

## Electronic Supplementary Information

for

# Synthesis of 3-phosphinoylquinolines via a phosphinylation-cyclization-aromatization process mediated by *tert*-butyl hydroperoxide

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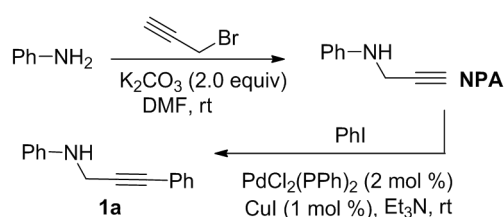
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## General:

$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were measured on Bruker 400 M spectrometers with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard or 85%  $\text{H}_3\text{PO}_4$  as external standard for  $^{31}\text{P}$  NMR. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the  $^1\text{H}$  spectrum as 0.00 ppm and  $\text{CDCl}_3$  resonance in the  $^{13}\text{C}$  spectrum as 77.16 ppm. All coupling constants ( $J$  values) were reported in Hertz (Hz). Chemical shifts of common trace  $^1\text{H}$  NMR impurities (ppm):  $\text{H}_2\text{O}$ : 1.56,  $\text{CHCl}_3$ : 7.26. HRMS spectra were recorded on a Bruker En Apex ultra 7.0 FT-MS apparatus. Column chromatography was performed on silica gel 300- 400 mesh. All new compounds were further characterized by HRMS (FT-ICR-MS) and electrospray ionization source in positive ion mode.

## 1. Experimental procedure for the synthesis of N-(3-phenyl-2-propynyl)aniline (1a)



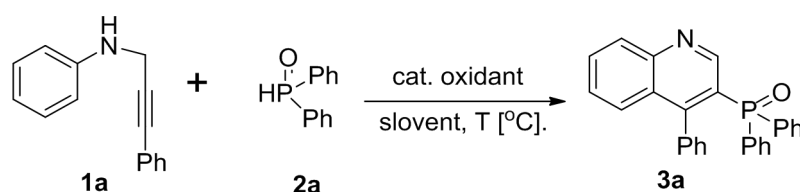
(1) An oven-dried round bottom flask (250 mL) with a magnetic stirring bar was charged with aniline (7.45 g, 80.0 mmol, 4.0 equiv), potassium carbonate (5.52 g, 40.0 mmol, 2.0 equiv), and *N,N*-dimethylformamide (DMF, 100 mL). A solution of propargyl bromide (2.38 g, 20.0 mmol, 1.0 equiv) in *N,N*-dimethylformamide (DMF, 8 mL) was added to the flask dropwise. The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was filtered, and then diluted with 250 mL of AcOEt. The mixture was washed with brine three times. The organic phase was dried over anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), filtered and concentrated under vacuum and the crude product was purified by silica gel chromatography using a petroleum ether/AcOEt mixture [20:1 (v/v)] as the eluent to give NPA (N-(2-propynyl)aniline, 2.15 g, 82% yield) as a light yellow oil.

(2) An oven-dried round bottom flask (250 mL) with a magnetic stir bar was charged with NPA (1.97 g, 15 mmol, 1.0 equiv), triethylamine (94 mL), iodobenzene (3.37 g, 16.5 mmol, 1.1 equiv), bis(triphenylphosphine)palladium dichloride (210.6 mg, 0.3 mmol, 0.02 equiv), and copper iodide (29 mg, 0.015 mmol, 0.01 equiv). The reaction mixture is stirred at 40 °C for 6 h. The reaction mixture was filtered, and then diluted with 250 mL of AcOEt. The mixture was washed with brine three times. The combined organic phases are dried over anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), filtered and concentrated under vacuum and the crude product was purified by silica gel chromatography using a petroleum ether/AcOEt mixture [20:1 (v/v)] as the eluent to give the N-(3-phenyl-2-propynyl)aniline (**1a**, 2.86 g, 92%) as a light yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.45-7.39 (m, 2H), 7.29-7.21 (m, 5H), 6.79 (t,  $J = 7.3$  Hz, 1H), 6.73 (d,  $J = 8.2$  Hz, 2H), 4.15 (s, 2H), 3.95 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  147.3, 131.9, 129.4, 128.5, 128.4, 123.0, 118.7, 113.8, 86.6, 83.5, 34.8.

**Experimental procedure for the synthesis of 3-phosphinoylquinolines:** An oven-dried Schlenk tube with a magnetic stir bar containing P(O)H (0.6 mmol), N-propargylanilines (0.2 mmol), DMF

(2.0 mL) was evacuated and purged with argon three times. TBHP (0.7 mmol) was added to the system at room temperature. The resulting mixture was stirred at 60 °C for 6 h. The reaction solution was allowed to cool to ambient temperature, and then diluted with ethyl acetate. The mixture was washed with brine three times. The organic layer was concentrated under vacuum and the crude product was purified by silica gel chromatography using a petroleum ether/AcOEt mixture [from 3:1 to 1:1 (v/v)] as the eluent to give the corresponding products.

**Table 1.** Optimization of reaction conditions<sup>a</sup>



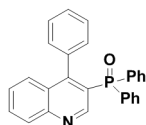
Entry	Catalyst	Oxidant (equiv)	Solvent	Temp (°C)	Yield <sup>b</sup> (%)
1	CuSO <sub>4</sub>	TBHP (3)	MeCN	60	40
2	AgNO <sub>3</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.3)	MeCN	100	trace
3	-	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O (3)	AcOH	60	trace
4	Bu <sub>4</sub> NI	TBHP (3)	MeCN	80	trace
5	-	TBHP (5)	MeCN	100	42
6	-	DTBP (5)	MeCN	100	30
7	-	TBPB (5)	MeCN	100	37
8	-	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (5)	MeCN	100	trace
9	-	H <sub>2</sub> O <sub>2</sub> (10)	MeCN	100	trace
10	-	TBHP (3.5)	MeCN	60	45
11	-	TBHP (3.5)	dioxane	60	42
<b>12</b>	-	<b>TBHP (3.5)</b>	<b>DMF</b>	<b>60</b>	<b>65</b>
13	-	TBHP (3.5)	DMSO	60	46
14	-	TBHP (3.5)	MeCN	60	45
15	-	TBHP (3.5)	DCE	60	46
16	-	TBHP (3.5)	EtOH	60	0
17	-	TBHP (3.5)	toluene	60	0
18 <sup>c</sup>	-	TBHP (3.5)	DMF	60	47
19	-	TBHP (3.5)	DMF	80	57
20	-	TBHP (3.5)	DMF	rt	20
21	-	TBHP (2.5)	DMF	60	44
22 <sup>d</sup>	-	TBHP (3.5)	DMF	60	50
23 <sup>e</sup>	-	TBHP (3.5)	DMF	60	trace

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.02 mmol), oxidant, DMF (2 mL), 60 °C (oil bath) under Ar for 6 h. TBHP = tertbutyl hydroperoxide 70% in water;

<sup>b</sup> Isolated yield based on **1a**. <sup>c</sup> TBHP(5-6M in decane). <sup>d</sup> **2a** (0.4 mmol). <sup>e</sup> Under air.

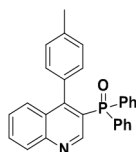
### Spectral data.

#### Diphenyl(4-phenylquinolin-3-yl)phosphine oxide (3a)



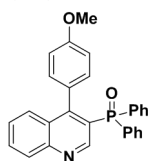
White solid; m.p. 193.9-195.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.86 (d, *J* = 6.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.82-7.77 (m, 1H), 7.64-7.58 (m, 4H), 7.49-7.43 (m, 4H), 7.39-7.34 (m, 4H), 7.26-7.22 (m, 1H), 7.17-7.13 (m, 2H), 7.09-7.06 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 155.6 (d, *J*<sub>C-P</sub> = 7.3 Hz), 151.8 (d, *J*<sub>C-P</sub> = 14.8 Hz), 149.4, 134.5 (d, *J*<sub>C-P</sub> = 5.0 Hz), 132.5 (d, *J*<sub>C-P</sub> = 105.6 Hz), 131.7 (d, *J*<sub>C-P</sub> = 9.6 Hz), 131.7, 131.6, 130.5, 129.7, 128.5 (d, *J*<sub>C-P</sub> = 12.2 Hz), 128.2, 127.7 (d, *J*<sub>C-P</sub> = 8.9 Hz), 127.4, 127.3, 127.2, 125.1 (d, *J*<sub>C-P</sub> = 100.8 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.6. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>20</sub>NNaOP<sup>+</sup>: 428.1175, found: 428.1182.

#### Diphenyl(4-(p-tolyl)quinolin-3-yl)phosphine oxide (3b)



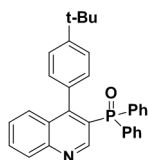
White solid; m.p. 239.6-241.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.84 (d, *J* = 6.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.78-7.73 (m, 1H), 7.61-7.55 (m, 4H), 7.52-7.40 (m, 4H), 7.36-7.30 (m, 4H), 6.95-6.89 (m, 4H), 2.29 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 155.9 (d, *J*<sub>C-P</sub> = 7.3 Hz), 152.0 (d, *J*<sub>C-P</sub> = 14.9 Hz), 149.4, 138.1, 132.7 (d, *J*<sub>C-P</sub> = 105.5 Hz), 131.8 (d, *J*<sub>C-P</sub> = 9.8 Hz), 131.7 (d, *J*<sub>C-P</sub> = 2.7 Hz), 131.61, 131.60, 131.59, 130.5, 129.7, 128.4 (d, *J*<sub>C-P</sub> = 12.2 Hz), 128.1, 127.9 (d, *J*<sub>C-P</sub> = 8.9 Hz), 127.4, 125.2 (d, *J*<sub>C-P</sub> = 101.4 Hz), 21.4; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.7. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>28</sub>H<sub>22</sub>NNaOP<sup>+</sup>: 442.1331, found: 442.1326.

#### (4-(4-Methoxyphenyl)quinolin-3-yl)diphenylphosphine oxide (3c)



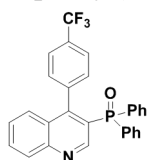
White solid; m.p. 195.7-198.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.81 (d, *J* = 6.0 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.83-7.45 (m, 1H), 7.63-7.52 (m, 5H), 7.46-7.41 (m, 3H), 7.37-7.32 (m, 4H), 7.01-6.98 (m, 2H), 6.66-6.63 (m, 2H), 3.78 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.6, 155.8 (d, *J*<sub>C-P</sub> = 7.3 Hz), 152.0 (d, *J*<sub>C-P</sub> = 15.2 Hz), 149.5, 132.6 (d, *J*<sub>C-P</sub> = 105.6 Hz), 132.0, 131.71 (d, *J*<sub>C-P</sub> = 9.3 Hz), 131.7 (d, *J*<sub>C-P</sub> = 3.1 Hz), 131.6, 129.7, 128.5 (d, *J*<sub>C-P</sub> = 12.4 Hz), 128.1 (d, *J*<sub>C-P</sub> = 8.9 Hz), 127.4, 127.3, 126.8 (d, *J*<sub>C-P</sub> = 5.1 Hz), 125.5 (d, *J*<sub>C-P</sub> = 101.2 Hz), 113.0, 55.4; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.5. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>28</sub>H<sub>22</sub>NNaO<sub>2</sub>P<sup>+</sup>: 458.1280, found: 458.1276.

#### (4-(4-(tert-Butyl)phenyl)quinolin-3-yl)diphenylphosphine oxide (3d)



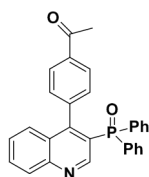
White solid; m.p. 273.1-273.9 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.84 (d,  $J = 6.0$  Hz, 1H), 8.13 (d,  $J = 8.4$  Hz, 1H), 7.80-7.75 (m, 1H), 7.63-7.54 (m, 5H), 7.47-7.40 (m, 3H), 7.35-7.29 (m, 4H), 7.13-7.10 (m, 2H), 7.05-7.02 (m, 2H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  156.1 (d,  $J_{\text{C-P}} = 7.4$  Hz), 152.1 (d,  $J_{\text{C-P}} = 14.9$  Hz), 151.1, 149.5, 132.6 (d,  $J_{\text{C-P}} = 106.3$  Hz), 131.7 (d,  $J_{\text{C-P}} = 9.7$  Hz), 131.66, 131.61 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.5 (d,  $J_{\text{C-P}} = 5.4$  Hz), 130.6, 129.8, 128.5 (d,  $J_{\text{C-P}} = 12.1$  Hz), 127.8 (d,  $J_{\text{C-P}} = 8.9$  Hz), 127.5, 127.4, 125.4 (d,  $J_{\text{C-P}} = 101.1$  Hz), 124.3, 34.7, 31.5;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.0. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{31}\text{H}_{29}\text{NOP}^+$ : 462.1981, found: 462.1984.

### Diphenyl(4-(4-(trifluoromethyl)phenyl)quinolin-3-yl)phosphine oxide (3e)



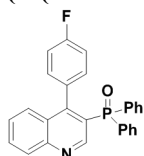
Pale yellow solid; m.p. 164.2-167.8 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.84 (d,  $J = 5.9$  Hz, 1H), 8.17 (d,  $J = 8.4$  Hz, 1H), 7.83-7.78 (m, 1H), 7.62-7.57 (m, 4H), 7.49-7.45 (m, 3H), 7.38-7.34 (m, 7H), 7.21-7.15 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  153.9 (d,  $J = 7.1$  Hz), 151.7 (d,  $J = 14.5$  Hz), 149.5, 138.3, 132.1 (d,  $J_{\text{C-P}} = 105.4$  Hz), 132.0 (d,  $J = 2.7$  Hz), 131.9, 131.8 (d,  $J_{\text{C-P}} = 9.5$  Hz), 131.1, 130.4 (q,  $J_{\text{C-F}} = 31.9$  Hz), 130.0, 128.8 (d,  $J_{\text{C-P}} = 12.4$  Hz), 127.9, 127.2 (d,  $J = 8.6$  Hz), 126.8, 125.6 (d,  $J_{\text{C-P}} = 99.5$  Hz), 124.4 (q,  $J_{\text{C-F}} = 4.0$  Hz), 124.0 (q,  $J_{\text{C-F}} = 272.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.1;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.9. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{28}\text{H}_{19}\text{F}_3\text{NNaOP}^+$ : 496.1049, found: 496.1050.

### 1-(4-(3-(Diphenylphosphoryl)quinolin-4-yl)phenyl)ethanone (3f)



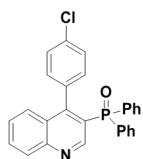
White solid; m.p. 201.3-204.9 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.79 (d,  $J = 5.9$  Hz, 1H), 8.15 (d,  $J = 8.5$  Hz, 1H), 7.82-7.72 (m, 3H), 7.61-7.55 (m, 4H), 7.49-7.43 (m, 3H), 7.38-7.34 (m, 5H), 7.17 (d,  $J = 8.2$  Hz, 2H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  197.9, 154.4 (d,  $J_{\text{C-P}} = 7.1$  Hz), 151.7 (d,  $J_{\text{C-P}} = 14.6$  Hz), 149.4, 139.6 (d,  $J_{\text{C-P}} = 5.1$  Hz), 136.6, 132.2 (d,  $J_{\text{C-P}} = 106.8$  Hz), 132.1 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.9, 131.8 (d,  $J_{\text{C-P}} = 9.5$  Hz), 130.9, 129.9, 128.7 (d,  $J_{\text{C-P}} = 12.6$  Hz), 127.8, 127.3, 127.2 (d,  $J_{\text{C-P}} = 8.9$  Hz), 126.8, 125.2 (d,  $J_{\text{C-P}} = 99.6$  Hz), 26.9;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.6. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{29}\text{H}_{23}\text{NO}_2\text{P}^+$ : 448.1461, found: 448.1465.

### (4-(4-Fluorophenyl)quinolin-3-yl)diphenylphosphine oxide (3g)



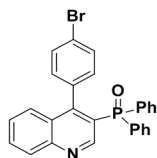
Pale yellow solid; m.p. 284.8-288.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.79 (d, *J* = 6.0 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.81-7.77 (m, 1H), 7.63-7.58 (m, 4H), 7.51-7.35 (m, 8H), 7.07-7.03 (m, 2H), 6.84-6.80 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 162.7 (d, *J*<sub>C-F</sub> = 248.2 Hz), 154.7 (d, *J* = 7.1 Hz), 151.8 (d, *J* = 14.7 Hz), 149.5, 132.6 (d, *J* = 8.3 Hz), 132.4 (d, *J*<sub>C-P</sub> = 105.6 Hz), 131.9 (d, *J* = 3.5 Hz), 131.8, 131.7 (d, *J* = 9.5 Hz), 130.4 (dd, *J*<sub>1</sub> = 4.7 Hz, *J*<sub>2</sub> = 3.4 Hz), 129.9, 128.7 (d, *J*<sub>C-P</sub> = 12.5 Hz), 127.8 (d, *J*<sub>C-P</sub> = 8.9 Hz), 127.7, 127.0, 125.7 (d, *J*<sub>C-P</sub> = 100.1 Hz), 114.5 (d, *J* = 21.7 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.3; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): δ -113.2. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>19</sub>FNNaOP<sup>+</sup>: 446.1081, found: 446.1084.

#### (4-(4-Chlorophenyl)quinolin-3-yl)diphenylphosphine oxide (3h)



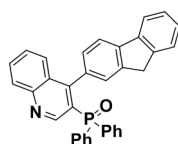
White solid; m.p. 195.4-197.6 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.75 (d, *J* = 6.0 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.74-7.70 (m, 1H), 7.55-7.50 (m, 4H), 7.43-7.29 (m, 8H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 154.1 (d, *J*<sub>C-P</sub> = 7.0 Hz), 151.6 (d, *J*<sub>C-P</sub> = 14.7 Hz), 149.3, 133.3 (d, *J*<sub>C-P</sub> = 5.2 Hz), 132.1 (d, *J*<sub>C-P</sub> = 105.9 Hz), 132.0, 131.8 (d, *J*<sub>C-P</sub> = 2.7 Hz), 131.7, 131.6 (d, *J*<sub>C-P</sub> = 9.8 Hz), 130.5, 129.7, 128.5 (d, *J*<sub>C-P</sub> = 12.5 Hz), 127.6, 127.2 (d, *J*<sub>C-P</sub> = 8.7 Hz), 126.7, 125.4 (d, *J*<sub>C-P</sub> = 100.1 Hz), 122.8; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.4. HRMS: [M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>20</sub>ClNOP<sup>+</sup>: 440.0966, found: 440.0970.

#### (4-(4-Bromophenyl)quinolin-3-yl)diphenylphosphine oxide (3i)



White solid; m.p. 153.0-156.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.81 (d, *J* = 6.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.81-7.76 (m, 1H), 7.63-7.57 (m, 4H), 7.50-7.46 (m, 4H), 7.40-7.35 (m, 4H), 7.12-7.08 (m, 2H), 7.01-6.97 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 154.4 (d, *J*<sub>C-P</sub> = 7.1 Hz), 151.8 (d, *J*<sub>C-P</sub> = 14.7 Hz), 149.5, 134.6, 133.0 (d, *J*<sub>C-P</sub> = 5.2 Hz), 132.3 (d, *J*<sub>C-P</sub> = 105.6 Hz), 132.0, 131.9 (d, *J*<sub>C-P</sub> = 2.8 Hz), 131.8, 131.7 (d, *J*<sub>C-P</sub> = 9.4 Hz), 129.9, 128.7 (d, *J*<sub>C-P</sub> = 12.1 Hz), 127.7, 127.6, 127.5 (d, *J*<sub>C-P</sub> = 8.9 Hz), 126.9, 125.6 (d, *J*<sub>C-P</sub> = 100.1 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.4. HRMS: [M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>20</sub>BrNOP<sup>+</sup>: 484.0460, found: 484.0462.

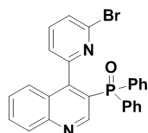
#### (4-(9H-fluoren-2-yl)quinolin-3-yl)diphenylphosphine oxide (3j)



White solid; m.p. 256.1-256.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.84 (d, *J* = 5.9 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.73-7.68 (m, 2H), 7.55-7.45 (m, 7H), 7.38-7.25 (m, 5H), 7.23-7.16 (m, 4H), 7.07-7.02 (m, 2H), 3.60 (dd, *J*<sub>1</sub> = 60.2 Hz, *J*<sub>2</sub> = 21.9 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 156.1 (d, *J*<sub>C-P</sub> = 7.4 Hz), 152.0 (d, *J*<sub>C-P</sub> = 14.7 Hz), 149.5, 143.6, 142.2, 141.9, 141.2, 133.0 (d, *J*<sub>C-P</sub> = 5.2

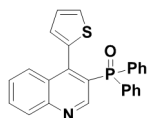
Hz), 132.7 (d,  $J_{C-P} = 105.5$  Hz), 132.4 (d,  $J_{C-P} = 105.5$  Hz), 131.8 (d,  $J_{C-P} = 9.7$  Hz), 131.77 (d,  $J_{C-P} = 9.7$  Hz), 131.7, 131.69 (d,  $J_{C-P} = 2.8$  Hz), 131.5 (d,  $J_{C-P} = 2.8$  Hz), 129.8, 129.5, 128.5 (d,  $J_{C-P} = 12.3$  Hz), 128.4 (d,  $J_{C-P} = 12.3$  Hz), 127.9 (d,  $J_{C-P} = 8.7$  Hz), 127.5, 127.4, 127.3, 127.2, 127.0, 125.5 (d,  $J_{C-P} = 101.0$  Hz), 125.2, 120.3, 118.9, 36.9;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.5. HRMS:  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_2\text{P}^+$ : 494.1668, found: 494.1666.

#### (4-(6-Bromopyridin-2-yl)quinolin-3-yl)diphenylphosphine oxide (3k)



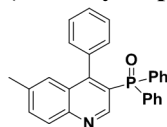
White solid; m.p. 219.7-220.8 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.87 (d,  $J = 5.7$  Hz, 1H), 8.32 (s, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 7.71-7.56 (m, 4H), 7.52-7.38 (m, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  152.4 (d,  $J_{C-P} = 5.4$  Hz), 151.8 (d,  $J_{C-P} = 14.3$  Hz), 151.7 (d,  $J_{C-P} = 6.7$  Hz), 150.1, 149.7, 138.4, 132.1 (d,  $J_{C-P} = 105.5$  Hz), 132.0, 131.98, 131.95 (d,  $J_{C-P} = 10.0$  Hz), 130.0, 128.7 (d,  $J_{C-P} = 12.3$  Hz), 128.2, 128.1, 126.6, 126.5 (d,  $J_{C-P} = 8.2$  Hz), 124.9 (d,  $J_{C-P} = 98.8$  Hz), 120.9;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  25.7. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{26}\text{H}_{18}\text{BrN}_2\text{NaOP}^+$ : 507.0232, found: 507.0231.

#### Diphenyl(4-(thiophen-2-yl)quinolin-3-yl)phosphine oxide (3l)



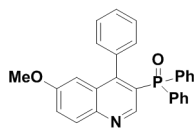
Pale yellow solid; m.p. 182.2-186.7 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.77 (d,  $J = 6.0$  Hz, 1H), 8.06 (d,  $J = 8.4$  Hz, 1H), 7.74-7.69 (m, 2H), 7.58-7.53 (m, 4H), 7.45-7.38 (m, 3H), 7.33-7.29 (m, 4H), 7.20-7.19 (m, 1H), 7.00 (d,  $J = 3.5$  Hz, 1H), 6.81 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 3.7$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  152.0 (d,  $J_{C-P} = 14.4$  Hz), 149.5, 148.5 (d,  $J_{C-P} = 6.4$  Hz), 134.3 (d,  $J_{C-P} = 5.6$  Hz), 132.2 (d,  $J_{C-P} = 106.3$  Hz), 132.1, 131.9 (d,  $J_{C-P} = 2.7$  Hz), 131.85, 131.8 (d,  $J_{C-P} = 9.8$  Hz), 131.7, 129.7, 128.64 (d,  $J_{C-P} = 12.4$  Hz), 128.63, 127.8, 127.0, 126.74, 126.7 (d,  $J_{C-P} = 100.1$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  25.1. HRMS:  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{25}\text{H}_{19}\text{NOP}^+$ : 412.0919, found: 412.0920.

#### (6-Methyl-4-phenylquinolin-3-yl)diphenylphosphine oxide (3m)



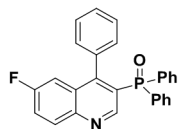
White solid; m.p. 239.6-241.7 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.75 (d,  $J = 6.0$  Hz, 1H), 8.03 (d,  $J = 8.5$  Hz, 1H), 7.62-7.56 (m, 5H), 7.46-7.42 (m, 2H), 7.36-7.32 (m, 4H), 7.26-7.18 (m, 2H), 7.15-7.11 (m, 2H), 7.06-7.03 (m, 2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  154.9 (d,  $J_{C-P} = 7.4$  Hz), 152.0 (d,  $J_{C-P} = 15.0$  Hz), 148.1, 137.6, 134.6 (d,  $J_{C-P} = 4.8$  Hz), 134.0, 132.6 (d,  $J_{C-P} = 105.6$  Hz), 131.8 (d,  $J_{C-P} = 9.5$  Hz), 131.7 (d,  $J_{C-P} = 2.8$  Hz), 130.7, 129.4, 128.5 (d,  $J_{C-P} = 12.3$  Hz), 128.2, 127.7 (d,  $J_{C-P} = 8.9$  Hz), 127.4, 125.8, 125.1 (d,  $J_{C-P} = 100.9$  Hz), 21.9;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.7. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{28}\text{H}_{22}\text{NNaOP}^+$ : 442.1331, found: 442.1326.

### (6-Methoxy-4-phenylquinolin-3-yl)diphenylphosphine oxide (3n)



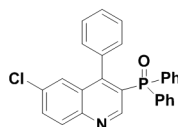
Pale yellow solid; m.p. 97.6-99.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.66 (d, *J* = 6.1 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.61-7.56 (m, 4H), 7.46-7.42 (m, 3H), 7.37-7.32 (m, 4H), 7.23-7.19 (m, 1H), 7.15-7.11 (m, 2H), 7.06-7.04 (m, 2H), 6.66 (d, *J* = 2.86 Hz, 1H), 3.62 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 158.4, 154.0 (d, *J*<sub>C-P</sub> = 7.4 Hz), 149.6 (d, *J*<sub>C-P</sub> = 15.0 Hz), 145.8, 134.8 (d, *J*<sub>C-P</sub> = 5.1 Hz), 132.6 (d, *J*<sub>C-P</sub> = 105.4 Hz), 131.8 (d, *J*<sub>C-P</sub> = 9.7 Hz), 131.7, 131.2, 130.5, 129.0 (d, *J*<sub>C-P</sub> = 9.1 Hz), 128.6 (d, *J*<sub>C-P</sub> = 12.5 Hz), 128.3, 127.6, 125.3 (d, *J*<sub>C-P</sub> = 100.7 Hz), 124.5, 104.6, 55.5; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.9. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>28</sub>H<sub>22</sub>NNaO<sub>2</sub>P<sup>+</sup>: 458.1280, found: 458.1276.

### (4-(4-Fluorophenyl)quinolin-3-yl)diphenylphosphine oxide (3o)



White solid; m.p. 209.4-213.4 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.79 (d, *J* = 5.9 Hz, 1H), 8.13 (dd, *J*<sub>1</sub> = 9.2 Hz, *J*<sub>2</sub> = 5.4 Hz, 1H), 7.61-7.50 (m, 5H), 7.47-7.42 (m, 2H), 7.37-7.32 (m, 4H), 7.26-7.20 (m, 1H), 7.15-7.10 (m, 2H), 7.06-7.01 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 161.0 (d, *J*<sub>C-F</sub> = 248.4 Hz), 155.0 (dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 5.9 Hz), 151.3 (dd, *J*<sub>1</sub> = 14.6 Hz, *J*<sub>2</sub> = 2.5 Hz), 146.6, 134.1 (d, *J* = 4.8 Hz), 132.30 (d, *J* = 9.1 Hz), 132.28 (d, *J*<sub>C-P</sub> = 101.7 Hz), 131.9, 131.8 (d, *J* = 9.5 Hz), 130.4, 128.8 (d, *J*<sub>C-P</sub> = 9.1 Hz), 128.6 (d, *J*<sub>C-P</sub> = 12.7 Hz), 128.56, 127.6, 126.0 (d, *J*<sub>C-P</sub> = 99.7 Hz), 122.0 (d, *J* = 26.1 Hz), 110.5 (d, *J* = 23.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.5; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): δ -110.6. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>19</sub>FNNaOP<sup>+</sup>: 446.1081, found: 446.1084.

