Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Artificial photoenzyme catalyzed aerobic oxidative cleavage of olefins in water

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Contents

1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred to are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relatives to the $CDCl_3$ residual peak (δ 7.26). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Flash column chromatography was performed on silica gel 60Å, 10-40μm. Mass spectra of chemicals were measured on an APCI-micro TOF. Mass spectra of proteins were run on a MALDI-TOF mass spectrometer (AB SCIEX 5800 MALDI TOF). The absorption spectra and emission spectra were recorded at room temperature using an automatic microplate reader. Alkenes were prepared by following literature methods.[1,2] Preparation of BSA-TXO is described in our previous study.[3]

2. Supplementary Data, Figures and Tables

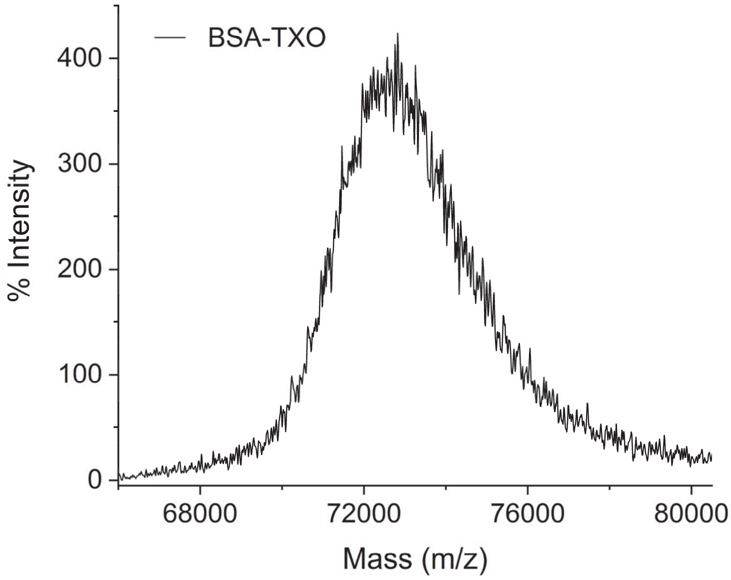
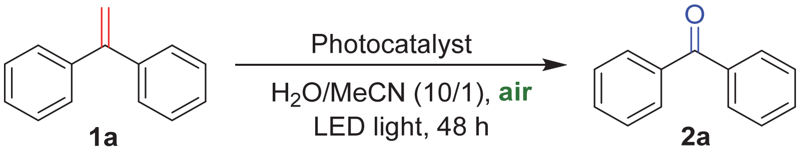


Figure S1. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of BSA-TXO.

Table S1. Optimization of the reaction conditions using TXO as photocatalyst.



Entry	Variation from standard conditions	Yield (%)
1	standard conditions	92
2	TXO (1.0 mol%), in H_2O	<5%
3	TXO (1.0 mol%), in MeCN	<5%
4	TXO (1.0 mol%), in H_2O/MeCN (v/v = 3/1)	<5%
5	TXO (1.0 mol%), in H_2O/MeCN (v/v = 1/1)	<5%
6	TXO (10 mol%), in H_2O/MeCN (v/v = 1/1)	34

Standard reaction conditions: 1,1-diphenylethylene **1a** (0.1 mmol), BSA-TXO (0.01 mol%) in H_2O/MeCN was stirred under LED light (λ = 405 nm) air for 48 h.

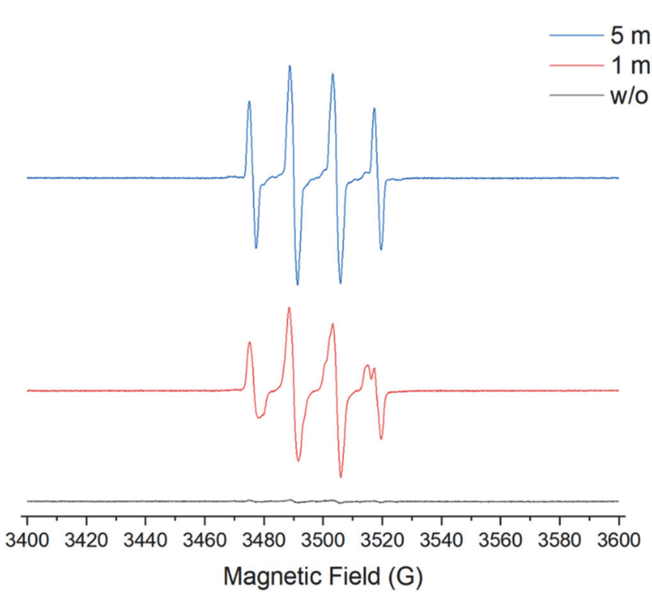


Figure S2. EPR experiments at (a) BSA-TXO in H_2O/MeCN = 10/1 without light. (b) BSA-TXO in H_2O/MeCN = 10/1 with DMPO irradiation for 1 min. (c) BSA-TXO in H_2O/MeCN = 10/1 with DMPO irradiation for 5 min.

MBTH method was applied for the testing of HCHO. The testing reagent was produced by mixing 3-methyl-2-benzothiazolone and ammonium ferric sulfate solution. Then one drop of the resulting reaction solution was added to the testing reagent, and the color turned blue very quickly, which, to some extent, demonstrated the presence of HCHO.[4]

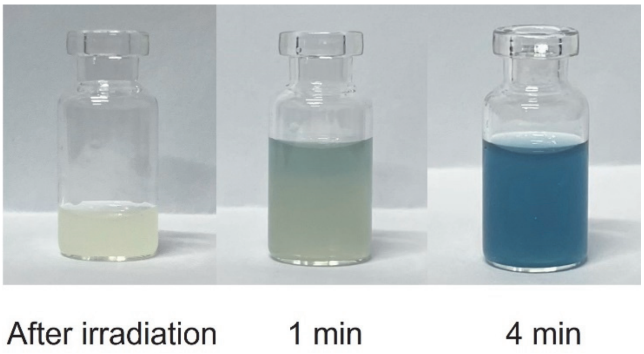


Figure S3. The identification of formaldehyde using the MBTH method.

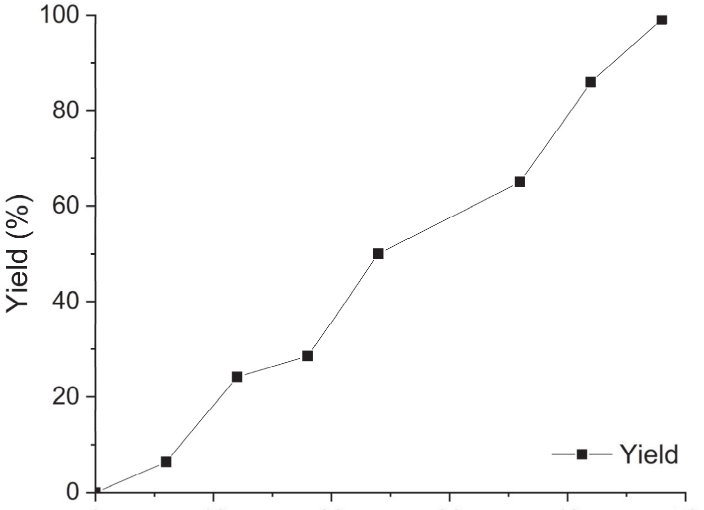
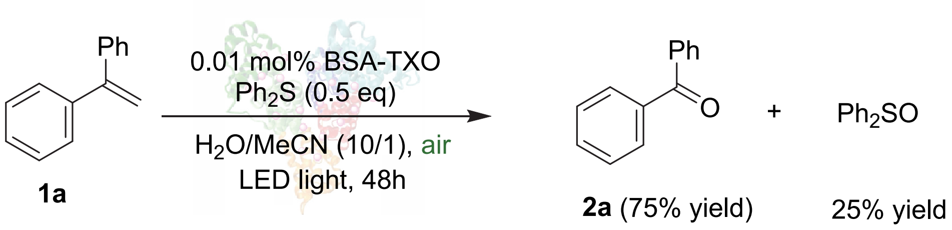


Figure S4. Reaction time course of aerobic oxidative cleavage of olefins in water. Standard reaction conditions: **1a** (0.1 mmol), BSA-TXO (0.01 mol%) in H_2O/MeCN (v/v = 10/1, 30 mL) was stirred under LED light (λ = 405 nm) in air.

Diphenyl sulfide being capable of rapidly reacting with dioxetanes while being inert toward endoperoxides, hydroperoxides, and singlet oxygen. By adding diphenyl sulfide (0.5 eq) to the reaction mixture of the model substrate **1a**, diphenyl sulfoxide was produced in 25% yield, and the yield of ketone 2a dropped from 92% to 75%. This observation supports the formation of proposed dioxetane intermediate.



Scheme S1. Trapping of dioxetane intermediate.

3. General procedure for photooxygenation

To a test tube containing purified water (20 mL) was added BSA-TXO catalyst (0.01 mmol%, 0.7 mg). The mixture was stirred, and an acetonitrile (2 mL) solution of substrate (0.1 mmol) was added. After the protein solution and the substrate solution are well mixed, a magnet was added, sealed with tin foil (left several holes by needle), and stirred at room temperature under 405 nm light for about 48 hours. After the reaction, the suspension was extracted three times with dichloromethane and the organic phase was collected. The collected filtrate was concentrated under reduced pressure, and purified by flash column chromatography (SiO_2, PE:EA = 50:1) to afford the desired product.

4. General procedure for recycling photocatalyst

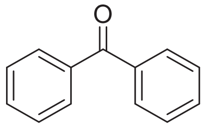
0.05 mmol of chalcone, 0.1 mol% of BSA-TXO were added into test tude containing purified water (20 mL) and acetonitrile (2 mL). Reaction was irradiated by 405 nm blue LED under nitrogen under room temperature. After the reaction, the mixture was extracted with ethyl ether (3×30 mL). The combined organic layer was concentrated in vacuum to give a crude product and water layer for next step. Water layer was moved to a another test tude, and an acetonitrile (2 mL) solution of substrate (0.05 mmol) was added.Then the above experimental procedures. Yield of cyclobutane was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

5. Gram-scale reaction of 1,1-diphenylethylene

To a test tube containing purified water (230 mL) was added BSA-TXO catalyst (0.01 mmol%, 14 mg). The mixture was stirred, and an acetonitrile (20 mL) solution of 1,1-diphenylethylene **1a** (2 mmol, 360 mg) was added. After the protein solution and the substrate solution are well mixed, a magnet was added, sealed with tin foil (left several holes by needle), and stirred at room temperature under 405 nm light for about 48 hours. After the reaction, the suspension was extracted three times with dichloromethane and the organic phase was collected. The collected filtrate was concentrated under reduced pressure, and purified by flash column chromatography (SiO_2, PE:EA = 50:1) to afford the desired benzophenone product (75%, 273 mg).

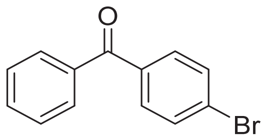
6. Characterization data for all products

Benzophenone (**2a**)



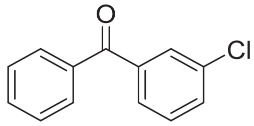
18 mg, 99% yield, yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86-7.80 (m, 4H), 7.65-7.58 (m, 2H), 7.51 (dd, *J* = 8.3, 7.0 Hz, 4H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

4-Bromophenyl)(phenyl)methanone (**2b**)



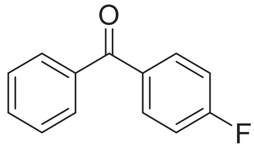
15 mg, 56% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80-7.76 (m, 2H), 7.70-7.58 (m, 5H), 7.53-7.46 (m, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[6]

3-Bhlorophenyl)(phenyl)methanone (**2c**)



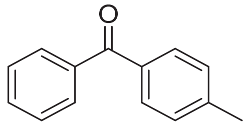
10 mg, 44% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dt, *J* = 8.7, 1.5 Hz, 3H), 7.69 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.67-7.61 (m, 1H), 7.59 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.53 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[7]

4-Fluorophenyl)(phenyl)methanone (**2d**)



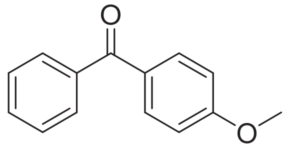
13 mg, 65% yield, white solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90-7.85 (m, 2H), 7.82-7.77 (m, 2H), 7.66-7.58 (m, 1H), 7.55-7.47 (m, 2H), 7.23-7.14 (m, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

Phenyl(p-tolyl)methanone (**2e**)



15 mg, 79% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83-7.79 (m, 2H), 7.77-7.73 (m, 2H), 7.63-7.57 (m, 1H), 7.53-7.47 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[6]

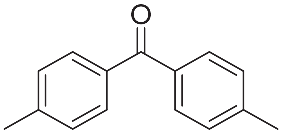
(4-methoxyphenyl)(phenyl)methanone (**2f**)



20 mg, 98% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88-7.83 (m, 2H),

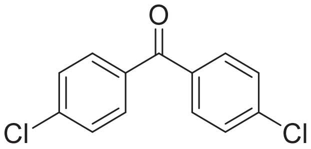
7.80-7.76 (m, 2H), 7.62-7.55 (m, 1H), 7.53-7.47 (m, 2H), 7.08-6.92 (m, 2H), 3.91 (s, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[6]

Di-p-tolylmethanone (**2g**)



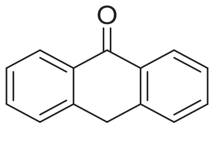
13 mg, 60% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76-7.64 (m, 4H), 7.27 (d, J = 9.7 Hz, 4H), 2.44 (s, 6H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

bis(4-chlorophenyl)methanone (**2h**)



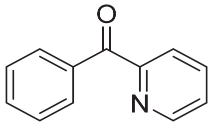
13 mg, 52% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77-7.70 (m, 4H), 7.51-7.45 (m, 4H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[8]

anthracen-9(10H)-one (**2i**)



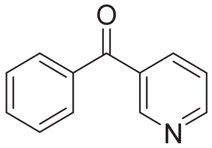
16 mg, 82% yield, yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42-8.37 (m, 2H), 7.66-7.60 (m, 2H), 7.50 (t, J = 7.3 Hz, 4H), 4.40 (s, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[9]

Phenyl(pyridin-2-yl)methanone (**2j**)



