Supporting Information

$Bi(NO_3)_3$/TEMPO dual catalysis for aerobic oxidation of alcohols

Zhenhua Xu,[a,*] Yi Xu, [a] Yamin Zhang, [a] Xiaoxiao Hu,[a] Yong Xie, [a] Zhiqiang Shi, [a] and Huawen Huang[b,c*]

[a] *School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Anhui 234000, People's Republic of China. E-mail: Xuzhenhua@ahszu.edu.cn.*
[b] *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China. E-mail: hwhuang@xtu.edu.cn.*
[c]*School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China.*

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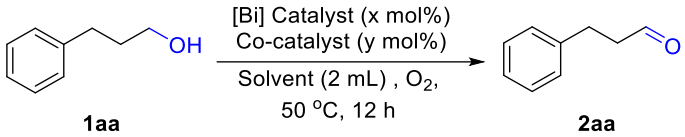
1. General information

Reactions via general procedure were carried out under an oxygen atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker-AV (400, 100, MHz, respectively) instrument using $CDCl_3$ as solvent. Chemical shifts are given in ppm and coupling constants in 400 Hz. Chemical shift values are reported in δ (ppm) relative to $CDCl_3$ (^{1}H NMR, δ = 7.26; ^{13}C NMR, δ = 77.00). Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. The structures of known compounds were further corroborated by comparing their ^{1}H NMR data with those in literature. In order to indicate the signal multiplicity, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them.

2. Optimization of reaction conditions. [a]

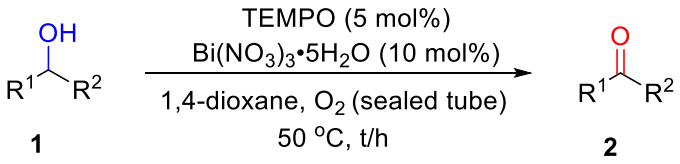


1aa **2aa**

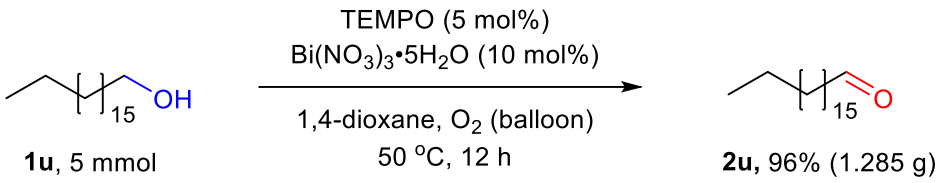
Entry	[Bi] Catalyst	co-catalyst	x/y	Solvent	Yield (%)[b]
1	**$Bi(NO_3)_3•5H_2O$**	**TEMPO**	**10/5**	**1,4-dioxane**	**90**
2	BiOCl	TEMPO	10/5	1,4-dioxane	25
3	[Bi]TPP	TEMPO	10/5	1,4-dioxane	40
4	$Bi(OTf)_3$	TEMPO	10/5	1,4-dioxane	30
5	$BiCl_3$	TEMPO	10/5	1,4-dioxane	trace
6	$Bi(NO_3)_3•5H_2O$	DTBP	10/5	1,4-dioxane	n.r
7	$Bi(NO_3)_3•5H_2O$	DDQ	10/5	1,4-dioxane	n.r
8	$Bi(NO_3)_3•5H_2O$	TBHP	10/5	1,4-dioxane	n.r
9	$Bi(NO_3)_3•5H_2O$	APS	10/5	1,4-dioxane	n.r
10	$Bi(NO_3)_3•5H_2O$	Et_3N	10/5	1,4-dioxane	n.r
11	$Bi(NO_3)_3•5H_2O$	TEMPO	5/5	1,4-dioxane	48
12	$Bi(NO_3)_3•5H_2O$	TEMPO	15/5	1,4-dioxane	92
13	$Bi(NO_3)_3•5H_2O$	TEMPO	20/5	1,4-dioxane	73
14	$Bi(NO_3)_3•5H_2O$	TEMPO	10/1	1,4-dioxane	60
15	$Bi(NO_3)_3•5H_2O$	TEMPO	10/10	1,4-dioxane	76
16	$Bi(NO_3)_3•5H_2O$	TEMPO	10/20	1,4-dioxane	78
17	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	DMSO	n.r
18	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	DCM	39
19	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	Toluene	44
20	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	CH_3CN	42
21	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	DCE	75
22	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	$CHCl_3$	91
23	---	TEMPO	10/5	1,4-dioxane	n.r
24	$Bi(NO_3)_3•5H_2O$	---	10/5	1,4-dioxane	n.r
25	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	---	37
26[c]	$Bi(NO_3)_3•5H_2O$	TEMPO	10/5	1,4-dioxane	71

[a] Reaction conditions: **1aa** (0.2 mmol), catalyst (10 mol%), co-catalyst (5 mol%), solvent (0.1 mol/L) under O_2 at 50 °C for 24 h. [b] NMR yield. [c] Under air.

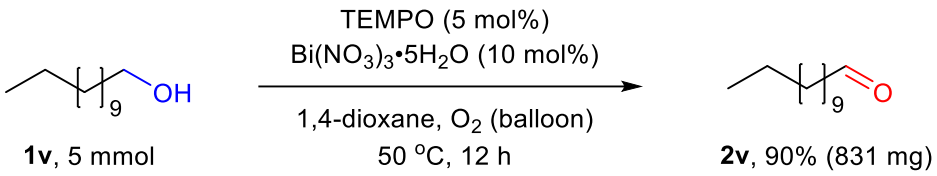
3. General procedure for the aerobic oxidation of alcohols.



Standard conditions: A 10 mL reaction vessel was charged with alcohol **1** (0.2 mmol, 1.0 equiv), TEMPO (1.6 mg, 0.01 mmol, 5 mol %), $Bi(NO_3)_3•5H_2O$ (9.7 mg, 0.02 mmol, 10 mol%) and 1,4-dioxane (2.0 mL). The atmosphere was exchanged by applying vacuum and backfilling with dioxygen (this process was carried out three times). The solution was stirred at 50 °C for identified reaction time under an oxygen atmosphere. After completion of the reaction (monitored by by TLC or GC-MS), the crude mixture was diluted with ethyl acetate (5.0 mL), filtered, and concentrated under reduced pressure to remove volatile components. Then, the crude products were obtained and used for NMR record. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give pure product **2** if the crude ^1H NMR contains impurities (petroleum ether/ethyl acetate, 20 : 1).



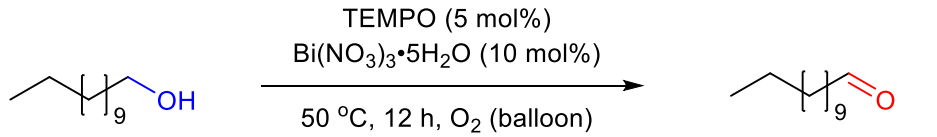
Gram-scale experiment (a): A 50 mL reaction vessel was charged with octadecan-1-ol **1u** (1.353 g, 5.0 mmol, 1.0 equiv), TEMPO (40 mg, 0.25 mmol, 5 mol %), $Bi(NO_3)_3•5H_2O$ (242 mg, 0.5 mmol, 10 mol%) and 1,4-dioxane (20 mL). The atmosphere was exchanged by applying vacuum and backfilling with dioxygen and the vessel was connected with an oxygen balloon. The solution was stirred at 50 °C for 12 h. After completion, the crude mixture was diluted with ethyl acetate (20 mL), filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh, petroleum ether/ethyl acetate, 20 : 1) to give pure product **2u** as white solid (96%, 1.285 g).



1v, 5 mmol

2v, 90% (831 mg)

Gram-scale experiment (b): A 50 mL reaction vessel was charged with octadecan-1-ol **1v** (1.13 mL, 5.0 mmol, 1.0 equiv), TEMPO (40 mg, 0.25 mmol, 5 mol %), $Bi(NO_3)_3 \cdot 5H_2O$ (242 mg, 0.5 mmol, 10 mol%) and 1,4-dioxane (20 mL). The atmosphere was exchanged by applying vacuum and backfilling with dioxygen and the vessel was connected with an oxygen balloon. The solution was stirred at 50 °C for 12 h. After completion, the crude mixture was diluted with ethyl acetate (20 mL), filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh, petroleum ether/ethyl acetate, 20 : 1) to give pure product **2v** as colorless oil (90%, 831 mg).



1v, 10 mmol

2v, 72% (1.325 g)

Gram-scale experiment (c): A 50 mL reaction vessel was charged with octadecan-1-ol **1v** (2.26 mL, 10 mmol, 1.0 equiv), TEMPO (80 mg, 0.5 mmol, 5 mol %), $Bi(NO_3)_3 \cdot 5H_2O$ (484 mg, 0.5 mmol, 10 mol%). The atmosphere was exchanged by applying vacuum and backfilling with dioxygen and the vessel was connected with an oxygen balloon. The solution was stirred at 50 °C for 12 h. After completion, the crude mixture was diluted with ethyl acetate (20 mL), filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh, petroleum ether/ethyl acetate, 20 : 1) to give pure product **2v** as colorless oil (72%, 1.325 g).

4. Metrics calculations

E-factor were calculated using Waste Mass/Product Mass.

(a) *Adv. Synth. Catal.*, **2010**, *352*, 113–118.

E-factor: [12.56 (sol.)+0.511 (SM1) +0.032 (Cat)+0.0276 (additive) +0.0406 (additive)-0.466 (Pro)]/0.466 =27.3

(b) *RSC Adv.*, **2016**, *6*, 35008–35013.

E-factor: [31.44 (sol.) +0.65 (SM1)+0.048(Cat) +0.088 (Cat) + 0.04 (additive)-0.609(Pro)]/0.609 =52

(c) *Org. Process Res. Dev.* **2019**, *23*, 825–8353.

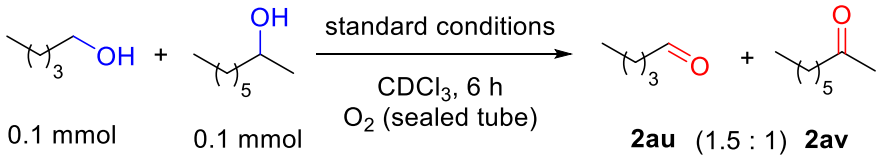
E-factor: [376.8 (sol.)+18.82 (SM1) +2.02 (Cat1)+1.72(Cat2) +0.585(Cat3)-16.30 (Pro)]/16.30 = 23.5

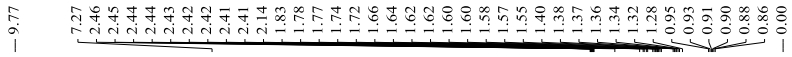
(d) **Our system in neat:**

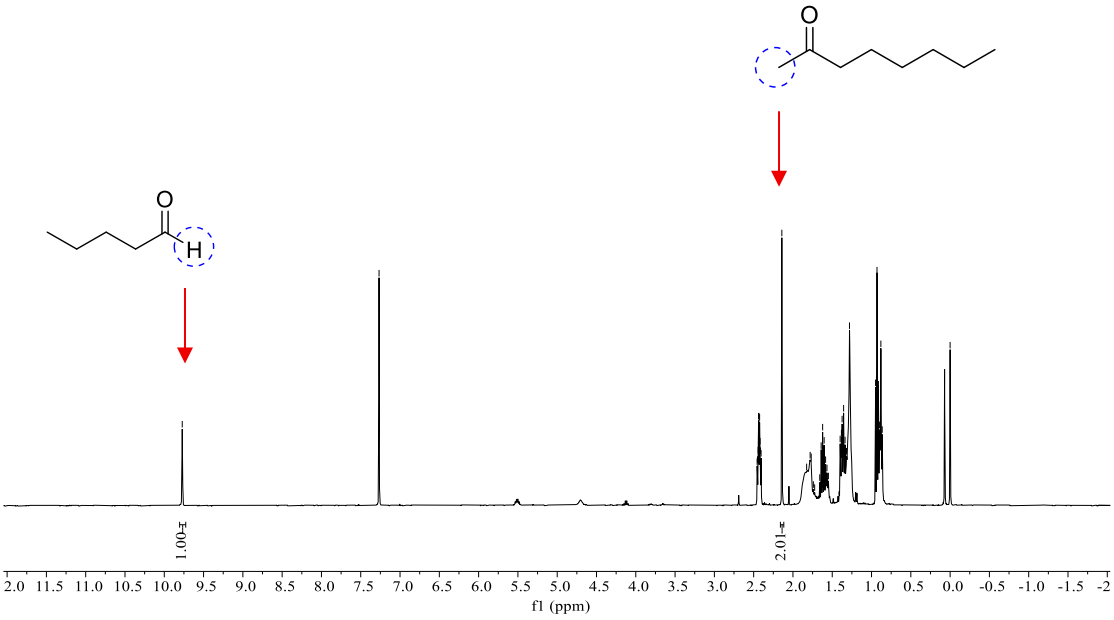
E-factor: [1.863 (SM1) +0.485 (Cat) +0.078 (co-Cat)-1.327]/1.327 = 0.83

5. competition reaction

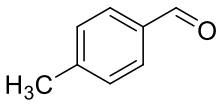
A 10 mL reaction vessel was charged with 1-pentanol (0.1 mmol), 2-octanol (0.1 mmol), TEMPO (1.6 mg, 0.01 mmol, 5 mol %), $Bi(NO_3)_3 \cdot 5H_2O$ (9.7 mg, 0.02 mmol, 10 mol%) and $CDCl_3$ (2.0 mL). The atmosphere was exchanged by applying vacuum and backfilling with dioxygen (this process was carried out three times). The solution was stirred at 50 °C for 6 h. After completion, the crude mixture was directed used for ^1H NMR, which suggests the molar ratio of corresponding pentanal (**2au**) and octan-2-one (**2av**) to be 1.5 : 1.



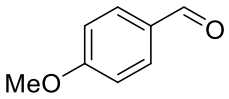




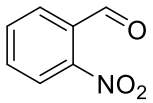
6. Characterization data of products



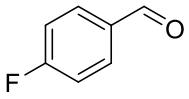
4-methylbenzaldehyde (2a, CAS: 104-87-0)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 23.8 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.95 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).



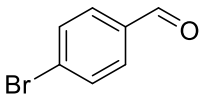
4-methoxybenzaldehyde (2b, CAS: 123-11-5)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 26.9 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.87 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H).



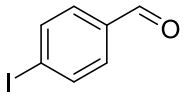
2-nitrobenzaldehyde (2c, CAS: 552-89-6)[2], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 29.9 mg, 99% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.41 (s, 1H), 8.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.94 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.82 - 7.72 (m, 2H).



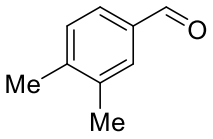
4-fluorobenzaldehyde (2d, CAS: 459-57-4)[3], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 24.6 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.96 (s, 1H), 7.93 – 7.87 (m, 2H), 7.24 – 7.16 (m, 2H).



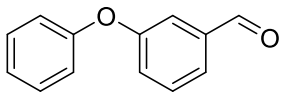
4-bromobenzaldehyde (2f, CAS: 1122-91-4)[4], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 36.6 mg, 99% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.96 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H).



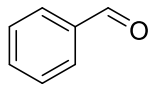
4-iodobenzaldehyde (2g, CAS: 15164-44-0)[4], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 45.9 mg, 99% yield, yellow solid. ^{1}H NMR (400 MHz, CDCl3, ppm) δ 9.94 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H).



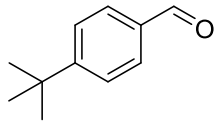
3,4-dimethylbenzaldehyde (2h, CAS: 5973-71-7)[5], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 26.6 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.92 (s, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H).



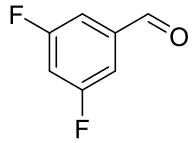
3-phenoxybenzaldehyde (2i, CAS: 39515-51-0)[6], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 39.2 mg, 99% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.95 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.46 (s, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H).



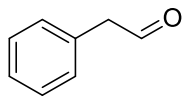
benzaldehyde (2j, CAS: 100-52-7)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 21.0 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.01 (s, 1H), 7.88 (d, *J* = 6.8 Hz, 2H), 7.66 - 7.60 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 2H).



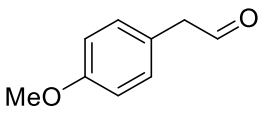
4-(tert-butyl)benzaldehyde (2k, CAS: 939-97-9)[7], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 31.7 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 9H).



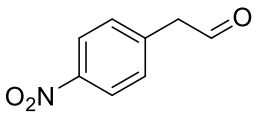
3,5-difluorobenzaldehyde (2l, CAS: 32085-88-4)[8], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.1 mg, 99% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.94 (s, 1H), 7.40 (d, *J* = 4.9 Hz, 2H), 7.08 (tt, *J* = 8.4, 2.2 Hz, 1H).



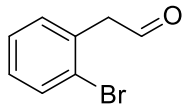
2-phenylacetaldehyde (2m, CAS: 122-78-1)[9], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 19.7 mg, 82% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.74 (t, *J* = 2.4 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 2H), 3.68 (d, *J* = 2.4 Hz, 2H).



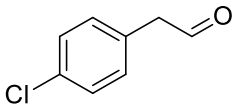
2-(4-methoxyphenyl)acetaldehyde (2n, CAS: 5703-26-4)[10], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 24.2 mg, 80% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.72 (t, *J* = 2.3 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.63 (d, *J* = 2.3 Hz, 2H).



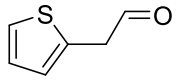
2-(4-nitrophenyl)acetaldehyde (2o, CAS: 1460-05-5)[11], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 15.9 mg, 48% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.81 (t, *J* = 1.7 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 3.87 (d, *J* = 1.7 Hz, 2H).



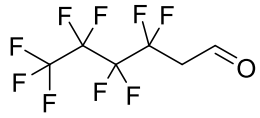
2-(2-bromophenyl)acetaldehyde (2p, CAS: 27200-79-9)[9], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.1 mg, 71% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.21 (m, 1H), 7.24 – 7.21 (m, 1H), 7.21 – 7.14 (m, 1H), 3.86 (d, *J* = 1.5 Hz, 2H).



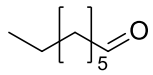
2-(4-chlorophenyl)acetaldehyde (**2q, CAS: 4251-65-4**)[12], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 21.6 mg, 70% yield, colorless liquid. ^{1}H NMR (400 MHz, CDCl3, ppm) δ 9.73 (t, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.67 (d, *J* = 2.1 Hz, 2H).



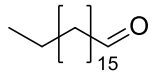
2-(thiophen-2-yl)acetaldehyde (**2r, CAS: 15022-15-8**)[10], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 22.7 mg, 90% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.27 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.94 (d, *J* = 3.2 Hz, 1H), 3.88 (d, *J* = 2.1 Hz, 2H).



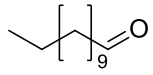
3,3,4,4,5,5,6,6,6-nonafluorohexanal (**2.2s**)[13], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 37.2 mg, 71% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.80 (s, 1H), 3.15 (t, *J* = 18.2 Hz, 2H).



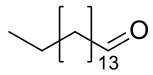
octanal (**2t, CAS: 124-13-0**)[6], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 21.8 mg, 85% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (s, 1H), 2.41 (td, *J* = 7.4, 1.9 Hz, 2H), 1.61 (t, *J* = 7.1 Hz, 2H), 1.33 – 1.24 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 3H).



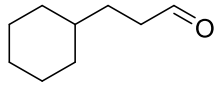
stearaldehyde (**2u, CAS: 638-66-4**)[14], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 51.0 mg, 95% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (s, 1H), 2.40 (td, *J* = 7.4, 1.9 Hz, 2H), 1.61 (t, *J* = 7.1 Hz, 2H), 1.30 – 1.23 (m, 28H), 0.86 (t, *J* = 6.7 Hz, 3H).



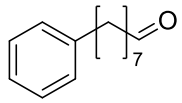
dodecanal (**2v, CAS: 112-54-9**)[7], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 33.2 mg, 90% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.79 (s, 1 H), 2.44 (td, *J* = 7.3, 1.71 Hz, 2 H), 1.65 (t, *J* = 7.1 Hz, 2 H), 1.40 – 1.14 (m, 16 H), 0.90 (t, *J* = 6.9 Hz, 3 H).



