

Supporting information for:

An Effective and Reusable Hyperbranched Polymer Immobilized Rhodium-Catalyst for the Hydroformylation of Olefins

Thomas Verheyen,[†] Niccolò Santillo,[‡] Davide Marinelli,[§] Elena Petricci,[‡] Wim M. De Borggraeve,[†] Luigi Vaccaro,[§] Mario Smet^{†}*

[†] Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

[‡] Department of Biochemistry, Chemistry and Pharmacy, University of Siena, Via A. Moro 2, 53100 Siena, Italy.

[§] Laboratory of Green Synthetic Organic Chemistry, CEMIN – Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia Via Elce di Sotto, 8, 06123 Perugia, Italy.

*email: mario.smet@kuleuven.be

1.	<u>General information</u>	3
2.	<u>Synthesis</u>	4
1.1	Synthesis of monomers.....	4
1.2	Synthesis of polymers	6
3.	<u>Characterization of HBPAOs</u>	6
4.	<u>Loading of HBPAOs</u>	12
5.	<u>Hydroformylation</u>	14
6.	<u>Leaching of Rhodium</u>	18
7.	<u>Aminocarbonylation</u>	19
8.	<u>NMR spectra</u>	20
7.1	¹ H NMR spectra	20
7.2	¹³ C NMR spectra	28
7.3	³¹ P NMR spectra	33

1. General information

Microwave: All microwave reactions are performed in a CEM Discover microwave oven equipped with a 10 mL tube for reactions under pressure and an external IR sensor to detect the reaction temperature during the irradiation. These glass vials, tested for resisting up to 250 psi (17 bar, 1723 KPa), are provided with a tube connection to an external pressure controlling system equipped with a valve and an exit tube for venting the vial at the end of the reaction. The exit tube was connected to a cylinder containing syngas through a three-way connector equipped with two taps to pressurize the system before microwave irradiation.

Mass: Mass spectra were recorded using a Thermo Electron LCQ Advantage fed by an Agilent 1100 pump and injection system.

NMR: ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300, 400 or 600 spectrometer at room temperature. Chemical shifts are reported in parts per million (ppm) and are referenced to the internal standard tetramethylsilane. ^{31}P NMR spectra were recorded on a Bruker Avance 600 spectrometer at room temperature. Chemical shifts are reported in ppm and are referenced to the external standard 25 vol% H_3PO_4 (present in a coaxial tube insert).

MPLC: MPLC flash chromatography was performed using a Büchi SepacoreTM flash apparatus, consisting of a C-660 Büchi fraction collector, C-615 pump manager, C-635 UV-photometer, two C-605 pump modules, and a Linseis D120S plotter. GraceResolvTM silica cartridges with Davisil[®] silica were used.

GPC: The first gel permeation chromatography (GPC) system consisted of a Shimadzu 10A with a Plgel 5 μm mixed D-column with an RID-10A and a SPD-10A detector. Measurements were performed in THF at 30 °C with a nominal flow rate of 1 mL/min, polystyrene standards were used for calibration, and the results were analyzed using the EZstart 7.2.1 software. The second GPC system, to determine absolute molecular weight, was equipped with a differential refractive index Un-2010 RI detector and a multiangle light scattering ($\lambda = 690 \text{ nm}$) DAWN EOS detector. The column contained a styrene-divinylbenzene copolymer network. Analyses were performed in THF at 35 °C with a nominal flow rate of 1 mL min⁻¹. Results were analyzed using ASTRA software. The refractive index increment dn dc^{-1} was measured independently in THF at 35 °C using an SEC-3010 dn dc^{-1} differential refractive index detector ($\lambda = 620 \text{ nm}$) and analyzed using BI-DNDCW software.

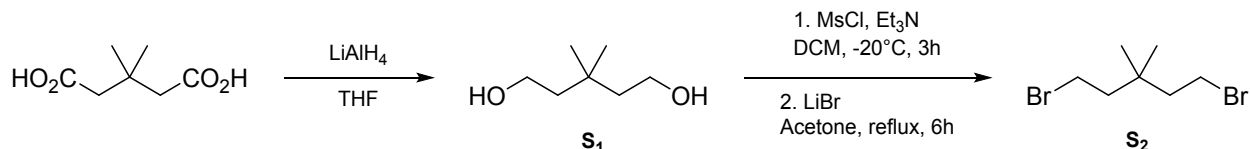
TGA: Thermogravimetric Analysis (TGA) was carried out using a SDT Q600 instrument under air from 25 °C to 800 °C. TGA was performed with a heating rate of 5.00 °C/min. The results were processed and analyzed using Advantage Software v5.5.20.

TXRF: Total-reflection X-ray fluorescence (TXRF) of the samples was measured on a Bruker S2 Picofox TXRF spectrometer, and the results were analyzed using XRF spectra 7 software.

FT-IR: IR spectra were recorded on a Bruker Alpha-T FT-IR spectrometer with a single reflection ATR sampling module (ZnSe ATR crystal) and processed using Opus software 7.5.

2. Synthesis

1.1 Synthesis of monomers

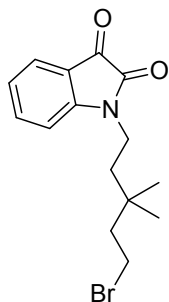


Scheme S1. Synthesis of **S1** and **S2**.

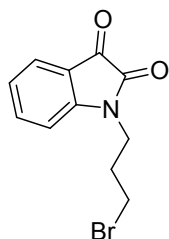
3,3-dimethylpentane-1,5-diol (S1): A dry, nitrogen purged flask was charged with LiAlH_4 (2.0 M in THF) (47 mL, 93.8 mmol) under nitrogen atmosphere. 3,3-dimethylglutaric acid (5.0 g, 31.2 mmol) in dry THF (17 mL) was added dropwise. The reaction mixture was refluxed overnight and cooled to 0°C the next day. Distilled H_2O (2.25 mL), NaOH 2M (2.25 mL) and distilled H_2O (4.5 mL) were added at 0°C . The mixture was diluted with EtOAc , the organic layer was separated and the water layer further extracted with EtOAc (2 X). The organic layer was dried over Na_2SO_4 , filtered and concentrated to obtain 3,3-dimethylpentane-1,5-diol (2.0 g, 50%) as a colorless oil. Procedure and spectroscopic data were identical to the reported values.¹ ^1H NMR (400 MHz, CDCl_3) δ = 3.74 (t, J =7.1 Hz, 4H), 1.58 (m, 6H), 0.95 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 59.7, 44.2, 31.7, 28.0.

1,5-dibromo-3,3-dimethylpentane (S2): 3,3-dimethylpentane-1,5-diol (1.7 g, 12.9 mmol) and Et_3N (8.9 mL, 64.5 mmol) were dissolved in dry DCM (40 mL) under nitrogen atmosphere and cooled to -20°C . MsCl (4.0 mL, 51.6 mmol) was added slowly and the reaction mixture was stirred for 1h at room temperature. The mixture was quenched with distilled H_2O and the mixture was extracted with DCM (3X). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. To a solution of the crude mixture in acetone (130 mL) was added LiBr (11.2 g, 129.0 mmol). The resulting suspension was stirred at reflux overnight. After cooling to room temperature, Et_2O was added and the organic layer was washed with distilled H_2O and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure, to give 1,5-dibromo-3,3-dimethylpentane (2.2 g, 67%). The crude mixture was used for the next step without purification. Procedure and spectroscopic data were identical to the reported values.² ^1H NMR (400 MHz, CDCl_3) δ = 3.34-3.39 (m, 4H), 1.83-1.89 (m, 4H), 0.94 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 45.3, 35.7, 28.4, 26.5.

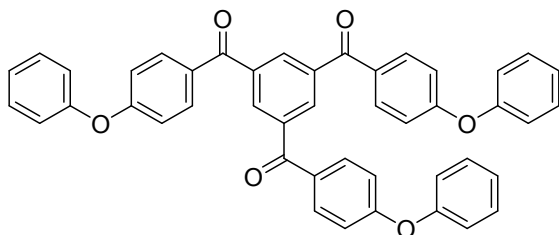
A₂ monomers 2a and 2b: In a flame-dried nitrogen flushed two-necked round-bottomed flask isatin (1.0 equiv) and K_2CO_3 (2.0 equiv), were dissolved in dry DMF (0.4 M) under nitrogen atmosphere. 1,5-dibromo-3,3-dimethylpentane (for **2a**) or 1,3-dibromopropane (for **2b**) (4.0 equiv) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated, Partitioned between distilled H_2O and DCM and the organic layers was separated. The water layer was further extracted with DCM (2 X). The organic layers were combined, washed with brine, dried over MgSO_4 , filtered and concentrated. The concentrate was purified by MPLC (DCM:MeOH 99:1) and the appropriate fractions were collected. The collected fractions were concentrated under reduced pressure and a solid was obtained after addition of C_7H_{16} followed by filtration and washing with C_7H_{16} .



1-(5-bromo-3,3-dimethylpentyl)indoline-2,3-dione (2a): Orange solid; ^1H NMR (400 MHz, CDCl_3) δ = 7.62-7.58 (m, 2H), 7.12 (t, J =7.5 Hz, 1H), 6.85 (d, J =7.8 Hz, 1H), 3.75-3.71 (m, 2H), 3.43-3.39 (m, 2H), 1.98-1.93 (m, 2H), 1.63-1.59 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ = 183.4, 157.9, 150.6, 138.3, 125.6, 123.7, 117.7, 109.8, 45.5, 38.2, 36.2, 33.9, 28.3, 26.4; IR: ν = 2956, 2867, 1730, 1606, 1466, 1354, 754, 473; MS (ESI) m/z : calculated for $\text{C}_{15}\text{H}_{18}\text{BrNO}_2$, 323.05; found, 346.02 $[\text{M} + \text{Na}]^+$.

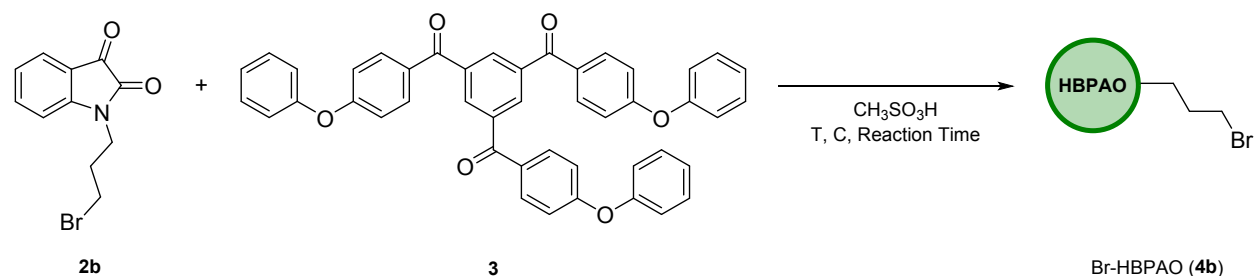


1-(3-bromopropyl)indoline-2,3-dione (2b): Orange solid; ^1H NMR (300 MHz, CDCl_3) δ = 7.68-7.55 (m, 2H), 7.14 (m, 1H), 7.03 (d, J =8.2 Hz, 1H), 3.91 (t, J =7.1 Hz, 2H), 3.48 (t, J =6.2 Hz, 2H), 2.36-2.22 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ = 183.2, 158.4, 150.8, 138.6, 125.6, 124.1, 117.5, 109.9, 38.8, 30.3, 30.0; IR: ν = 2957, 1730, 1608, 1464, 1352, 757, 548, 468; MS (ESI) m/z : calculated for $\text{C}_{11}\text{H}_{10}\text{BrNO}_2$, 266.99; found, 289.98 $[\text{M} + \text{Na}]^+$.



Benzene-1,3,5-triyltris(4-phenoxyphenyl)methanone (3): AlCl_3 (7.8 g, 58.8 mmol) was dissolved in DCE (70 mL) in a flame-dried nitrogen flushed 250 mL two-necked round-bottomed flask under nitrogen atmosphere. Diphenyl ether (23.4 mL, 147 mmol) was added to the reaction mixture in one portion. A solution of Benzene-1,3,5-tricarbonyl trichloride (2.6 g, 9.8 mmol) in DCE (30 mL) was added dropwise at room temperature over 1 hour. The reaction mixture was refluxed for 2 hours. The reaction mixture was quenched in a cold solution of distilled $\text{H}_2\text{O}:\text{HCl}$ (1 M) (1:1). The quenched mixture was extracted with DCM (3 X). The organic layers were combined, washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The concentrate was further purified via precipitation from $\text{DCM}:\text{C}_7\text{H}_{16}$ and $\text{DCM}:\text{MeOH}$. The product was obtained as a white powder (4.8 g, 74%). ^1H NMR (300 MHz, CDCl_3) δ = 8.32 (s, 3H), 7.84 (d, J =8.8 Hz, 6H), 7.45 – 7.39 (m, 6H), 7.21 (t, J =7.4 Hz, 3H), 7.11 (d, J =7.6 Hz, 6H), 7.04 (d, J =8.8 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ = 193.7, 162.4, 155.2, 138.5, 133.5, 132.6, 130.7, 130.2, 124.9, 120.4, 117.2; IR: ν = 1656, 1580, 1486, 1239, 1160, 843, 735, 693, 496 MS (ESI) m/z : calculated for $\text{C}_{45}\text{H}_{30}\text{O}_6$, 666.20; found, 667.60 $[\text{M} + \text{H}]^+$.

1.2 Synthesis of polymers



Scheme S2. Optimization of polymerization.

A flame-dried nitrogen flushed vial was filled with A₂ monomer **2b** and B₃ monomer **3** (equimolar). In CH₃SO₃H (c = 0.05 M). The reaction mixture was heated to the appropriate temperature (rt, 40 °C or 50 °C) and stirred (7, 16 or 48h). The reaction mixture was quenched in distilled H₂O. The precipitate was filtered and washed with distilled H₂O dried and analyzed via GPC (in THF). The results are shown in figure S1 and table 1.

3. Characterization of HBPAOs

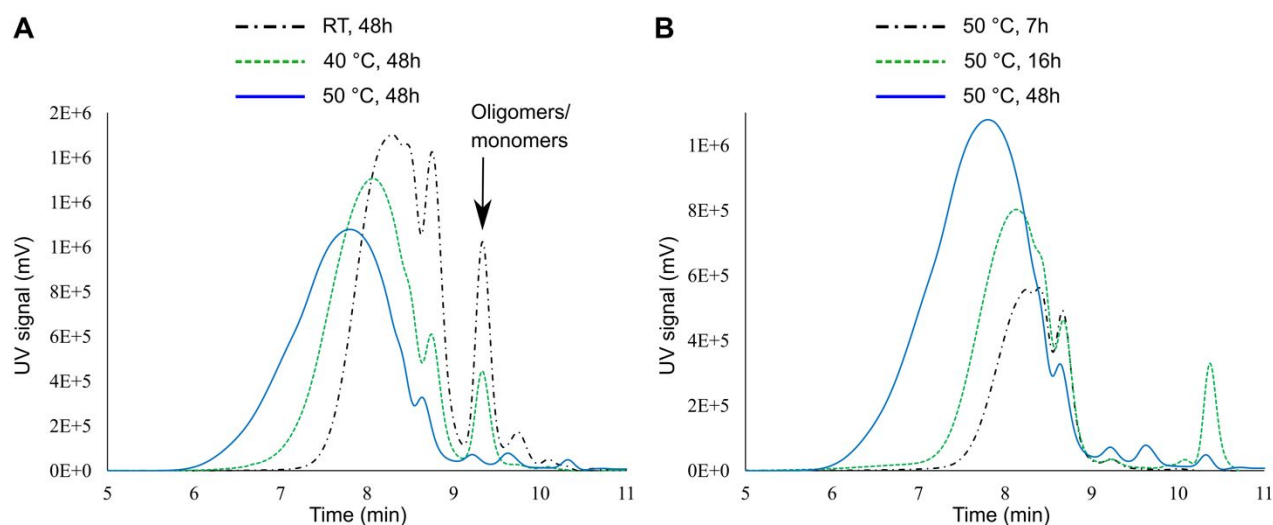


Figure S1. Gel permeation chromatograms for optimization of Br-HBPAO **4b**. Superelectrophilic arylation at different temperatures (**A**) superelectrophilic arylation at different times (**B**). Corresponding data shown in Table 1 in the manuscript.

Additional information on the polymerization was obtained by comparing ¹H NMR spectra of both the A₂ monomer **2b** and B₃ monomer **3** with Br-HBPAO **4b** (Figure S2). Broadened signals are observed in the aromatic region of the Br-HBPAO **4b** spectrum corresponding to equivalent signals in the spectra of the monomers. In the alkyl region three peaks (assignment based on ¹H, ¹³C and HSQC of **2b**) with a ratio of 1:1:1 are observed at similar chemical shift as the A₂ monomer **2b** (peaks k, m and l). ¹³C NMR spectra of both the monomer **2b** and **3** with Br-HBPAO **4b** (Figure S3) confirmed the results of ¹H NMR. Carbonyl carbons C₁ and C₂ peaks of **2b** shifted (C₁ from 158.4 to 177.5 ppm) or disappeared (C₂ at 183.2 ppm) after

polymerization while a new peak at 61.3 ppm appears due to a quaternary carbon center formed.

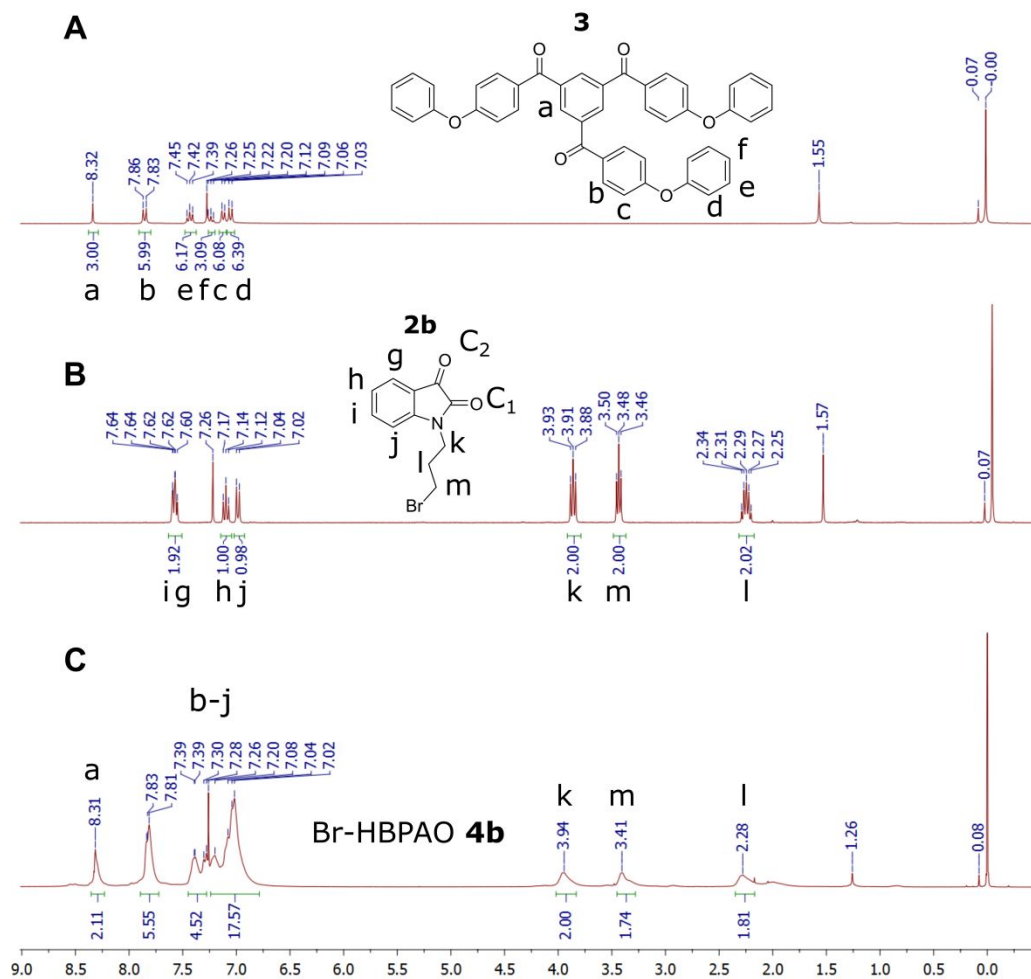


Figure S2. ^1H NMR (CDCl_3) comparison of B_3 monomer **3** (A), monomer **2b** (B) and Br-HBPAO **4b** (C).

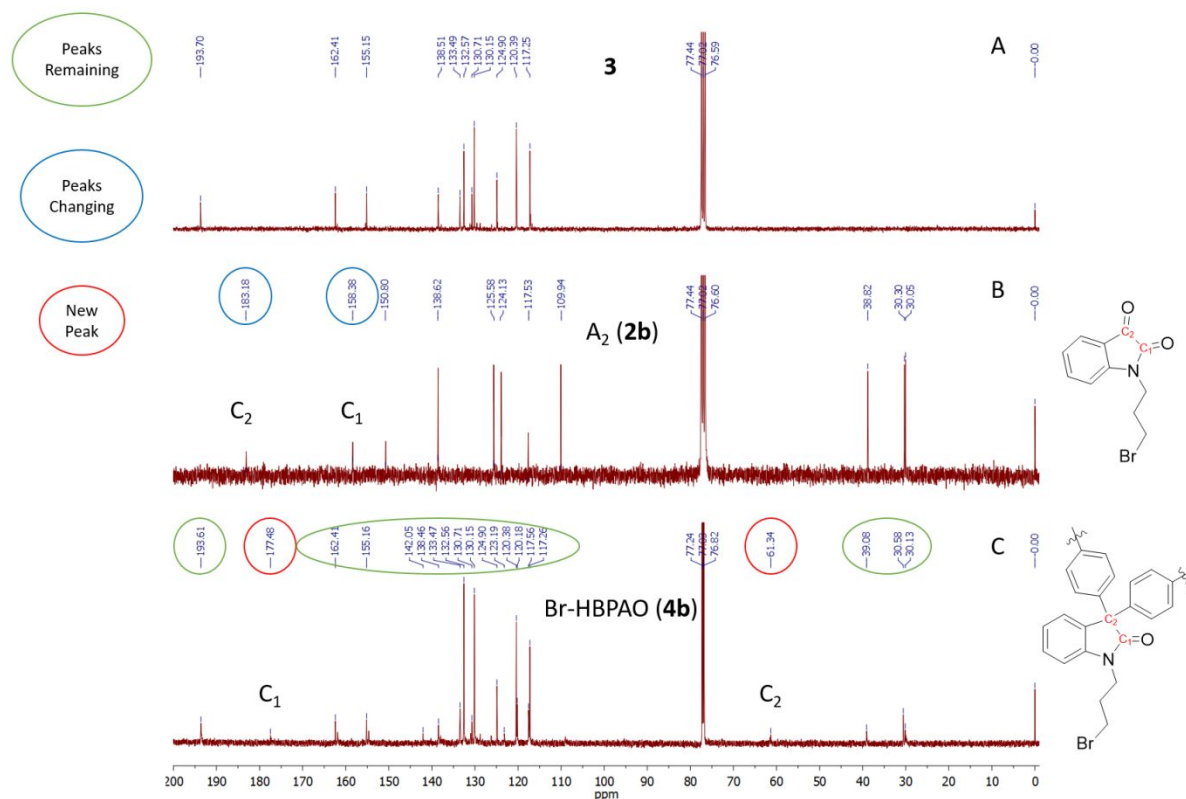


Figure S3. ^{13}C NMR (CDCl₃) comparison of B₃ monomer **3** (A), A₂ monomer **2b** (B) and Br-HBPAO **4b** (C).

Functionalization with NiXantphos was validated via ^1H NMR. Shift of respective signals of the propyl chain was observed after functionalization (Figure S4 and S5).

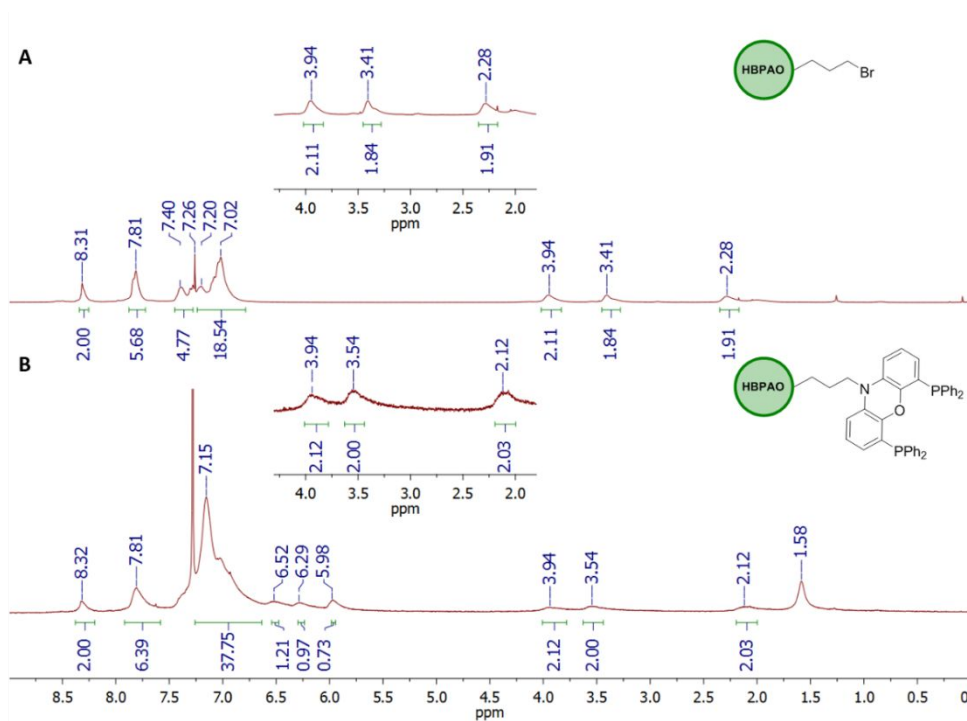


Figure S4. ^1H NMR (CDCl₃) comparison of Br-HBPAO **4b** (A) and NiX-HBPAO **1b** (B).

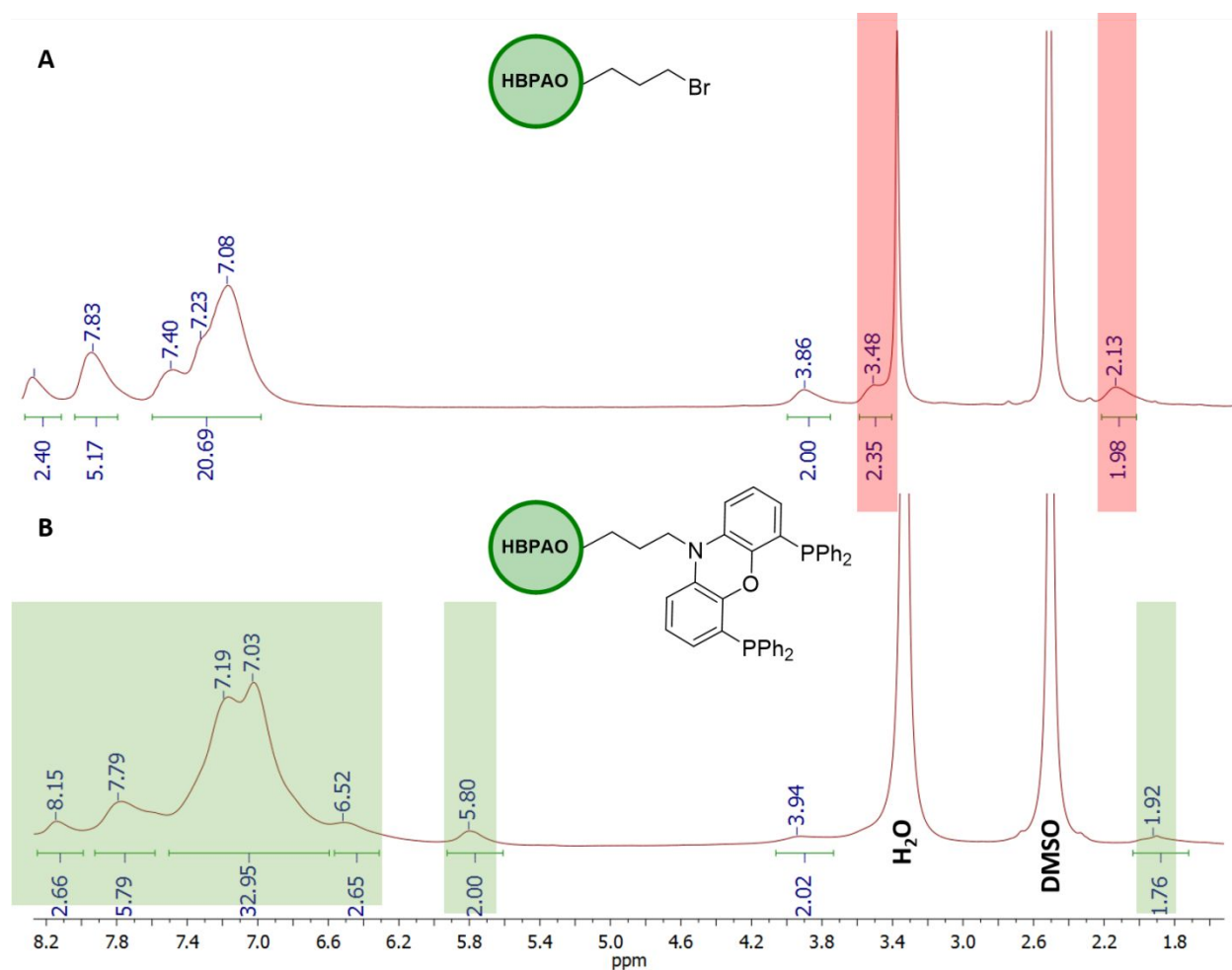


Figure S5. ^1H -NMR ($\text{DMSO}-d_6$) of Br-HBPAO **4b** (A) and NiX-HBPAO **1b** (B). Red band indicates the signals disappearing after functionalization and the green band indicates the new signals appearing after functionalization.

Functionalization with NiXantphos was validated via FT-IR. Disappearance of the free *N*-H of NiXantphos and signals of NiXantphos in the lower region were observed for NiX-HBPAO **1b**.

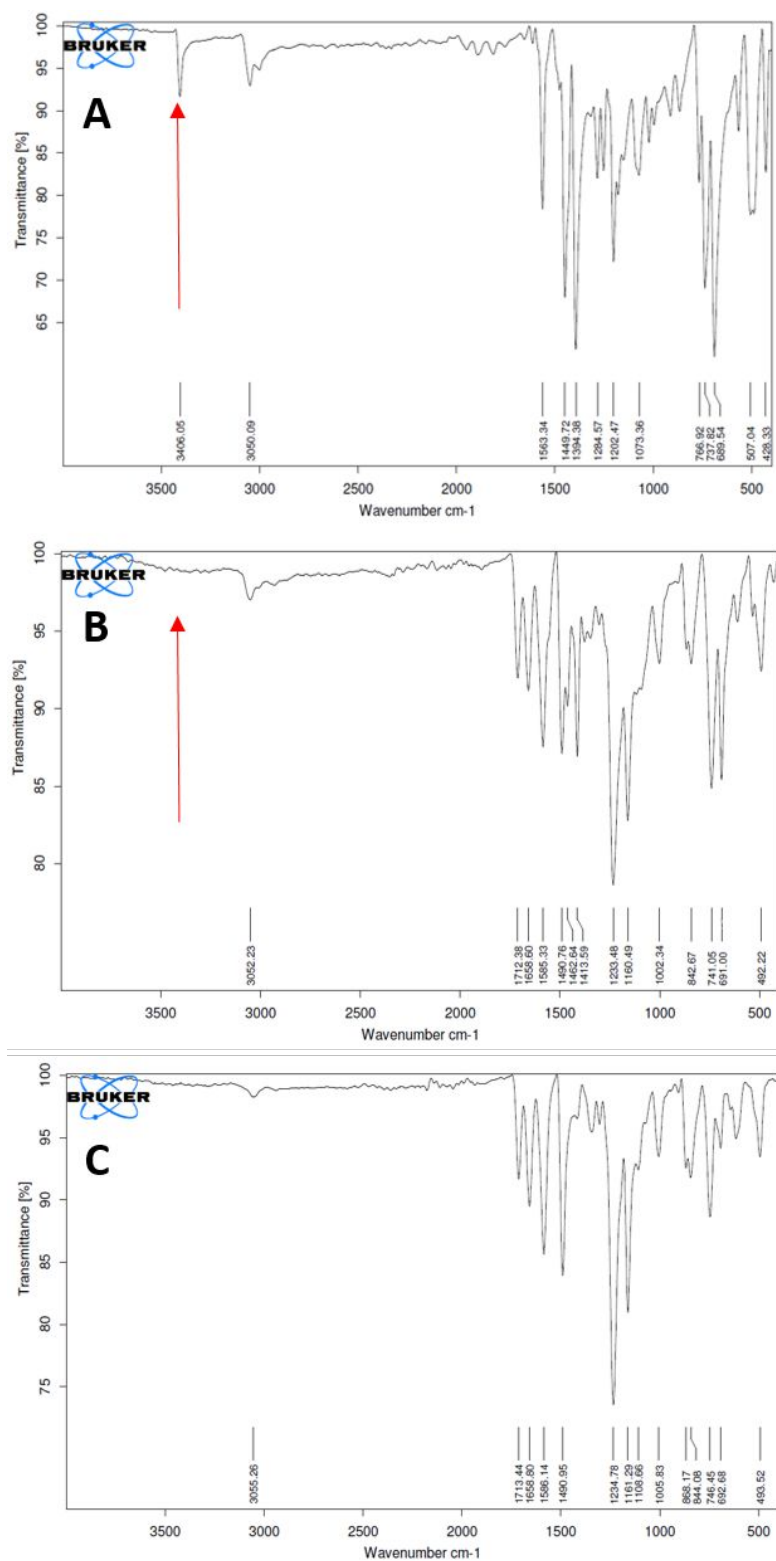


Figure S6. FT-IR trace of NiXantphos **5** (A) of NiX-HBPAO **1b** (B) and of Br-HBPAO **4b** (C).

Functionalization with NiXantphos was validated via GPC. GPC profiles changed after functionalization.

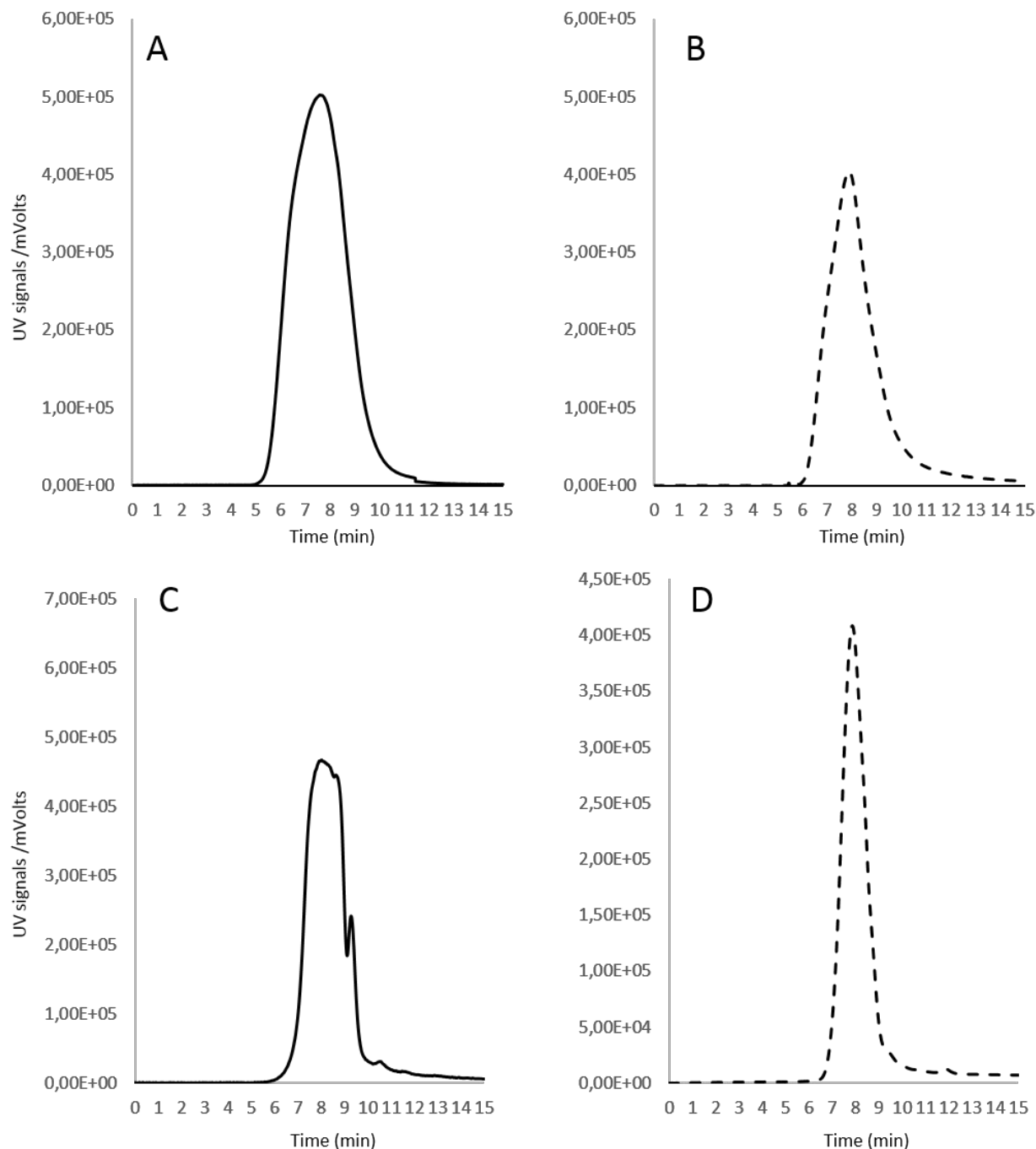


Figure S7. GPC-UV spectra at 254 nm of (A) Br-HBPAO **4b** in THF:DMF 1:1 + 0.05 M LiBr (B) NiX-HBPAO **1b** in THF:DMF 1:1 + 0.05 M LiBr (C) Br-HBPAO **4a** in THF (D) NiX-HBPAO **4b** in THF.

Functionalization with NiXantphos was validated via TGA. TGA profiles changed after functionalization.

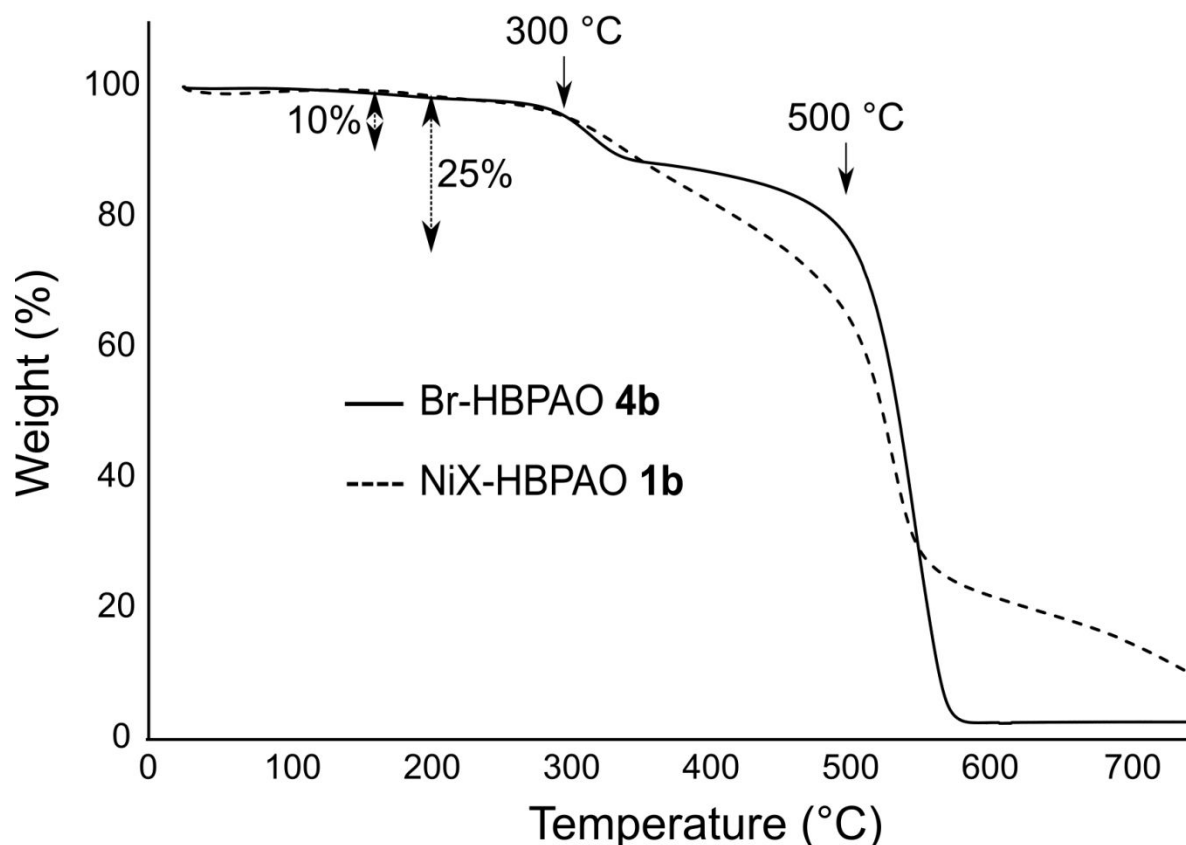


Figure S8. TGA-trace of Br-HBPAO **4b** (solid line) and NiX-HBPAO **1b** (dotted line).

4. Loading of HBPAOs

Br-HBPAOs: The loading of Nix-HBPAOs **4a** and **4b** was determined by TXRF.

Br-HBPAOs: An Eppendorf tube was filled with an exactly determined amount of Br-HBPAO **4b** or **4a** (1-2 mg). The sample was dissolved in THF (900 μ L p.a.). The copper internal standard solution (100 μ L of a copper ICP standard of 1000 ppm Cu in 3 % HNO₃ solution) was added and the mixture was sonicated. A small amount of this prepared solution (5 μ L) was put on a small quartz plate, which was pre-coated with a hydrophobic silicone solution (30 μ L), and dried in an oven at 60 °C. The samples were measured on a Bruker S2 Picofox TXRF spectrometer after evaporation of the solvent. For each Br-HBPAO three samples were measured. The loading of Br-HBPAO **4a** was 1.10 mmol/g and of Br-HBPAO **4b** was 1.34 mmol/g.

Table S1. TXRF results and calculation of loading for Br-HBPAO **4a** and **4b**.

Sample	m (mg)	C ₁ (mg/L) ^a	Loading (mmol/g) ^b
Br-HBPAO 4a	0.50	44.306	1.11
Br-HBPAO 4a	0.80	68.172	1.01
Br-HBPAO 4a	1.29	116.615	1.13
Br-HBPAO 4b	1.23	125.437	1.27

Br-HBPAO 4b	1.44	160.809	1.39
Br-HBPAO 4b	1.22	132.024	1.36

^a determined by TXRF

^b calculated via: $Loading \left[\frac{mmol}{g} \right] = \left(\frac{c_{TXRF} \left[\frac{mg}{L} \right] \times 0.001 L}{A_r \left[\frac{g}{mol} \right] \times m_{Br-HBP} [mg]} \right) \times 1000 \left[\frac{mmol}{mol} \right]$ with A_r the standard atomic weight of bromine and a factor 1000 to convert mol to mmol.

Nix-HBPAOs: The loading of Nix-HBPAOs **1a** and **1b** was determined by qNMR and CHN elemental analysis.

1) qNMR³⁻⁴

An NMR tube was filled with an exactly determined amount of Nix-HBPAOs **1a** or **1b** and triphenylphosphine oxide (cas: 791-28-6) ($\pm 1-2$ mg) dissolved in 700 μ L DMF:DMSO- d_6 (3:1). ³¹P NMR spectra (600 Mhz) was recorded. After determining the optimal parameters (optimal parameters: 01p= 2.5 ppm, d1= 20 sec, NS= 128, SW= 100, 600 Mhz) the procedure was repeated two more times.

Table S2. qNMR results and calculation of loading for Nix-HBPAO **1a** and **1b**.

Sample	Nix-HBPAO m (mg)	OPPh ₃ m (mg)	OPPh ₃ n (mmol)	Peak area OPPh ₃	Peak area Nix-HBPAO	Loading Nix-HBPAO (mmol/g) ^a
NiX-HBPAO 1a	0.9	1.4	0.005	1	0.22	0.62
NiX-HBPAO 1a	0.8	1.1	0.004	1	0.25	0.62
NiX-HBPAO 1a	1.0	1.2	0.004	1	0.28	0.60
NiX-HBPAO 1b	3.4	1.7	0.006	1	0.86	0.77
NiX-HBPAO 1b	3.3	1.7	0.006	1	0.84	0.78
NiX-HBPAO 1b	3.0	1.5	0.005	1	0.85	0.76

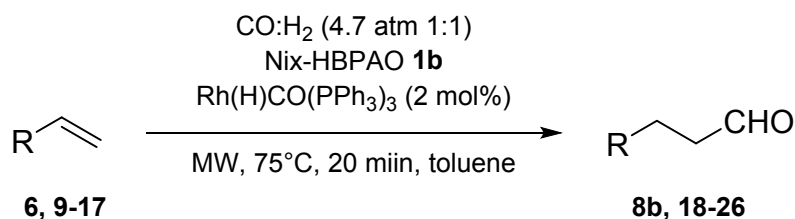
^a calculated via: $Loading \left[\frac{mmol}{g} \right] = \left(n_{OPPh_3} [mmol] \cdot \left(\frac{Peak\ area\ Nix-HBPAO}{2} \right) \right) \cdot \left(\frac{1000}{mass\ Nix-HBPAO [mg]} \right)$

2) CHN elemental analysis⁵⁻⁸

The difference in nitrogen content before functionalization (Br-HBPAO **4a/4b**) and after (NiX-HBPAO **1a/1b**) was determined by CHN elemental analysis resulting in a loading of 0.68 mmol/g **1a** and of 0.84 mmol/g for **1b**, respectively.

5. Hydroformylation

General procedure:



Scheme S3. Hydroformylation.

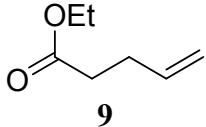
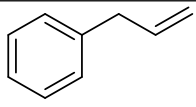
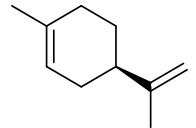
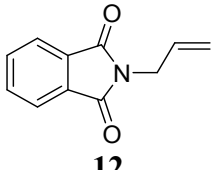
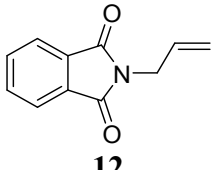
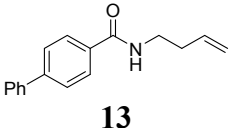
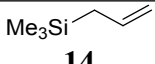
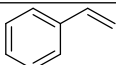
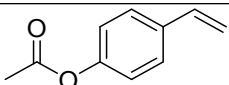
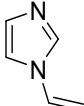
General procedure: NiX-HBPAO **1b** (16 mol%) was added to a solution of Rh(CO)H(PPh₃)₃ (2 mol%) in toluene (1.4 mL) and stirred at room temperature under nitrogen atmosphere for 10 minutes. The proper olefin (0.0375 mmol) was added in one portion and the mixture was pressurized with syngas (4.8 bar) and irradiated with microwaves for 20 minutes, at 75 °C (max power 150 W). The tube was cooled and the internal gas released. The reaction mixture was filtered, to recover NiX-HBPAO **1b**, washed with C₆H₁₄ (2 X 1 mL) and the filtrate evaporated under reduced pressure. The crude mixture was further purified by flash chromatography when necessary.

Table S3. Additional experiments for 1-octene hydroformylation

Entry	Ligand	Ligand:cat	Conditions	7 (%)	8a:8b (Conv%)	Conv (%)
1	1a	8:1	CO/H ₂ (2.7 bar), toluene, 110 °C, MW, 4 min	80	-	80
2	1a	8:1	CO/H ₂ (4.8 bar), toluene, 90 °C, MW, 10 min	46	-	46
3	1a	8:1	CO/H ₂ (2.7 bar), EtOH, 110 °C, MW, 4 min	35	1:1 (5)	40
4	1a	8:1	CO/H ₂ (2.7 bar), EtOH, 110 °C, MW, 20 min	40	1:1 (5)	50
5	1a	8:1	CO/H ₂ (4.8 bar), EtOH, 110 °C, MW, 4 min	50	-	50
6	1b	8:1	CO/H ₂ (2.7 bar), toluene, 90 °C, MW, 10 min	25	6:1 (20)	49
7	1b	8:1	CO/H ₂ (4.8 bar), toluene, 90 °C, MW, 20 min	50	n.d.	54

Table S4. Additional data for hydroformylation scope.

Entry	Alkene	Conversion ^a	hydrogenation ^a	Linear hydroformylation ^b	l/b ratio ^c
-------	--------	-------------------------	----------------------------	--------------------------------------	------------------------

1	 9	>99%	0%	85%	99:1
2	 10	65%	1%	60%	15:1
3 ^d	 11	6%	0%	0%	0:1
4	 12	93%	46%	41%	7:1
5 ^e	 12	98%	21%	62%	12:1
6	 13	>99%	-	70%	70:1
7	 14	>99%	0%	95%	1:0
8 ^f	 15	80%	<1%	50%	2:1
9 ^f	 16	95%	14%	58%	2.5:1
10	 17	>99%	>99%	0%	-

General conditions: **9-17** (0.04 mmol), **1b** (16 mol%), Rh(H)CO(PPh₃)₃ (2 mol%) (8:1 ratio) in 1.4 mL toluene 20 min microwave (MW) at 75 °C under 4.8 bar CO:H₂ (1:1).

^a Determined by GC with benzoquinone as internal standard.

^b Isolated yield.

^c determined by ¹H NMR.

^d **1b** (32 mol%), Rh(H)CO(PPh₃)₃ (2 mol%) (16:1 ratio).

^e **1b** (32 mol%), Rh(H)CO(PPh₃)₃ (2 mol%) (16:1 ratio) under 4.0 bar CO:H₂ (1:1).

^f Homogeneous conditions ratio **1b**:**15b**:**15c** 1:9 and ratio **16b**:**16c** 1:15.

Nonanal (8a)⁹: ¹H NMR (200 MHz, CDCl₃) δ = 0.85 (t, J = 6.6 Hz, 3H), 1.20 (m, 10H), 1.59 (m, 2H), 2.41 (m, 2H), 9.73 (s, 1H). MS (EI) m/z: 142. Yield: 95%

Ethyl 6-oxohexanoate (18)⁹: ¹H NMR (200 MHz, CDCl₃) δ = 9.67 (s, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.48-2.32 (m, 2H), 2.30-2.21 (m, 2H), 1.61-1.49 (m, 4H), 1.16 (t, J = 7.1 Hz, 3H). MS (ESI) m/z: 159 [M + H]⁺, 290 [M + Na]⁺. Yield: 85%

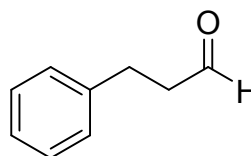
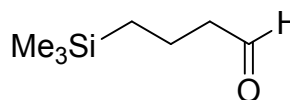
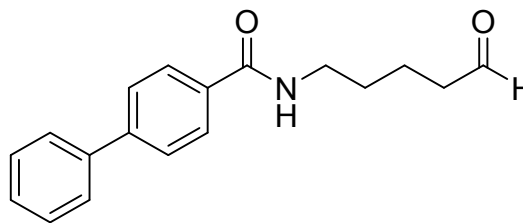
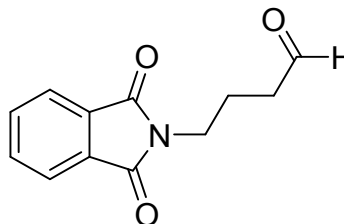
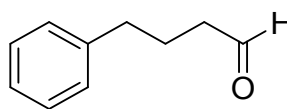
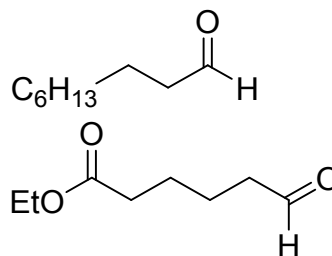
4-phenylbutanal (19)⁹: ¹H NMR (200 MHz, CDCl₃) δ = 1.95 (m, 2H), 2.45 (t, J = 7.2, 2H), 2.65 (t, J = 7.2, 2H), 7.25 (m, 5H), 9.86 (s, 1H). MS (ESI) m/z: 149 [M + H]⁺. Yield: 60 %

4-(1,3-dioxoisindolin-2-yl)butanal (21)⁹: ¹H NMR (400 MHz, CDCl₃) δ = 9.77 (s, 1H), 7.82 (d, J = 5.5 Hz, 2H), 7.69 (d, J = 5.5 Hz, 2H), 3.71 (t, J = 6.8 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.02-1.95 (m, 2H). MS (ESI) m/z: 218 [M + H]⁺, 240 [M + Na]⁺. Yield: 62%

N-(4-oxobutyl)-[1,1'-biphenyl]-4-carboxamide (22)¹⁰: ¹H NMR (400 MHz, CDCl₃) δ = 9.75 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.77–7.53 (m, 4H), 7.56–7.27 (m, 3H), 7.27–7.10 (m, 1H), 3.45 (q, J = 6.3 Hz, 2H), 2.50 (t, J = 6.7 Hz, 2H), 1.70-1.64 (m, 2H). MS (ESI) m/z: 268 [M + H]⁺, 290 [M + Na]⁺. Yield: 70%

4-(trimethylsilyl)butanal (23)¹¹: ¹H NMR (400 MHz, CDCl₃) δ = 9.75 (s, 1H), 2.48 (t, J = 7.2 Hz, 2H), 1.65 (m, 2H), 0.51 (t, J = 8.4 Hz, 2H), 0.02 (s, 9H). MS (EI) m/z: 144. Yield: 95%

3-phenylpropanal (24)¹²: ¹H NMR (400 MHz, CDCl₃) δ = 9.80 (t, J = 1.4 Hz, 1H), 7.30 (d, J = 8.4, 2H), 7.26–7.16 (m, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.92–2.64 (m, 2H). MS (ESI) m/z: 135 [M + H]⁺. Yield: 50%



4-(3-oxopropyl)phenyl acetate (25)¹³: ¹H NMR (400 MHz, CDCl₃) δ = 9.79 (s, 1H), 7.17 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.26 (s, 3H). MS (ESI) m/z: 193 [M + H]⁺, 215 [M + Na]⁺. Yield: 58%

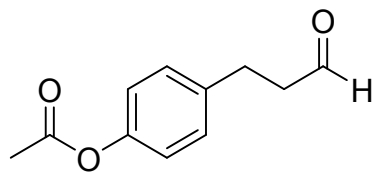


Table S5. Additional experiments substrate scope

Entry	Alkene	Ligand (1b) :Cat	Conditions	SM	Hydrogenation	Product
1		8:1	CO:H ₂ 1:1 (4.8 bar), toluene, 90 °C, MW, 20 min	68%	20%	-
2		16:1	CO:H ₂ 1:1 (4.8 bar), toluene, 90 °C, MW, 20 min	70%	25%	-
3		16:1	CO:H ₂ 1:1 (5.8 bar), toluene, 90 °C, MW, 20 min	50%	40%	5%
4		16:1	CO:H ₂ 1:1 (4.8 bar), toluene, 75 °C, MW, 20 min	64%	30%	5%
5		16:1	CO:H ₂ 1:1 (4.0 bar), toluene, 75 °C, MW, 20 min	-	85%	-
6		16:1	CO:H ₂ 1:1 (2.7 bar), toluene, 75 °C, MW, 20 min	90%	-	-
7		16:1	CO:H ₂ 1:1 (2.7 bar), toluene, 90 °C, MW, 10 min	70%	30%	-

6. Leaching of Rhodium

General procedure:

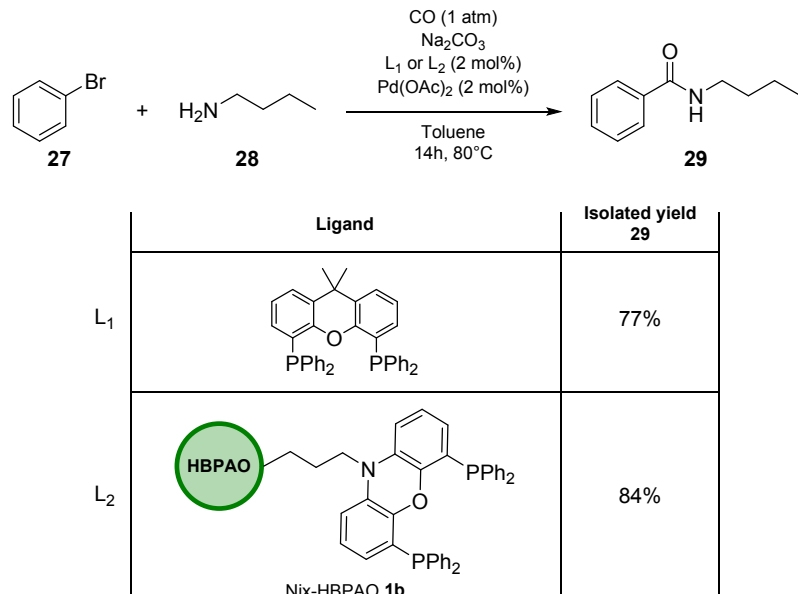
1) Complexation of rhodium

The solid catalyst **1b** (105 mg, 0.081 mmol) was added to a solution of $\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_3$ (100 mg, 0.11 mmol) in toluene (2 mL). The mixture was pressurized with syngas (4.8 bar) and irradiated with microwaves for 20 minutes, at 75 °C (max power 150 W). The tube was cooled and the internal gas released. After centrifugation (3500 rpm, 1 min, 25 °C) the solvent was removed and the catalyst washed with toluene (1 mL X 10), centrifugated and the solvent removed, the procedure was repeated for consecutive 5 times. The solutions collected were evaporated and the rhodium quantity determined by ICP analysis. After drying the catalyst overnight, the solid was suspended in toluene (2 mL). The mixture was pressurized with syngas (4.8 bar) and irradiated with microwaves for 20 minutes, at 75 °C (max power 150 W). The tube was cooled and the internal gas released. After centrifugation (3500 rpm, 1 min, 25 °C) the solvent was removed and the catalyst washed with toluene (1 mL X 5), centrifugated and the solvent removed, the procedure was repeated for consecutive 5 times. The solutions collected were evaporated and the rhodium quantity determined by ICP analysis to check if rhodium leaching was still observed.

2) Hydroformylation with rhodium complexed catalyst

The preformed solid catalyst (loading 0.01 mmol/g, 100 mg, 0.001 mmol) was suspended in toluene (0.5 mL). 1-octene (8 μL , 0.05 mmol) was added in one portion and the mixture was pressurized with syngas (4.8 bar) and irradiated with microwaves for 20 minutes, at 75 °C (max power 150 W). The tube was cooled and the internal gas released. After centrifugation (3500 rpm, 1 min, 25 °C) the solvent was removed and the catalyst washed with toluene (1 mL X 5), centrifugated and the solvent removed 5 times. The solutions collected were evaporated and the rhodium quantity determined by ICP analysis and the conversion determined by GC analysis. The catalyst was dried under vacuum over-night and used for additional 4 times, in the same reaction conditions.

7. Aminocarbonylation



Scheme S4. Aminocarbonylation of bromobenzene.

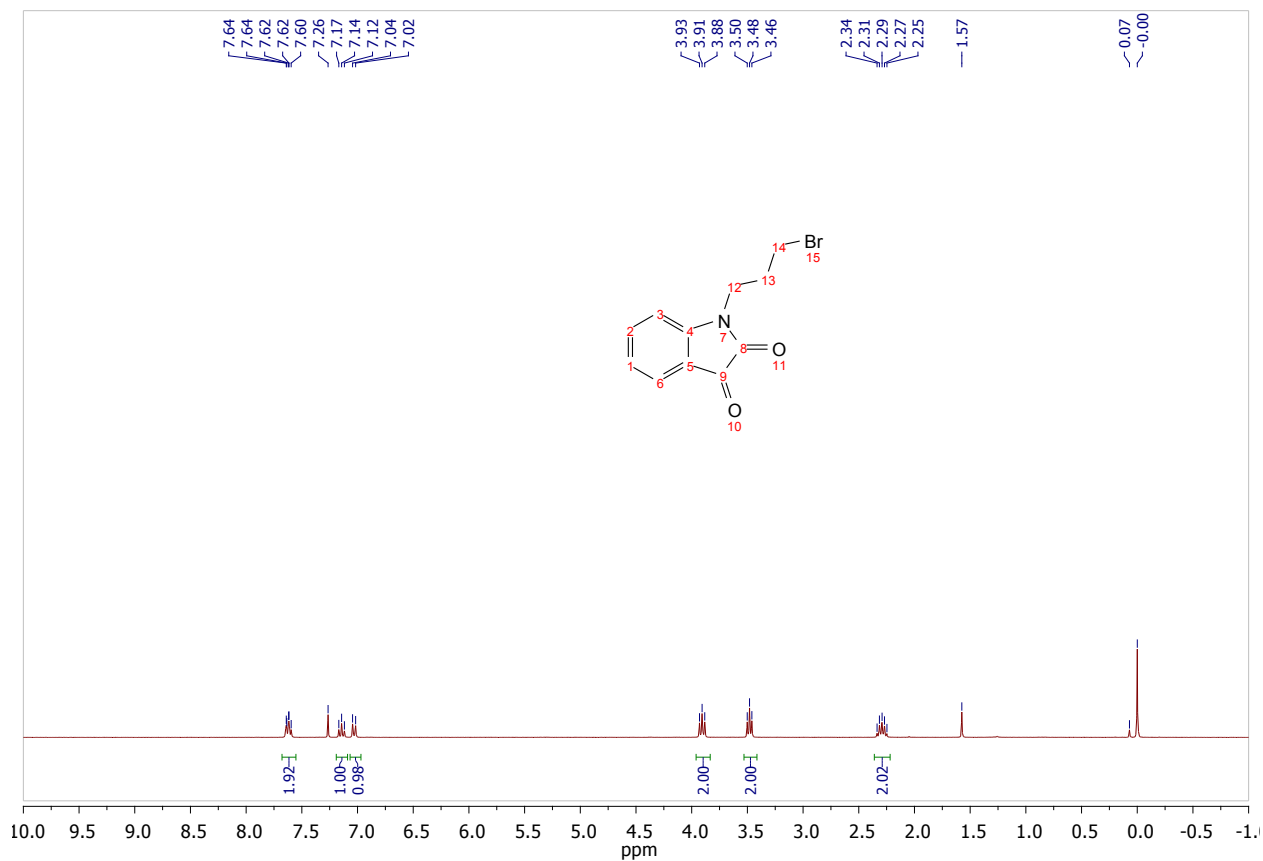
***N*-butylbenzamide (**29**):** A flame dried vial was filled with Na₂CO₃ (318 mg, 3.0 mmol), Pd(OAc)₂ (4.5 mg, 2 mol%) and L₁ or L₂ (2 mol%) under argon atmosphere. The vial was purged with argon (3 X). Dry degassed toluene (2 mL), bromobenzene (105 µL, 1.0 mmol) and benzylamine (149 µL, 1.5 mmol) were subsequently added in one portion. Carbon monoxide (CO) was bubbled through the mixture for 5 min. The mixture was stirred at 80 °C overnight under carbon monoxide atmosphere.

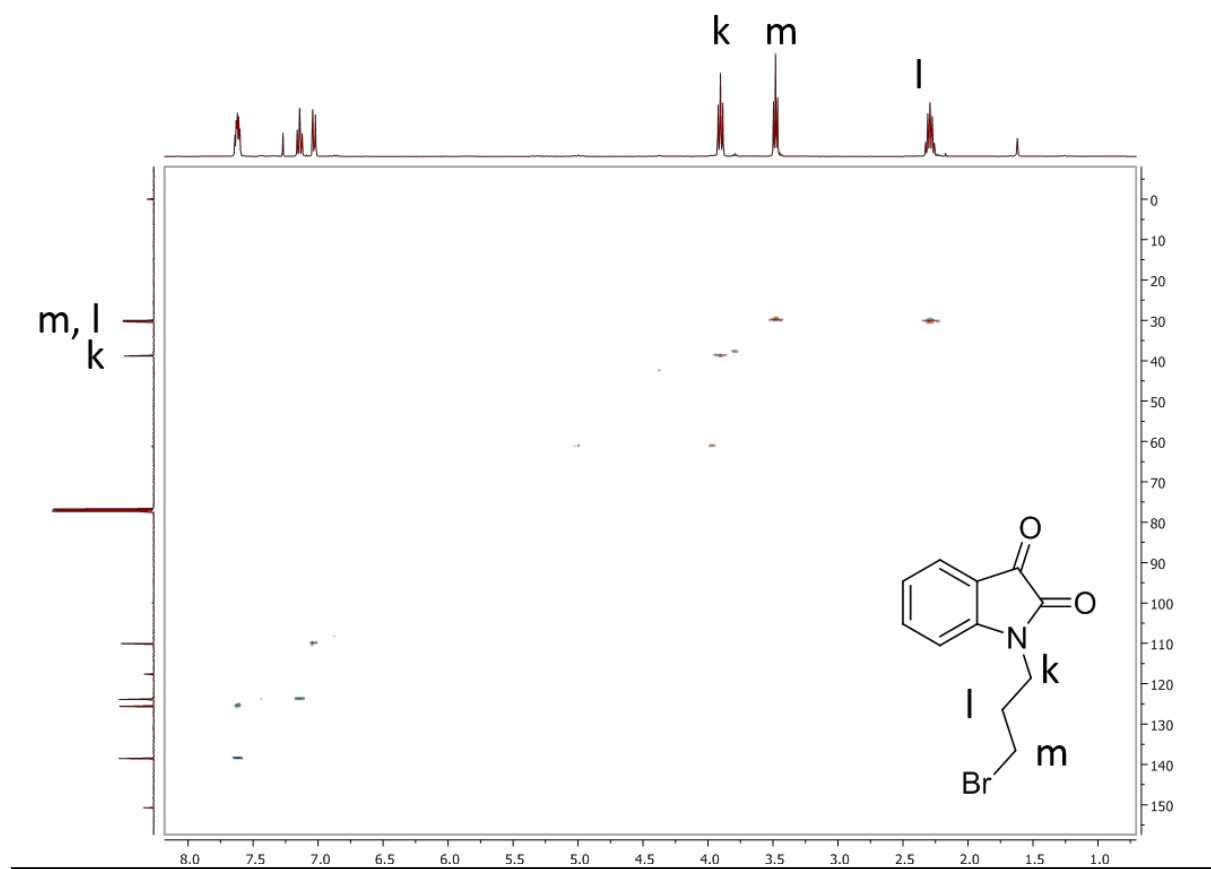
For Xantphos: The reaction mixture was diluted with EtOAc and filtered over celite®, concentrated and further purified by MPLC (C₇H₁₆:EtOAc 8:2) to obtain *N*-butylbenzamide (136 mg, 77%) as a colorless oil. Spectroscopic data were identical to the reported values. ¹H NMR (300 MHz, CDCl₃) δ = 7.77-7.74 (m, 2H), 7.49-7.40 (m, 3H), 6.13 (br. s, 1H), 3.49-3.43 (m, 2H), 1.65-1.56 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, J = 7.3Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ = 167.5, 134.9, 131.3, 128.6, 126.8, 39.8, 31.8, 20.2, 13.8

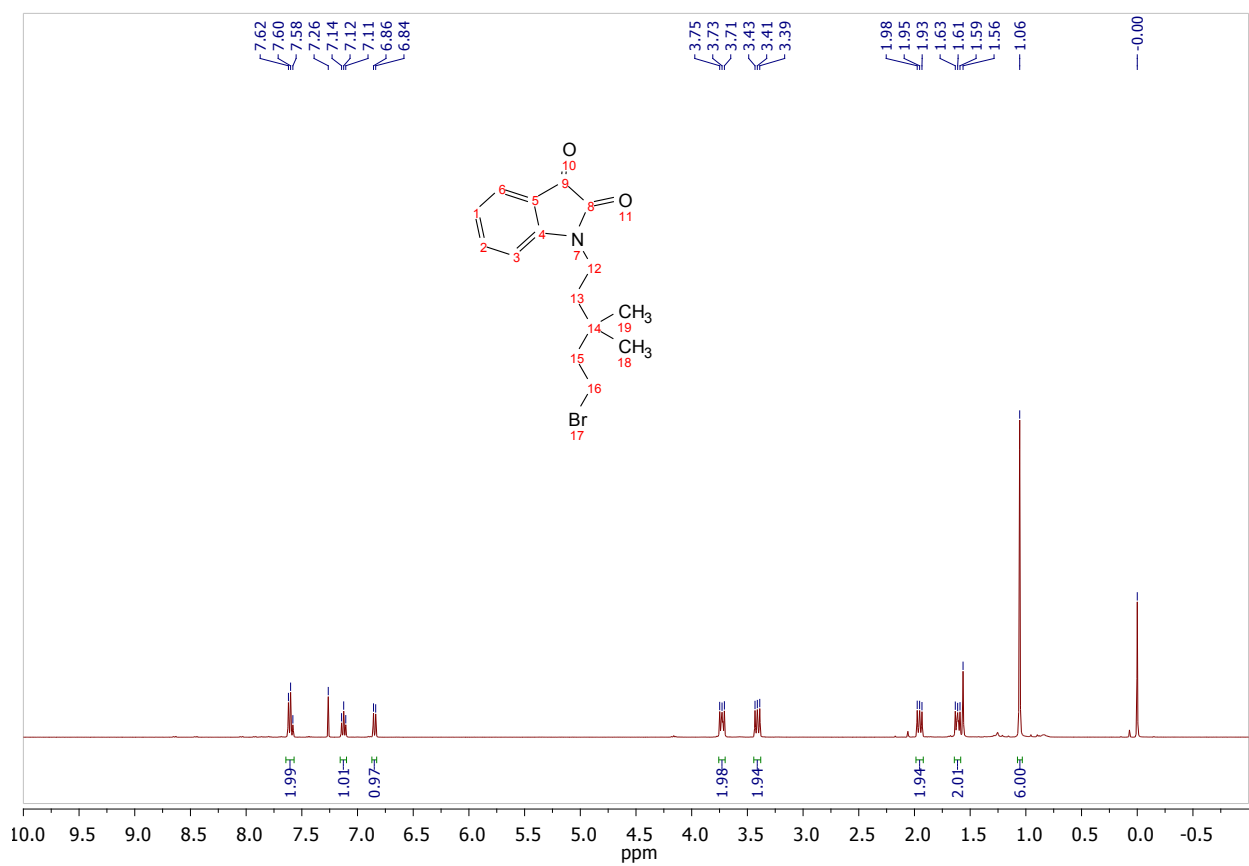
For Nix-HBPAO **1b:** The reaction mixture was diluted with EtOAc and the catalyst was filtered off. The filtrate was concentrated and further purified by MPLC (C₇H₁₆:EtOAc 8:2) to obtain *N*-butylbenzamide (149 mg, 84%) as a colorless oil. Spectroscopic data were identical to the reported values. ¹H NMR (300 MHz, CDCl₃) δ = 7.77-7.74 (m, 2H), 7.49-7.40 (m, 3H), 6.13 (br. s, 1H), 3.49-3.43 (m, 2H), 1.65-1.56 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, J = 7.3Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ = 167.5, 134.9, 131.3, 128.6, 126.8, 39.8, 31.8, 20.2, 13.8

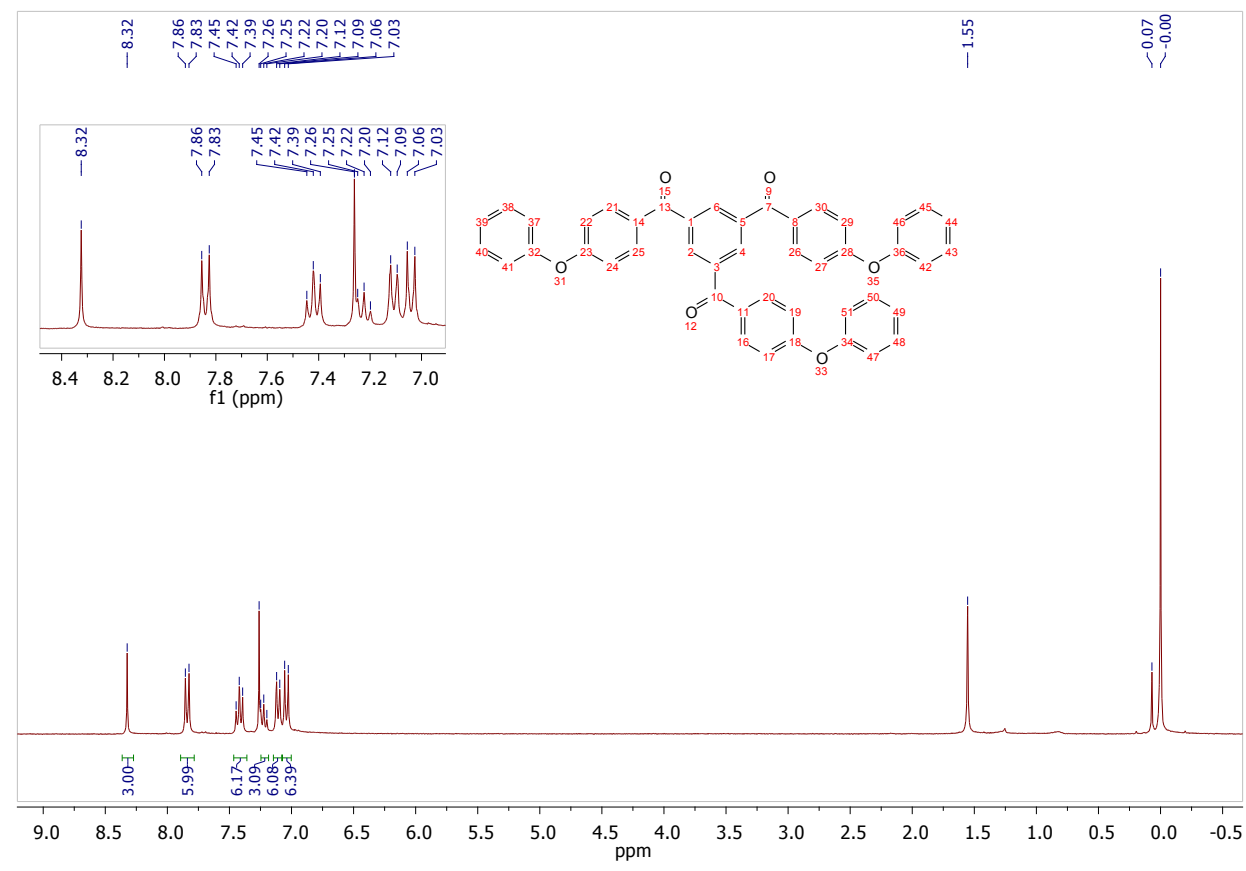
8. NMR spectra

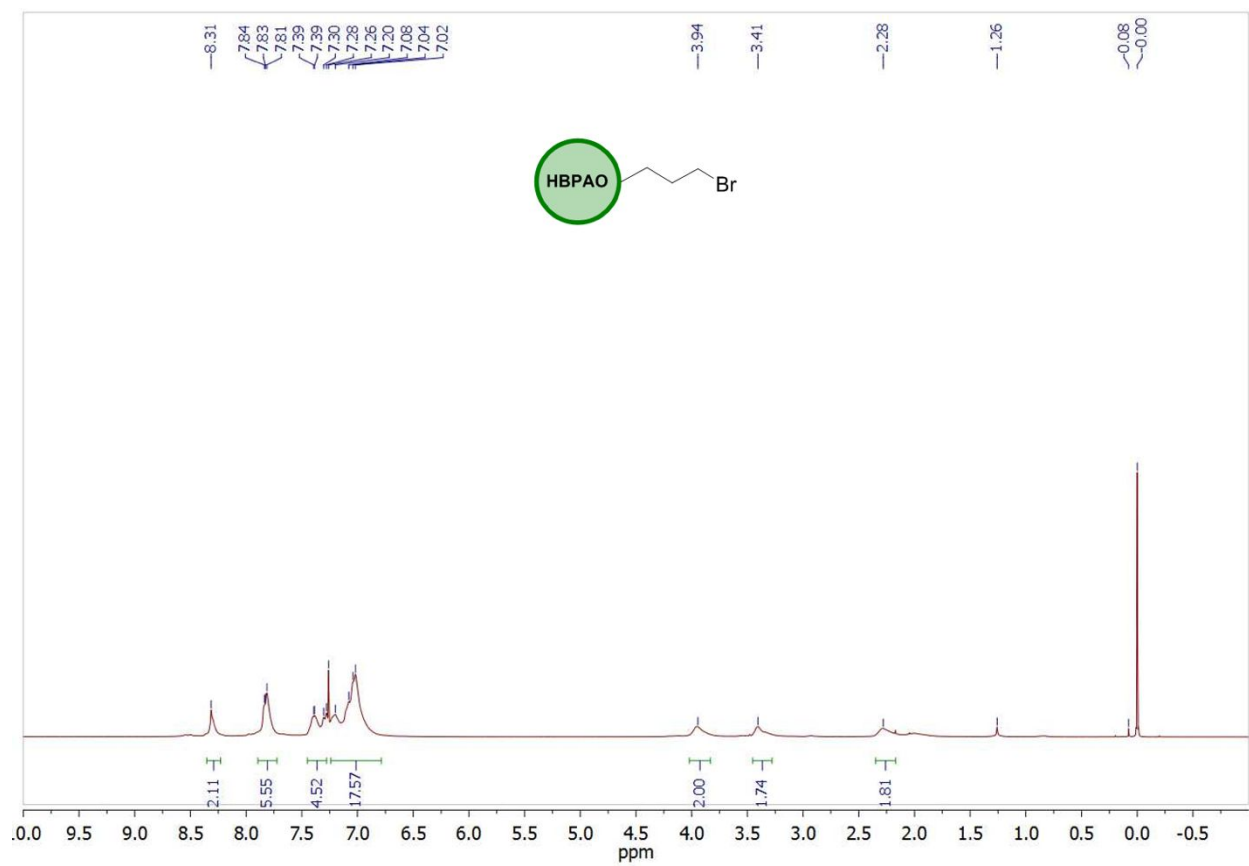
7.1 ^1H NMR spectra

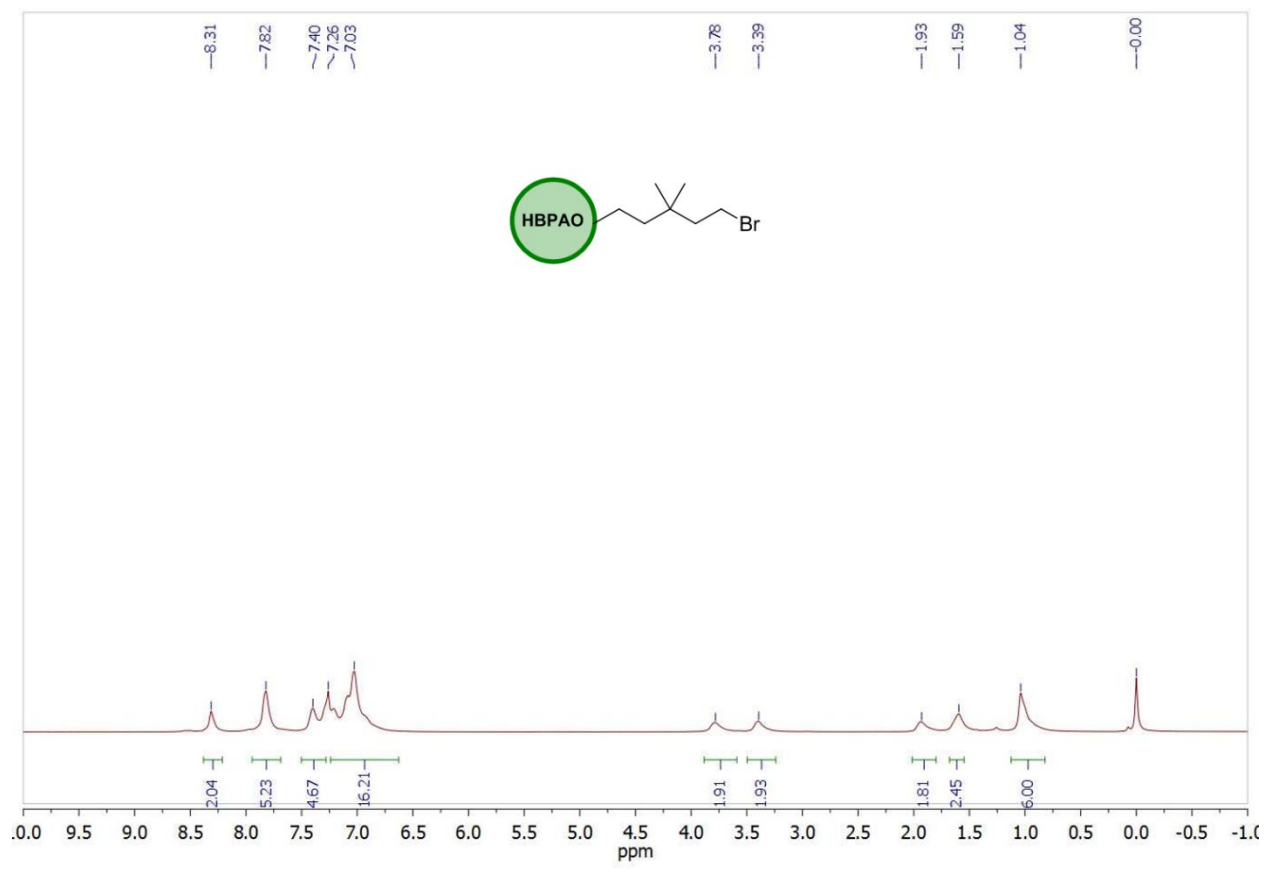


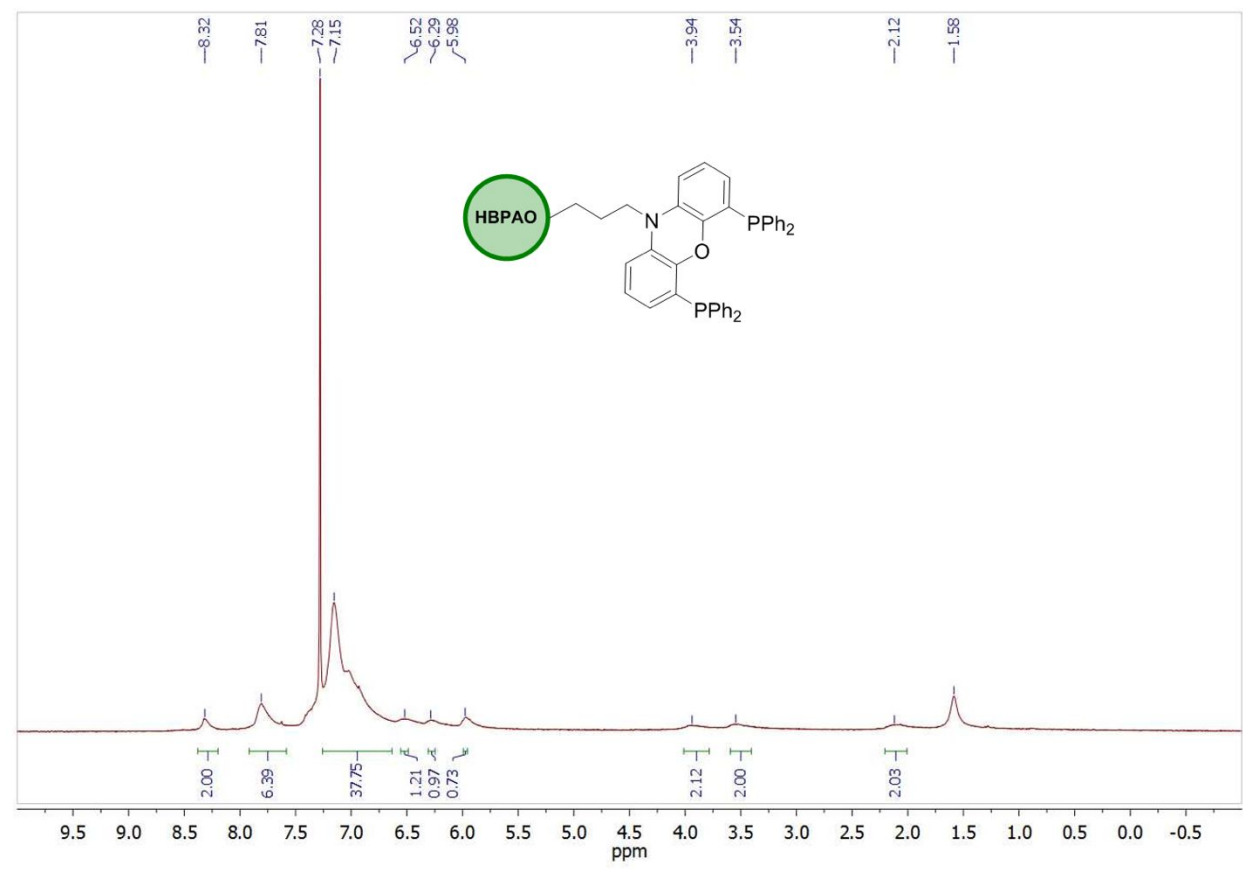


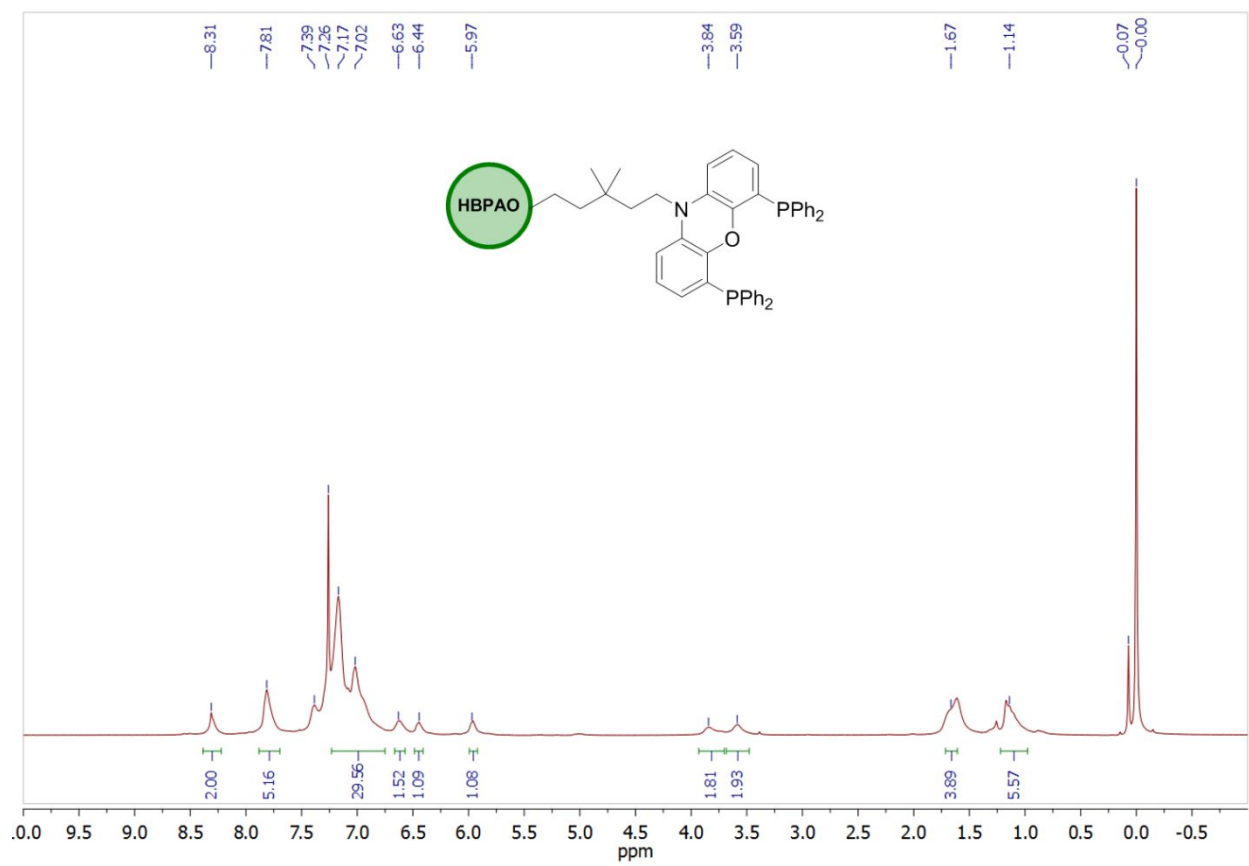




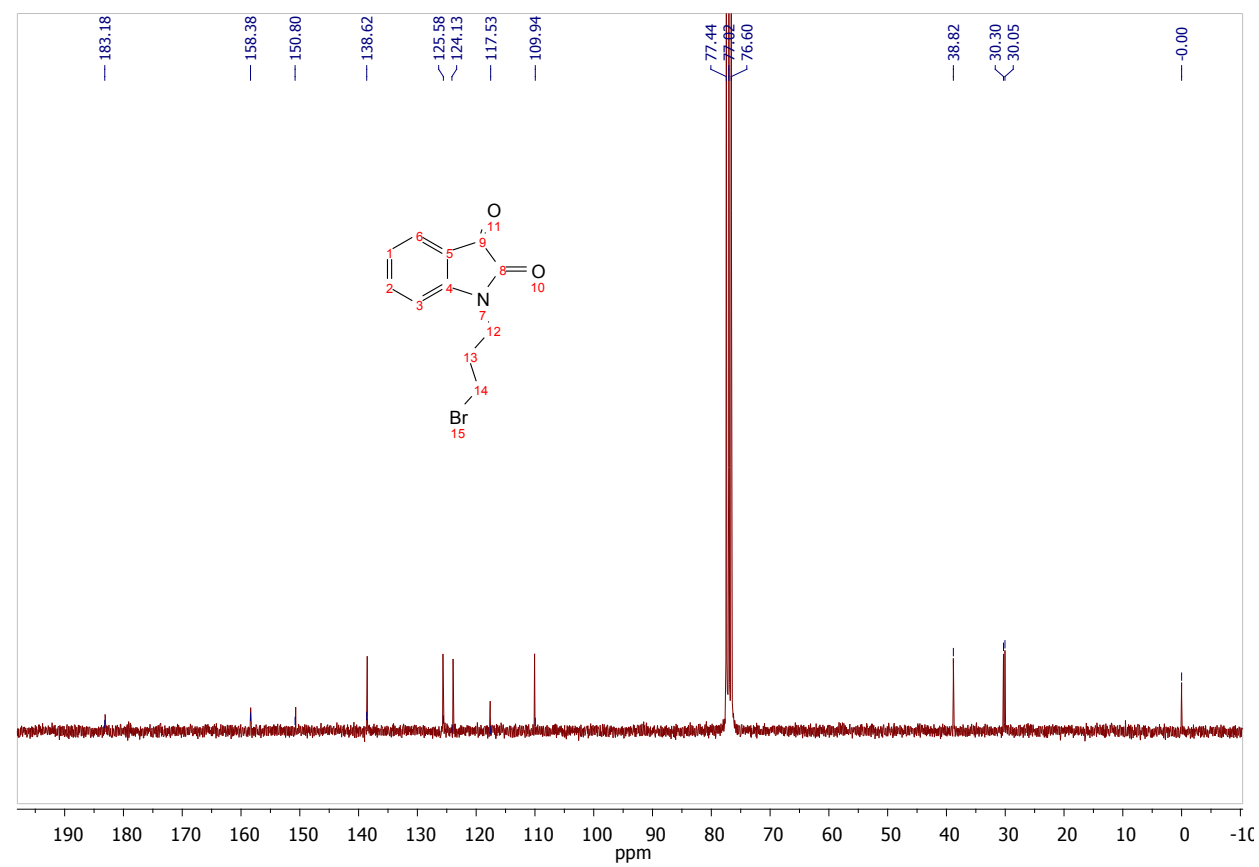


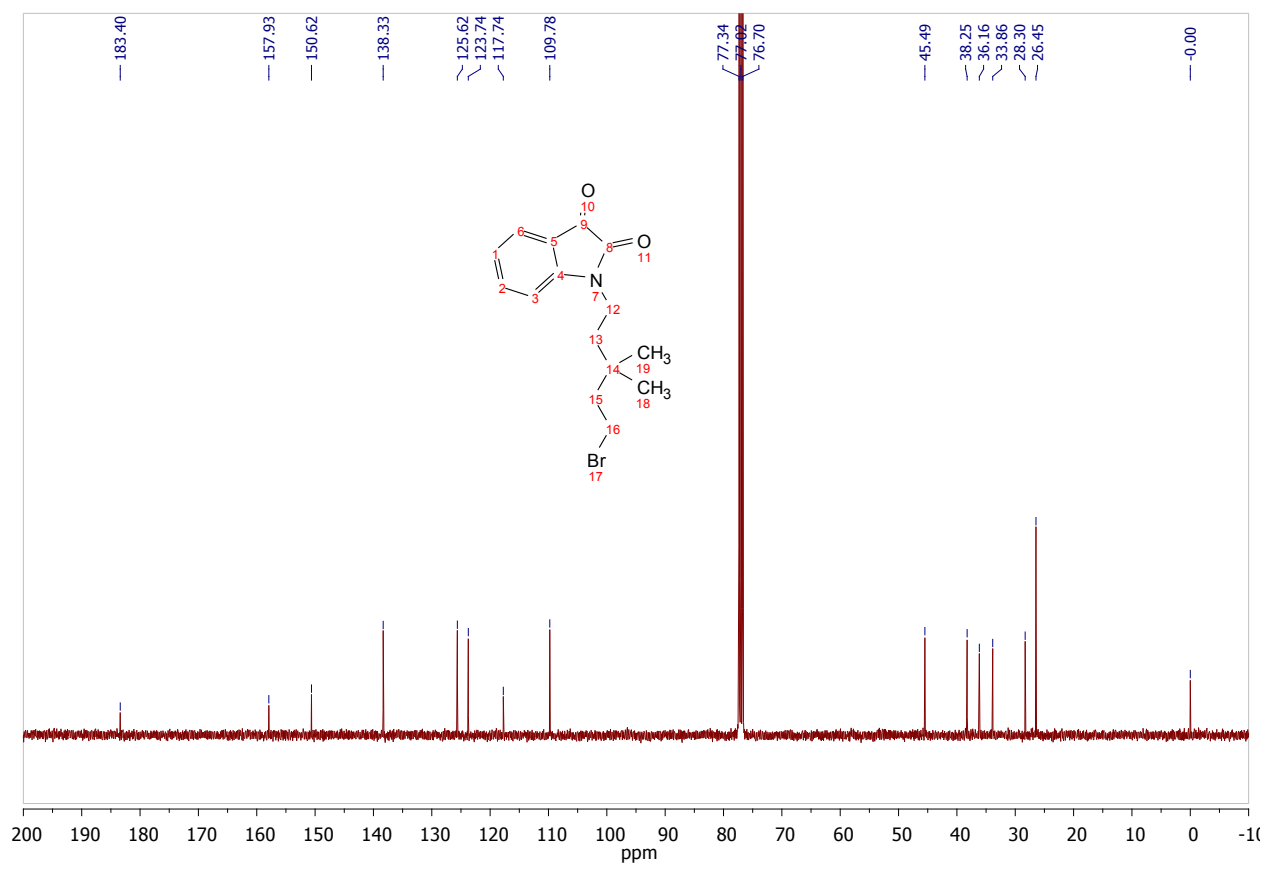




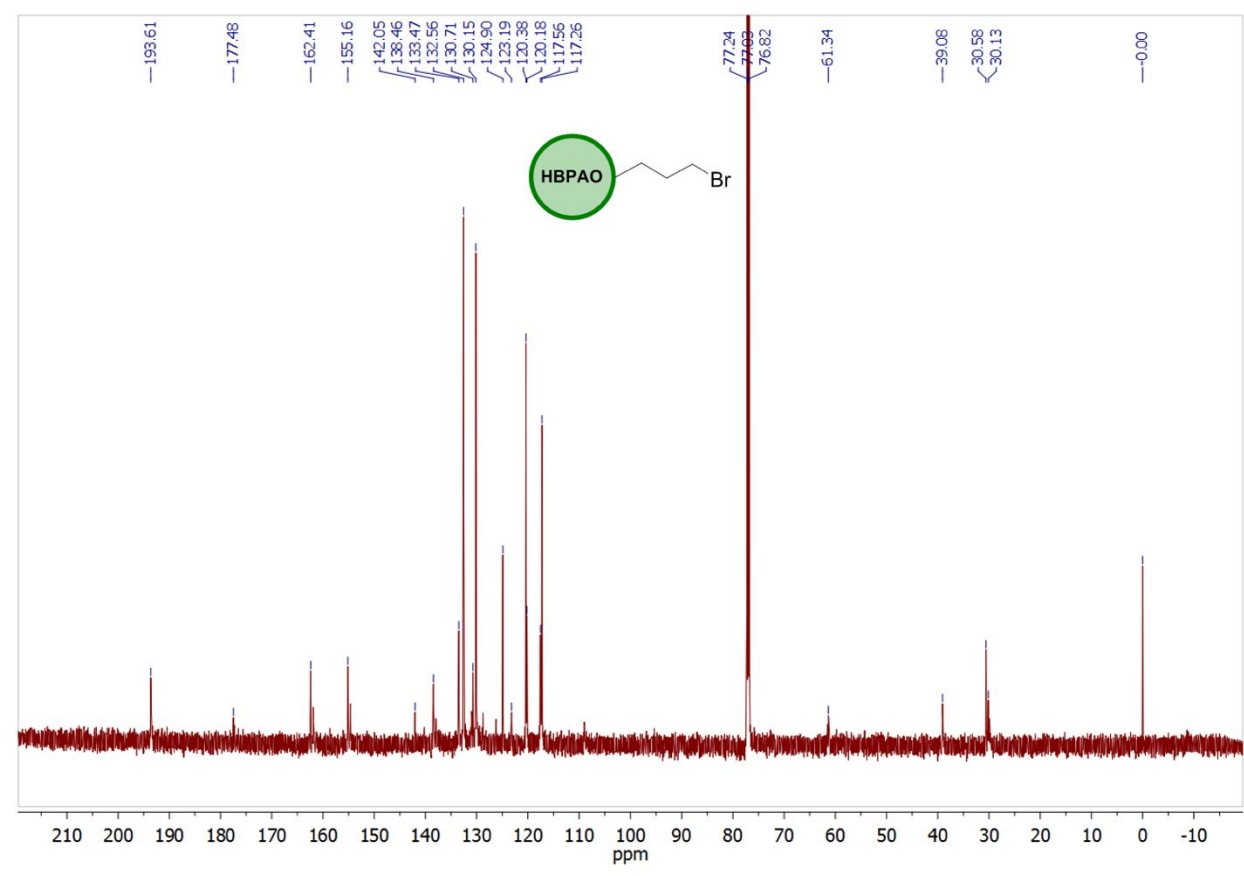


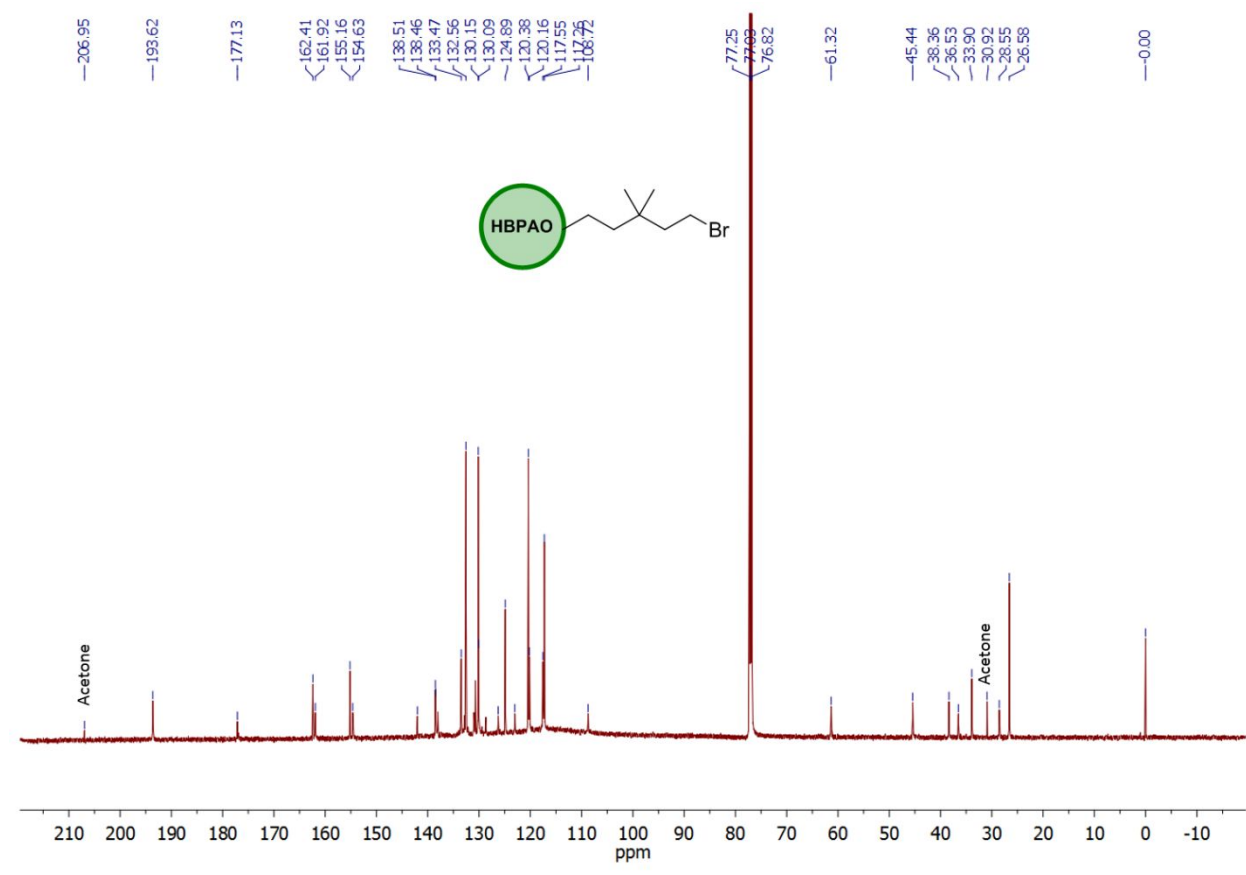
7.2 ¹³C NMR spectra



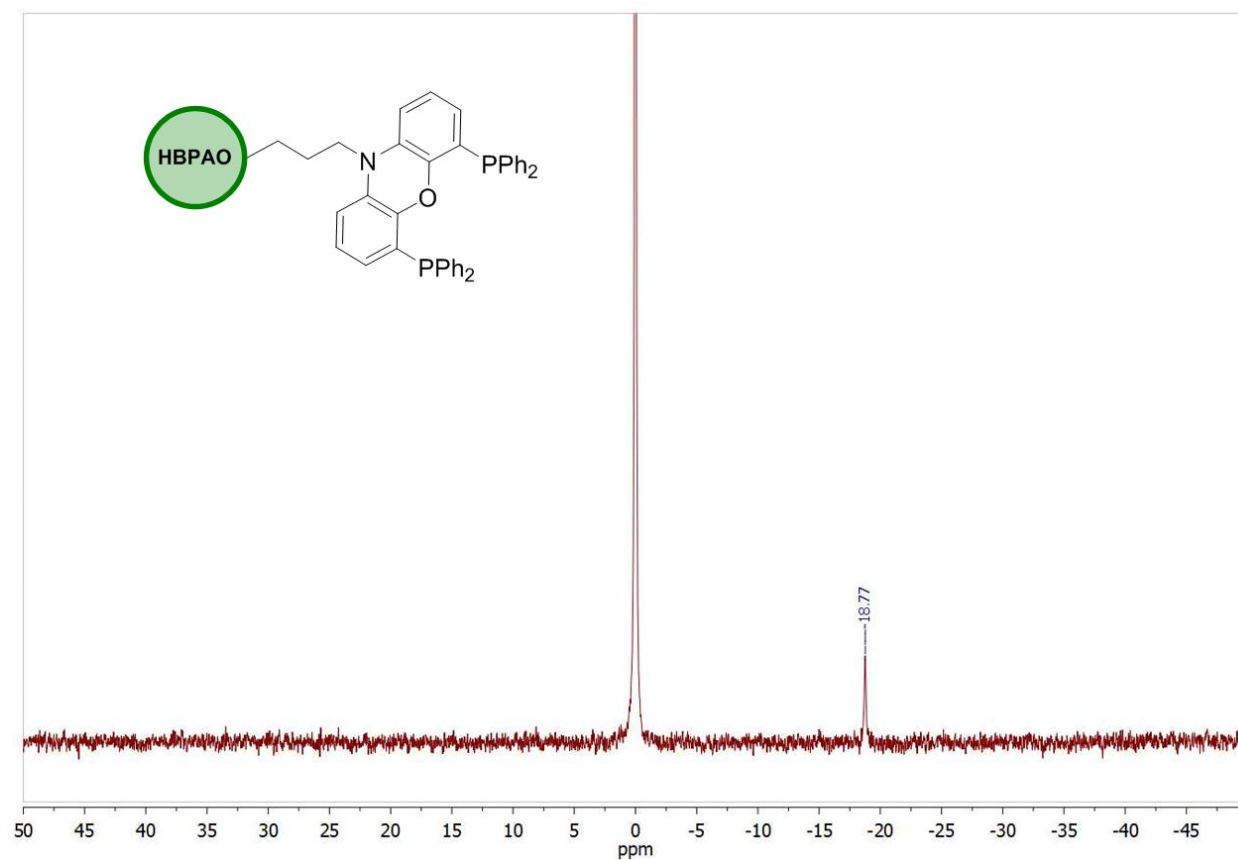


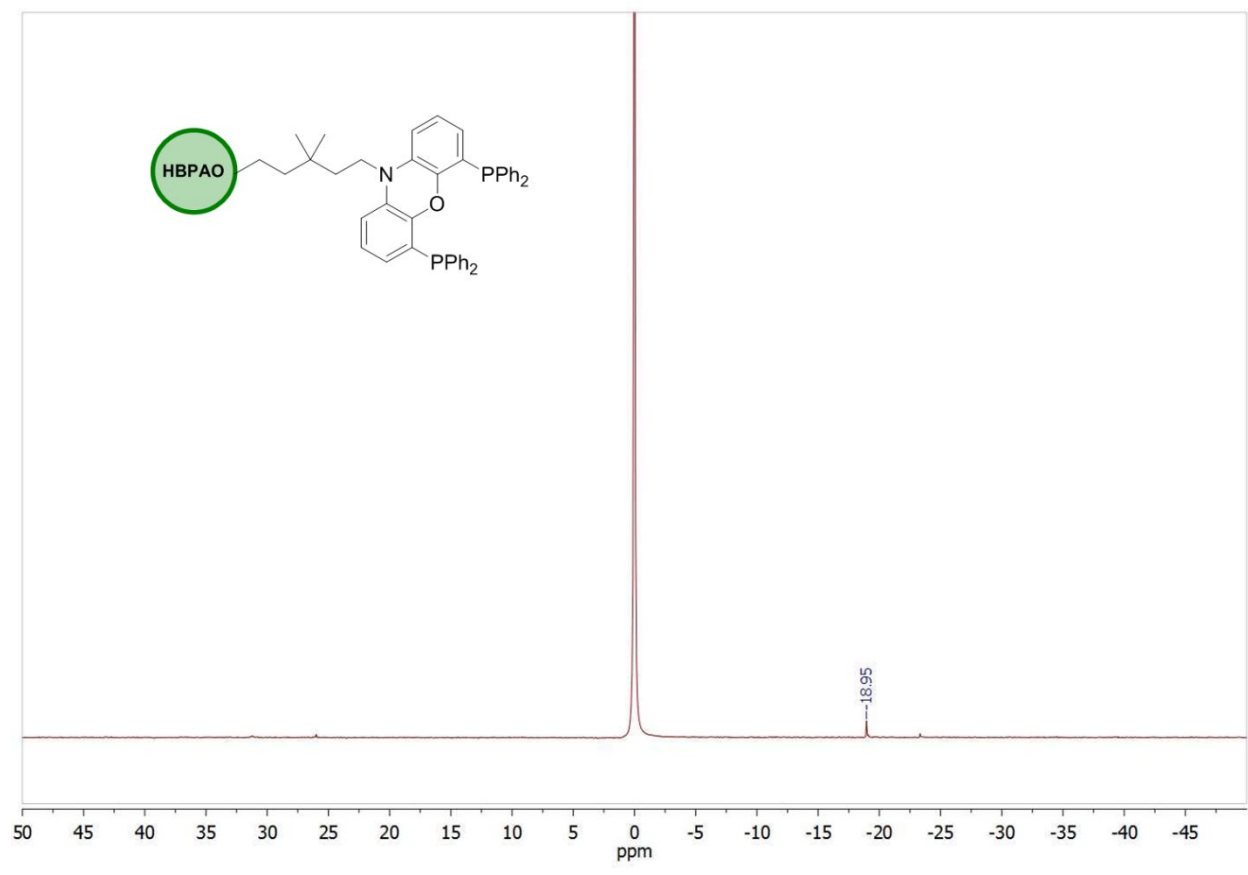






7.3 ^{31}P NMR spectra





References

- (1) Kelly, B. D.; Lambert, T. H. Cyclopropenium-Activated Cyclodehydration of Diols. *Org. Lett.* **2011**, *13*, 740-743.
- (2) Takasu, N.; Oisaki, K.; Kanai, M. Iron-Catalyzed Oxidative C (3)-H Functionalization of Amines. *Org. Lett.* **2013**, *15*, 1918-1921.
- (3) Maniara, G.; Rajamoorthi, K.; Rajan, S.; Stockton, G. W. Method Performance and Validation for Quantitative Analysis by ¹H and ³¹P NMR Spectroscopy. Applications to Analytical Standards and Agricultural Chemicals. *Anal. Chem.* **1998**, *70*, 4921-4928.
- (4) Bharti, S. K.; Roy, R. Quantitative ¹H NMR Spectroscopy. *Trac-Trends Anal. Chem.* **2012**, *35*, 5-26.
- (5) Gheorghe, A.; Matsuno, A.; Reiser, O. Expedient Immobilization of TEMPO by Copper-Catalyzed Azide-Alkyne [3+2]-Cycloaddition onto Polystyrene Resin. *Adv. Synth. Catal.* **2006**, *348*, 1016-1020.
- (6) Reger, T. S.; Janda, K. D. Polymer-Supported (Salen)Mn Catalysts for Asymmetric Epoxidation: A Comparison Between Soluble and Insoluble Matrices. *J. Am. Chem. Soc.* **2000**, *122*, 6929-6934.
- (7) Sugimura, R.; Qiao, K.; Tomida, D.; Yokoyama, C. Immobilization of Acidic Ionic Liquids by Copolymerization with Styrene and their Catalytic use for Acetal Formation. *Catal. Commun.* **2007**, *8*, 770-772.
- (8) Yan, B.; Jewell, C. F.; Myers, S. W. Quantitatively Monitoring of Solid-Phase Organic Synthesis by Combustion Elemental Analysis. *Tetrahedron* **1998**, *54*, 11755-11766.
- (9) Petricci, E.; Mann, A.; Schoenfelder, A.; Rota, A.; Taddei, M. Microwaves Make Hydroformylation a Rapid and Easy Process. *Org. Lett.* **2006**, *8*, 3725-3727.

- (10) Johns, A.; Nash, D. J.; Stemp, G. Patent 9850363 A1. 1998.
- (11) Zhang, X. W.; Coo, B. N.; Yu, S. C.; Zhang, X. M. Rhodium-Catalyzed Asymmetric Hydroformylation of *N*-Allylamides: Highly Enantioselective Approach to β^2 -Amino Aldehydes. *Angew. Chem., Int. Ed.* **2010**, *49*, 4047-4050.
- (12) Tanaka, H.; Chou, J. Y.; Mine, M.; Kuroboshi, M. The Oxidation of Alcohols in *N*-Oxyl-Immobilized Silica Gel/Aqueous NaOCl Disperse Systems. A Prominent Access to a Column-Flow System. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1745-1755.
- (13) Kantee, K.; Rukachaisirikul, V.; Tadpetch, K. Synthesis of Tetrahydropyranyl Diarylheptanoids From *Dioscorea Villosa*. *Tetrahedron Lett.* **2016**, *57*, 3505-3509.