SUPPORTING INFORMATION

Cobalt-catalyzed, Aminoquinoline-Directed Functionalization of Phosphinic Amide sp^2 C-H Bonds

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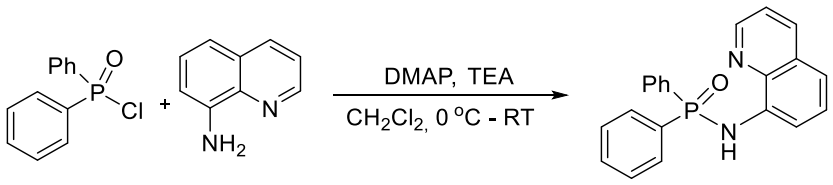
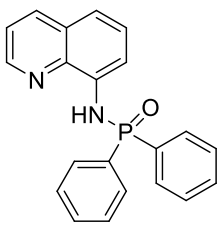
General considerations

Reactions were performed using standard glassware or were run in 6-dram vials with PTFE/Liner screw caps. Column chromatography was performed on 60 Å silica gel (Dynamic Adsorbents Inc.). The ^{1}H, ^{13}C, ^{19}F, ^{31}P, and 2D-NMR spectra were recorded on JEOL EC-400, JEOL EC-500, or JEOL EC-600 spectrometers using TMS or residual solvent peak as a reference. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent QTOF mass spectrometer at the Mass Spectrometry Facility (MSF) of the Department of Chemistry and Biochemistry of University of Texas-Austin. IR spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. All procedures were performed under ambient air unless otherwise noted. Reagents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted. Due to the complexity of C-P coupling in ^{13}C-NMR, signals were listed without analysis of coupling.

Synthesis and characterization of starting phosphinamides.



_P,P_-Diphenyl-_N_-(quinolin-8-yl)phosphinic amide (3, Table 1)



Solution of 8-aminoquinoline (3.0 g, 21 mmol), *N*,*N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), and triethylamine (3.3 mL, 24 mmol) in anhydrous CH_2Cl_2 (30 mL) was cooled to 0 °C followed by slow addition of diphenylphosphinic chloride (3.8 mL, 20 mmol) under N_2 with vigorous stirring. After addition, the solution was warmed to room temperature and stirred overnight. Reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 x 50 mL). Combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Recrystallization from hexanes/EtOAc 3:1 afforded 5.9 g (86%) of *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide as a tan solid. R_f = 0.21 (hexane/EtOAc 1:1), mp 152-154 °C (hexanes/EtOAc 3:1).

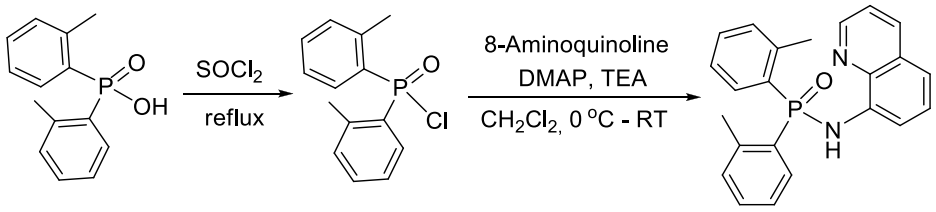
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.74 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 8.03-7.89 (m, 5H), 7.56-7.49 (m, 2H), 7.48-7.43 (m, 4H), 7.42-7.34 (m, 2H), 7.31-7.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 148.2, 138.8, 138.7, 137.8, 136.4, 132.7, 132.38, 132.36, 132.0, 131.9, 131.4, 129.0, 128.9, 128.5, 127.2, 121.8, 119.5, 113.9, 113.8.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 19.8.

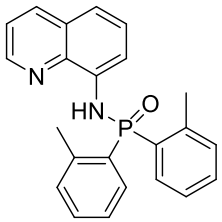
HRMS (ESI) calcd. for $C_{21}H_{17}N_2OPNa$ $[M+Na]^+$: 367.0971; found: 367.0971.

FT-IR (neat, cm^{-1}) υ 1504, 1472, 1317, 1112, 1091.



Scheme S1. Synthesis of *P*,*P*-di-*o*-tolyl-*N*-(quinolin-8-yl)phosphinic amide

***P*,*P*-Di-*o*-tolyl-*N*-(quinolin-8-yl)phosphinic amide (5, Scheme 1)**



Product was synthesized in two step procedure from the known di-o-tolylphosphinic acid[1], according to Scheme S1.

Solution of di-*o*-tolylphosphinic acid (1.35 g, 5.5 mmol) in $SOCl_2$ (5 mL) was refluxed for 3 h, then cooled to room temperature and evaporated to dryness to afford the crude phosphinic chloride.

Solution of freshly prepared phosphinic chloride in anhydrous CH_2Cl_2 (10 mL) was added dropwise to a solution of 8-aminoquinoline (833 mg, 5.78 mmol), *N*,*N*-dimethyl-4-aminopyridine (22 mg, 0.18 mmol), and triethylamine (0.9 mL, 6.6 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0 °C under N_2. The reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 4:1 to 2:1) afforded 1.37 g (67%) of *P*,*P*-di-*o*-tolyl-*N*-(quinolin-8-yl)phosphinic amide as a tan solid.

R_f = 0.39 (hexanes/EtOAc 1:1), mp 162-164 °C (Et_2O).

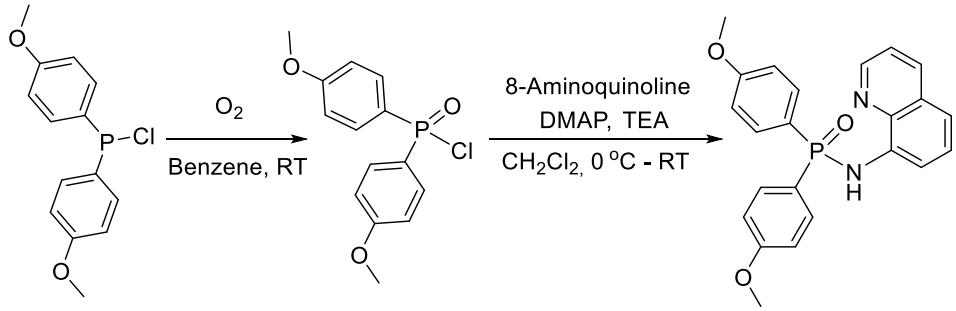
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.70 (d, *J* = 3.0 Hz, 1H), 8.07 (d, *J* = 8 Hz, 1H), 7.89 (d, *J* = 13.9 Hz, 1H), 7.70-7.65 (m, 3H), 7.42-7.35 (m, 3H), 7.29-7.26 (m, 4H), 7.19-7.16 (m, 2H), 2.63 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 148.1, 142.8, 142.7, 138.73, 138.66, 138.3, 136.5, 135.09, 135.07, 134.8, 133.3, 133.1, 132.4, 132.3, 132.2, 132.1, 131.0, 129.8, 128.6, 127.5, 125.9, 125.7, 121.8, 119.2, 113.90, 113.88, 21.9, 21.8.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 24.9.

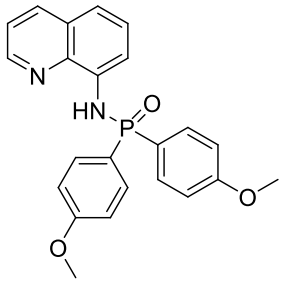
HRMS (ESI) calcd. for $C_{23}H_{21}N_2OPNa$ $[M+Na]^+$: 395.1284; found: 395.1284.

FT-IR (neat, cm^{-1}) υ 1505, 1474, 1448, 1313, 1208, 1133.



Scheme S2. *P,P*-Bis(4-methoxyphenyl)-*N*-(quinolin-8-yl)phosphinic amide

***P,P*-Bis(4-methoxyphenyl)-*N*-(quinolin-8-yl)phosphinic amide (7, Scheme 1)**



Product was synthesized in two step procedure from chlorobis(4-methoxyphenyl)phosphine[2] according to Scheme S2.

Inside glovebox, a 25 mL Schlenk flask was charged with chloro-bis-(4-methoxyphenyl)phosphine (500 mg, 1.78 mmol) and anhydrous benzene (2.5 mL). The mixture was stirred at room temperature for 5 h under oxygen stream. After completion, the reaction mixture was evaporated to dryness and crude bis(4-methoxyphenyl)phosphinic chloride was used without further purification.

Solution of freshly prepared bis(4-methoxyphenyl)phosphinic chloride in anhydrous CH_2Cl_2 (5 mL) was added dropwise to a solution of 8-aminoquinoline (270 mg, 1.87 mmol), *N,N*-dimethyl-4-aminopyridine (11 mg, 89 μmol), and triethylamine (0.37 mL, 2.67 mmol) in anhydrous CH_2Cl_2 (2.5 mL) at 0 °C under N_2. The mixture was warmed up to room temperature and stirred overnight. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). Combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 1:1 to 1:3, then EtOAc) afforded 243 mg (34% over 2 steps) of *P,P*-bis(4-methoxyphenyl)-*N*-(quinoline-8-yl)phosphinic amide as a white solid.

R_f = 0.19 (hexane/EtOAc 1:4), mp 182-184 °C (Et_2O).

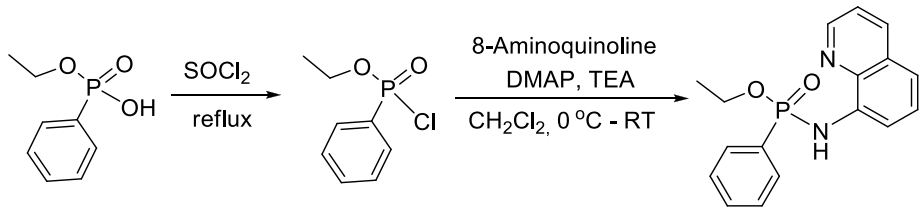
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.68 (d, *J* = 3.1 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.77 (m, 5H), 7.39 – 7.29 (m, 2H), 7.23 (s, 2H), 6.96 – 6.84 (m, 4H), 3.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 162.7, 148.0, 138.83, 138.76, 138.1, 136.4, 133.9, 133.8, 128.5, 127.3, 124.4, 123.1, 121.7, 119.2, 114.5, 114.3, 113.80, 113.76, 55.4.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 20.0.

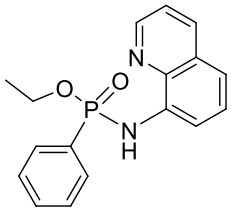
HRMS (ESI) calcd. For $C_{23}H_{21}N_2O_3PNa$ $[M+Na]^+$: 427.1182; found: 427.1182.

FT-IR (neat, cm^{-1}) υ 1566, 1500, 1257, 1209, 1124, 1022.



Scheme S3. Synthesis of *N*-(quinolin-8-yl)phenylphosphonamide monoethyl ester

_N_-(Quinolin-8-yl)phenylphosphonamide monoethyl ester (9, Scheme 1)



Product was synthesized in two step procedure from the known phenylphosphonic acid monoethyl ester[3] according to Scheme S3.

Solution of phenylphosphinic acid monoethyl ester (1.92 g, 10.3 mmol) in $SOCl_2$ (5 mL) was refluxed for 2 h, then cooled to room temperature and evaporated to dryness to afford the crude phenylphosphinic chloride monoethyl ester.

Solution of freshly prepared phenylphosphinic chloride monoethyl ester in anhydrous CH_2Cl_2 (5 mL) was added dropwise to a solution of 8-aminoquinoline (1.51 g, 10.5 mmol), *N*,*N*-dimethyl-4-aminopyridine (40 mg, 0.325 mmol), and triethylamine (1.67 mL, 12 mmol) in anhydrous CH_2Cl_2 (20 mL) at 0 °C under N_2. The reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). Combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 4:1 to 2:3) afforded 1.14 g (36%, over 2 steps) of *N*-(quinolin-8-yl)phenylphosphonamide monoethyl ester as a yellow oil.

R_f = 0.20 (hexane/EtOAc 1:1).

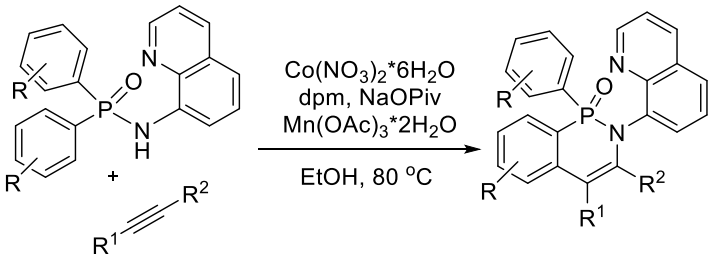
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.99 – 7.86 (m, 3H), 7.52 – 7.44 (m, 1H), 7.41 (dq, *J* = 5.0, 3.5 Hz, 4H), 7.35 – 7.26 (m, 2H), 4.35 – 4.27 (m, 1H), 4.27 – 4.19 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 148.2, 138.57, 138.50, 137.5, 136.3, 132.31, 132.29, 131.65, 131.57, 131.0, 129.6, 128.7, 128.58, 128.47, 127.2, 121.8, 119.3, 112.5, 61.46, 61.41, 16.53, 16.48.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 17.8.

Cobalt-catalyzed sp^2 C-H functionalization

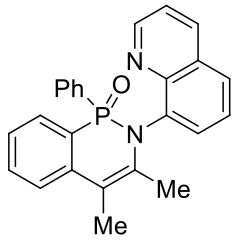
1. Cobalt-catalyzed coupling between phosphinic amides and alkynes



General procedure.

A 6-dram vial (w/polyseal screw cap) equipped with a magnetic stir bar was charged with phosphinic amide (0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2*6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), and EtOH (5 mL). Reaction mixture was stirred at room temperature for 5 min, then $Mn(OAc)_3*2H_2O$ (134 mg, 0.5 mmol, 1 equiv) and alkyne (0.6 mmol, 1.2 equiv) was added at once. The reaction was heated at 80 °C and monitored by TLC (vial opened after 2 h and 16 h to determine the completion time). Opening of the vial allows for introduction of oxygen from air. After completion, the mixture was cooled to room temperature and diluted with EtOH (5 mL). Solvent was evaporated, and Na K tartrate (10 mL, 1 M aqueous solution) was added to the residue followed by extraction with CH_2Cl_2 (3 x 20 mL). Combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Purification by column chromatography on silica gel using appropriate eluent followed by concentrating the fraction of product and drying the residue under vacuum yielded pure product.

***N*-(Quinolin-8-yl)-3,4-dimethyl-1-phenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 1)**



P,P-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1 mmol, 2 equiv), $Co(NO_3)_2*6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3*2H_2O$ (134 mg, 0.5 mmol, 1 equiv), 2-butyne (47 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 155 mg (78%) of a beige solid was obtained.

Large scale: A 75-mL pressure tube was charged with *P,P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (1.03 g, 3.0 mmol), NaOPiv (744 mg, 6.0 mmol, 2.0 equiv), $Co(NO_3)_2*6H_2O$ (175 mg, 0.6 mmol, 20 mol%), dipivaloylmethane (0.31 mL, 1.5 mmol, 50 mol%), and EtOH (30 mL). Reaction mixture was stirred at room temperature for 5 min, then $Mn(OAc)_3*2H_2O$ (804 mg, 3 mmol, 1 equiv) and 2-butyne (0.28 mL, 3.6 mmol, 1.2 equiv) was added at once. The reaction was heated at 80 °C and monitored by TLC after 16 h and 24 h to determine the completion time. After 24 h, the mixture was cooled to room temperature and diluted with EtOH (15 mL). Solvent was evaporated, and potassium sodium tartrate (50 mL, 1M aqueous solution) was added to the residue followed by extraction with CH_2Cl_2 (3 x 50 mL). Combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 1:1 to 1:2) yielded 935 mg (79%) of a beige solid.

R_f = 0.15 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (d, *J* = 7.3 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.63 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.60-7.53 (m, 4H), 7.38-7.23 (m, 3H, overlaps with chloroform signal), 7.16 (td, *J* = 7.3, 2.4 Hz, 1H), 7.05 (t, *J* = 7.1 Hz, 1H), 6.90 (td, *J* = 7.6, 3.3 Hz, 2H), 2.30 (s, 3H), 1.85 (s, 3H).

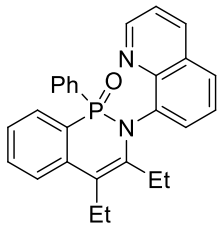
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.3, 145.2, 145.2, 139.72, 139.69, 137.7, 136.9, 136.0, 133.4, 133.3, 131.5, 131.3, 131.1, 131.0, 130.7, 130.6, 129.9, 128.7, 127.8, 127.0, 126.9, 126.0, 124.8, 124.7, 124.4, 123.7, 123.6, 123.3, 121.3, 107.0, 106.9, 19.3, 19.2, 16.1.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 16.7.

HRMS (ESI) calcd. For $C_{25}H_{21}N_2OPNa$ $[M+Na]^+$: 419.1284; found: 419.1285.

FT-IR (neat, cm^{-1}) υ 1202, 1184, 1134.

***N*-(Quinolin-8-yl)-3,4-diethyl-1-phenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 2)**



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 3-hexyne (68 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 2:1 to 1:1), 184 mg (87%) of a brownish oil that slowly solidifies was obtained. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond.

R_f = 0.18 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.75 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.2, 4.9 Hz, 1H), 7.60- 7.47 (m, 4H), 7.34 – 7.27 (m, 2H), 7.25 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.14 (td, *J* = 7.3, 2.6 Hz, 1H), 7.04 (td, *J* = 7.4, 1.1 Hz, 1H), 6.89 (td, *J* = 7.7, 3.4 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 2.47 (ddt, *J* = 13.2, 7.4, 6.6 Hz, 1H), 1.79 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.30 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

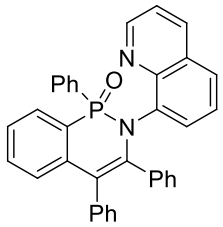
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.2, 145.34, 145.31, 142.3, 139.1, 139.0, 137.4, 135.9, 133.4, 133.2, 131.44, 131.35, 131.3, 131.2, 130.9, 130.8, 130.6, 130.0, 128.6, 127.5, 127.0, 126.8, 125.8, 125.4, 125.0, 124.8, 124.1, 123.6, 123.5, 121.3, 114.0, 113.9, 24.9, 22.5, 15.1, 13.4.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 16.6.

HRMS (ESI) calcd. For $C_{27}H_{25}N_2OPNa$ $[M+Na]^+$: 447.1597; found: 447.1597.

FT-IR (neat, cm^{-1}) υ 1214, 1195, 1175, 1130.

***N*-(Quinolin-8-yl)-1,3,4-triphenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 3)**



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3.2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), diphenylacetylene (107 mg, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 203 mg (78%) of a brownish oil that slowly solidifies was obtained. Product exists as a 15:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond.

R_f = 0.24 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.08 (d, *J* = 7.3 Hz, 1H), 7.82-7.70 (m, 2H), 7.65 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.47 (dd, *J* = 14.4, 7.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31-7.26 (m, 1H), 7.23-7.09 (m, 8H), 7.05 (ddd, *J* = 7.4, 5.2, 4.3 Hz, 2H), 7.00-6.90 (m, 4H), 6.54-6.47 (m, 3H).

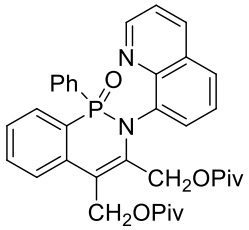
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.4, 144.5, 142.6, 139.4, 139.3, 138.8, 137.7, 136.70, 136.66, 135.6, 133.6, 133.5, 132.5, 132.3, 131.6, 131.51, 131.46, 131.1, 131.0, 130.8, 129.7, 128.2, 127.8, 127.5, 127.1, 127.0, 126.6, 126.5, 126.4, 125.9, 125.8, 125.7, 125.5, 124.5, 123.8, 123.2, 122.2, 121.1, 119.2, 117.8, 117.7.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 16.9.

HRMS (ESI) calcd. For $C_{35}H_{25}N_2OPNa$ $[M+Na]^+$: 543.1597; found: 543.1594.

FT-IR (neat, cm^{-1}) υ 1469, 1273, 1216, 1107, 1097.

_N_-(Quinolin-8-yl)-3,4-di-(*tert*-butylcarbonyloxy)methyl-1-phenyl-1,2-dihydrobenzo[*c*][1,2]aza-phosphinine 1-oxide (Table 2, Entry 4)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 1,4-di-*tert*-butylcarbonyloxy-2-butyne (153 mg, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 2:3), 183 mg (61%) of a colorless oil that slowly solidifies was obtained Product exists as a 9:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond.

R_f = 0.24 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.67 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.73 (dd, *J* = 8.2, 4.9 Hz, 1H), 7.60-7.45 (m, 4H), 7.36 (dd, *J* = 10.3, 3.9 Hz, 1H), 7.28 (ddd, *J* = 12.4, 11.9, 6.0 Hz, 4H), 7.04 (td, *J* = 7.6, 0.9 Hz, 1H), 6.88 (td, *J* = 7.7, 3.5 Hz, 2H), 5.45 (d, *J* = 13.2 Hz, 1H), 5.30 (d, *J* = 13.1 Hz, 1H), 5.03 (dd, *J* = 13.5, 1.7 Hz, 1H), 4.32 (d, *J* = 13.6 Hz, 1H), 1.21 (s, 9H), 1.03 (s, 9H).

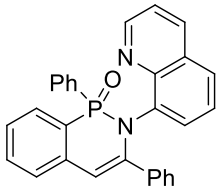
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 178.6, 177.6, 150.4, 144.7, 140.3, 137.8, 137.7, 136.1, 135.7, 133.3, 133.2, 131.9, 131.7, 131.6, 131.0 130.9, 130.3, 129.2, 128.60, 128.55, 127.1, 127.0, 126.7, 126.5, 125.8, 125.5, 124.5, 124.4, 124.3, 121.6, 112.0, 111.9, 61.9, 61.3, 39.0, 38.7, 27.3, 27.2.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 16.9.

HRMS (ESI) calcd. For $C_{35}H_{37}N_2O_5PNa$ $[M+Na]^+$: 619.2332; found: 619.2335.

FT-IR (neat, cm^{-1}) υ 1722, 1212, 1134, 1114.

_N_-(Quinolin-8-yl)-1,3-diphenyl-1,2-dihydrobenzo[_c_][1,2]azaphosphinine 1-oxide (Table 2, Entry 5)



_P,P_-Diphenyl-_N_-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), phenylacetylene (66 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 180 mg (81%) of a colorless oil that slowly solidifies was obtained. Product was isolated as a 9:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.2 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.72 (dd, _J_ = 4.1, 1.4 Hz, 1H), 8.14-8.10 (m, 1H), 7.76-7.65 (m, 3H), 7.56-7.51 (m, 1H), 7.49-7.40 (m, 2H), 7.35 (dd, _J_ = 6.8, 2.9 Hz, 3H), 7.27-7.21 (m, 2H, overlapped with chloroform), 7.12 (ddd, _J_ = 15.2, 8.4, 4.4 Hz, 2H), 6.97 (td, _J_ = 7.6, 3.3 Hz, 2H), 6.90 (dd, _J_ = 7.1, 2.9 Hz, 3H), 6.32 (d, _J_ = 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.1, 149.4, 145.3, 144.01, 143.99, 138.44, 138.41, 138.1, 138.0, 137.78, 137.76, 135.5, 133.1, 133.0, 131.8, 131.5, 131.0, 130.9, 130.43, 130.38, 129.0, 128.4, 128.2, 127.7, 127.5, 127.4, 127.2, 127.1, 127.0, 126.8, 126.7, 126.1, 125.9, 125.5, 124.0, 123.0, 121.1, 107.72, 107.66.

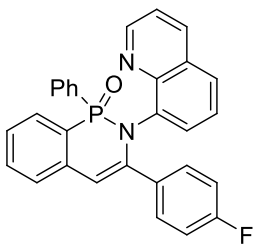
^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 19.4.

HRMS (ESI) calcd. For $C_{29}H_{21}N_2OPNa$ $[M+Na]^+$: 467.1284; found: 467.1285.

FT-IR (neat, cm^{-1}) υ 1467, 1198, 1177, 1114.

Repeating reaction on the same scale: after column chromatography (gradient hexanes/EtOAc 1:1 to EtOAc/MeOH 10:1) 222 mg (>99%) of a product was obtained.

_N_-(Quinolin-8-yl)-1-phenyl-3-(4-fluorophenyl)-1,2-dihydrobenzo[_c_][1,2]azaphosphinine 1-oxide (Table 2, Entry 6)



_P,P_-Diphenyl-_N_-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 4-fluorophenylacetylene (72 mg, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 185 mg (80%) of a colorless oil that slowly solidifies was

obtained. Product was isolated as a 9:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.2 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.70 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.72 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69-7.63 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46-7.39 (m, 2H), 7.36-7.29 (m, 3H), 7.25-7.18 (m, 2H), 7.11 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.06 (d, *J* = 6.2 Hz, 1H), 6.94 (td, *J* = 7.7, 3.4 Hz, 2H), 6.57 (t, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 1.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, couplings not resolved) δ 162.9, 160.9, 149.4, 144.2, 143.9, 138.0, 137.9, 137.6, 135.60, 134.6, 133.1, 133.0, 131.9, 131.6, 131.4, 131.0, 130.9, 130.8, 130.7, 130.3, 128.5, 127.5, 127.2, 127.1, 126.8, 126.7, 126.1, 126.0, 125.5, 124.1, 123.1, 121.2, 114.1, 113.9, 107.6, 107.5.

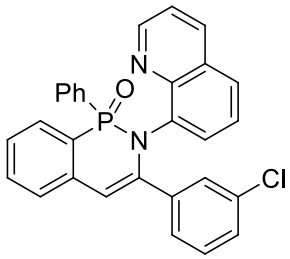
^{19}F NMR (471 MHz, $CDCl_3$, ppm) δ -113.9 (tt, *J* = 8.8, 5.4 Hz).

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 19.4.

HRMS (ESI) calcd. For $C_{29}H_{20}FN_2OPNa$ $[M+Na]^+$: 485.1189; found: 485.1190.

FT-IR (neat, cm^{-1}) υ 1212, 1201, 1116.

_N_-(Quinolin-8-yl)-1-phenyl-3-(3-chlorophenyl)-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 7)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 3-chlorophenylacetylene (74 μL, 0.6 mmol), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 200 mg (84%) of a colorless oil that slowly solidifies was obtained. Product was isolated as a 9:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.23 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.71 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.69-7.62 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25-7.19 (m, 3H), 7.12 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.08 (td, *J* = 7.5, 0.9 Hz, 1H), 6.95 (td, *J* = 7.7, 3.5 Hz, 2H), 6.85-6.81 (m, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 1.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.4, 143.8, 140.3, 140.2, 137.73, 137.69, 137.5, 135.6, 133.1, 133.0, 132.9, 131.9, 131.6, 131.2, 131.0, 130.9, 130.2,

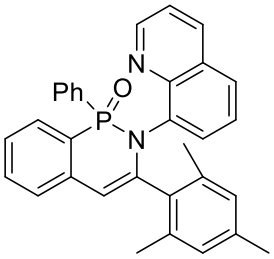
129.1, 128.5, 128.2, 128.1, 127.54, 127.53, 127.3, 127.2, 127.1, 126.9, 126.8, 126.3, 126.2, 125.6, 124.3, 123.2, 121.3, 108.1, 108.0.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 19.2.

HRMS (ESI) calcd. For $C_{29}H_{20}ClN_2OPNa$ $[M+Na]^+$: 501.0894; found: 501.0892.

FT-IR (neat, cm^{-1}) υ 1471, 1352, 1212, 1203, 1112.

_N_-(Quinolin-8-yl)-1-phenyl-3-(1,3,5-trimethylphenyl)-1,2-dihydrobenzo[_c_][1,2]azaphosphinine 1-oxide (Table 2, Entry 8)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (344 mg, 1.0 mmol), NaOPiv (248 mg, 2.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (58 mg, 0.2 mmol, 20 mol%), dipivaloylmethane (104 μL, 0.5 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (268 mg, 1.0 mmol, 1.0 equiv), 2-ethynyl-1,3,5-trimethylbenzene (188 μL, 1.2 mmol, 1.2 equiv), EtOH (10 mL), 80 °C, 16 h. Reaction was carried out in a 8-dram vial. After column chromatography (gradient hexanes/EtOAc from 2:1 to 3:2), 117 mg (24%) of a colorless oil that slowly solidifies was obtained. Product was isolated as a 14:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.17 (hexanes/EtOAc 1:1).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.70-8.63 (m, 1H), 8.23 (d, *J* = 7.4 Hz, 1H), 7.72-7.63 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45-7.35 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 (td, *J* = 7.4, 2.2 Hz, 1H), 7.17-7.08 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93-6.83 (m, 2H), 6.49 (s, 1H), 6.39 (s, 1H), 6.15 (s, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 1.93 (s, 3H).

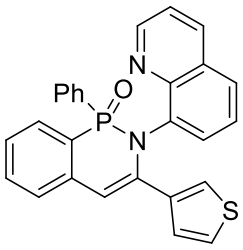
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.0, 145.0, 143.0, 138.11, 138.08, 137.8, 137.5, 137.1, 136.7, 135.4, 133.5, 133.4, 131.7, 131.4, 130.7, 130.6, 130.3, 129.2, 128.2, 128.0, 127.9, 127.7, 126.8, 126.7, 126.43, 126.36, 125.7, 125.5, 125.2, 123.8, 122.7, 121.1, 107.62, 107.55, 21.2, 20.9, 20.6.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 19.6.

HRMS (ESI) calcd. For $C_{32}H_{27}N_2OPNa$ $[M+Na]^+$: 509.1753; found: 509.1754.

FT-IR (neat, cm^{-1}) υ 1591, 1197, 1131, 1176, 1116, 1054, 1024.

***N*-(Quinolin-8-yl)-1-phenyl-3-thiophenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 9)**



P,P-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 3-ethynylthiophene (59 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 ^oC, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 180 mg (80%) of a light yellow oil that slowly solidifies was obtained. Product was isolated as a 10:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.2 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.69 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.12 (d, *J* = 7.3 Hz, 1H), 7.76 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.73-7.63 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.47-7.37 (m, 3H), 7.25 (d, *J* = 15.5 Hz, 1H, overlaps with chloroform signal), 7.23-7.18 (m, 1H), 7.12 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.11-7.06 (m, 2H), 6.96 (td, *J* = 7.7, 3.5 Hz, 2H), 6.89 (dd, *J* = 4.7, 0.9 Hz, 1H), 6.73 (dd, *J* = 5.1, 2.9 Hz, 1H), 6.40 (d, *J* = 1.8 Hz, 1H).

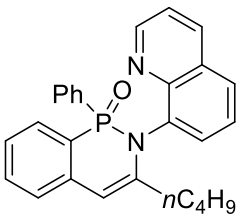
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.5, 144.2, 140.3, 139.32, 139.29, 138.01, 137.97, 137.7, 135.6, 133.1, 133.0, 131.9, 131.6, 131.5, 130.9, 130.8, 130.4, 130.2, 128.5, 128.2, 127.6, 127.3, 127.1, 126.73, 126.65, 126.1, 126.0, 125.6, 124.5, 123.9, 123.7, 122.9, 121.2, 107.1, 107.0.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 19.6.

HRMS (ESI) calcd. For $C_{27}H_{19}N_2OPSNa$ $[M+Na]^+$: 473.0848; found: 473.0848.

FT-IR (neat, cm^{-1}) υ 1468, 1205, 1107.

***N*-(Quinolin-8-yl)-3-*n*-hexyl-1-phenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (Table 2, Entry 10)**



P,P-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 1-hexyne (69 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 157 mg (74%) of a light yellow oil was obtained. Product was isolated as a >20:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.75- 8.72 (m, 1H), 8.20 (d, *J* = 7.3 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.59-7.46 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.39-7.34 (m, 1H), 7.34-7.28 (m, 2H), 7.21 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.08 (td, *J* = 7.5, 2.6 Hz, 1H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.84 (td, *J* = 7.5, 3.3 Hz, 2H), 6.08 (s, 1H), 2.11-2.03 (m, 1H), 1.99-1.88 (m, 1H), 1.51-1.34 (m, 2H), 1.11 (dt, *J* = 21.5, 7.2 Hz, 1H), 1.00 (dt, *J* = 21.7, 7.2 Hz, 1H), 0.62 (t, *J* = 7.3 Hz, 3H).

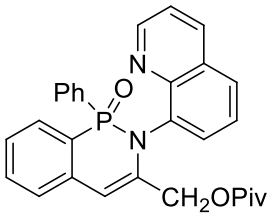
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.3, 145.3, 145.1, 145.0, 138.5, 138.4, 136.0, 135.9, 133.2, 133.1, 132.03, 132.01, 131.6, 131.29, 131.26, 131.1, 130.8, 130.6, 129.8, 128.6, 128.3, 126.9, 126.7, 126.2, 126.1, 125.9, 125.0, 124.9, 123.0, 121.7, 121.3, 102.8, 102.7, 34.7, 30.7, 22.2, 13.8.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 18.7.

HRMS (ESI) calcd. For $C_{27}H_{25}N_2OPNa$ $[M+Na]^+$: 447.1597; found: 447.1598.

FT-IR (neat, cm^{-1}) υ 1201, 1181, 1114, 1102.

_N_-(Quinolin-8-yl)-3-(*tert*-butylcarbonyloxy)methyl-1-phenyl-1,2-dihydro-benzo[*c*][1,2]aza-phosphinine 1-oxide (Table 2, Entry 11)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), prop-2-ynyl pivalate (84 mg, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 2:1 to 1:1 then 2:3), 156 mg (65%) of a colorless oil that slowly solidifies was obtained. Product was isolated as a 14:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.22 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.73 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.55-7.48 (m, 3H), 7.43-7.35 (m, 3H), 7.24 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.20 (td, *J* = 7.5, 2.8 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (td, *J* = 7.7, 3.5 Hz, 1H), 6.35 (d, *J* = 1.4 Hz, 1H), 4.57 (d, *J* = 13.4 Hz, 1H), 4.36 (d, *J* = 13.5 Hz, 1H), 1.07 (s, 9H).

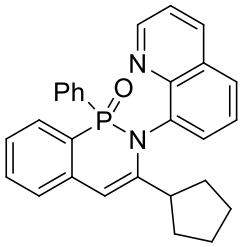
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 177.8, 150.5, 144.7, 138.7, 137.42, 137.39, 136.2, 134.7, 133.24, 133.16, 132.5, 132.4, 131.9, 131.6, 131.3, 131.2, 131.0, 130.8, 130.5, 129.4, 128.8, 128.7, 128.5, 128.4, 127.0, 126.9, 126.9, 126.3, 126.2, 125.9, 123.9, 122.9, 121.5, 105.84, 105.77, 65.13, 65.11, 38.8, 27.2.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 18.7.

HRMS (ESI) calcd. For $C_{29}H_{27}N_2O_3PNa$ $[M+Na]^+$: 505.1652; found: 505.1655.

FT-IR (neat, cm^{-1}) υ 1212, 1183, 1116, 1088.

