Supporting Information

Transition Metal Free Quinoline Synthesis from Acetophenones and Anthranils *via* Sequential One Carbon Homologation/Conjugate addition/Annulation Cascade

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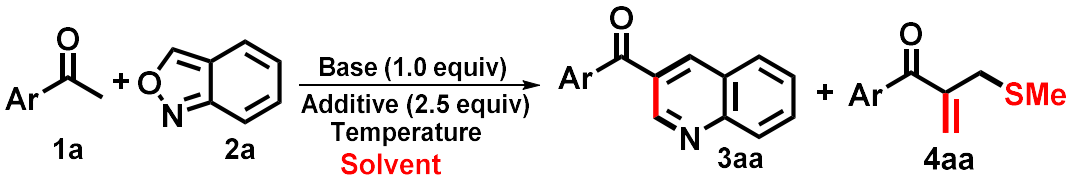
1. General techniques:

All reagents were purchased from Sigma Aldrich, Alfa Aesar and TCI were used without further purification. All experiments were carried out under nitrogen atmosphere. All the solvents used for the reaction were distilled before use. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^{1}H and ^{13}C NMR spectra were recorded with 300, 400 and 500 MHz NMR instruments with tertramethylsilane (TMS) as an internal standard. High-resolution mass spectra (ESI-HRMS) were recorded on ESI-QTOP mass spectrometer. Chemical shifts (δ =) are reported in ppm using TMS as an internal standard, and spin -spin coupling constants (*J*) are given in Hz. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units.

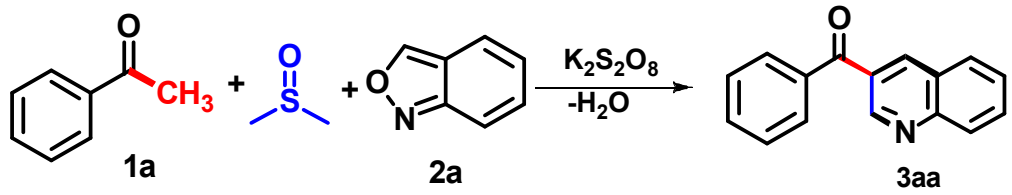
2. Optimization of reaction conditions (Table-S1)[a]



Entry	Additive	Base	Solvent	Temp/[°C]	Yield(%)[b]	
					3aa	4aa
1	$K_2S_2O_8$	DABCO	DMSO	rt	n.o.	n.o
2	$K_2S_2O_8$	DABCO	DMSO	60	n.o.	n.o.
3	$K_2S_2O_8$	DABCO	DMSO	120	26	45
4	$K_2S_2O_8$	DBU	DMSO	120	21	26
5	$K_2S_2O_8$	Et_3N	DMSO	120	11	15
6	$K_2S_2O_8$	K_2CO_3	DMSO	120	54	trace
7	$K_2S_2O_8$	Cs_2CO_3	DMSO	120	51	trace
8	$K_2S_2O_8$	NaOAc	DMSO	120	43	trace
9	$K_2S_2O_8$	-	DMSO	120	76	n.o.
10	$(NH_4)_2S_2O_8$	-	DMSO	120	37	n.o
11	$KHSO_4$	-	DMSO	120	n.o	n.o.
12	TBHP	-	DMSO	120	n.o.	n.o.
13	TEMPO	-	DMSO	120	n.o.	n.o.
14	$K_2S_2O_8$	-	DMSO	120	52	n.o.[c]
15	$K_2S_2O_8$	-	DMF	120	26	n.o.
16	$K_2S_2O_8$	-	DMA	120	32	n.o.
17	$K_2S_2O_8$	-	NMP	120	21	n.o.

[a]Reaction was performed using **1a** (1.0 mmol), **2a** (1.1 mmol), DMSO (2.0 mL) and additive (2.5 mmol) under nitrogen, 24 h. [b]Isolated yield. [c]When (1.5 equiv) of $K_2S_2O_8$ was used.

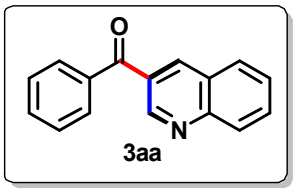
3. General experimental procedure for the synthesis of quinolines (3aa):



To a solution of acetophenone **1a** (0.12 mL, 1.0 mmol) and anthranil **2a** (0.14 gm, 1.2 mmol) in DMSO (1.4 mL) was added $K_2S_2O_8$ (0.68 gm, 2.5 mmol) at room temperature under argon atmosphere. The temperature of oil bath was increased up to 120 °C and mixture was stirred at same temperature for another 24 h. The reaction mixture was then allowed to attain room temperature and diluted with ethyl acetate (10 mL). The organic layer was washed with water (10 mL), sodium bicarbonate (10 mL) and brine (10 mL). The organic layer was further dried over anhydrous sodium sulphate and solvent was evaporated under reduced pressure to get crude product which was purified by column chromatography using 100-200 mesh silica gel.

4. Spectral data of compounds obtained in this study:

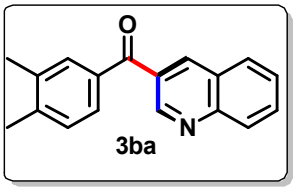
Phenyl(quinolin-3-yl)methanone (3aa):[1]



The title compound was prepared according to general procedure on 1.0 mmol scale.

A white solid (170 mg, 76%); m.p. 74 -75 °C, {Lit 73 – 75 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.33 (d, *J* = 2.2 Hz, 1H), 8.56 – 8.55 (m, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.69 – 7.61 (m, 2H), 7.54 7.55 (dd, *J*=9.6, 5.4, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 194.72, 150.11, 149.05, 139.19, 136.96, 133.18, 132.90, 132.11, 130.07, 129.17, 128.72, 127.79, 126.72; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{12}NO$ [M+H] is 234.09134 and found 234.09123.

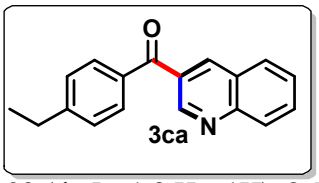
(3,4-dimethylphenyl)(quinolin-3-yl)methanone (3ba):



The title compound was prepared according to general procedure on 0.3 mmol scale.

A white solid, (57 mg, 73%); white solid, **^{1}H NMR (500 MHz, $CDCl_3$)** 9.29 (d, *J* = 2.1 Hz, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.83 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.66 (s, 1H), 7.62 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 194.73, 150.36, 149.29, 142.80, 138.56, 137.19, 134.75, 131.63, 131.11, 130.58, 129.76, 129.40, 129.08, 127.97, 127.48, 126.68, 20.07, 19.77; **HRMS** (ESI, Orbitrap) calcd for $C_{18}H_{16}NO$ [M+H] is 262.12264 and found 262.12254.

(4-ethylphenyl)(quinolin-3-yl)methanone (3ca):

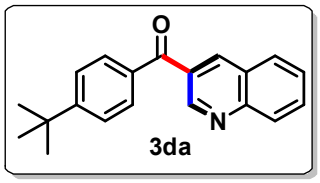


The title compound was prepared according to general procedure on 0.3 mmol scale.

A white solid (58 mg, 74%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.32 (d, *J* = 1.8 Hz, 1H), 8.56 (d, *J* = 1.7 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 194.58, 150.41, 150.24, 149.42, 138.61, 134.62, 131.71, 130.48, 130.41,

129.51, 129.12, 128.20, 127.55, 126.69, 29.05, 15.22; **HRMS** (ESI, Orbitrap) calcd for $C_{18}H_{16}NO$ [M+H] is 262.12264 and found 262.12268.

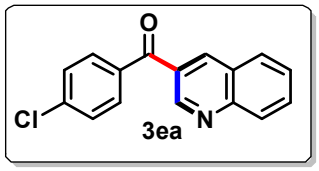
(4-(*tert*-butyl)phenyl)(quinolin-3-yl)methanone (3da):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (62 mg, 72%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.33 (d, *J* = 2.2 Hz, 1H), 8.57 (d, *J* = 2.9 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.65 – 7.61 (m, 1H), 7.58 – 7.55 (m, 2H), 1.39 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 194.49, 156.98, 150.36, 149.35, 138.61, 134.27, 131.68, 130.39, 130.11, 129.44, 129.09, 127.51, 126.64, 125.61, 35.21, 31.10; **HRMS** (ESI, Orbitrap) calcd for $C_{20}H_{20}NO$ [M+H] is 290.15394 and found 290.15399.

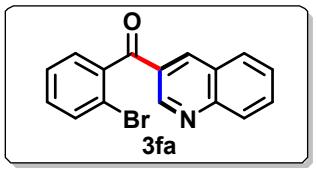
(4-chlorophenyl)(quinolin-3-yl)methanone (3ea):[2]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (63 mg, 79%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.28 (s, 1H), 8.52 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.96 (m, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.50, 149.98, 149.42, 139.54, 138.64, 135.21, 131.94, 131.31, 129.65, 129.42, 129.08, 128.93, 127.65, 126.46; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}ClNO$ [M+H] is 268.05237 and found 268.05343.

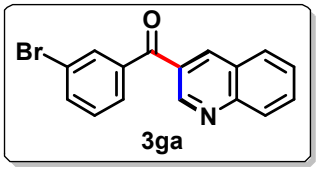
(2-bromophenyl)(quinolin-3-yl)methanone (3fa):[3]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (73 mg, 78%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.35 (d, *J* = 2.1 Hz, 1H), 8.48 (d, *J* = 1.7 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.82 (m, 2H), 7.71 (dd, *J* = 7.9, 2.5 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.54 – 7.37 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 194.63, 150.11, 139.68, 135.07, 133.52, 132.46, 131.88, 129.57, 129.33, 127.69, 127.62, 125.57, 125.35, 119.69, 113.21; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}BrNO$ [M+H] is 312.00185 and found 312.00189.

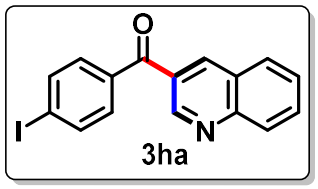
(3-bromophenyl)(quinolin-3-yl)methanone (3ga):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (72 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.31 (d, *J* = 2.2 Hz, 1H), 8.56 (d, *J* = 1.9 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.01 (t, *J* = 1.8 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.88 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.66 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 193.43, 150.11, 149.65, 138.94, 138.89, 135.96, 132.77, 132.18, 130.23, 129.58, 129.48, 129.27, 128.55, 127.80, 126.58, 123.03; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}BrNO$ [M+H] is 312.00185 and found 312.00205.

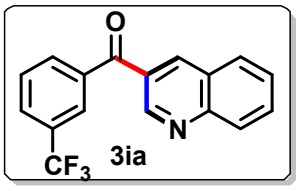
(4-iodophenyl)(quinolin-3-yl)methanone (3ha):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (85 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.30 (d, *J* = 1.5 Hz, 1H), 8.53 (d, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 – 7.84 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.13, 150.13, 149.61, 138.81, 138.02, 136.33, 132.09, 131.38, 129.58, 129.20, 127.78, 126.58, 101.02; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}INO$ [M+H] is 359.98798 and found 359.98842.

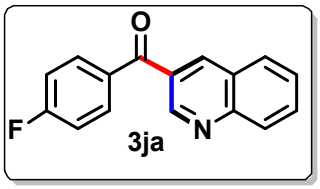
quinolin-3-yl(3-(trifluoromethyl)phenyl)methanone (3ia):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (70 mg, 78%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.33 (d, *J* = 2.2 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.25 – 8.21 (m, 1H), 8.15 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.99 – 7.87 (m, 3H), 7.73 – 7.65 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 193.51, 150.02, 149.74, 138.99, 137.75, 135.05, 133.10, 132.29, 131.33, 129.63, 129.51, 129.48 (*J* = 4.4 Hz), 129.35, 129.27, 127.88, 126.69 (q, *J* = 14.7 Hz), 125.45 (d, *J* = 21.9 Hz), 113.21; **HRMS** (ESI, Orbitrap) calcd for $C_{17}H_{11}F_3NO$ [M+H] is 302.07873 and found 302.07882.

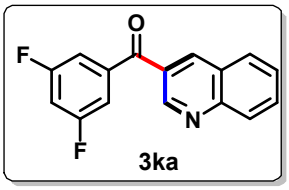
(4-fluorophenyl)(quinolin-3-yl)methanone (3ja):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (59 mg, 79%); white solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.27 (d, *J* = 1.5 Hz, 1H), 8.51 (d, *J* = 1.5 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.80 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 193.23, 166.64 (d, *J* = 255.5 Hz), 150.01, 149.36, 138.52, 133.22, 132.59 (d, *J* = 9.3 Hz), 131.85, 129.89, 129.39, 129.04, 127.62, 126.48, 115.81 (d, *J* = 21.9 Hz); **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}FNO$ [M+H] is 252.08192 and found 252.08192.

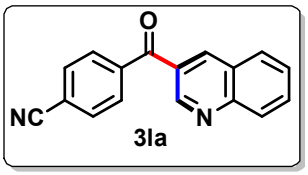
(3,5-difluorophenyl)(quinolin-3-yl)methanone (3ka):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (65 mg, 80%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.30 (s, 1H), 8.54 (d, *J* = 1.9 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.940 - 7.86 (m, 1H), 7.69 – 7.64 (m, 1H), 7.39 – 7.34 (m, 2H), 7.10 (tt, *J* = 8.5, 2.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 192.20, 162.86 (dd, *J* = 251.19, 11.61 Hz), 149.82, 139.89, 138.96, 132.38, 129.57, 129.26, 128.92, 127.92, 126.46, 113.07 (dd, *J* = 18.9, 8.45 Hz), 112.89 (d, *J* = 18.8 Hz), 108.65 (d, *J* = 24.9 Hz); **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{10}F_2NO$ [M+H] is 270.07250 and found 270.07325.

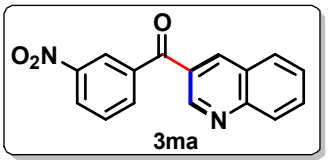
4-(quinoline-3-carbonyl)benzonitrile (3la):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (63 mg, 82%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.32 (d, *J* = 2.1 Hz, 1H), 8.54 (d, *J* = 2.1 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.89 (m, 4H), 7.89 – 7.84 (m, 2H), 7.72 – 7.65 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 193.40, 149.89, 149.79, 140.51, 139.16, 132.54, 130.27, 129.63, 129.30, 128.89, 128.01, 126.48, 117.83, 116.37; **HRMS** (ESI, Orbitrap) calcd for $C_{17}H_{11}N_2O$ [M+H] is 259.08659 and found 259.08661.

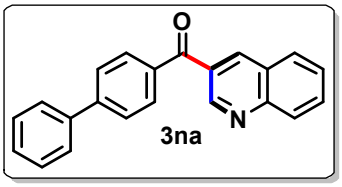
(3-nitrophenyl)(quinolin-3-yl)methanone (3ma):[1]



The title compound was prepared according to general procedure on 0.3 mmol scale.

Yellow solid, (65 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.32 (d, *J* = 2.0 Hz, 1H), 8.69 (s, 1H), 8.57 (s, 1H), 8.50 (dd, *J* = 4.6, 3.6 Hz, 1H), 8.25 – 8.17 (m, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 192.55, 149.84, 148.35, 139.04, 138.48, 135.36, 132.51, 130.04, 129.65, 129.32, 128.83, 128.01, 127.31, 126.49, 124.65; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{11}N_2O_3$ [M+H] is 279.07642 and found 279.07724.

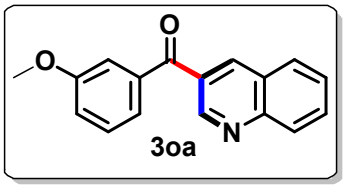
[1,1'-biphenyl]-4-yl(quinolin-3-yl)methanone (3na):[ref]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (70 mg, 76%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.36 (s, 1H), 8.59 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.91 (m, 3H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.59 (m, 3H), 7.55 – 7.39 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 194.42, 150.34, 149.46, 145.90, 139.70, 138.76, 135.66, 131.87, 130.75, 130.27, 129.51, 129.20, 129.06, 128.42, 127.65, 127.33, 126.67; **HRMS** (ESI, Orbitrap) calcd for $C_{22}H_{16}NO$ [M+H] is 310.12264 and found 31012264.

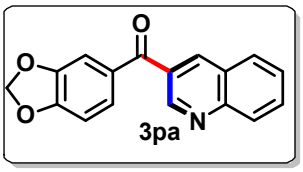
(3-methoxyphenyl)(quinolin-3-yl)methanone (3oa):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (53 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.33 (d, *J* = 2.0 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.86 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.47 – 7.37 (m, 3H), 7.22 – 7.19 (m, 1H), 3.89 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 194.53, 159.76, 150.17, 149.29, 138.76, 138.20, 131.78, 129.49, 129.32, 129.09, 127.52, 122.73, 119.44, 114.14, 55.43; **HRMS** (ESI, Orbitrap) calcd for $C_{17}H_{14}NO_2$ [M+H] is 64.10191 and found 264.10191.

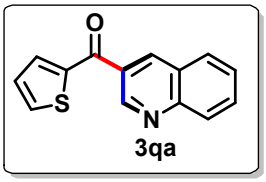
Benzo[1,3]dioxol-5-yl(quinolin-3-yl)methanone (3pa):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (56 mg, 67%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.26 (s, 1H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.85 - 7.82 (m, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.38 (m, 2H), 6.92 – 6.87 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 193.03, 152.07, 150.13, 149.24, 148.30, 138.20, 131.62, 131.42, 129.41, 129.01, 127.54, 127.01, 109.64, 107.93, 102.03, 77.32, 77.00, 76.68; **HRMS** (ESI, Orbitrap) calcd for $C_{17}H_{12}NO_3$ [M+H] is 278.08117 and found 278.08125.

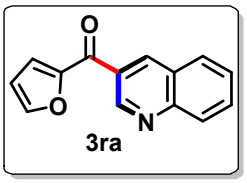
Quinolin-3-yl(thiophen-2-yl)methanone (3qa):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (52 mg, 72%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.28 (s, 1H), 8.59 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.79 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.74 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.65 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.16 (dd, *J* = 4.9, 3.8 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 186.17, 149.63, 149.47, 143.24, 137.80, 135.11, 131.82, 130.75, 129.52, 129.11, 128.37, 127.72, 126.72; **HRMS** (ESI, Orbitrap) calcd for $C_{14}H_{10}NOS$ [M+H] is 240.04776 and found 240.04763.

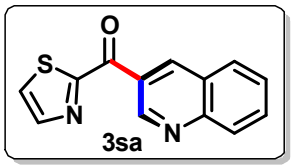
Furan-2-yl(quinolin-3-yl)methanone (3ra):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (51 mg, 73%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.47 (s, 1H), 8.85 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.86 (ddd, *J* = 6.9, 4.9, 1.5 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.70 – 7.62 (m, 1H), 7.45 – 7.34 (m, 1H), 6.68 (dd, *J* = 3.5, 1.7 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.39, 152.43, 149.81, 149.54, 147.51, 138.36, 131.92, 129.69, 129.48, 129.29, 127.60, 126.79, 120.81, 112.71; **HRMS** (ESI, Orbitrap) calcd for $C_{14}H_{10}NO_2$ [M+H] is 224.07060 and found 224.07046.

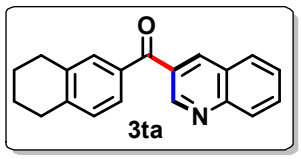
Quinolin-3-yl(thiazol-2-yl)methanone (3sa):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (60 mg, 84%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.78 (d, *J* = 2.1 Hz, 1H), 9.58 (d, *J* = 1.9 Hz, 1H), 8.19 (t, *J* = 6.4 Hz, 2H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.88 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.81 (d, *J* = 3.1 Hz, 1H), 7.66 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 182.31, 167.22, 150.50, 149.48, 145.08, 141.23, 132.35, 129.79, 129.19, 127.59, 127.42, 126.80, 126.64; **HRMS** (ESI, Orbitrap) calcd for $C_{14}H_{10}NO_2$ [M+H] is 241.04301 and found 241.04374.

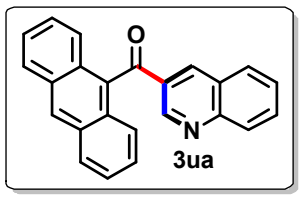
Quinolin-3-yl(5,6,7,8-tetrahydronaphthalen-2-yl)methanone (3ta):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (63 mg, 74%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.31 (d, *J* = 1.8 Hz, 1H), 8.55 (d, *J* = 1.7 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.66 – 7.56 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 1H), 2.90 – 2.78 (m, 4H), 1.86 – 1.82 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 194.84, 150.44, 149.36, 143.45, 138.60, 137.79, 134.42, 131.68, 131.01, 130.66, 129.48, 129.38, 129.14, 127.52, 127.32, 126.75, 29.74, 29.42, 22.95, 22.83; **HRMS** (ESI, Orbitrap) calcd for $C_{20}H_{18}NO$ [M+H] is 288.13829 and found 288.13810.

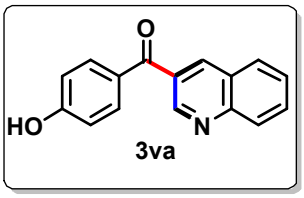
Anthracen-9-yl(quinolin-3-yl)methanone (3ua):



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (71 mg, 72%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.49 (d, *J* = 1.8 Hz, 1H), 8.65 (s, 1H), 8.33 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.85 - 779 (m, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.44 – 7.39 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 199.03, 150.18, 149.92, 139.92, 132.75, 132.50, 131.10, 130.47, 129.63, 129.57, 129.12, 128.87, 128.70, 127.57, 127.04, 126.91, 125.69, 124.99; **HRMS** (ESI, Orbitrap) $C_{24}H_{16}NO$ [M+H] is 334.12264 and found 334.12273.

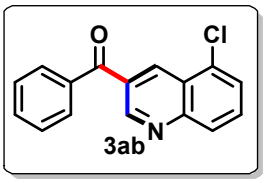
(4-hydroxyphenyl)(quinolin-3-yl)methanone (3va):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (38 mg, 52%); **^{1}H NMR (300 MHz, DMSO d_6)** δ = 9.26 (d, *J* = 1.8 Hz, 1H), 8.94 (d, *J* = 1.5 Hz, 1H), 8.26 (dd, *J* = 16.4, 8.3 Hz, 2H), 8.02 (t, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 3H), 6.97 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (75 MHz, DMSO d_6)** δ = 191.82, 162.71, 148.57, 145.75, 140.05, 132.85, 130.92, 129.83, 128.24, 127.35, 126.64, 115.58.

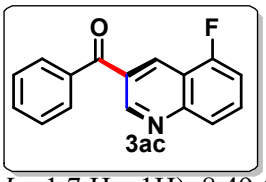
(5-chloroquinolin-3-yl)(phenyl)methanone (3ab):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (54 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.30 (s, 1H), 8.47 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.91 (s, 1H), 7.88 – 7.85 (m, 2H), 7.81 – 7.77 (m, 1H), 7.71 – 7.65 (m, 1H), 7.55 – 7.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 194.55, 150.53, 147.85, 137.67, 136.78, 133.49, 133.33, 132.69, 131.15, 130.87, 130.08, 128.77, 127.64, 127.32; **HRMS** (ESI, Orbitrap) $C_{16}H_{11}ClNO$ [M+H] is 268.05273 and found 268.05342.

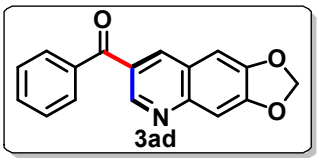
(5-fluoroquinolin-3-yl)(phenyl)methanone (3ac):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (50 mg, 66%)**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.26 (d, *J* = 1.7 Hz, 1H), 8.49 (d, *J* = 1.9 Hz, 1H), 8.19 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.68 – 7.59 (m, 2H), 7.56 – 7.51 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 194.62, 160.89 (d, *J* = 250.5 Hz), 149.59, 146.51, 137.97 (d, *J* = 5.4 Hz), 137.89, 136.78, 133.24, 132.08 (d, *J* = 9.1 Hz), 130.72, 130.02, 128.69, 127.42, 127.35, 122.01 (d, *J* = 25.8 Hz), 111.97 (d, *J* = 21.8 Hz); **HRMS** (ESI, Orbitrap) $C_{16}H_{11}FNO$ [M+H] is 252.08192 and found 252.08281.

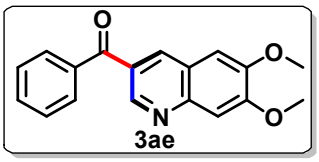
[1,3]dioxolo[4,5-g]quinolin-7-yl(phenyl)methanone (3ad):[4]



The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (55 mg, 66%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.07 (d, *J* = 1.5 Hz, 1H), 8.37 (d, *J* = 1.3 Hz, 1H), 7.82 (dd, *J* = 7.3, 0.7 Hz, 2H), 7.66 – 7.58 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.44 (s, 1H), 7.11 (s, 1H), 6.15 (d, *J* = 0.7 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 194.91, 152.77, 148.70, 148.53, 148.39, 137.30, 132.83, 129.95, 128.67, 128.55, 123.94, 105.85, 103.70, 102.23.

(6,7-dimethoxyquinolin-3-yl)(phenyl)methanone (3ae):[4]

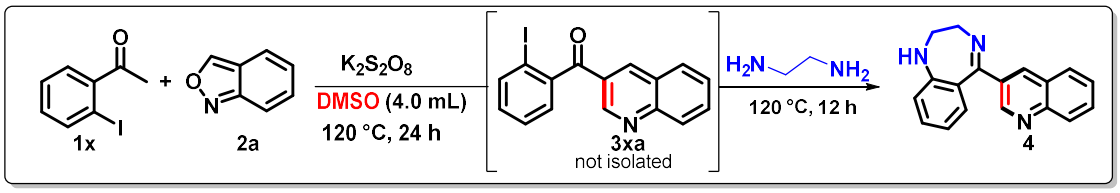


The title compound was prepared according to general procedure on 0.3 mmol scale.

White solid, (56 mg, 64%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.11 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 7.89 - 7.81 (m, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 10.3, 5.0 Hz, 3H), 7.12 (s, 1H), 4.07 (s, 3H), 4.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.05, 154.52, 150.57, 148.48, 147.01, 137.43, 136.95, 132.75, 129.96, 128.55, 122.41, 107.84, 106.05, 56.38, 56.18.

