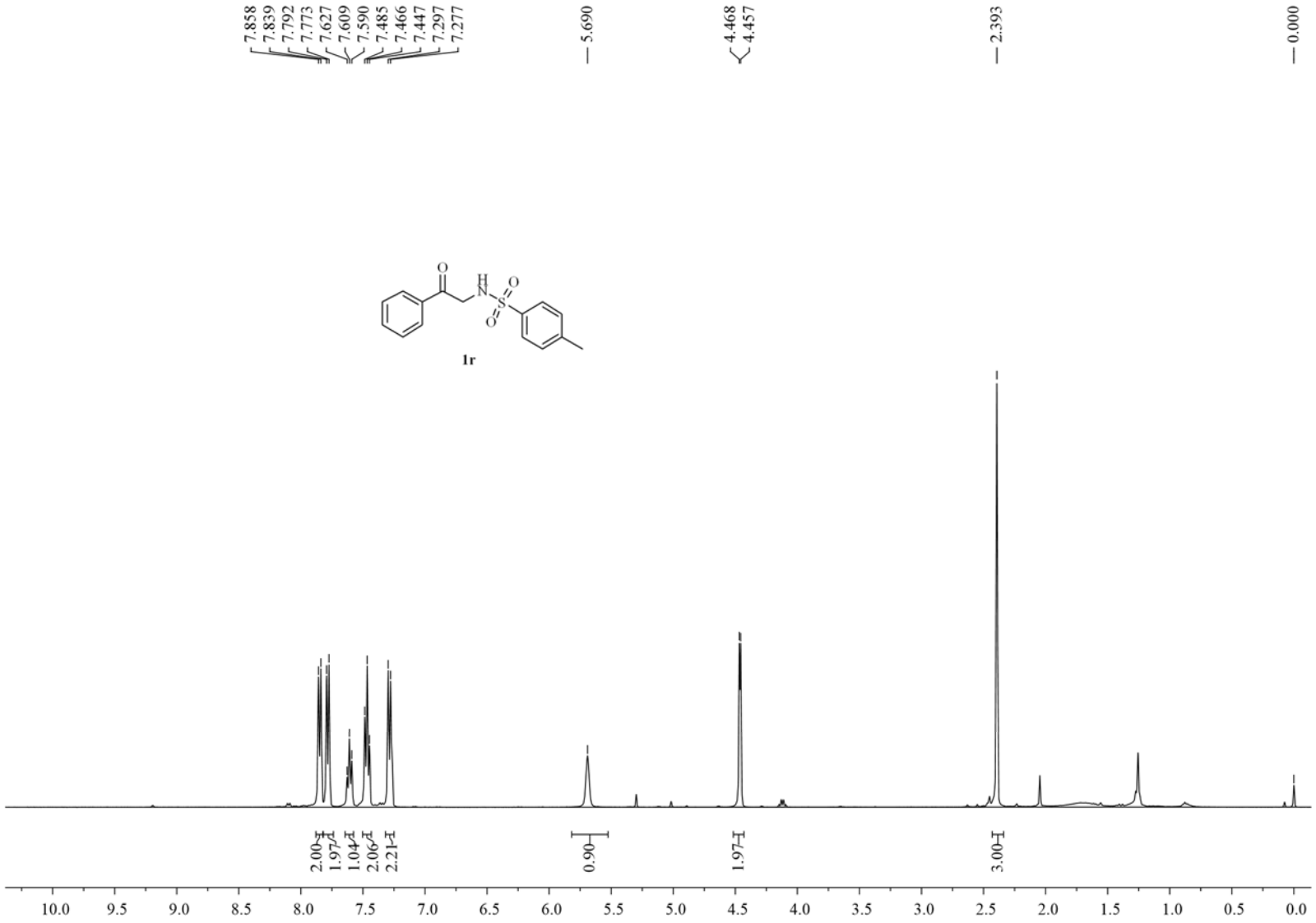
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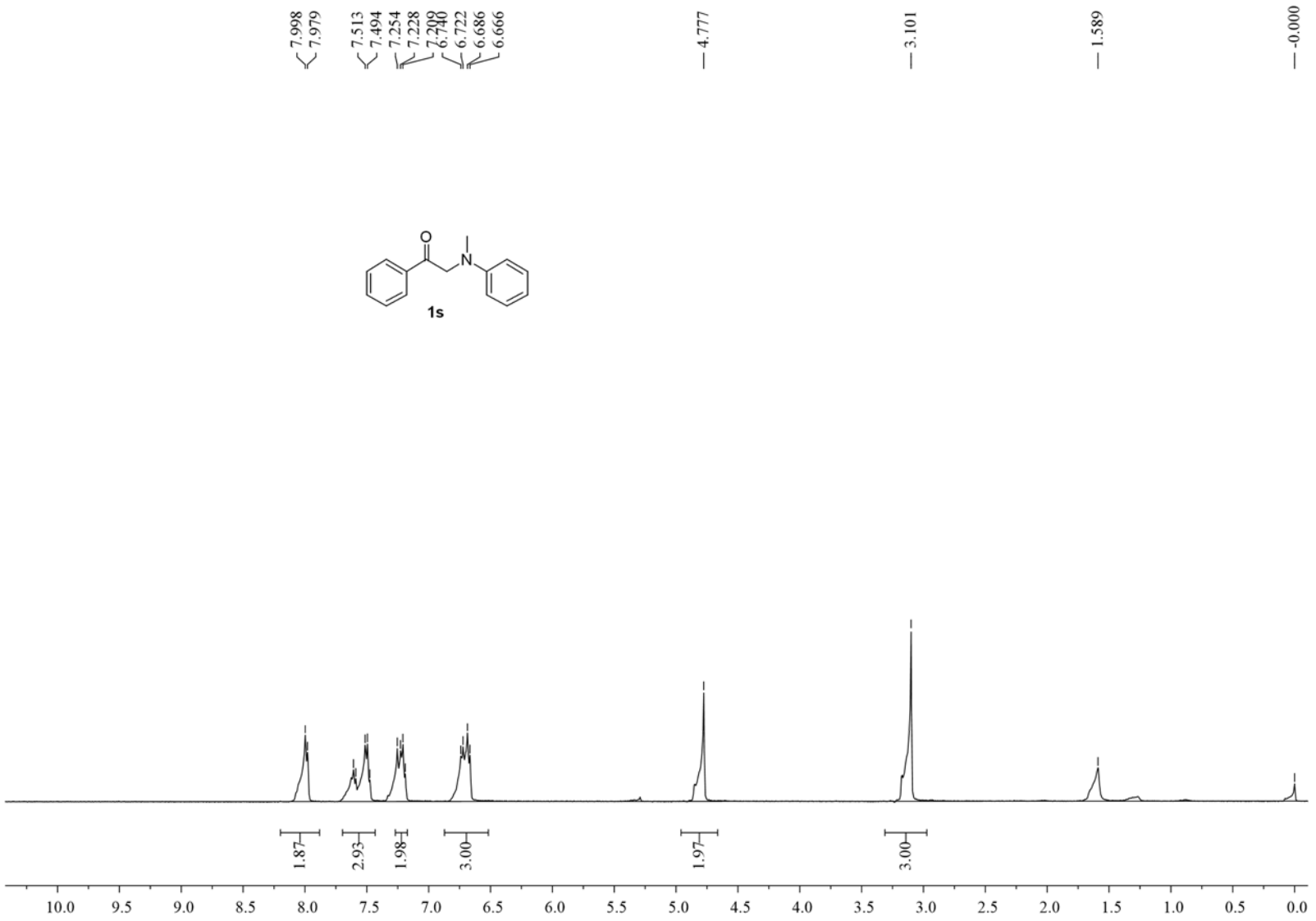
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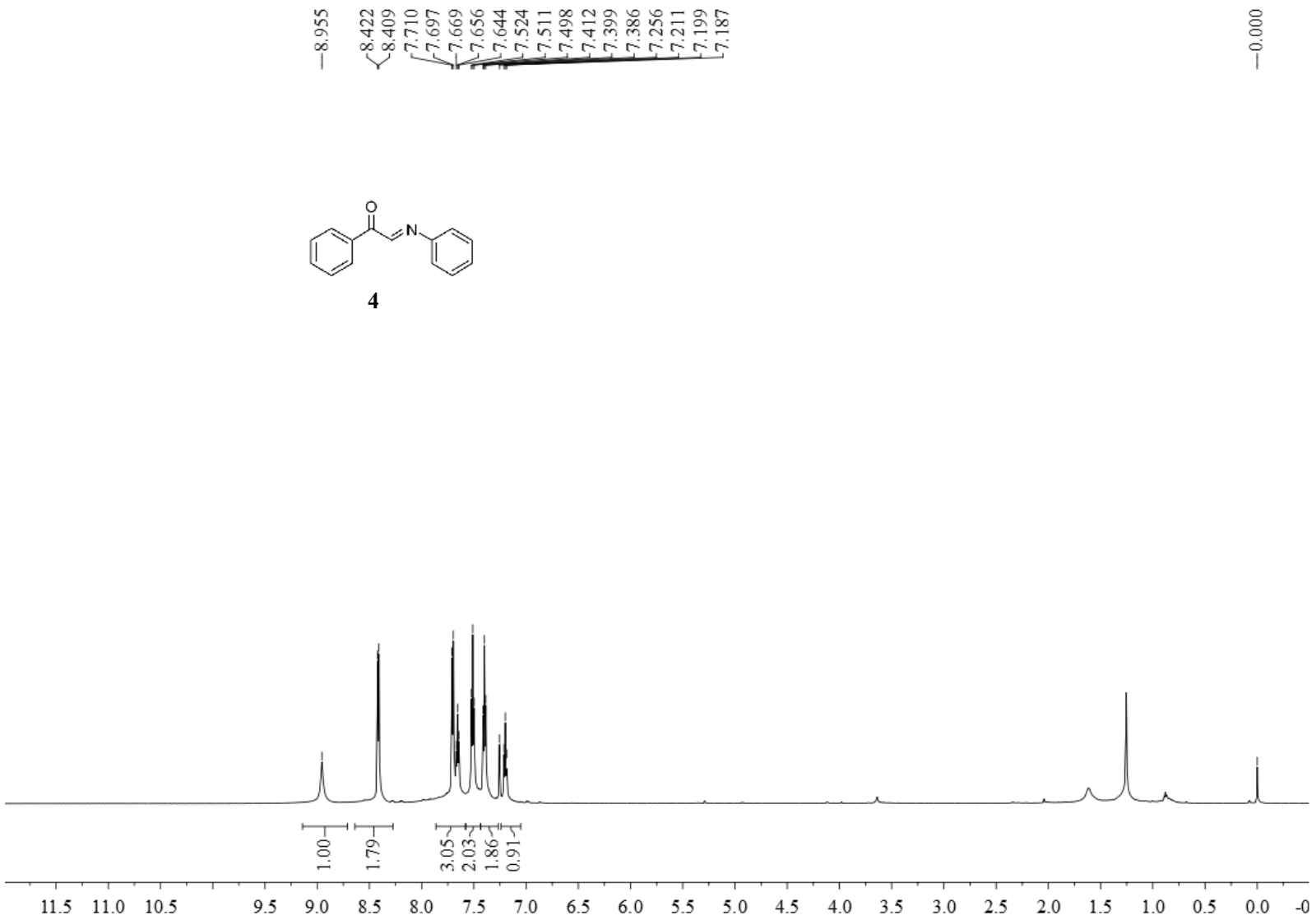
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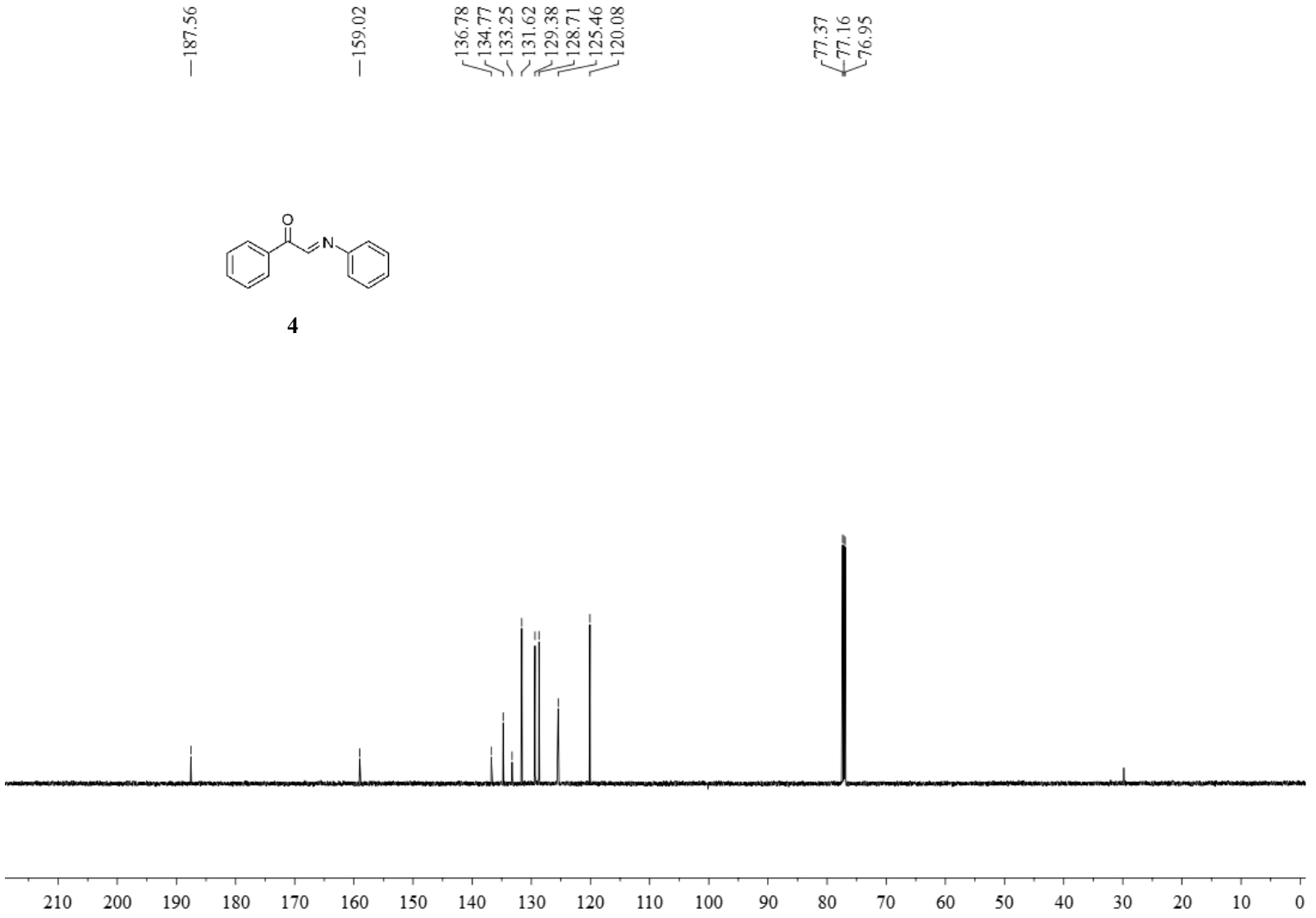
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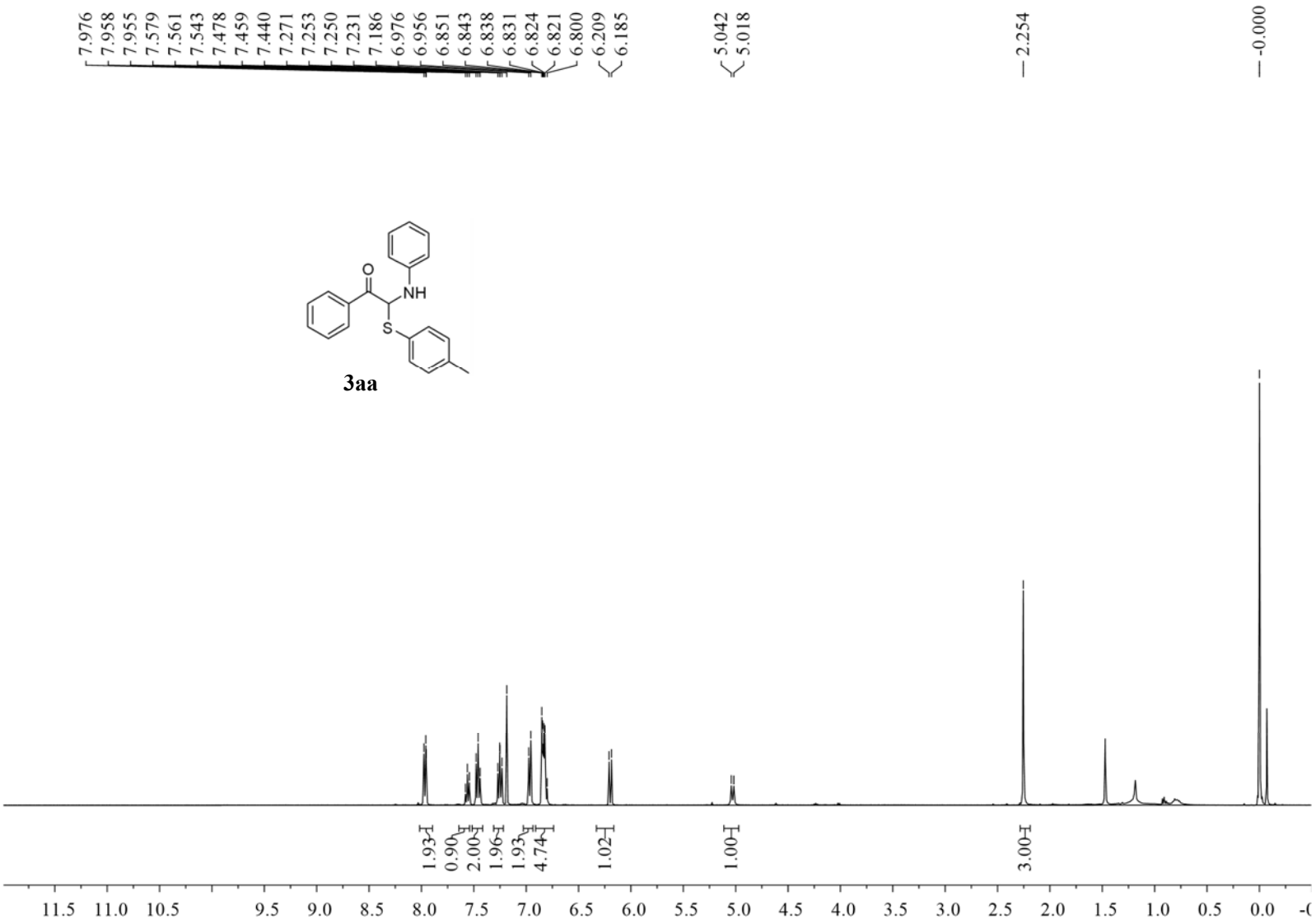
4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6.821
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NH
S
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3.00
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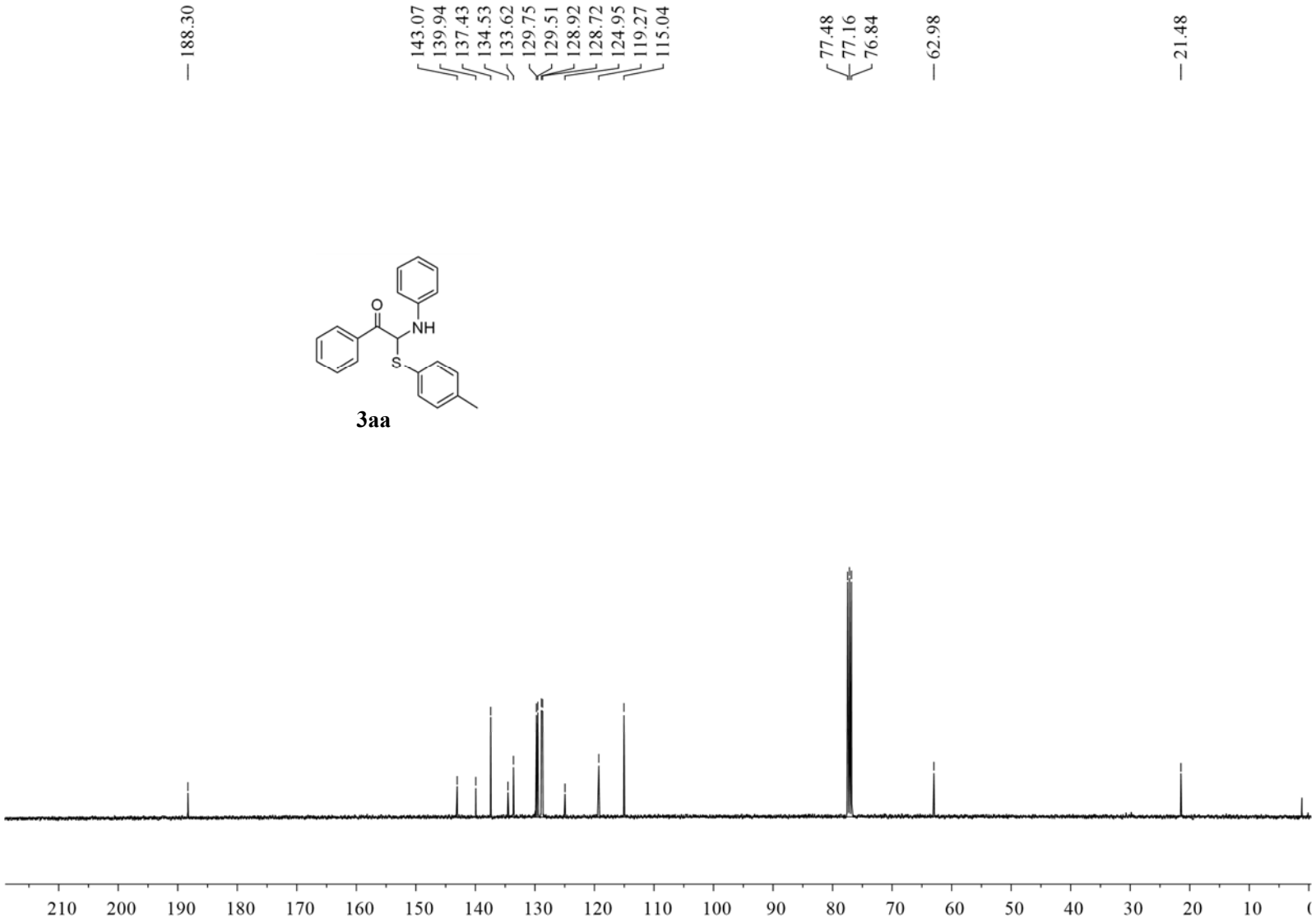
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77.16
76.84
62.98
21.48
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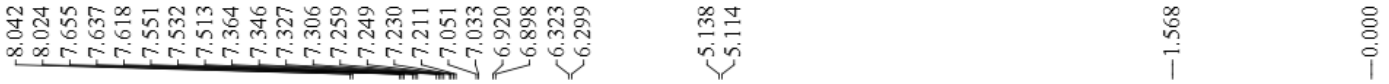
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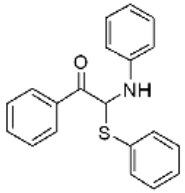
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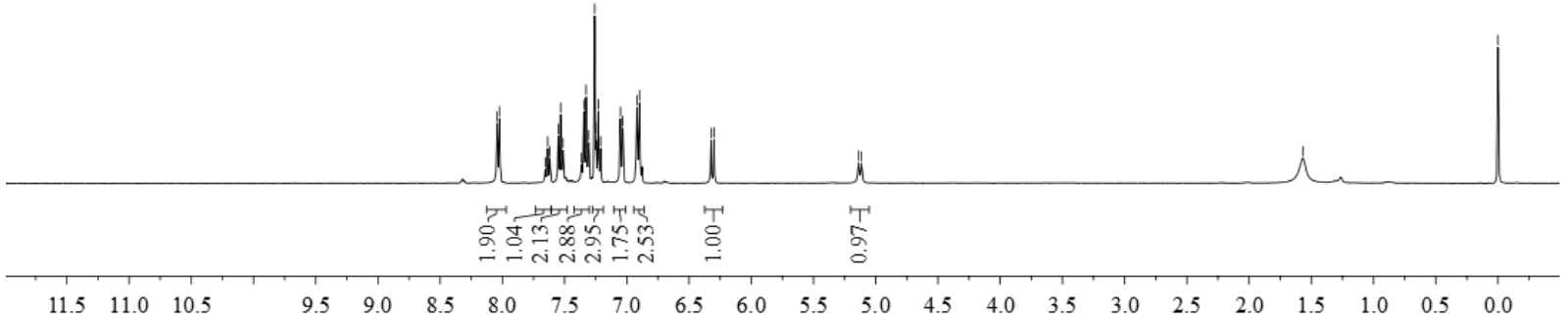
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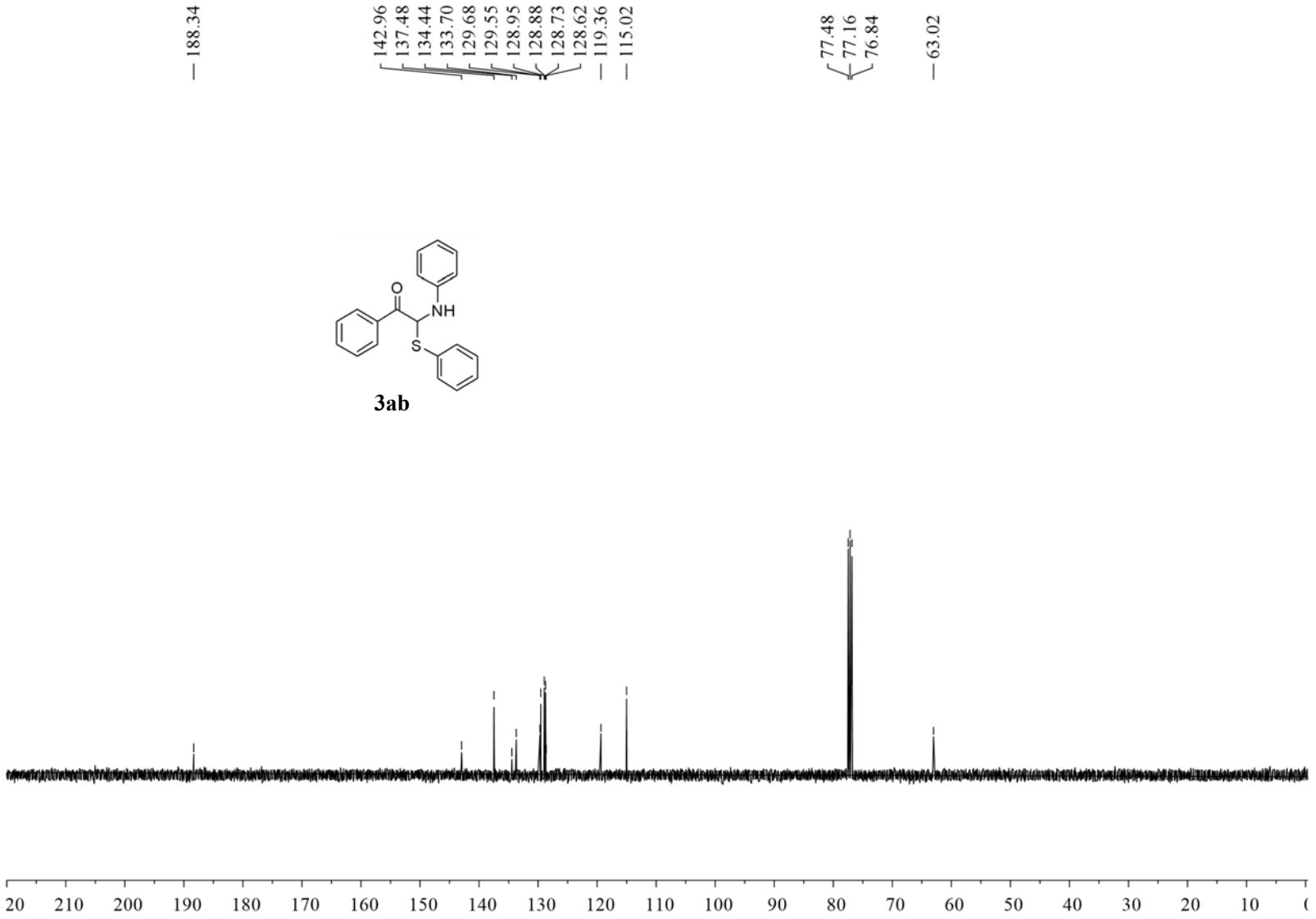
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77.16
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63.02
O
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S
3ab
20
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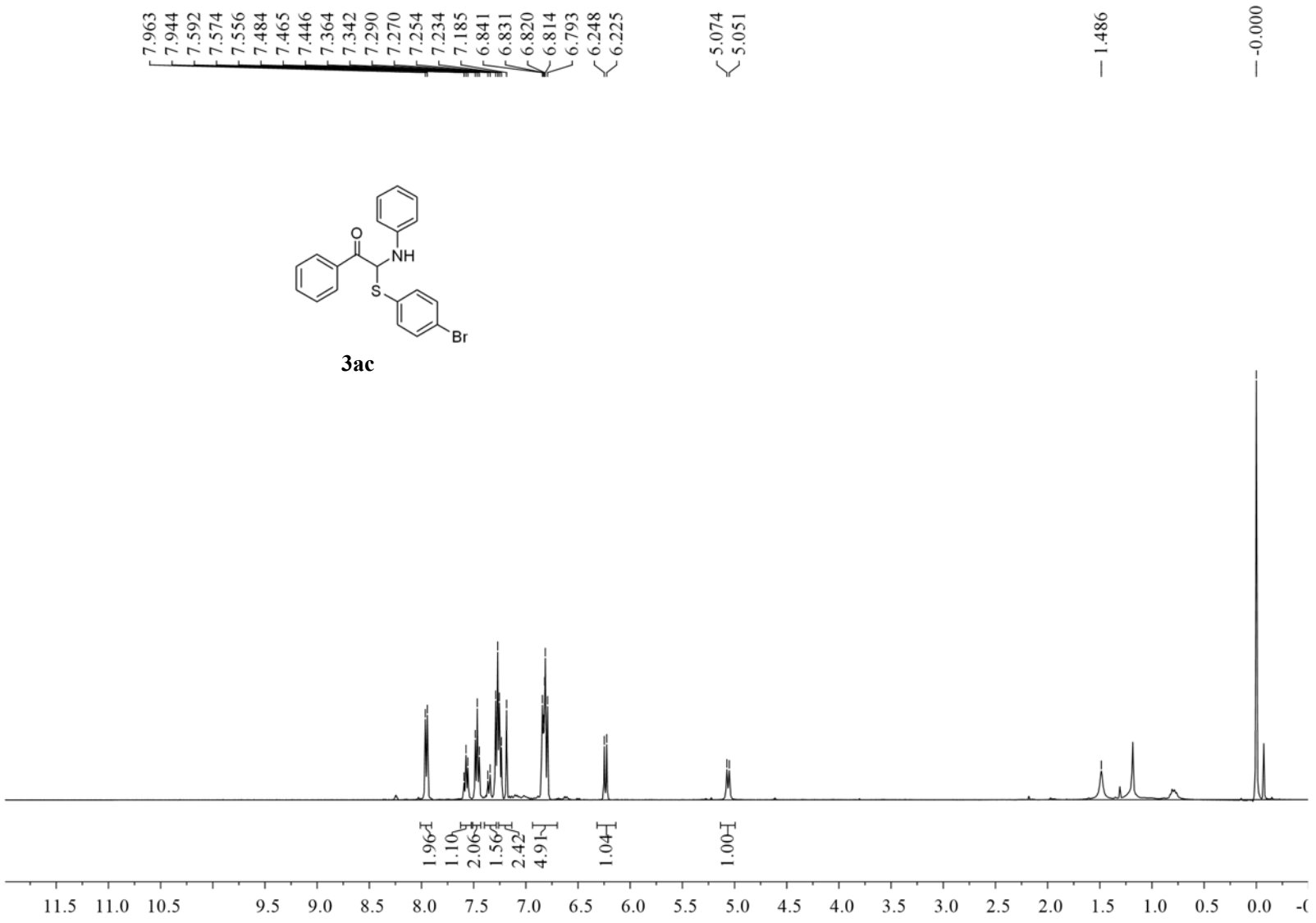
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S
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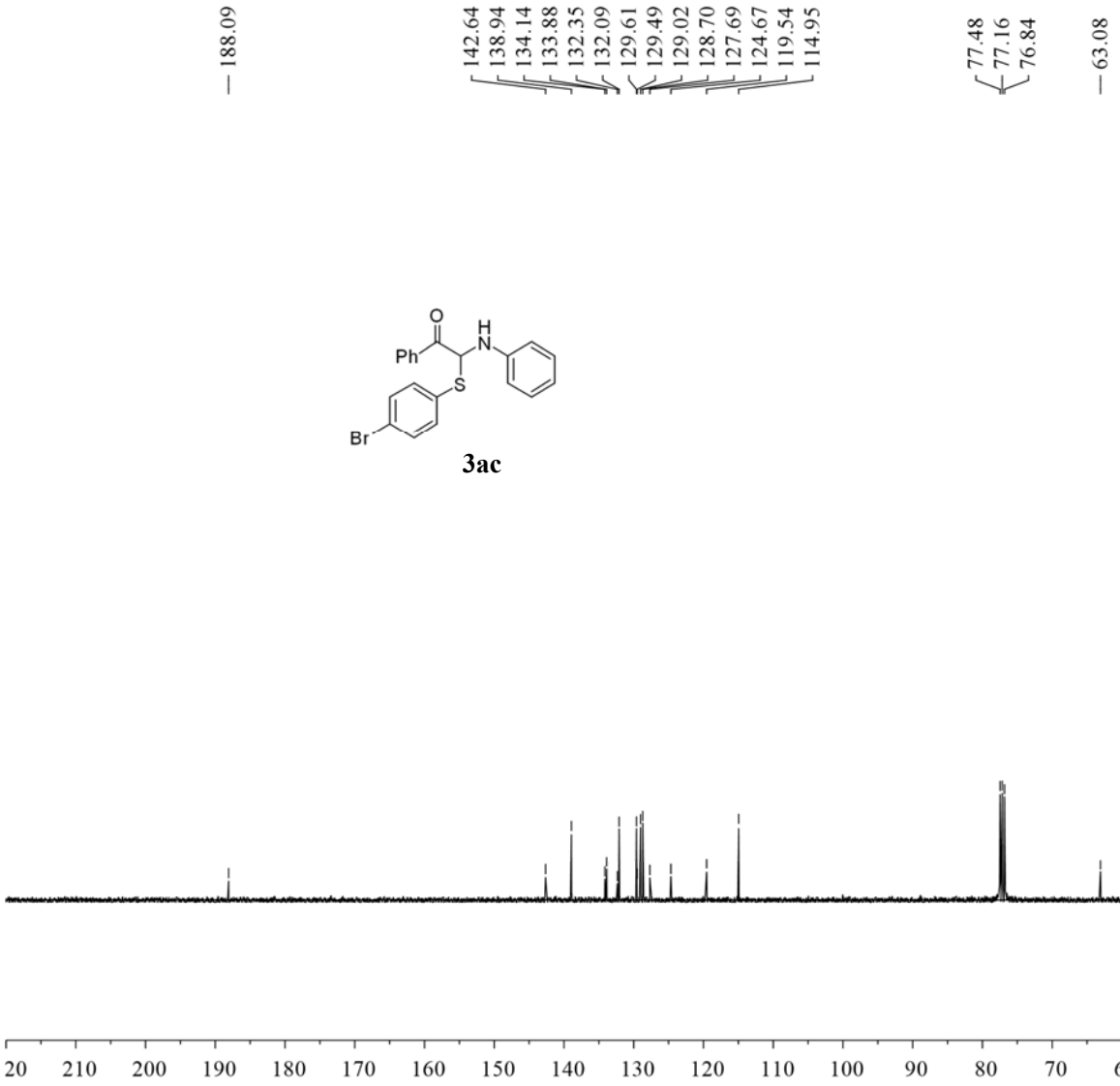
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77.16
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H
N
Ph
S
Br
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10

3ac


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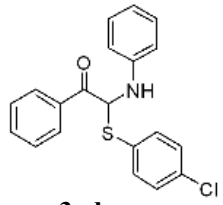
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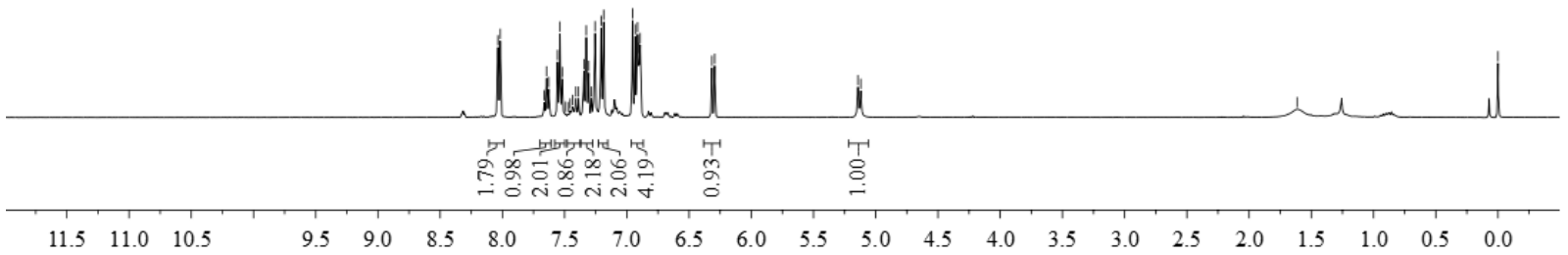
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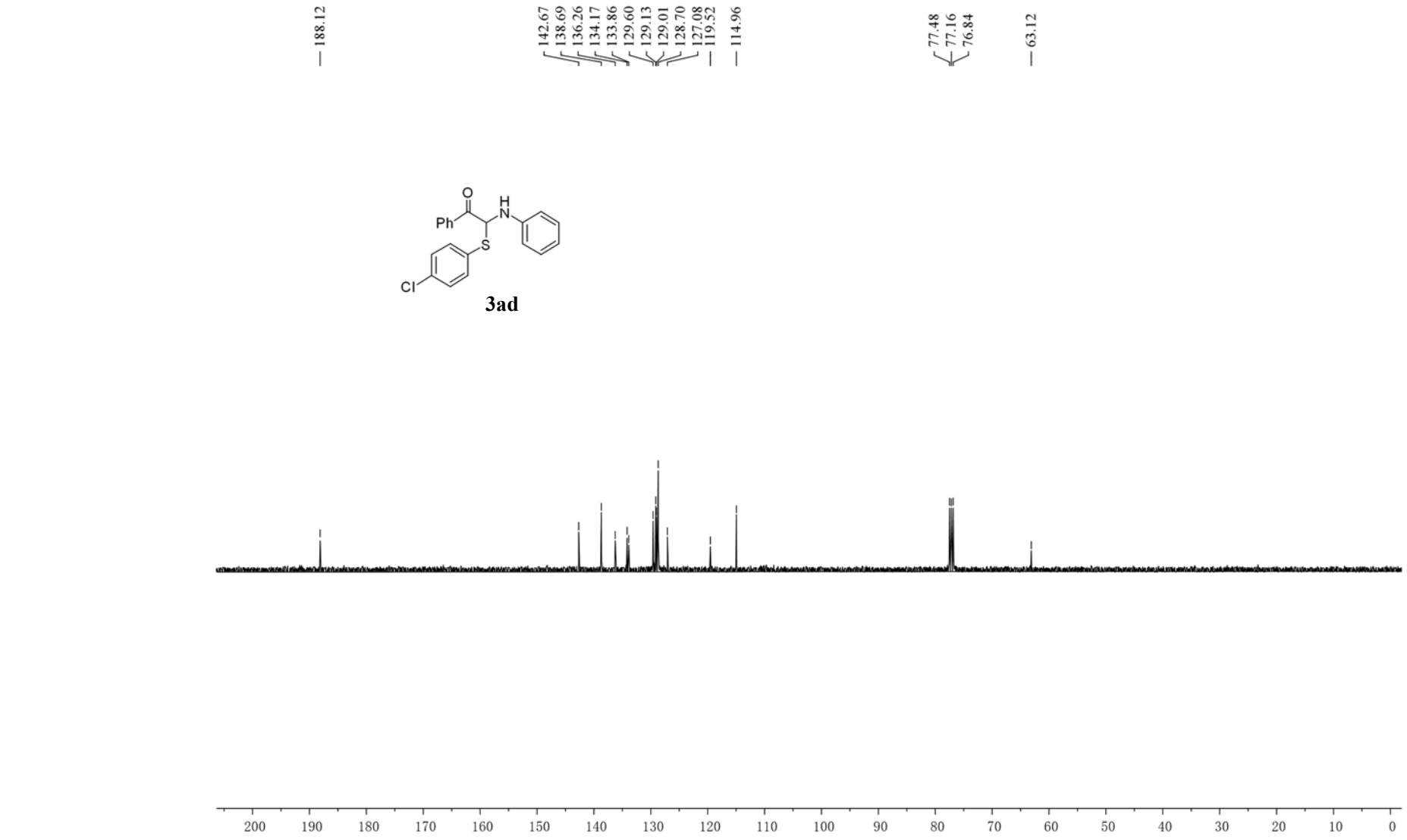
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76.84
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Ph
H
N
S
Cl
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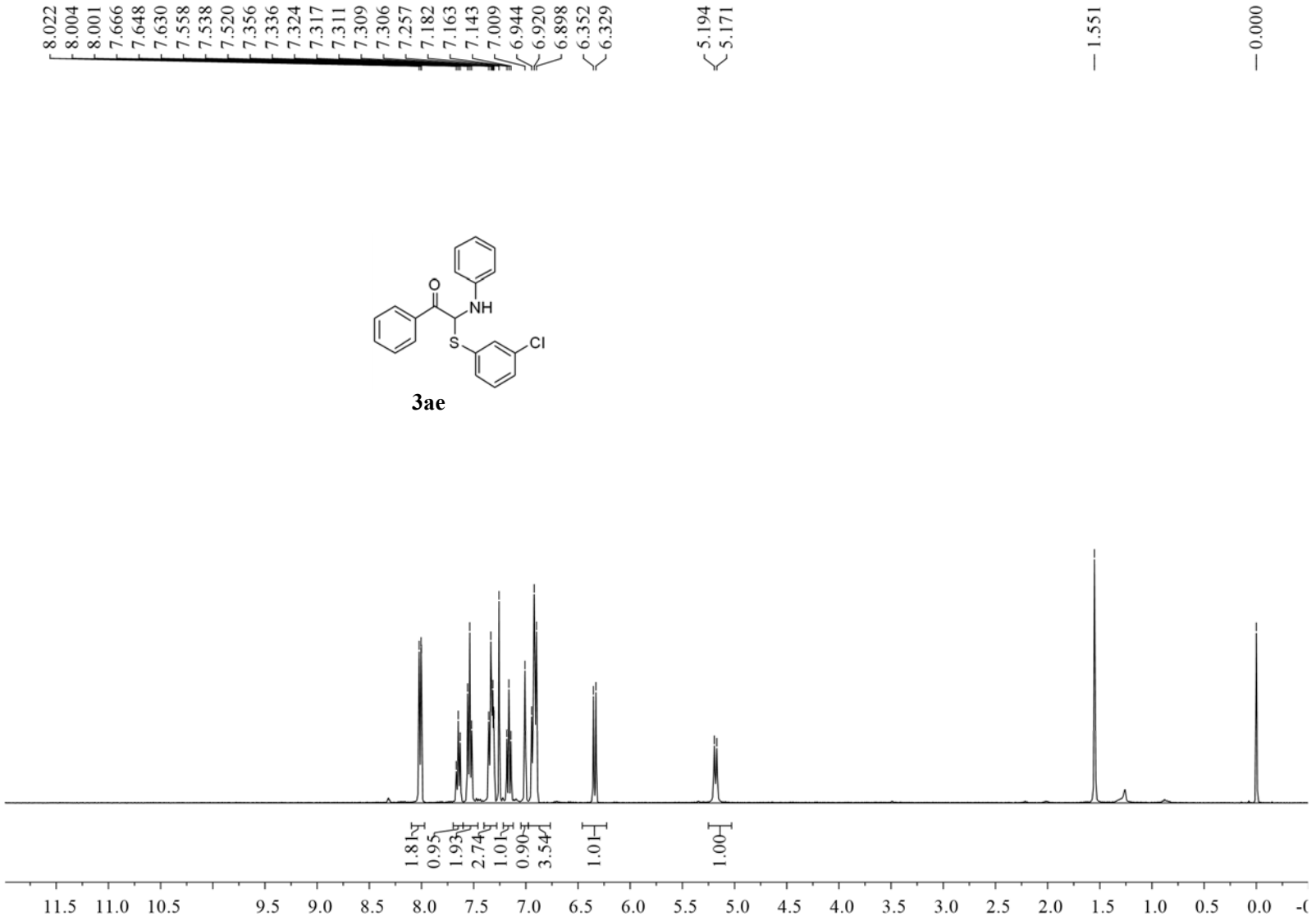
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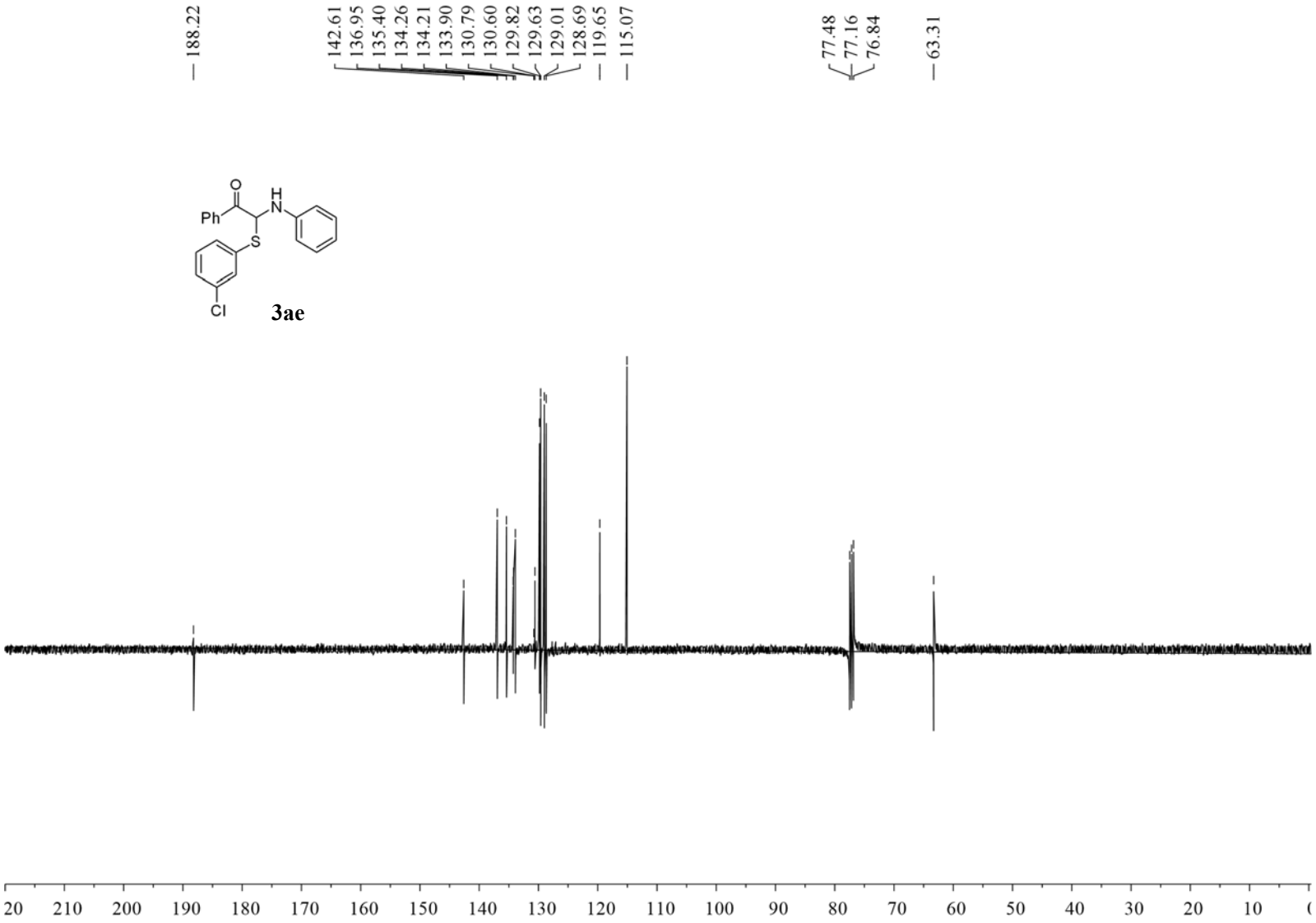
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63.31
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Ph
H
N
S
Cl
3ae
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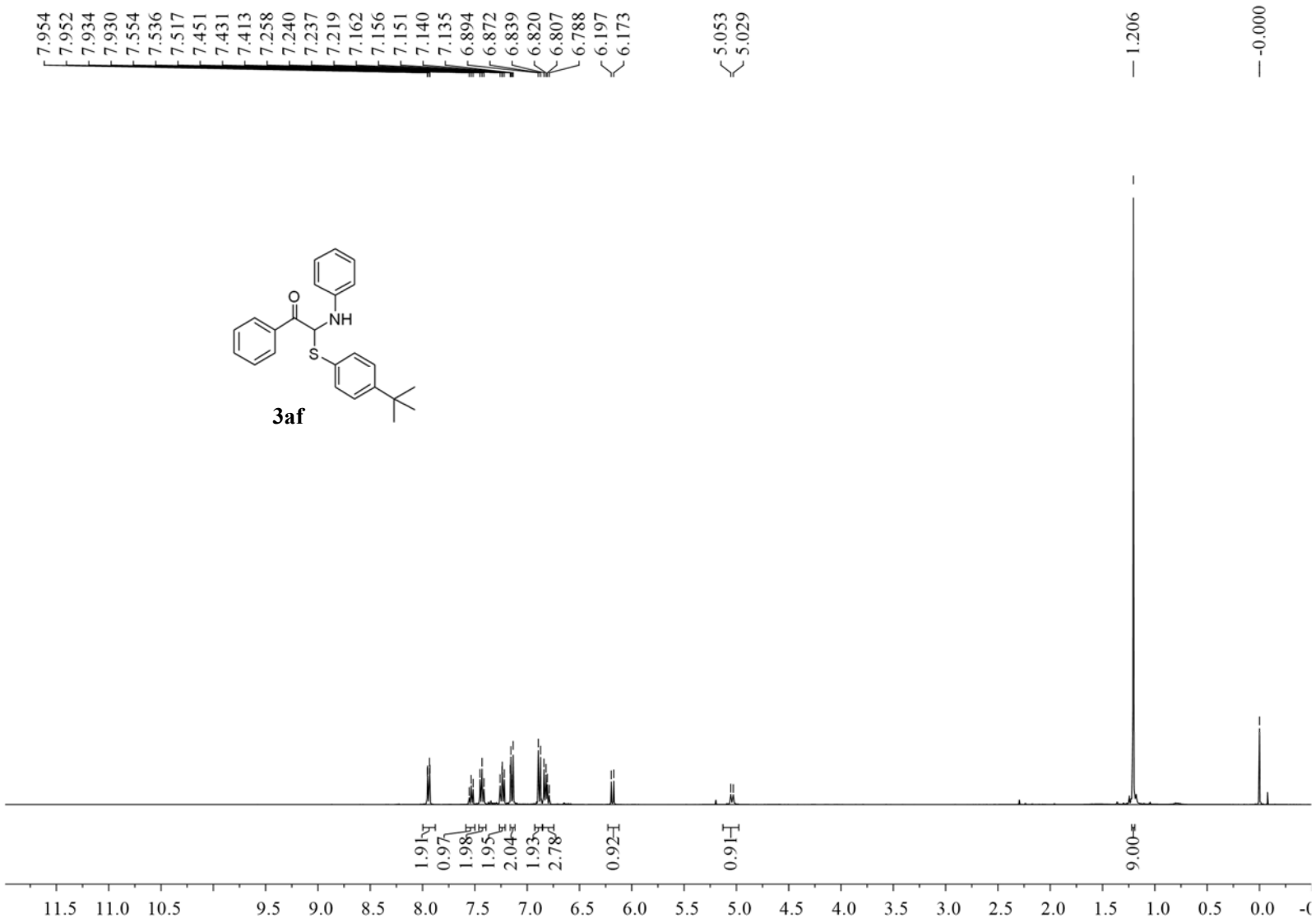
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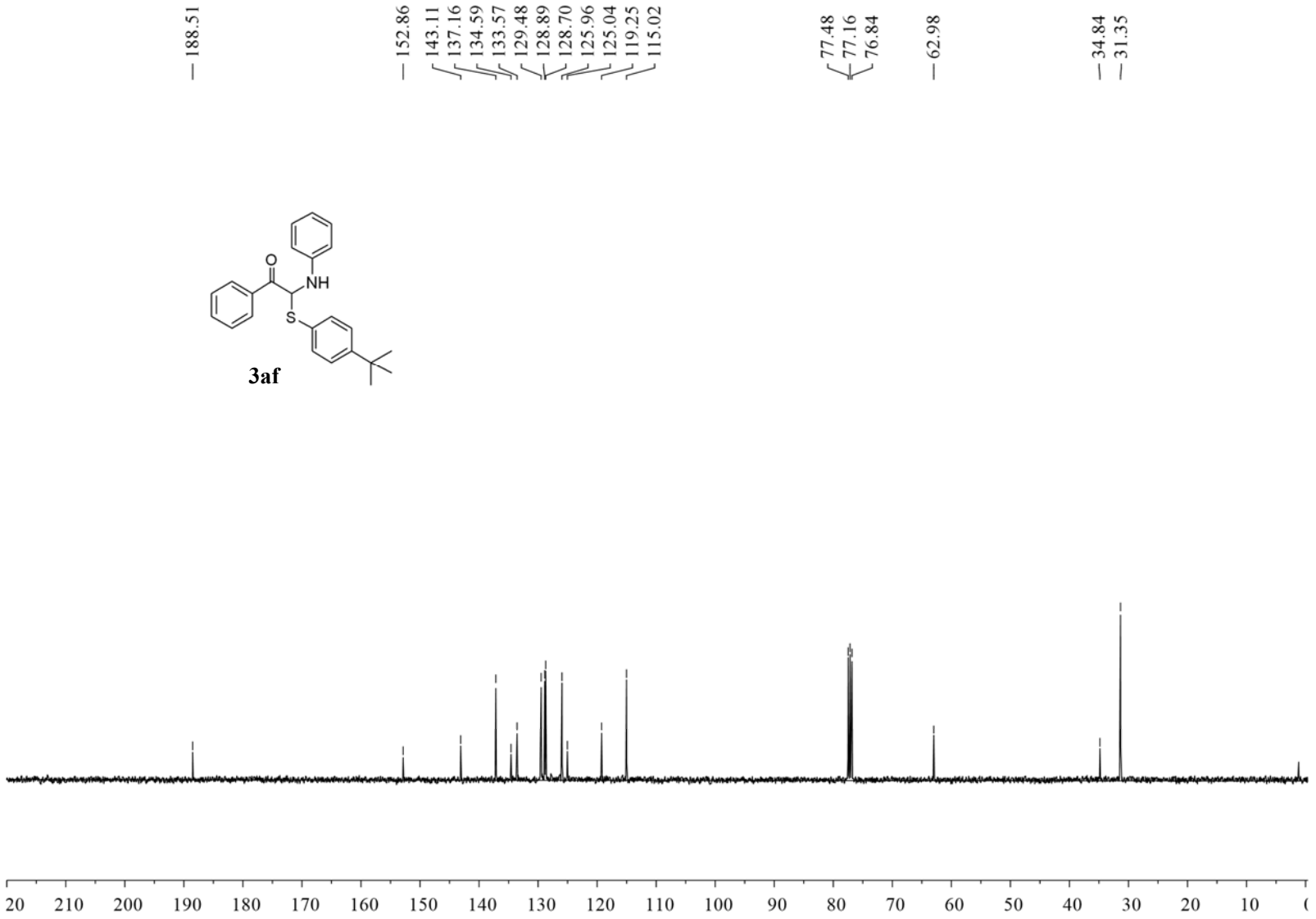
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31.35
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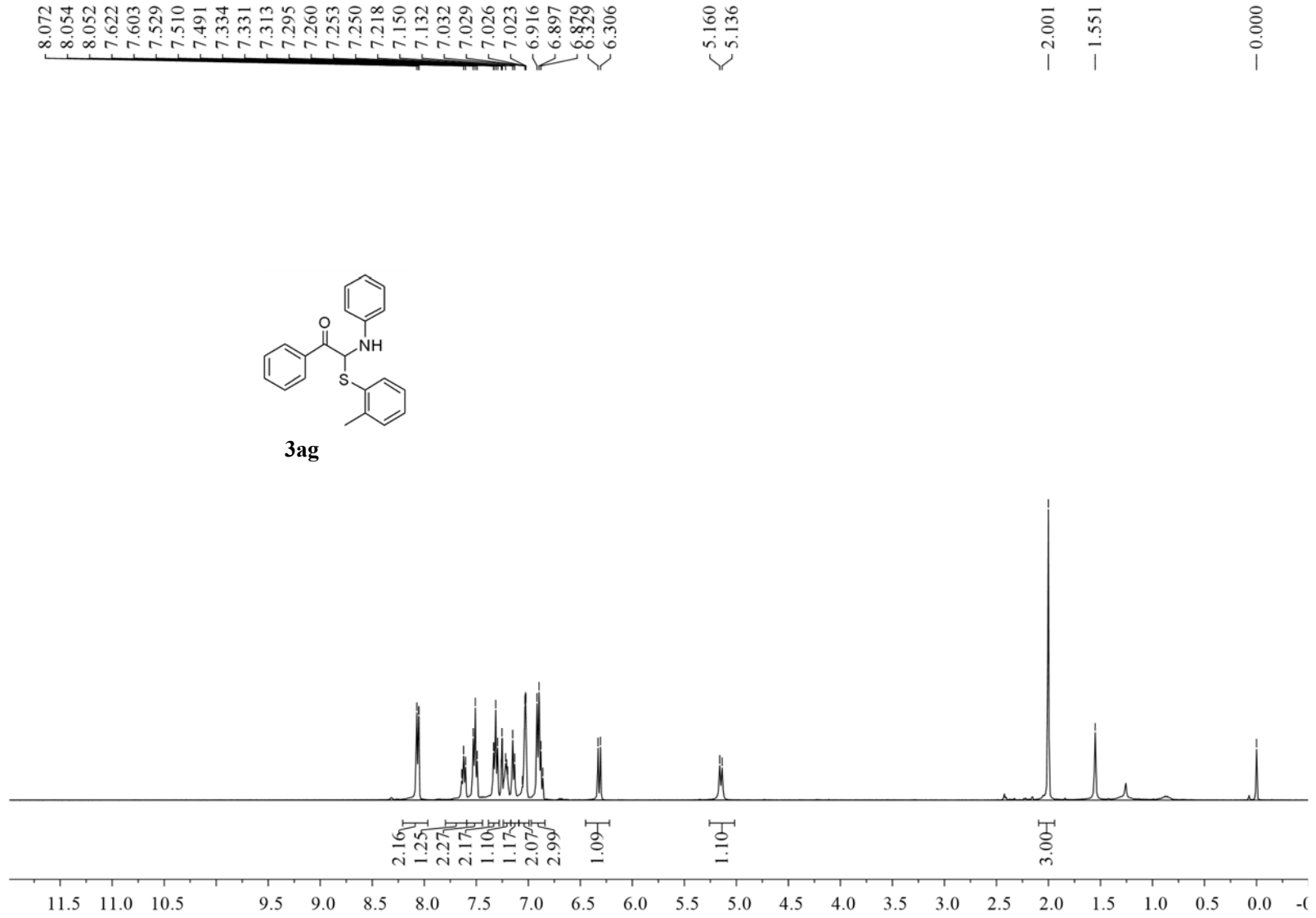
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7.150
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2.27
