Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light-Induced Tandem Phosphorylation Cyclization of Vinyl Azides under Mild Conditions

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1. General information

^{1}H NMR (400 MHz) and ^{13}CNMR (100 MHz) spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. ^{31}P NMR (162 MHz) spectra and ^{19}F NMR(376 MHz) were recorded on the same instrument. Mass spectra were mearsured using Thermo Scientific DSQ II. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. The safety issues for handling of azido compounds[1,2]

2.1. Sodium azide (NaN_3)

Sodium azide is toxic (LD50 oral = 27 mg/kg for rats) and can be absorbed through skin. Appropriate gloves are necessary when using it. It decomposes explosively upon heating to above 275 ℃. Sodium azide is relatively safe especially in aqueous solution, *unless acidified to form* HN_3, which is volatile and highly toxic.

2.2. Organic azides

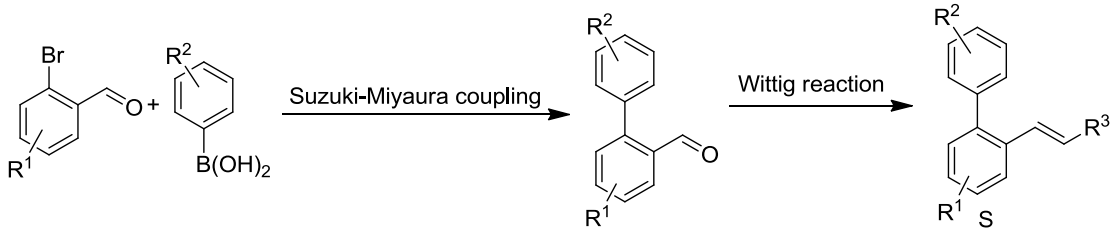
Organic azides are potentially explosive substances that can decompose with the slight input of energy from external sources (heat, light, pressure, etc). When designing the organic azides used for the project, we keep in mind the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group. All organic azides prepared in this work are satisfied with the equation above and they are enough stable to be stored under –20 ℃ at leatst for 6 months. We have never experienced a safety problem with these materials.

$(N_C+N_O)/N_N>3$ (N_C: number of the carbon atom, N_C: number of the oxygen atom, N_N: number of the carbon atom)

3. Synthesis of biaryl vinyl azides

3.1. Synthesis of biaryl alkenes

Biaryl alkenes were prepared by a two-step sequences including Suzuki-Miyaura coupling and Wittig reaction. The preparation of biaryl alkenes was described in previous reports, and the NMR spectroscopya was consisted with those data.[1]



A general procedure for synthesis of biaryl alkene **S1**(R_1 =H, R_2 = Me):

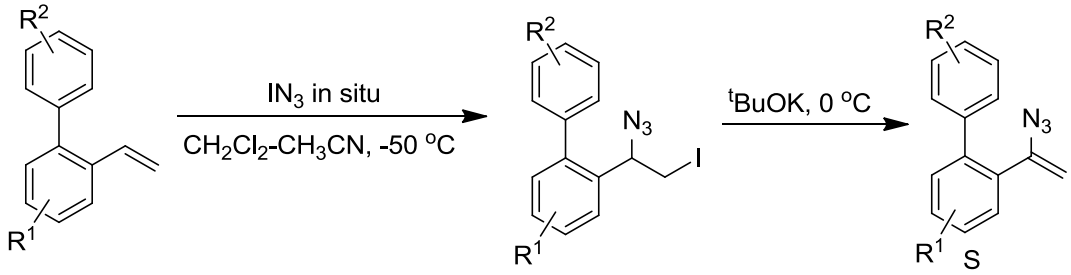
To a solution of 2-bromobenzaldehyde (9.41g, 50.9 mmol) and p-tolylboronic acid (8.31 g,61.1 mmol) in ethanol (60 mL) and 1,2-dimethoxyethane (DME) (80 mL) was added an aqueous solution of Na_2CO_3 2M (100 mL, 200 mmol), followed by $Pd(PPh_3)_4$(4.62 g, 4.0 mmol).The reaction was stirred at 90 ℃ under nitrogen atmosphere for 6 h. After completion, the reaction mixture was filter through a short pad of celite and washed with Et_2O. The aqueousphase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column

chromatography (hexane : EtOAc = 95 : 5) to biphenyl-2-carbaldehyde.

To a suspension of $MePPh_3Br$ (27.29 g, 76.4 mmol) in THF (120 mL), *t*-BuOK (8.57 g, 76.4mmol) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to -78 ℃ and a solution of the intermediate aldehyde (8.81g, 48.3 mmol) in THF (50 mL) was added dropwise. The mixture was stirred at -78 ℃ for 1 h and then warmed to room temperature for 1 h. The reaction was quenched with water. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over$MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : EtOAc = 97 : 3) to afford 2-vinylbiphenyl from 2-bromobenzaldehyde **S1**.

All biaryl alkenes **S** were prepared through the same synthetic route as that of **S1.**

3.2. Synthesis of biaryl vinyl azides (Hassner's method)



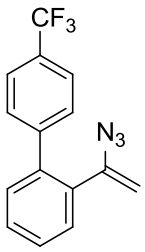
A general procedure of method A (R_1 = H, R_2 = Me): this procedure was slightly modified from Hassner's method.[3]

To a suspension of NaN_3 (2.119 g, 32.4 mmol) in acetonitrile (8.0 mL) was added dropwise a solution of iodine monochloride (3.175 g, 19.6 mmol) in CH_2Cl_2 (30 mL) at 0 ℃. The mixture was stirred at the same temperature for 30 min and then cooled to –50 ℃. A solution of 4'-methyl-2-vinylbiphenyl (2.520 g, 13.0 mmol) in CH_2Cl_2 (15 mL) was added slowly over 30 min. After that,the mixture was further kept at the same temperature for 15 min, and then was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted two times with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification. This step only led to a single regioisomer.

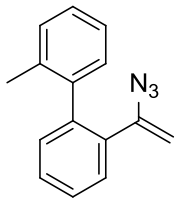
To a solution of the obtained compounds above in Et_2O (30 mL) was added *t*-BuOK (1.602 g,14.3 mmol) at 0 ℃, and the mixture was stirred for 2 h at the same temperature. The reaction was quenched with water, and the organic materials were extracted with Et_2O. The Et_2O solution was washed with brine, and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography silica gel (hexane :EtOAc = 99 : 1) to give vinyl azide 2-vinyl-1,1'-biphenyl **S2** as a pale yellow liquid.

All biarylvinyl azides were prepared through the same synthetic route as that of **S2**.

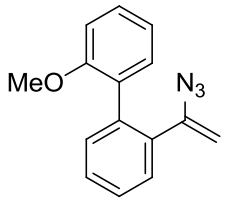
3.3. Characterization data of new biarylvinylazides



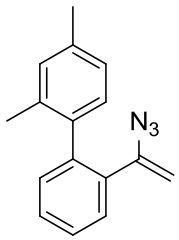
2-(1-azidovinyl)-4'-(trifluoromethyl)biphenyl(1e): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (2H, d, *J* = 9.0 Hz), 7.32-7.47 (4H, m), 7.56 (2H, d, *J* = 9.0 Hz), 4.94 (1H, s), 4.81 (1H, s); ^{19}F NMR (376 MHz,$CDCl_3$) δ 63.38; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.22, 144.23, 138.98, 133.82, 130.30, 130.10, 129.69, 129.53, 129.25, 129.06, 128.17, 125.11, 125.16, 103.96.



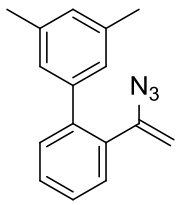
2-(1-azidovinyl)-2'-methylbiphenyl(1f): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ7.44-7.47 (1H, m), 7.31-7.39 (2H, m), 7.15-7.25 (5H, m), 4.81 (1H, d, *J* = 3.0 Hz), 4.63 (1H, d, *J* = 3.0 Hz), 2.11 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ144.80, 140.46, 140.41, 135.52, 134.24, 130.58, 129.89, 129.43, 128.82, 128.70, 127.42, 127.22, 125.38, 103.24, 20.05.



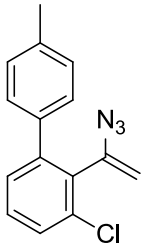
2-(1-azidovinyl)-2'-methoxybiphenyl(1g): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.42 (5H, m), 7.22 (1H, d, *J* = 9.0 Hz), 6.98 (1H, d, *J* = 9.0 Hz), 6.90 (1H, d, *J* = 9.0 Hz), 4.73 (1H, s), 4.42 (1H, s), 3.72 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.08, 144.63, 137.47, 134.76, 131.05, 130.69, 129.73, 128.84, 128.77, 128.19, 127.23, 120.45, 110.54, 102.78, 55.01.



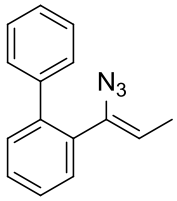
2'-(1-azidovinyl)-2,4-dimethylbiphenyl(1k): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.46 (1H, m), 7.30-7.37 (2H, m), 7.17-7.20 (1H, m), 7.10 (1H, d, *J* = 9.0 Hz), 7.05 (1H, d, *J* = 9.0 Hz), 7.00 (1H, s), 4.80 (1H, s), 4.62 (1H, s), 2.31 (3H, s), 2.06 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.76, 140.59, 140.33, 134.68, 134.16, 132.33, 130.60, 130.07, 129.76, 128.72, 128.65, 128.12, 127.11, 103.20, 20.87, 19.51.



2'-(1-azidovinyl)-3,5-dimethylbiphenyl(1l): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ7.29-7.40 (4H, m), 7.06 (2H, s), 6.97 (1H, s), 4.90 (1H, s), 4.77 (1H, s), 2.33 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.78, 140.70, 140.47, 137.47, 133.61, 130.37, 129.82, 129.18, 128.94, 127.11, 126.54, 103.45, 21.28.



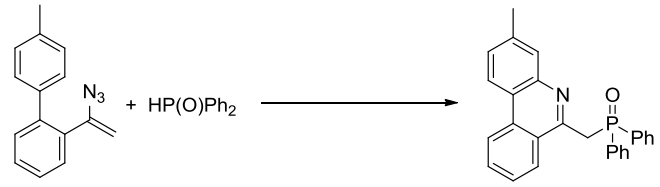
2-(1-azidovinyl)-3-chloro-4'-methylbiphenyl(1n): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (1H, d, *J* = 3.0 Hz), 7.29-7.36 (3H, m), 7.24 (1H, d, *J* = 9.0 Hz), 7.18 (2H, d, *J* = 7.5 Hz), 4.92 (1H, s), 4.79 (1H, s), 2.36 (3H, s),; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.60, 138.79, 137.41, 136.29, 135.02, 132.85, 131.65, 129.77, 129.25, 128.97, 128.39, 104.05, 21.14.

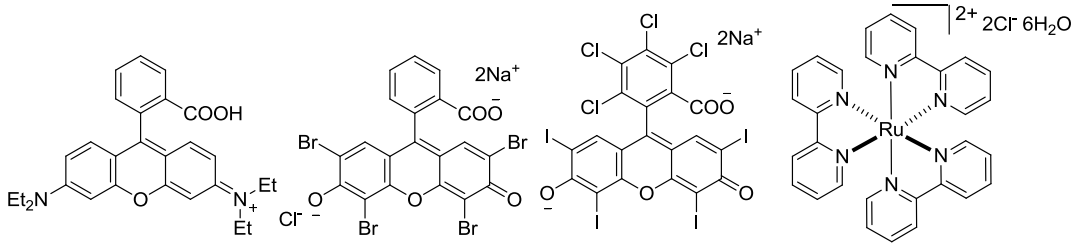


2-(1-azidoprop-1-enyl)biphenyl(1o): yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.48 (2H, m), 7.32-7.39 (7H, m), 5.01 (1H, q, *J* = 12.0 Hz), 1.65 (3H, d, *J* = 9.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.63, 140.28, 137.03, 133.92, 130.60, 130.36, 129.20, 128.82, 128.10, 127.53, 127.47, 115.89, 12.53.

4. General Procedures.

4.1. Optimization of Reaction Conditions





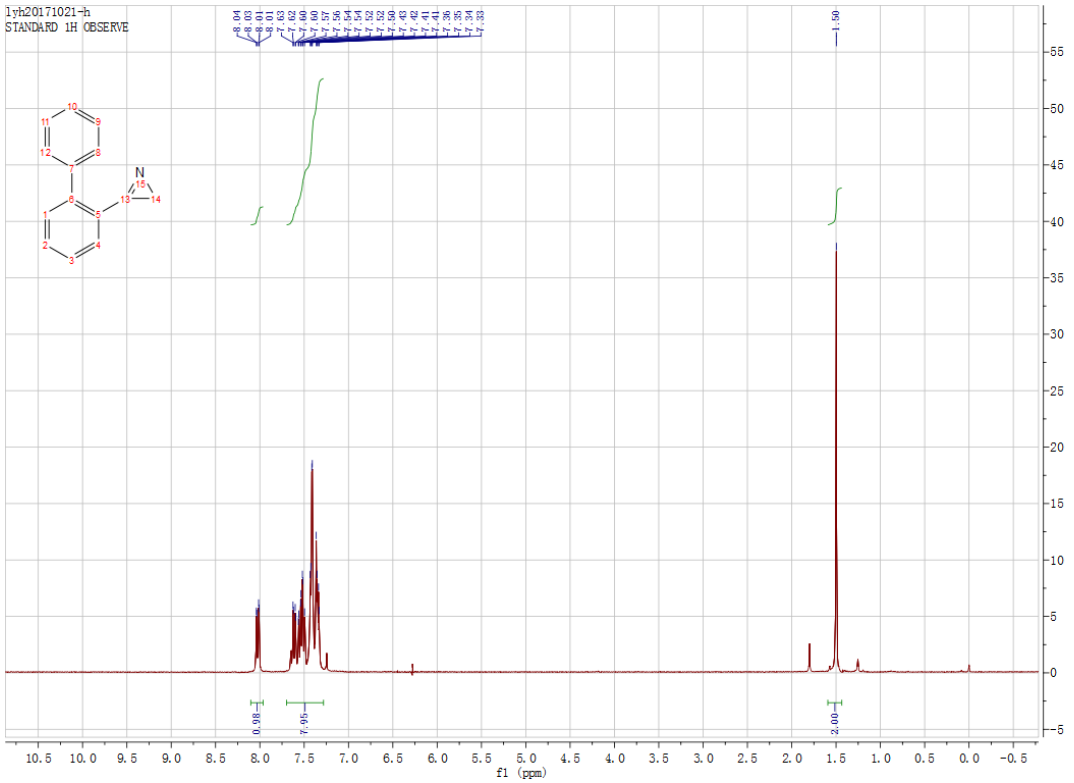
Rhodamine B EOSIN Y Rose bengal $Ru(bpy)_3Cl_2·6H_2O$

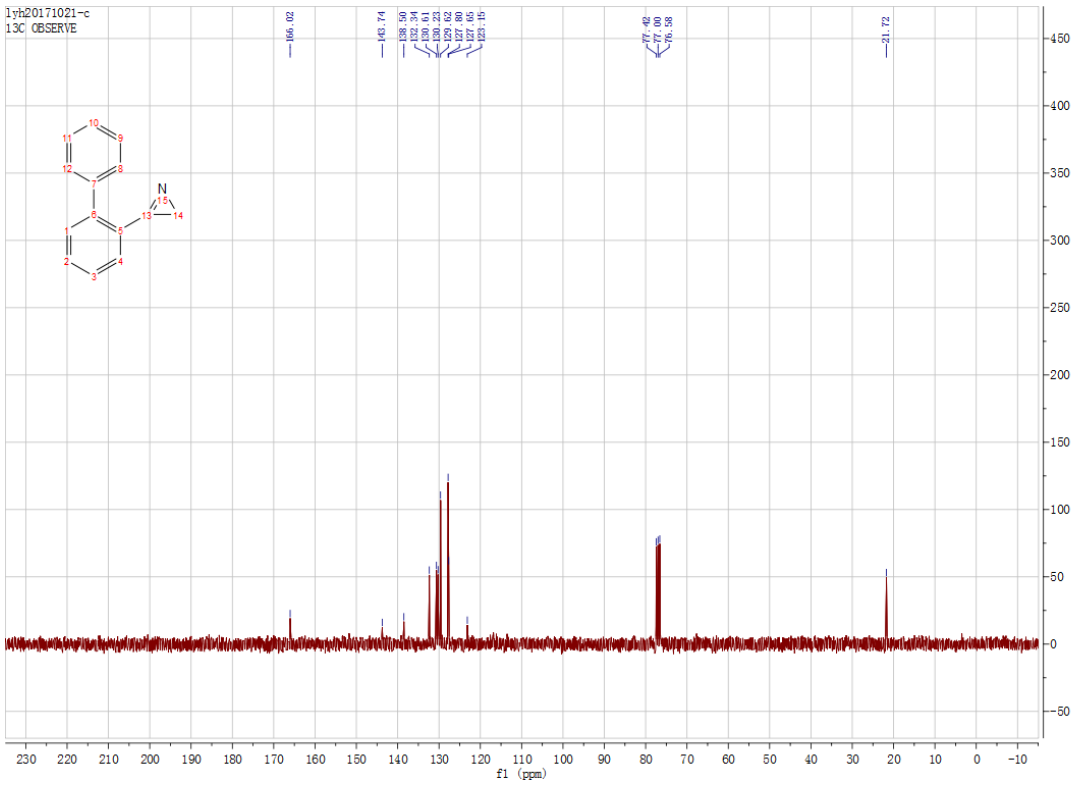
entry	S_1/S_2(mol/mol)	cat	oxidant	base	solvent	result[b]
1[c]	1.4	10 mol % $CuCl_2$	1.5 eq. BPO		CH_3CN	azirine
2[c]	1.4	10 mol % $CuCl_2$	1.5 eq. DICP		CH_3CN	azirine
3[c]	1.4	10 mol % $CuCl_2$	1.5 eq. DTBP		CH_3CN	azirine
4[c]	1.4	10 mol % $CuCl_2$	1.5 eq. TBHP		CH_3CN	azirine
5[c]	1.4	10 mol % $CuCl_2$	1.5 eq. TBPB		CH_3CN	azirine
6[c]	1.4	10 mol % $CuCl_2$	1.5 eq. $K_2S_2O_8$		CH_3CN	azirine
7[c]	1.4	10 mol % $AgNO_3$	1.0 eq. $Mg(NO3)_2$		CH_3CN	azirine
8[c]	1.4	10 mol % $AgNO_3$	1.0 eq. $Zr(NO3)_4$		CH_3CN	azirine
9[c]	1.4	10 mol % $AgNO_3$	1.0 eq. $Zn(NO3)_2$		CH_3CN	azirine
10	1.4	10 mol % $AgNO_3$	1.5 eq. $K_2S_2O_8$		CH_3CN	n.d.

11	1.4	10 mol % $CuCl_2$	1.5 eq. $K_2S_2O_8$		CH_3CN	n.d.
12	1.4	2 mol % Rhodamine B	air		CH_3CN	trace
13	1.4	2 mol % Eosin Y	air		CH_3CN	trace
14	1.4	2 mol % Rose bengal	air		CH_3CN	trace
15	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	air		CH_3CN	13%
16	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. BPO		CH_3CN	n.d.
17	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. DICP		CH_3CN	21%
18	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. DTBP		CH_3CN	trace
19	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBHP		CH_3CN	trace
20	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB		CH_3CN	43%
21	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB		THF	n.d.
22	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB		DCE	23%
23	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB		DMF	trace
24	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB		Tol	n.d.
25	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. Na_2CO_3	CH_3CN	81%
26	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. K_2CO_3	CH_3CN	63%
27	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. K_3PO_4	CH_3CN	59%
28	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. Li_2CO_3	CH_3CN	57%
29	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. NaOAc	CH_3CN	70%
30	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. K_2HPO_4	CH_3CN	75%
31	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.5 eq. DABCO	CH_3CN	64%
32	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.5 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	80%
33	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	90%
34	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	2.0 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	90%
35	1.4	1 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	66%
36[d]	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	n.d.
37	1.4		1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	n.d.
38	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$		1.2 eq. Na_2CO_3	CH_3CN	n.d.
39[e]	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	71%
40[f]	1.4	2 mol % $Ru(bpy)_3Cl_2$ $6H_2O$	1.8 eq. TBPB	1.2 eq. Na_2CO_3	CH_3CN	n.d.

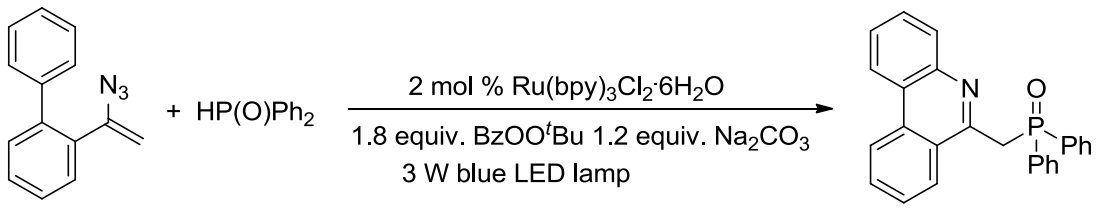
[a] Reaction conditions: a solution of 1a, 2a, oxidant and photocatalyst (1equiv.=0.2 mmol) in the indicated solvent (0.1 M) was irradiated by 3W blue LED lamp at rt for 12 h under Ar. [b] Isolated yield. [c] at 80 ℃ [d] No irradiation. [e] Irradiated by 3W green LED lamp. [f] Irradiated by 9W white LED lamp.

3-([1,1'-biphenyl]-2-yl)-2H-azirine: Colorless liquid, ^1H NMR (300 MHz, $CDCl_3$) δ 8.04-8.01(1H, m), 7.33-7.63 (8H, m), 1.50 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.02, 143.74, 138.50, 132.34, 130.61, 130.23, 129.62, 127.80, 127.65, 123.15, 21.72.

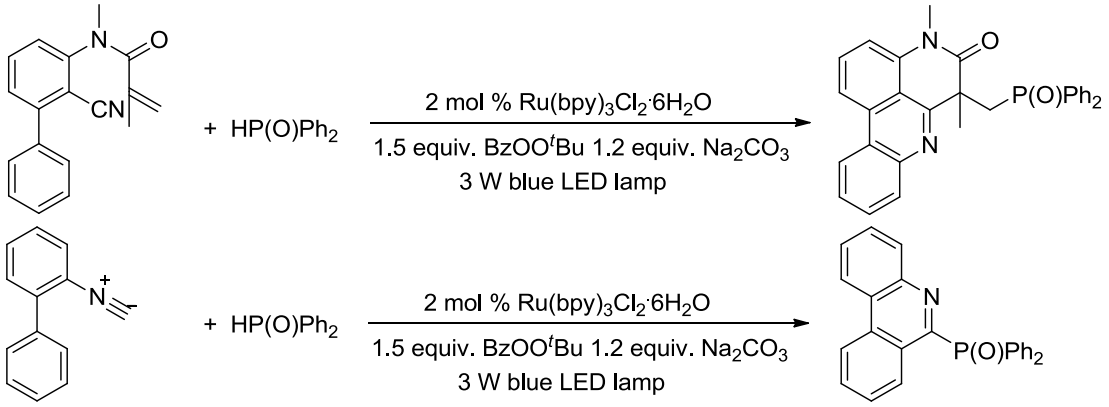




4.2. General procedure for Phosphoryl radical onto vinyl azides

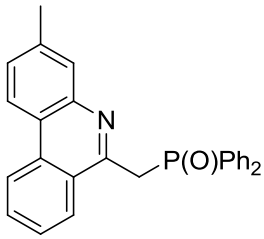


A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with vinyl azides (0.42 mmol, 1.4 equiv.), $Ru(bpy)_3Cl_2·6H_2O$ (0.006 mmol, 0.02 equiv.), $HP(O)R_4R_5$ (0.3 mmol, 1.0 equiv.), Na_2CO_3 (0.36 mmol, 1.2 equiv.). The flask was evacuated and backfilled with Ar for 3 times. tert-butylbenzoperoxoate (0.54 mmol, 1.8 equiv.) and CH_3CN (3.0 mL, 0.1 M) were added with syringe under N_2. The mixture was then irradiated by a 3 W blue LED lamp (away from tube 5-10 cm) at room temperature for 12 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product.

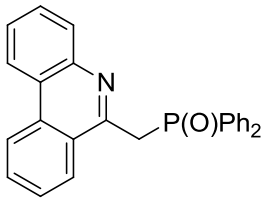


A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with nitriles and isocyanides (0.2 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2·6H_2O$ (0.004 mmol, 0.02 equiv.), $HP(O)R_4R_5$ (0.24 mmol, 1.2 equiv.), Na_2CO_3 (0.24 mmol, 1.2 equiv.). The flask was evacuated and backfilled with Ar for 3 times. tert-butylbenzoperoxoate (0.3 mmol, 1.5 equiv.) and CH_3CN (2.0 mL, 0.1 M) were added with syringe under N_2. The mixture was then irradiated by a 3 W blue LED lamp (away from tube 5-10 cm) at room temperature for 12 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product.

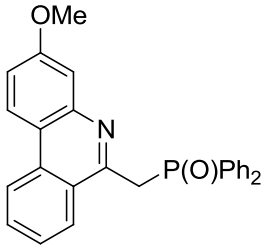
4.3. Characterization data of new phenanthridine



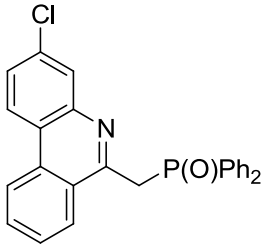
6-((diphenylphosphoryl)methyl)-3-methylphenanthridine(3a), 110 mg, Yield: 90 %, white solid (M.P. = 189-190 ^oC), ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (2H, d, *J* = 8.9 Hz), 8.27 (1H, d, *J* = 8.4 Hz), 7.84-7.90 (4H, m), 7.67-7.70 (2H, m), 7.57 (1H, t, *J* = 8.1 Hz), 7.32-7.42 (7H, m), 4.49 (2H, d, *J* = 15.2 Hz), 2.50 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.83; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.74(d, *J* = 7.9 Hz), 143.27(d, *J* = 2.2 Hz), 132.69, 132.20 (d, *J* = 100.8 Hz), 131.54, 131.52 (d, *J* = 2.7 Hz), 131.20 (d, *J* = 9.5 Hz), 130.36, 128.69, 128.34, 128.12 (d, *J* = 12.1 Hz), 127.54, 126.76, 125.61 (d, *J* = 2.1 Hz), 121.56, 121.15, 39.76 (d, *J* = 62.9 Hz), 21.38. HRMS calcd for $C_{27}H_{22}NOP$: $[M+H]^+$408.1512, found 408.1516.



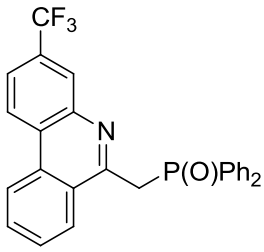
6-((diphenylphosphoryl)methyl)phenanthridine(3b), 111 mg, Yield: 94 %, white solid (M.P. = 202-203 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (1H, d, *J* = 8.3 Hz), 8.45-8.48 (2H, m), 7.84-7.89 (4H, m), 7.78 (1H, t, *J* = 8.1 Hz), 7.56-7.68 (3H, m), 7.35-7.45 (6H, m), 4.54 (2H, d, *J* = 15.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.96; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.86 (d, *J* = 8.0 Hz), 143.38, 138.37, 132.69, 132.46 (d, *J* = 101.1 Hz), 132.31(d, *J* = 8.2 Hz), 131.60 (d, *J* = 2.6 Hz), 131.26 (d, *J* = 9.5 Hz), 130.53, 129.22, 128.35, 128.18 (d, *J* = 12.1 Hz), 127.66, 127.34, 126.64, 125.99 (d, *J* = 2.1 Hz), 123.53, 121.83, 39.78 (d, *J* = 62.9 Hz). HRMS calcd for $C_{26}H_{20}NOP$: $[M+H]^{+}$394.1355, found 394.1358.



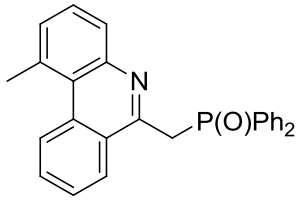
6-((diphenylphosphoryl)methyl)-3-methoxyphenanthridine(3c), 115 mg, Yield: 91 %, white solid (M.P. = 196-197 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.42 (3H, m), 7.82-7.88 (4H, m), 7.72 (1H, t, *J* = 9.0 Hz), 7.56 (1H, t, *J* = 9.0 Hz), 7.37-7.46 (6H, m), 7.27 (1H, s), 7.21 (1H, dd, *J* = 9.0 Hz, *J* = 3.0 Hz), 4.52 (2H, d, *J* = 15.2 Hz), 3.93 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.70; ^{13}C NMR (100 MHz, $CDCl_3$) δ159.85, 154.39 (d, *J* = 7.9 Hz), 144.85, 133.00, 132.55 (d, *J* = 100.8 Hz), 131.63 (d, *J* = 2.8 Hz), 131.29 (d, *J* = 9.5 Hz), 130.67, 128.23 (d, *J* = 12.1 Hz), 127.73, 126.30, 125.14, 123.11, 121.38, 117.70, 117.57, 109.15, 55.46, 39.89 (d, *J* = 62.8 Hz); HRMS calcd for $C_{27}H_{22}NO_2P$: $[M+H]^{+}$424.1461, found 424.1464.



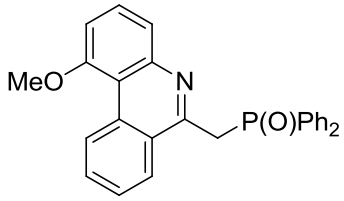
3-chloro-6-((diphenylphosphoryl)methyl)phenanthridine(3d): 70 mg, Yield: 55 %, white solid (M.P. = 203-204 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (2H, d, *J* = 4.5 Hz), 8.47 (1H, d, *J* = 4.5 Hz), 8.38 (1H, d, *J* = 8.8 Hz), 7.84-7.89 (4H, m), 7.80 (1H, t, *J* = 8.2 Hz), 7.69 (1H, t, *J* = 8.0 Hz), 7.53 (1H, dd, *J* = 8.8 Hz, *J* = 2.0 Hz), 7.38-7.48 (6H, m), 4.52 (2H, d, *J* = 15.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.84; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.44 (d, *J* = 7.9 Hz), 143.96, 133.98, 132.36 (d, *J* = 101.1 Hz), 132.34, 131.79 (d, *J* = 2.6 Hz), 131.27 (d, *J* = 9.5 Hz), 131.03, 128.42, 128.32 (d, *J* = 11.9 Hz), 127.96, 127.74, 127.23, 126.00, 123.32, 122.11, 121.82, 39.83 (d, *J* = 62.5 Hz); HRMS calcd for $C_{26}H_{19}ClNOP$: $[M+H]^{+}$428.0966, found 428.0969.



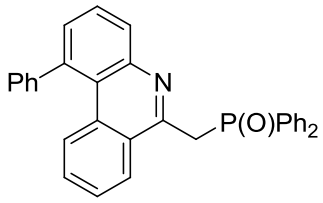
6-((diphenylphosphoryl)methyl)-3-(trifluoromethyl)phenanthridine(3e): 119 mg, Yield: 86 %, white solid (M.P. = 205-207 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.54 (3H, m), 8.13 (1H, s), 7.84-7.90 (4H, m), 7.82 (1H, t, *J* = 8.2 Hz), 7.74 (2H, t, *J* = 7.3 Hz), 7.38-7.49 (6H, m), 4.53 (2H, d, *J* = 14.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.84; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.74 (d, *J* = 8.0 Hz), 142.58 (d, *J* = 2.3 Hz), 132.32 (d, *J* = 101.4 Hz), 131.92, 131.83 (d, *J* = 2.3 Hz), 131.22 (d, *J* = 9.5 Hz), 131.14, 130.14 (q, *J* = 65.6 Hz), 128.58, 128.35 (d, *J* = 12.2 Hz), 128.03, 126.70 (d, *J* = 4.3 Hz), 126.63 (d, *J* = 1.6 Hz), 125.87, 122.96, 122.49 (d, *J* = 2.9 Hz), 122.24, 39.89 (d, *J* = 62.2Hz). HRMS calcd for $C_{27}H_{19}F_3NOP$: $[M+H]^+$462.1629, found 462.1236.



