Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Silver(I)-Promoted Romote C5–H Phosphonation of 8-Aminoquinoline Amides with H-phosphonates

Mengmeng Sun,[a] Suyan Sun,[a] Huijie Qiao,[a] Fan Yang,*[a] Yu Zhu,[a] Jianxun Kang,[a] Yusheng Wu,*[b,c] and Yangjie Wu*[a]

[a] The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, PR China

[b] TetranovBiopharm, LLC. 75 Daxue Road, Zhengzhou, 450052, PR China

[c] Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province, PR China

*E-mail: yangf@zzu.edu.cn; wyj@zzu.edu.cn; yusheng.wu@tetranovglobal.com

Contents

1. General Information

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ 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. Dichloromethane, ethyl acetate, and hexane were used for column chromatography. The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted.

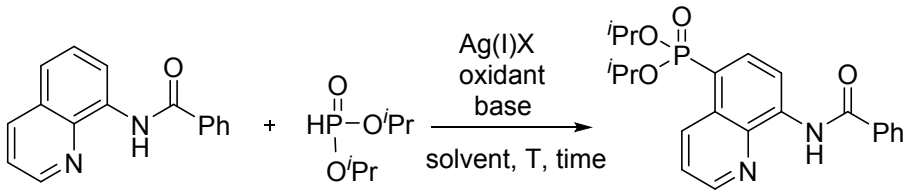
2. Preparation of Substrates

(a) Amides **3a-3o** were prepared from the corresponding acids and 8-aminoquinoline according to the reported procedure.[1]
(b) The substrate **3p** was prepared from benzyl alcohol and 8-aminoquinoline according to the reported procedure.[2]

3. Optimization of Reaction Conditions

A 25 mL schlenk tube was equipped with a magnetic stir bar and charged with N-(quinolin-8-yl)benzamide **1a** (24.8 mg, 0.1 mmol), diisopropyl H-phosphonate **2a** (33.2 mg, 0.2 mmol, 2 equiv), AgX (0.25 mmol, 2.5 equiv), oxidant (0.2 mmol, 2 equiv), base (0.2 mmol, 2 equiv), and solvent (1.0 mL). The resulting mixture was heated at 120 ^{o}C under a nitrogen atmosphere for 24 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 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/EtOAc as an eluent (10:1, V/V) to afford the pure product **3aa**.

Table S1 Screening of Reaction Conditions[a]



1a **2a** **3aa**

entry	AgX	oxidant	base	solvent	yield (%)[b]
1	Ag_2CO_3	$K_2S_2O_8$	K_2CO_3	toluene	41
2	$AgNO_3$	$K_2S_2O_8$	K_2CO_3	toluene	24
3	Ag_2O	$K_2S_2O_8$	K_2CO_3	toluene	18
4	Ag_2SO_4	$K_2S_2O_8$	K_2CO_3	toluene	<5

5	AgOAc	$K_2S_2O_8$	K_2CO_3	toluene	<5
6	AgI	$K_2S_2O_8$	K_2CO_3	toluene	nr
7	$AgSO_3CF_3$	$K_2S_2O_8$	K_2CO_3	toluene	nr
8	-	$K_2S_2O_8$	K_2CO_3	toluene	<5
9	Ag_2CO_3	NMO	K_2CO_3	toluene	<5
10	Ag_2CO_3	BQ	K_2CO_3	toluene	nr
11	Ag_2CO_3	$PhI(OAc)_2$	K_2CO_3	toluene	12
12	Ag_2CO_3	TBHP	K_2CO_3	toluene	nr
13	Ag_2CO_3	$Cu(OAc)_2$	K_2CO_3	toluene	nr
14	Ag_2CO_3	-	K_2CO_3	toluene	25
15	Ag_2CO_3	$K_2S_2O_8$	KOH	toluene	37
16	Ag_2CO_3	$K_2S_2O_8$	NaOH	toluene	46
17	Ag_2CO_3	$K_2S_2O_8$	^{t}BuOLi	toluene	36
18	Ag_2CO_3	$K_2S_2O_8$	-	toluene	<5
19	Ag_2CO_3	$K_2S_2O_8$	Na_2CO_3	toluene	22
20	Ag_2CO_3	$K_2S_2O_8$	^{t}BuOK	toluene	<5
21	Ag_2CO_3	$K_2S_2O_8$	pyridine	toluene	38
22	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	51
23	Ag_2CO_3	$K_2S_2O_8$	NaOH	^{t}AmOH	48
24	Ag_2CO_3	$K_2S_2O_8$	NaOH	PhCl	46
25	Ag_2CO_3	$K_2S_2O_8$	NaOH	DCE	<5
26	Ag_2CO_3	$K_2S_2O_8$	NaOH	CH_3COCH_3	<5
27	Ag_2CO_3	$K_2S_2O_8$	NaOH	THF	<5
28[d]	**Ag_2CO_3**	**$K_2S_2O_8$**	**NaOH**	**dioxane**	**68**
29[e]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	60
30[f]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	39
31[g]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	53
32[h]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	60
33[i]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	46
34[j]	Ag_2CO_3	$K_2S_2O_8$	NaOH	dioxane	53

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), AgX (0.2 mmol), oxidant (0.2 mmol), base (0.2 mmol), solvent (1 mL) at 120 °C under N_2 for 24 h. [b]Isolated yield. [c]Silver salt (0.25 mmol). [d]Silver salt (0.3 mmol). [e]Silver salt (0.25 mmol) in air. [f]Silver salt (0.25 mmol) at 130 °C. [g]Silver salt (0.25 mmol) at 110 °C. [h]Silver salt (0.25 mmol) for 12h. [i]Silver salt (0.25 mmol) for 48h. DCE (1,2-dichloroethane). THF (tetrahydrofuran). BQ (*p*-benzoquinone). TBHP (^{t}Butyl hydroperoxide). NMO (4-methylmorpholine N-oxide).

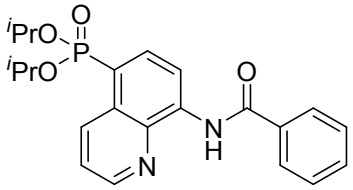
4. Typical Procedure for the Products

A 25 mL schlenk tube was equipped with a magnetic stir bar and charged with **1** (0.1 mmol), **2** (0.2 mmol, 2 equiv), Ag_2CO_3 (69 mg, 0.25 mmol, 2.5 equiv), $K_2S_2O_8$ (54 mg, 0.2 mmol, 2 equiv), NaOH (8 mg, 0.2 mmol, 2 equiv), and dioxane (1.0 mL). The

resulting mixture was heated at 120 °C under a nitrogen atmosphere for 24 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 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/EtOAc as an eluent to afford the pure products **3**.

5. Characterization Data of the Products

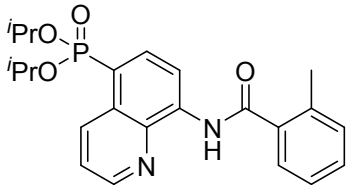
Diisopropyl(8-benzamidoquinolin-5-yl)phosphonate (3aa):



3aa

Light yellow solid (68%); mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.97−8.93 (m, 2H), 8.89−8.88 (m, 1H), 8.30 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 8.08−8.06 (m, 2H), 7.59−7.53 (m, 4H), 4.77−4.69 (m, 2H), 1.39 (d, J = 6.2 Hz, 6H), 1.16 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.4, 138.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 138.5 (d, $J_{C\text{-}P}$ = 3.7 Hz), 136.0 (d, $J_{C\text{-}P}$ = 14.3 Hz), 135.9, 134.7, 132.2, 128.9, 128.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 127.3, 122.5, 119.8 (d, $J_{C\text{-}P}$ = 189.2 Hz), 114.7 (d, $J_{C\text{-}P}$ = 16.6 Hz), 71.1 (d, $J_{C\text{-}P}$ = 5.5 Hz), 24.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.7 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.2; HRMS (ESI+): calcd for $C_{22}H_{25}N_2O_4P$ $[M+H]^+$: 413.1625, Found: 413.1629.

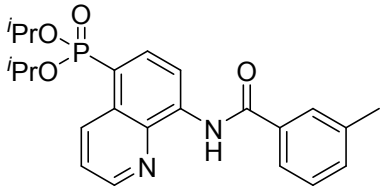
Diisopropyl[8-(2-methylbenzamido)quinolin-5-yl]phosphonate (3ba) :



3ba

Light yellow solid (56%); mp 101−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.98−8.93 (m, 2H), 8.81 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 8.31 (dd, $J_{H\text{-}P}$ = 15.9 Hz, J = 8.0 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.57 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 7.45−7.41 (m, 1H), 7.34 (t, J = 7.5 Hz, 2H), 4.79−4.71 (m, 2H), 2.61 (s, 3H), 1.41 (d, J = 6.1 Hz, 6H), 1.17 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 148.4, 138.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.4 (d, $J_{C\text{-}P}$ = 13.4 Hz), 136.9, 136.1, 136.0 (d, $J_{C\text{-}P}$ = 9.2 Hz), 135.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 131.5, 130.7, 128.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 127.3, 126.1, 122.5, 119.9 (d, $J_{C\text{-}P}$ = 189.3 Hz), 114.6 (d, $J_{C\text{-}P}$ = 16.7 Hz), 71.1 (d, $J_{C\text{-}P}$ = 5.4 Hz), 24.2 (d, $J_{C\text{-}P}$ = 3.7 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.8 Hz), 20.2; ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.2; HRMS (ESI+): calcd for $C_{23}H_{27}N_2O_4P$ $[M+H]^+$: 427.1781, Found: 427.1781.

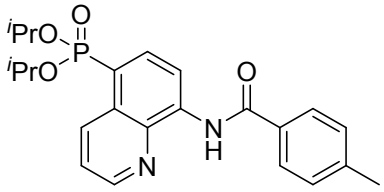
Diisopropyl[8-(3-methylbenzamido)quinolin-5-yl]phosphonate (3ca) :



3ca

Light yellow solid (52%); mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 8.98−8.94 (m, 2H), 8.91−8.90 (m, 1H), 8.32 (dd, J_{H-P} = 15.8 Hz, J = 8.0 Hz, 1H), 7.89−7.86 (m, 2H), 7.59 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 7.47−7.42 (m, 2H), 4.79−4.71 (m, 2H), 2.49 (s, 3H), 1.41 (d, J = 6.1 Hz, 6H), 1.17 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 148.4, 138.8, 138.7, 138.6 (d, J_{C-P} = 9.6 Hz), 136.0 (d, J_{C-P} = 9.0 Hz), 135.9 (d, J_{C-P} = 3.6 Hz), 134.7, 132.9, 128.7, 128.1, 128.0, 124.3, 122.5, 119.7 (d, J_{C-P} = 189.3 Hz), 114.4 (d, J_{C-P} = 16.6 Hz), 71.1 (d, J_{C-P} = 5.5 Hz), 24.1 (d, J_{C-P} = 4.0 Hz), 23.8 (d, J_{C-P} = 4.9 Hz), 21.5; ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.2; HRMS (ESI+): calcd for $C_{23}H_{27}N_2O_4P$ $[M+H]^+$: 427.1781, Found: 427.1782.

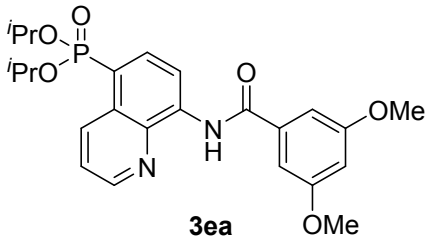
Diisopropyl[8-(4-methylbenzamido)quinolin-5-yl]phosphonate (3da):



3da

Light yellow solid (61%); mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.89−8.84 (m, 2H), 8.80 (d, J = 3.0 Hz, 1H), 8.22 (dd, J_{H-P} = 15.8 Hz, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.50 (dd, J = 8.5 Hz, J = 4.2 Hz, 1H), 7.26−7.24 (m, 2H), 4.68−4.62 (m, 2H), 2.35 (s, 3H), 1.31 (d, J = 6.0 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.4, 142.8, 138.7 (d, J_{C-P} = 3.6 Hz), 138.5 (d, J_{C-P} = 13.4 Hz), 136.0 (d, J_{C-P} = 9.1 Hz), 135.8 (d, J_{C-P} = 3.5 Hz), 131.8, 129.5, 128.0 (d, J_{C-P} = 11.2 Hz), 127.3, 122.5, 119.5 (d, J_{C-P} = 189.4 Hz), 114.6 (d, J_{C-P} = 16.6 Hz), 71.1 (d, J_{C-P} = 5.4 Hz), 24.1 (d, J_{C-P} = 3.8 Hz), 23.8 (d, J_{C-P} = 4.8 Hz), 21.5; ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.3; HRMS (ESI+): calcd for $C_{23}H_{27}N_2O_4P$ $[M+H]^+$: 427.1781, Found: 427.1785.

Diisopropyl[8-(3,5-dimethoxybenzamido)quinolin-5-yl]phosphonate (3ea):

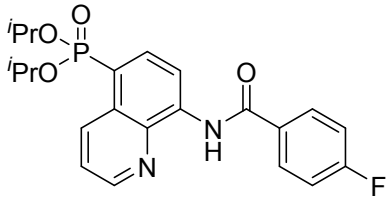


3ea

Light yellow solid (59%); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.91 (s, 1H),

8.95−8.88 (m, 3H), 8.31 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.59 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 7.21 (d, J = 2.1 Hz, 2H), 6.69 (s, 1H), 4.78−4.70 (m, 2H), 3.90 (s, 6H), 1.40 (d, J = 6.2 Hz, 6H), 1.17 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.1, 148.4, 138.6 (d, $J_{C\text{-}P}$ = 10.7 Hz), 138.5, 136.9, 136.0 (d, $J_{C\text{-}P}$ = 17.2 Hz), 135.9 (d, $J_{C\text{-}P}$ = 4.7 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 122.5, 119.8 (d, $J_{C\text{-}P}$ = 189.4 Hz), 114.7 (d, $J_{C\text{-}P}$ = 16.5 Hz), 105.4, 104.1, 71.2 (d, $J_{C\text{-}P}$ = 5.4 Hz), 55.7, 24.1 (d, $J_{C\text{-}P}$ = 3.9 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.2; HRMS (ESI+): calcd for $C_{24}H_{29}N_2O_6P$ $[M+H]^+$: 473.1836, Found: 473.1841.

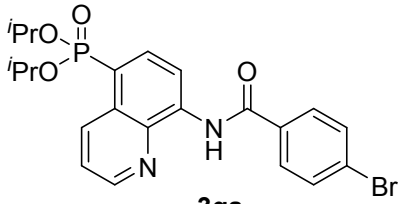
Diisopropyl(8-[4-fluorobenzamido)quinolin-5-yl]phosphonate (3fa):



3fa

Light yellow solid (58%); mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.97−8.90 (m, 3H), 8.32 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 8.12−8.09 (m, 2H), 7.60 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 7.26−7.22 (m, 2H), 4.80−4.72 (m, 2H), 1.41 (d, J = 6.2 Hz, 6H), 1.18 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, $J_{C\text{-}F}$ = 253.0 Hz), 164.5, 148.4, 138.5 (d, $J_{C\text{-}P}$ = 13.3 Hz), 138.4 (d, $J_{C\text{-}P}$ = 3.6 Hz), 136.0, 135.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 130.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 122.5, 119.9 (d, $J_{C\text{-}P}$ = 189.3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 114.7 (d, $J_{C\text{-}P}$ = 16.6 Hz), 71.2 (d, $J_{C\text{-}P}$ = 5.3 Hz), 24.1 (d, $J_{C\text{-}P}$ = 3.9 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.1; HRMS (ESI+): calcd for $C_{22}H_{24}FN_2O_4P$ $[M+H]^+$: 431.1531, Found: 431.1535.

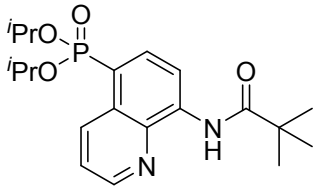
Diisopropyl[8-(4-bromobenzamido)quinolin-5-yl]phosphonate (3ga):



3ga

Saffron yellow solid (53%); mp 117−119 °C; 1H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.97−8.90 (m, 3H), 8.31 (dd, $J_{H\text{-}P}$ = 15.9 Hz, J = 8.0 Hz, 1H), 7.96−7.94 (m, 2H), 7.71−7.69 (m, 2H), 7.61 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 4.80−4.72 (m, 2H), 1.41 (d, J = 6.2 Hz, 6H), 1.18 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.5, 138.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 138.3 (d, $J_{C\text{-}P}$ = 3.7 Hz), 136.0, 135.9 (d, $J_{C\text{-}P}$ = 13.4 Hz), 133.5, 132.2, 129.0, 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 127.0, 122.6, 120.1 (d, $J_{C\text{-}P}$ = 189.4 Hz), 114.8 (d, $J_{C\text{-}P}$ = 16.7 Hz), 71.2 (d, $J_{C\text{-}P}$ = 5.5 Hz), 24.2 (d, $J_{C\text{-}P}$ = 4.0 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.7 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.1; HRMS (ESI+): calcd for $C_{22}H_{24}BrN_2O_4P$ $[M+H]^+$: 491.0730, Found: 491.0733.

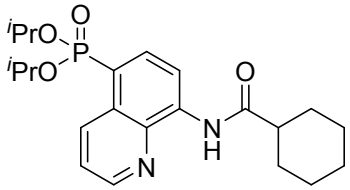
Diisopropyl(8-pivalamidoquinolin-5-yl)phosphonate (3ia):



3ia

Light yellow oil (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.91 (dd, J = 8.6 Hz, J = 1.5 Hz, 1H), 8.88 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 8.83 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 8.28 (dd, $J_{H\text{-}P}$ = 15.9 Hz, J = 8.0 Hz, 1H), 7.59 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 4.79−4.67 (m, 2H), 1.44 (s, 9H), 1.40 (d, J = 6.2 Hz, 6H), 1.15 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 148.3, 138.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.5 (d, $J_{C\text{-}P}$ = 13.3 Hz), 136.1 (d, $J_{C\text{-}P}$ = 9.2 Hz), 135.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 127.9 (d, $J_{C\text{-}P}$ = 11.3 Hz), 122.4, 119.1 (d, $J_{C\text{-}P}$ = 189.3 Hz), 114.3 (d, $J_{C\text{-}P}$ = 16.5 Hz), 71.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 40.5, 27.6, 24.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.4; HRMS (ESI+): calcd for $C_{20}H_{29}N_2O_4P$ $[M+H]^+$: 393.1938, Found: 393.1942.

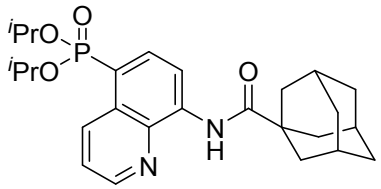
Diisopropyl[8-(cyclohexanecarboxamido)quinolin-5-yl]phosphonate (3ja):



3ja

Light yellow solid (55%); mp 99−101 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.92 (d, J = 8.5 Hz, 1H), 8.86 (d, J = 3.0 Hz, 1H), 8.83 (dd, J = 8.0 Hz, J = 3.6 Hz, 1H), 8.26 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 4.77−4.69 (m, 2H), 2.54−2.47 (m, 1H), 2.09 (d, J = 11.9 Hz, 2H), 1.90−1.86 (m, 2H), 1.74 (d, J = 11.6 Hz, 1H), 1.68−1.59 (m, 2H), 1.40 (d, J = 6.1 Hz, 8H), 1.35 (s, 1H), 1.15 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 148.2, 138.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.2 (d, $J_{C\text{-}P}$ = 13.3 Hz), 136.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 135.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 122.4, 119.2 (d, $J_{C\text{-}P}$ = 189.4 Hz), 114.5 (d, $J_{C\text{-}P}$ = 16.6 Hz), 71.0 (d, $J_{C\text{-}P}$ = 5.3 Hz), 46.8, 29.6, 25.7, 25.6, 24.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.4; HRMS (ESI+): cacld for $C_{22}H_{31}N_2O_4P$ $[M+H]^+$: 419.2094, found: 419.2097.

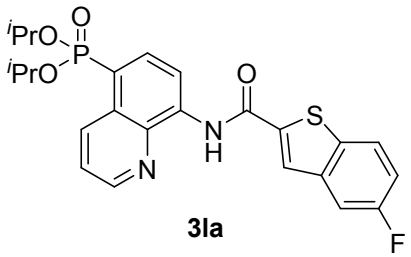
Diisopropyl{8-[(3*r*,5*r*,7*r*)-adamantane-1-carboxamido]quinolin-5-yl}phosphonate (3ka):



3ka

Light yellow solid (64%); mp 39−41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.93−8.88 (m, 2H), 8.85 (dd, J = 8.0 Hz, J = 3.6 Hz, 1H), 8.27 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.57 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 4.76−4.68 (m, 2H), 2.15 (s, 3H), 2.11 (s, 5H), 1.81 (s, 6H), 1.40 (d, J = 6.2 Hz, 6H), 1.15 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 148.3, 138.7, 138.6 (d, $J_{C\text{-}P}$ = 9.3 Hz), 136.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 135.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 122.3, 119.1 (d, $J_{C\text{-}P}$ = 189.3 Hz), 114.4 (d, $J_{C\text{-}P}$ = 16.7 Hz), 71.0 (d, $J_{C\text{-}P}$ = 5.3 Hz), 42.3, 39.2, 36.4, 28.1, 24.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.4; HRMS (ESI+): cacld for $C_{26}H_{35}N_2O_4P$ $[M+H]^+$: 471.2407, Found: 471.2413.

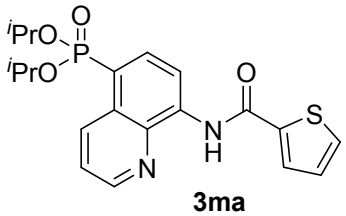
Diisopropyl{8-(5-fluorobenzo[*b*]thiophene-2-carboxamido)quinolin-5-yl}phosphonate (3la):



3la

Light yellow solid (31%); mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.98−8.94 (m, 2H), 8.89 (dd, J = 7.9 Hz, J = 3.4 Hz, 1H), 8.31 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.85 (dd, J = 8.8 Hz, J = 4.6 Hz, 1H), 7.64−7.59 (m, 2H), 7.26−7.21 (m, 1H), 4.81−4.72 (m, 2H), 1.42 (d, J = 6.1 Hz, 6H), 1.18 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, $J_{C\text{-}F}$ = 243.3 Hz), 160.2, 148.6, 141.6, 140.0 (d, $J_{C\text{-}F}$ = 9.6 Hz), 138.3 (d, $J_{C\text{-}P}$ = 13.3 Hz), 137.9 (d, $J_{C\text{-}F}$ = 3.6 Hz), 137.0, 136.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 135.9 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.6 Hz), 125.2 (d, $J_{C\text{-}F}$ = 4.5 Hz), 124.1 (d, $J_{C\text{-}F}$ = 9.3 Hz), 122.7, 120.2 (d, $J_{C\text{-}P}$ = 189.3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 25.5 Hz), 114.9 (d, $J_{C\text{-}P}$ = 16.5 Hz), 110.5 (d, $J_{C\text{-}F}$ = 23.0 Hz), 71.2 (d, $J_{C\text{-}P}$ = 5.4 Hz), 24.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.8 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.0; HRMS (ESI+): cacld for $C_{24}H_{24}FN_2O_4PS$ $[M+H]^+$: 487.1251, Found: 487.1254.