_N_-(Quinolin-8-yl)-3-cyclopentyl-1-phenyl-1,2-dihydrobenzo[_c_][1,2]azaphosphinine 1-oxide (Table 2, Entry 12)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), cyclopentylacetylene (70 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 2:3), 166 mg (76%) of a colorless oil that slowly solidifies was obtained. Product was isolated as a >20:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown.

R_f = 0.24 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.74 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.51-7.42 (m, 3H), 7.40-7.34 (m, 2H), 7.31 (dd, *J* = 13.5, 7.6 Hz, 1H), 7.23 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.11 (td, *J* = 7.3, 2.8 Hz, 1H), 6.98 (td, *J* = 7.5, 0.8 Hz, 1H), 6.83 (td, *J* = 7.7, 3.4 Hz, 2H), 6.19 (d, *J* = 1.8 Hz, 1H), 2.26 (dd, *J* = 15.4, 7.7 Hz, 1H), 1.78 (ddd, *J* = 16.2, 10.3, 6.3 Hz, 1H), 1.69-1.52 (m, 5H), 1.33-1.16 (m, 2H).

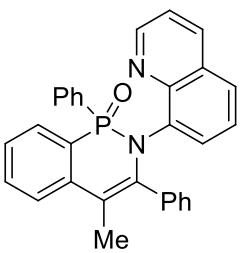
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.3, 149.7, 145.3, 145.2, 138.50, 138.47, 136.3, 135.9, 133.2, 133.1, 132.30, 132.28, 131.6, 131.2, 131.0, 130.7, 130.6, 130.0, 128.5, 128.2, 126.8, 126.7, 126.5, 126.4, 125.9, 125.1, 124.9, 122.8, 121.8, 121.3, 100.2, 100.1, 43.37, 43.35, 34.2, 31.4, 25.5, 25.2.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 18.6.

HRMS (ESI) calcd. For $C_{28}H_{25}N_2OPNa$ $[M+Na]^+$: 459.1597; found: 459.1599.

FT-IR (neat, cm^{-1}) υ 1624, 1208, 1116, 1104.

_N_-(Quinolin-8-yl)-4-methyl-1,3-diphenyl-1,2-dihydrobenz[c-1,2]azaphosphinine 1-oxide (Table 2, Entry 13)



P,*P*-Diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 1-phenyl-1-propyne (75 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 164 mg (72%) of a colorless oil that slowly solidifies was obtained. Product was

obtained as a 20:1 mixture of regioisomers inseparable by column chromatography, structure of major isomer shown. It exists as a 13:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond.

R_f = 0.2 (hexane/EtOAc 1:2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.76 (dd, *J* = 4.1, 1.5 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.69 (td, *J* = 8.6, 4.2 Hz, 4H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.40-7.34 (m, 1H), 7.24-7.03 (m, 7H), 6.93 (td, *J* = 7.7, 3.4 Hz, 3H), 6.82 (bs, 3H), 2.10 (s, 3H).

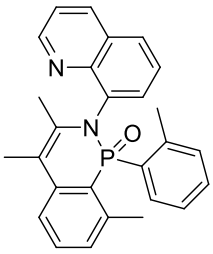
^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.4, 144.4, 140.8, 139.69, 139.66, 138.2, 137.2, 137.1, 135.6, 133.43, 133.35, 131.6, 131.5, 131.1, 130.8, 130.71, 130.66, 130.6, 129.6, 128.3, 127.20, 127.16, 127.13, 127.10, 126.6, 125.9, 125.8, 125.4, 124.54, 124.46, 124.4, 121.1, 109.7, 109.7, 17.5.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 16.7.

HRMS (ESI) calcd. For $C_{30}H_{23}N_2OPNa$ $[M+Na]^+$: 481.1440; found: 481.1441.

FT-IR (neat, cm^{-1}) υ 1204, 1183, 1138, 1115.

_N_-(Quinolin-8-yl)-1-(2-methyl)phenyl-3,4-dimethyl-1,2-dihydro-8-methylbenzo[*c*][1,2]aza-phosphinine 1-oxide (6, Scheme 1)



P,*P*-Di-*o*-tolyl-*N*-(quinolin-8-yl)phosphinic amide (186 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1 equiv), 2-butyne (47 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 2:1 to 3:2), 118 mg (56%) of a colorless oil that slowly solidifies was obtained.

R_f = 0.25 (hexane/EtOAc 1:2).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.66 (bs, 1H), 8.26 (bs, 1H), 7.88-7.82 (m, 2H), 7.57-7.37 (m, 3H), 7.34-7.33 (m, 1H), 7.19-7.18 (m, 1H), 7.00-6.91 (m, 1H), 6.83 (bs, 2H), 6.51 (s, 1H), 2.24 (s, 3H), 2.06 (s, 3H), 1.85-1.83 (2 overlapped singlets, 6H).

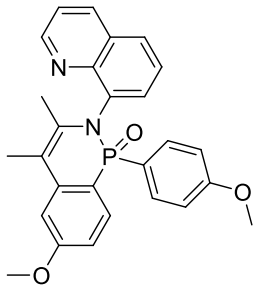
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 149.7, 145.3, 141.8, 141.7, 140.34, 140.29, 140.2, 140.1, 137.42, 137.40, 136.9, 135.8, 134.8, 134.7, 131.5, 131.4, 131.1, 130.5, 130.4, 130.2, 128.6, 127.6, 127.5, 125.8, 124.6, 124.4, 123.6, 122.3, 122.2, 122.1, 121.2, 106.0, 105.9, 21.7, 21.6, 19.5, 16.9.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 12.5.

HRMS (ESI) calcd. For $C_{27}H_{25}N_2OPNa$ $[M+Na]^+$: 447.1597; found: 447.1599.

FT-IR (neat, cm^{-1}) υ 1201, 1184, 1131.

***N*-(Quinolin-8-yl)-1-(4-methoxy)phenyl-3,4-dimethyl-1,2-dihydro-6-methoxylbenzo[*c*][1,2]aza-phosphinine 1-oxide (8, Scheme 1)**



P,*P*-Bis(4-methoxyphenyl)-*N*-(quinolin-8-yl)phosphinic amide (202 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 2-butyne (47 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:2 to 1:4, then EtOAc), 172 mg (75%) of a brownish oil that slowly solidifies was obtained.

R_f = 0.1 (hexane/EtOAc 1:4).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.76 (d, *J* = 2.8 Hz, 1H), 8.14 (d, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 12.2, 8.7 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.30-7.15 (m, 2H), 7.12-7.00 (m, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.40 (dd, *J* = 8.6, 2.2 Hz, 2H), 3.85 (s, 3H), 3.56 (s, 3H), 2.25 (s, 3H), 1.81 (s, 3H).

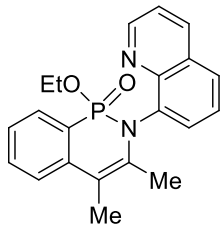
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 162.0, 161.8, 150.2, 145.2, 141.8, 141.7, 137.8, 137.6, 136.0, 135.2, 135.1, 132.6, 132.4, 131.1, 131.0, 128.7, 127.7, 126.0, 122.5, 121.3, 121.0, 117.6, 116.2, 112.6, 112.5, 111.6, 111.4, 108.1, 108.0, 106.5, 106.4, 55.3, 55.1, 19.4, 16.2.

^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ 17.2.

HRMS (ESI) calcd. For $C_{27}H_{25}N_2O_3PNa$ $[M+Na]^+$: 479.1495; found: 479.1494.

FT-IR (neat, cm^{-1}) υ 1592, 1196, 1176, 1131, 1115.

***N*-(Quinolin-8-yl)-1-ethoxy-3,4-dimethyl-1,2-dihydrobenzo[c][1,2]aza-phosphinine 1-oxide (10, Scheme 1)**



N-(Quinolin-8-yl)phenylphosphonamide monoethyl ester (156 mg, 0.5 mmol), NaOPiv (124 mg, 1.0 mmol, 2.0 equiv), $Co(NO_3)_2$*$6H_2O$ (44 mg, 0.15 mmol, 30 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), $Mn(OAc)_3$*$2H_2O$ (134 mg, 0.5 mmol, 1.0 equiv), 2-butyne (47 μL, 0.6 mmol, 1.2 equiv), EtOH (5 mL), 80 °C, 16 h. After column chromatography (gradient hexanes/EtOAc from 1:1 to 1:2), 74 mg (41%) of a brownish oil that slowly solidifies was obtained. Product exists as a 10:8 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond.

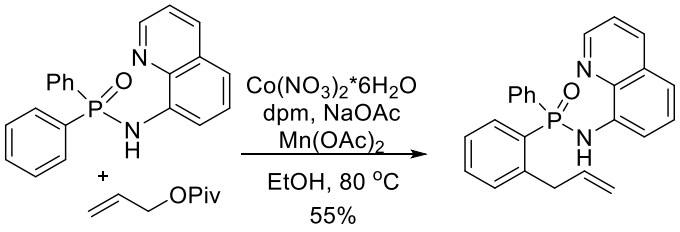
R_f = 0.23 (hexanes/EtOAc 1:2).

^{1}H NMR (600 MHz, DMSO-d_6, 100 ºC, ppm) δ 8.85 (bs, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.66 (m, 5H), 7.53 (bs, 1H), 7.40 (bs, 1H), 4.11 (bs, 2H), 2.22 (s, 3H), 1.77 (s, 3H), 1.10 (bs, 3H).

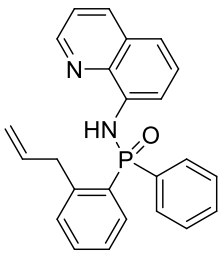
^{13}C NMR (MHz, DMSO-d_6, ppm; mixture of atropisomers, list of signals, C-P coupling not resolved) δ 151.3, 151.0, 146.0, 145.6, 141.05, 141.01, 140.45, 140.41, 138.0, 137.1, 137.0, 136.9, 135.7, 132.6, 132.3, 131.0, 130.1, 129.4, 128.53, 128.49, 128.43, 128.3, 128.10, 128.05, 127.0, 126.7, 126.2, 126.1, 125.7, 125.6, 124.5, 124.4, 124.3, 124.2, 123.1, 123.0, 122.43, 122.35, 121.9, 111.38, 111.33, 108.32, 108.27, 62.91, 62.86, 61.15, 61.11, 18.73, 18.61, 16.77, 16.57, 16.1, 15.9.

^{31}P NMR (MHz, DMSO-d_6, ppm; mixture of atropisomers) δ 11.7, 10.2.

2. Cobalt-catalyzed coupling between phosphinamides and alkenes



***P*-(2-Allylphenyl)-*P*-phenyl-*N*-(quinolin-8-yl)phosphinic amide (11, Scheme 2)**



A 8 dram vial equipped with a magnetic stir bar was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), allyl pivalate (85 mg, 0.6 mmol, 1.2 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), NaOAc (82 mg, 1.0 mmol, 2.0 equiv), $Mn(OAc)_2$ (178 mg, 1.0 mmol, 2.0 equiv), and EtOH (5 mL). Reaction mixture was heated at 80 °C for 5 h and monitored by TLC. Reaction solvent was evaporated. After column chromatography on silica gel (gradient hexanes/EtOAc from 8:1 to 4:1, then 2:1) 106 mg (55%) of a colorless oil that slowly solidifies was obtained.

R_f = 0.58 (hexanes/EtOAc 1:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.74 (dd, *J* = 4.1, 1.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.61 – 7.53 (m, 3H), 7.50 – 7.46 (m, 3H), 7.44 – 7.38 (m, 2H), 7.34 – 7.29 (m, 2H), 7.19 (dd, *J* = 7.2, 5.9 Hz, 1H), 6.01 – 5.83 (m, 1H), 4.97 (d, *J* = 12.0 Hz, 2H), 4.01 (dd, *J* = 15.8, 6.6 Hz, 1H), 3.90 (dd, *J* = 15.8, 6.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 147.9, 145.04, 144.98, 138.64, 138.59, 138.0, 137.4, 136.9, 136.3, 133.13, 133.05, 132.7, 132.28, 132.26, 132.19,

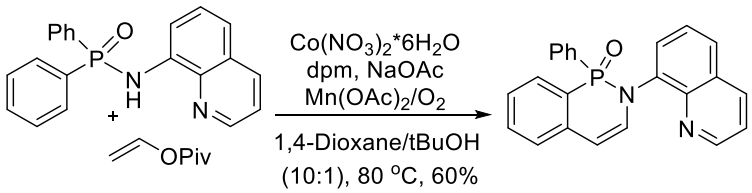
132.17, 132.1, 132.0, 131.8, 131.2, 131.1, 130.5, 129.6, 128.8, 128.7, 128.4, 127.3, 126.0, 125.9, 122.4, 121.6, 119.2, 116.4, 113.90, 113.88, 38.30, 38.27.

^{31}P NMR (243 MHz, $CDCl_3$, ppm) δ 23.4.

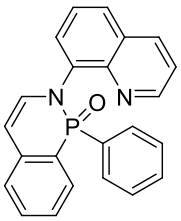
HRMS (ESI) calcd. For $C_{24}H_{21}N_2OPNa$ $[M+Na]^+$: 407.1284; found: 407.1285.

FT-IR (neat, cm^{-1}) υ 1505, 1317, 1212, 1091.

Control experiment without $Mn(OAc)_2$ gave product in 12% yield (determined by ^{1}H-NMR using triphenylmethane as internal standard).



1-Phenyl-2-(quinolin-8-yl)-1,2-dihydrobenzo[*c*][1,2]azaphosphinine 1-oxide (12, Scheme 2)



A 8 dram vial equipped with a magnetic stir bar was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), vinyl pivalate (89 μL, 0.6 mmol, 1.2 equiv), $Co(NO_3)_2$*$6H_2O$ (29 mg, 0.1 mmol, 20 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), NaOAc (82 mg, 1.0 mmol, 2.0 equiv), $Mn(OAc)_2$ (178 mg, 1.0 mmol, 2.0 equiv), and the mixture of 1,4-dioxane/*t*-BuOH (10:1) (5.5 mL). Resulting solution was purged with O_2 gas for 1 min, heated at 80 °C for 22 h, monitored by TLC after 2, 6, 16 h. After each opening, the reaction mixture was purged with O_2 for 1 minute. Reaction solvent was evaporated. After column chromatography on silica gel (gradient hexanes/EtOAc from 2:1 to 1:1) 110 mg (60%) of a colorless oil that slowly solidifies was obtained. R_f = 0.23 (hexanes/EtOAc 1:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.95 – 8.80 (m, 1H), 8.39 – 8.14 (m, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.66 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.42 – 7.32 (m, 3H), 7.23 – 7.14 (m, 2H), 7.13 – 7.02 (m, 2H), 6.93 – 6.75 (m, 1H), 6.06 (d, *J* = 7.4 Hz, 1H).

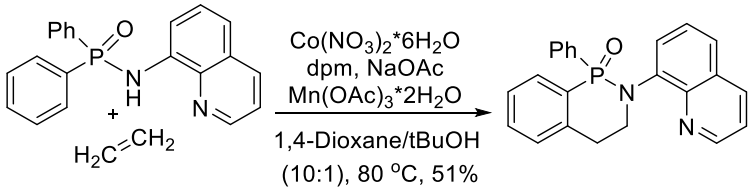
^{13}C NMR (150 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 150.0, 143.9, 138.1, 137.6, 136.2, 136.1, 133.0, 132.2, 131.7, 131.6, 131.1, 131.0, 129.22, 129.15, 127.6, 127.5, 127.4, 126.1, 126.01, 125.96, 125.7, 125.6, 121.3, 102.3.

^{31}P NMR (243 MHz, $CDCl_3$, ppm) δ 17.6.

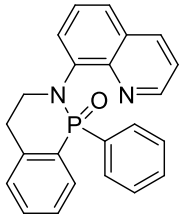
HRMS (ESI) calcd. For $C_{23}H_{17}N_2OPNa$ $[M+Na]^+$: 391.0971; found: 391.0972.

FT-IR (neat, cm^{-1}) υ 1633, 1469, 1322, 1260, 1195, 1111, 1100.

Control experiment without $Mn(OAc)_2/O_2$ gave product in 24% yield (determined by ^{1}H-NMR using triphenylmethane as internal standard).



1-Phenyl-2-(quinolin-8-yl)-1,2,3,4-tetrahydrobenzo[*c*][1,2]azaphosphinine 1-oxide (13, Scheme 2)



A 8 dram vial equipped with a magnetic stir bar was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (172 mg, 0.5 mmol), $Co(NO_3)_2$*$6H_2O$ (44 mg, 0.15 mmol, 30 mol%), dipivaloylmethane (52 μL, 0.25 mmol, 50 mol%), NaOAc (82 mg, 1.0 mmol, 2 equiv), $Mn(OAc)_3$*$2H_2O$ (268 mg, 1.0 mmol, 2.0 equiv), and the mixture of 1,4-dioxane/*t*-BuOH (10:1) (5.5 mL). Resulting solution was cooled to 0 °C and purged with ethylene gas for 1 min, then heated at 80 °C for 24 h. Reaction was monitored by TLC after 2, 6, 16 h. After each opening, the reaction mixture was cooled to 0 °C and purged with ethylene gas for 1 minute. Reaction solvent was evaporated. After column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) 94 mg (51%) of a colorless oil that slowly solidifies was obtained.

R_f = 0.37 (hexanes/EtOAc 1:2).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.81 – 8.76 (m, 1H), 8.30 (dd, *J* = 11.5, 8.1 Hz, 2H), 8.08 – 8.00 (m, 2H), 7.74 – 7.68 (m, 1H), 7.68 – 7.63 (m, 2H), 7.38 – 7.31 (m, 3H), 7.18 – 7.12 (m, 2H), 6.99 – 6.85 (m, 2H), 4.47 – 4.34 (m, 1H), 3.95 – 3.89 (m, 1H), 3.37 – 3.31 (m, 1H), 3.26 – 3.19 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 148.4, 144.14, 144.08, 140.5, 140.4, 138.0, 136.0, 133.43, 133.36, 132.59, 132.57, 132.0, 131.9, 131.5, 131.3, 131.2, 131.1, 130.98, 130.97, 130.1, 129.7, 129.4, 129.1, 128.9, 128.8, 128.0, 126.8, 125.8, 125.7, 120.9, 120.5, 37.27, 37.25, 31.0.

^{31}P NMR (202 MHz, $CDCl_3$, ppm) δ 28.5.

HRMS (ESI) calcd. For $C_{23}H_{19}N_2OPNa$ $[M+Na]^+$: 393.1127; found: 393.1126.

FT-IR (neat, cm^{-1}) υ 1504, 1437, 1412, 1308, 1207, 1114, 1091.

3. Control experiments

Procedure for control experiment without catalyst (Table S1, entry 4).

A 2-dram vial equipped with a magnetic stir bar was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (86 mg, 0.25 mmol), NaOPiv (62 mg, 0.5 mmol, 2.0 equiv), $Mn(OAc)_3*2H_2O$ (68 mg, 0.25 mmol, 1 equiv), 2-butyne (24 μL, 0.3 mmol, 1.2 equiv), and EtOH (2.5 mL). Resulting solution was heated at 80 °C for 24 h. After completion, the reaction mixture was cooled to room temperature and solvent was evaporated. Reaction mixture was analyzed by TLC (hexanes/EtOAc 1:1) and ^{1}H-NMR spectroscopy. Product formation was not observed. After flash column chromatography on silica gel (gradient hexanes/EtOAc from 1:1 to 1:2) 80 mg (93%) of phosphinic amide was recovered.

General procedure for control experiments (Table S1, entries 1-3, 6).

A 2-dram vial equipped with a magnetic stir bar was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (34 mg, 0.1 mmol), $Co(NO_3)_2*6H_2O$ (5.8 mg, 0.02 mmol, 20 mol%), ligand (50 mol%), NaOPiv (25 mg, 0.2 mmol, 2.0 equiv), $Mn(OAc)_3*2H_2O$ (0.5-1.0 equiv), 2-butyne (9.4 μL, 0.12 mmol, 1.2 equiv), Ph_3CH (24 mg, 0.1 mmol, 1.0 equiv), and EtOH (1 mL). Resulting mixture was heated at 80 °C for 3.5 h, cooled to room temperature and solvent was evaporated. To the residue potassium sodium tartrate (5 mL of 1M aqueous solution) was added and mixture was extracted with CH_2Cl_2 (3 x 10 mL). Combined organic phase was dried over $MgSO_4$, filtered, and solvent was evaporated. Reaction mixture was analyzed by ^{1}H-NMR spectroscopy.

Procedure for control experiment under inert atmosphere (Table S1, entry 10).

Inside glovebox, a 2-dram vial equipped with a magnetic stir bar and septum was charged with *P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinic amide (34 mg, 0.1 mmol), $Co(NO_3)_2*6H_2O$ (5.8 mg, 0.02 mmol, 20 mol%), dipivaloylmethane (10.4 μL, 0.05 mmol, 50 mol%), NaOPiv (25 mg, 0.2 mmol, 2.0 equiv), $Mn(OAc)_3*2H_2O$ (27 mg, 0.1 mmol, 1.0 equiv), 2-butyne (9.4 μL, 0.12 mmol, 1.2 equiv), Ph_3CH (24 mg, 0.1 mmol, 1.0 equiv). Outside glovebox degassed EtOH (1 mL) was added The resulting mixture was flushed with argon and heated at 80 °C for 3.5 h. After cooling to room temperature and addition of potassium sodium tartrate (5 mL of 1M aqueous solution) the mixture was extracted with CH_2Cl_2 (3 x 10 mL). Combined organic phase was dried over $MgSO_4$, filtered, and solvent was evaporated. Reaction mixture was analyzed by ^{31}P and ^{1}H-NMR spectroscopy.

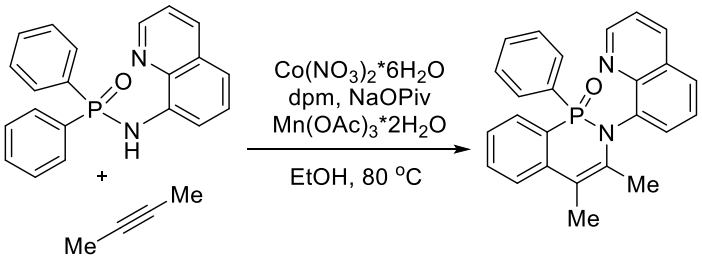
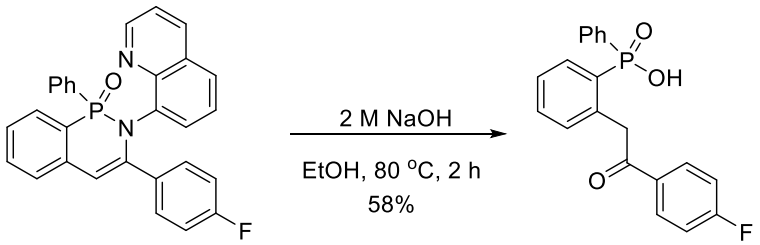


Table S1 Control experiments

Entry	Change in standard conditions	Time, h	Substrate : Product ratio[a]	Product yield[b]
1	-	3.5	0 : 1	99%
2	4,4-dimethyl-1-phenylpentane-1,3-dione instead of dpm	3.5	1 : 5	74%
3	dbm instead of dpm	3.5	1 : 1.9	53%
4	without $Co(NO_3)_2*6H_2O$, dpm	24	1 : 0	-
5	without $Mn(OAc)_3*2H_2O$	3.5	1 : 1	49%
6	50 mol% $Mn(OAc)_3*2H_2O$	3.5	1 : 10	82%
7	without dpm	3.5	2.3 : 1	30%
8	cat. $Co(acac)_2$	3.5	1 : 2.4	69%
9[c]	cat $Co(acac)_2$, acac	3.5	1 : 3	76%
10	inert atmosphere, degassed EtOH	3.5	97 : 3	<5%

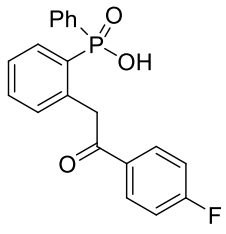
[a] Determined by ^{31}P NMR spectroscopy. [b] ^{1}H NMR yield using triphenylmethane as internal standard. [c] 20 mol% $Co(acac)_2$, 10 mol% acac. dpm = dipivaloylmethane, dbm = dibenzoylmethane, acac = acetylacetone

Removal of directing group



2-(2-(4-Fluorophenyl)-2-oxoethyl)phenyl(phenyl)phosphinic acid (15)

A 6-dram vial equipped with magnetic stir bar was charged with *N*-(quinolin-8-yl)-1-phenyl-3-(4-fluorophenyl)-1,2-dihydrobenzo[c][1,2]aza-phosphinine 1-oxide (116 mg, 0.25 mmol), NaOH (0.25 mL, 2 M aqueous solution, 0.5 mmol), and EtOH (2 mL). The mixture was stirred at 80 °C for 2 h.



After completion, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL) and 10% HCl aqueous solution (10 mL). Combined organic phase was concentrated *in vacuo*. The crude product was treated with 2 M NaOH aqueous solution (5 mL), and the aqueous phase was further washed with CH_2Cl_2 (2 x 10 mL). Combined aqueous phase was acidified with 2 M HCl aqueous solution (2 mL), and extracted with CH_2Cl_2 (2 x 10 mL). Combined organic phase was dried over Na_2SO_4, filtered, and evaporated to give 51 mg (58%) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (bs, 1H), 7.84 (dd, *J* = 13.3, 7.7 Hz, 1H), 7.78 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.50 (dd, *J* = 12.7, 7.6 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 6.9 Hz, 1H), 7.18 (td, *J* = 7.4, 2.9 Hz, 2H), 7.12 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.93 (t, *J* = 8.6 Hz, 2H), 4.43 (s, 2H).

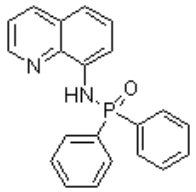
^{13}C NMR (101 MHz, $CDCl_3$, ppm; list of signals, C-P coupling not resolved) δ 195.6, 166.9, 164.4, 138.0, 137.9, 133.5, 133.4, 132.8, 132.3, 132.2, 131.9, 131.7, 131.6, 131.2, 131.1, 130.2, 128.4, 128.3, 126.9, 126.8, 115.6, 115.4, 77.5, 77., 76.8, 43.8.

^{31}P NMR (202 MHz, $CDCl_3$) δ 33.3.

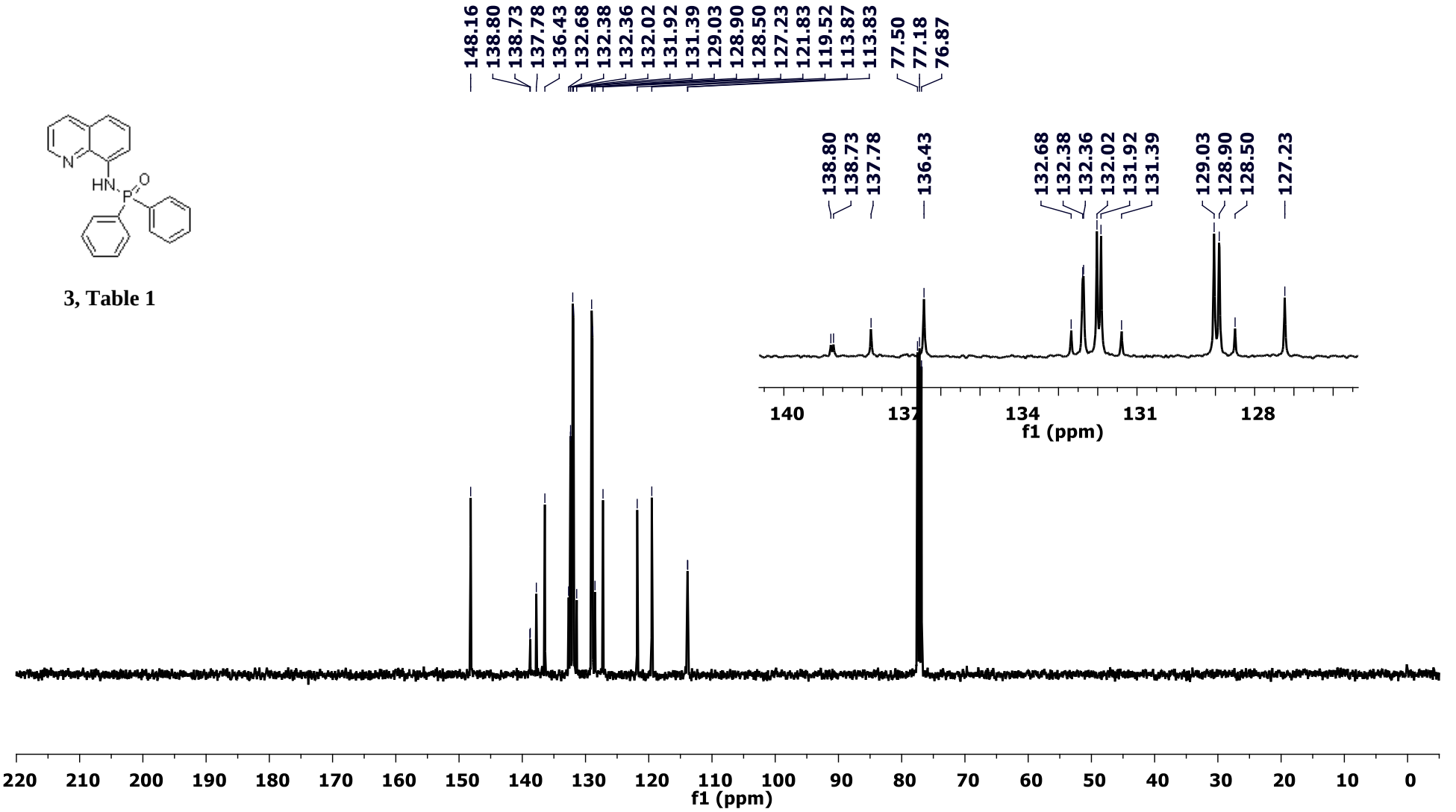
^{19}F NMR (471 MHz, $CDCl_3$) δ -105.4 (tt, *J* = 8.3, 5.5 Hz).

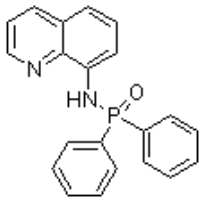
HRMS (ESI) calcd. For $C_{20}H_{16}FO_3P$ $[M-H]^-$: 353.0748; found: 353.0751.