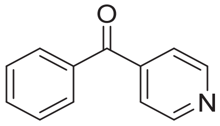
15 mg, 80% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (dt, *J* = 4.7, 1.3 Hz, 1H), 8.13-8.04 (m, 3H), 7.93 (td, *J* = 7.7, 1.7 Hz, 1H), 7.65-7.58 (m, 1H), 7.56-7.48 (m, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[10]

Phenyl(pyridin-3-yl)methanone (**2k**)



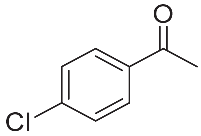
10 mg, 53% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 2.2 Hz, 1H), 8.84 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.15 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.84 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.73-7.62 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.48 (dd, *J* = 7.9, 4.8 Hz, 1H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

phenyl(pyridin-4-yl)methanone (**2l**)



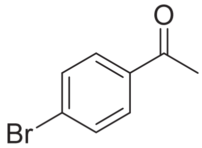
8 mg, 42% yield, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.87-8.81 (m, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.64-7.59 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[7]

1-Chloro-4-(prop-1-en-2-yl)benzone (**2m**)



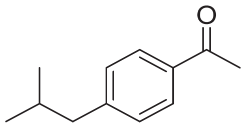
13 mg, 82% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96-7.84 (m, 2H), 7.49-7.39 (m, 2H), 2.59 (s, 3H). The ^{1}H NMR data are in consistent with those reported in the literature. Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

1-(4-Bromophenyl)ethan-1-one (**2n**)



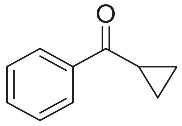
11 mg, 56% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 2.61 (s, 3H). The ^{1}H NMR data are in consistent with those reported in the literature. Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

1-(4-Isobutylphenyl)ethan-1-one (**2o**)



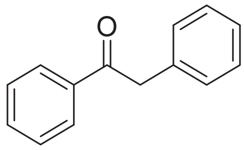
9 mg, 49% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90-7.86 (m, 2H), 7.29-7.21 (m, 2H), 2.59 (s, 3H), 2.54 (d, J = 7.2 Hz, 2H), 1.90 (dp, J = 13.6, 6.8 Hz, 1H), 0.91 (d, J = 6.6 Hz, 6H). The ^{1}H NMR data are in consistent with those reported in the literature. Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[11]

Cyclopropyl(phenyl)methanone (**2p**)



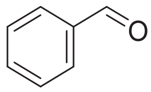
13 mg, 87% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08-8.01 (m, 2H), 7.64-7.54 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 2.71 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.27 (dt, *J* = 6.9, 3.4 Hz, 2H), 1.07 (dq, *J* = 7.3, 3.6 Hz, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[12]

1,2-diphenylethan-1-one (**2q)**



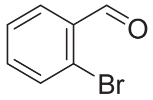
18 mg, 92% yield, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 8.2, 5.3 Hz, 3H), 4.32 (s, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[6]

Benzaldehyde (**2r**)



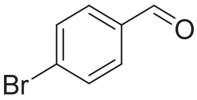
5 mg, 47% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 7.94-7.88 (m, 2H), 7.68-7.63 (m, 1H), 7.56 (dd, *J* = 8.3, 6.9 Hz, 2H). The ^{1}H NMR data are in consistent with those reported in the literature. Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

2-bromobenzaldehyde (**2s**)



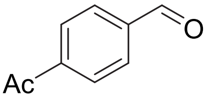
16 mg, 85% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.35 (s, 1H), 7.91-7.88 (m, 1H), 7.66-7.61 (m, 1H), 7.45-7.41 (m, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

4-Bromobenzaldehyde (**2t**)



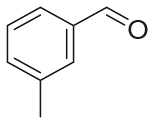
11 mg, 60% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.84-7.74 (m, 2H), 7.74-7.68 (m, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[5]

4-acetylbenzaldehyde (**2u**)



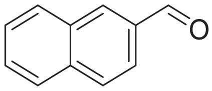
9 mg, 61% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.95-7.90 (m, 2H), 7.31-7.24 (m, 3H), 2.35 (s, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[13]

3-Methylbenzaldehyde (**2v**)



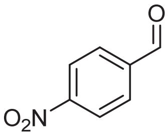
7 mg, 61% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.70-7.67 (m, 2H), 7.47-7.39 (m, 2H), 2.44 (s, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[14]

2-Naphthaldehyde (**2w**)



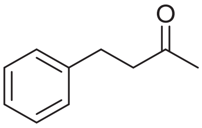
7 mg, 47% yield, yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.19 (s, 1H), 8.38 (d, *J* = 1.4 Hz, 1H), 8.06-8.02 (m, 1H), 8.01-7.96 (m, 2H), 7.96-7.92 (m, 1H), 7.68 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported. [10]

4-nitrobenzaldehyde (**2x**)



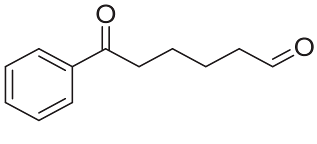
3 mg, 10%yield, white solid, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.46 – 8.36 (m, 2H), 8.14 – 8.03 (m, 2H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[15]

4-phenylbutan-2-one (**2y**)



3 mg, 22% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.4, 6.5 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[16]

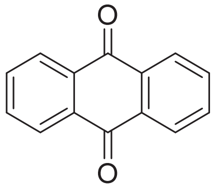
6-oxo-6-phenylhexanal (**2ab**)



11 mg, 57% yield, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.81 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 3.03 (td, *J* = 7.1,

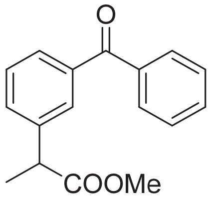
2.0 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.86-1.71 (m, 4H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[17]

Anthracene-9,10-dione (**2ac**)



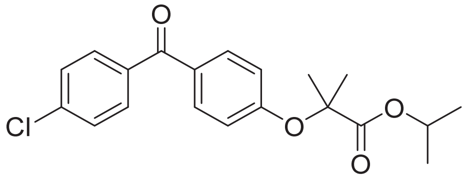
10 mg, 45% yield, yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 5.7, 3.3 Hz, 4H), 7.84 (dd, *J* = 5.8, 3.3 Hz, 4H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[18]

methyl 2-(3-benzoylphenyl)propanoate (**2ad)**



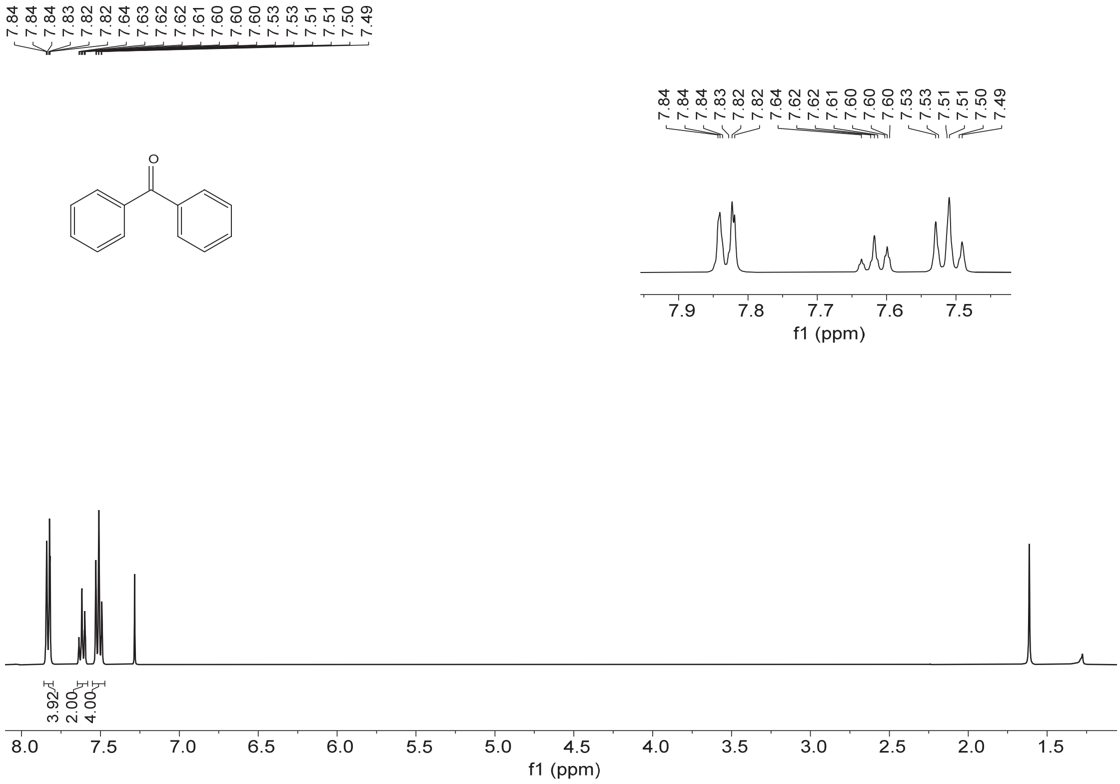
25 mg, 94% yield, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.60-7.56 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50-7.45 (m, 2H), 7.43 (td, *J* = 7.7, 1.9 Hz, 1H), 3.81 (qd, *J* = 7.2, 1.9 Hz, 1H), 3.67 (d, *J* = 2.2 Hz, 3H), 1.54 (dd, *J* = 7.2, 2.1 Hz, 3H). Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[19]

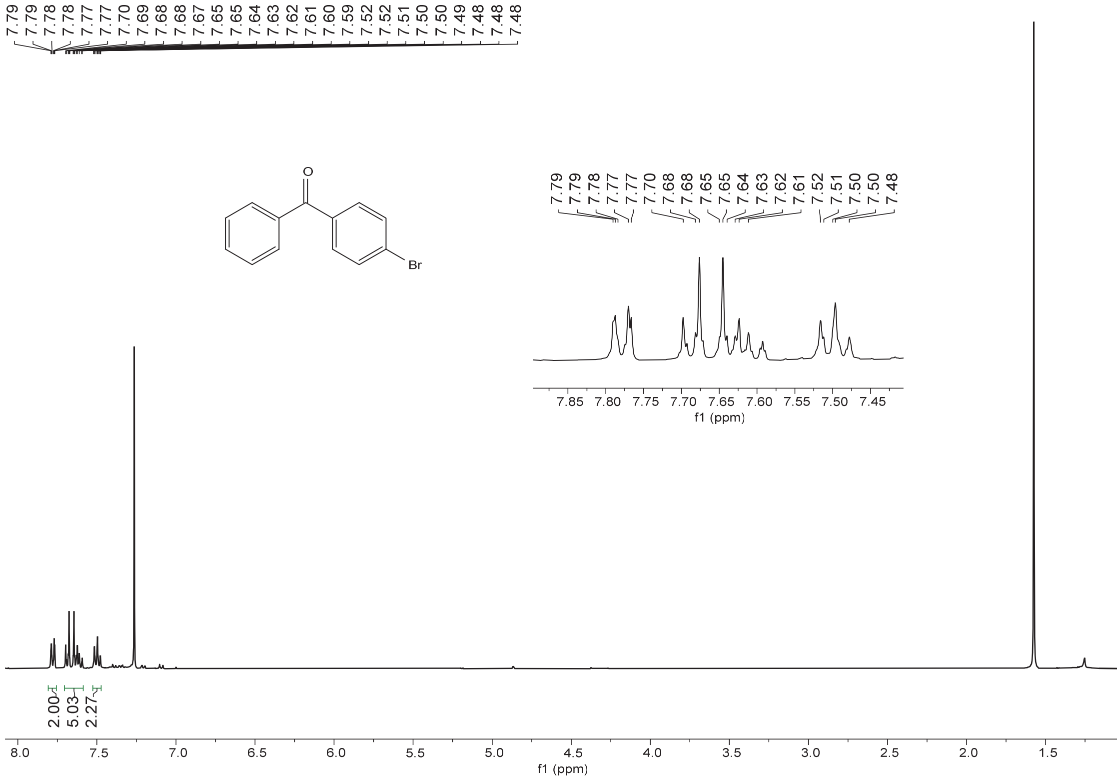
isopropyl 2-methyl-2-(4-(4-methylbenzoyl)phenoxy)propanoate (**2ae**)

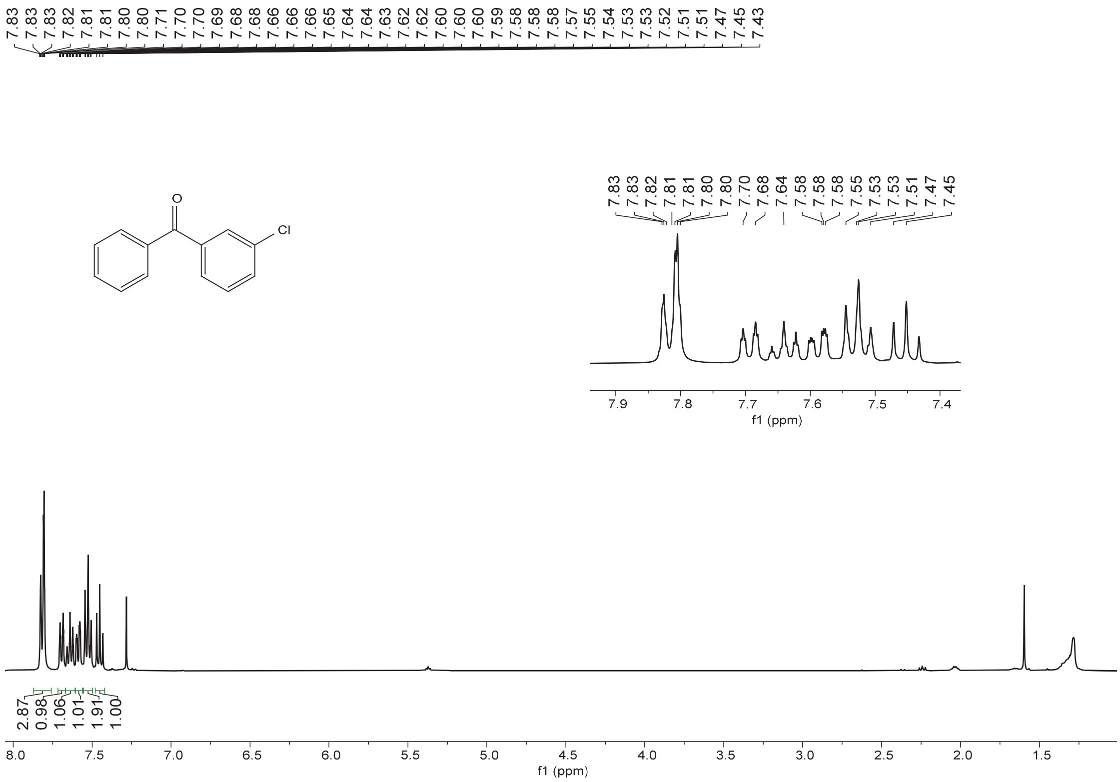


32 mg, 90% yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79-7.67 (m, 4H), 7.55-7.43 (m, 2H), 6.97-6.83 (m, 2H), 5.11 (p, J = 6.2 Hz, 1H), 1.68 (s, 6H), 1.23 (s, 3H), 1.22 (s, 3H).Known compound. The ^{1}H NMR spectroscopic data matched those previously reported.[20]

