

Supporting Information for

Aryne-induced dearomatic phosphonylation of electron-deficient azaarenes

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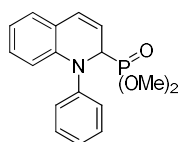
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General procedure for the three-component reaction of arynes with N-heteroaromatics and dialkyl phosphites:

A 10 mL round-bottom flask containing KF (35 mg, 0.6 mmol) and 18-crown-6 (159 mg, 0.6 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled THF (2.0 mL), aryne precursor (110 μ L, 0.45 mmol), quinoline (36 μ L, 0.3 mmol), and dimethyl phosphite (42 μ L, 0.45 mmol) were subsequently added to the system and the reaction mixture was stirred at room temperature for 14 h. The mixture was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford the pure product **4a** in 89% yield (84 mg) as a dark brown oil.

1,2-Dihydro-1-phenyl-2- dimethyl phosphate-quinoline (4a):

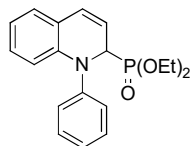


^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.39 (d, J = 10.4 Hz, 3H), 3.60 (d, J = 10.4 Hz, 3H), 5.0 (ddd, J = 7.5, 6.4, 1.1 Hz, 1H), 5.75-5.80 (m, 1H), 6.6 (dd, J = 9.4, 5.3 Hz, 1H), 6.85-6.89 (m, 2H), 7.01-7.09 (m, 2H), 7.13 (dd, J = 7.4, 1.2 Hz, 1H), 7.2-7.3 (m, 4H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 148.4, 141.2, 129.6, 128.7, 127.6, 127.5, 127.4, 127.3, 126.3, 123.2, 122.0, 121.6, 120.8, 120.0, 59.8, 58.3, 53.2; IR (KBr): ν = 2978, 2855, 1663, 1593,

1493, 1462, 1377, 1327, 1246, 1188, 1045, 968, 829, 760, 698 cm⁻¹;

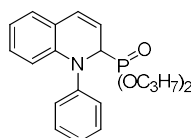
HRMS (ESI) found: 315.1017, calcd for C₁₇H₁₈NO₃P: 315.1024.

1,2-Dihydro-1-phenyl-2-diethyl phosphite-quinoline (4b):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4b** as the pure product. Yield 70% (72 mg); dark brown oil; ¹H NMR (400 MHz, dimethyl sulfoxide-d₆): δ 0.96 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 3.65-3.75 (m, 1H), 3.86-4.01 (m, 3H), 4.93 (ddd, J = 7.5, 6.4, 1.1 Hz, 1H), 5.78 (ddd, J = 9.5, 6.4, 4.8 Hz, 1H), 6.64 (dd, J = 9.5, 5.4 Hz, 1H), 6.82-6.87 (m, 2H), 7.01-7.12 (m, 3H), 7.27-7.36 (m, 4H); ¹³C NMR (100MHz, dimethyl sulfoxide-d₆): δ 148.6, 141.4, 129.5, 128.6, 127.4, 127.3, 127.2, 126.5, 126.4, 123.2, 122.2, 121.4, 121.0, 120.0, 62.6, 62.5, 62.4, 60.3, 58.8; IR (KBr.): ν=3063, 2982, 1667, 1593, 1493, 1450, 1393, 1366, 1254, 1161, 1072, 1022, 964, 756, 698 cm⁻¹; HRMS (ESI) found: 343.1332, calcd for C₁₉H₂₂NO₃P: 343.1337.

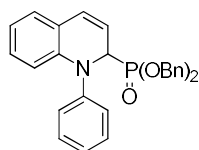
1,2-Dihydro-1-phenyl-2-dinpropyl phosphite-quinoline (4c):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 8/1) to afford **4c** as the pure product. Yield 75% (83 mg); pale yellow oil; ¹H NMR

(400 MHz, dimethyl sulfoxide- d_6): δ 0.80 (d, $J = 6.2$ Hz, 3H), 4.38-4.67 (m, 3H), 4.83 (ddd, $J = 7.5, 6.4, 1.1$ Hz, 1H), 5.75 (ddd, $J = 9.6, 6.3, 4.6$ Hz, 1H), 6.48-6.70 (m, 2H), 6.82-7.11 (m, 6H), 7.20-7.42 (m, 7H), 7.52-7.65 (m, 2H), 7.75-8.05 (m, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 161.6, 148.9, 141.4, 140.7, 138.1, 130.9, 130.5, 129.4, 128.5, 127.4, 126.5, 123.0, 122.6, 122.1, 121.4, 120.3, 115.7, 74.1, 71.1, 60.9, 59.3; IR (KBr): $\nu=2928, 1767, 1643, 1204, 1049, 1026, 1003$ cm^{-1} ; HRMS (ESI) found: 371.1646, calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{P}$: 371.1650.

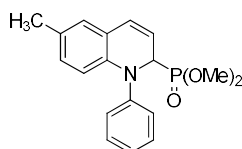
1,2-Dihydro-1-phenyl-2-dibenzyl phosphite-quinoline (4d):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4d** as the pure product. Yield 71% (99 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 5.06 (d, $J = 9.4$ Hz, 1H), 6.51 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 9.6$ Hz, 2H), 7.22-7.27 (m, 2H), 7.29-7.35 (m, 4H), 7.38-7.45 (m, 4H), 7.53-7.65 (m, 7H), 7.78 (d, $J = 7.7$ Hz, 2H), 8.04 (d, $J = 9.6$ Hz, 2H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 161.6, 141.3, 140.7, 138.1, 131.0, 130.5, 129.5, 129.2, 129.1, 129.0, 128.8, 128.4, 122.6, 122.1, 120.3, 115.7, 99.9, 66.9; IR (KBr): $\nu=1771, 1643, 1585, 1566, 1450, 1404, 1331,$

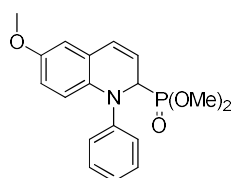
1250, 1215, 1196, 1142, 760, 698 cm^{-1} ; HRMS (ESI) found: 467.1646, calcd for $\text{C}_{29}\text{H}_{26}\text{NO}_3\text{P}$: 467.1650.

6-methyl -2- dimethyl phosphate -1-phenyl-1, 2-dihydroquinoline (4f):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4f** as the pure product. Yield 72% (71 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 2.34 (s, 3H), 3.32 (s, 6H), 6.41 (d, $J = 8.6$ Hz, 1H), 6.65 (d, $J = 9.5$ Hz, 1H), 7.23 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.28-7.32 (m, 2H), 7.51-7.65 (m, 5H), 7.97 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 161.4, 140.4, 139.3, 138.2, 132.1, 131.7, 130.5, 129.4, 129.1, 128.6, 122.1, 120.2, 115.7, 20.5; IR (KBr): $\nu=3838, 2924, 2496, 1971, 1724, 1659, 1566, 1493, 1381, 1331, 1242, 760$ cm^{-1} ; HRMS (ESI) found: 329.1173, calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{P}$: 329.1181.

6-methoxy-2-dimethyl phosphate -1-phenyl-1, 2-dihydroquinoline (4g):

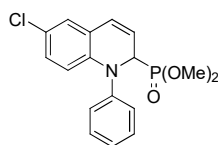


Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4g** as the pure product. Yield 67% (69 mg); pale yellow oil; ^1H NMR

(400 MHz, dimethyl sulfoxide- d_6): δ 3.32 (s, 6H), 3.79 (m, 3H), 6.44 (d, $J = 9.2$ Hz, 1H), 6.68 (d, $J = 9.2$ Hz, 1H), 7.06 (dd, $J = 9.2$, 2.9 Hz, 1H), 7.28-7.31 (m, 2H), 7.33-7.35 (m, 1H), 7.52-7.64 (m, 4H), 7.98 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 161.1, 154.8, 140.2, 138.3, 135.8, 131.9, 131.8, 130.5, 129.5, 129.3, 129.2, 122.6, 121.0, 119.5, 117.0, 110.9, 56.1, 53.0; IR (KBr): $\nu = 2951, 2855, 1778, 1728, 1435, 1381, 1342, 1292, 1207, 760$ cm^{-1} ; HRMS (ESI) found: 345.1039, calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{P}$: 345.1052.

6-chloro-2-dimethyl phosphate -1-phenyl-1,2-dihydroquinoline

(4h):



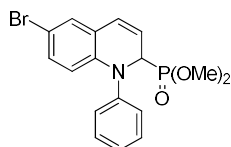
Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4h** as the pure product. Yield 72% (75 mg); dark brown oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.45 (d, $J = 10.6$ Hz, 3H), 3.63 (d, $J = 10.6$ Hz, 3H), 5.08 (dd, $J = 16.3, 6.1$ Hz, 1H), 5.80-5.87 (m, 1H), 6.66 (dd, $J = 9.2, 5.8$ Hz, 1H), 6.82-6.87 (m, 1H), 7.05-7.11 (m, 2H), 7.23 (s, 1H), 7.31-7.35 (m, 4H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 148.0, 140.2, 129.7, 128.3, 127.9, 127.8, 126.8, 126.5, 126.4, 124.8, 123.8, 122.4, 122.2, 121.4, 59.8, 58.2, 53.4; IR

(KBr): $\nu=1667, 1481, 1369, 1258, 1204, 1030, 826, 760 \text{ cm}^{-1}$;

HRMS (ESI) found: 349.0625, calcd for $\text{C}_{17}\text{H}_{17}\text{ClNO}_3\text{P}$: 349.0635.

6-bromo-2-dimethyl phosphate -1-phenyl-1,2-dihydroquinoline

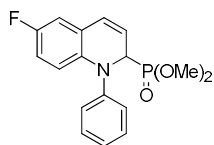
(4i):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4i** as the pure product. Yield 78% (92 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.44 (d, $J = 10.6$ Hz, 3H), 3.62 (d, $J = 10.6$ Hz, 3H), 5.08 (ddd, $J = 7.5, 6.4, 1.1$ Hz, 1H), 5.82 (ddd, $J = 9.5, 6.4, 4.8$ Hz, 1H), 6.66 (dd, $J = 9.6, 5.4$ Hz, 1H), 6.76-6.80 (m, 1H), 7.05-7.11 (m, 1H), 7.17-7.21 (m, 1H), 7.31-7.36 (m, 5H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 147.9, 147.8, 140.7, 131.1, 129.8, 129.6, 128.3, 126.4, 126.3, 123.8, 122.5, 122.1, 121.7, 112.5, 59.8, 58.2, 53.3; IR (KBr): $\nu=3044, 2982, 2824, 1663, 1589, 1497, 1416, 1377, 1269, 1215, 1030, 826, 760 \text{ cm}^{-1}$; HRMS (ESI) found: 393.0131, calcd for $\text{C}_{17}\text{H}_{17}\text{BrNO}_3\text{P}$: 393.0129.

6-fluoro-2-dimethyl phosphate -1-phenyl-1,2-dihydroquinoline

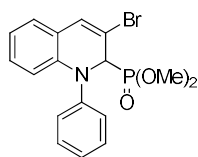
(4j):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4j**

as the pure product. Yield 75% (75 mg); dark brown oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.44 (d, $J = 10.6$ Hz, 3H), 3.62 (d, $J = 10.6$ Hz, 3H), 5.07 (ddd, $J = 7.5, 6.5, 1.1$ Hz, 1H), 5.82-5.89 (m, 1H), 6.66 (dd, $J = 9.6, 5.2$ Hz, 1H), 6.88-6.93 (m, 2H), 7.01-7.07 (m, 2H), 7.24-7.33 (m, 4H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 158.5, 156.2, 148.9, 137.3, 129.7, 128.1, 126.7, 123.1, 122.7, 122.2, 121.5, 115.3, 113.6, 113.3, 59.8, 58.2, 53.3; IR (KBr): $\nu=3059, 2955, 2924, 2855, 1663, 1593, 1543, 1442, 1369, 1250, 1146, 1030, 872, 818, 764, 698, 602$ cm^{-1} ; HRMS (ESI) found: 333.0917, calcd for $\text{C}_{17}\text{H}_{17}\text{FNO}_3\text{P}$: 333.0930.

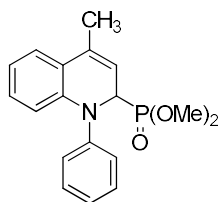
3-Bromo-2- dimethyl phosphate -1-phenyl-1,2-dihydroquinoline (4k):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4k** as the pure product. Yield 60% (71 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.41 (d, $J = 10.6$ Hz, 3H), 3.66 (d, $J = 10.6$ Hz, 3H), 5.08 (d, $J = 16.8$ Hz, 1H), 6.94-6.98 (m, 2H), 7.05-7.10 (m, 1H), 7.13-7.27 (m, 5H), 7.30-7.35 (m, 2H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 147.9, 139.5, 130.3, 130.2, 129.8, 129.2, 127.3, 126.9, 123.7, 122.5, 121.8, 120.8, 108.5, 65.8, 64.2, 53.7, 53.4; IR (KBr): $\nu=3059, 2955, 2855, 1593, 1493, 1450, 1362, 1285, 1184, 1119, 1072, 1026, 837, 802, 698$ cm^{-1} ; HRMS (ESI) found: 393.0134, calcd for

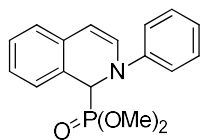
C₁₇H₁₇BrNO₃P: 393.0129.

4-methyl-2- dimethyl phosphate -1-phenyl-1,2-dihydroquinoline (4l):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4l** as the pure product. Yield 55% (54 mg); pale blue oil; ¹H NMR (400 MHz, dimethyl sulfoxide-d₆): δ 2.05 (d, *J* = 5.3 Hz, 3H), 3.36 (d, *J* = 10.6 Hz, 3H), 3.58 (d, *J* = 10.6 Hz, 3H), 4.97 (ddd, *J* = 7.6, 6.6, 1.1 Hz, 1H), 5.59-5.63 (m, 1H), 6.89-6.95 (m, 2H), 6.99-7.04 (m, 1H), 7.07-7.13 (m, 1H), 7.27-7.32 (m, 5H); ¹³C NMR (100MHz, dimethyl sulfoxide-d₆): δ 148.4, 141.1, 132.6, 132.4, 129.6, 128.6, 127.8, 127.7, 124.5, 122.9, 121.6, 121.5, 120.2, 117.5, 99.9, 59.5, 57.9, 53.1; IR (KBr): ν=2859, 2338, 1663, 1593, 1489, 1447, 1366, 1254, 1026, 818, 760 cm⁻¹; HRMS (ESI) found: 329.1173, calcd for C₁₈H₂₀NO₃P: 329.1181.

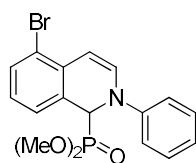
1,2-Dihydro-1-phenyl-2-dimethyl phosphate-isoquinoline (4m):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4m** as the pure product. Yield 83% (78 mg); pale yellow oil; ¹H NMR (400 MHz, dimethyl sulfoxide-d₆): δ 3.58 (d, *J* = 10.4 Hz, 3H), 3.66

(d, $J = 10.4$ Hz, 3H), 5.55 (dd, $J = 12.9, 1.2$ Hz, 1H), 5.99 (d, $J = 7.4$ Hz, 1H), 6.64 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.03 (t, $J = 7.3$ Hz, 1H), 7.08-7.11 (m, 1H), 7.14-7.21 (m, 4H), 7.22-7.28 (m, 1H), 7.33-7.38 (m, 2H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 145.1, 132.8, 129.9, 129.6, 129.5, 128.6, 127.9, 127.5, 126.4, 124.9, 123.7, 121.5, 116.9, 106.9, 58.7, 57.2, 53.3; IR (KBr): $\nu = 2955, 2924, 2855, 1659, 1597, 1493, 1462, 1231, 1038, 760, 690, 548, 471$ cm^{-1} ; HRMS (ESI) found: 315.1019, calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{P}$: 315.1024.

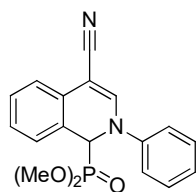
5-bromo-2-dimethyl phosphate-1-phenyl-1, 2-dihydroisoquinoline (4n):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4n** as the pure product. Yield 77% (91 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.50 (d, $J = 10.6$ Hz, 3H), 3.55 (d, $J = 10.6$ Hz, 3H), 5.99 (d, $J = 13.3$ Hz, 1H), 6.04 (d, $J = 7.5$ Hz, 1H), 6.96-7.09 (m, 3H), 7.20-7.26 (m, 3H), 7.32-7.38 (m, 2H), 7.49 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 172.5, 170.8, 144.5, 132.5, 132.4, 132.2, 129.5, 127.6, 127.5, 126.8, 122.2, 118.4, 117.4, 104.6, 58.8, 57.3, 53.4; IR (KBr): $\nu = 3888, 3707, 3595, 2943, 2851, 2284, 1593, 1443, 1423, 1265, 1234, 1037, 760,$

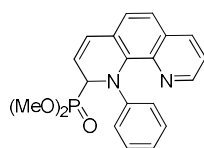
694 cm^{-1} ; HRMS (ESI) found: 393.0131, calcd for $\text{C}_{17}\text{H}_{17}\text{BrNO}_3\text{P}$: 393.0129.

3-acetonitril-2-dimethyl phosphate-1-phenyl-1, 2-dihydroisoquinoline (4o):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 3/1) to afford **4o** as the pure product. Yield 50% (51 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ =3.44 (d, J = 10.6 Hz, 3H), 3.51 (d, J = 10.6 Hz, 3H), 6.18 (d, J = 12.2 Hz, 1H), 7.17-7.23 (m, 2H), 7.27-7.32 (m, 2H), 7.36-7.51 (m, 5H), 7.94 (d, J = 1 Hz, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 143.8, 143.2, 129.7, 129.5, 128.9, 128.6, 128.5, 127.8, 125.0, 123.1, 121.1, 120.1, 118.7, 87.7, 87.6, 58.9, 57.4, 53.6; IR (KBr): ν =3838, 3738, 3657, 2928, 2859, 2307, 2203, 1879, 1678, 1489, 1450, 1350, 1242, 1022, 748 cm^{-1} ; HRMS (ESI) found: 340.0971, calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3\text{P}$: 340.0977.

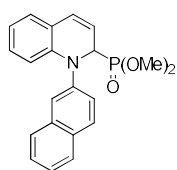
1,2-Dihydro-1-phenyl-2-dimethyl phosphate-1, 10-Phenanthroline hydrate (4p):



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 2/1) to afford **4p**

as the pure product. Yield 70% (77 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.32 (s, 1H), 3.46-3.49 (m, 2H), 3.62 (d, $J = 10.2$ Hz, 3H), 5.19 (dd, $J = 21.4, 5.9$ Hz, 1H), 5.88-5.95 (m, 1H), 6.79-6.93 (m, 4H), 7.09-7.16 (m, 2H), 7.34 (dd, $J = 8.2, 4.1$ Hz, 1H), 7.44-7.48 (m, 1H), 7.61-7.65 (m, 1H), 8.21-8.25 (m, 1H), 8.49 (dd, $J = 4.1, 1.6$ Hz, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 151.7, 149.2, 142.2, 136.7, 136.4, 129.2, 128.9, 128.4, 127.8, 126.3, 123.3, 122.4, 122.0, 121.4, 120.9, 70.3, 61.9, 60.3, 54.2, 53.5; IR (KBr): $\nu=3946, 3761, 3561, 3051, 2951, 2870, 2338, 2164, 1979, 1902, 1593, 1493, 1447, 1373, 1250, 1111, 1068, 961, 837, 806, 756, 660, 579$ cm^{-1} ; HRMS (ESI) found: 366.1127, calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3\text{P}$: 366.1133.

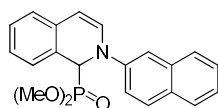
1-(2-naphthylphenyl)-2-dimethyl phosphate-1, 2-dihydroquinoline (4q):



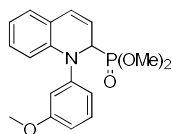
Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4q** as the pure product. Yield 82% (90 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.42 (d, $J = 10.6$ Hz, 3H), 3.63 (d, $J = 10.6$ Hz, 3H), 5.21 (ddd, $J = 7.5, 6.5, 1$ Hz, 1H), 5.83 (ddd, $J = 9.4, 6.3, 4.8$ Hz, 1H), 6.67-6.73 (m, 1H), 6.89-6.96 (m, 2H), 7.07-7.13 (m, 1H), 7.17 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.36-7.41 (m, 1H),

7.43-7.49 (m, 2H), 7.73-7.80 (m, 2H), 7.80-7.85 (m, 2H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 145.9, 141.0, 134.3, 130.0, 129.0, 128.7, 127.9, 127.6, 127.5, 126.9, 126.5, 126.4, 125.0, 122.4, 121.9, 121.1, 120.0, 118.1, 59.9, 58.3, 53.3; IR (KBr): ν =2920, 2789, 2368, 1709, 1674, 1574, 1254, 1137, 1115, 806, 796, 401 cm^{-1} ; HRMS (ESI) found: 365.1176, calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{P}$: 365.1181.

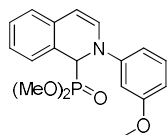
**1-(2-naphthylphenyl)-2-dimethyl phosphate-1,
2-dihydroisoquinoline (4r):**



Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4r** as the pure product. Yield 88% (96 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.51 (d, J = 10.6 Hz, 3H), 3.54 (d, J = 10.6 Hz, 3H), 6.01 (d, J = 7.4 Hz, 1H), 6.07 (d, J = 13.2 Hz, 1H), 6.96 (dd, J = 7.4, 1.1 Hz, 1H), 7.09-7.19 (m, 2H), 7.21-7.28 (m, 2H), 7.31-7.36 (m, 1H), 7.43-7.49 (m, 1H), 7.52-7.57 (m, 2H), 7.82 (t, J = 8.7 Hz, 2H), 7.87-7.91 (m, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 142.8, 134.2, 132.8, 130.0, 129.2, 129.0, 128.7, 128.0, 127.8, 127.3, 127.0, 126.5, 125.1, 124.3, 123.8, 118.3, 112.2, 107.5, 58.7, 57.2, 53.3; IR (KBr): ν =3900, 2947, 2276, 1663, 1470, 1350, 1281, 1254, 1107, 1030, 961, 829 cm^{-1} ; HRMS (ESI) found: 365.1176, calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{P}$: 365.1181.

1-(3-Methoxyphenyl)-2-dimethyl**phosphate-1,****2-dihydroquinoline (4s):**

Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4s** as the pure product. Yield 86% (89 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.39 (d, $J = 10.6$ Hz, 3H), 3.59 (d, $J = 10.6$ Hz, 3H), 3.71 (s, 3H), 5.07 (dd, $J = 16.6, 6.4$ Hz, 1H), 5.78 (ddd, $J = 9.5, 6.3, 4.9$ Hz, 1H), 6.59-6.67 (m, 2H), 6.83-6.95 (m, 4H), 7.05-7.21 (m, 3H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): $\delta = 160.5, 149.7, 141.0, 130.2, 128.6, 127.5, 127.4, 126.4, 121.8, 121.1, 120.4, 114.1, 108.4, 107.9, 59.7, 58.2, 55.5, 53.3$; IR (KBr): $\nu = 3943, 2959, 2924, 2859, 1778, 1724, 1663, 1593, 1489, 1450, 1288, 1258, 1161, 1103, 1038, 694$ cm^{-1} ; HRMS (ESI) found: 345.1130, calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{P}$: 345.1130.

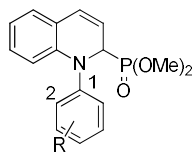
1-(3-Methoxyphenyl)-2-dimethyl**phosphate-1,****2-dihydroisoquinoline (4t):**

Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4t** as the pure product. Yield 90% (93 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.48 (d, $J = 10.6$ Hz, 3H), 3.53

(d, $J = 10.6$ Hz, 3H), 3.78 (s, 3H), 5.86 (d, $J = 13.1$ Hz, 1H), 5.93 (d, $J = 7.4$ Hz, 1H), 6.54-6.58 (m, 1H), 6.72-6.76 (m, 2H), 6.79 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.05-7.09 (m, 1H), 7.11-7.16 (m, 1H), 7.19-7.24 (m, 3H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 160.5, 146.4, 132.8, 130.2, 129.9, 128.6, 127.9, 126.4, 125.1, 123.7, 109.3, 107.1, 103.0, 58.8, 57.3, 55.5, 53.3, 53.2; IR (KBr): $\nu=2847, 1856, 1663, 1601, 1489, 1454, 1269, 1246, 1207, 1177, 1045, 999, 837, 787, 694$ cm^{-1} ; HRMS (ESI) found: 345.1124, calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{P}$: 345.1130.

1-(2-methylphenyl)-2-dimethyl phosphate-1, 2-dihydroquinoline

(4u):

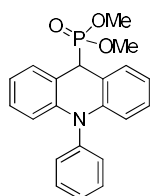


R= 2CH₃, 3CH₃

Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 5/1) to afford **4u** as the pure product. Yield 80% (79 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 2.24 (s, 3H), 3.39 (d, $J = 10.6$ Hz, 3H), 3.59 (d, $J = 10.6$ Hz, 3H), 5.01 (ddd, $J = 7.2, 6.5, 1.0$ Hz, 1H), 5.76 (ddd, $J = 9.5, 6.4, 4.9$ Hz, 1H), 6.62-6.67 (m, 2H), 6.82-6.88 (m, 3H), 7.04-7.14 (m, 4H), 7.16-7.21 (m, 1H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): $\delta = 166.3, 153.3, 146.1, 143.6, 134.2, 133.4, 132.3, 132.1, 131.0, 128.8, 127.4, 126.2, 125.5, 124.9, 124.1, 64.7, 63.1, 57.9$; IR (KBr): $\nu=2920, 2851, 2326, 1724, 1663,$

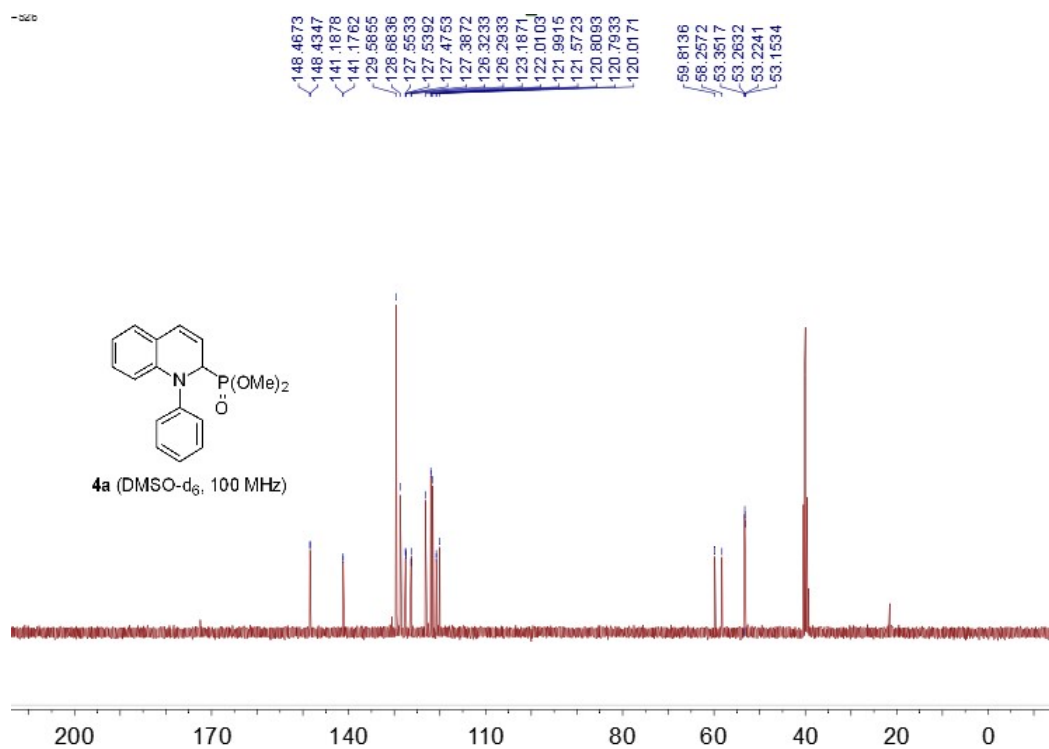
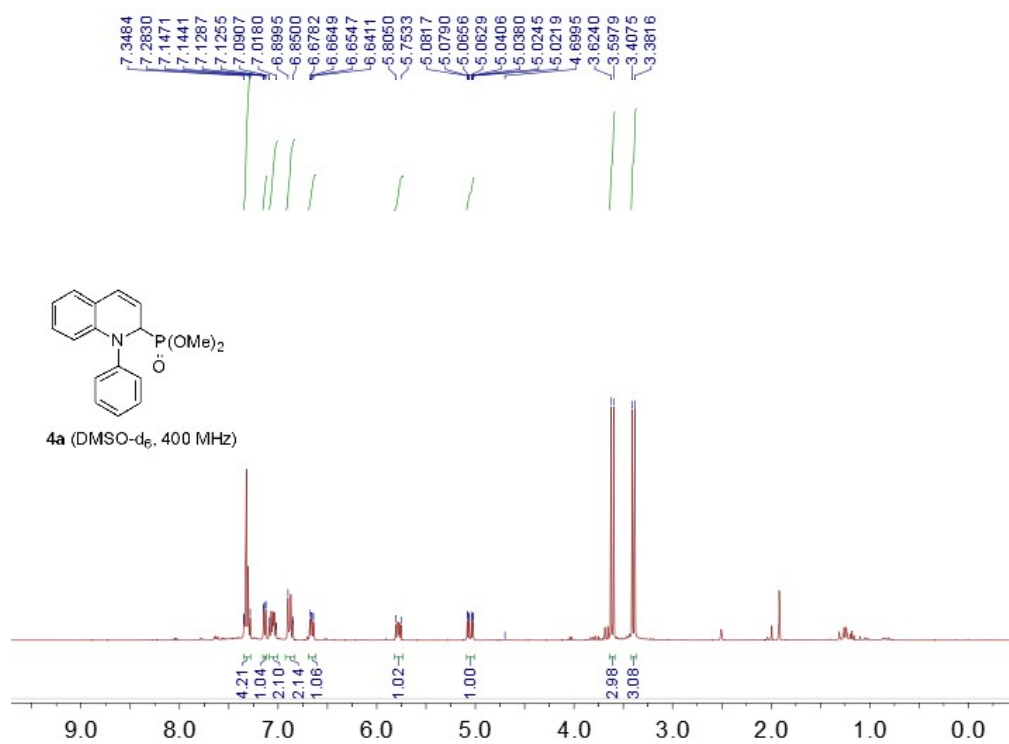
1593, 1489, 1450, 1366, 1258, 1177, 1057, 964, 945, 833, 752, 698 cm^{-1} ; HRMS (ESI) found: 329.1175, calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{P}$: 329.1181.

