Supplementary Information

For

Visible light-mediated oxidative quenching reaction to electron-rich epoxides: highly regioselective synthesis of α-bromo (di)ketones and mechanism study

Lin Guo,[†] Chao Yang,[†] Lewei Zheng, [†] Wujiong Xia[*,†,‡]

[†]*State Key Lab of Urban Water Resource and Environment, the Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080*

[‡]*State Key Lab of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*

E-mail: xiawj@hit.edu.cn

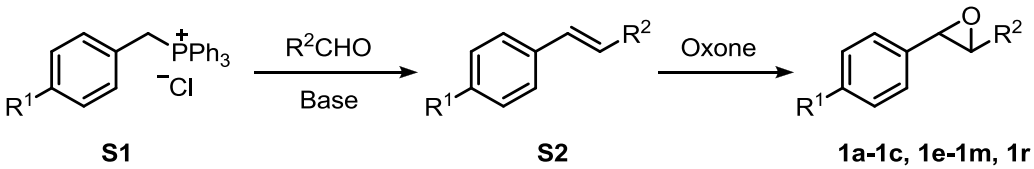
Contents

1. General Information

All reagents were purchased from commercial sources unless otherwise noted. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by treatment with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating/or by staining with a solution of 12 g 2,4-dinitrophenylhydrazine in 60 mL conc. H_2SO_4 , 80 mL H_2O and 200 mL 95% EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for 1H NMR spectra were reported in δ ppm referenced to an internal $SiMe_4$ standard. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the $CDCl_3$ triplet at 77.16 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent.

2. Preparation and Characterization of Substrates

1) Synthesis of **1a-1c, 1e-1m, 1r**



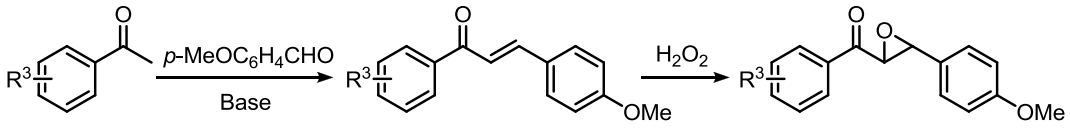
S1 **S2** **1a-1c, 1e-1m, 1r**

Substrates **1a-1c, 1e-1m, 1r** were prepared from the corresponding alkenes by using Oxone as epoxidation reagent. Take **1a** as an example. To a mixture of *p*-$MeOC_6H_4CH_2PPh_3Cl$ (2.5 g, 5.98 mmol) and LiOH (195.7 mg, 8.15 mmol) in THF (40 mL) was added benzaldehyde (576.6 mg, 5.44 mmol). The reaction mixture was stirred at 70 ℃ for 5 h. The reaction mixture was cooled to r.t. and then quenched with water. The mixture was extracted with EtOAc (3 × 40 mL) and the combined organic layers were washed with brine, dried, filtered and concentrated *in vacuo*. The product was purified by recrystallization to afford (E)-1-methoxy-4- styrylbenzene

(**S2**) as white solid.

To a solution of **S2** (210.1 mg, 1.0 mmol) in acetone/acetonitrile (20 mL, 1:1) was added saturated $NaHCO_3$ solution (10 mL) and then cooled to 0 ℃. To this solution was added a water solution (10 mL) of potassium monopersulfate triple salt (1.35 g, 2.2 mmol), the mixture was stirred for 5 h at 0 ℃ before it was quenched by water, and extracted with ethyl acetate (3 × 30 mL). The organic layer was washed with brine (50 mL), dried over anhydrous $NaSO_4$, and concentrated *in vacuo*. The product was purified by column chromatography (hexanes: EtOAc = 30:1) to afford 205.7 mg (91%) of **1a** as white solid.

2) Synthesis of **1d, 1n-1q**

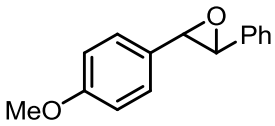


Substrates **1d**, **1n-1q** were prepared from the corresponding chalcones by utilizing H_2O_2 as epoxidation reagent. Take **1d** as an example. To a mixture of *p*-$MeOC_6H_4CHO$ (1.0 g, 7.35 mmol) and phenyl methyl ketone (882.7 mg, 7.35 mmol) in MeOH (15 mL) was added a 5N NaOH solution (4.5 mL, 22.05 mmol). The reaction mixture was stirred at r.t. for 2 h, and then the solvent was removed *in vacuo*. The mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with brine, dried, filtered and concentrated *in vacuo*. The product was purified by recrystallization or column chromatography to afford (E)-3-(4-methoxyphenyl)-1 -phenylprop-2-en-1-one (**S4**) as yellow solid.

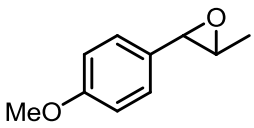
To a solution of **S4** (119 mg, 0.5 mmol) in MeOH (10 mL) was added a 5N NaOH solution (0.15 mL, 0.75 mmol) and hydrogen peroxide (30% in water, 0.15 mL). The reaction mixture was stirred at room temperature for 15 min and then the solvent was removed *in vacuo*. The mixture was extracted with EtOAc (3 × 10 mL), washed with brine, dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (hexanes: EtOAc = 16:1) to afford 108.0 mg (80%) of **1d** as white

solid.

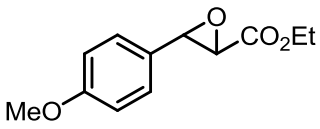
3) Characterization of **1a** – **1r**



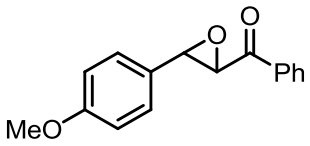
trans-2-(4-methoxyphenyl)-3-phenyloxirane (1a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.33 (m, 5H), 7.28 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 3.85 (d, J = 2.0 Hz, 1H), 3.83-3.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 137.4, 129.3, 128.7, 128.4, 127.0, 125.6, 114.2, 62.9, 62.8, 55.5.



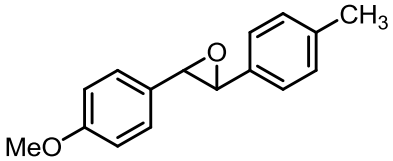
trans-2-(4-methoxyphenyl)-3-methyloxirane (1b): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.52 (d, J = 1.5 Hz, 1H), 3.03 (qd, J = 5.1, 2.0 Hz, 1H), 1.43 (d, J = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 129.8, 126.9, 117.0, 59.5, 58.8, 55.3, 17.9.



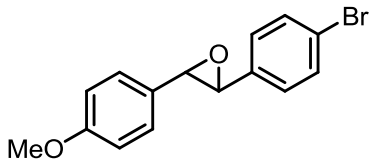
ethyl trans-3-(4-methoxyphenyl)oxirane-2-carboxylate (1c): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 4.32 – 4.23 (m, 2H), 4.04 (d, J = 1.5 Hz, 1H), 3.80 (s, 3H), 3.50 (d, J = 1.7 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 160.4, 127.4, 127.0, 114.2, 61.8, 58.0, 56.8, 55.5, 14.3.



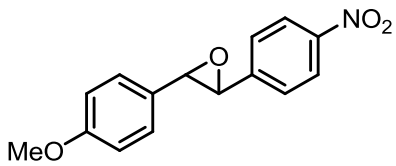
(trans-3-(4-methoxyphenyl)oxiran-2-yl)(phenyl)methanone (1d): ^{1}H-NMR (400 MHz, CDCl3): 8.01 (d, J = 8.2 Hz, 2H), 7.41–7.36(m, 5 H), 6.96–6.94 (m, 2 H), 4.25 (d, J = 1.2 Hz, 1H), 4.07 (d, J = 1.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 160.6, 133.4, 131.0, 129.1, 127.8, 127.6, 115.0, 114.2, 61.1, 60.1, 55.3.



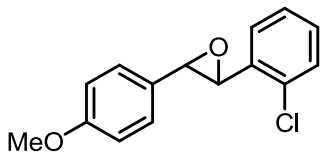
trans-2-(4-methoxyphenyl)-3-p-tolyloxirane (1e): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.15 (m, 6H), 6.89 (d, J = 8.7 Hz, 2H), 3.81 (d, J = 1.5 Hz, 1H), 3.80-3.78 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 138.1, 134.4, 129.4, 129.3, 126.9, 125.5, 114.1, 62.8, 62.7, 55.4, 21.2.



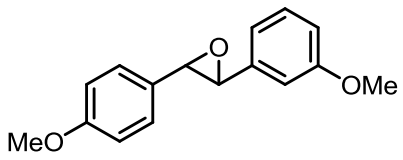
trans-2-(4-bromophenyl)-3-(4-methoxyphenyl)oxirane (1f): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 4H), 7.06 (t, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.84 (d, J = 1.4 Hz, 1H), 3.82 (s, 3H), 3.77 (d, J = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 129.0, 127.3, 127.2, 126.9, 115.8, 115.5, 114.2, 62.9, 62.2, 55.5.



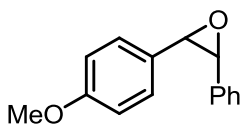
trans-2-(4-methoxyphenyl)-3-(4-nitrophenyl)oxirane (1g): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 4.00 (d, J = 1.2 Hz, 1H), 3.86 (s, 3H), 3.83 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 130.2, 128.0, 126.9, 126.4, 123.8, 123.1, 114.2, 63.3, 61.6, 55.3.



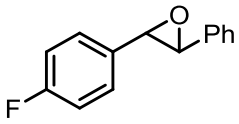
trans-2-(2-chlorophenyl)-3-(4-methoxyphenyl)oxirane (1h): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.7 Hz, 2H), 7.42-7.35 (m, 3H), 7.29-7.26 (m, 1H), 6.88 (d, J = 8.7 Hz, 2H), 3.97 (d, J = 1.3 Hz, 1H), 3.85 (s, 3H), 3.83 (d, J = 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.5, 129.2, 127.4, 127.1, 126.0, 115.9, 115.2, 114.7, 62.5, 62.1, 55.4.



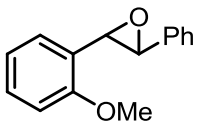
trans-2-(3-methoxyphenyl)-3-(4-methoxyphenyl)oxirane (1i): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 3H), 6.99 – 6.88 (m, 5H), 3.88 (d, J = 1.7 Hz, 1H), 3.86 – 3.83 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 159.9, 139.0, 129.7, 126.9, 118.0, 114.1, 110.5, 62.8, 62.7, 55.4, 55.3.



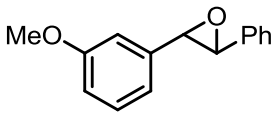
cis-2-(4-methoxyphenyl)-3-phenyloxirane (1j): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 5H), 7.12 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 4.35 (q, J = 4.2 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 134.7, 128.2, 127.9, 127.6, 127.0, 126.5, 113.4, 59.9, 59.6, 55.2.



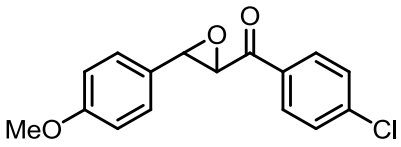
2-(4-fluorophenyl)-3-phenyloxirane (1k): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.32 (m, 7H), 7.11 (d, J = 10 Hz, 1H), 7.09 (d, J = 10 Hz, 1H), 3.89 (brs, 1H), 3.86 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 136.8, 132.8, 128.5, 128.4, 127.1, 125.4, 115.5, 62.7, 62.2.



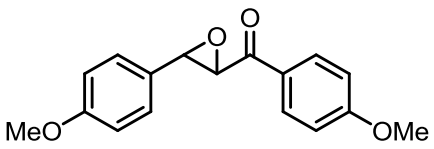
trans-2-(2-methoxyphenyl)-3-phenyloxirane (1l): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.33 (m, 7H), 7.06 (dd, J = 7.5, 7.5 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 4.34 (d, J = 1.8 Hz, 1H), 3.86 (d, J = 1.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 137.4, 128.8, 128.3, 128.0, 125.6, 124.9, 120.6, 110.1, 62.2, 58.2, 55.2.



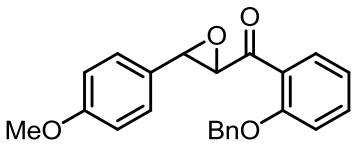
trans-2-(3-methoxyphenyl)-3-phenyloxirane (1m): ^{1}H NMR (400 MHz, CDCl3): δ 7.60 – 7.50 (m, 6H), 7.20-7.15 (m, 3H), 4.10 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl3): δ 160.0, 138.9, 137.1, 129.7, 128.6, 128.4, 125.6, 118.0, 114.2, 110.5, 62.8, 55.3, 55.2.



(4-chlorophenyl)(trans-3-(4-methoxyphenyl)oxiran-2-yl)methanone (1n): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 4.22 (d, J = 0.8 Hz, 1H), 4.02 (d, J = 0.8 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 160.6, 140.7, 133.9, 129.9, 129.4, 127.3, 127.2, 114.4, 61.3, 59.6, 55.5.

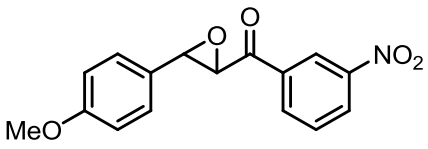


(4-methoxyphenyl)(trans-3-(4-methoxyphenyl)oxiran-2-yl)methanone (1o): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 6.94 (t, J = 9.4 Hz, 4H), 4.25 (d, J = 1.3 Hz, 1H), 4.02 (d, J = 1.3 Hz, 1H), 4.02 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 164.3, 160.4, 130.9, 128.8, 127.7, 127.3, 114.3, 114.2, 61.0, 59.3, 55.7, 55.5.

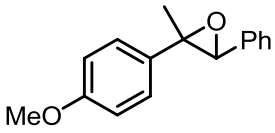


(2-(benzyloxy)phenyl)(trans-3-(4-methoxyphenyl)oxiran-2-yl)methanone (1p): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 1.6, 8.0 Hz, 1H), 7.48-7.52 (m, 1H),

7.30-7.34 (m, 3H), 7.24-7.29 (m, 5H), 7.19 (d, J = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 2H), 4.50 (d, *J* = 1.6 Hz, 1H), 4.07 (d, J = 1.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.32, 158.52, 136.14, 135.64, 134.68, 130.93, 128.70, 128.59, 128.25, 127.38, 126.67, 125.83, 121.26, 113.04, 70.77, 63.44, 59.98.



(trans-3-(4-methoxyphenyl)oxiran-2-yl)(3-nitro phenyl)methanone (1q): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 – 8.85 (m, 1H), 8.46 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.26 (d, *J* = 1.7 Hz, 1H), 4.07 (d, *J* = 1.7 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 160.7, 136.7, 134.1, 130.8, 130.3, 128.2, 127.3, 126.7, 123.5, 114.5, 61.5, 59.8, 55.5.



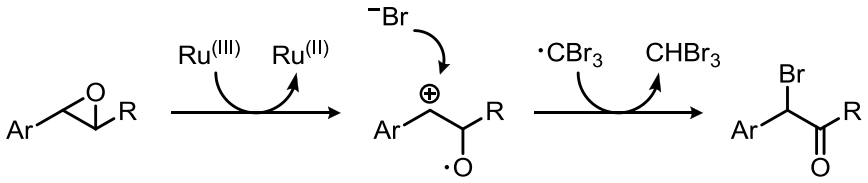
trans-2-(4-methoxyphenyl)-2-methyl-3-phenyloxirane (1r): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 8.3 Hz, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 1H), 3.81 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 142.5, 128.5, 128.1, 127.9, 127.5, 125.2, 113.7, 67.0, 63.1, 55.3, 16.7.

3. General Procedure for Photocatalytic Reaction

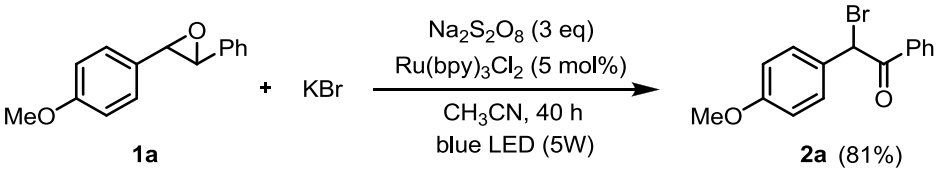
A 10 mL round bottom flask was equipped with magnetic stir bar and was charged with substrate **1a** (45 mg, 0.20 mmol), carbon tetrabromide (99.1 mg, 0.30 mmol), CH_3CN (3.0 mL) and $Ru(bpy)_3Cl_2$ (7.5 mg, 0.01 mmol). The mixture was irradiated by a blue LEDs (5 W) for 5 h. After the reaction was completed, the solvent was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexanes: EtOAc = 12:1) to afford the desired product **2a** in 92% yield.

4. Mechanistic Research

1) Carbocation Trapping Mechanism (*Passway A*)

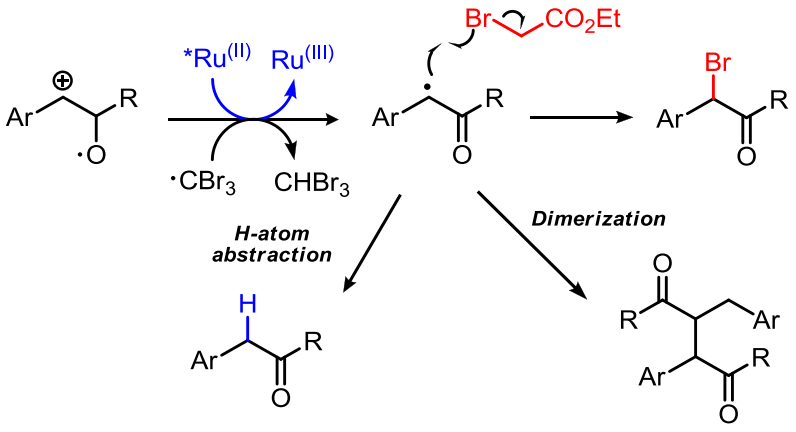


To understand this mechanism further, we were able to trap the benzyl cation intermediate **5** with bromide by utilizing sodium persulfide as single electron transfer reagent and potassium bromide as external bromo-source via a nucleophilic S_N1 process.



A 10 mL round bottom flask was equipped with epoxide **1a** (49.5 mg, 0.22 mmol), sodium persulfide (156.4 mg, 0.66 mmol), potassium bromide (130.3 mg, 1.10 mmol), CH_3CN (5.0 mL) and $Ru(bpy)_3Cl_2$ (8.2 mg, 0.011 mmol). The reaction mixture was irradiated with 5 W blue LED for 40 h. Then the solvent was removed *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexanes: EtOAc = 12:1) to afford the desired product **2a** in 81% yield.

2) Propagation mechanism (*Passway B*)



In our investigation we discovered that two kinds of byproducts derived from benzyl radical intermediate **6** were separated during which process a small quantity of oxidative quencher was used. Experiment was also conducted by adding various

amounts of oxidative quencher to a mixture of **1a** and 5 mol% $Ru(bpy)_3Cl_2$ in acetonitrile, forming the desired product **2a** along with reduced ketone **7** as main byproduct after 12 h irradiation. The NMR analysis was shown in Figure 1.

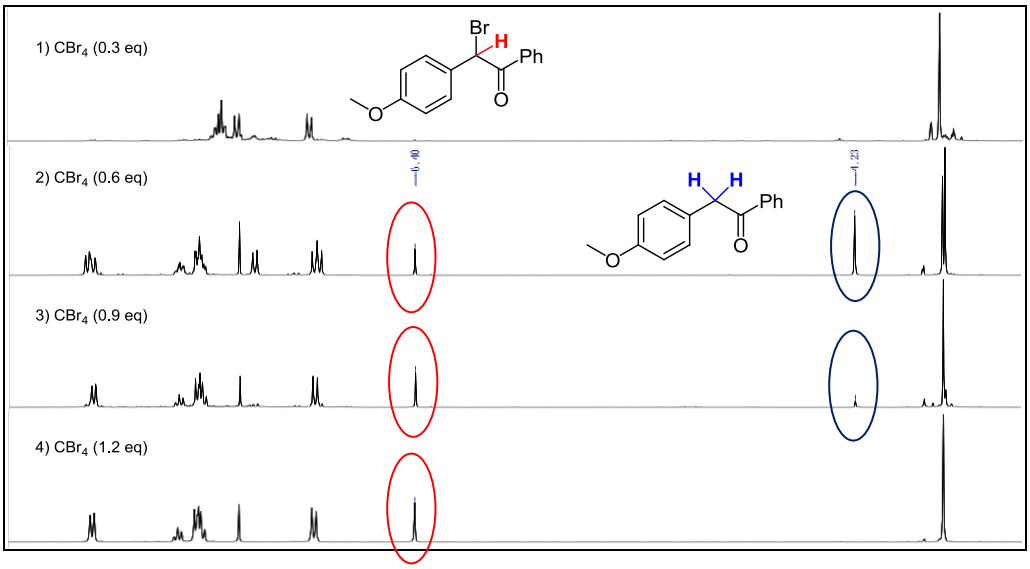
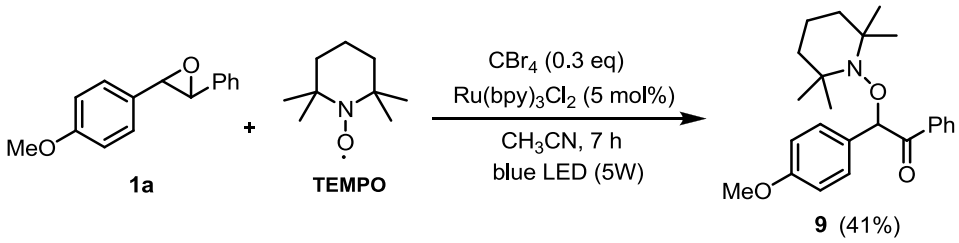


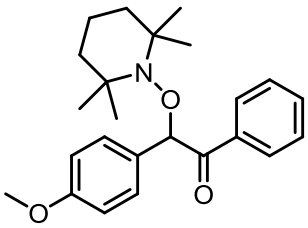
Figure 1 NMR analysis for different amount of CBr_4 addition

To explain this phenomenon, possible mechanistic *Pathway B* was proposed on condition that less than 1.0 equiv oxidative quencher was used. Secondary photocatalytic reaction was performed during which process benzyl radical **6** was obtained from carbocation **5** by performing another photocatalytic cycle. Thus, we were able to set up a control experiment with TEMPO to scavenge the radical **6** and prove its existence.