NMR spectra

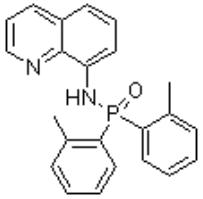


3, Table 1


148.16
138.80
138.73
137.78
136.43
132.68
132.38
132.36
132.02
131.92
131.39
129.03
128.90
128.50
127.23
121.83
119.52
113.87
113.83
77.50
77.18
76.87
HN
P
O
N
3, Table 1
f1 (ppm)
f1 (ppm)

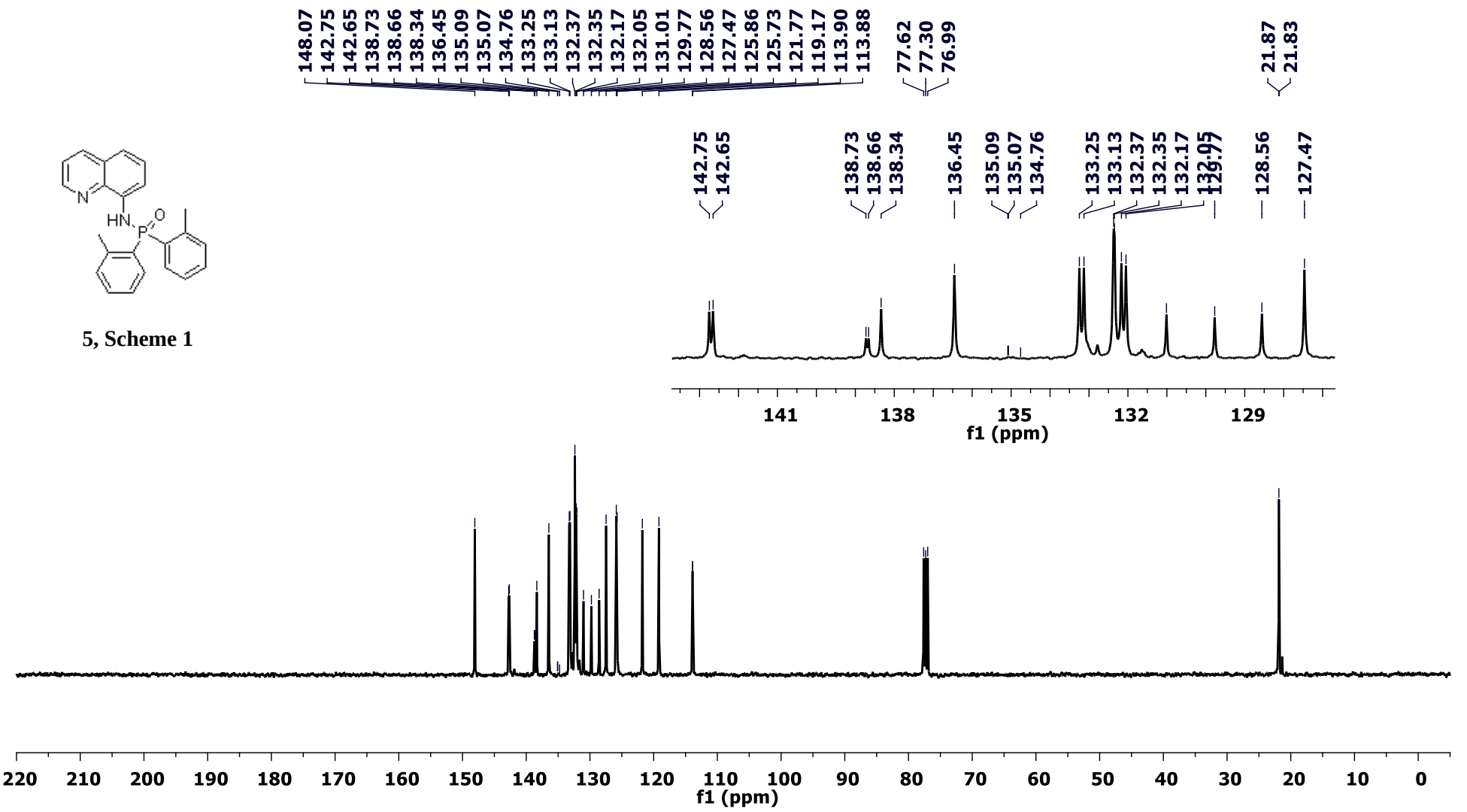


3, Table 1

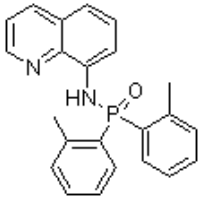

N
HN
P
O

5, Scheme 1

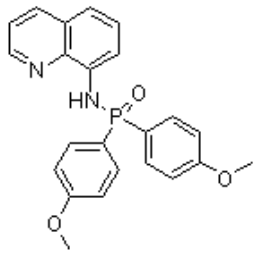
8.70
8.70
8.08
8.06
7.91
7.87
7.70
7.68
7.67
7.65
7.42
7.40
7.38
7.36
7.35
7.34
7.32
7.29
7.27
7.26
7.19
7.17
7.16
2.63
2.25
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.00
1.03
1.26
2.96
4.34
3.89
2.19
5.99
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.07
142.75
142.65
138.73
138.66
138.34
136.45
135.09
135.07
134.76
133.25
133.13
132.37
132.35
132.17
132.05
131.01
129.77
128.56
127.47
125.86
125.73
121.77
119.17
113.90
113.88
77.62
77.30
76.99
21.87
21.83
HN
P
O
N
141
138
135
132
129
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5, Scheme 1

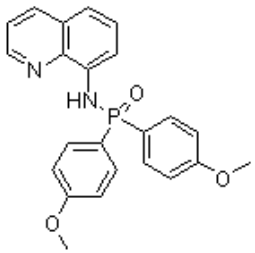


5, Scheme 1


N
HN
P
O
O
O

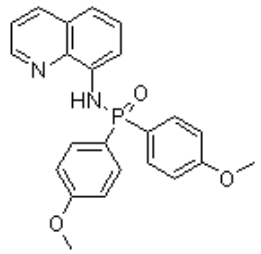
7, Scheme 1

8.69
8.68
7.85
7.83
7.82
7.80
7.36
7.35
7.34
7.33
7.32
7.31
7.23
7.21
6.93
6.92
6.91
3.74
8.1
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
1.00
1.10
5.42
2.16
2.01
4.17
6.53
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

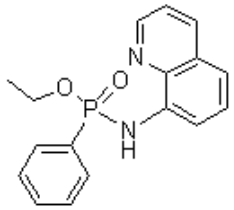

N
HN
P
O
O
O

7, Scheme 1

162.68
148.03
138.83
138.76
138.08
136.37
133.88
133.76
128.48
127.29
124.43
123.07
121.71
119.18
114.48
114.33
113.80
113.76
77.47
77.15
76.84
55.43
f1 (ppm)
f1 (ppm)

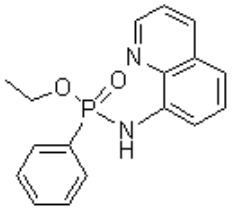


7, Scheme 1



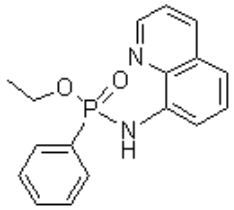
9, Scheme 1

8.79 8.78 8.78 8.78 8.09 8.09 8.07 8.07 7.91 7.88 7.42 7.41 7.41 7.40 7.40 7.39 7.31 7.30 7.30 5.28 4.33 4.32 4.31 4.30 4.30 4.28 4.26 4.25 4.24 4.23 4.23 4.21 1.41 1.39 1.38 -0.01
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4
f1 (ppm)
1.00 1.05 1.05 2.08 1.01 4.12 2.13 2.07 3.12
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



9, Scheme 1

148.17
138.57
138.50
137.46
136.28
132.31
132.29
131.65
131.57
130.96
129.56
128.70
128.58
128.47
127.19
121.84
119.31
112.53
77.41
77.15
76.90
61.46
61.41
16.53
16.48
f1 (ppm)
f1 (ppm)



9, Scheme 1

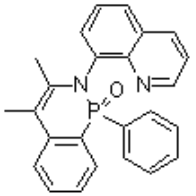
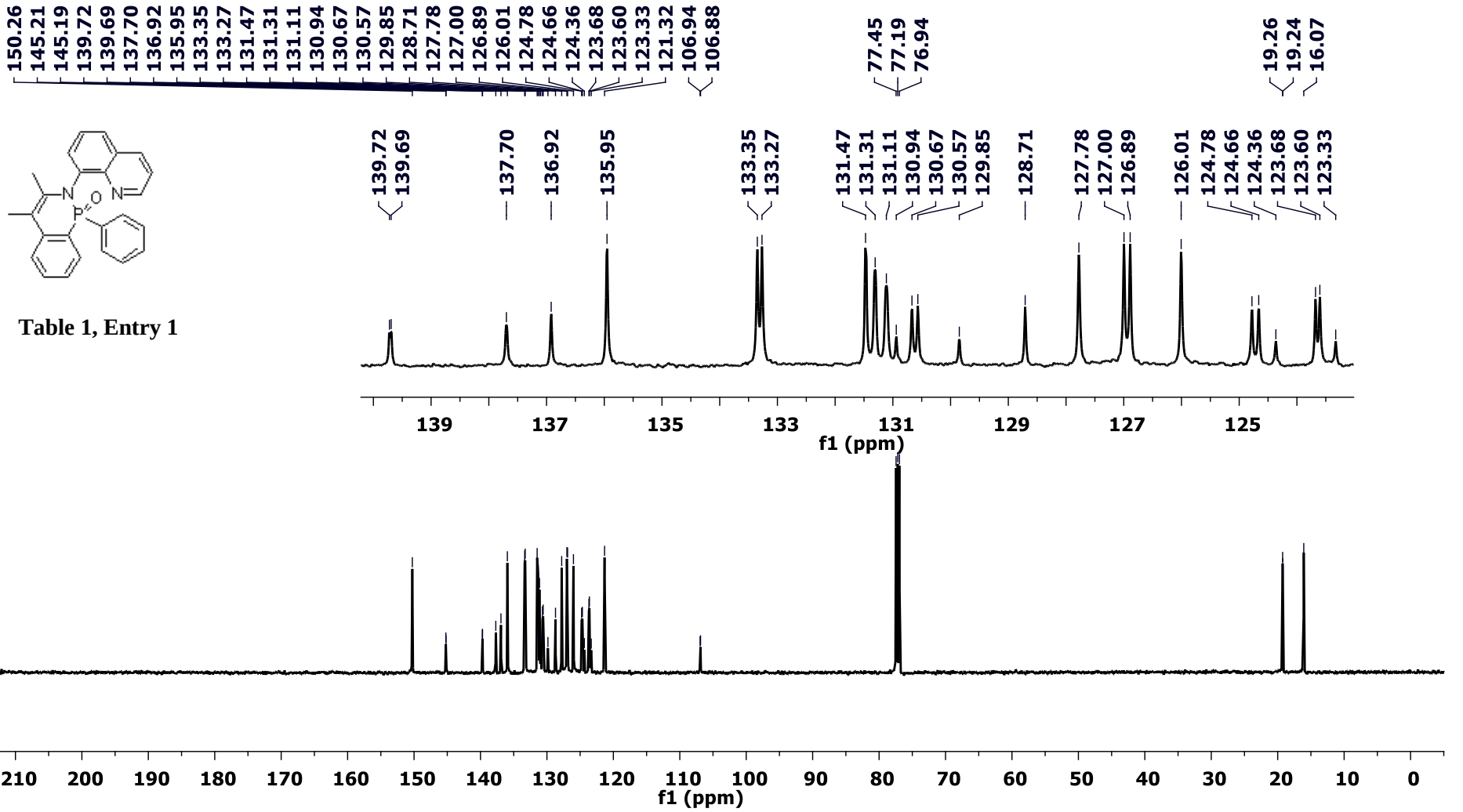


Table 1, Entry 1



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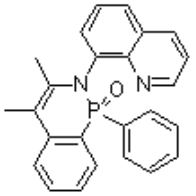
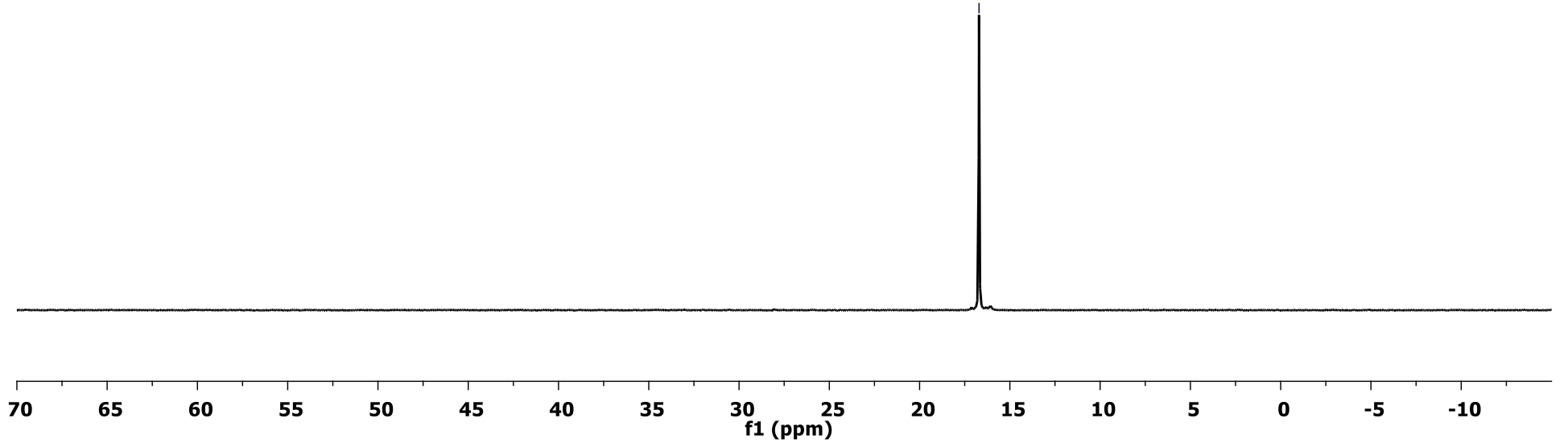
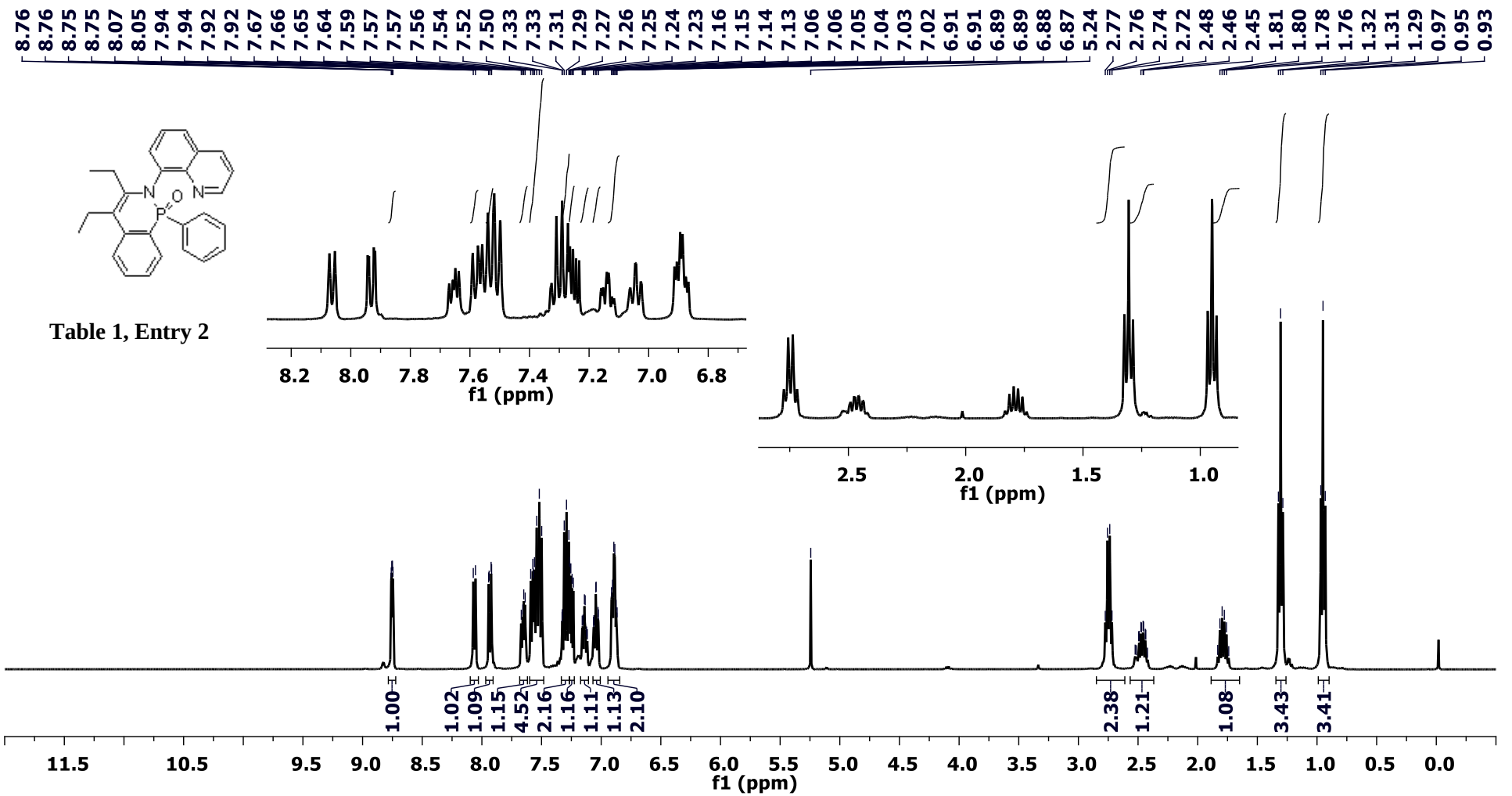


Table 1, Entry 1





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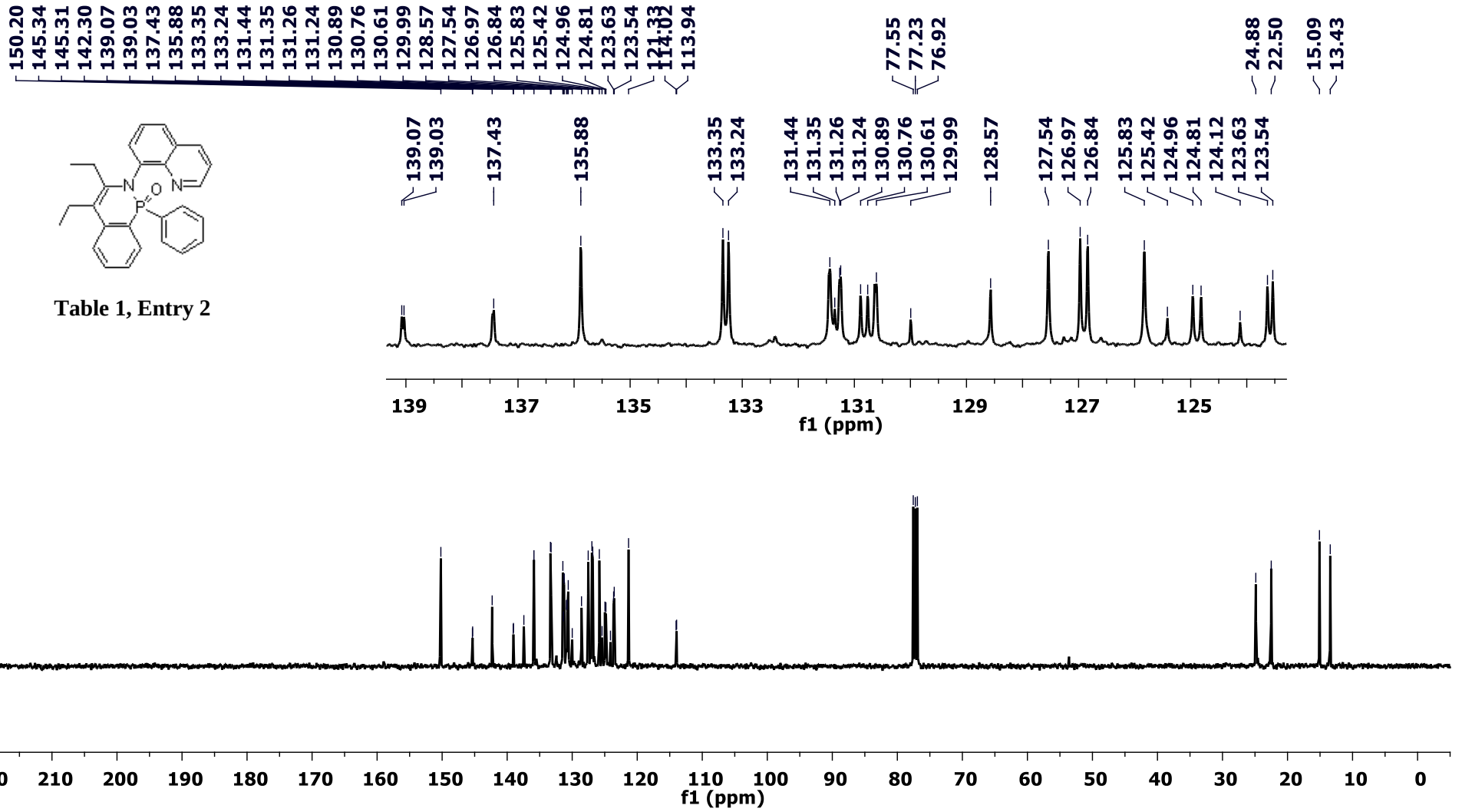

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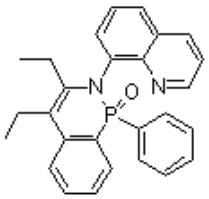
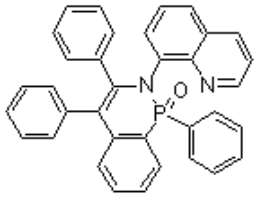


Table 1, Entry 2



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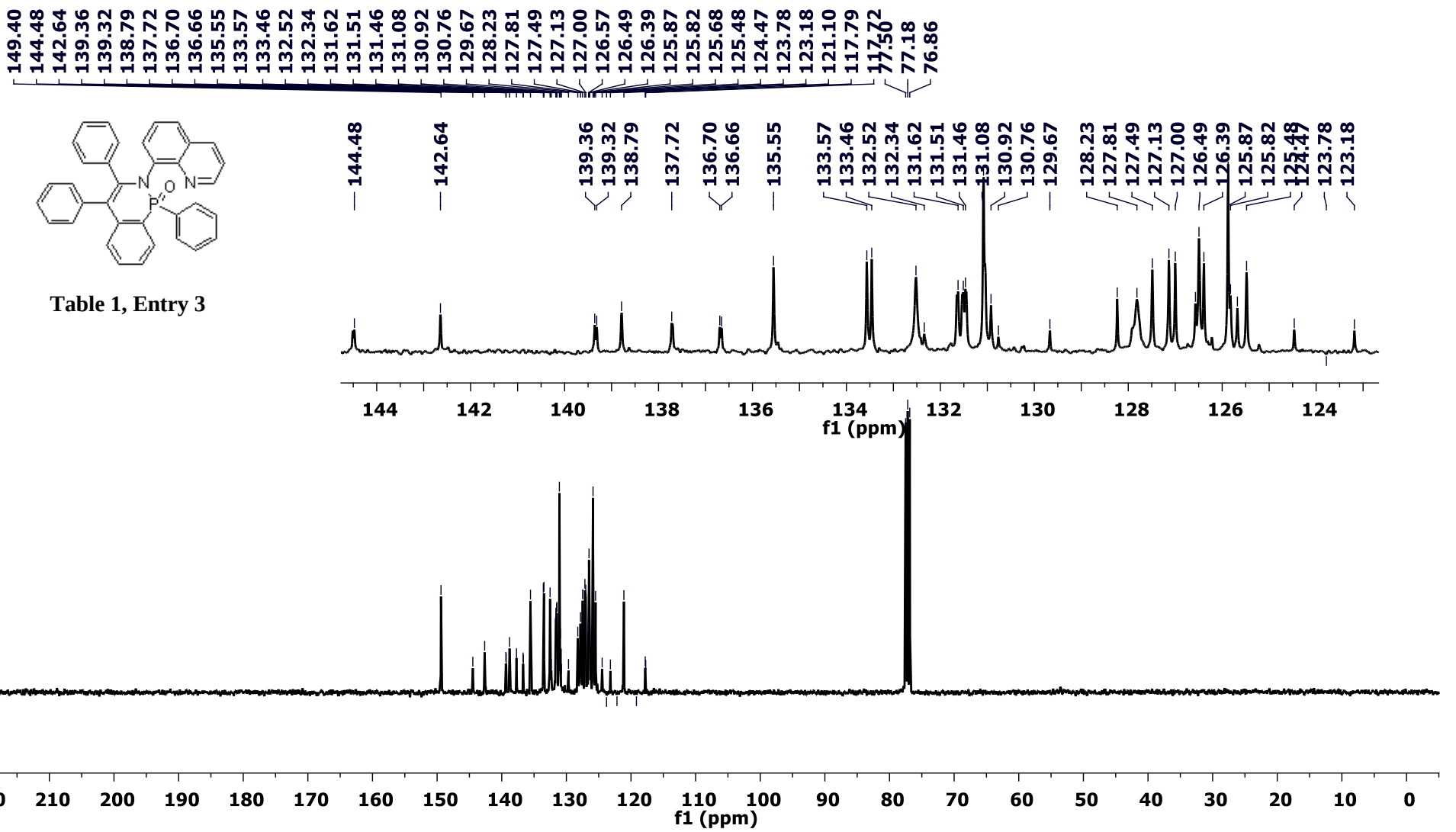

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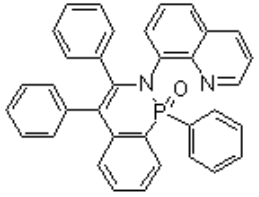
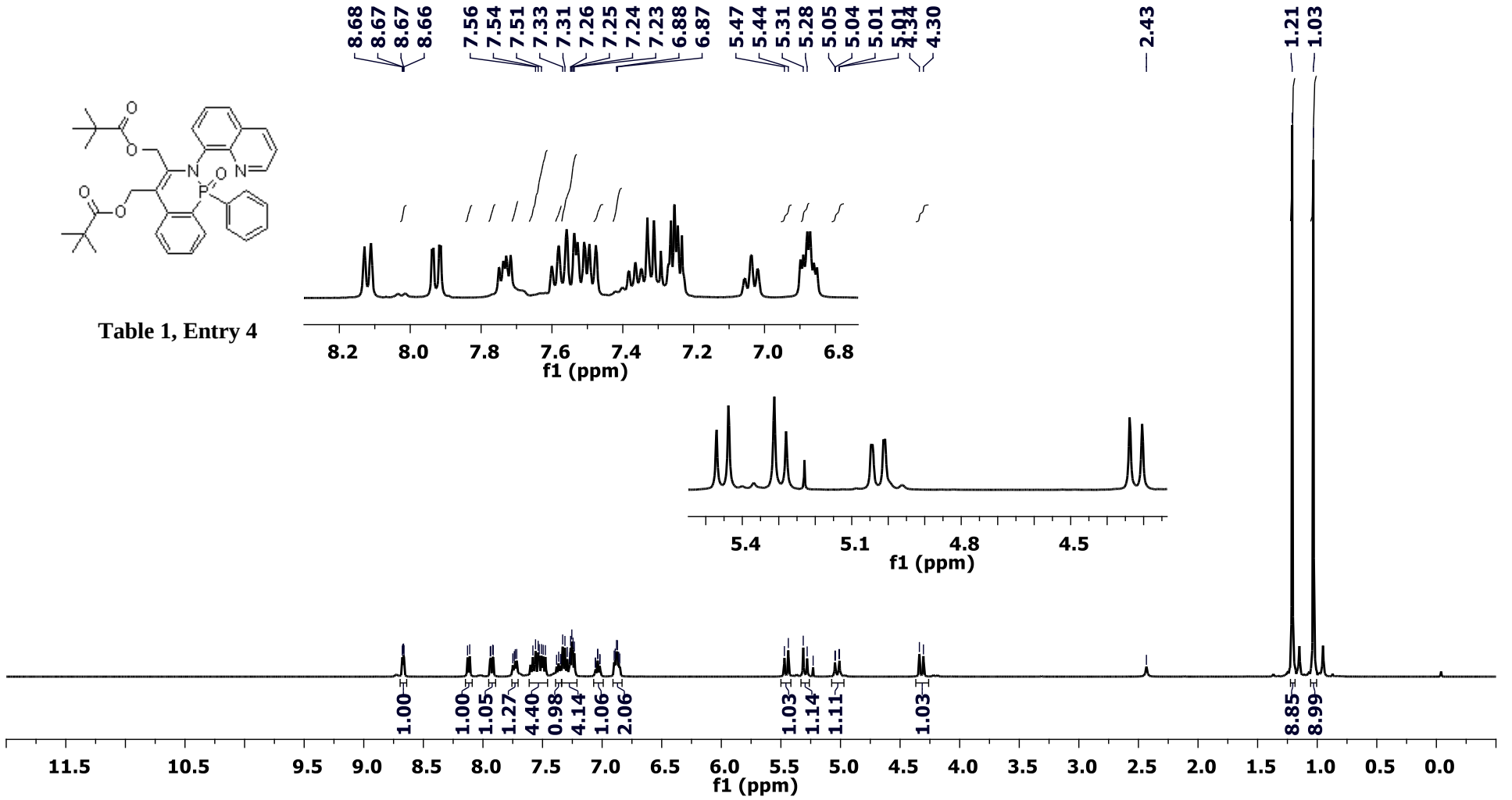


Table 1, Entry 3



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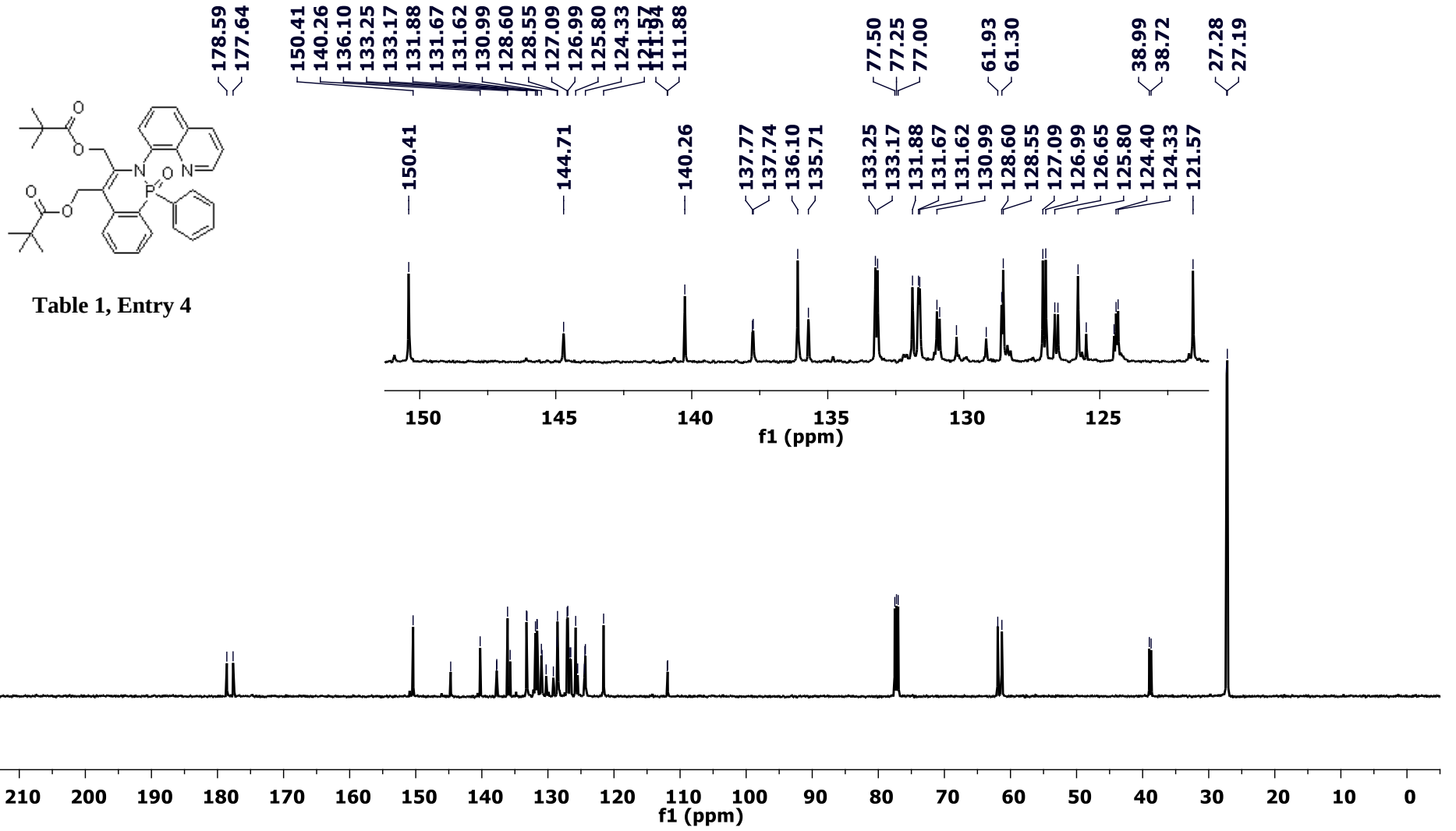


Table 1, Entry 4

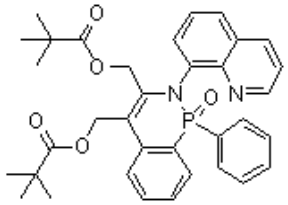
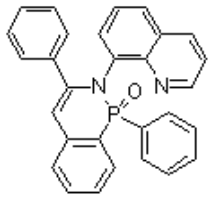


Table 1, Entry 4



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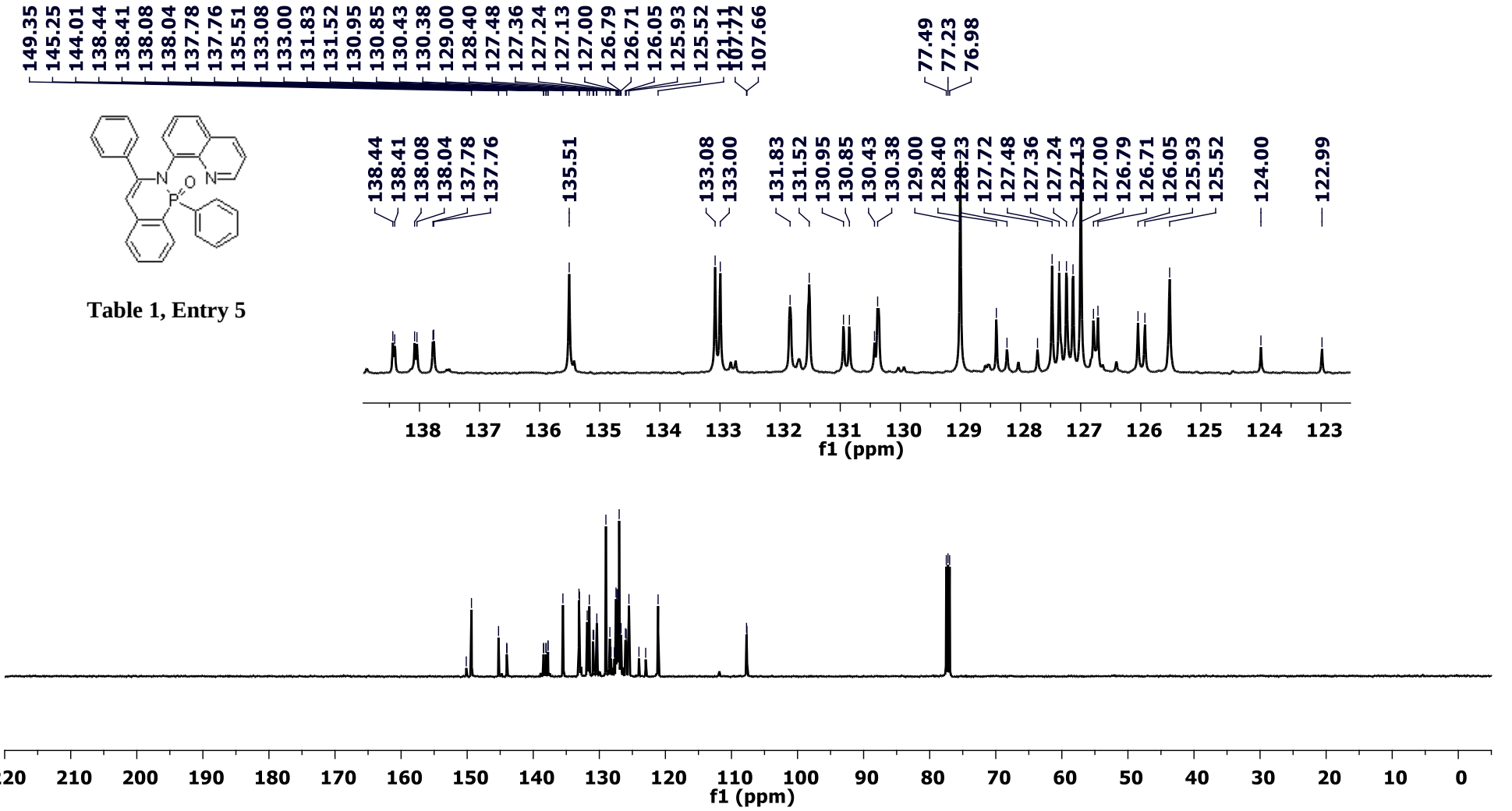