7. NMR spectra of isolated products



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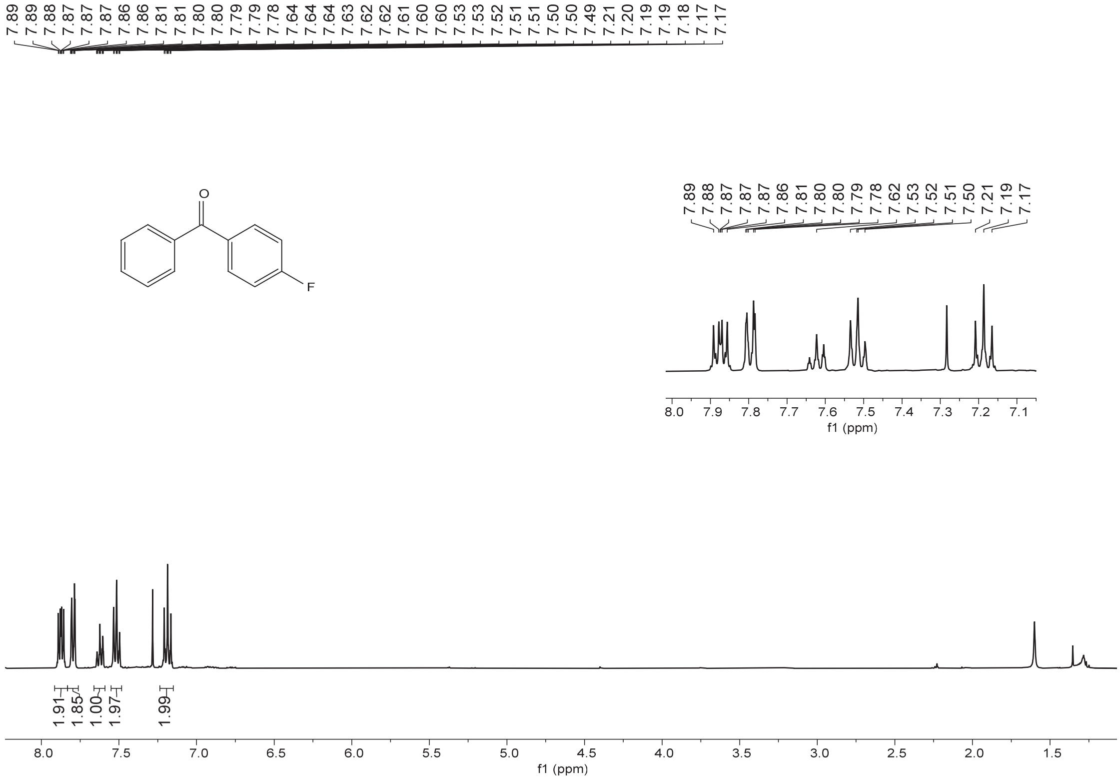
O
Cl
7.83 7.83 7.82 7.81 7.81 7.80 7.80 7.70 7.68 7.64 7.58 7.58 7.58 7.55 7.53 7.53 7.51 7.47 7.45
7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
2.87 0.98 1.06 1.01 1.91 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)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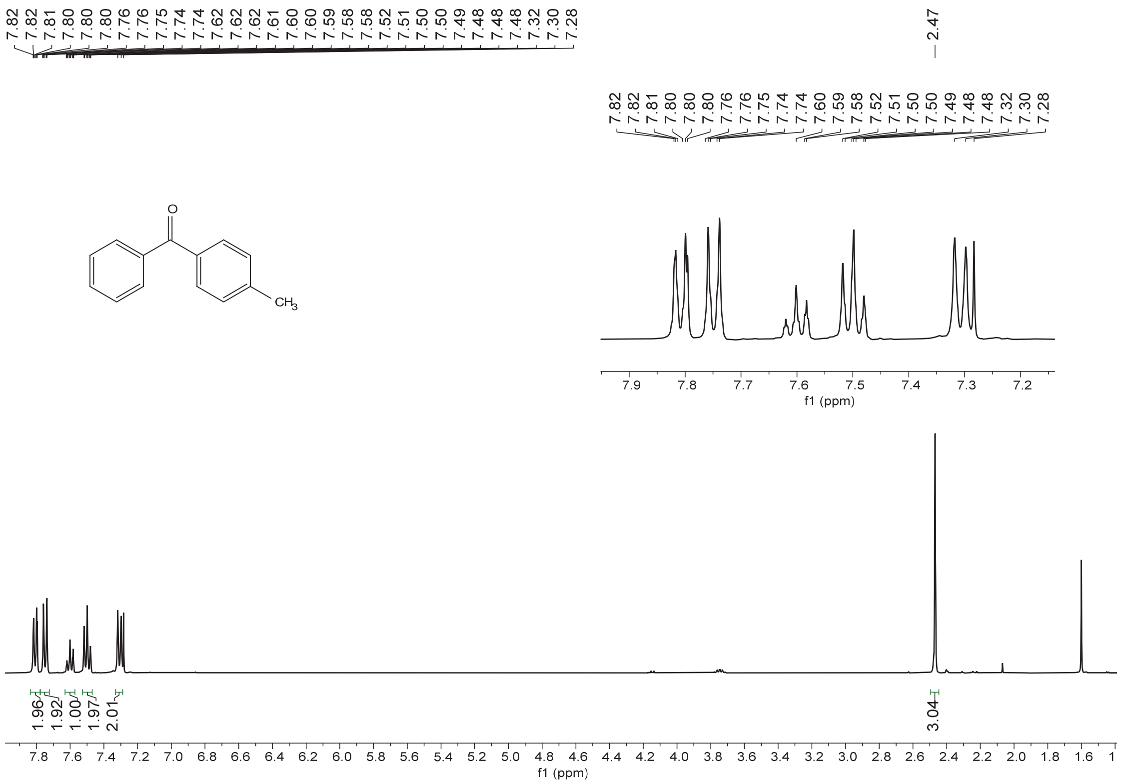
O
F
7.89 7.88 7.87 7.87 7.86 7.81 7.80 7.80 7.79 7.78 7.62 7.53 7.52 7.51 7.50 7.21 7.19 7.17
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.91 1.85 1.00 1.97 1.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)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7.62
7.61
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7.58
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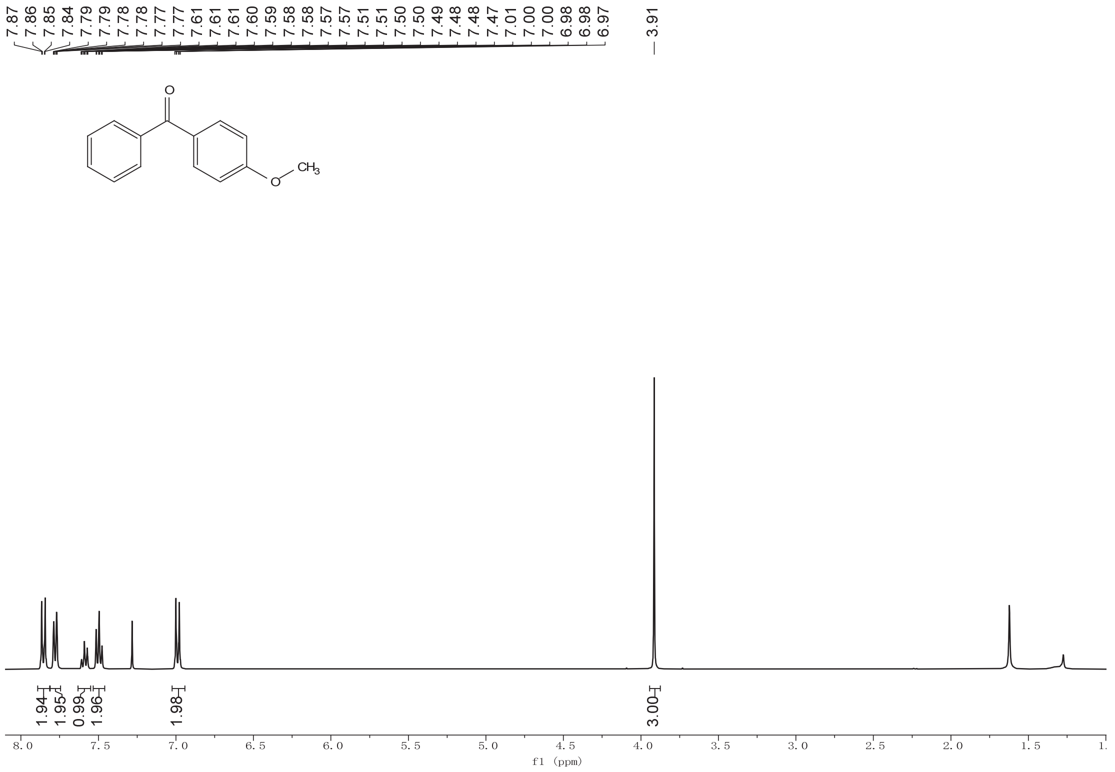
7.59
7.58
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.32
7.30
7.28
O
CH3
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.96
1.92
1.00
1.97
2.01
3.04
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1
f1 (ppm)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7.47
7.01
7.00
7.00
6.98
6.98
6.97
3.91
O
O
CH3
1.94
1.95
0.99
1.96
1.98
3.00
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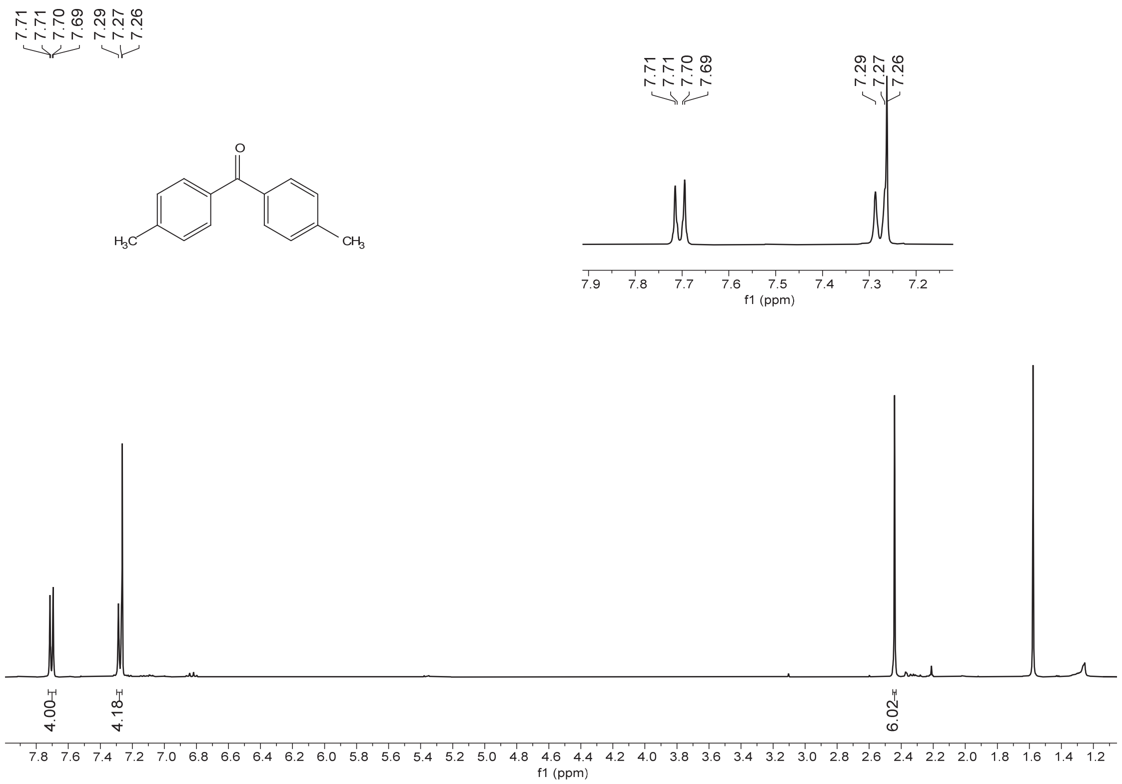
f1 (ppm)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H3C
CH3
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f1 (ppm)
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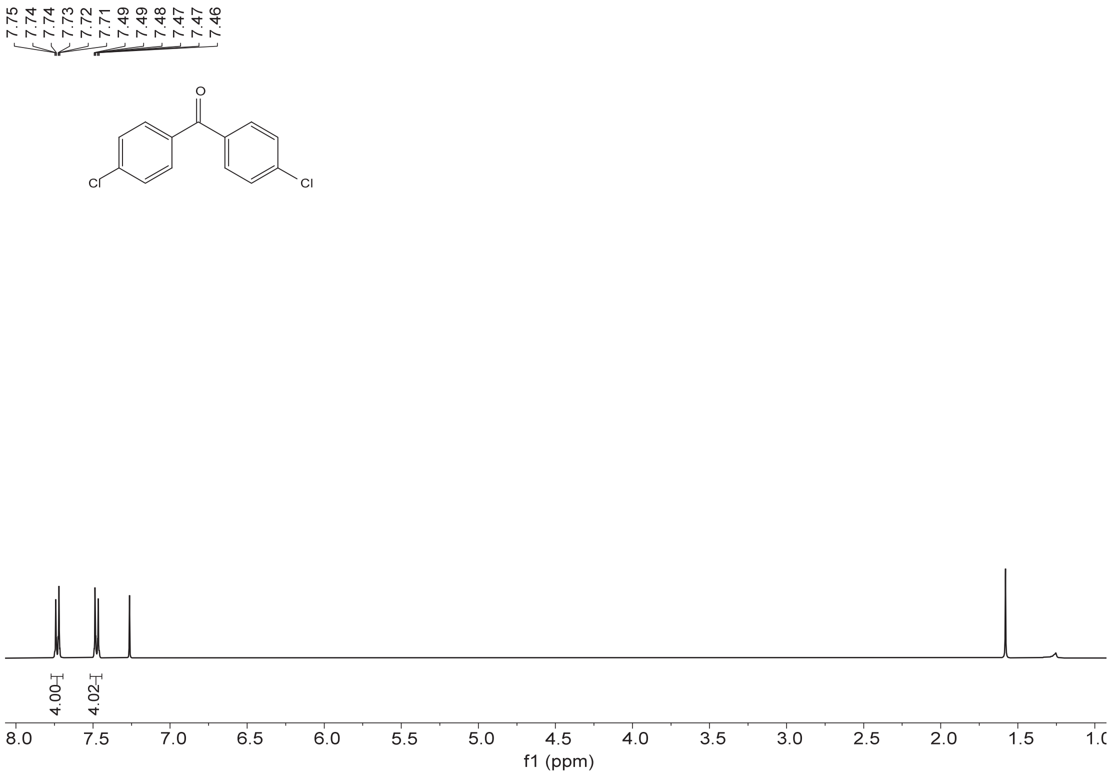
4.18
6.02
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)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7.49
7.48
7.47
7.47
7.46
O
Cl
Cl
4.00
4.02
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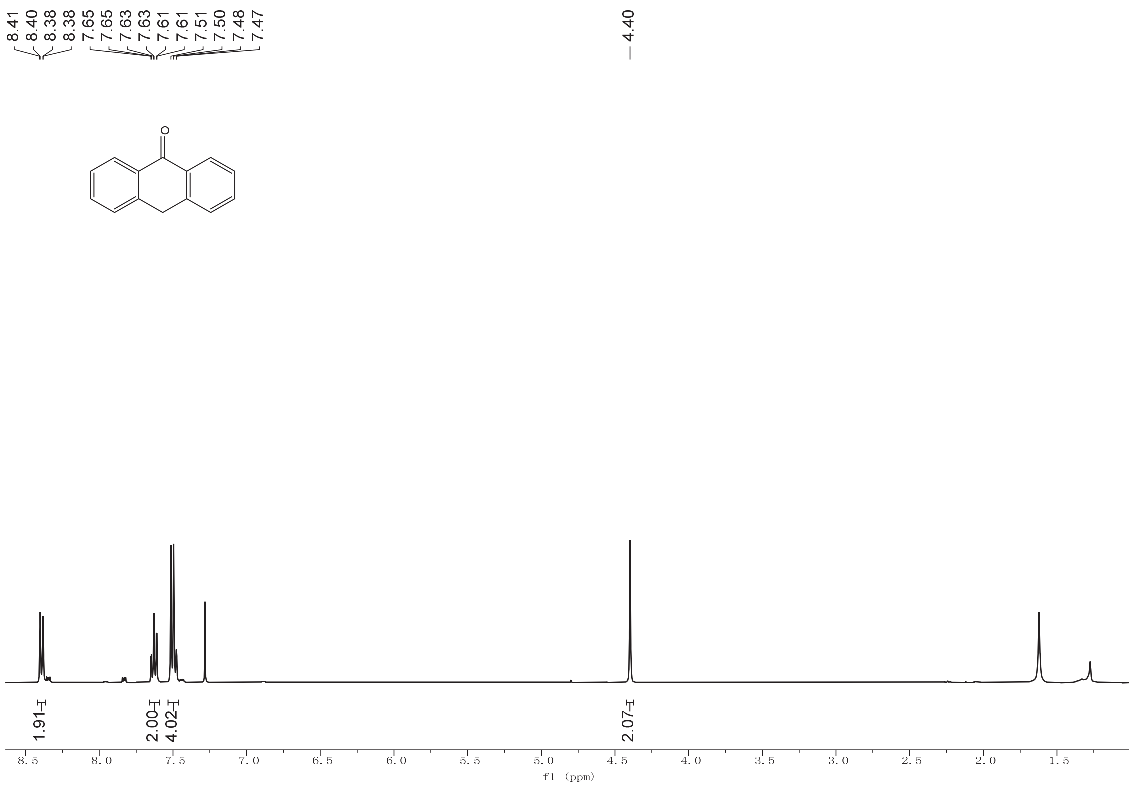
f1 (ppm)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7.48
7.47
4.40
O
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2.00
4.02
2.07
8.5
8.0
7.5
7.0
6.5
6.0
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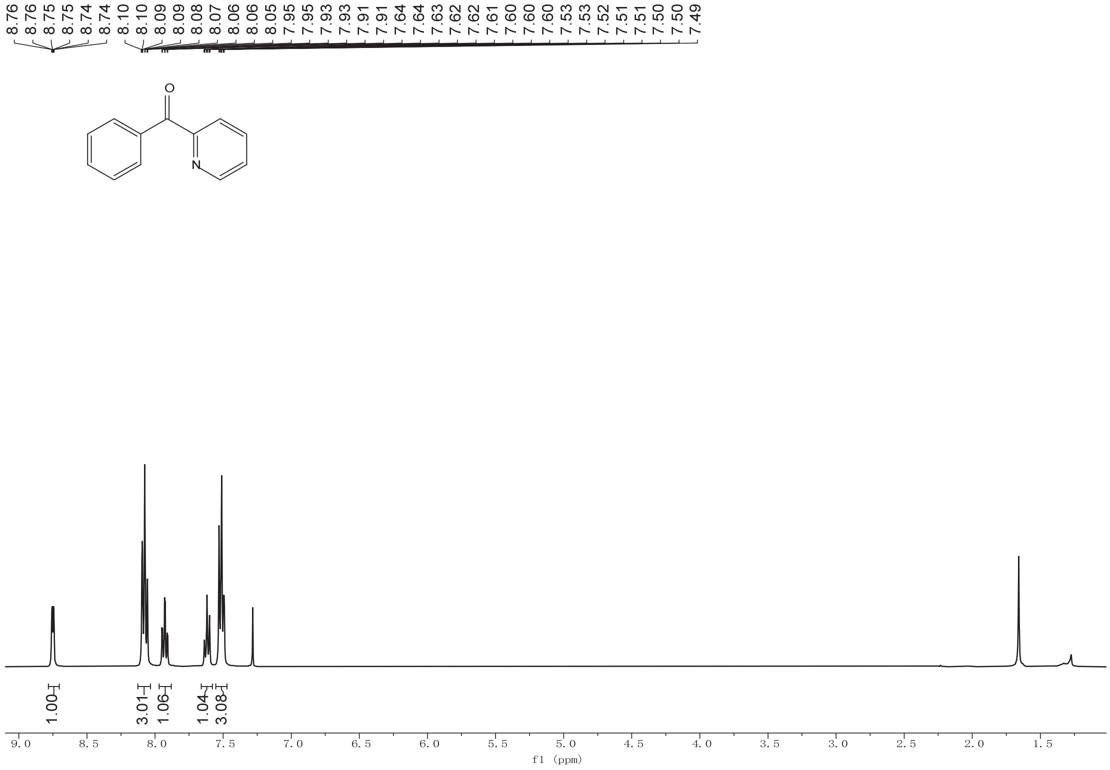
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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8.06
8.05
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1.04
3.08
9.0
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8.0
7.5
7.0
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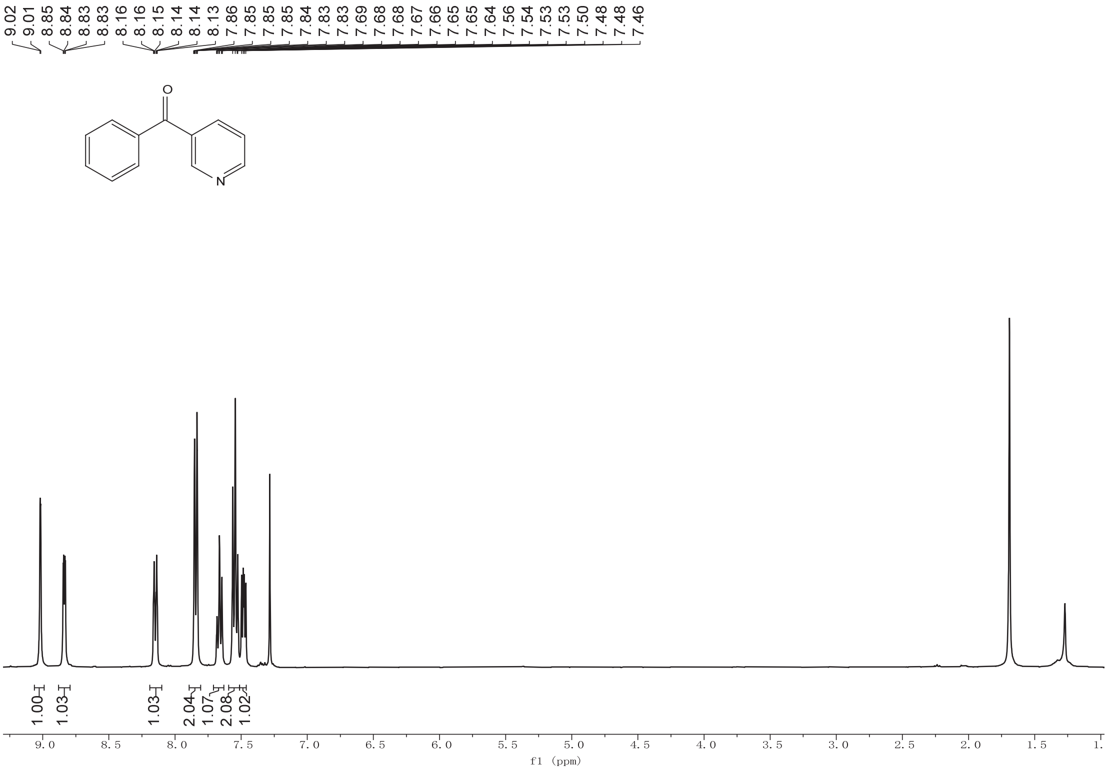
1.5