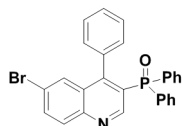
### (6-Chloro-4-phenylquinolin-3-yl)diphenylphosphine oxide (3p)



White solid; m.p. 268.2-271.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.74 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, *J*<sub>1</sub> = 8.9 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H), 7.53-7.49 (m, 4H), 7.41-7.34 (m, 3H), 7.31-7.26 (m, 4H), 7.19-7.15 (m, 1H), 7.09-7.05 (m, 2H), 6.98-6.95 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 154.8 (d, *J*<sub>C-P</sub> = 7.7 Hz), 152.1 (d, *J*<sub>C-P</sub> = 14.7 Hz), 147.9, 133.8 (d, *J*<sub>C-P</sub> = 2.7 Hz), 133.6, 132.6, 132.2 (d, *J*<sub>C-P</sub> = 104.2 Hz), 131.9 (d, *J*<sub>C-P</sub> = 2.7 Hz), 131.8 (d, *J*<sub>C-P</sub> = 9.7 Hz), 131.4, 130.5, 128.7 (d, *J*<sub>C-P</sub> = 12.1 Hz), 128.6, 128.56 (d, *J*<sub>C-P</sub> = 8.2 Hz), 127.6, 126.3 (d, *J*<sub>C-P</sub> = 100.9 Hz), 125.9; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 24.4. HRMS: [M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>20</sub>ClNOP<sup>+</sup>: 440.0966, found: 440.0970.

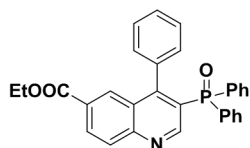
### (6-Bromo-4-phenylquinolin-3-yl)diphenylphosphine oxide (3q)





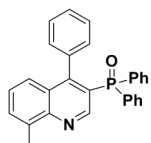
Pale yellow solid; m.p. 263.4-264.9 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.75 (d,  $J = 5.9$  Hz, 1H), 7.93 (d,  $J = 9.0$  Hz, 1H), 7.76 (dd,  $J_1 = 8.9$  Hz,  $J_2 = 1.9$  Hz, 1H), 7.53-7.48 (m, 5H), 7.40-7.36 (m, 2H), 7.30-7.26 (m, 4H), 7.20-7.15 (m, 1H), 7.09-7.05 (m, 2H), 6.96-6.95 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  154.7 (d,  $J_{\text{C-P}} = 7.7$  Hz), 152.2 (d,  $J_{\text{C-P}} = 14.8$  Hz), 148.1, 135.1, 133.8 (d,  $J_{\text{C-P}} = 5.1$  Hz), 132.2 (d,  $J_{\text{C-P}} = 105.8$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.7 (d,  $J_{\text{C-P}} = 9.5$  Hz), 131.5, 130.5, 129.2, 129.0 (d,  $J_{\text{C-P}} = 9.0$  Hz), 128.7, 128.6 (d,  $J_{\text{C-P}} = 12.5$  Hz), 127.6, 126.2 (d,  $J_{\text{C-P}} = 99.3$  Hz), 121.8 (d,  $J_{\text{C-P}} = 1.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.5. HRMS:  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{27}\text{H}_{20}\text{BrNOP}^+$ : 484.0460, found: 484.0458.

### Ethyl 3-(diphenylphosphoryl)-4-phenylquinoline-6-carboxylate (3r)



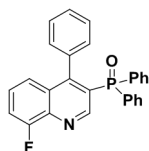
White solid; m.p. 196.2-198.9 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.91 (d,  $J = 6.0$  Hz, 1H), 8.37 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 1.9$  Hz, 1H), 8.23 (d,  $J = 1.7$  Hz, 1H), 8.18 (d,  $J = 8.8$  Hz, 1H), 7.62-7.57 (m, 4H), 7.48-7.44 (m, 2H), 7.38-7.34 (m, 4H), 7.28-7.23 (m, 1H), 7.18-7.14 (m, 2H), 7.10-7.07 (m, 2H), 4.32 (q,  $J = 7.1$  Hz, 2H), 1.31 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  165.9, 157.1 (d,  $J_{\text{C-P}} = 7.3$  Hz), 153.9 (d,  $J_{\text{C-P}} = 14.7$  Hz), 153.1, 133.8 (d,  $J_{\text{C-P}} = 5.1$  Hz), 133.2 (d,  $J_{\text{C-P}} = 105.0$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.7 (d,  $J_{\text{C-P}} = 9.5$  Hz), 131.0, 130.6, 130.3, 130.1, 129.4, 128.7, 128.6 (d,  $J_{\text{C-P}} = 12.4$  Hz), 127.6, 127.2 (d,  $J_{\text{C-P}} = 8.9$  Hz), 126.2 (d,  $J_{\text{C-P}} = 99.7$  Hz), 61.7, 14.3;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.4. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{30}\text{H}_{24}\text{NNaO}_3\text{P}^+$ : 500.1386, found: 500.1385.

### (8-Methyl-4-phenylquinolin-3-yl)diphenylphosphine oxide (3s)



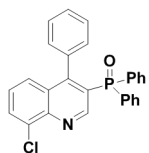
White solid; m.p. 169.0-172.7 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.81 (d,  $J = 6.0$  Hz, 1H), 7.63-7.57 (m, 5H), 7.47-7.42 (m, 2H), 7.37-7.29 (m, 6H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 2H), 7.07-7.04 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  156.0 (d,  $J_{\text{C-P}} = 7.2$  Hz), 150.7 (d,  $J_{\text{C-P}} = 15.1$  Hz), 148.5, 137.4, 134.9 (d,  $J_{\text{C-P}} = 4.9$  Hz), 132.5 (d,  $J_{\text{C-P}} = 105.4$  Hz), 131.84, 131.8 (d,  $J_{\text{C-P}} = 9.5$  Hz), 131.7 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.7, 128.6 (d,  $J_{\text{C-P}} = 12.1$  Hz), 128.2, 127.8 (d,  $J_{\text{C-P}} = 8.4$  Hz), 127.3, 127.1, 125.3, 124.9 (d,  $J_{\text{C-P}} = 101.1$  Hz), 18.4;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.6. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{28}\text{H}_{22}\text{NNaOP}^+$ : 442.1331, found: 442.1326

### (8-Fluoro-4-phenylquinolin-3-yl)diphenylphosphine oxide (3t)



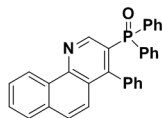
White solid; m.p. 178.1-179.8 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.77 (d,  $J = 5.9$  Hz, 1H), 7.55-7.50 (m, 4H), 7.43-7.38 (m, 3H), 7.34-7.27 (m, 5H), 7.19-7.15 (m, 2H), 7.09-7.05 (m, 2H), 7.00-6.97 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.2 (d,  $J_{\text{C-F}} = 257.7$  Hz), 155.7 (dd,  $J_1 = 7.9$  Hz,  $J_2 = 2.9$  Hz), 152.1 (d,  $J_1 = 15.3$  Hz), 139.9 (d,  $J = 12.1$  Hz), 134.3 (d,  $J = 4.9$  Hz), 132.2 (d,  $J_{\text{C-P}} = 106.0$  Hz), 132.0 (d,  $J = 2.5$  Hz), 131.8 (d,  $J_{\text{C-P}} = 9.6$  Hz), 130.6, 129.5 (d,  $J = 8.7$  Hz), 128.7 (d,  $J_{\text{C-P}} = 12.4$  Hz), 128.6, 127.5, 127.1 (d,  $J = 8.0$  Hz), 126.6 (d,  $J_{\text{C-P}} = 99.2$  Hz), 123.1 (d,  $J = 4.7$  Hz), 115.6 (d,  $J = 18.5$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.3;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -125.2. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{27}\text{H}_{19}\text{FNNaOP}^+$ : 446.1081, found: 446.1084.

### (8-Chloro-4-phenylquinolin-3-yl)diphenylphosphine oxide (3u)



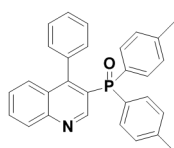
White solid; m.p. 268.2-271.3 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.87 (d,  $J = 5.9$  Hz, 1H), 7.89 (dd,  $J_1 = 7.2$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.61-7.56 (m, 4H), 7.48-7.32 (m, 8H), 7.26-7.21 (m, 1H), 7.16-7.11 (m, 2H), 7.06-7.03 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  156.4 (d,  $J_{\text{C-P}} = 7.3$  Hz), 152.4 (d,  $J_{\text{C-P}} = 15.3$  Hz), 145.7, 134.2 (d,  $J_{\text{C-P}} = 5.1$  Hz), 134.0, 132.1 (d,  $J_{\text{C-P}} = 106.4$  Hz), 132.0 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.8 (d,  $J_{\text{C-P}} = 9.8$  Hz), 131.6, 130.6, 129.3 (d,  $J_{\text{C-P}} = 8.9$  Hz), 128.7 (d,  $J_{\text{C-P}} = 12.2$  Hz), 128.6, 127.5, 127.2, 126.6 (d,  $J_{\text{C-P}} = 99.5$  Hz), 126.5;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.3. HRMS:  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{27}\text{H}_{20}\text{ClNOP}^+$ : 440.0966, found: 440.0970.

### Diphenyl(4-phenylbenzo[h]quinolin-3-yl)phosphine oxide (3v)



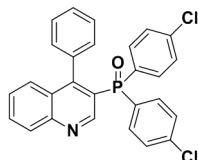
White solid; m.p. 209.2-211.7 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.32 (d,  $J = 6.1$  Hz, 1H), 8.90 (d,  $J = 6.4$  Hz, 1H), 7.91-7.88 (m, 1H), 7.81-7.74 (m, 2H), 7.72-7.63 (m, 5H), 7.52-7.48 (m, 2H), 7.42-7.38 (m, 5H), 7.28-7.25 (m, 1H), 7.20-7.16 (m, 2H), 7.12-7.10 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  154.8 (d,  $J_{\text{C-P}} = 7.5$  Hz), 150.9 (d,  $J_{\text{C-P}} = 15.1$  Hz), 148.6, 134.9 (d,  $J_{\text{C-P}} = 4.9$  Hz), 134.3, 132.5 (d,  $J_{\text{C-P}} = 105.7$  Hz), 131.9 (d,  $J_{\text{C-P}} = 9.8$  Hz), 131.8 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.2, 130.8, 129.6, 128.63 (d,  $J_{\text{C-P}} = 12.7$  Hz), 128.6, 128.3, 128.0, 127.7, 127.4, 126.0 (d,  $J = 101.4$  Hz), 125.8 (d,  $J_{\text{C-P}} = 8.3$  Hz), 125.3, 123.5;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  24.8. HRMS:  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{31}\text{H}_{22}\text{NNaOP}^+$ : 478.1331, found: 478.1334.

### (4-Phenylquinolin-3-yl)di-p-tolylphosphine oxide (3w)



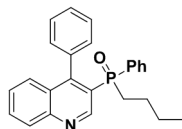
White solid; m.p. 169.0-172.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.84 (d, *J* = 6.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.87-7.74 (m, 1H), 7.48-7.42 (m, 6H), 7.26-7.21 (m, 1H), 7.16-7.11 (m, 6H), 7.05-7.03 (m, 2H), 2.36 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 155.5 (d, *J*<sub>C-P</sub> = 7.2 Hz), 152.1 (d, *J*<sub>C-P</sub> = 14.7 Hz), 149.4, 142.2 (d, *J*<sub>C-P</sub> = 2.7 Hz), 134.8 (d, *J*<sub>C-P</sub> = 5.1 Hz), 131.8 (d, *J*<sub>C-P</sub> = 10.0 Hz), 131.5, 130.6, 129.8, 129.5 (d, *J*<sub>C-P</sub> = 108.7 Hz), 129.3 (d, *J*<sub>C-P</sub> = 12.7 Hz), 128.2, 127.9 (d, *J*<sub>C-P</sub> = 8.9 Hz), 127.4, 127.33, 127.3, 125.6 (d, *J*<sub>C-P</sub> = 100.1 Hz), 21.7; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 25.1. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>29</sub>H<sub>25</sub>NOP<sup>+</sup>: 434.1668, found: 434.1668.

### Bis(4-chlorophenyl)(4-phenylquinolin-3-yl)phosphine oxide (3x)



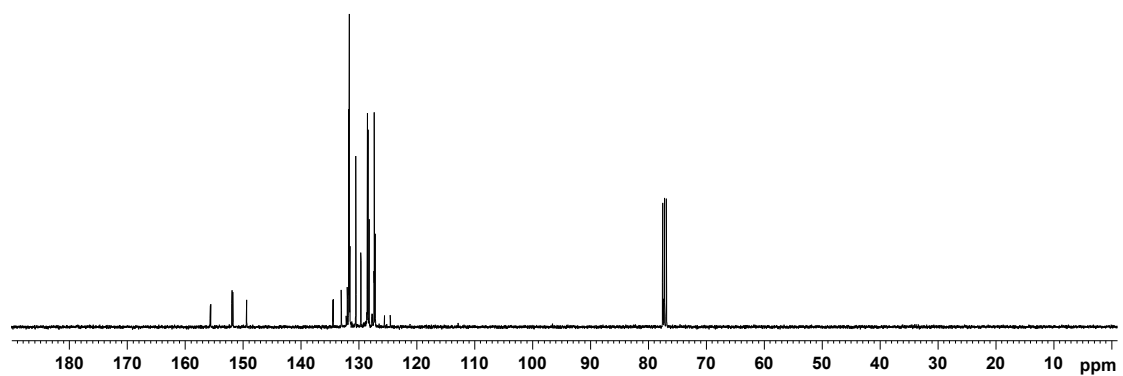
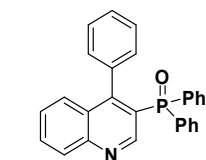
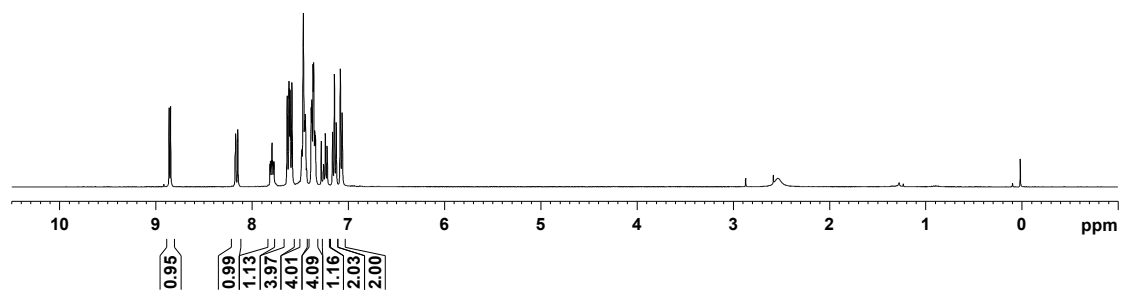
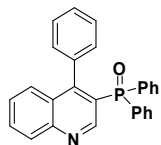
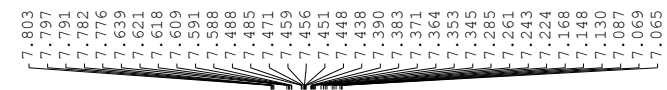
White solid; m.p. 111.8-114.7 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.77 (d, *J* = 6.0 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.76-7.71 (m, 1H), 7.46-7.39 (m, 6H), 7.28-7.25 (m, 4H), 7.23-7.19 (m, 1H), 7.13-7.08 (m, 2H), 7.00-6.98 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 155.8 (d, *J*<sub>C-P</sub> = 7.8 Hz), 151.5 (d, *J*<sub>C-P</sub> = 14.9 Hz), 149.6, 138.7 (d, *J*<sub>C-P</sub> = 3.5 Hz), 134.4 (d, *J*<sub>C-P</sub> = 4.8 Hz), 133.1 (d, *J*<sub>C-P</sub> = 10.5 Hz), 132.1, 130.8 (d, *J*<sub>C-P</sub> = 107.3 Hz), 130.6, 129.9, 129.1 (d, *J*<sub>C-P</sub> = 12.8 Hz), 128.7, 127.8, 127.6 (d, *J*<sub>C-P</sub> = 7.8 Hz), 127.6, 127.3, 124.2 (d, *J*<sub>C-P</sub> = 103.0 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 23.2. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>18</sub>Cl<sub>2</sub>NNaOP<sup>+</sup>: 496.0395, found: 496.0398.

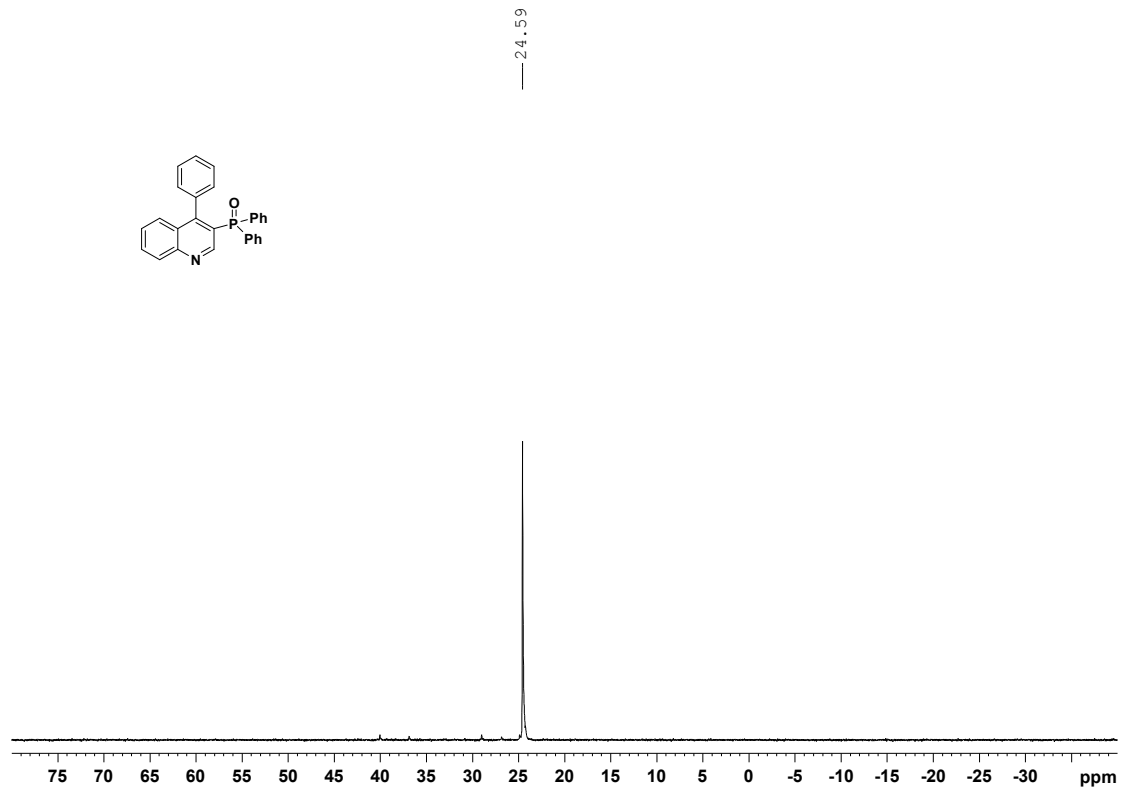
### Butyl(phenyl)(4-phenylquinolin-3-yl)phosphine oxide (3y)



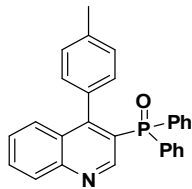
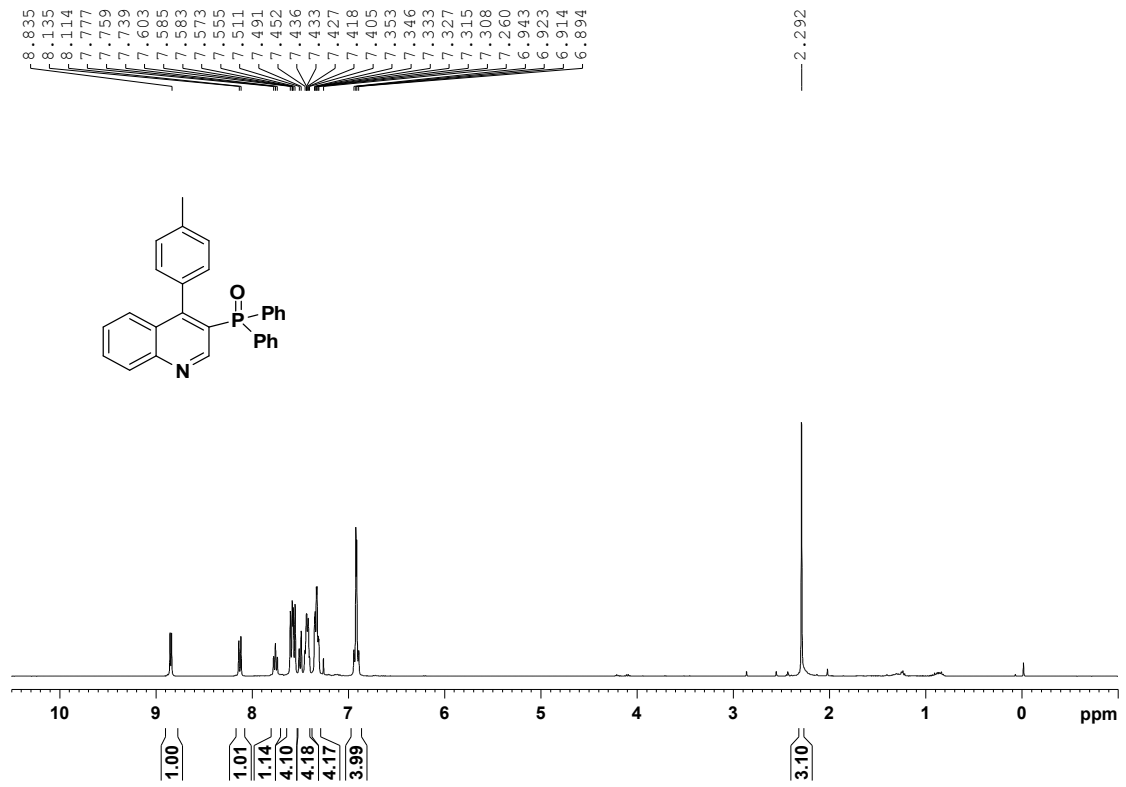
Colorless gum; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.40 (d, *J* = 5.1 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.38-7.31 (m, 3H), 7.30-7.24 (m, 4H), 7.23-7.15 (m, 3H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 1.93-1.78 (m, 2H), 1.45-1.34 (m, 2H), 1.27-1.22 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 153.4 (d, *J*<sub>C-P</sub> = 7.8 Hz), 151.5 (d, *J*<sub>C-P</sub> = 11.3 Hz), 149.4, 135.2 (d, *J*<sub>C-P</sub> = 4.5 Hz), 133.9 (d, *J*<sub>C-P</sub> = 100.3 Hz), 131.6 (d, *J*<sub>C-P</sub> = 2.6 Hz), 131.5, 130.7 (d, *J*<sub>C-P</sub> = 9.7 Hz), 130.4, 129.7 (d, *J*<sub>C-P</sub> = 10.5 Hz), 128.8, 128.6 (d, *J*<sub>C-P</sub> = 11.9 Hz), 128.1 (d, *J*<sub>C-P</sub> = 17.3 Hz), 127.6 (d, *J*<sub>C-P</sub> = 8.5 Hz), 127.4, 127.1, 124.9 (d, *J*<sub>C-P</sub> = 93.0 Hz), 28.8 (d, *J*<sub>C-P</sub> = 72.6 Hz), 24.2 (d, *J*<sub>C-P</sub> = 15.6 Hz), 23.5 (d, *J*<sub>C-P</sub> = 3.7 Hz), 13.7; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 32.2. HRMS: [M+Na]<sup>+</sup> *m/z* calcd for C<sub>25</sub>H<sub>24</sub>NNaOP<sup>+</sup>: 408.1488, found: 408.1485.

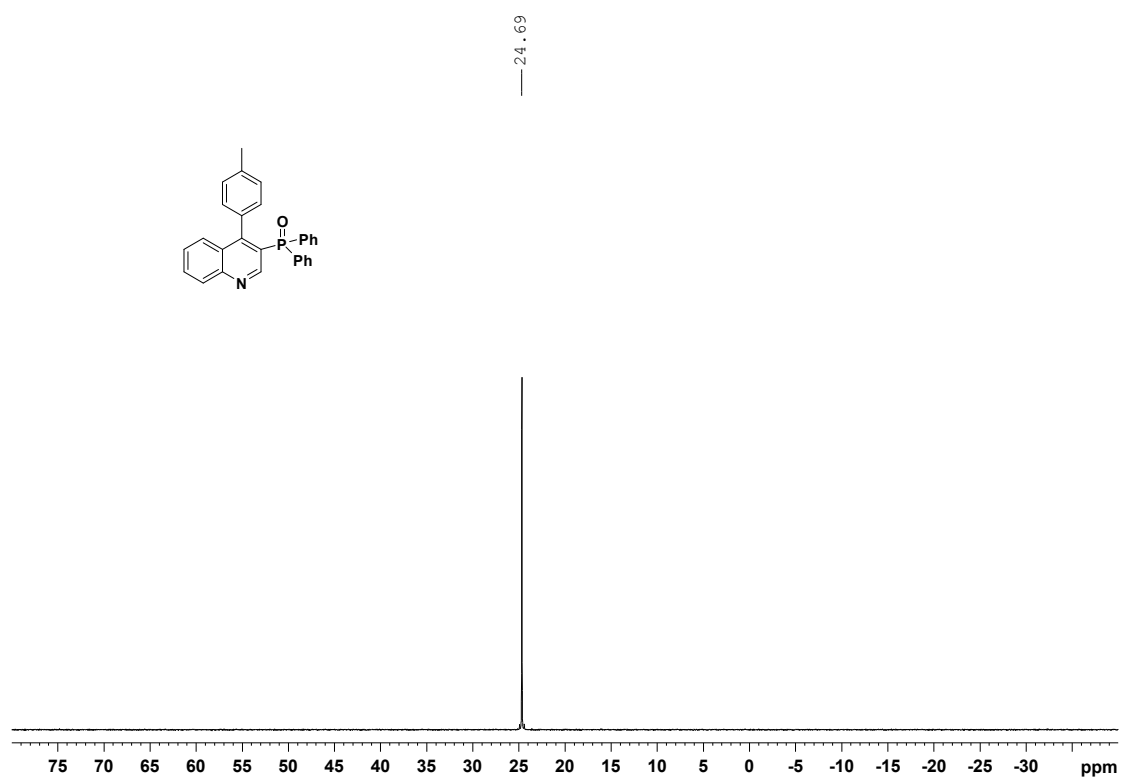
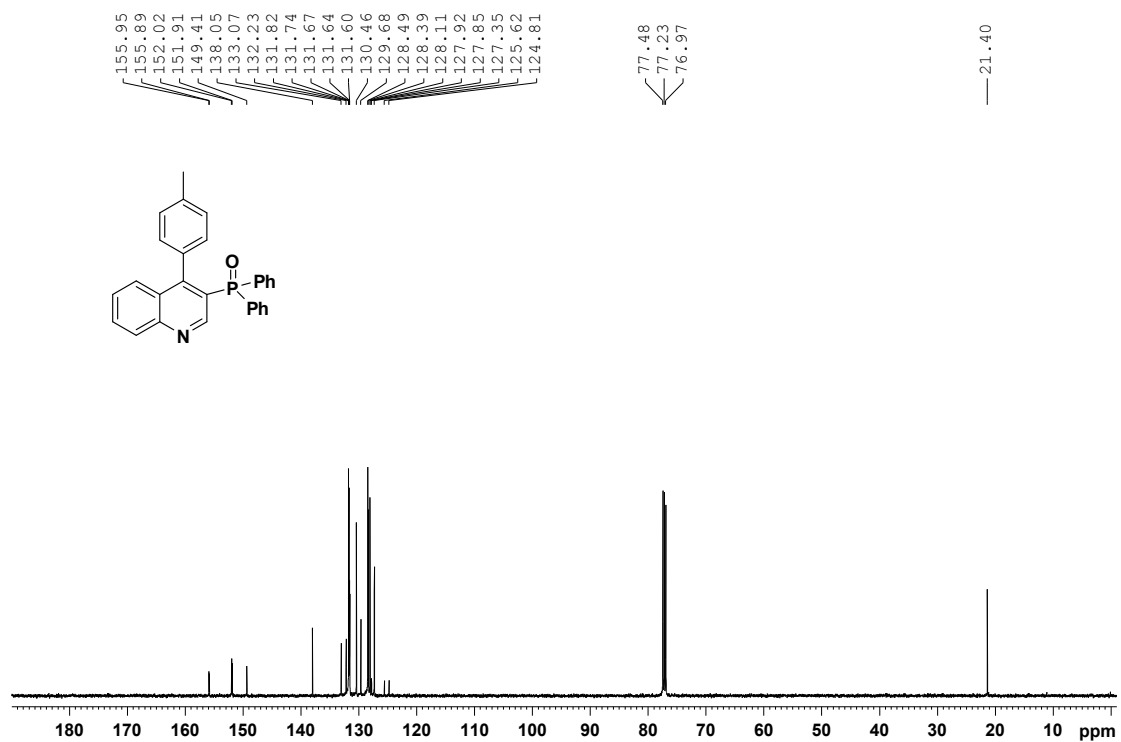
**3a**