Table 1, Entry 5

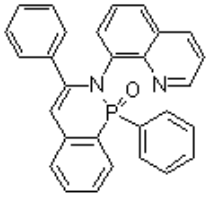
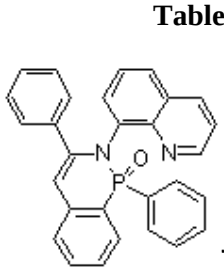
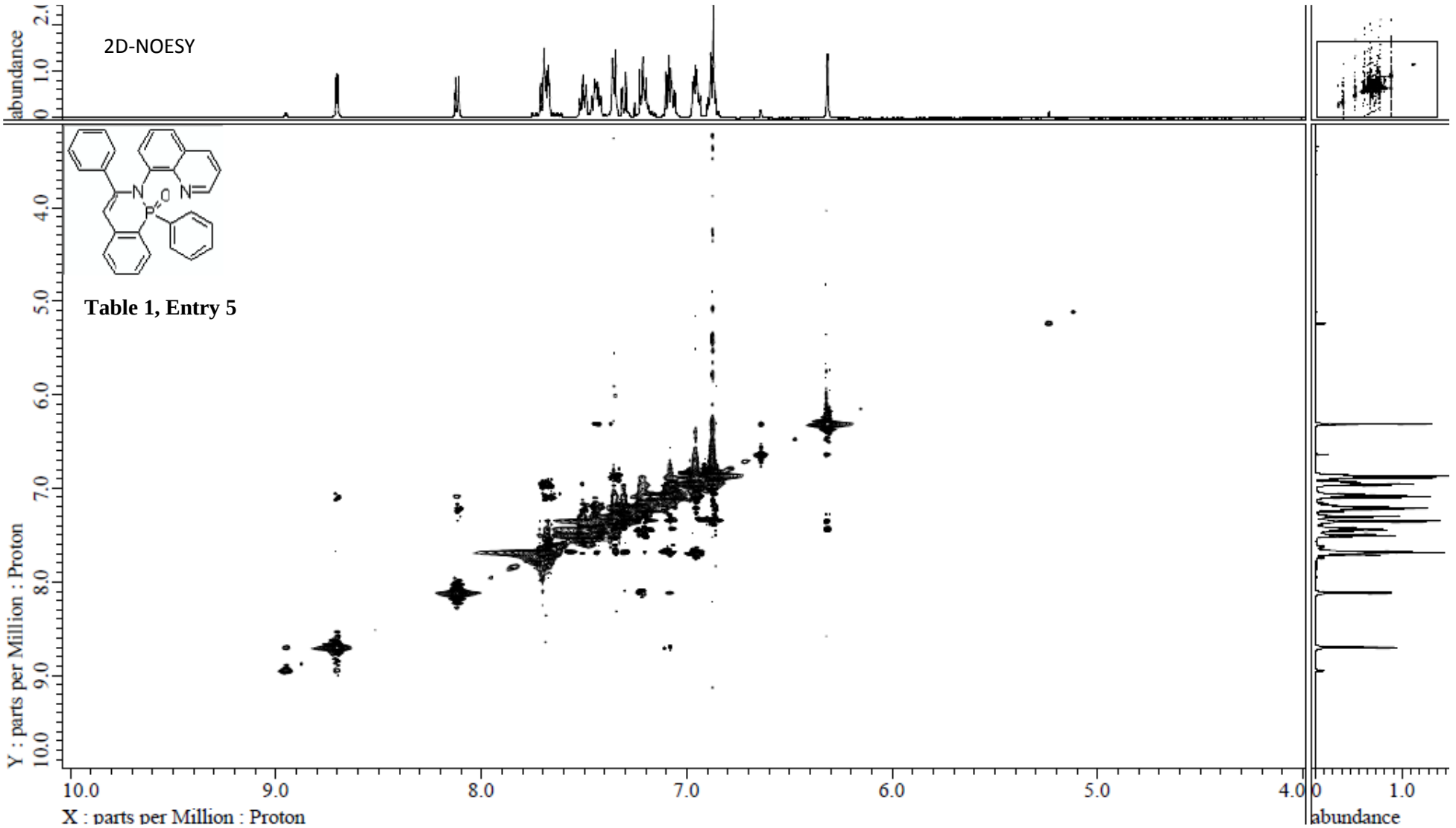


Table 1, Entry 5

Table 1, Entry 5



2D-COSY


2D-NOESY
abundance
Table 1, Entry 5
Y : parts per Million : Proton
X : parts per Million : Proton
10.0
9.0
8.0
7.0
6.0
5.0
4.0
1.0
0

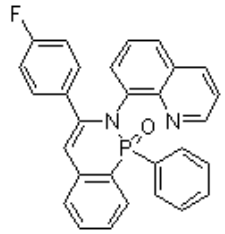
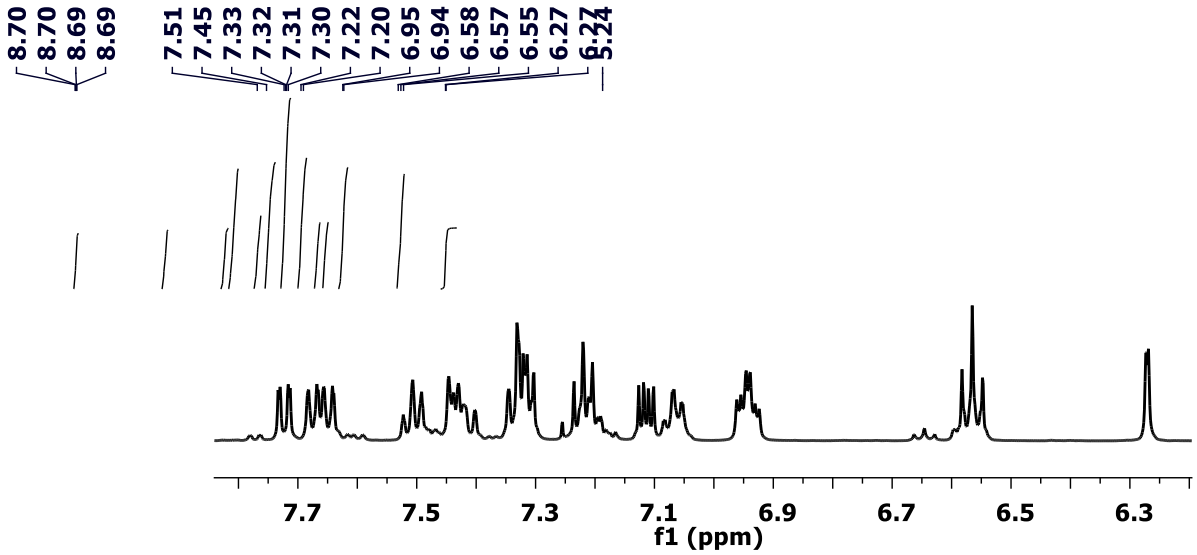
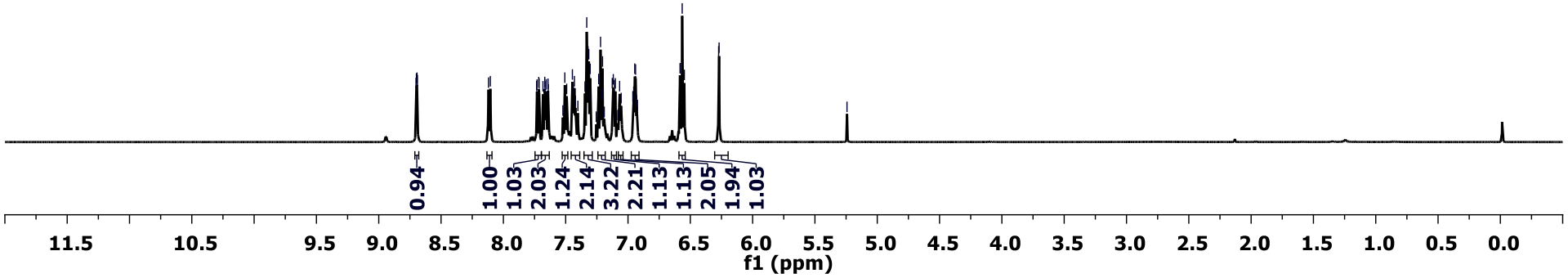


Table 1, Entry 6





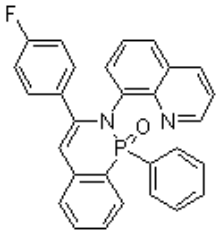


Table 1, Entry 6

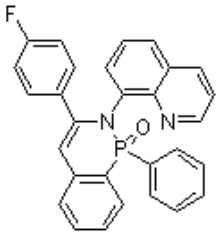


Table 1, Entry 6

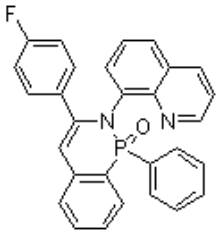
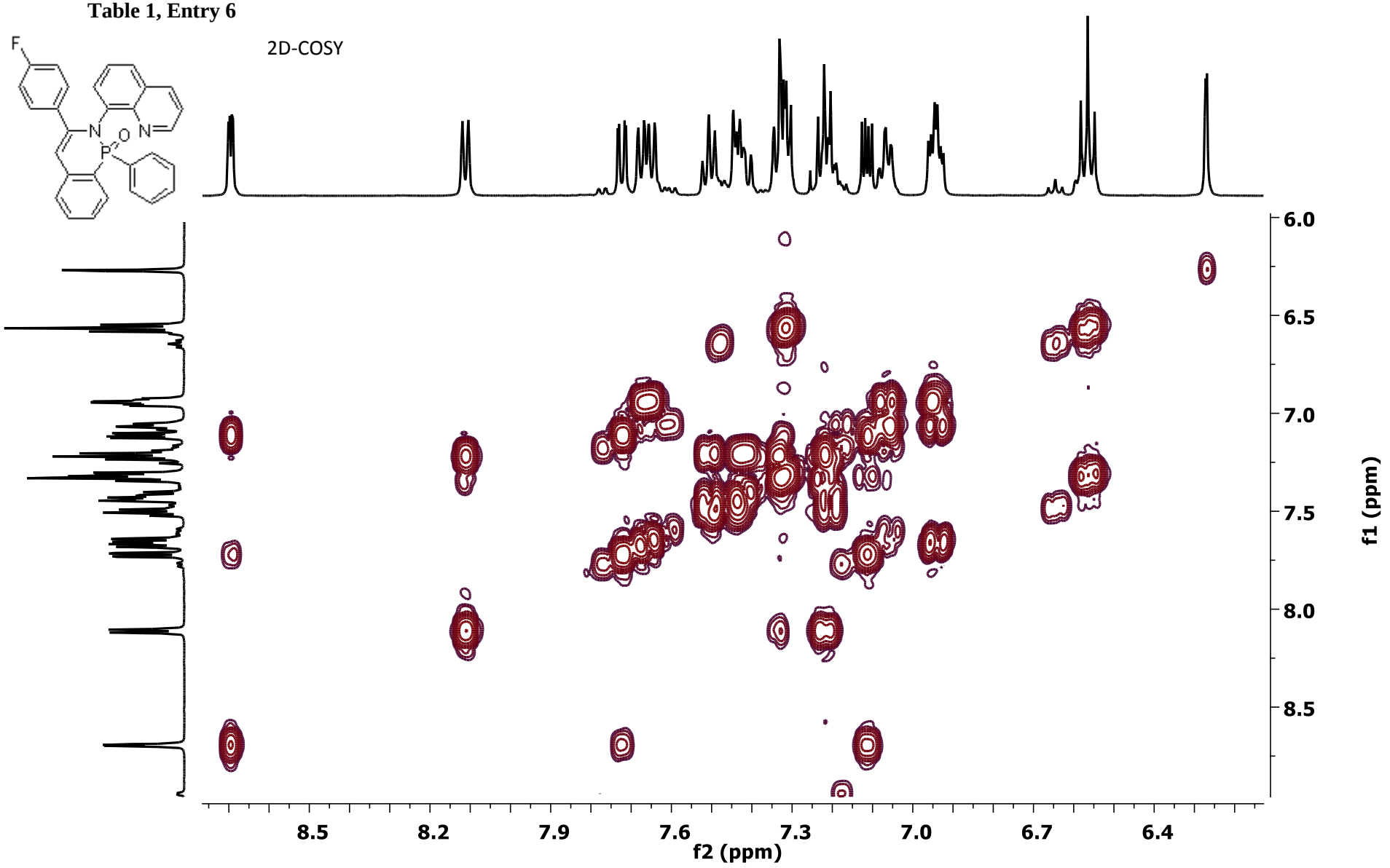
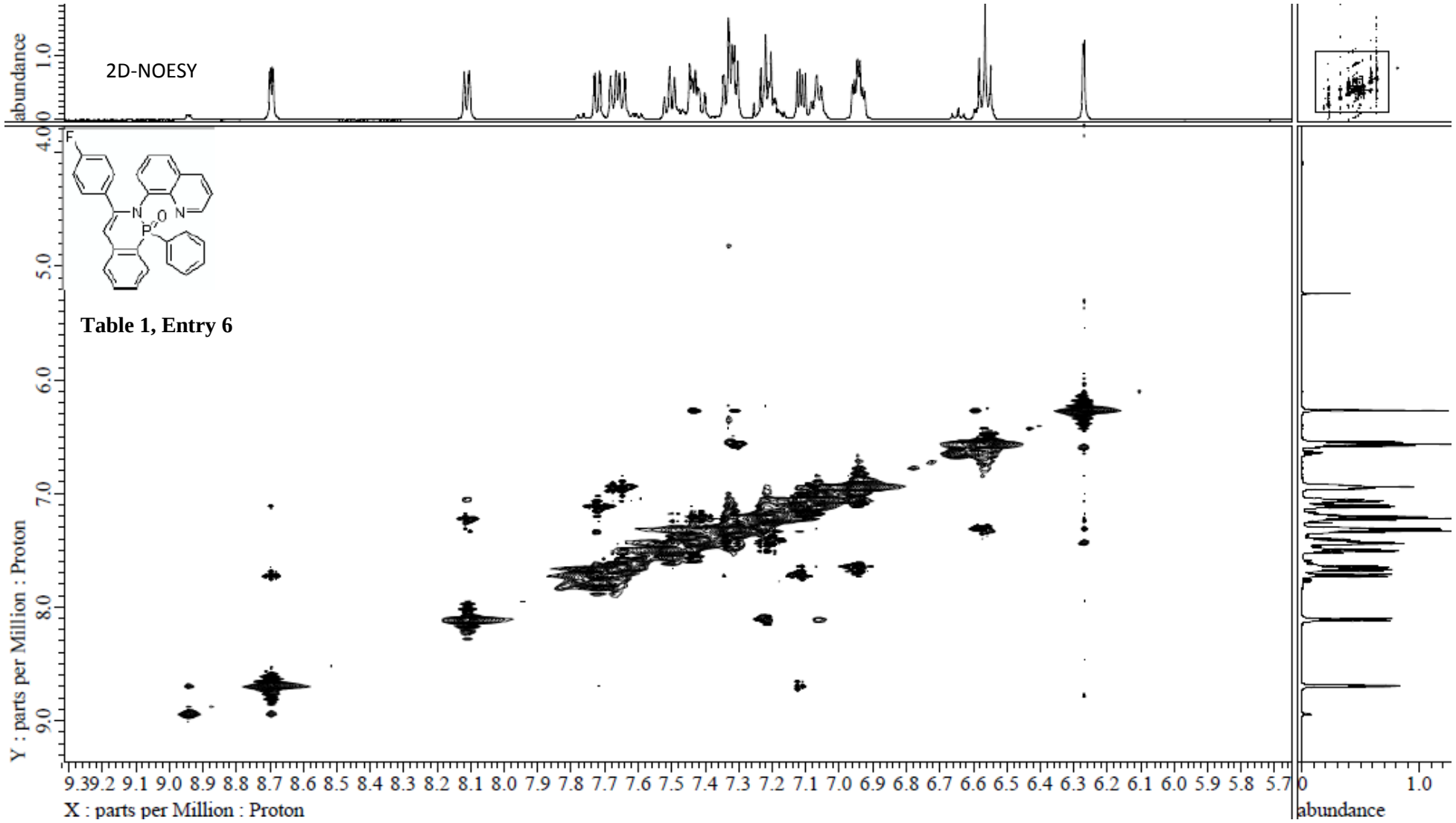
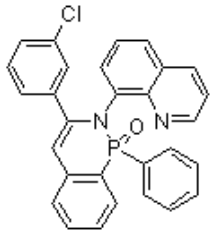


Table 1, Entry 6

Table 1, Entry 6




2D-NOESY
abundance
F
N
O
P
N
Table 1, Entry 6
Y : parts per Million : Proton
X : parts per Million : Proton
abundance



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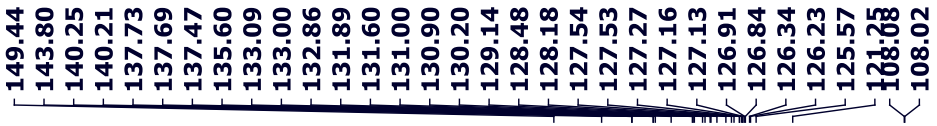


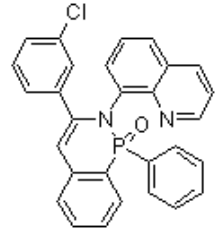
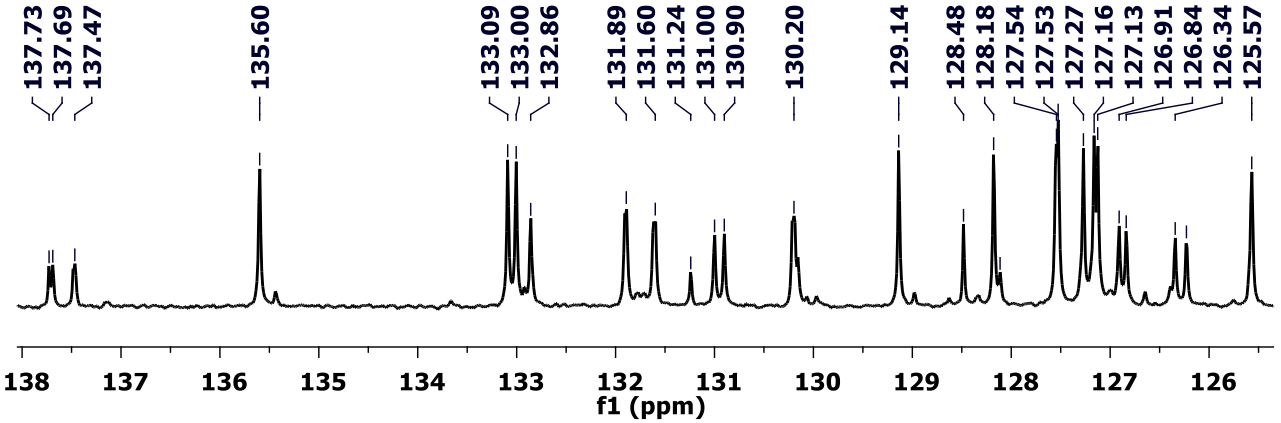
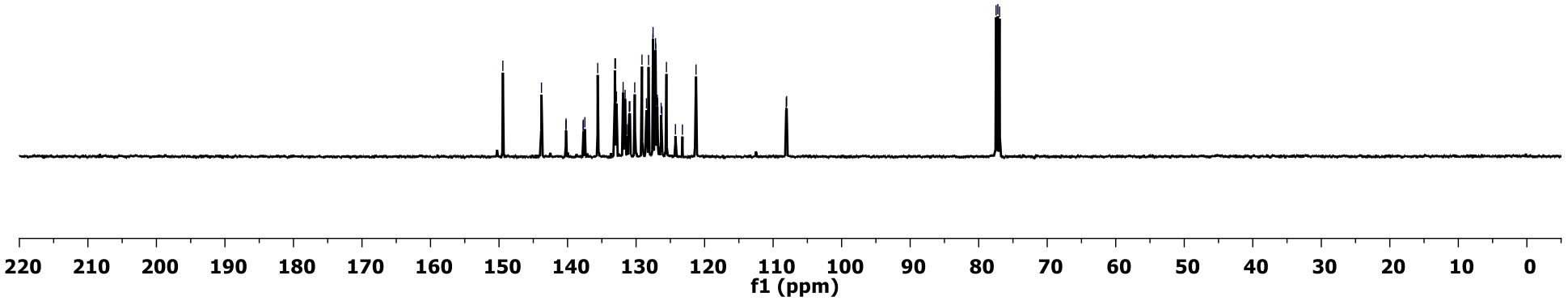


Table 1, Entry 7





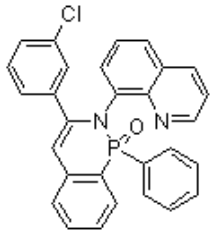
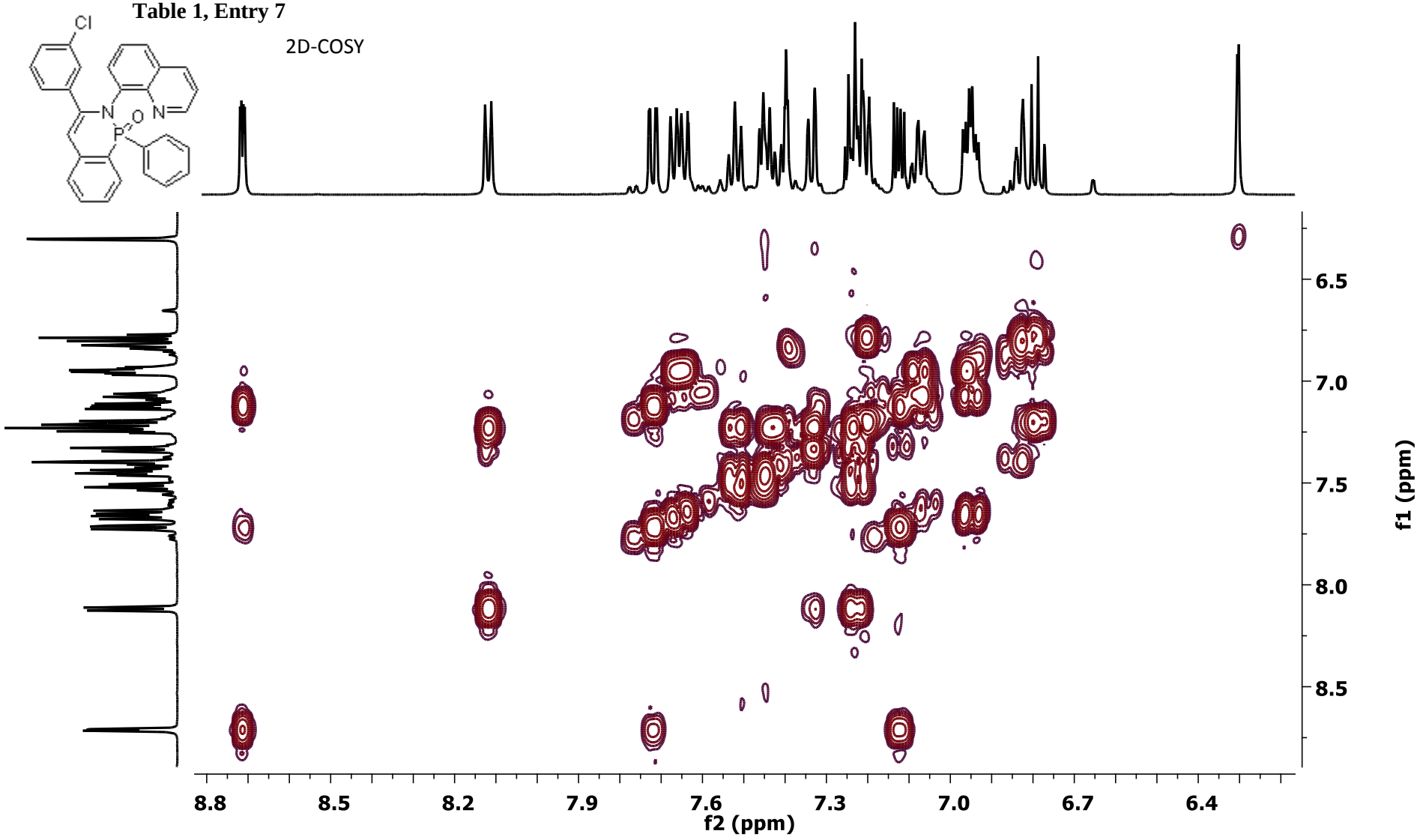
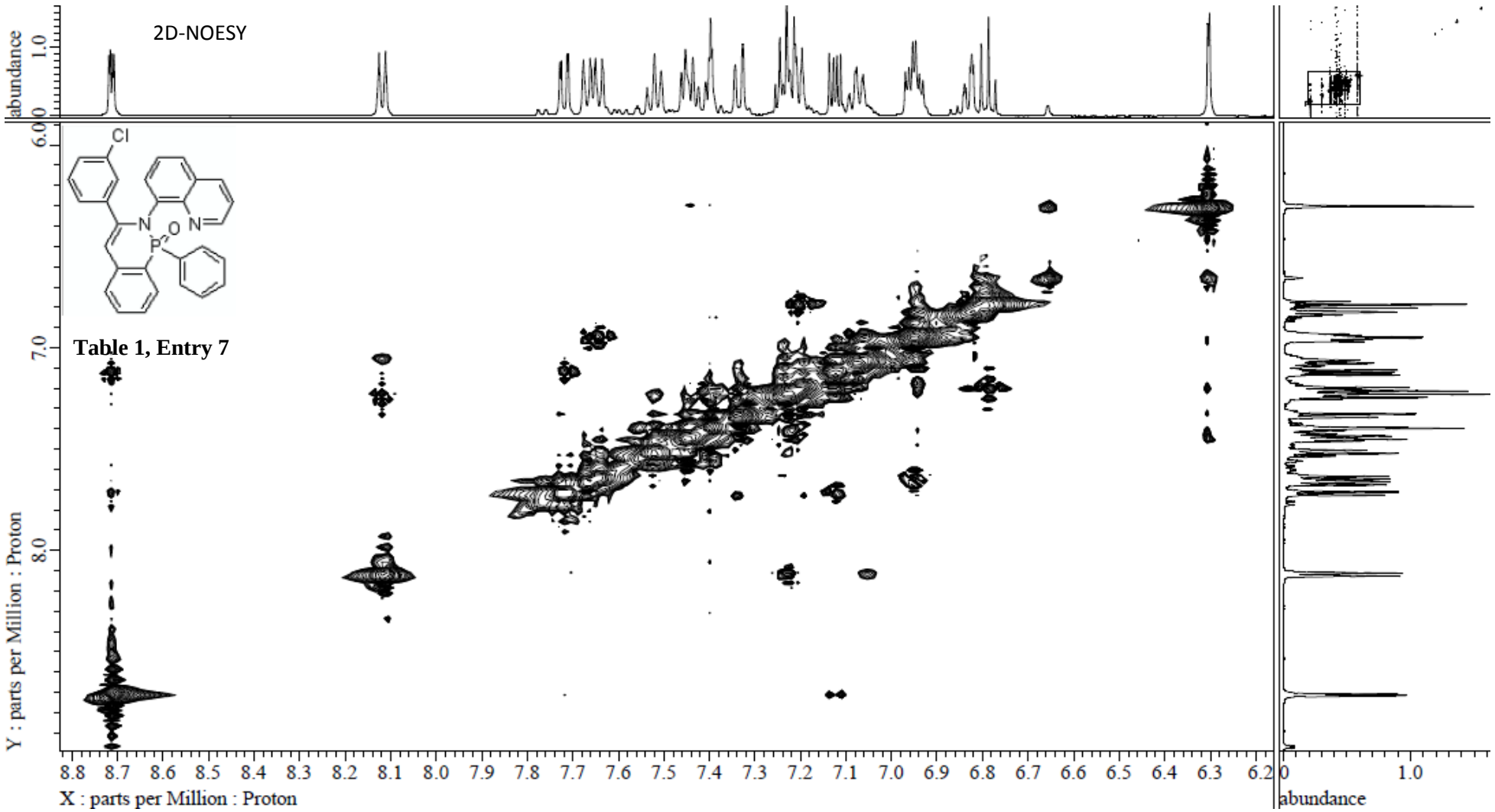
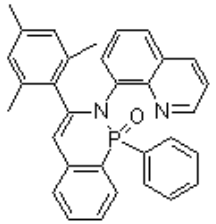


Table 1, Entry 7

Table 1, Entry 7




2D-NOESY
abundance
1.0
0
Cl
N
O
N
P
Table 1, Entry 7
6.0
7.0
8.0
Y : parts per Million : Proton
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2
X : parts per Million : Proton
0
1.0
abundance



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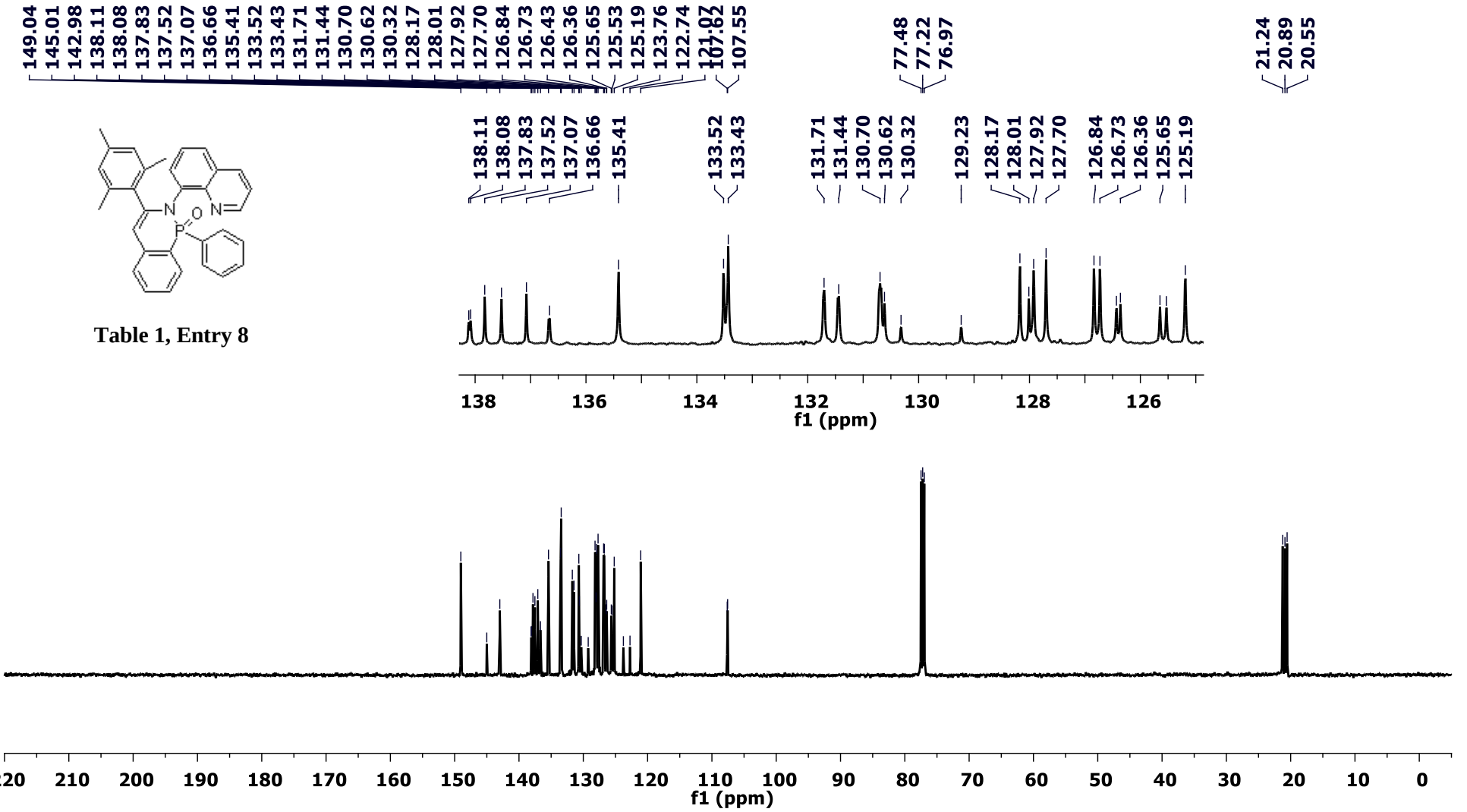

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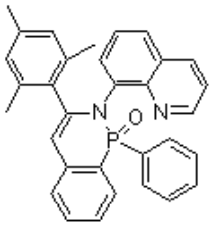
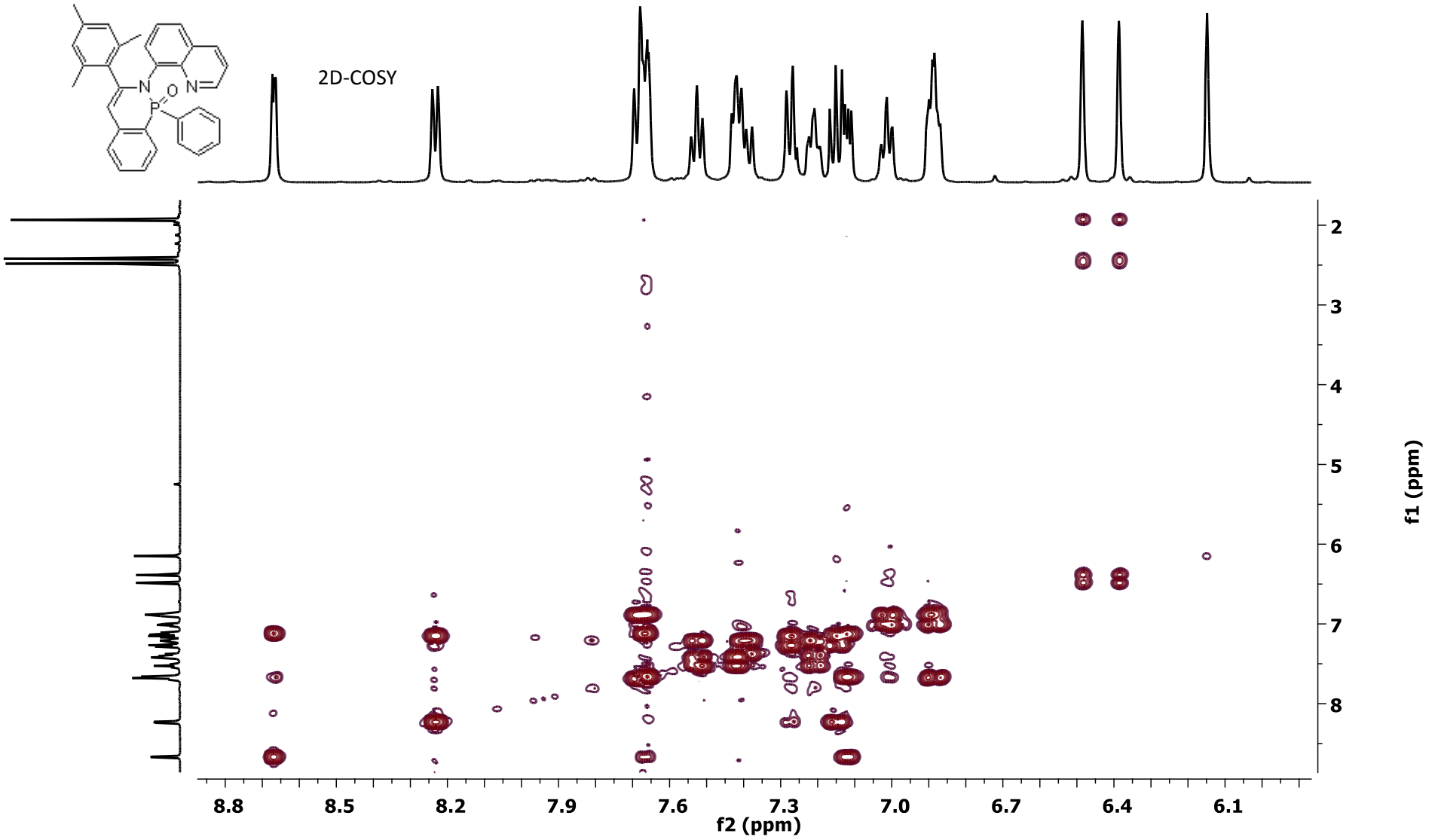


Table 1, Entry 8

Table 1, Entry 8



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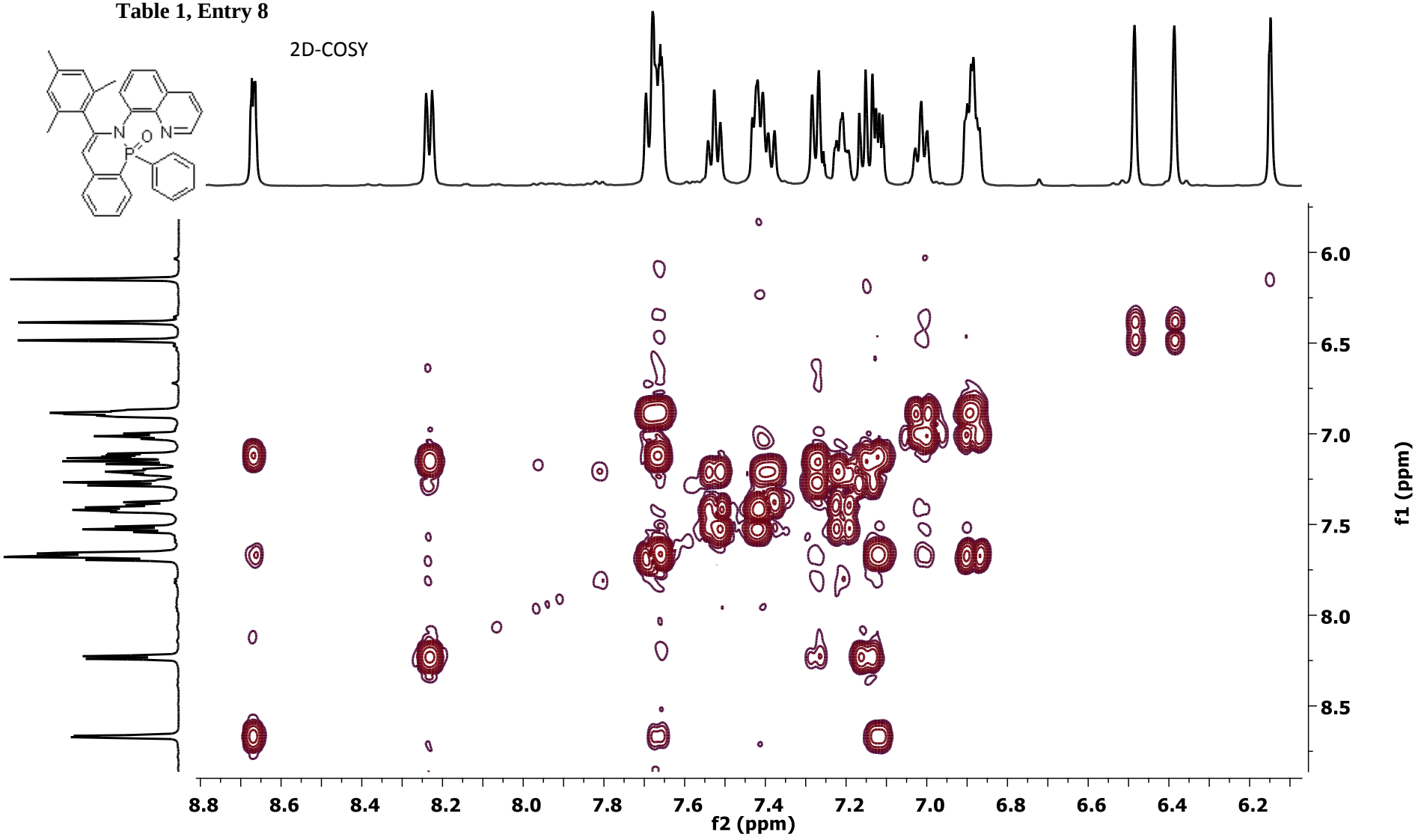
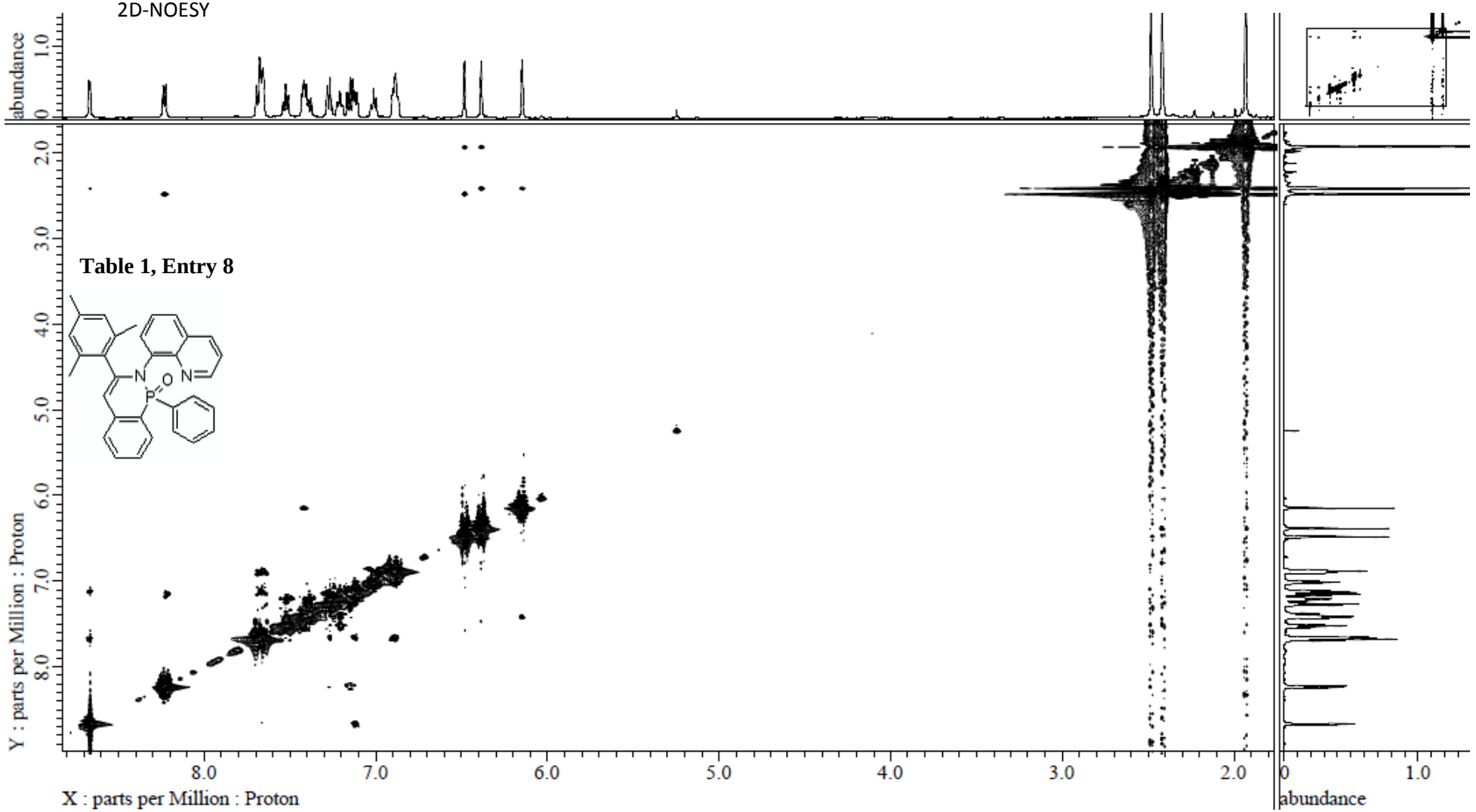


2D-NOESY



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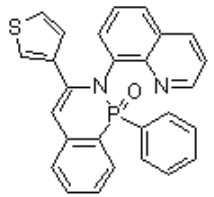
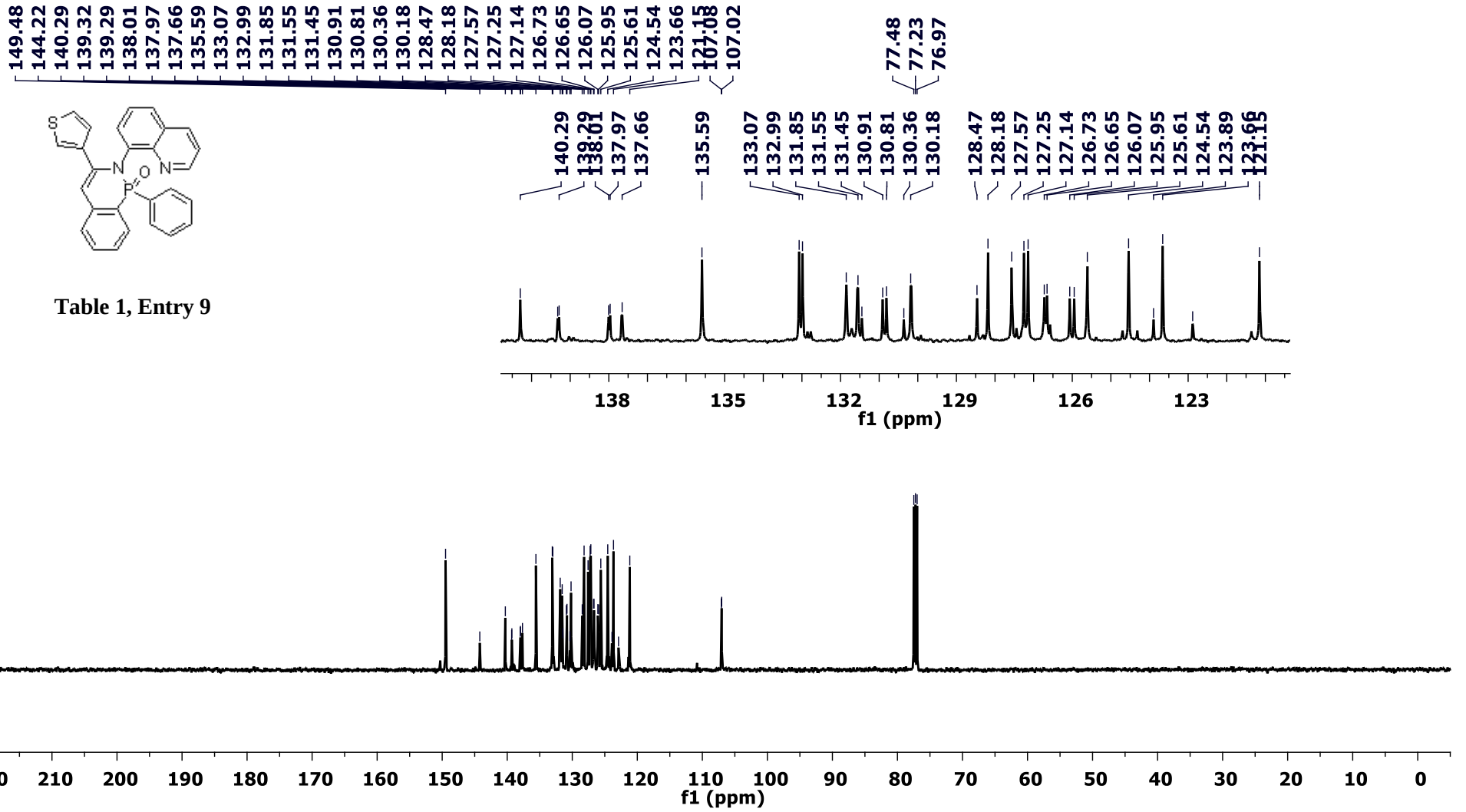


Table 1, Entry 9



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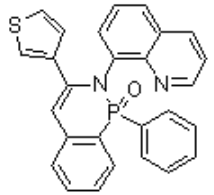
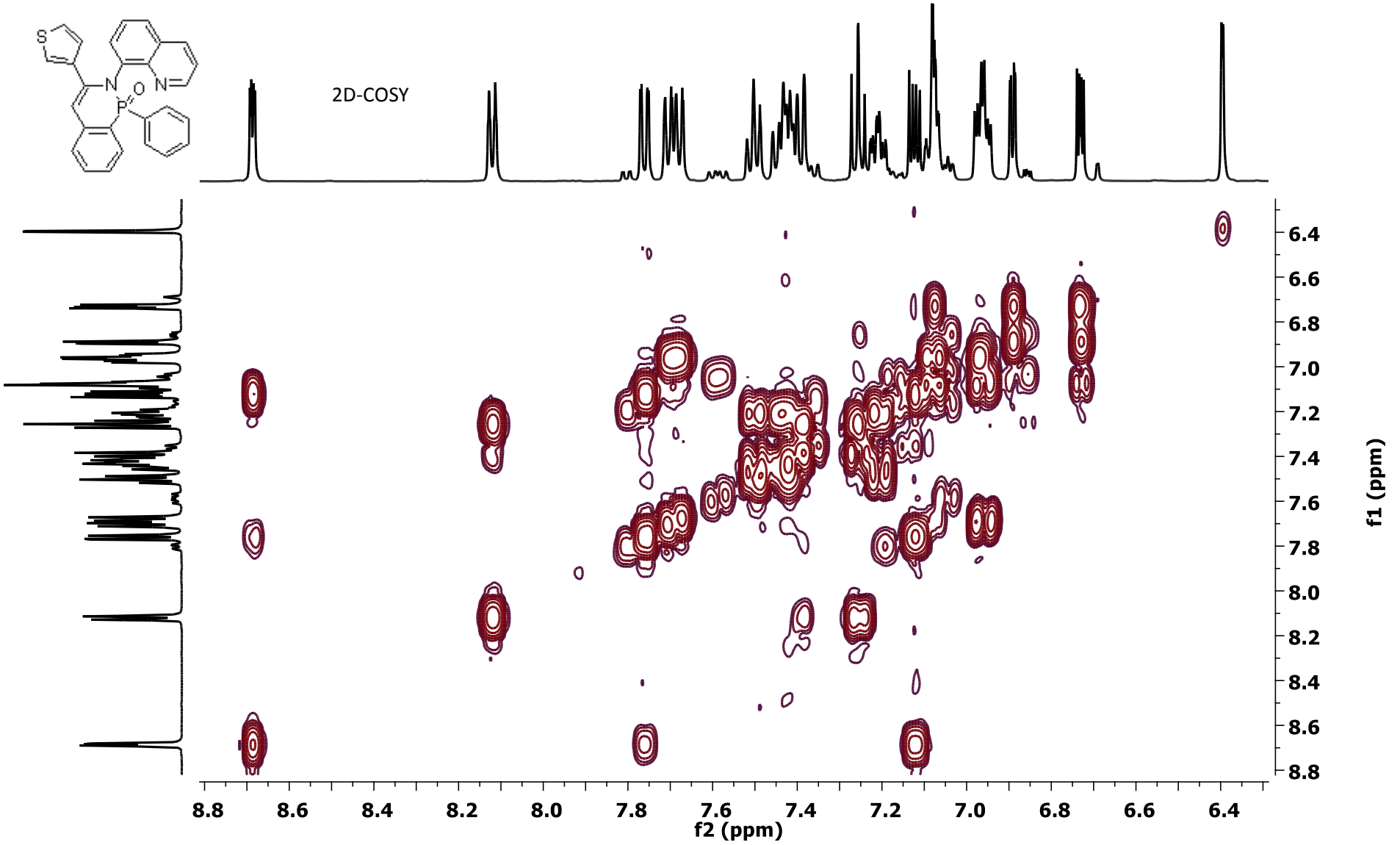
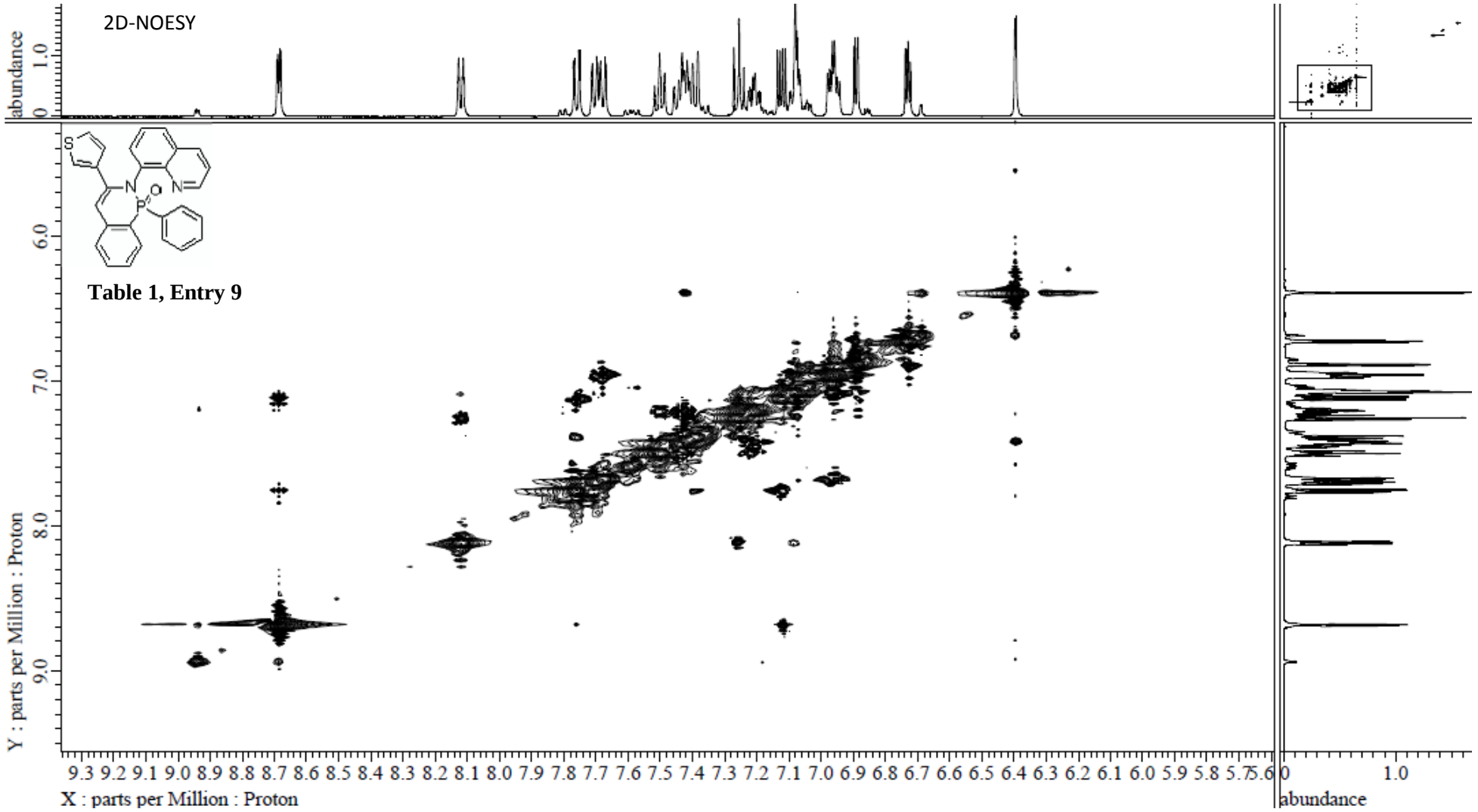


Table 1, Entry 9

Table 1, Entry 9





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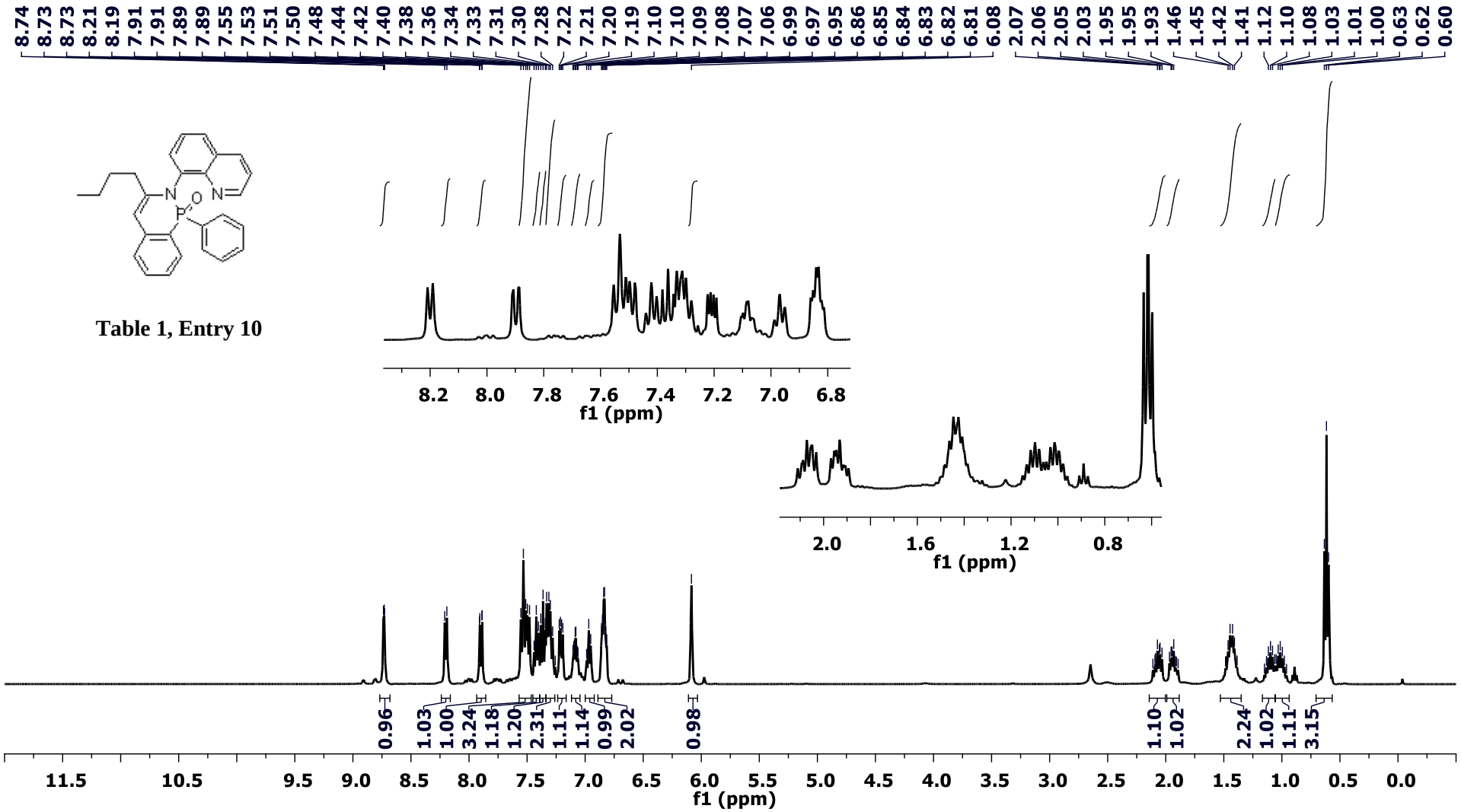

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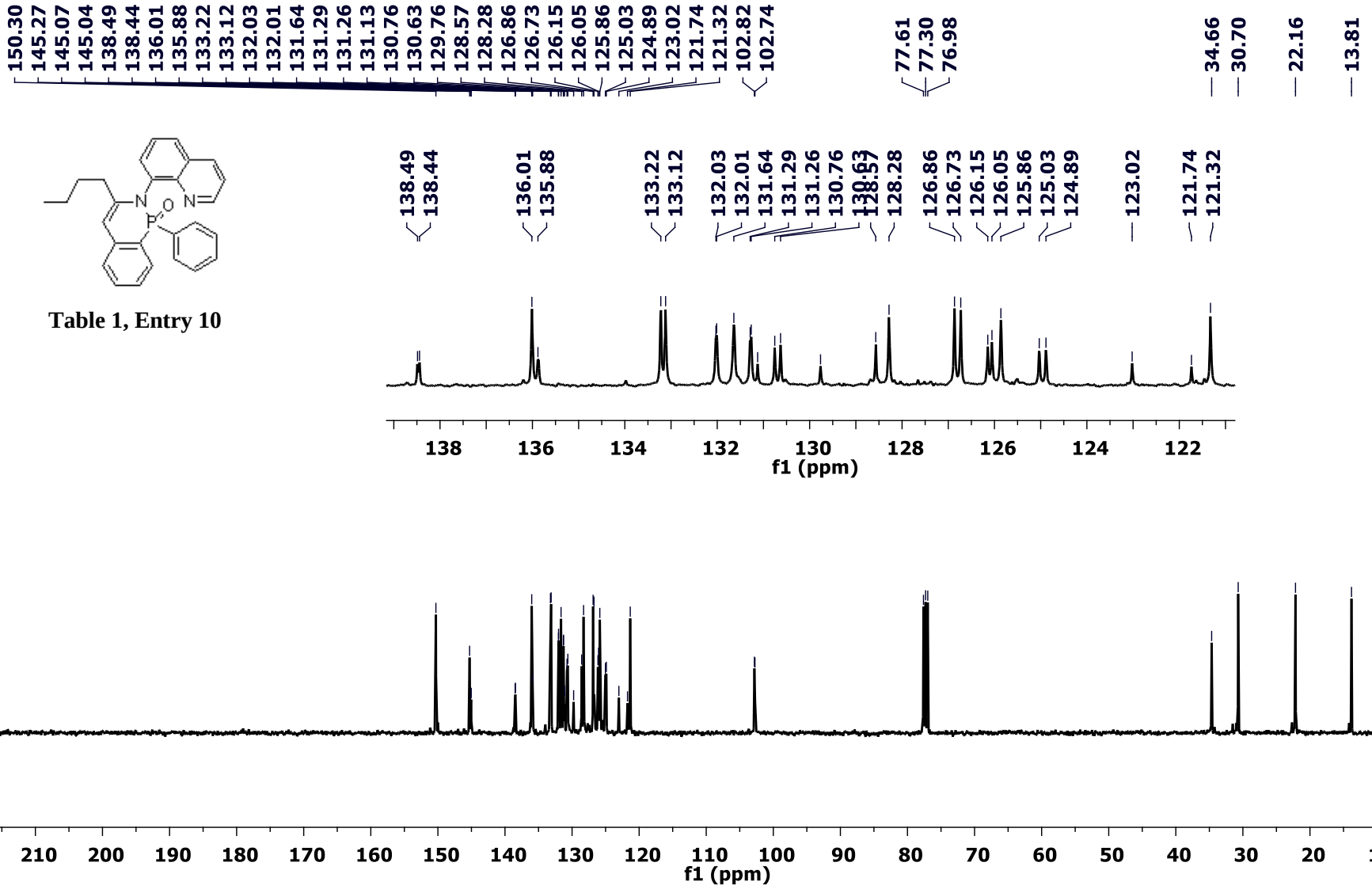


Table 1, Entry 10

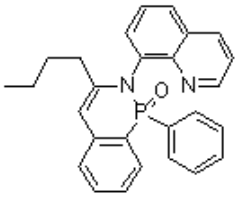


Table 1, Entry 10

Table 1, Entry 10

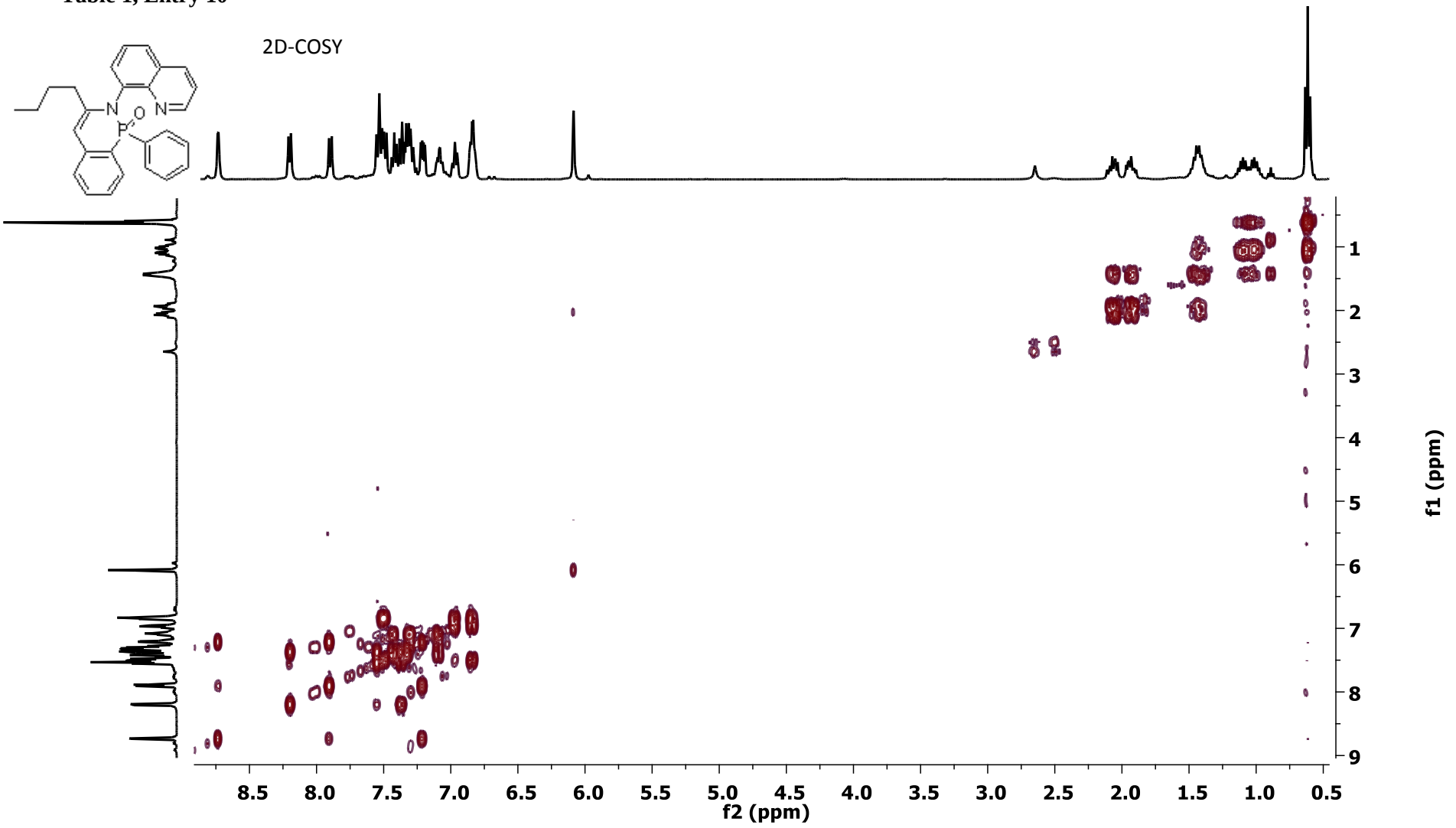
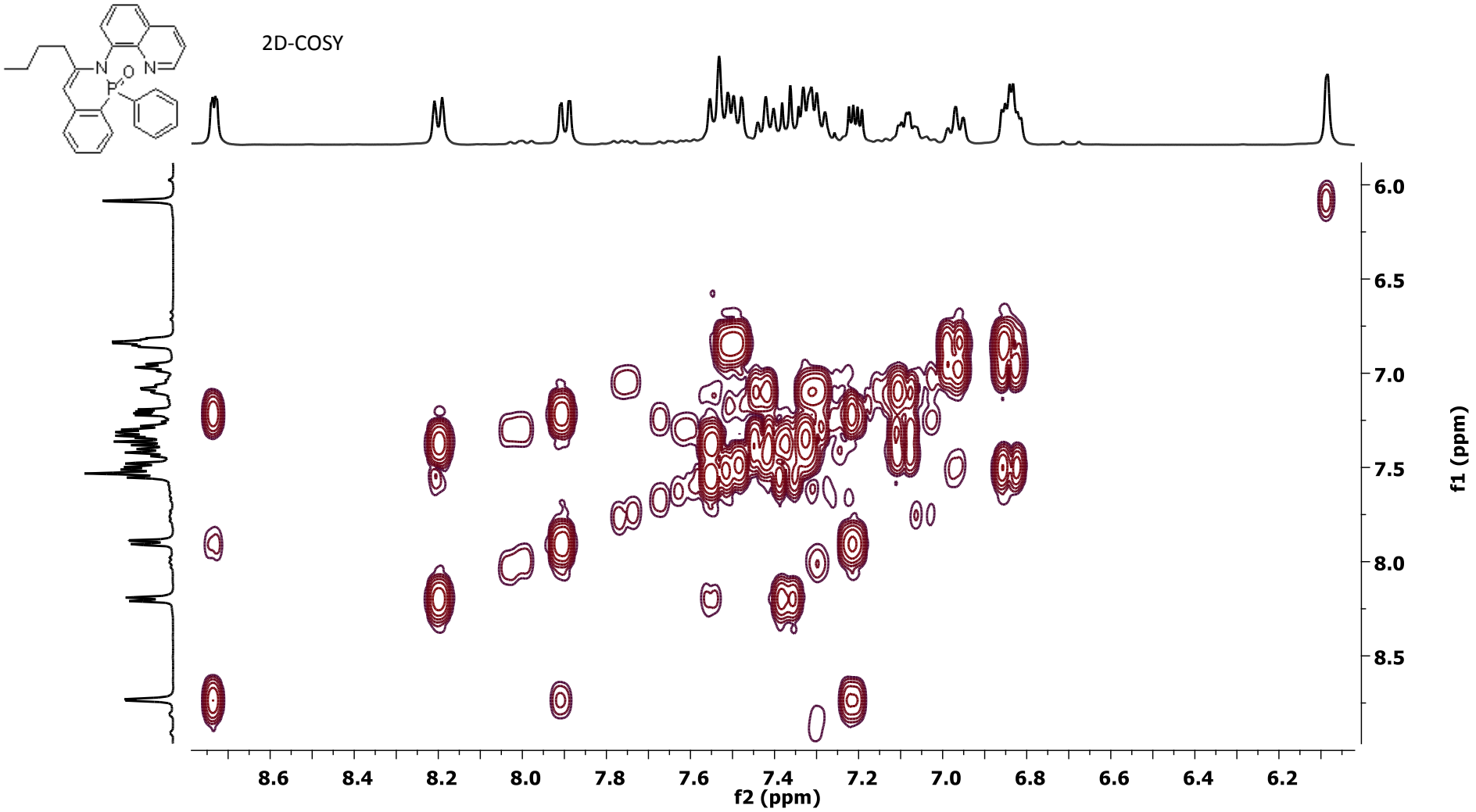
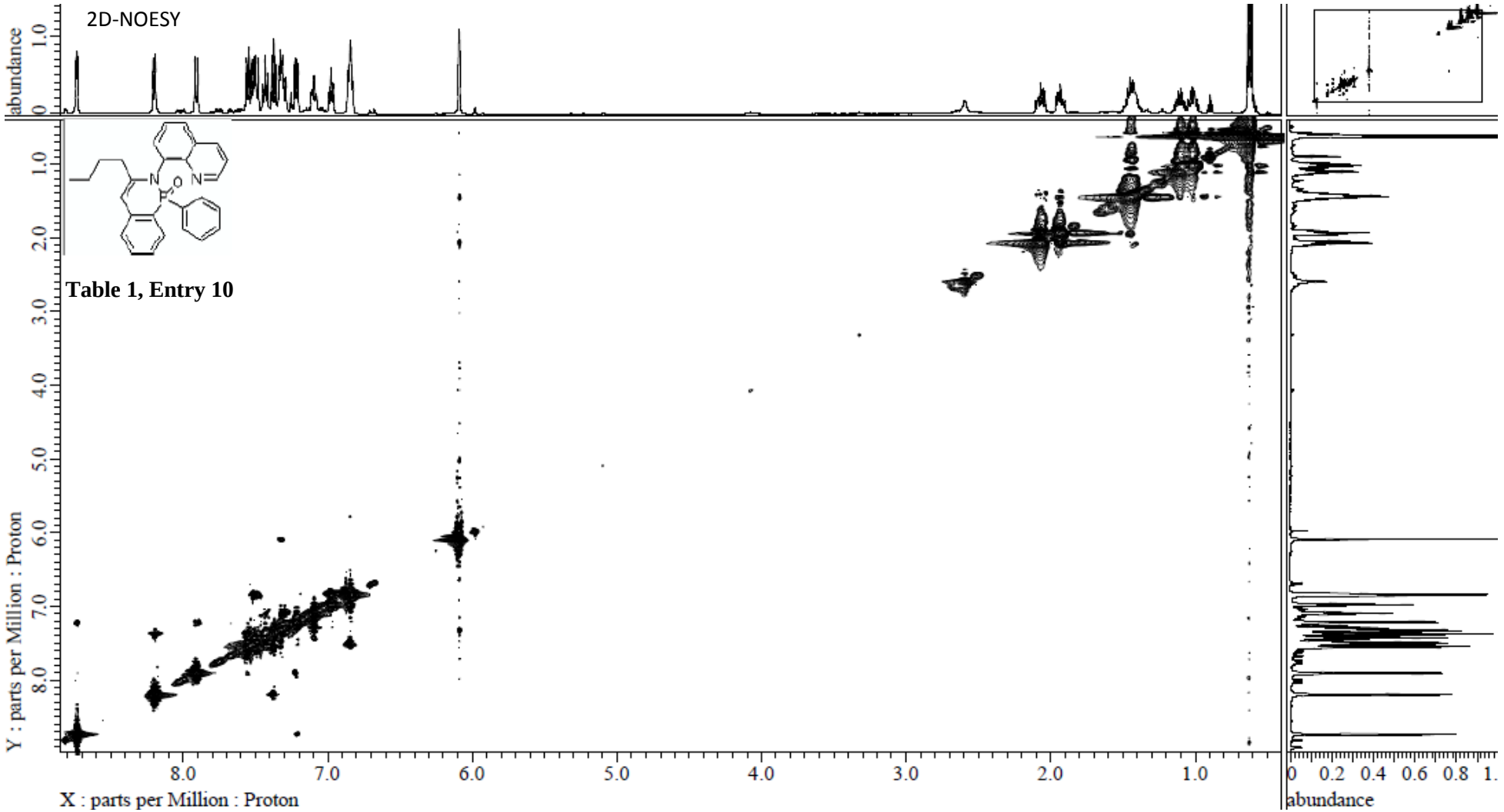


