

Supporting Information

Methanol as a Formylating Agent in Nitrogen Heterocycles

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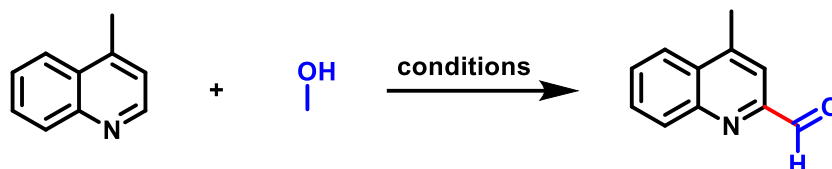
General Information

¹H and ¹³C NMR spectra were recorded on a Bruker advance III 400 spectrometer in CDCl₃ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by ¹H and ¹³C NMR, MS, HRMS. The starting materials were purchased from Aldrich, Energy Chemical, Acros Organics, J&K Chemicals or TCI and used without further purification.

Typical procedure

A mixture of 4-methylquinoline (1 equiv., 0.2 mmol), Fe(acac)₃ (3%, 0.006 mmol), TBHP (2 equiv., 0.4 mmol), acetic acid (2.0 equiv., 0.4 mmol) and methanol (2 mL) was heated at 110°C for 9 h. After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.

The modification of the reaction condition



Substrate: 0.2 mmol (1 equiv.);

TBHP: *t*-BuOOH; DTBP: (*t*-BuO)₂

Entry	Methanol (mL)	Initiator (equiv.)	Catalyst (mol %)	T (°C)	Time (h)	Yield (%)
1	2	TBHP (2)	Fe(acac) ₃ (3)	80	9	NR
2	2	TBHP (2)	Fe(acac) ₃ (3)	90	9	16
3	2	TBHP (2)	Fe(acac) ₃ (3)	100	9	47
4	2	TBHP (2)	Fe(acac) ₃ (3)	110	9	76
5	2	TBHP (2)	Fe(acac) ₃ (3)	120	9	72
6	2	TBHP (2)	Fe(acac) ₃ (3)	130	9	43
7	2	TBHP (2)	-	110	9	trace
8	3	TBHP (2)	Cu (3)	110	9	trace
9	3	TBHP (2)	CuCl (3)	110	9	trace
10	3	TBHP (2)	CuBr (3)	110	9	trace

11	3	TBHP (2)	CuI (3)	110	9	trace
12	3	TBHP (2)	Cu ₂ O (3)	110	9	trace
13	3	TBHP (2)	CuBr ₂ (3)	110	9	trace
14	3	TBHP (2)	Cu(AcO) ₂ ·H ₂ O (3)	110	9	trace
15	3	TBHP (2)	Cu(acac) ₂ (3)	110	9	trace
16	3	TBHP (2)	Mn(acac) ₂ (3)	110	9	trace
17	3	TBHP (2)	Ni(acac) ₂ (3)	110	9	trace
18	3	TBHP (2)	Pd(acac) ₂ (3)	110	9	trace
19	3	TBHP (2)	AgNO ₃ (3)	110	9	trace
20	3	TBHP (2)	FeCl ₂ (3)	110	9	trace
21	3	TBHP (2)	Fe(OTf) ₂ (3)	110	9	58
22	3	TBHP (2)	Fe(AcO) ₂ (3)	110	9	65
23	3	TBHP (2)	Fe(acac) ₂ (3)	110	9	72
24	3	TBHP (2)	FeCl ₃ · 6H ₂ O (3)	110	9	52
25	3	TBHP (2)	Fe(OTf) ₃ (3)	110	9	60
26	3	TBHP (2)	Fe(AcO) ₃ (3)	110	9	68
27	4	TBHP (2)	FeNO ₃ · 9H ₂ O (3)	110	9	32

28	2	DTBP (2)	Fe(acac) ₃ (3)	110	9	trace
29	1	DCP (2)	Fe(acac) ₃ (3)	110	9	trace
30	2	K ₂ S ₂ O ₈ (2)	Fe(acac) ₃ (3)	110	9	trace
31	2	TBHP (1)	Fe(acac) ₃ (3)	110	9	58
32	2	TBHP (3)	Fe(acac) ₃ (3)	110	9	70
33	2	TBHP (2)	Fe(acac) ₃ (1)	110	9	67
34	2	TBHP (2)	Fe(acac) ₃ (5)	110	9	73
35	1	TBHP (2)	Fe(acac) ₃ (3)	110	9	57
36	3	TBHP (2)	Fe(acac) ₃ (3)	110	9	63
37	5	TBHP (2)	Fe(acac) ₃ (3)	110	9	54
38	2	TBHP (2)	Fe(acac) ₃ (3)	110	6	62
39	2	TBHP (2)	Fe(acac) ₃ (3)	110	12	67
40	2	TBHP (2) AcOH (2)	Fe(acac)₃ (3)	110	9	82
41	2	TBHP (2) CF ₃ COOH (2)	Fe(acac) ₃ (3)	110	9	73

42	PhMe (1 mL) CH ₃ OH (1 mL)	TBHP (2) AcOH (2)	Fe(acac) ₃ (3)	110	9	43
43	EA (1 mL) CH ₃ OH (1 mL)	TBHP (2) AcOH (2)	Fe(acac) ₃ (3)	110	9	56
44	<i>t</i> -BuOH (1 mL) CH ₃ OH (1 mL)	TBHP (2) AcOH (2)	Fe(acac) ₃ (3)	110	9	60

Physical data and references for the following products

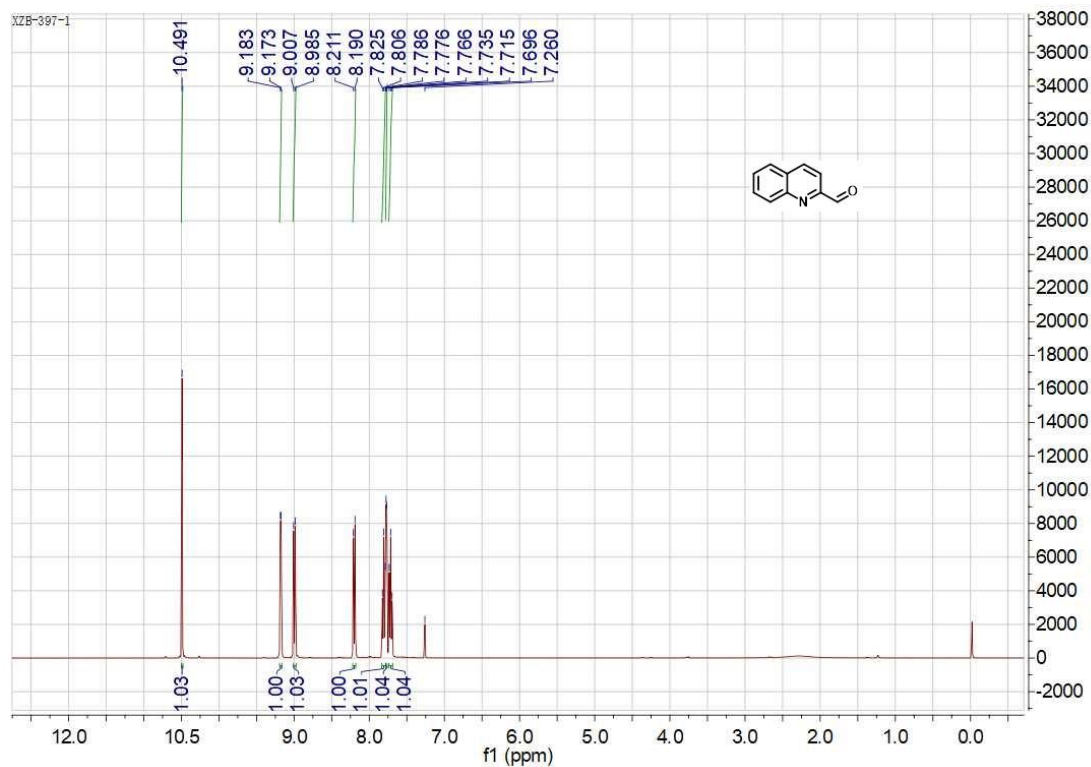
All known compounds are determined by ¹H NMR and ¹³C NMR, MS analysis and compared with which were cited in the following references^[1-4] and the new compounds were further confirmed by HRMS.

References:

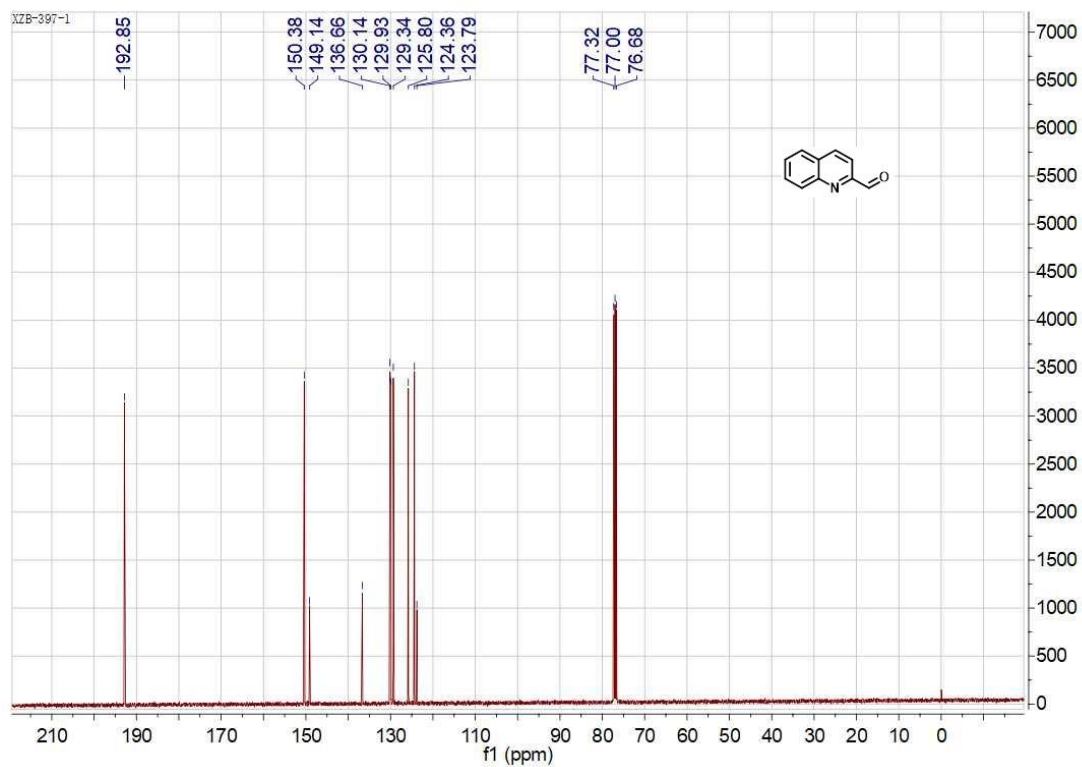
1. J. Dong, X. Wang, H. Song, Y. Liu, Q. Wang, *Adv. Synth. Catal.*, 2020, **362**, 2155.
2. Q. Wang, K. Xu, Y. Jiang, Y. Liu, B. Sun, C. Zeng, *Org. Lett.*, 2017, **19**, 5517.
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5. L. Jiang, Y. Huang, Y. Yan, Y. Xie, *Tetrahedron Lett.*, 2016, **57**, 4149.
6. Y. Wu, P. Guo, L. Chen, W. Duan, Z. Yang, T. Wang, T. Chen, F. Xiong, *Chem. Commun.*, 2021, **57**, 3271.
7. W. Jia, Y. Jian, B. Huang, C. Yang, W. Xia, *Synlett.*, 2018, **29**, 1881.