f1 (ppm)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7.48
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2.08
1.02
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7.0
6.5
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3.5
3.0
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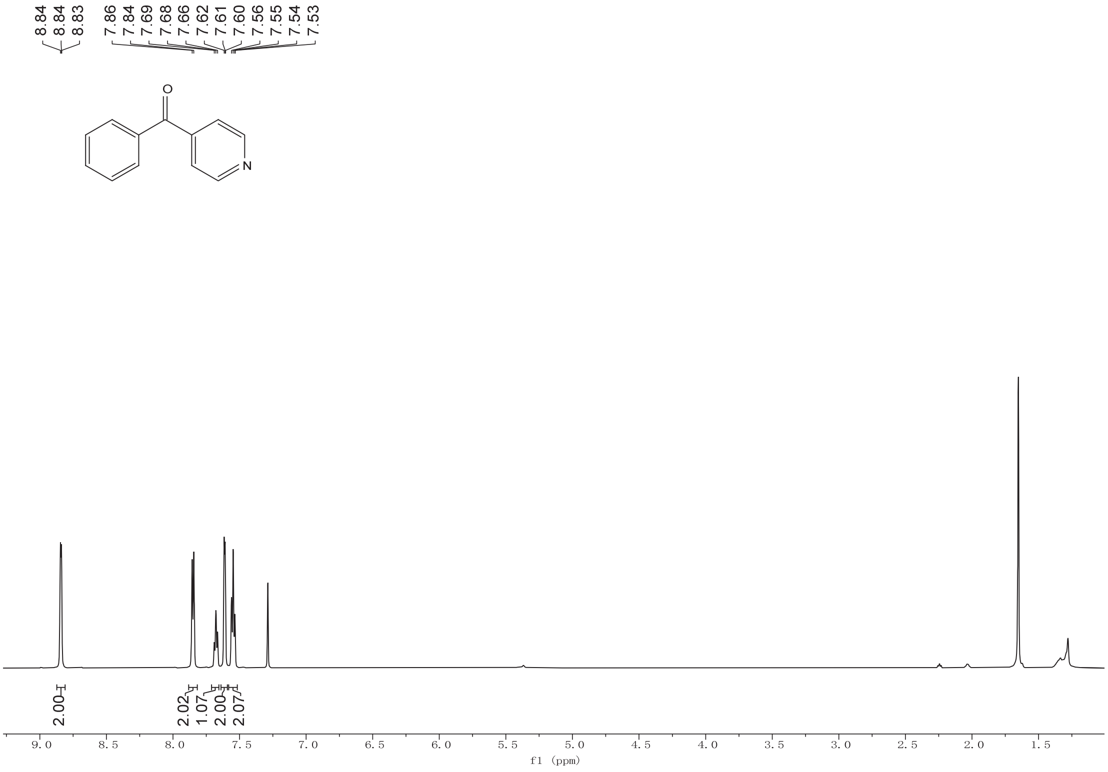
1.5
1.
f1 (ppm)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2.02
1.07
2.00
2.07
9.0
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8.0
7.5
7.0
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4.0
3.5
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2.5
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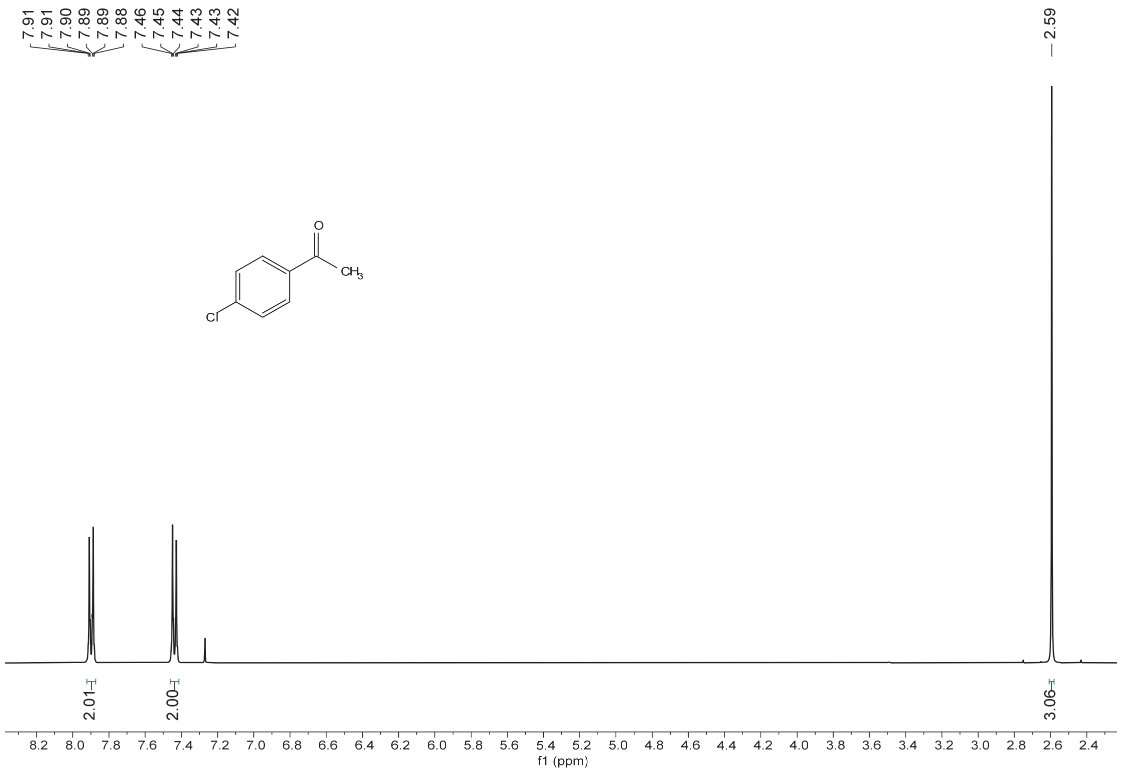
1.5
f1 (ppm)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7.45
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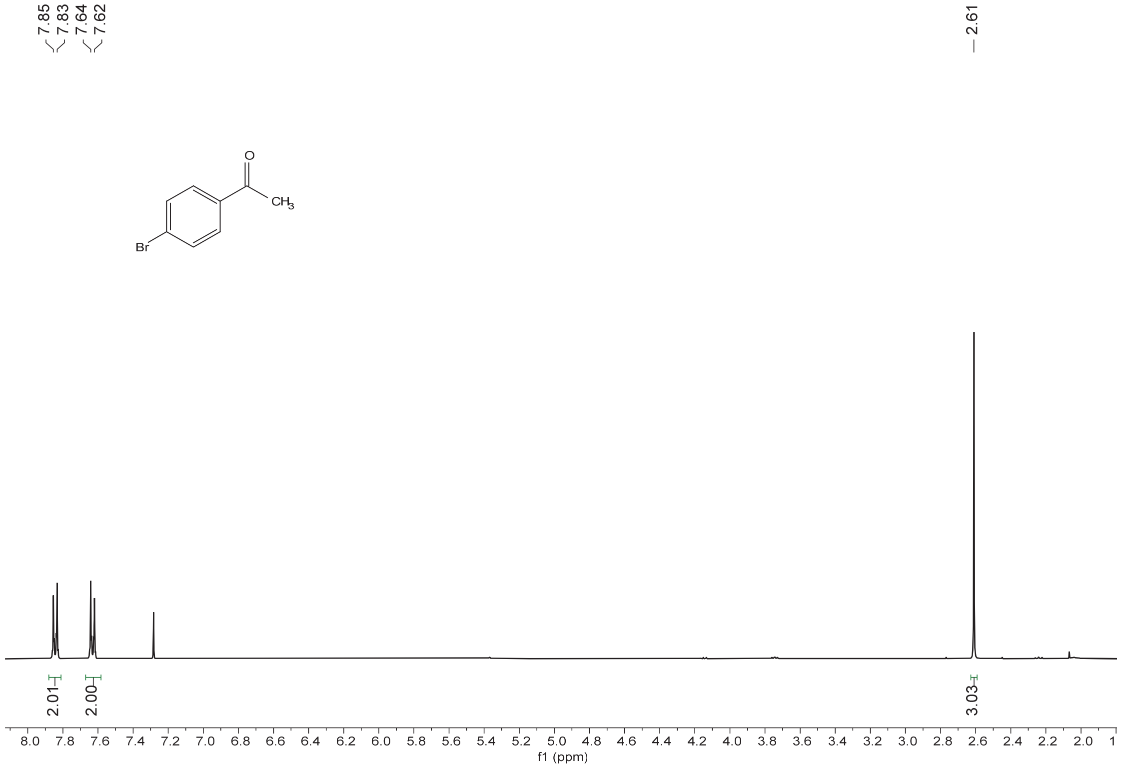
2.59
O
CH3
Cl
2.01
2.00
3.06
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)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3.03
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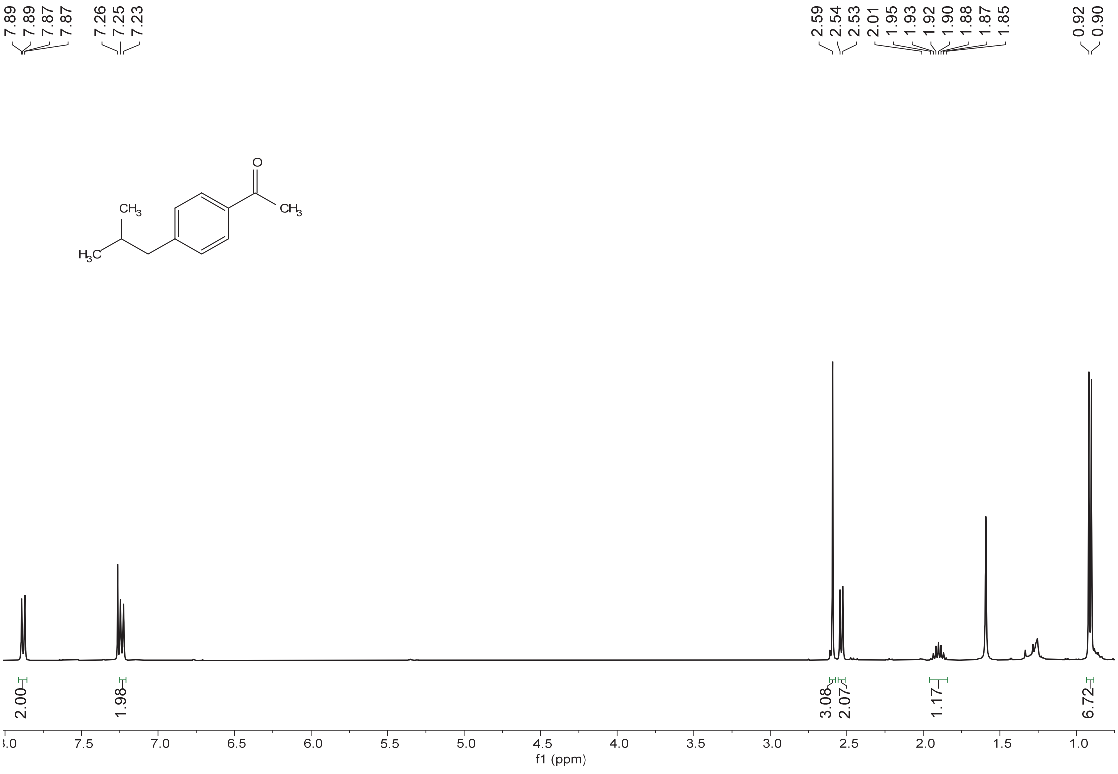
f1 (ppm)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1.90
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1.87
1.85
0.92
0.90
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CH3
H3C
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2.07
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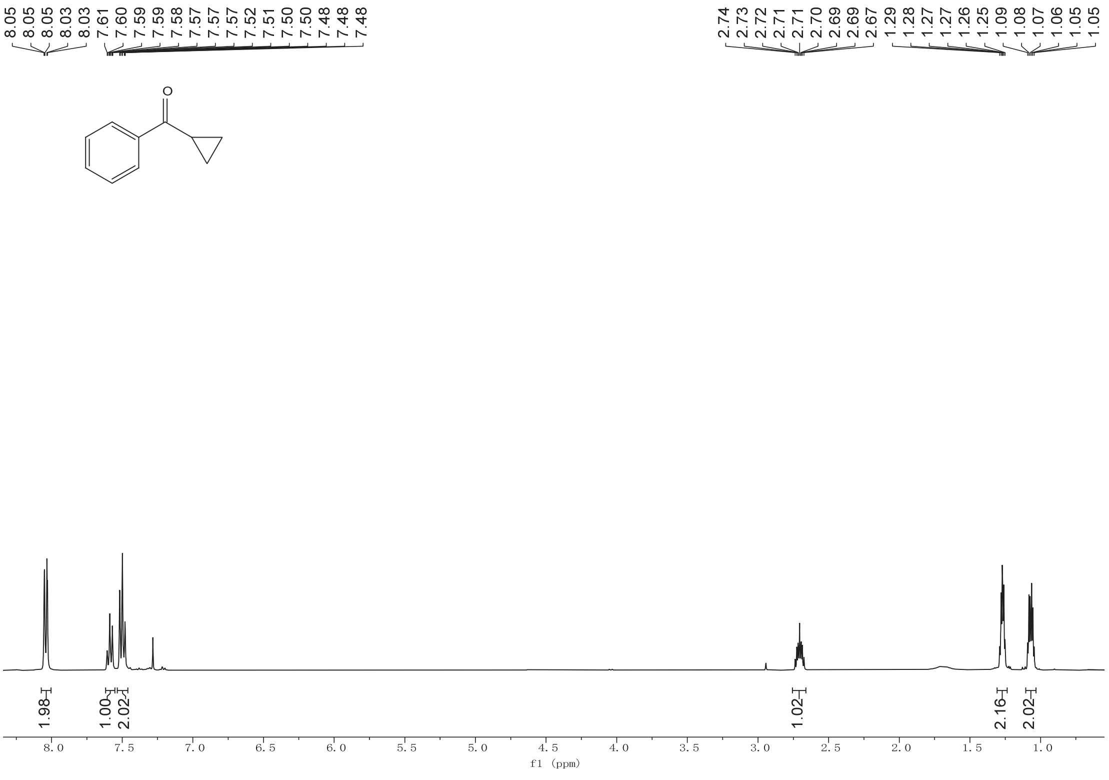
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2.67
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1.28
1.27
1.27
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1.08
1.07
1.06
1.05
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O
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1.0
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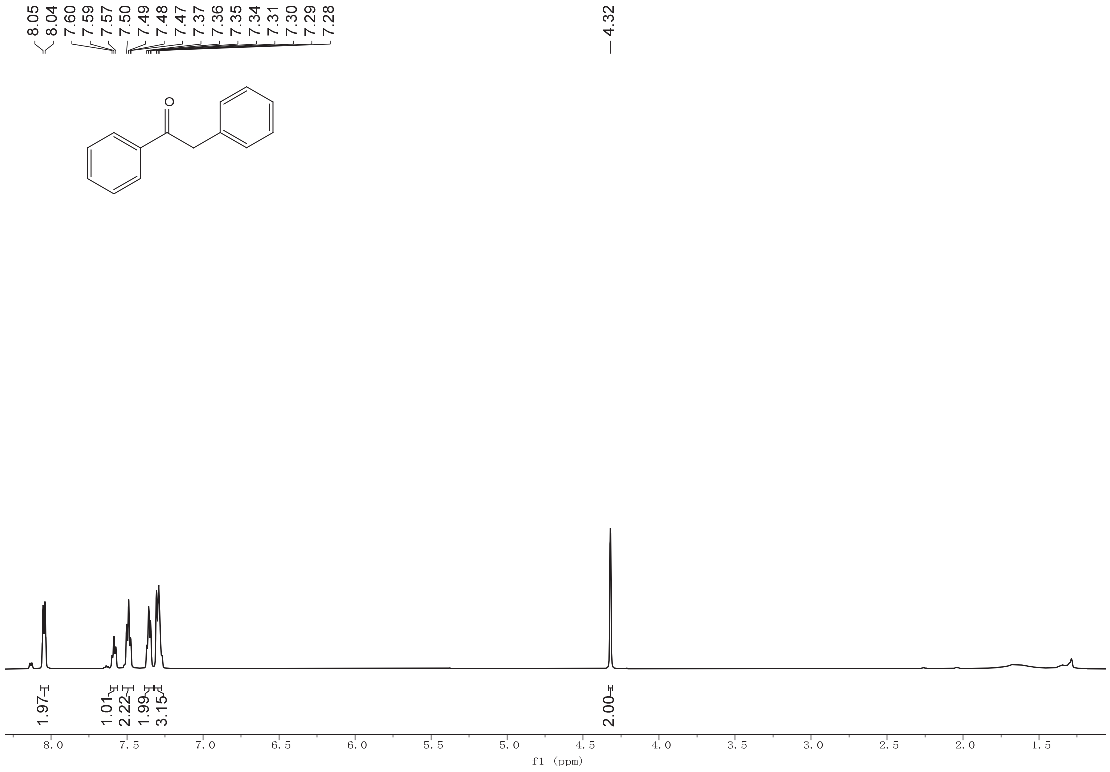
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7.29
7.28
4.32
O
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1.01
2.22
1.99
3.15
2.00
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7.5
7.0
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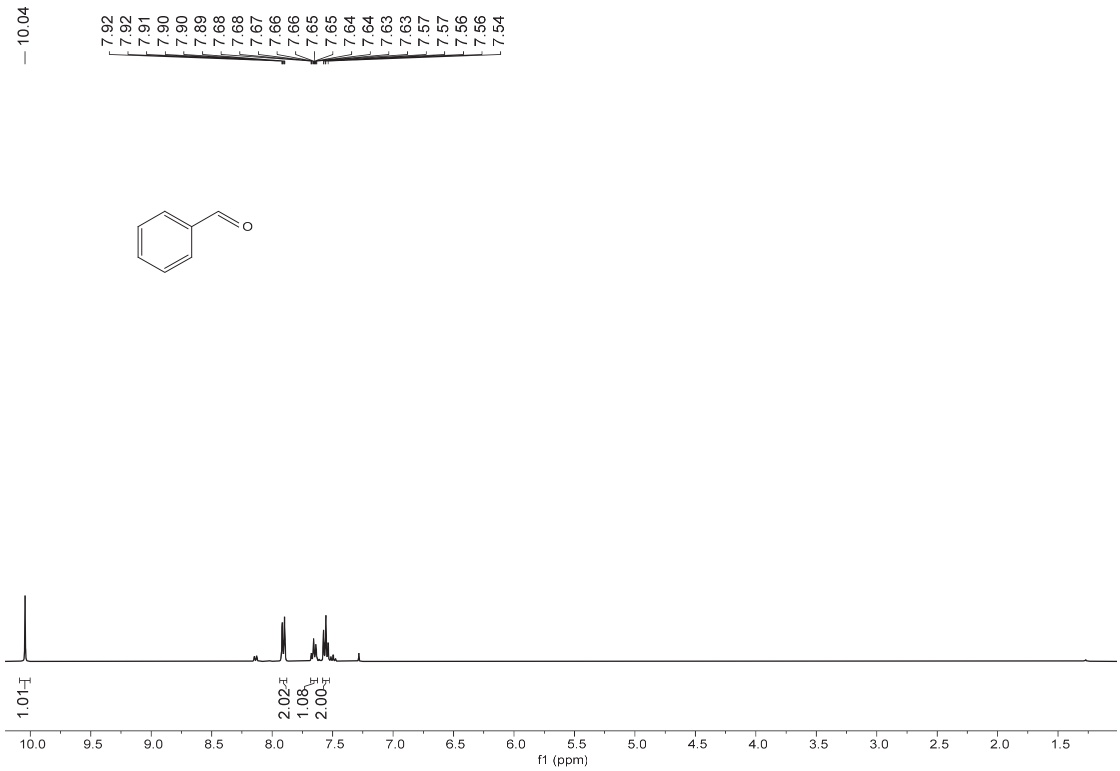
f1 (ppm)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7.63
7.63
7.57
7.57
7.56
7.56
7.54
O
1.01
2.02
1.08
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
4.0
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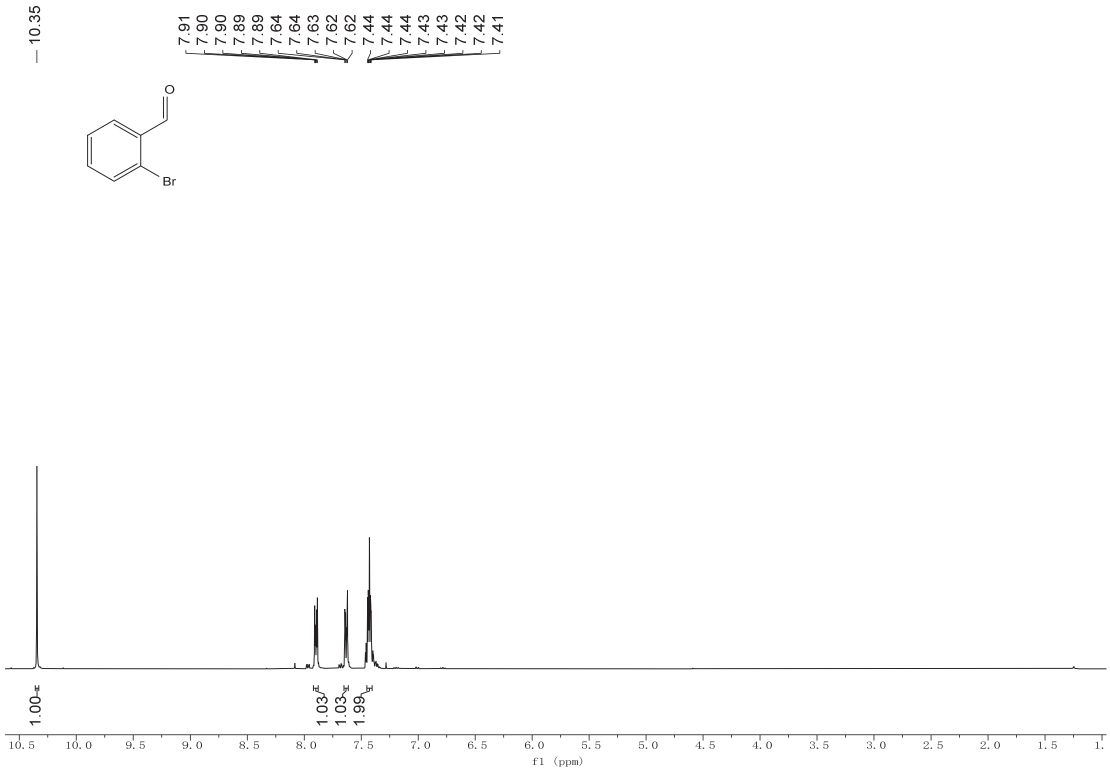
1.5
f1 (ppm)