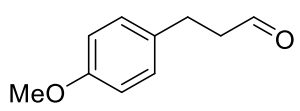
palmitaldehyde (2w, CAS: 629-80-1)[14], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 45.2 mg, 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.74 (s, 1H), 2.40 (td, *J* = 7.4, 1.9 Hz, 2H), 1.61 (t, *J* = 7.0 Hz, 2H), 1.30 – 1.20 (m, 24H), 0.86 (t, *J* = 6.7 Hz, 3H).



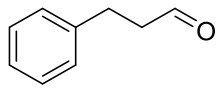
3-cyclohexylpropanal (**2x, CAS: 4361-28-8**)[7], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 25.5 mg, 91% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (s, 1H), 2.42 (td, *J* = 8.2, 7.8, 1.9 Hz, 2H), 1.72 – 1.63 (m, 5H), 1.50 (q, *J* = 7.3 Hz, 2H), 1.27 – 1.12 (m, 4H), 0.93 – 0.80 (m, 2H).



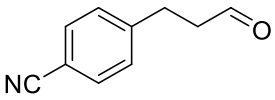
8-phenyloctanal (**2y**)[15], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.4 mg, 94% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (t, *J* = 1.7 Hz, 1H), 7.31 - 7.23 (m, 2H), 7.21 - 7.13 (m, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.41 (td, *J* = 7.3, 1.9 Hz, 2H), 1.65 - 1.56 (m, 4H), 1.33 (d, *J* = 2.3 Hz, 6H).



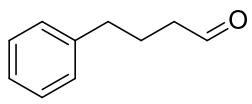
3-(4-methoxyphenyl)propanal (2z, CAS: 20401-88-1)[16], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 31.2 mg, 95% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.80 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H).



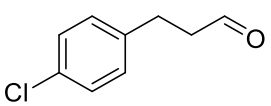
3-phenylpropanal (**2aa, CAS: 104-53-0**)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 24.1 mg, 91% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.82 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.16 (m, 3H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.9 Hz, 2H).



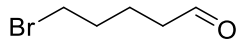
4-(3-oxopropyl)benzonitrile (**2ab, CAS: 136295-53-9**)[17], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 29.3 mg, 92% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.81 (s, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 3.00 (t, J = 7.4 Hz, 2H), 2.82 (t, J = 7.3 Hz, 2H).



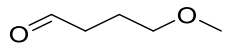
4-phenylbutanal (**2ac, CAS: 18328-11-5**)[17], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.1 mg, 95% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.75 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.45 (td, *J* = 7.3, 1.6 Hz, 2H), 1.96 (p, *J* = 7.4 Hz, 2H).



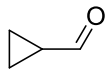
3-(4-chlorophenyl)propanal (**2ad, CAS: 75677-02-0**)[18], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 30.2 mg, 90% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.80 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H).



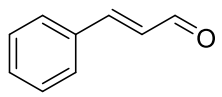
5-bromopentanal (**2ae, CAS: 1191-30-6**)[19], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 26.6 mg, 81% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.78 (t, J = 1.5 Hz, 1H), 3.42 (t, J = 6.5 Hz, 2H), 2.49 (td, J = 7.1, 1.5 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.84 – 1.76 (m, 2H).



4-methoxybutanal (**2af, CAS: 21071-24-9**)[20], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 16.3 mg, 80% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.76 (s, 1H), 3.39 (t, *J* = 6.1 Hz, 2H), 3.30 (s, 3H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.89 (p, *J* = 6.6 Hz, 2H).

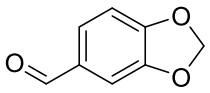


cyclopropanecarbaldehyde (**2ag, CAS: 1489-69-6**)[8], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 10.5 mg, 75% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 5.9 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.09 – 1.04 (m, 4H).

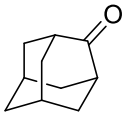


cinnamaldehyde (**2ah, CAS: 104-55-2**)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 16.4 mg, 62% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.69 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.47 (d, *J* =

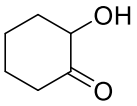
16.0 Hz, 1H), 7.44 – 7.38 (m, 3H), 6.71 (dd, *J* = 15.9, 7.7 Hz, 1H).



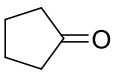
Piperonal (**2ai, CAS: 120-57-0**)[1], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.5 mg, 95% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.79 (s, 1H), 7.39 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H).



2-adamantane ketone (**2aj, CAS: 700-58-3**), by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 29.7 mg, 99% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.52 (s, 2H), 2.10 – 2.03 (m, 4H), 2.02 – 1.93 (m, 6H), 1.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.7, 47.0, 39.3, 36.3, 27.4.

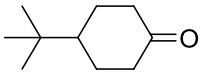


2-hydroxycyclohexan-1-one (**2ak, CAS: 533-60-8**), by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 21.4 mg, 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 4.11 (dd, *J* = 11.4, 7.2 Hz, 1H), 2.55 (ddt, *J* = 13.6, 3.9, 1.7 Hz, 1H), 2.45 (ddq, *J* = 12.7, 6.1, 2.9 Hz, 1H), 2.35 (tdd, *J* = 13.7, 6.4, 1.5 Hz, 1H), 2.10 (ddt, *J* = 12.4, 5.9, 2.7 Hz, 1H), 1.88 (dd, *J* = 13.4, 3.1 Hz, 1H), 1.72 (tt, *J* = 13.2, 3.2 Hz, 1H), 1.67 - 1.56 (m, 1H), 1.49 (td, *J* = 12.6, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 75.4, 39.5, 36.7, 27.6, 23.4.

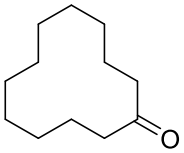


cyclopentanone (2al, CAS: 120-92-3), by silica gel column chromatography

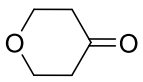
(petroleum ether/ethyl acetate = 20:1), 14.4 mg, 90% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.18 – 2.11 (m, 4H), 1.98 - 1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 38.4, 23.2.



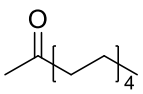
4-(tert-butyl)cyclohexan-1-one (**2am, CAS: 98-53-3**)[21], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 28.0 mg, 91% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.41 – 2.21 (m, 4H), 2.11 – 2.00 (m, 2H), 1.49 – 1.36 (m, 3H), 0.89 (s, 9H).



cyclododecanone (2an, CAS: 830-13-7), by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 34.6 mg, 95% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.49 – 2.40 (m, 4H), 1.74 – 1.65 (m, 4H), 1.32 – 1.21 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 40.4, 24.7, 24.6, 24.2, 22.6, 22.3; ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 40.4, 24.7, 24.6, 24.2, 22.6, 22.3.

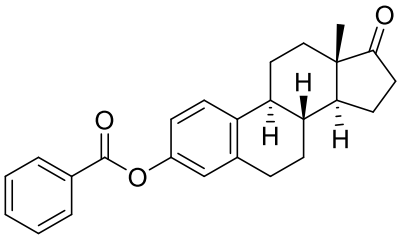


tetrahydro-4H-pyran-4-one (2ao, CAS: 108-97-4)[22], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 19.0 mg, 95% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.95 (t, J = 5.9 Hz, 4H), 2.48 (t, J = 5.9 Hz, 4H).

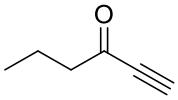


undecan-2-one (**2ap, CAS: 112-12-9**), by silica gel column chromatography

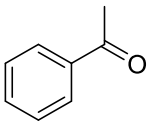
(petroleum ether/ethyl acetate = 20:1), 28.9 mg, 85% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.40 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.59 – 1.50 (m, 2H), 1.29 – 1.20 (m, 12H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 43.8, 31.9, 29.9, 29.4 (2 C), 29.3, 29.2, 23.9, 22.7, 14.1; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 43.8, 31.9, 29.9, 29.4, 29.4, 29.3, 29.2, 23.9, 22.7, 14.1.



Estrone benzoate (2aq, CAS: 2393-53-5), by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 70.3 mg, 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 – 8.15 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.02 – 6.92 (m, 2H), 2.98 – 2.87 (m, 2H), 2.57 – 2.38 (m, 2H), 2.35 – 2.26 (m, 1H), 2.20 – 1.94 (m, 4H), 1.67 – 1.42 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 165.5, 148.9, 138.1, 137.5, 133.6, 130.2, 129.7, 128.6, 126.5, 121.8, 118.9, 50.4, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.4, 25.8, 21.6, 13.9.



hex-1-yn-3-one (2ar, CAS: 689-00-9), by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 17.7 mg, 92% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.19 (s, 1H), 2.56 (t, *J* = 7.3 Hz, 2H), 1.76 – 1.64 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 81.5, 78.3, 47.3, 17.3, 13.5.



acetophenone (**2as, CAS: 98-86-2**)[14], by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1), 22.8 mg, 95% yield, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.61 (s, 3H).

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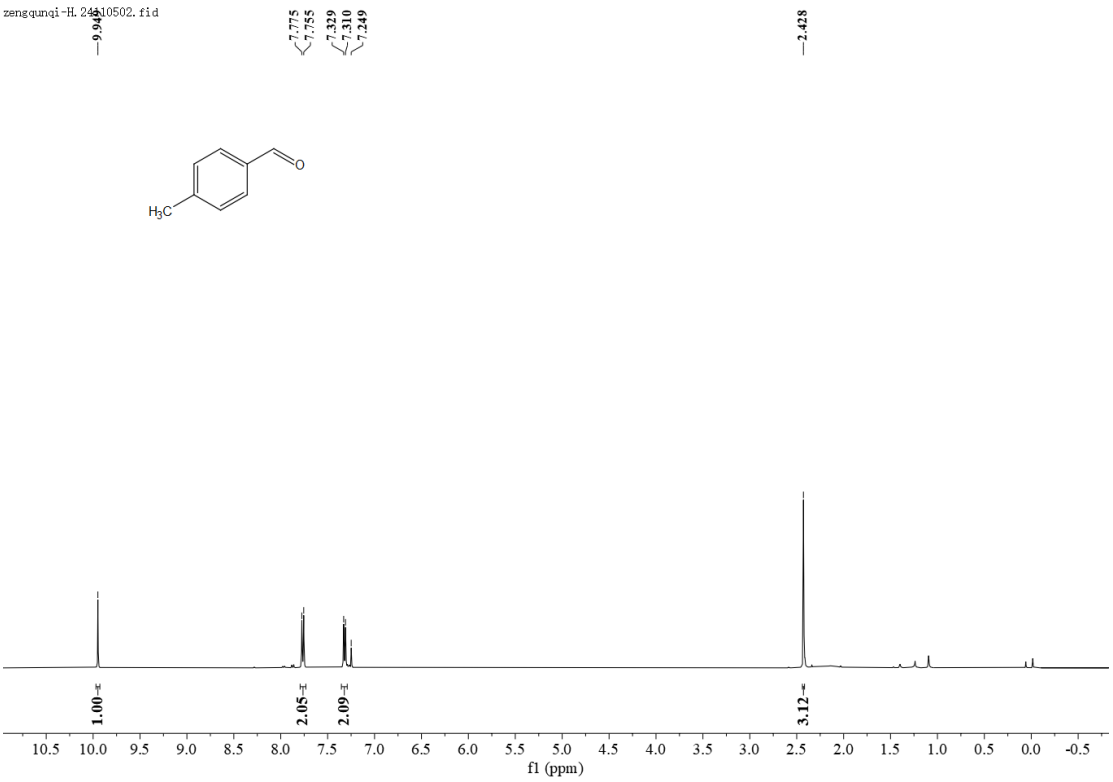
8. NMR Spectra of products

4-methylbenzaldehyde (2a)



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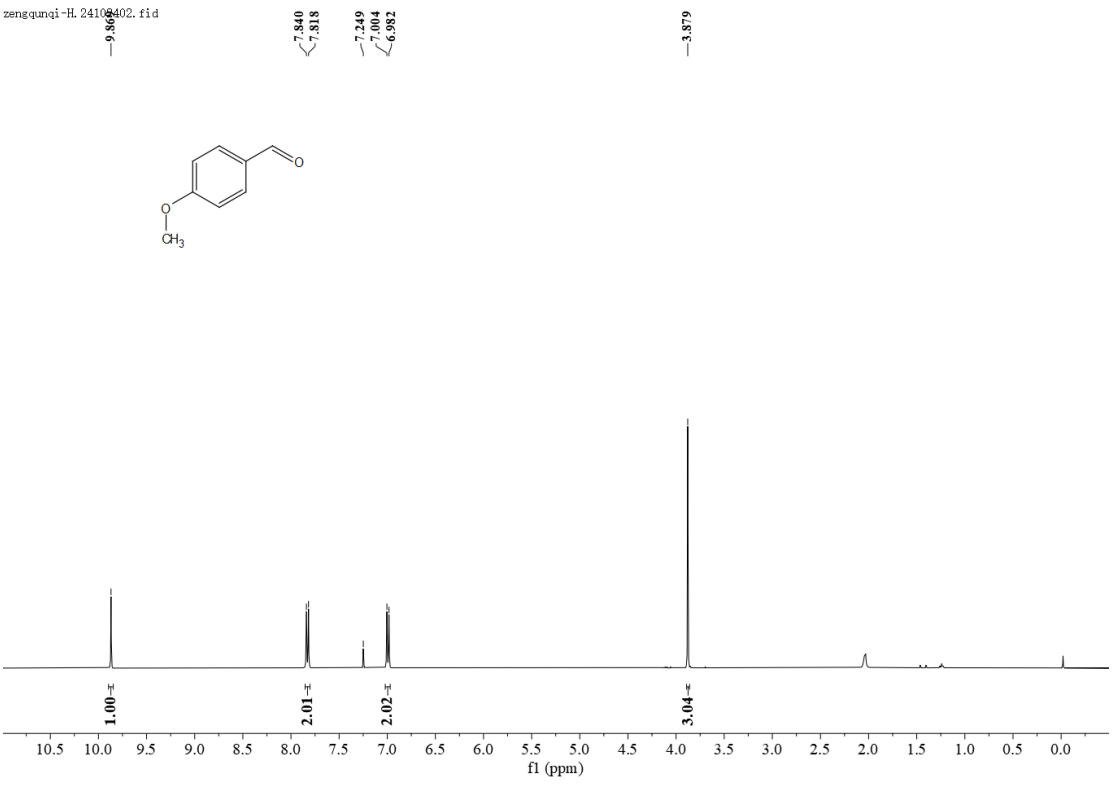

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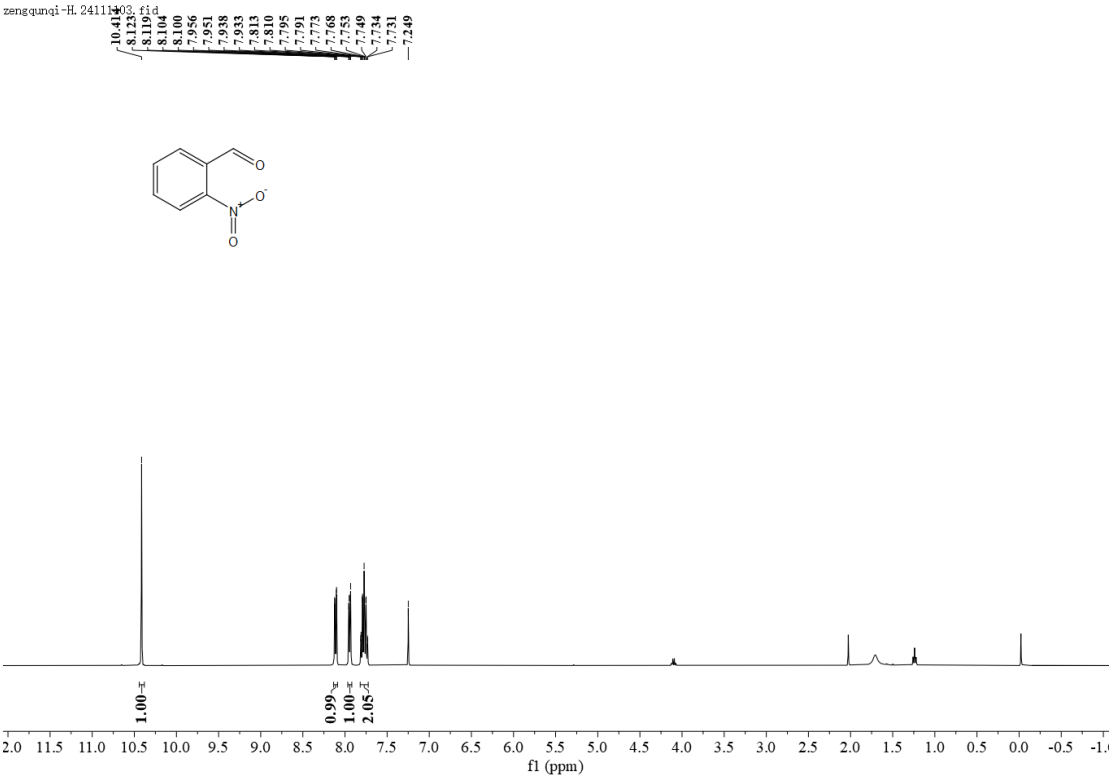

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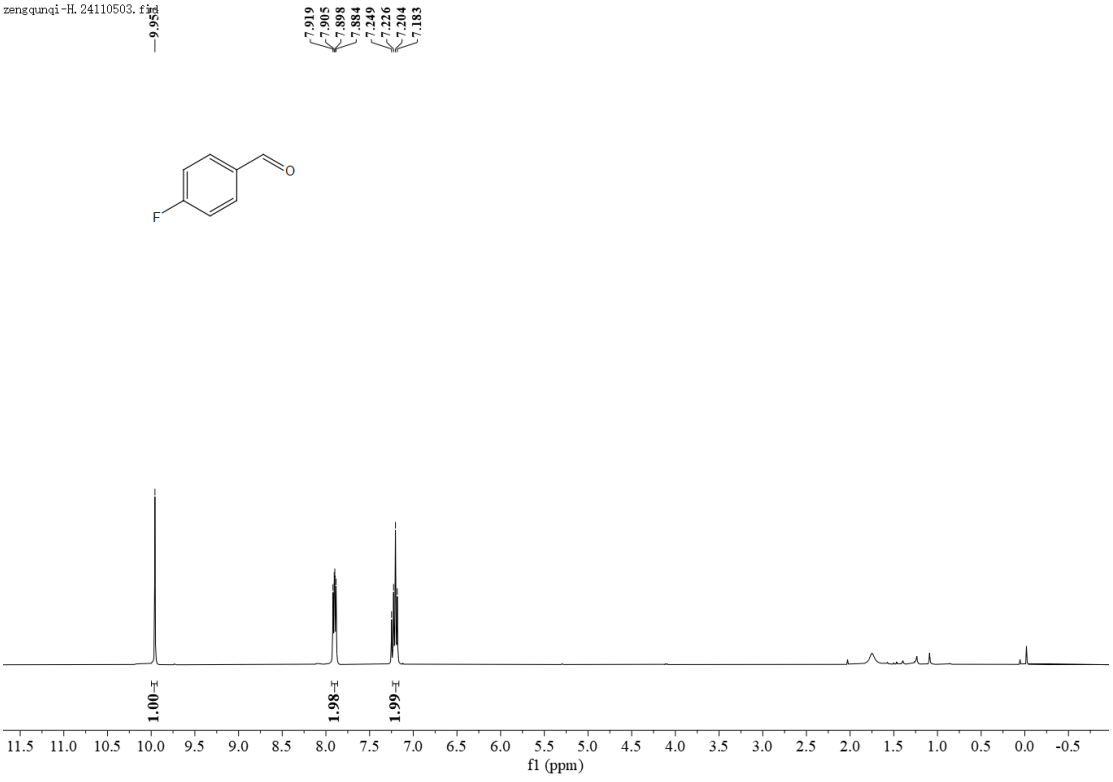
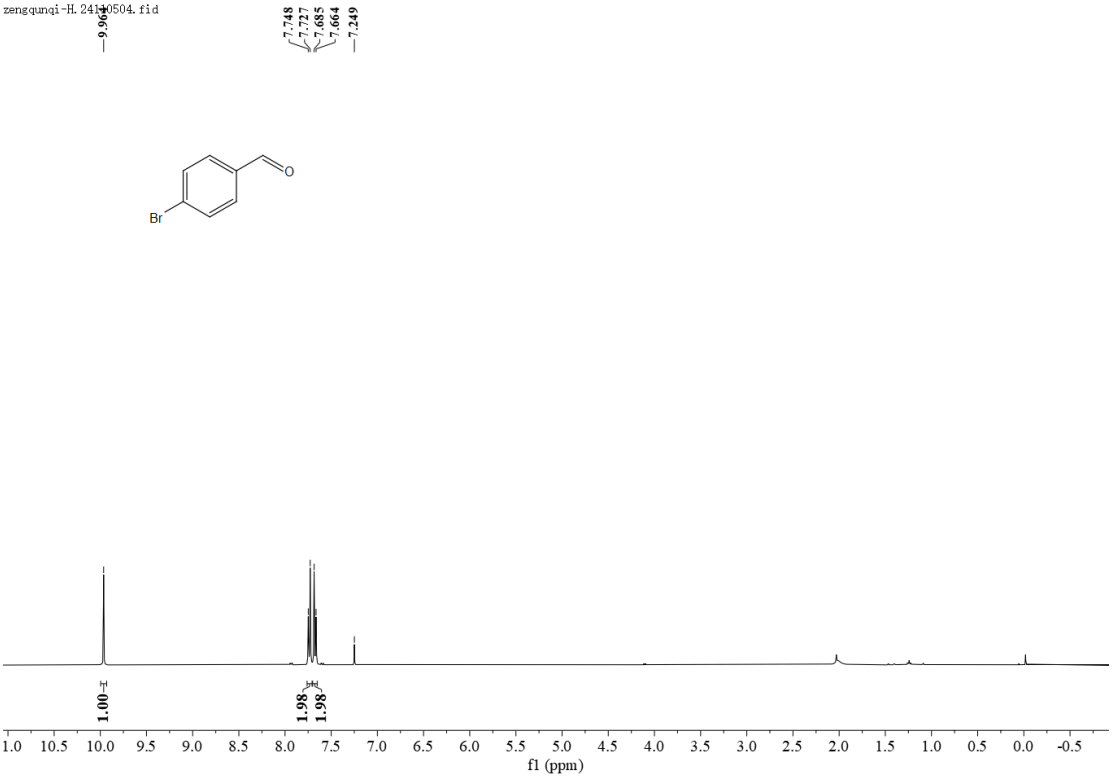