Copies of the ^1H NMR, ^{13}C NMR

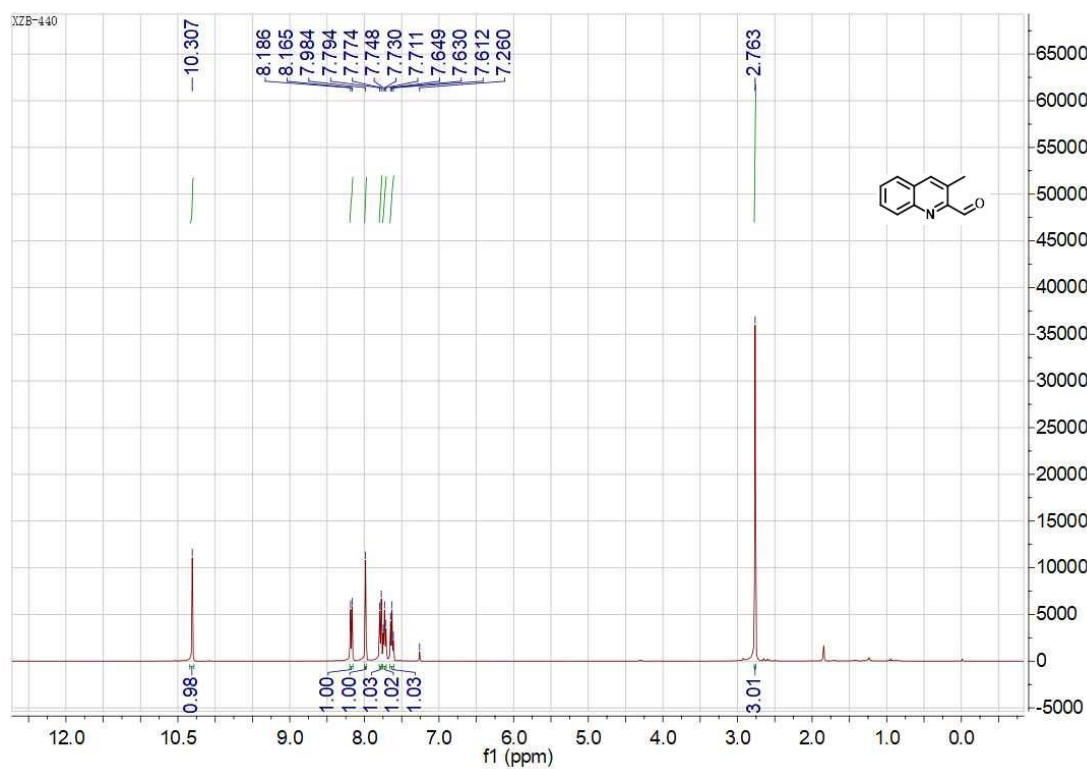
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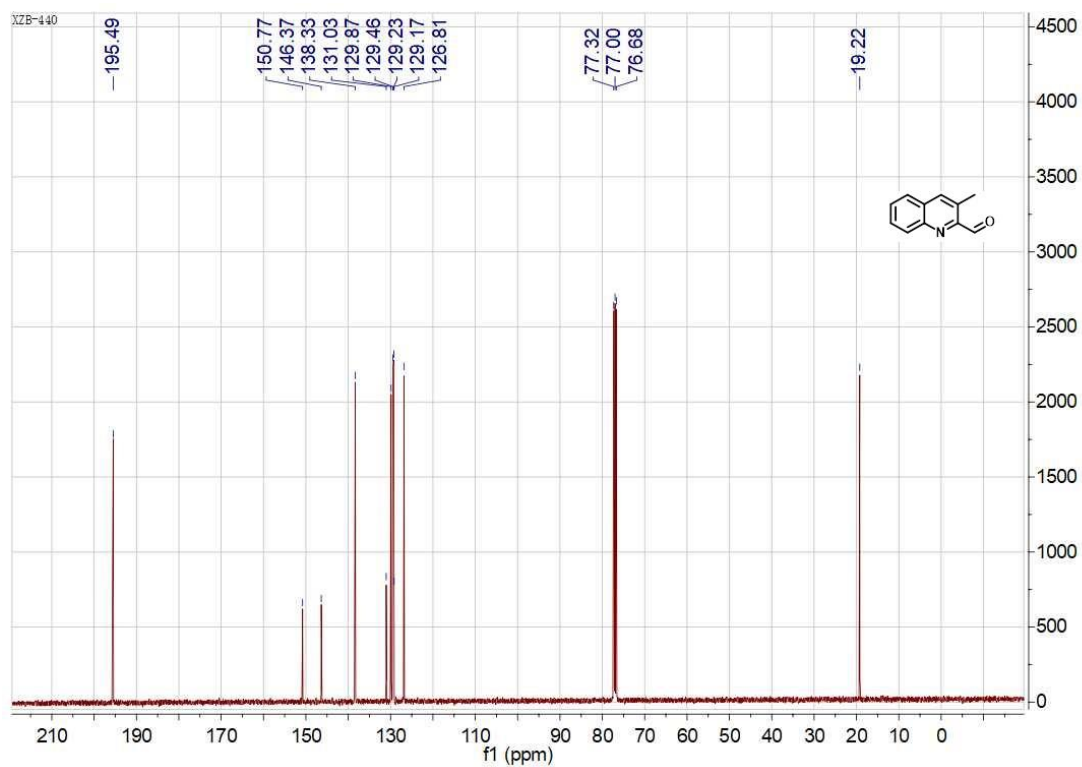
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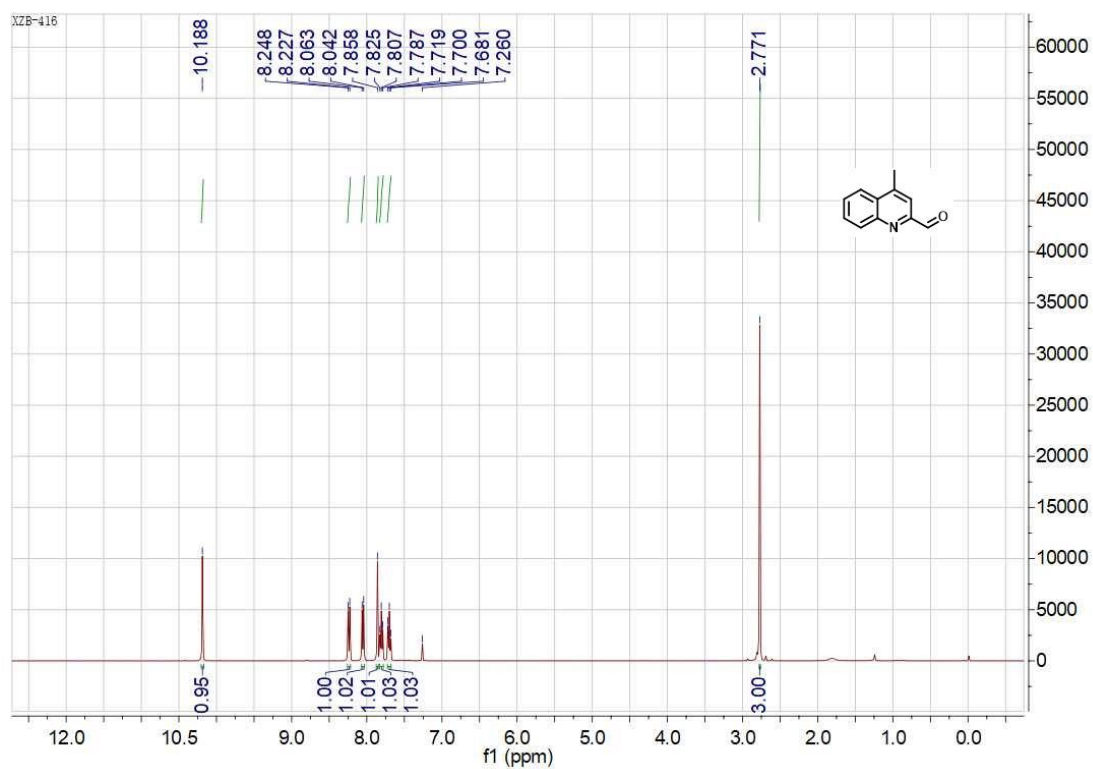
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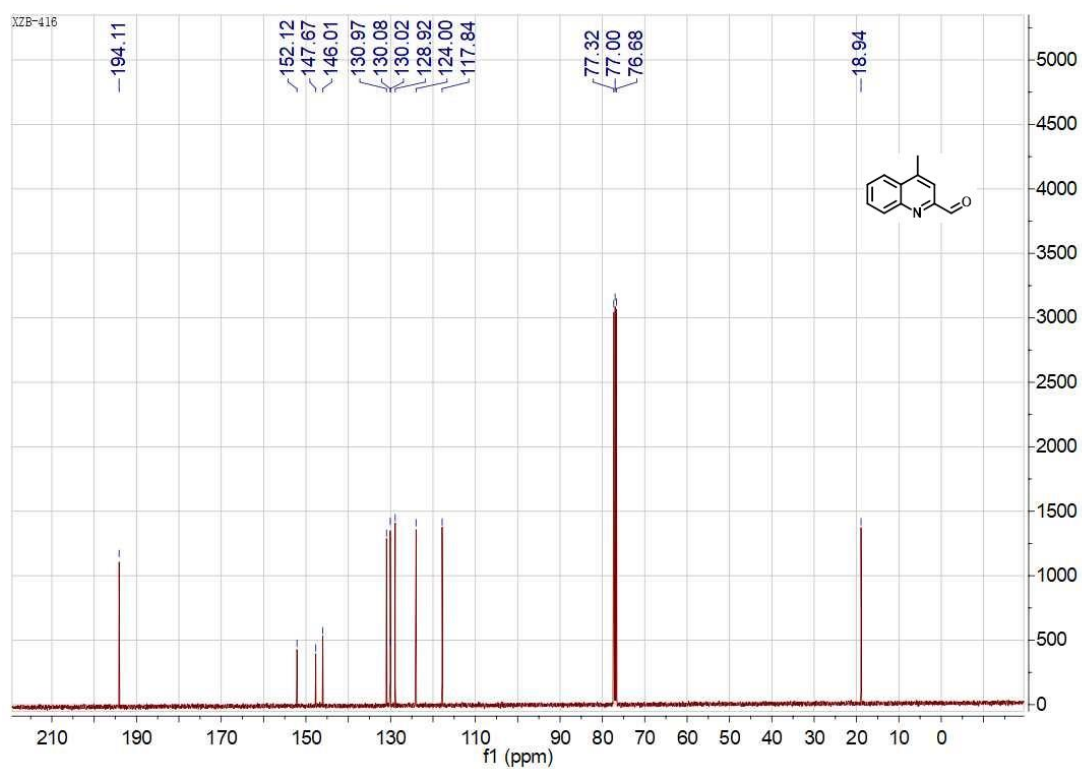
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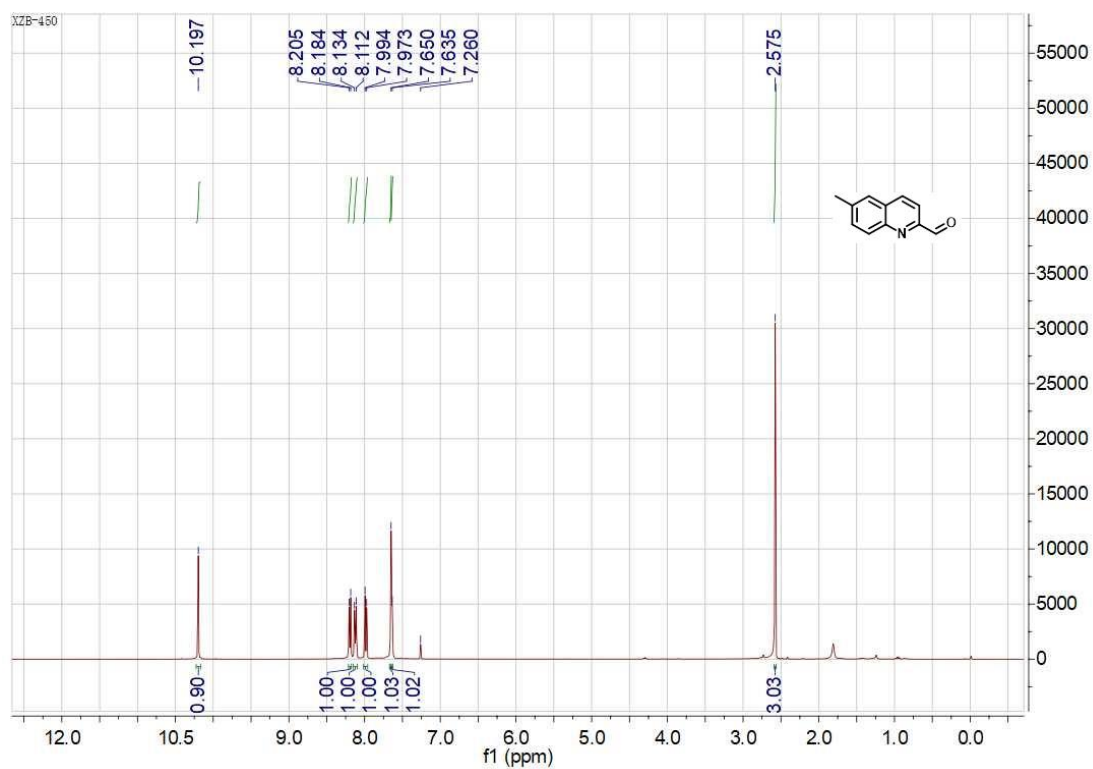
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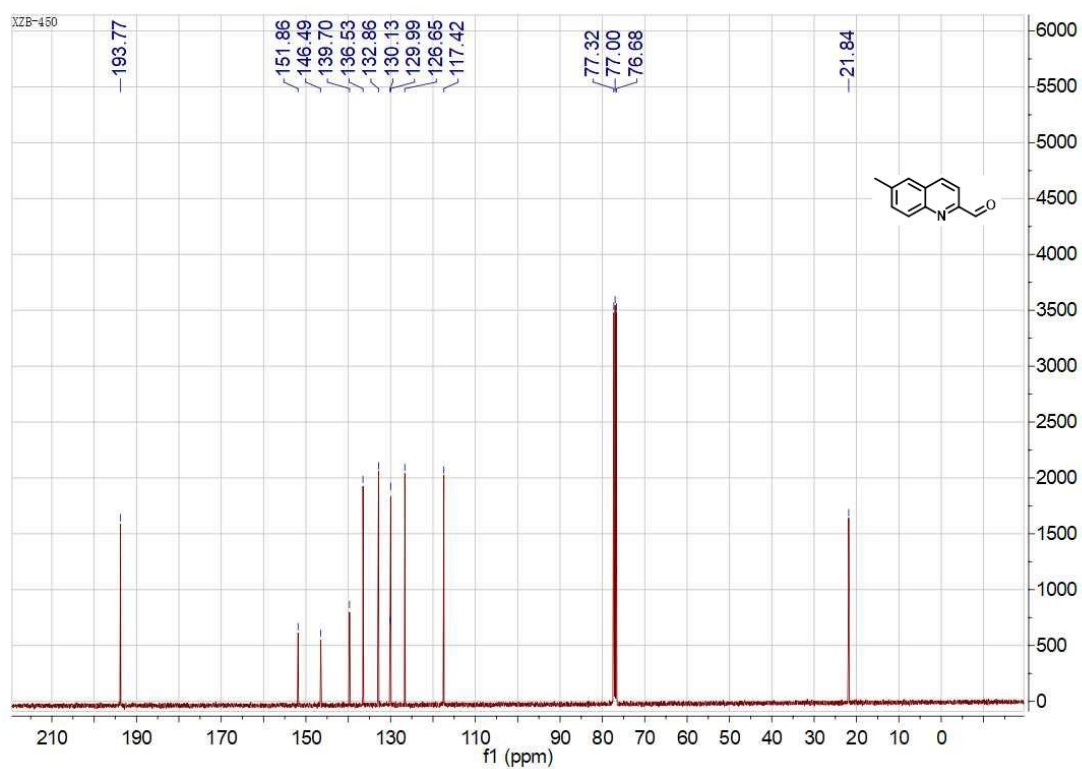
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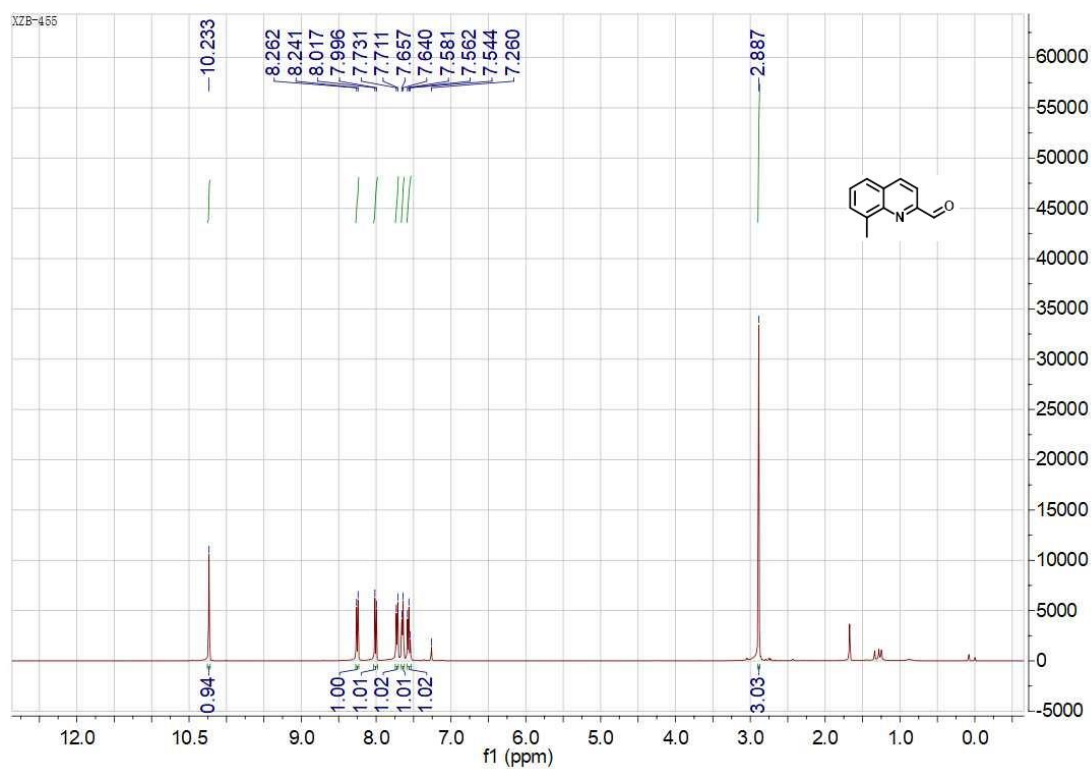
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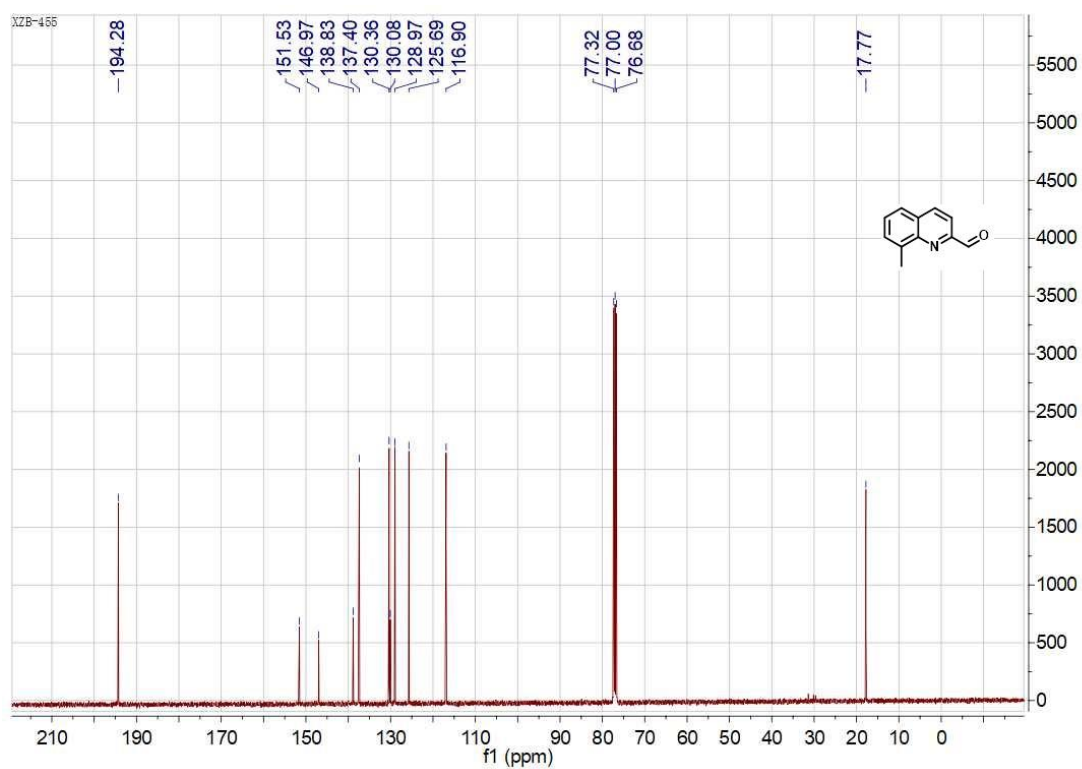