10.35
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7.90
7.90
7.89
7.89
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7.64
7.63
7.62
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7.44
7.44
7.43
7.42
7.42
7.41
O
Br
1.00
1.03
1.03
1.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.5
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3.5
3.0
2.5
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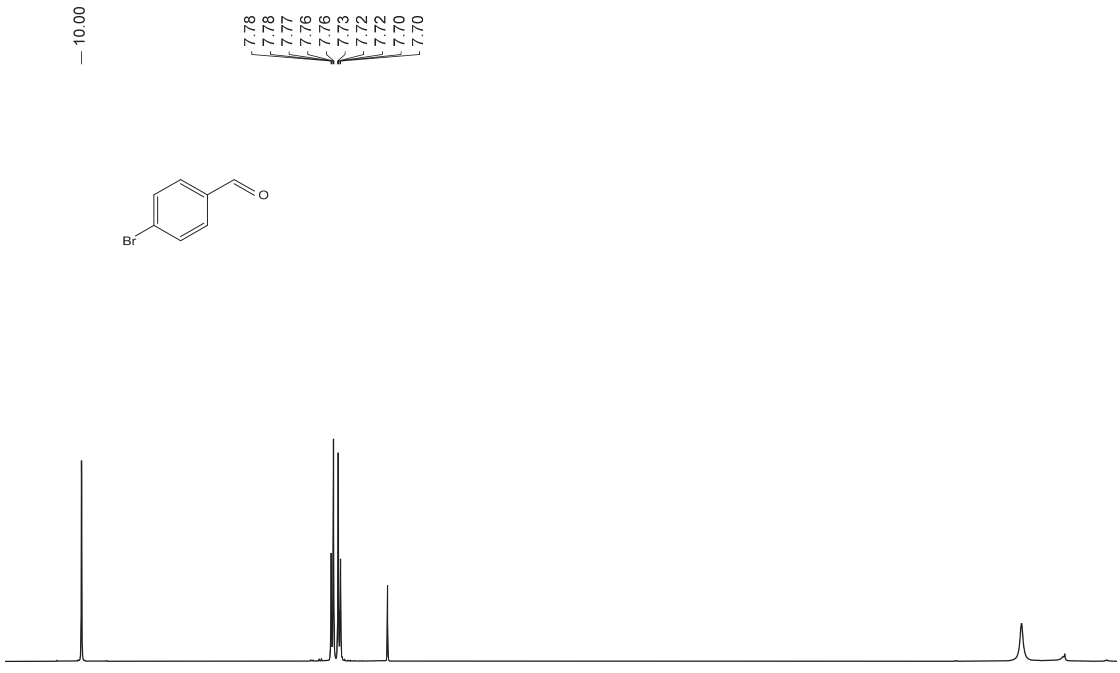
1.5
1.
f1 (ppm)



