Experimental section

General procedures. Chromatographic purifications were performed on silica gel (35-70 mesh, Merck) columns. Thin-layer chromatography was carried out using Merck Kiesegel 60-F254 plates. ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM 400 instrument using tetramethylsilane (TMS) as an internal standard. FAB Mass spectra were measured on a VG-Quattro spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. GC-MS spectra were obtained with a VG-Quattro spectrometer equipped with a 30 m Supelco SPB-5 capillary column.

GC separation conditions. The products yield and the isomeric ratios for all the reactions were determined by GC analyses performed on a Carlo Erba HRGC 5160 instrument equipped with a 30 m Supelco SPB-5 capillary column and a FID detector. Chemical yields were determined by adding a suitable internal standard (tetradecane) to the reaction mixture at the end of each experiment and were reproducible within ±2% for multiple experiments.

Reactions

a) Typical procedure for the reaction catalysed by metalloporphyrins **4**: 1.3 mg of catalyst, (1.7 μmol), were dissolved in 3 mL of the ionic liquids and 1 mL of phenylacetylene (9.77 mmol) were added. The resulting solution was warmed at 150 °C for 18 hours, under nitrogen. At the end of the reaction, tetradecane was added as an internal standard and the mixture was extracted three times with 3 mL portions of diethyl ether. The organic solution was dried on anhydrous Na_2SO_4, filtered, concentrated under vacuum and analysed by GC.

b) Typical procedure for the reaction catalyzed by metalloporphyrin **4** in 1,2-dichlorobenzene: 1.3 mg of catalyst, (1.7 μmol), were dissolved in 3 mL of 1,2-dichlorobenzene and 1 mL of phenylacetylene (9.1 mmol) were added. The resulting solution was warmed at 150 °C for for 18 hours, under nitrogen. At the end of the reaction, tetradecane was added as an internal standard.

An authentic sample of 1-phenylnaphthalene, available from Aldrich, was used for the identification of the reaction products from phenylacetylene. All the elemental analysis gave satisfactory results.

Analytical data

8-methoxy-1-(3-methoxyphenyl)naphthalene: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 1H, *J*=9.2 Hz), 7.72 (d, 1H, *J*=8 Hz), 7.45 (t, 1 H, *J*=7.6 Hz), 7.36 (t, 1H, *J*= 7.6 Hz), 7.26 (d, 1 H, *J*=6.8 Hz), 7.23 (s, 1 H), 6.93-7.08 (m, 4 H), 3.91 (s, 3 H), 3.82 (s, 3 H); EI MS: *m/z*(%) 264(100).

6-methoxy-1-(3-methoxyphenyl)naphthalene: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, *J*=8 Hz), 7.35-7.48 (m, 3 H), 7.21-7.26 (m, 3 H), 6.84-6.90 (m, 2H), 6.76 (d, 1 H, *J*=7.6 Hz), 3.79 (s, 3 H), 3.48 (s, 3 H); EI MS: *m/z*(%) 264(100).