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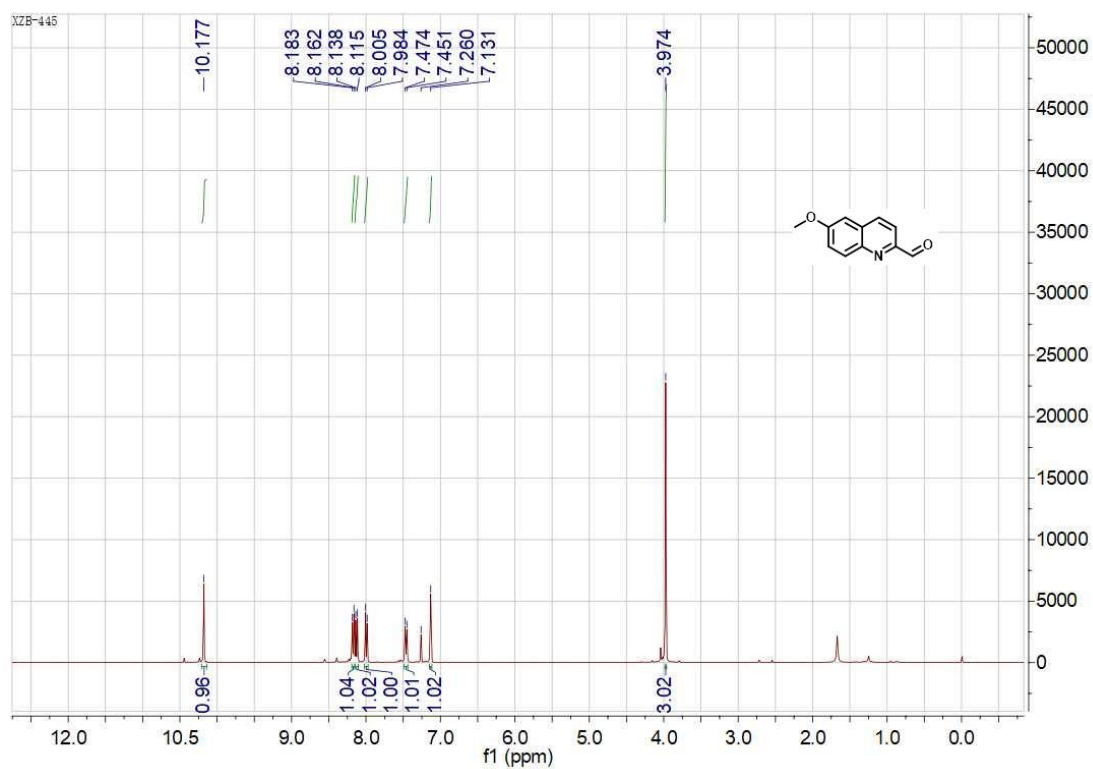
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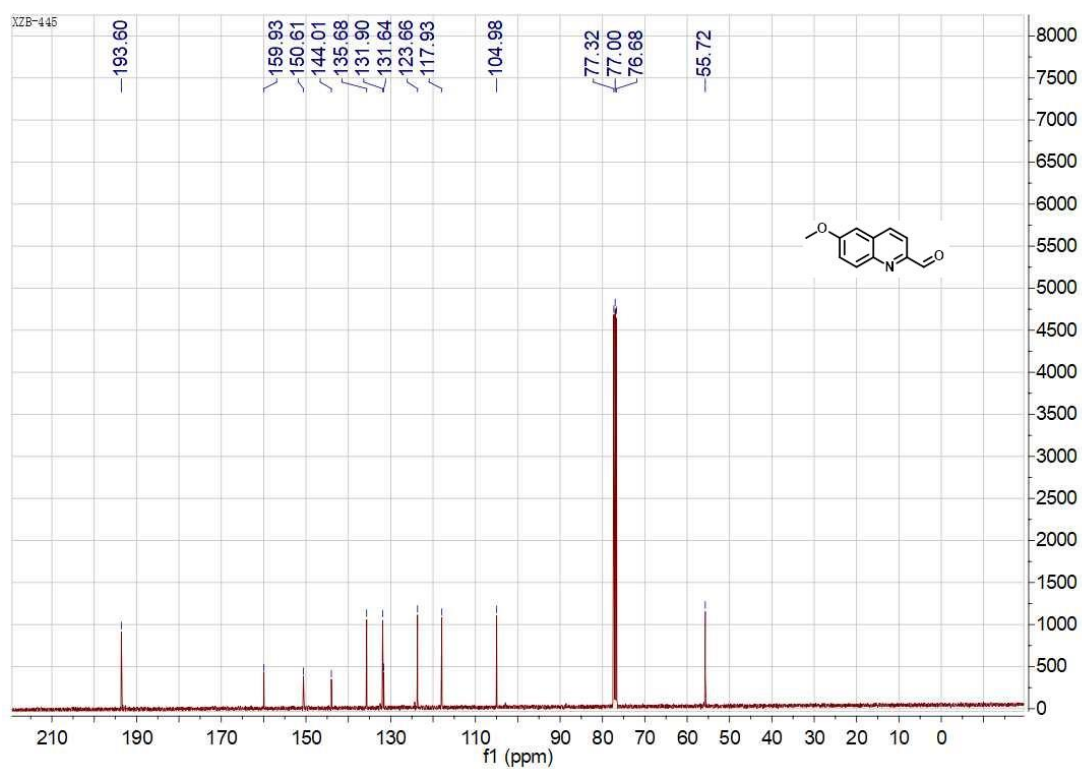
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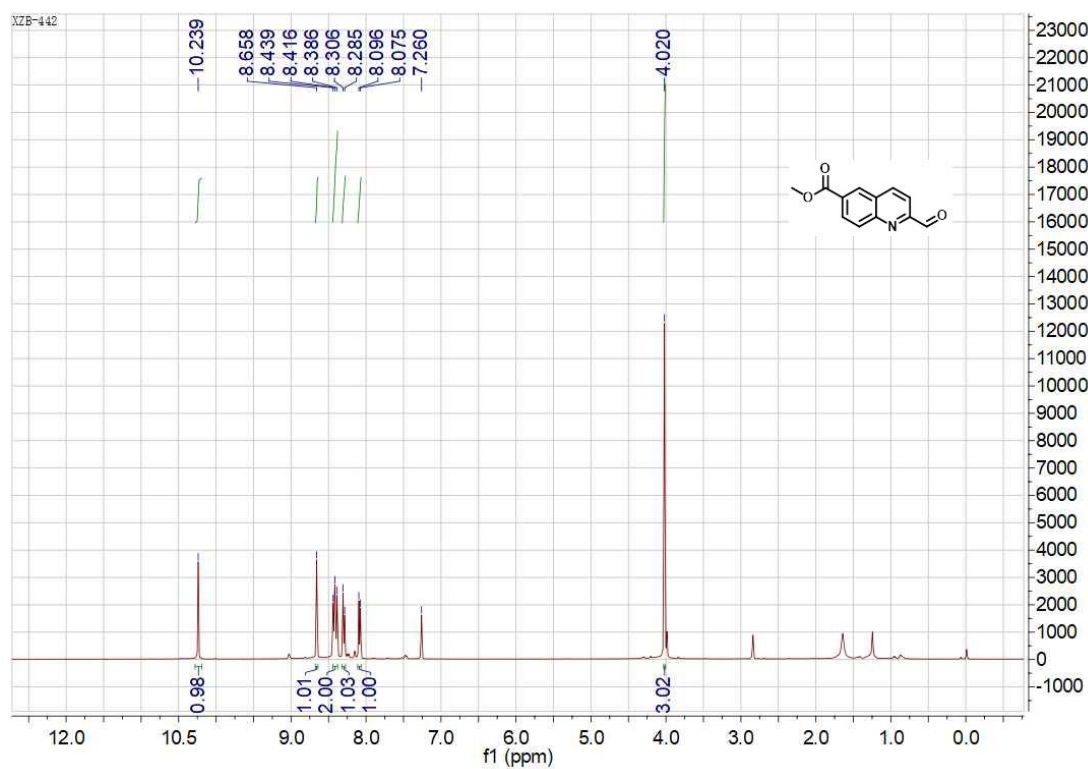
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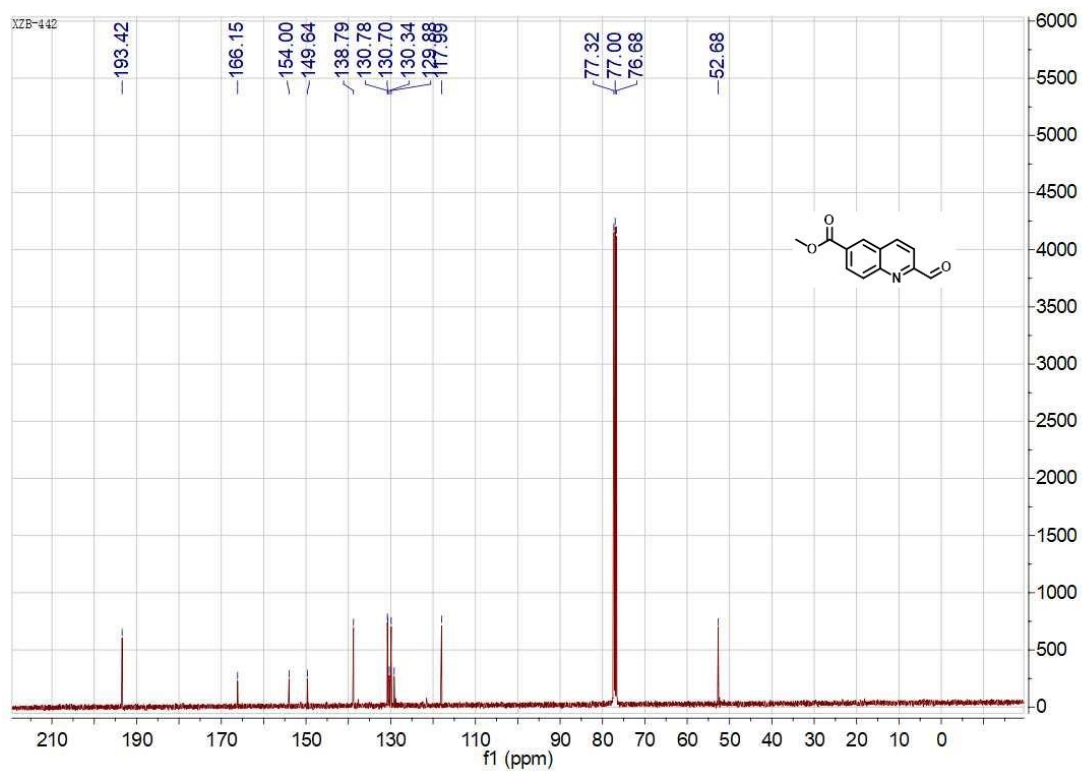
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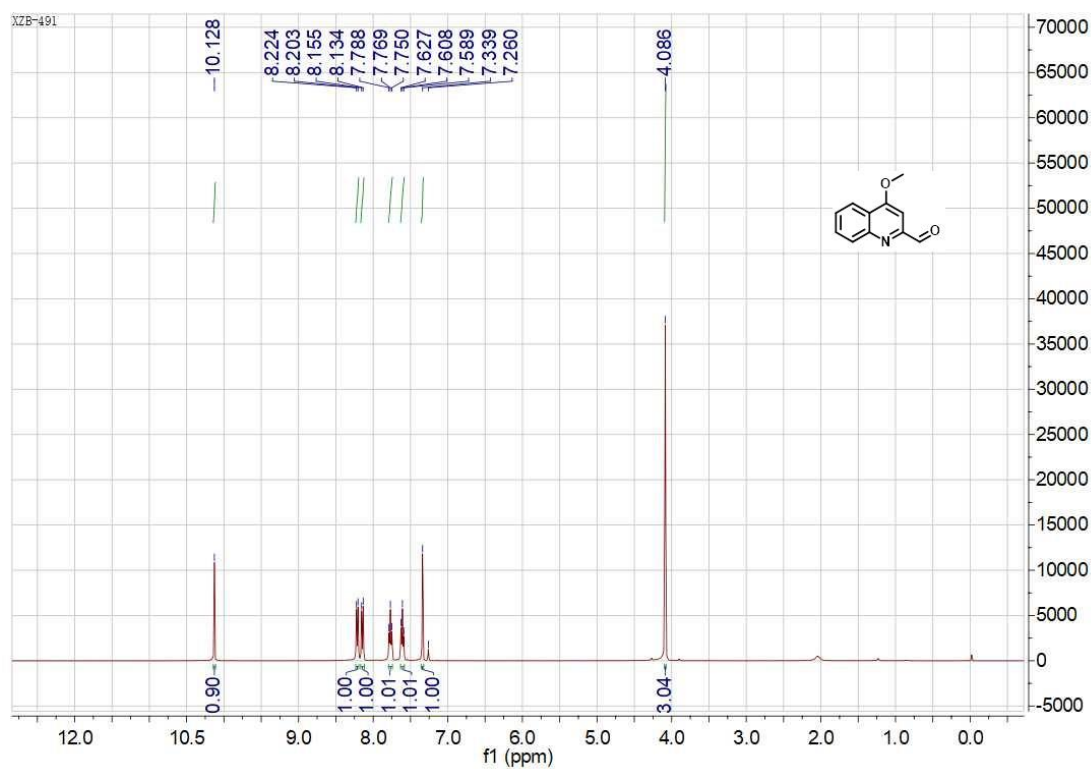
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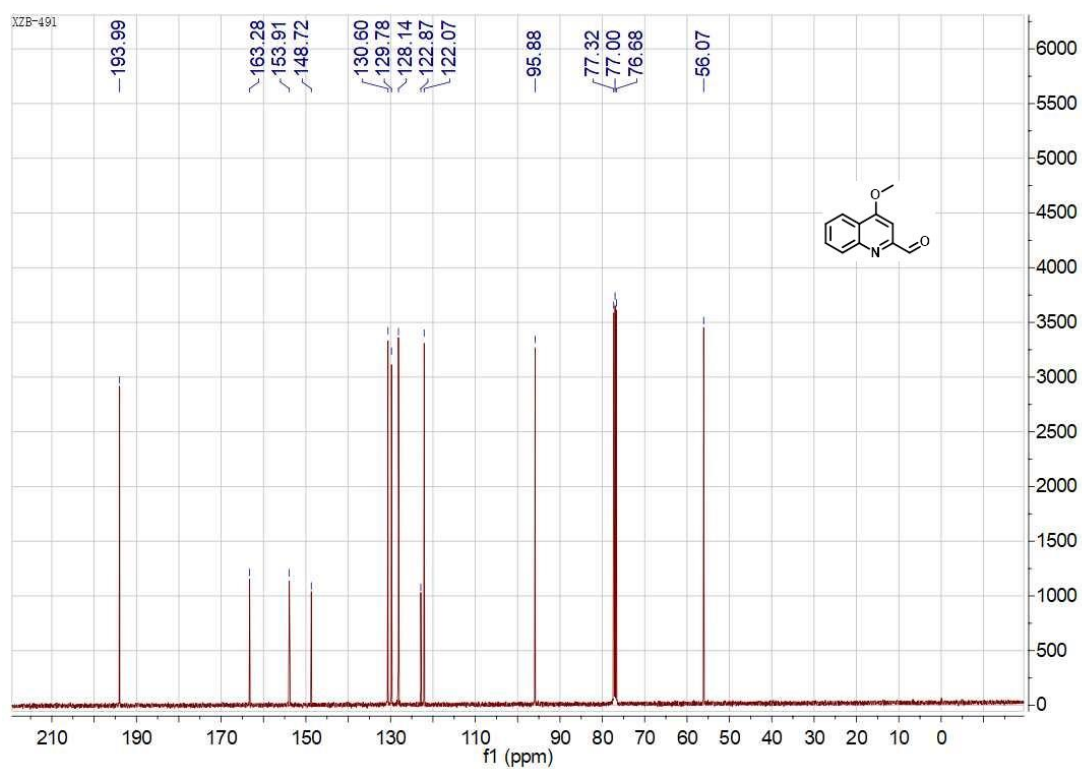
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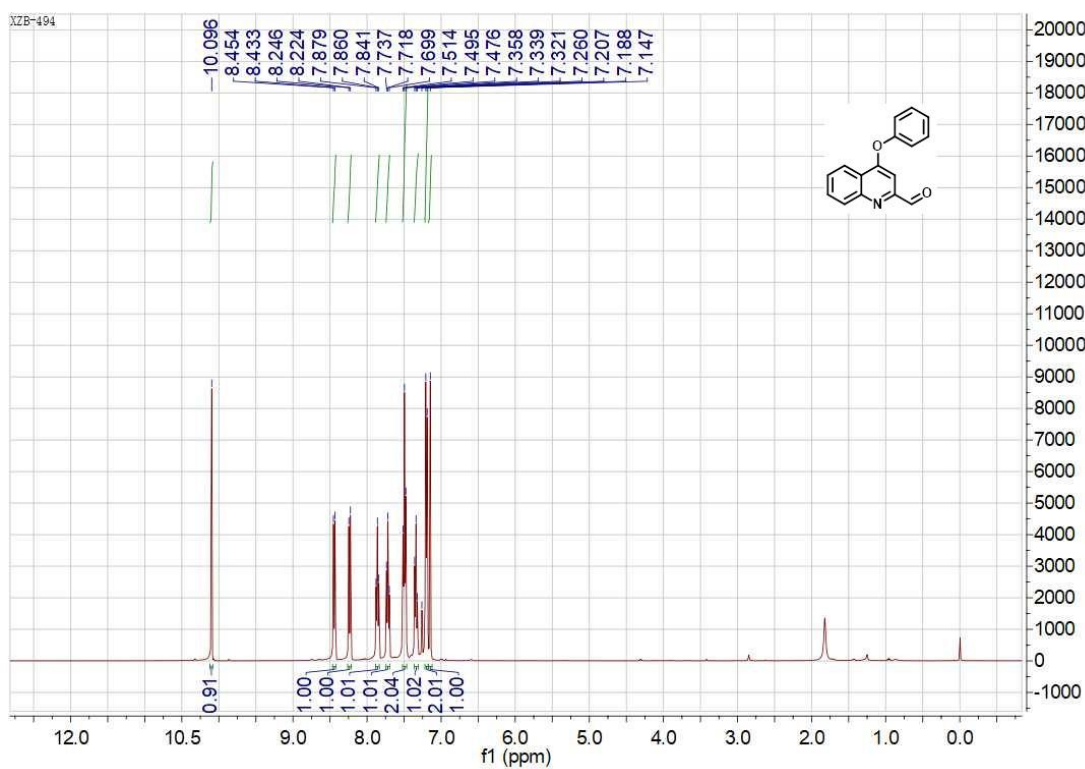
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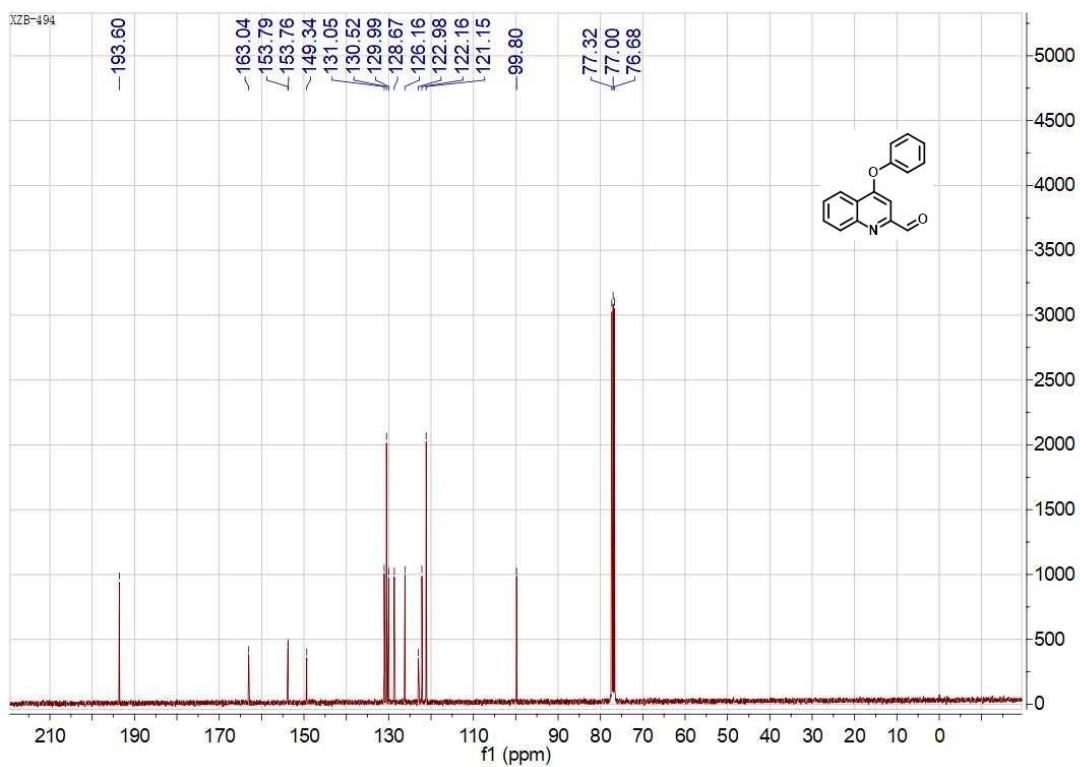
