Supporting Information

Direct C4-H Phosphonation of 8-Hydroxyquinoline Derivatives Employing Photoredox Catalysis and Silver Catalysis

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1. General Information

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used directly without further purification. Petroleum ether, ethyl acetate and hexane were used for column chromatography. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, td = triplet doublet). Unless otherwise mentioned, all materials were commercially obtained and used without further purification.

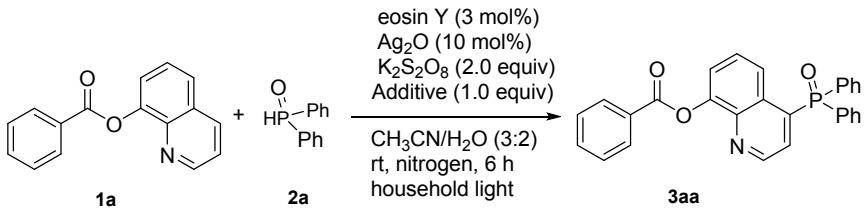
2. Preparation of Substrates

All of the esters substrates were prepared from the corresponding acids and 8-hydroxyquinoline according to the reported procedure.[1]

3. Optimization of Reaction Conditions

A 20 mL Schlenk tube was equipped with a magnetic stir bar and charged with 8-hydroxylquinoline ester **1a** (24.9 mg, 0.1 mmol), diphenylphosphine oxide **2a** (0.2 mmol, 2.0 equiv), photocatalyst (0.003 mmol, 3 mol%), AgX (0.01 mmol, 10 mol%), oxidant (0.2 mmol, 2 equiv), and solvent (1.0 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 6 h. Upon completion, the mixture was added into H_2O (20 mL) and extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using CH_2Cl_2/ethyl acetate as an eluent (2:1, V/V) to afford the pure product **3aa**.

Table S1 Screening of Reaction Conditions[a]



Entry	Photocatalyst	AgX	Oxidant	Solvent	Addition	yield (%)[b]
1	acid red 94	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	50%
2	acid red 94	AgOAc	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	trace
3	acid red 94	AgI	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	trace
4	acid red 94	$AgNO_2$	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	37%
5	acid red 94	Ag_3PO_4	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	trace
6	acid red 94	$AgNO_3$	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	44%
7	acid red 94	Ag_2CO_3	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	48%
8	acid red 94	Ag_2SO_4	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	trace
9	acid red 94	AgOTf	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	trace

10	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	74%
11	eosin B	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	43%
12	$[Ru(bpy)_3]Cl_2$	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	42%
13	alizarin red S	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	20%
14	$Ir(bpy)_2$	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	43%
15	eosin Y	Ag_2O	NMO	CH_3CN/H_2O(3:2)	-	trace
16	eosin Y	Ag_2O	BQ	CH_3CN/H_2O(3:2)	-	trace
17	eosin Y	Ag_2O	TBHP	CH_3CN/H_2O(3:2)	-	38%
18	eosin Y	Ag_2O	DTBP	CH_3CN/H_2O(3:2)	-	20%
19	eosin Y	Ag_2O	TBPB	CH_3CN/H_2O(3:2)	-	trace
20	eosin Y	Ag_2O	$(NH_4)_2S_2O_8$	CH_3CN/H_2O(3:2)	-	45%
21	eosin Y	Ag_2O	$Na_2S_2O_8$	CH_3CN/H_2O(3:2)	-	57%
22	eosin Y	Ag_2O	$PhI(OAc)_2$	CH_3CN/H_2O(3:2)	-	NR
23	eosin Y	Ag_2O	-	CH_3CN/H_2O(3:2)	-	NR
24	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	NaOAC	trace
25	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	PivONa	trace
26	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	K_3PO_4	NR
27	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	Na_2CO_3	trace
28	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	PivOH	trace
29	eosin Y	Ag_2O	$K_2S_2O_8$	DCE	-	NR
30	eosin Y	Ag_2O	$K_2S_2O_8$	Dioxane	-	NR
31	eosin Y	Ag_2O	$K_2S_2O_8$	Acetone	-	NR
32	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(1:1)	-	39%
33	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(2:1)	-	10%
34	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(2:3)	-	18%
35	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(10:0)	-	NR
36	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(0:10)	-	22%
37	eosin Y	Ag_2O	$K_2S_2O_8$	Acetone/H_2O(1:1)	-	54%
38[c]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	60%
39[d]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	<5%
40[e]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	<5%
41[f]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	20%
42[fg]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	<5%
43[fh]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	<5%
44[fi]	-	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	NR
45[j]	**eosin Y**	**Ag_2O**	**$K_2S_2O_8$**	**CH_3CN/H_2O(3:2)**	**-**	**78%**
46[k]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	65%
47[l]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	34%
48[m]	eosin Y	Ag_2O	$K_2S_2O_8$	CH_3CN/H_2O(3:2)	-	NR

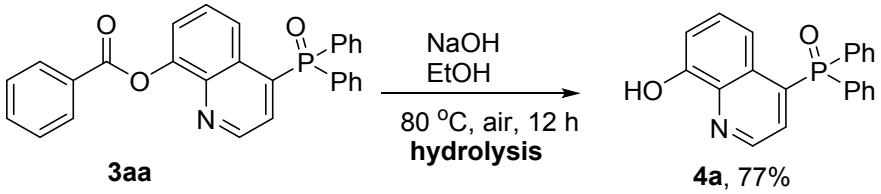
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), AgX (10 mol%), photocatalyst (3 mol%, 26 W household light), oxidant (0.2 mmol, 2 equiv), additive (1.0 equiv), solvent (1.0 mL) under nitrogen for 8 h. [b]Isolated yield. [c]Under green LED. [d]Under red LED. [e]Under blue LED. [f]Under dark. [g]For Ag_2O (1.0 equiv). [h]For Ag_2O (2.0 equiv). [i]For no eosin Y. [j]For 6 h, [k]For 10 h, [l]Under air, [m]Under O_2.

4. Typical Procedure for the Products

(**a**) Procedure for the synthesis of **3**:

A 20 mL Schlenk tube was equipped with a magnetic stir bar and charged with 8-hydroxylquinoline ester **1** (0.1 mmol), diaryphosphine oxide **2** (0.2 mmol), eosin Y (2.1 mg, 0.003 mmol, 3 mol%), $K_2S_2O_8$ (0.2 mmol, 2 equiv), Ag_2O (2.3 mg, 0.01 mmol, 10 mol%) in CH_3CN/H_2O (3:2) (1.5 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 6 h. Upon completion, the mixture was added into H_2O (20 mL) and extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using CH_2Cl_2/ethyl acetate as an eluent (2:1, V/V) to afford the pure product **3**.

(**b**) Procedure for the hydrolysis of **4a:**

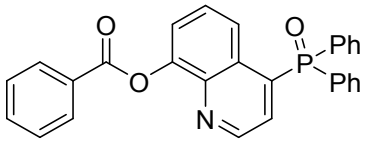


3aa **4a**, 77%

To a solution of **3aa** (0.2 mmol) in ethyl alcohol (3 mL), NaOH (0.22 mmol, 1.1 equiv) was added, and the resulting mixture was stirred at 80 °C for 12 h. The solvent was removed by vacuum, and then 3 mL H_2O was added to the residue. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using CH_2Cl_2/ethyl acetate (2:1, V/V) as an eluent to afford the pure product **4a**.

5. Characterization Data of the Products

4-(diphenylphosphoryl)quinolin-8-yl benzoate (3aa):



3aa

Light yellow solid (78% yield); mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.53−8.51 (m, 1H), 8.34−8.32 (m, 2H), 7.72−7.49 (m, 15H), 7.15 (dd, J= 15.1, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.9 (d,

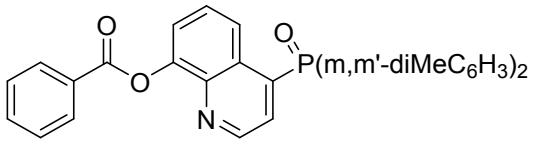
$J_{C\text{-}P}$ = 7.1 Hz), 138.8 (d, $J_{C\text{-}P}$ = 94.3 Hz), 133.7, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 106.3 Hz), 130.6, 129.4, 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.9, 128.6, 127.7, 126.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 125.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 122.2; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for $C_{28}H_{21}NO_3P$ $[M+H]^+$: 450.1254, Found: 450.1255.

4-(di-p-tolylphosphoryl)quinolin-8-yl benzoate (3ab):

3ab

Light yellow solid (66% yield); mp 194−195 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 3.8 Hz, 1H), 8.53 (d, J= 7.9 Hz, 1H), 8.33 (d, J= 7.6 Hz, 2H), 7.67−7.63 (m, 1H), 7.59−7.51 (m, 8H), 7.31−7.29 (m, 4H), 7.15 (dd, J= 14.8, 4.2 Hz, 1H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 143.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 139.2 (d, $J_{C\text{-}P}$ = 93.9 Hz), 133.7, 132.0 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6, 129.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 129.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 128.6, 127.9 (d, $J_{C\text{-}P}$ = 107.8 Hz), 127.6, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.2, 21.7; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 31.1; HRMS (ESI-TOF): Calcd for $C_{30}H_{25}NO_3P$ $[M+H]^+$: 478.1567, Found: 478.1569.

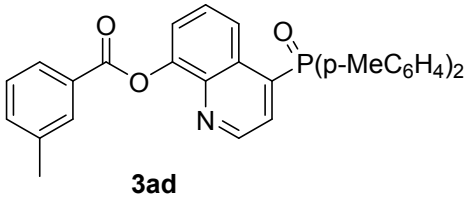
4-(bis(3,5-dimethylphenyl)phosphoryl)quinolin-8-yl benzoate (3ac):



3ac

Light yellow solid (53% yield); mp 109−110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 3.9 Hz, 1H), 8.56-8.54 (m, 1H), 8.35-8.32 (m, 2H), 7.68−7.64 (m, 1H), 7.58−7.53 (m, 4H), 7.29 (d, J= 12.6 Hz, 4H), 7.21 (s, 2H), 7.16 (dd, J= 14.8, 4.2 Hz, 1H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 141.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 139.3 (d, $J_{C\text{-}P}$ = 92.7 Hz), 138.6 (d, $J_{C\text{-}P}$ = 13.0 Hz), 134.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 133.7, 130.9 (d, $J_{C\text{-}P}$ = 104.1 Hz), 130.7, 129.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 129.4, 129.1 (d, $J_{C\text{-}P}$ = 6.6 Hz), 128.6, 127.5, 126.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 125.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.1, 21.4; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 31.3; HRMS (ESI-TOF): Calcd for $C_{32}H_{29}NO_3P$ $[M+H]^+$: 506.1880, Found: 506.1881.

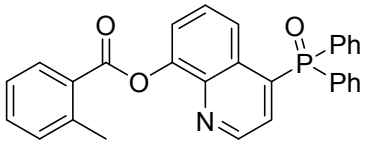
4-(di-p-tolylphosphoryl)quinolin-8-yl 3-methylbenzoate (3ad):



3ad

Light yellow solid (48% yield); mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 3.8 Hz, 1H), 8.54−8.52 (m, 1H), 8.15−8.12 (m, 2H), 7.59−7.53 (m, 6H), 7.48−7.40 (m, 2H), 7.31−7.29 (m, 4H), 7.14 (dd, J= 14.8, 4.2 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 149.1 (d, $J_{C\text{-}P}$ = 11.3 Hz), 148.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 143.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 141.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 139.3 (d, $J_{C\text{-}P}$ = 93.7 Hz), 138.4, 134.5, 132.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 131.0, 129.6 (d, $J_{C\text{-}P}$ = 12.8 Hz), 129.3, 129.0 (d, $J_{C\text{-}P}$ = 6.6 Hz), 128.5, 127.7, 127.5, 127.5, 126.6 (d, $J_{C\text{-}P}$ = 9.3 Hz), 125.8 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.1, 21.7, 21.4; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 31.0; HRMS (ESI-TOF): Calcd for $C_{31}H_{27}NO_3P$ $[M+H]^+$: 492.1723, Found: 492.1724.

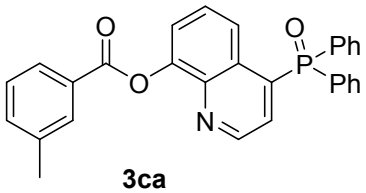
4-(diphenylphosphoryl)quinolin-8-yl 2-methylbenzoate (3ba):



3ba

Light yellow solid (67% yield); mp 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (t, J= 4.0 Hz, 1H), 8.51−8.48 (m, 1H), 8.38−8.36 (m, 1H), 7.72−7.49 (m, 13H), 7.38-7.33 (m, 2H), 7.16 (dd, J= 14.9, 4.2 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 149.0 (d, $J_{C\text{-}P}$ = 11.3 Hz), 148.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 142.0 (d, $J_{C\text{-}P}$ = 7.2 Hz),141.5, 138.8 (d, $J_{C\text{-}P}$ = 93.7 Hz), 132.8, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz),131.9,131.7, 131.2 (d, $J_{C\text{-}P}$ = 105.0 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.9, 128.6, 127.7, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 126.0,125.6 (d, $J_{C\text{-}P}$ = 5.6 Hz), 122.3, 21.9; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF) Calcd for $C_{29}H_{23}NO_3P$ $[M+H]^+$: 464.1410, Found: 464.1413.

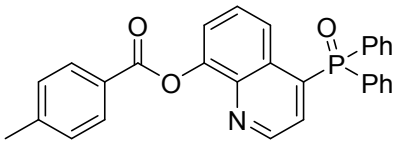
4-(diphenylphosphoryl)quinolin-8-yl 3-methylbenzoate (3ca):



3ca

Light yellow solid (68% yield); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.53−8.50 (m, 1H), 8.15−8.12 (m, 2H), 7.72−7.41 (m, 15H), 7.15 (dd, J= 14.9, 4.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 149.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 148.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 142.0 (d, $J_{C\text{-}P}$ = 7.3 Hz), 138.8 (d, $J_{C\text{-}P}$ = 94.0 Hz),138.5, 134.5, 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 105.1 Hz), 131.0, 129.3, 128.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.9, 128.5, 127.7, 127.7, 126.6 (d, $J_{C\text{-}P}$ = 9.5 Hz),125.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.2, 21.3; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF) Calcd for $C_{29}H_{23}NO_3P$ $[M+H]^+$: 464.1410, Found: 464.1412.

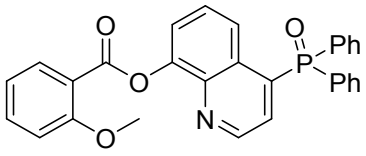
4-(diphenylphosphoryl)quinolin-8-yl 4-methylbenzoate (3da):



3da

Light yellow solid (66% yield); mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.52−8.49 (m, 1H), 8.23−8.21 (m, 1H), 7.72−7.49 (m, 13H), 7.35-7.33 (m, 2H), 7.14 (dd, J= 14.9, 4.2 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 149.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 148.3 (d, $J_{C\text{-}P}$ = 3.2 Hz), 144.5, 142.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 138.7 (d, $J_{C\text{-}P}$ = 94.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 108.4 Hz),129.4, 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.7, 126.7, 126.6, 126.6, 125.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.3, 21.8; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF) Calcd for $C_{29}H_{23}NO_3P$ $[M+H]^+$: 464.1410, Found: 464.1413.

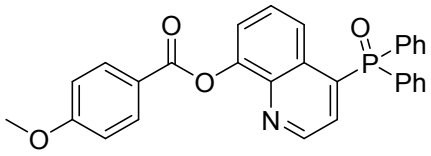
4-(diphenylphosphoryl)quinolin-8-yl 2-methoxybenzoate (3ea):



3ea

Light yellow solid (58% yield); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (t, J= 4.0 Hz, 1H), 8.48 (d, J= 8.2 Hz, 1H), 8.32−8.29 (m, 1H), 7.71−7.48 (m, 13H), 7.15 (dd, J= 15.0, 4.2 Hz, 1H), 7.10-7.04 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2,160.3, 149.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 148.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 142.1 (d, $J_{C\text{-}P}$ = 7.2 Hz),139.1, 138.1, 134.85, 132.9, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.1 Hz),132.0, 131.2 (d, $J_{C\text{-}P}$ = 105.1 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.8, 127.6, 126.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.4 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.4, 119.5 (d, $J_{C\text{-}P}$ = 161.4 Hz) 112.3, 56.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF) Calcd for $C_{29}H_{23}NO_4P$ $[M+H]^+$: 480.1359, Found: 480.1362.

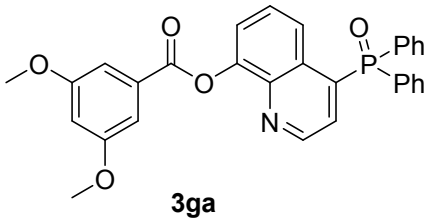
4-(diphenylphosphoryl)quinolin-8-yl 4-methoxybenzoate (3fa):



3fa

Light yellow solid (61% yield); mp 208−209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.51-8.49 (m, 1H), 8.29−8.27 (m, 2H), 7.71−7.66 (m, 4H), 7.62-7.48 (m, 8H), 7.14 (dd, J= 15.0, 4.2 Hz, 1H), 7.03-7.00 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 164.0, 148.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 142.1 (d, $J_{C\text{-}P}$ = 7.2 Hz), 139.2, 138.3, 132.7, 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 105.2 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.7, 126.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.0 (d, $J_{C\text{-}P}$ = 63.4 Hz), 55.6; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF) Calcd for $C_{29}H_{23}NO_4P$ $[M+H]^+$: 480.1359, Found: 480.1361.

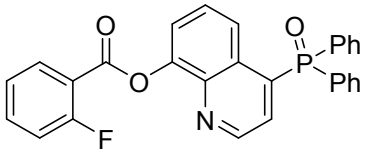
4-(diphenylphosphoryl)quinolin-8-yl 3,5-dimethoxybenzoate (3ga):



3ga

Light yellow solid (60% yield); mp 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (t, J= 4.0 Hz, 1H), 8.54-8.51 (m, 1H), 7.72−7.67 (m, 4H),7.63-7.49 (m, 8H), 7.48 (s, 1H), 7.47 (s, 1H), 7.15 (dd, J= 14.9, 4.2 Hz, 1H), 6.75 (t, J= 2.4 Hz, 1H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 160.8, 149.1 (d, J_{C-P} = 11.4 Hz), 148.2 (d, J_{C-P} = 2.8 Hz), 141.9 (d, J_{C-P} = 7.2 Hz), 139.2, 138.3, 132.6 (d, J_{C-P} = 2.7 Hz), 132,0 (d, J_{C-P} = 10.0 Hz), 131.1 (d, J_{C-P} = 105.1 Hz), 131.1, 128.9 (d, J_{C-P} = 12.4 Hz), 127.7, 126.6 (d, J_{C-P} = 9.4 Hz), 125.7 (d, J_{C-P} = 5.4 Hz), 122.2, 108.0, 106.7, 55.7; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF) Calcd for $C_{30}H_{25}NO_3P$ $[M+H]^+$: 510.1465, Found: 510.1469.

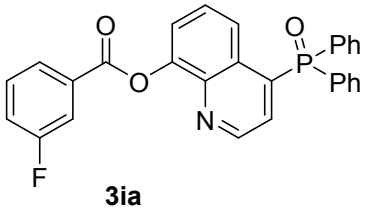
4-(diphenylphosphoryl)quinolin-8-yl 2-fluorobenzoate (3ha):



3ha

Light yellow solid (63% yield); mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.89 (t, J= 3.9 Hz, 1H), 8.54 (d, J= 8.2, 1H), 8.32-8.28 (m, 1H), 7.73-7.68 (m, 4H), 7.65−7.58 (m, 4H),7.56-7.51 (m, 5H), 7.35−7.31 (m, 1H), 7.26−7.23 (m, 1H),7.18 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9, 162.8 (d, J_{C-F} = 3.9 Hz), 161.3, 149.1 (d, J_{C-P}= 11.4 Hz), 147.8 (d, J_{C-P} = 2.7 Hz), 141.7 (d, J_{C-F} = 7.2 Hz), 138.8 (d, J_{C-P} = 93.9 Hz), 135.3 (d, J_{C-P} = 9.1 Hz), 133.0, 132.6 (d, J_{C-P} = 2.6 Hz), 132.0 (d, J_{C-P} = 9.8 Hz), 131.1 (d, J_{C-P} = 105.1 Hz), 129.0 (d, J_{C-P} = 12.4 Hz), 127.7, 126.7 (d, J_{C-P} = 9.4 Hz), 125.8 (d, J_{C-P}= 5.4 Hz), 124.2 (d, J_{C-P} = 4.0 Hz), 122.2, 117.9 (d, J_{C-P} = 9.2 Hz), 117.2 (d, J_{C-F} = 21.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.912; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}FNO_3P$ $[M+H]^+$: 468.1159, Found: 468.1159.

4-(diphenylphosphoryl)quinolin-8-yl 3-fluorobenzoate (3ia):

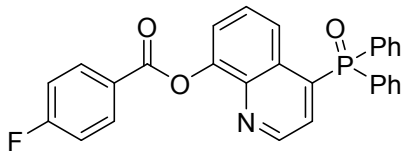


3ia

Light yellow solid (66% yield); mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 3.8 Hz,

1H), 8.53 (d, *J*= 8.0, 1H), 8.11 (d, *J*= 7.7, 1H), 8.00 (d, *J*= 8.9, 1H), 7.72−7.67 (m, 4H), 7.62-7.55 (m, 3H), 7.53−7.50 (m, 6H), 7.37−7.33 (m, 1H), 7.16 (dd, *J*= 15.0, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 162.6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 157.2, 149.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 147.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.7 (d, $J_{C\text{-}F}$ = 7.2 Hz), 138.7 (d, $J_{C\text{-}P}$ = 94.1 Hz), 132,7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.9 (d, $J_{C\text{-}P}$ = 105.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 7.7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.7, 126.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 126.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.2, 120.8 (d, $J_{C\text{-}P}$ = 21.1 Hz), 117.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 115.6; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 31.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -108.038; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}FNO_3P$ $[M+H]^+$: 468.1159, Found: 468.1163.

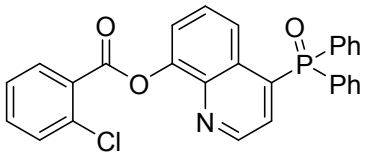
4-(diphenylphosphoryl)quinolin-8-yl 4-fluorobenzoate (3ja):



3ja

Light yellow solid (65% yield); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (t, *J*= 3.9Hz, 1H), 8.54 (d, *J*= 7.3, 1H), 8.38-8.34 (m, 2H), 7.74-7.69 (m, 4H), 7.64−7.58 (m, 4H),7.56-7.51 (m, 5H), 7.28−7.25 (m, 1H), 7.17 (dd, *J*= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.5, 165.0, 164.5, 149.1 (d, $J_{C\text{-}P}$= 11.3 Hz), 148.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 141.8 (d, $J_{C\text{-}F}$ = 7.1 Hz), 138.8 (d, $J_{C\text{-}P}$ = 93.8 Hz), 133.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 105.2 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.7, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.8 (d, $J_{C\text{-}P}$= 5.4 Hz), 125.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 122.2, 115.9 (d, $J_{C\text{-}P}$ = 21.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.355; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}FNO_3P$ $[M+H]^+$: 468.1159, Found: 468.1161.

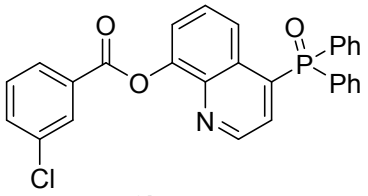
4-(diphenylphosphoryl)quinolin-8-yl 2-chlorobenzoate (3ka):



3ka

Light yellow (66% yield); mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (t, *J*= 4.0 Hz, 1H), 8.52 (d, *J*= 8.4 Hz, 1H), 8.37−8.34 (m, 1H), 7.72−7.67 (m, 4H), 7.62−7.58 (m, 3H), 7.56−7.48 (m, 7H), 7.44−7.40 (m, 1H), 7.18 (dd, *J*= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 147.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.8 (d, $J_{C\text{-}P}$ = 93.9 Hz), 134.8, 133.3, 132.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 132.6, 132,0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.4, 131.1 (d, $J_{C\text{-}P}$ = 105.1 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.9, 127.6, 126.8, 126.8, 126.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 5.4 Hz), 122.2; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}ClNO_3P$ $[M+H]^+$: 484.0864, Found: 484.0867.

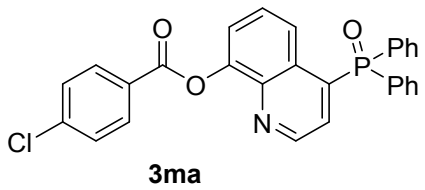
4-(diphenylphosphoryl)quinolin-8-yl 3-chlorobenzoate (3la):



3la

Light yellow solid (65% yield); mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.55-8.52 (m, 1H), 8.32−8.31 (m, 1H), 8.2 2−8.19 (m, 1H), 7.72−7.67 (m, 4H), 7.65−7.58 (m, 3H), 7.56−7.47 (m, 7H), 7.15 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2, 149.2 (d, $J_{C\text{-}P}$ = 11.3 Hz), 147.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 139.0 (d, $J_{C\text{-}P}$ = 93.7 Hz), 133.7, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.5, 131.2, 131.1 (d, $J_{C\text{-}P}$ = 105.1 Hz), 130.3, 130.2 (d, $J_{C\text{-}P}$ = 3.7 Hz), 129.3, 129.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.7, 127.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 126.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.5; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}ClNO_3P$ $[M+H]^+$: 484.0864, Found: 484.0866.

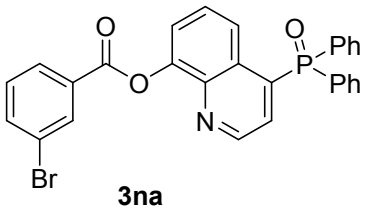
4-(diphenylphosphoryl)quinolin-8-yl 4-chlorobenzoate (3ma):



3ma

Light yellow solid (63% yield); mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 3.9 Hz, 1H), 8.54-8.52 (m, 1H), 8.28−8.25 (m, 2H), 7.72−7.67 (m, 4H), 7.63−7.58 (m, 2H), 7.57−7.56 (m, 1H), 7.54−7.49 (m, 7H), 7.15 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.6, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.8 (d, $J_{C\text{-}P}$ = 7.1 Hz), 140.2, 138.9 (d, $J_{C\text{-}P}$ = 93.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1, 132,0 (d, $J_{C\text{-}P}$ = 1.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 105.1 Hz), 129.0, 129.0, 128.9, 127.9, 127.6, 126.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.2; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}ClNO_3P$ $[M+H]^+$: 484.0864, Found: 484.0865.

4-(diphenylphosphoryl)quinolin-8-yl 3-bromobenzoate (3na):

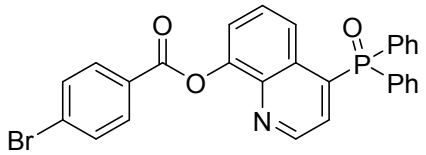


3na

Light yellow solid (49% yield); mp 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 4.0 Hz, 1H), 8.55−8.53 (m, 1H), 8.47−8.46 (m, 1H), 8.26−8.23 (m, 1H), 7.79−7.76 (m, 1H), 7.72−7.67 (m, 4H), 7.62−7.58 (m, 2H), 7.56 (m, 1H), 7.54−7.49 (m, 5H), 7.42 (t, J= 7.9 Hz, 1H), 7.16 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 149.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 147.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.9 (d, $J_{C\text{-}P}$ = 93.8 Hz), 136.6, 133.5, 132.6 (d, $J_{C\text{-}P}$ = 2.6

Hz), 132,0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.3, 131.1 (d, $J_{C\text{-}P}$ = 105.1 Hz), 130.2, 129.1, 129.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 129.0, 127.6, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 122.7, 122.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}BrNO_3P$ $[M+H]^+$: 528.0359, Found: 528.0360.

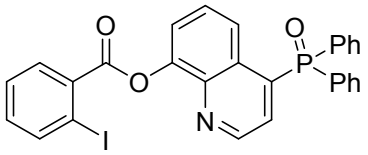
4-(diphenylphosphoryl)quinolin-8-yl 4-bromobenzoate (3oa):



3oa

Light yellow solid (54% yield); mp 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 3.9 Hz, 1H), 8.54−8.52 (m, 1H), 8.19-8.17 (m, 2H), 7.72−7.67 (m, 7H), 7.63−7.58 (m, 2H), 7.56 (m, 1H), 7.54−7.49 (m, 5H), 7.15 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.8 149.1 (d, $J_{C\text{-}P}$ = 11.3 Hz), 148.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 141.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.8 (d, $J_{C\text{-}P}$ = 93.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1, 132.0, 132.0, 131.0 (d, $J_{C\text{-}P}$ = 105.1 Hz), 129.0, 129.0, 128.9, 128.3, 127.7, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 122.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}BrNO_3P$ $[M+H]^+$: 528.0359, Found: 528.0359.

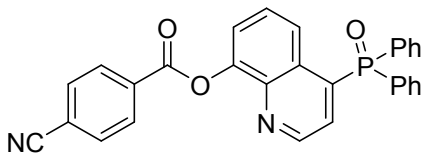
4-(diphenylphosphoryl)quinolin-8-yl 2-iodobenzoate (3pa):



3pa

Light yellow solid (45% yield); mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (t, J= 3.9Hz, 1H), 8.52 (d, J= 2.1, 1H), 8.42-8.39 (m, 1H), 8.12 (d, J= 7.8, 1H), 7.74-7.69 (m, 4H), 7.65−7.61 (m, 3H),7.58-7.52 (m, 6H), 7.27−7.25 (m, 1H),7.19 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 149.1 (d, $J_{C\text{-}P}$= 11.3 Hz), 147.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 141.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 138.8 (d, $J_{C\text{-}P}$ = 93.7 Hz), 133.5, 133.4, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.4, 132.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 105.2 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.9, 128.6, 128.2, 127.6, 126.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.8 (d, $J_{C\text{-}P}$= 5.4 Hz), 122.2, 95.3; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; HRMS (ESI-TOF): Calcd for $C_{28}H_{20}INO_3P$ $[M+H]^+$: 476.0220, Found: 476.0218.

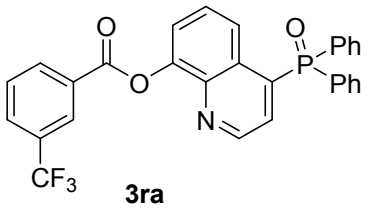
4-(diphenylphosphoryl)quinolin-8-yl 4-cyanobenzoate (3qa):



3qa

Light yellow solid (58% yield); mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 4.0 Hz, 1H), 8.56−8.54 (m, 1H), 8.44−8.42 (m, 2H), 7.86−7.84 (m, 2H), 7.72−7.67 (m, 4H), 7.62−7.58 (m, 3H), 7.56−7.50 (m, 5H), 7.16 (dd, J= 14.9, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9, 149.2 (d, J_{C-P} = 11.5 Hz), 147.7 (d, J_{C-P} = 2.8 Hz), 141.5 (d, J_{C-P} = 7.2 Hz), 139.0 (d, J_{C-P} = 93.5 Hz), 133.3, 132.7 (d, J_{C-P} = 2.7 Hz), 132.5, 132,0 (d, J_{C-P} = 10.0 Hz), 131.0, 130.9 (d, J_{C-P} = 105.3 Hz), 129.0, 129.0 (d, J_{C-P} = 12.5 Hz), 127.7, 126.8 (d, J_{C-P} = 9.4 Hz), 126.1 (d, J_{C-P} = 5.6 Hz), 122.0, 117.5 (d, J_{C-P} = 96.4 Hz) ; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for $C_{29}H_{20}N_2O_3P$ $[M+H]^+$: 475.1206, Found: 475.1209.

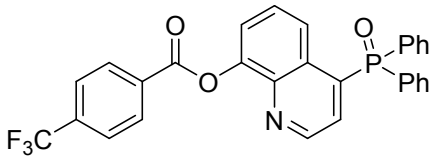
4 diphenylphosphoryl)quinolin-8-yl 3-(trifluoromethyl)benzoate (3ra):



3ra

Light yellow solid (67% yield); mp 99−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.60 (s, 1H), 8.57−8.54 (m, 1H), 8.52−8.50 (m, 1H), 7.93−7.91 (m, 1H), 7.72−7.67 (m, 5H), 7.63−7.56 (m, 4H), 7.54−7.50 (m, 4H), 7.16 (dd, J= 14.9, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2, 149.2 (d, J_{C-P} = 11.5 Hz), 147.9 (d, J_{C-P} = 2.9 Hz), 141.7 (d, J_{C-P} = 7.0 Hz), 139.0 (d, J_{C-P} = 93.8 Hz), 133.7, 132.6 (d, J_{C-P} = 2.7 Hz), 132,0 (d, J_{C-P} = 10.0 Hz), 131.3 (q, J_{C-F} = 32.9 Hz), 131.1 (d, J_{C-P} = 105.1 Hz), 130.3, 130.2 (d, J_{C-P} = 3.6 Hz), 129.3, 129.0 (d, J_{C-P} = 12.3 Hz), 128.9, 127.7, 127.5 (d, J_{C-P} = 3.8 Hz), 126.7 (d, J_{C-P} = 9.5 Hz), 126.0 (q, J_{C-F} = 5.4 Hz), 123.7 (q, J_{C-F} = 270.7 Hz), 122.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.704; HRMS (ESI-TOF): Calcd for $C_{29}H_{20}F_3NO_3P$ $[M+H]^+$: 518.1127, Found: 518.1132.

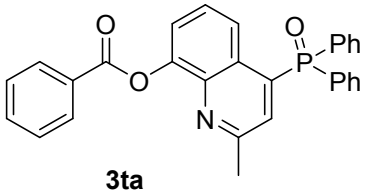
4-(diphenylphosphoryl)quinolin-8-yl 4-(trifluoromethyl)benzoate (3sa):



3sa

Light yellow solid (52% yield); mp 99−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (t, J= 3.8 Hz, 1H), 8.56-8.54 (m, 1H), 8.45 (d, J= 8.3 Hz, 2H), 7.82 (d, J= 8.3 Hz, 2H), 7.72−7.67 (m, 4H), 7.64−7.56 (m, 4H), 7.54−7.50 (m, 4H), 7.16 (dd, J= 14.9, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 149.1 (d, J_{C-P} = 11.4 Hz), 147.9 (d, J_{C-P} = 2.8 Hz), 141.6 (d, J_{C-P} = 7.1 Hz), 139.0 (d, J_{C-P} = 93.8 Hz), 135.3, 134.9, 132.6 (d, J_{C-P} = 2.7 Hz), 132,0 (d, J_{C-P} = 10.0 Hz), 131.1 (d, J_{C-P} = 105.1 Hz), 130.9, 129.0 (d, J_{C-P} = 12.4 Hz), 127.6, 126.7 (d, J_{C-P} = 9.3 Hz), 126.0 (d, J_{C-F} = 5.4 Hz), 125.7 (d, J_{C-P} = 3.7 Hz), 122.1; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.100; HRMS (ESI-TOF): Calcd for $C_{29}H_{20}F_3NO_3P$ $[M+H]^+$: 518.1127, Found: 518.1133.

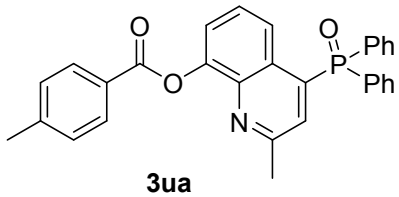
4-(diphenylphosphoryl)-2-methylquinolin-8-yl benzoate (3ta):



3ta

Light yellow solid (69% yield); mp 200−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37−8.31 (m, 3H), 7.72−7.64 (m, 4H), 7.61−7.48 (m, 10H), 7.45−7.41 (m, 1H), 7.12-7.08 (d, *J*= 15.4 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 158.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 147.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.5 (d, $J_{C\text{-}P}$ = 7.7 Hz), 138.6 (d, $J_{C\text{-}P}$ = 94.0 Hz), 133.5, 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132,0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 104.9 Hz), 130.5, 129.7, 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.6, 127.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 127.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 126.5, 125.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 122.0, 25.8; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.4; HRMS (ESI-TOF): Calcd for $C_{29}H_{23}NO_3P$ $[M+H]^+$: 464.1410, Found: 464.1414.

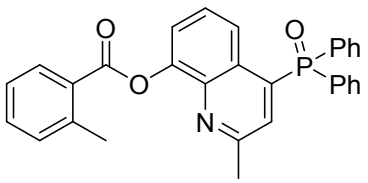
4-(diphenylphosphoryl)-2-methylquinolin-8-yl 4-methylbenzoate (3ua):



3ua

Light yellow solid (67% yield); mp 157−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J*= 8.4 Hz, 1H), 8.21 (d, *J*= 8.1 Hz, 2H), 7.71−7.67 (m, 4H), 7.60−7.57 (m, 2H), 7.52-7.48 (m, 5H), 7.44-7.40 (m, 1H), 7.34 (d, *J*= 8.0 Hz, 2H), 7.10 (d, *J*= 15.3 Hz, 1H), 2.54 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 158.0 (d, $J_{C\text{-}P}$ = 11.3 Hz), 147.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 144.3, 141.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 138.6 (d, $J_{C\text{-}P}$ = 93.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132,0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 104.8 Hz), 130.5, 129.3, 128.9 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 127.0 (d, $J_{C\text{-}P}$ = 6.7 Hz), 126.9, 126.5, 125.2 (d, $J_{C\text{-}P}$ = 5.2 Hz), 122.1, 25.8, 21.8; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.3; HRMS (ESI-TOF): Calcd for $C_{30}H_{25}NO_3P$ $[M+H]^+$: 478.1567, Found: 478.1567.

4-(diphenylphosphoryl)-2-methylquinolin-8-yl 2-methylbenzoate (3va):

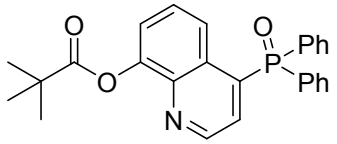


3va

Light yellow solid (64% yield); mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34-8.32 (m, 2H), 8.72-8.67 (m, 4H), 7.62−7.58 (m, 2H), 7.52−7.48 (m, 6H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 2H), 7.12 (d, *J*= 15.3 Hz, 1H), 2.72 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 158.0 (d, $J_{C\text{-}P}$ = 11.3 Hz), 147.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.4 (d, $J_{C\text{-}P}$ = 7.4 Hz), 140.9, 138.6 (d, $J_{C\text{-}P}$ = 93.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.5, 132,0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.7, 131.4, 131.3 (d, $J_{C\text{-}P}$ = 104.9

Hz), 129.2, 128.9 (d, $J_{C\text{-}P}$ = 12.2 Hz), 127.8 (d, $J_{C\text{-}P}$ = 9.1 Hz), 127.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 126.5, 125.9, 125.2 (d, $J_{C\text{-}P}$ = 5.2 Hz), 122.1, 25.7, 21.6; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.3; HRMS (ESI-TOF): Calcd for $C_{30}H_{25}NO_3P$ $[M+H]^+$: 478.1567, Found: 478.1567.

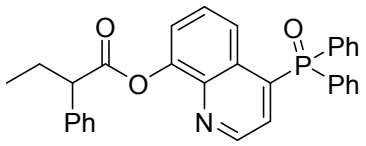
4-(diphenylphosphoryl)quinolin-8-yl pivalate (3wa):



3wa

Light yellow solid (34% yield); mp 185−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (t, J= 4.0 Hz, 1H), 8.44 (d, J= 8.4 Hz, 1H), 7.70−7.64 (m, 4H), 7.62−7.59 (m, 2H), 7.52−7.46 (m, 5H), 7.42−7.40 (m, 1H), 7.13 (dd, J= 15.0, 4.2 Hz, 1H), 1.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.5, 148.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 148.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 142.0 (d, $J_{C\text{-}P}$ = 9.2 Hz), 138.5 (d, $J_{C\text{-}P}$ = 93.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.2 (d, $J_{C\text{-}P}$ = 104.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7, 127.6, 126.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 121.9, 39.3, 27.4; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for $C_{26}H_{25}NO_3P$ $[M+H]^+$: 430.1567, Found: 430.1569.

4-(diphenylphosphoryl)quinolin-8-yl 2-phenylbutanoate (3xa):



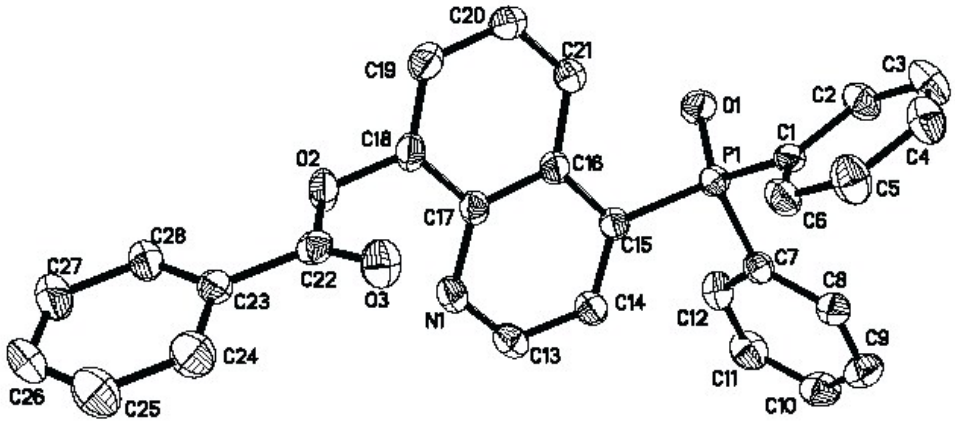
3xa

Light yellow solid (37% yield); mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (t, J= 3.9 Hz, 1H), 8.42 (d, J= 8.5 Hz, 1H), 7.68−7.58 (m, 6H), 7.50−7.48 (m, 6H), 7.45−7.36 (m, 3H), 7.32−7.28 (m, 2H), 7.13 (dd, J= 14.9, 4.2 Hz, 1H), 3.97 (t, J= 7.6 Hz, 1H), 2.40−2.33 (m, 1H) 2.02−2.00 (m, 1H), 1.08 (t, J= 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.0, 148.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 148.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 141.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 138.7, 138.6 (d, $J_{C\text{-}P}$ = 94.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.2 Hz), 132,0 (d, $J_{C\text{-}P}$ = 18.2 Hz), 132.0, 131.6 (d, $J_{C\text{-}P}$ = 7.2 Hz), 130.5 (d, $J_{C\text{-}P}$ = 7.6 Hz), 129.0, 128.9, 128.6, 128.4, 127.6, 127.4, 126.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 125.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 121.9, 53.2, 29.7, 27.0; ^{31}P NMR (163 MHz, $CDCl_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for $C_{31}H_{27}NO_3P$ $[M+H]^+$: 492.1723, Found: 492.1727.

6. References

1. Truong, T.; Klimovica, K.; Daugulis, O. *J. Am. Chem. Soc.* **2013**, *135*, 9342.

7. The Single Crystal X-ray Diffraction Study of 3aa.



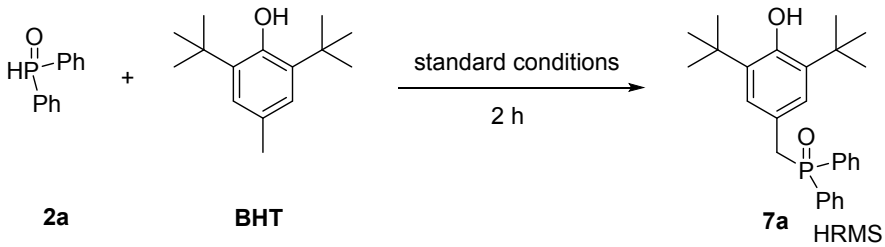
CCDC 1580532 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

Table S2 Crystal Data and Structure Refinement for **3aa**

Identification code	20170595
Empirical formula	$C_{28}H_{22}NO_4P$
Formula weight	467.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3199(11)
b/Å	22.2918(14)
c/Å	9.1023(9)
α/°	90
β/°	108.630(9)
γ/°	90
Volume/Å^3	2368.8(4)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.151
F(000)	976.0
Crystal size/mm^3	0.22 × 0.18 × 0.15

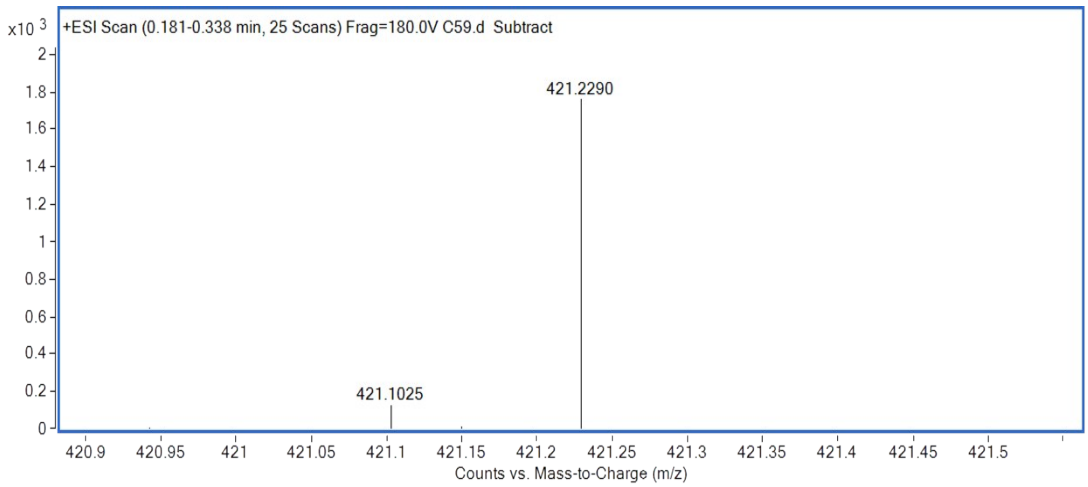
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.956 to 52.732
Index ranges	-15 ≤ h ≤ 14, -27 ≤ k ≤ 26, -6 ≤ l ≤ 11
Reflections collected	10630
Independent reflections	4823 [R_{int} = 0.0316, R_{sigma} = 0.0539]
Data/restraints/parameters	4823/0/307
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1154
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.1371
Largest diff. peak/hole / e Å^{-3}	0.25/-0.29

8. The Experiment of Trapping the Phosphonyl Radical

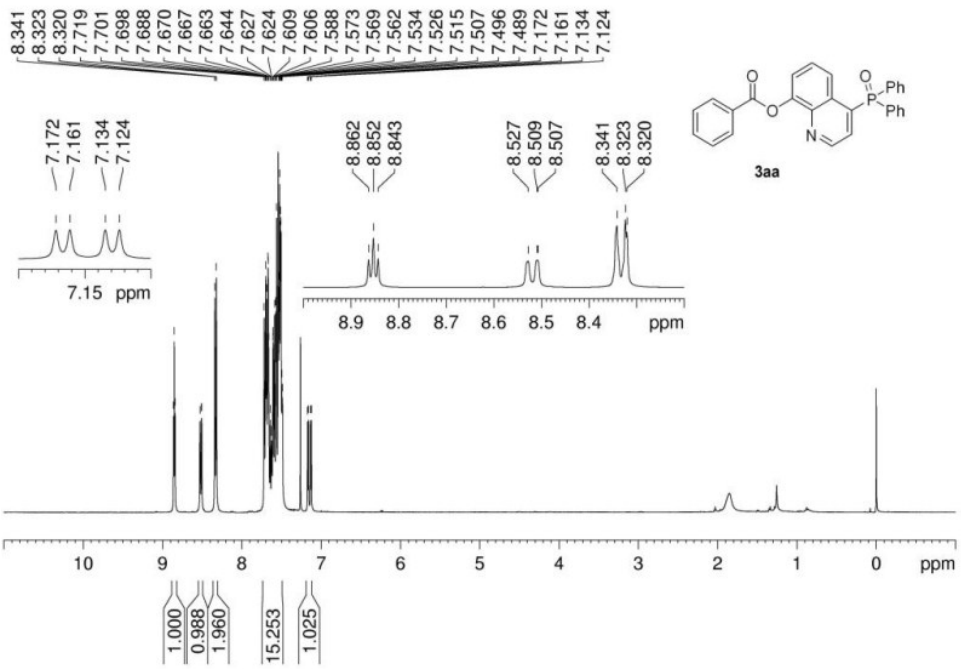


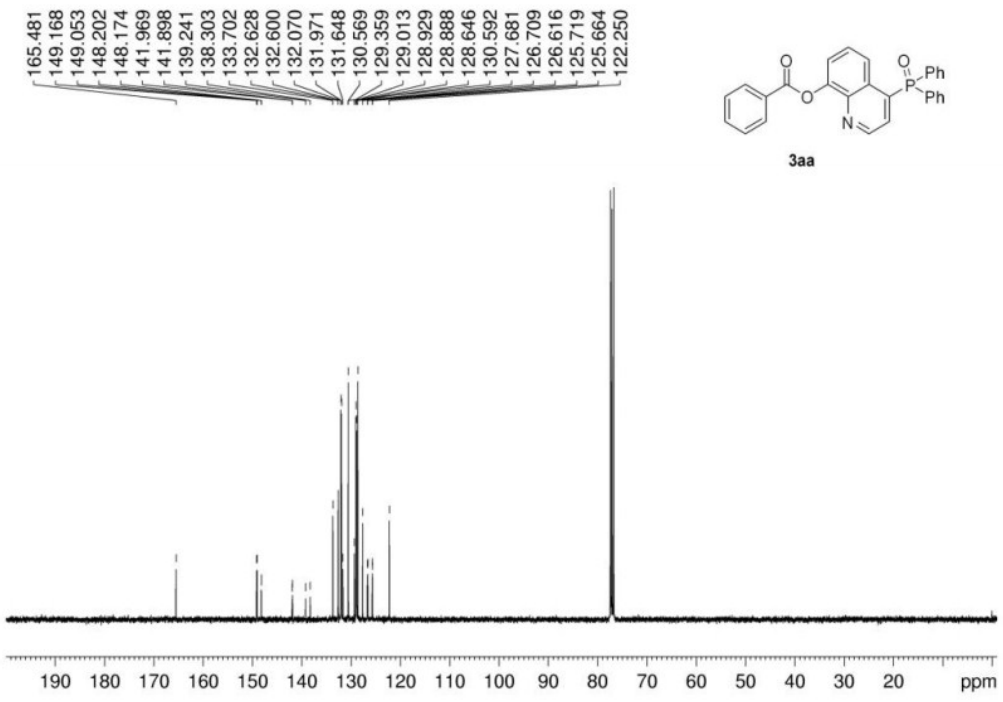
2a **BHT** **7a**

HRMS (ESI+) m/z:[M+Na]+
Calcd for $C_{27}H_{33}O_2P$
421.2291;found:421.2290



9. Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra for the Products


8.341
8.323
8.320
7.719
7.701
7.698
7.688
7.670
7.667
7.663
7.644
7.627
7.624
7.609
7.606
7.588
7.573
7.569
7.562
7.534
7.526
7.515
7.507
7.496
7.489
7.172
7.161
7.134
7.124
7.172
7.161
7.134
7.124
7.15 ppm
8.862
8.852
8.843
8.527
8.509
8.507
8.341
8.323
8.320
8.9 8.8 8.7 8.6 8.5 8.4 ppm
3aa
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
0.988
1.960
15.253
1.025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149.168
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148.202
148.174
141.969
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139.241
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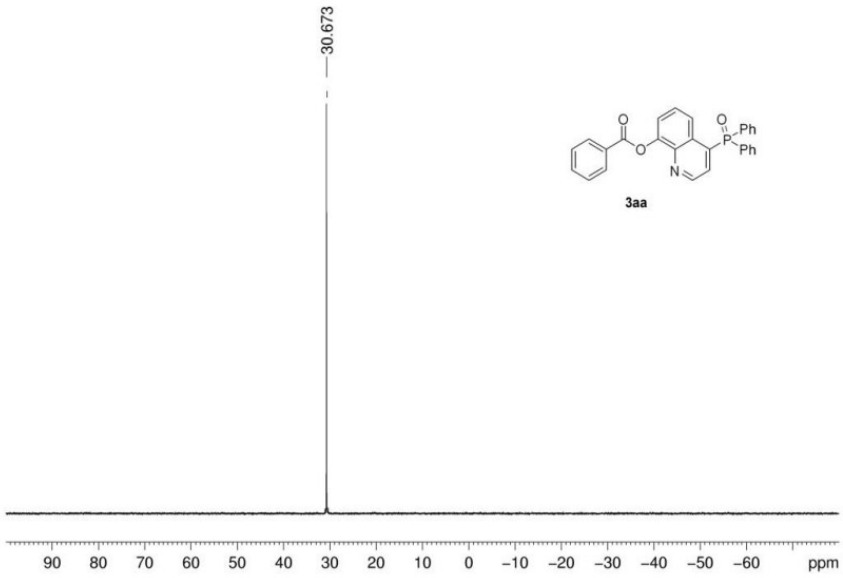
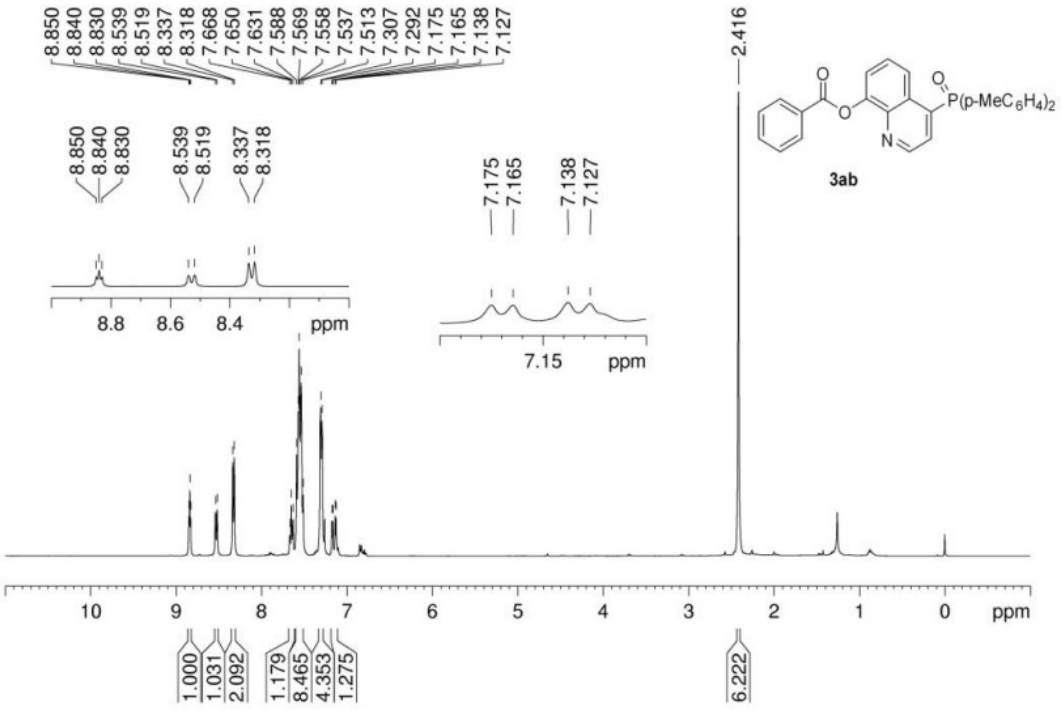
133.702
132.628
132.600
132.070
131.971
131.648
130.569
129.359
129.013
128.929
128.888
128.646
130.592
127.681
126.709
126.616
125.719
125.664
122.250
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


30.673
Ph
Ph
3aa
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm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8.840
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8.318
7.668
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7.631
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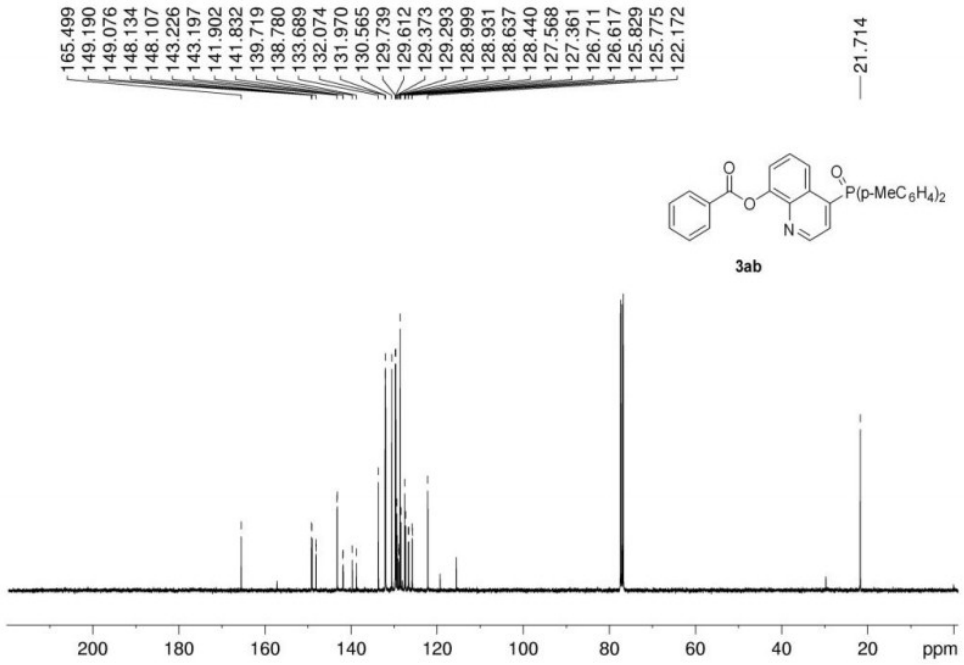
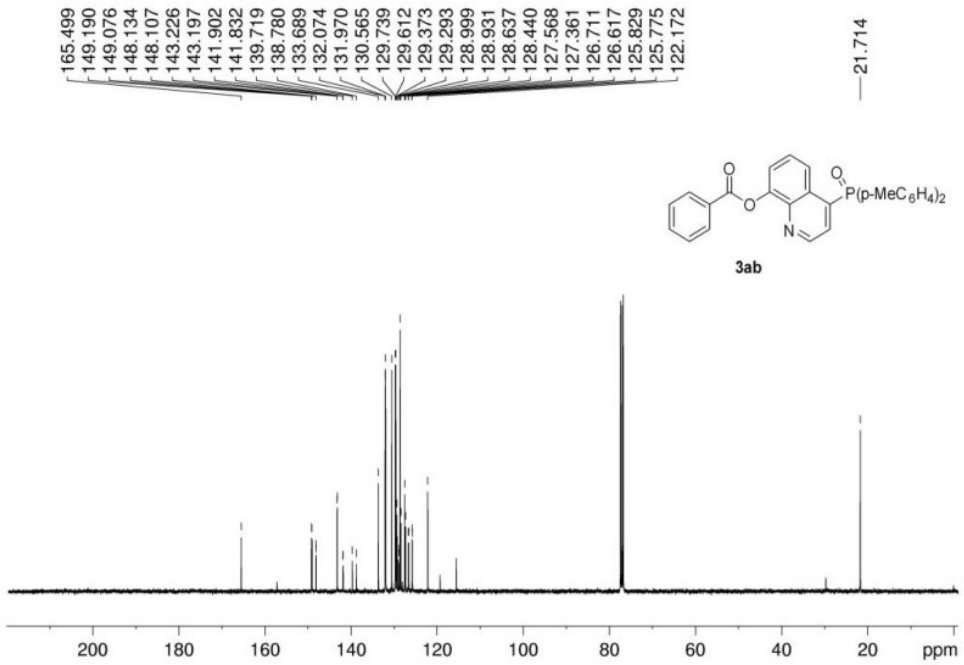
7.537
7.513
7.307
7.292
7.175
7.165
7.138
7.127
2.416
P(p-MeC6H4)2
3ab
8.8 8.6 8.4 ppm
7.15 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.031
2.092
1.179
8.465
4.353
1.275
6.222


165.499
149.190
149.076
148.134
148.107
143.226
143.197
141.902
141.832
139.719
138.780
133.689
132.074
131.970
130.565
129.739
129.612
129.373
129.293
128.999
128.931
128.637
128.440
127.568
127.361
126.711
126.617
125.829
125.775
122.172
21.714
P(p-MeC6H4)2
3ab
200
180
160
140
120
100
80
60
40
20
ppm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149.190
149.076
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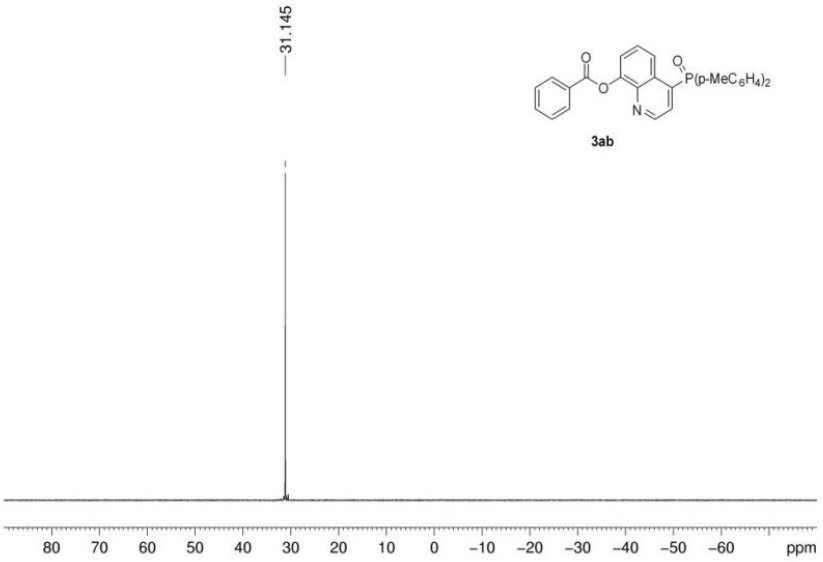
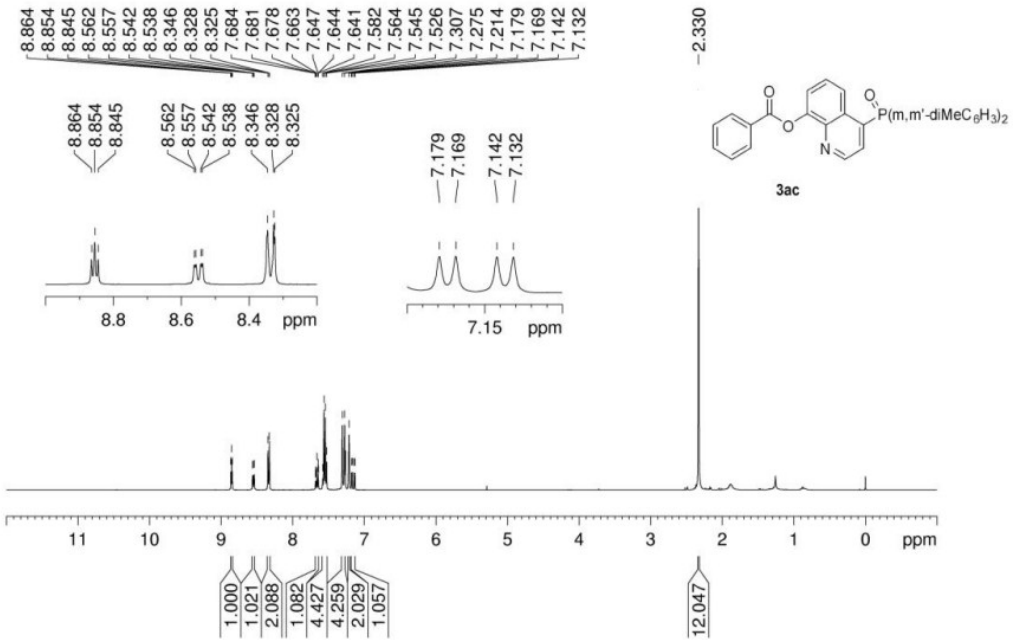
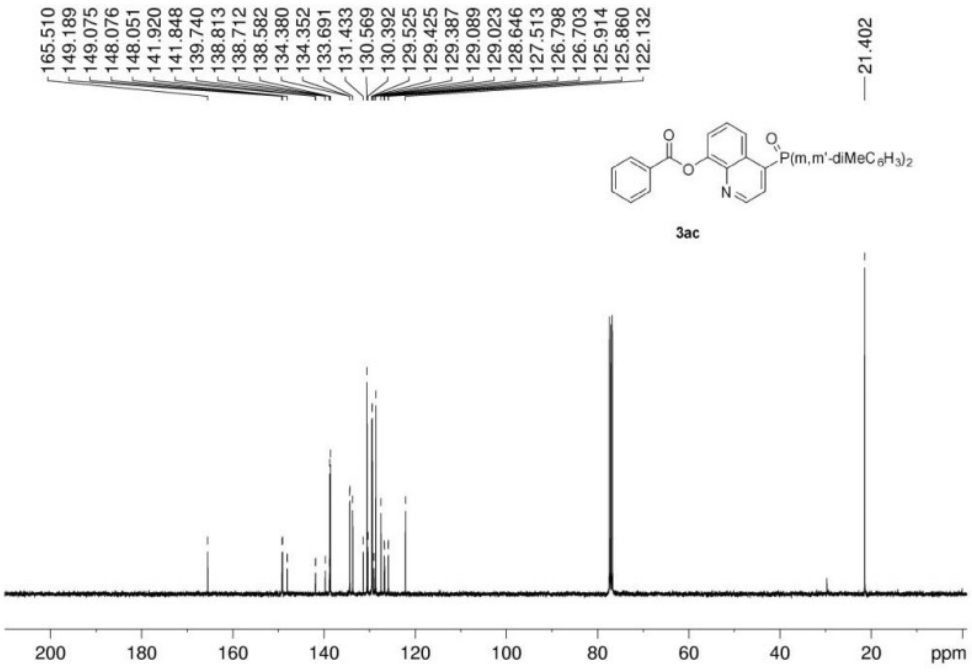
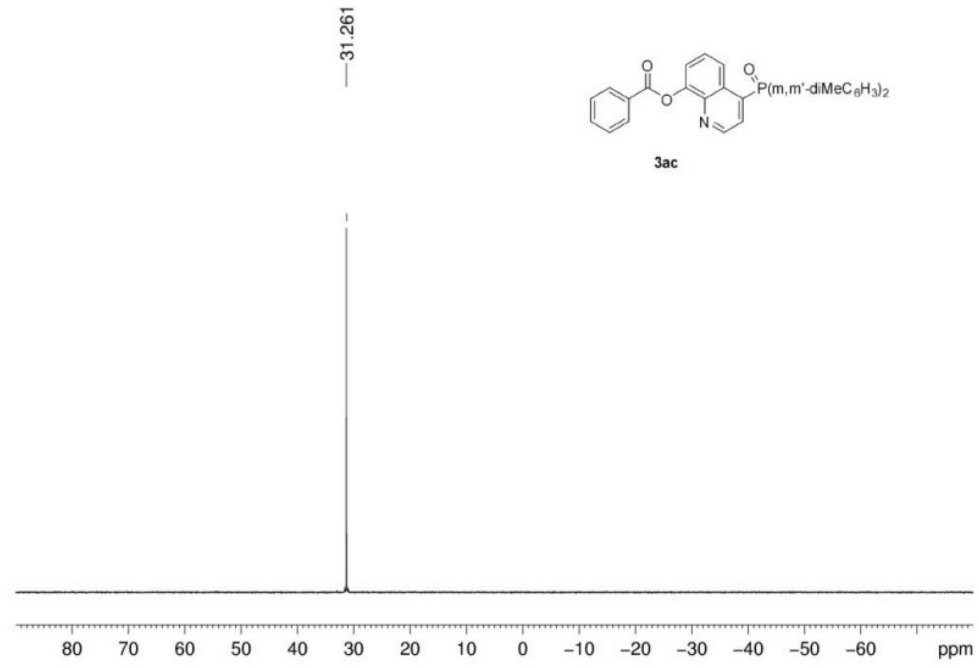
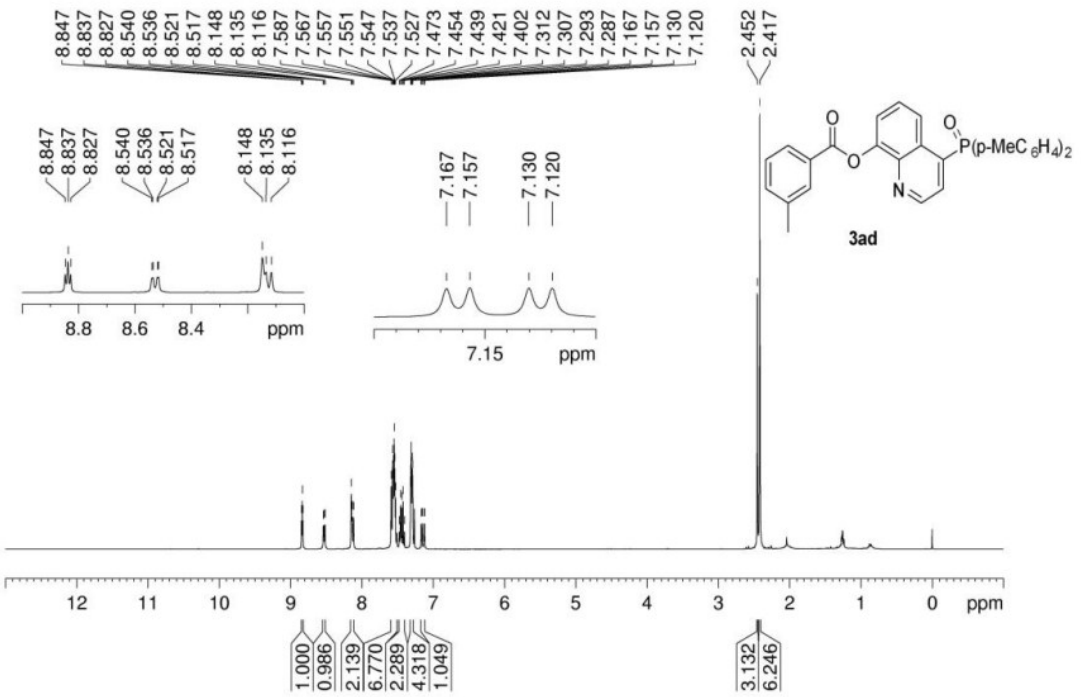
143.197
141.902
141.832
139.719
138.780
133.689
132.074
131.970
130.565
129.739
129.612
129.373
129.293
128.999
128.931
128.637
128.440
127.568
127.361
126.711
126.617
125.829
125.775
122.172
21.714
P(p-MeC6H4)2
3ab
200
180
160
140
120
100
80
60
40
20
ppm

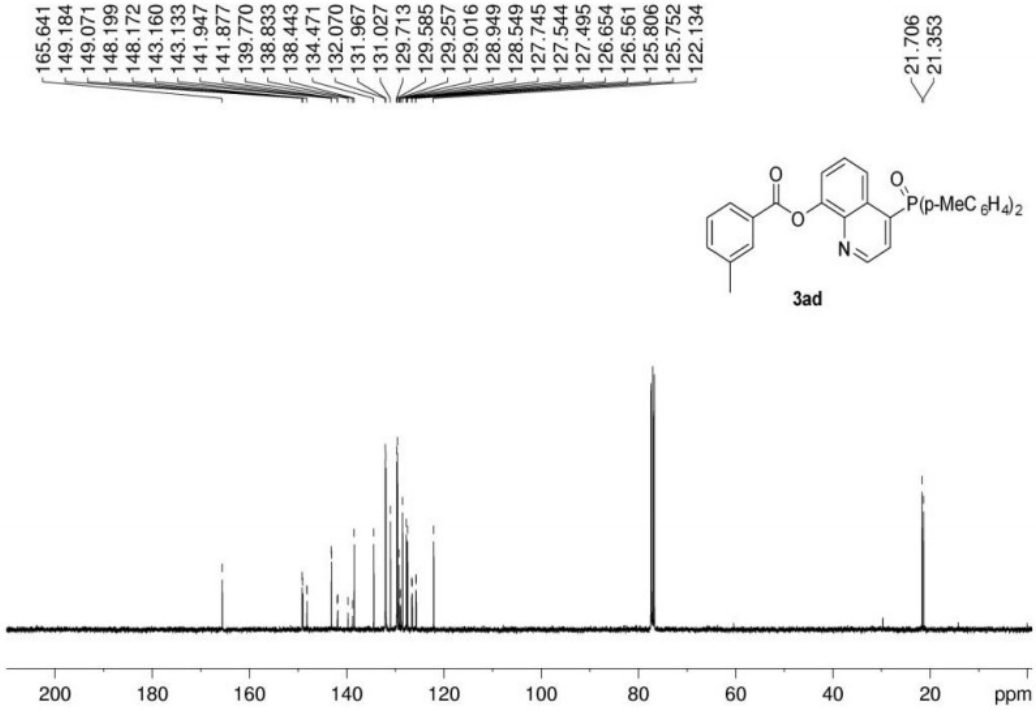

31.145
P(p-MeC6H4)2
3ab
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

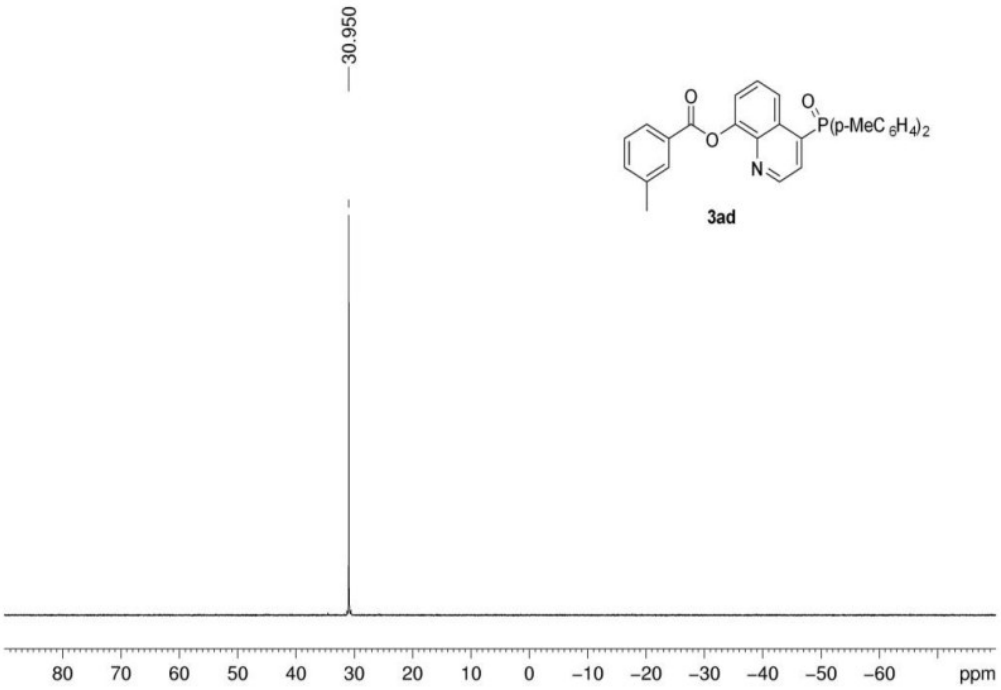

8.864 8.854 8.845 8.562 8.557 8.542 8.538 8.346 8.328 8.325 7.684 7.681 7.678 7.663 7.647 7.644 7.641 7.582 7.564 7.545 7.526 7.307 7.275 7.214 7.179 7.169 7.142 7.132
2.330
P(m,m'-diMeC6H3)2
3ac
8.8 8.6 8.4 ppm
7.15 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.021 2.088 1.082 4.427 4.259 2.029 1.057
12.047

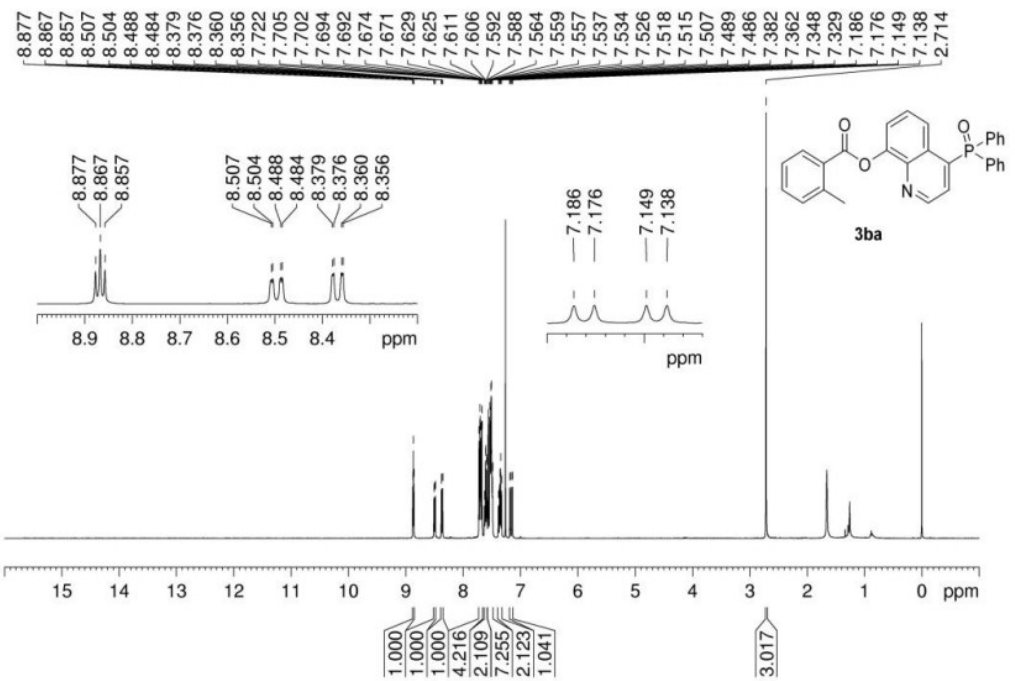

165.510
149.189
149.075
148.076
148.051
141.920
141.848
139.740
138.813
138.712
138.582
134.380
134.352
133.691
131.433
130.569
130.392
129.525
129.425
129.387
129.089
129.023
128.646
127.513
126.798
126.703
125.914
125.860
122.132
21.402
P(m,m'-diMeC6H3)2
3ac
200
180
160
140
120
100
80
60
40
20
ppm

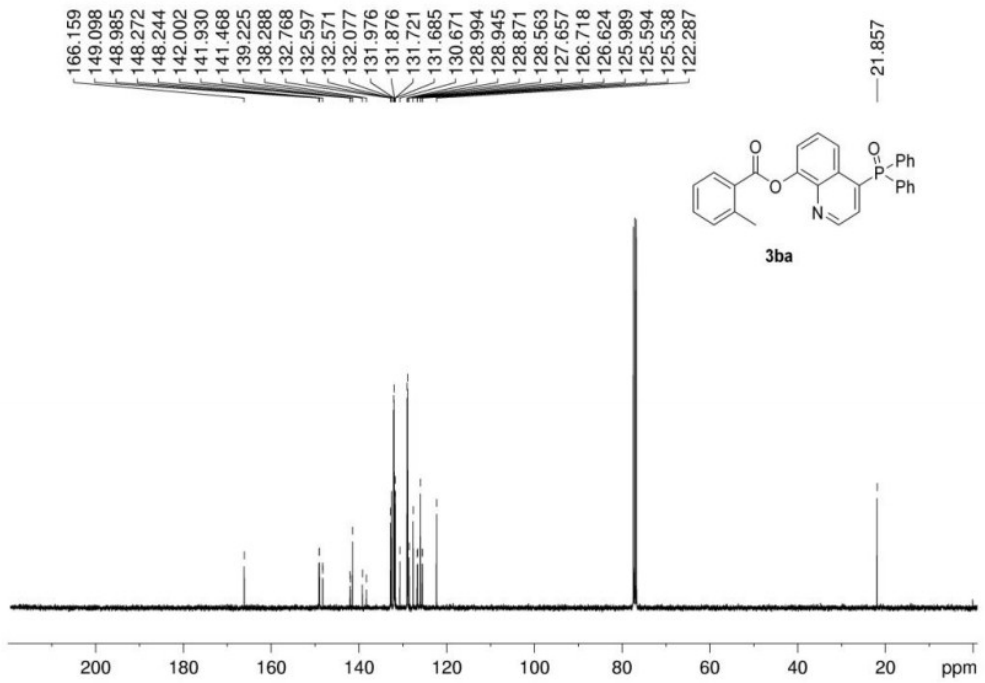

31.261
P(m,m'-diMeC6H3)2
3ac
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

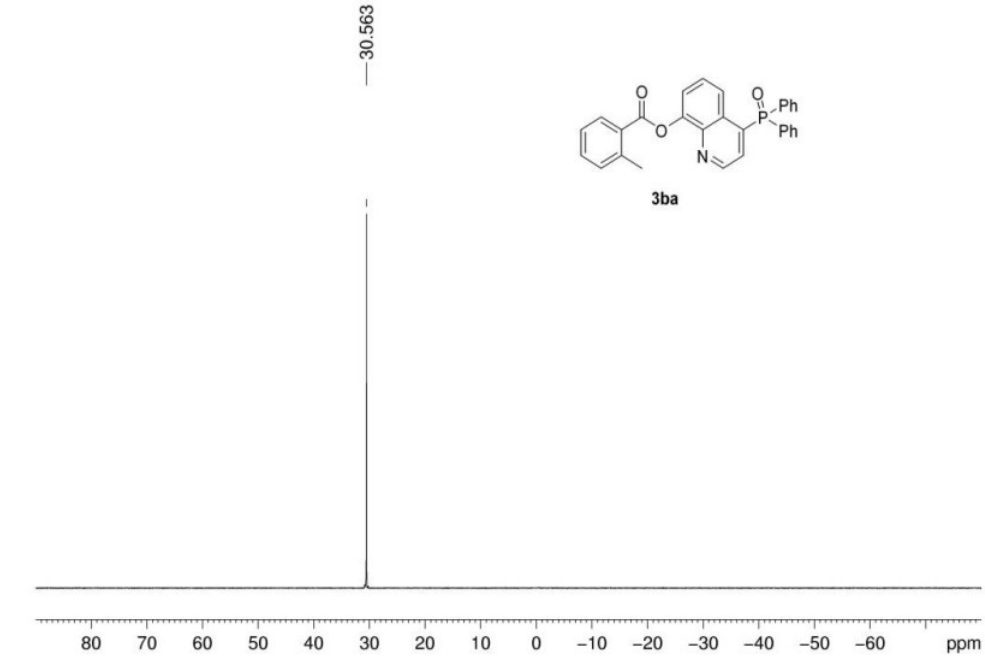

8.847
8.837
8.827
8.540
8.536
8.521
8.517
8.148
8.135
8.116
7.587
7.567
7.557
7.551
7.547
7.537
7.527
7.473
7.454
7.439
7.421
7.402
7.312
7.307
7.293
7.287
7.167
7.157
7.130
7.120
2.452
2.417
8.8
8.6
8.4
ppm
7.15
ppm
3ad
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.986
2.139
6.770
2.289
4.318
1.049
3.132
6.246

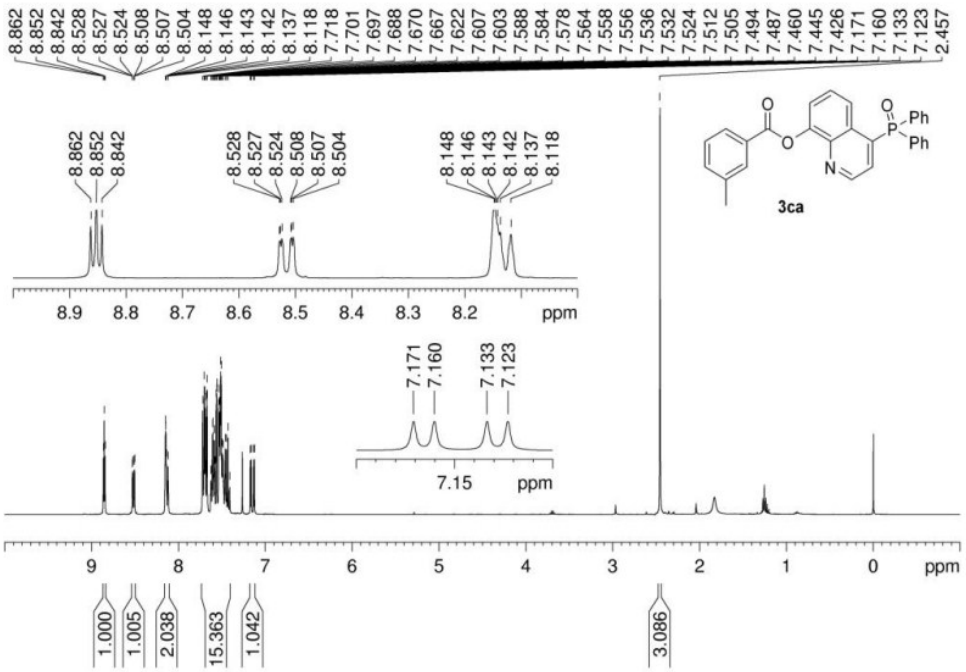

165.641
149.184
149.071
148.199
148.172
143.160
143.133
141.947
141.877
139.770
138.833
138.443
134.471
132.070
131.967
131.027
129.713
129.585
129.257
129.016
128.949
128.549
127.745
127.544
127.495
126.654
126.561
125.806
125.752
122.134
21.706
21.353
3ad
200
180
160
140
120
100
80
60
40
20
ppm

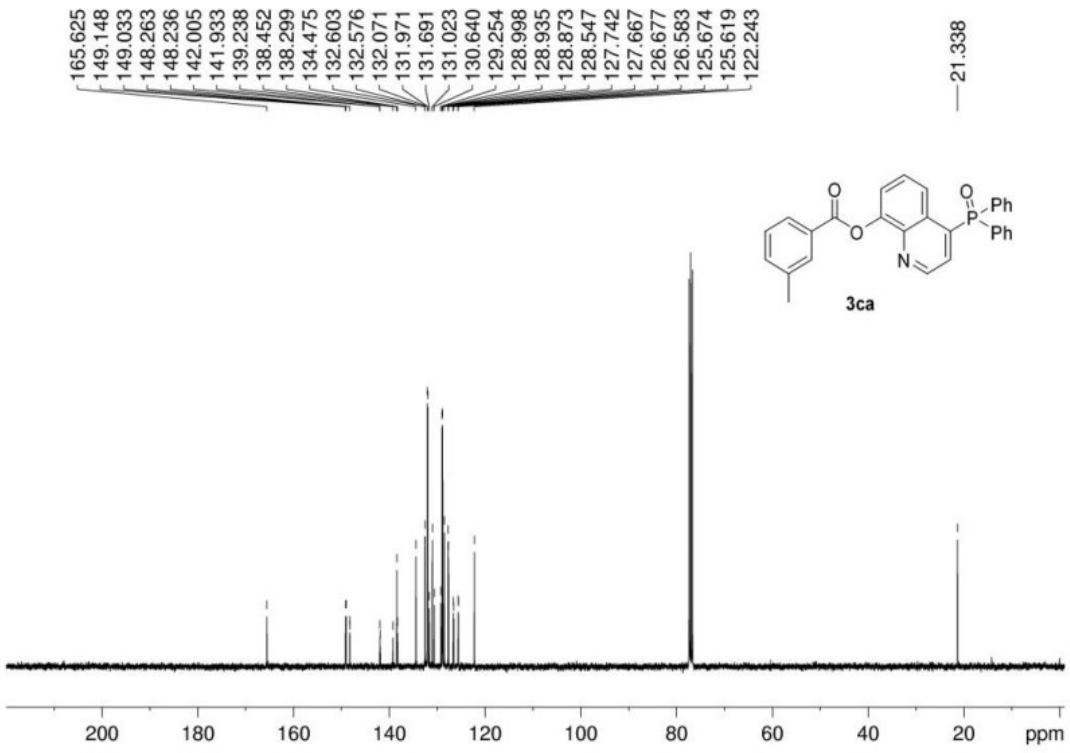

30.950
O
O
O
P(p-MeC6H4)2
N
3ad
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

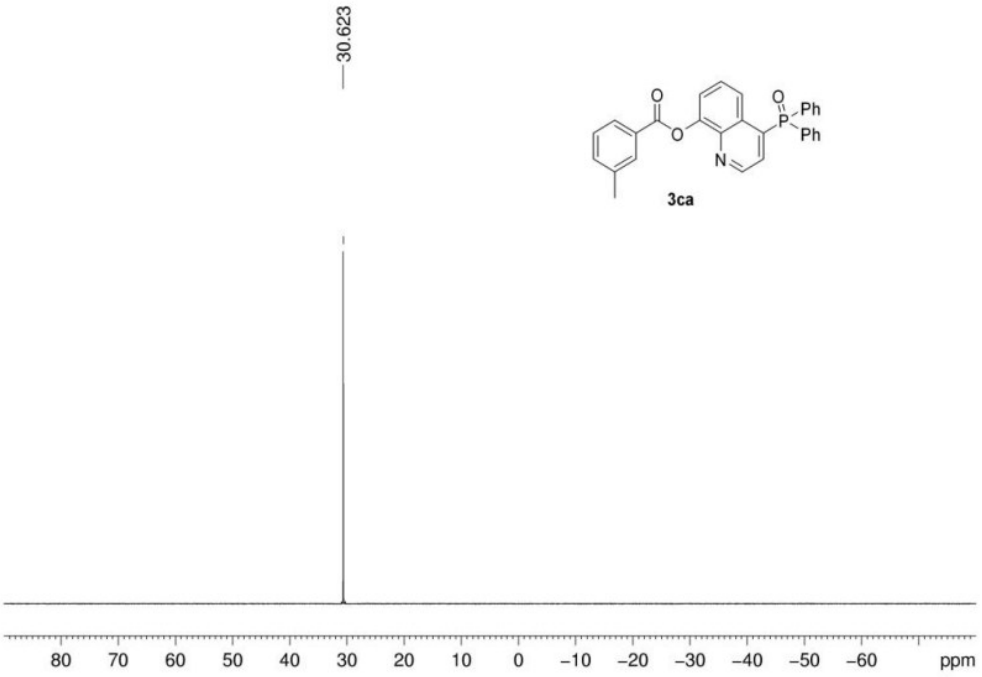

8.877 8.867 8.857 8.507 8.504 8.488 8.484 8.379 8.376 8.360 8.356 7.722 7.705 7.702 7.694 7.692 7.674 7.671 7.629 7.625 7.611 7.606 7.592 7.588 7.564 7.559 7.557 7.537 7.534 7.526 7.518 7.515 7.507 7.489 7.486 7.382 7.362 7.348 7.329 7.186 7.176 7.149 7.138 2.714
8.877 8.867 8.857
8.507 8.504 8.488 8.484 8.379 8.376 8.360 8.356
8.9 8.8 8.7 8.6 8.5 8.4 ppm
7.186 7.176
7.149 7.138
ppm
O
O
P
Ph
Ph
N
3ba
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.000 1.000 4.216 2.109 7.255 2.123 1.041
3.017

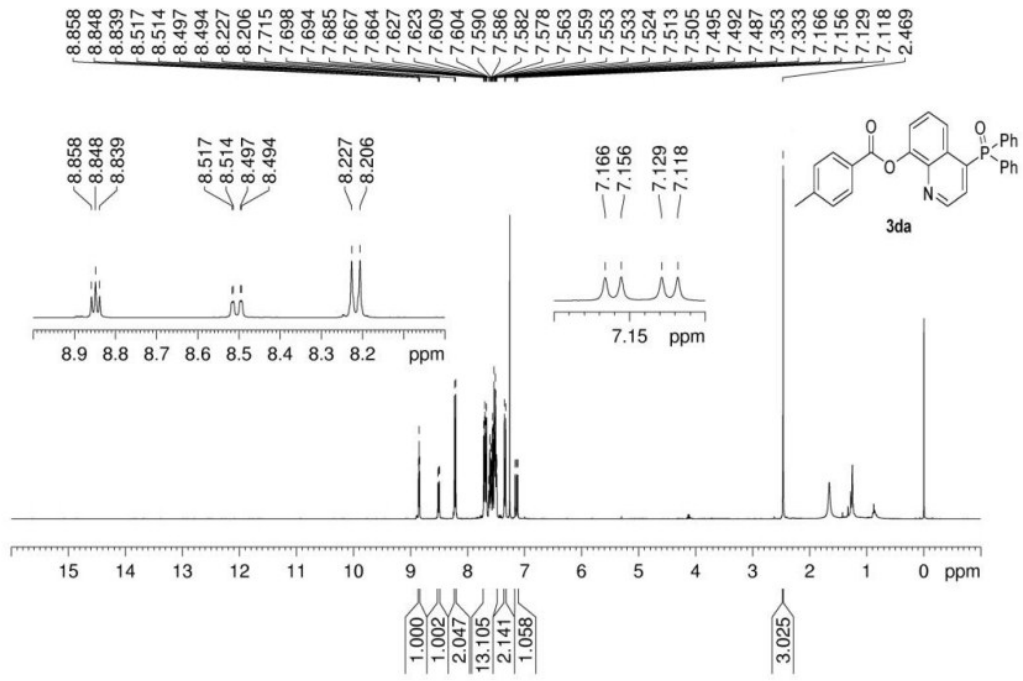

166.159
149.098
148.985
148.272
148.244
142.002
141.930
141.468
139.225
138.288
132.768
132.597
132.571
132.077
131.976
131.876
131.721
131.685
130.671
128.994
128.945
128.871
128.563
127.657
126.718
126.624
125.989
125.594
125.538
122.287
21.857
O
O
P
Ph
Ph
N
3ba
200
180
160
140
120
100
80
60
40
20
ppm

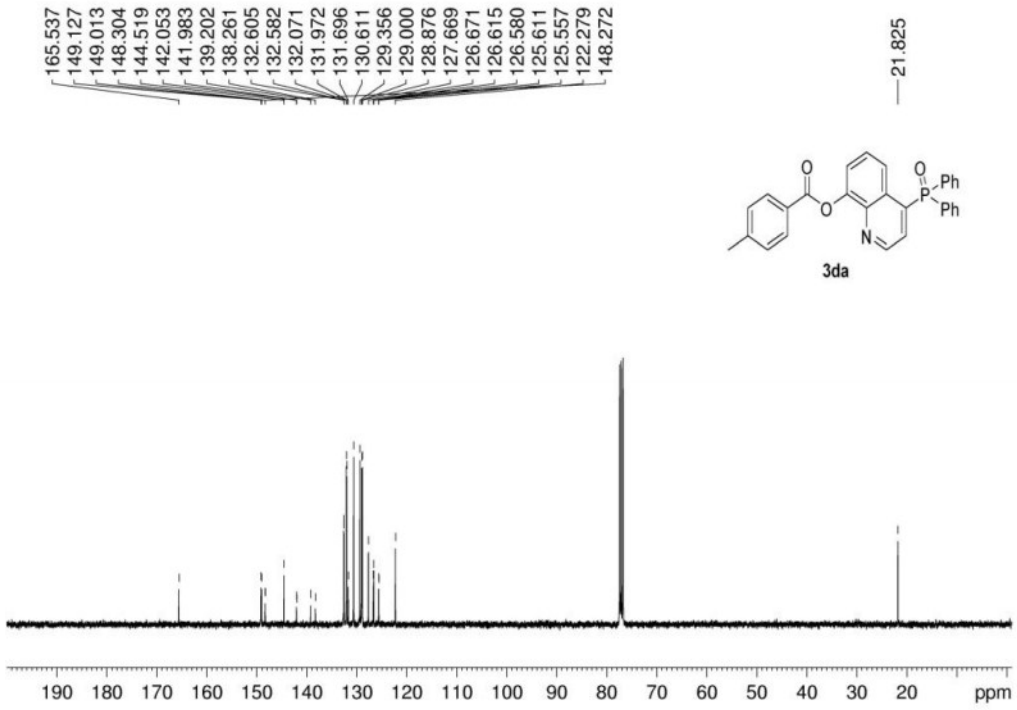

30.563
O
O
P
Ph
Ph
N
3ba
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm


8.862
8.852
8.842
8.528
8.527
8.524
8.508
8.507
8.504
8.148
8.146
8.143
8.142
8.137
8.118
7.718
7.701
7.697
7.688
7.670
7.667
7.622
7.607
7.603
7.588
7.584
7.578
7.564
7.558
7.556
7.536
7.532
7.524
7.512
7.505
7.494
7.487
7.460
7.445
7.426
7.171
7.160
7.133
7.123
2.457
3ca
ppm
1.000
1.005
2.038
15.363
1.042
3.086


165.625
149.148
149.033
148.263
148.236
142.005
141.933
139.238
138.452
138.299
134.475
132.603
132.576
132.071
131.971
131.691
131.023
130.640
129.254
128.998
128.935
128.873
128.547
127.742
127.667
126.677
126.583
125.674
125.619
122.243
21.338
3ca
ppm


30.623
3ca
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm


8.858 8.848 8.839 8.517 8.514 8.497 8.494 8.227 8.206 7.715 7.698 7.694 7.685 7.667 7.664 7.627 7.623 7.609 7.604 7.590 7.586 7.582 7.578 7.563 7.559 7.553 7.533 7.524 7.513 7.505 7.495 7.492 7.487 7.353 7.333 7.166 7.156 7.129 7.118 2.469
3da
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 ppm
7.15 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.002 2.047 13.105 2.141 1.058
3.025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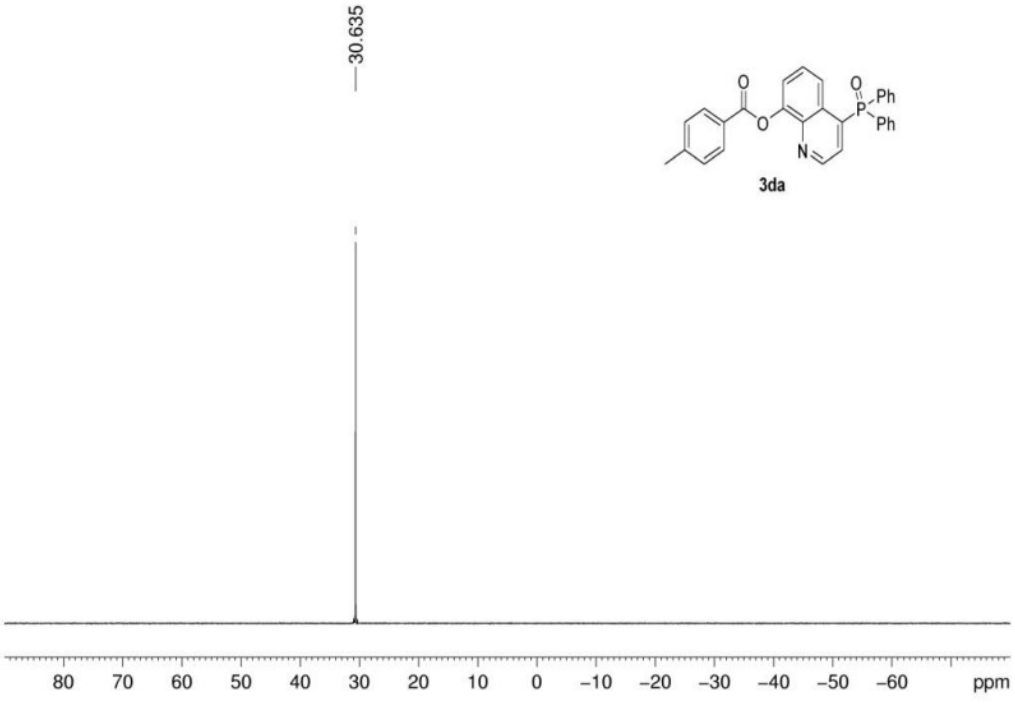
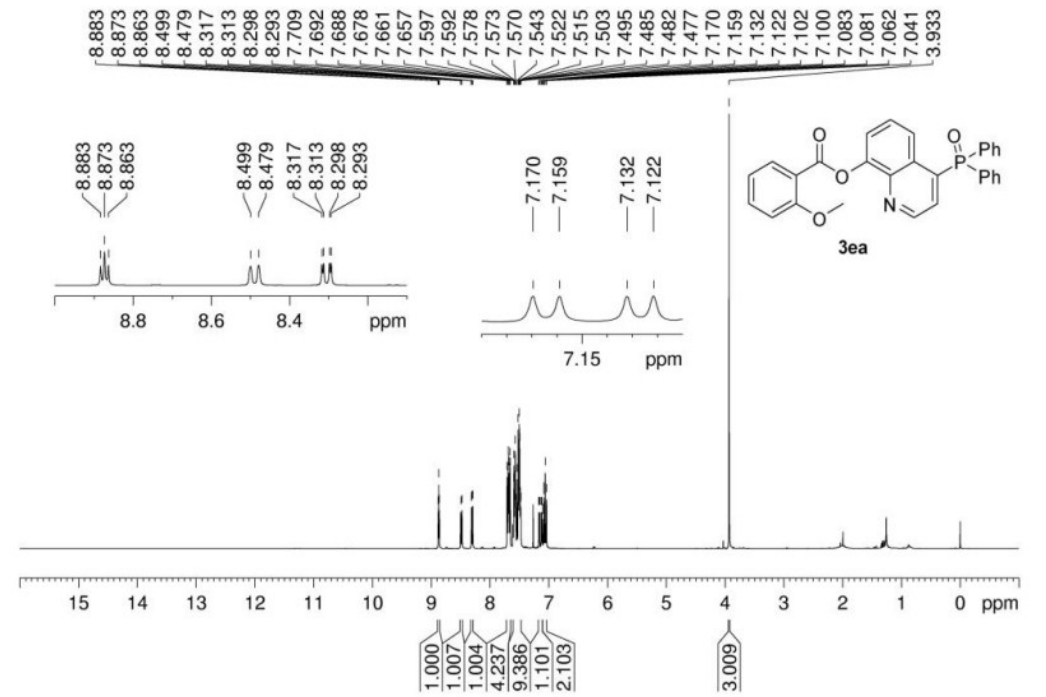
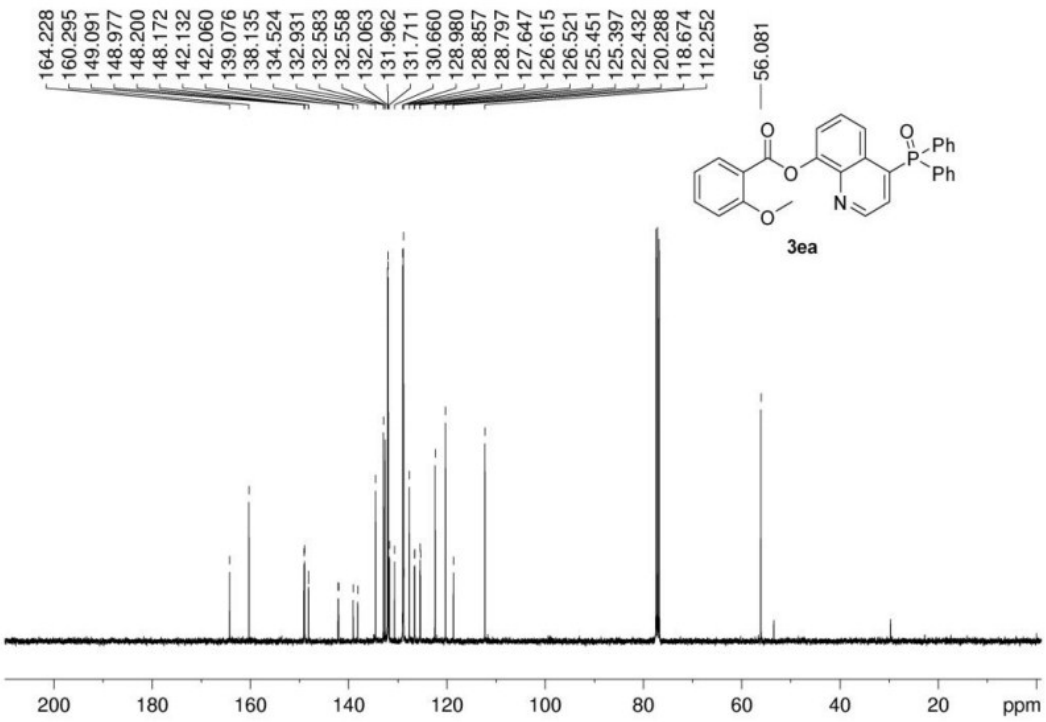
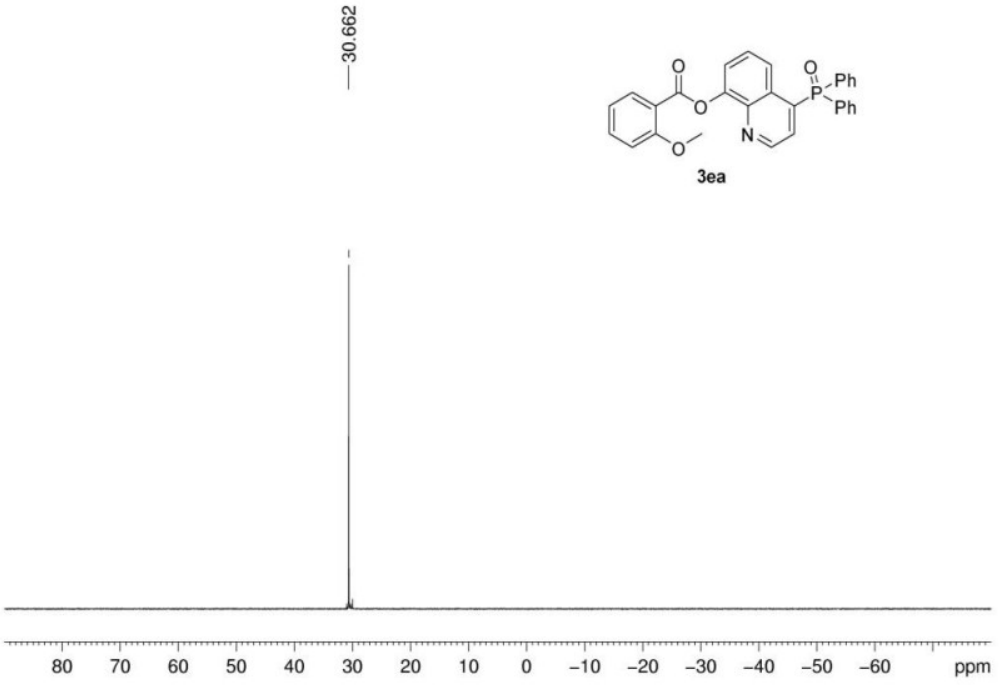
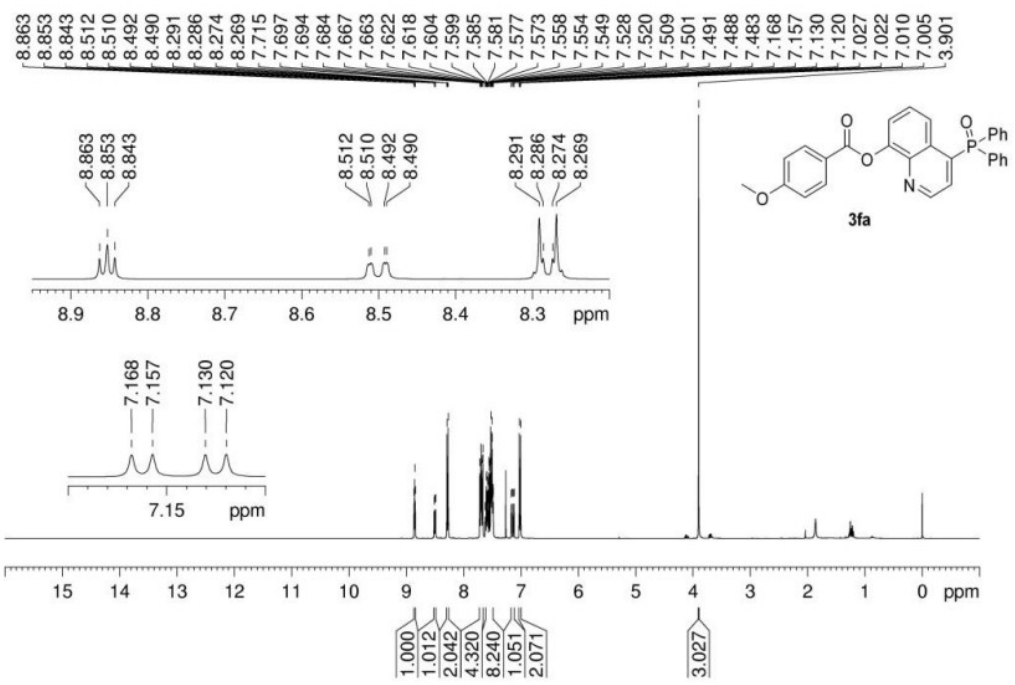
149.127
149.013
148.304
144.519
142.053
141.983
139.202
138.261
132.605
132.582
132.071
131.972
131.696
130.611
129.356
129.000
128.876
127.669
126.671
126.615
126.580
125.611
125.557
122.279
148.272
21.825
O
O
O
P
Ph
Ph
N
3da
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

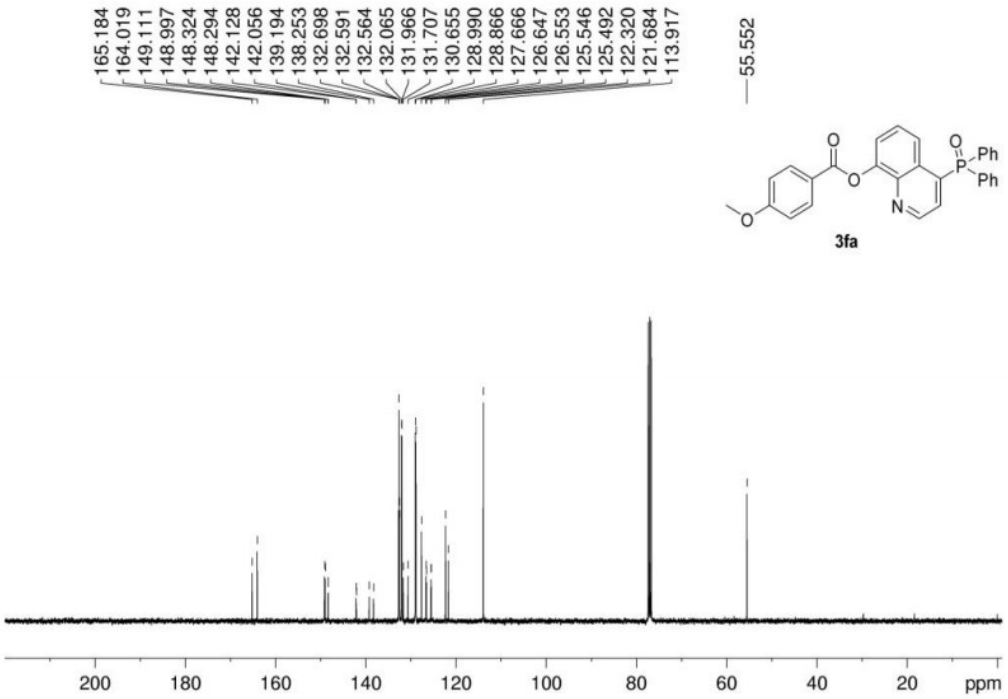

30.635
O
O
O
P
Ph
Ph
N
3da
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

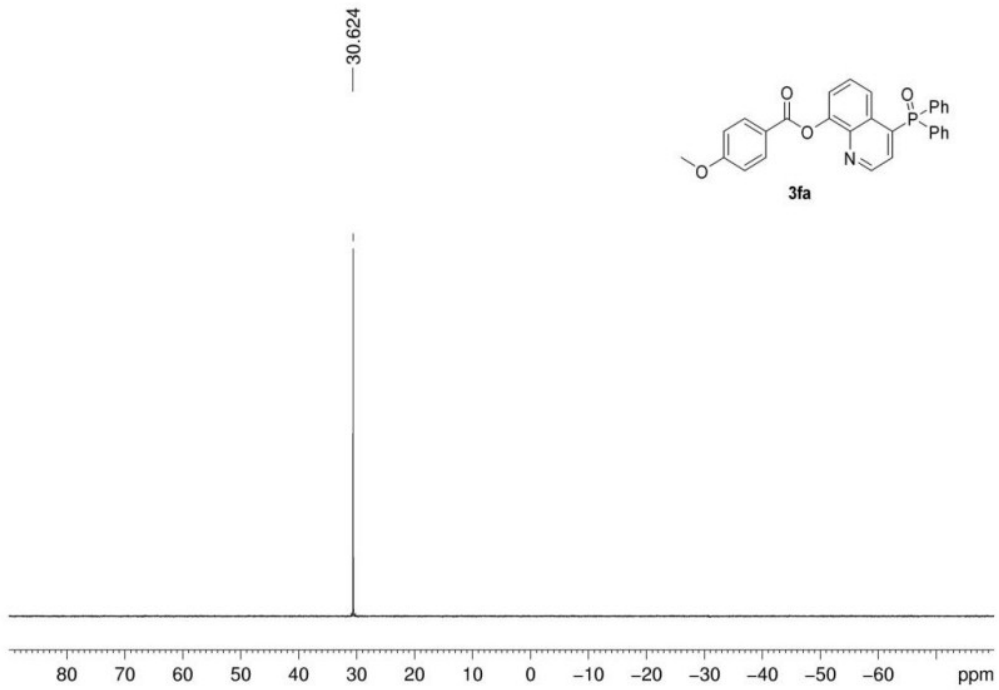

8.883
8.873
8.863
8.499
8.479
8.317
8.313
8.298
8.293
7.709
7.692
7.688
7.678
7.661
7.657
7.597
7.592
7.578
7.573
7.570
7.543
7.522
7.515
7.503
7.495
7.485
7.482
7.477
7.170
7.159
7.132
7.122
7.102
7.100
7.083
7.081
7.062
7.041
3.933
8.8
8.6
8.4
ppm
7.15
ppm
Ph
Ph
3ea
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.007
1.004
4.237
9.386
1.101
2.103
3.009

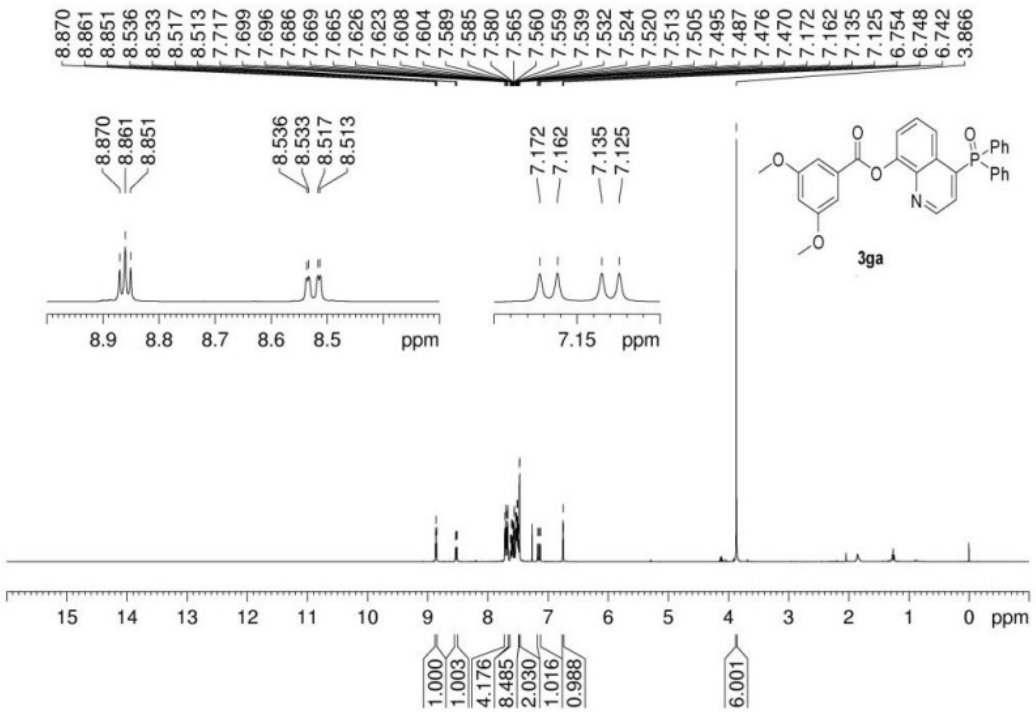

164.228
160.295
149.091
148.977
148.200
148.172
142.132
142.060
139.076
138.135
134.524
132.931
132.583
132.558
132.063
131.962
131.711
130.660
128.980
128.857
128.797
127.647
126.615
126.521
125.451
125.397
122.432
120.288
118.674
112.252
56.081
Ph
Ph
3ea
200 180 160 140 120 100 80 60 40 20 ppm

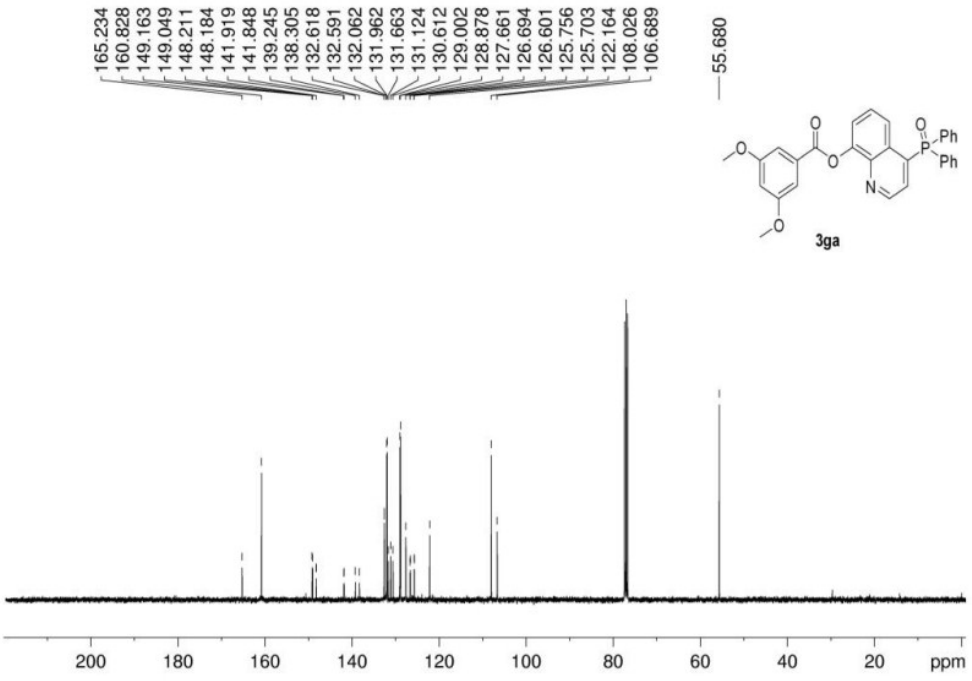

30.662
3ea
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

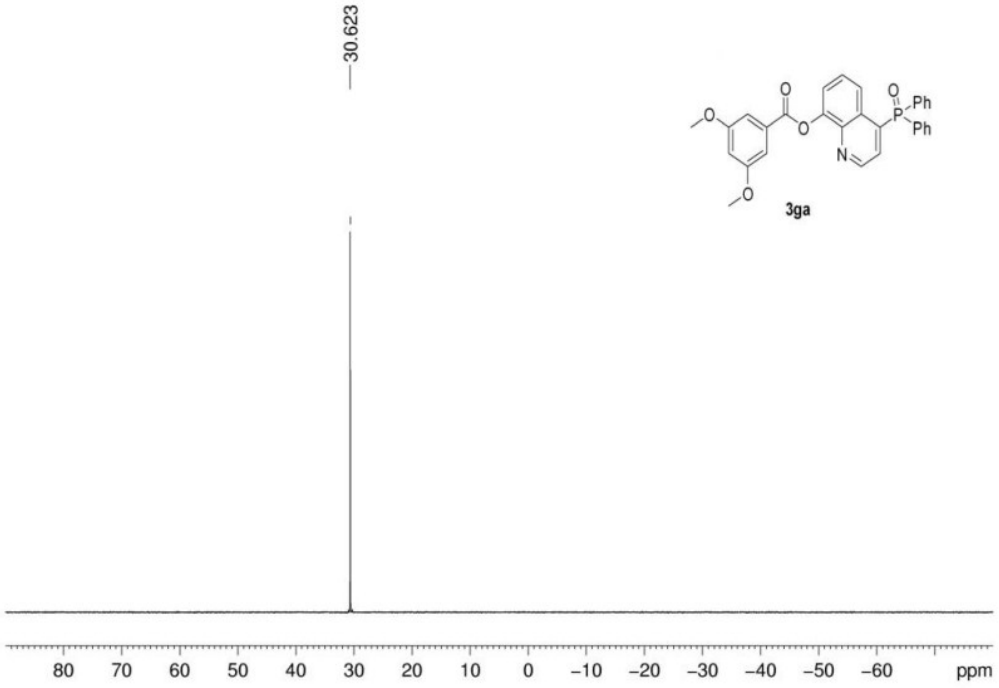

8.863 8.853 8.843 8.512 8.510 8.492 8.490 8.291 8.286 8.274 8.269 7.715 7.697 7.694 7.684 7.667 7.663 7.622 7.618 7.604 7.599 7.585 7.581 7.577 7.573 7.558 7.554 7.549 7.528 7.520 7.509 7.501 7.491 7.488 7.483 7.168 7.157 7.130 7.120 7.027 7.022 7.010 7.005 3.901
3fa
8.9 8.8 8.7 8.6 8.5 8.4 8.3 ppm
7.15 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.012 2.042 4.320 8.240 1.051 2.071 3.027

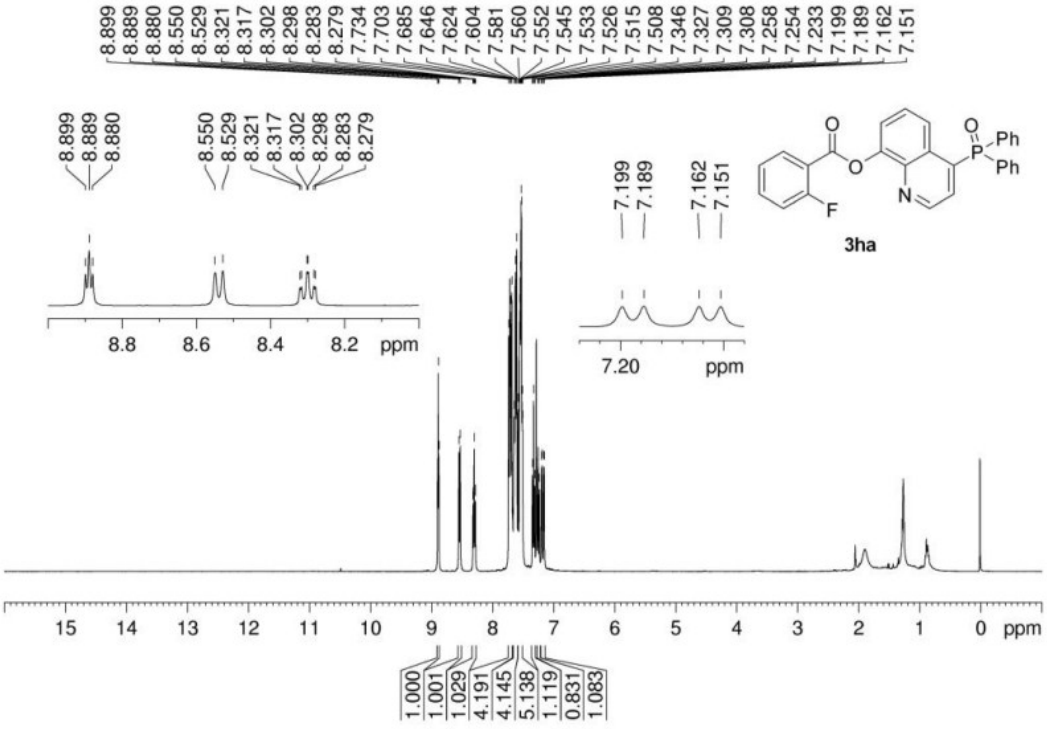

165.184
164.019
149.111
148.997
148.324
148.294
142.128
142.056
139.194
138.253
132.698
132.591
132.564
132.065
131.966
131.707
130.655
128.990
128.866
127.666
126.647
126.553
125.546
125.492
122.320
121.684
113.917
55.552
O
O
O
P
Ph
Ph
N
O
3fa
200
180
160
140
120
100
80
60
40
20
ppm

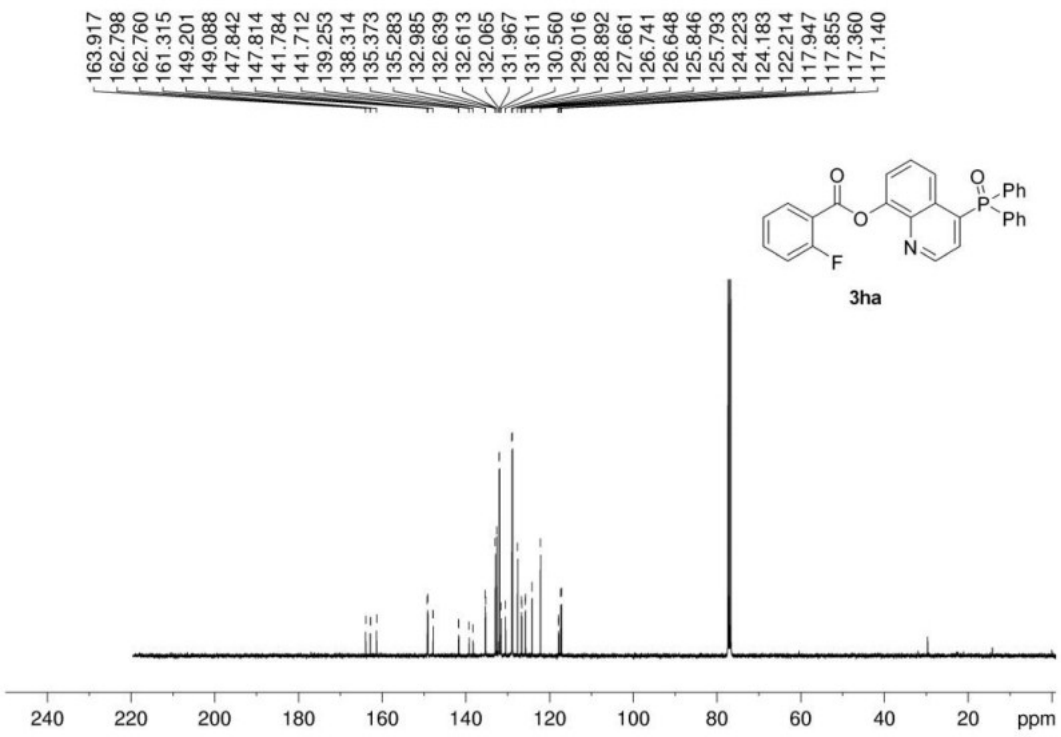

30.624
O
O
O
P
Ph
Ph
N
O
3fa
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

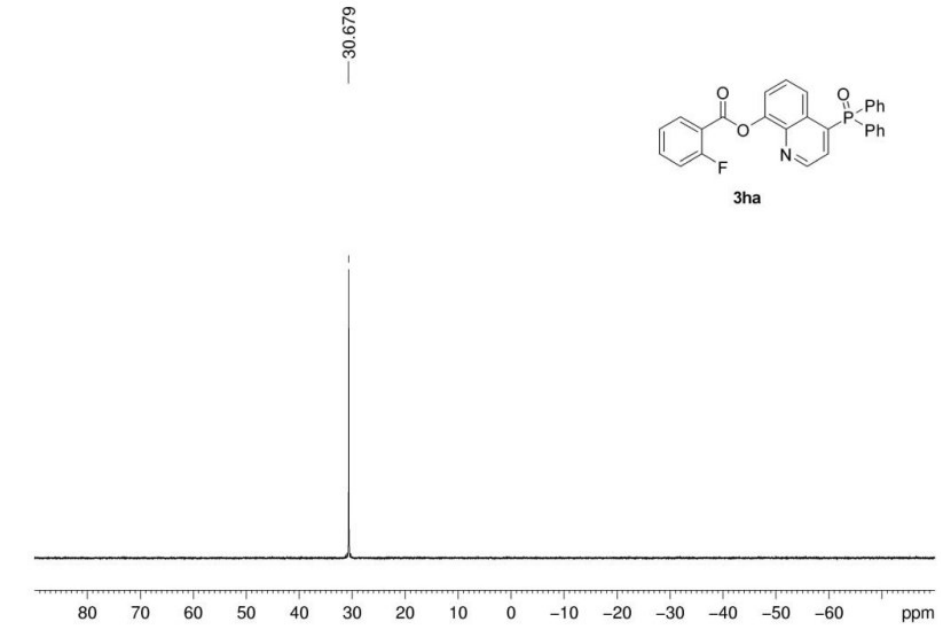

8.870
8.861
8.851
8.536
8.533
8.517
8.513
7.717
7.699
7.696
7.686
7.669
7.665
7.626
7.623
7.608
7.604
7.589
7.585
7.580
7.565
7.560
7.559
7.539
7.532
7.524
7.520
7.513
7.505
7.495
7.487
7.476
7.470
7.172
7.162
7.135
7.125
6.754
6.748
6.742
3.866
8.9 8.8 8.7 8.6 8.5 ppm
7.15 ppm
3ga
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.003
4.176
8.485
2.030
1.016
0.988
6.001

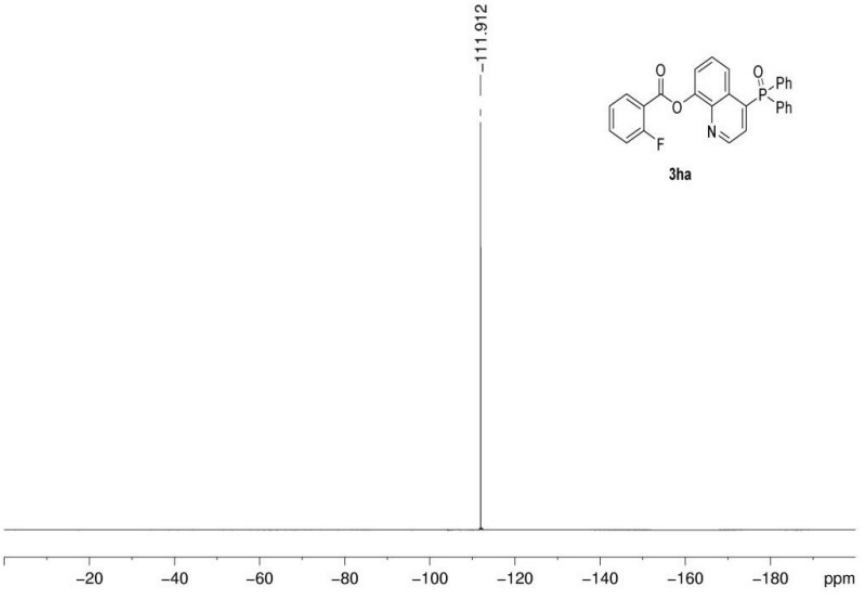

165.234
160.828
149.163
149.049
148.211
148.184
141.919
141.848
139.245
138.305
132.618
132.591
132.062
131.962
131.663
131.124
130.612
129.002
128.878
127.661
126.694
126.601
125.756
125.703
122.164
108.026
106.689
55.680
3ga
200 180 160 140 120 100 80 60 40 20 ppm

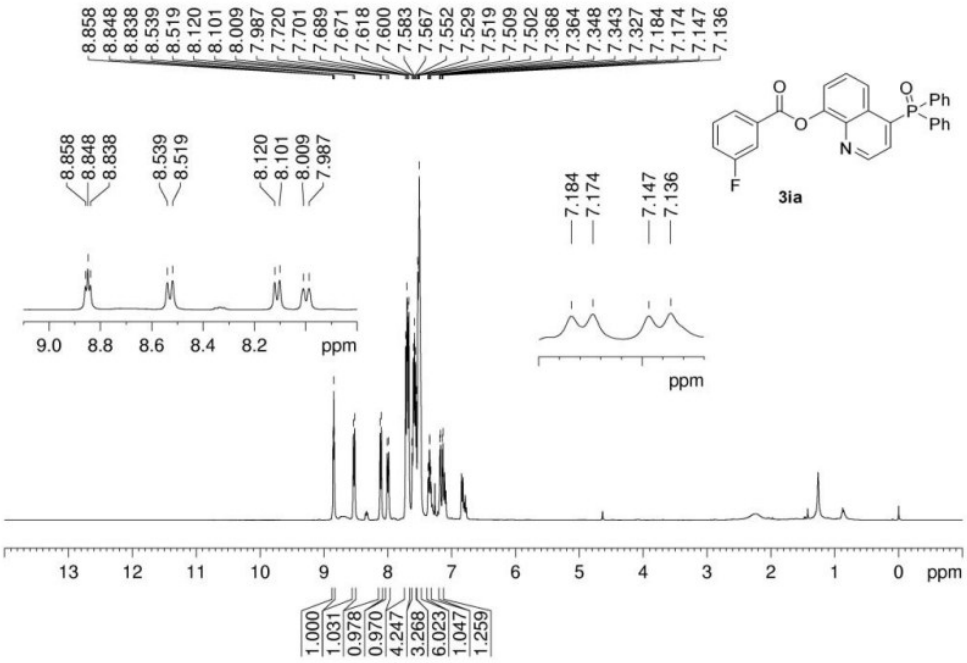

30.623
3ga
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

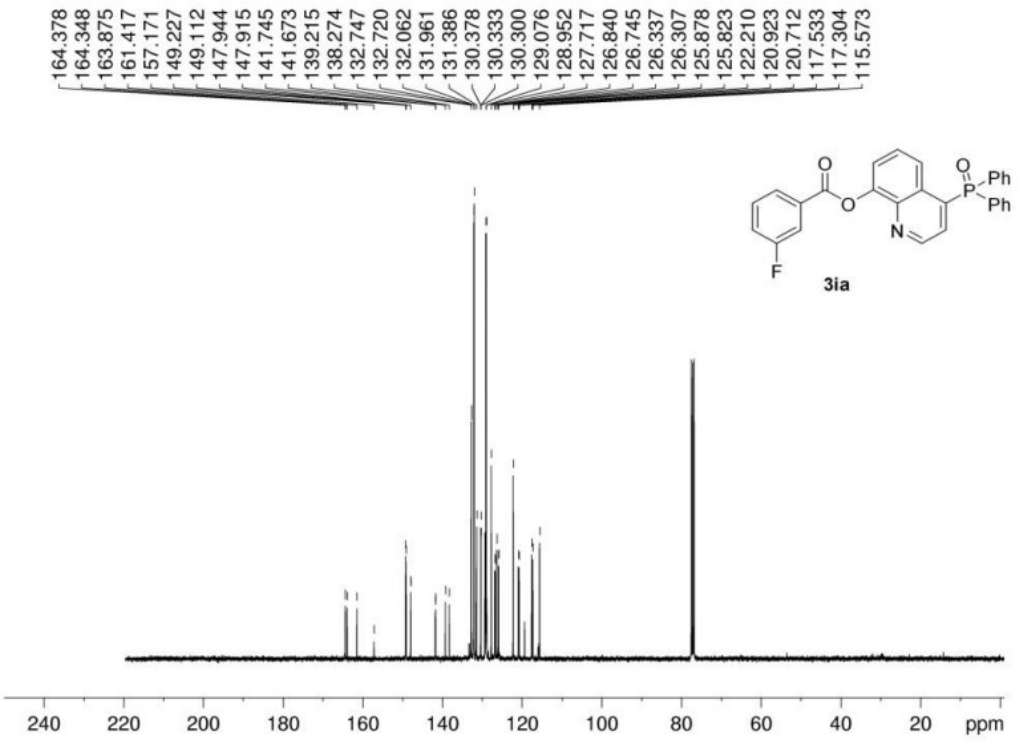

8.899 8.889 8.880 8.550 8.529 8.321 8.317 8.302 8.298 8.283 8.279 7.734 7.703 7.685 7.646 7.624 7.604 7.581 7.560 7.552 7.545 7.533 7.526 7.515 7.508 7.346 7.327 7.309 7.308 7.258 7.254 7.233 7.199 7.189 7.162 7.151
3ha
8.8 8.6 8.4 8.2 ppm
7.20 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.001 1.029 4.191 4.145 5.138 1.119 0.831 1.083

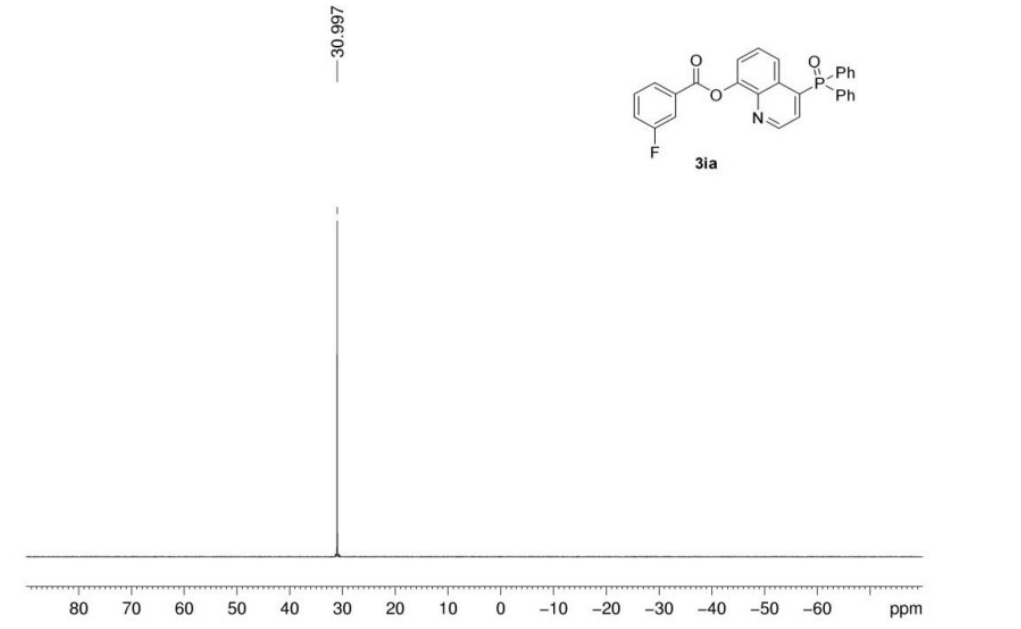

163.917
162.798
162.760
161.315
149.201
149.088
147.842
147.814
141.784
141.712
139.253
138.314
135.373
135.283
132.985
132.639
132.613
132.065
131.967
131.611
130.560
129.016
128.892
127.661
126.741
126.648
125.846
125.793
124.223
124.183
122.214
117.947
117.855
117.360
117.140
O
O
P
Ph
Ph
O
N
F
3ha
240
220
200
180
160
140
120
100
80
60
40
20
ppm

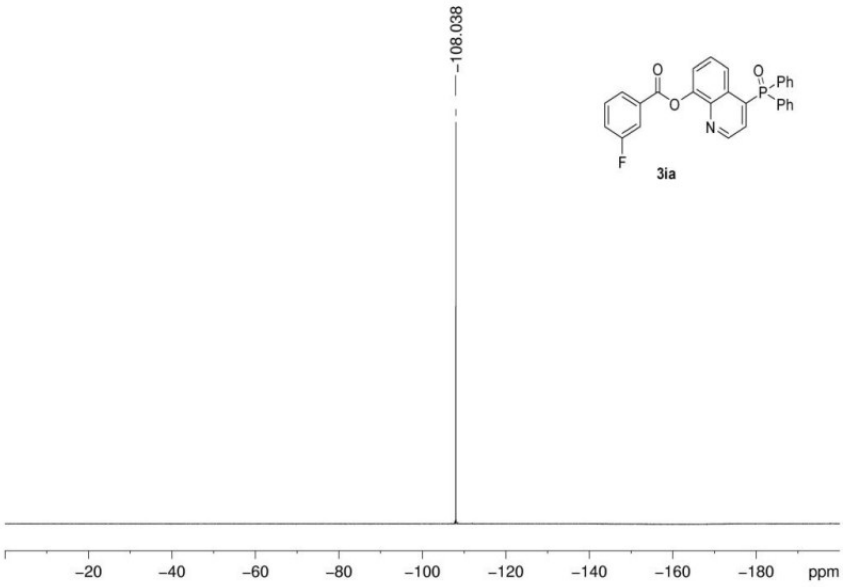

30.679
O
O
P
Ph
Ph
O
N
F
3ha
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

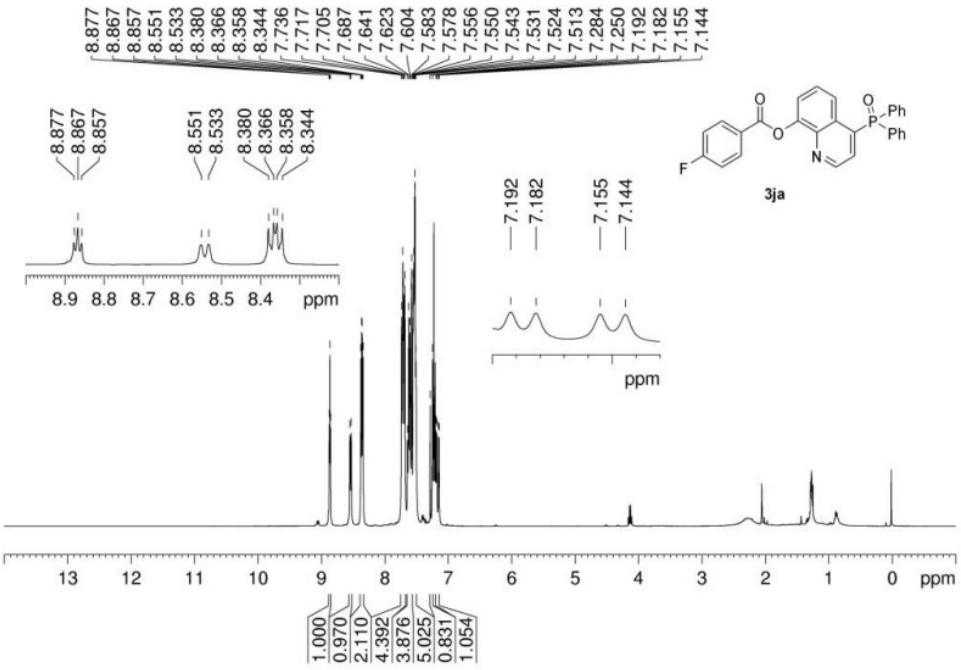

-111.912
3ha
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

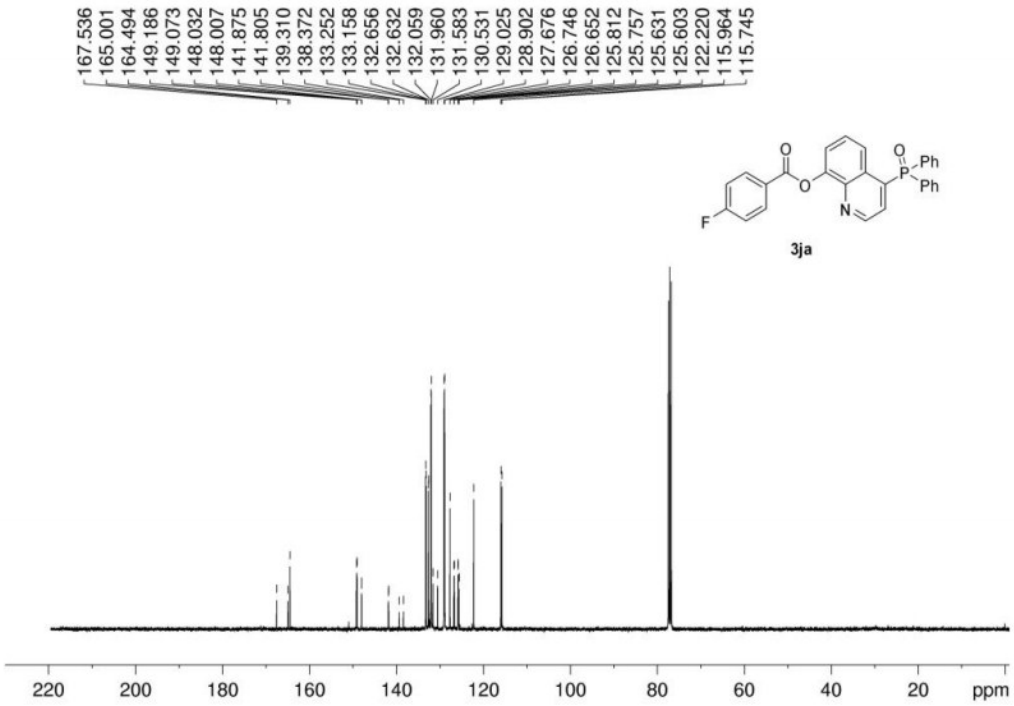

8.858
8.848
8.838
8.539
8.519
8.120
8.101
8.009
7.987
7.720
7.701
7.689
7.671
7.618
7.600
7.583
7.567
7.552
7.529
7.519
7.509
7.502
7.368
7.364
7.348
7.343
7.327
7.184
7.174
7.147
7.136
3ia
9.0
8.8
8.6
8.4
8.2
ppm
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.031
0.978
0.970
4.247
3.268
6.023
1.047
1.259

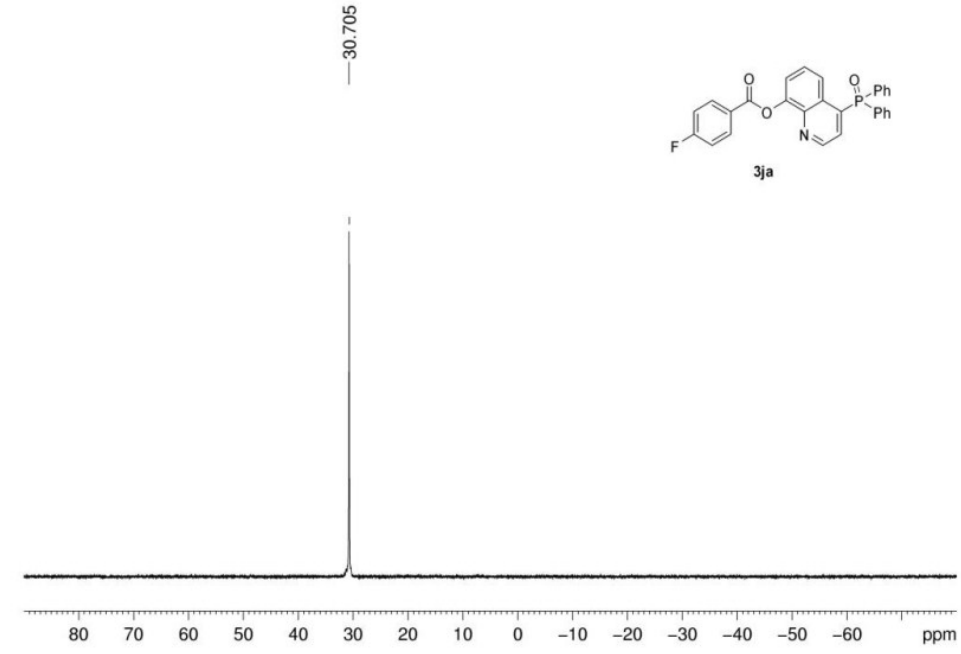

164.378
164.348
163.875
161.417
157.171
149.227
149.112
147.944
147.915
141.745
141.673
139.215
138.274
132.747
132.720
132.062
131.961
131.386
130.378
130.333
130.300
129.076
128.952
127.717
126.840
126.745
126.337
126.307
125.878
125.823
122.210
120.923
120.712
117.533
117.304
115.573
O
O
Ph
P
Ph
O
N
F
3ia
240
220
200
180
160
140
120
100
80
60
40
20
ppm

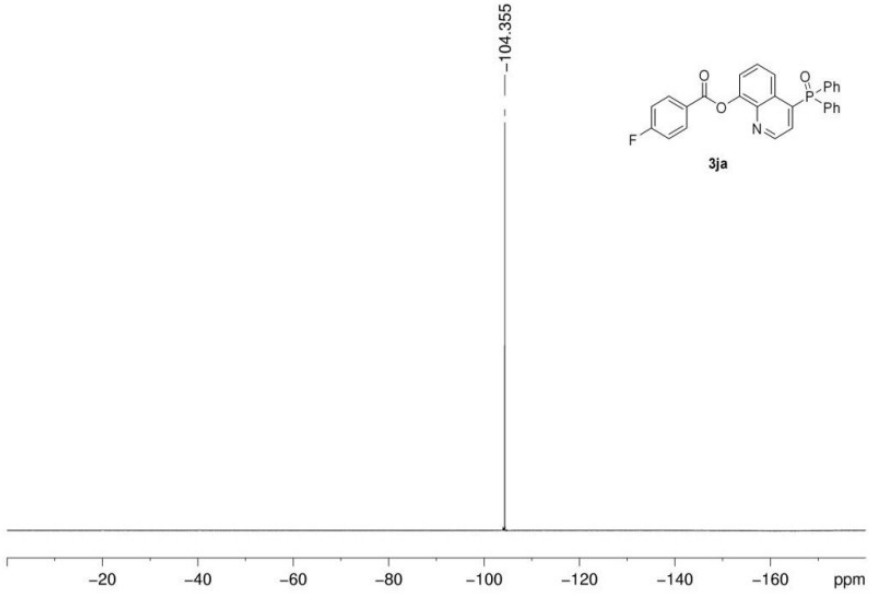

30.997
O
O
Ph
P
Ph
O
N
F
3ia
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

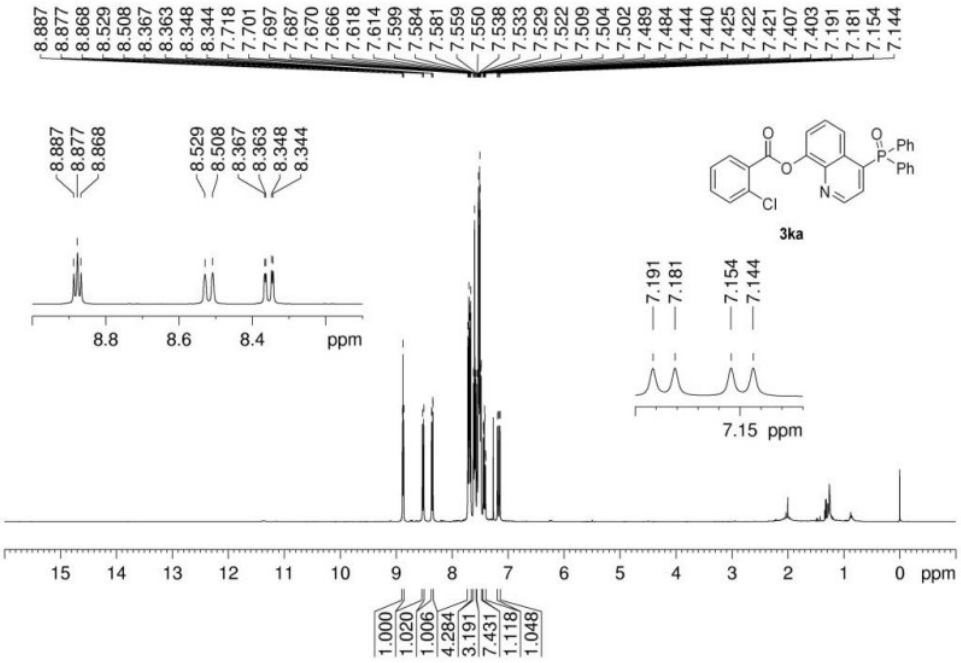

108.038
3ia
−20 −40 −60 −80 −100 −120 −140 −160 −180 ppm


8.877 8.867 8.857 8.551 8.533 8.380 8.366 8.358 8.344 7.736 7.717 7.705 7.687 7.641 7.623 7.604 7.583 7.578 7.556 7.550 7.543 7.531 7.524 7.513 7.284 7.250 7.192 7.182 7.155 7.144
3ja
8.9 8.8 8.7 8.6 8.5 8.4 ppm
ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 0.970 2.110 4.392 3.876 5.025 0.831 1.054

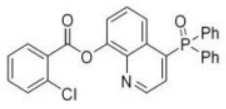

167.536
165.001
164.494
149.186
149.073
148.032
148.007
141.875
141.805
139.310
138.372
133.252
133.158
132.656
132.632
132.059
131.960
131.583
130.531
129.025
128.902
127.676
126.746
126.652
125.812
125.757
125.631
125.603
122.220
115.964
115.745
O
O
Ph
P
Ph
F
N
3ja
220
200
180
160
140
120
100
80
60
40
20
ppm


30.705
O
O
Ph
P
Ph
F
N
3ja
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

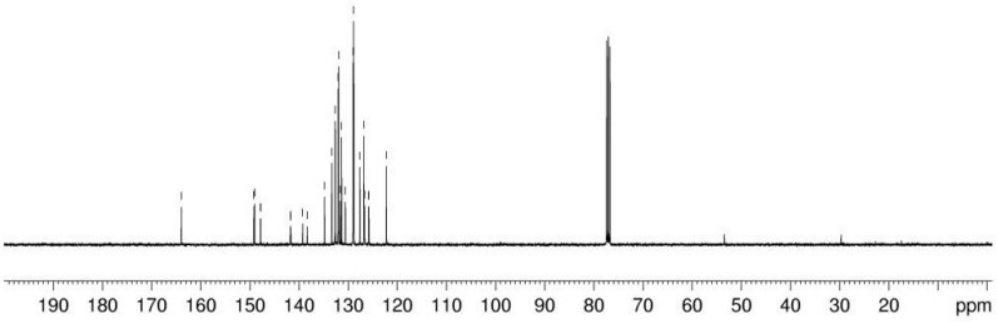

-104.355
3ja
-20
-40
-60
-80
-100
-120
-140
-160
ppm


8.887
8.877
8.868
8.529
8.508
8.367
8.363
8.348
8.344
7.718
7.701
7.697
7.687
7.670
7.666
7.618
7.614
7.599
7.584
7.581
7.559
7.550
7.538
7.533
7.529
7.522
7.509
7.504
7.502
7.489
7.484
7.444
7.440
7.425
7.422
7.421
7.407
7.403
7.191
7.181
7.154
7.144
3ka
8.8
8.6
8.4
ppm
7.15 ppm
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.020
1.006
4.284
3.191
7.431
1.118
1.048

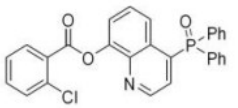

163.932
149.188
149.073
147.834
147.806
141.769
141.698
139.274
138.336
134.846
133.341
132.660
132.641
132.613
132.060
131.961
131.627
131.356
130.576
129.015
128.935
128.891
127.639
126.800
126.769
126.675
125.846
125.792
122.215


O
O
P
Ph
Ph
N
Cl

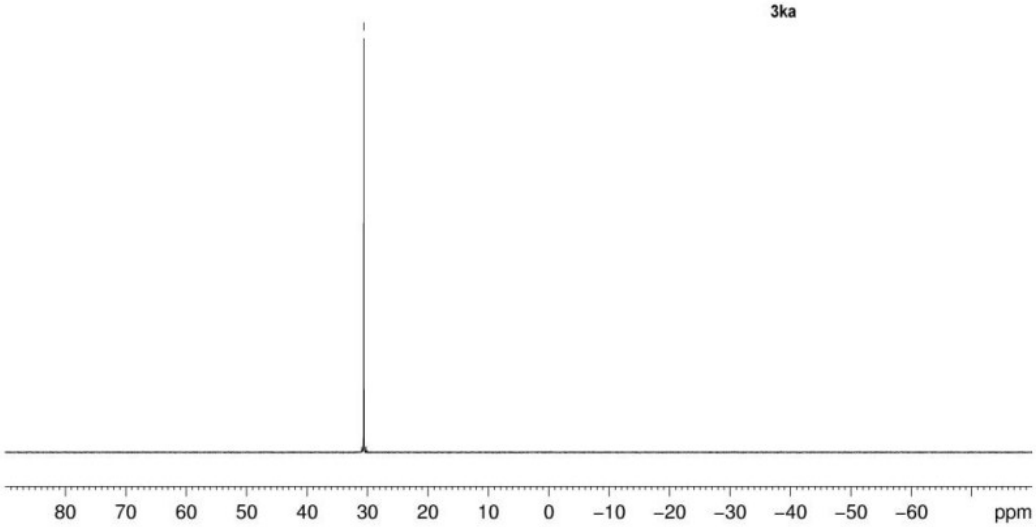
3ka

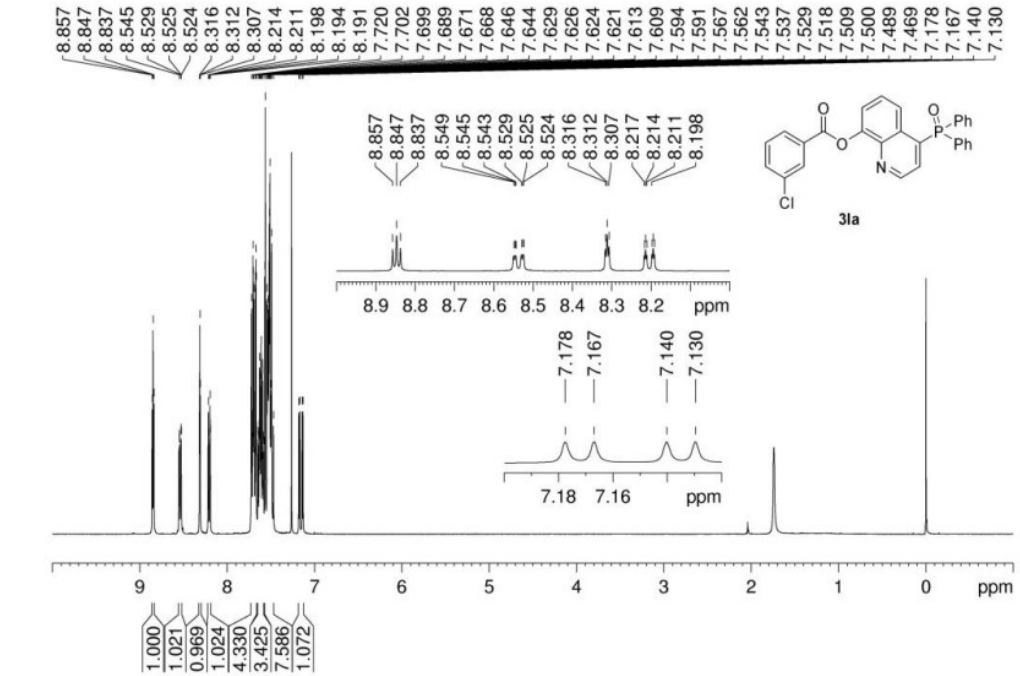

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

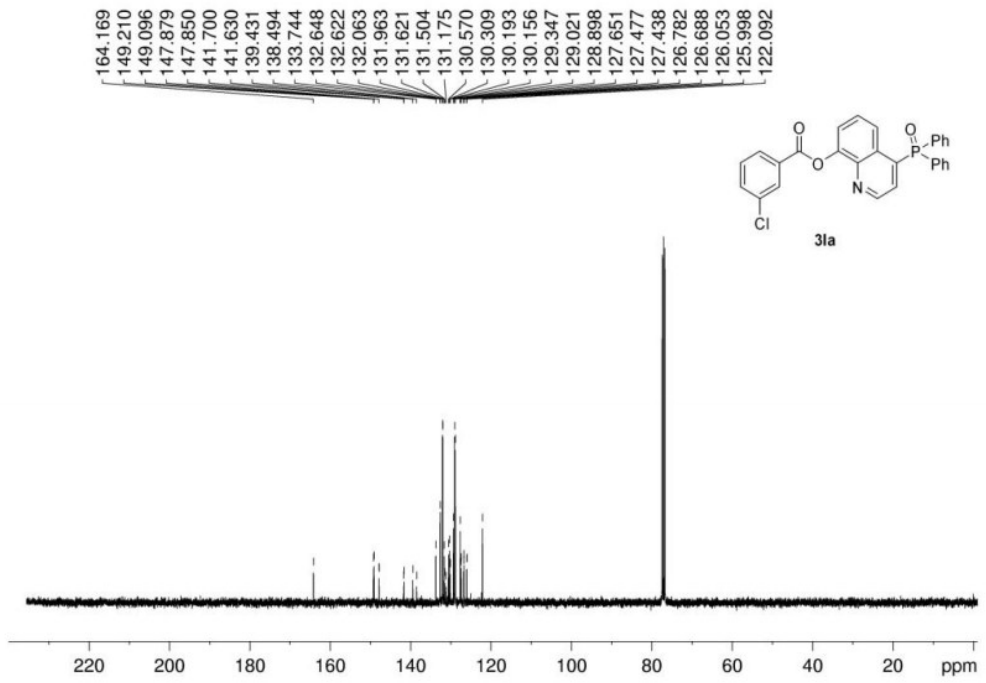

30.585

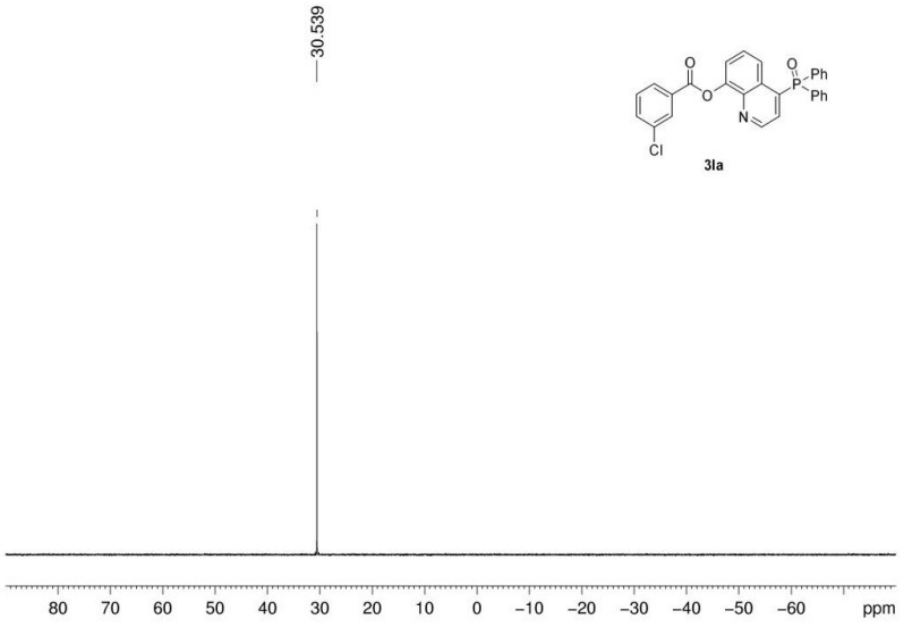

O
O
P
Ph
Ph
N
Cl

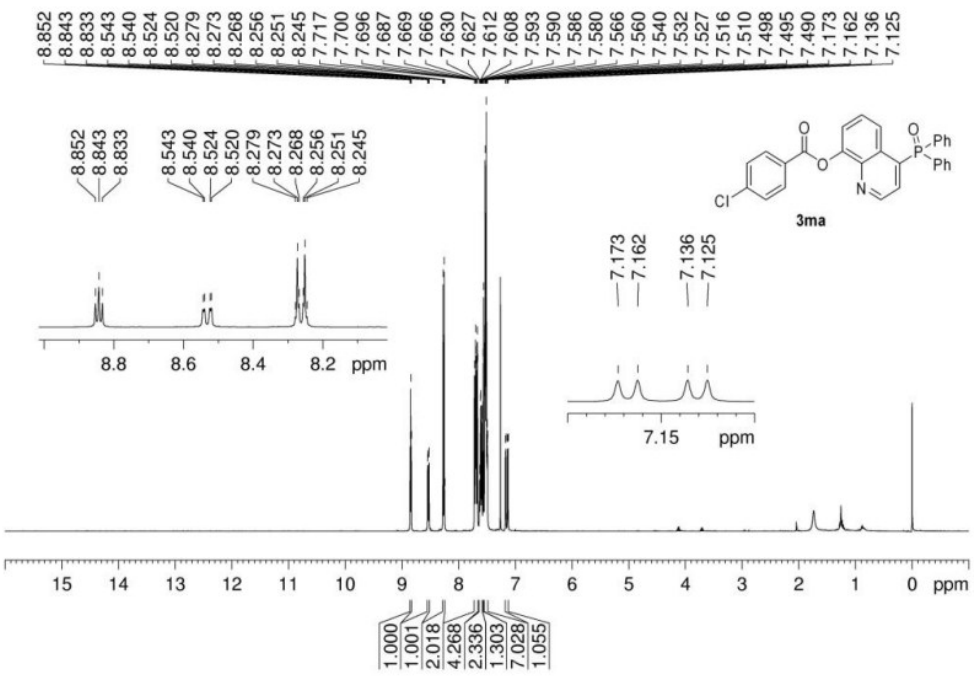
3ka

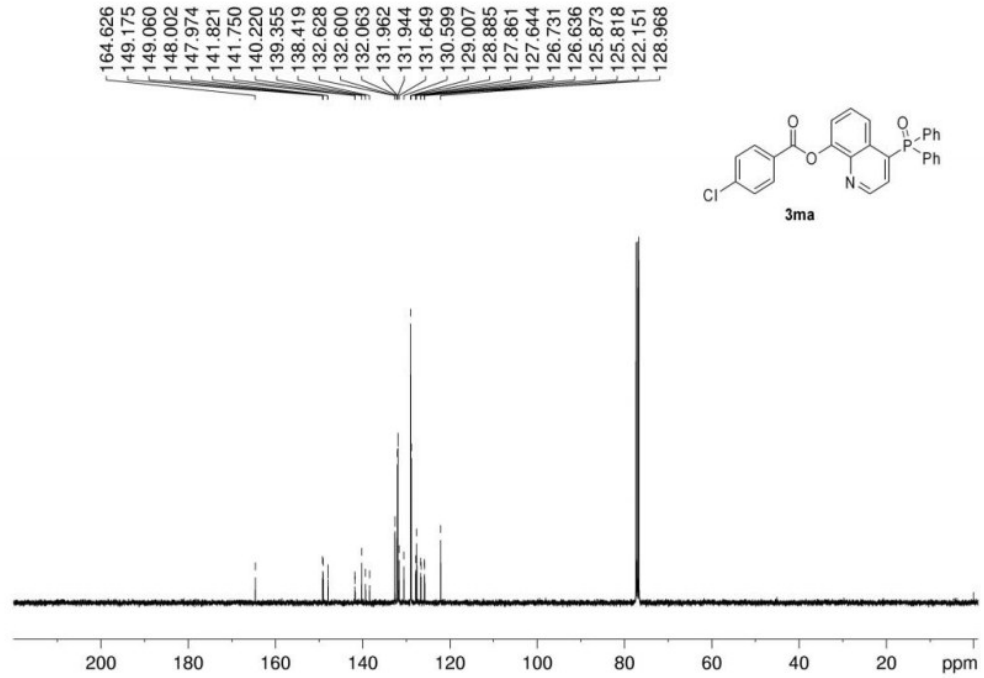

80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

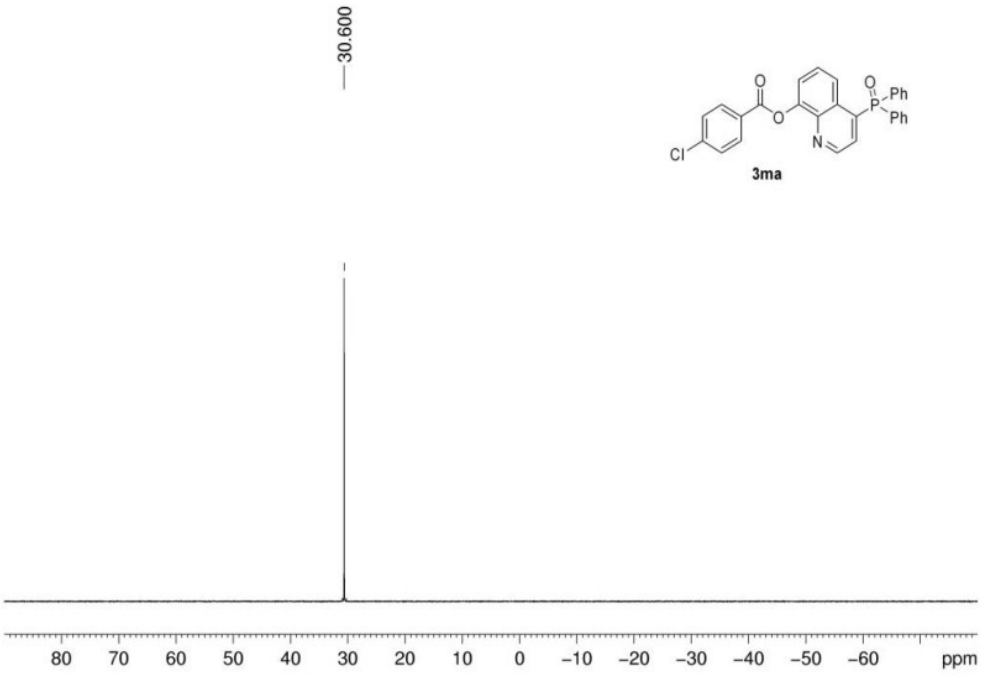

8.857
8.847
8.837
8.545
8.529
8.525
8.524
8.316
8.312
8.307
8.214
8.211
8.198
8.194
8.191
7.720
7.702
7.699
7.689
7.671
7.668
7.646
7.644
7.629
7.626
7.624
7.621
7.613
7.609
7.594
7.591
7.567
7.562
7.543
7.537
7.529
7.518
7.509
7.500
7.489
7.469
7.178
7.167
7.140
7.130
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 ppm
7.18 7.16 ppm
3la
9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.021
0.969
1.024
4.330
3.425
7.586
1.072

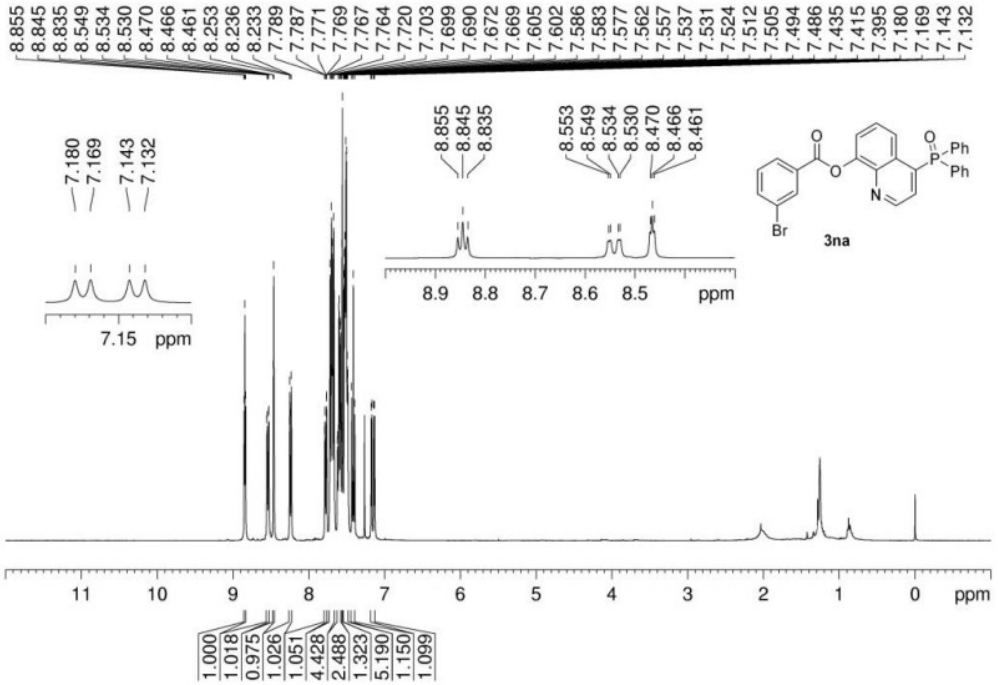

164.169
149.210
149.096
147.879
147.850
141.700
141.630
139.431
138.494
133.744
132.648
132.622
132.063
131.963
131.621
131.504
131.175
130.570
130.309
130.193
130.156
129.347
129.021
128.898
127.651
127.477
127.438
126.782
126.688
126.053
125.998
122.092
3la
220 200 180 160 140 120 100 80 60 40 20 ppm

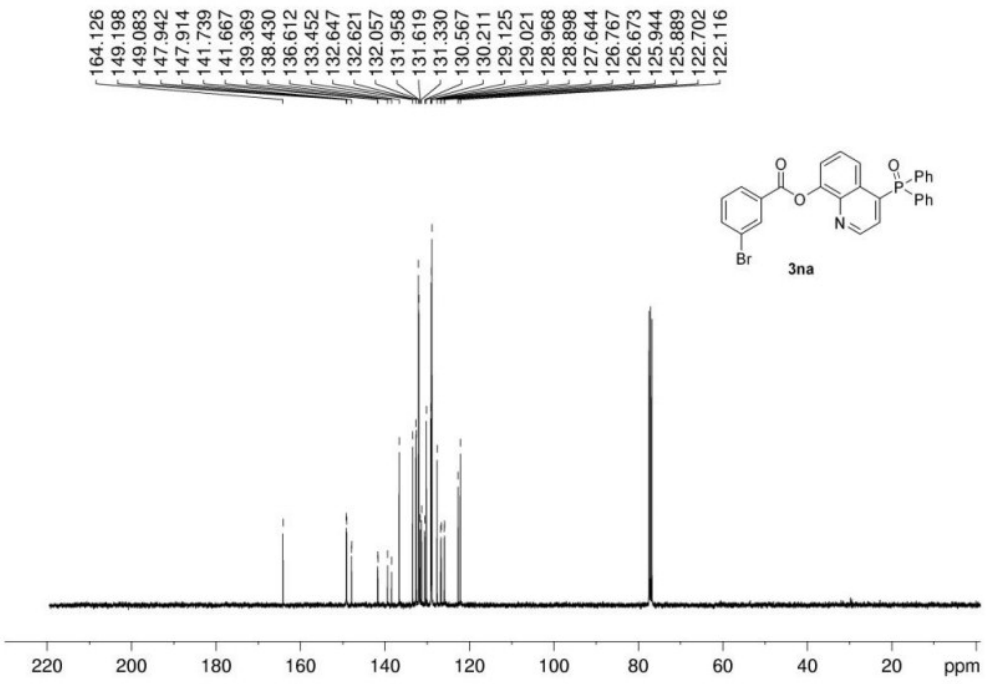

30.539
3la
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

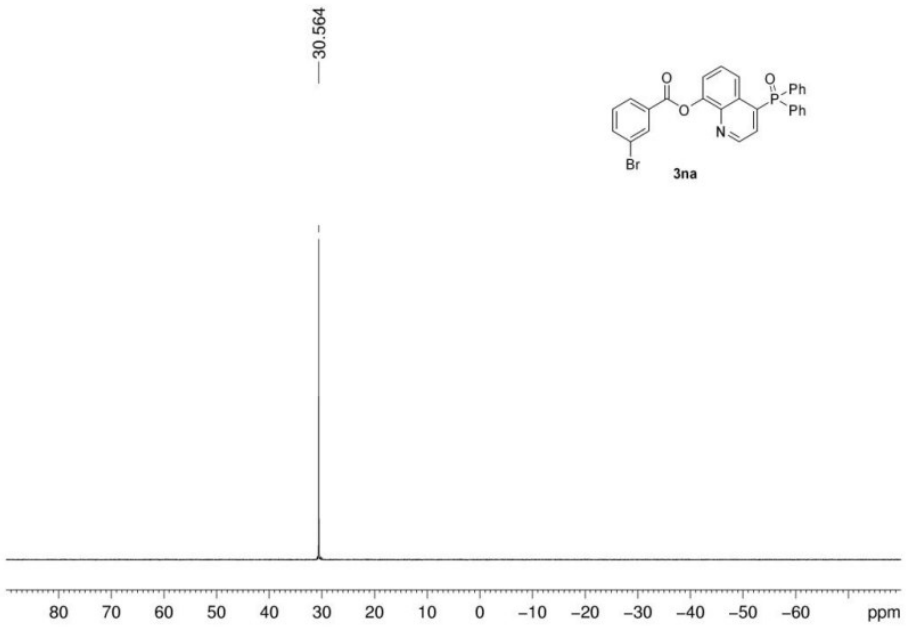

8.852 8.843 8.833 8.543 8.540 8.524 8.520 8.279 8.273 8.268 8.256 8.251 8.245 7.717 7.700 7.696 7.687 7.669 7.666 7.630 7.627 7.612 7.608 7.593 7.590 7.586 7.580 7.566 7.560 7.540 7.532 7.527 7.516 7.510 7.498 7.495 7.490 7.173 7.162 7.136 7.125
3ma
7.173 7.162 7.136 7.125
7.15 ppm
8.8 8.6 8.4 8.2 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.001 2.018 4.268 2.336 1.303 7.028 1.055

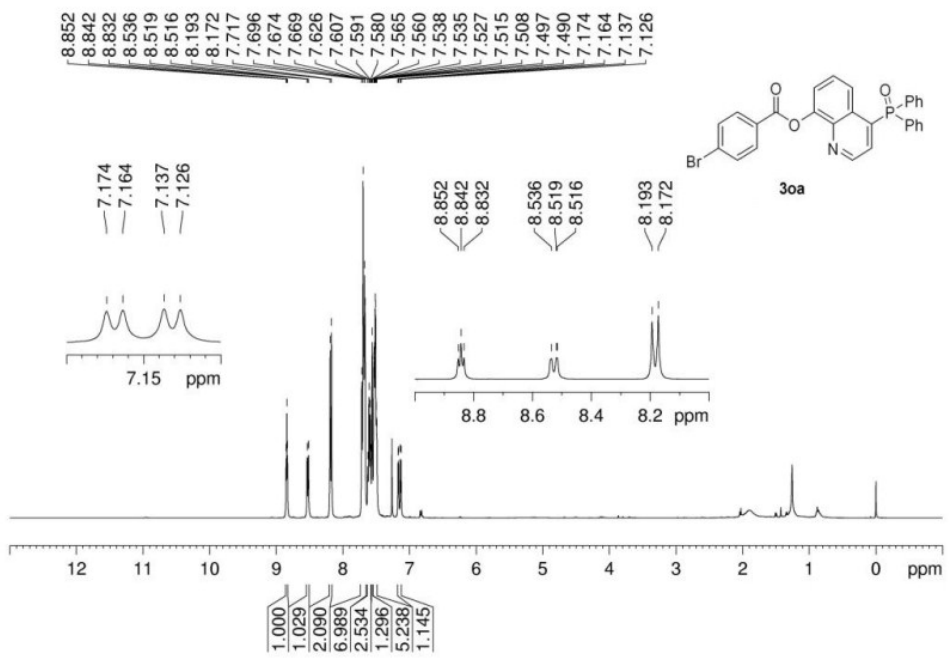

164.626
149.175
149.060
148.002
147.974
141.821
141.750
140.220
139.355
138.419
132.628
132.600
132.063
131.962
131.944
131.649
130.599
129.007
128.885
127.861
127.644
126.731
126.636
125.873
125.818
122.151
128.968
O
O
P
Ph
Ph
N
Cl
3ma
200
180
160
140
120
100
80
60
40
20
ppm


30.600
O
O
P
Ph
Ph
N
Cl
3ma
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm


8.855
8.845
8.835
8.549
8.534
8.530
8.470
8.466
8.461
8.253
8.236
8.233
7.789
7.787
7.771
7.769
7.767
7.764
7.720
7.703
7.699
7.690
7.672
7.669
7.605
7.602
7.586
7.583
7.577
7.562
7.557
7.537
7.531
7.524
7.512
7.505
7.494
7.486
7.435
7.415
7.395
7.180
7.169
7.143
7.132
7.15 ppm
8.9 8.8 8.7 8.6 8.5 ppm
Br
3na
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.018
0.975
1.026
1.051
4.428
2.488
1.323
5.190
1.150
1.099


164.126
149.198
149.083
147.942
147.914
141.739
141.667
139.369
138.430
136.612
133.452
132.647
132.621
132.057
131.958
131.619
131.330
130.567
130.211
129.125
129.021
128.968
128.898
127.644
126.767
126.673
125.944
125.889
122.702
122.116
Br
3na
220 200 180 160 140 120 100 80 60 40 20 ppm


30.564
Ph
Ph
O
O
P
N
Br
3na
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm


8.852
8.842
8.832
8.536
8.519
8.516
8.193
8.172
7.717
7.696
7.674
7.669
7.626
7.607
7.591
7.580
7.565
7.560
7.538
7.535
7.527
7.515
7.508
7.497
7.490
7.174
7.164
7.137
7.126
Ph
Ph
O
O
P
N
Br
3oa
7.15 ppm
8.8 8.6 8.4 8.2 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.029
2.090
6.989
2.534
1.296
5.238
1.145


164.794
149.186
149.072
147.975
147.948
141.782
141.710
139.318
138.380
132.662
132.634
132.060
132.011
131.964
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128.949
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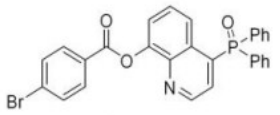
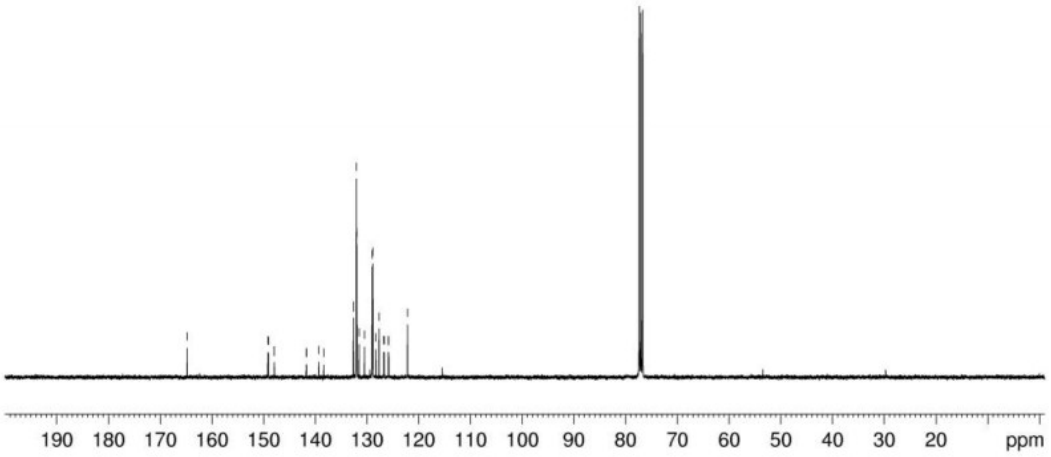
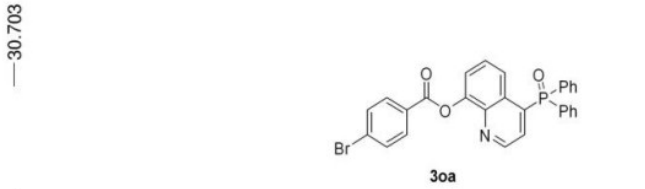
128.297
127.673
126.760
126.667
125.872
125.816
122.170


O
O
P
Ph
Ph
N
Br

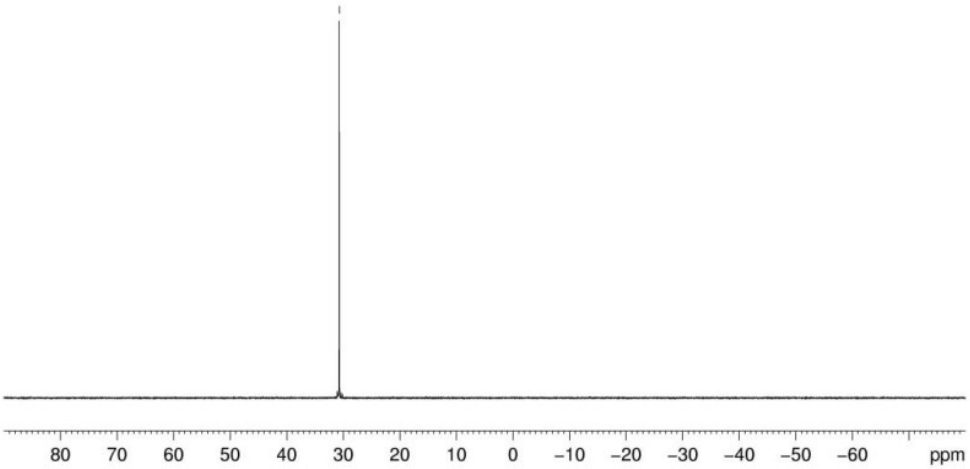
3oa

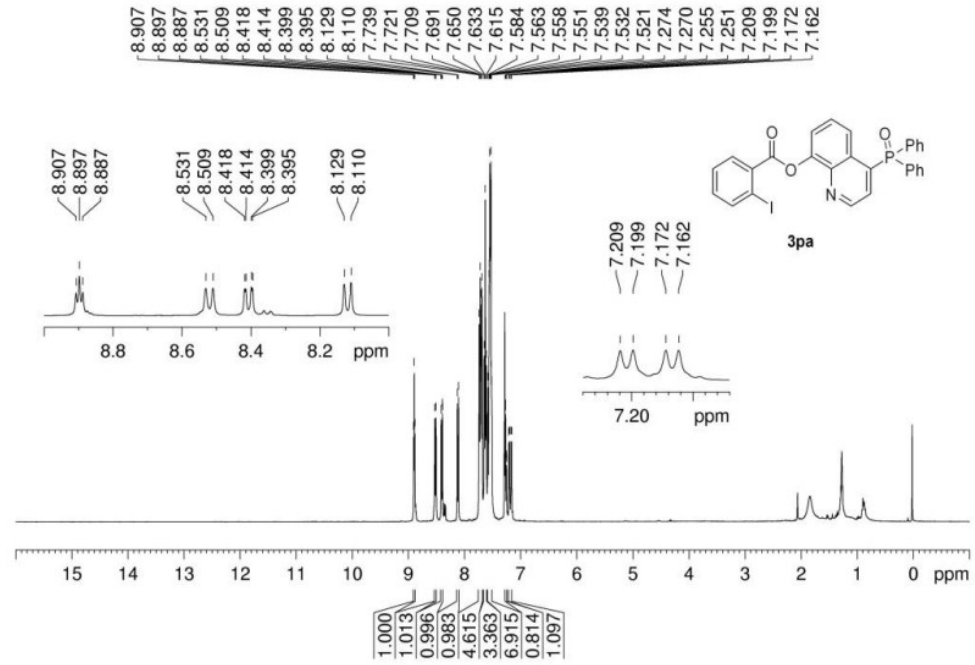

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

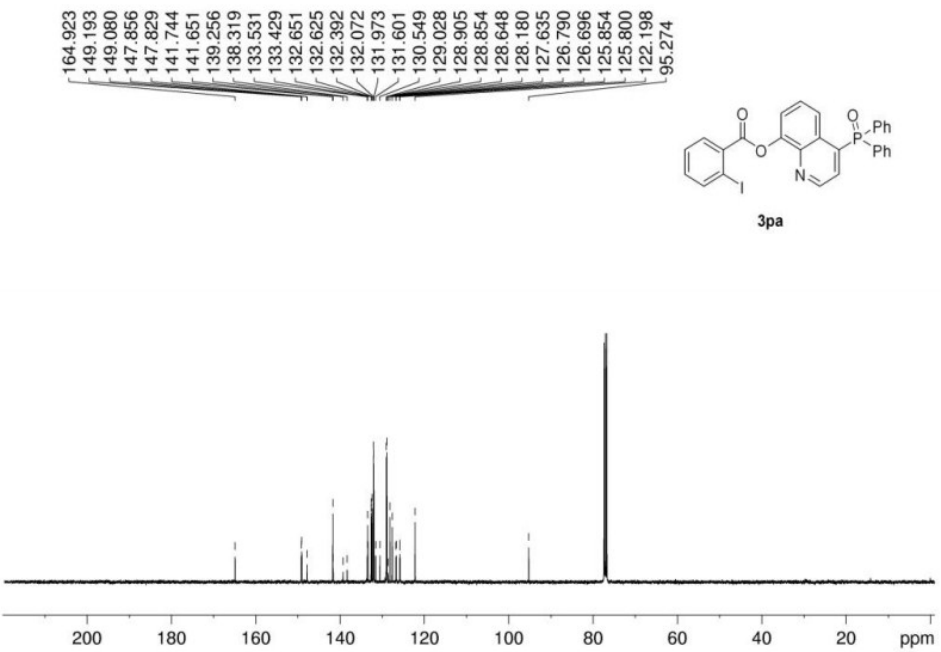

30.703

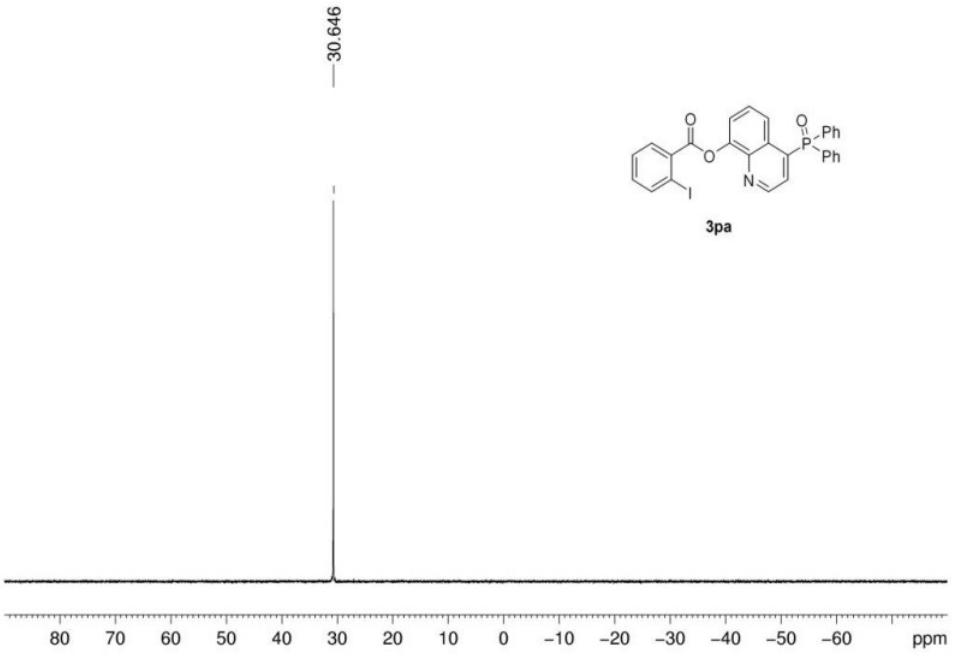
O
O
P
Ph
Ph
N
Br

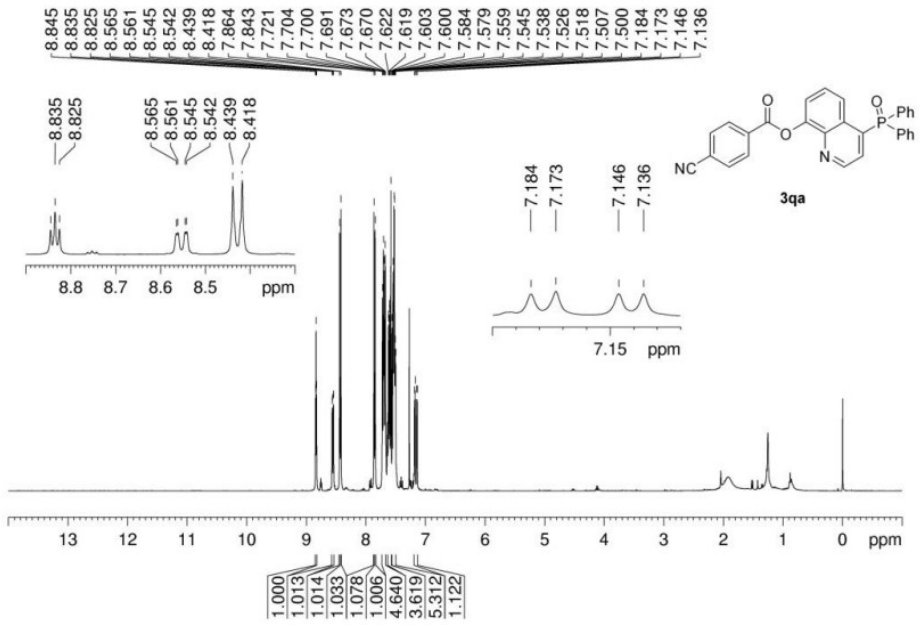
3oa

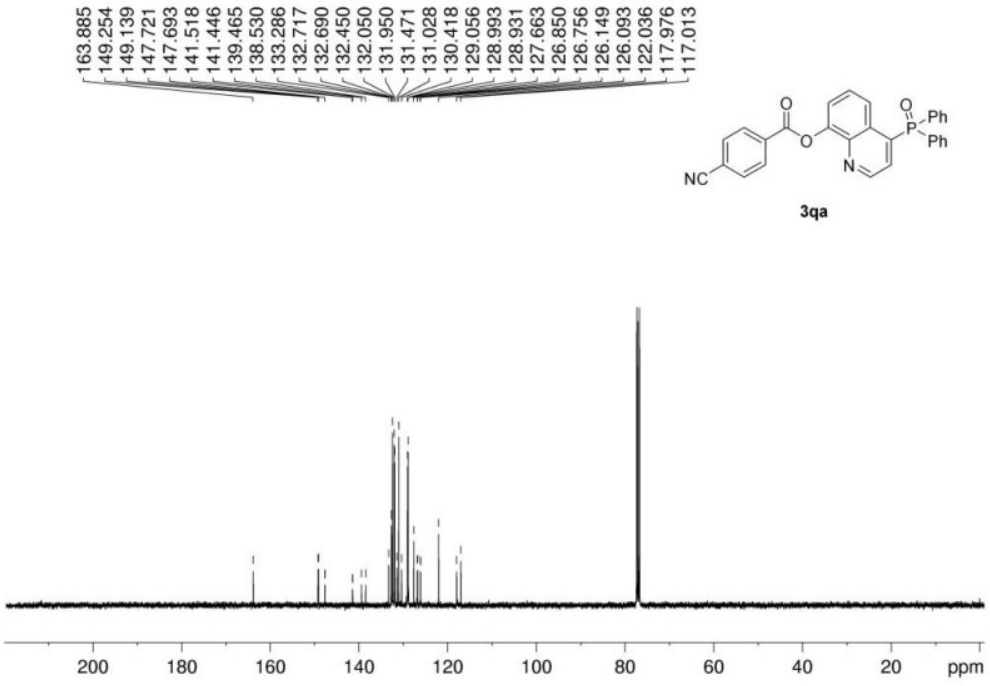

80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

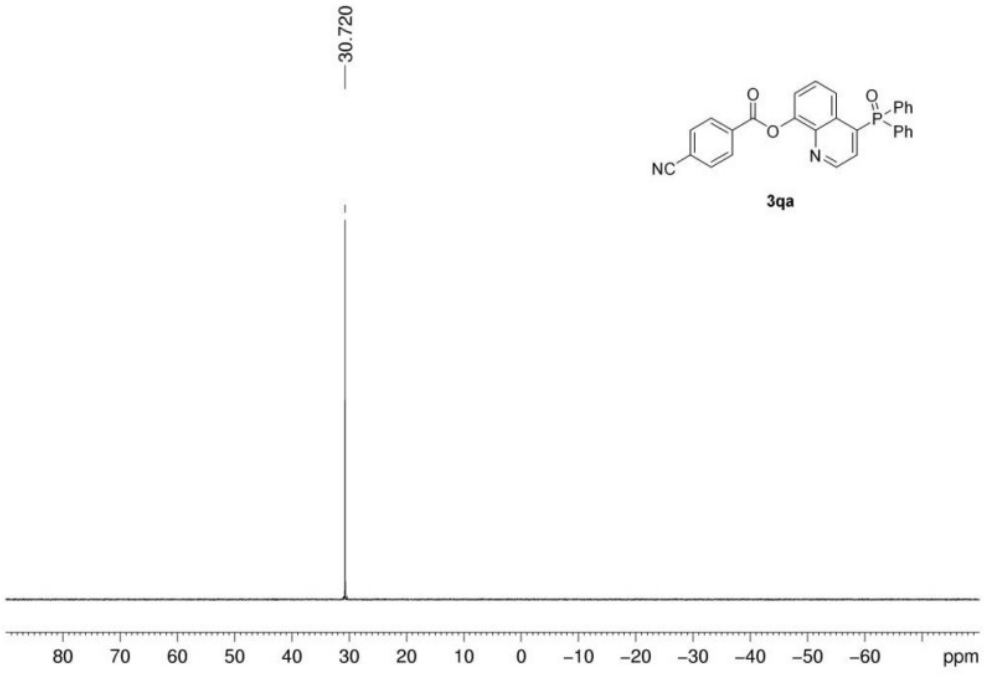

8.907
8.897
8.887
8.531
8.509
8.418
8.414
8.399
8.395
8.129
8.110
7.739
7.721
7.709
7.691
7.650
7.633
7.615
7.584
7.563
7.558
7.551
7.539
7.532
7.521
7.274
7.270
7.255
7.251
7.209
7.199
7.172
7.162
8.8
8.6
8.4
8.2
ppm
7.20
ppm
3pa
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.013
0.996
0.983
4.615
3.363
6.915
0.814
1.097

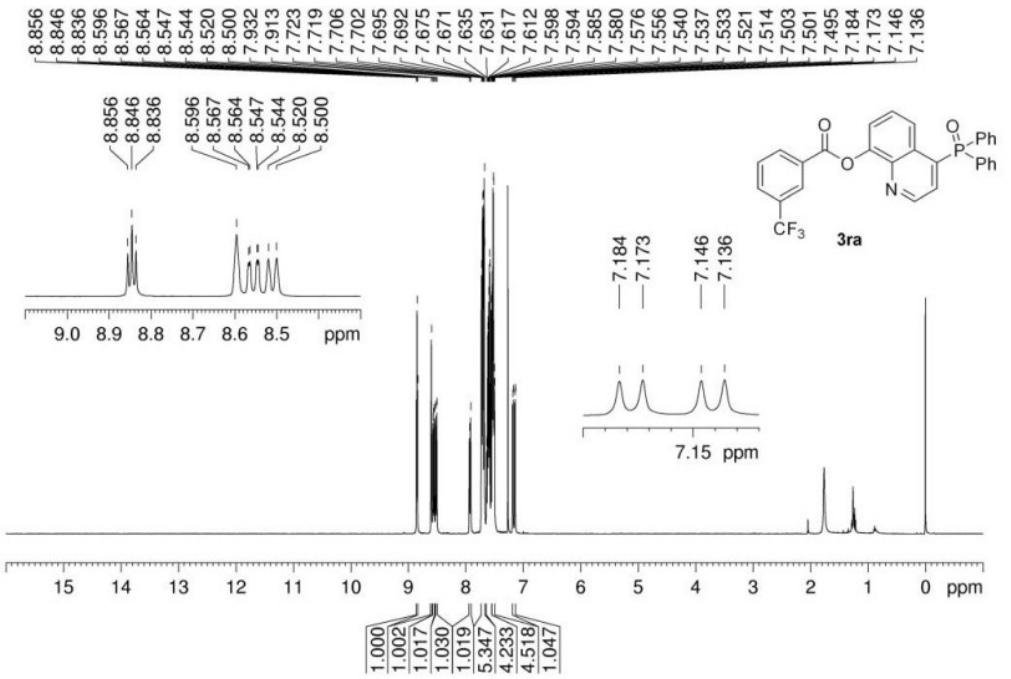

164.923
149.193
149.080
147.856
147.829
141.744
141.651
139.256
138.319
133.531
133.429
132.651
132.625
132.392
132.072
131.973
131.601
130.549
129.028
128.905
128.854
128.648
128.180
127.635
126.790
126.696
125.854
125.800
122.198
95.274
3pa
200
180
160
140
120
100
80
60
40
20
ppm

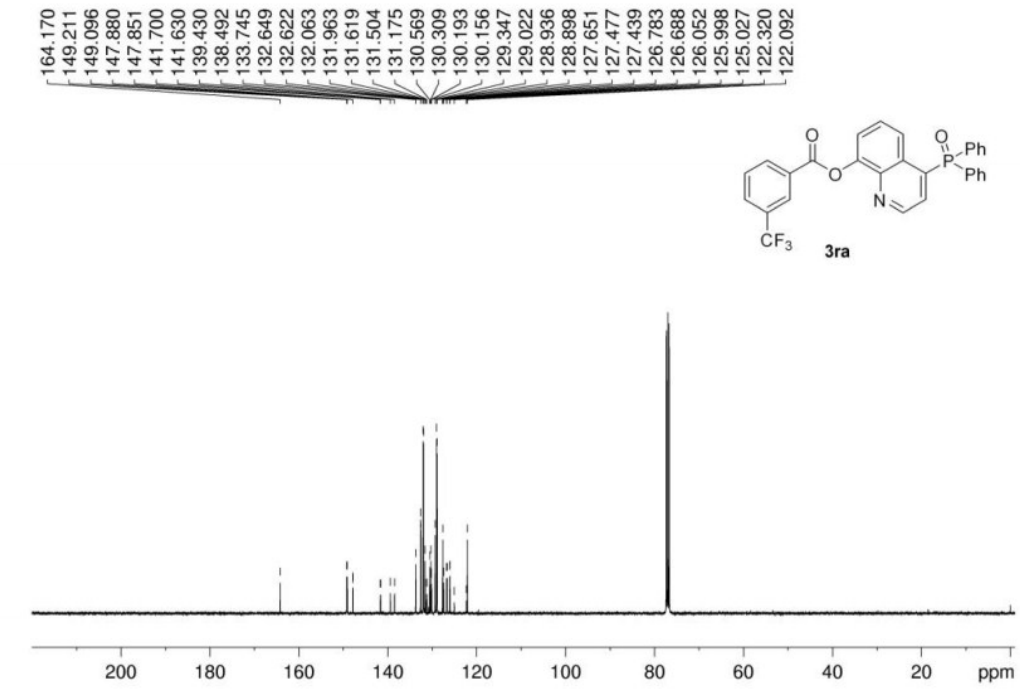

30.646
3pa
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

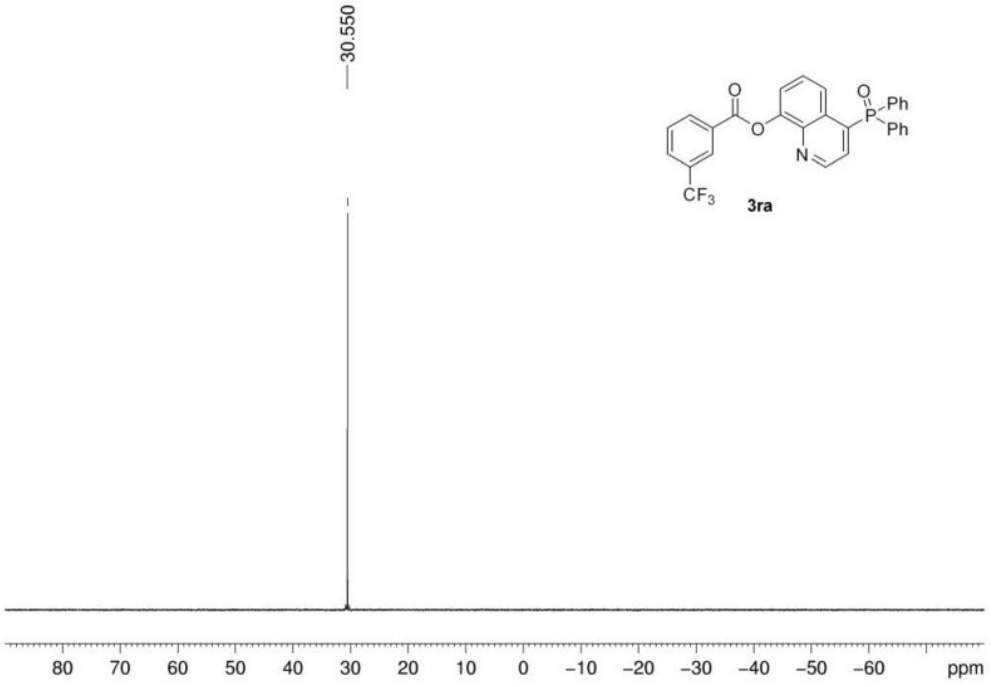

8.845 8.835 8.825 8.565 8.561 8.545 8.542 8.439 8.418 7.864 7.843 7.721 7.704 7.700 7.691 7.673 7.670 7.622 7.619 7.603 7.600 7.584 7.579 7.559 7.545 7.538 7.526 7.518 7.507 7.500 7.184 7.173 7.146 7.136
3qa
8.8 8.7 8.6 8.5 ppm
7.15 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 1.013 1.014 1.033 1.078 1.006 4.640 3.619 5.312 1.122

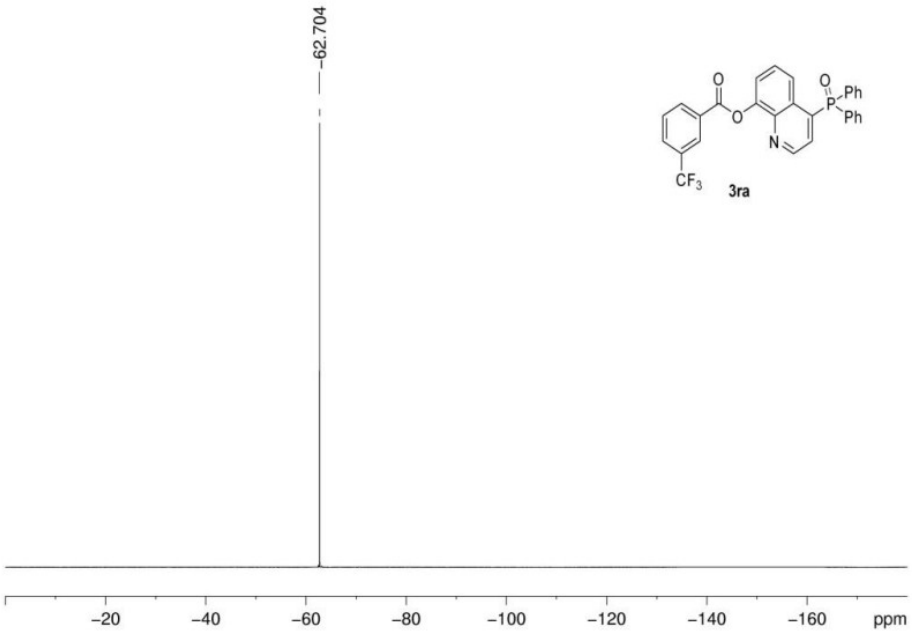

163.885
149.254
149.139
147.721
147.693
141.518
141.446
139.465
138.530
133.286
132.717
132.690
132.450
132.050
131.950
131.471
131.028
130.418
129.056
128.993
128.931
127.663
126.850
126.756
126.149
126.093
122.036
117.976
117.013
O
O
P
Ph
Ph
N
NC
3qa
200
180
160
140
120
100
80
60
40
20
ppm

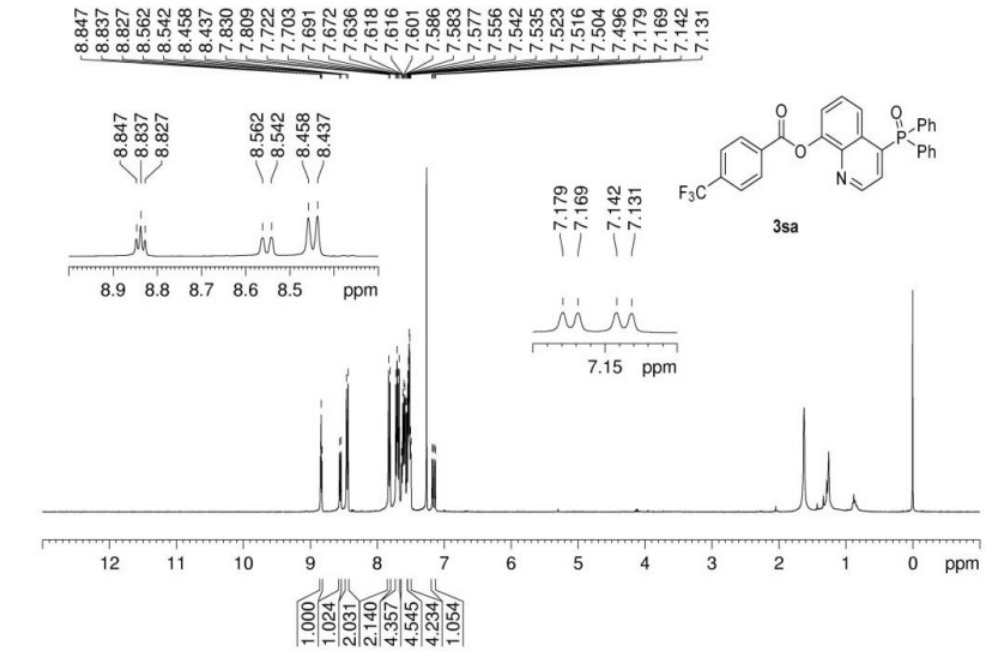

30.720
O
O
P
Ph
Ph
N
NC
3qa
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

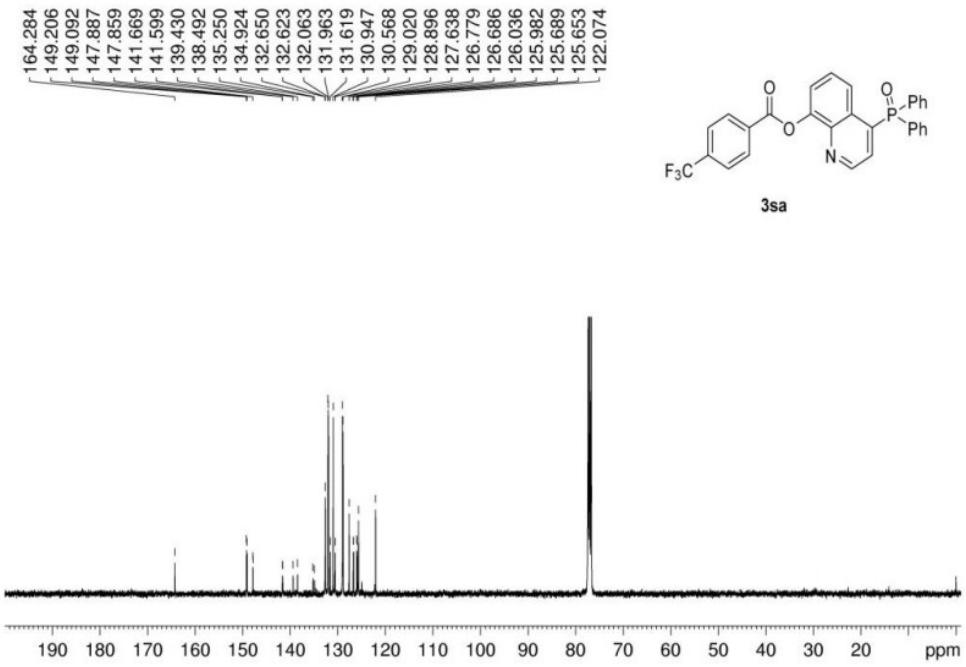

8.856
8.846
8.836
8.596
8.567
8.564
8.547
8.544
8.520
8.500
7.932
7.913
7.723
7.719
7.706
7.702
7.695
7.692
7.675
7.671
7.635
7.631
7.617
7.612
7.598
7.594
7.585
7.580
7.576
7.556
7.540
7.537
7.533
7.521
7.514
7.503
7.501
7.495
7.184
7.173
7.146
7.136
9.0 8.9 8.8 8.7 8.6 8.5 ppm
7.15 ppm
Ph
Ph
CF3
3ra
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.002
1.017
1.030
1.019
5.347
4.233
4.518
1.047

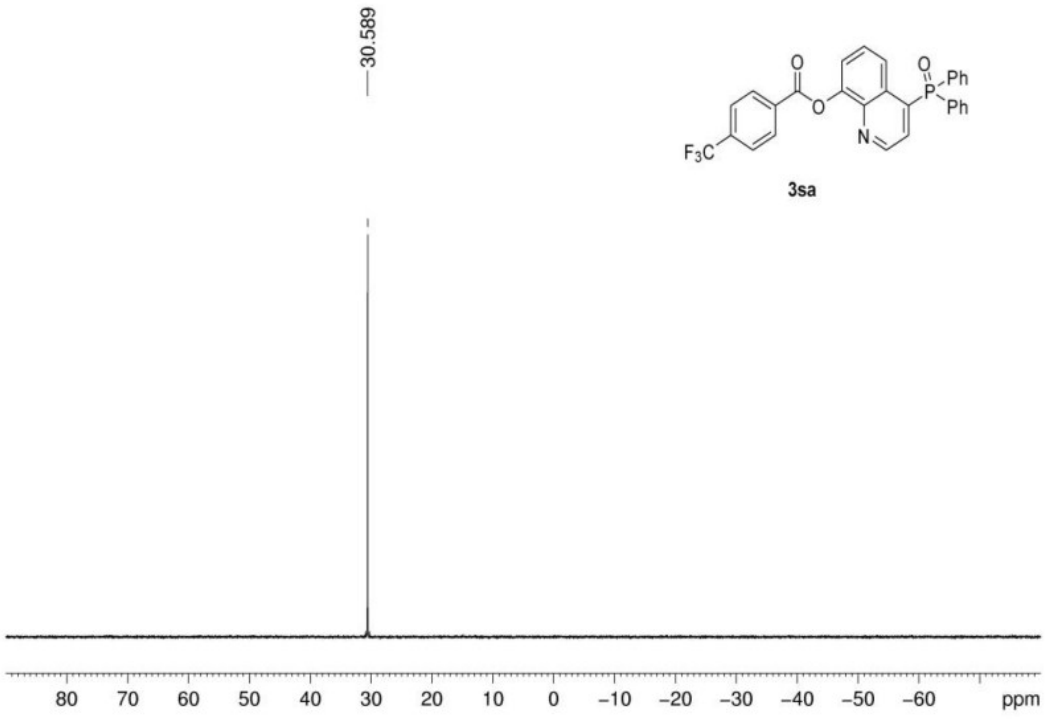

164.170
149.211
149.096
147.880
147.851
141.700
141.630
139.430
138.492
133.745
132.649
132.622
132.063
131.963
131.619
131.504
131.175
130.569
130.309
130.193
130.156
129.347
129.022
128.936
128.898
127.651
127.477
127.439
126.783
126.688
126.052
125.998
125.027
122.320
122.092
Ph
Ph
CF3
3ra
200 180 160 140 120 100 80 60 40 20 ppm

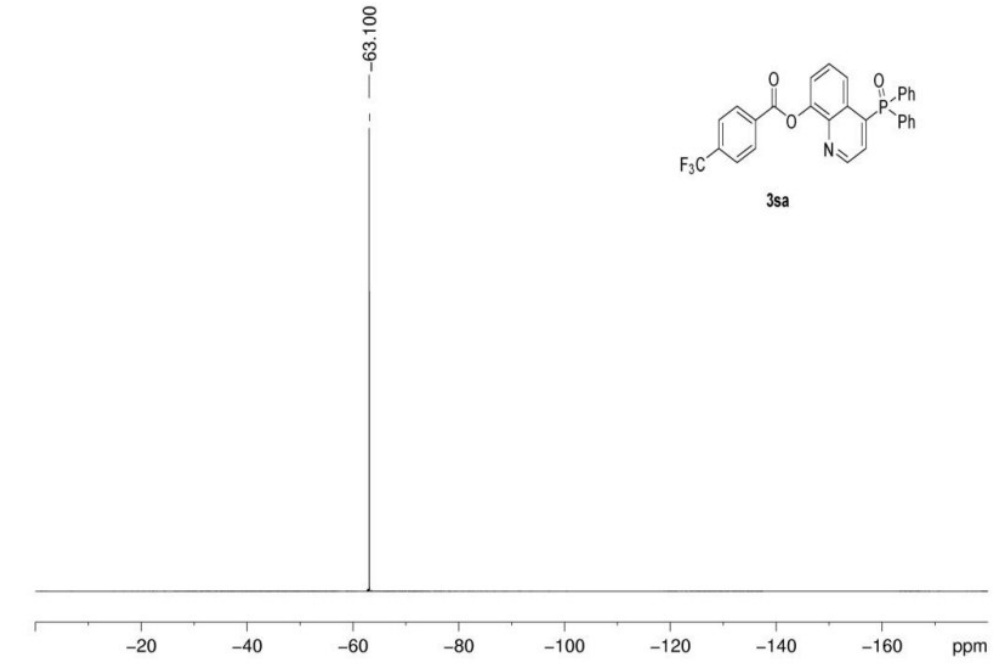

30.550
O
O
P
Ph
Ph
N
CF3
3ra
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

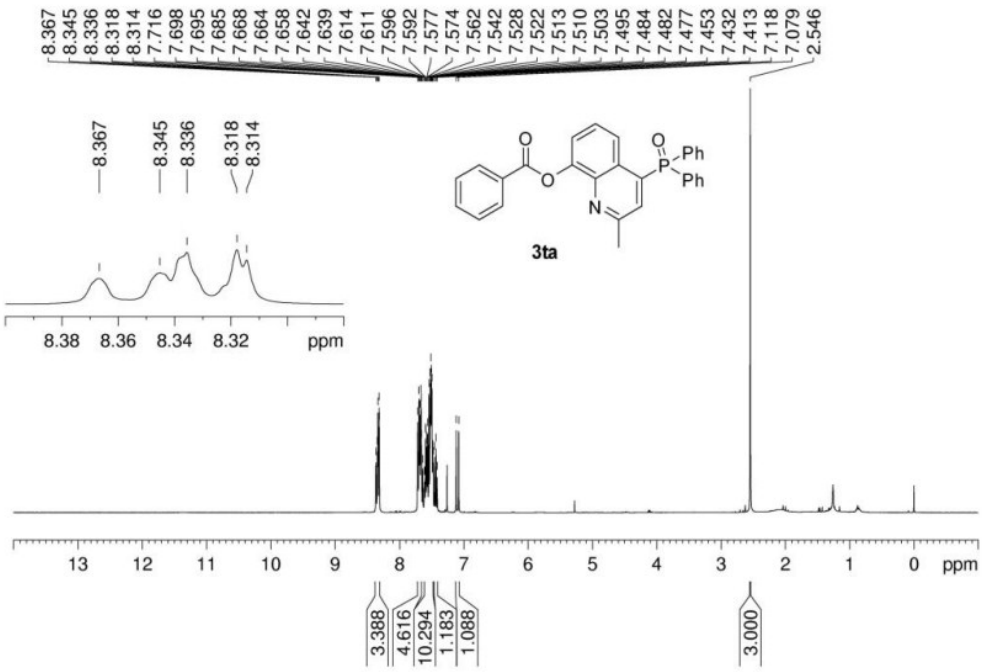

62.704
O
O
P
Ph
Ph
N
CF3
3ra
−20
−40
−60
−80
−100
−120
−140
−160
ppm

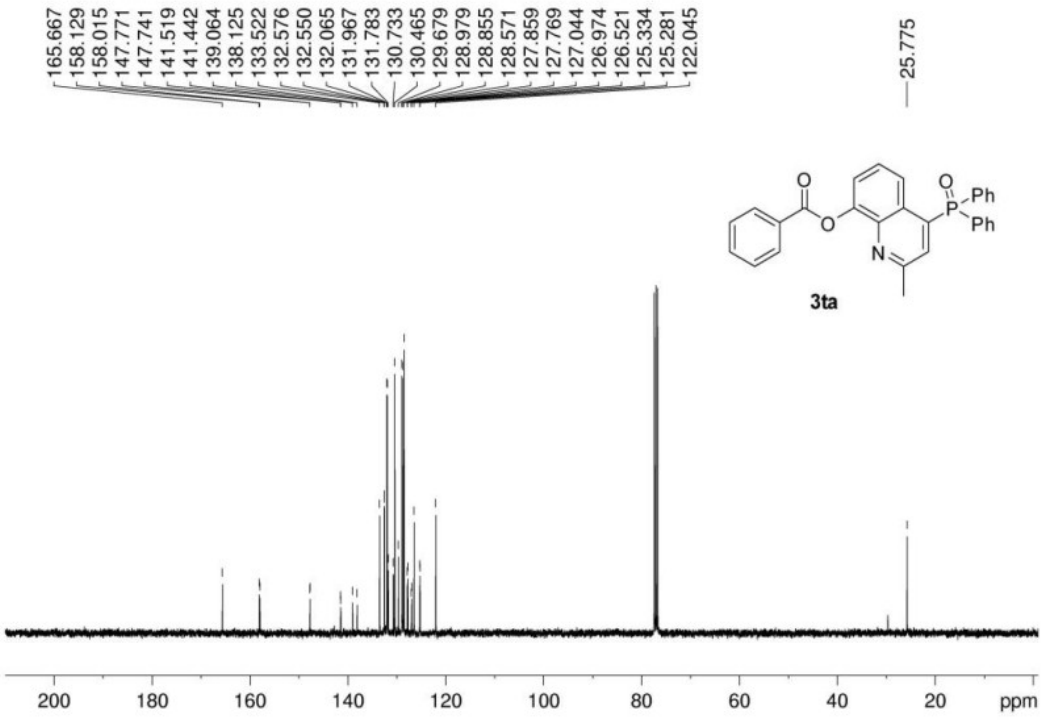

8.847
8.837
8.827
8.562
8.542
8.458
8.437
7.830
7.809
7.722
7.703
7.691
7.672
7.636
7.618
7.616
7.601
7.586
7.583
7.577
7.556
7.542
7.535
7.523
7.516
7.504
7.496
7.179
7.169
7.142
7.131
8.9 8.8 8.7 8.6 8.5 ppm
7.15 ppm
3sa
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.024
2.031
2.140
4.357
4.545
4.234
1.054

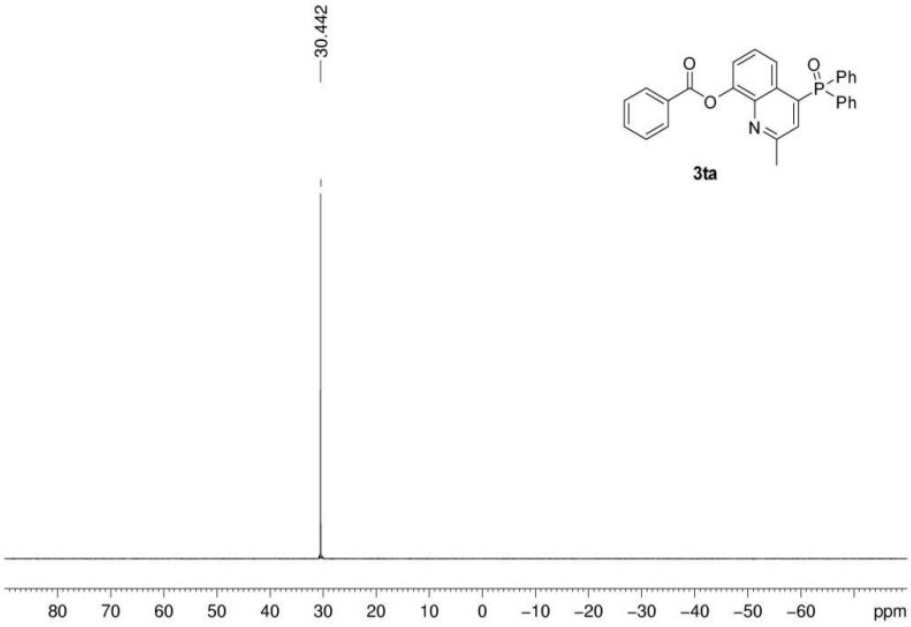

164.284
149.206
149.092
147.887
147.859
141.669
141.599
139.430
138.492
135.250
134.924
132.650
132.623
132.063
131.963
131.619
130.947
130.568
129.020
128.896
127.638
126.779
126.686
126.036
125.982
125.689
125.653
122.074
3sa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

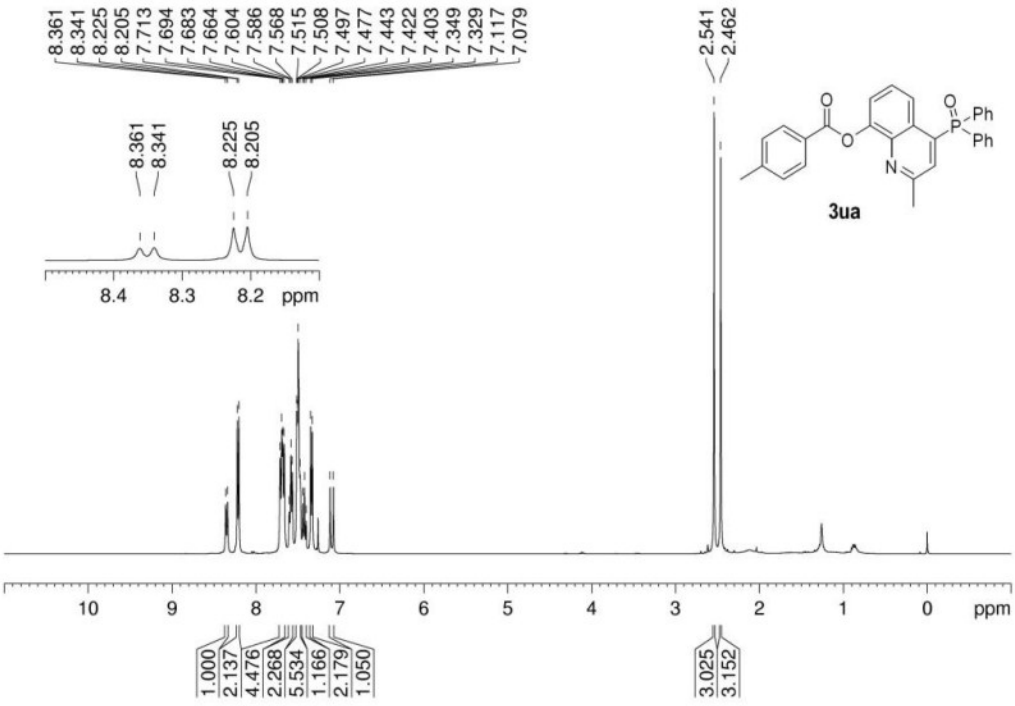

30.589
3sa
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

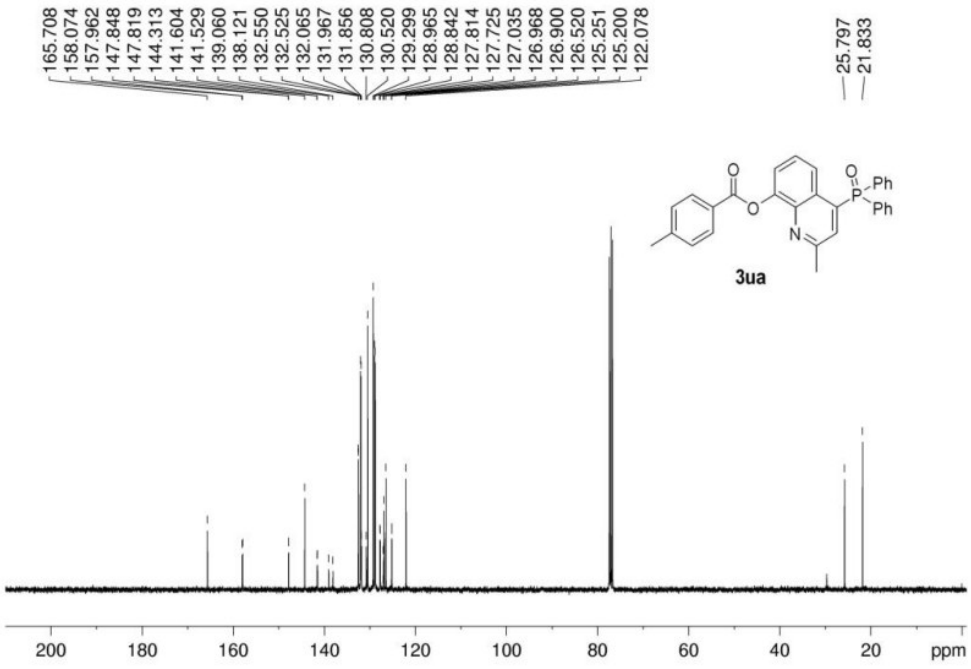

−63.100
3sa
−20 −40 −60 −80 −100 −120 −140 −160 ppm

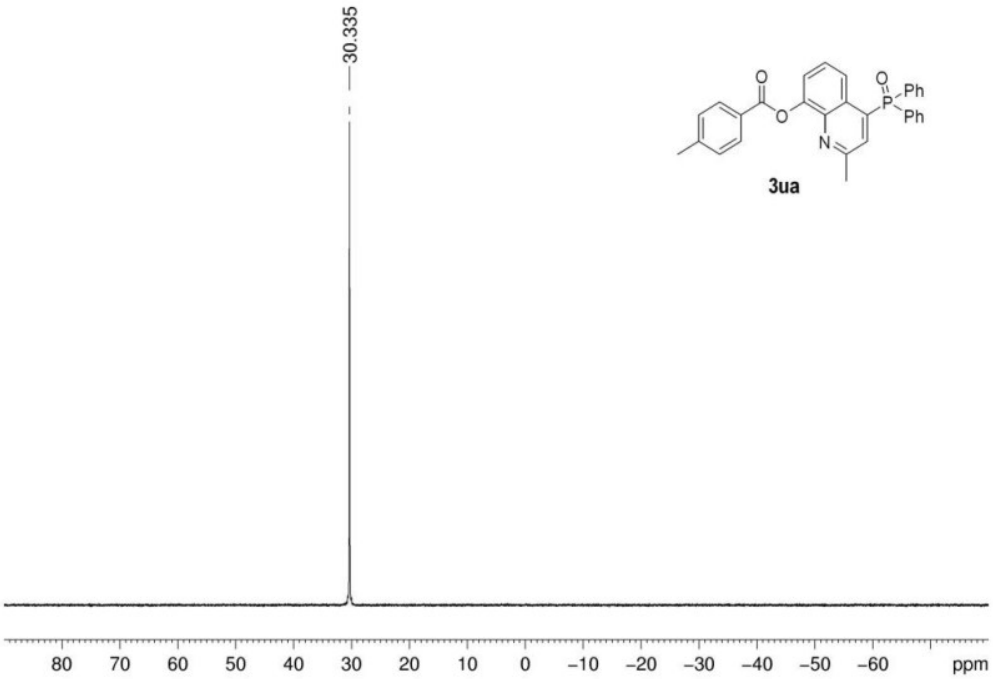

8.367
8.345
8.336
8.318
8.314
7.716
7.698
7.695
7.685
7.668
7.664
7.658
7.642
7.639
7.614
7.611
7.596
7.592
7.577
7.574
7.562
7.542
7.528
7.522
7.513
7.510
7.503
7.495
7.484
7.482
7.477
7.453
7.432
7.413
7.118
7.079
2.546
8.38 8.36 8.34 8.32 ppm
O
O
P
Ph
Ph
N
3ta
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.388
4.616
10.294
1.183
1.088
3.000

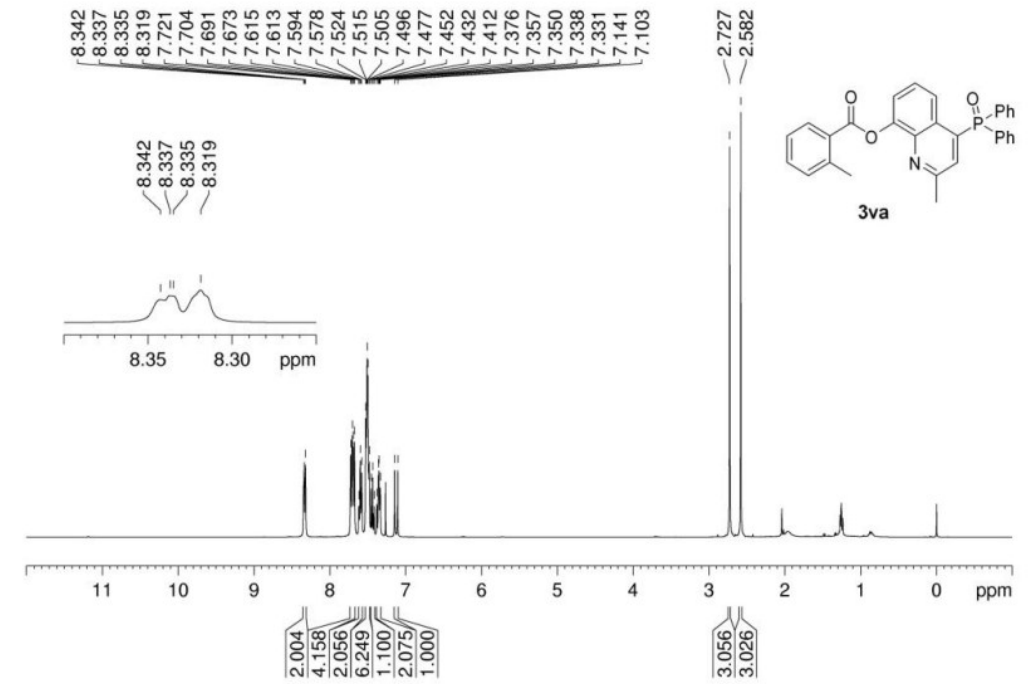

165.667
158.129
158.015
147.771
147.741
141.519
141.442
139.064
138.125
133.522
132.576
132.550
132.065
131.967
131.783
130.733
130.465
129.679
128.979
128.855
128.571
127.859
127.769
127.044
126.974
126.521
125.334
125.281
122.045
25.775
O
O
P
Ph
Ph
N
3ta
200 180 160 140 120 100 80 60 40 20 ppm

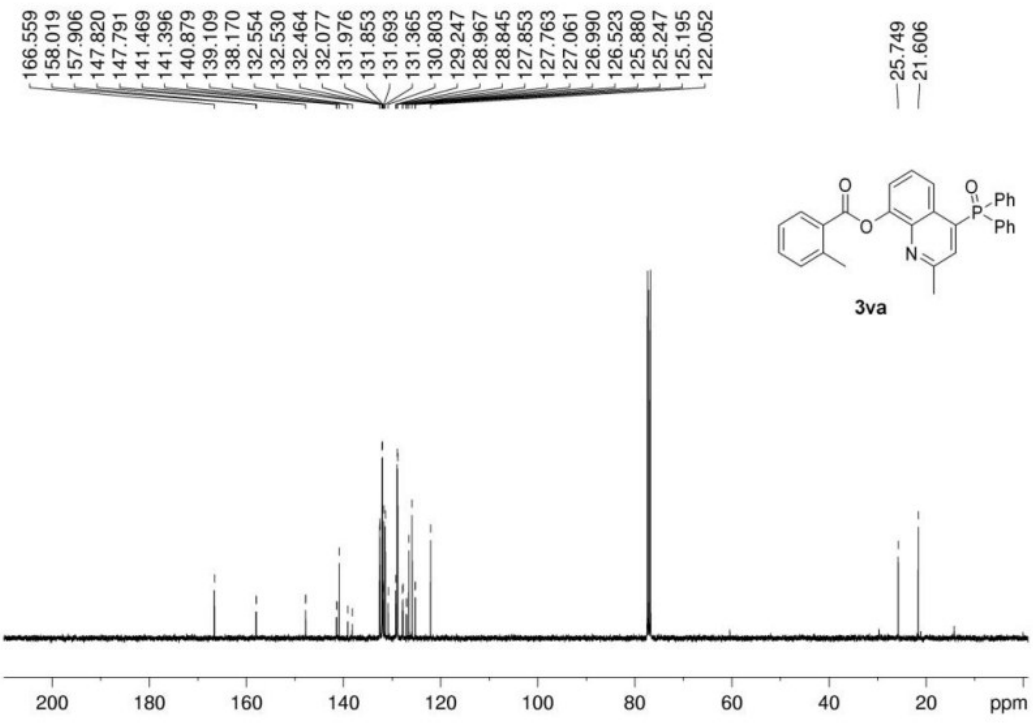

30.442
3ta
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm

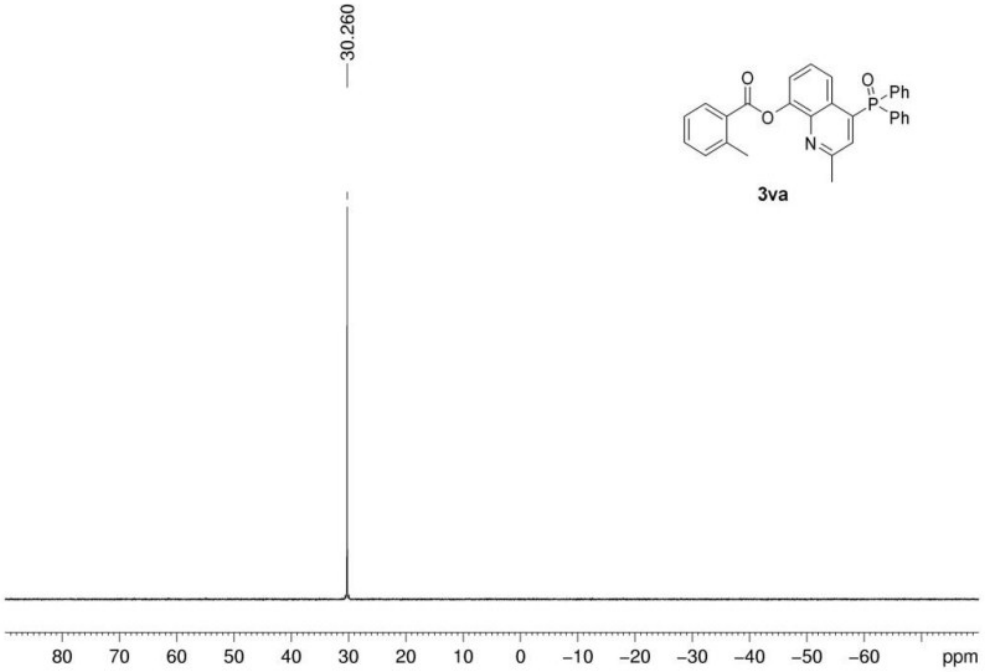

8.361
8.341
8.225
8.205
7.713
7.694
7.683
7.664
7.604
7.586
7.568
7.515
7.508
7.497
7.477
7.443
7.422
7.403
7.349
7.329
7.117
7.079
2.541
2.462
3ua
8.4 8.3 8.2 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
2.137
4.476
2.268
5.534
1.166
2.179
1.050
3.025
3.152

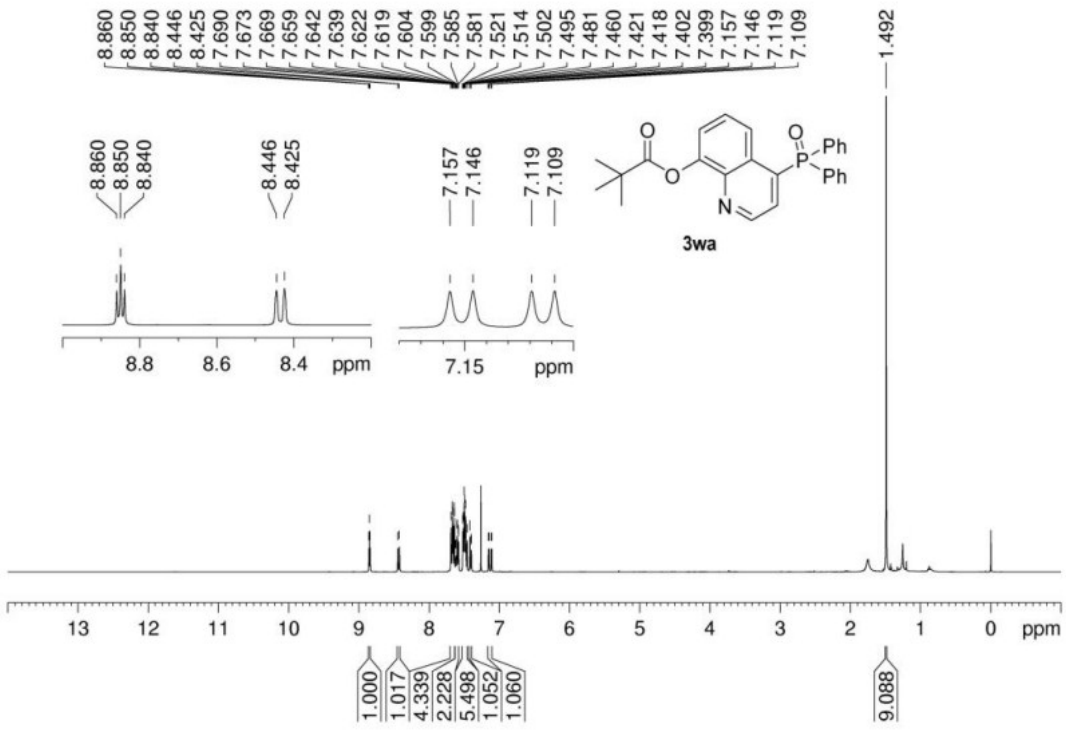

165.708
158.074
157.962
147.848
147.819
144.313
141.604
141.529
139.060
138.121
132.550
132.525
132.065
131.967
131.856
130.808
130.520
129.299
128.965
128.842
127.814
127.725
127.035
126.968
126.900
126.520
125.251
125.200
122.078
25.797
21.833
O
O
O
P
Ph
Ph
N
3ua
200
180
160
140
120
100
80
60
40
20
ppm

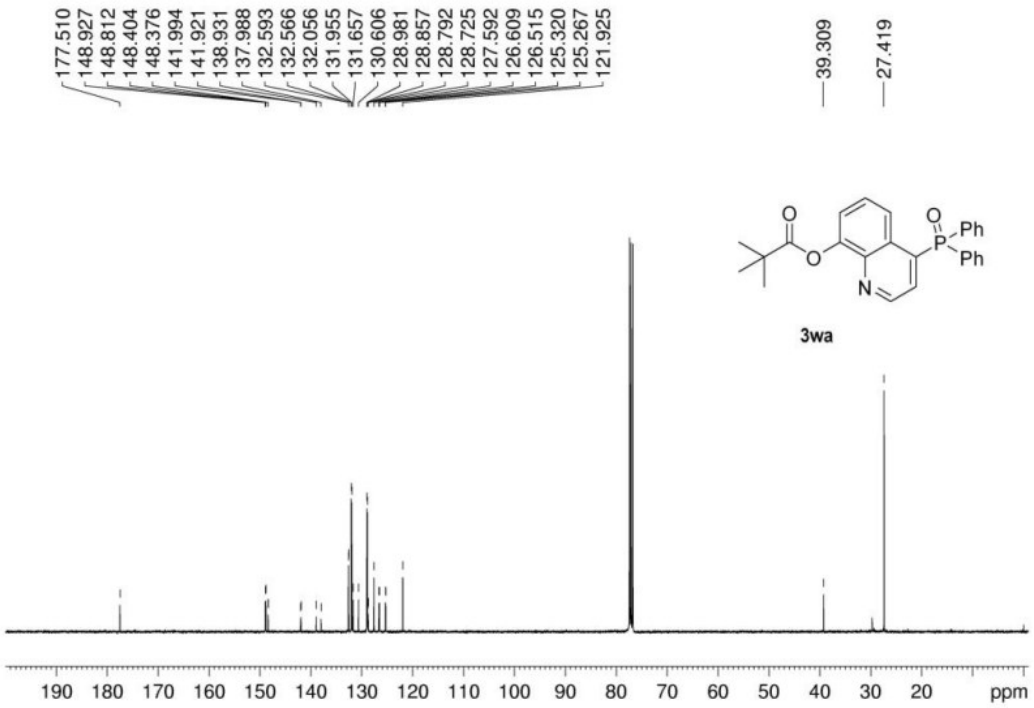

30.335
O
O
O
P
Ph
Ph
N
3ua
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm

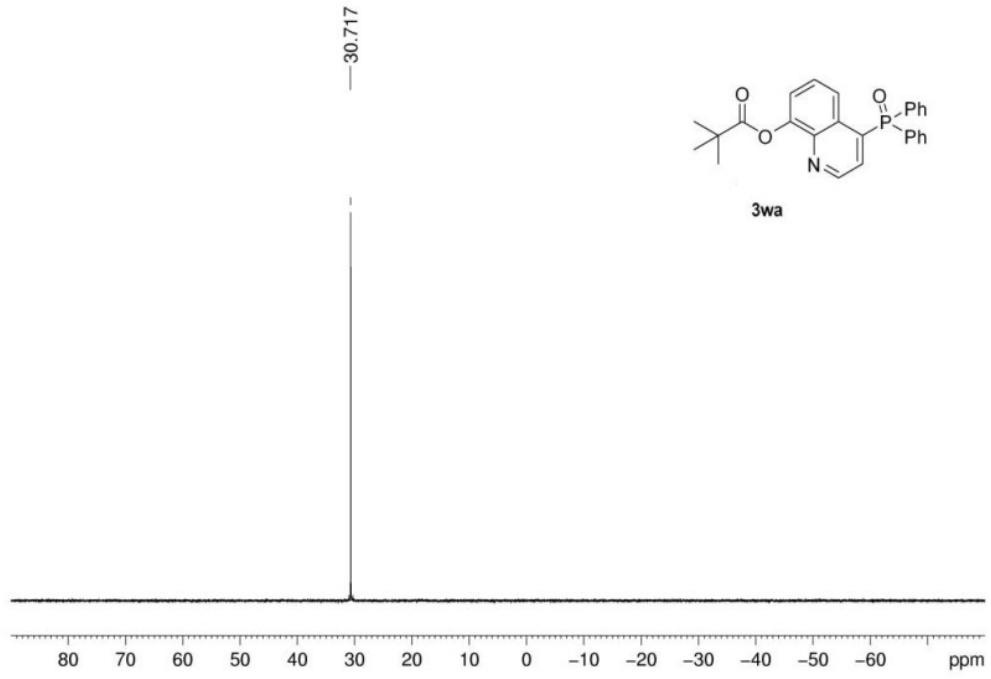

8.342
8.337
8.335
8.319
7.721
7.704
7.691
7.673
7.615
7.613
7.594
7.578
7.524
7.515
7.505
7.496
7.477
7.452
7.432
7.412
7.376
7.357
7.350
7.338
7.331
7.141
7.103
2.727
2.582
3va
8.35
8.30
ppm
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.004
4.158
2.056
6.249
1.100
2.075
1.000
3.056
3.026

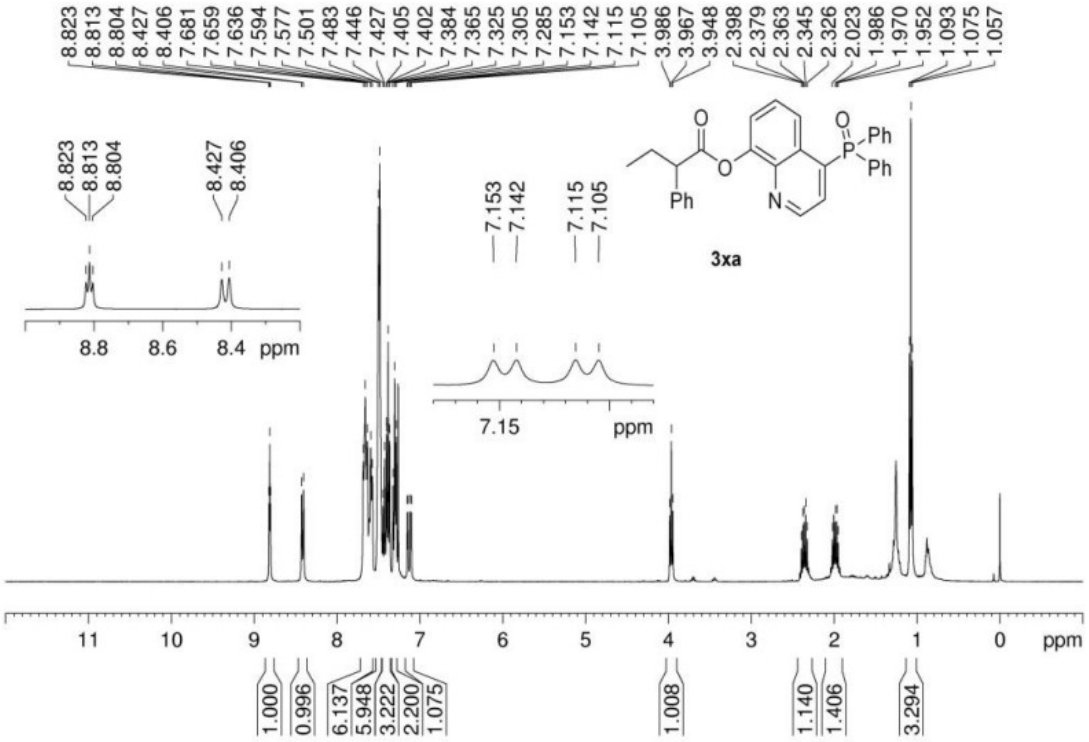

166.559
158.019
157.906
147.820
147.791
141.469
141.396
140.879
139.109
138.170
132.554
132.530
132.464
132.077
131.976
131.853
131.693
131.365
130.803
129.247
128.967
128.845
127.853
127.763
127.061
126.990
126.523
125.880
125.247
125.195
122.052
25.749
21.606
3va
200
180
160
140
120
100
80
60
40
20
ppm


30.260
3va
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm


8.860
8.850
8.840
8.446
8.425
7.690
7.673
7.669
7.659
7.642
7.639
7.622
7.619
7.604
7.599
7.585
7.581
7.521
7.514
7.502
7.495
7.481
7.460
7.421
7.418
7.402
7.399
7.157
7.146
7.119
7.109
1.492
3wa
8.8 8.6 8.4 ppm
7.15 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.017
4.339
2.228
5.498
1.052
1.060
9.088


177.510
148.927
148.812
148.404
148.376
141.994
141.921
138.931
137.988
132.593
132.566
132.056
131.955
131.657
130.606
128.981
128.857
128.792
128.725
127.592
126.609
126.515
125.320
125.267
121.925
39.309
27.419
O
O
Ph
P
Ph
O
N
3wa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


30.717
O
O
Ph
P
Ph
O
N
3wa
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 ppm


8.823
8.813
8.804
8.427
8.406
7.681
7.659
7.636
7.594
7.577
7.501
7.483
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7.427
7.405
7.402
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7.153
7.142
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7.105
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3.967
3.948
2.398
2.379
2.363
2.345
2.326
2.023
1.986
1.970
1.952
1.093
1.075
1.057
8.8
8.6
8.4 ppm
7.15 ppm
3xa
11 10 9 8 7 6 5 4 3 2 1 0 ppm
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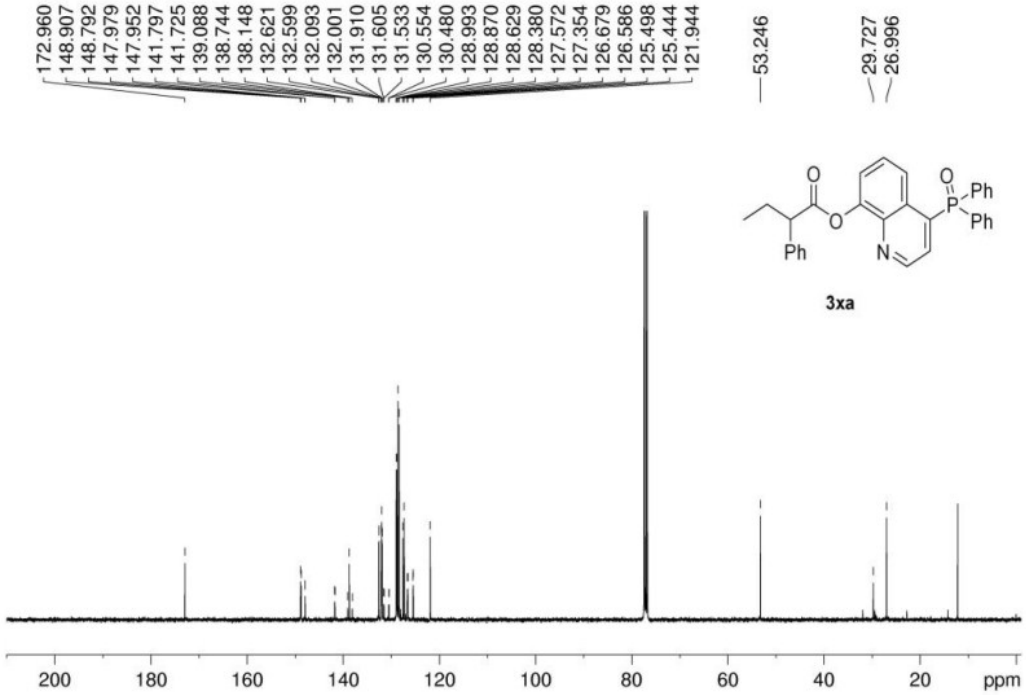
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132.001
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131.605
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130.554
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128.993
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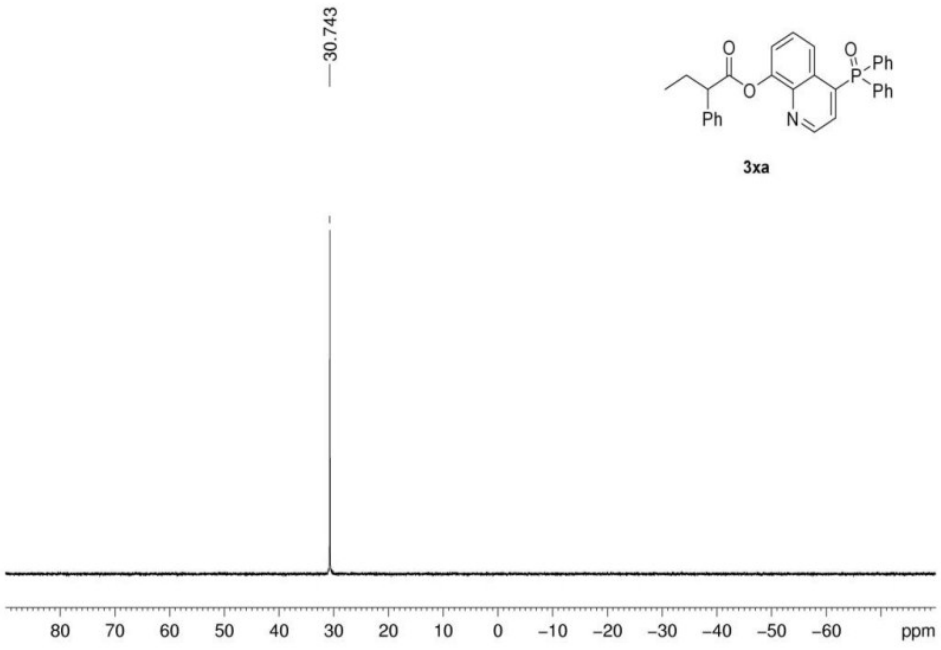
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O
O
O
P
Ph
Ph
Ph
N
3xa
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60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
ppm