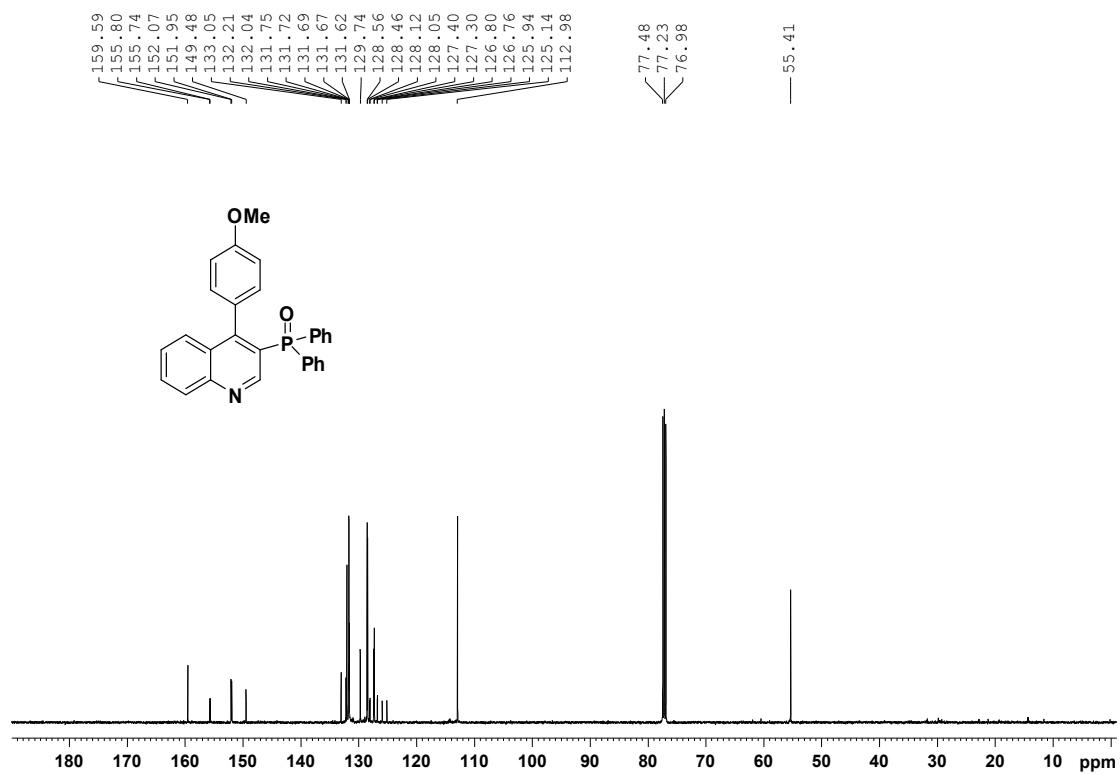
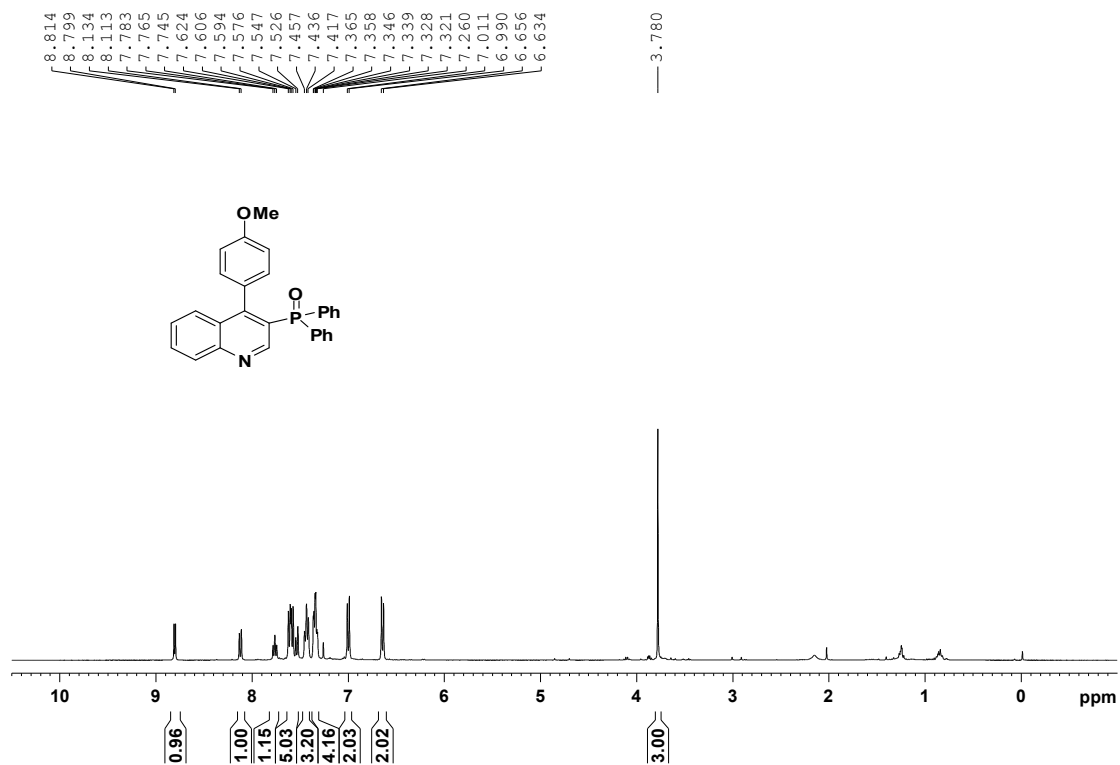


**3b**

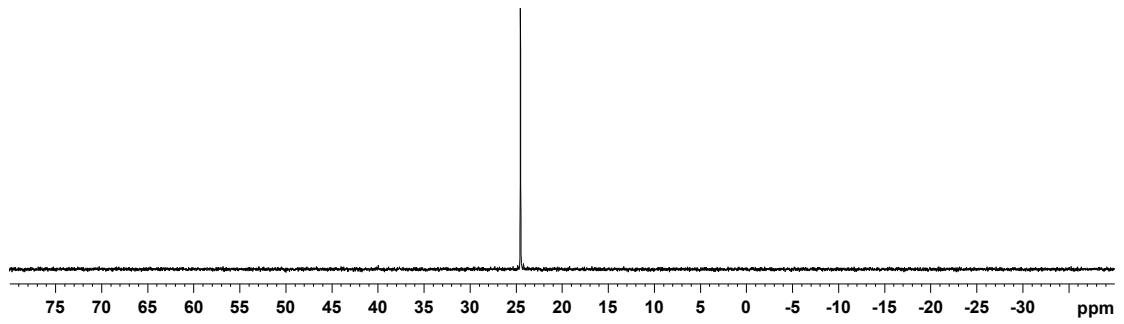
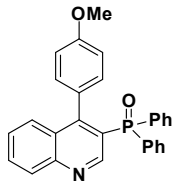




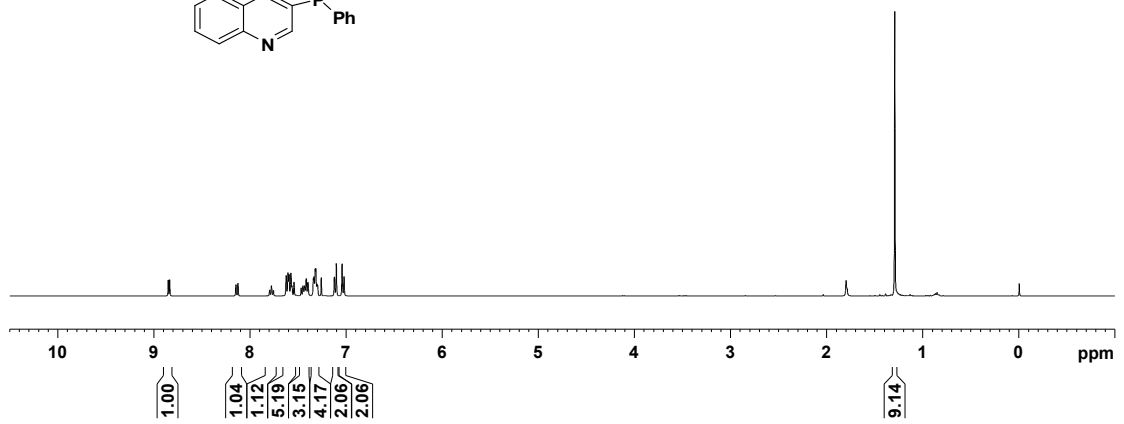
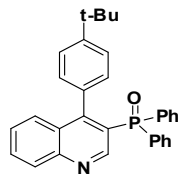
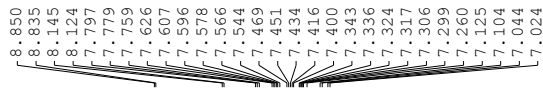
3c



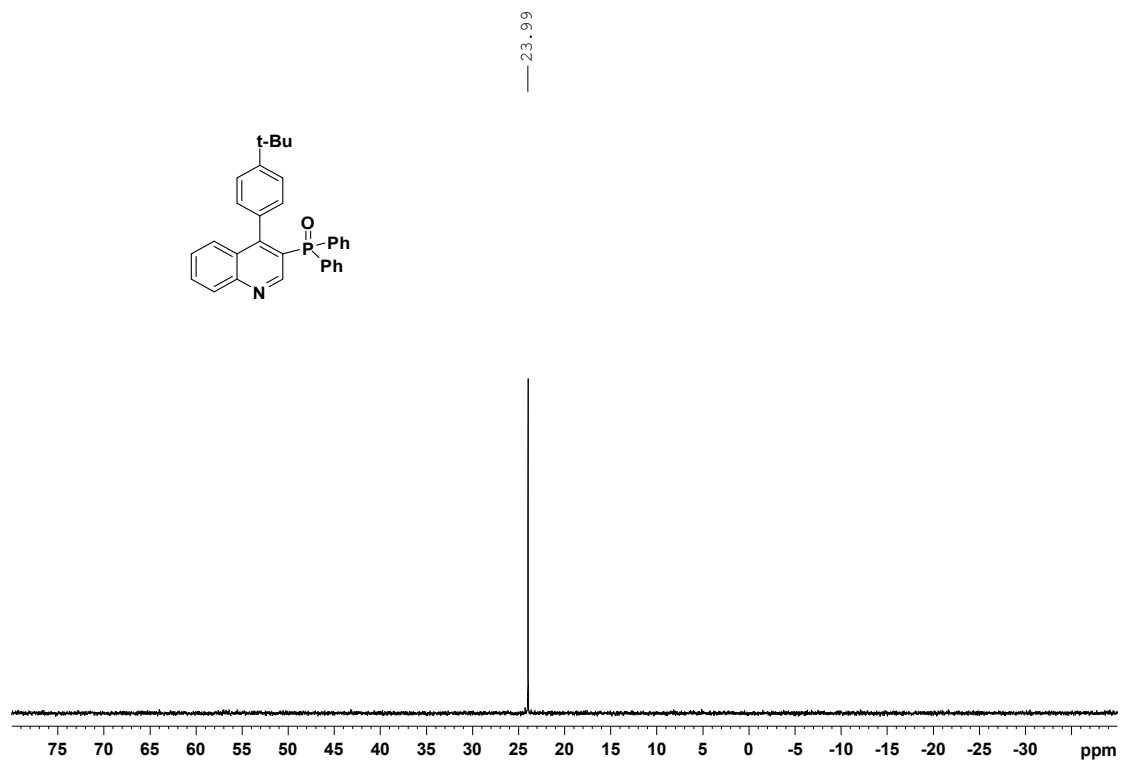
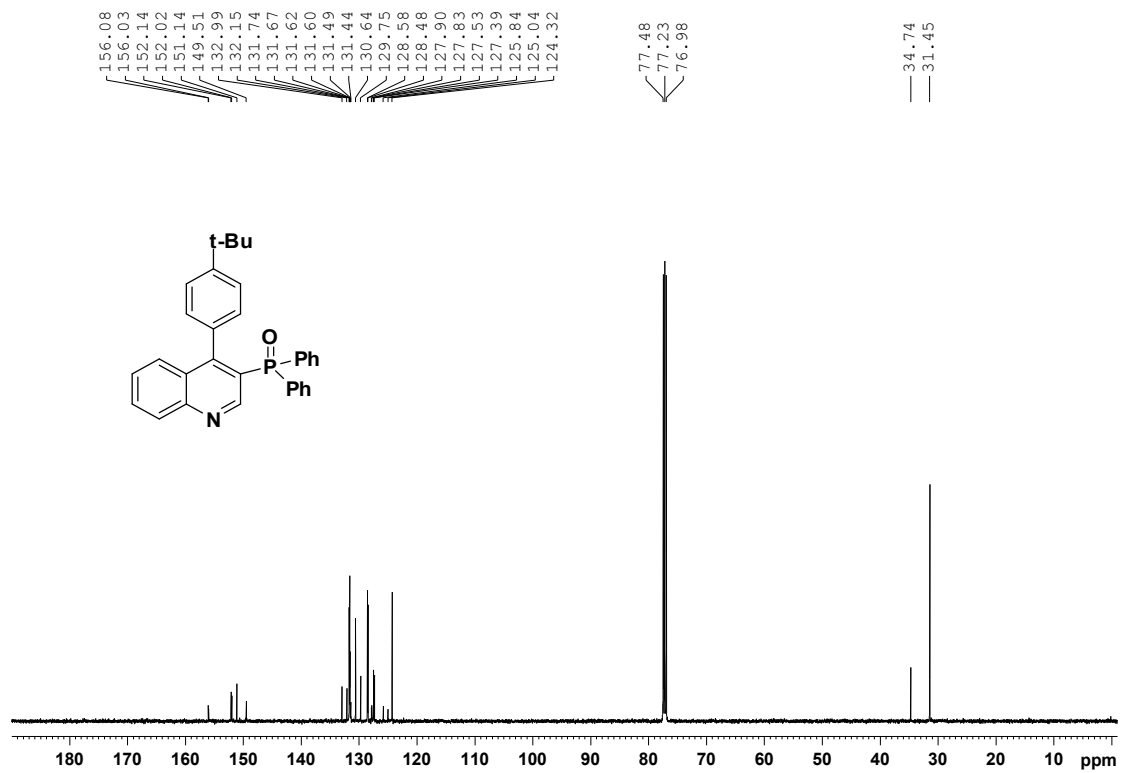
— 24.51



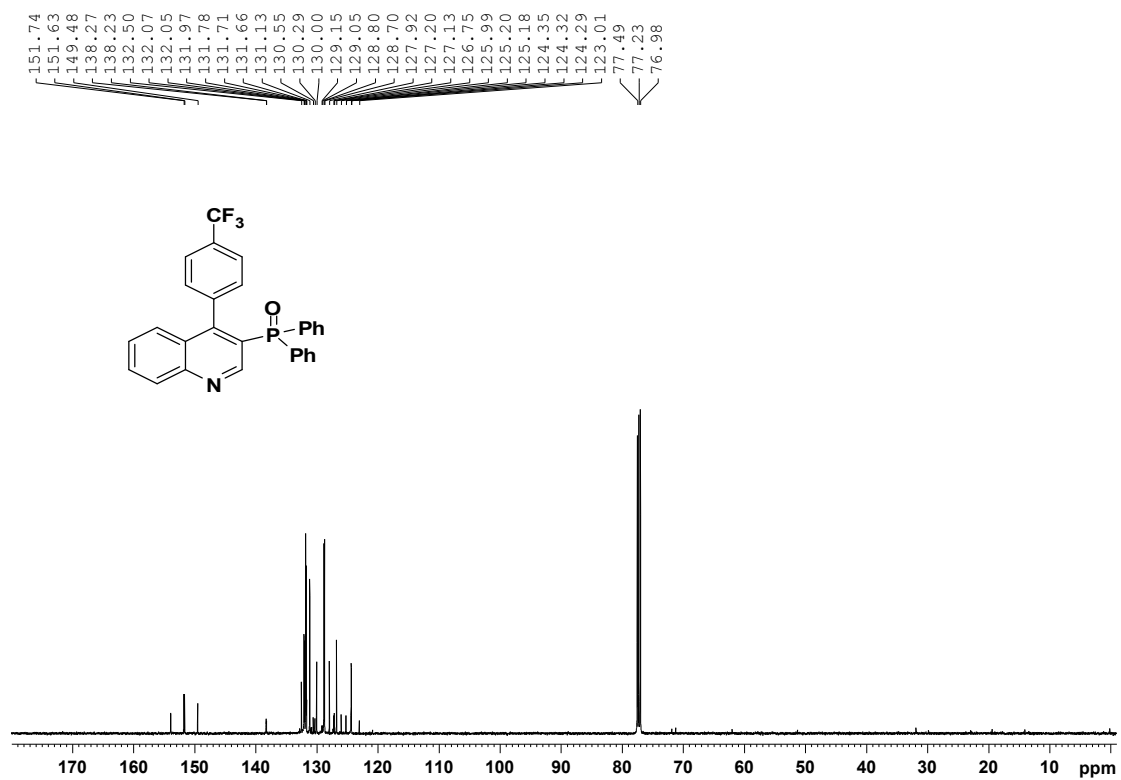
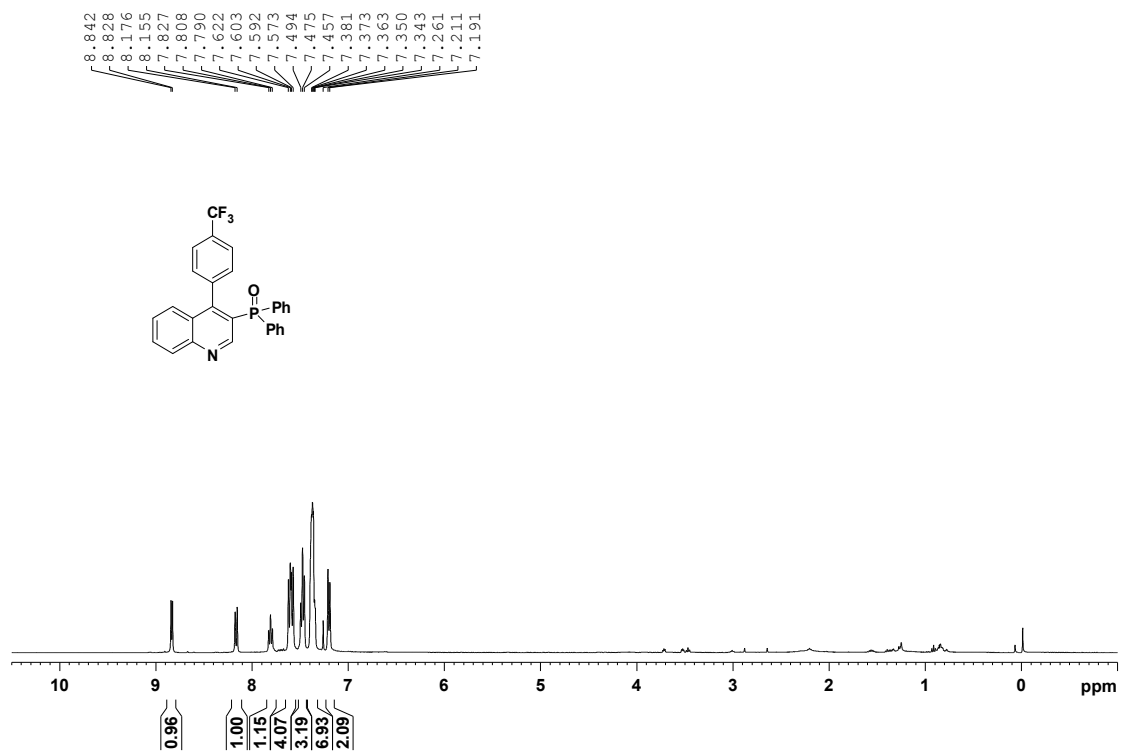
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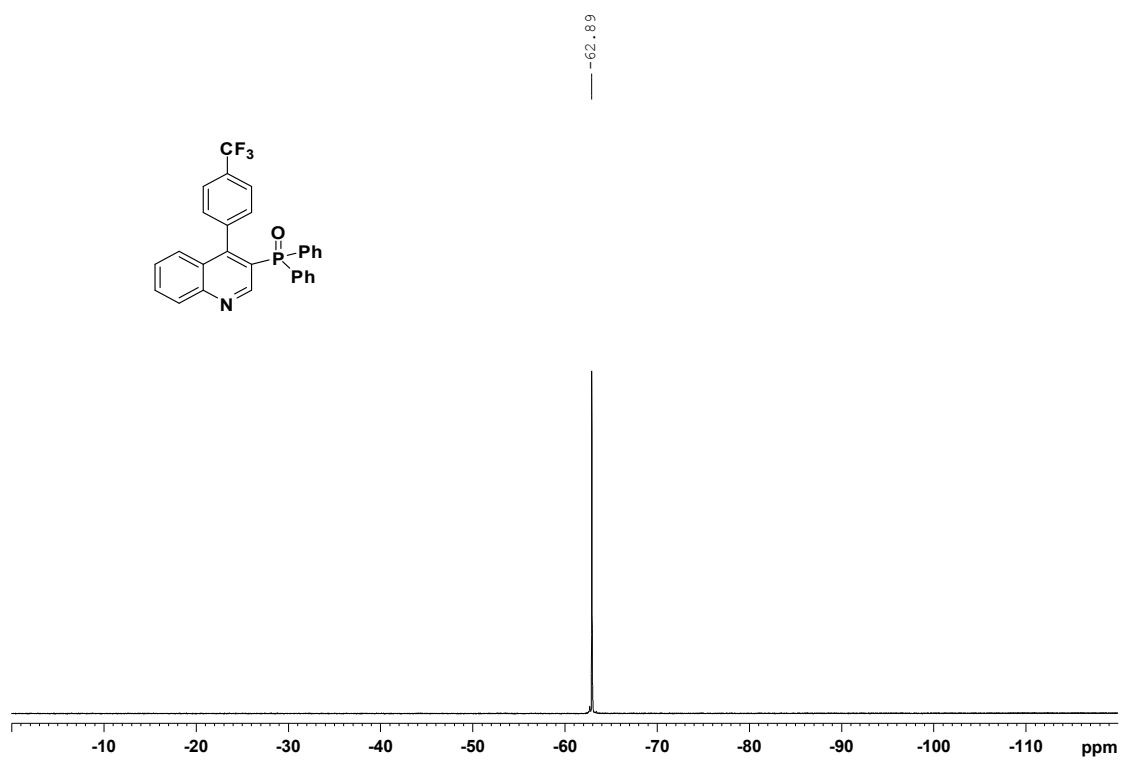
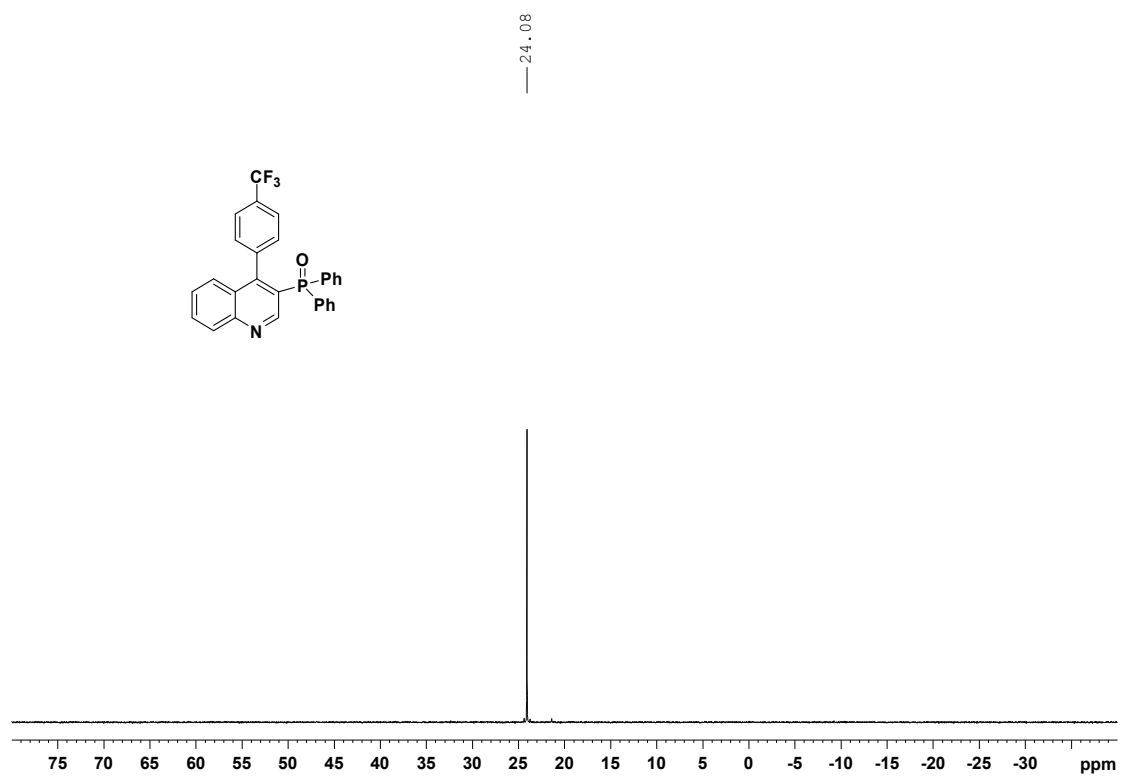




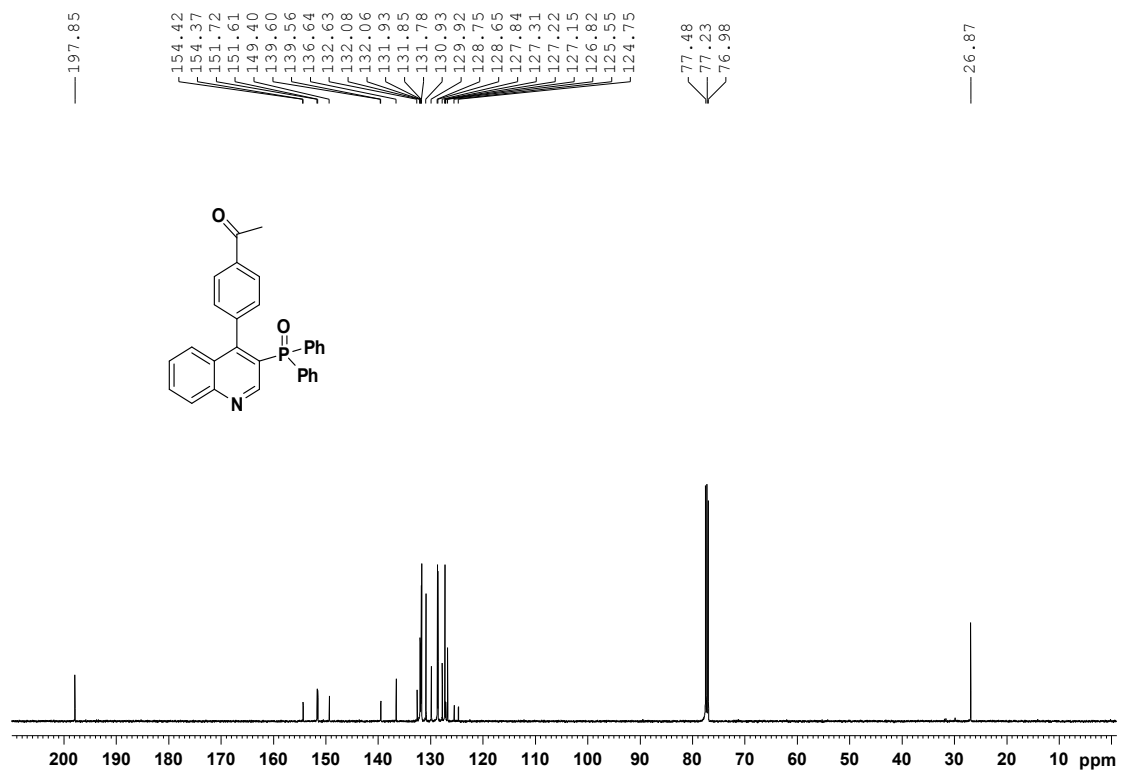
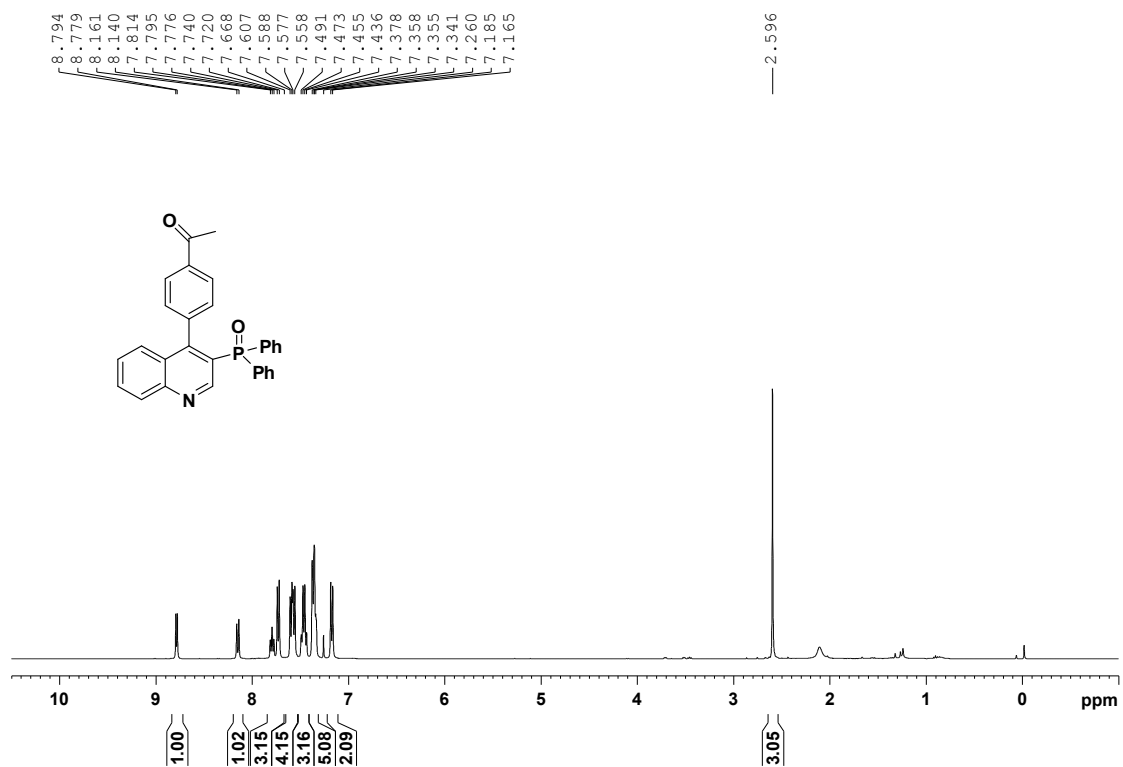


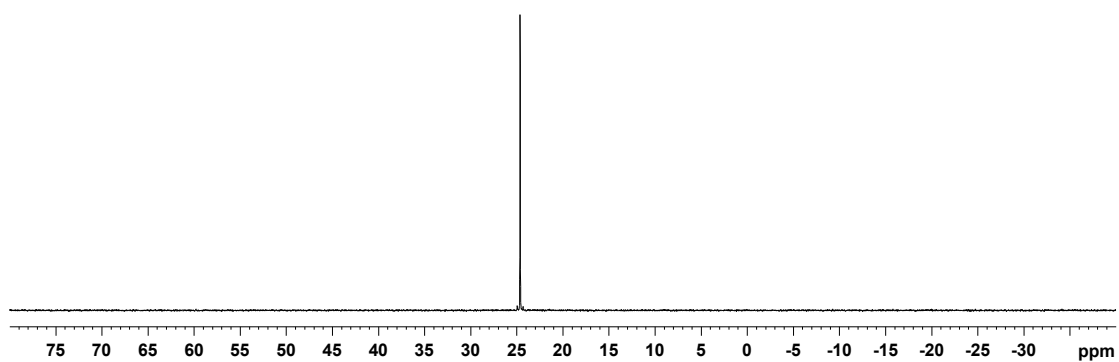
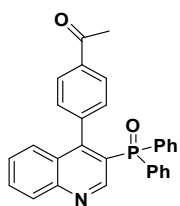
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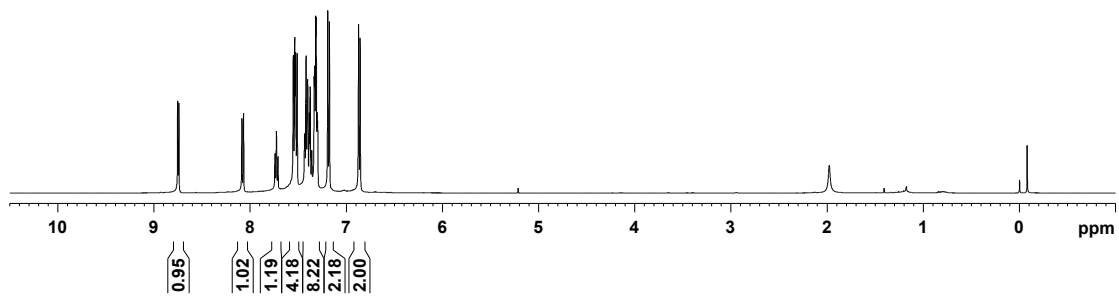
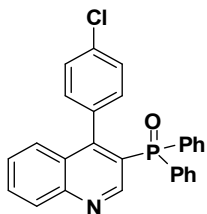


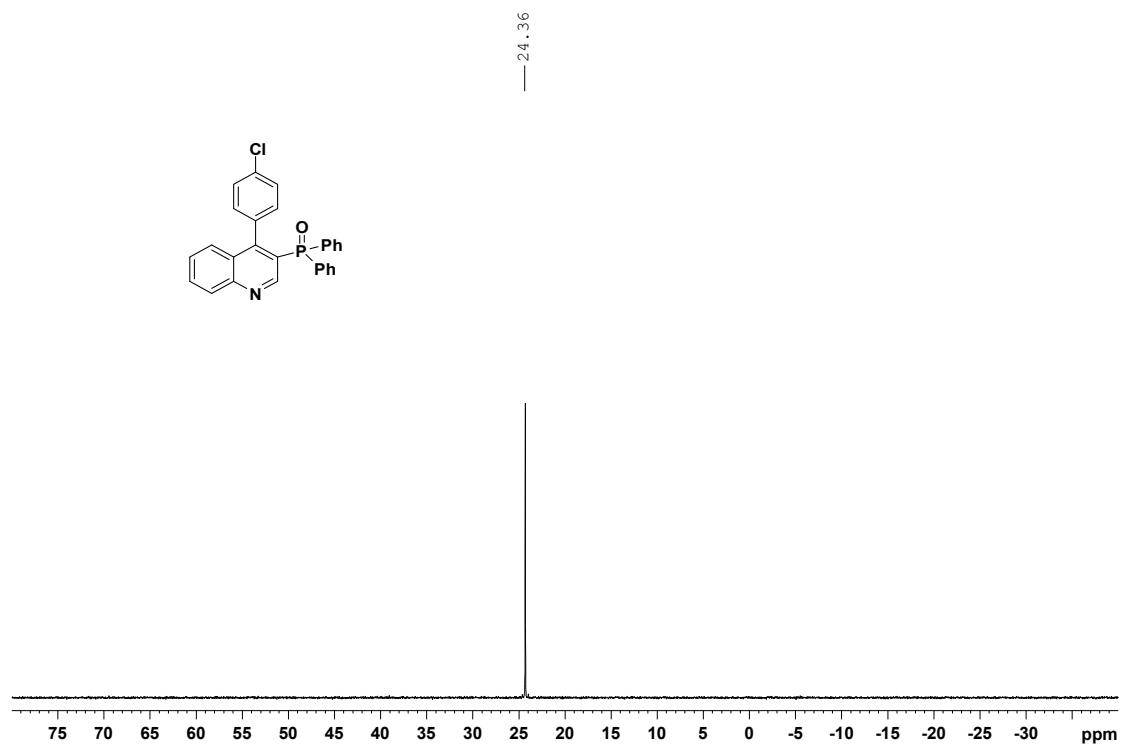
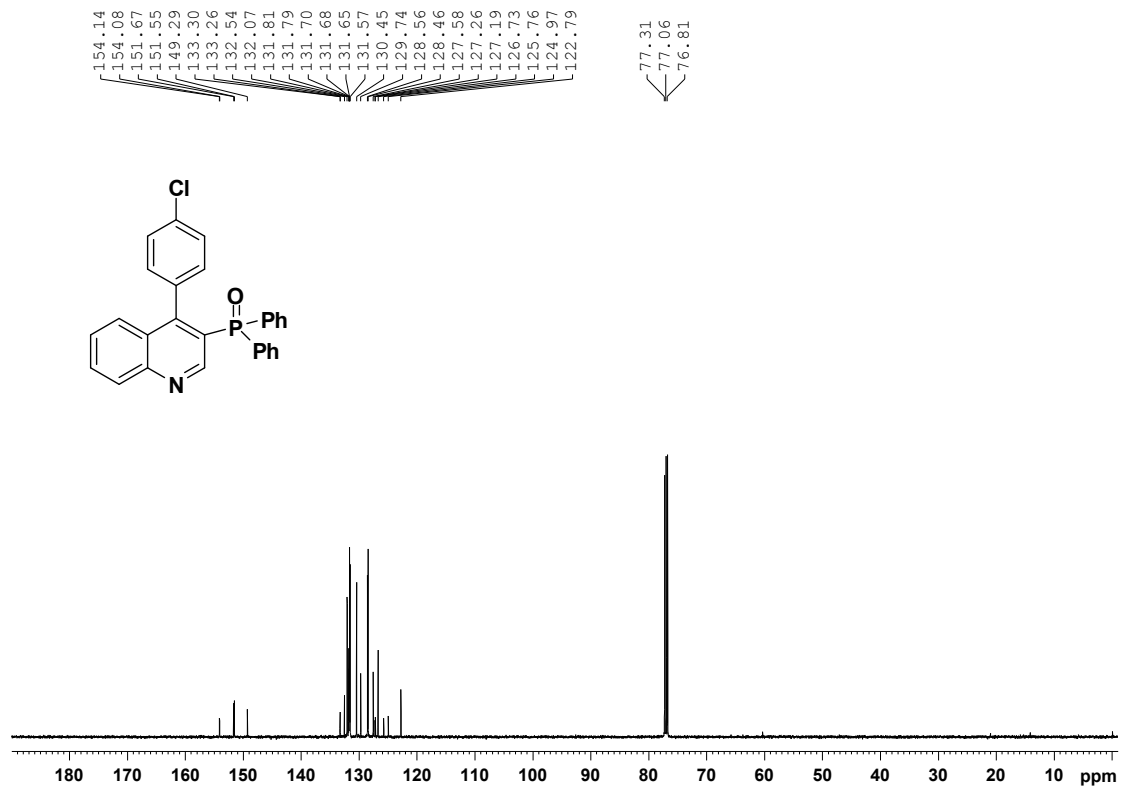
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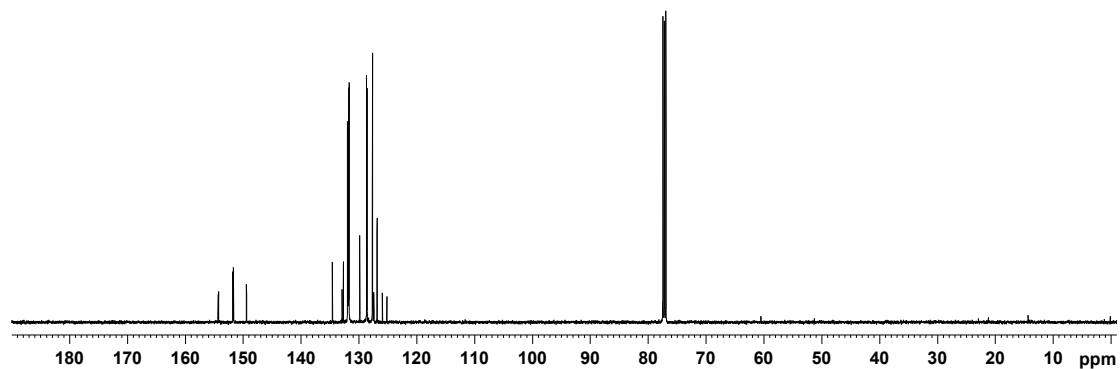
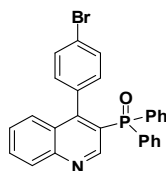
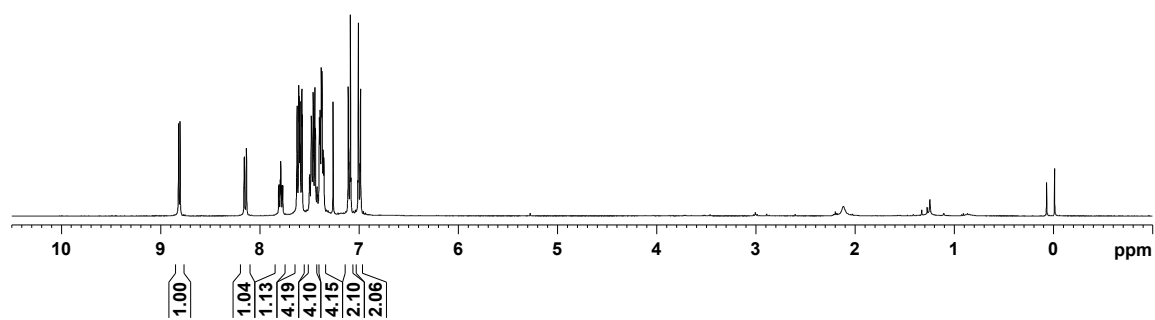
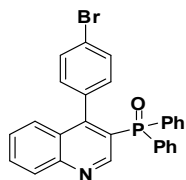
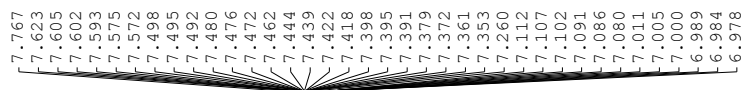


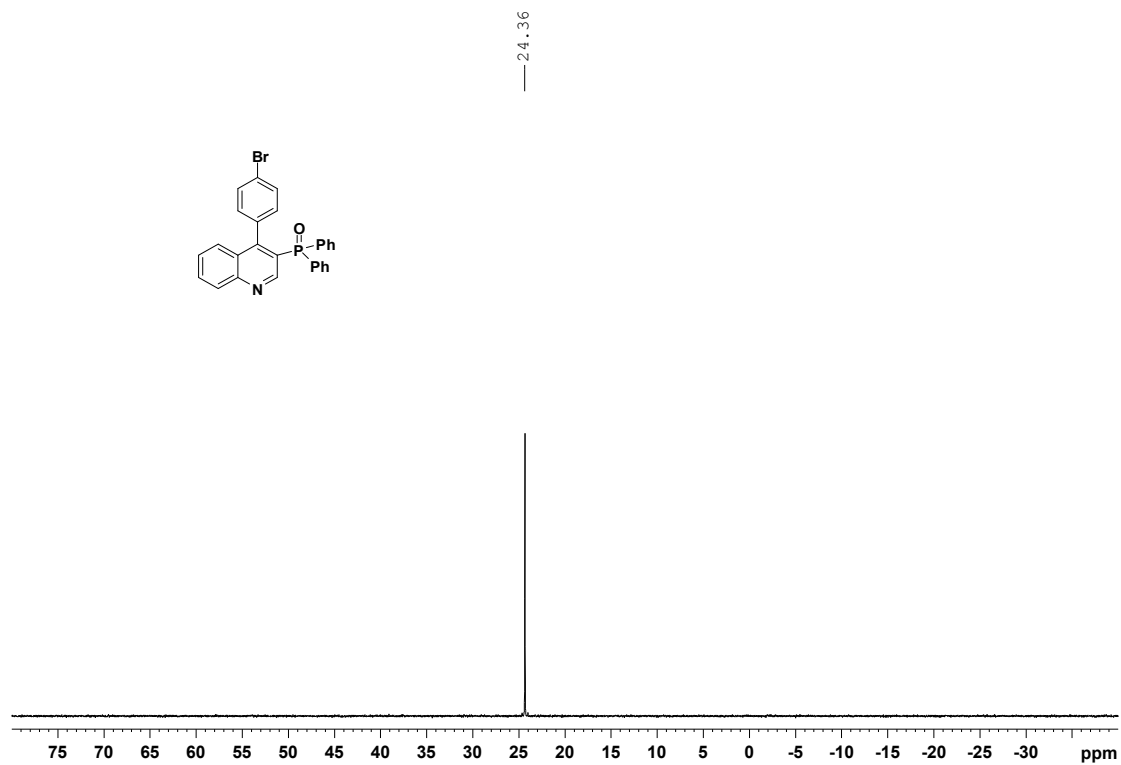
### 3h



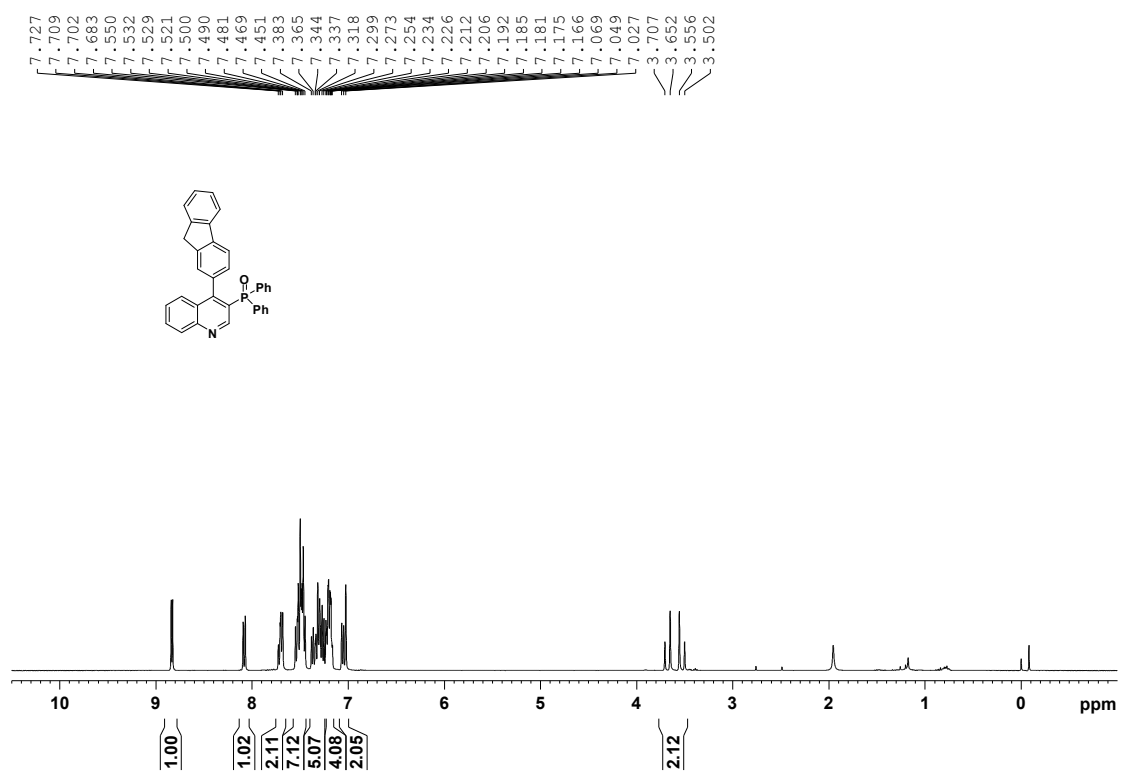


3i

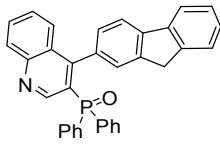
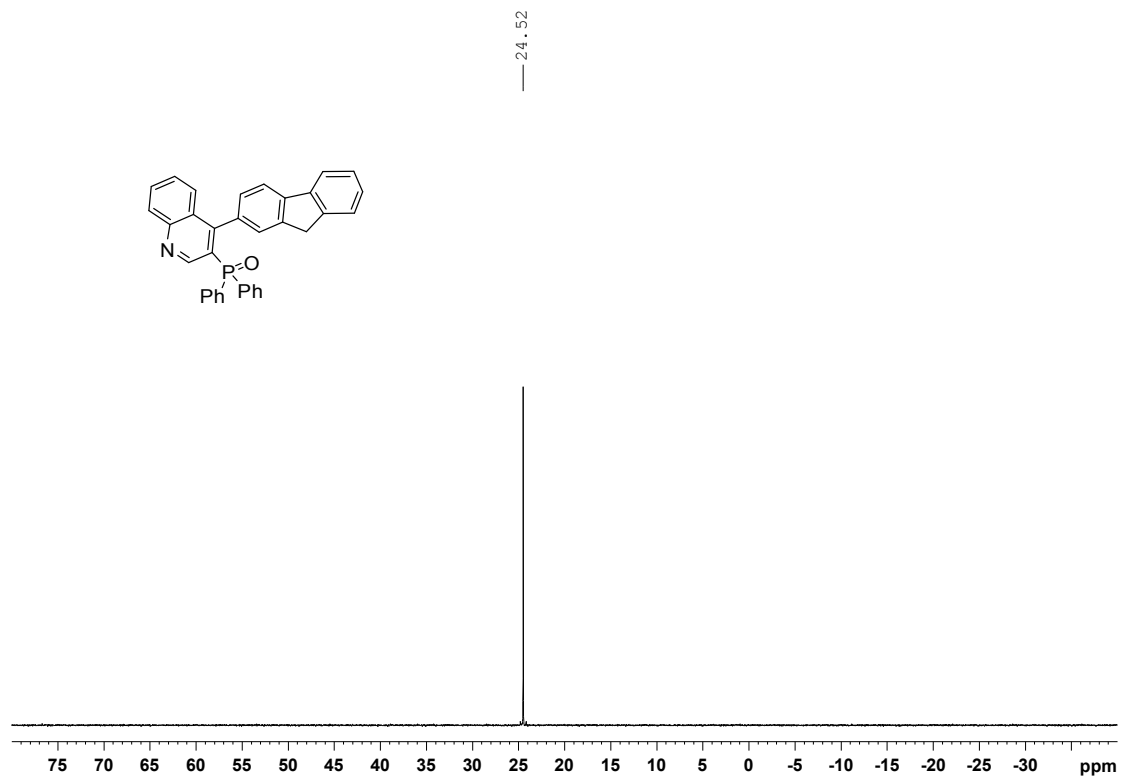
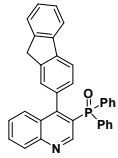
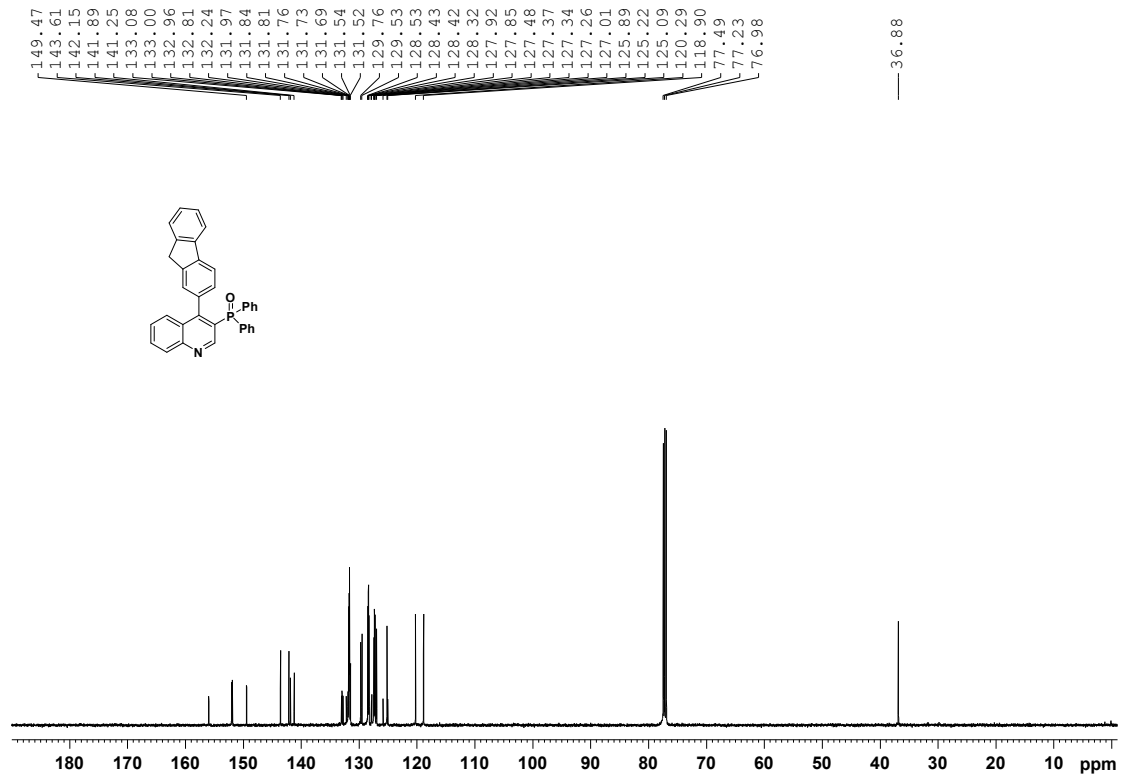




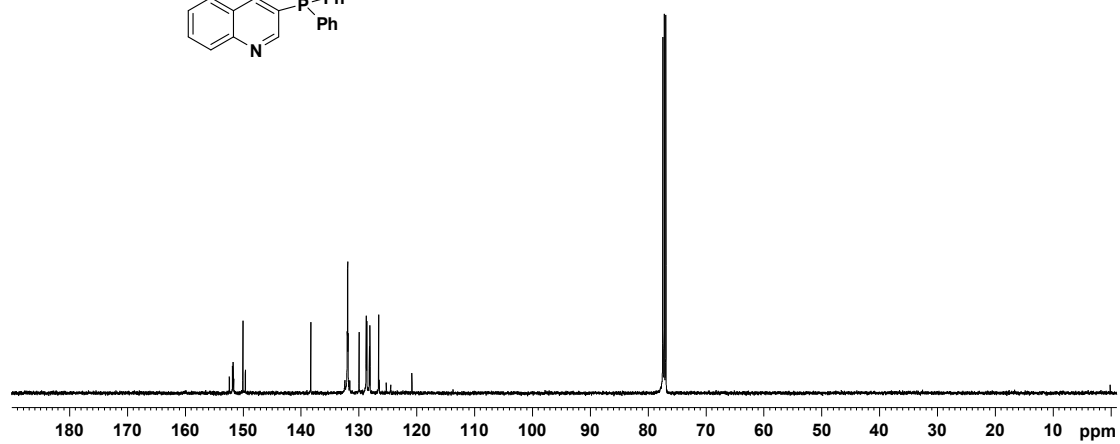
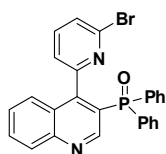
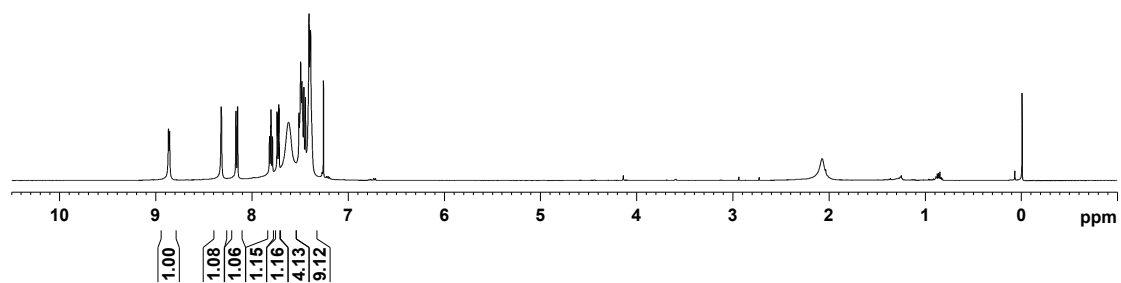
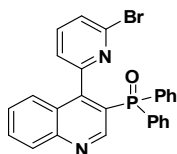
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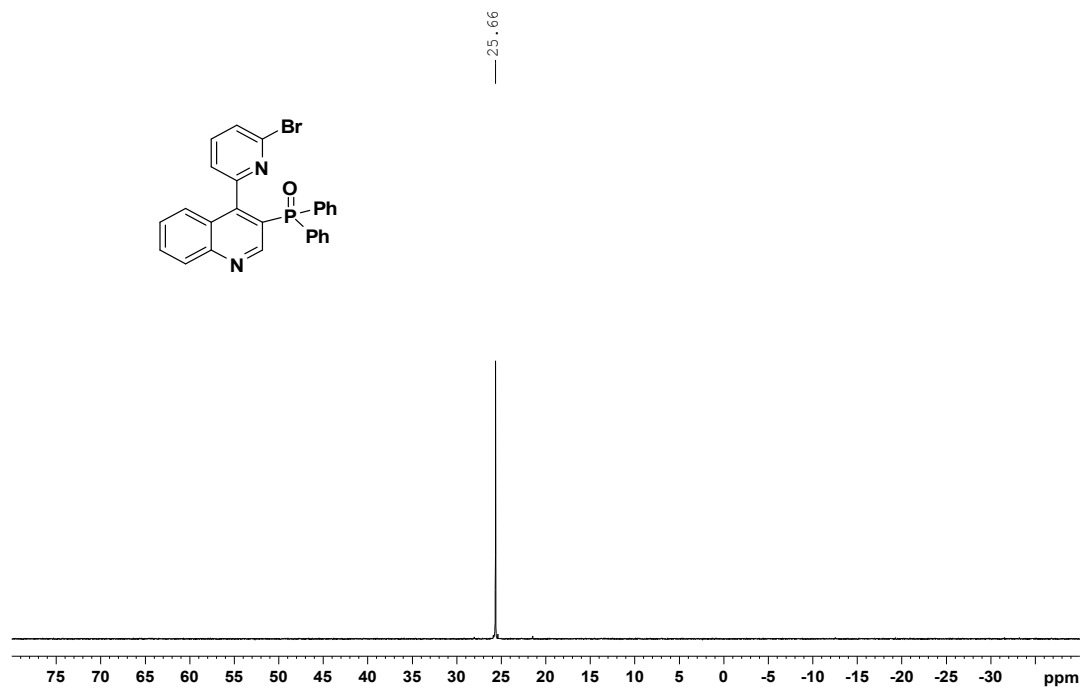