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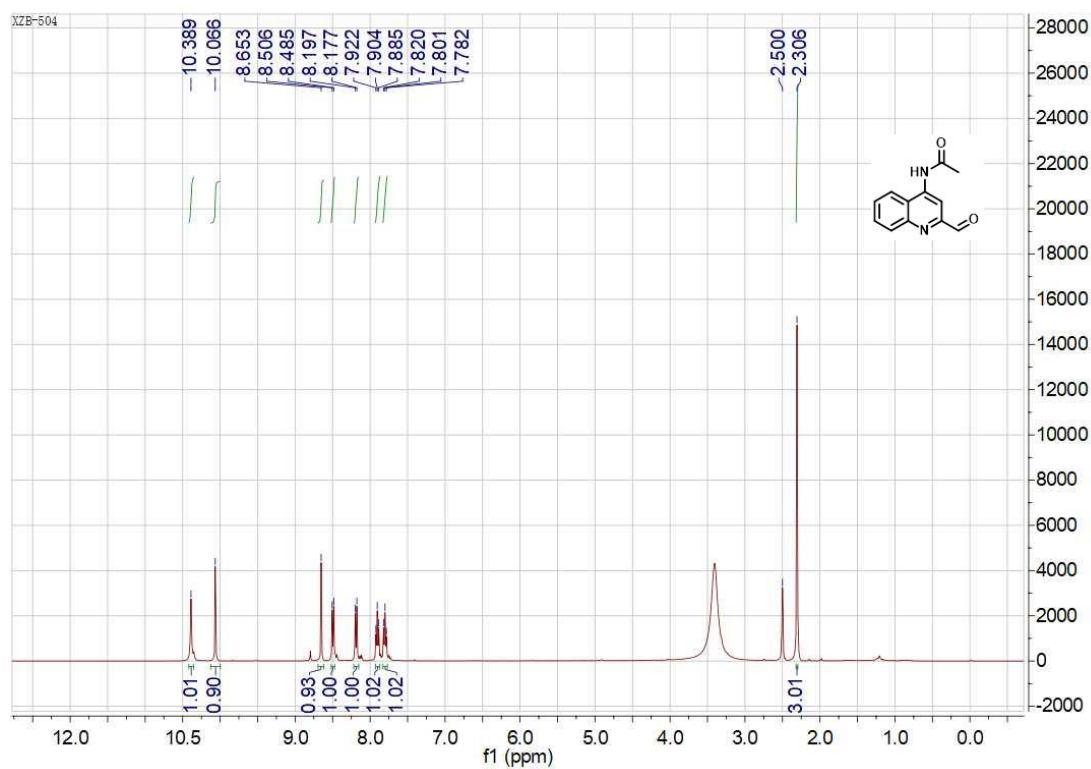
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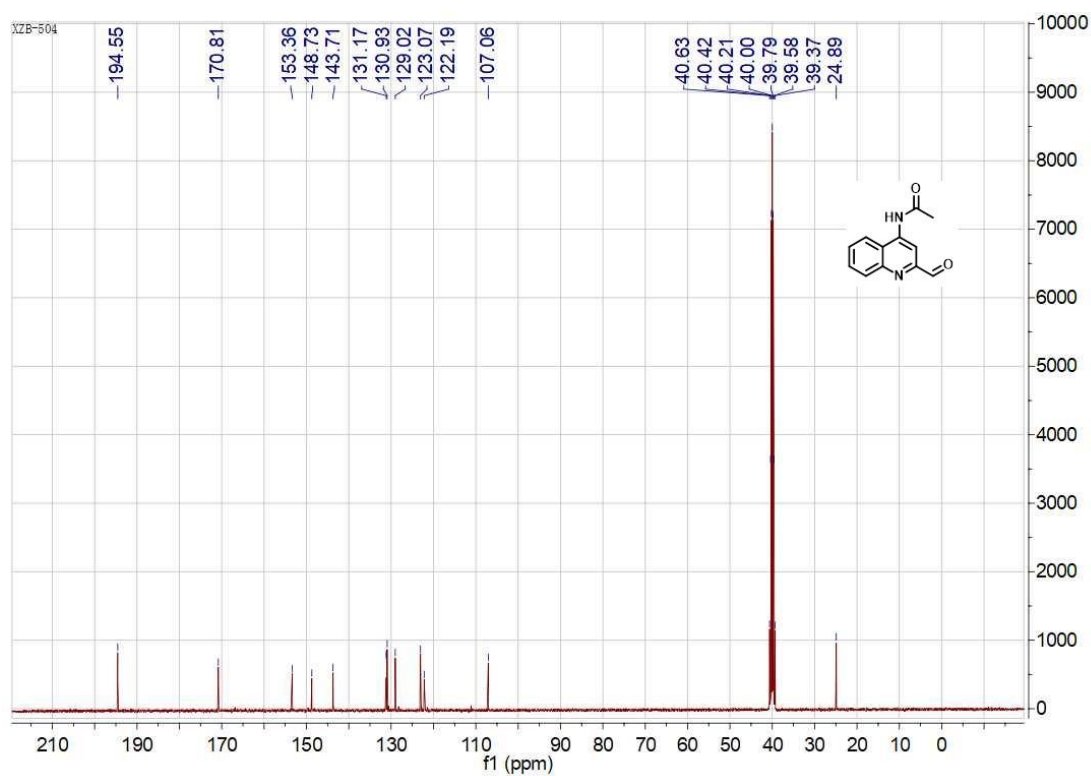
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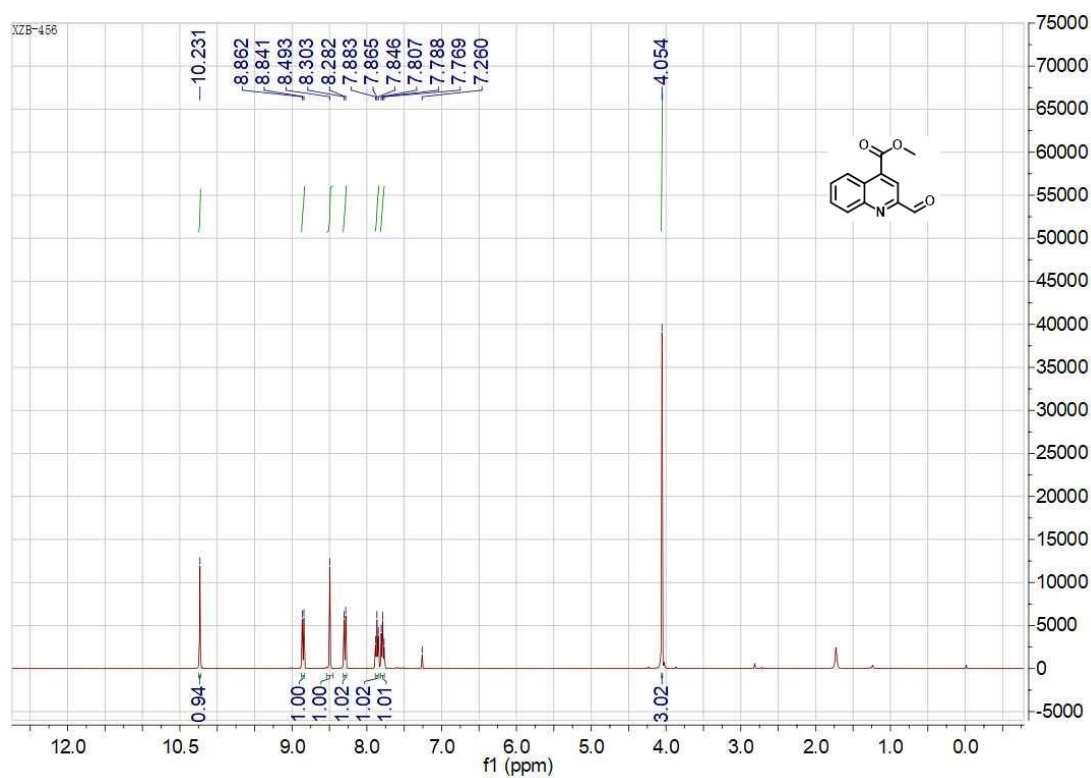
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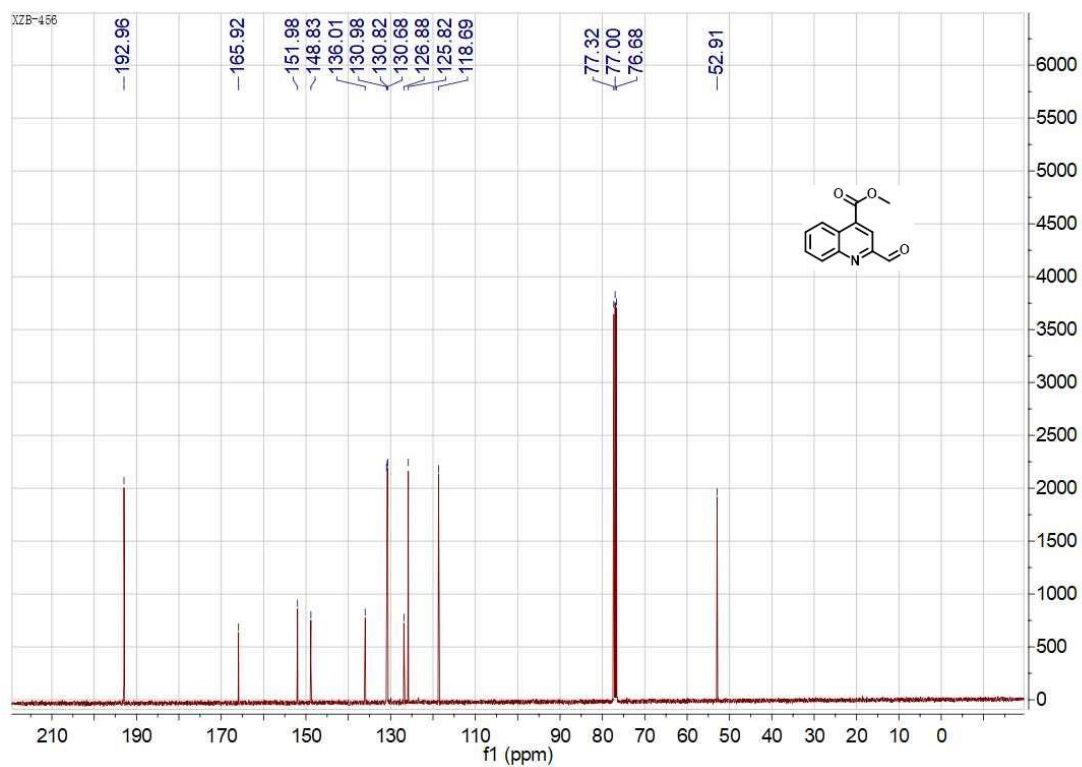
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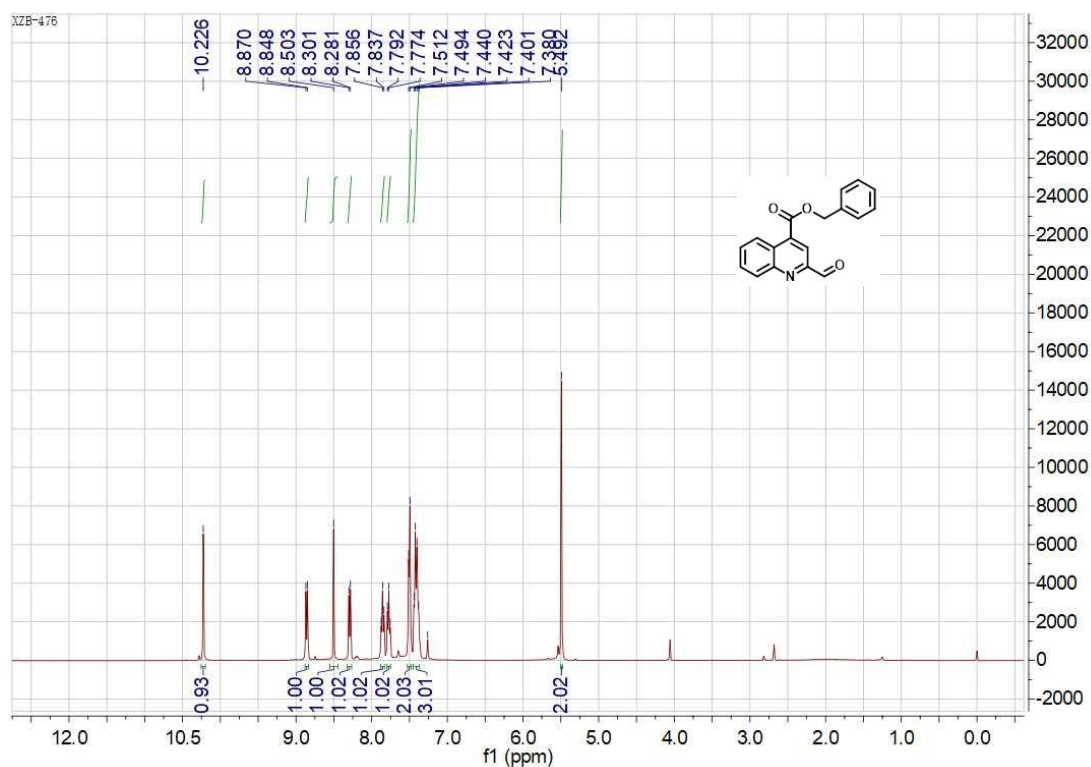
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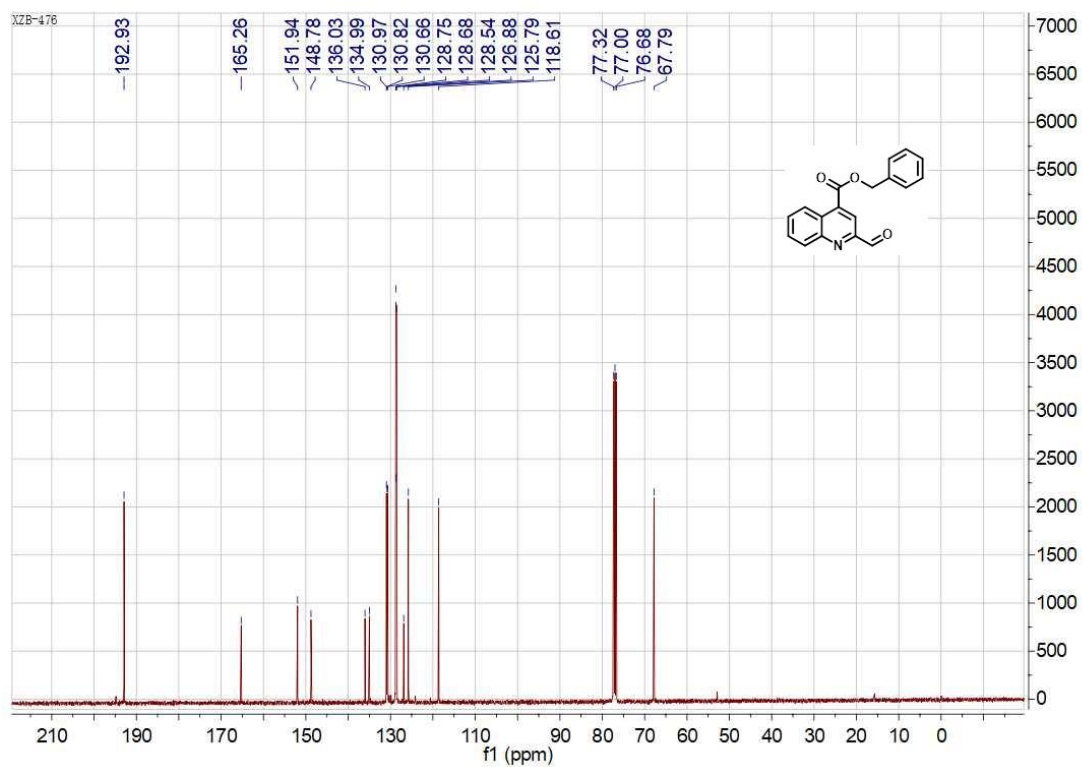
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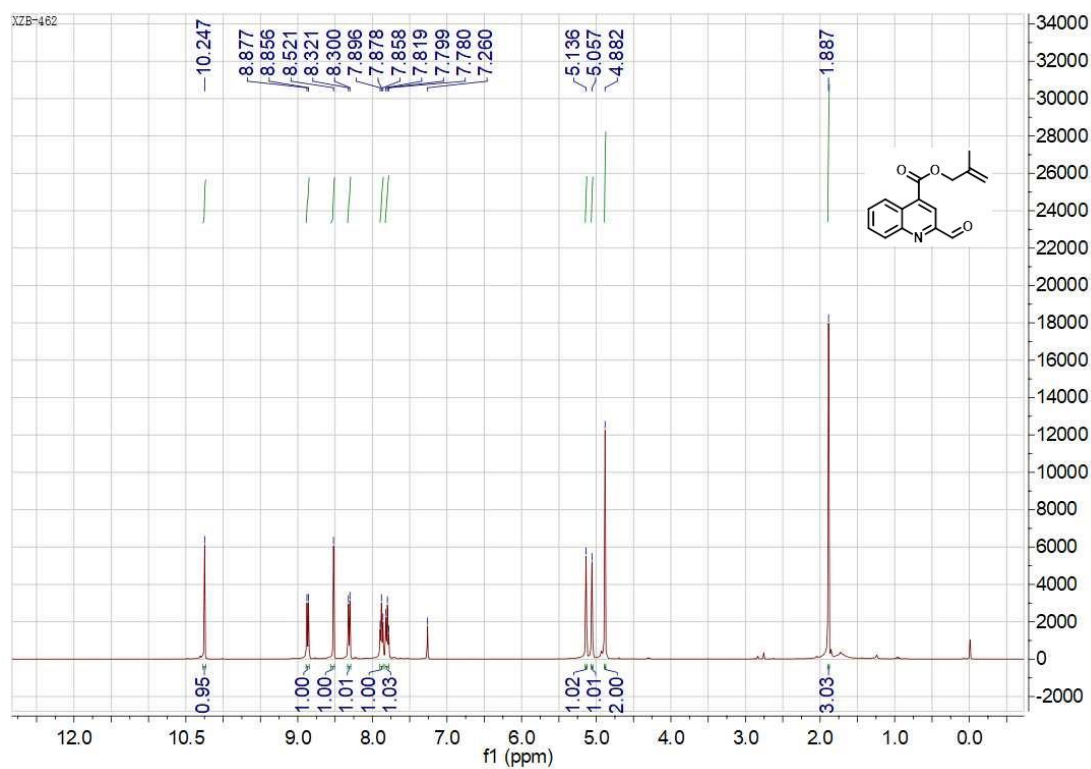
