Supporting Information

A Chiral Porous Organic Polymer as Heterogeneous Ligand for Enantioselective Pd-Catalyzed C(sp^3)–H Functionalization

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1. General Information

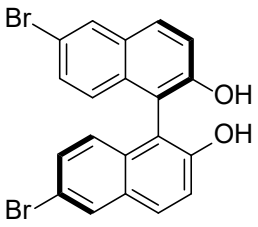
Chemicals

All chemicals were reagent grade and used as received without further purification. 4-iodotoluene was acquired from Fluka Chemie Ag and the remaining chemicals were from Sigma Aldrich: (*R*)-1,1'-Bi-2-naphthol, bromine, tetrakis(triphenylphosphine)palladium(0), 5 wt.% Pd/C (catalog number 75992), potassium vinyltrifluoroborate, K_2CO_3, PCl_3, $P(NMe_2)_3$, morpholine, *N*-methyl-2-pyrrolidone, Et_3N, dibenzylether, $Pd(dba)_2$, $Pd_2(dba)_3$, $Pd_2(dba)_3 \cdot CHCl_3$, Cs_2CO_3, *m*-xylene, *p*-xylene, 4-iodoanisole, 4-iodotoluene, 4-fluoro-1-iodobenzene, styrene, divinylbenzene, AIBN, thionylchloride, 3-(3-methoxyphenyl)-1-propionic acid, 3-(3-methylphenyl)-1-propionic acid, 3-(3-fluorophenyl)-1-propionic acid, 3-(4-fluorophenyl)-1-propionic acid, 3-(3,5-dimethylphenyl)-1-propionic acid, 3-phenylpropionyl chloride, and 8-aminoquinoline.

Equipment

Anhydrous solvents were dried/purified using the solvent purification system Puresolv MD-7. TEM images were obtained from a Technai T20 G2 microscope from TEI. STEM images are from a FEI Titan 80-300ST with 300 kV voltage. SEM images were taken on a Quanta 200 ESEM FEG microscope from FEI. Samples were deposited on 300 mesh Cu grids with no prior treatment. N_2-physisorption was conducted on a Micrometrics 3Flex instrument at 77 K. Samples for N_2-physisorption were degassed 24 hours before the analysis on a Micrometrics VacPrep 061 Sample Degas System at room temperature. TGA was performed on a Mettler Toledo TGa/DSC 1 STARe System. XRF analysis was conducted on a PANalytical Epsilon3 system. X-ray Powder diffraction was measured with a Cu-Kα radiation source on a HUBER G760 Guinier camera. The enantiomeric excess was determined by HPLC with a chiral stationary phase. ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR were measured on a Bruker Ascend 400 (400 Hz) with chemical shifts in ppm reported relative to the solvent peak. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublets of doublets; dt, doublet of triplets. ^{31}P MAS NMR spectra were recorded with a Bruker AVANCE III HD spectrometer operating at a 14.1 T magnetic field with a 4 mm o.d. CP/MAS BBFO probe. A ^{31}P-^{1}H CP/MAS spectrum was acquired using a ramped contact pulse of 3 ms, an interscan delay of 3 seconds and 392 transient scans. In addition, a simple *bloch-decay* experiment was acquired with an interscan delay of 90 seconds and 1024 transient scans allowing for a quantitative analysis of the present phosphor sites. High-power SPINAL-64 ^{1}H decoupling was employed for all experiments. Spectra were acquired with spinning frequencies between 8 and 15 kHz in order to identify the isotropic chemical shifts. These are reported relative to $NH_4H_2PO_4$ (0.81 ppm).

2. Synthesis of POPs containing Chiral Phosphoramidites

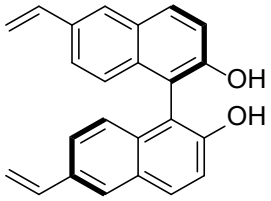


(*R*)-6,6'-Dibromo-2,2'-dihydroxy-1,1'-dinaphthyl (1)[1]

(*R*)-BINOL (5 g, 17.5 mmol) was dissolved in anhydrous CH_3CN (90 mL) with a magnetic stir bar and kept at 0 °C. Br_2 (8.38 g, 2.7 mL, 52.4 mmol) was added dropwise to the solution and left to stir for 3 hours. The mixture was quenched with Na_2SO_3, and the organic phase was extracted 3 times with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, and the solvent removed yielding a white powder (6.70 g, 86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$,) δ 8.05 (d, *J* = 2.0 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.44-7.34 (m, 4H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.05 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.0, 131.9, 130.9, 130.7, 130.6, 130.4, 125.9, 119.0, 118.0, 110.6.



(*R*)-6,6'-Divinyl-2,2'-dihydroxy-1,1'-dinaphthyl (2)[2]

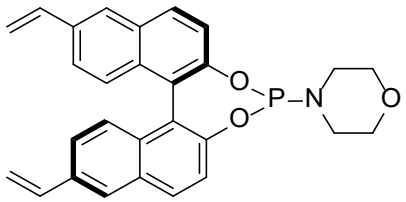
(*R*)-6,6'-Dibromo-2,2'-dihydroxy-1,1'-dinaphthyl (**1**) (888 mg, 2.00 mmol), potassium vinyltrifluoroborate (964 mg, 7.20 mmol), and $Pd(PPh_3)_4$ (231 mg, 0.20 mmol) were weighed off in a round-bottom flask and a stir bar was added. The setup was connected to a reflux condenser and made inert by 3 vacuum/N_2 cycles with Schlenk techniques. Degassed THF (60 mL) and degassed 1M K_2CO_3 (12 mL) were added and the mixture was kept at refluxing conditions at 75 °C for 24 h. Next, the reaction was cooled down to room temperature, water (30 mL) was added, and the organic residues were extracted with heptane. The combined organic phase was dried over $MgSO_4$, concentrated, and purified by silica gel chromatography (9:1 heptane:EtOAc) affording the product as a white solid (490 mg, 72% yield).

[1] The synthesis of (*R*)-6,6'-dibromo-2,2'-dihydroxy-1,1'-dinapthyl (**1**) was adapted from Aoyagi, N.; Ogawa, N.; Izumi, T. *Tetrahedron Lett.*, **2006**, *47*, 4797-4801.

[2] The synthesis of (*R*)-6,6'-divinyl-2,2'-dihydroxy-1-1'-dinapthyl (**2**) was adapted from Liang, Z.; Chen, J.; Chen, X.; Zhang, K.; Lv, J.; Zhao, H.; Zhang, G.; Xie, C.; Zong, L.; Jia, X. *Chem. Commun.,* **2019**, *55*, 13721-13724.

^{1}H-NMR (400 MHz, $CDCl_3$,) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 1.7 Hz, 2H), 7.46 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.85 (dd, *J* = 17.6 Hz, 10.9 Hz, 2H), 5.79 (d, *J* = 17.6 Hz, 2H), 5.29 (d, *J* = 10.9 Hz, 2H) 5.10 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.8, 136.5, 133.5, 133.0, 131.6, 129.5, 126.7, 124.9, 124.5, 118.1, 113.9, 110.9.



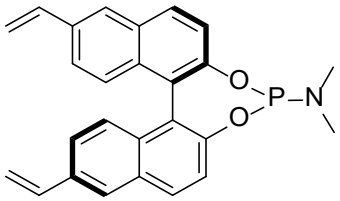
***O*,*O*'-(*R*)-(6,6'-Divinyl-1,1'-Dinaphthyl-2,2'-diyl)-*N*-(1-morpholinyl)phosphoramidite (3)**

Inside an argon filled glovebox, (*R*)-6,6'-divinyl-2,2'-dihydroxy-1,1'-dinaphthyl (**2**) (200 mg, 0.60 mmol) was mixed with one drop of NMP (*N*-methyl-2-pyrrolidone), PCl_3 (2 mL), and a magnetic stir bar in a round-bottom flask. The flask was sealed with a rubber septum. Outside the glovebox, the mixture was heated to 60 °C for 1 hour. The excess amount of PCl_3 was removed under vacuum before anhydrous THF (2 mL) was added to the mixture. A solution of morpholine (520 µL, 6.00 mmol) in anhydrous THF (2 mL) was added slowly to the mixture at 0 °C. After stirring overnight at room temperature, the mixture was quenched with water (6 mL) followed by extraction with EtOAc (3x 10 mL). The organic phase was combined, dried over $MgSO_4$, and concentrated before purified by silica gel chromatography (8:2 heptane:EtOAc) yielding the product as a white powder (146 mg, 53% yield).

^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.10 (m, 2H), 8.03 (d, *J* = 6.2 Hz, 2H), 7.64-7.56 (m, 4H), 7.16 (dd, *J* = 20.1, 8.9 Hz, 2H), 6.89 (m, 2H), 5.92 (dd, *J* = 17.6, 3.9, 2H), 5.35 (dd, *J* = 11.0, 3.5 Hz, 2H), 3.44 (t, *J* = 4.7 Hz, 4H) 2.99 (m, 2H), 2.85 (m, 2H).

^{13}C-NMR (101 MHz, d_6-DMSO) δ 149.3, 149.2, 148.9, 136.2, 133.9, 133.7, 131.6, 131.6, 131.4, 131.2, 130.8, 130.6, 126.9, 126.3, 126.2, 123.8, 123.2, 123.1, 122.4, 122.2, 121.7, 121.7, 115.0, 114.9, 66.9, 66.8, 44.1, 43.9.

^{31}P-NMR (162 MHz, d_6-DMSO) δ 144.



***O*,*O*'-(*R*)-6,6'-Divinyl-1,1'-dinathyl-2,2'-diyl)-*N*,*N*-dimethylphosphoramidite (4)**

(*R*)-6,6'-Divinyl-2,2'-dihydroxy-1,1'-dinaphthyl (**2**) (200 mg, 0.60 mmol) was weighed off in a round-bottom flask before a stir bar was added. The setup was connected to a condenser and made inert by 3 vacuum/N_2

cycles with Schlenk techniques before adding anhydrous toluene (3 mL). PMe_3 (98.0 mg, 108 µL, 0.60 mmol) was slowly added to the solution and the mixture was left to stir at refluxing conditions at 120 °C for 2 h. The mixture was cooled down to room temperature before being purified by silica gel chromatography (9:1 heptane:EtOAc) yielding the product as a white powder (86 mg, 35% yield).

^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.10 (dd, *J* = 19.2, 8.8 Hz, 2H), 8.03 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.58 (d, *J* = 8.7, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.16 (dd, *J* = 17.8, 8.9 Hz, 2H), 6.89 (ddd, *J* = 17.7, 11.0, 2.9, 2H), 5.93 (dd, *J* = 17.6, 4.3, 2H), 5.35 (dd, *J* = 11.0, 3.7 Hz, 2H), 2.48 (d, *J* = 9.8 Hz, 6H).

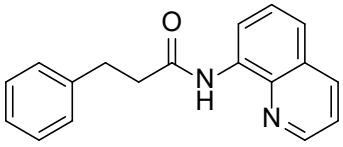
^{13}C-NMR (101 MHz, d_6-DMSO) δ 149.7, 149.7, 149.0, 136.3, 136.2, 133.8, 133.6, 131.6, 131.4, 131.1, 130.8, 130.7, 130.6, 126.9, 126.9, 126.3, 126.2, 123.8, 123.2, 123.2, 122.4, 122.3, 121.8, 121.8, 115.0, 114.9, 35.5, 35.3.

^{31}P-NMR (162 MHz, d_6-DMSO) δ 148.

Synthesis of (*R*)-P-amidite-POP

In a round-bottom flask connected to a condenser, phosphoramidite (**3**: 800 mg, 1.76 mmol or **4**: 723 mg, 1.76 mmol) and AIBN (1.35 g, 8.25 mmol) were weighed off and a stir bar was added. The setup made inert by 3 vacuum/N_2 cycles with Schlenk techniques before divinylbenzene (0.24 g, 0.27 mL, 1.87 mmol), styrene (9.09 g, 10.0 mL, 88.0 mmol), and THF (30 mL) were added and the resulting mixture was left to stir at refluxing conditions at 85 °C overnight. The POP was precipitated out by adding the reaction mixture to a stirring solution of CH_3OH. The POP was collected on a glass sintered funnel, washed with 5x CH_3OH, and dried under vacuum affording a white solid (7.46 g).

3. Synthesis of Starting Materials



3-Phenyl-*N*-(quinolin-8-yl)propionamide[3]

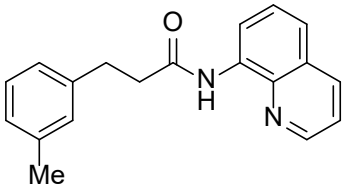
In a round-bottom flask, 8-aminoquinoline (432 mg, 3.00 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and a stir bar was added. The setup was made inert by 3 vacuum/N_2 cycles with Schlenk techniques. 3-Phenylpropionyl chloride (504 mg, 444 µL, 3.00 mmol) and Et_3N (830 µL, 6.00 mmol) were added dropwise at 0 °C. The reaction was kept at 40 °C overnight. Water (30 mL) was added to the reaction and the organic phase was extracted with 3x EtOAc. The combined organic phase was dried over $MgSO_4$, concentrated, and purified by silica gel chromatography (90:10 heptane:EtOAc) yielding a white powder (679 mg, 82% yield). NMR of the isolated product was in accordance with previous reports.[3]

[3] Synthetic procedure adapted from Tong, H-R.; Zheng, S.; Li, X.; Deng, Z.; Wang, H.; He, G.; Peng, Q.; Chen. G.; *ACS Catal.* **2018**, *8*, 11502-11512.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.83-8.76 (m, 2H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.58-7.48 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.21 (m, 1H), 3.15 (dd, *J* = 9.0, 6.7 Hz, 2H) 2.90 (dd, *J* = 9.0, 6.8 Hz, 2H).

General Procedure for Remaining substrates (not optimized)

3-Aryl-1-propionic acid (3.00 mmol) was weighed off in a round-bottom flask and a stir bar was added. The setup was made inert by 3 vacuum/N_2 cycles with Schlenk techniques. Anhydrous CH_2Cl_2 (10 mL) was added to dissolve the solid before $SOCl_2$ (322 mg, 197 µL, 2.70 mmol) was slowly added to the solution and the mixture was kept at 45 °C overnight while stirring. Next, the CH_2Cl_2 was removed under vacuum and fresh anhydrous CH_2Cl_2 (10 mL) was added. In another round-bottom flask, 8-aminoquinoline (388.8 mg, 2.7 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and a stir bar was added. The setup was made inert by 3 vacuum/N_2 cycles with Schlenk techniques. The acid chloride solution was slowly added to the solution of 8-aminoquinoline at 0 °C followed by Et_3N (830 µL, 6.00 mmol) before the reaction was heated and kept to 40 °C overnight. Next, water (30 mL) was added to the reaction and the organic phase was extracted with 3x EtOAc. The combined organic phase was washed with 1M HCl (aq) and brine before being dried over $MgSO_4$, concentrated, and purified by silica gel chromatography (90:10 heptane:EtOAc). All starting materials are known compounds with NMR in accordance with previously reports.[4]

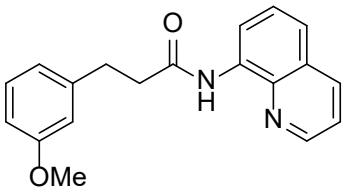


3-(3-Methylphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the general procedure and was isolated as a pale yellow solid (282 mg, 39% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.82-8.77 (m, 2H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59-7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.14-7.08 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 3.11 (dd, *J* = 9.2, 6.6 Hz, 2H) 2.89 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.32 (s, 3H).

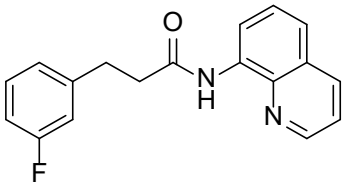
[4]Tong, H-R.; Zheng, S.; Li, X.; Deng, Z.; Wang, H.; He, G.; Peng, Q.; Chen. G.; *ACS Catal.* **2018**, *8*, 11502-11512.



3-(3-Methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the general procedure and was isolated as a yellow oil (124 mg, 15% yield).

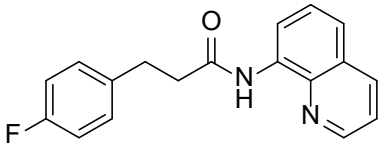
^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.84-8-72 (m, 2H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.58-7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 2.1 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.78 (s, 3H), 3.13 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.89 (dd, *J* = 9.0, 6.7 Hz, 2H).



3-(3-Fluorophenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the general procedure from 3-(3-methylphenyl)-*N*-(quinolin-8-yl)propionamide and was isolated as a pale brown solid (459 mg, 62% yield).

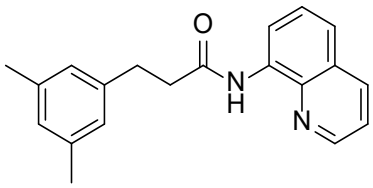
^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.87-8.63 (m, 2H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.59-7.49 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28-7.21 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.01 (dt, *J* = 9.9, 2.1 Hz, 1H), 6.93-6.85 (m, 1H), 3.15 (dd, *J* = 8.7, 6.8 Hz, 2H) 2.90 (dd, *J* = 8.7, 6.8 Hz, 2H).



3-(4-Fluorophenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the general procedure from 3-(3-methylphenyl)-*N*-(quinolin-8-yl)propionamide and was isolated as a pale yellow solid (350 mg, 48% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.84-8.67 (m, 2H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.58-7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.29-7.21 (m, 2H), 7.02-6.93 (m, 2H), 3.12 (t, *J* = 7.7 Hz, 2H) 2.87 (dd, *J* = 8.5, 6.9 Hz, 2H).



3-(3,5-Dimethylphenyl)-*N*-(quinolin-8-yl)propionamide

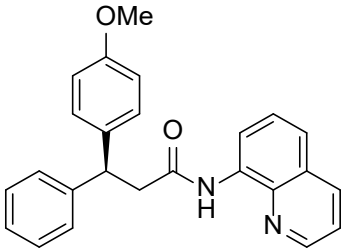
The compound was prepared according to the general procedure from 3-(3-methylphenyl)-*N*-(quinolin-8-yl)propionamide and was isolated as a yellow oil (454 mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.83-8.76 (m, 2H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.59-7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.92 (s, 2H), 6.84 (s, 1H), 3.08 (dd, *J* = 9.3, 6.6 Hz, 2H) 2.87 (dd, *J* = 9.3, 6.6 Hz, 2H), 2.28 (s, 6H).

4. Catalytic Evaluation

Standard Catalytic Reaction

In a standard catalytic experiment, Pd source (0.010-0.015 mmol Pd), 3-phenyl-*N*-(quinolin-8-yl)propionamide (0.10 mmol), aryliodide (0.30-0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and POP (0.02-0.03 mmol ligand) were mixed with a stir bar in a 4 mL vial inside an argon filled glovebox. Solvent (0.6 mL) was added to the mixture and the vial was sealed with a PTFE-lined screw cap. Outside the glovebox, the vial was put into an aluminum heating block at 100 °C for the specified time at 1000 rpm. After the specified time, the reaction mixture was cooled down to rt. before a stock solution of dibenzylether in EtOAc was added as a NMR standard – 0.5 mL of a 0.05 M stock solution. The mixture was filtered through a 0.22 µm syringe filter and concentrated on vacuum before analysis by NMR for assessing conversion and yield. The enantiomeric excess was quantified by HPLC after purification of crude mixture by silica gel chromatography (85:15 heptane:EtOAc).

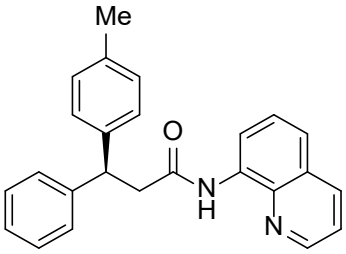


3-Phenyl-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide[5]

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02

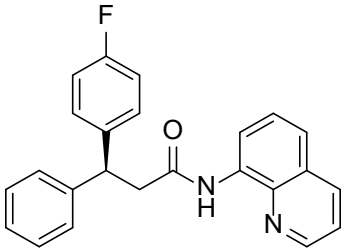
[5] The absolute configuration was determined from: Yan, S-B.; Zhang, S.; Duan, W-L. *Org. Lett.* **2015**, *17*, 2458-2461.

mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralcel-OD-H column with hexane/*i*-PrOH = 80:20, flow rate 0.9 mL/min, retention times = 22.3 min for major isomer and 26.9 min for minor isomer.



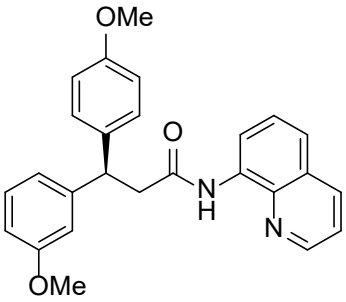
3-Phenyl-3-(4-methylphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-iodotoluene (87.2 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralpack-AD column with hexane/i-PrOH = 85:15, retention times = 15.0 min for minor isomer and 18.5 min for major isomer.



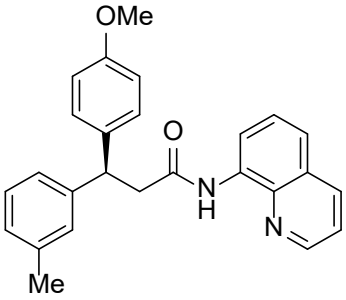
3-Phenyl-3-(4-fluorophenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-fluoro-1-iodobenzene (88.8 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralcel-OD-H column with hexane/*i*-PrOH = 80:20, retention times = 20.1 min for major isomer and 29.9 min for minor isomer.



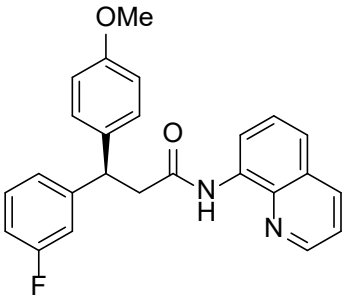
3-(3-Methoxyphenyl)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-(3-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide (30.6 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralcel-OD-H column with hexane/*i*-PrOH = 80:20, retention times = 27.6 min for major isomer and 35.1 min for minor isomer.



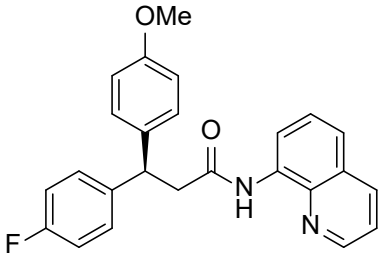
3-(3-Methylphenyl)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-(3-methylphenyl)-*N*-(quinolin-8-yl)propionamide (29.0 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralcel-OD-H column with hexane/*i*-PrOH = 85:15, retention times = 25.9 min for major isomer and 31.8 min for minor isomer.



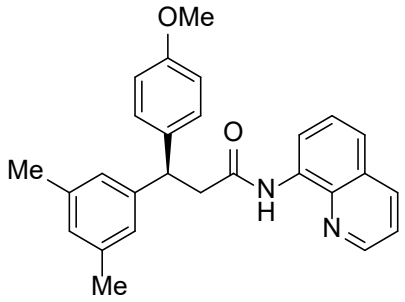
3-(3-Fluorophenyl)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-(3-fluorophenyl)-*N*-(quinolin-8-yl)propionamide (29.4 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C.
The enantiomeric excess was determined by a Chiralpack AD column with hexane/*i*-PrOH = 85:15, retention times = 25.1 min for minor isomer and 35.5 min for major isomer.



3-(4-Fluorophenyl)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-(4-fluorophenyl)-*N*-(quinolin-8-yl)propionamide (29.4 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C.
The enantiomeric excess was determined by a Chiralpack AD column with hexane/*i*-PrOH = 80:20, retention times = 27.0 min for minor isomer and 32.3 min for major isomer.



3-(3,5-Dimethylphenyl)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide

The compound was prepared according to the procedure above (standard catalytic reaction) using, Pd_2dba_3 (6.9 mg, 0.0075 mmol), 3-(3,5-dimethylphenyl)-*N*-(quinolin-8-yl)propionamide (30.4 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) applying *m*-xylene as solvent. The reaction time was 72 h at 100 °C. The enantiomeric excess was determined by a Chiralcel-OD-H column with hexane/*i*-PrOH = 85:15, retention times = 22.9 min for major isomer and 27.2 min for minor isomer.

Recycling Experiment

An experiment was started as described for 3-phenyl-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide with $Pd_2(dba)_3$ (6.9 mg, 0.0075 mmol), 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) were mixed with a stir bar in a 4 mL vial inside an argon filled glovebox. *m*-Xylene (0.6 mL) was added to the mixture and the vial was sealed with a PTFE-lined screw cap. Outside the glovebox, the vial was put into an aluminum heating block at 100 °C for 72 h at 1000 rpm. After the specified time, the reaction mixture was cooled down to rt. before a stock solution of dibenzylether in EtOAc was added as a NMR standard – 0.5 mL of a 0.05 M stock solution. The organic residues were extracted from the solids with hexane 3 times and the combined organic phase was concentrated and analyzed by NMR. The crude mixture was purified by silica gel chromatography (85:15 heptane:EtOAc) before the enantiomeric excess was quantified by HPLC on a Chiralcel-OD-H column with hexane/*i*-PrOH = 80:20, flow rate 0.9 mL/min, 22.3 min for major isomer and 26.9 min for minor isomer. The remaining solids from the extraction with hexane were dried before being taken into a glovebox and reused while either adding or not adding a fresh amount of $Pd_2(dba)_3$. Thereafter, the procedure was repeated as described in the beginning with the addition of 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), and Cs_2CO_3 (65.2 mg, 0.20 mmol) and *m*-xylene (0.6 mL).

Leaching Test

An experiment was started as described for 3-phenyl-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)propionamide with $Pd_2(dba)_3$ (6.9 mg, 0.0075 mmol), 3-phenyl-*N*-(quinolin-8-yl)propionamide (27.6 mg, 0.10 mmol), 4-iodoanisole (93.6 mg, 0.40 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and (*R*)-P-amidite-POP (187 mg, 0.02 mmol) were mixed with a stir bar in a 4 mL vial inside an argon filled glovebox. *m*-Xylene (0.6 mL) was added to the mixture and the vial was sealed with a PTFE-lined screw cap. Outside the glovebox, the vial was put into an aluminum heating block at 100 °C for 72 h at 1000 rpm. After the

specified time, the reaction mixture was cooled down to room temperature and the organic residues were extracted from the solids with hexane 3 times. The solvent was removed from the combined organic phase and the resulting mixture was dissolved 2% HNO_3 for ICP-OES, EtOAc for analysis XRF, or $CDCl_3$ for NMR.

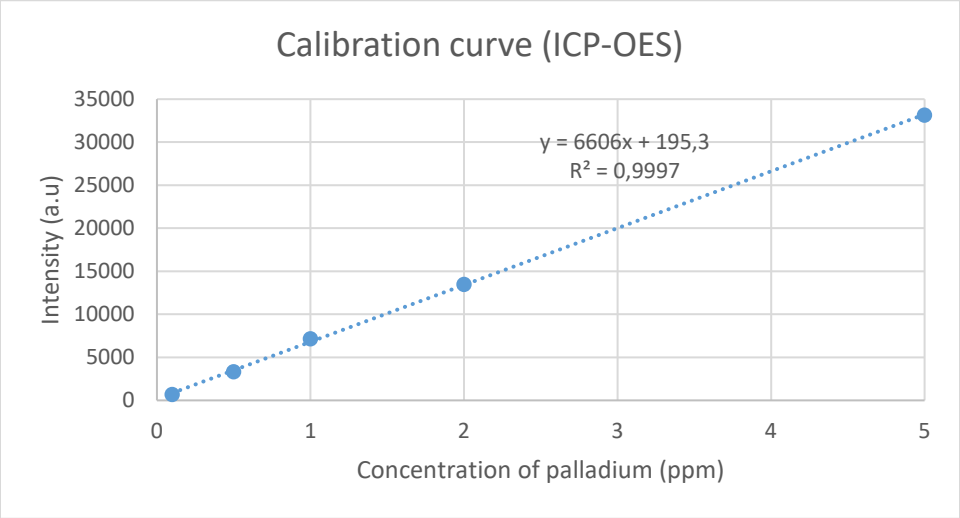


Figure S1. Calibration curve used to quantify the palladium concentration by ICP-OES.

A sample was prepared as described above in 2% HNO_3 and provided a concentration of 0.0034 ppm after being diluted 30 times from the original reaction, thus the Pd concentration from the extracted phase was 0.11 ppm or 0.004% of the original Pd loading.

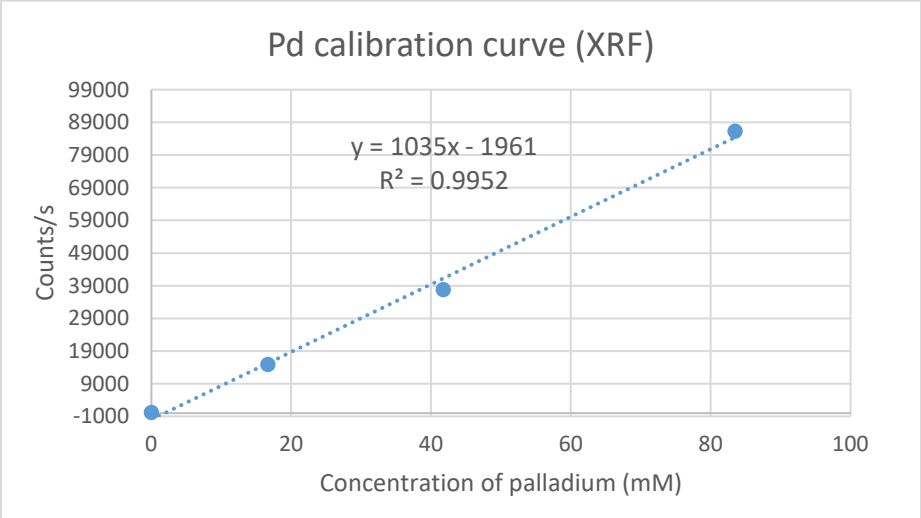


Figure S2. Calibration curve of Pd in an EtOAc solution measured on XRF with values given in table.

A sample was prepared as described above in EtOAc and provided 2612 counts/s with correlates to a Pd concentration of 0.63 mM or 2.5% of the original Pd concentration showcasing that metal leaching is not an issue for this catalytic system.

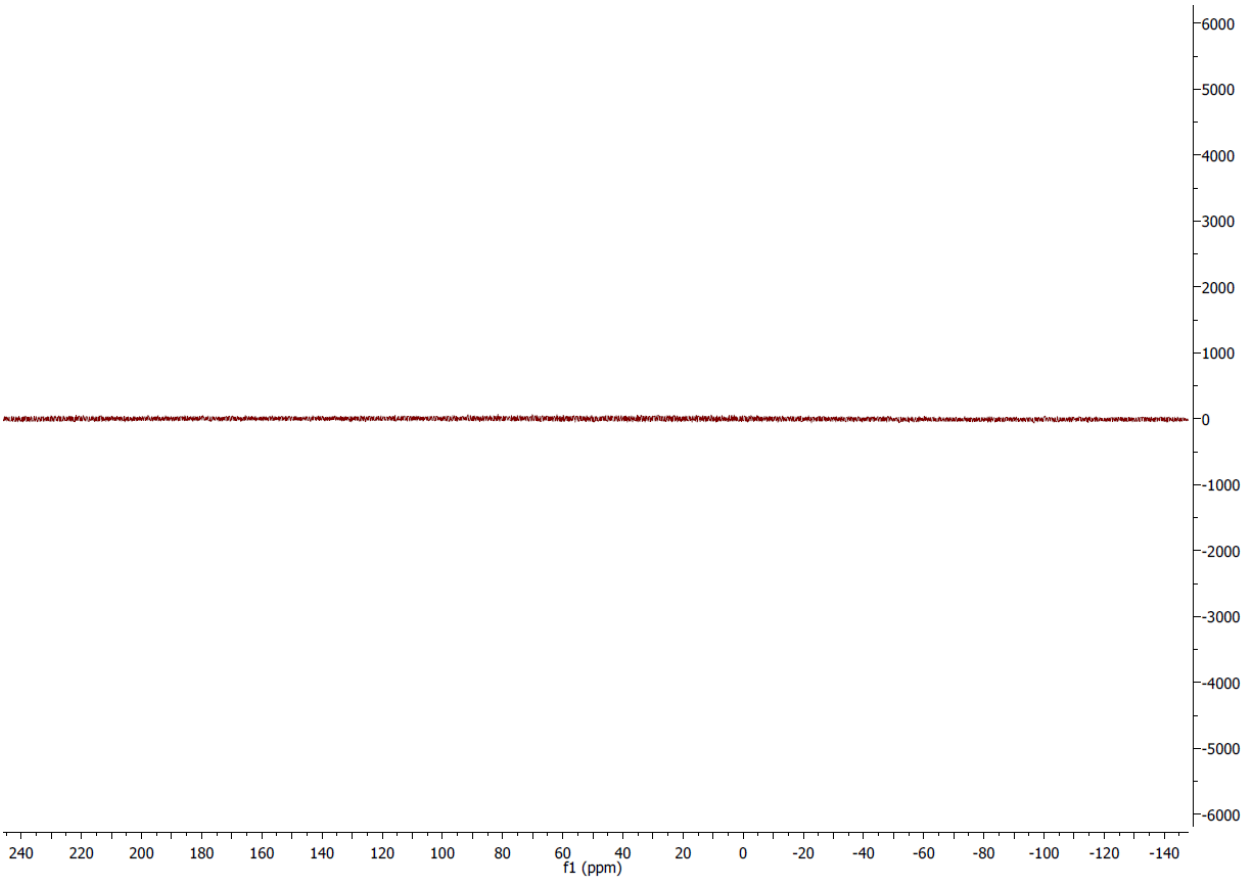


Figure S3. ^{31}P-NMR of the extracted liquid phase in $CDCl_3$.

The spectrum does not show any sign of leached phosphor containing species showcasing the heterogeneity of the ligand.

5. ^{31}P CP/MAS NMR Data and Phosphorus Quantification

Site	δ(iso) ppm	δ(CSA) ppm	ηCSA)	Relative amount
1	143.6	-145.3	0.58	0.86
2	9.6	-129	0.05	0.14

Table S1. Detailed NMR values for solid state NMR of fresh (*R*)-P-amidite-POP.

A *bloch-decay* experiment was carried out to attempt to provide quantitate data for the phosphor using $NH_4H_2PO_4$ as a reference material.

129.6 mg $NH_4H_2PO_4$ (34.9 mg P): I = 35725785.9 a.u. with 4 scans -> I = 255915 au/mg/scan.

Polymer sample: I = 101314620 au with 1024 scans.

Mass of phosphorus: P = 101314620/1024/255915 = 0.38 mg.

Polymer sample mass = 110.9 mg, m%(P) = 0.34 %wt.

Thereby, the ligand concentration in the polymer is approximately 0.11 mmol/g.

6. Modification of POP Backbone

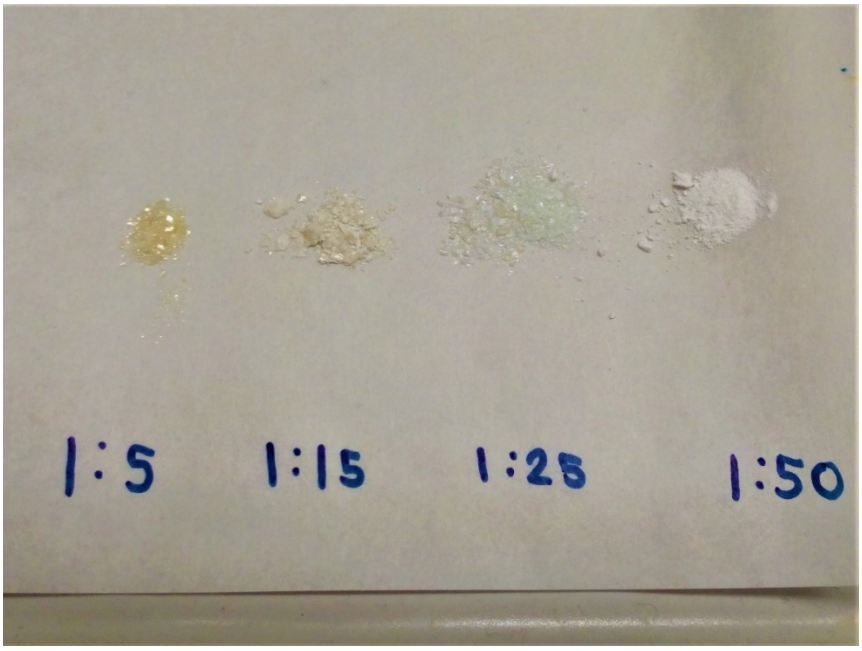


Figure S4. Picture of the synthesized POPs with various ligand to styrene ratio. From left to right the ratio increases starting from 1:5 up to 1:50.

7. Additional Characterization of the POP

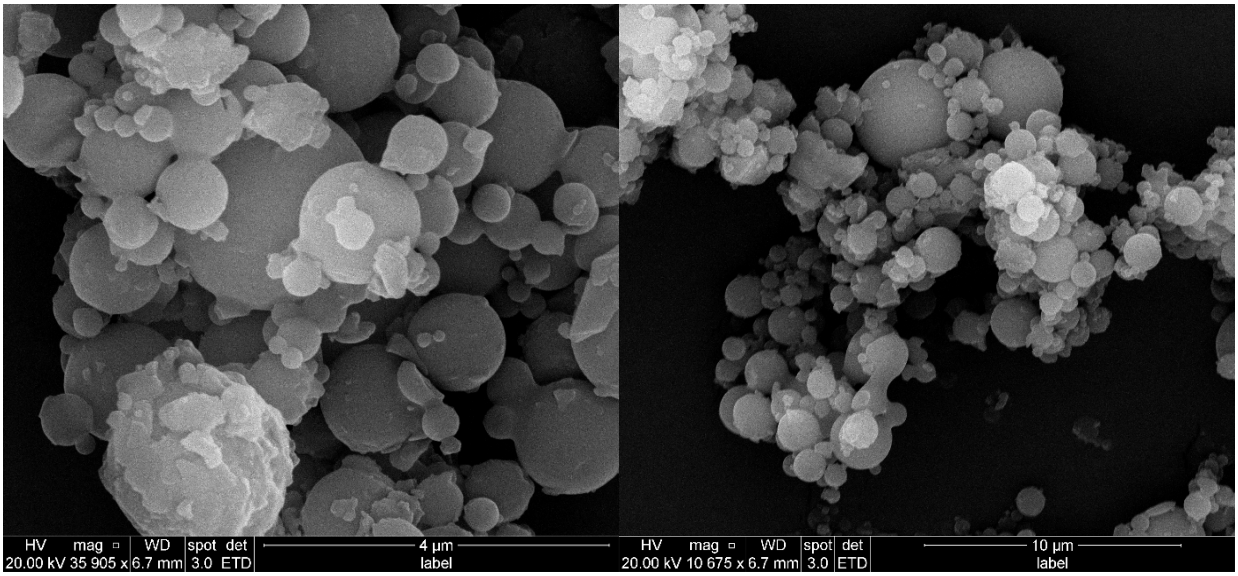


Figure S5. SEM image of the (*R*)-P-amidite-POP showing the morphology and particle size of the synthesized POP.

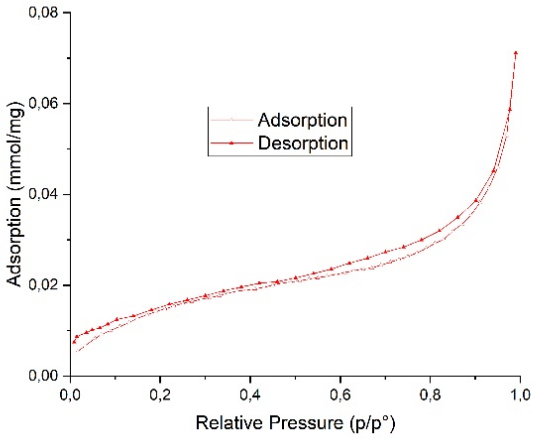


Figure S6. N_2-physisorption curve of the (*R*)-P-amidite-POP

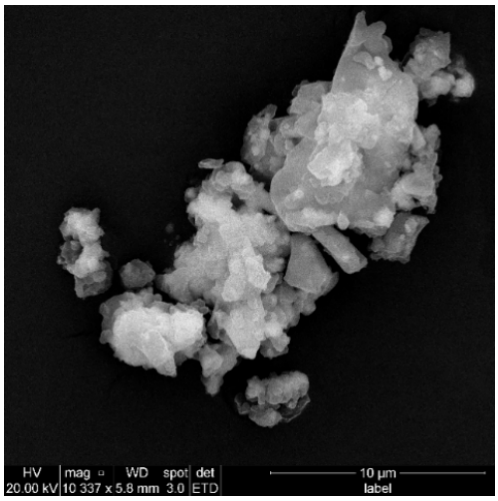


Figure S7. SEM image of the recycled (*R*)-P-amidite-POP.

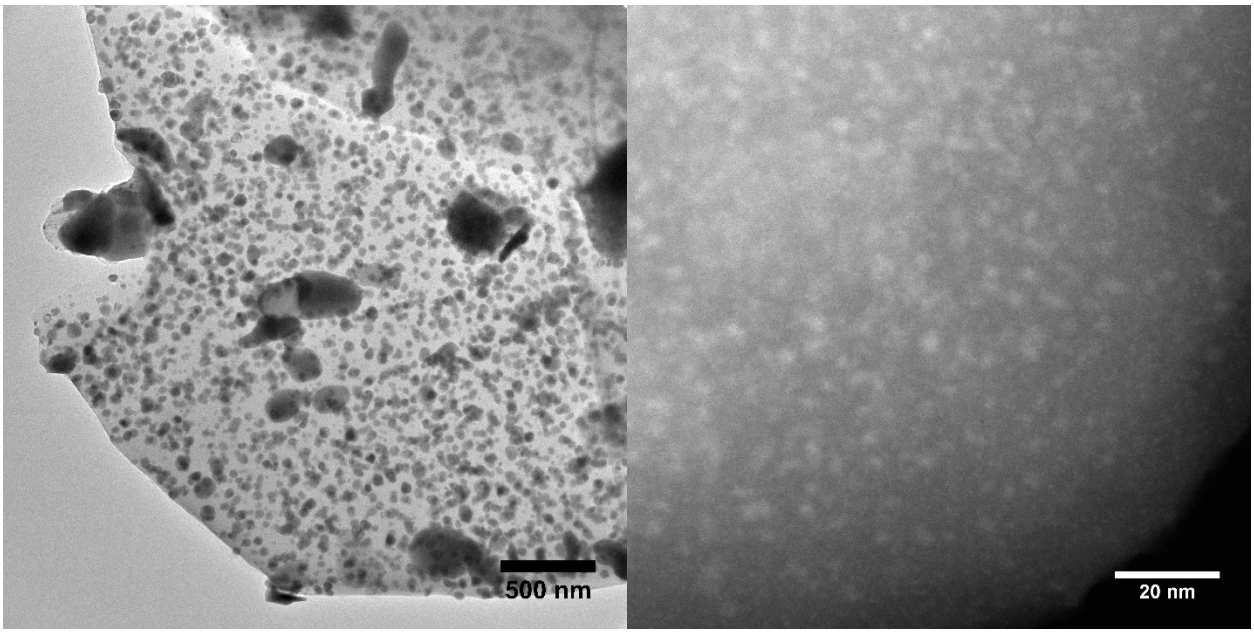


Figure 8. Additional STEM images of the used (*R*)-P-amidite-POP.

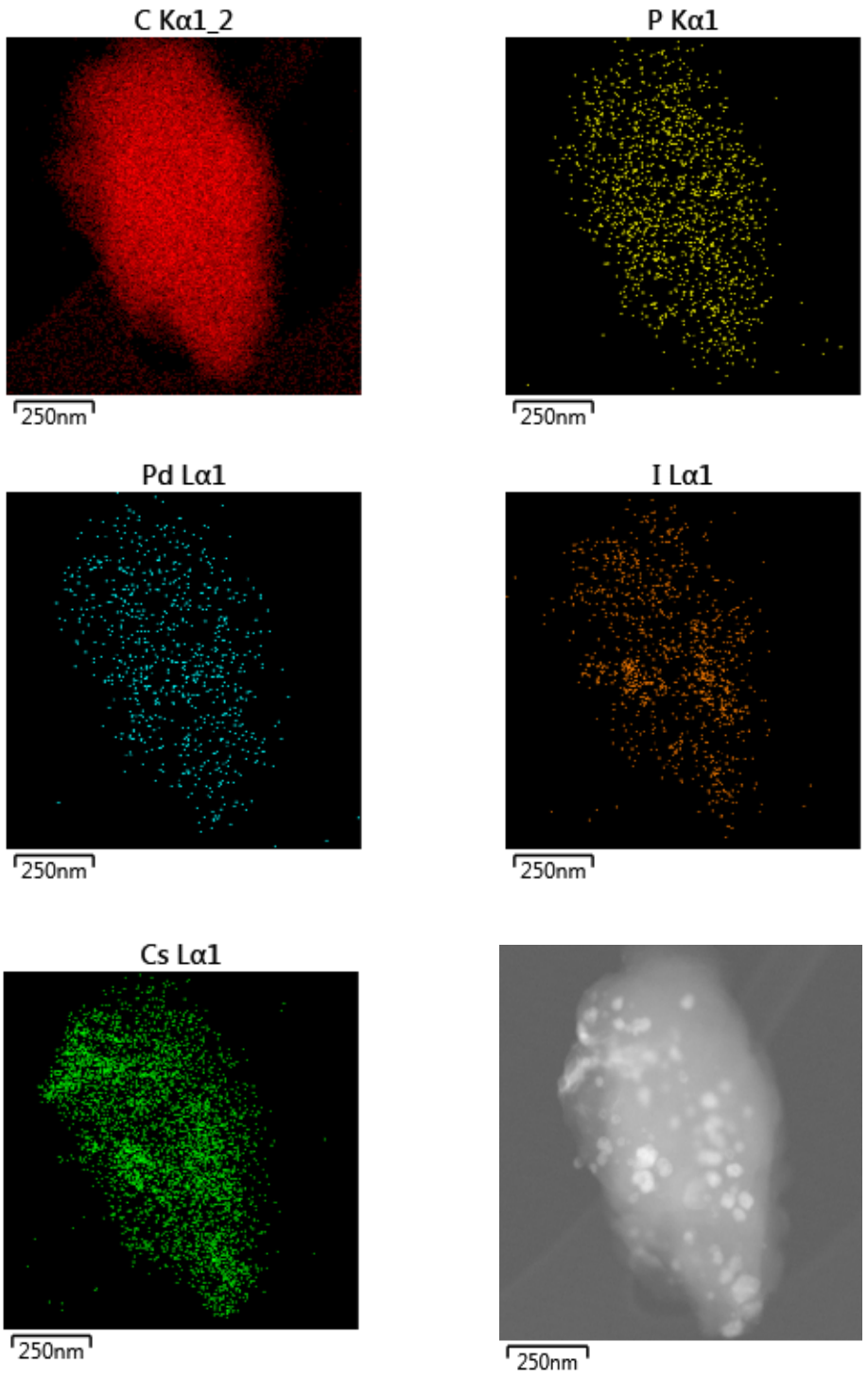
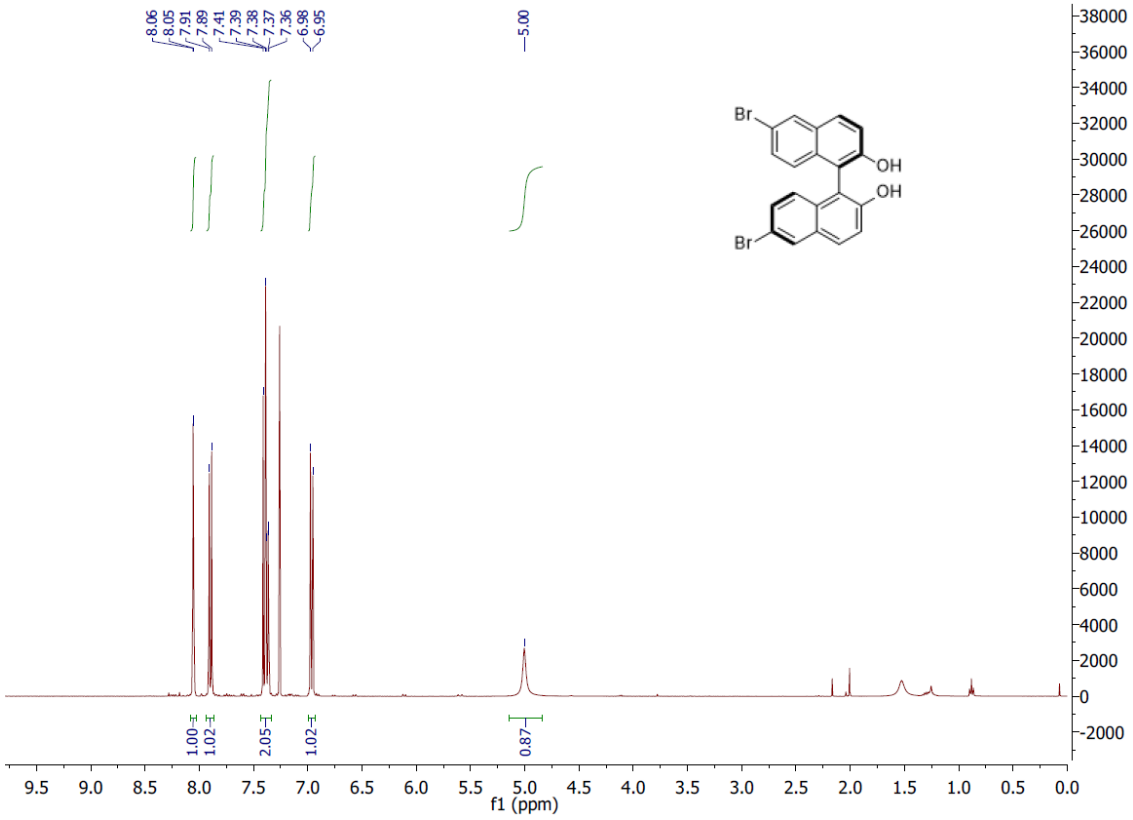
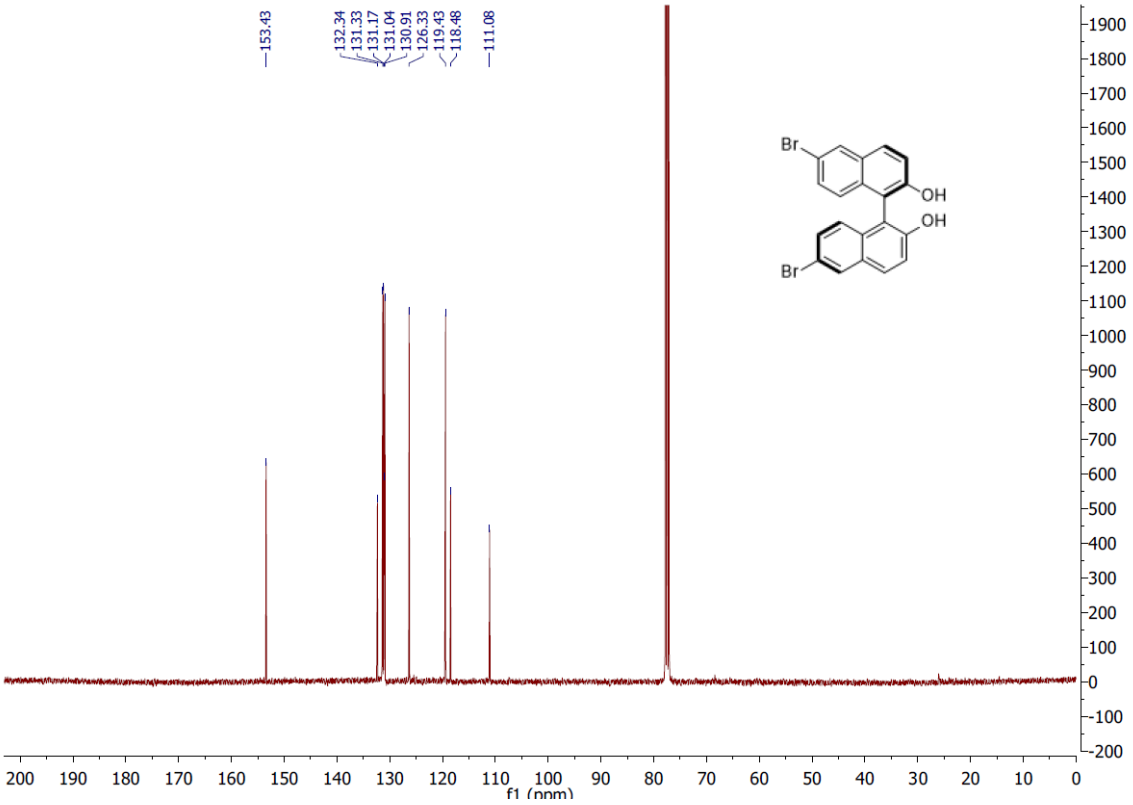
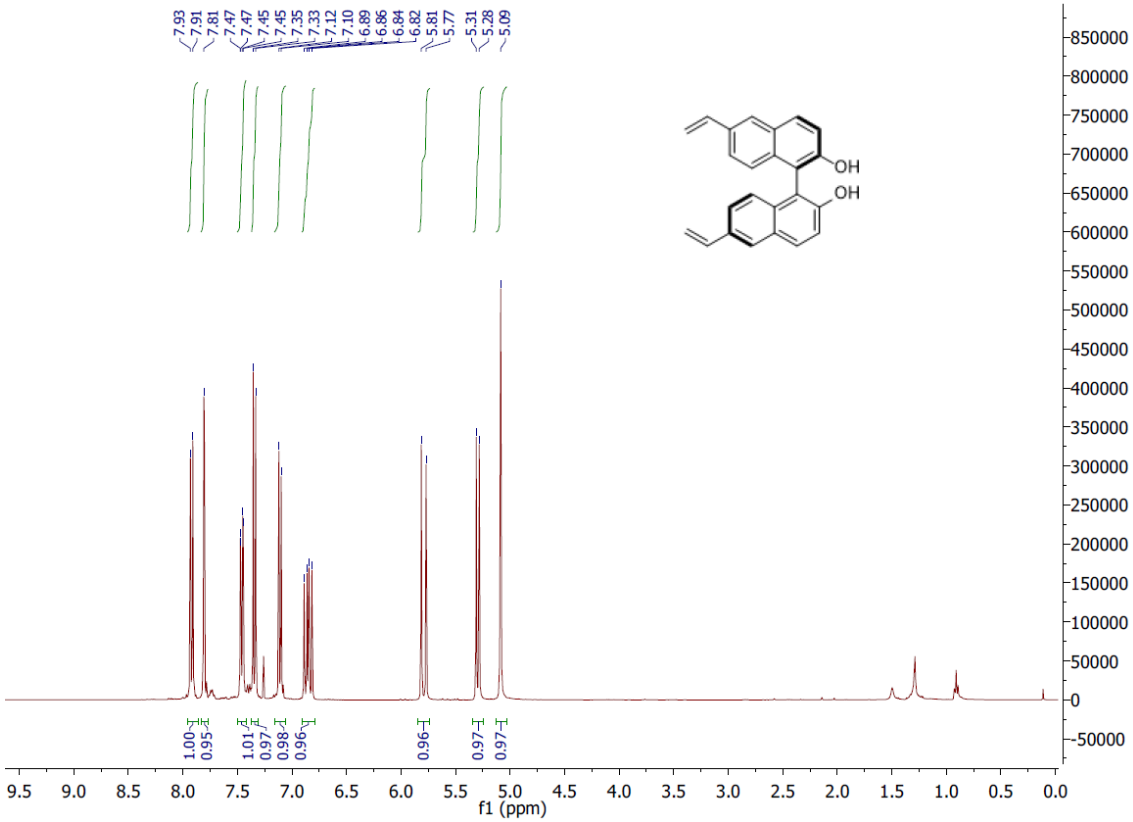


Figure S9. EDX analysis of the used (*R*)-P-amidite-POP indicating the presence of phosphorous, CsI particles, and Pd throughout the sample.

8. NMR Spectra



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7.91
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7.47
7.47
7.45
7.45
7.35
7.33
7.12
7.10
6.89
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6.84
6.82
5.81
5.77
5.31
5.28
5.09
OH
OH
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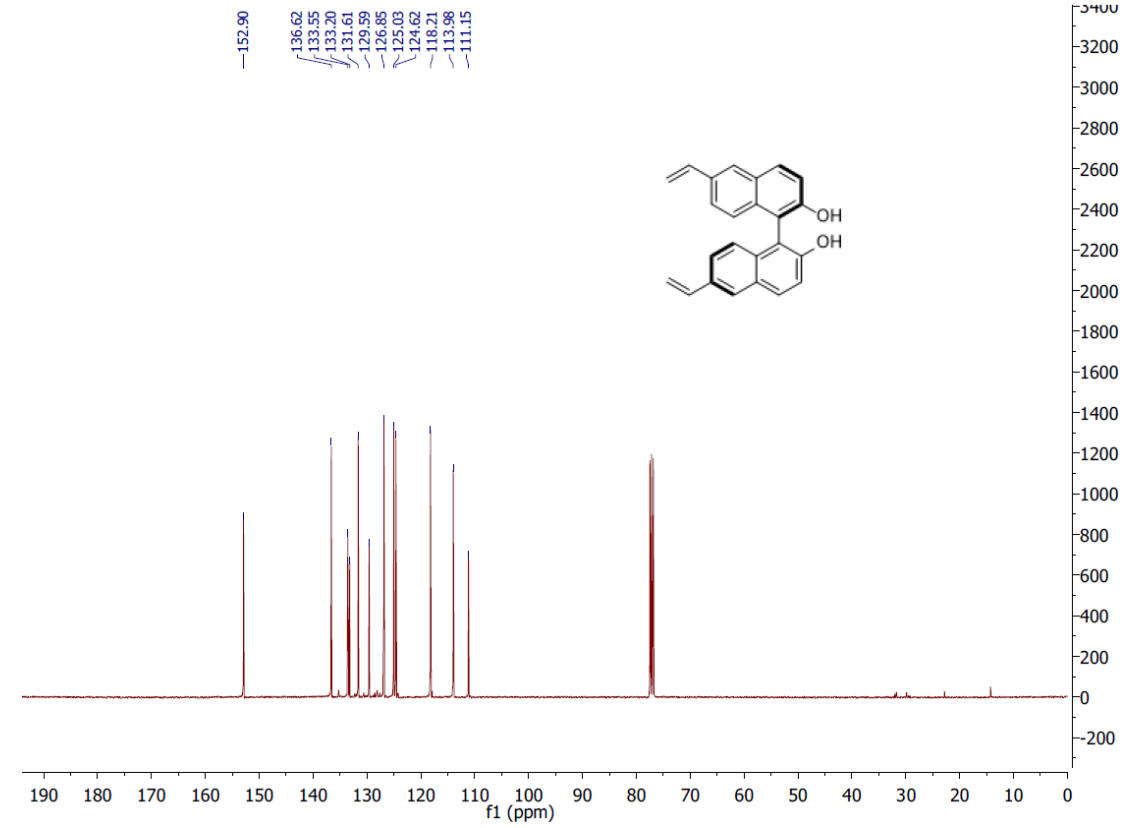
0.95
1.01
0.97
0.98
0.96
0.96
0.97
0.97
f1 (ppm)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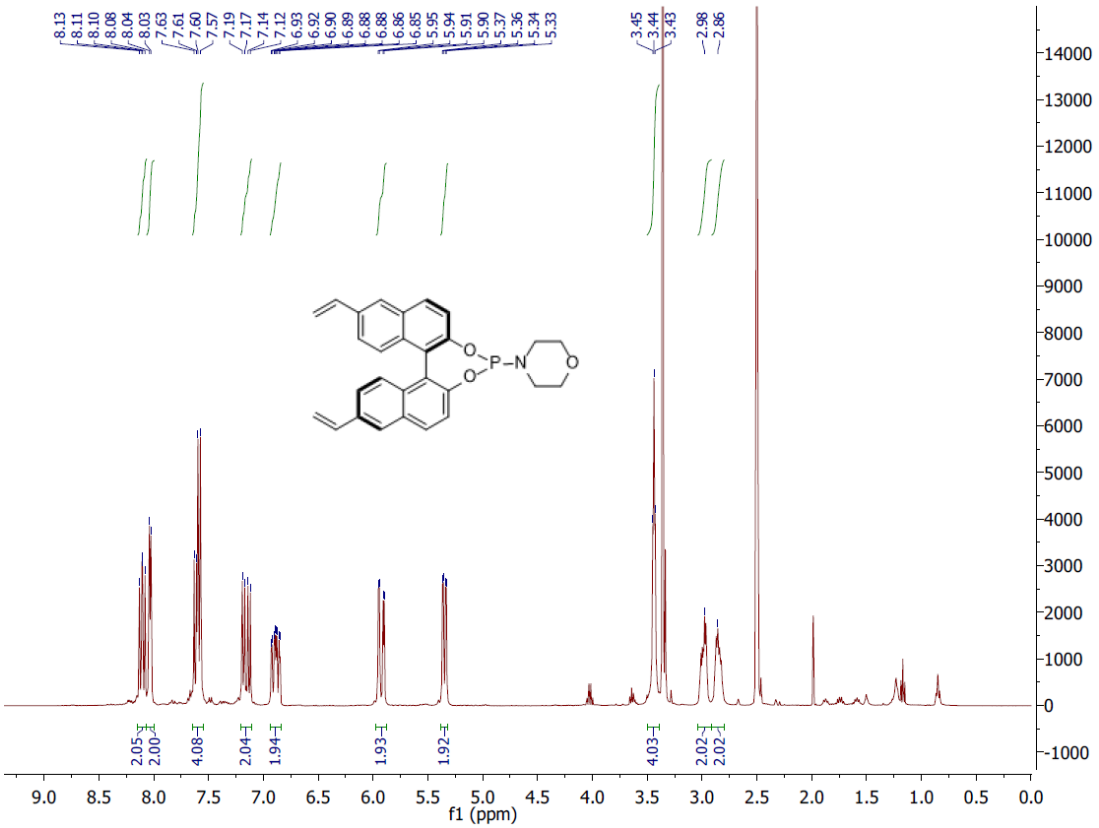
124.62
118.21
113.98
111.15
OH
OH
f1 (ppm)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8.10
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8.03
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7.61
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7.57
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6.93
6.92
6.90
6.89
6.88
6.88
6.86
6.85
5.95
5.94
5.91
5.90
5.37
5.36
5.34
5.33
3.45
3.44
3.43
2.98
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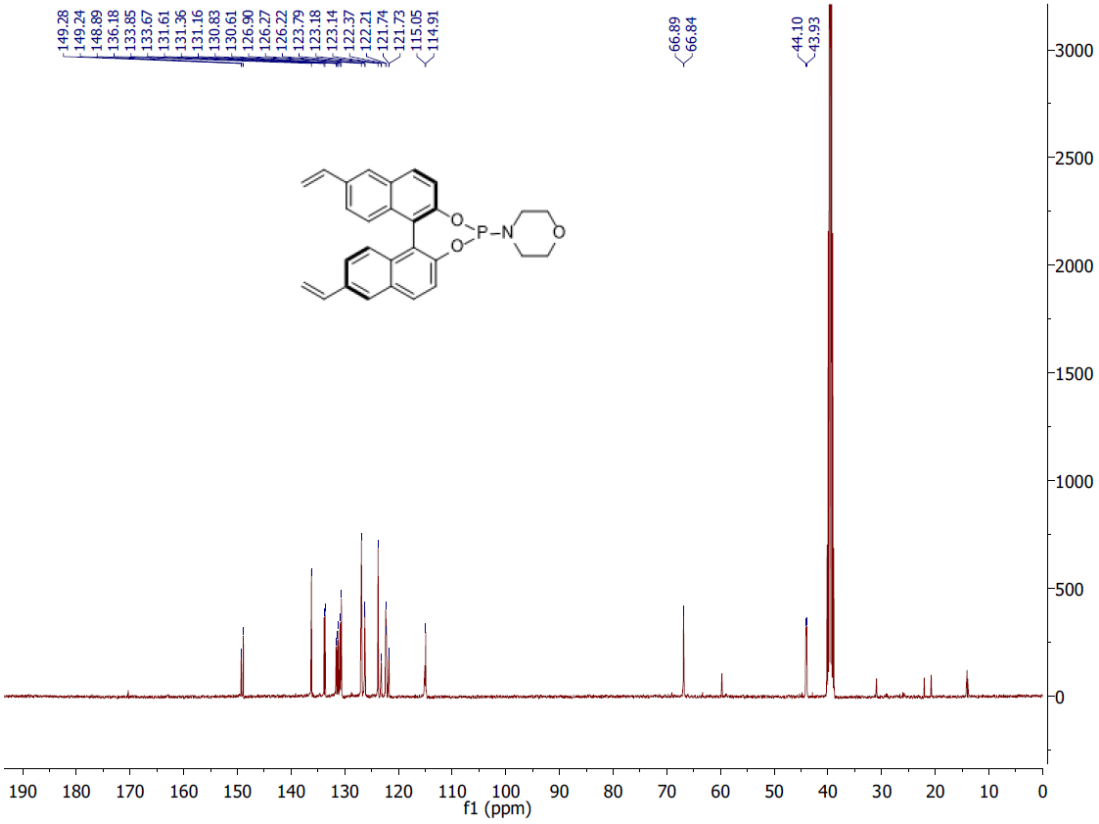
1.92
4.03
2.02
2.02
f1 (ppm)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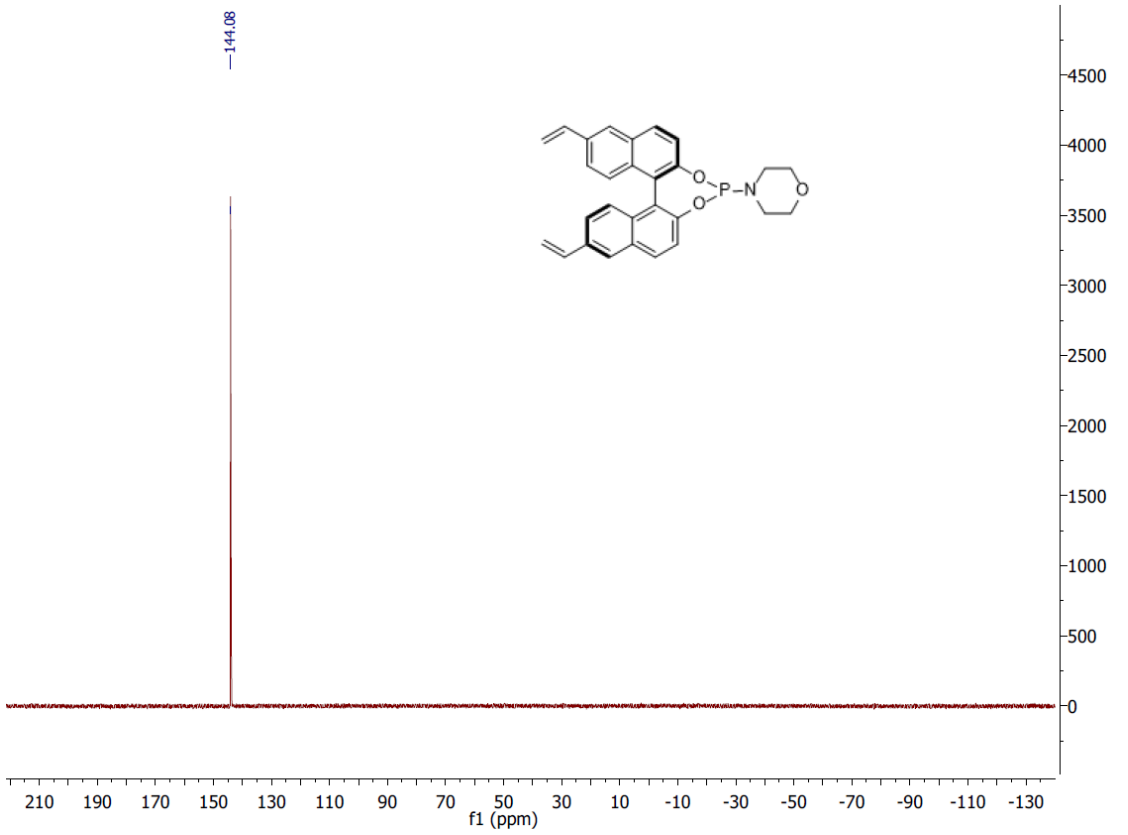
43.93
f1 (ppm)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P–N
O
O
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3000
2500
2000
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1000
500
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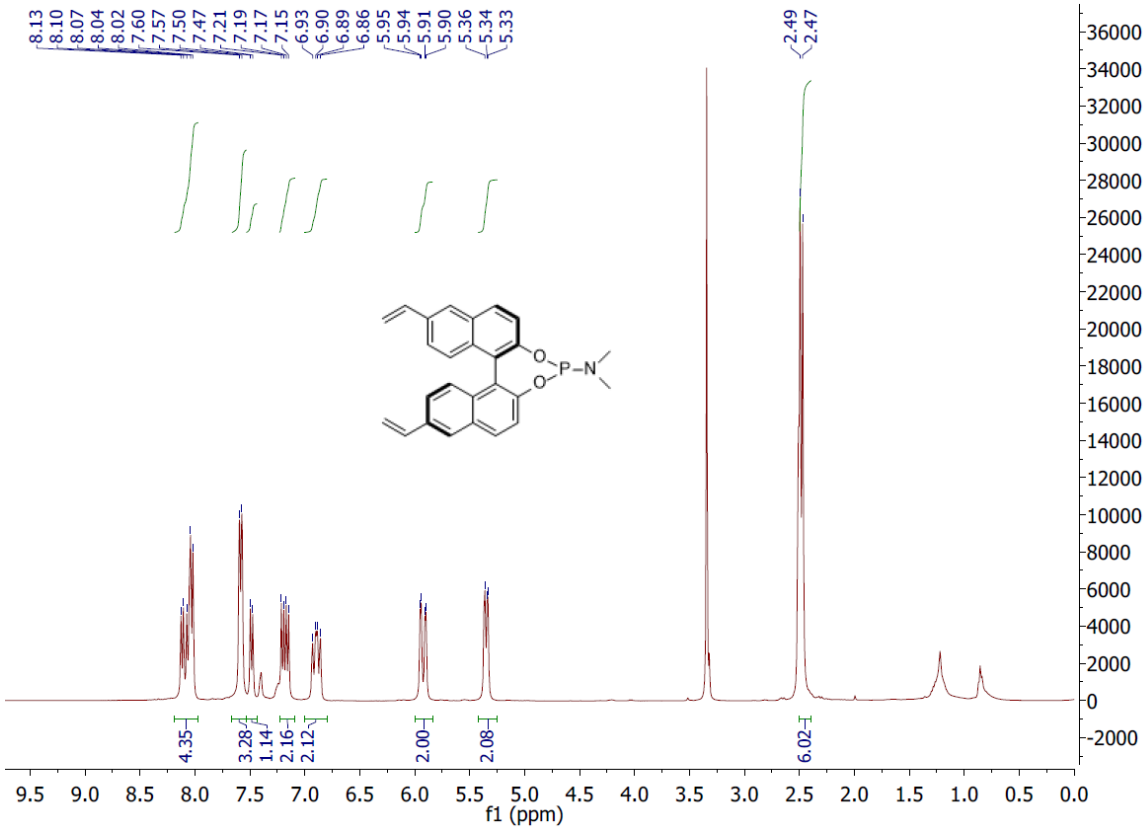
f1 (ppm)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8.02
7.60
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7.50
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7.21
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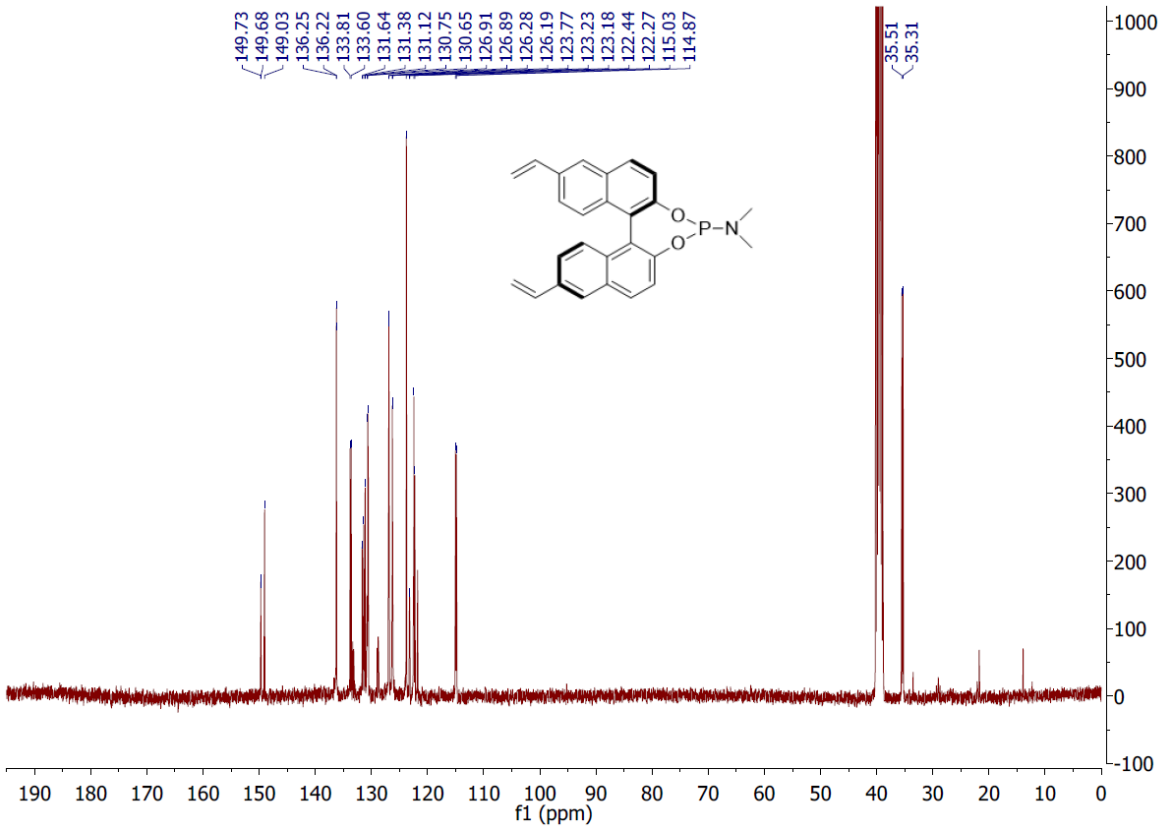
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
4.35
3.28
1.14
2.16
2.12
2.00
2.08
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.28
126.19
123.77
123.23
123.18
122.44
122.27
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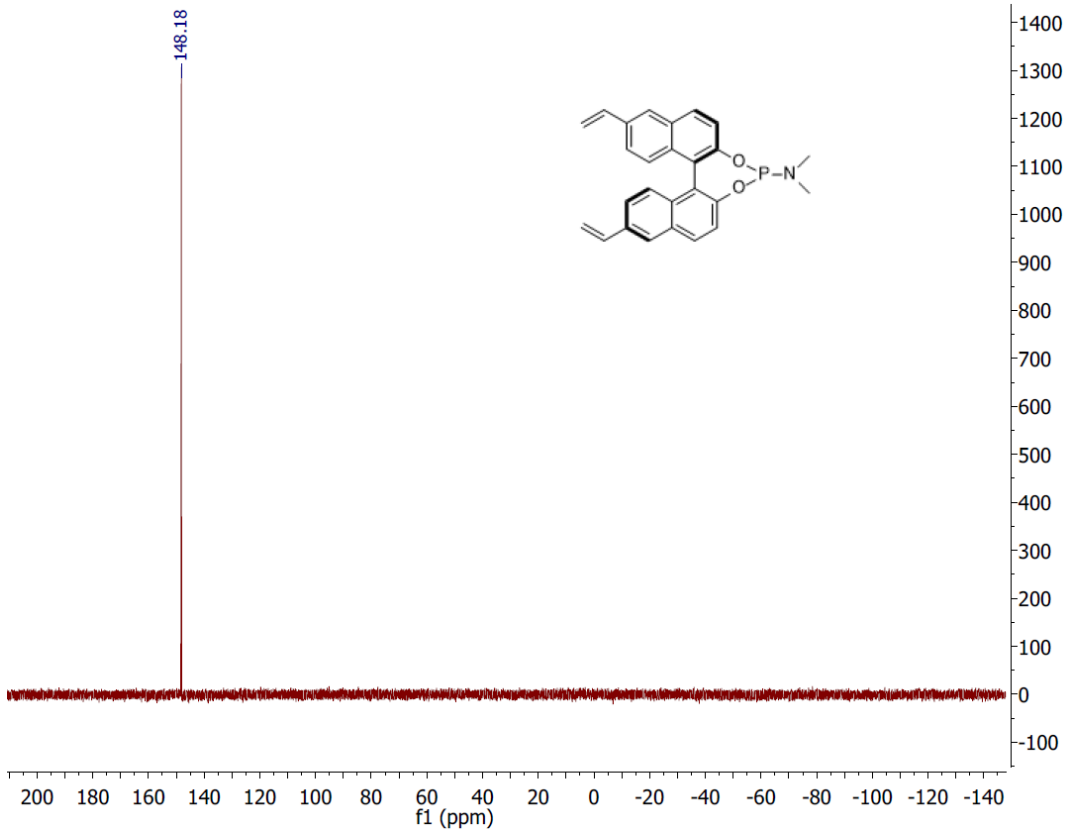
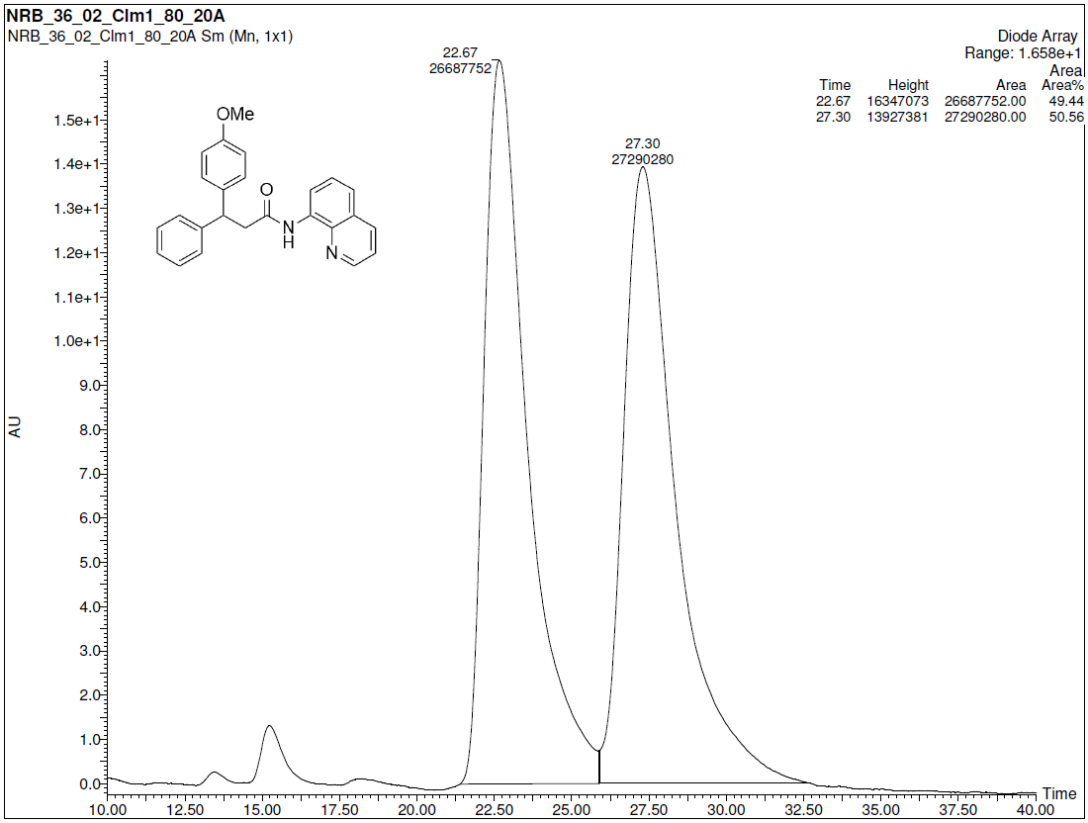
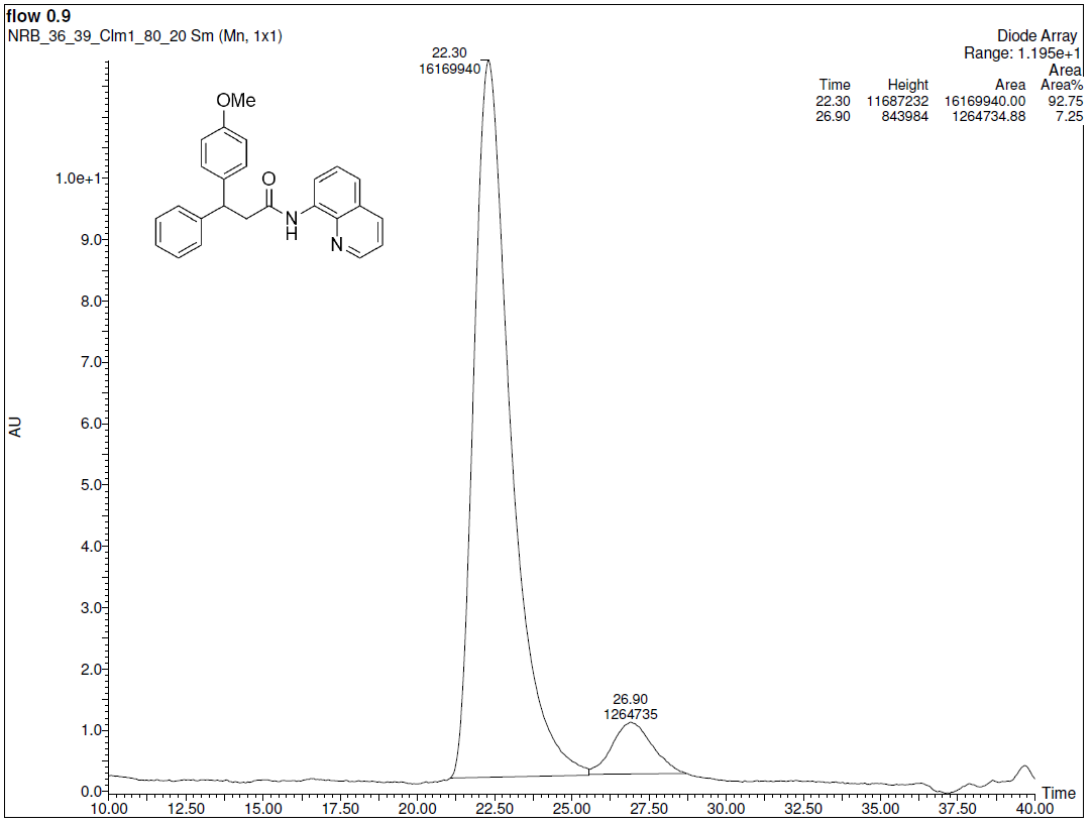
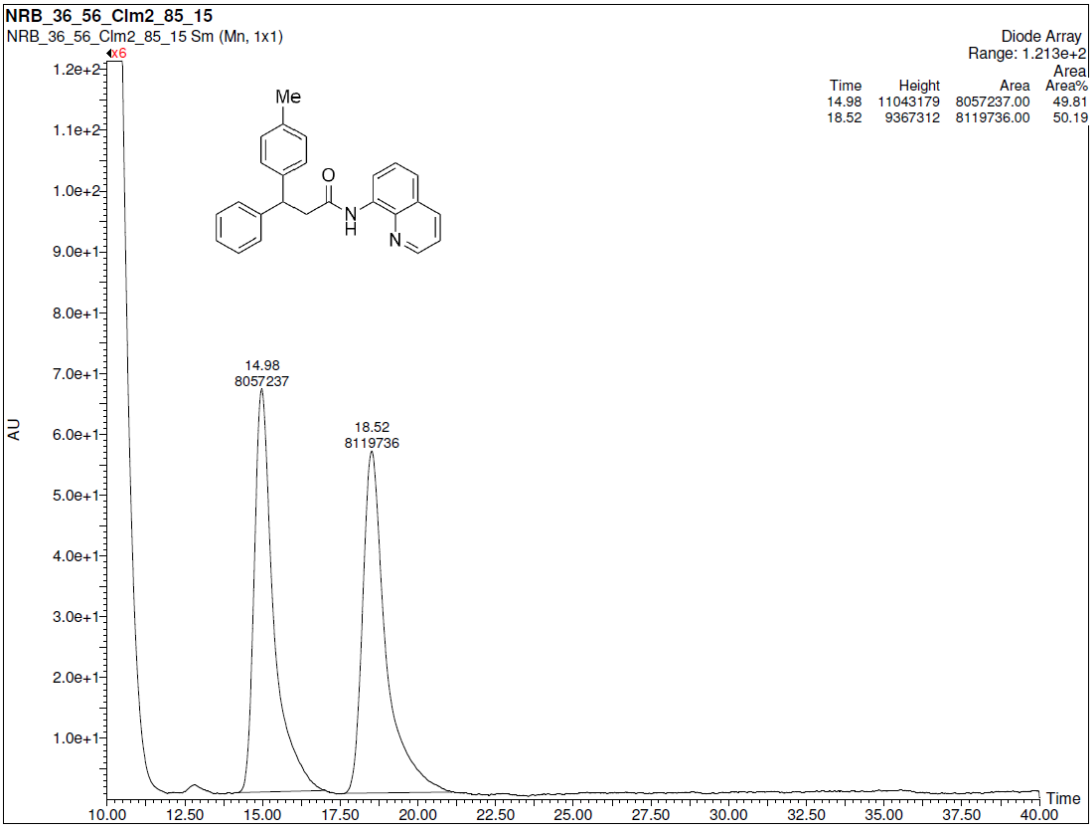
35.31
O
P–N
O
f1 (ppm)


148.18
O
P–N
O
f1 (ppm)

9. HPLC Traces



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NRB_36_56_Clm2_85_15 Sm (Mn, 1x1)
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Range: 1.213e+2
Area
Time Height Area Area%
14.98 11043179 8057237.00 49.81
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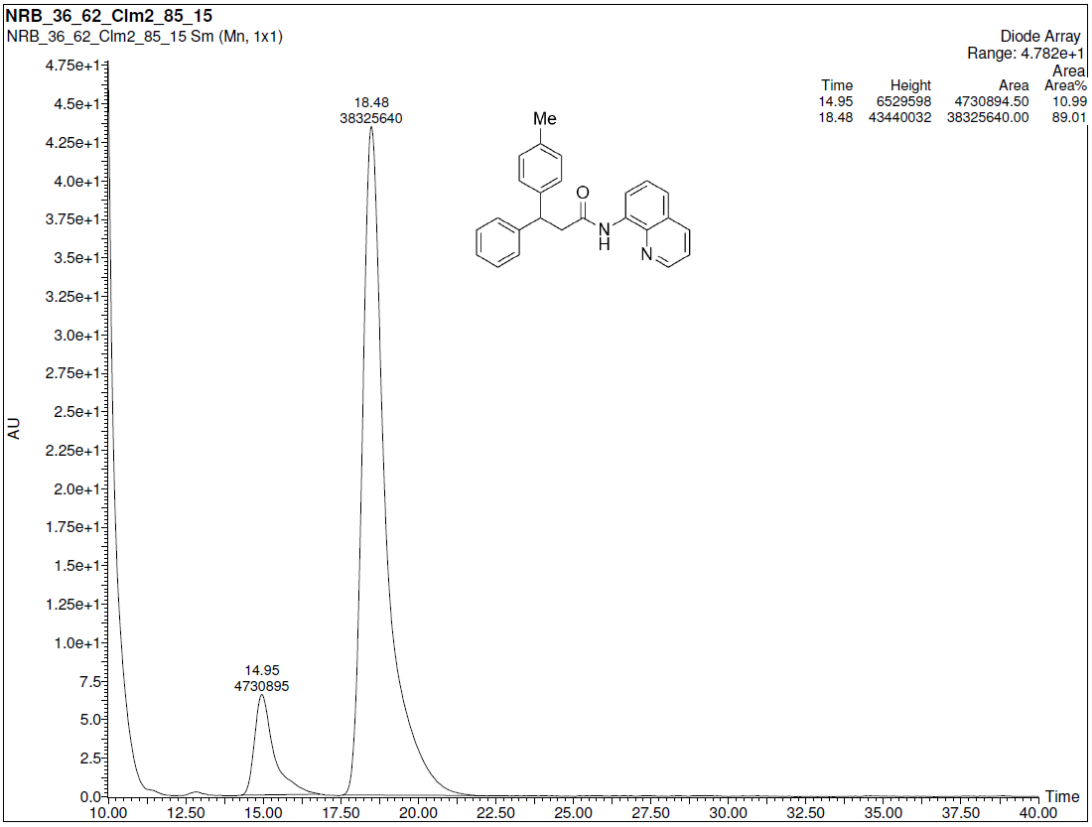
AU
Time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Diode Array
Range: 4.782e+1
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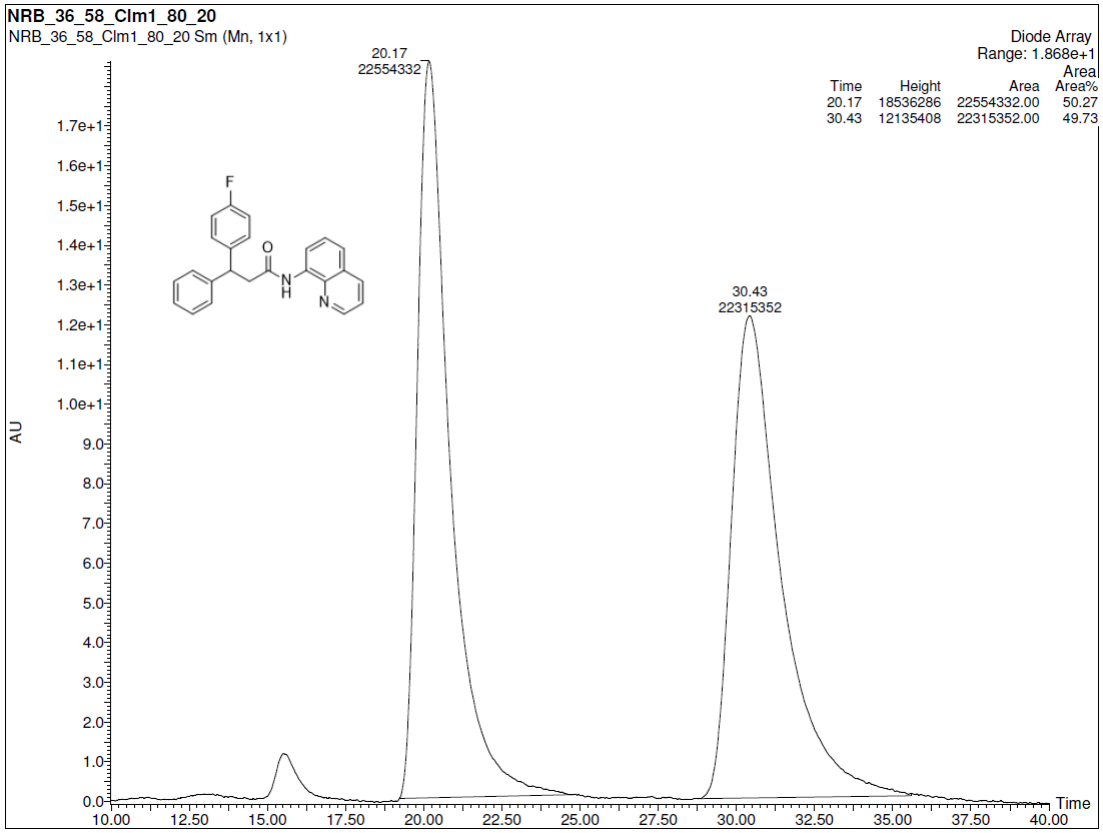
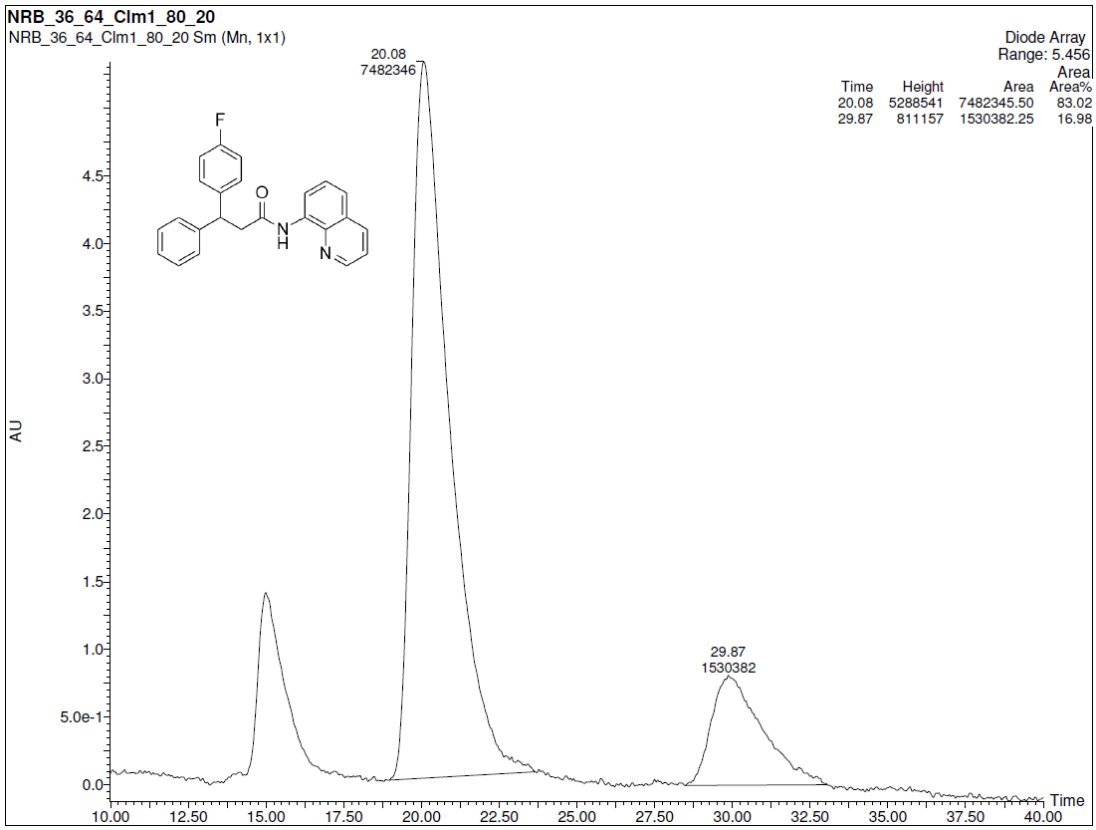
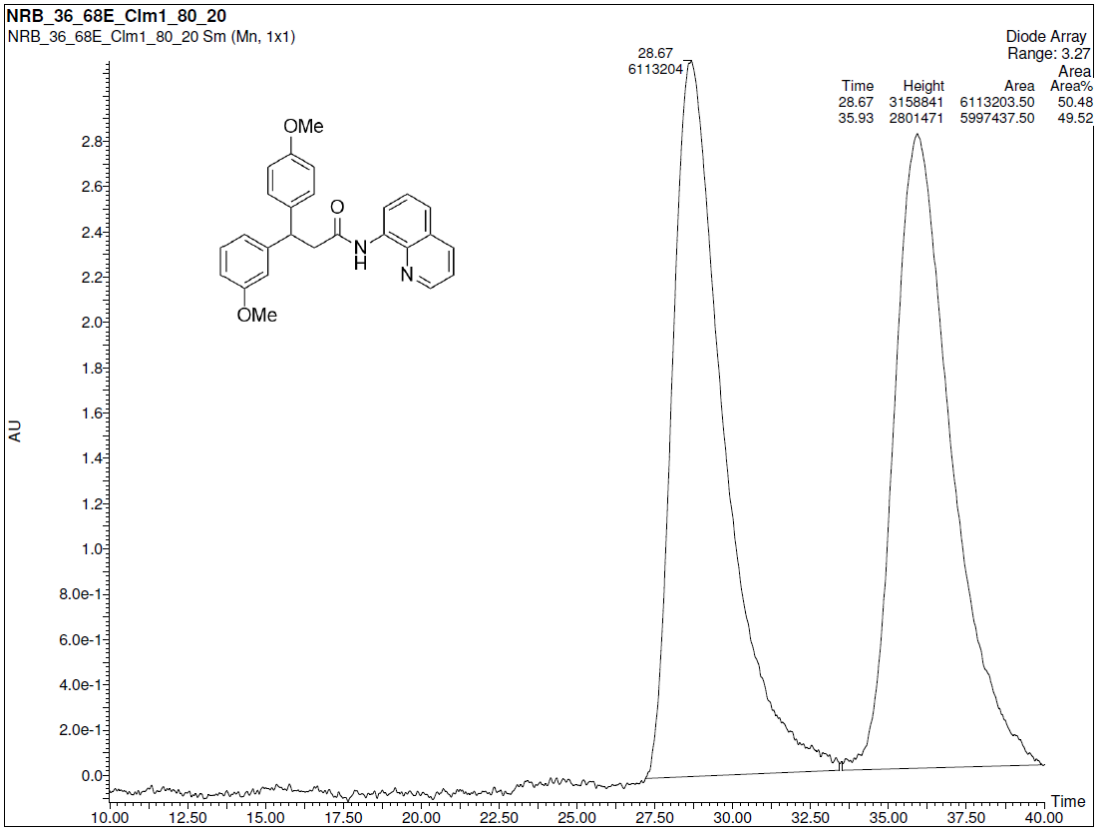
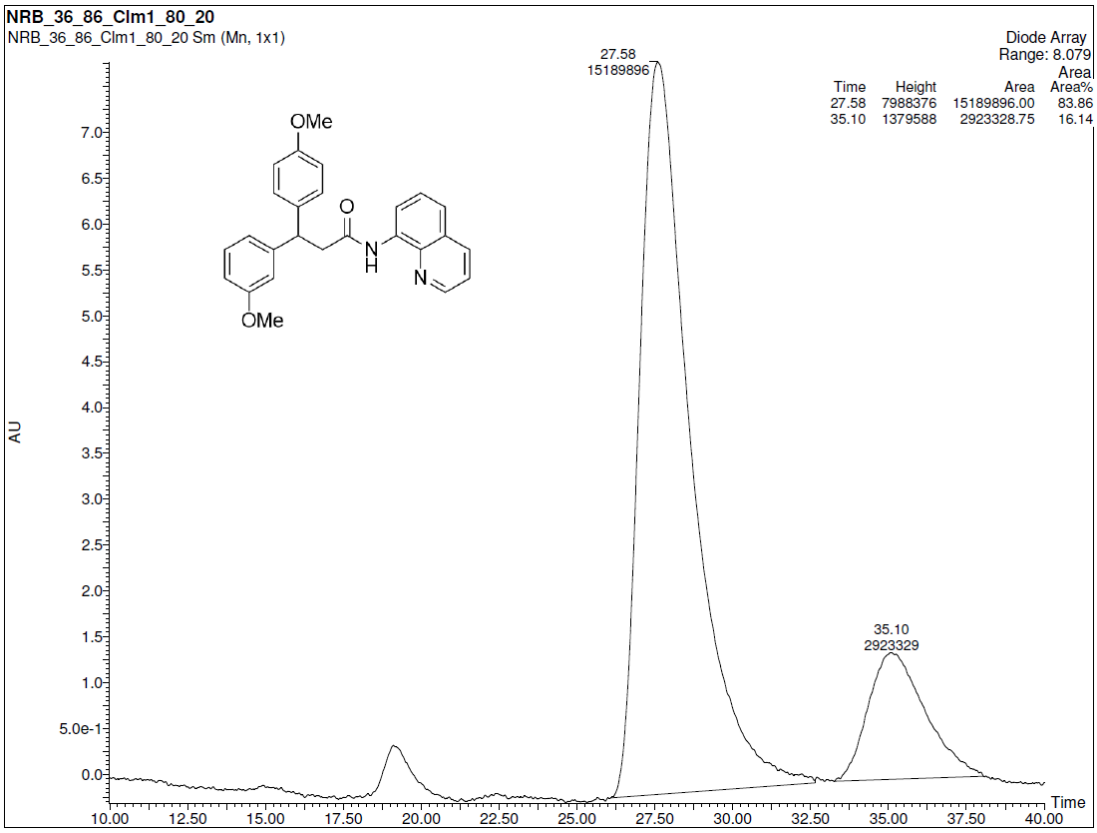
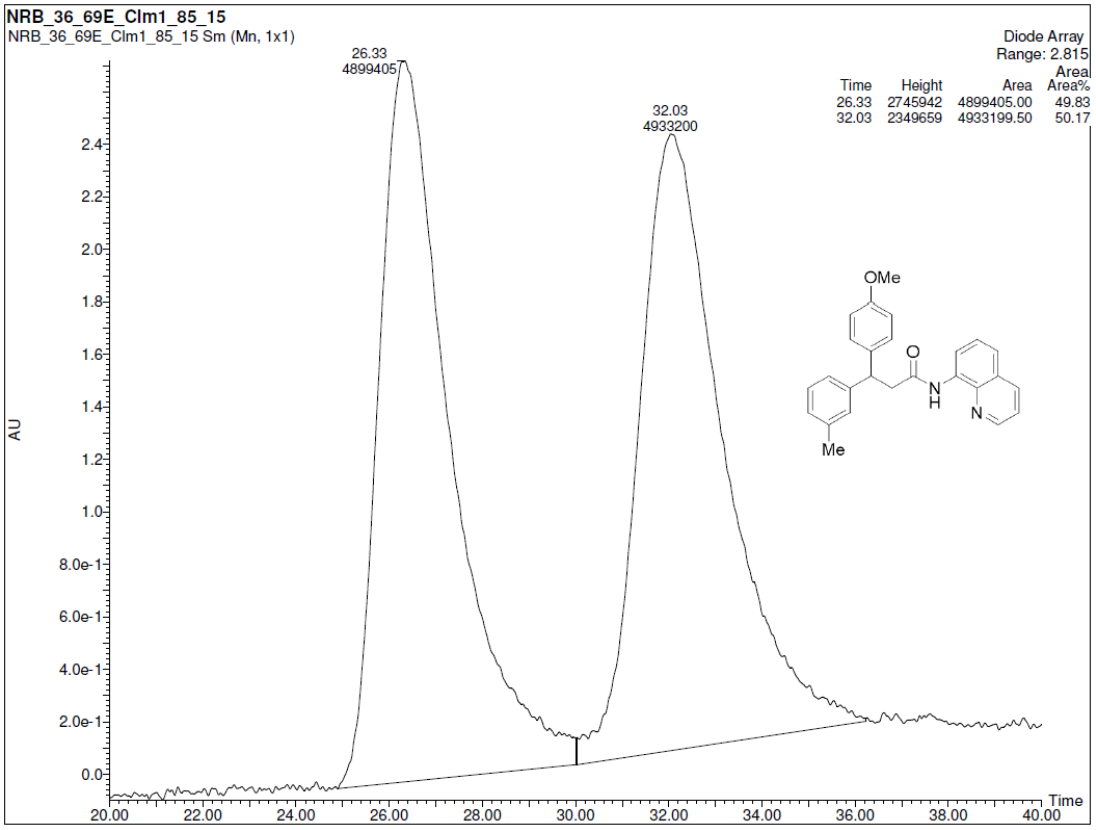
18.48
38325640
Me
O
N
H
N
14.95
4730895
AU
Time

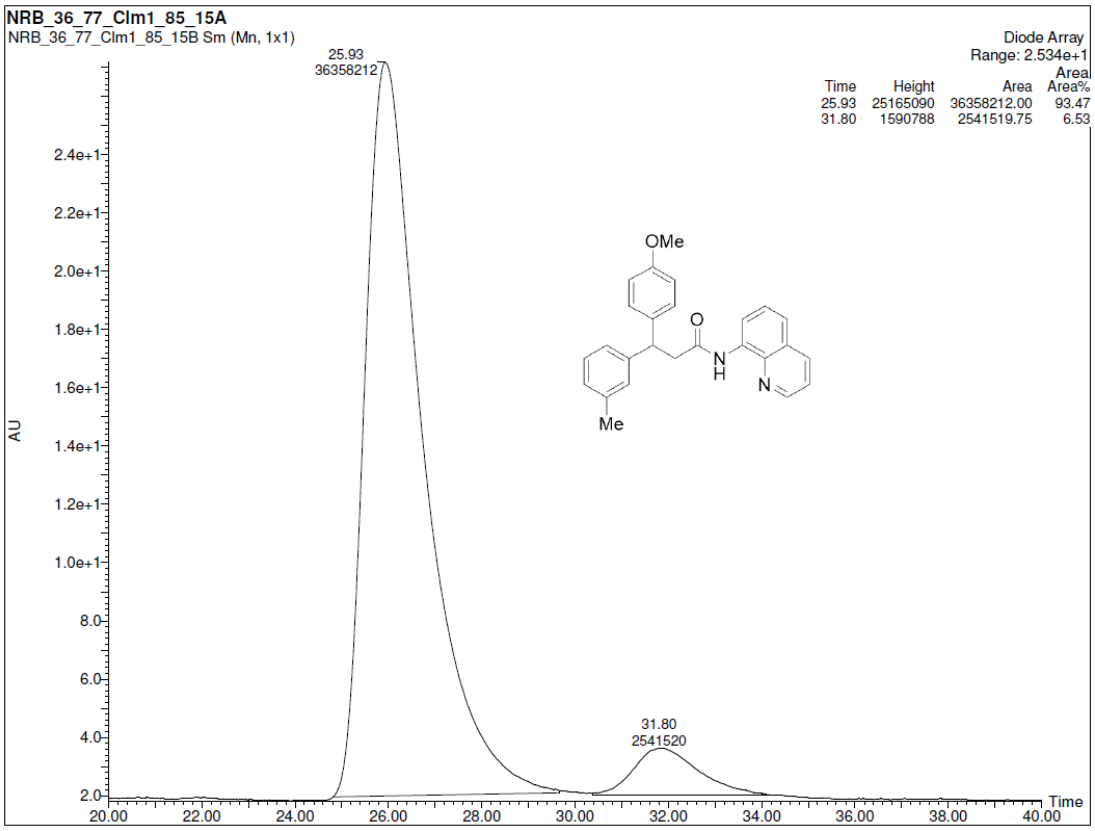

NRB_36_58_Clm1_80_20
NRB_36_58_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 1.868e+1
Area
Time Height Area Area%
20.17 18536286 22554332.00 50.27
30.43 12135408 22315352.00 49.73
20.17
22554332
30.43
22315352
AU
Time
F
O
N
H
N

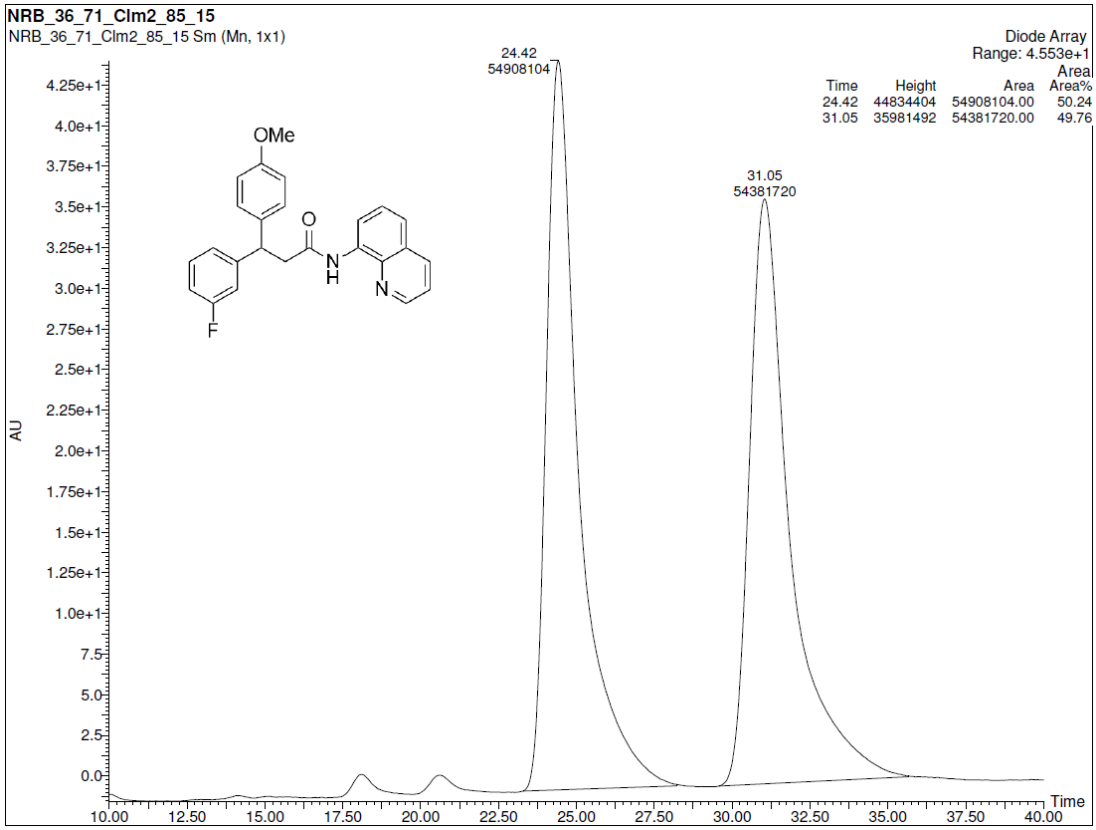

NRB_36_64_Clm1_80_20
NRB_36_64_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 5.456
Area
Time Height Area Area%
20.08 5288541 7482345.50 83.02
29.87 811157 1530382.25 16.98
20.08
7482346
29.87
1530382
AU
Time
F
O
N
H
N

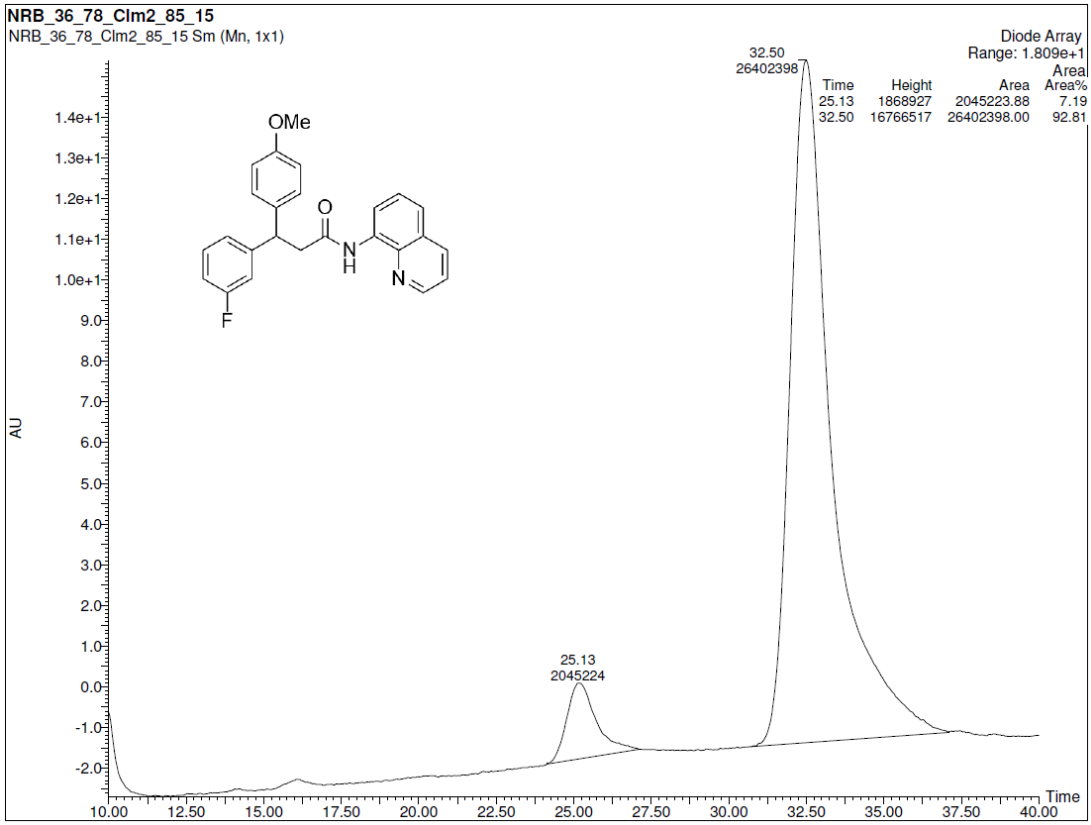

NRB_36_68E_Clm1_80_20
NRB_36_68E_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 3.27
28.67
6113204
Time Height Area Area%
28.67 3158841 6113203.50 50.48
35.93 2801471 5997437.50 49.52
OMe
O
N
H
N
OMe
AU
Time

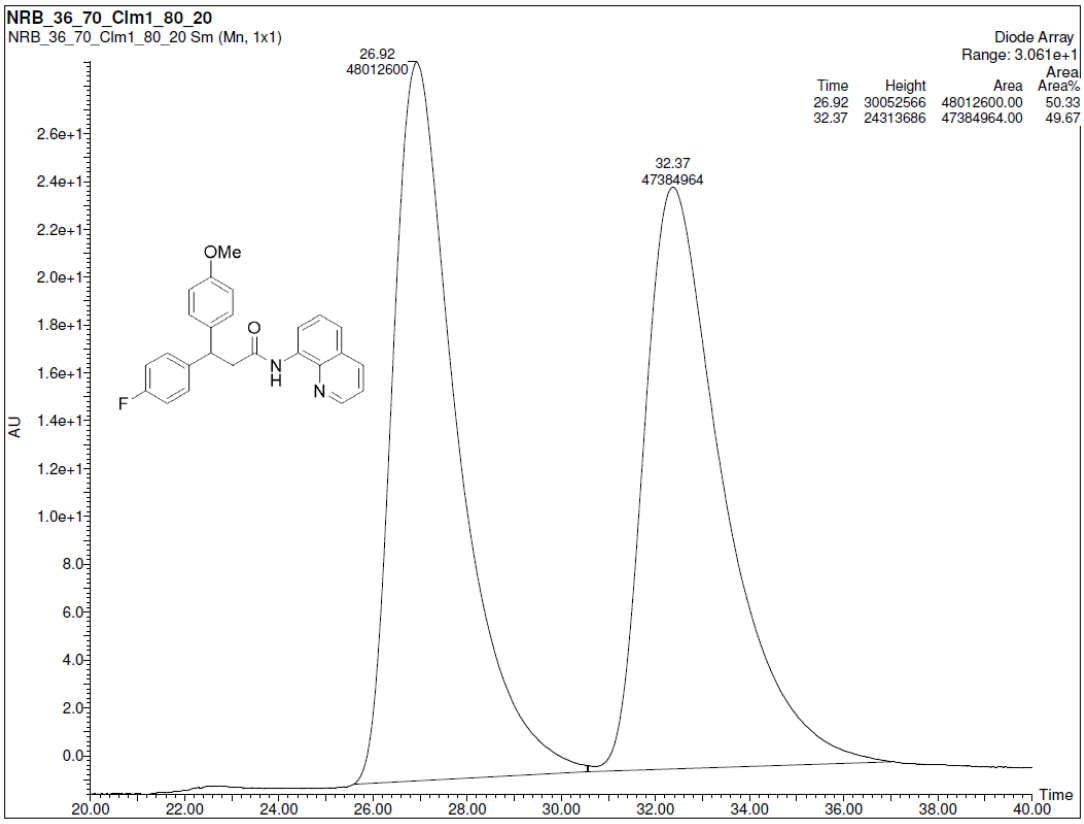

NRB_36_86_Clm1_80_20
NRB_36_86_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 8.079
27.58
15189896
Time Height Area Area%
27.58 7988376 15189896.00 83.86
35.10 1379588 2923328.75 16.14
OMe
O
N
H
N
OMe
35.10
2923329
AU
Time

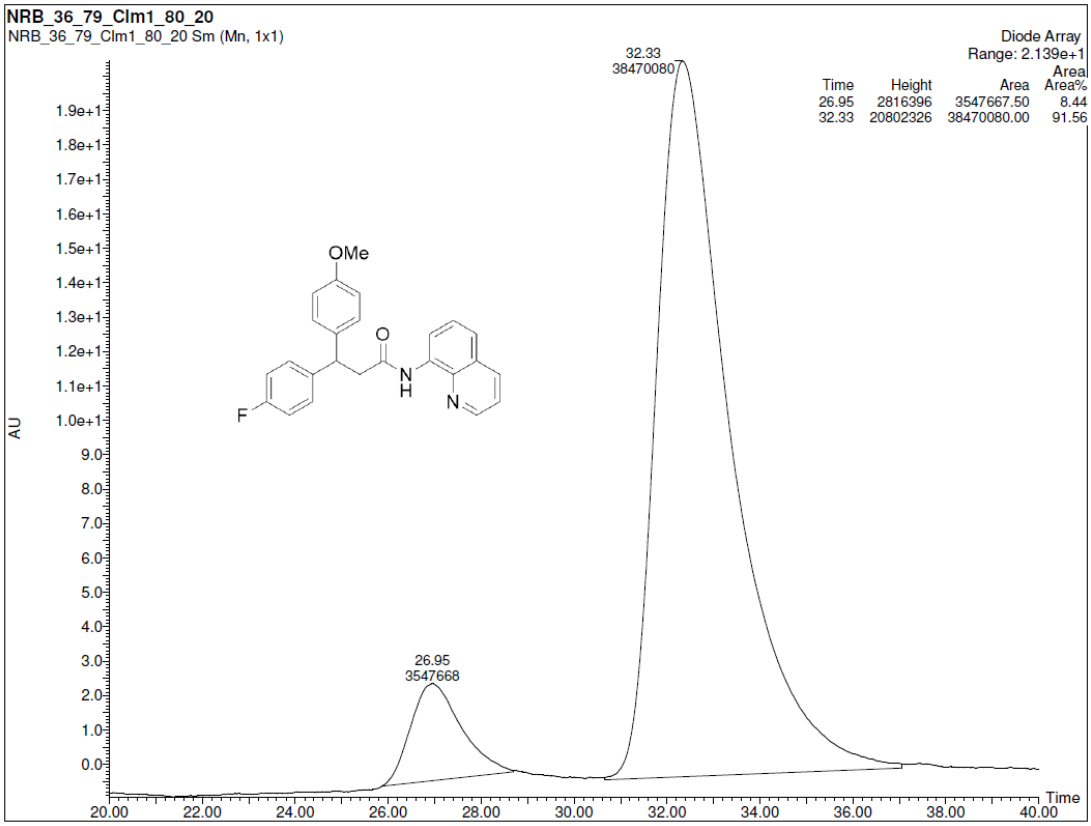

NRB_36_69E_Clm1_85_15
NRB_36_69E_Clm1_85_15 Sm (Mn, 1x1)
Diode Array
Range: 2.815
Area
Time Height Area Area%
26.33 2745942 4899405.00 49.83
32.03 2349659 4933199.50 50.17
26.33
4899405
32.03
4933200
OMe
O
N
H
N
Me
AU
Time

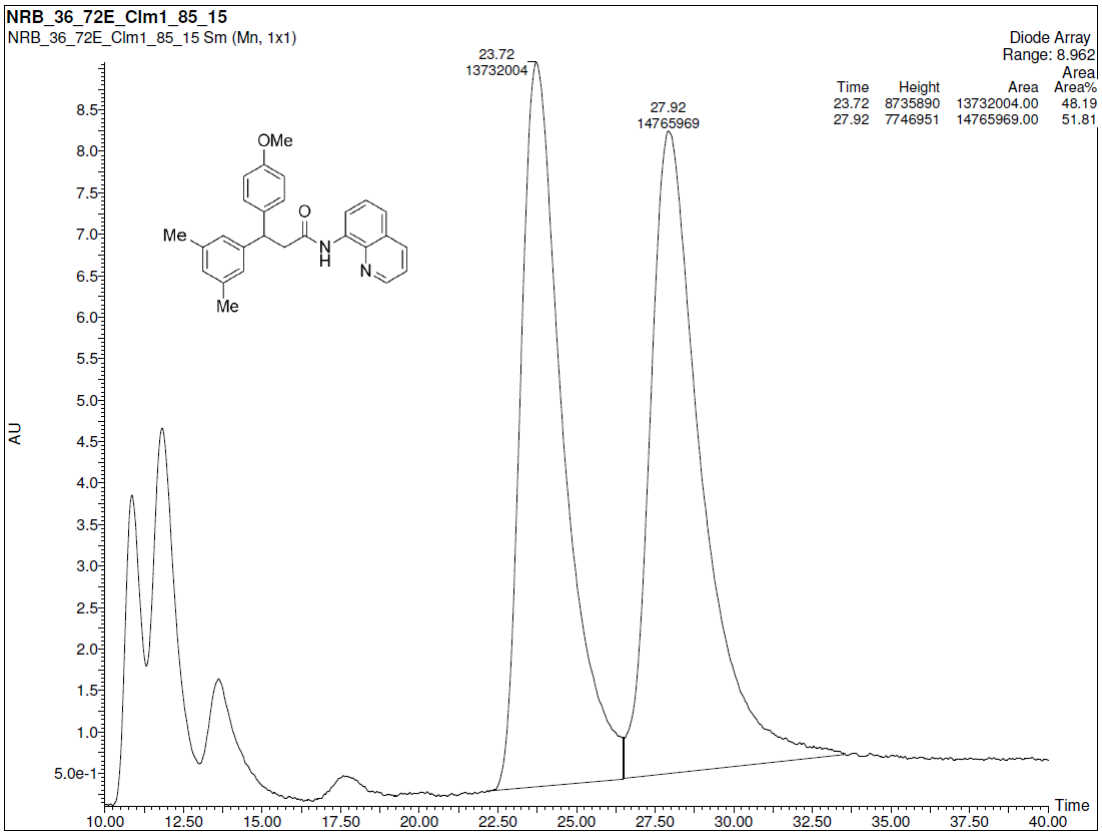

NRB_36_77_Clm1_85_15A
NRB_36_77_Clm1_85_15B Sm (Mn, 1x1)
Diode Array
Range: 2.534e+1
Area
Time Height Area Area%
25.93 25165090 36358212.00 93.47
31.80 1590788 2541519.75 6.53
25.93
36358212
OMe
O
N
H
N
Me
31.80
2541520
AU
Time

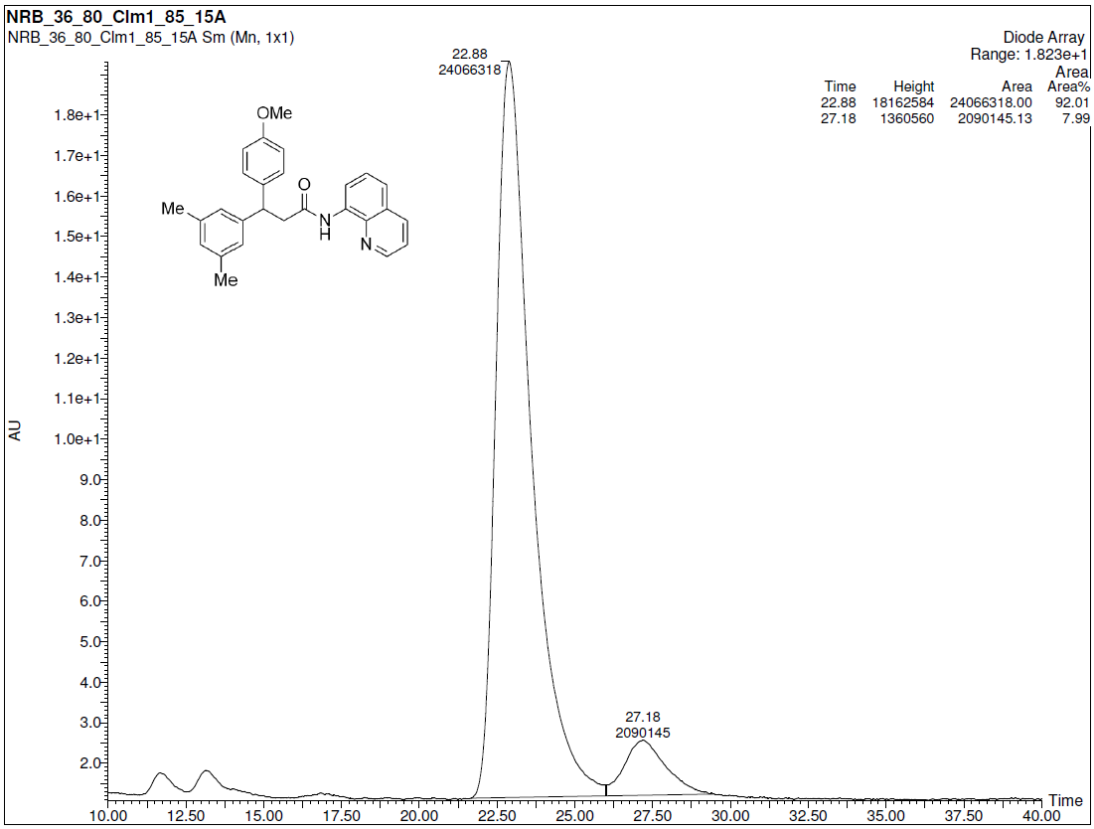

NRB_36_71_Clm2_85_15
NRB_36_71_Clm2_85_15 Sm (Mn, 1x1)
Diode Array
Range: 4.553e+1
Area
Time Height Area Area%
24.42 44834404 54908104.00 50.24
31.05 35981492 54381720.00 49.76
24.42
54908104
31.05
54381720
OMe
O
N
H
N
F
AU
Time


NRB_36_78_Clm2_85_15
NRB_36_78_Clm2_85_15 Sm (Mn, 1x1)
Diode Array
Range: 1.809e+1
Area
Time Height Area Area%
25.13 1868927 2045223.88 7.19
32.50 16766517 26402398.00 92.81
32.50
26402398
25.13
2045224
OMe
O
N
H
N
F
AU
Time


NRB_36_70_Clm1_80_20
NRB_36_70_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 3.061e+1
Time Height Area Area%
26.92 30052566 48012600.00 50.33
32.37 24313686 47384964.00 49.67
26.92
48012600
32.37
47384964
OMe
O
N
H
N
F
AU
Time


NRB_36_79_Clm1_80_20
NRB_36_79_Clm1_80_20 Sm (Mn, 1x1)
Diode Array
Range: 2.139e+1
Time Height Area Area%
26.95 2816396 3547667.50 8.44
32.33 20802326 38470080.00 91.56
32.33
38470080
26.95
3547668
OMe
O
N
H
N
F
AU
Time


NRB_36_72E_Clm1_85_15
NRB_36_72E_Clm1_85_15 Sm (Mn, 1x1)
Diode Array
Range: 8.962
Time Height Area Area%
23.72 8735890 13732004.00 48.19
27.92 7746951 14765969.00 51.81
23.72
13732004
27.92
14765969
OMe
Me
Me
O
N
H
N
AU
Time


NRB_36_80_Clm1_85_15A
NRB_36_80_Clm1_85_15A Sm (Mn, 1x1)
Diode Array
Range: 1.823e+1
Time Height Area Area%
22.88 18162584 24066318.00 92.01
27.18 1360560 2090145.13 7.99
22.88
24066318
27.18
2090145
OMe
Me
Me
O
N
H
N
AU
Time

Resolution of enantiomers with the dimethylamino phosphoramidite based POP.