General Proceedure for one pot synthesis of 5-(quinolin-3-yl)-2,3-dihydro-1H-benzo[e][1,4]diazepine (4):[4]

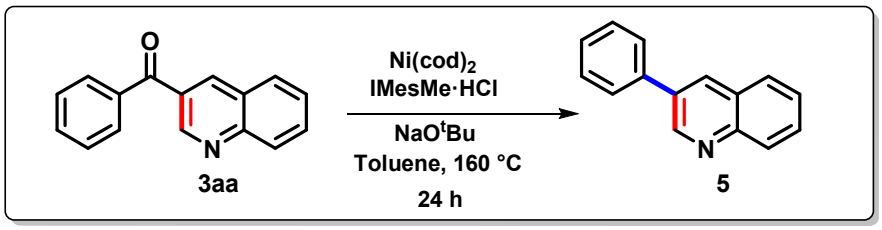
To a solution of acetophenone **1x** (0.25 g, 1.0 mmol) and anthranil **2a** (0.14 g, 1.2 mmol) in DMSO (4.0 mL) was added $K_2S_2O_8$ (0.68 gm, 2.5 mmol) at room temperature under nitrogen atmosphere. The temperature of oil bath was increased up to 120 °C and mixture was stirred at same temperature for another 24 h. The reaction mixture was cooled to room temperature and ethylenediamine (0.67 mL, 10 mmol) was added to it and the mixture was again heated at 120 °C for 12 h. The reaction temperature was cooled down to room temperature and and diluted with ethyl acetate (15 mL). The organic layer was washed with water (15 mL), sodium bicarbonate (15 mL) and brine (15 mL). The organic layer was further dried over anhydrous sodium sulphate and solvent was evaporated under reduced pressure to get crude product which was purified by coloumn chromatography using 100-200 mesh silica gel.



White solid, (139 mg, 51%); m.p. 201 - 203 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.14 (d, *J* = 2.2 Hz, 1H), 8.26 (d, *J* = 1.9 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.76 (m, 1H), 7.55 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.03 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.79 – 6.69 (m, 2H), 4.12 – 4.06 (m, 2H), 3.91 - 3.86 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 170.22, 150.93, 148.32, 136.67, 134.10, 132.30, 131.70, 130.16, 129.19, 128.49, 127.27, 126.90, 120.83, 119.07, 117.76, 77.32, 77.00, 76.68, 53.61, 51.77.

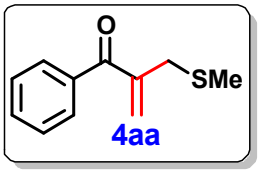
General procedure for Nickel mediated decarbonylation of 3-keto-quinoline:[5]

To a solution of $Ni(cod)_2$ (0.034 g, 0.12 mmol), IMesMe·HCl (0.046 g, 0.12 mmol), NaO^tBu (0.012 g, 0.125 mmol) in anhydrous toluene (0.5 mL) was added a solution of 3-keto quinoline (**3aa**, 0.03 g, 0.12 mmol) in anhydrous toluene 0.5 mL under nitrogen atmosphere at room temperature. The reaction mixture was stirred at room temperature for 10 mins and then refluxed at 160 °C for another 24 hrs. The reaction was allowed to come to room temperature and the crude mixture was filtered through a small pad of celite. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel eluting with a solvent gradient of hexane: ethyl acetate (90:10 changing to 94 : 16, by volume) to give the title product (0.011 g) as a yellow oil.



Yellow oil, (11 mg, 40%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.19 (d, *J* = 2.3 Hz, 1H), 8.30 (d, *J* = 2.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.74 – 7.71(m, 3H), 7.58 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.44 – 7.22 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.96, 147.35, 137.91, 133.89, 133.29, 129.98, 129.44, 129.22, 128.15, 128.04, 127.47, 127.05.

2-((methylthio)methyl)-1-phenylprop-2-en-1-one (4aa):[6]

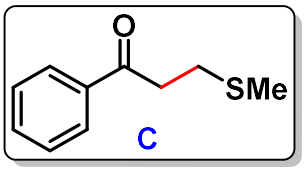


Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.89 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.48 – 7.42 (m, 1H), 5.92 (s, 1H), 5.68 (s, 1H), 3.54 (s, 1H), 2.13 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 196.99, 143.85, 137.53, 132.52, 129.54, 128.31, 125.97, 77.41, 77.09, 76.77, 35.33, 15.56.

General procedure for the synthesis of C and D:

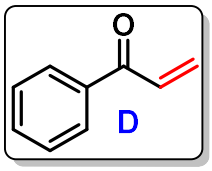
To a solution of acetophenone **1a** (0.12 mL, 1.0 mmol) in DMSO (1.4 mL) was added $K_2S_2O_8$ (0.54 gm, 2.0 mmol) at room temperature under argon atmosphere. The temperature of oil bath was increased up to 120 °C and mixture was stirred at same temperature for another 12 h. The reaction mixture was then allowed to attain room temperature and diluted with ethyl acetate (10 mL). The organic layer was washed with water (10 mL), sodium bicarbonate (10 mL) and brine (10 mL). The organic layer was further dried over anhydrous sodium sulphate and solvent was evaporated under reduced pressure to get crude product which was purified by coloumn chromatography using 100-200 mesh silica gel furnished **C** and **D** in 46% and 20% yields respectively.

3-(methylthio)-1-phenylpropan-1-one (C):[6]



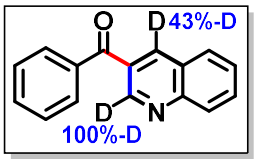
Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.99 – 7.95 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 3.29 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.17 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 196.90, 143.75, 137.44, 132.42, 129.45, 128.22, 125.87, 77.32, 77.00, 76.68, 35.23, 15.47.

1-phenylprop-2-en-1-one (D):[6]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.09 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.37 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.87 (dd, *J* = 10.6, 1.7 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 191.12, 137.30, 133.02, 132.42, 130.23, 128.73, 128.65.

Phenyl(quinolin-3-yl-2,4-d2)methanone (3aa-d_2)



^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.57 (s, 0.42 H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.92 - 7.84 (m, 3H), 7.70 – 7.63 (m, 2H), 7.59 – 7.51 (m, 2H).