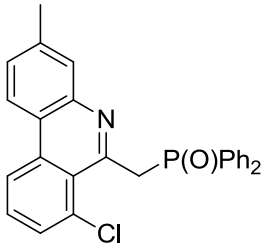
6-((diphenylphosphoryl)methyl)-1-methylphenanthridine(3f): 93 mg, Yield: 76 %, white solid (M.P. = 147-149 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (1H, d, *J* = 8.5 Hz), 8.51 (1H, d, *J* = 8.0 Hz), 7.85-7.90 (4H, m), 7.75-7.79 (2H, m), 7.68 (1H, t, *J* = 7.4 Hz), 7.52 (1H, t, *J* = 7.8 Hz), 7.34-7.43 (7H, m), 4.53 (2H, d, *J* = 15.1 Hz), 3.04 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.06; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.51 (d, *J* = 7.9 Hz), 144.83, 134.85, 134.07, 132.61 (d, *J* = 100.8 Hz), 131.62 (d, *J* = 2.7 Hz), 131.32 (d, *J* = 9.5 Hz), 130.97, 129.75, 128.22 (d, *J* = 11.8 Hz), 127.73, 127.53, 126.98 (d, *J* = 2.2 Hz), 126.66, 126.39, 123.38, 39.77 (d, *J* = 63.1 Hz), 26.66. HRMS calcd for $C_{27}H_{22}NOP$: $[M+H]^+$408.1512, found 408.1514.



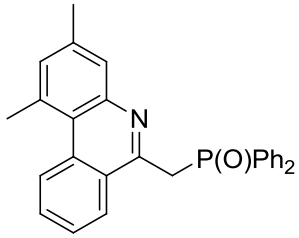
6-((diphenylphosphoryl)methyl)-1-methoxyphenanthridine(3g): 50 mg, Yield: 40 %, white solid (M.P. = 151-153 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (1H, d, *J* = 8.6 Hz), 8.45 (1H, d, *J* = 8.0 Hz), 7.84-7.89 (4H, m), 7.76 (1H, t, *J* = 8.2 Hz), 7.64 (1H, t, *J* = 7.3 Hz), 7.50-7.56 (2H, m), 7.33-7.43 (6H, m), 7.21 (1H, dd, *J* = 7.1 Hz, *J* = 2.0 Hz), 4.53 (2H, d, *J* = 15.2 Hz), 4.07 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.98; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.91, 154.44 (d, *J* = 7.6 Hz), 145.38, 132.79, 132.60 (d, *J* = 100.8 Hz), 131.59 (d, *J* = 2.7 Hz), 131.33 (d, *J* = 9.5 Hz), 130.41, 128.19 (d, *J* = 11.9 Hz), 127.84, 127.72, 127.12, 126.69, 126.34 (d, *J* = 2.2 Hz), 122.13, 114.33, 107.85, 55.77, 39.87 (d, *J* = 63.0 Hz). HRMS calcd for $C_{27}H_{22}NO_2P$: $[M+H]^+$424.1461, found 424.1463.



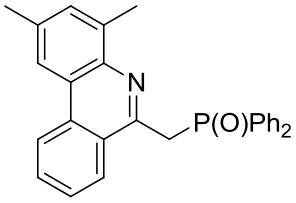
6-((diphenylphosphoryl)methyl)-1-phenylphenanthridine(3h): 104 mg, Yield: 74 %, white solid (M.P. = 183-185 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (1H, d, *J* = 8.2 Hz), 7.87-7.93 (5H, m), 7.61 (1H, t, *J* = 7.5 Hz), 7.58 (1H, d, *J* = 8.6 Hz), 7.50 (1H, t, *J* = 7.7 Hz), 7.33-7.45 (12H, m), 7.50 (1H, t, *J* = 7.5 Hz), 4.54 (2H, d, *J* = 15.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.00; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.12(d, *J* = 7.8 Hz), 144.48, 144.07, 139.80, 132.90, 132.64 (d, *J* = 101.1 Hz), 131.66 (d, *J* = 2.6 Hz), 131.34 (d, *J* = 9.5 Hz), 130.46, 129.02, 128.98, 128.92, 128.89, 128.25 (d, *J* = 11.9 Hz), 127.33 (d, *J* = 2.3 Hz), 127.27, 127.06 (d, *J* = 2.0 Hz), 127.02, 126.85, 121.95, 39.70 (d, *J* = 63.1 Hz). HRMS calcd for $C_{32}H_{24}NOP$: $[M+H]^+$470.1668, found 470.1671.



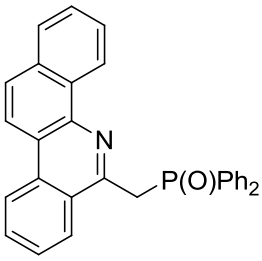
7-chloro-6-((diphenylphosphoryl)methyl)-3-methylphenanthridine(3i): 113 mg, Yield: 85 %, white solid (M.P. = 202-204 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, d, *J* =8.9 Hz), 8.26 (1H, d, *J* = 1.9 Hz), 8.24 (1H, d, *J* = 8.4 Hz), 7.83-7.89 (4H, m), 7.68 (1H, s), 7.62 (1H, dd, *J* = 8.8 Hz, *J* = 2.0 Hz), 7.36-7.45 (7H, m), 4.45 (2H, d, *J* = 15.2 Hz), 2.53 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.56; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.75 (d, *J* = 7.9 Hz), 143.39 (d, *J* = 2.1 Hz), 138.93, 132.68, 132.47 (d, *J* = 101.0 Hz), 131.73 (d, *J* = 2.7 Hz), 131.29 (d, *J* = 9.5 Hz), 131.16, 130.93, 128.95, 128.88, 128.27 (d, *J* = 12.1 Hz), 126.75, 126.50 (d, *J* = 2.2 Hz), 123.41, 121.50, 120.59, 39.57 (d, *J* = 62.8 Hz), 21.46. HRMS calcd for $C_{27}H_{21}ClNOP$: $[M+H]^+$442.1122, found 442.1126.



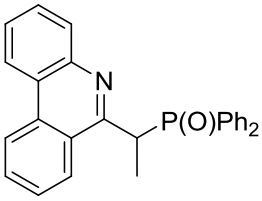
6-((diphenylphosphoryl)methyl)-1,3-dimethylphenanthridine(3j): 95 mg, Yield: 75 %, white solid (M.P. = 171-173 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (1H, d, *J* = 8.5 Hz), 8.45 (1H, d, *J* = 8.1 Hz), 7.86-7.91 (4H, m), 7.73 (1H, t, *J* = 7.2 Hz), 7.65 (1H, t, *J* = 7.4 Hz), 7.35-7.45 (7H, m), 7.29 (1H, d, *J* = 15.0 Hz), 4.53(2H, d, *J* = 15.0 Hz), 2.99 (3H, s), 2.54 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.00; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.69 (d, *J* = 8.0 Hz), 143.20 (d, *J* = 2.2 Hz), 135.50, 134.38, 132.89 (d, *J* = 100.9 Hz), 132.25, 131.53 (d, *J* = 2.7 Hz), 131.29 (d, *J* = 9.5 Hz), 130.40, 129.32, 128.32, 128.23 (d, *J* = 12.0 Hz), 127.28, 126.83 (d, *J* = 2.3 Hz), 126.57, 126.48, 123.28 (d, *J*= 1.4 Hz), 39.24 (d, *J*= 64.3 Hz), 26.59, 18.65. HRMS calcd for $C_{28}H_{24}NOP$: $[M+H]^+$422.1668, found 422.1670.



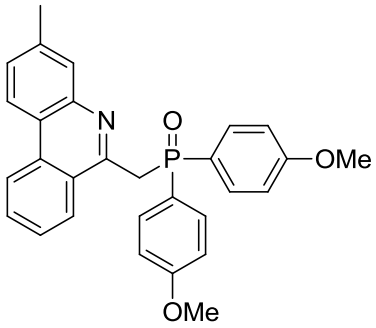
6-((diphenylphosphoryl)methyl)-2,4-dimethylphenanthridine(3k): 116 mg, Yield: 92 %, white solid (M.P. = 174-176 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (1H, d, *J* = 8.3 Hz), 8.34 (1H, d, *J* = 8.2 Hz), 8.08 (1H, s), 7.85-7.91 (4H, m), 7.70 (1H, t, *J* = 8.0 Hz), 7.59 (1H, t, *J* = 7.2 Hz), 7.33-7.44 (6H, m), 7.30 (1H, s), 4.50 (2H, d, *J* = 15.1 Hz), 2.55 (3H, s), 2.50 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.20; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.02 (d, *J* = 8.1 Hz), 140.34 (d, *J* = 2.2 Hz), 136.97, 135.93, 132.84 (d, *J* = 100.6 Hz), 132.81, 131.50 (d, *J* = 2.7 Hz), 131.31 (d, *J* = 9.4Hz), 130.81, 129.99, 128.16 (d, *J* = 12.0 Hz), 127.17, 126.98, 125.88 (d, *J* = 2.3 Hz), 123.26, 122.11, 119.22, 39.08 (d, *J* = 64.3 Hz), 21.85, 18.04. HRMS calcd for $C_{28}H_{24}NOP$: $[M+H]^+$ 422.1668, found 422.1670.



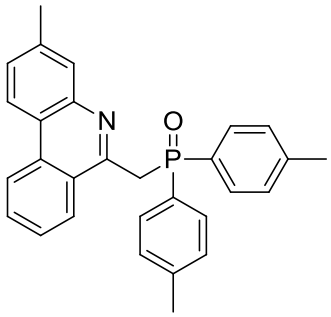
6-((diphenylphosphoryl)methyl)benzo[c]phenanthridine(3l): 70 mg, Yield: 53 %, white solid (M.P. = 186-188 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88-8.91 (1H, m), 8.59 (1H, d, *J* = 8.3 Hz), 8.45 (2H, t, *J* = 10.3 Hz), 7.89-7.96 (6H, m), 7.80 (1H, t, *J* = 7.4 Hz), 7.61-7.69 (3H, m), 7.36-7.45 (6H, m), 4.66 (2H, d, *J* = 15.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.14; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.33 (d, *J* = 8.2 Hz), 140.01 (d, *J* = 2.2 Hz), 133.15, 133.10, 132.74 (d, *J* = 100.9 Hz), 131.65 (d, *J* = 2.7 Hz), 131.35 (d, *J* = 9.4 Hz), 130.44, 128.32 (d, *J* = 12.0 Hz), 127.44, 127.30, 127.16, 126.51, 126.48, 124.80, 122.38, 120.44, 119.75, 39.21 (d, *J* = 64.2 Hz). HRMS calcd for $C_{30}H_{22}NOP$: $[M+H]^+$444.1512, found 444.1515.



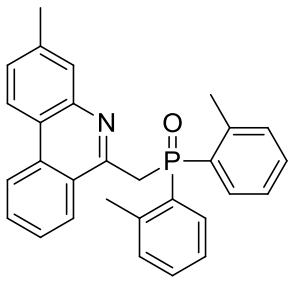
6-(1-(diphenylphosphoryl)ethyl)phenanthridine(3m): 67 mg, Yield: 55 %, white solid (M.P. = 194-197 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (1H, d, *J* = 8.2 Hz), 8.49 (1H, d, *J* = 8.0 Hz), 8.39 (1H, d, *J* = 7.3 Hz), 8.01-8.05 (3H, m), 7.67-7.77 (4H, m), 7.57-7.64 (2H, m), 7.25-7.41 (6H, m), 4.45 (2H, td, *J* = 22.9Hz, *J* = 7.4 Hz), 1.88 (3H, dd, *J* = 16.0 Hz, *J* = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.25; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.85 (d, *J* = 4.1 Hz), 143.12, 132.92, 132,28 (d, *J* = 97.2 Hz), 131.78 (dd, *J* = 62.3 Hz, *J* = 9.0 Hz), 131.34 (dd, *J* = 11.3 Hz, *J*= 2.6 Hz), 131.11, 130.22, 129.50, 128.48, 127.99 (dd, *J* = 11.45 Hz, *J* = 3.7 Hz), 127.19, 126.78, 125.18 (d, *J* = 3.5 Hz), 123.35, 122.23, 121.51, 42.44 (d, *J* = 68.2 Hz), 15.12 (d, *J* = 2.3 Hz). HRMS calcd for $C_{27}H_{22}NOP$: $[M+H]^+$408.1512, found 408.1515.



6-((bis(4-methoxyphenyl)phosphoryl)methyl)-3-methylphenanthridine(3n): 98 mg, Yield: 70 %, white solid (M.P. = 142-144 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (1H, d, *J* = 8.2 Hz), 8.41 (1H, d, *J* = 8.2 Hz), 8.33 (1H, d, *J*= 8.4 Hz), 7.70-7.79 (6H, m), 7.60 (1H, t, *J* = 7.4 Hz), 7.39 (1H, d, *J* = 8.1 Hz), 6.86 (4H, dd, *J* = 8.8 Hz, *J* = 2.1 Hz), 4.45 (2H, d, *J* = 15.4 Hz), 3.76 (6H, s), 2.54 (3H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.96; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.70 (d, *J* = 2.8 Hz), 154.28 (d, *J* = 7.8 Hz), 143.51, 138.42, 133.11 (d, *J* = 10.9 Hz), 132.75, 130.38, 128.79, 128.33, 128.28 (d, *J* = 101.6 Hz), 126.81, 125.74 (d, *J* = 2.0 Hz), 124.64, 123.57, 121.61 (d, *J* = 5.0 Hz), 121.24, 113.70 (d, *J* = 13.9 Hz), 55.17, 40.38 (d, *J* = 62.9 Hz), 21.44. HRMS calcd for $C_{29}H_{26}NO_3P$: $[M+H]^+$468.1723, found 468.1724.

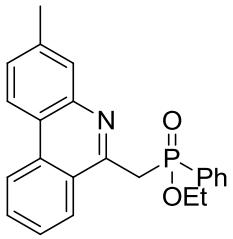


6-((dip-tolylphosphoryl)methyl)-3-methylphenanthridine(3o): 82 mg, Yield: 63 %, white solid (M.P. = 158-160 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (6H, s), 2.54 (3H, s), 4.48 (2H, d, *J* = 15.2 Hz), 7.15-7.18 (4H, m), 7.40 (1H, d, *J* = 8.4 Hz), 7.61(1H, d, *J* = 7.8 Hz), 7.70-7.77 (6H, m), 8.34 (1H, d, *J* = 8.4 Hz), 7.43-7.48 (2H, m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.19; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.47, 22.61, 40.16 (d, *J* = 62.8 Hz), 121,31, 121.60, 121.66, 125.80, 126.86, 127.86, 128.36, 128.82, 128.94 (d, *J* = 12.3 Hz), 129.63 (d, *J* = 103.2 Hz), 130.42, 131,30 (d, *J* = 9.9 Hz), 132.82, 138.43, 141.93 (d, *J* = 2.6 Hz), 143.53, 154.19 (d, *J* = 7.8 Hz). HRMS calcd for $C_{29}H_{26}NOP$: $[M+H]^+$436.1825, found 436.1824.

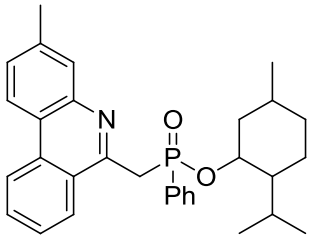


6-((dio-tolylphosphoryl)methyl)-3-methylphenanthridine(3p): 70 mg, Yield: 54 %, white solid (M.P. = 168-170 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (1H, t, *J* = 8.2 Hz), 8.47 (1H, t, *J* = 8.2 Hz), 8.37 (1H, t, *J* = 8.4 Hz), 8.03 (1H, t, *J* = 7.5 Hz), 8.00 (1H, t, *J* = 7.7 Hz), 7.77 (1H, t, *J* = 7.4 Hz), 7.62 (1H, t, *J* = 7.6 Hz), 7.62 (1H, s), 7.42 (1H, d, *J* = 8.2 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.24

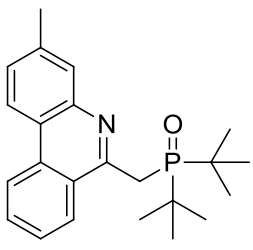
(3H, t, *J* = 7.6 Hz), 7.12 (4H, d, *J* = 4.5 Hz), 7.10 (1H, d, *J* = 4.6 Hz), 4.61 (2H, d, *J* = 14.7 Hz), 2.54 (3H, s), 2.24 (6H, s); ^{31}P NMR (162 MHz $CDCl_3$) δ 32.71; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.12, 141.92 (d, *J* = 2.0 Hz), 138.38, 132.80, 132.22, 132.12, 131.94, 131.62, 131.59, 131.48, 130.97, 130.40, 128.78, 128.38, 128.03, 126.68, 126.00(d, *J* = 2.0 Hz), 125.46, 125.34, 121.62, 121.55, 121.24 (d, *J* = 6.5 Hz), 39.06 (d, *J* = 62.5 Hz), 21.45, 21.17 (d, *J*= 4.2 Hz). HRMS calcd for $C_{29}H_{26}NOP$: $[M+H]^+$436.1825, found 436.1823.



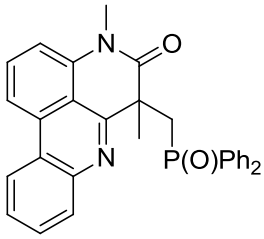
ethyl (3-methylphenanthridin-6-yl)methyl(phenyl)phosphinate(3q): 27 mg, Yield: 24 %, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (1H, d, *J* = 8.2 Hz), 8.38 (1H, d, *J* = 8.4 Hz), 8.24 (1H, d, *J* = 8.2 Hz), 7.67-7.78 (4H, m), 7.58 (1H, t, *J* = 8.1 Hz), 7.42-7.47 (2H, m), 7.26-7.36 (2H, m), 3.86-4.16 (2H, m), 4.15 (2H, d, *J* = 18.5 Hz), 2.55 (3H, s), 1.20 (3H, t, *J* = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.34; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.54 (d, *J* = 8.1 Hz), 143.64 (d, *J* = 2.7 Hz), 138.57, 132.85, 131.13 (d, *J* = 2.8 Hz), 131.88 (d, *J* = 9.9 Hz), 130.48 (d, *J* = 129.8 Hz), 130.38, 16.30 (d, *J* = 6.5 Hz), 129.03, 128.41, 128.19 (d, *J* = 13.0 Hz), 127.27, 126.65, 125.36 (d, *J* = 2.8 Hz), 121.80, 121.61, 121.27 (d, *J* = 1.5 Hz), 61.10 (d, *J* = 6.4 Hz), 39.32 (d, *J* = 91.6 Hz), 21.45. HRMS calcd for $C_{23}H_{22}NOP$: [M＋H]＋ 375.1388, found 375.1386.



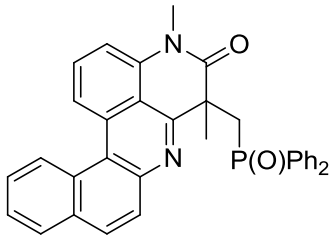
2-isopropyl-5-methylcyclohexyl(3-methylphenanthridin-6-yl)methyl(phenyl)phosphinate(3r): 41 mg, Yield: 28 %, white solid (M.P. = 127-129 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (1H, d, *J* = 8.2 Hz), 8.41 (2H, d, *J* = 8.3 Hz), 7.83-7.89 (3H, m), 7.39 (1H, t, *J* = 7.3 Hz), 7.66 (1H, t, *J* = 7.2 Hz), 7.38-7.51 (4H, m), 4.16-4.25 (1H, m), 4.10 (2H, dd, *J* = 17.4 Hz, *J* = 4.5 Hz), 2.57 (3H, s), 1.66-1.70 (2H, m), 1.45-1.51 (2H, m), 1.18-1.22 (2H, m), 0.70-0.92 (3H, m), 0.67 (3H, d, *J* = 6.5 Hz), 0.52 (3H, d, *J* = 7.0 Hz), 0.24 (3H, d, *J* = 6.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.46; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.84 (d, *J* = 9.2 Hz), 143.77, 138.48, 133.40 (d, *J* = 128.5 Hz), 131.92 (d, *J* = 2.8 Hz), 132.91, 131.67 (d, *J* = 10.1 Hz), 130.45, 129.16, 128.35, 128.14 (d, *J* = 13.0 Hz), 127.93, 126.75, 125.58 (d, *J* = 2.2 Hz), 121.67, 121.62, 121.41 (d, *J* = 1.4 Hz), 48.45 (d, *J* = 6.0 Hz), 42.90, 41.15, 40.23, 32.93, 31.34, 24.84, 22.42, 21.83, 21.49, 20.72, 14.63. HRMS calcd for $C_{31}H_{36}NO_2P$: $[M+H]^+$485.2484, found 485.2487.



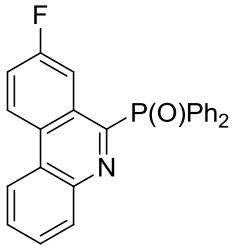
6-((di-tert-butylphosphoryl)methyl)-3-methylphenanthridine (3s): 78 mg, Yield: 71 %, white solid (M.P. = 166-168 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (1H, d, *J* = 8.1 Hz), 8.52 (1H, d, *J* = 8.2 Hz), 8.41 (1H, d, *J* = 8.4 Hz), 7.84 (1H, s), 7.79 (1H, t, *J* = 7.7 Hz), 7.71 (1H, t, *J* = 7.2 Hz), 7.45 (1H, d, *J* = 8.3 Hz), 3.97 (2H, d, *J* = 12.2 Hz), 2.58 (3H, s), 1.31 (9H, s), 1.27 (9H, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.00; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.21 (d, *J* = 7.0 Hz), 143.53, 138.55, 132.71, 130.67, 129.31, 128.72, 128.40, 126.92, 126.09, 121.82, 121.48, 121.28, 36.82 (d, *J* = 44.5 Hz), 34.68 (d, *J* = 58.4 Hz), 26.92, 21.47. HRMS calcd for $C_{23}H_{30}NOP$: $[M+H]^+$ 368.2138, found 368.2139.



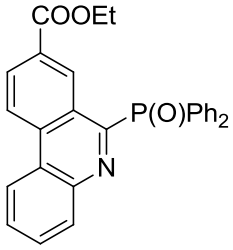
6-((diphenylphosphoryl)methyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one(5a): 68 mg, Yield: 71 %, white solid (M.P. = 233-235 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.33 (1H, m), 8.12 (1H, dd, *J* = 8.3 Hz, *J* = 4.7 Hz), 7.67-7.79 (3H, m), 7.49-7.54 (3H, m), 7.34-7.41 (3H, m), 7.10-7.22 (3H, m), 6.91-6.96 (1H, m), 6.82-6.87 (2H, m), 3.72 (2H, ddd, *J* = 40.8 Hz, *J* = 14.2 Hz, *J* = 14.2 Hz), 3.61 (3H, s), 1.88 (3H, d, *J* = 2.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.08; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.22, 158.06 (d, *J* = 1.9 Hz), 143.84, 139.05, 134.82 (d, *J* = 98.9 Hz), 133.08 (d, *J* = 98.9 Hz), 133.00, 131.66, 131.20 (d, *J* = 2.6 Hz), 130.48 (d, *J* = 9.5 Hz), 130.05 (d, *J* = 9.5 Hz), 129.95 (d, *J* = 2.6 Hz), 129.12, 128.22, 128.21 (d, *J* = 11.7 Hz), 127.19 (d, *J* = 11.7 Hz), 126.19, 122.77, 122.13, 115.45, 111.88, 110.75, 48.43 (d, *J* = 4.2 Hz), 40.94 (d, *J*= 70.2 Hz), 32.03 (d, *J* = 14.3 Hz), 29.95. HRMS calcd for $C_{30}H_{25}N_2O_2P$: $[M+H]^+$ 477.1726, found 477.1728.



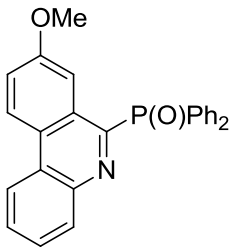
6-((diphenylphosphoryl)methyl)-4,6-dimethyl-4H-benzo[a]pyrido[4,3,2-gh]phenanthridin-5(6H)-one(5b): 62 mg, Yield: 57 %, white solid (M.P. = 199-200 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (1H, d, *J* = 8.4 Hz), 8.61 (1H, d, *J* = 8.7 Hz), 7.97 (1H, d, *J* = 7.6 Hz), 7.83 (1H, d, *J* = 8.8 Hz), 7.80 (1H, t, *J* = 8.3 Hz), 7.66-7.72 (3H, m), 7.62 (1H, d, *J* = 7.0 Hz), 7.43 (1H, d, *J* = 8.8 Hz), 7.34-7.42 (3H, m), 7.24 (1H, d, *J* = 7.9 Hz), 7.06-7.12 (2H, m), 6.65-6.74 (3H, m), 3.70-3.78 (2H, m), 3.67 (3H, s), 1.88 (3H, d, *J* = 2.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.82; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23(d, *J* = 1.6 Hz), 157.22, 143.89, 138.93, 134.86 (d, *J* = 99.0 Hz), 132.98, 132.93, 132.68 (d, *J* = 98.8 Hz), 131.36, 131.31 (d, *J* = 2.5 Hz), 130.48 (d, *J* = 9.5 Hz), 130.03 (d, *J* = 9.6 Hz), 129.87 (d, *J* = 2.8 Hz), 129.70, 129.22, 128.50, 128.31 (d, *J* = 11.7 Hz), 127.75, 127.48, 127.25 (d, *J* = 11.8 Hz), 126.31, 126.00, 120.30, 119.41, 113.32, 110.03, 48.43 (d, *J* = 4.2 Hz), 40.94 (d, *J* = 70.2 Hz), 32.06 (d, *J* = 14.4 Hz), 30.15; HRMS calcd for $C_{34}H_{27}N_2O_2P$: $[M+H]^+$527.1883, found 527.1884.



6-(diphenylphosphoryl)-8-fluorophenanthridine(7a): 57 mg, Yield: 72 %, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (dd, 1H, *J* = 2.6 Hz, *J* = 10.2 Hz), 8.62-8.59 (m, 1H), 8.50-8.48 (m, 1H), 8.07-8.05 (m, 1H), 7.98-7.93 (m, 4H), 7.73-7.66 (m, 2H), 7.59-7.43 (m, 7H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.44; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.58; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 247.8 Hz), 155.8 (dd, *J* = 4.3 Hz, *J* = 127.7 Hz), 142.3 (d, *J* = 22.6 Hz), 132.6 (d, *J* = 104.3 Hz), 132.2 (d, *J* = 9.0 Hz), 131.8 (d, *J* = 2.7 Hz), 131.1, 128.8 (d, *J* = 62.7 Hz), 128.2 (d, *J* = 12.2 Hz), 124.5 (d, *J* = 8.7 Hz), 123.8, 121.8, 120.4 (d, *J* = 24.3 Hz), 113.1 (d, *J* = 23.1 Hz); HRMS calcd for $C_{25}H_{17}FNOP$ $[M+H]^+$ 398.1105, found 398.1103.



ethyl 6-(diphenylphosphoryl)phenanthridine-8-carboxylate(7b): 46 mg, Yield: 51 %, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (d, 1H, *J* = 1.2 Hz), 8.67-8.65 (m, 1H), 8.59-8.57 (m, 1H), 8.45-8.42 (m, 1H), 8.09-8.07 (m, 1H), 8.02-7.97 (m, 4H), 7.77-7.72 (m, 2H), 7.55-7.44 (m, 6H), 4.43 (q, 2H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.12; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 157.6 (d, *J* = 126.5 Hz), 143.3 (d, *J* = 22.6 Hz), 135.3 (d, *J* = 6.6 Hz), 132.6 (d, *J* = 104.3 Hz), 132.2 (d, *J* = 9.2 Hz), 131.7 (d, *J* = 2.6 Hz), 131.1, 130.8, 130.5, 129.7, 129.5, 129.1, 128.2 (d, *J* = 12.0 Hz), 127.0 (d, *J* = 22.8 Hz), 123.6 (d, *J* = 2.2 Hz), 122.5 (d, *J* = 19.3 Hz), 61.3, 14.3; HRMS calcd for $C_{28}H_{22}NO_3P$ $[M+H]^+$452.1410, found 452.1409.



6-(diphenylphosphoryl)-8-methoxyphenanthridine(7c): 50 mg, Yield: 61 %, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, 1H, *J* = 2.6 Hz), 8.55-8.48 (m, 2H), 8.05-8.03 (m, 1H), 7.99-7.94 (m, 4H), 7.70-7.62 (m, 2H), 7.54-7.43 (m, 7H), 3.94 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.60; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 155.4 (d, *J* = 128.4 Hz), 142.0 (d, *J* = 23.1 Hz), 132.9 (d, *J* = 104.0 Hz), 132.2 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 2.7 Hz), 131.0, 129.4 (d, *J* = 23.0 Hz), 128.8, 128.1 (d, *J* = 12.1 Hz), 127.6, 127.0 (d, *J* = 6.7 Hz), 124.5 (d, *J* = 2.3 Hz), 123.6, 122.6, 121.6, 107.4, 55.6; HRMS calcd for $C_{26}H_{20}NO_2P$ $[M+H]^+$ 410.1304, found 410.1299.

