Electronic Supporting Information for: "Online monitoring by infrared spectroscopy using multivariate analysis – background theory and application to catalytic dehydrogenative coupling of alcohols to esters"

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S1 General Procedure

S1.1 Experimental equipment and reagents

Infrared monitoring was realized with attenuated total reflectance Fourier-transform infrared (ATR-FTIR) technology using ReactIR™ 15 workstation from Mettler Toledo. Additional analyses were performed using a Shimadzu 2030 GC equipped with FID detector and a DB5 column (5 m x 0.05 mm x 0.05 µm). Tetradecane was used as an internal standard.

All the experiments were carried out under argon atmosphere using vacuum line and standard Schlenk techniques. Anhydrous 1-butanol (99.8%), butyraldehyde (99.5%), butyl butyrate (98%) were purchased from Aldrich. 1-Butanol was dried over activated 3A molecular sieves, butyraldehyde and

butyl butyrate were fractionally distilled under argon with appropriate drying agents.[1] Liquids were outgassed by extensive argon bubbling. Complex $RuH(CO)BH_4[HM(CH_2CH_2PiPr_2)_2]$ was prepared according the reported procedure.[2,3]

S1.2 IR measurement procedure for calibration

Prior to samples analysis baseline background spectrum was recorded in air. For calibration, initial solutions of interest were prepared by mixing weighted proportions of 1-butanol, butyraldehyde and butyl butyrate. Solution was added to the vessel and mixture was heated at appropriated temperature. Absorbance spectra were recorded. Then, gravimetrically measured portions of compounds were added and absorbance spectrums of new solutions were recorded for supplementary calibration points.

S1.3 Experimental procedure with online IR measurement

A 100 mL round bottom flask equipped with a condenser topped by an argon bubbler was inerted using standard Schlenk techniques. Prior to experiment, analysis baseline background spectrum was recorded in argon atmosphere. Substrates (0.3 mol) were added to the vessel, heated to 110°C using an oil bath and vigorously stirred (1400 rpm) with a magnetic stirring bar. Argon was bubbled through the liquid. A solution of the catalytic complex (0.07 mmol, 240 ppm) in 1-butanol prepared under argon was transferred to the mixture *via* a syringe under argon stream.

S2 Molar composition for IR calibration

S2.1 Molar composition of the standard solutions analysed at 383 K

N°	Butanol	Butyraldehyde	Butyl butyrate
1	100%	0%	0%
2	90%	5%	5%
3	82%	4%	14%
4	79%	16%	5%
5	76%	24%	0%
6	75%	24%	1%
7	74%	5%	21%
8	74%	24%	2%
9	73%	23%	4%
10	72%	23%	5%
11	71%	23%	7%
12	70%	25%	5%
13	70%	22%	8%
14	69%	16%	15%
15	68%	22%	10%
16	67%	5%	29%
17	66%	21%	13%
18	65%	14%	21%
19	65%	21%	15%
20	64%	21%	15%
21	64%	20%	16%
22	63%	20%	17%
23	61%	20%	19%
24	60%	19%	21%

25	59%	26%	15%
26	59%	19%	22%
27	58%	14%	28%
28	57%	18%	24%
29	56%	5%	39%
30	56%	18%	26%
31	55%	18%	27%
32	54%	17%	29%
33	53%	17%	30%
34	52%	17%	31%
35	52%	27%	21%
36	50%	16%	34%
37	49%	13%	38%
38	45%	26%	29%
39	41%	15%	43%
40	40%	21%	39%
41	40%	34%	27%
42	39%	31%	30%
43	38%	5%	57%
44	38%	37%	25%
45	37%	29%	33%
46	37%	35%	28%
47	36%	25%	39%
48	35%	33%	32%
49	33%	31%	36%
50	32%	26%	41%
51	32%	27%	41%
52	31%	16%	53%
53	29%	22%	49%
54	27%	29%	45%
55	24%	17%	59%
56	23%	10%	67%
57	22%	24%	54%
58	21%	5%	74%
59	18%	8%	74%
60	16%	19%	65%
61	15%	27%	58%
62	9%	0%	91%
63	9%	16%	75%
64	9%	26%	65%
65	8%	9%	83%
66	5%	5%	90%
67	4%	19%	77%
68	0%	0%	100%

S2.2 Molar composition of the standard solutions analysed at various temperatures

N°	Temperature (°C)	Butanol	Butyraldehyde	Butyl butyrate
1	61 75 92 109	87%	7%	5%
2	51 72 88 105	67%	12%	21%
3	52 71 89	54%	17%	29%

	107			
4	60 77 96 114	28%	25%	47%
5	56 75 91 111	10%	0%	90%
6	56 75 93 111	15%	5%	81%
7	58 76 95 112	51%	0%	49%

References

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