Table 1, Entry 10




2D-NOESY
abundance
Table 1, Entry 10
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

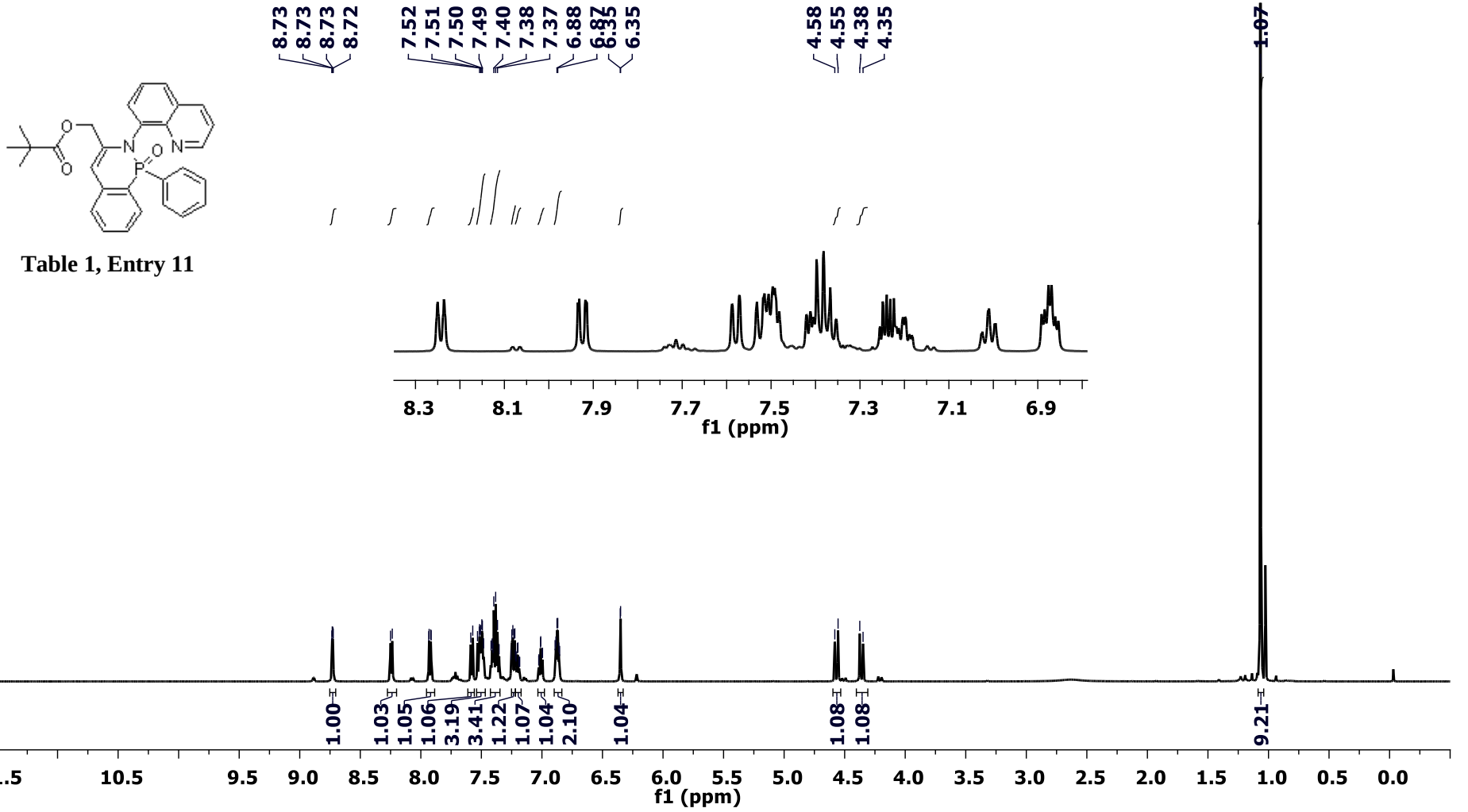


Table 1, Entry 11

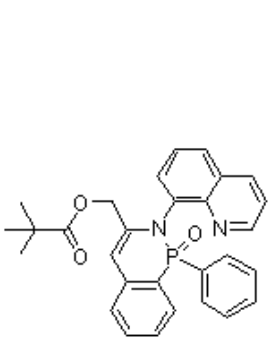


Table 1, Entry 11

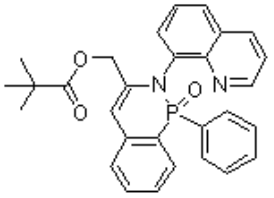
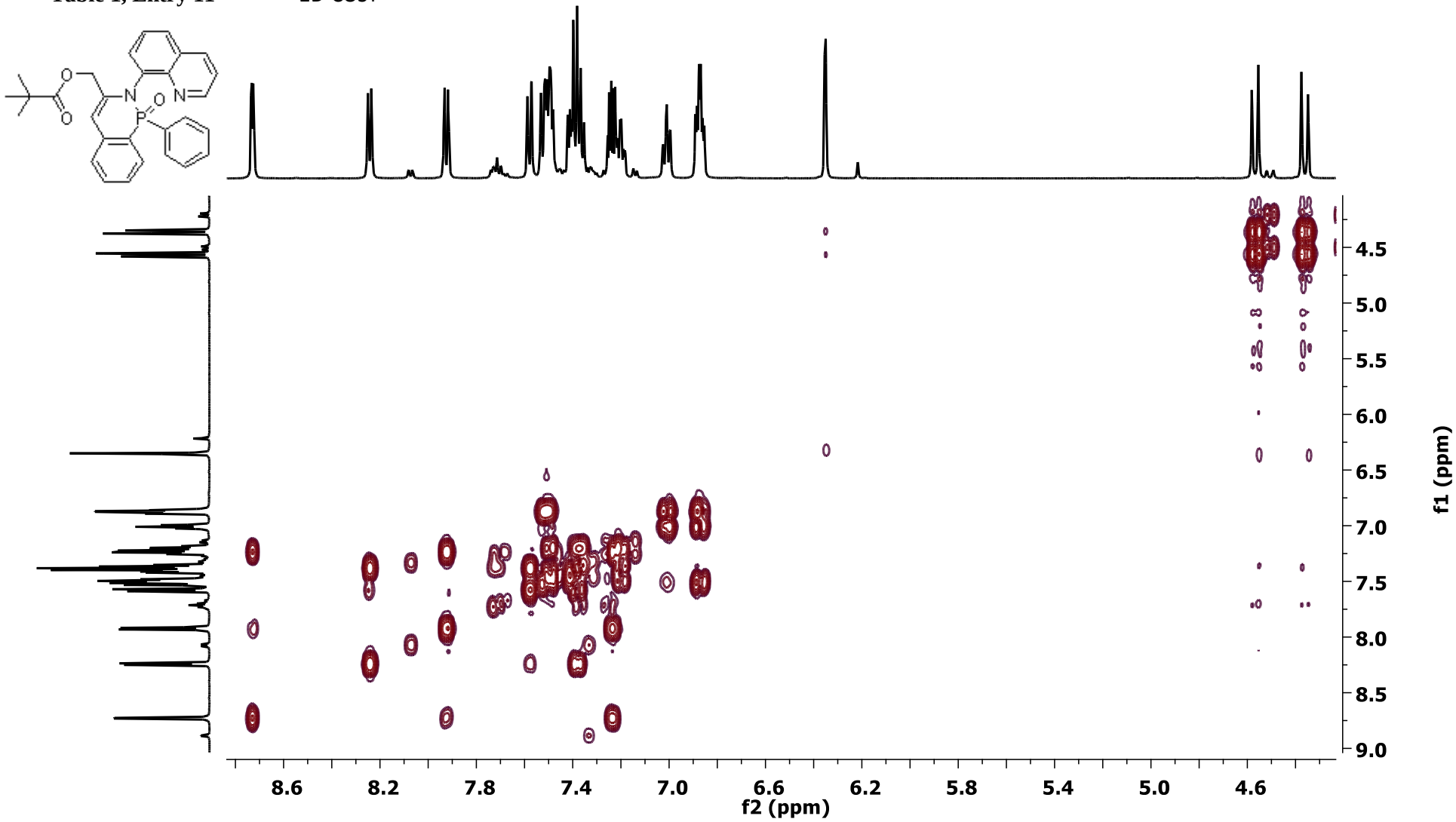
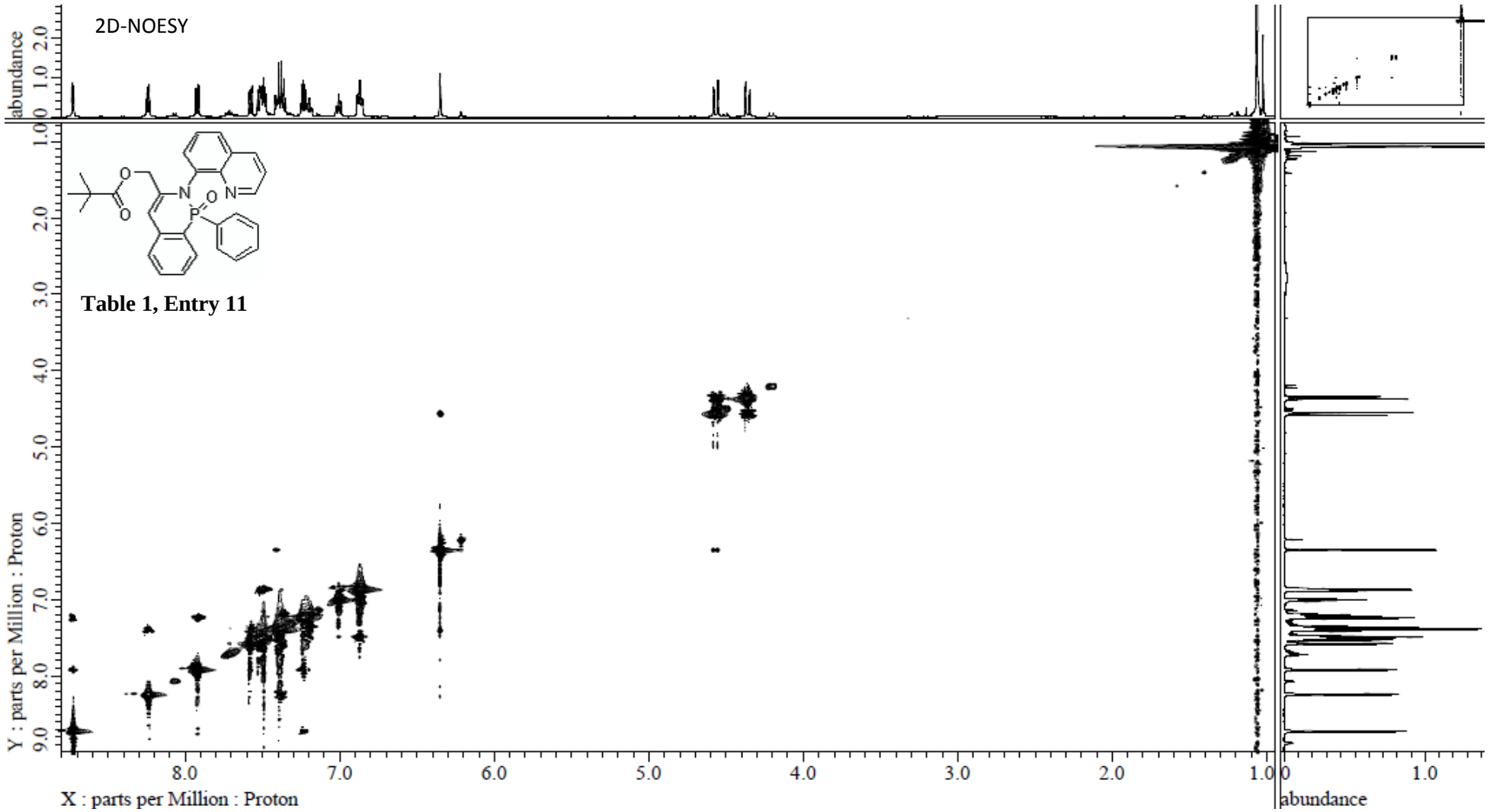


Table 1, Entry 11

Table 1, Entry 11 2D-COSY




2D-NOESY
abundance
Table 1, Entry 11
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

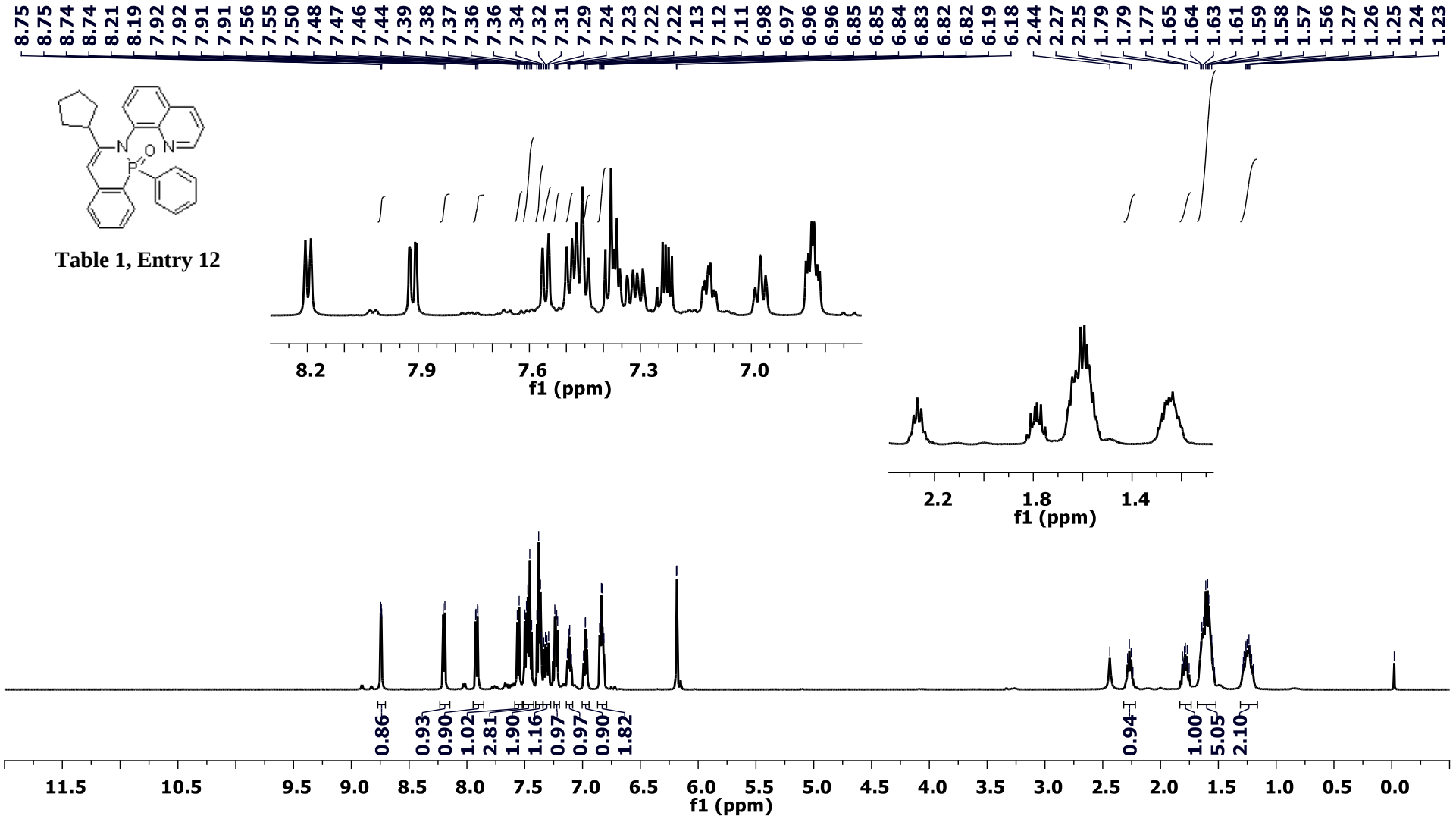


Table 1, Entry 12

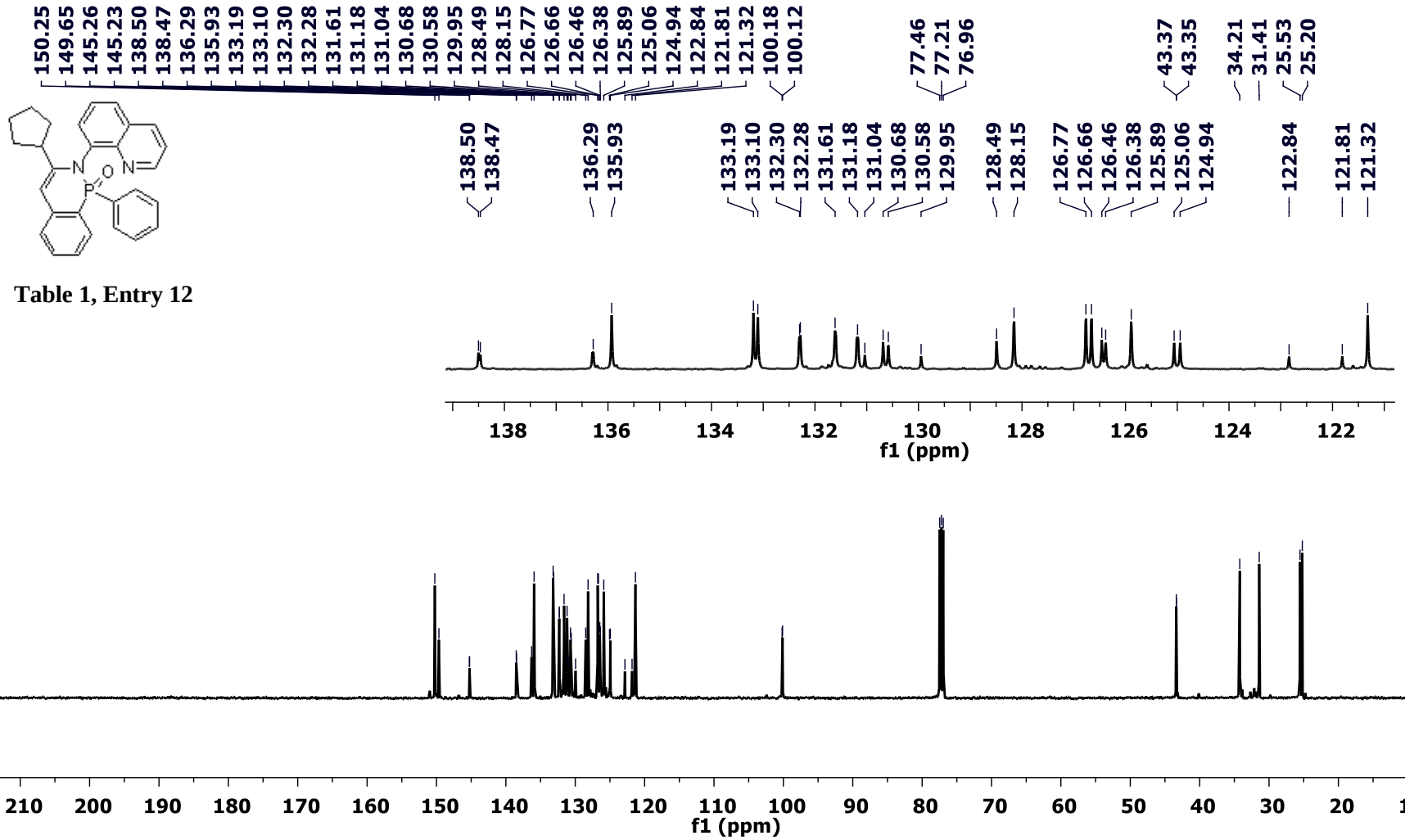


Table 1, Entry 12

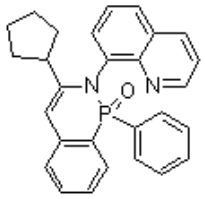


Table 1, Entry 12

Table 1, Entry 12

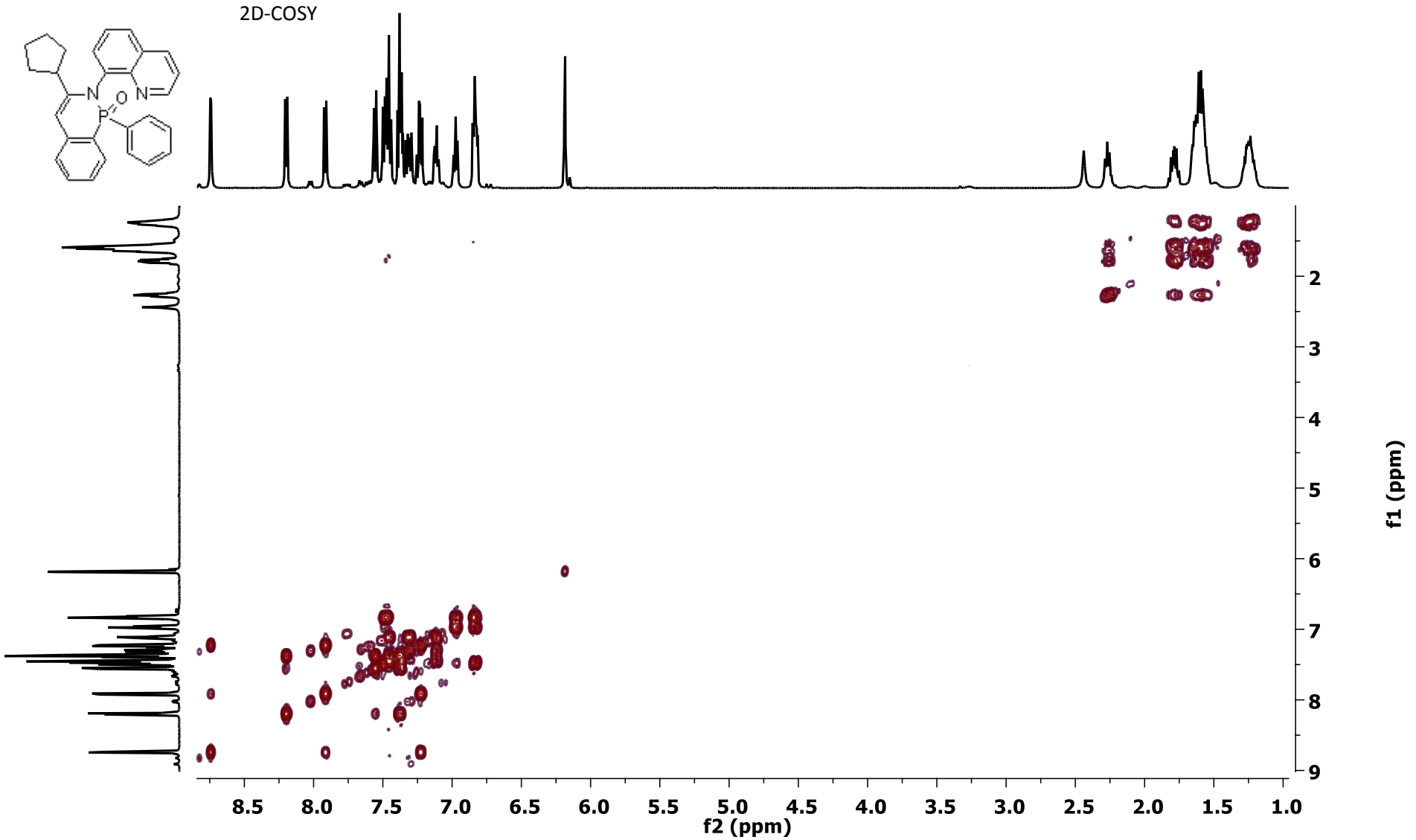
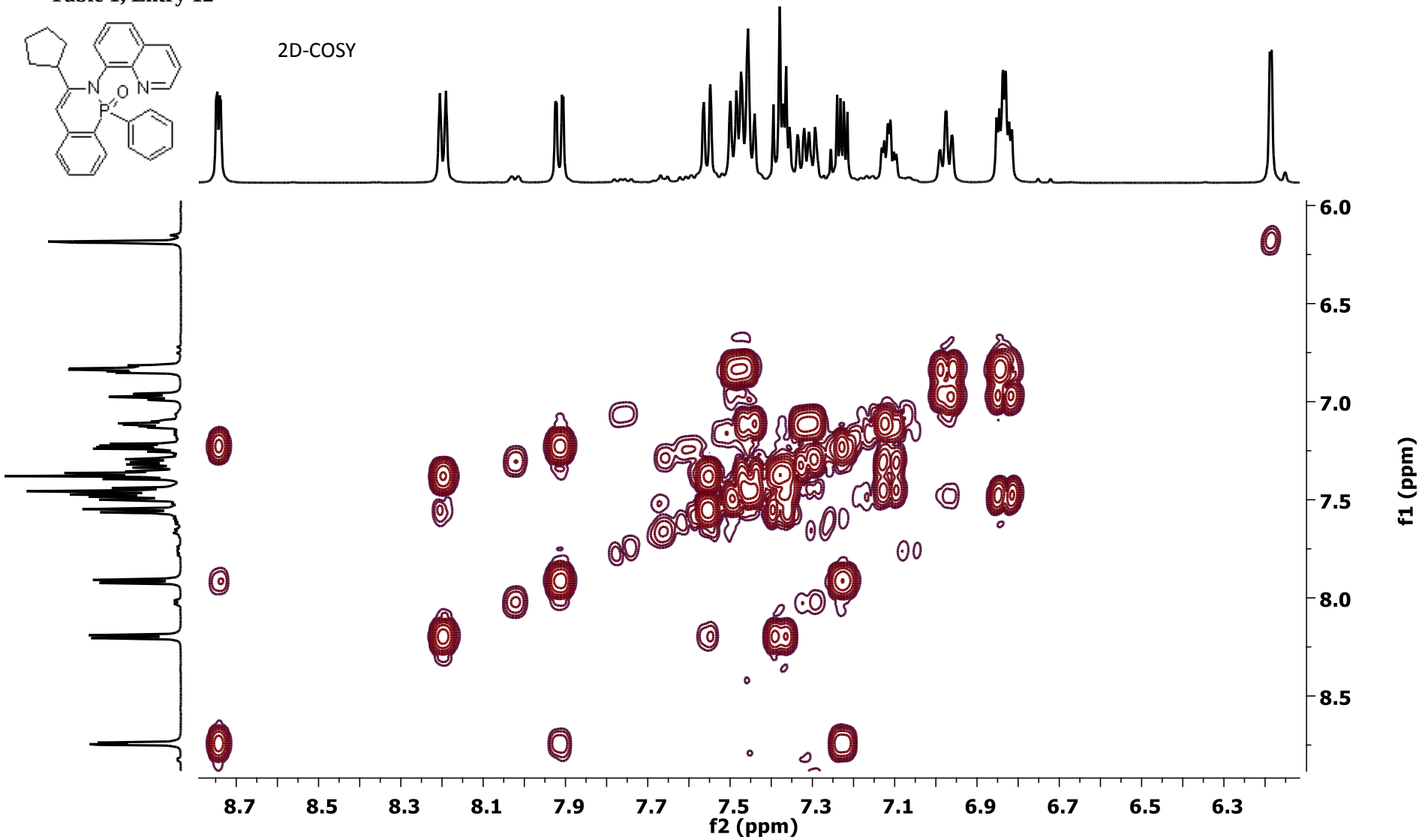
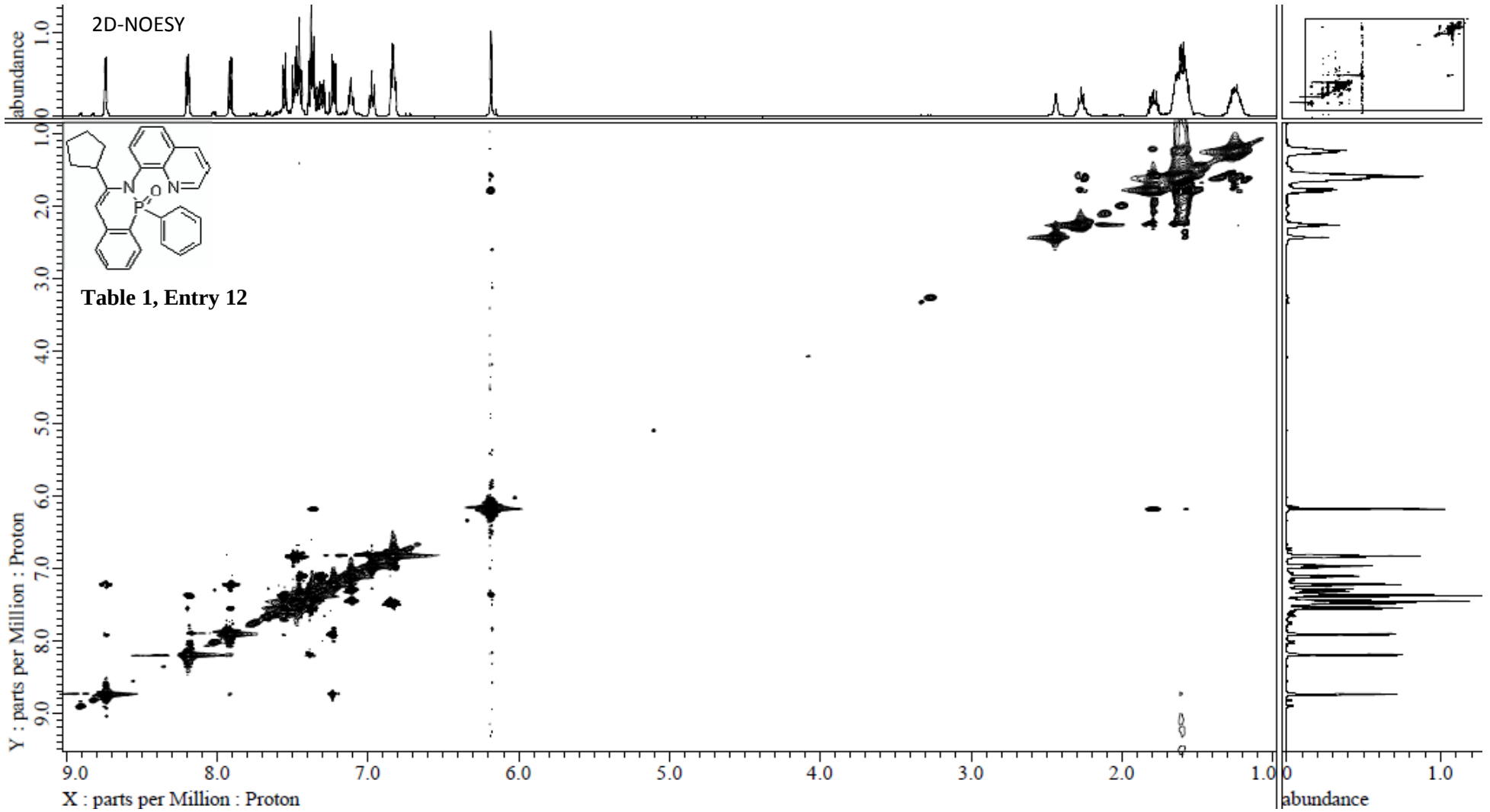


Table 1, Entry 12




2D-NOESY
abundance
Table 1, Entry 12
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