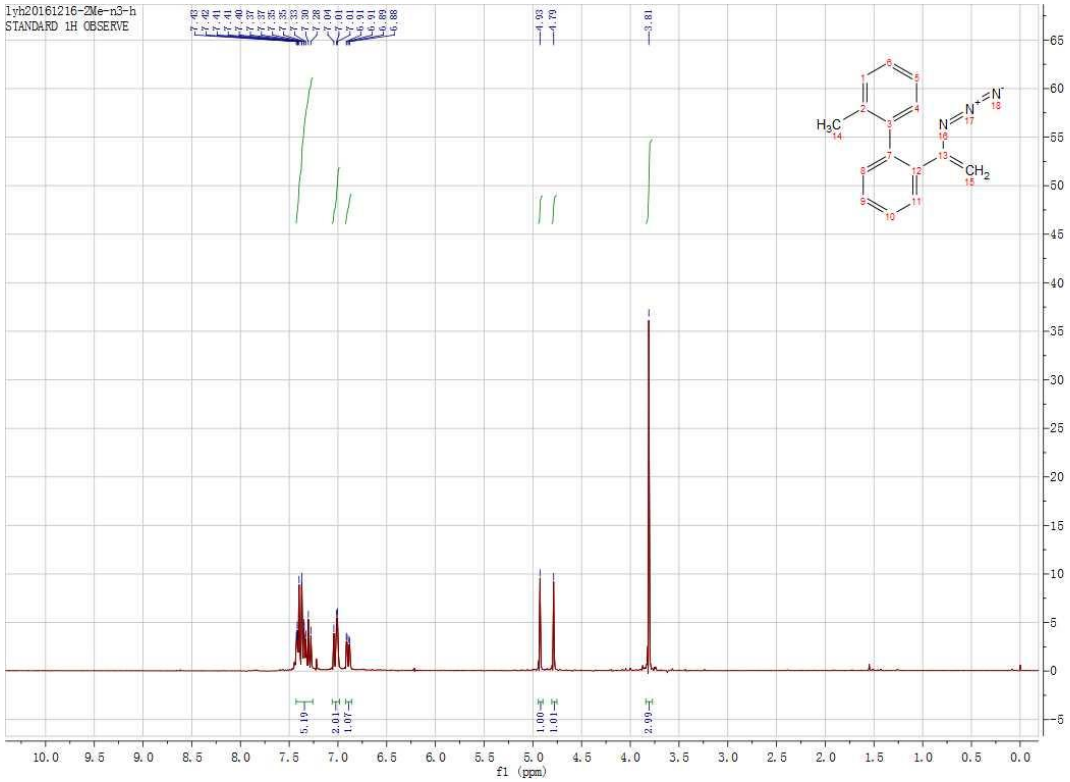
5. References

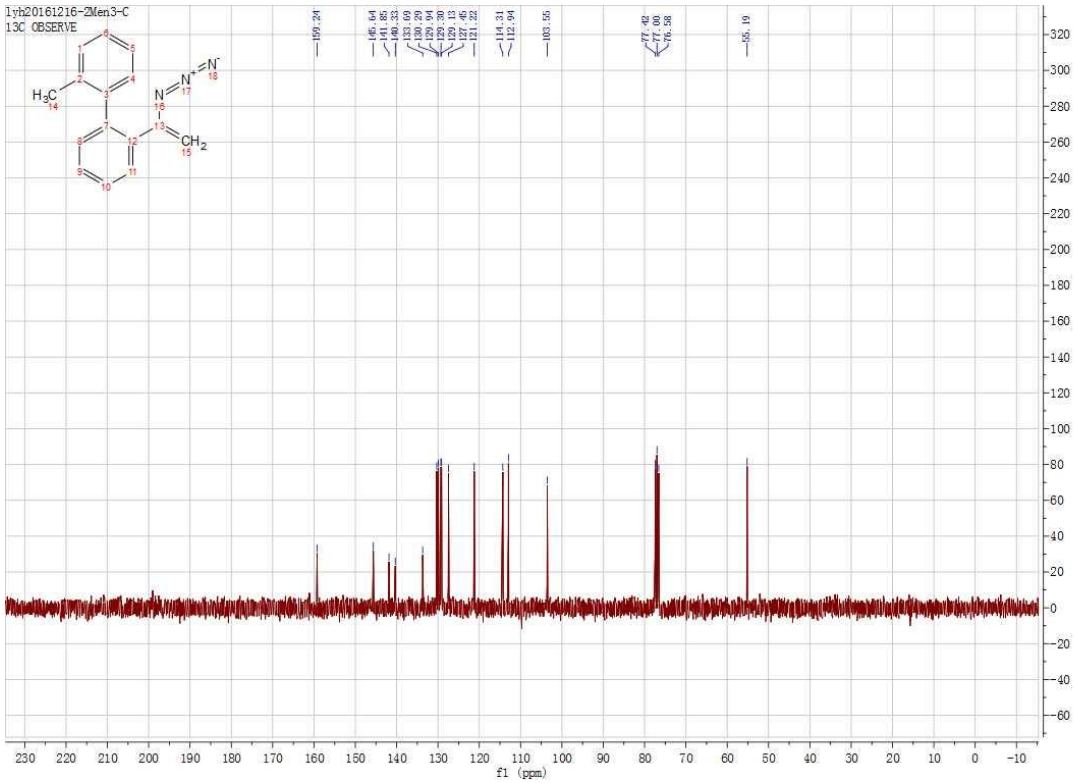
[1]Keicher, T.; Löbbecke, S. Lab-Scale Synthesis of Azido Compounds: Safety Measures andAnalysis. In *Organic Azides: Syntheses and Applications;* Bräse, S., Banert, K. Eds.; Wiley:Chichester, 2010; pp 3.

[2] Smith, P. A. S. *The Chemistry of Open-Chain Organic Nitrogen Compounds*; Vol. 2; W.A.Benjamin Inc.: New York, 1966; pp 211.

[3] (a) Hassner, A.; Fowler, F. W. *Tetrahedron Lett*. **1967**, *8*, 1545. (b) Fowler, F. W.; Hassner,A.; Levy, L. A. *J. Am. Chem. Soc*. **1967**, *89*, 2077.

6. Spectra

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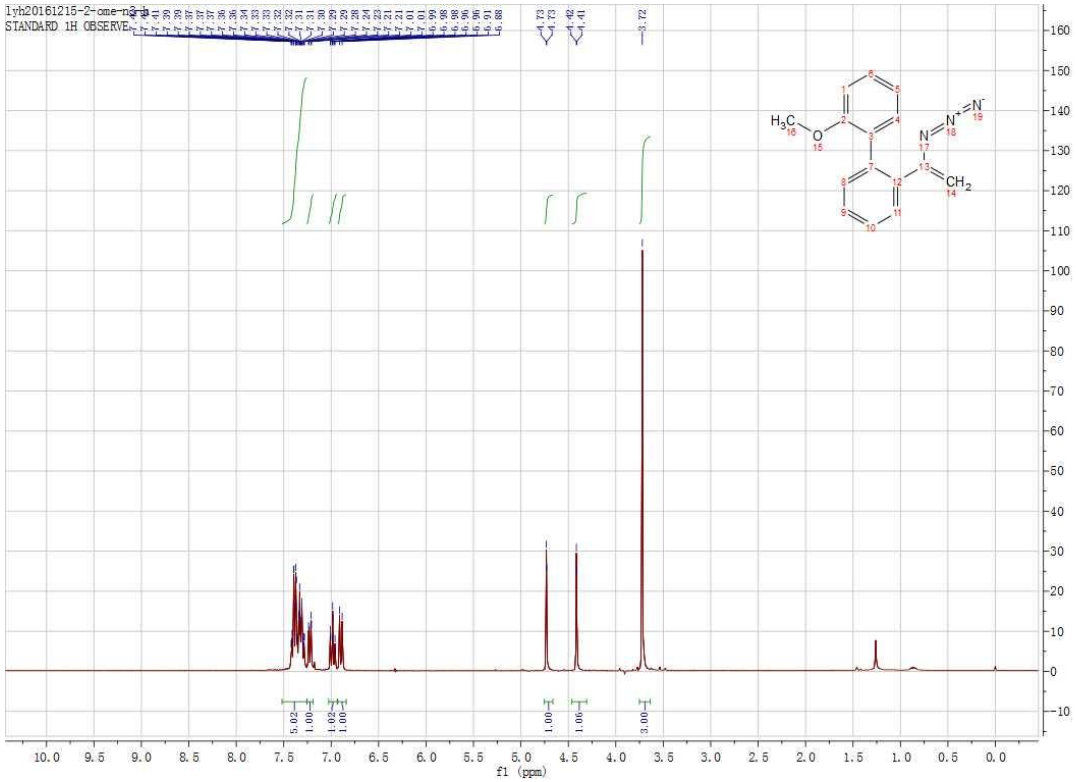
55.19
f1 (ppm)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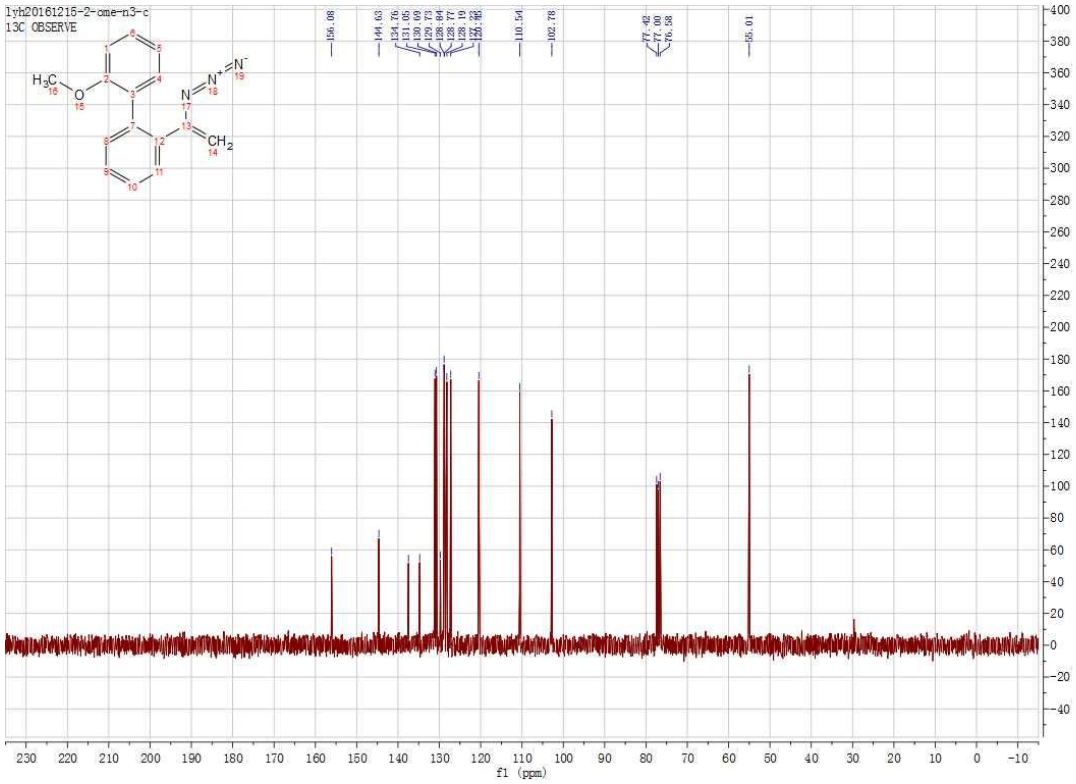
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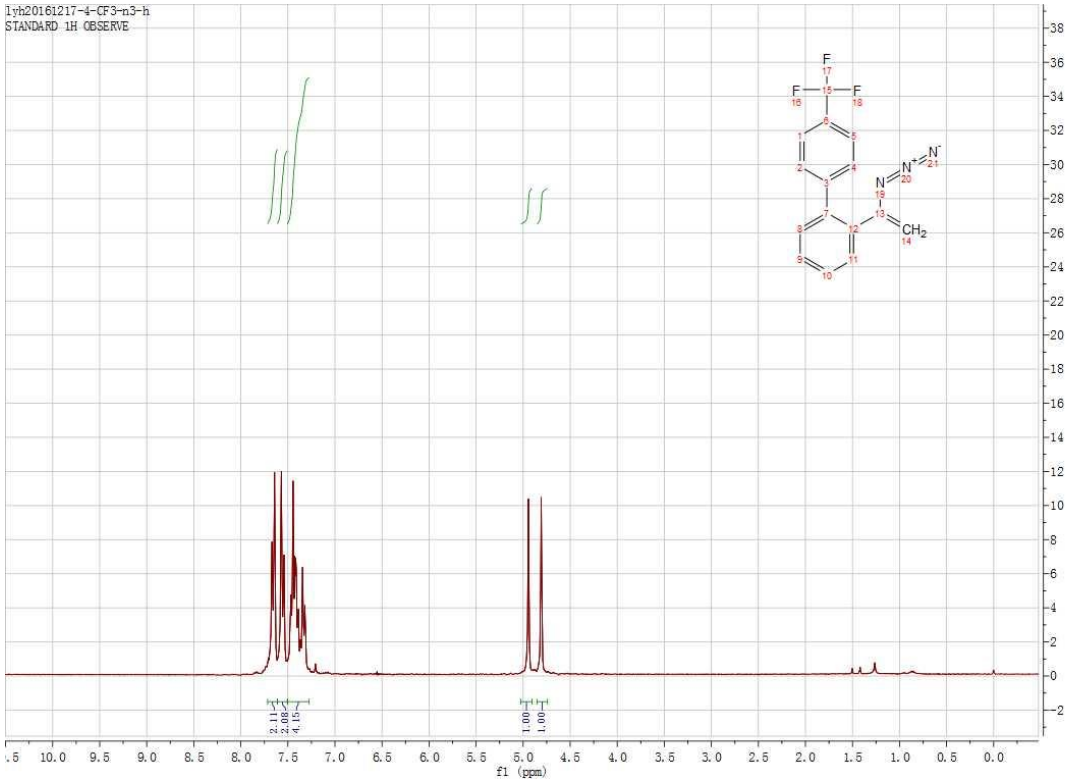
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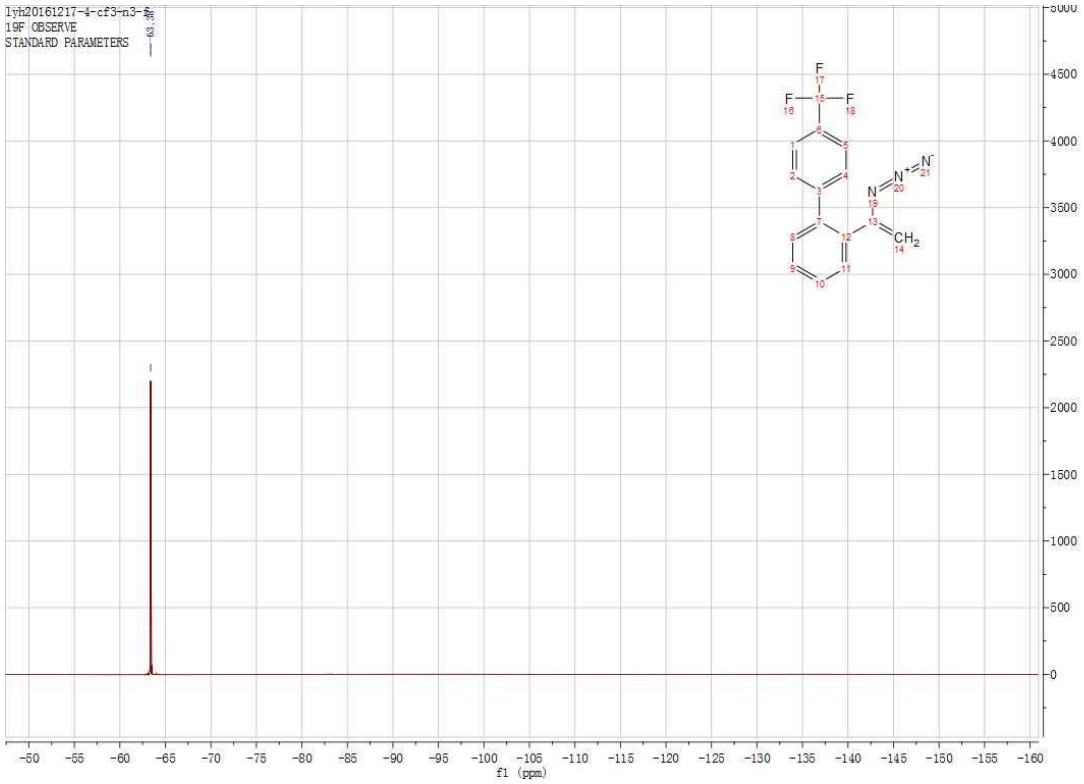
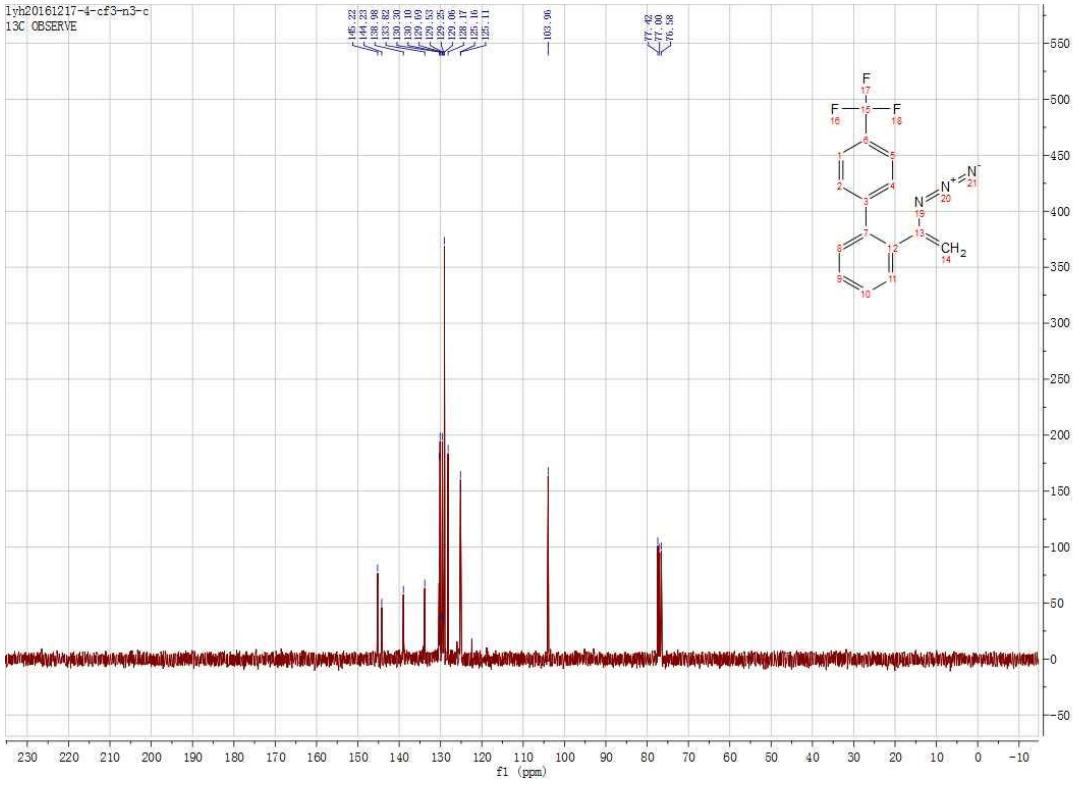
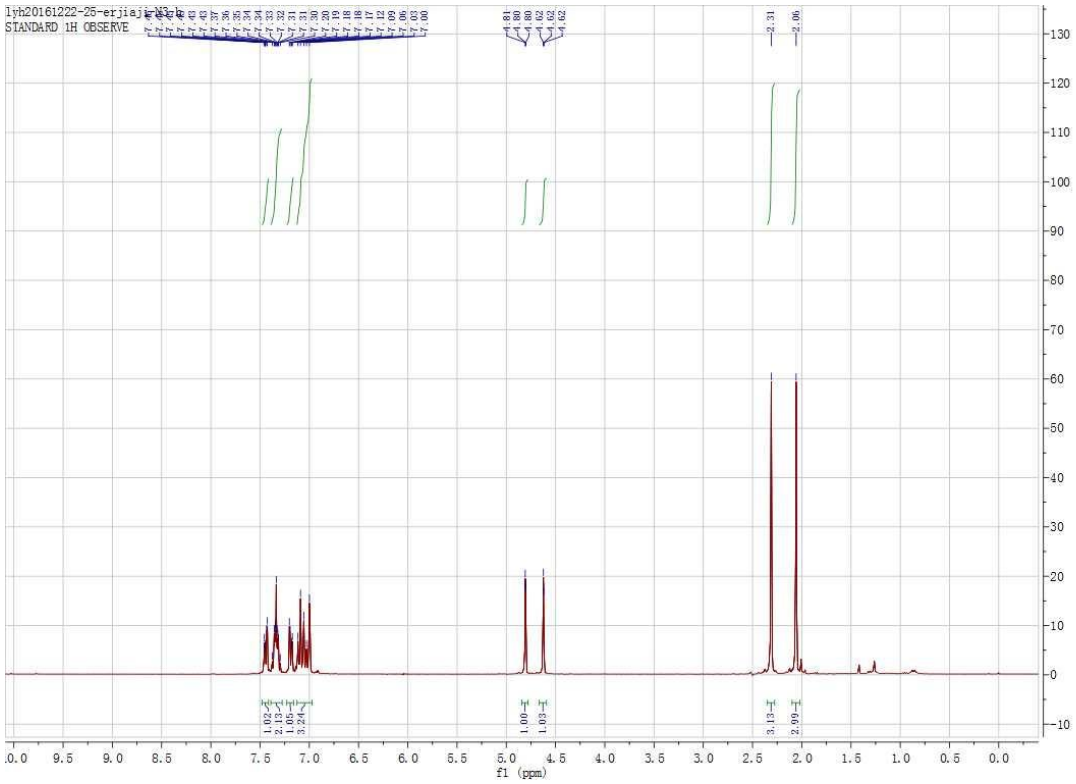
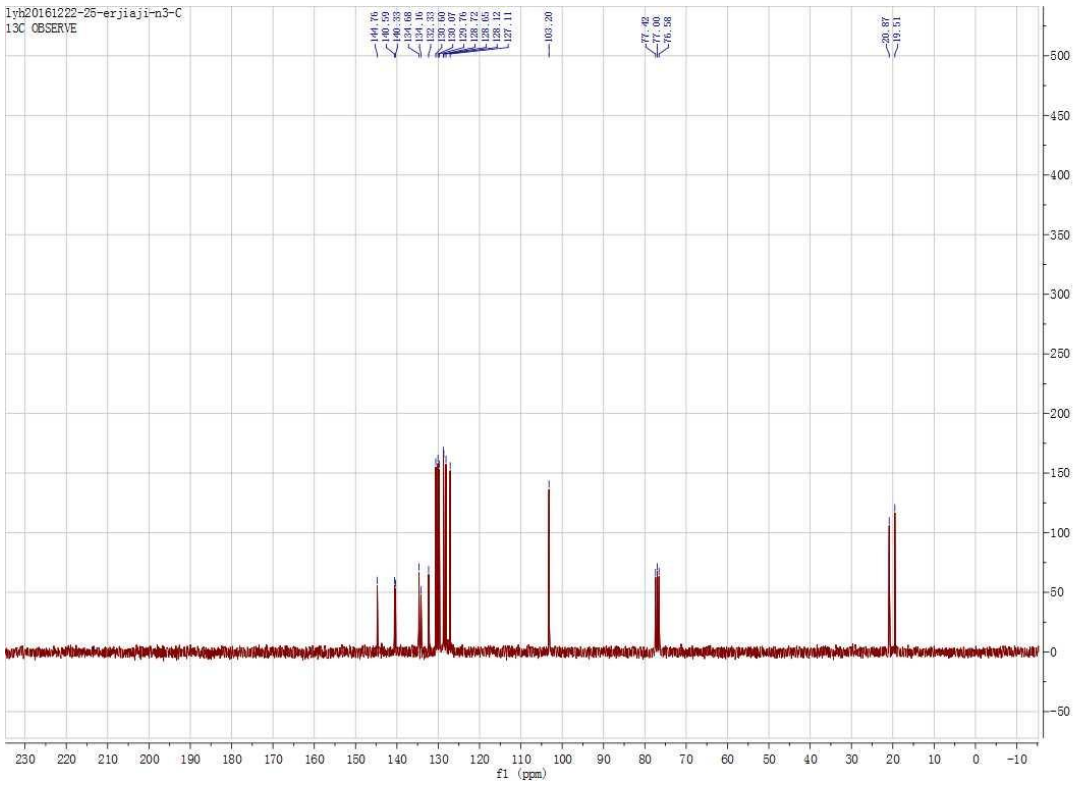
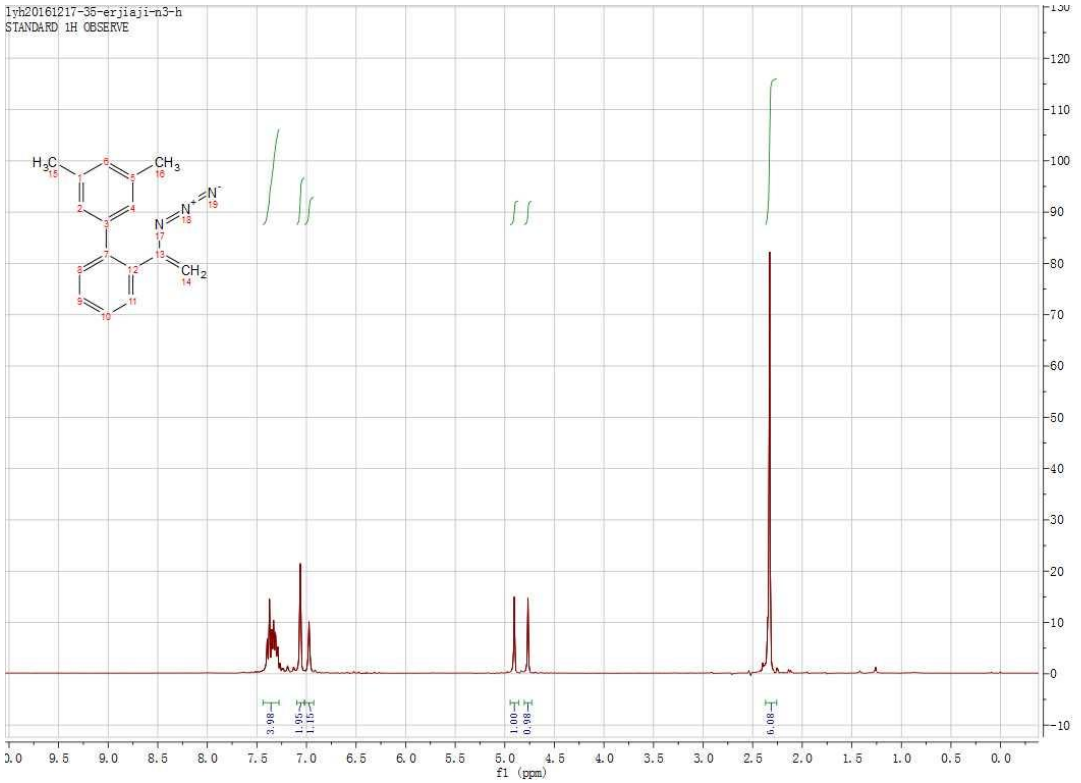
1.00
f1 (ppm)

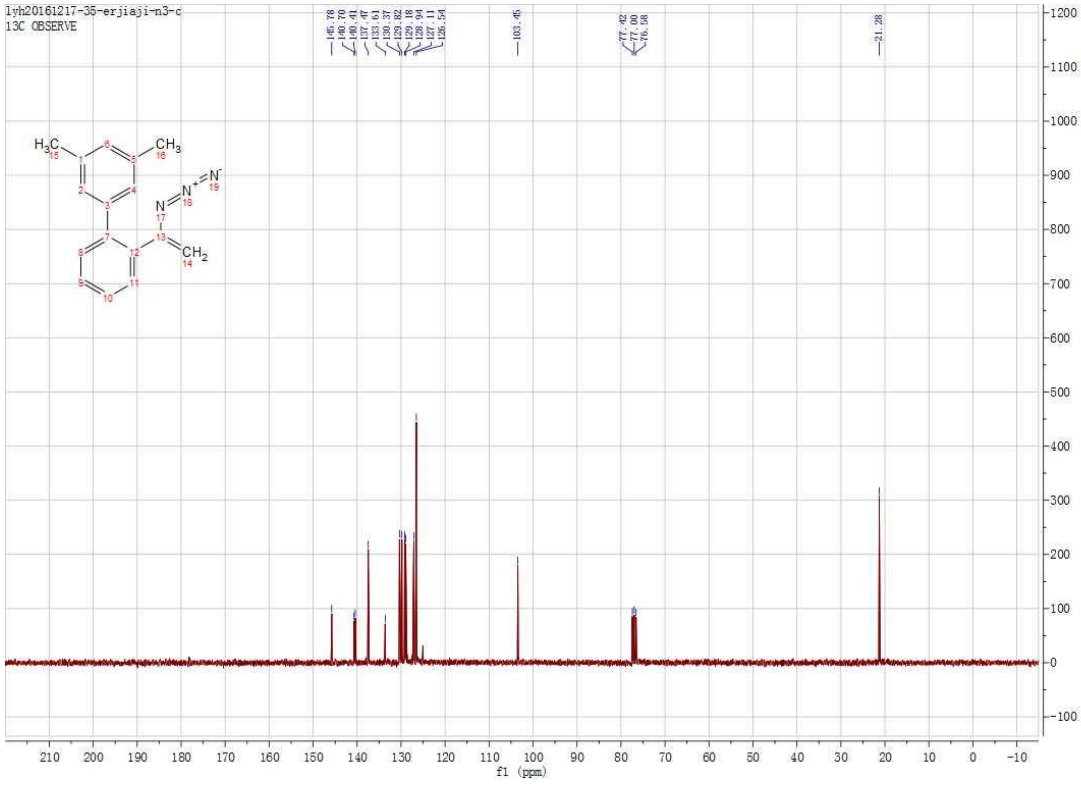

lyh20161217-4-cf3-n3-
19F OBSERVE
STANDARD PARAMETERS
f1 (ppm)

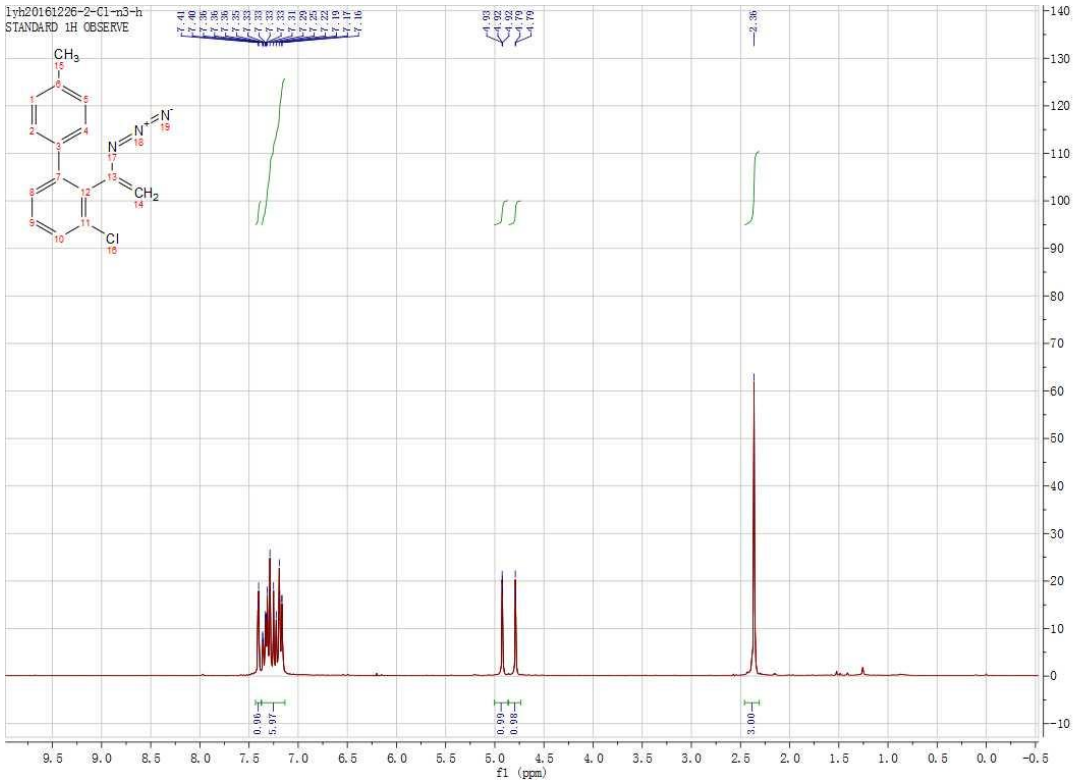

lyh20161217-4-cf3-n3-c
13C OBSERVE
f1 (ppm)

