Electronic Supplementary Material (ESI) for Dalton Transactions

Tailoring Metal-Organic Framework Catalysts by Click Chemistry

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1. General remarks

Chemicals

Dimethylformamide, DMF, C_3H_7NO (Aldrich, 99.8%); dichloromethane, CH_2Cl_2 (Acros Organics, 99.99%); tetrahydrofuran, THF, C_4H_8O (Aldrich, 99%); methanol, MeOH, CH_4O (Aldrich, 98 %), 2-ethyl-1-butanol, $C_6H_{14}O$ (Aldrich, 98 %); 2-aminoterephthalic acid, NH_2-bdc, $C_8H_7NO_4$ (Alfa Aesar, 99%); 1,4-diazabicyclo[2.2.2] octane, DABCO, $C_6H_{12}N_2$ (Aldrich, 98%); zinc nitrate, $Zn(NO_3)_2 \cdot 4H_2O$ (Merck, 98.5%); *tert*-butyl nitrite, tBuONO, $C_4H_9NO_2$ (Aldrich, 90%); trimethylsilyl azide, $TMSN_3$, $C_3H_9N_3Si$ (Aldrich, 99.5%); tetrakis(acetonitrile)copper(I) hexafluorophosphate, $Cu^I(CH_3CN)_4PF_6$ (Aldrich, n.c); phenylacetylene, C_8H_6 (Aldrich, 98%); diethylpropargylamine, $C_7H_{13}N$ (Fluka, 90%); deuterium chloride, DCl (Aldrich, 99% D); deuterated dimethyl sulfoxide, DMSO-d_6, C_2D_6OS (Eurisotop, 99.8% D);

^{1}H NMR Analysis:

All NMR spectra were recorded with the same automated procedure for routine analysis on a Bruker Avance 250 spectrometer operating at 250 MHz for ^{1}H. Spectra are calibrated using the deuterium signals of DMSO. Approximately 5mg of **(1), (1b), (1c)** and **(1d)** were digested and dissolved in 0.45 mL of DMSO-d_6 and 0.05 mL of dilute DCl (35% DCl in D_2O).

XRD Analysis:

Powder X-ray diffraction patterns were recorded using a Bruker D5005 diffractometer (Bragg–Brentano geometry, graphite monochromator, Cu Kα radiation) and a Bruker D8 ADVANCE diffractometer (Bragg–Brentano geometry, Cu Kα radiation, 50 kV, 35 mA, λ= 0.154184 nm).

Gas Sorption Analysis:

N_2 isotherms were carried out at 77 K using a BELSORP-max (BEL Japan). All derivatives of **(1)** were degassed for one night at 100°C under vacuum.

Infrared Spectroscopy.

IR spectra were recorded on a Fourier Transform Vector 22 Bruker spectrometer in KBr pellets in the 400-4000 cm^{-1} region.

Starting MOF material: DMOF-NH_2 (1)

1 was synthesized as described previously [1].
^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 3.52 (s, 6.68H, DABCO), 7.13 (d, 1H, J = 8.3Hz), 7.47 (s, 1H), 7.79 (d, 1H, J = 8.3Hz).BET surface area: 1320 $m^2.g^{-1}$

2. Generic Post-Functionalization

In a typical synthesis, the freshly-dried DMOF-NH_2 **(1)** (80 mg, 0.27 mmol) is treated with tBuONO (0.22 mL, 1.84 mmol, 7eq) and $TMSN_3$ (0.2 mL, 1.51 mmol, 6eq) in THF for one night at room temperature to produce the corresponding intermediate azide compound, DMOF-N_3 **(1a)**. In the same vessel, **(1b)** is obtained by adding an excess of phenylacetylene (0.96 mL, 8.8 mmol, 32eq) in the presence of $Cu^I(CH_3CN)_4PF_6$ (48 mg, 0.13 mmol, 0.5 eq) in THF, whereas **(1c)** is obtained by adding an excess of diethylpropargylamine (0.33 mL, 2.3 mmol, 8.5eq) in the presence of $Cu^I(CH_3CN)_4PF_6$ (24 mg, 0.06 mmol, 0.25 eq). The mixtures were continuously stirred for 24 h. After decantation, the supernates were removed. The solids were washed three times by THF (x 8 mL) and three times by CH_2Cl_2 (x 8 mL) in order to remove unreactive substrates. The solids were then dried under vacuum at room temperature to yield the final compounds.

Table S1. Experimental conditions of the control of the degree of modification with phenylacetylene (b) and diethylpropargylamine (c)

Degree of modification	Amount of $Cu(ACN)_4PF_6$ used	Amount of alkyne **b** used
15± 5% **(1b-15)**	6 mg (0.016 mmol, 0,06 eq)	0.12 mL (1.1 mmol, 4 eq)
40± 5% **(1b-40)**	12 mg (0.032 mmol, 0.125 eq)	0.24 mL (2.2 mmol, 8 eq)
65 ± 5% **(1b-65)**	24 mg (0.065 mmol, 0.25 eq)	0.48 mL (4.4 mmol, 16 eq)
80± 5% **(1b-80)**	36mg (0.1 mmol, 0,375 eq)	0.72 mL (6.6 mmol, 24 eq)
(1b)	48 mg (0.13 mmol, 0.5 eq)	0.96 mL (8.8 mmol, 32 eq)

Degree of modification	Amount of $Cu(ACN)_4PF_6$ used	Amount of alkyne **c** used
40± 5% **(1c-40)**	6 mg (0.014 mmol, 0.05 eq)	0.08 mL (0.54 mmol, 2 eq)
85± 5% **(1c-85)**	17 mg (0.04 mmol, 0.15 eq)	0.25 mL (1.7 mmol, 6.3 eq)
(1c)	24 mg (0.06 mmol, 0.2 eq)	0.33 mL (2.3 mmol, 8.5 eq)

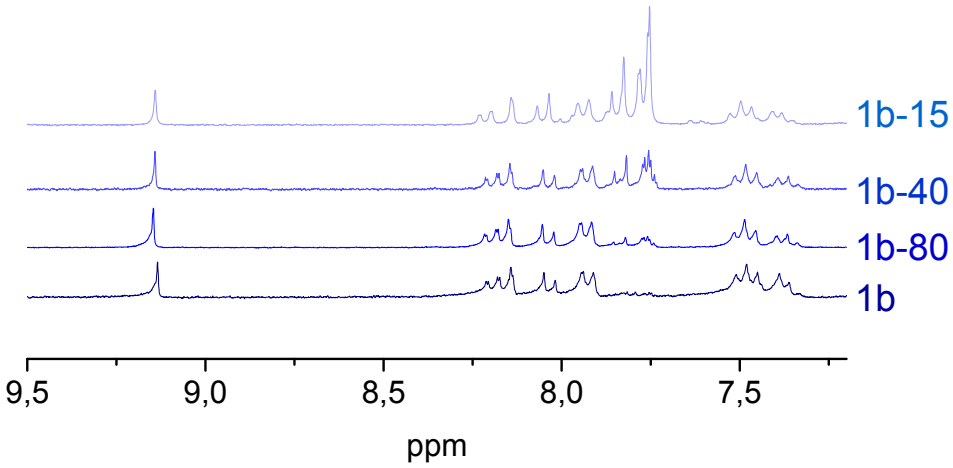


Figure S1. ^{1}H NMR of (1b-15), (1b-40), (1b-80) and (1b)

Experimental Conditions for Tandem Modification

DMOF-N_3 (80 mg, 0.25 mmol eq of -N_3) was placed into a vial (10 mL capacity) with 3.0 mL of THF, 18 mg (0.045 mmol, 0.2 eq) of $Cu^{I}(CH_3CN)_4PF_6$ and 0.36 mL (2.5 mmol, 10 eq) of phenylacetylene **(b)**. The sample was left to react for one night at room temperature. Next, 80 mg (0.2 mmol, 0.8 eq) of $Cu^{I}(CH_3CN)_4PF_6$ and 2 mL (14 mmol, 56 eq) of diethylpropargylamine **(c)** in THF were added and the mixture was stirred continuously for 24 h. After decantation, the supernate was removed. The solid was washed three times by THF (x 8 mL) and three times by CH_2Cl_2 (x 8 mL) in order to remove unreactive substrates. The solid was then dried under vacuum at room temperature to yield **(1d).**

3. Characterizations

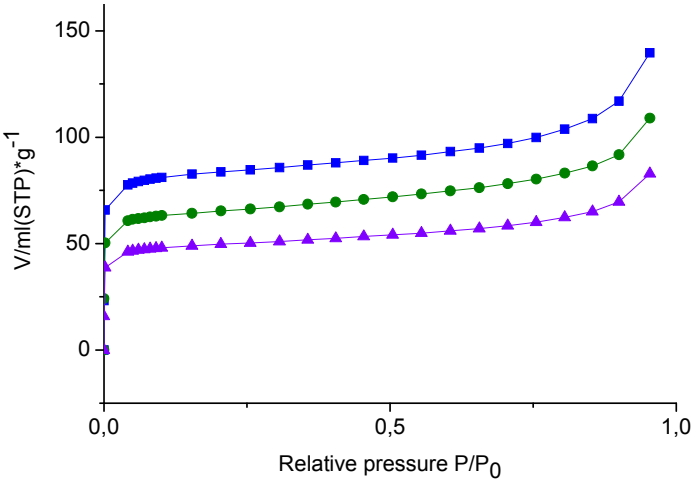


Figure S2. N_2 adsorption isotherms of 1b-40 (■), 1c- 40 (●) and 1d (▲)

Table S2. BET surface area of representative compounds

compound	BET surface area ($m^2.g^{-1}$)
1	1320
1b-40	520
1c-40	400
1d	310

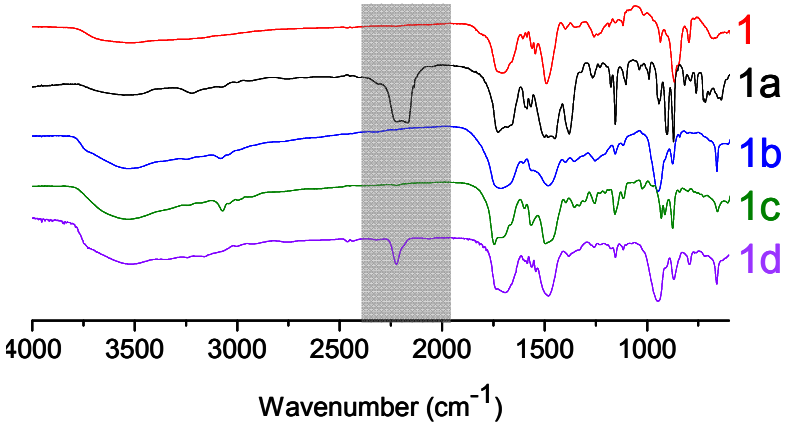


Figure S3. FT-IR of 1, 1a, 1b, 1c and 1d compounds

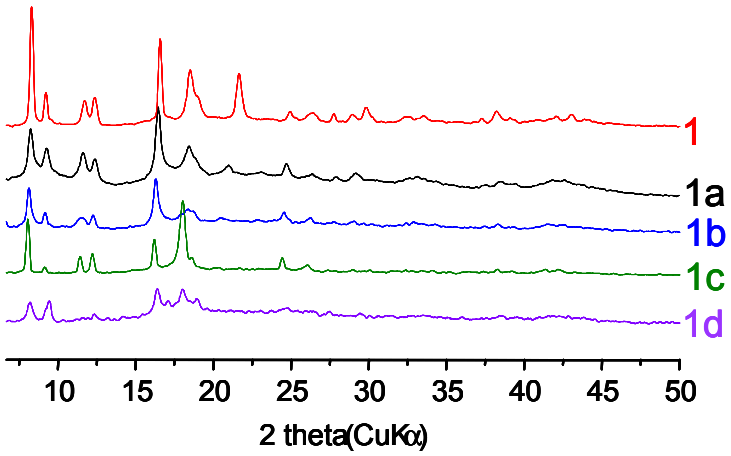


Figure S4. Powder XRD patterns of 1, 1a, 1b, 1c and 1d compounds

Elemental analyses

1b- 80

$Zn_2(C_{16}H_9O_4N_3)_{1,6}(C_8H_3O_4N_3)_{0,4}(C_6H_{12}N_2)(CH_2Cl_2)_{0,8}$

Calculated: Zn 14.79, C 48.34, H 3.33, N 12.67.

Found: Zn 14.29, C 46.46, H 3.24, N 12.58, Cu 0.64.

1b- 80

$Zn_2(C_{16}H_9O_4N_3)_{1,6}(C_8H_3O_4N_3)_{0,4}(C_6H_{12}N_2)(CH_2Cl_2)_2$

Calculated: Zn 13.84

Found: Zn 13.74, Cu 1.64

1b- 40

$Zn_2(C_{16}H_9N_3O_4)_{0,8}(C_8H_3N_3O_4)_{1,2}(C_6H_{12}N_2)(CH_2Cl_2)_{1,4}$

Calculated: Zn 15.25

Found: Zn 15.27, Cu 1.47

1c-85

$Zn_2(C_{15}H_{16}N_4O_4)_{1,7}(C_8H_3N_3O_4)_{0,3}(C_6H_{12}N_2)(CH_2Cl_2)_{0,6}$

Calculated: Zn 14.65

Found: Zn 14.68, Cu 1.05

1d

$Zn_2(C_{16}H_9N_3O_4)_{0,6}(C_8H_3N_3O_4)_{0,8}(C_{15}H_{16}N_4O_4)_{0,6}(C_6H_{12}N_2)(CH_2Cl_2)_3(H_2O)_2$

Calculated: Zn 12.2, C 38.09, H 3.7, N 11.2

Found: Zn 13.01, C 36.9, H 2.91, N 8.04

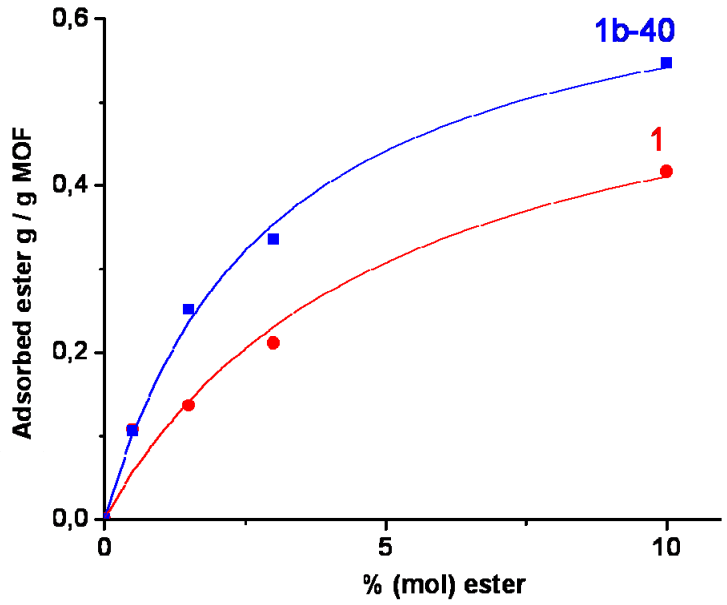


Figure S5. Liquid adsorption isotherms of ethyldecanoate in the ethyldecanoate/isooctane mixture for 1 (●) and 1b-40 (■)

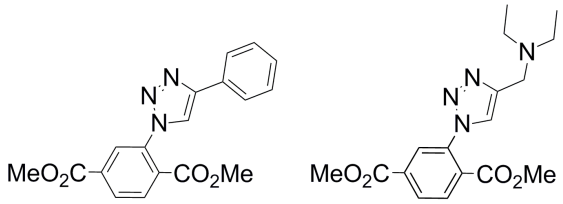
4. Catalytic run

All catalytic measurements for the transesterification reaction were carried out in a Teflon®-lined stainless steel digestion bomb (TopIndustrie) under stirring. Ethyldecanoate (2.5 mL) and methanol (10 mL) were made to react in the presence of 20 mg catalyst for 20 h at 130°C. After the reaction, the catalyst was recovered by filtration, and a sample of the filtrate was diluted in CH_2Cl_2 and analyzed by gas chromatography (HP 6890N equipped with a 30 m HP5 column). Carbon mass balances always exceeded 97%.

Table S3. Transesterification yield using functionalized MOFs and reference catalysts [a]

Entry	Catalyst	b (%)	c (%)	yield (%)
1	**none**	-	-	10
2	**1**	-	-	10
3	**1a**	-	-	10
4	**1b-40**	40	-	48
5	**1b-40** [b]	40	-	8
6	**1b-80**	80	-	80
7	**1c-40**	-	40	21
8	**1c-85**	-	85	28
9	**1d**	**30**	**30**	**84**
10	$Cu(ACN)_4PF_6$ [c]	-	-	32
11	$Cu(OAc)_2$ [c]	-	-	40
13	**linker b** [c]	100	-	30
14	**linker c** [c]	-	100	21

[a] Conditions: ethyldecanoate (2.5 mL) is allowed to react in methanol (10 mL) using 20 mg of DMOF catalyst (~0.03 mmol MOF, c.a 0.06 mmol $–NH_2$) at 130°C for 20h [b] 2-ethyl-1-butanol is used instead of methanol [c] Homologue catalysts used under homogenous conditions (scheme 2); 0.3 mmol of catalyst are used.



linker b linker c

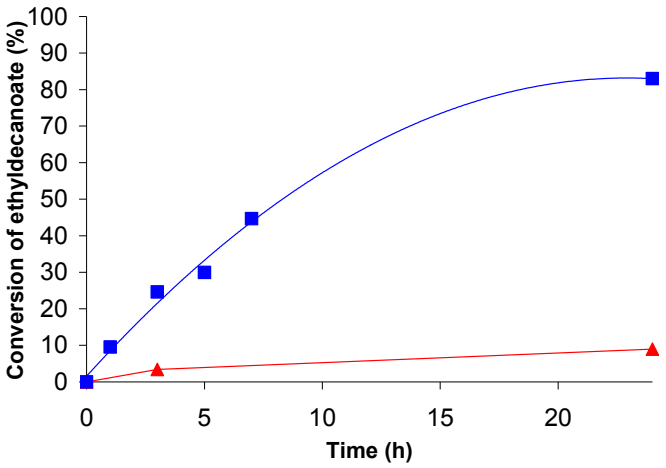
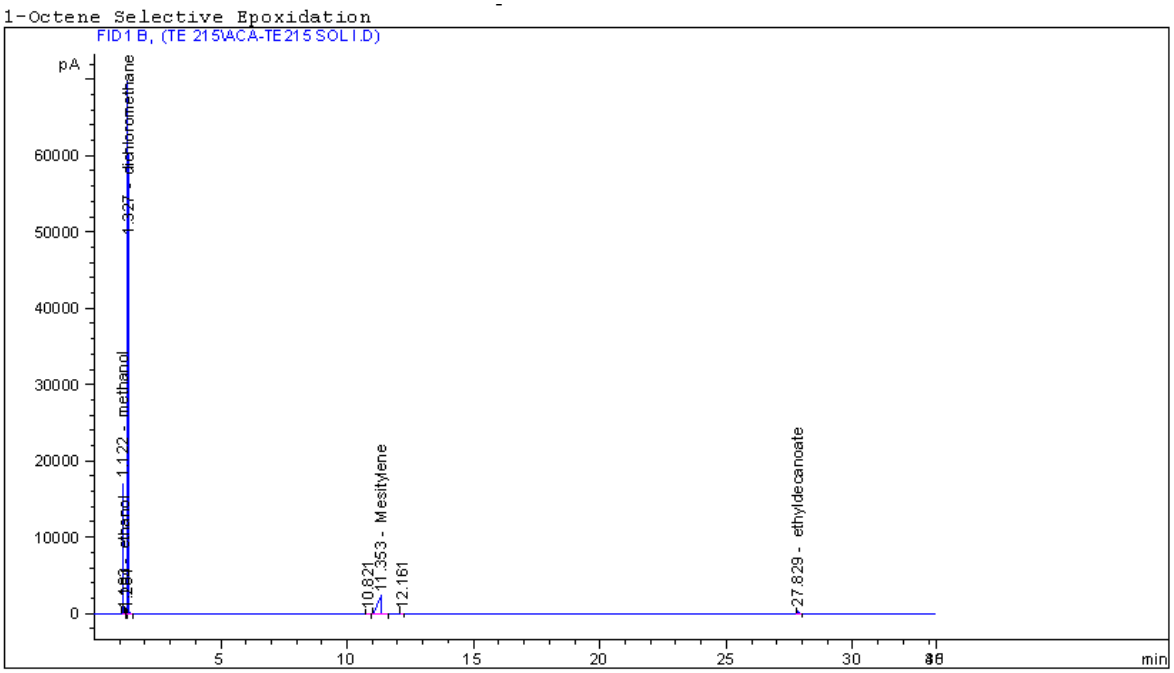


Figure S6. Kinetic studies of ethyldecanoate conversion for 1 (▲) and 1b-80 (■)



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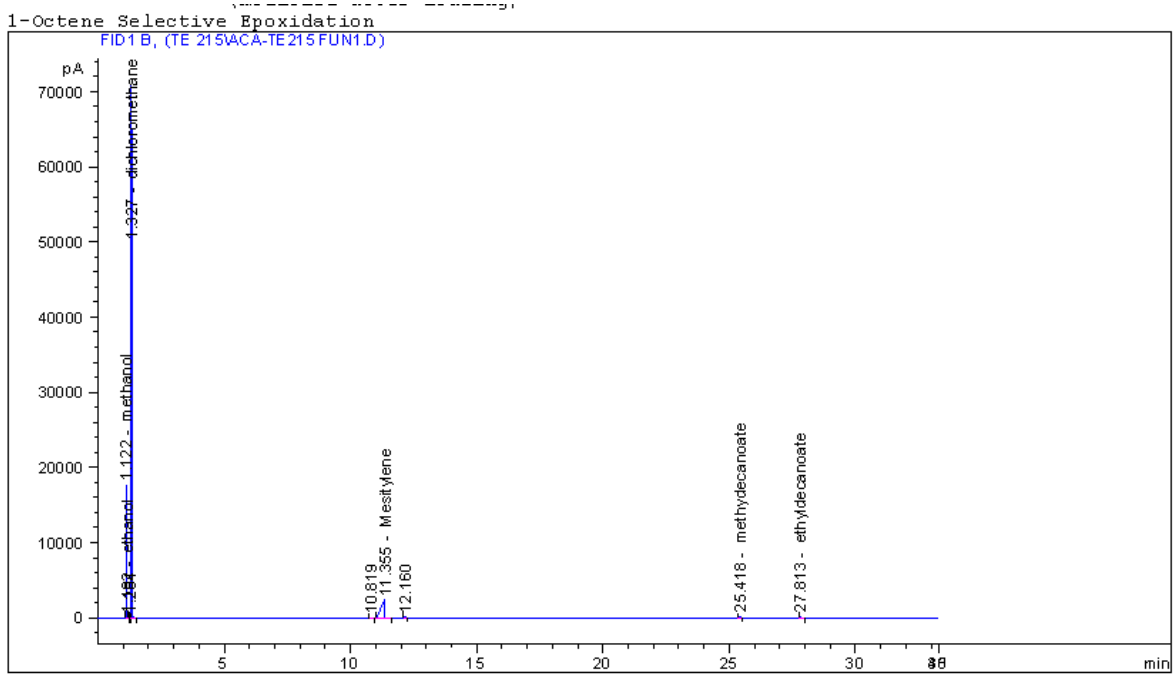
RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [g/mL]	Grp	Name
1.122	BV S	1.45796e4	5.87688e-6	8.56827e-2		methanol
1.183	BV X	13.17490	3.70227e-3	4.87770e-2		ethanol
1.327	VB S	8.14711e4	0.00000	0.00000		dichloromethane
11.353	BB	2.38319e4	1.43987e-6	3.43150e-2		Mesitylene
25.490		-	-	-		methydecanoate
27.829	BB	921.49493	2.00538e-6	1.84795e-3		ethyldecanoate

Totals : 1.70623e-1

Figure S7: GC trace of initial transesterification solution.



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Signal 1: FID1 B,

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [g/mL]	Grp	Name
1.122	BV S	1.48571e4	5.87862e-6	8.73392e-2		methanol
1.182	BB X	69.50404	3.75320e-3	2.60862e-1		ethanol
1.327	VB S	8.22345e4	0.00000	0.00000		dichloromethane
11.355	BB	2.43697e4	1.43996e-6	3.50915e-2		Mesitylene
25.418	BB	450.13925	2.01563e-6	9.07316e-4		methydecanoate
27.813	BB	429.00256	2.01662e-6	8.65136e-4		ethyldecanoate

Totals : 3.85065e-1

Figure S8: GC trace of product from 1b-40 catalyzed reaction.

5. Catalyst stability

In order to assess the stability of the DMOF catalyst, PXRD, NMR measurement and leaching tests were performed.

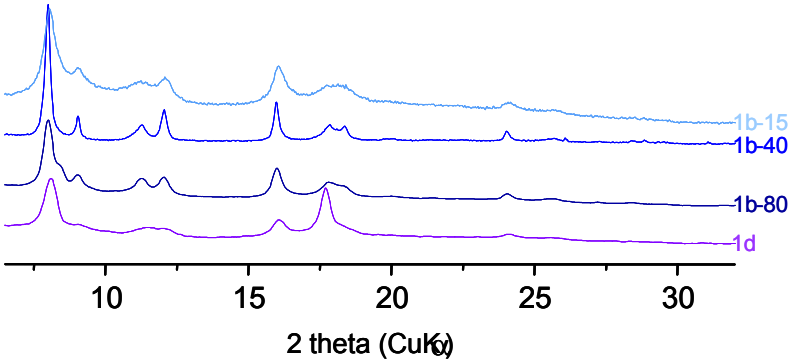


Figure S9. PXRD patterns of post-catalysis 1b-15, 1b-40, 1b-80 and 1d

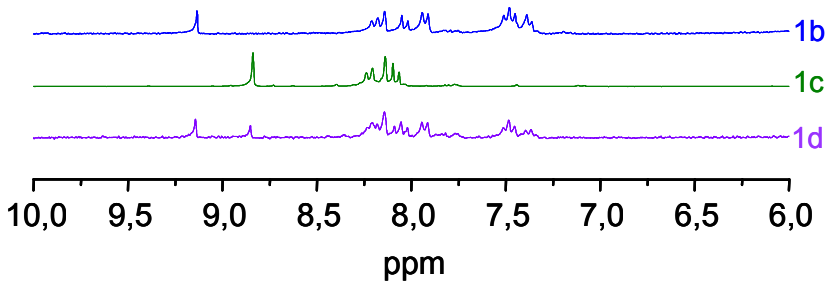


Figure S10: ^{1}HNMR of post-catalysis 1b, 1c and 1d

The unstable azide groups started to decompose up to 100°C. After catalysis, we observed therefore the disappearance of aromatic DMOF-N_3 signals.

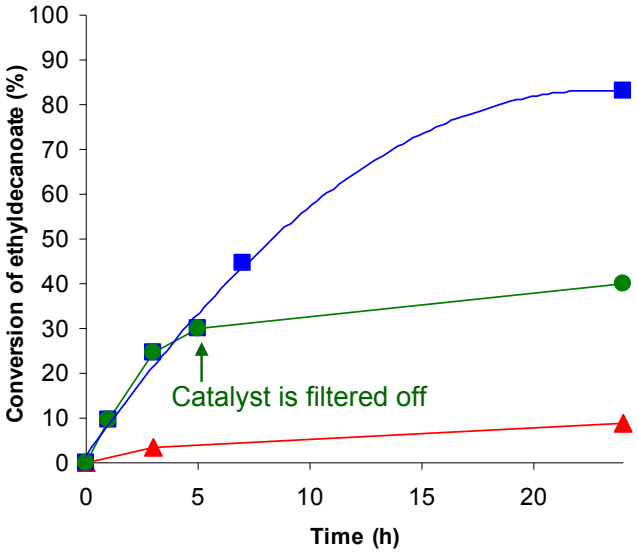


Figure S11. Kinetic studies of ethyldecanoate conversion for (1) (▲), (1b-80) (■) and for leaching test (●)

6. Synthesis of homogeneous analogues of the linkers

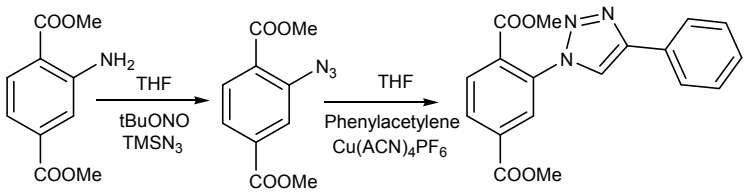
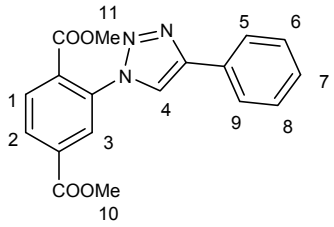


Figure S12: Synthesis of linker b

Dimethyl-2-aminoterephthalate (0.190 g, 0.91 mmol) was dissolved in THF (4 mL) in a 25 mL round-bottomed flask and cooled to 0°C in an ice bath. To this stirred mixture was added tBuONO (141 mg, 0.16 mL, 1.37 mmol), followed by a dropwise addition of $TMSN_3$ (126 mg, 0.14 mL, 1.10 mmol). The resulting solution was stirred at room temperature for one night. Phenylacetylene (140 mg, 0.150 mL, 1.37 mmol) and $Cu^{I}(CH_3CN)_4PF_6$ (48 mg, 0.26 mmol) were then added, and this mixture was stirred overnight at room temperature. The mixture was concentrated under vacuum and the organics were extracted by CH_2Cl_2 and washed with water, saturated $NaHCO_3$ (aq) and brine. After drying over Na_2SO_4, the solvent was taken off under reduced pressure. The yield obtained was 80%.



^{1}H NMR 250 MHz, (DMSO-d_6) δ: 9.22 (s, 1H, H_4), 8.24 (d, J= 7Hz, 2H, H_3, H_2), 8.07 (d, 1H, J= 8.5Hz, H_1), 7.95 (d, 2H, J= 8 Hz, H_5, H_9), 7.45 (m, 3H, H_6, H_7, H_8), 3.93 (s, 3H, H_{10}), 3.69 (s, 3H ,H_{11})

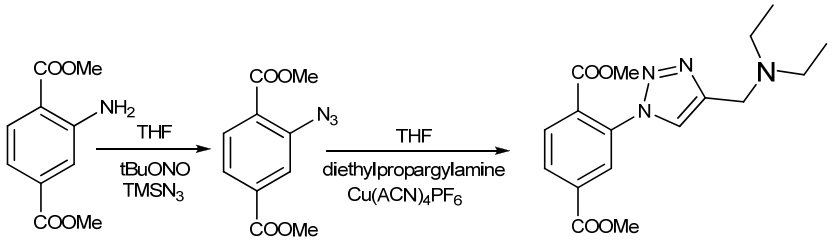


Figure S13: Synthesis of linker c

Dimethyl-2-aminoterephthalate (0.190 g, 0.91 mmol) was dissolved in THF (4 mL) in a 25 mL round-bottomed flask and cooled to 0°C in an ice bath. To this stirred mixture was added tBuONO (141 mg, 0.16 mL, 1.37 mmol), followed by a dropwise addition of $TMSN_3$ (126 mg, 0.14 mL, 1.10 mmol). The resulting solution was stirred at room temperature for one night. Diethylpropargylamine (0.190 mL, 1.37 mmol) and $Cu^{I}(CH_3CN)_4PF_6$ (48 mg, 0.26 mmol) were then added, and this mixture was stirred overnight at room temperature. The mixture was concentrated under vacuum and the organics were extracted by CH_2Cl_2 and washed with water, saturated $NaHCO_3$ (aq) and brine. After drying over Na_2SO_4, the solvent was taken off under reduced pressure. The yield obtained was 70%.

^{1}H NMR 250 MHz, (DMSO-d_6) δ: 8.62 (s, 1H), 8.19 (t, 2H, J= 8Hz), 8.04 (d, 1H, J= 8Hz), 3.92 (s, 3H), 3.64 (s, 3H), 3.64 (s, 2H), 3.48(s, 2H), 2.44 (q, 4H, J= 7Hz), 1.02(t, 6H, J= 7Hz).

7. References

[1] M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel, D. Farrusseng, *J. Am. Chem. Soc.* **2010**, *132*, 4518-4519.