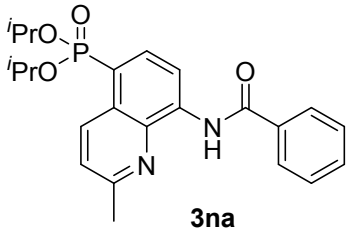
Diisopropyl[8-(thiophene-2-carboxamido)quinolin-5-yl]phosphonate (3ma):



3ma

Light yellow solid (33%); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 8.87−8.77 (m, 3H), 8.21 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.77 (d, J = 3.3 Hz, 1H), 7.53−7.50 (m, 2H), 7.12−7.09 (m, 1H), 4.70−4.62 (m, 2H), 1.32 (d, J = 6.2 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.4, 138.5, 137.3 (d, $J_{C\text{-}P}$ = 3.6 Hz), 137.2 (d, $J_{C\text{-}P}$ = 13.3 Hz), 135.0, 134.9, 130.5, 127.9, 127.1, 127.0, 121.5, 118.6 (d, $J_{C\text{-}P}$ = 189.9 Hz), 113.6 (d, $J_{C\text{-}P}$ = 16.7 Hz), 70.2 (d, $J_{C\text{-}P}$ = 5.5 Hz), 23.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 22.8 (d, $J_{C\text{-}P}$ = 4.7 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.2; HRMS (ESI+): cacld for $C_{20}H_{23}N_2O_4PS$ $[M+H]^+$: 419.1189, Found: 419.1192.

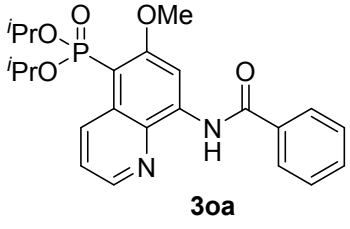
Diisopropyl(8-benzamido-2-methylquinolin-5-yl)phosphonate (3na):



3na

Saffron yellow solid (56%); mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.84 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 8.73 (d, J = 8.7 Hz, 1H), 8.15 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 8.00−7.98 (m, 2H), 7.52−7.46 (m, 3H), 7.37 (d, J = 8.7 Hz, 1H), 4.69−4.60 (m, 2H), 2.71 (s, 3H), 1.31 (d, J = 6.2 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 156.5, 137.0, 136.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 134.9 (d, $J_{C\text{-}P}$ = 3.5 Hz), 133.9 (d, $J_{C\text{-}P}$ = 9.1 Hz), 133.8, 131.1, 127.9, 126.3, 125.1 (d, $J_{C\text{-}P}$ = 11.2 Hz), 122.3, 118.4 (d, $J_{C\text{-}P}$ = 188.7 Hz), 113.6 (d, $J_{C\text{-}P}$ = 16.7 Hz), 70.0 (d, $J_{C\text{-}P}$ = 5.3 Hz), 24.2, 23.1 (d, $J_{C\text{-}P}$ = 3.9 Hz), 22.7 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 15.5; HRMS (ESI+): calcd for $C_{23}H_{27}N_2O_4P$ $[M+H]^+$: 427.1781, Found: 427.1785.

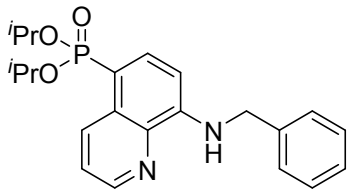
Diisopropyl(8-benzamido-6-methoxyquinolin-5-yl)phosphonate (3oa):



3oa

Light yellow solid (61%); mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 9.90 (d, J = 8.5 Hz, 1H), 8.92 (d, J = 5.9 Hz, 1H), 8.70 (d, J = 2.8 Hz, 1H), 8.10−8.08 (m, 2H), 7.62−7.55 (m, 3H), 7.52 (dd, J = 8.8 Hz, J = 4.1 Hz, 1H), 4.74−4.66 (m, 2H), 4.11 (s, 3H), 1.40 (d, J = 6.2 Hz, 6H), 1.19 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.1, 145.8, 140.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 135.8, 134.5, 134.1 (d, $J_{C\text{-}P}$ = 14.0 Hz), 132.3, 131.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.9, 127.3, 123.2, 103.3 (d, $J_{C\text{-}P}$ = 10.2 Hz), 102.9 (d, $J_{C\text{-}P}$ = 185.8 Hz), 70.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 56.5, 24.1 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.7 (d, $J_{C\text{-}P}$ = 4.8 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 14.2; HRMS (ESI+): calcd for $C_{23}H_{27}N_2O_5P$ $[M+H]^+$: 443.1731, Found: 443.1730.

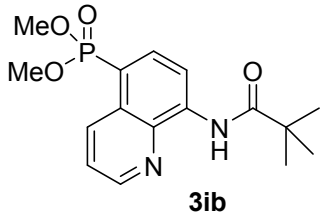
Diisopropyl[8-(benzylamino)quinolin-5-yl]phosphonate (3ra):



3ra

Light yellow solid (41%); mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76−8.71 (m, 2H), 8.08 (dd, $J_{H\text{-}P}$ = 15.6 Hz, J = 8.0 Hz, 1H), 7.46 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 7.43−7.41 (m, 2H), 7.38−7.34 (m, 2H), 7.31−7.28 (m, 1H), 7.12 (s, 1H), 6.63 (dd, J = 8.0 Hz, J = 3.6 Hz, 1H), 4.69−4.61 (m, 2H), 4.58 (d, J = 5.7 Hz, 2H), 1.38 (d, J = 6.2 Hz, 6H), 1.12 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 146.9, 138.2, 138.0 (d, $J_{C\text{-}P}$ = 13.6 Hz), 137.2 (d, $J_{C\text{-}P}$ = 10.0 Hz), 135.4 (d, $J_{C\text{-}P}$ = 3.6 Hz), 128.8, 128.7, 128.6, 127.4, 122.3, 109.6 (d, $J_{C\text{-}P}$ = 195.2 Hz), 103.0 (d, $J_{C\text{-}P}$ = 17.6 Hz), 70.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 47.2, 24.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.8 (d, $J_{C\text{-}P}$ = 5.0 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 18.2; HRMS (ESI+): cacld for $C_{22}H_{27}N_2O_3P$ $[M+H]^+$: 399.1832, Found: 399.1832.

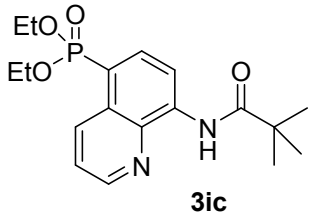
Dimethyl(8-pivalamidoquinolin-5-yl)phosphonate (3ib):



3ib

Saffron yellow solid (30%); mp 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.88−8.82 (m, 3H), 8.21 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.5 Hz, J = 4.3 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 148.5, 139.2 (d, $J_{C\text{-}P}$ = 3.7 Hz), 138.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 136.6 (d, $J_{C\text{-}P}$ = 8.9 Hz), 135.4 (d, $J_{C\text{-}P}$ = 3.7 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.7 Hz), 122.8, 116.1 (d, $J_{C\text{-}P}$ = 190.1 Hz), 114.3 (d, $J_{C\text{-}P}$ = 16.7 Hz), 52.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 40.6, 27.6; ^{31}P NMR (163 MHz, $CDCl_3$) δ 20.9; HRMS (ESI+): cacld for $C_{16}H_{21}N_2O_4P$ $[M+H]^+$: 337.1312, Found: 337.1315.

Diethyl(8-pivalamidoquinolin-5-yl)phosphonate (3ic):

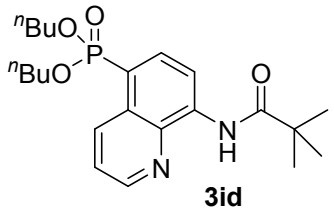


3ic

Light yellow oil (36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51(s, 1H), 8.91 (dd, J = 8.6 Hz, J = 1.5 Hz, 1H), 8.87 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 8.82 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 8.23 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.6 Hz, J = 4.2 Hz, 1H), 4.22−4.16 (m, 2H), 4.12−4.05 (m, 2H), 1.44 (s, 9H), 1.30 (t, J = 7.1 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 148.4, 138.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 136.3 (d, $J_{C\text{-}P}$ = 8.9 Hz), 135.6 (d, $J_{C\text{-}P}$ = 3.7 Hz), 128.0 (d, $J_{C\text{-}P}$ =11.4 Hz), 122.6, 117.6 (d, $J_{C\text{-}P}$ = 189.0 Hz), 114.3 (d, $J_{C\text{-}P}$ = 16.6 Hz), 62.3 (d, $J_{C\text{-}P}$ = 5.2 Hz), 40.5, 27.6, 16.3 (d, $J_{C\text{-}P}$ = 6.5 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 17.8; HRMS (ESI+): cacld for $C_{18}H_{25}N_2O_4P$ $[M+H]^+$: 365.1625, Found: 365.1628.

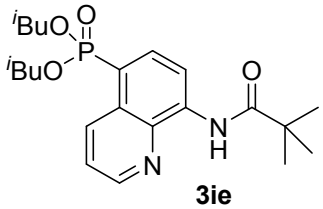
Dibutyl(8-pivalamidoquinolin-5-yl)phosphonate (3id):



3id

Saffron yellow oil (57%); ^{1}H MNR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.90 (dd, J = 8.6 Hz, J = 1.4 Hz, 1H), 8.87 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 8.83 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 8.22 (dd, $J_{H\text{-}P}$ = 15.7 Hz, J = 8.0 Hz, 1H), 7.57 (dd, J = 8.5 Hz, J = 4.2 Hz, 1H), 4.16−4.08 (m, 2H), 4.04−3.96 (m, 2H), 1.67−1.59 (m, 4H), 1.44 (s, 9H), 1.38−1.32 (m, 4H), 0.87 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 148.4, 138.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 136,2 (d, $J_{C\text{-}P}$ = 8.9 Hz), 135.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 122.5, 117.5 (d, $J_{C\text{-}P}$ = 189.2 Hz), 114.3 (d, $J_{C\text{-}P}$ = 16.5 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 40.5, 32.4 (d, $J_{C\text{-}P}$ = 6.6 Hz), 27.6, 18.7, 13.5; ^{31}P NMR (163 MHz, $CDCl_3$) δ 17.9; HRMS (ESI+): cacld for $C_{22}H_{33}N_2O_4P$ $[M+H]^+$: 421.2251, Found: 421.2253.

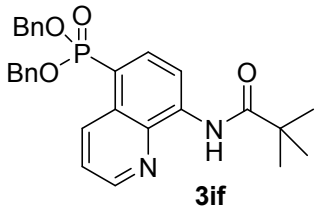
Diisobutyl(8-pivalamidoquinolin-5-yl)phosphonate (3ie):



3ie

Light yellow oil (41%); ^{1}H MNR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.91 (dd, J = 8.6 Hz, J = 1.5 Hz, 1H), 8.87 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 8.84 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 8.23 (dd, $J_{H\text{-}P}$ = 15.8 Hz, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.6 Hz, J = 4.3 Hz, 1H), 3.93−3.87 (m, 2H), 3.79-3.73 (m, 2H), 1.98−1.88 (m, 2H), 1.44 (s, 9H), 0.90 (dd, J = 6.7 Hz, J = 1.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 148.4, 138.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 138.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 136.3 (d, $J_{C\text{-}P}$ = 8.8 Hz), 135.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 122.5, 117.5 (d, $J_{C\text{-}P}$ = 189.9 Hz), 114.3 (d, $J_{C\text{-}P}$ = 16.6 Hz), 72.1 (d, $J_{C\text{-}P}$ = 5.8 Hz), 40.5, 29.1 (d, $J_{C\text{-}P}$ = 7.1 Hz), 27.6, 18.8; ^{31}P NMR (163 MHz, $CDCl_3$) δ 17.9; HRMS (ESI+): cacld for $C_{22}H_{33}N_2O_4P$ $[M+H]^+$: 421.2251, Found: 421.2254.

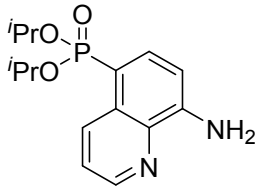
Dibenzyl(8-pivalamidoquinolin-5-yl)phosphonate (3if):



3if

Light yellow oil (47%); ^{1}H MNR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.86−8.78 (m, 3H), 8.23 (dd, $J_{H\text{-}P}$ = 16.0 Hz, J = 8.1 Hz, 1H), 7.47 (dd, J = 8.6 Hz, J = 4.3 Hz, 1H), 7.27 (s, 10H), 5.17−5.12 (m, 2H), 5.06−5.02 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 148.4, 139.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 138.5 (d, $J_{C\text{-}P}$ = 13.8 Hz), 136.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 135.9 (d, $J_{C\text{-}P}$ = 6.8 Hz), 135.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 128.5, 128.4, 128.1, 128.0 (d, $J_{C\text{-}P}$ = 11.7 Hz), 122.6, 117.0 (d, $J_{C\text{-}P}$ = 190.8 Hz), 114.2 (d, $J_{C\text{-}P}$ = 16.8 Hz), 67.8 (d, $J_{C\text{-}P}$ = 5.2 Hz), 40.6, 27.7; ^{31}P NMR (163 MHz, $CDCl_3$) δ 18.7; HRMS (ESI+): cacld for $C_{28}H_{29}N_2O_4P$ $[M+H]^+$: 489.1938, Found: 489.1941.

Diisopropyl(5-aminoquinolin-8-yl)phosphonate (7a):



7a

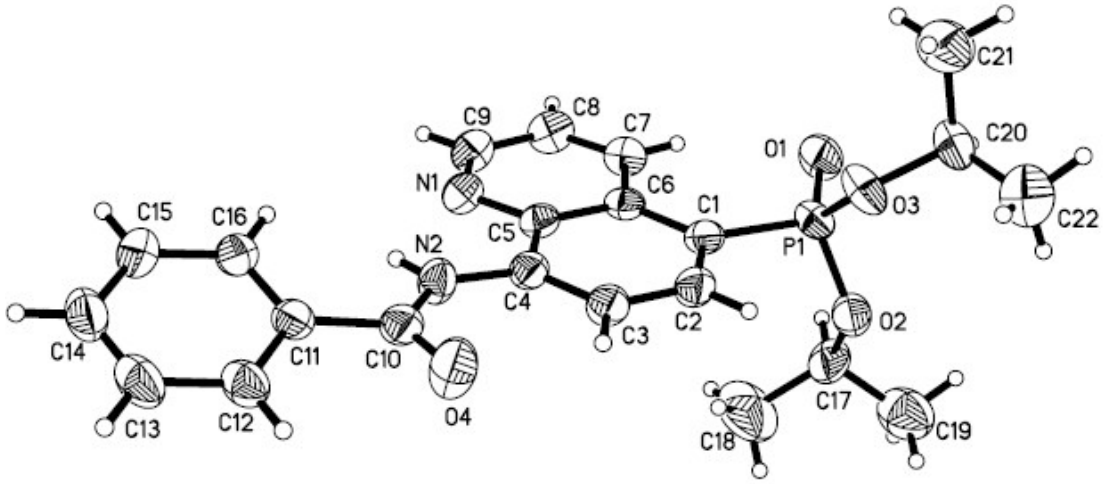
Light yellow solid (68%); mp 97-99 ^{o}C; ^{1}H MNR (400 MHz, $CDCl_3$) δ 8.77-8.75 (m, 2H), 8.07 (dd, $J_{C\text{-}P}$ = 15.4 Hz, J = 7.8 Hz, 1H), 7.46 (dd, J = 8.3 Hz, J = 4.4 Hz, 1H), 6.88 (dd, J = 7.8 Hz, J = 3.6 Hz, 1H), 5.57 (s, 2H), 4.71-4.63 (m, 2H), 1.39 (d, J = 6.2 Hz, 6H), 1.12 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 147.3, 138.0 (d, $J_{C\text{-}P}$ = 13.6 Hz), 136.7 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.3 (d, $J_{C\text{-}P}$ = 3.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.6 Hz), 122.3, 111.6 (d, $J_{C\text{-}P}$ = 193.8 Hz), 107.5 (d, $J_{C\text{-}P}$ = 17.7 Hz), 70.5 (d, $J_{C\text{-}P}$ = 5.1 Hz), 24.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.9 Hz); ^{31}P NMR (163 MHz, $CDCl_3$) δ 17.7; HRMS (ESI+): cacld for $C_{15}H_{21}N_2O_3P$ $[M+H]^+$: 309.1363, Found: 309.1368.

6. References

1. (a) L. D. Tran, J. Roane and O. Daugulis, *Angew. Chem., Int. Ed.,* 2013, **52**, 6043−6046. (b) T. Truong, K. Klimovica and O. Daugulis, *J. Am. Chem. Soc.*, 2013, **135**, 9342−9345.

2. C. Wang, C. P. Chen, J. Han, J. Y. Zhang, Y. M. Yao and Y. S. Zhao, *Eur. J. Org. Chem*., 2015, 2972−2977.

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



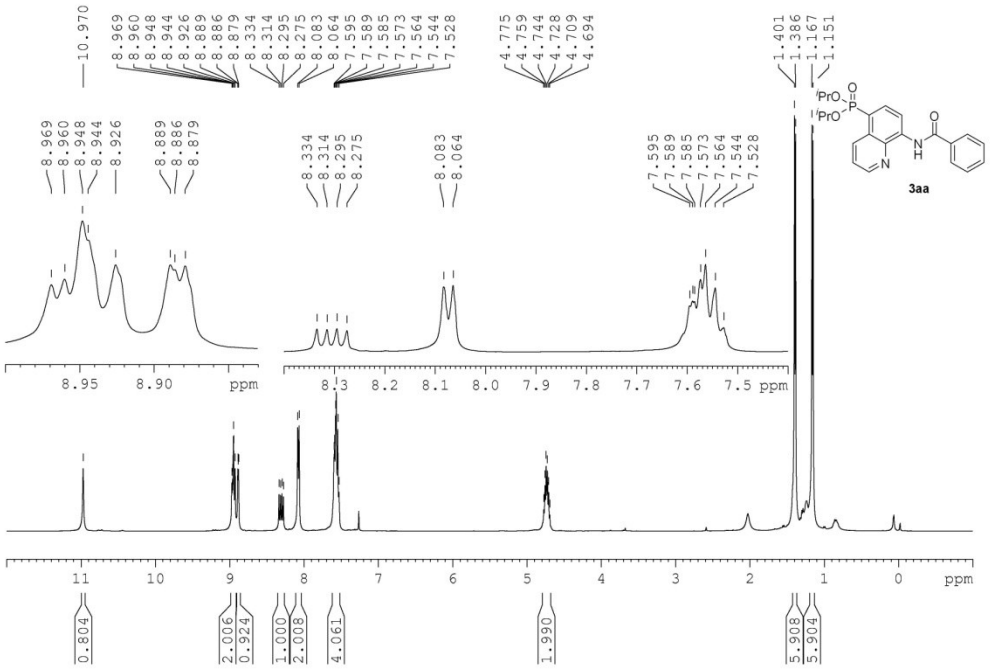
CCDC 1474469 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

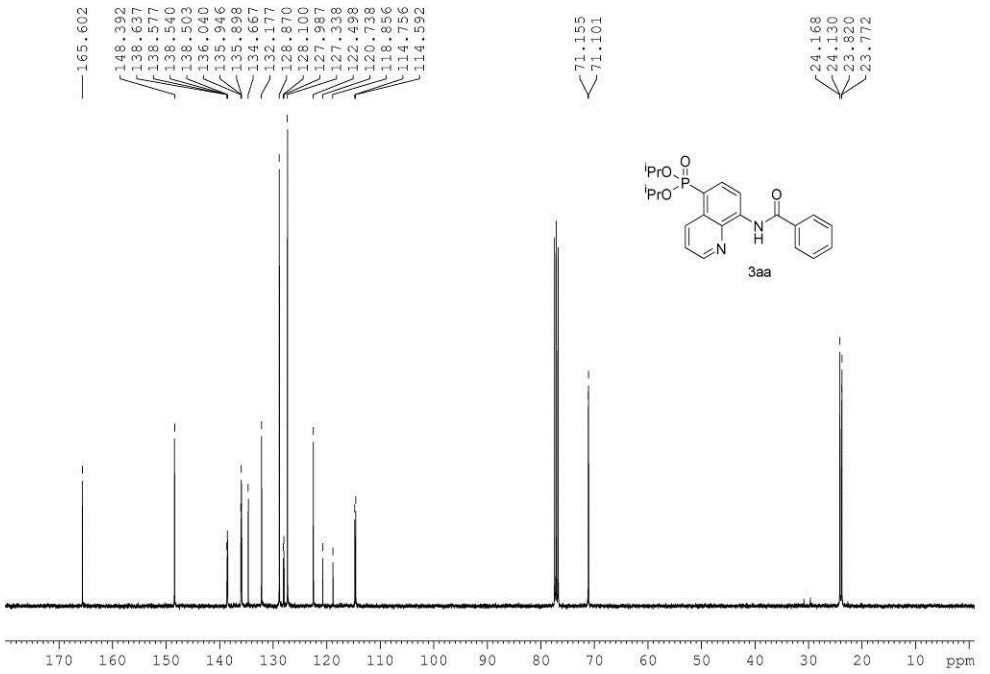
Table S3 Crystal Data and Structure Refinement for **3aa**

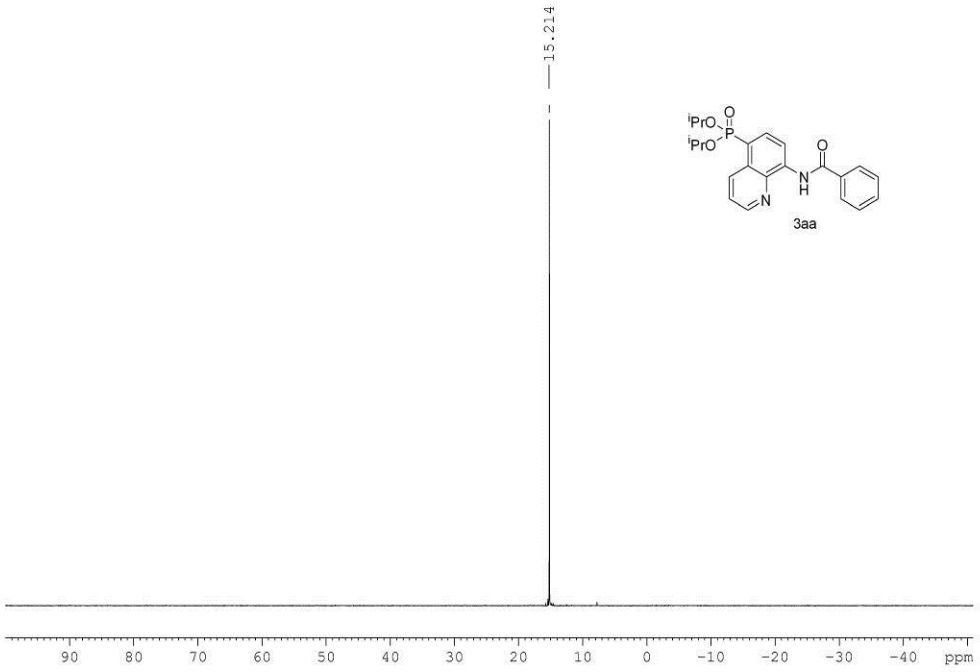
Empirical formula	$C_{22}H_{25}N_2O_4P$
Formula weight	412.41
Temperature/K	291.15
Crystal system	triclinic
Space group	P-1
a/Å	8.9115(7)
b/Å	11.1099(7)
c/Å	11.8272(9)
α/°	83.858(6)
β/°	86.228(6)
γ/°	67.922(6)
Volume/Å^3	1078.45(14)
Z	2
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.157
F(000)	436.0
Crystal size/mm^3	0.21 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.932 to 52.744
Index ranges	$-11 \le h \le 10$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	8712
Independent reflections	4383 [R_{int} = 0.0373, R_{sigma} = 0.0592]
Data/restraints/parameters	4383/33/293
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0776, wR_2 = 0.2075

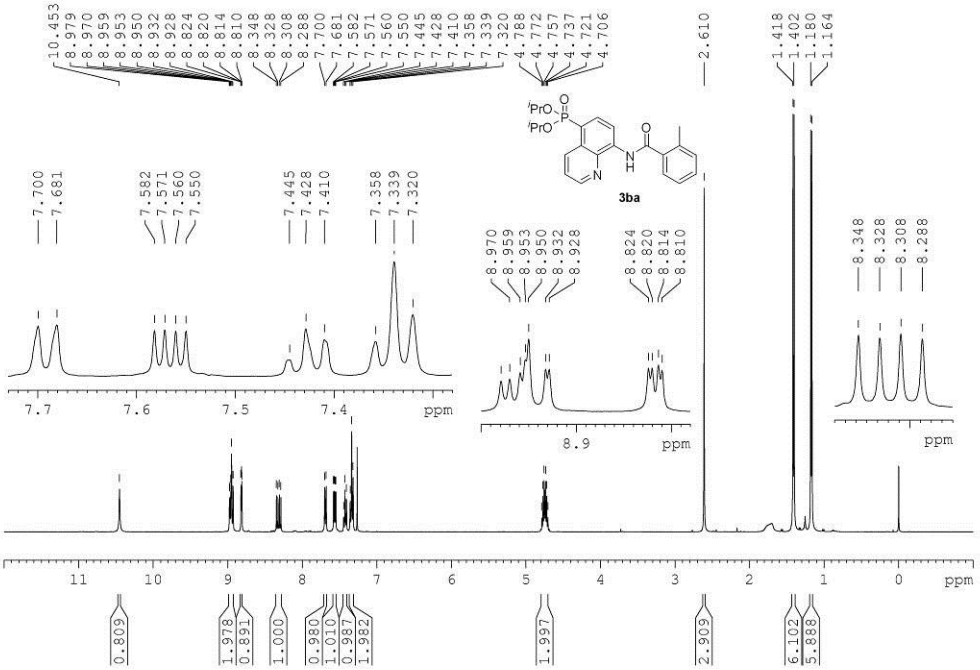
Final R indexes [all data]	$R_1 = 0.1204$, $wR_2 = 0.2482$
Largest diff. peak/hole / e Å^{-3}	0.62/-0.43

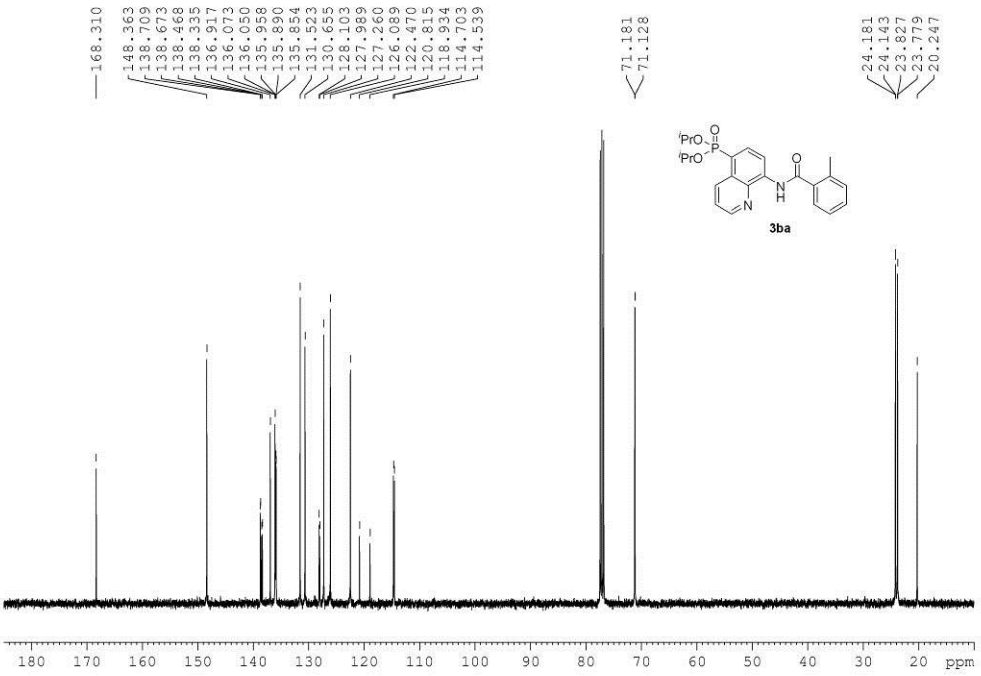
8. Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra for the Products

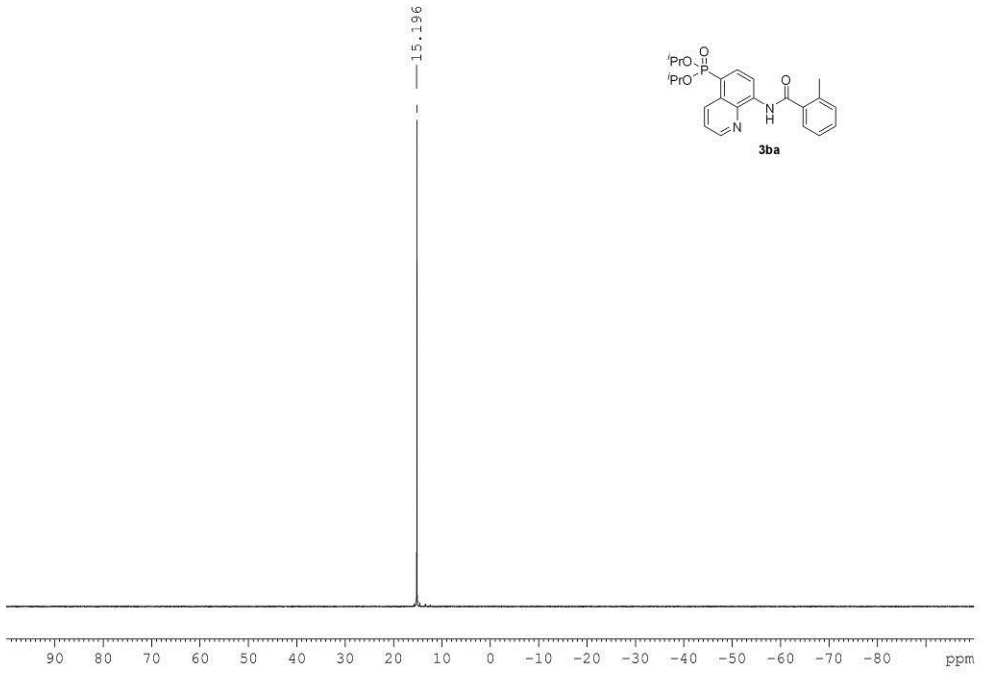





15.214
3aa
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


10.453
8.979
8.970
8.959
8.953
8.950
8.932
8.928
8.824
8.820
8.814
8.810
8.348
8.328
8.308
8.288
7.700
7.681
7.582
7.571
7.560
7.550
7.445
7.428
7.410
7.358
7.339
7.320
4.788
4.772
4.757
4.737
4.721
4.706
2.610
1.418
1.402
1.180
1.164
3ba
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.809
1.978
0.891
1.000
0.980
1.010
0.987
1.982
1.997
2.909
6.102
5.888


168.310
148.363
138.709
138.673
138.468
138.335
136.917
136.073
136.050
135.958
135.830
135.854
131.523
130.655
128.103
127.989
127.260
126.089
122.470
120.815
118.934
114.703
114.539
71.181
71.128
24.181
24.143
23.827
23.779
20.247
3ba
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


15.196
3ba
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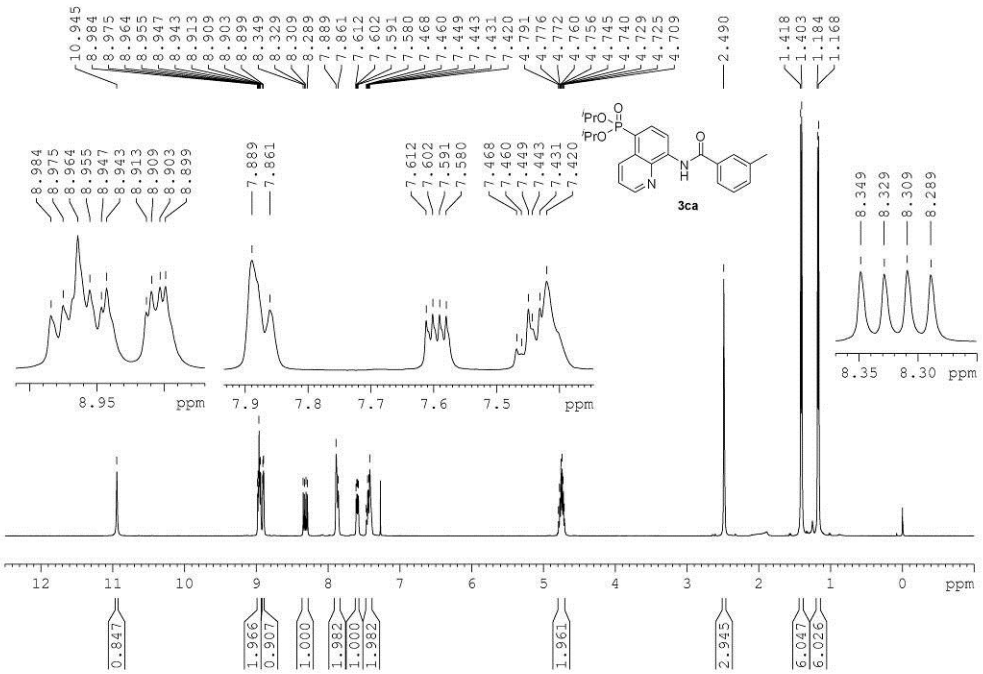
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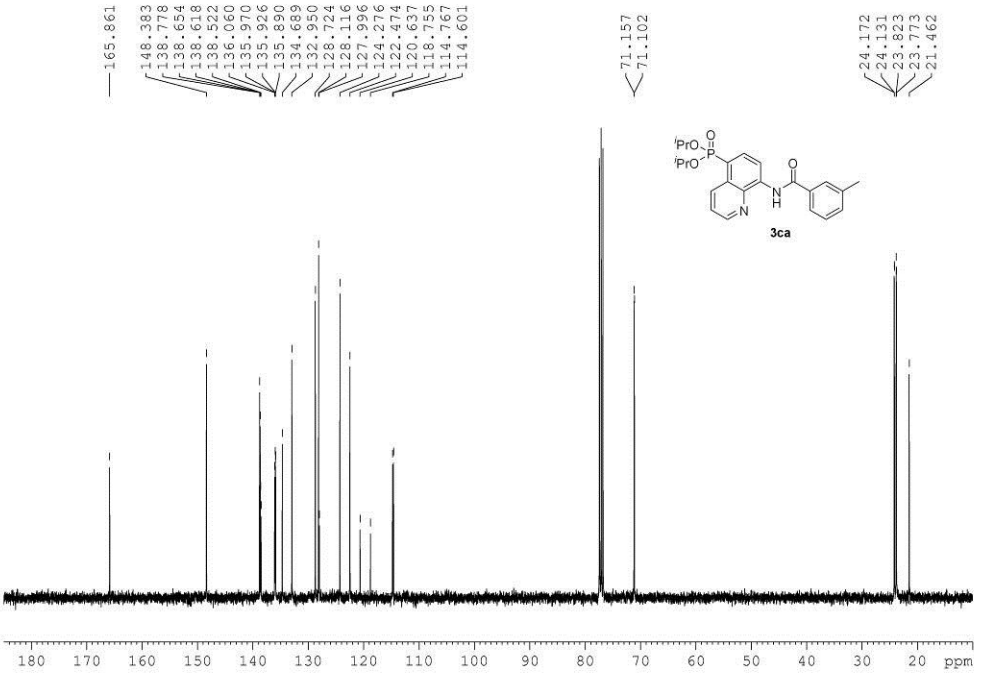
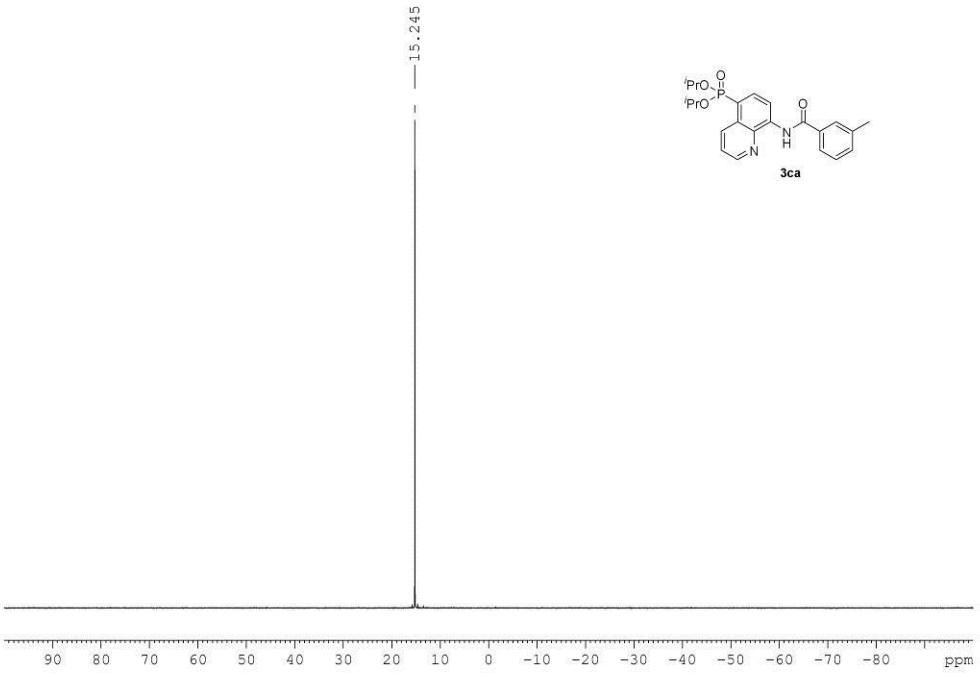
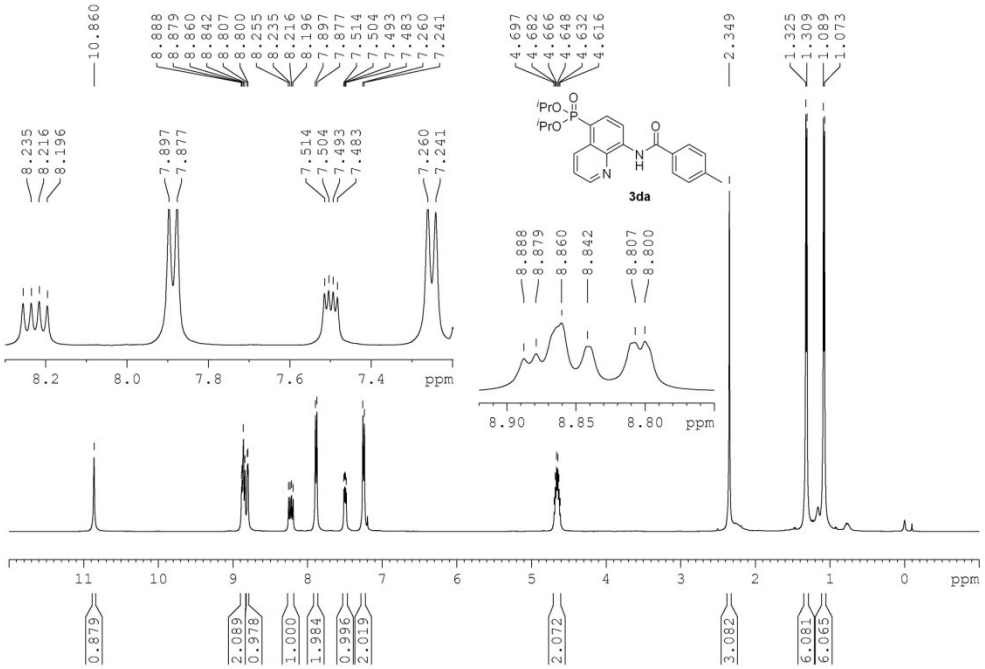
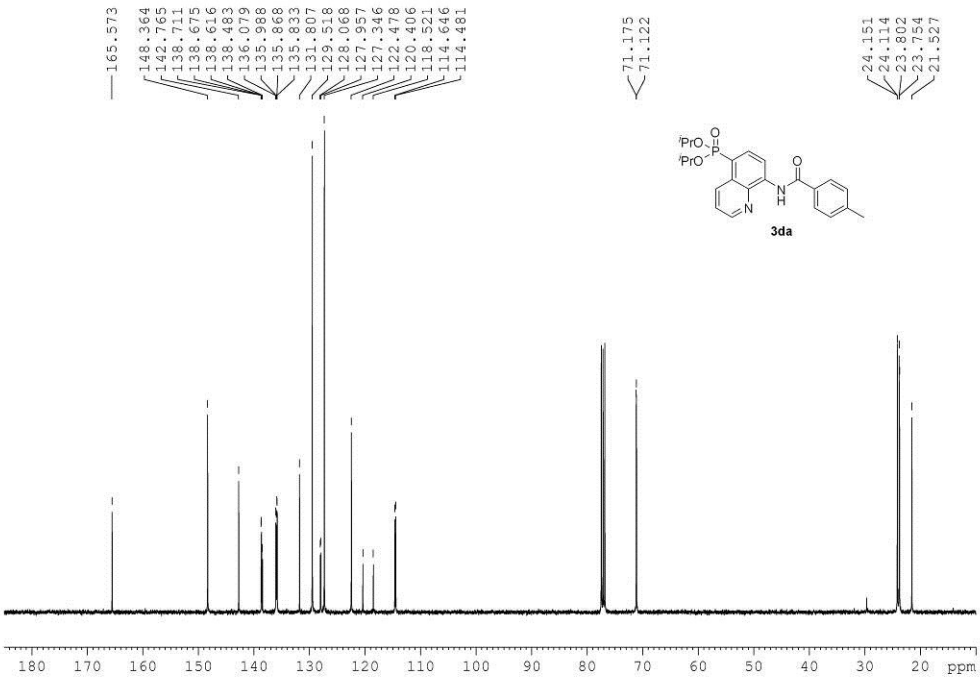
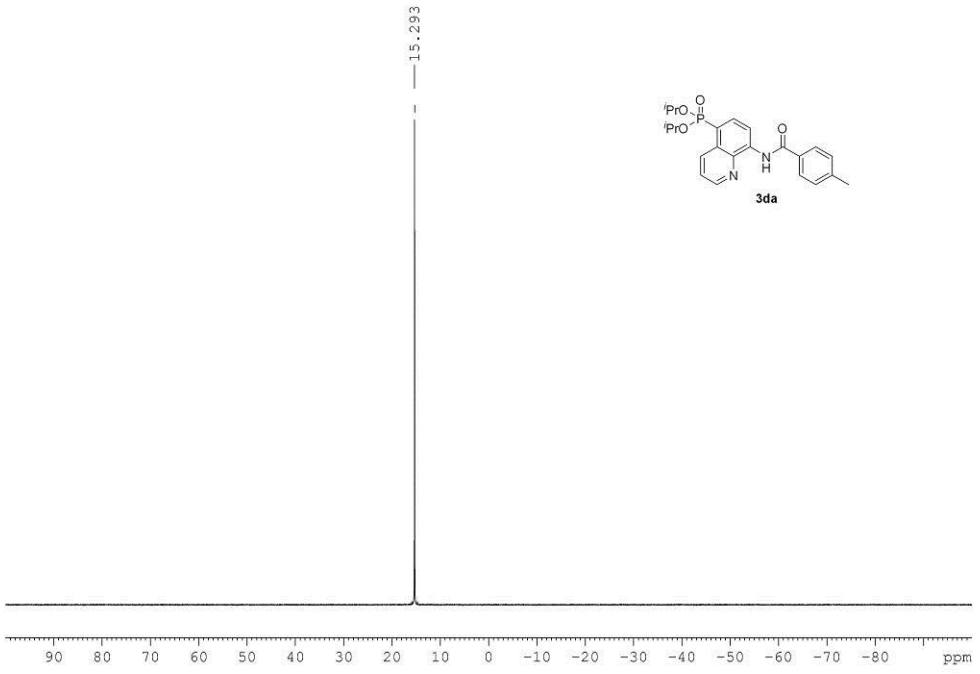
8.984
8.975
8.964
8.955
8.947
8.943
8.913
8.909
8.903
8.899
8.349
8.329
8.309
8.289
7.889
7.861
7.612
7.602
7.591
7.580
7.468
7.460
7.449
7.443
7.431
7.420
4.791
4.776
4.772
4.760
4.756
4.745
4.740
4.729
4.725
4.709
2.490
1.418
1.403
1.184
1.168
3ca
8.95 ppm
7.9 7.8 7.7 7.6 7.5 ppm
8.35 8.30 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.847
1.966
0.907
1.000
1.982
1.000
1.982
1.961
2.945
6.047
6.026

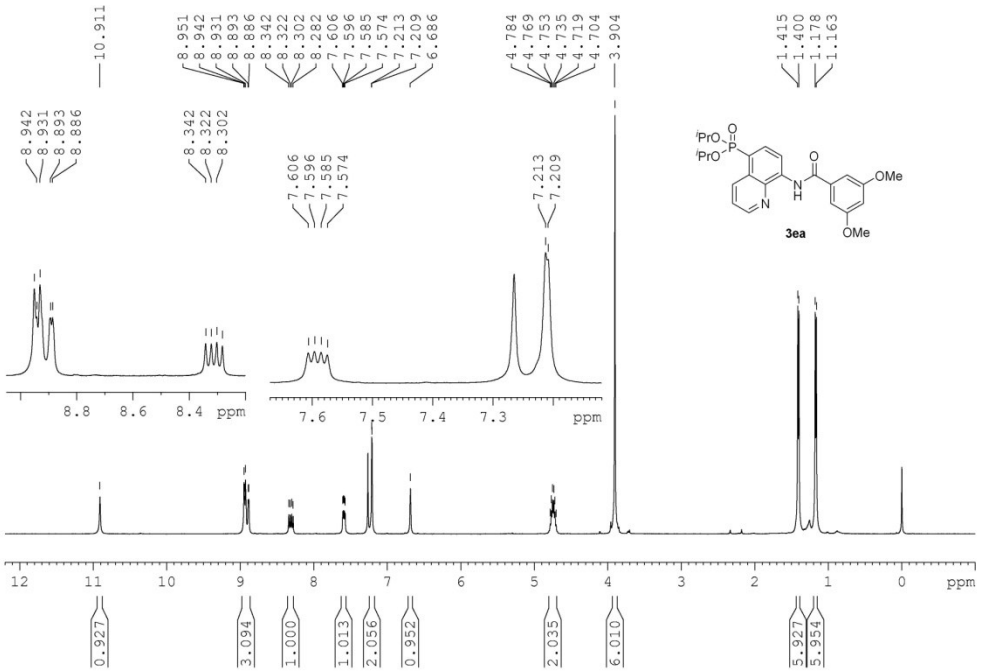

165.861
148.383
138.778
138.654
138.618
138.522
136.060
135.970
135.926
135.890
134.689
132.950
128.724
128.116
127.996
124.276
122.474
120.637
118.755
114.767
114.601
71.157
71.102
24.172
24.131
23.823
23.773
21.462
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