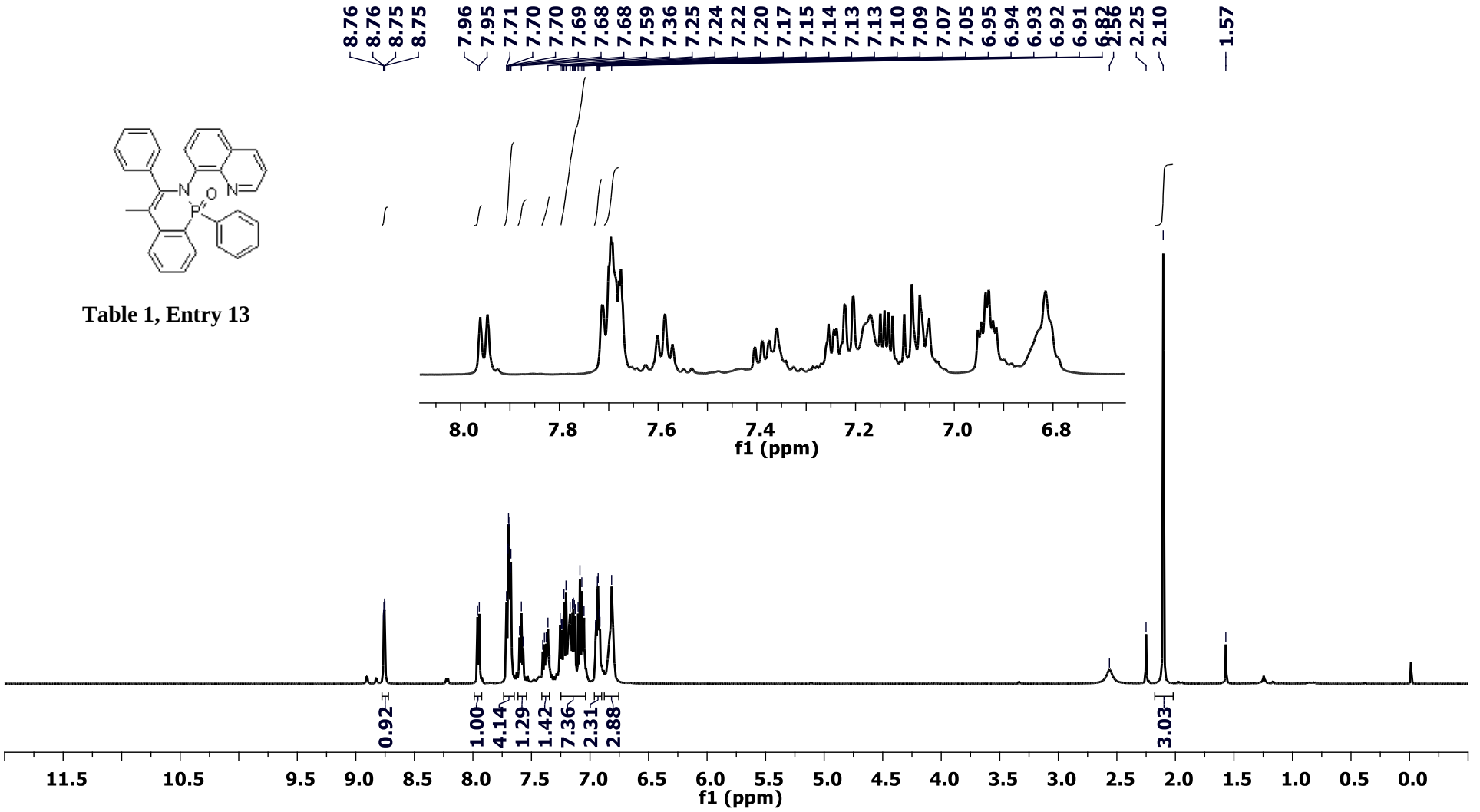


Table 1, Entry 13

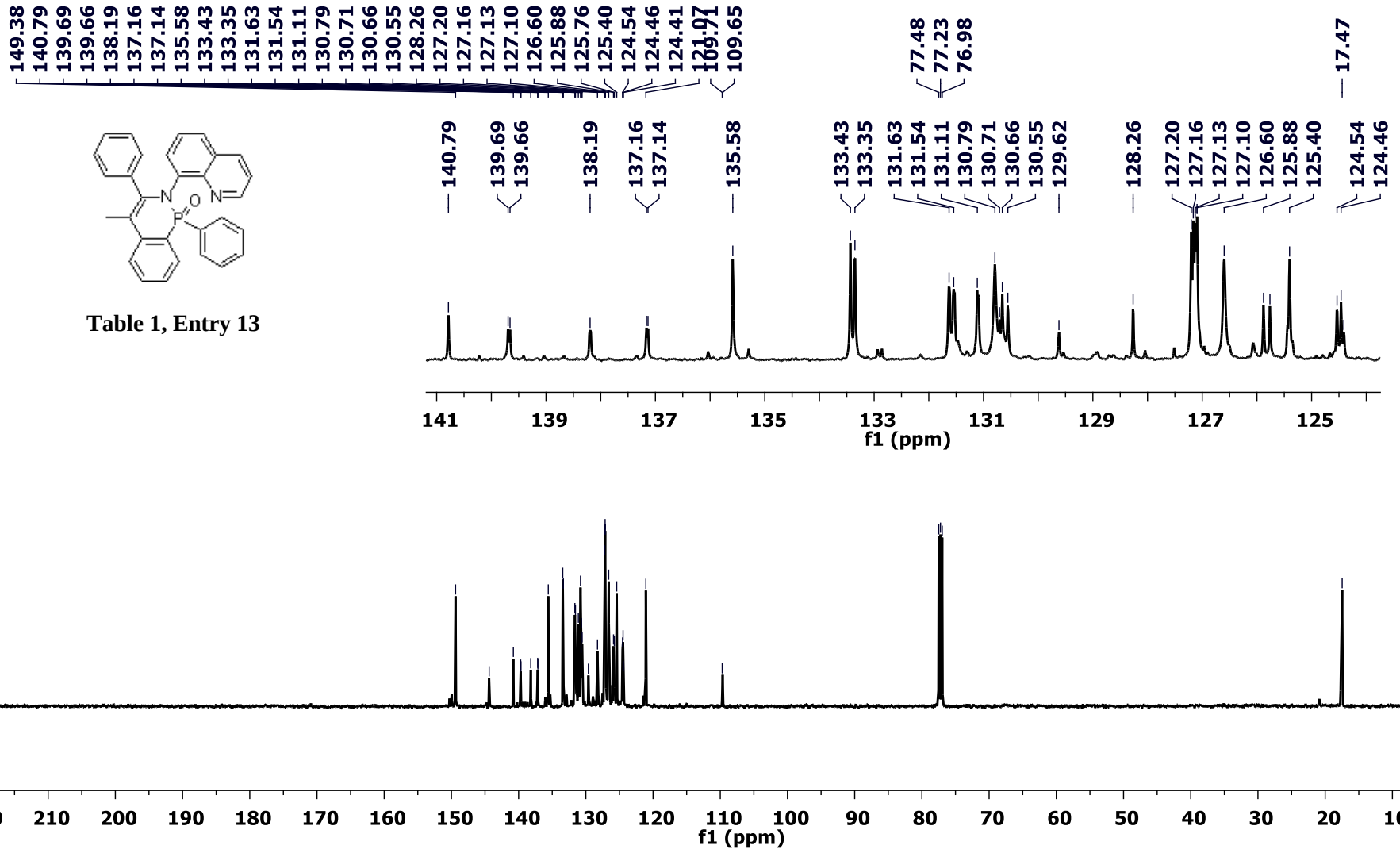


Table 1, Entry 13

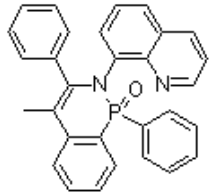
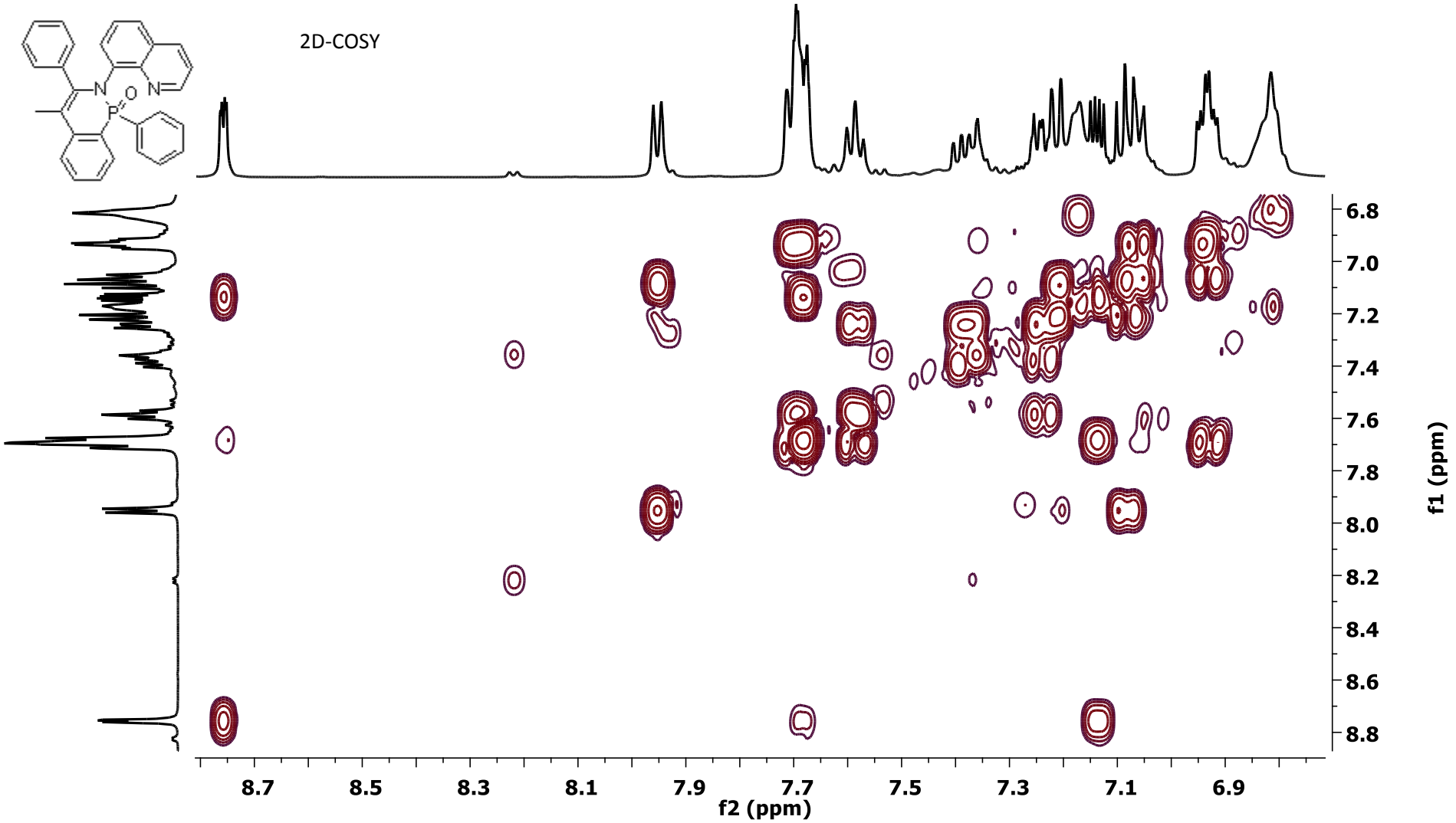
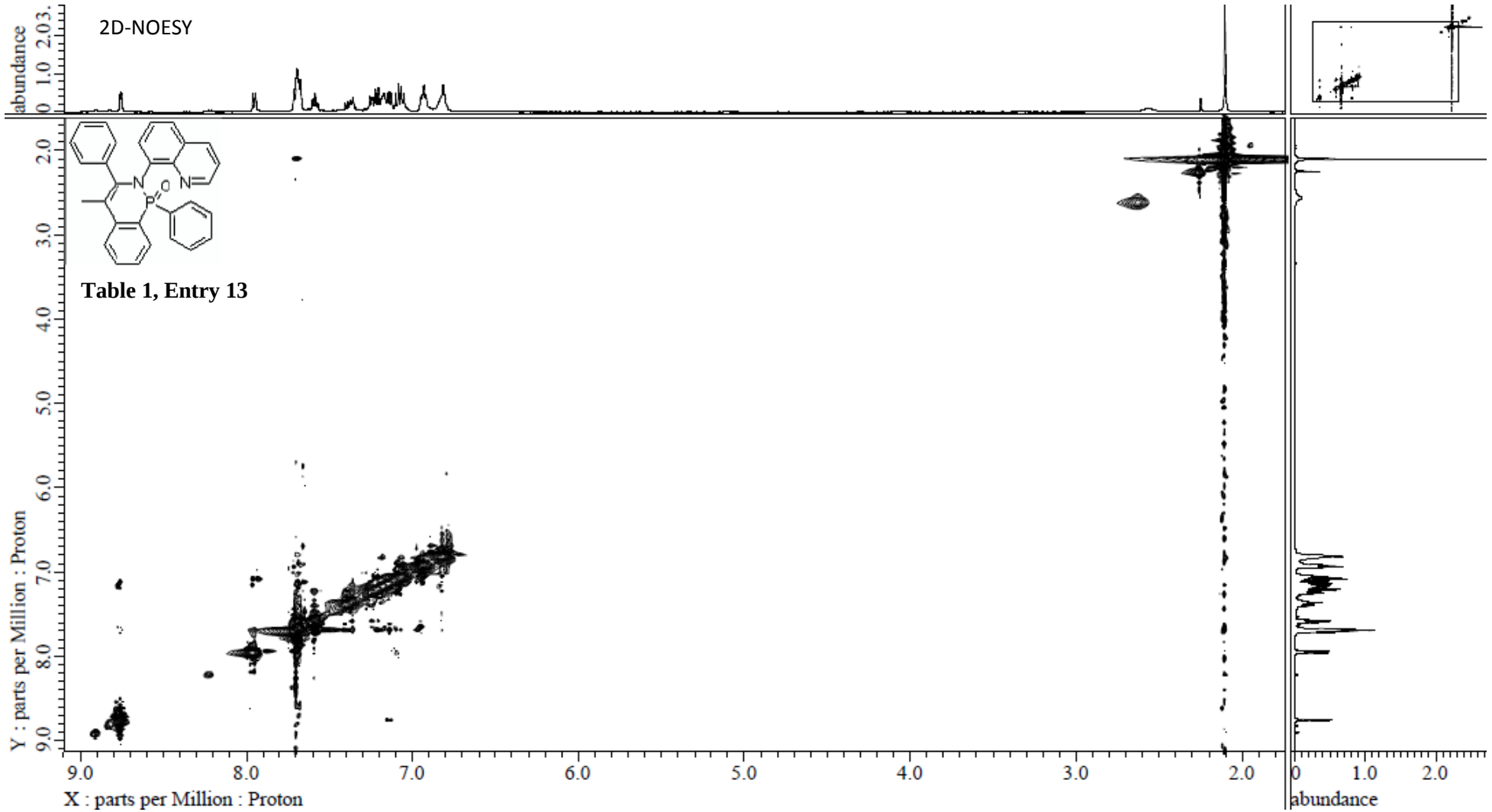
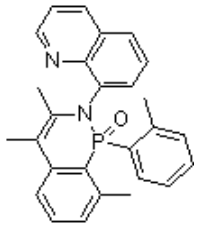


Table 1, Entry 13

Table 1, Entry 13

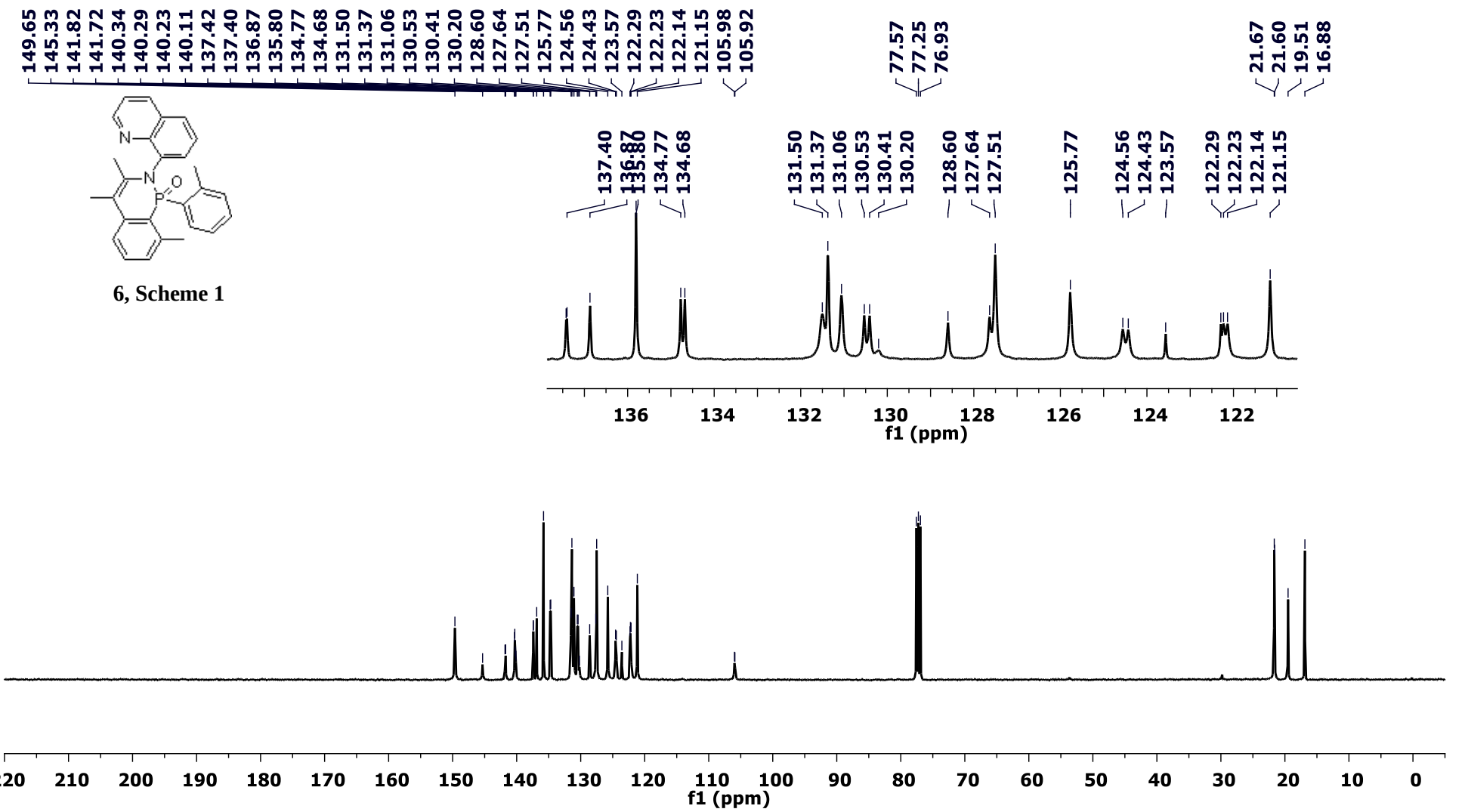



2D-NOESY
abundance
0 1.0 2.0 3.
Table 1, Entry 13
Y : parts per Million : Proton
X : parts per Million : Proton
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0 1.0 2.0
abundance

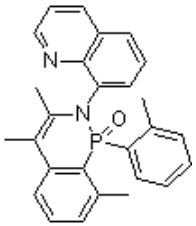


6, Scheme 1

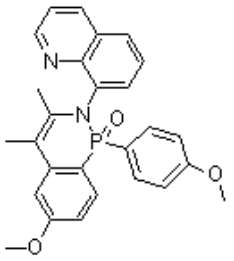
8.66
7.88
7.87
7.50
7.48
7.47
7.46
7.44
7.42
7.33
7.19
7.19
7.18
6.96
6.95
6.93
6.83
5.24
2.24
2.06
1.85
1.83
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
0.94
0.90
2.06
3.24
1.00
1.09
1.19
2.01
0.90
3.05
2.94
5.92
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.65
145.33
141.82
141.72
140.34
140.29
140.23
140.11
137.42
137.40
136.87
135.80
134.77
134.68
131.50
131.37
131.06
130.53
130.41
130.20
128.60
127.64
127.51
125.77
124.56
124.43
123.57
122.29
122.23
122.14
121.15
105.98
105.92
77.57
77.25
76.93
21.67
21.60
19.51
16.88
N
N
O
P
136
134
132
130
128
126
124
122
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6, Scheme 1

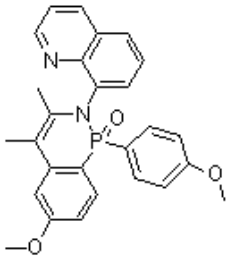


6, Scheme 1

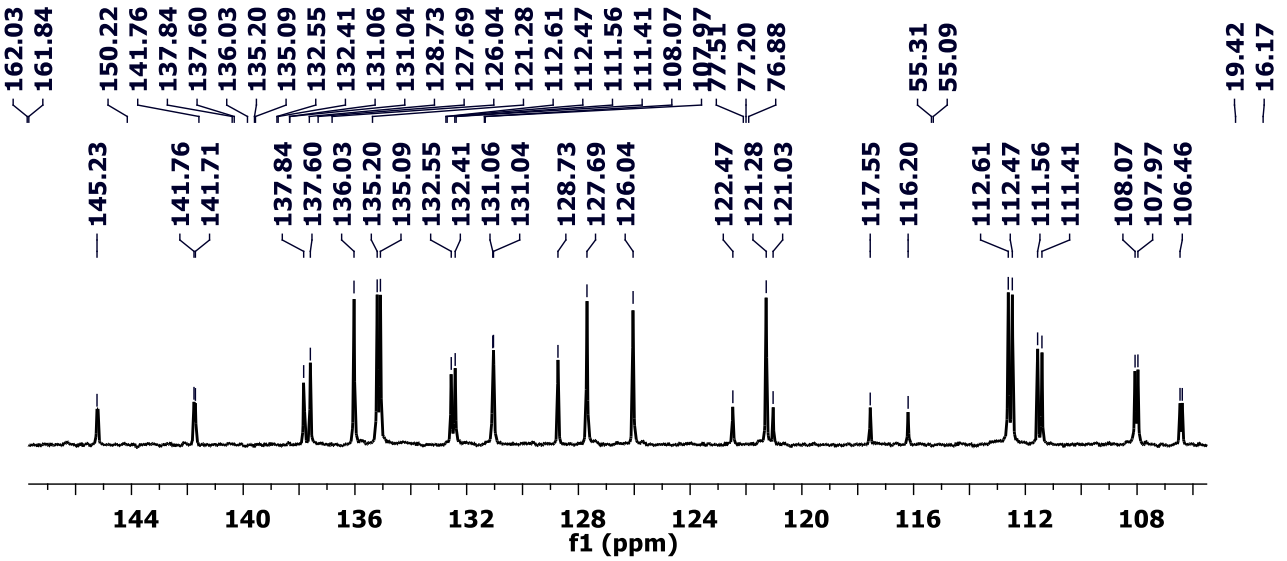


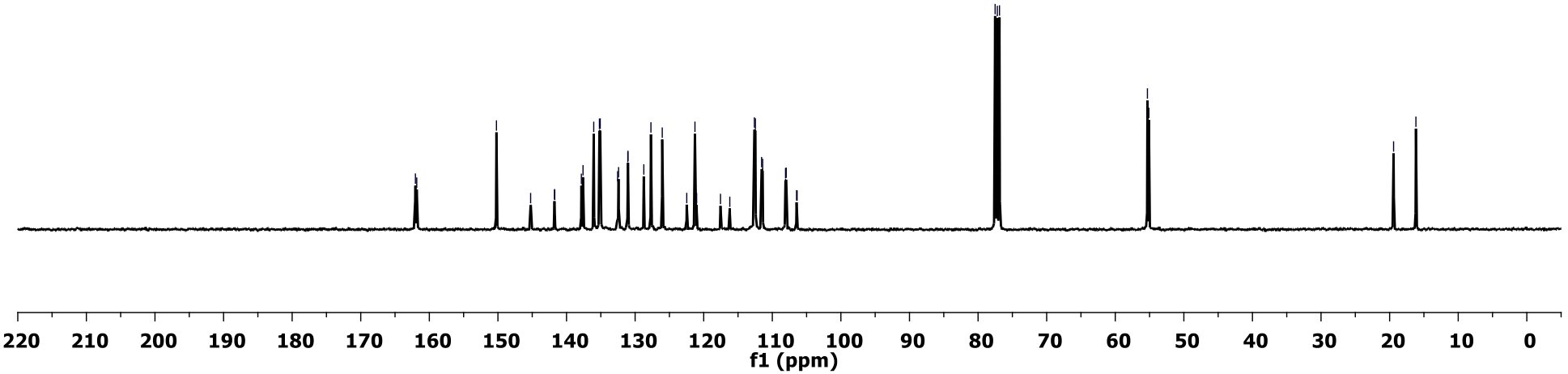
8, Scheme 1

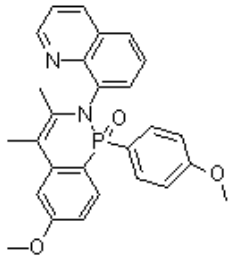
8.77
8.76
8.15
8.13
7.96
7.94
7.55
7.53
7.50
7.48
7.47
7.45
7.35
7.27
7.26
7.25
7.24
7.07
7.06
7.05
6.73
6.41
6.40
6.39
3.89
3.56
2.25
1.81
8.3
8.0
7.7
7.4
7.1
6.8
6.5
f1 (ppm)
0.90
0.92
1.00
1.08
1.90
0.99
2.12
1.08
1.04
1.93
3.16
2.95
2.98
2.95
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



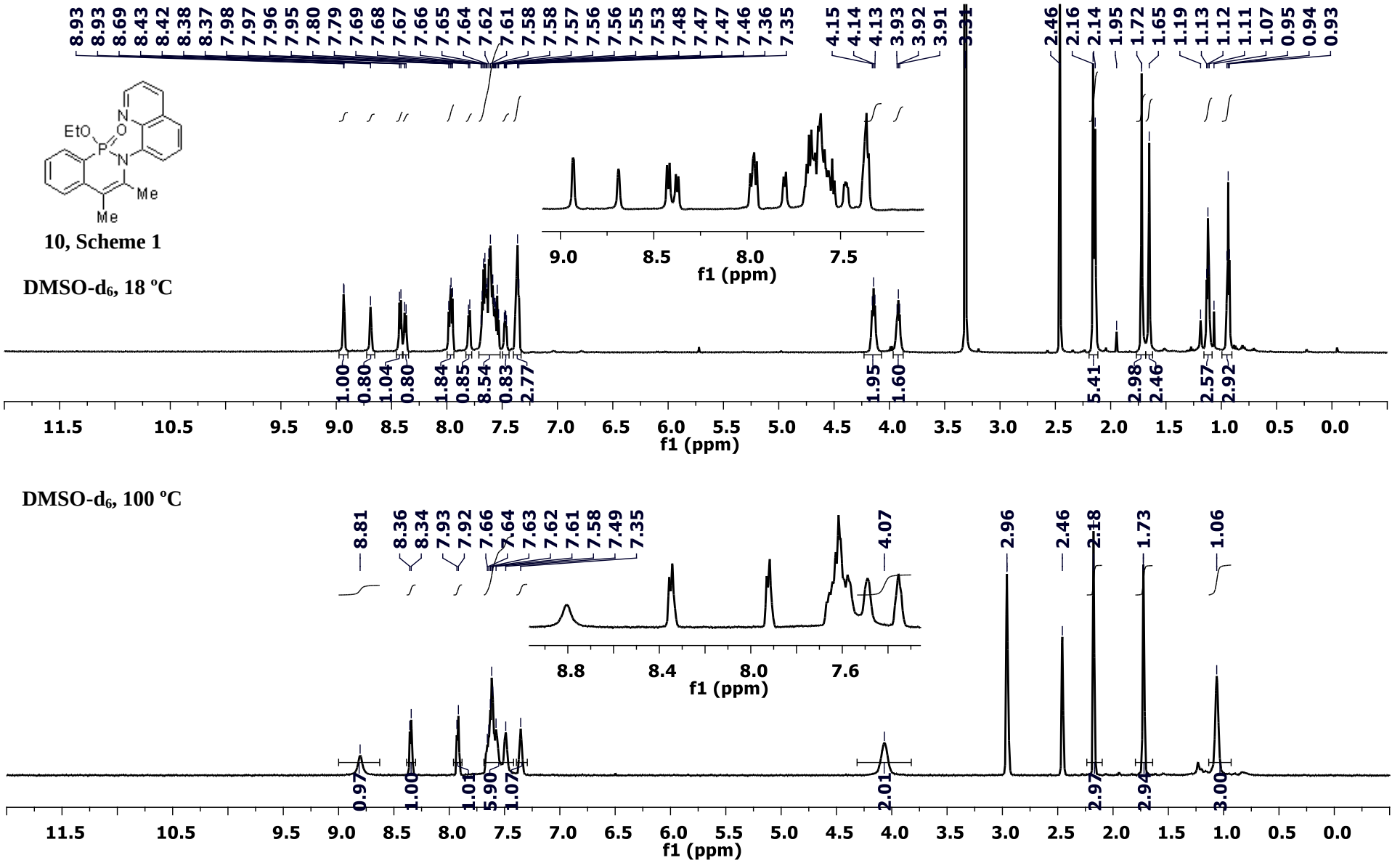
8, Scheme 1

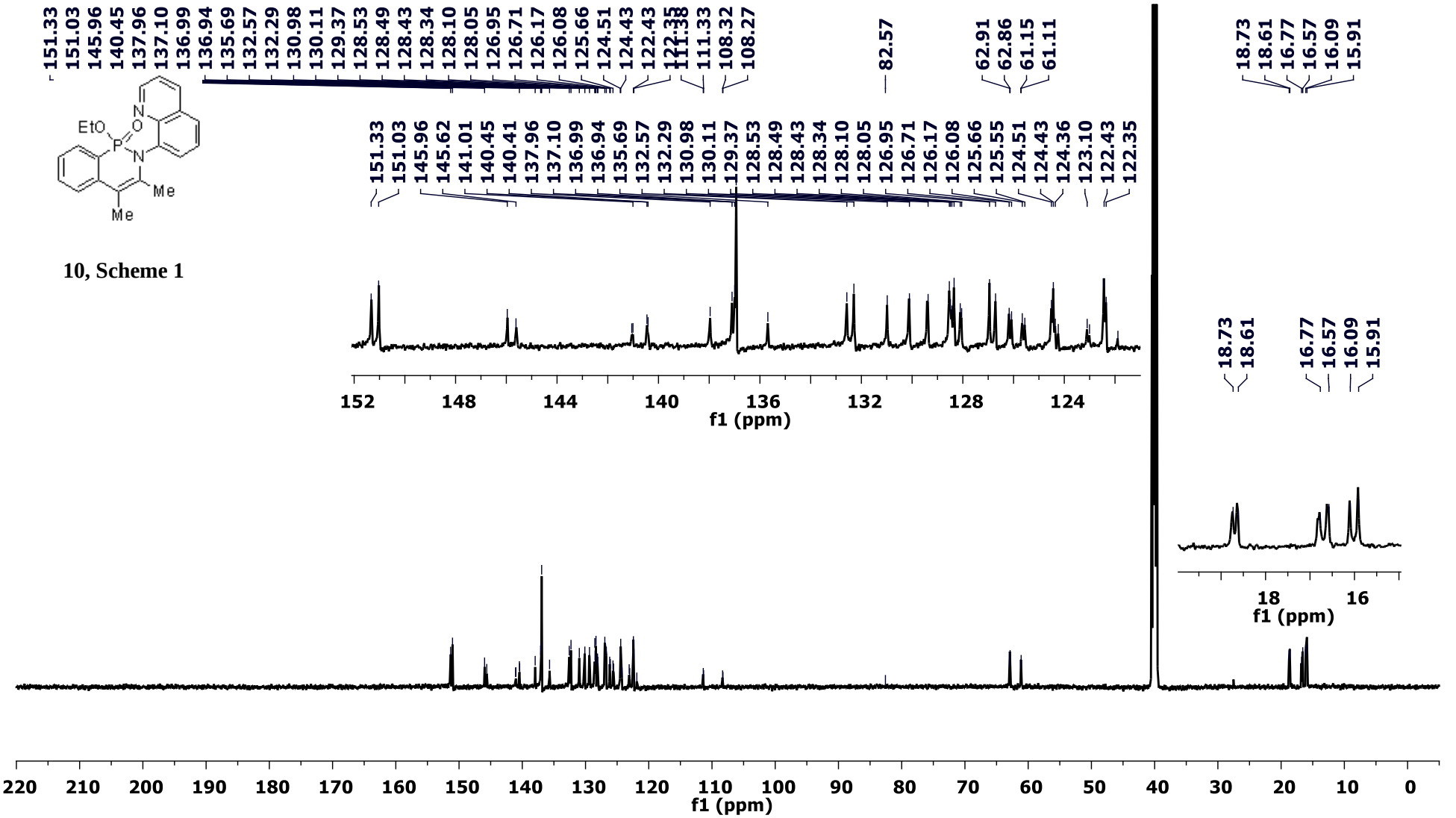

162.03
161.84
150.22
141.76
137.84
137.60
136.03
135.20
135.09
132.55
132.41
131.06
131.04
128.73
127.69
126.04
121.28
112.61
112.47
111.56
111.41
108.07
107.97
77.51
77.20
76.88
55.31
55.09
19.42
16.17
145.23
141.76
141.71
137.84
137.60
136.03
135.20
135.09
132.55
132.41
131.06
131.04
128.73
127.69
126.04
122.47
121.28
121.03
117.55
116.20
112.61
112.47
111.56
111.41
108.07
107.97
106.46
144
140
136
132
128
124
120
116
112
108
f1 (ppm)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

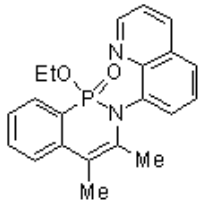


8, Scheme 1


10, Scheme 1
DMSO-d6, 18 °C
DMSO-d6, 100 °C
f1 (ppm)

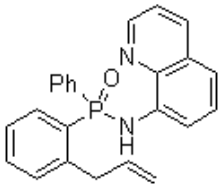

151.33
151.03
145.96
140.45
137.96
137.10
136.99
136.94
135.69
132.57
132.29
130.98
130.11
129.37
128.53
128.49
128.43
128.34
128.10
128.05
126.95
126.71
126.17
126.08
125.66
124.51
124.43
122.43
122.35
111.38
111.33
108.32
108.27
82.57
62.91
62.86
61.15
61.11
18.73
18.61
16.77
16.57
16.09
15.91
EtO
O
P
N
N
Me
Me
f1 (ppm)
f1 (ppm)
f1 (ppm)

