Supporting Information

Eosin Y Catalyzed Visible Light Oxidative C-C and C-P bond Formation

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1. Experimental details and characterization data for all compounds

a) General information

^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (δ) referenced to the internal solvent signal (peak at 7.26 ppm). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet)); coupling constants (*J*) are in Hertz (Hz). ^{13}C NMR were obtained at 75 MHz spectrometer in $CDCl_3$ solution and referenced to the internal solvent signal (central peak is 77.00 ppm). ^{31}P NMR were obtained at 121 MHz and calibrated with (peak at 0.00 ppm). All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254; visualization was accomplished with UV light and/or staining with appropriate stains (anisaldehyde, orphosphomolybdic acid). Standard flash chromatography procedures were followed (particle size 40−63 μm). Commercially available reagents and solvents were used without further purification. Irradiation with green light was performed using high-power LEDs Philips LUXEON® Rebel (1W, λ = 530±10 nm, 145 lm @700mA).

b) General Procedures

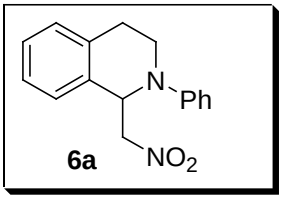
General procedure for the preparation of 2-aryl-1,2,3,4-tetrahydroisoquinolines[1]

Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a Schlenk-tube. The Schlenk-tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (2.0 mL, 15.0 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively at room temperature. The reaction mixture was heated at 85-90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using hexane/ethyl acetate as eluent.

General procedure for the preparation of *β*-nitro amine derivatives

In a 5 mL snap vial equipped with magnetic stirring bar the tetrahydroisoquinoline derivative (1 eq) and Eosin Y (0.02 eq) were dissolved in nitroalkane (0.25 mmol/mL) and the resulting mixture was irradiated through the vial's plane bottom side using green LEDs. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane/ethyl acetate as eluent.

1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6a)[2]



6a

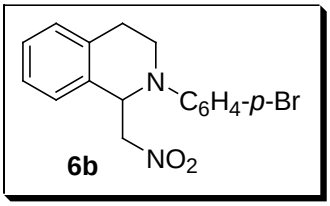
^{1}H NMR (300 MHz, $CDCl_3$):

δ ppm 7.33-7.13(m, 6H), 7.01-6.98(m, 2H), 6.87(t, *J* = 7.3 Hz, 1H), 5.57(t, *J* = 7.2 Hz, 1H), 4.88(dd, *J* = 11.8, 7.8 Hz, 1H), 4.57(dd, *J* = 11.8, 6.6 Hz, 1H), 3.70-3.58(m, 2H), 3.15-3.05(m, 1H), 2.84-2.76(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):

δ ppm 148.4, 135.3, 132.9, 129.5, 129.2, 128.1, 127.0, 126.6, 119.4, 115.1, 78.8, 58.2, 42.0, 26.4.

2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (6b)[3]



6b

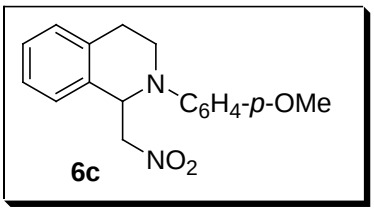
^{1}H NMR (300 MHz, $CDCl_3$):

δ ppm 7.34(d, *J* = 9.1 Hz, 2H), 7.27-7.12(m, 4H), 6.85(d, *J* = 8.8 Hz, 2H), 5.49(t, *J* = 7.6 Hz, 1H), 4.87-4.80(m, 1H), 4.59-4.53(m, 1H), 3.63-3.59(m, 2H), 3.09-3.04(m, 1H), 2.83-2.74(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):

δ ppm 147.5, 135.0, 132.6, 132.2, 129.3, 128.3, 126.8, 126.8, 116.7, 111.5, 78.6, 58.1, 42.1, 26.2.

2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (6c)[4]

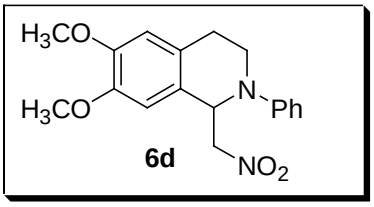


6c

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.26-7.22(m, 2H), 7.19-7.14(m, 2H), 6.94(d, *J* = 9.1 Hz, 2H), 6.83(d, *J* = 9.1 Hz, 2H), 5.41(dd, *J* = 8.6, 5.8 Hz, 1H), 4.83(dd, *J* = 11.9, 8.6 Hz, 1H), 4.57(dd, *J* = 11.9, 5.8 Hz, 1H), 3.76(s, 3H), 3.50-3.55(m, 2H), 3.08-2.97(m, 1H), 2.74-2.67(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 153.9, 143.0, 135.4, 132.9, 129.5, 127.9, 126.9, 126.6, 118.8, 114.7, 78.9, 58.9, 55.6, 43.1, 25.8.

6,7-Dimethoxy-1-nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6d)[5]

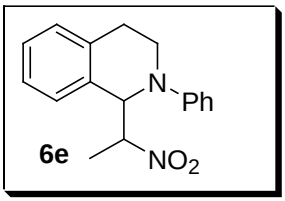


6d

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.29-7.23(m, 2H), 6.98(d, *J* = 8.1 Hz, 2H), 6.85(t, *J* = 7.3 Hz, 1H), 6.65(s, 1H), 6.61(s, 1H), 5.47(dd, *J* = 8.0, 6.3 Hz, 1H), 4.85(dd, *J* = 11.8, 8.1 Hz, 1H), 4.57(dd, *J* = 11.8, 6.3 Hz, 1H), 3.86(s, 3H), 3.85(s, 3H), 3.67-3.64(m, 1H), 3.57(m, 1H), 3.00(ddd, *J* = 15.4, 9.4, 5.6 Hz, 1H), 2.67(dt, *J* = 16.2, 4.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 148.8, 148.6, 147.7, 129.4, 127.4, 124.5, 119.5, 115.5, 111.7, 109.6, 78.8, 58.0, 56.1, 55.9, 42.0, 25.8.

1-(1-Nitro-ethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6e)[4]

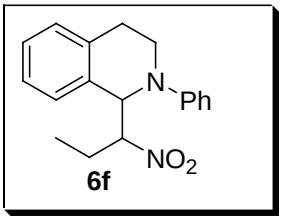


6e

^{1}H NMR (300 MHz, $CDCl_3$):
The major isomer: δ ppm 5.23(d, *J* = 6.7 Hz, 1H), 5.10-5.00(m, 1H), 3.65-3.55(m, 2H), 1.55(d, *J* = 6.8 Hz, 3H); The minor isomer: δ ppm 5.24(d, *J* = 7.0 Hz, 1H), 4.91-4.86(m, 1H), 3.84(ddd, *J* = 13.6, 8.1, 5.7 Hz, 2H), 1.71(d, *J* = 6.8 Hz, 3H). Other overlapped peaks: δ ppm 7.30-7.21(m), 7.18-7.09(m), 7.02-6.98(m), 6.86-6.79(m), 3.11-3.00(m), 2.95-2.85(m).