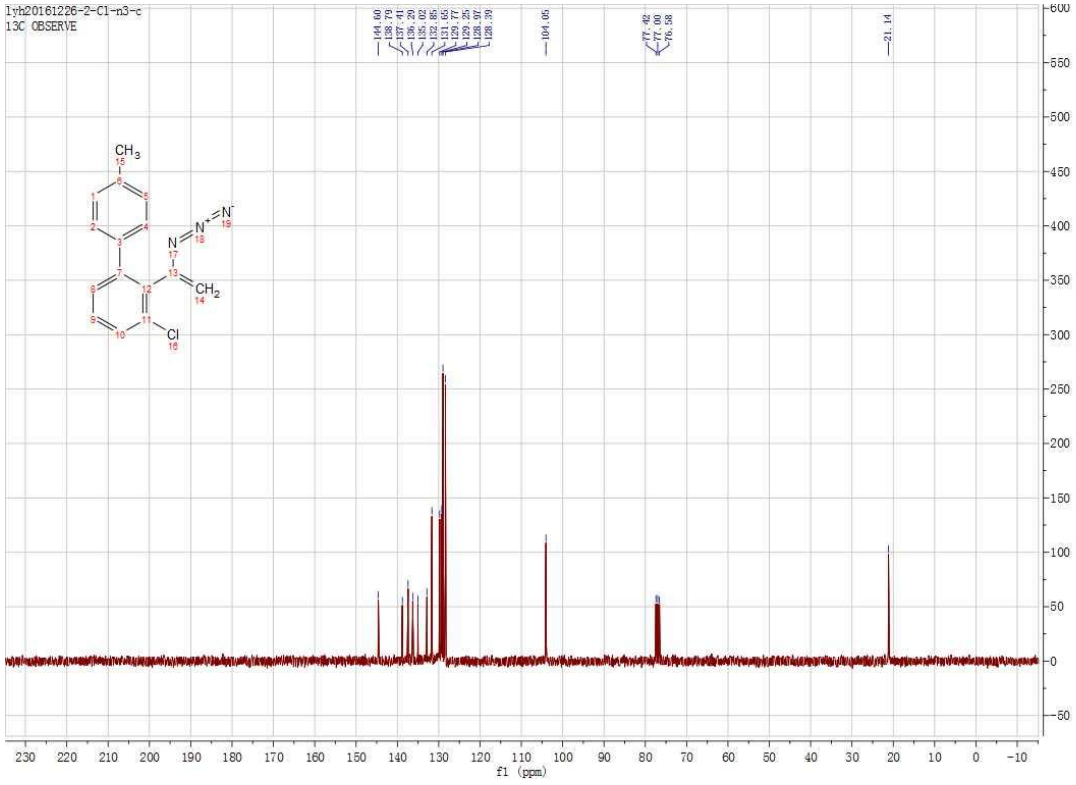

STANDARD 1H OBSERVE
f1 (ppm)

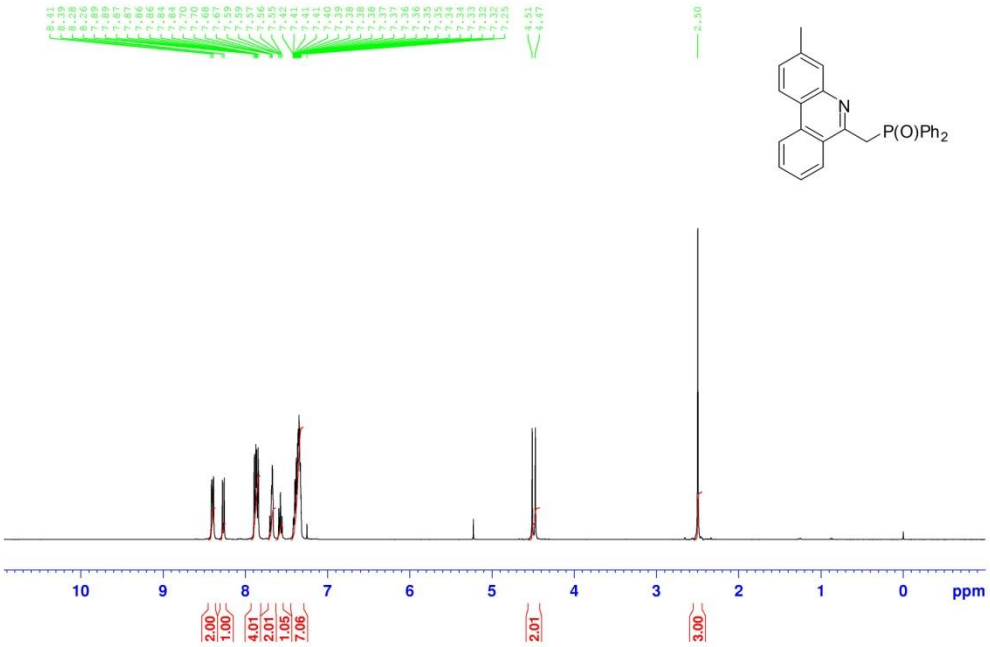

13C OBSERVE
f1 (ppm)

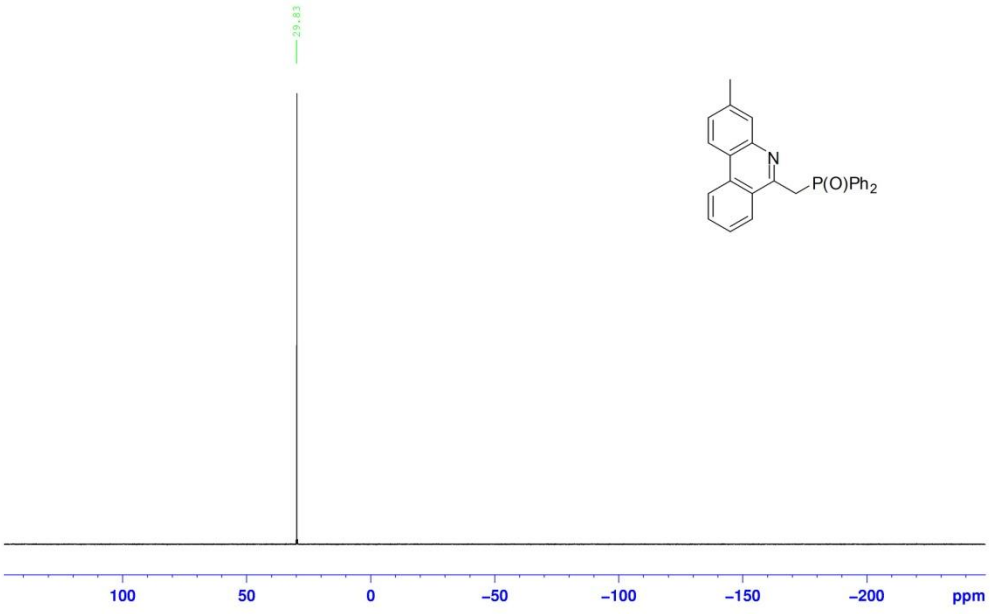

lyh20161217-35-erjiaji-n3-h
STANDARD 1H OBSERVE
f1 (ppm)

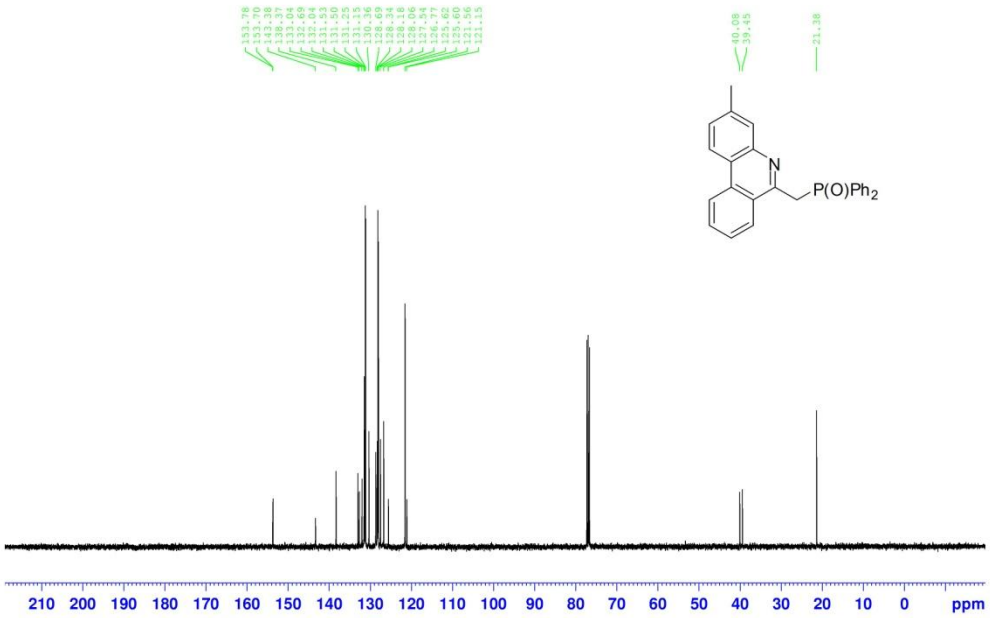

lyh20161217-35-erjiaji-n3-c
13C OBSERVE
f1 (ppm)

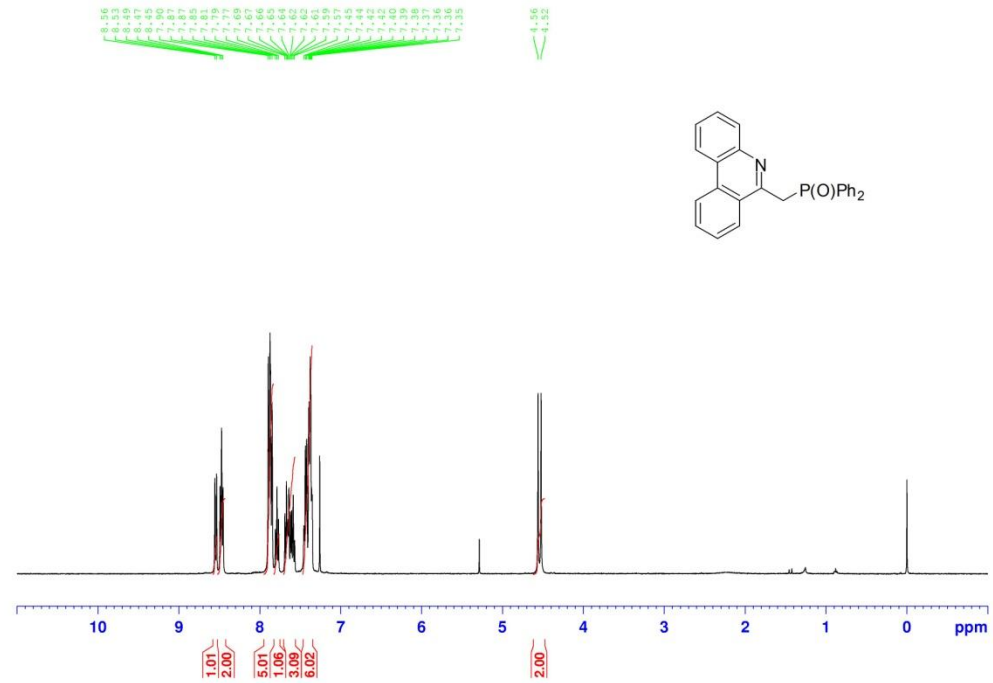

lyh20161226-2-Cl-n3-h
STANDARD 1H OBSERVE
f1 (ppm)

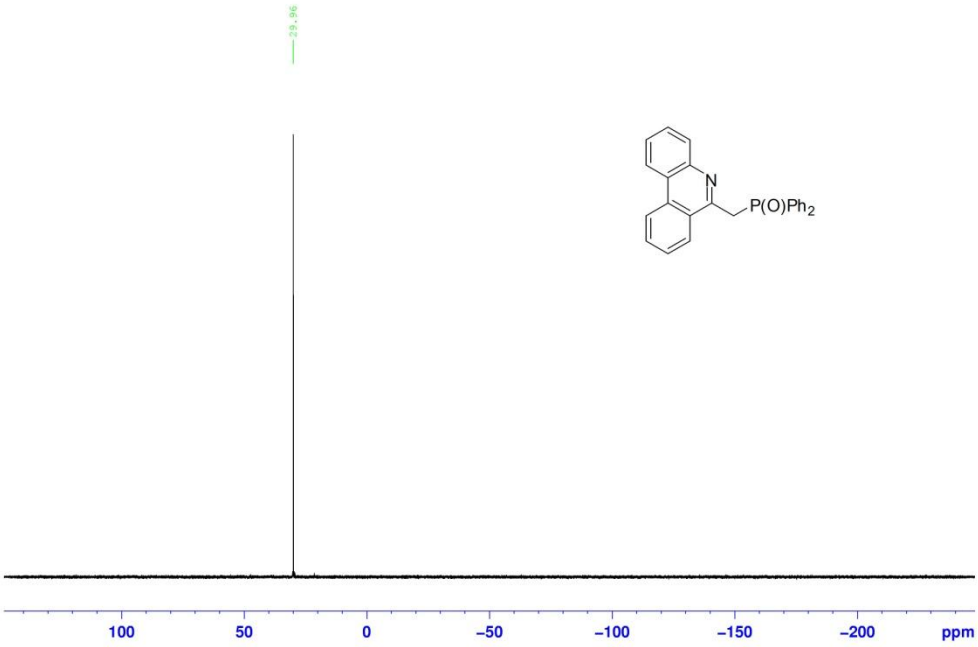

lyh20161226-2-Cl-n3-c
13C OBSERVE
f1 (ppm)

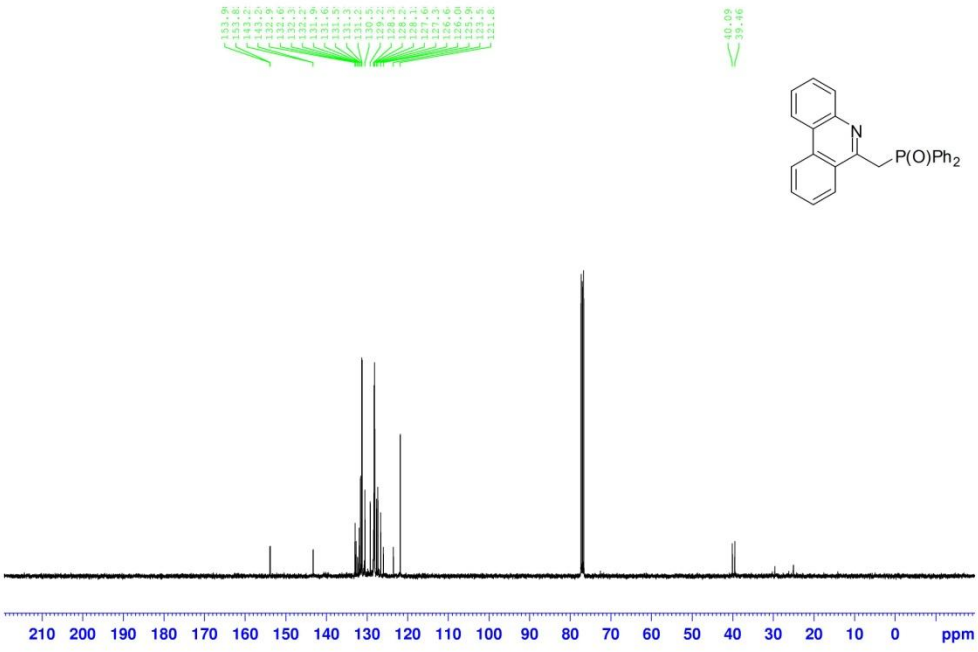

8.41
8.39
8.28
8.26
7.89
7.87
7.87
7.86
7.86
7.84
7.84
7.70
7.70
7.68
7.67
7.59
7.57
7.56
7.55
7.42
7.41
7.41
7.41
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.25
4.51
4.47
2.50
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
4.01
2.01
1.05
7.06
2.01
3.00

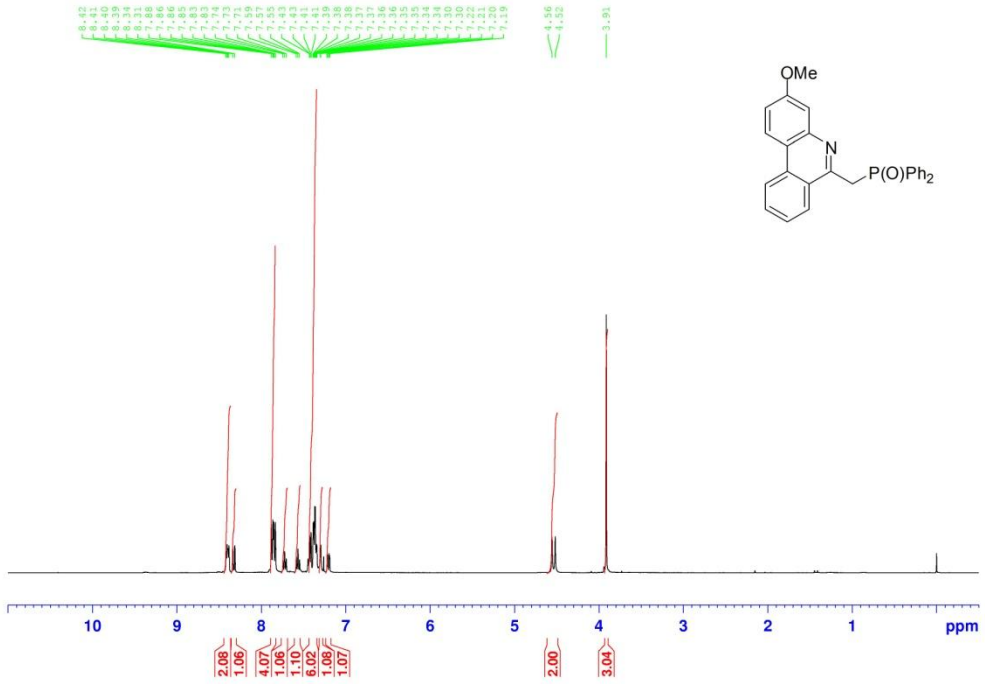

29.83
N
P(O)Ph2
100
50
0
-50
-100
-150
-200
ppm

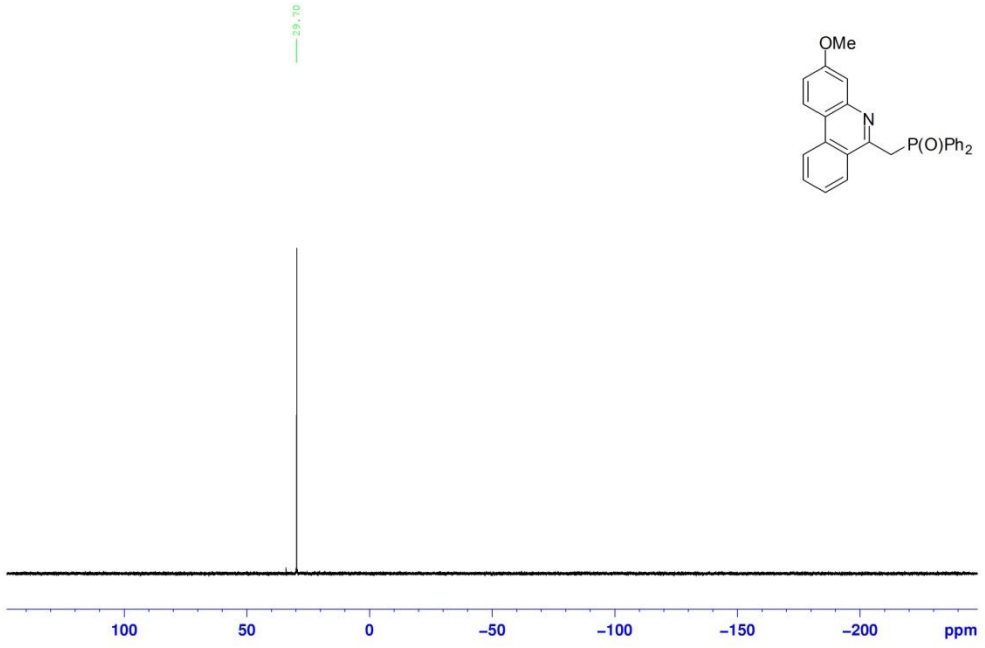

153.78
153.70
143.38
143.37
139.04
132.69
132.04
131.53
131.50
131.25
131.15
130.36
128.69
128.54
128.18
128.06
127.54
126.77
126.67
125.60
121.56
121.15
40.08
39.45
21.38
N
P(O)Ph2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

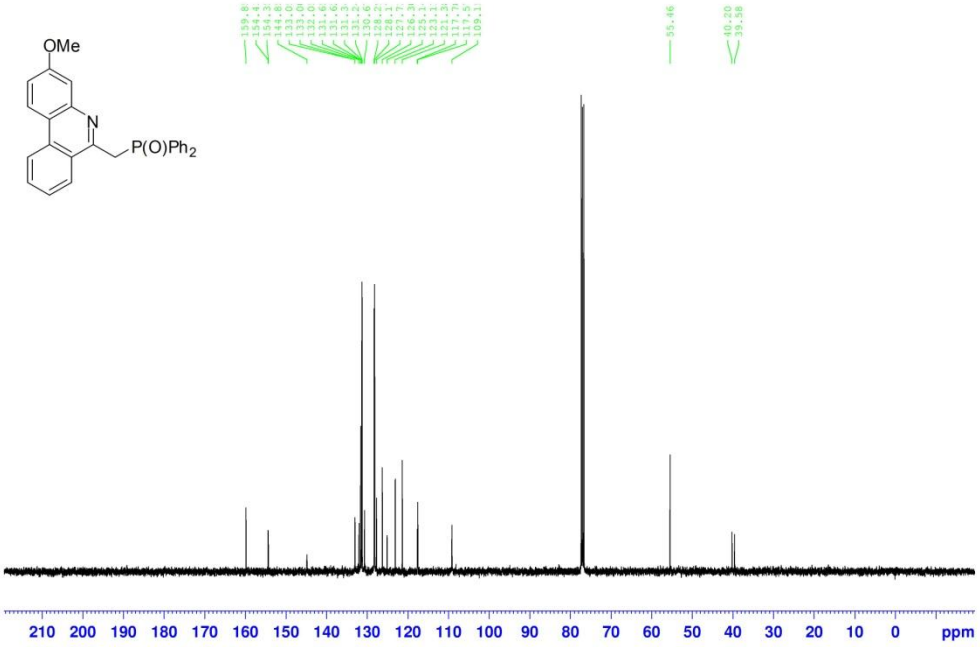

8.56
8.53
8.49
8.47
8.45
7.90
7.87
7.85
7.85
7.81
7.79
7.77
7.69
7.67
7.66
7.65
7.64
7.62
7.62
7.61
7.59
7.57
7.45
7.44
7.42
7.40
7.39
7.38
7.37
7.36
7.36
7.35
4.56
4.32
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
2.00
5.01
1.06
3.09
6.02
2.00

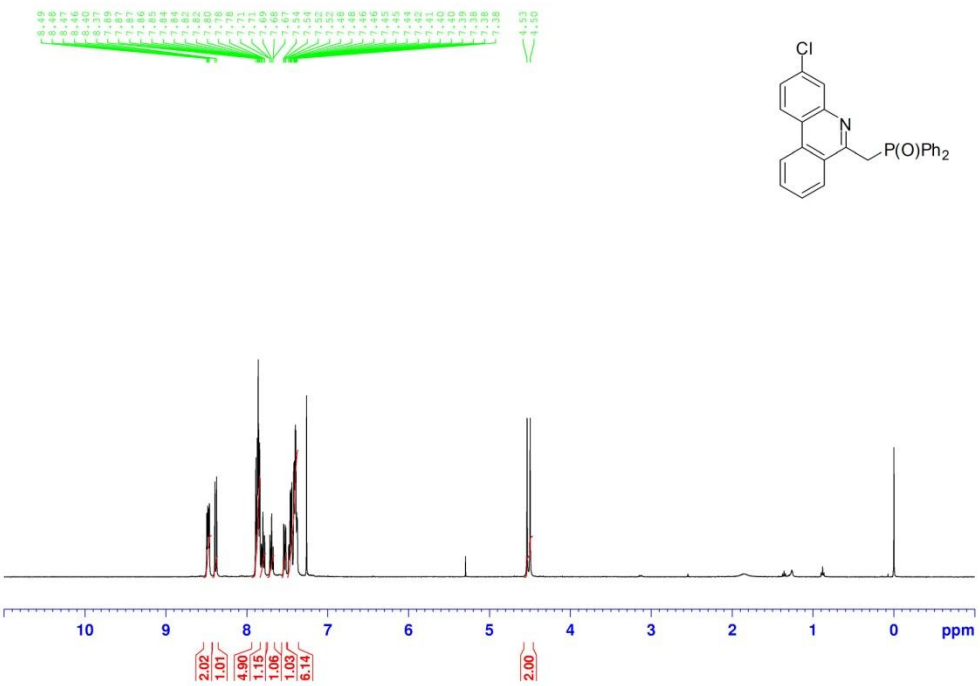

29.96
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

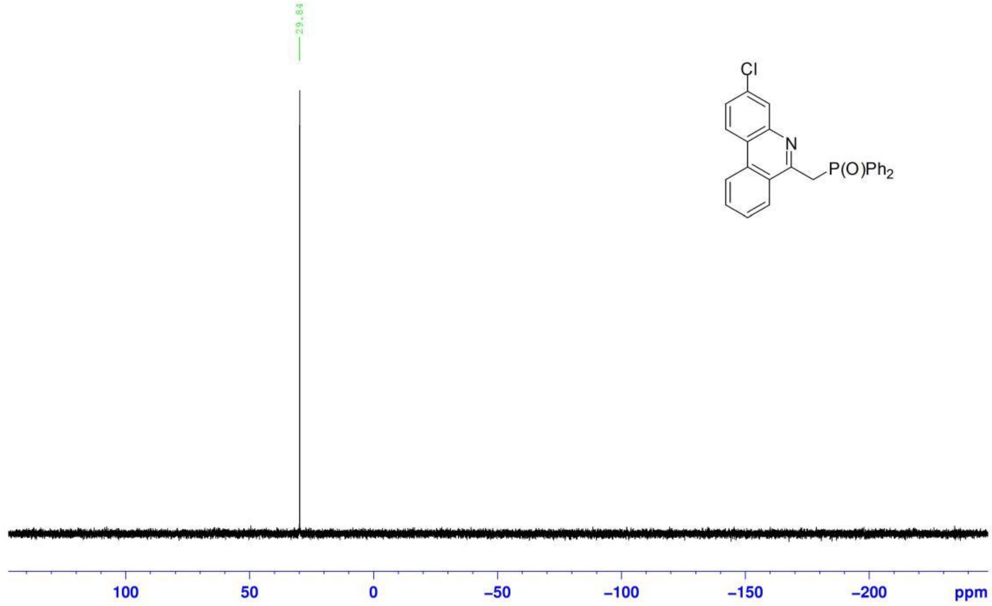

153.9
153.4
143.2
143.2
132.9
132.6
132.3
132.2
131.9
131.6
131.5
131.3
131.2
130.5
129.2
129.1
128.2
128.1
127.6
127.5
126.6
126.0
125.9
123.5
121.8
40.09
39.46
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
ppm

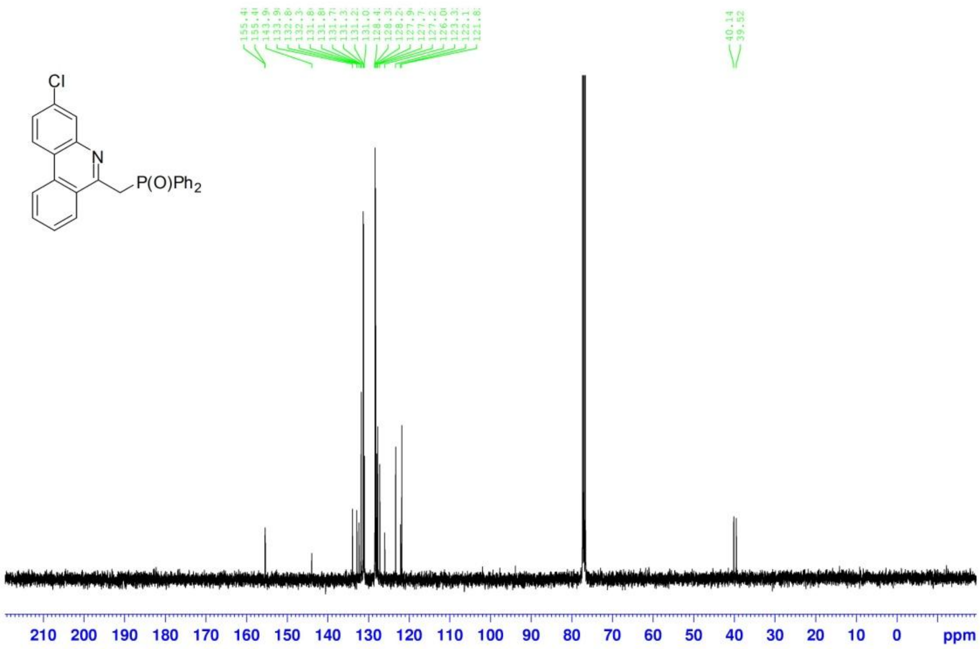

OMe
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm


OMe
N
P(O)Ph2
159.8
154.4
154.3
144.6
133.0
132.0
131.6
131.5
131.3
131.2
130.6
128.7
128.1
127.7
126.3
125.1
123.1
121.3
117.7
117.5
109.1
55.46
40.20
39.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

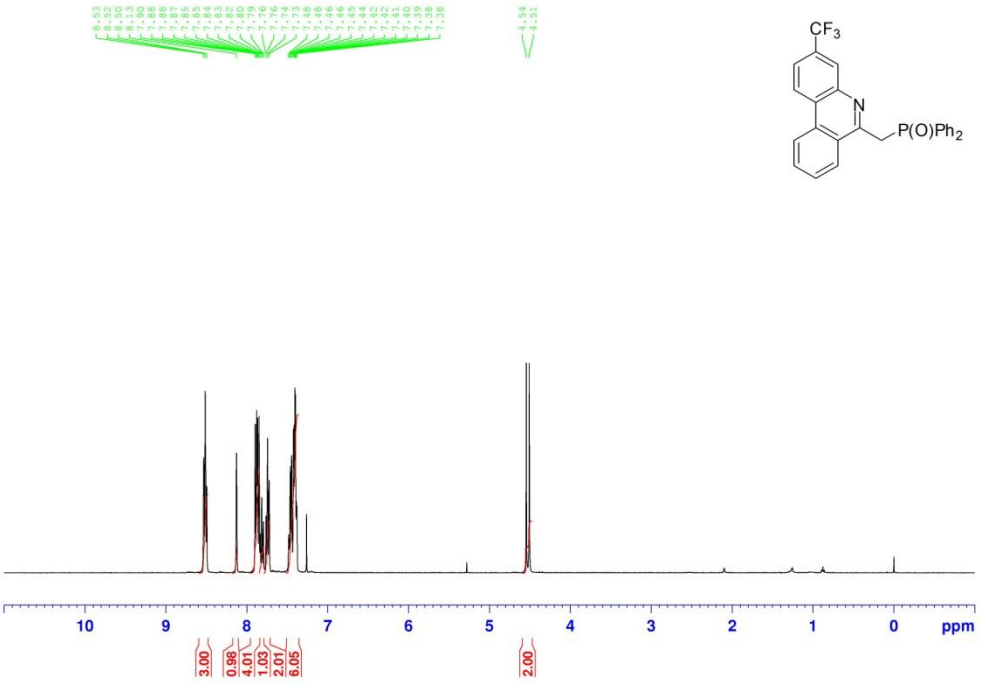

8.49
8.48
8.47
8.46
8.40
8.37
7.89
7.87
7.86
7.85
7.84
7.82
7.80
7.78
7.71
7.69
7.68
7.67
7.54
7.54
7.52
7.48
7.46
7.46
7.45
7.45
7.44
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
4.53
4.50
Cl
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
2.02
1.01
4.90
1.15
1.06
1.03
6.14
2.00

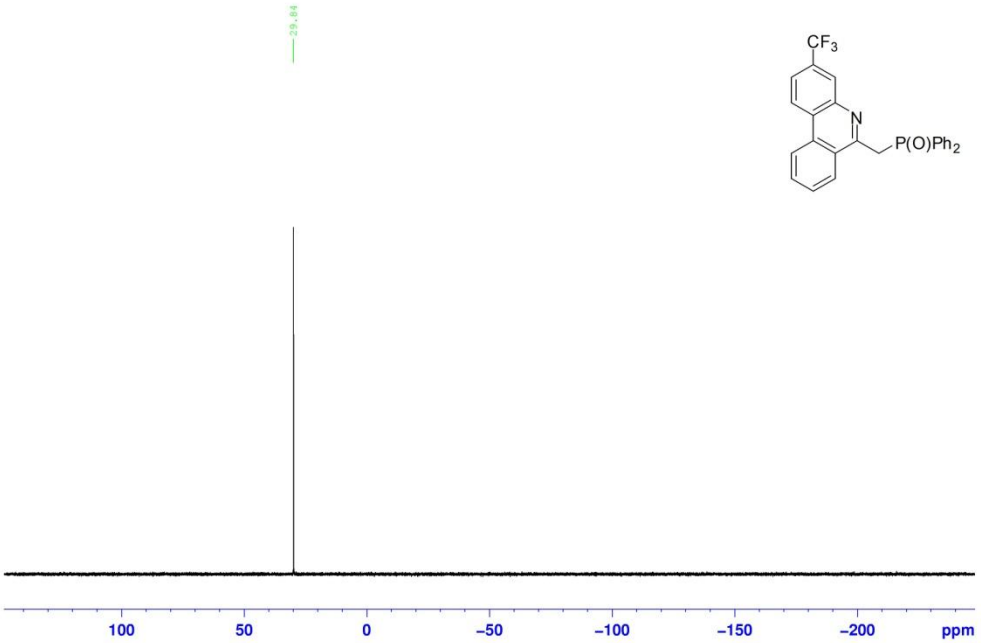


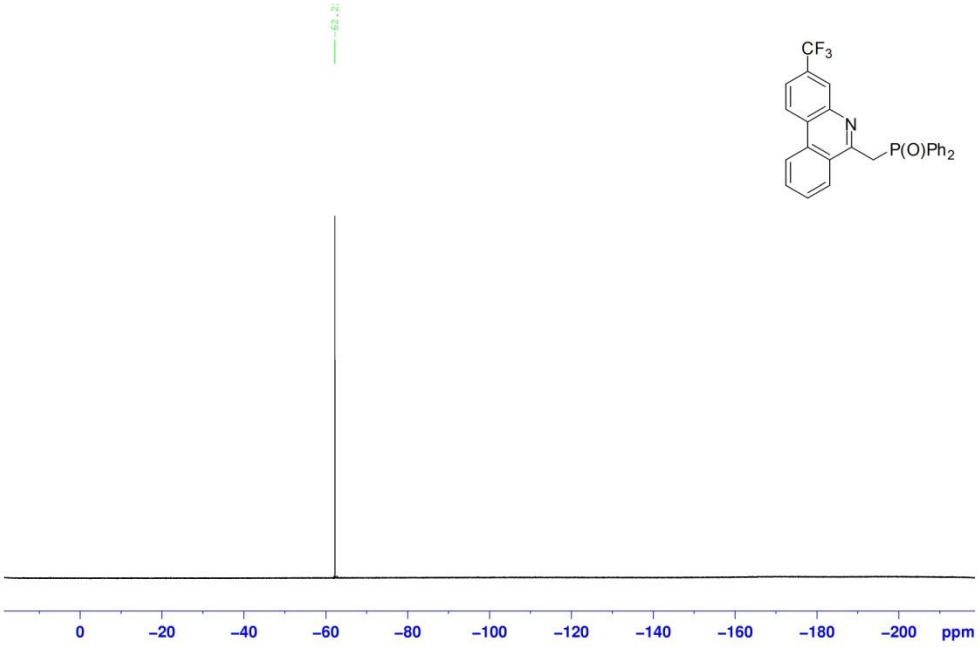
29.84
Cl
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

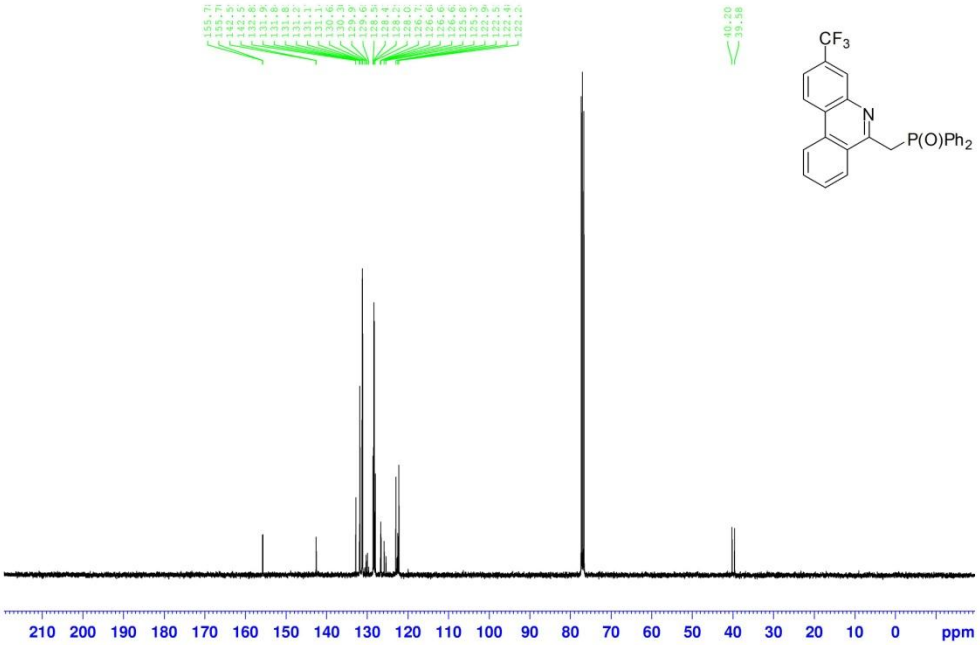


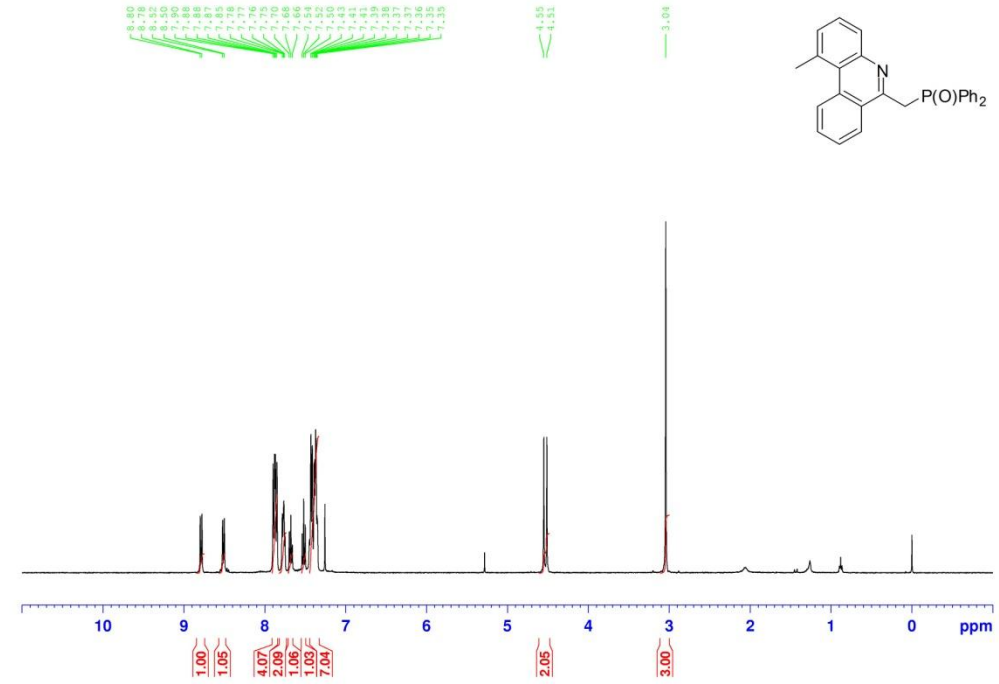
155.4
155.4
143.9
133.9
132.8
132.3
131.8
131.8
131.7
131.3
131.2
131.0
128.4
128.3
128.2
127.9
127.7
127.2
126.0
123.3
122.1
121.8
40.14
39.52
Cl
N
P(O)Ph2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

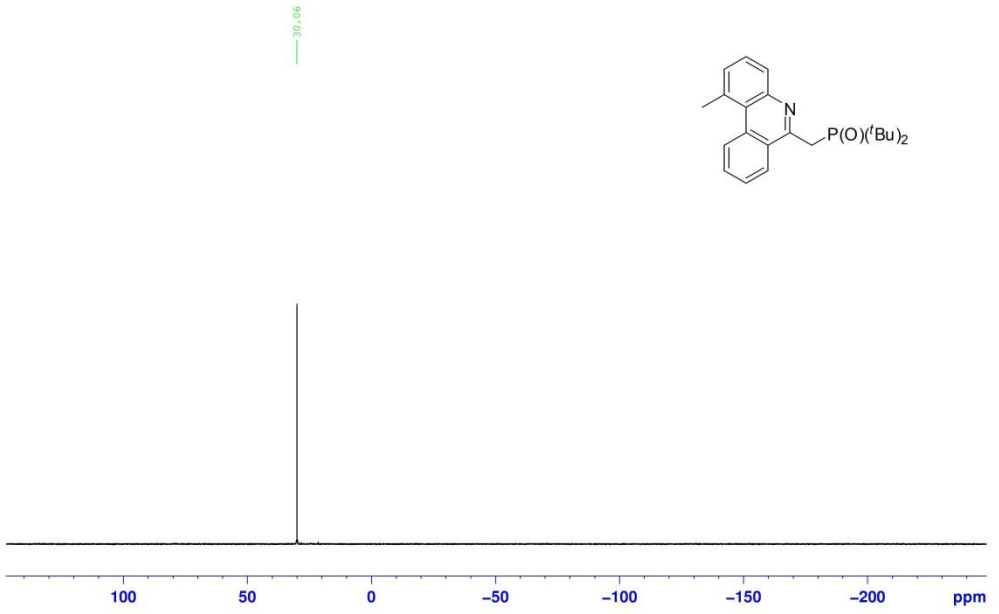

CF3
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
3.00
0.96
4.01
1.03
2.01
6.05
2.00

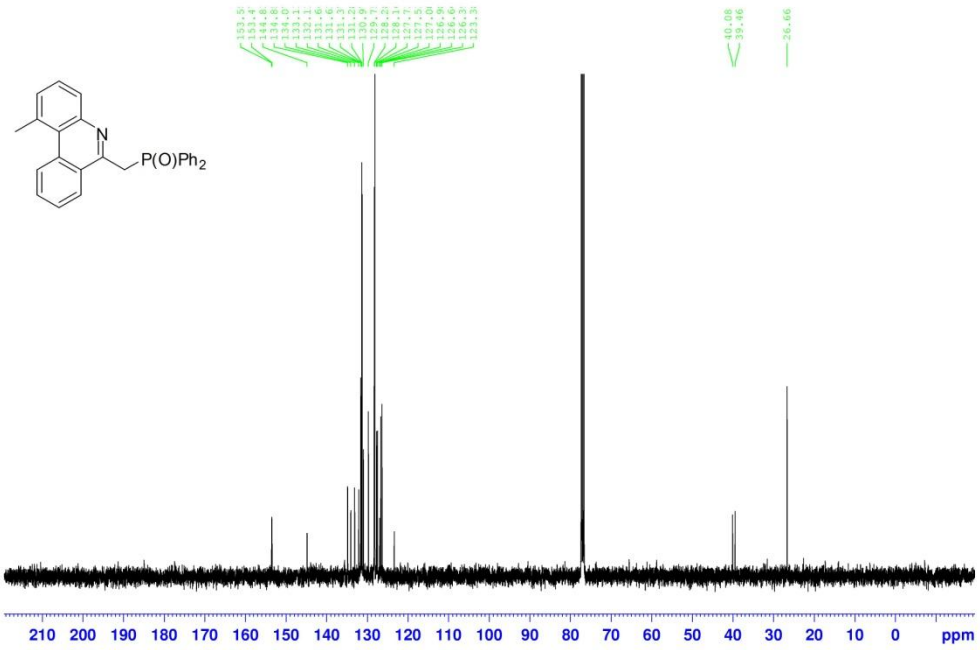

29.84
CF3
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

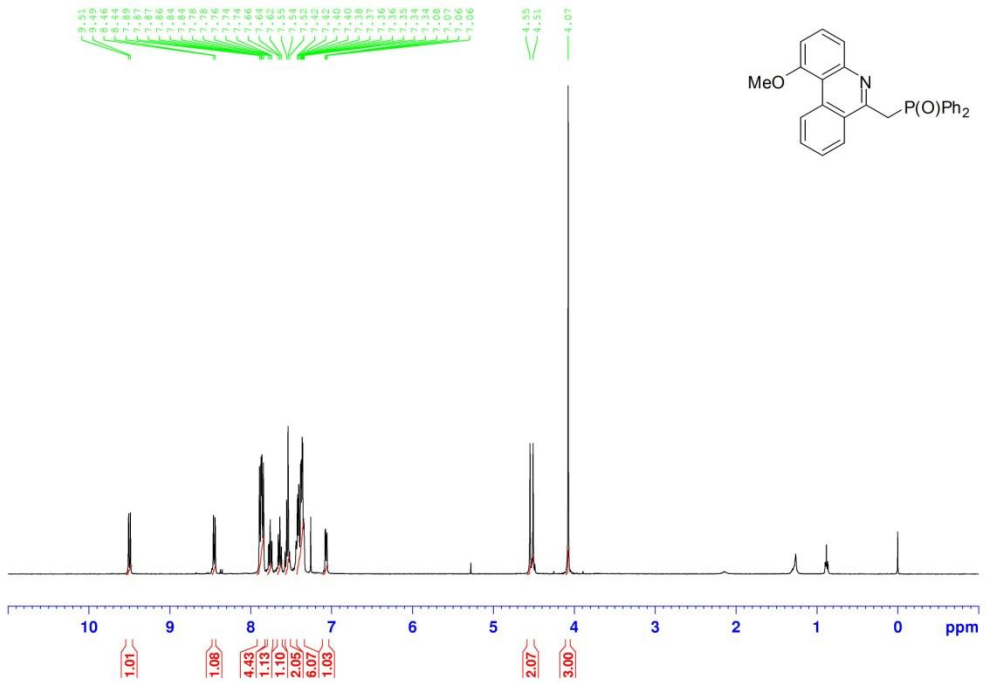

-62.2
CF3
N
P(O)Ph2
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

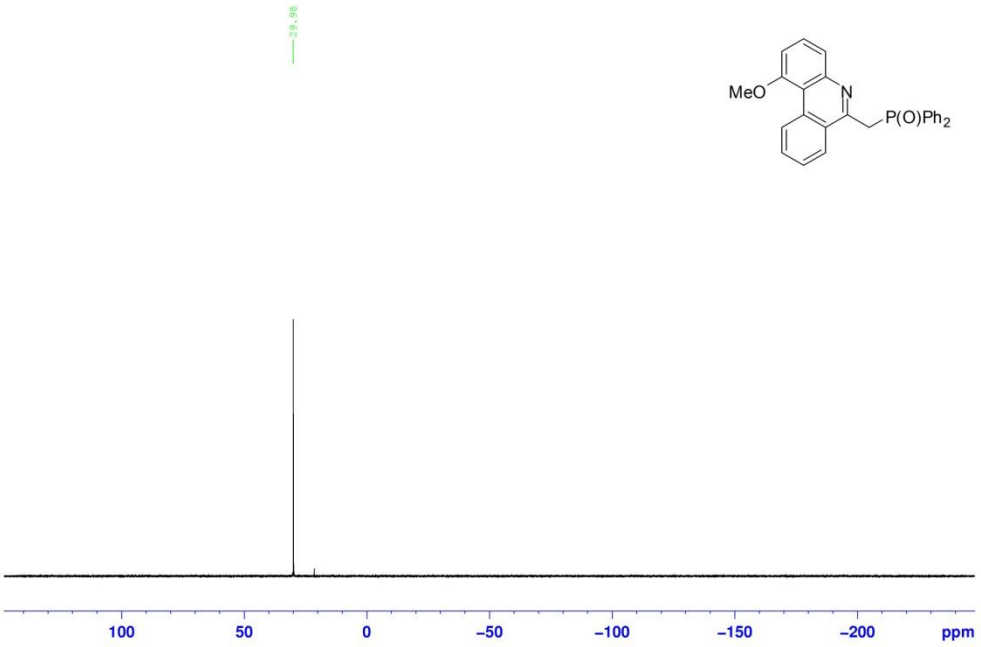

155.7
153.7
142.5
140.8
133.8
131.8
131.2
131.1
130.6
130.3
129.9
129.6
128.5
128.4
128.2
128.0
127.7
126.6
126.4
125.8
123.3
122.9
122.5
122.4
122.2
40.20
39.58
CF3
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

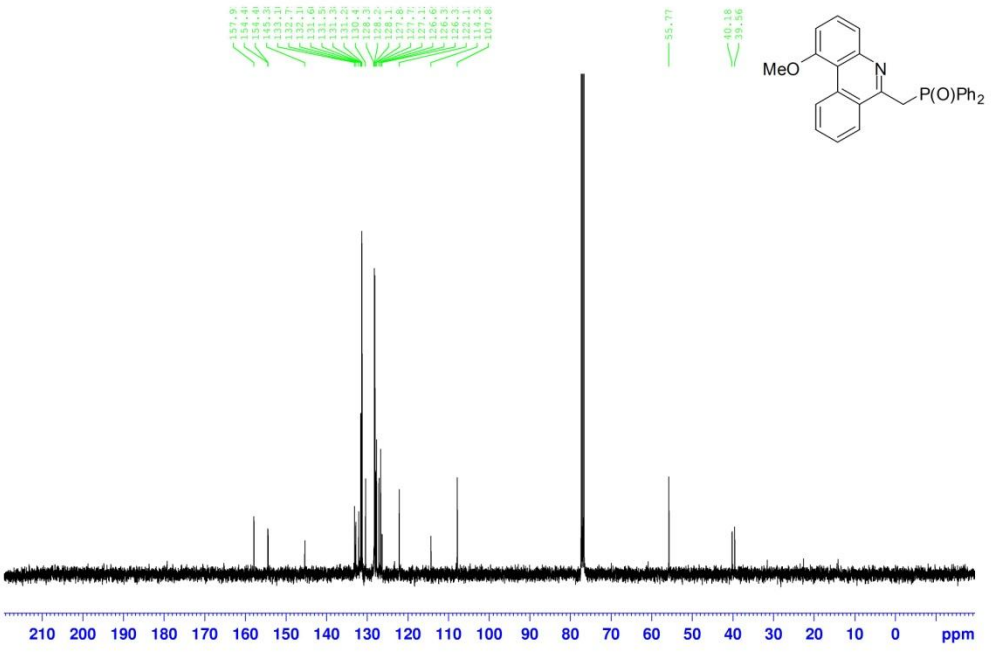

8.80
8.79
8.52
8.50
7.90
7.88
7.87
7.85
7.78
7.77
7.76
7.75
7.70
7.68
7.66
7.54
7.52
7.50
7.43
7.41
7.39
7.38
7.37
7.37
7.36
7.35
7.35
4.55
4.51
3.04
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
4.07
2.09
1.06
1.03
7.04
2.05
3.00

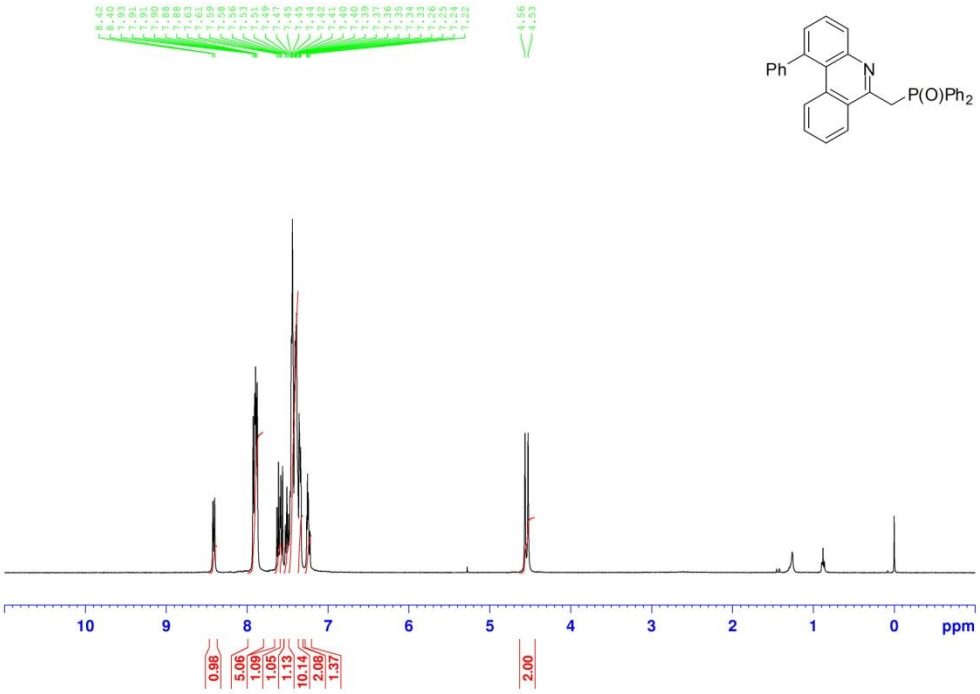

30.06
N
P(O)(tBu)2
100
50
0
−50
−100
−150
−200
ppm

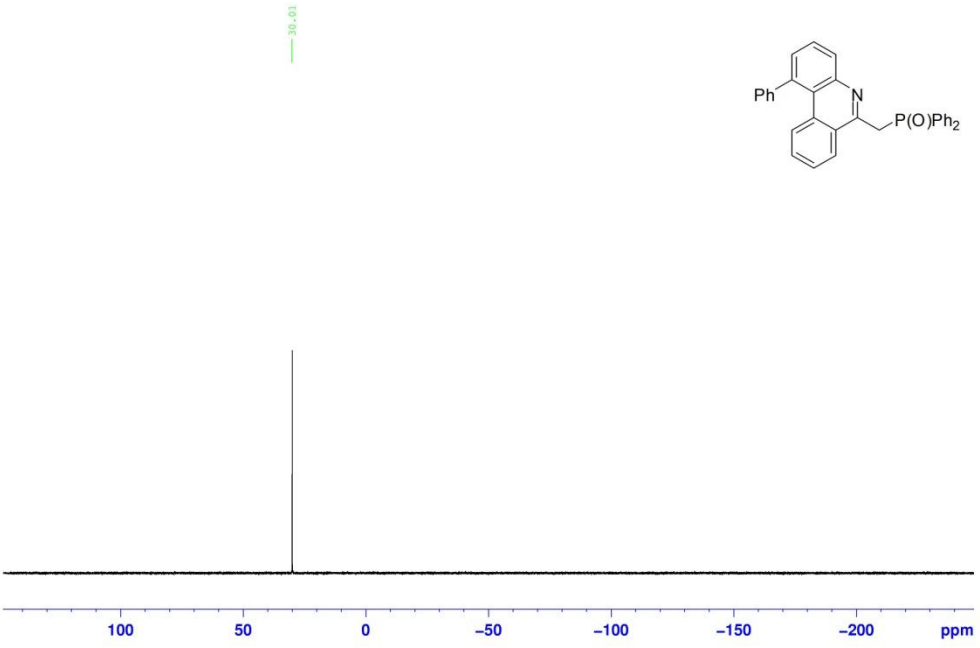

N
P(O)Ph2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

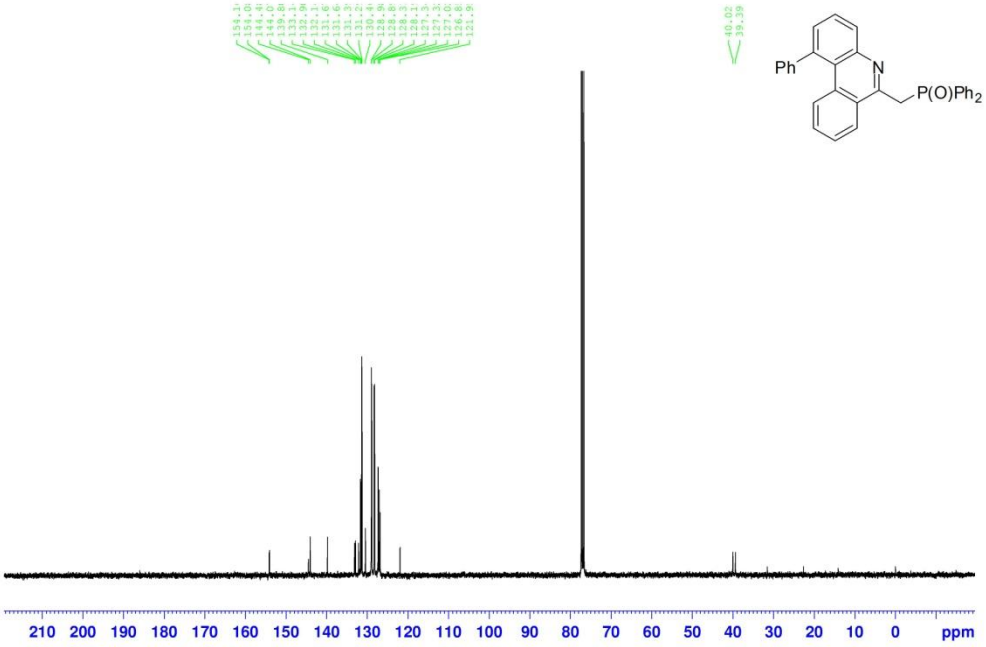

MeO
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.08
4.43
1.13
1.10
2.05
6.07
1.03
2.07
3.00

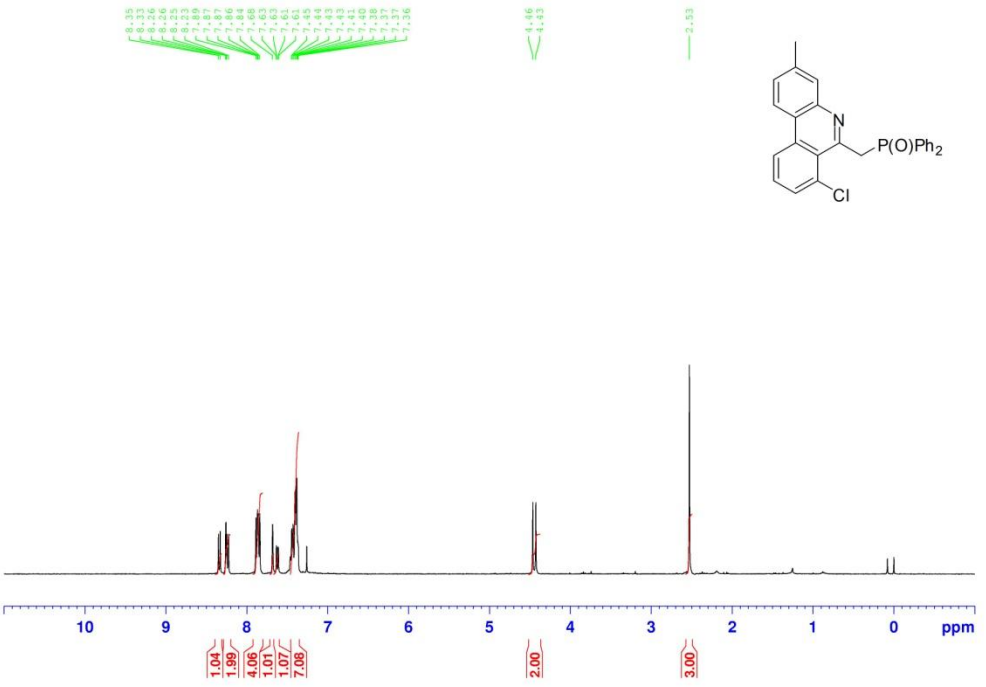

29.98
MeO
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

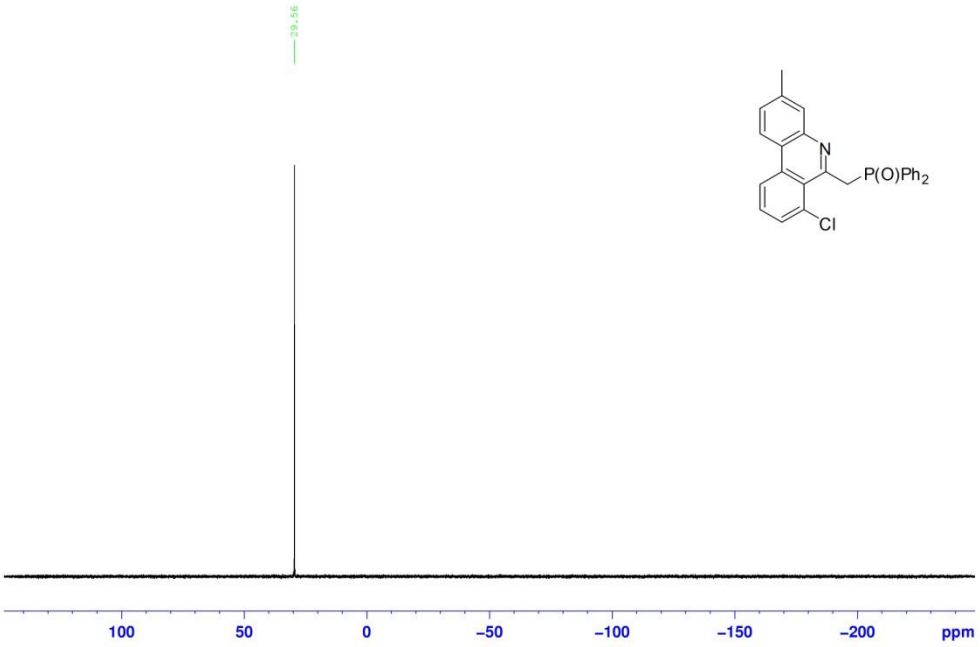

157.9
154.4
154.0
133.3
132.7
132.1
131.6
131.5
131.4
131.2
130.4
128.3
128.2
128.1
127.8
127.7
127.1
126.6
126.3
122.1
114.3
107.6
55.77
40.18
39.56
MeO
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

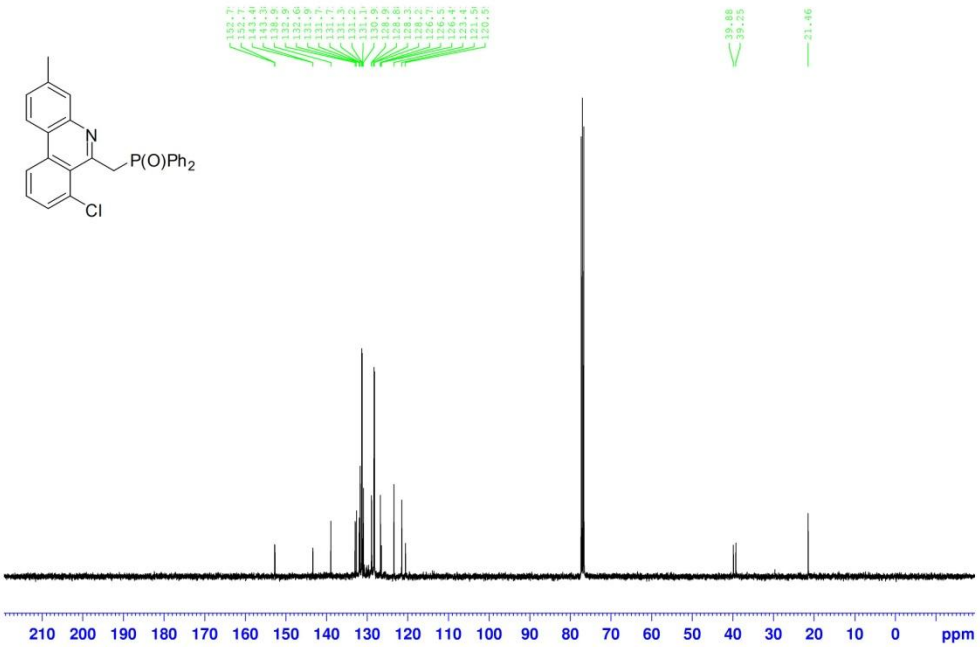

Ph
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
5.06
1.09
1.05
1.13
10.14
2.08
1.37
2.00

