Electronic Supplementary Material (ESI) for Green Chemistry.

Visible−Light Induced Phosphonation of Quinoxalines and Quinoxalin-2(1H)-ones Under Aerobic Metal-free Conditions

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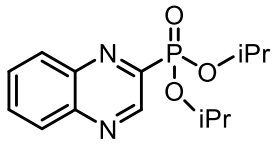
1. Characterisation data:

Diisopropyl quinoxalin-2-ylphosphonate (3a):

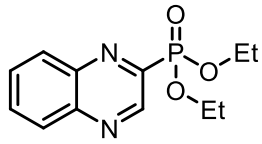
(Eluent: 30 %EtOAc/hexane); 81% yield (43 mg); brown liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ



9.28 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.82 (m, 2H), 4.95 (dd, *J* = 12.6, 6.2 Hz, 2H), 1.43 (d, *J* = 6.1 Hz, 6H), 1.33 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.29 (d, *J*= 223.8 Hz), , 146.34 (d, *J*= 27.5 Hz), 142.97, 142.41 (d, *J*= 20.6 Hz), 132.01, 130.83, 130.43, 129.59, 72.67 (d, *J*=5.8 Hz), 24.13 (dd, *J*= 33.7, 4.7 Hz); **^{31}P NMR** (242 MHz, $CDCl_3$) δ 7.85; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{14}H_{20}N_2O_3P$ 295.1212 found 295.1207.

Diethyl quinoxalin-2-ylphosphonate (3b): [1]

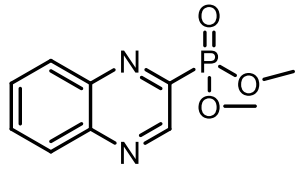
(Eluent: 30 %EtOAc/hexane); 84% yield (45 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.26 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.83 – 7.70 (m, 2H), 4.34 – 4.25 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.05 (d, *J* = 223.2 Hz), 146.20 (d, *J*= 27.7 Hz), 143.04, 142.33 (d, *J*= 21.3 Hz), 132.15, 130.91, 130.32, 129.53, 63.65 (d, *J*= 6.2 Hz), 16.44 (d, *J*= 6.2 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.14.

Dimethyl quinoxalin-2-ylphosphonate (3c):

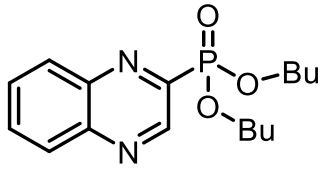
(Eluent: 30 %EtOAc/hexane); 90 % yield (43 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.21 (s, 1H), 8.17 (dd, *J* = 8.1, 1H), 8.07 (dd, *J* = 9.0 Hz, 1H), 7.82 – 7.75 (m, 2H), 3.90 (d, *J* = 11.0 Hz, 6H); δ **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.97 (d, *J* = 224.4 Hz), 146.11 (d, *J* = 27.3 Hz), 143.05, 142.22 (d, *J* = 21.6 Hz), 132.25, 130.96, 130.20, 129.48, 53.91 (d, *J* = 6.4 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.51; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{10}H_{11}KN_2O_3P$ 277.0144 found 277.0166.

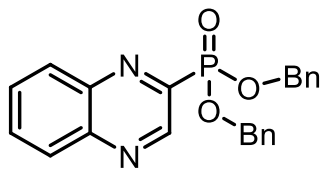
Dibutyl quinoxalin-2-ylphosphonate (3d):

(Eluent: 20 %EtOAc/hexane); 77% yield (50 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.12 – 8.10 (m, 1H), 7.85 – 7.78 (m, 2H), 4.26 - 4.19 (m, 4H), 1.70 – 1.66 (m, 4H), 1.40 - 1.36 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.15 (d, *J* = 223.4 Hz), 146.22 (d, *J* = 27.5 Hz), 143.01, 142.36 (d, *J* = 21.5 Hz),132.11, 130.88, 130.33, 129.54, 67.31 (d, *J* = 6.6 Hz), 32.49 (d, *J* = 6.1 Hz), 18,71, 13.59; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.15; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{16}H_{24}N_2O_3P$ 323.1525 found 323.1528.



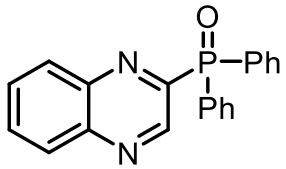
Dibenzyl quinoxalin-2-ylphosphonate (3e):

(Eluent: 20 % EtOAc/hexane); 86 % yield (67 mg); brown liquid;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.39 – 7.28 (m, 10H), 5.29 (d, *J* = 8.4 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.87 (d, *J* = 224.6 Hz), 146.13 (d, *J* = 28.3 Hz), 142.99 (s), 142.26 (d, *J* = 21.9 Hz), 135.63 (d, *J* = 6.1 Hz), 132.26, 130.95, 130.32, 129.55, 128.70, 128.67, 128.29, 69.11 (d, *J* = 5.5 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 10.57; **HRMS**-ESI (m/z) $[M+K]^+$calcd. For $C_{22}H_{19}KN_2O_3P$ 429.0770 found 429.0787.



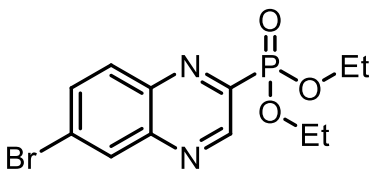
Diphenyl(quinoxalin-2-yl)phosphine oxide (3f):[1]

(Eluent: 20 %EtOAc/hexane); 80 % yield (53 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.31 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.94- 7.87 (m, 2H), 7.34 - 7.30 (m, 8H), 7.19 – 7.16 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.13 (d, *J* = 7.9 Hz), 146.56 (d, *J* = 29.6 Hz), 146.26 (d, *J* = 229.8 Hz), 143.35, 142.48 (d, *J* = 22.4 Hz), 132.08 (d, *J* = 189.8 Hz), 130.55, 129.99, 129.73, 125.75, 120.91, 120.88; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 2.45.



Diethyl (6-bromoquinoxalin-2-yl)phosphonate (3g):

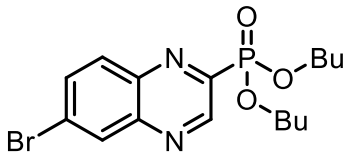
(Eluent: 20 %EtOAc/hexane); 52 % yield (36 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (dd, *J* = 8.1, 2.8 Hz, 1H), 8.55-8.45 (m, 1H), 8.23-8.13 (m, 1H), 8.07-8.02 (m, 1H), 4.51 – 4.42 (m, 4H), 1.54- 1.51 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.58 (d, *J* = 223.4 Hz), 146.51 (d, *J* = 27.7 Hz),141.90, 141.15 (d, *J* = 27.7 Hz), 134.72, 131.97,



130.94, 125.19, 63.83 (t, *J* = 7.4 Hz), 16.55 (d, *J* = 6.1 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.74; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{12}H_{15}BrN_2O_3P$ 345.0004 found 345.0035.

Dibutyl (6-bromoquinoxalin-2-yl)phosphonate (3h):

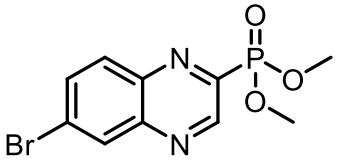
(Eluent: 20 %EtOAc/hexane); 36 % yield (29 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.26 (s, 1H), 8.34 (d, *J* = 2.1 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.92 (dd, *J* = 9.0, 2.1 Hz, 1H), 4.31 – 4.21 (m, 4H), 1.75 – 1.70 (m, 4H), 1.45 – 1.38 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.66 (d, *J* = 223.5 Hz), 147.07 (d, *J* = 27.4 Hz), 143.55, 141.17 (d, *J* = 21.7 Hz), 134.73, 131.98, 131.61, 126.70, 67.51 (d, *J* = 6.0 Hz), 32.59 (d, *J* = 5.7 Hz), 18.80, 13.68; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.73; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{16}H_{22}BrNaN_2O_3P$ 423.0449 found 423.0468.

Dimethyl (6-bromoquinoxalin-2-yl)phosphonate (3i):

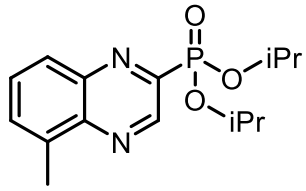
(Eluent: 30 %EtOAc/hexane); 63 % yield (40 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.28 (d, *J* = 7.2 Hz, 1H), 8.43-8.34 (m, 1H), 8.11 – 7.92 (m, 2H), 3.97 (d, *J* = 11.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.29 (d, *J* = 223.1 Hz), 146.52 (d, *J* = 27.8 Hz), 143.70, 142.81 (d, *J* = 21.4 Hz), 135.95, 132.56, 131.59, 126.96, 54.20 (t, *J* = 6.6 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.20 (s). **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{10}H_{11}BrN_2O_3P$ 316.9691 found 316.9697.

Diisopropyl (5-methylquinoxalin-2-yl)phosphonate (3j):

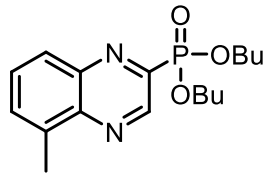
(Eluent: 20 %EtOAc/hexane); 42 % yield (26 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.29 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 2H), 4.96 – 4.91 (m, 2H), 2.81 (s, 3H), 1.43 (d, *J* = 6.1 Hz, 6H), 1.34 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.69 (d, *J* = 224.2 Hz), 145.11 (d, *J* = 26.9 Hz), 142.60 (d, *J* = 21.3 Hz), 142.20, 137.95, 131.91, 130.58, 128.28, 72.62 (d, *J* = 5.7 Hz), 29.83, 24.13 (d, *J* = 29.7 Hz), 17.34; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 7.60; **HRMS-ESI** (m/z) $[M+K]^+$ calcd. For $C_{15}H_{21}KN_2O_3P$ 347.0927 found 347.0908.

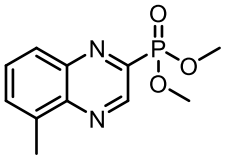
Dibutyl (5-methylquinoxalin-2-yl)phosphonate (3k):

(Eluent: 20 %EtOAc/hexane); 60 % yield (40 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.04 – 7.99 (m, 1H), 7.68 – 7.63 (m, 2H), 4.23 – 4.16 (m, 4H), 2.75 (s, 3H), 1.66 (dd, *J* = 8.5, 6.3 Hz, 4H), 1.38 – 1.33 (m, 4H), 0.87 – 0.83 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.65 (d, *J* = 223.2 Hz), 145.08 (d, *J* = 27.3 Hz), 142.64 (d, *J* = 21.5 Hz), 142.34, 138.00, 132.04, 130.67, 128.27, 67.31 (d, *J* = 6.3 Hz), 32.59 (d, *J* = 6.2 Hz), 18.83, 17.35, 13.70; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.49; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{17}H_{26}N_2O_3P$ 337.1681 found 337.1662.



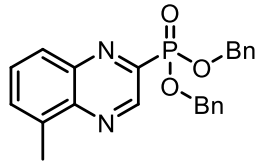
Dimethyl (5-methylquinoxalin-2-yl)phosphonate (3l):

(Eluent: 20 %EtOAc/hexane); 79 % yield (40 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 – 7.70 (m, 2H), 3.95 (d, *J* = 11.0 Hz, 6H), 2.81 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.52 (m, *J*= 223.9 Hz), 145.10 (d, *J* = 28.5 Hz), 142.70, 142.52, 138.10, 132.23, 130.83, 128.23, 54.00 (d, *J* = 5.8 Hz), 17.33; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.96; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{11}H_{14}N_2O_3P$ 253.0742 found 253.0758.



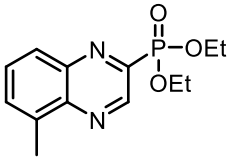
Dibenzyl (5-methylquinoxalin-2-yl)phosphonate (3m):

(Eluent: 15 %EtOAc/hexane); 55 % yield (44 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.07 – 8.01 (m, 1H), 7.73 – 7.69 (m, 2H), 7.39 – 7.28 (m, 10H), 5.28 (d, *J* = 8.2 Hz, 4H), 2.80 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.30 (d, *J* = 224.7 Hz), 144.95 (d, *J* = 27.9 Hz), 142.50 (d, *J* = 21.7 Hz), 142.31, 137.98, 135.77 (d, *J* = 6.0 Hz), 132.12, 130.70, 128.81, 128.68, 128.26, 128.20, 69.03 (d, *J* = 5.6 Hz), 17.31; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.89 (s). **HRMS-ESI** (m/z) $[M+H]^+$ calcd. For $C_{23}H_{22}N_2O_3P$ 405.1368 found 405.1369.



Diethyl (5-methylquinoxalin-2-yl)phosphonate (3n):

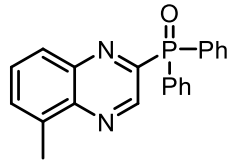
(Eluent: 10 %EtOAc/hexane); 53 % yield (30 mg); brown liquid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.11 – 8.06 (m, 1H), 7.74 – 7.69 (m, 2H), 4.37 – 4.30 (m, 4H), 2.82 – 2.81 (m, 3H), 1.39 (td, *J* = 7.0, 0.6 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.57 (d, *J* = 223.2 Hz), 145.08 (d, *J* = 27.7 Hz), 142.62 (d, *J*=



20.7 Hz), 142.37, 138.01, 132.05, 130.69, 128.26, 63.64 (d, *J* = 6.1 Hz), 17.33, 16.52 (d, *J* = 6.2 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.50; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{13}H_{18}N_2O_3P$ 281.1055 found 281.1094.

(5-methylquinoxalin-2-yl)diphenylphosphine oxide (3o):

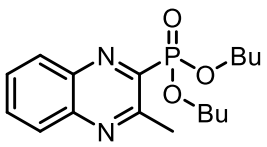
(Eluent: 20 %EtOAc/hexane); 45 % yield (31 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



9.41 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.33- 7.29 (m, 8H), 7.19 – 7.16 (m, 2H), 2.83 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.23 (d, *J* = 7.8 Hz), 145.71 (d, *J* = 229.7 Hz), 145.39 (d, *J* = 29.3 Hz), 142.63, 138.23, 132.66, 131.07, 130.00, 128.39, 125.71, 120.93, 120.92 17.35; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 2.25 (s). **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{21}H_{17}N_2OP$ 345.1157 found 345.0377.

Dibutyl (3-methylquinoxalin-2-yl)phosphonate (3p):

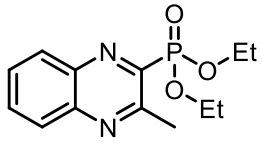
(Eluent: 15 %EtOAc/hexane); 43 % yield (29 mg); brown liquid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.16 – 8.13 (m, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.74 (td, *J* = 7.6, 7.0, 1.3 Hz, 1H), 4.32 – 4.24 (m, 4H), 3.01 (s, 3H), 1.75 (dd, *J* = 8.2, 6.7 Hz, 4H), 1.49 – 1. 42 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.49 (d, *J* = 28.8 Hz), 147.90 (d, *J* = 222.1 Hz), 142.18, 140.19 (d, *J* = 21.4 Hz), 132.01, 130.07, 129.64, 128.65, 67.33 (d, *J* = 6.4 Hz), 32.61 (d, *J* = 5.9 Hz); 23.70, 18.88, 13.72; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 10.82; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{17}H_{26}N_2O_3P$ 337.1681 found 337.1683.

Diethyl (3-methylquinoxalin-2-yl)phosphonate (3q):

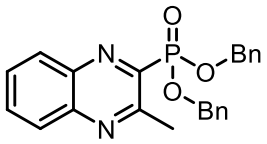
(Eluent: 20 %EtOAc/hexane); 91% yield (51 mg); brown liquid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.14 – 8.11 (m, 1H), 8.01 – 7.98 (m, 1H), 7.80- 7.76 (m, 1H), 7.72 - 7.69 (m, 1H), 4.37 – 4.29 (m, 4H), 3.00 – 2.98 (m, 3H), 1.42 – 1.39 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.41 (d, *J* = 28.9 Hz), 147.69 (d, *J* = 222.2 Hz), 142.12, 140.11 (d, *J* = 21.4 Hz), 132.03, 130.00, 129.64, 128.57, 63.67 (d, *J* = 6.2 Hz), 23.60, 16.43 (d, *J* = 5.9 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 10.74; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{13}H_{18}N_2O_3P$ 281.1055 found 281.1096.

dibenzyl (3-methylquinoxalin-2-yl)phosphonate (3r):

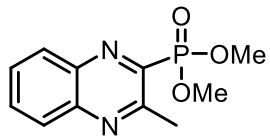
(Eluent: 20 %EtOAc/hexane); 72 % yield (58 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.11 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.83 (t, *J* = 7.1 Hz, 1H), 7.76 (t, *J* = 7.1 Hz, 1H), 7.41 – 7.30 (m, 10 H), 5.34- 5.25 (m, 4H), 3.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.60 (d, *J* = 31.0 Hz), 150.54 (d, *J* = 8.3 Hz), 146.22 (d, *J* = 229.3 Hz), 142.47 (s), δ 140.26 (d, *J* = 22.4 Hz), 132.69, 130.21, 130.05, 129.94, 128.77, 125.61, 120.93 (d, *J* = 3.8 Hz), 23.84; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.04; **HRMS-ESI** (m/z) [M+H]+calcd. For $C_{23}H_{22}N_2O_3P$ 405.1368 found 405.1360.

Dimethyl (3-methylquinoxalin-2-yl)phosphonate (3s):

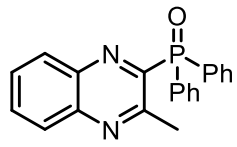
(Eluent: 20 %EtOAc/hexane); 86 % yield (43 mg); yellow solid (Melting point 78-79 ℃): **^{1}H NMR**



(500 MHz, $CDCl_3$ δ 8.10 (d, *J* = 8.1, 1H), 7.96 (d, *J* = 8.4, 1H), 7.83 - 781 (m, 1H), 7.76- 7.73 (m, 1H), 741 - 3.93 (d, *J* = 11.0 Hz, 6H), 2.94 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.44 (d, *J* = 29.1 Hz), 147.00 (d, *J* = 223.0 Hz), 142.23, 140.10 (d, *J* = 21.4 Hz), 132.22, 130.0, 129.79, 128.65, 54.13 (d, *J* = 6.6 Hz), 29.77, 23.56; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 13.00; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{11}H_{14}N_2O_3P$ 253.0742 found 253.0727.

(3-methylquinoxalin-2-yl)diphenylphosphine oxide (3t):

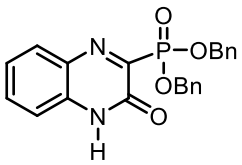
(Eluent: 10 %EtOAc/hexane); 69 % yield (47 mg); brown liquid; **^{1}H NMR** (500 MHz, CDCl3) δ



8.20 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.30 (m, 8H), 7.19 (tt, *J* = 5.2, 2.2 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.60 (d, *J* = 31.0 Hz), 150.54 (d, *J* = 8.3 Hz), 146.22 (d, *J* = 229.3 Hz), 142.47 (s), 140.26 (d, *J* = 22.4 Hz), 132.70 (s), 130.22 (s), 130.05 (s), 129.94 (s), 128.77 (s), 125.62 (s), 120.93 (d, *J* = 3.8 Hz), 23.85 (s); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 2.86 (s). **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{21}H_{17}KN_2OP$ 383.0716 found 383.0783.

Dibenzyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5a): [2]

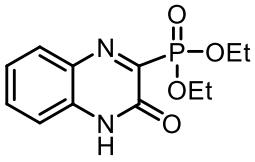
(Eluent: 40 %EtOAc/hexane); 86 % yield (72 mg); yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



12.77 (s, 1H), 7.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.50 (m, 1H), 7.44 – 7.41 (m, 4H), 7.38 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.34 – 7.27 (m, 7H), 5.39 (d, *J* = 7.8 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.01 (d, *J* = 31.9 Hz), 152.44 (d, *J* = 231.3 Hz), 136.24 (d, *J* = 6.9 Hz), 133.30, 132.17, 132.83 (d, *J* = 25.8 Hz), 130.58, 128.58, 128.46, 128.12, 124.72, 116.55, δ 69.51 (d, *J* = 6.1 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.41.

Diethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5b): [2]

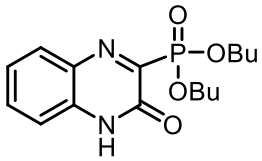
(Eluent: 40 %EtOAc/hexane); 83 % yield (49 mg); yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



12.82 (s, 1H), 7.94 – 7.91 (m, 1H), 7.60 – 7.56 (m, 1H), 7.49 – 7.47 (d, *J* = 8.2 Hz, 1H), 7.37 - 7.34 (m, 1H), 4.48 - 4.42 (m, 4H), 1.44 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.00 (d, *J* = 32.1 Hz), 152.84 (d, *J* = 229.5 Hz), 133.07, 132.80 (d, *J* = 25.3 Hz), 132.27, 130.57, 124.50, 116.56, 64.32 (d, *J* = 6.1 Hz), 16.58 (d, *J* = 6.2 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.09.

dibutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5c): [2]

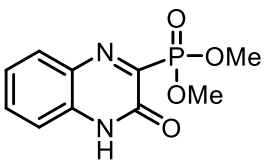
(Eluent:40 %EtOAc/hexane); 49 % yield (33 mg); yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



12.90 (s, 1H), 7.9 - 7.92 (m, 1H), 7.60 - 7.57 (m, 1H), 7.50 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.38 – 7.35 (m, 1H), 4.41 – 4.36, (m, 4H), 1.81 (m, 4H), 1.52 – 1.44 (m, 4H), 0.97 (td, *J* = 7.4, 1.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.10 (d, *J* = 31.4 Hz), 152.92 (d, *J* = 229.8 Hz), 133.02, 132.84 (d, *J* = 25.4 Hz), 132.22, 130.56, 124.62, 116.56, 67.94 (d, *J* = 6.6 Hz), 32.70 (d, *J* = 6.2 Hz), 18.85, 13.77; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 7.98.

Dimethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5d): [2]

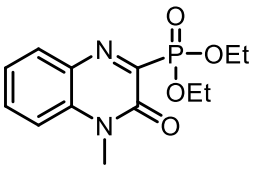
(Eluent: 40 %EtOAc/hexane); 61% yield (31 mg); yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



12.48 (s, 1H), 7.95 - 7.94 (m, 1H), 7.62 – 7.59 (m, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.36 (m, 1H), 4.07 (d, *J* = 11.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.82, 152.50 (d, *J* = 231.7 Hz), 133.37, 132.88 (d, *J* = 23.0 Hz), 132.07, 130.80, 124.89, 116.43, 54.83 (d, *J* = 5.8 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 10.38.

Diethyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5e):

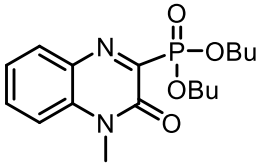
(Eluent:40 %EtOAc/hexane); 69 % yield (41 mg); yellow liquid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



7.99 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.42 – 7.34 (m, 2H), 4.48 – 4.41 (m, 4H), 3.71 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.16 (d, *J* = 32.4 Hz), 152.60 (d, *J* = 230.3 Hz), 134.08, 133.07, 132.89 (d, *J* = 26.6 Hz), 131.88, 124.08, 113.95, 64.21 (d, *J* = 6.2 Hz), 16.59 (d, *J* = 6.2 Hz), 28.99; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.60; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{13}H_{18}N_2O_4P$ 297.1004 found 268.1069.

Dibutyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5f):

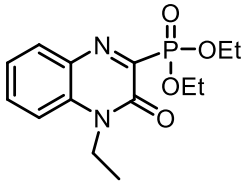
(Eluent: 40 %EtOAc/hexane); 66 % yield (47 mg); yellow liquid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ



7.89 (dt, *J* = 8.1, 2.1 Hz, 1H), 7.61 - 7.59 (m, 1H), 7.33 – 7.26 (m, 2H), 4.33 – 4.24 (m, 4H), 3.62 (d, *J* = 1.8 Hz, 3H), 1.72 – 1.67 (m, 4H), 1.43- 1.36 (m, 4H), 0.88 (td, *J* = 7.4, 1.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.11 (d, *J* = 32.0 Hz), 152.66 (d, *J* = 230.0 Hz), 133.04, 133.00, 132.75, 131.80, 124.02, 113.91, 67.85 (d, *J* = 6.3 Hz), 32.71 (d, *J* = 6.2 Hz), 28.96, 18.81, 13.75; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.53; **HRMS-ESI** (m/z) $[M+H]^+$calcd. For $C_{17}H_{26}N_2O_4P$ 353.1630 found 353.1626.

Diethyl (4-ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5g):

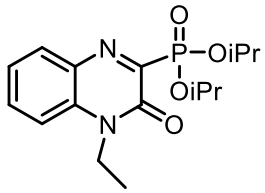
(Eluent: 40 %EtOAc/hexane); 77 % yield (48 mg); yellow liquid ;**^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69 – 7.65 (m,1H), 7.40 – 7.37 (m, 2H), 4.49 - 4.42 (m, 4H), 4.35 - 4.30 (m, 2H), 1.45 (t, *J* = 7.1 Hz, 6H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.66 (d, *J* = 34.7 Hz), 152.60 (d, *J* = 231.4 Hz), 133.21, 132.99, 132.97, 132.05, 123.82, 113.75, 64.20 (d, *J* = 6.3 Hz), 37.37, 16.55 (d, *J* = 6.4 Hz), 12.39; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.75; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{14}H_{19}KN_2O_4P$ 349.0720 found 349.0743.

Diisopropyl (4-ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5h):

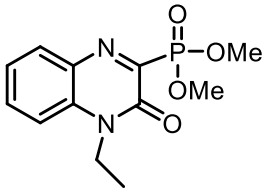
(Eluent: 40 %EtOAc/hexane); 78 % yield (53 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.09 (d, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.47 (m, 2H), 5.19 -5.15 (m, 2H), 4.44 (q, *J* = 8.0, 7.5 Hz, 2H), 1.61 – 1.54 (m, 12H), 1.52 – 1.48 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.52 (d, *J* = 32.4 Hz), 153.14 (d, *J* = 230.3 Hz), 133.12, 133.12 (d, *J* = 26.3 Hz),132.79, 132.03, 123.71, 113.70, 72.85 (d, *J* = 6.3 Hz), 37.33, 24.50, 23.87 (d, *J* = 6.0 Hz), 12.45; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 6.92; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{16}H_{23}N_2NaO_4P$ 361.1293 found 361.1271.

Dimethyl (4-ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5i): [2]

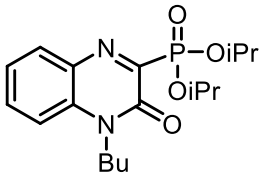
(Eluent: 40 %EtOAc/hexane); 73 % yield (43 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



8.03 – 8.00 (m, 1H), 7.70 – 7.66 (m, 1H), 7.42 – 7.37 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.07 (d, *J* = 11.1 Hz, 6H), 1.40 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.81 (d, *J* = 32.3 Hz), 152.20 (d, *J* = 231.5 Hz), 133.30, 133.19, 133.08, 133.06, 132.17, 123.99, 113.83, 54.72 (d, *J* = 6.2 Hz), 37.48, 12.43; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.26.

Diisopropyl (4-butyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5j):

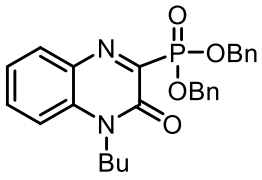
(Eluent: 40 %EtOAc/hexane); 76 % yield (56 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.39 – 7.32 (m, 2H), 5.06 (m, 2H), 4.26 – 4.23 (m, 2H), 1.77 -1.71 (m, 2H), 1.48 (dd, *J* = 20.7, 6.2 Hz, 14H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.63 (d, *J* = 32.1 Hz), 153.02 (d, *J* = 229.9 Hz), 132.99 (d, *J* = 26.6 Hz), 132.66, 131.88, 123.60, 113.79, 72.70 (d, *J* = 6.2 Hz), 41.99, 29.21, 24.40, 23.78 (d, *J* = 5.9 Hz), 20.24, 13.77; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 6.85; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{18}H_{27}KN_2O_4P$ 405.1346 found 405.1356.

Dibenzyl (4-butyl-3,4-dihydroquinoxalin-2-yl)phosphonate (5k):

(Eluent: 40 %EtOAc/hexane); 61% yield (56 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



7.91 – 7.89 (m, 1H), 7.66 – 7.62 (m, 1H), 7.44 - 7.42 (m, 4H), 7.37 -7.26 (m, 8H),5.43 – 5.36 (m,4H), 4.23 – 4.20 (m, 2H), 1.76 – 1.70 (m, 2H), 1.52 – 1.54 (m, 2H), 1.01 – 0.98 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.90 (d, *J* = 32.6 Hz), 152.33 (d, *J* = 231.3 Hz), 136.45 (d, *J* = 6.3 Hz),

133.31, 133.24, 132.03, 132.07, 128.49, 128.30, 128.14, 123.86, 113.96, 69.45 (d, *J* = 6.1 Hz), 42.21, 29.30, 20.37, 13.86; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 9.15; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{26}H_{27}NaN_2O_4P$ 485.1606 found 485.1604.

Dimethyl (4-butyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5l):

(Eluent: 40 %EtOAc/hexane); 87 % yield (54 mg); yellow solid; (Melting point129- 130 °C): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.42 – 7.35 (m, 2H), 4.26 (t, *J* = 8.0 Hz, 2H), 4.07 (d, *J* = 10.9 Hz, 6H), 1.77 – 1.72 (m, 2H), 1.52 – 1.47 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.85 (d, *J* = 32.1 Hz), 151.97 (d, *J* = 231.3 Hz), 133.17, 133.04, 133.01(d, *J* = 27.4 Hz), 131.95, 123.84, 113.89, 54.57 (d, *J* = 6.2 Hz), 42.15, 29.14, 20.24, 13.69; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.24; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{14}H_{19}N_2NaO_4P$ 333.0980 found 333.0973.

(3-(diethoxyphosphoryl)-2-oxoquinoxalin-1*(2H)*methyl propionate (5m):

(Eluent: 40 %EtOAc/hexane); 61% yield (45 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.34 – 7.31 (m, 1H), 7.07 (dd, *J* = 8.6, 1.1 Hz, 1H), 4.96 (s, 2H), 4.40 - 4.33 (m, 4H), 4.19 – 4.15 (m, 2H), 1.39 – 1.35 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.58, 153.31, 152.52 (d, *J* = 266.6 Hz), 133.07, 132.72 (d, *J* = 26.2 Hz), 131.89, 124.21, 113.45, 64.13 (d, *J* = 6.3 Hz), 62.12, 43.14, 16.40 (d, *J* = 6.2 Hz), 14.01 ; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 7.89 (s); **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{16}H_{21}KN_2O_6P$ 407.0774 found 407.0766.

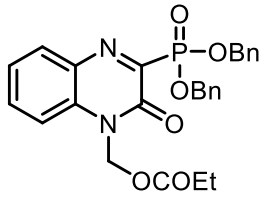
(3-(dibutoxyphosphoryl)-2-oxoquinoxalin-1(2H)-yl)methyl propionate (5n):

(Eluent: 40 %EtOAc/hexane); 44 % yield (31 mg); brown liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.39 – 7.36 (m, 1H), 7.10 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.01 (s, 2H), 4.39 - 4.29 (m, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.78 – 1.72 (m, 4H), 1.47 – 1.43 (m, 4H), 1.26 – 1.23 (m 3H), 0.94 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.73, 153.57 (d, *J* = 32.6 Hz), 152.68 (d, *J* = 230.4 Hz), 133.22, 133.10, 132.91(d, *J* = 26.4 Hz), 132.08,

124.31, 113.48, 67.94 (d, *J* = 6.6 Hz), 62.27, 43.28, 32.68(d, *J* = 6.2Hz), 18.80, 14.15, 13.74; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 7.89; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{20}H_{29}N_2NaO_6P$ 447.1661 found 447.1640.

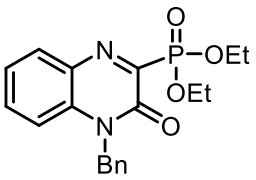
(3-(bis(benzyloxy)phosphoryl)-2-oxoquinoxalin-1(2*H*)-yl)methyl propionate (5o):

(Eluent: 40 %EtOAc/hexane); 68 % yield (67 mg); yellow liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 4H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.28 (m, 6H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.40 – 5.37 (m, 4H), 5.02 (s, 2H), 4.25 (d, *J* = 7.1 Hz, 2H), 1.28 – 1.26 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.74, 153.69 (d, *J* = 33.0 Hz), 152.38 (d, *J* = 231.7 Hz), 136.39, 136.34, 133.33, 133.00 (d, *J* = 26.2 Hz), 132.23, 128.58, 128.42, 128.23, 124.45, 113.54, 69.59 (d, *J* = 6.0 Hz), 62.40, 43.41, 29.81 (d, *J* = 7.0 Hz), 14.23; **^{31}P NMR** (242 MHz, $CDCl_3$) δ 7.68; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{26}H_{25}N_2NaO_6P$ 515.1348 found 515.1346.



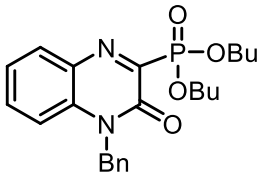
Diethyl (4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5p):[2]

(Eluent: 30 % EtOAc/hexane); 83 % yield (62 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.55 – 7.52 (m, 1H), 7.55 – 7.43 (m, 1H), 7.51 – 7.43 (m, 6H), 5.69 (s, 2H), 4.72 – 4.66 (m, 4H), 1.66 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.12 (d, *J* = 32.4 Hz), 152.69 (d, *J* = 229.9 Hz), 134.74, 133.28, 133.10, 132.91, 131.77, 128.94, 127.83, 127.00, 124.01, 114.69, 64.23 (d, *J* = 6.2 Hz), 45.74, 16.50 (d, *J* = 6.3 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.46.



Dibutyl (4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5q):

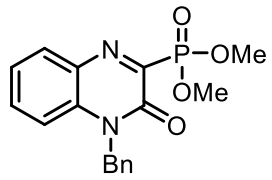
(Eluent: 40 %EtOAc/hexane); 59 % yield (51 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.0, 1.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.35 – 7.26 (m, 7H), 5.49 (s, 2H), 4.43 – 4.37 (m, 4H), 1.81 – 1.75 (m, 4H), 1.52 – 1.44 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.25 (d, *J* = 32.5 Hz), 153.02 (d, *J* = 229.9 Hz), 134.93, 133.20 (d, *J* = 26.3 Hz), 133.09, 132.94, 131.97, 129.10, 127.99, 127.15, 124.10, 114.76, 68.03 (d, *J* = 6.6 Hz), 45.88, 32.78 (d, *J*



= 6.1 Hz), 18.89, 13.82; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.40; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{23}H_{29}KN_2O_4P$ 467.1502 found 467.1509.

Dimethyl (4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (5r):[2]

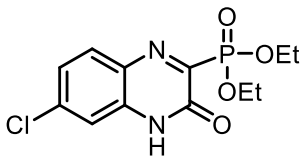
(Eluent: 40 %EtOAc/hexane); 86 % yield (59 mg); yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ



7.99 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.37 – 7.24 (m, 8H), 5.49 (s, 2H), 4.08 (d, *J* = 11.0 Hz, 6H); ^{13}C **NMR** (125 MHz, $CDCl_3$) δ 154.35 (d, *J* = 32.4 Hz), 152.39 (d, *J* = 232.9 Hz), 134.74, 133.41, 133.19, 133.17 (d, *J* = 26.3 Hz), 132.01, 129.11, 128.02, 127.12, 124.25, 114.84, 54.82 (d, *J* = 6.2 Hz), 45.96; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 11.01.

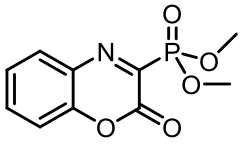
Diethyl (6-chloro-3-oxo-3,4-dihydroquinoxali-2-yl)phosphonate (5s):

(Eluent: 40 %EtOAc/hexane); 77% yield (49 mg); yellow solid, (Melting point 209- 210 °C): **^{1}H**



NMR (500 MHz, $CDCl_3$) δ 12.79 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.53 – 7.51 (m, 1H), 4.70 – 4.63 (m, 4H), 1.67 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.54 (d, *J* = 31.8 Hz), 153.04 (d, *J* = 229.5 Hz), 139.10, 131.25 (d, *J* = 25.8 Hz), 131.36, 131.15, 125.15, 116.18, 64.51 (d, *J* = 6.3 Hz), 16.58 (d, *J* = 6.2 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$) δ 8.20; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{12}H_{14}ClKN_2O_4P$ 355.0017 found 355.0020.

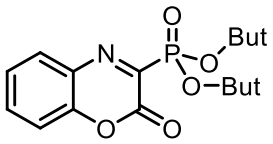
Dimethyl (2-oxo-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(6a):



(Eluent: 20 %EtOAc/hexane); 63% yield (32 mg); yellow liquid, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.63- 7.60 (m, 1H), 7.42- 7.40 (m, 1H), 7.32 (dd, *J* = 8.3, 1.3 Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.05 (d, *J* =37.3), 149.98 (d, *J* = 233.6 Hz), 146.82 (d, *J* = 21 Hz), 134.22, 134.02 (d, J= 23.2 Hz), 130.86, 126.19, 116.97, 55.05 (d, J = 6.3 Hz); **^{31}P NMR** (242 MHz, $CDCl_3$) δ 7.46; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{10}H_{10}NNaO_5P$ 278.0194 found 278.0195.

Dibutyl (2-oxo-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (6b):

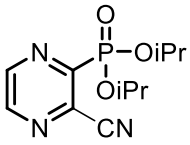
(Eluent: 20 %EtOAc/hexane); 34% yield (23 mg); yellow liquid, **^{1}H NMR** (600 MHz, $CDCl_3$) δ



7.89 – 7.85 (m, 1H), 7.61-7.58 (m, 1H), 7.41-7.38 (m, 1H), 7.32 – 7.29 (m, 1H), 4.35-4.29 (m, 4H), 1.75-1.70 (m, 4H), 1.45-1.41 (m , 4H), 0.92 (dd, *J* = 7.5, 2.4 Hz, 6H), **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.29, 151.02, 149.75, 146.88, 133.99, 131.16, 131.00, 130.80, 126.06, 116.92, 68.40, 68.35, 32.65, 32.61, 18.79, 13.72; **^{31}P NMR** (242 MHz, $CDCl_3$) δ 4.96; **HRMS-ESI** (m/z) $[M+Na]^+$calcd. For $C_{16}H_{22}NNaO_5P$ 362.1133 found 362.1130.

diisopropyl (5-cyanopyrazin-2-yl)phosphonate (6c):

(Eluent: 30 %EtOAc/hexane); 37 % yield (68 mg); colourless liquid, **^{1}H NMR** (600 MHz, $CDCl_3$)



δ 9.16 (s, 1H), 9.04 (s, 1H), 4.94-4.89 (m, 2H), 1.43-1.42 (m, 6H), 1.34-1.32 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.33 (d, *J* = 224.3 Hz), 147.93, 147.80, 147.77, 132.19, 115.01, 73.52(d, *J* = 6.8 Hz), 24.21 (d, *J* = 4.4 Hz); 24.01 (d, *J* = 4.4 Hz); **^{31}P NMR** (242 MHz, $CDCl_3$) δ 1.93; **HRMS-ESI** (m/z) $[M+K]^+$calcd. For $C_{11}H_{16}KN_3O_3P$ 308.0566 found 308.0873.

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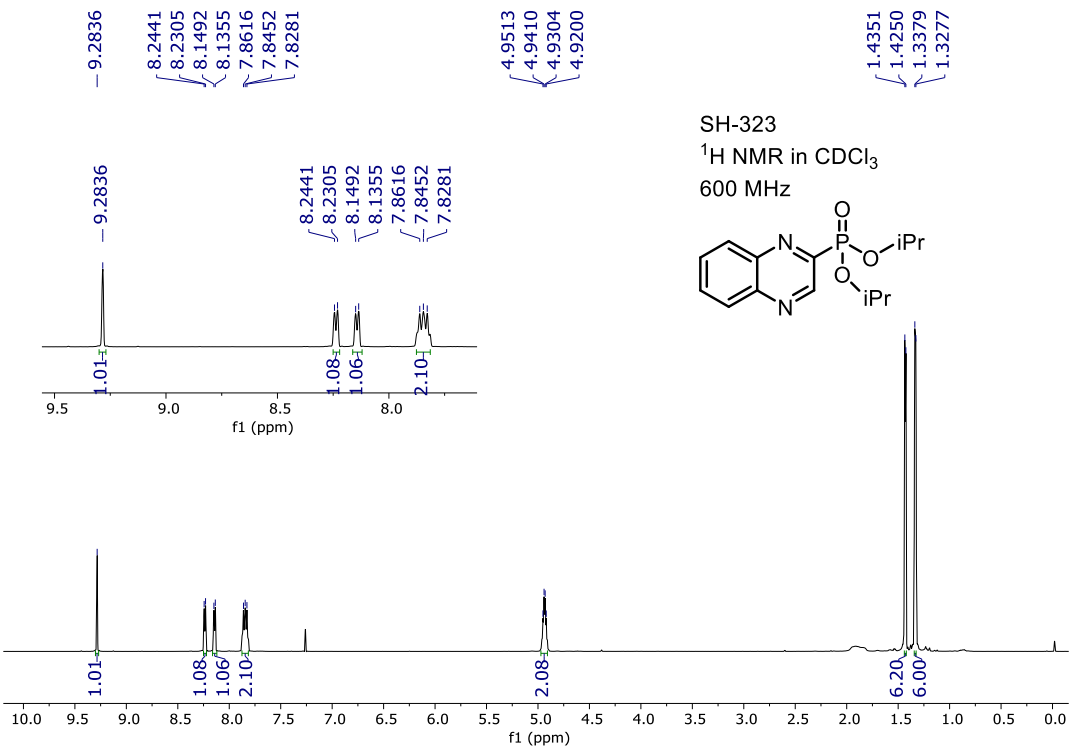
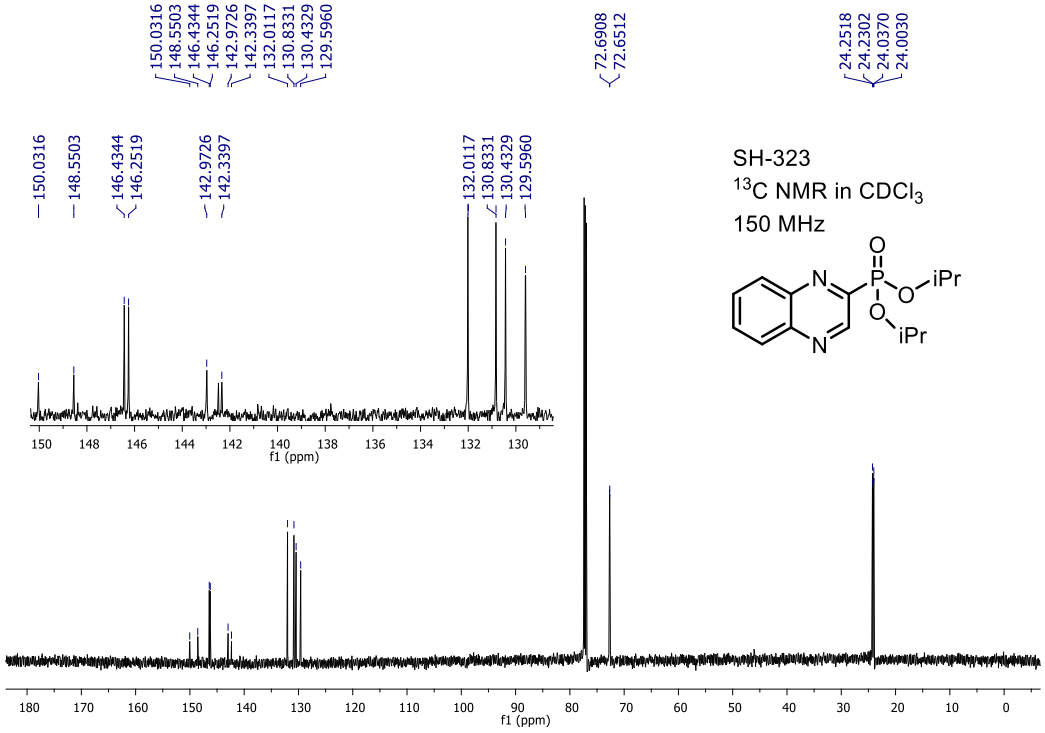
2. References:

1. Y. Liu, X. Chen, F. Zeng, K. Sun, C. Qu, L. Fan, Z. An, R. Li, C. Jing, S. Wei, L. Qu, B. Yu, Y. Sun and Y. Zhao *J. Org. Chem.*, 2018, **83**, 11727.
2. K. Li, Y. Jiang, K. Xu, C. Zeng and B. Suna Green Chem., 2019, **21**, 4412.

