Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Threefold Reactivity of a COF-Embedded Rhenium Catalyst: Reductive Etherification, Oxidative Esterification or Transfer Hydrogenation

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Contents **Page**

Materials, Methods and Instrumentation	2
Synthetic Procedures	4
Materials Characterization	8
Reactivity Studies	15

Materials, Methods, and Instrumentation

4,5-Dichloroanthracene-9(10*H*)-one was prepared according to literature procedure.[1]

Magnesium (Fisher Chemical), 1-bromododecane (Alfa Aesar), pyridine-3-boronic acid (Fisher Chemical), sodium carbonate (Alfa Aesar), tris(dibenzylacetone)dipalladium(0) (Acros), dicyclohexyl[2',4',6'-tris(propan-2-yl)[1,1'-biphenyl]-2-yl]-phosphane (Strem), bromopentacarbonylrhenium(I) (Strem), benzaldehyde (Sigma-Aldrich), potassium *tert*-butoxide (Chem-Impex International), pentacarbonylrhenium(I) bromide (Strem), sodium borohydride (Oakwood), silver tetrafluoroborate (Oakwood), d_8-isopropanol (Sigma), 1,3,5-triformylbenzene (Sigma-Aldrich), benzidine (Sigma-Aldrich), and acetic acid (Sigma-Aldrich) were purchased and used without further purification. Commercial reagents and solvents were obtained from diverse suppliers and used as received.

Reaction progress was monitored by analytical thin-layer chromatography (TLC) on ALUGRAM® Xtra SIL G/UV_{254} aluminium sheets from Macherey Nagel. TLC plates were rendered visible by exposure to ultraviolet light. All purifications were carried out under flash-chromatographic conditions on silica gel (60 Å, 40–63 µm, 230–400 mesh, Macherey Nagel).

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected on a Varian DirecDrive 400 MHz instrument at The University of Texas at Austin. Chemical shifts are given in ppm (δ) and calibrated using residual non-deuterated solvent peak as internal reference ($CDCl_3$: δ 7.26; d_8-THF: δ 3.58; d_8-^{i}PrOH: δ 3.89). Multiplicities are reported as follow: s (singlet), d (doublet), t (triplet), m (multiplet), or combinations thereof. Coupling constants *J* are given in Hz.

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO MRD diffractometer operating at 45 Kv and 40 mA.

Small and wide angle X-ray scattering (SAXS) measurements were performed in an Anton Paar SAXSess mc2 instrument operating at 40 kV and 50 mA. Data were collected with an image plate detector. Samples were placed in a holder with Mylar windows for the measurement. All data are background corrected.

Nitrogen (N_2) sorption measurements were performed using a Quantachrome Autosorb IQ2 automated analyzer. Prior to the measurements, samples were outgassed by heating to 120 °C (heating rate: 5 °C min^{-1}, dwelling time: 720 min). Multipoint Brunauer–Emmett–Teller (BET) method using ASIQwin™ software was used to estimate the surface areas of the obtained powders. Pore size distributions were assessed using quenched-solid density functional theory (QSDFT) adsorption branch model for slit/cylindrical pores (N_2 at 77 K on carbon).

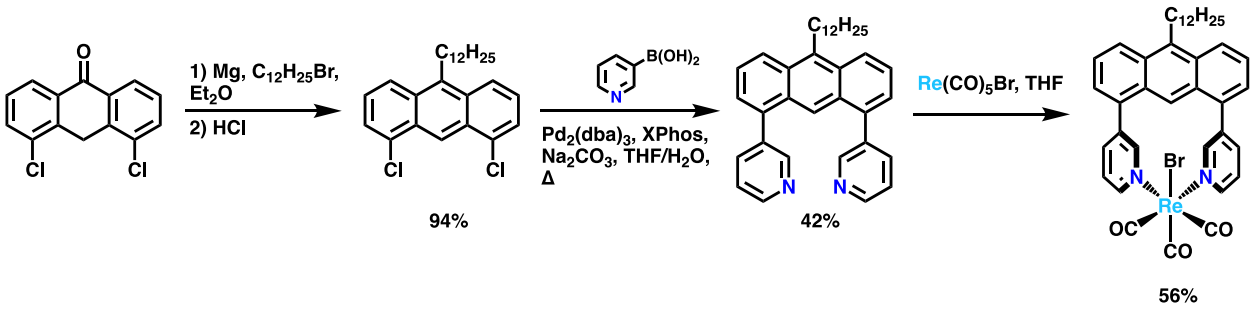
Infrared (IR) spectra were recorded on a Bruker VERTEX 80v FT–IR spectrometer in ATR mode. IR data are background corrected and reported in frequency of adsorption (cm^{-1}).

Raman spectra (Witec alpha300R Access mini confocal Raman microscope) were acquired at room temperature using a 785 nm laser line with a power of 5.0 mW, acquisition time of 3 s and 20 accumulations, and an objective of 20×. The spectra were processed using SpectraGriph 1.2.14 software (Software for optical spectroscopy 2016-20 developed by Dr.Friedrich Menges, Oberstdorf, Germany).

Thermogravimetric analysis (TGA) were performed on a TGA/DSC 1 STAR^e system (Mettler-Toledo). The samples were heated from 303.15 to 1173.15 K at 283.15 K min^{-1} under a continuous flow of argon of 20 mL min^{-1}.

High-angle annular dark field scanning transmission electron microscopy (HAADF–STEM), aberration-corrected high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy in STEM (STEM–EDX) were carried out at the INL on a double aberration-corrected Titan Themis 60–300 (FEI Co., Hillsboro, OR, USA), equipped with an X-FEG gun and superX EDX configuration with four detector system, operating at 200 kV. The TEM grids were prepared by placing the dry COF powder onto a 400 mesh copper grid with a lacey carbon support (TedPella) and then shaking off loose powder.

Synthetic Procedures



Scheme S1. Synthesis of [Re(^{C12}Anth-py$_2$) (CO)$_3$Br].

1,8-Dichloro-10-dodecylanthracene

In an oven-dried Schlenk flask under a nitrogen atmosphere, magnesium powder (1.66 g, 68.4 mmol) was activated by heating with iodine. The iodine was removed under vacuum. To the magnesium, 100 mL of dry Et_2O was added by syringe. The mixture was cooled to 0 °C on an ice bath, and 1-bromododecane (16.4 mL, 68.4 mmol) was slowly added by syringe. When addition was complete, the ice bath was removed, and the mixture was stirred at room temperature for approximately 1.5 hours or until the mixture appeared as a hazy grey suspension. This mixture was again cooled to 0 °C on an ice bath, and 4,5-dichloroanthracene-9(10*H*)-one (4.50 g, 17.1 mmol) was added as a solid in one portion. The mixture was allowed to gradually warm to room temperature and was allowed to react for 12 hours. The resulting yellow suspension was cooled to 0 °C on an ice bath, and 1 M HCl (50 mL) was slowly added, resulting in the evolution of hydrogen gas. After addition was complete, the mixture was allowed to stir for another 30 minutes. The mixture was then added to a separatory funnel, and the organic layer was isolated. The aqueous layer was extracted with 3 × 15 mL of Et_2O. The organic extracts were combined, washed with saturated sodium chloride solution, and dried over anhydrous Na_2SO_4. The Et_2O was removed under vacuum affording an oily yellow liquid. This crude product was purified by silica gel flash chromatography (hexane eluant) to yield the product as a yellow solid.