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7.72
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Br
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2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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3.5
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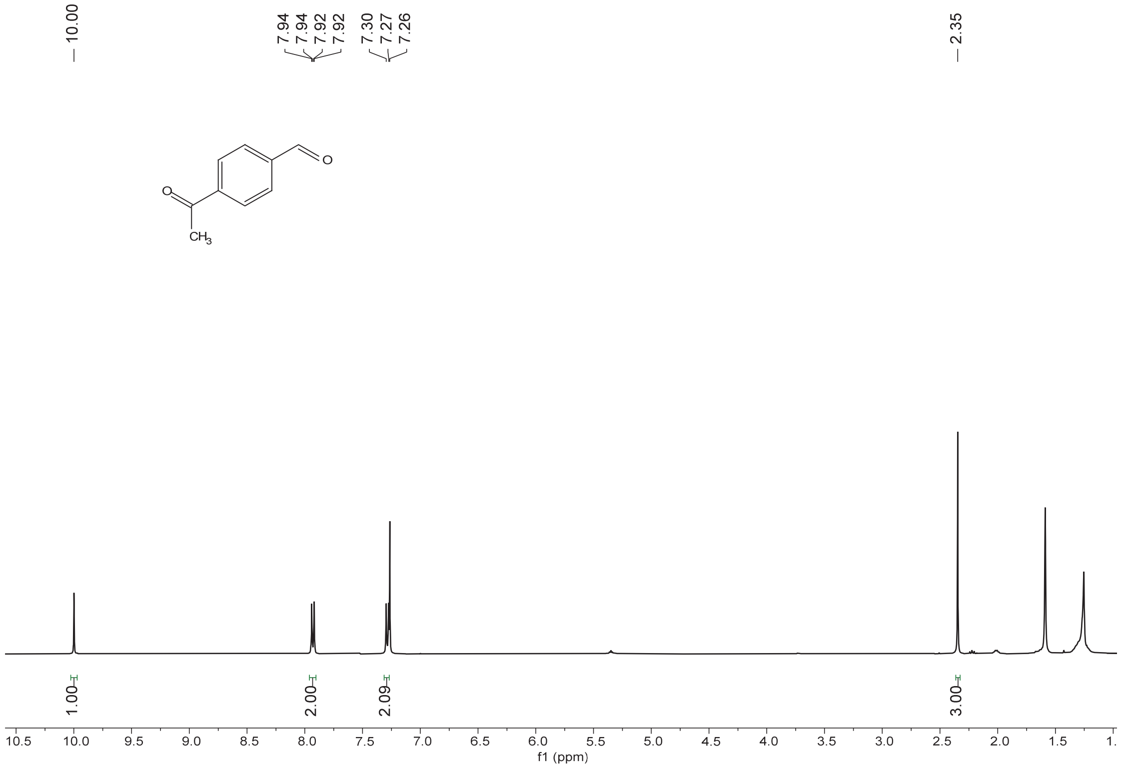
1.5
1.0
f1 (ppm)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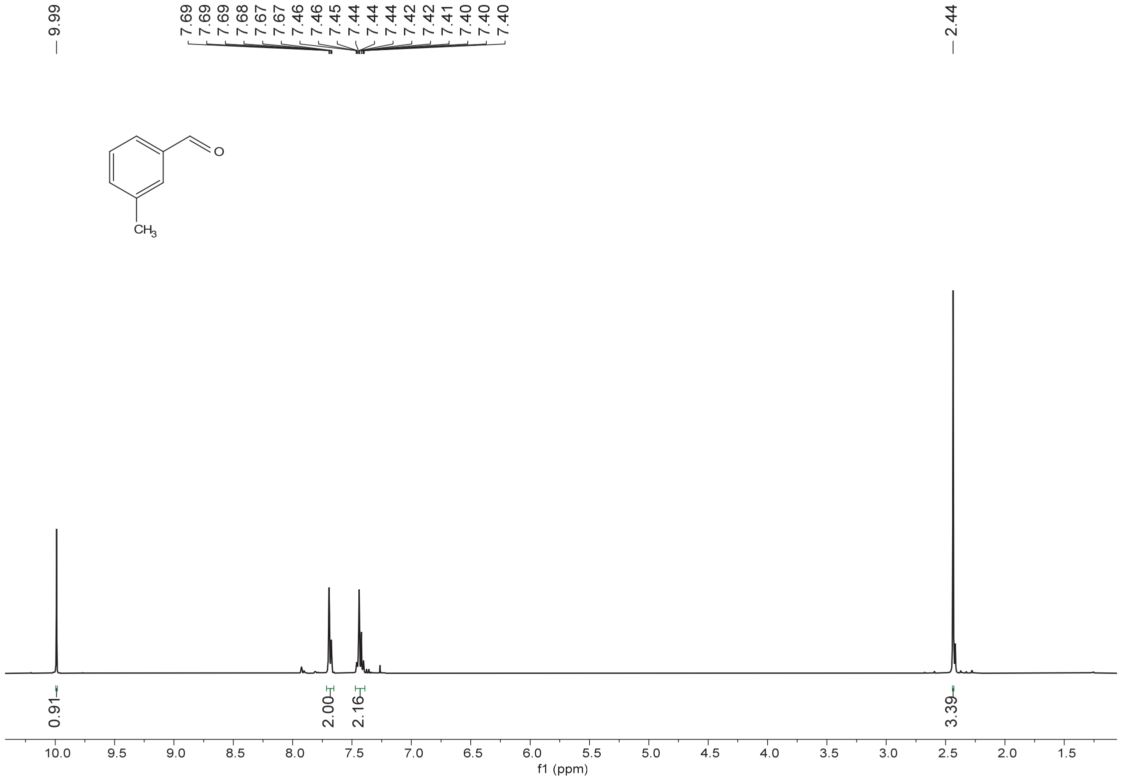
2.09
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.
f1 (ppm)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7.69
7.69
7.68
7.67
7.67
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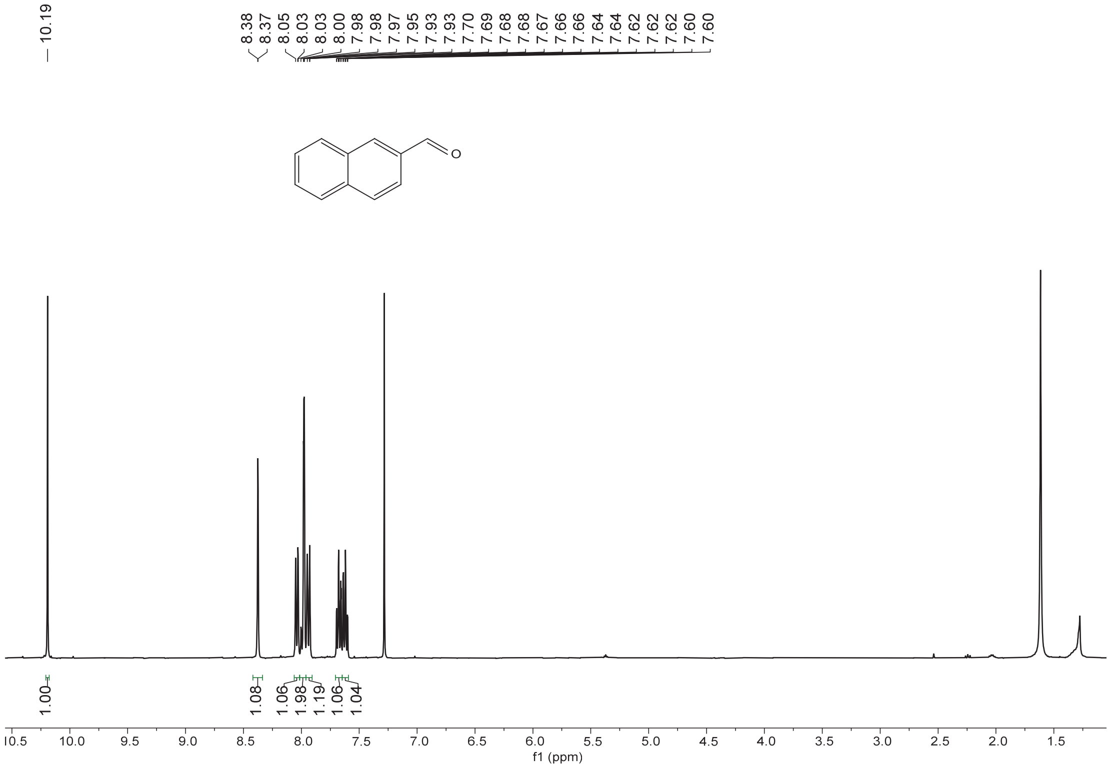
7.46
7.45
7.44
7.44
7.44
7.42
7.42
7.41
7.40
7.40
7.40
2.44
O
CH3
0.91
2.00
2.16
3.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)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8.37
8.05
8.03
8.03
8.00
7.98
7.98
7.97
7.95
7.93
7.93
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.64
7.64
7.62
7.62
7.62
7.60
7.60
O
1.00
1.08
1.06
1.98
1.19
1.06
1.04
10.5
10.0
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
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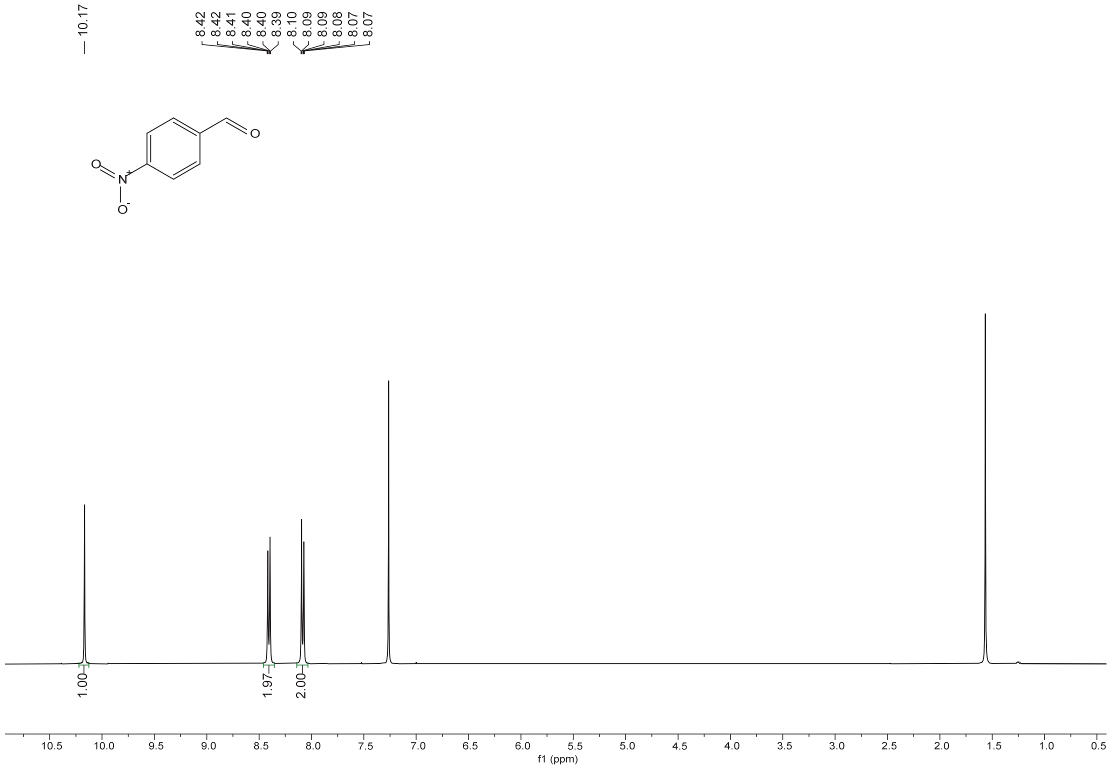
2.5
2.0
1.5
f1 (ppm)


10.17
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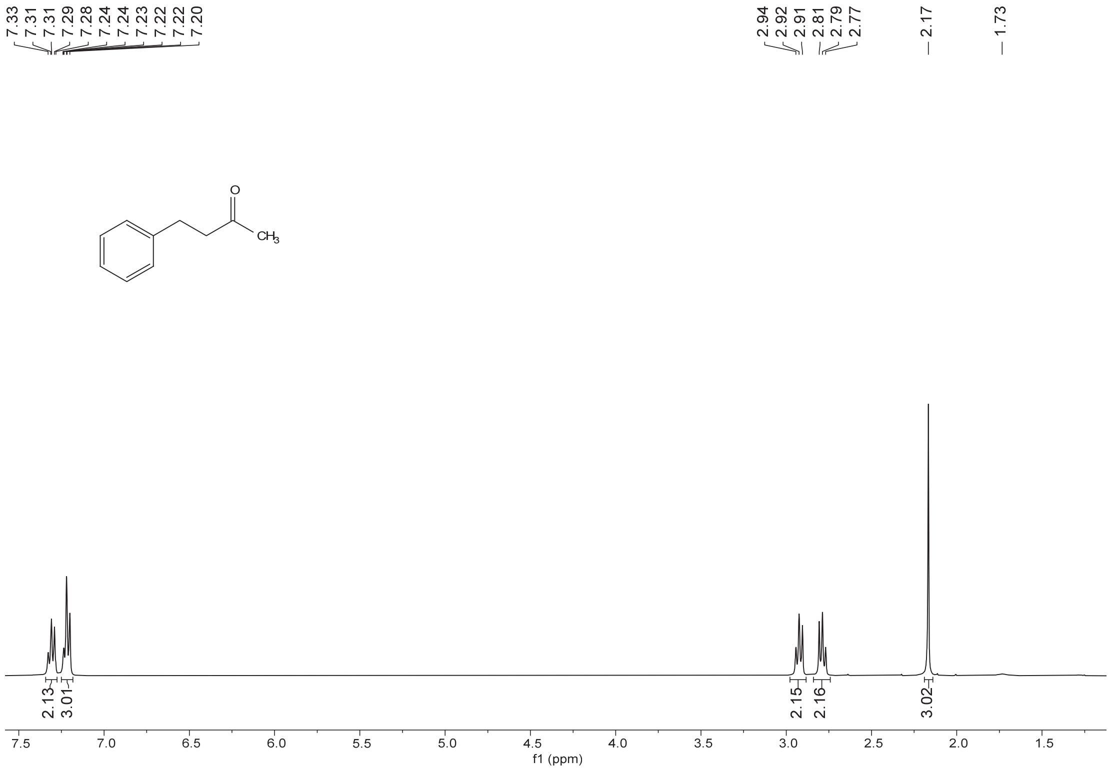
8.42
8.41
8.40
8.40
8.39
8.10
8.09
8.09
8.08
8.07
8.07
O
N+
O
O-
1.00
1.97
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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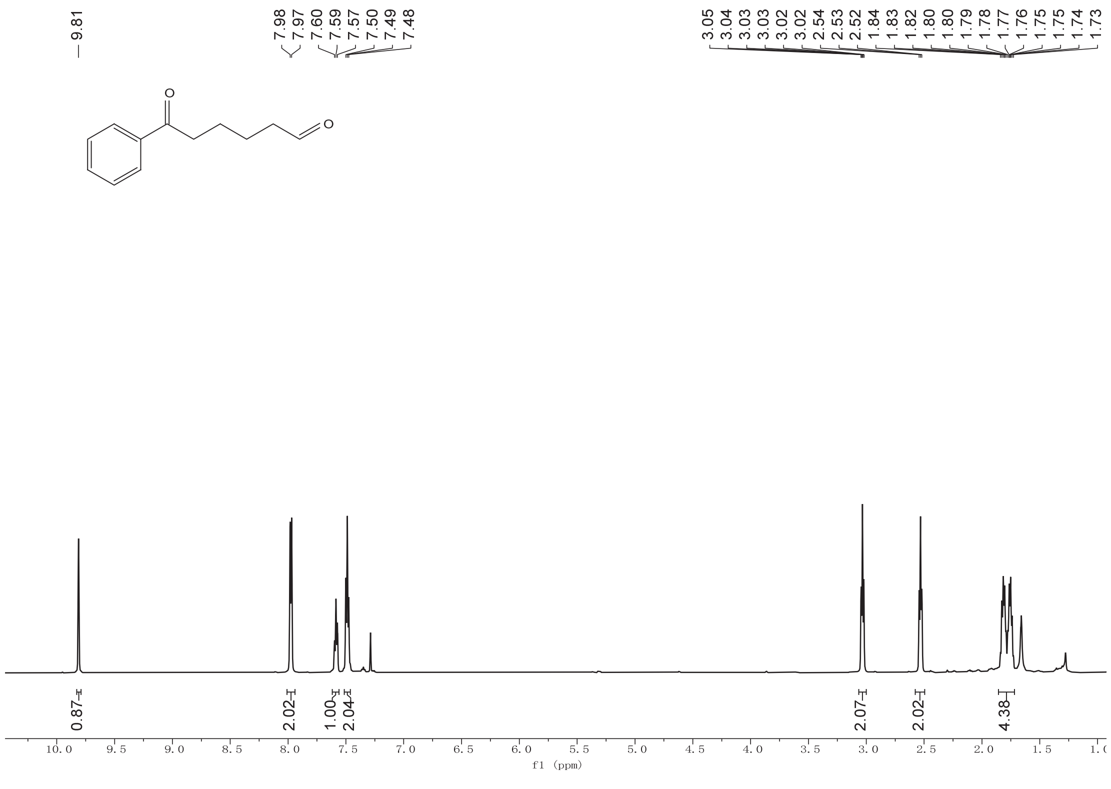
7.31
7.29
7.28
7.24
7.24
7.23
7.22
7.22
7.20
2.94
2.92
2.91
2.81
2.79
2.77
2.17
1.73
O
CH3
2.13
3.01
2.15
2.16
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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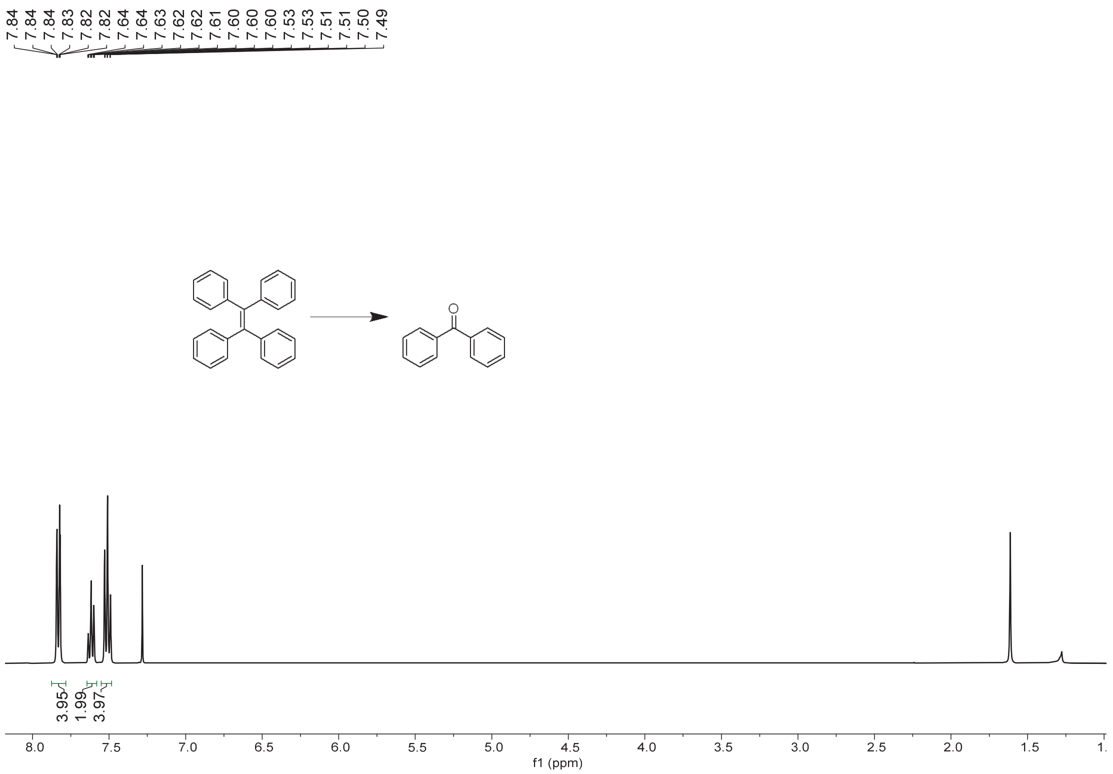
7.49
7.48
3.05
3.04
3.03
3.02
3.02
2.54
2.53
2.52
1.84
1.83
1.82
1.80
1.80
1.79
1.78
1.77
1.76
1.75
1.75
1.74
1.73
O
O
0.87
2.02
1.00
2.04
2.07
2.02
4.38
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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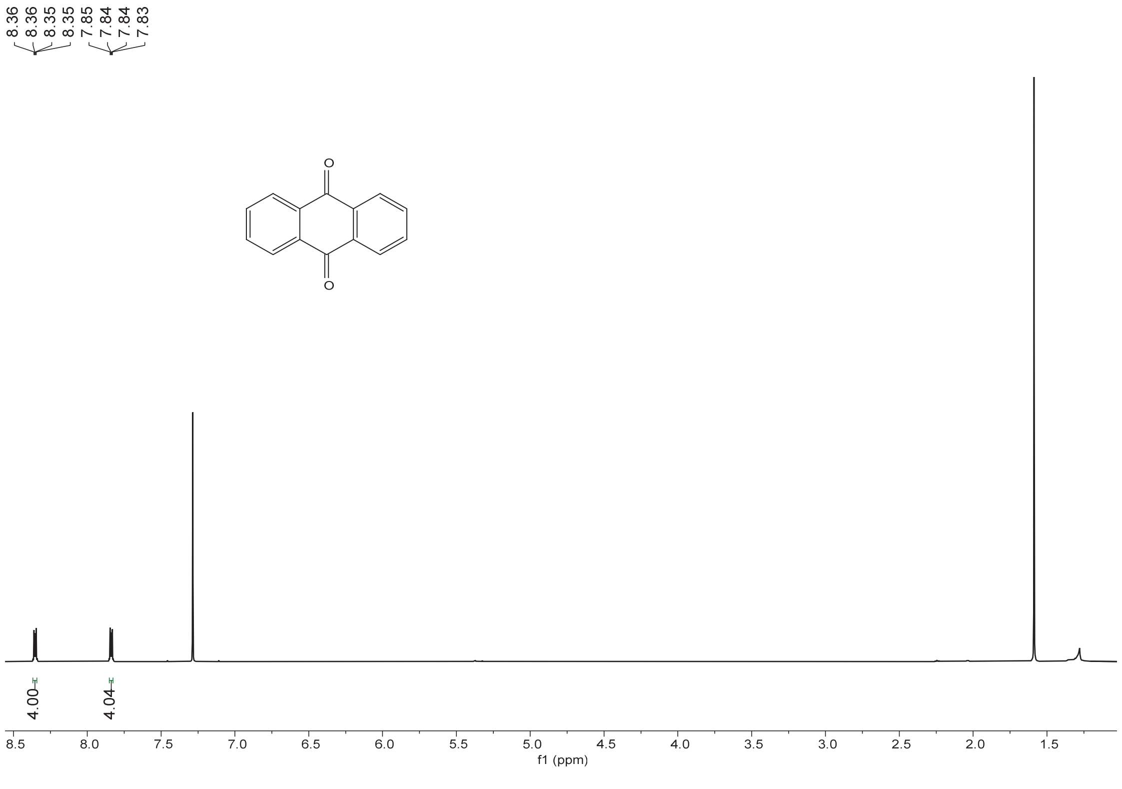
7.84
7.84
7.83
7.82
7.82
7.64
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.60
7.53
7.51
7.51
7.50
7.49
O
3.95
1.99
3.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.
f1 (ppm)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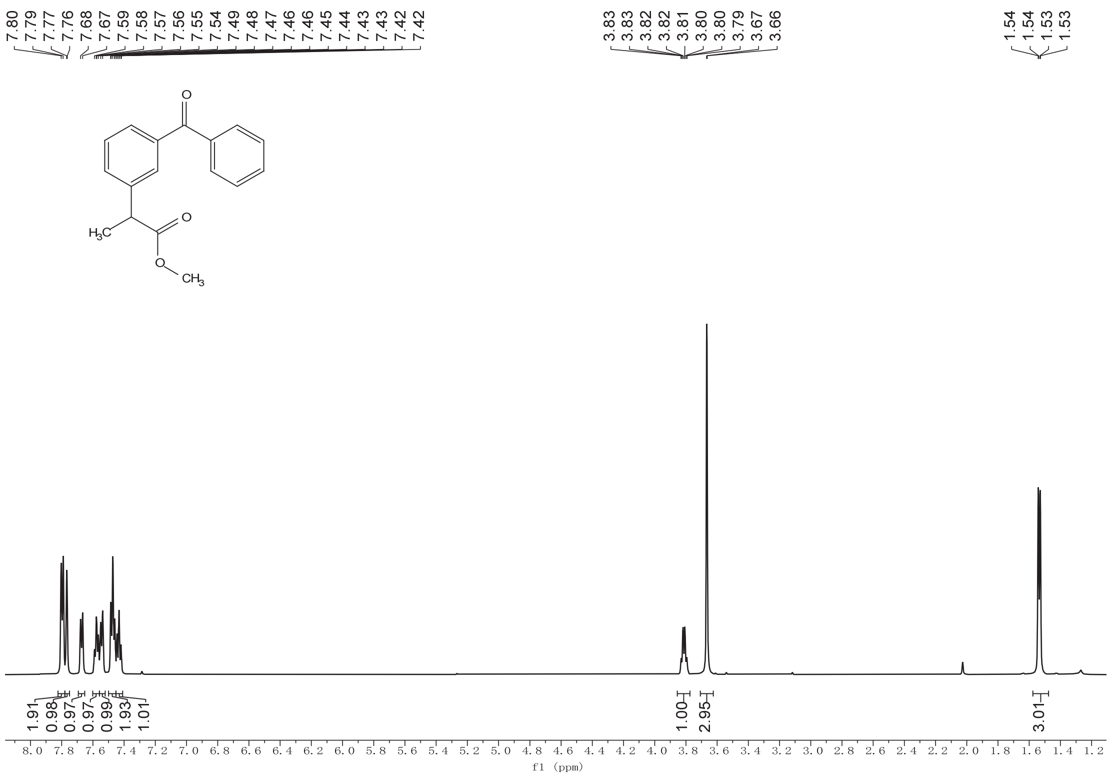
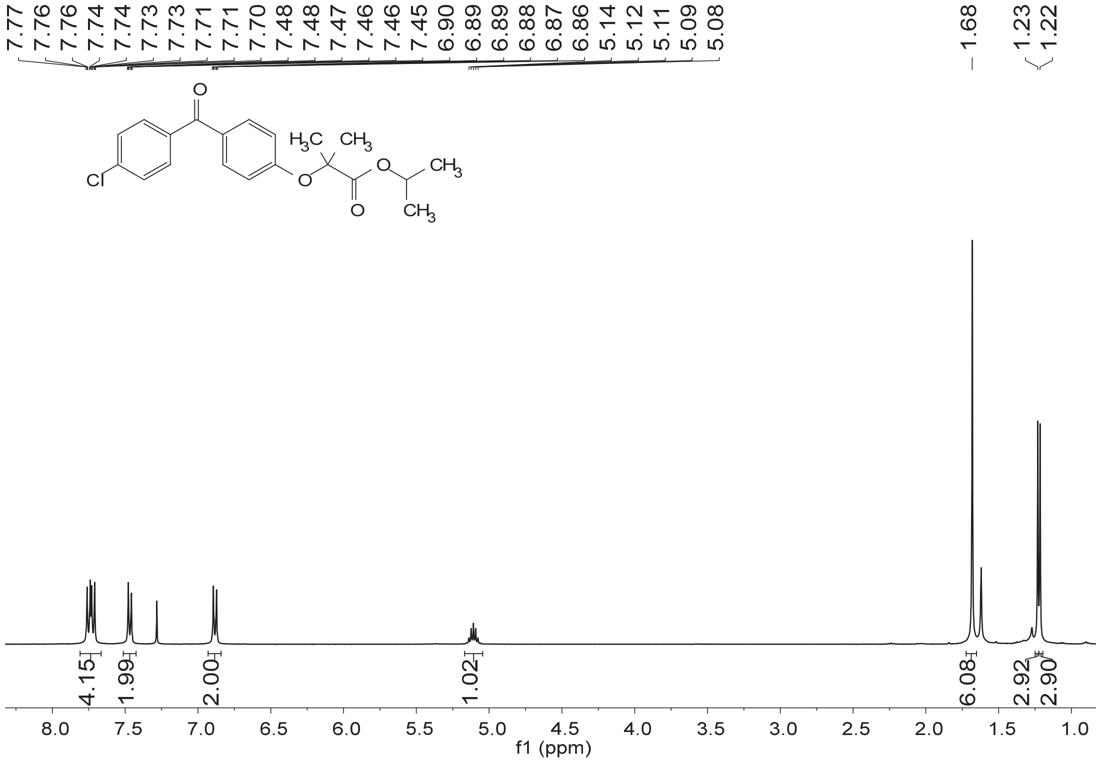
8.36
8.35
8.35
7.85
7.84
7.84
7.83
O
O
4.00
4.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