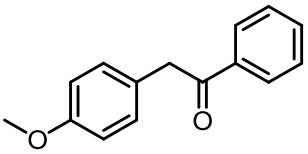


To a solution of 2-(4-methoxyphenyl)-3-phenyloxirane (30.0 mg, 0.133 mmol) in acetonitrile (3 mL) was added CBr_4 (52.9 mg, 0.159 mmol), TEMPO (31.2 mg, 0.200 mmol) and $Ru(bpy)_3Cl_2$ (5.0 mg, 0.0067 mmol). The mixture was stirred at room temperature for 7 hours under 5W blue LED irradiation. Then the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel to afford 20.8

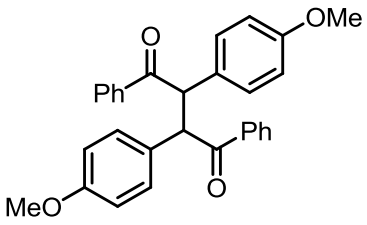
mg (0.055 mmol, 41% yield) of compound **9** as an orange solid (mp: 96-97 ℃).



2-(4-methoxyphenyl)-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (9): R_f (hexane/EtOAc 10:1): 0.5. IR (neat): 2991, 2926, 2870, 2851, 1677, 1598, 1510, 1080,810, 798. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.40 (dd, J = 8.1, 6.3 Hz, 4H), 6.81 (d, J = 8.7 Hz, 2H), 5.95 (s, 1H), 3.75 (s, 3H), 1.60-1.28 (m, 6H), 1.17 (d, J = 7.2 Hz, 6H), 0.99 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 198.4, 159.1, 135.4, 132.9, 129.9, 129.3, 128.8, 128.5, 113.9, 92.5, 60.1, 59.8, 55.2, 40.3, 33.9, 33.4, 20.4, 20.3, 17.1. HRMS-ESI (TOF, m/z): [M + H]+ calcd for $C_{24}H_{32}NO_3$, 382.2377; found, 382.2399.

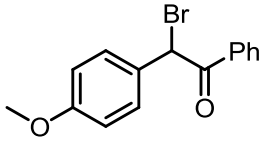


2-(4-methoxyphenyl)-1-phenylethanone (7): R_f (hexane/ EtOAc 8:1): 0.35. IR (neat): 3055, 3024, 3000, 2928, 1692, 1514, 1447, 1035, 793, 756. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.23 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 158.7, 136.8, 133.2, 130.6, 128.8, 128.7, 126.7, 114.3, 55.4, 44.8. HRMS-ESI (TOF, m/z): [M + H]+ calcd for $C_{15}H_{15}O_2$, 227.1067; found, 227.1064.



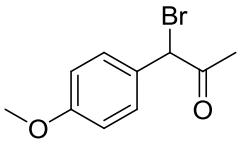
2,3-bis(4-methoxyphenyl)-1,4-diphenylbutane-1,4-dione (8): d.r. 3:1. R_f (hexane/ EtOAc 5:1): 0.25. IR (neat): 3052, 2932, 1689, 1512, 1205, 1044, 802, 795. ^{1}H NMR (400 MHz, $CDCl_3$): Major δ 7.97 (d, J = 7.7 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 5.29 (s, 1H), 3.70 (s, 3H); Minor δ 7.87 (d, J = 7.7 Hz, 2H), 7.48 – 7.31 (m, 5H), 6.74 (d, J = 8.7 Hz, 2H), 5.68 (s, 1H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): Major δ 200.0, 158.8, 136.7, 130.0, 129.0, 128.6, 128.5, 114.3, 55.3, 29.9; Minor δ 200.0, 158.8, 133.0, 132.9, 130.3, 128.7, 128.6, 114.4, 57.8, 29.9. HRMS-ESI (TOF, m/z): [M + H]+ calcd for $C_{30}H_{27}O_4$, 451.1904; found, 451.1896.

5. Characterization of Products

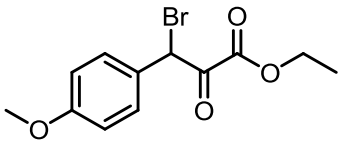


2-bromo-2-(4-methoxyphenyl)-1-phenylethanone (2a): According

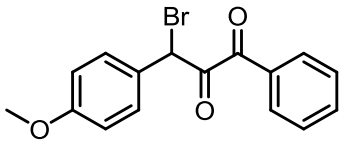
to the general procedure, compound **2a** was obtained in 92% yield (7 h) as light-yellow solid. R_f (hexane /EtOAc 6:1): 0.3. IR (neat): 3012, 2932, 2836, 1691, 1607, 1511, 1448, 1253, 1031, 823, 744, 538. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.49-7.42 (m, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.40 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 160.3, 134.3, 133.8, 130.6, 129.2, 128.9, 127.9, 114.6, 55.4, 51.4. HRMS-ESI (TOF, m/z): $[M + H]^+$ Calcd for $C_{15}H_{14}BrO_2$, 305.0172; found, 305.0159. $[M - Br]^+$ Calcd for $C_{15}H_{13}O_2$, 225.0910; Found, 225.0903.



1-bromo-1-(4-methoxyphenyl)propan-2-one (2b): According to the general procedure, compound **2b** was obtained in 88% yield (8 h) as white solid. R_f (hexane/EtOAc 10:1): 0.35. IR (neat): 2951, 2877, 1730, 1514, 1248, 1178, 1035, 821. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 1H), 3.80 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 160.3, 130.2, 127.2, 114.6, 56.4, 55.5, 26.4. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{10}H_{11}O_2$, 163.0754; Found, 163.0751.

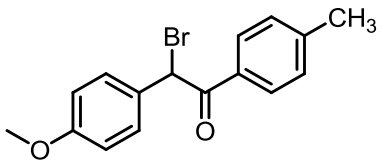


ethyl 3-bromo-3-(4-methoxyphenyl)-2-oxopropanoate (2c): According to the general procedure, compound **2c** was obtained in 67% yield (9 h) as light yellow oil. R_f (hexane/EtOAc 8:1): 0.3. IR (neat): 3001, 2935, 1733, 1608, 1513, 1257, 1177, 1054, 831, 531. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.22 (s, 1H), 4.32 (qd, *J* = 7.2, 3.7 Hz, 2H), 3.81 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 160.7, 160.3, 131.2, 125.0, 114.6, 63.3, 55.5, 50.1, 14.0. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{12}H_{13}O_4$, 221.0808; Found, 221.0807.

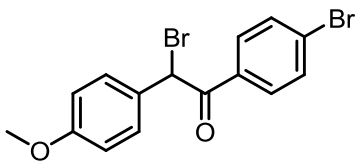


3-bromo-3-(4-methoxyphenyl)-1-phenylpropane-1,2-dione (2d): According to the general procedure, compound **2d** was obtained in 78% yield (11 h) as yellow oil. R_f (hexane/EtOAc 8:1): 0.45. IR (neat): 2962, 2838, 1720, 1673, 1607, 1512, 1257, 1030, 735, 685. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 8.00 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 15.8, 8.3 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 1H), 3.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 189.9, 160.7, 135.1, 132.4, 131.4, 130.5, 129.0, 125.0, 114.6, 55.5, 50.0. HRMS (ESI-TOF) m/z: [M -

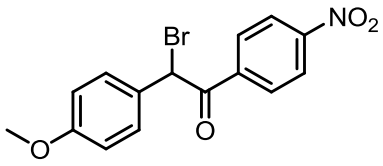
Br]$^+$ Calcd for $C_{16}H_{13}O_3$, 253.0859; Found, 253.0837.



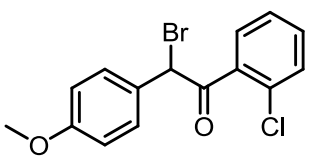
2-bromo-2-(4-methoxyphenyl)-1-p-tolylethanone (2e): According to the general procedure, compound **2e** was obtained in 75% yield (6 h) as yellow oil. R_f (hexane/EtOAc 5:1): 0.35. IR (neat): 2925, 2849, 1676, 1600, 1511, 1264, 1166, 1025, 843, 758, 601. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.39 (s, 1H), 3.79 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 190.8, 160.3, 144.8, 131.7, 130.6, 129.6, 129.4, 128.2, 114.6, 55.4, 51.5, 21.8. HRMS (ESI-TOF) m/z: [M - Br]$^+$ Calcd for $C_{16}H_{15}O_2$, 239.1067; Found, 239.1064.



2-bromo-1-(4-bromophenyl)-2-(4-methoxyphenyl)ethanone (2f): According to the general procedure, compound **2f** was obtained in 86% yield (10 h) as light-yellow solid. R_f (hexane/EtOAc 5:1): 0.35. IR (neat): 2957, 2836, 1691, 1584, 1512, 1253, 1071, 1032, 805, 775, 540. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.83 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.32(s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 190.2, 160.4, 133.0, 132.2, 130.7, 130.6, 129.0, 127.5, 114.6, 55.4, 51.2. HRMS (ESI-TOF) m/z: [M - Br]$^+$ Calcd for $C_{15}H_{12}O_2Br$, 303.0015; Found, 303.0033.

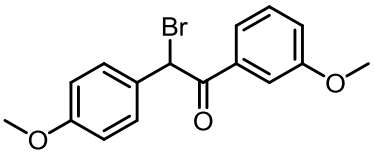


2-bromo-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethanone (2g): According to the general procedure, compound **2g** was obtained in 72% yield (8 h) as yellow oil. R_f (hexane/EtOAc 5:1): 0.5. IR (neat): 2935, 2839, 1699, 1606, 1526, 1347, 1255, 1177, 811 , 743, 542. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.27 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.33(s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 189.8, 160.6, 150.5, 139.1, 130.7, 130.3, 126.7, 124.0, 114.8, 55.5, 51.1. HRMS (ESI-TOF) m/z: [M - Br]$^+$ Calcd for $C_{15}H_{12}NO_4$, 270.0761; Found, 270.0759.

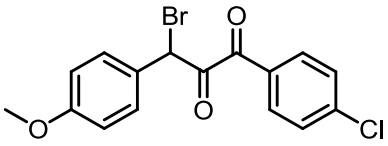


2-bromo-1-(2-chlorophenyl)-2-(4-methoxyphenyl)ethanone (2h): According to the general procedure, compound **2h** was obtained in 85% yield (6 h) as light-yellow solid. R_f (hexane/EtOAc 6:1): 0.3.

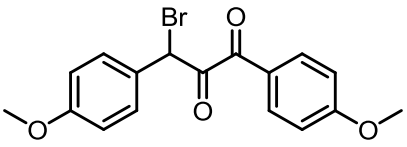
IR (neat): 2933, 2840, 1669, 1597, 1512, 1255, 1031, 842, 746, 609. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.7 Hz, 2H), 7.40-7.35 (m, 3H), 7.30-7.27 (m, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.23 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 160.5, 137.5, 132.2, 131.1, 130.7, 130.4, 130.2, 127.1, 126.7, 114.5, 55.5, 53.8. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{15}H_{12}O_2Cl$, 259.0520; Found, 259.0519.



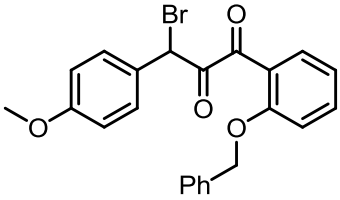
2-bromo-1-(3-methoxyphenyl)-2-(4-methoxyphenyl)ethanone (2i): According to the general procedure, compound **2i** was obtained in 77% yield (6 h) as yellow oil. R_f (hexane/EtOAc 6:1): 0.3. IR (neat): 3003, 2935, 2836, 1688, 1597, 1512, 1252, 1177, 1032, 785, 687, 520. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.2, 2.4 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.38 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 160.3, 160.0, 135.6, 130.6, 129.8, 128.0, 121.6, 120.2, 114.6, 113.7. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{16}H_{15}O_3$, 255.1016; Found, 255.1022.



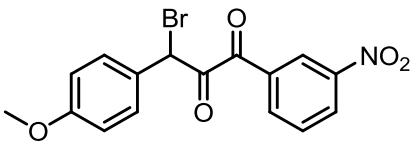
3-bromo-1-(4-chlorophenyl)-3-(4-methoxyphenyl)propane-1,2-dione (2n): According to the general procedure, compound **2n** was obtained in 75% yield (10 h) as light-yellow solid. R_f (hexane/EtOAc 5:1): 0.4. IR (neat): 2960, 2917, 2848, 1721, 1677, 1587, 1512, 1259, 1176, 1089, 783, 535. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 9.5 Hz, 2H), 6.37 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 189.4, 160.8, 141.9, 131.8, 131.4, 130.7, 129.5, 124.8, 114.6, 55.5, 49.8. GC-MS (EI): 51.1, 77.1, 91.1, 105.1, 135.0, 150.1, 288.0



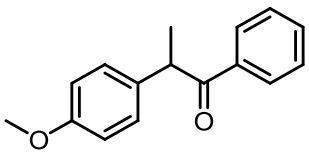
3-bromo-1,3-bis(4-methoxyphenyl)propane-1,2-dione (2o): According to the general procedure, compound **2o** was obtained in 65% yield (14 h) as light-yellow solid. R_f (hexane/EtOAc 5:1): 0.35. IR (neat): 2956, 1680, 1588, 1502, 1314, 1248, 1030, 748, 655. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.9 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.39 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 189.5, 165.2, 160.6, 133.0, 131.3, 125.4, 125.3, 114.5, 114.4, 55.8, 55.5, 50.2. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{16}H_{12}O_2Cl$, 287.0469; Found, 287.0459.



1-(2-(benzyloxy)phenyl)-3-bromo-3-(4-methoxyphenyl)propane-1,2-dione (2p): According to the general procedure, compound **2p** was obtained in 68% yield (11 h) as yellow oil. R_f (hexane/EtOAc 5:1): 0.4. IR (neat): 2837, 1660, 1596, 1512, 1305, 1255, 1030, 755, 698. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.48-7.39 (m, 5H), 7.19 (d, J = 8.6Hz, 2H), 7.08 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.5Hz, 1H), 6.79 (d, J = 8.6Hz, 2H), 5.72 (s, 1H), 5.14 (d, J = 2.7Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 192.5, 160.2, 159.4, 136.5, 135.3, 131.1, 129.0, 128.7, 128.3, 127.1, 122.9, 121.6, 114.3, 113.3, 71.4, 55.4, 51.3. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{17}H_{15}O_4$, 283.0965; Found, 283.0969.

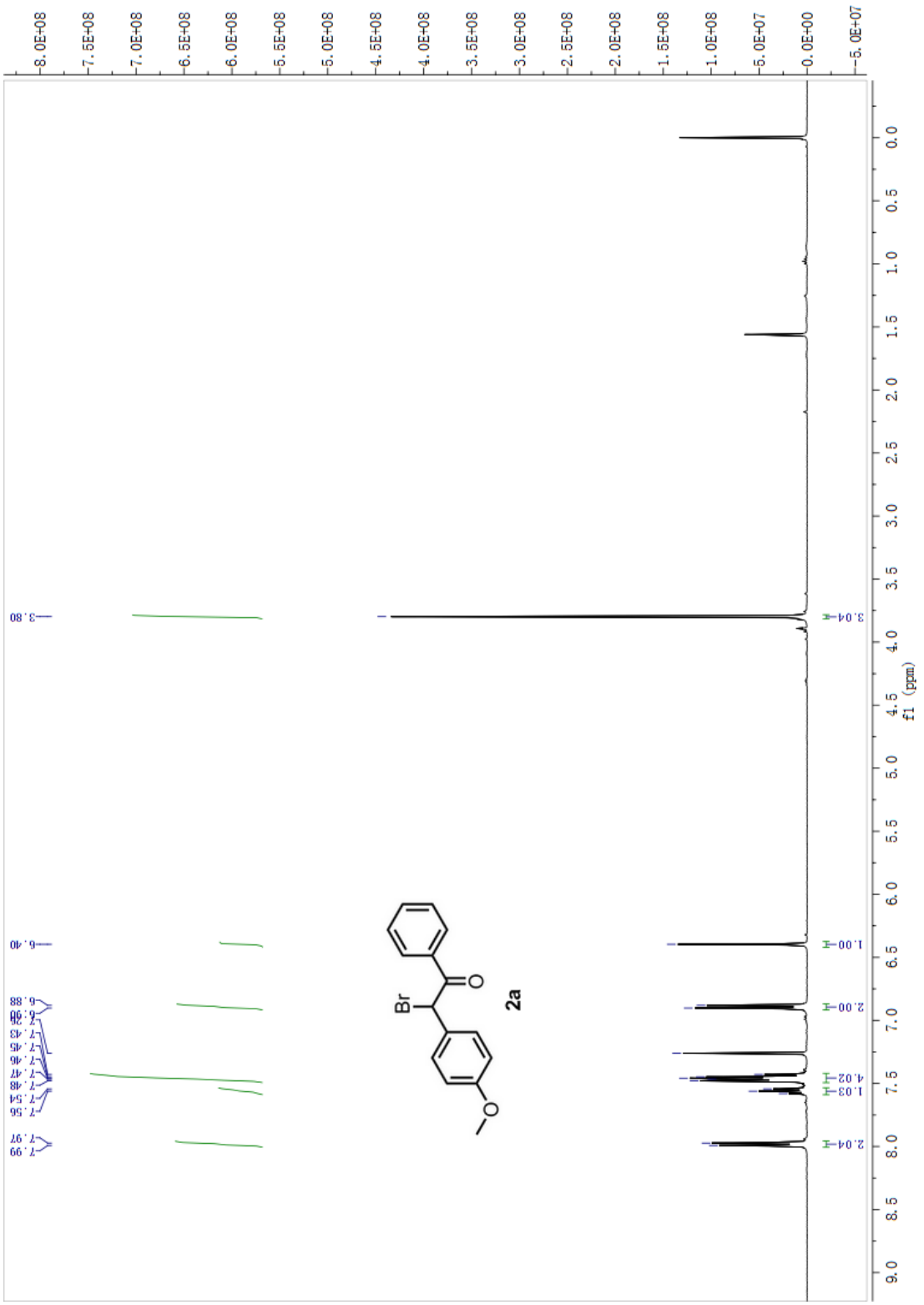


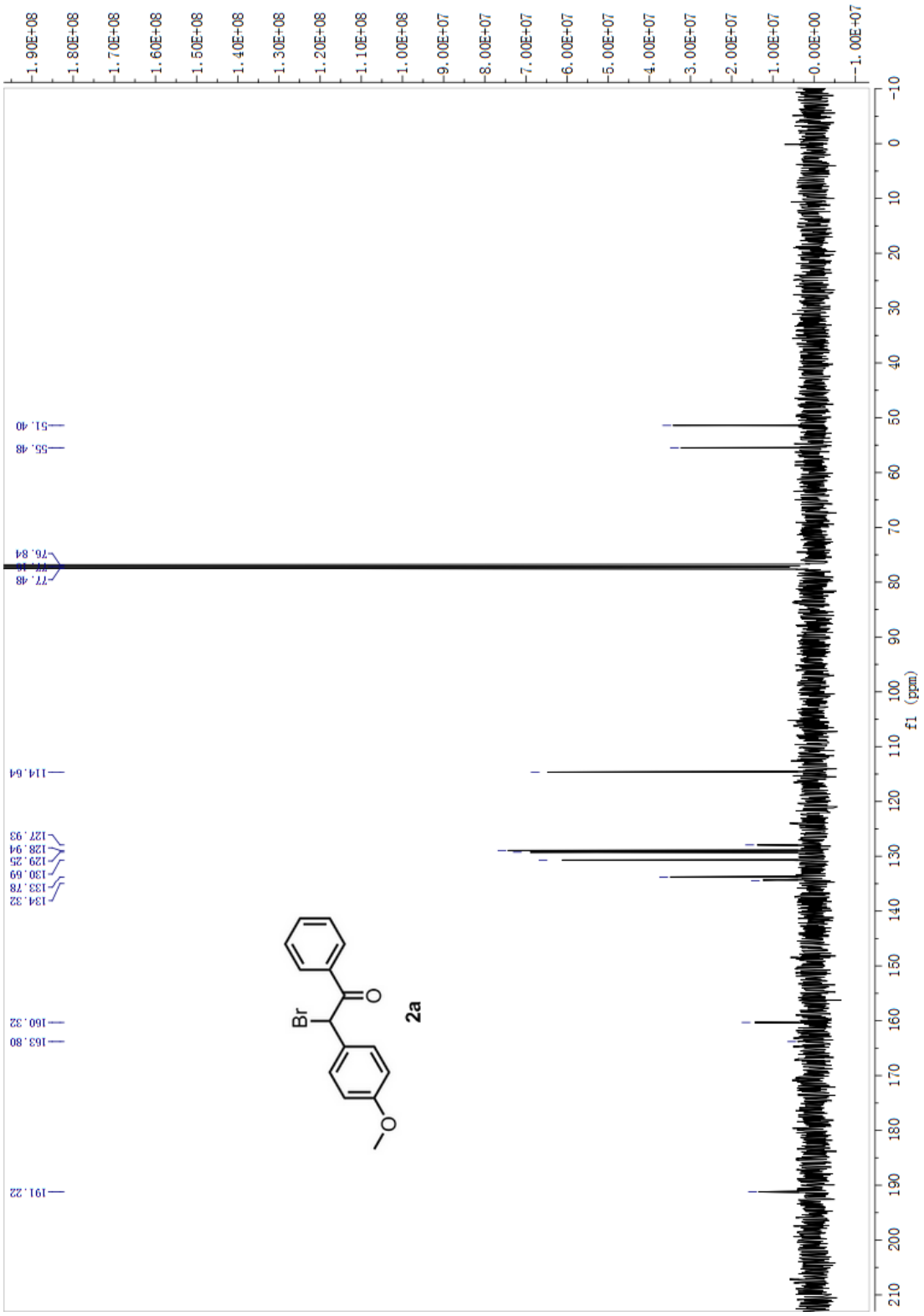
3-bromo-3-(4-methoxyphenyl)-1-(3-nitrophenyl)propane-1,2-dione (2q): According to the general procedure, compound **2q** was obtained in 77% yield (14 h) as yellow oil. R_f (hexane/EtOAc 8:1): 0.4. IR (neat): 3087, 1702, 1592, 1533, 1350, 1257, 1178, 1029, 831, 720. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.51 (d, J = 8.1 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.40 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 188.4, 161.0, 135.8, 135.5, 133.8, 131.5, 130.3, 129.0, 125.2, 124.3, 114.7, 55.5, 49.5. HRMS (ESI-TOF) m/z: $[M - Br]^+$ Calcd for $C_{23}H_{19}O_4$, 359.1278; Found, 359.1280.