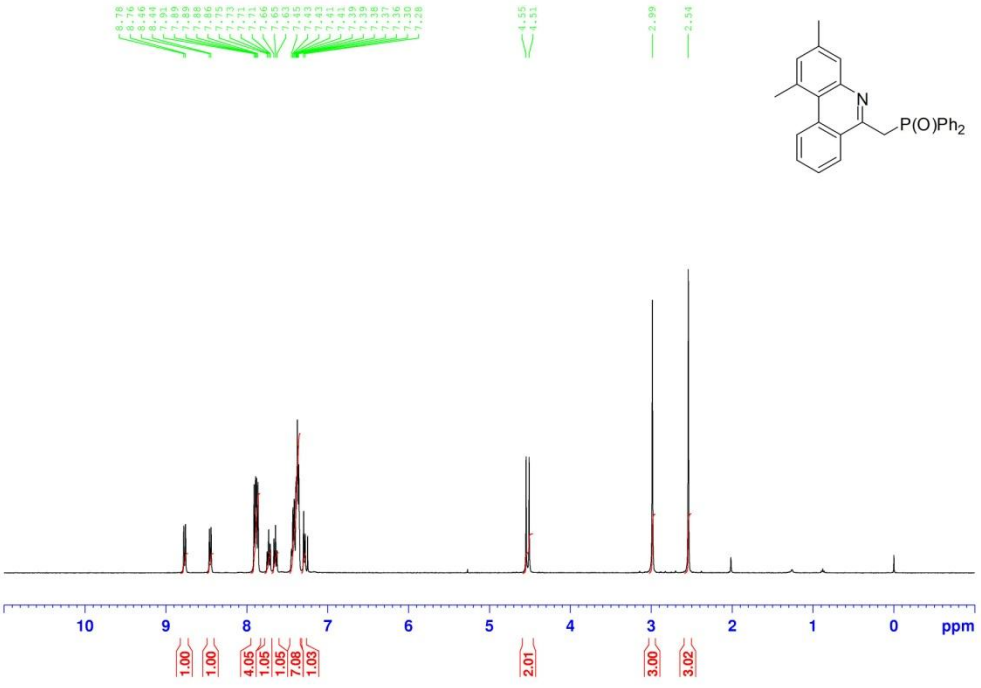

30.01
Ph
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

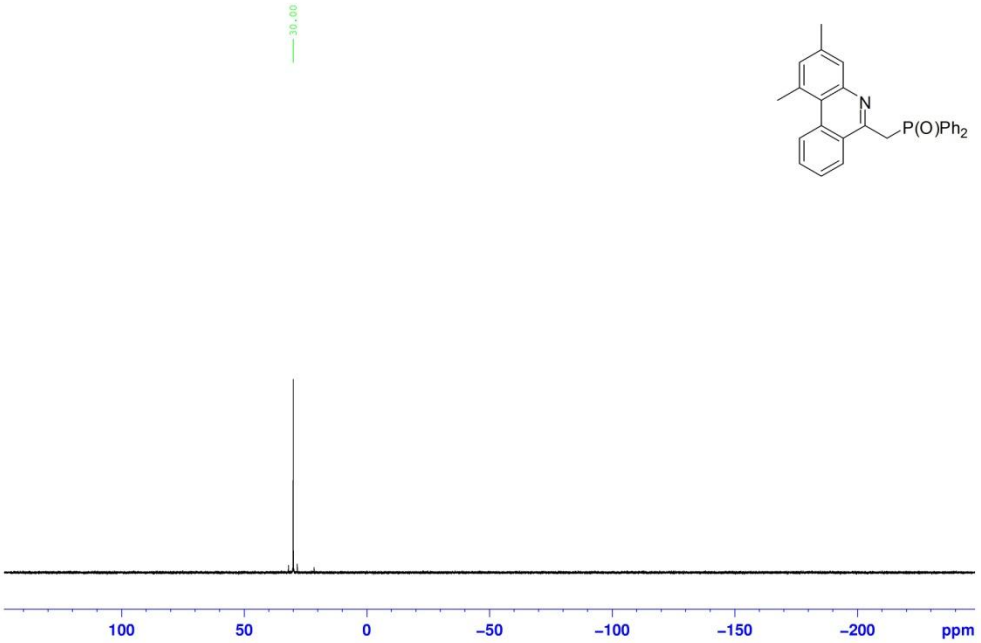

Ph
N
P(O)Ph2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

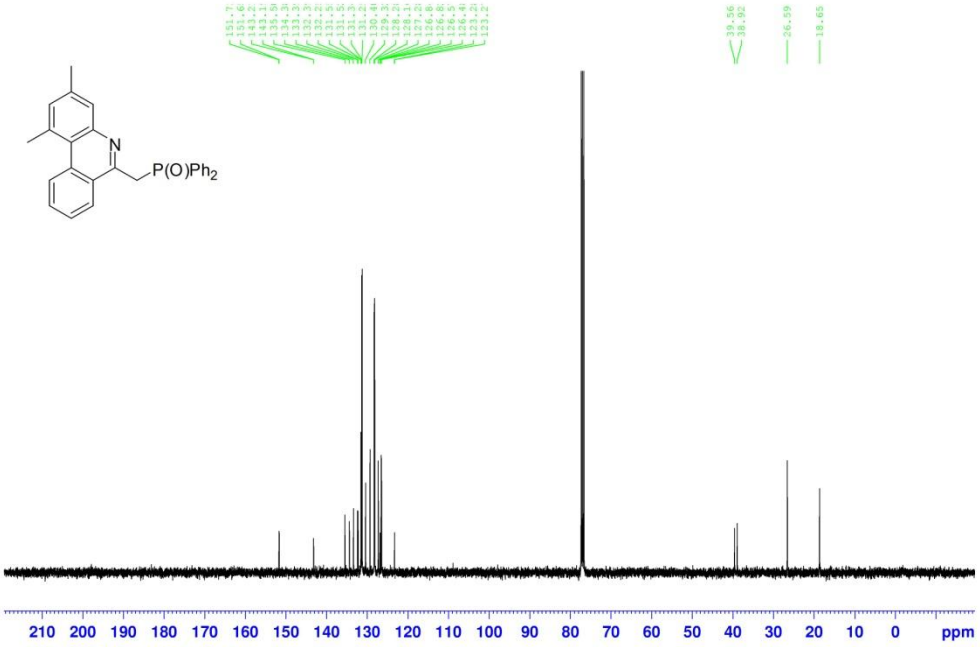

N
P(O)Ph2
Cl
10 9 8 7 6 5 4 3 2 1 0 ppm
1.04
1.99
4.06
1.01
1.07
7.08
2.00
3.00

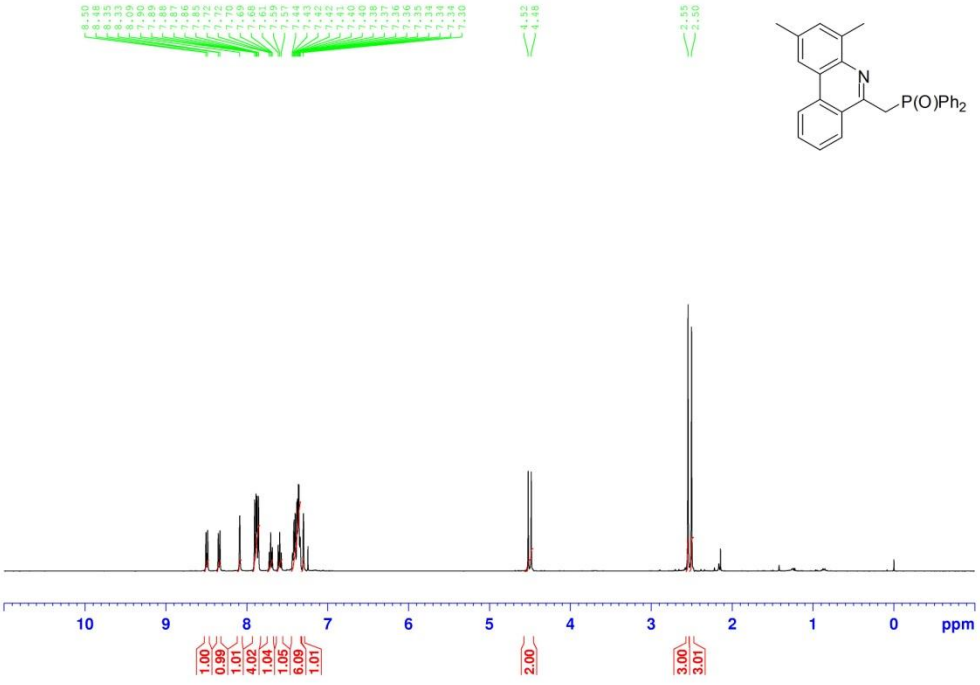

29.56
N
P(O)Ph2
Cl
100
50
0
−50
−100
−150
−200
ppm

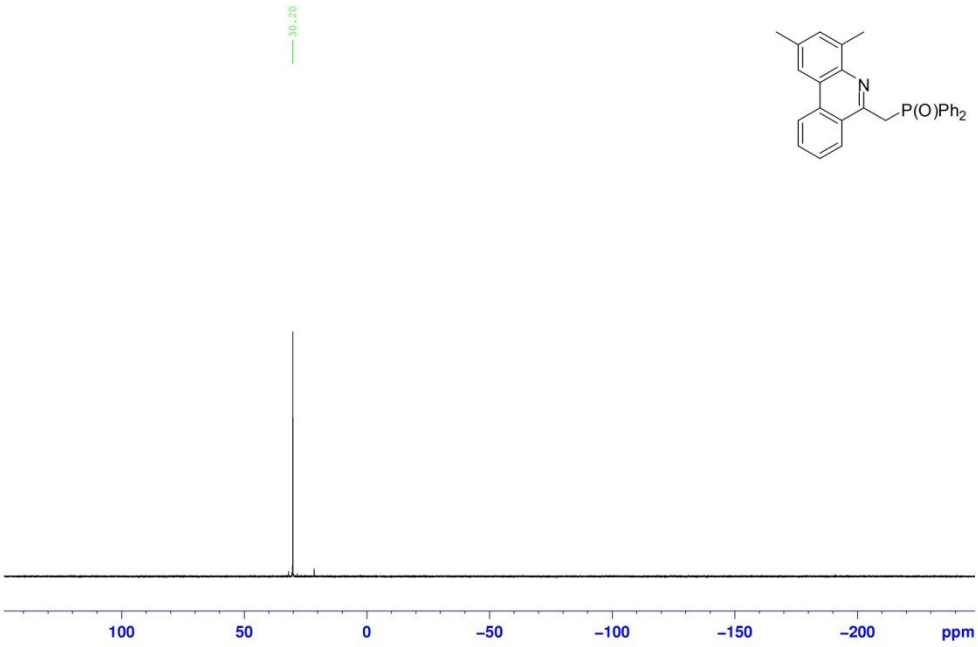

N
P(O)Ph2
Cl
39.88
39.25
21.46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

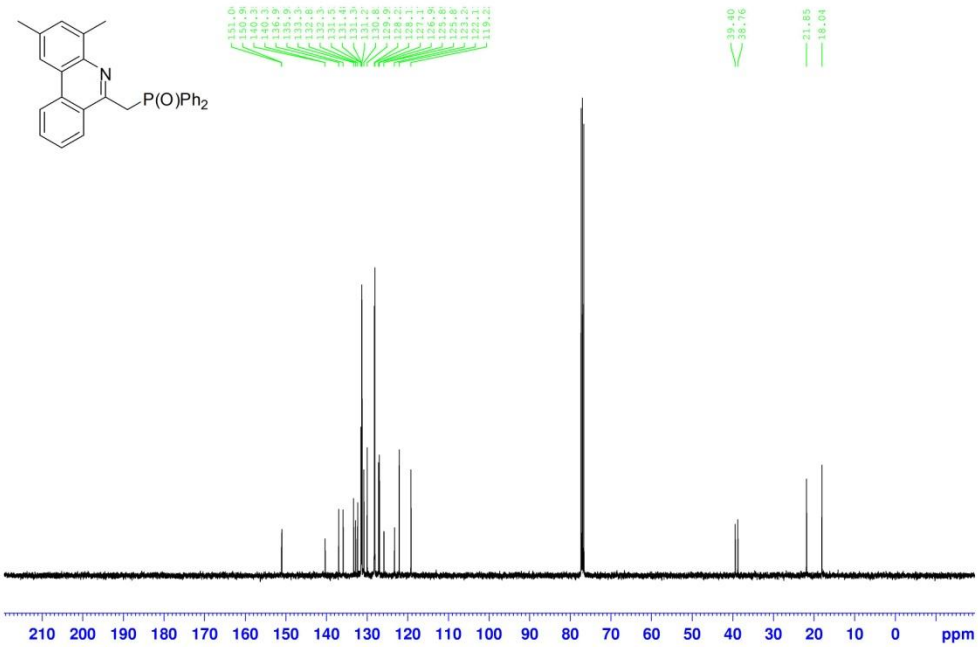

8.78
8.76
8.46
8.45
7.91
7.89
7.88
7.86
7.75
7.73
7.71
7.66
7.65
7.63
7.45
7.43
7.41
7.39
7.38
7.37
7.36
7.30
7.28
4.55
4.51
2.99
2.54
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
4.05
1.05
1.05
7.08
1.03
2.01
3.00
3.02

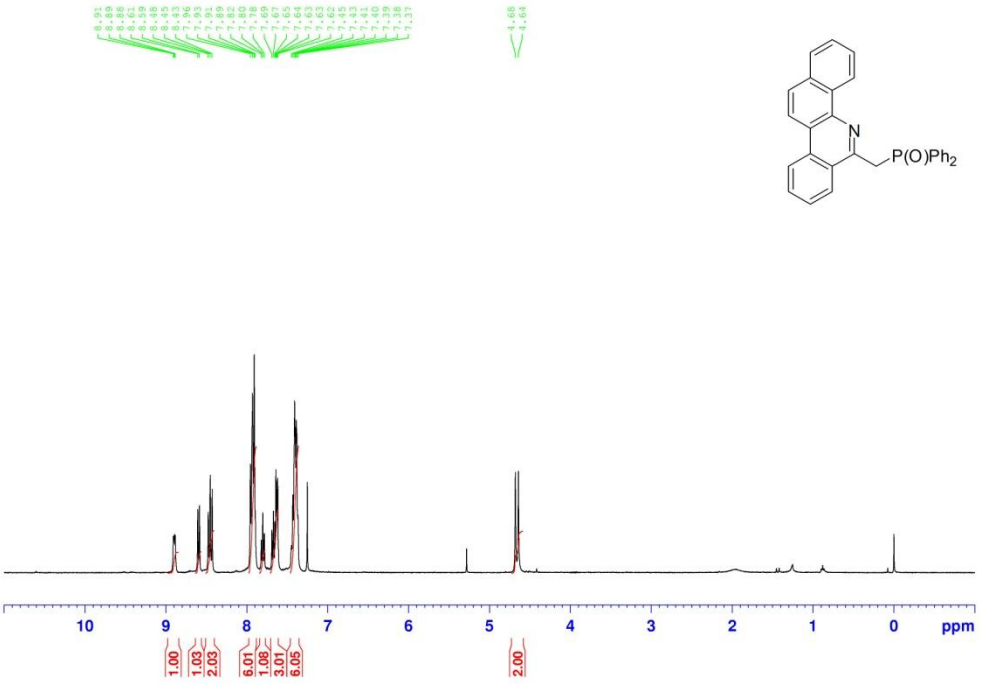

30.00
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

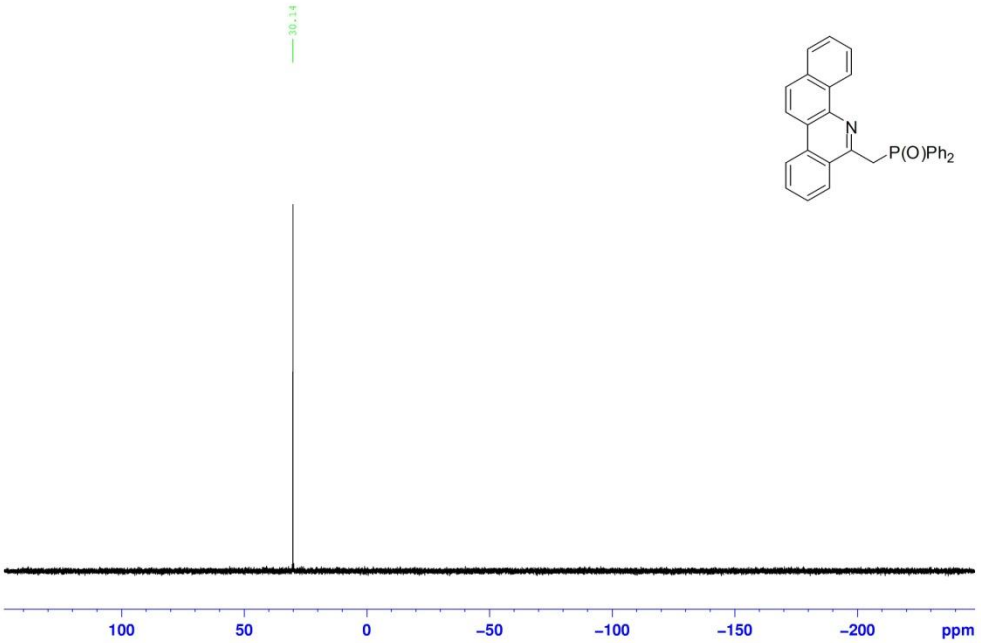

N
P(O)Ph2
39.56
39.92
26.59
18.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

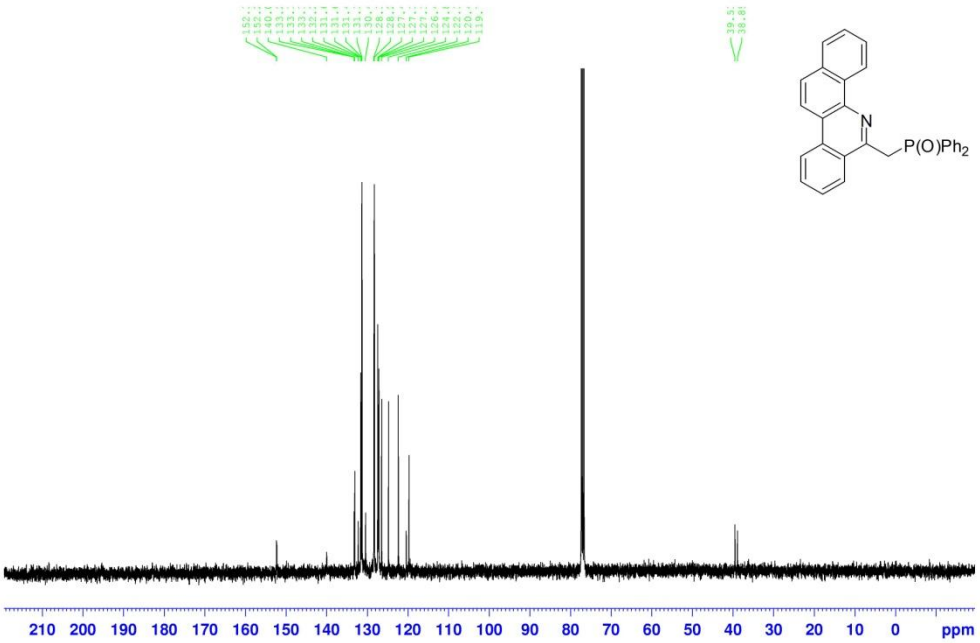

4.52
4.48
2.55
2.50
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.99
1.01
4.02
1.04
1.05
6.09
1.01
2.00
3.00
3.01

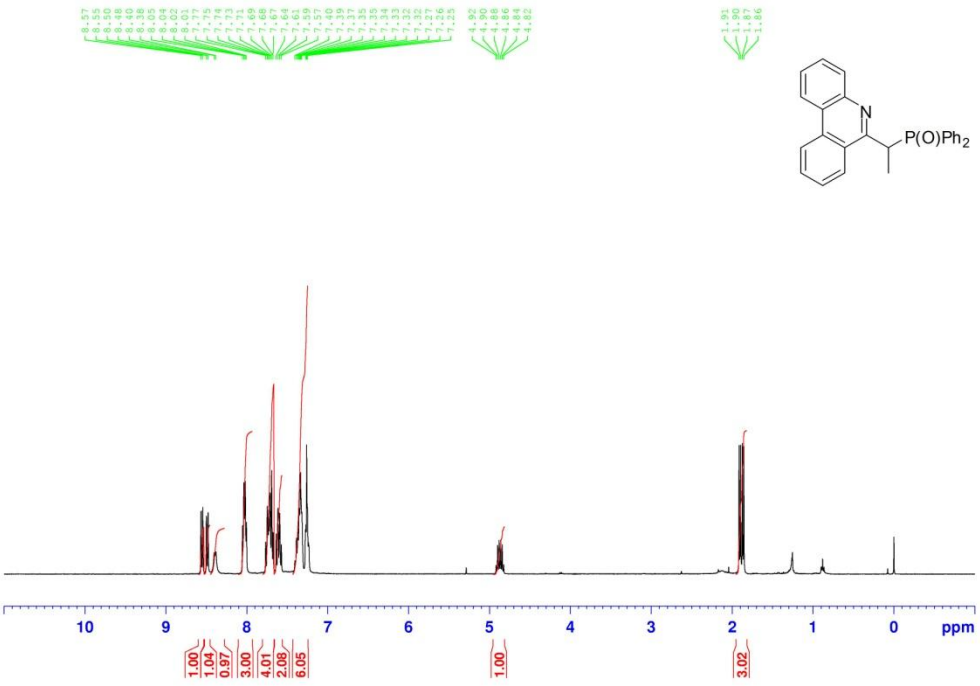

30.20
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

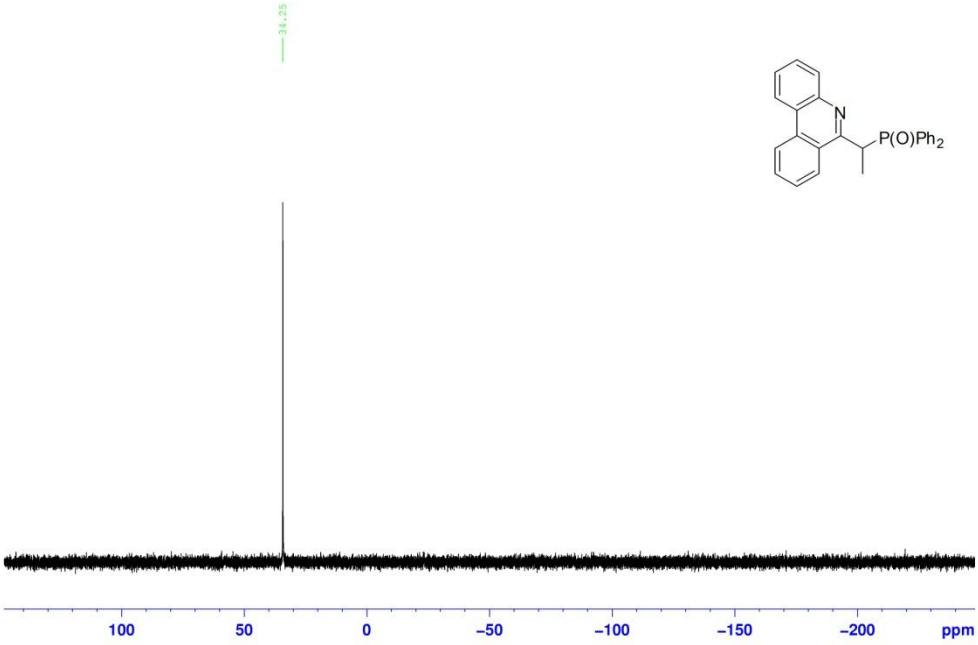

N
P(O)Ph2
39.40
38.76
21.85
18.04
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

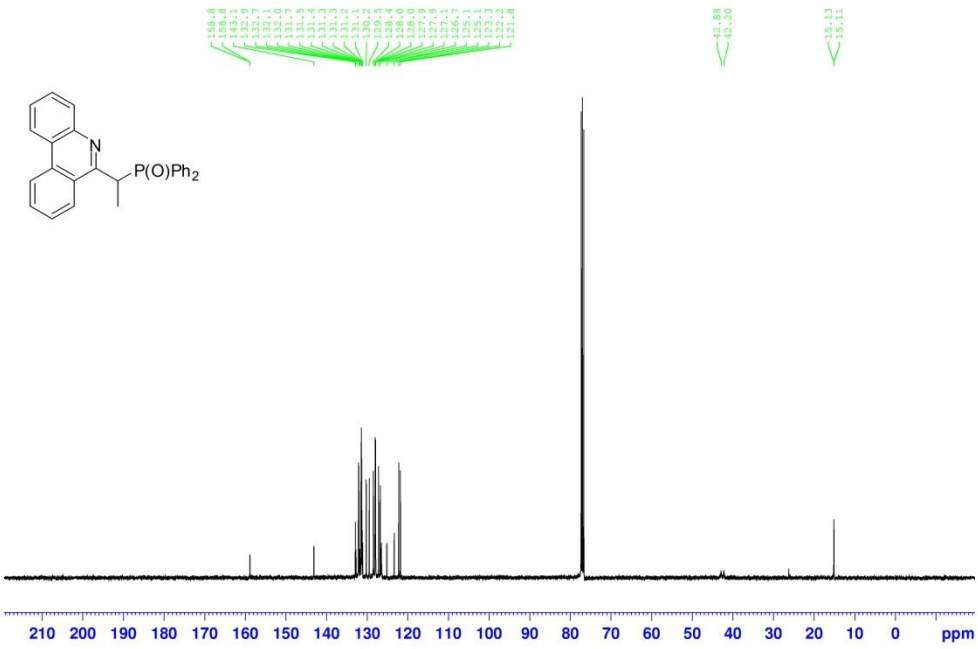

8.91
8.89
8.88
8.61
8.59
8.45
8.43
7.96
7.93
7.91
7.89
7.82
7.80
7.68
7.67
7.65
7.64
7.63
7.62
7.45
7.43
7.41
7.39
7.38
7.37
4.68
4.64
N
P(O)Ph2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.03
6.01
1.08
3.01
6.05
2.00

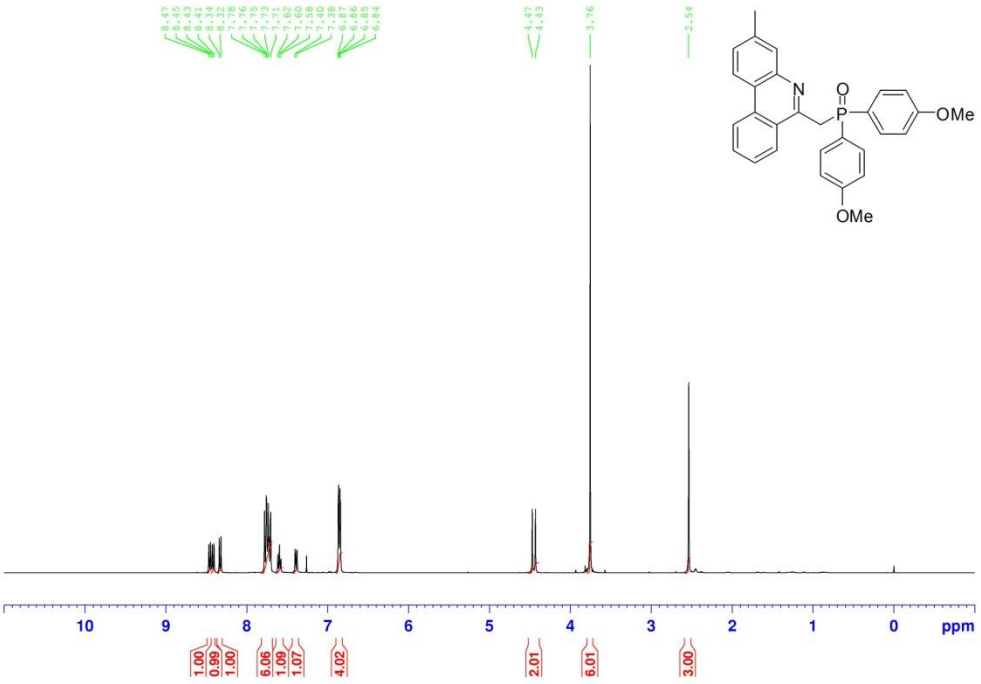

30.14
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

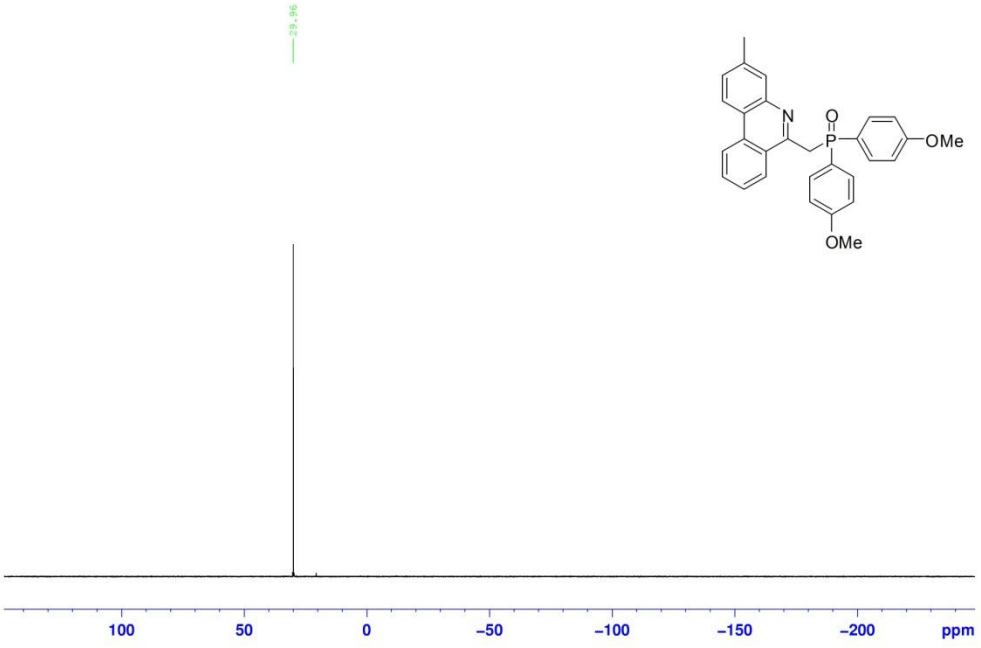

N
P(O)Ph2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

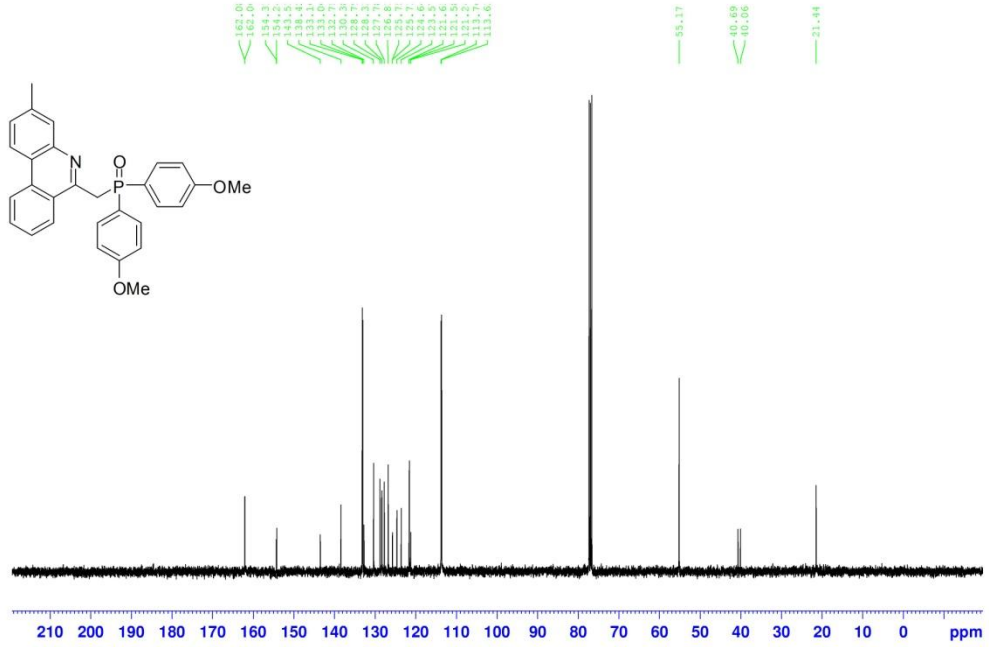

N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.04
0.97
3.00
4.01
2.08
6.05
1.00
3.02