^{13}C NMR (75 MHz, $CDCl_3$):
The major isomer: δ ppm 148.8, 135.5, 131.9, 129.4, 129.2, 128.3, 128.1, 126.1, 119.3, 115.3, 85.4, 62.7, 42.6, 26.3, 16.3; The minor isomer: δ ppm 149.1, 134.7, 133.8, 129.2, 129.0, 128.6, 127.2, 126.5, 118.7, 114.4, 88.9, 61.1, 43.5, 26.7, 17.4.

1-(1-Nitro-propyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6f)[6]

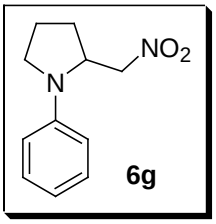


6f

^{1}H NMR (300 MHz, $CDCl_3$):
The major isomer: δ ppm 5.18(d, *J* = 9.6 Hz, 1H), 4.95-4.87(m, 1H), 3.93-3.84(m, 1H); The minor isomer: δ ppm 5.29(d, *J* = 9.3 Hz, 1H), 4.76-4.68(m, 1H); Other overlapped peaks: δ ppm 7.34-7.15(m), 7.04-6.97(m), 6.88-6.80(m), 3.74-3.50(m), 3.16-2.85(m), 2.30-2.09(m), 1.90-1.82(m), 1.00-0.94(m).

^{13}C NMR (75 MHz, $CDCl_3$):
The major isomer: δ ppm 149.0, 135.4, 132.4, 129.3, 129.1, 128.6, 128.1, 125.8, 119.2, 115.7, 92.9, 62.1, 42.1; The minor isomer: δ ppm 148.9, 134.6, 133.8, 129.2, 128.6, 128.1, 127.1, 126.5, 118.4, 114.0, 96.0, 60.6, 43.4, 26.7, 24.9, 10.6; Other overlapped peaks: δ ppm 129.5, 129.5, 129.1, 128.5, 128.5, 128.1, 128.1, 127.1, 126.5, 125.8, 26.7, 25.6, 24.9, 24.5, 10.6.

2-Nitromethyl-1-phenyl-pyrrolidine (6g)[1a]



6g

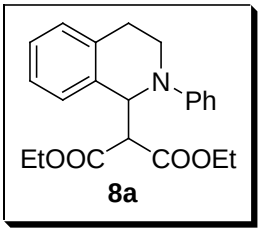
^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.30-7.22(m, 2H), 6.81-6.76(m, 1H), 6.72-6.69(m, 2H), 4.64(dd, *J* = 11.3, 3.0 Hz, 1H), 4.45-4.37(m, 1H), 4.19(dd, *J* = 11.4, 9.8 Hz, 1H), 3.54-3.47(m, 1H), 3.26-3.17(m, 1H), 2.20-2.08(m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 145.7, 129.6, 117.2, 111.9, 75.8, 57.5, 48.2, 29.4, 22.9.

General procedure for the preparation of *β*-diester amine derivatives

In a 5 mL snap vial equipped with magnetic stirring bar the tetrahydroisoquinoline derivative (1 eq) and Eosin Y (0.02 eq) were dissolved in dialkyl malonates (0.25 mmol/mL) and the resulting mixture was irradiated through the vial's plane bottom side using green LEDs. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and distilled off excess dialkyl malonates using a Kugelrohr apparatus yielding the analytically pure reaction products.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-malonic acid diethyl ester (8a)[4]

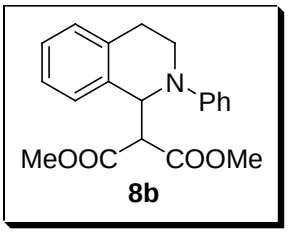


8a

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.35-7.08(m, 6H), 7.02(d, *J* = 8.0 Hz, 2H), 6.78(t, *J* = 7.3 Hz, 1H), 5.78(d, *J* = 9.2 Hz, 1H), 4.23- 3.98(m, 4H), 3.95(d, *J* = 9.2 Hz, 1H), 3.81-3.61(m, 2H), 3.14-3.04(m, 1H), 2.87(dt, *J* = 16.4, 5.2 Hz, 1H), 1.20(t, *J* = 7.1 Hz, 3H), 1.12(t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 167.9, 167.1, 148.8, 135.9, 134.8, 129.0, 128.8, 127.5, 127.1, 126.0, 118.4, 115.0, 61.5, 59.5, 57.8, 42.2, 26.1, 13.9, 13.8.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-malonic acid dimethyl ester (8b)[2]

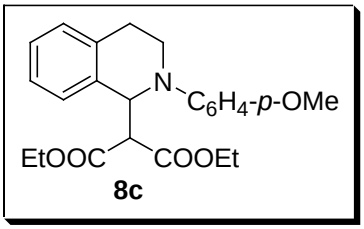


8b

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.30-7.10(m, 6 H), 7.03(d, *J* = 8.1 Hz, 2H), 6.80(t, *J* = 7.3 Hz, 1H), 5.76(d, *J* = 9.4 Hz, 1H), 4.00(d, *J* = 9.4 Hz, 1H), 3.78-3.66(m, 5H), 3.58(s, 3H), 3.15-3.03(m, 1H), 2.85(dt, *J* = 16.5, 5.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 168.2, 167.4, 148.7, 135.6, 134.7, 129.1, 128.9, 127.6, 126.9, 126.0, 118.6, 115.1, 59.0, 58.1, 52.5, 42.1, 26.0.

2-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]-malonic acid diethyl ester (8c)[4]

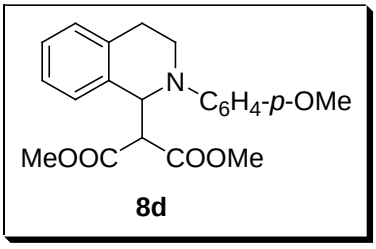


8c

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.28-7.22(m, 1H), 7.19-7.09(m, 3H), 6.92(d, *J* = 9.1 Hz, 2H), 6.78(d, *J* = 9.1 Hz, 2H), 5.52(d, *J* = 9.2 Hz, 2H), 4.15-4.01(m, 4H), 3.91(d, *J* = 9.2 Hz, 2H), 3.72(s, 3H), 3.69-3.63(m, 1H), 3.59- 3.53(m, 1H), 3.06-2.95(m, 1H), 2.76(dt, *J* = 16.6, 4.3 Hz, 1H), 1.17-1.10(m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 167.9, 167.1, 153.0, 143.4, 135.5, 134.7, 129.0, 127.2, 127.1, 125.8, 117.9, 114.3, 61.3, 61.3, 59.4, 58.8, 55.4, 42.9, 25.5, 13.9, 13.8.