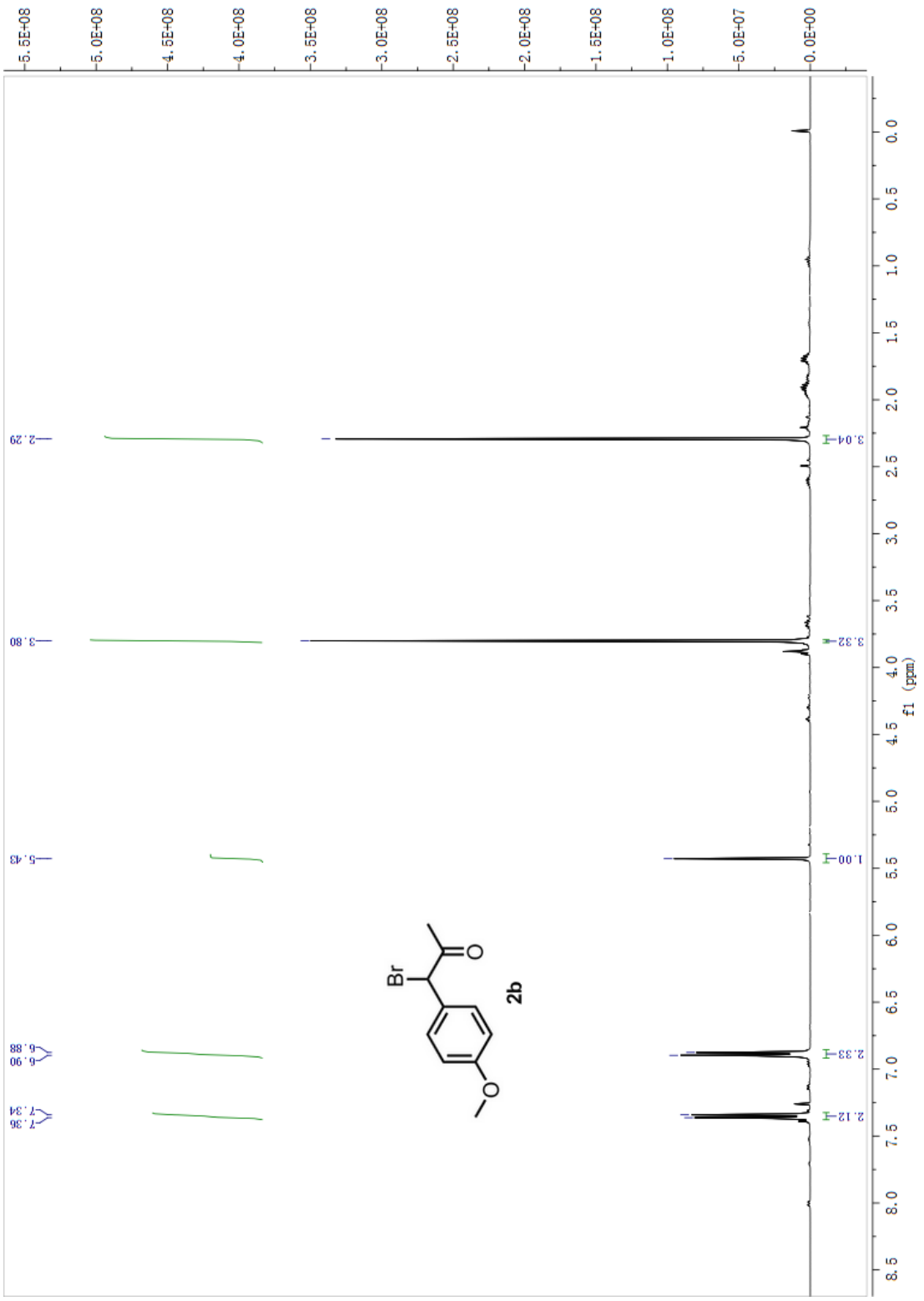


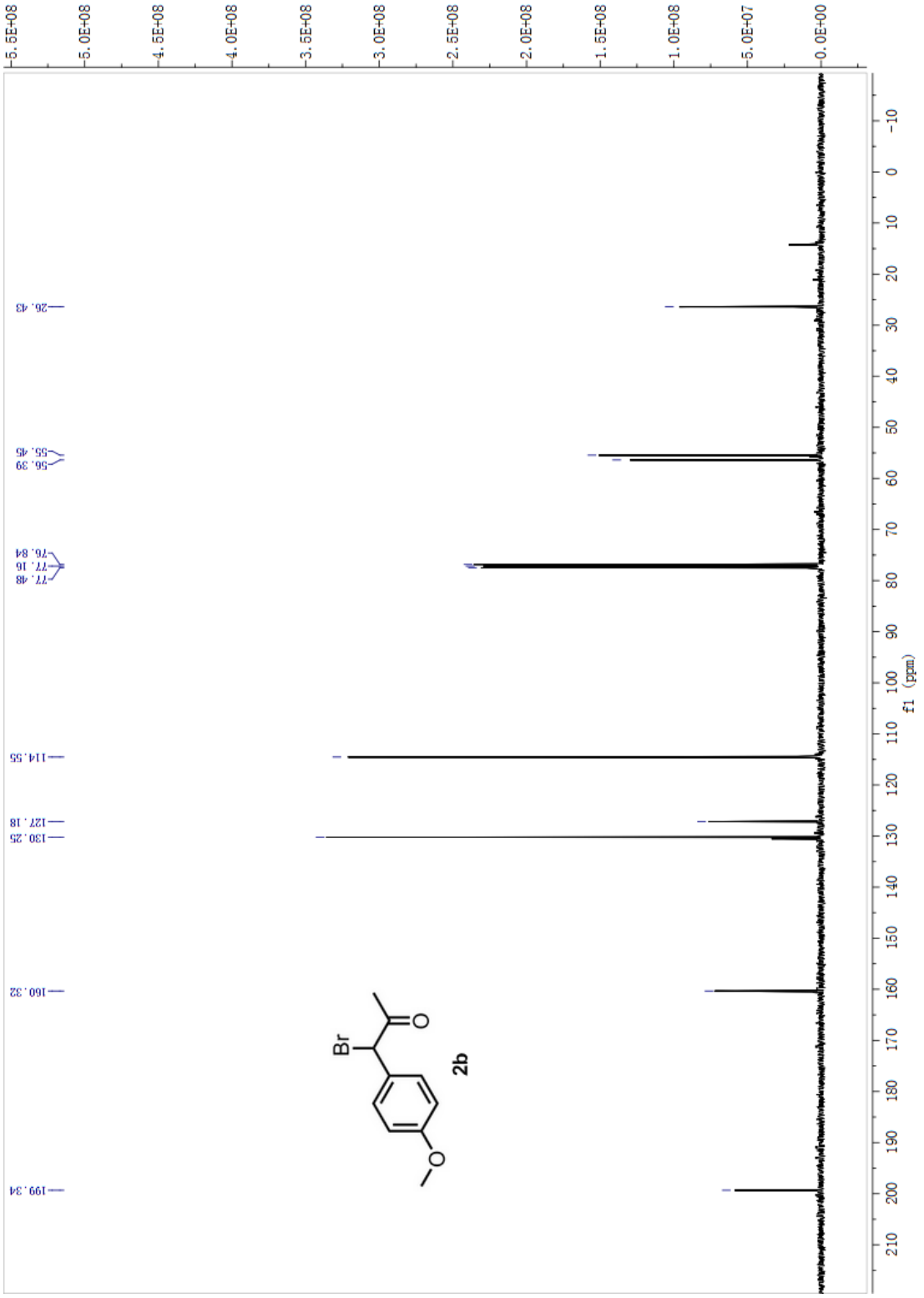
2-(4-methoxyphenyl)-1-phenylpropan-1-one(3r):According to the general procedure, compound **3r** was obtained in 82% yield (9 h) as yellow oil. R_f (hexane/EtOAc 8:1): 0.5. IR (neat): 3048, 2977, 2926, 1677, 1620, 1521, 1466, 1233, 1208. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.65 (q, J = 6.8 Hz, 1H), 3.75 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 158.6, 136.6, 133.6, 132.8, 128.9, 128.8, 128.6, 114.5, 55.3, 47.1, 19.6. HRMS-ESI (TOF, m/z): [M + H]+ calcd for $C_{16}H_{17}O_2$, 241.1223; found, 241.1249.

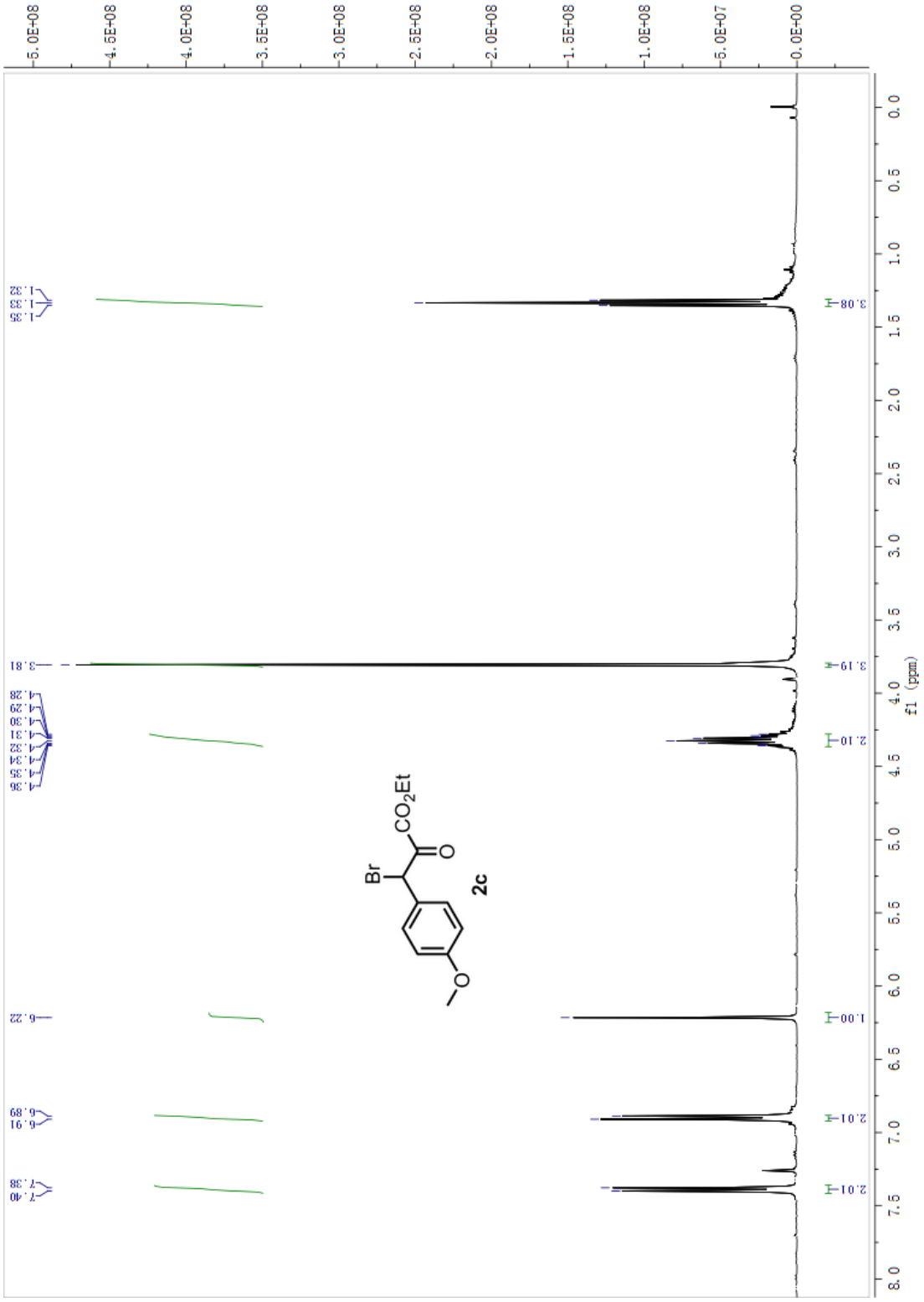
6. ^{1}H NMR and ^{13}C NMR Spectra for Products

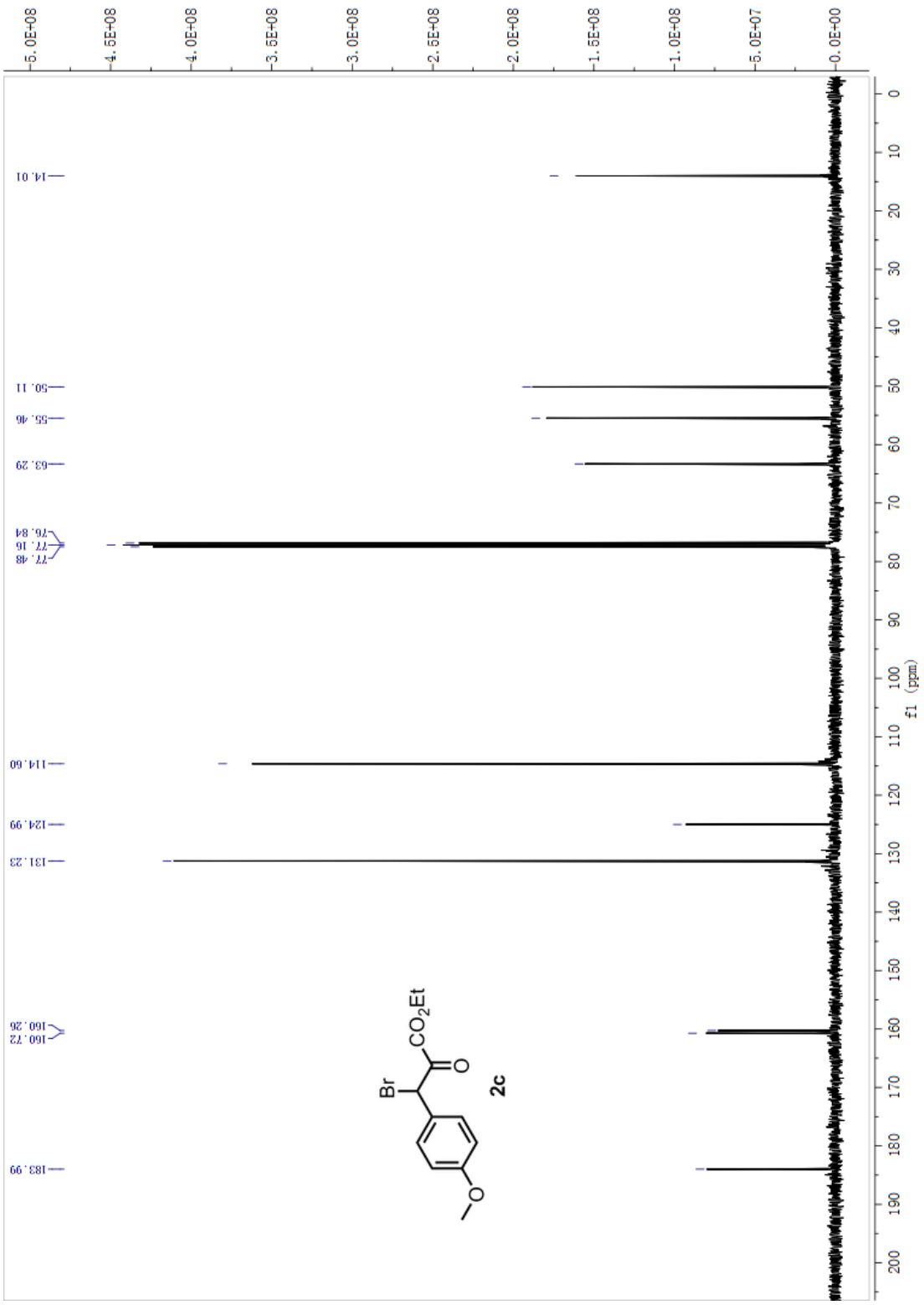


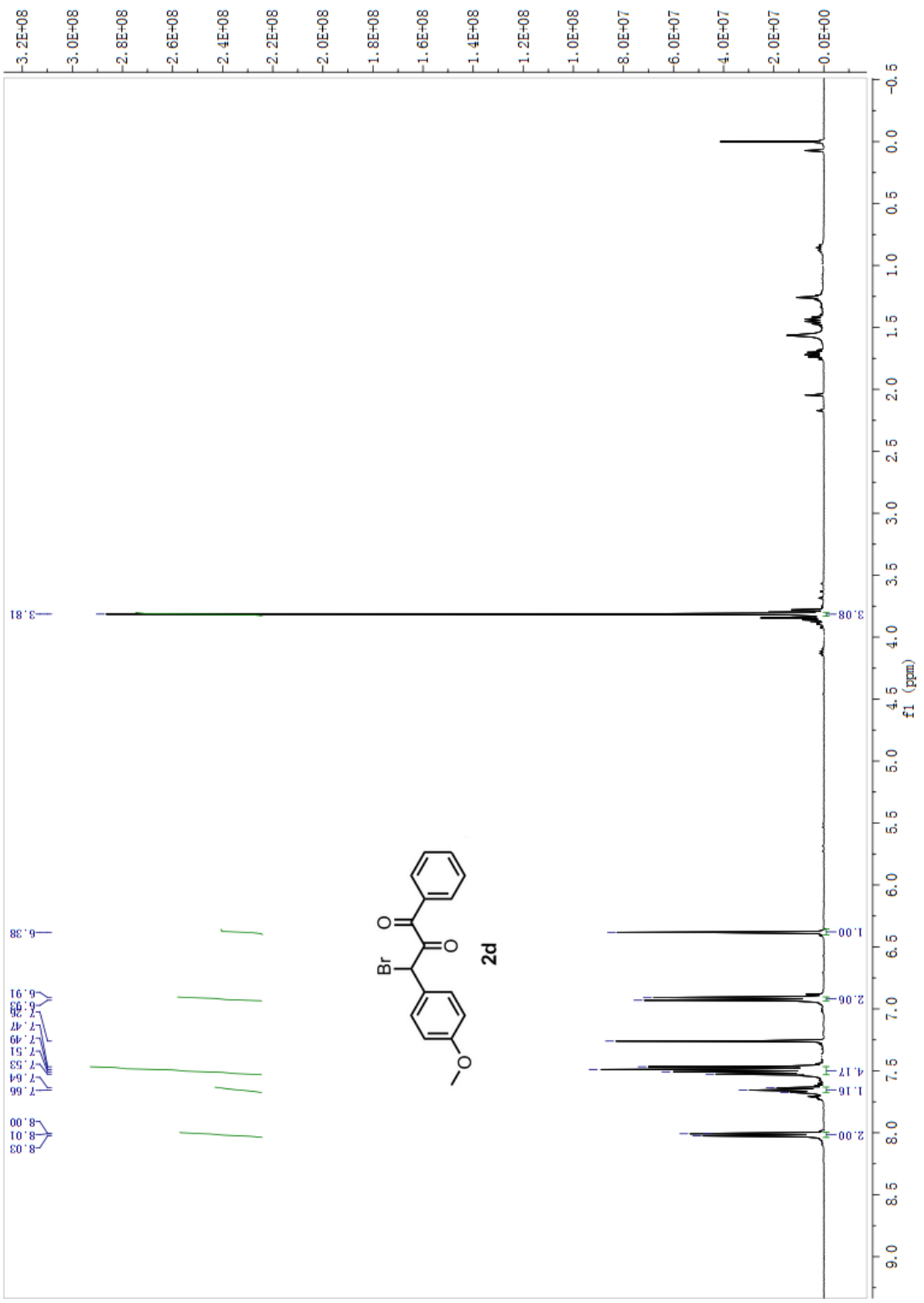

51.40
55.48
76.84
77.48
114.64
127.93
128.94
129.25
130.69
133.78
134.32
160.32
163.80
191.22
Br
O
O
2a
f1 (ppm)