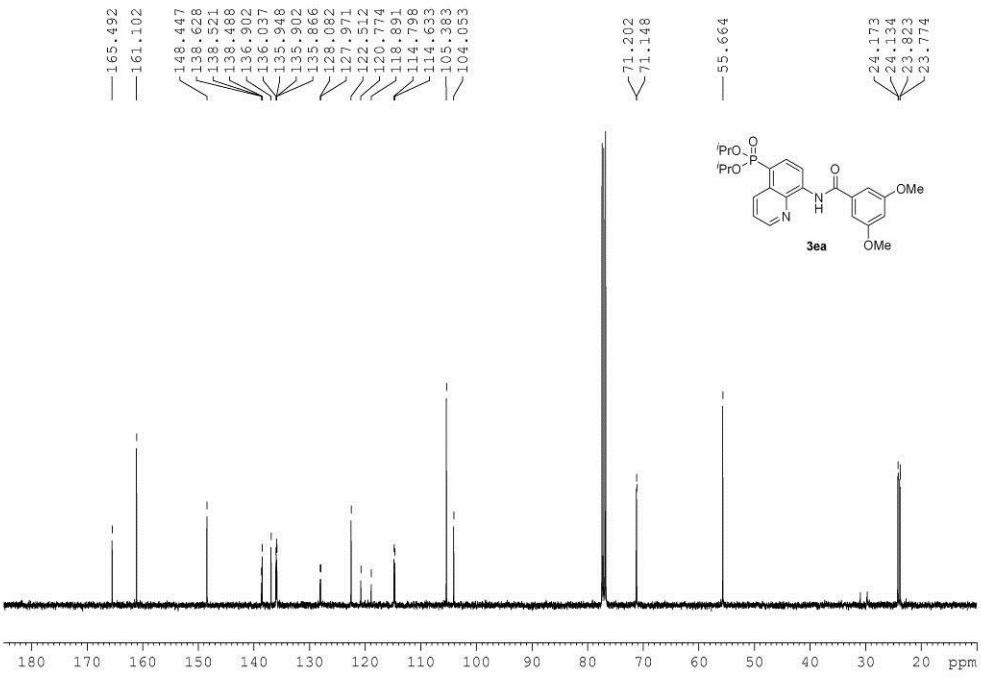

15.245
3ca
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


10.860
8.888 8.879 8.860 8.842 8.807 8.800 8.255 8.235 8.216 8.196 7.897 7.877 7.514 7.504 7.493 7.483 7.260 7.241
4.697 4.682 4.666 4.648 4.632 4.616
2.349
1.325 1.309 1.089 1.073
3da
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.879 2.089 0.978 1.000 1.984 0.996 2.019 2.072 3.082 6.081 6.065


165.573
148.364
142.765
138.711
138.675
138.616
138.483
136.079
135.988
135.868
135.833
131.807
129.518
128.068
127.957
127.346
122.478
120.406
118.521
114.646
114.481
71.175
71.122
24.151
24.114
23.802
23.754
21.527
3da
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


15.293
3da
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


10.911
8.951
8.942
8.931
8.893
8.886
8.342
8.322
8.302
8.282
7.606
7.596
7.585
7.574
7.213
7.209
6.686
4.784
4.769
4.753
4.735
4.719
4.704
3.904
1.415
1.400
1.178
1.163
3ea
OMe
OMe
ppm
0.927
3.094
1.000
1.013
2.056
0.952
2.035
6.010
5.927
5.954


165.492
161.102
148.447
138.628
138.521
138.488
136.902
136.037
135.948
135.902
135.866
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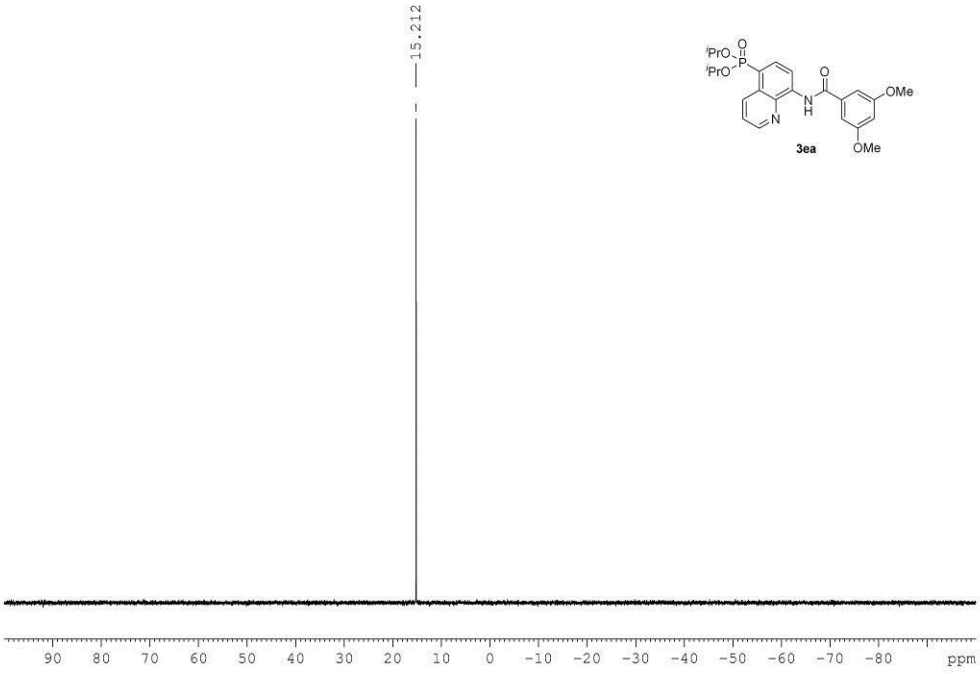
127.971
122.512
120.774
118.891
114.798
114.633
105.383
104.053
71.202
71.148
55.664
24.173
24.134
23.823
23.774
3ea
OMe
OMe
ppm


15.212
3ea
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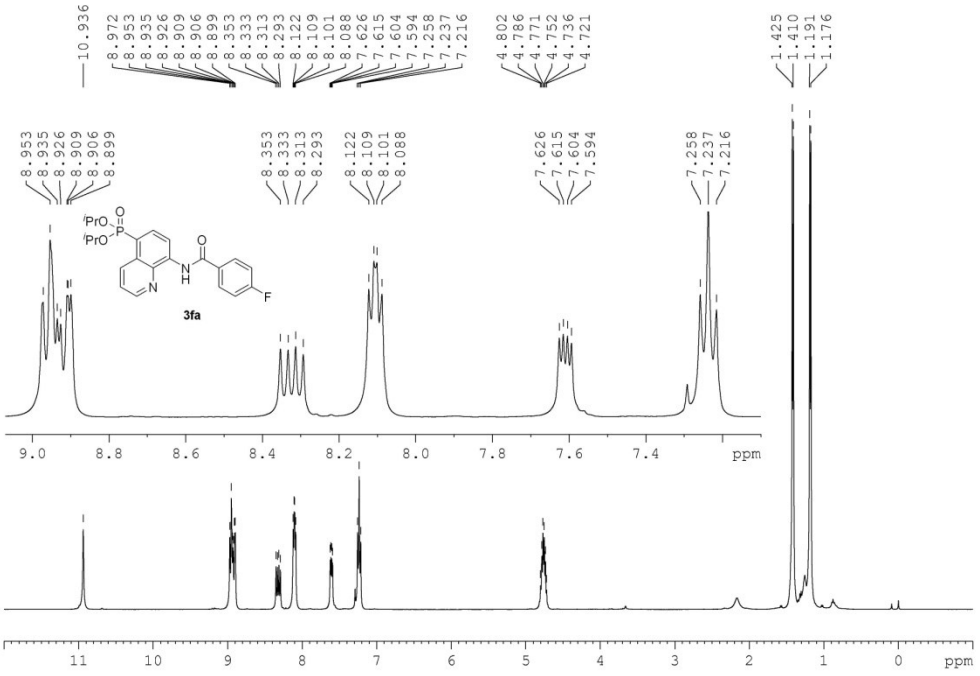
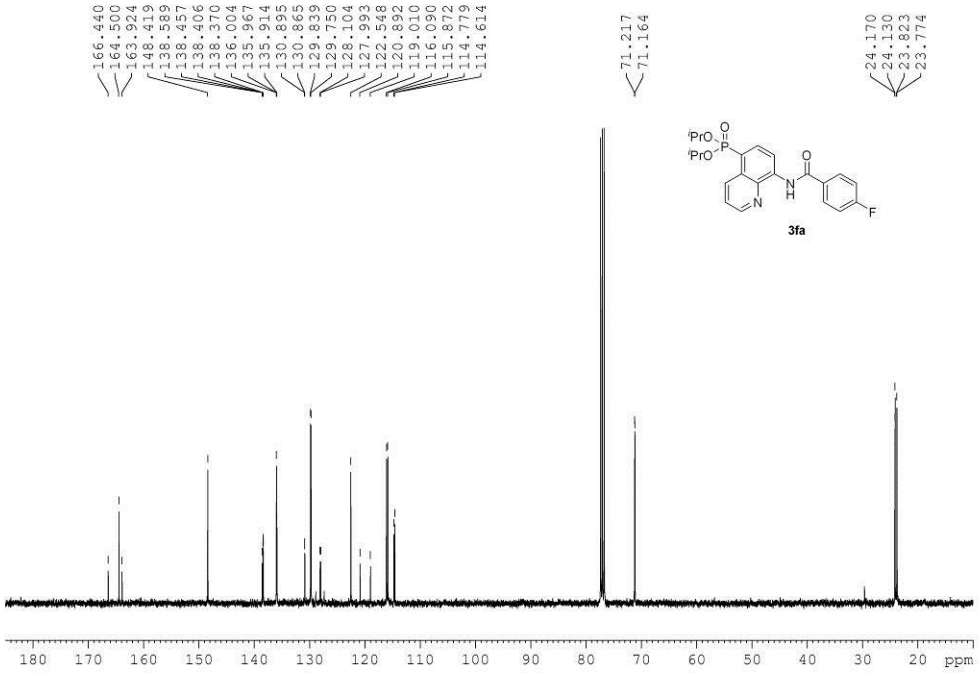
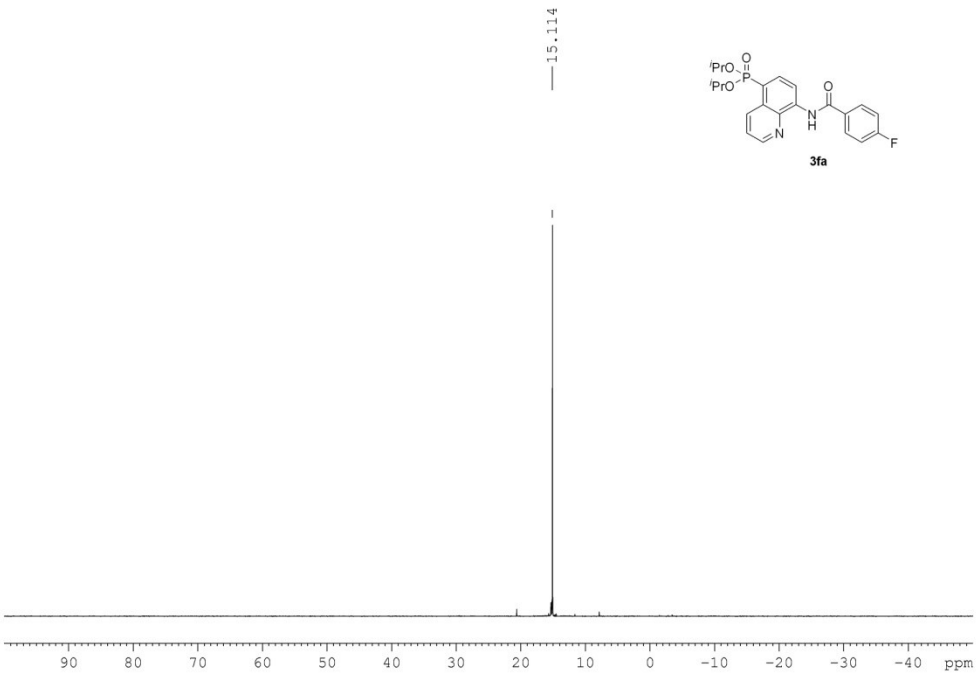

10.936
8.972 8.953 8.935 8.926 8.909 8.906 8.899 8.353 8.333 8.313 8.293 8.122 8.109 8.101 8.088 7.626 7.615 7.604 7.594 7.258 7.237 7.216
4.802 4.786 4.771 4.752 4.736 4.721
1.425 1.410 1.191 1.176
3fa
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm


166.440
164.500
163.924
148.419
138.589
138.457
138.406
138.370
136.004
135.967
135.914
130.895
130.865
129.839
129.750
128.104
127.993
122.548
120.892
119.010
116.090
115.872
114.779
114.614
71.217
71.164
24.170
24.130
23.823
23.774
iPrO
iPrO
O
P
O
N
H
N
F
3fa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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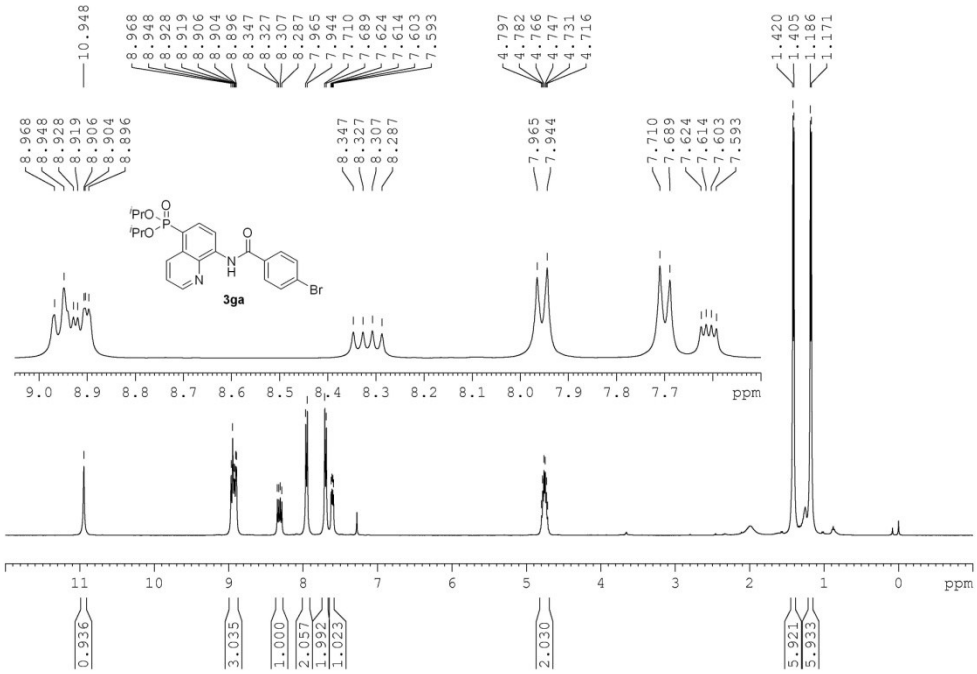
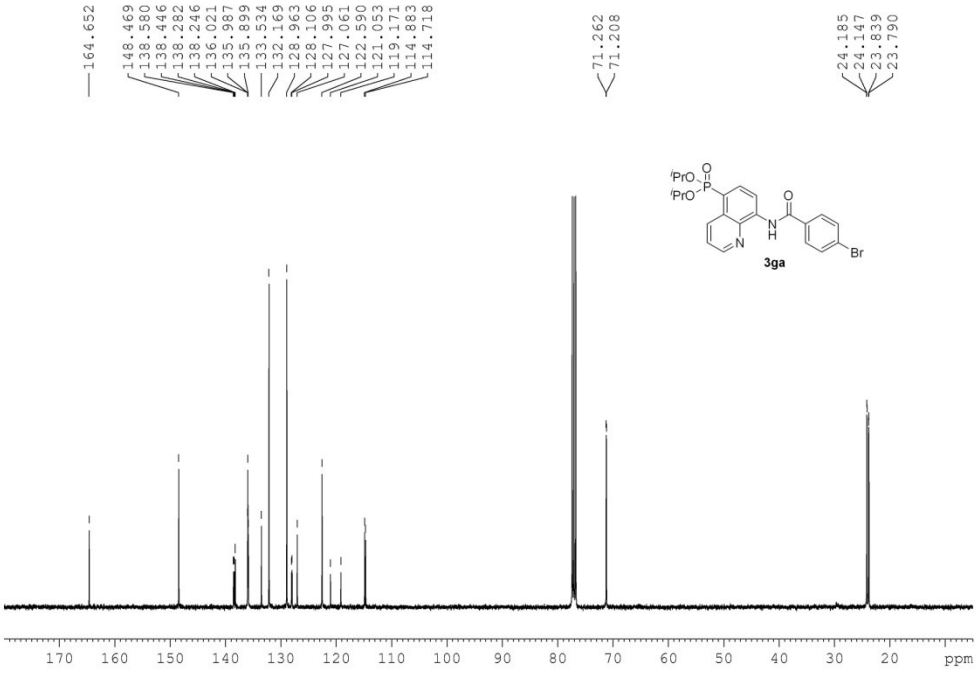
iPrO
iPrO
O
P
O
N
H
N
F
3fa
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


10.948
8.968
8.948
8.928
8.919
8.906
8.904
8.896
8.347
8.327
8.307
8.287
7.965
7.944
7.710
7.689
7.624
7.614
7.603
7.593
4.797
4.782
4.766
4.747
4.731
4.716
1.420
1.405
1.186
1.171
3ga
ppm
0.936
3.035
1.000
2.057
1.992
1.023
2.030
5.921
5.933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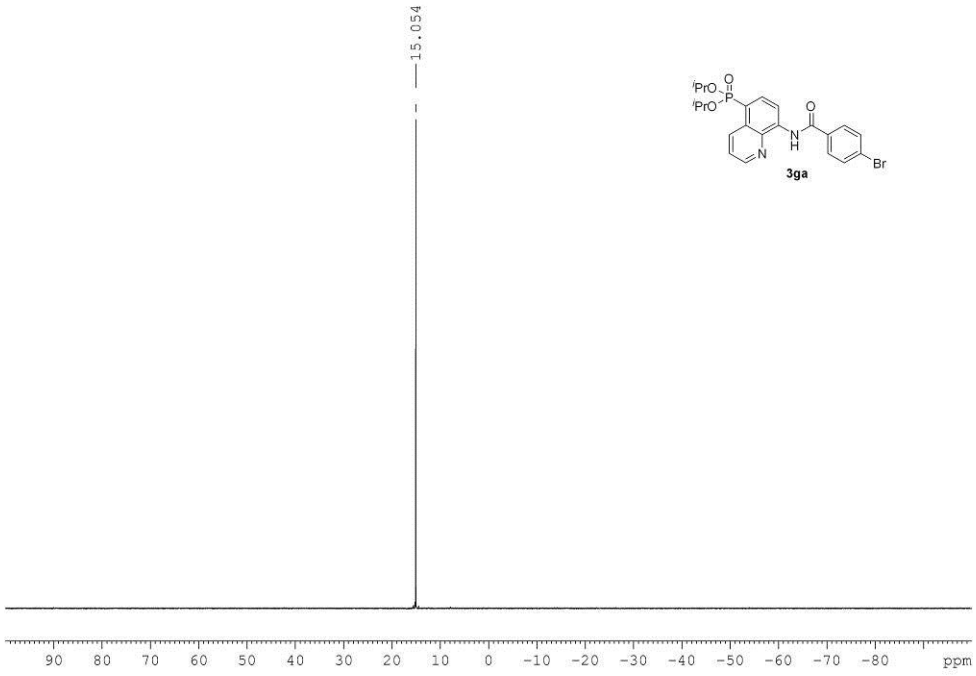
138.580
138.446
138.282
138.246
136.021
135.987
135.899
133.534
132.169
128.963
128.106
127.995
127.061
122.590
121.053
119.171
114.883
114.718
71.262
71.208
24.185
24.147
23.839
23.790
3ga
ppm