4-bromobenzaldehyde (2f)



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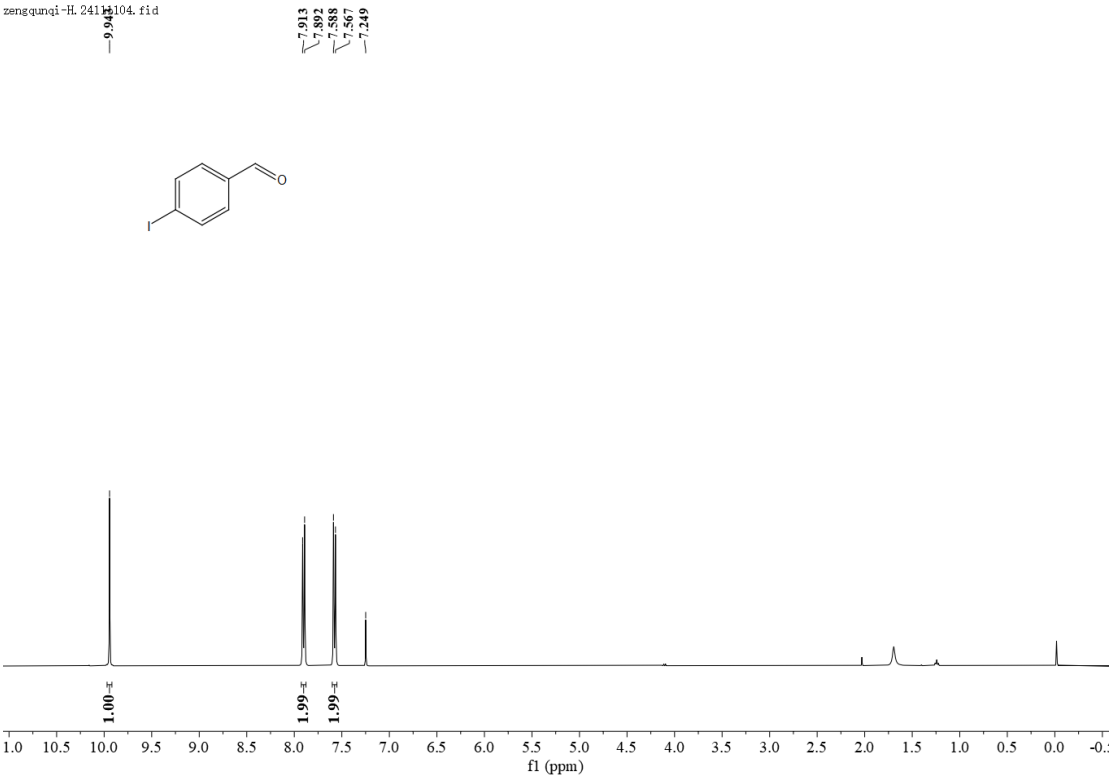

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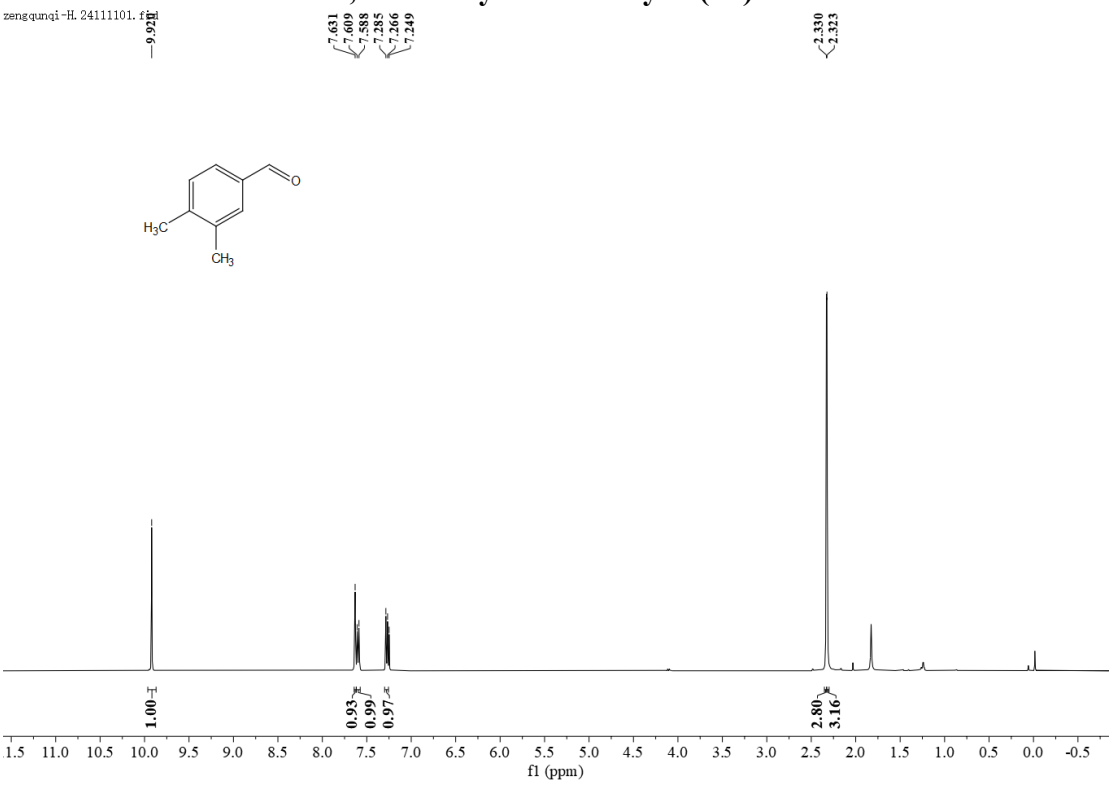

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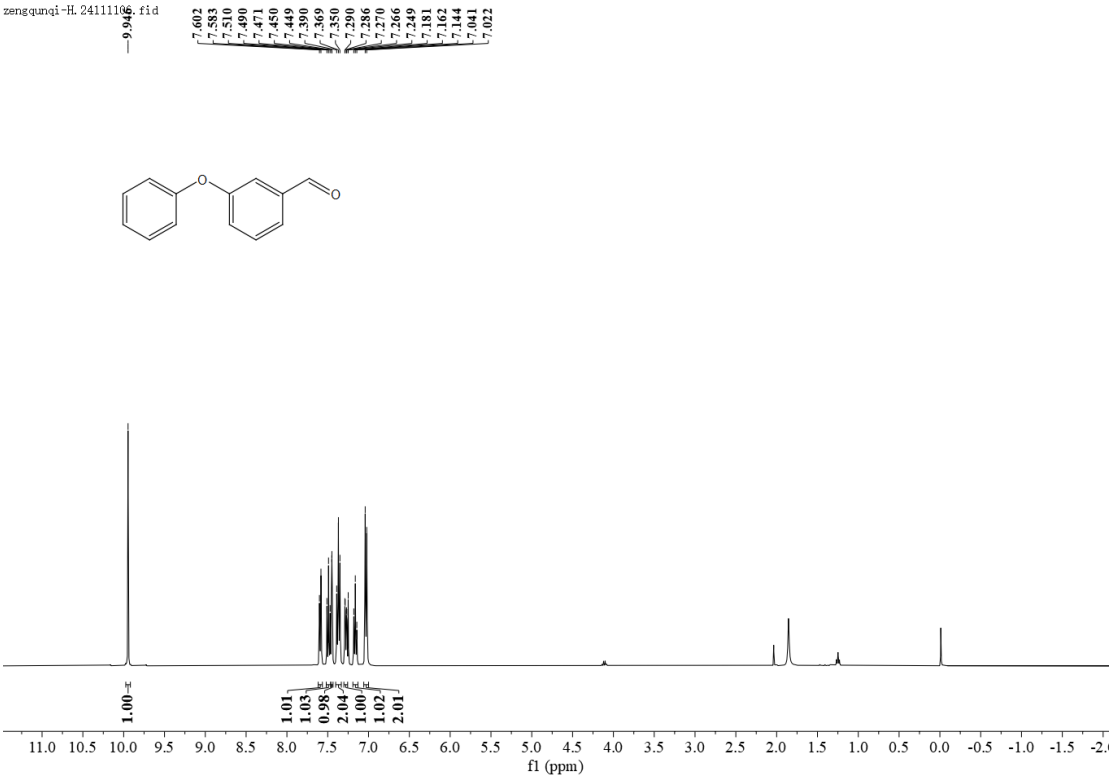
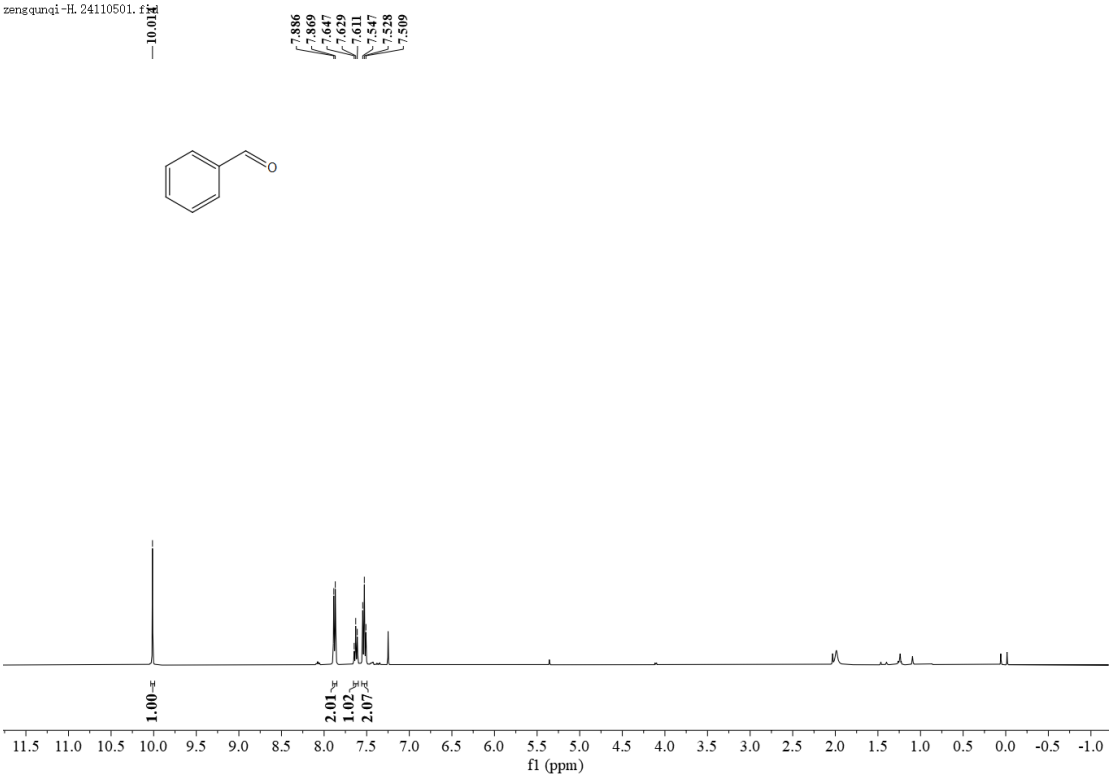


benzaldehyde (2j)



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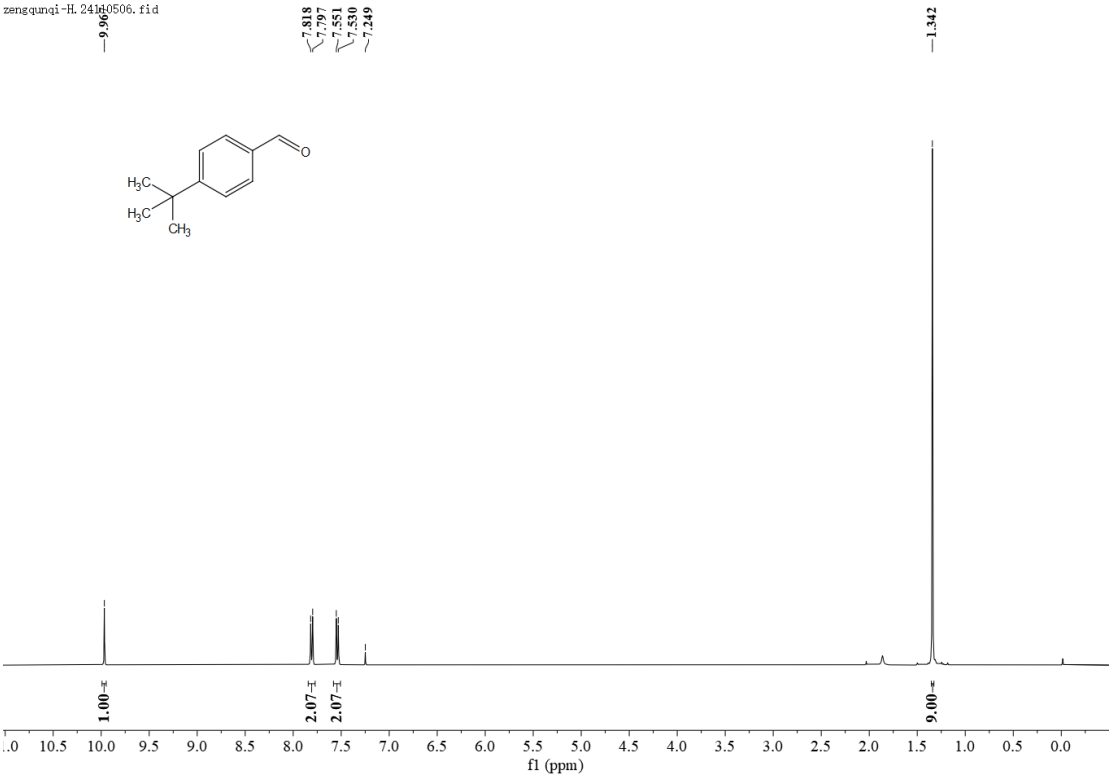

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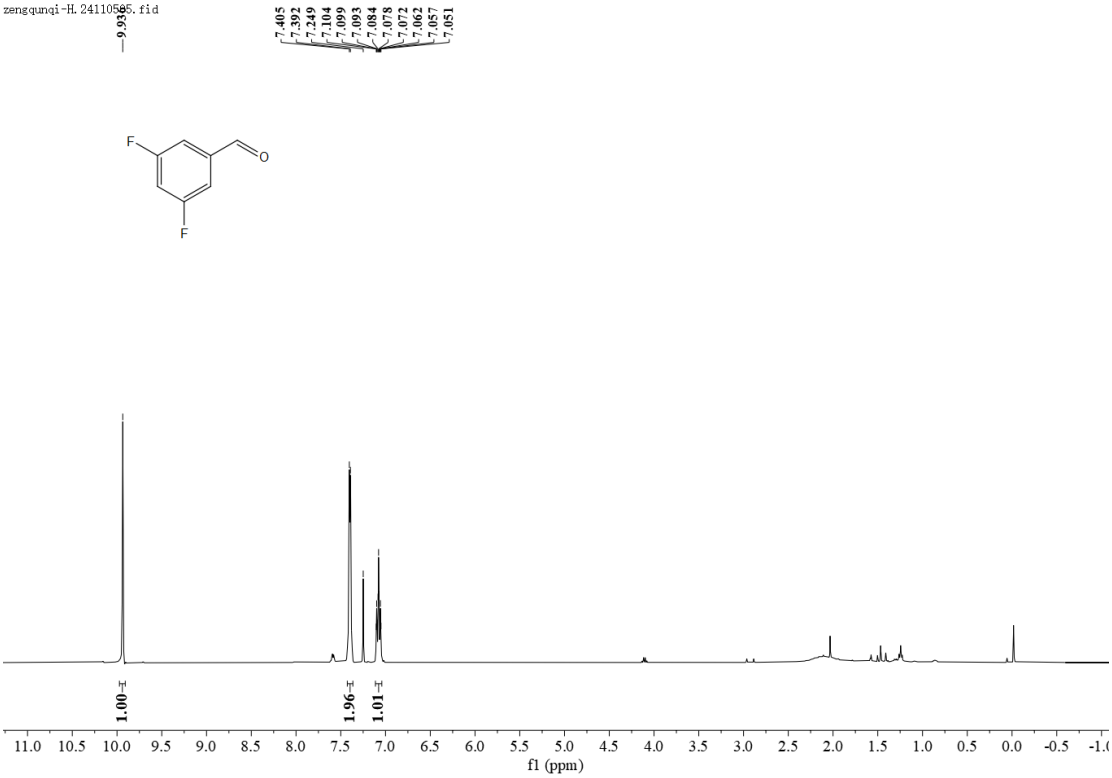

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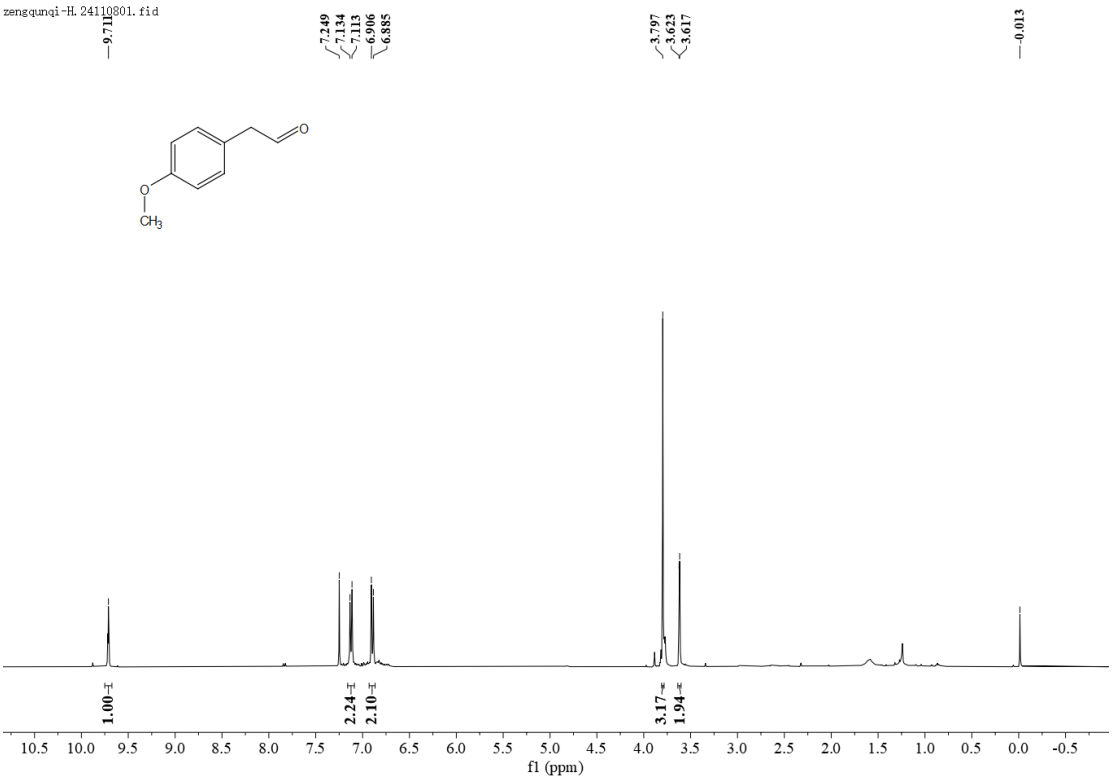