Yield: 6.69 g (94%)

^{1}H NMR (400 MHz, $CDCl_3$). δ = 9.27 (s 1H), 8.20 (d 2H), 7.63 (d 2H), 7.44 (dd 2H), 3.58 (t 2H), 1.78 (tt 2H), 1.55 (tt 2H), 1.45-1.15 (m 16 H), 0.88 (t 3H) ppm

^{13}C NMR (400 MHz, $CDCl_3$). δ = 136.26, 128.63, 128.02, 125.58, 125.41, 123.74, 120.15, 119.74, 31.91, 29.69, 29.65, 29.35, 22.68, 14.11 ppm

HRMS (CI) calculated for $[C_{26}H_{32}Cl_2]^+$: *m*/*z* = 414.1881, found: *m*/*z* = 414.1882.

3,3'-(10-Dodecylanthracene-1,8-diyl)dipyridine

A Schlenk flask was charged with Anth-$C_{12}H_{25}$-Cl_2 (3.00 g, 5.99 mmol), pyridine-3-boronic acid (1.47 g, 12.0 mmol), and sodium carbonate (1.27 g, 12.0 mmol). The flask was transferred to a drybox where tris(dibenzylacetone)dipalladium(0) (0.165 g, 0.180 mmol) and dicyclohexyl[2',4',6'-tris(propan-2-yl)[1,1'-biphenyl]-2-yl]-phosphane (XPhos) (0.080 g, 0.180 mmol) were added. This was dissolved in 200 mL of THF. The flask was removed from the drybox where 30 mL of degassed water was added. The mixture was refluxed overnight to afford a dark orange solution. This solution was cooled to room temperature and transferred to a separatory funnel. The solution was partitioned by adding 50 mL of brine. The organic layer was separated off, and the aqueous layer was extracted with 3 × 15 mL of EtOAc. The organic extracts were combined with the previously isolated organic layer and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford an orange oil. This crude product was purified by silica gel column flash chromatography (mobile phase was EtOAc, then 10:1 EtOAc/MeOH to elute the product). The product was isolated as a yellow-orange solid.

Yield: 1.27 g (42%)

^{1}H NMR (400 MHz, $CDCl_3$). δ = 8.67 (d 2H), 8.59 (dd 2H), 8.36 (d 2H), 8.17 (s 1H), 7.75 (dt 2H), 7.60 (dd 2H), 7.40 (d 2H), 7.34 (dd 2H), 3.70 (dd 2H), 1.89 (q 2H), 1.66 (q 2H), 1.46 (q 2H), 1.28 (m 14H), 0.89 (t 3H) ppm

^{13}C NMR (400 MHz, $CDCl_3$). δ = 150.42, 148.53, 137.40, 136.68, 136.45, 130.05, 129.66, 126.62, 125.37, 125.03, 122.96, 121.65, 32.03, 31.66, 30.52, 29.81, 29.75, 29.73, 29.46, 28.74, 22.80, 14.24 ppm.

HRMS (ESI+) calculated for $[C_{36}H_{40}N_2+H]^+$: *m*/*z* = 501.3264, found: *m*/*z* = 501.3265.

[Re(^{C12}Anth-py$_2$) (CO)$_3$Br]

In a dry box under nitrogen atmosphere, Anth-$C_{12}H_{25}$-py_2 (100 mg, 0.200 mmol) and $Re(CO)_5Br$ were dissolved in 2 mL of THF in a Schlenk flask. The flask was removed from the dry box and attached to a Schlenk line under nitrogen atmosphere. The solution was refluxed for 16 hours, resulting in the formation of a yellow precipitate. The mixture was cooled to room temperature, and the precipitate was isolated by vacuum filtration. The product was washed once with Et_2O to

afford a vibrant yellow solid. Diffraction-quality crystals were obtained by vapor diffusion of pentane into a THF solution of the product at –20 °C.

Yield: 94.5 mg (56%)

FTIR $\nu_{C\equiv O}$ = 2030, 1926, 1902 cm^{-1}.

HRMS (FIA+) calculated for $[C_{39}H_{40}BrN_2O_3Re+Na]^+$: *m*/*z* = 873.1656, found: *m*/*z* = 873.1641.

(μ-H)[Re(^{C12}Anth-py$_2$) (CO)$_3$]$_2$

Procedure adapted from literature preparation.[2]

In a 10 mL glass pressure vessel, [Re(^{C12}Anth-py$_2$) (CO)$_3$Br] (25.0 mg, 29.4 μmol) was dissolved in 3 mL of THF. $AgBF_4$ (5.7 mg, 29.4 μmol) was added and the solution was heated to 60 °C for 1 h. The mixture was filtered to remove the AgBr precipitate. The yellow supernatant was transferred to a scintillation vial, and 0.5 mL of water was added. $NaBH_4$ (5.6 mg, 147 μmol) was added to this solution and the solution was allowed to stir at room temperature for 12 h. The reaction mixture was dried of Na_2SO_4 and filtered through Celite. The filtrate was collected and the solvent was removed under vacuum at room temperature to afford a yellow residue. Formation of Re–H products was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, d_8-THF) δ = –5.34, –17.21 ppm.

TFB-BD

To a 10 mL ampoule (Wheaton, pre-scored, borosilicate, 19 × 107 mm) were placed 1,3,5-triformylbenzene (TFB) (29 mg, 0.18 mmol), benzidine (BD) (50 mg, 0.27 mmol), mesitylene (1.5 mL), and 1,4-dioxane (1.5 mL), and the mixture was sonicated for 10 min. Then, aq. acetic acid 6 M was added (300 µL), and the mixture was sonicated further for 10 min to obtain a homogenous dispersion. The mixture was frozen in a bath of liquid N_2 and the ampoule was sealed under vacuum. The mixture was heated in the oven at 120 ºC for 3 d. The precipitate was collected by filtration without vacuum, washed with 1,4-dioxane until the washing solution showed no color, then with tetrahydrofuran and hexane, and dried under nitrogen at 90 ºC, to afford TFB-BD as yellow solid.

Yield: 20 mg (95%)

The powder X-ray diffraction (XRD) pattern exhibited reflections at 2θ = 3.5, 6.1, 7.1 and 16.2° (Fig. 1b), consistent with the literature report.[3] COF formation was further supported by the Fourier-transform infrared (FTIR) spectrum that exhibited a feature at 1623 cm^{-1} corresponding to the C=N stretch, similar to the reported data[3] (Fig. 1c, main text). The accessible surface area of TFB-BD was examined by N_2 sorption measurement at 77 K, evidencing a type I isotherm (Fig. S1) that is typical of microporous materials. The BET surface area of TFB-BD was 847 $m^2\ g^{-1}$, and the pore size distribution calculated using the QSDFT model for slit/cylindrical pores (adsorption branch) showed a maximum at 1.5 nm (Fig. S1 and S2) also in agreement with literature.[4]

[Re]@TFB-BD

[Re(^{C12}Anth-py_2) $(CO)_3$Br] (7.2 mg, 0.008 mmol) was dissolved in dichloromethane (1.5 mL) and added dropwise to 155 mg of TFB-BD, so that the COF remains wet, but not submerged in the solvent. Then, the solid was dried under nitrogen at 90 ºC for 48 h to evaporate the solvent.