1-phenyl-6-dimethyl phosphate-Acridine (4v):

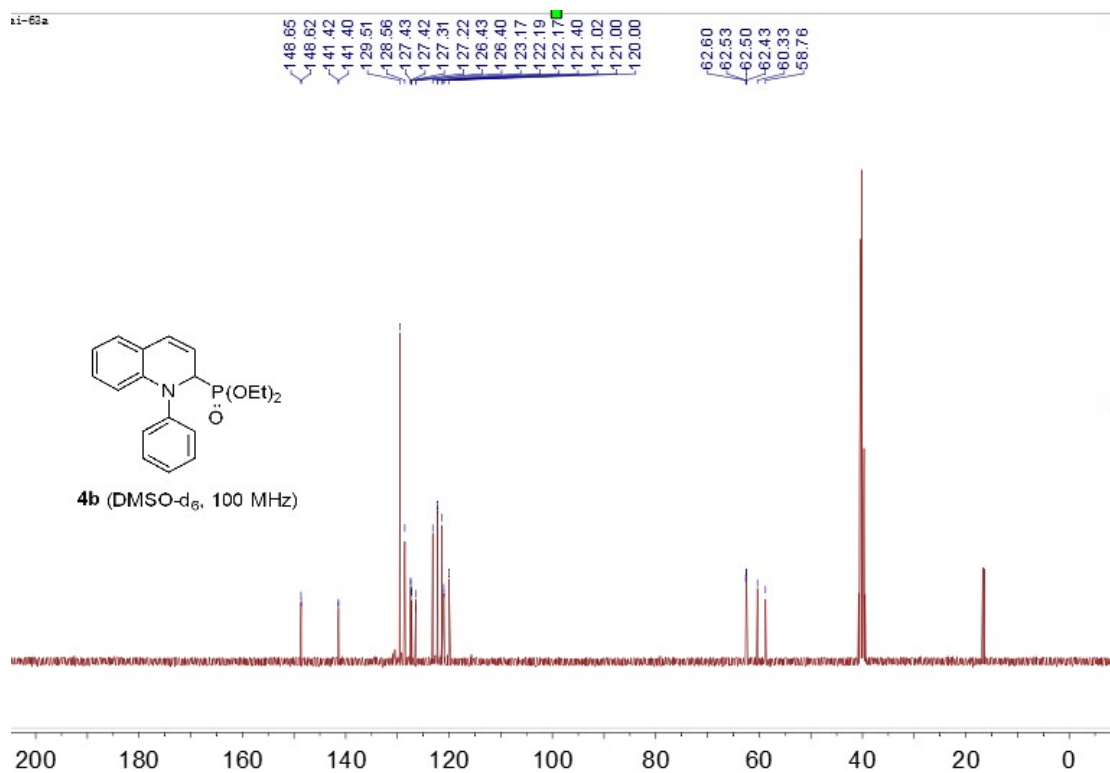
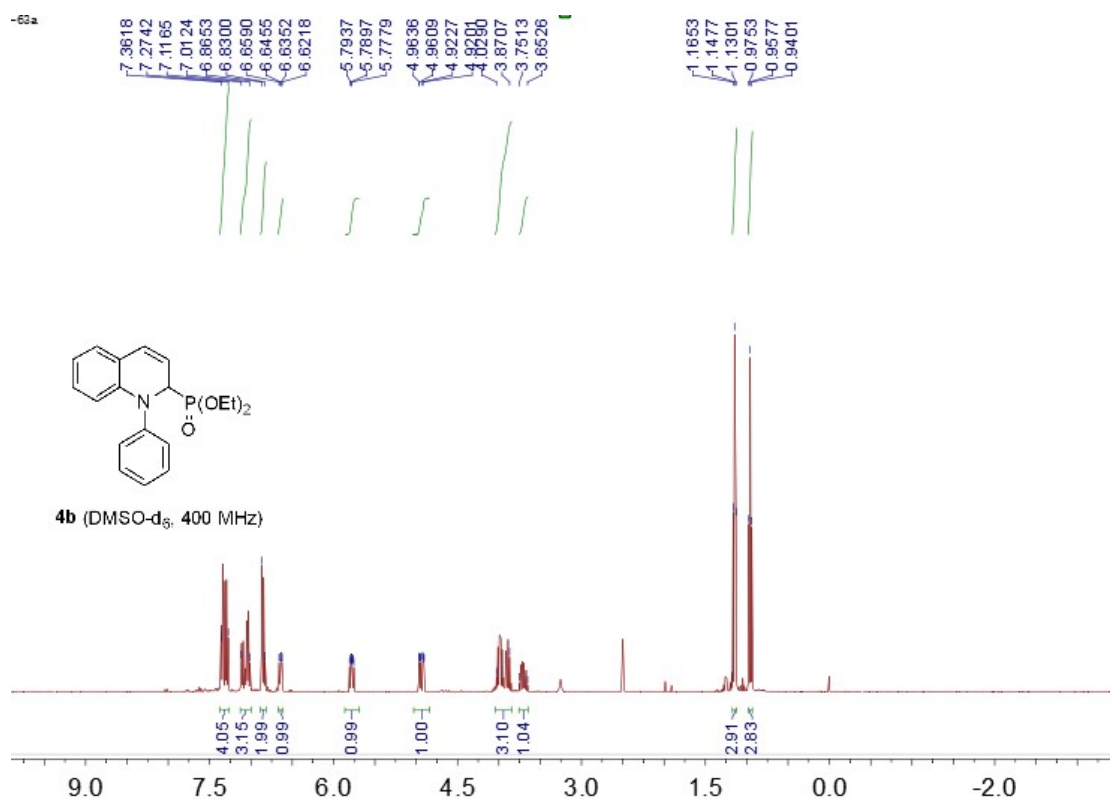


Prepared according to general procedure and purified by column chromatography on silica gel (PE/EA = 1/1) to afford **4v** as the pure product. Yield 55% (60 mg); pale yellow oil; ^1H NMR (400 MHz, dimethyl sulfoxide- d_6): δ 3.50 (d, $J = 10.4$ Hz, 6H), 4.92 (d, $J = 25.2$ Hz, 1H), 6.20 (d, $J = 8.2$ Hz, 2H), 6.87-6.93 (m, 2H), 7.00-7.06 (m, 2H), 7.25 (d, $J = 7.6$ Hz, 2H), 7.36-7.40 (m, 2H), 7.54-7.60 (m, 1H), 7.66-7.72 (m, 2H); ^{13}C NMR (100MHz, dimethyl sulfoxide- d_6): δ 142.7, 142.6, 140.6, 131.4, 131.2, 130.5, 130.4, 129.0, 128.2, 128.1, 121.1, 121.0, 117.0, 116.9, 114.3, 114.2, 53.6, 53.5, 42.8, 41.5.

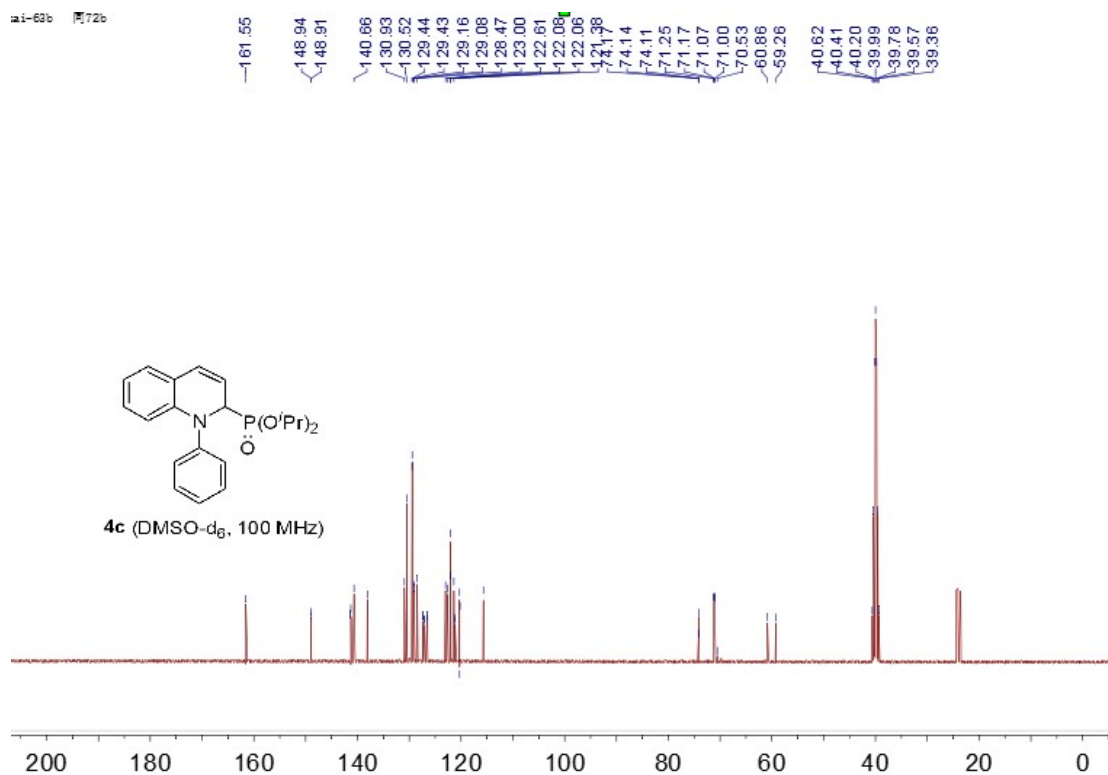
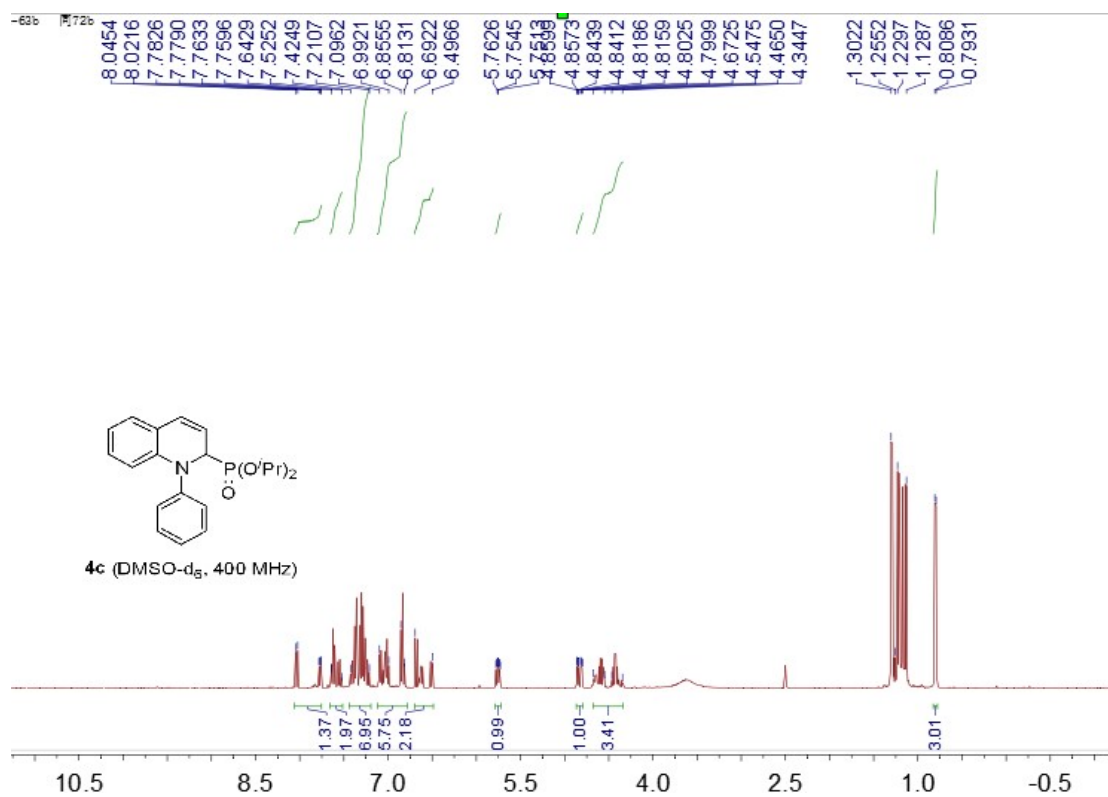
Compound 4a



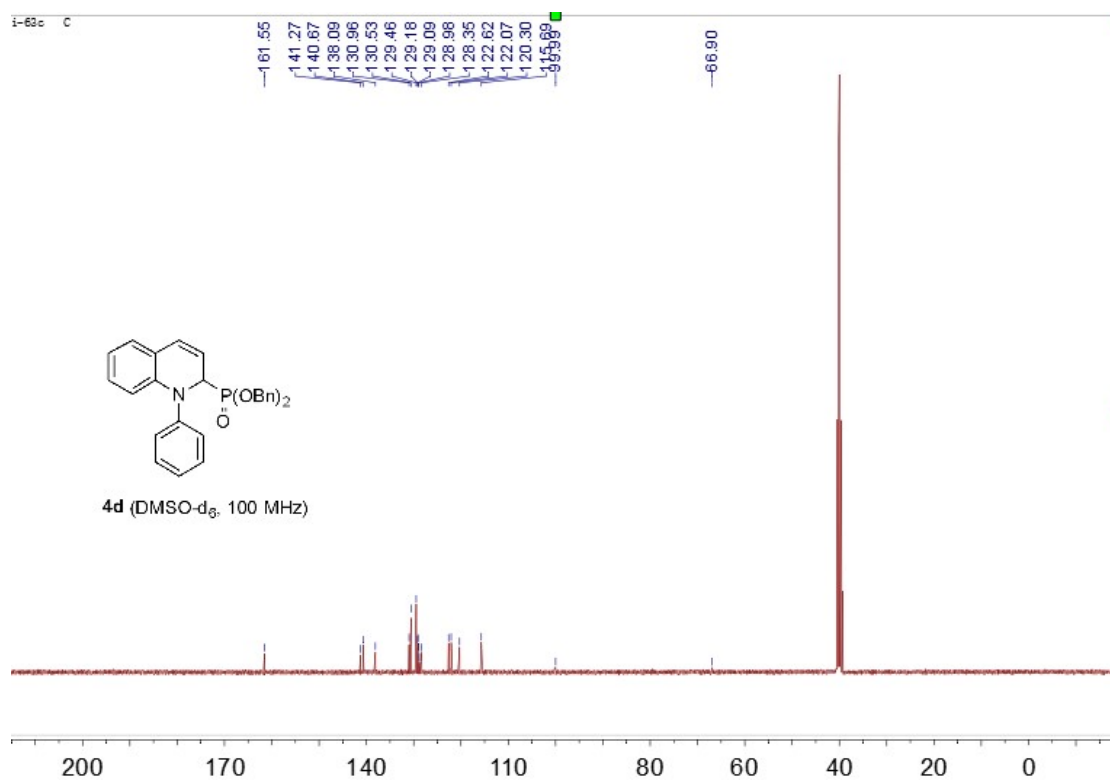
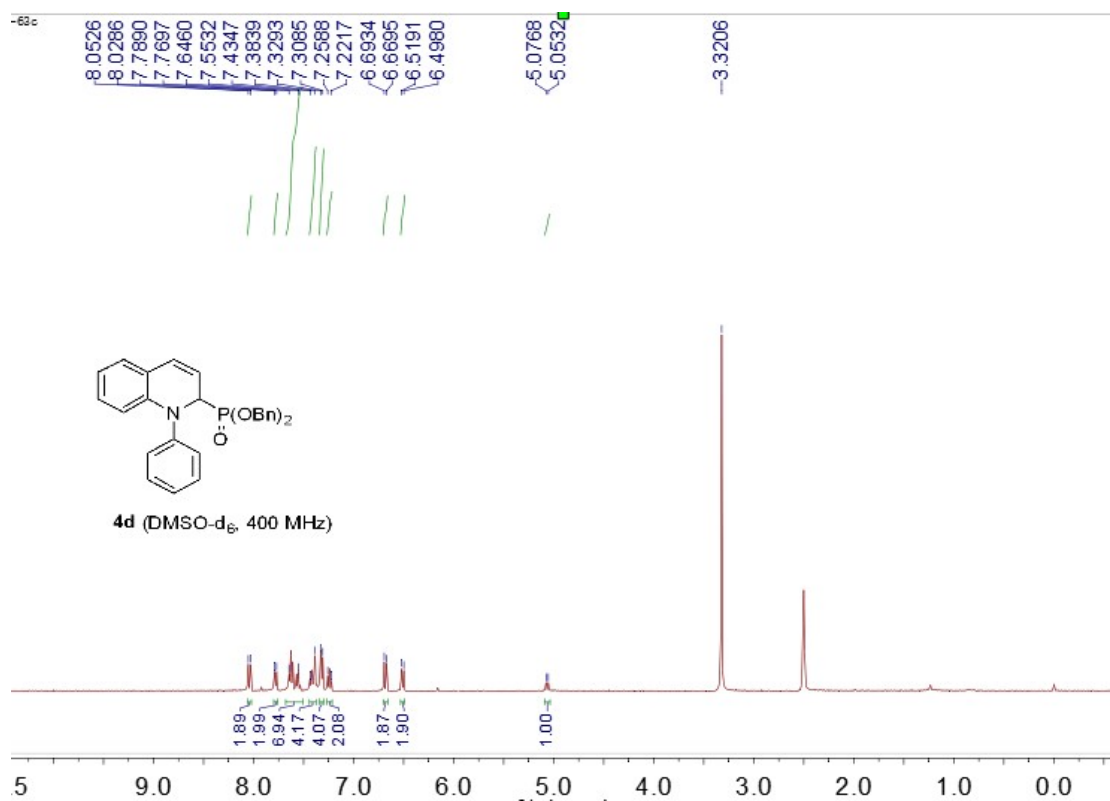
Compound 4b



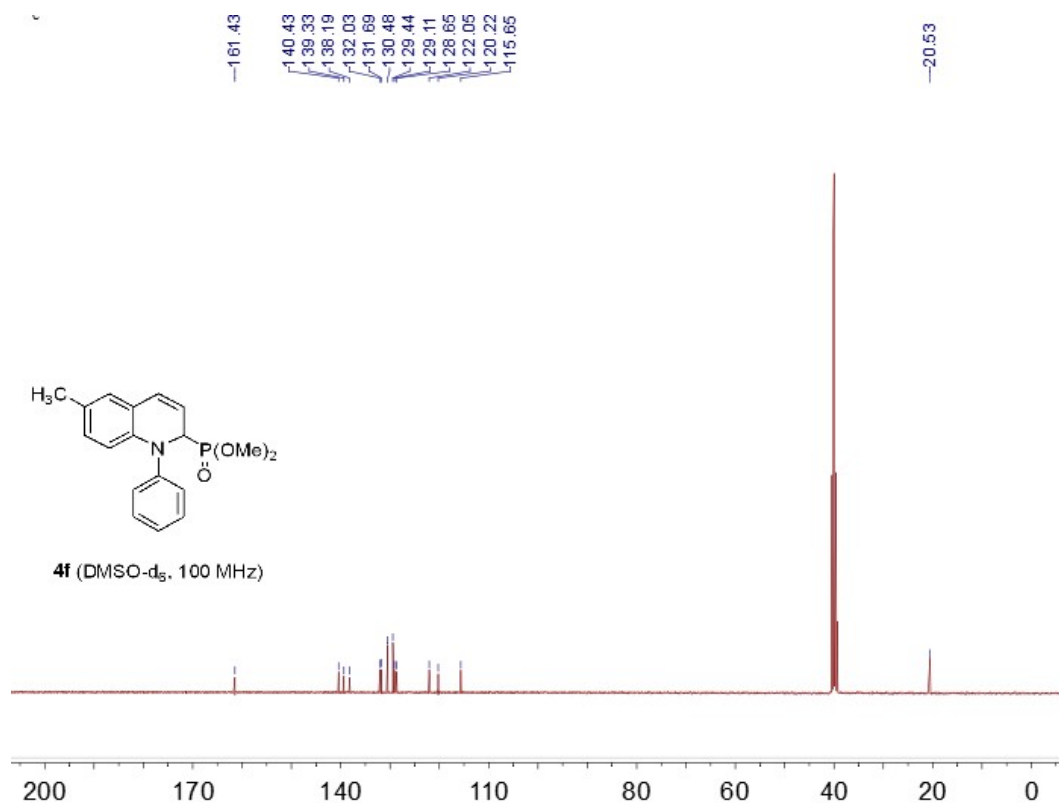
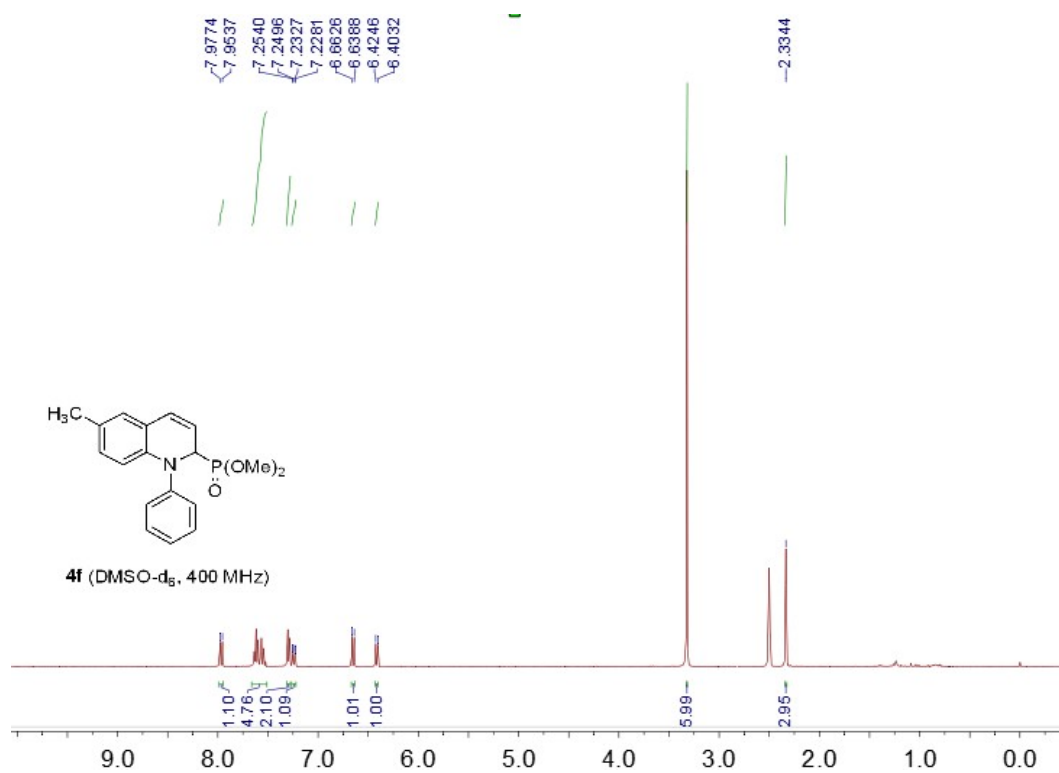
Compound 4c



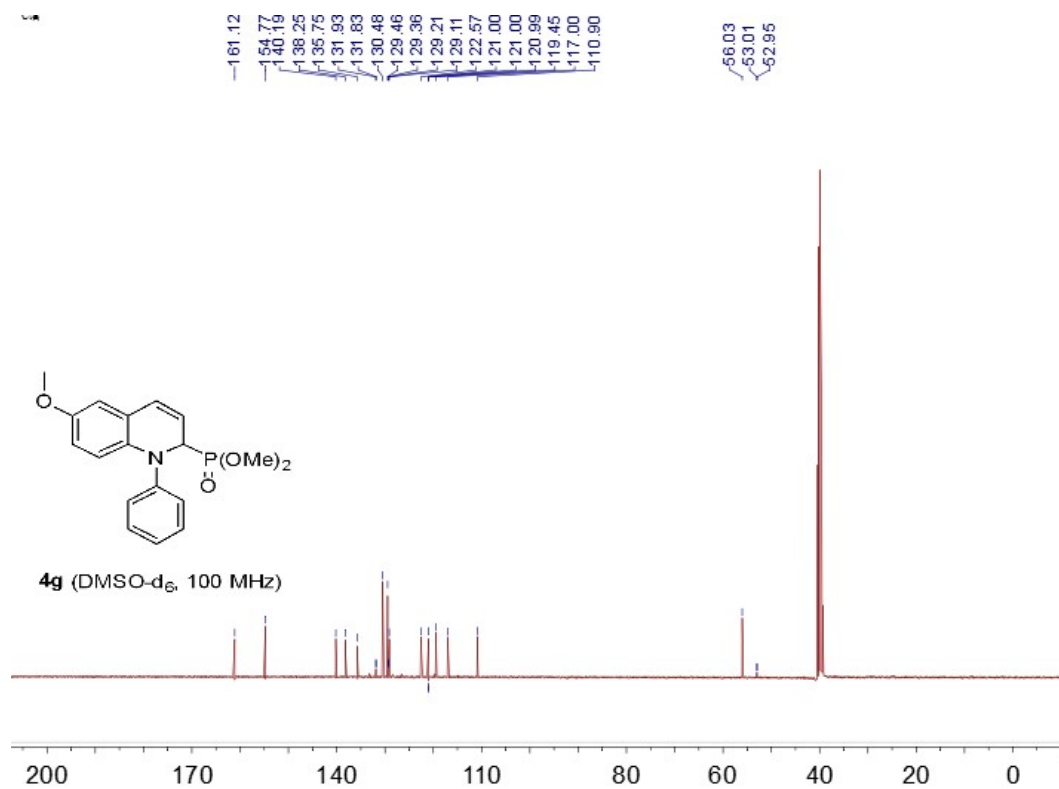
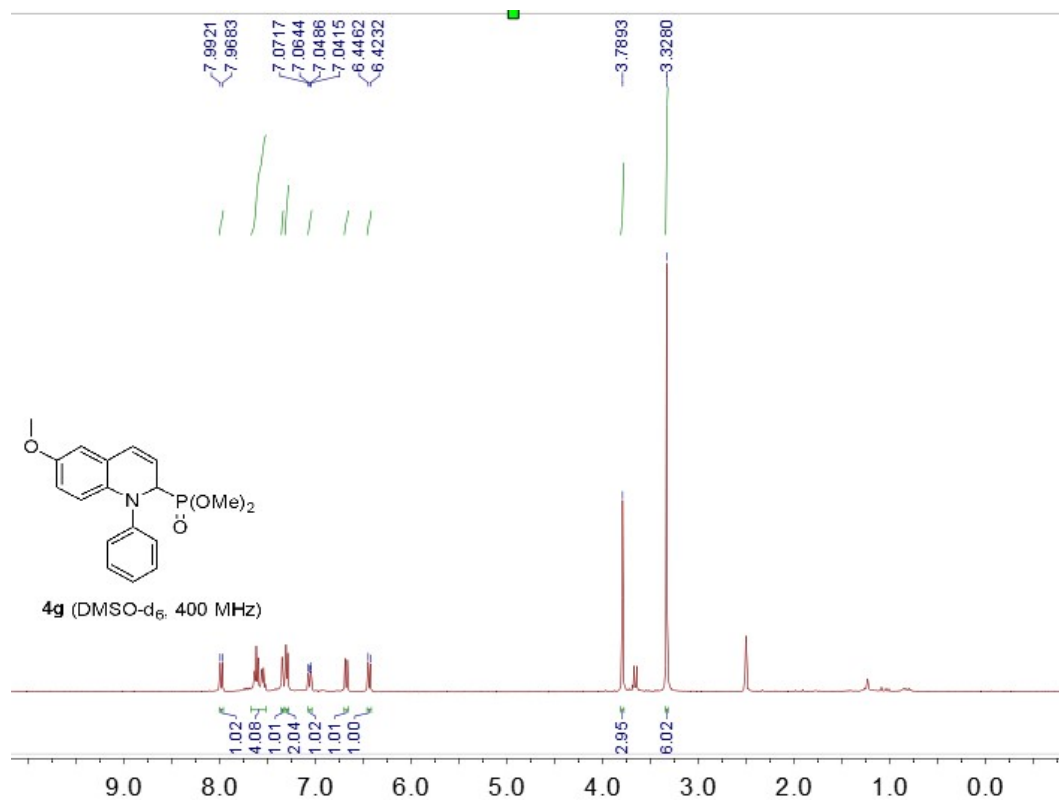
Compound 4d



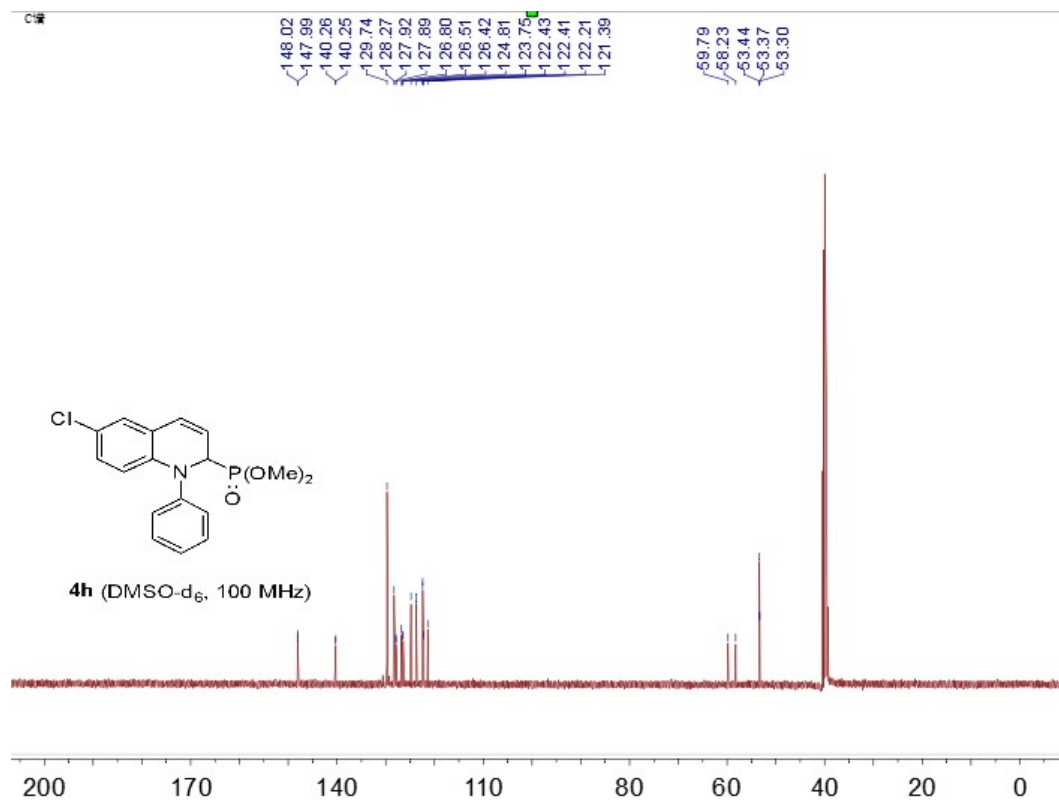
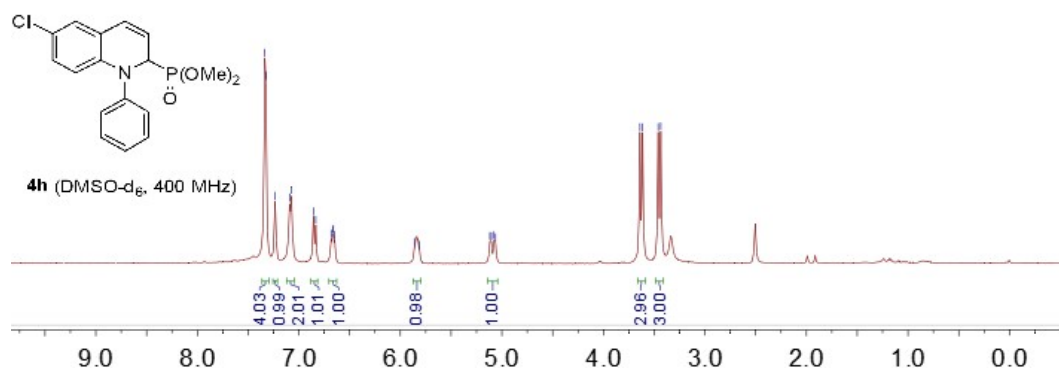
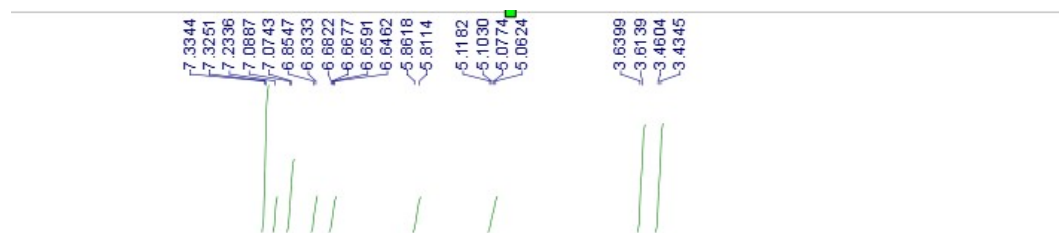
Compound 4f



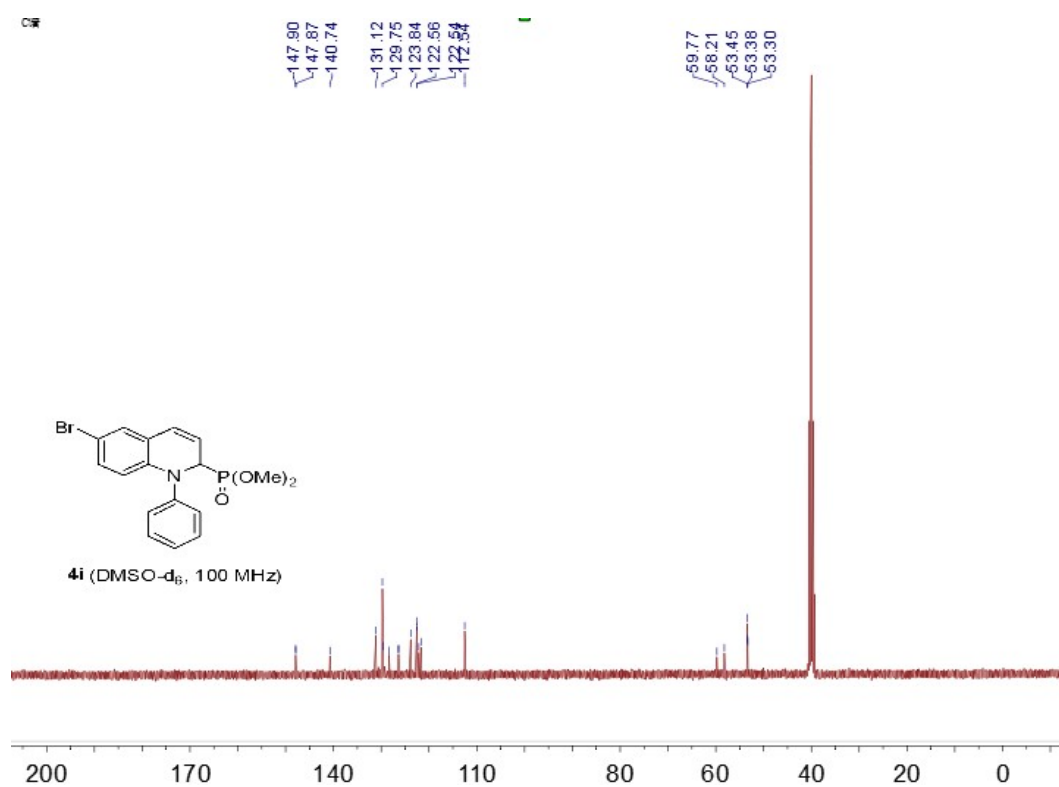
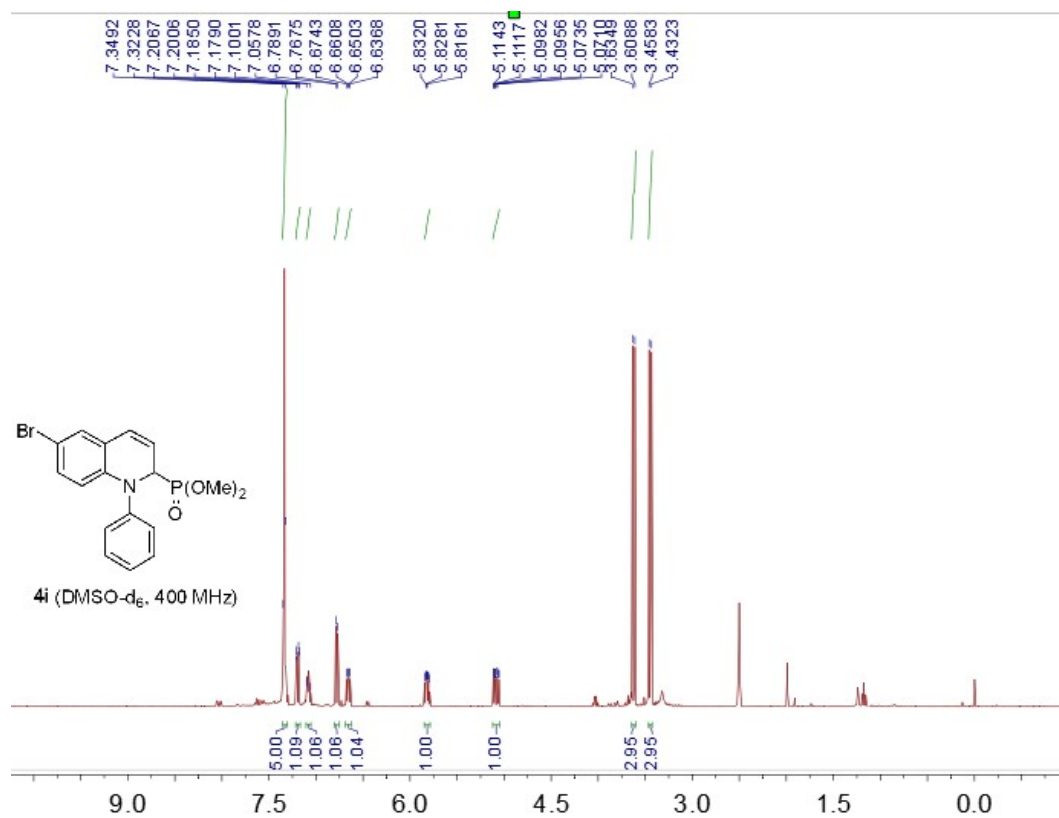
Compound 4g



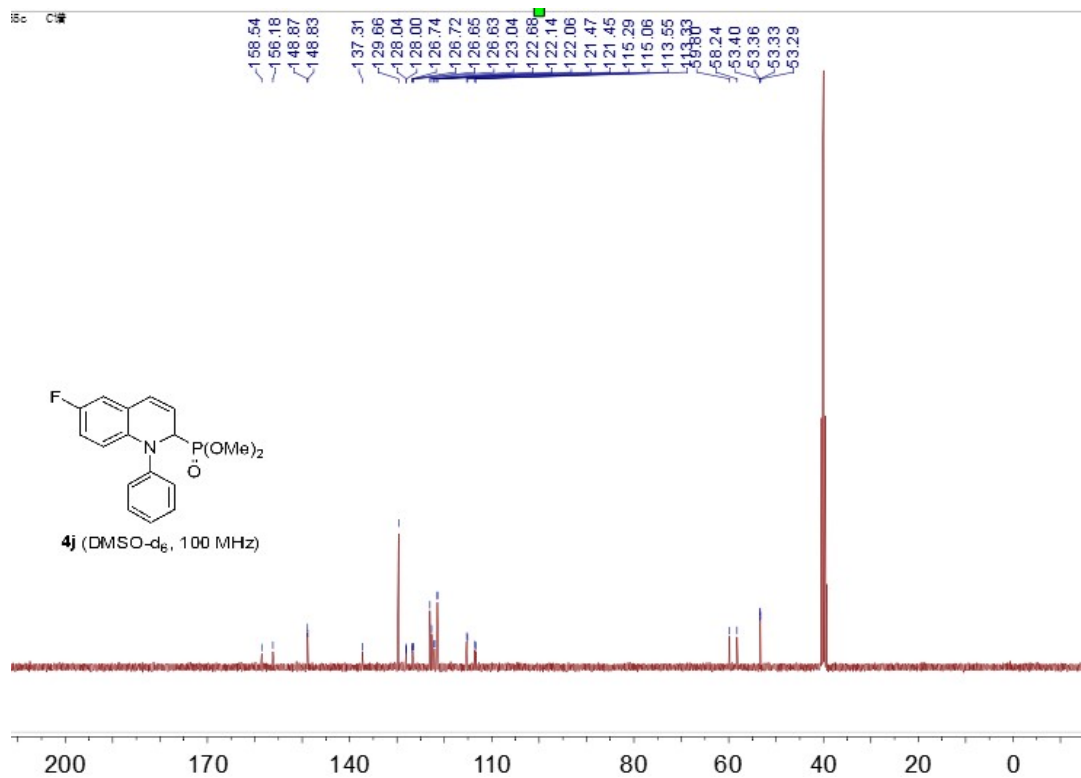
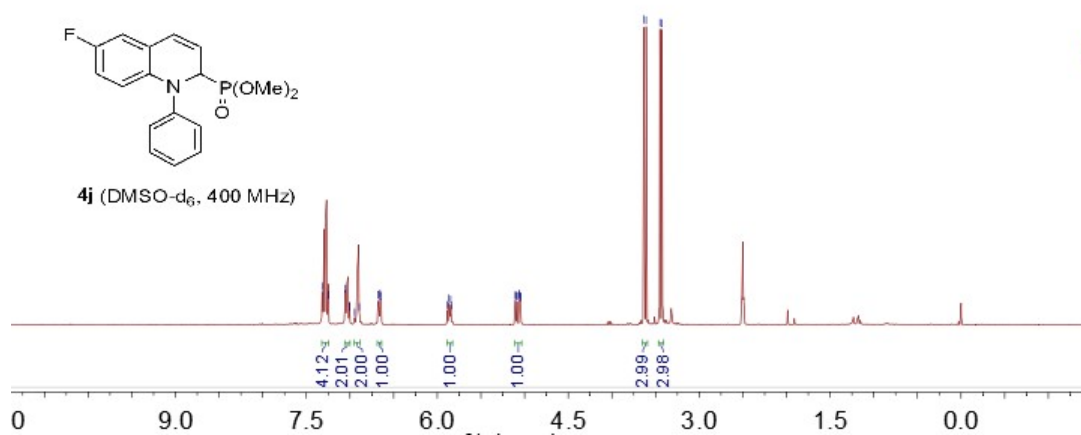
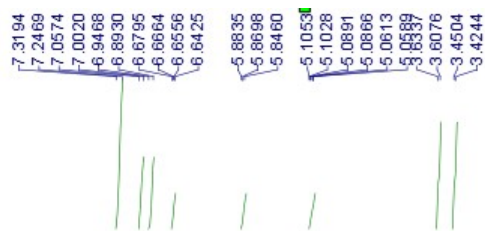
Compound 4h



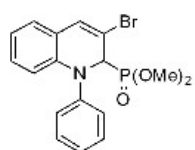
Compound 4i



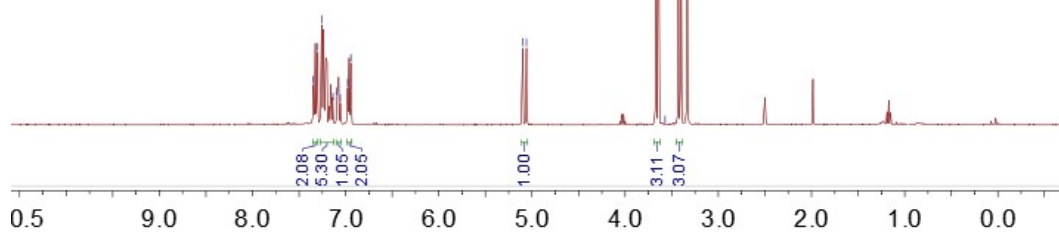
Compound 4j



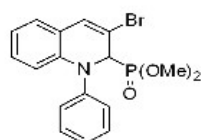
Compound 4k



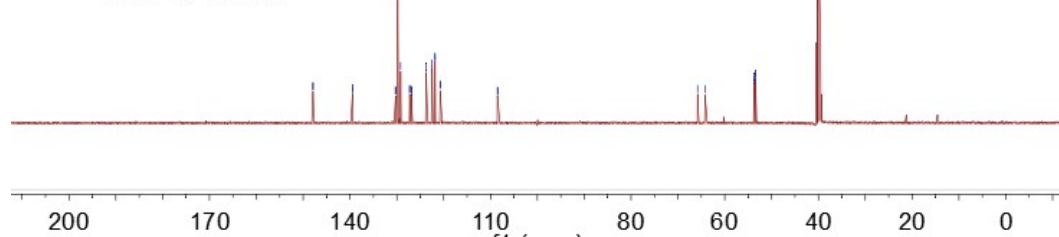
4k (DMSO-d₆, 400 MHz)



66a C¹³

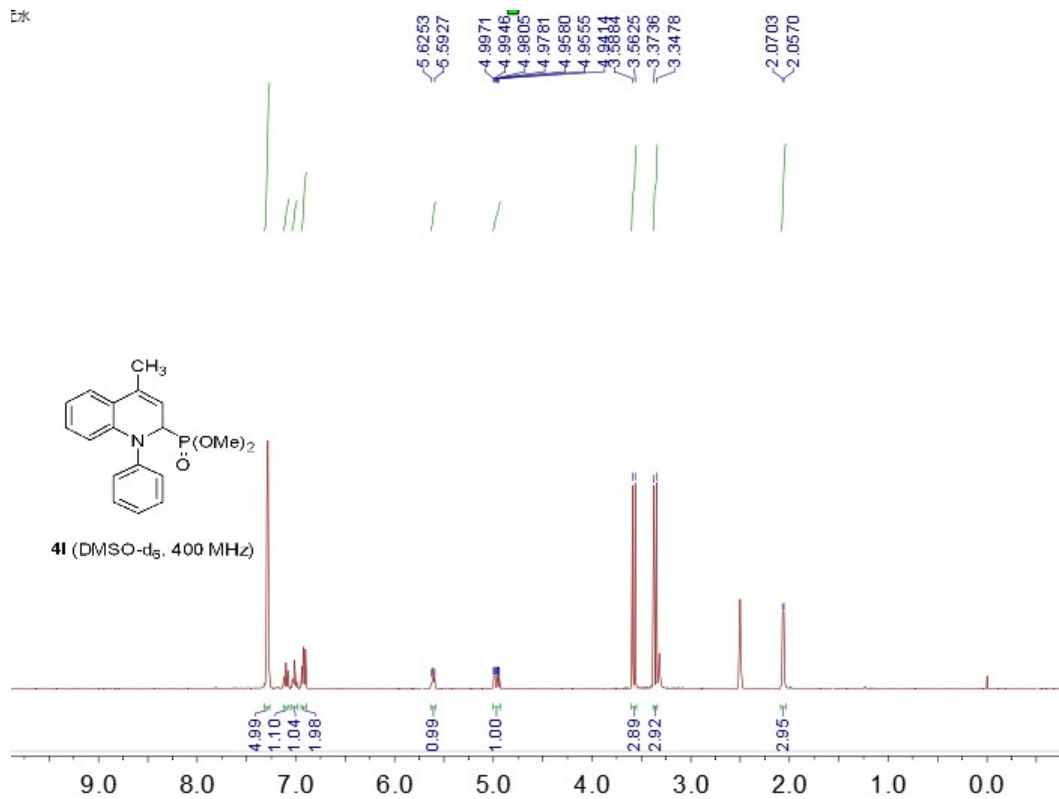


4k (DMSO-d₆, 100 MHz)

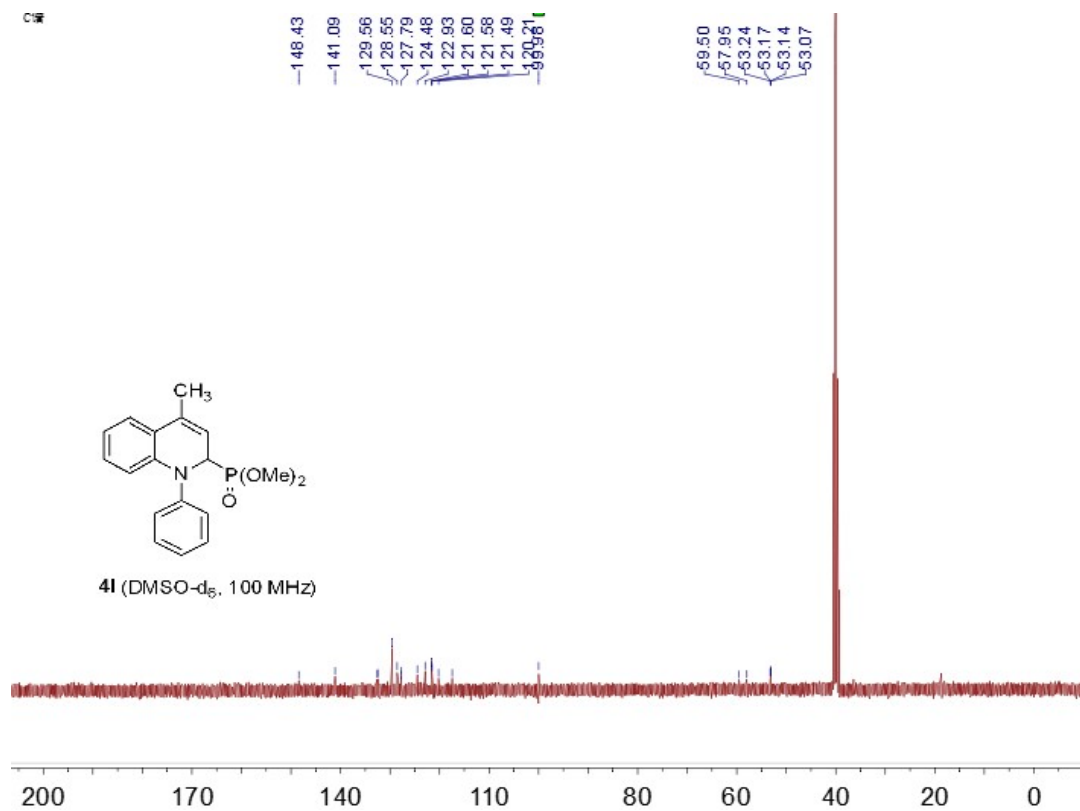


Compound 4I

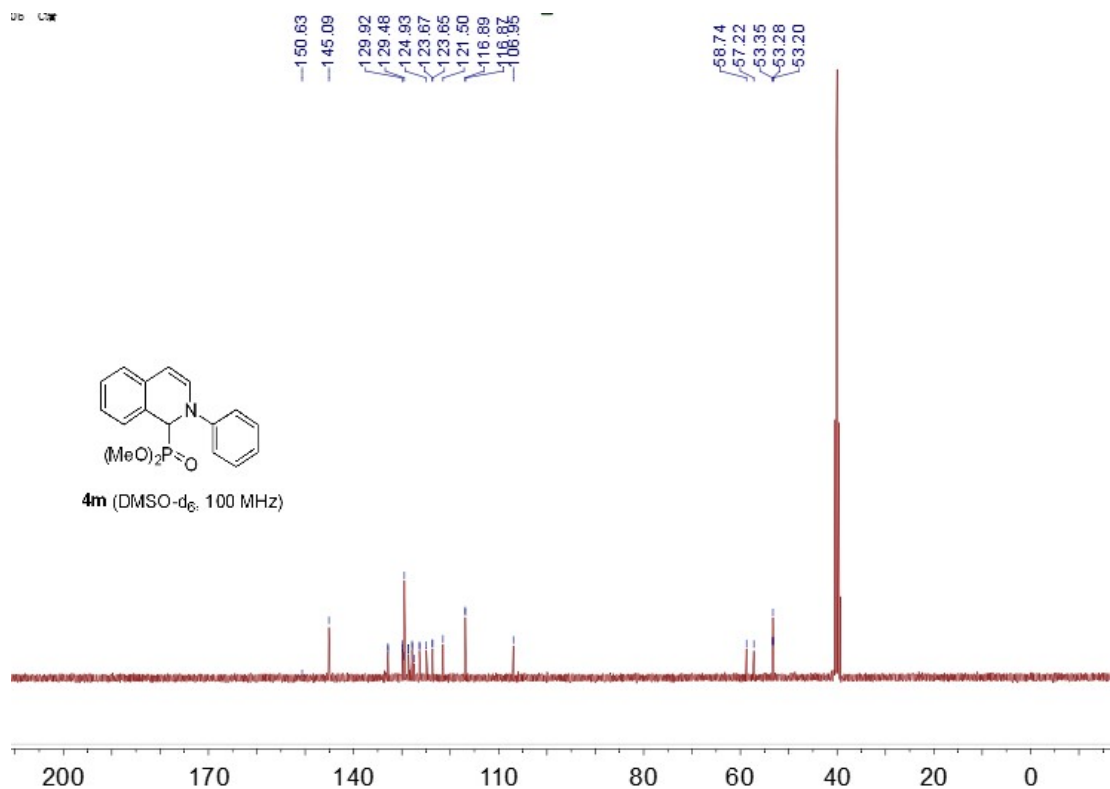
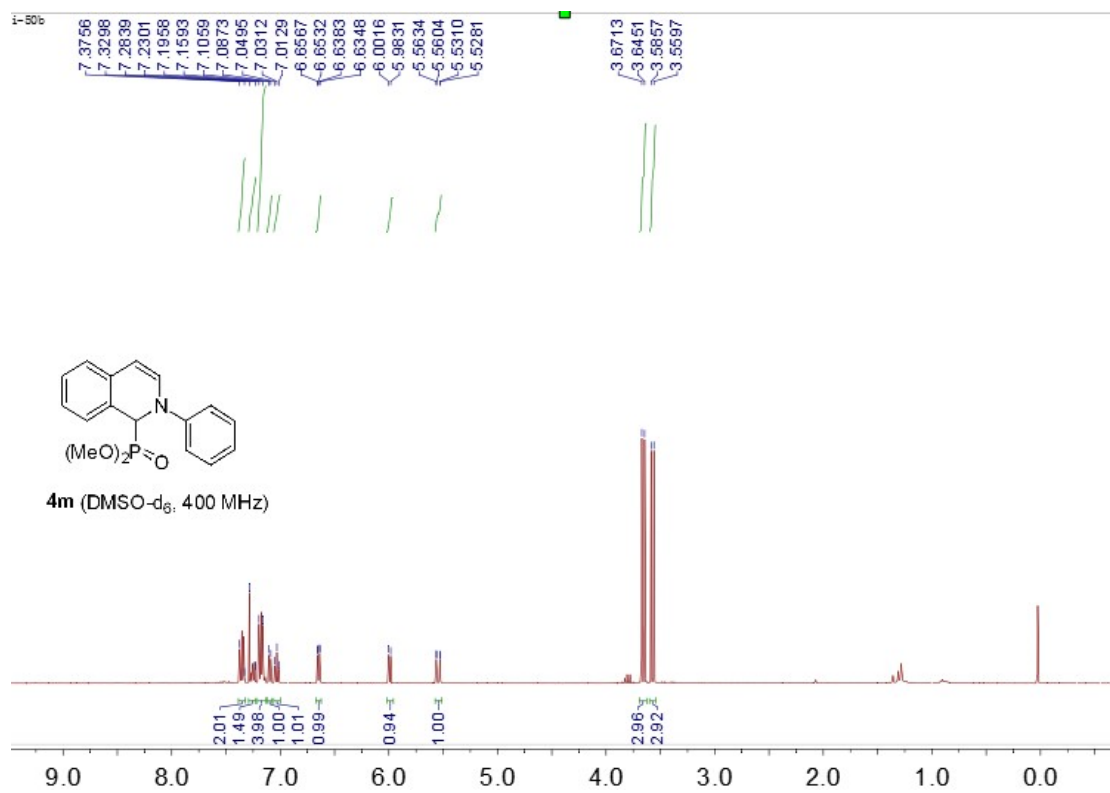
1H



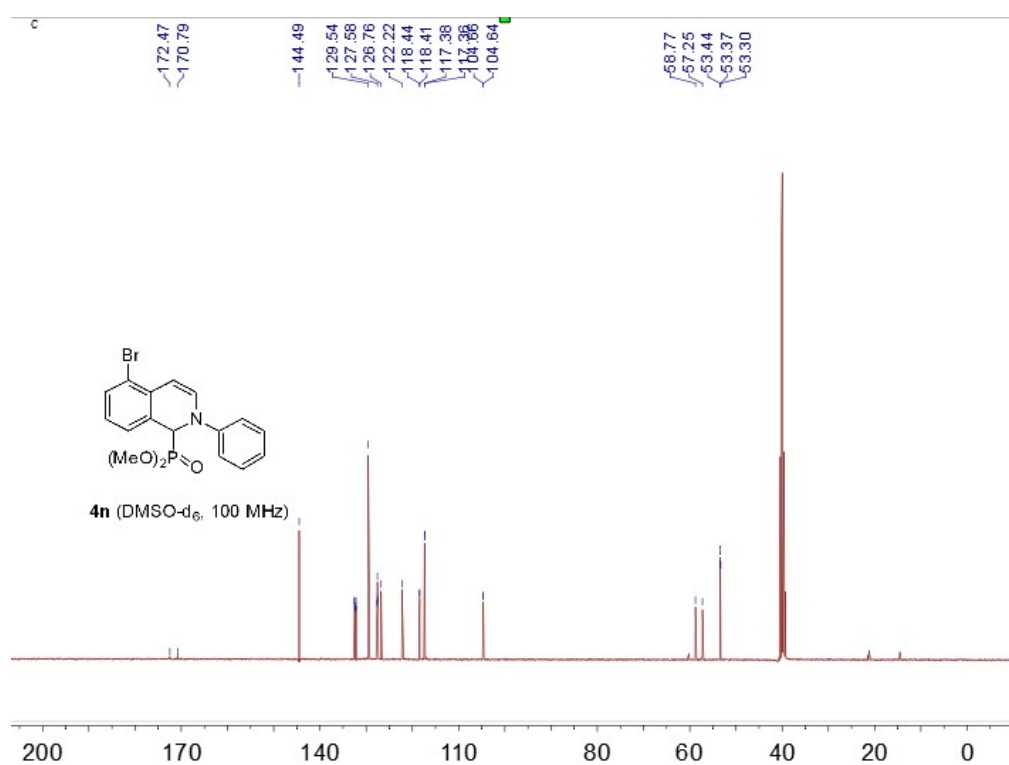
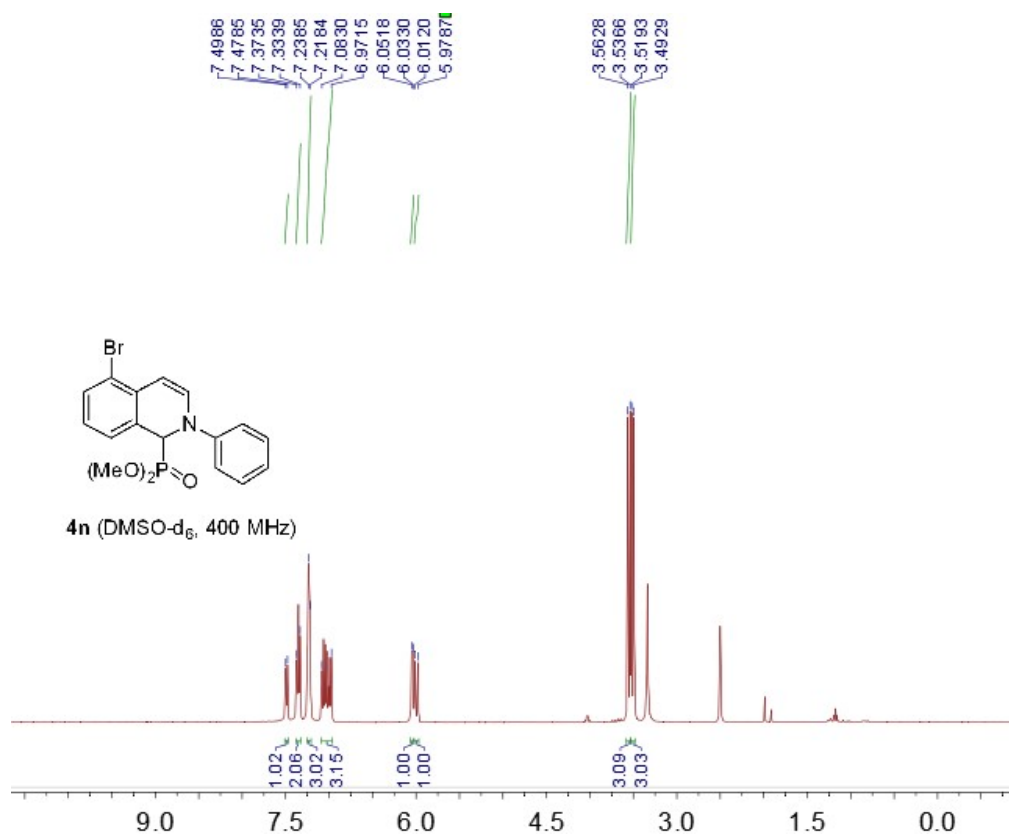
13C



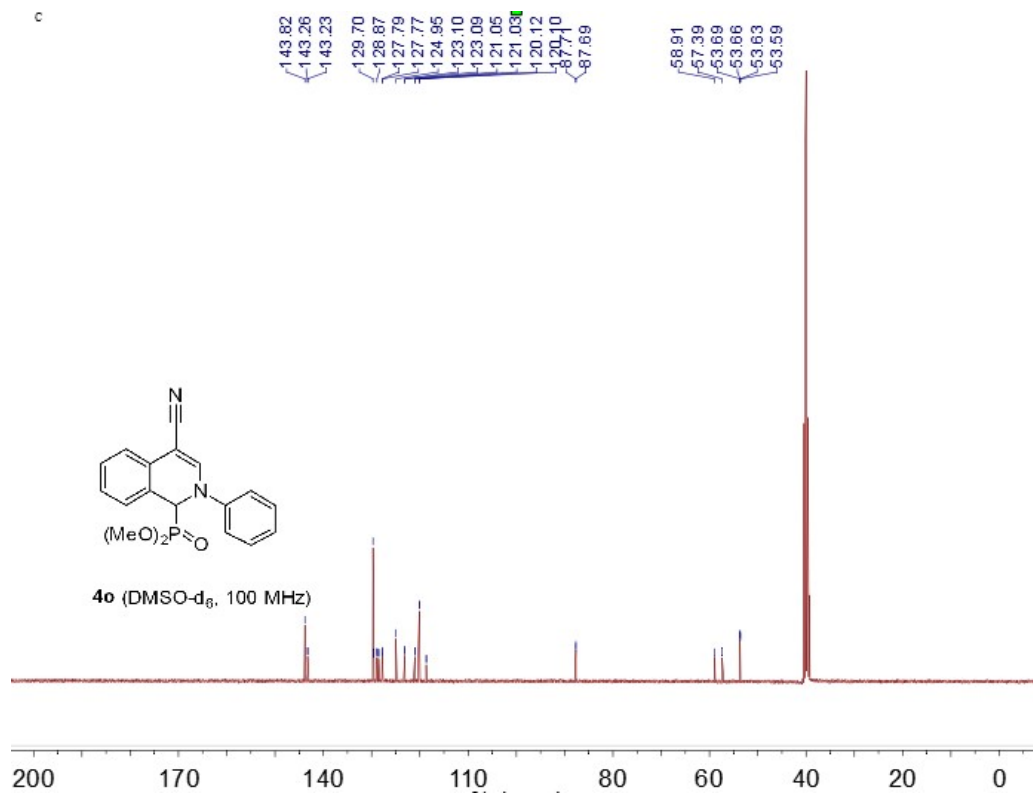
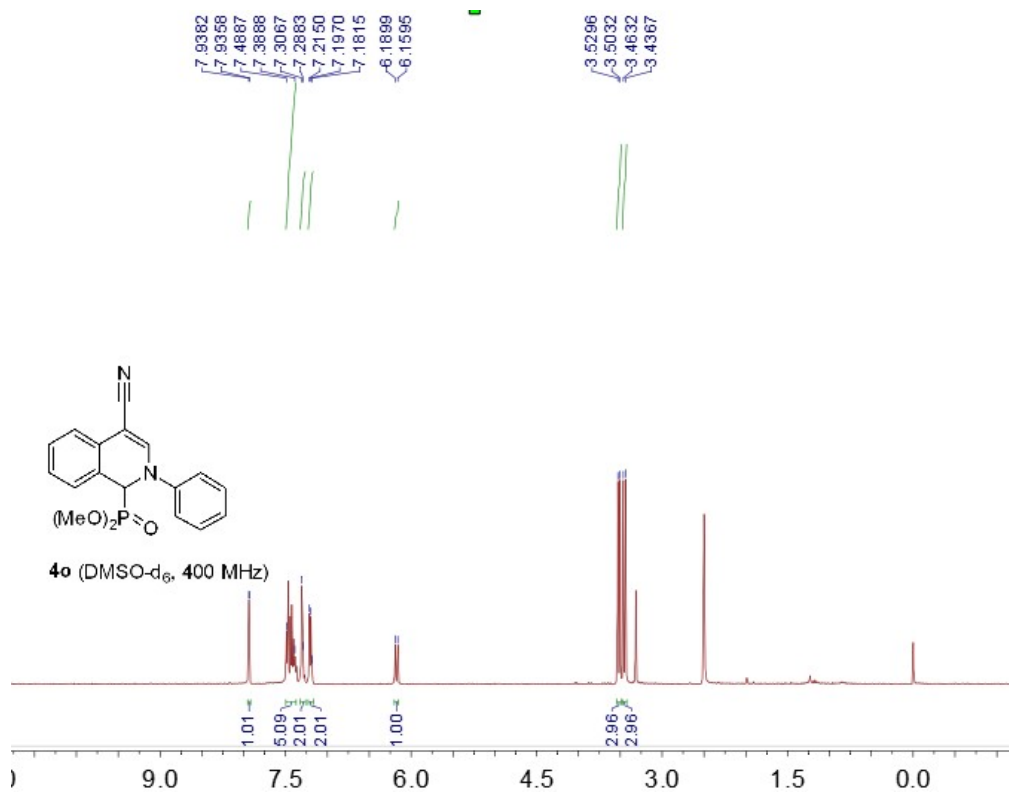
Compound 4m



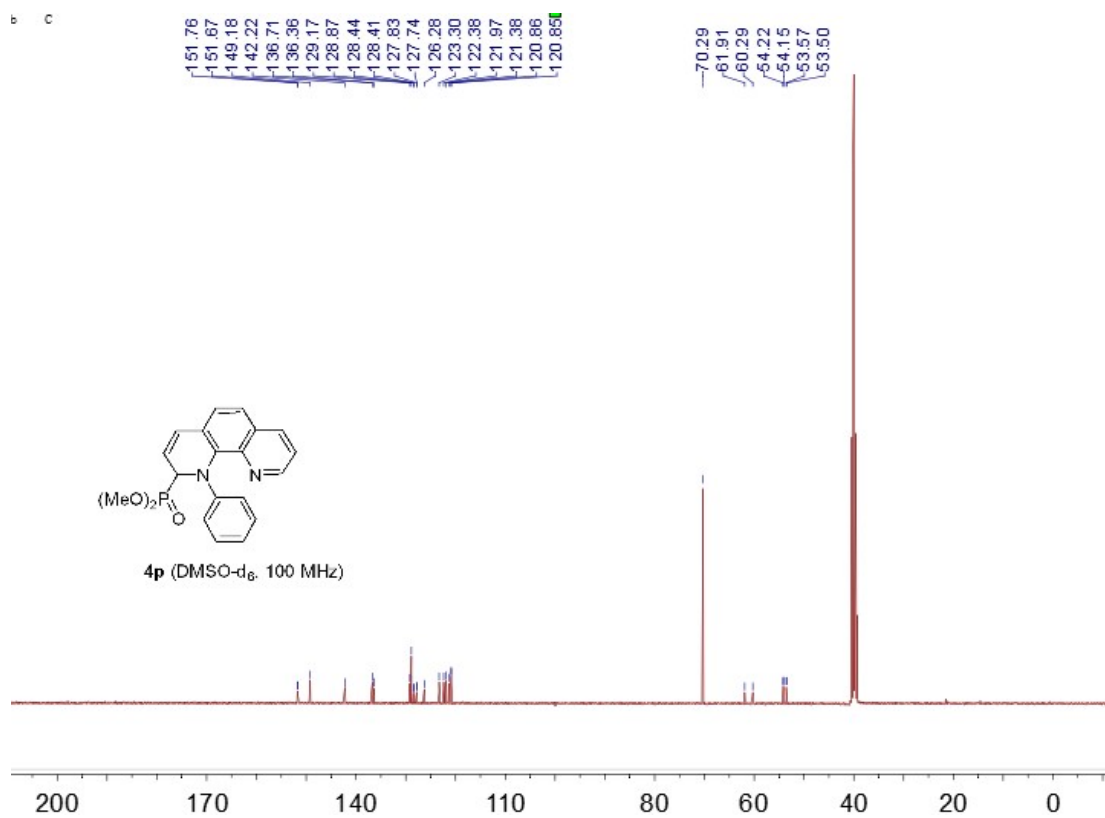
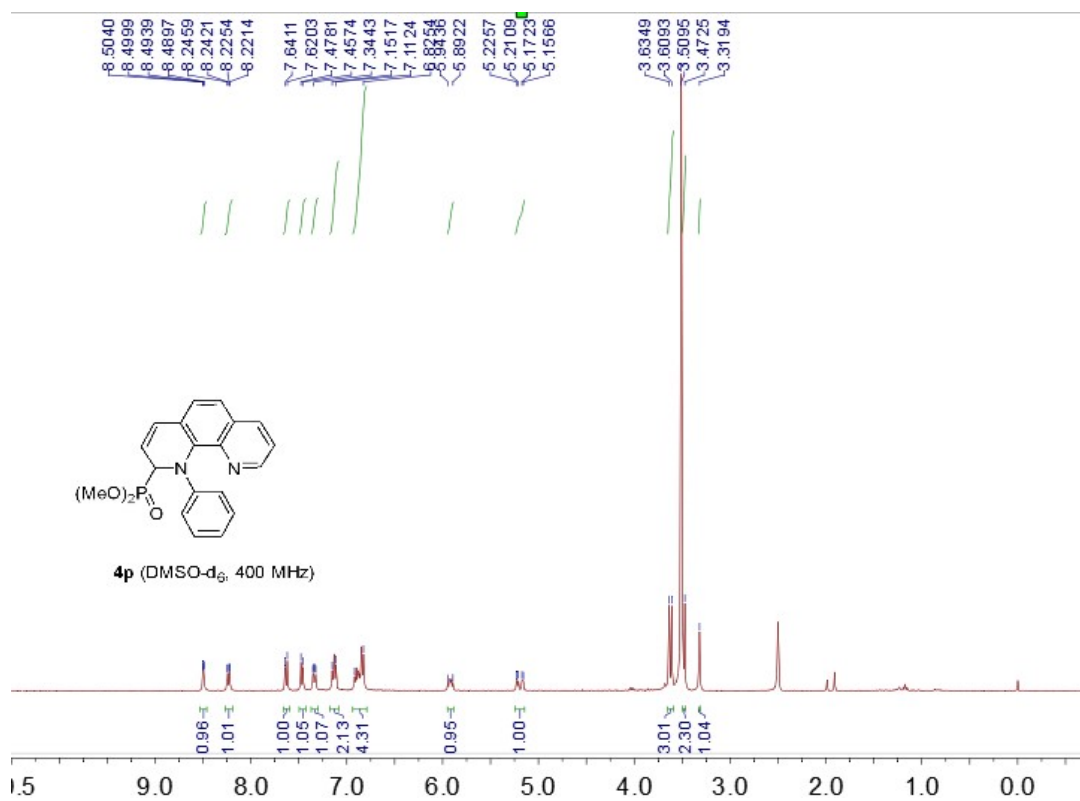
Compound 4n



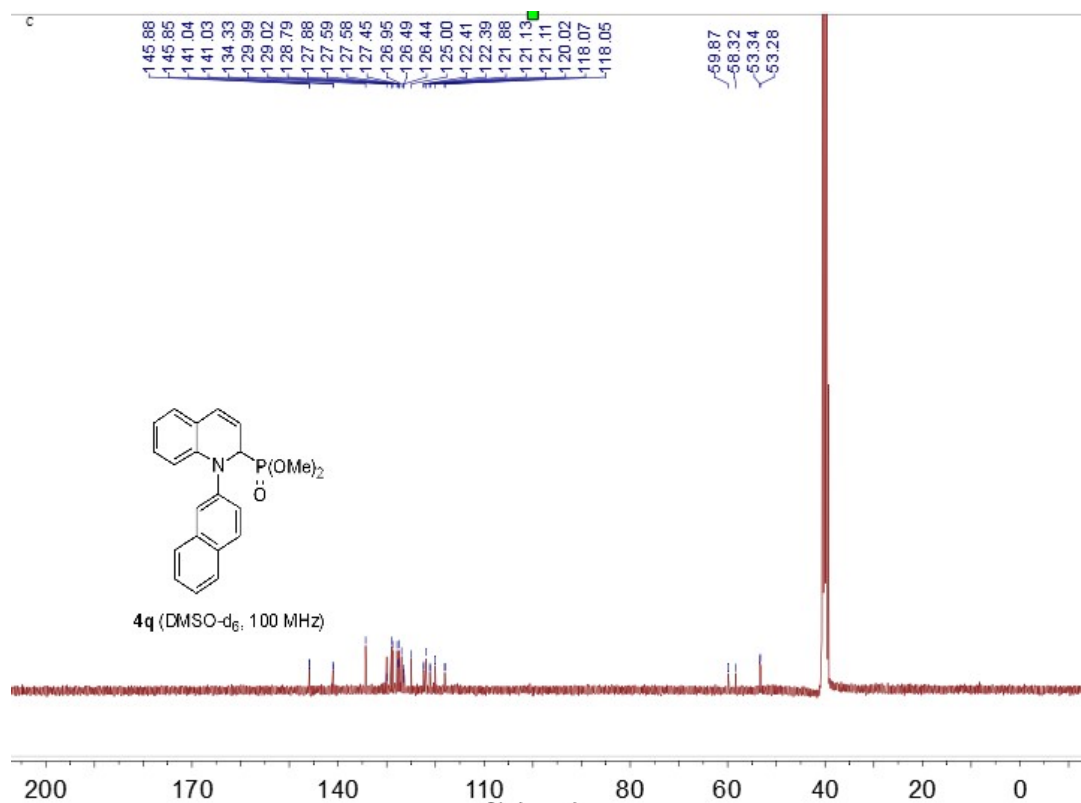
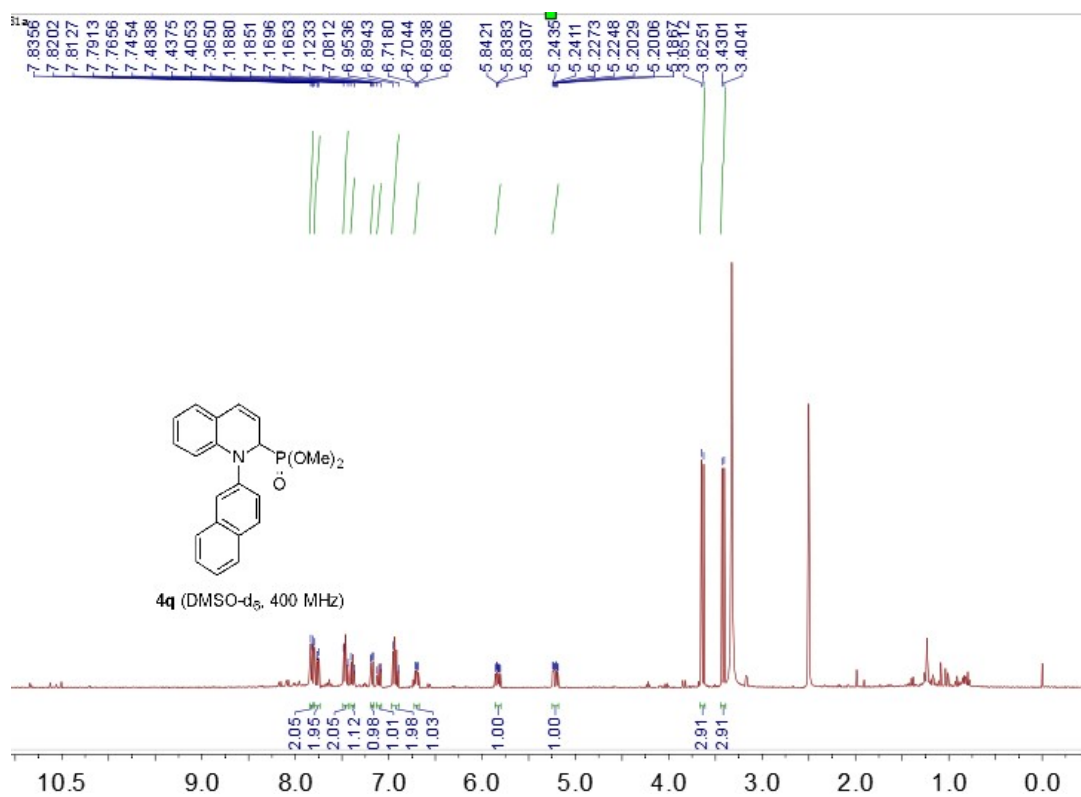
Compound 4o



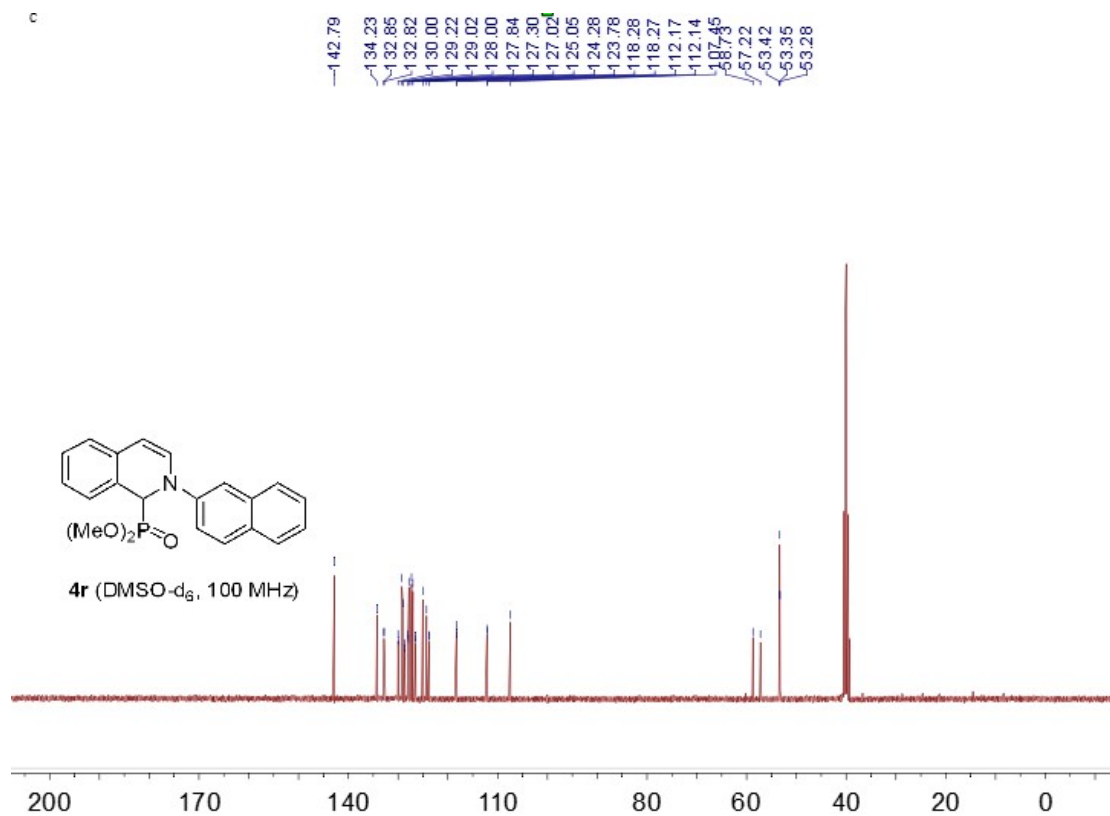
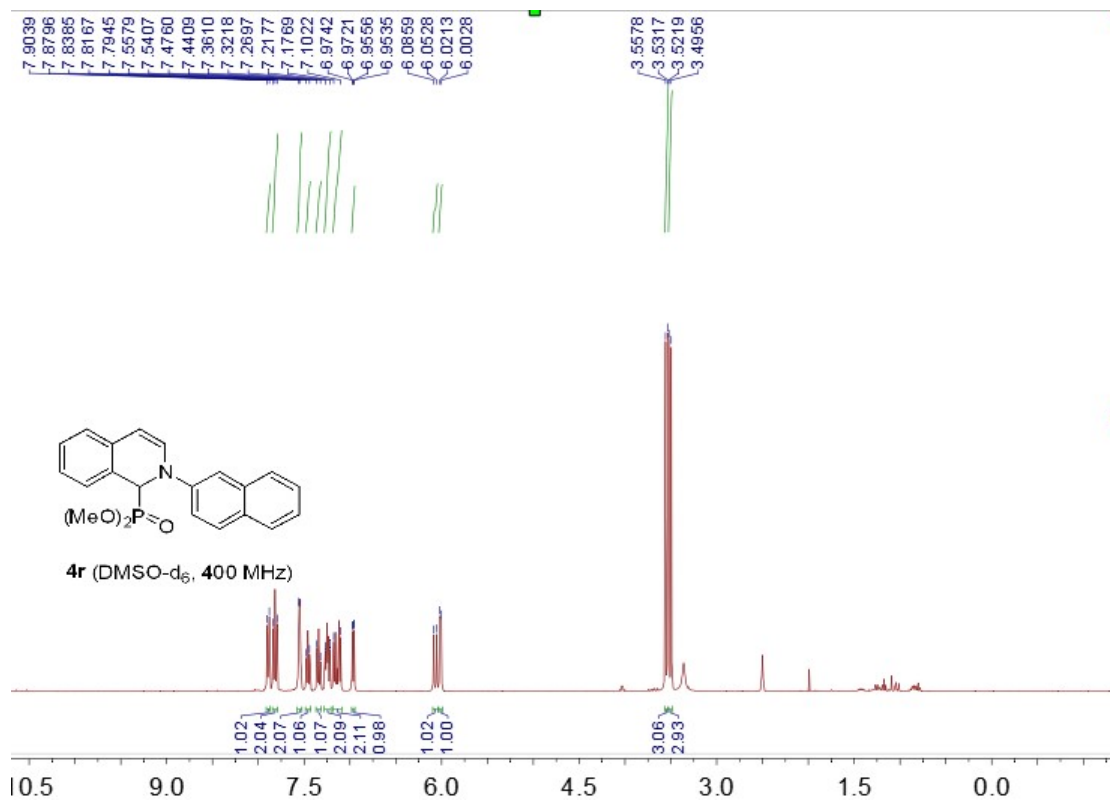
Compound 4p



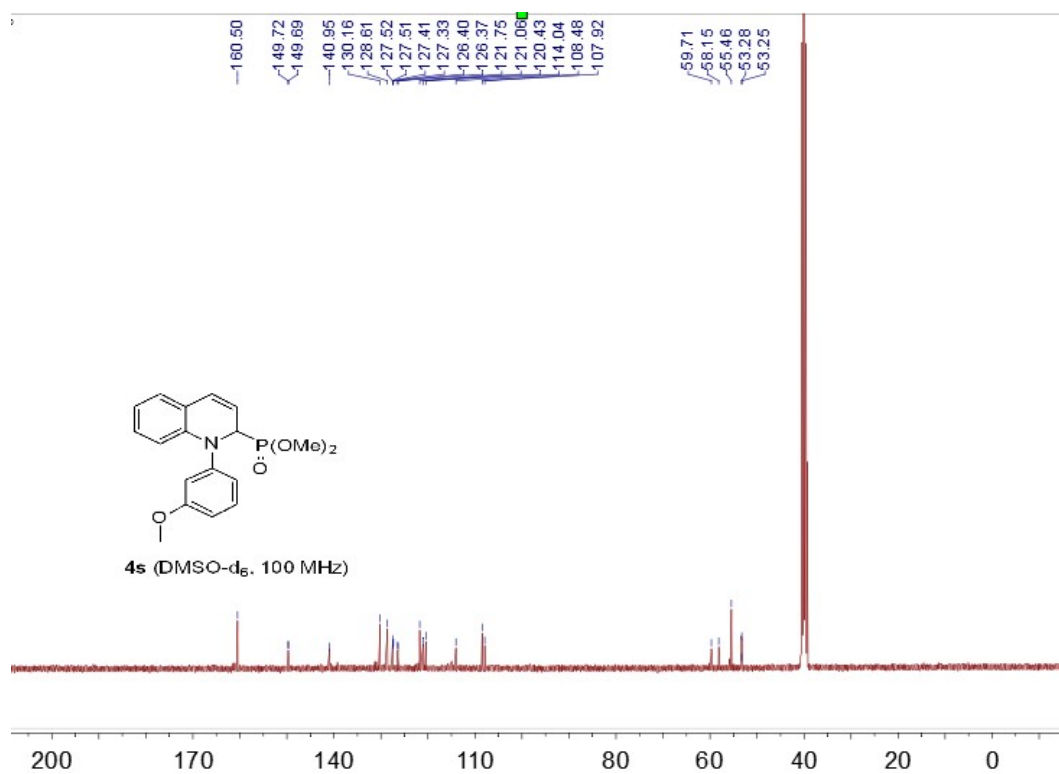
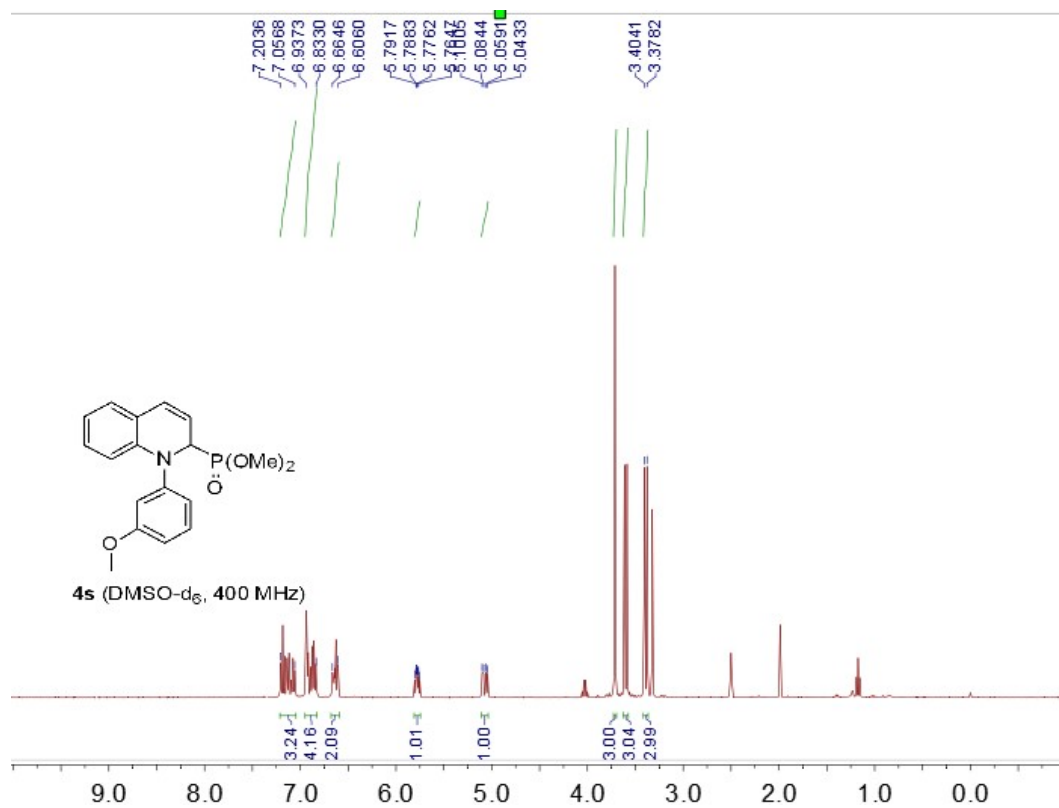
Compound 4q



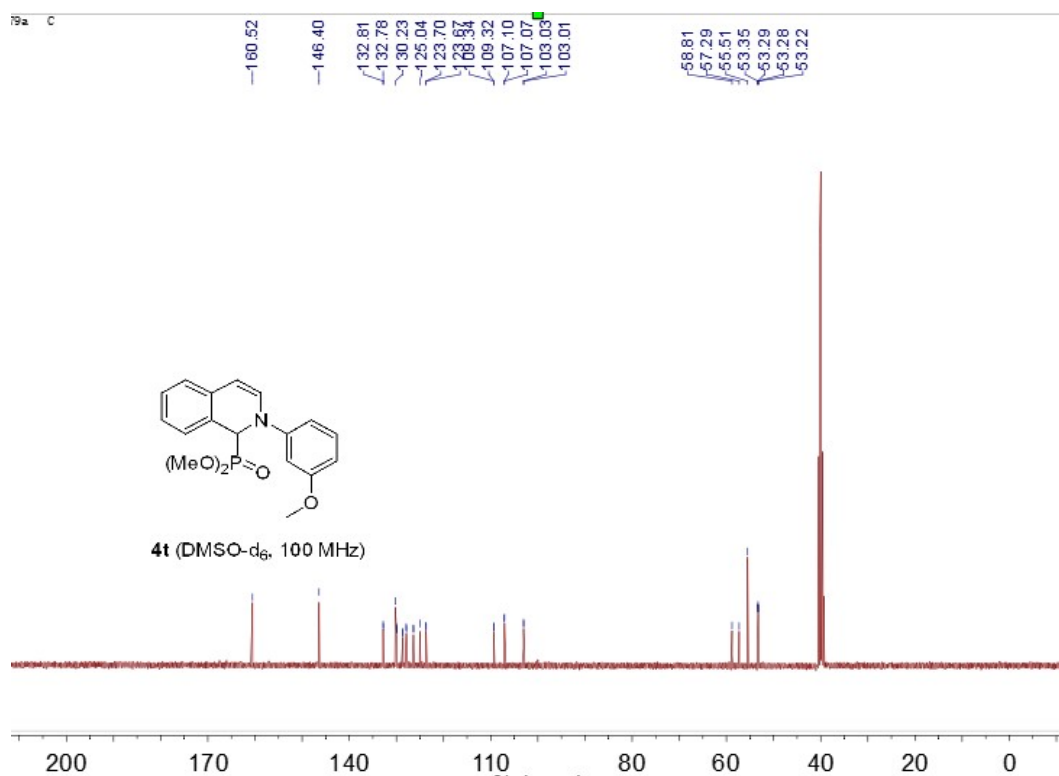
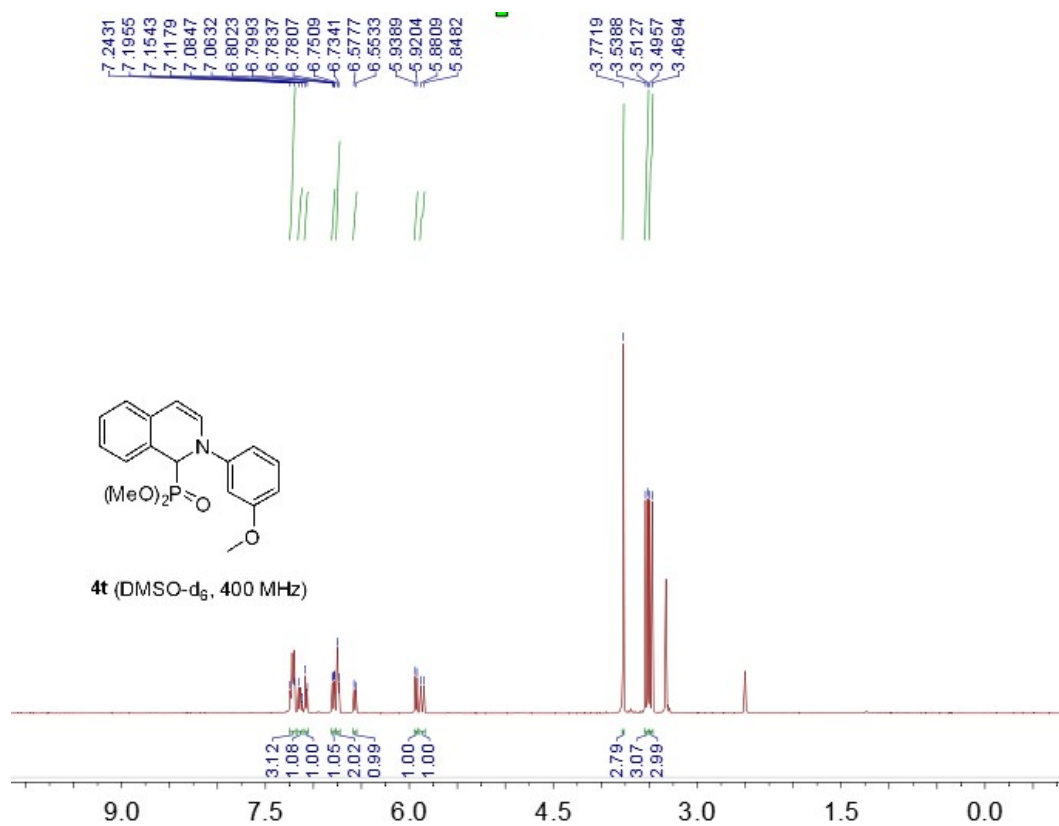
Compound 4r



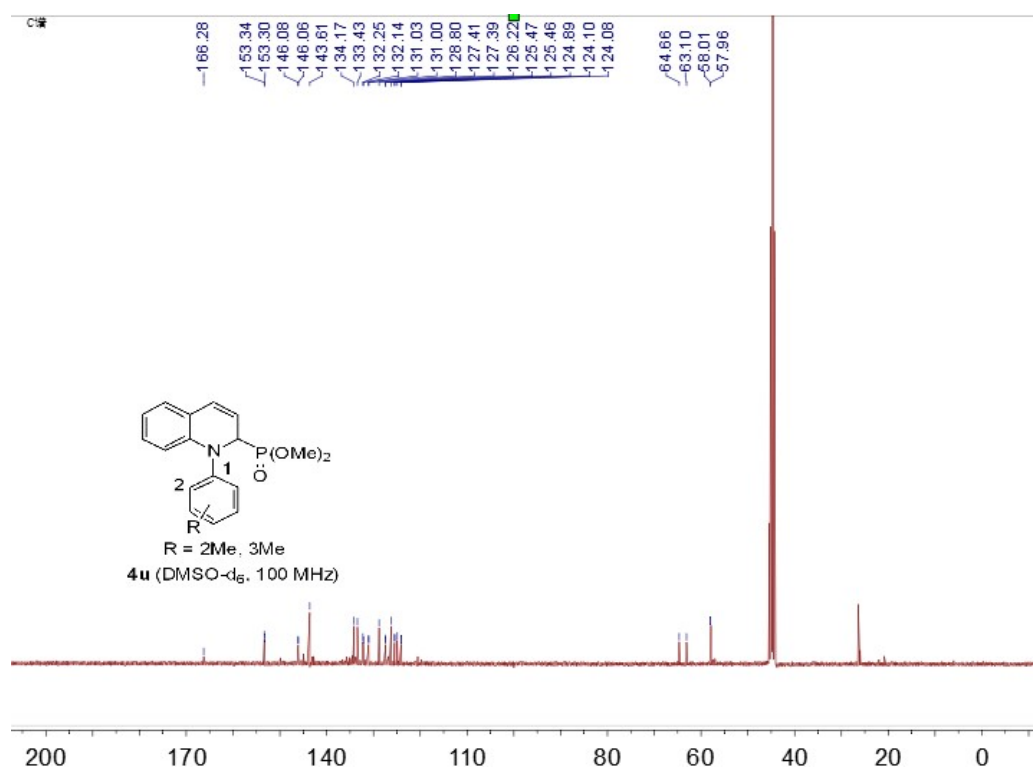
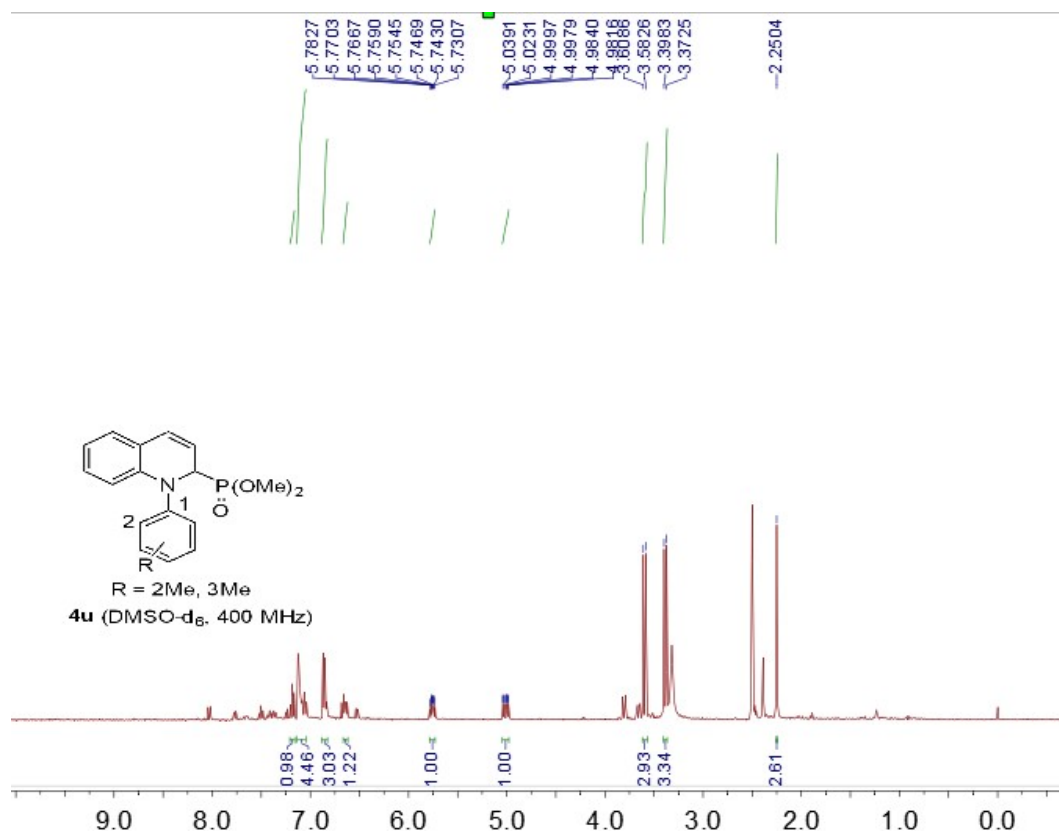
Compound 4s



Compound 4t



Compound 4u



Compound 4v