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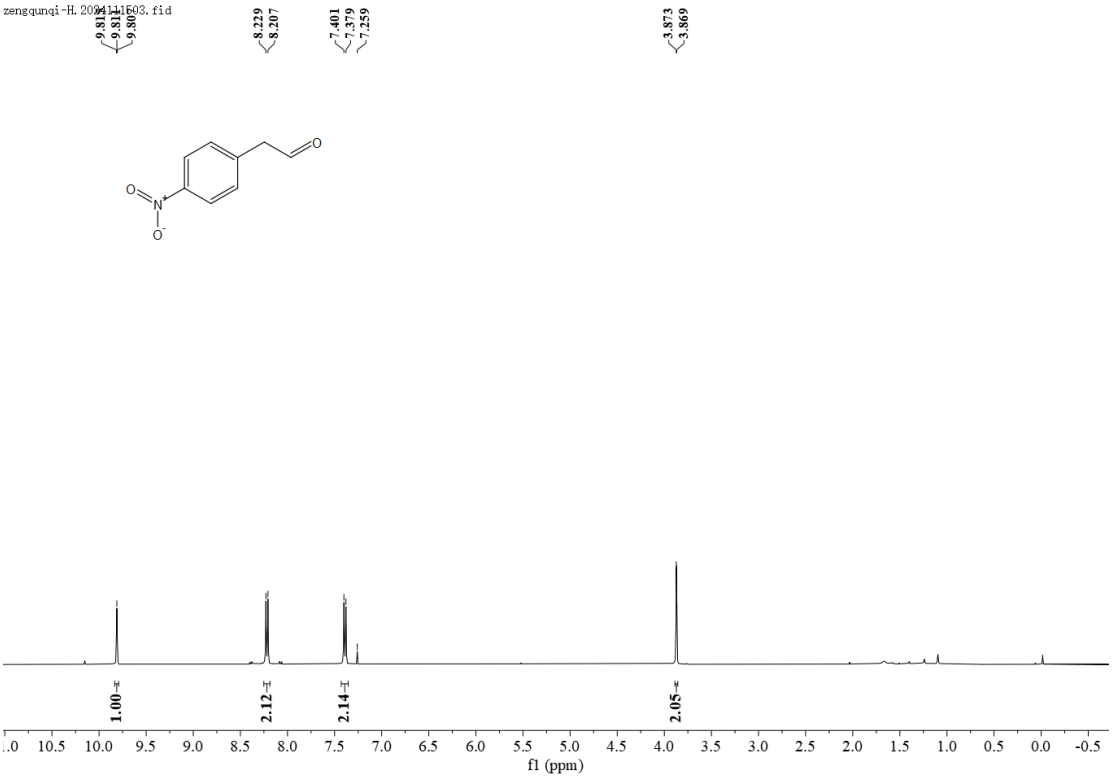

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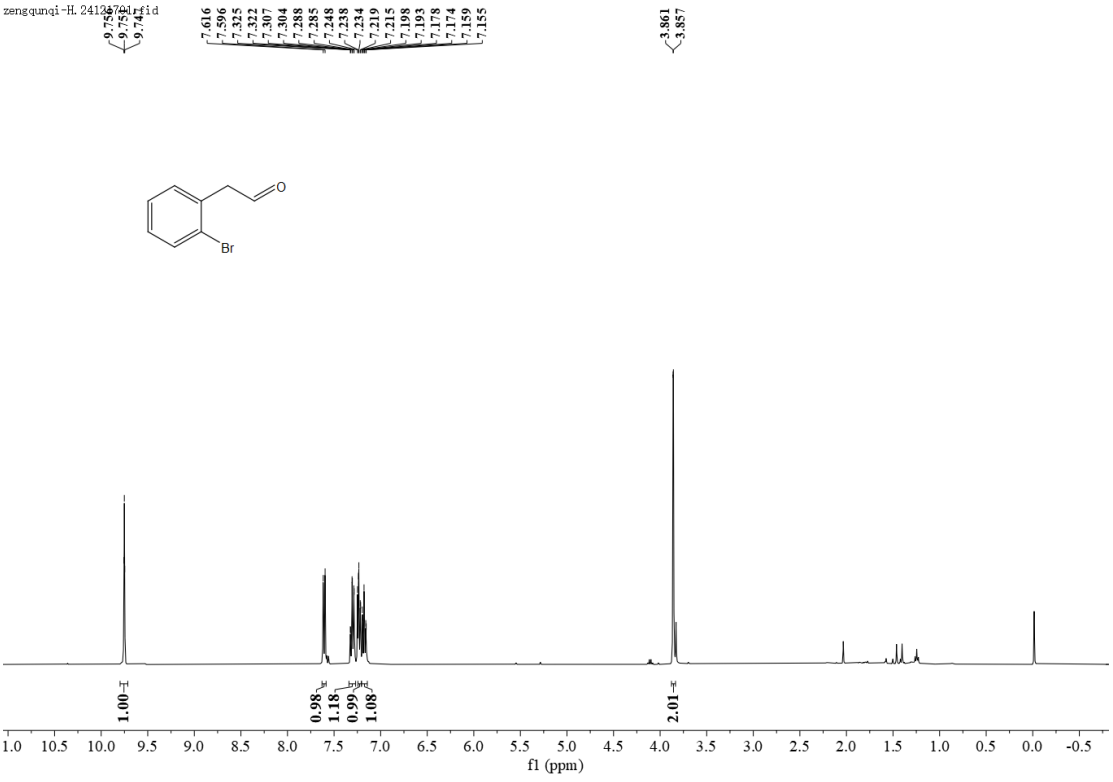

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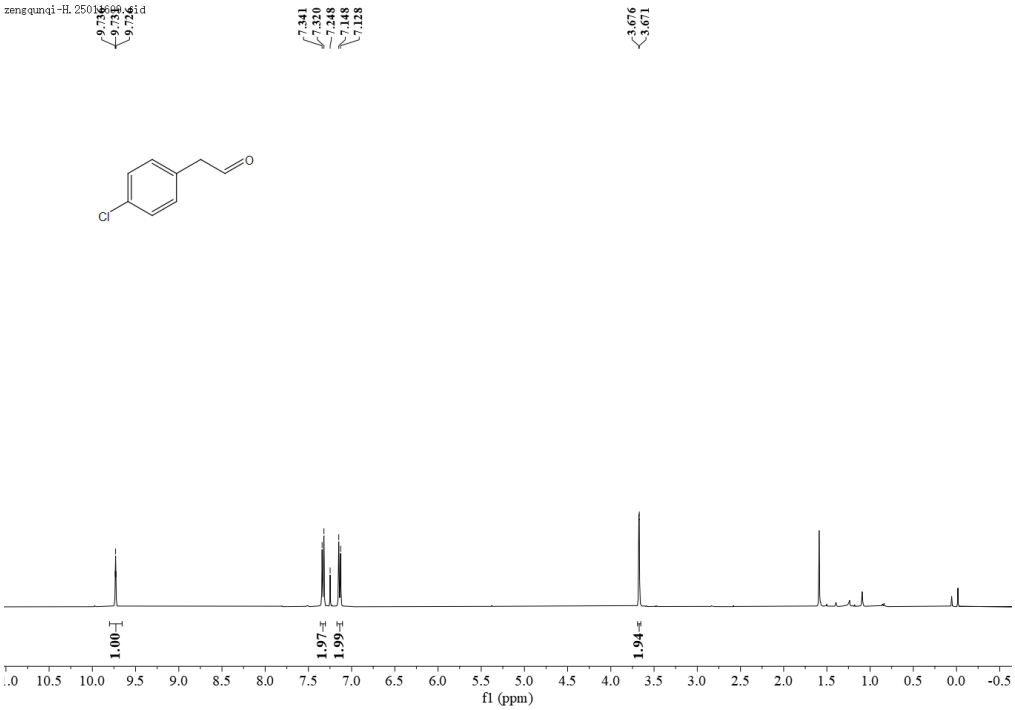
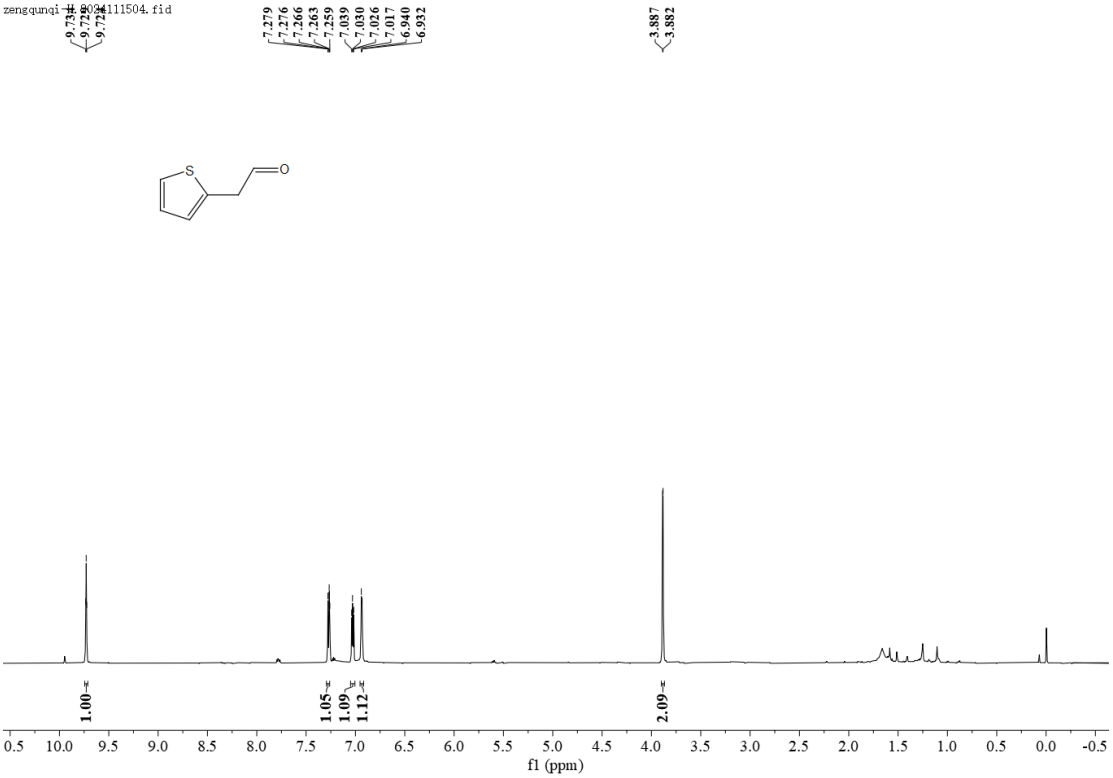
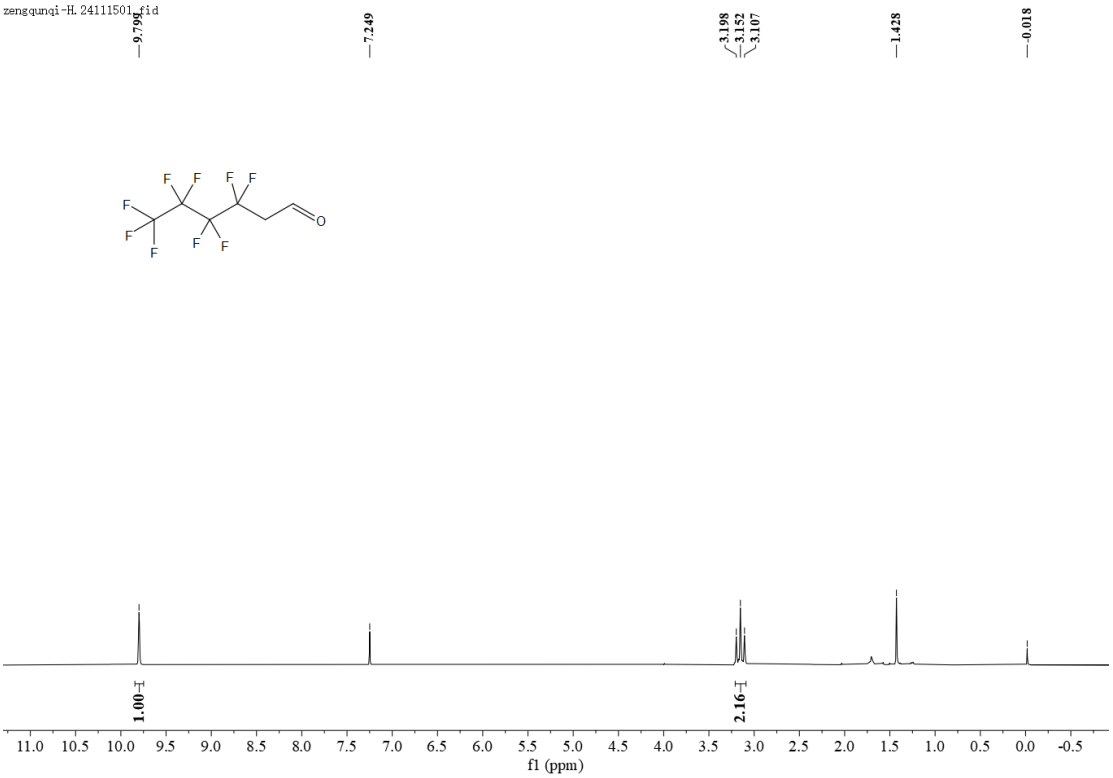


2-(thiophen-2-yl)acetaldehyde (2r)



3,3,4,4,5,5,6,6,6-nonafluorohexanal (2s)



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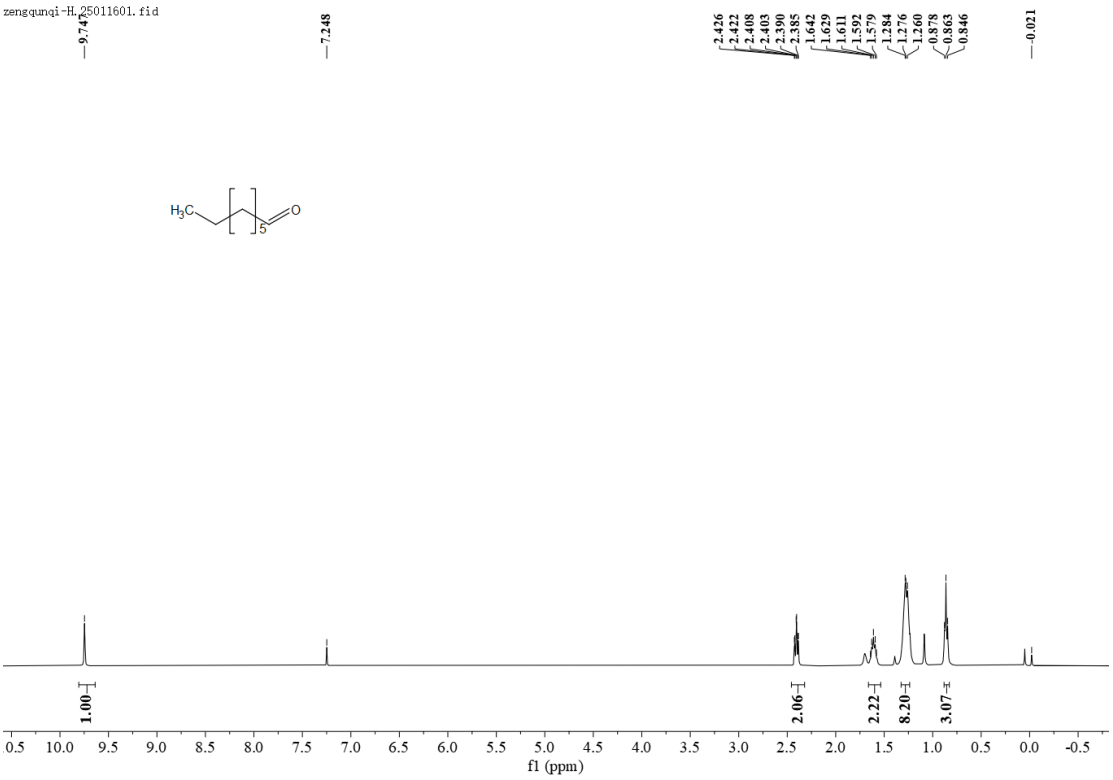

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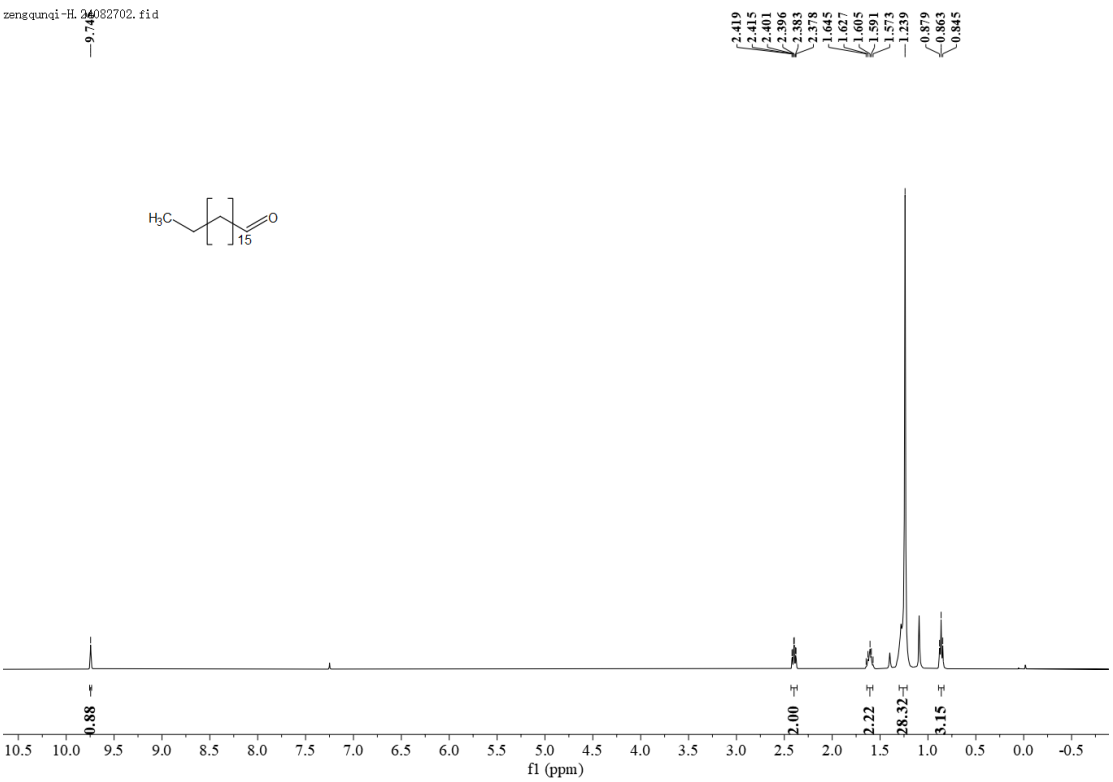
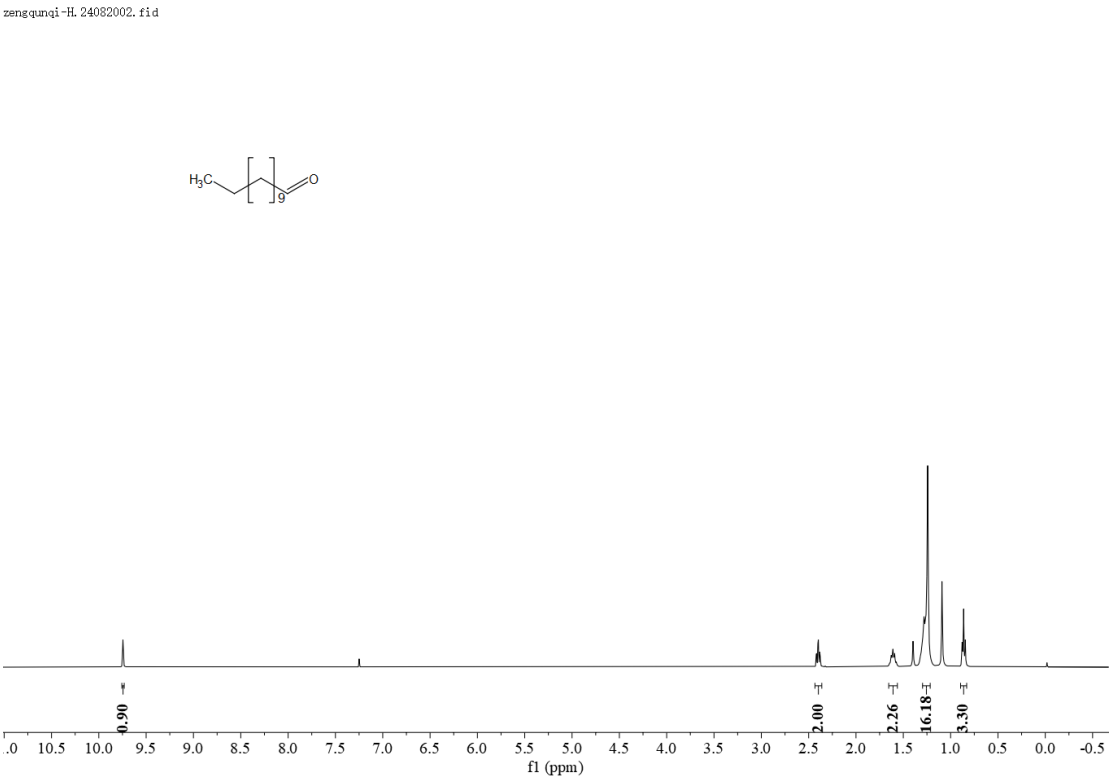


dodecanal (2v)