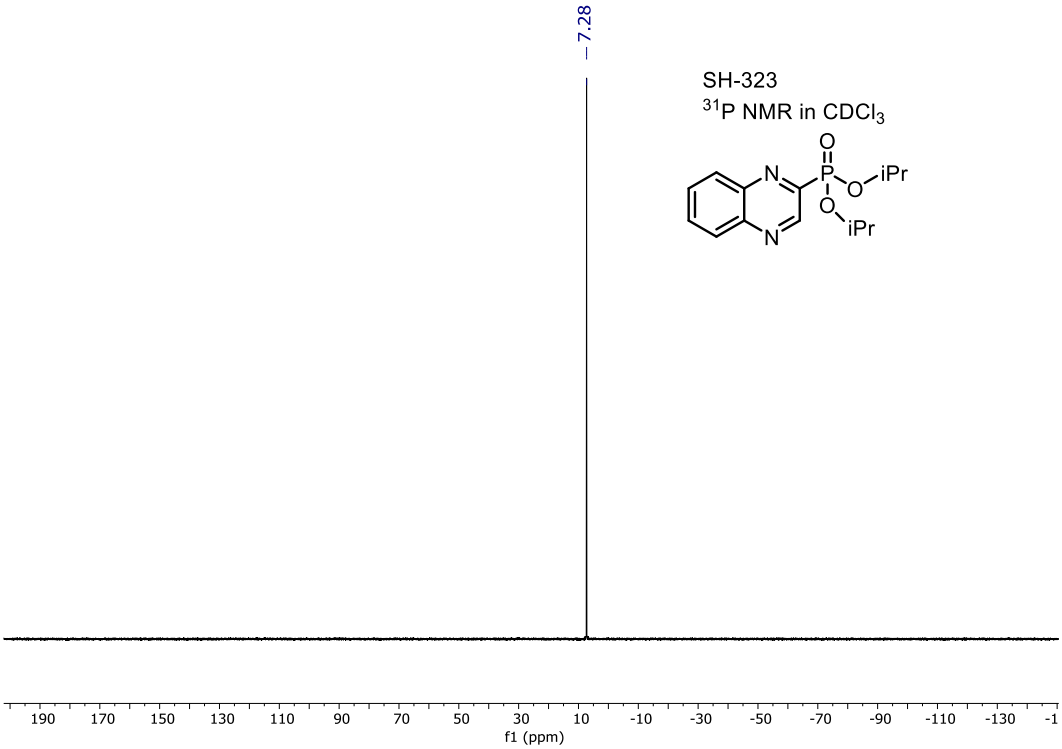
3. ^{1}H , ^{13}C and ^{31}P NMR Spectra of all products:



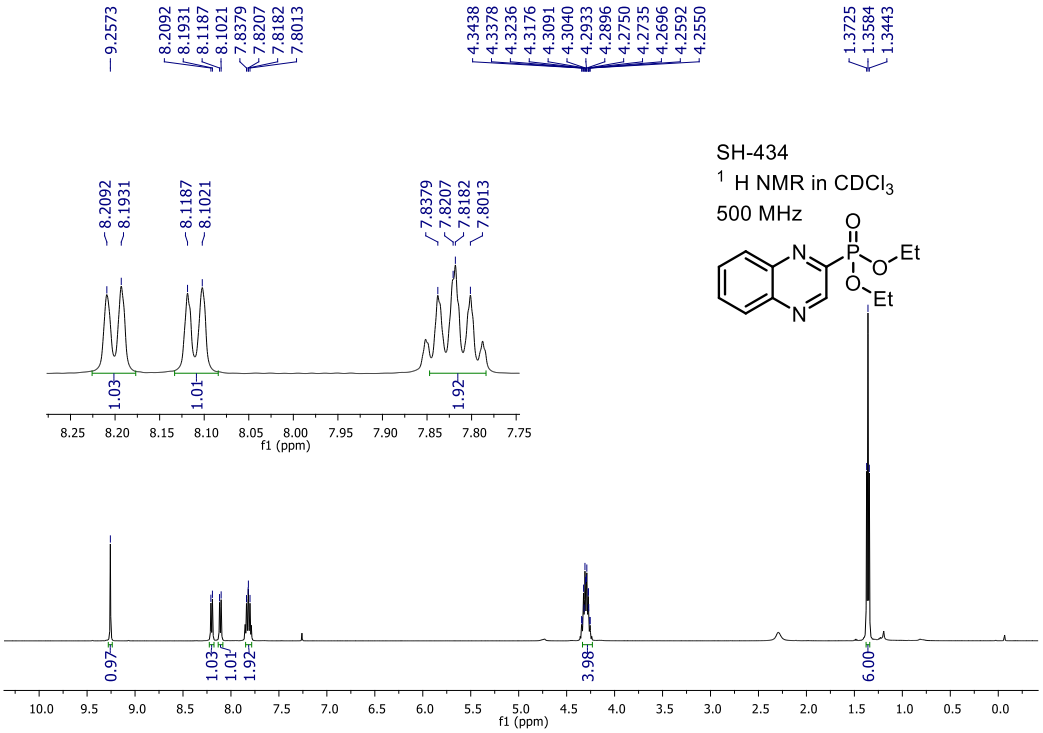
^{1}H NMR **3a**



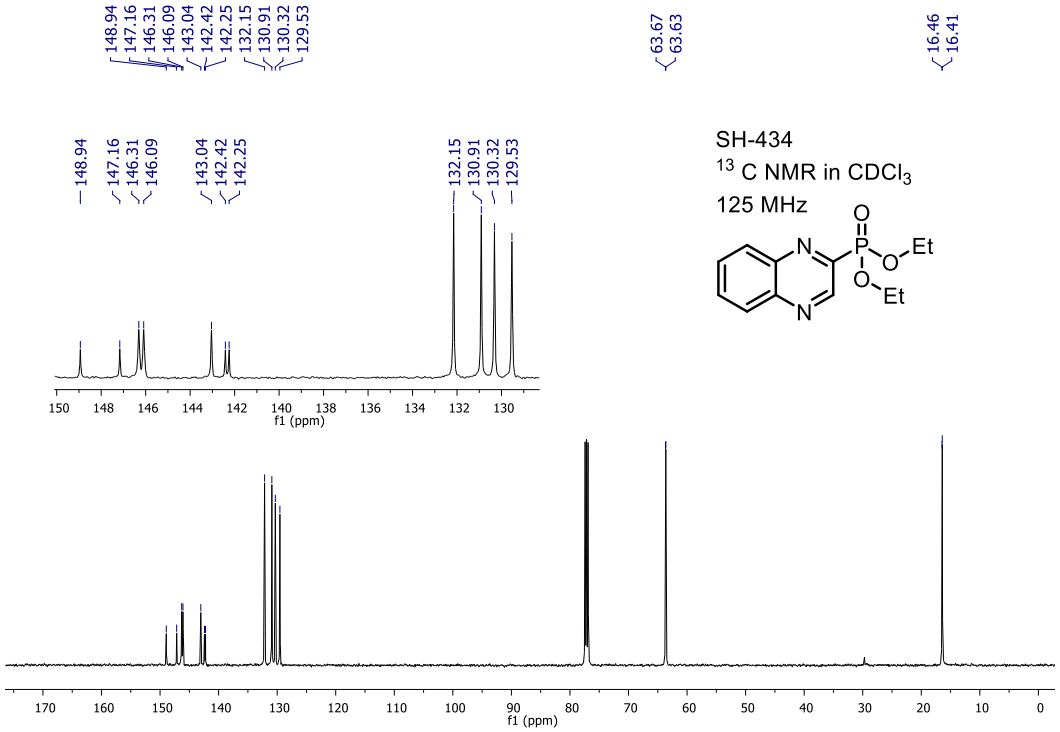
^{13}C NMR **3a**



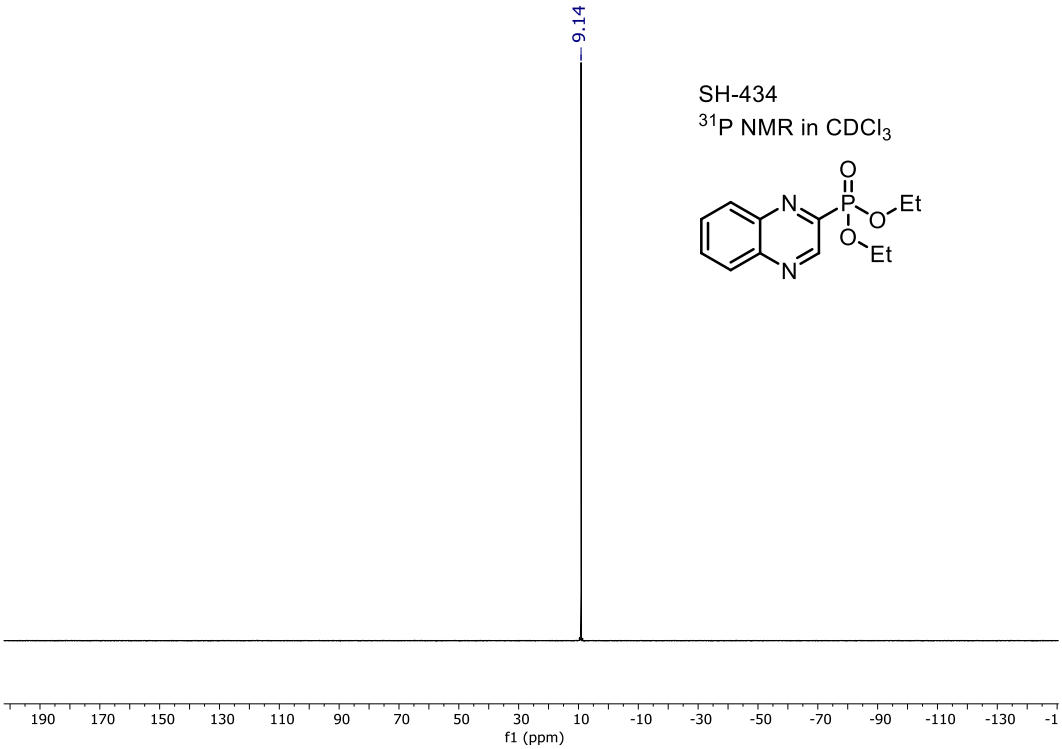
^{31}P NMR **3a**



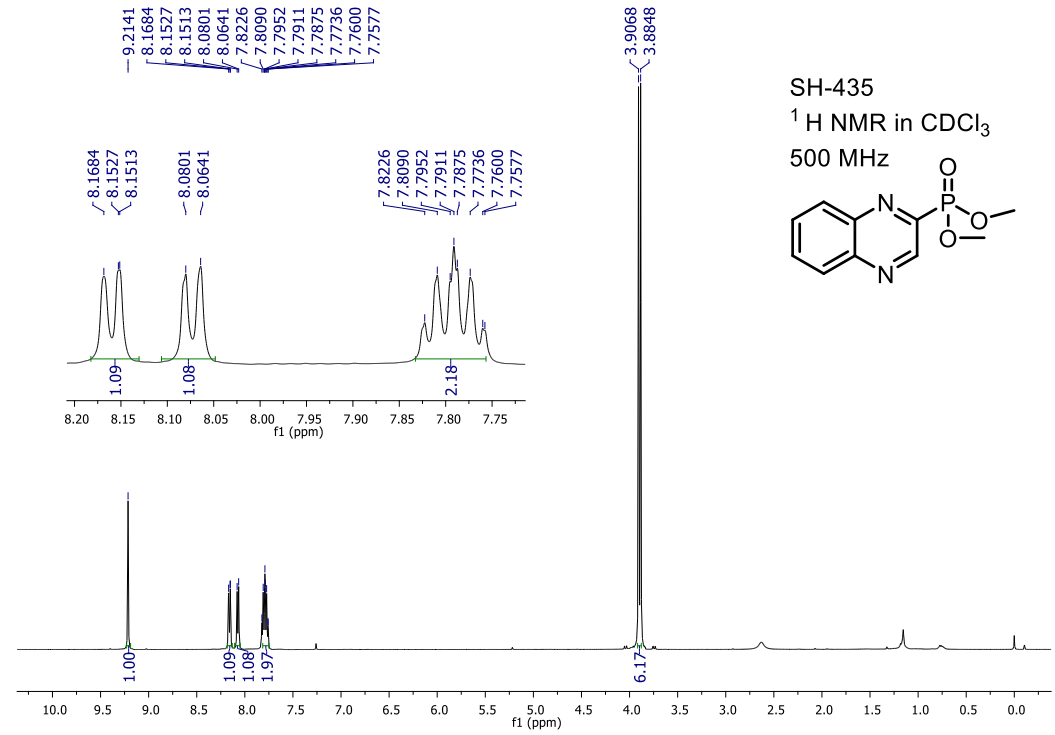
^{1}H NMR **3b**



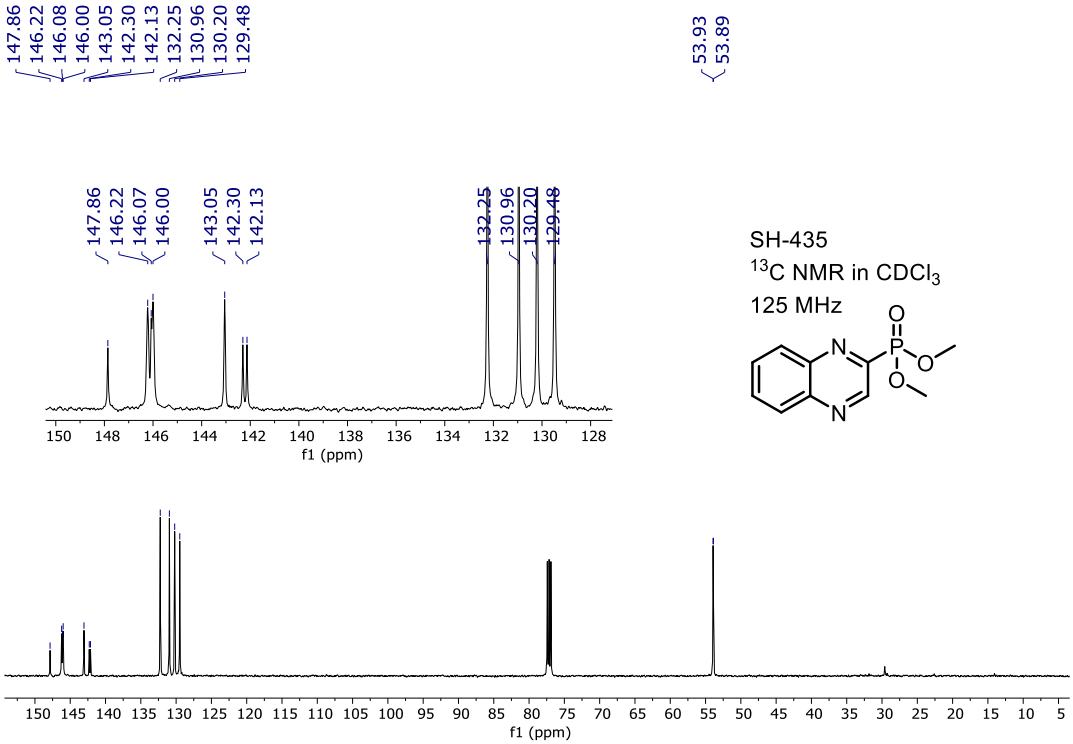
^{13}C NMR **3b**



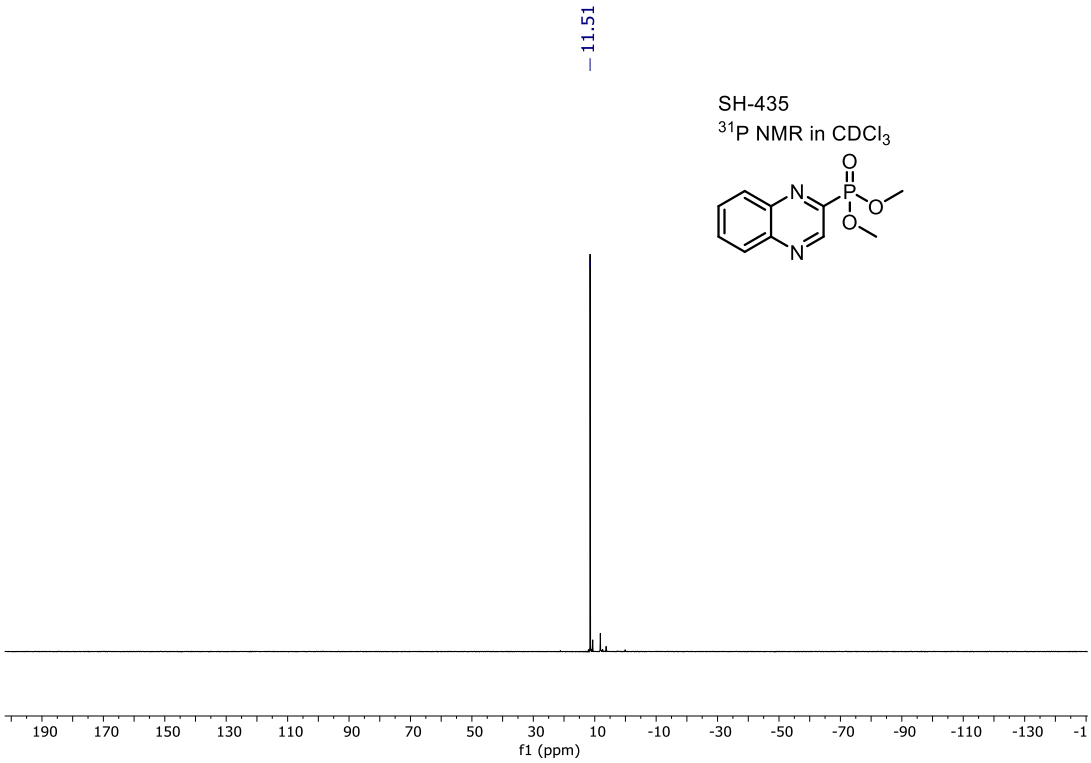
^{31}P NMR **3b**



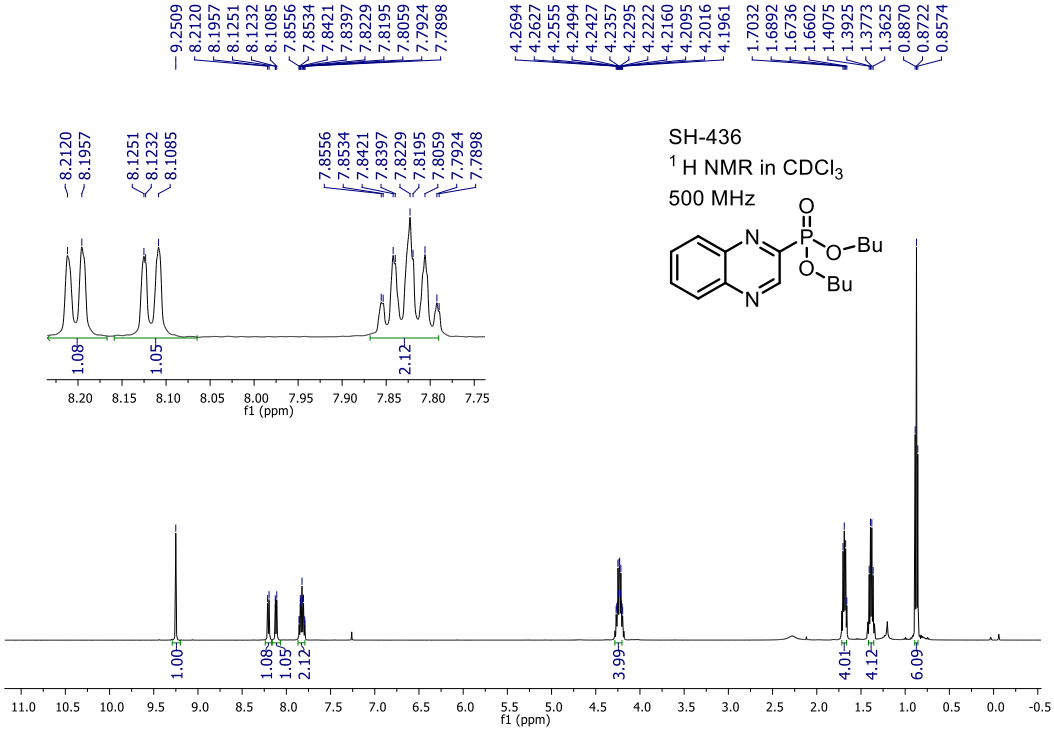
^{1}H NMR **3c**



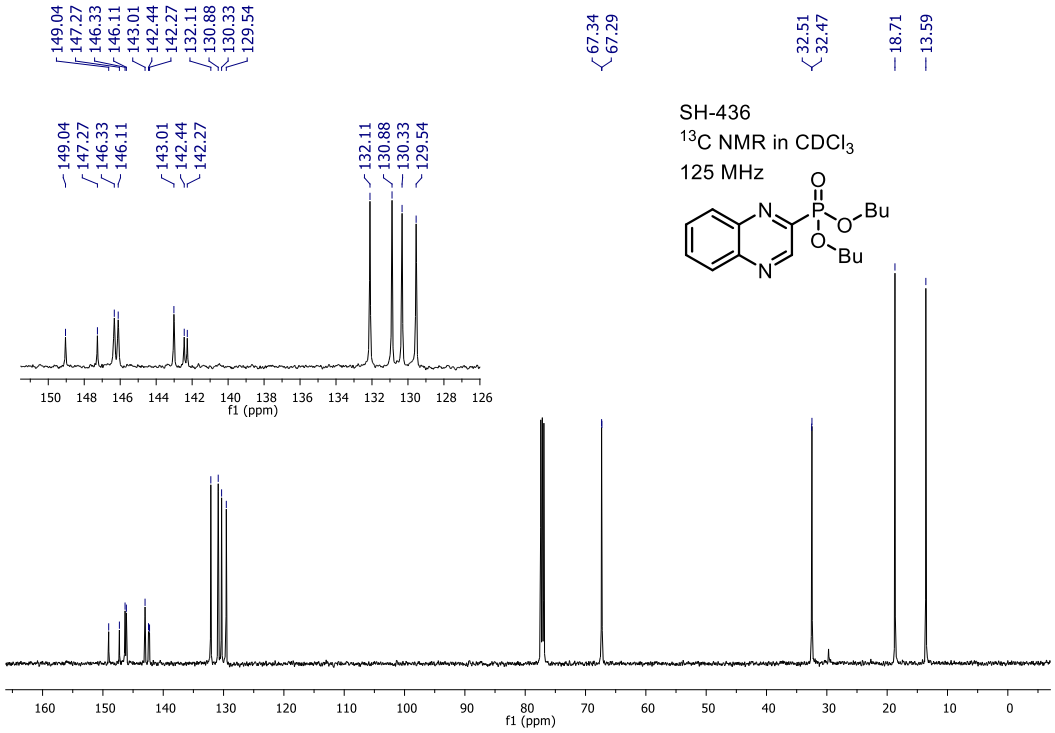
^{13}C NMR **3c**



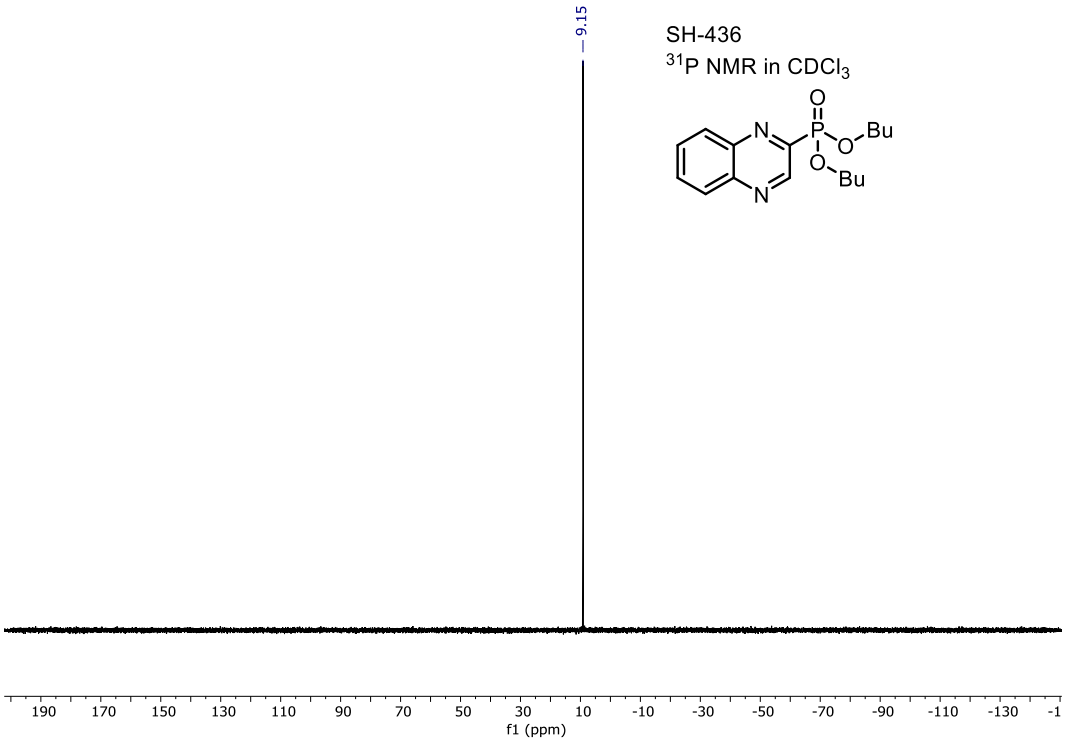
^{31}P NMR **3c**



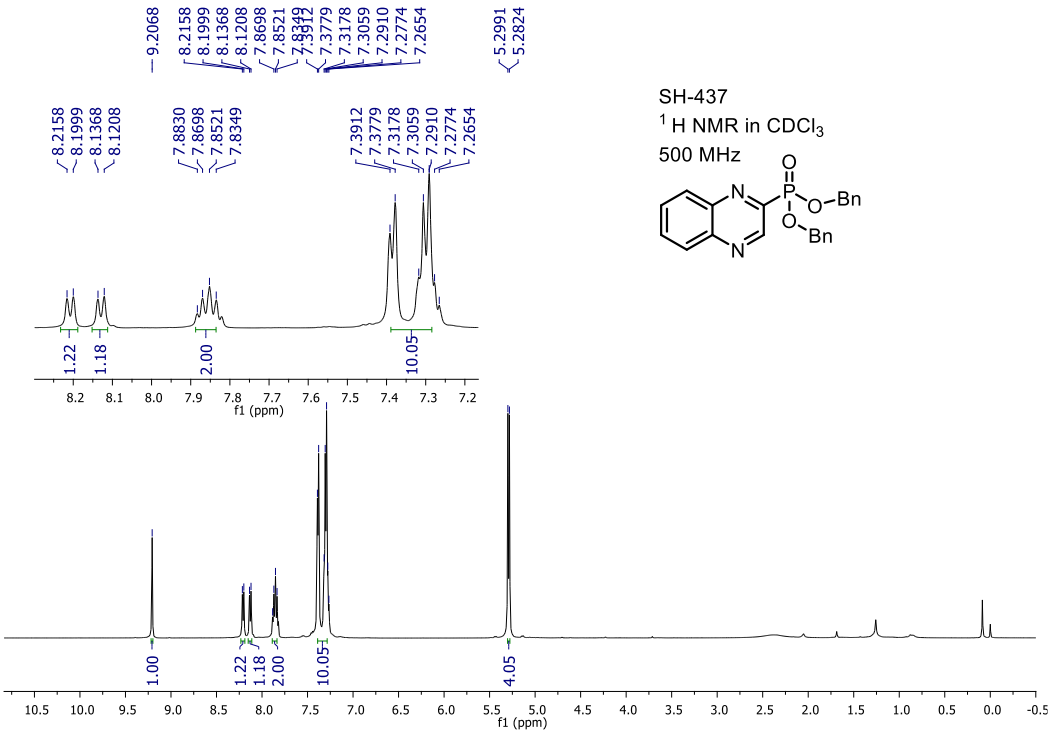
^{1}H NMR **3d**



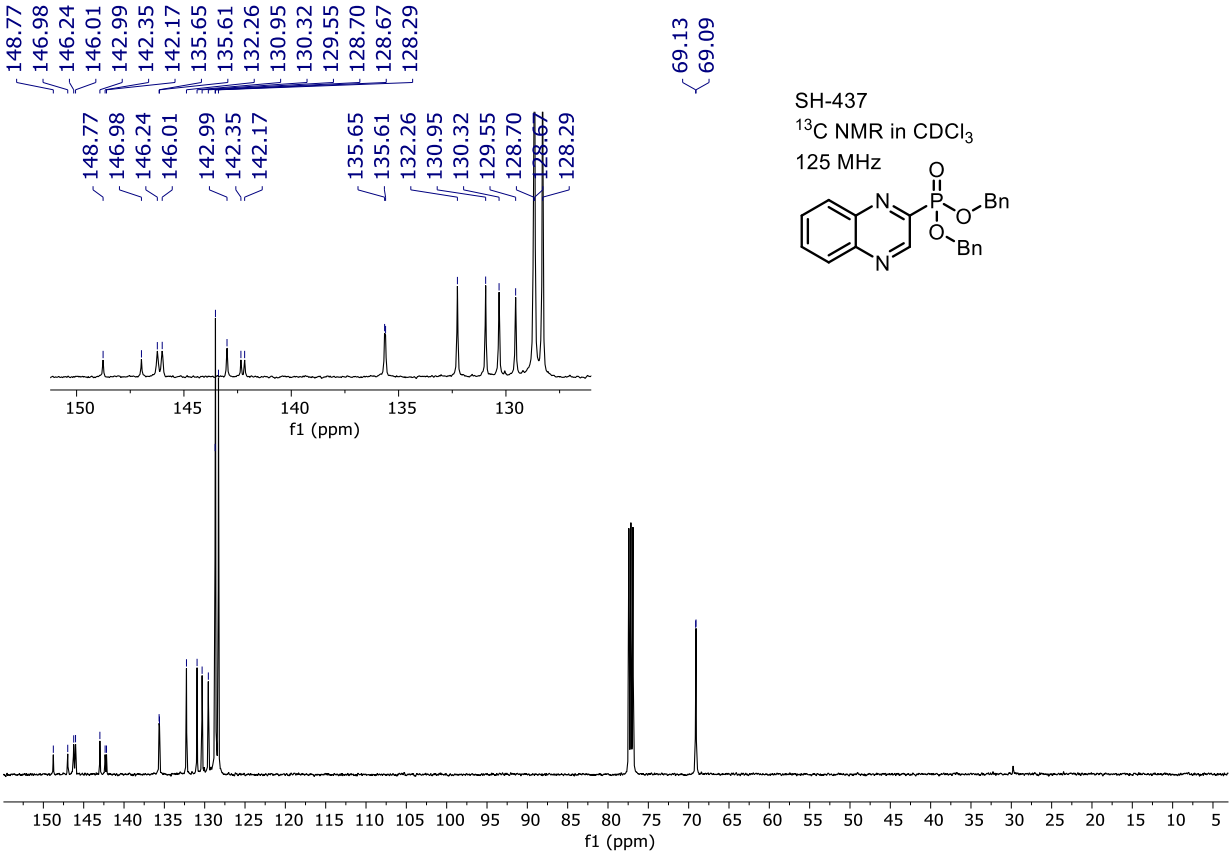
^{13}C NMR **3d**



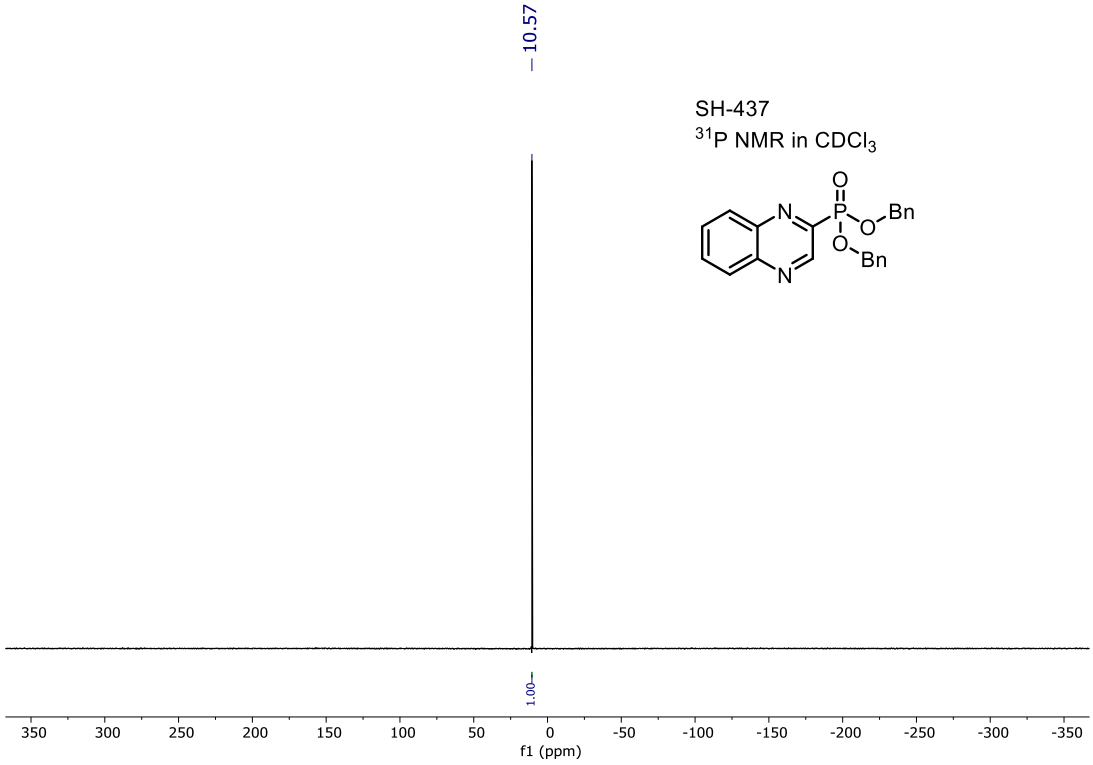
^{31}P NMR **3d**



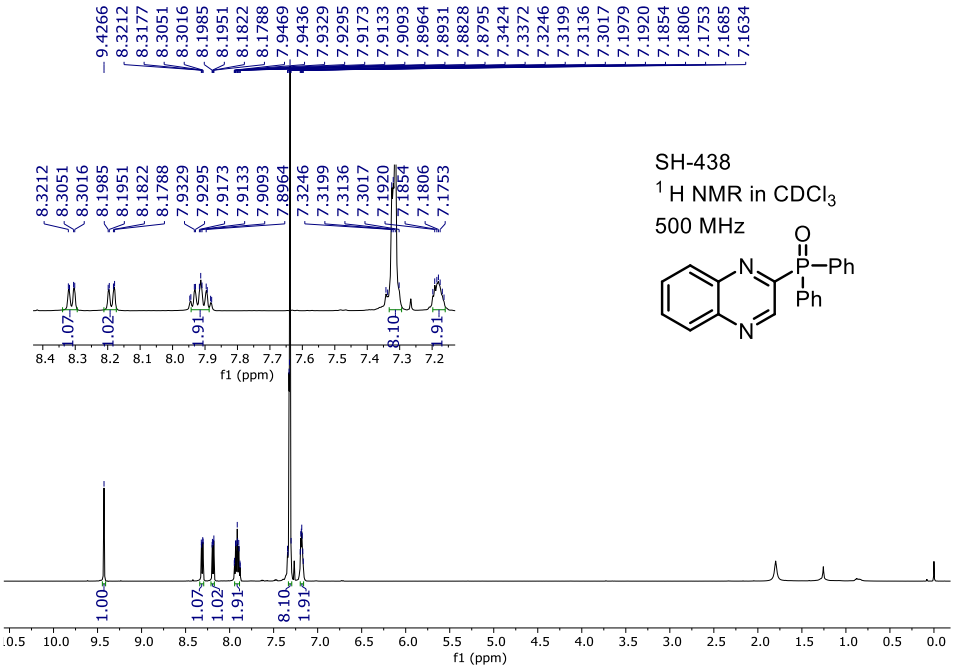
^{1}H NMR **3e**



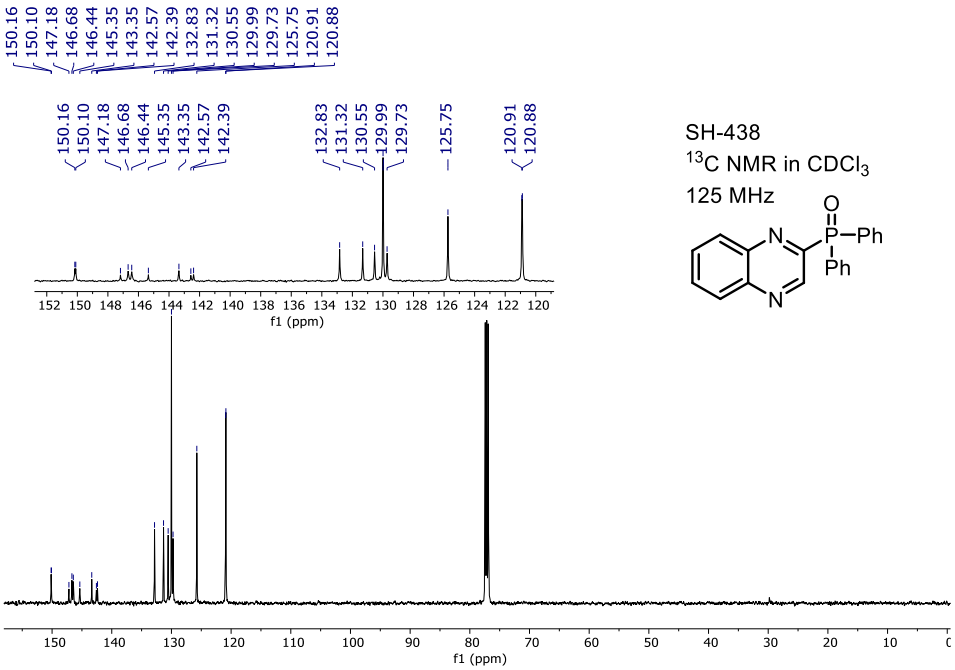
^{13}C NMR **3e**



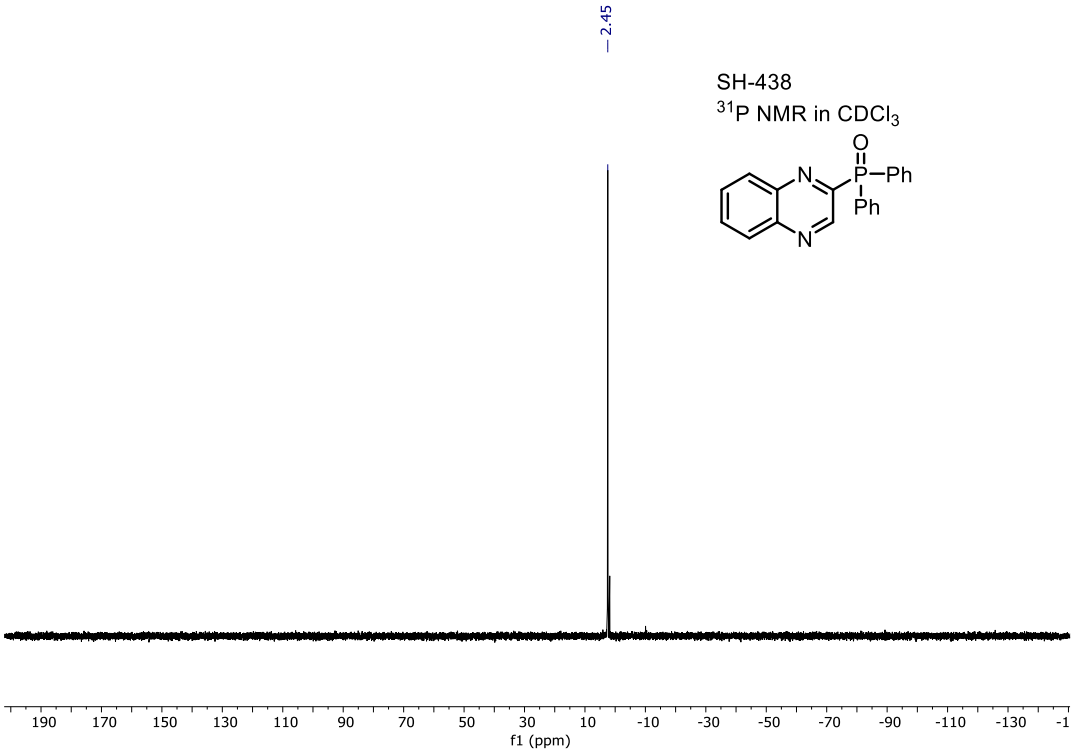
^{31}P NMR **3e**



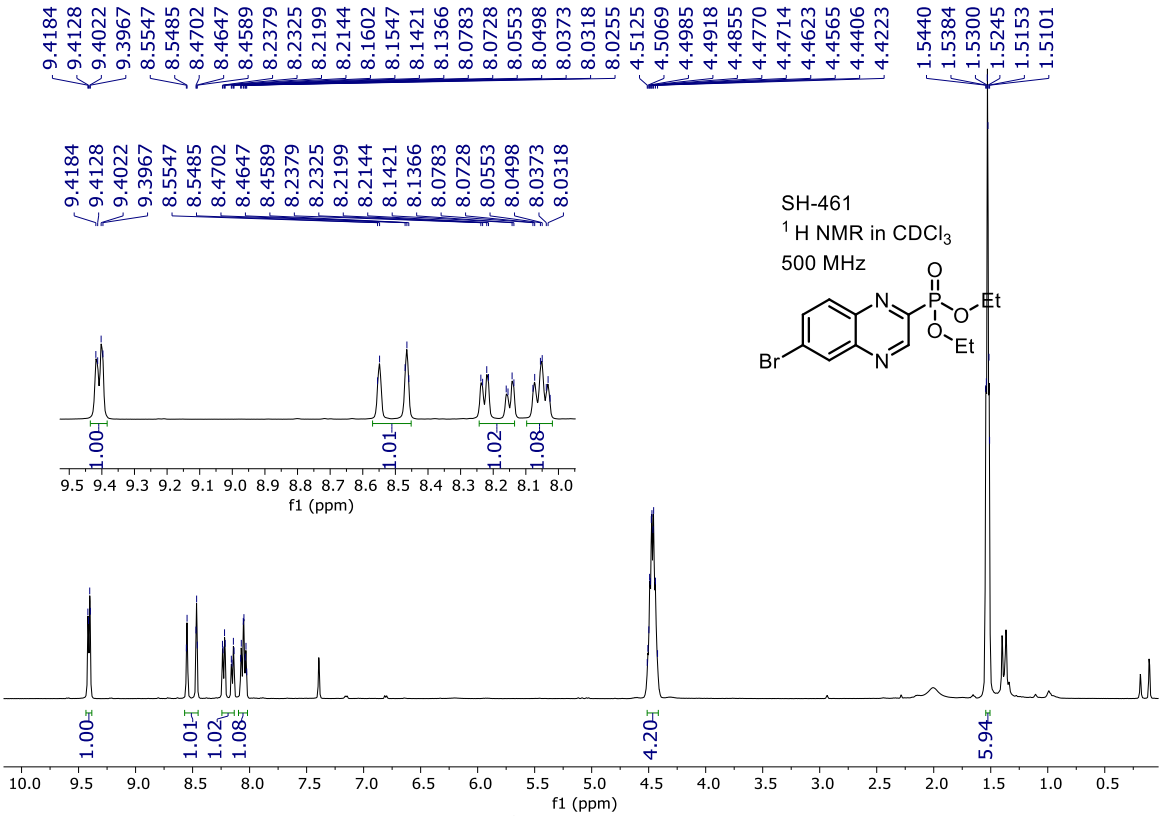
^{1}HNMR **3f**



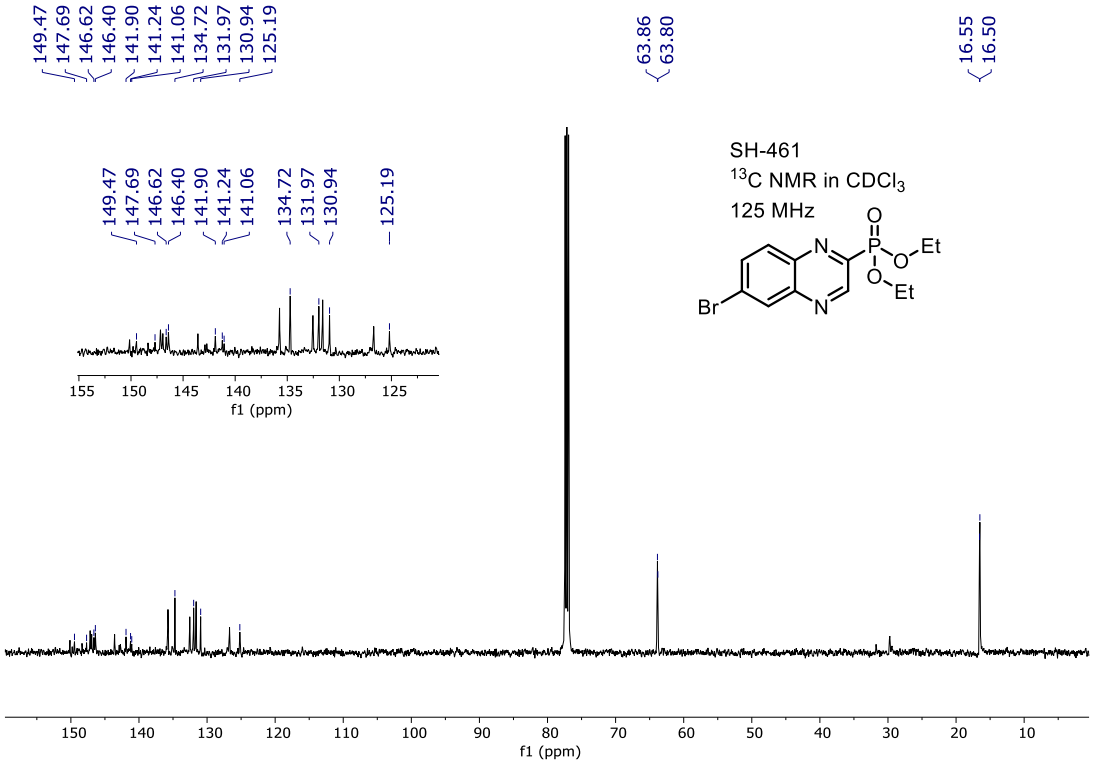
^{13}C NMR **3f**



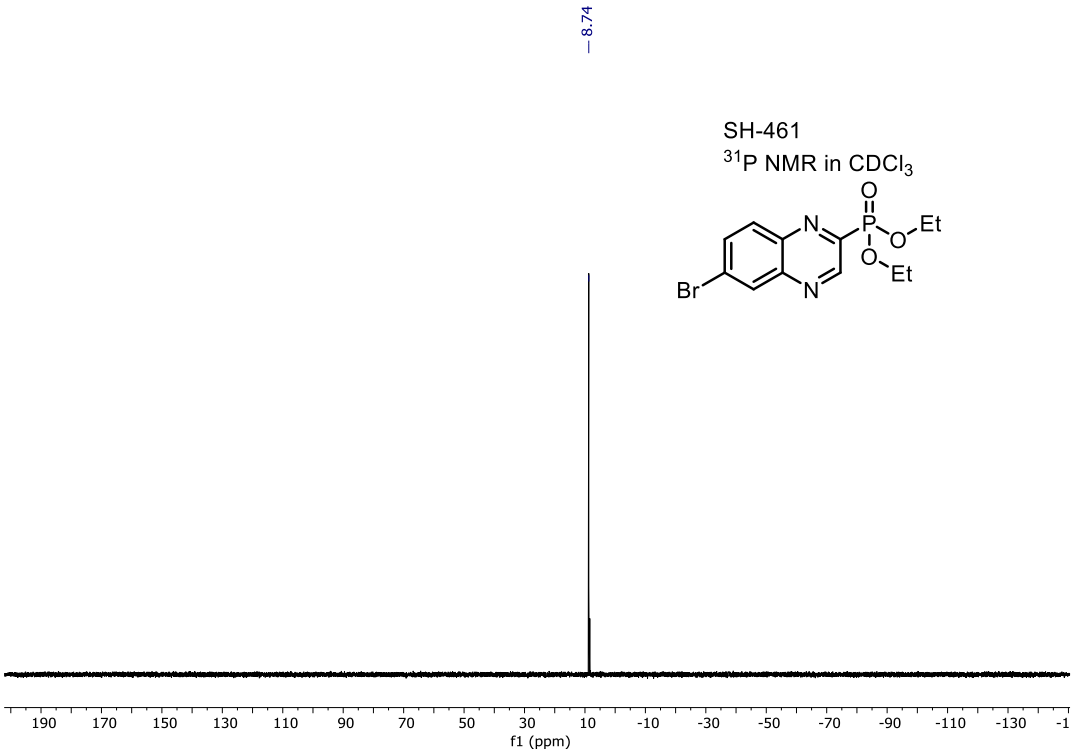
^{31}P NMR **3f**



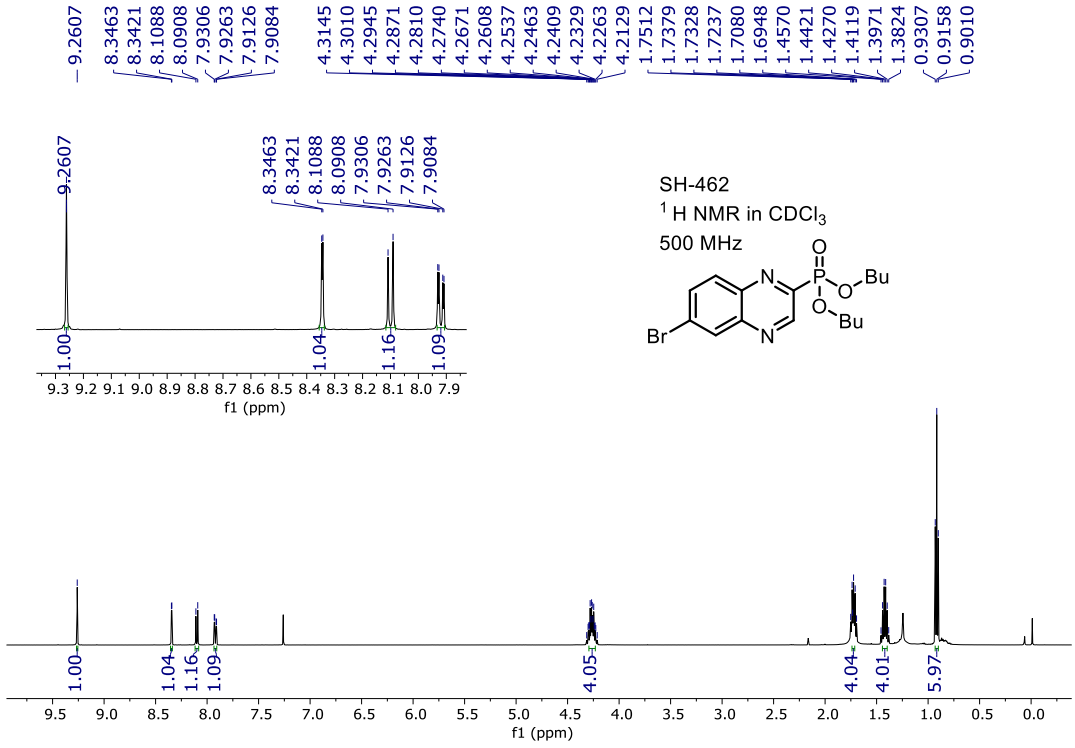
^{1}HNMR **3g**



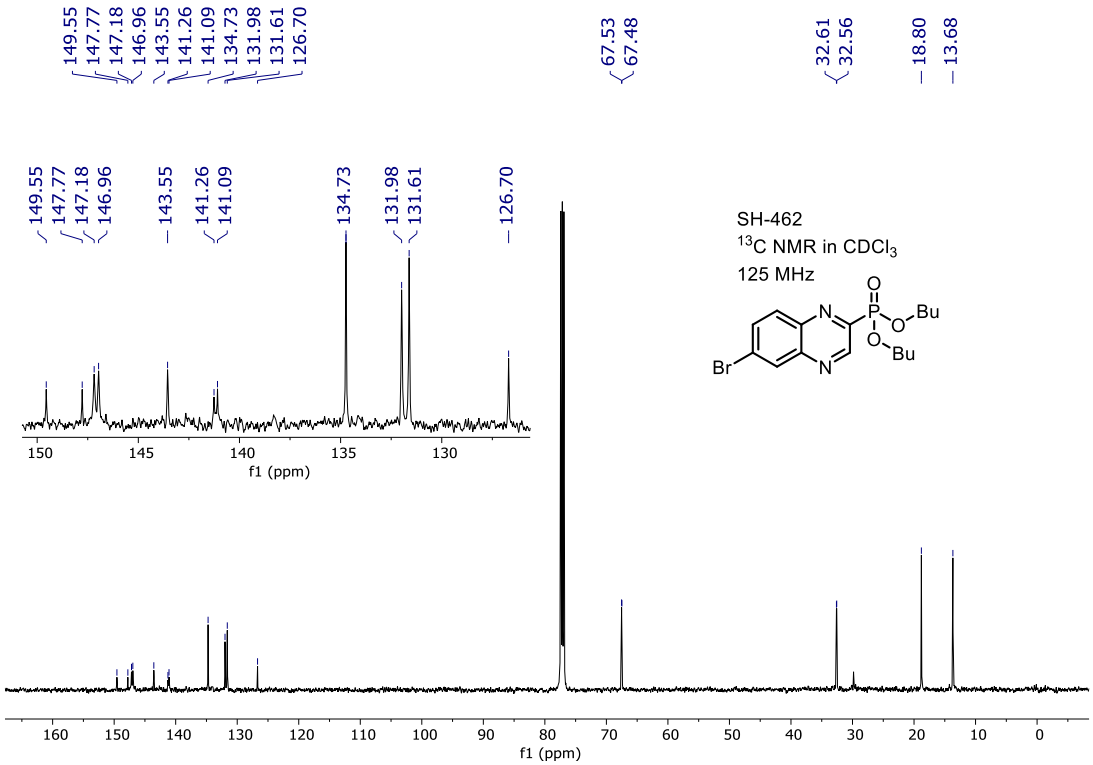
^{13}C NMR **3g**



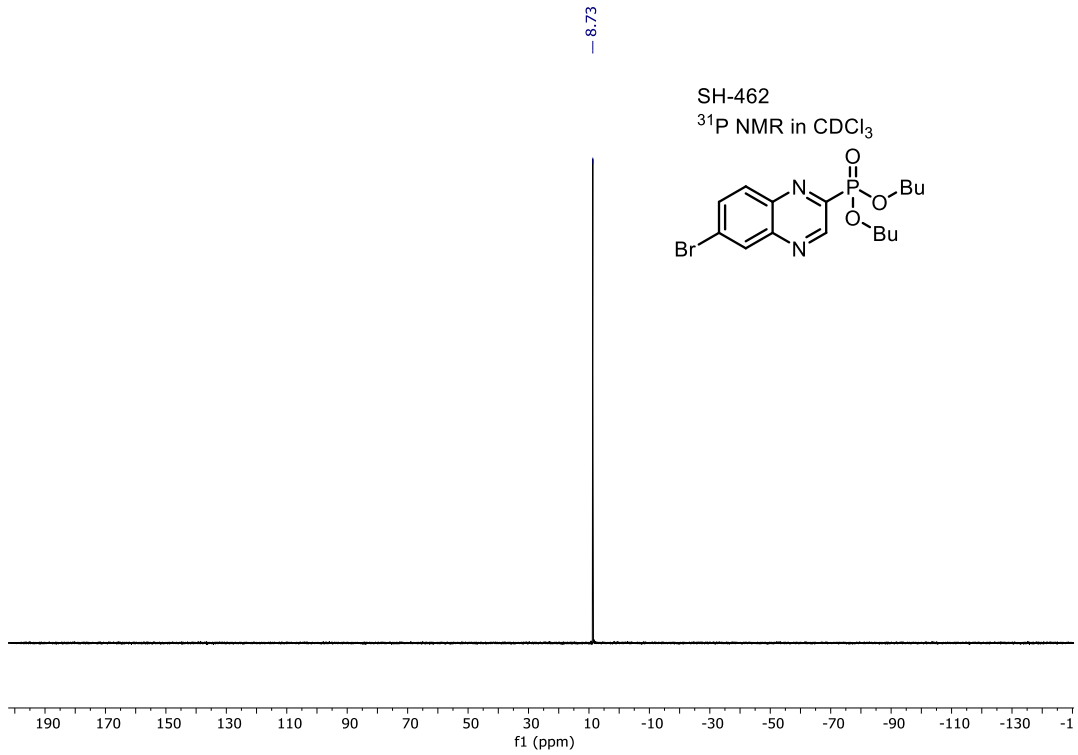
^{31}P NMR **3g**



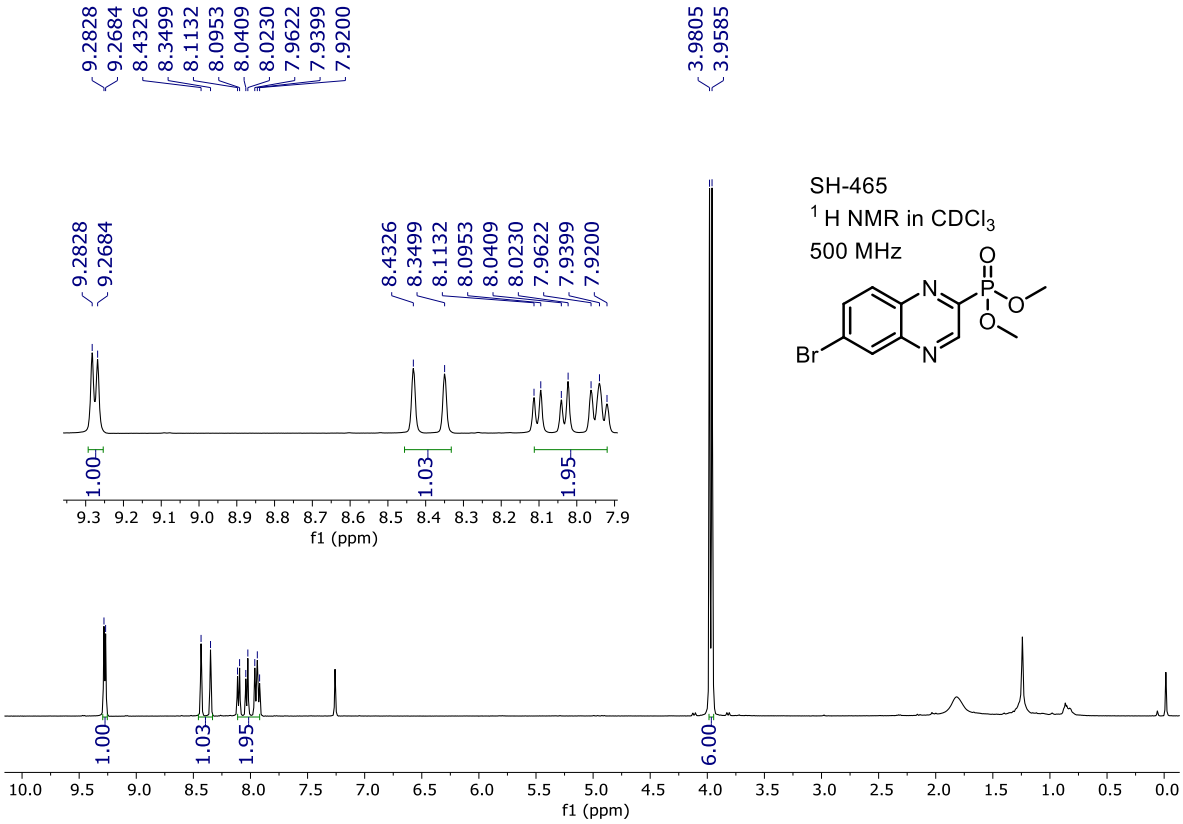
^{1}HNMR **3h**



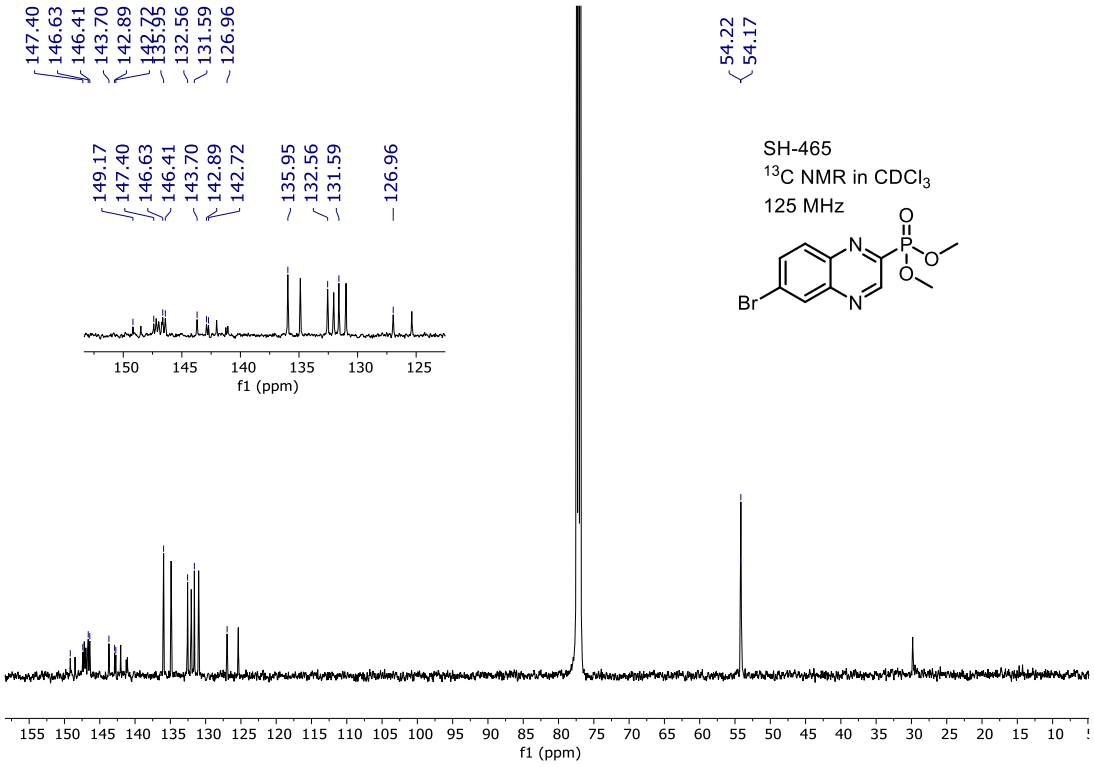
^{13}C NMR **3h**



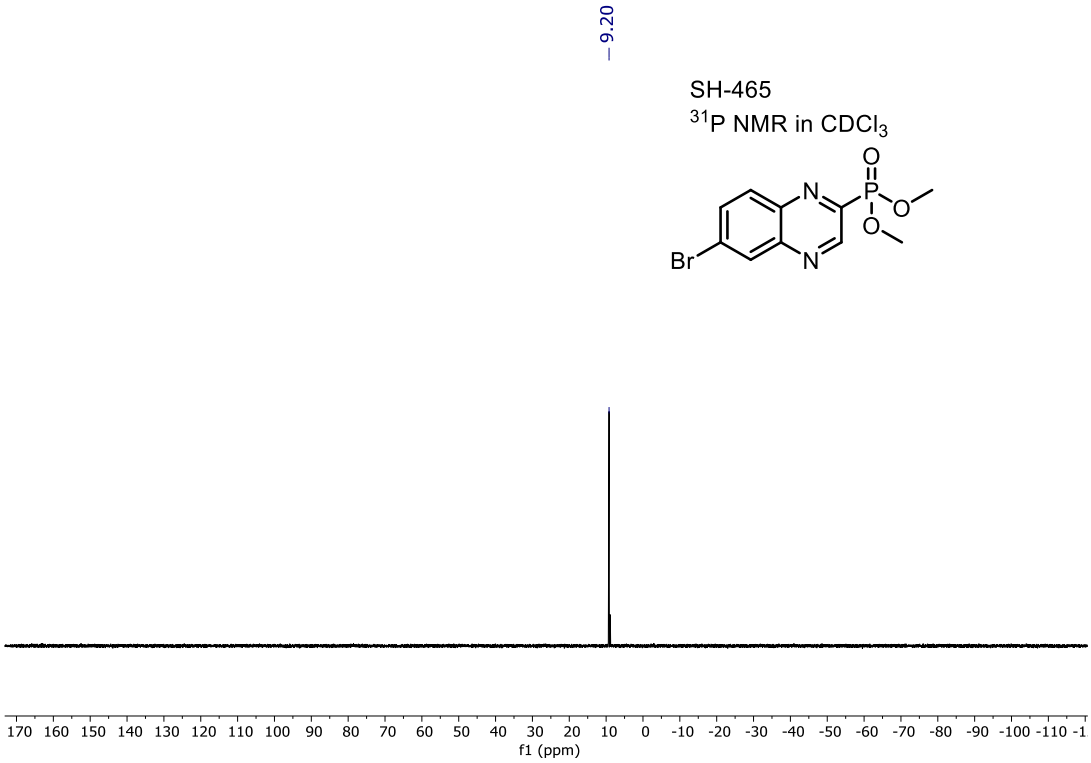
^{31}P NMR **3h**



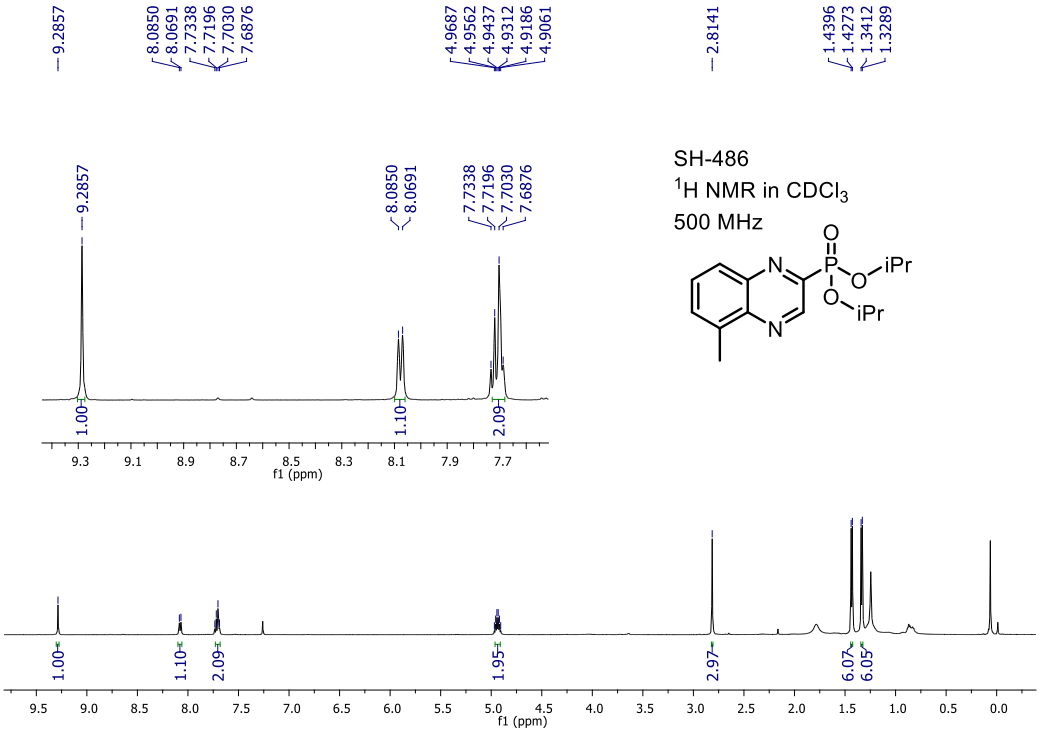