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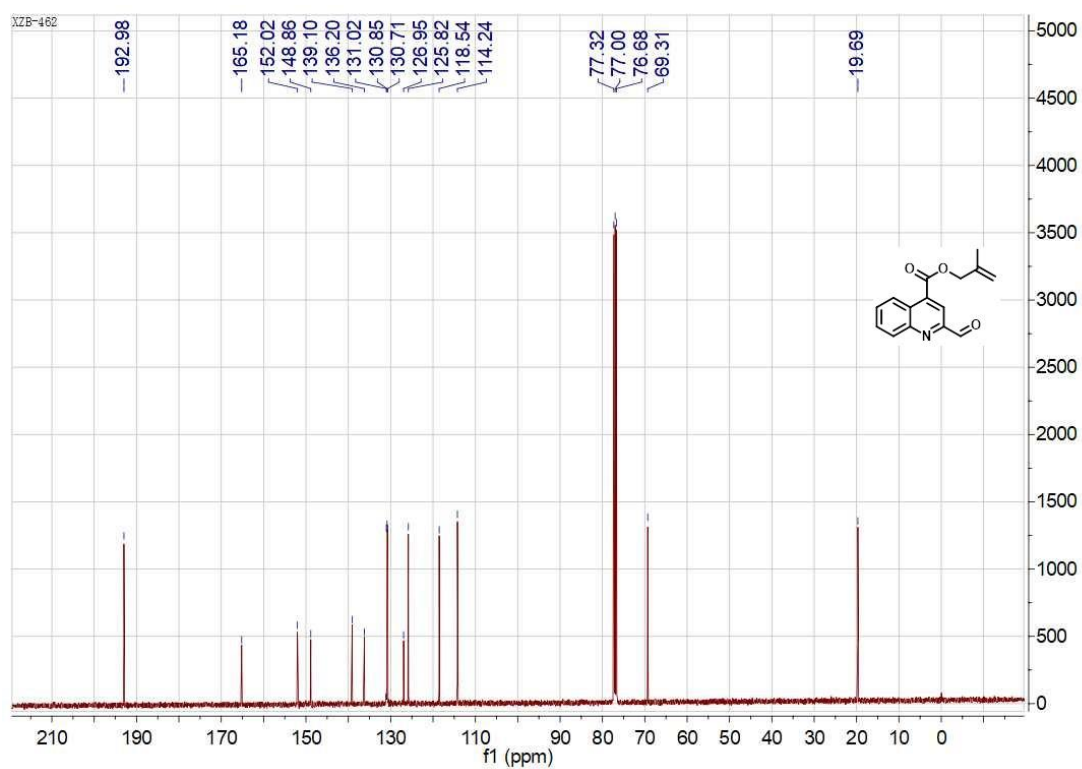
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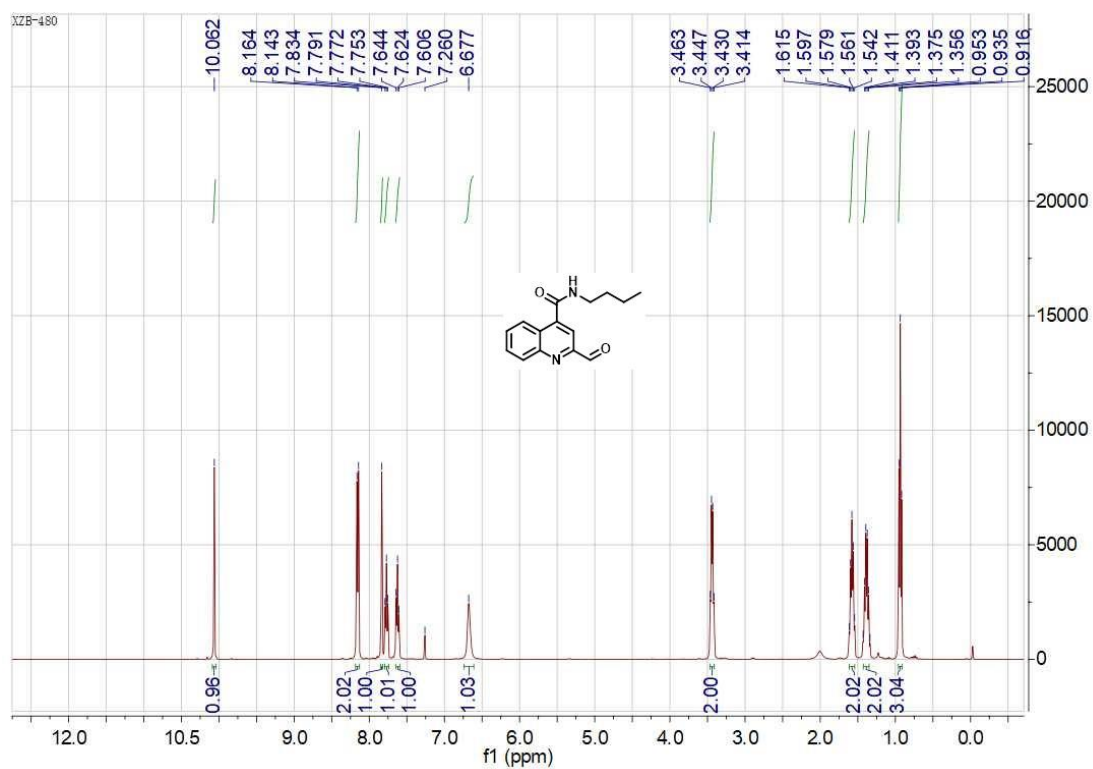
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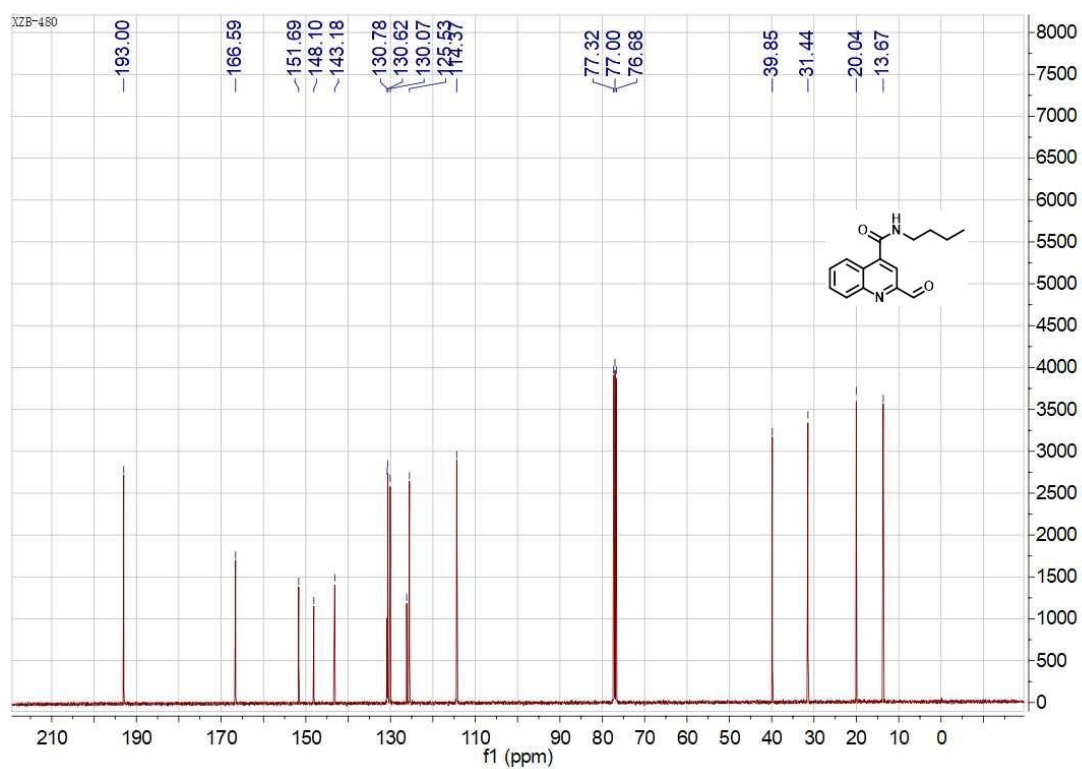
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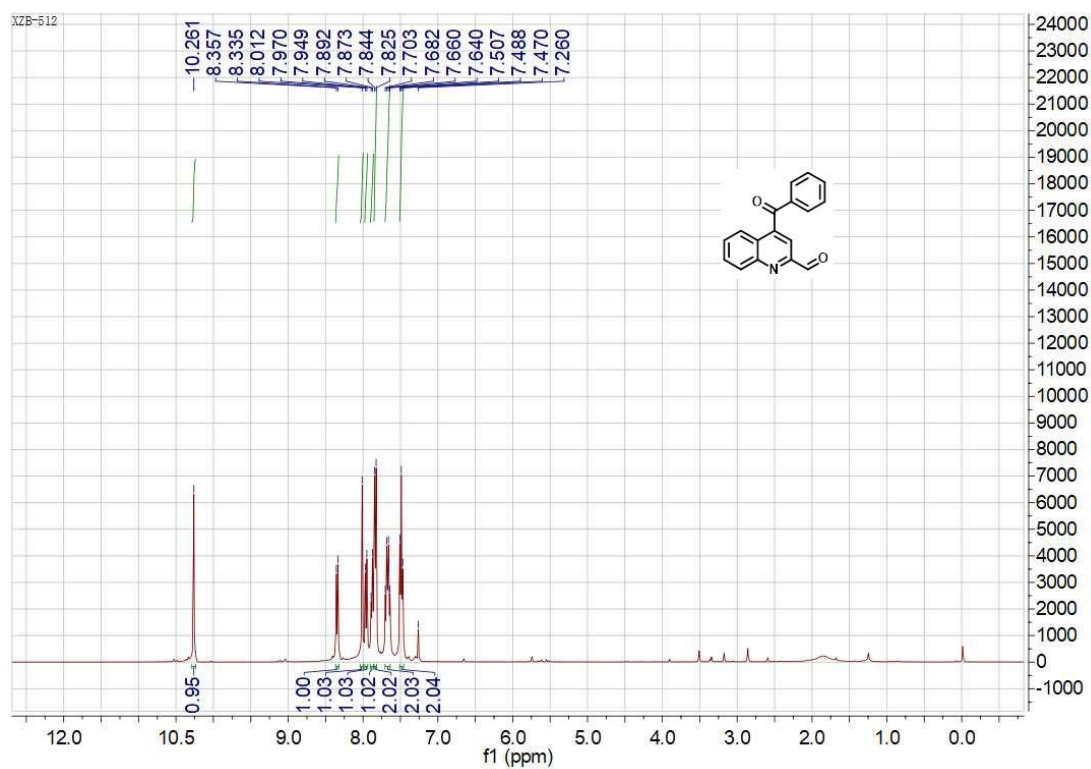
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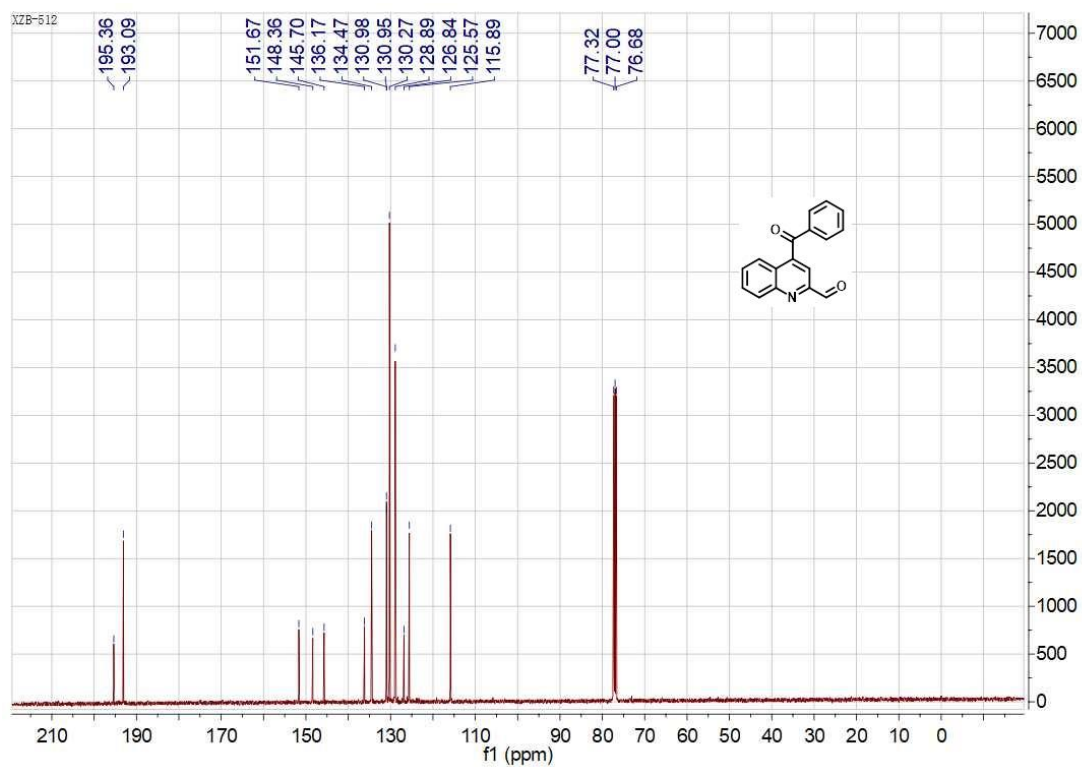
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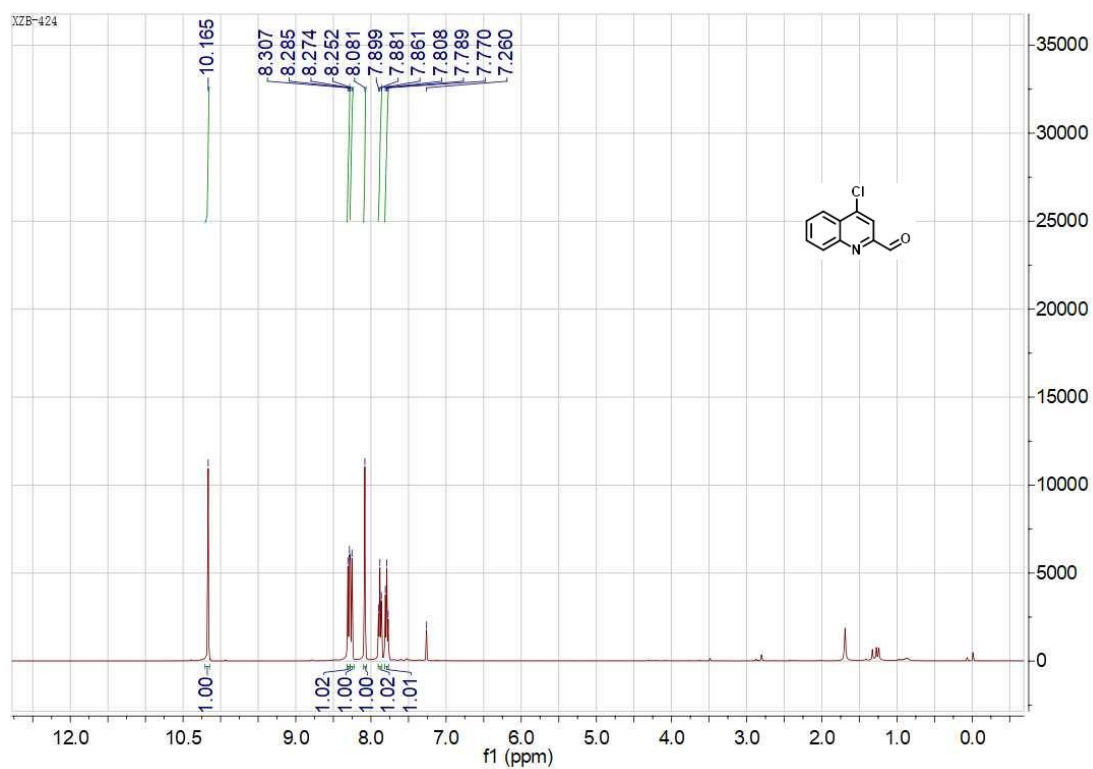
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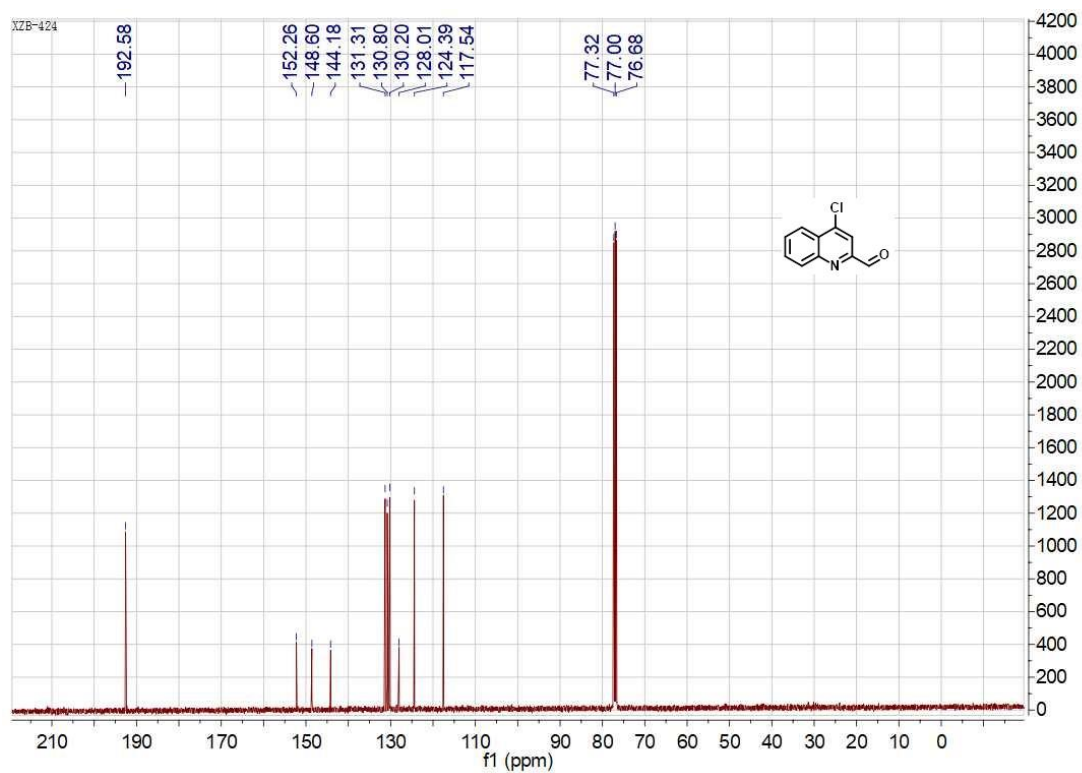
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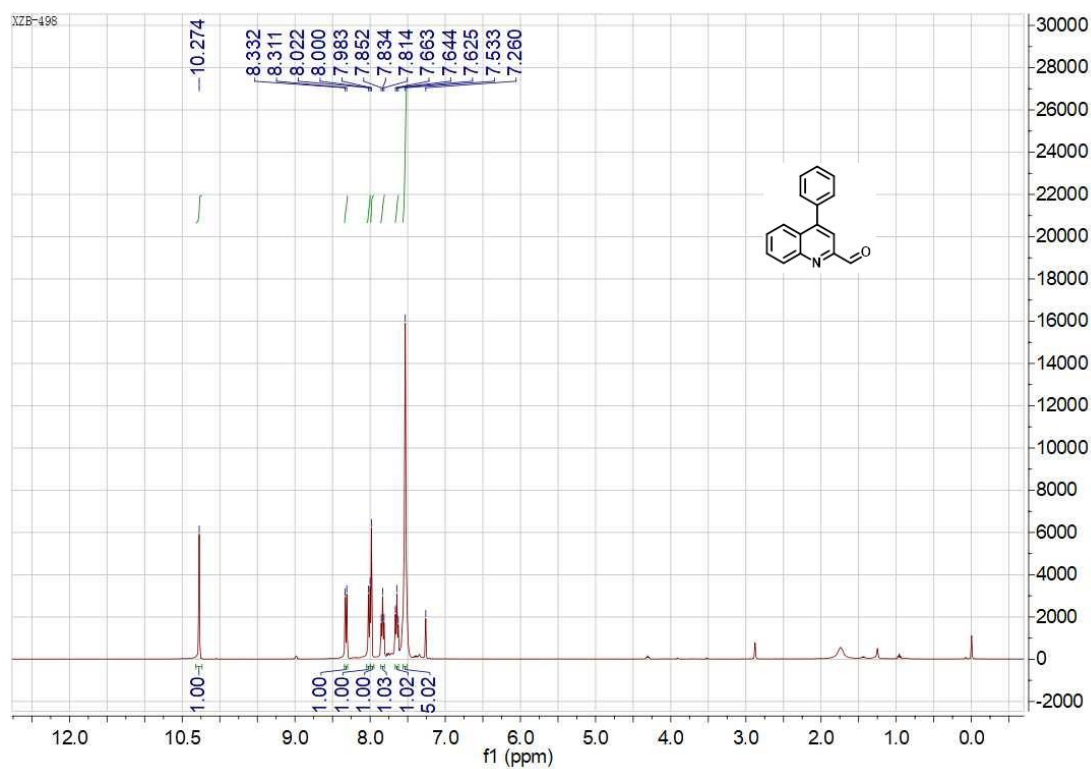