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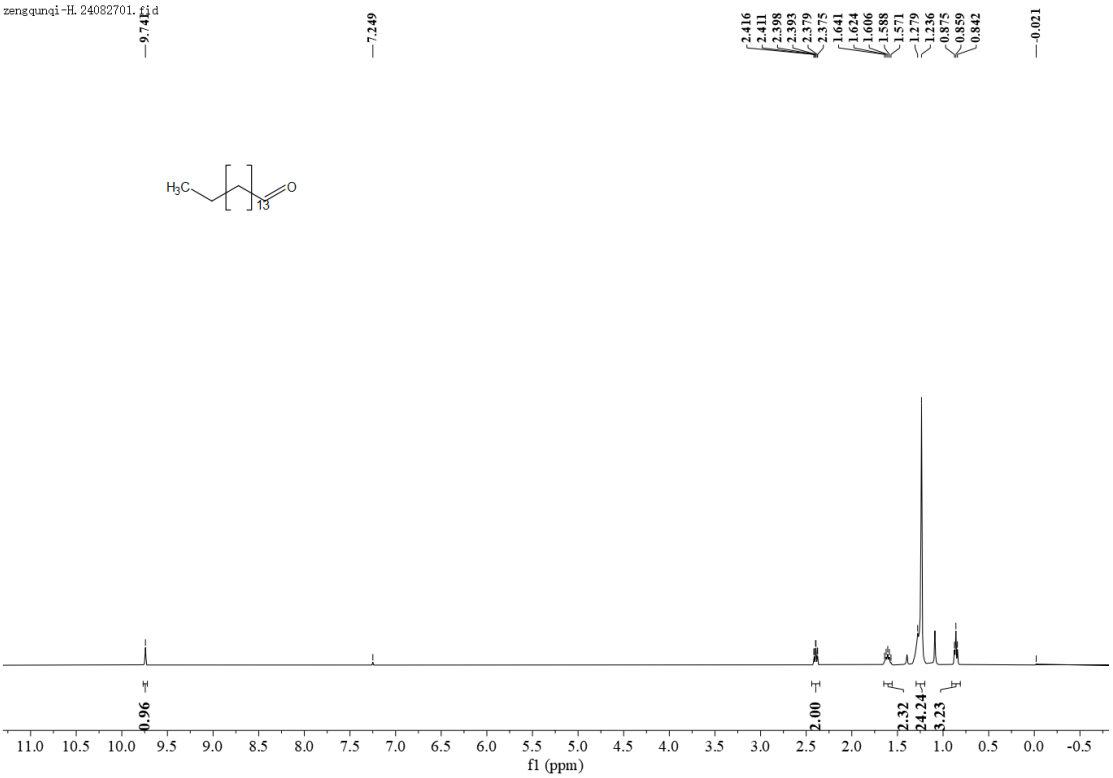
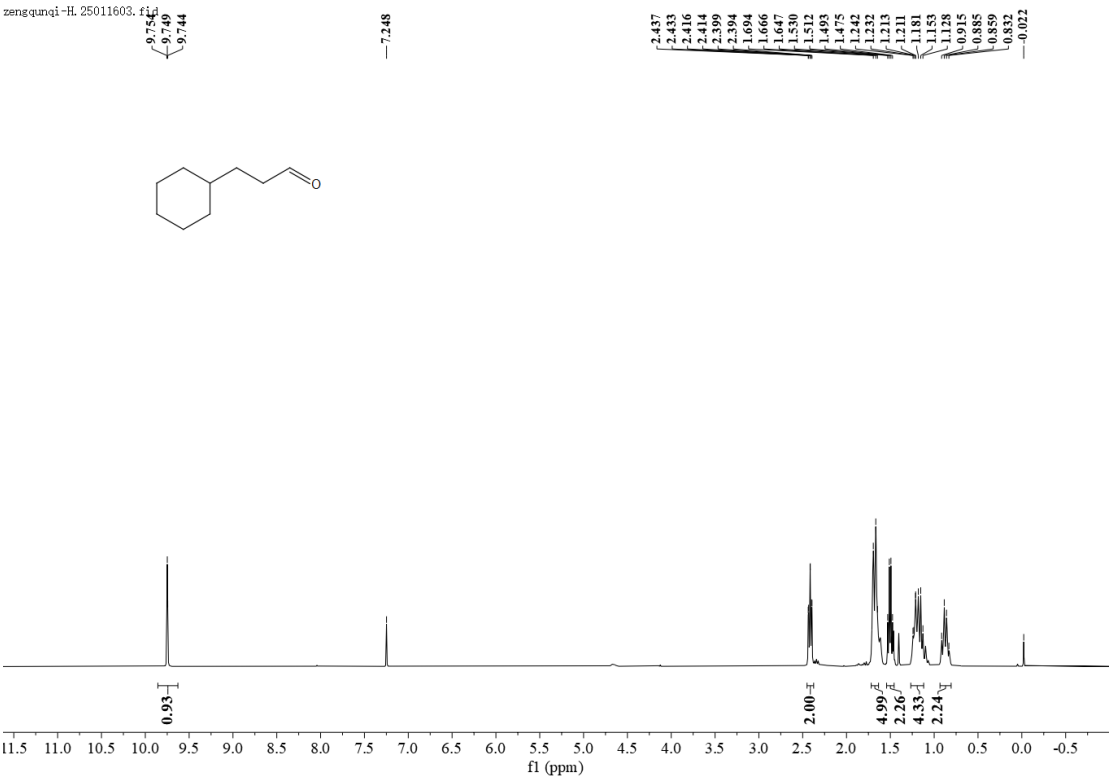


3-cyclohexylpropanal (2x)



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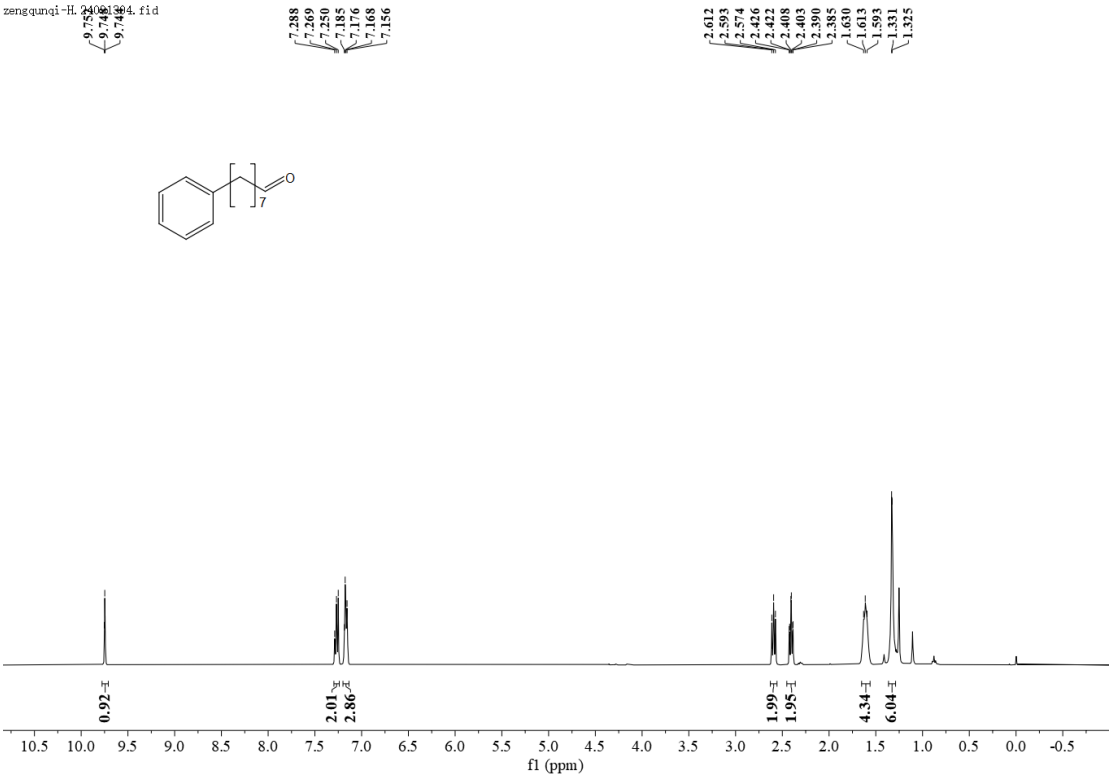
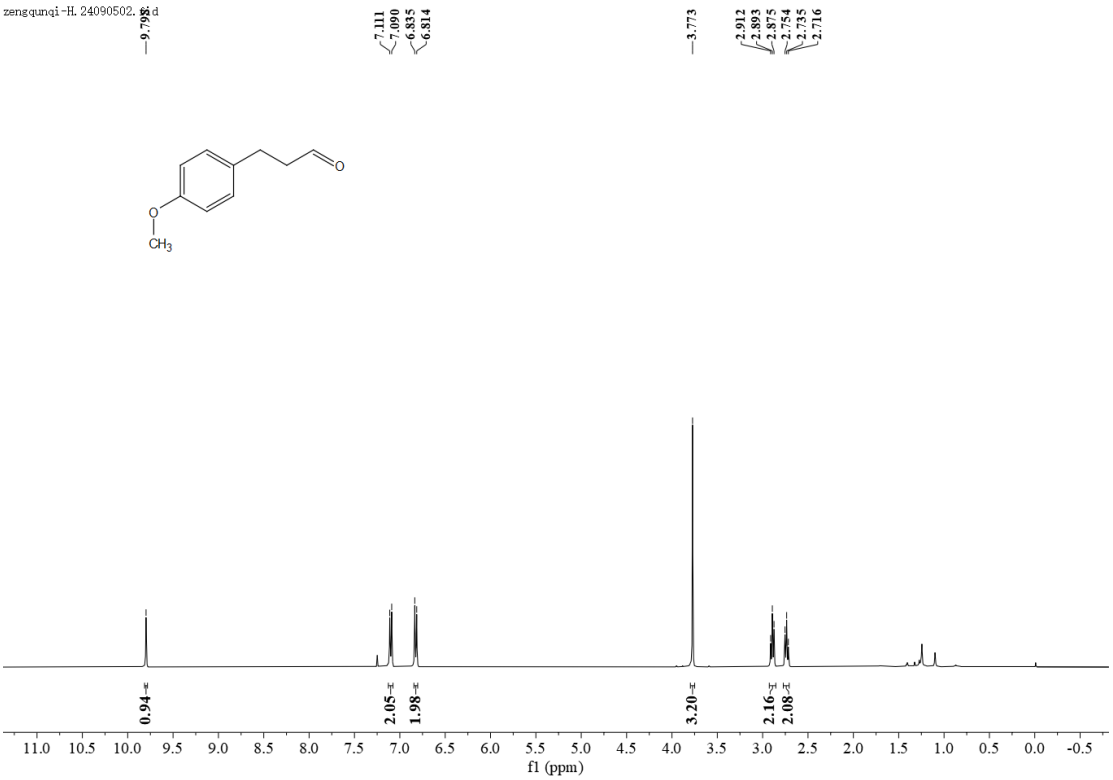
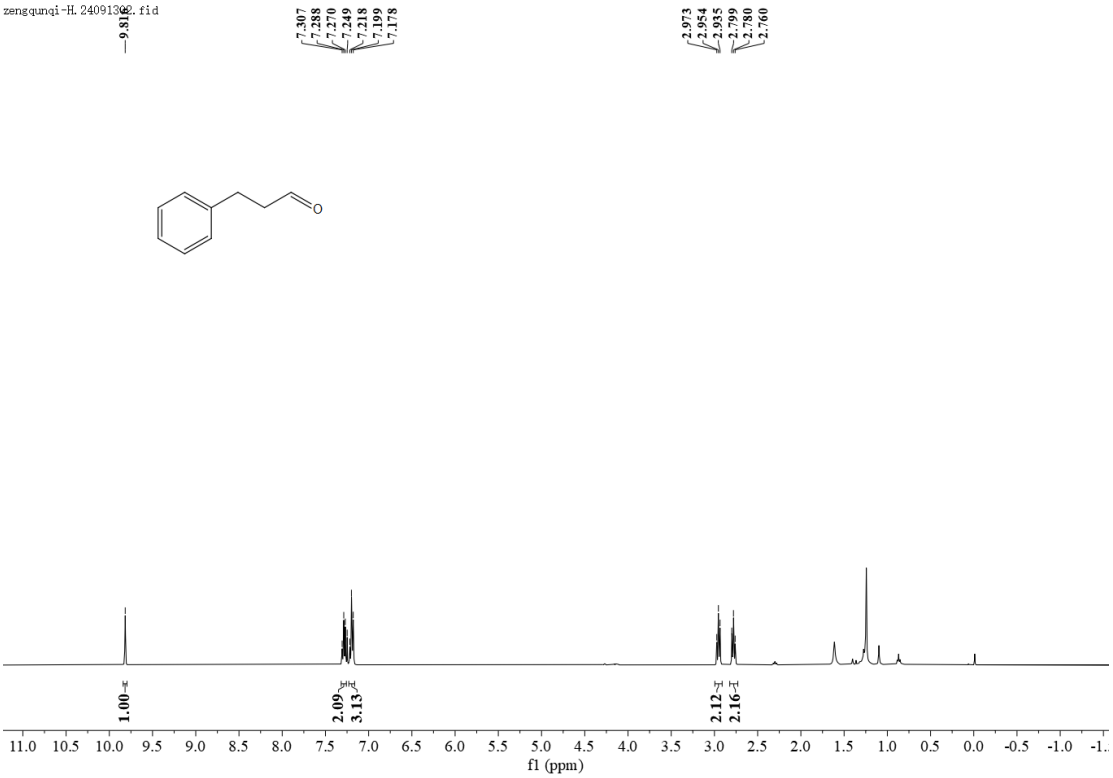


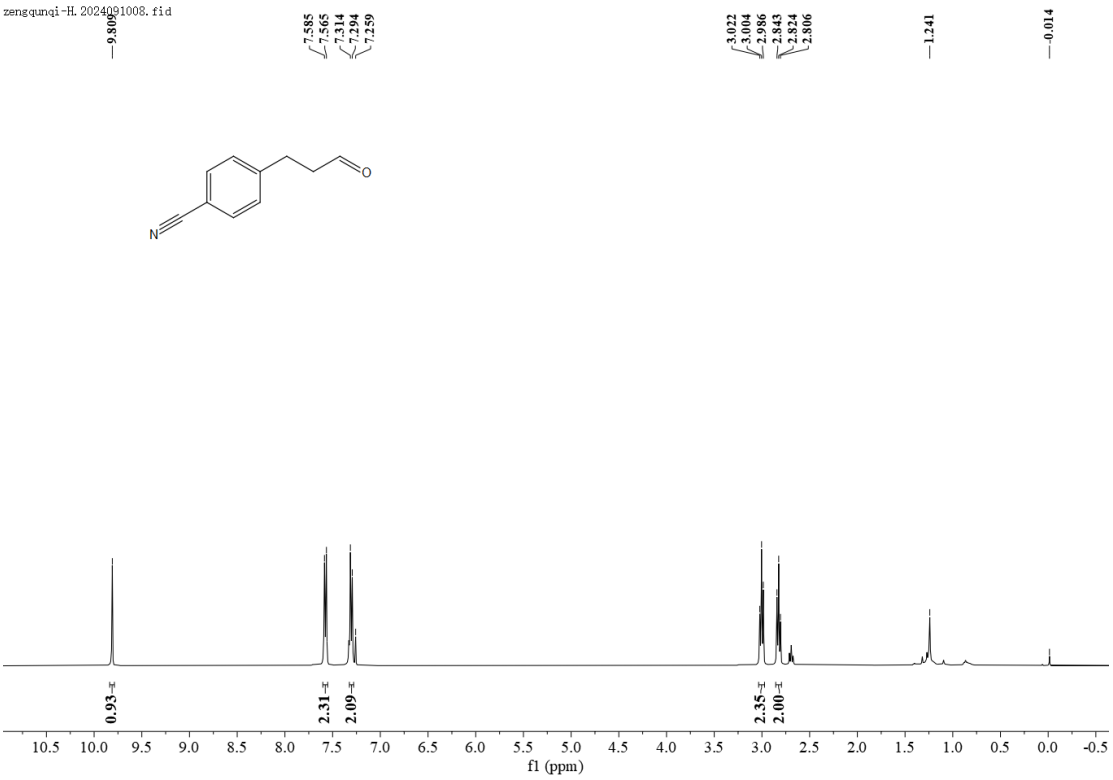
3-(4-methoxyphenyl)propanal (2z)



3-phenylpropanal (2aa)



4-(3-oxopropyl)benzonitrile (2ab)