7.80 7.79 7.77 7.76 7.68 7.67 7.59 7.58 7.57 7.56 7.55 7.54 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.43 7.42 7.42
3.83 3.83 3.82 3.82 3.81 3.80 3.80 3.79 3.67 3.66
1.54 1.54 1.53 1.53
O
H3C
O
O
CH3
1.91 0.98 0.97 0.97 0.99 1.93 1.01
1.00 2.95
3.01
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)


7.77 7.76 7.76 7.74 7.74 7.73 7.73 7.71 7.71 7.70 7.48 7.48 7.47 7.46 7.46 7.45 6.90 6.89 6.89 6.88 6.87 6.86 5.14 5.12 5.11 5.09 5.08
1.68
1.23 1.22
O
Cl
H3C
CH3
O
O
CH3
O
CH3
4.15 1.99 2.00
1.02
6.08 2.92 2.90
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
f1 (ppm)

8. References

[1] Nakano Y, Black M J, Meichan A J, et al. Photoenzymatic Hydrogenation of Heteroaromatic Olefins Using ‘Ene’-Reductases with Photoredox Catalysts. *Angew. Chem. Int. Ed.* **2020**, 59, 10484

[2]Miyazawa K, Koike T, Akita M. Regiospecific Intermolecular Aminohydroxylation of Olefins by Photoredox Catalysis. *Chem. Eur. J.,* **2015**, 21: 11677-11680.

[3] Fu y, Xia Y, Xu Y R, et al. A Recyclable Supramolecular Photocatalyst for the Chemoselective [2 + 2] Photocycloaddition of Chalcones in Water. *ACS Sustainable Chemistry & Engineering.* **2023**, 11 (50), 17752-17759

[4] Xu W H, Mou K, Zhou H N, Xu J , et al. Transformation of triolein to biogasoline by photo-chemo-biocatalysis. *Green Chem*. **2022**, *24*, 6589

[5] Xie P, Xue C, Luo J, et al. Decatungstate-mediated solar photooxidative cleavage of C=C bonds using air as an oxidant in water. *Green Chem.* **2021**, *23*, 5936-5943.

[6] Zhao B, Lu X. Cationic palladium (II)-catalyzed addition of arylboronic acids to nitriles. One-step synthesis of benzofurans from phenoxyacetonitriles. *Org. Lett.* **2006**, *8*, 5987-5990.

[7] Wang Z J, Wang X Y, Wang X, et al. Carbonylative suzuki cross-coupling reaction catalyzed by bimetallic Pd-Pt nanodendrites under ambient CO pressure. *Catal. Commun.* **2017**, *101*, 10-14.

[8] Fu Y, Ma X Z, Shi C Z, Shen T, et al. MeZnOMe-mediated reaction of aldehydes with Grignard reagents: A glance into nucleophilic addition/Oppenauer oxidation pathway. *Applied Organometallic Chemistry*. **2018**, *32(9)*, e4462.

[9] Bazyar Z, Hosseini-Sarvari M. On/Off O_2 switchable photocatalytic oxidative and protodecarboxylation of carboxylic acids[J]. *The Journal of organic chemistry,* **2019**, *84(21)*: 13503-13515.

[10] Liu J, Zhang X, Yi H, et al. Chloroacetate-Promoted Selective Oxidation of Heterobenzylic Methylenes under Copper Catalysis[J]. *Angewandte Chemie International Edition*, **2015**, *54(4)*: 1261-1265.

[11] Bellale E V, Bhalerao D S, Akamanchi K G. Oxidative conversion of α, α-disubstituted acetamides to corresponding one-carbon-shorter ketones using hypervalent iodine (λ5) reagents in combination with tetraethylammonium bromide. *J.*

Org. Chem. **2008**, *73*, 9473-9475.

[12] Wang X, Wang C, Liu Y, et al. Acceptorless dehydrogenation and aerobic oxidation of alcohols with a reusable binuclear rhodium (II) catalyst in water[J]. *Green Chemistry,* **2016**, *18(17)*: 4605-4610.

[13] Despras G, Zamaleeva A I, Dardevet L, et al. H-Rubies, a new family of red emitting fluorescent pH sensors for living cells[J]. *Chem. Sci.* **2015**, *6*, 5928-5937.

[14] Wang D, Wang P, Wang S, et al. Direct electrochemical oxidation of alcohols with hydrogen evolution in continuous-flow reactor. *Nat. Commun*, **2019**, *10*, 2796.

[15] Shengming M, Jinxian L, Suhua L, et al. Development of a General and Practical Iron Nitrate/TEMPO-Catalyzed Aerobic Oxidation of Alcohols to Aldehydes/Ketones: Catalysis with Table Salt. *Adv. Synth. Catal.,* **2011**, *353*: 1005-1017.

[16] Pochampalli S, Owk R, Prathap R M, et al. Copper catalyzed oxygen assisted C(CNOH)–C(alkyl) bond cleavage: a facile conversion of aryl/aralkyl/vinyl ketones to aromatic acids. *Chem. Commun*, **2019**, *55*, 4817.

[17] Fujihara T, Cong C, Terao J, et al. Palladium-Catalyzed Reduction of Carboxylic Acids to Aldehydes with Hydrosilanes in the Presence of Pivalic Anhydride[J]. *Advanced Synthesis & Catalysis,* **2013**, *355(17)*: 3420-3424.

[18] Zhao J L, Jiang X K, Wu C, et al. An unprecedented photochemical reaction for anthracene-containing derivatives. *ChemPhysChem*, **2016**, *17,* 3217-3222.

[19] Dang T T, Seayad A M. A Convenient Ruthenium-Catalysed α-Methylation of Carbonyl Compounds using Methanol[J]. *Advanced Synthesis & Catalysis,* **2016**, *358(21)*: 3373-3380.

[20] Sagadevan A, Charpe V P, Ragupathi A, et al. Visible Light Copper Photoredox-Catalyzed Aerobic Oxidative Coupling of Phenols and Terminal Alkynes: Regioselective Synthesis of Functionalized Ketones via C≡C Triple Bond Cleavage. *Journal of the American Chemical Society*, **2017**, *139 (8)*, 2896-2899