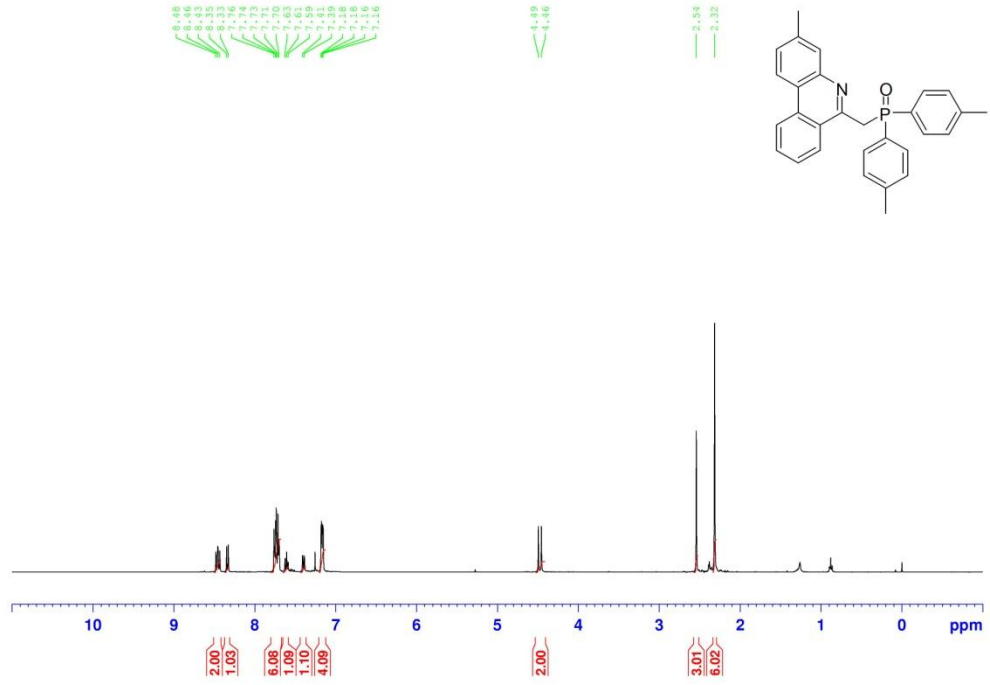

34.25
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm

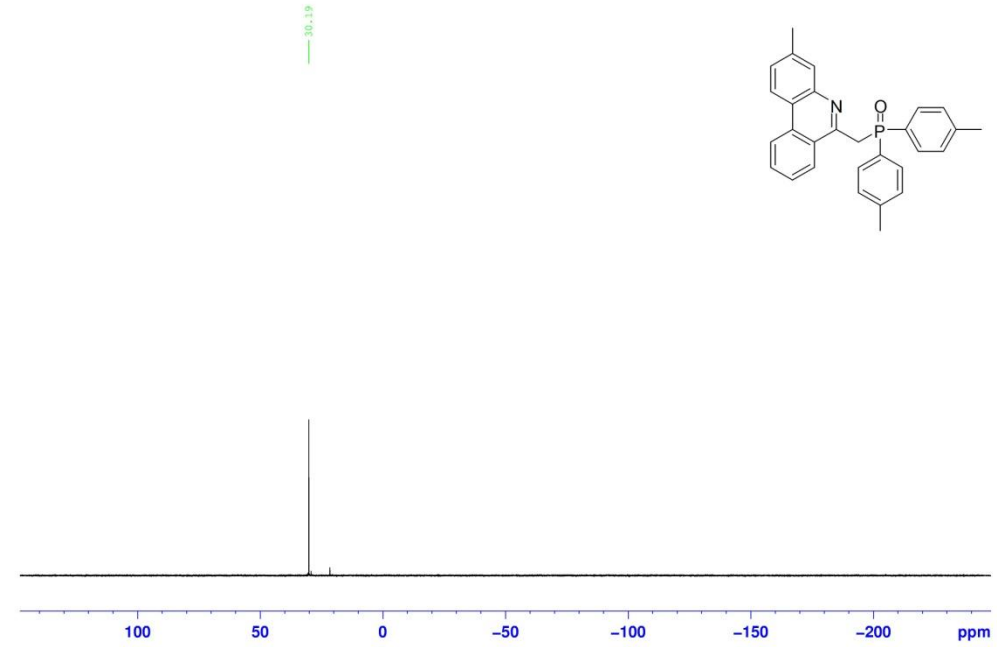

158.8
156.8
143.1
132.9
132.7
132.1
132.0
131.7
131.5
131.4
131.3
131.3
131.2
131.1
130.2
130.1
129.4
128.4
128.0
127.9
127.8
127.1
126.7
125.1
123.1
122.2
121.8
42.88
42.50
15.13
15.11
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

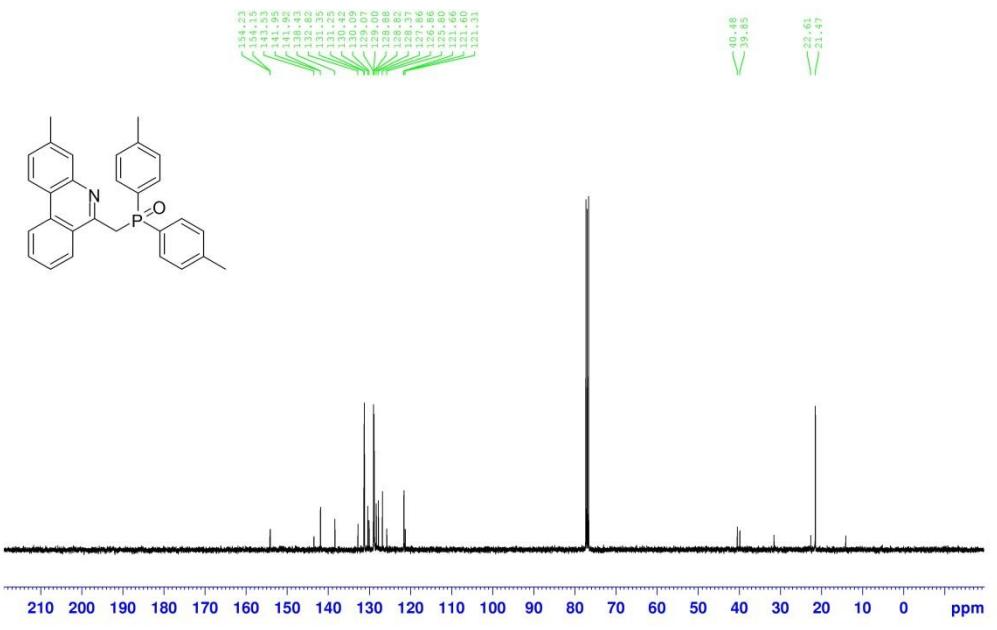

8.47
8.45
8.43
8.41
8.34
8.32
7.78
7.76
7.75
7.73
7.71
7.62
7.60
7.58
7.40
7.38
6.87
6.86
6.85
6.84
4.47
4.43
3.76
2.54
N
O
P
OMe
OMe
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.00
6.06
1.09
1.07
4.02
2.01
6.01
3.00

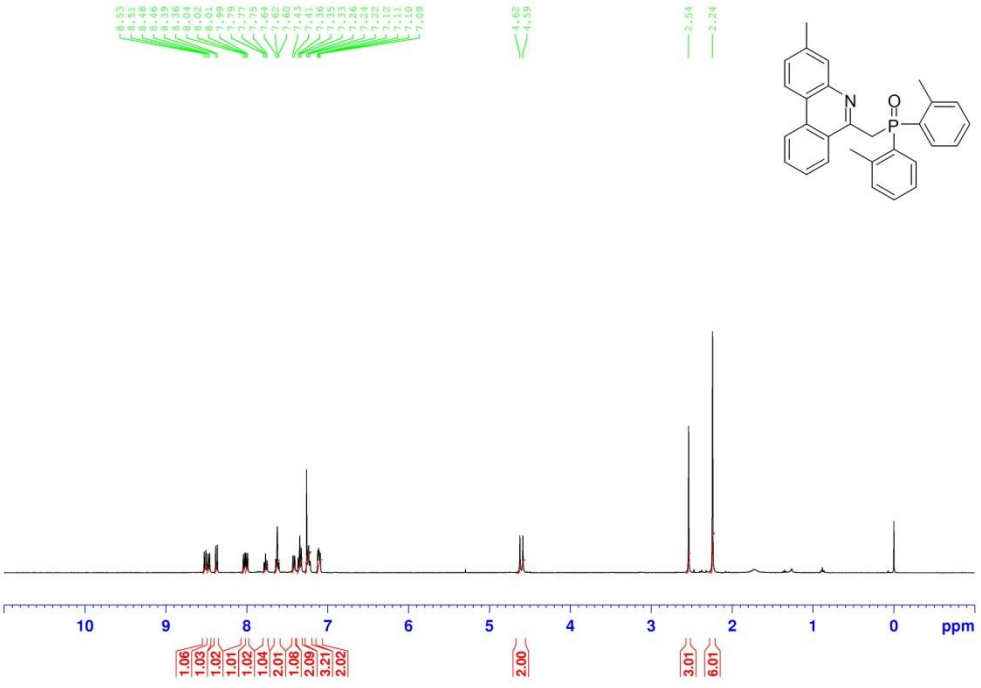

29.96
N
O
P
OMe
OMe
100
50
0
−50
−100
−150
−200
ppm

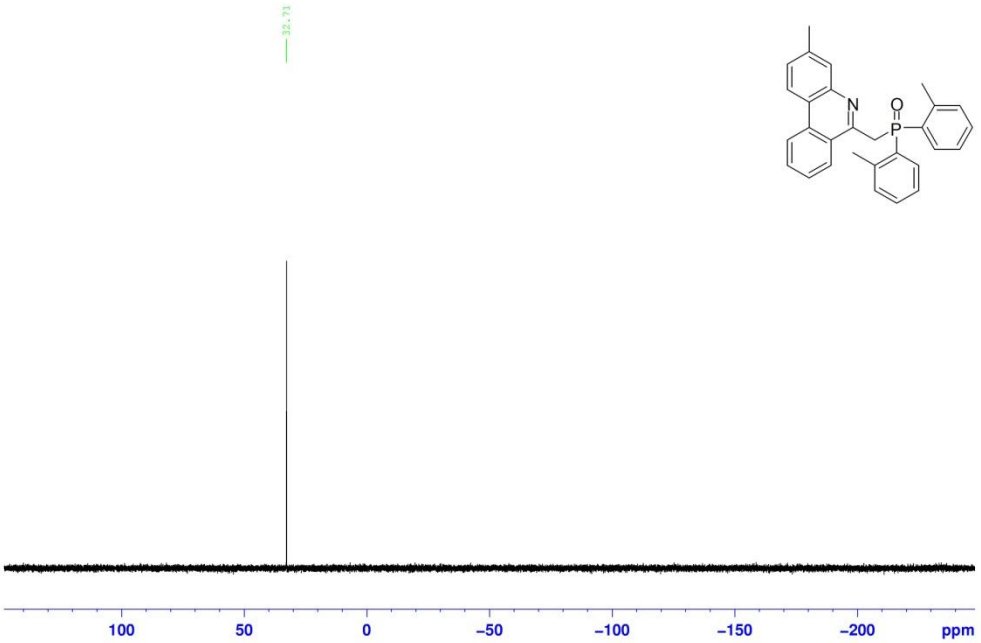

OMe
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

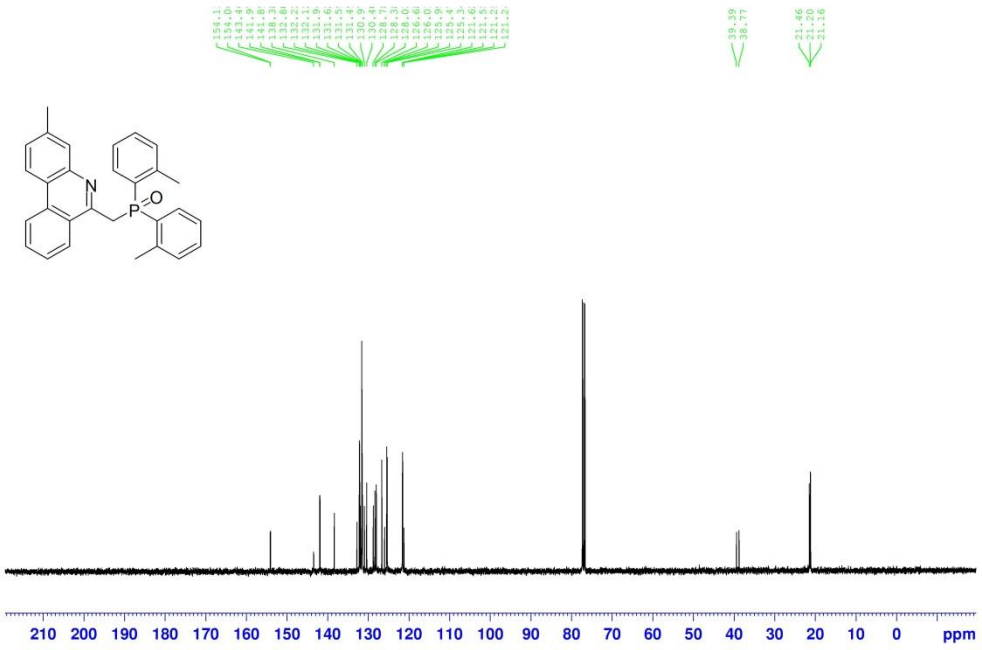

10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.03
6.08
1.09
1.10
4.09
2.00
3.01
6.02

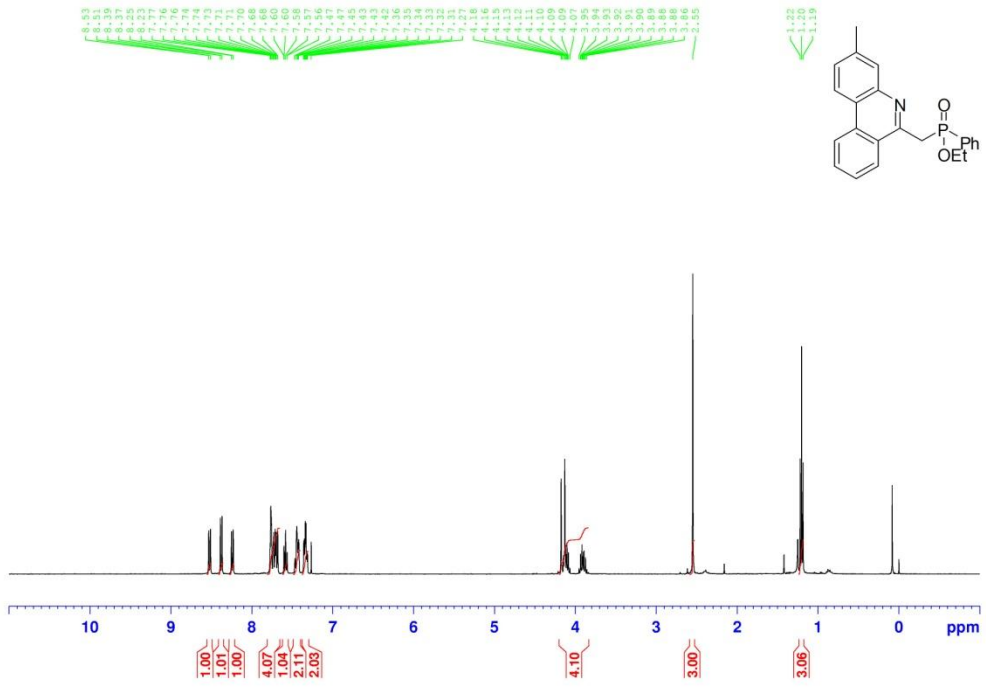

30.19
N
O
P
100
50
0
−50
−100
−150
−200
ppm

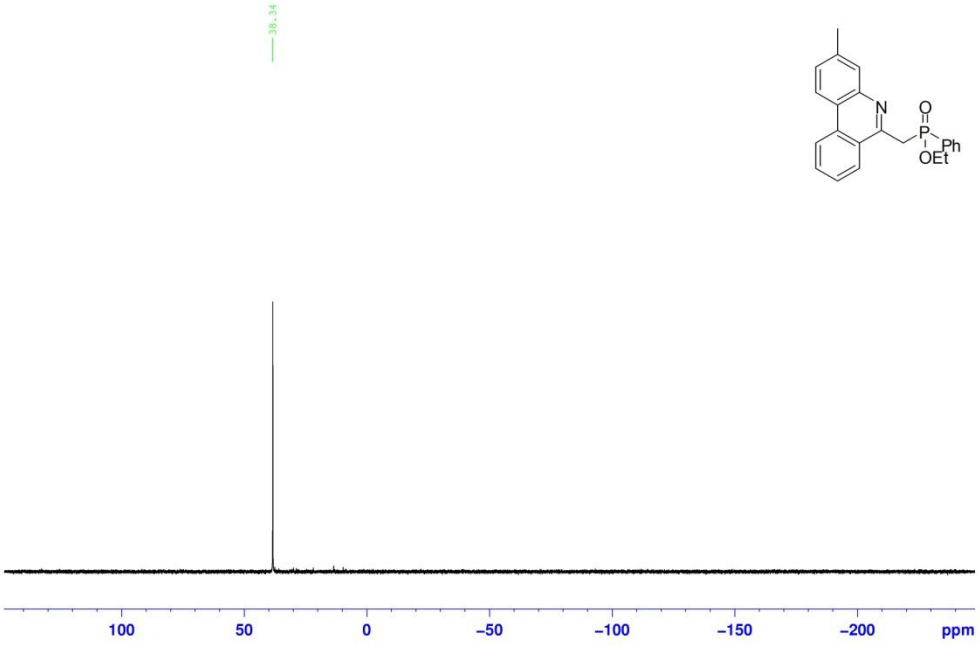

154.23
144.15
143.53
141.95
141.92
138.43
132.80
131.35
131.25
130.42
130.09
129.07
129.00
128.88
128.82
128.77
127.86
126.86
125.80
121.66
121.60
121.31
40.48
39.85
22.61
21.47
N
O
P
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

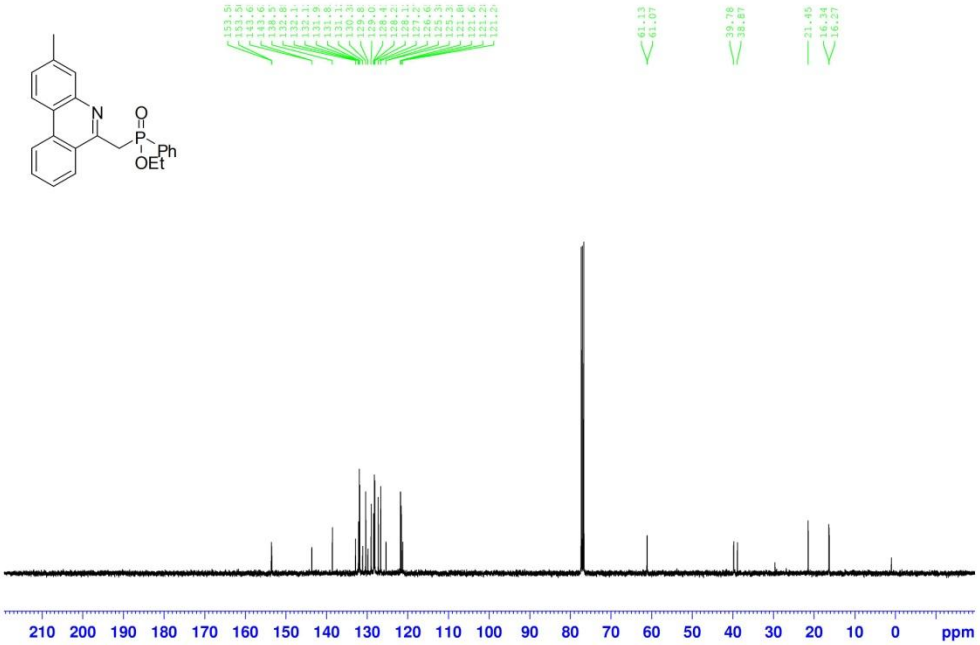

8.53
8.51
8.48
8.46
8.39
8.36
8.04
8.02
8.01
7.99
7.79
7.77
7.75
7.64
7.62
7.60
7.43
7.41
7.36
7.35
7.33
7.26
7.24
7.22
7.12
7.11
7.10
7.09
4.62
4.59
2.54
2.24
N
O
P
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.03
1.02
1.01
1.02
1.04
2.01
1.08
2.09
3.21
2.02
2.00
3.01
6.01

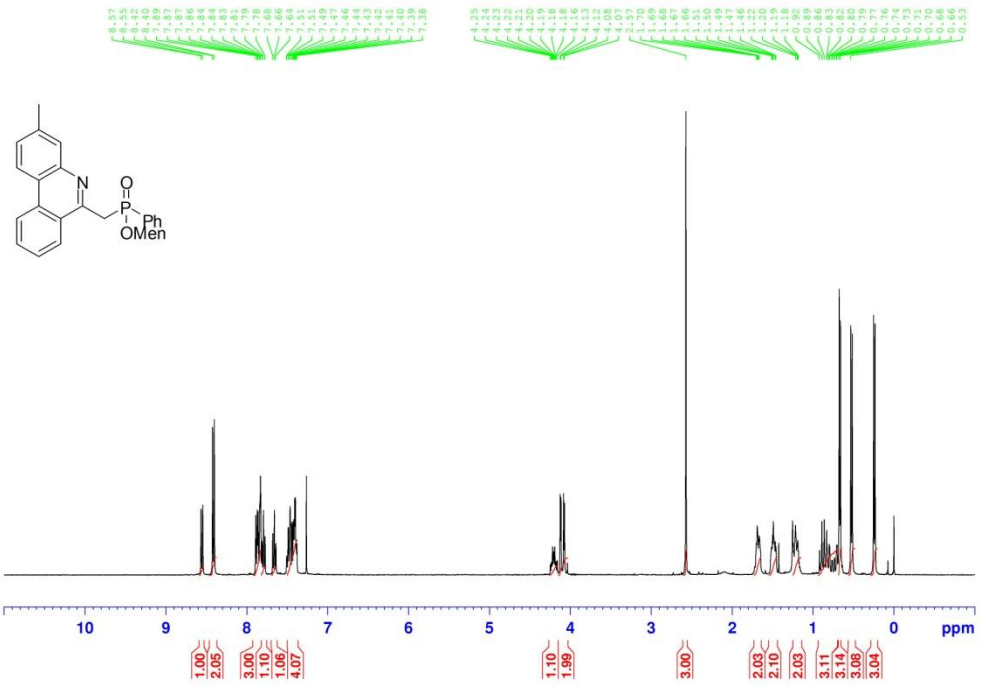

32.71
N
O
P
100
50
0
−50
−100
−150
−200
ppm

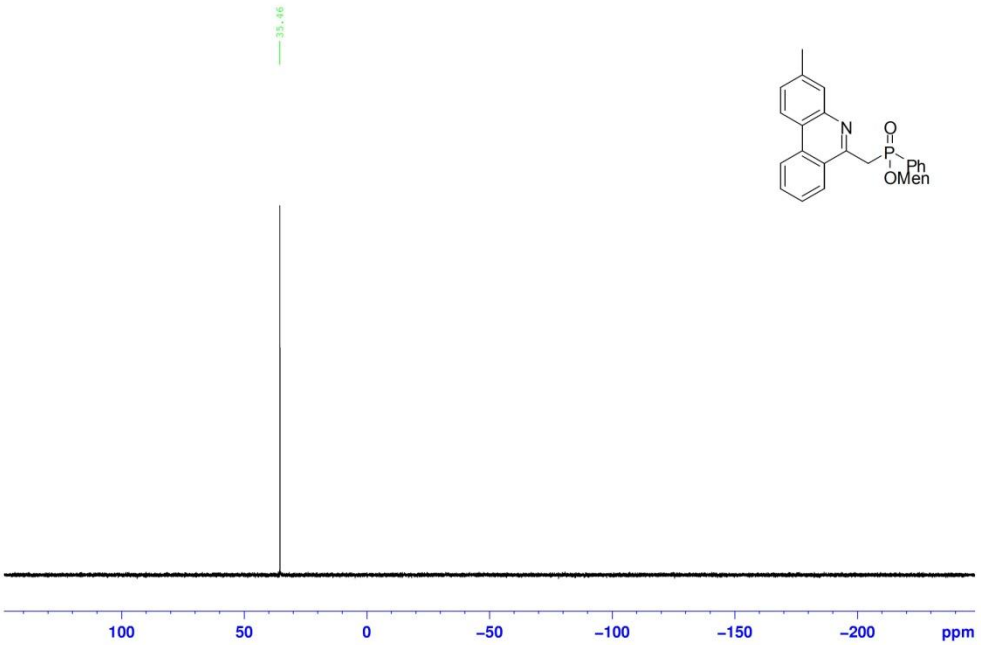

N
P
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

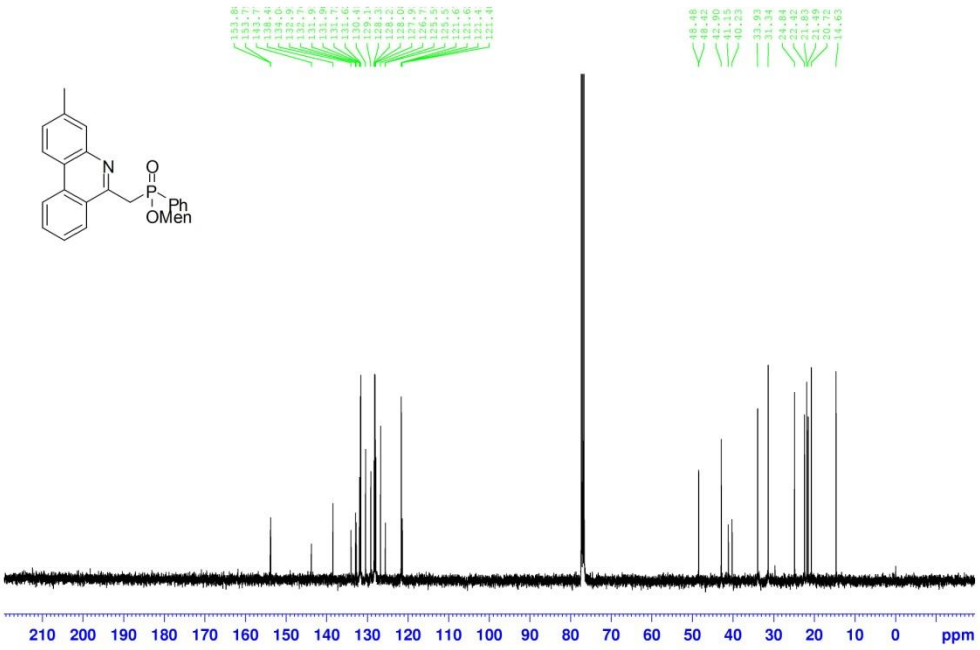

N
O
P
Ph
OEt
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.01
1.00
4.07
1.04
2.11
2.03
4.10
3.00
3.06

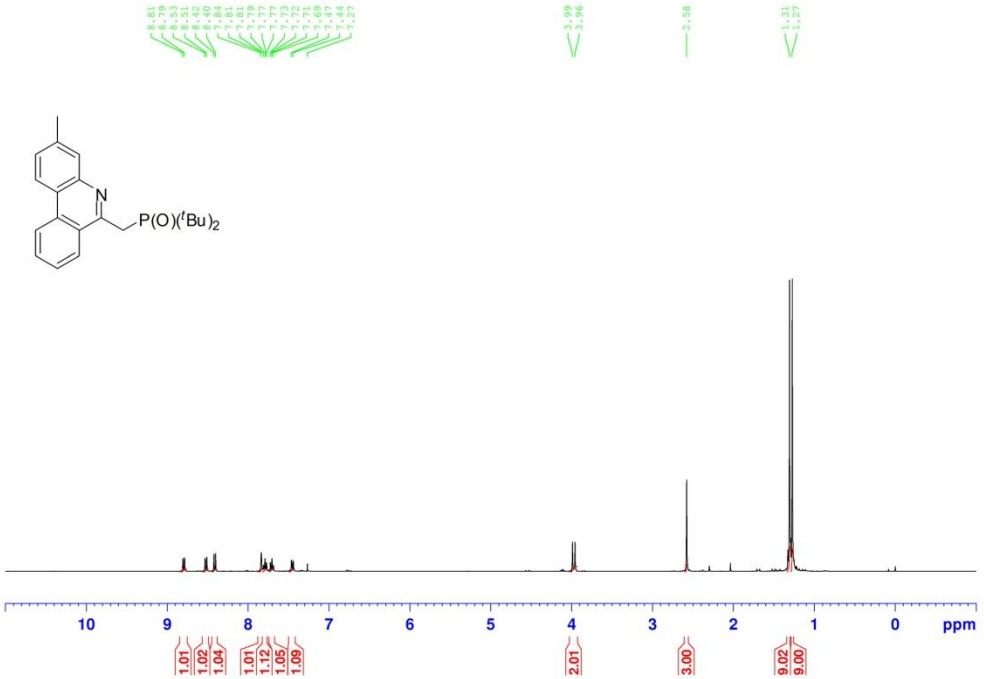

38.34
N
O
P
Ph
OEt
100
50
0
−50
−100
−150
−200
ppm

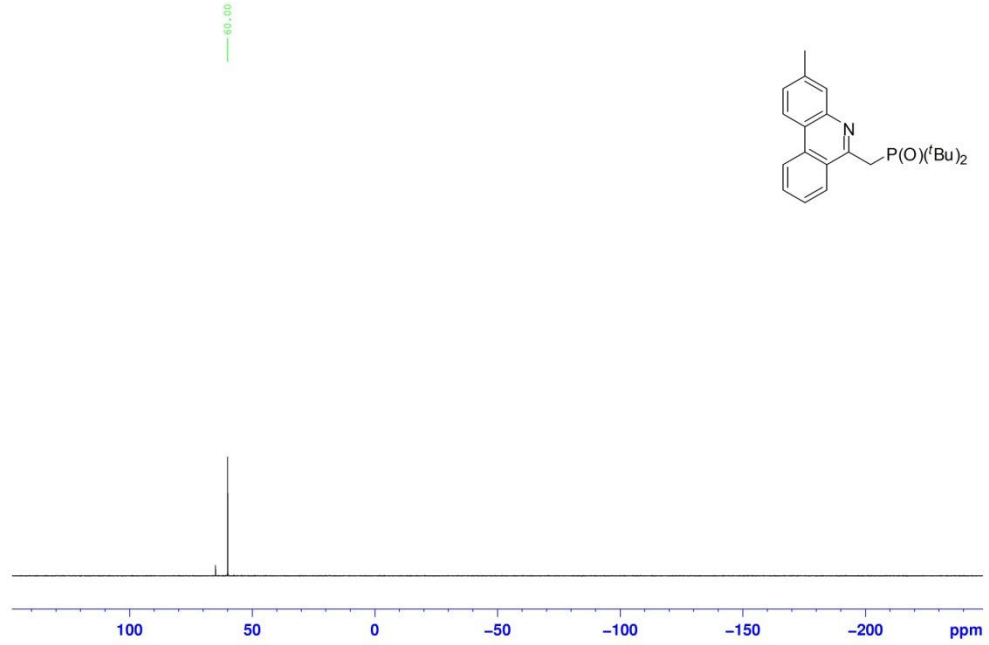

153.5
153.3
143.6
138.5
132.8
132.1
131.9
131.8
131.3
130.8
129.8
129.0
128.4
128.2
128.1
127.2
126.6
125.3
123.3
121.8
121.6
121.2
61.13
61.07
39.78
38.67
21.45
16.34
16.27
N
O
P
Ph
OEt
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