15.054
3ga
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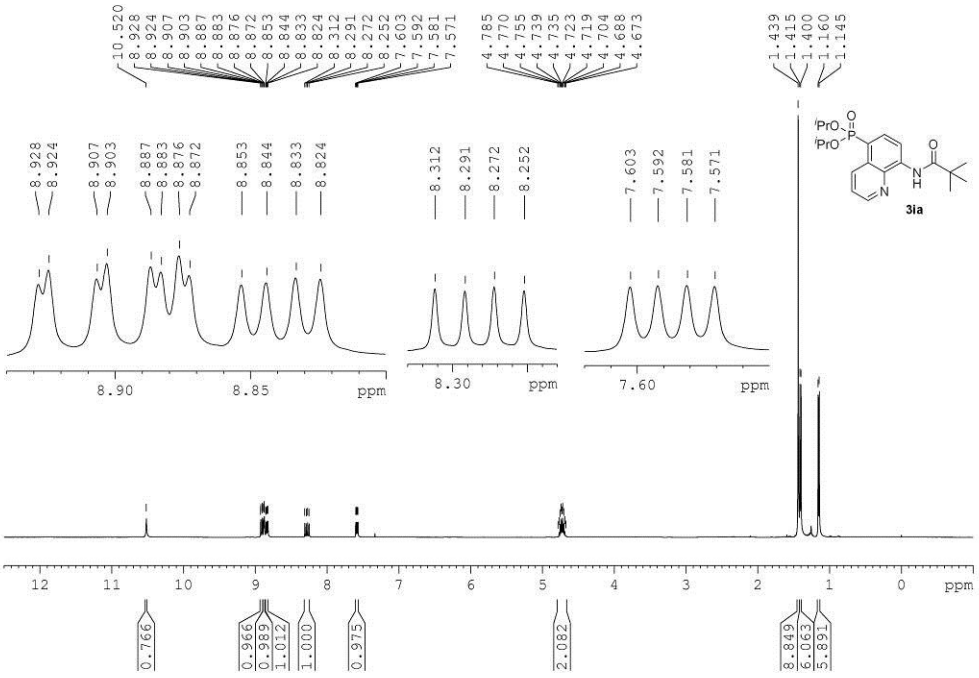
10.520
8.928
8.924
8.907
8.903
8.887
8.883
8.876
8.872
8.853
8.844
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8.824
8.312
8.291
8.272
8.252
7.603
7.592
7.581
7.571
4.785
4.770
4.755
4.739
4.735
4.723
4.719
4.704
4.688
4.673
1.439
1.415
1.400
1.160
1.145
3ia
8.90
8.85
8.30
7.60
ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
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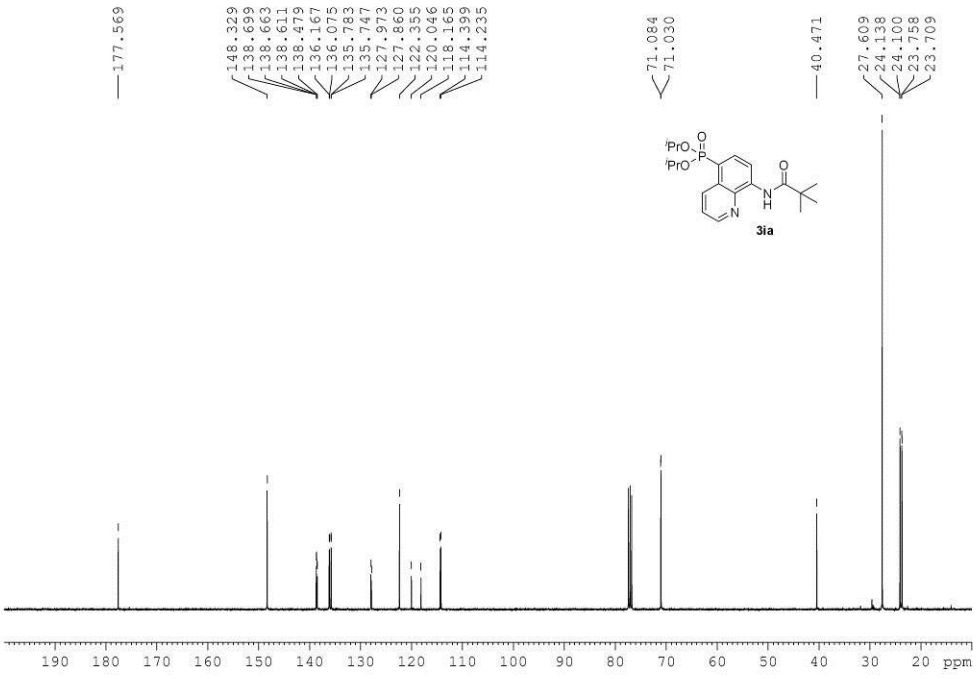
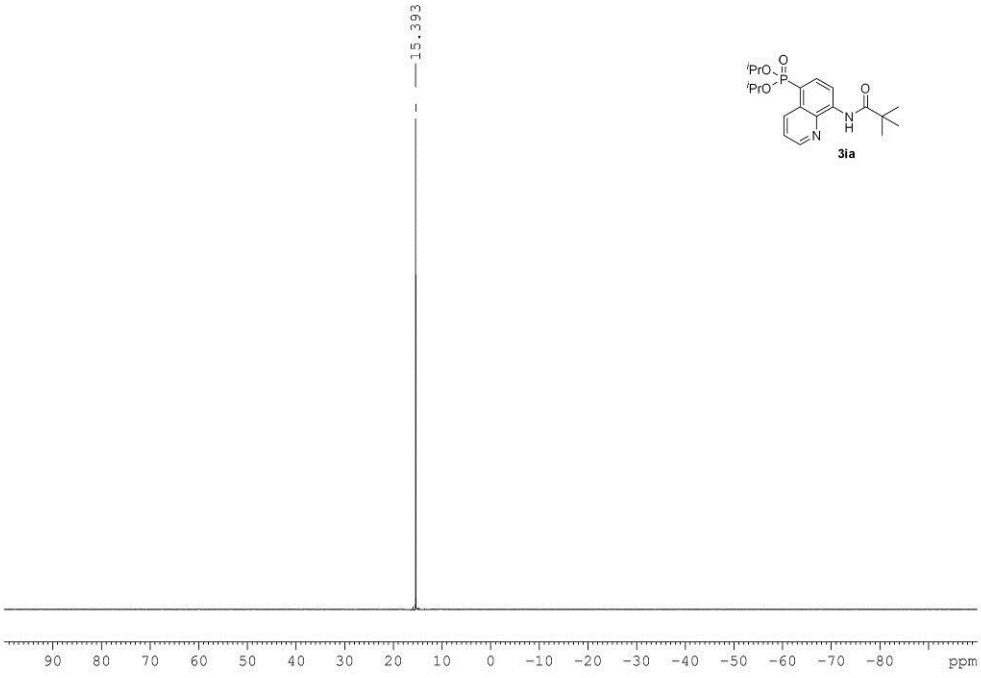
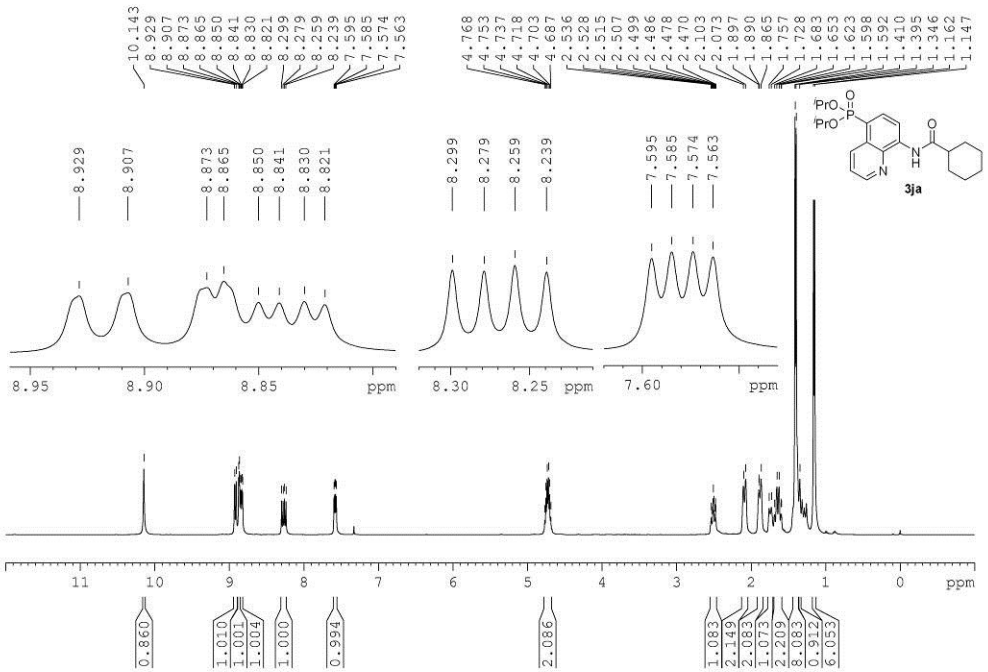
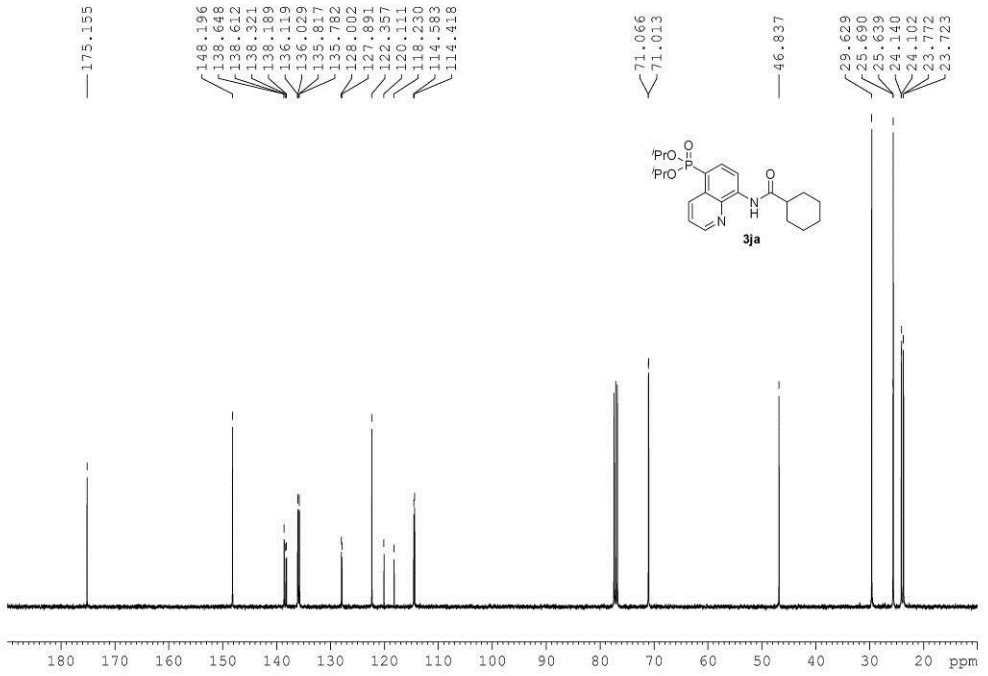
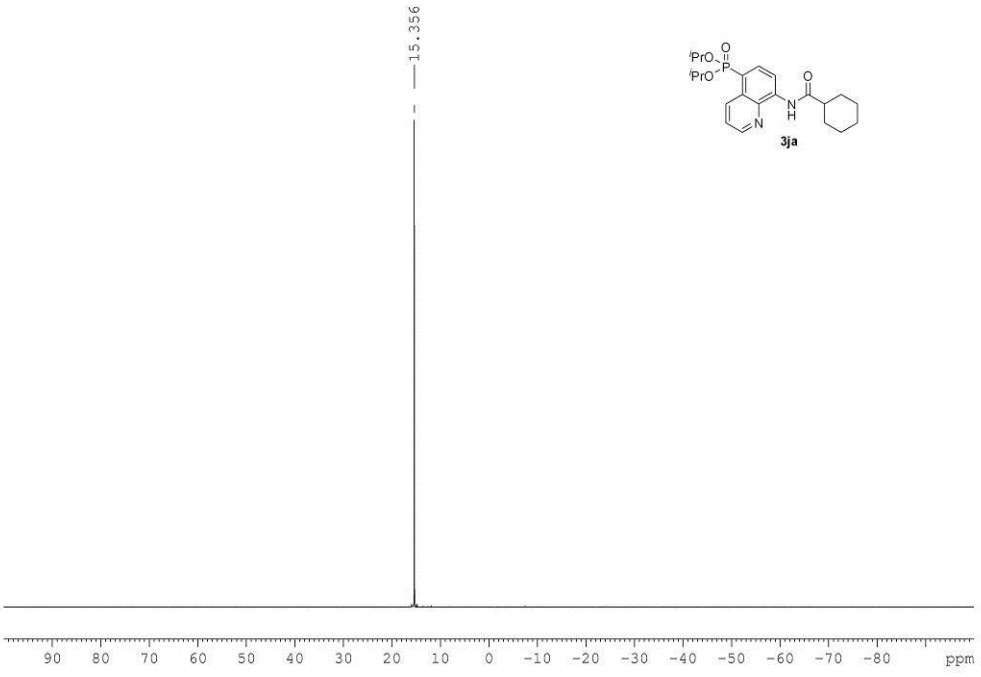
0.966
0.989
1.012
1.000
0.975
2.082
8.849
6.063
5.891

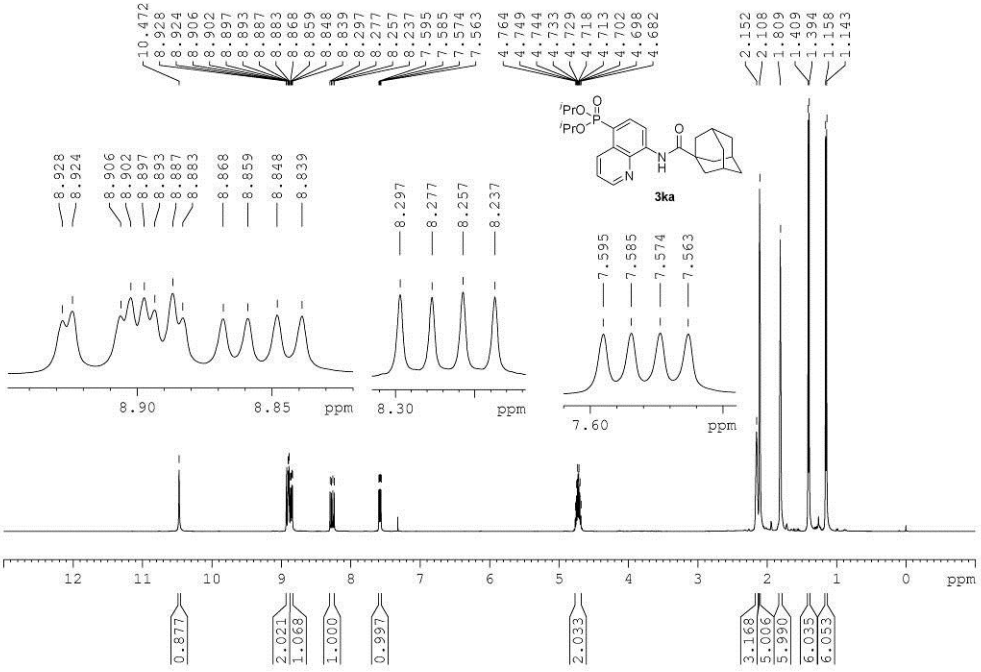

177.569
148.329
138.699
138.663
138.611
138.479
136.167
136.075
135.783
135.747
127.973
127.860
122.355
120.046
118.165
114.399
114.235
71.084
71.030
40.471
27.609
24.138
24.100
23.758
23.709
3ia
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

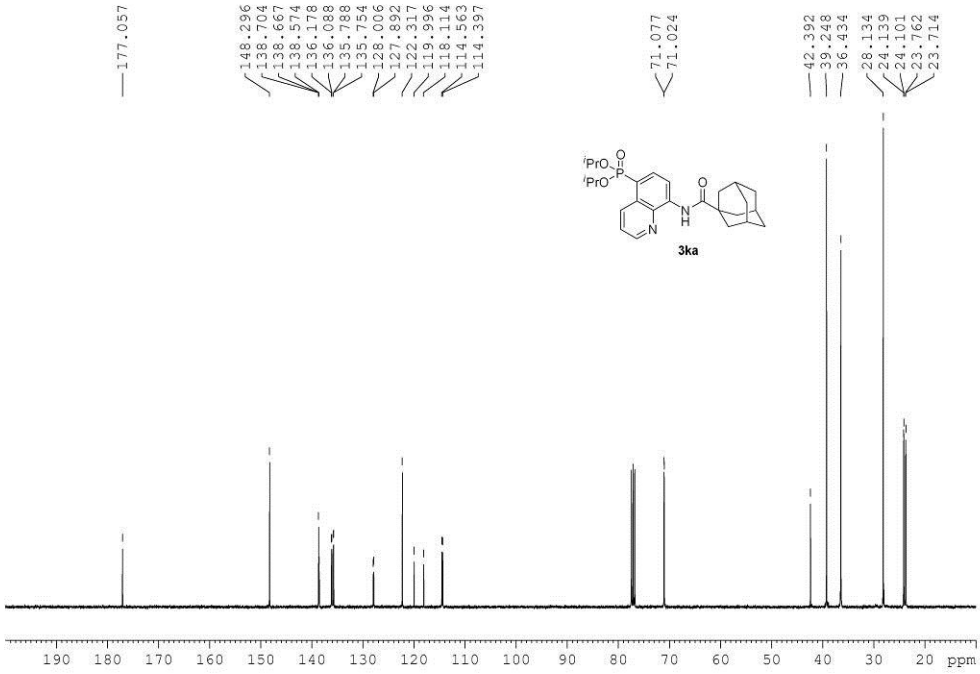

15.393
3ia
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

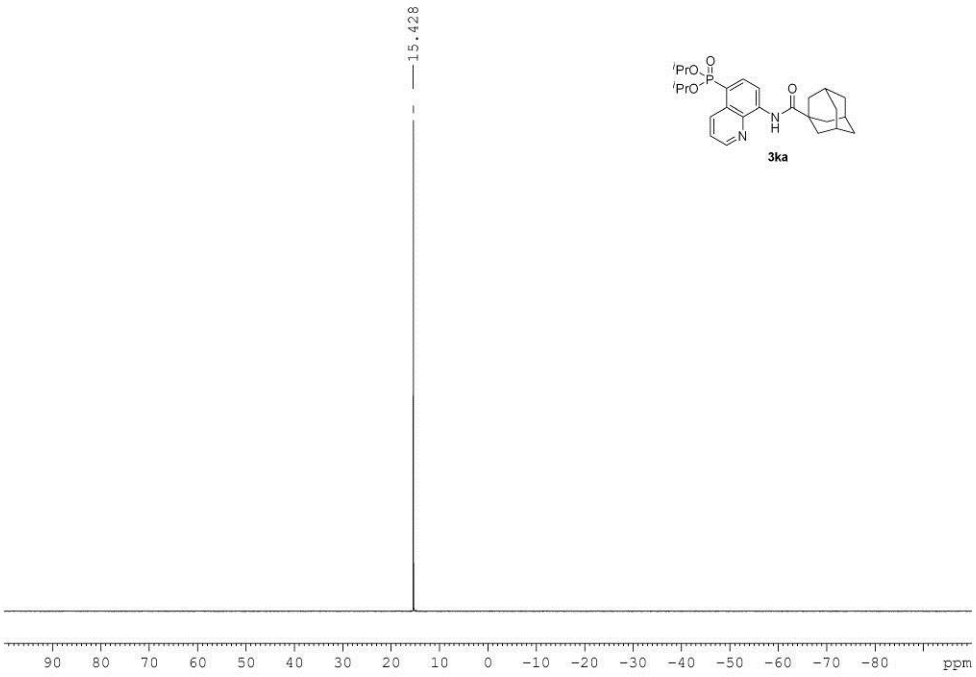

10.143
8.929
8.907
8.873
8.865
8.850
8.841
8.830
8.821
8.299
8.279
8.259
8.239
7.595
7.585
7.574
7.563
4.768
4.753
4.737
4.718
4.703
4.687
2.536
2.528
2.515
2.507
2.499
2.486
2.478
2.470
2.103
2.073
1.897
1.890
1.865
1.757
1.728
1.683
1.653
1.623
1.598
1.592
1.410
1.395
1.346
1.162
1.147
3ja
8.95
8.90
8.85
ppm
8.30
8.25
ppm
7.60
ppm
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.860
1.010
1.001
1.004
1.000
0.994
2.086
1.083
2.149
2.083
1.073
2.209
8.083
0.912
6.053

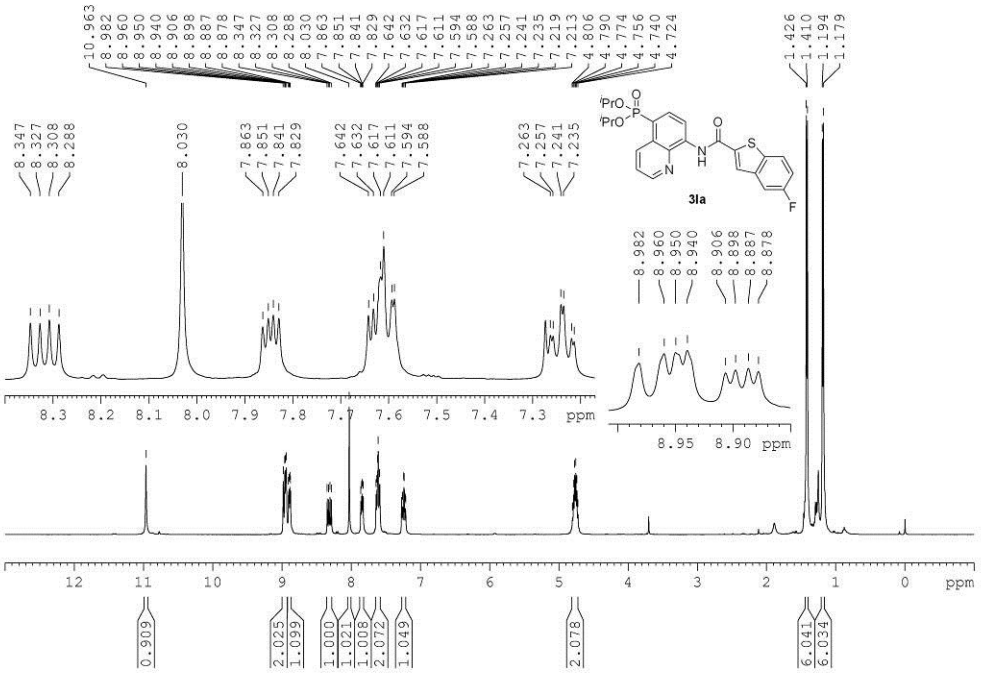

175.155
148.196
138.648
138.612
138.321
138.189
136.119
136.029
135.817
135.782
128.002
127.891
122.357
120.111
118.230
114.583
114.418
71.066
71.013
46.837
29.629
25.690
25.639
24.140
24.102
23.772
23.723
3ja
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

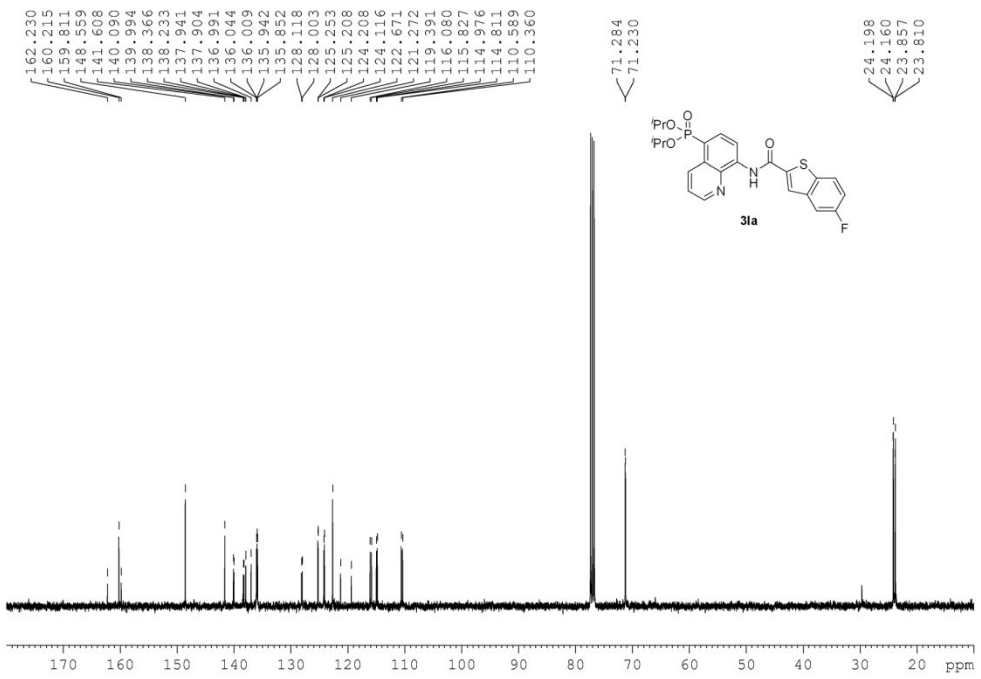

15.356
3ja
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

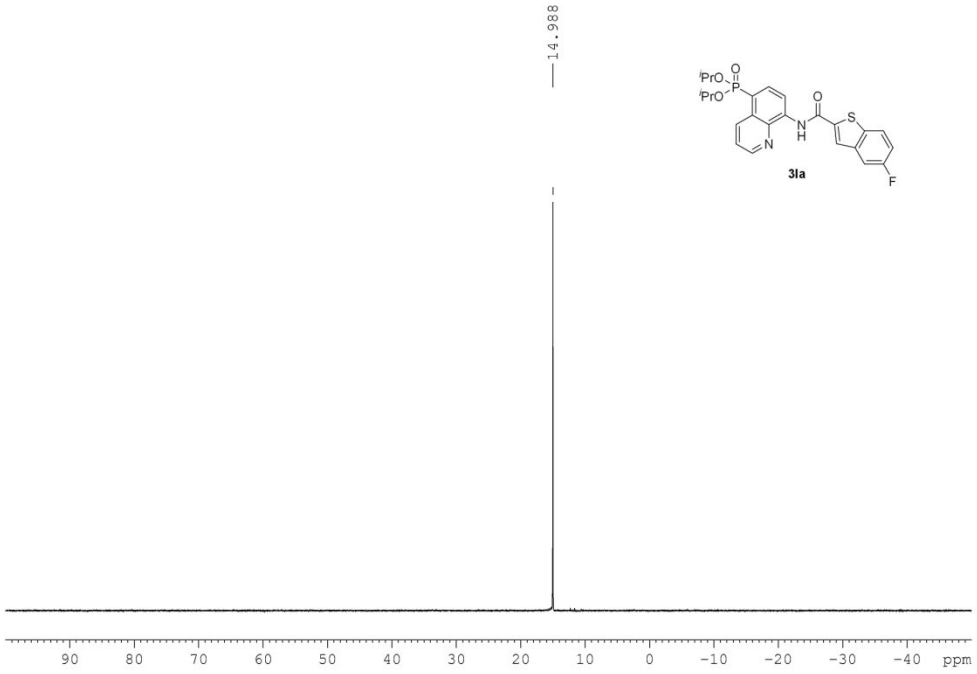

10.472
8.928
8.924
8.906
8.902
8.897
8.893
8.887
8.883
8.868
8.859
8.848
8.839
8.297
8.277
8.257
8.237
7.595
7.585
7.574
7.563
4.764
4.749
4.744
4.733
4.729
4.718
4.713
4.702
4.698
4.682
2.152
2.108
1.809
1.409
1.394
1.158
1.143
3ka
8.90
8.85
ppm
8.30
ppm
7.60
ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.877
2.021
1.068
1.000
0.997
2.033
3.168
5.006
5.990
6.035
6.053