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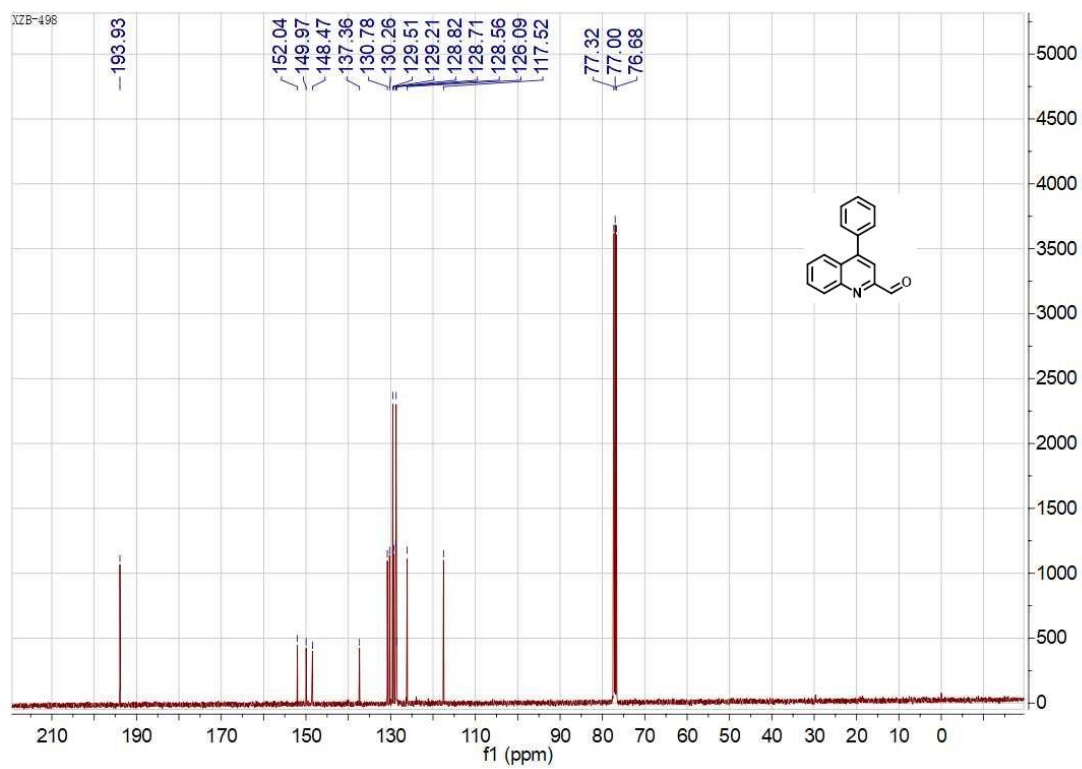
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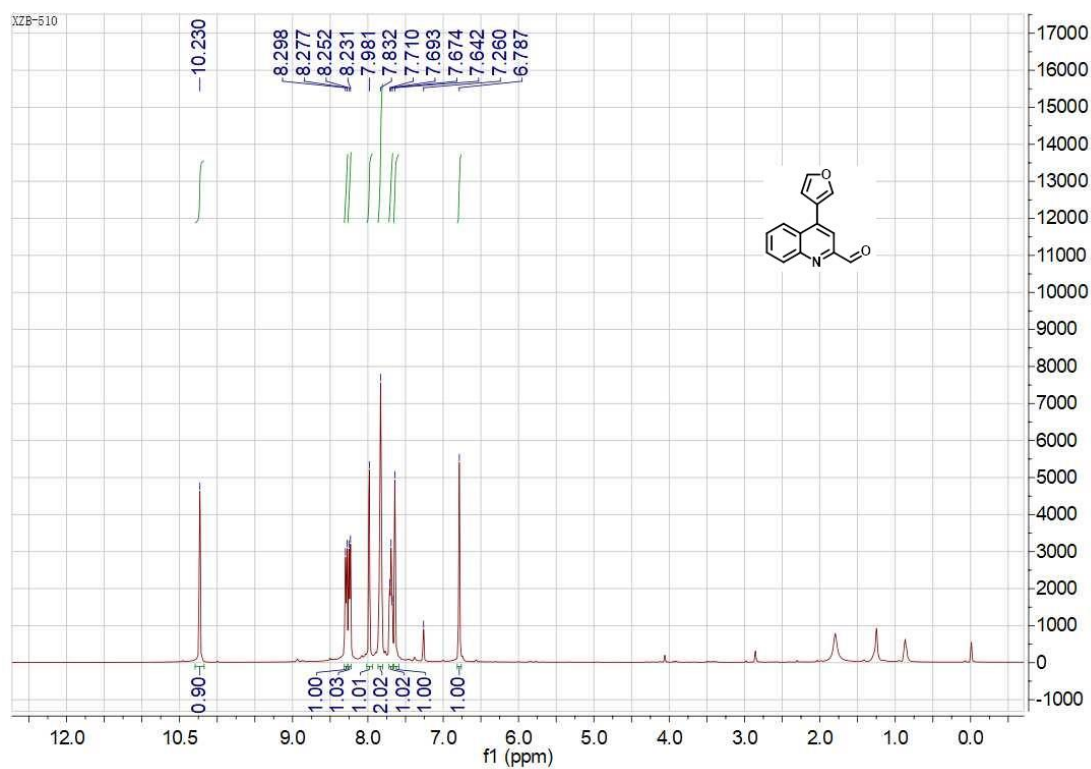
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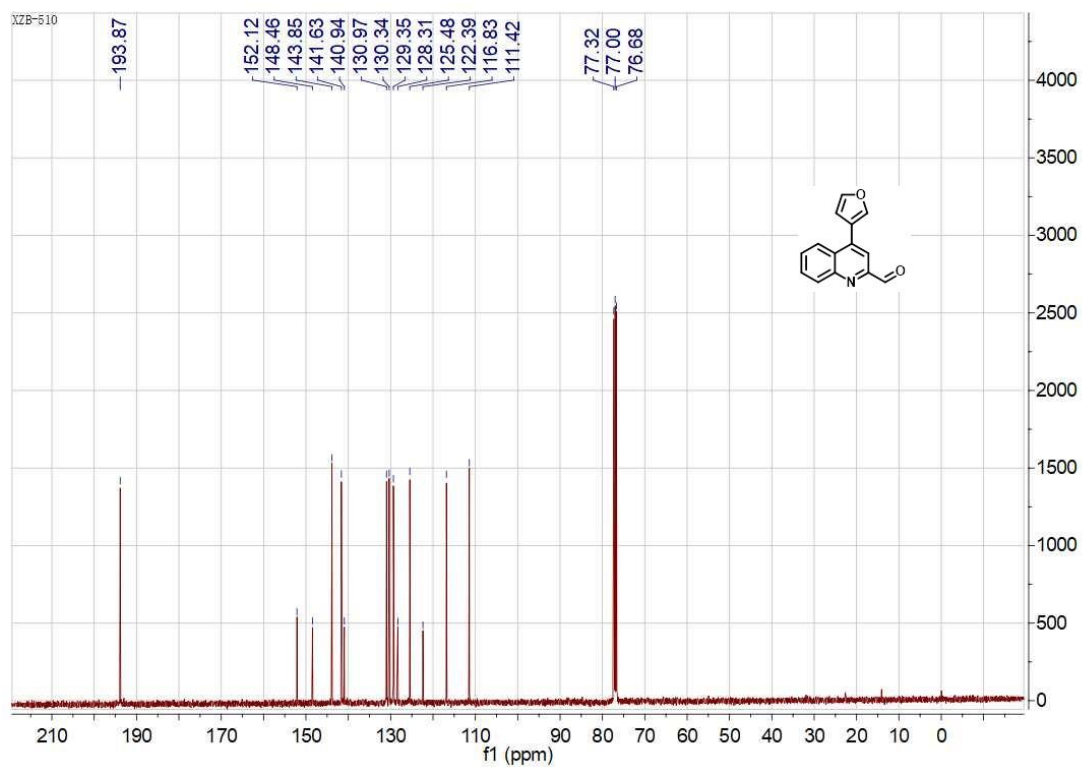
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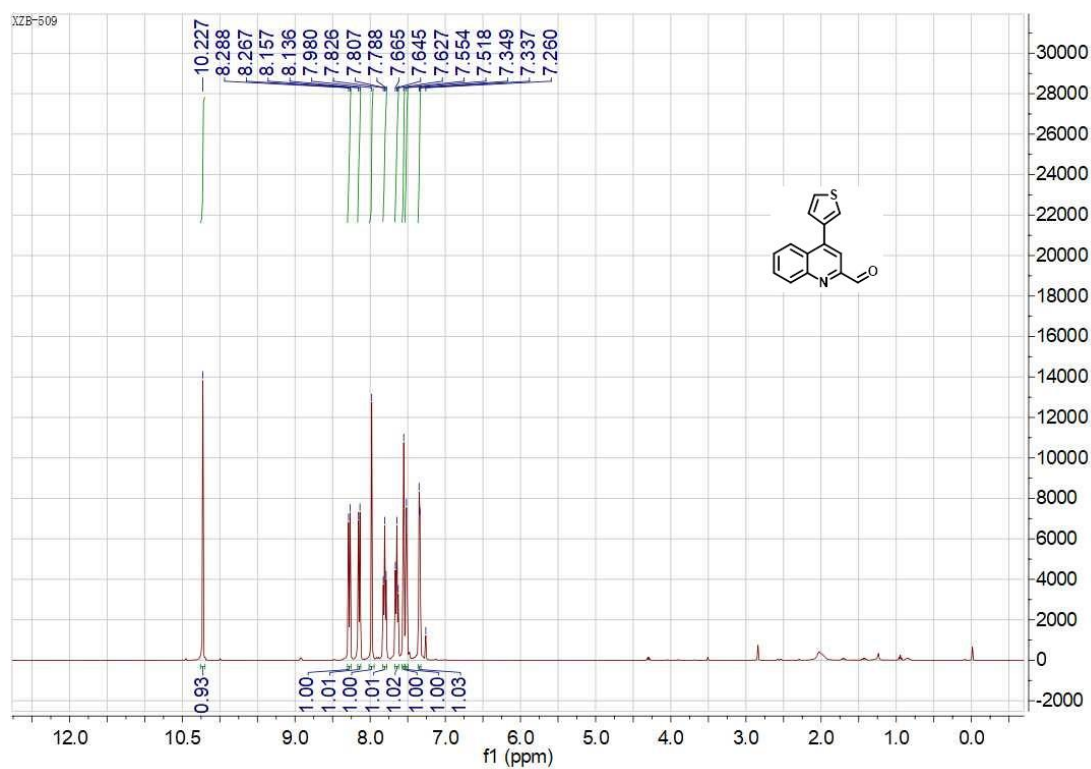
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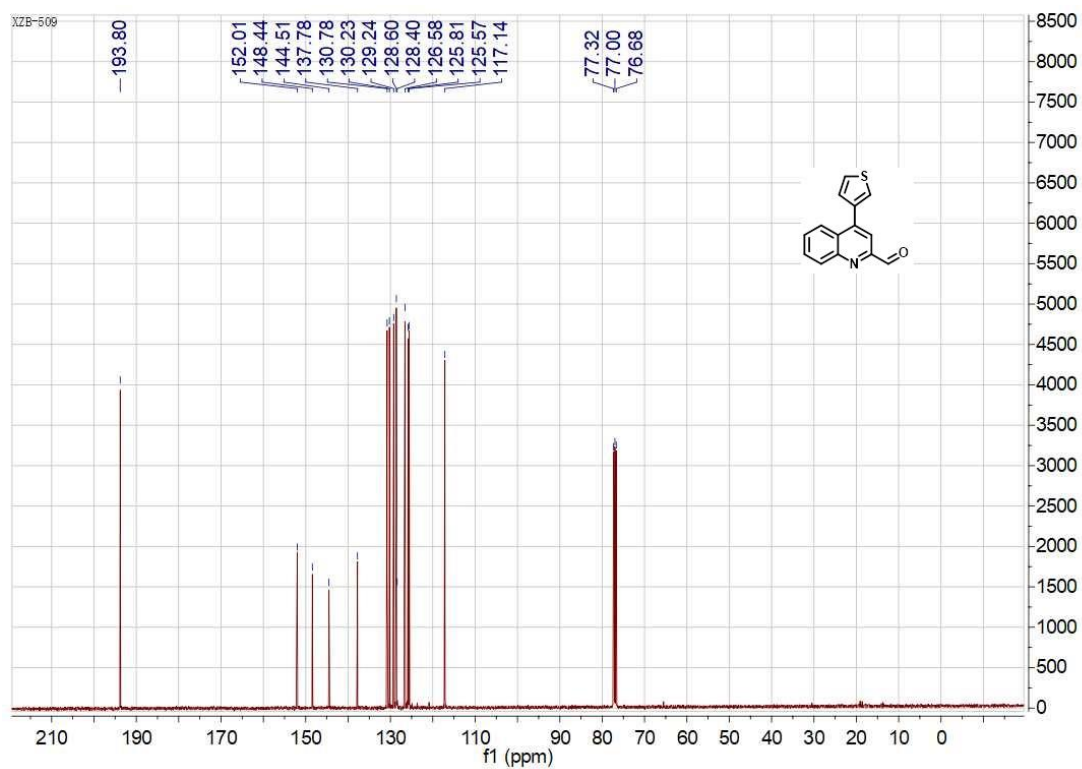
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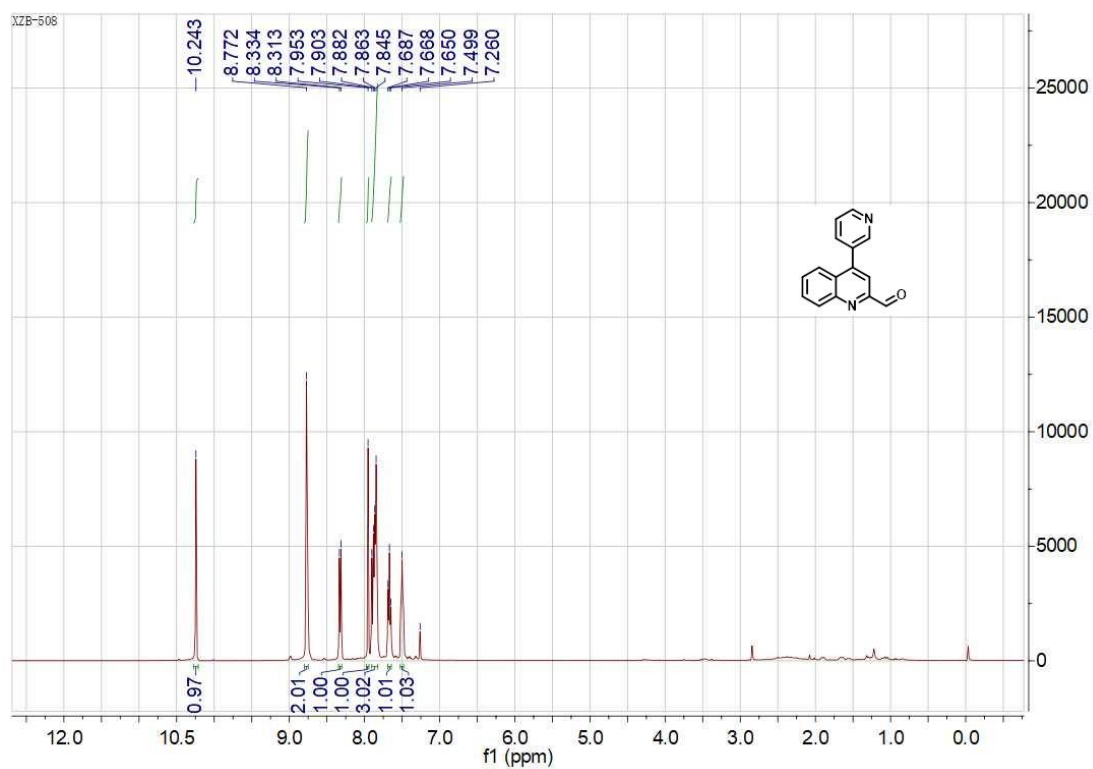
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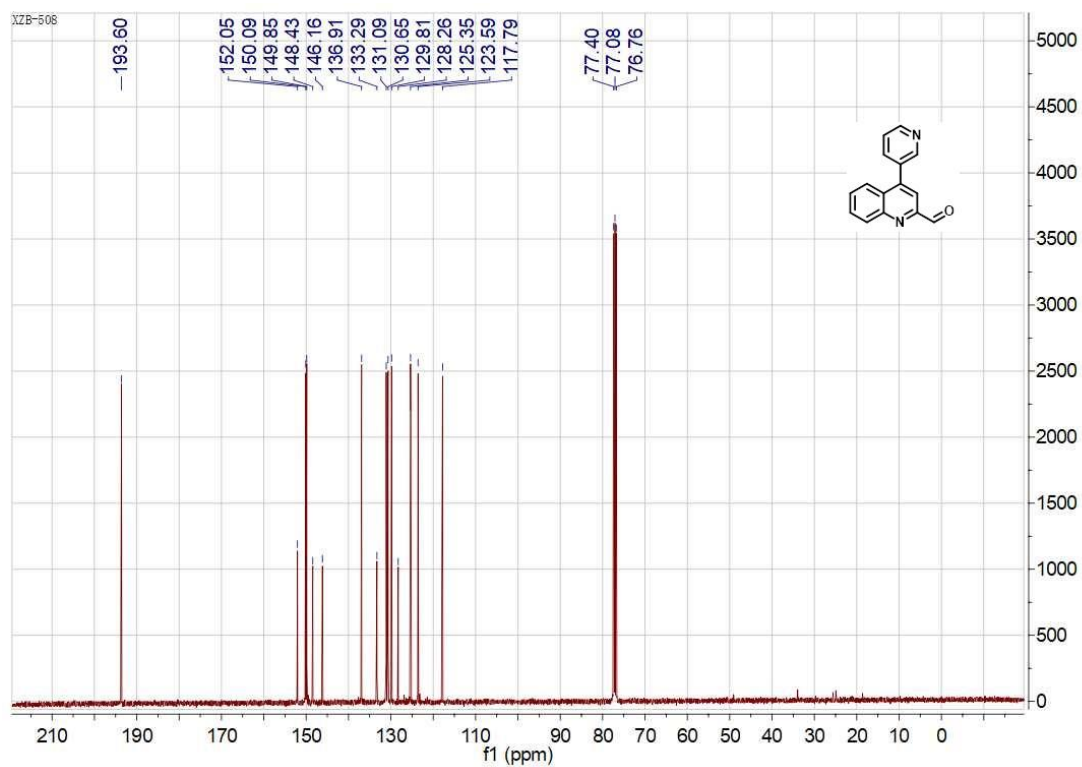
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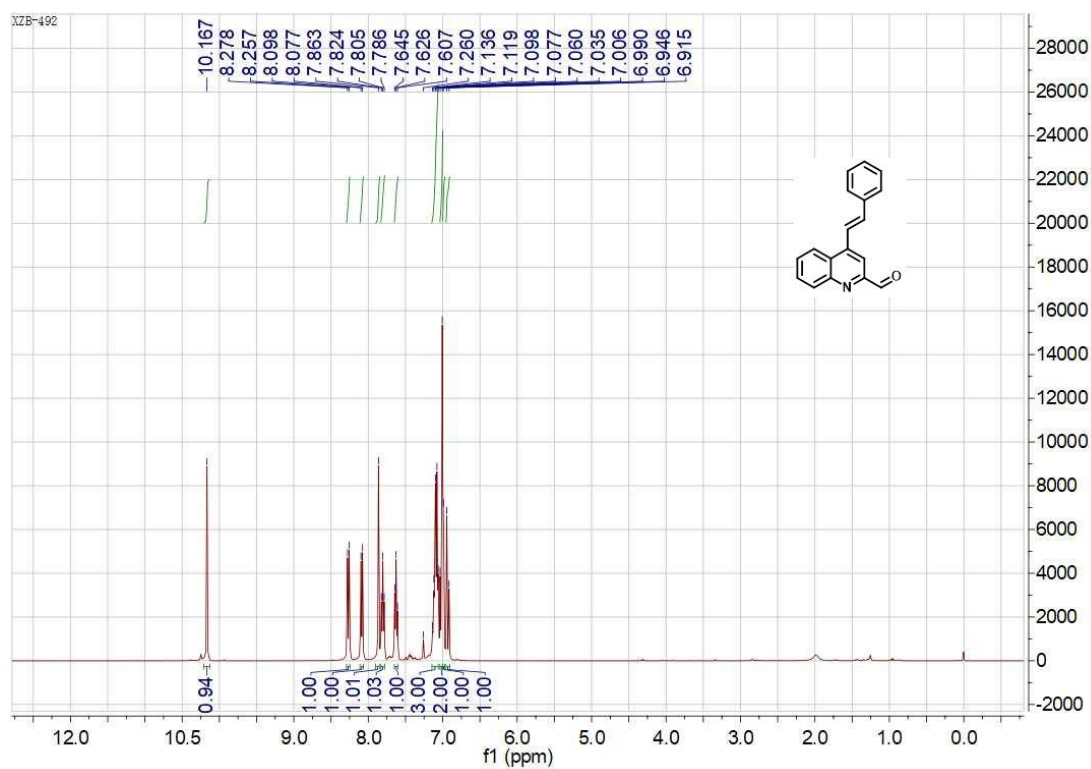