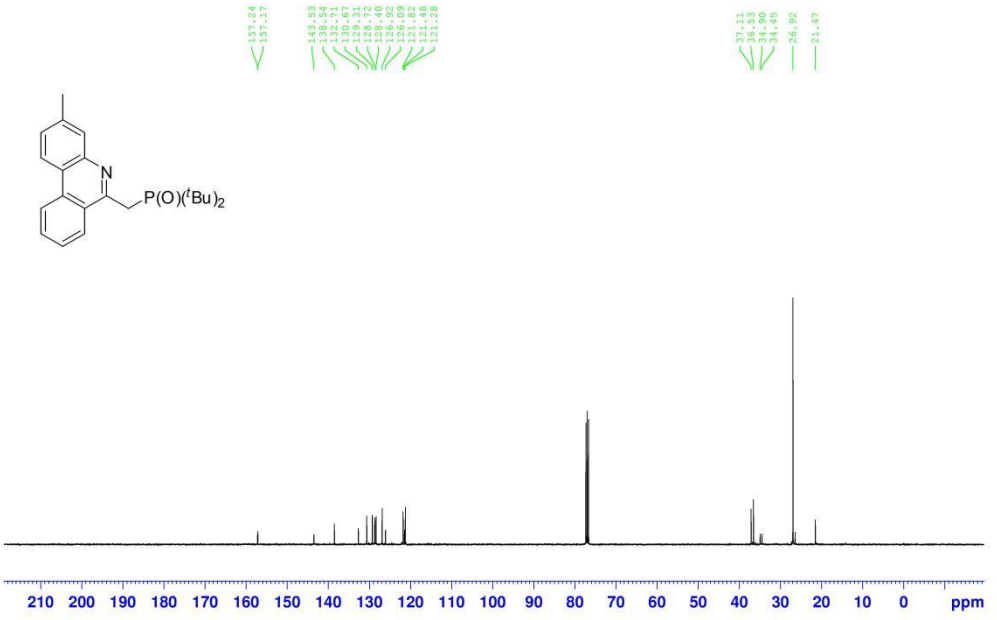

N
O
P
Ph
OMen
10
9
8
7
6
5
4
3
2
1
0
ppm


35.46
N
O
P
Ph
OMen
100
50
0
−50
−100
−150
−200
ppm

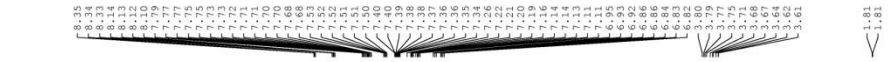

N
O
P
Ph
OMen
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

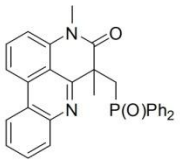

N
P(O)(tBu)2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.02
1.04
1.01
1.12
1.05
1.09
2.01
3.00
9.02
9.00

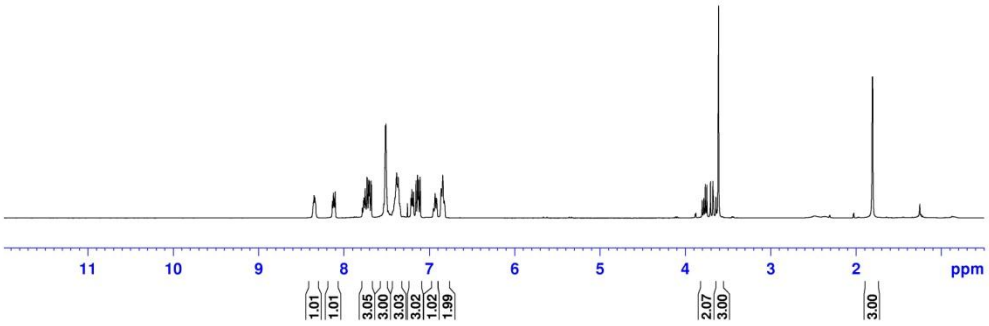

60.00
N
P(O)(tBu)2
100
50
0
−50
−100
−150
−200
ppm


157.24
157.17
149.53
138.54
132.71
130.67
129.31
128.72
128.40
126.92
126.09
121.82
121.48
121.28
37.11
36.53
34.90
34.45
26.92
21.47
N
P(O)(tBu)2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

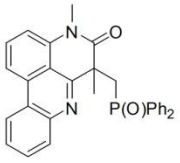
hurb-33

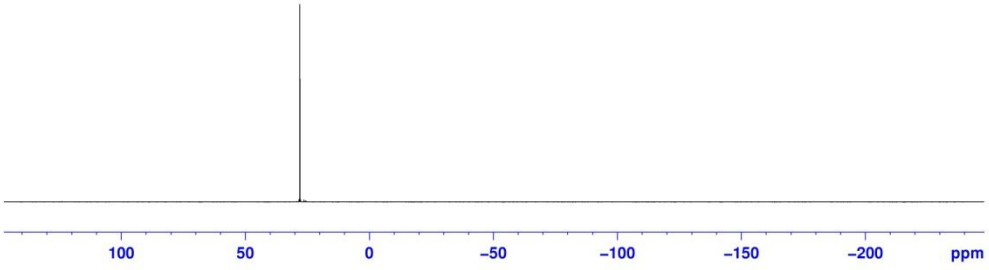




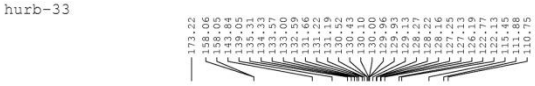


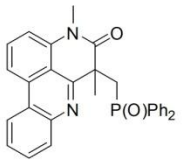
hurb-33

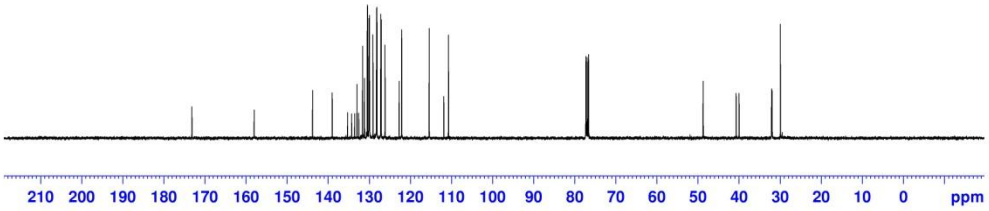




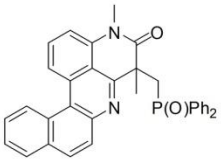
hurb-33

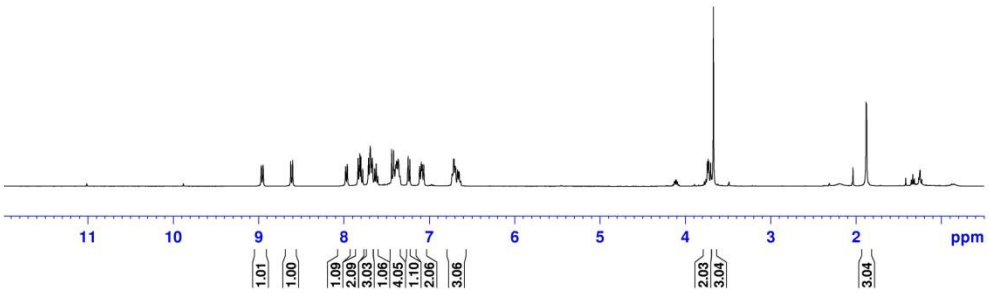




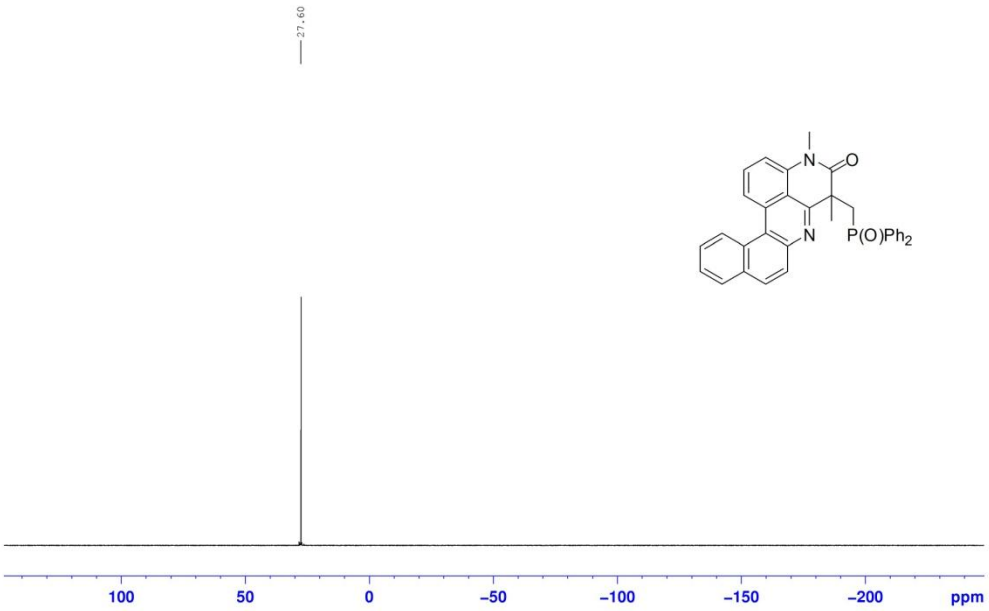


hurb-34

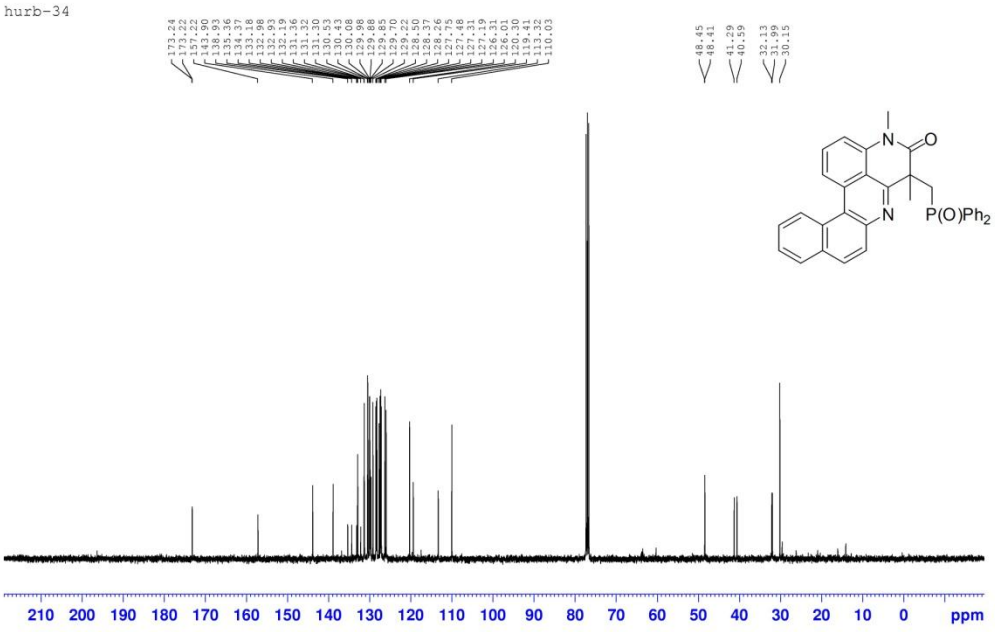


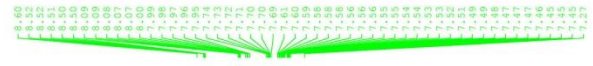


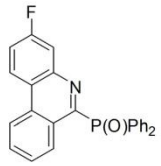
hurb-36

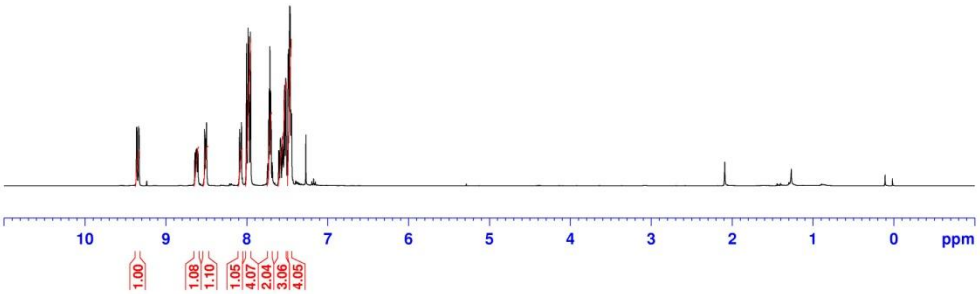


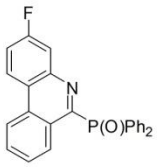
hurb-34

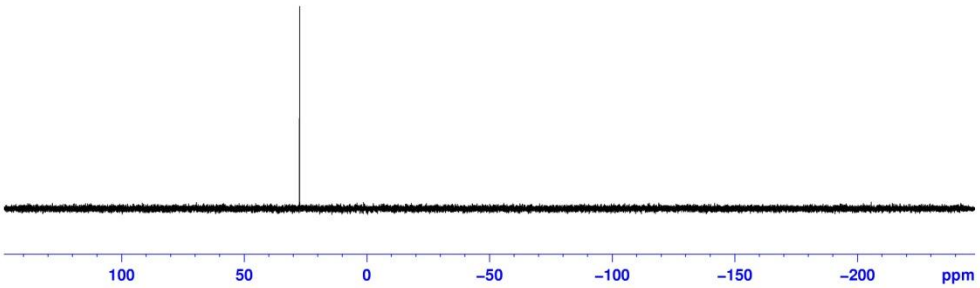


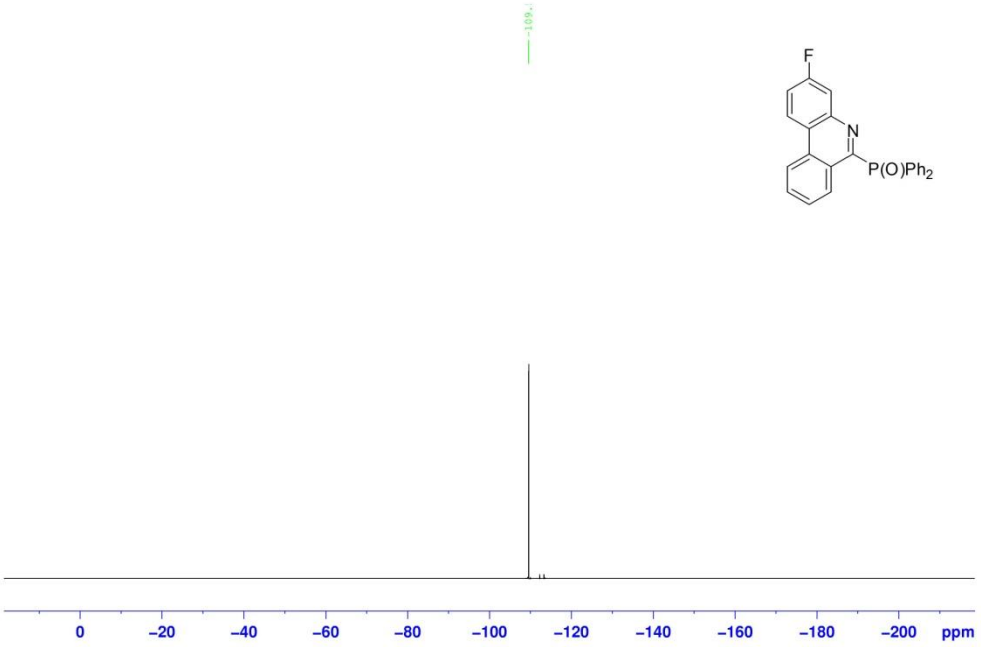


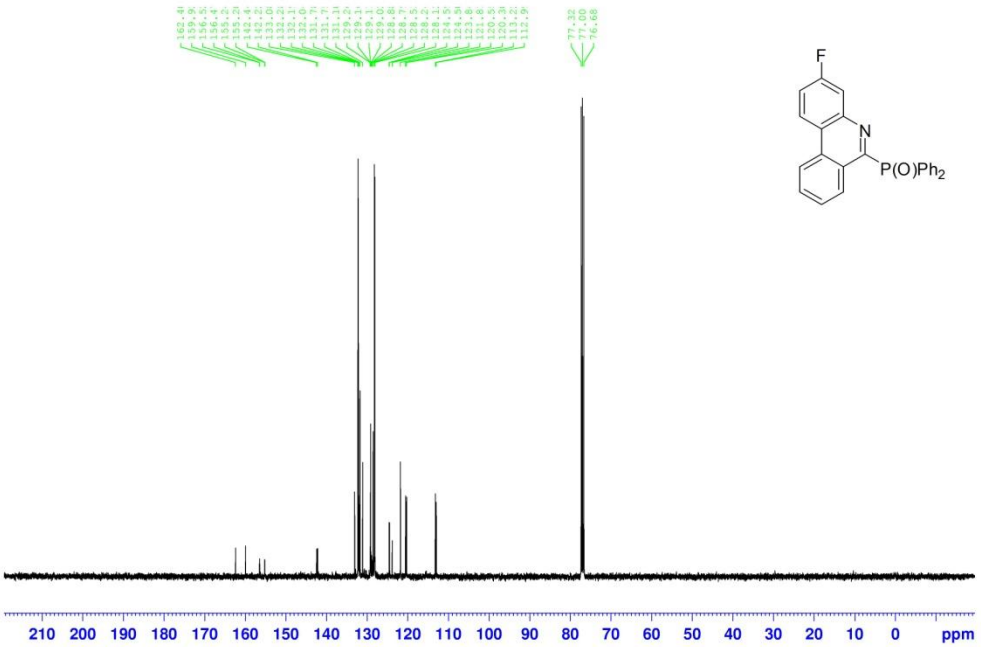

F
N
P(O)Ph2

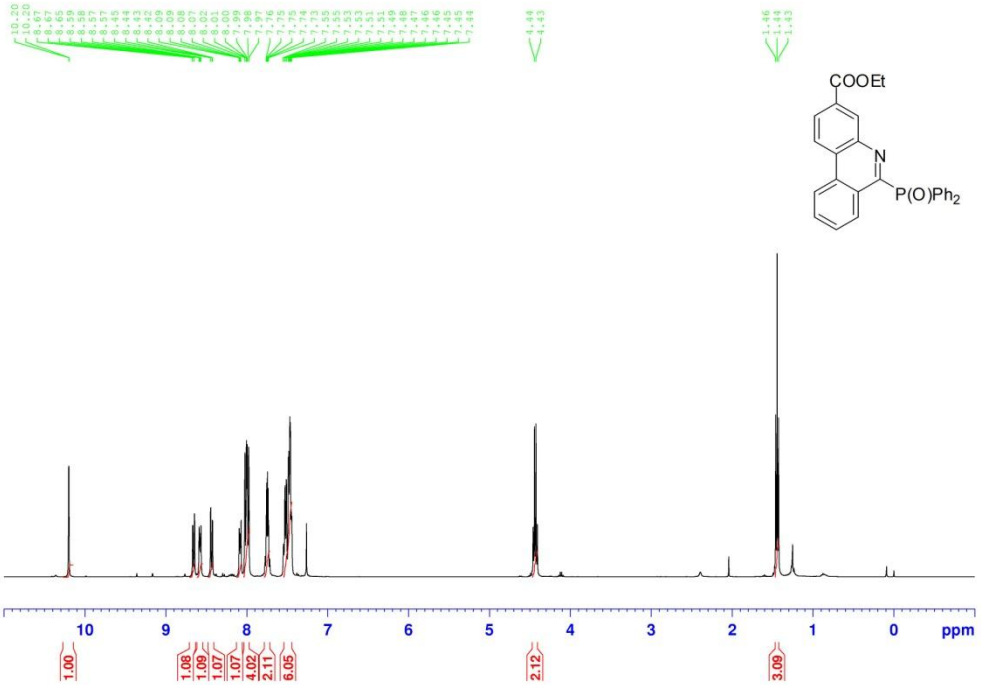

10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.08
1.10
1.05
4.07
2.04
3.06
4.05

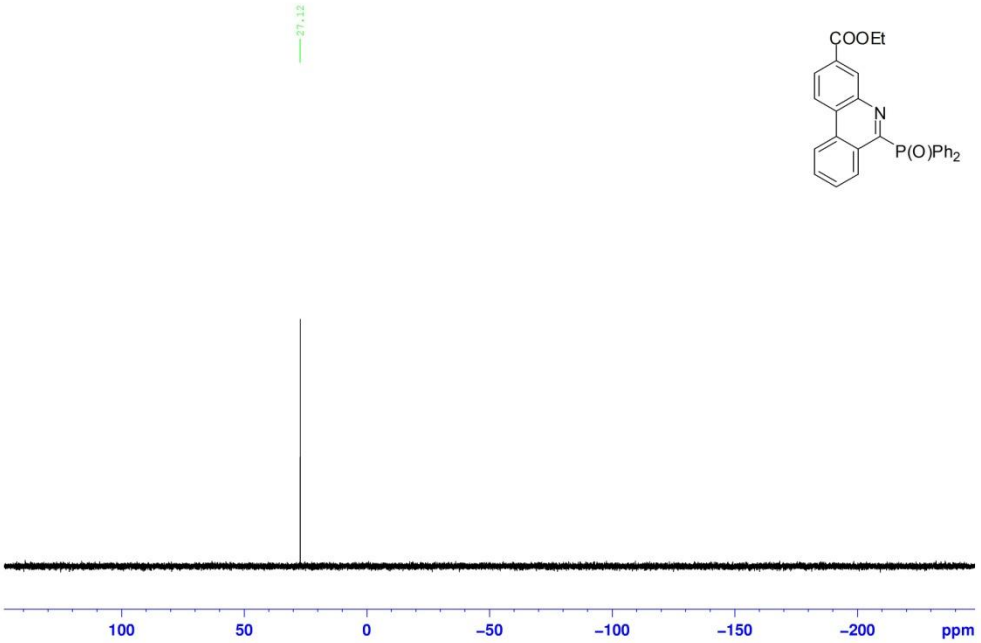

F
N
P(O)Ph2

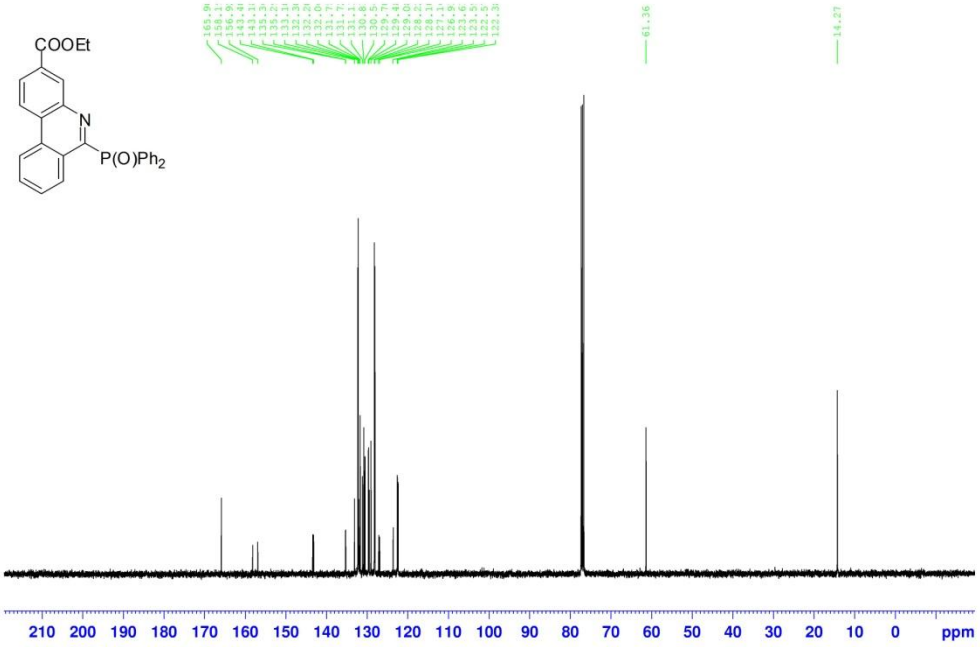

100
50
0
−50
−100
−150
−200
ppm

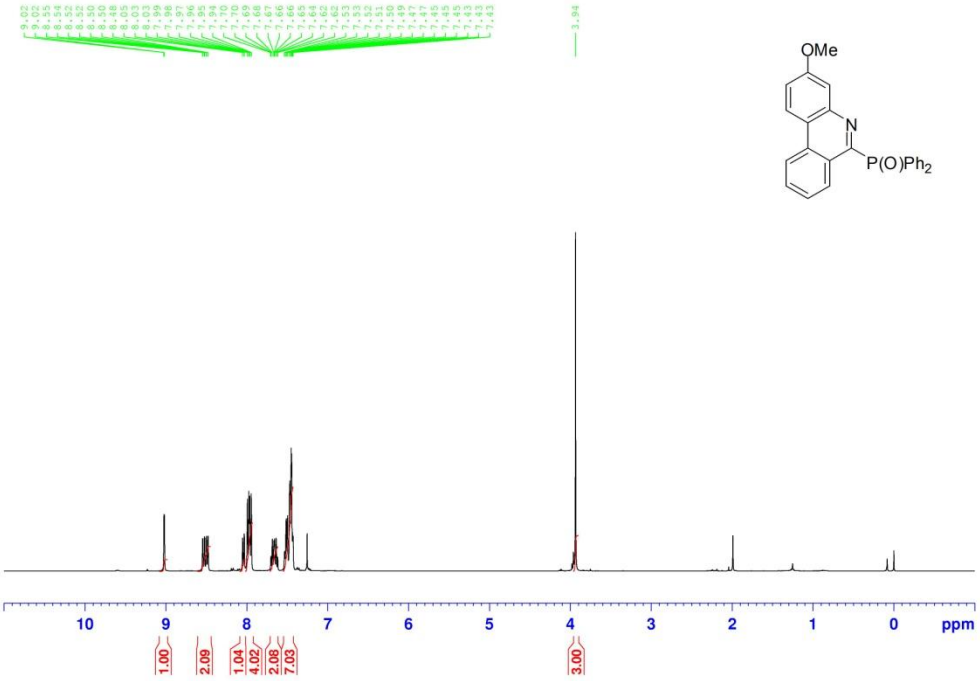

F
N
P(O)Ph2
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm

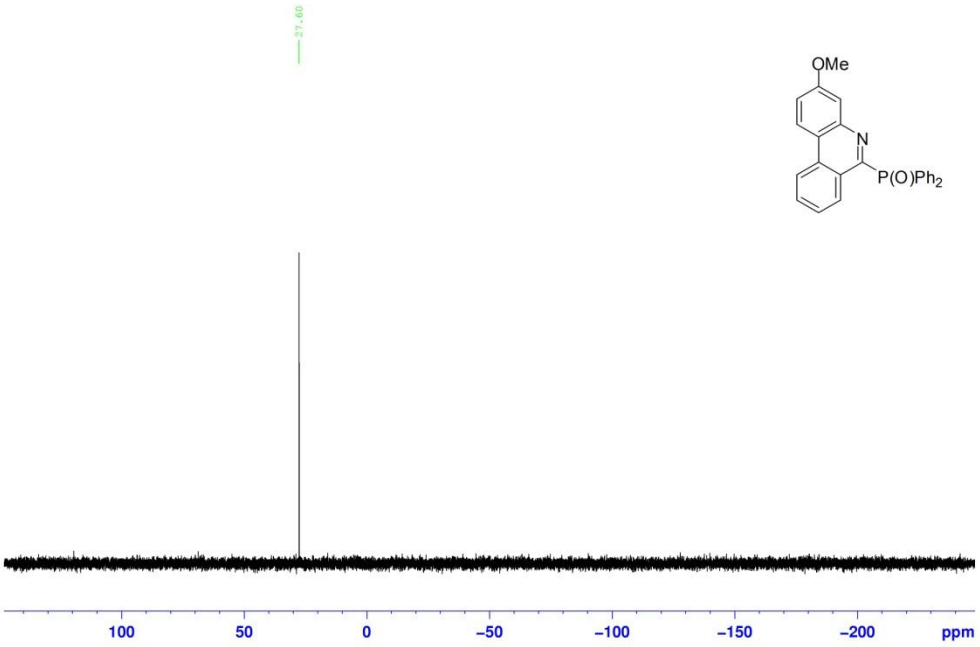

F
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

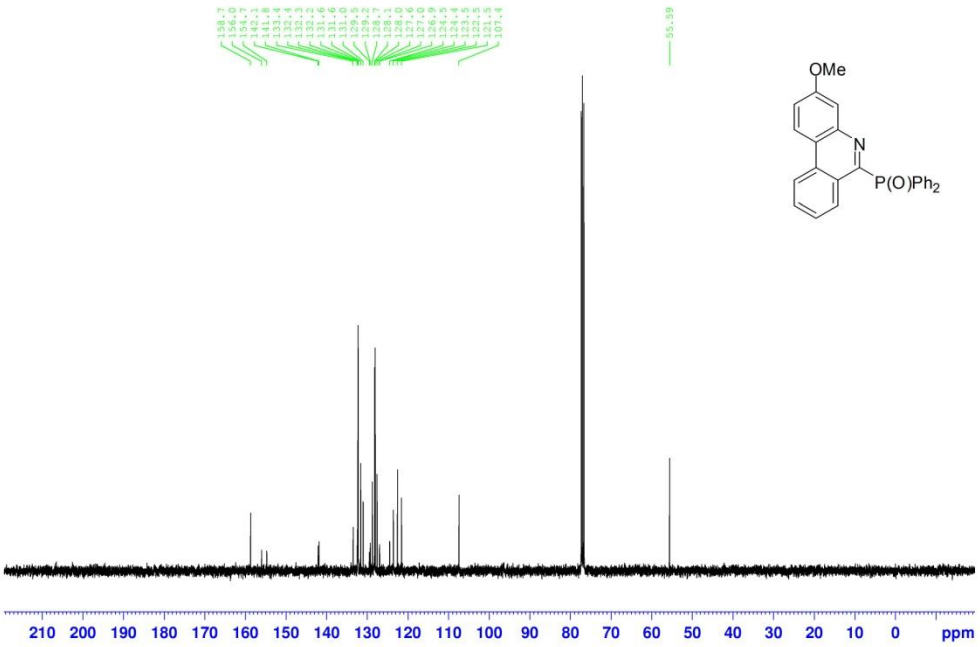

COOEt
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.08 1.09 1.07 1.07 4.02 2.11 6.05 2.12 3.09


27.12
COOEt
N
P(O)Ph2
100 50 0 −50 −100 −150 −200 ppm


COOEt
N
P(O)Ph2
61.36
14.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3.94
OMe
N
P(O)Ph2
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.09
1.04
4.02
2.08
7.03
3.00


27.60
OMe
N
P(O)Ph2
100
50
0
−50
−100
−150
−200
ppm


158.7
156.0
154.7
142.1
141.8
133.4
132.3
132.2
131.6
131.6
131.0
129.5
129.2
129.1
128.1
128.0
127.6
127.1
127.0
124.5
124.4
123.5
123.5
121.5
107.4
55.39
OMe
N
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm