Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Base-free, acceptorless dehydrogenative coupling of ethanol to ethyl acetate with PNP complexes

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1. General information

Absolute Ethanol (purity 99.98%), toluene (purity 99.99%), *o*-xylene (purity ≥ 98%), *m*-xylene (purity ≥ 99%), *p*-xylene (purity ≥ 99%), ethylbenzene (purity ≥ 99.%), mesitylene (purity 98%), *p*-cymene (purity ≥ 99%), chlorobenzene (purity ≥ 99%), anisole (purity 99.7%), cyclohexane (purity 99.5%), methylcyclohexane (purity ≥ 99%), 1,3-dimethylcyclohexane (purity 99%), tetrahydrofuran (purity 99.99%), 1,4-dioxane (purity 99.8%), cyclopentyl methyl ether (purity 99.99%), γ-valerolactone (purity 99%) were purchased from Sigma Aldrich or TCI. The complexes **Ru**-**1** to **Ru**-**6** and **Ir**-**1** are commercially available and used without further purification. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. Dimethyl sulfoxide (100 µL, purity 99.9%) was added as the internal standard to quantify the conversion of ethanol and the yield of ethyl acetate. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer and were referenced on the deuterated solvent peak. Catalysts were added to the reaction vessel inside an argon-filled glovebox. Substrates and co-solvents (Figure S1) were loaded into the 50 mL reaction flask using standard Schlenk techniques. Unless otherwise specified, the volume of the reaction vessel is a 50 mL Schlenk flask and the stirring rate is 600 rpm.

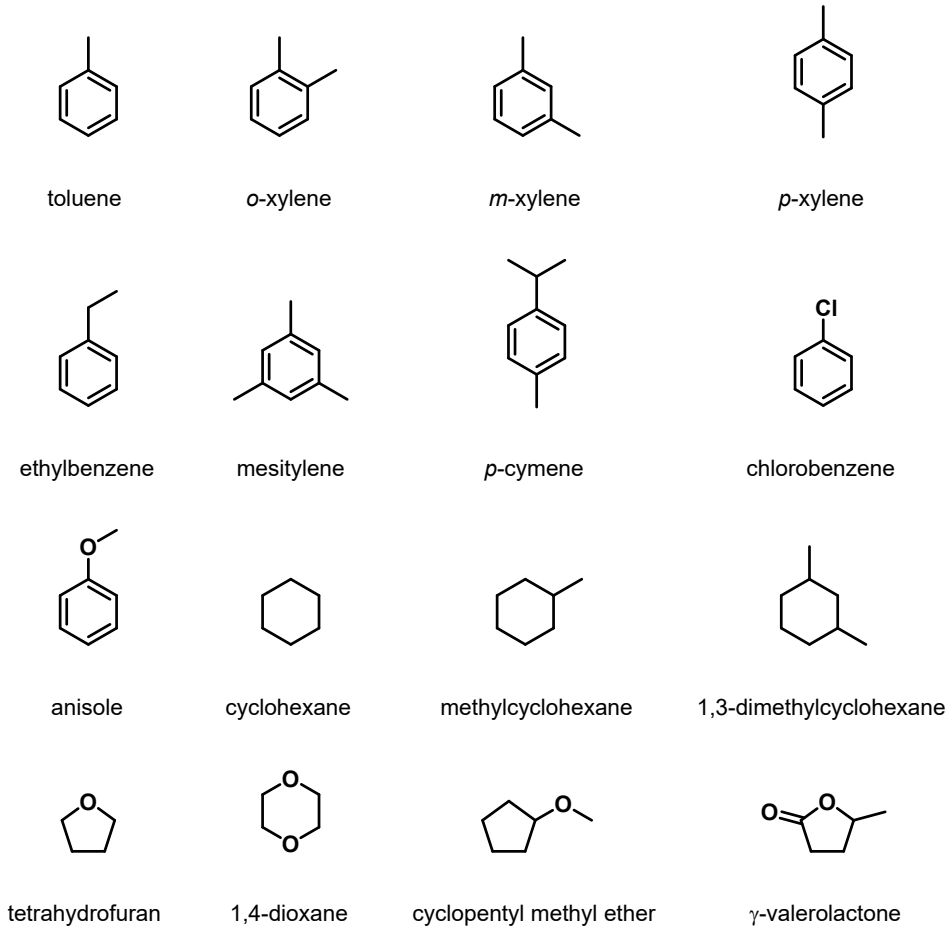


Figure S1. Used organic compounds as co-solvents in this work

Table S1. Properties of the different solvents used in this study.[1,2]

Solvent	Boiling point (°C)	Dielectric constant (20 °C)
cyclohexane	80.8	2.02
methylcyclohexane	101	2.02
1,3-dimethylcyclohexane	120-125	/
p-xylene	138.4	2.27
1,4-dioxane	101	2.2 (25 °C)
p-cymene	177	2.3
m-xylene	139	2.36
toluene	110.6	2.4
mesitylene	164.7	2.4
ethylbenzene	136	2.5
o-xylene	144	2.56
anisole	153.8	4.3
cyclopentyl methyl ether	106	4.76 (25 °C)
chlorobenzene	132	5.6 (25 °C)
tetrahydrofuran	66	7.58 (25 °C)
acetaldehyde	20.2	21.8 (18 °C)
ethanol	78.4	24.5
γ-valerolactone	207	36.47 (25 °C)

2. Experimental section

General procedure for a catalytic reaction. A 50 mL Schlenk flask equipped with a magnetic stir bar was loaded with the catalyst (0.05 – 0.1 mol%) inside a glovebox. The sealed flask was removed from the glovebox. Then dried and degassed EtOH (2mL) and co-solvent (2.5 – 15 mL) were added with a Hamilton® syringe. The flask was purged three times with argon before carrying out the experiments at the desired, external, temperature (100-120 °C) for 18-72 h at a stirring rate of 600 rpm under reflux.

After the reaction time, the flask was cooled to room temperature and 0.5-1 mL of extra co-solvent was loaded under argon. Dimethyl sulfoxide (100 µL) was added as internal standard to quantify the conversion of EtOH and the yield of AcOEt. Finally, the resulting solution was analyzed by ^{1}H and ^{13}C NMR using $CDCl_3$ or CD_3OD.

Conversion and yield calculation.

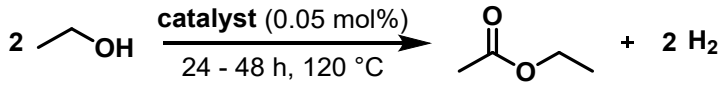
$$left\ EtOH\ amount = \frac{NMR\ integration\ of\ H\ on\ methylene\ groups\ of\ EtOH * 6 * added\ amount\ of\ DMSO}{2 * NMR\ integration\ of\ DMSO}$$

$$Produced\ EtOAc = \frac{NMR\ integration\ of\ H\ on\ methylene\ groups\ of\ EtOAc * 6 * added\ amount\ of\ DMSO}{2 * NMR\ integration\ of\ DMSO}$$

$$Conversion = \frac{(initial\ EtOH\ amount - \ left\ EtOH\ amount)}{initial\ ethanol\ amount} * 100\%$$

$$Yield = \frac{Produced\ EtOAc\ amount * 2}{initial\ EtOH\ amount} * 100\%$$

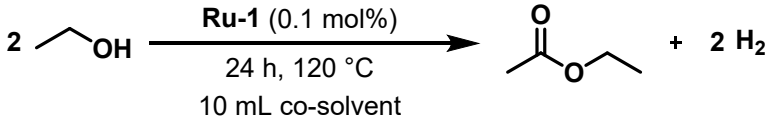
Table S2. Initial attempts for ethanol conversion to ethyl acetate with **Ru**-**1** in the absence of solvent.



Entry	Catalyst (0.05 mol%)	Time [h]	Conversion [%][a]	Yield [%][a]	Selectivity [%]
1	**Ru**-**1**	24	43	34	61
2	**Ru**-**2**	48	42	31	74
3	**Ru**-**3**	24	< 5	< 5	-
4	**Ru**-**4**	24	0	0	-
5	**Ru**-**5**	24	0	0	-
6	**Ru**-**6**	24	0	0	-
7	**Ir**-**1**	24	0	0	-

[a]Determined by NMR, dimethyl sulfoxide (DMSO) as the internal standard.

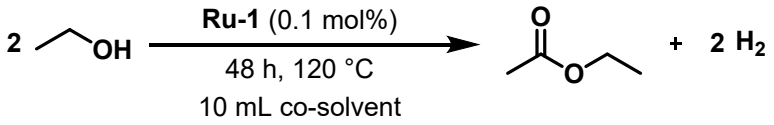
Table S3. Screening of ethanol conversion using 10 mL co-solvent with 0.1 mol% **Ru**-**1** at 120 °C for 24 h.



Entry	Solvent	Conversion [%][a]	Yield [%][a]	Selectivity [%]
1	toluene	63	46	73
2	*m*-xylene	87	79	91
3	*o*-xylene	58	51	88
4	*p*-xylene	40	27	68
5	mesitylene	30	15	50
6	ethylbenzene	68	55	81
7	*p*-cymene	66	53	80
8	chlorobenzene	10	5	50
9	cyclohexane	52	50	96
10	methylcyclohexane	55	50	91
11	1,3-dimethylcyclohexane	51	46	90
12	anisole	61	49	80
13	tetrahydrofuran	22	20	91
14	1,4-dioxane	53	41	77
15	cyclopentyl methyl ether	52	46	88
16	γ-valerolactone	12	7	58

[a] Determined by NMR, dimethyl sulfoxide (DMSO) as the internal standard.

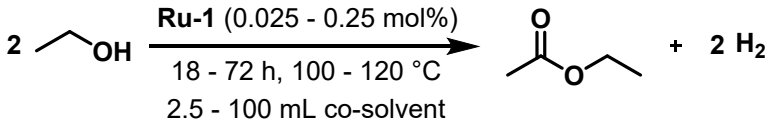
Table S4. Screening of ethanol conversion using 10 mL co-solvent with 0.1 mol% **Ru**-**1** at 120 °C for 48 h.



Entry	Solvent	Conversion [%][a]	Yield [%][a]	Selectivity [%]
1	toluene	72	52	72
2	*m*-xylene	95	76	80
3	*o*-xylene	58	54	93
4	*p*-xylene	45	28	62
5	mesitylene	0	0	0
6	ethylbenzene	72	55	76
7	*p*-cymene	59	48	81
8	chlorobenzene	0	0	0
9	cyclohexane	51	34	67
10	methylcyclohexane	46	45	98
11	1,3-dimethylcyclohexane	57	55	96
12	anisole	73	57	78
13	tetrahydrofuran	63	58	92
14	1,4-dioxane	59	43	73
15	cyclopentyl methyl ether	56	45	80
16	γ-valerolactone	14	8	57

[a] Determined by NMR, dimethyl sulfoxide (DMSO) as the internal standard.

Table S5. Optimization of ethanol conversion under different conditions.



Entry	**Ru-1** [mol%]	Solvent	Volume [mL]	Time [h]	Conversion [%][a]	Yield [%][a]	Selectivity [%]
1	0.025	Toluene	10	72	39	13	33
2	0.05	Toluene	10	24	43	25	58
3	0.05	Toluene	10	72	72	54	75
4	0.05	Toluene	2.5	24	47	43	91
5	0.1	Toluene	2.5	18	89	84	94
6	0.1	Toluene	2.5	24	98	92	94
7[b]	0.1	Toluene	2.5	24	37	34	92
8	0.1	Toluene	5	24	91	87	96
9	0.1	Toluene	15	24	53	52	98
10	0.1	Toluene	10	72	92	86	93
11	0.1	*m*-xylene	2.5	24	76	71	93
12	0.1	*m*-xylene	5	24	86	78	91
13	0.1	*m*-xylene	15	24	69	68	99
14	0.25	*m*-xylene	5	24	> 99	> 99	> 99
15	0.25	*m*-xylene	10	24	> 99	97	99
16	0.3	*m*-xylene	10	24	> 99	93	93
17[c]	0.25	*m*-xylene	100	24	> 99	87	87
18	0.05	*o*-xylene	10	48	52	33	63
19	0.1	Ethylbenzene	5	24	58	48	83
20	0.1	Ethylbenzene	15	24	69	50	72
21	0.05	Cyclohexane	10	24	25	25	100
22	0.1	Tetrahydrofuran	10	72	65	63	97

[a] Determined by NMR, dimethyl sulfoxide (DMSO) as the internal standard.

[b] 100 °C.

[c] 20 mL EtOH.

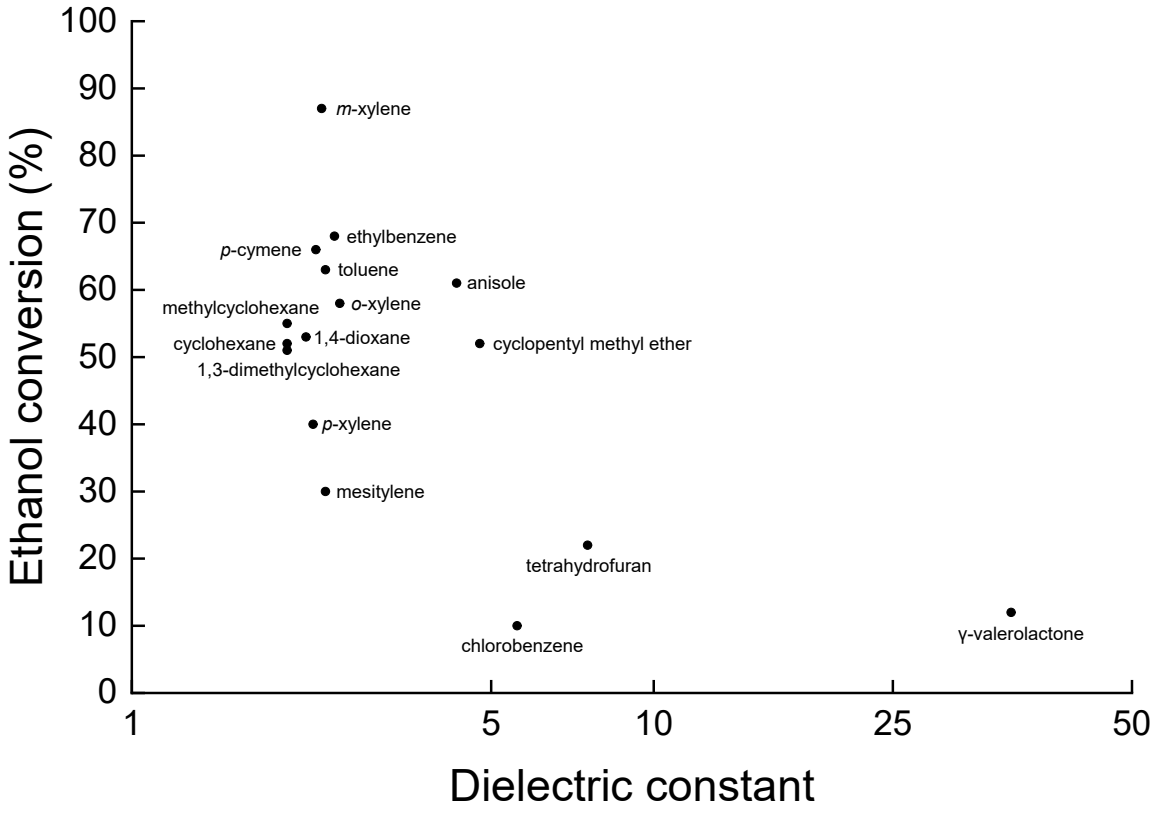


Figure S2. Distribution of EtOH conversion in sixteen solvents with different dielectric constant in presence of **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

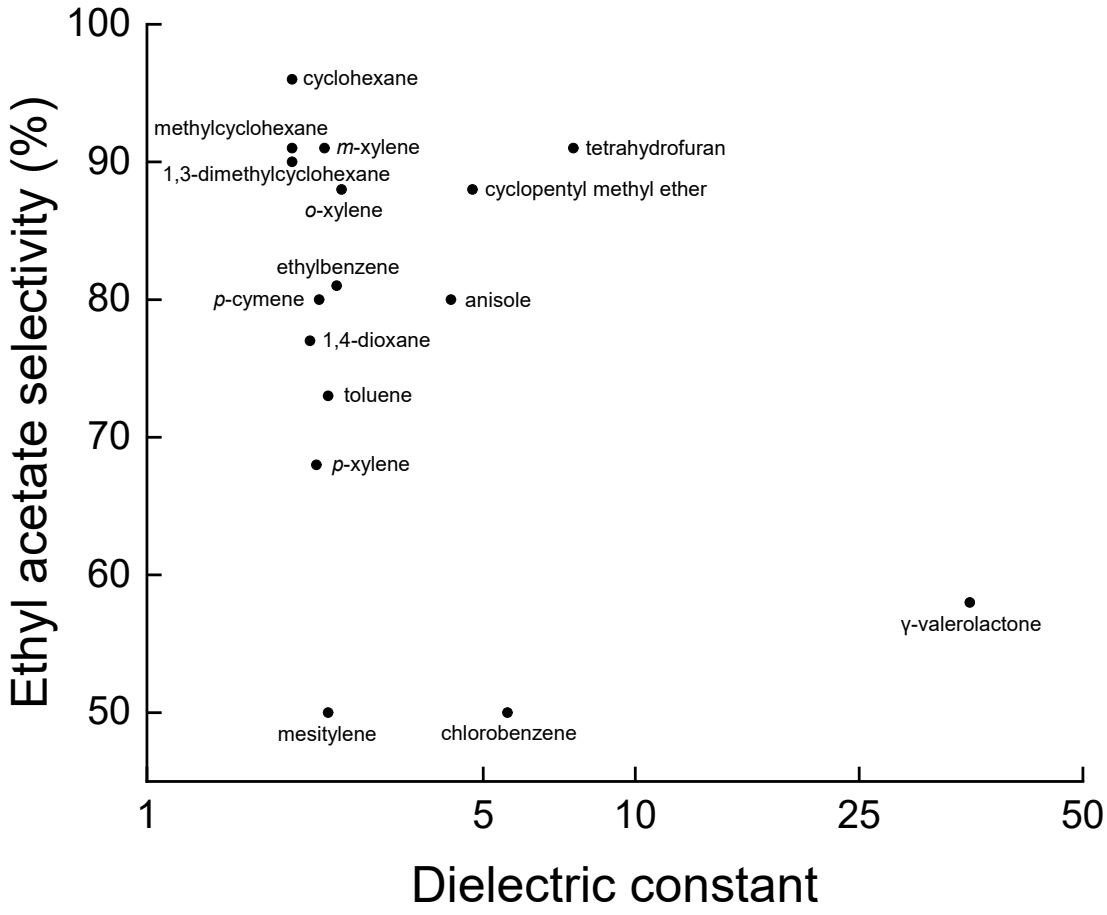


Figure S3. Distribution of AcOEt selectivity in sixteen solvents with different dielectric constant in presence of **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

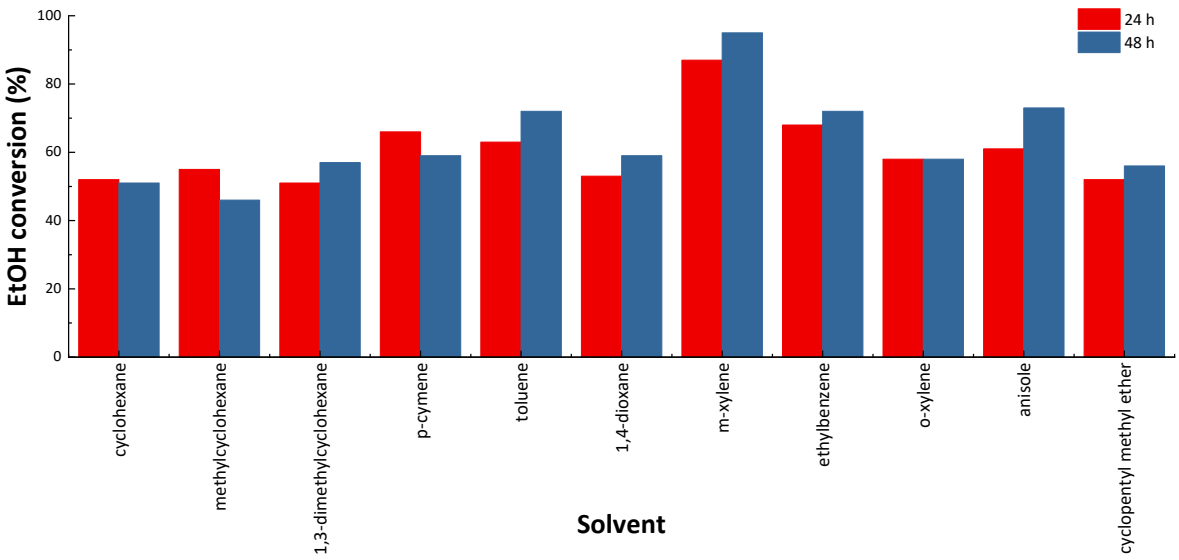


Figure S4. Solvent effect in the ADC of EtOH with **Ru**-**1** (0.1 mol%) at 120 °C between 24 and 48 h.

3. NMR spectra of crude reactions

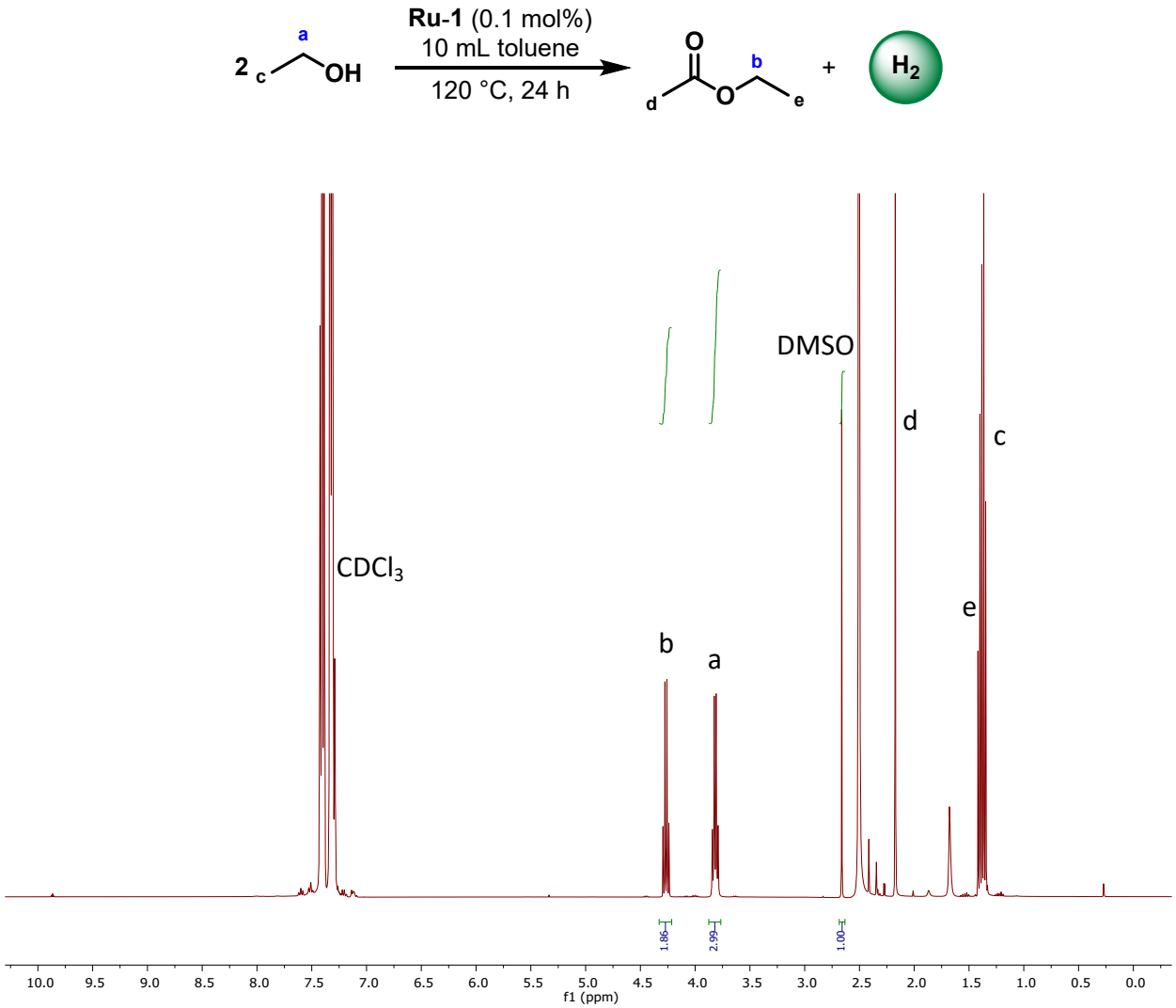


Figure S5. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL toluene, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

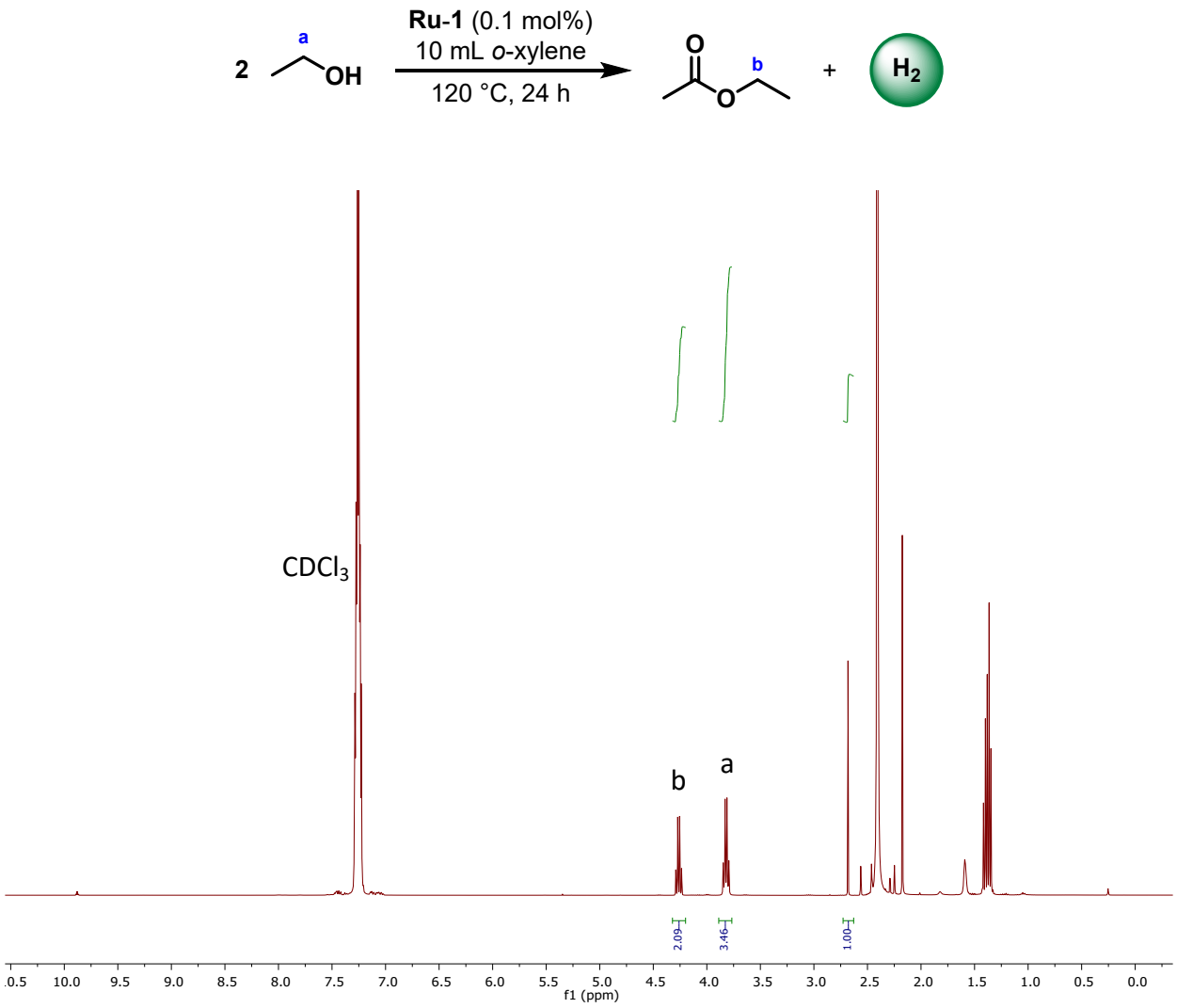


Figure S6. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL *o*-xylene, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

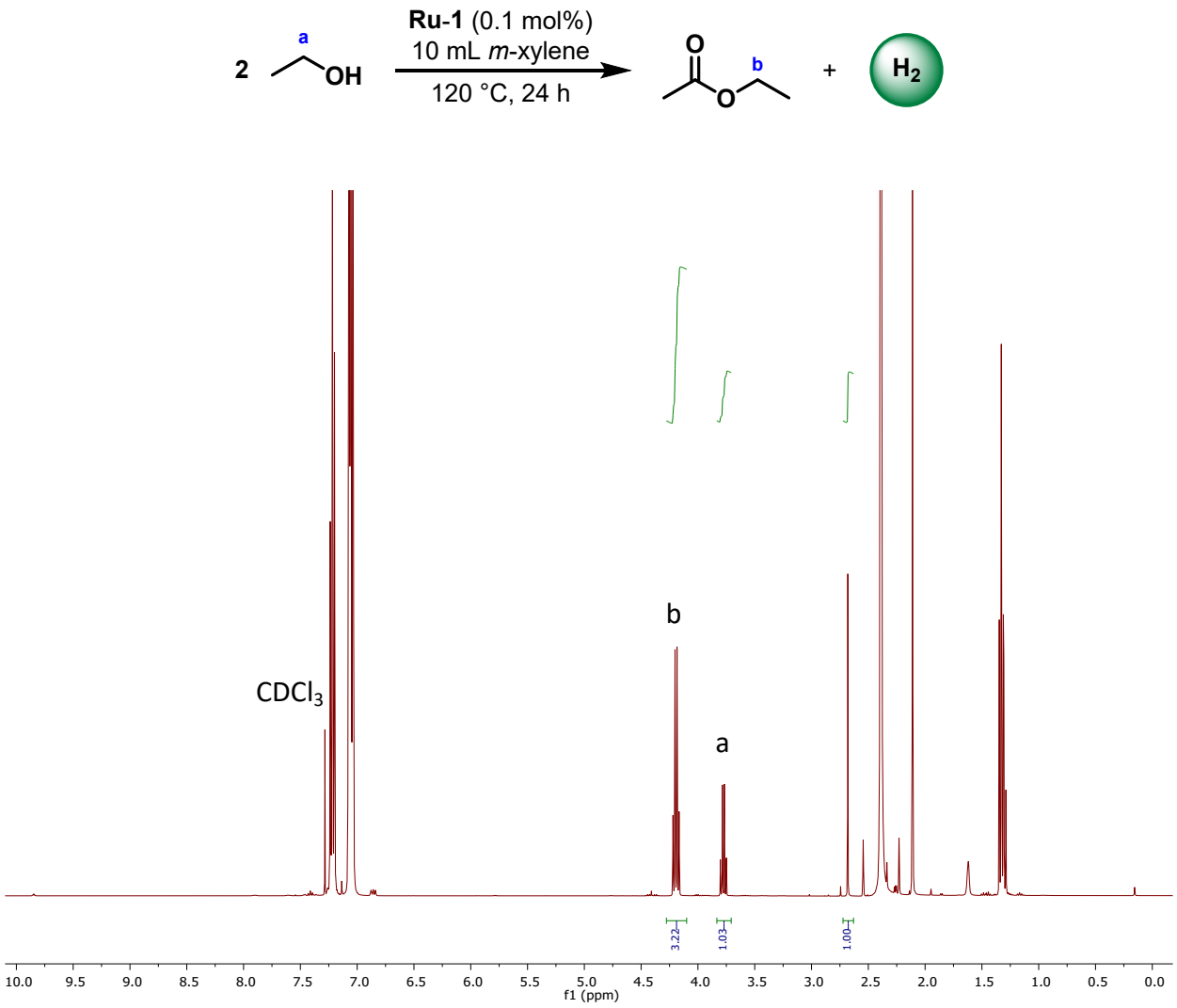


Figure S7. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL *m*-xylene, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

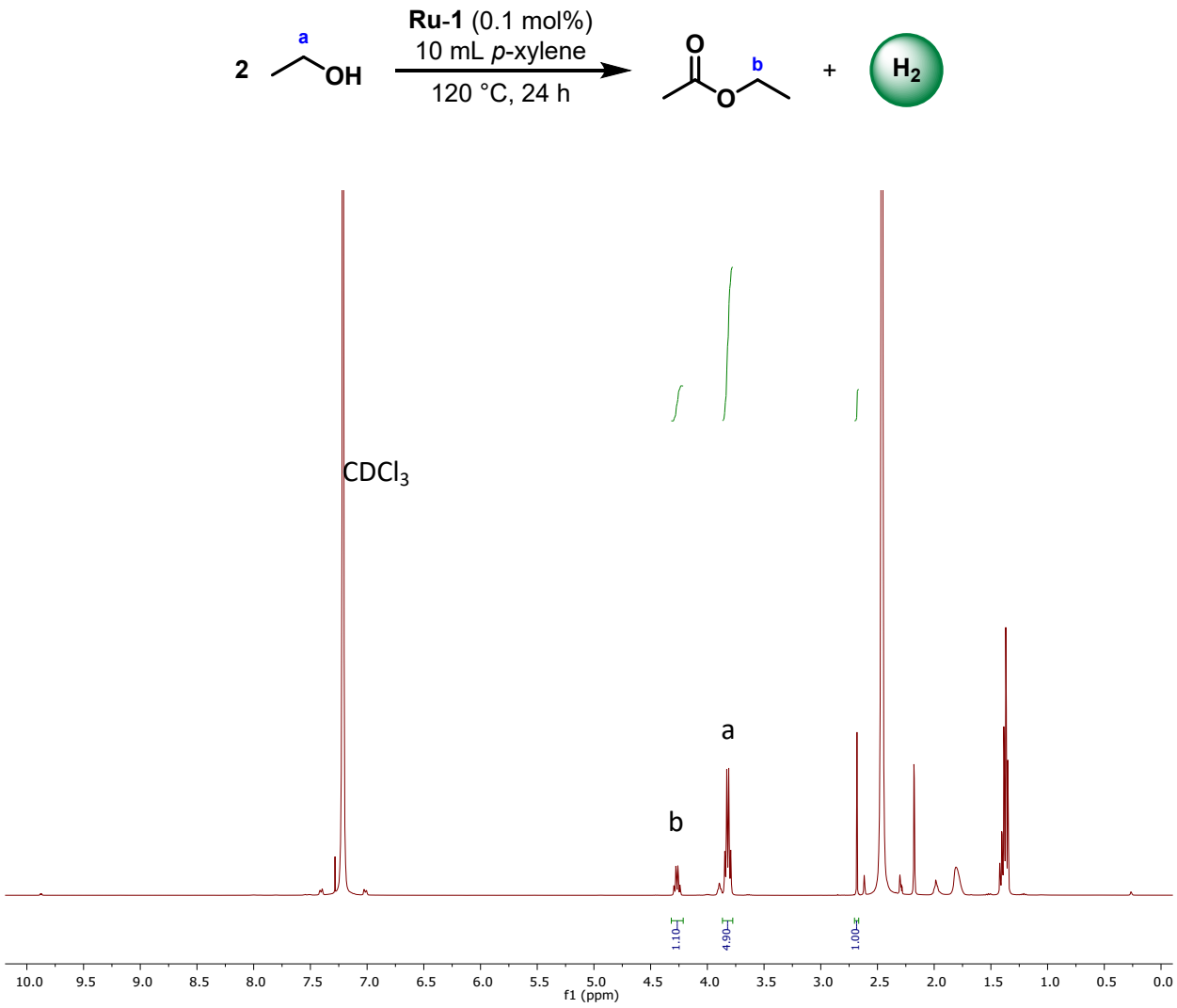


Figure S8. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL *p*-xylene, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

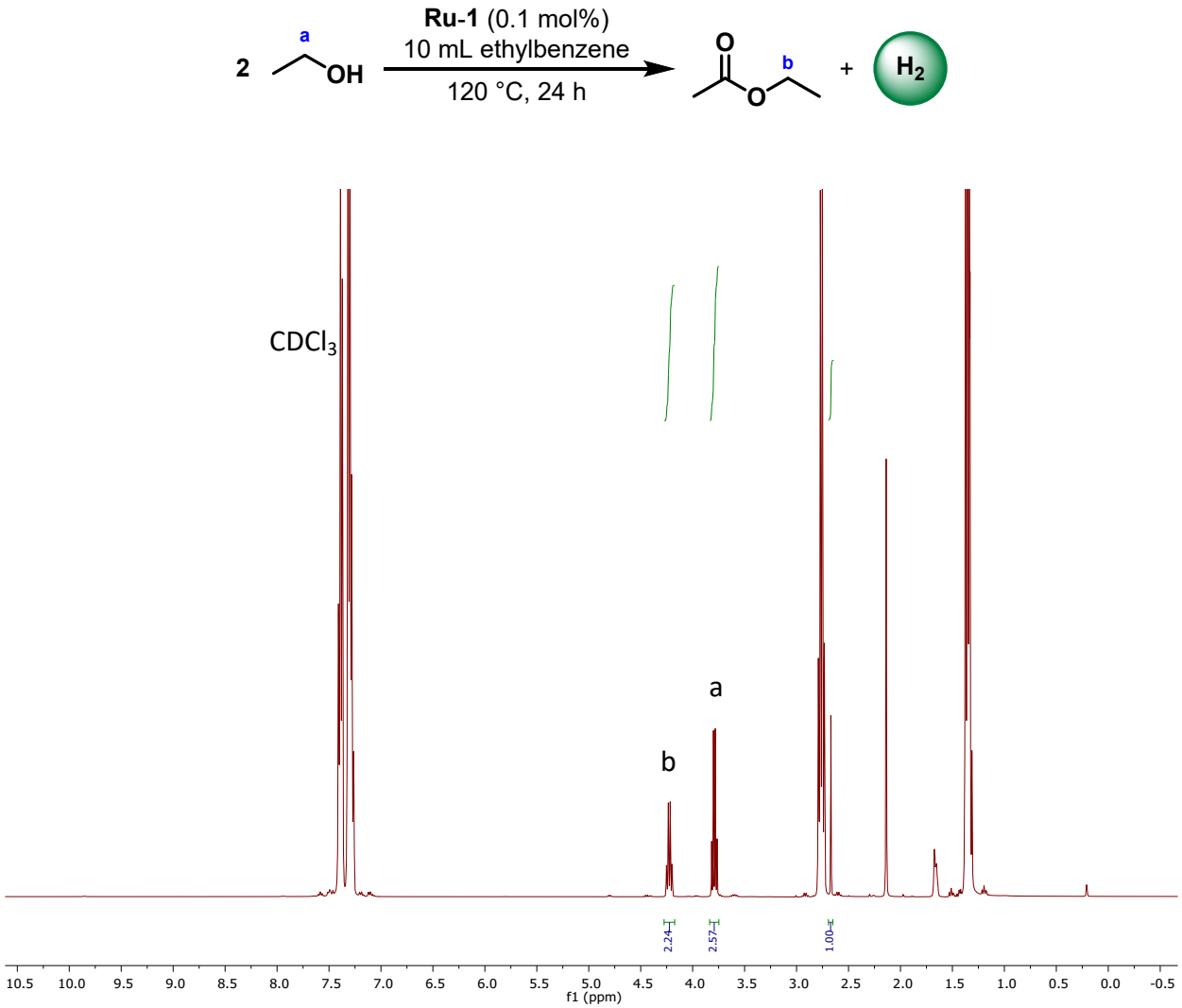


Figure S9. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL ethylbenzene, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

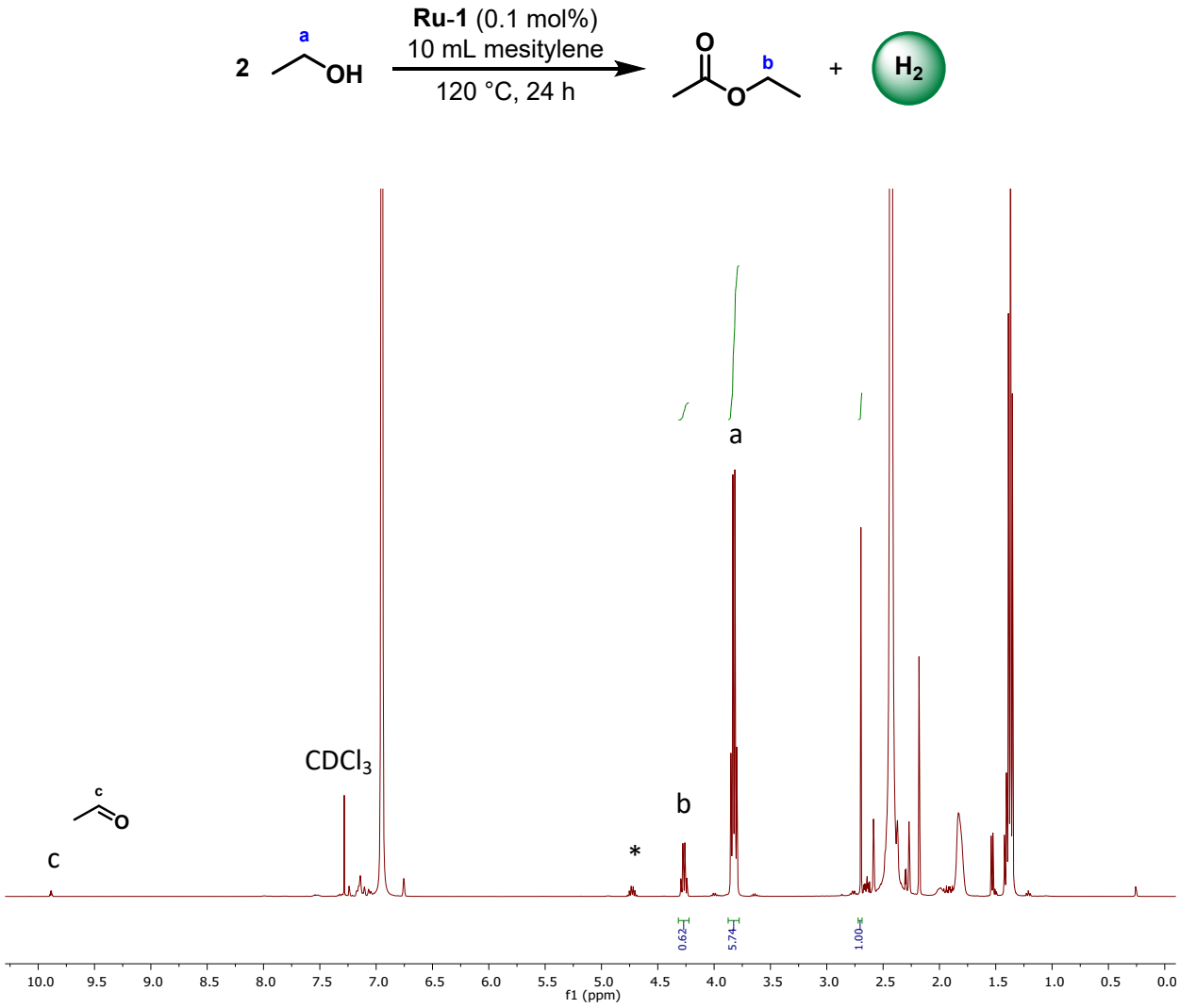


Figure S10. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL mesitylene, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

* unknown peak

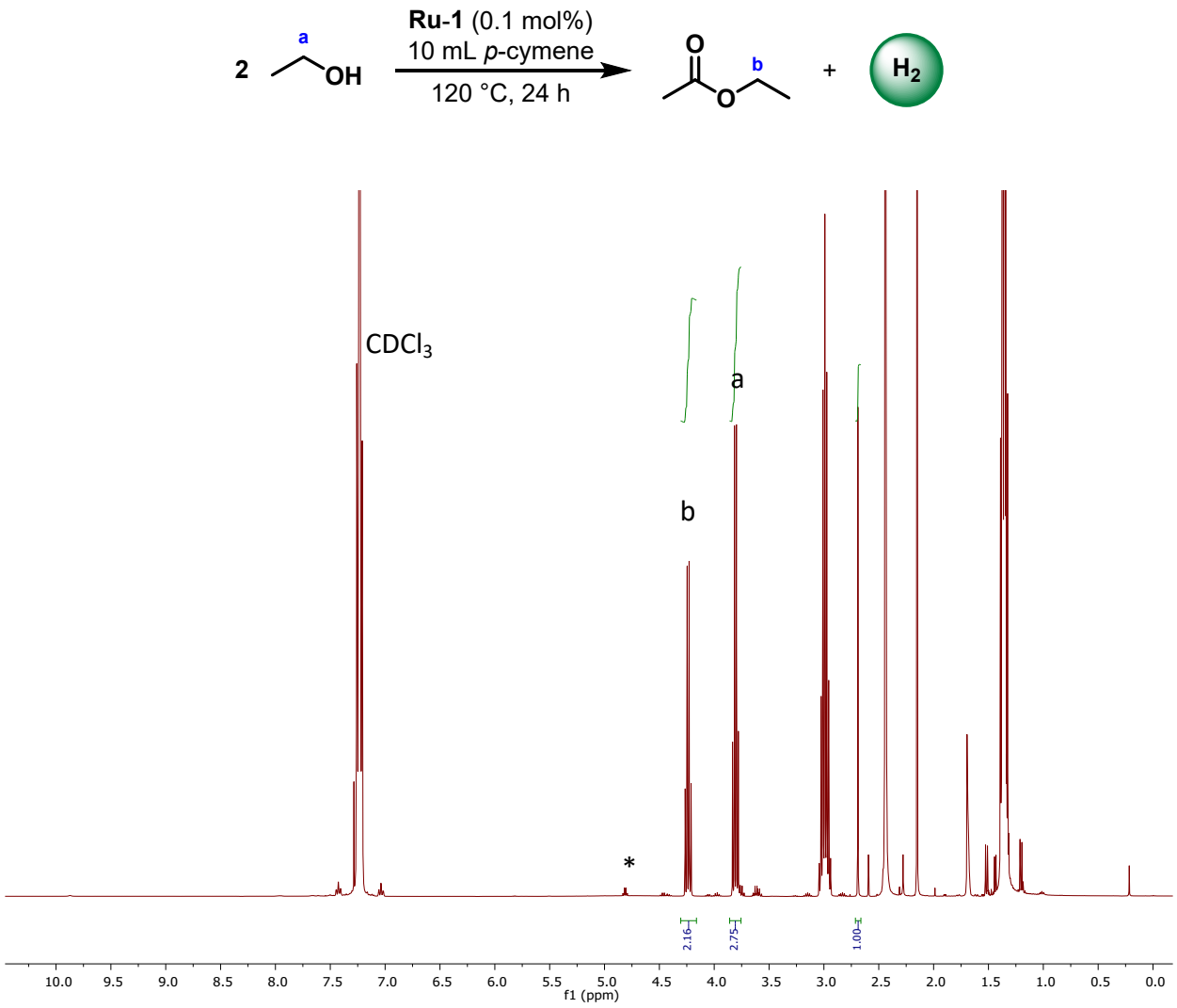


Figure S11. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL *p*-cymene, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

* unknown peak

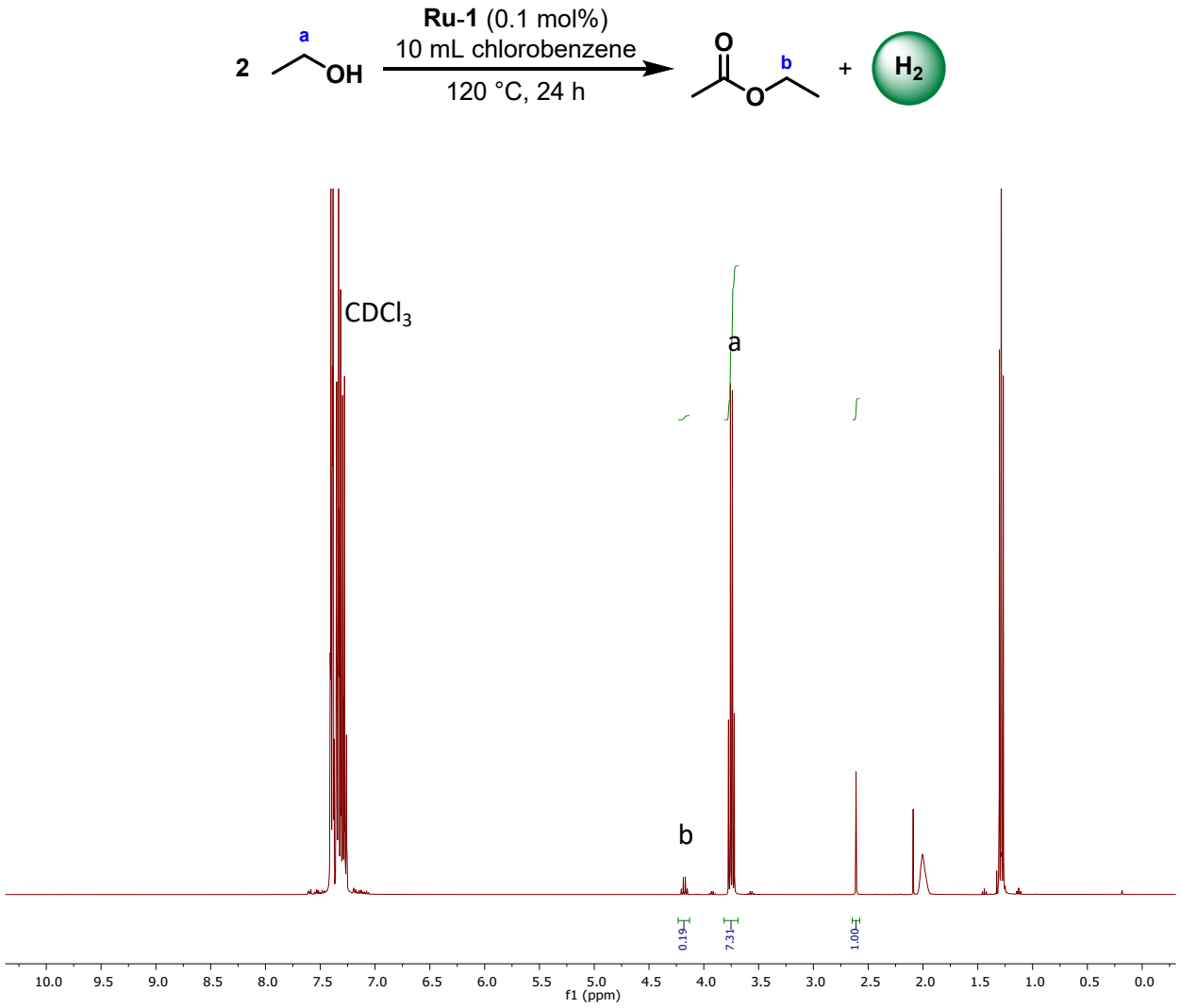


Figure S12. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL chlorobenzene, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

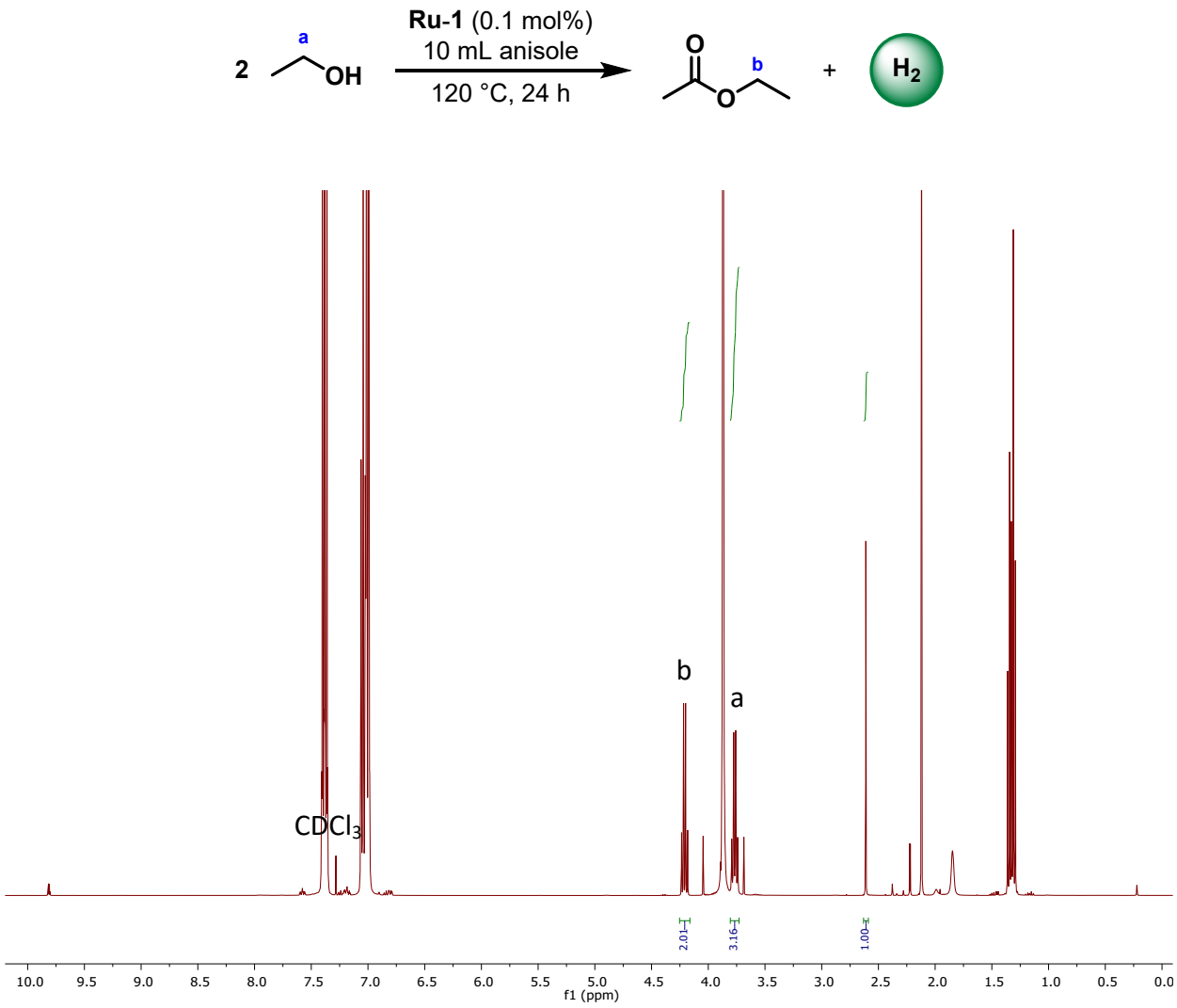


Figure S13. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL anisole, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

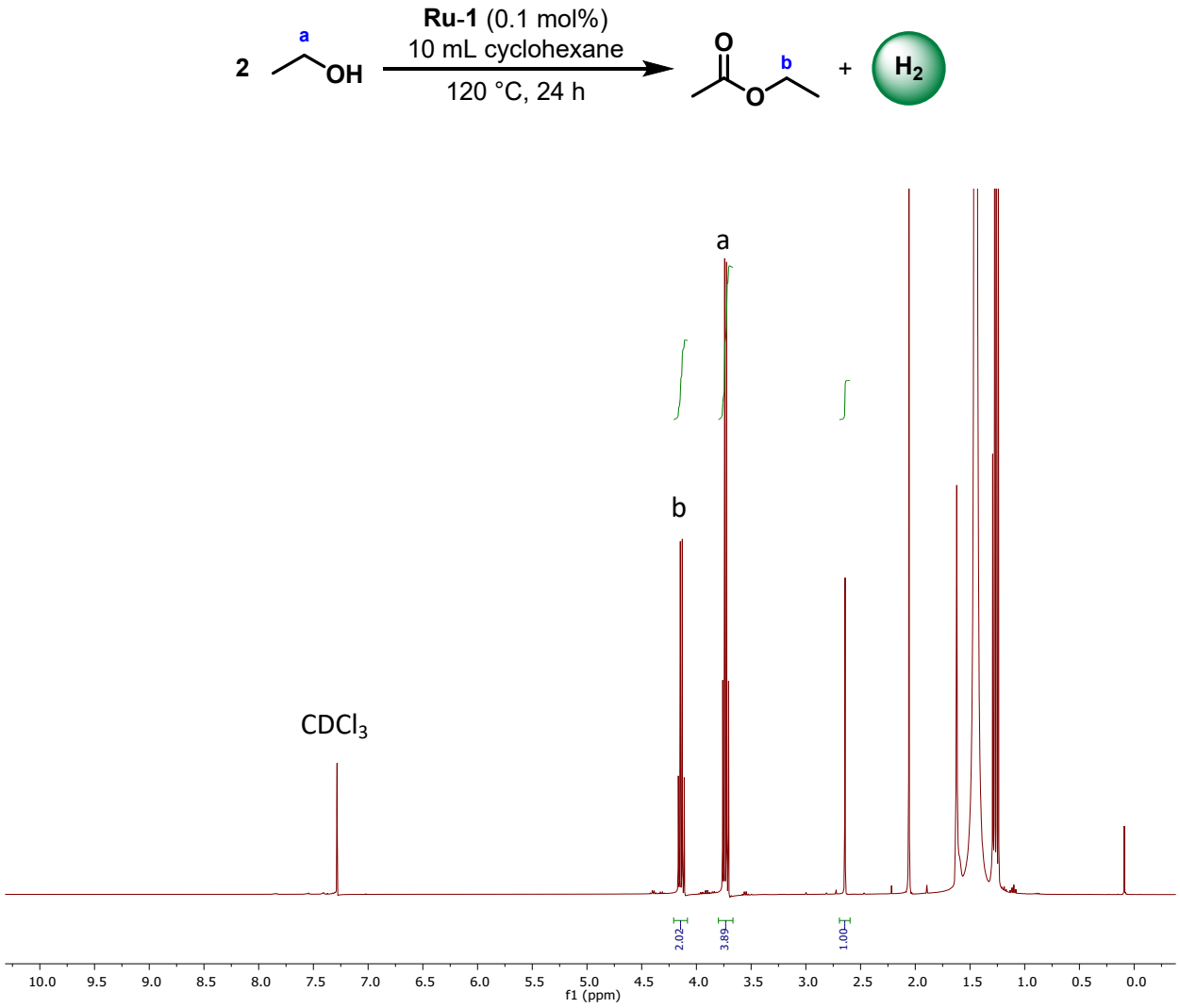


Figure S14. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL cyclohexane, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

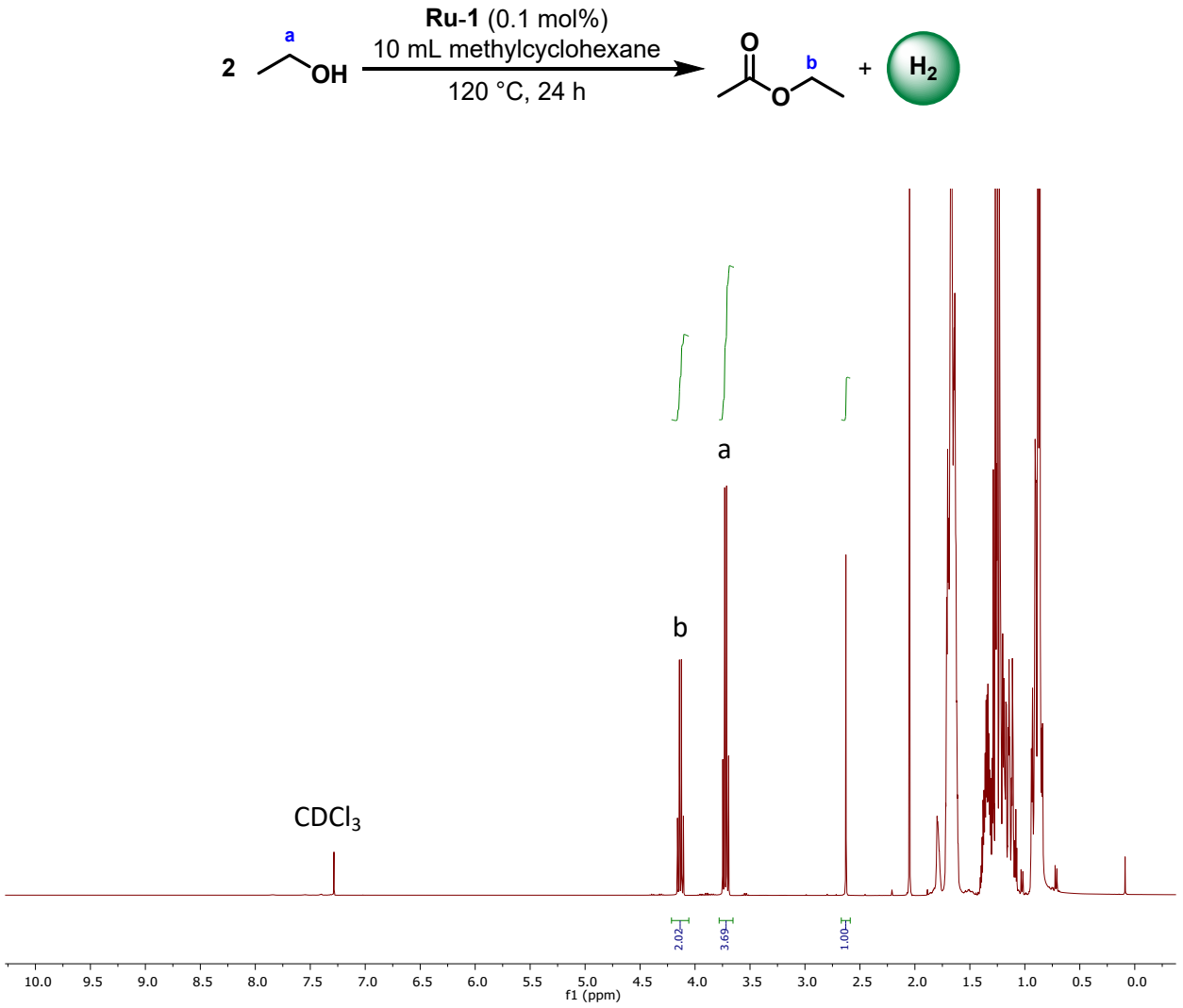


Figure S15. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL methylcyclohexane, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

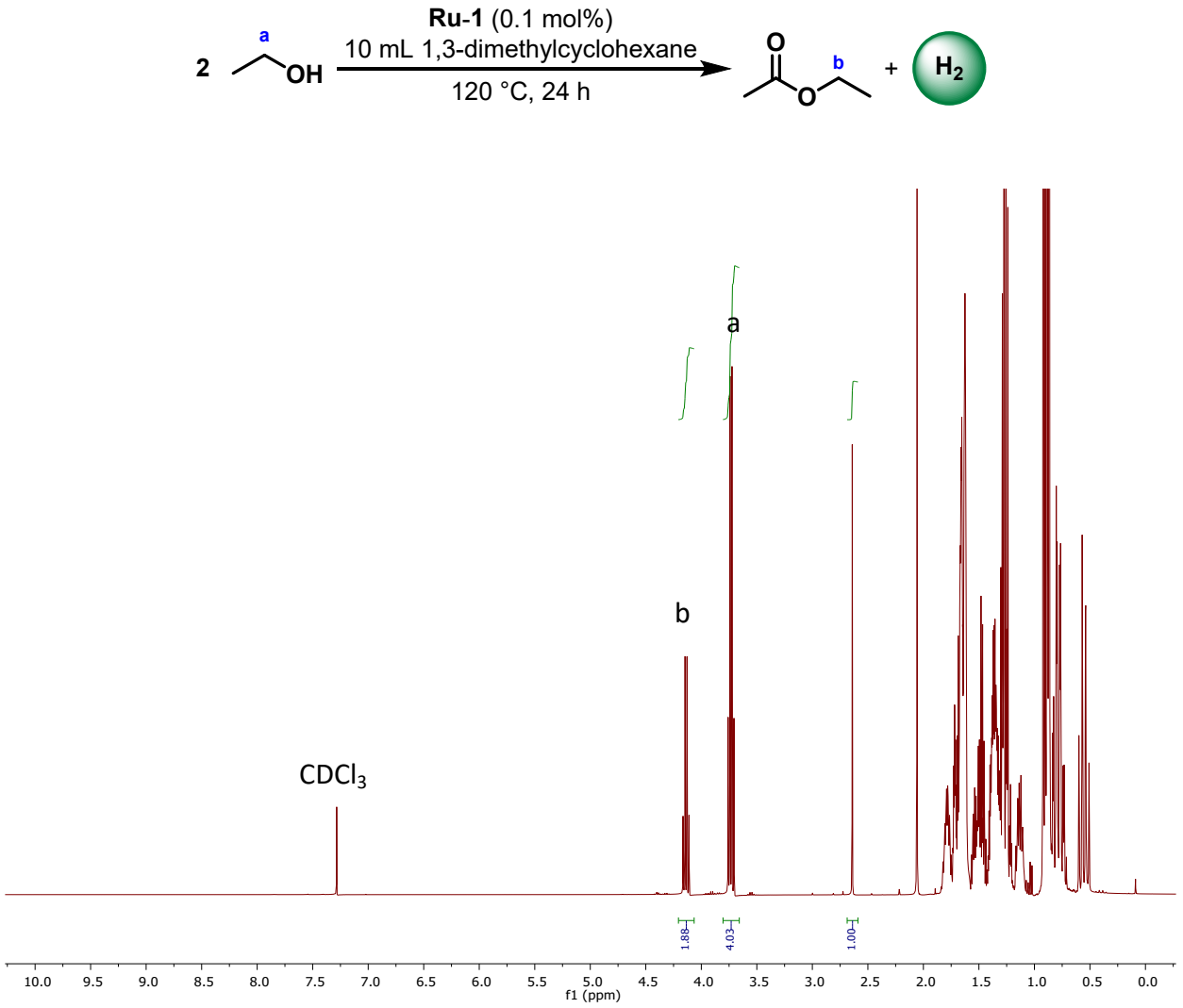


Figure S16. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL 1,3-dimethylcyclohexane, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

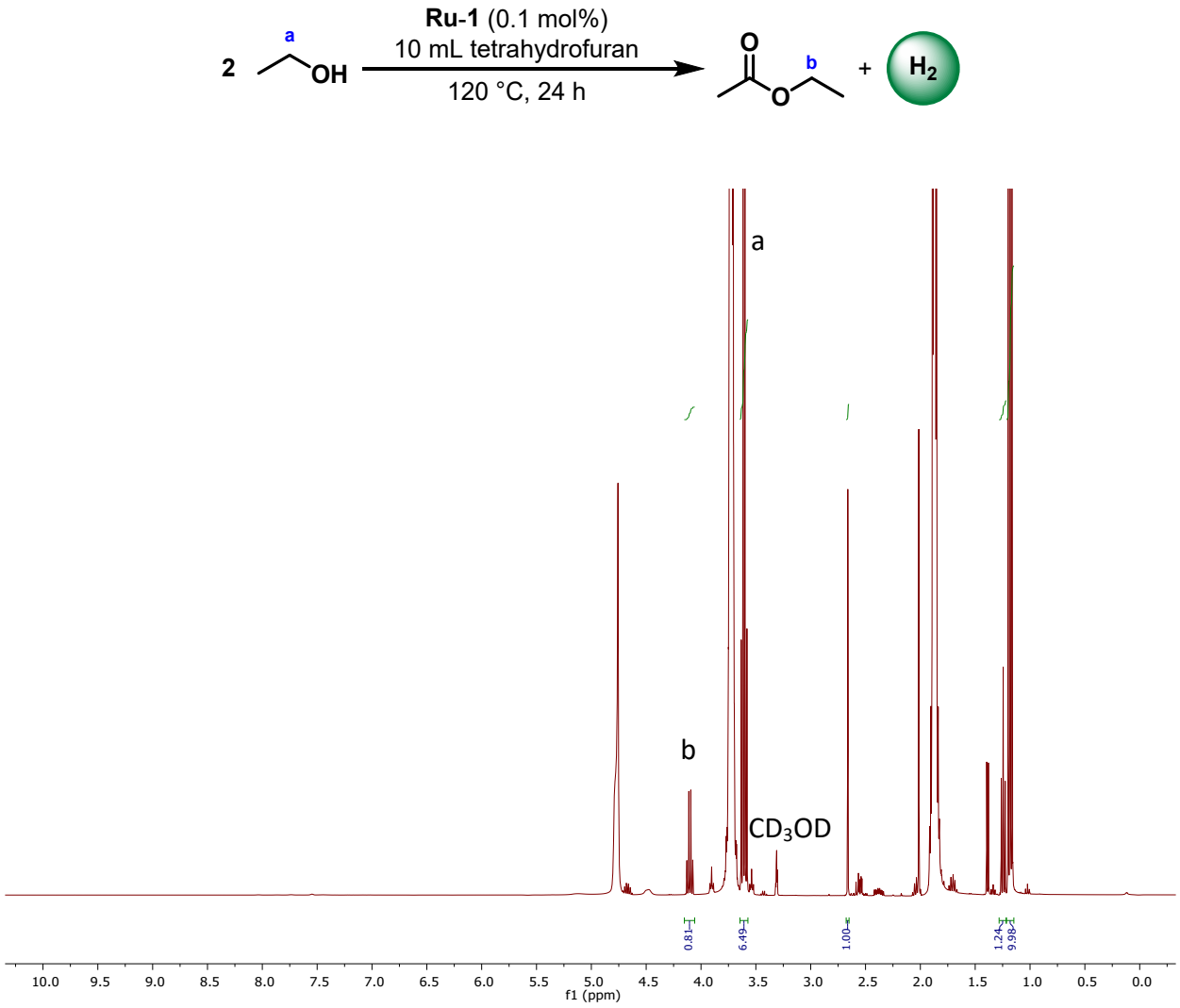


Figure S17. ^{1}H NMR of ADC of EtOH to AcOEt (CD_3OD, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL tetrahydrofuran, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

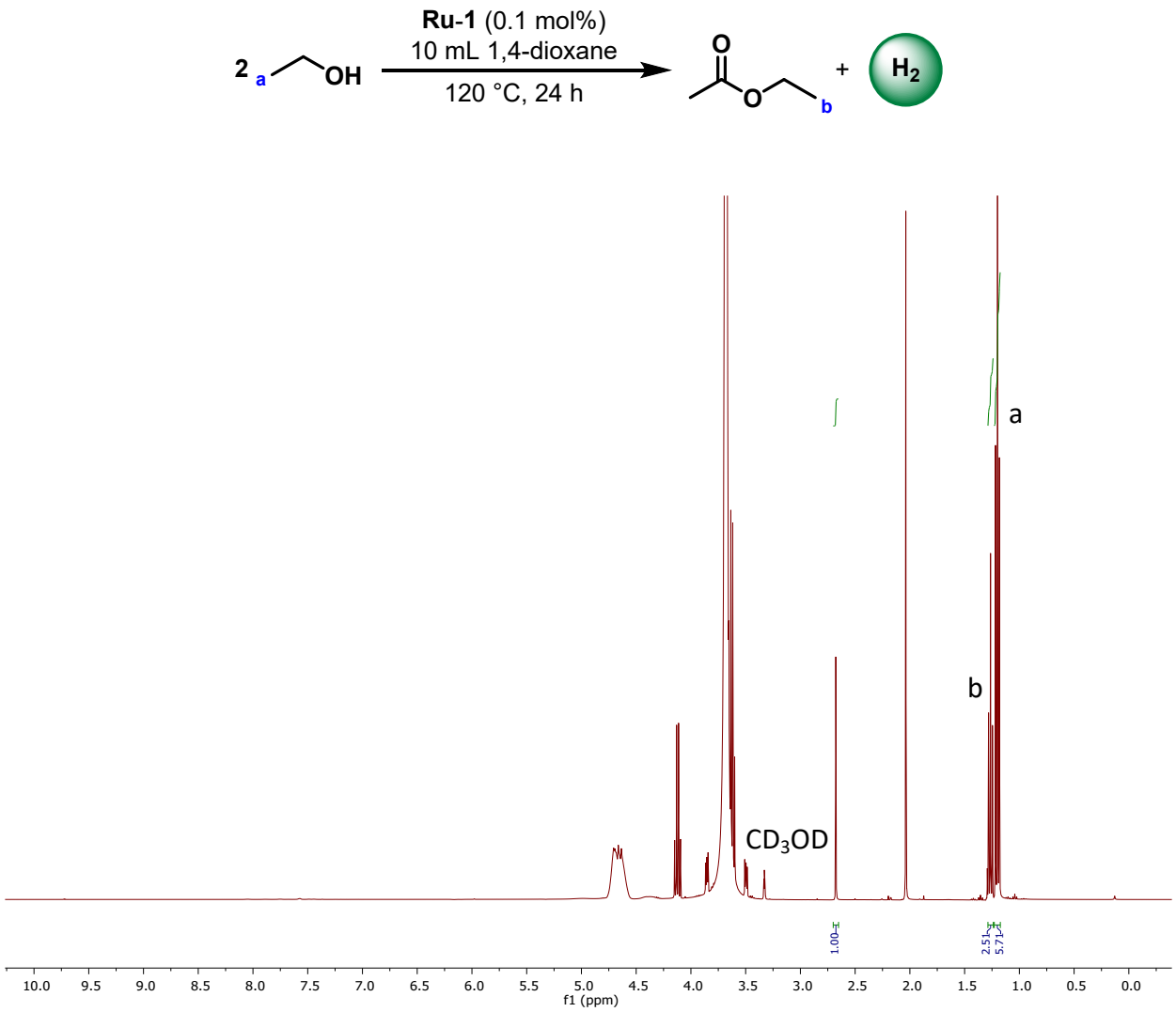


Figure S18. ^{1}H NMR of ADC of EtOH to AcOEt (CD_3OD, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL 1,4-dioxane, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

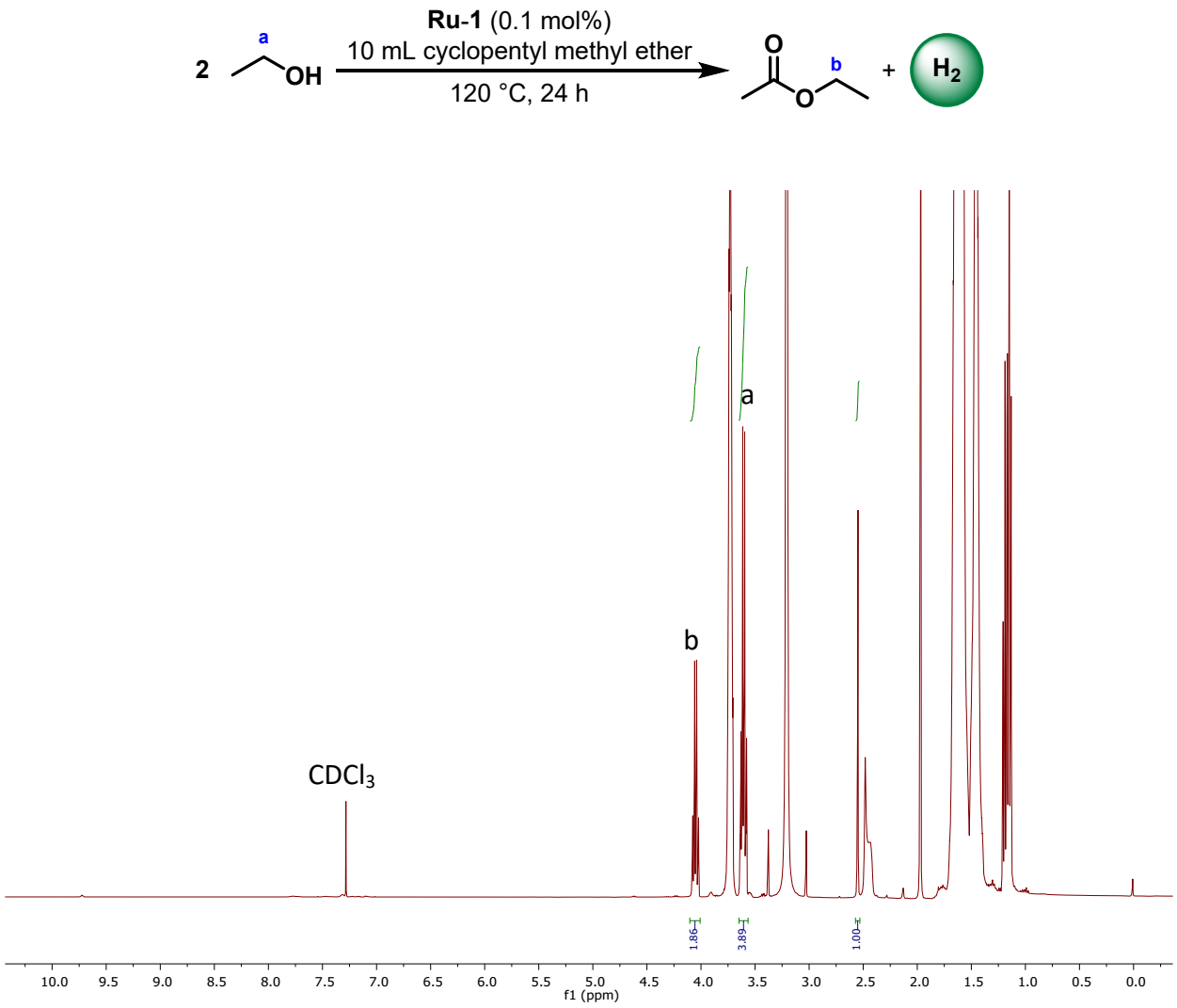


Figure S19. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL cyclopentyl methyl ether, **Ru**-**1** (0.1 mol%) at 120 °C for 24 h.

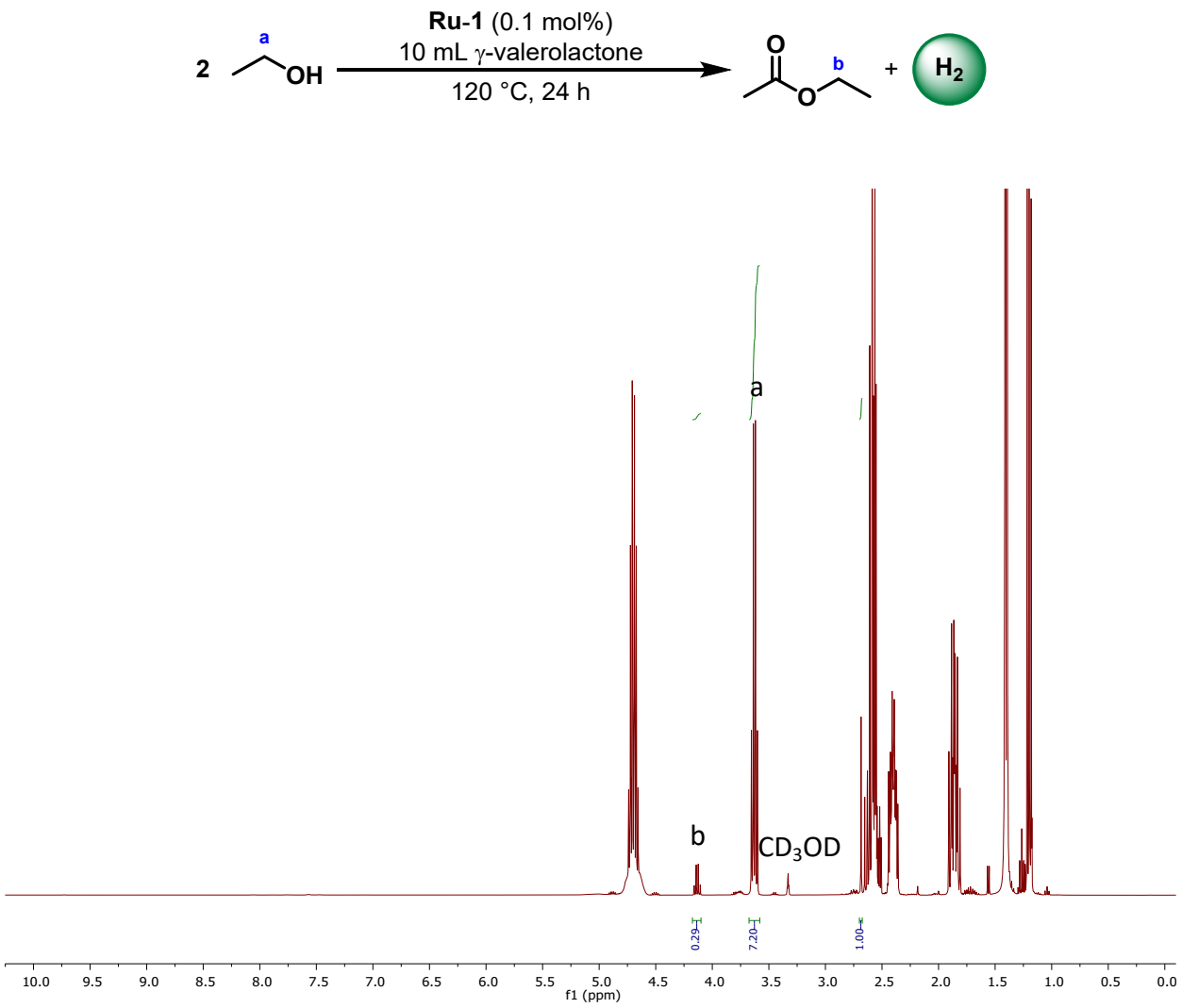


Figure S20. ^{1}H NMR of ADC of EtOH to AcOEt (CD_3OD, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL γ-valerolactone, **Ru-1** (0.1 mol%) at 120 °C for 24 h.

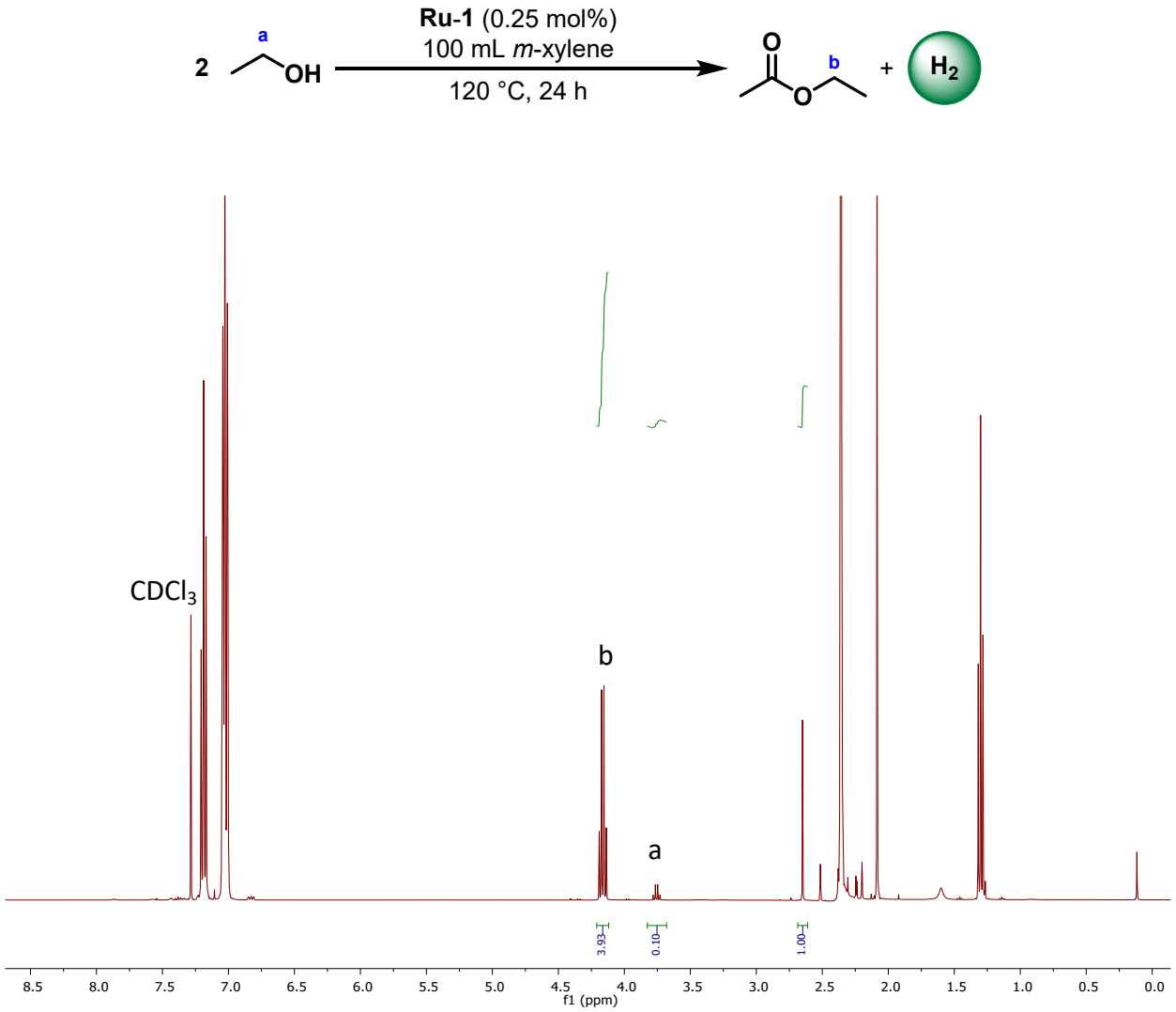


Figure S21. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 2 mL EtOH, 10 mL *m*-xylene, **Ru-1** (0.25 mol%) at 120 °C for 24 h.

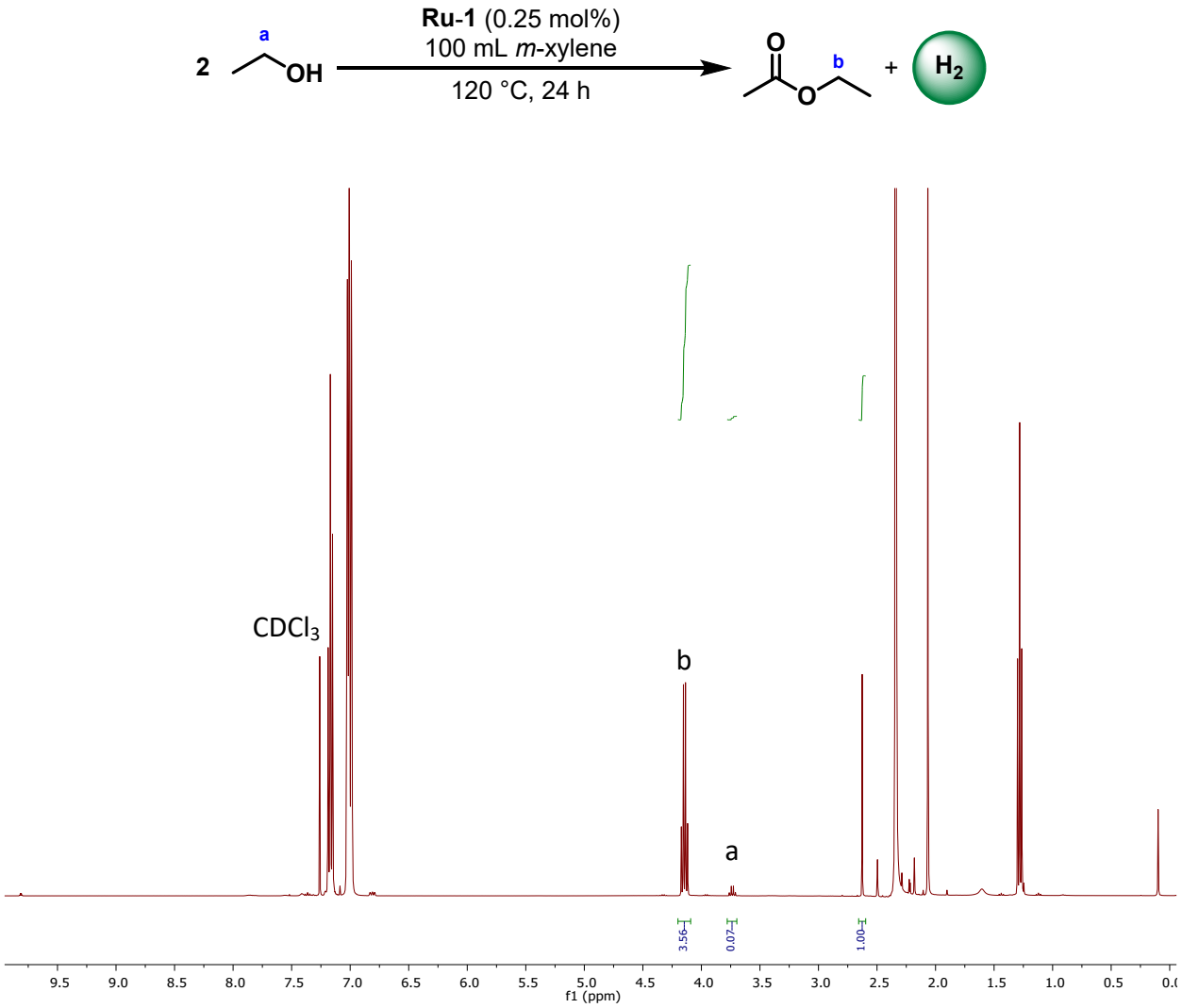


Figure S22. ^{1}H NMR of ADC of EtOH to AcOEt ($CDCl_3$, 25 °C, 400 MHz). Reaction conditions: 20 mL EtOH, 100 mL *m*-xylene, **Ru-1** (0.25 mol%) at 120 °C for 24 h.

4. References

1 The Engineering ToolBox, https://www.engineeringtoolbox.com/liquid-dielectric-constants-d_1263.html, (accessed 1st November)

2 Not Voodoo X.4, http://www.chem.rochester.edu/notvoodoo/pages/reagents.php?page=solvent_polarity, (accessed 1st November)