2-[2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]-malonic acid dimethyl ester (8d)[4]

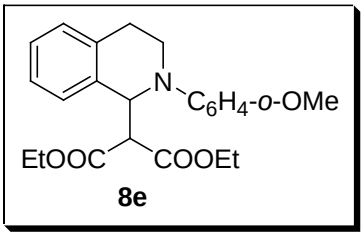


8d

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.22-7.15(m, 2H), 7.13-7.08(m, 2H), 6.92(d, *J* = 9.1 Hz, 2H), 6.78(d, *J* = 9.1 Hz, 2H), 5.50(d, *J* = 9.4 Hz, 2H), 3.97(d, *J* = 9.4 Hz, 2H), 3.72(s, 3H), 3.69-3.63(m, 4H), 3.61(s, 3H), 3.58-3.53(m, 1H), 3.01(ddd, *J* = 16.6, 10.2, 6.3 Hz, 1H), 2.74(dt, *J* = 16.7, 4.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 168.2, 167.4, 153.2, 143.3, 135.3, 134.7, 129.1, 127.4, 127.0, 125.9, 118.2, 114.3, 59.1, 55.5, 52.4, 52.4, 43.0, 25.5.

2-[2-(2-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]-malonic acid diethyl ester (8e)[4]

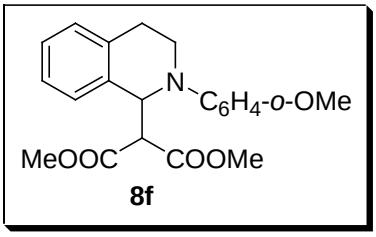


8e

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.29-7.08(m, 4H), 7.01-6.95(m, 1H), 6.83-6.77(m, 3H), 5.47(d, *J* = 8.5 Hz, 1H), 4.10-3.97(m, 4H), 3.95(d, *J* = 8.5 Hz, 1H), 3.81(s, 3H), 3.52-3.34(m, 2H), 2.94-2.83(m, 1H), 2.71-2.64(m, 1H), 1.13(t, *J* = 5.7 Hz, 3H), 1.08(t, *J* = 5.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 168.0, 167.3, 152.6, 141.0, 139.4, 135.6, 135.0, 129.0, 127.0, 125.6, 123.2, 121.7, 120.6, 111.4, 61.2, 61.1, 58.9, 55.3, 42.7, 26.2, 13.7.

2-[2-(2-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]-malonic acid dimethyl ester (8f)[4]



8f

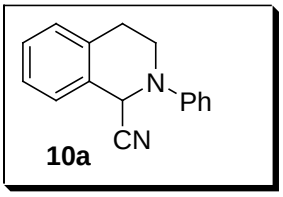
^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.24-7.09(m, 4H), 7.01-6.94(m, 1H), 6.85-6.77(m, 3H), 5.43(d, *J* = 8.9 Hz, 1H), 4.01(d, *J* = 8.9 Hz, 1H), 3.82(s, 3H), 3.66-3.51(m, 2H), 3.58(s, 3H), 3.56(s, 3H), 2.93-2.82(m, 1H), 2.72-2.64(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 168.3, 167.5, 152.8, 139.3, 135.5, 135.0, 129.2, 127.1, 126.7, 125.7, 123.3, 121.9, 120.6, 111.5, 59.2, 58.7, 55.3, 52.3, 52.2, 42.8, 26.1.

General procedure for the preparation of *α*-amino nitriles

In a 5 mL snap vial equipped with magnetic stirring bar the tetrahydroisoquinoline derivative (1 eq) and eosin Y (0.02 eq) were dissolved in DMF (0.25 mmol/mL). Then malononitrile (1.5 eq) was added and the resulting mixture was irradiated through the vial's plane bottom side using green LEDs. After the reaction was completed (monitored by TLC), the mixture was transferred to the separating funnel, diluted with diethyl ether and washed with water. The aqueous phase was extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate as eluent.

2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (10a)[7]

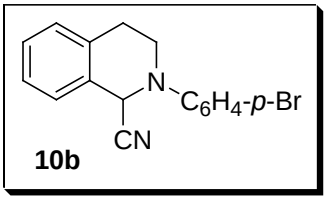


10a

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.42-7.24(m, 6H), 7.12-7.02(m, 3H), 5.54(s, 1H), 3.83-3.76(m, 1H), 3.55-3.46(m, 1H), 3.23-3.12(m, 1H), 2.96(td, *J* = 16.3, 3.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 148.4, 134.6, 129.6, 129.4, 128.8, 127.1, 126.9, 121.9, 117.6, 117.6, 53.2, 44.2, 28.6.

2-(4-Bromo-phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (10b)[3]

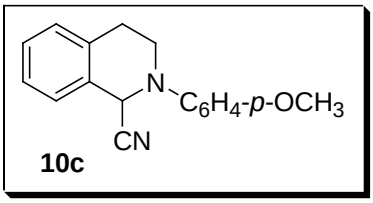


10b

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.46(d, *J* = 9.0 Hz, 2H), 7.34-7.23(m, 4H), 6.96(d, *J* = 9.0 Hz, 2H), 5.46(s, 1H), 3.69-3.75(m, 1H), 3.51-3.42(m, 1H), 3.21-3.10(m, 1H), 3.02-2.94(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 147.4, 134.4, 132.54, 129.3, 129.2, 128.9, 127.0, 127.0, 119.1, 117.4, 114.4, 52.9, 44.2, 28.4

2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (10c)[7]

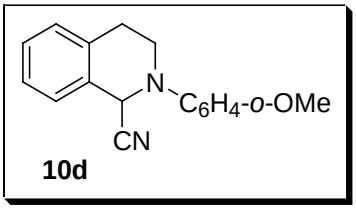


10c

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.34-7.22(m, 4H), 7.10(d, *J* = 9.0 Hz, 2H), 6.93(d, *J* = 9.0 Hz, 2H), 5.37(s, 1H), 3.80(s, 3H), 3.62-3.56(m, 1H), 3.48-3.39(m, 1H), 3.23-3.11(m, 1H), 2.97-2.90(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 155.7, 142.6, 134.3, 129.7, 129.5, 128.6, 127.1, 126.7, 121.0, 117.6, 114.8, 55.6, 55.5, 44.9, 28.7.