Materials Characterization

N_2 Physisorption

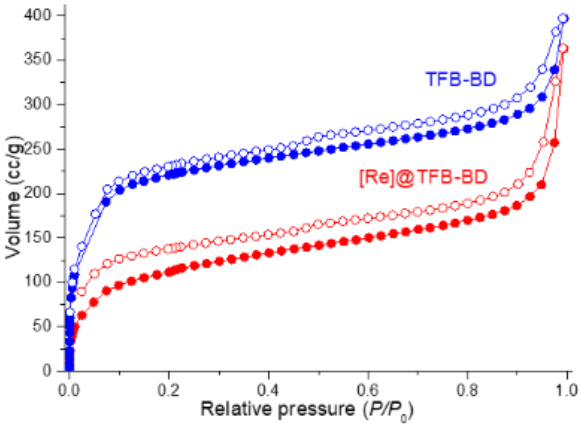


Figure S1. N_2 adsorption (*filled*) and desorption (*hollow*) isotherm profiles of TFB-BD (*blue*) and [Re]@TFB-BD (*red*) measured at 77 K.

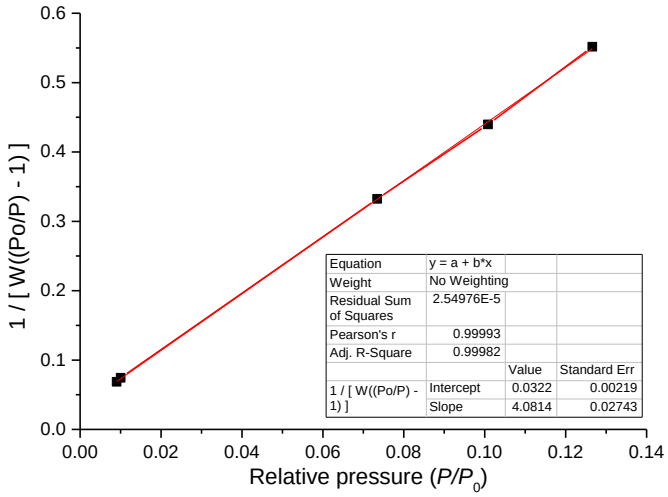


Figure S2. Multi-point BET plot and linear fit for TFB-BD.

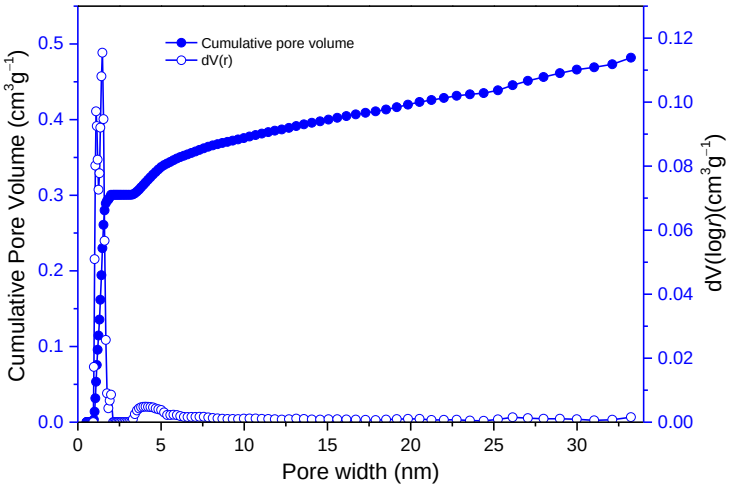


Figure S3. Pore size distribution (*hollow*) and cumulative pore volume (*filled*) profiles for TFB-BD.

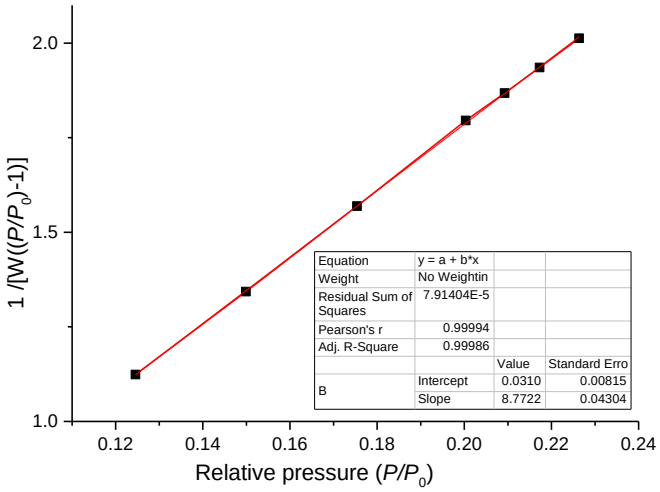


Figure S4. Multi-point BET plot and linear fit for [Re]@TFB-BD.

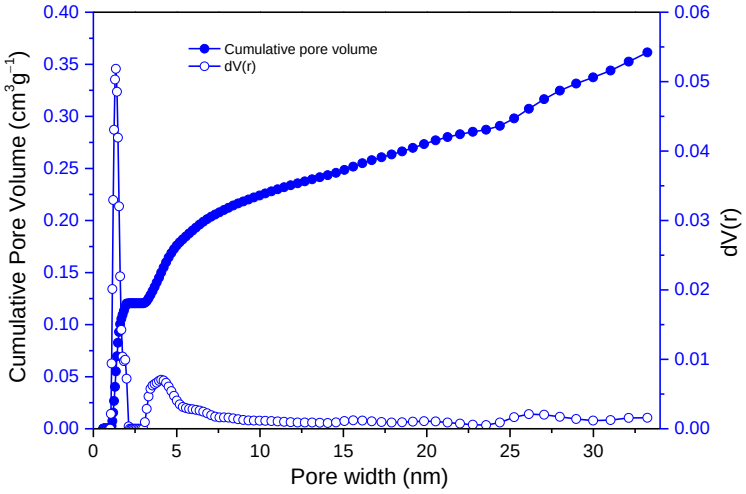


Figure S5. Pore size distribution (*hollow*) and cumulative pore volume (*filled*) profiles for [Re]@TFB-BD.

Raman spectroscopy

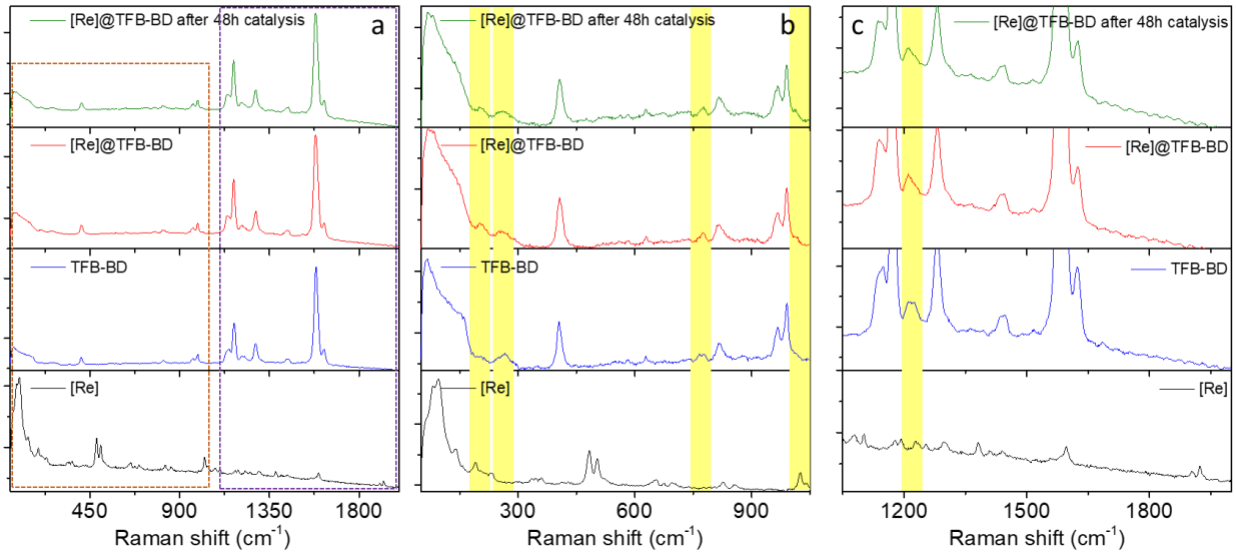


Figure S6. (a) Raman spectra of [Re(^{C12}Anth-py$_2$) (CO)$_3$Br] (*black*), pristine TFB-BD (*blue*), [Re]@TFB-BD before (*red*) and after 48 h catalysis (*green*) upon excitation with a 785 nm laser line. The orange and purple dashed rectangles indicate the spectral windows of interest; (b) Raman spectra from 50 to 1050 cm^{-1}, and (c) 1050 to 2000 cm^{-1}, in which can be clearly identified the differences after [Re] catalyst impregnation (highlighted in yellow).

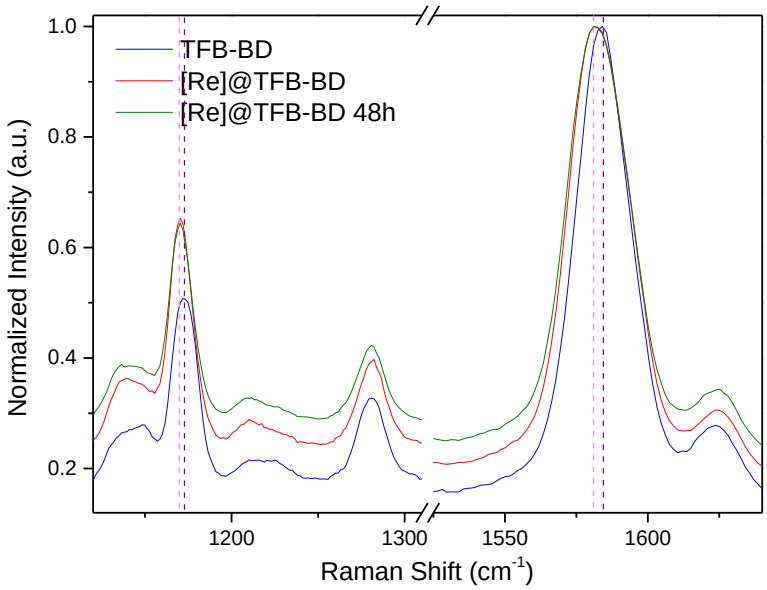


Figure S7. Raman spectral window from 1100 to 1650 cm^{-1}, which shows that features at 1172 and 1584 cm^{-1} of TFB-BD COF (*blue*) present slightly blue-shifted and broadened in [Re]@TFB-BD before (*red*) and after (*green*) the catalytic reaction. Raman spectra were normalized at maximum intensity of 1554 cm^{-1} peak for better comparison.

TGA

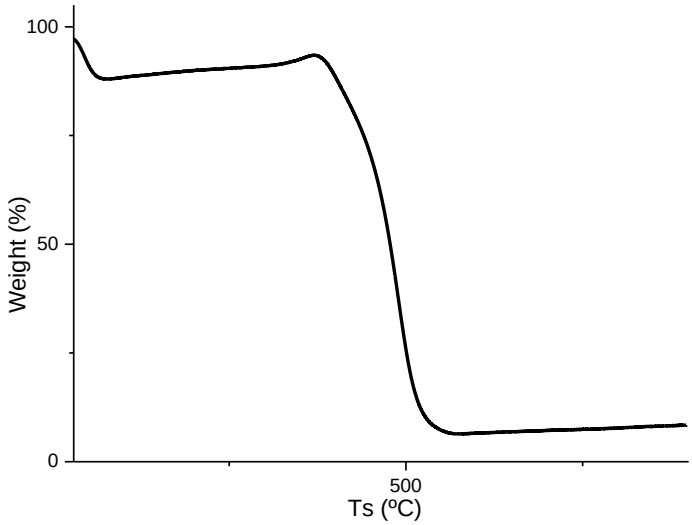


Figure S8. TGA of TFB-BD.

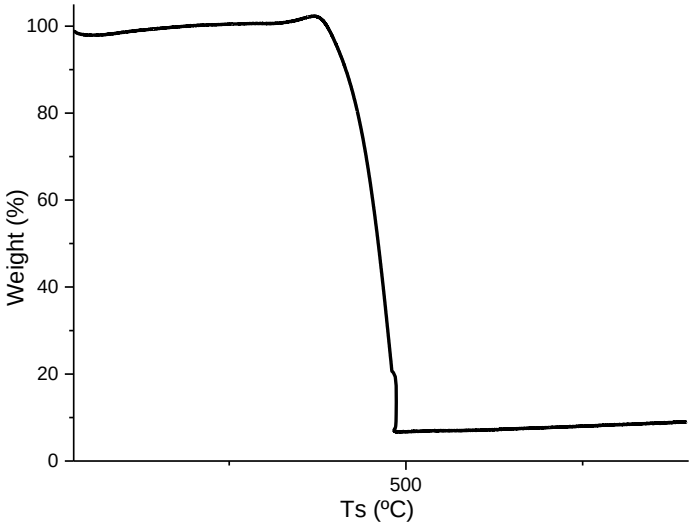


Figure S9. TGA of [Re]@TFB-BD.

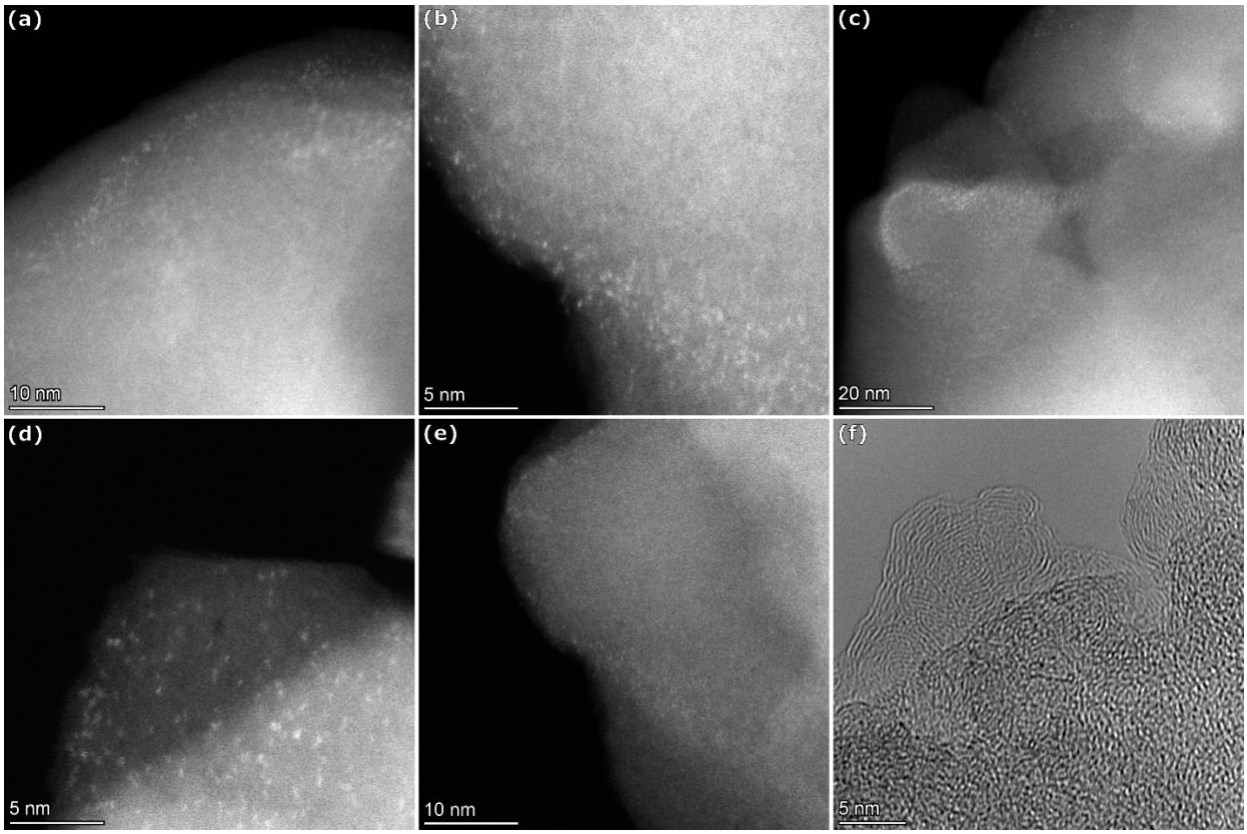


Figure S10. A–E) HAADF–STEM images of the single atoms on [Re]@TFB-BD, shown as bright spots on the lower atomic weight carbon background. The single atoms are easier to resolve on the edges of the COF due to its thinness. F) TEM image of [Re]@TFB-BD.

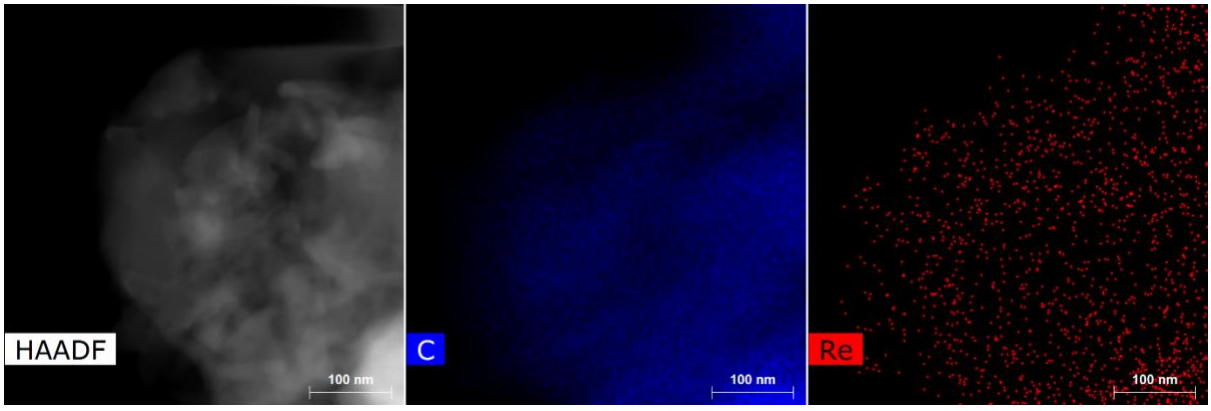


Figure S11. STEM–EDX maps, with the HAADF–STEM image and the maps of the carbon Kα edge and Re Lα edge.

Reactivity Studies

Homogenous catalysis reaction:

A 10 mL glass pressure vessel was charged with 1.75 mL ^{i}PrOH, 1.0 μL benzaldehyde (9.8 μmol, 1 eq), 250 μL of 0.2 mM KO^{t}Bu in ^{i}PrOH (0.50 μmol, 0.05 eq), and 0.5 mg [Re(^{C12}Anth-py$_2$)(CO)$_3$Br] (0.49 μmol, 0.05 eq). The pressure vessel was sealed, and the mixture was heated to 70 °C. The mixture was allowed to react with stirring for 18 h. The mixture was cooled to room temperature and any precipitate that had formed was removed by filtration through Celite. The supernatant was isolated, and the volume was reduced to approximately 100 μL under vacuum at room temperature. This colorless residue was dissolved in 1 mL of hexanes and submitted for GCMS analysis.

Heterogeneous reactions:

A 10 mL glass pressure vessel was charged with 1.75 mL ^{i}PrOH, 1.0 μL benzaldehyde (9.8 μmol, 1 equiv), 250 μL of 0.2 mM KO^{t}Bu in ^{i}PrOH (0.50 μmol, 0.05 eq), and 7.0 mg of [Re]@TFB-BD. The pressure vessel was sealed, and the mixture was heated to 70 °C. The mixture was allowed to react with stirring for 48 h. The mixture was cooled to room temperature and any precipitate that had formed was removed by filtration through Celite. The supernatant was isolated, and the volume was reduced to approximately 100 μL under vacuum at room temperature. This colorless residue was dissolved in 1 mL of hexanes and submitted for GCMS analysis.

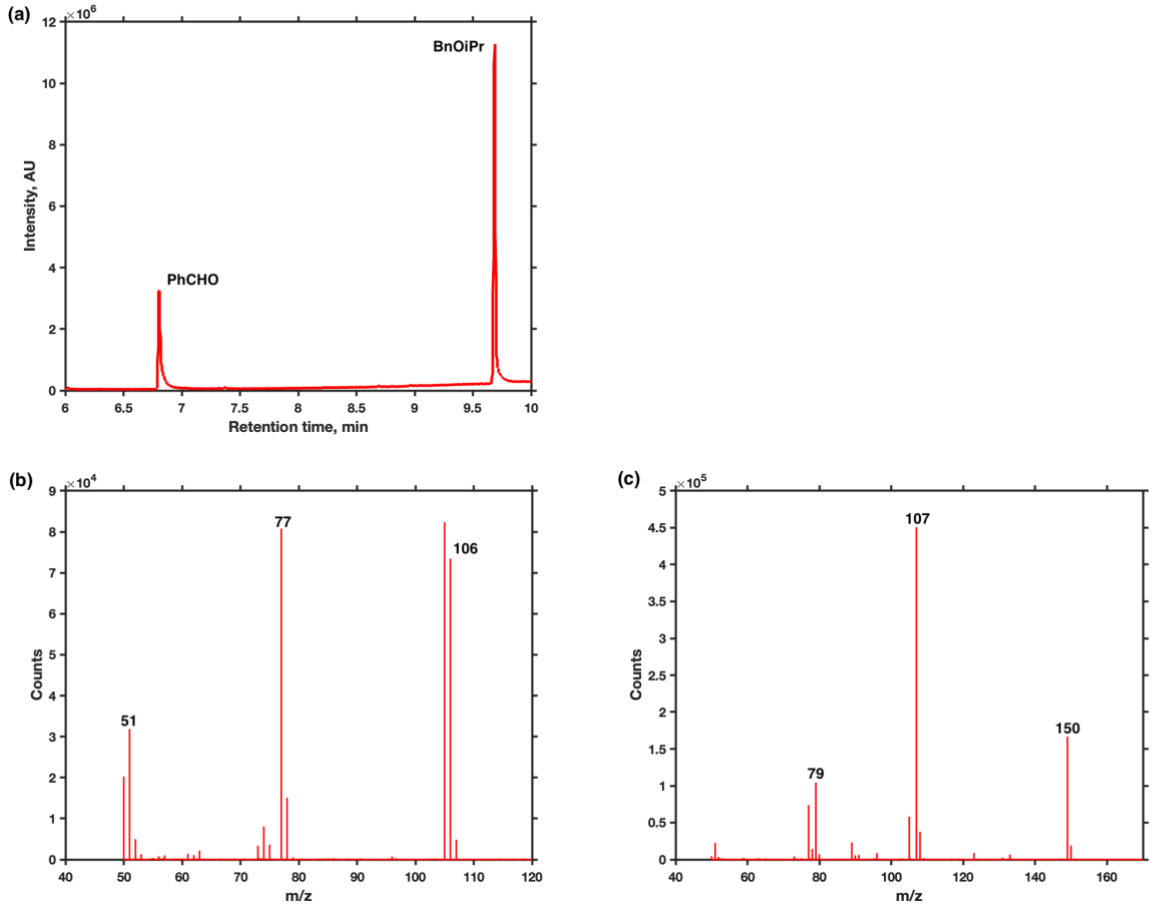


Figure S12. a) Total ion chromatograph of the reaction products of the reductive etherification of benzaldehyde ([Re]@TFB-BD heterogeneous phase reaction). PhCHO retention time = 6.80 min, PhCOO^{i}Pr retention time = 9.69 min. b) Extracted mass spectrum for benzaldehyde product eluted at 6.80 min. c) Extracted mass spectrum for Bn^{i}OPr product eluted at 9.69 min.

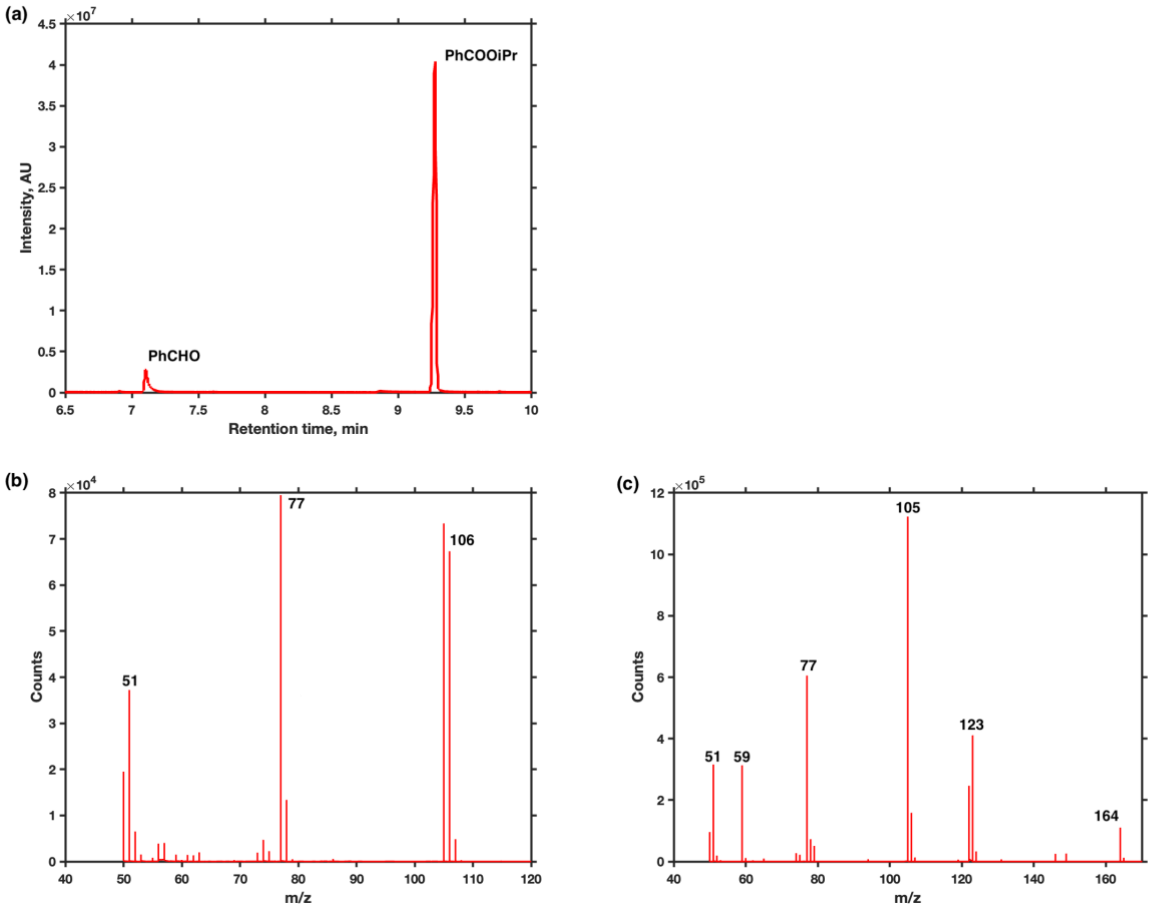


Figure S13. a) Total ion chromatograph of the reaction products of the oxidative esterification of benzaldehyde (homogenous phase reaction). PhCHO retention time = 7.10 min, PhCOO^{i}Pr retention time = 9.28 min. b) Extracted mass spectrum for PhCHO product eluted at 7.10 min. c) Extracted mass spectrum for PhCOO^{i}Pr product eluted at 9.28 min.

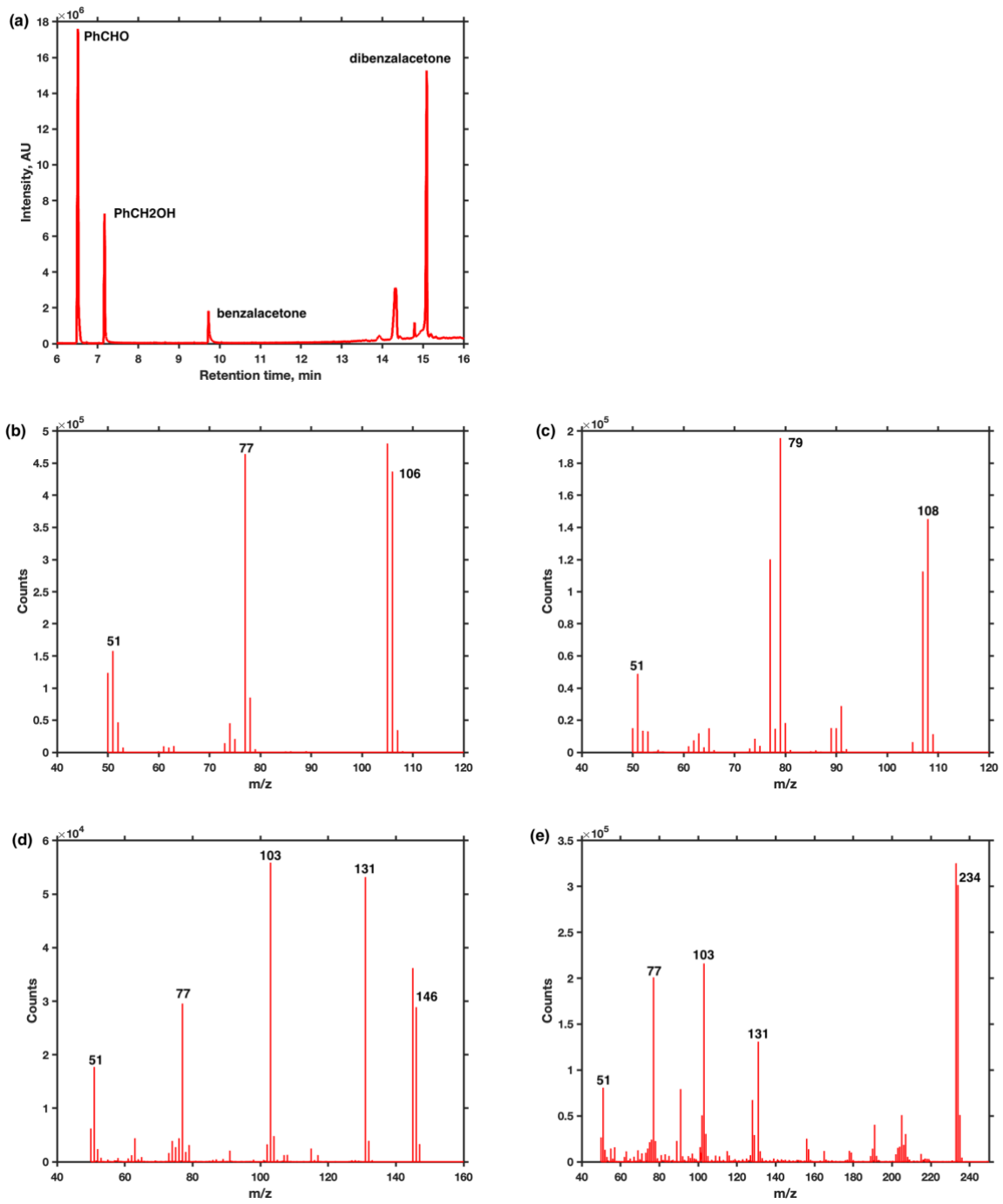


Figure S14. a) Total ion chromatograph of the reaction products of the transfer hydrogenation/aldol condensation of benzaldehyde (homogenous Re in the presence of TFB-BD). Benzaldehyde retention time = 6.71 min, $PhCH_2OH$ retention time = 7.12 min, benzalacetone retention time = 9.87 min, dibenzalacetone retention time = 15.07 min. b) Extracted mass spectrum for benzaldehyde product eluted at 6.71 min. c) Extracted mass spectrum for $PhCH_2OH$ product eluted at 7.12 min. d) Extracted mass spectrum for benzalacetone product eluted at 9.87 min. e) Extracted mass spectrum for dibenzalacetone product eluted at 15.07 min.

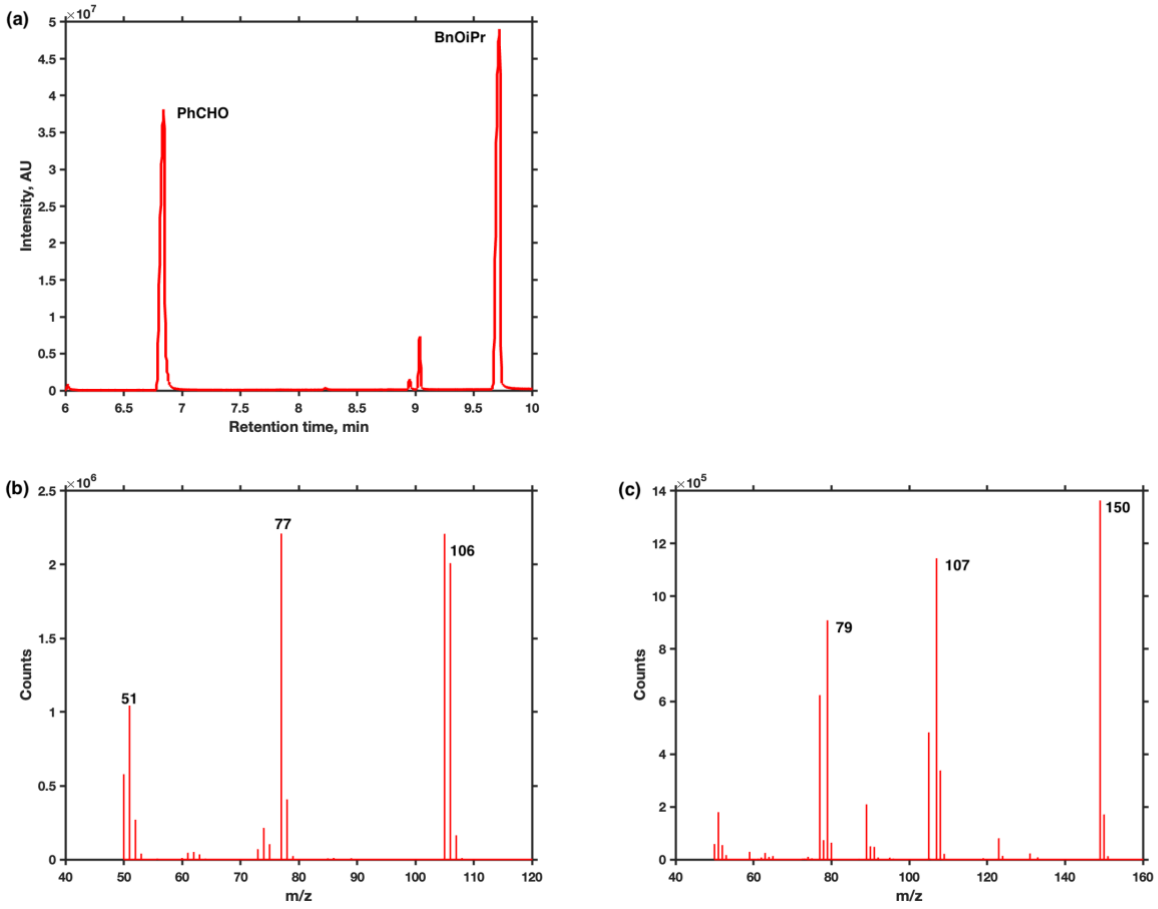


Figure S15. a) Total ion chromatograph of the reaction products of the reductive etherification of benzaldehyde (heterogeneous phase reaction, recycled). PhCHO retention time = 6.84 min, PhCOO^{i}Pr retention time = 9.72 min. b) Extracted mass spectrum for PhCHO product eluted at 6.84 min. c) Extracted mass spectrum for PhCHO product eluted at 9.72 min.

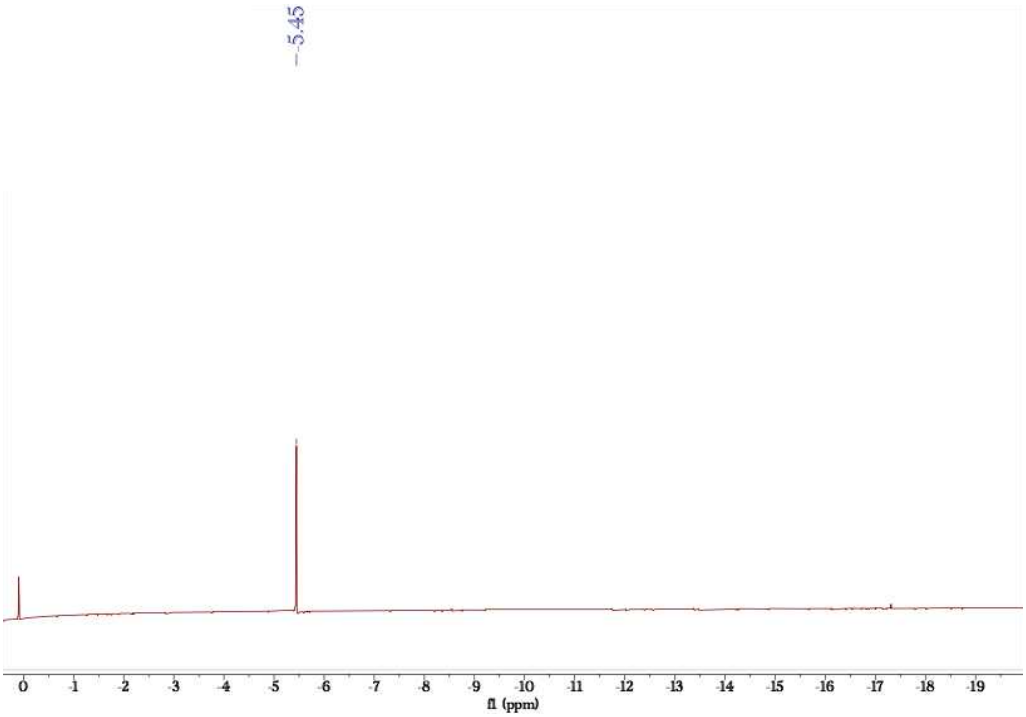


Figure S16. ^{1}H NMR spectrum of the reaction of benzaldehyde, KO^{t}Bu (5 mol%), [Re(^{C12}Anth-py$_2$) (CO)$_3$Br] (5 mol%) in d_8-^{i}PrOH after heating for 18 h at 70 °C. Re–H–Re dimer formation evidenced by peak at –5.45 ppm (referenced to ^{i}PrOH).

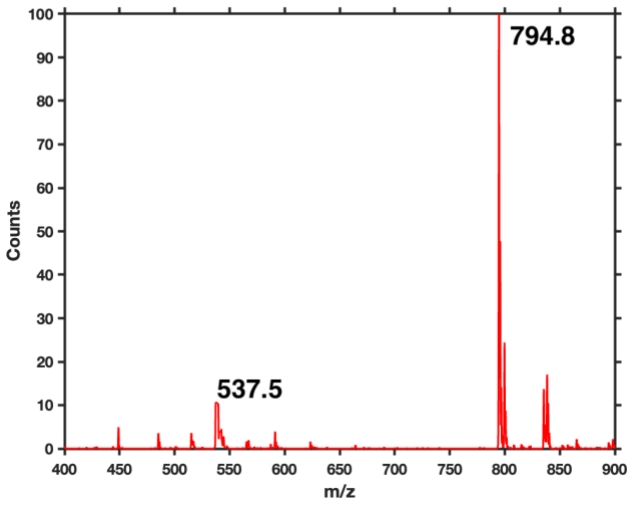


Figure S17. Mass spectrum (ESI+) of precipitate that formed during the homogenous-phase reaction of [Re(^{C12}Anth-py$_2$) (CO)$_3$Br] (5 mol%) with benzaldehyde in ^{i}PrOH with KO^{t}Bu (5 mol%), which is identified as [(μ-H)[Re(^{C12}Anth-py$_2$)(CO)$_3$]$_2$]$^{+}$. [M+2Na]$^{2+}$m/z = 794.8, predicted for $C_{78}H_{81}N_4Na_2O_3Re_2$ = 794.75428; [M+3Na]$^{3+}$ m/z = 537.5, predicted for $C_{78}H_{81}N_4Na_3O_3Re_2$ = 537.499218.

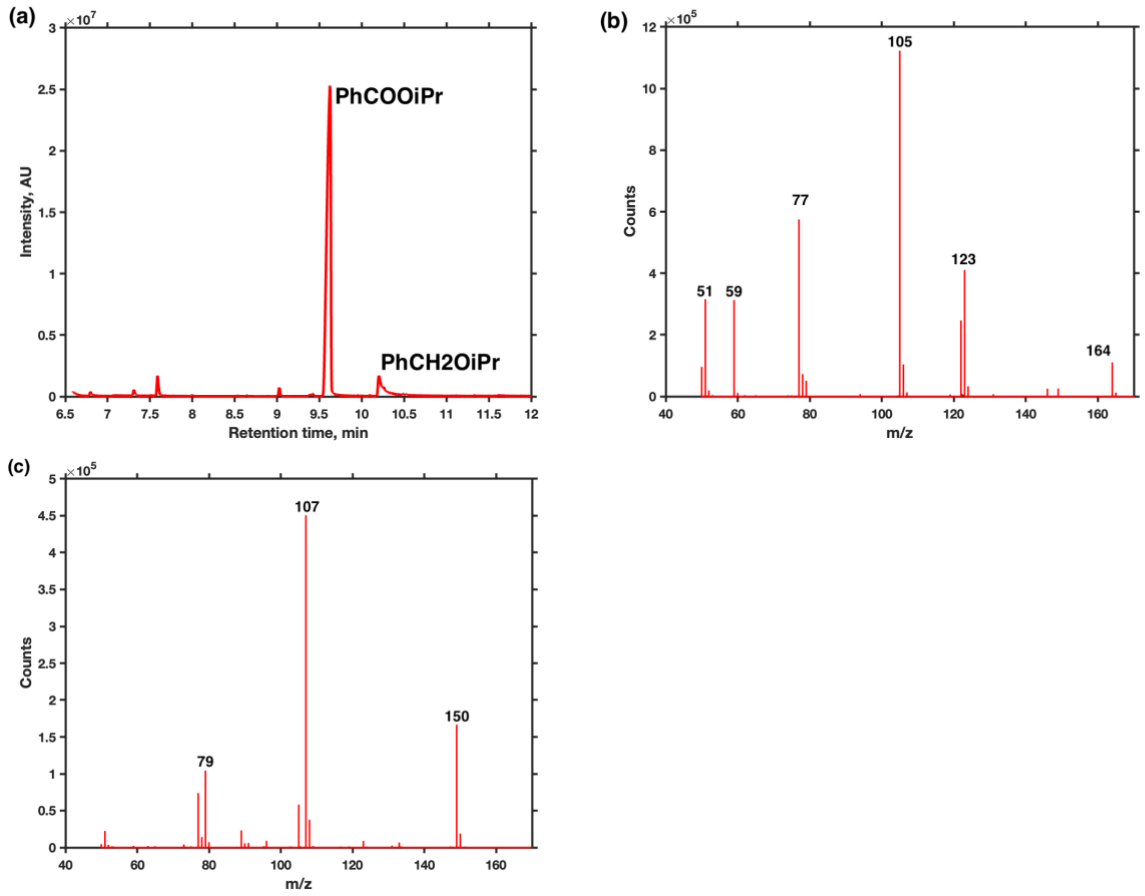


Figure S18. a) Total ion chromatograph of the reaction products of the reaction of isopropyl benzoate with TFB-BD@[Re] (heterogeneous phase reaction). PhCOO^{i}Pr retention time = 9.62 min, PhCH$_2$O^{i}Pr retention time = 10.2 min. b) Extracted mass spectrum for PhCOO^{i}Pr product eluted at 9.62 min. c) Extracted mass spectrum for PhCH$_2$O^{i}Pr product eluted at 10.2 min.

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