5. References:

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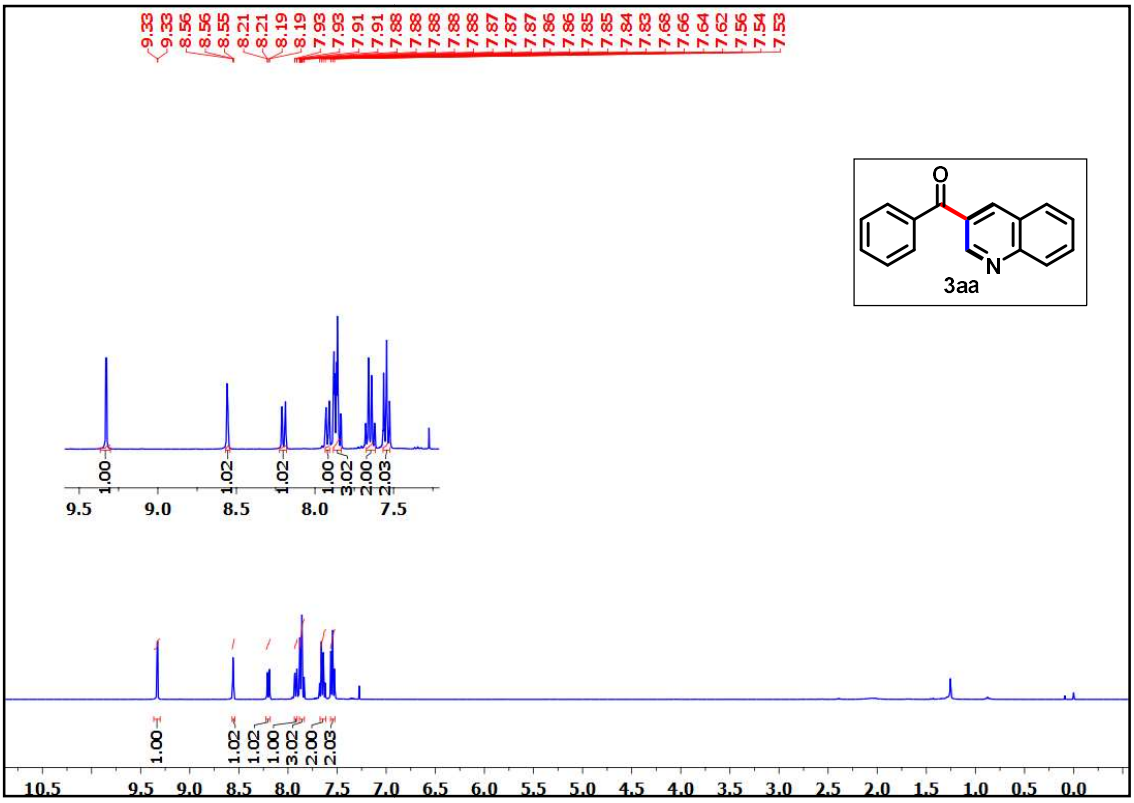
^{1}H and ^{13}C NMR copies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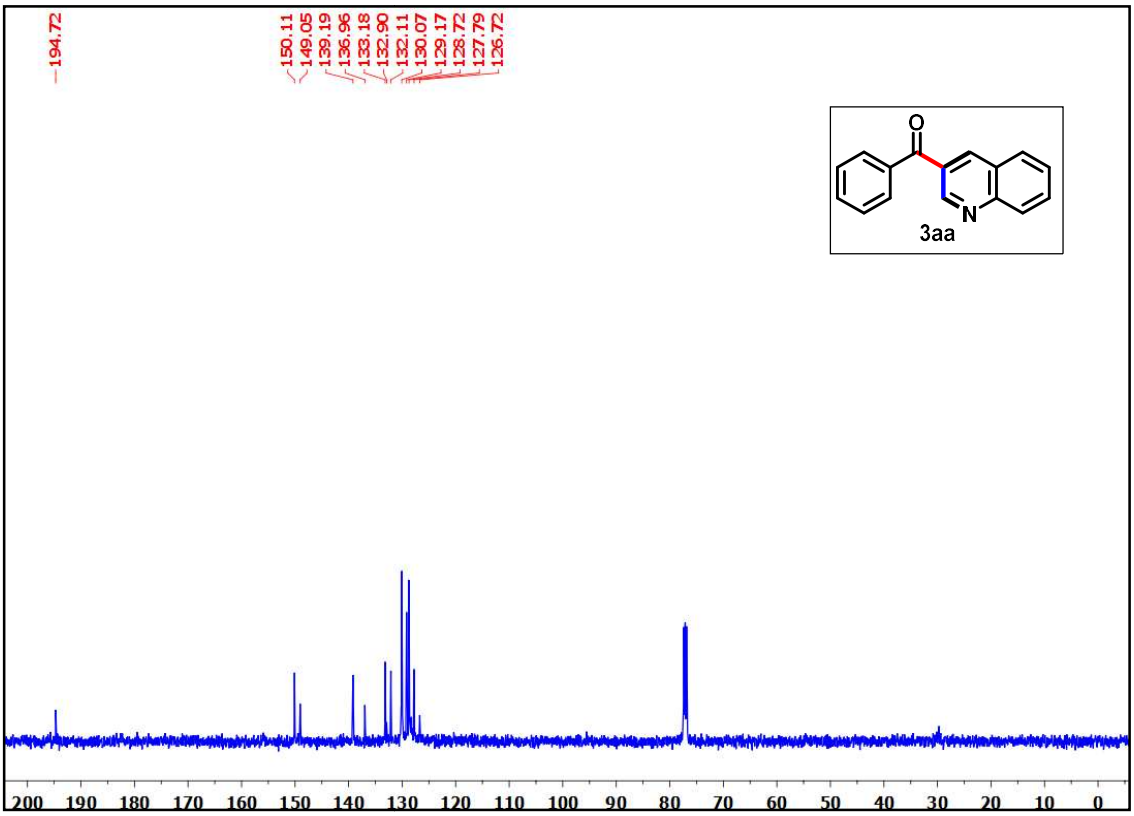
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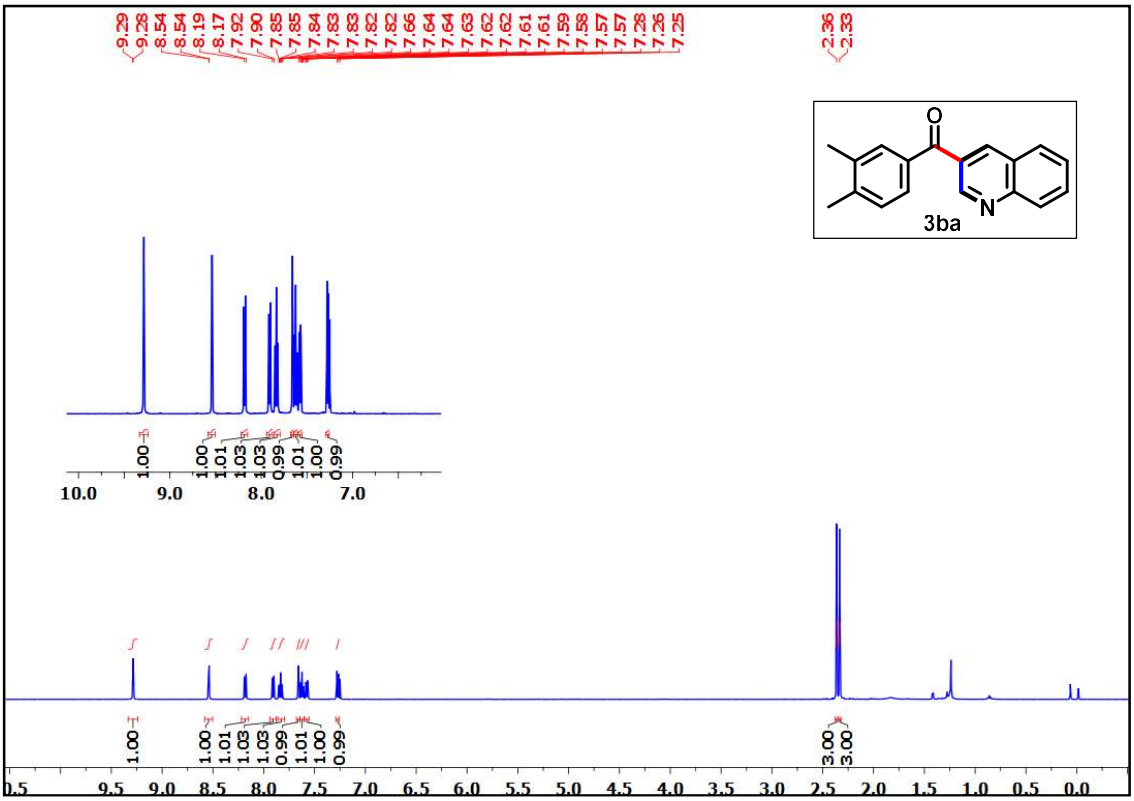
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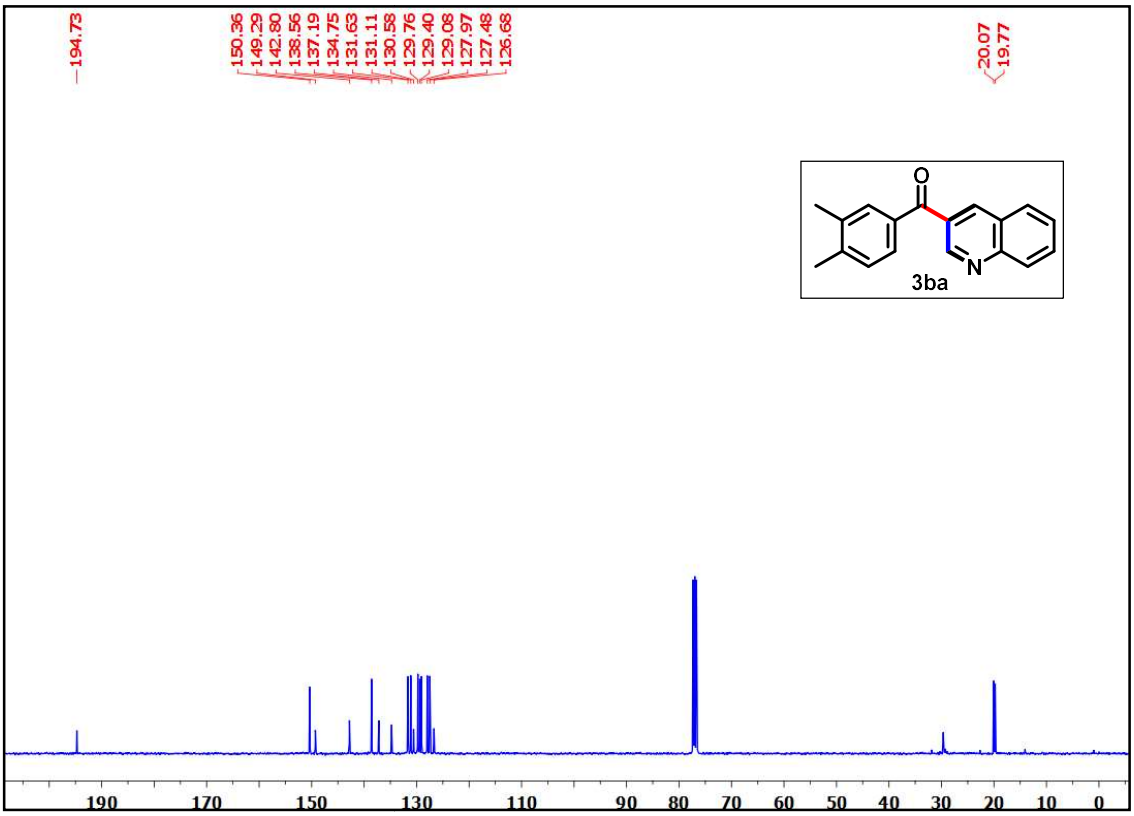
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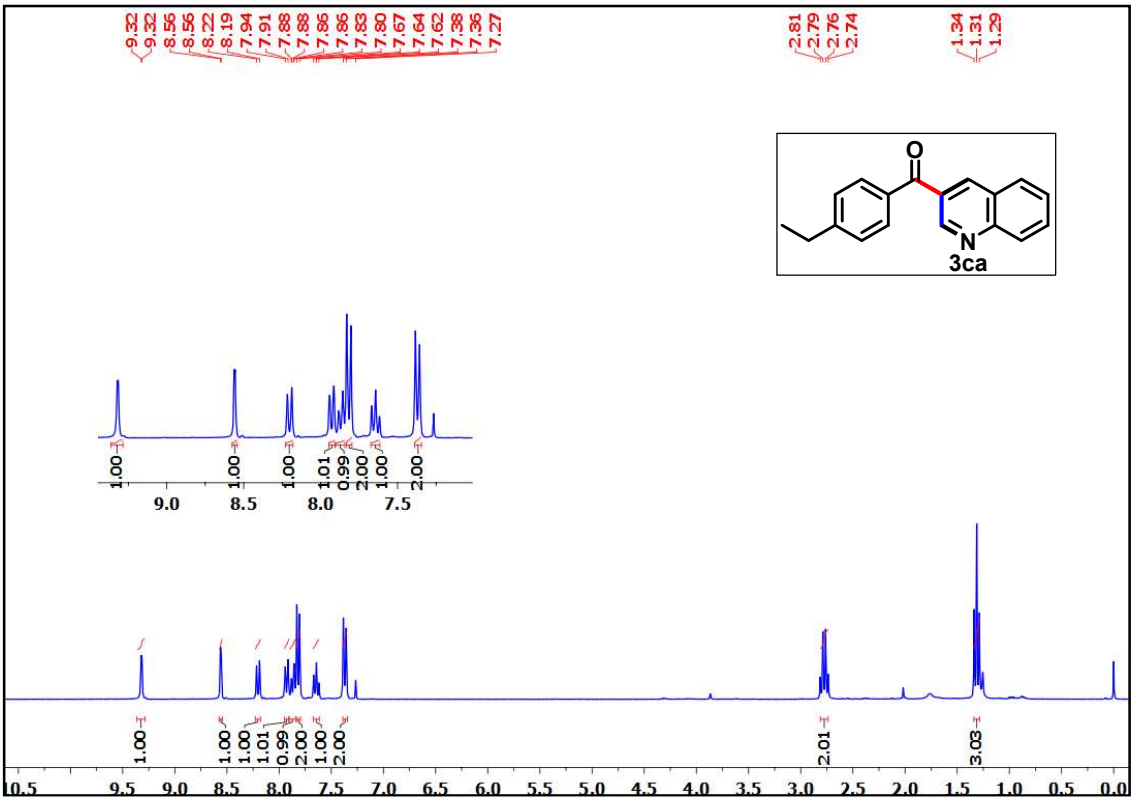
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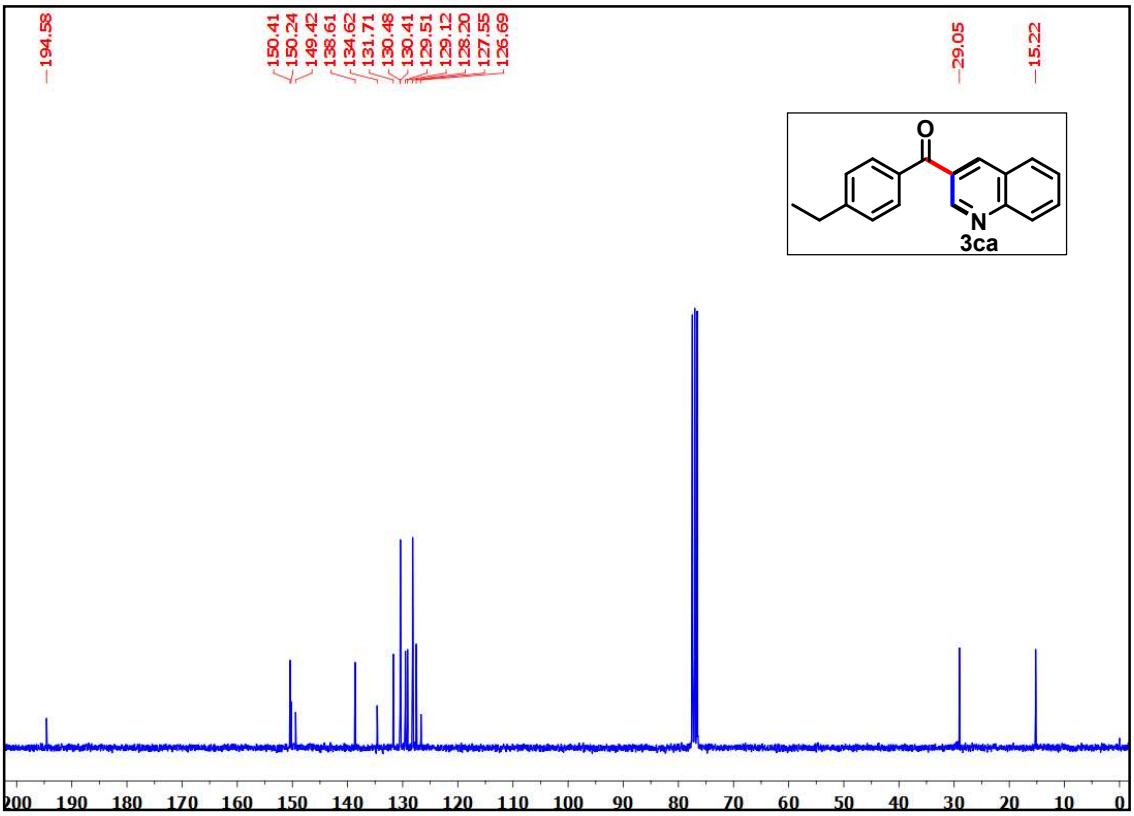
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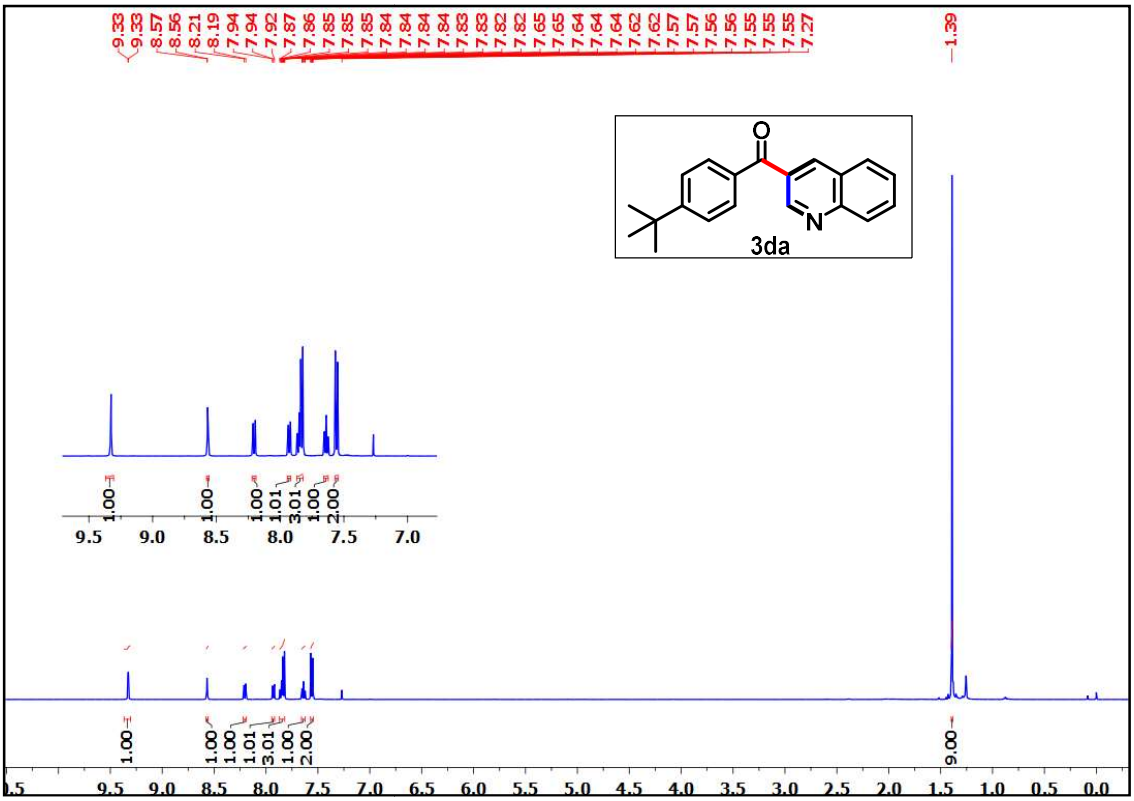
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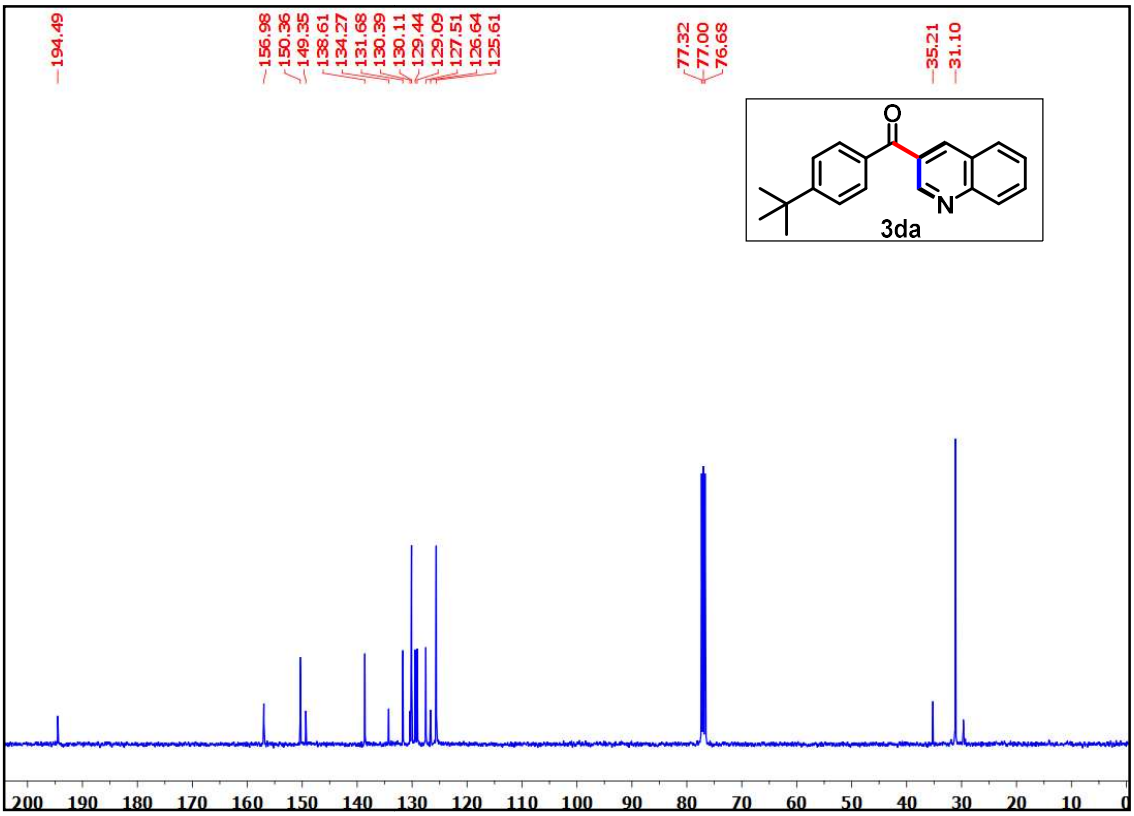
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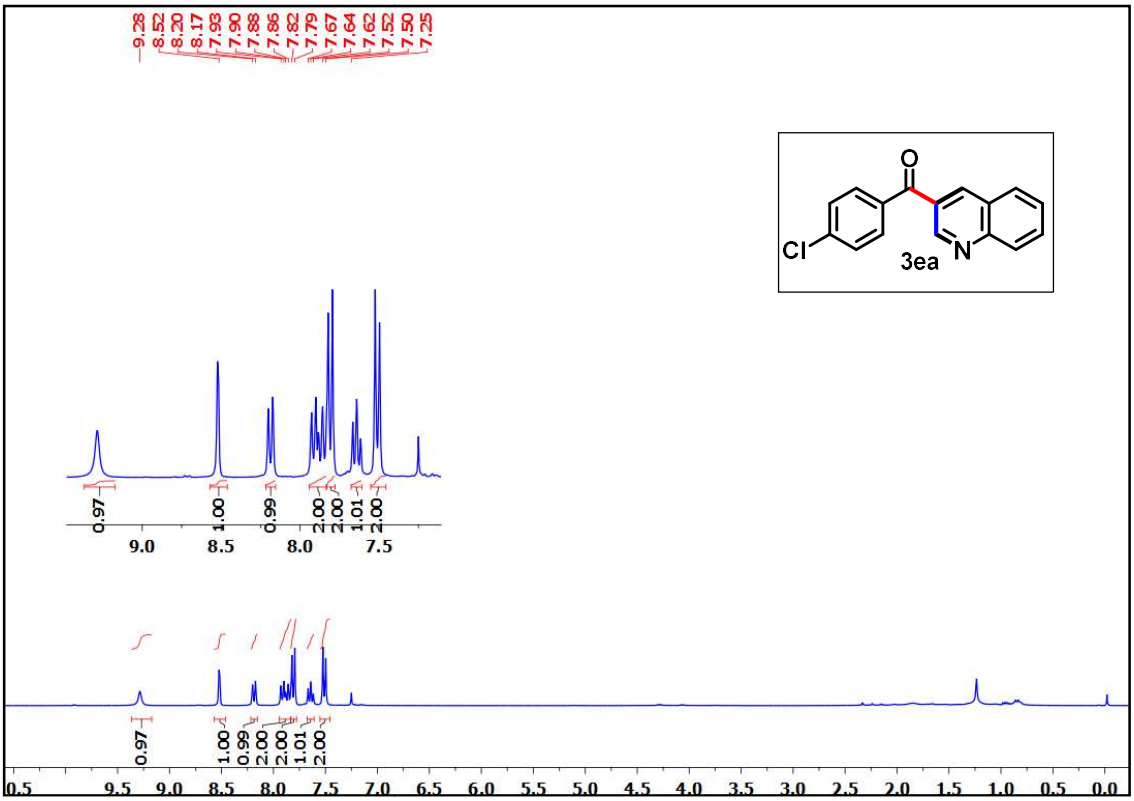
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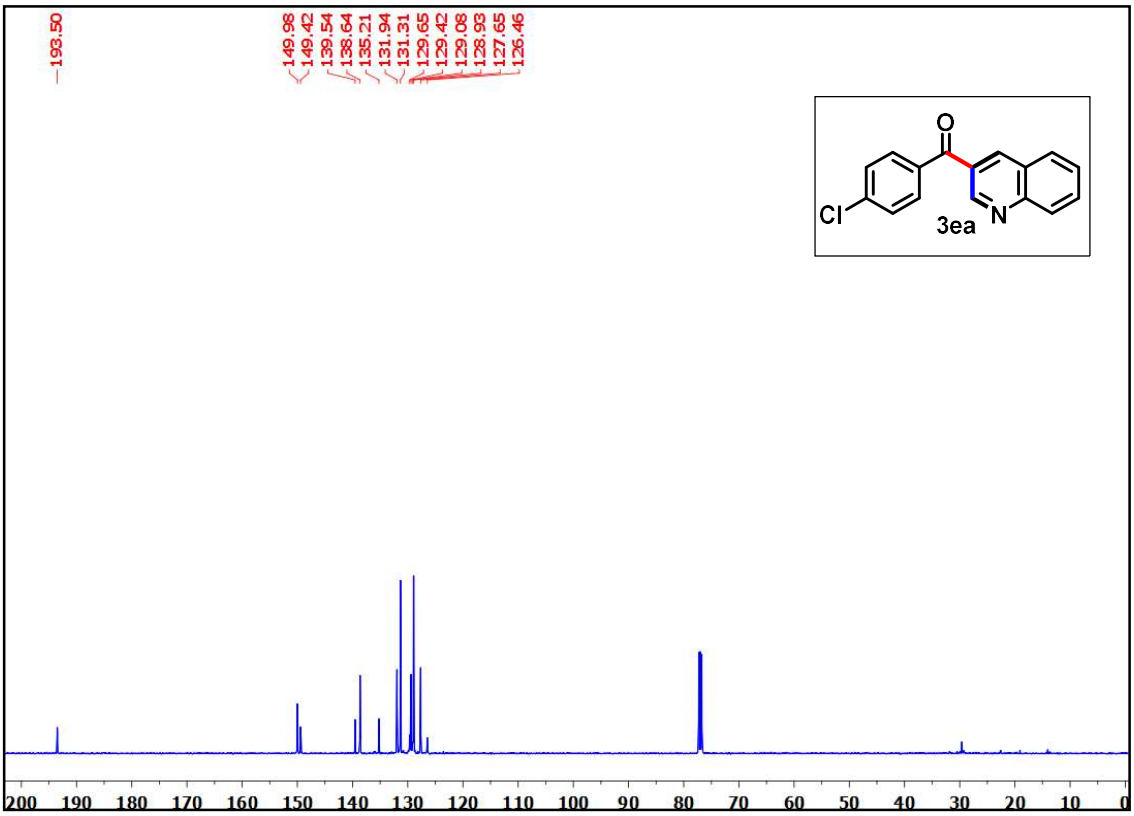