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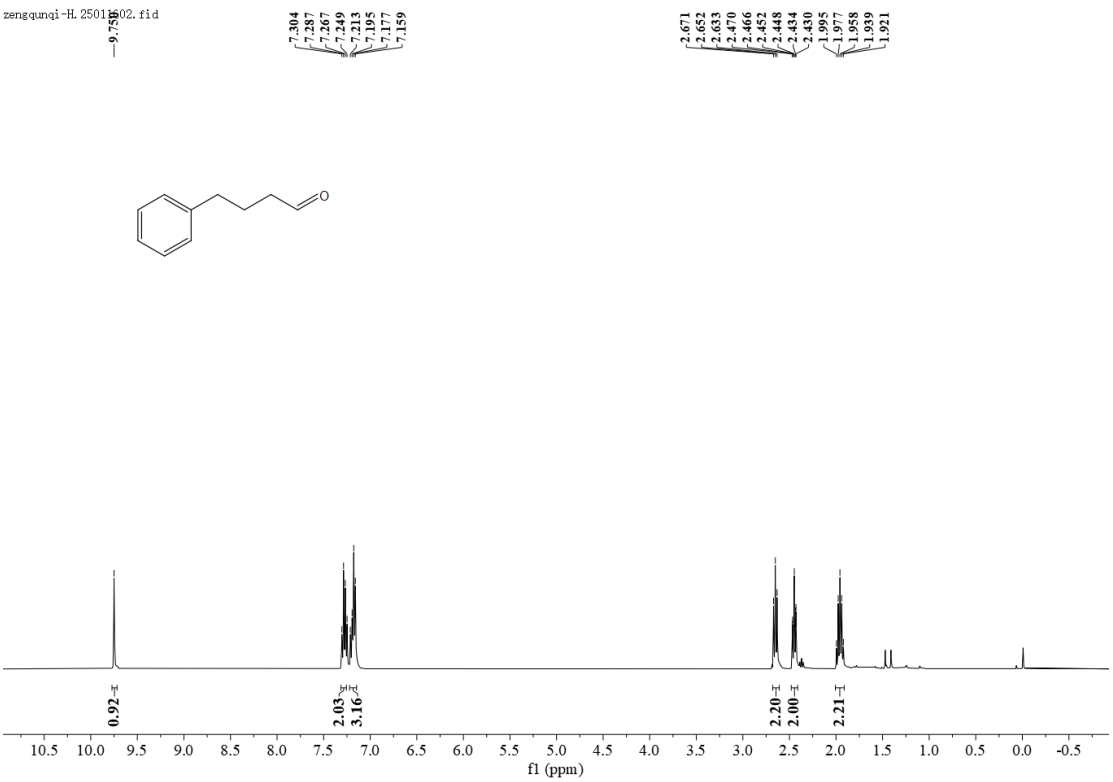
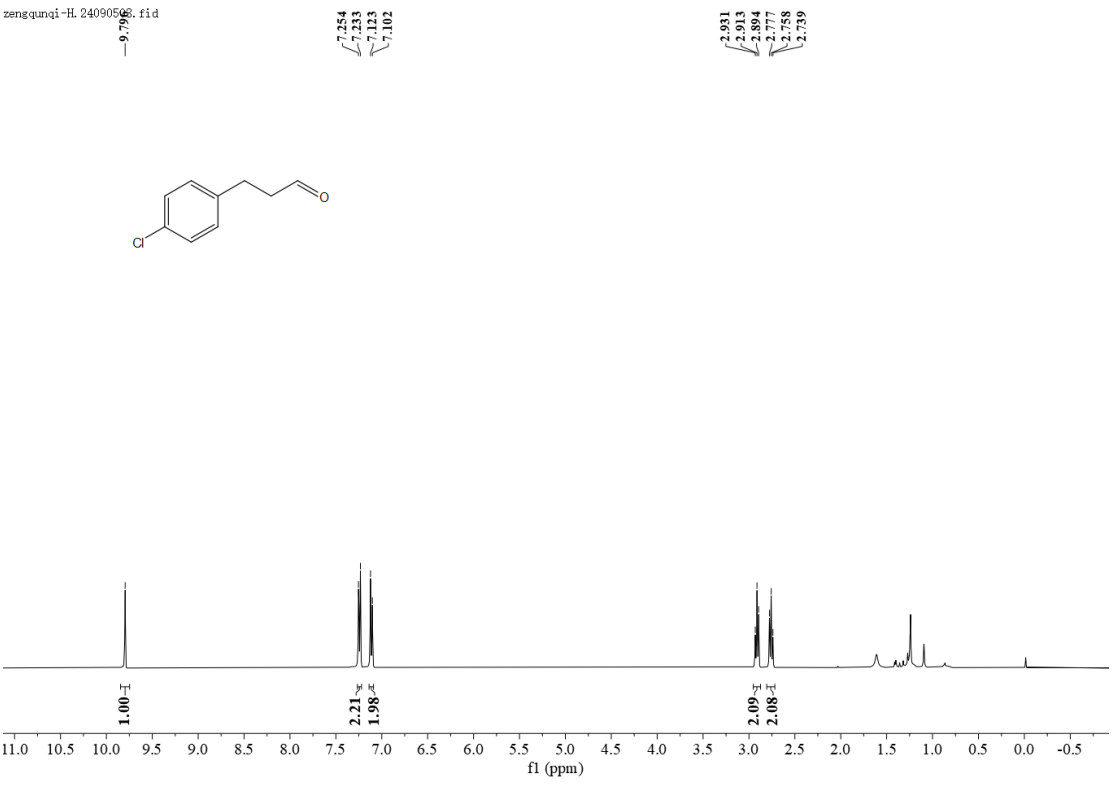


3-(4-chlorophenyl)propanal (2ad)



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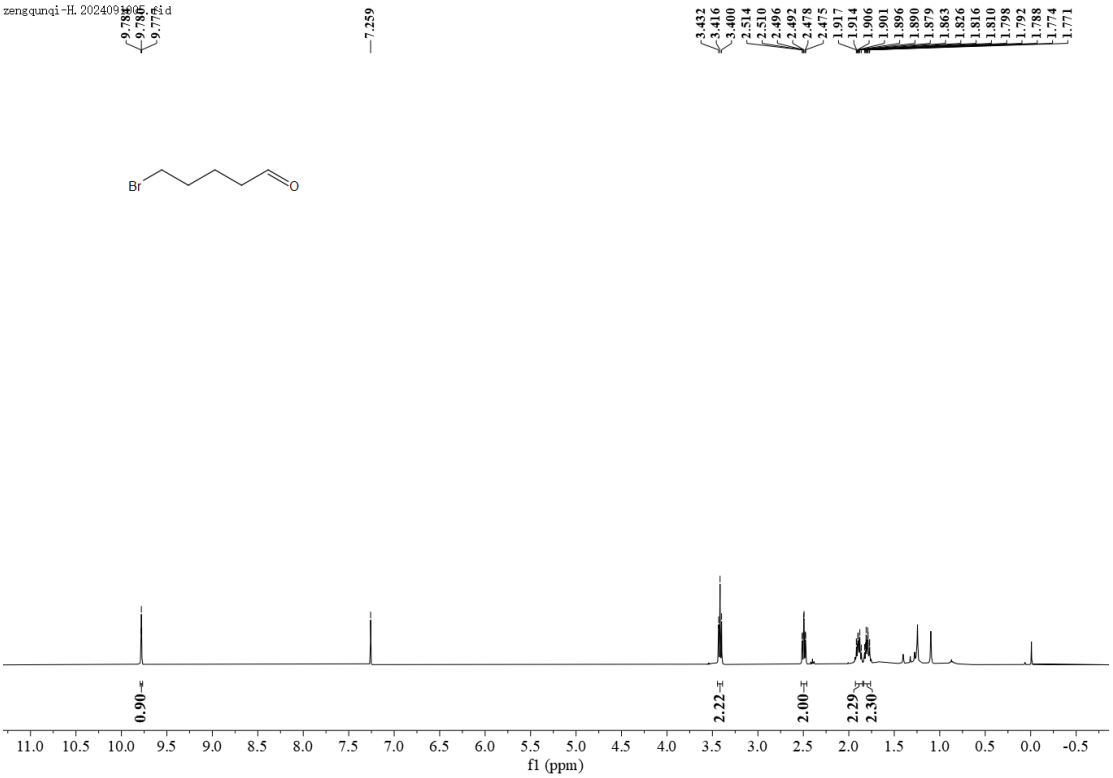

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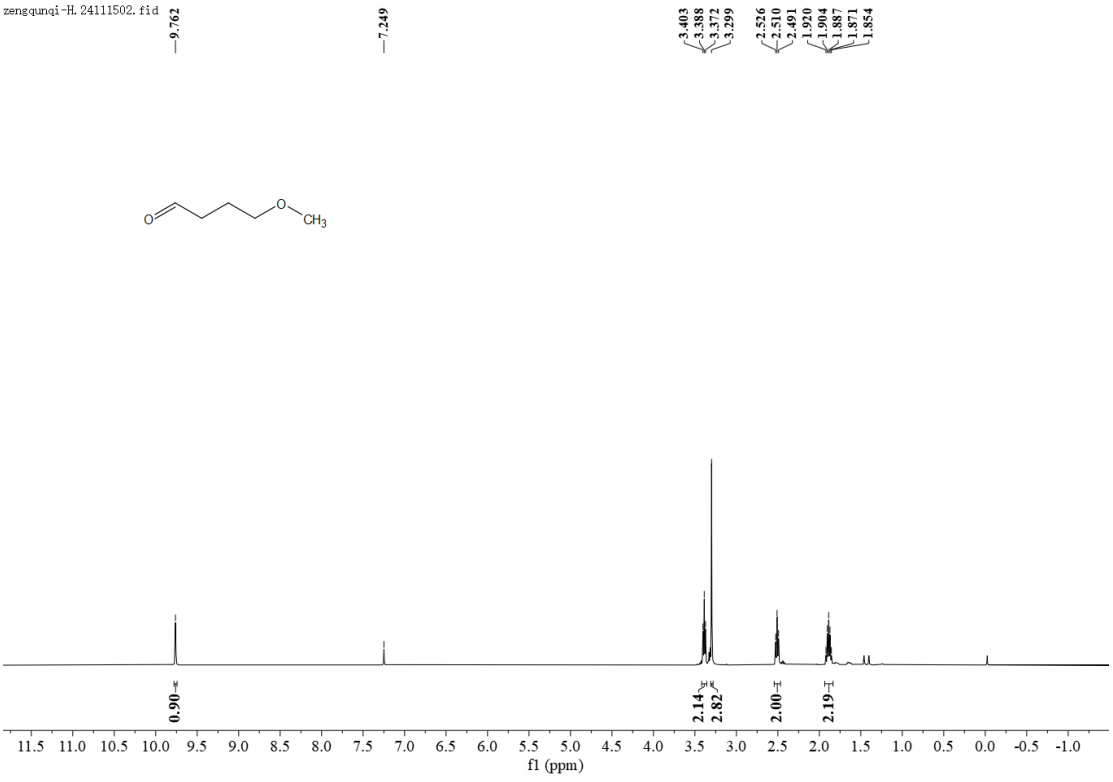
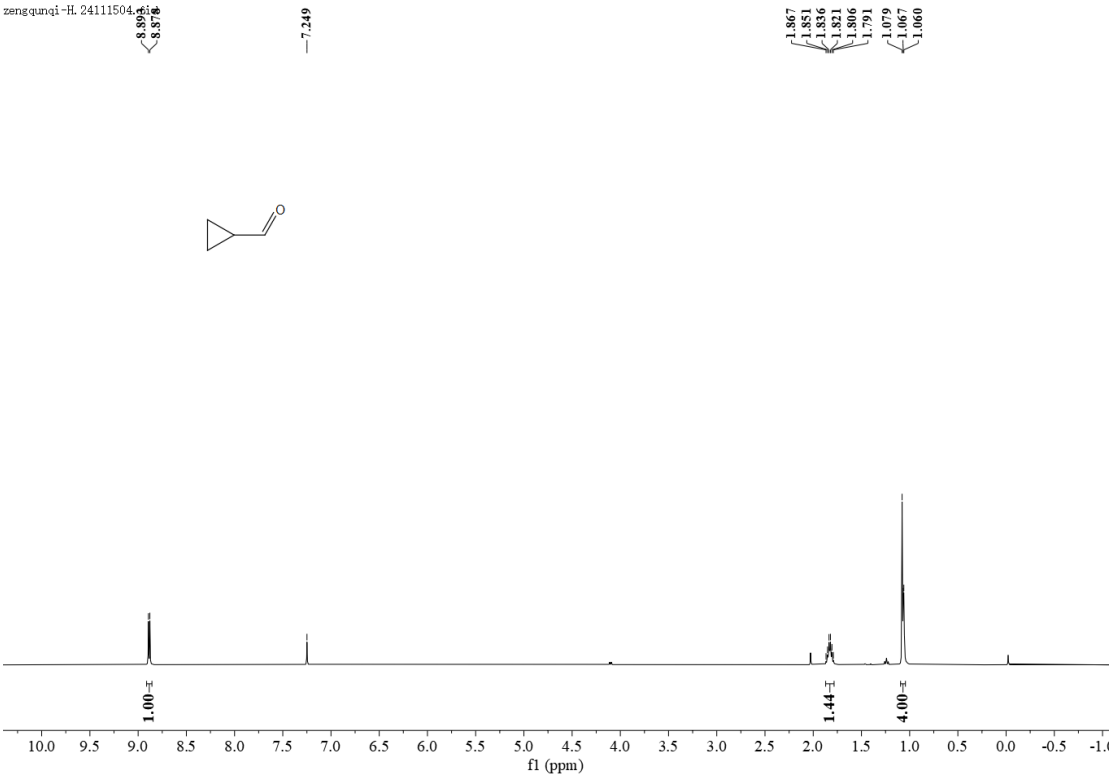
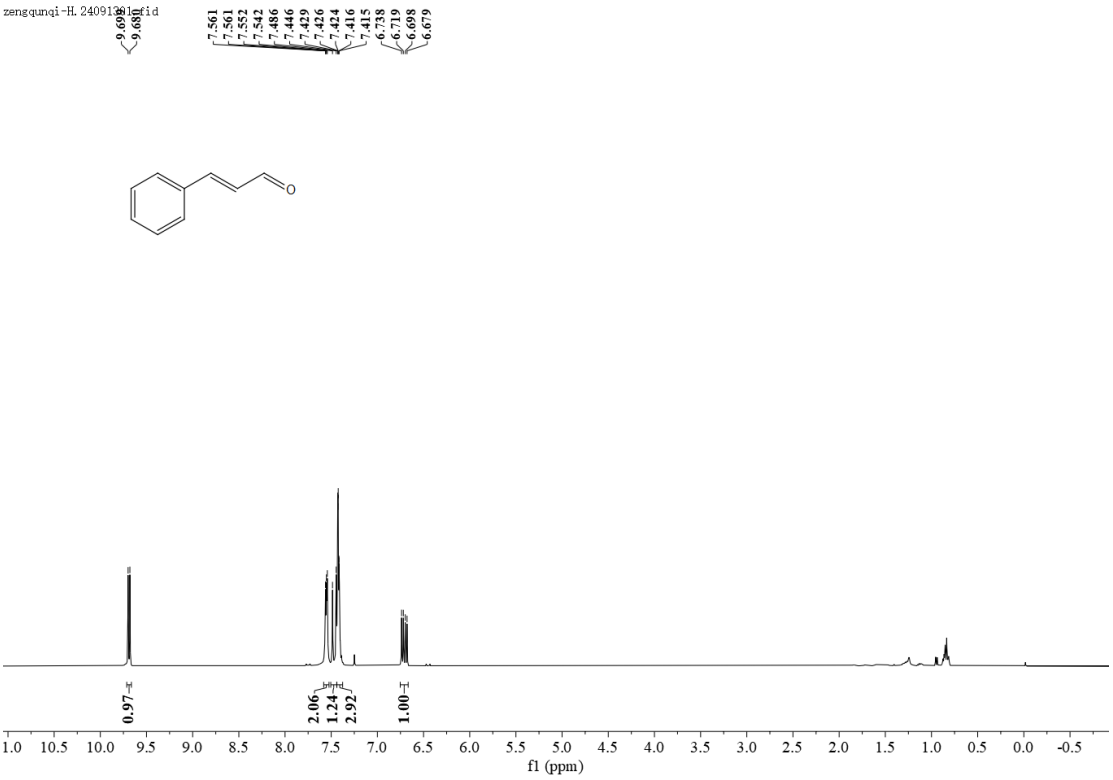


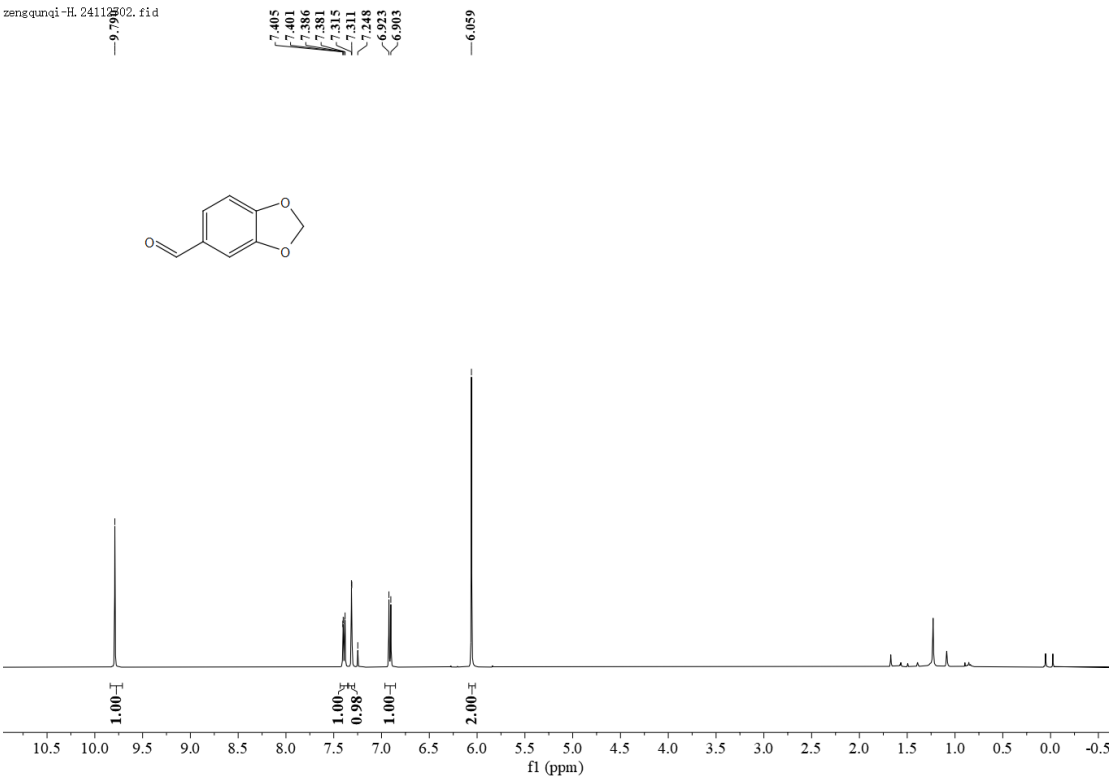
cyclopropanecarbaldehyde (2ag)



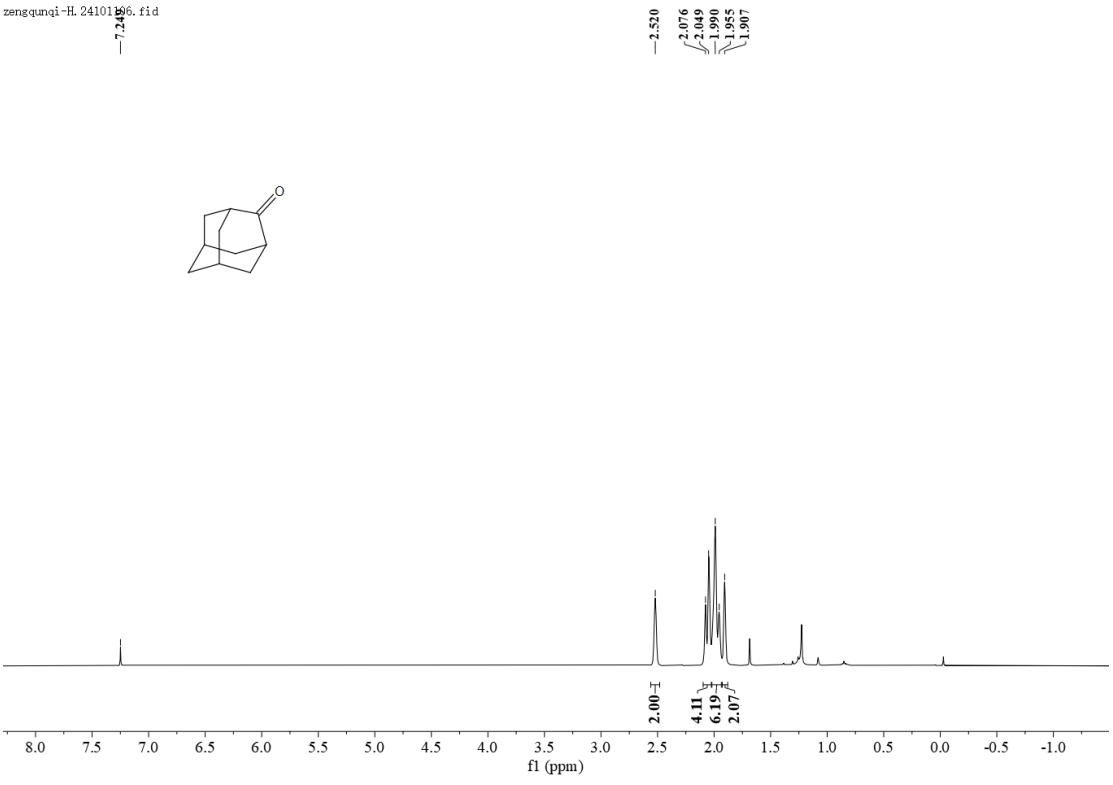
cinnamaldehyde (2ah)