10, Scheme 1


EtO
O
P
N
N
Me
Me

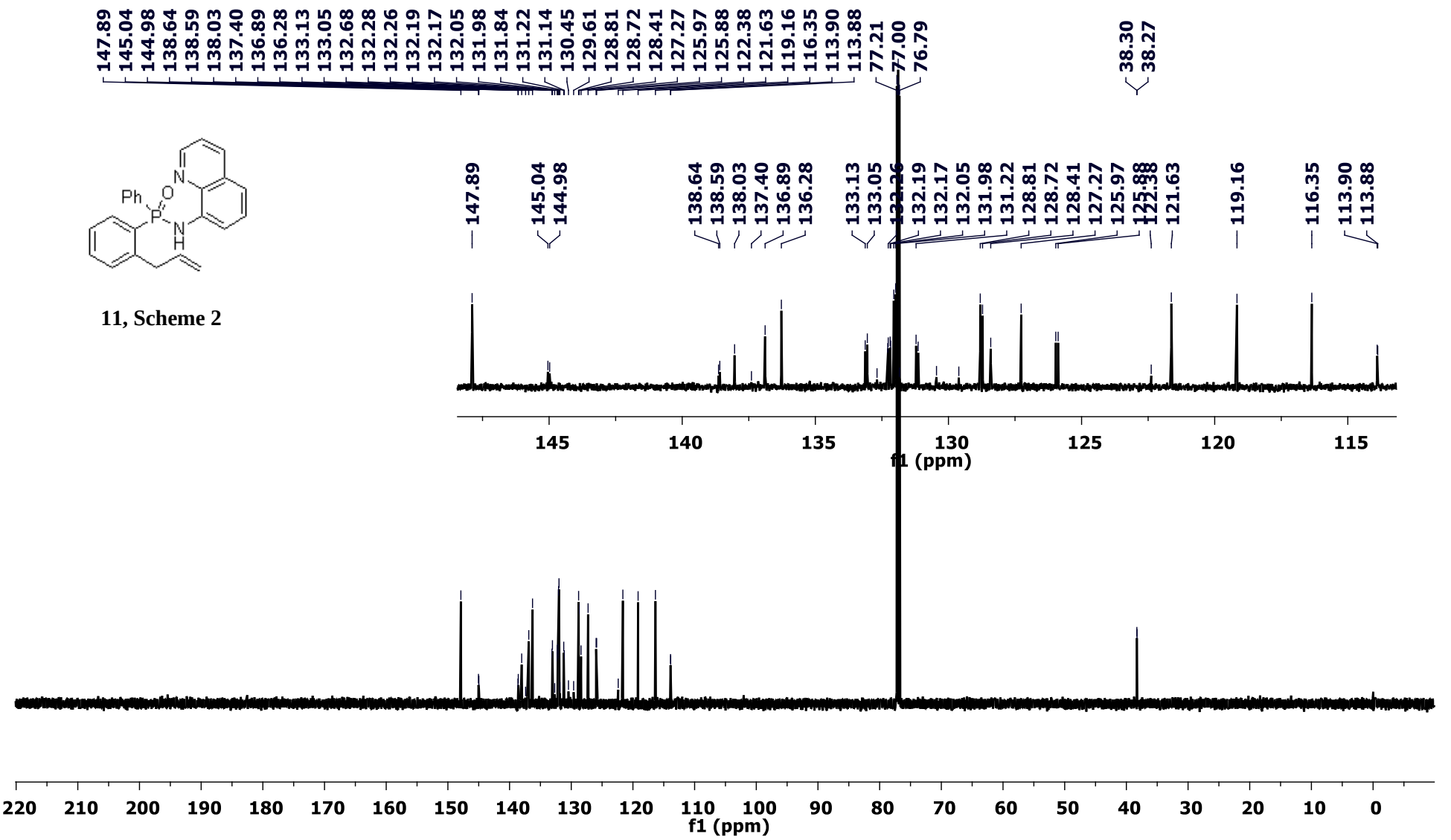
10, Scheme 1

11.70
10.18
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
f1 (ppm)

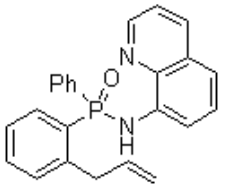

Ph
O
P
N
H
N

11, Scheme 2

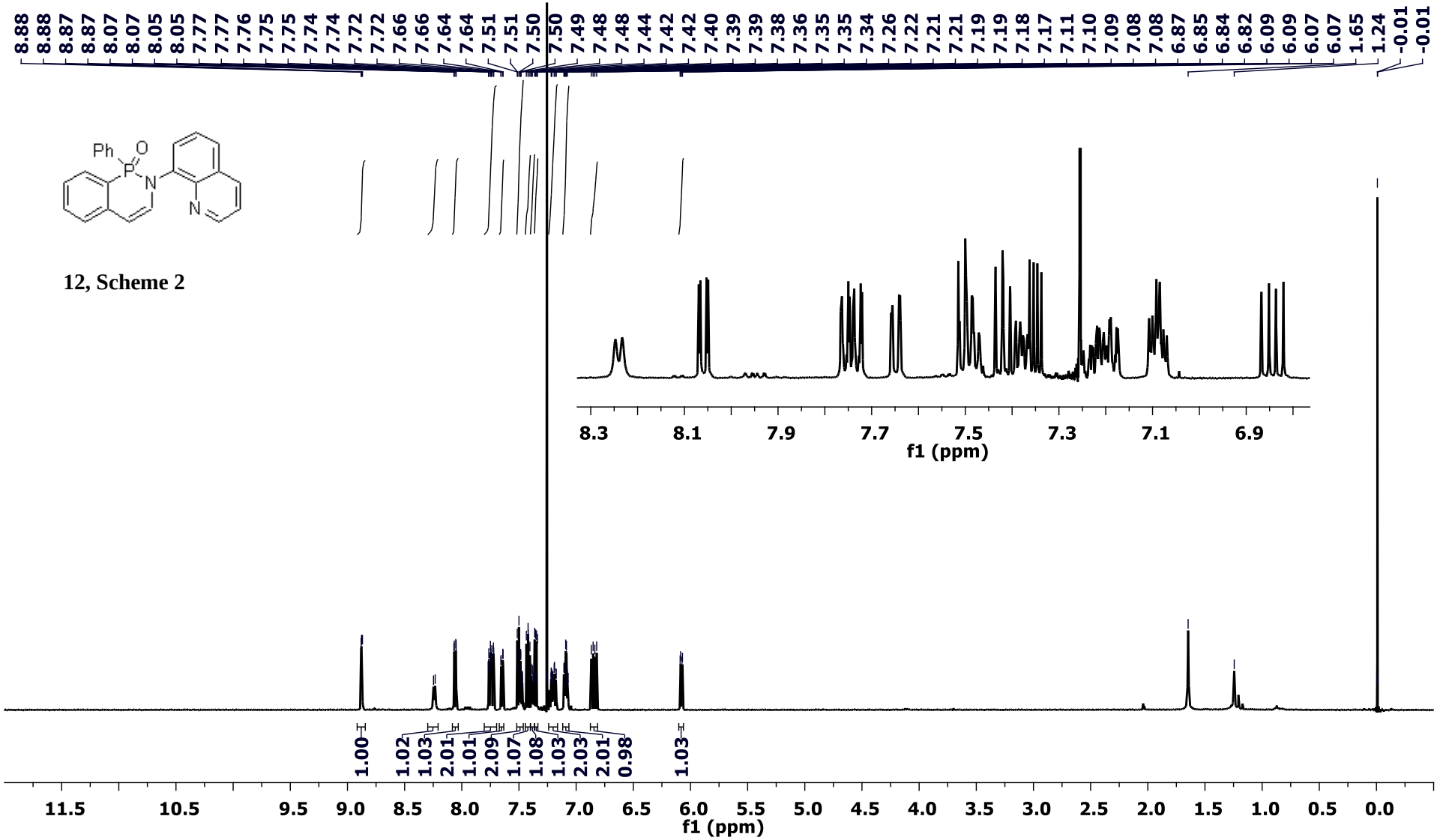
8.74
8.74
8.74
8.73
7.90
7.89
7.88
7.57
7.49
7.49
7.48
7.32
7.32
7.31
5.92
5.91
5.89
5.88
4.98
4.96
4.03
4.02
4.00
3.99
3.92
3.91
3.89
3.88
1.78
-0.00
8.7
8.5
8.3
8.1
7.9
7.7
7.5
7.3
f1 (ppm)
5.8
5.4
5.0
4.6
4.2
f1 (ppm)
1.00
1.00
3.04
3.04
3.05
2.07
2.11
1.04
0.93
2.08
1.01
1.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

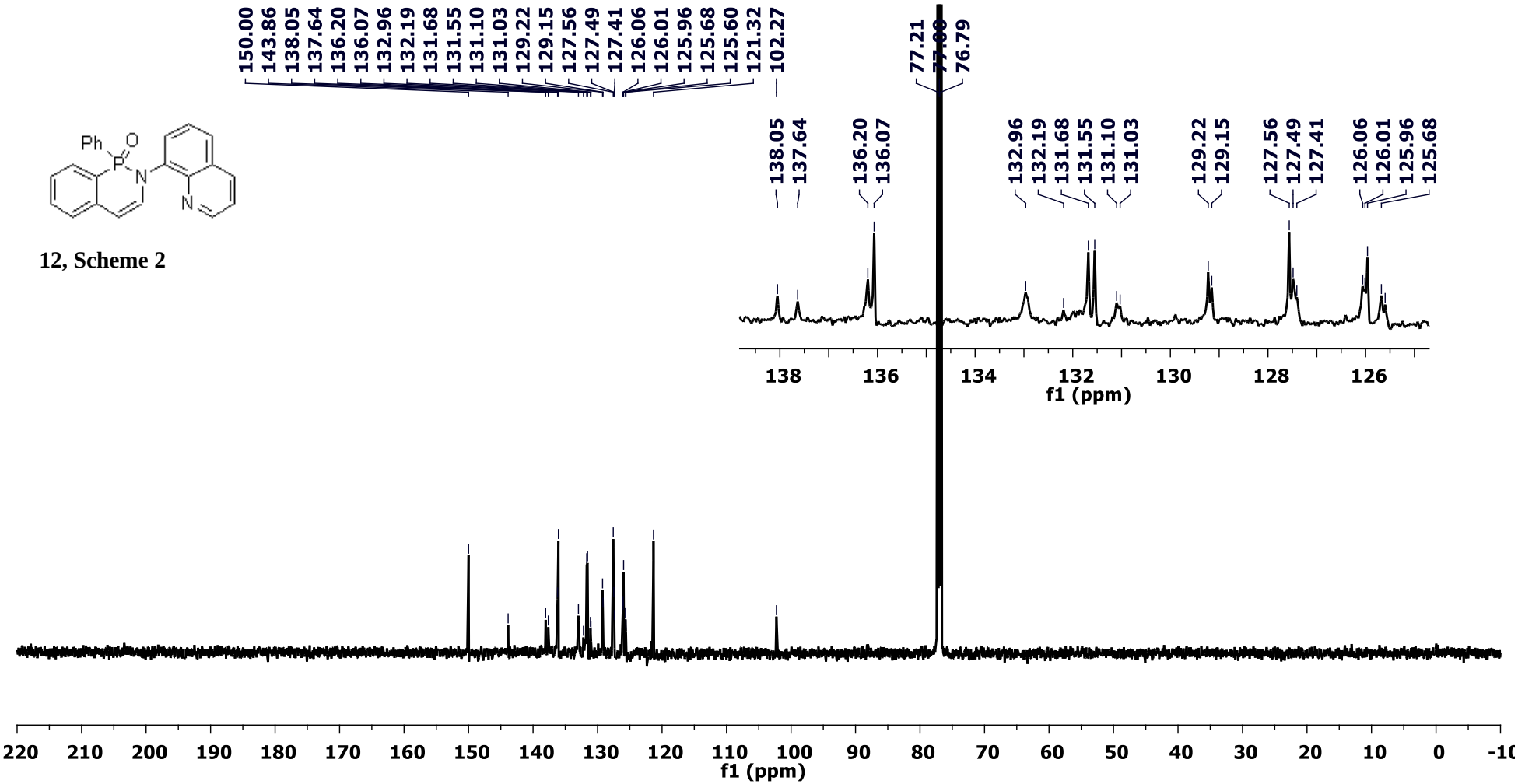

147.89
145.04
144.98
138.64
138.59
138.03
137.40
136.89
136.28
133.13
133.05
132.68
132.28
132.26
132.19
132.17
132.05
131.98
131.84
131.22
131.14
130.45
129.61
128.81
128.72
128.41
127.27
125.97
125.88
122.38
121.63
119.16
116.35
113.90
113.88
77.21
77.00
76.79
38.30
38.27
Ph
O
P
N
N
H
145
140
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11, Scheme 2

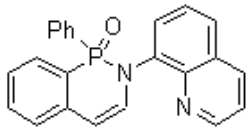


11, Scheme 2


8.88 8.88 8.87 8.87 8.07 8.07 8.05 8.05 7.77 7.77 7.76 7.75 7.75 7.74 7.74 7.72 7.72 7.66 7.66 7.64 7.64 7.51 7.51 7.50 7.50 7.49 7.48 7.48 7.44 7.42 7.42 7.40 7.39 7.39 7.38 7.36 7.35 7.35 7.34 7.26 7.22 7.21 7.21 7.19 7.19 7.18 7.17 7.11 7.10 7.09 7.08 7.08 6.87 6.85 6.84 6.82 6.09 6.09 6.07 6.07 1.65 1.24 -0.01 -0.01
Ph
O
P
N
N
12, Scheme 2
8.3 8.1 7.9 7.7 7.5 7.3 7.1 6.9
f1 (ppm)
1.00 1.02 1.03 2.01 1.01 2.09 1.07 1.08 1.03 2.03 2.01 0.98 1.03
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

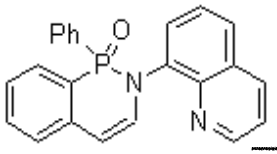

150.00
143.86
138.05
137.64
136.20
136.07
132.96
132.19
131.68
131.55
131.10
131.03
129.22
129.15
127.56
127.49
127.41
126.06
126.01
125.96
125.68
125.60
121.32
102.27
77.21
77.00
76.79
Ph
O
P
N
N
138.05
137.64
136.20
136.07
132.96
132.19
131.68
131.55
131.10
131.03
129.22
129.15
127.56
127.49
127.41
126.06
126.01
125.96
125.68
138
136
134
132
130
128
126
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

12, Scheme 2

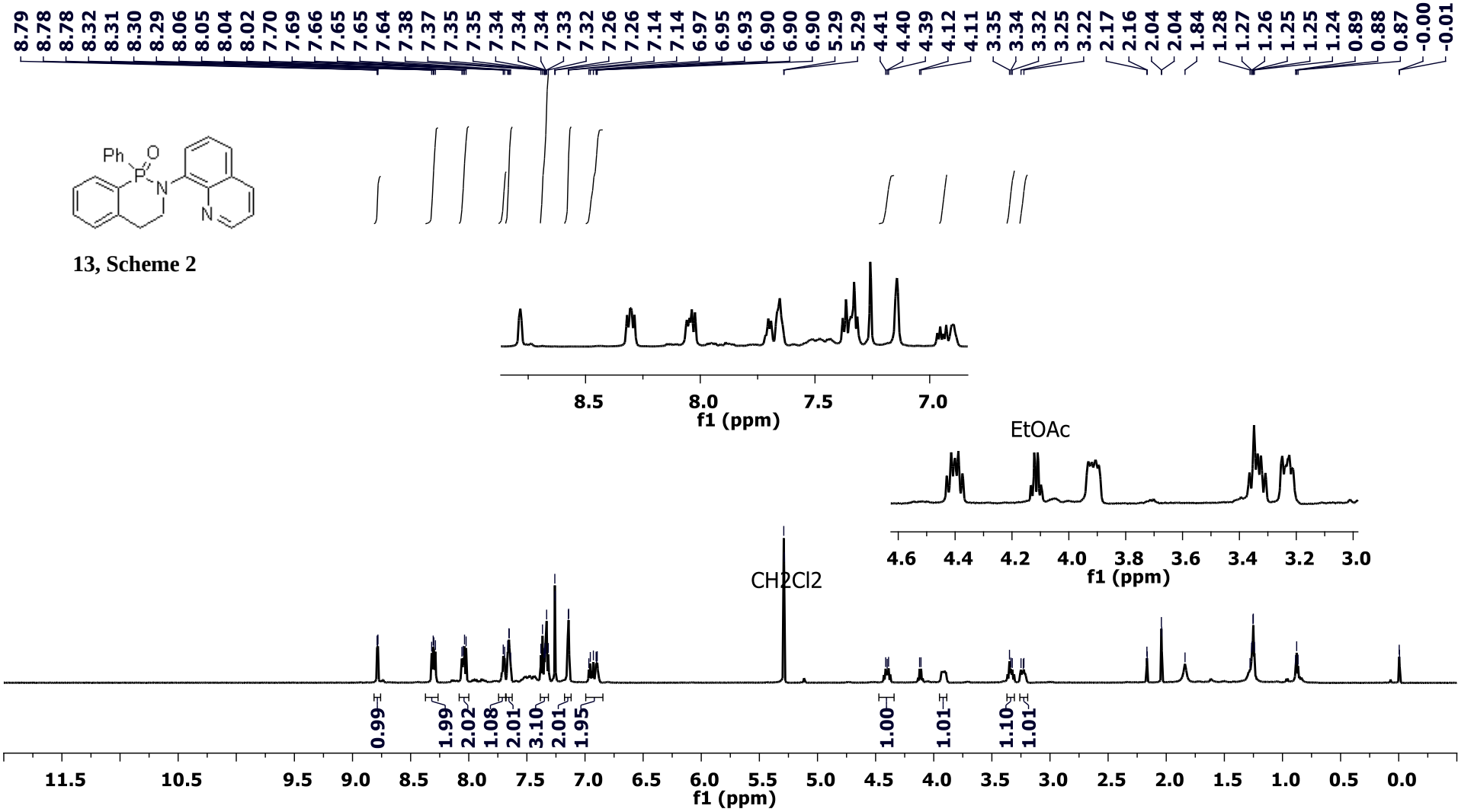


12, Scheme 2

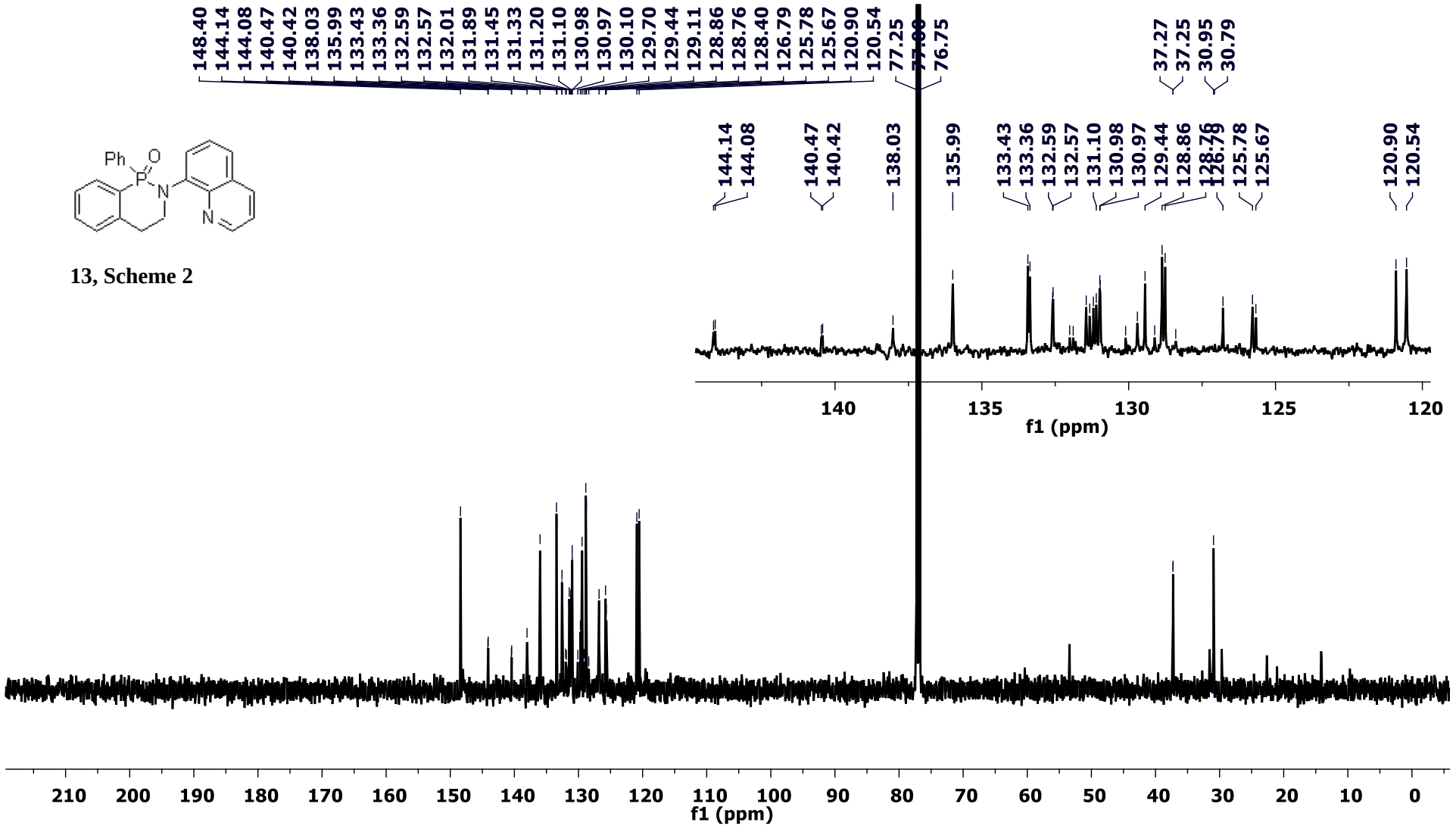
12, Scheme 2



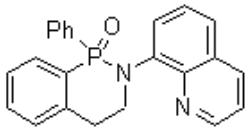
2D-COSY


8.79 8.78 8.78 8.32 8.31 8.30 8.29 8.06 8.05 8.04 8.02 7.70 7.69 7.66 7.65 7.65 7.64 7.38 7.37 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.26 7.26 7.14 7.14 6.97 6.95 6.93 6.90 6.90 6.90 5.29 5.29 4.41 4.40 4.39 4.12 4.11 3.35 3.34 3.32 3.25 3.22 2.17 2.16 2.04 2.04 1.84 1.28 1.27 1.26 1.25 1.25 1.24 0.89 0.88 0.87 -0.00 -0.01
Ph
O
P
N
N
8.5 8.0 7.5 7.0
f1 (ppm)
EtOAc
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
f1 (ppm)
CH2Cl2
0.99 1.99 2.02 1.08 2.01 3.10 2.01 1.95 1.00 1.01 1.10 1.01
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

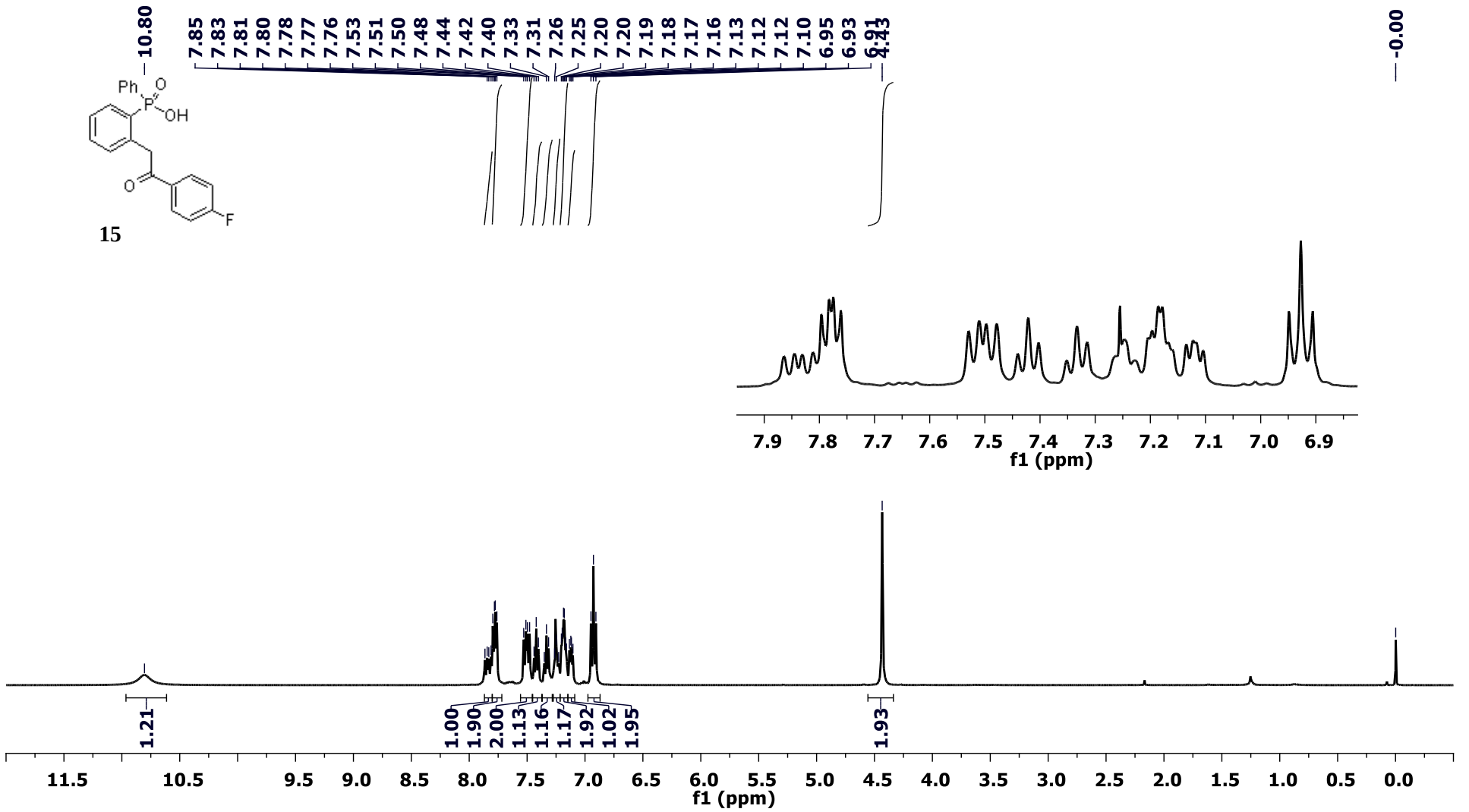
13, Scheme 2

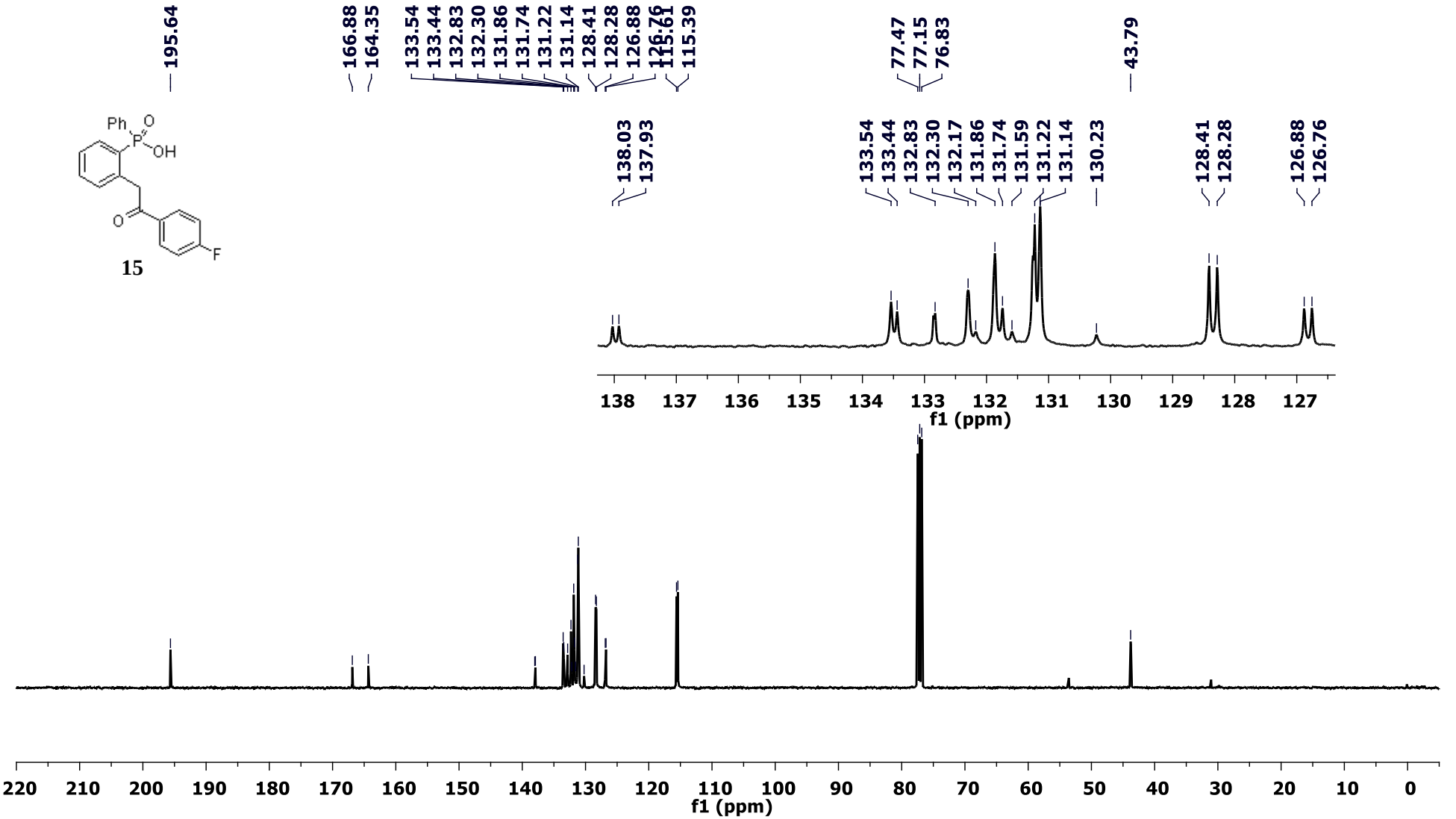

148.40
144.14
144.08
140.47
140.42
138.03
135.99
133.43
133.36
132.59
132.57
132.01
131.89
131.45
131.33
131.20
131.10
130.98
130.97
130.10
129.70
129.44
129.11
128.86
128.76
128.40
126.79
125.78
125.67
120.90
120.54
77.25
77.00
76.75
37.27
37.25
30.95
30.79
Ph
O
P
N
N
144.14
144.08
140.47
140.42
138.03
135.99
133.43
133.36
132.59
132.57
131.10
130.98
130.97
129.44
128.86
128.76
128.40
126.79
125.78
125.67
120.90
120.54
140
135
130
125
120
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

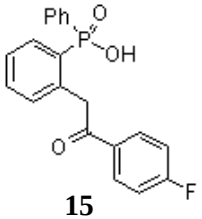
13, Scheme 2



13, Scheme 2

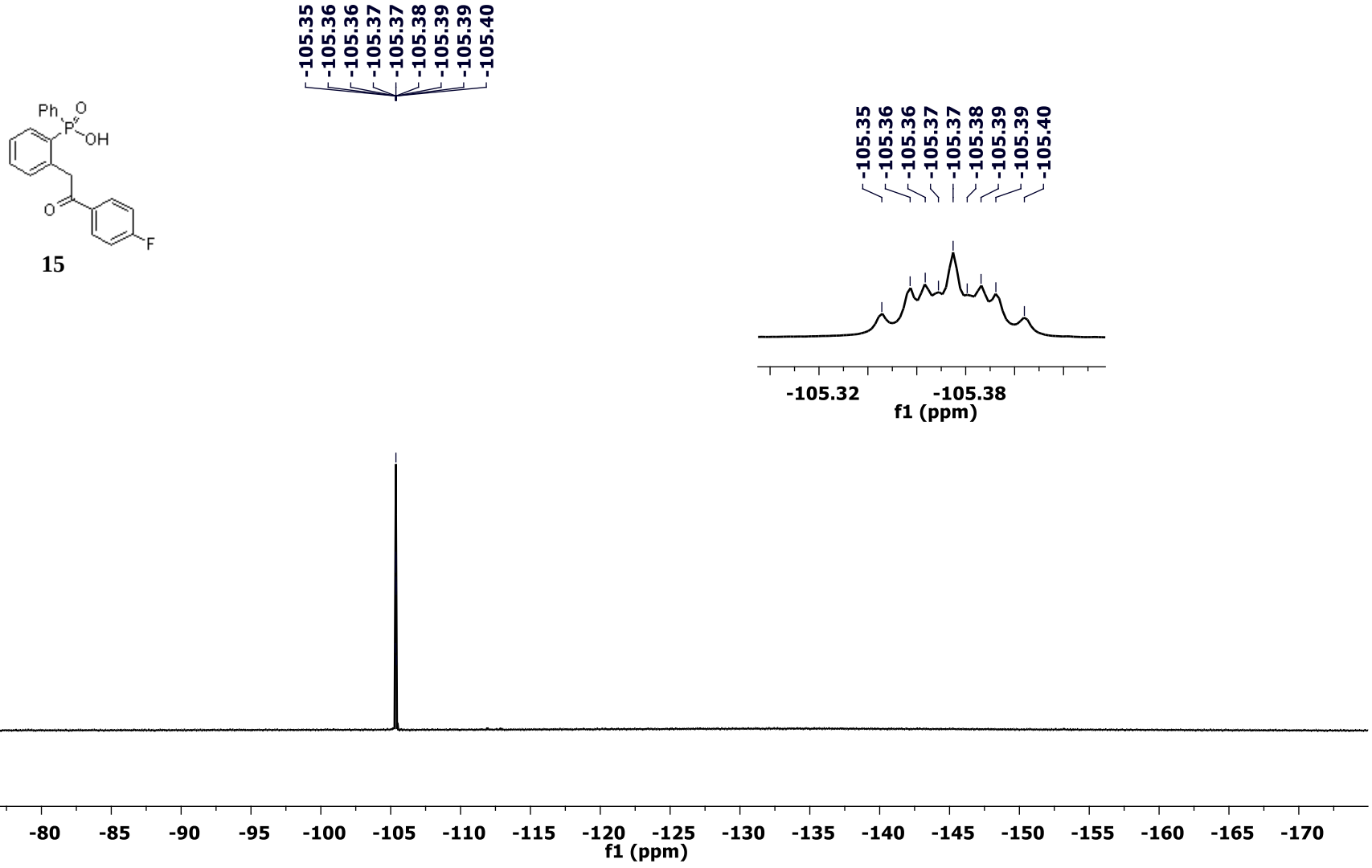

10.80
7.85
7.83
7.81
7.80
7.78
7.77
7.76
7.53
7.51
7.50
7.48
7.44
7.42
7.40
7.33
7.31
7.26
7.25
7.20
7.20
7.19
7.18
7.17
7.16
7.13
7.12
7.12
7.10
6.95
6.93
6.91
4.43
-0.00
Ph
O
P
OH
O
F
15
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.21
1.00
1.90
2.00
1.13
1.16
1.17
1.92
1.02
1.95
1.93
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.64
166.88
164.35
133.54
133.44
132.83
132.30
131.86
131.74
131.22
131.14
128.41
128.28
126.88
126.76
115.61
115.39
77.47
77.15
76.83
43.79
Ph
O
P
OH
O
F
15
138.03
137.93
133.54
133.44
132.83
132.30
132.17
131.86
131.74
131.59
131.22
131.14
130.23
128.41
128.28
126.88
126.76
138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
P
OH
O
F

15

33.26
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)


-105.35
-105.36
-105.36
-105.37
-105.37
-105.38
-105.39
-105.39
-105.40
Ph
O
P
OH
O
F
15
-105.35
-105.36
-105.36
-105.37
-105.37
-105.38
-105.39
-105.39
-105.40
-105.32
-105.38
f1 (ppm)
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
f1 (ppm)

References

1. Carpino, L. A.; Xia, J.; Zhang, C.; El-Faham, A. *J. Org. Chem.* **2004**, *69*, 62-71.
2. Wu, H. C.; Yu, J. Q.; Spencer, J. B. *Org. Lett.* **2004**, *6*, 4675-4678.
3. Smith, A. B.; Ducry, L.; Corbett, R. M.; Hirschmann, R. *Org. Lett.* **2000**, *2*, 3887-3890.