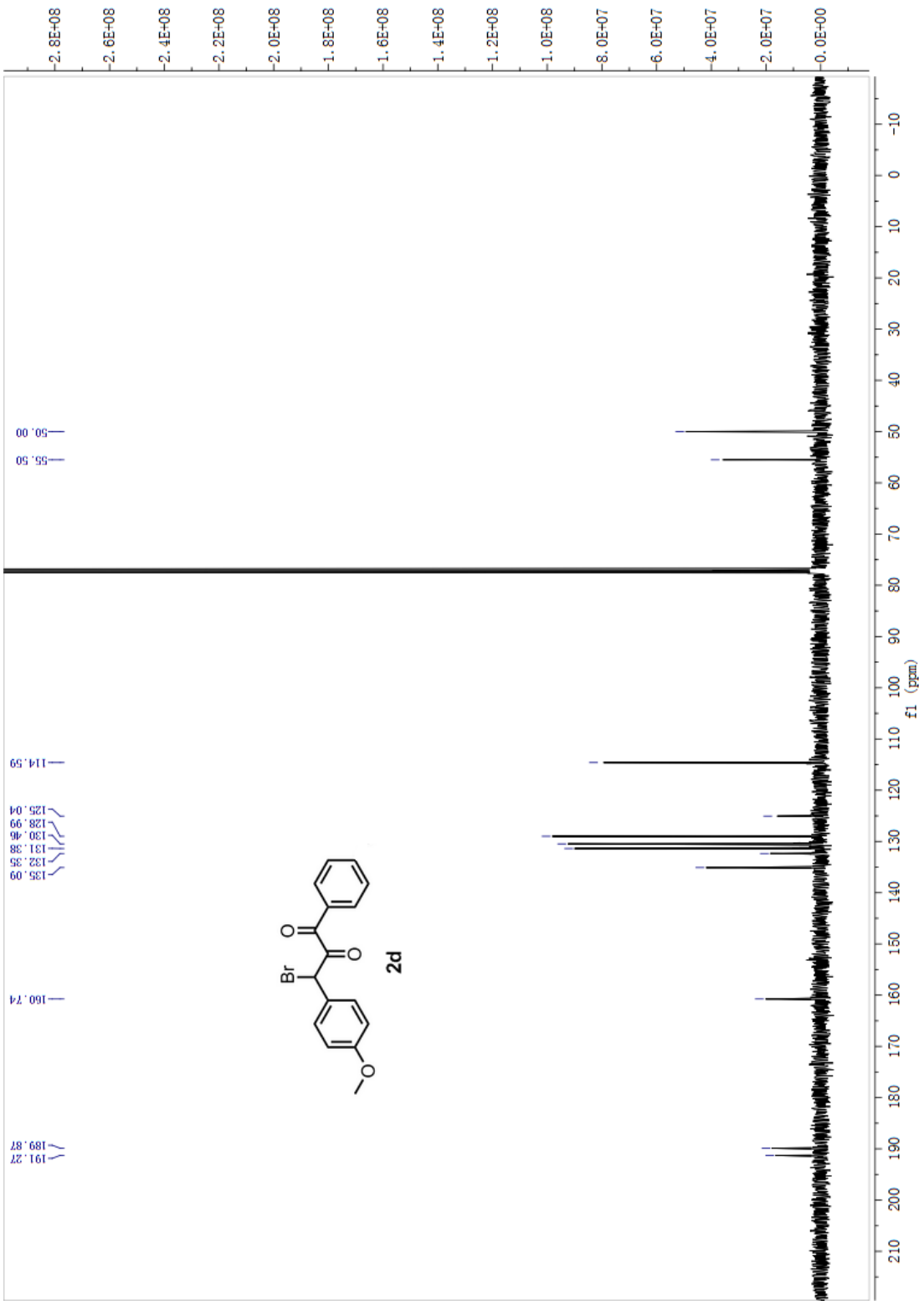


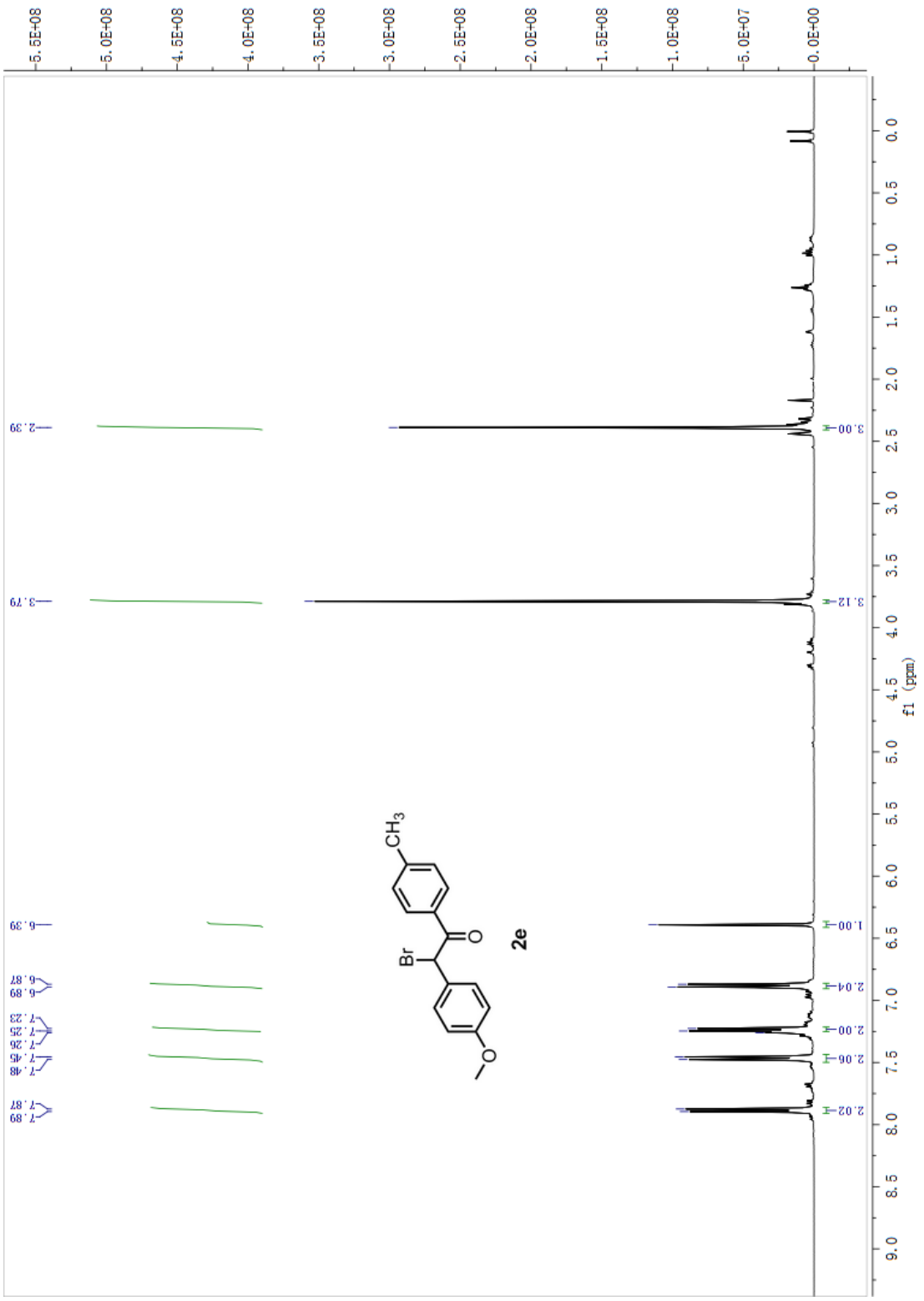


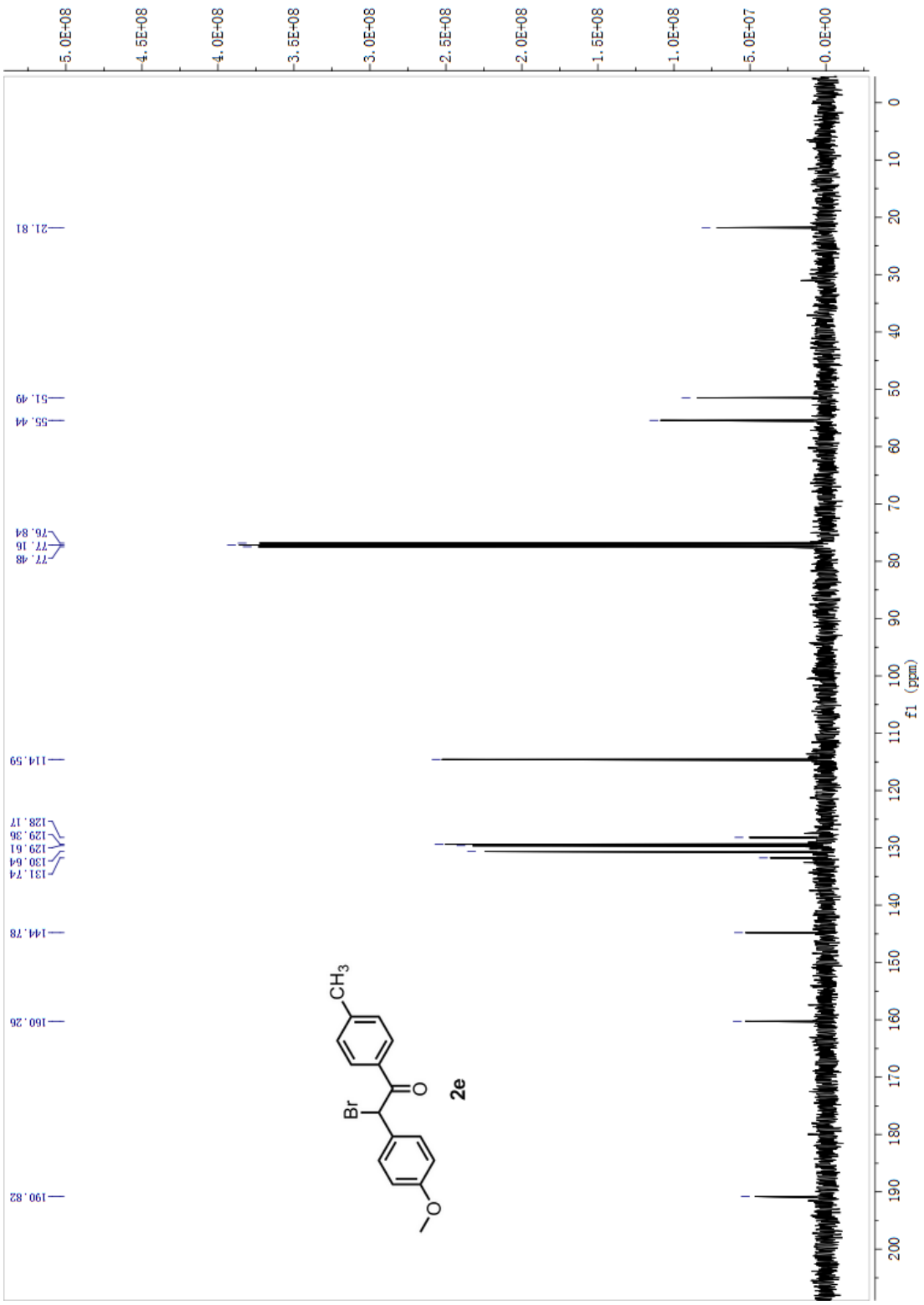


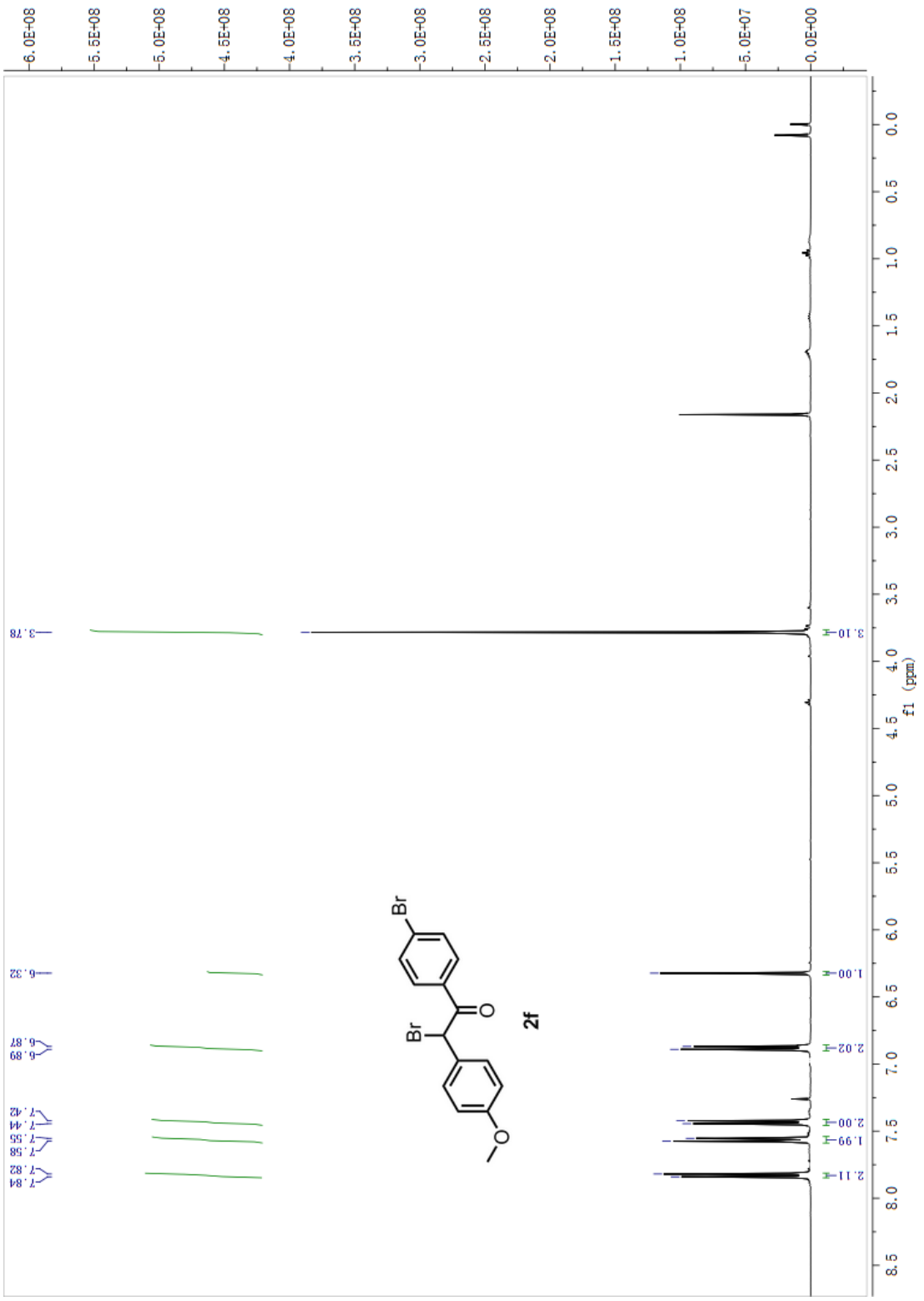


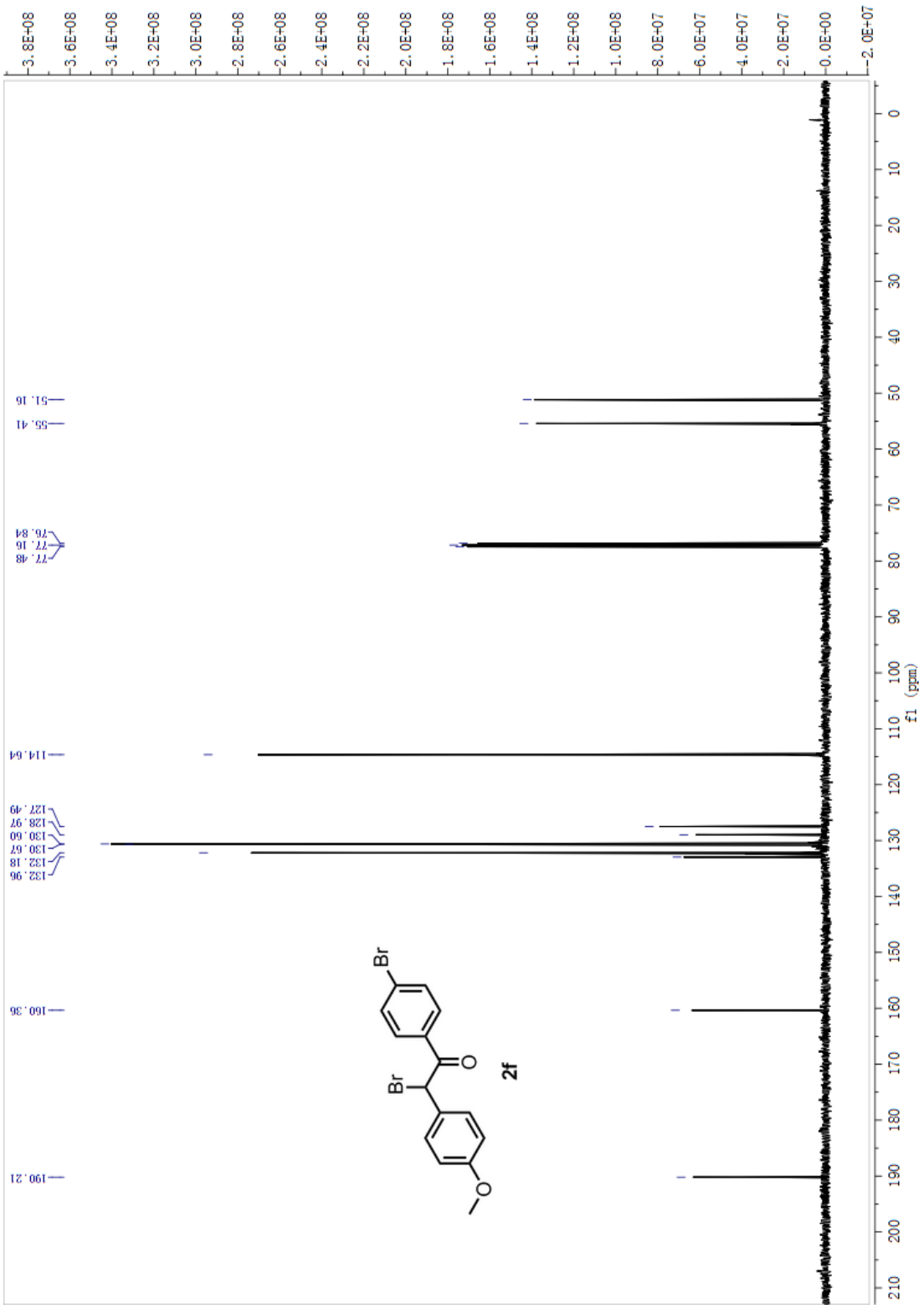


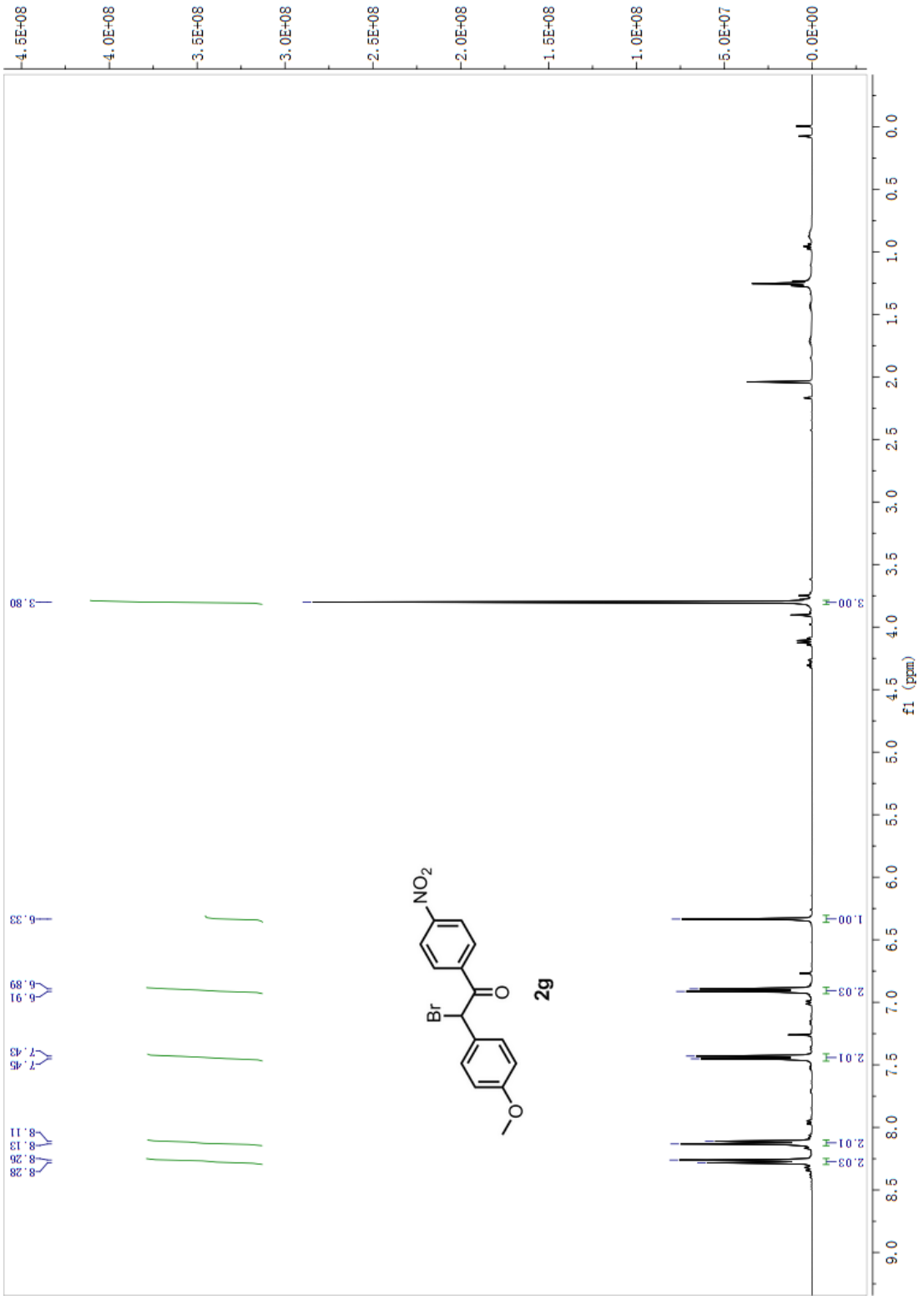


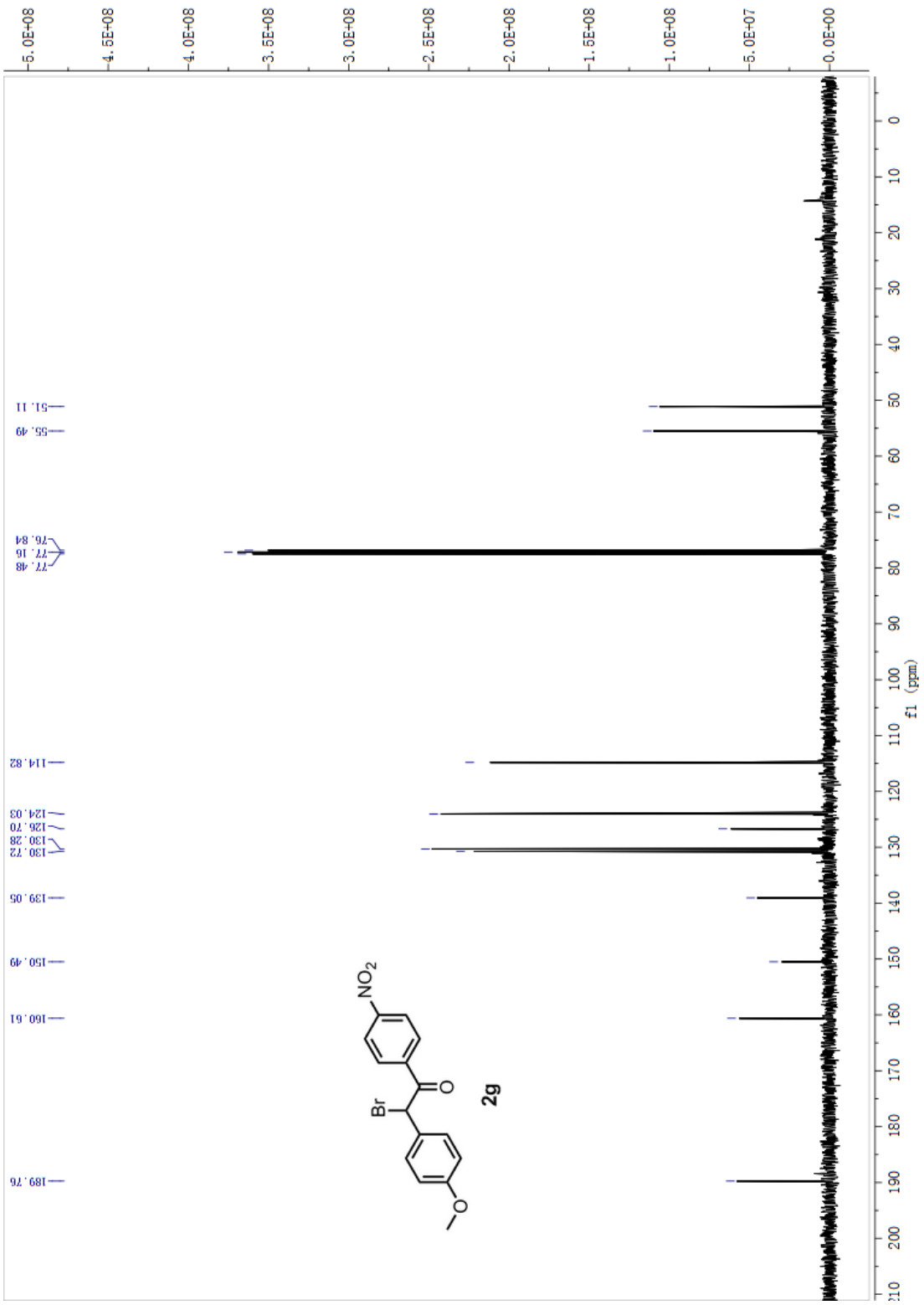


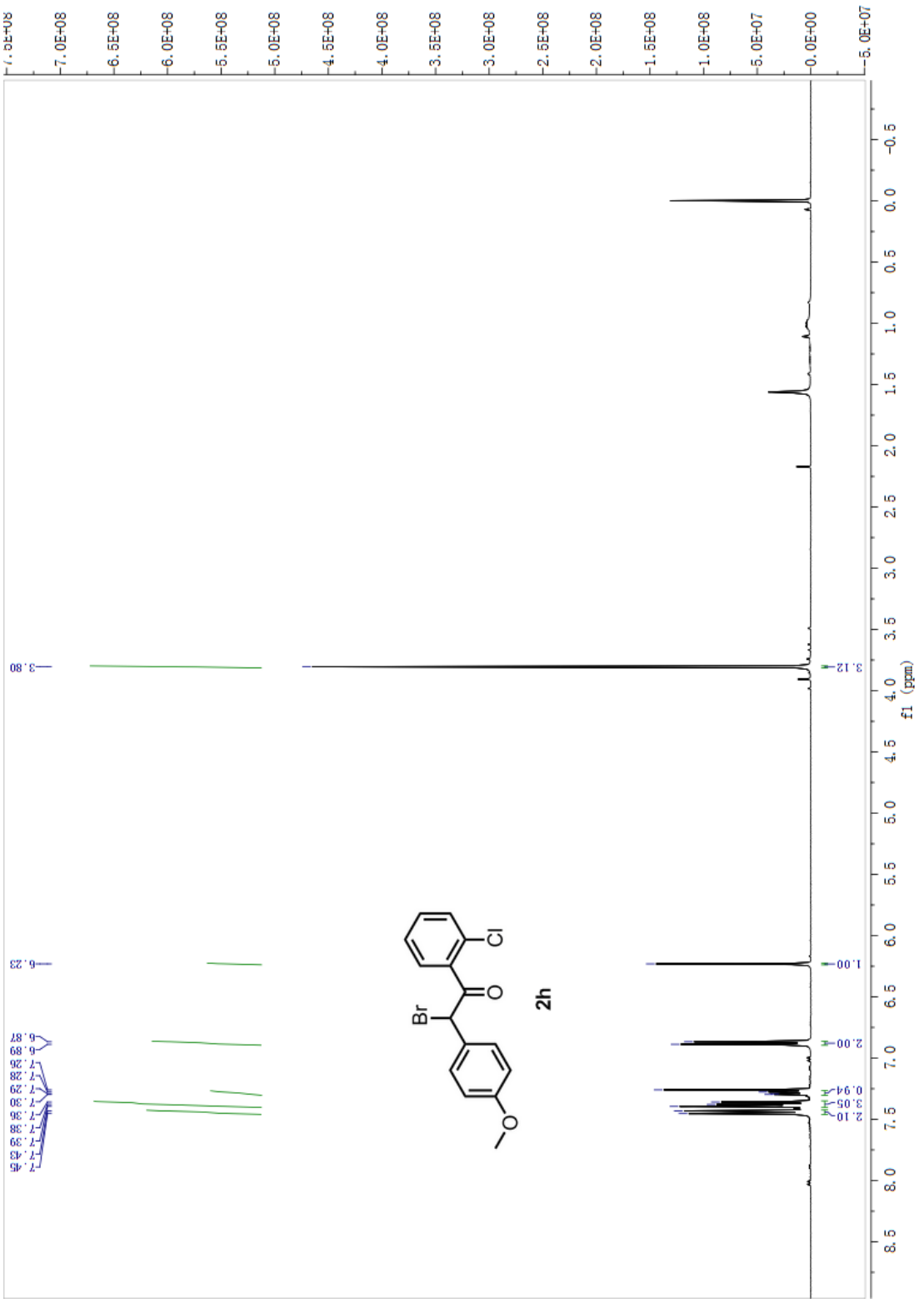



Br
Br
O
O
2f
f1 (ppm)





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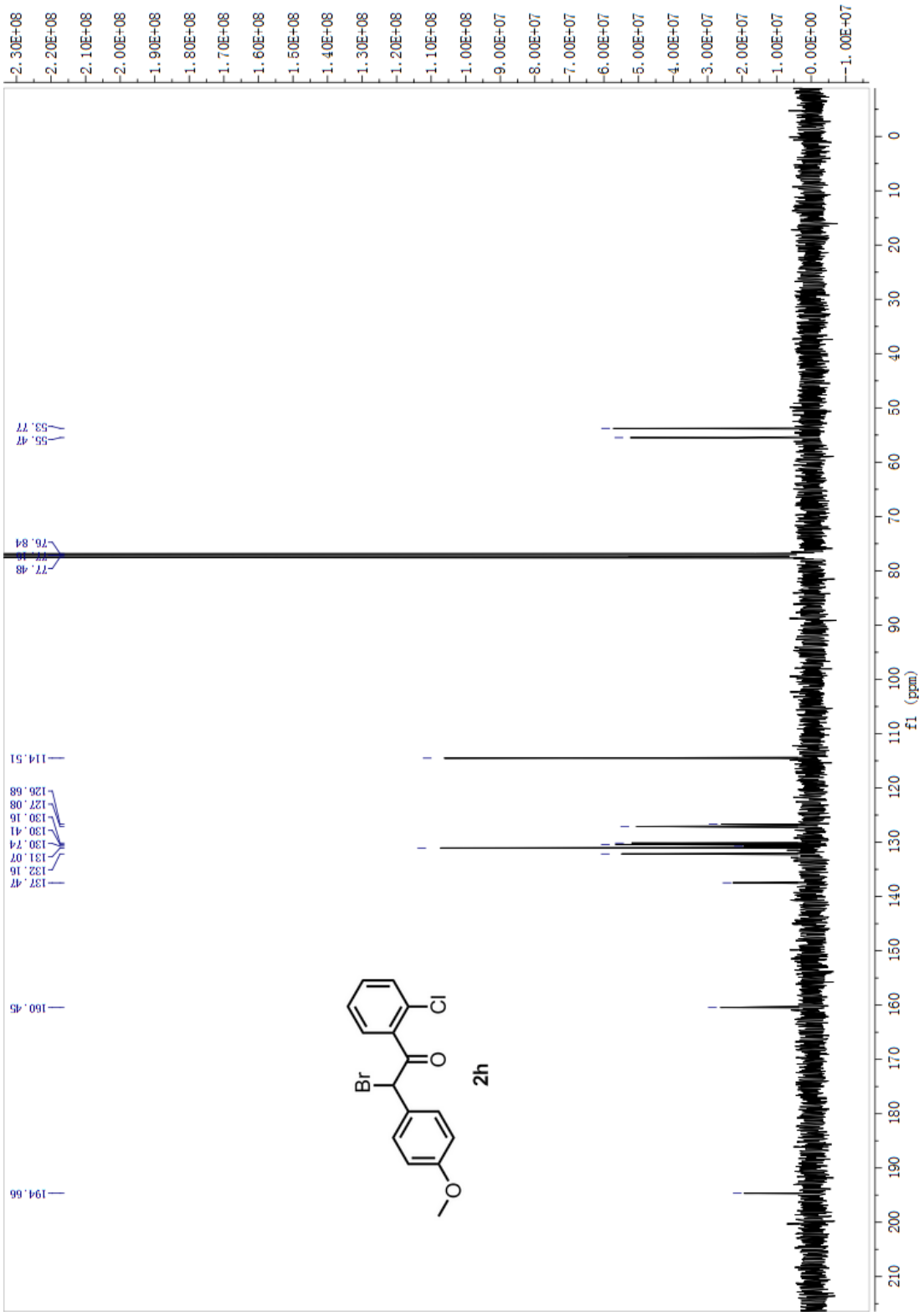
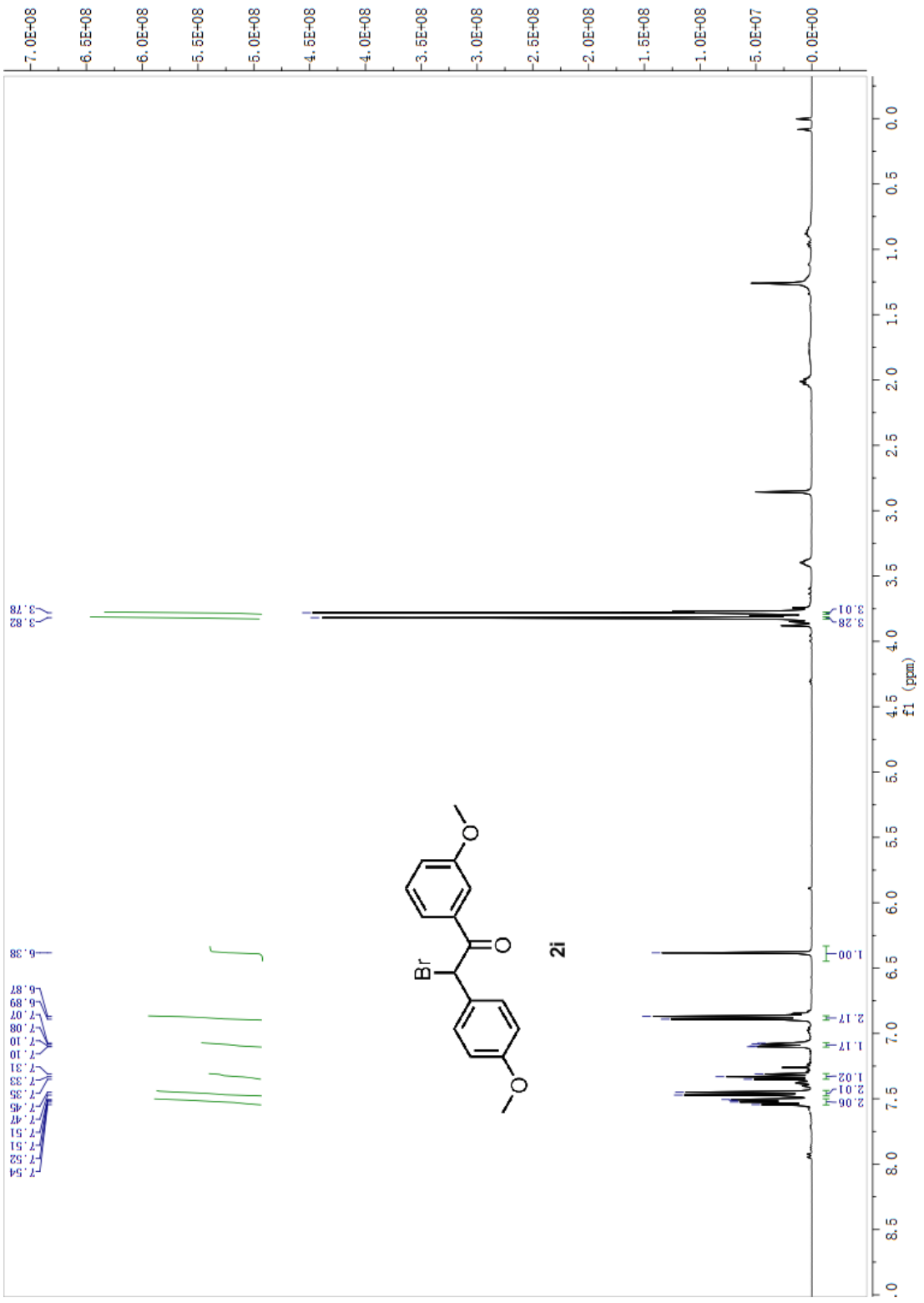
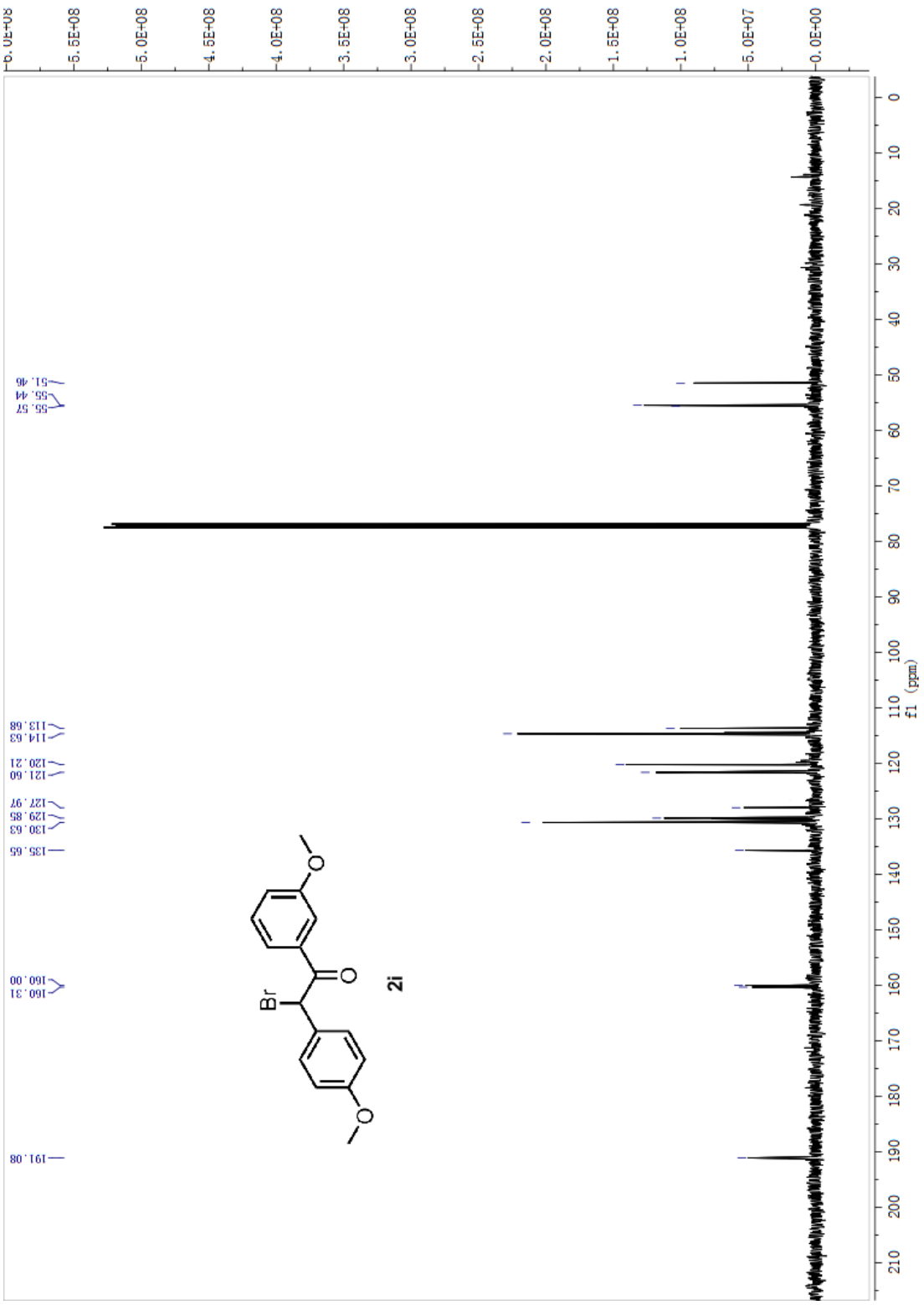
6.89
7.26
7.28
7.29
7.30
7.36
7.38
7.39
7.43
7.45
3.12
1.00
2.00
0.94
3.05
2.10
Br
O
Cl
O
2h



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160.31
160.00
135.65
130.63
129.85
127.97
121.60
120.21
114.63
113.68
55.57
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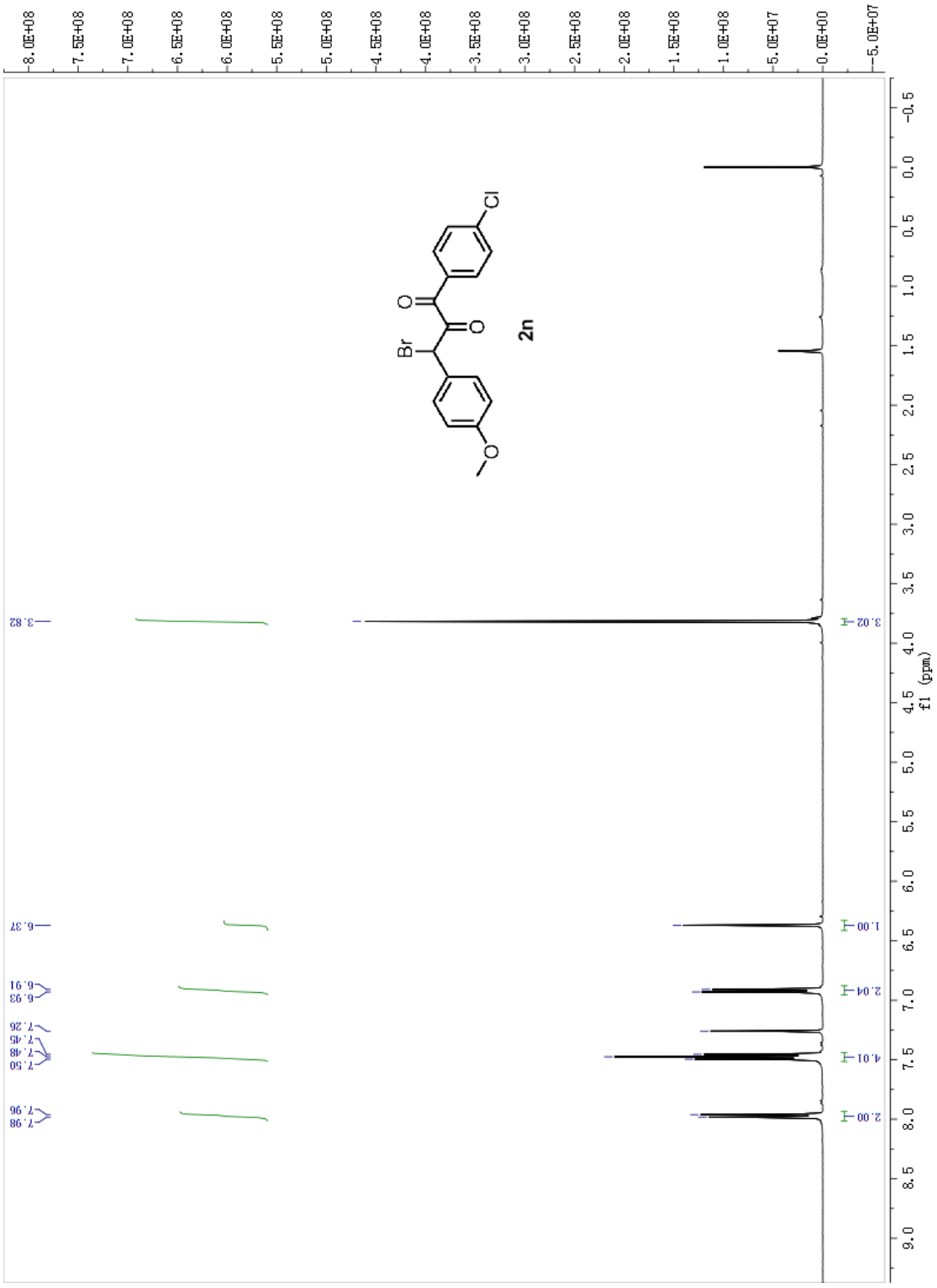
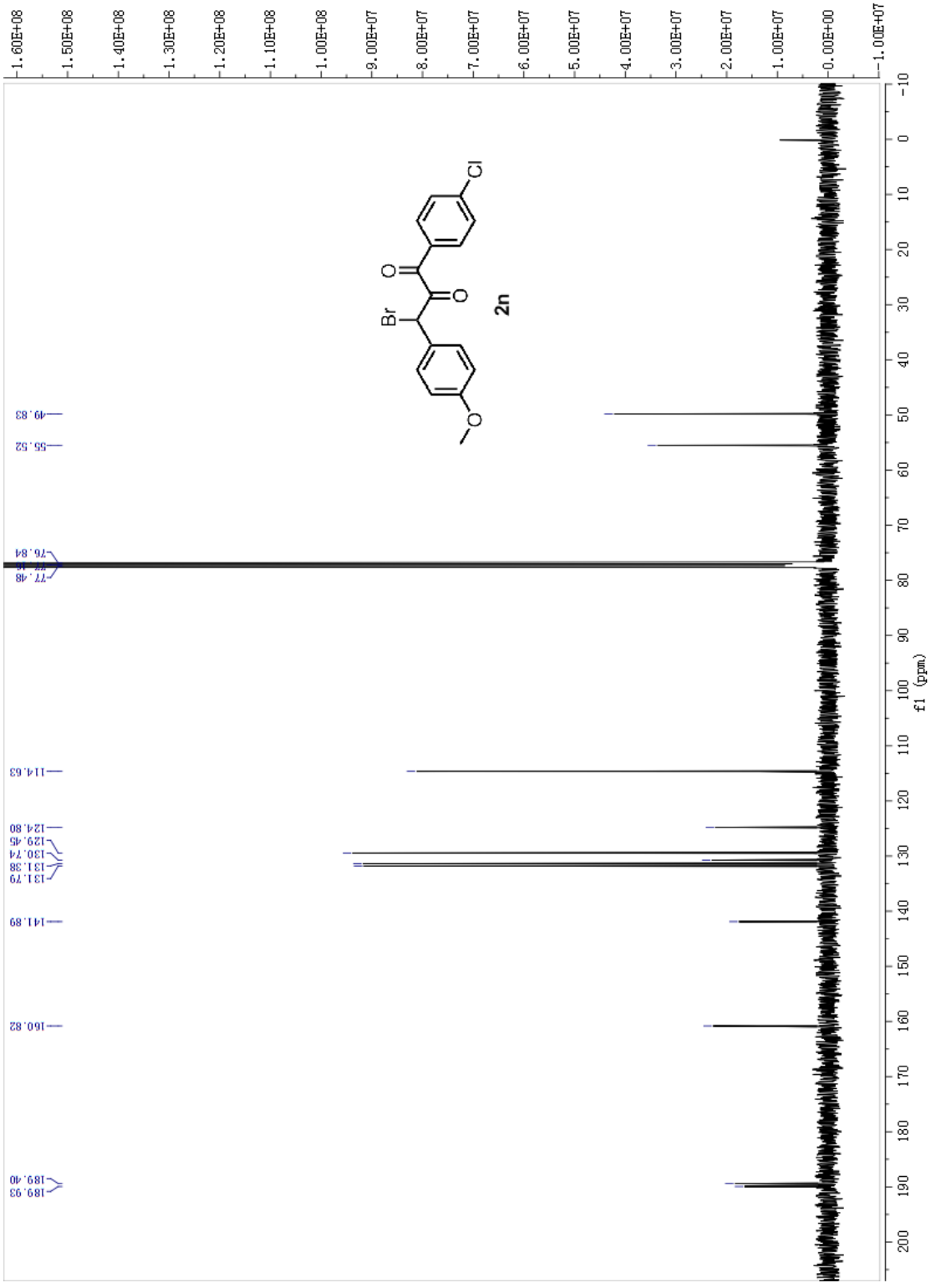
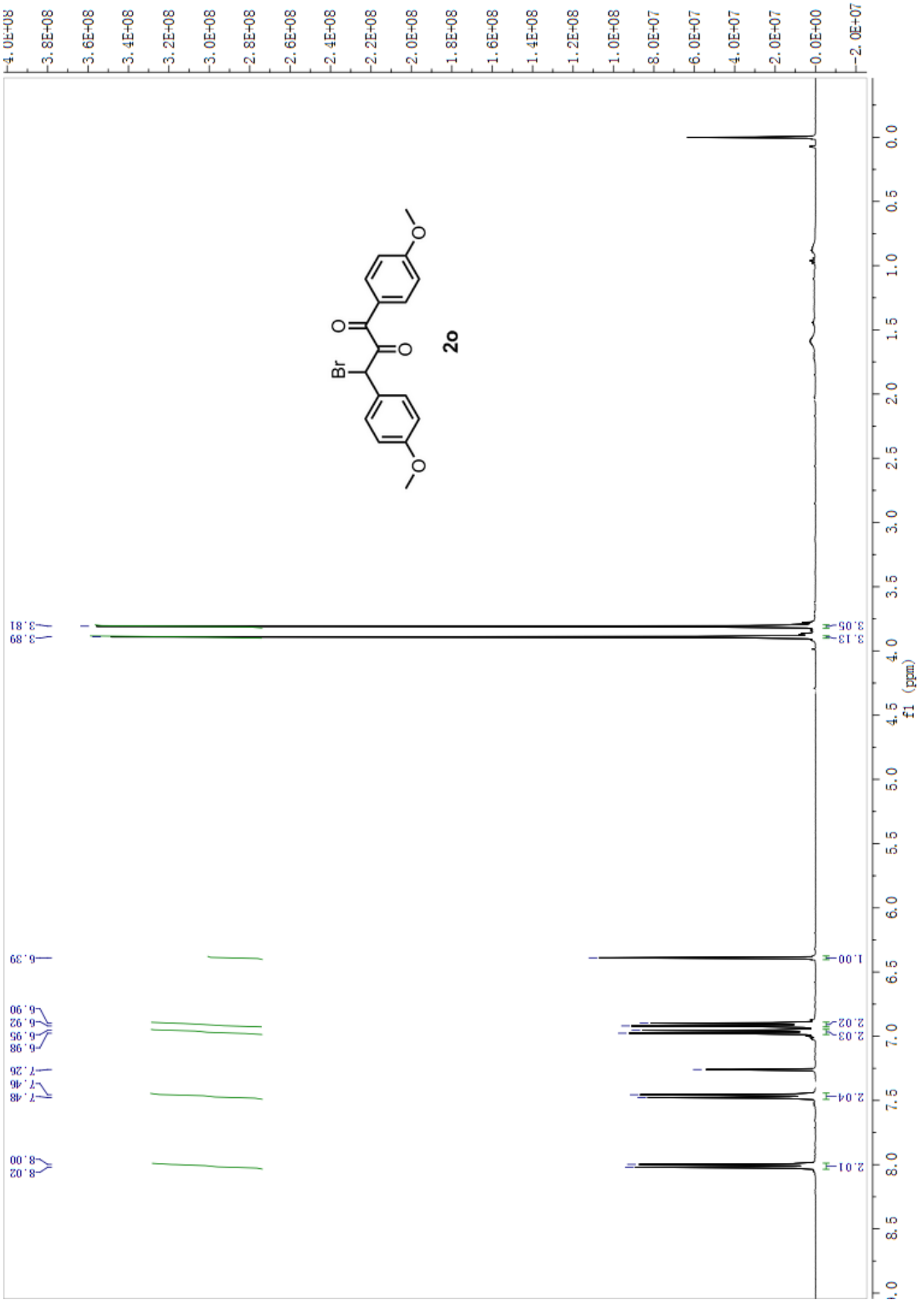
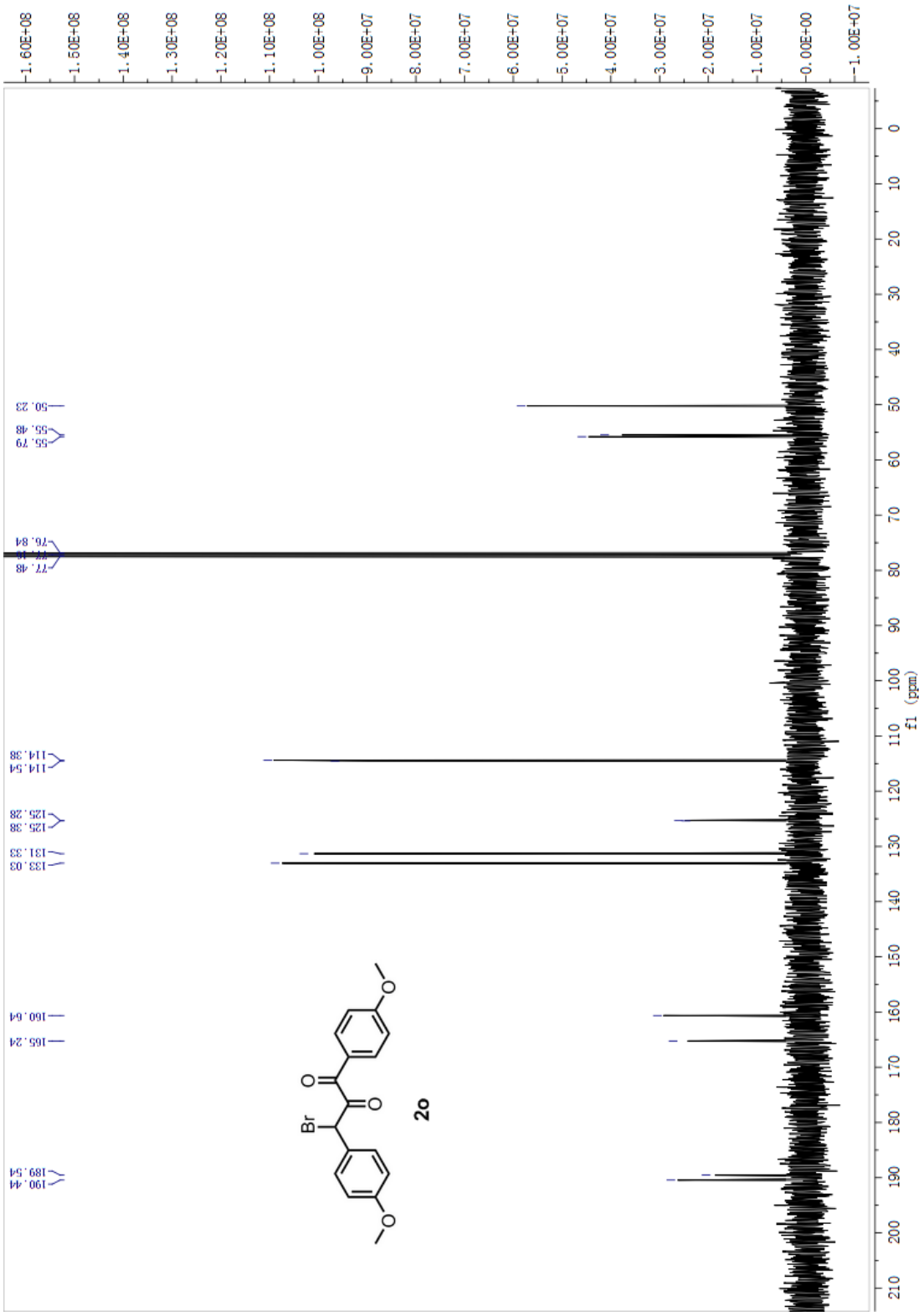
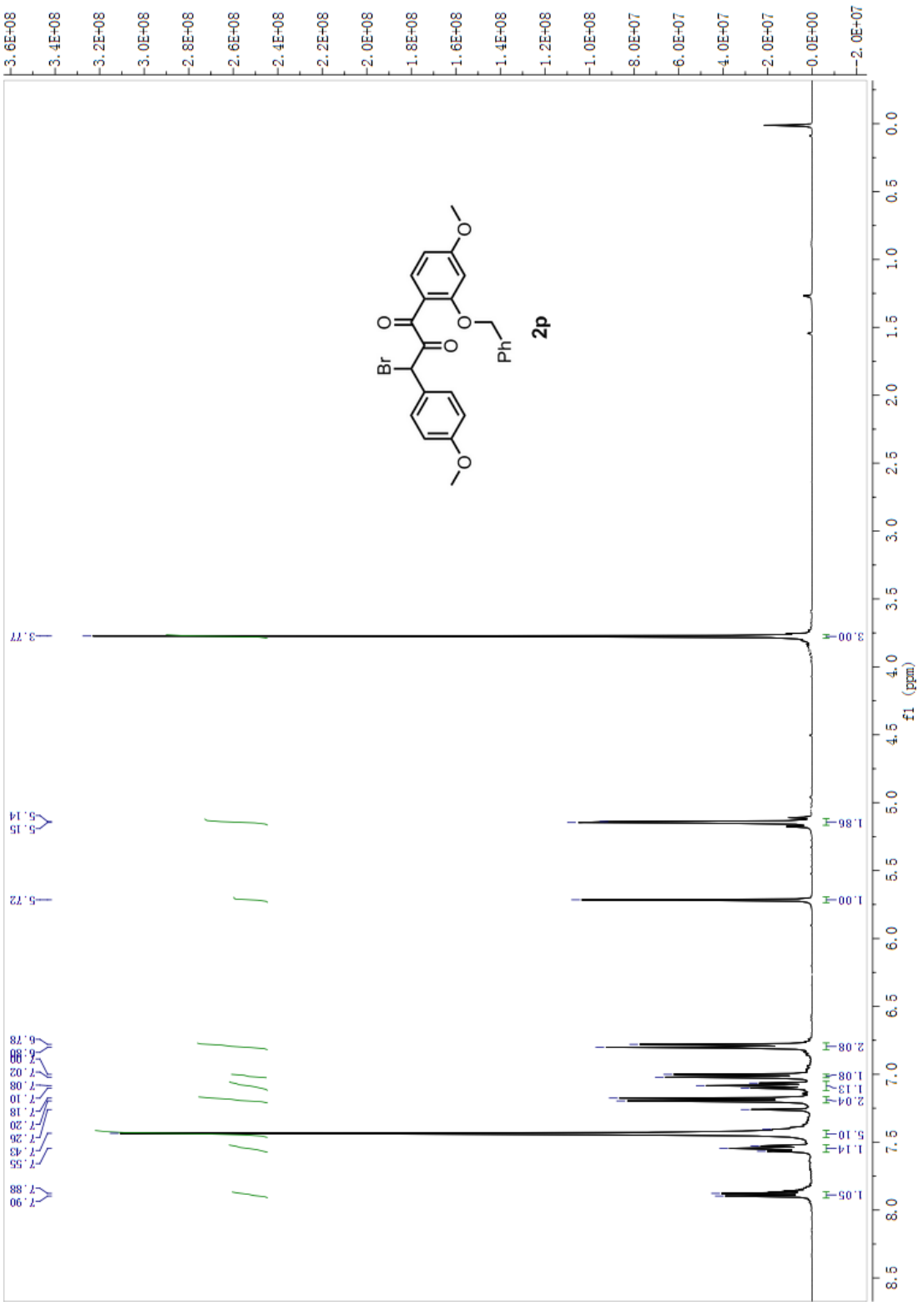
51.46
f1 (ppm)
Br
O
O
O
2i

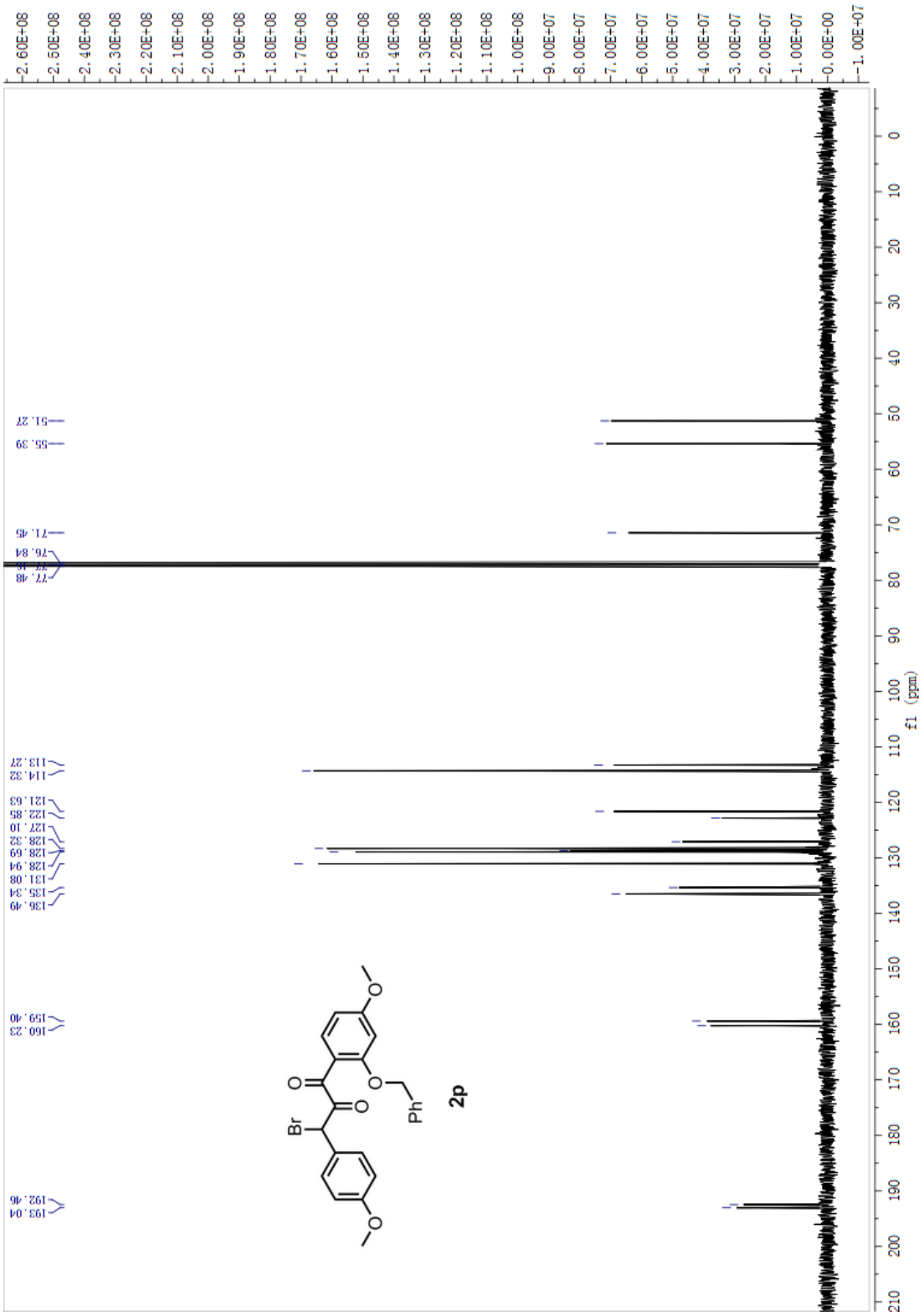





Br
O
O
O
O
2o
f1 (ppm)