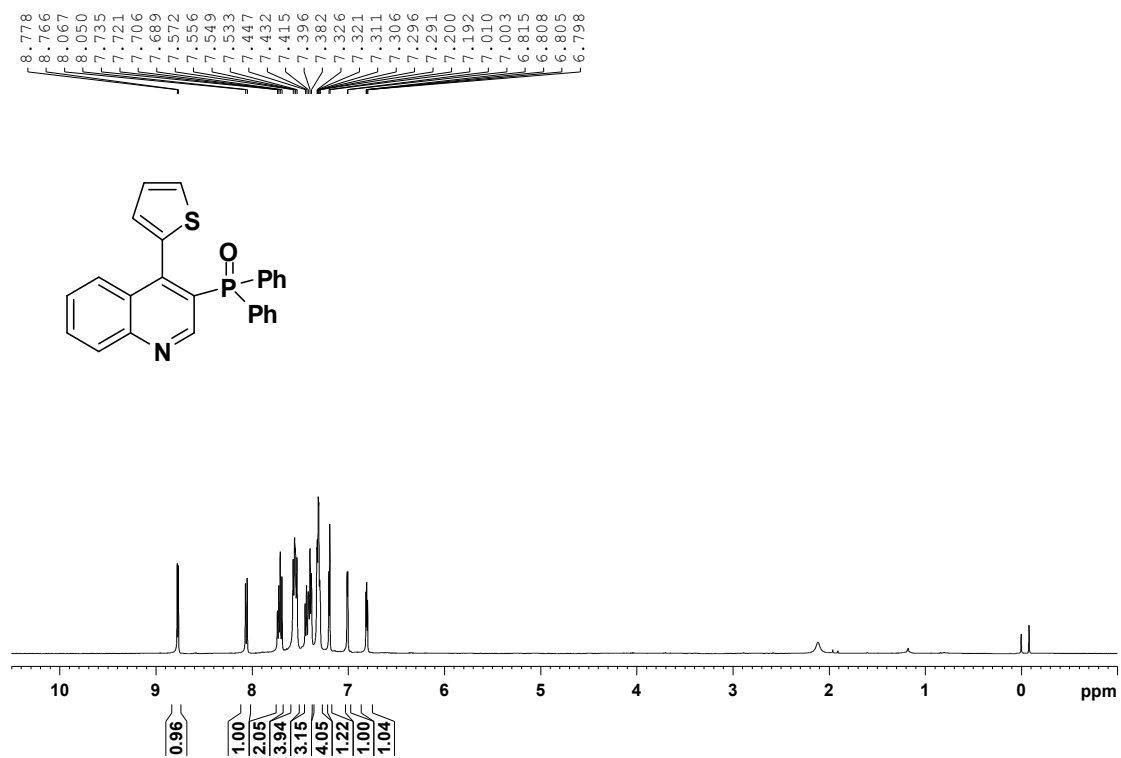


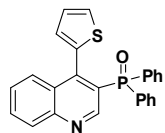
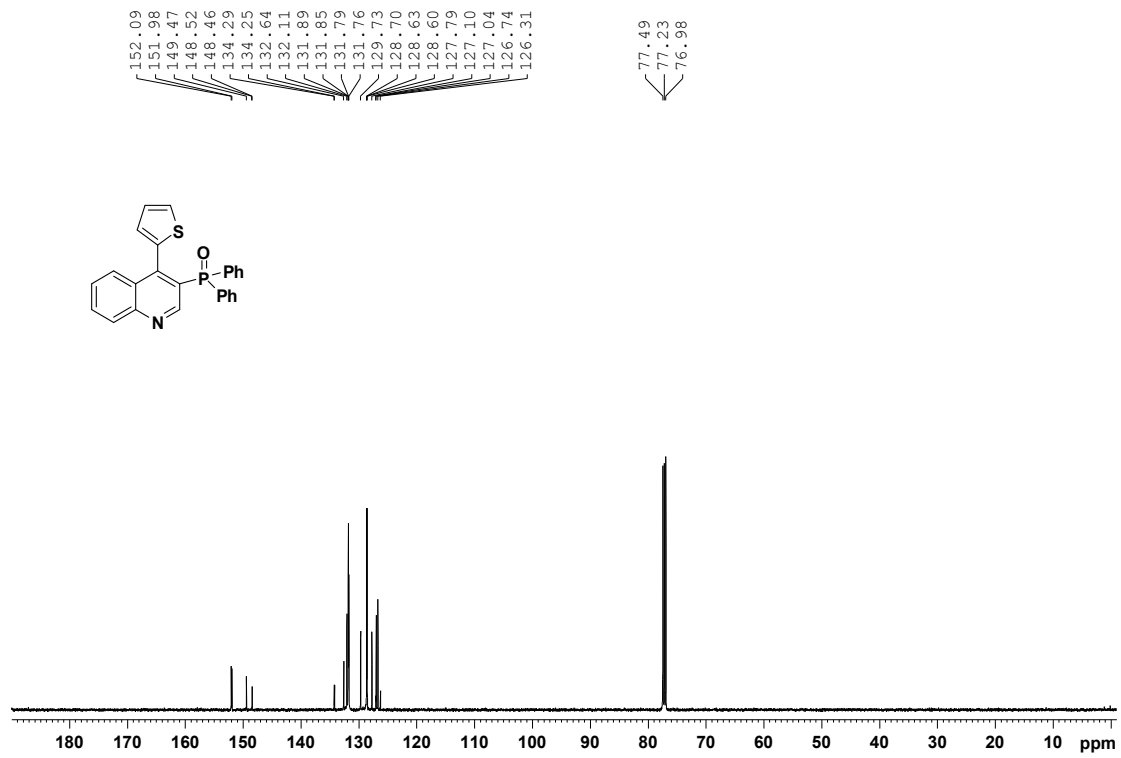
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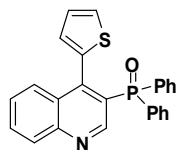
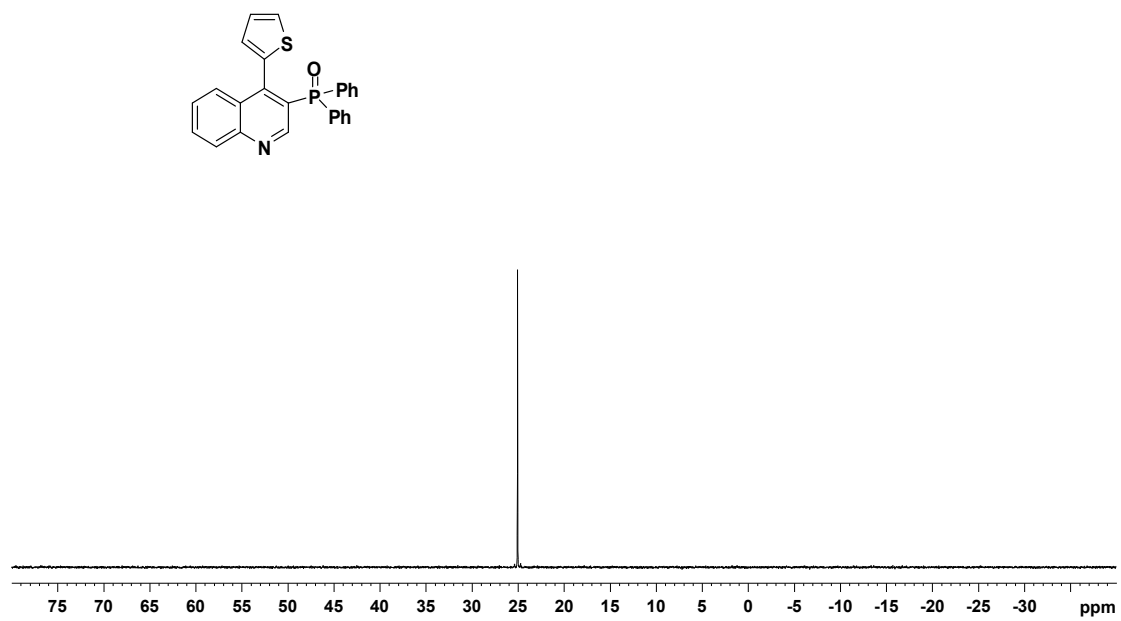


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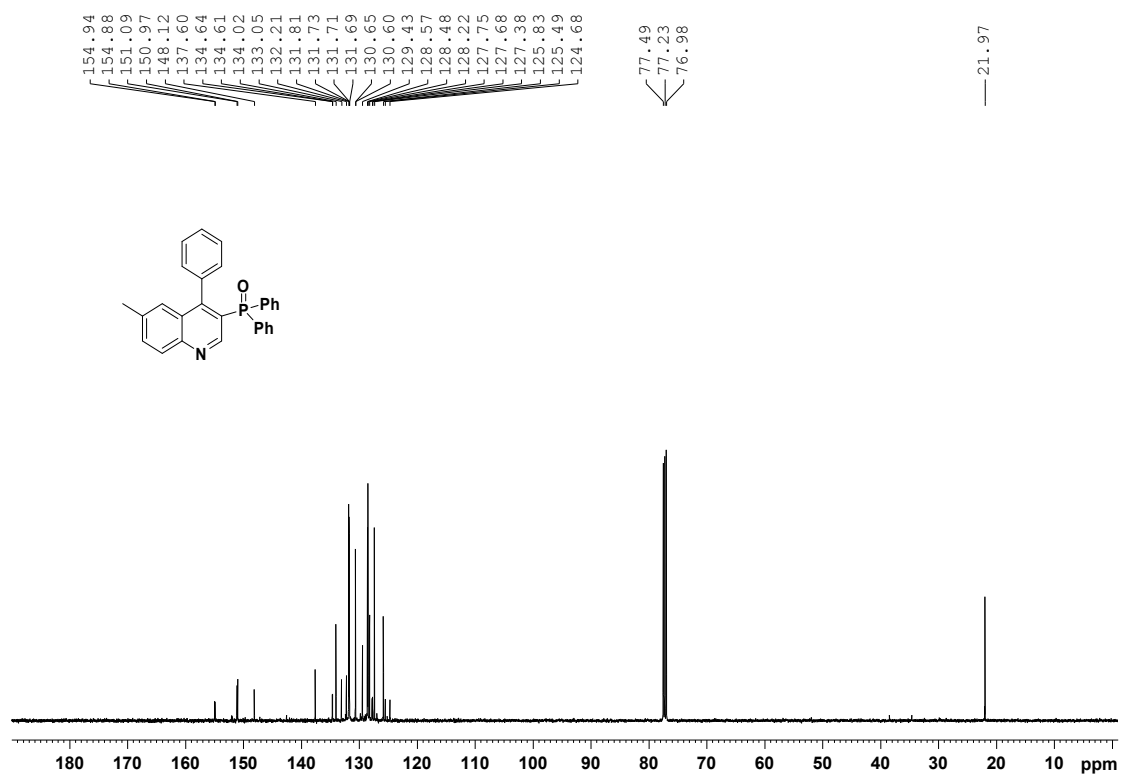
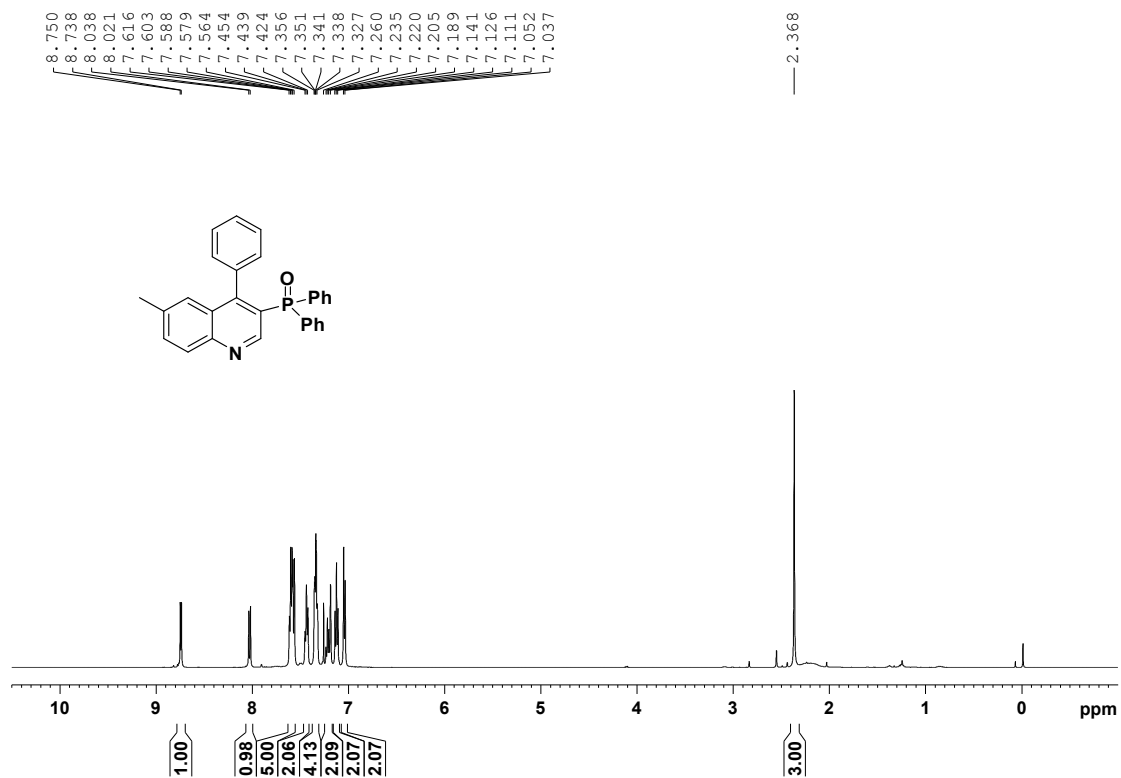




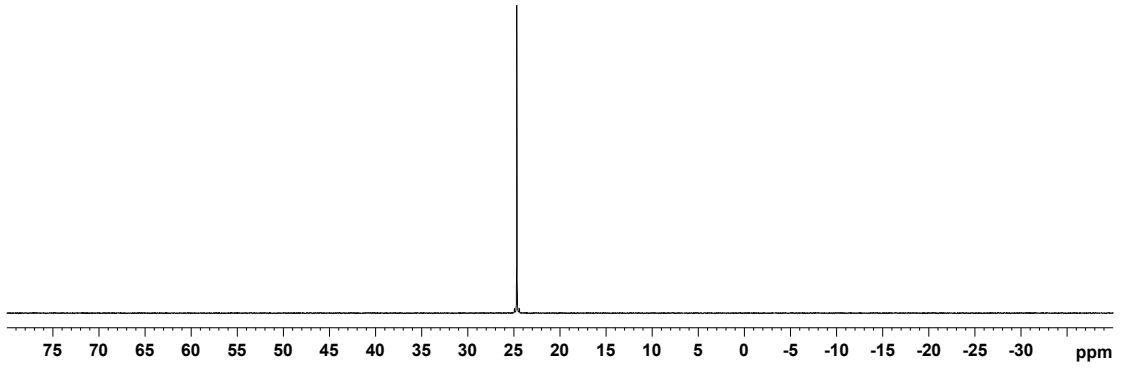
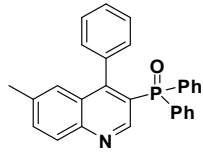
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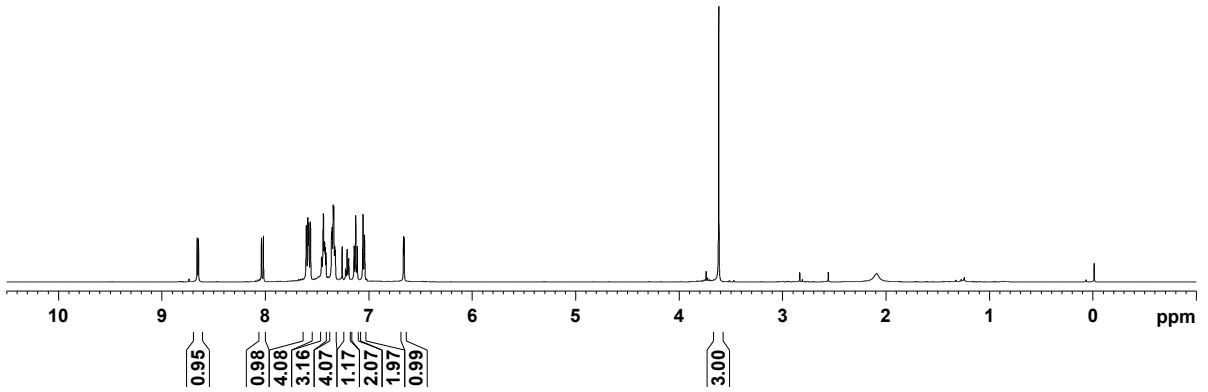
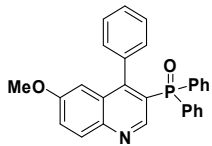
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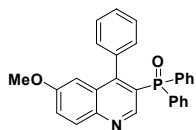
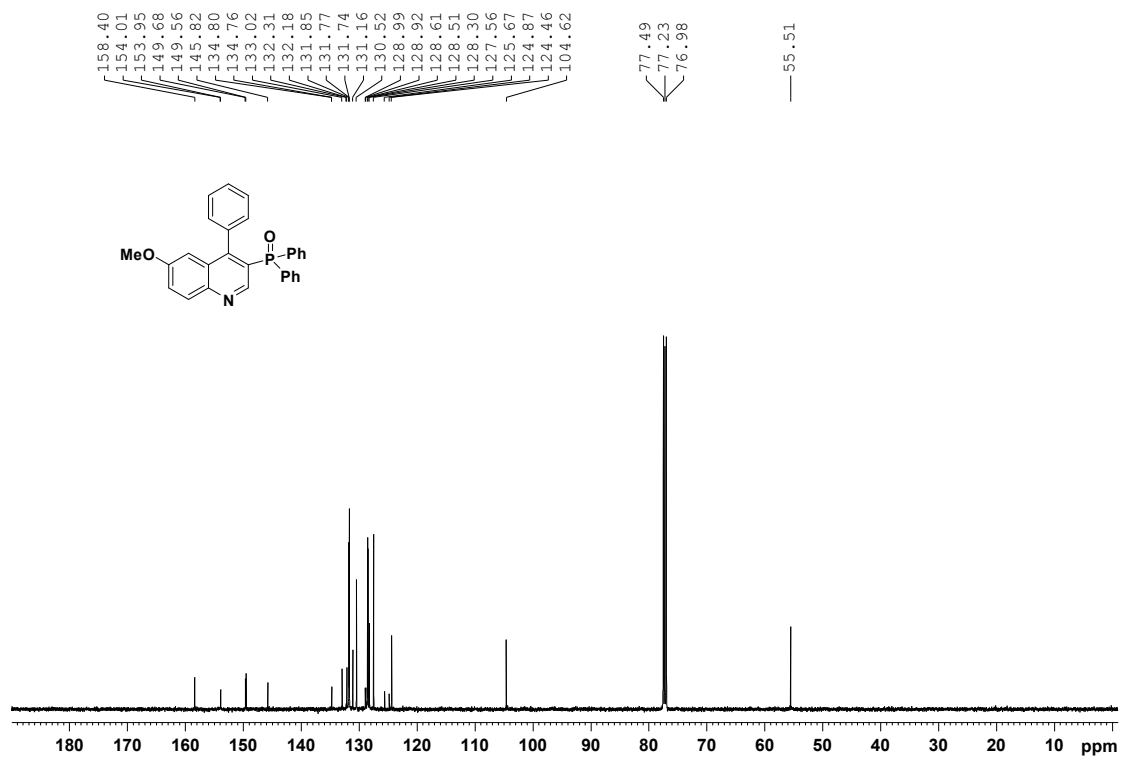


— 24.69

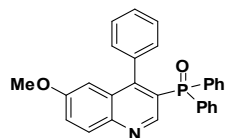
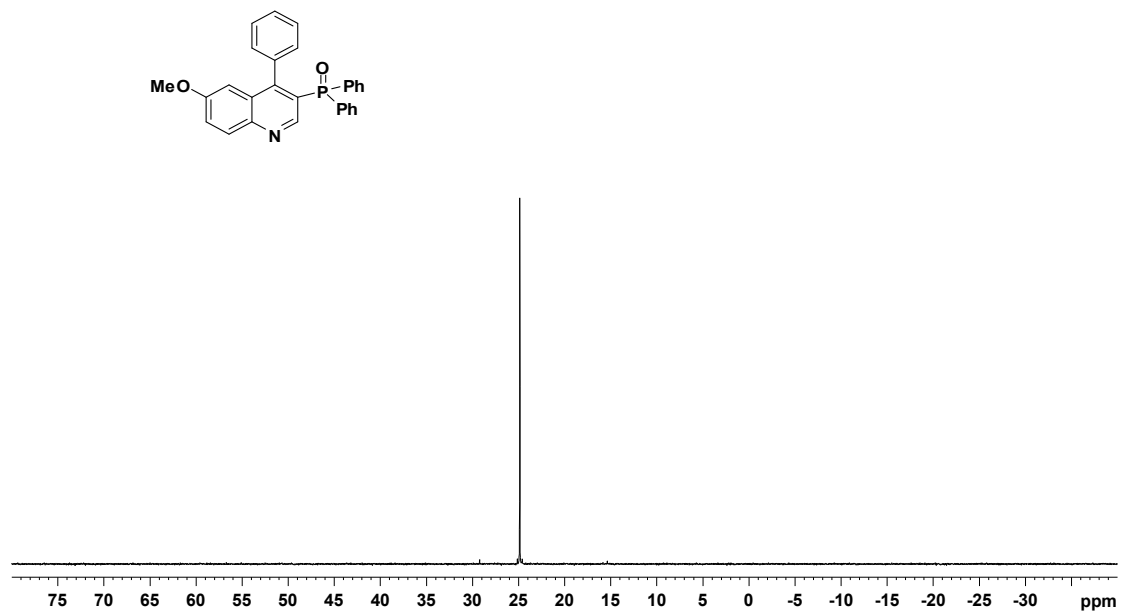


**3n**

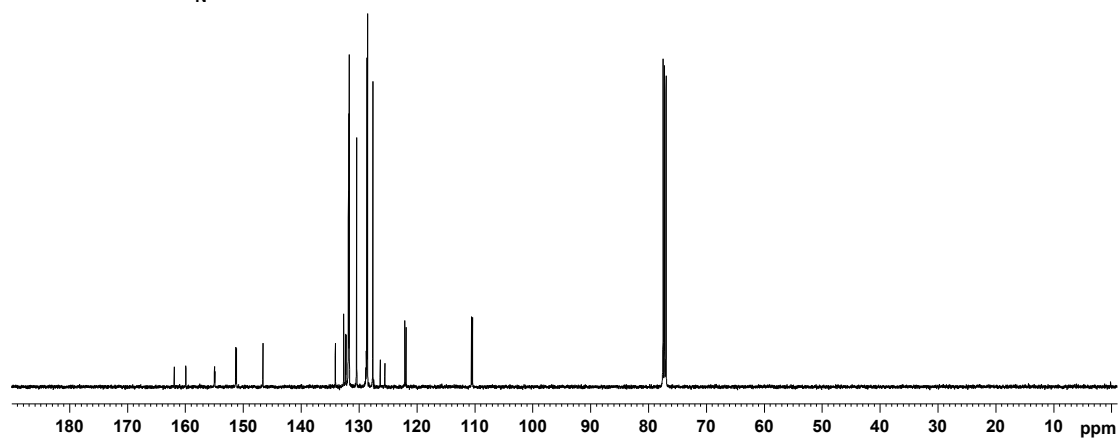
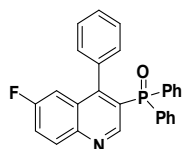
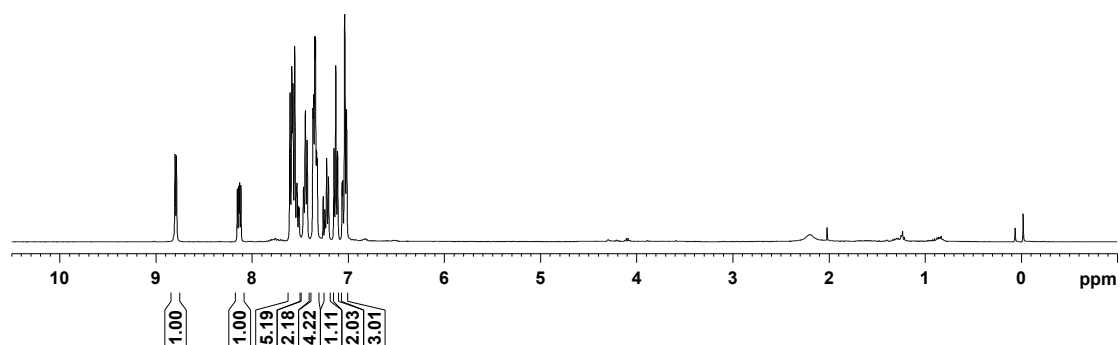
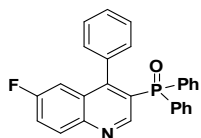




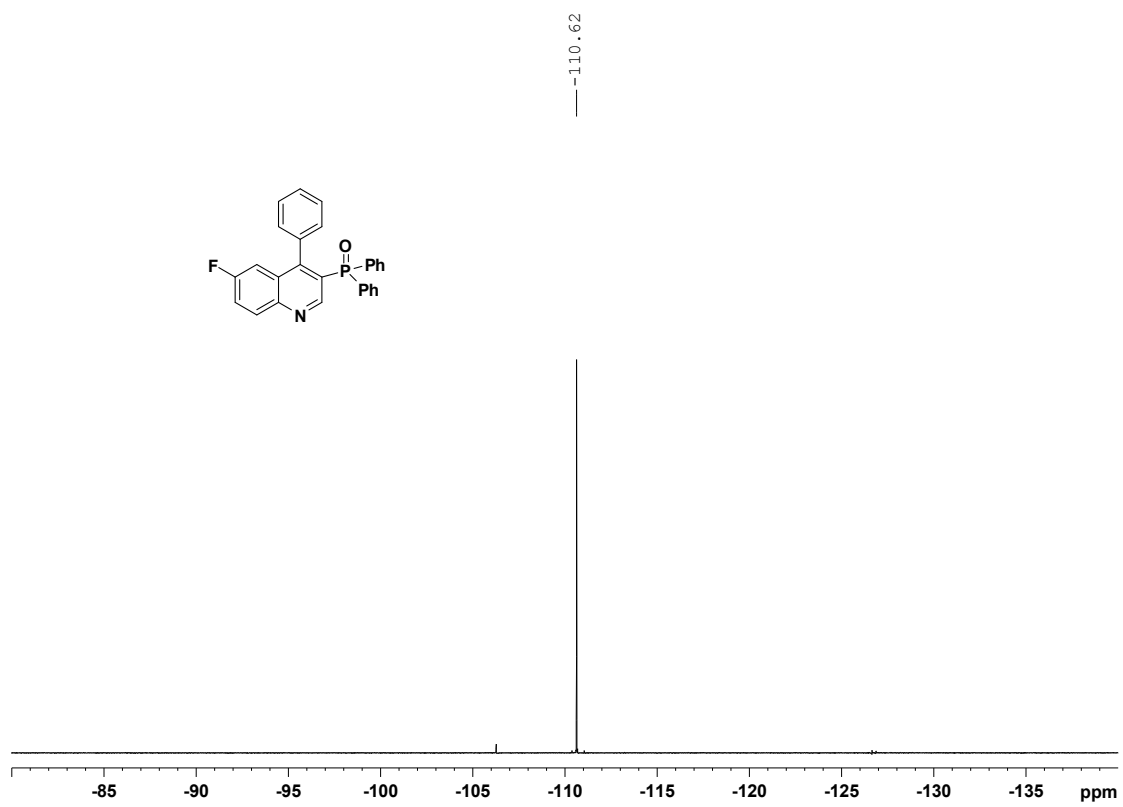
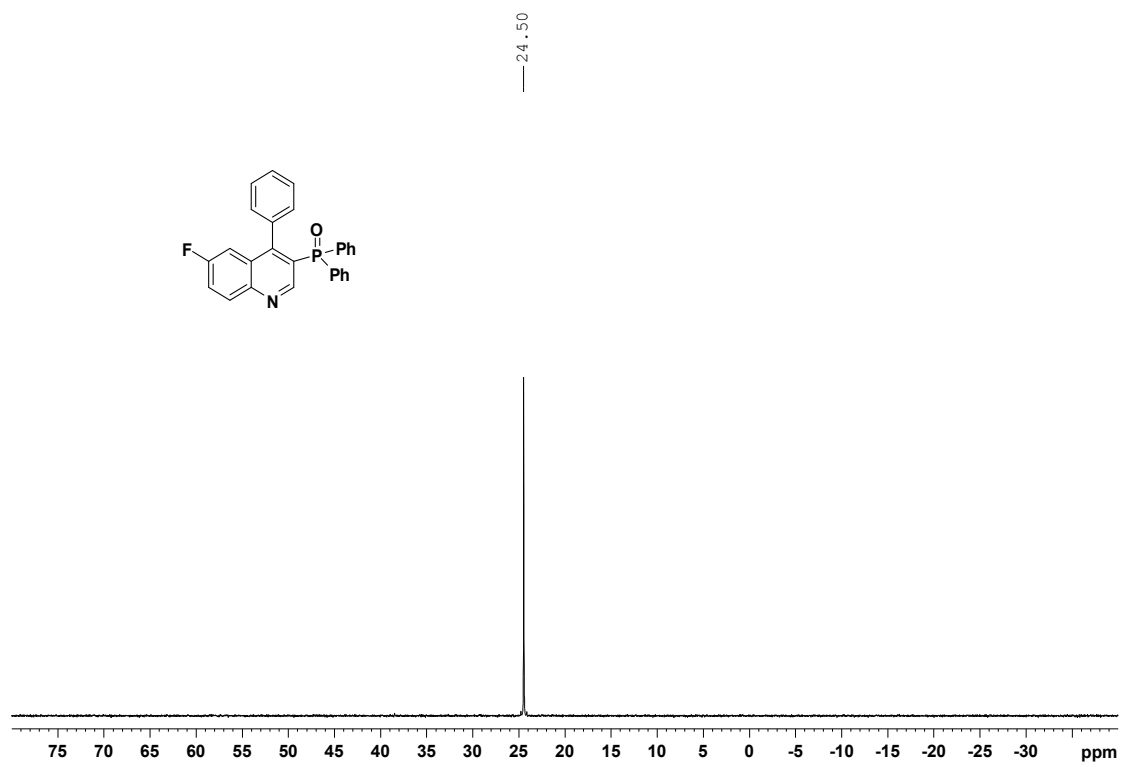
—24.89



30

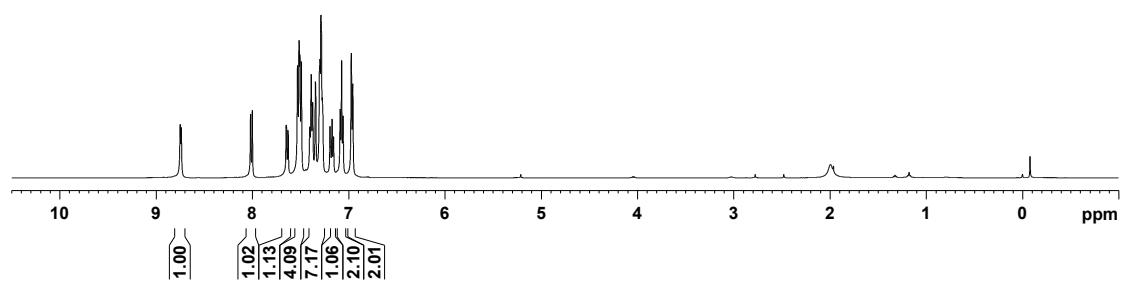
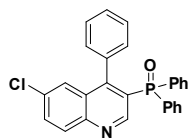






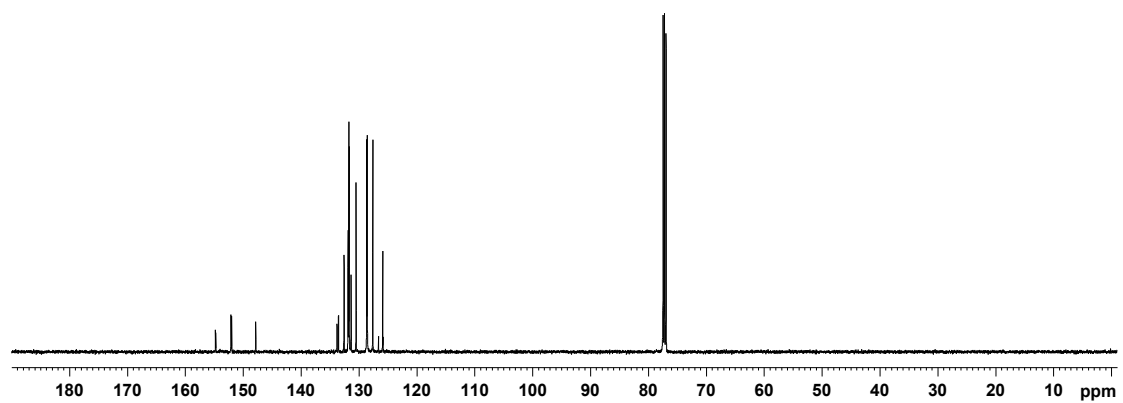
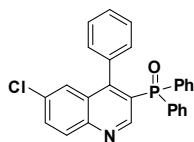
3p

8.749  
8.737  
8.018  
8.000  
7.648  
7.644  
7.630  
7.627  
7.530  
7.514  
7.506  
7.491  
7.443  
7.402  
7.388  
7.373  
7.344  
7.301  
7.297  
7.287  
7.283  
7.273  
7.193  
7.186  
7.171  
7.156  
7.087  
7.072  
7.057  
6.971  
6.956

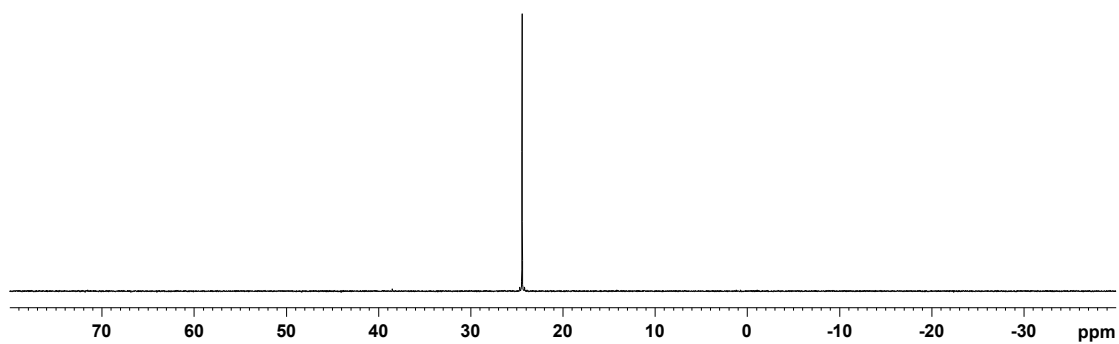
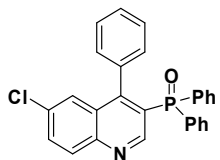


154.84  
154.78  
152.16  
152.05  
147.88  
133.86  
133.82  
133.58  
132.63  
132.60  
131.93  
131.91  
131.79  
131.72  
131.41  
130.53  
128.70  
128.65  
128.60  
128.53  
127.65  
126.66  
125.93  
125.86

77.88  
77.23  
76.97

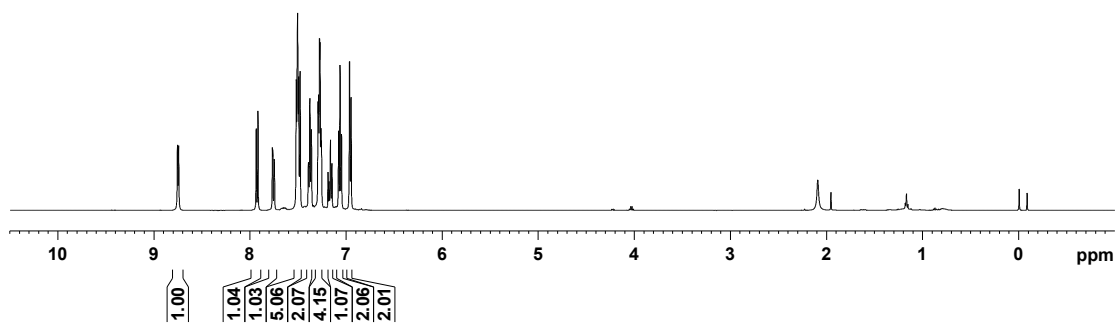
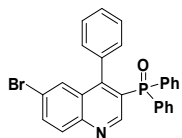


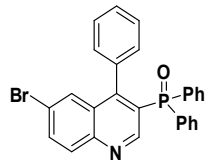
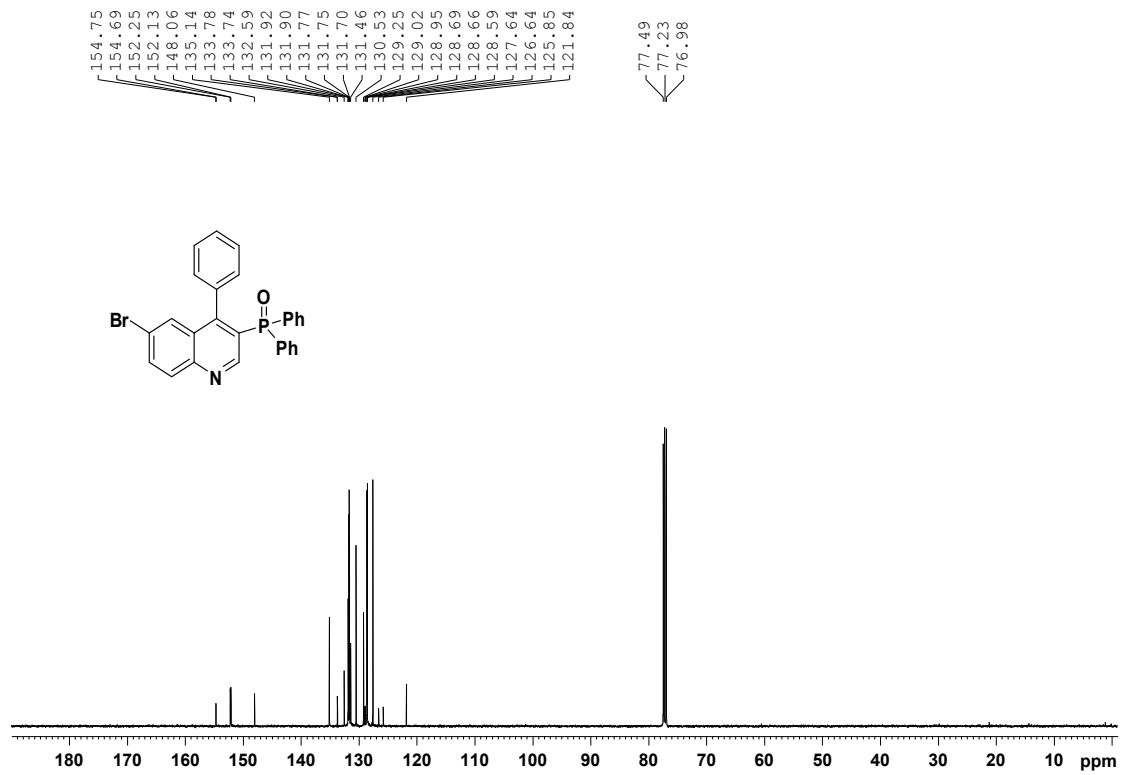
— 24.45



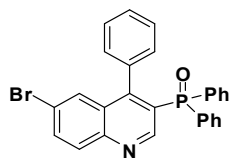
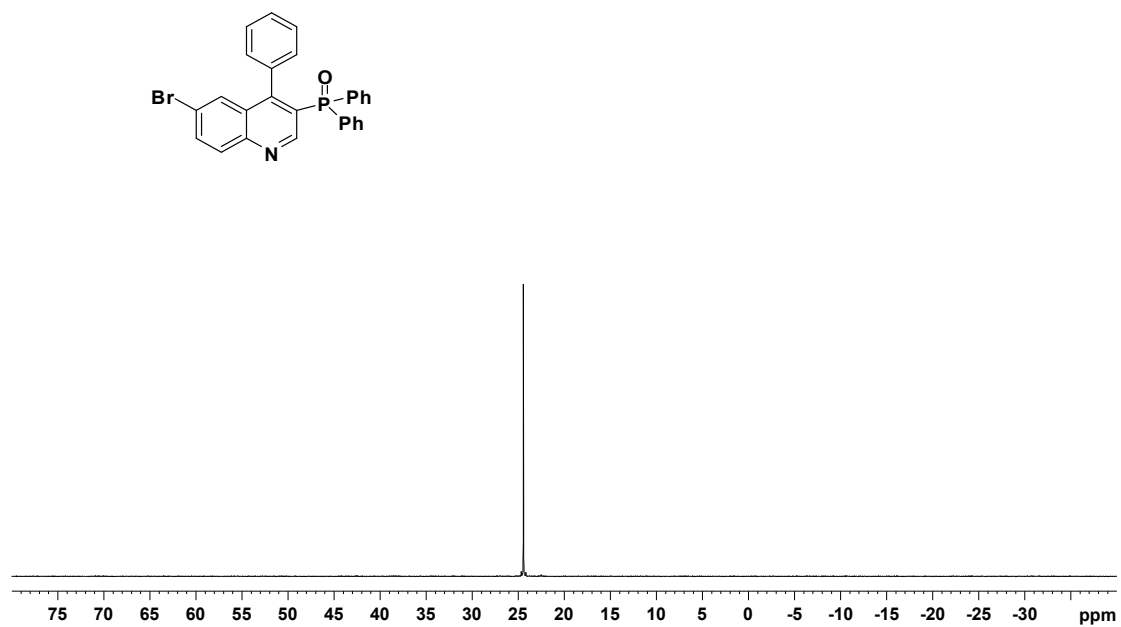
**3q**

8.756  
8.745  
7.941  
7.923  
7.772  
7.769  
7.755  
7.751  
7.524  
7.510  
7.500  
7.485  
7.398  
7.383  
7.368  
7.298  
7.292  
7.282  
7.277  
7.267  
7.261  
7.194  
7.183  
7.168  
7.153  
7.084  
7.068  
7.053  
6.970  
6.955

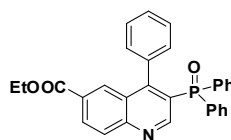
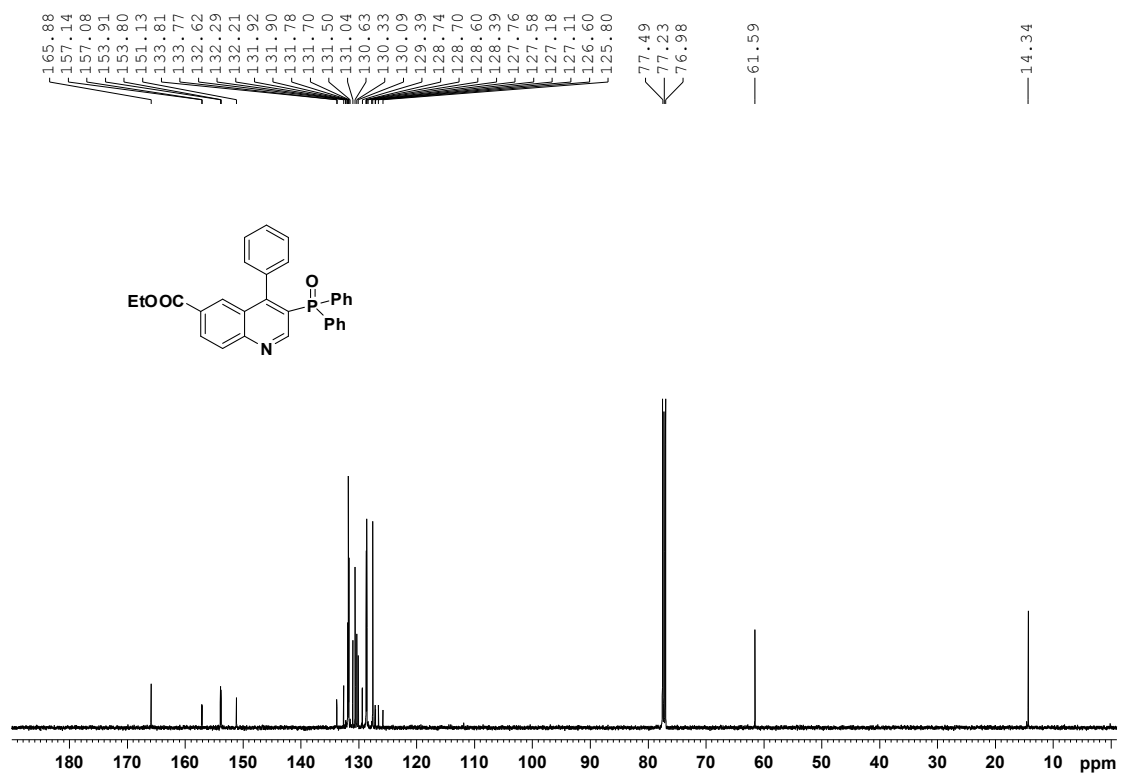
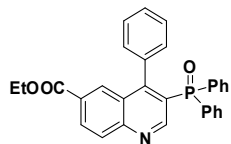
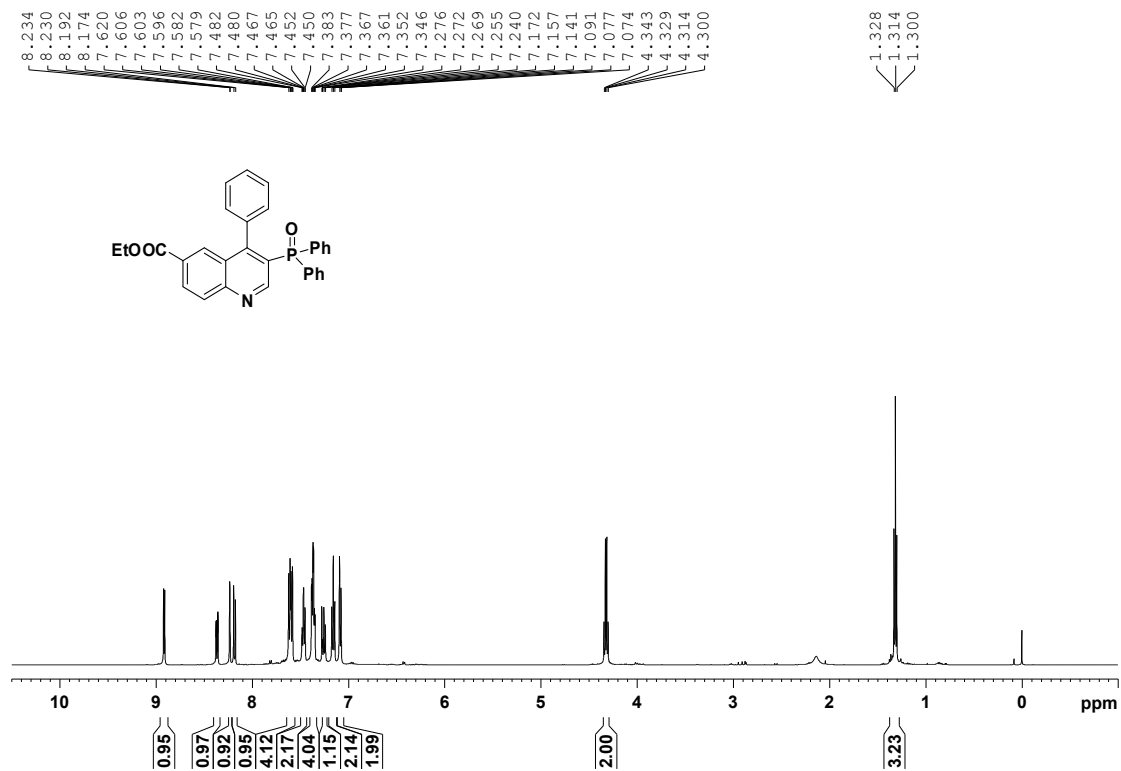


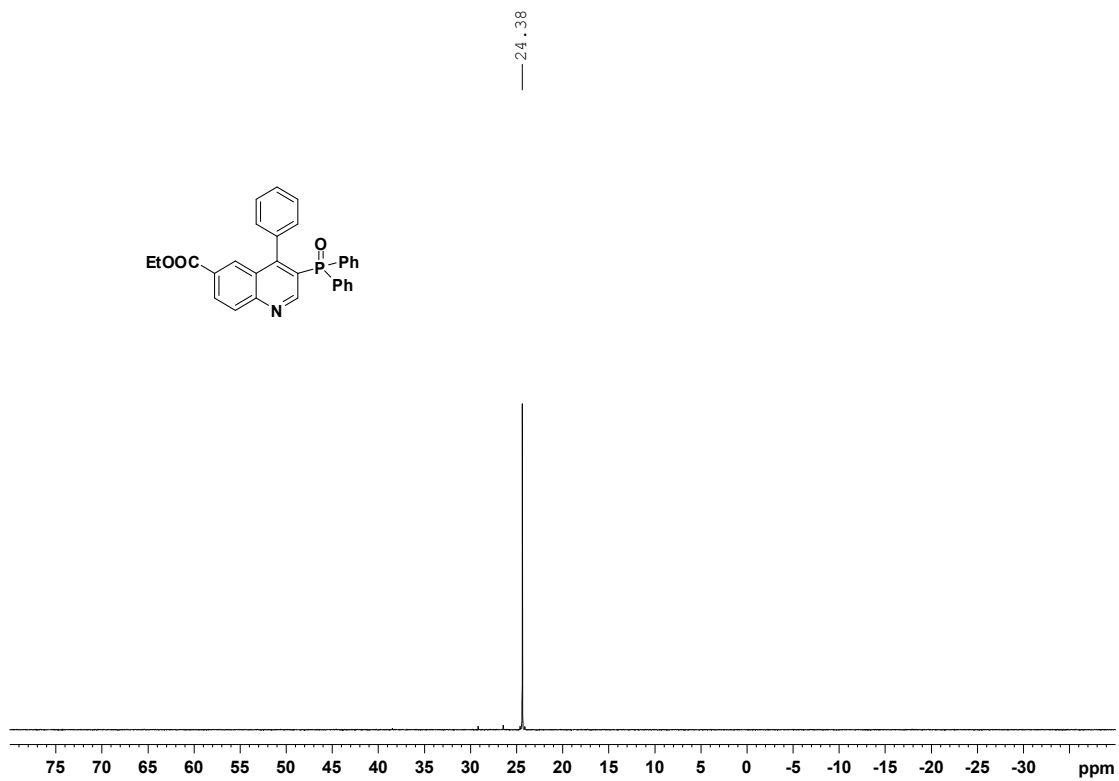
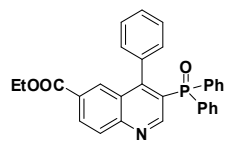


— 24.46

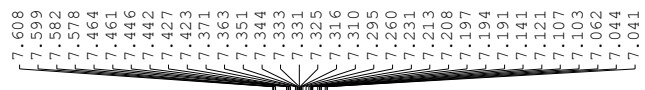


3r

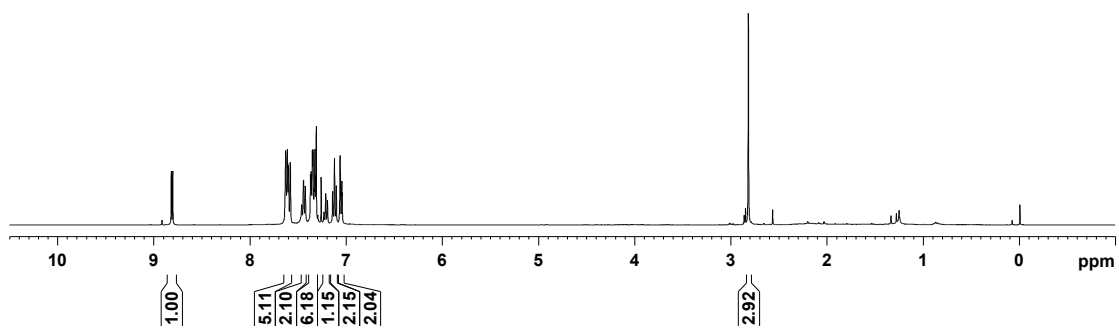
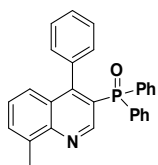




3s



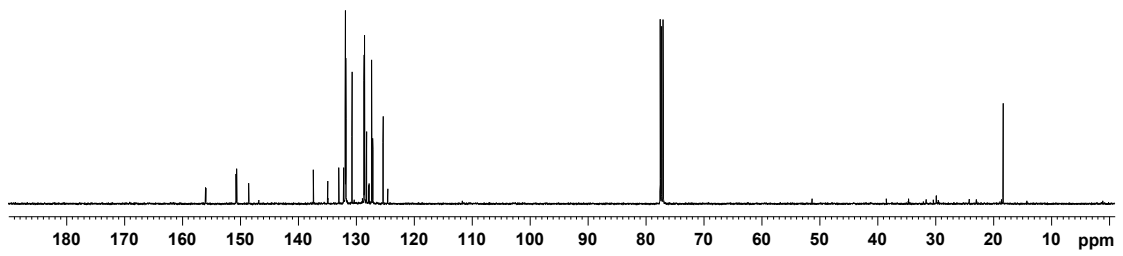
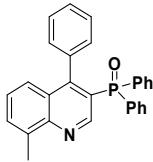
— 2.817



155.97  
155.91  
150.71  
150.59  
148.51  
137.35  
134.88  
134.84  
132.96  
132.12  
131.84  
131.76  
131.73  
131.71  
130.68  
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128.52  
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127.82  
127.75  
127.28  
127.09  
125.32  
124.51

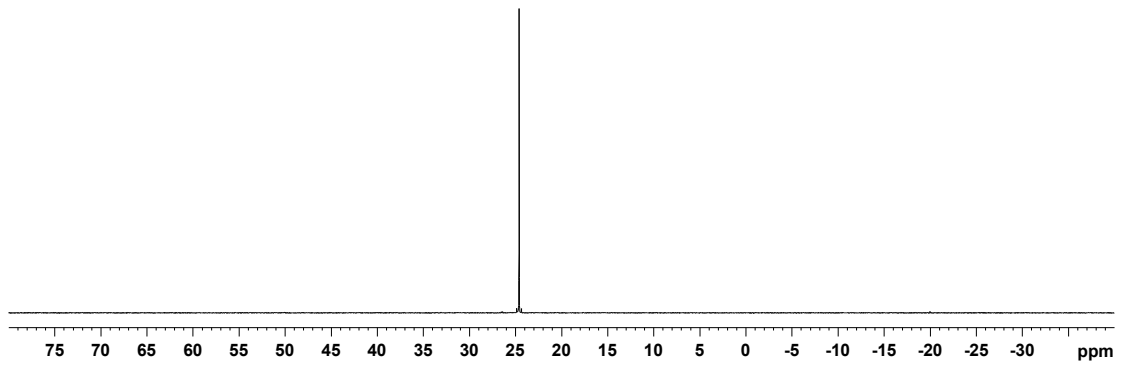
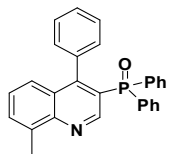
77.49  
77.23  
76.98

18.37



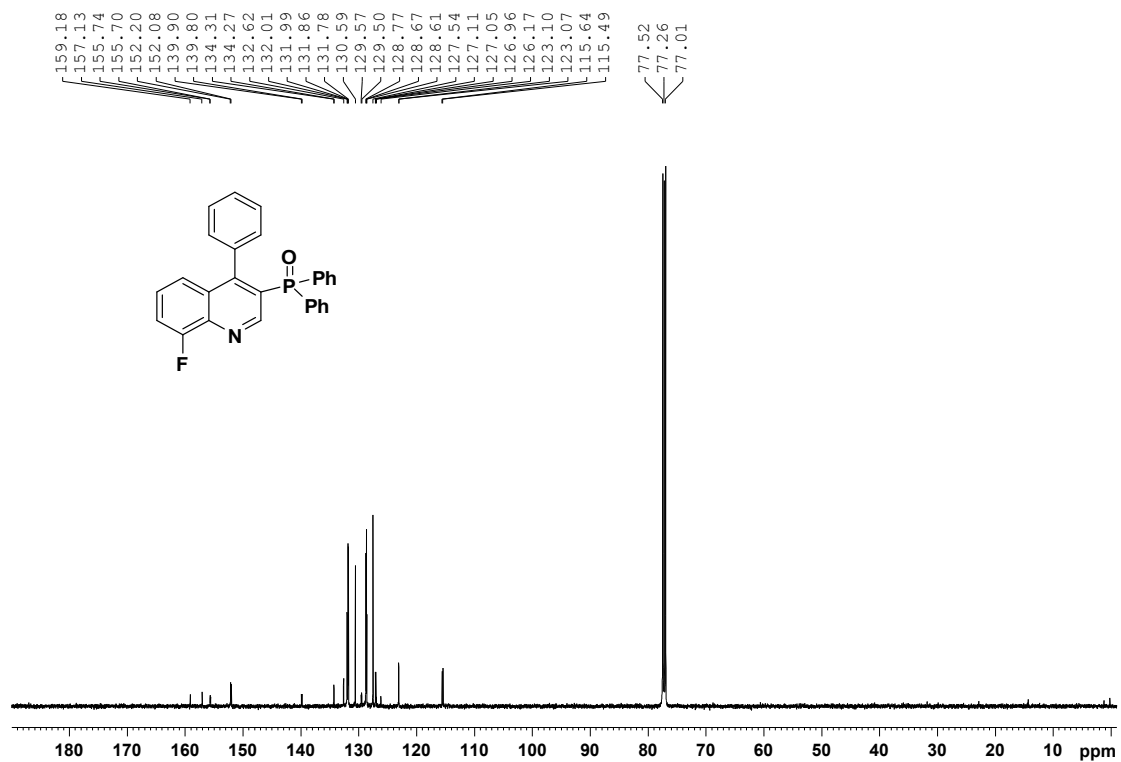
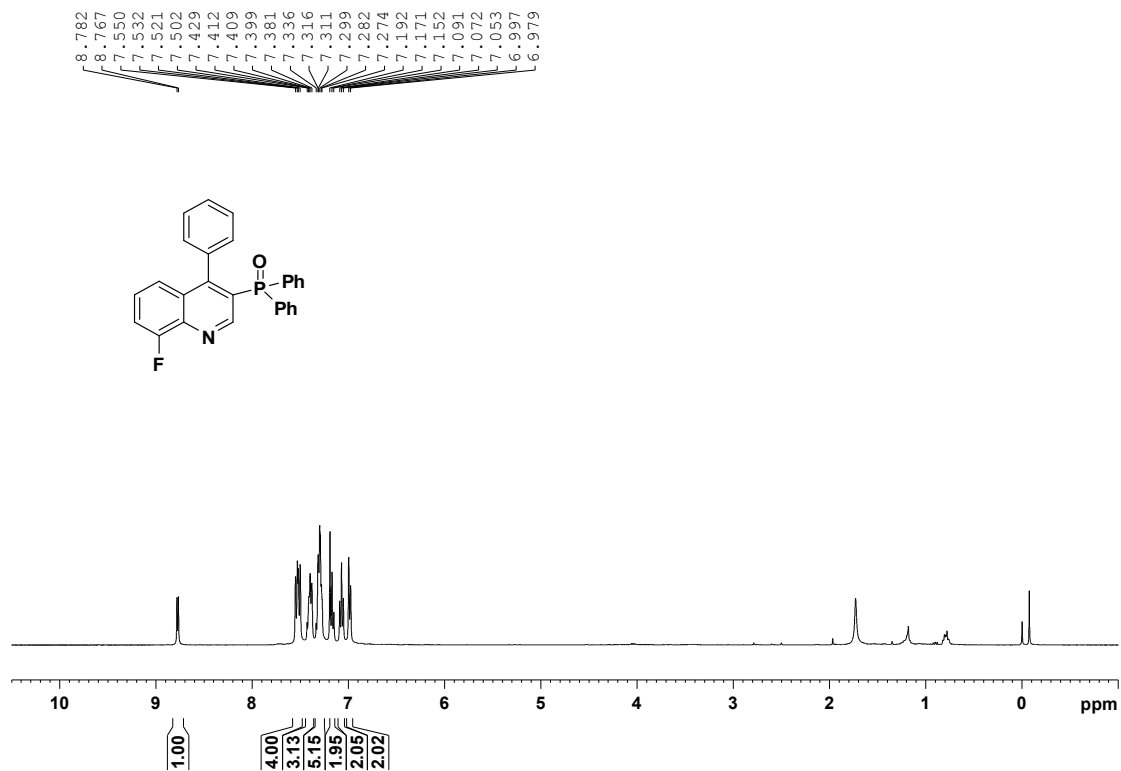
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

24.64

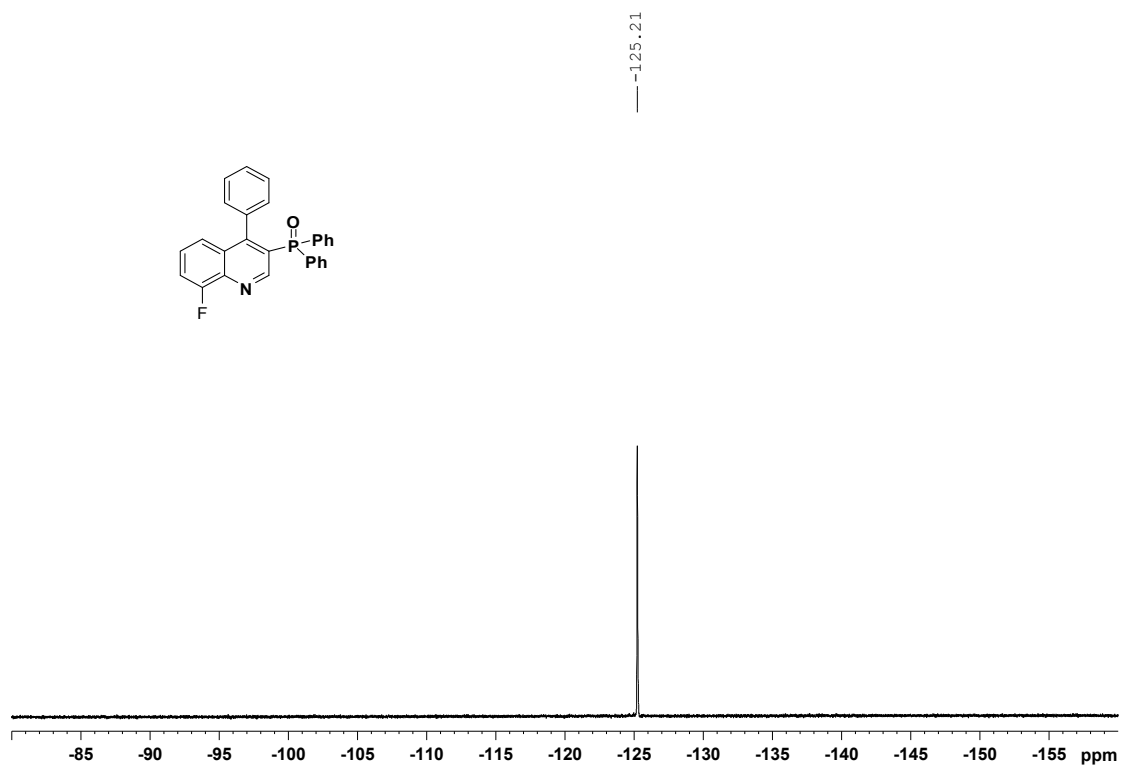
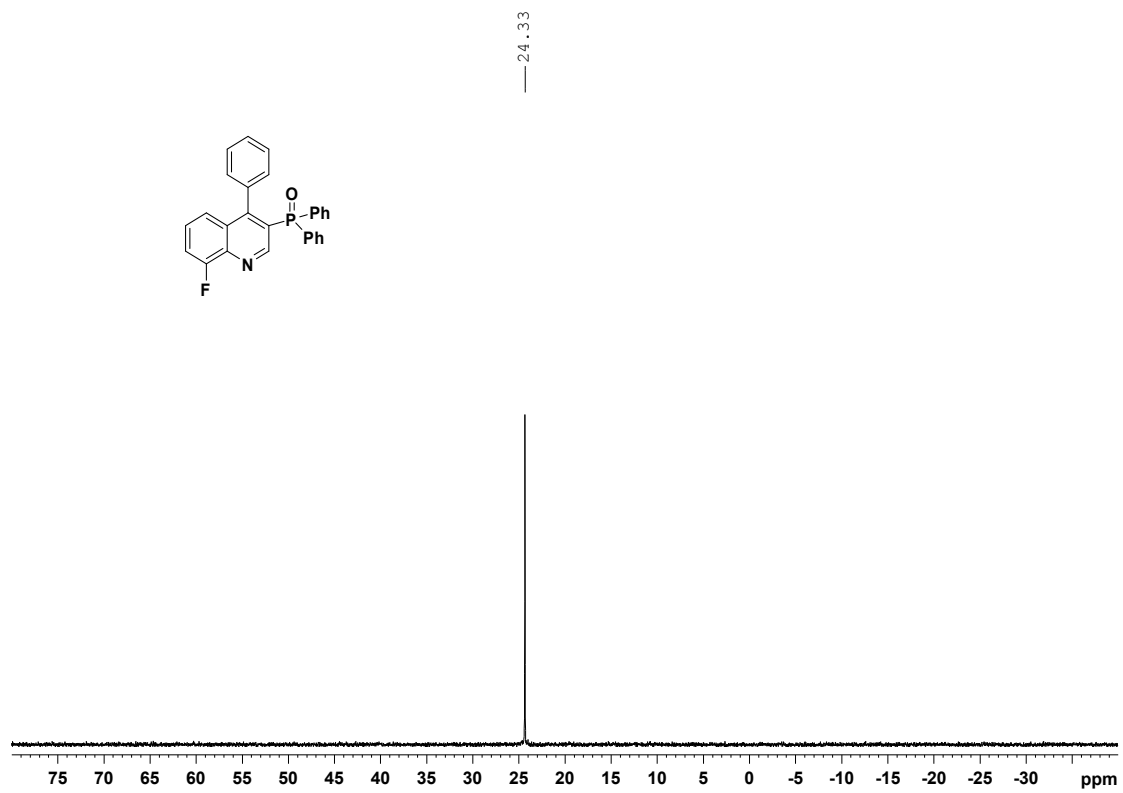


75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

3t

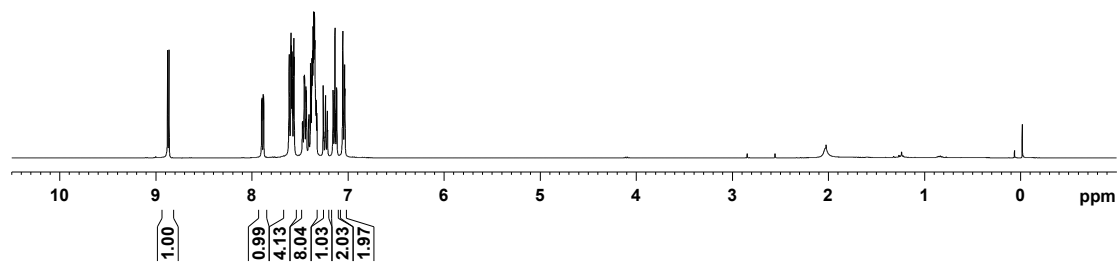
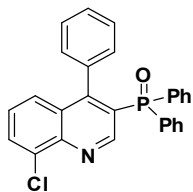






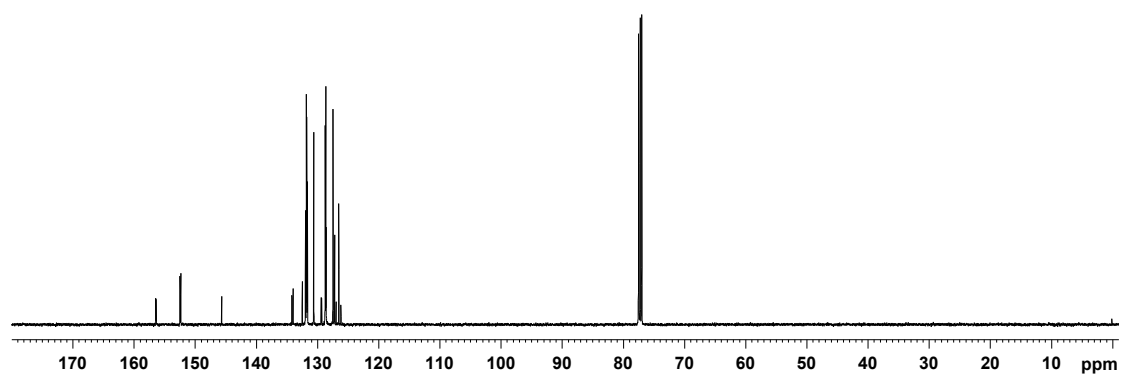
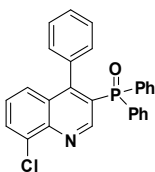
3u

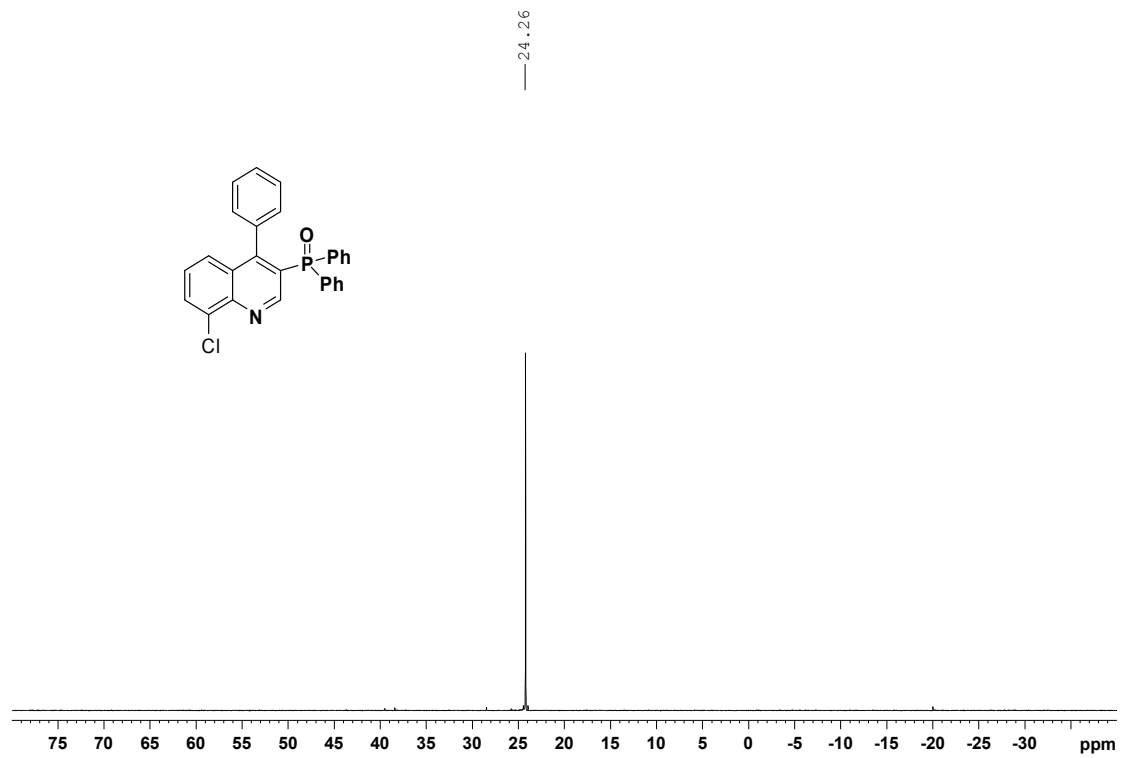
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7.473  
7.470  
7.458  
7.454  
7.439  
7.436  
7.412  
7.409  
7.391  
7.387  
7.378  
7.374  
7.370  
7.365  
7.359  
7.351  
7.347  
7.344  
7.341  
7.333  
7.326  
7.260  
7.255  
7.252  
7.241  
7.236  
7.231  
7.221  
7.217  
7.214  
7.157  
7.138  
7.124  
7.119  
7.054  
7.037  
7.033



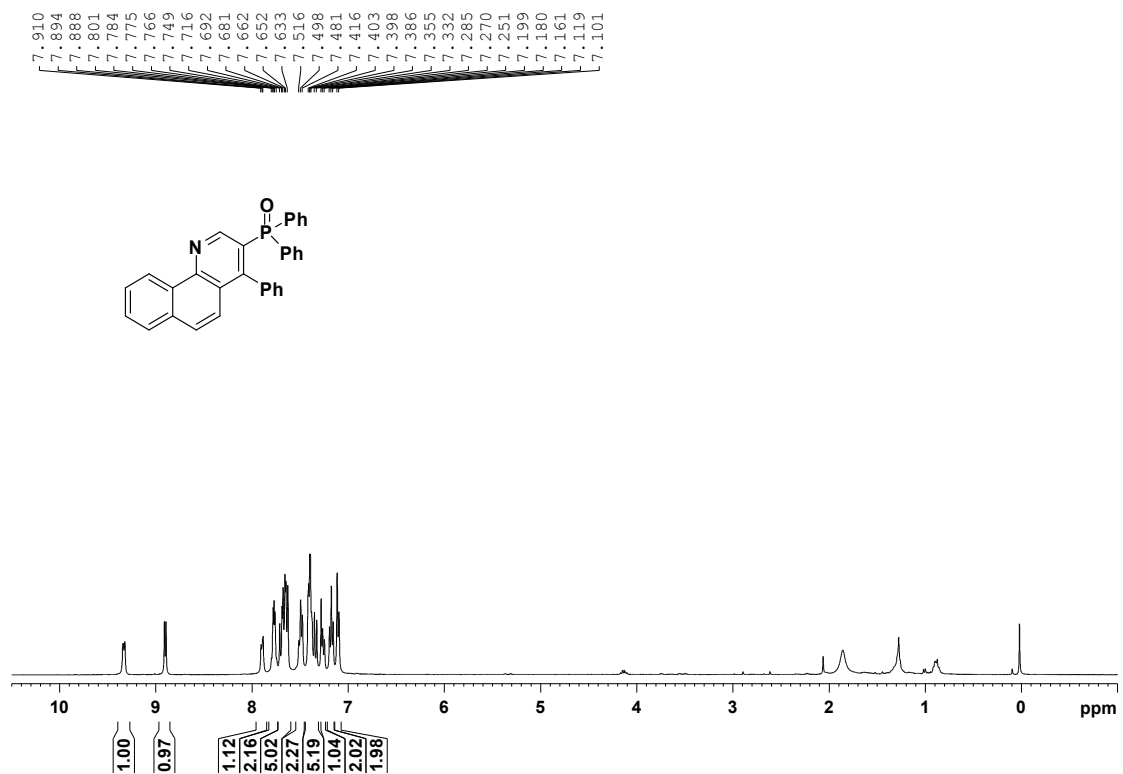
156.43  
156.37  
152.47  
152.35  
145.65  
134.20  
134.15  
133.97  
132.48  
131.96  
131.94  
131.81  
131.73  
131.63  
130.61  
129.38  
129.31  
128.73  
128.63  
128.57  
127.46  
127.19  
126.95  
126.51  
126.16

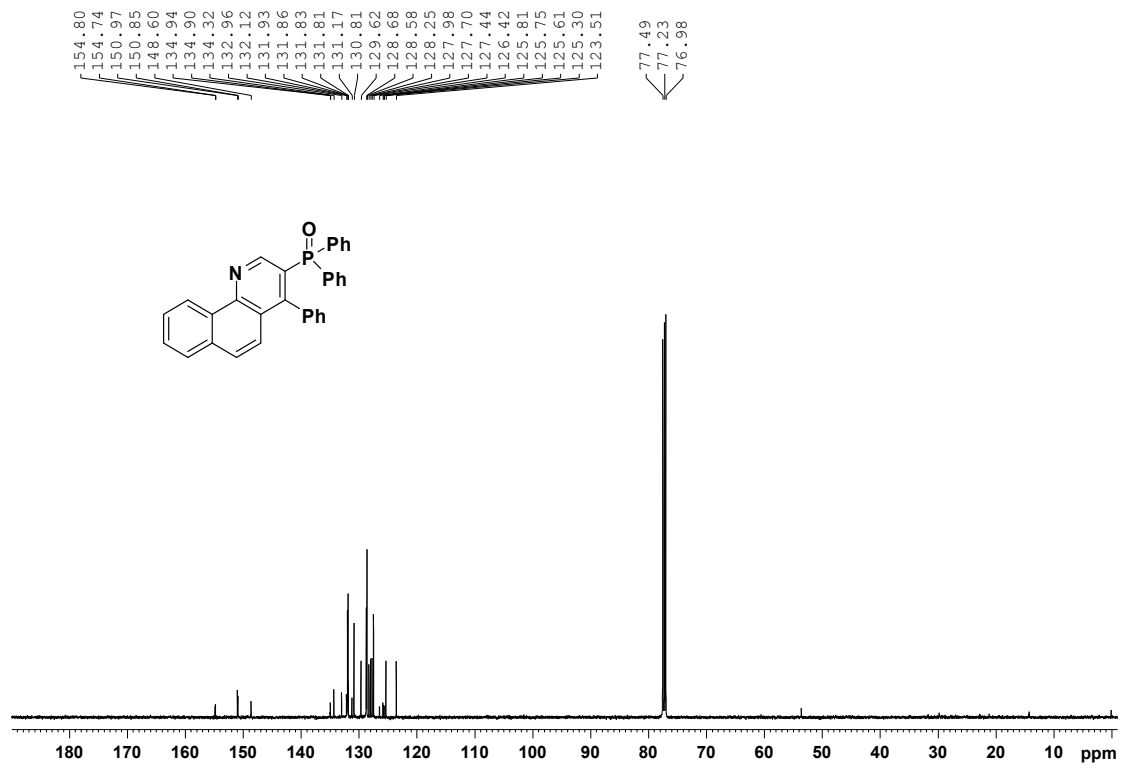
77.49  
77.23  
76.98



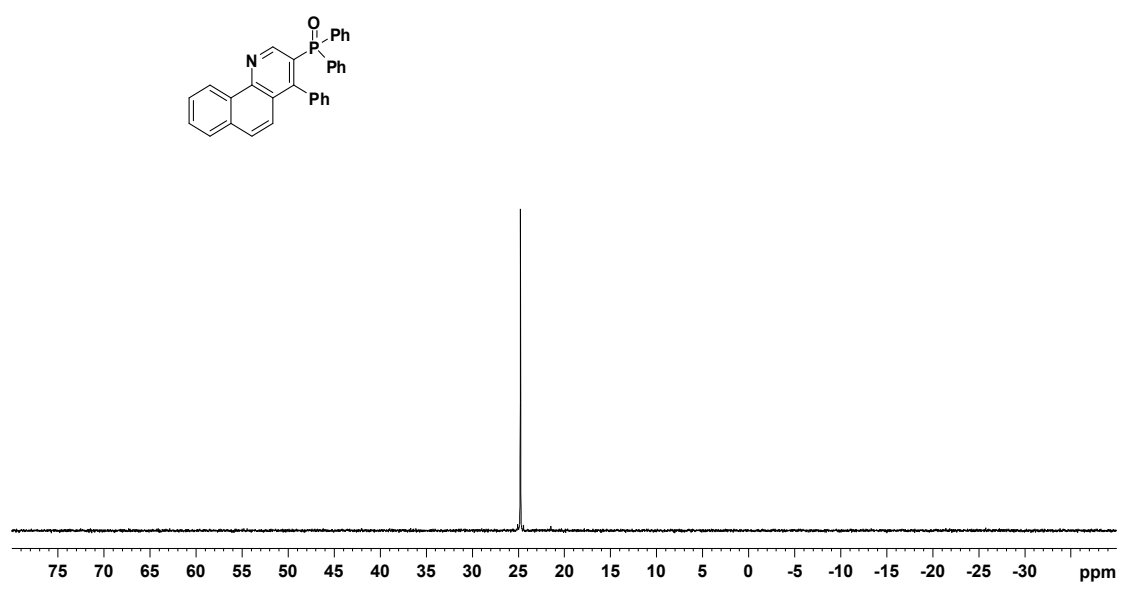


**3v**

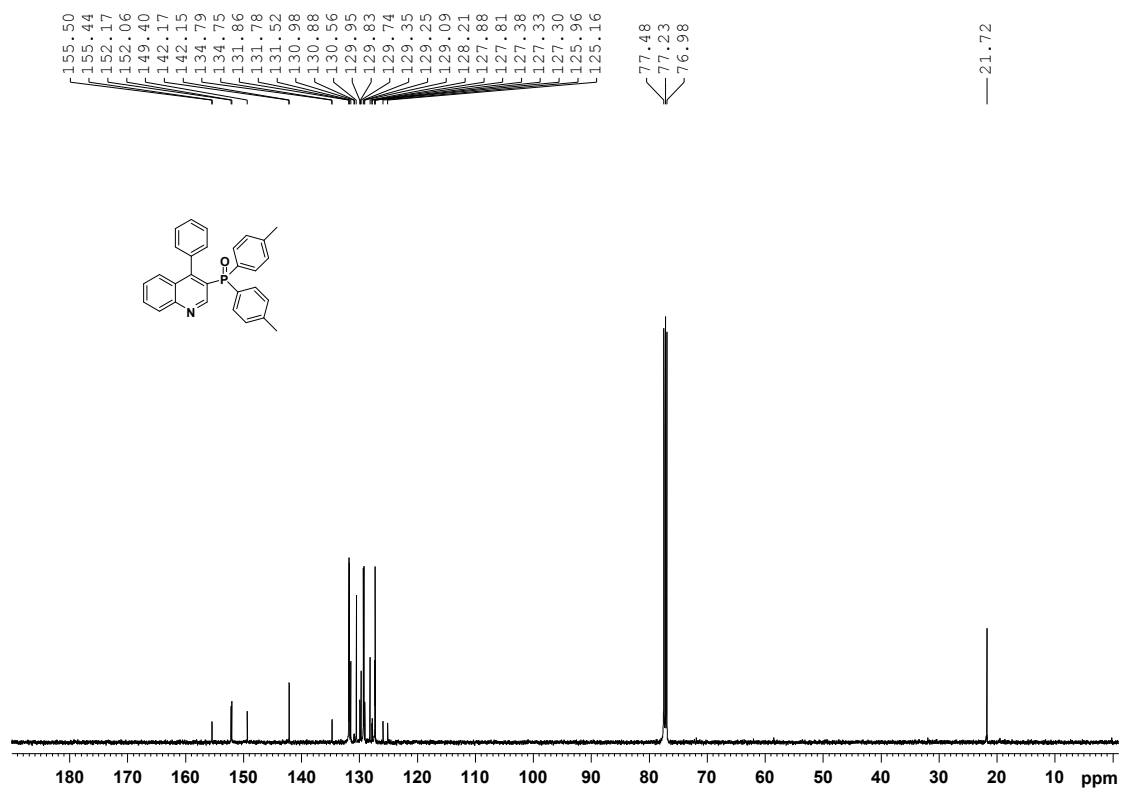
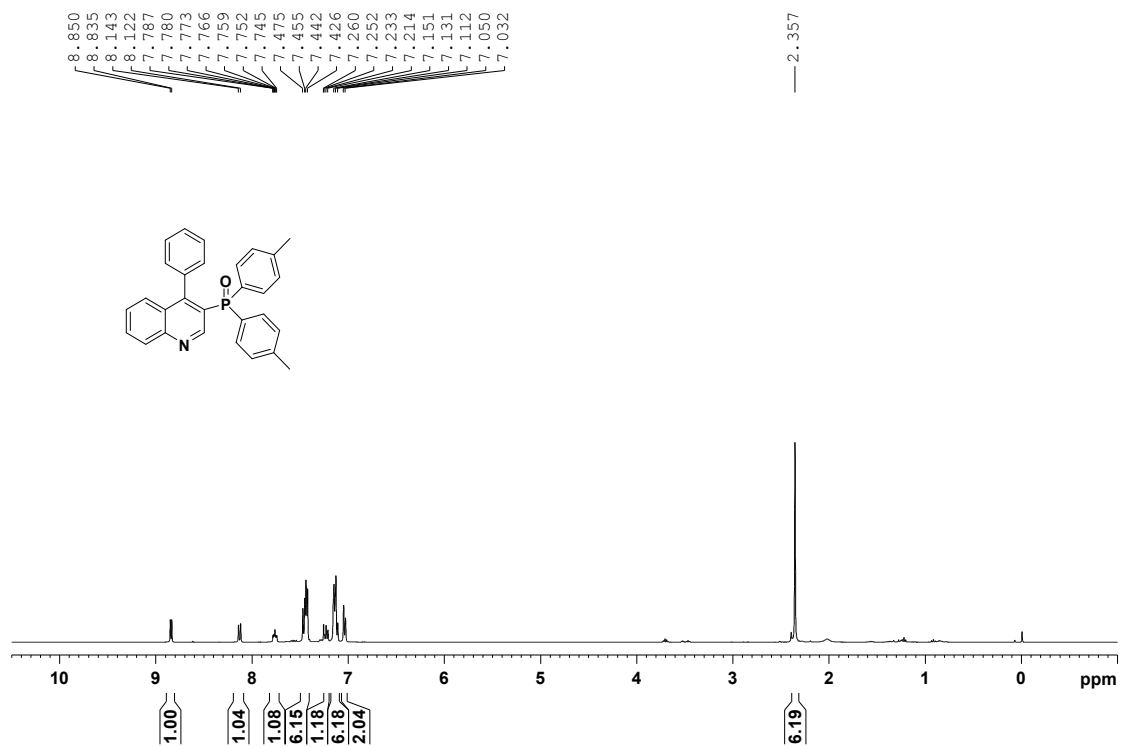