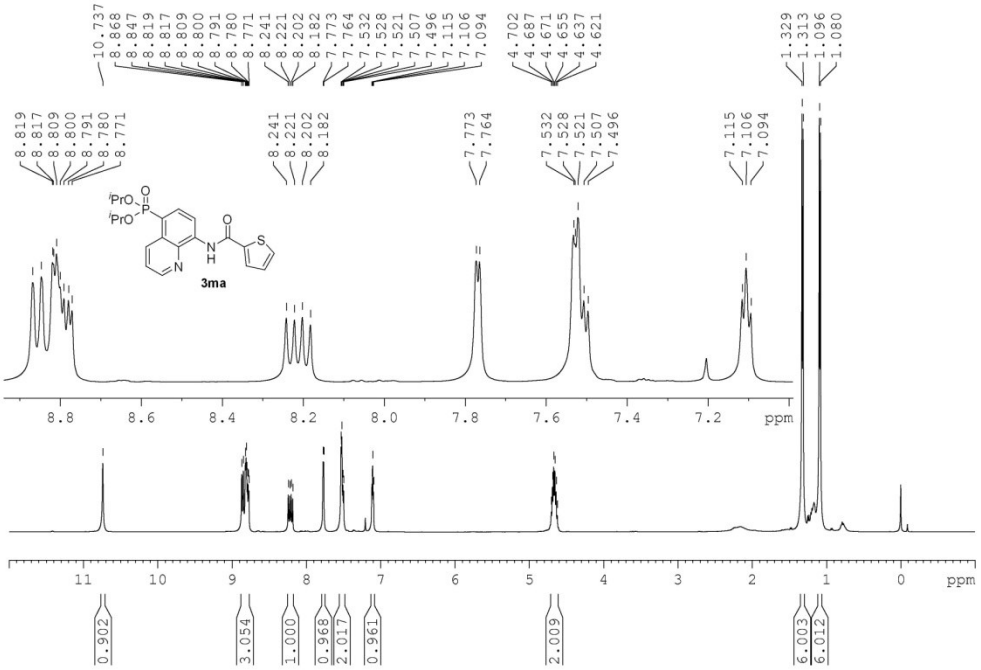

177.057
148.296
138.704
138.667
138.574
136.178
136.088
135.788
135.754
128.006
127.892
122.317
119.996
118.114
114.563
114.397
71.077
71.024
42.392
39.248
36.434
28.134
24.139
24.101
23.762
23.714
3ka
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

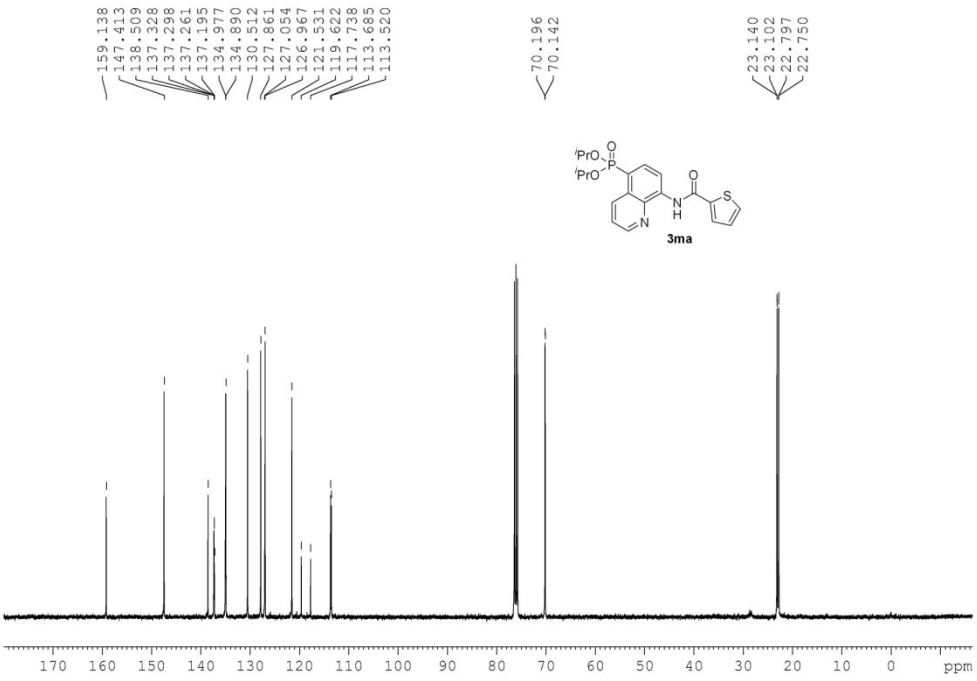

15.428
3ka
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

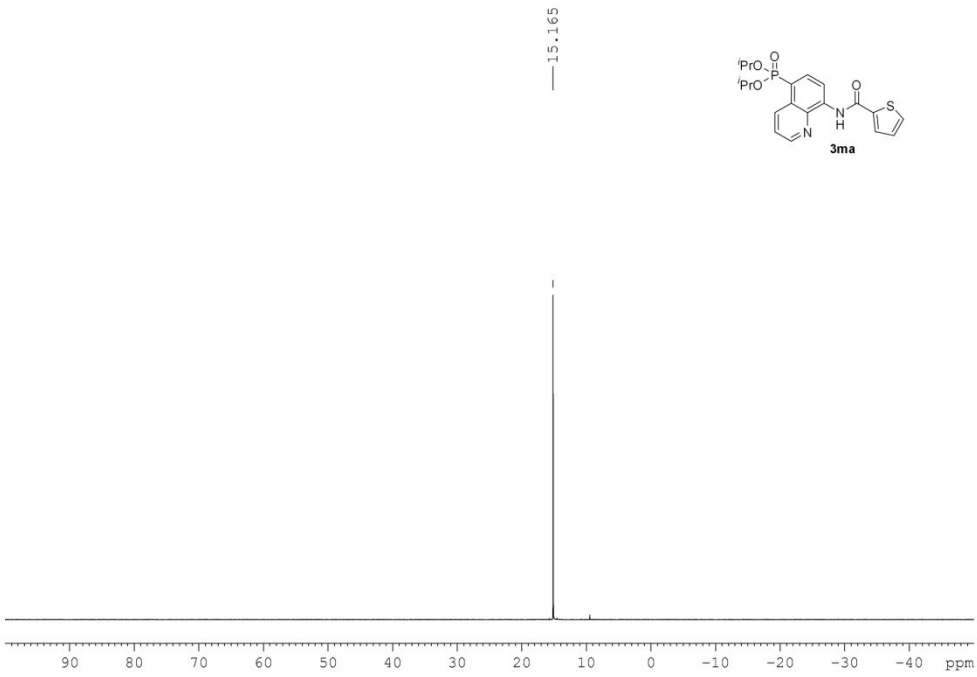

10.963
8.982
8.960
8.950
8.940
8.906
8.898
8.887
8.878
8.347
8.327
8.308
8.288
8.030
7.863
7.851
7.841
7.829
7.642
7.632
7.617
7.611
7.594
7.588
7.263
7.257
7.241
7.235
7.219
7.213
4.806
4.790
4.774
4.756
4.740
4.724
1.426
1.410
1.194
1.179
3Ia
ppm
0.909
2.025
1.099
1.000
1.021
1.008
2.072
1.049
2.078
6.041
6.034

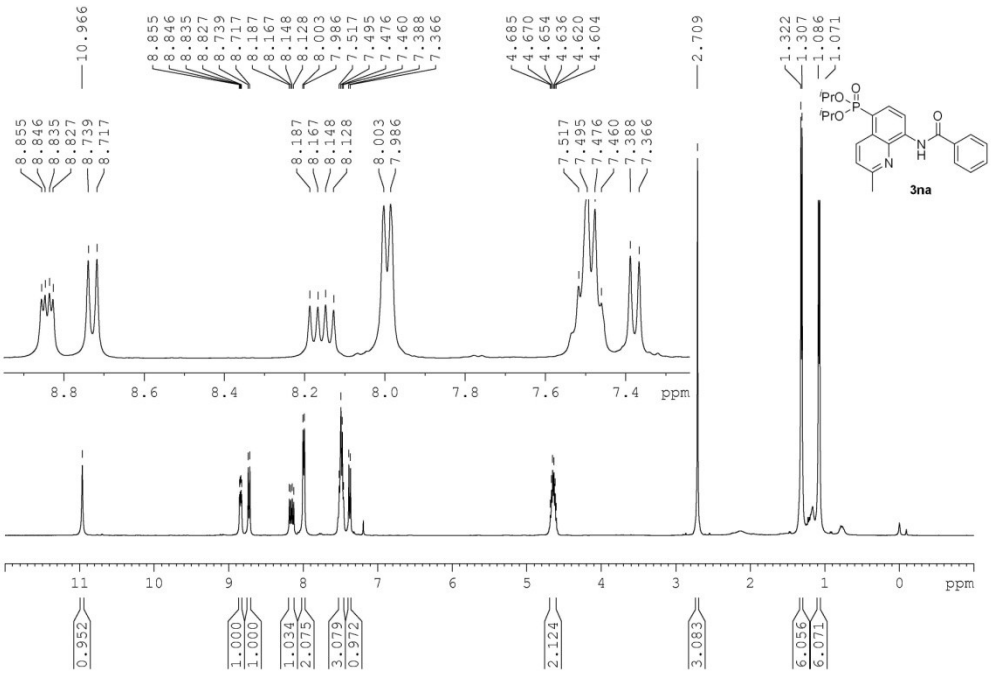

162.230
160.215
159.811
148.559
141.608
140.090
139.994
138.366
138.233
137.941
137.904
136.991
136.044
136.009
135.942
135.852
128.118
128.003
125.253
125.208
124.208
124.116
122.671
121.272
119.391
116.080
115.827
114.976
114.811
110.589
110.360
71.284
71.230
24.198
24.160
23.857
23.810
3Ia
ppm

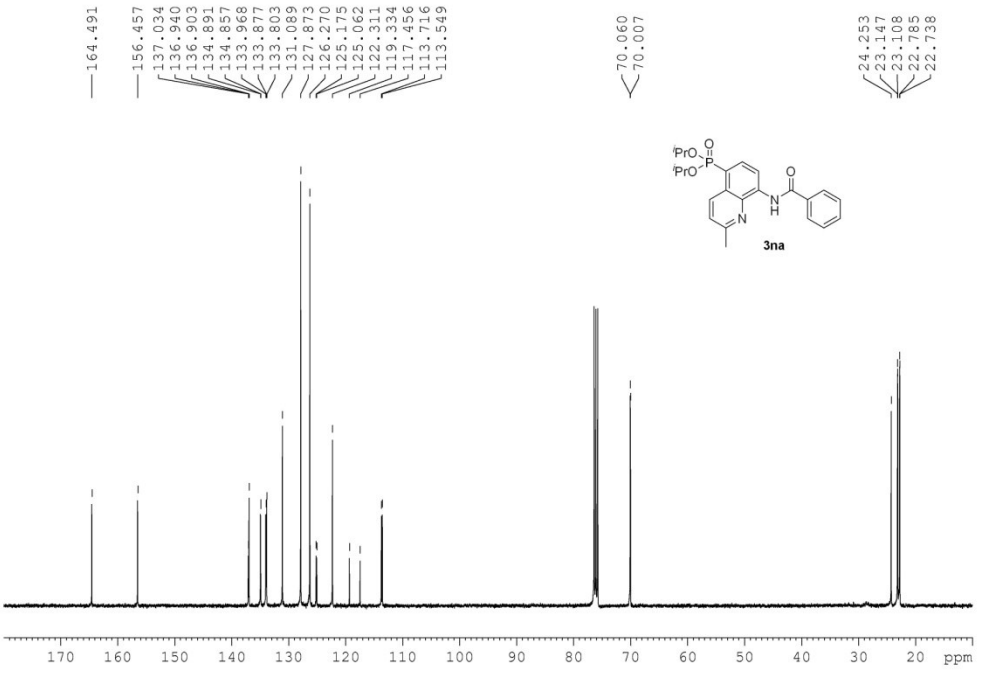

14.988
3la
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

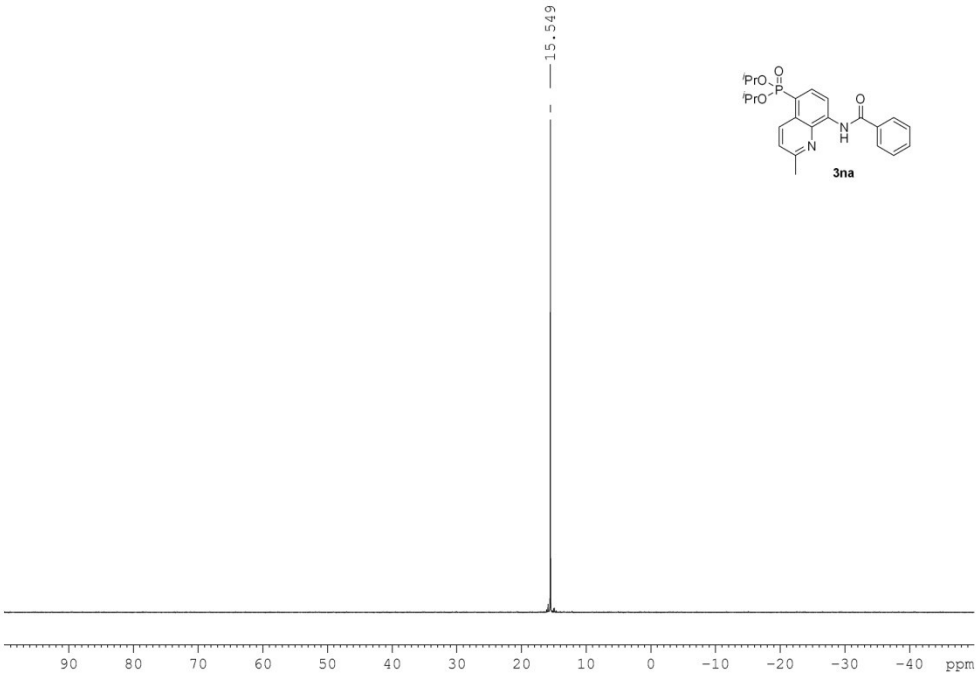

10.737
8.868
8.847
8.819
8.817
8.809
8.800
8.791
8.780
8.771
8.241
8.221
8.202
8.182
7.773
7.764
7.532
7.528
7.521
7.507
7.496
7.115
7.106
7.094
4.702
4.687
4.671
4.655
4.637
4.621
1.329
1.313
1.096
1.080
3ma
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.902
3.054
1.000
0.968
2.017
0.961
2.009
6.003
6.012

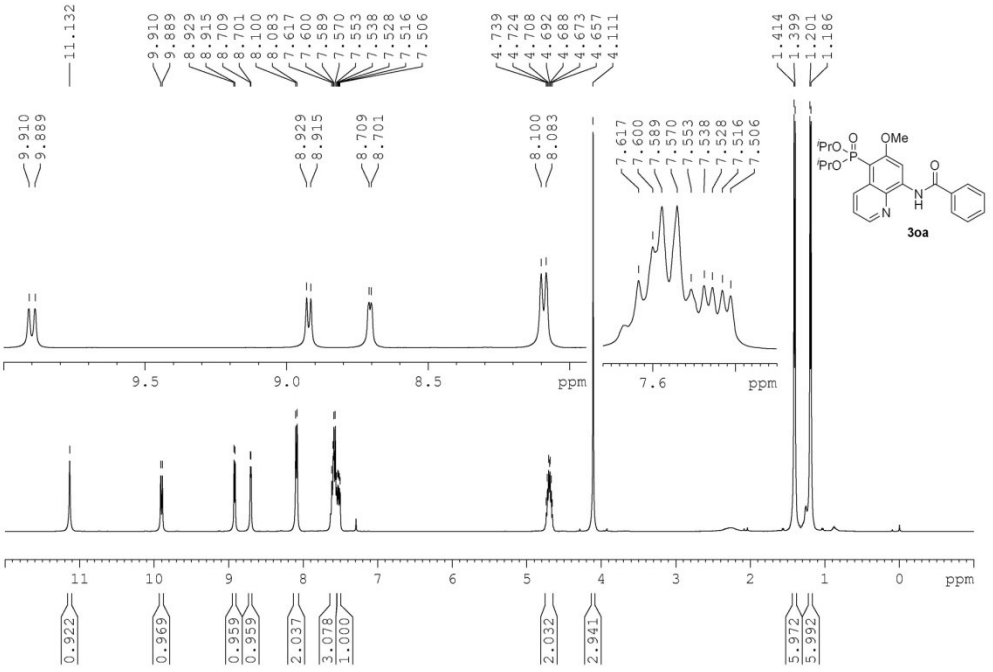

159.138
147.413
138.509
137.328
137.298
137.261
137.195
134.977
134.890
130.512
127.861
127.054
126.967
121.531
119.622
117.738
113.685
113.520
70.196
70.142
23.140
23.102
22.797
22.750
3ma
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

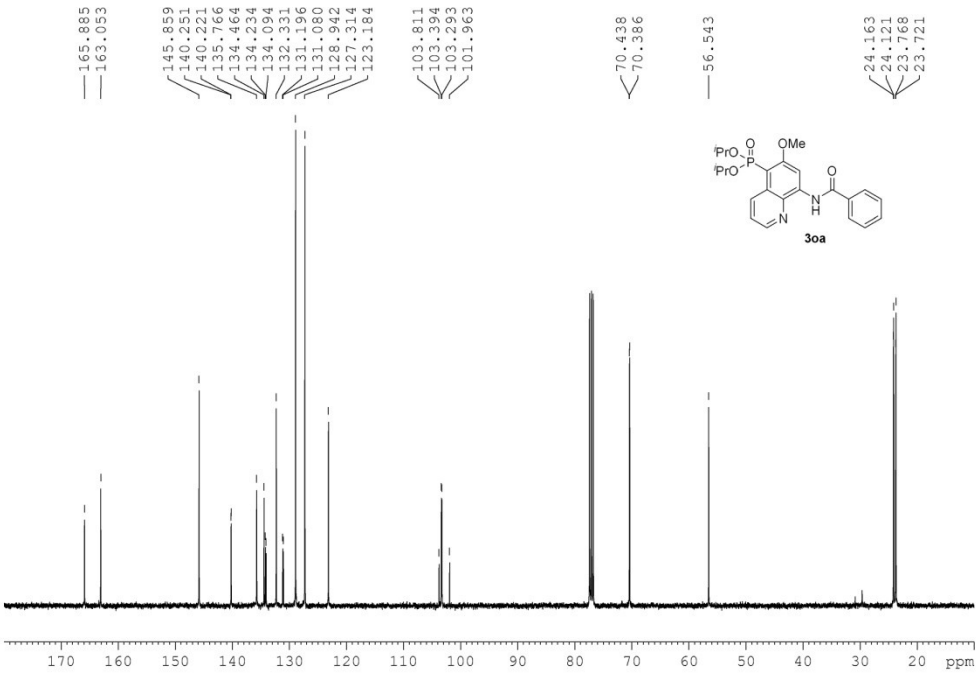

15.165
3ma
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 ppm

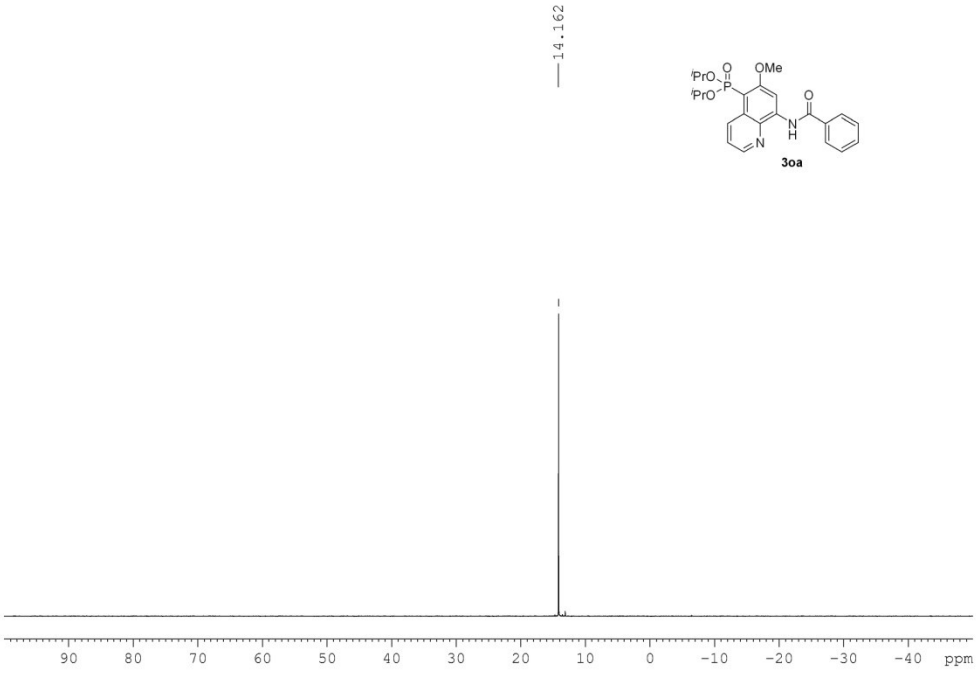

10.966
8.855
8.846
8.835
8.827
8.739
8.717
8.187
8.167
8.148
8.128
8.003
7.986
7.517
7.495
7.476
7.460
7.388
7.366
4.685
4.670
4.654
4.636
4.620
4.604
2.709
1.322
1.307
1.086
1.071
3na
ppm
0.952
1.000
1.000
1.034
2.075
3.079
0.972
2.124
3.083
6.056
6.071

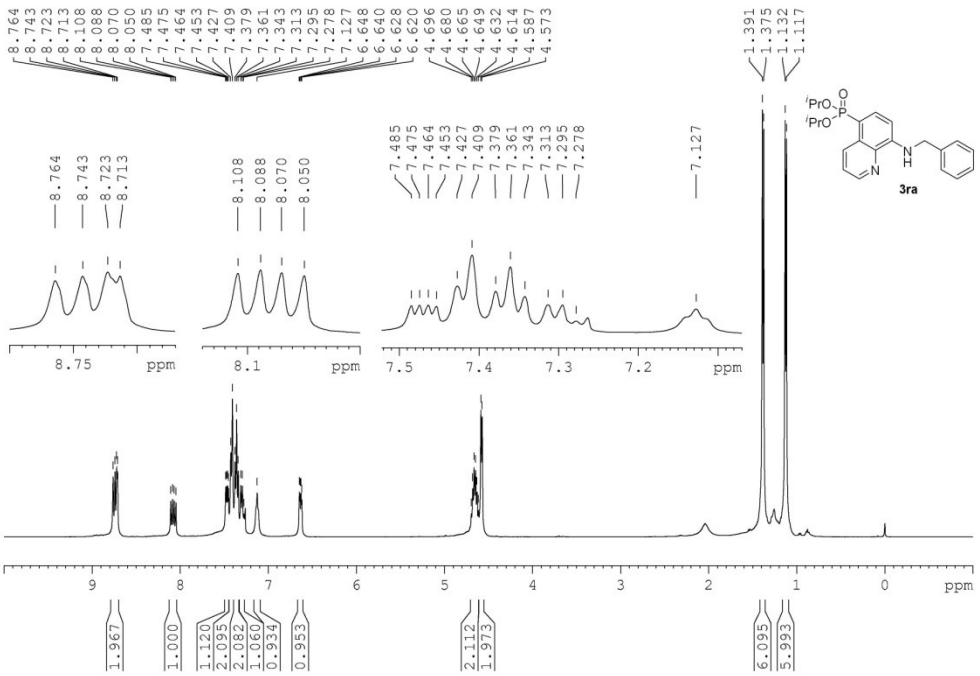

164.491
156.457
137.034
136.940
136.903
134.891
134.857
133.968
133.877
133.803
131.089
127.873
126.270
125.175
125.062
122.311
119.334
117.456
113.716
113.549
70.060
70.007
24.253
23.147
23.108
22.785
22.738
3na
ppm