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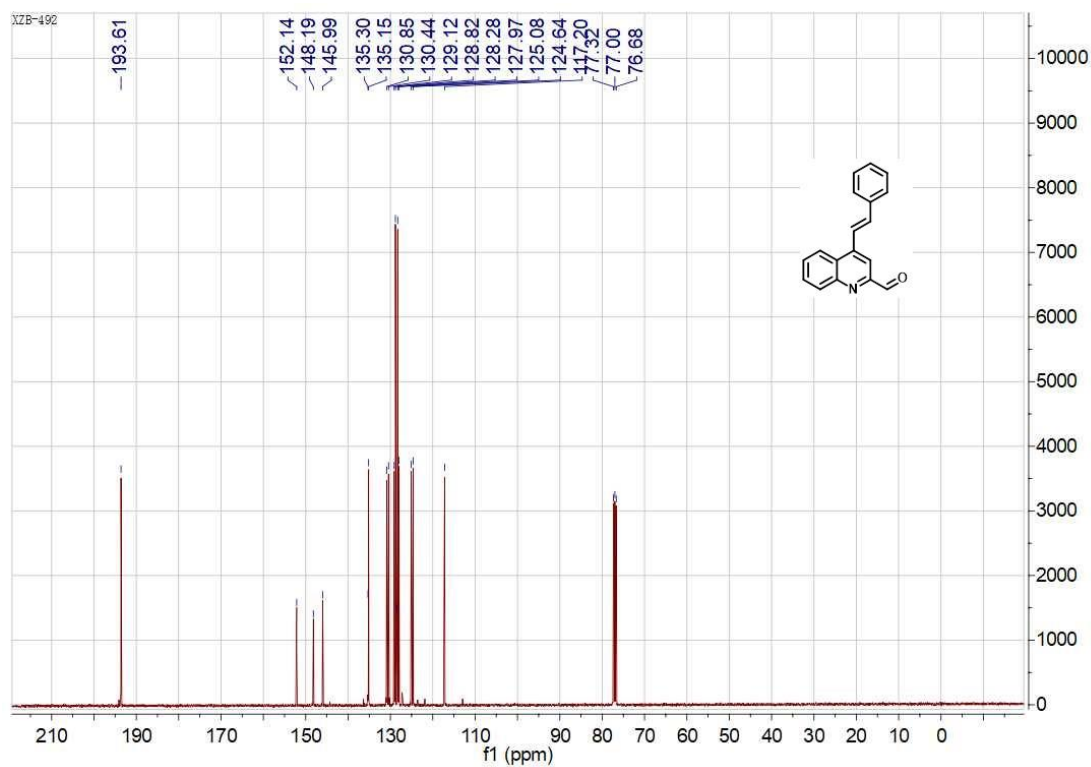
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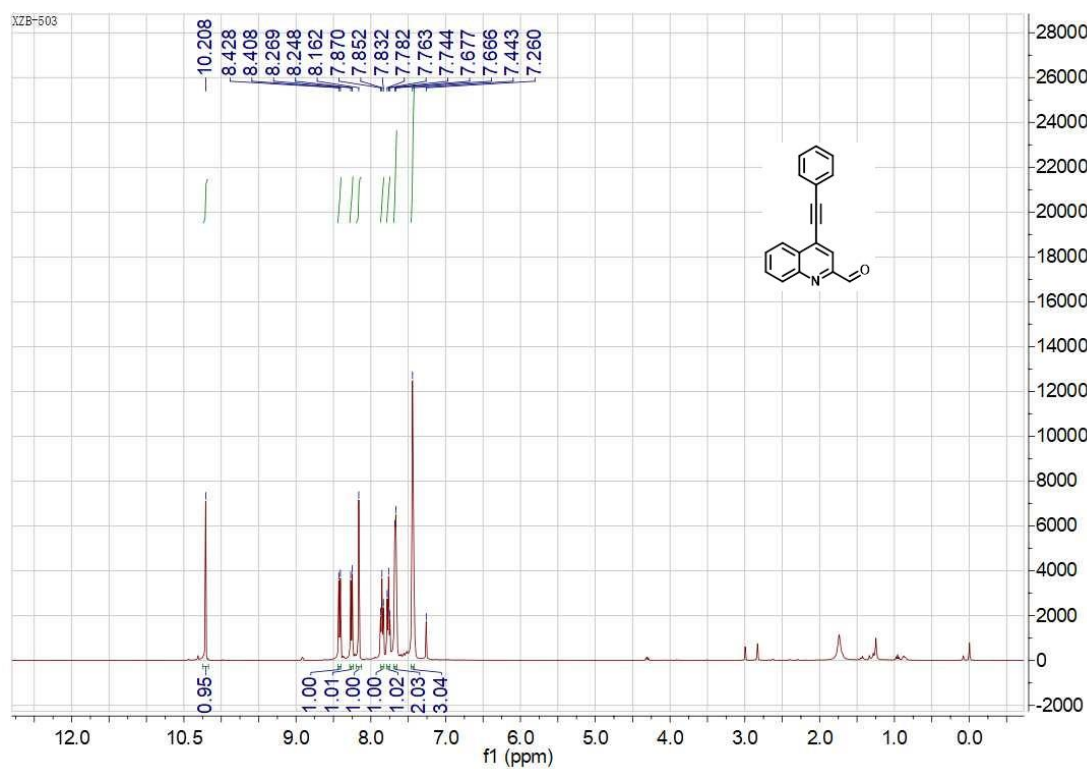
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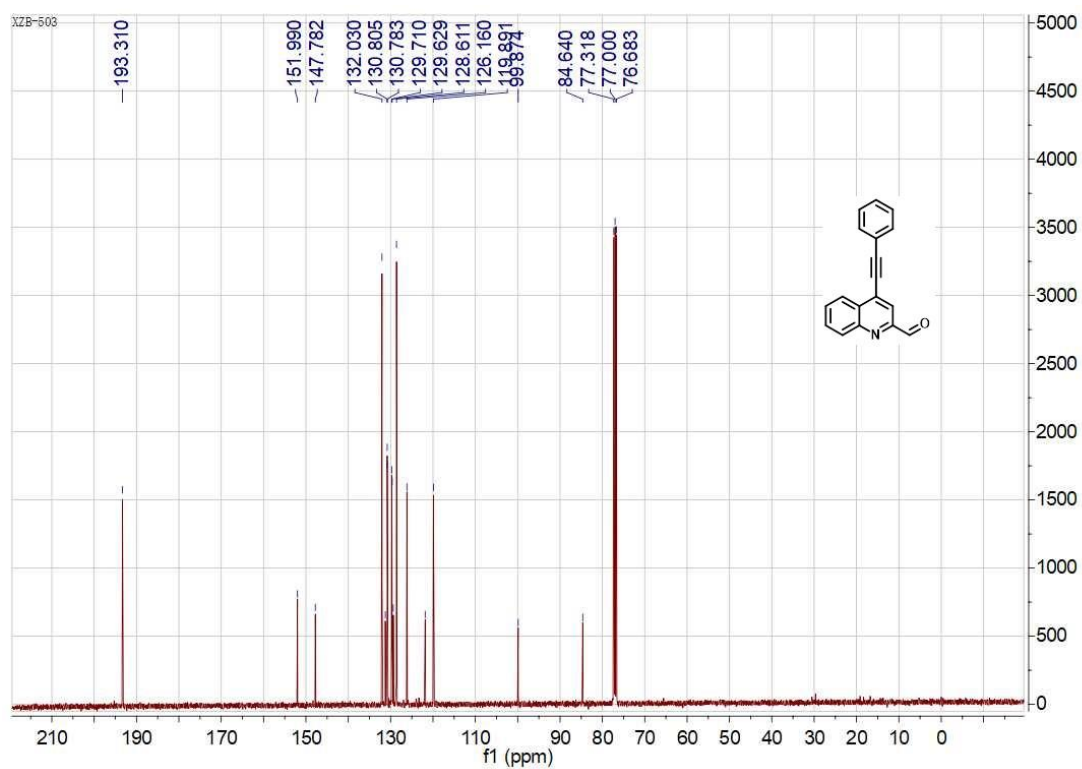
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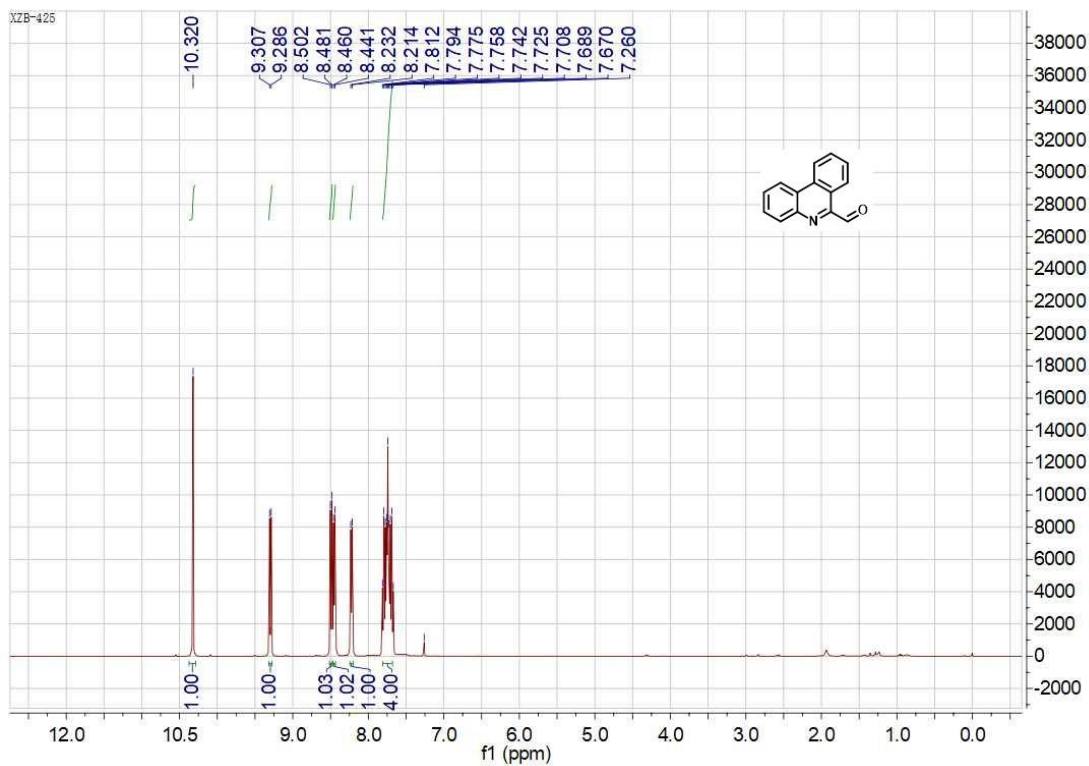
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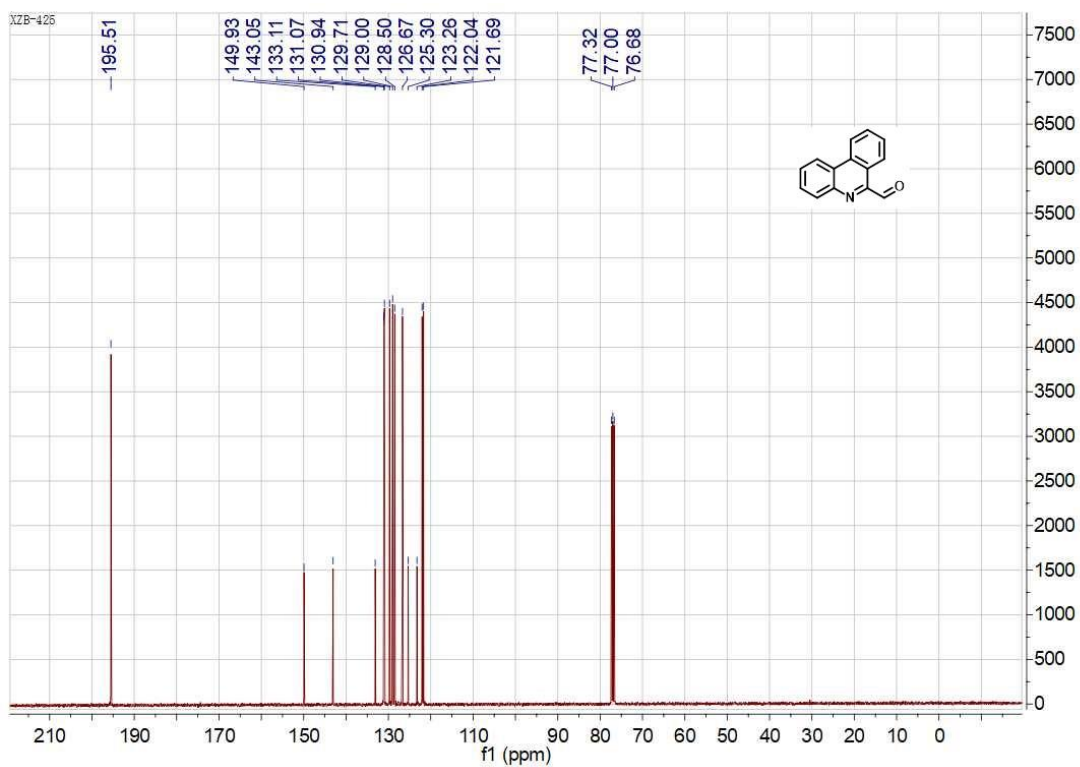
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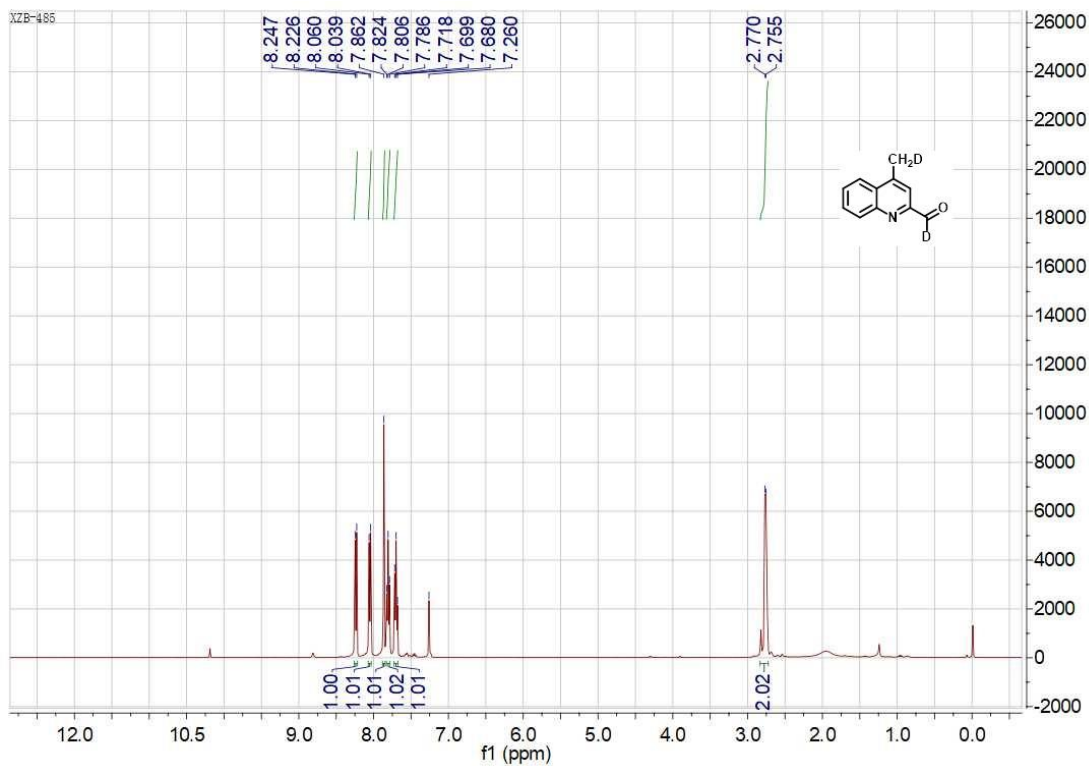
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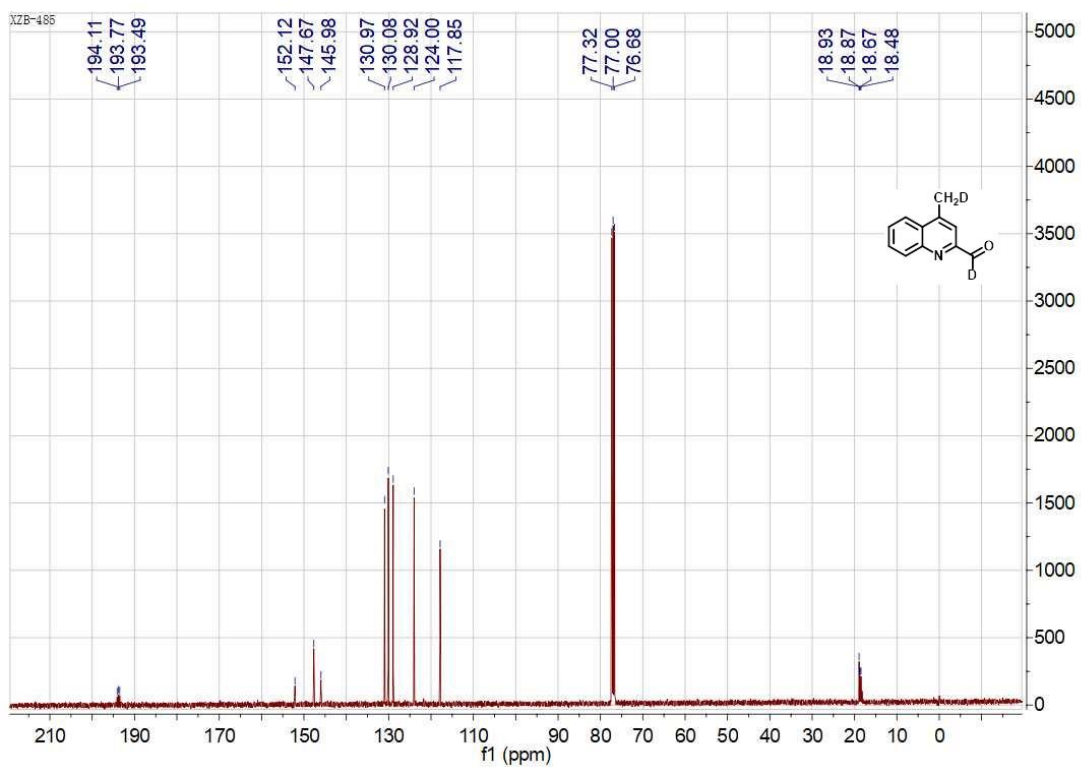