2-(2-Methoxy-phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (10d)



10d

^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.34-7.13(m, 6H), 7.07-7.01(m, 1H), 6.96-6.93(m, 1H), 5.76(s, 1H), 3.87(s, 3H), 3.55-3.51(m, 2H), 3.31-3.20(m, 1H), 2.97-2.90(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 155.7, 137.6, 133.9, 129.8, 129.4, 128.4, 127.1, 126.4, 125.0, 121.3, 120.8, 117.6, 111.3, 55.5, 53.0, 44.6, 28.6.

mp: 162-164°C

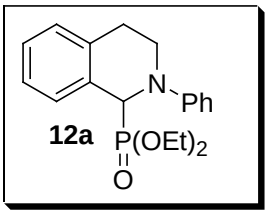
IR: ν_{max} /cm^{-1} 2979, 2929, 2844, 2225 (C≡N), 1657, 1588, 1494, 1388, 1289, 1246, 1161, 1021, 966, 829, 806, 741.

MS (EI, 70 eV): m/z = 120.1 (39.25), 233.1 (95.19), 264.2 (100.00) [M^+].

General procedure for the preparation of *α*-amino phosphonates

In a 5 mL snap vial equipped with magnetic stirring bar the tetrahydroisoquinoline derivative (1 eq) and eosin Y (0.02 eq) were dissolved in DMF (0.238 mmol/mL). Then dialkyl phosphonate (4 eq) was added and the resulting mixture was irradiated through the vial's plane bottom side using green LEDs. After the reaction was completed (monitored by TLC), the mixture was transferred to the separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by silica gel column chromatography using hexane/ethyl acetate as eluent.

1-Phenyl-2-diethylphosphonate-1,2,3,4-tetrahydroisoquinoline (12a)[8]



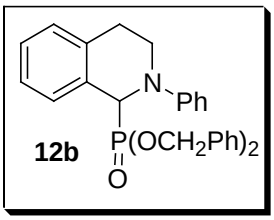
^{1}H NMR (300MHz, $CDCl_3$):

δ ppm 7.39-7.36(m, 1H), 7.29-7.13(m, 5H), 6.99(d, *J* = 8.3 Hz, 2H), 6.80(t, *J* = 7.3 Hz, 1H), 5.20(d, *J* = 20.0 Hz, 1H), 4.14-3.86(m, 5H), 3.65-3.61(m, 1H), 3.07-3.02(m, 2H), 1.25(t, *J* = 7.1 Hz, 3H), 1.15(t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):

δ ppm 149.4(d, *J* = 5.7 Hz), 136.4(d, *J* = 5.4 Hz), 130.7, 129.1, 128.7(d, *J* = 2.4 Hz), 128.1(d, *J* = 4.5 Hz), 127.4(d, *J* = 3.5 Hz), 125.9(d, *J* = 2.7 Hz), 118.4, 114.6, 63.3(d, *J* = 7.3 Hz), 62.3(d, *J* = 7.6 Hz), 58.8(d, *J* = 159.2 Hz), 43.5, 26.7, 16.4(d, *J* = 6.3 Hz), 16.4(d, *J* = 6.4 Hz).

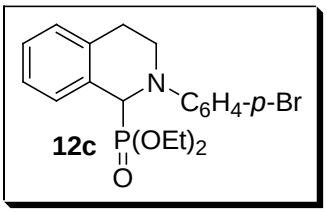
1-Phenyl-2-dibenzylphosphonate-1,2,3,4-tetrahydroisoquinoline (12b)[8]



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.38-7.11(m, 16H), 6.98(d, *J* = 8.3 Hz, 2H), 6.81(t, *J* = 7.2 Hz, 1H), 5.30(d, *J* = 19.6 Hz, 1H), 5.05-4.69(m, 4H), 4.07- 3.99(m, 1H), 3.67-3.59(m, 1H), 3.08-2.99(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 149.2(d, *J* = 5.4 Hz), 136.5(d, *J* = 5.5 Hz), 136.3(d, *J* = 6.1 Hz), 136.2(d, *J* = 6 Hz), 130.4, 129.2, 128.8(d, *J* = 2.4 Hz), 128.4(d, *J* = 6.4 Hz), 128.2, 128.2, 128.1, 128.0(d, *J* = 3.7 Hz), 127.5(d, *J* = 3.6 Hz), 126.0(d, *J* = 2.9 Hz), 118.6, 114.8, 68.6(d, *J* = 7.3 Hz), 67.7(d, *J* = 7.7 Hz), 59.0(d, *J* = 158.1 Hz), 43.5, 26.8.

1-*(*4-Bromophenyl)-2-diethylphosphonate-1,2,3,4-tetrahydroisoquinoline (12c)



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.39-7.29(m, 3H), 7.22-7.14(m, 3H), 6.84(d, *J* = 9.1 Hz, 2H), 6.83-6.79(m, 2H), 5.10(d, *J* = 19.2 Hz, 1H), 4.20-3.73(m, 5H), 3.57-3.49(m, 1H), 3.20- 3.10(m, 2H), 1.23(t, *J* = 7.0 Hz, 3H), 1.14(t, *J* = 7.1 Hz, 3H).

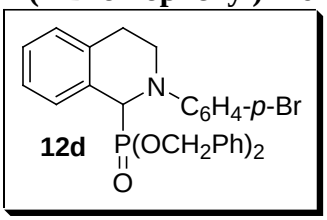
^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 148.3(d, *J* = 5.0 Hz), 136.3(d, *J* = 5.6 Hz), 131.8, 130.3, 128.6(d, *J* =2.7 Hz), 128.1(d, *J* = 4.6 Hz), 127.6(d, *J* = 3.4 Hz), 126.0(d, *J* = 2.7 Hz), 116.1, 110.3, 63.3(d, *J* = 7.3 Hz), 62.4(d, *J* = 7.7 Hz), 58.7(d, *J* = 159.6 Hz), 43.6, 26.9, 16.4(d, *J* = 5.5 Hz), 16.4(d, *J* = 5.5 Hz).

^{31}P NMR (121 MHz, $CDCl_3$):
δ ppm 22.41(s).

IR: ν_{max} /cm^{-1} 3065, 3028, 2929, 2906, 1594, 1588, 1504, 1493, 1389, 1245, 1048, 1022, 964.

HRMS:
Calculated for $C_{19}H_{23}BrNO_3P$ ($M^{+\cdot}$) : 423.0599; Found: 423.0604.

1-(4-Bromophenyl)-2-dibenzylphosphonate-1,2,3,4-tetrahydroisoquinoline (12d)



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.32-7.14(m, 14H), 7.11-7.08(m, 2H), 6.81(d, *J* = 9.1 Hz, 2H), 5.19(d, *J* = 18.7 Hz, 1H), 5.02-4.70(m, 4H), 3.98-3.89(m, 1H), 3.55-3.47(m, 1H), 3.12-2.96(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 148.1(d, *J* = 4.6 Hz), 136.3(d, *J* = 5.3 Hz), 136.1(d, *J* = 3.0 Hz), 136.0(d, *J* = 3.1 Hz), 131.8, 130.1, 128.7(d, *J* = 2.7 Hz), 128.6, 128.5, 128.4, 128.4, 128.3, 128.2(d, *J* = 5.0 Hz), 128.0, 127.9, 127.8(d, *J* = 3.5 Hz), 126.1(d, *J* = 2.9 Hz), 116.2, 110.4, 68.6(d, *J* = 7.4 Hz), 67.8(d, *J* = 7.9 Hz), 58.9(d, *J* = 158 Hz), 43.6, 27.0.

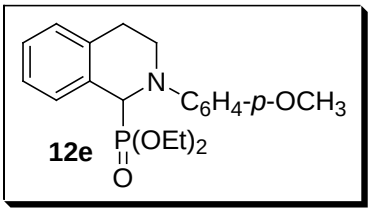
^{31}P NMR (121 MHz, $CDCl_3$):
δ ppm 23.5(s).

mp: 172-173°C

IR: ν_{max} /cm^{-1} 3031, 2946, 2895, 1508, 1495, 1259, 988, 994, 917, 764, 747.

HRMS:
Calculated for $C_{29}H_{27}BrNO_3P$ ($M^{+\cdot}$) : 547.0912; Found: 547.0919.

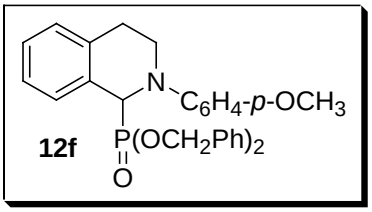
1-(4-Methoxyphenyl)-2-diethylphosphonate-1,2,3,4-tetrahydroisoquinoline (12e)[8]



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.40-7.30(m, 1H), 7.18-7.10(m, 3H), 6.94-6.89(m, 2H), 6.81-6.78(m, 2H), 5.02(d, 1H, *J* = 21.5 Hz), 4.19-3.87(m, 5H), 3.73(s, 3H), 3.57-3.49(m, 1H), 2.94- 2.89(m, 2H), 1.25(t, *J* = 7.1 Hz, 3H), 1.15(t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 153.1, 144.1(d, *J* = 8.2 Hz), 136.4(d, *J* = 5.8 Hz), 130.5, 128.9(d, *J* = 2.4 Hz), 128.1(d, *J* = 4.4 Hz), 127.2(d, *J* = 3.5 Hz), 125.8(d, *J* = 2.9 Hz), 117.5, 114.5, 63.3(d, *J* = 7.3 Hz), 62.2(d, *J* = 7.6 Hz), 59.4(d, *J* = 158.6 Hz), 55.6, 44.6, 26.1, 16.5(d, *J* = 5.6 Hz), 16.4(d, *J* = 5.7 Hz).

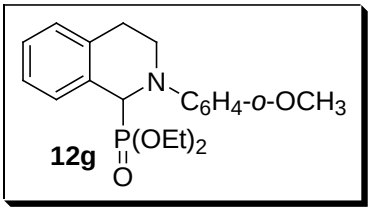
1-(4-Methoxyphenyl)-2-dibenzylphosphonate-1,2,3,4-tetrahydroisoquinoline (12f)[8]



^{1}H NMR (300 MHz, $CDCl_3$):
δ ppm 7.39-7.13(m, 14H), 6.93(d, *J* = 9.1 Hz, 2H), 6.81(d, *J* = 9.1 Hz, 2H), 5.16(d, *J* = 22.1 Hz, 1H), 5.08-4.82(m, 4H), 4.10-4.02(m, 1H), 3.75(s, 3H), 3.59-3.51(m, 1H), 3.02-2.88(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 153.2, 144.0(d, *J* = 8.1 Hz), 136.5(d, *J* = 5.8 Hz), 136.3(d, *J* = 6.0 Hz), 130.2, 129.0(d, *J* = 2.7 Hz), 128.4(d, *J* = 5.8 Hz), 128.3, 128.2, 128.1, 128.0, 127.9, 127.4(d, *J* = 3.0 Hz), 125.9(d, *J* = 2.9 Hz), 117.7, 114.5, 68.7(d, *J* = 7.3 Hz), 67.7(d, *J* = 7.9 Hz), 59.7(d, *J* = 157.2 Hz), 55.6, 44.7, 26.2.

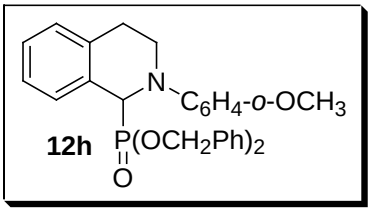
1-*(*2-Methoxyphenyl)-2-diethylphosphonate-1,2,3,4-tetrahydroisoquinoline (12g)[8]



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.46-7.43(m, 1H), 7.20-7-16(m, 2H), 7.12-7.09(m, 1H), 6.99-6.93(m, 1H), 6.91-6.81(m, 3H), 5.16(d, *J* = 21.8 Hz, 1H), 4.04- 3.80(m, 5H), 3.81(s, 3H), 3.61-3.54(m, 1H), 2.97-2.84(m, 1H), 2.75-2.69(m, 1H), 1.18(t, *J* =7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 152.5, 140.1(d, *J* = 7.8 Hz), 135.8(d, *J* = 6.0 Hz), 130.7, 129.2(d, *J* = 2.5 Hz), 128.1(d, *J* = 4.0 Hz), 127.0(d, *J* = 3.6 Hz), 125.5(d, *J* = 3.1 Hz), 123.0, 121.7, 120.8, 111.6, 63.0(d, *J* = 7.3 Hz), 61.9(d, *J* = 7.3 Hz), 58.7(d, *J* = 146.9 Hz), 55.4, 44.3, 26.5, 16.3(d, *J* = 6.0 Hz).

1-(2-Methoxyphenyl)-2-dibenzylphosphonate-1,2,3,4-tetrahydroisoquinoline (12h)[8]



^{1}H NMR (300MHz, $CDCl_3$):
δ ppm 7.47(d, *J* = 7.4 Hz, 1H), 7.37-7.09(m, 12H), 7.03-6.97(m, 1H), 6.92- 6.79(m, 3H), 5.29(d, *J* = 22.5 Hz, 1H), 5.06-4.90(m, 3H), 4.85-4.78(m, 1H), 4.16-4.10(m, 1H), 3.77(s, 3H), 3.67-3.60(m, 1H), 2.95-2.80(m, 1H), 2.74- 2.69(m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$):
δ ppm 152.6, 141.3, 139.9(d, *J* = 8.5 Hz), 136.9(d, *J* = 6.8 Hz), 136.5(d, *J* = 6.1 Hz), 136.0(d, *J* = 6.3 Hz), 130.4, 129.4(d, *J* = 2.5 Hz), 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 127.2(d, *J* = 3.7 Hz), 125.7(d, *J* = 3.2 Hz), 123.3, 121.8, 120.9, 111.6, 68.5(d, *J* = 7.2 Hz), 67.4(d, *J* = 7.5 Hz), 59.3(d, *J* = 149.6 Hz), 55.3, 44.6, 26.3.

Starch-Iodine test for the detection of H_2O_2

After the reaction was completed (monitored by TLC), aqueous potassium iodide was added. The aqueous layer turned to light brown-blue color and the color was enhanced by addition of starch. To the same aqueous layer, aqueous sodium thiosulfate was added and the solution immediately turned colorless.

The chemical equations involved in this reaction:

$$H_2O_2 + 2KI_{(aq)} \longrightarrow I_{2(aq)} + 2K^+_{(aq)}$$ (light brown color solution)

$$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$ (colorless solution)

Δ*G* values of electron transfer calculated from Rehm-Weller equation

Singlet excited state energy of eosin Y[9]

E_{00} (^{1}S) = 2.31 V

Oxidation and reduction potentials of eosin Y[9,10]

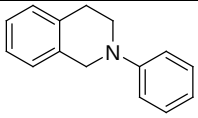
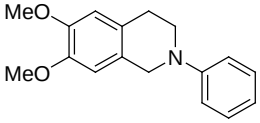
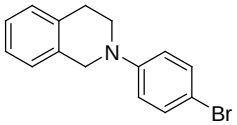
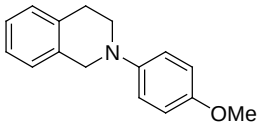
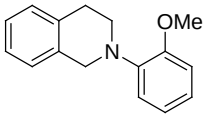
For rough estimation of excited state redox potentials we can also use the following equation[11]

E^0 ($D^{\cdot+}$/D*) = E^0 ($D^{\cdot+}$/D) – E_{00}
E^0 (A*/$A^{\cdot-}$) = E^0 (A/$A^{\cdot-}$) + E_{00}

Gibbs free energy of the electron transfer from tetrahydroisoquinoline to the excited eosine Y in acetonitrile can be calculated using Rehm-Weller equation[12]

ΔG (kcal/mol) = 23.06($E_{ox} - E_{red} - e_0^2/a\varepsilon - E_{00}$)

where E_{ox} and E_{red} are oxidation potential of tetrahydroisoquinoline and reduction potential of eosine Y, $e^2/\varepsilon a$ is Coulombic term (0.06 kcal mol^{-1}; lit.[12]).

Tetrahydroisoquinoline	Oxidation potential / V	ΔG / kcal.mol^{-1}
	0.82	-11.3
	0.82	-11.3
	0.88	-7.6
	0.62	-15.9
	0.81	-11.5

Note: (a) Eosin Y potentials are in reference to SCE in acetonitrile. (b) All oxidation potentials of tetrahydroisoquinoline derivatives are reported in reference to the SCE in acetonitrile (the potentials were measured in reference to ferrocene/ferrocenium and then converted in to SCE according to Pavlishchuk, V. V.; Addison, A. W. *Inorganica. Chimica. Acta* **2000**, *298*, 97-102.)

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1 *(a) Li, Z.; Li, C.-J. J. Am. Chem. Soc.* **2005**, *127,* 3672-3673. (b) Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 581-584.

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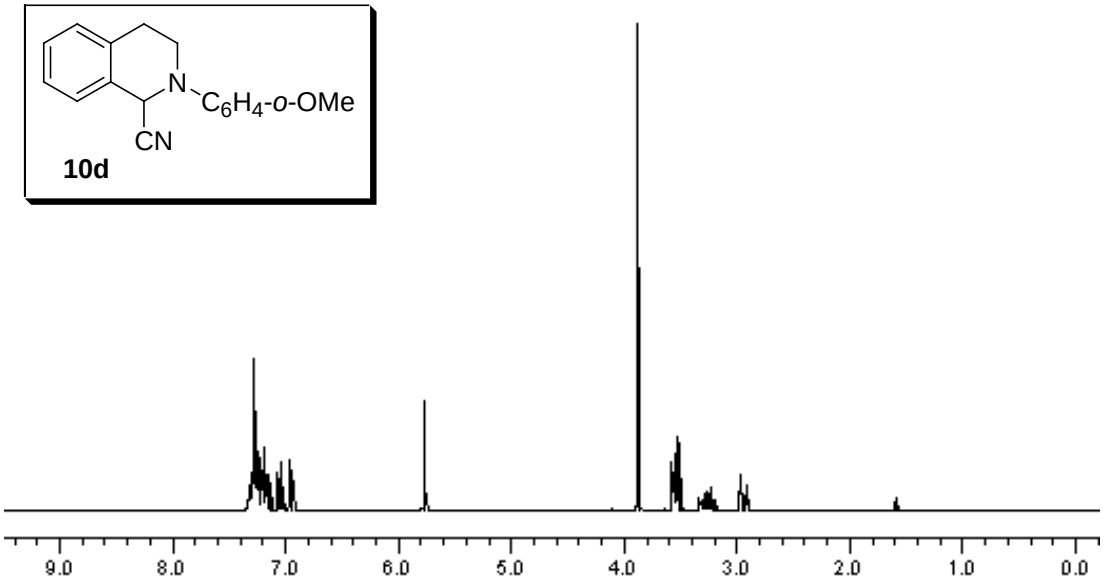
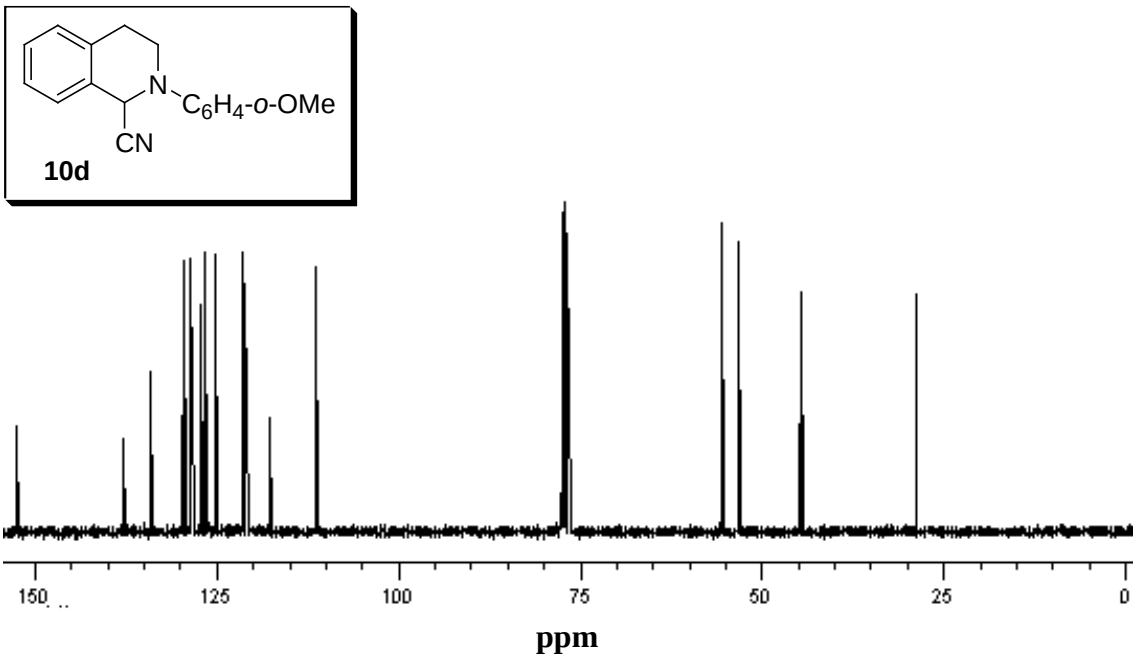
2) ^{1}H and ^{13}C NMR spectra of all new compounds

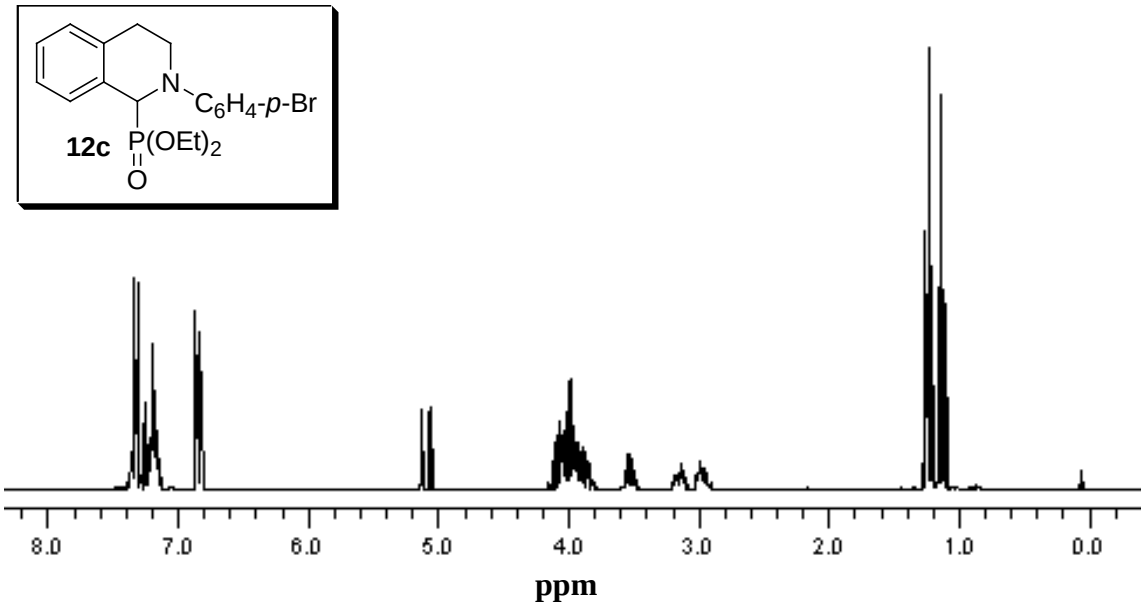
^{1}H NMR (300MHz, $CDCl_3$)



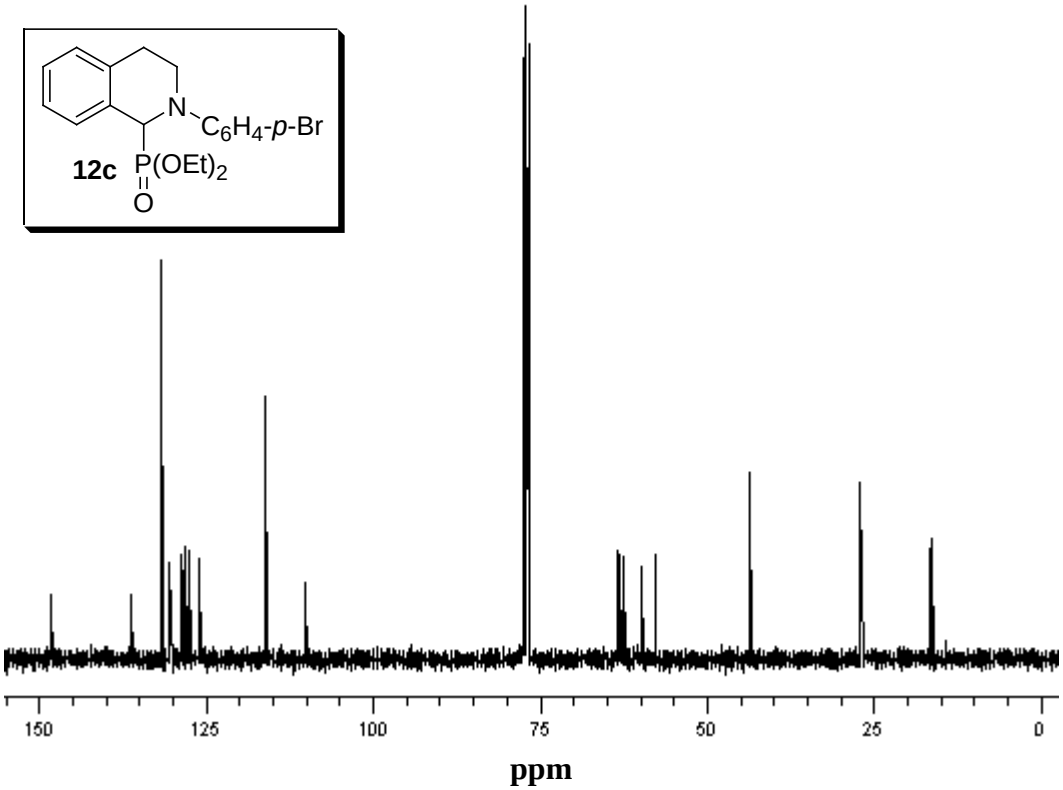
^{13}C NMR (75 MHz, $CDCl_3$)