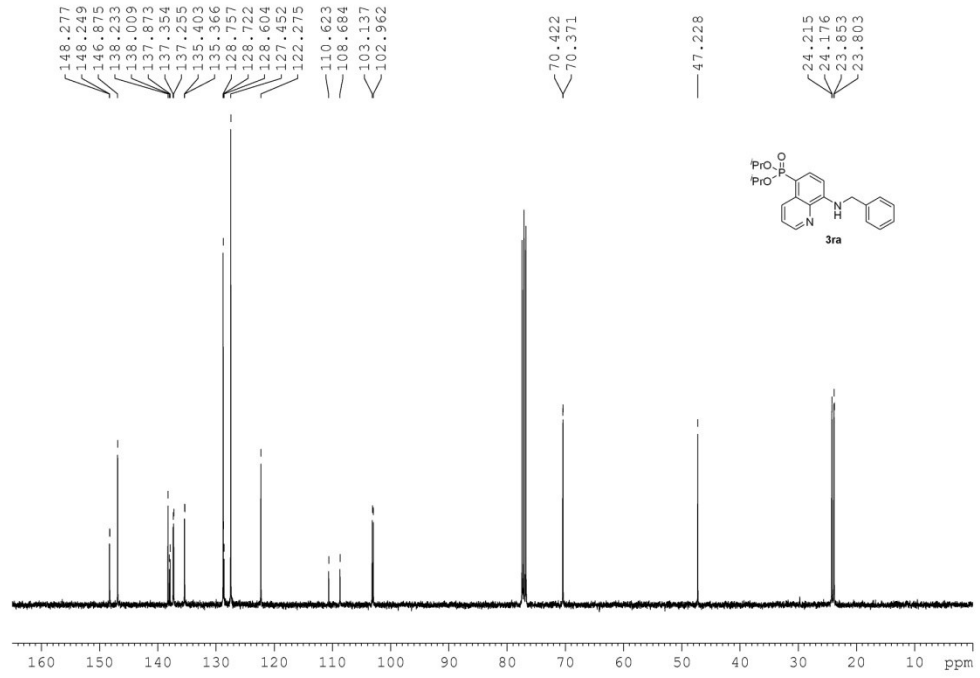

15.549
3na
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

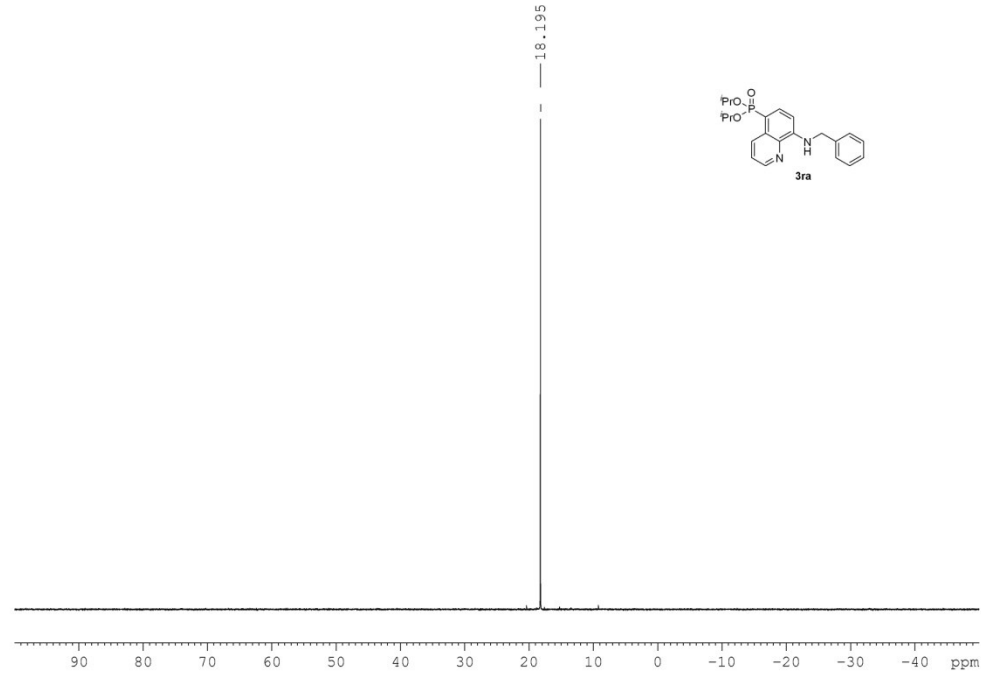

11.132
9.910
9.889
8.929
8.915
8.709
8.701
8.100
8.083
7.617
7.600
7.589
7.570
7.553
7.538
7.528
7.516
7.506
4.739
4.724
4.708
4.692
4.688
4.673
4.657
4.111
1.414
1.399
1.201
1.186
OMe
3oa
9.5 9.0 8.5 ppm
7.6 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.922
0.969
0.959
0.959
2.037
3.078
1.000
2.032
2.941
5.972
5.992

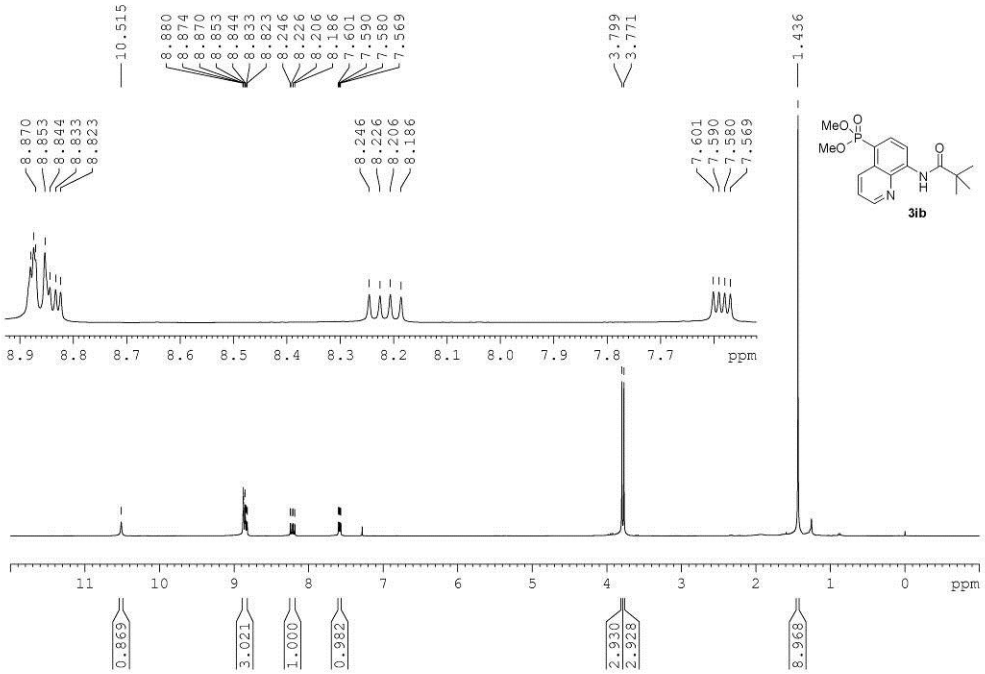

165.885
163.053
145.859
140.251
140.221
135.766
134.464
134.234
134.094
132.331
131.196
131.080
128.942
127.314
123.184
103.811
103.394
103.293
101.963
70.438
70.386
56.543
24.163
24.121
23.768
23.721
OMe
iPrO
iPrO
P
O
N
H
O
3oa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

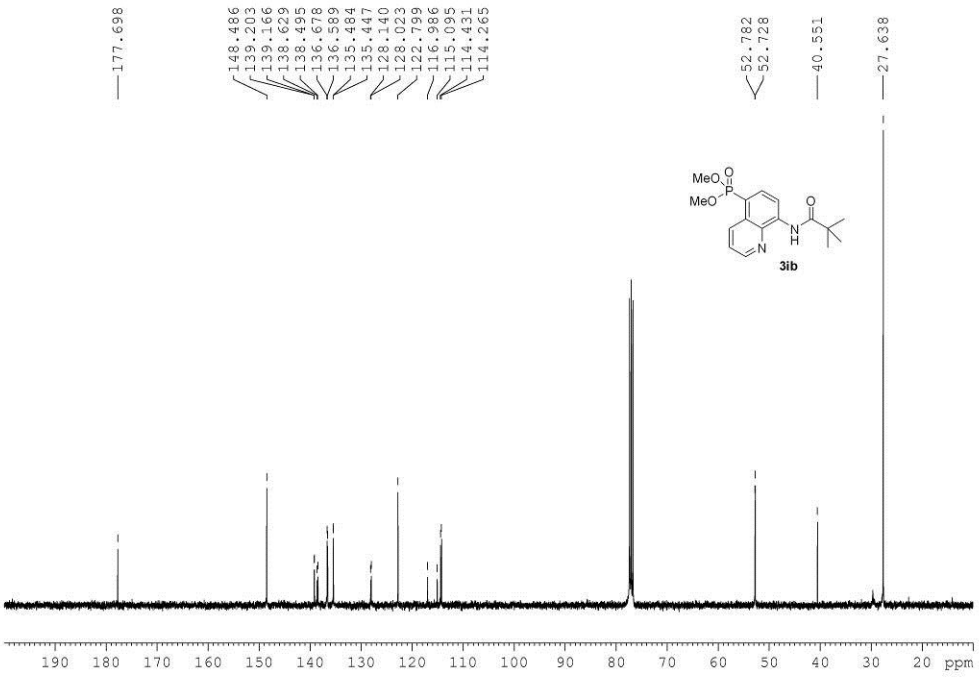

14.162
OMe
iPrO
iPrO
P
O
N
H
O
3oa
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

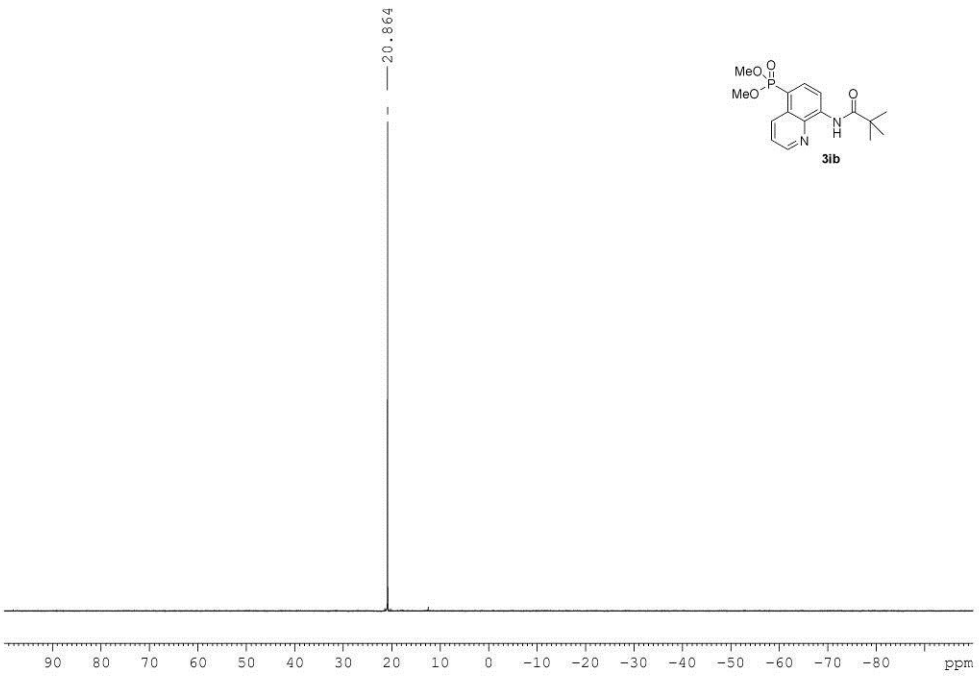

8.764
8.743
8.723
8.713
8.108
8.088
8.070
8.050
7.485
7.475
7.464
7.453
7.427
7.409
7.379
7.361
7.343
7.313
7.295
7.278
7.127
6.648
6.640
6.628
6.620
4.696
4.680
4.665
4.649
4.632
4.614
4.587
4.573
1.391
1.375
1.132
1.117
3ra
8.75 ppm
8.1 ppm
7.5 7.4 7.3 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.967
1.000
1.120
2.095
2.082
1.060
0.934
0.953
2.112
1.973
6.095
5.993

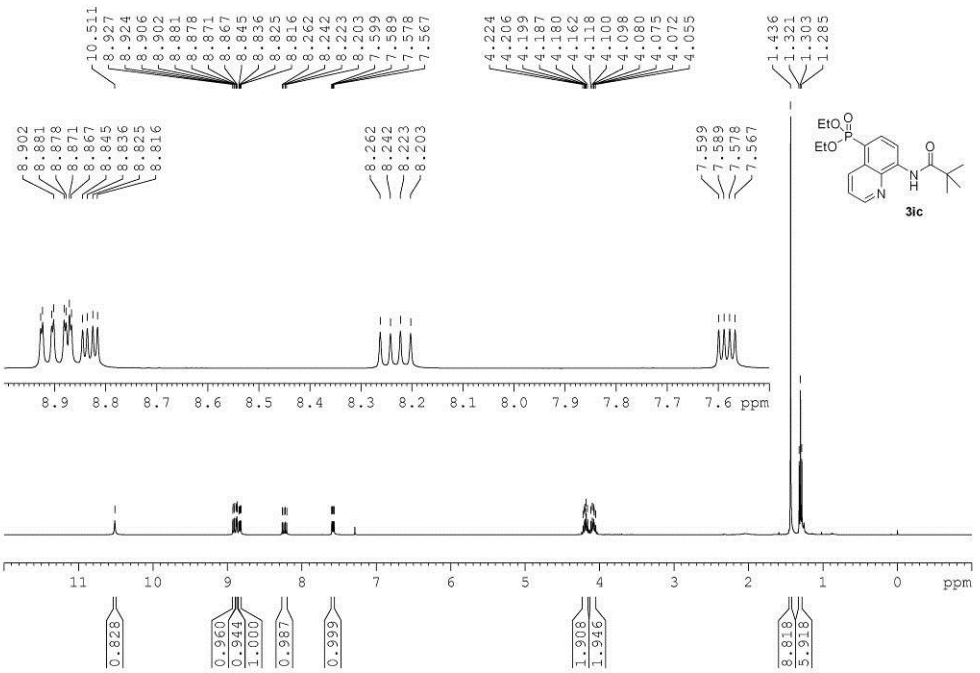

148.277
148.249
146.875
138.233
138.009
137.873
137.354
137.255
135.403
135.366
128.757
128.722
128.604
127.452
122.275
110.623
108.684
103.137
102.962
70.422
70.371
47.228
24.215
24.176
23.853
23.803
3ra
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

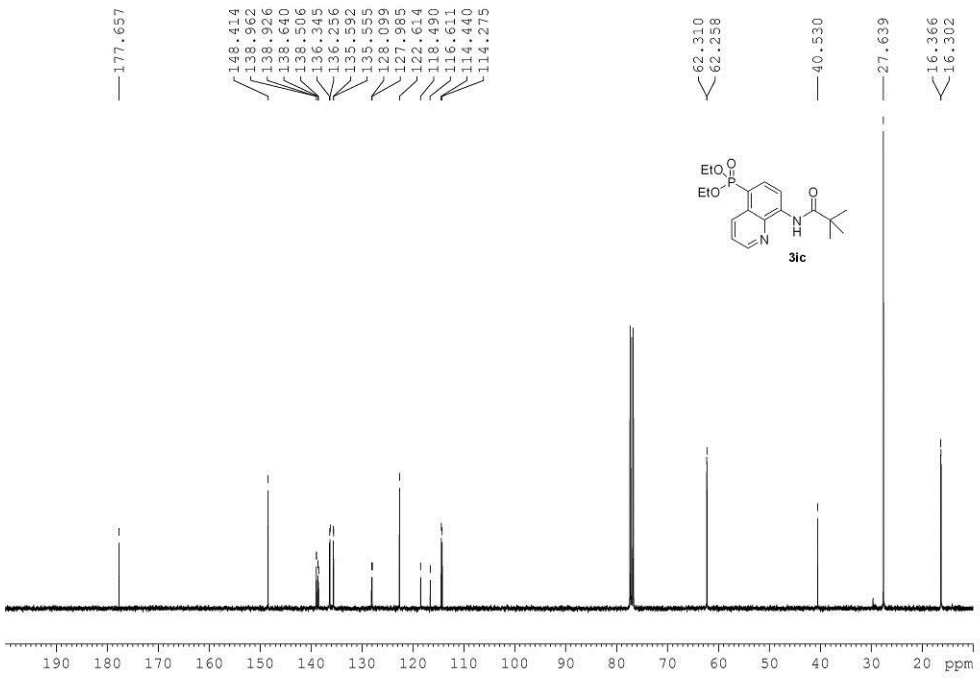

18.195
3ra
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

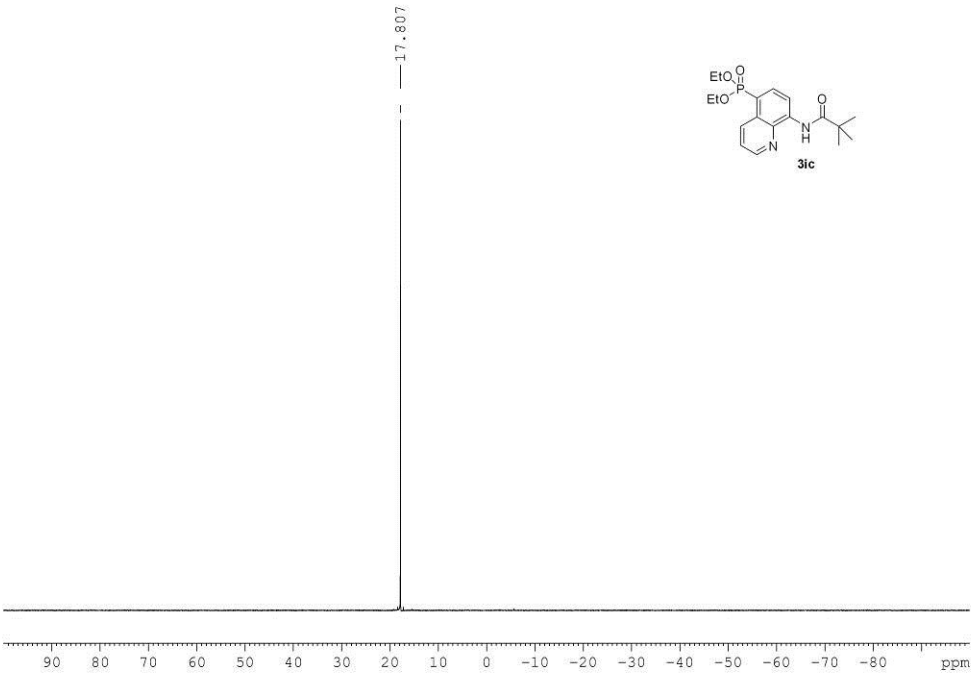

10.515
8.880
8.874
8.870
8.853
8.844
8.833
8.823
8.246
8.226
8.206
8.186
7.601
7.590
7.580
7.569
3.799
3.771
1.436
3ib
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.869
3.021
1.000
0.982
2.930
2.928
8.968

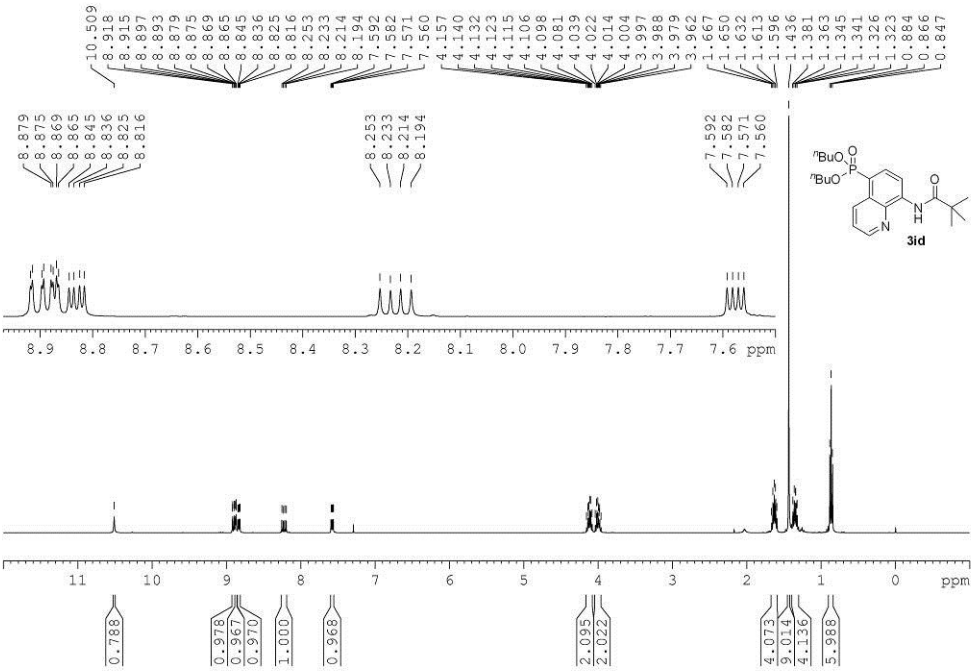

177.698
148.486
139.203
139.166
138.629
138.495
136.678
136.589
135.484
135.447
128.140
128.023
122.799
116.986
115.095
114.431
114.265
52.782
52.728
40.551
27.638
MeO
MeO
P
O
N
H
O
N
3ib
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

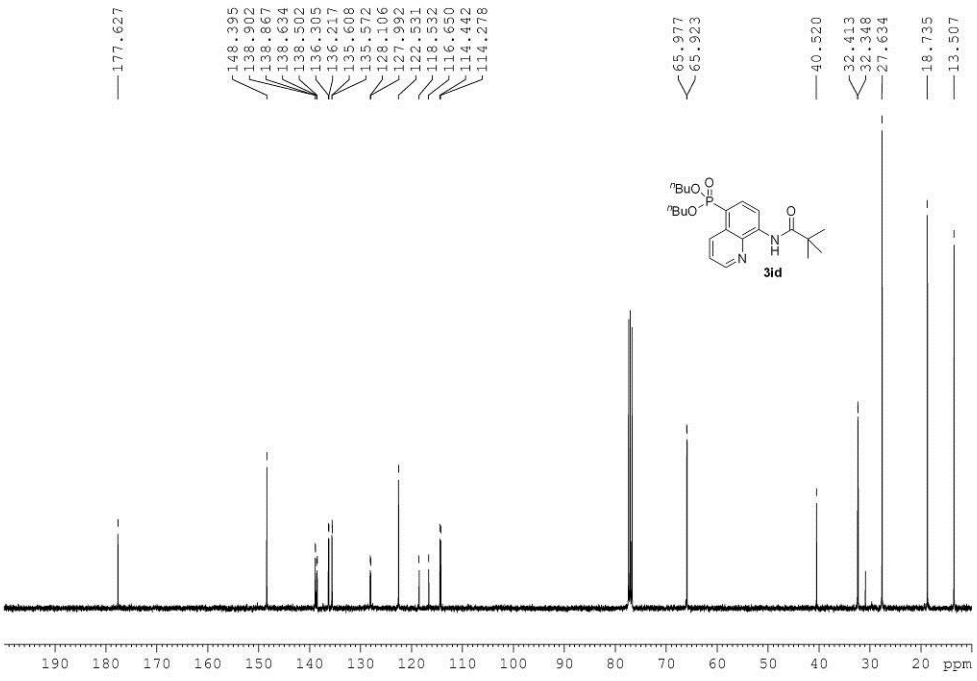

20.864
MeO
MeO
P
O
N
H
O
N
3ib
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

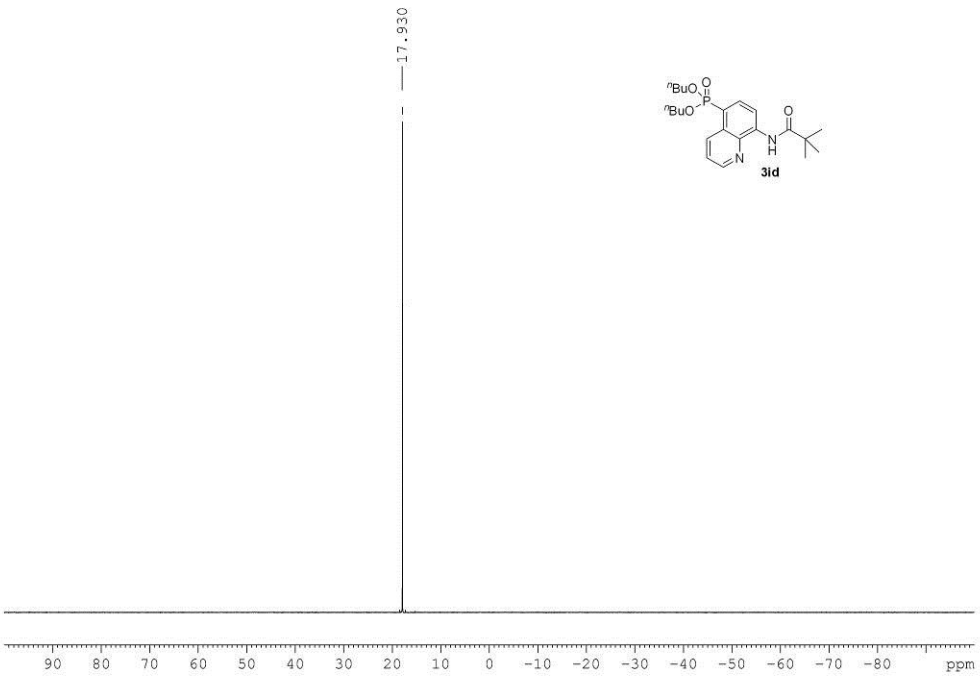

10.511
8.927
8.924
8.906
8.902
8.881
8.878
8.871
8.867
8.845
8.836
8.825
8.816
8.262
8.242
8.223
8.203
7.599
7.589
7.578
7.567
4.224
4.206
4.199
4.187
4.180
4.162
4.118
4.100
4.098
4.080
4.075
4.072
4.055
1.436
1.321
1.303
1.285
3ic
ppm
0.828
0.960
0.944
1.000
0.987
0.999
1.908
1.946
8.818
5.918

