

Supporting Information

Phosphine-Pyridonate Ligands Containing Octahedral Ruthenium Complexes : Access to Esters and Formic Acid

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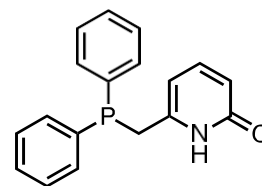
A. General Experimental Methods

All reactions were carried out under an inert argon atmosphere with standard schlenk techniques. Solvents were degassed and stored in argon atmosphere before use. Reagents were used as received without further purification, unless otherwise stated. ^1H NMR spectra were recorded using a Bruker Avance^{III} 300 MHz and 400 MHz NMR spectrometers. All ^1H -NMR data are reported in δ units, parts per million (ppm) and were calibrated relative to the reported residual solvent signals in the corresponding deuterated solvents. All ^{13}C -NMR and ^{31}P -NMR data are reported in ppm and were recorded with ^1H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, quint = quintet, br = broad, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

B. Synthesis of the Ligands

6-((Diphenylphosphaneyl)methyl)pyridin-2(1H)-one: (L1-H)

6-Methylpyridin-2-ol (1.0 g, 9.16 mmol, 1.0 equiv.) was dissolved in 10.0 mL THF, cooled at 0 °C followed by the slow addition of *n*-BuLi (12 mL, 19.2 mmol, 2.1equiv.). This solution was stirred for an hour. Then it was cooled to -78 °C and was added to another solution containing Diphenylphosphinechloride (1.6 mL, 9.16 mmol, 1.0 equiv.) in 2.5 mL of THF at -78 °C. This solution was stirred at -78 °C for one hour. Then the solution was allowed to warm up naturally to room temperature and was stirred at room temperature for 16 hours. After the completion of reaction, solvent was evaporated followed by addition of 10 mL degassed water to dissolve the oily liquid. After 10 mL dichloromethane was added and the solution was acidified slowly with 5% HCl solution (degassed) till the pH was around 3. Addition of degassed acetone gradually precipitated the ligand as off-white solid. Further washing with degassed acetone afforded the expected ligand as white powder with 70% yield (1.9g, 6.4 mmol).



Spectroscopic details are consistent with the reported literature.¹

¹ F. Jiang, M. Achard, T. Roisnel, V. Dorcet, C. Bruneau, *Eur. J. Inorg. Chem.* 2015, **26**, 4312.

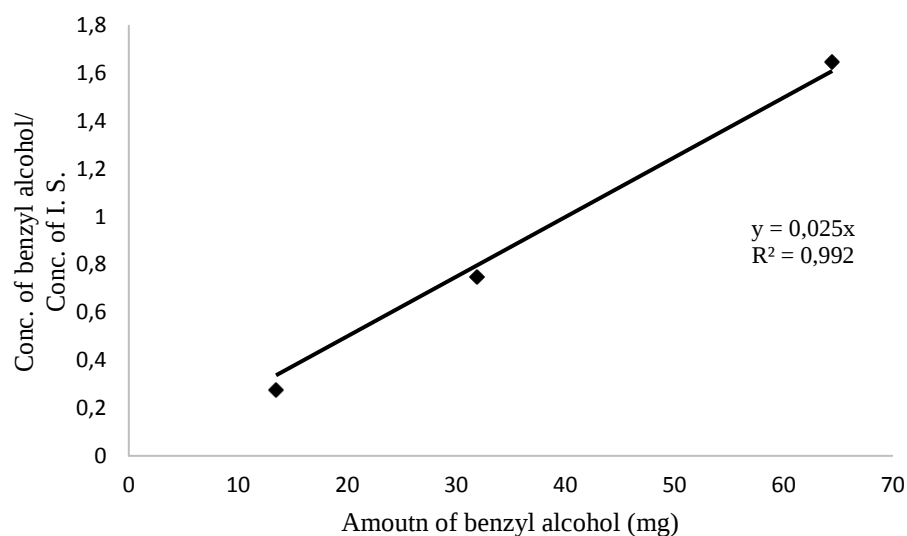
6,6'-(phenylphosphinediyl)bis(methylene)dipyridin-2(1H)-one [P(NOH)₂]: (L2-H)

Ligand **L2-H** is prepared by the reported procedure.²

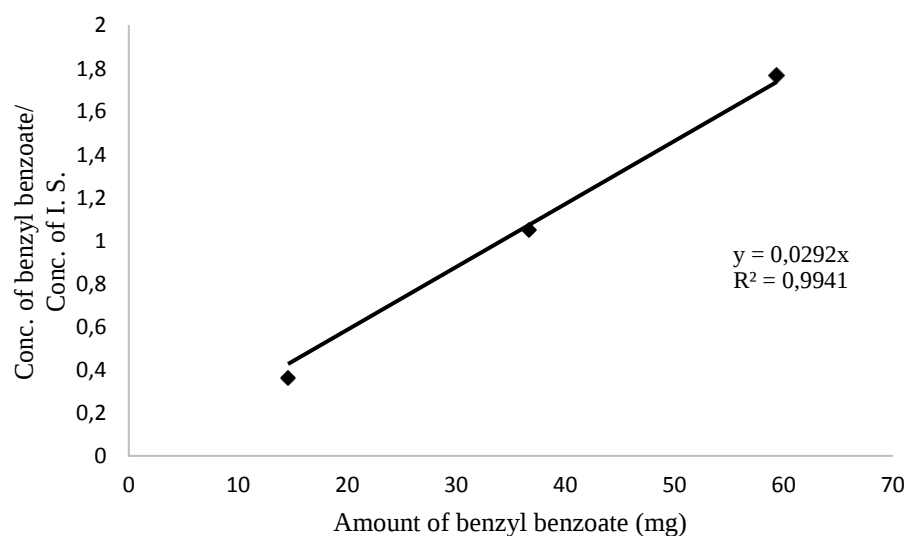
6,6'-(tert-butylphosphinediyl)bis(methylene)dipyridin-2(1H)-one [tBuP(NOH)₂]: (L3-H)

Ligand **L3-H** is prepared by the reported procedure.²

C. Internal Standard Studies

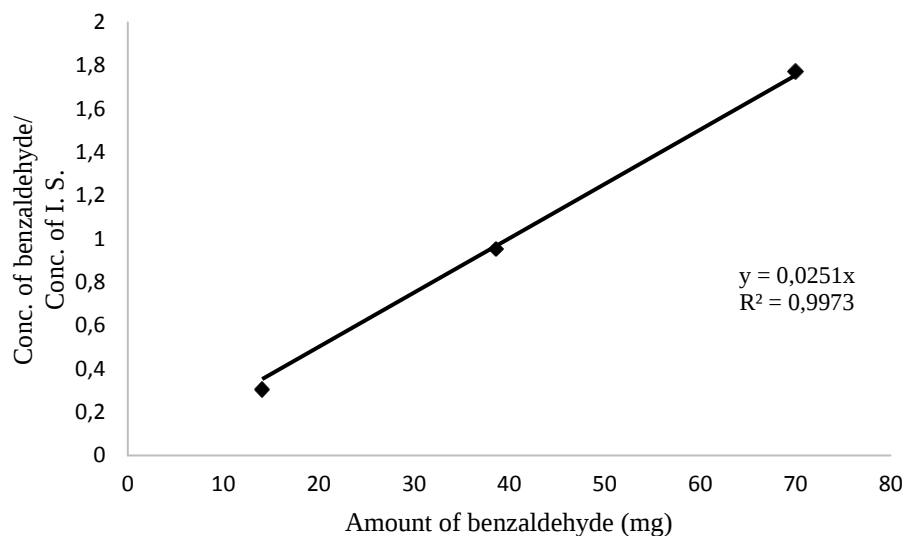


Internal standard graph for calculation of conversion of benzyl alcohol



Internal standard graph for calculation of yield of benzyl benzoate

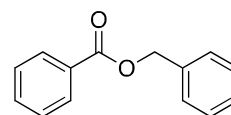
² A.R. Sahoo, F. Jiang, C. Bruneau, G.V.M. Sharma, S. Suresh, M. Achard, *RSC Adv.* 2016, **6**, 100554.



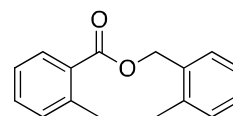
Internal standard graph for calculation of yield of benzaldehyde

D. Analytical Data

Benzyl benzoate (3a)⁴: Obtained by the reaction of benzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 16h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless liquid with 94% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.11-8.09 (m, ArCH, 2H), 7.59-7.55 (m, ArCH, 1H), 7.48-7.34 (m, ArCH, 7H), 5.39 (s, OCH₂, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 166.6 (quat-C), 136.2 (quat-C), 133.1 (ArCH), 130.3 (quat-C), 129.8 (ArCH), 128.7 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 66.8 (OCH₂).



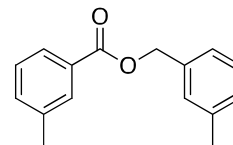
2-Methylbenzyl 2-methylbenzoate (3b)³: Obtained by the reaction of 2-methylbenzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 20h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 25 : 1) afforded the product as a colourless oil with 72% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 7.9 Hz, ArCH, 1H), 7.46-7.40 (m, ArCH, 2H), 7.32-7.24 (m, ArCH, 5H), 5.39 (s, OCH₂, 2H), 2.64 (s, CH₃, 3H), 2.45 (s, CH₃, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 167.4 (quat-C), 140.5 (quat-C), 137.1 (quat-C), 134.2 (quat-C), 132.2 (ArCH), 131.9 (ArCH), 130.8 (ArCH), 130.5 (ArCH), 129.6 (quat-C), 129.4 (ArCH), 128.6 (ArCH), 126.2 (ArCH), 125.8 (ArCH), 65.0 (OCH₂), 21.9



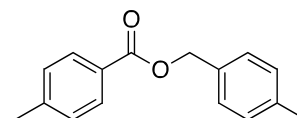
³ C. Liu, S. Tang, A. Lei, *Chem. Comm.* 2013, **49**, 1324.

(CH₃), 19.1 (CH₃).

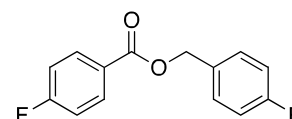
3-Methylbenzyl 3-methylbenzoate (3c)⁴: Obtained by the reaction of 3-methylbenzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 20h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 25 : 1) afforded the product as a colourless oil with 63% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.90-7.88 (m, ArCH, 2H), 7.38-7.27 (m, ArCH, 4H), 7.25-7.06 (m, ArCH, 2H), 5.33 (s, OCH₂, 2H), 2.40 (s, CH₃, 3H), 2.38 (s, CH₃, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 166.8 (*quat-C*), 138.4 (*quat-C*), 138.3 (*quat-C*), 136.2 (*quat-C*), 133.9 (ArCH), 130.4 (ArCH), 130.2 (*quat-C*), 129.1 (ArCH), 129.1 (ArCH), 128.6 (ArCH), 128.4 (ArCH), 127.0 (ArCH), 125.4 (ArCH), 66.8 (OCH₂), 21.5 (CH₃), 21.4 (CH₃).



4-Methylbenzyl 4-methylbenzoate (3d)⁴: Obtained by the reaction of 4-methylbenzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 20h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 25 : 1) afforded the product as a colourless oil with 89% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.2 Hz, ArCH, 2H), 7.36 (d, *J* = 7.9 Hz, ArCH, 2H), 7.23 (dd, *J*₁ = 10.8 Hz, *J*₂ = 8.2 Hz, ArCH, 4H), 5.33 (s, OCH₂, 2H), 2.42 (s, CH₃, 3H), 2.38 (s, CH₃, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 166.6 (*quat-C*), 143.7 (*quat-C*), 138.1 (*quat-C*), 133.3 (*quat-C*), 129.8 (ArCH), 129.4 (ArCH), 129.2 (ArCH), 128.4 (ArCH), 127.6 (*quat-C*), 66.6 (OCH₂), 21.8 (CH₃), 21.3 (CH₃).

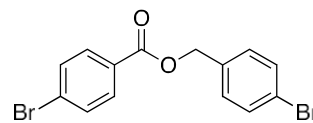


4-Fluorobenzyl 4-fluorobenzoate (3e)⁴: Obtained by the reaction of 4-fluorobenzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 78% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.06 (m, ArCH, 2H), 7.44-7.41 (m, ArCH, 2H), 7.12-7.05 (m, ArCH, 4H), 5.32 (s, OCH₂, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 166.0 (d, ¹*J*_{C-F} = 255 Hz, *quat-C*), 165.5 (*quat-C*), 162.8 (d, ¹*J*_{C-F} = 247 Hz, *quat-C*), 132.3 (d, ³*J*_{C-F} = 9.3 Hz, ArCH), 131.9 (d, ⁴*J*_{C-F} = 3.2 Hz, *quat-C*), 130.4 (d, ³*J*_{C-F} = 8.3 Hz, ArCH), 126.4 (d, ⁴*J*_{C-F} = 3.0 Hz, *quat-C*), 115.7 (d, ²*J*_{C-F} = 21.8 Hz, ArCH), 66.2 (OCH₂).

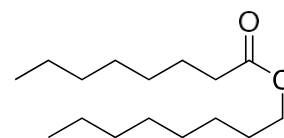


⁴ R. Ray, R.D. Jana, M. Bhadra, D. Maiti, G. K. Lahiri, *Chem. Eur. J.* 2014, **47**, 15618.

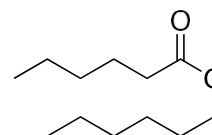
4-Bromobenzyl 4-bromobenzoate (3f)⁴: Obtained by the reaction of 4-bromobenzyl alcohol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a white solid with 83% yield. ¹H NMR (300 MHz, CDCl₃): δ 7.94-7.89 (m, ArCH, 2H), 7.60-7.50 (m, ArCH, 4H), 7.33-7.2 (m, ArCH, 2H), 5.30 (s, OCH₂, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 165.7 (*quat-C*), 134.9 (*quat-C*), 131.9 (ArCH), 131.9 (ArCH), 130.1 (ArCH), 128.9 (*quat-C*), 128.5 (*quat-C*), 122.6 (*quat-C*), 66.3 (OCH₂).



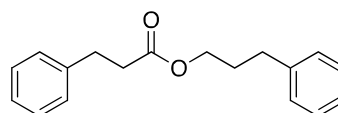
Octyl octanoate (3g)³: Obtained by the reaction of 1-octanol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a white solid with 85% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.05 (t, *J* = 6.7 Hz, OCH₂, 2H), 2.28 (t, *J* = 7.5 Hz, CH₂CO, 2H), 1.64-1.57 (m, 4H), 1.29-1.27 (m, 18H), 0.89-0.85 (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 174.1 (*quat-C*), 64.5 (OCH₂), 34.6 (CH₂), 31.9 (CH₂), 31.8 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 26.1 (CH₂), 25.2 (CH₂), 22.8 (CH₂), 22.7 (CH₂), 14.2 (CH₃), 14.2 (CH₃).



Hexyl hexanoate (3h)⁵: Obtained by the reaction of 1-hexanol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a white solid with 77% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.05 (t, *J* = 6.7 Hz, OCH₂, 2H), 2.28 (t, *J* = 7.5 Hz, CH₂CO, 2H), 1.63-1.59 (m, 4H), 1.30 (br, 10H), 0.90-0.87 (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 174.1 (*quat-C*), 64.5 (OCH₂), 34.5 (CH₂), 31.6 (CH₂), 31.5 (CH₂), 28.8 (CH₂), 25.7 (CH₂), 24.9 (CH₂), 22.7 (CH₂), 22.5 (CH₂), 14.1 (CH₃), 14.0 (CH₃).



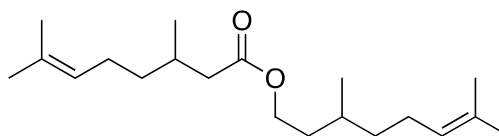
3-Phenylpropyl 3-phenylpropanoate (3i)⁴: Obtained by the reaction of 3-phenylpropan-1-ol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a white solid with 78% yield. ¹H NMR (300 MHz,



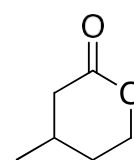
⁵ N. Yamamoto, Y. Obora, Y. Ishii, *J. Org. Chem.* 2011, **76**, 2937.

CDCl₃): δ 7.35-7.17 (m, ArCH, 10H), 4.12 (t, J = 6.5 Hz, OCH₂, 2H), 2.99 (t, J = 7.8 Hz, CH₂CO, 2H), 2.69-2.64 (m, 4H), 1.96 (q, J = 6.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 173.0 (*quat-C*), 141.3 (*quat-C*), 140.6 (*quat-C*), 128.6 (ArCH), 128.5 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 126.4 (ArCH), 126.1 (ArCH), 63.9 (OCH₂), 36.0 (CH₂), 32.3 (CH₂), 31.1 (CH₂), 30.3 (CH₂).

3,7-Dimethyloct-6-en-1-yl 3,7-dimethyloct-6-enoate (3j): Obtained by the reaction of Citronellol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 82% yield. ¹H NMR (400 MHz, CDCl₃): δ 5.08 (t, J = 6.6 Hz, 2H), 4.14-4.04 (m, 2H), 2.29 (dd, J_1 = 14.6 Hz, J_2 = 5.9 Hz, 1H), 2.09 (dd, J_1 = 14.5 Hz, J_2 = 8.2 Hz, 1H), 2.01-1.91 (m, 5H), 1.67 (s, 3H), 1.59 (s, 3H), 1.57-1.13 (m, 7H), 0.93 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 173.5 (d, *quat-C*), 131.5 (d, *quat-C*), 124.6 (d, CH), 62.8 (d, CH₂), 42.0 (d, CH₂), 37.1 (CH₂), 36.9 (CH₂), 35.7 (CH₂), 30.2 (CH), 29.6 (d, CH), 25.8 (d, CH₃), 25.5 (d, CH₂), 19.8 (CH₃), 19.5 (CH₃), 17.8 (CH₃). *Two adjacent peaks are due to the two diastereoisomers. HRMS(ESI-TOF): calc'd for C₂₀H₃₆O₂Na [M+Na]⁺ 331.26075; found 331.2608.



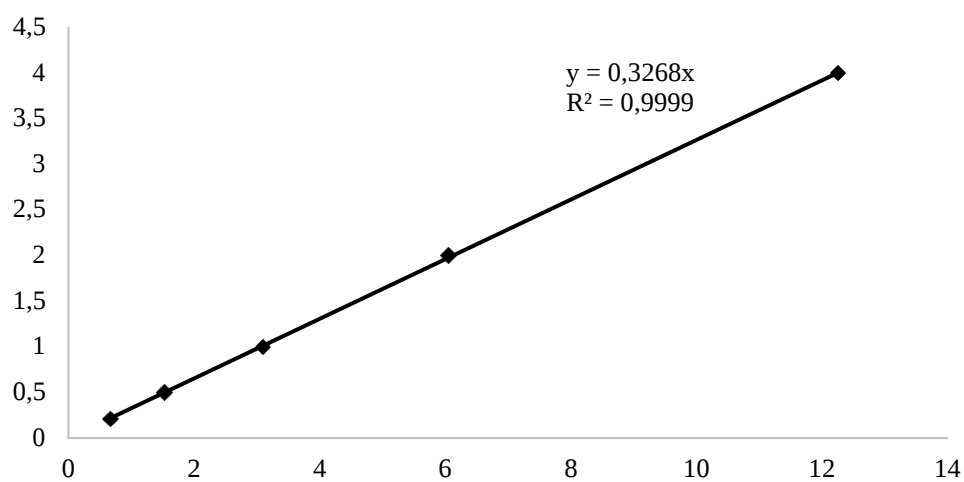
4-Methyltetrahydro-2H-pyran-2-one (3k)⁶: Obtained by the reaction of 3-methylpentane-1,5-diol (0.5 mmol) in presence of complex **Ru-1** and NaOH in toluene (2 mL) at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 2 : 1) afforded the product as a colourless oil with 81% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.40 (ddd, J_1 = 11.4 Hz, J_2 = 4.9 Hz, J_3 = 4.0 Hz, 1H), 4.25 (td, J_1 = 11.0 Hz, J_2 = 3.8 Hz, 1H), 2.70-2.62 (m, 1H), 2.13-2.03 (m, 2H), 1.94-1.87 (m, 1H), 1.55-1.46 (m, 1H), 1.05 (d, J = 6.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 171.3 (*quat-C*), 68.7 (CH₂), 38.4 (CH₂), 30.8 (CH₂), 26.7 (CH), 21.6 (CH₃).



⁶ A. S. Touchy, K. Shimizu, *RSC Adv.* 2015, 5, 29072.

E. Internal Standard Studies for Formic Acid Production

$$[\text{HCO}_2\text{H}] = 0.3268 \cdot \left(\frac{\text{int. HC}(\text{HCO}_2\text{H})}{\text{int. HCO}(\text{DMF})} \right)$$



Internal standard curve for the calculation of Formic acid concentration