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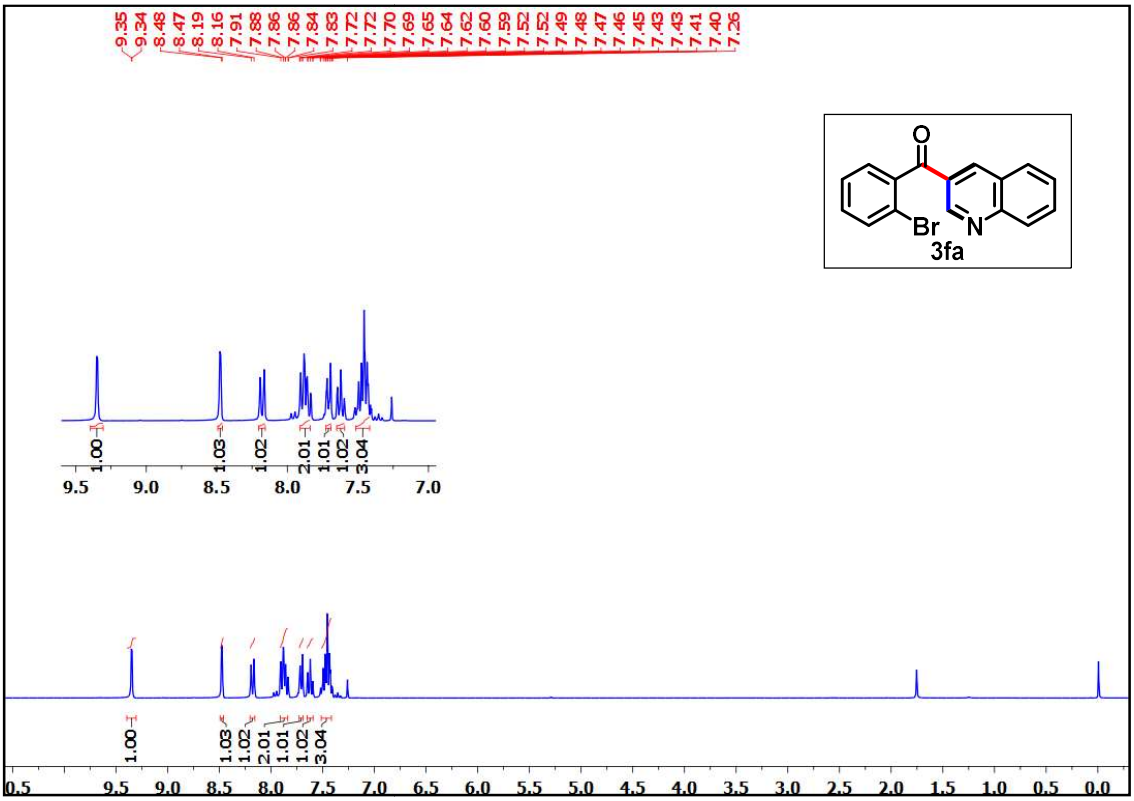
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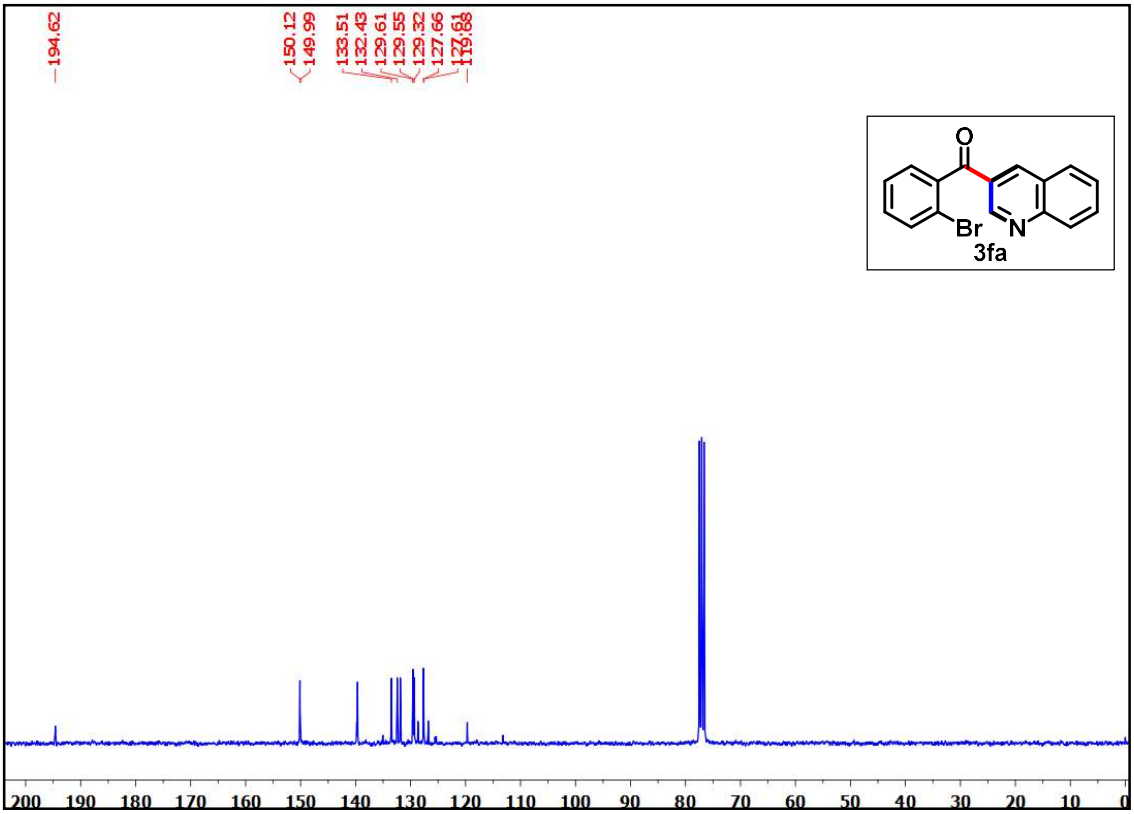
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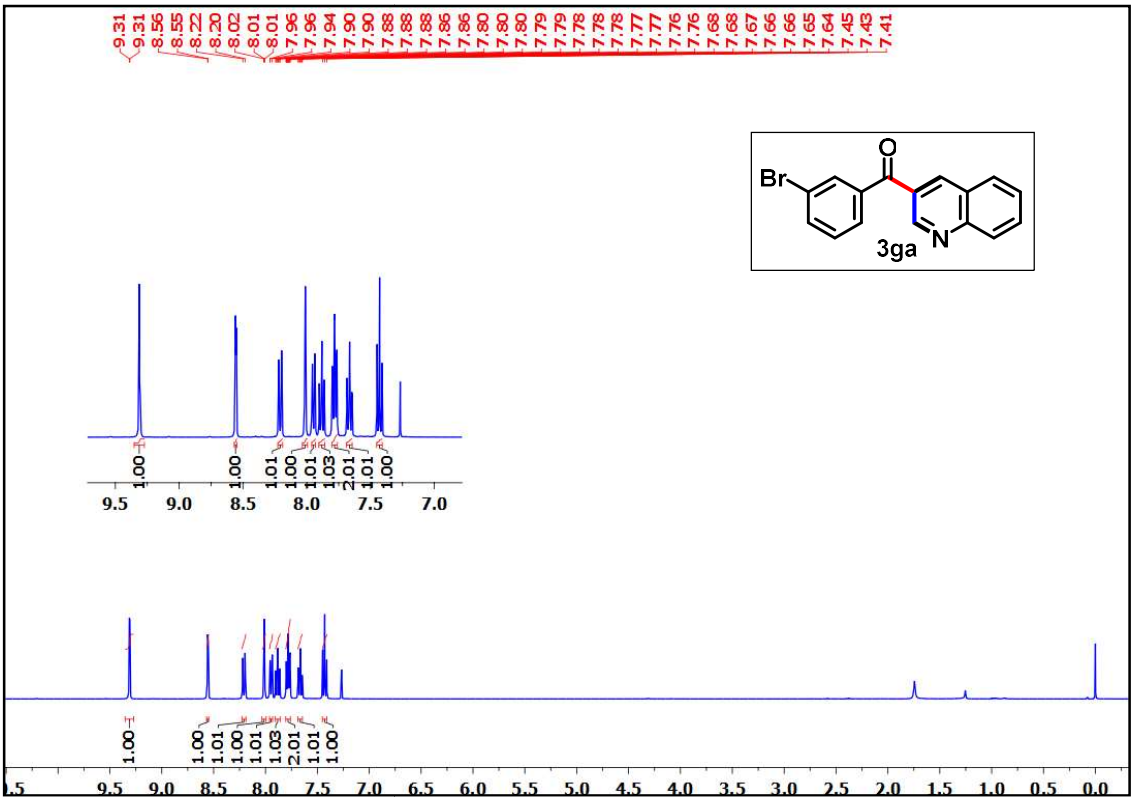
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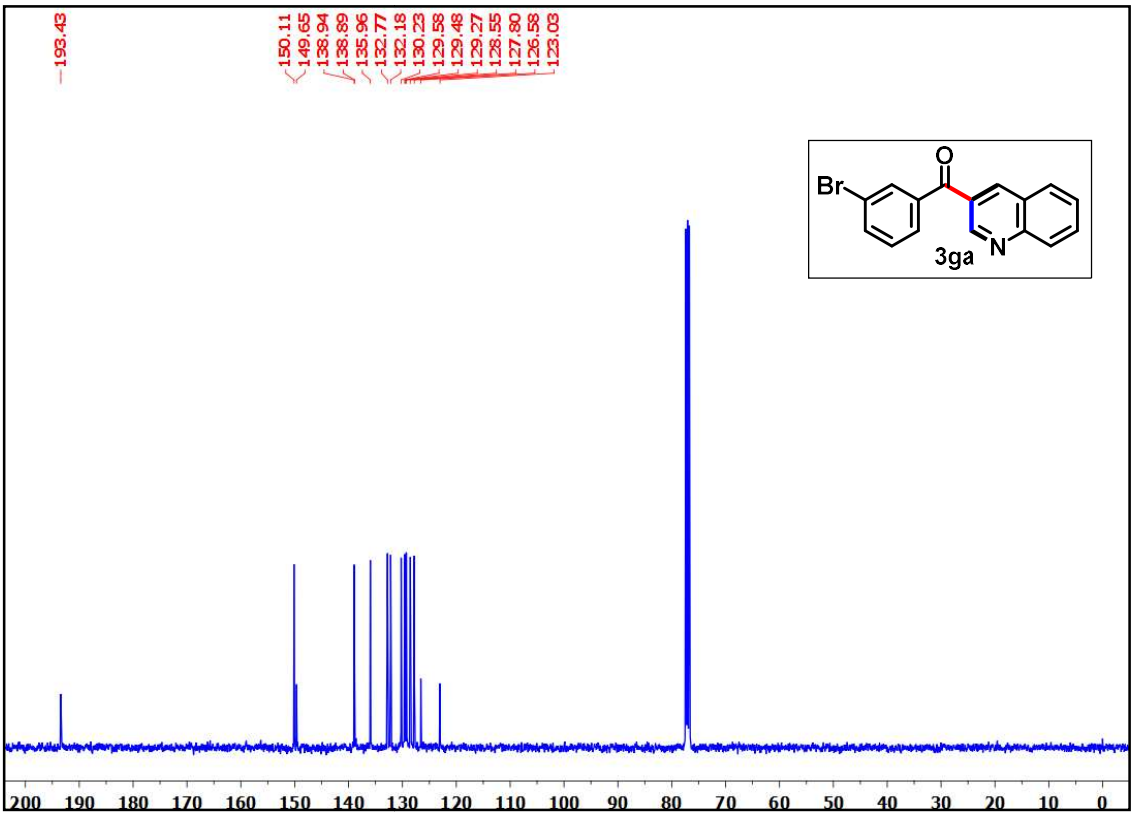
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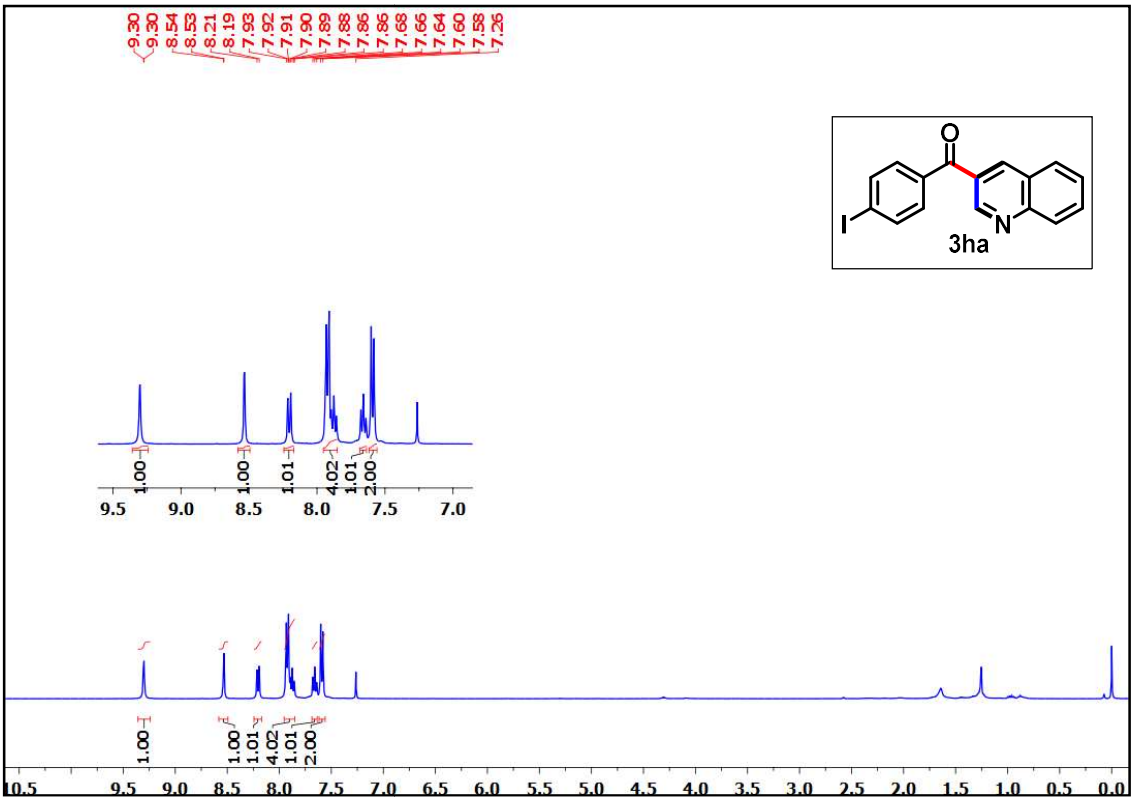
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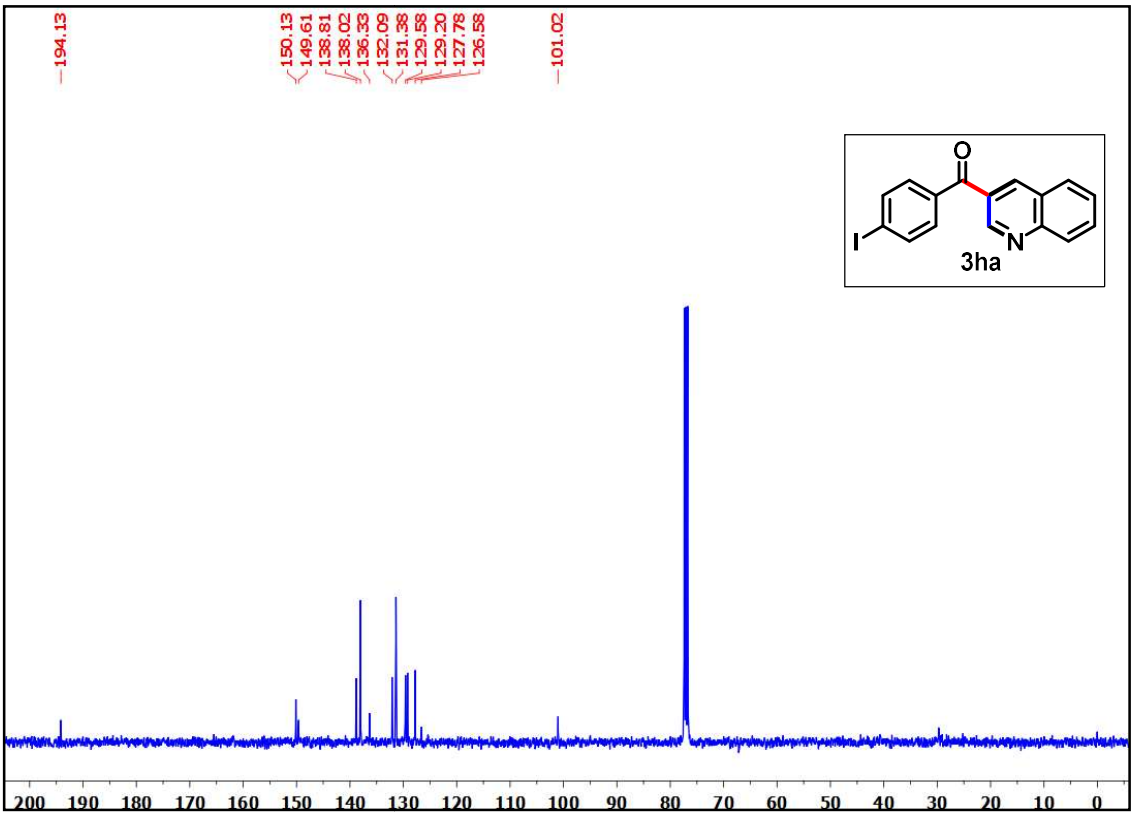
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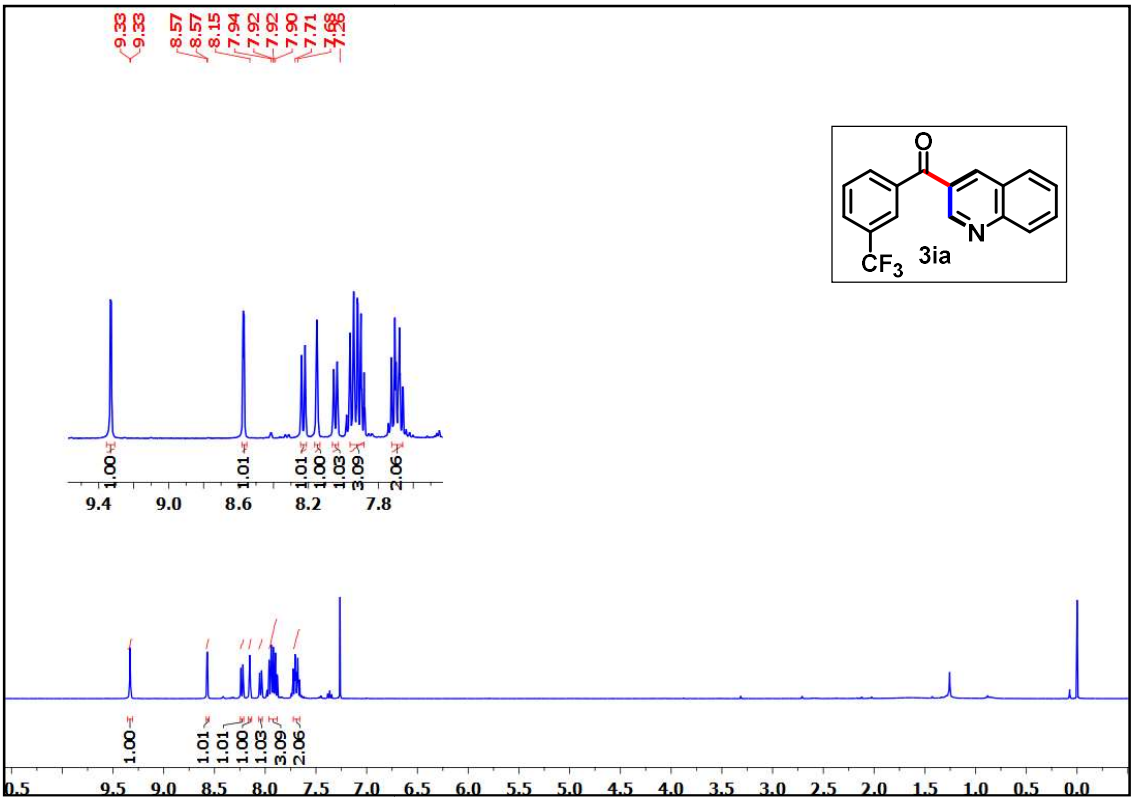
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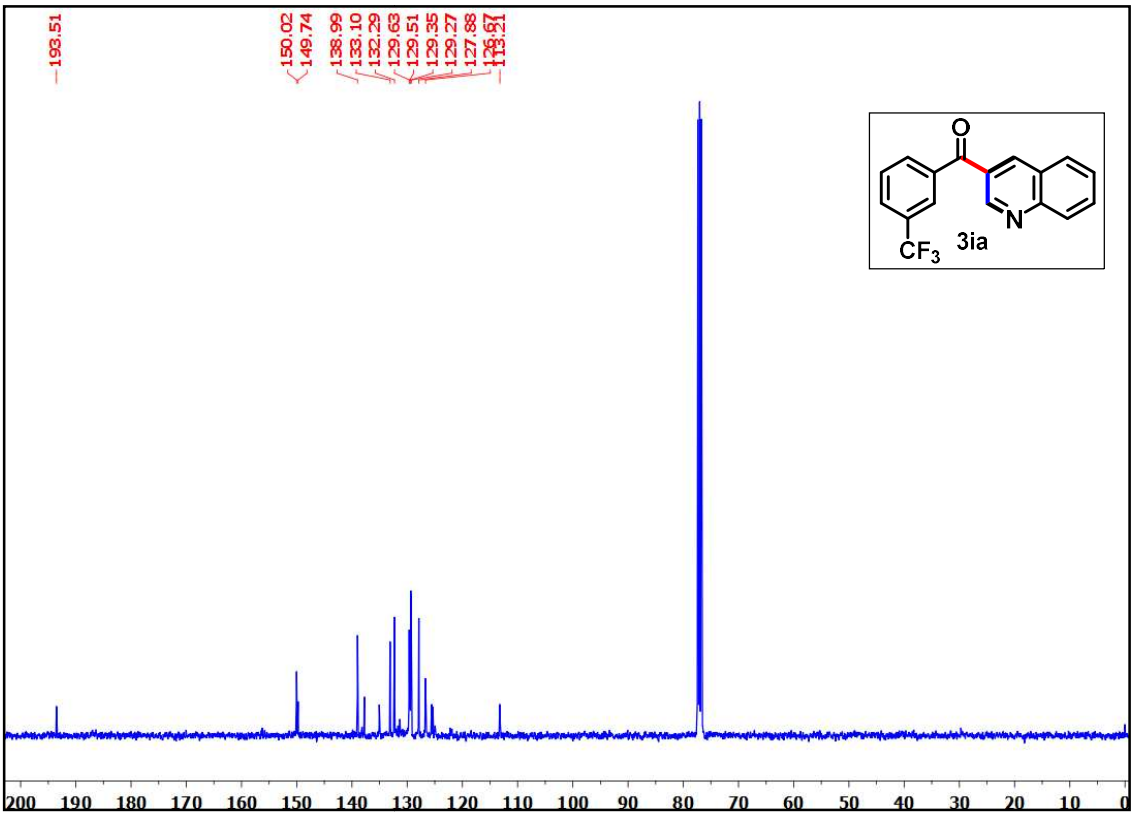
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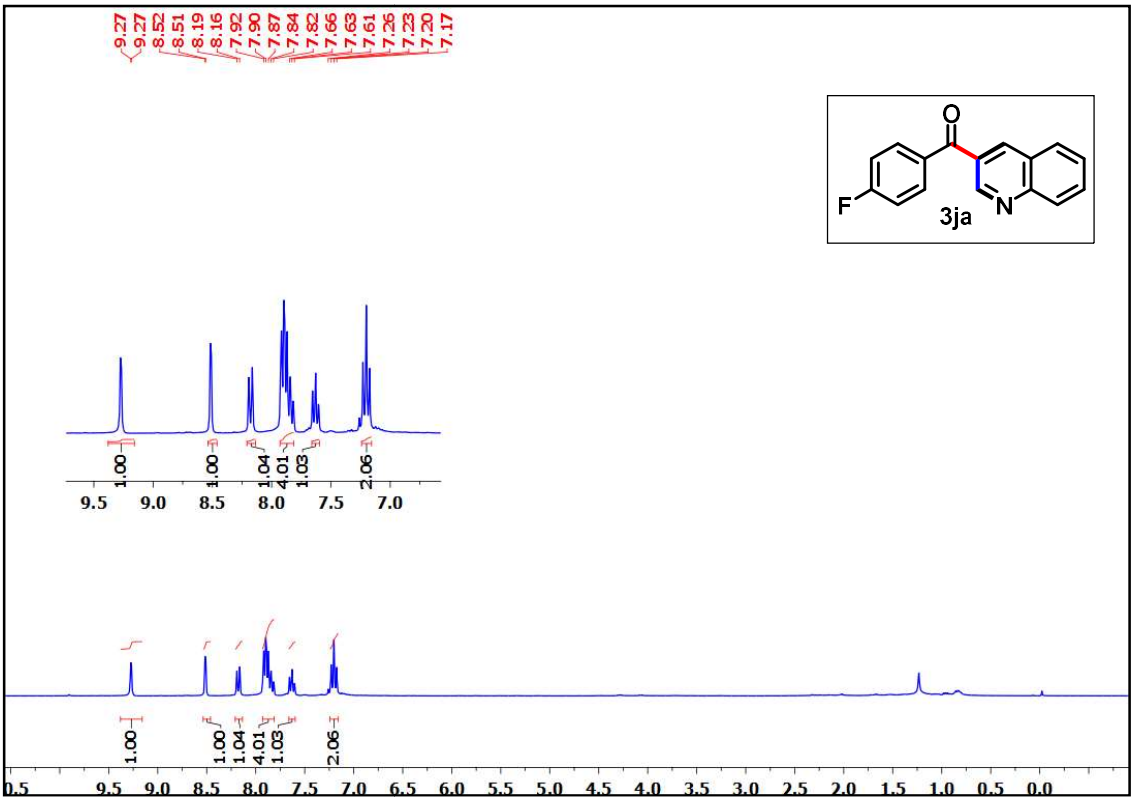
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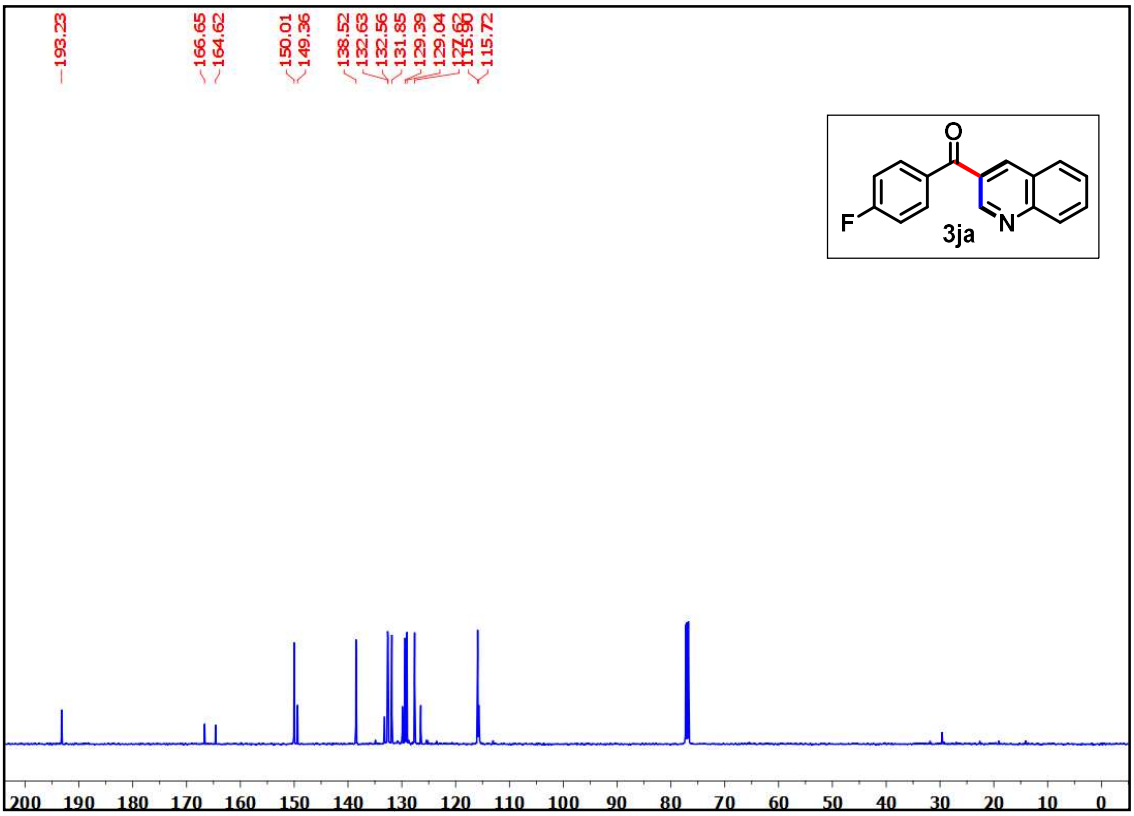
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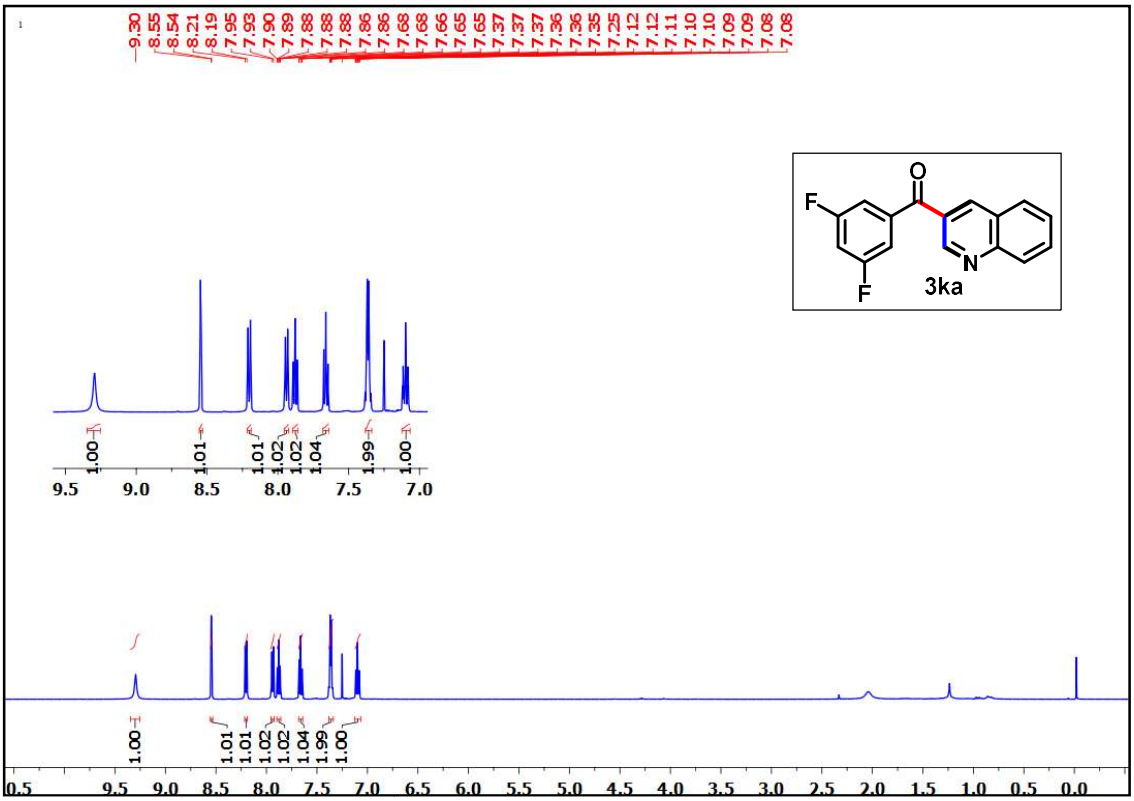
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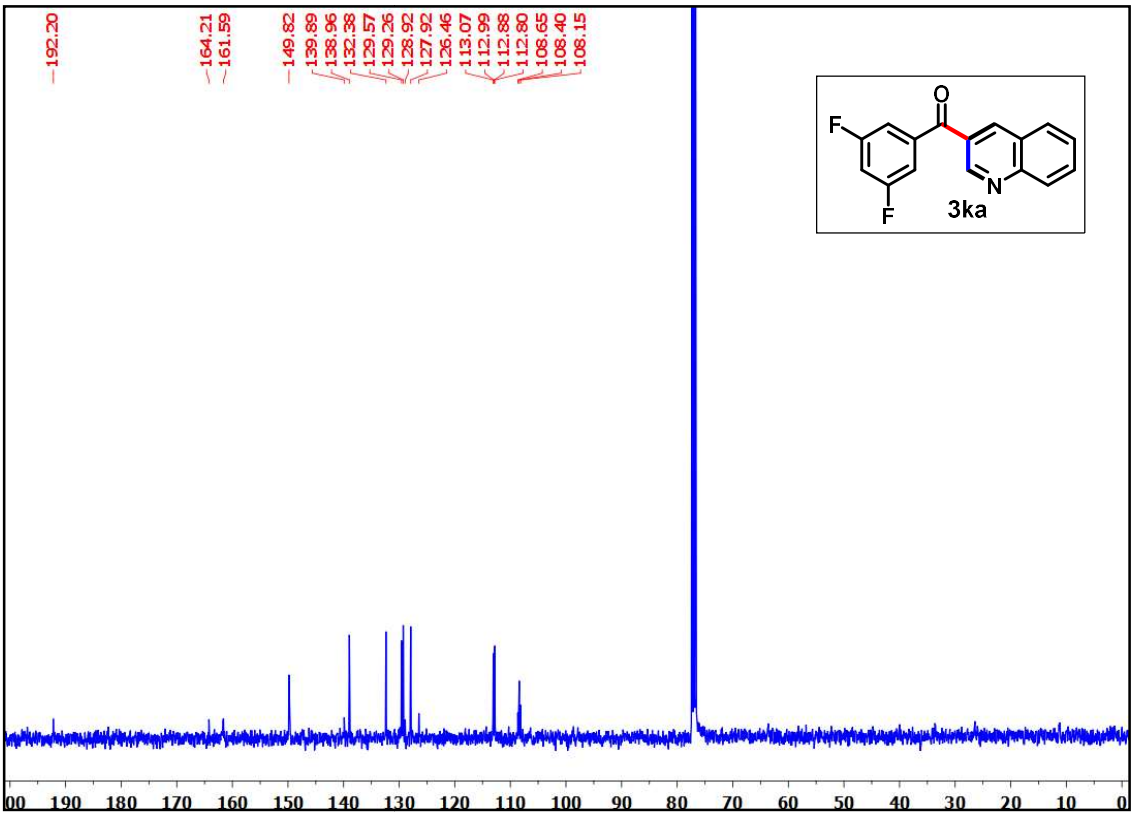
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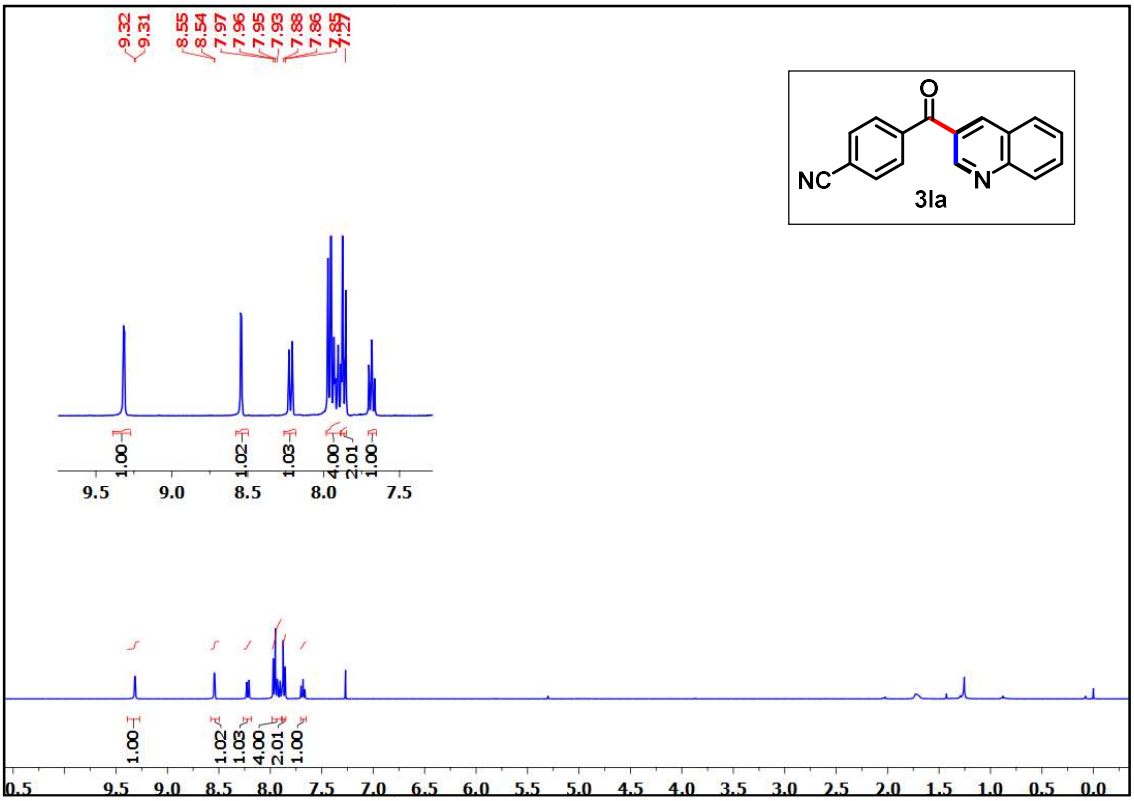
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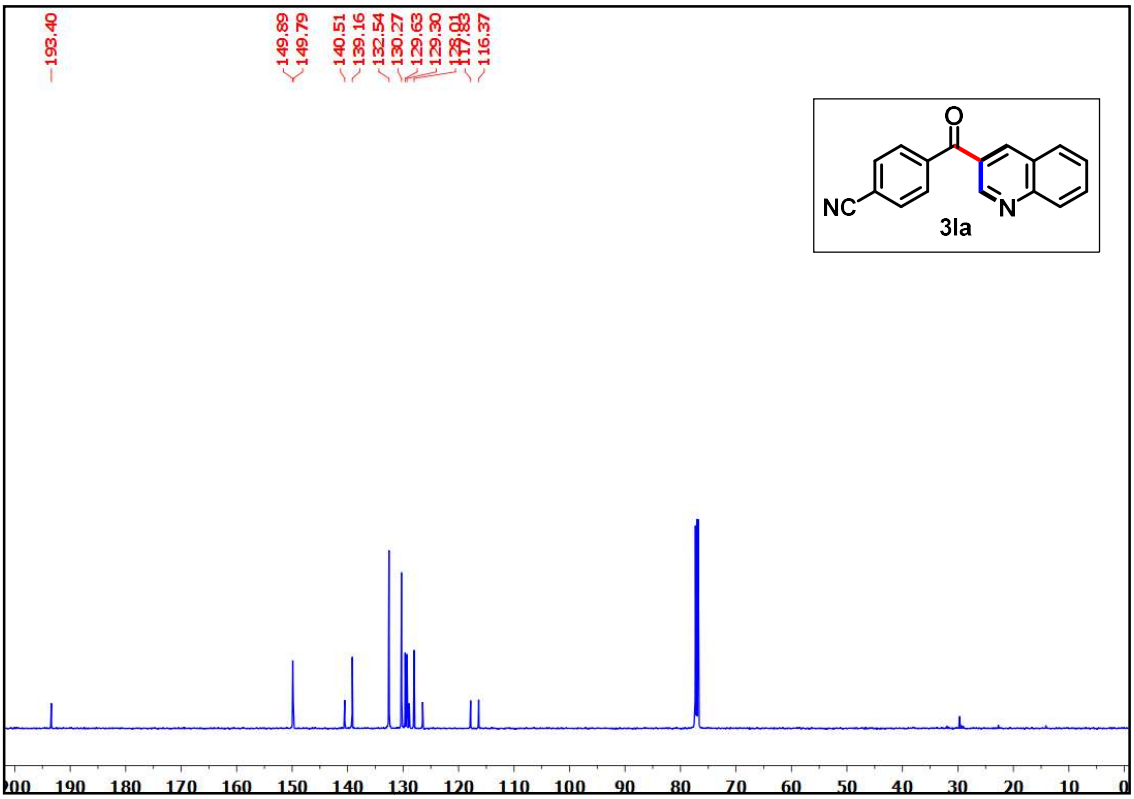
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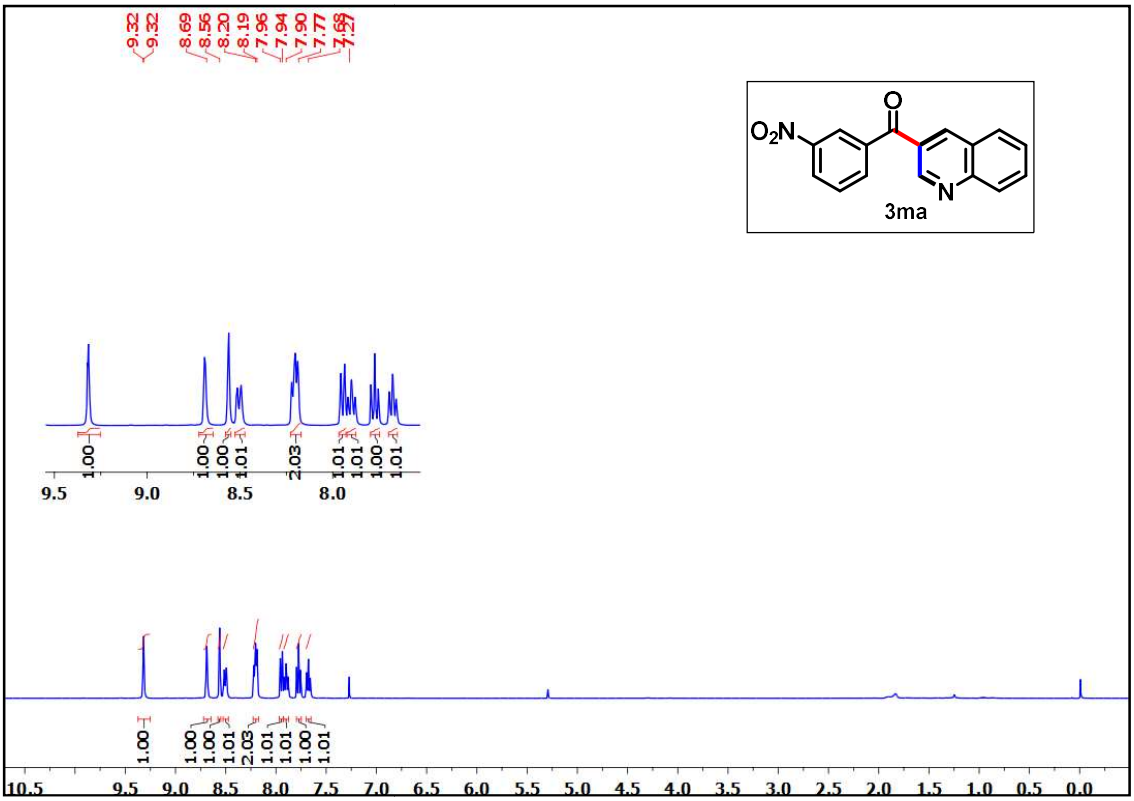
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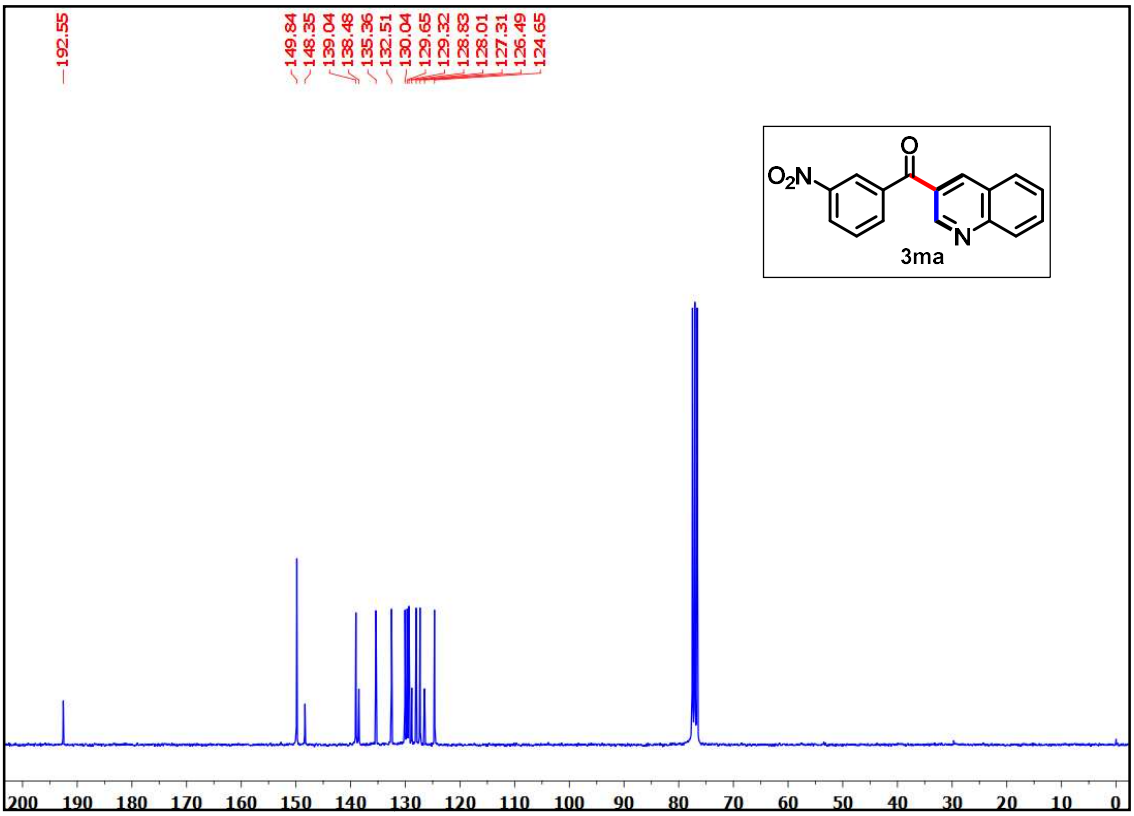
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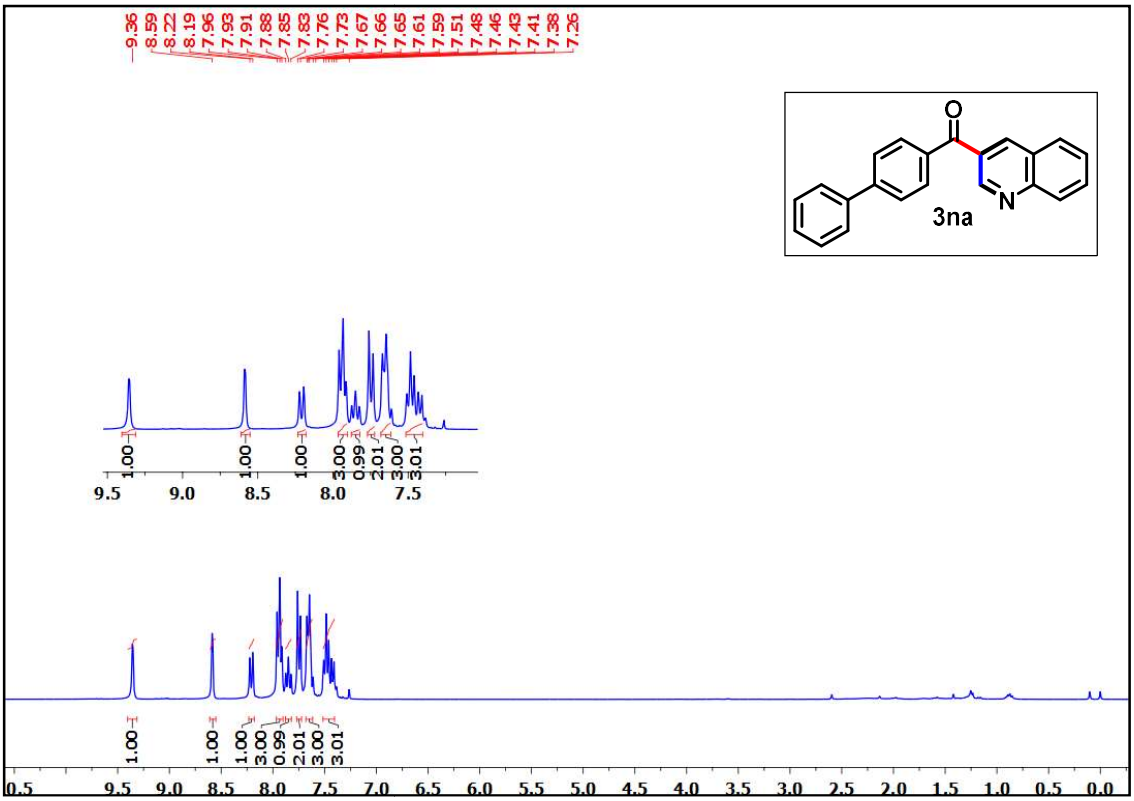
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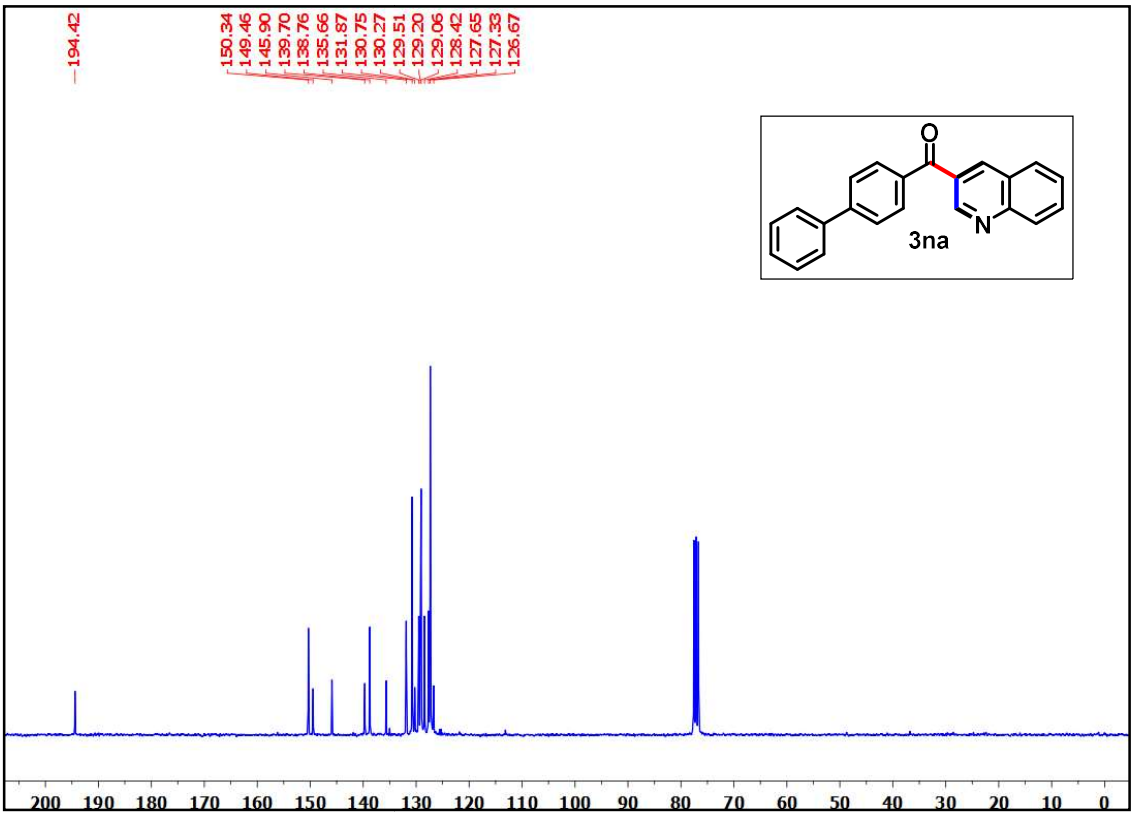
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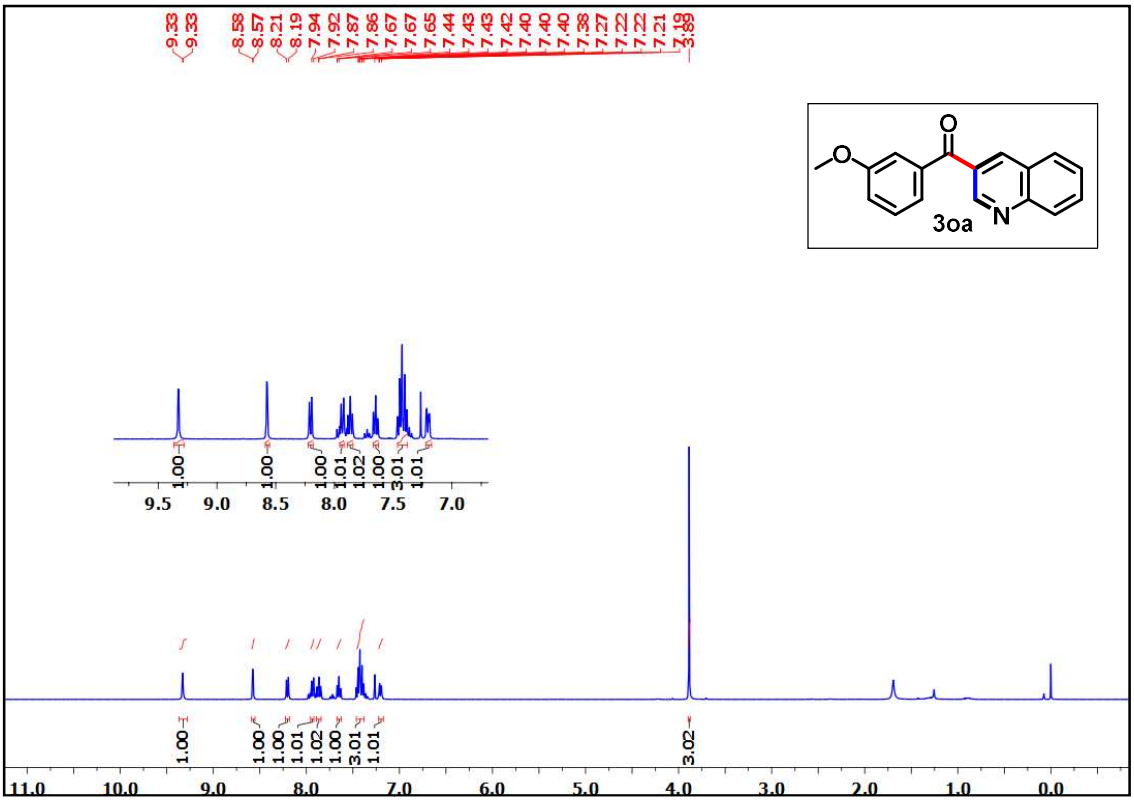
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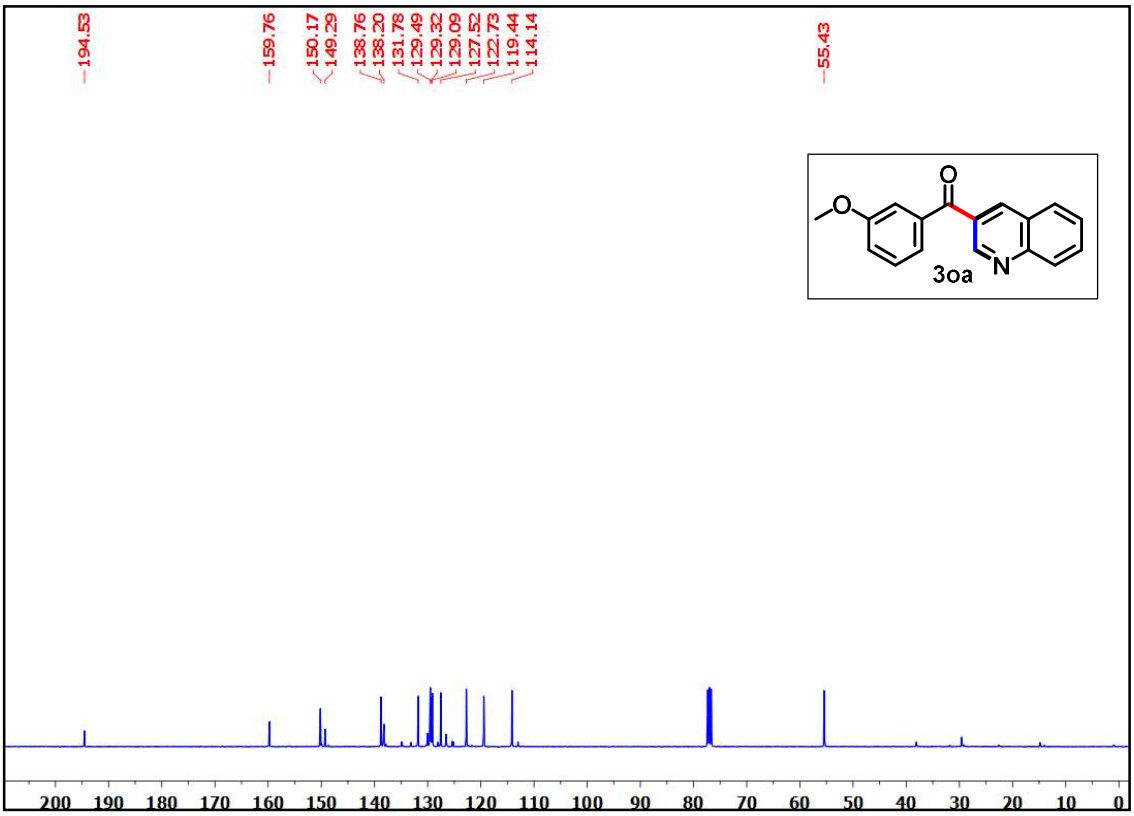
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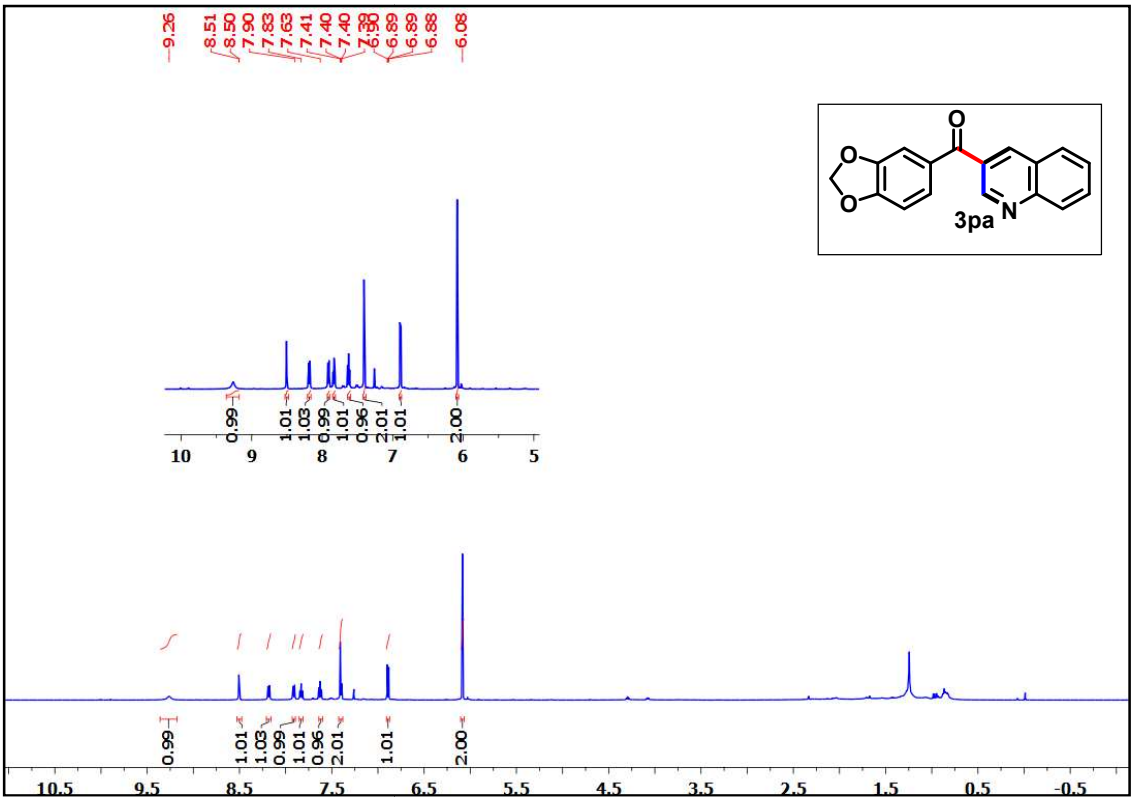
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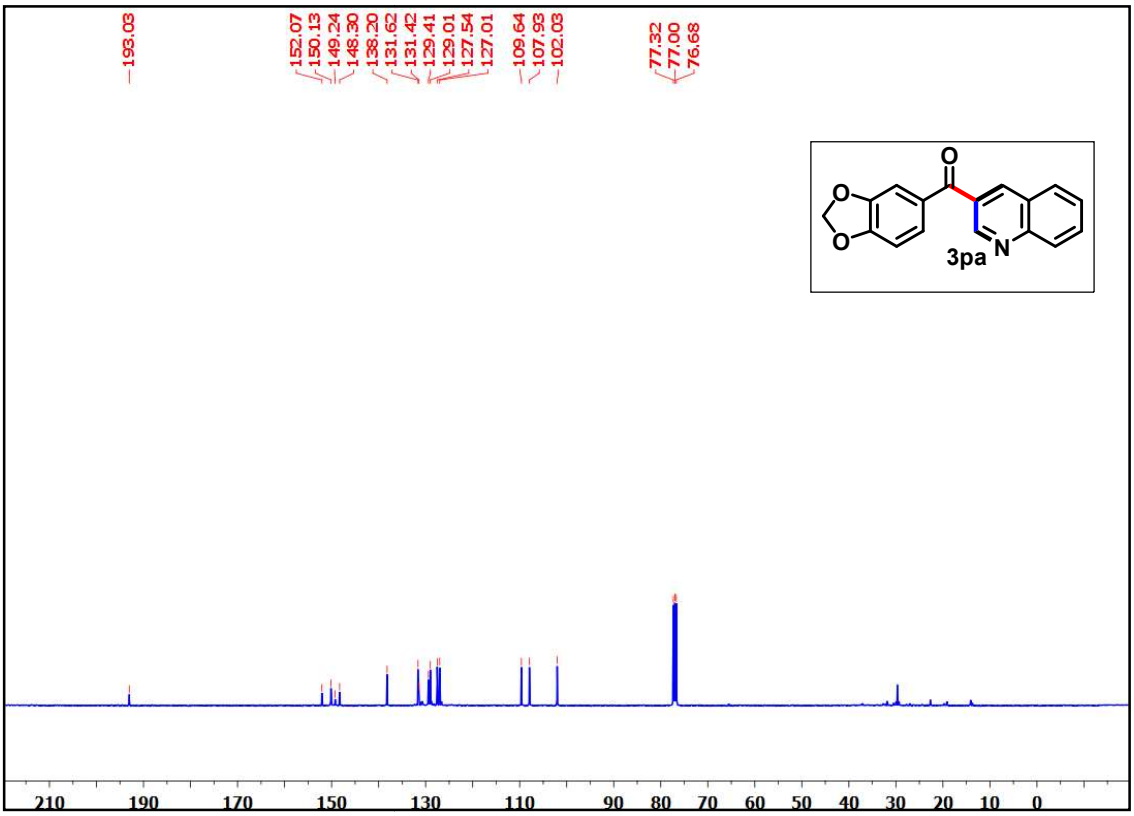
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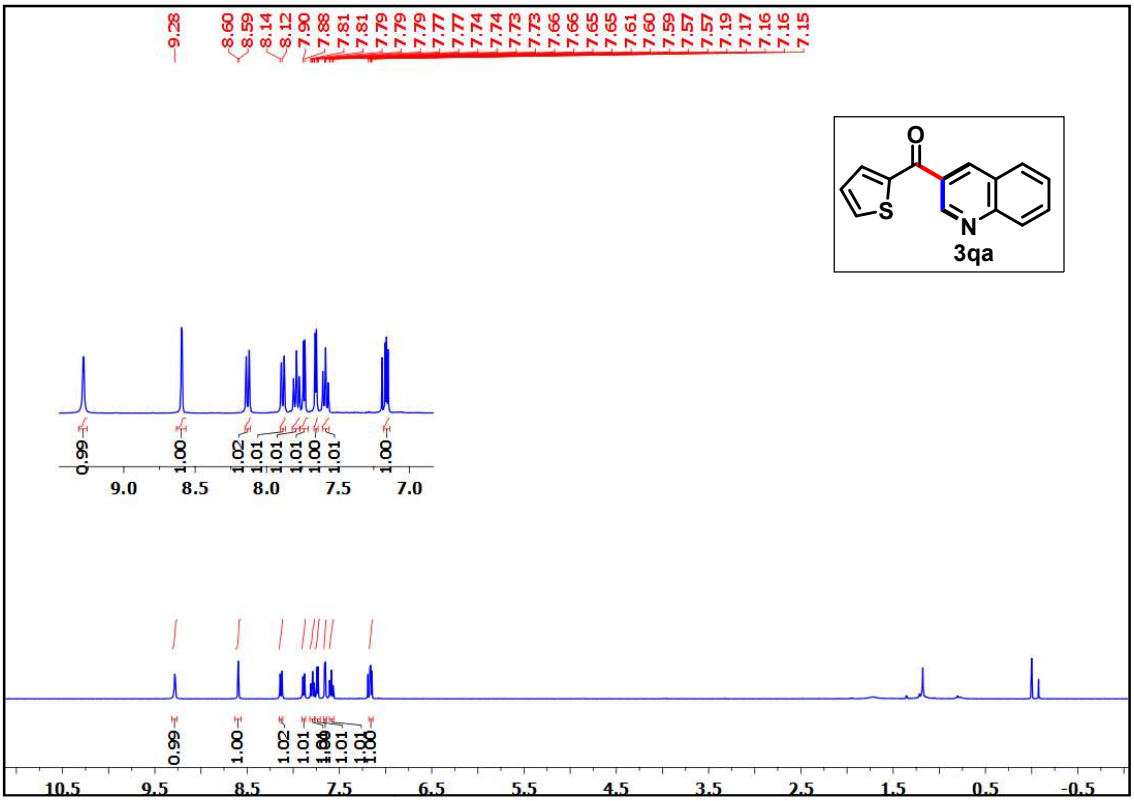
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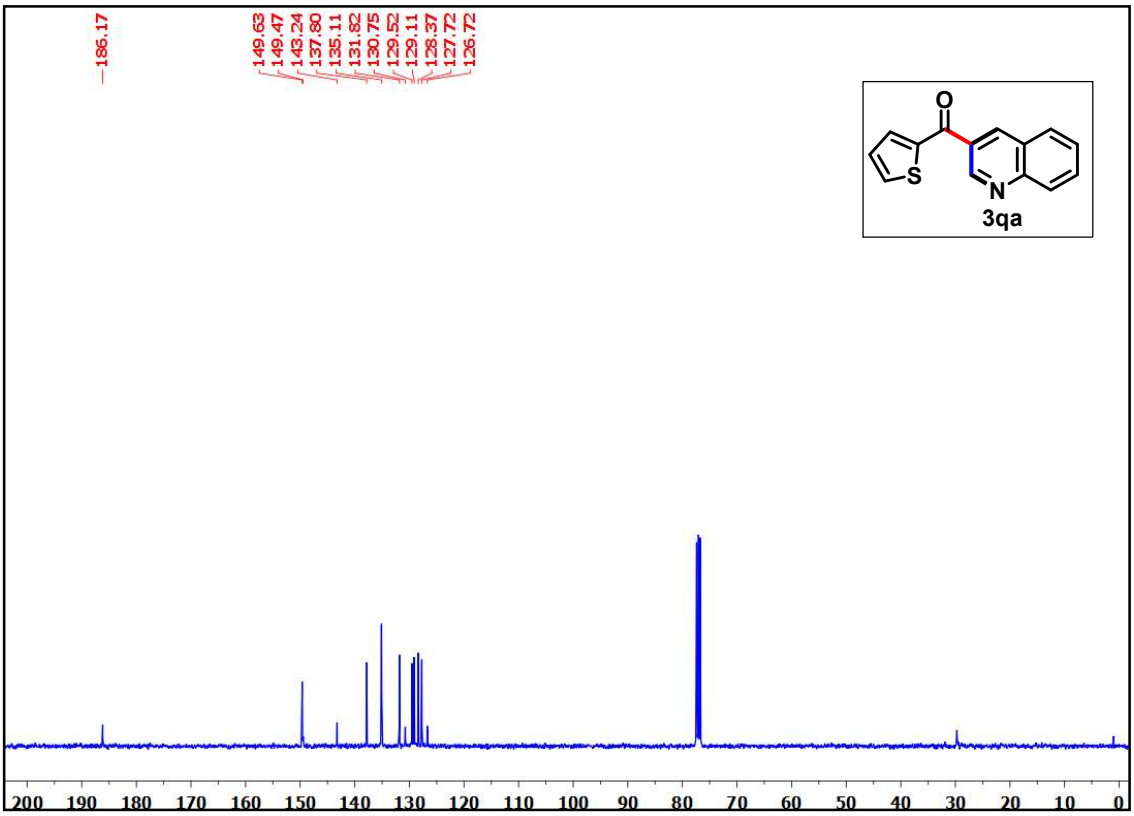
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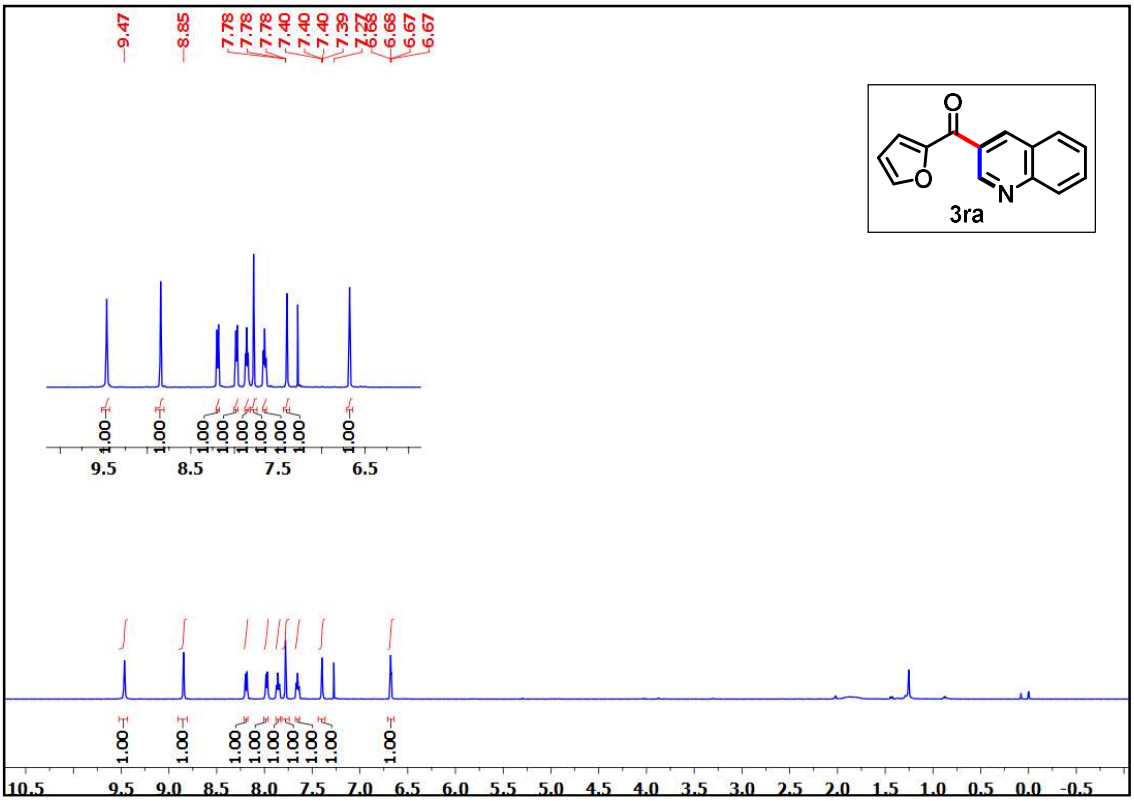
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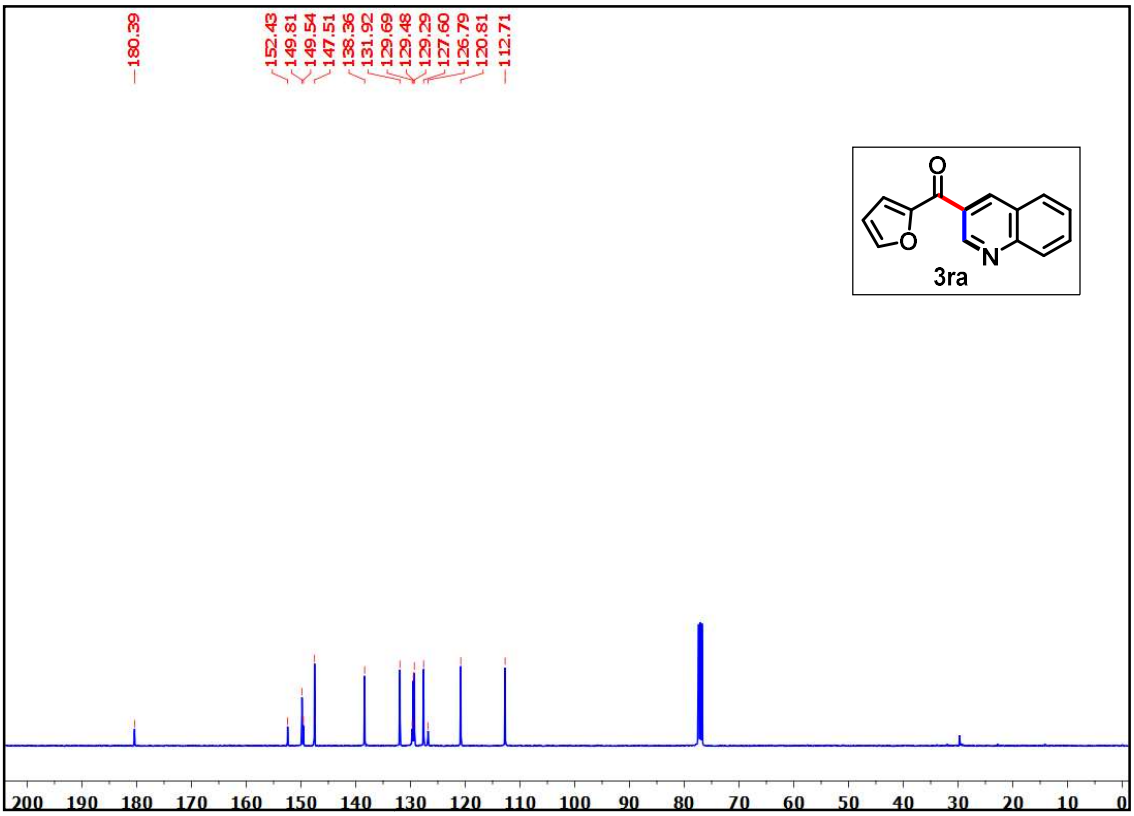
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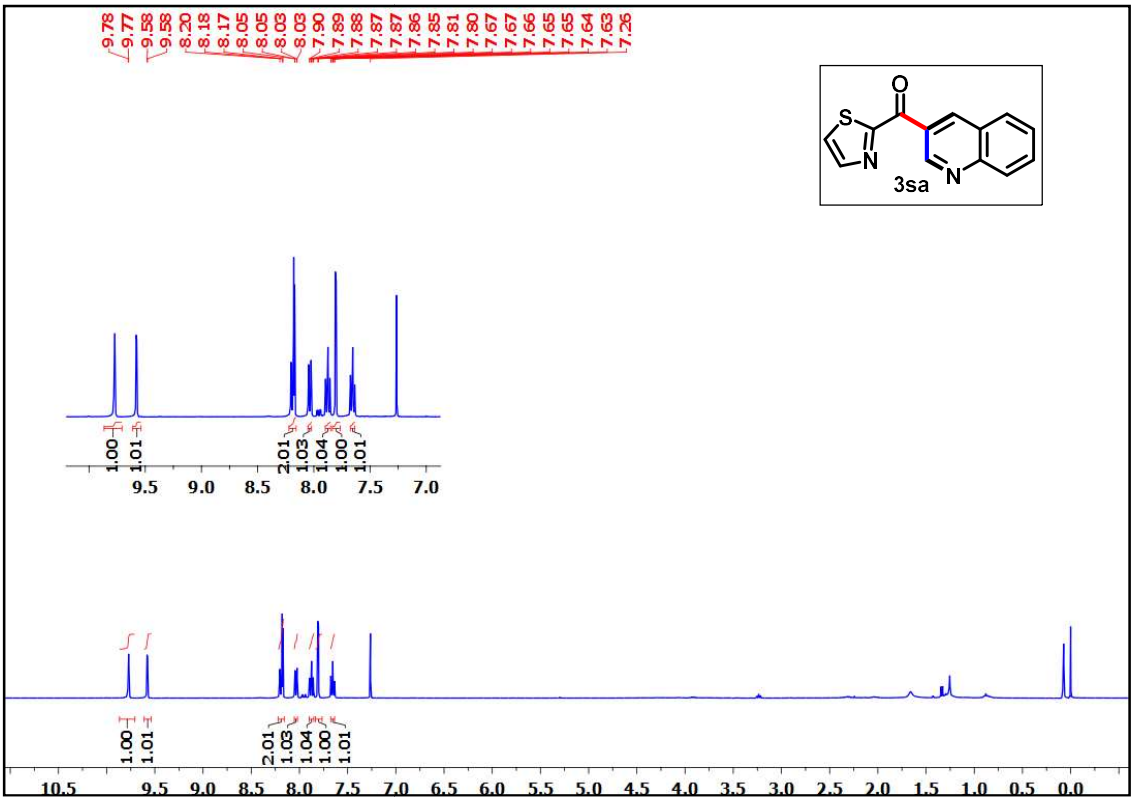
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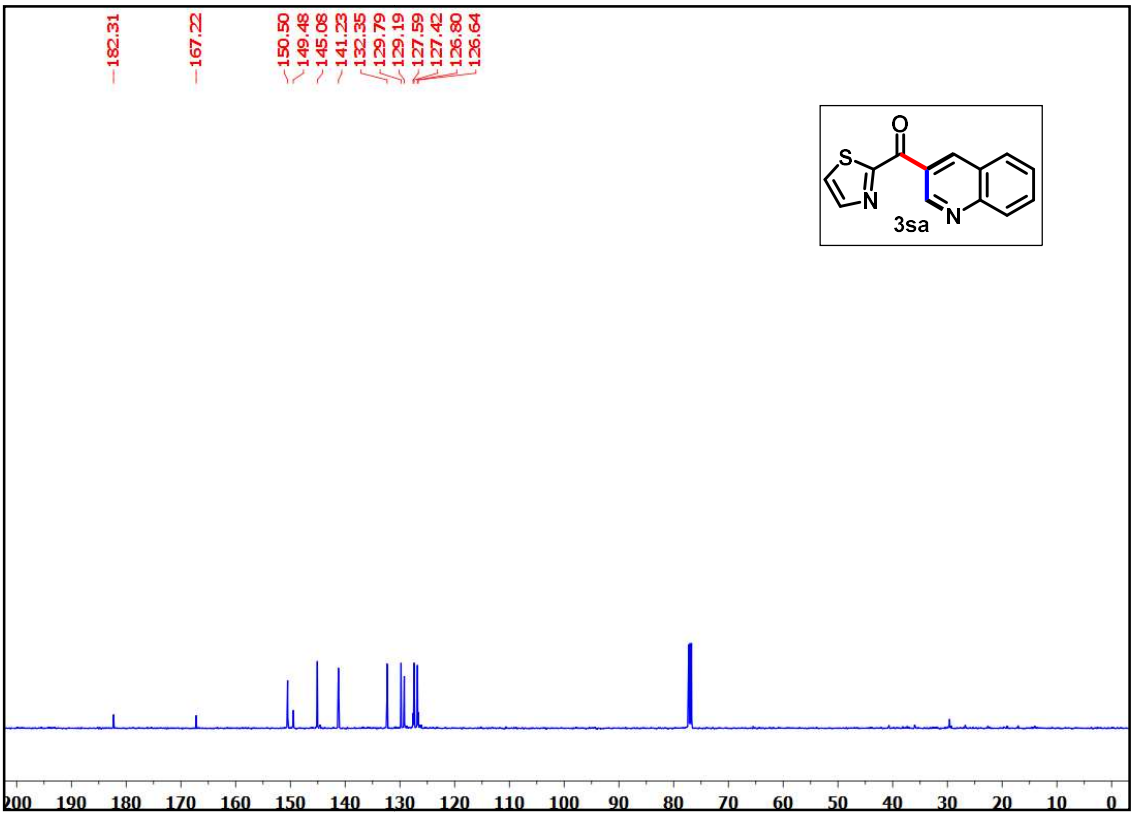
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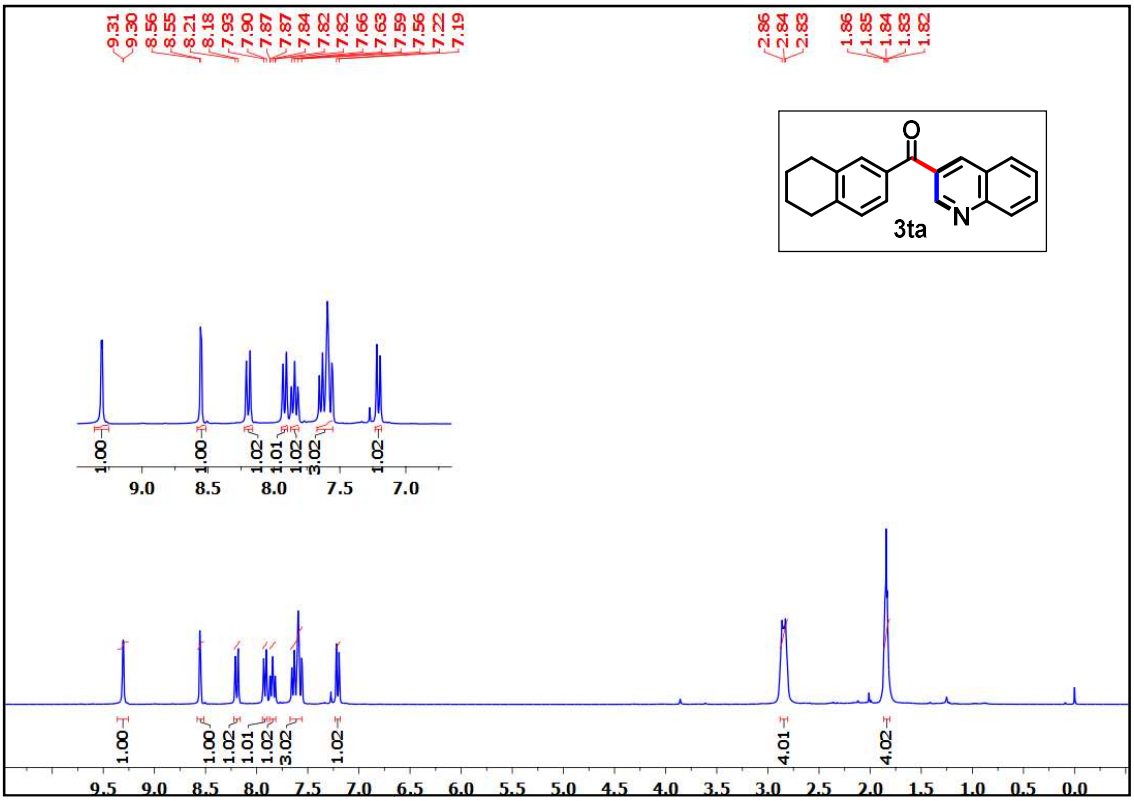
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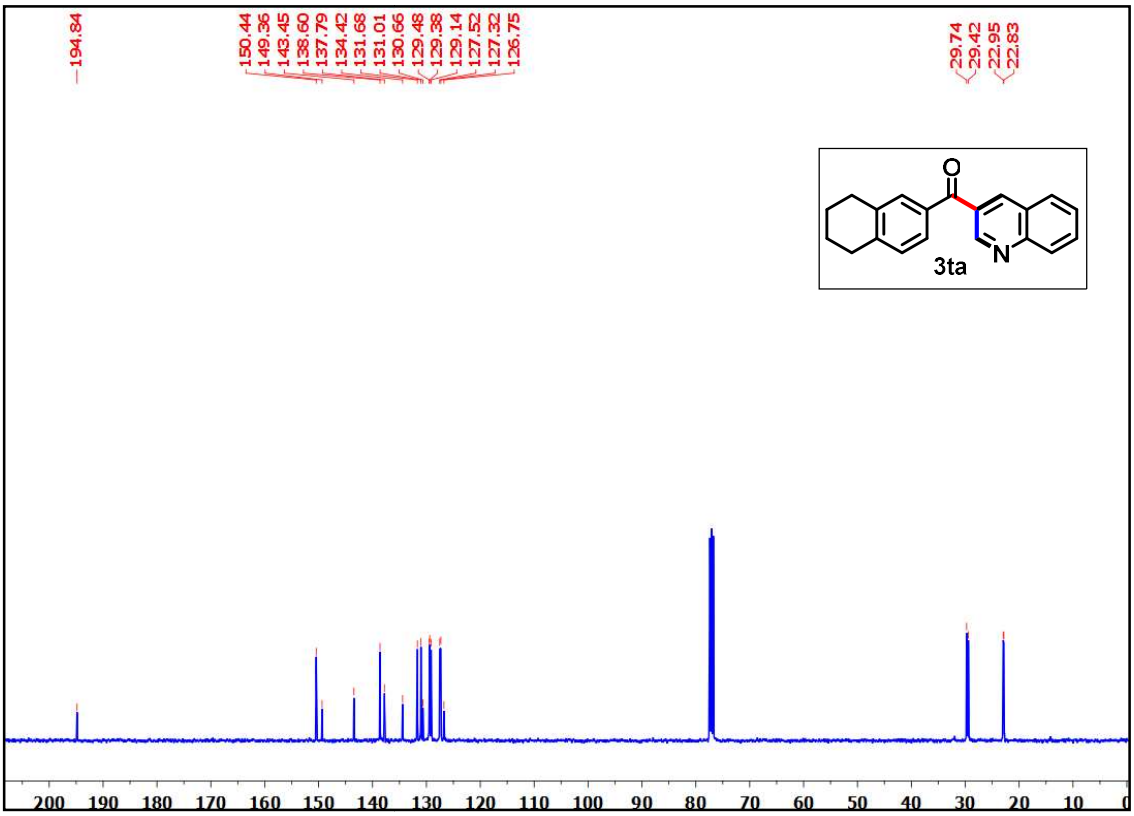
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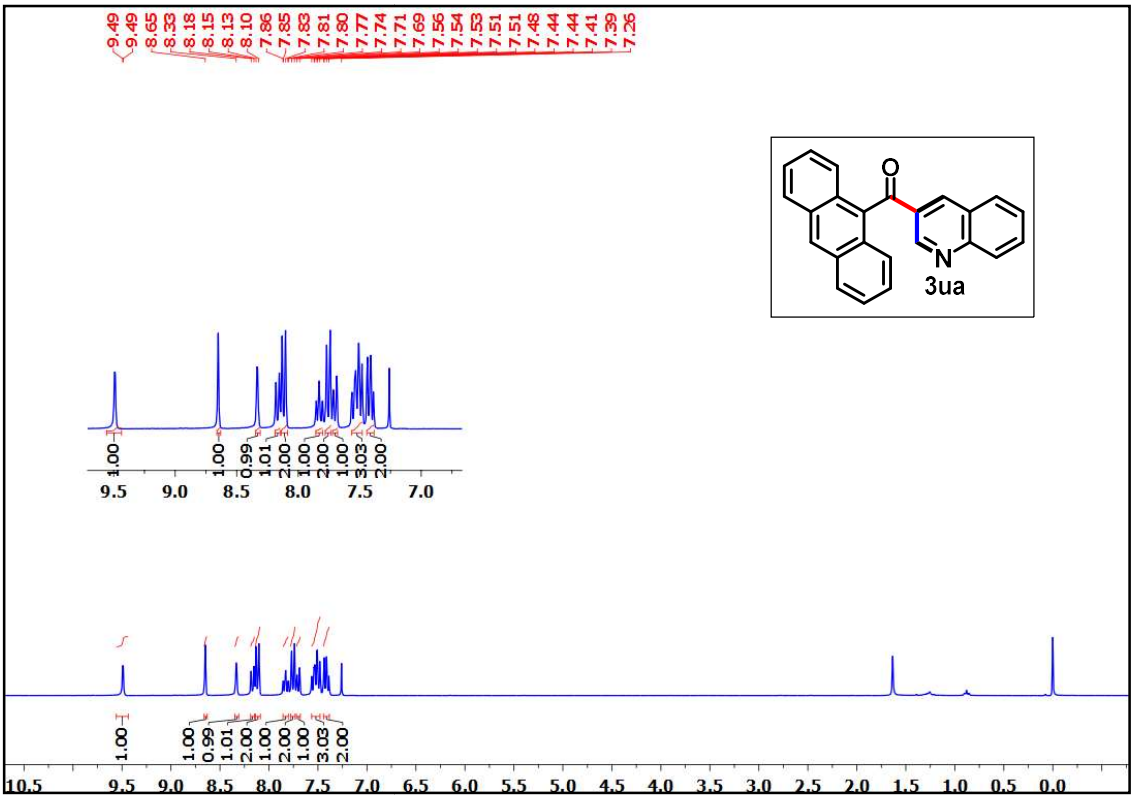
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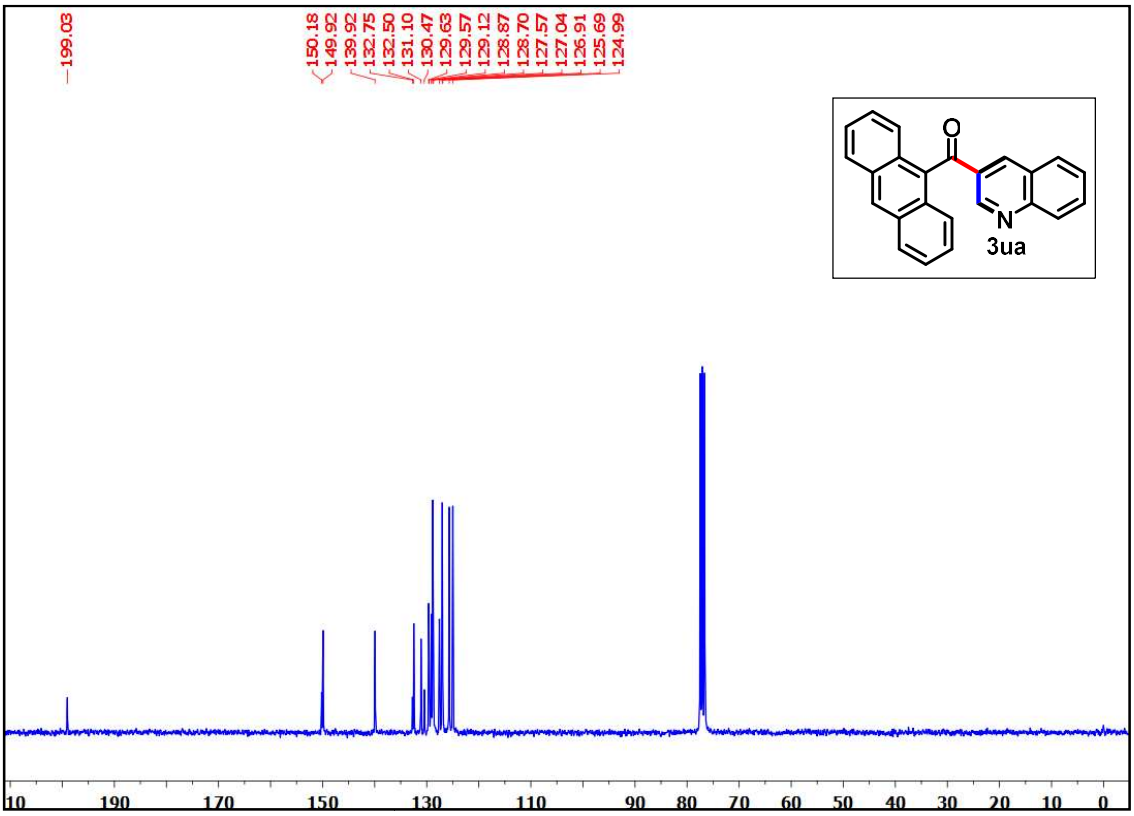
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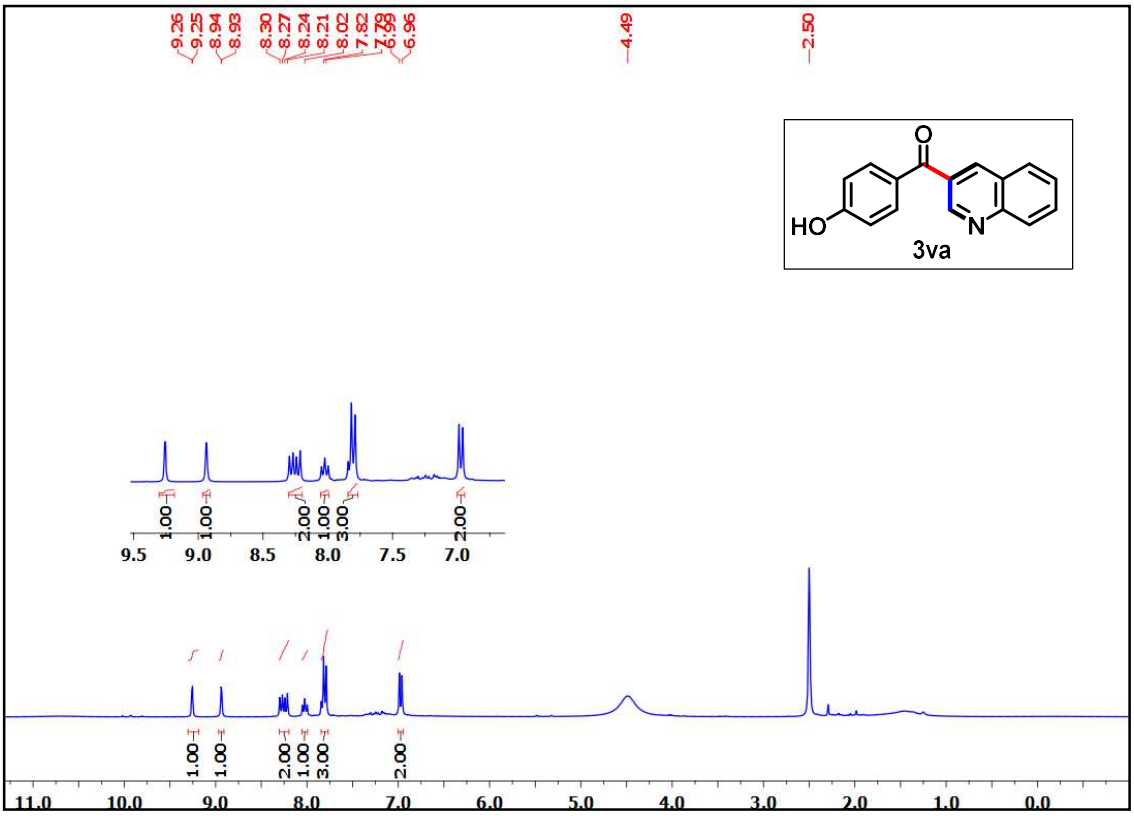
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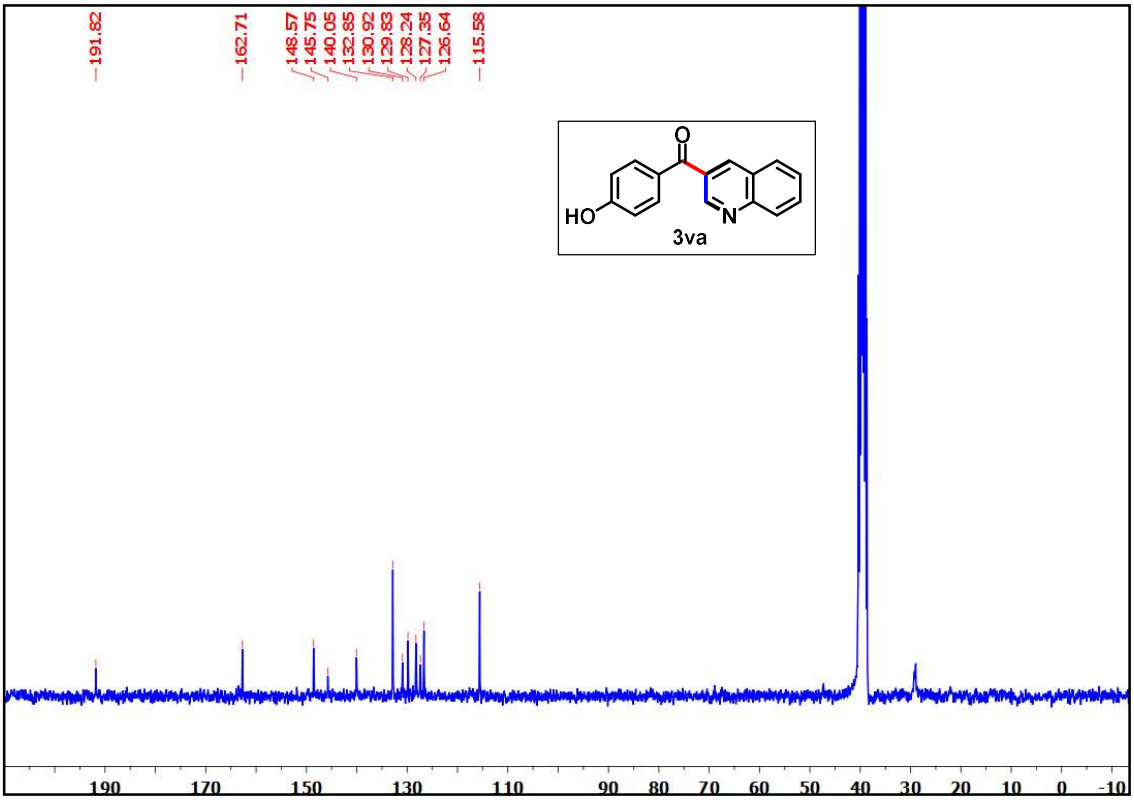
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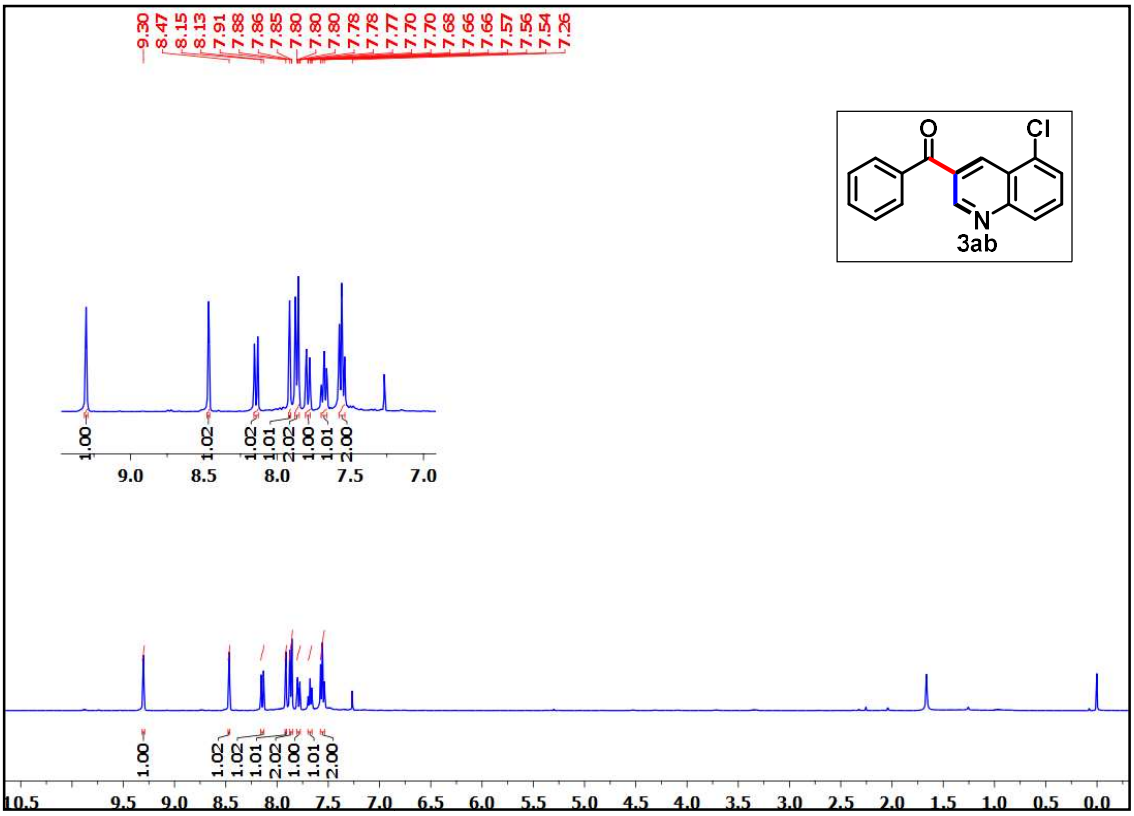
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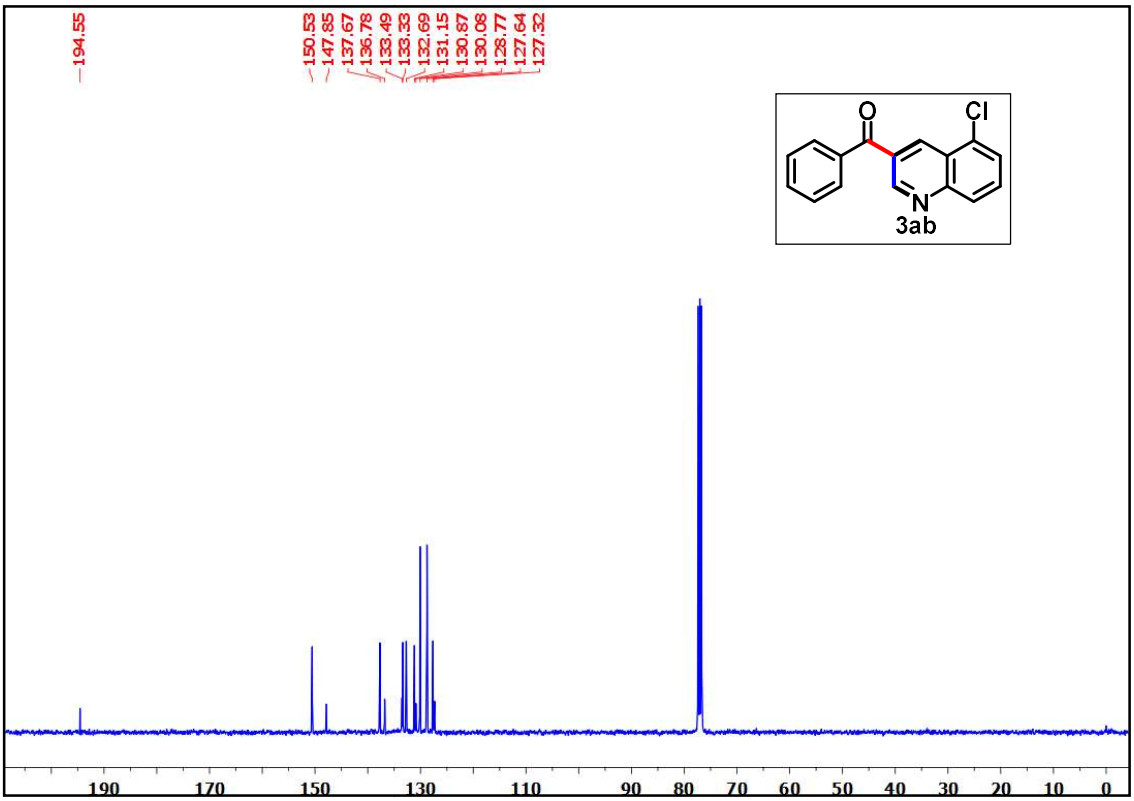
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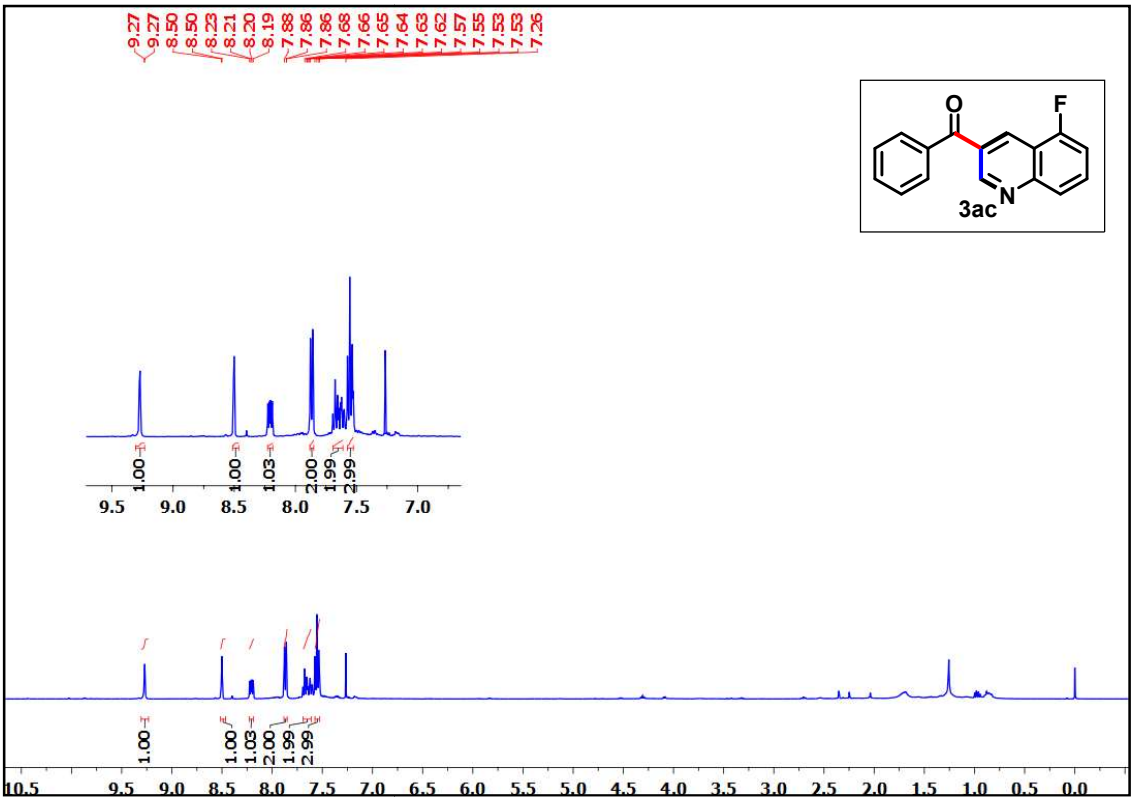
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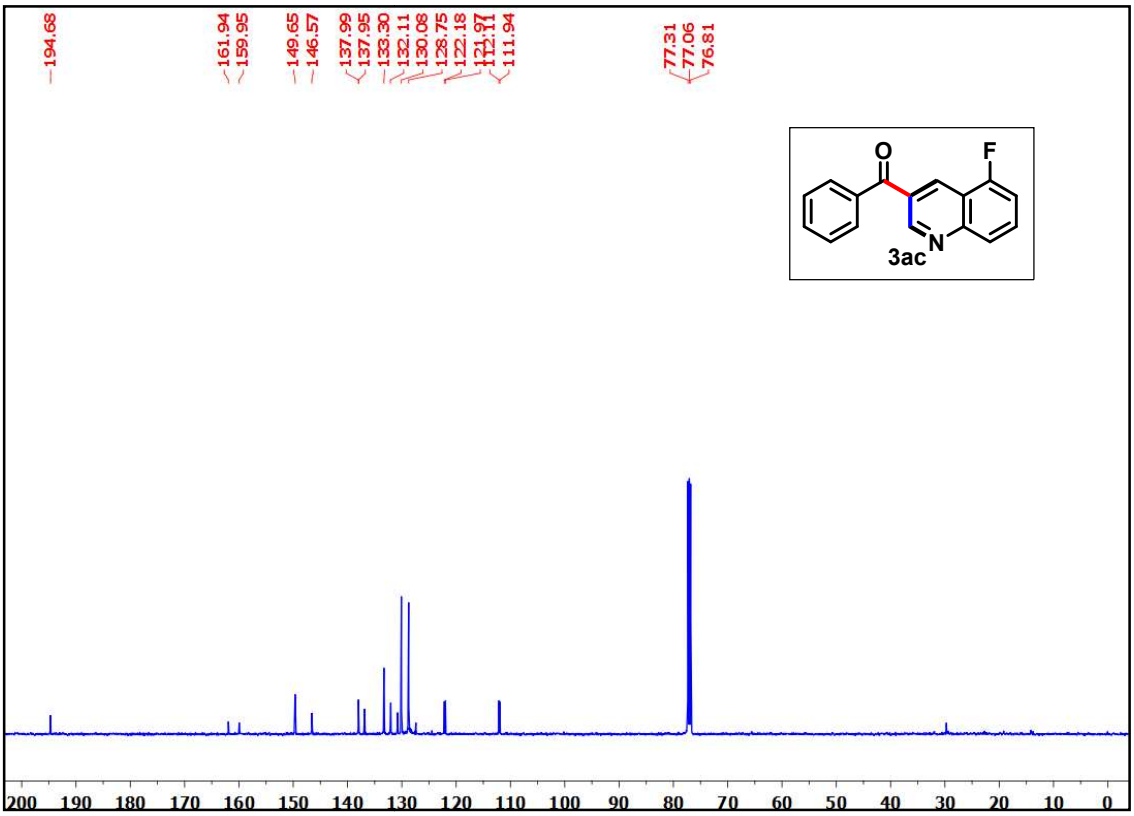
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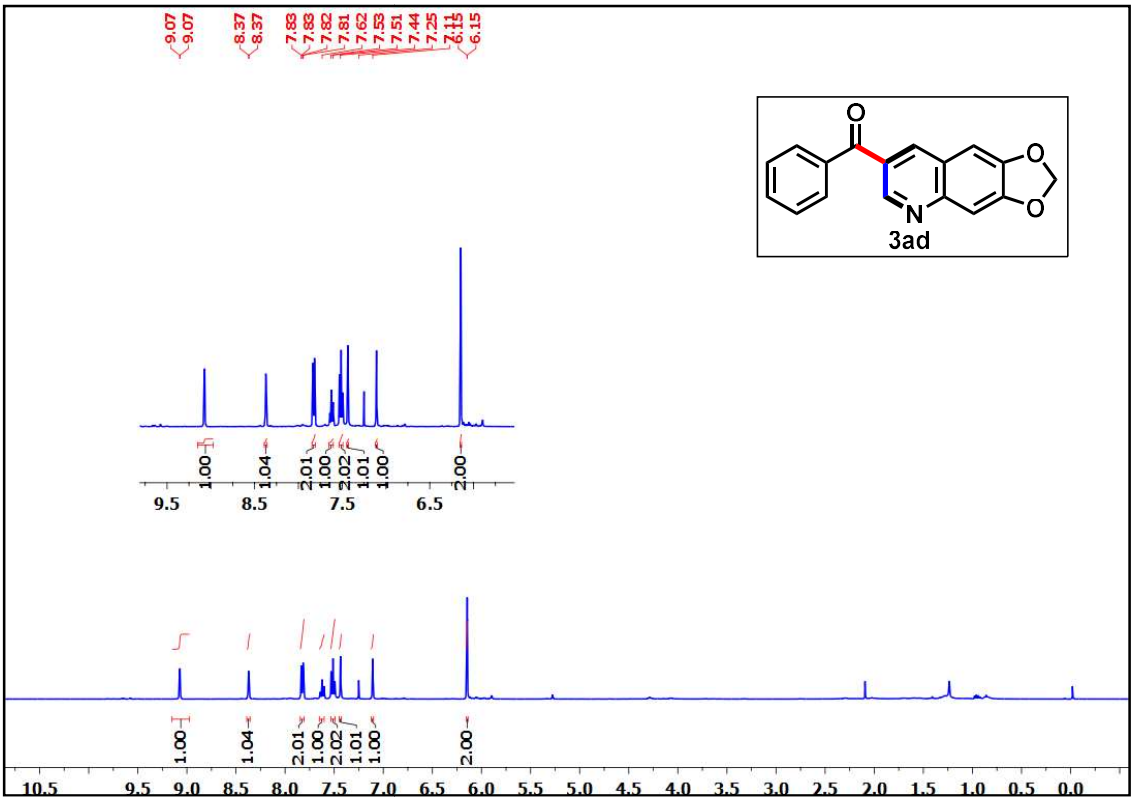
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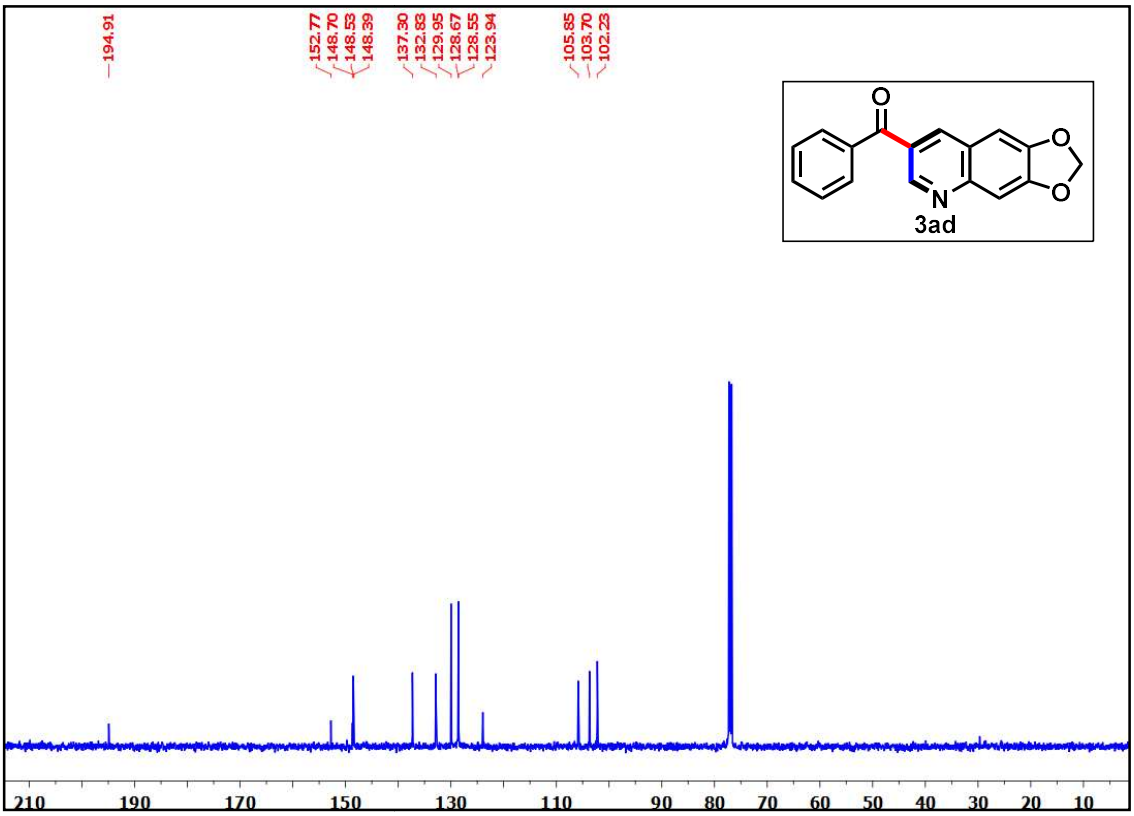
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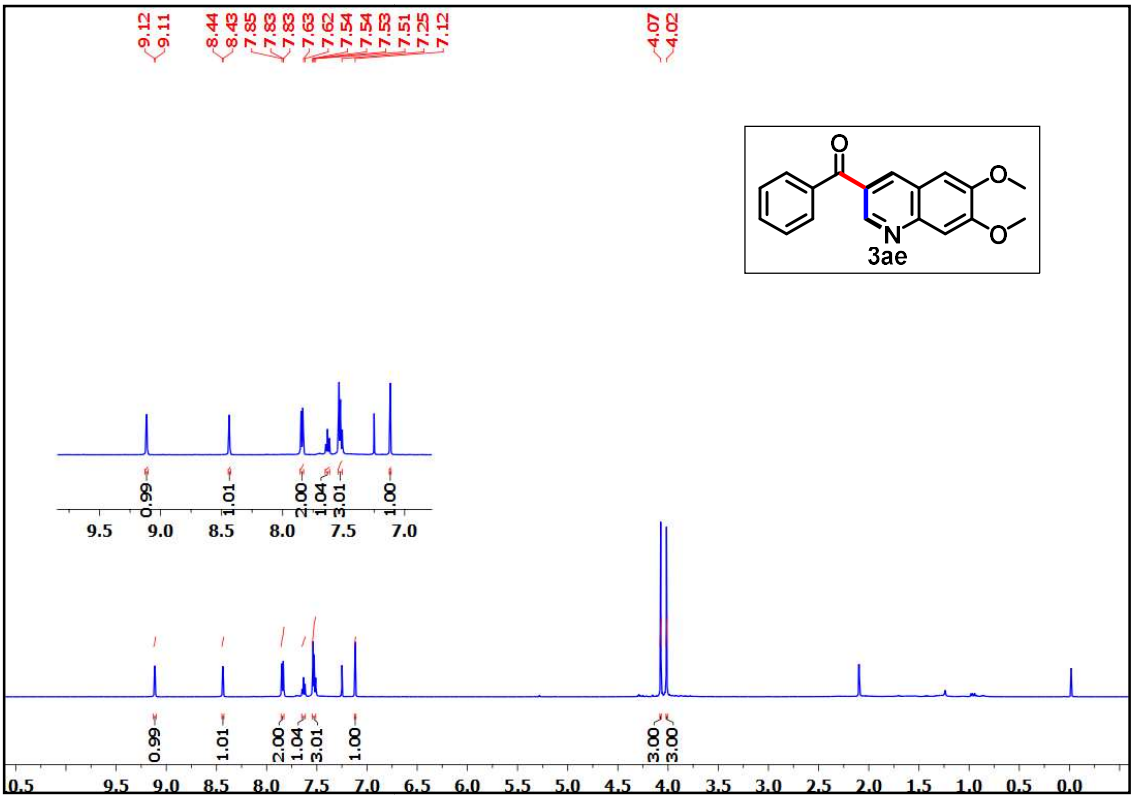
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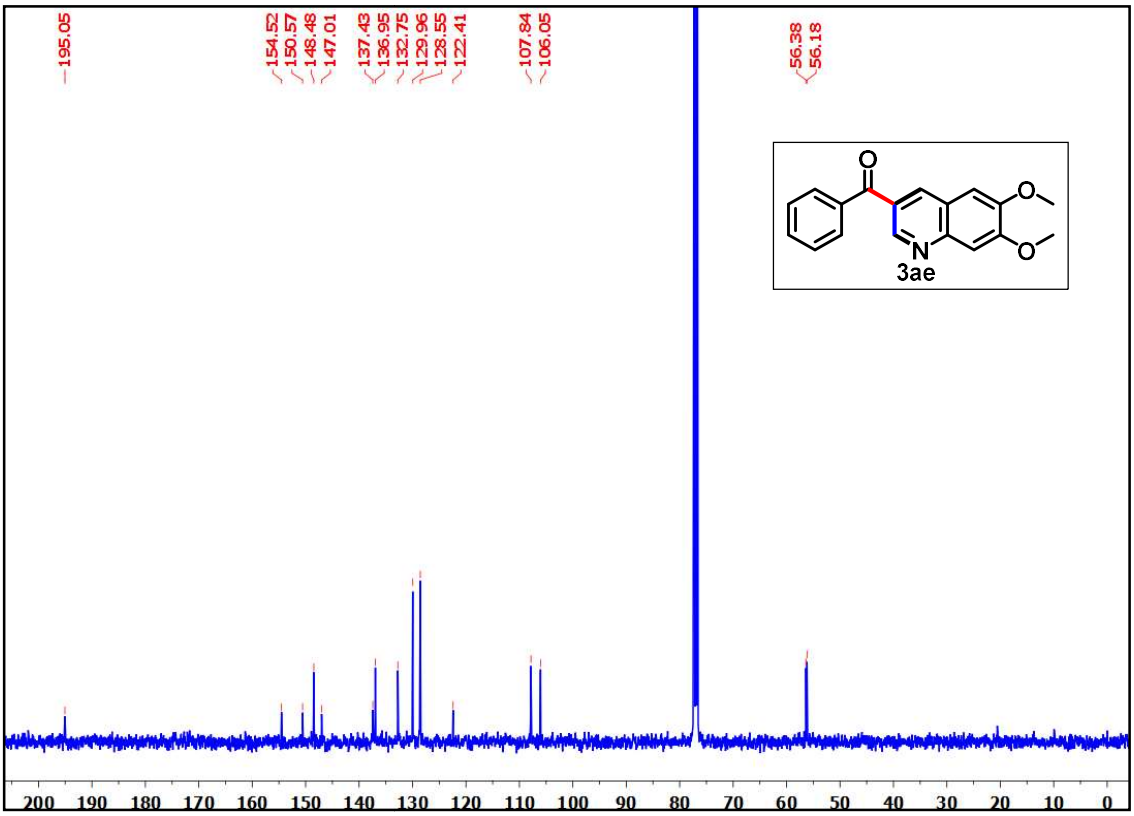
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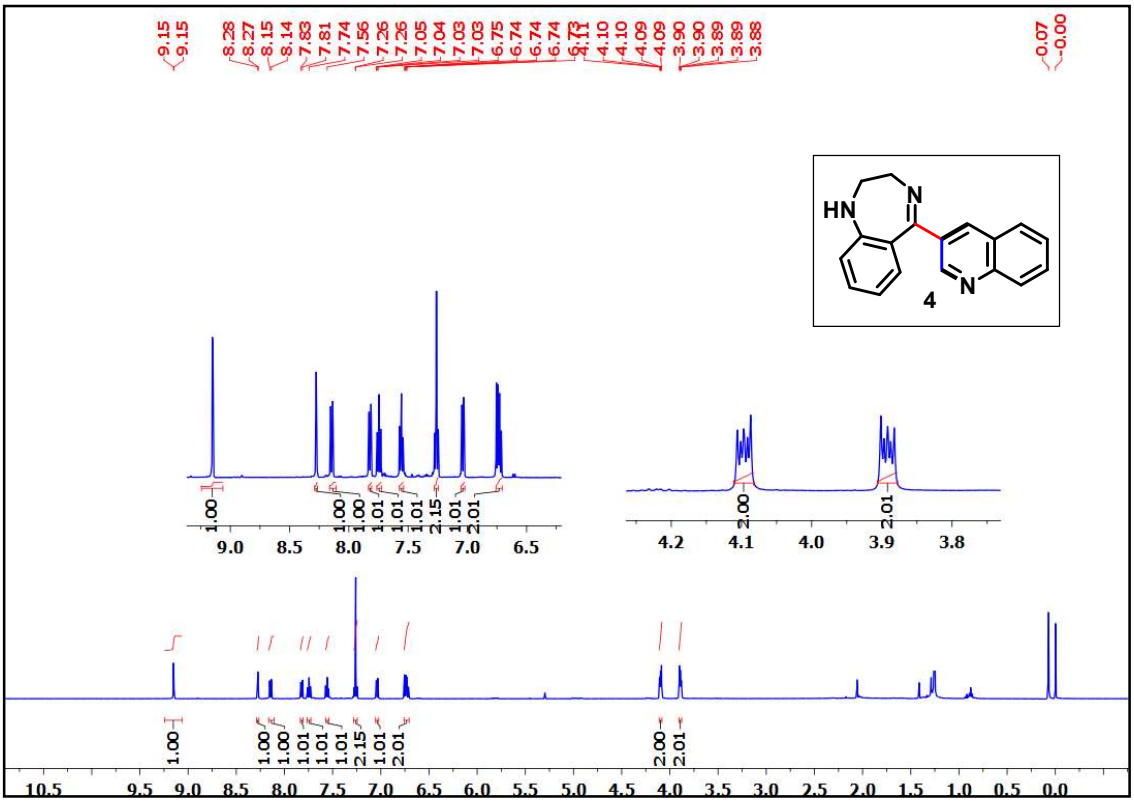
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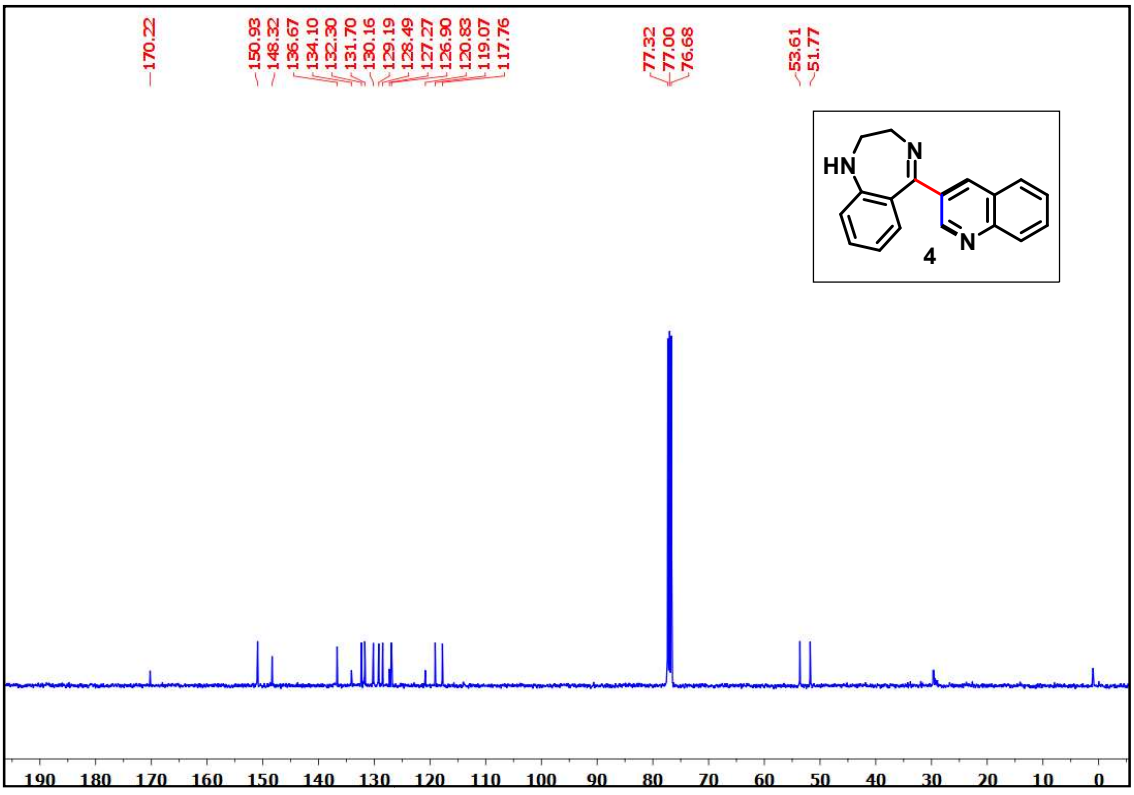
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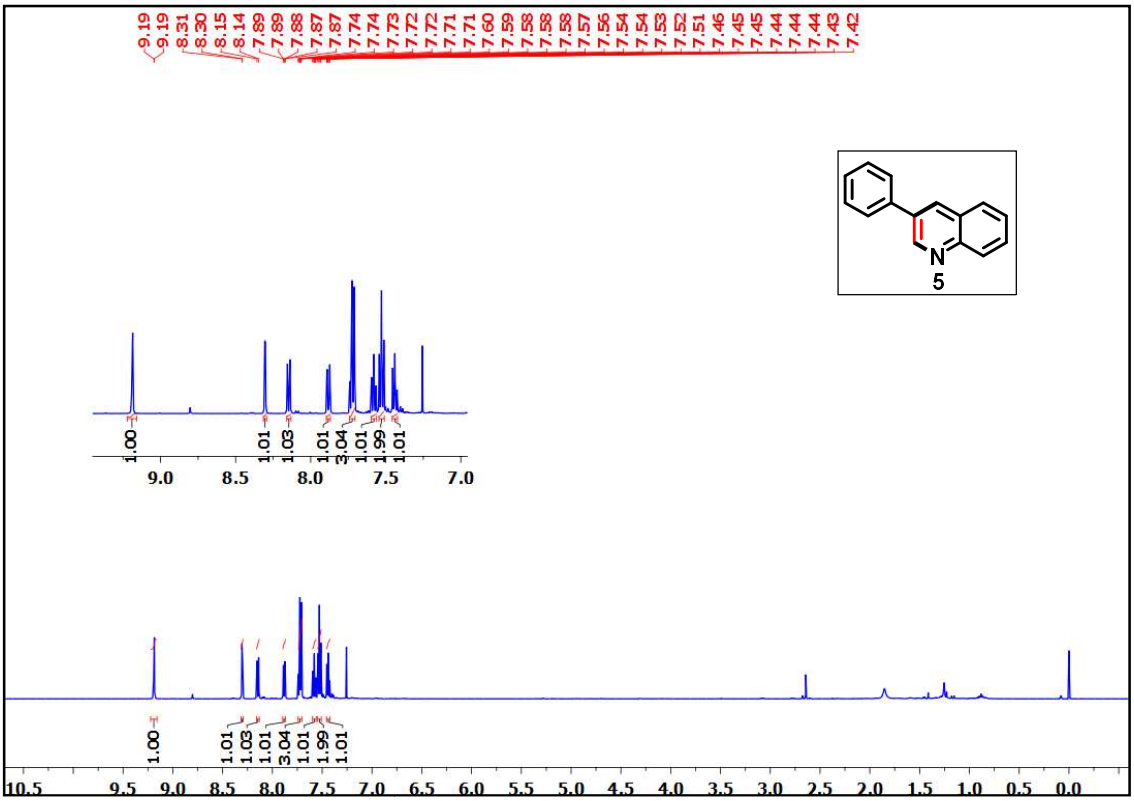
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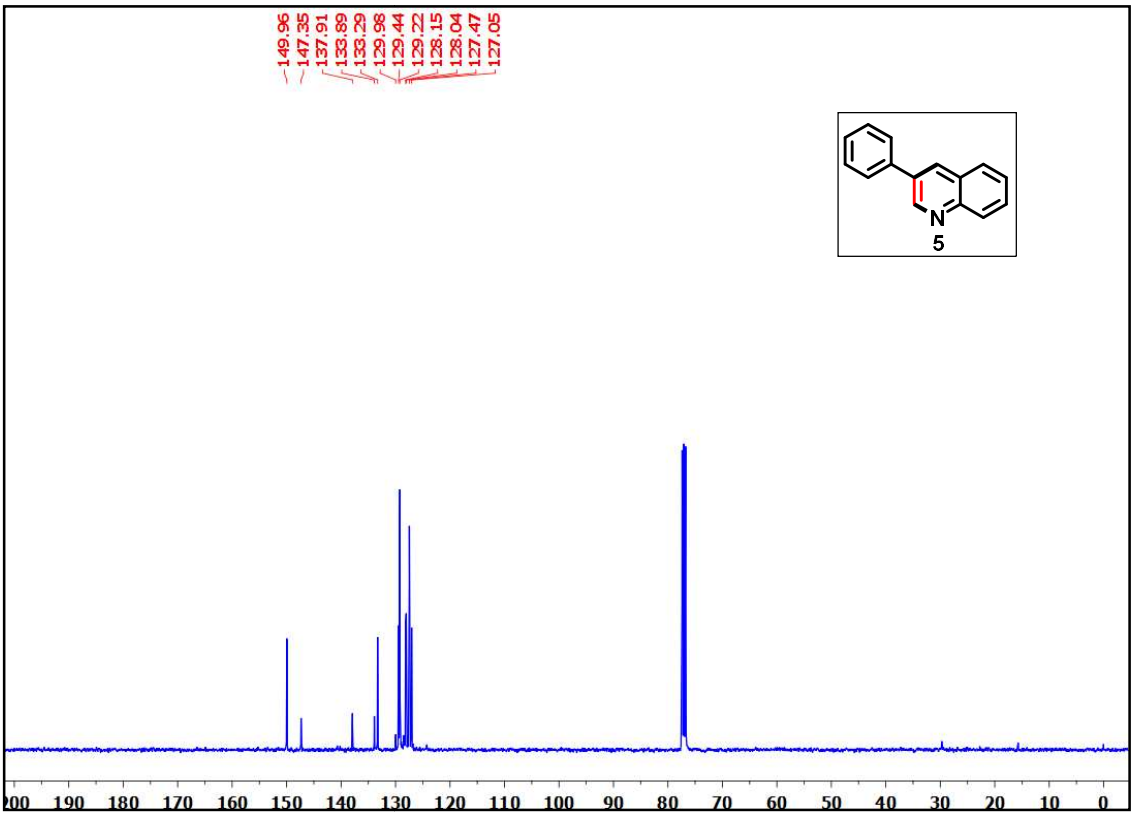
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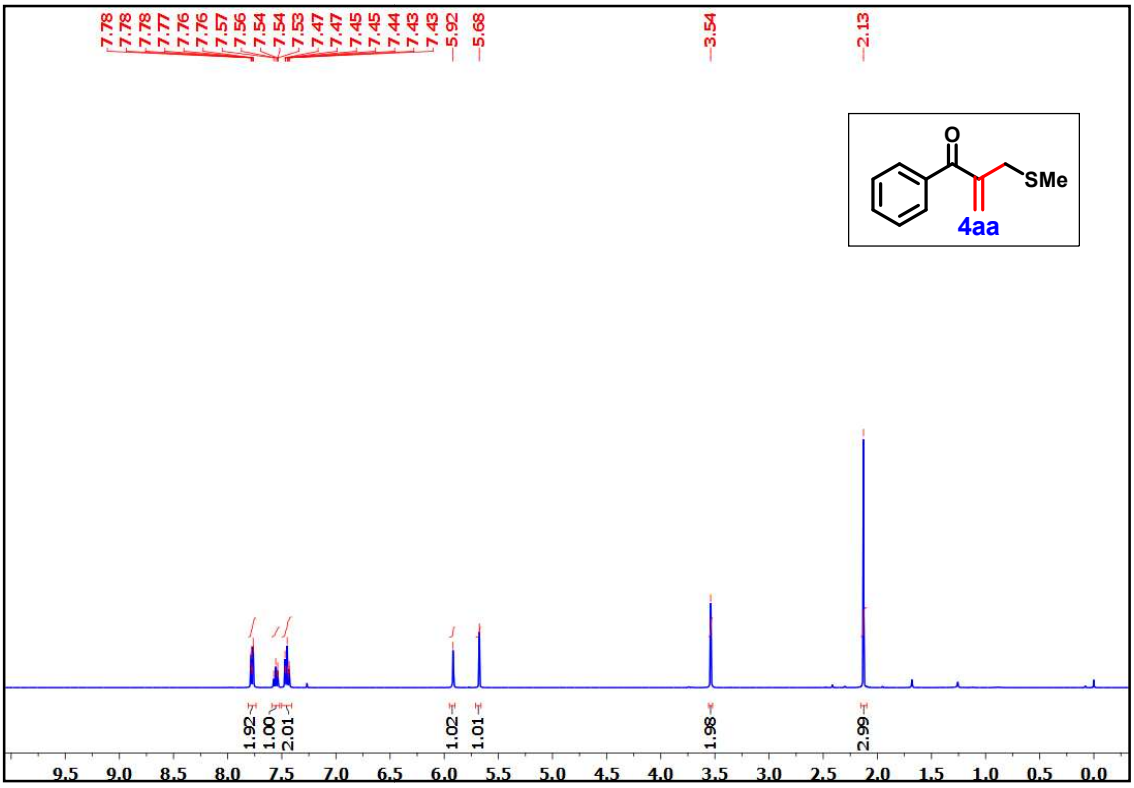
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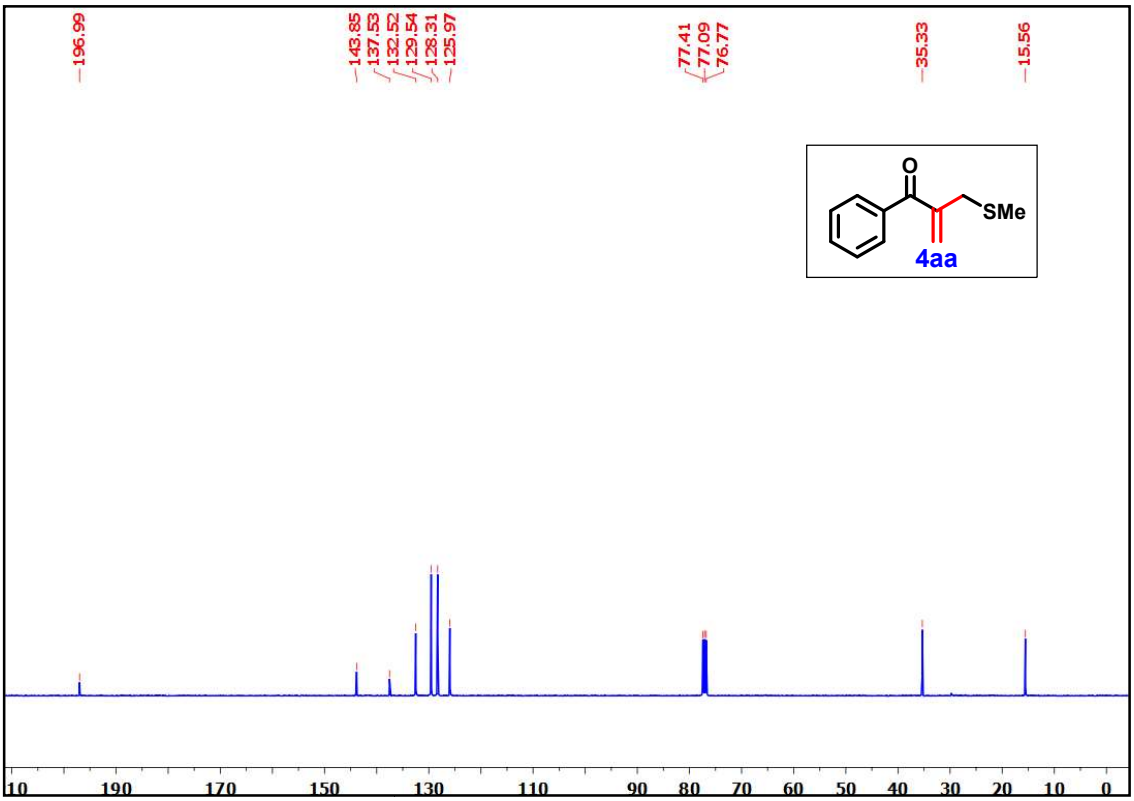
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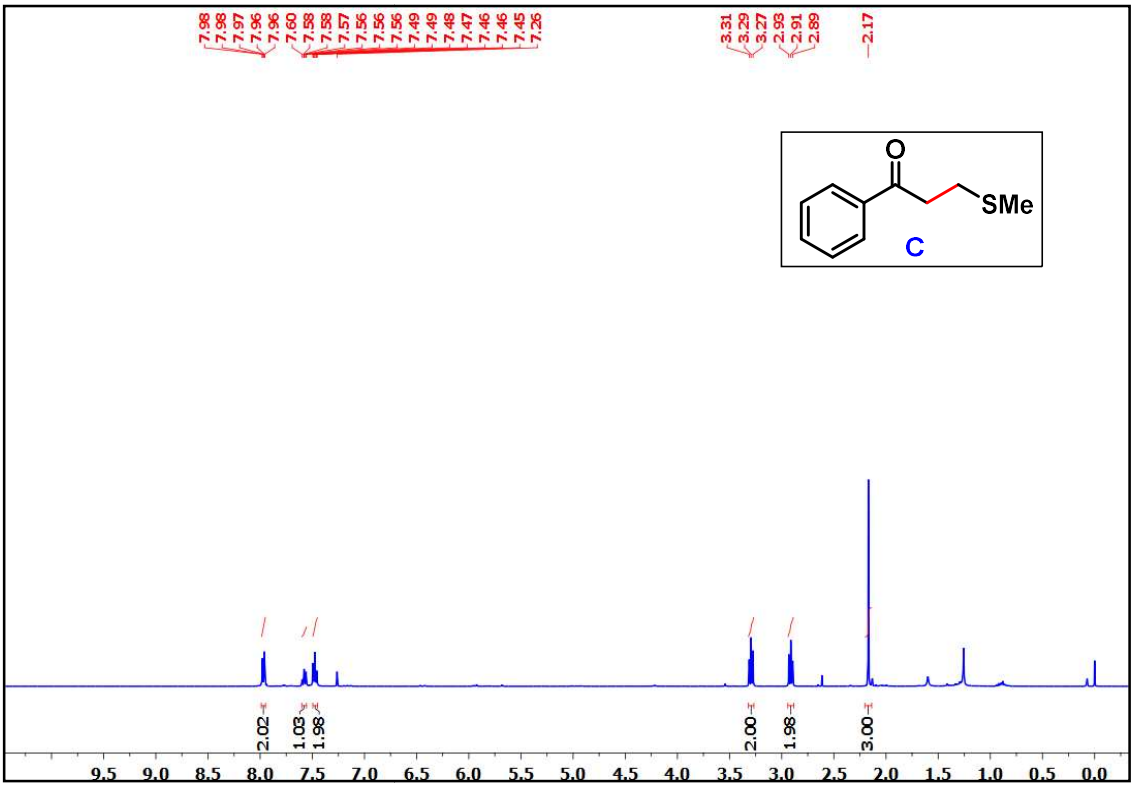
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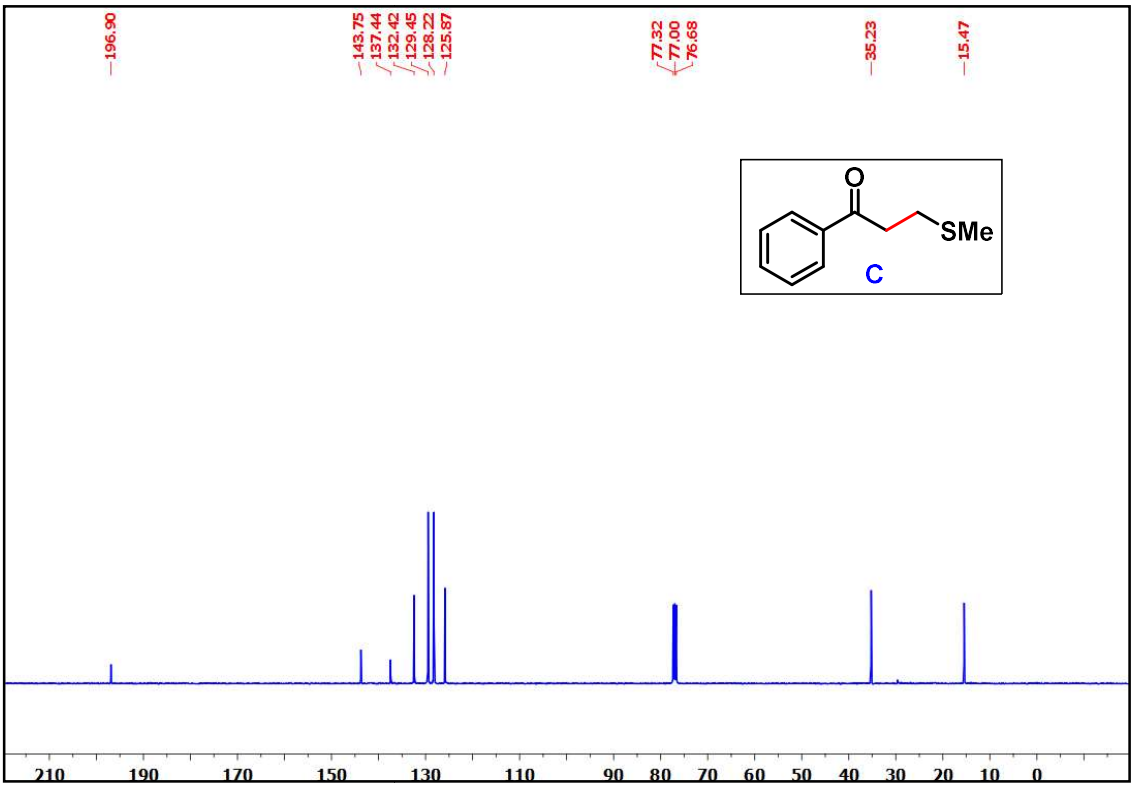
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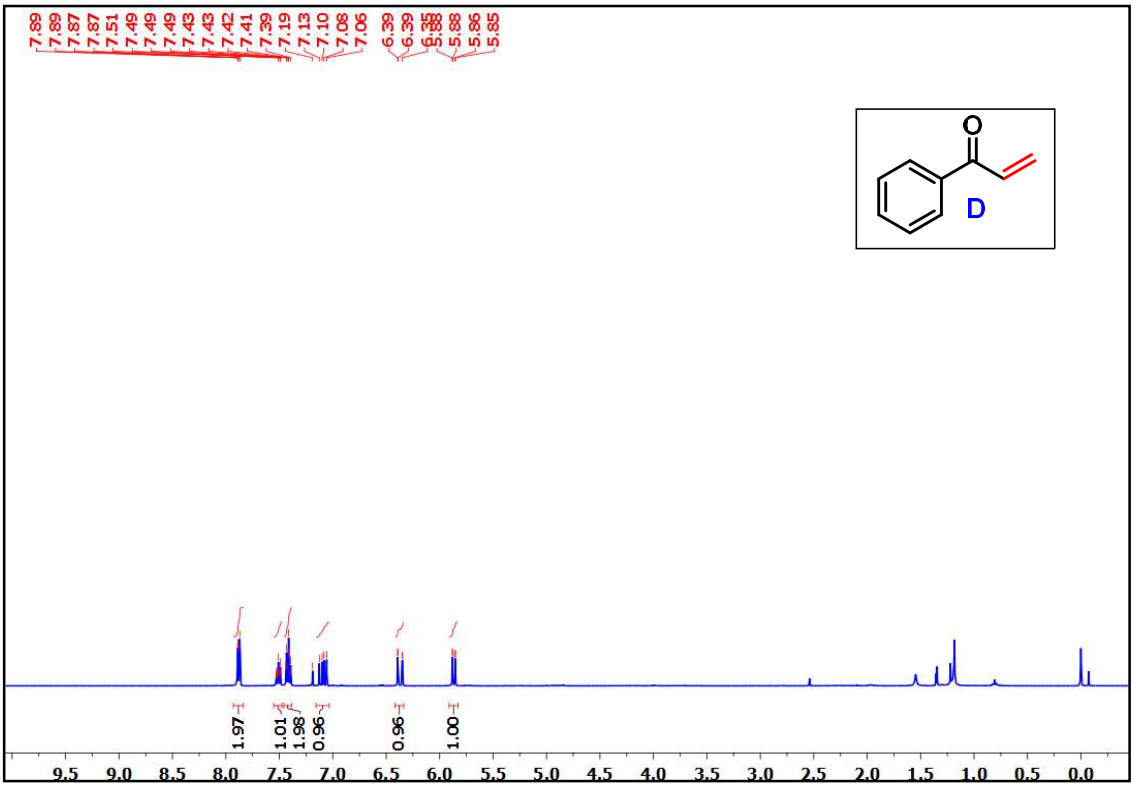
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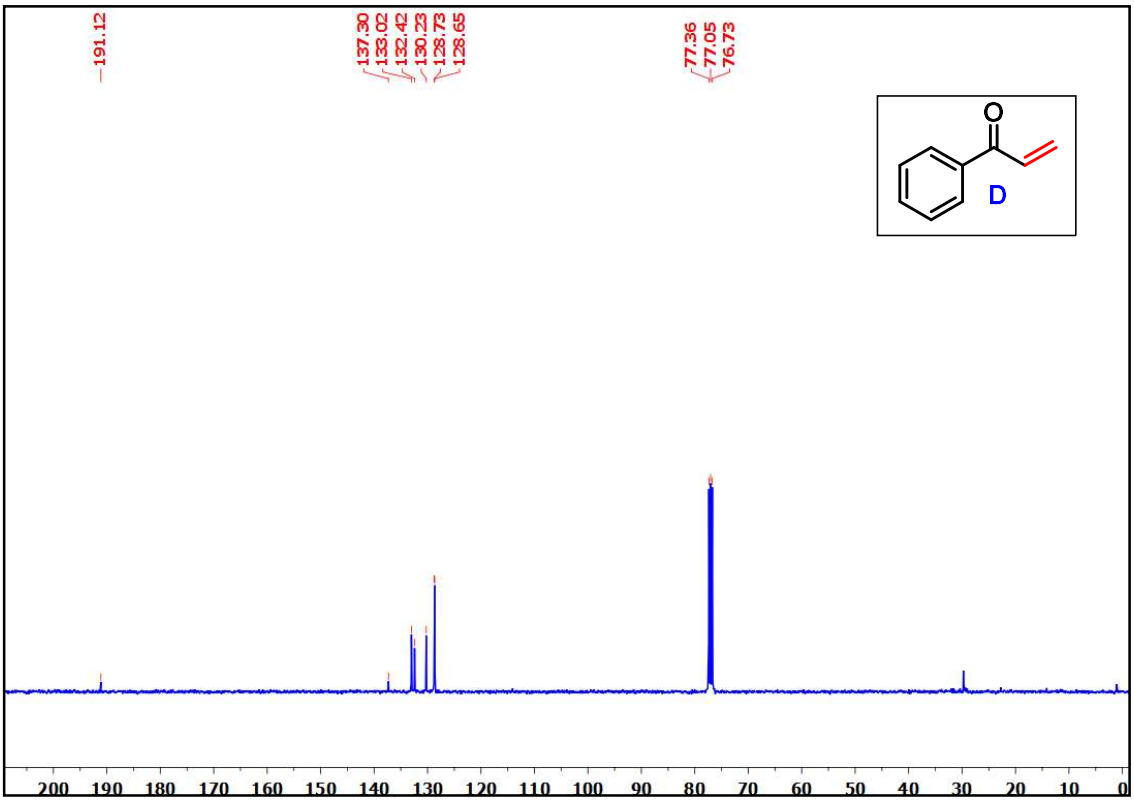
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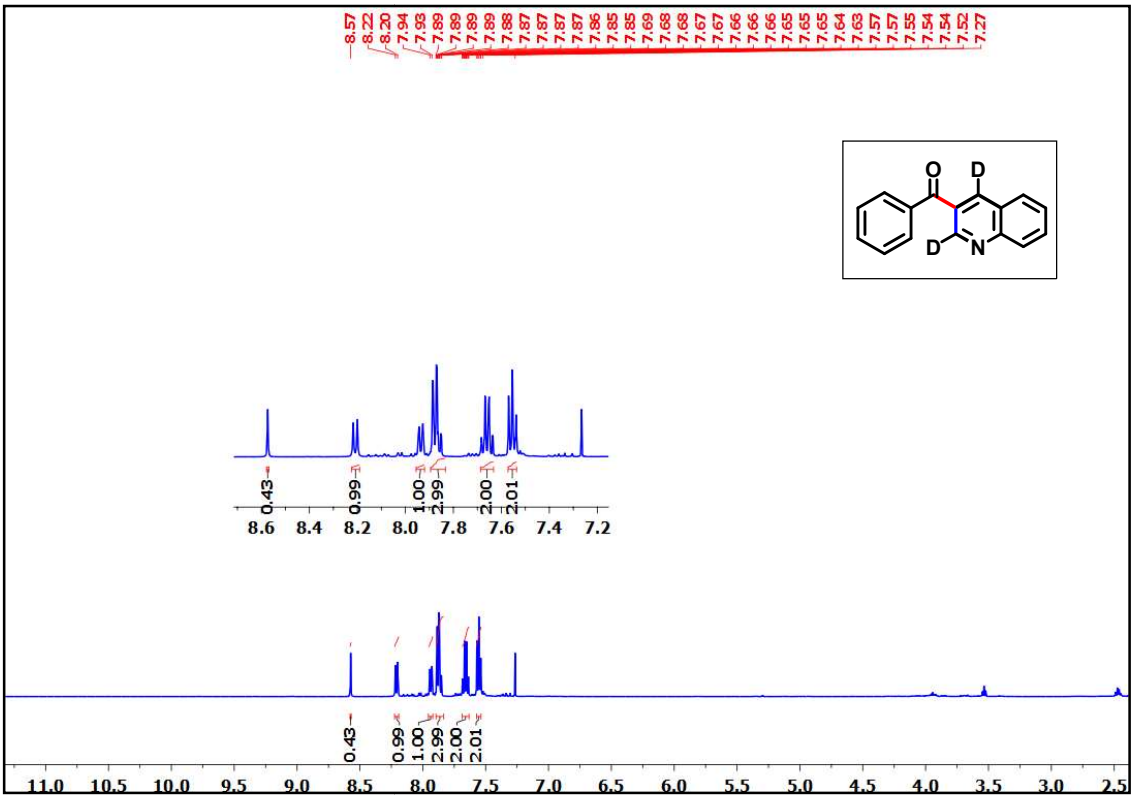
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