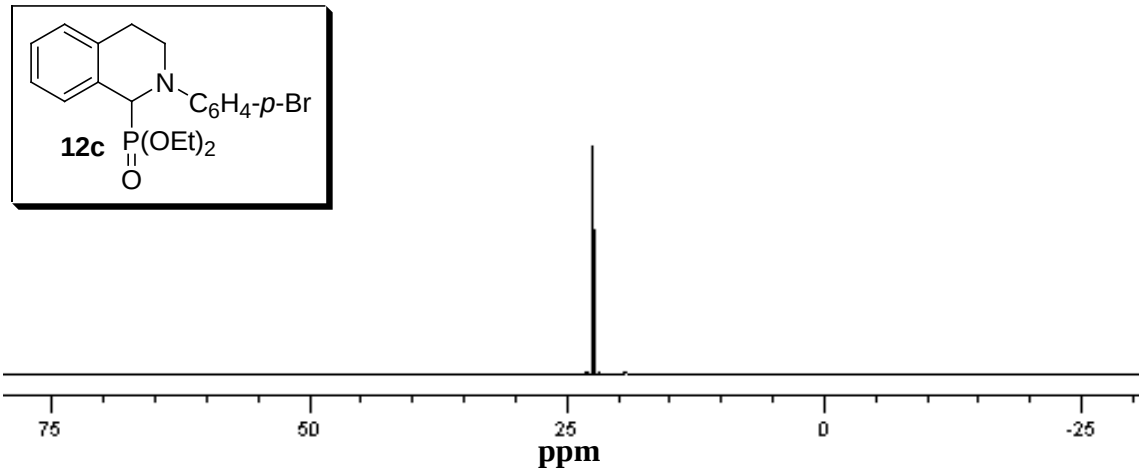
^{1}H NMR (300MHz, $CDCl_3$)



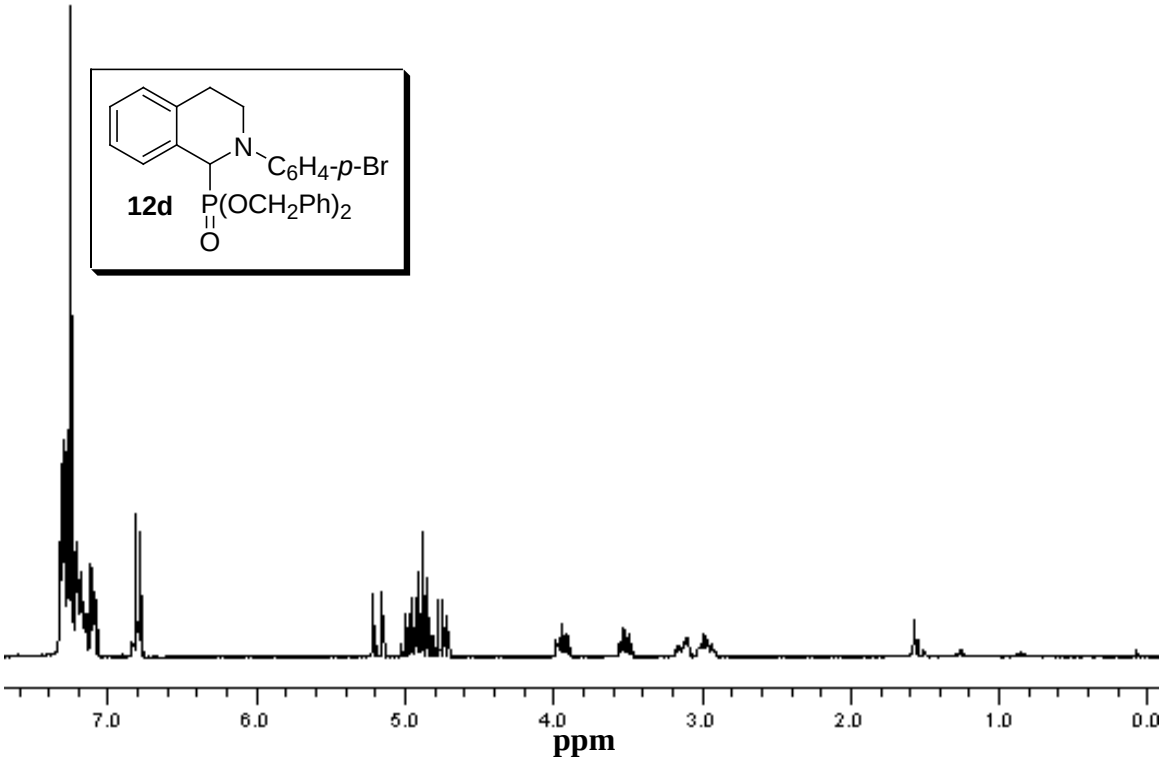
^{13}C NMR (75 MHz, $CDCl_3$)



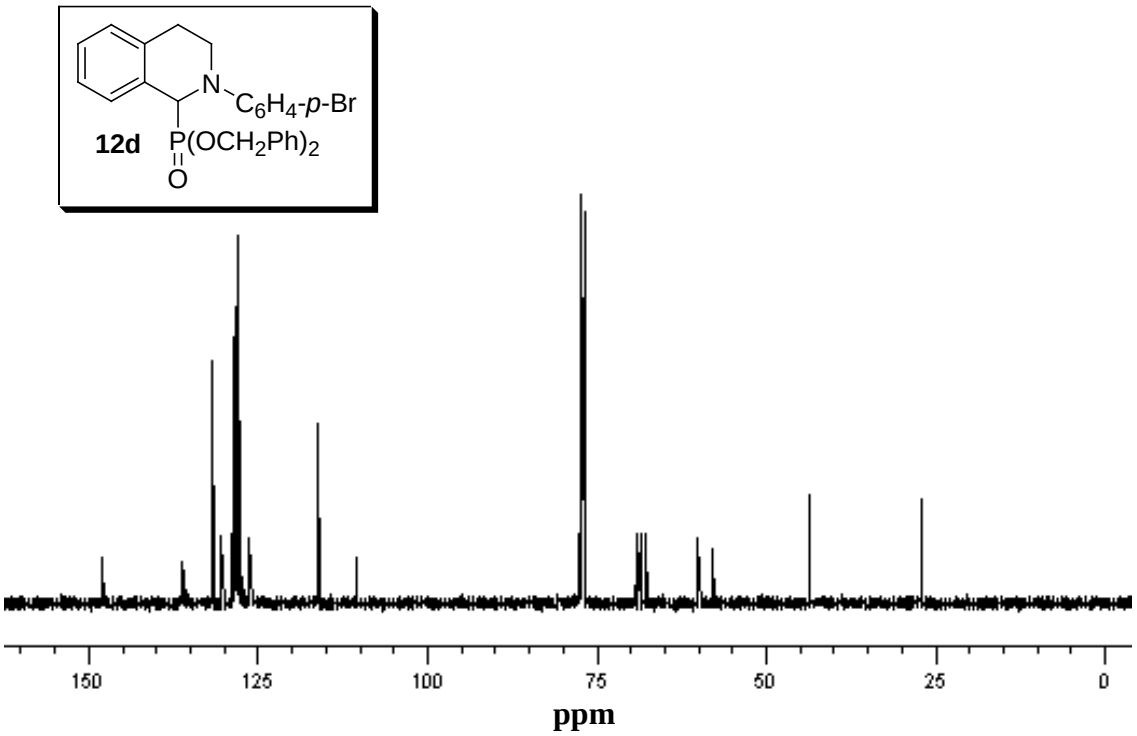
^{31}P NMR (121 MHz, $CDCl_3$)



^{1}H NMR (300MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{31}P NMR (121 MHz, $CDCl_3$)