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2.99
1.09
1.10
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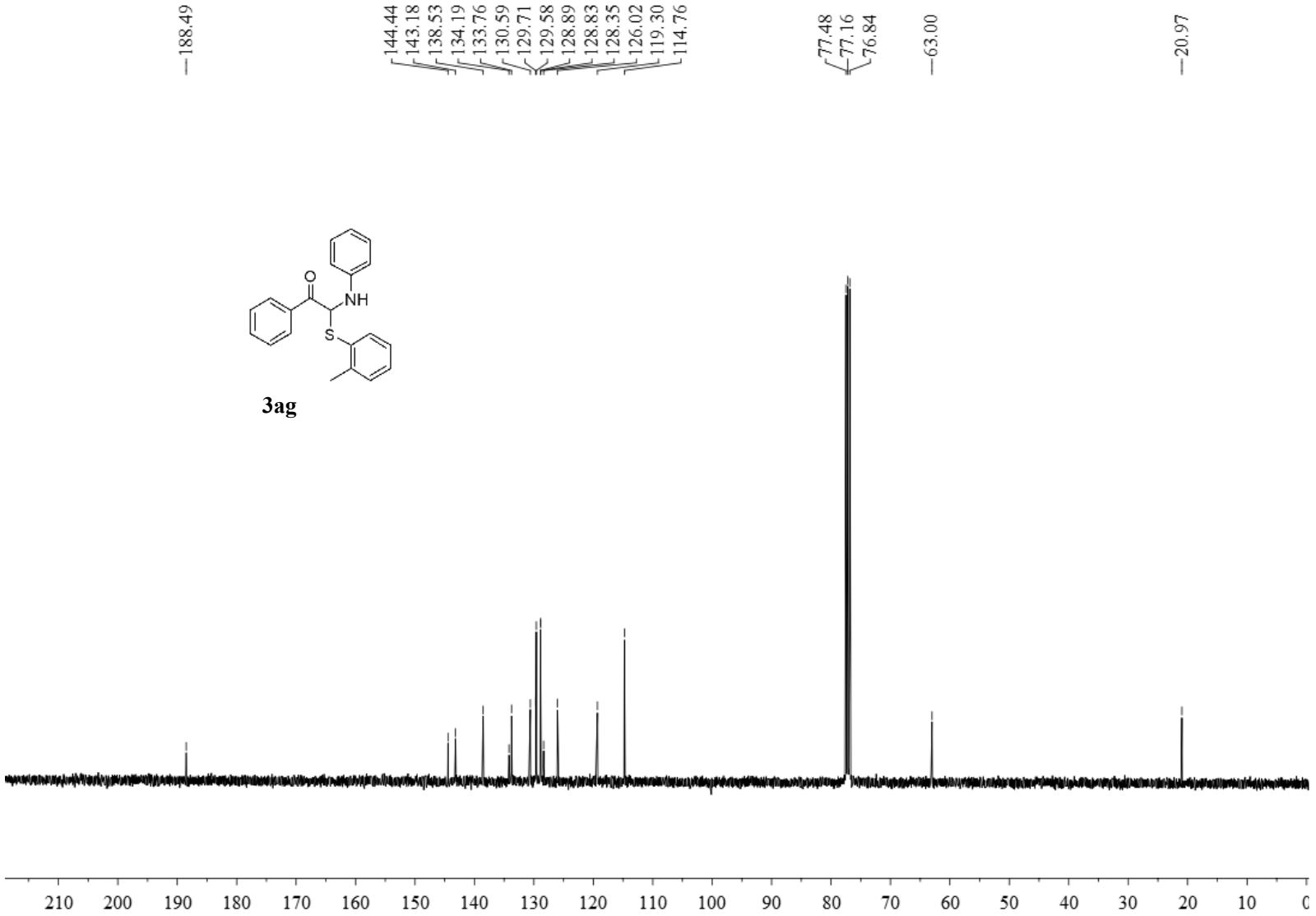
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3ag


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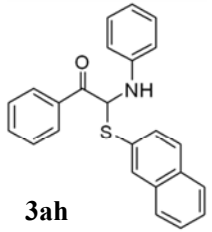
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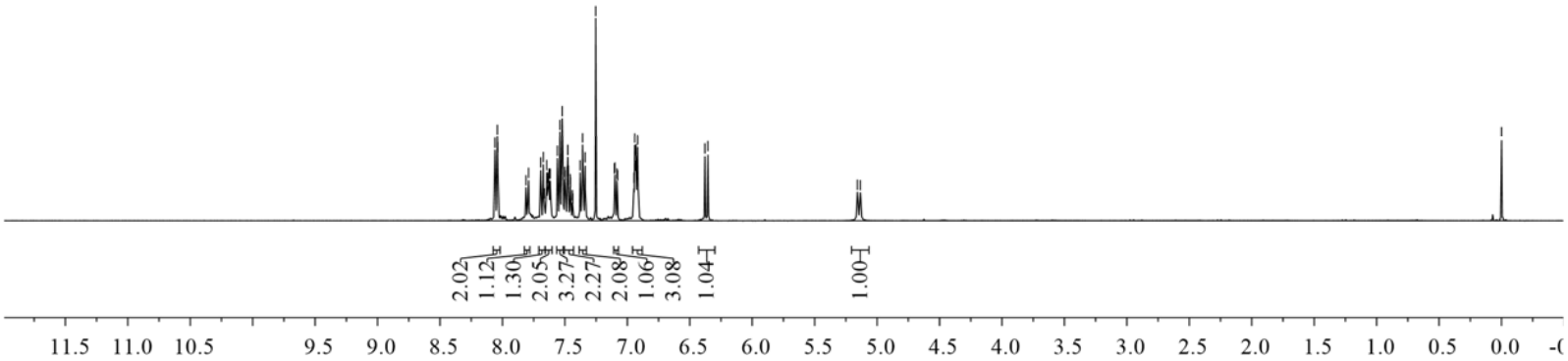
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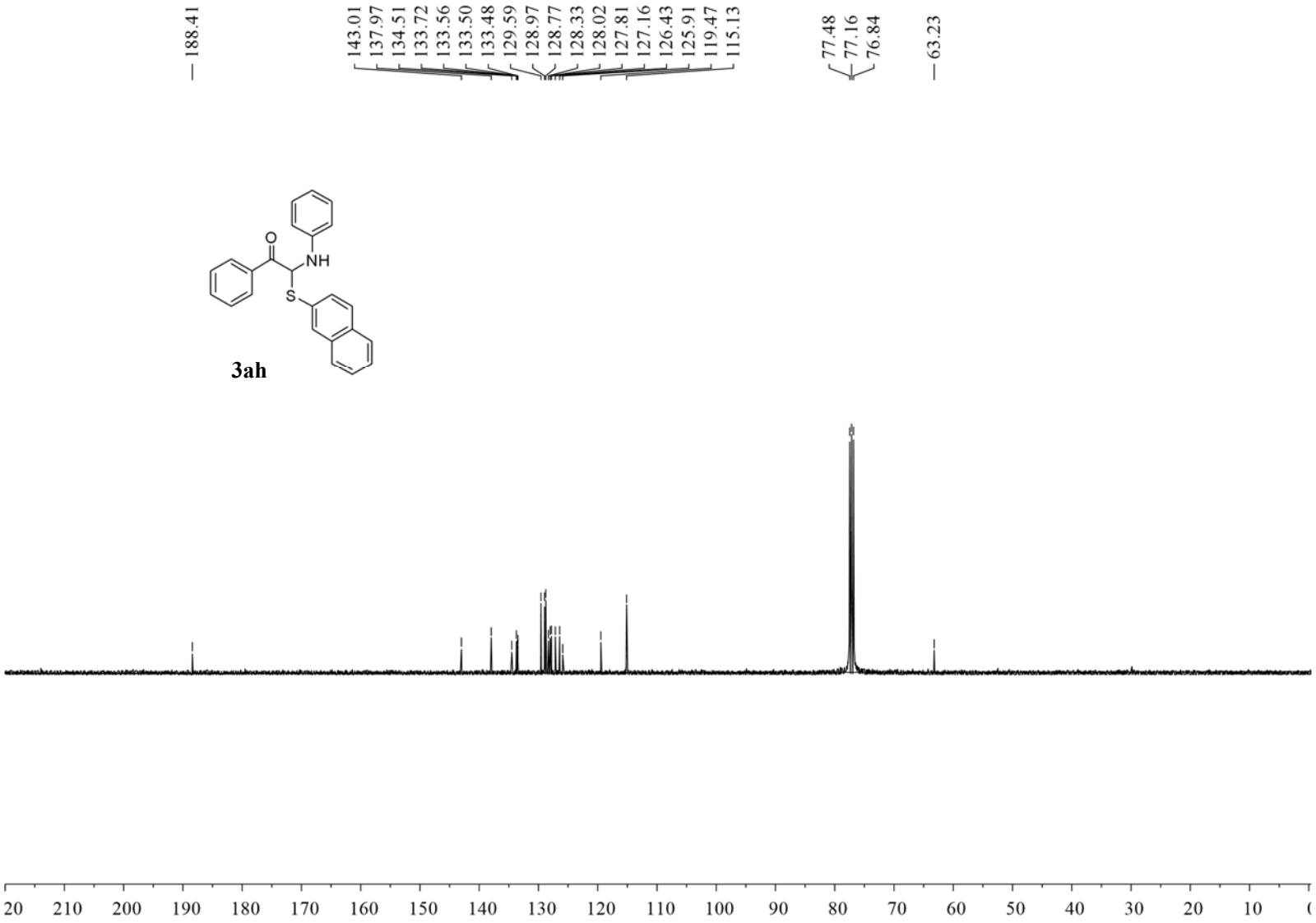
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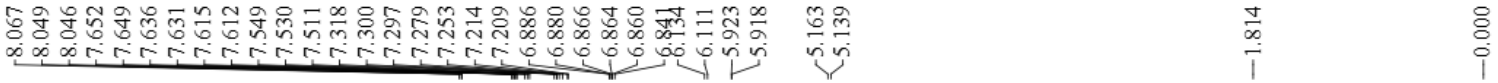
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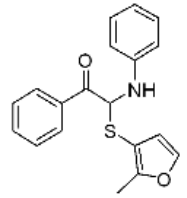
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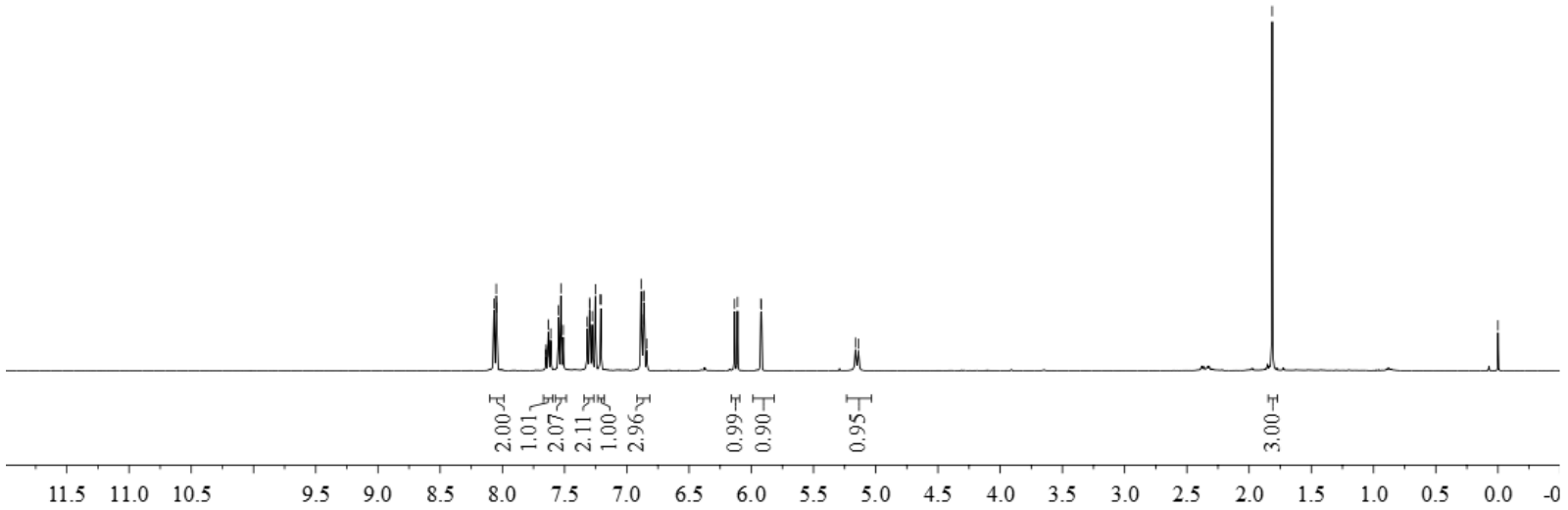
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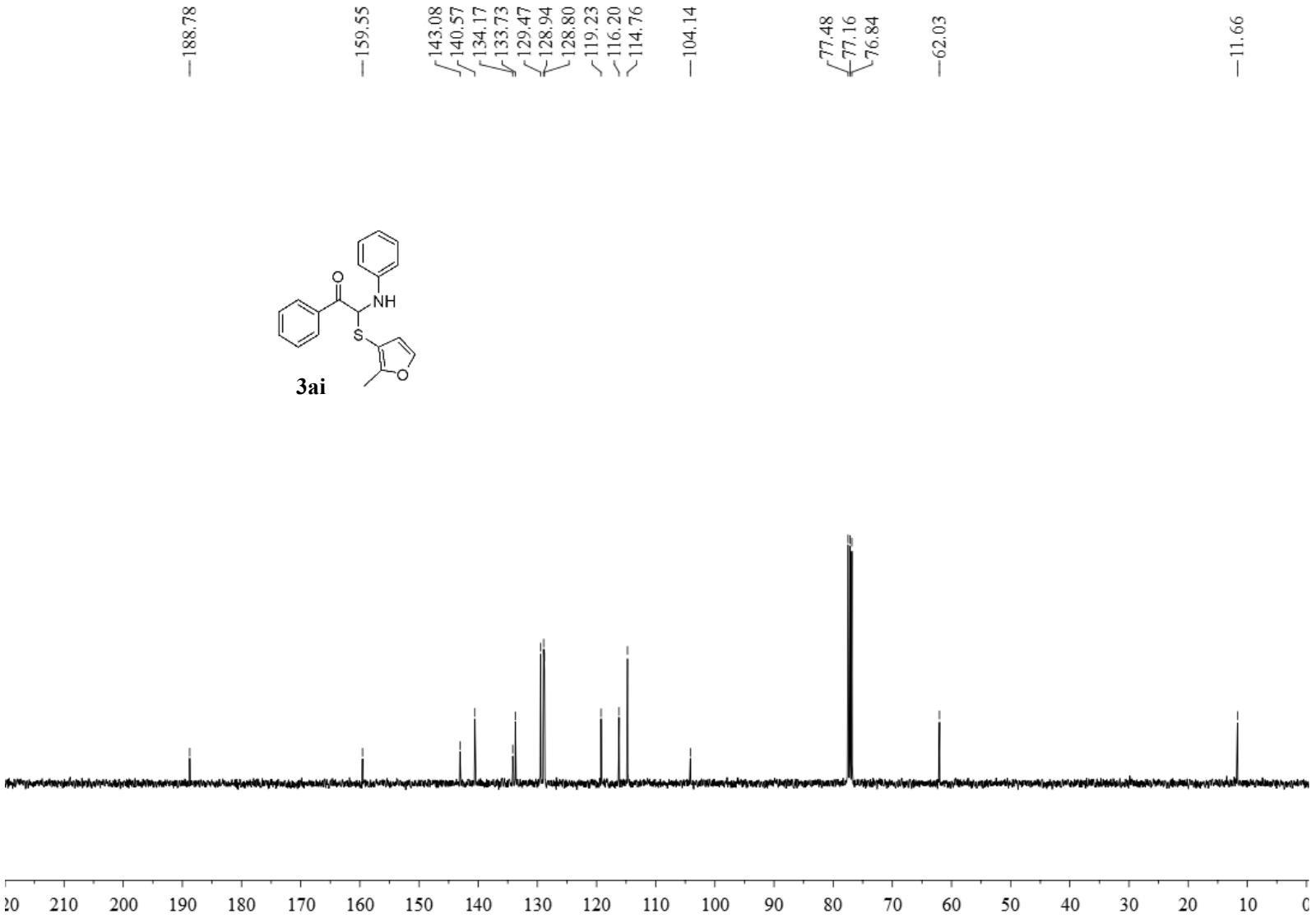
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76.84
62.03
11.66
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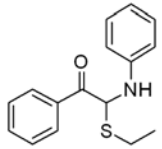
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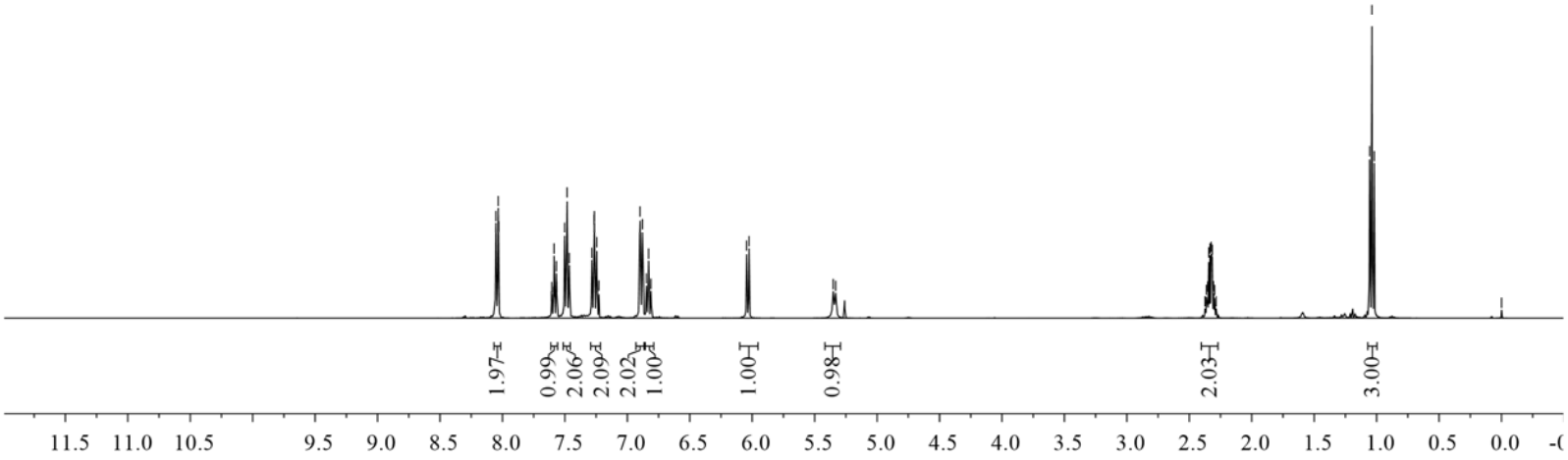
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0.98
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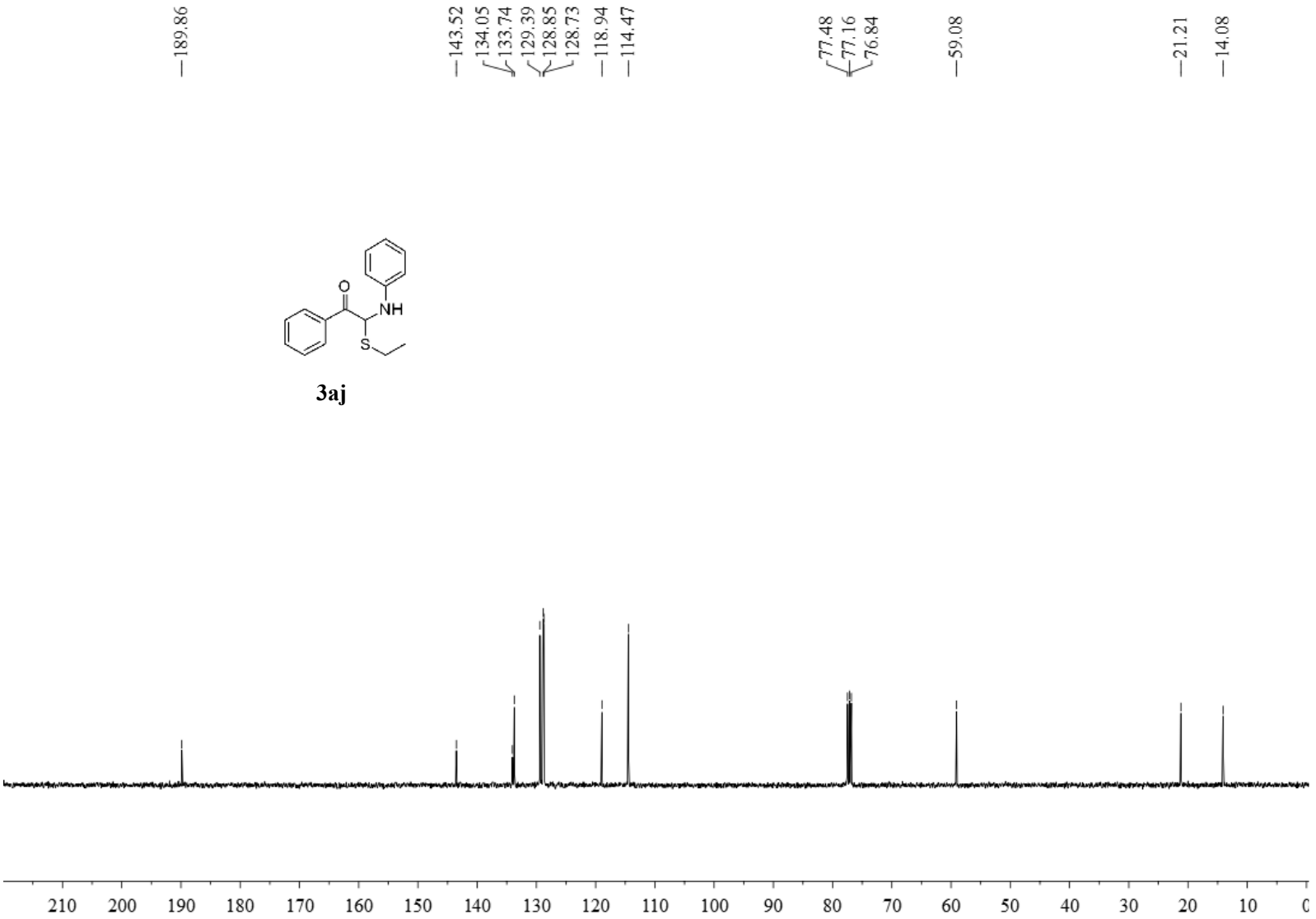
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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21.21
14.08
O
NH
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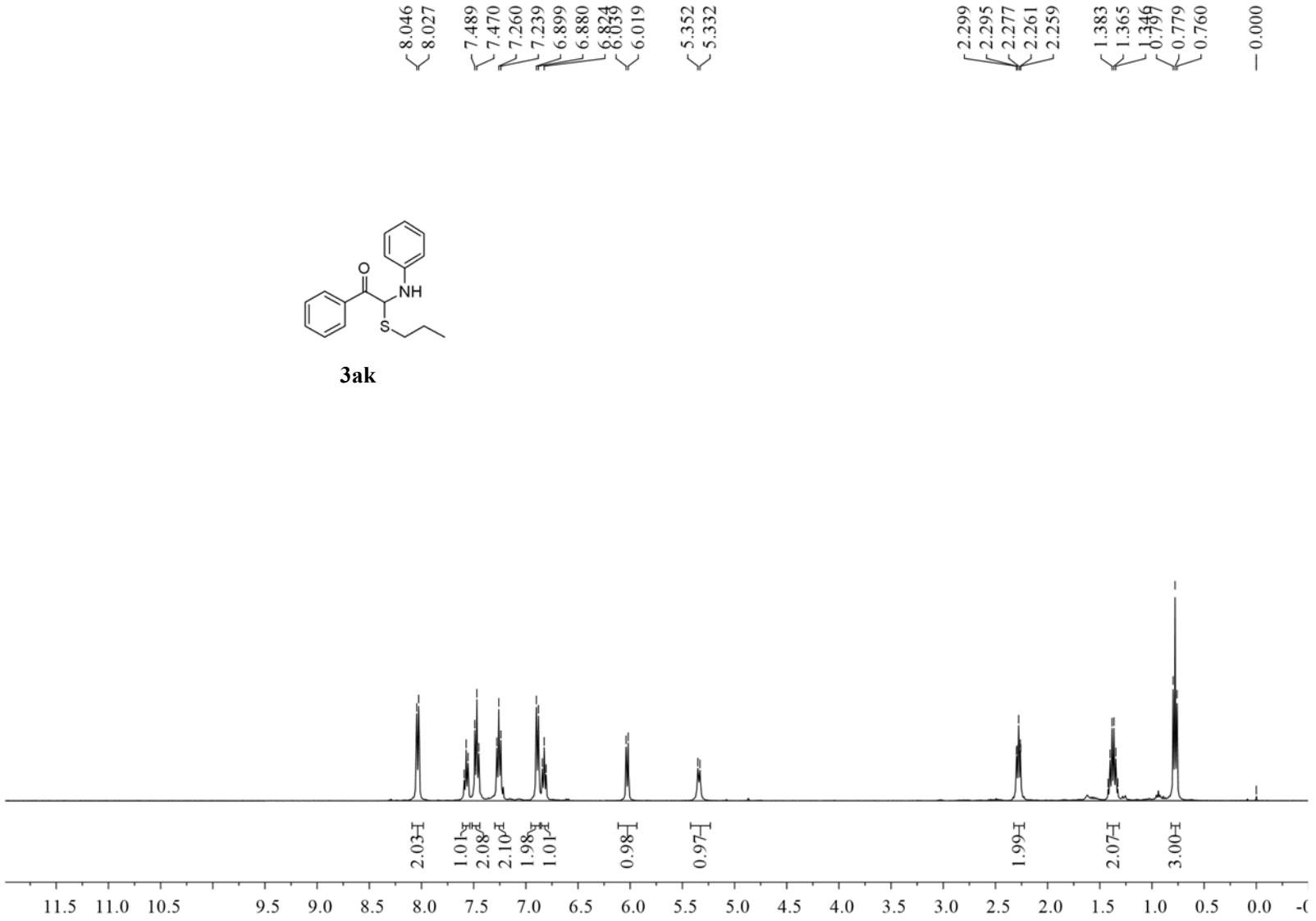
3aj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2.261
2.259
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1.346
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0.000
O
NH
S
2.03
1.01
2.08
2.10
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1.99
2.07
3.00
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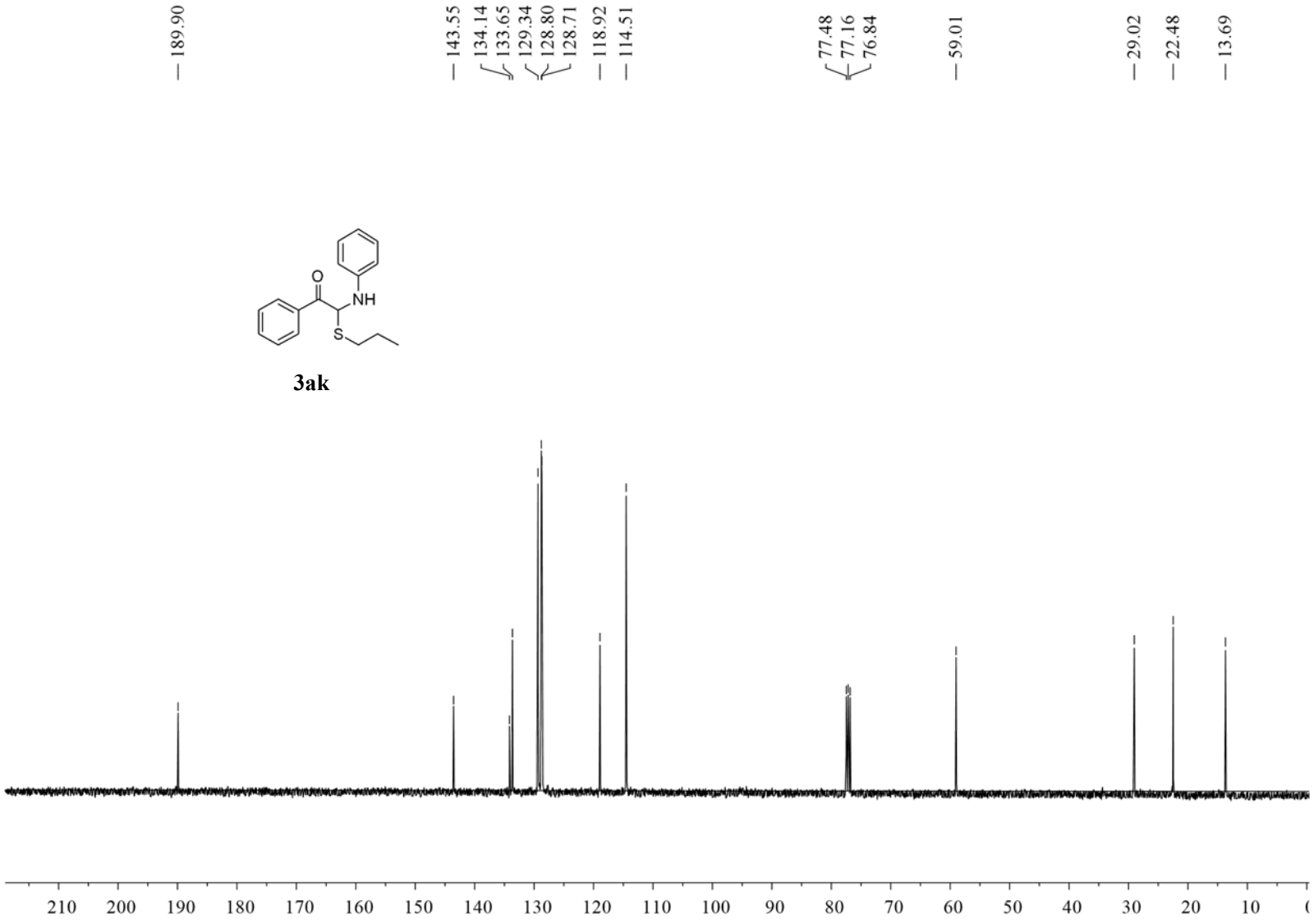
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O
NH
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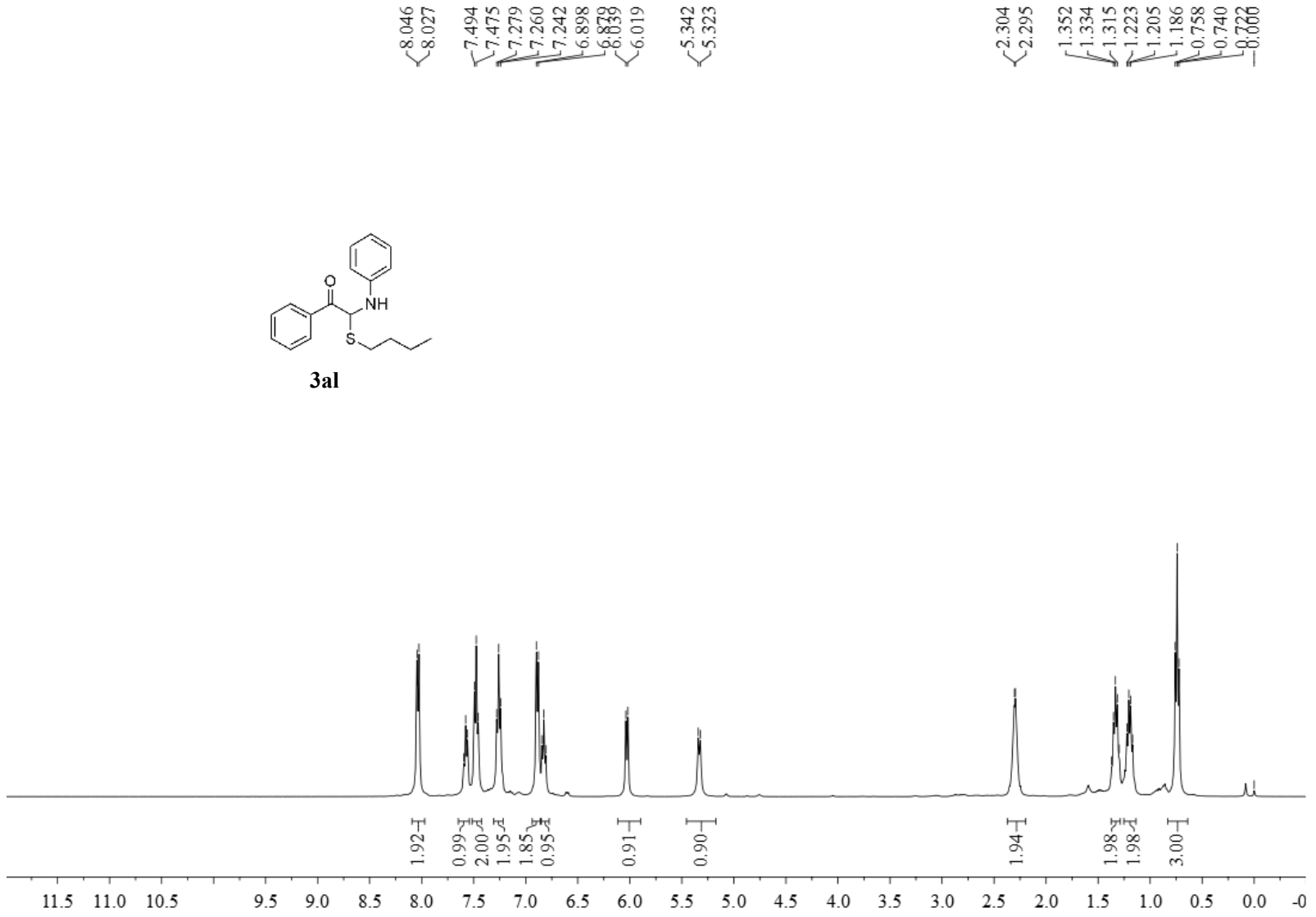
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NH
S
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0.95
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1.98
1.98
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

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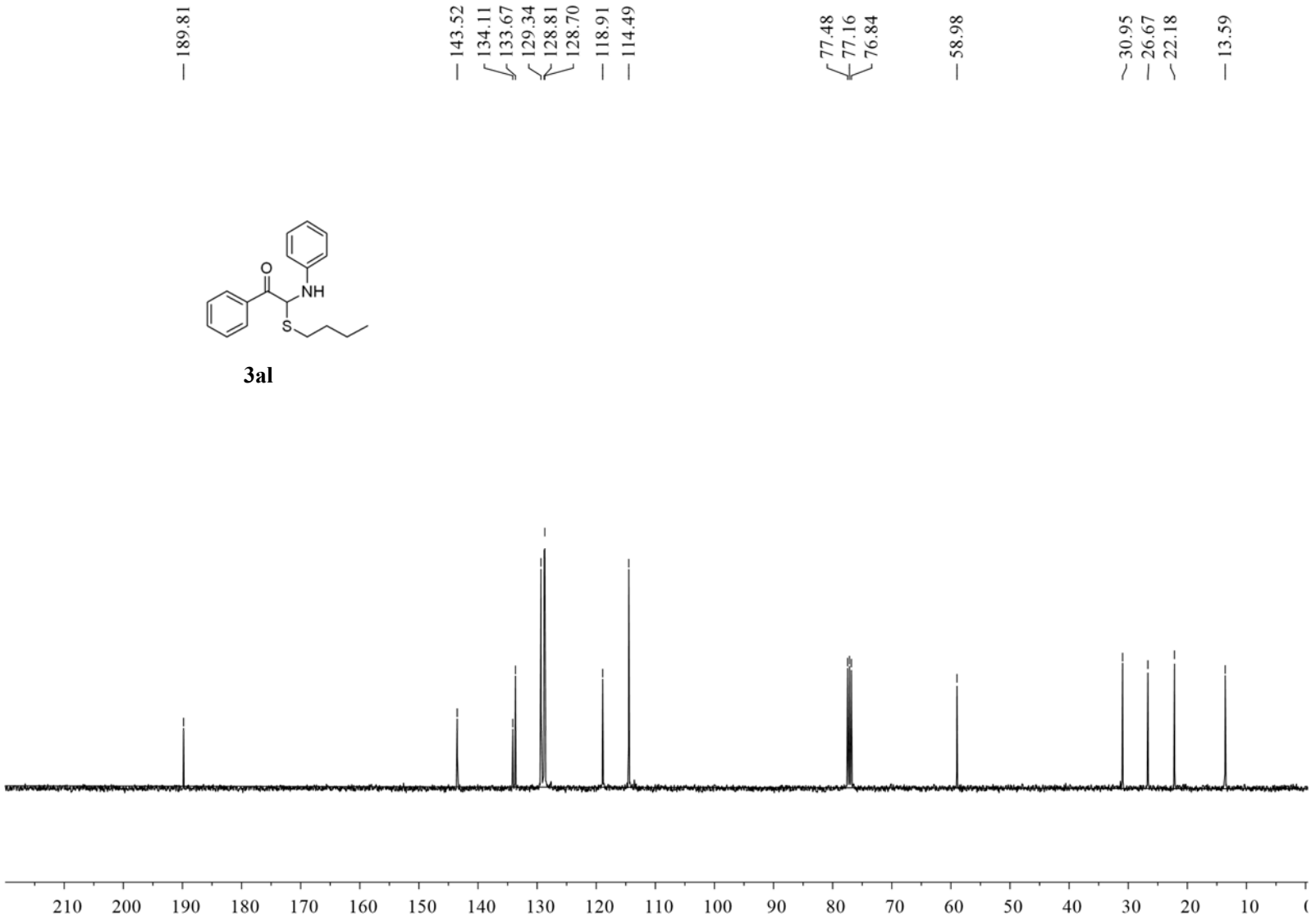
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26.67
22.18
13.59
O
NH
S
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200
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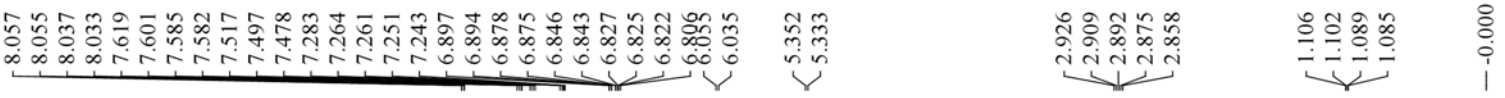
3al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7.261
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6.825
6.822
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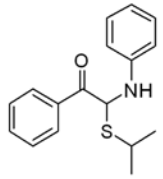
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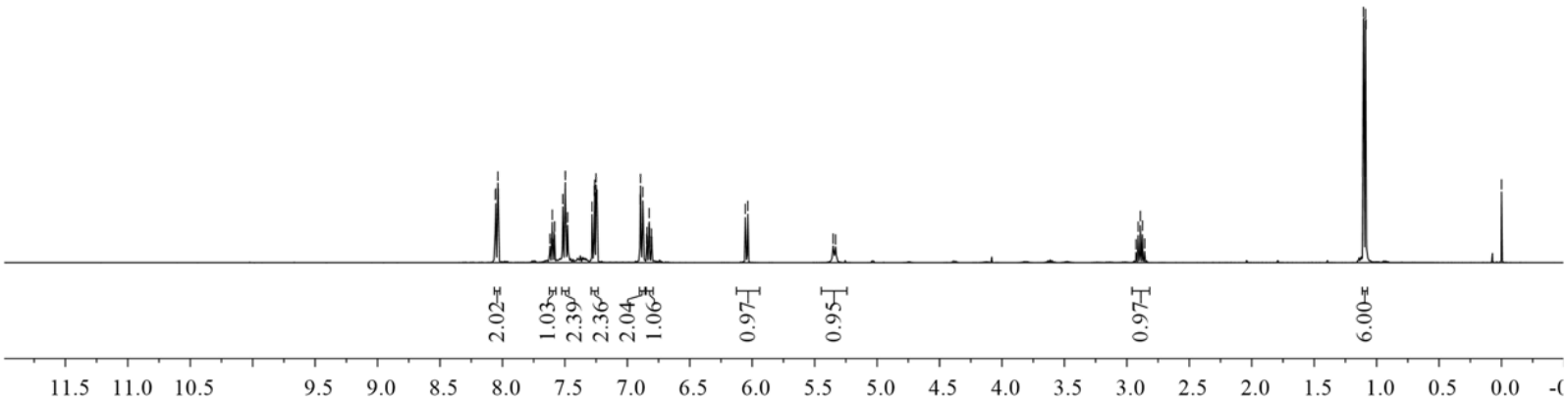
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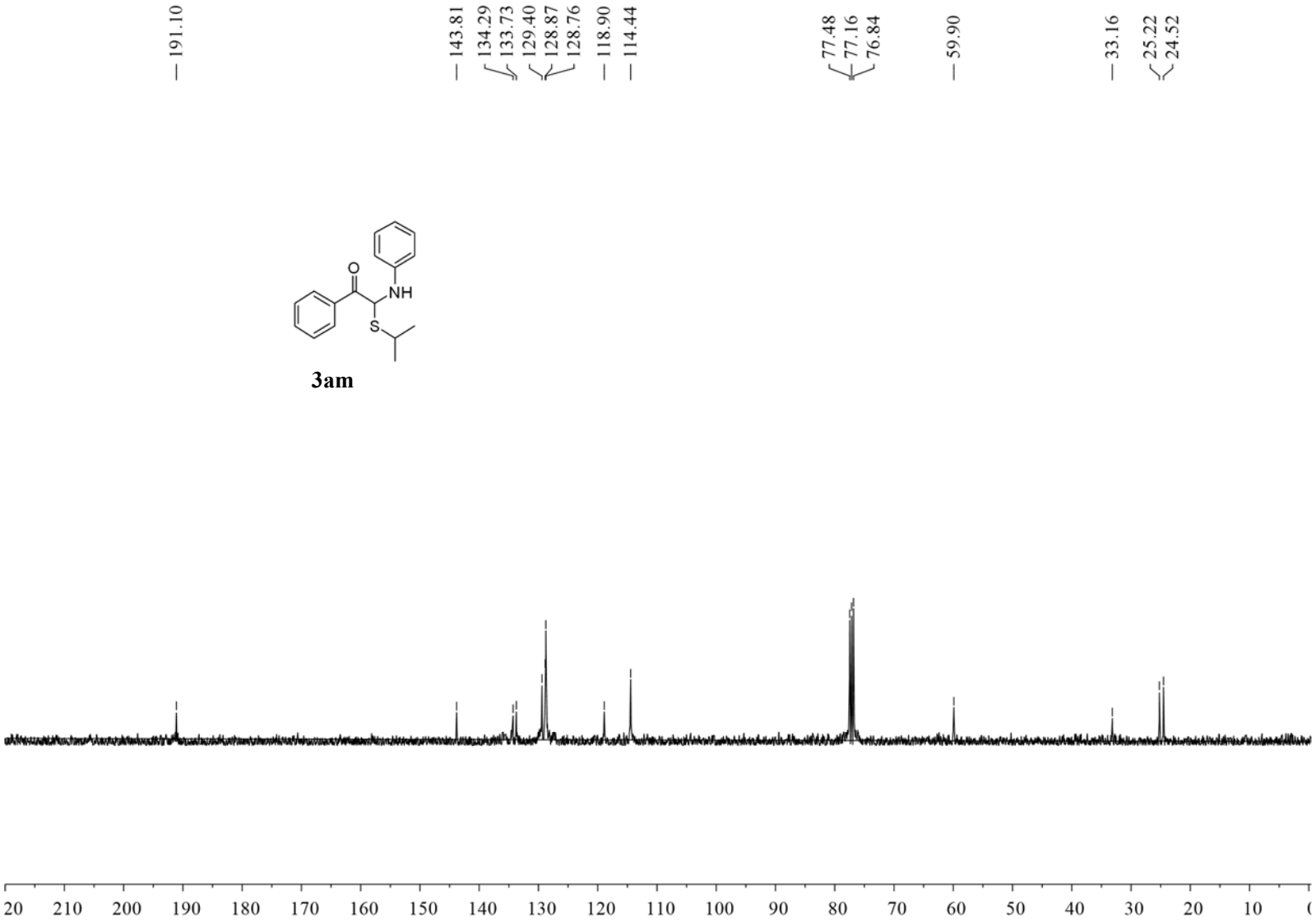
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33.16
25.22
24.52
O
NH
S
20
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200
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100
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20
10

3am


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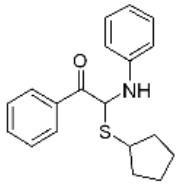
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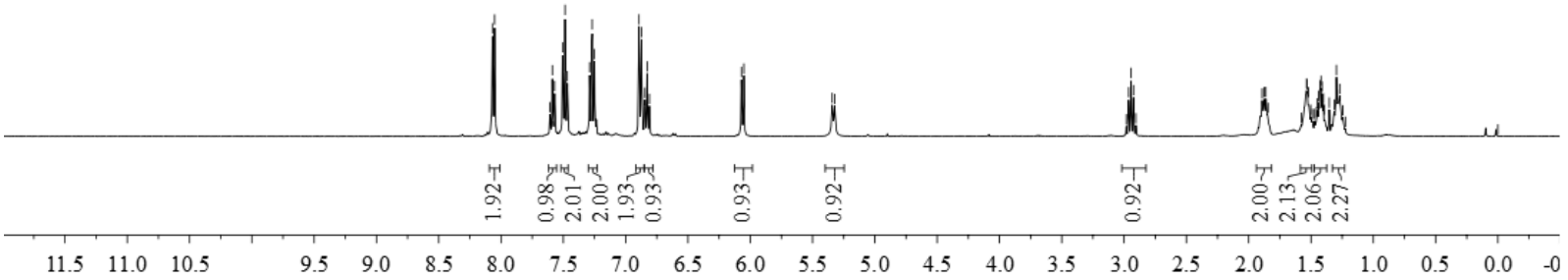
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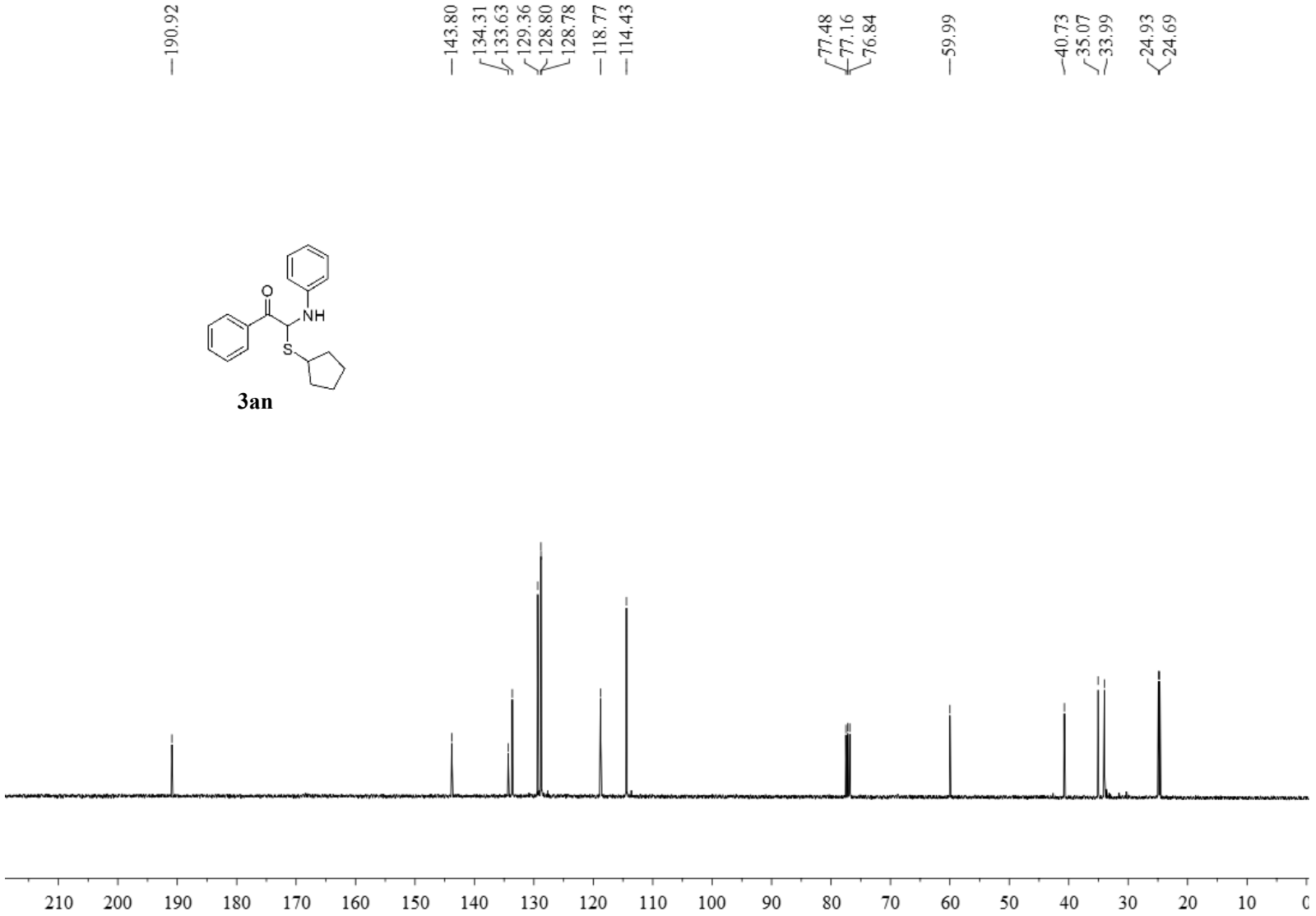
2.27
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0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35.07
33.99
24.93
24.69
O
NH
S
3an
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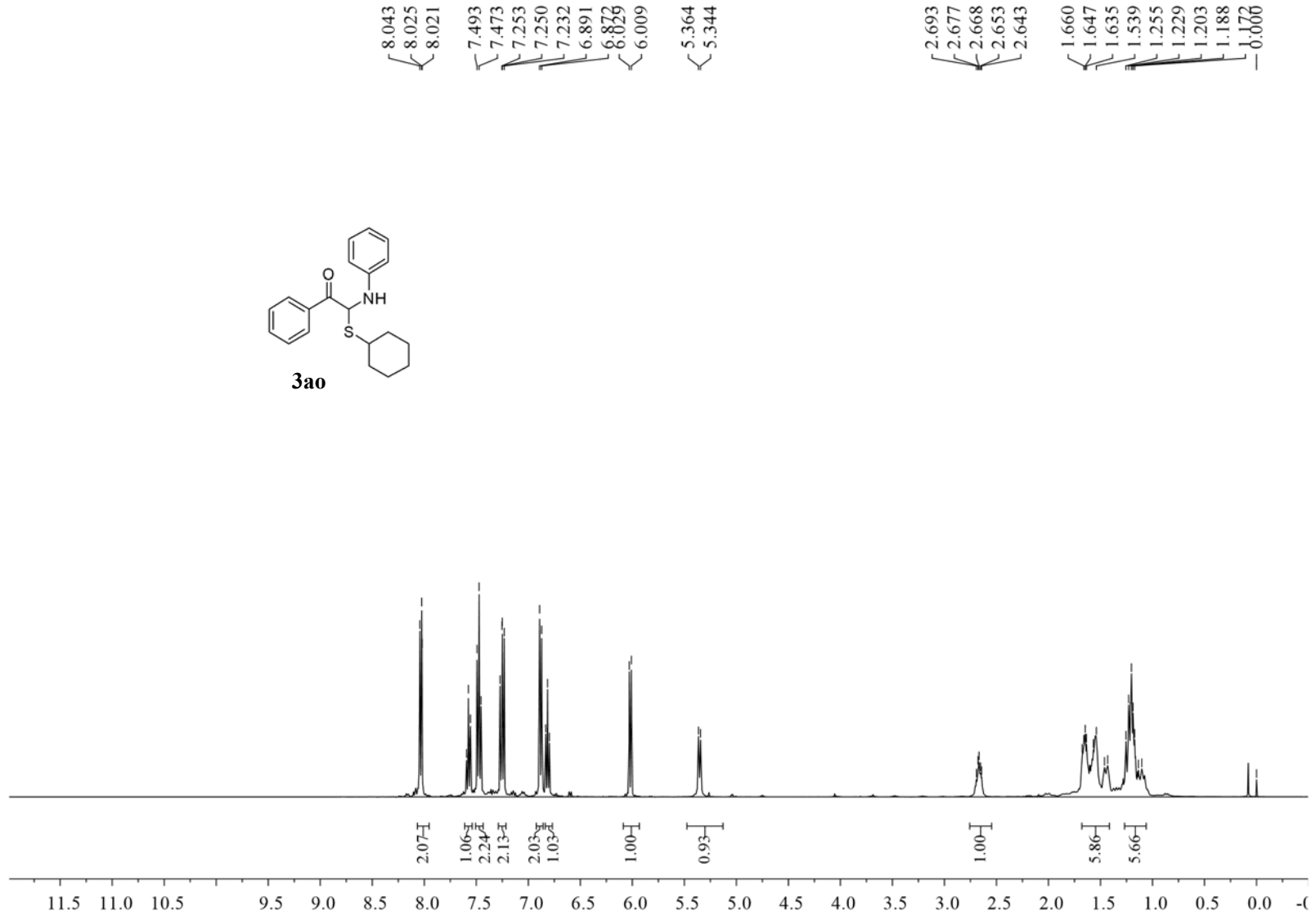
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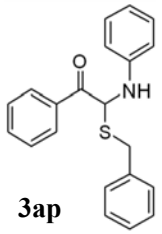
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S

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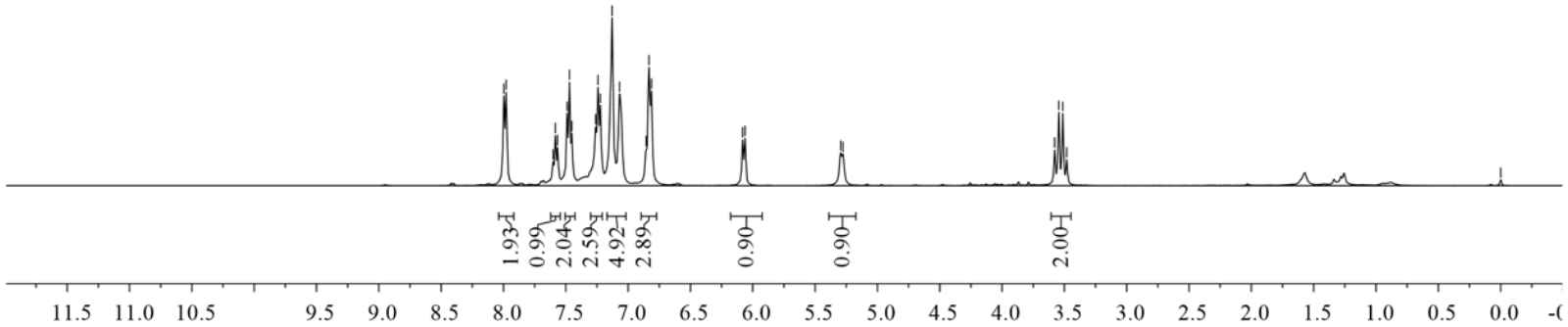
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2.00
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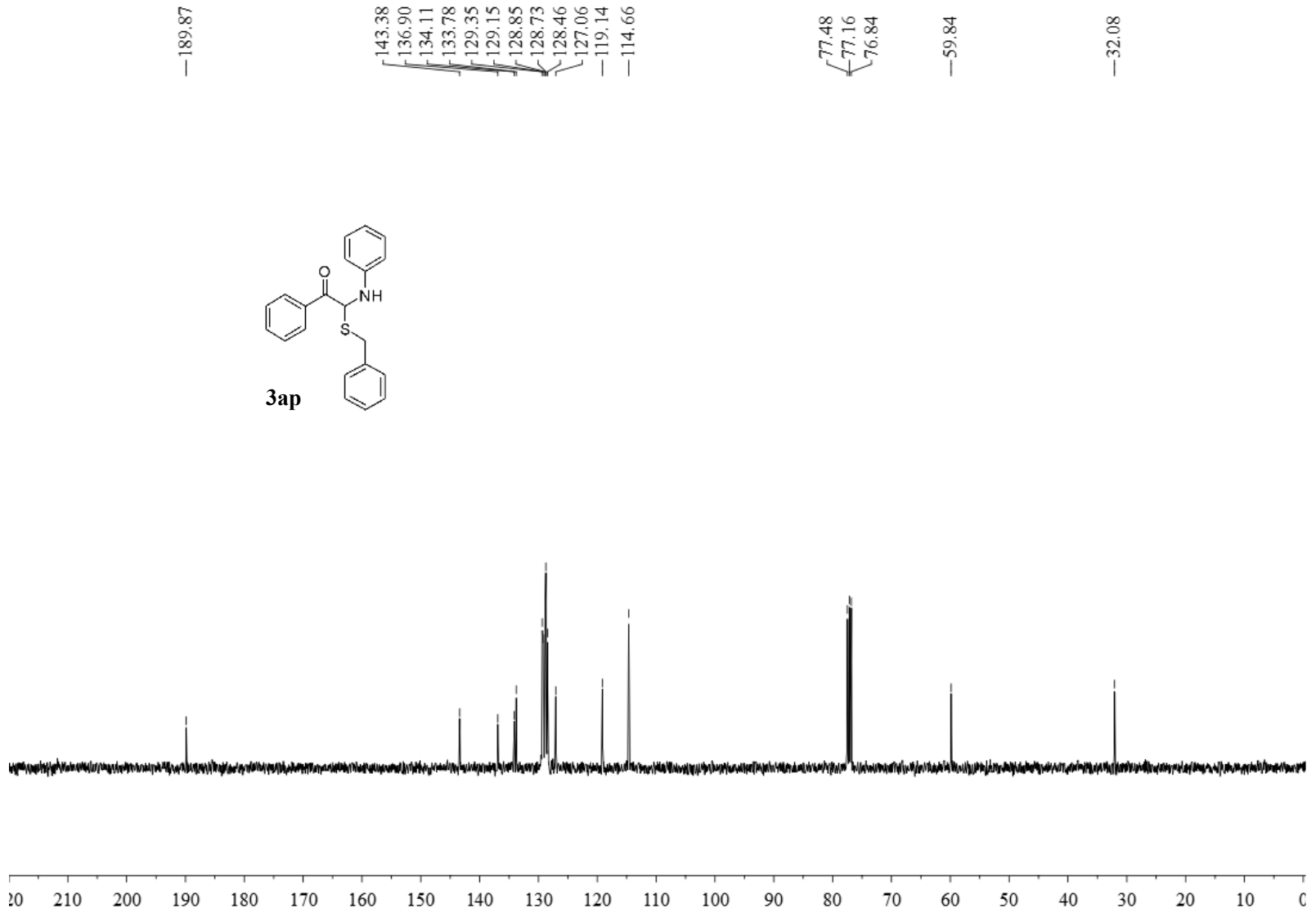
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77.16
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59.84
32.08
O
NH
S
3ap
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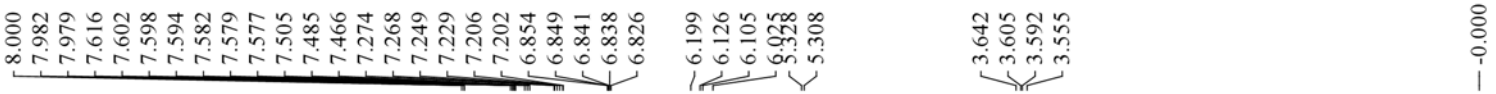
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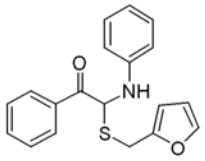
O
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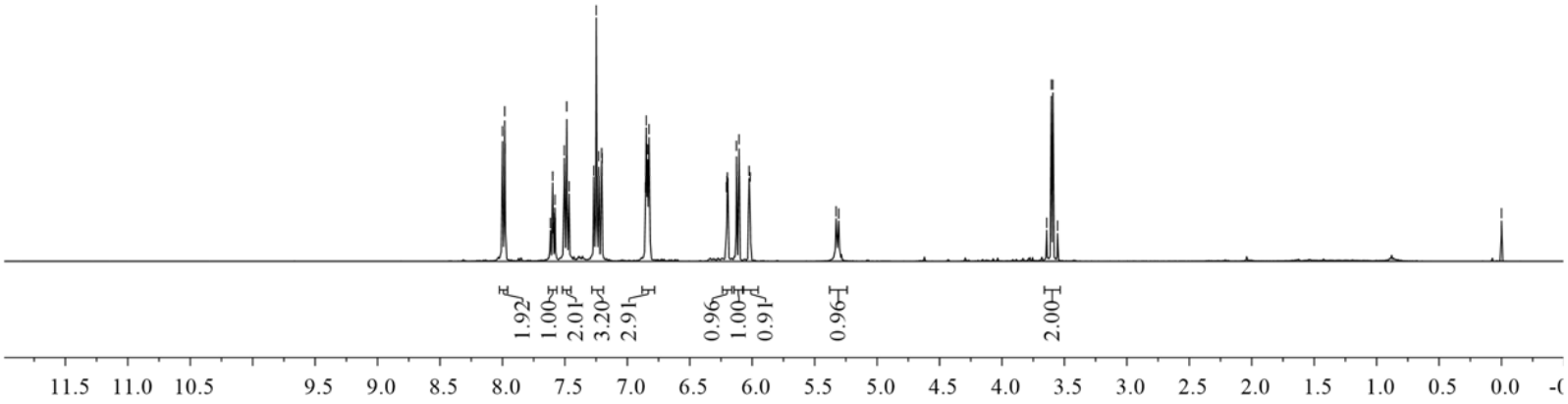
O

3aq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6.0
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1.0
0.5
0.0

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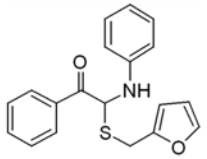
24.58



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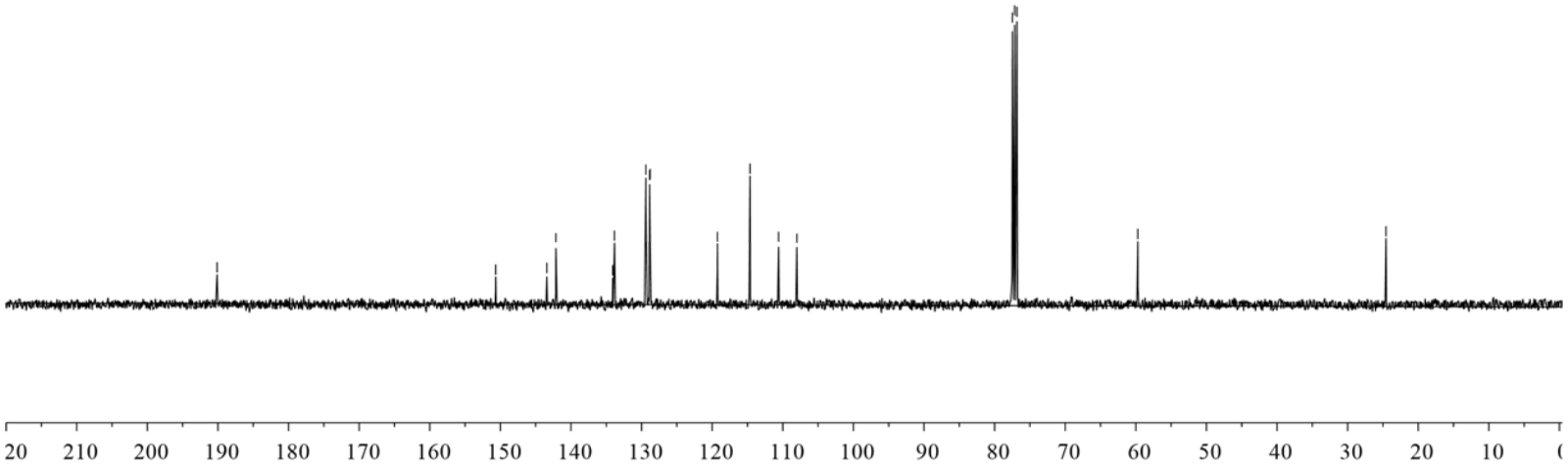


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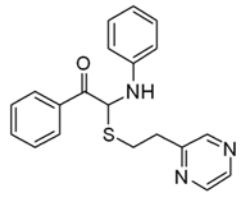
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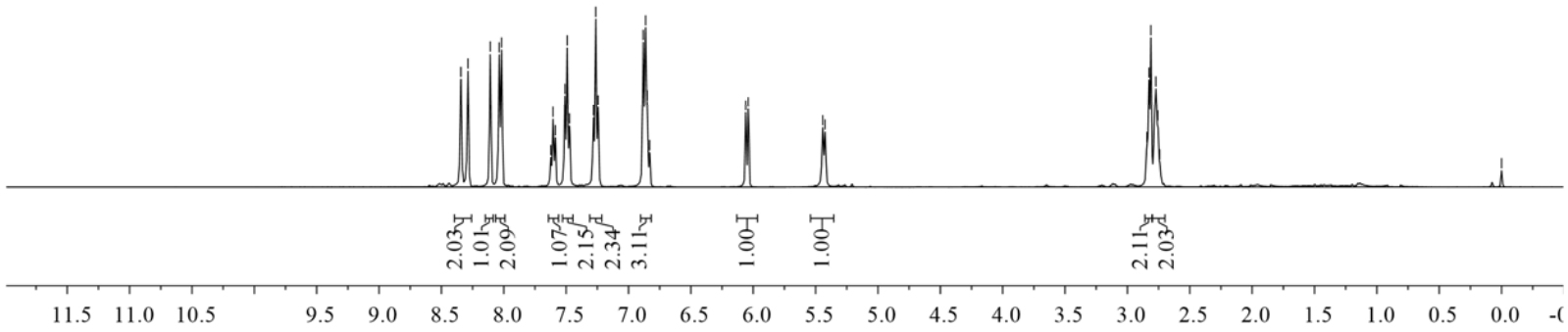
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2.11
2.03
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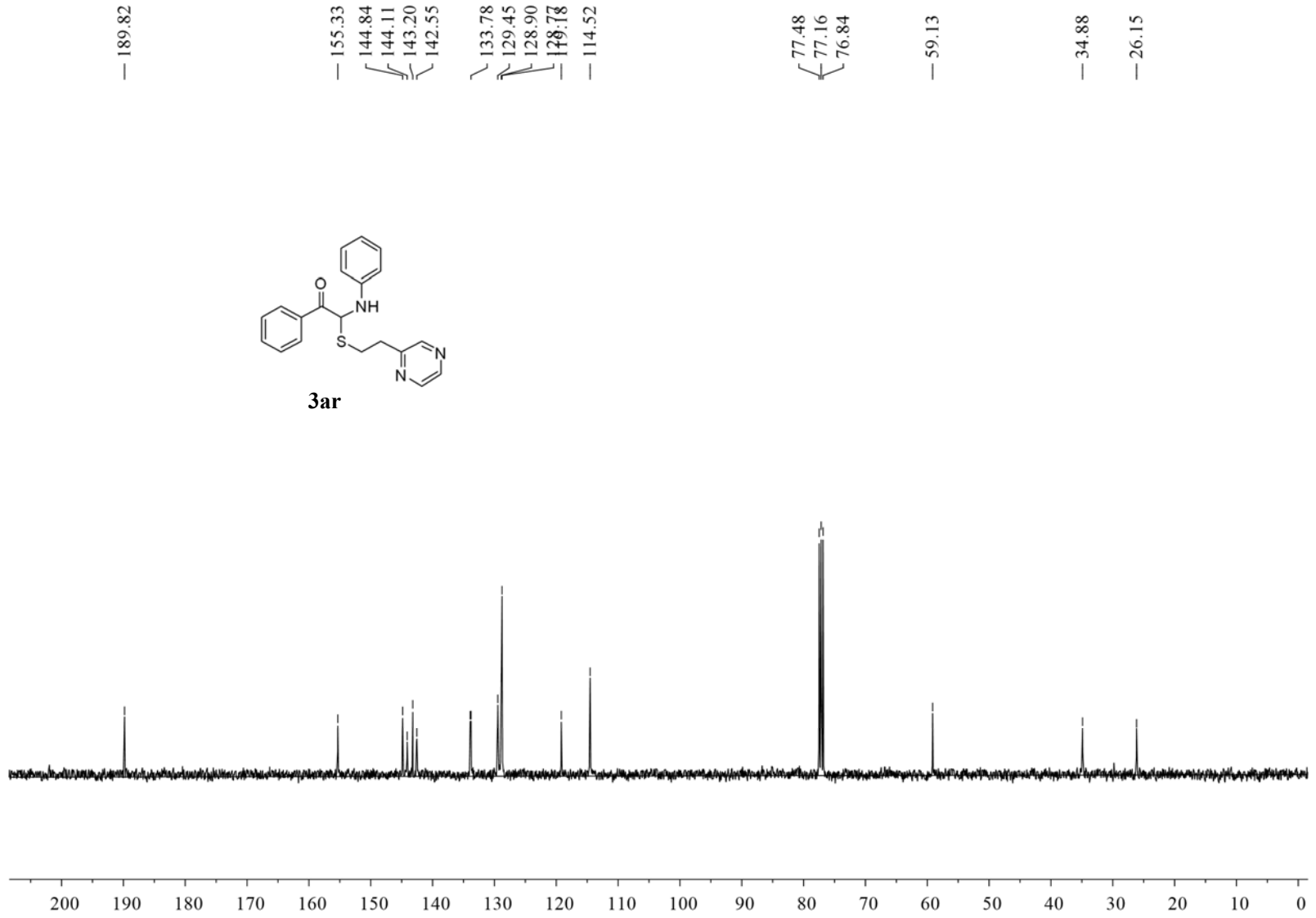
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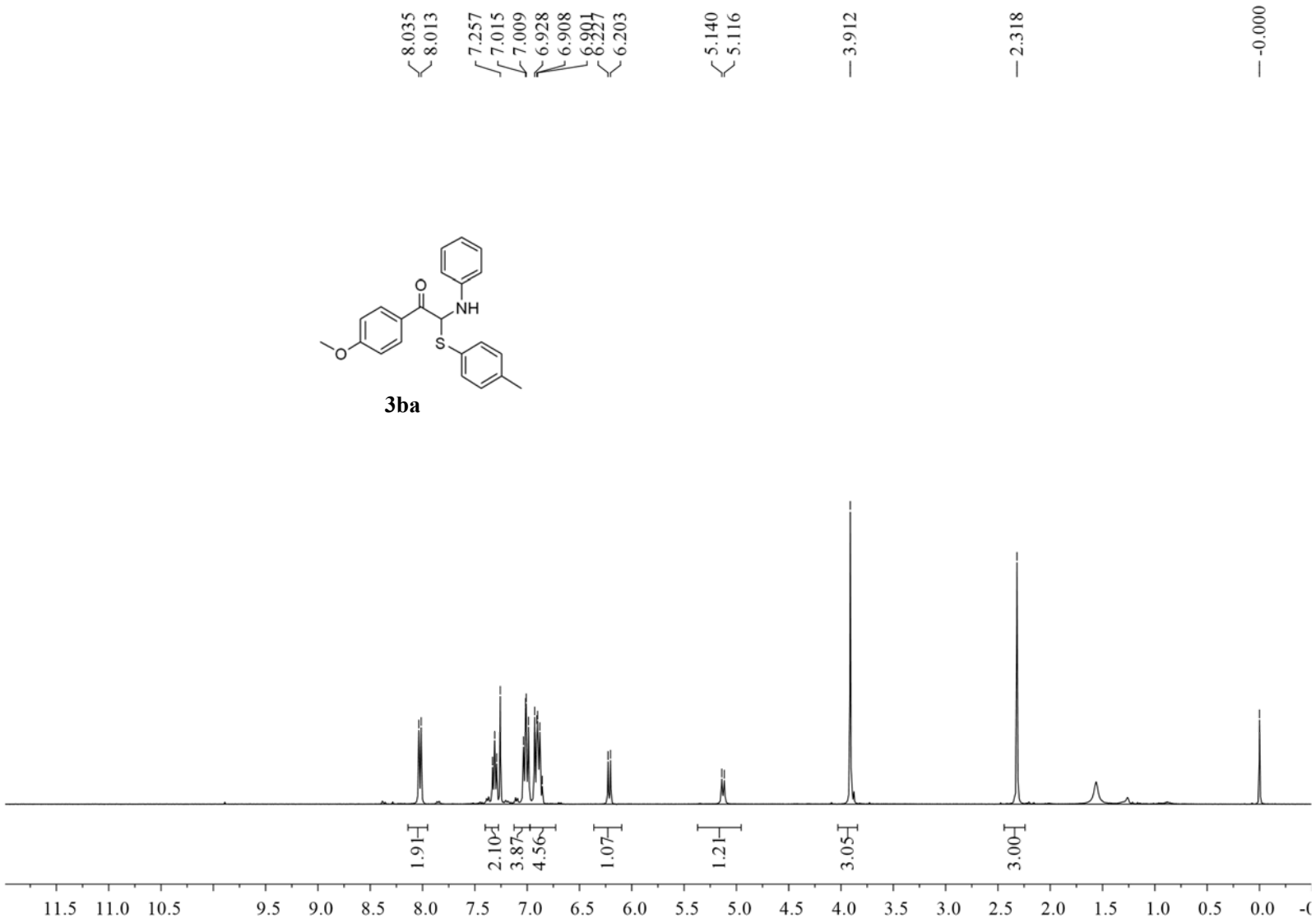
3ar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S
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2.10
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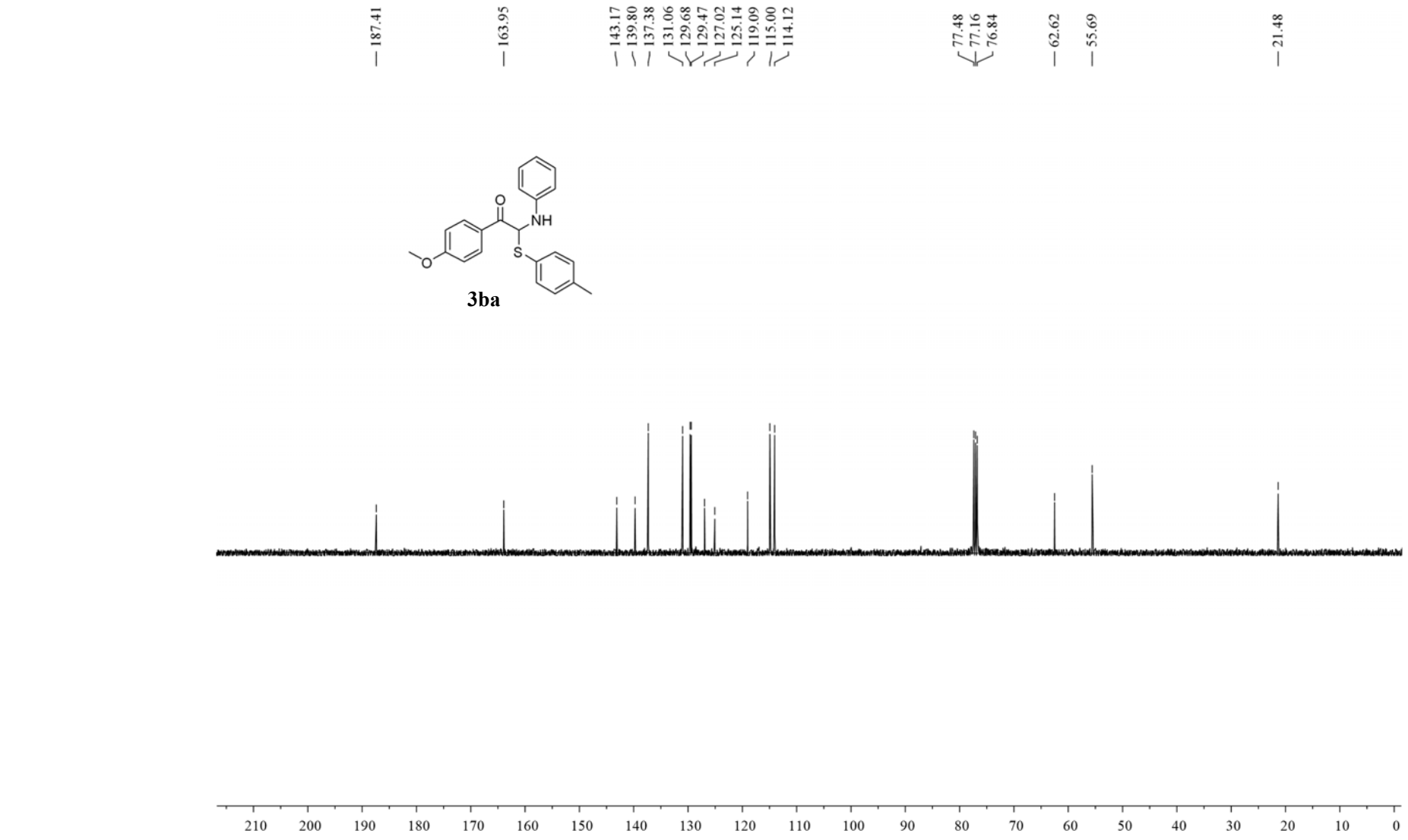
1.07
1.21
3.05
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3ba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3ba
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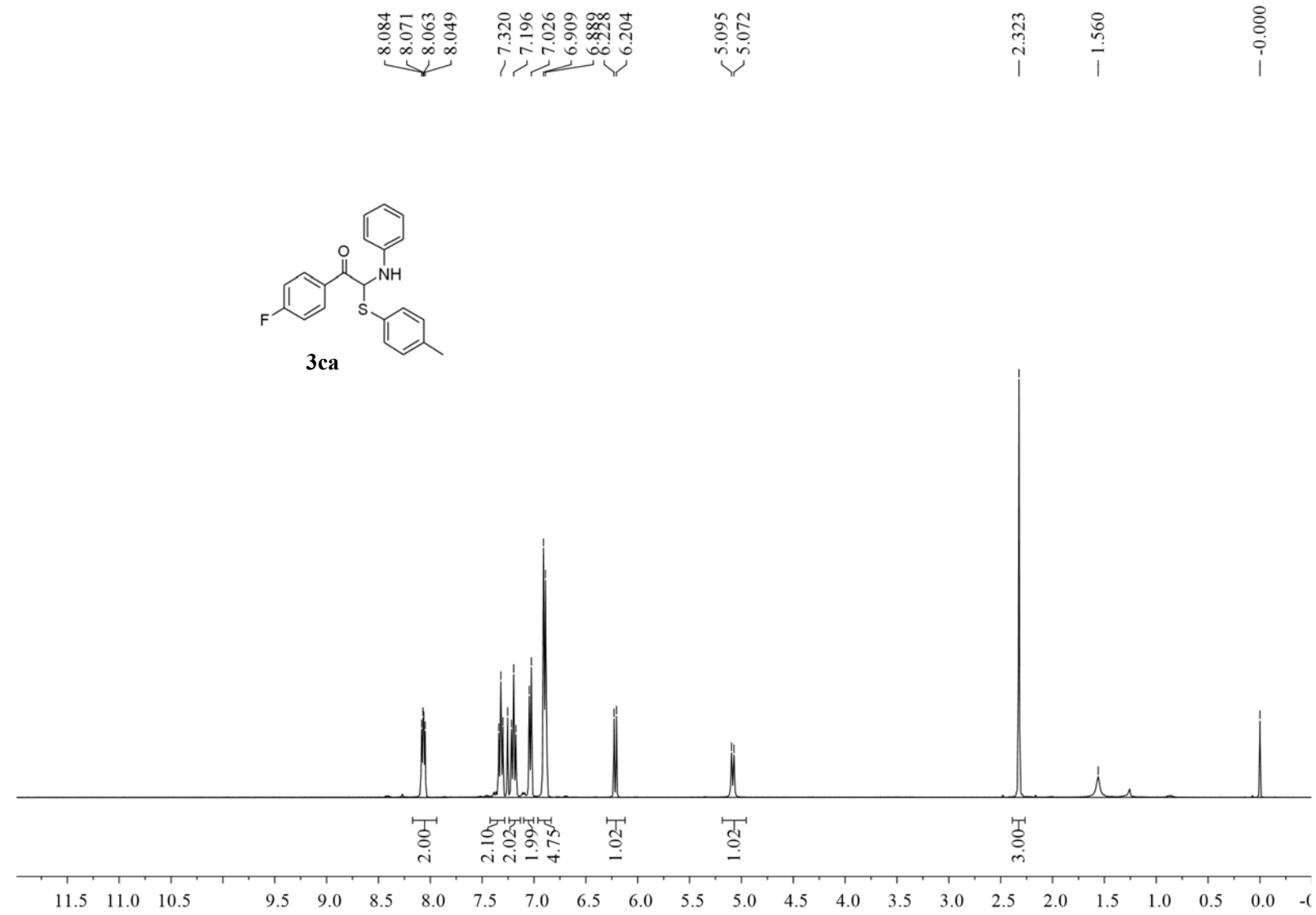
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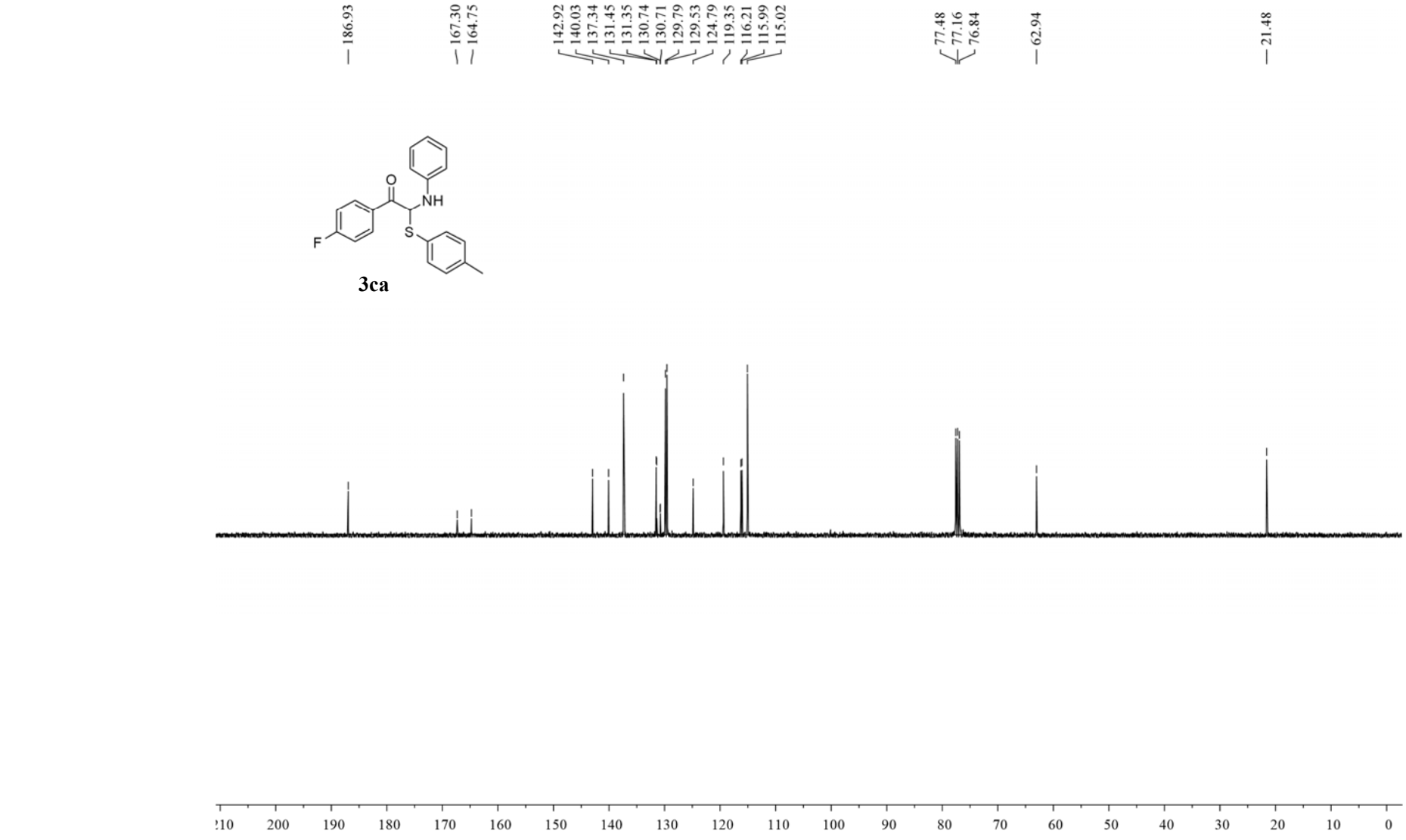
1.99
4.75
1.02
1.02
3.00
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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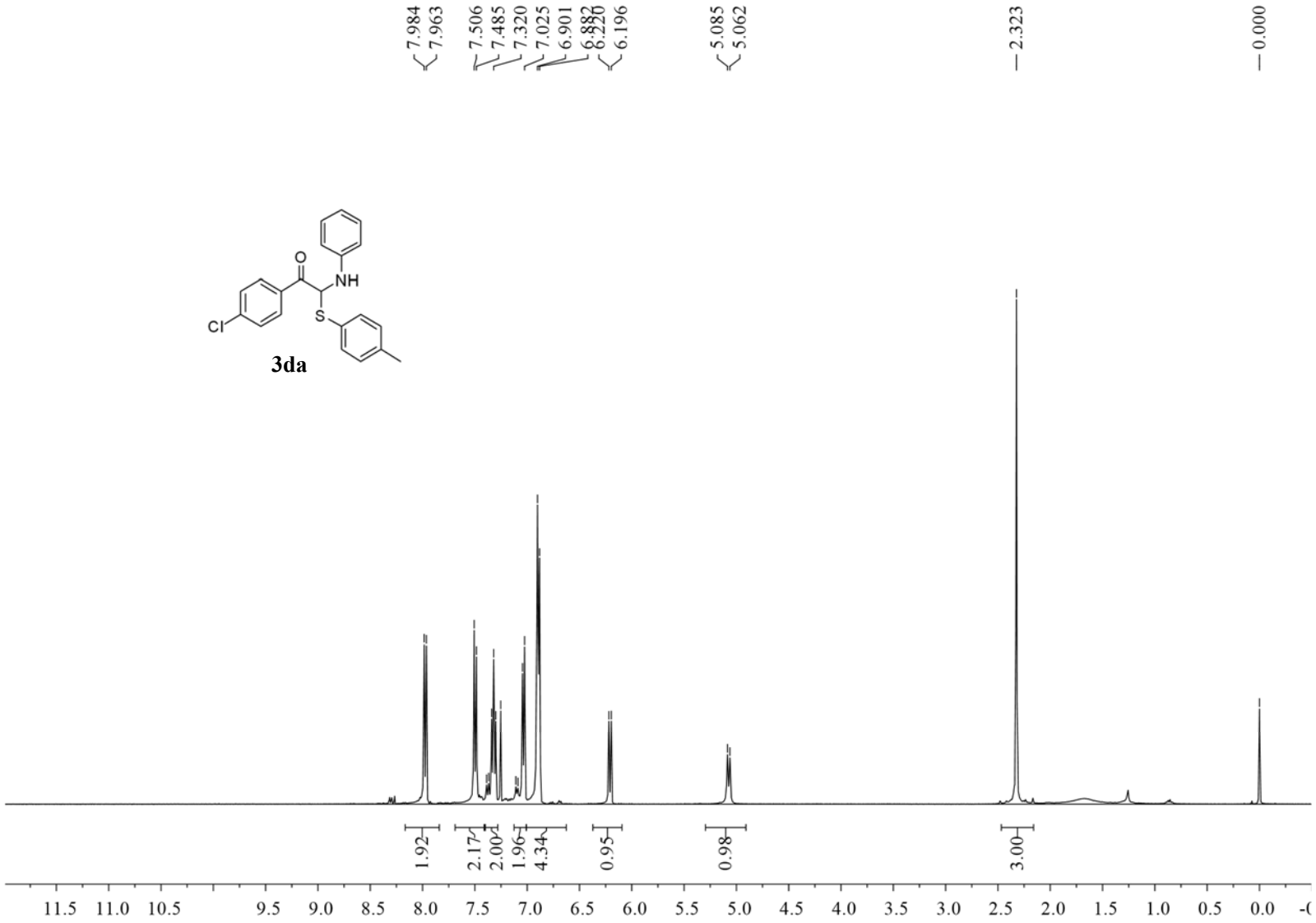
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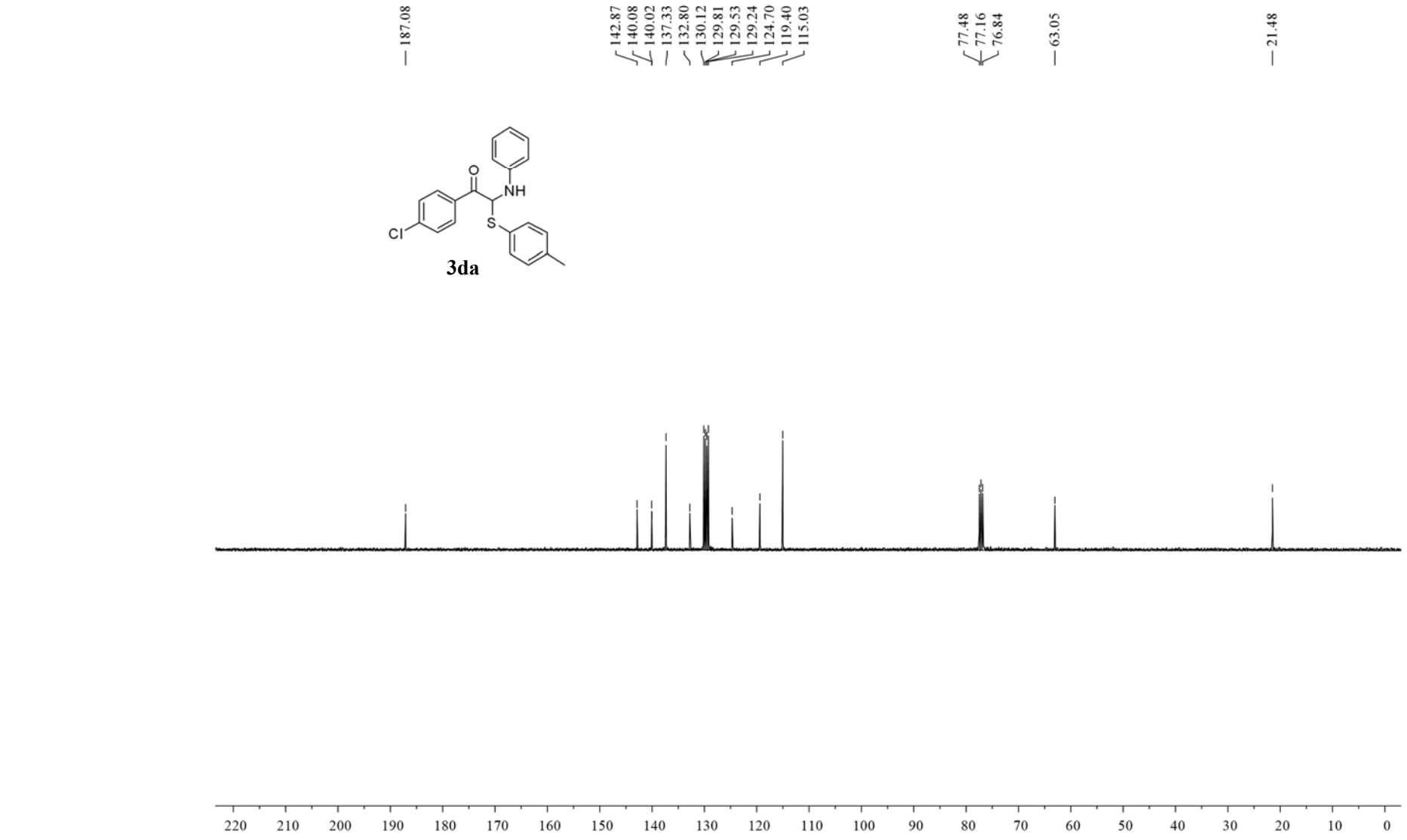
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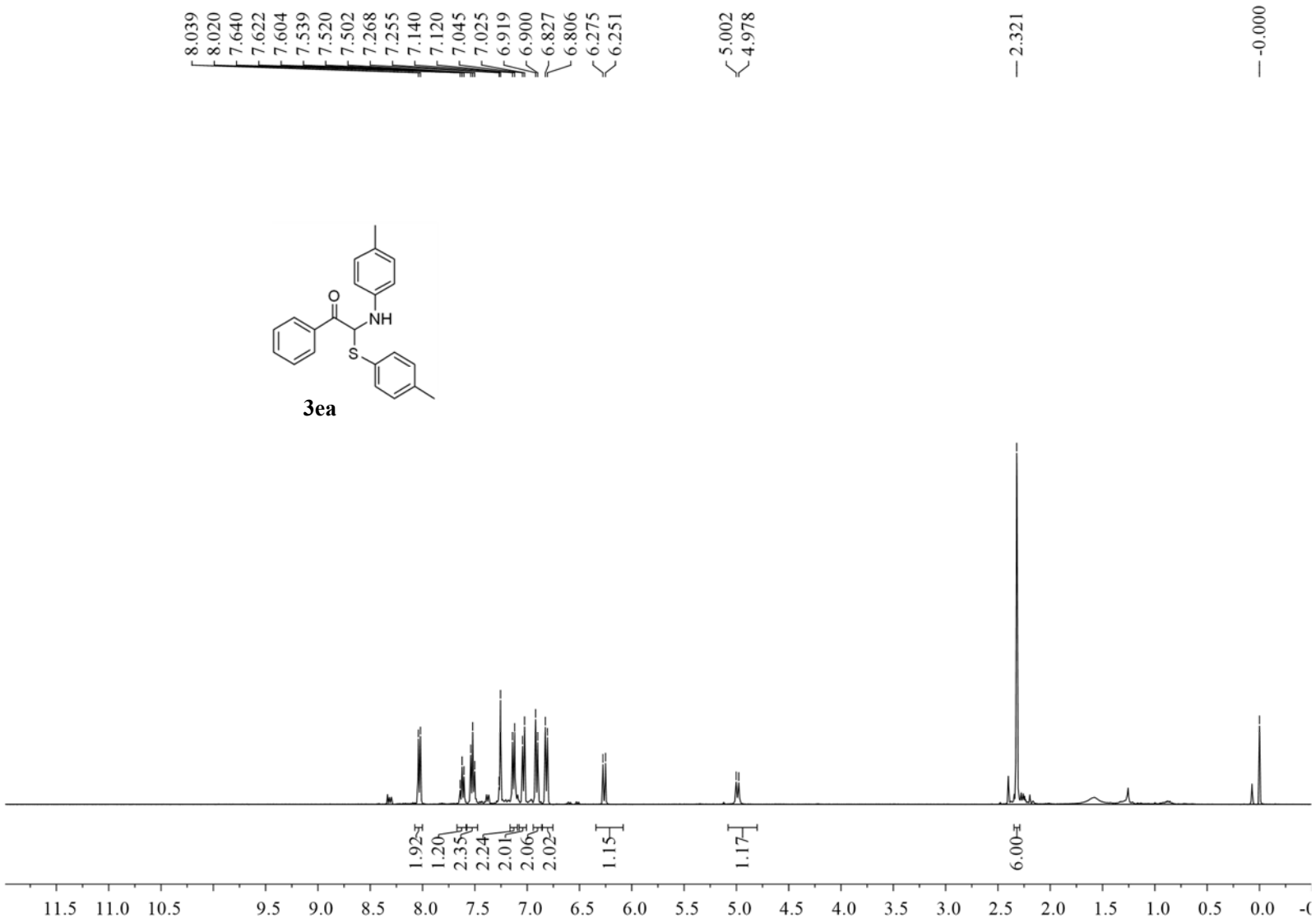
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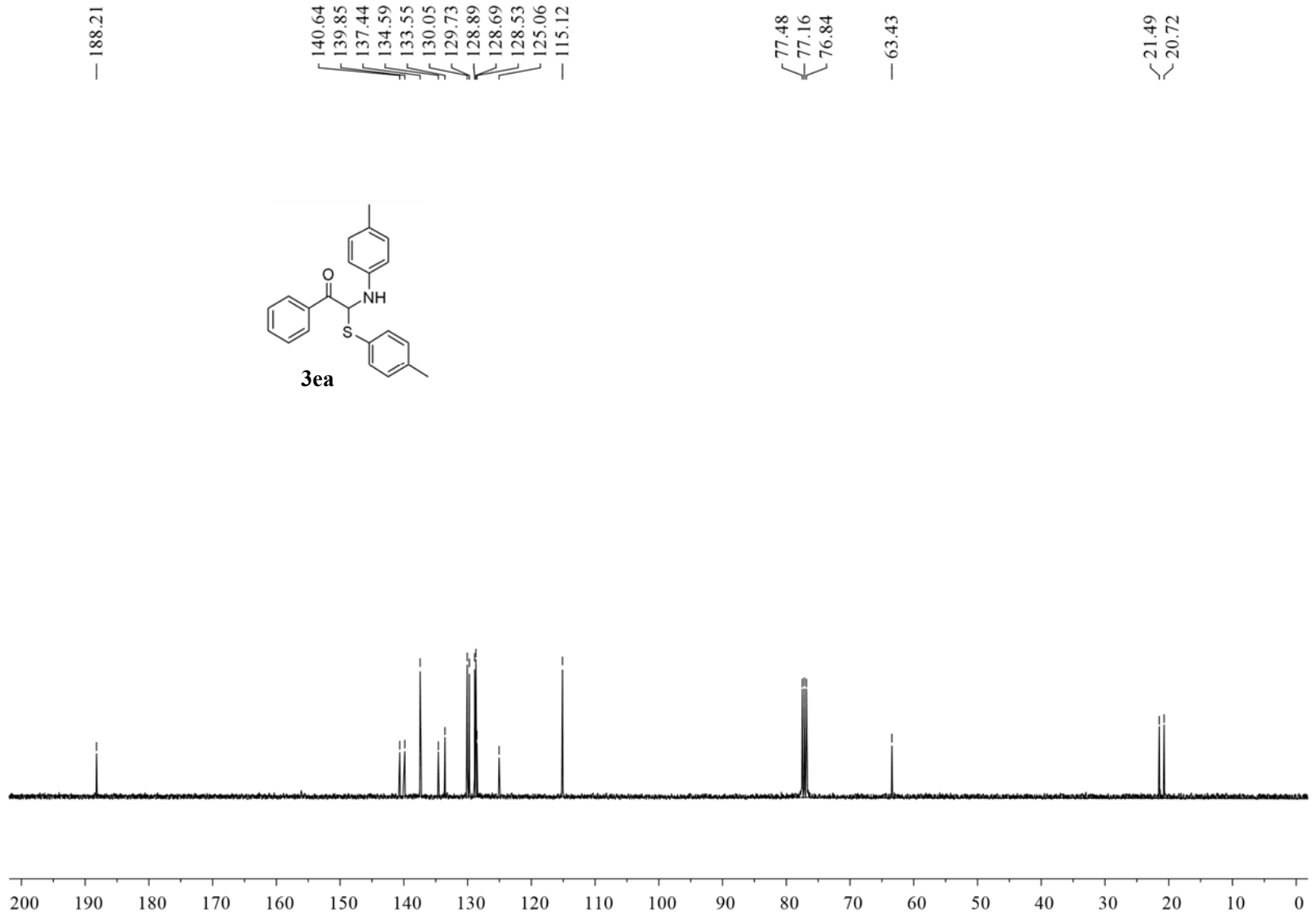
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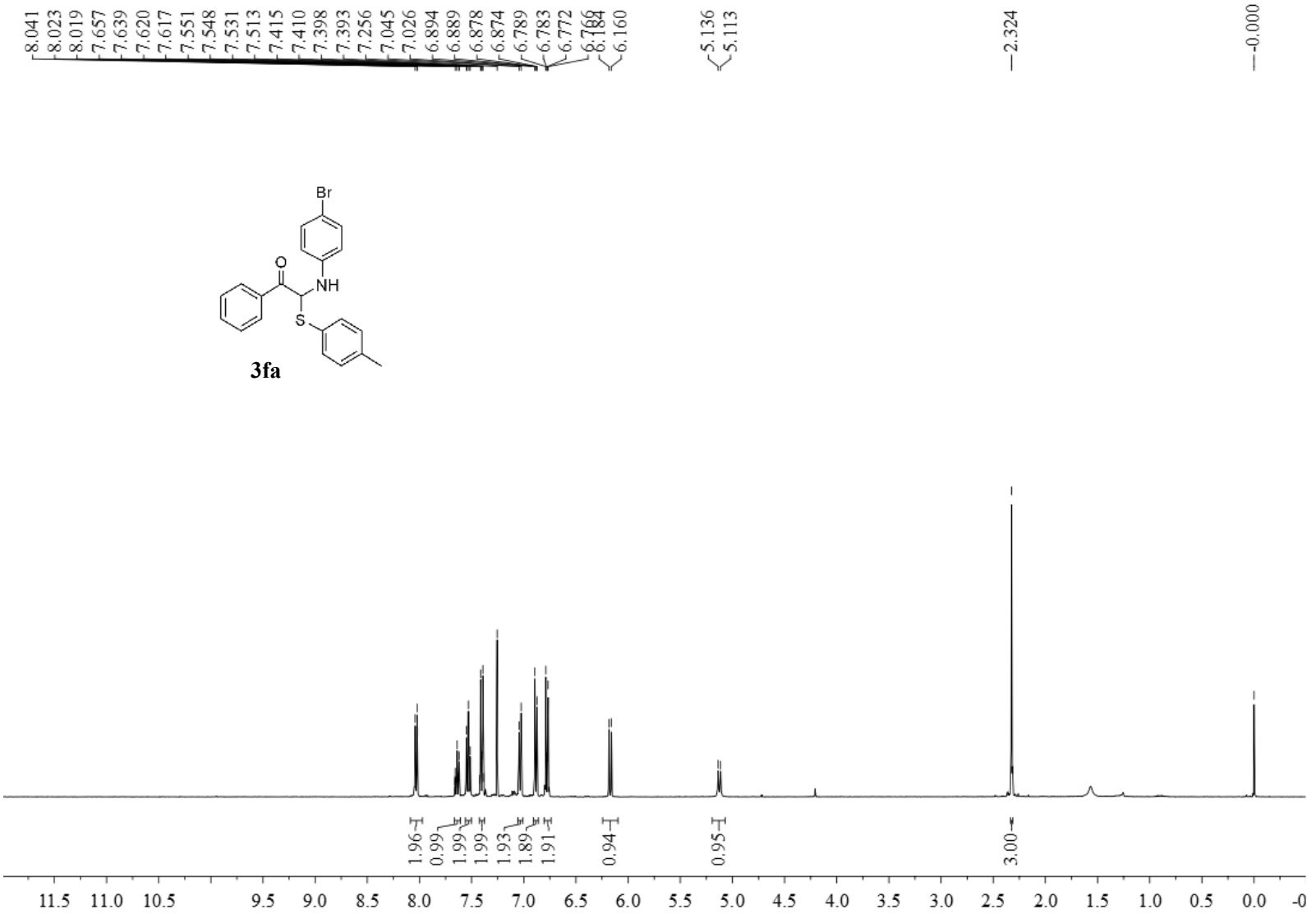
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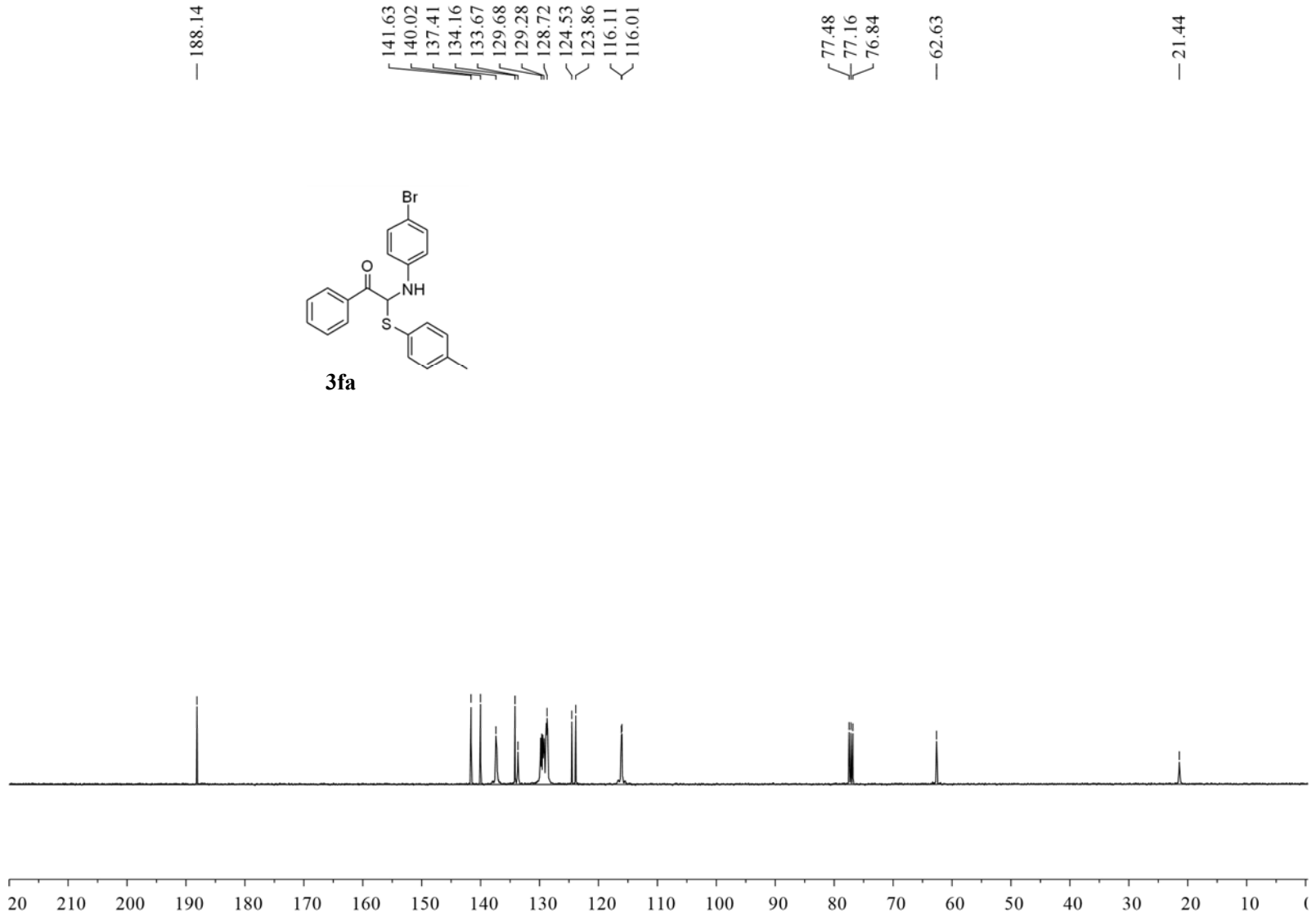
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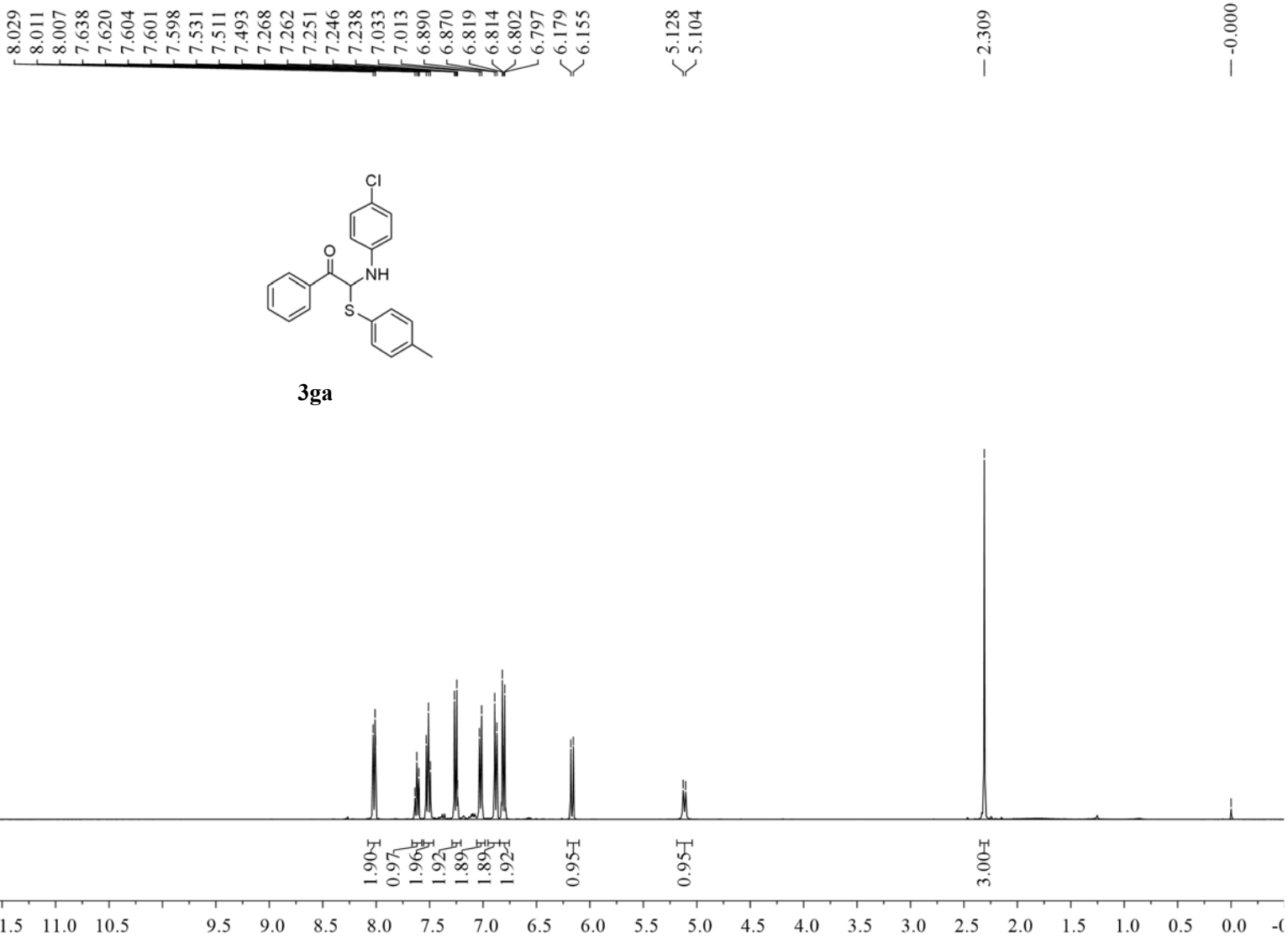
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1.89
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0.95
3.00
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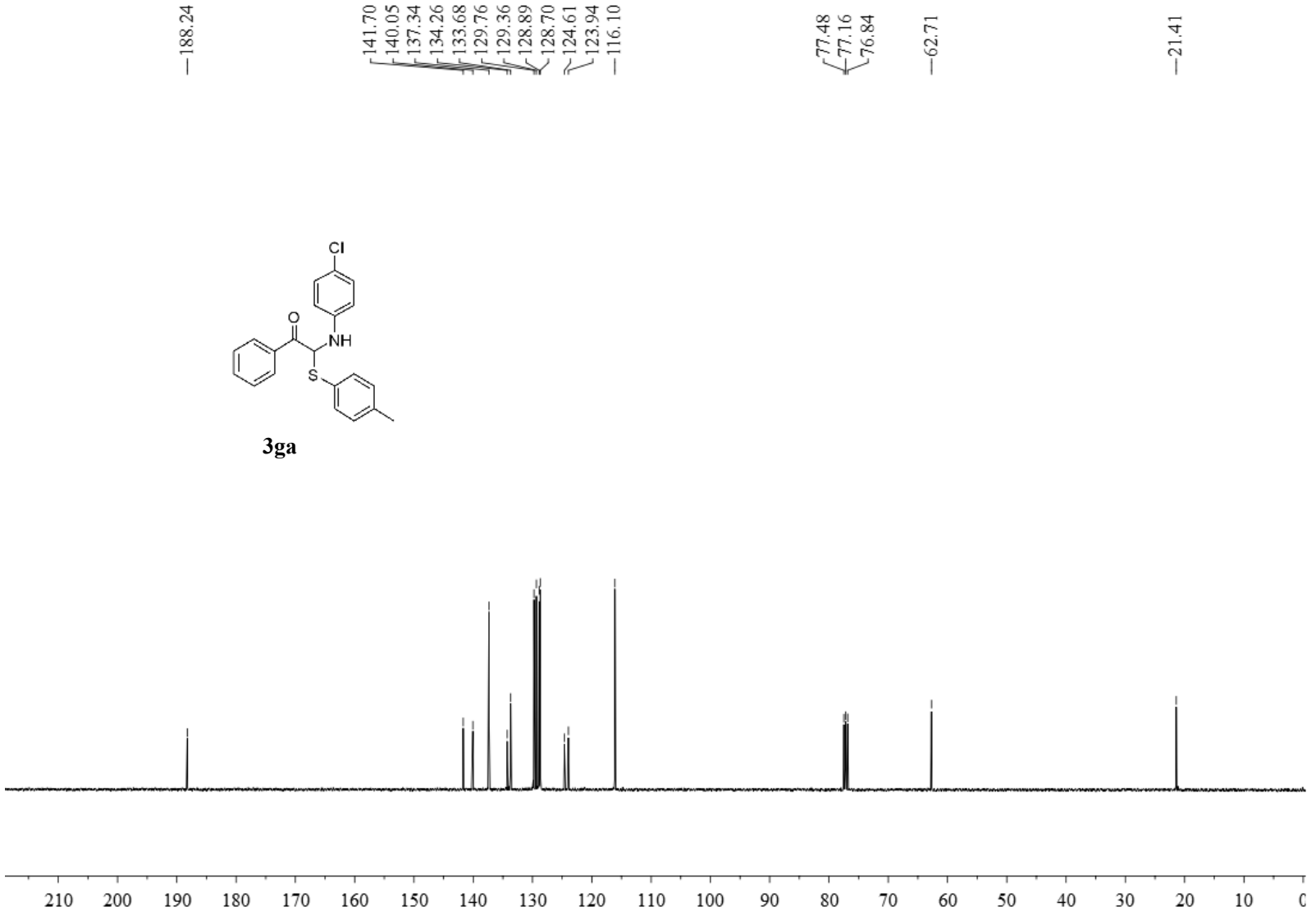
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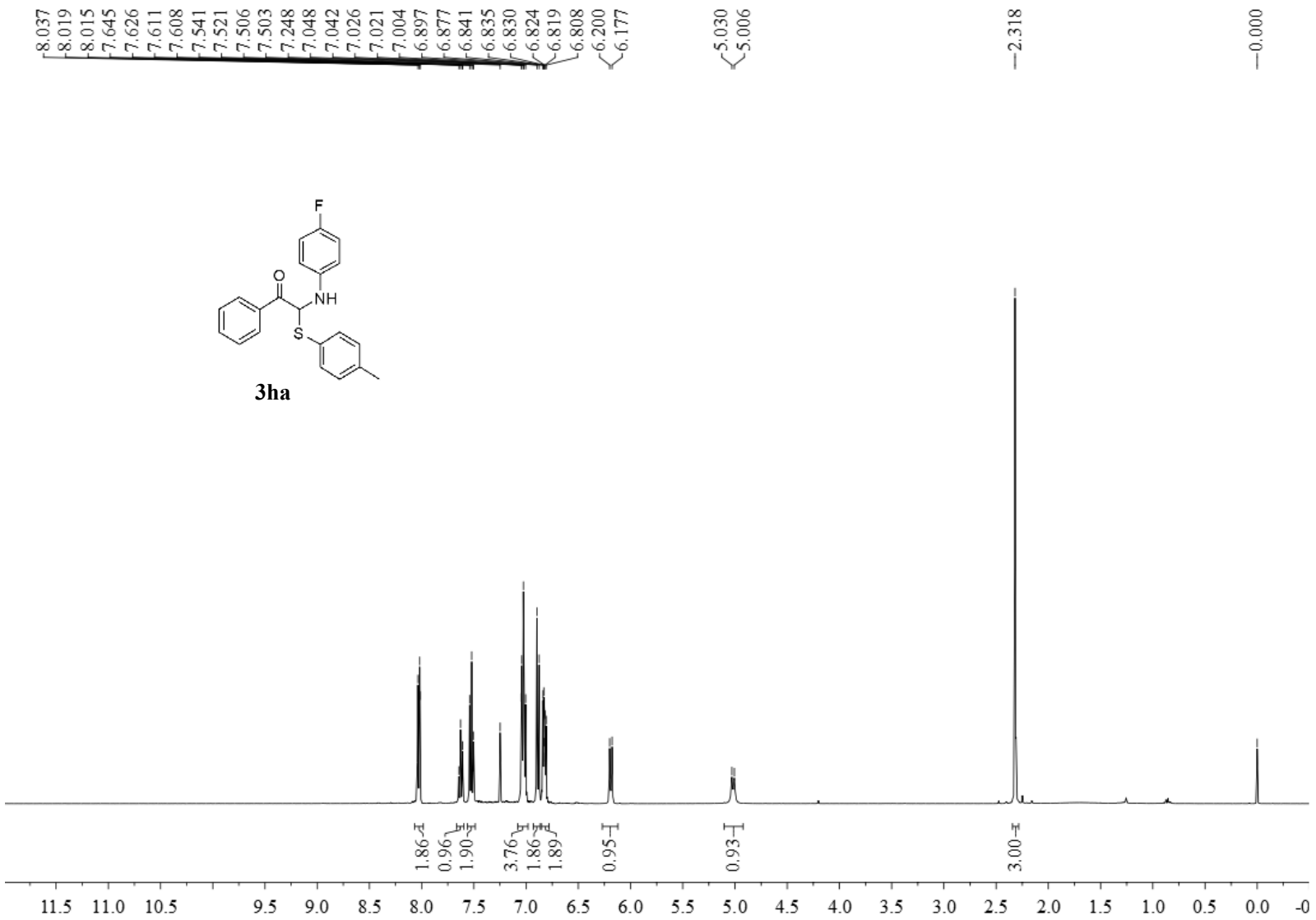
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3.00
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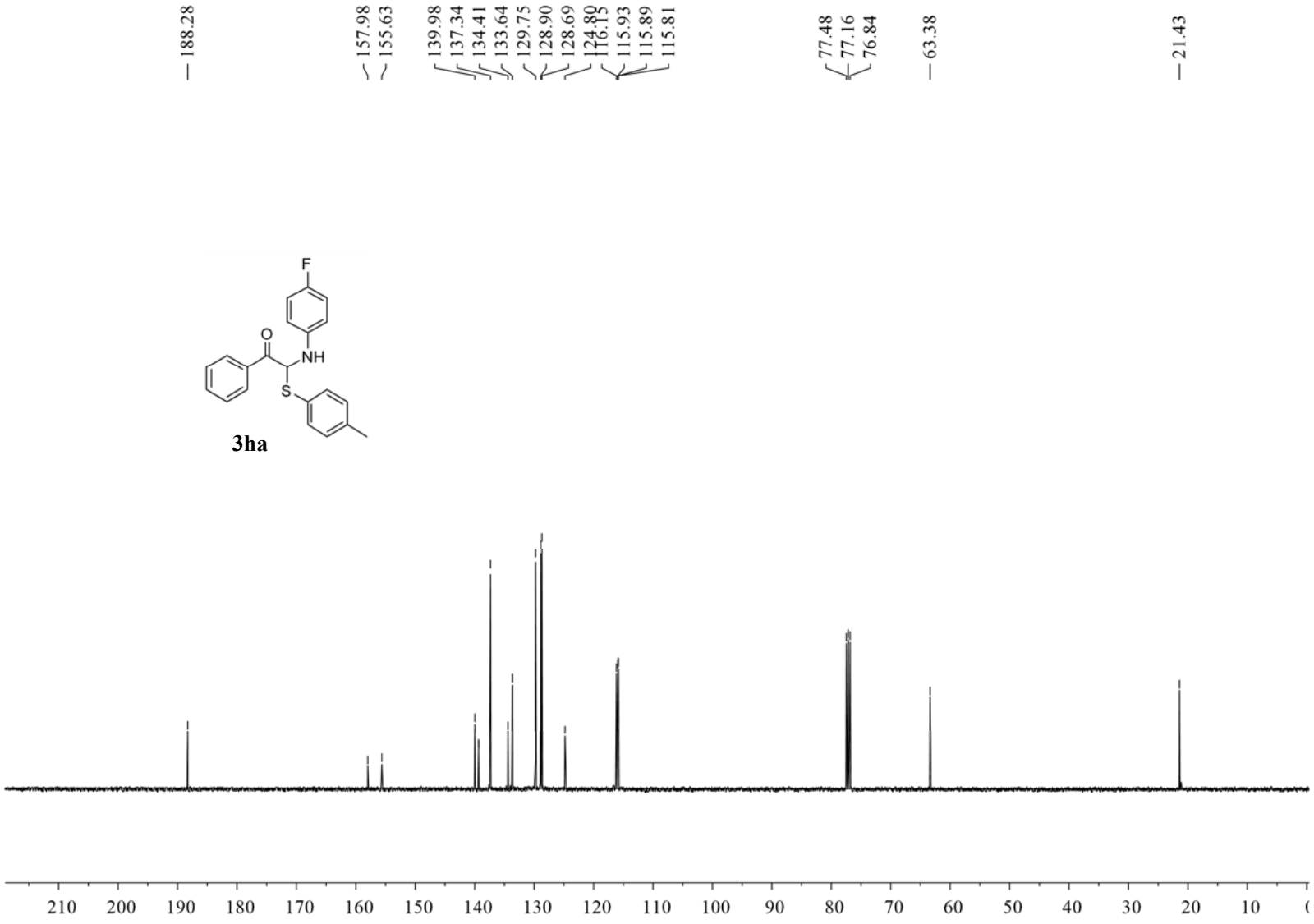
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O
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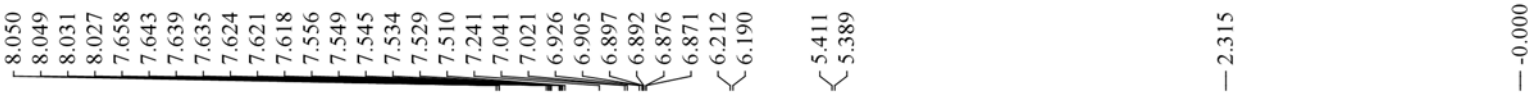
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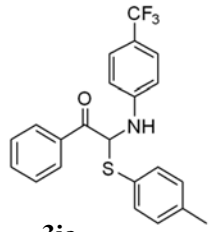
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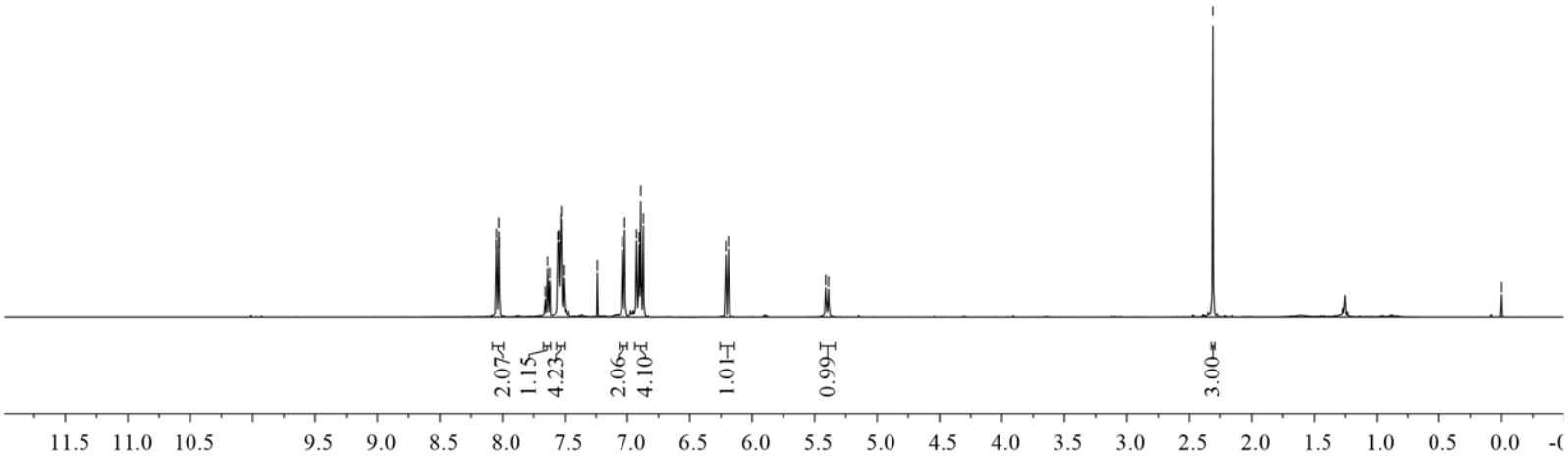
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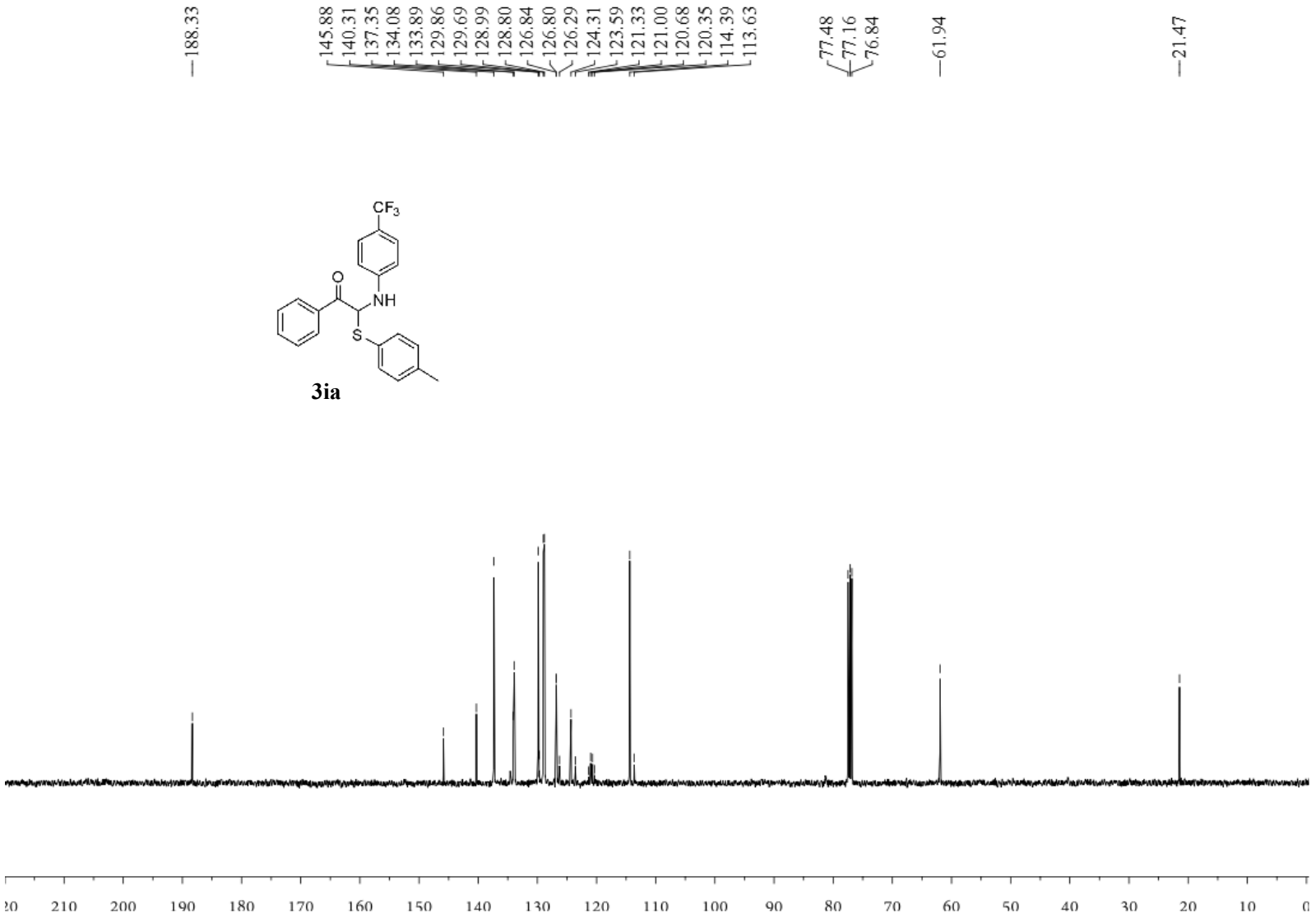
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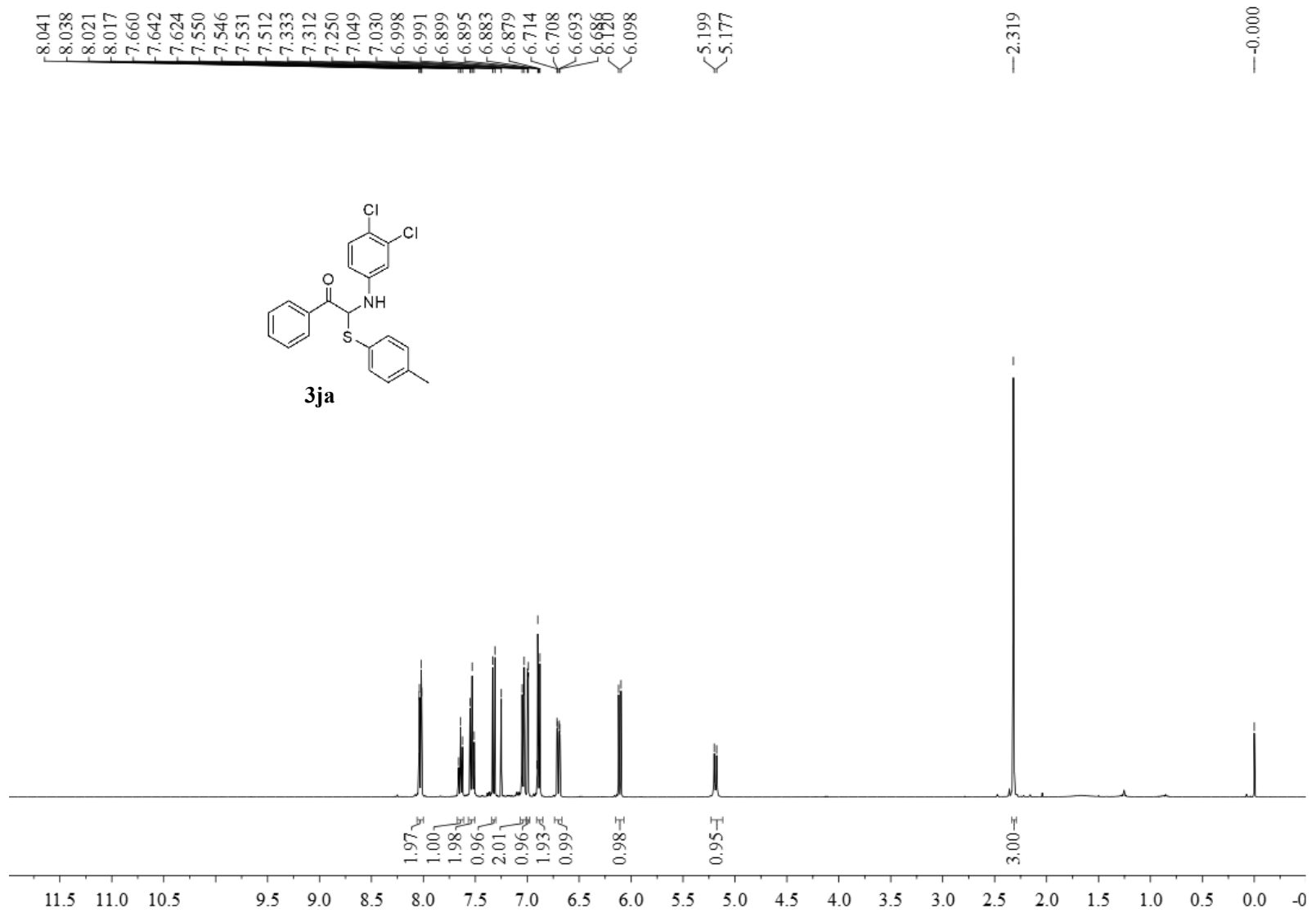
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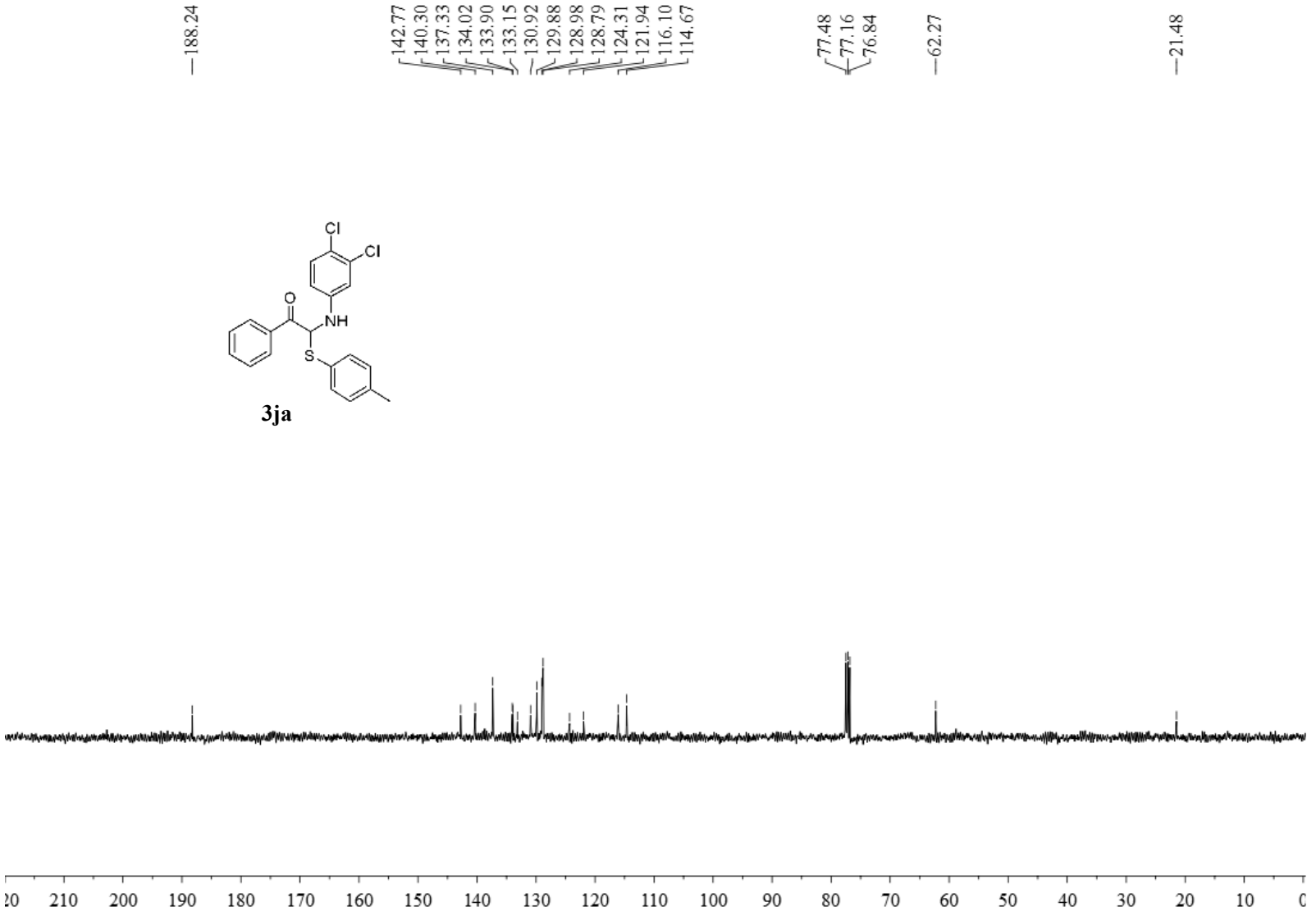
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Cl
Cl
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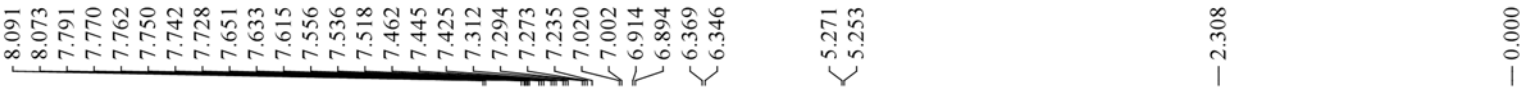
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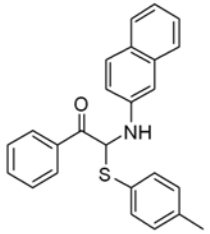
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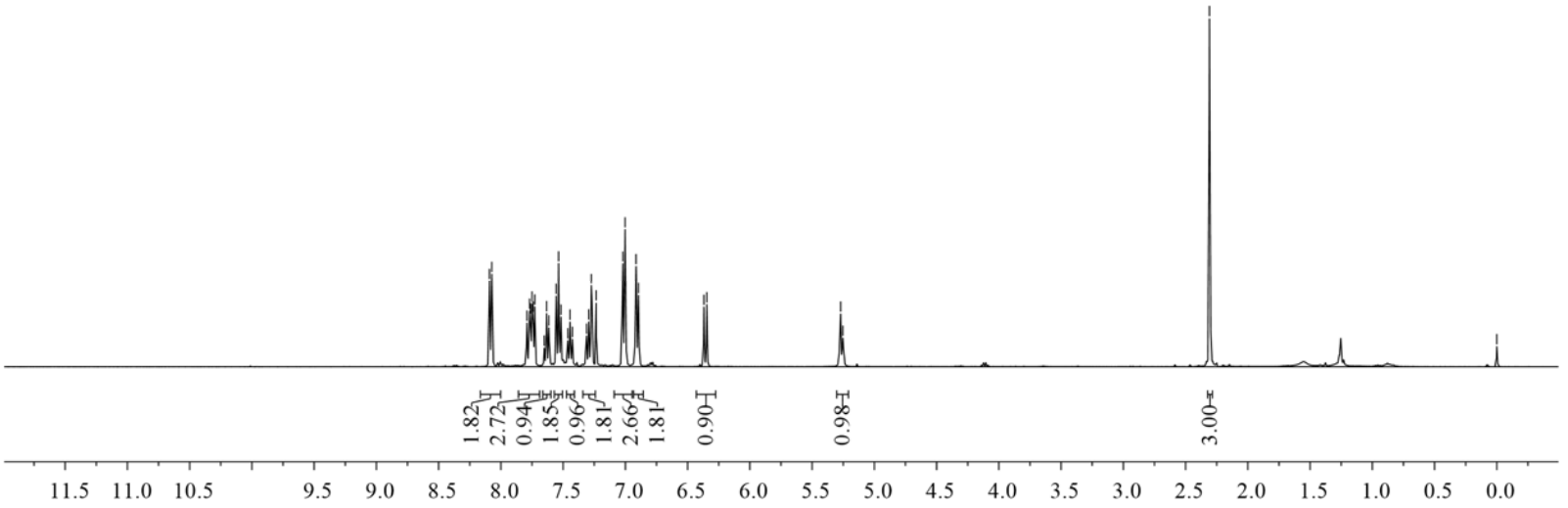
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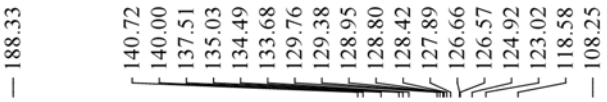
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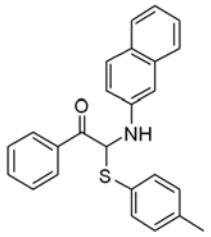
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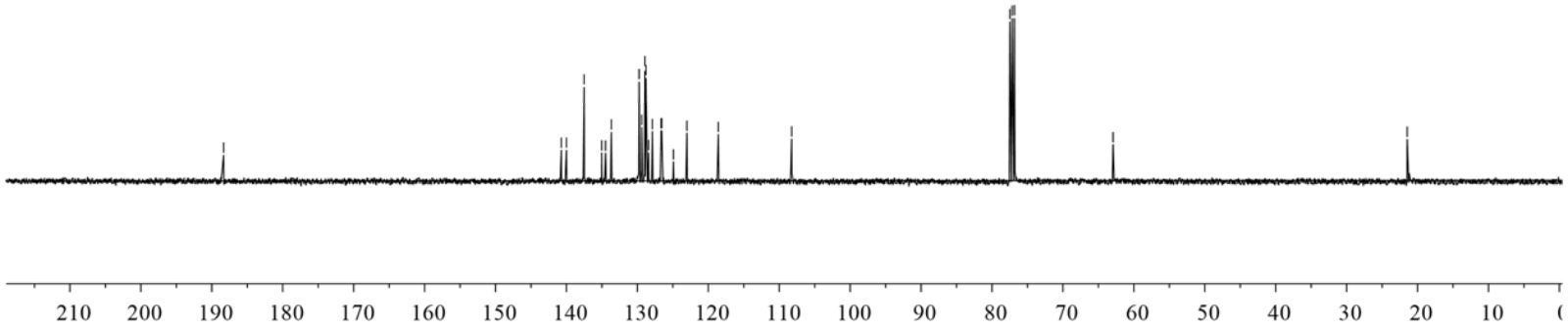
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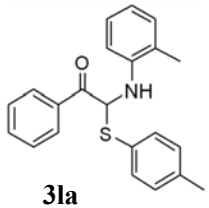
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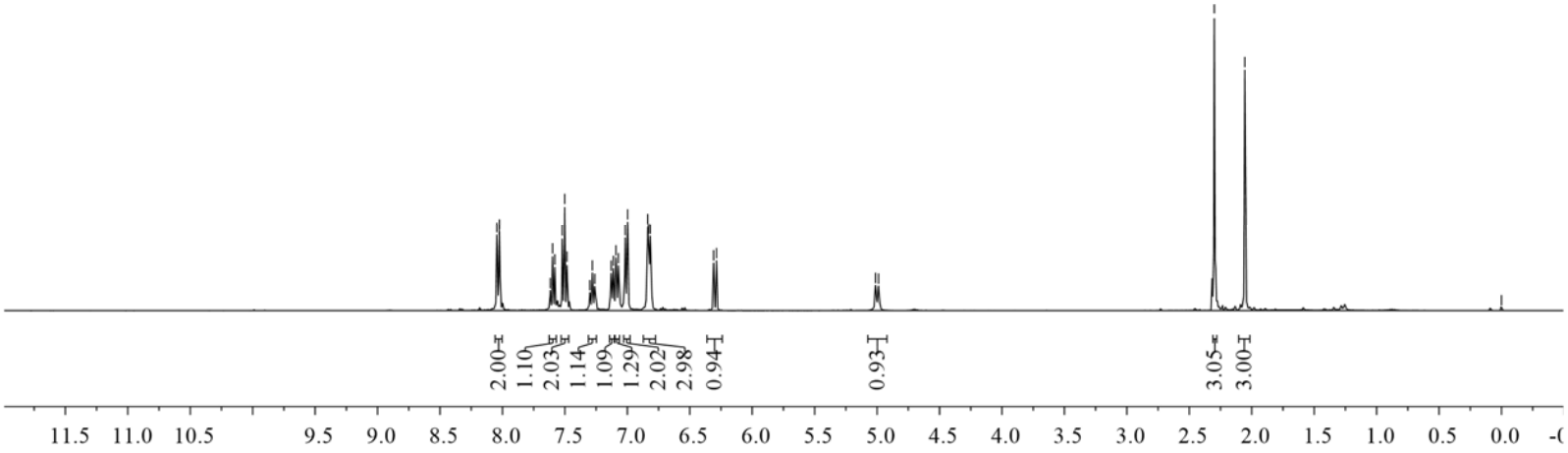
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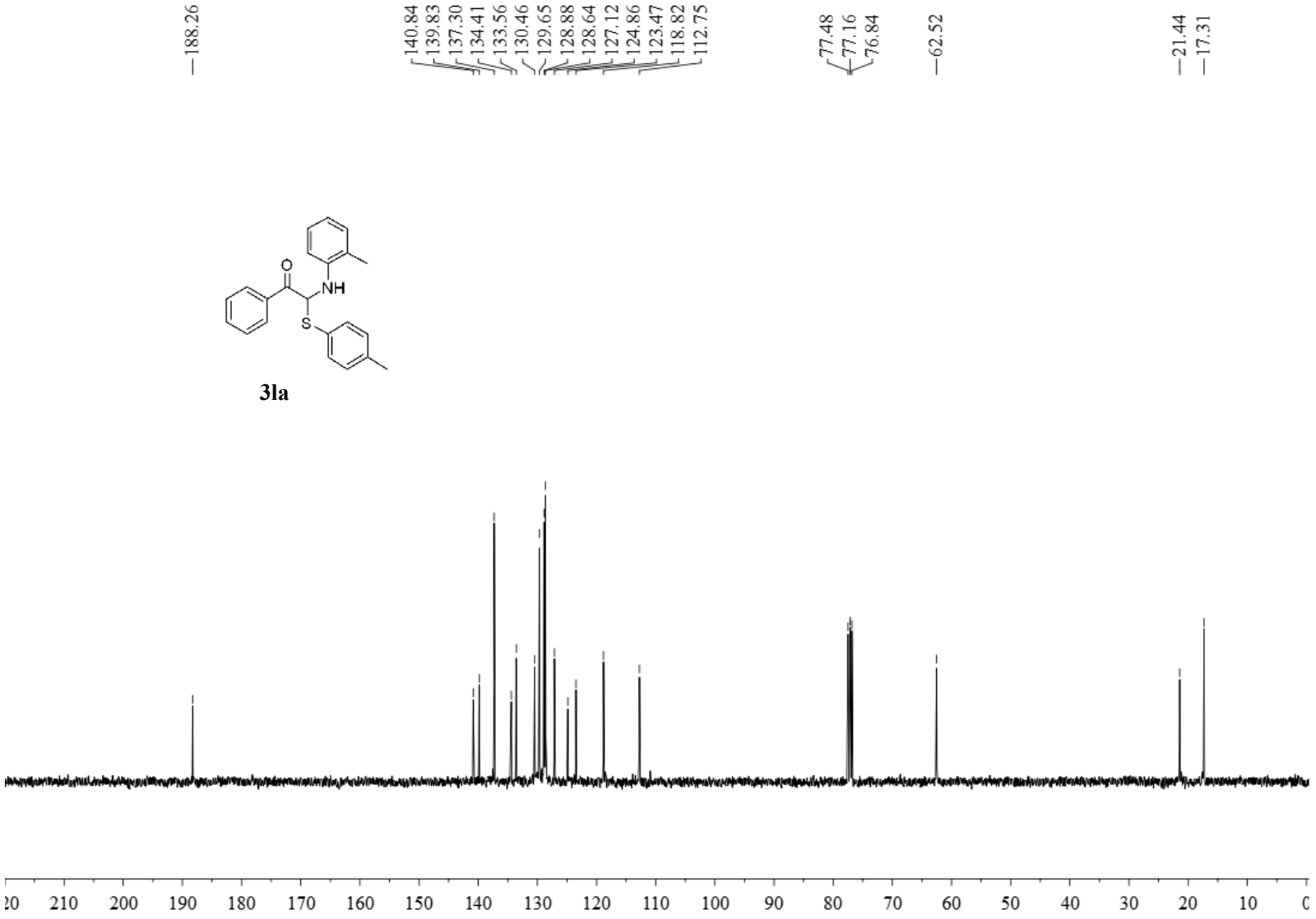
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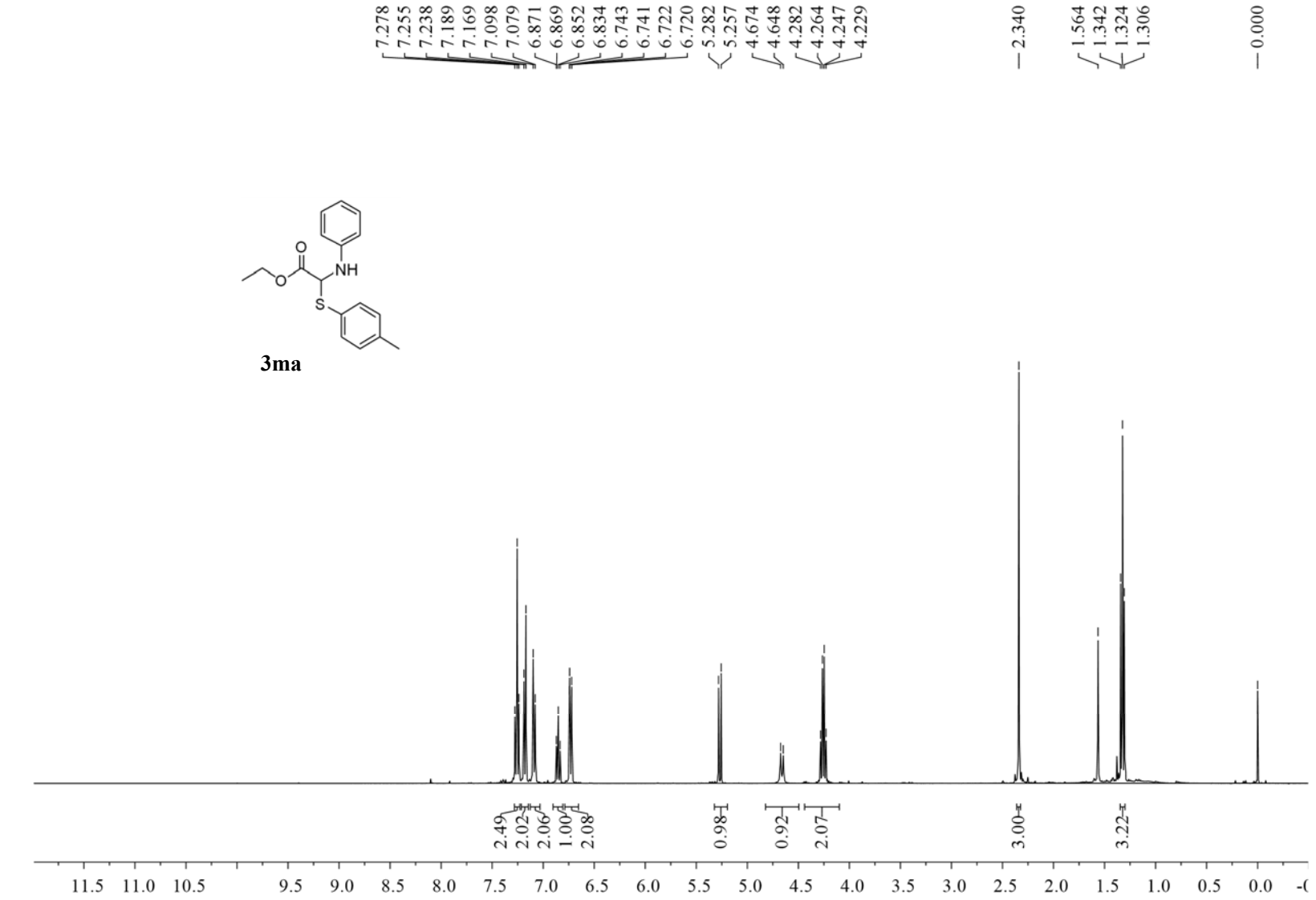
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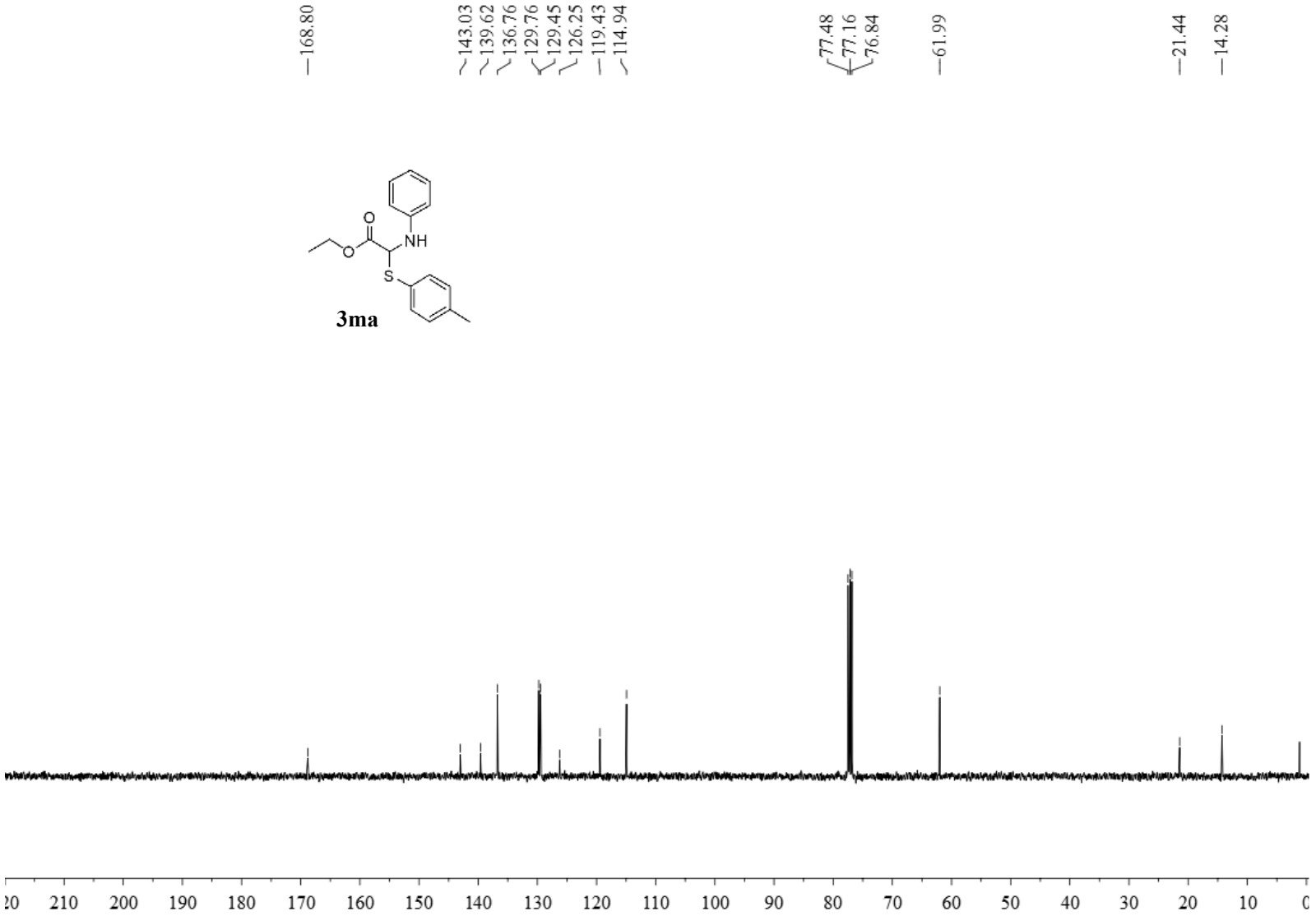
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