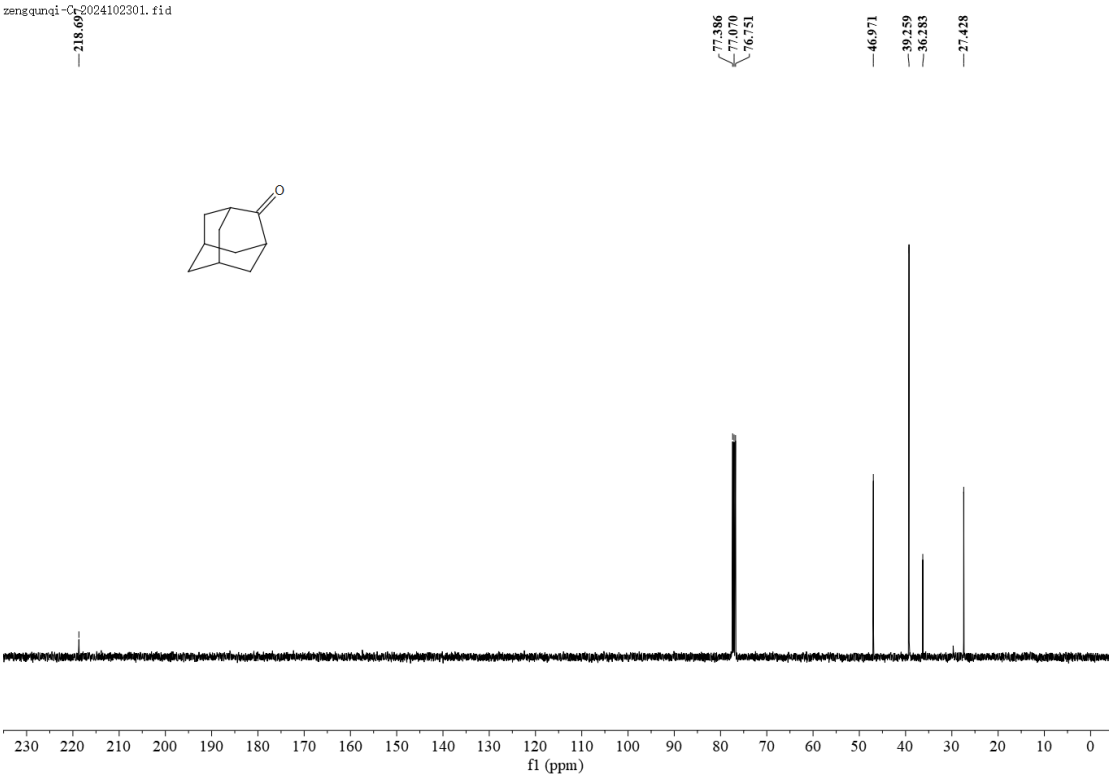


Piperonal (2ai)

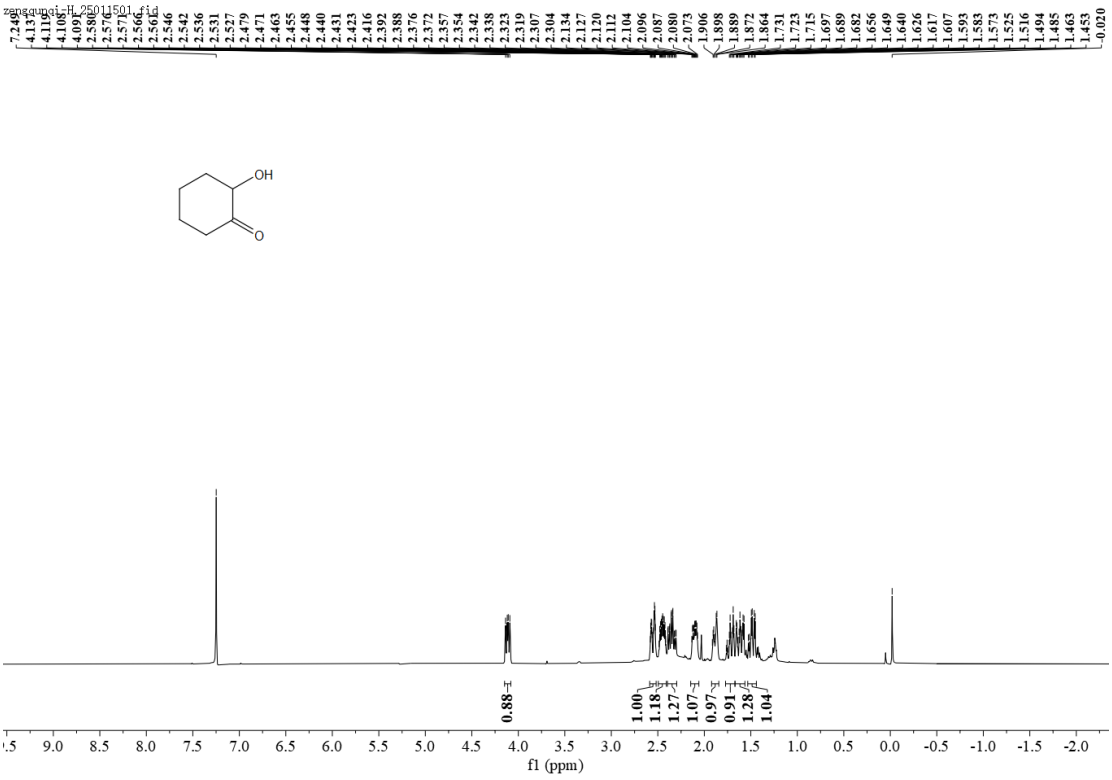


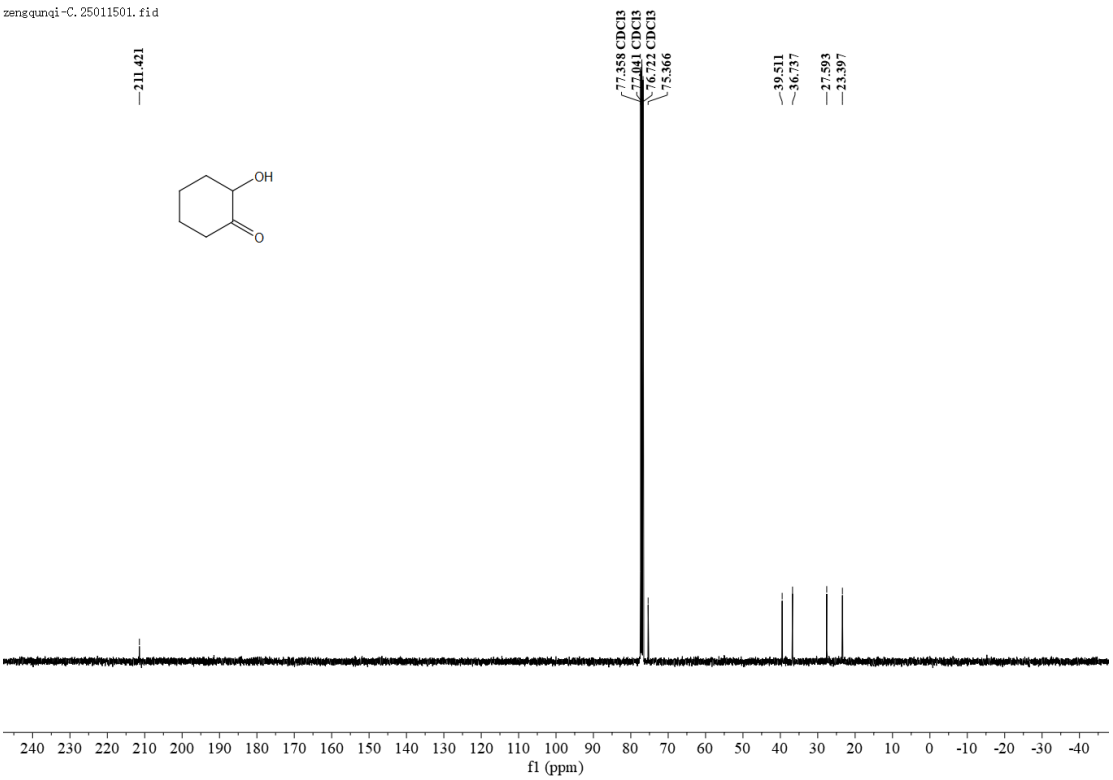
2-adamantane ketone (2aj)



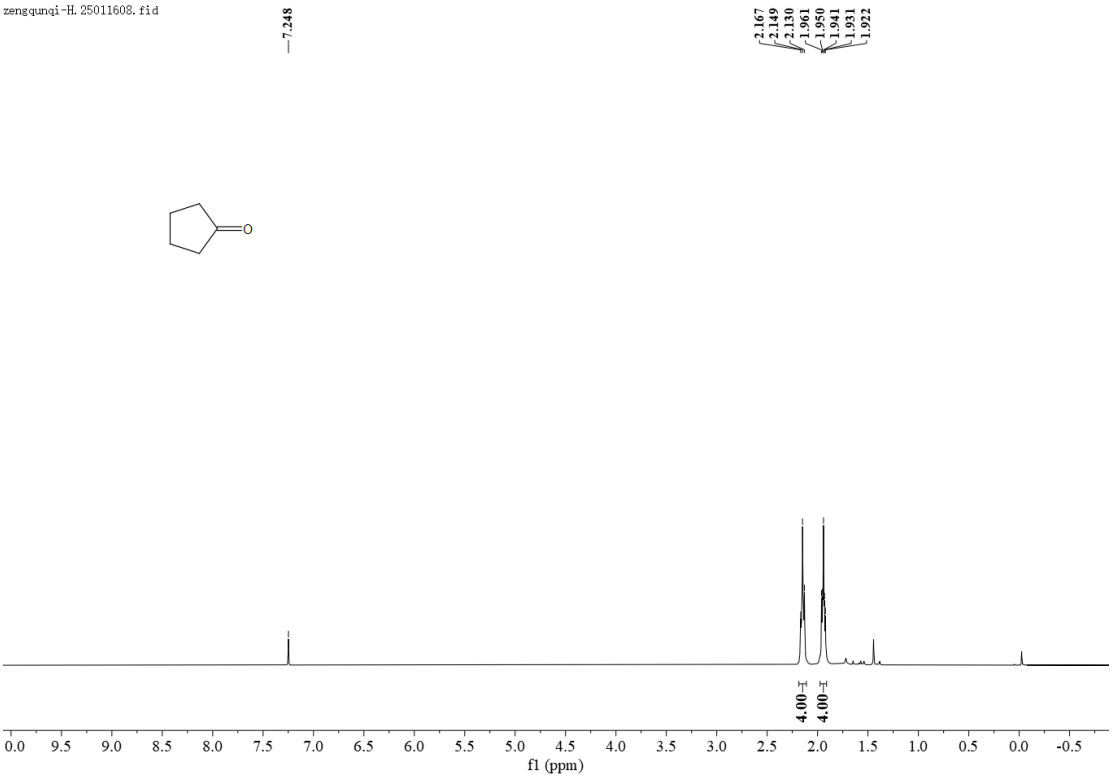


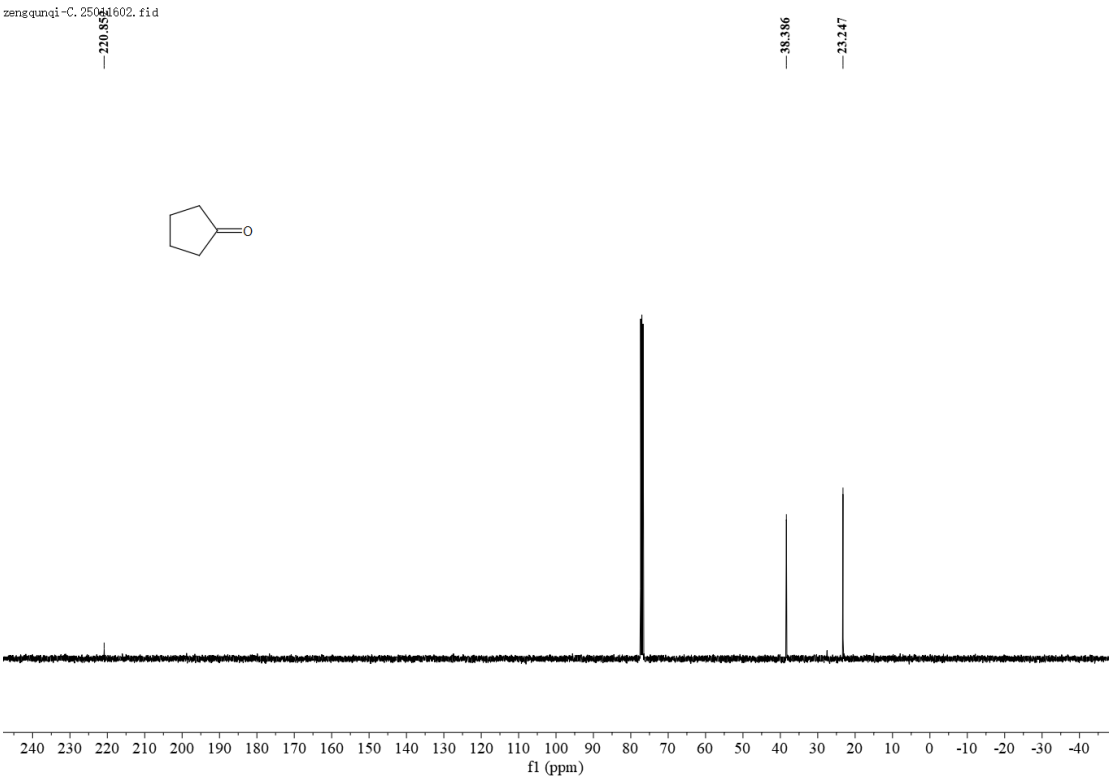
2-hydroxycyclohexan-1-one (2ak)



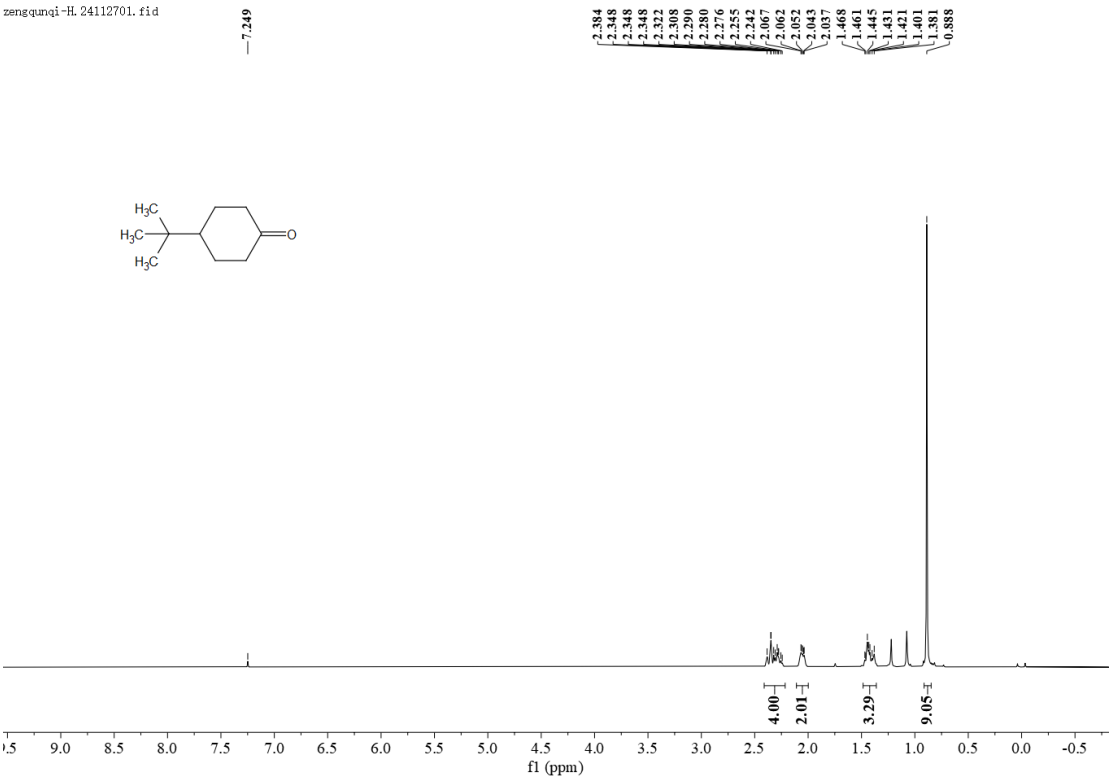


cyclopentanone (2al)

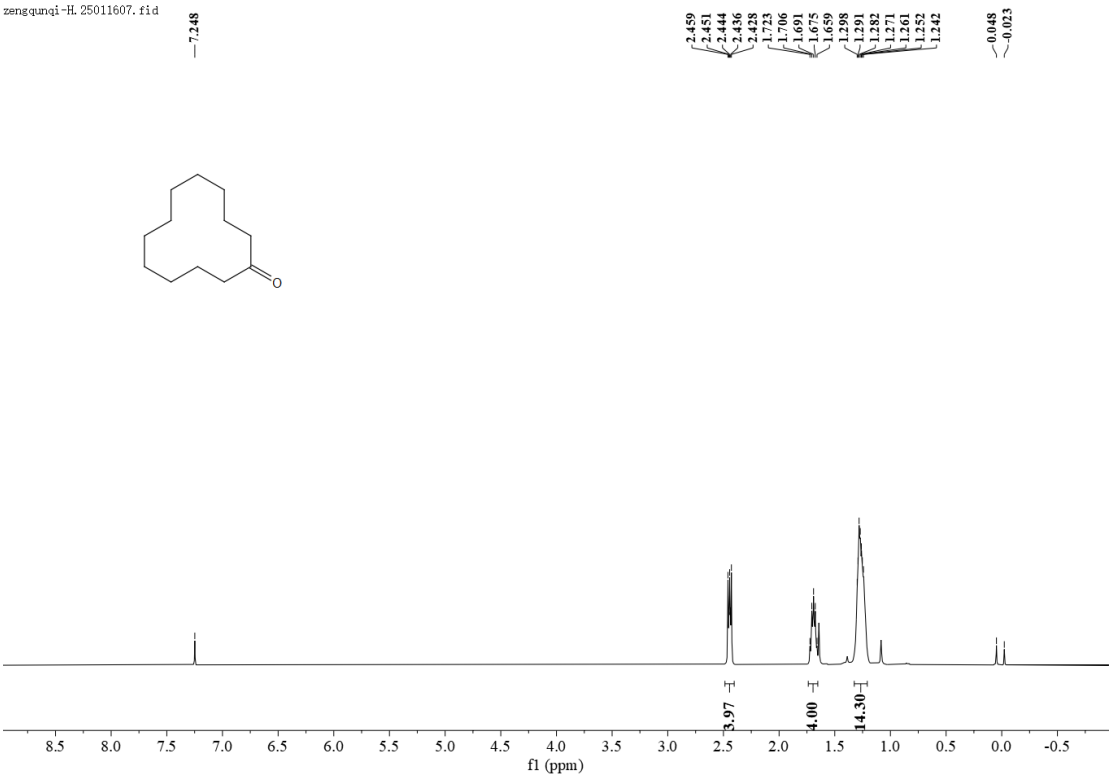


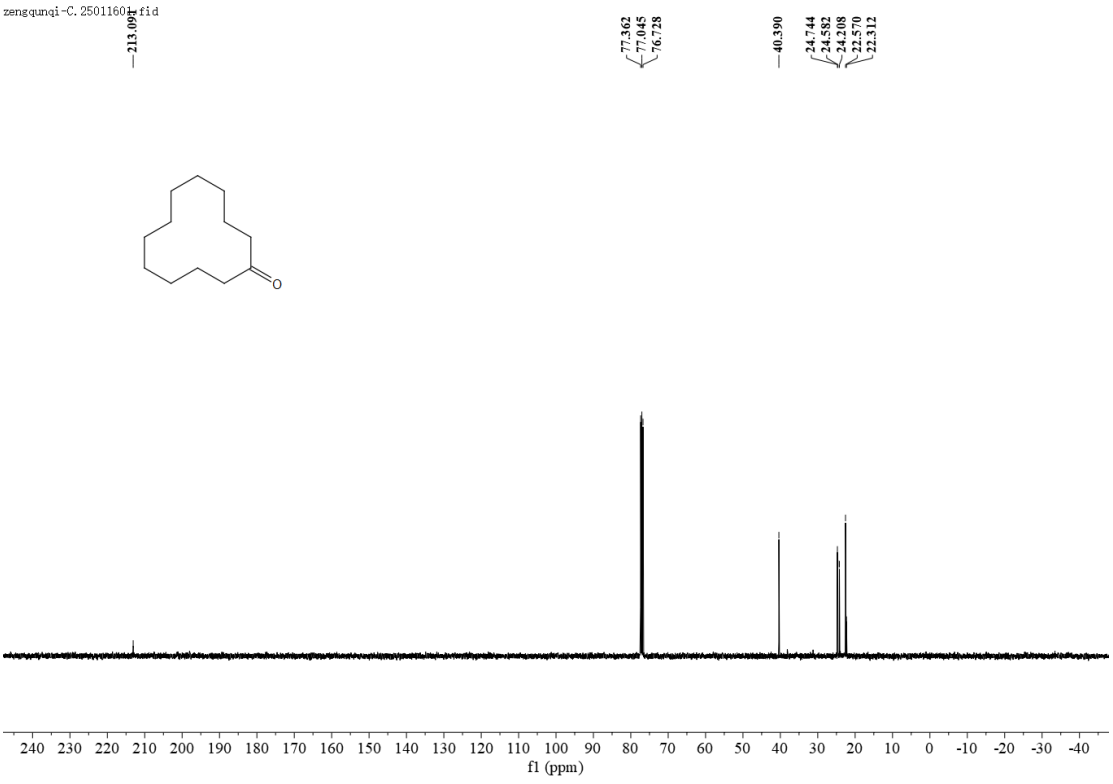


4-(tert-butyl)cyclohexan-1-one (2am)