^{1}H NMR **3i**



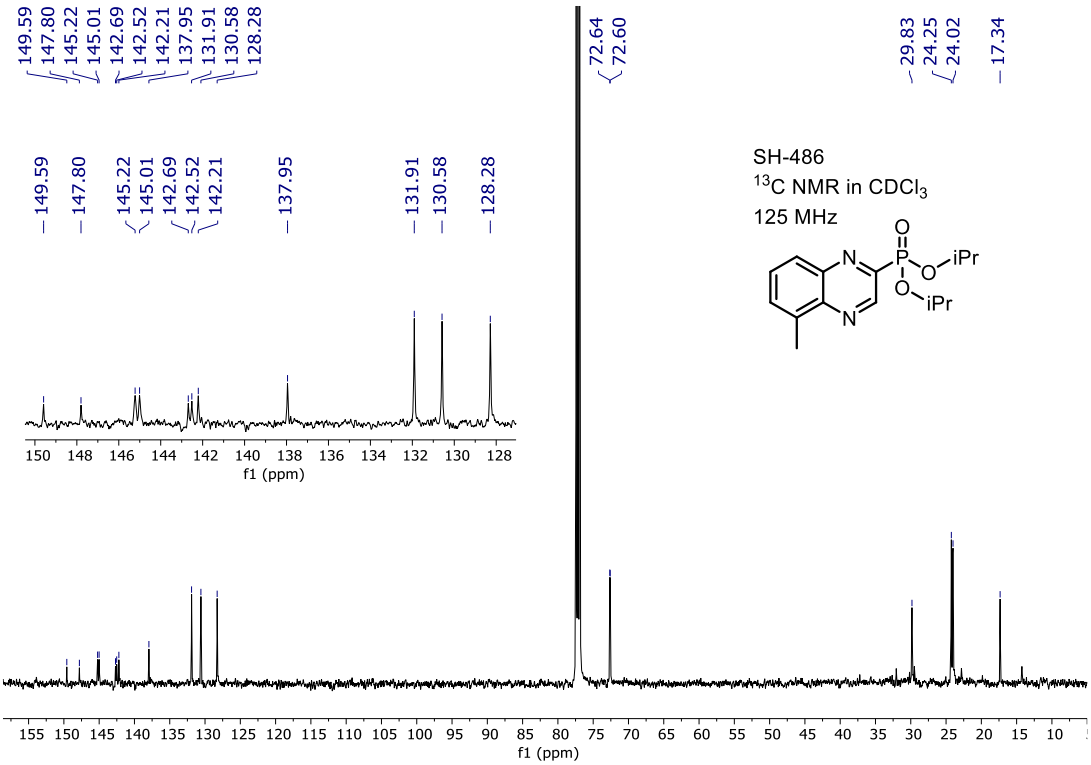
^{13}C NMR **3i**



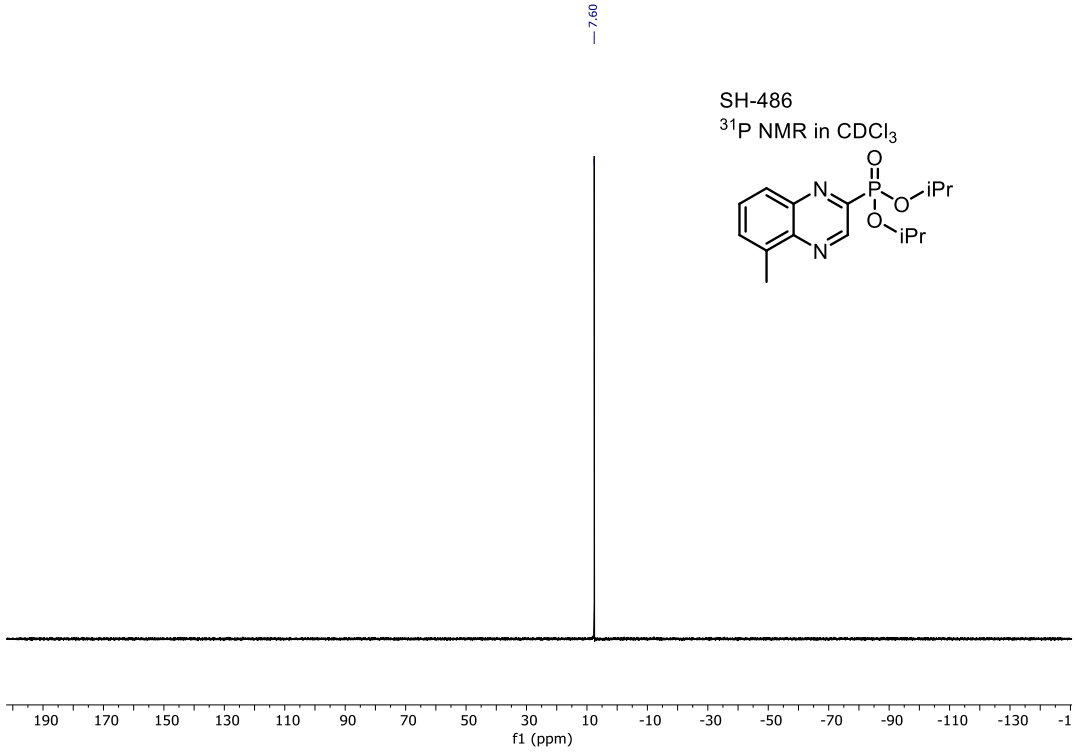
^{31}P NMR **3i**



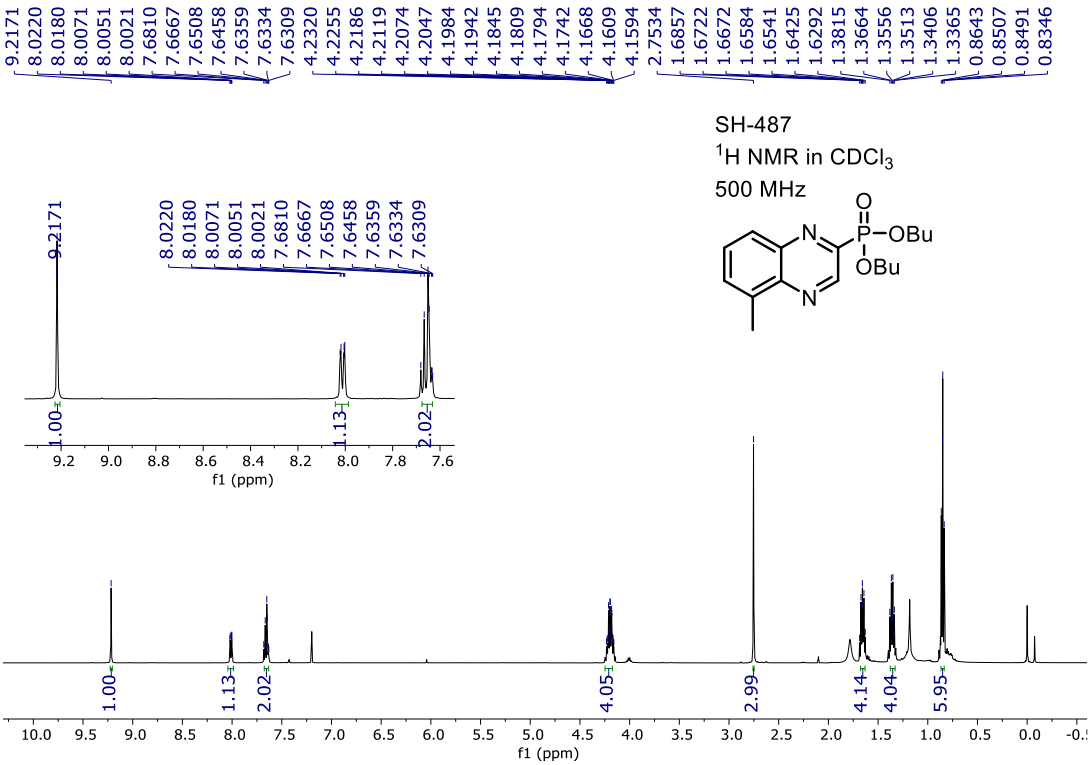
^{1}H NMR **3j**



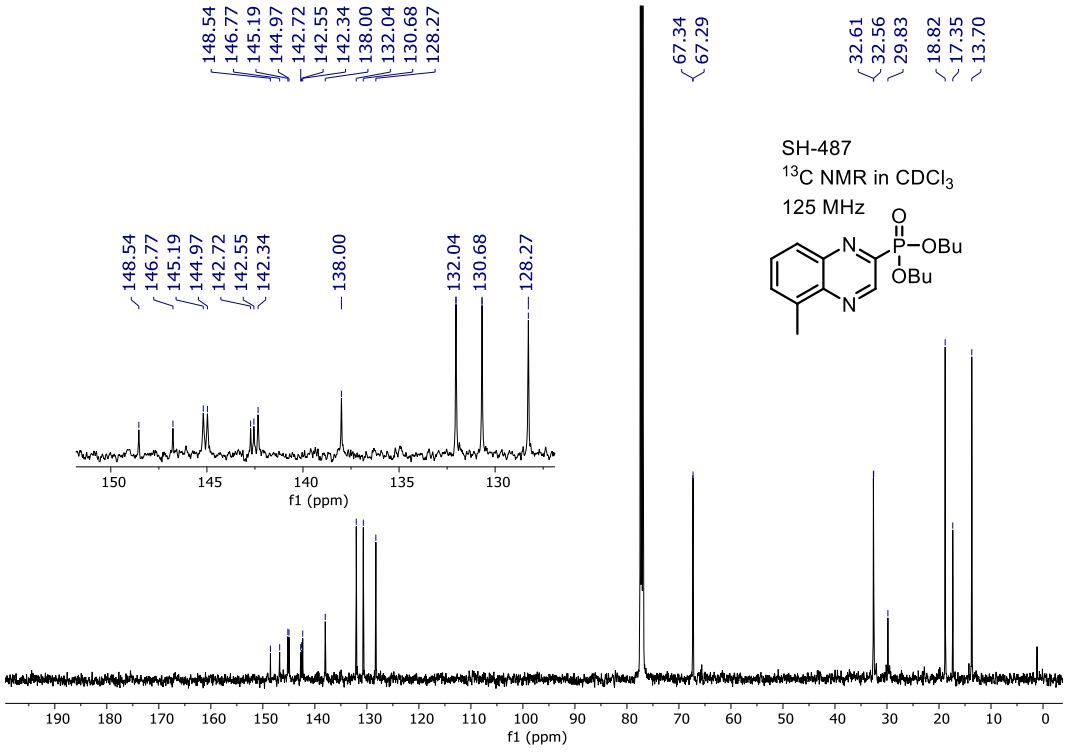
^{13}C NMR **3j**



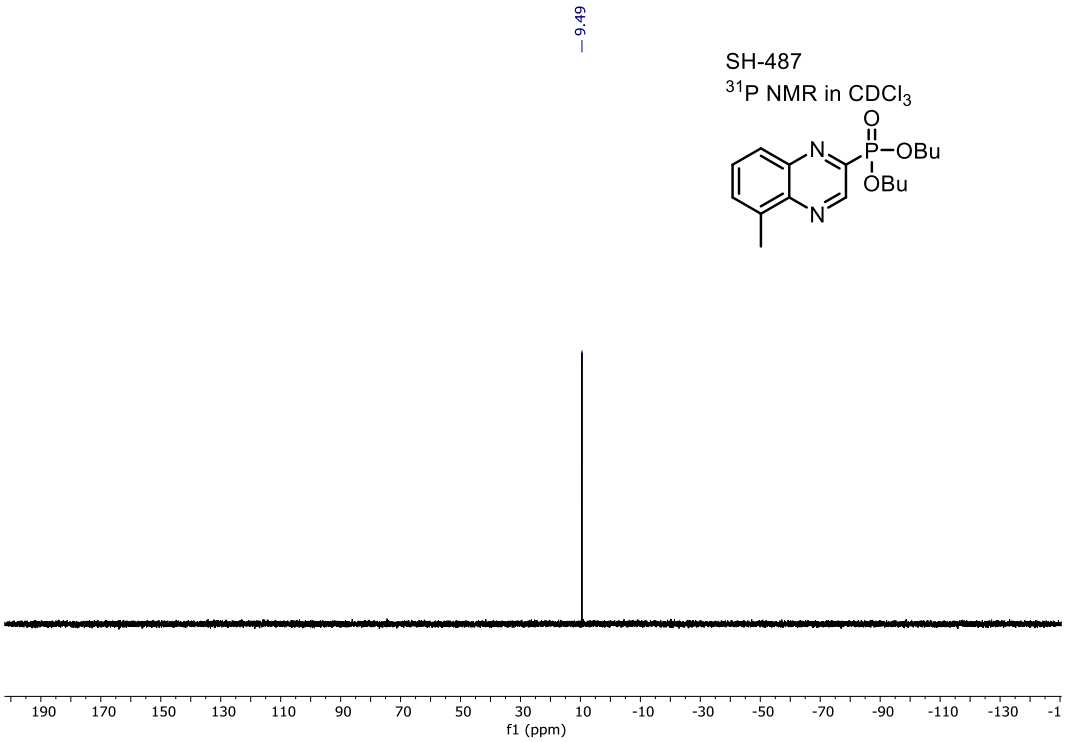
^{31}P NMR **3j**



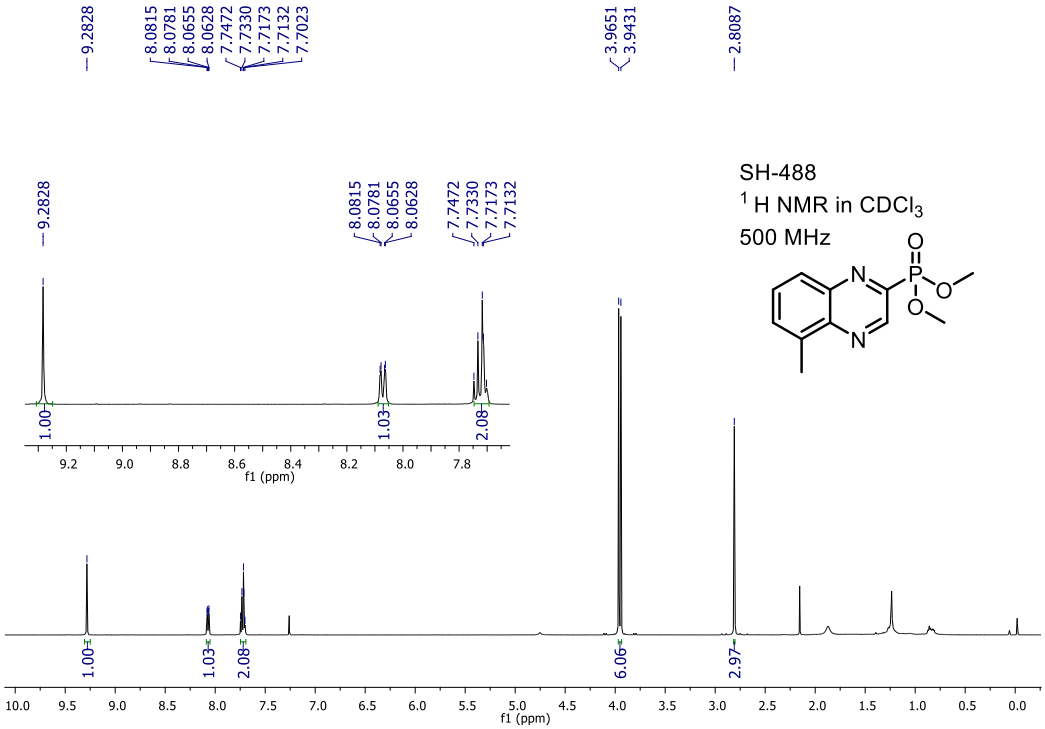
^{1}H NMR **3k**



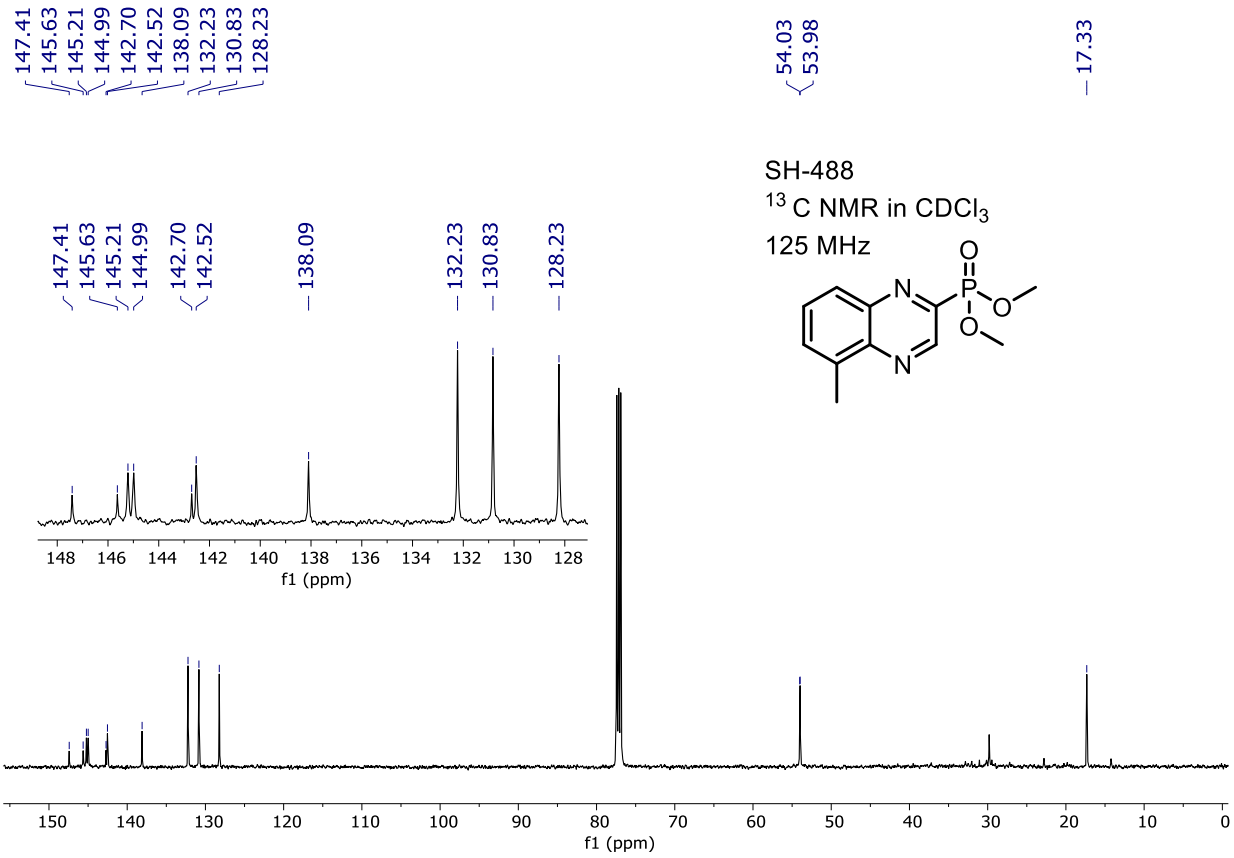
^{13}C NMR **3k**



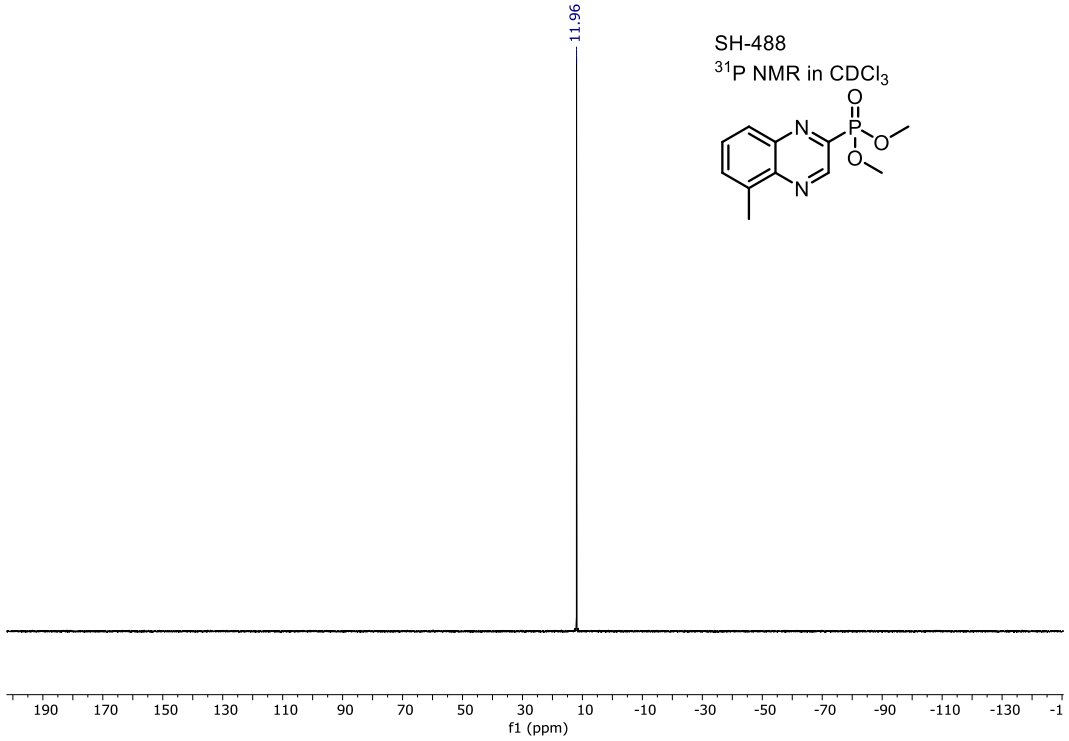
^{31}P NMR **3k**



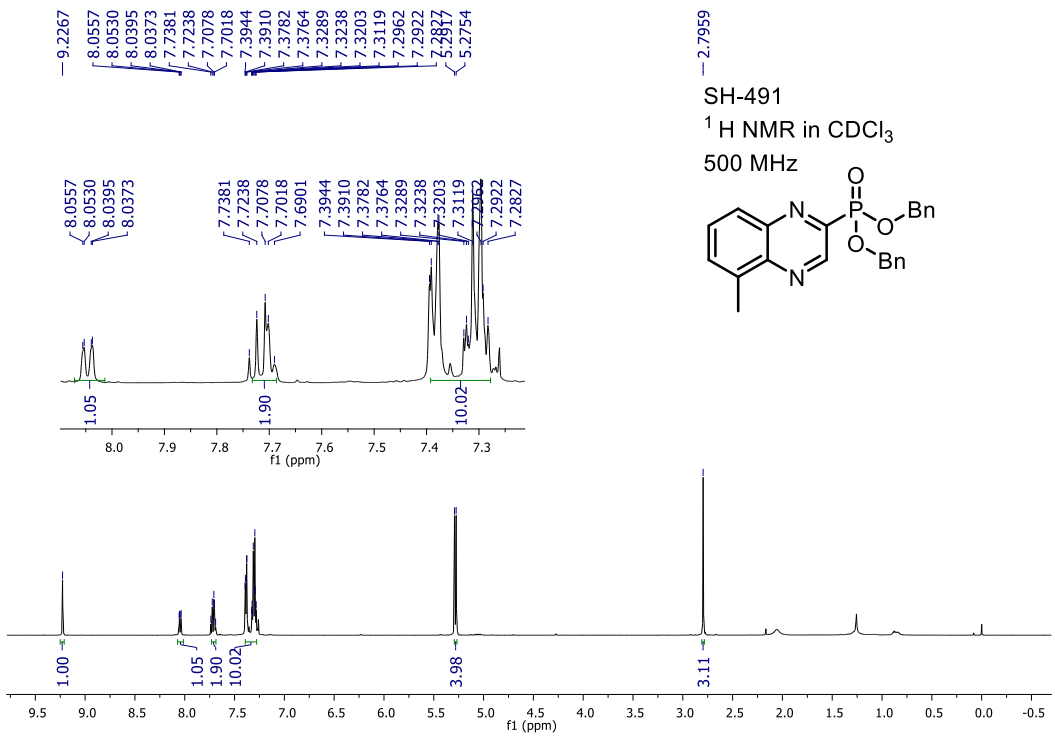
^{1}H NMR **3l**



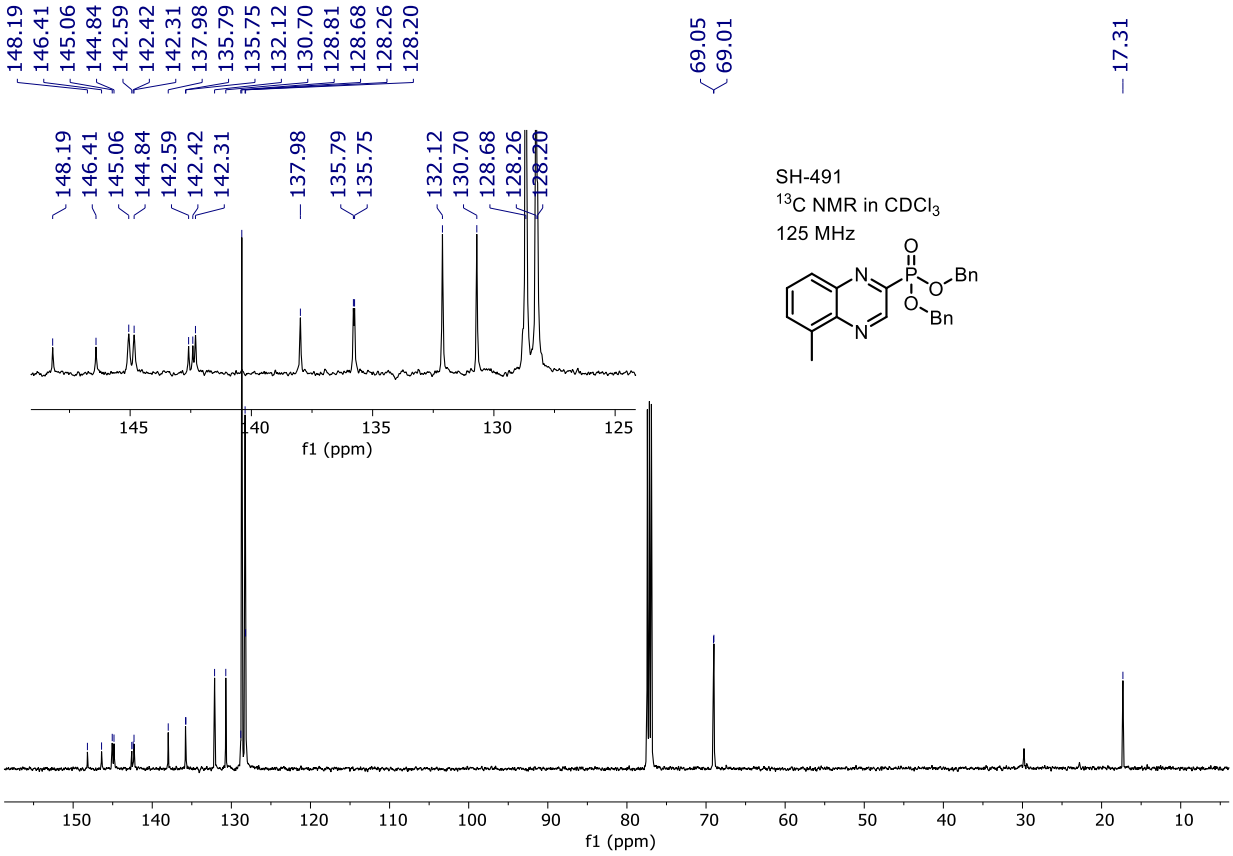
^{13}C NMR **3l**



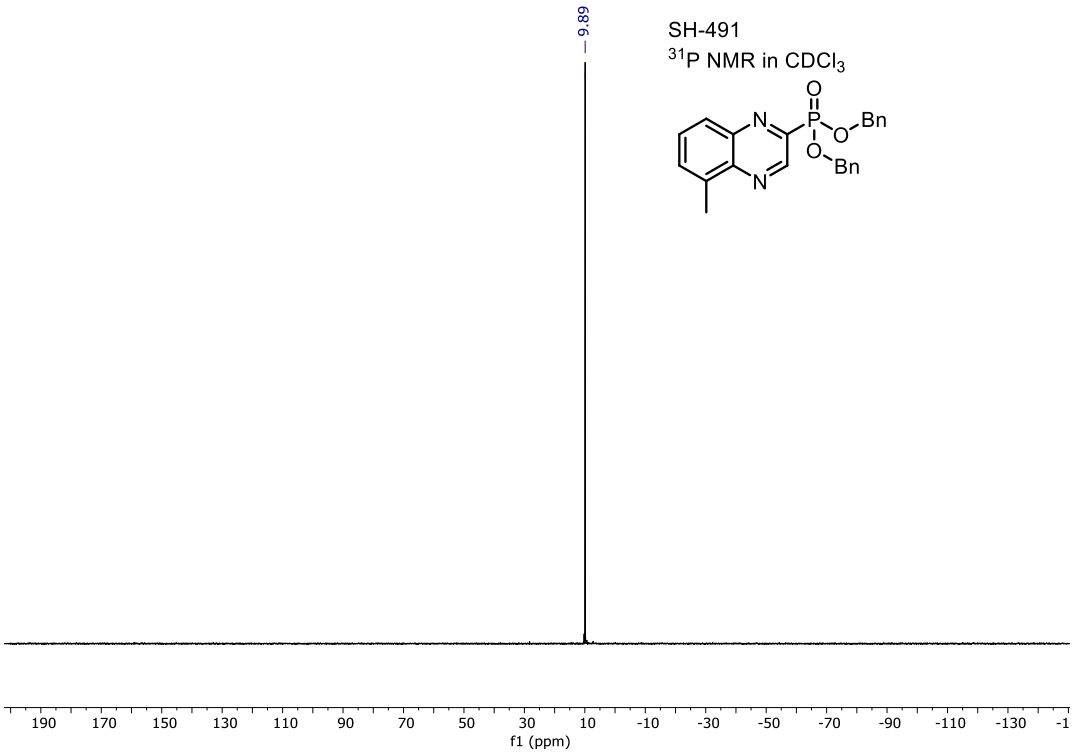
^{31}P NMR **3l**



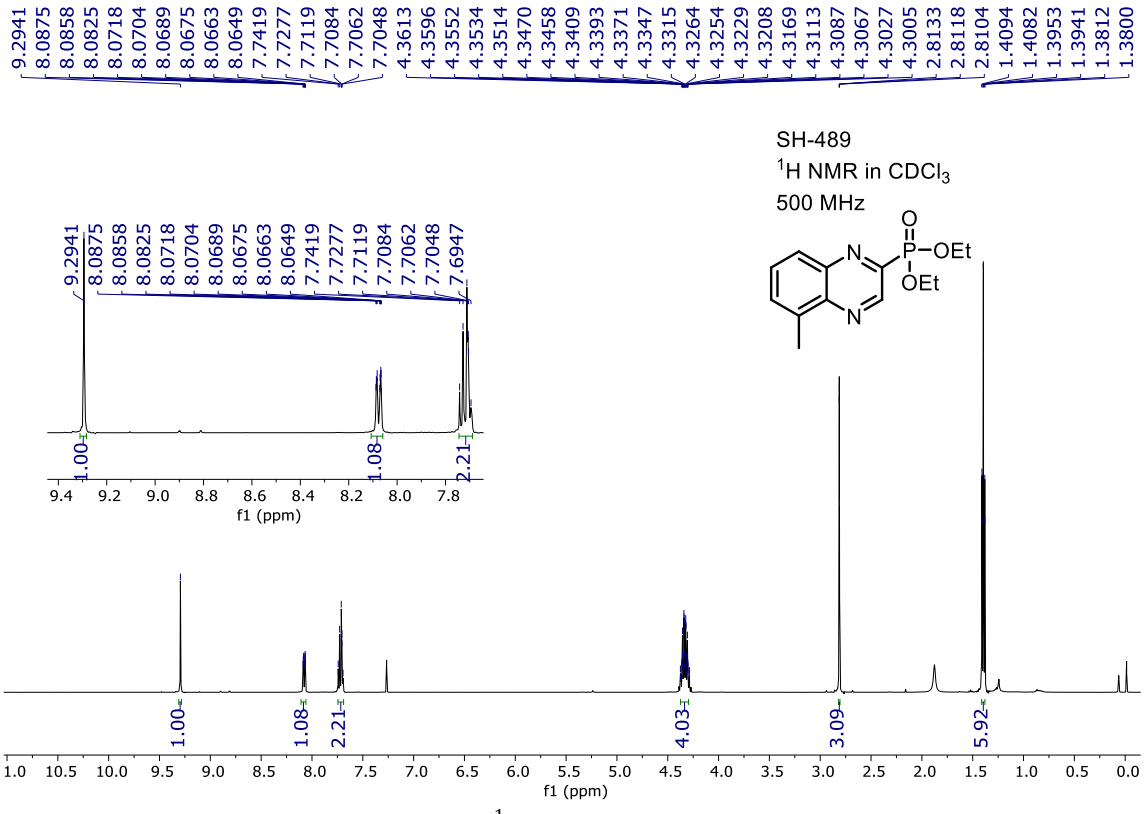
^{1}H NMR **3m**



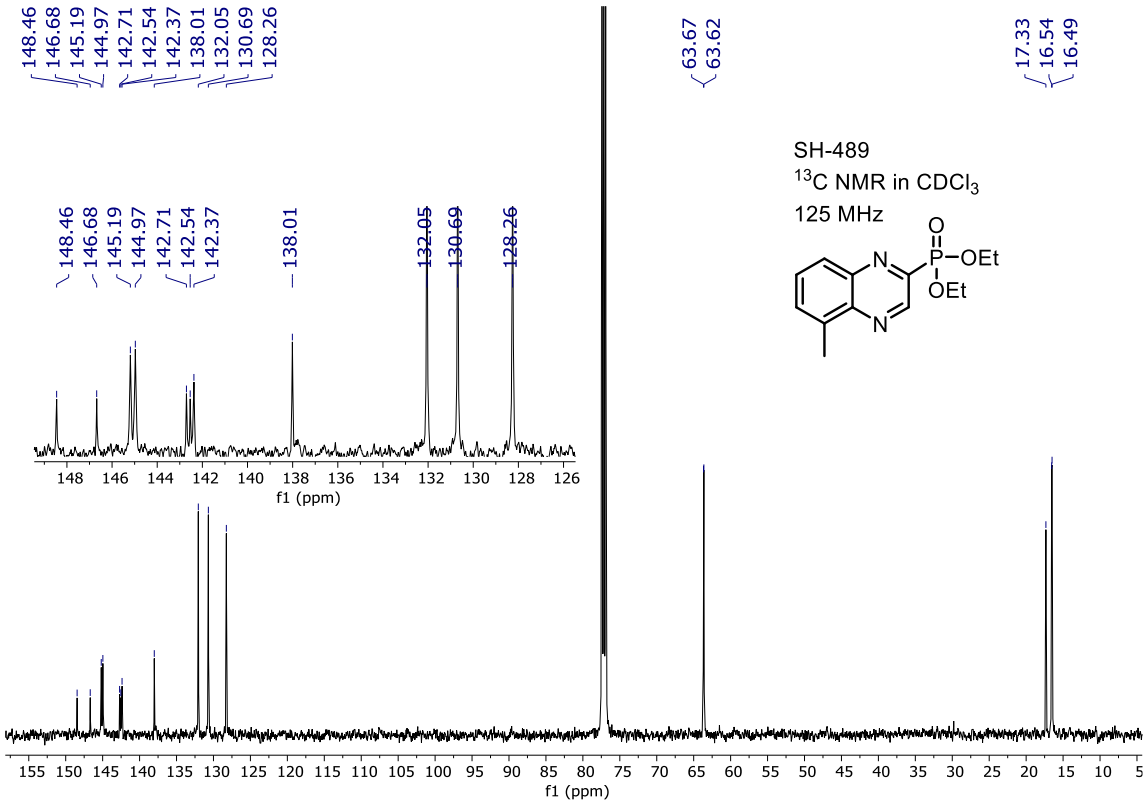
^{13}C NMR **3m**



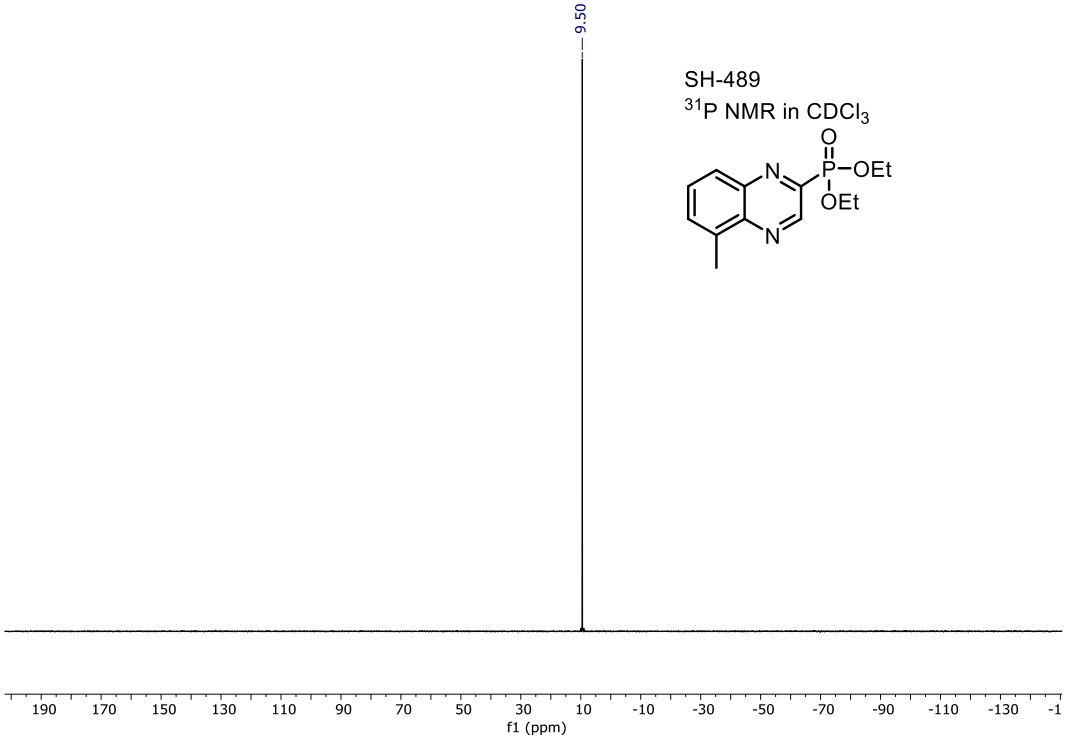
^{31}P NMR **3m**



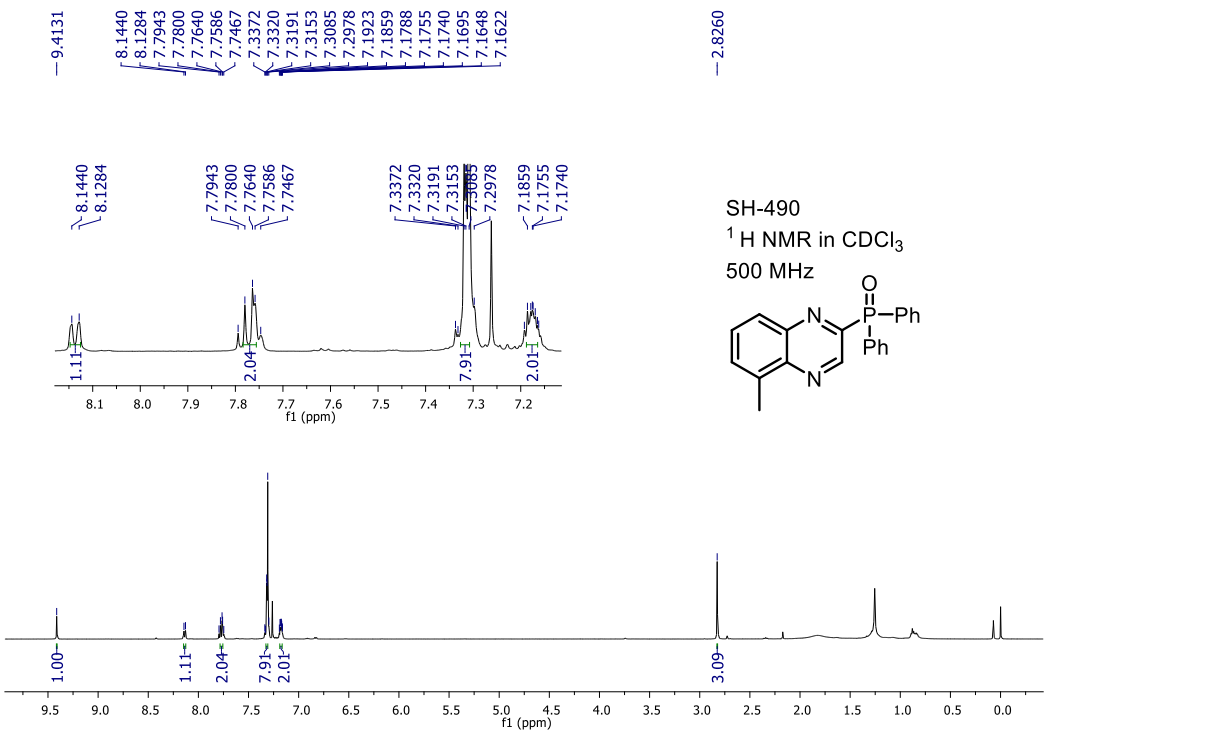
^{1}H NMR **3n**



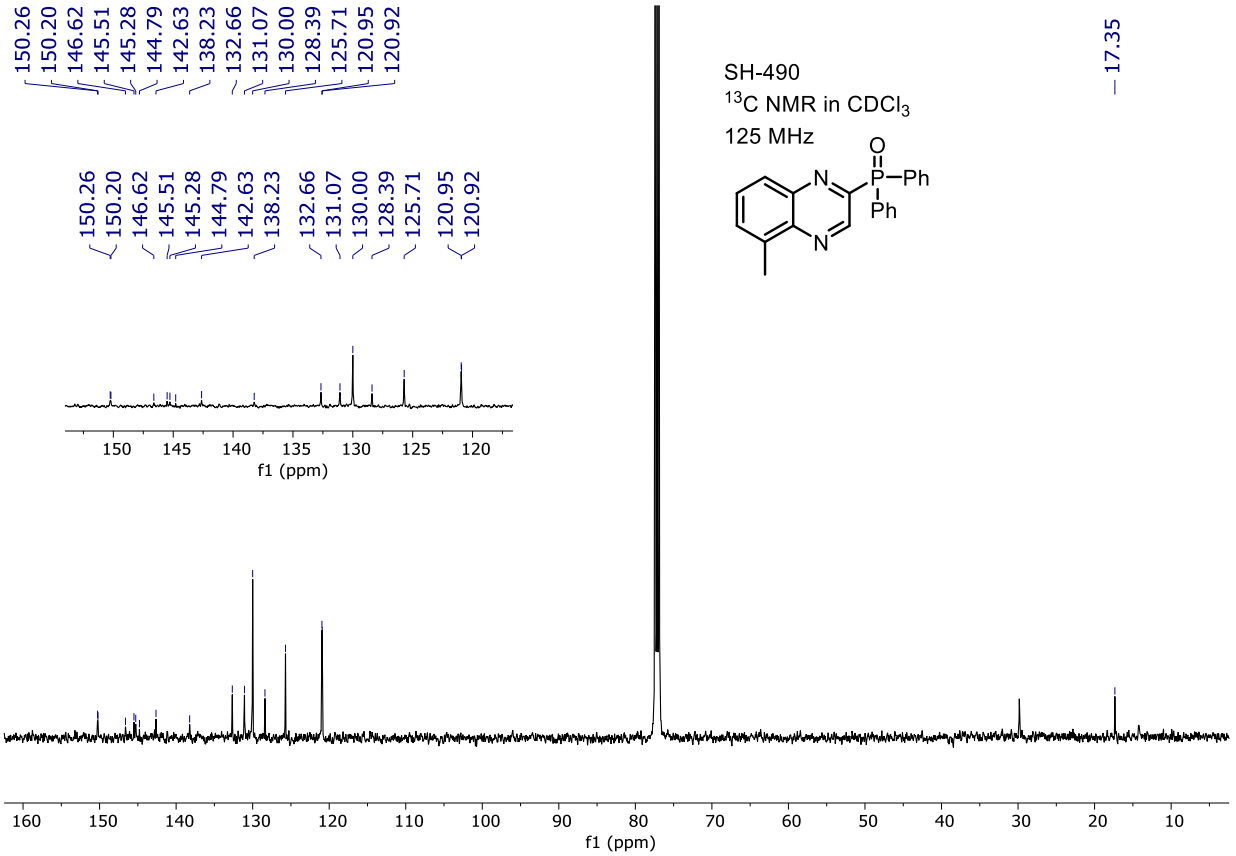
^{13}C NMR **3n**



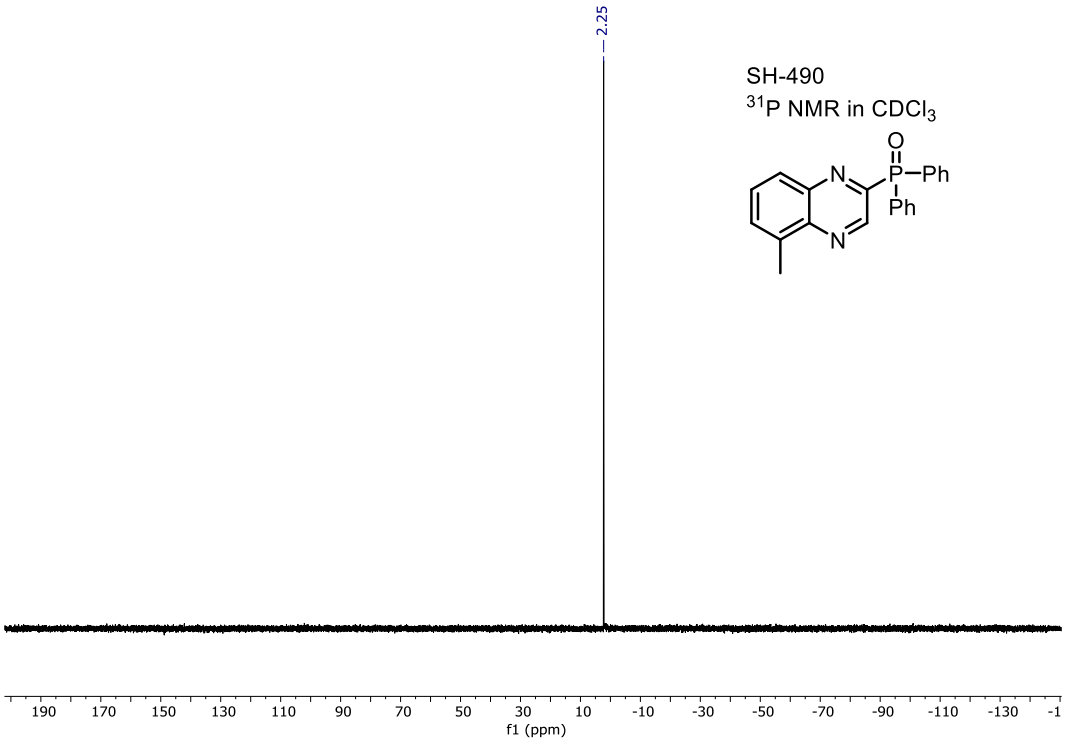
^{31}P NMR **3n**



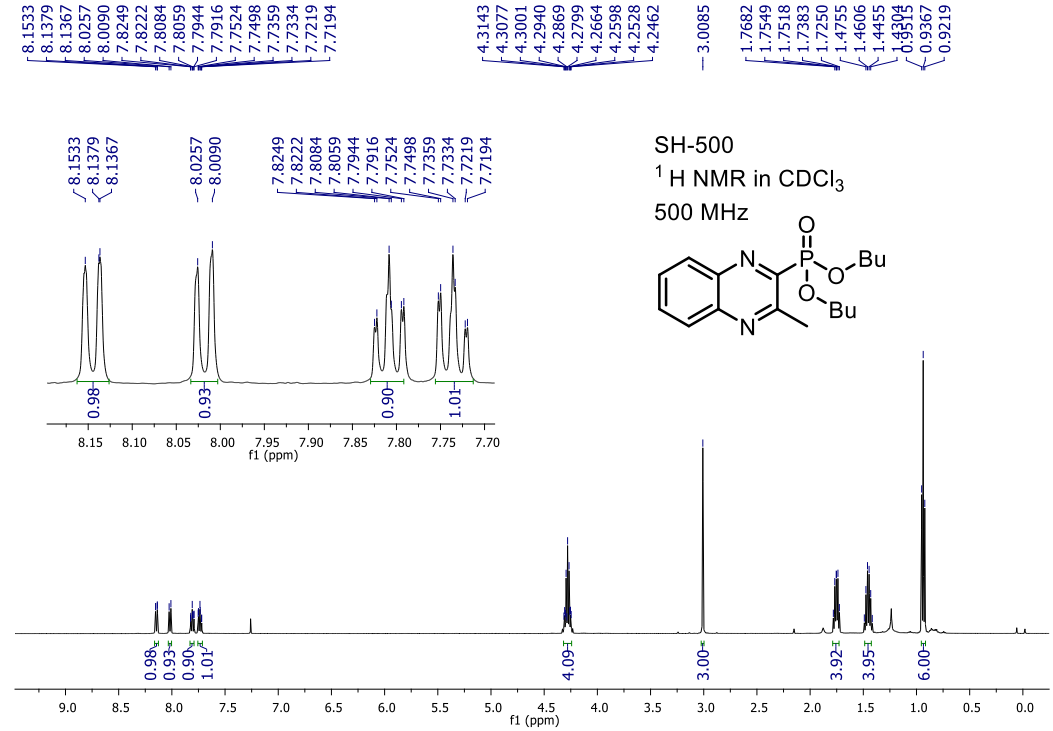
^{1}H NMR **3o**



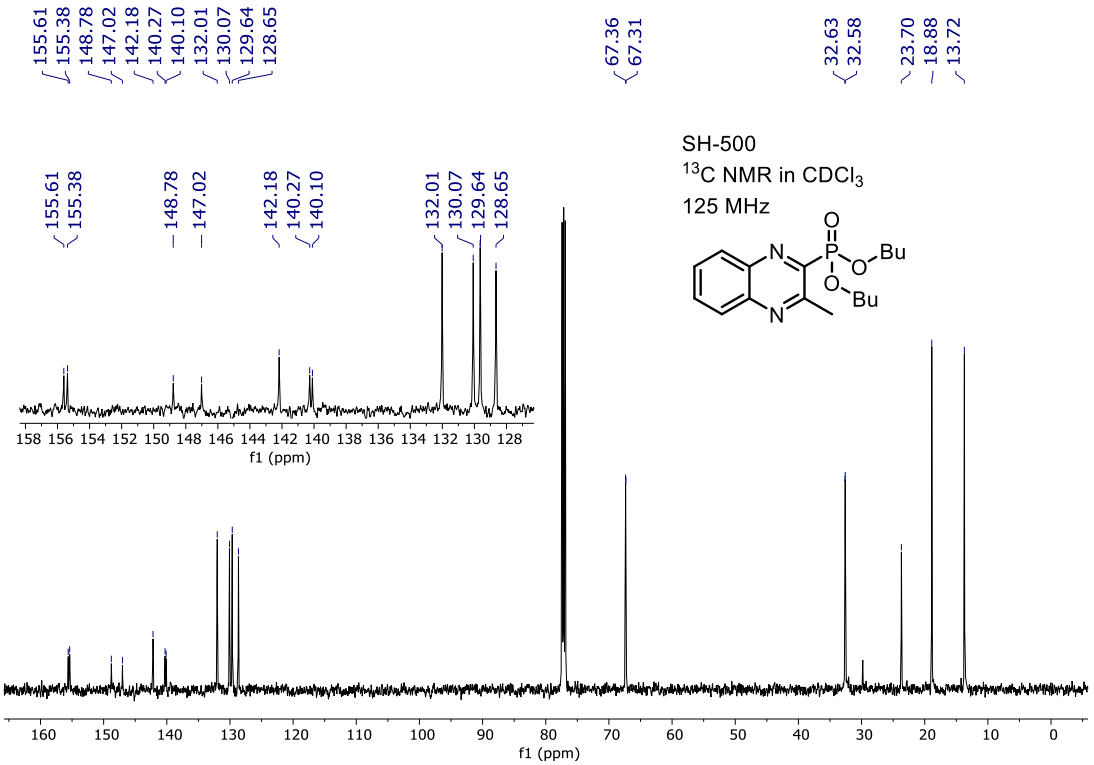
^{13}C NMR **3o**



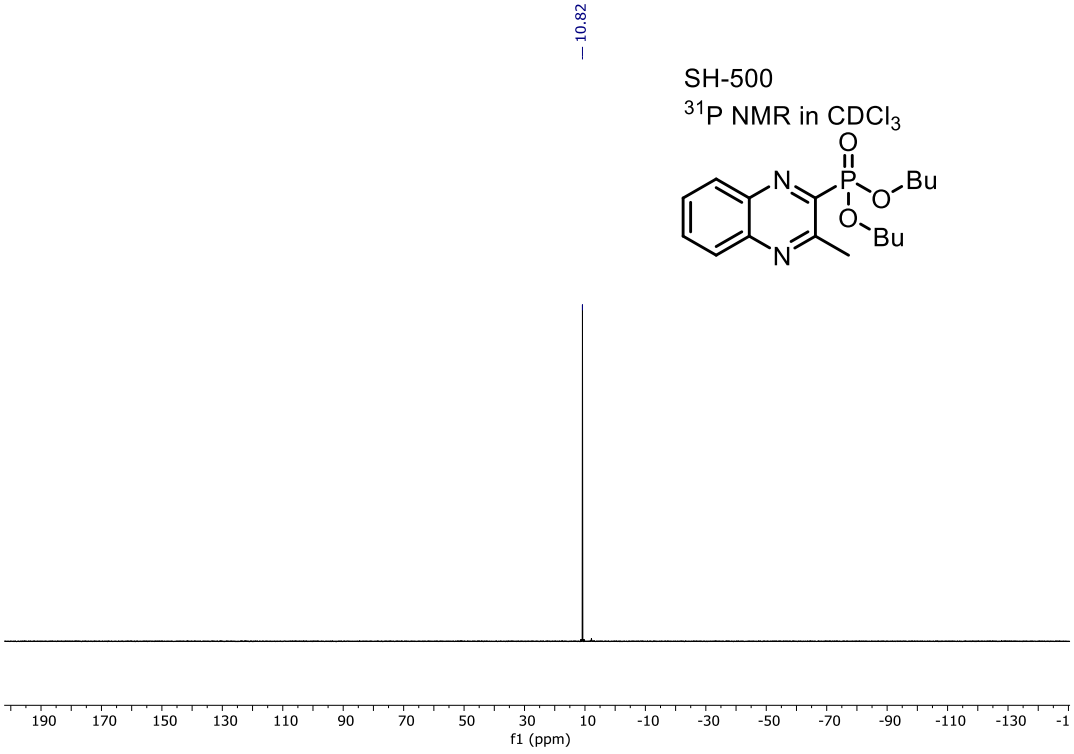
^{31}P NMR **3o**



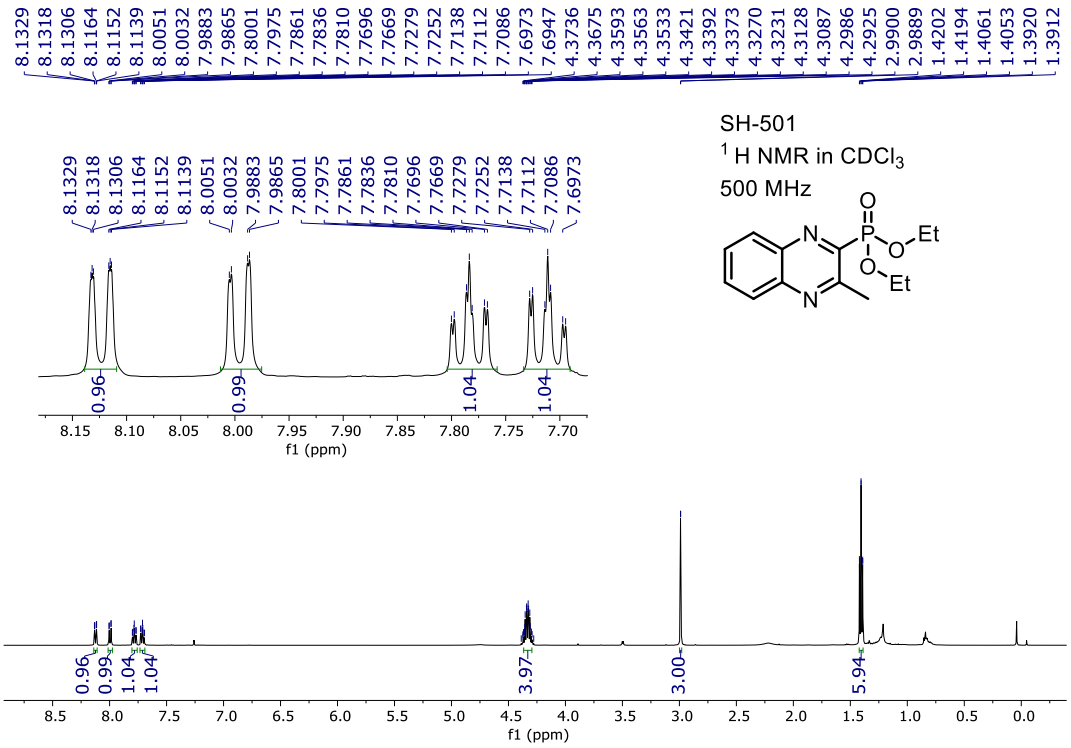
^{1}H NMR **3p**



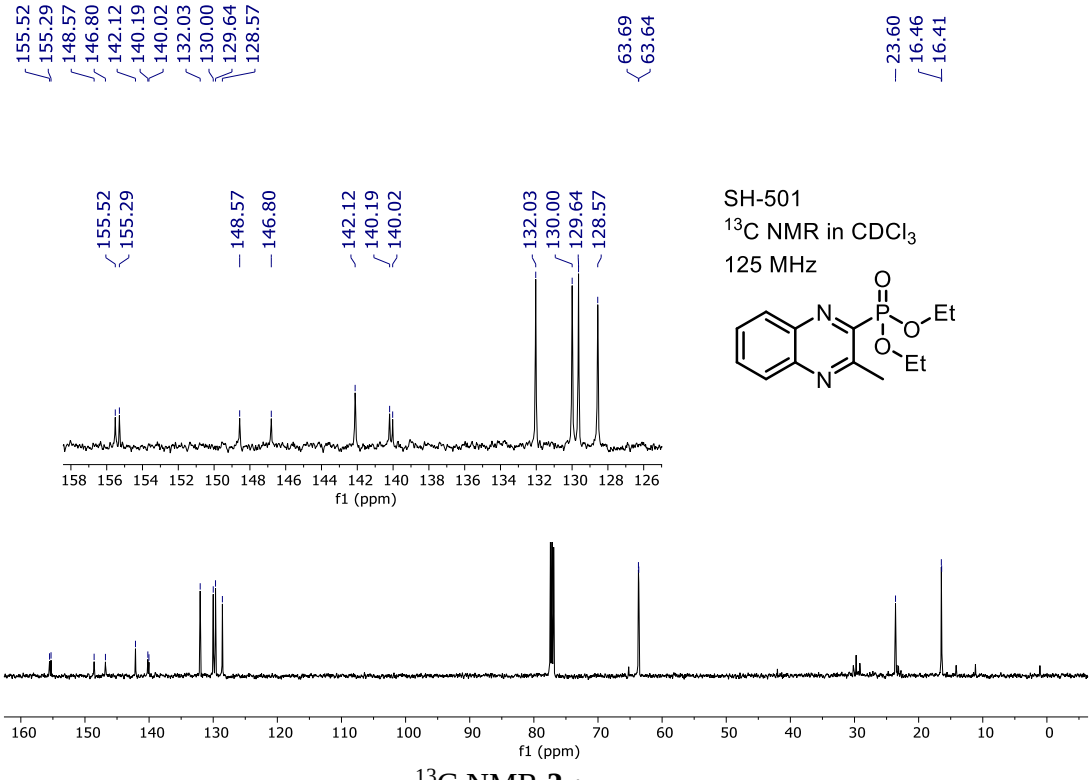
^{13}C NMR **3p**



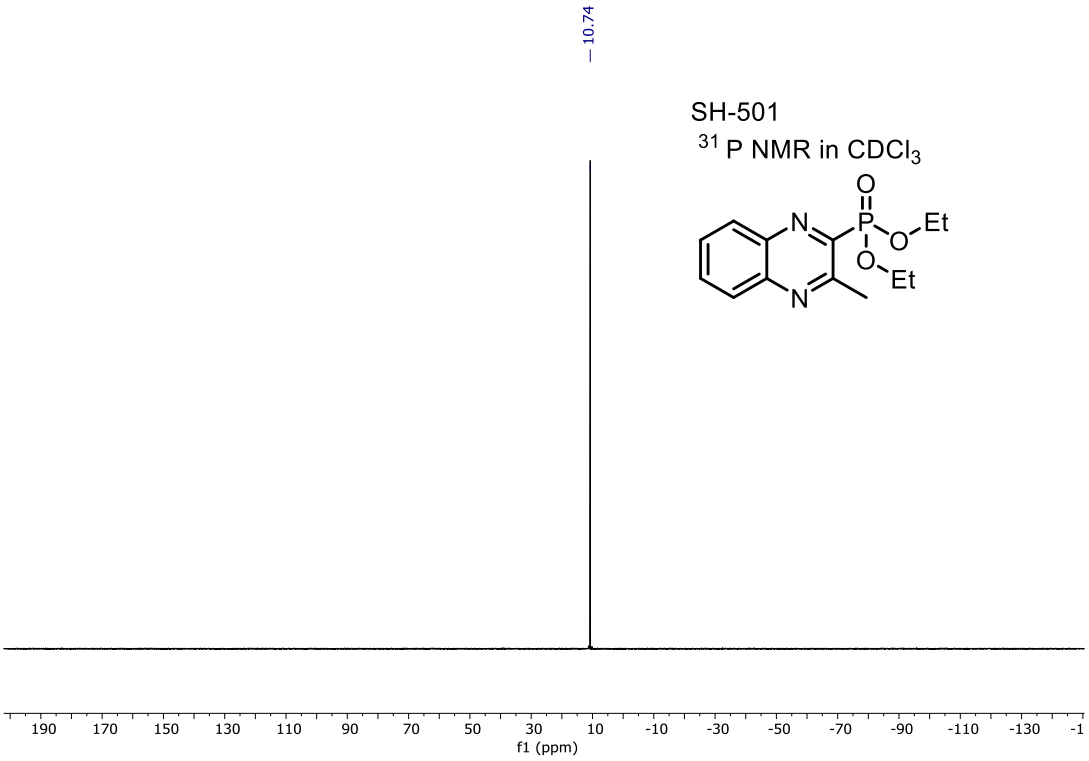
^{31}P NMR **3p**



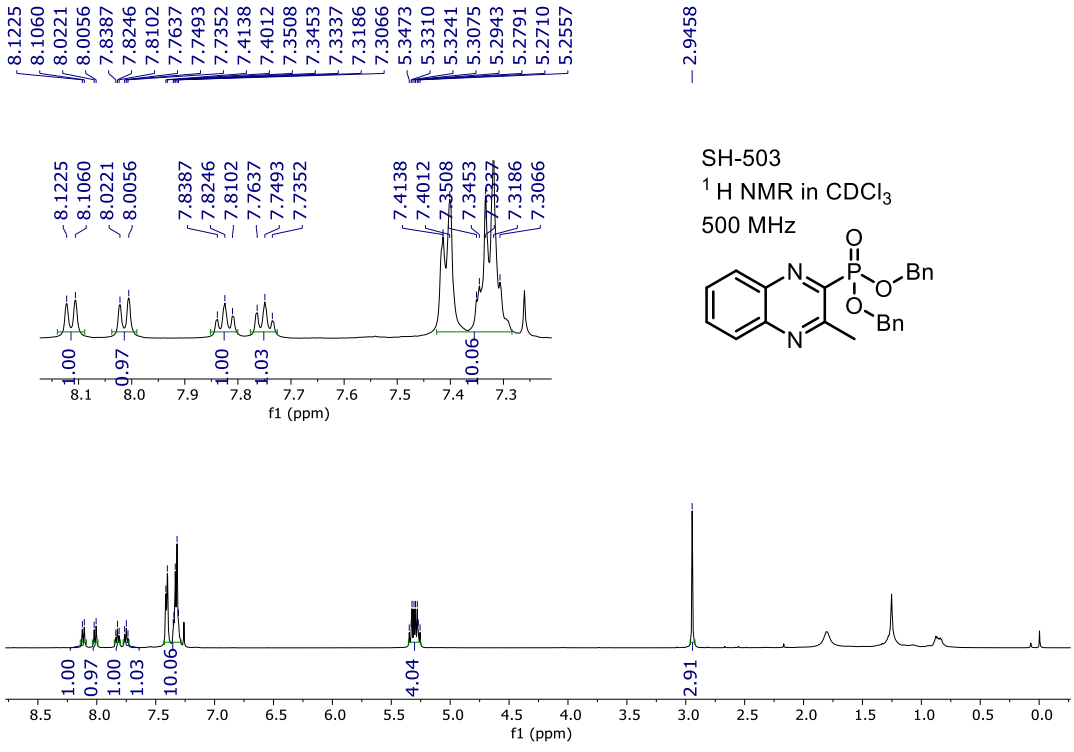
^{1}H NMR **3q**



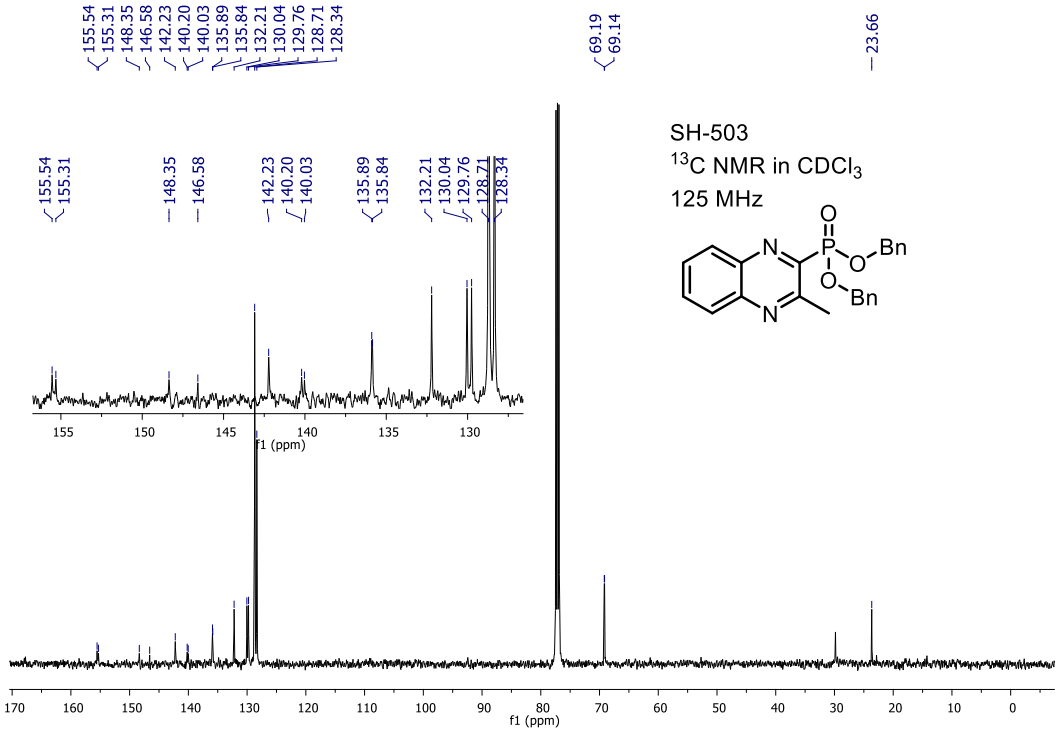
^{13}C NMR **3q**



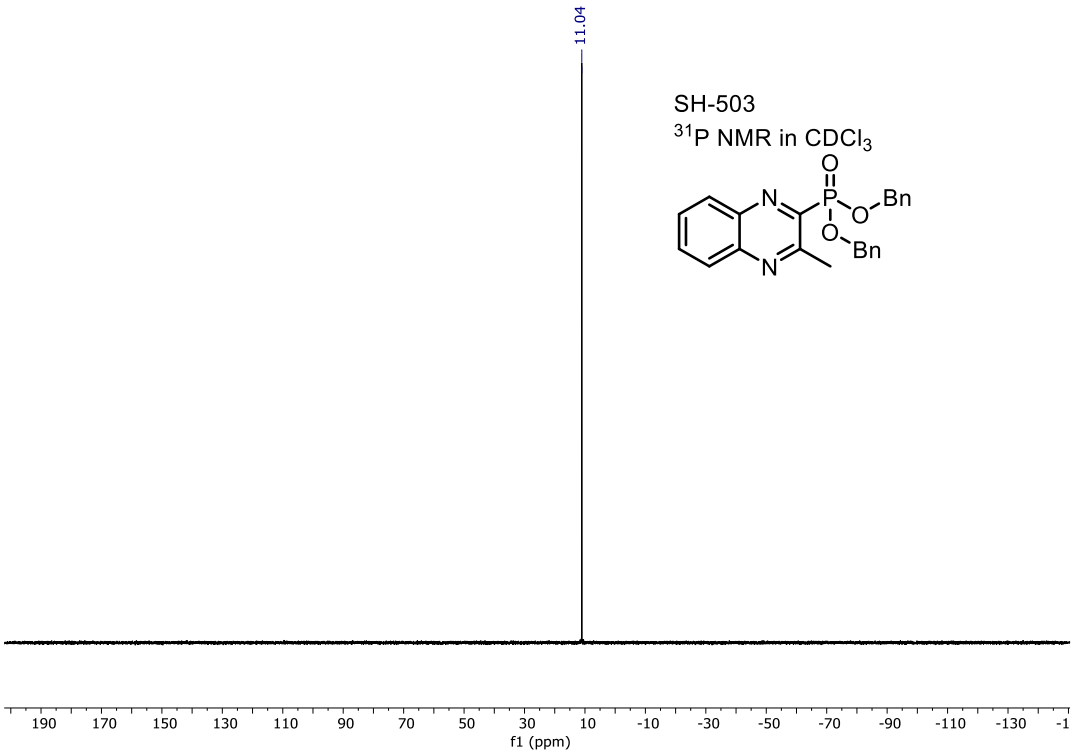
^{31}P NMR **3q**



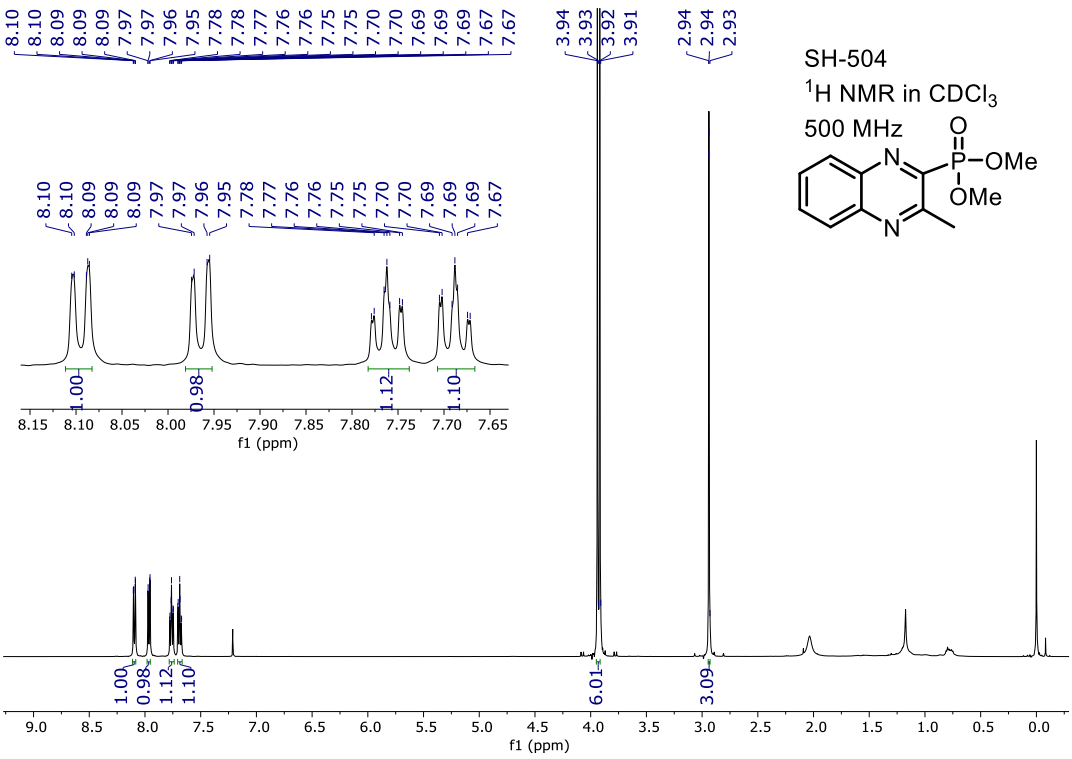
^{1}H NMR **3r**



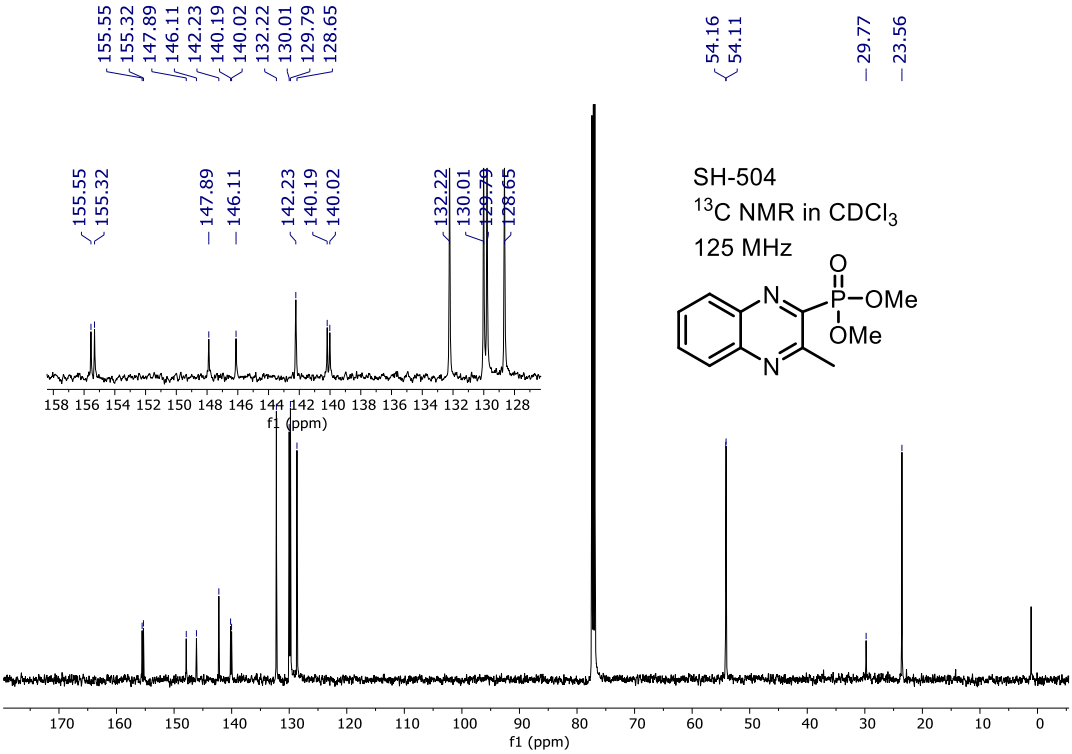
^{13}C NMR **3r**



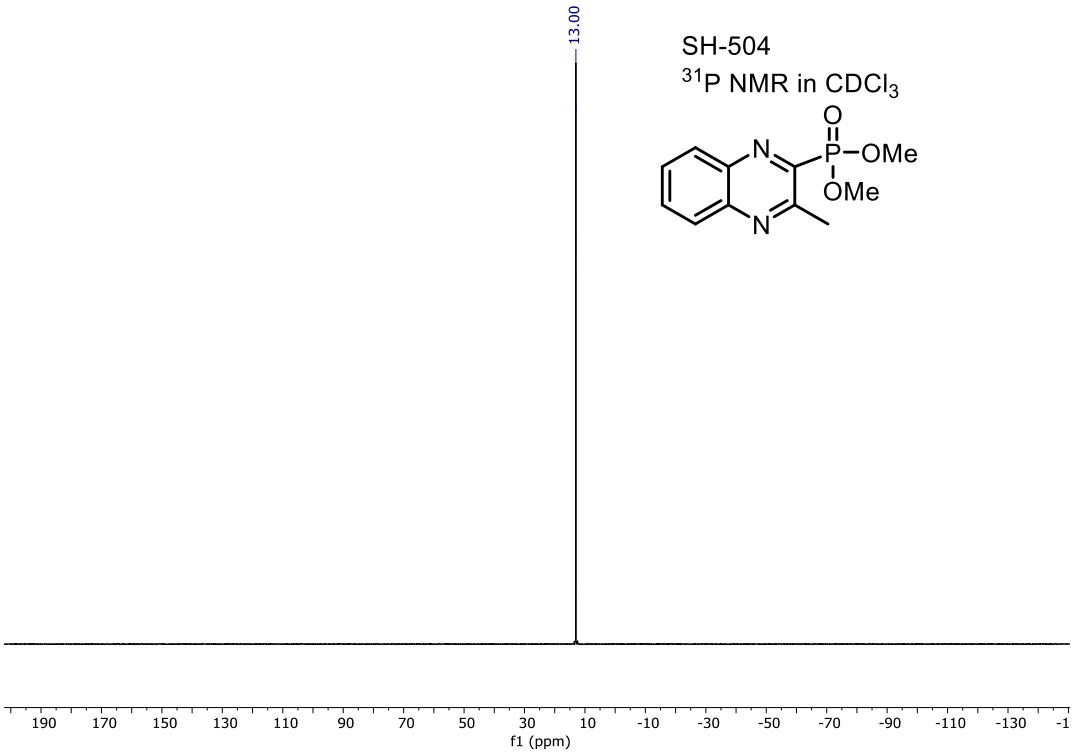
^{31}P NMR **3r**



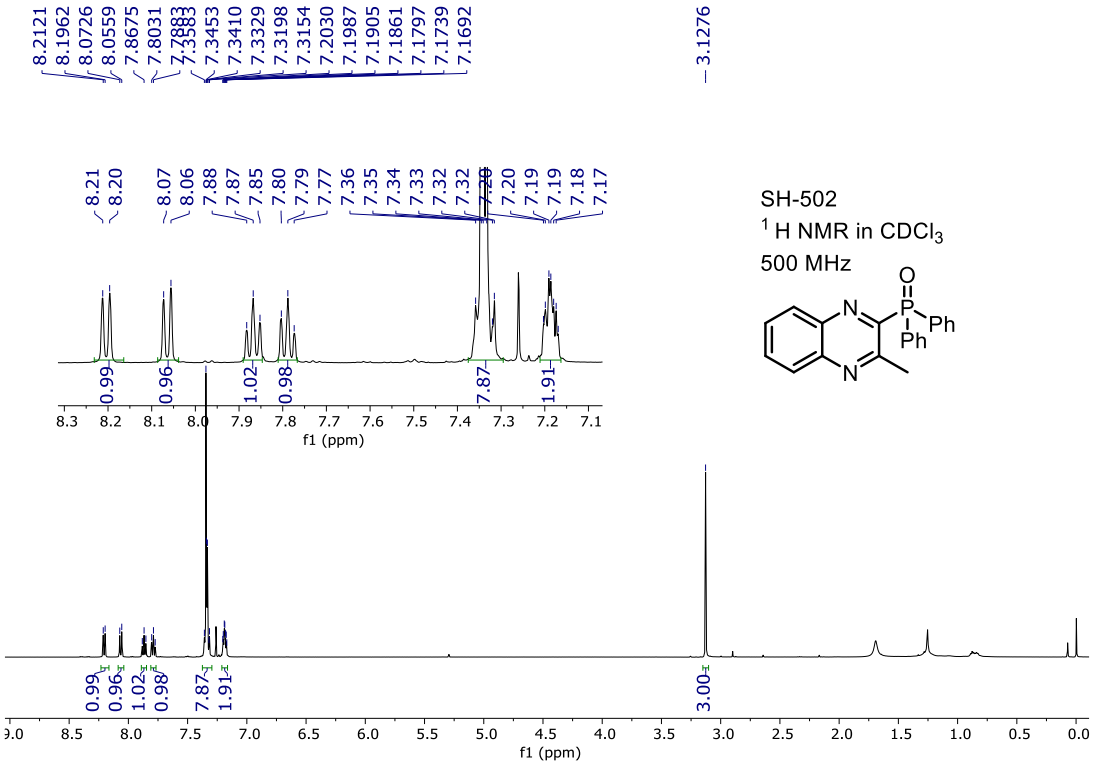
^{1}H NMR **3s**



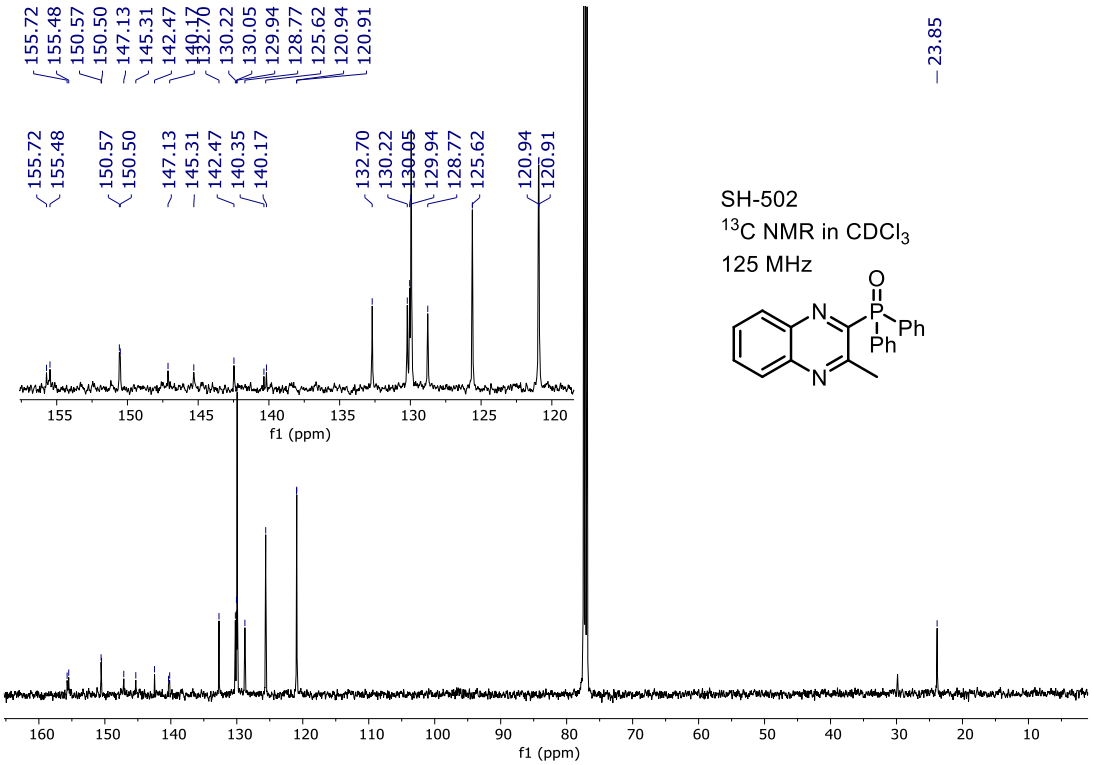
^{13}C NMR **3s**



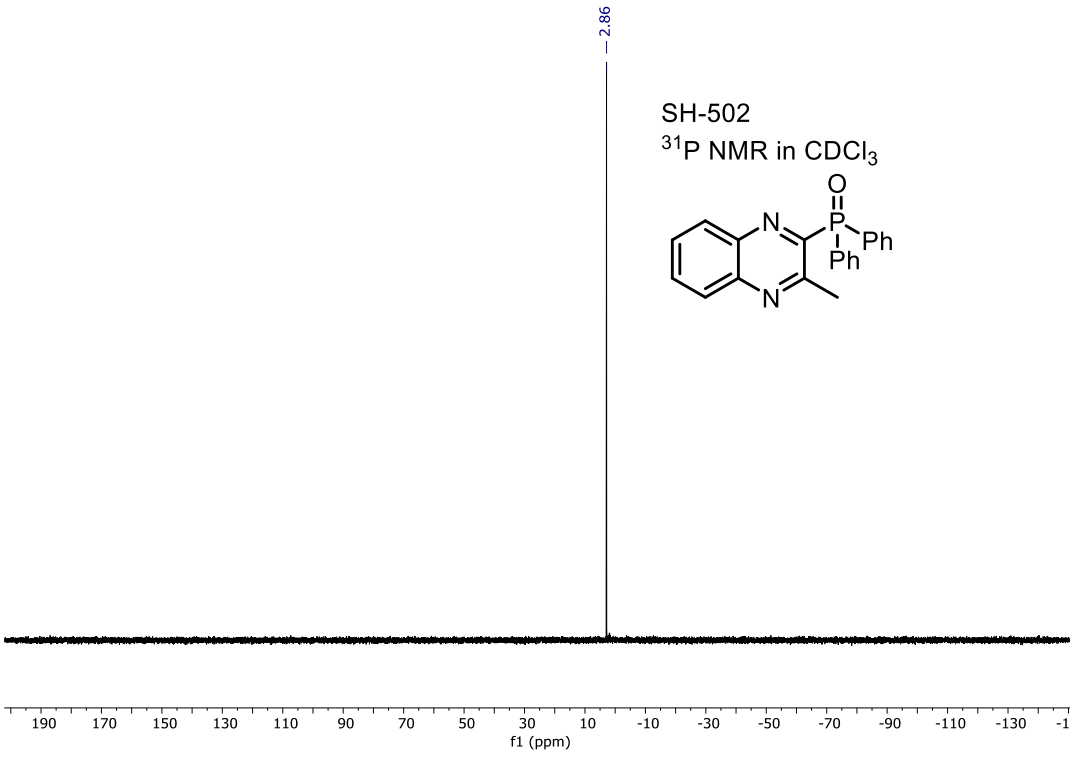
^{31}P NMR **3s**



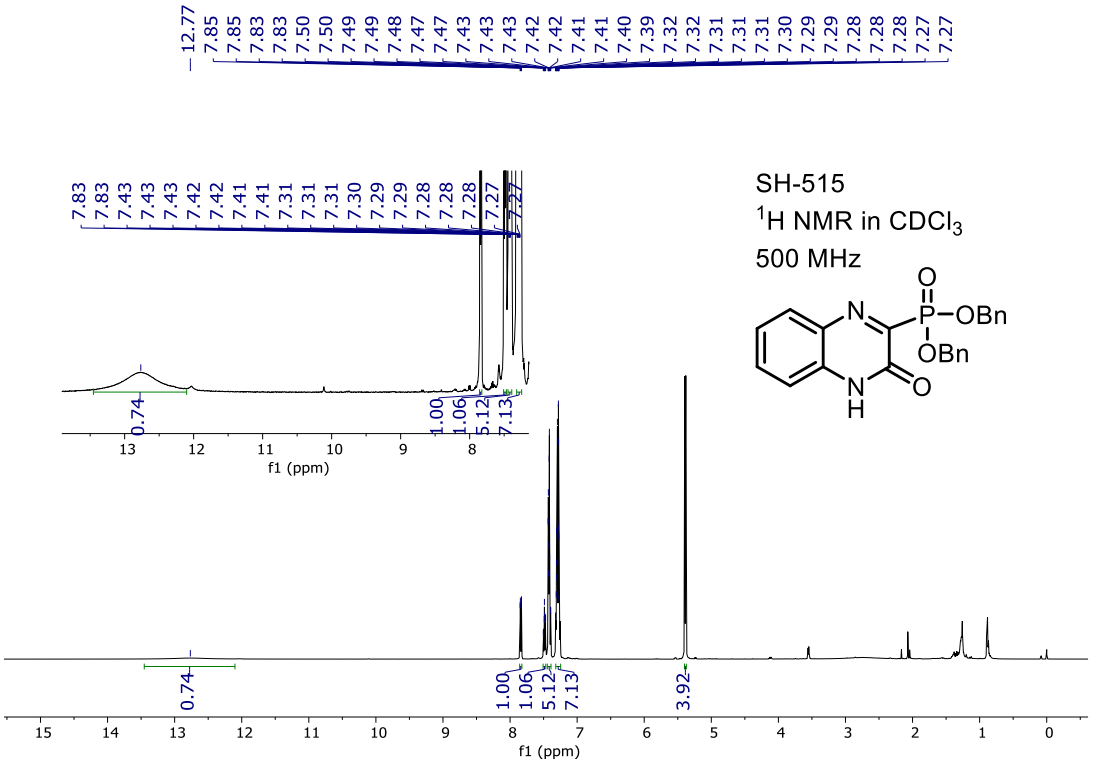
^{1}H NMR **3t**



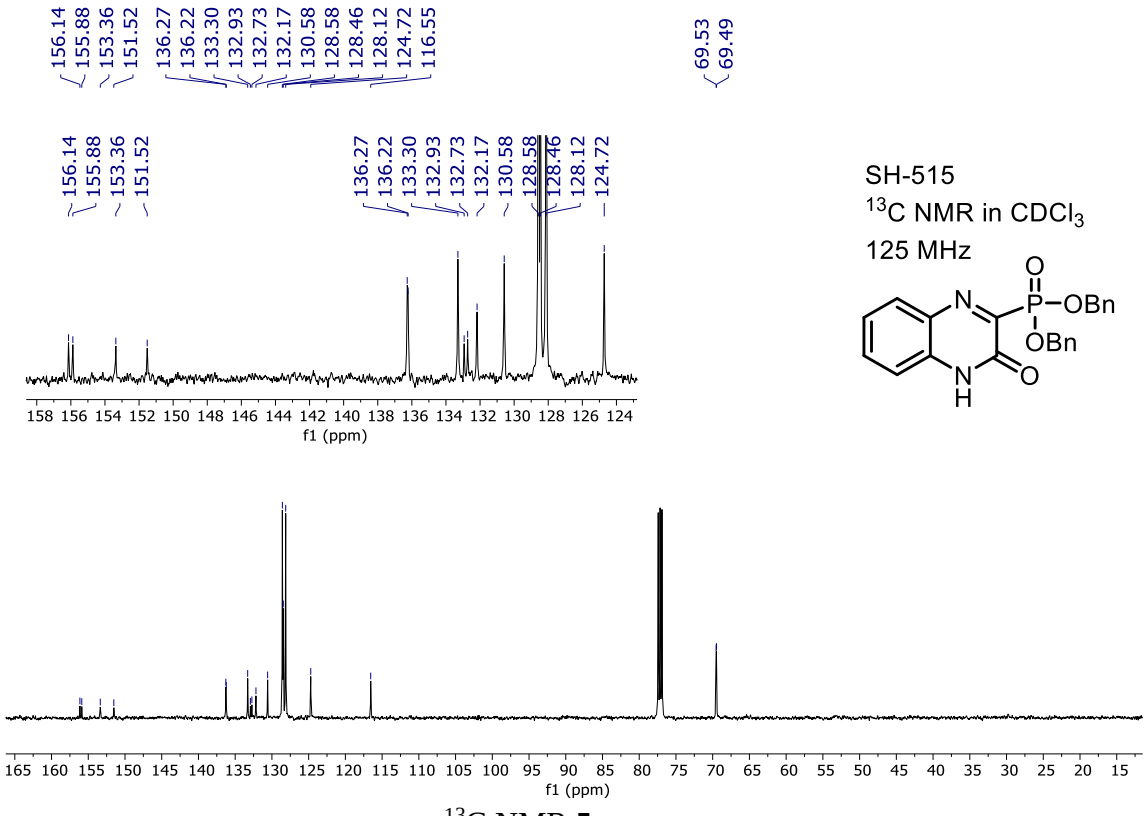
^{13}C NMR **3t**



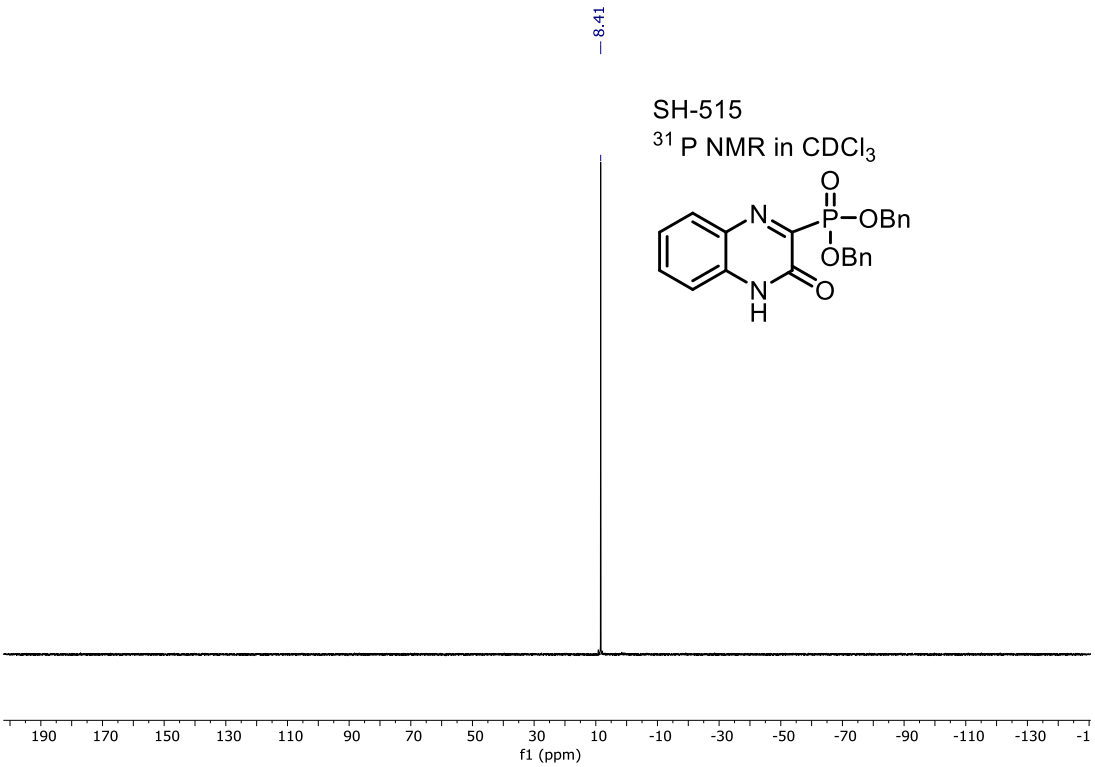
^{31}P NMR **3t**



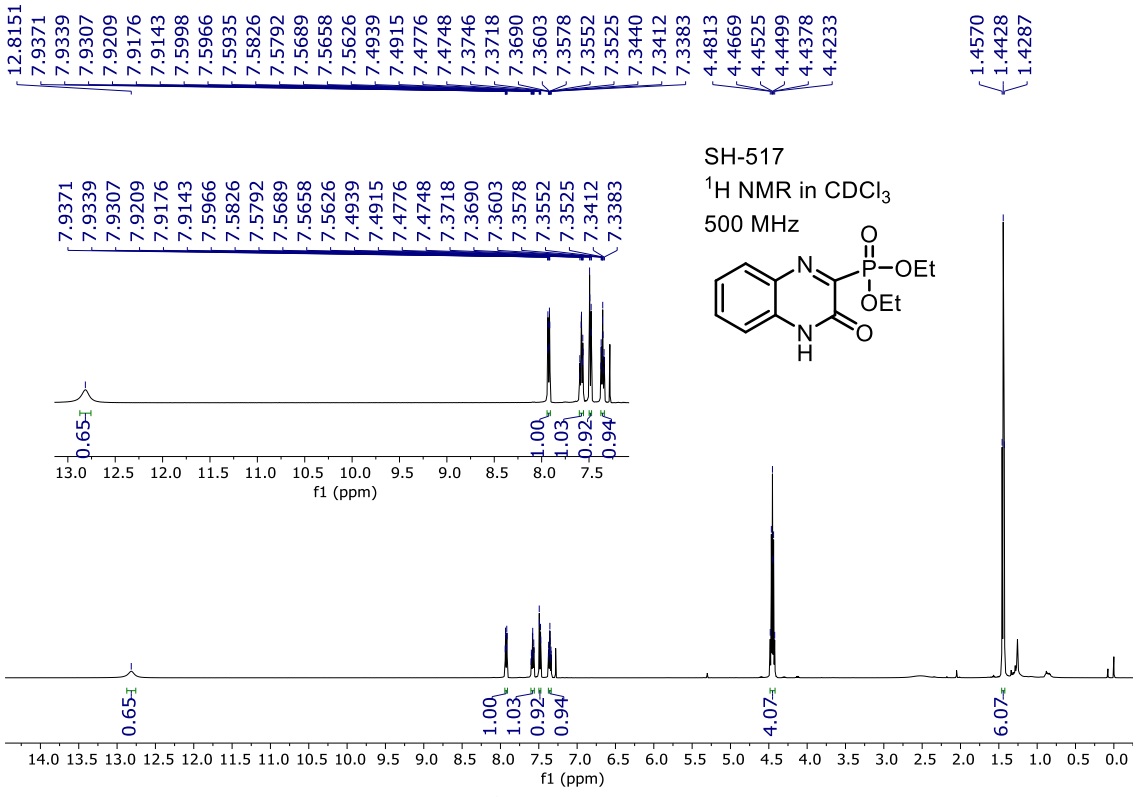
^{1}H NMR **5a**



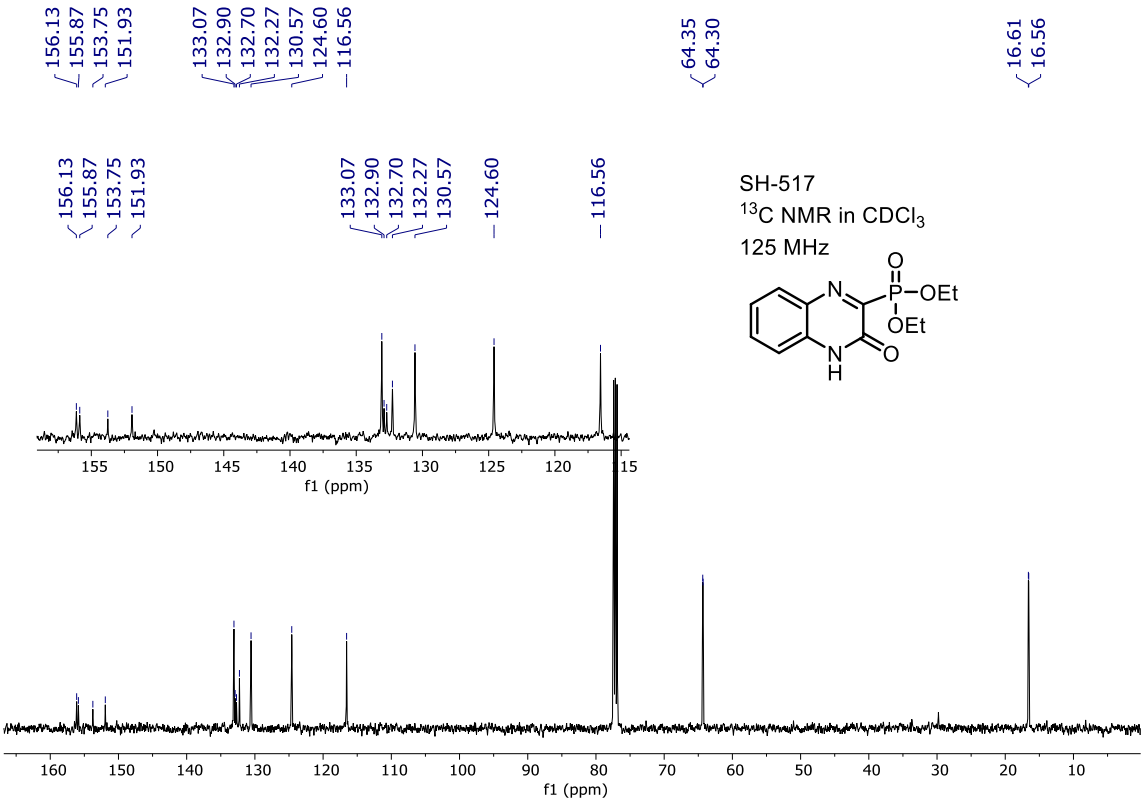
^{13}C NMR **5a**



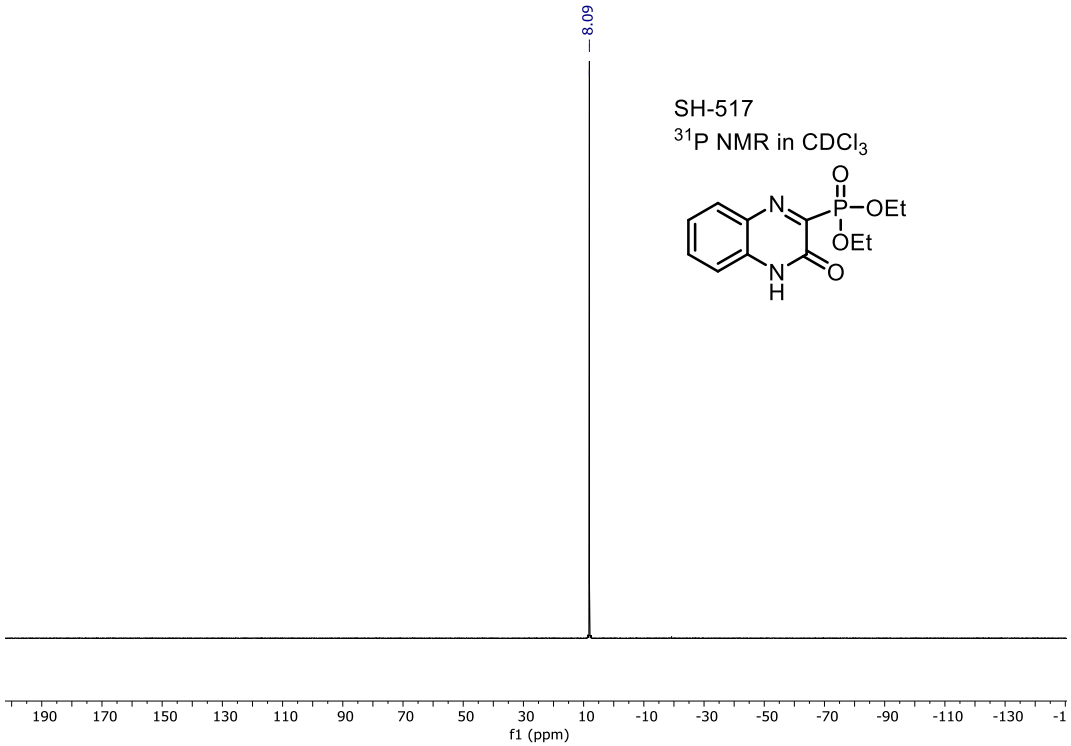
^{31}P NMR **5a**



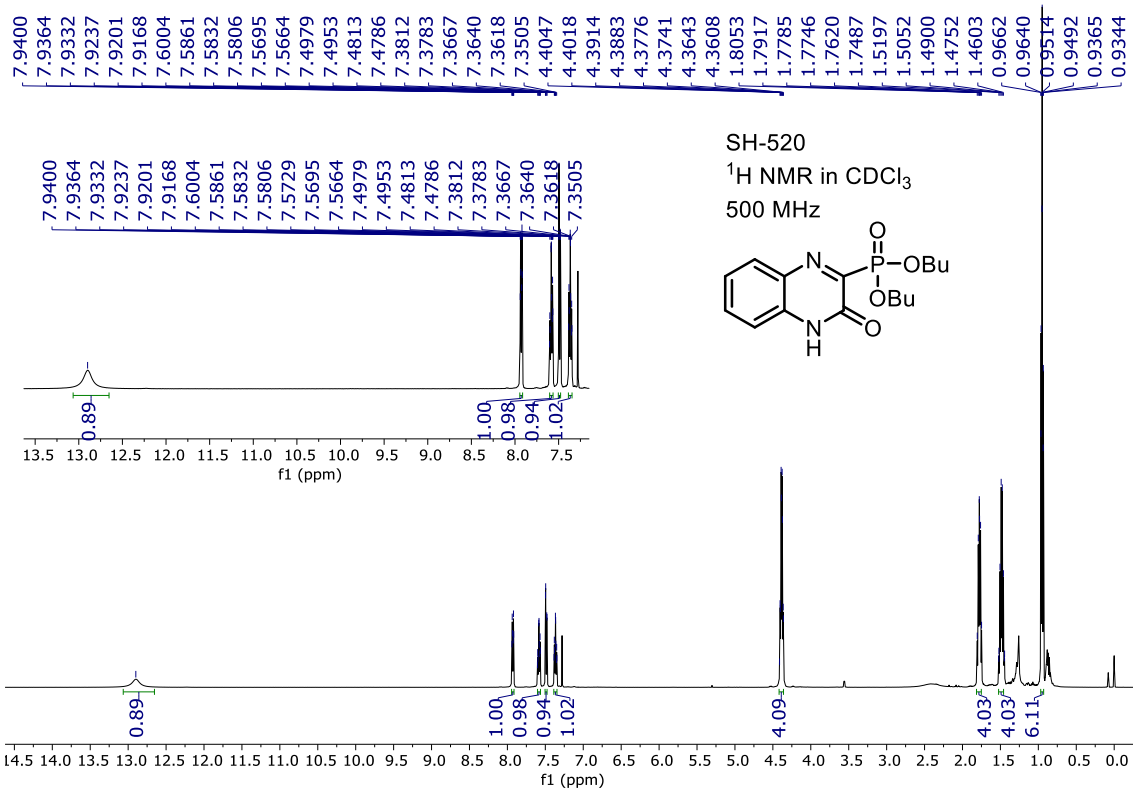
^{1}H NMR **5b**



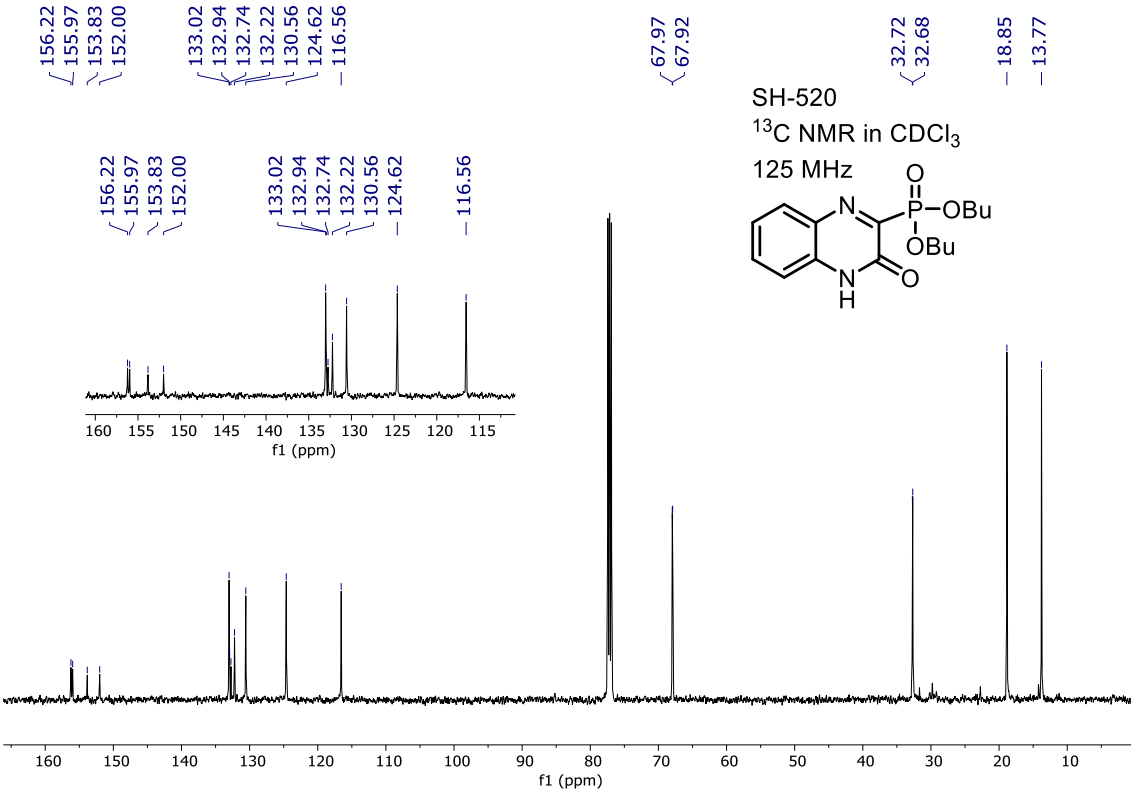
^{13}C NMR **5b**



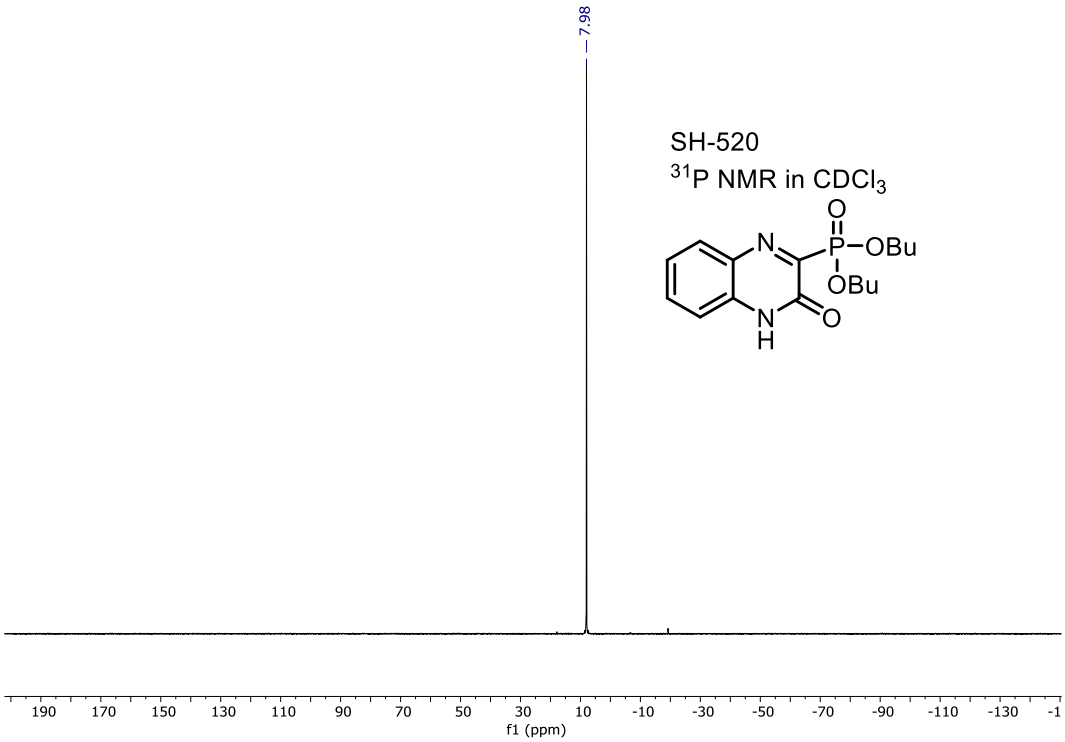
^{31}P NMR **5b**



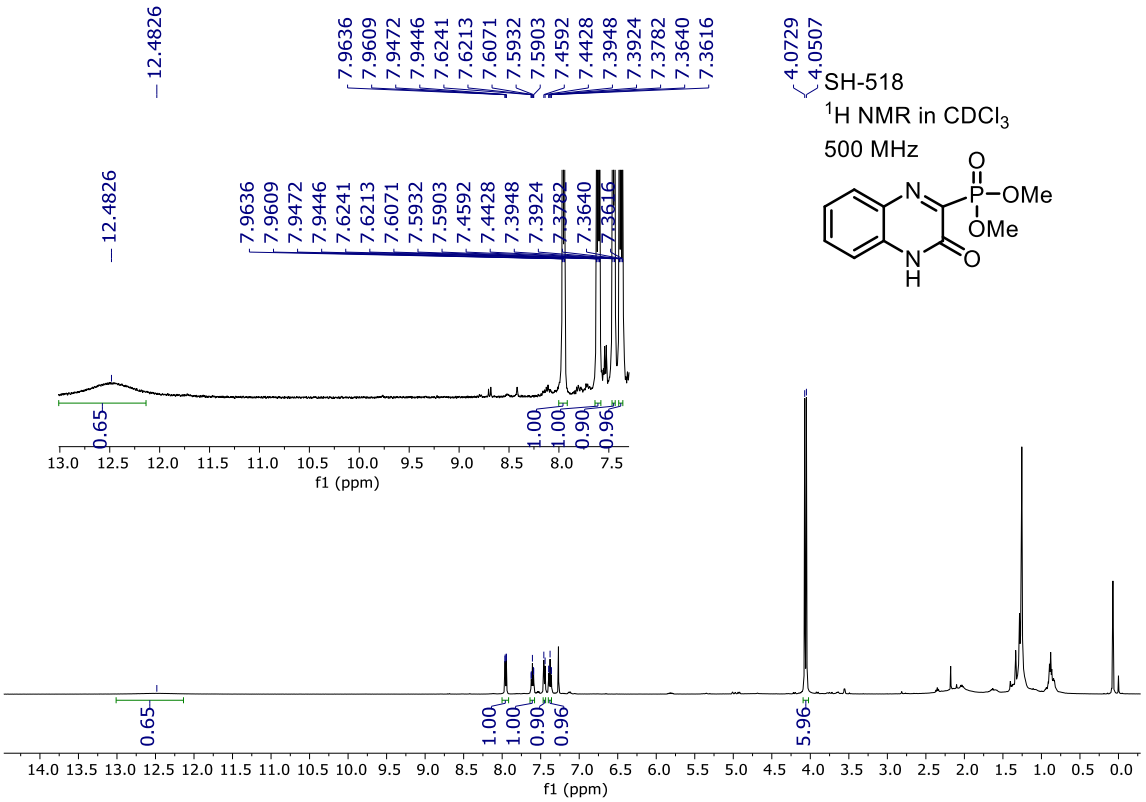
^{1}H NMR **5c**



^{13}C NMR **5c**



^{31}P NMR **5c**



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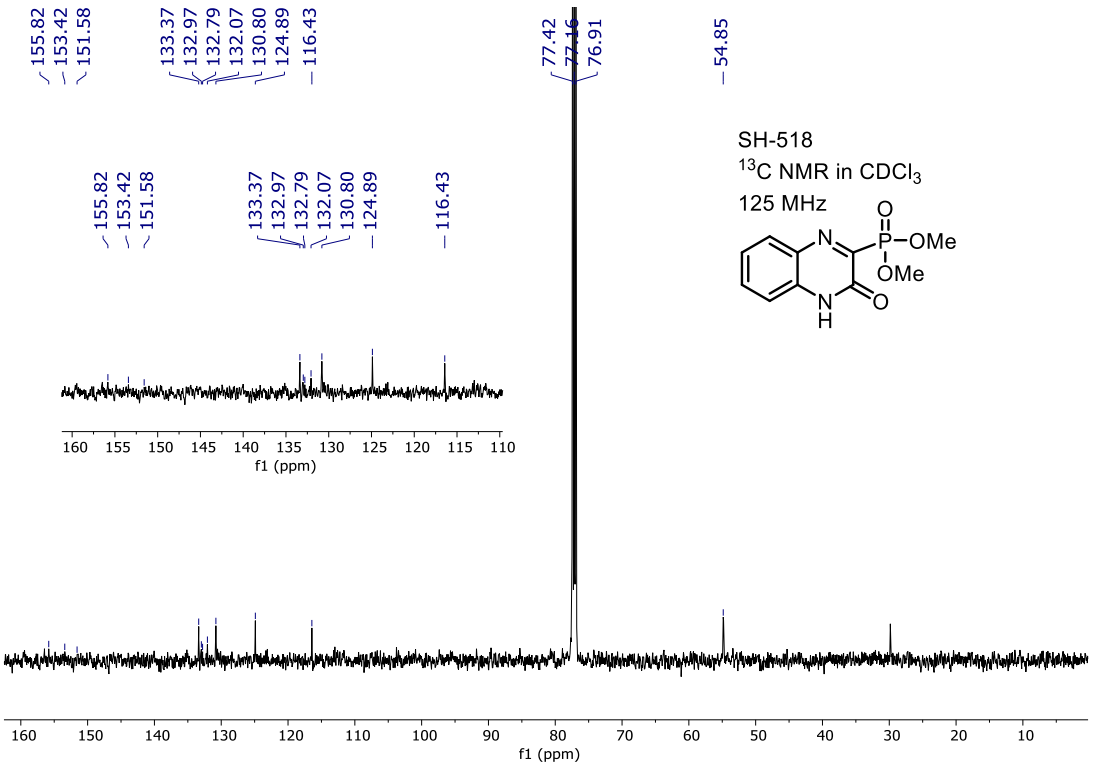

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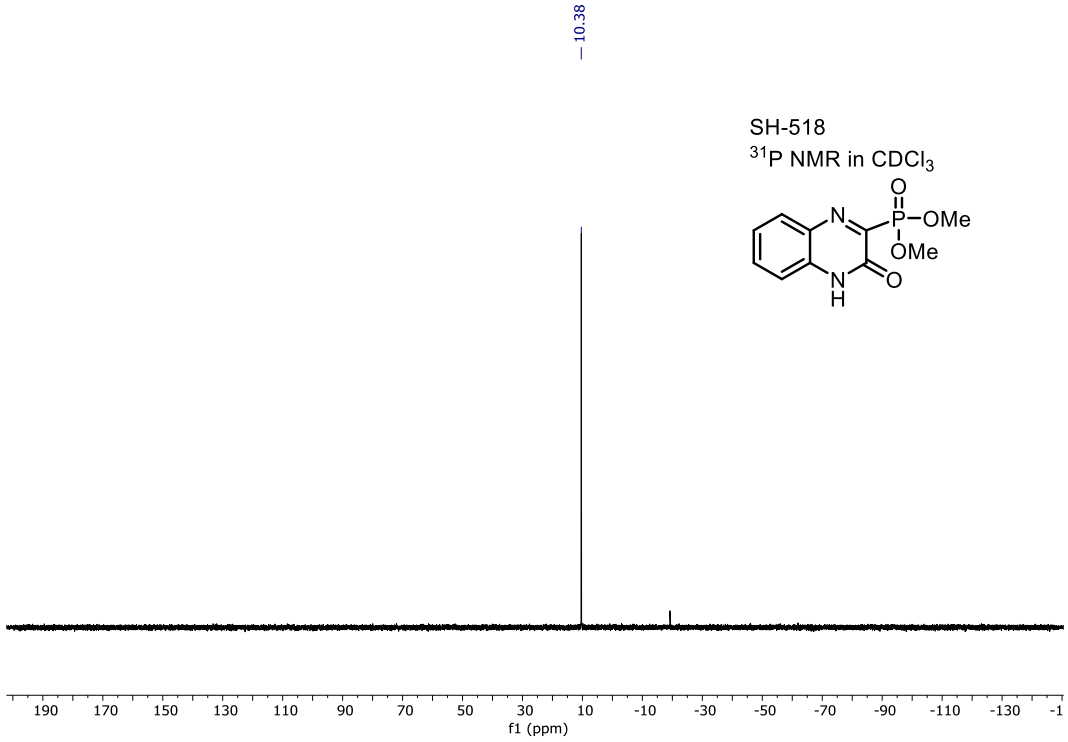

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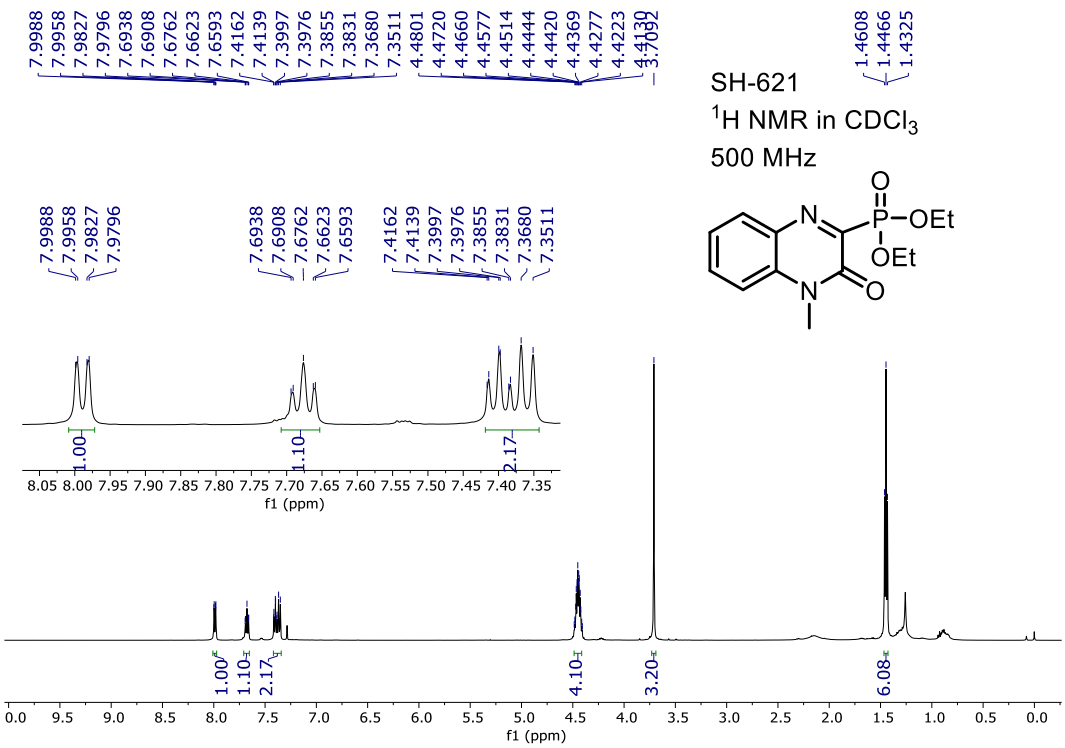
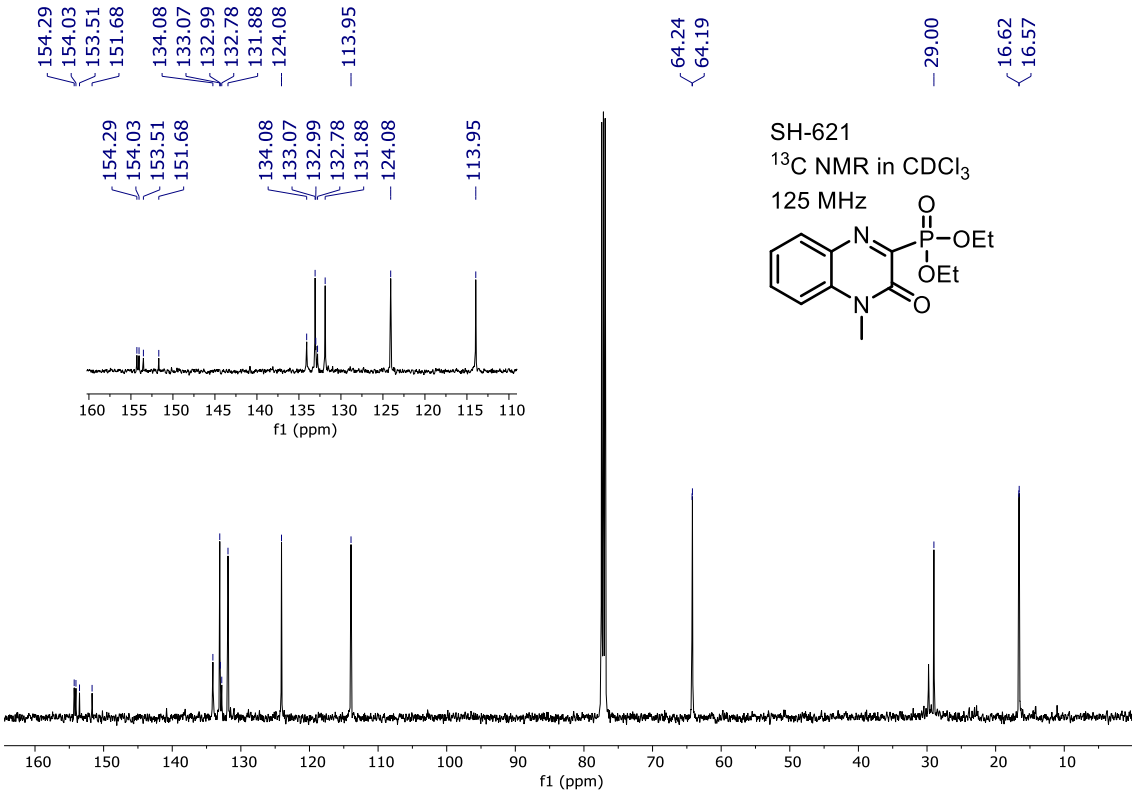
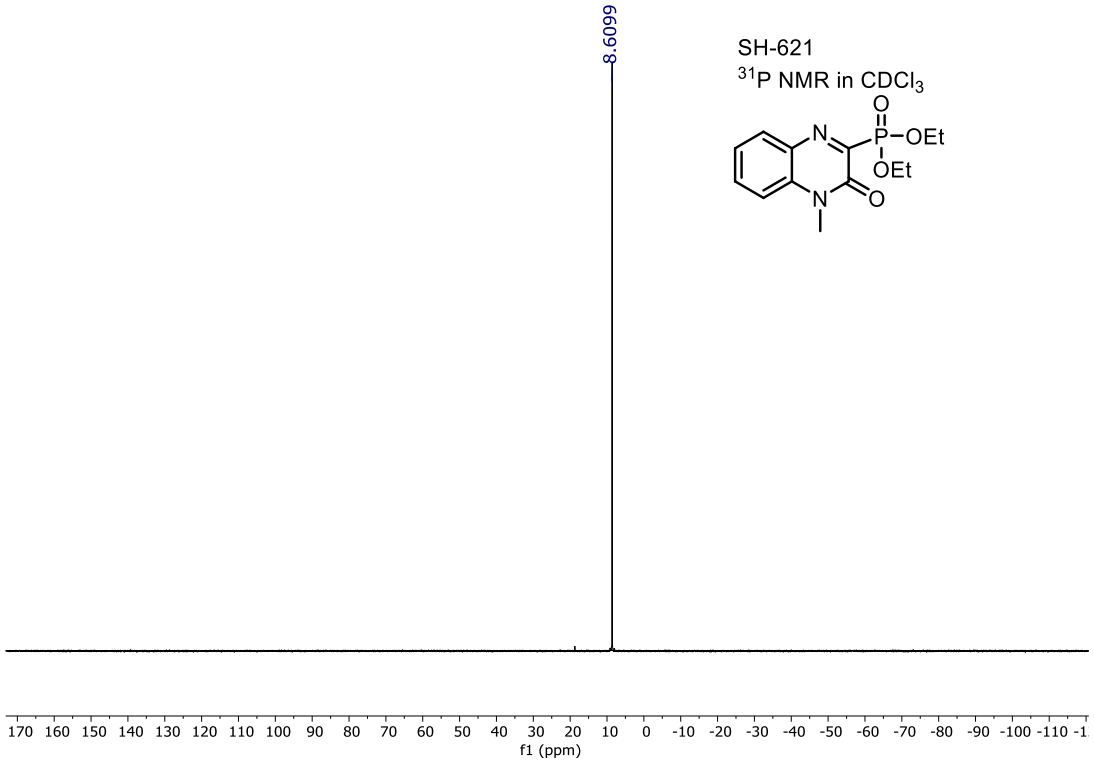