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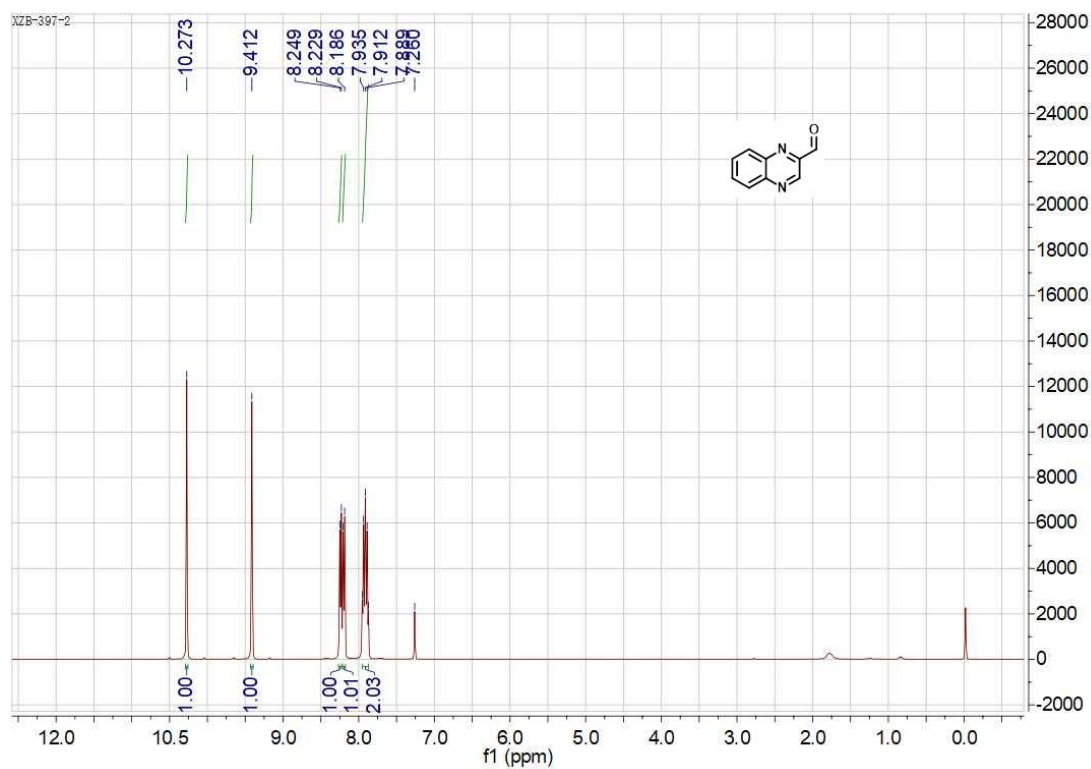
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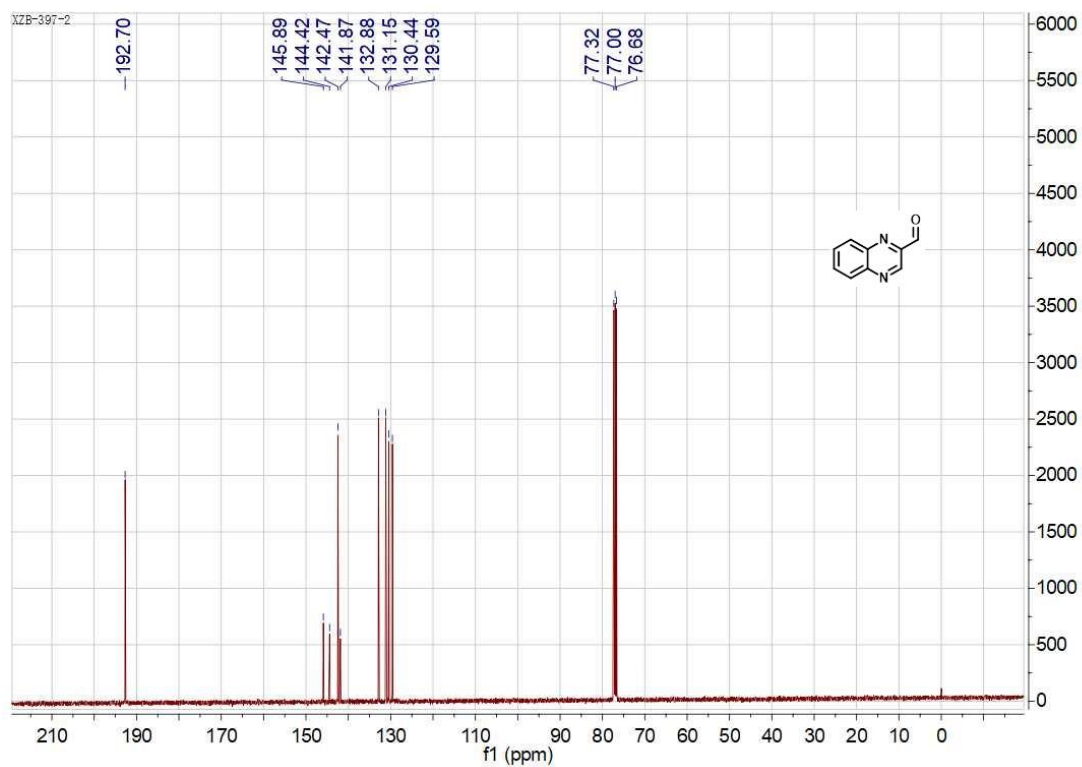
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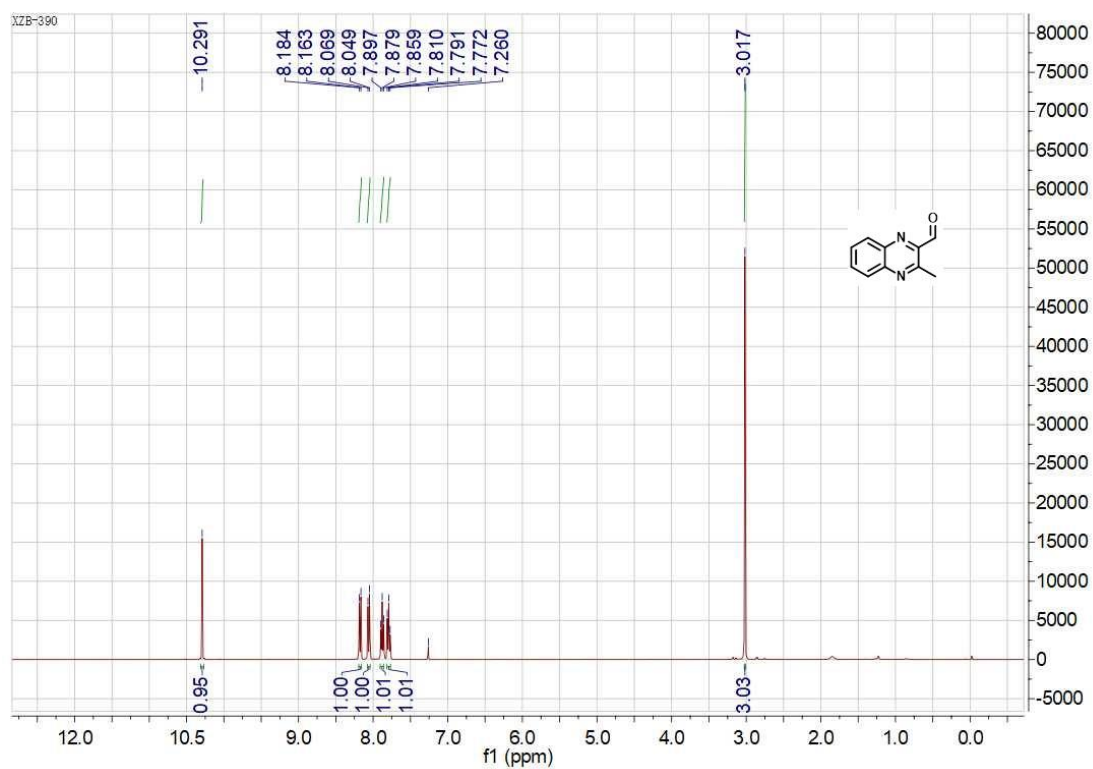
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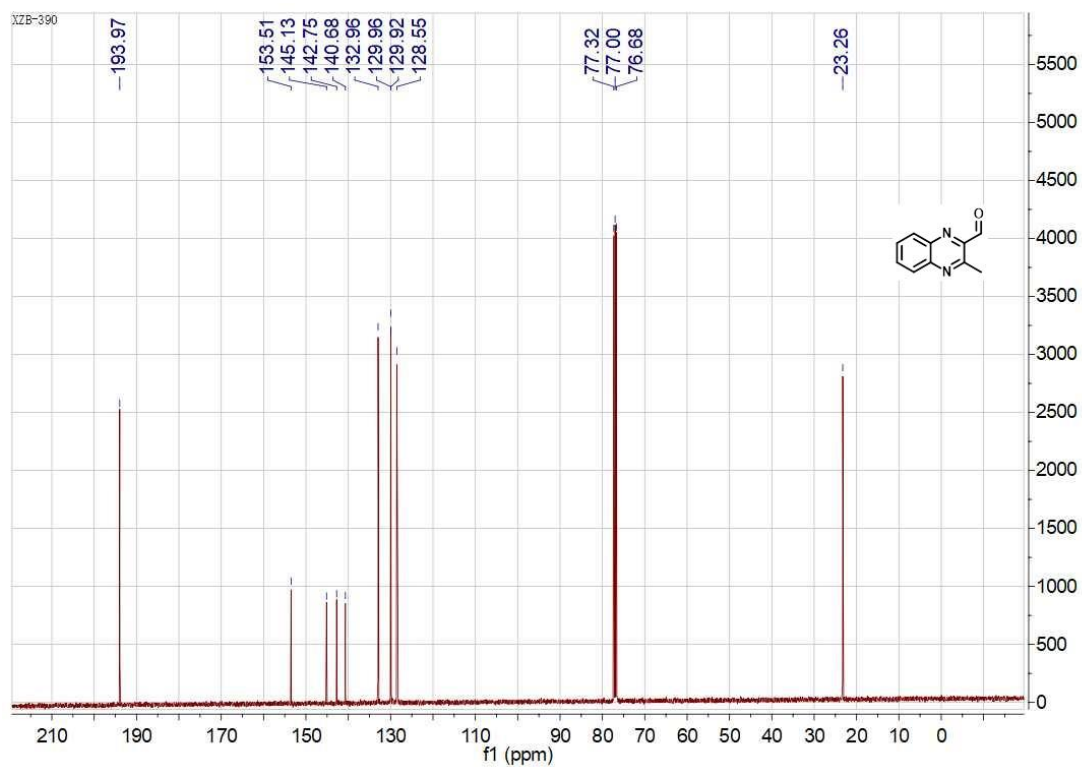
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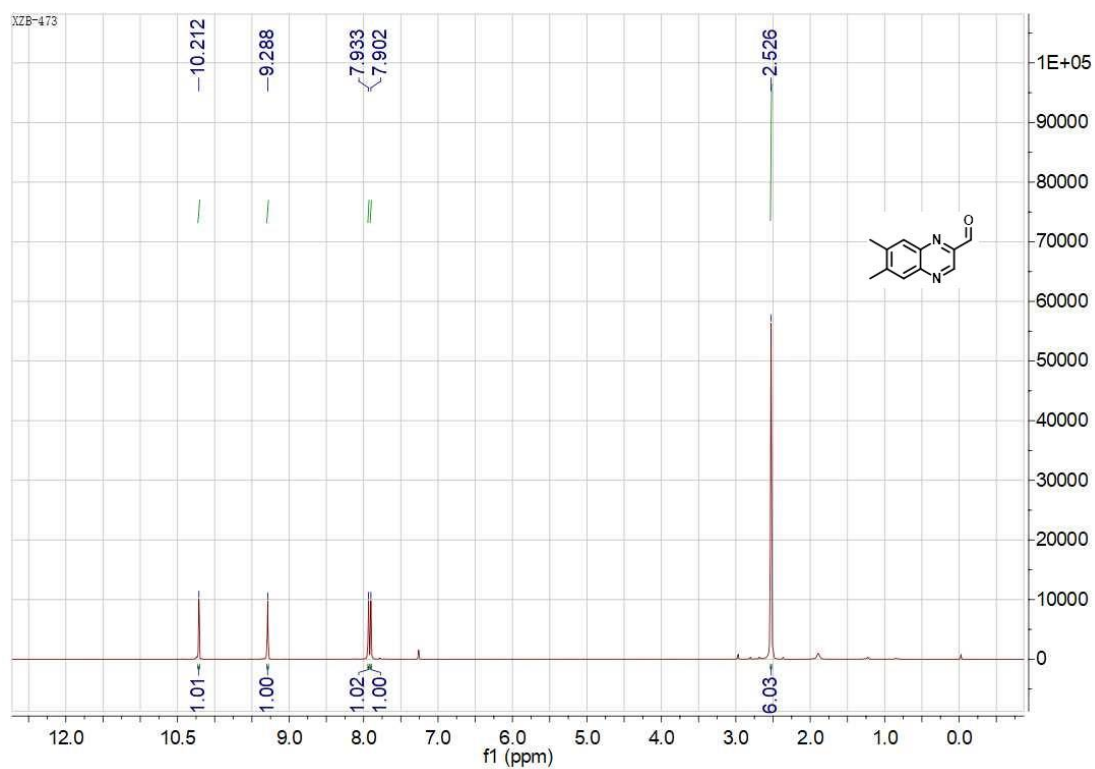
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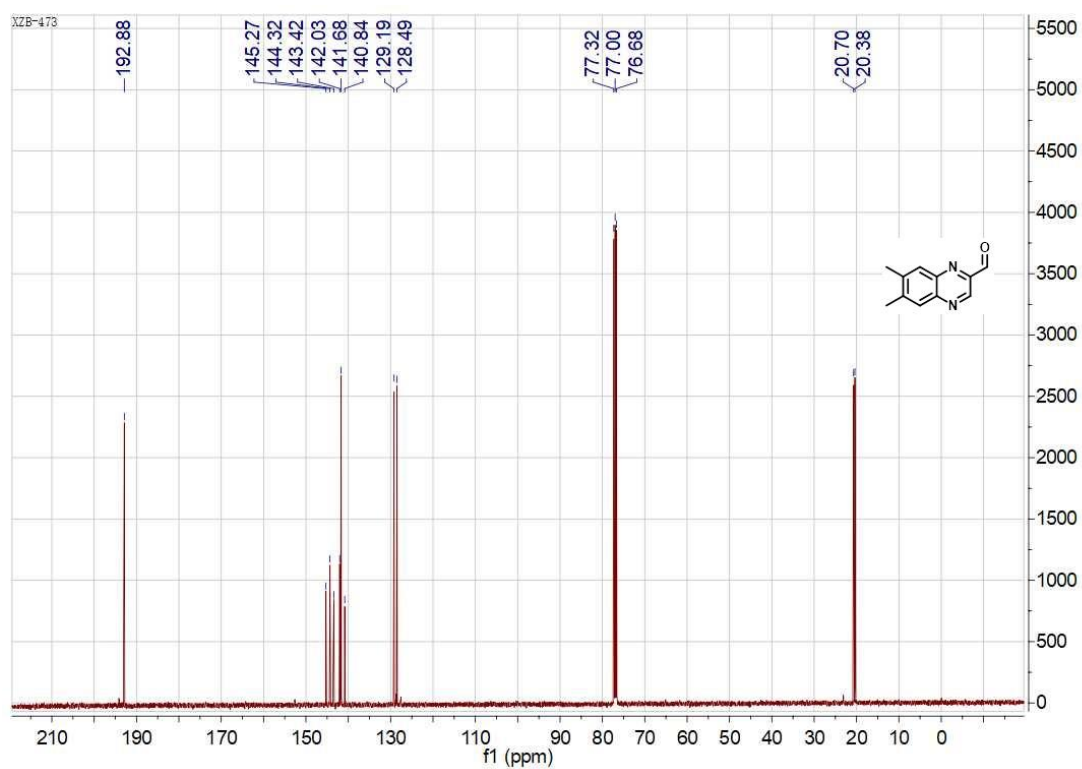
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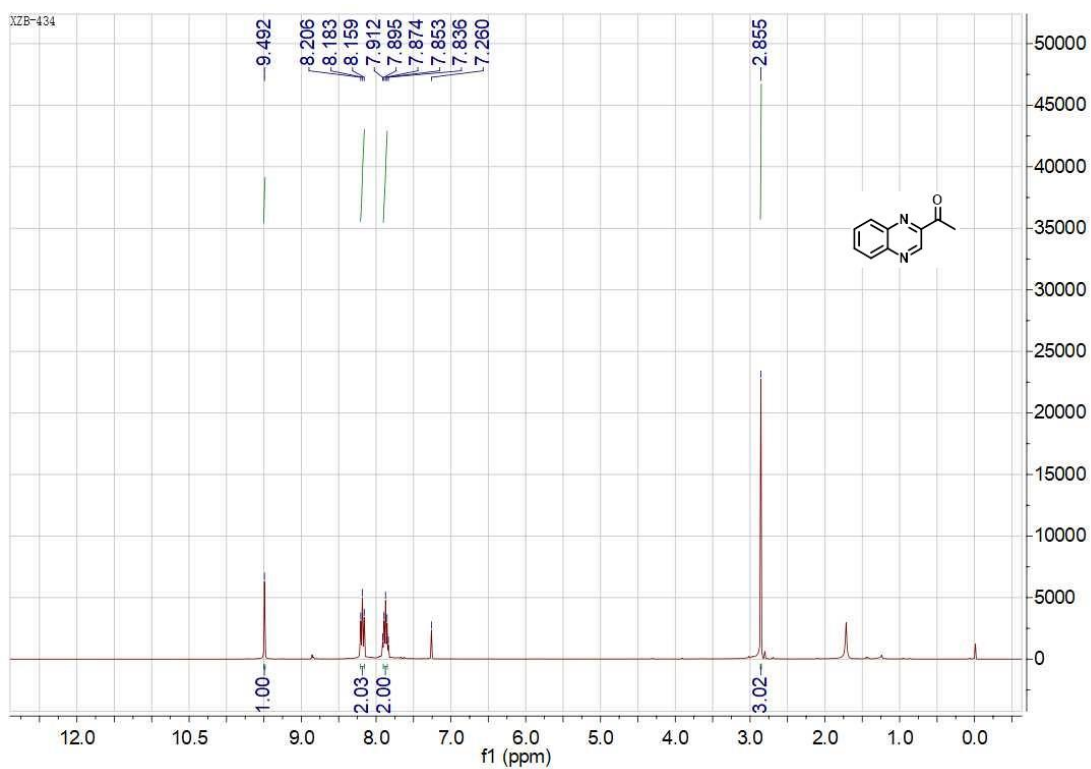
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27-¹³C NMR



28-¹H NMR



28-¹³C NMR