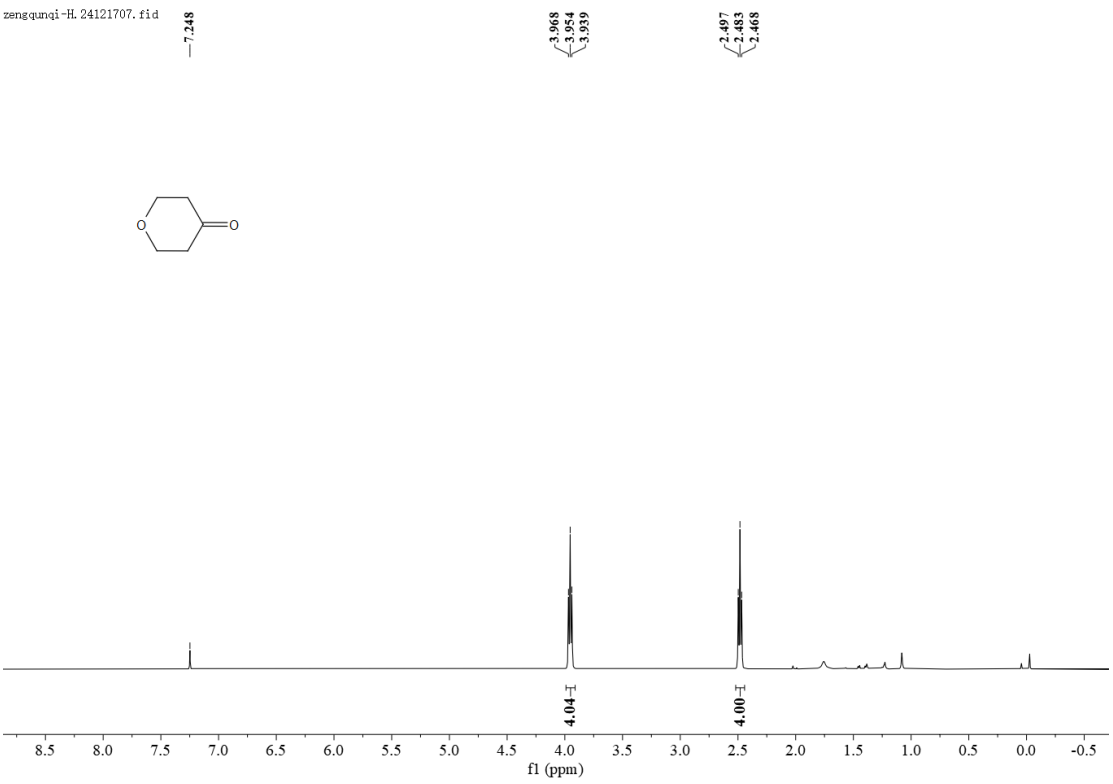


cyclododecanone (2an)

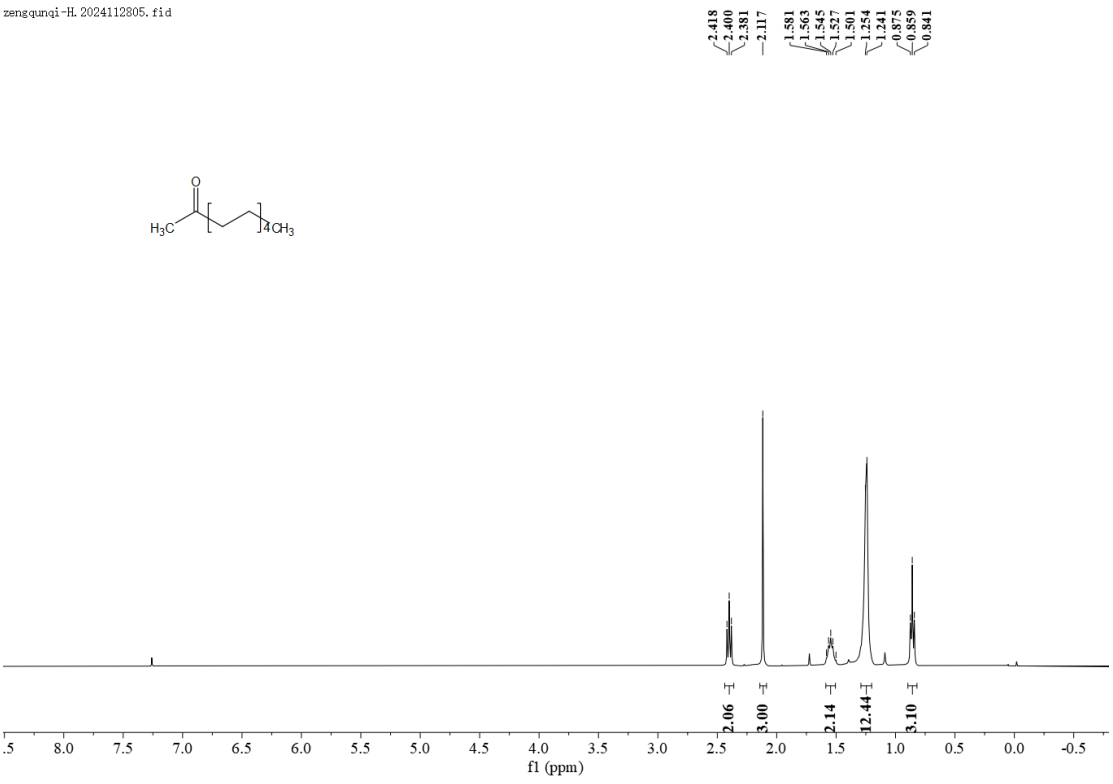


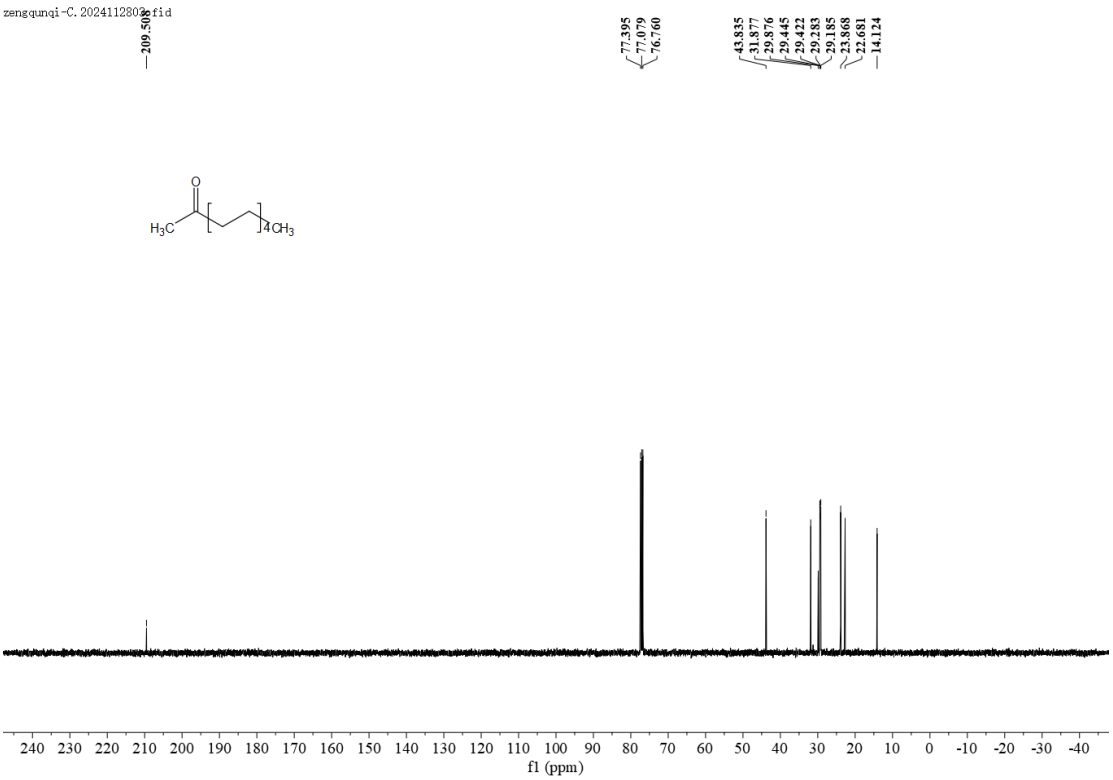


tetrahydro-4H-pyran-4-one (2ao)

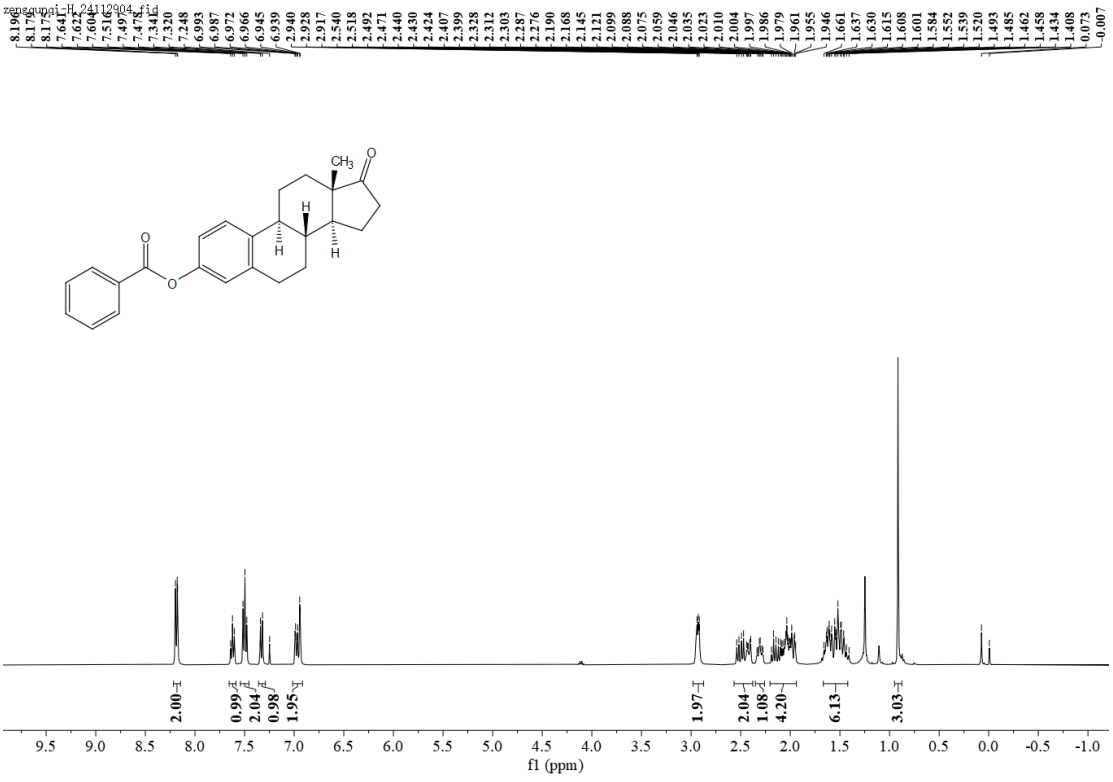


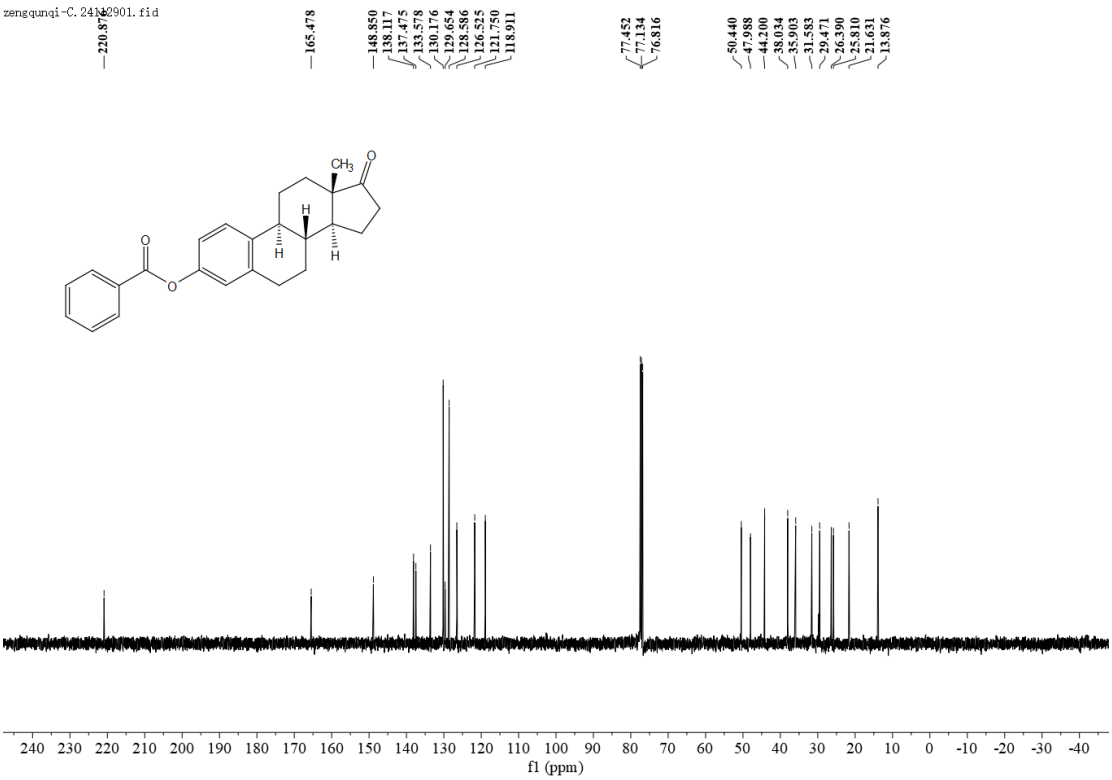
undecan-2-one (2ap)



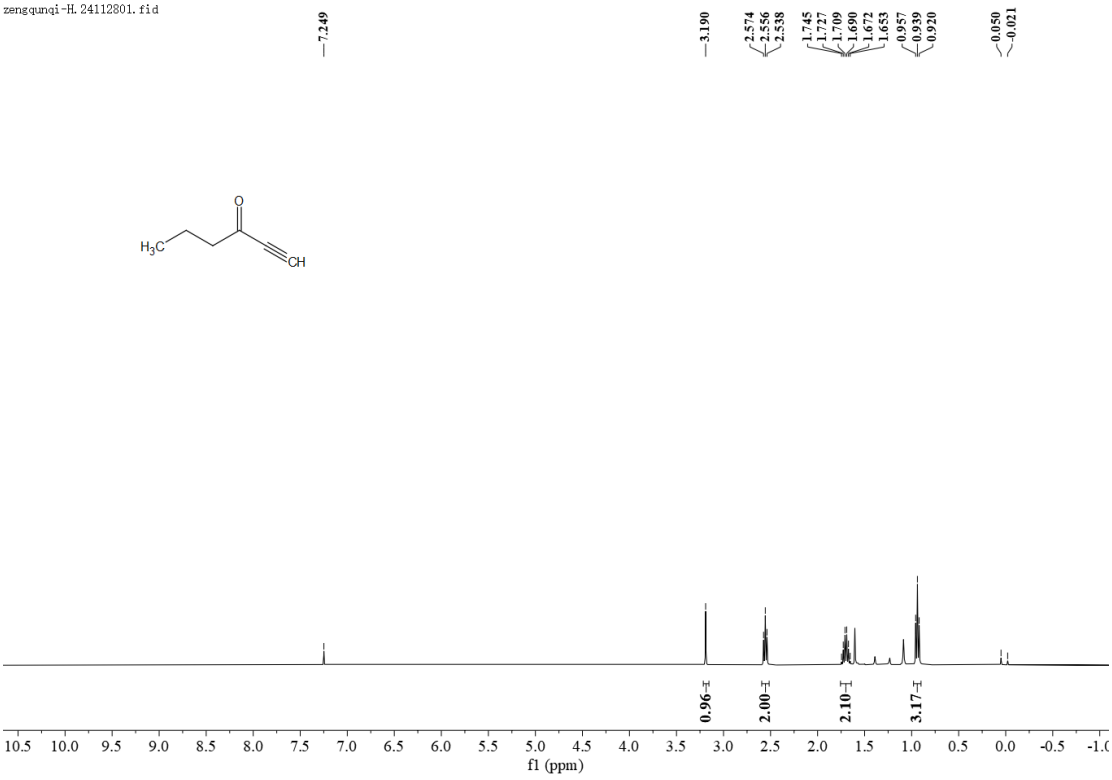


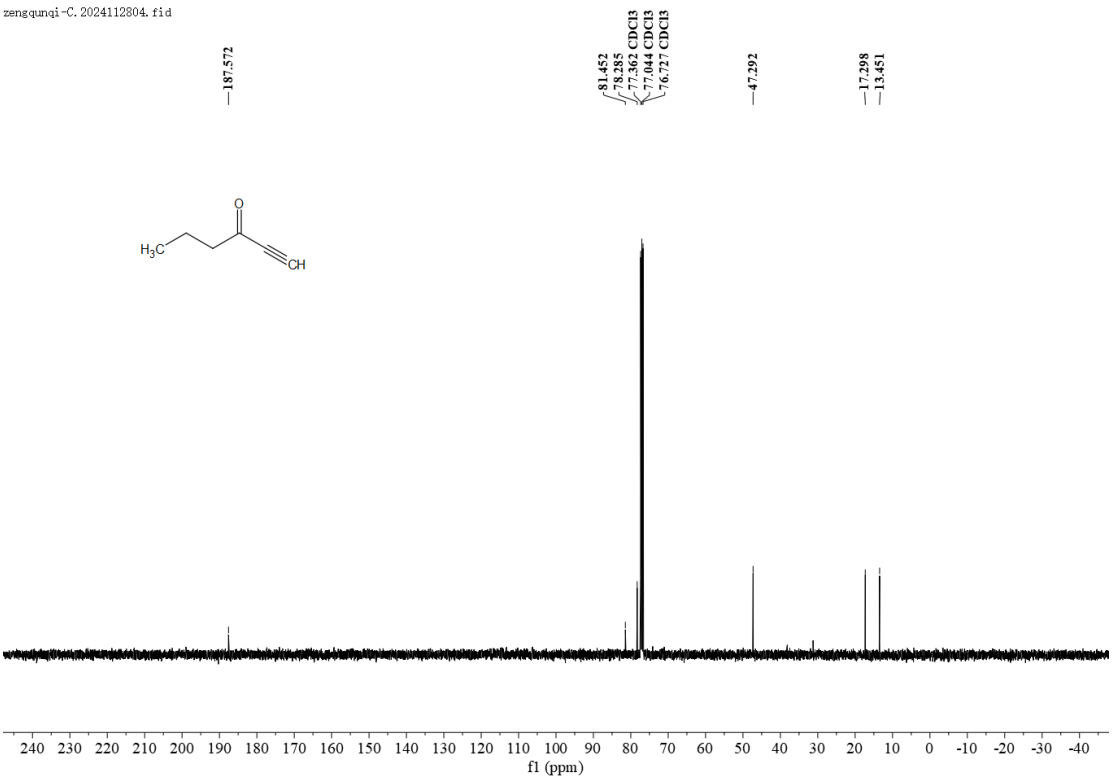
Estrone benzoate (2aq)





hex-1-yn-3-one (2ar)





acetophenone (2as)