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55.39
71.45
76.84
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113.27
114.32
121.63
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128.32
128.69
128.94
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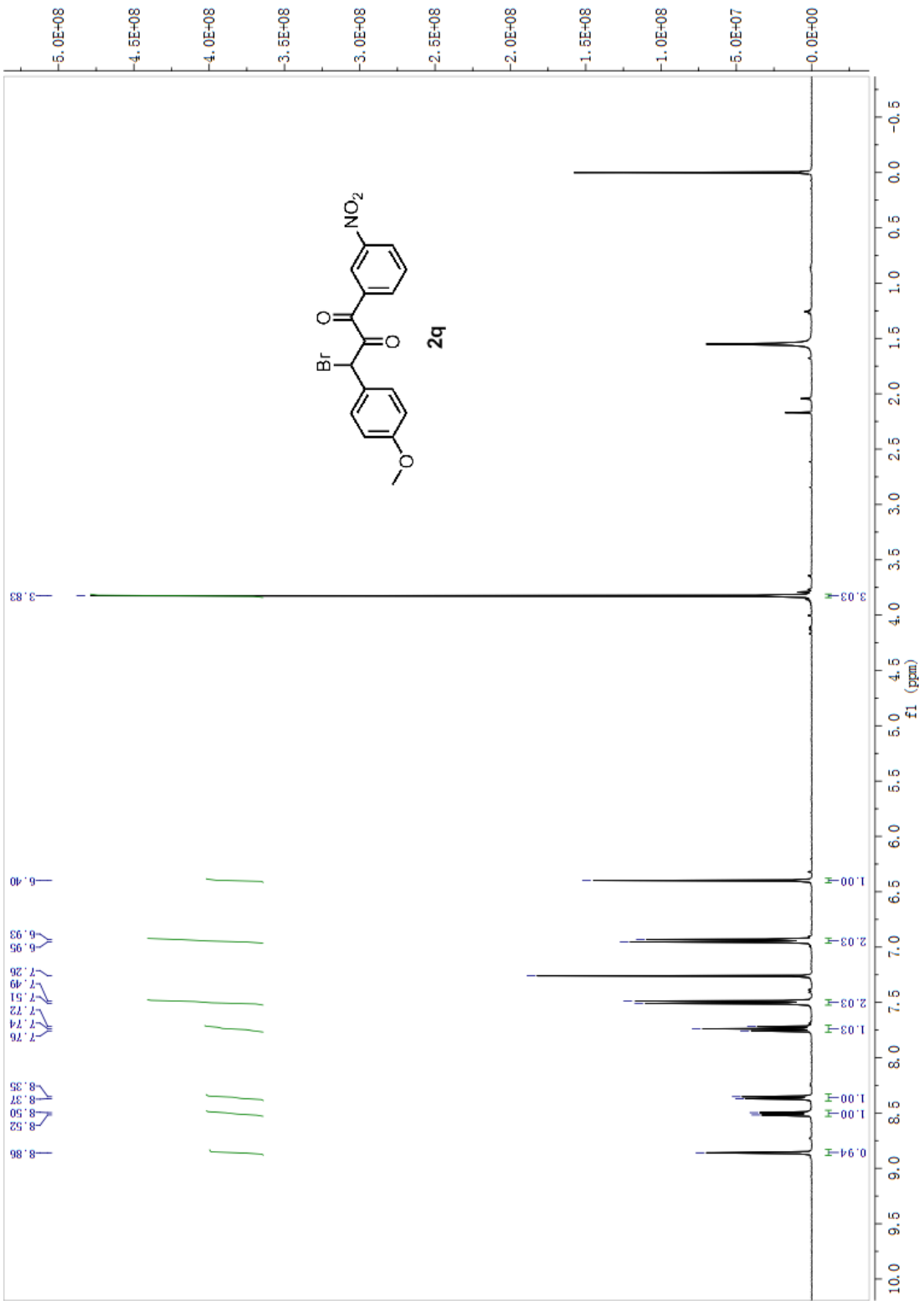
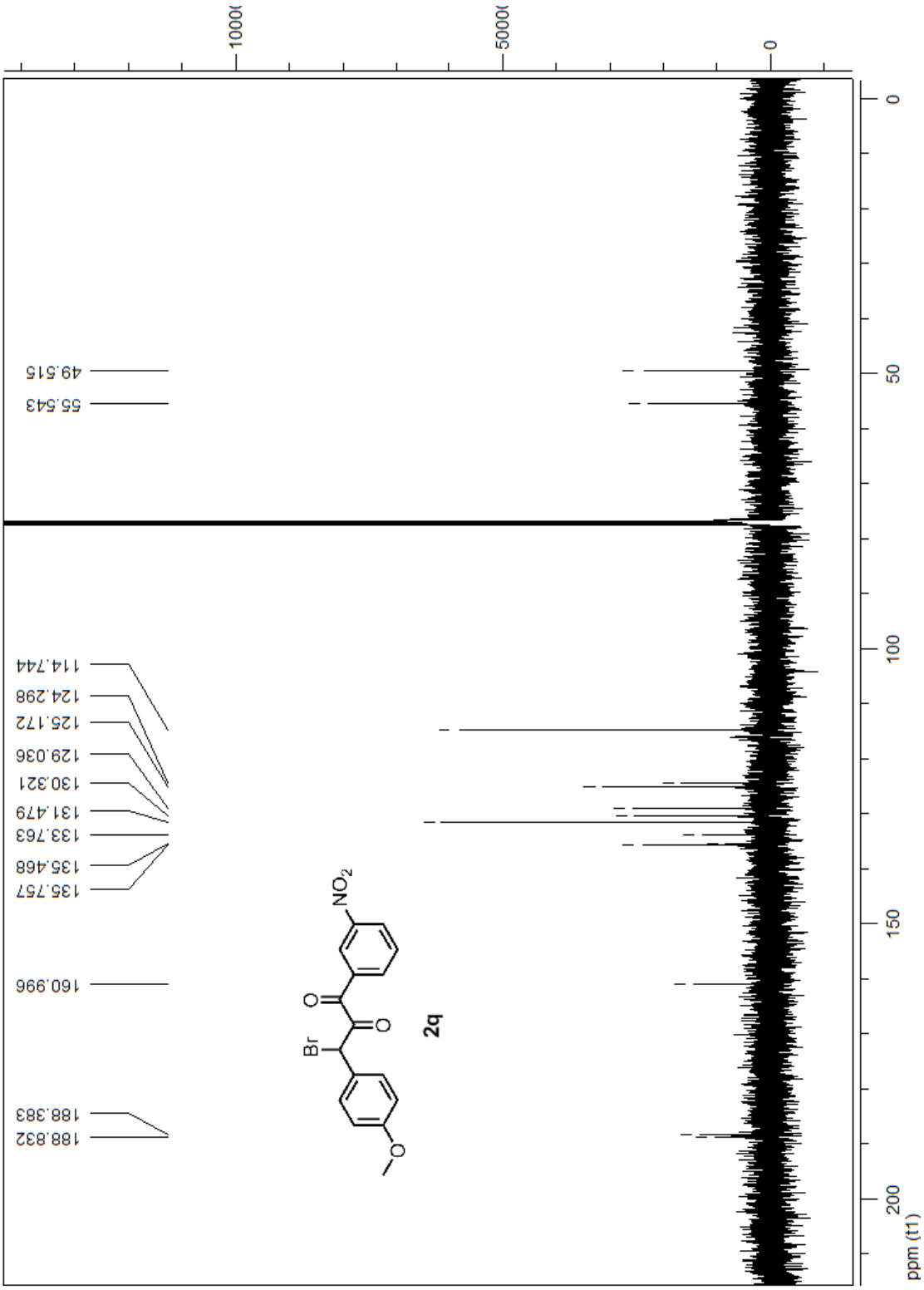
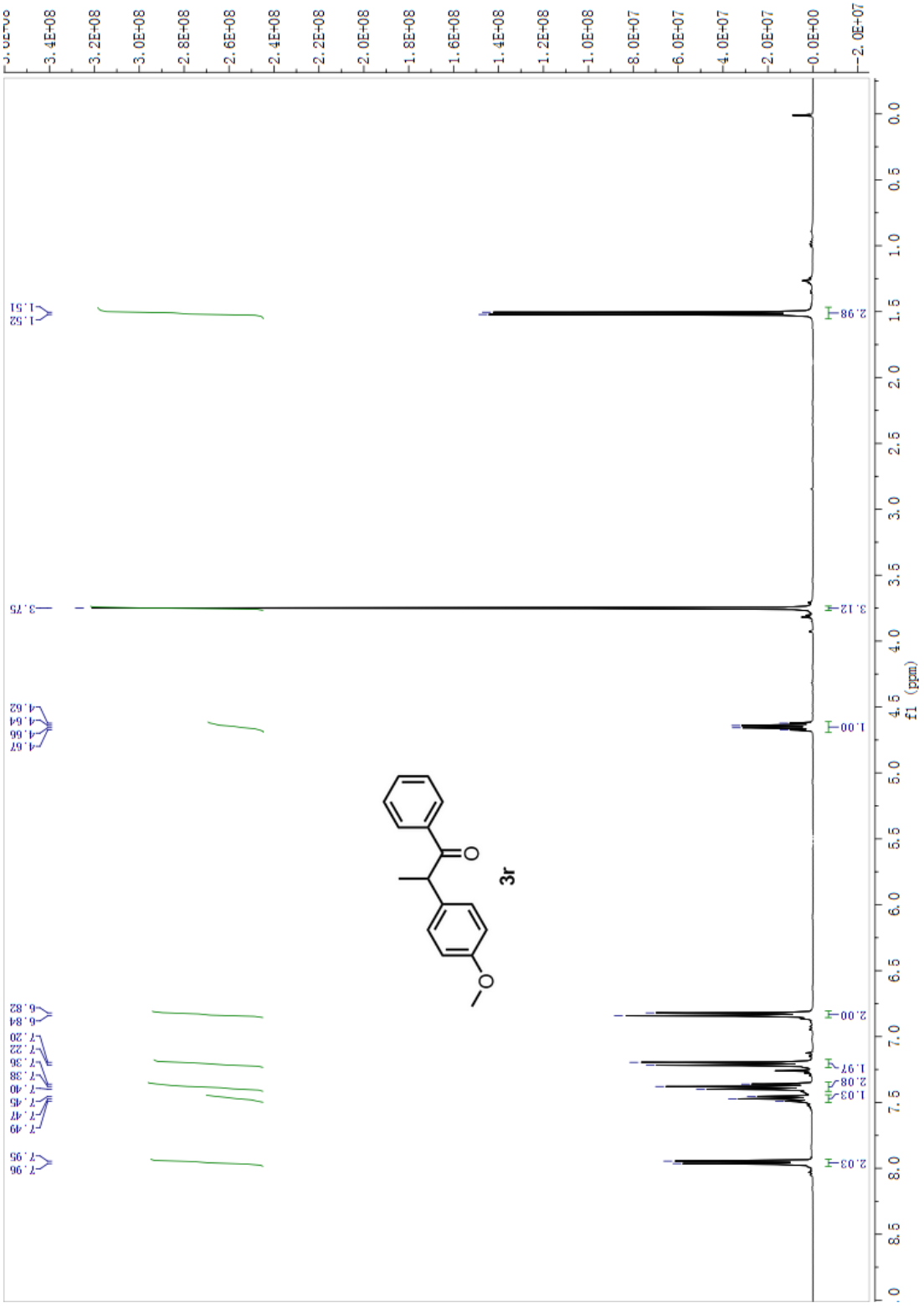
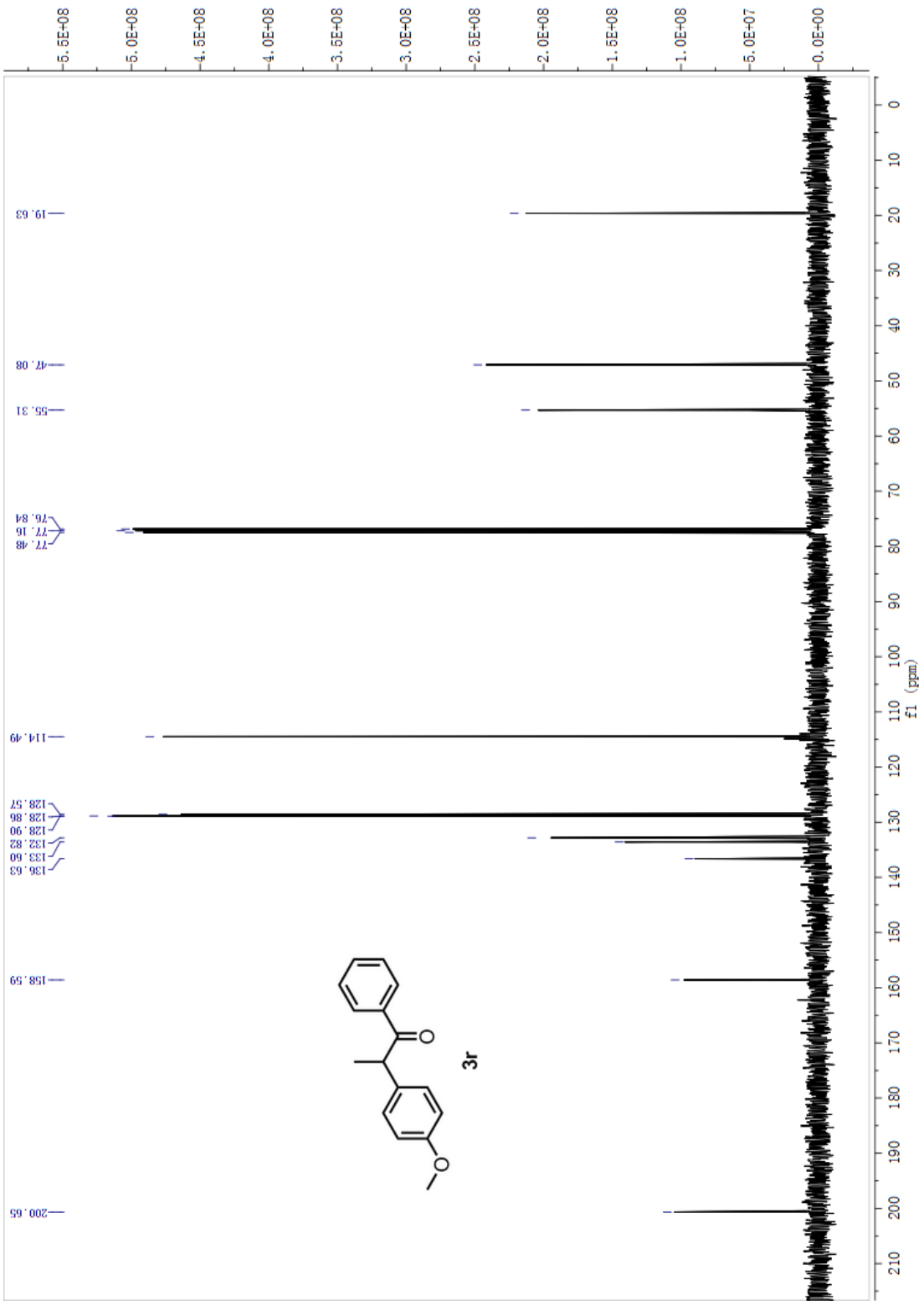
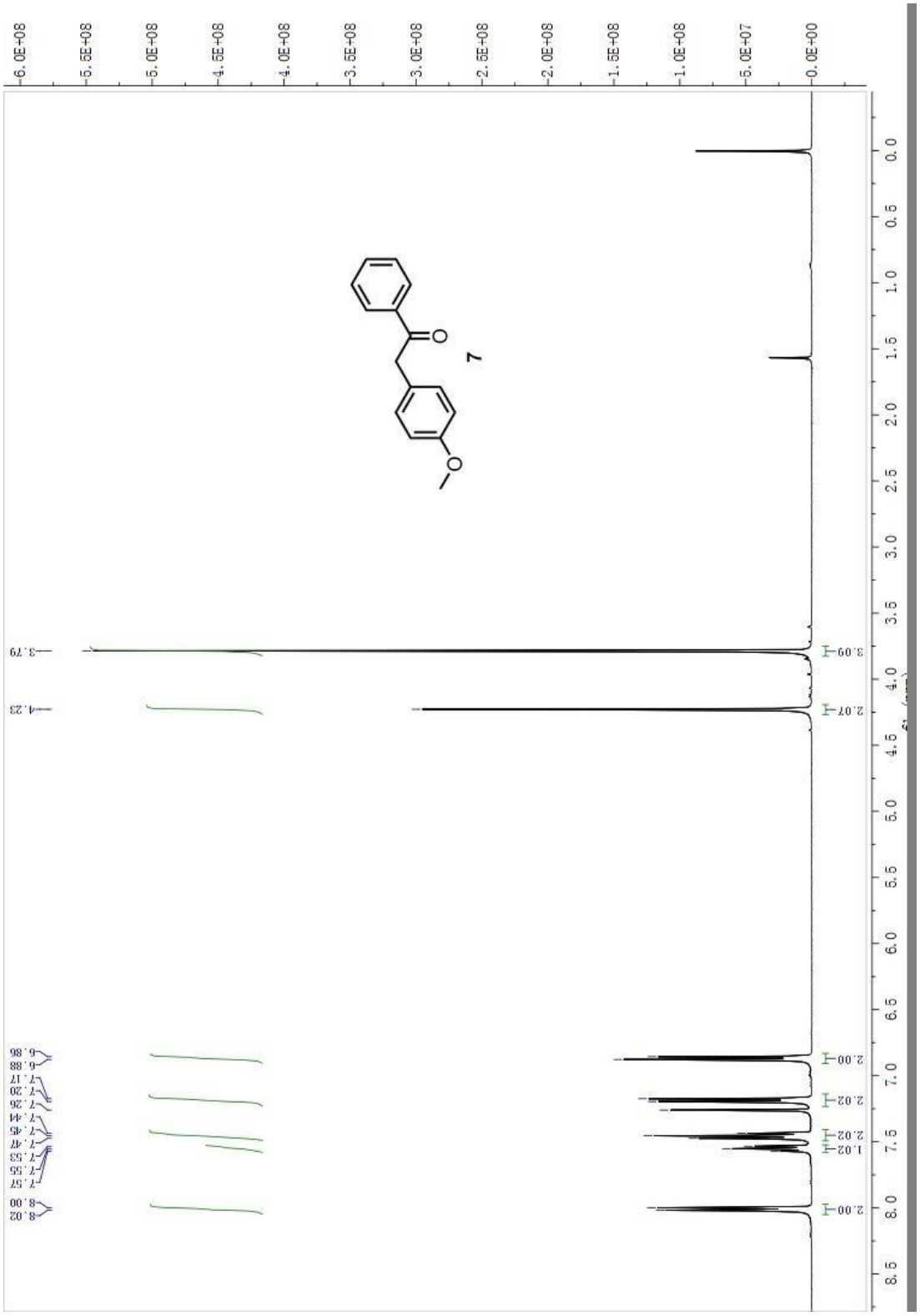
135.34
136.49
159.40
160.23
192.46
193.04
Br
O
Ph
2p
f1 (ppm)

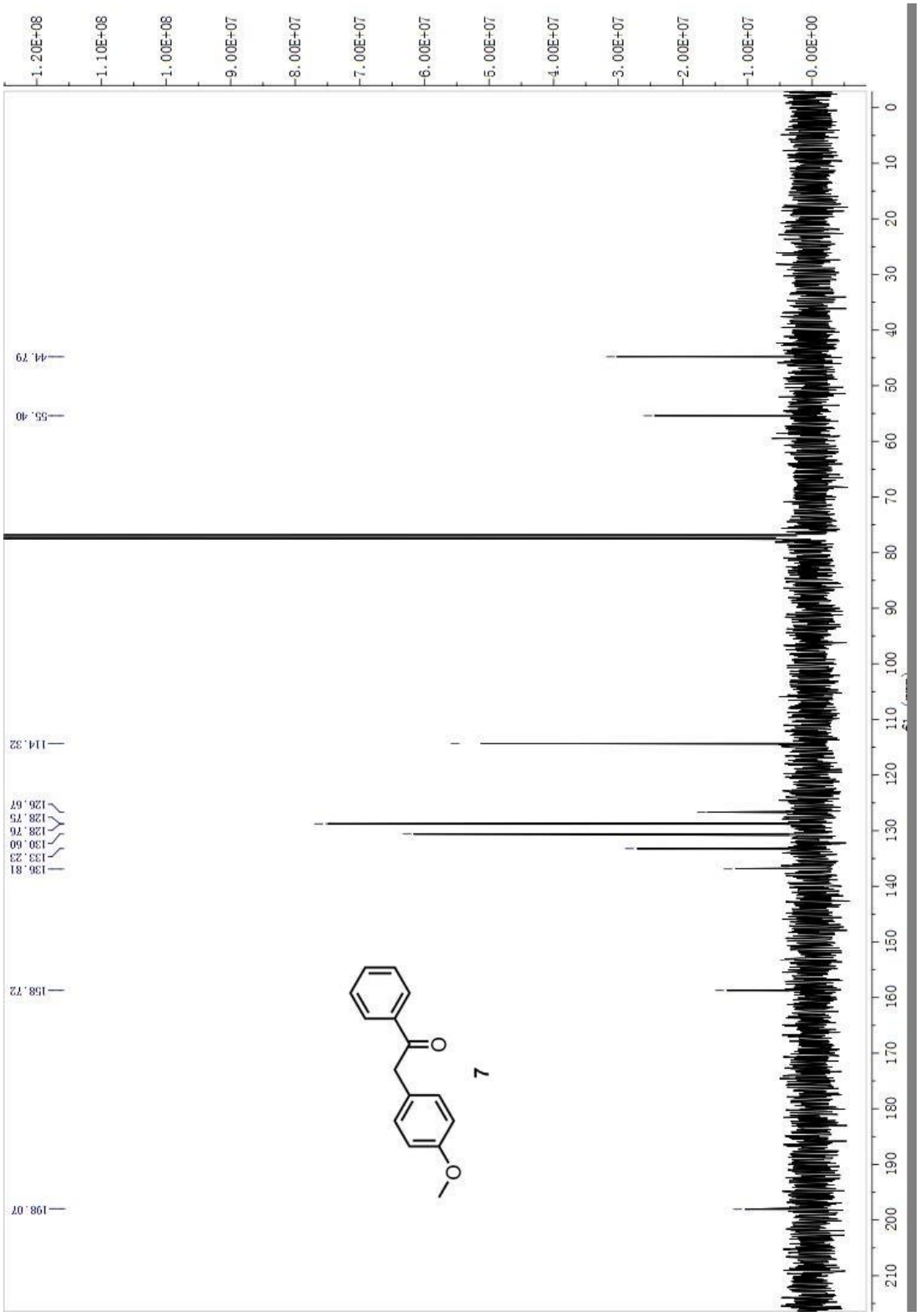

NO2
O
O
Br
O
2q
f1 (ppm)

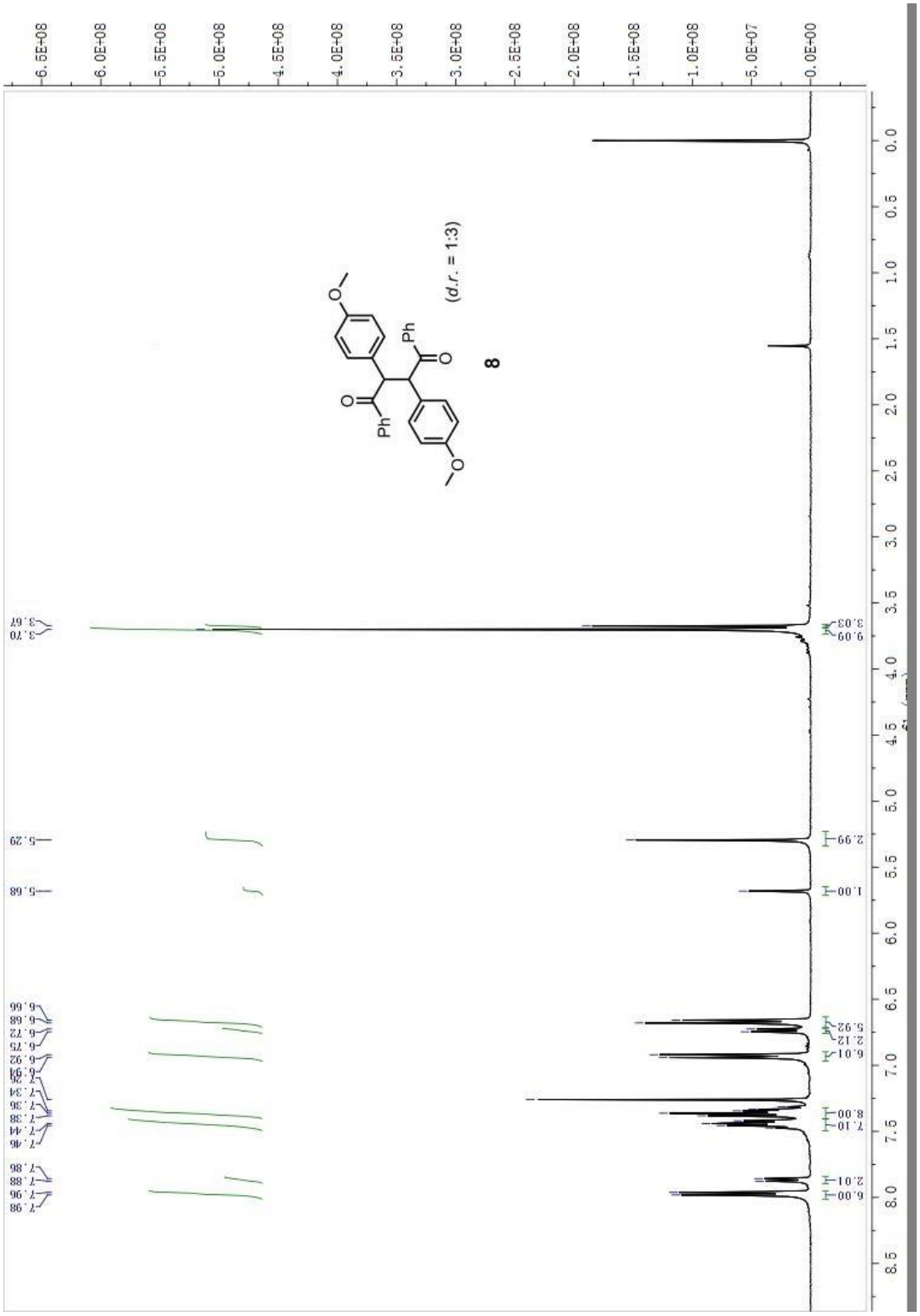


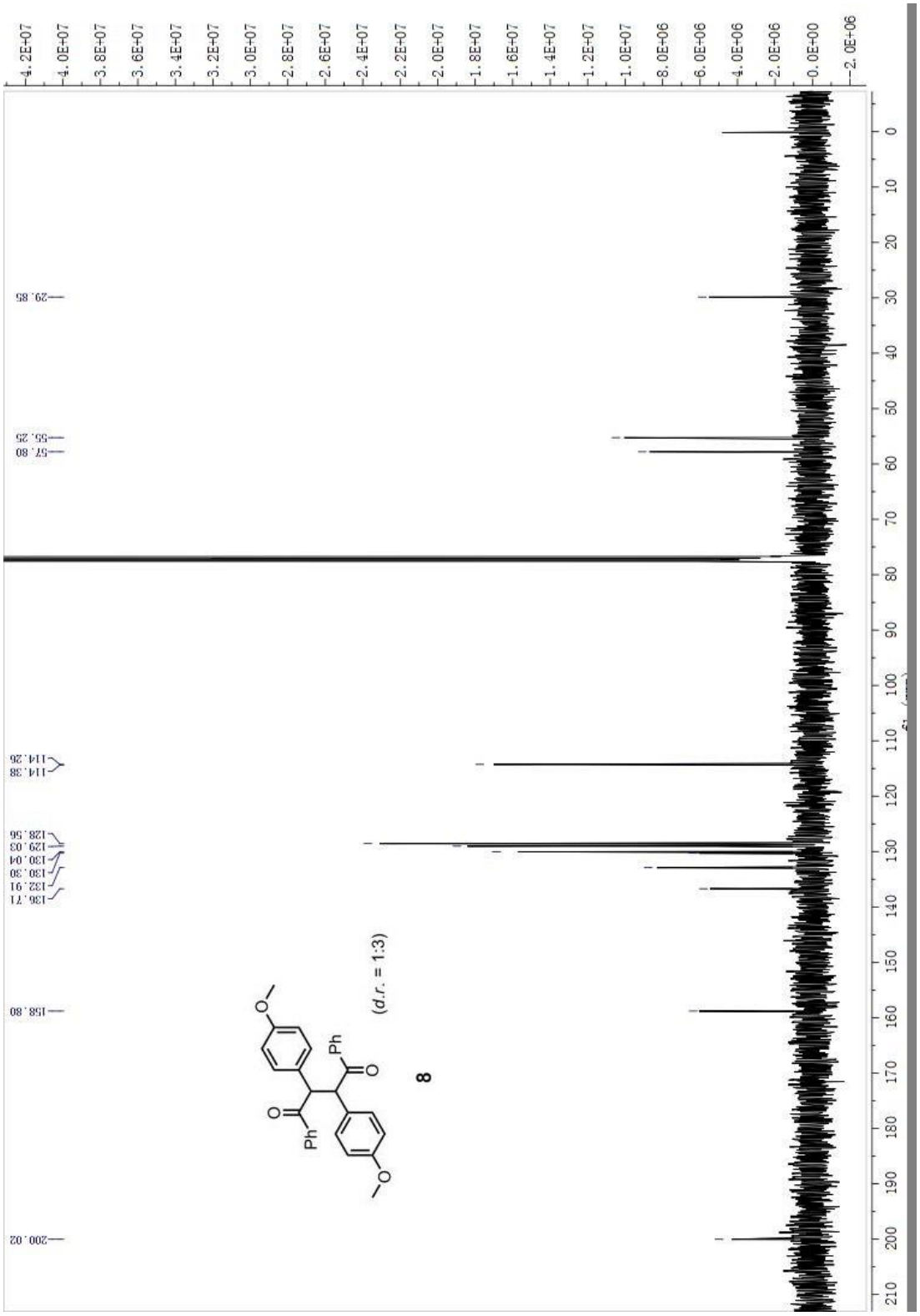


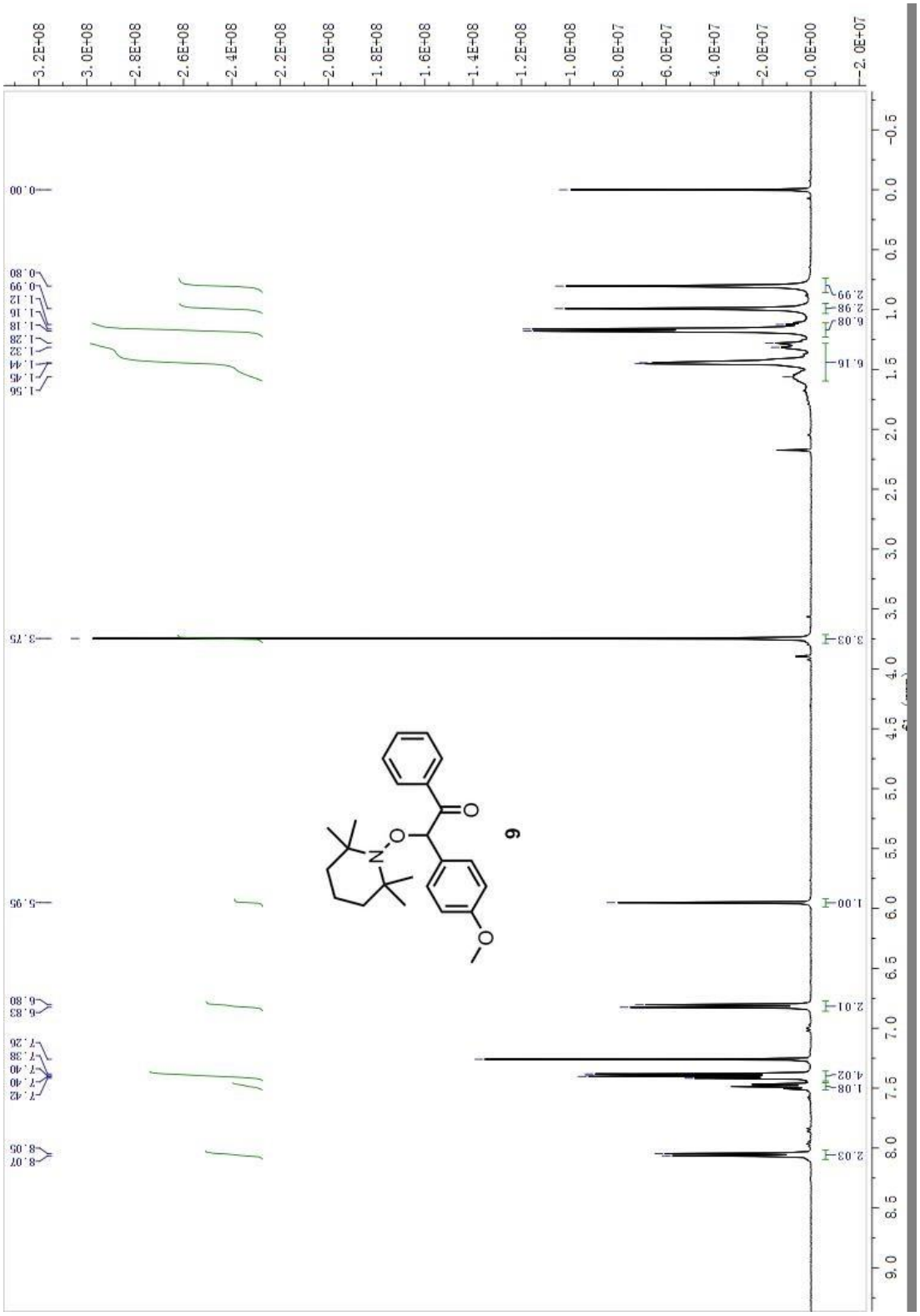



7
3.79
4.23
6.86
6.88
7.17
7.20
7.26
7.44
7.45
7.47
7.53
7.55
7.57
8.00
8.02
3.09
2.07
2.00
2.02
2.02
1.02
2.00





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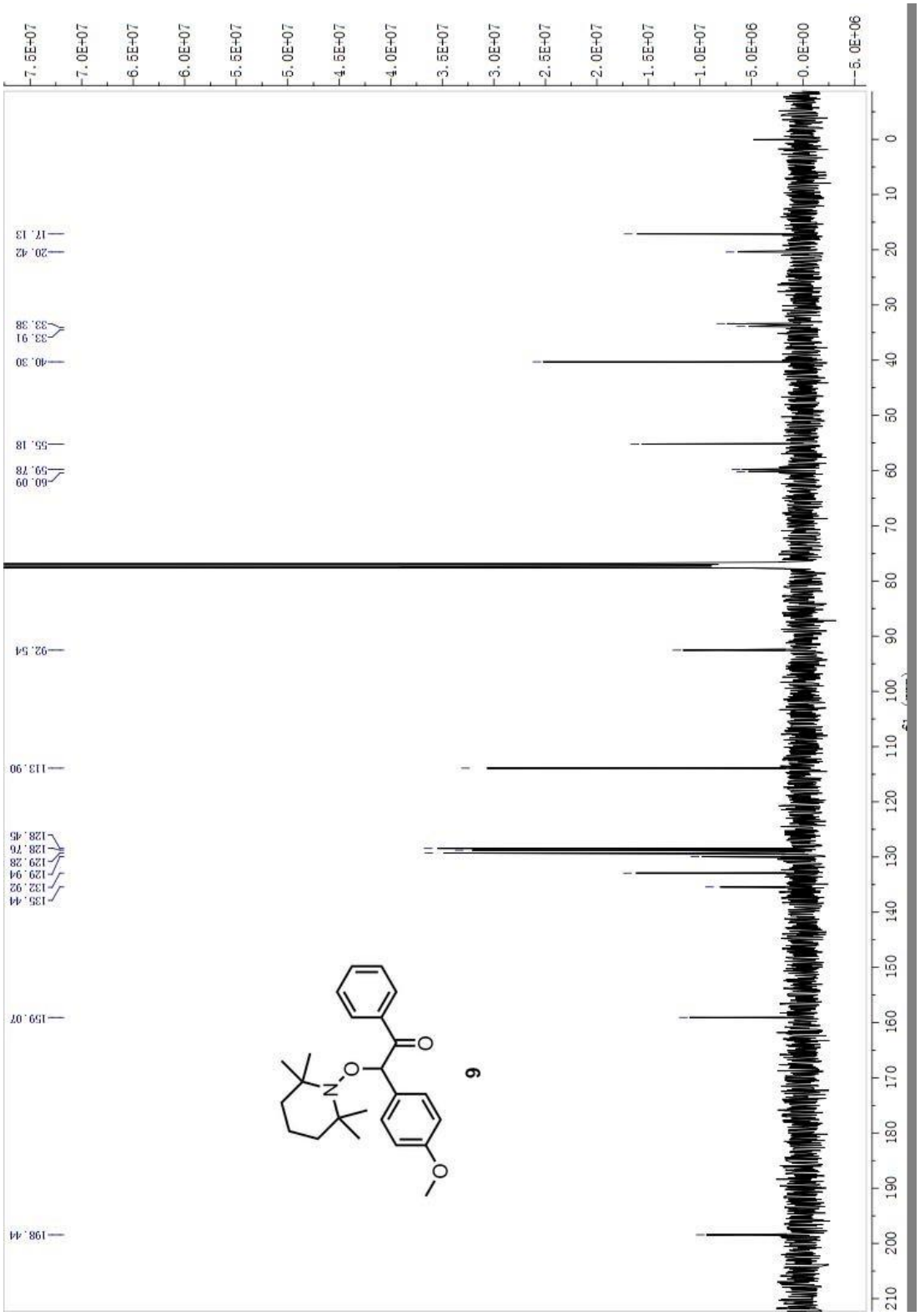
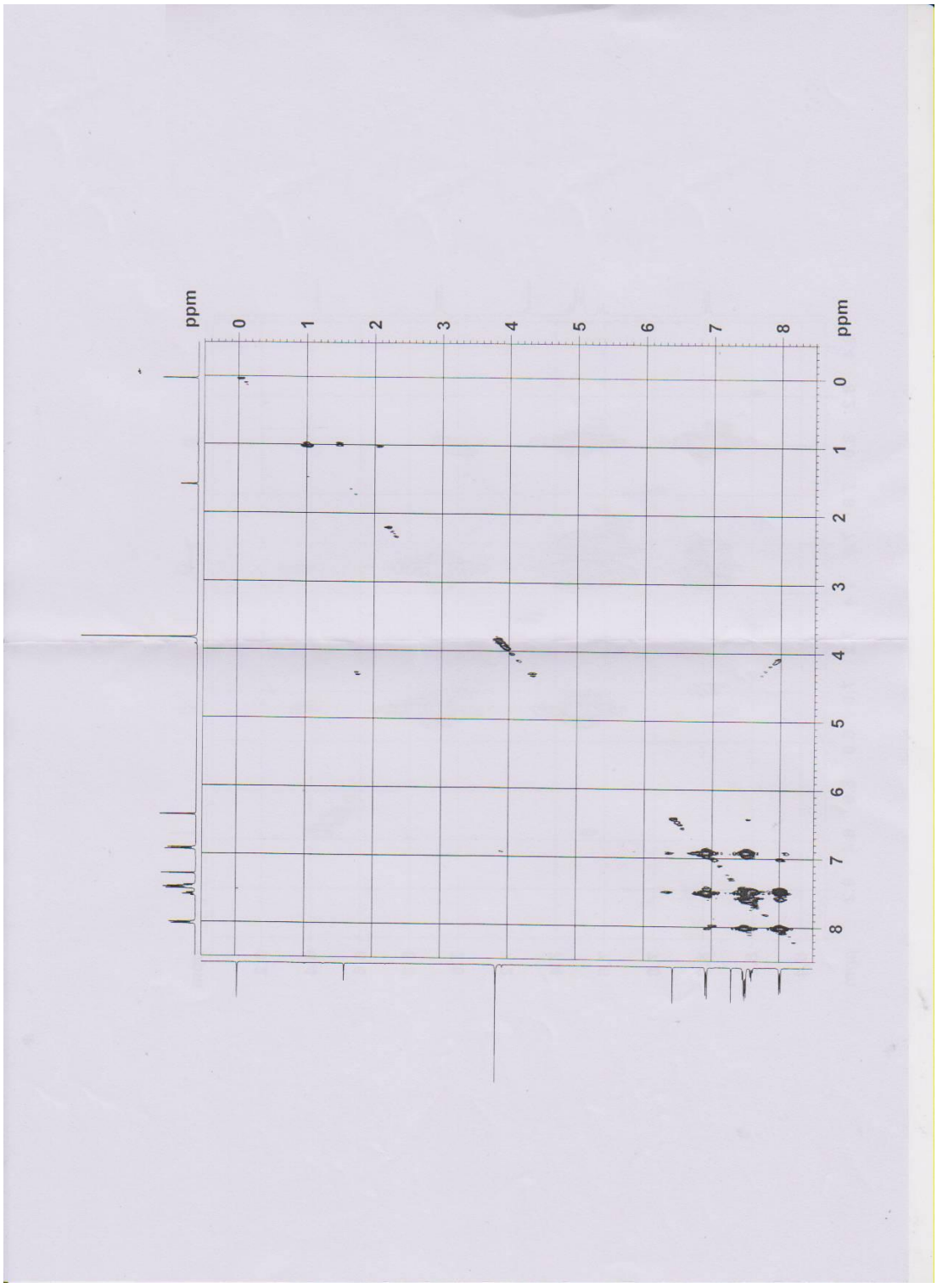
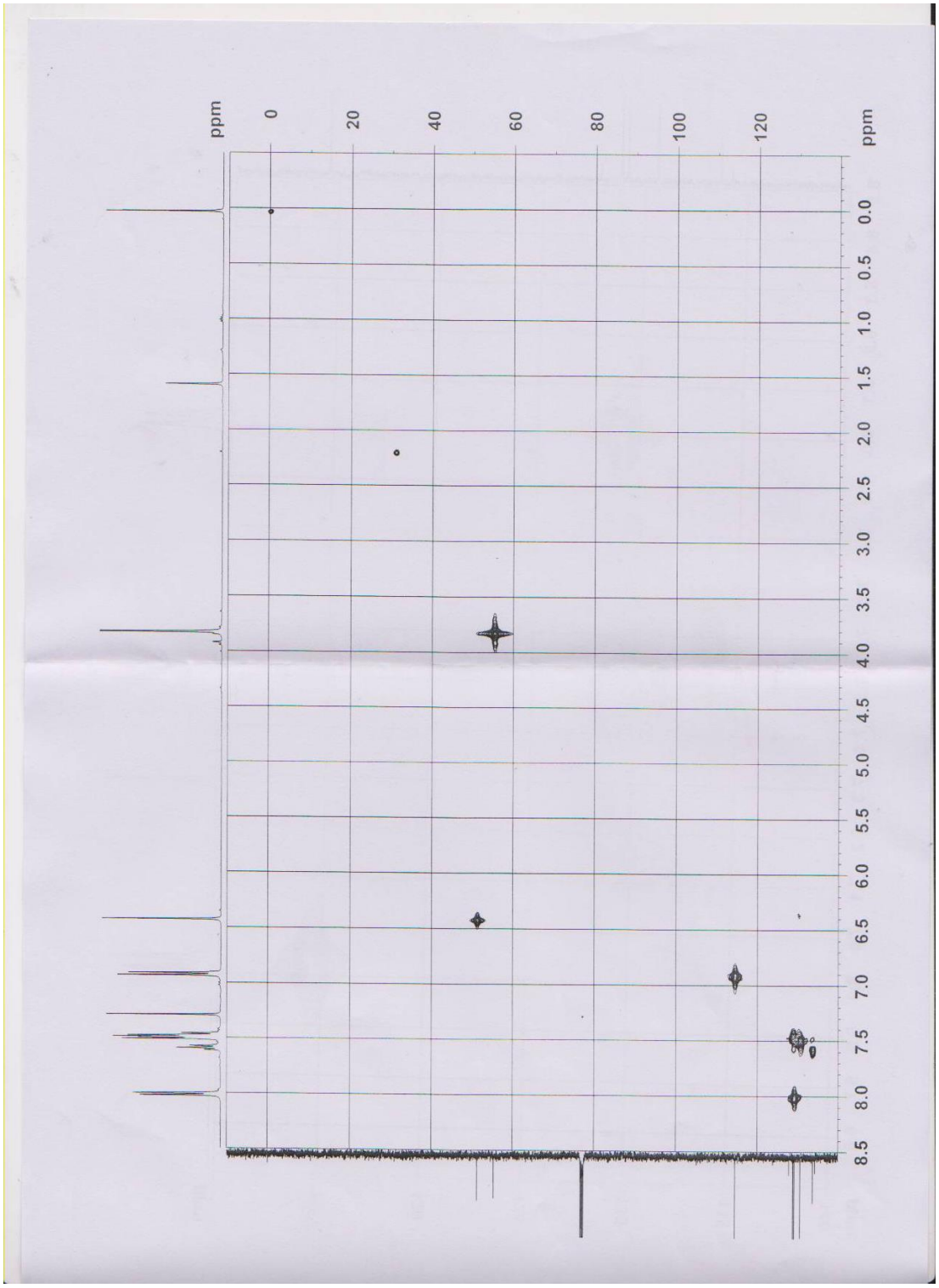


COSY spectra for 2a



HMQC spectra for 2a



HMBC spectra for 2a