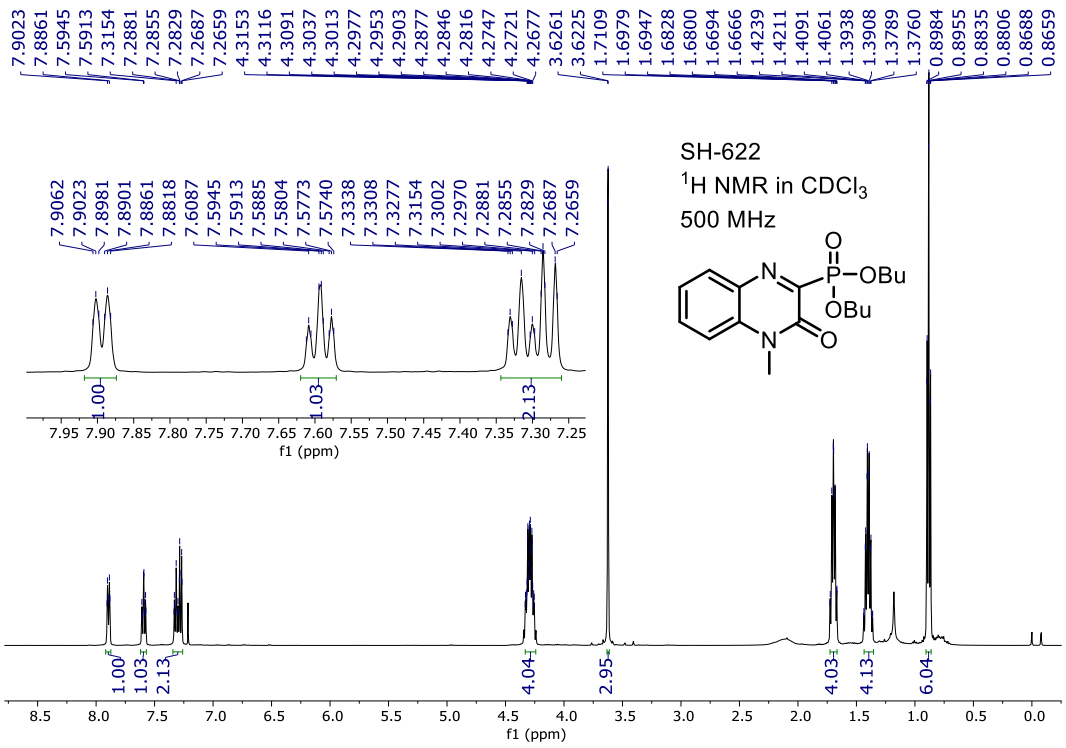
^{1}H NMR **5e**



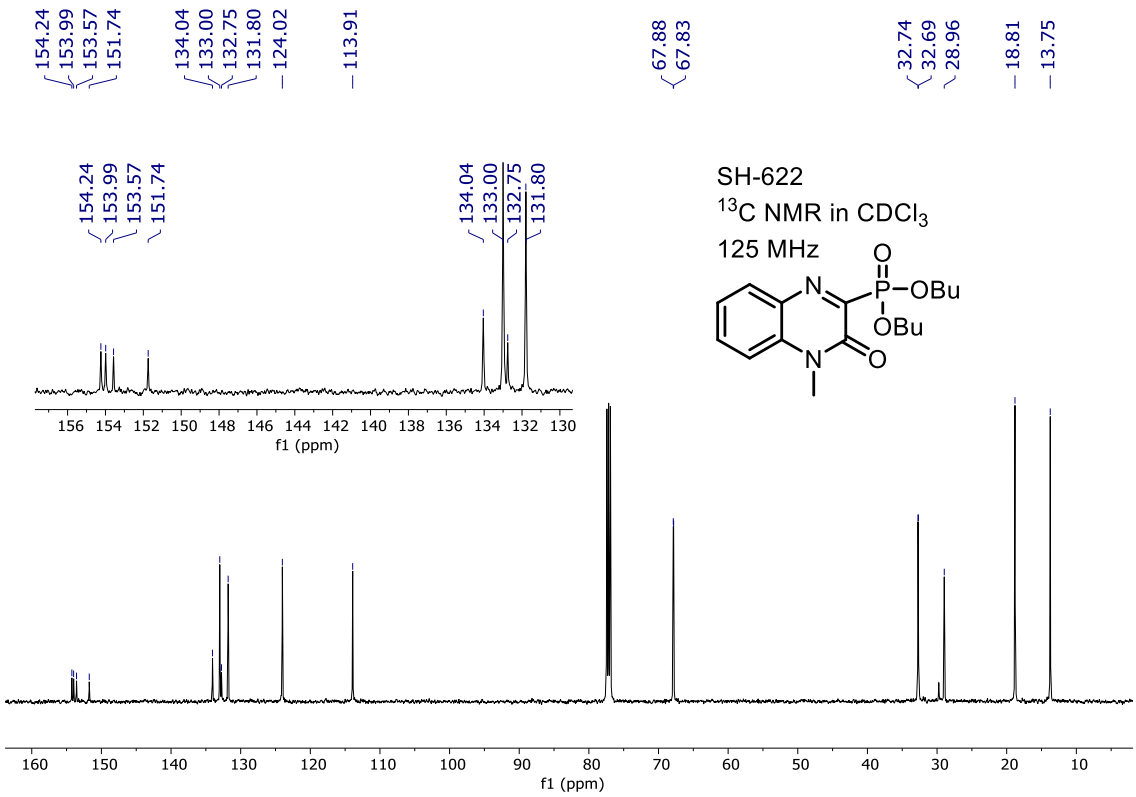
^{13}C NMR **5e**



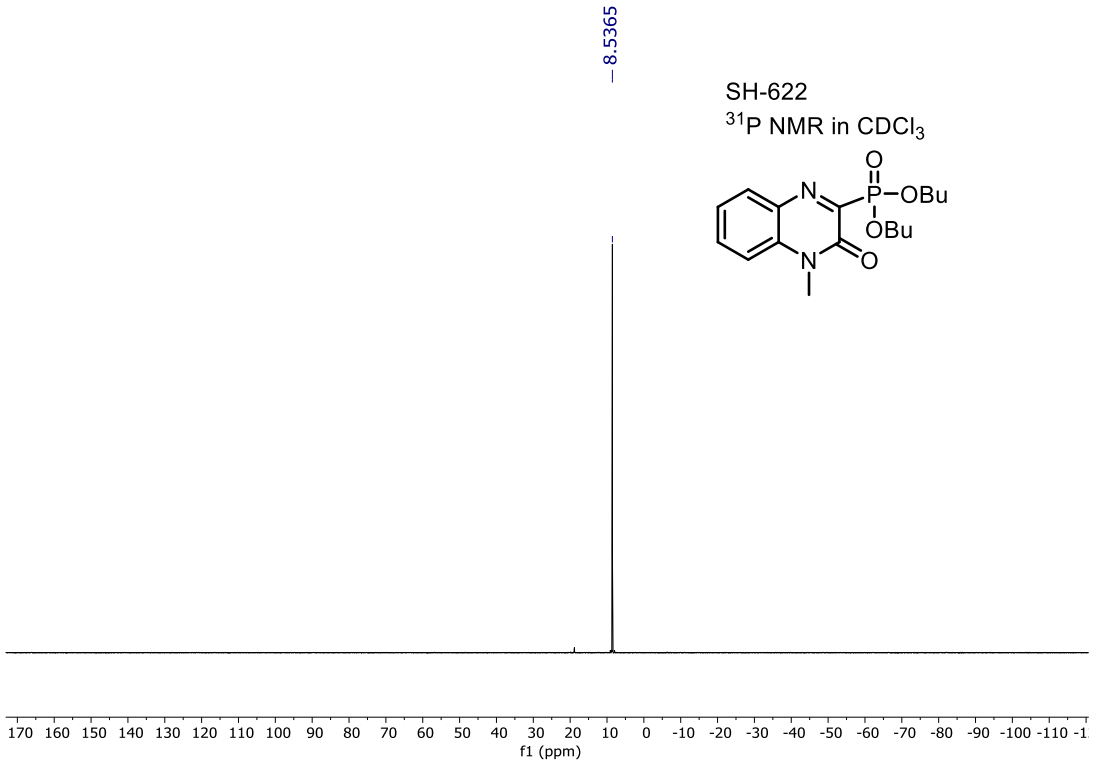
^{31}P NMR **5e**



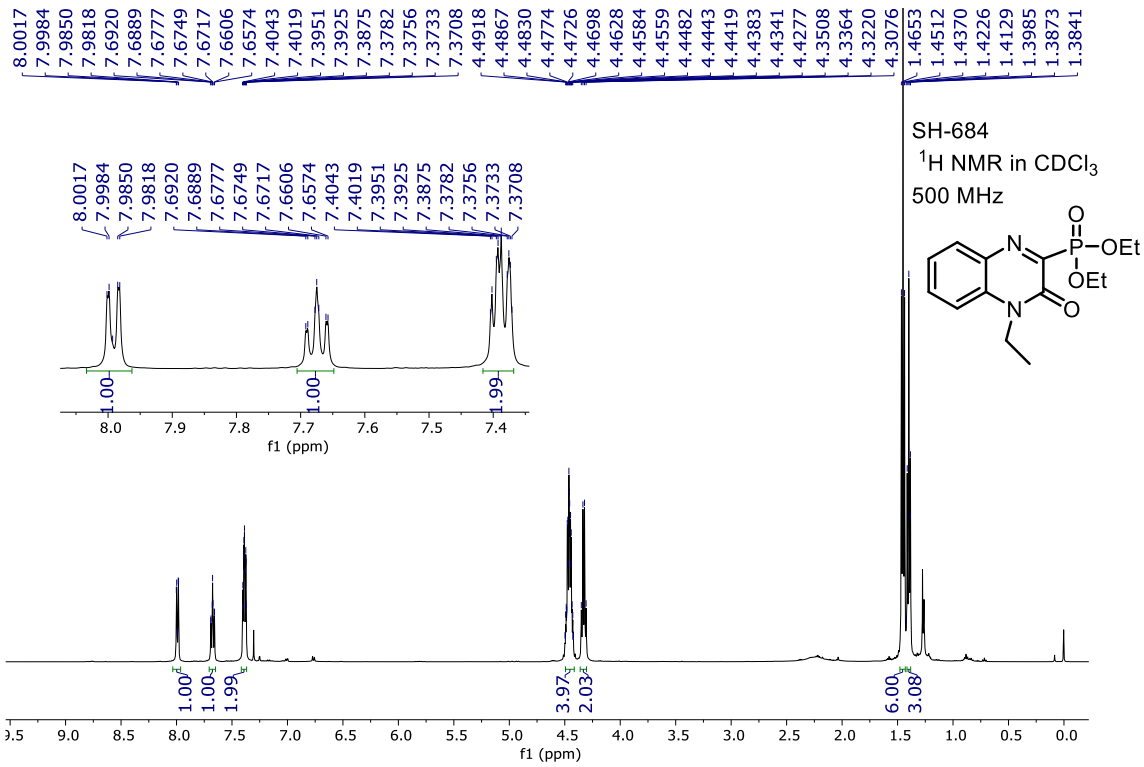
^{1}H NMR **5f**



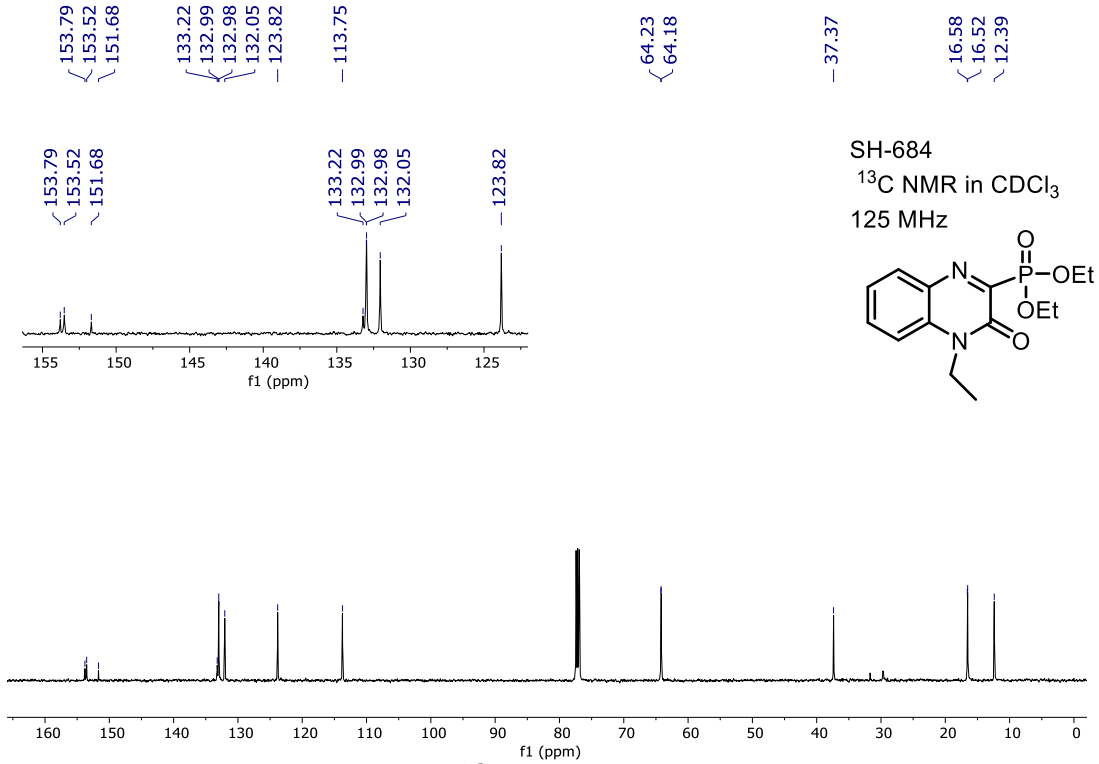
^{13}C NMR **5f**



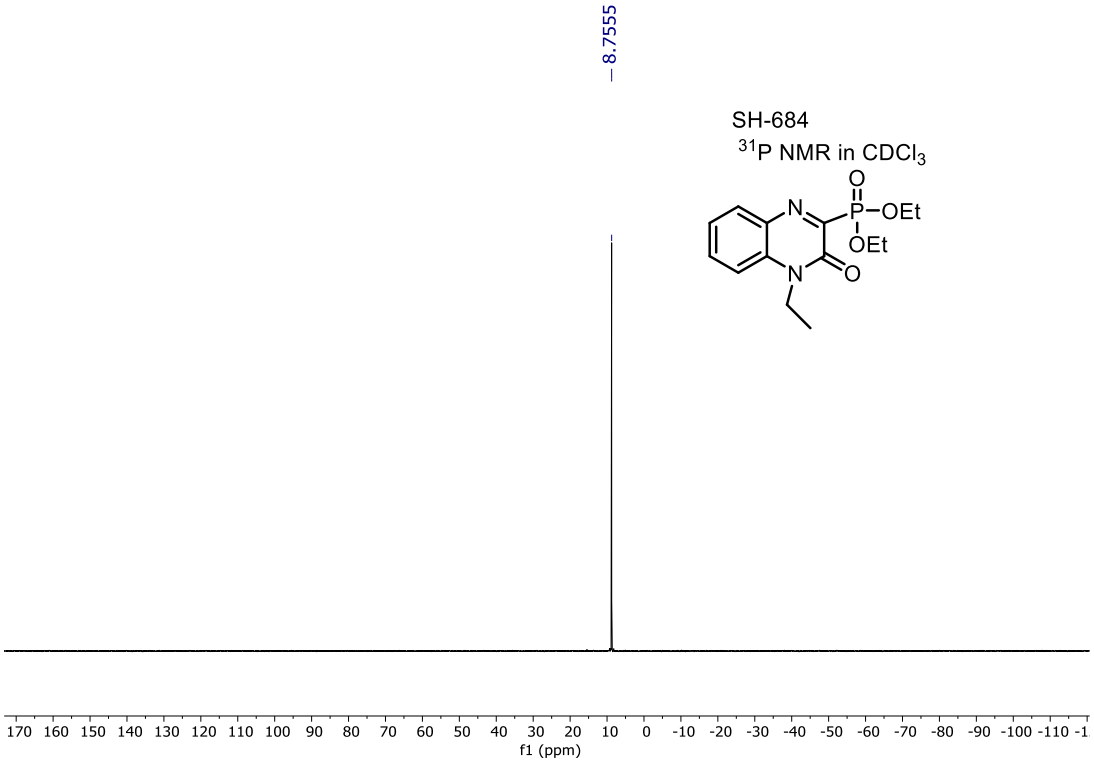
^{31}P NMR **5f**



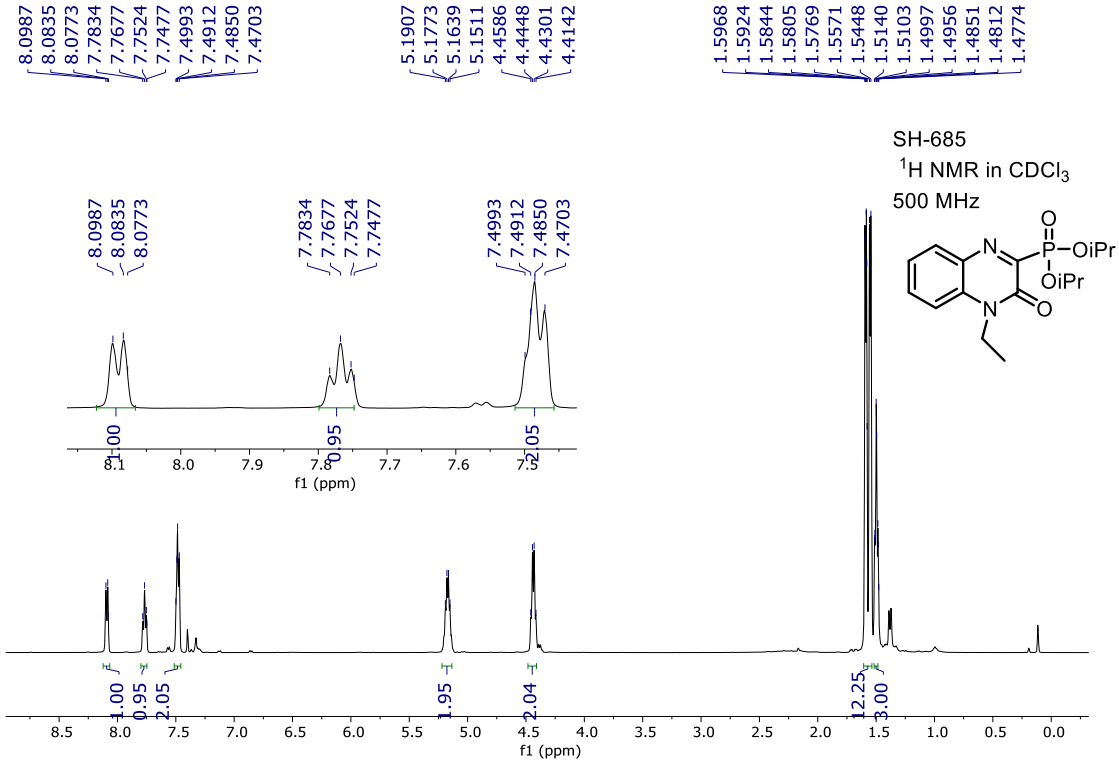
^{1}H NMR **5g**



^{13}C NMR **5g**



^{31}P NMR **5g**



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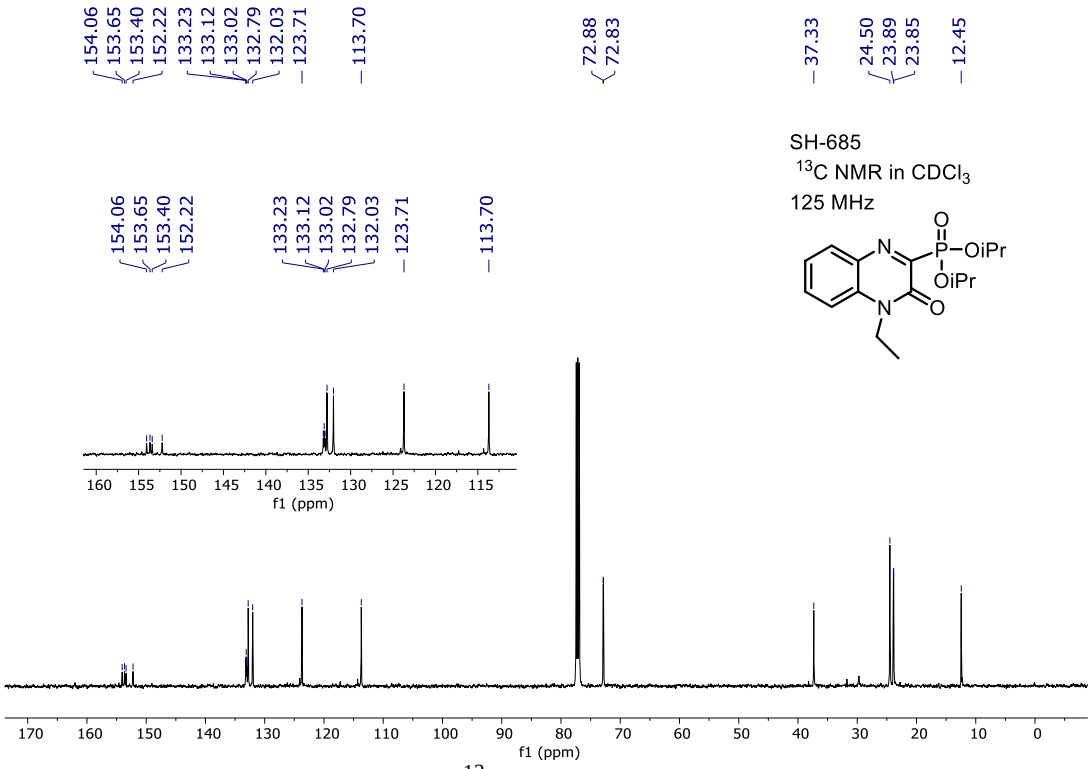
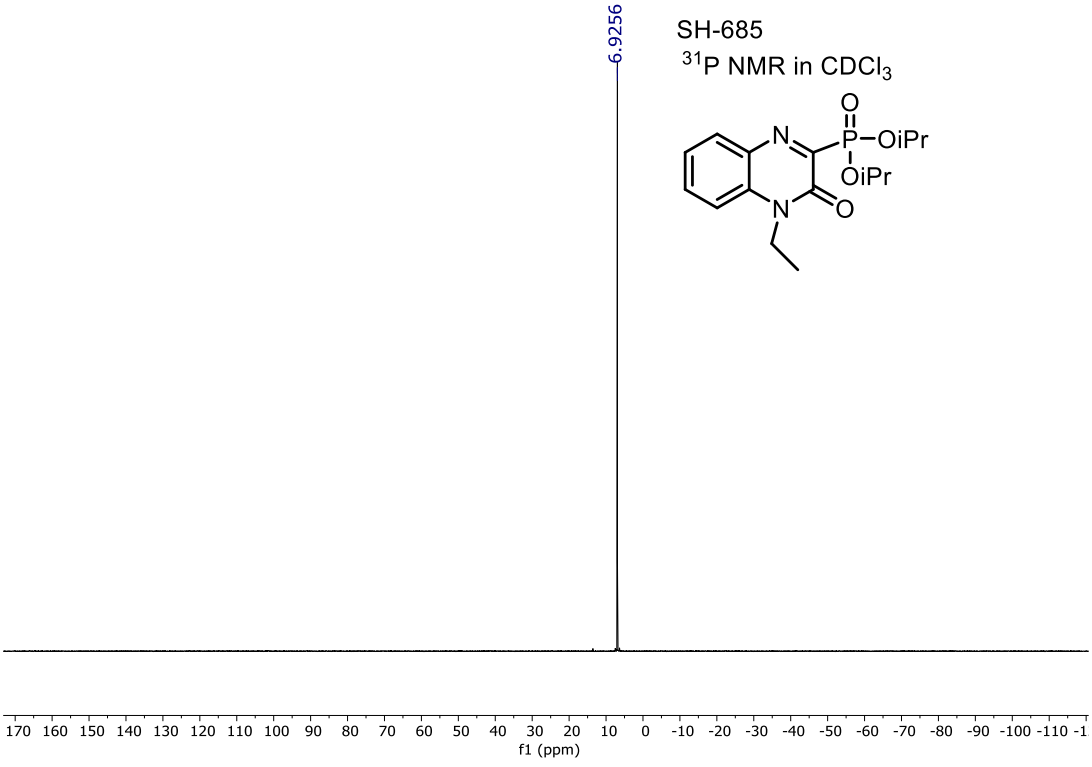


^{13}C NMR **5h**



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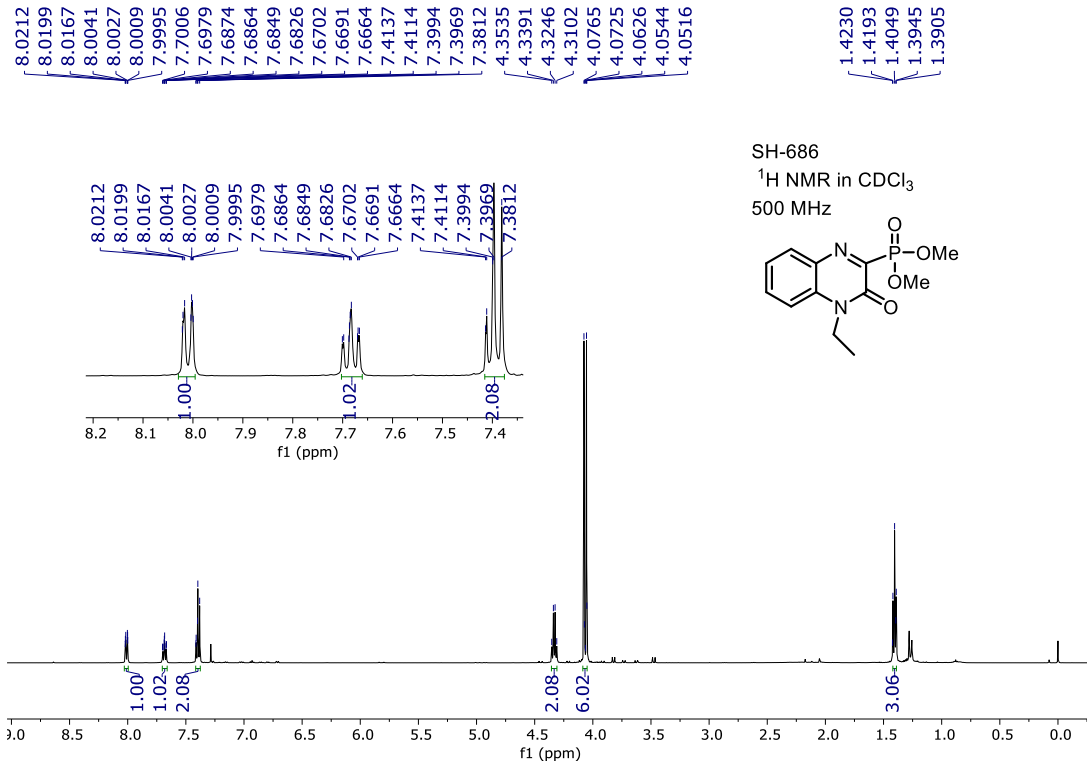
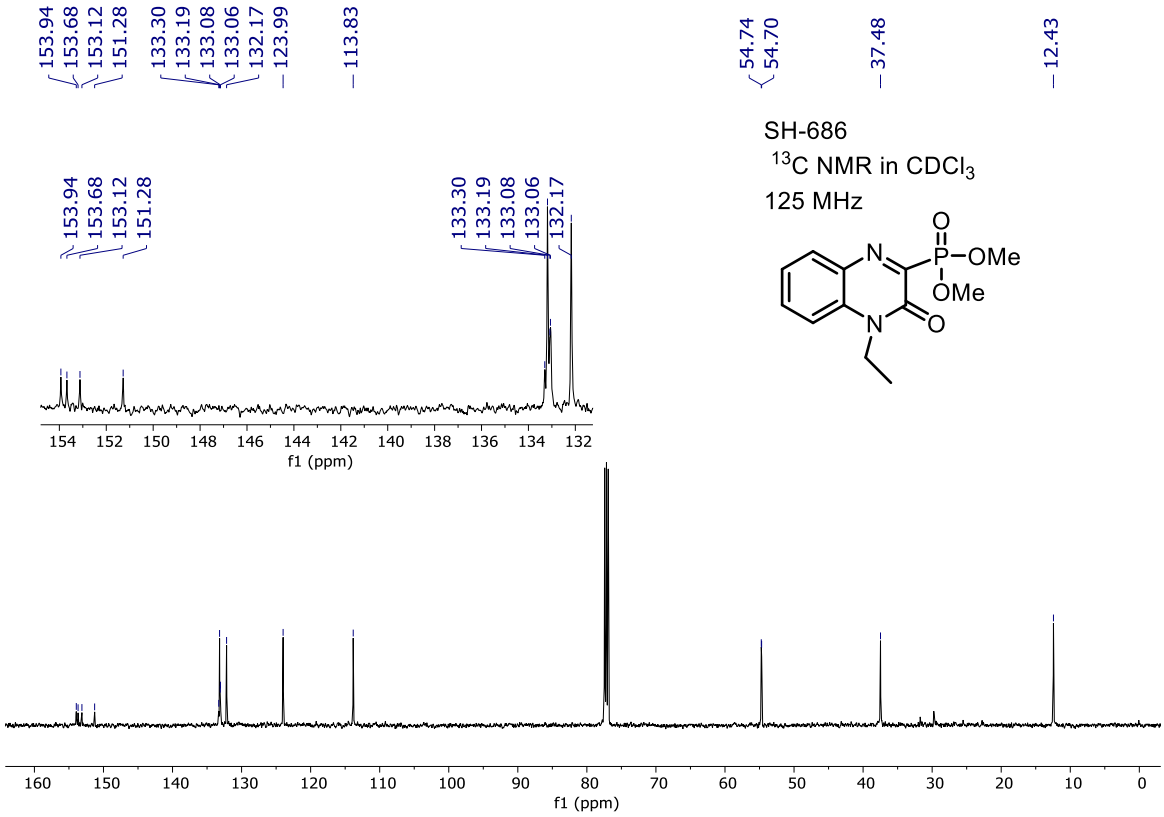
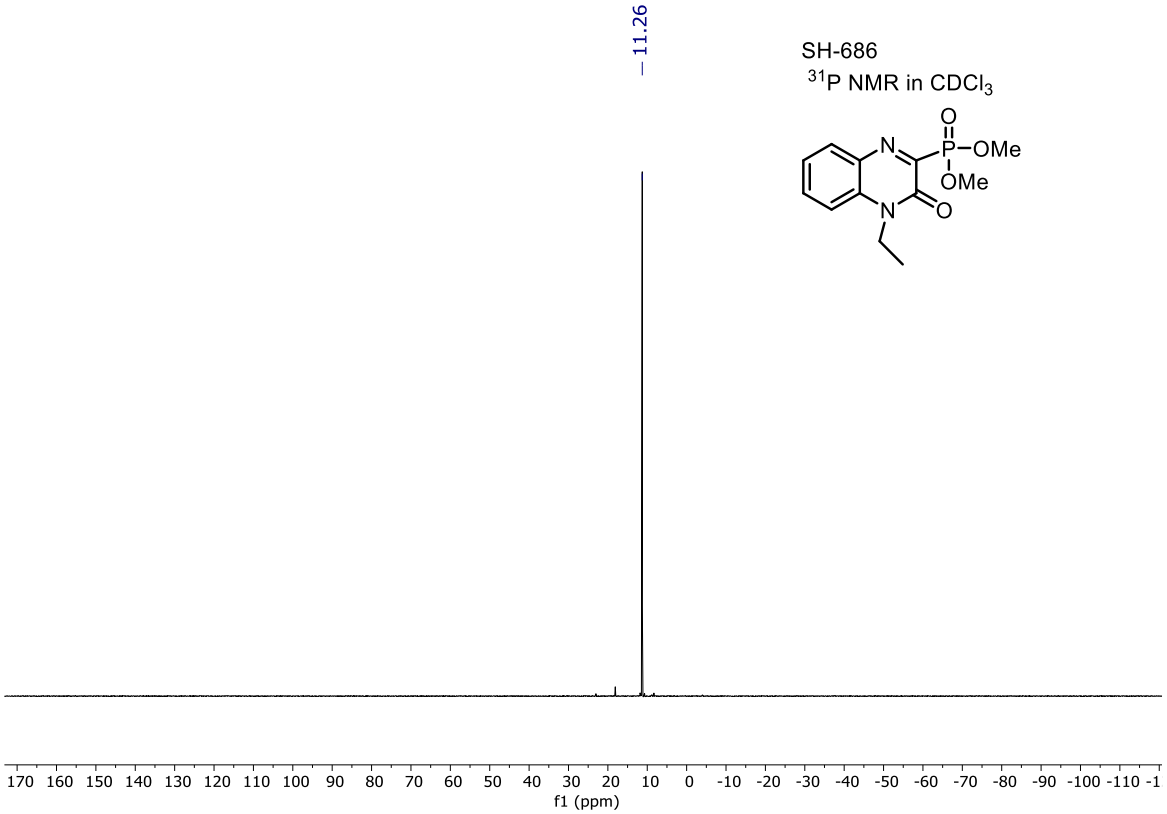


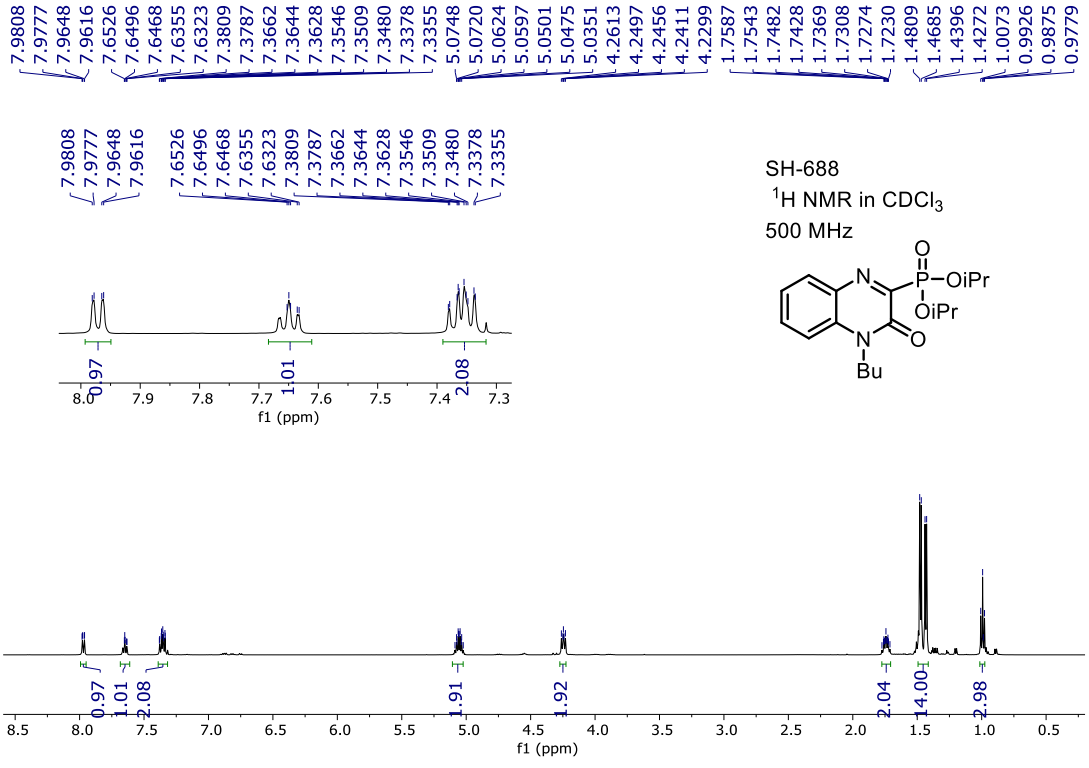
^{1}H NMR **5i**



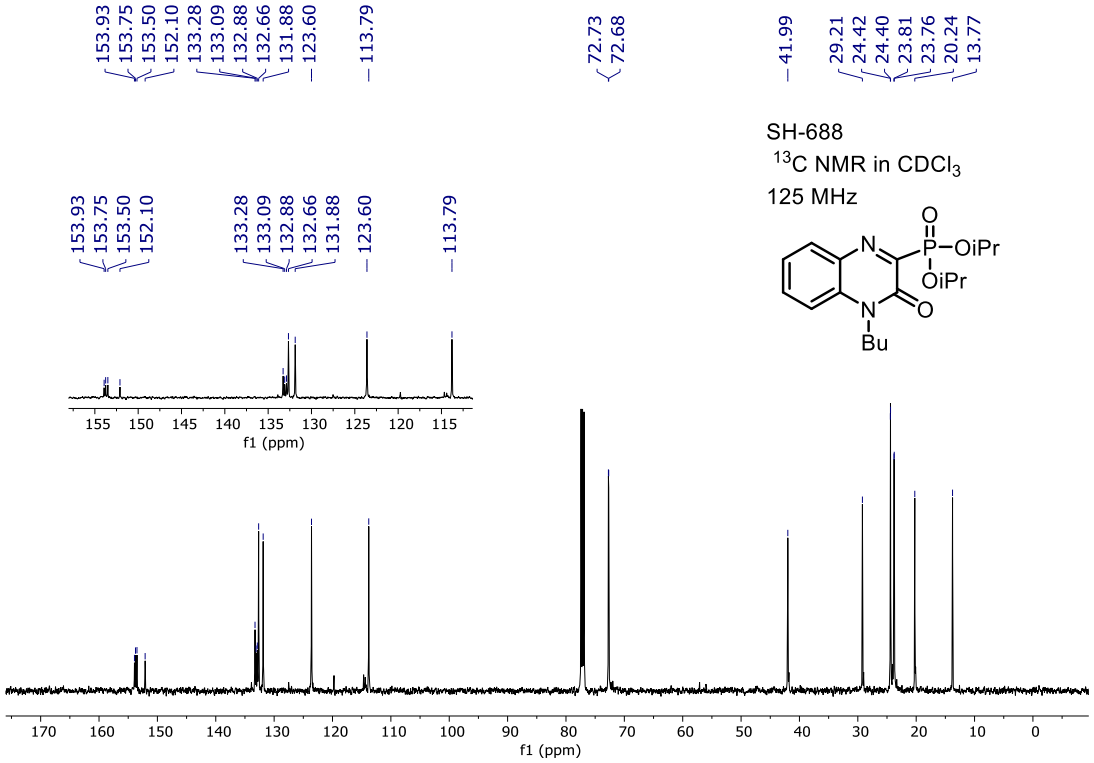
^{13}C NMR **5i**



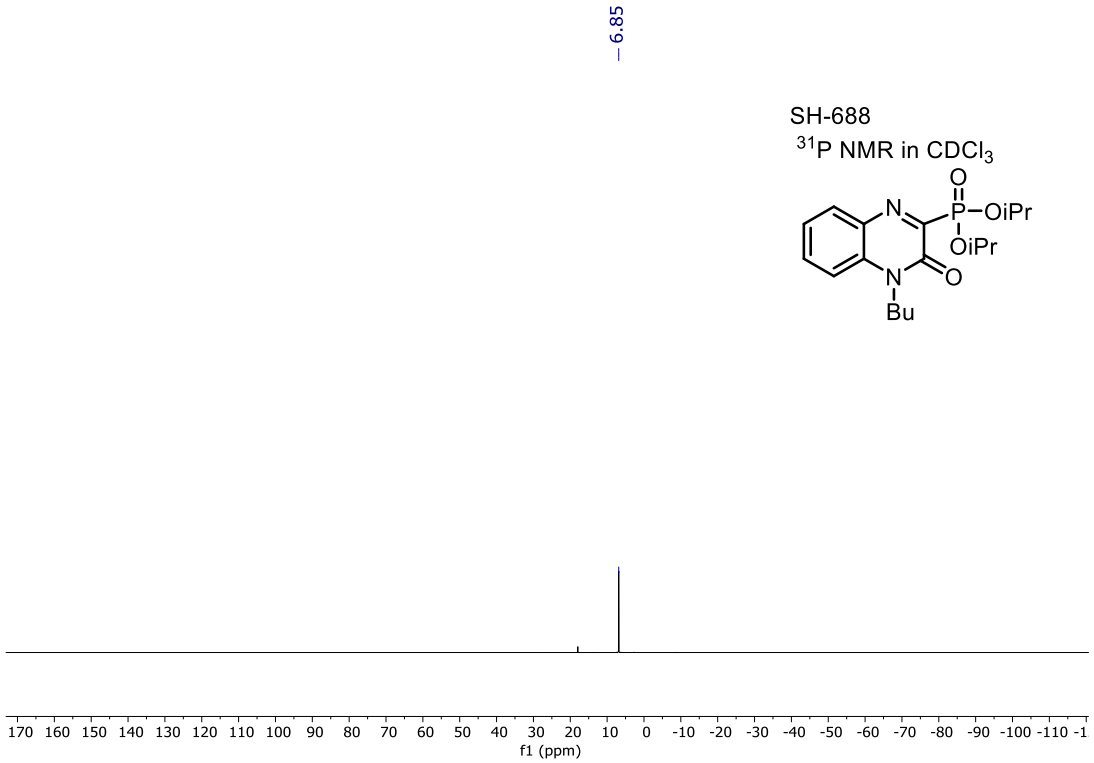
^{31}P NMR **5i**



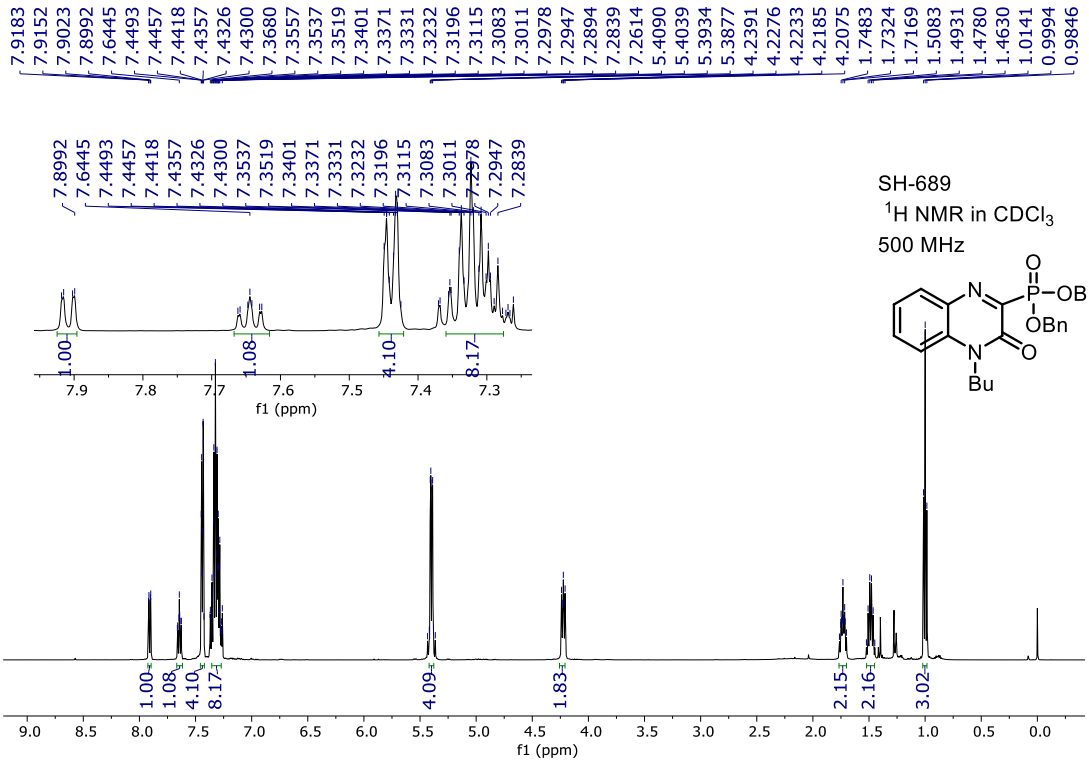
^{1}H NMR **5j**



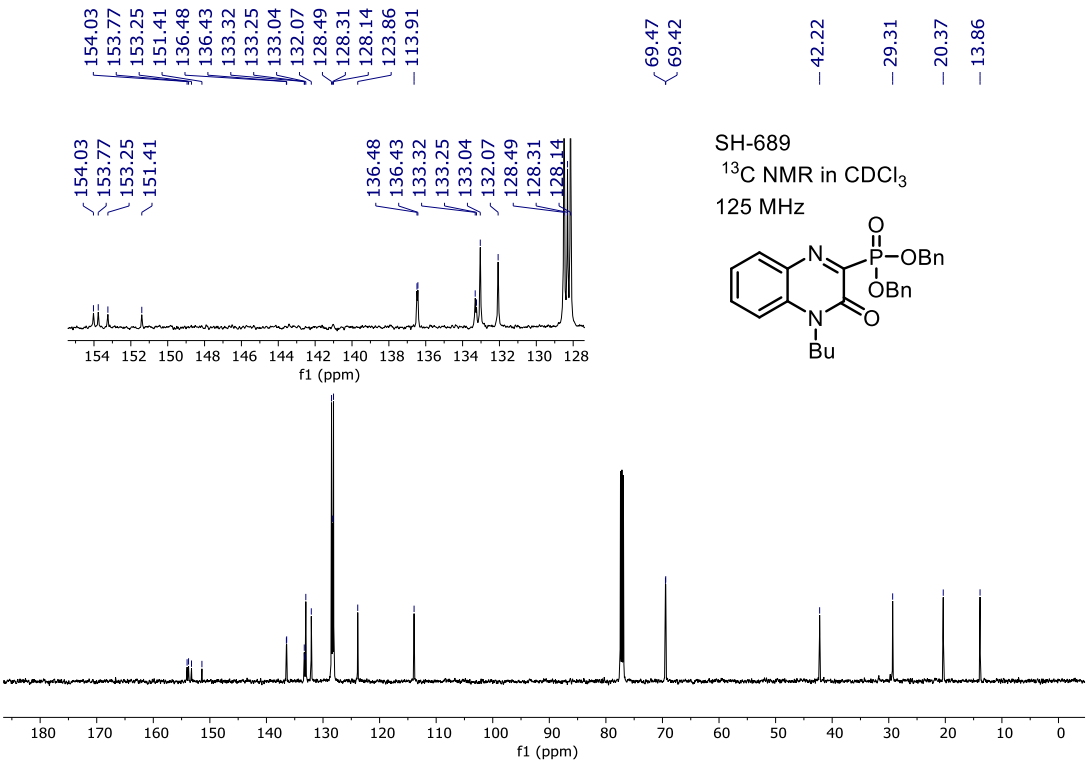
^{13}C NMR **5j**



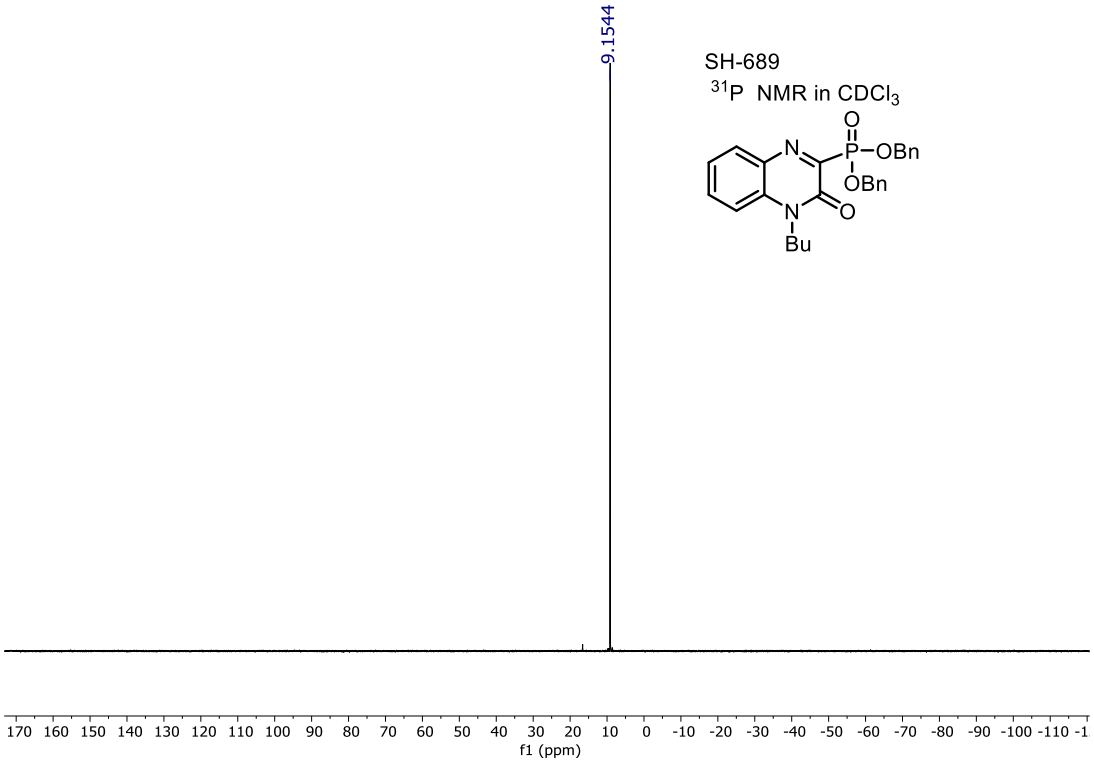
^{31}P NMR **5j**



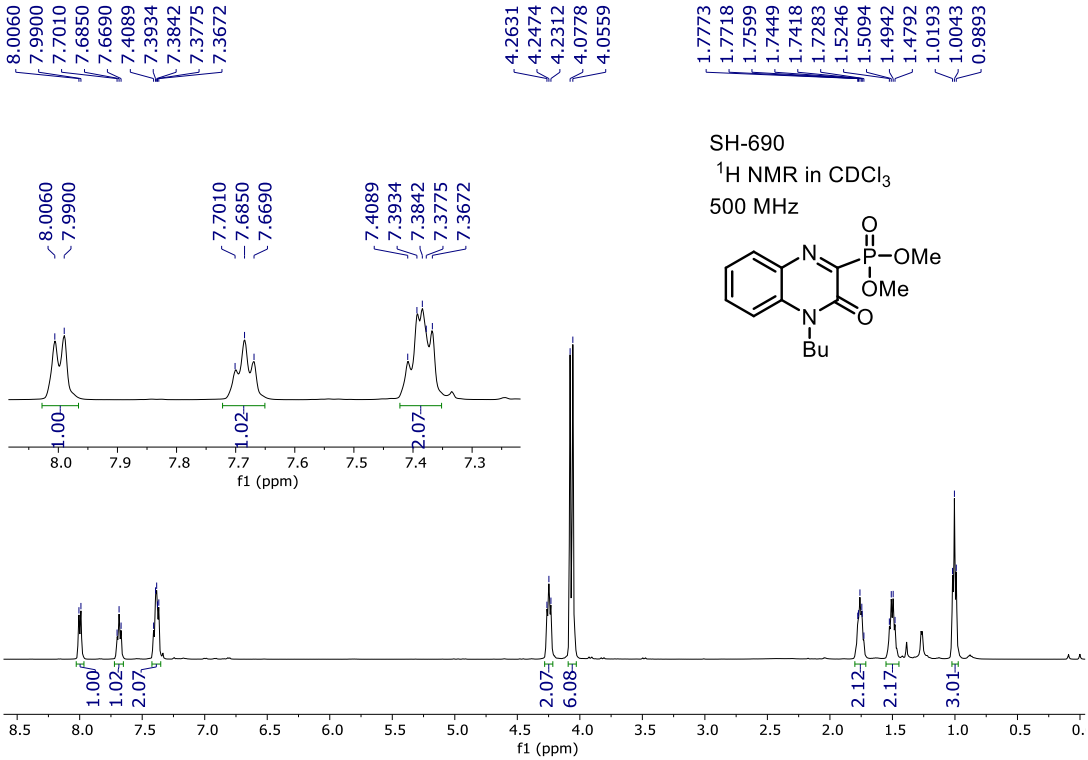
^{1}H NMR **5k**



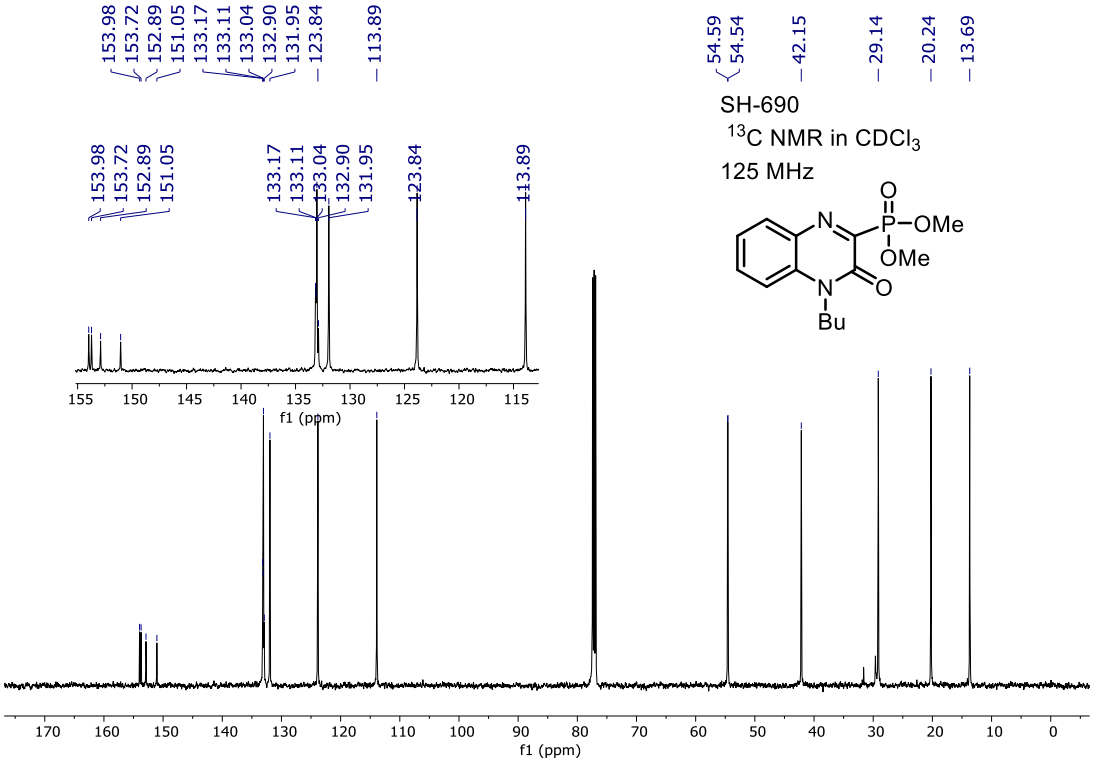
^{13}C NMR **5k**



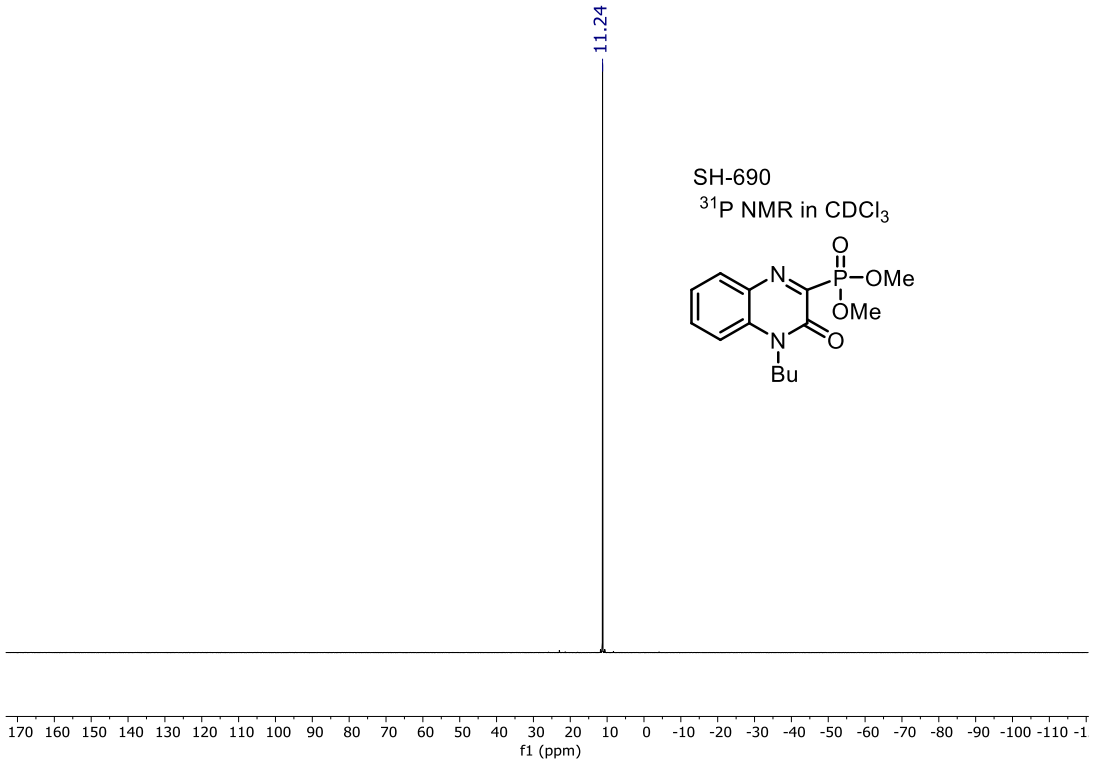
^{31}P NMR **5k**



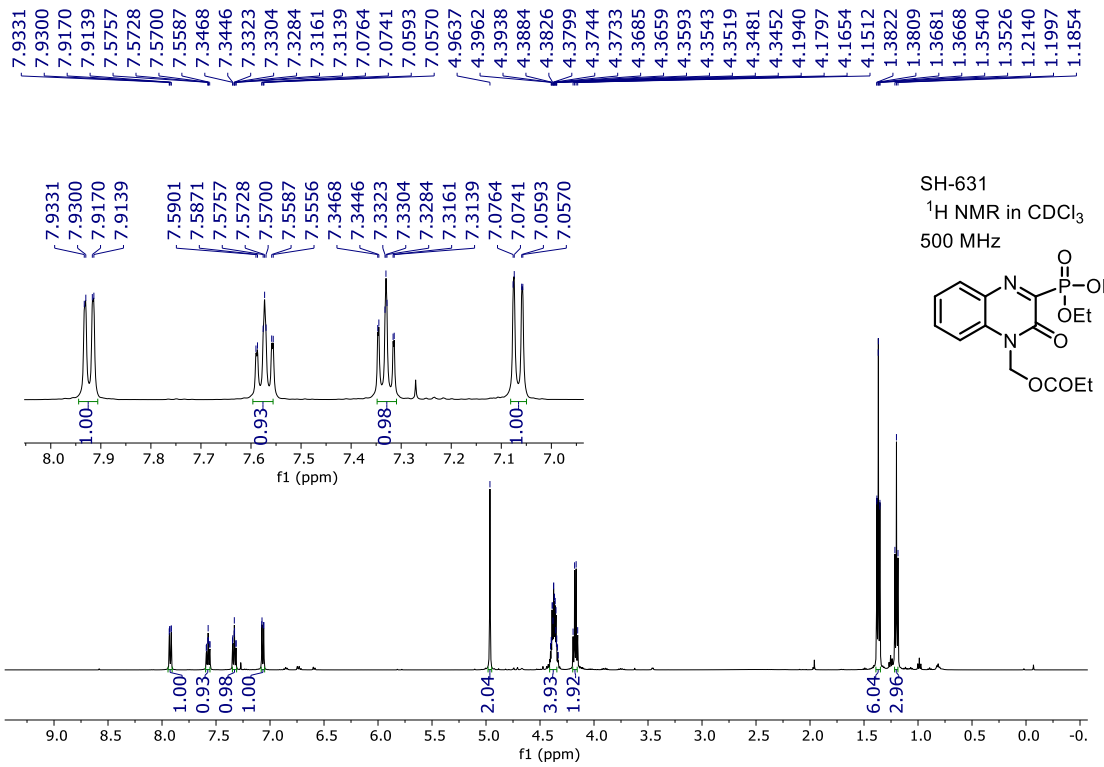
^{1}H NMR **5l**



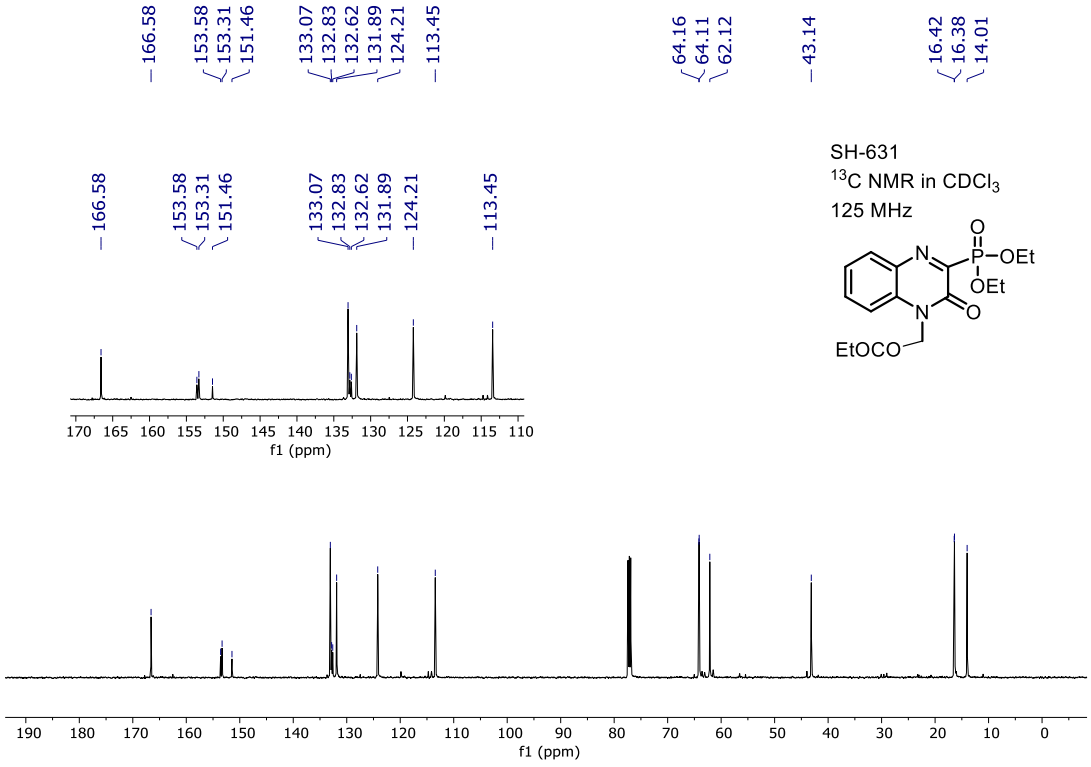
^{13}C NMR **5l**



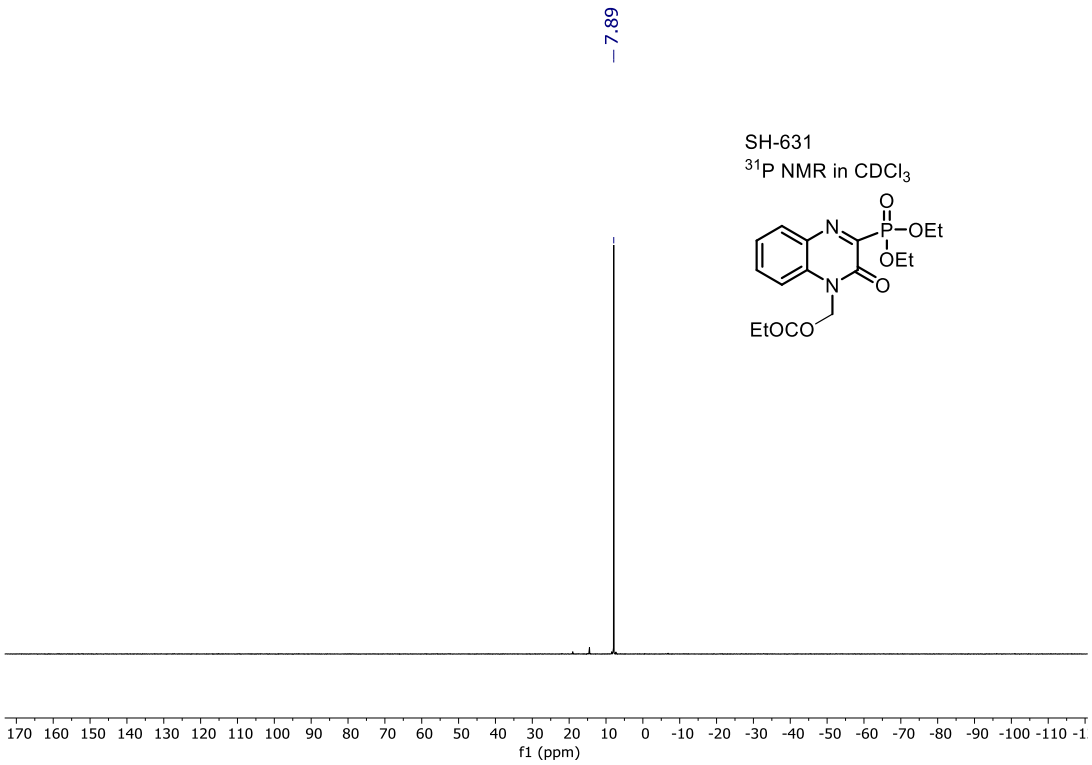
^{31}P NMR **5l**



^{1}H NMR **5m**



^{13}C NMR **5m**



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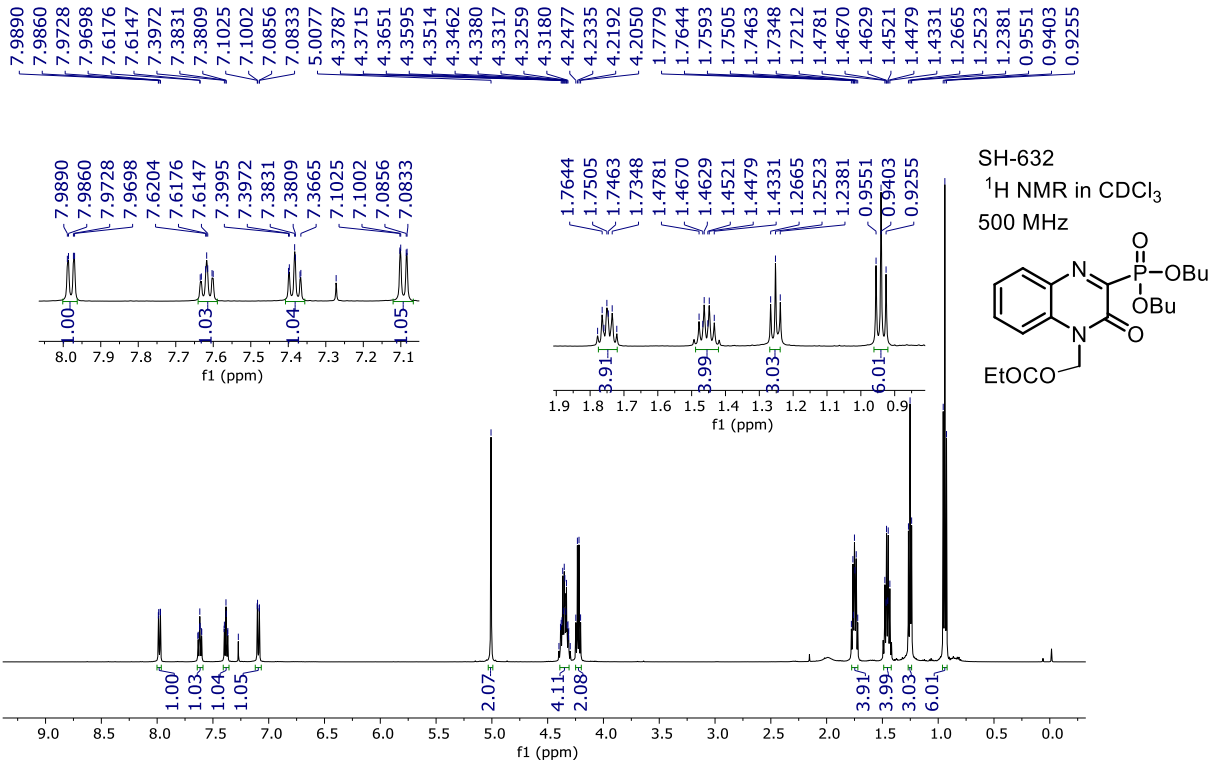
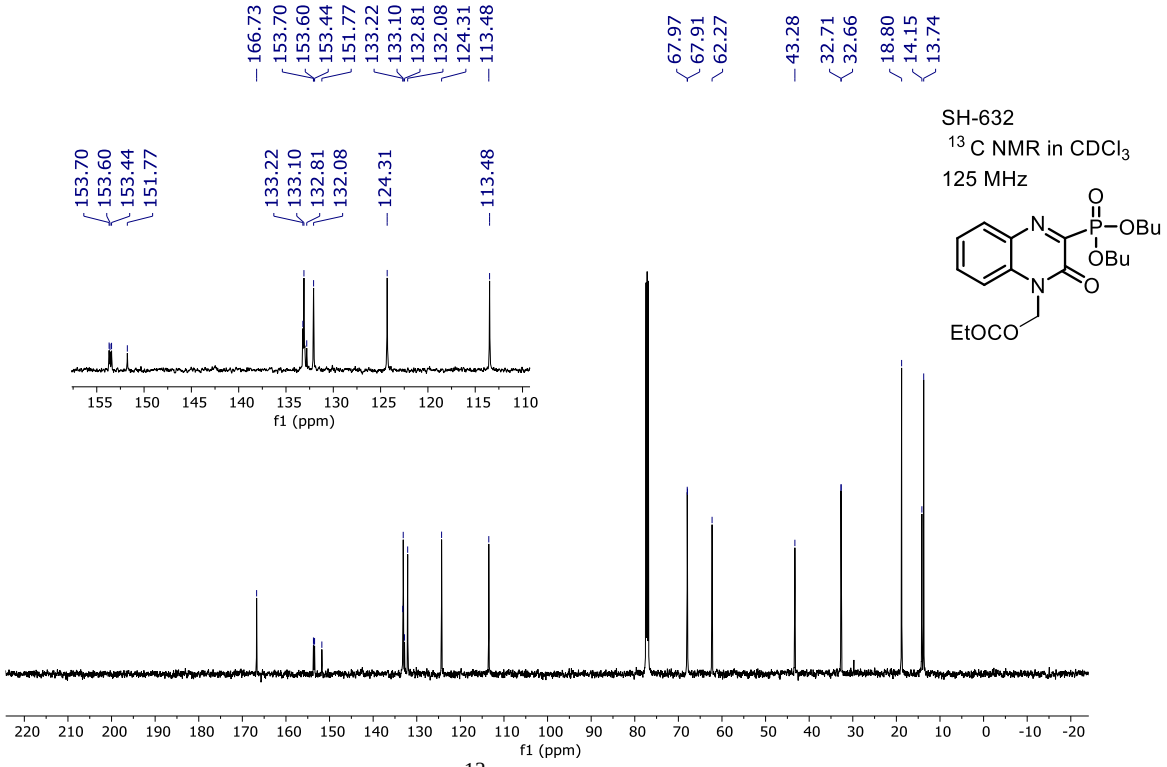
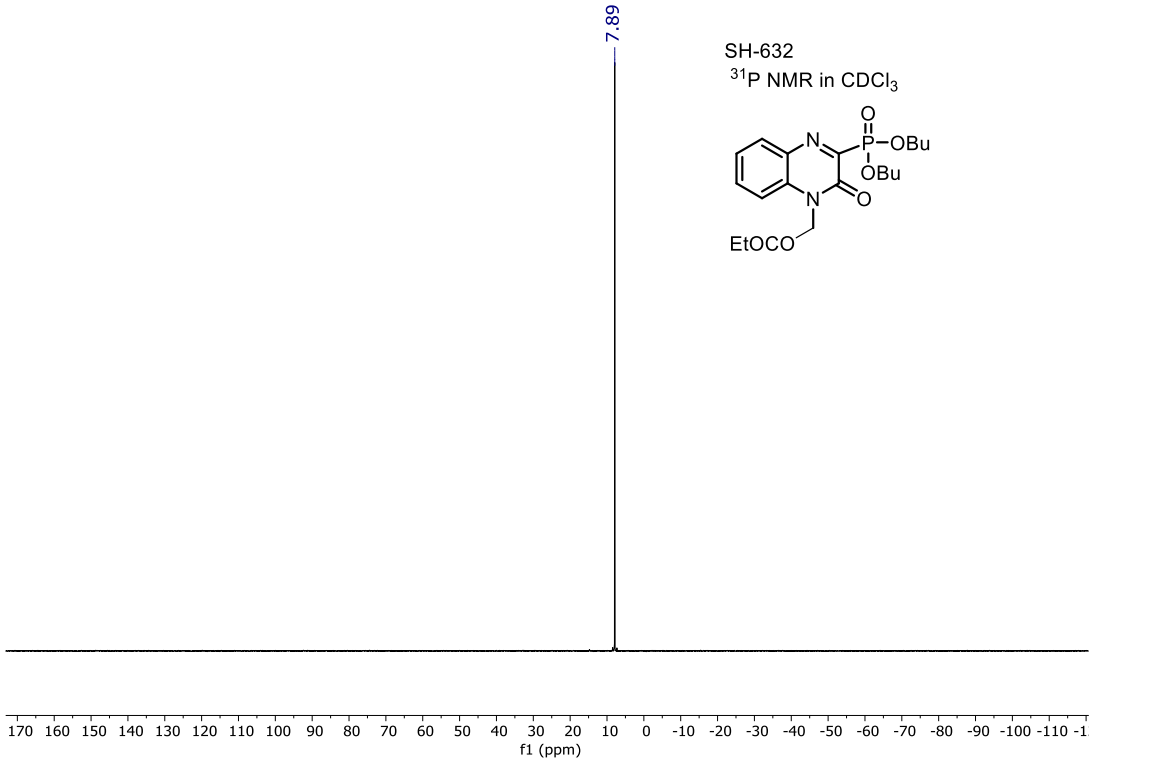


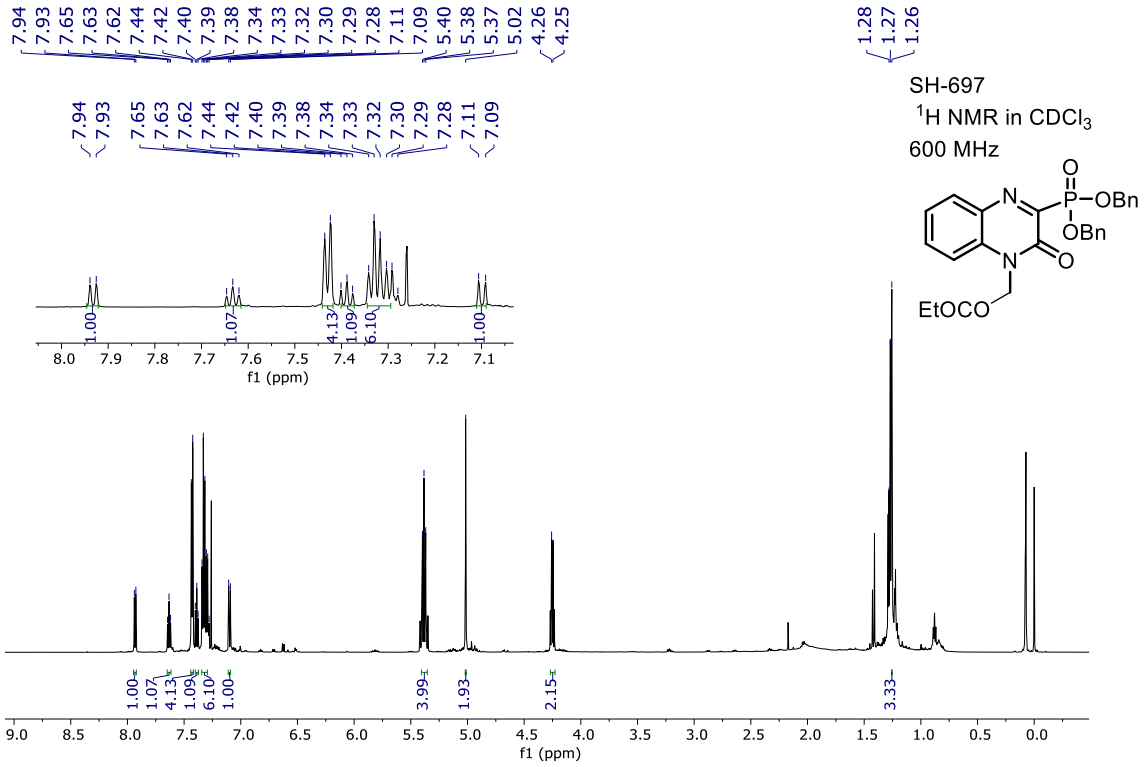
^{1}H NMR **5n**



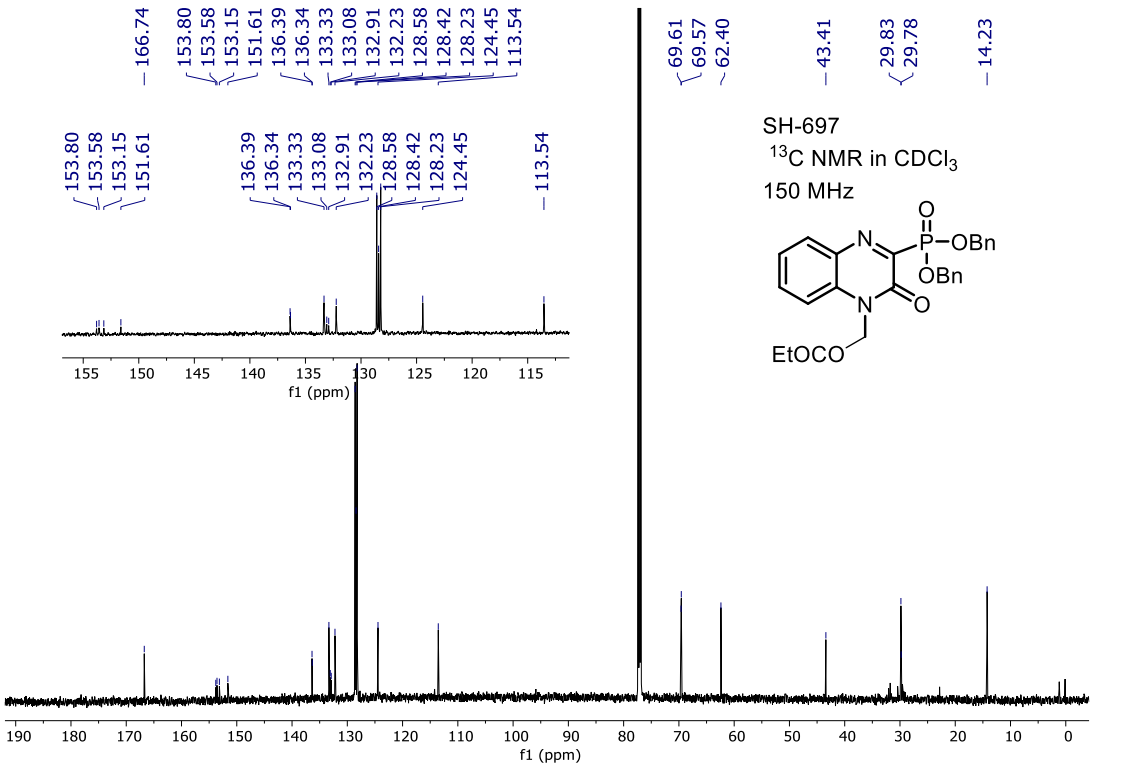
^{13}C NMR **5n**



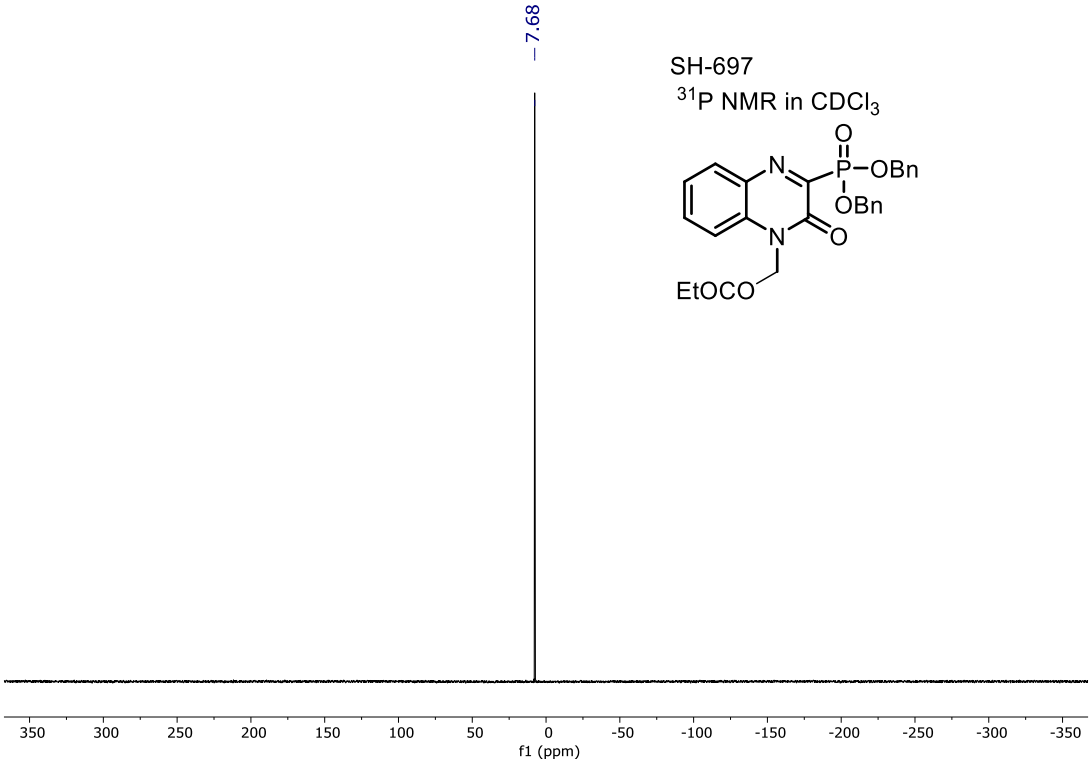
^{31}P NMR **5n**



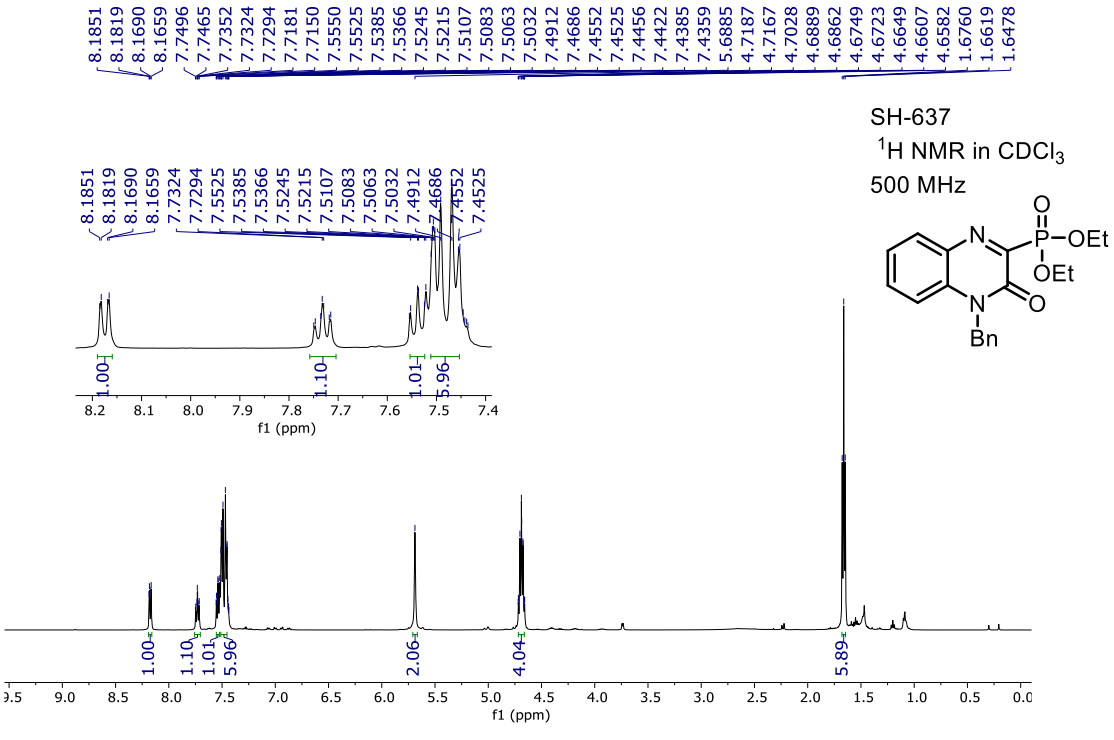
^{1}H NMR **5o**



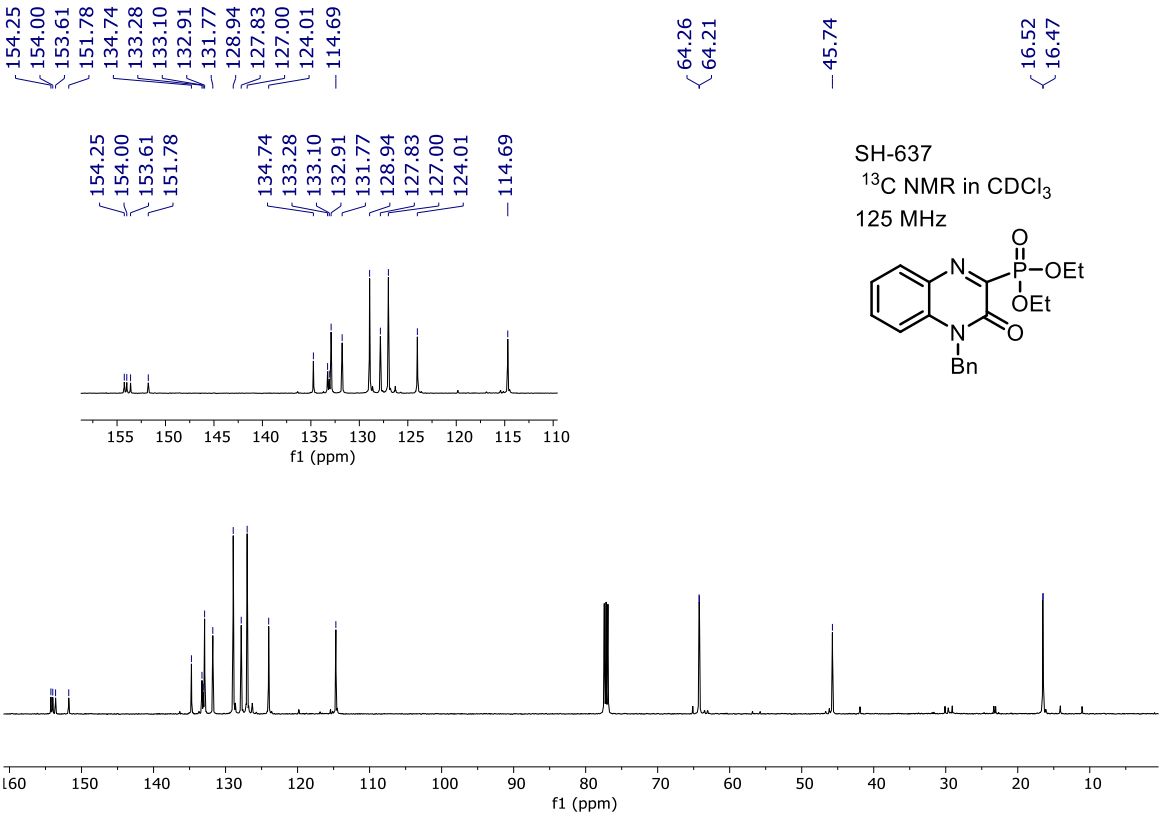
^{13}C NMR **5o**



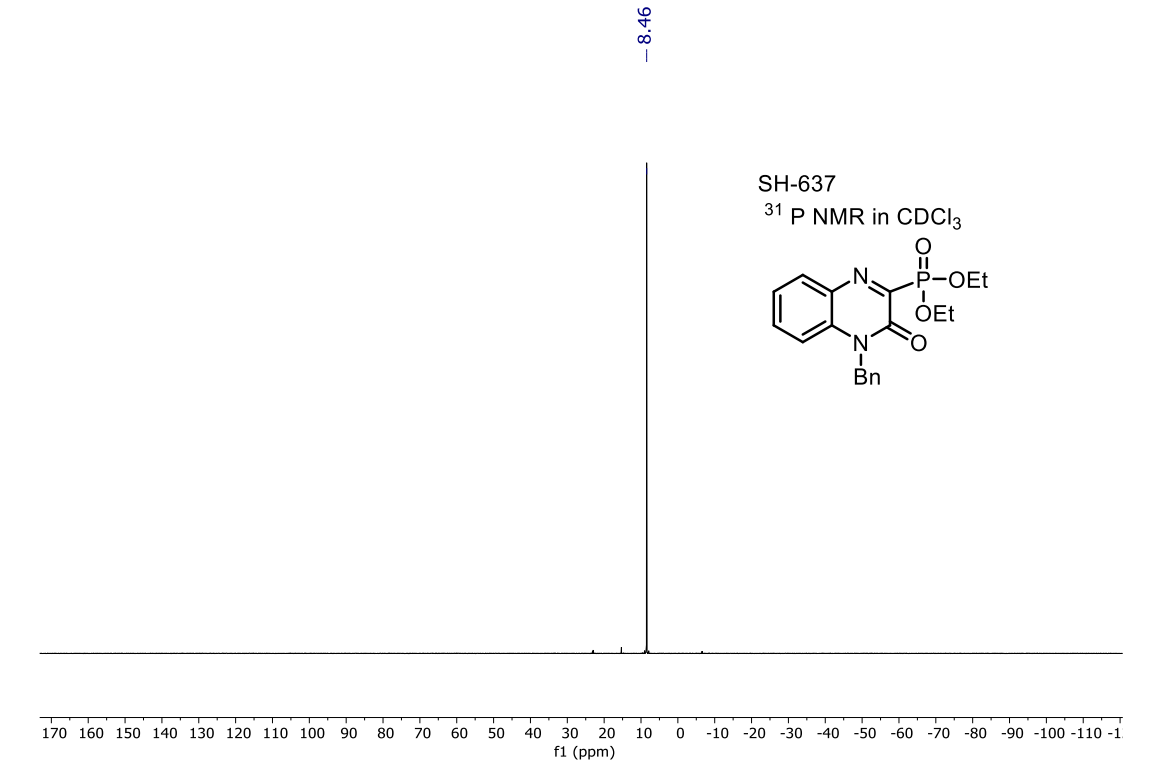
^{31}P NMR **5o**



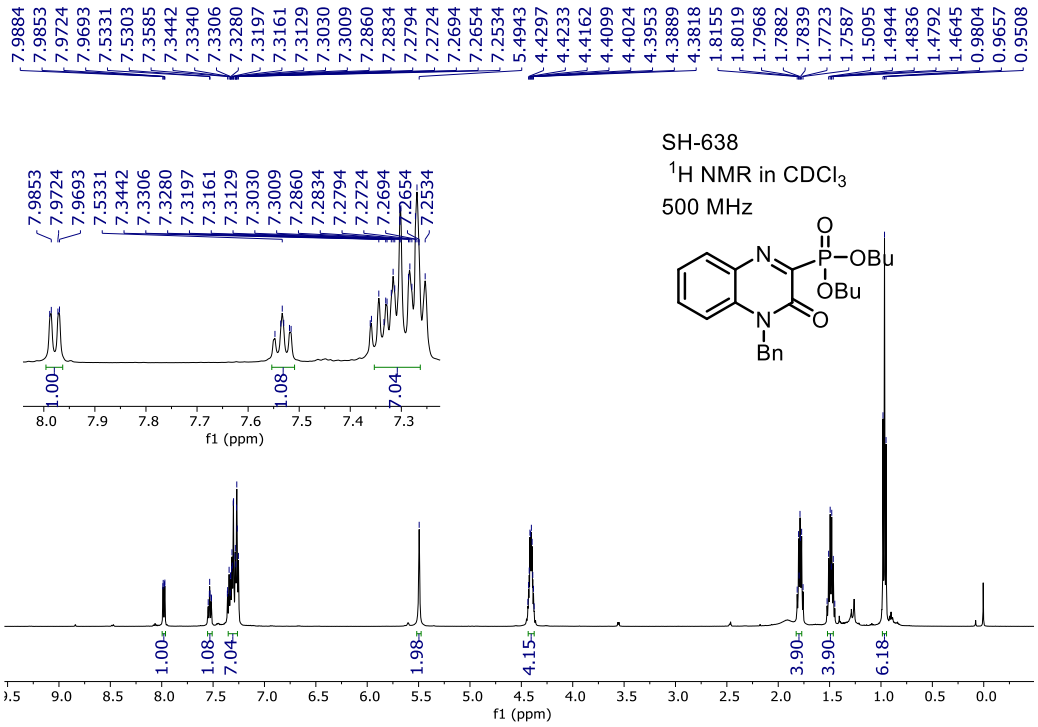
^{1}H NMR **5p**



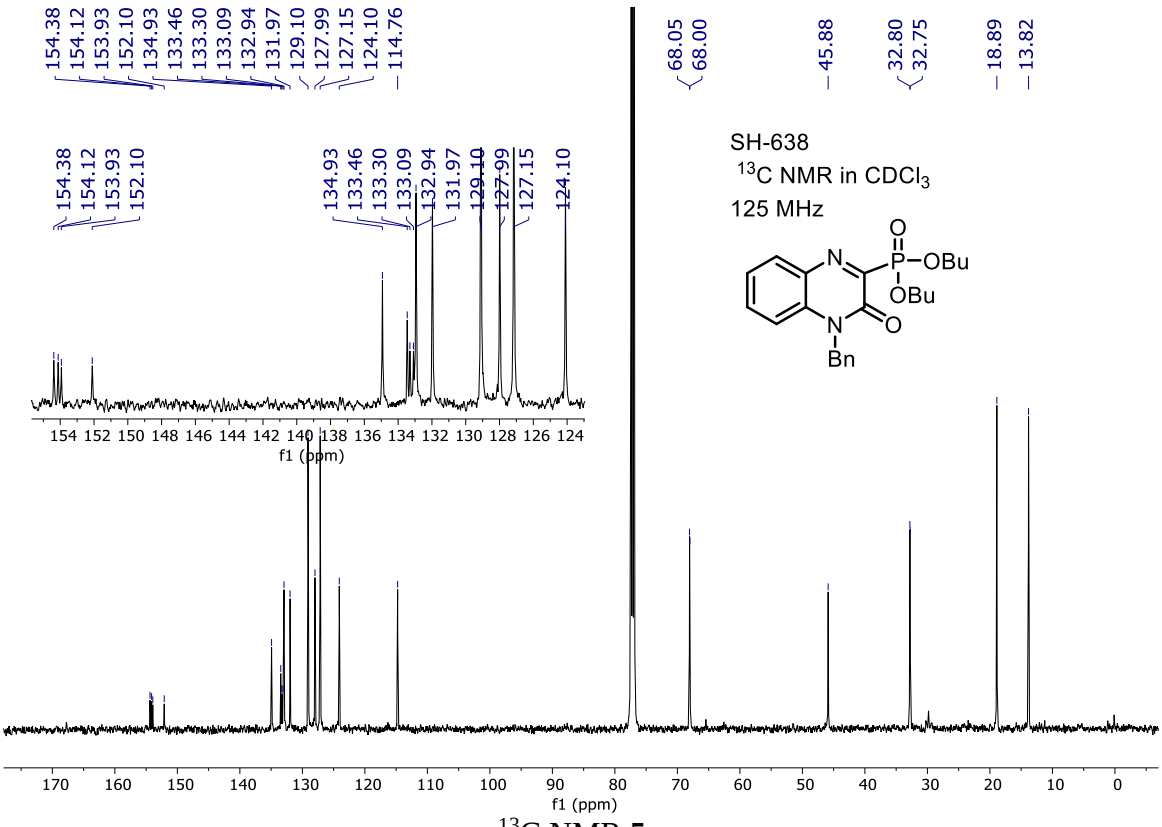
^{13}C NMR **5p**



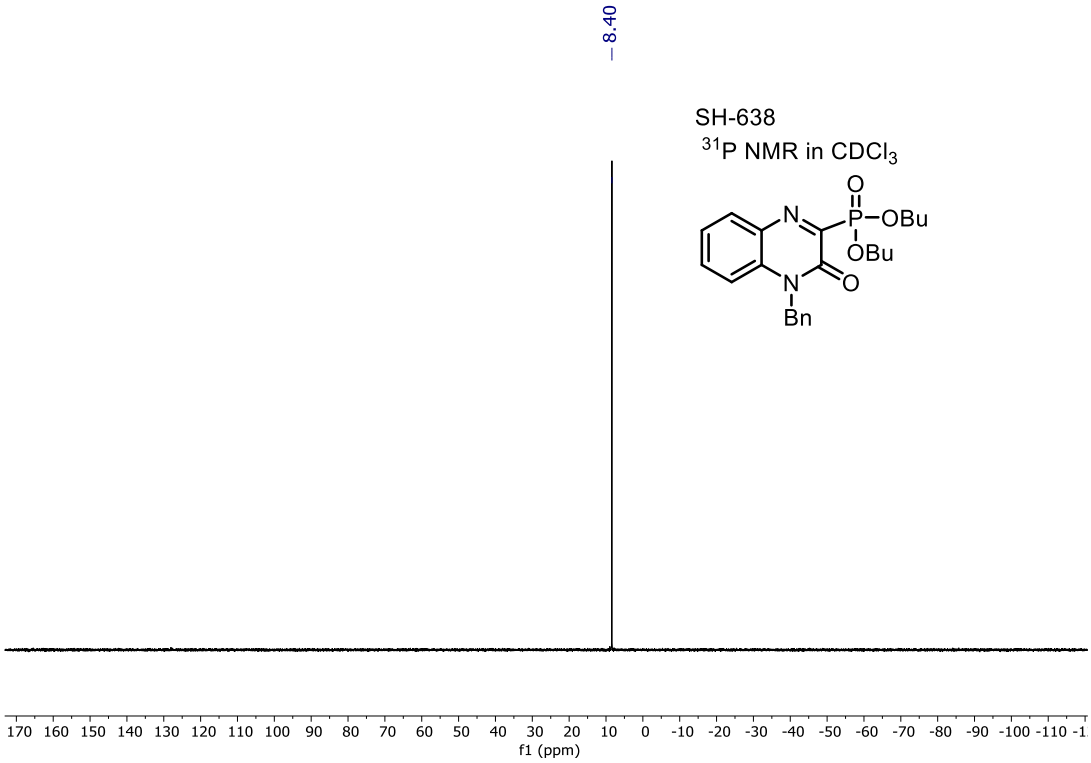
^{31}P NMR **5p**



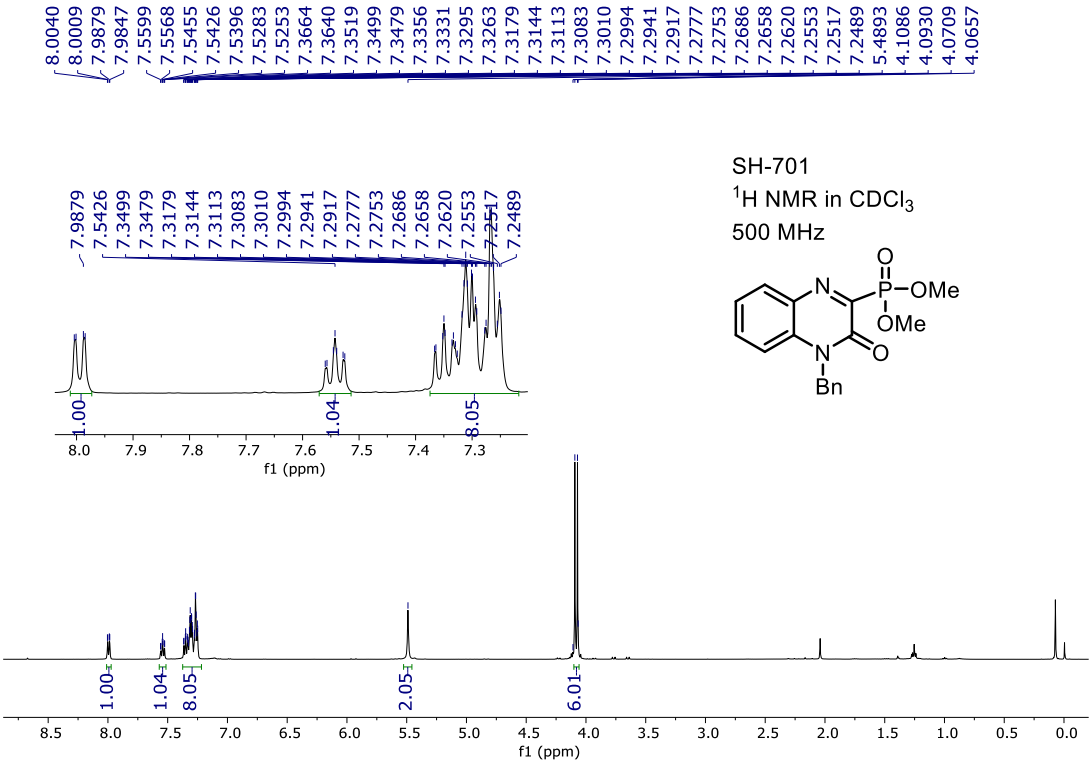
^{1}H NMR **5q**



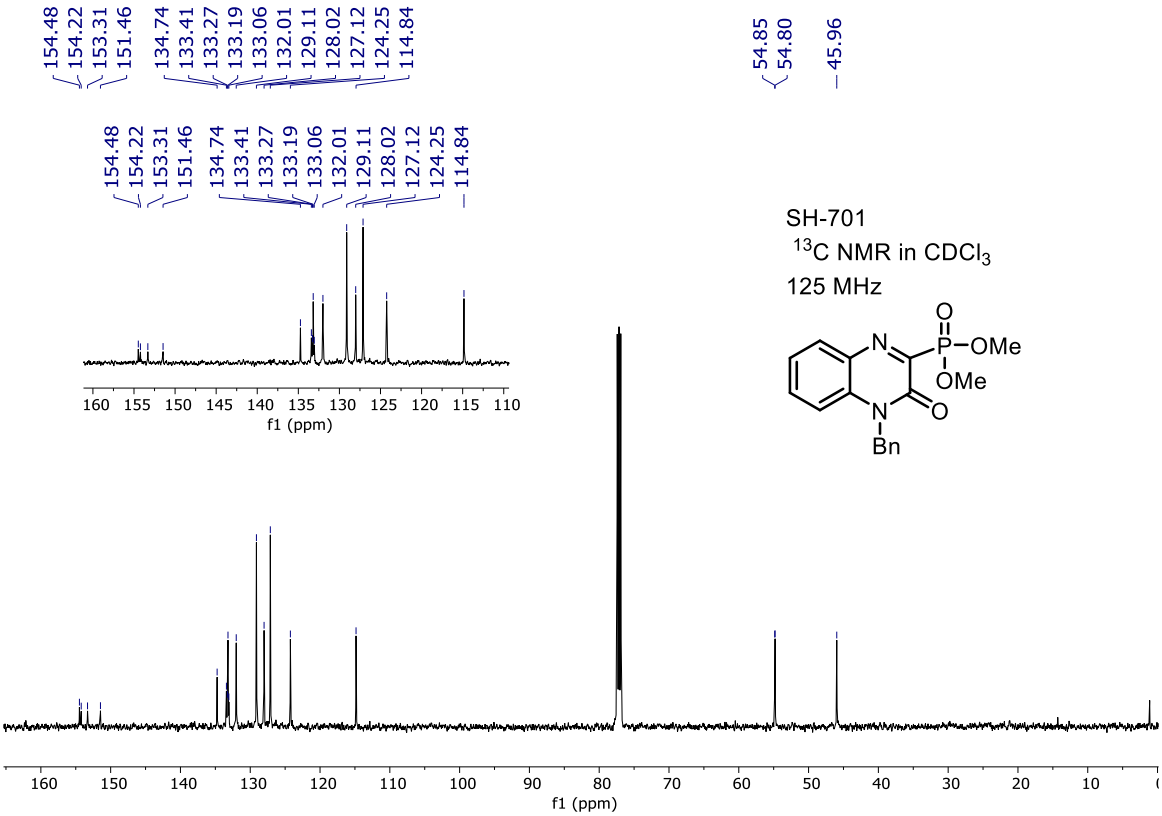
^{13}C NMR **5q**



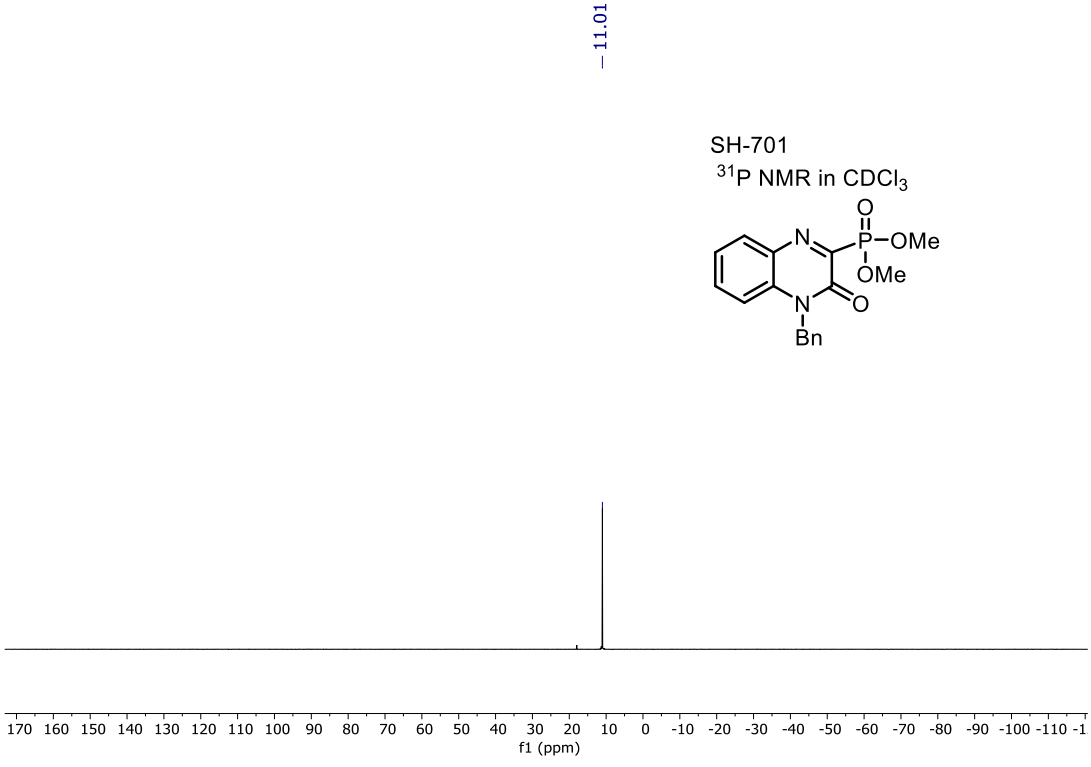
^{31}P NMR **5q**



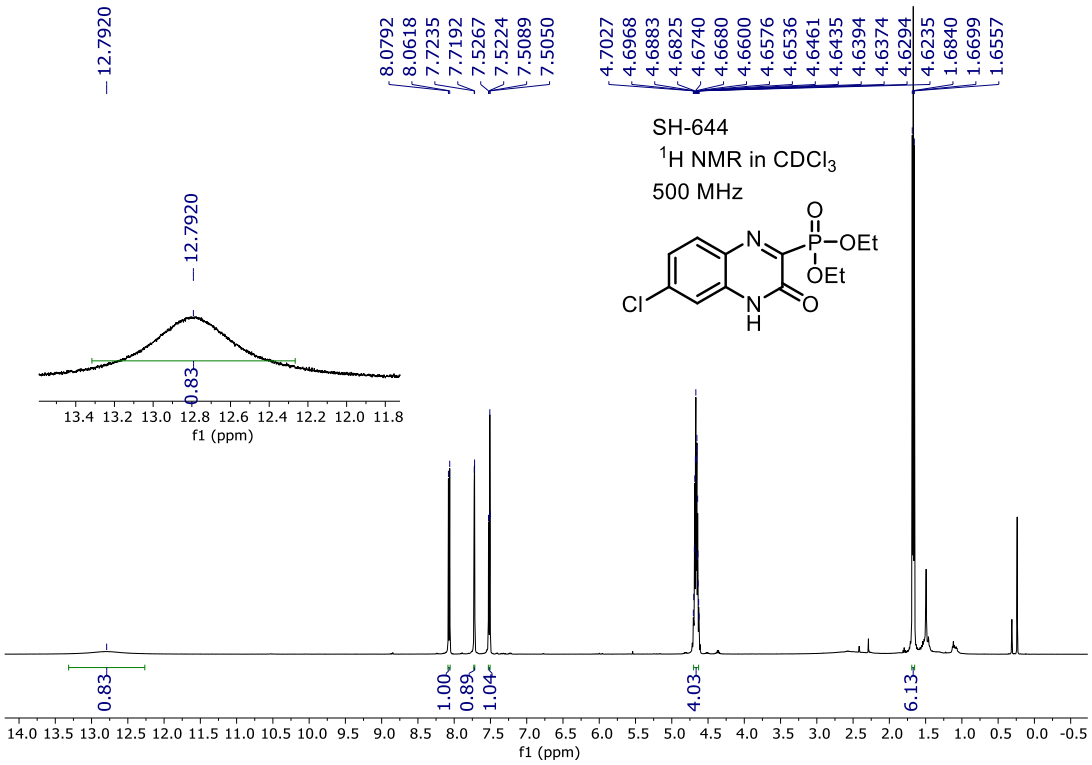
^{1}H NMR **5r**



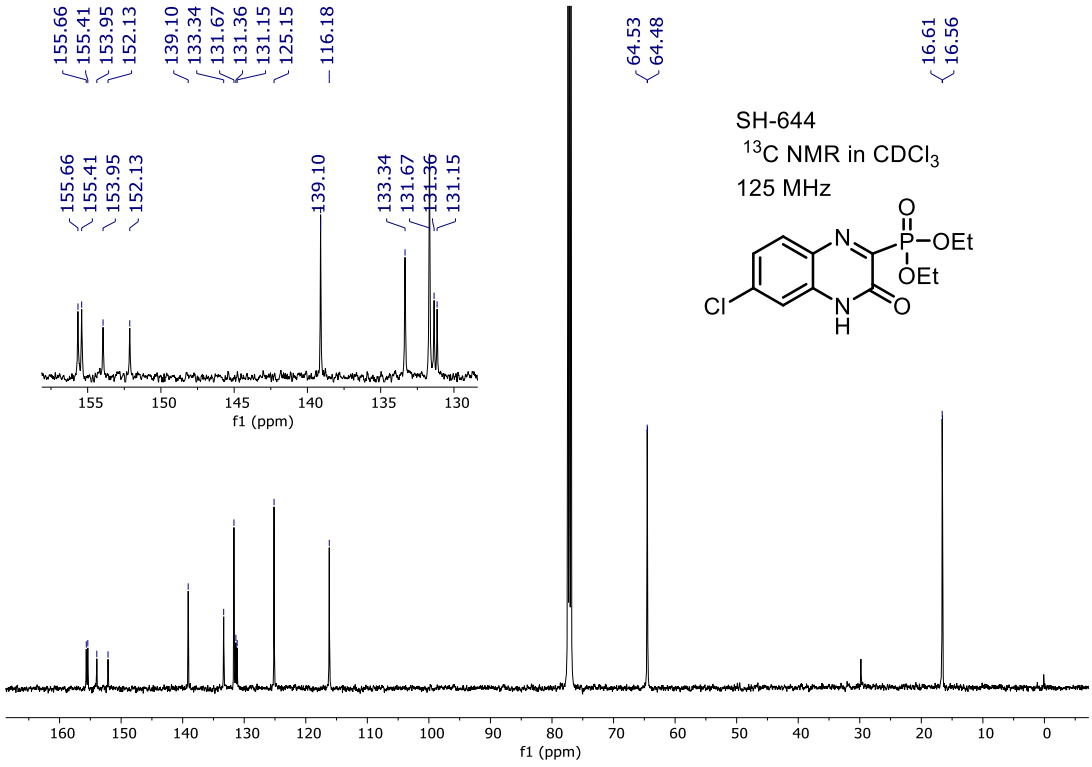
^{13}C NMR **5r**



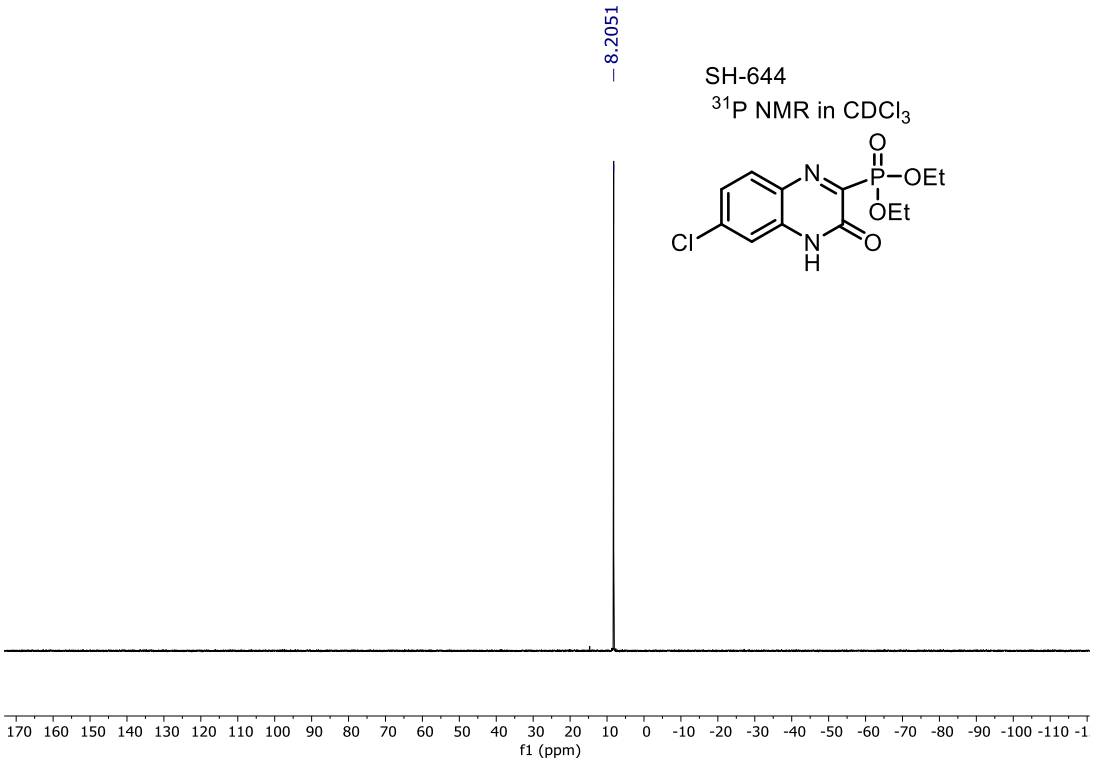
^{31}P NMR **5r**



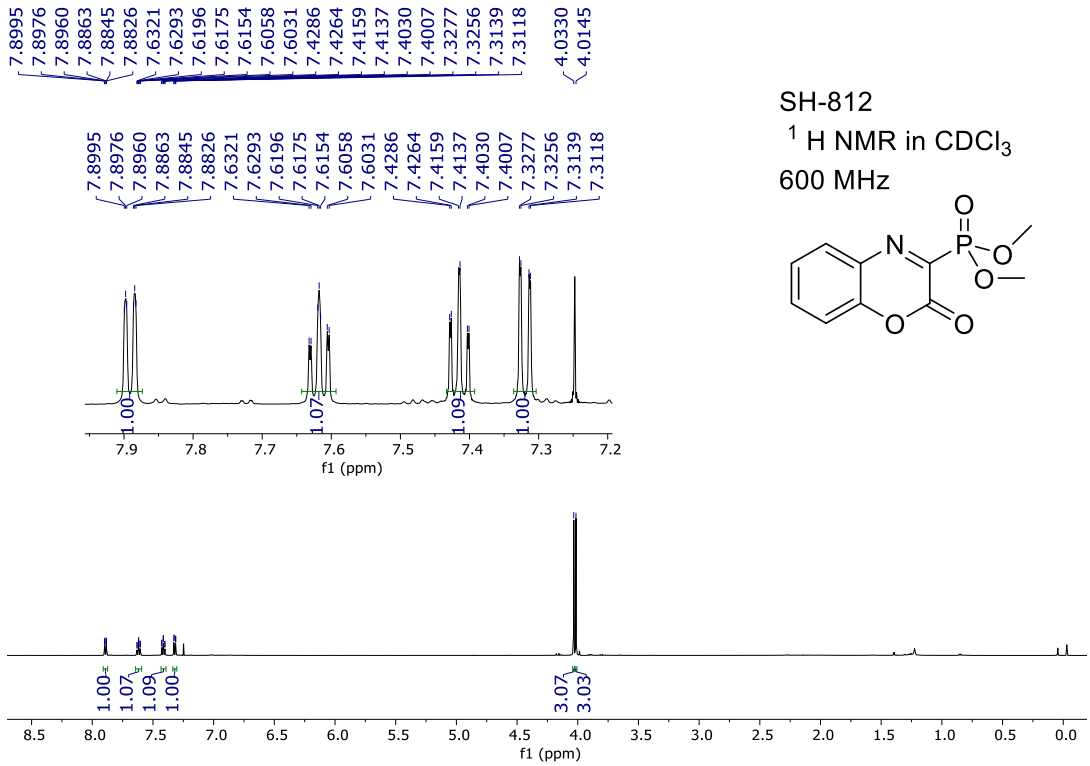
^{1}H NMR **5s**



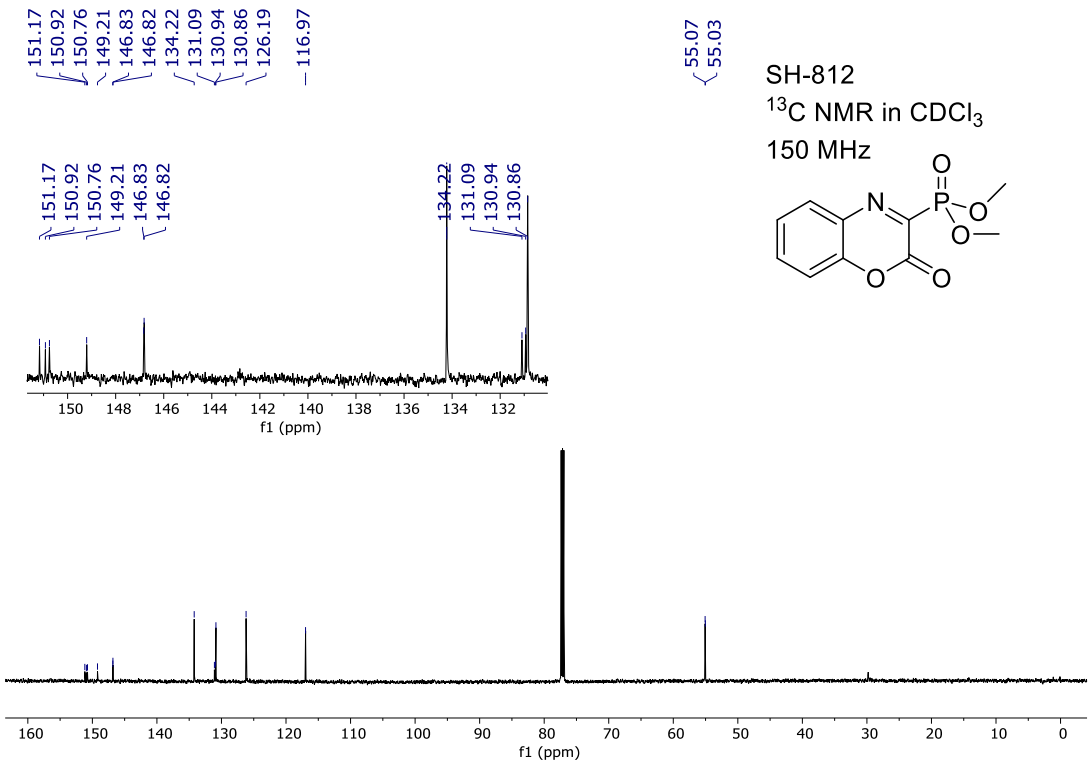
^{13}C NMR **5s**



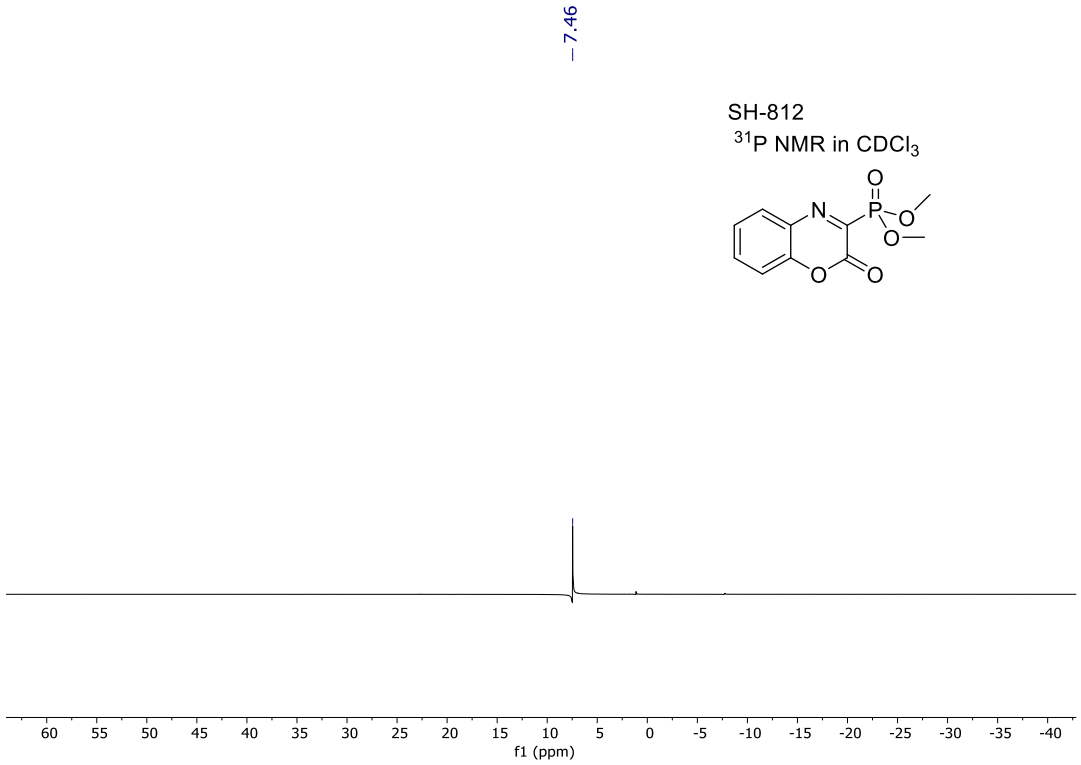
^{31}P NMR **5s**



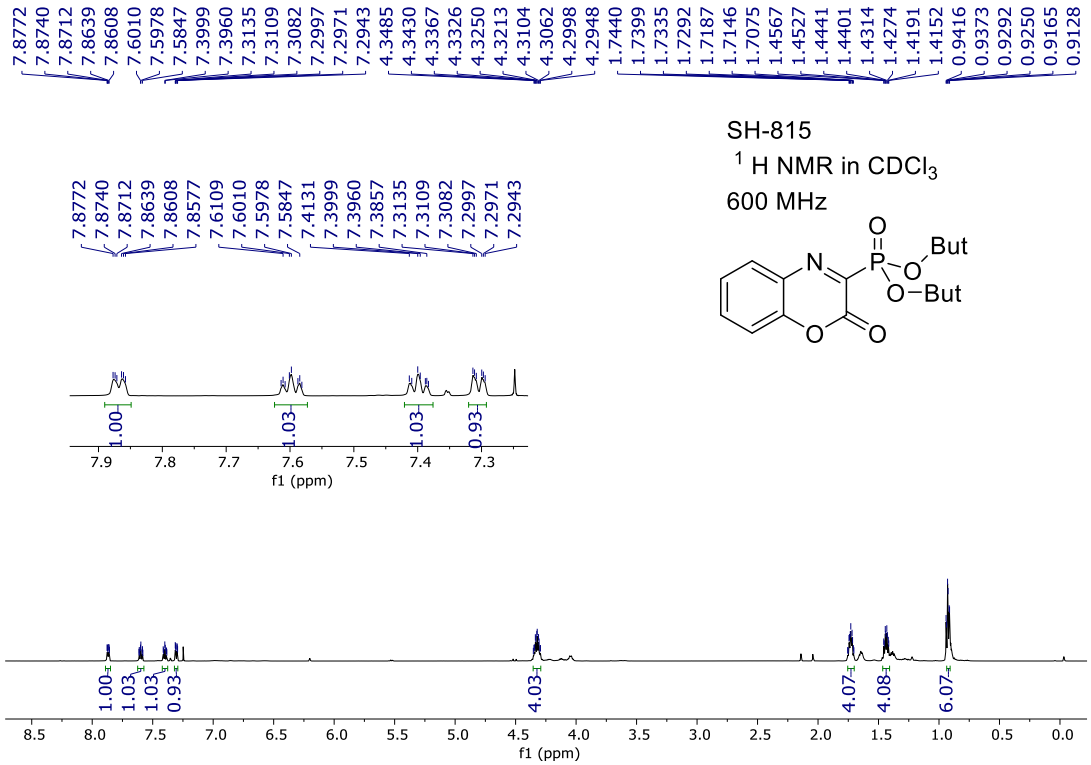
^{1}H NMR **6a**



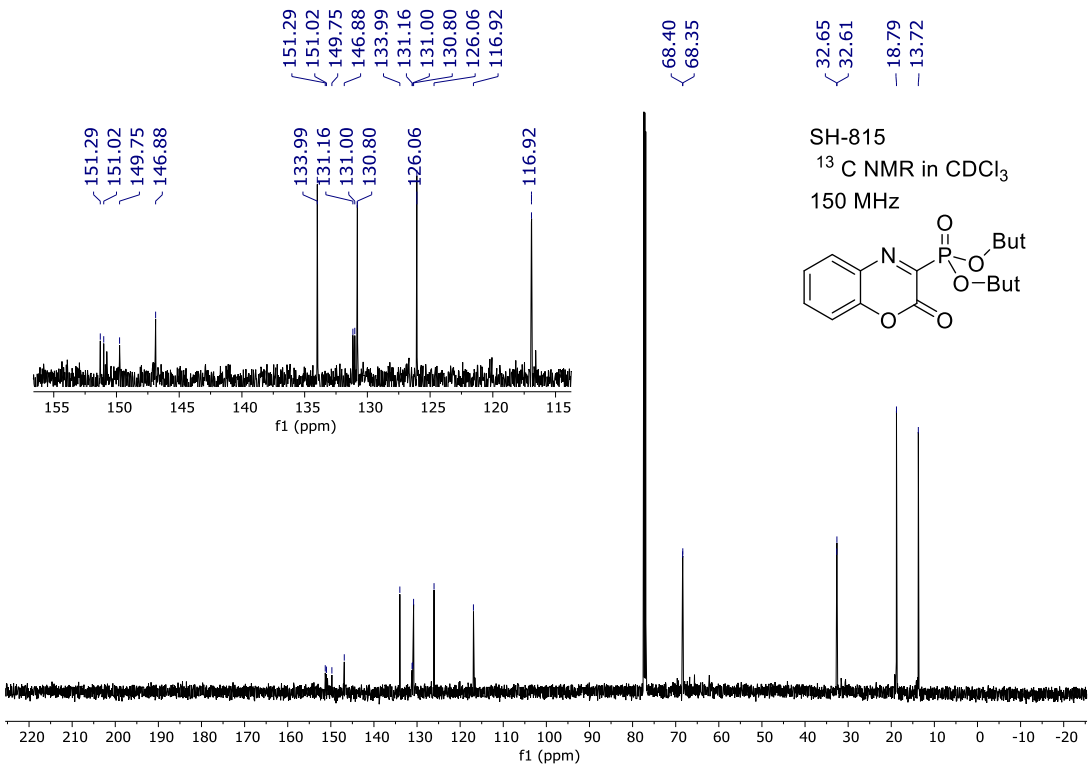
^{13}C NMR **6a**



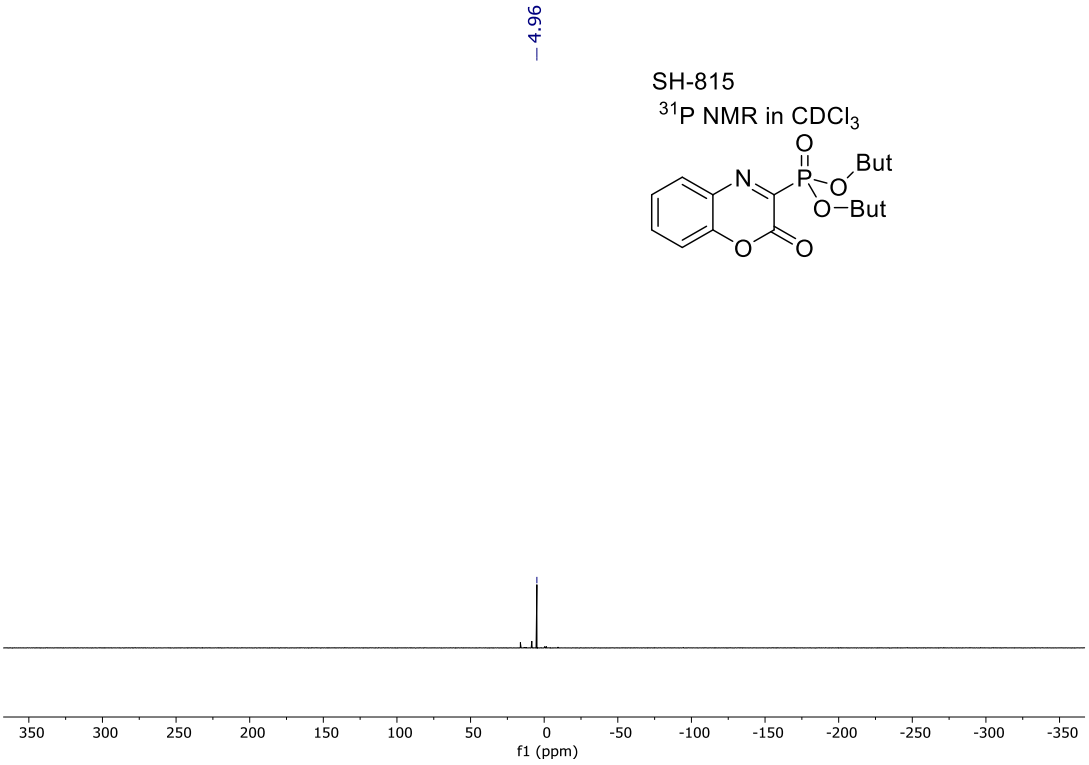
^{31}P NMR **6a**



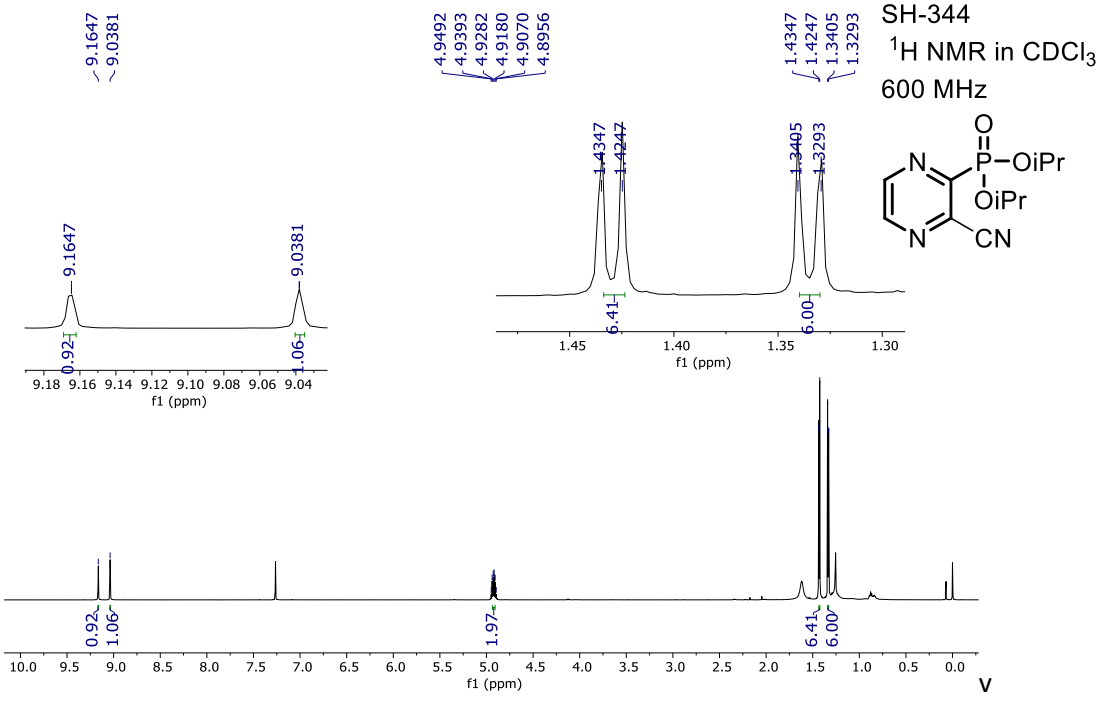
^{1}H NMR **6b**



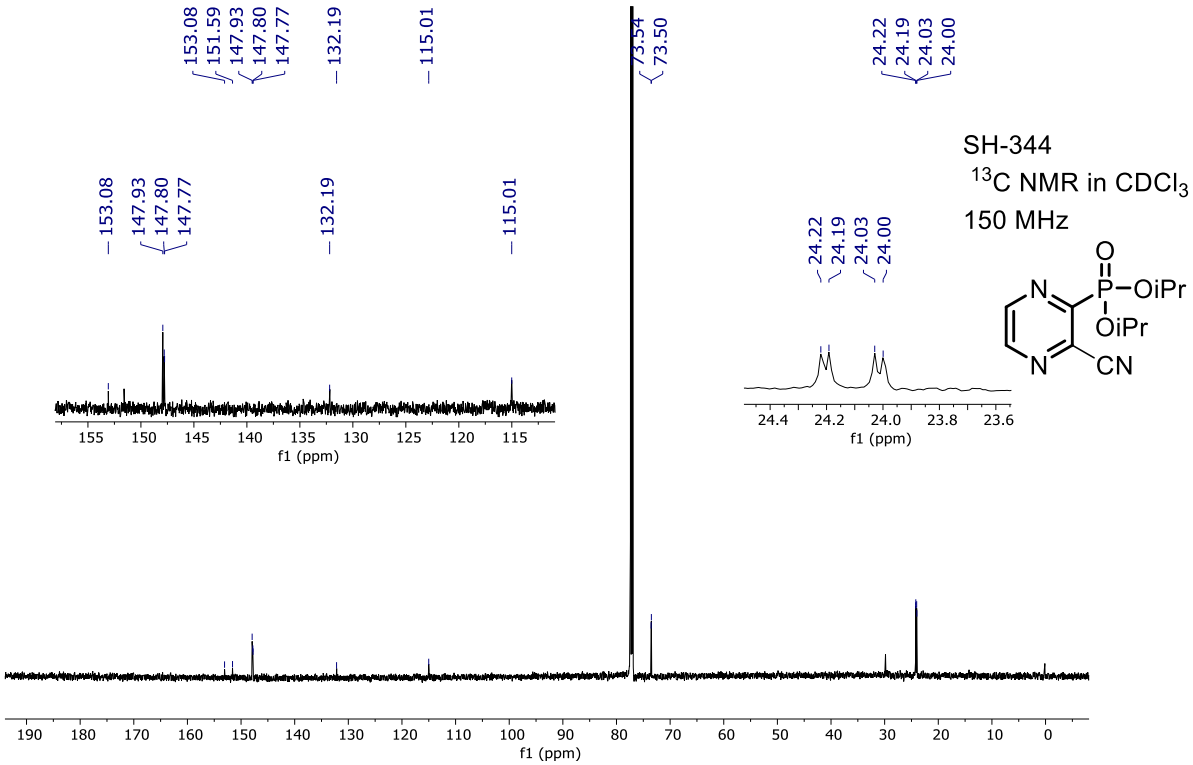
^{13}C NMR **6b**



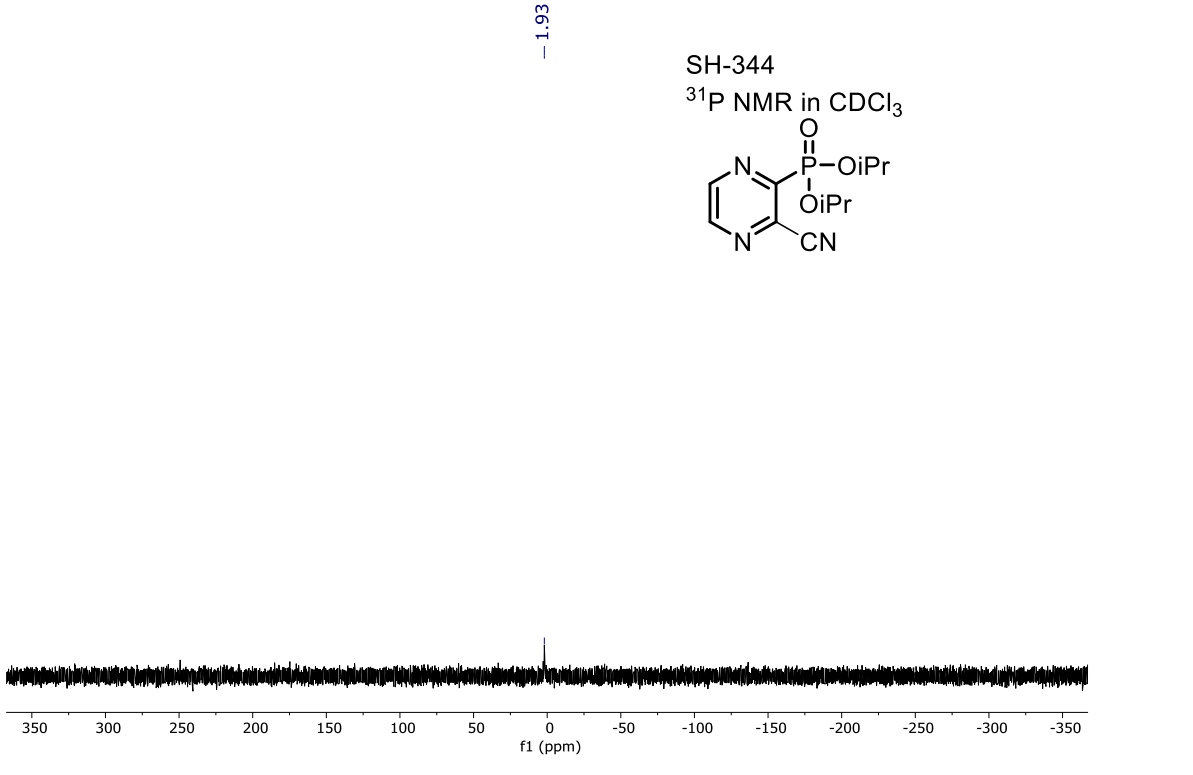
^{31}P NMR **6b**



^{1}H NMR **6c**



^{13}C NMR **6c**



^{31}P NMR **6c**

4. Photograph of the reaction system

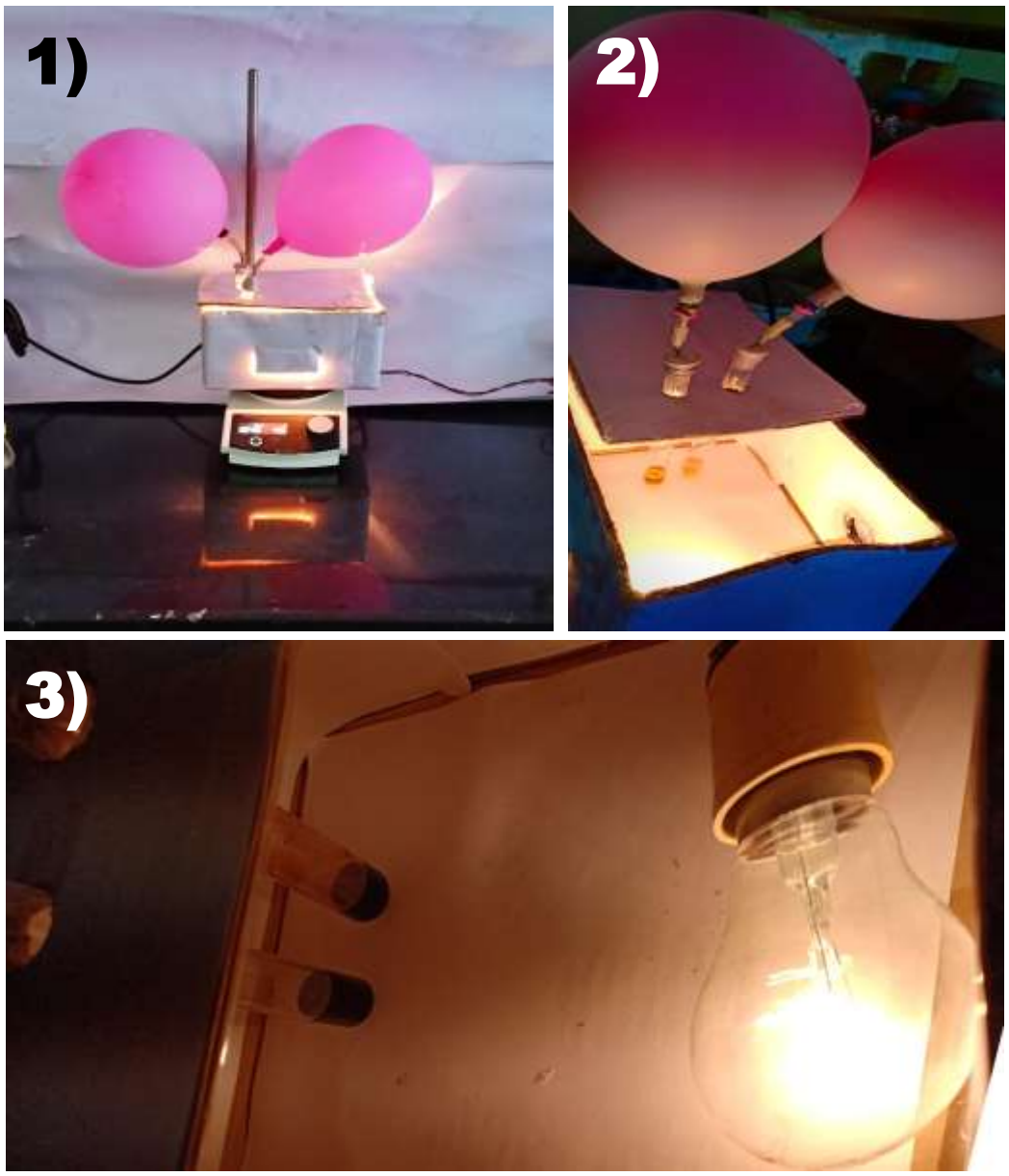
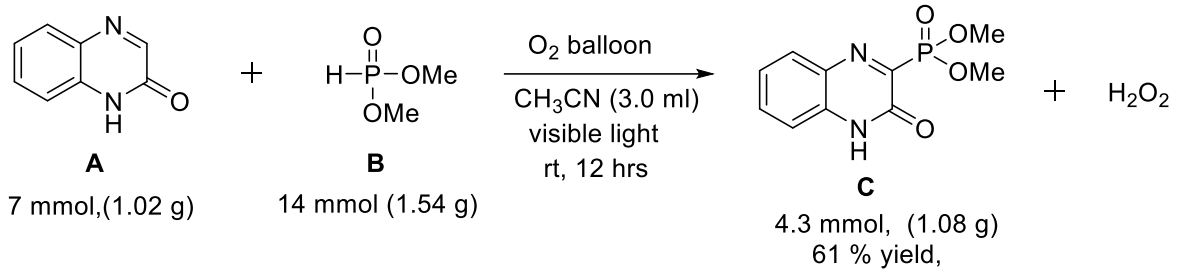


Figure S1. Photographs of reaction system; **1)**. Entire reaction setup with magnetic stirrer, **2)**. Visible light system (wooden box) with O_2 balloons, **3)**. Incandescent bulb and reaction tubes inside the wooden box (The distance between the bulb and reaction tubes is approximately 10-12 cm).

5. Detection of hydrogen peroxide formation by $KMNO_4$ titration method

Estimation of H_2O_2



To an oven dried completely evacuated reaction tube equipped with a magnetic stir bar, added quinoxalin-2(1H)-one **(A)** (1.02g, 7 mmol), dimethyl phosphate **(B)** (1.54 g, 14 mmol), mixture purged with oxygen balloon (O_2) for 10 min. Then the reaction mixture with diluted with CH_3CN (3.0 ml) and stirred in a closed reaction tube with oxygen balloon at room temperature under visible light conditions by using 40 W incandescent lamp for 12 h at room temperature. After completion of reaction the quantification of H_2O_2 was performed by volumetric estimation by titrating against $KMnO_4$ solution with the reaction mixture. In 1-liter beaker 2.5 ml of reaction mixture is diluted with 500 ml water. From that solution 25 ml taken and diluted with 25 ml 10% H_2SO_4. Take it into conical flask and this sample solution is treated with 0.1 N $KMnO_4$.The end point determined when the solution becomes permanent pink in colour.

Product **(c)** yield is 61 %, So theoretically calculated 61 % H_2O_2 should present in reaction mixture is 0.145 g

Theoretically calculated amount of H_2O_2 in reaction mixture = 0.145 g

So, amount of H_2O_2 should present in reaction mixtu**re** = 0.145/ Molecular weight of H_2O_2

= 4.3 mmol

Practically estimated amount of H_2O_2 in reaction mixture

$2KMNO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

Molecular equivalent weight of H_2O_2 = 17 g

So, 1000 ml Molecular equivalent weight is = 17

1ml molecular equivalent weight is = 17/1000 = 0.017 g

In 500 ml water the amount of sample is 2.5 ml

So,25 ml of water the amount of sample is = (2.5×25) / 500 = 0.125

Normality of $KMNO_4$ is 0.1 N

Volume used of $KMNO_4$ is 2.83

Strength of H_2O_2 % =

((N ×V) $KMNO_4$ × Molecular equivalent weight of H_2O_2 / Sample amount) × 100

= (0.1× 2.83 × 0.017 / 0.125) ×100

= 3.84 %

Therefore the total reaction mixture was 3 ml

So, amount of H_2O_2 in reaction mixture = (3.84/100) ×3 = 0.1152 g

= 0.1152/Molecular weight of H_2O_2

= 3.38 mmol