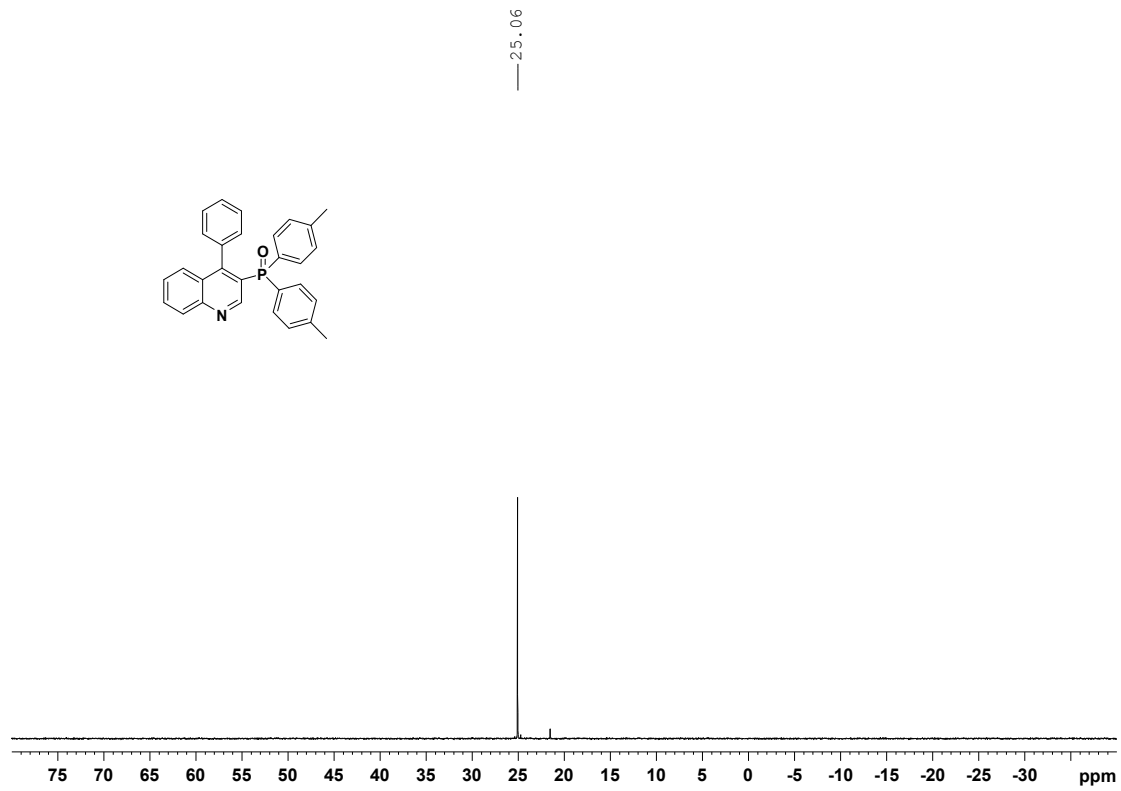


— 24.75

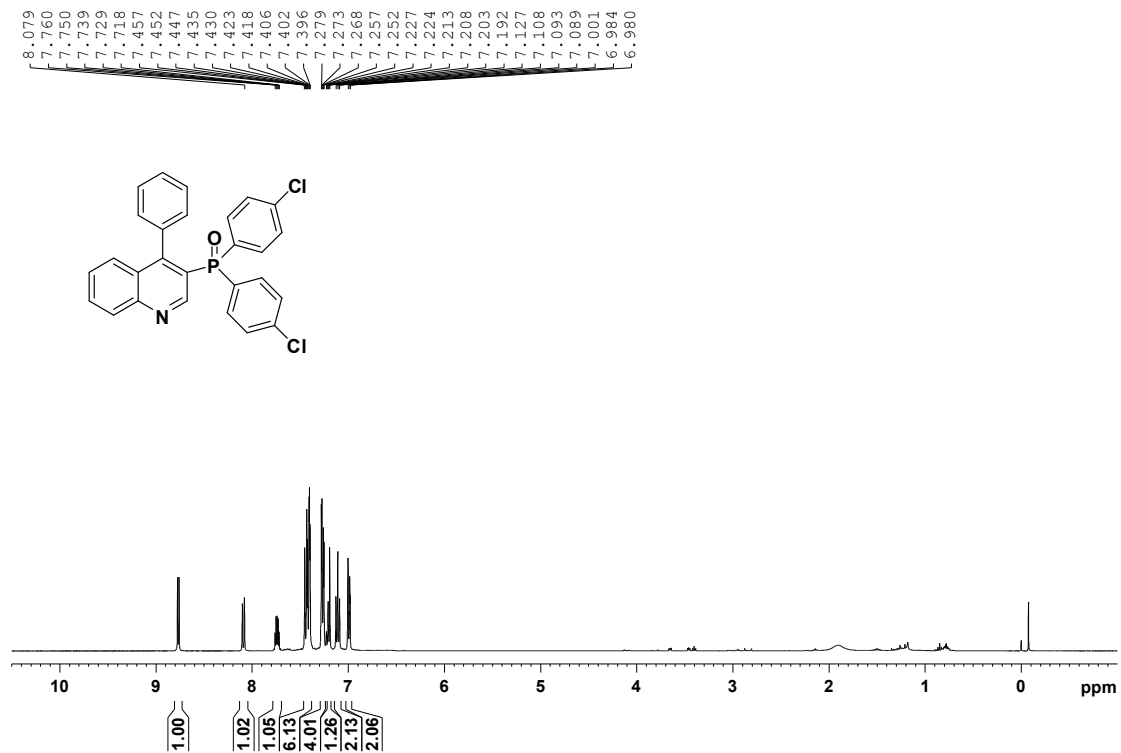


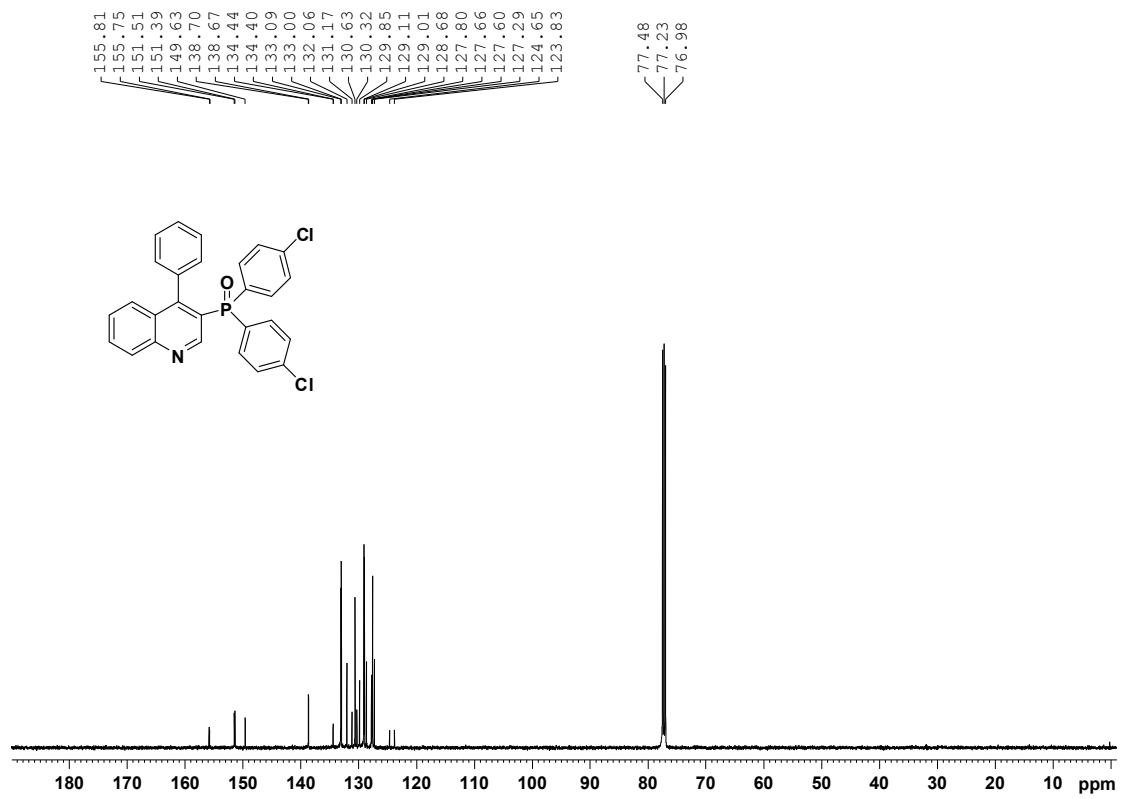
3w



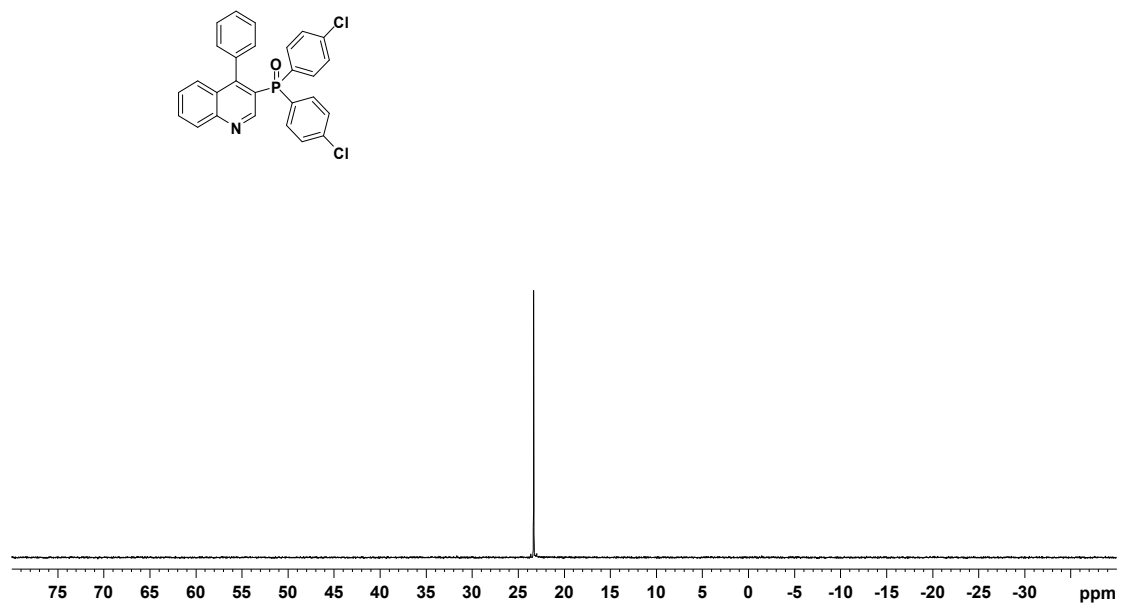


**3x**

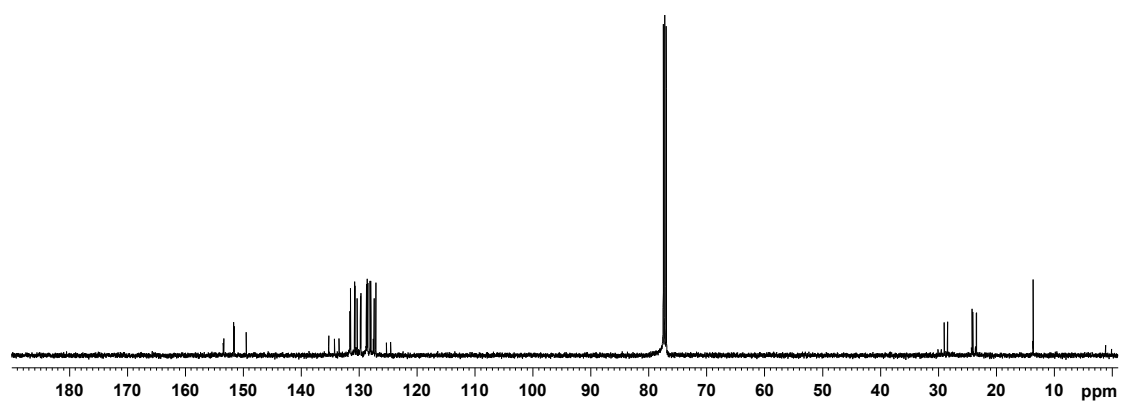
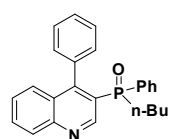
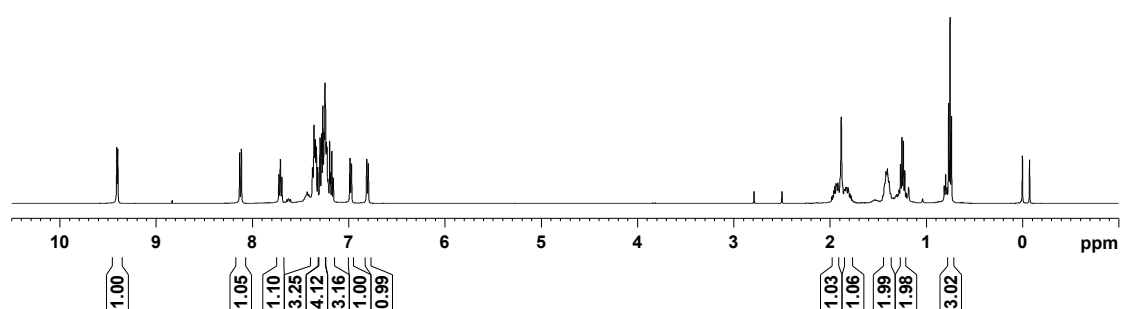
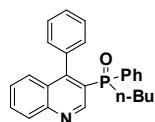
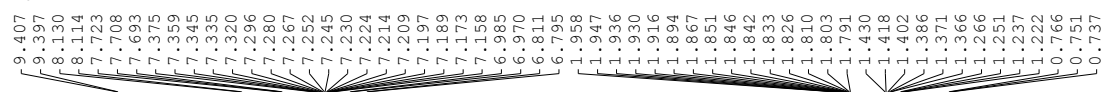




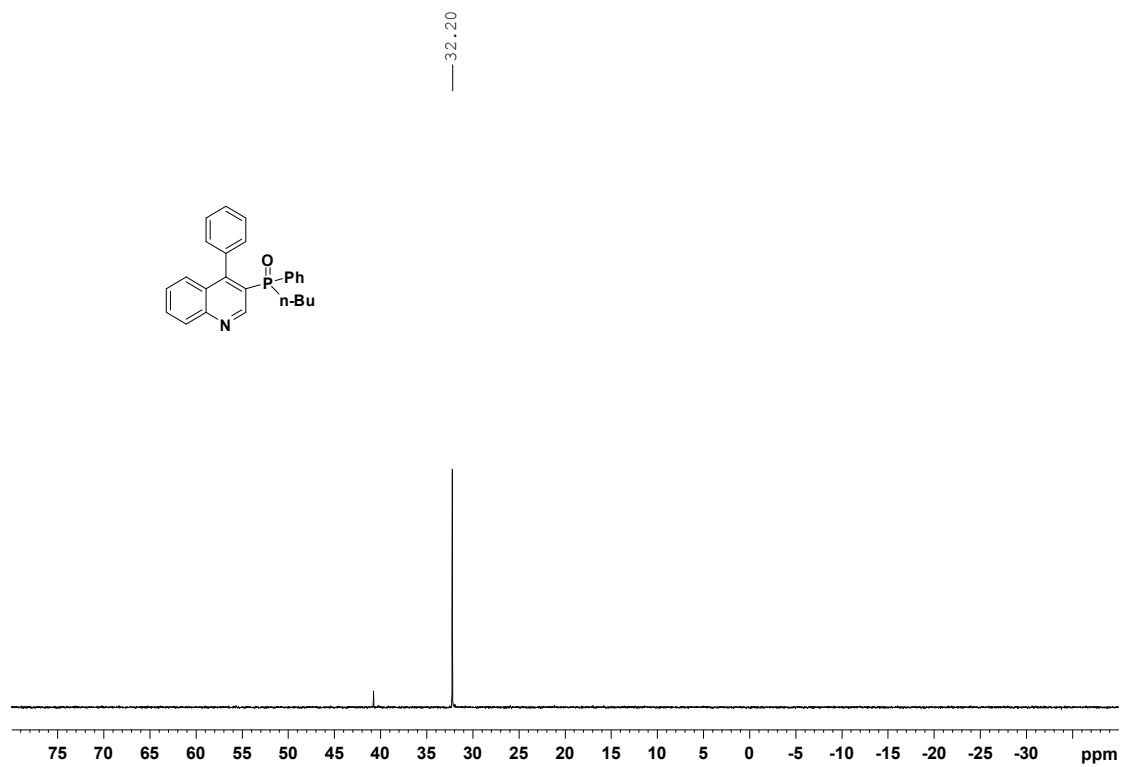
—23.31



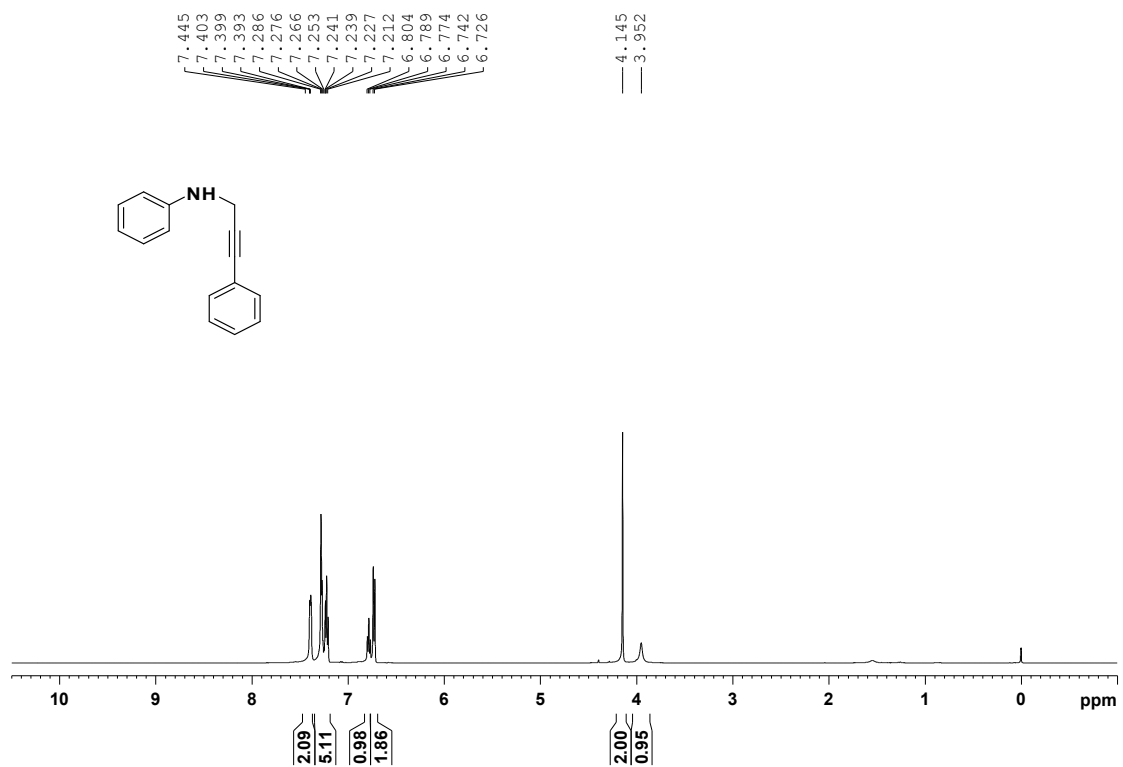
3y

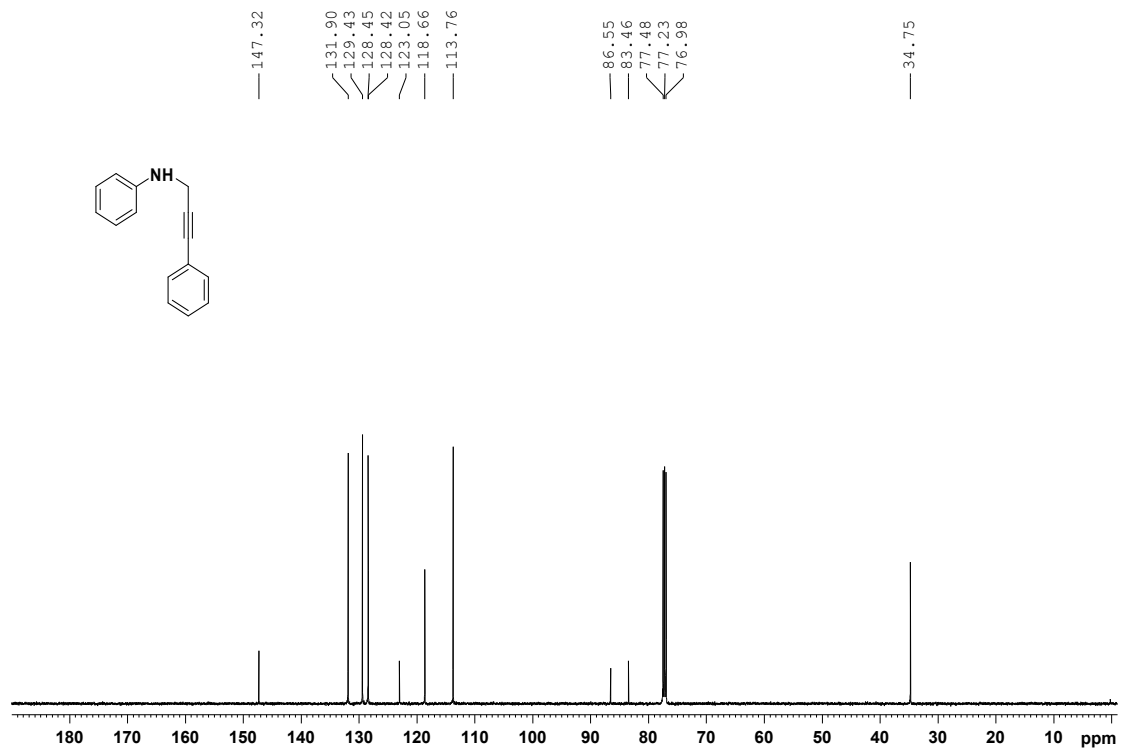






1a



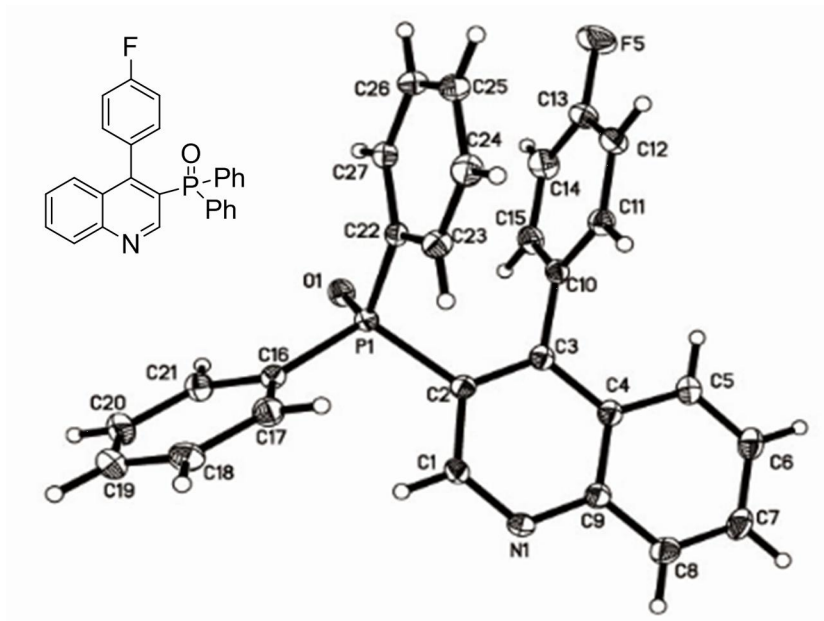


**3g**

X-ray Crystallographic Analysis X-ray structural data were collected on a Bruker Smart APEX diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation and a CCD area detector. Using Olex2, the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimisation.

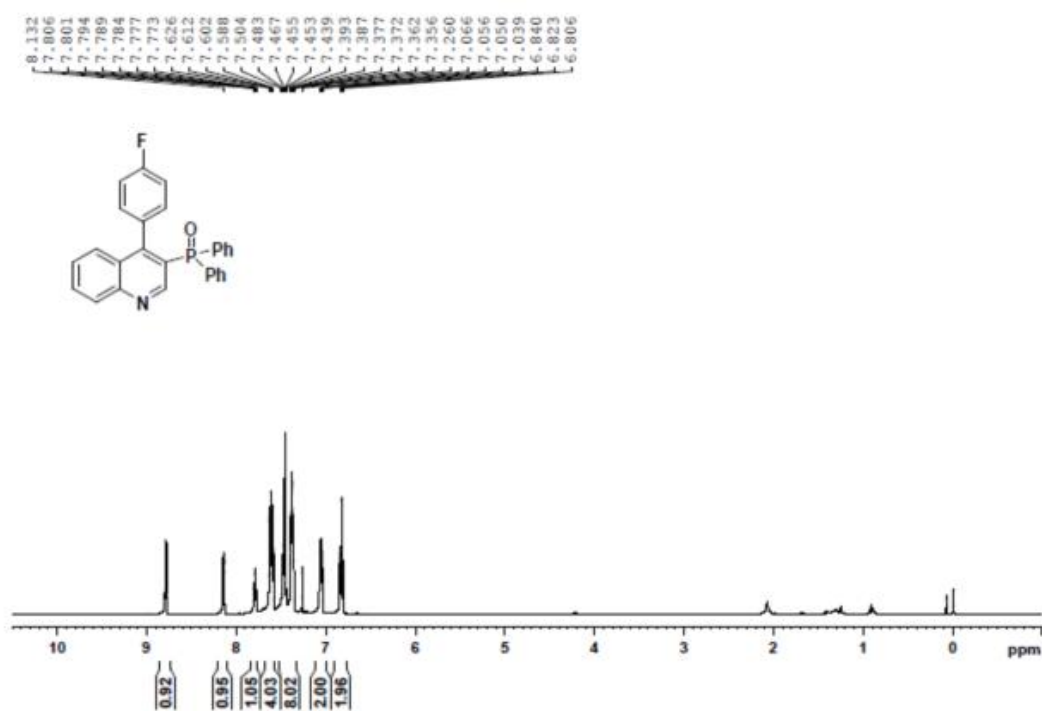
**Table 1 Crystal data and structure refinement for t1217m.**

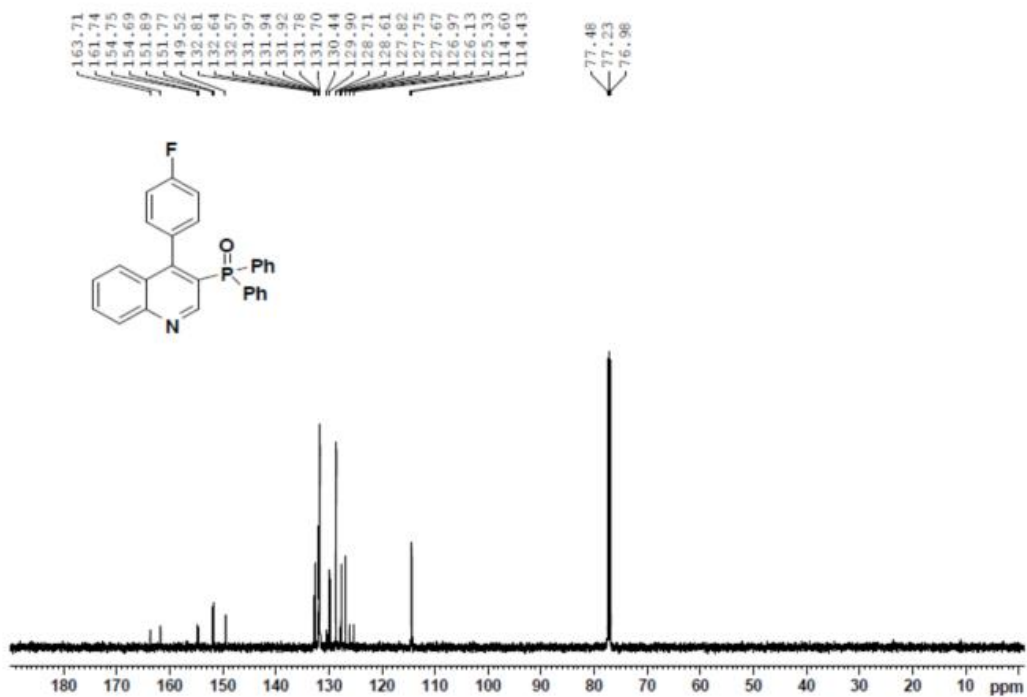
Identification code	t1217m
Empirical formula	CHNOPF <sub>0.03</sub> Cl <sub>0.03</sub>
Formula weight	75.88
Temperature/K	273.15
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	12.481(3)
b/Å	10.625(2)
c/Å	17.678(4)
$\alpha$ /°	90.00
$\beta$ /°	108.484(3)
$\gamma$ /°	90.00
Volume/Å <sup>3</sup>	2223.3(8)
Z	29
$\rho_{\text{calc}}/\text{cm}^3$	1.643
$\mu/\text{mm}^{-1}$	0.651
F(000)	1099.0
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	3.52 to 57.5
Index ranges	-16 $\leq$ h $\leq$ 16, -13 $\leq$ k $\leq$ 13, -23 $\leq$ l $\leq$ 23
Reflections collected	19034
Independent reflections	5358 [ $R_{\text{int}} = 0.0278$ , $R_{\text{sigma}} = 0.0266$ ]
Data/restraints/parameters	5358/0/280
Goodness-of-fit on F <sup>2</sup>	1.628
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0649$ , $wR_2 = 0.2024$
Final R indexes [all data]	$R_1 = 0.0697$ , $wR_2 = 0.2066$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.70/-0.27



**Figure 1.** X-ray structure of **3g**.

Molecular structure of **3g** with the anisotropic displacement parameters depicted at the 30% probability level.





— 24.33