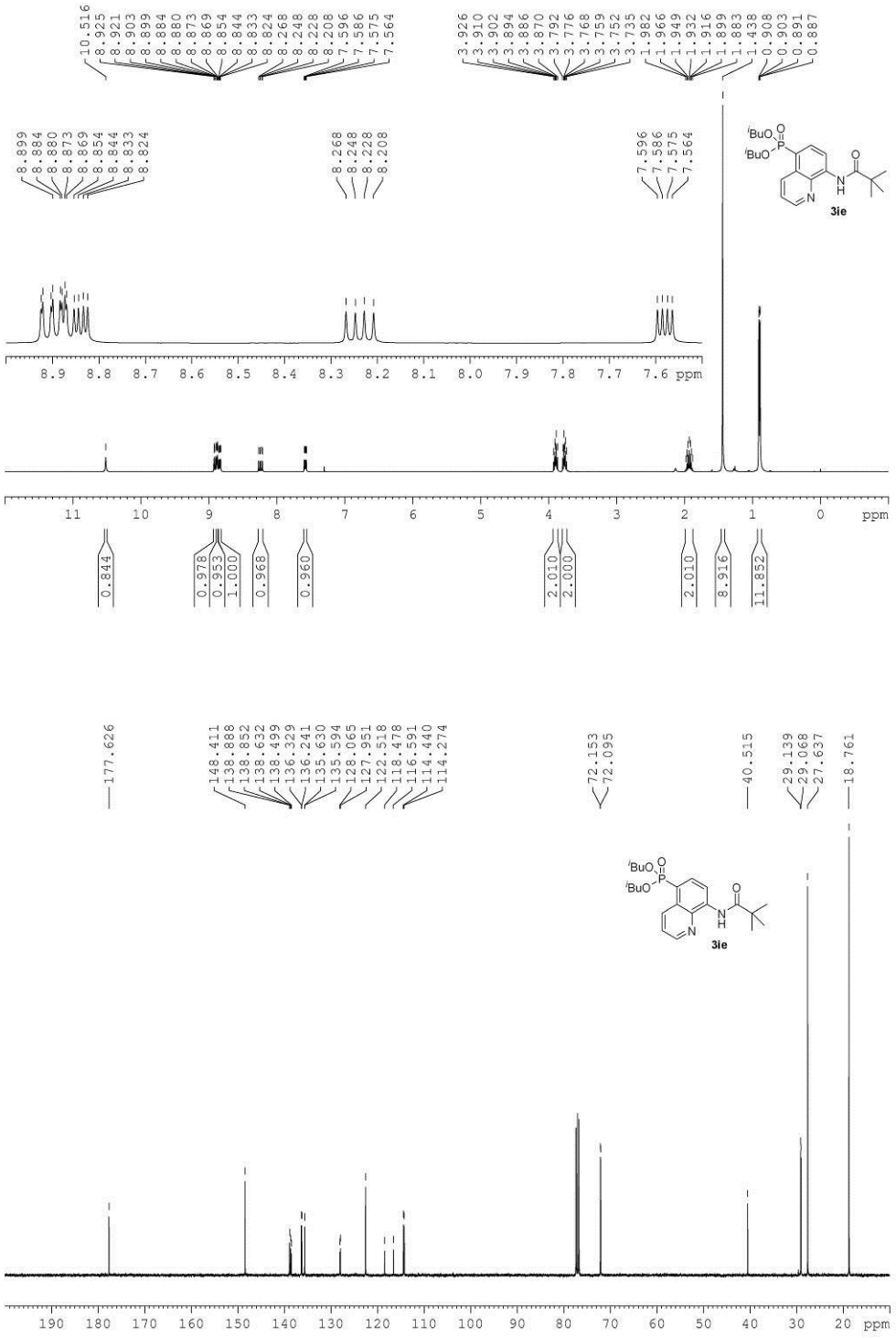

177.657
148.414
138.962
138.926
138.640
138.506
136.345
136.256
135.592
135.555
128.099
127.985
122.614
118.490
116.611
114.440
114.275
62.310
62.258
40.530
27.639
16.366
16.302
3ic
ppm

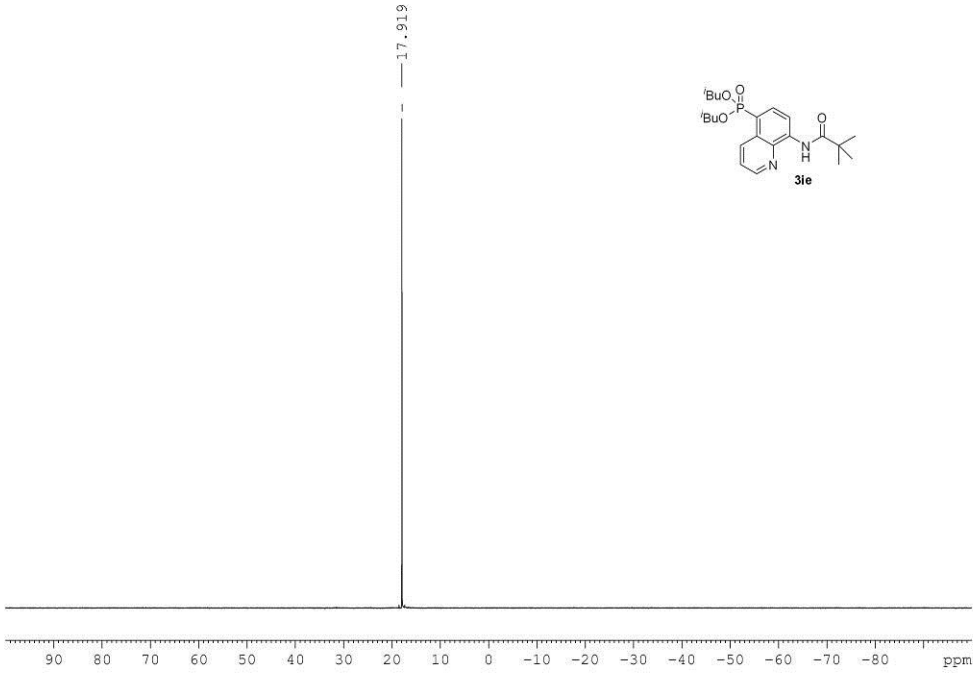

17.807
EtO
EtO
O
P
N
H
N
O
3ic
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

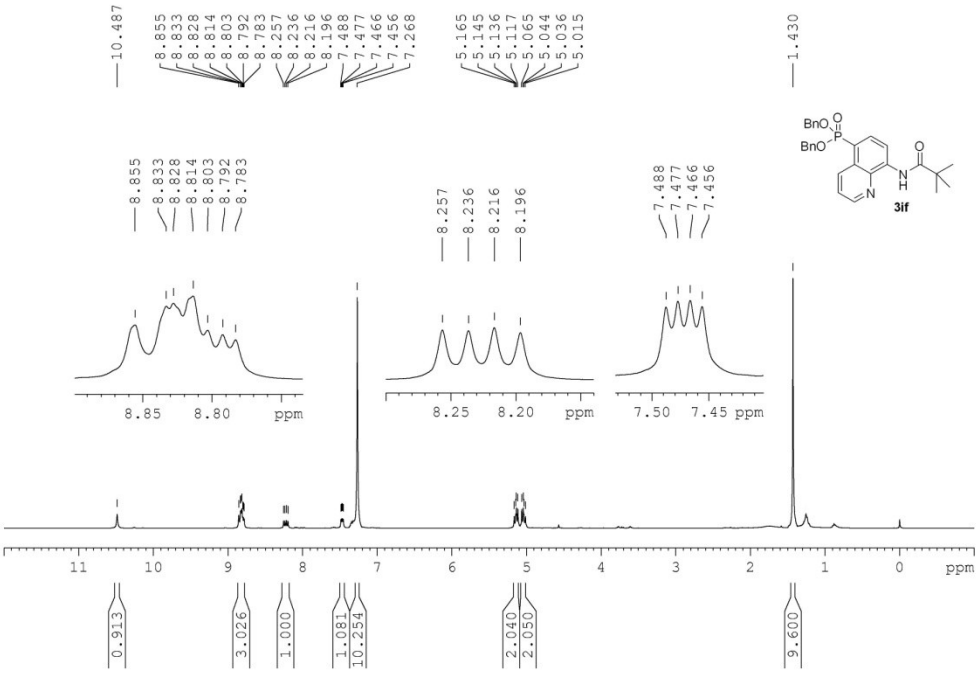

10.509
8.918
8.915
8.897
8.893
8.879
8.875
8.869
8.865
8.845
8.836
8.825
8.816
8.253
8.233
8.214
8.194
7.592
7.582
7.571
7.560
4.157
4.140
4.132
4.123
4.115
4.106
4.098
4.081
4.039
4.022
4.014
4.004
3.997
3.988
3.979
3.962
1.667
1.650
1.632
1.613
1.596
1.436
1.381
1.363
1.345
1.341
1.326
1.323
0.884
0.866
0.847
nBuO
nBuO
O
P
N
H
N
O
3id
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.788
0.978
0.967
0.970
1.000
0.968
2.095
2.022
4.073
9.014
4.136
5.988

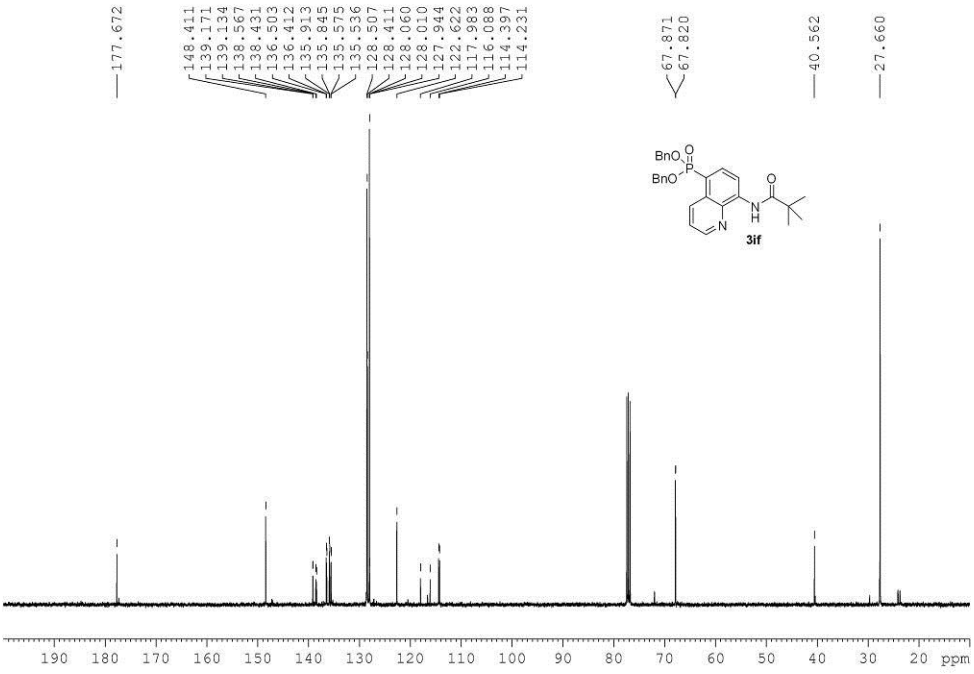

177.627
148.395
138.902
138.867
138.634
138.502
136.305
136.217
135.608
135.572
128.106
127.992
122.531
118.532
116.650
114.442
114.278
65.977
65.923
40.520
32.413
32.348
27.634
18.735
13.507
3id
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

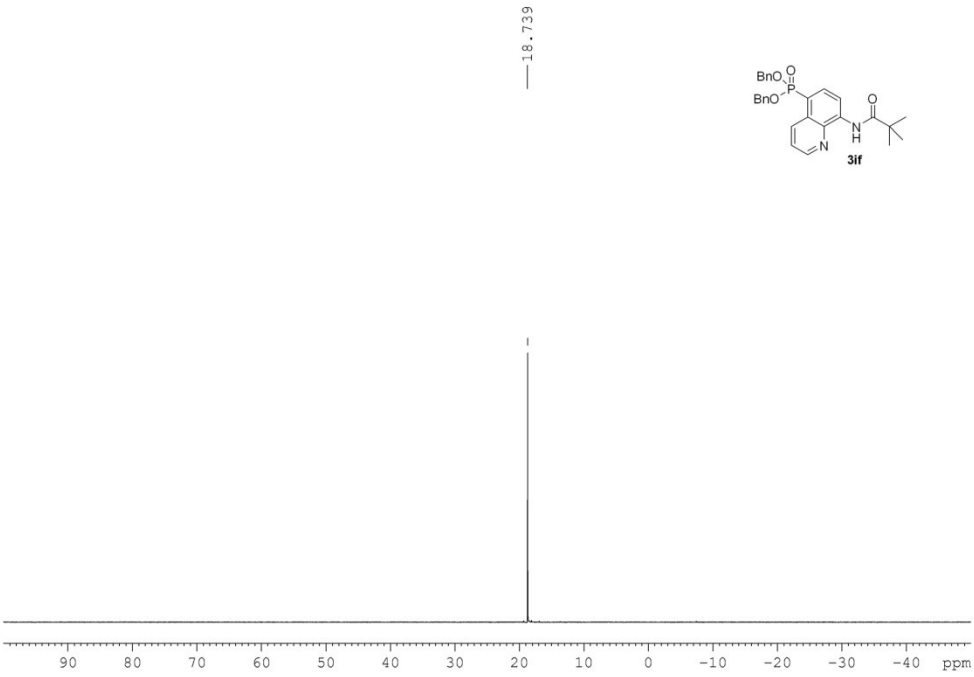

17.930
3id
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

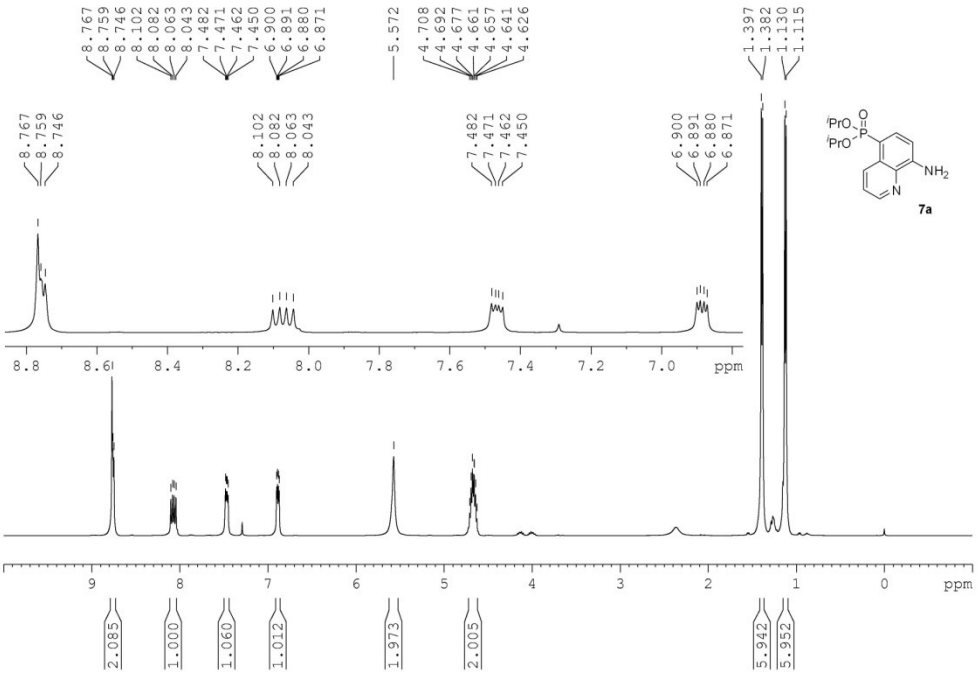

10.516
8.925
8.921
8.903
8.899
8.884
8.880
8.873
8.869
8.854
8.844
8.833
8.824
8.268
8.248
8.228
8.208
7.596
7.586
7.575
7.564
3.926
3.910
3.902
3.894
3.886
3.870
3.792
3.776
3.768
3.759
3.752
3.735
1.982
1.966
1.949
1.932
1.916
1.899
1.883
1.438
1.908
0.903
0.891
0.887
3ie
0.844
0.978
0.953
1.000
0.968
0.960
2.010
2.000
2.010
8.916
11.852
ppm
177.626
148.411
138.888
138.852
138.632
138.499
136.329
136.241
135.630
135.594
128.065
127.951
122.518
118.478
116.591
114.440
114.274
72.153
72.095
40.515
29.139
29.068
27.637
18.761
3ie
ppm

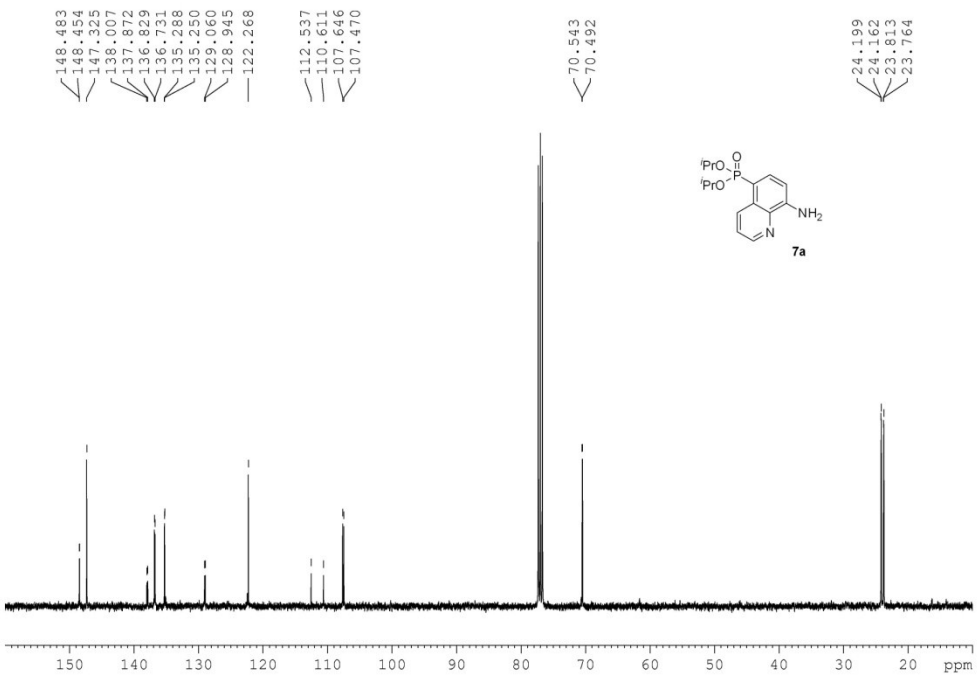

17.919
3ie
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

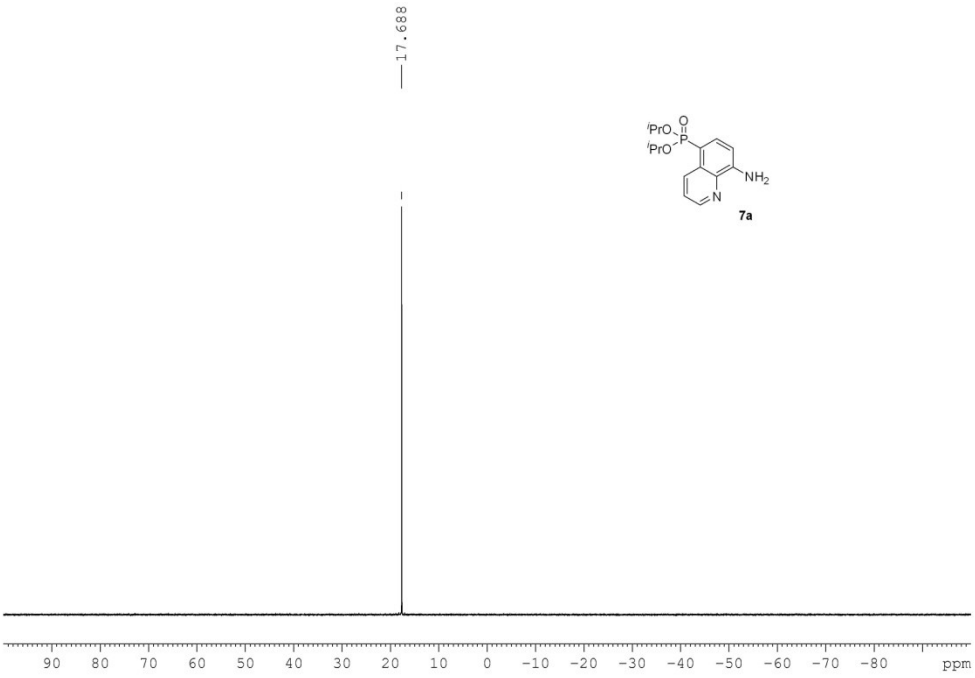

10.487
8.855
8.833
8.828
8.814
8.803
8.792
8.783
8.257
8.236
8.216
8.196
7.488
7.477
7.466
7.456
7.268
5.165
5.145
5.136
5.117
5.065
5.044
5.036
5.015
1.430
3if
8.85 8.80 ppm
8.25 8.20 ppm
7.50 7.45 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.913
3.026
1.000
1.081
10.254
2.040
2.050
9.600


177.672
148.411
139.171
139.134
138.567
138.431
136.503
136.412
135.913
135.845
135.575
135.536
128.507
128.411
128.060
128.010
127.944
122.622
117.983
116.088
114.397
114.231
67.871
67.820
40.562
27.660
BnO
BnO
P
O
N
H
3if
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


18.739
BnO
BnO
P
O
N
H
3if
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


8.767
8.759
8.746
8.102
8.082
8.063
8.043
7.482
7.471
7.462
7.450
6.900
6.891
6.880
6.871
5.572
4.708
4.692
4.677
4.661
4.657
4.641
4.626
1.397
1.382
1.130
1.115
ppm
2.085
1.000
1.060
1.012
1.973
2.005
5.942
5.952
7a


148.483
148.454
147.325
138.007
137.872
136.829
136.731
135.288
135.250
129.060
128.945
122.268
112.537
110.611
107.646
107.470
70.543
70.492
24.199
24.162
23.813
23.764
ppm
7a


17.688
iPrO
iPrO
O
P
NH2
N
7a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm