General considerations

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used as received. Catalytic reactions were generally conducted on a Radley's 12-place reaction carousel. Reactions under microwave irradiation were conducted in a Biotage Initiator Eight microwave using 2-5 mL Biotage Microwave vials sealed with aluminium crimp caps fitted with a silicon septum. All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F 254 precoated plates (0.25 mm) The developed chromatogram was analysed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H) or 75.4 MHz (^{13}C). The chemical shift values (δ) are given in parts per million and are referred to the residual peak of the deuterated solvent used ($CDCl_3$). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets t = triplet, td = triplet of doublets, m = multiplet, br = broad signal), coupling constant (Hz), and integration. ESI-TOF high-resolution mass spectra were provided by the mass spectrometry service of the University of Seville (Spain).

A representative experimental procedure (thermal conditions)

A Radley tube was charged with a magnetic stir bar, $RuCl_3 \cdot nH_2O$ (13 mg, 0.05 mmol, 5 mol %), AcONa (0.25 g, 3 mmol), Zn (8.2 mg, 0.125 mmol) and 2 mL of deoxygenated water. Soon after 2-phenylpyridine (0,143 mL, 1 mmol) and the required aryl/heteroaryl halide (1.2 mmol) were added by Eppendorf Research® (100-1000 μL) micropipette. The reaction vessel was positioned in the carousel and the reaction mixture was stirred at 110 ºC for 16-20h. After the reaction mixture had cooled to room temperature, the organic layer was extracted with 3 mL of DCM, dried over $MgSO_4$ and filtered through a short silica-pad using EtOAc as eluent. The filtrate was rotary evaporated and the residue analysed by ^{1}H NMR to determine the conversion and product distribution. Unknown products were purified by silica column chromatography, with hexane/ethyl acetate (10-30% in ethyl acetate) as eluent and characterized by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry.

A representative experimental procedure (micro-wave conditions)

Reactions under microwave irradiation were conducted in a Biotage Initiator Eight microwave using 2-5 mL Biotage Microwave vials sealed with aluminium crimp caps fitted with a silicon septum. Temperature was set to 140 ºC and the stirring rate to 600 rpm. Typical graphs for the reactions carried under microwave irradiation are shown below (Figure 1). After the reaction mixture had cooled to room temperature the same protocol as used for the thermal version of the reaction was followed.

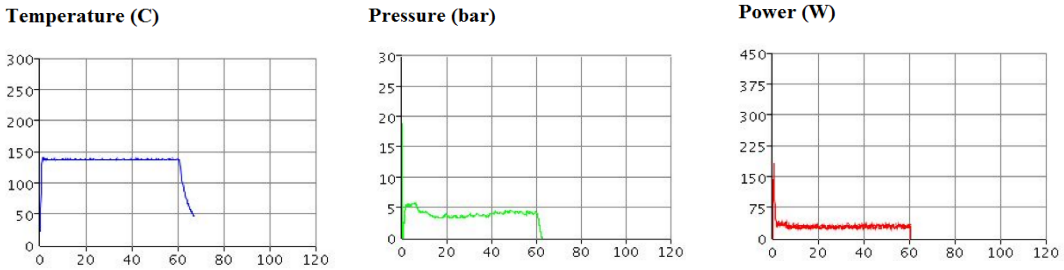
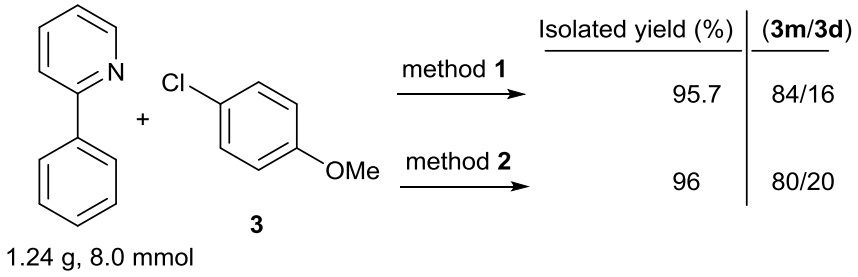


Figure 1.

Multigram synthesis

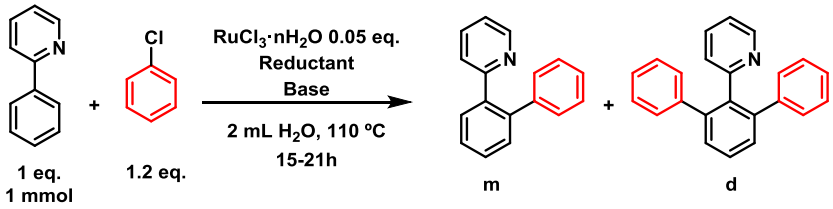
a) Thermal conditions: The thermal reaction was carried out using 8-times the amounts described for the standard experiment (see above) in a 25 mL vial sealed with an aluminium crimp-cap. The vial was kept at 110 ºC for 16 h in an oil bath time after which the resultant solution was extracted with DCM dried over $MgSO_4$ and purified by silica column chromatography using Hex/AcOEt (85/15) as the mobile phase.

b) micro-wave conditions: Same protocol as in thermal conditions was used, but in this case, the 25 mL vial sealed with an aluminium crimp-cap was placed in a Biotage Initiator Eight microwave, where the temperature was set to 140 ºC and the reaction time to 1h. The final solution was extracted with DCM, dried over $MgSO_4$ and subjected to purification by silica column chromatography using Hex/AcOEt (85/15) as the eluent.



Scheme 1. Isolated yields in preparative scale

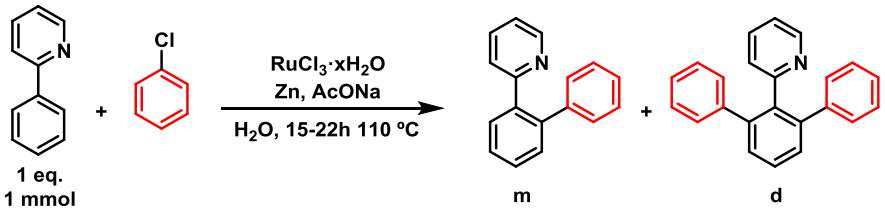
Table 1. Screening conditions for the reaction of 2-phenylpyridine with chlorobenzene



Entry	Base (eq.)	Reductant (eq.)	Conversion (m/d)[b]
1	NaOAc (3)	-	0 (-/-)
2	Na(acac) (1.1)	Zn (0.25)	80 (87/13)
3	Na(acac) (3)	Zn (0.25)	86 (89/11)
4[a]	Na(acac) (3)	Zn (0.125)	99 (42/58)
5	Na(acac) (3)	H_3PO_2 (0.1)	87 (83/17)
6	Na(acac) (3)	H_3PO_2 (0.3)	13 (only m)
7	NaOAc (3)	Zn (0.6)	84 (86/14)
8	NaOAc (3)	Zn (0.15)	82 (88/12)
9	NaOAc (1)	Zn (5)	69 (94/6)
10	NaOAc (1)	Zn (0.25)	72 (90/10)
11	NaOAc (3)	H_3PO_2 (0.1)	65 (93/7)
12	NaOAc (3)	H_3PO_2 (0.05)	68 (86/14)
13	NaOAc (3)	NaH_2PO_2 (0.6)	0 (-/-)
14	NaOAc (3)	Hydrazine (2.5)	0 (-/-)
15	NaOAc (3)	$NaBH_4$ (3)	14 (83/17)
16	NaOH (1.1)	Zn (0.25)	0 (-/-)
17	Cs_2CO_3 (1.1)	Zn (0.25)	0 (-/-)
18	Na_2CO_3 (1.1)	Zn (0.25)	0 (-/-)
19	NaOAc(3) + Cs_2CO_3 (1.1)	Zn (0.15)	0 (-/-)

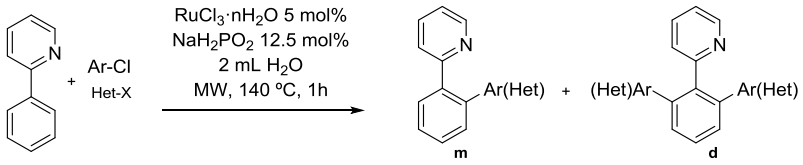
Reaction conditions: $RuCl_3 \cdot nH_2O$ (0.05 mmol, 5 mol %), 2-phenylpyridine (1 mmol), phenyl chloride (1.2 mmol), base, 110 °C for 16-20h in 2mL of water. [a](1.5 mmol of phenyl chloride); [b]conversion and product ratio determined by NMR.

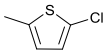
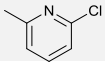
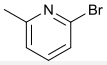
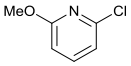
Further optimisations



Entry	Optimisations	Conv. (%)	m/d
1	rt	0	-
2	1 mL H_2O	67	89/11
3	6 eq. Ar-Cl	100	37/63
4	10 mL H_2O/ 1.5 eq. Ar-Cl	71	88/12
5	10% cat.	81	85/15
6	15% cat.	80	83/17

Table 2. Functionalization of 2-phneylpyridine with arylchlorides and heteroarylchlorides using microwave heating and NaH_2PO_4 as reductant.



Entry	ArCl or Het-X	Conv. (m/d)[a]
1	 R = H	81 (86/14)
2	R = *p*-CH_3	84 (85/15)[b]
3	R = *p*-OCH_3	83 (86/14)
4	R = *p*-CN	39 (51/49)[c]
5	R = *p*-OH	28 (52/48*)
6	R = *m*-$N(CH_3)_2$	77 (78/22)
7	R = *o*-NH_2	28 (79/21*)
8		86 (54/46)
9		67 (54/46)
10		70 (55/45)
11		46 (38/62)
12		25 (80/20)[g]

Method 3:. $RuCl_3 \cdot nH_2O$ (0.05 mmol, 5 mol %), 2-phenylpyridine (1 mmol), aryl/heteroaryl halide (1.2 mmol), NaOAc (3 mmol), NaH_2PO_2 (0.125 mmol), 140 °C under μw irradiation for 1h in 2mL of water. [a]Conversion and product ratio determined by NMR, [b]1.5 eq. Ar-Cl; [c]1.2 eq. NaOAc, * Homocoupling of 2-phenylpyridine instead of the diarylated product.

Electrospray ionization mass spectrometry (ESI-MS) and sample preparation

ESI-MS studies were conducted on a QTOF Premier instrument with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK) operating in the W-mode at a resolution of ca. 15000 (FWHM). The drying and cone gas was nitrogen set to flow rates of 300 and 30 L/h, respectively. A capillary voltage of 3.5 kV or 3.3 kV was used in the positive ESI(+) and negative ESI(-) scan mode, respectively. The cone voltage was adjusted in both ESI(+) or ESI(-) scan modes to a low value (typically Uc = 5−15 V) to control the extent of fragmentation in the source region. Aqueous or THF solutions were introduced through a fused-silica capillary to the ESI source via syringe pump at a flow rate of 10 µL/min. The chemical composition of each Ru-containing species was facilitated by the characteristic isotopic pattern at natural abundance of Ru and it was carried out by comparison of the isotope experimental and theoretical patterns using the MassLynx 4.1 program.

A series of ESI-MS experiments were designed using closely related experimental conditions to those used in the catalytic study depicted in Table 1. An important consideration of the present system is that the presence of an excess of NaOAc in the catalytic system produces strong ion suppression of all species but NaOAc, thus resulting in ESI(+) and ESI(-) mass spectra dominated by $[Na_x(OAc)_{(x-1)}]^+$ and $[Na_{(x-1)}(OAc)_x)]^-$ species, respectively. Our ESI-MS study revealed that using an excess larger than 6 equivalents resulted in complete ion suppression of all metal-containing species, so that a limited excess of NaOAc was employed in the ESI-MS study to be compatible with the ESI-MS technique. The $RuCl_3{\cdot}nH_2O$ to reducing agent molar ratio was fixed to 1:2 which falls within the molar ratio tested in the catalytic study (see Table 1). Experiments in the presence of the substrates were also performed using typically 2 equivalents of phenylpyridine or chlorobenzene with respect to $RuCl_3{\cdot}nH_2O$.

Experiments using $RuCl_3{\cdot}nH_2O$ / Zn / NaOAc in a 1:2:6 molar ratio in water or THF.

$RuCl_3{\cdot}nH_2O$ (22 mg, 0.084 mmol) / Zn (11 mg, 0.168 mmol) / NaOAc (41 mg, 0.504 mmol) were suspended in 2 mL of H_2O or THF under an inert N_2 atmosphere and stirred at 90 ºC and 60 ºC, respectively for 1 hour. The resulting black suspension was filtered through 0.2 µm filters and the resulting solution was 50-fold diluted with H_2O or THF and directly introduced into the ESI mass spectrometer. Each experiment was investigated in triplicate and satisfactory reproducibility was observed. ESI(-) mass spectra did not reveal the presence of Ru-containing species but $[ZnX_3]^-$ anions (X = Cl or OAc) were observed along with the expected series of $[Na_{(x-1)}(OAc)_x]^-$ anions due to the presence of an excess of NaOAc. ESI(+) mass spectra display peaks characteristic of the presence of Ru; illustrative ESI(+) mass spectra are shown in **figure S1** and **S2** for H_2O or THF solutions, respectively.

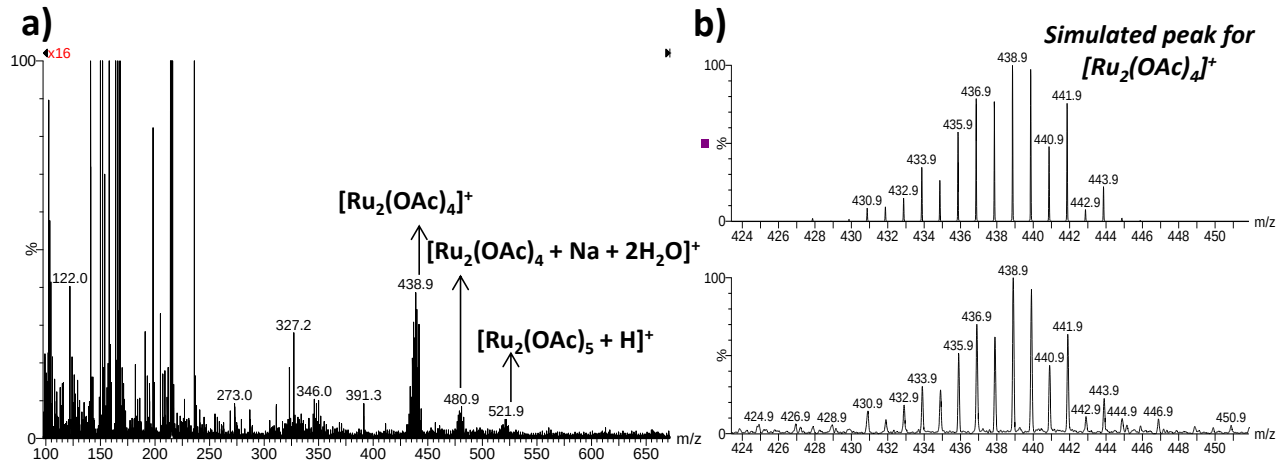


Figure S1. a) ESI(+) mass spectrum of the catalytic system $RuCl_3 \cdot nH_2O$ / Zn / NaOAc in a 1:2:6 molar ratio in water recorded at Uc = 15 V. Notice that the vertical scale has been increase 16-fold to bring the peak due to $[Ru_2(OAc)_4]^+$ species at m/z 438.9 to a reasonable scale. Other lower intensity dimeric species are also observed at m/z 480.9 for $[Ru_2(OAc)_4 + Na + 2H_2O]^+$ and m/z 521.9 for $[Ru_2(OAc)_5 + H]^+$; b) simulated (top) and experimental (bottom) isotopic pattern for the $[Ru_2(OAc)_4]^+$ cation.

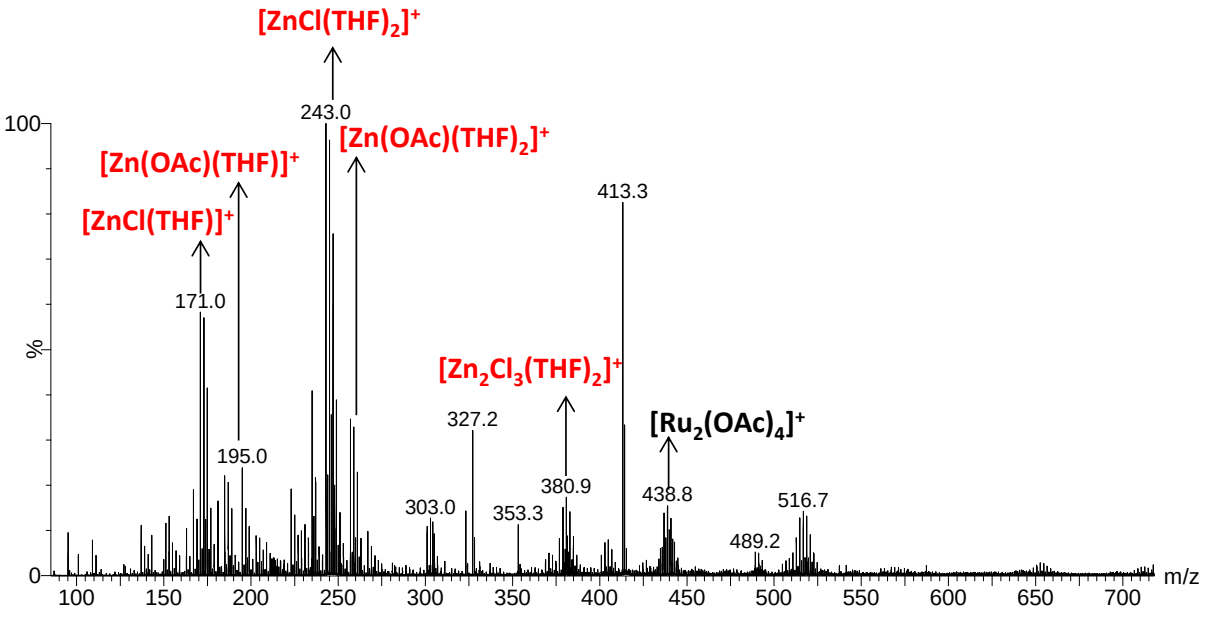


Figure S2. ESI(+) mass spectrum of the catalytic system $RuCl_3 \cdot nH_2O$ / Zn / NaOAc in a 1:2:6 molar ratio in THF recorded at Uc = 15 V. Like the ESI(+) mass spectrum of the reaction in water in **figure S1**, the dominant Ru-containing species is $[Ru_2(OAc)_4]^+$; however, a number of Zn-containing species are also observed in the ESI(+) mass spectrum as THF adducts (see peak assignment in red).

Experiment using $RuCl_3 \cdot nH_2O$ / H_3PO_2 / NaOAc in a 1:2:6 molar ratio in water.

$RuCl_3 \cdot nH_2O$ (22 mg, 0.084 mmol) / H_3PO_2 (30µL of a 50 % H_3PO_2 solution in H_2O, 0.168 mmol)/ NaOAc (41 mg, 0.504 mmol) were suspended in 2 mL of H_2O under an inert N_2 atmosphere and stirred at 90 ºC for 1 hour. The resulting black suspension was filtered through 0.2 µm filters and the resulting solution was 50-fold diluted with H_2O and directly introduced into the ESI mass spectrometer. Each experiment was investigated in triplicate and satisfactory reproducibility was observed. ESI(-) mass spectra did not reveal the presence of Ru-containing species but the series of $[Na_{(x-1)}(OAc)_x]^-$ and $[(H_2PO_2)_xNa_{(x-1)}]^-$ adducts were observed. The ESI(+) mass spectrum in **figure S3** displays a barely detected peak characteristic of the presence of Ru.

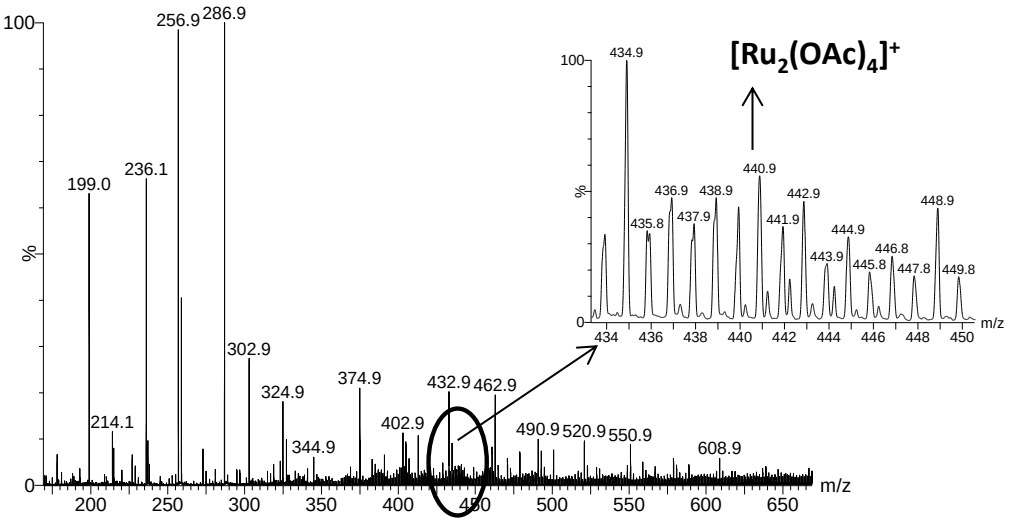


Figure S3. ESI(+) mass spectrum of the catalytic system $RuCl_3 \cdot nH_2O$ / H_3PO_2 / NaOAc in a 1:2:6 molar ratio in water recorded in water at Uc = 15 V. In this particular case, the peak due to $[Ru_2(OAc)_4]^+$ species at m/z 438.9 is barely observed (see inset).

Experiments using $RuCl_3 \cdot nH_2O$ / Zn / NaOAc in a 1:2:6 molar ratio in the presence of 2 eq. of phenylpyridine or phenyl chloride in water.

$RuCl_3 \cdot nH_2O$ (22 mg, 0.084 mmol) / Zn (11 mg, 0.168 mmol) / NaOAc (41 mg, 0.504 mmol) were suspended in 2 mL of H_2O under an inert N_2 atmosphere and stirred at 90 ºC for 1 hour. The resulting black suspension was filtered through 0.2 µm filters and the resulting solution was 50-fold diluted with H_2O and directly introduced into the ESI mass spectrometer. ESI(+) mass spectra display peaks characteristic of the presence of Ru; illustrative ESI(+) mass spectra are shown in **figure S4** and **S5** for reaction in the presence of phenylpyridine or chlorobenzene, respectively. We also investigate the chemical speciation of our catalytic system in the presence of both substrates. In this case, the ESI(+) mass spectrum revealed that ion

suppression effects for Ru-containing species were very pronounced, the spectrum being dominated by $[Na_x(OAc)_{(x-1)}]^+$, [phenylpyridine + H]$^+$, [phenylpyridine + Na]$^+$ adducts and no Ru-containing species being detected at all.

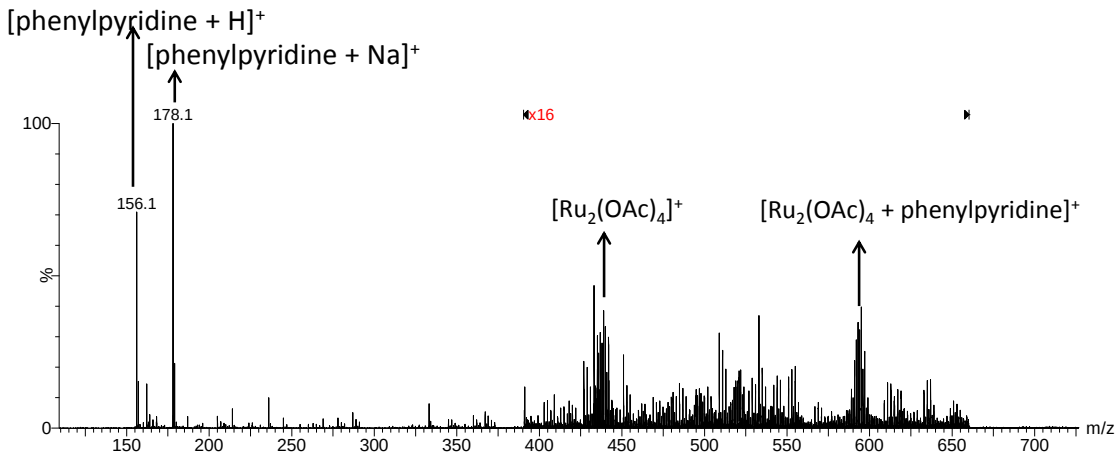


Figure S4. a) ESI(+) mass spectrum of the catalytic system $RuCl_3{\cdot}nH_2O$ / Zn / NaOAc in a 1:2:6 and phenylpyridine (2 eqs.) molar ratio in water recorded at Uc = 15 V. Notice that the vertical scale has been increase 16-fold to bring the peaks due to $[Ru_2(OAc)_4]^+$ species at m/z 438.9 and $[Ru_2(OAc)_4$+phenylpyridine]+ species at m/z 594.9 to a reasonable scale.

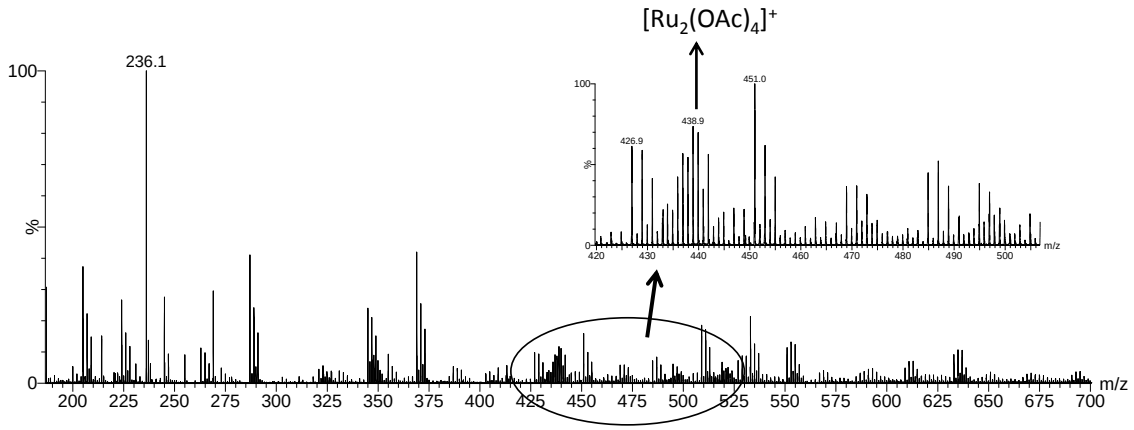
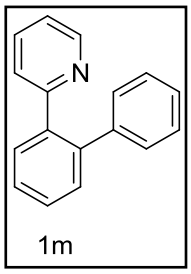


Figure S5. a) ESI(+) mass spectrum of the catalytic system $RuCl_3{\cdot}nH_2O$ / Zn / NaOAc in a 1:2:6 and PhCl (2 eqs.) molar ratio in water recorded at Uc = 15 V.

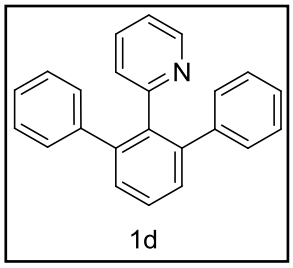
^{1}H and ^{13}C NMR characterization



NMR data are consistent with previously reported data

Angewandte Chemie, **2012** , 11, 2744 - 2748

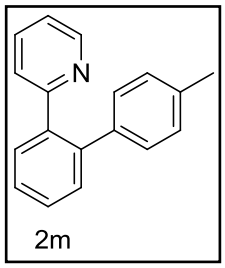
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (d, *J* = 4.2 Hz, 1H), 7.71 – 6.68 (m, 1H), 7.48 – 7.43 (m, 3H), 7.37 (td, *J* = 7.8, 1.8 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.17 – 7.14 (m, 2H), 9.09 (dd, *J* = 6.6, 5.1 Hz, 1H), 6.88 (d, *J* = 8.1, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 149.4, 141.4, 140.7, 139.5, 135.1, 130.5 (2C), 129.7, 128.5, 128.0, 127.6, 126.7, 125.4, 121.3.



NMR data are consistent with previously reported data

Angewandte Chemie, **2012** , 11, 2744 - 2748

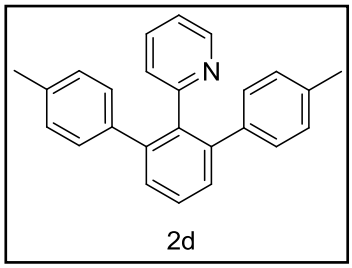
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J* = 3.9 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (m, 1H), 7.42 (t, *J* = 2.7 Hz, 1H), 7.25 (t, *J* = 4.8 Hz, 1H), 7.12 – 7.08 (m, 10H), 6.89 – 6.84 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 148.4, 141.8, 141.5, 138.5, 134.8, 129.6, 129.4, 128.1, 127.6, 126.7, 126.2, 120.8.



NMR data are consistent with previously reported data

Journal Organic Chemistry, **2011**, 76, 8543 – 8548

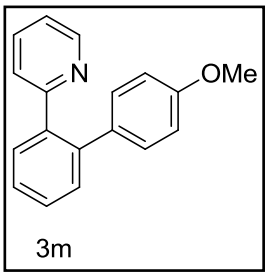
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, *J* = 3.2 Hz, 1H), 7.70 – 71 (m, 1H), 7.40 – 7.47 (m, 4H), 7.13 (t, *J* = 5.6 Hz, 1H), 7.06 – 7.07 (m, 4H), 6.92 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 149.1, 141.1, 140.3, 139.2, 134.9, 130.2, 129.4, 128.2, 127.7, 126.4, 125.1, 121.0, 22.4.



NMR data are consistent with previously reported data

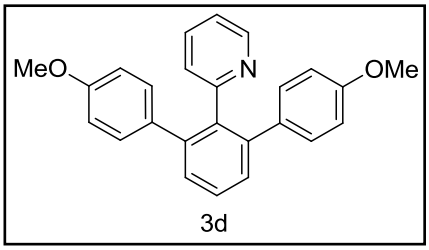
J. Am. Chem. Soc., **2010**, 132, 12212 – 12213.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.42 (s, 1H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.32 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.99 – 6.94 (m, 9H), 6.91 – 6.88 (m, 1H), 2.27 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 148.5, 141.7, 138.6, 138.4, 135.8, 134.9, 129.5, 129.3, 128.3, 128.1, 126.8, 120.8, 21.0.



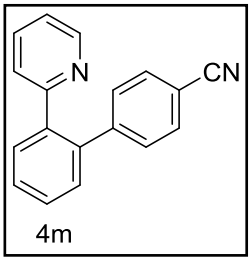
3m

NMR data are consistent with previously reported data
Journal Organic Chemistry, **2011**, 76, 8543 – 8548
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.70 (m, 1H), 7.43 – 7.46 (m, 4H), 7.08 – 7.13 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 158.3, 149.4, 140.2, 139.3, 135.3, 133.7, 130.8, 130.5, 130.4, 128.5, 127.3, 125.4, 121.3, 113.5, 55.2.



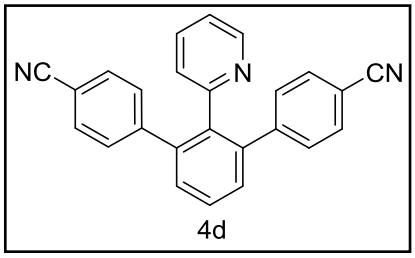
3d

NMR data are consistent with previously reported data
J. Am. Chem. Soc., **2010**, 132, 12212 – 12213.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 4.4 Hz, 0.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.41 (s, 1H), 7.39 (d, *J* = 1.2 Hz, 1H), 7.33 (td, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.00 (dt, *J* = 8.8 Hz, 2.0 Hz, 4H), 6.94 – 6.91 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.69 (dt, *J* = 8.8 Hz, 2.0 Hz, 2H), 3.75 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 158.0, 148.6, 141.4, 138.4, 135.0, 134.0, 130.6, 129.2, 128.1, 126.8, 120.8, 113.1, 55.1.



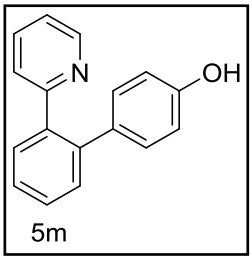
4m

NMR data are consistent with previously reported data
J. Am. Chem. Soc., **2010**, 132, 12212 – 12213.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.0 Hz, 1H), 7.68 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 7.54 – 7.47 (m, 5H), 7.41 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 7.24 (s, 2H), 7.16 – 7.14 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 149.6, 146.4, 139.6, 138.8, 135.7, 131.8, 130.7, 130.3, 130.2, 128.8, 128.7, 125.0, 121.8, 118.9, 110.4.

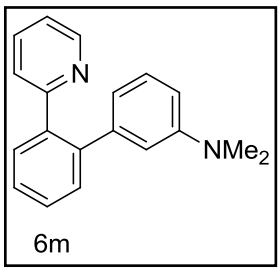


4d

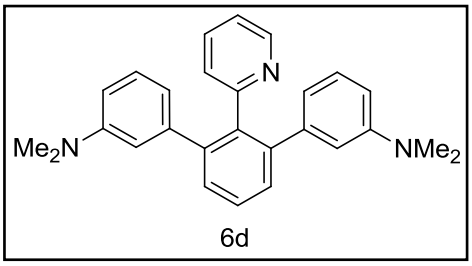
NMR data are consistent with previously reported data
J. Am. Chem. Soc., **2010**, 132, 12212 – 12213.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (s, 2H), 7.46 (d, *J* = 7.0 Hz, 4H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 4H), 7.01 (t, *J* = 5.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 149.1, 146.0, 140.4, 138.4, 135.5, 131.6, 130.2, 130.1, 128.8, 126.6, 121.8, 118.7, 110.5.



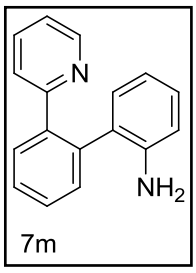
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, *J* = 4.3 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.53 (ddd, *J* = 8.0, 7.1, 1.7 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.24 – 7.17 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.55, 157.41, 149.68, 142.59, 140.70, 140.51, 139.17, 134.69, 132.86, 132.61, 131.31, 129.42, 128.30, 123.96, 117.36. ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.55, 157.41, 149.68, 142.59, 139.17, 134.69, 132.86, 132.61, 131.31, 129.42, 128.30, 123.96, 117.36. HRMS (EI+) exact mass calculated for $C_{17}H_{12}NO$ $[M]^+$ requires m/z 246.0920, found m/z 246.0919.



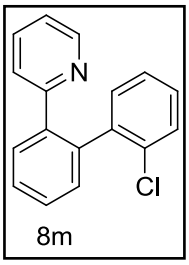
NMR data are consistent with previously reported data
Organometallics, **2011**, 30 (21), 6010–6016
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.68 (m, 1H), 7.48 – 7.42 (m, 3H), 7.37 (td, *J* = 7.8, 1.8 Hz, 1H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.08 (m, 1H), 6.92 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.62 – 6.56 (m, 2H), 6.45 (br t, *J* = 2.5 Hz, 1H), 2.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.6, 149.3, 142.0, 141.5, 139.6, 135.2, 130.4, 130.3, 128.8, 128.5, 127.5, 125.5, 121.3, 118.3, 114.8, 111.3, 40.6.



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.34 (td, *J* = 7.7, 1.8 Hz, 1H), 7.09 (dd, *J* = 13.9, 6.0 Hz, 2H), 6.97 (dt, *J* = 7.8, 1.0 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.63 – 6.51 (m, 4H), 6.45 – 6.37 (m, 2H), 2.74 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.48, 149.73, 148.20, 142.41, 142.22, 138.04, 135.13, 129.30, 128.39, 128.12, 126.79, 120.78, 118.64, 115.01, 111.05, 40.73. HRMS (EI+) exact mass calculated for $C_{27}H_{27}N_3$ [M] requires m/z 393.2206, found m/z 393.2205.



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 – 8.58 (m, 1H), 7.85 – 7.73 (m, 1H), 7.55 – 7.43 (m, 2H), 7.43 – 7.32 (m, 2H), 7.14 – 7.05 (m, 2H), 7.01 (ddd, *J* = 7.2, 5.0, 1.5 Hz, 2H), 6.70 (td, *J* = 7.4, 1.0 Hz, 1H), 6.60 – 6.55 (m, 1H), 3.41 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.39, 149.14, 143.65, 139.85, 137.43, 135.51, 130.96, 130.91, 130.47, 129.07, 128.49, 128.14, 126.79, 124.37, 121.64, 118.32, 115.26. HRMS (EI+) exact mass calculated for $C_{17}H_{13}N_2$ $[M]^+$ requires m/z 245.1073, found m/z 245.1078.

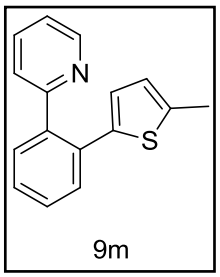


8m

NMR data are consistent with previously reported data

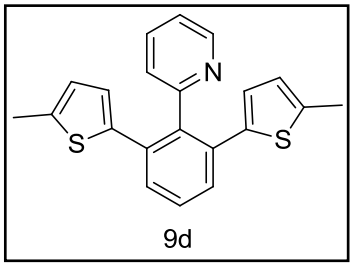
Organic Letters, **2009**, 11 (15), 3174–3177

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.5 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.51 (m, 3H), 7.32 – 7.37 (m, 3H), 7.15 – 7.16 (m, 2H), 7.04 – 7.06 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 149.9, 140.8, 140.6, 138.4, 135.9, 133.8, 132.6, 131.4, 130.6, 130.0, 129.0, 128.9, 128.7, 126.4, 124.8, 122.0.



9m

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 – 8.67 (m, 1H), 7.62 – 7.57 (m, 1H), 7.57 – 7.49 (m, 2H), 7.46 – 7.38 (m, 2H), 7.25 – 7.16 (m, 2H), 6.57 – 6.51 (m, 1H), 6.47 (d, *J* = 3.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.33, 149.28, 140.38, 140.27, 139.37, 135.64, 133.39, 130.52, 130.48, 128.51, 127.67, 126.93, 125.41, 125.07, 121.78, 15.27. HRMS (EI+) exact mass calculated for $C_{16}H_{13}NS$ $[M]^+$ requires m/z 250.0685, found m/z 250.0690.

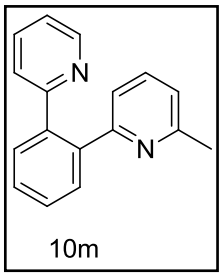


9d

NMR data are consistent with previously reported data:

Angewandte Chemie, **2010**, 49, 6629 - 6632

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (ddd, 1 H, *J* = 4.8 Hz, *J* = 1.8 Hz, *J* = 1.0 Hz), 7.54 (td, 2H, *J* = 7.7 Hz, *J* = 1.83 Hz), 7.53 (d, 1H, *J* = 7.7 Hz), 7.45–7.43 (dd, 1 H, *J* = 8.2 Hz, *J* = 7.1 Hz), 7.18 (ddd, 1 H, *J* = 7.6 Hz, *J* = 5.1 Hz, *J* = 1.2 Hz), 7.15 – 7.13 (m, 1H), 6.48 (m, 2H), 6.42 (d, 2 H, *J* = 3.6 Hz), 2.38 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 148.9, 140.4, 140.2, 137.8, 135.9, 134.9, 129.5, 128.3, 127.0, 126.3, 125.1, 122.1, 15.2.

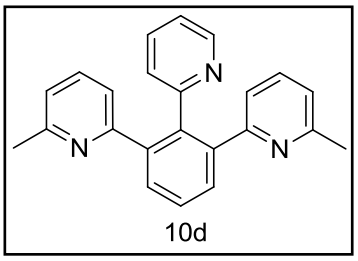


10m

NMR data are consistent with previously reported data

Advanced Synthesis and Catalysis, **2009**, vol. 351, 1737 - 1743

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.9 Hz, 1H), 7.66 (dt, *J* = 7.8, 2.9 Hz, 2H), 7.56 – 7.46 (m, 2H), 7.43 (td, *J* = 7.7, 1.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.06 (m, 1H), 6.98 (dd, *J* = 7.9, 1.1 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.35, 158.38, 157.95, 149.22, 139.71, 139.59, 135.87, 135.41, 130.28, 128.67, 128.51, 125.14, 121.97, 121.38, 121.01, 24.50.

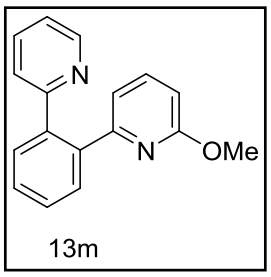


10d

NMR data are consistent with previously reported data

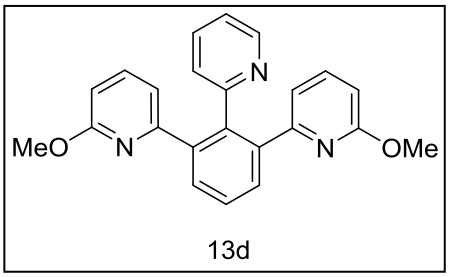
Advanced Synthesis and Catalysis, **2009**, vol. 351, 1737 - 1743

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 4.8 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.59 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.28 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 158.4, 157.4, 148.2, 140.9, 138.4, 135.4, 134.7, 130.4, 128.4, 126.7, 125.4, 121.7, 120.6, 120.5, 30.2, 24.4.



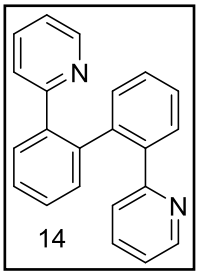
13m

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (ddd, *J* = 5.0, 1.8, 0.9 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.56 – 7.44 (m, 4H), 7.16 (ddd, *J* = 7.5, 5.0, 1.1 Hz, 1H), 7.06 (ddd, *J* = 7.8, 3.2, 2.1 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.3 Hz, 1H), 3.51 – 3.48 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.16, 162.08, 158.51, 151.04, 141.87, 141.46, 140.55, 137.57, 132.65, 132.50, 132.14, 130.52, 126.80, 123.23, 118.96, 110.66, 54.95. HRMS (EI+) exact mass calculated for $C_{17}H_{12}N_2O$ $[M]^{++}$ requires m/z 260.0942, found m/z 260.0950



13d

Isolated together with 13m.



14

NMR data are consistent with previously reported data

Tetrahedron, **2009**, *65*, 3085–3089

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 4.9, 0.7 Hz, 1H), 7.61 – 7.50 (m, 1H), 7.50 – 7.33 (m, 4H), 7.06 (dd, *J* = 7.0, 5.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 148.4, 139.7, 139.07, 136.0, 131.3, 130.1, 128.9, 127.9, 124.7, 121.5.