Supporting Information

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Biomimetic Synthesis of Pd Nanocatalysts for the Stille Coupling Reaction.

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(17 pages)

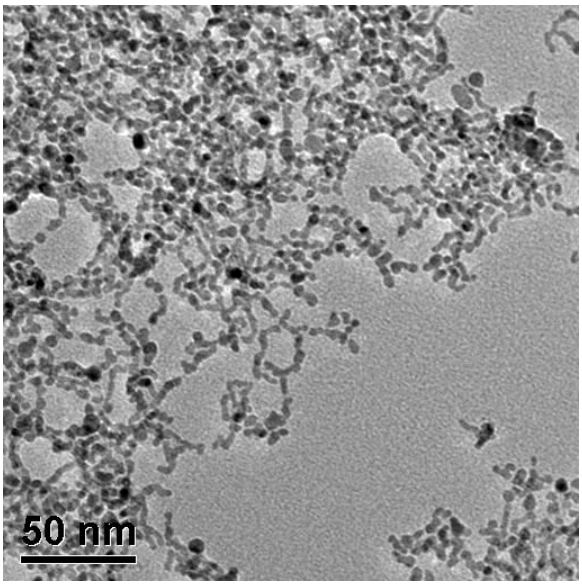


Figure S1. Irregular Pd nanostructures produced when the Pd4 peptide is substituted with the R5 peptide.

4-iodobenzoic acid

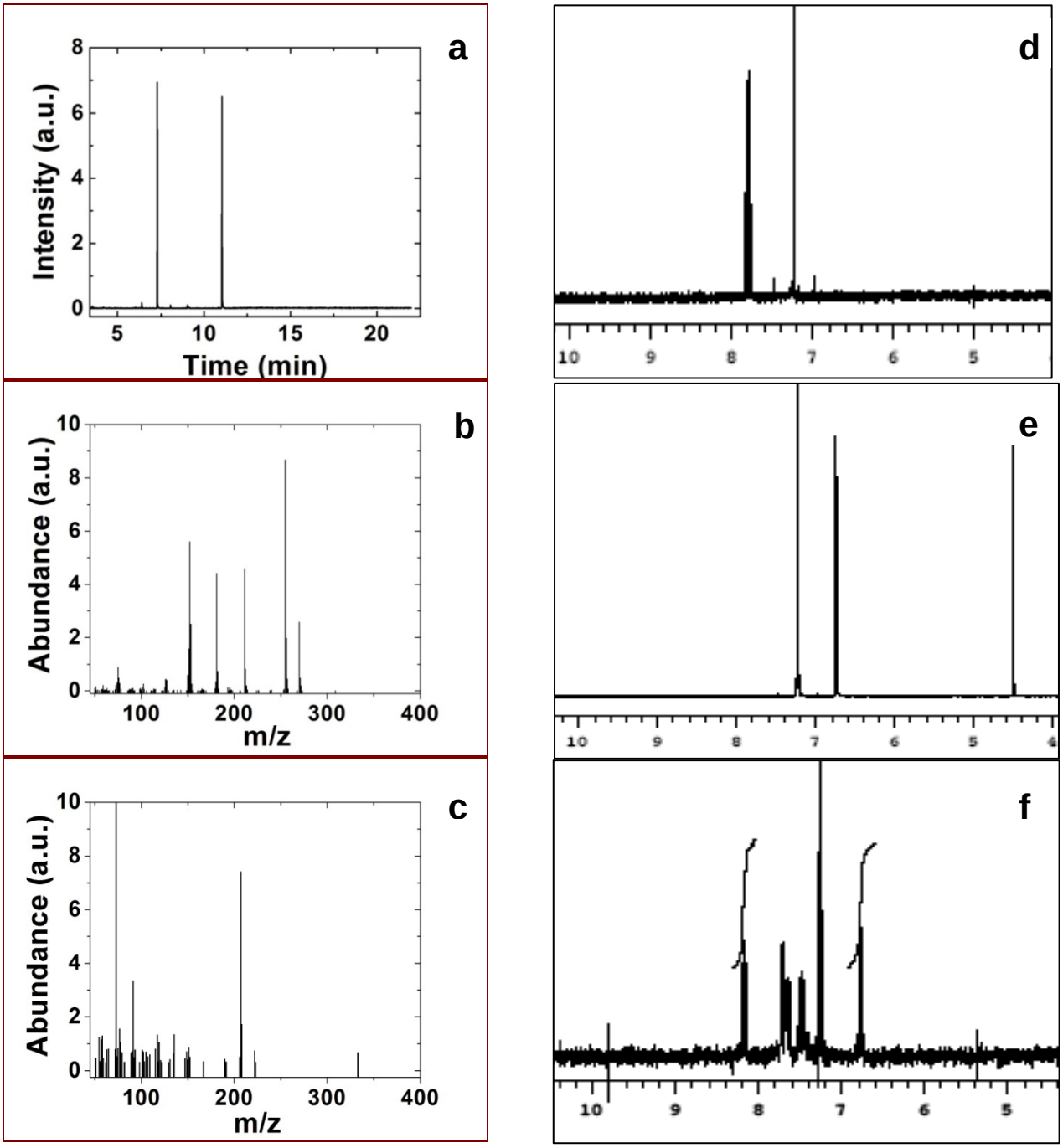


Figure S2. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-iodobenzoic acid and $PhSnCl_3$ (0.005 mol% Pd, 24 h), after derivatization with MSTFA. The mass spectrum (b) of the peak at 11.04 min, corresponds to the biphenyl-4-carboxylic acid trimethylsilyl ester (m/z = 270). The mass spectrum (c) of the peak at 7.29 min corresponds to the internal standard 4-tertbutylphenol (TBP) trimethylsilyl derivative (m/z = 222). ^{1}H NMR spectrum of 4-iodobenzoic acid (d), TBP (e) and the crude product of the Stille reaction added with 0.5 mmols of TBP (f). The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

3-iodobenzoic acid

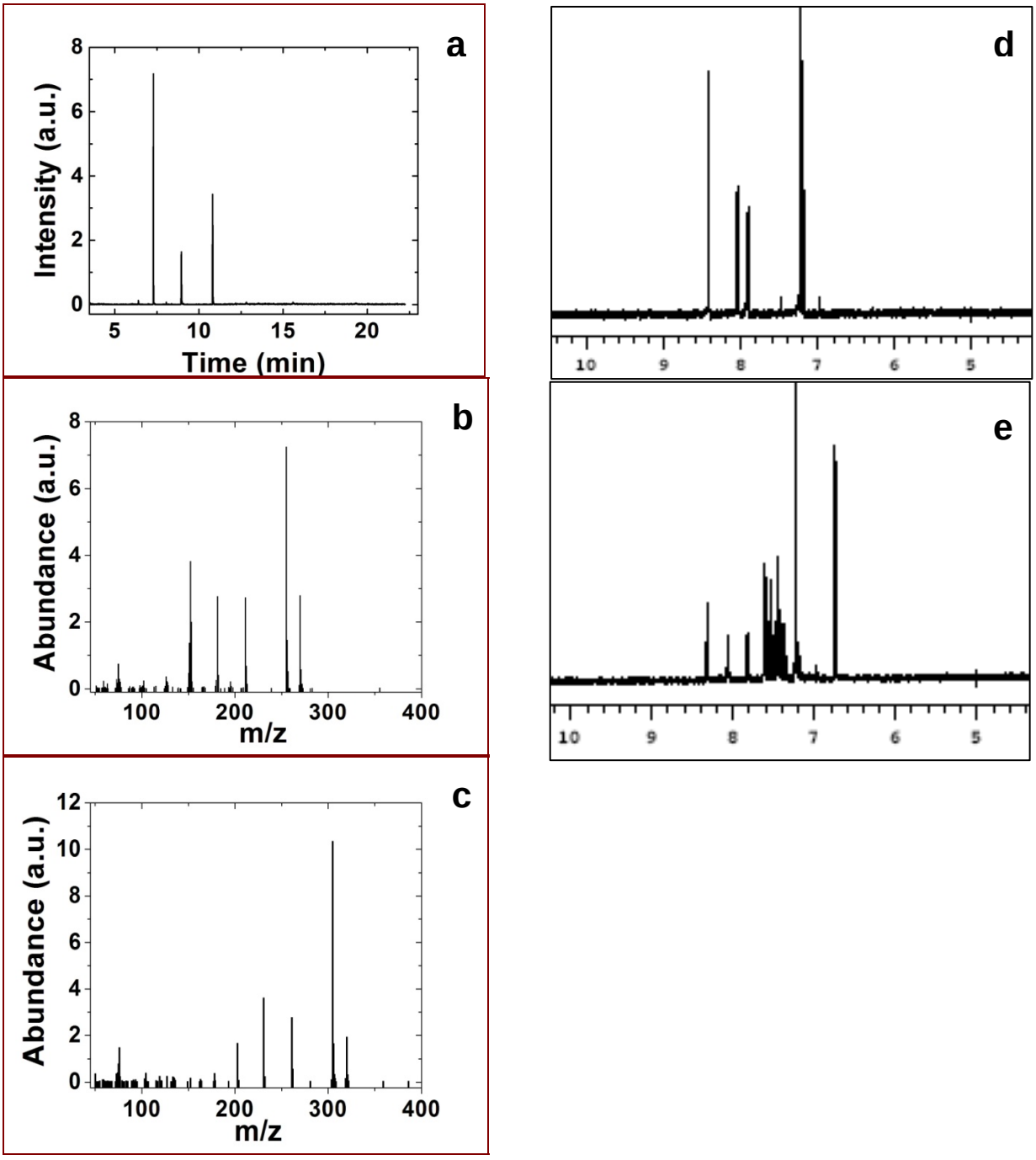


Figure S3. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 3-iodobenzoic acid and $PhSnCl_3$ (0.05 mol% Pd, 24 h), after derivatization with MSTFA. The mass spectrum (b) of the peak at 10.81 min, corresponds to the biphenyl-3-carboxylic acid trimethylsilyl ester (m/z = 270). The mass spectrum (c) of the peak at 8.95 min corresponds to the starting material, 3-iodobenzoic acid (m/z = 320). ^{1}H NMR spectrum of 3-iodobenzoic acid (d) and the crude product of the Stille reaction added with 0.5 mmols of TBP (e). The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

2-iodobenzoic acid

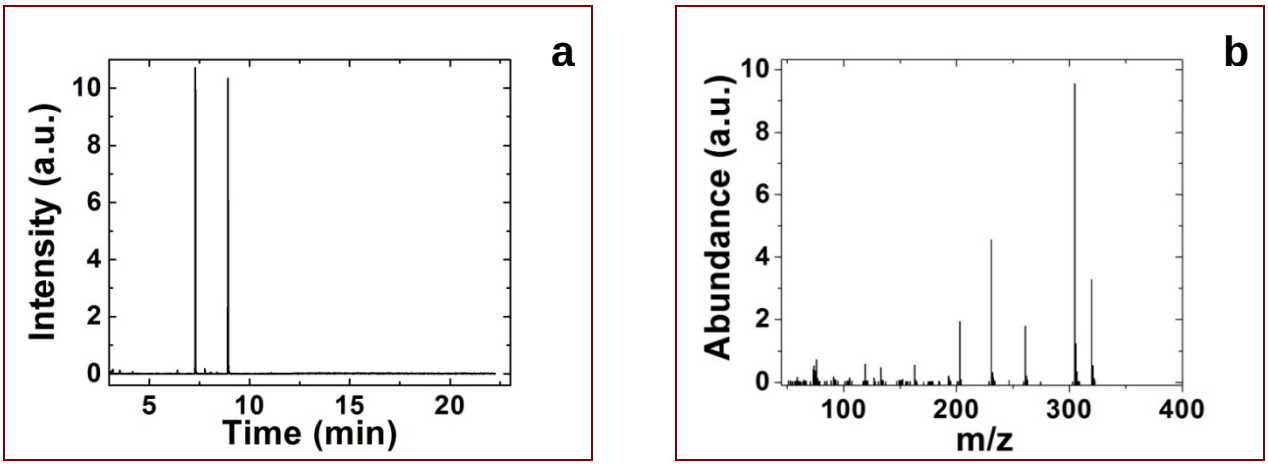


Figure S4. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 2-iodobenzoic acid and $PhSnCl_3$ (0.05 mol% Pd, 24 h), after derivatization with MSTFA. The mass spectrum (b) of the peak at 8.93 min, corresponds to the 2-iodobenzoic acid trimethylsilyl ester (m/z = 320). No product is formed in this reaction.

4-bromobenzoic acid, 0.10 mol% Pd, 3.0 d

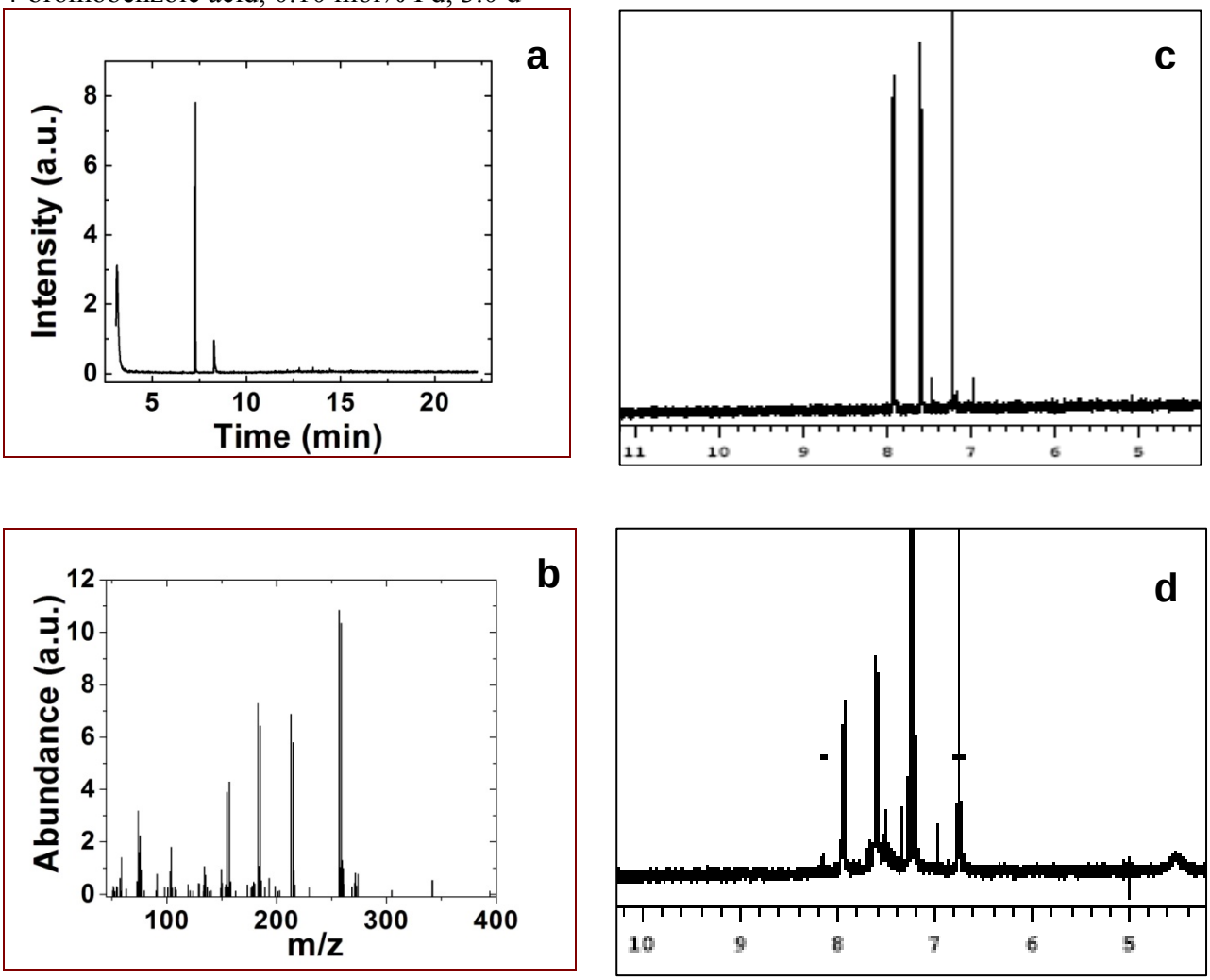


Figure S5. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromobenzoic acid and $PhSnCl_3$ (0.10 mol% Pd, 3.0 d), after derivatization with MSTFA. The mass spectrum (b) of the peak at 8.28 min, corresponds to the 4-bromobenzoic acid trimethylsilyl ester (m/z = 272). ^{1}H NMR spectrum of 4-bromobenzoic acid (c) and the crude product of the Stille reaction added with 0.5 mmols of TBP (d). The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

4-bromobenzoic acid, 0.10 mol% Pd, 7.0 d

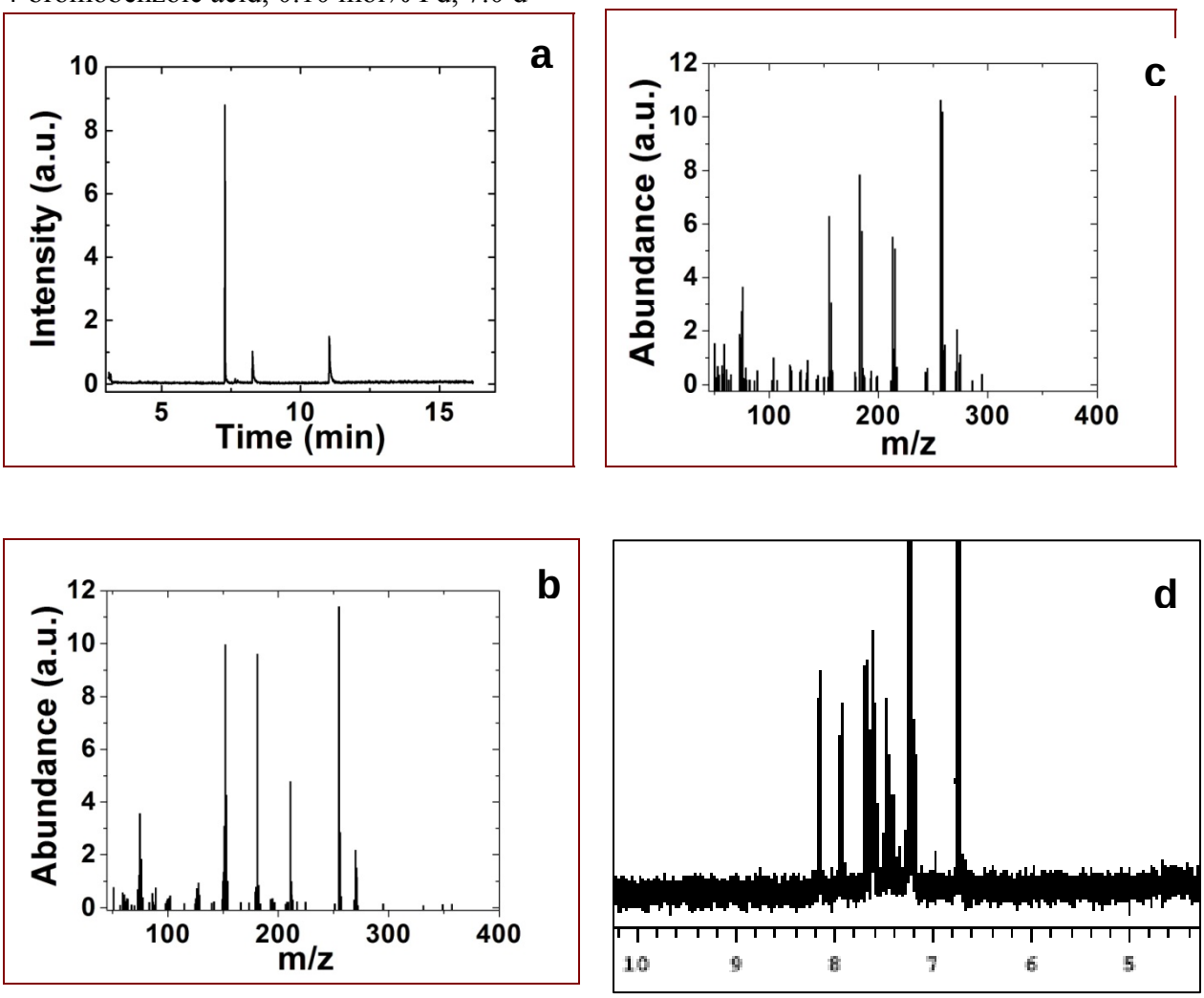


Figure S6. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromobenzoic acid and $PhSnCl_3$ (0.10 mol% Pd, 7.0 d), after derivatization with MSTFA. The mass spectrum (b) of the peak at 11.03 min, corresponds to the biphenylcarboxylic acid trimethylsilyl ester (m/z = 270). The mass spectrum (c) of the peak at 8.28 min corresponds to the 4-bromobenzoic acid trimethylsilyl ester (m/z = 272). (d) ^{1}H NMR spectrum of the crude product of the Stille reaction added with 0.5 mmol of TBP. The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

4-bromobenzoic acid, 0.50 mol% Pd, 3.0 d

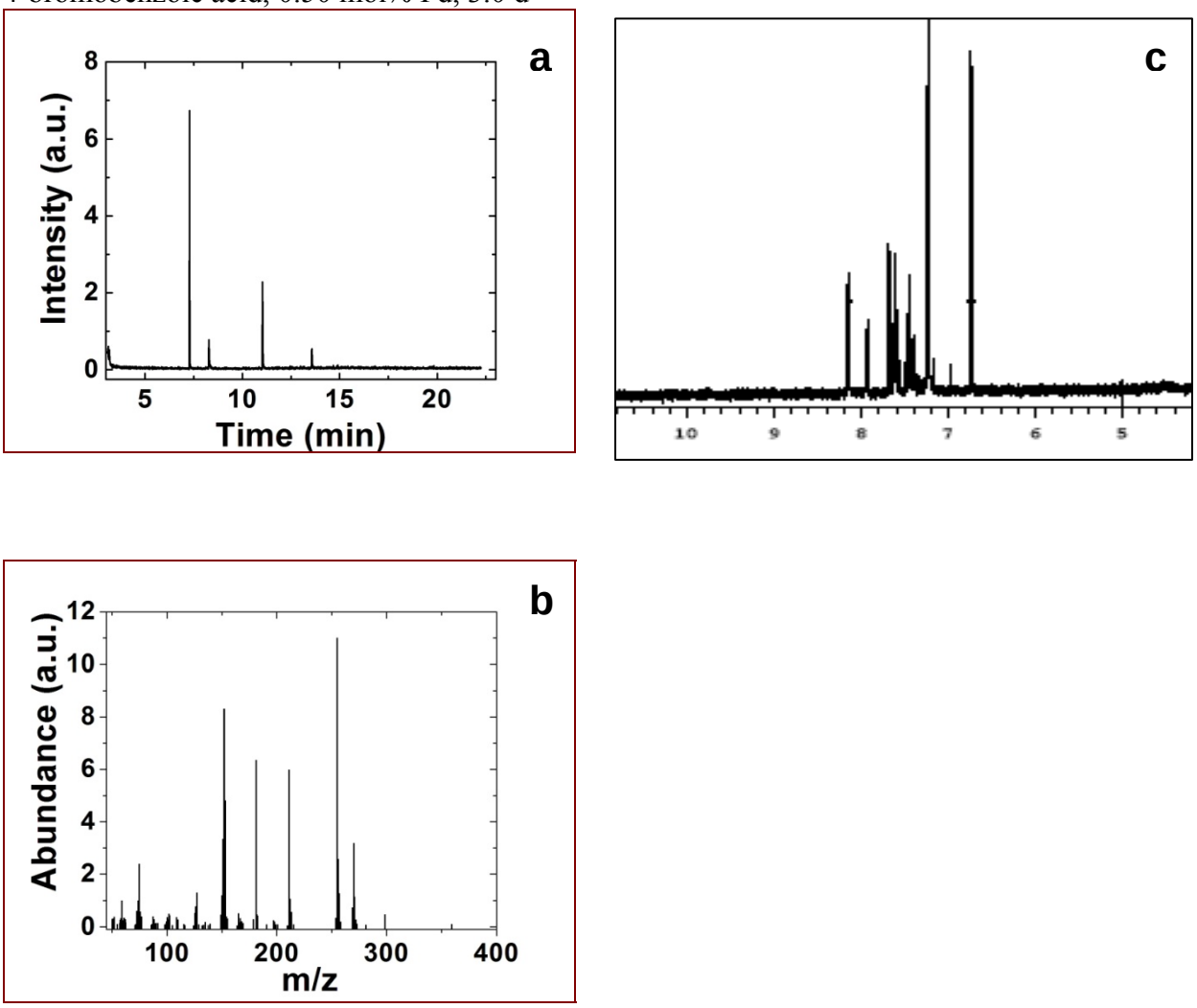


Figure S7. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromobenzoic acid and $PhSnCl_3$ (0.50 mol% Pd, 3.0 d), after derivatization with MSTFA. The mass spectrum (b) of the peak at 11.03 min, corresponds to the biphenyl-4-carboxylic acid trimethylsilyl ester (m/z = 270). (c) ^{1}H NMR spectrum of the crude product of the Stille reaction added with 0.5 mmols of TBP. The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

4-bromobenzoic acid, 0.50 mol% Pd, 7.0 d

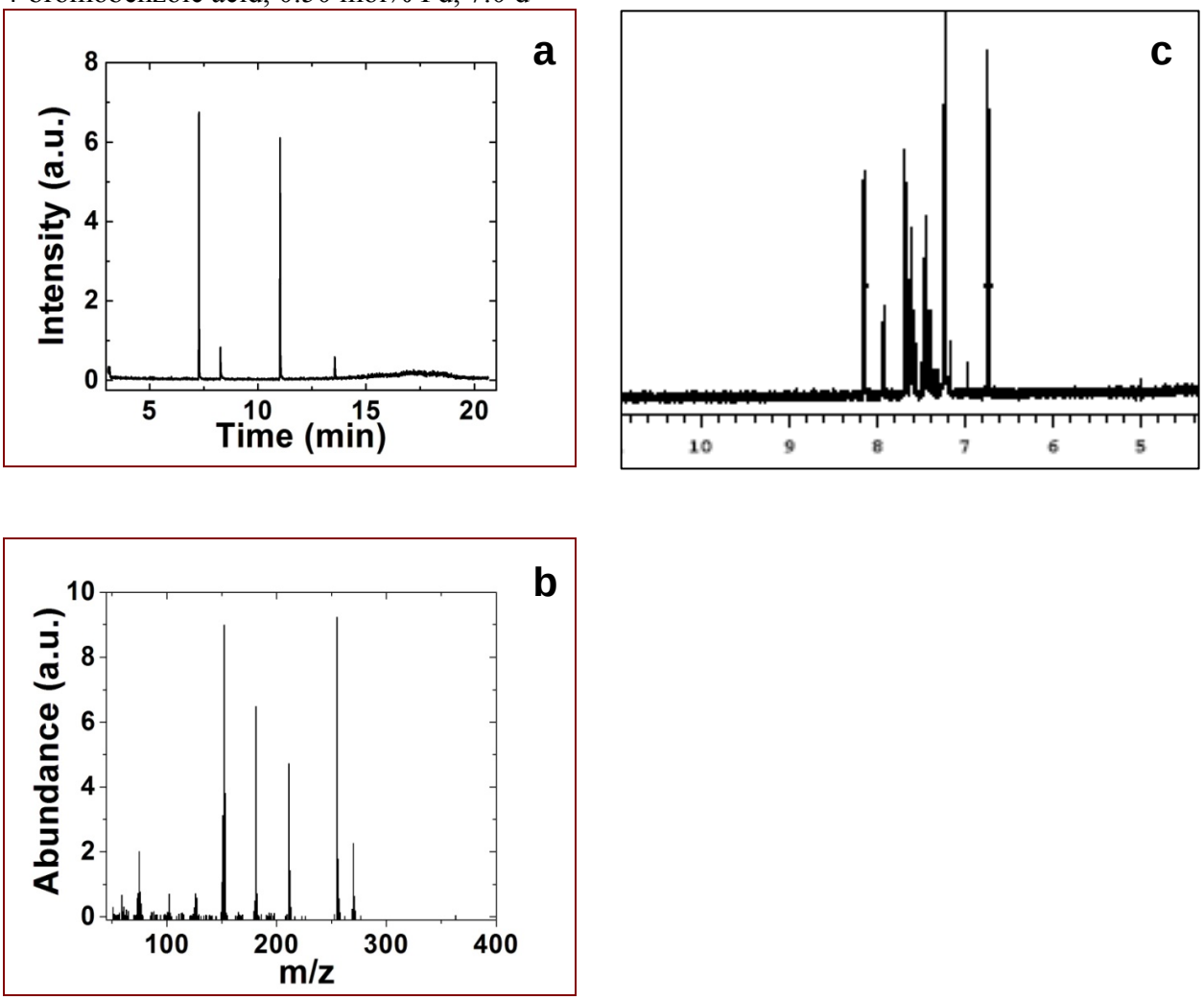


Figure S8. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromobenzoic acid and $PhSnCl_3$ (0.50 mol% Pd, 7.0 d) after derivatization with MSTFA. The mass spectrum (b) of the peak at 11.03 min, corresponds to the biphenyl-4-carboxylic acid trimethylsilyl ester (m/z = 270). (c) ^1H NMR spectrum of the crude product of the Stille reaction added with 0.5 mmols of TBP. The integration of the peak at δ 8.15 ppm (product) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.

4-chlorobenzoic acid

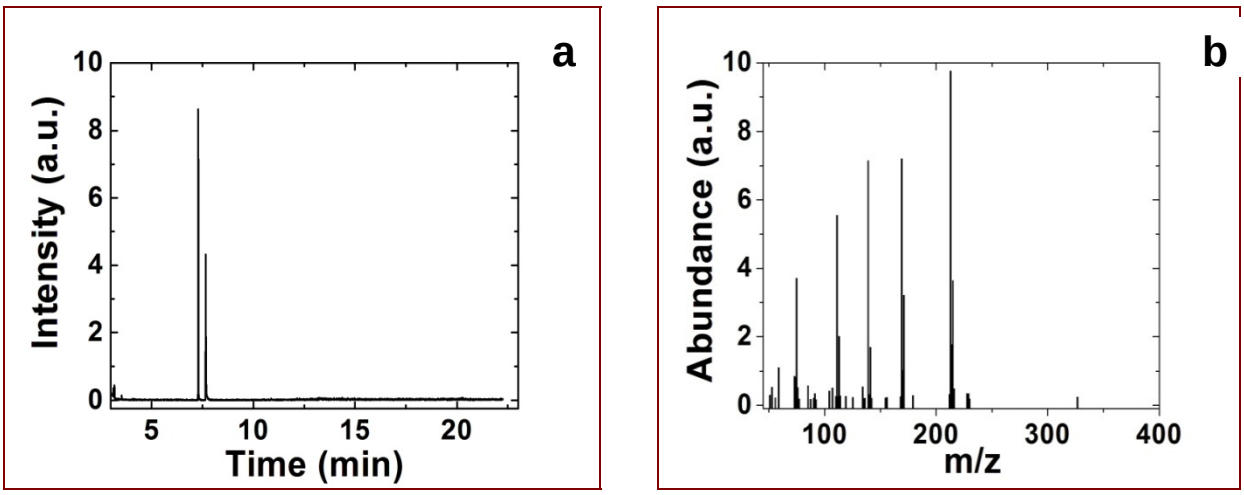


Figure S9. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-chlorobenzoic acid and $PhSnCl_3$ (0.05 mol% Pd, 24 h), after derivatization with MSTFA. The mass spectrum (b) of the peak at 7.66 min corresponds to the 4-chlorobenzoic acid trimethylsilyl ester (m/z = 242). No product is formed in this reaction.

4-iodophenol

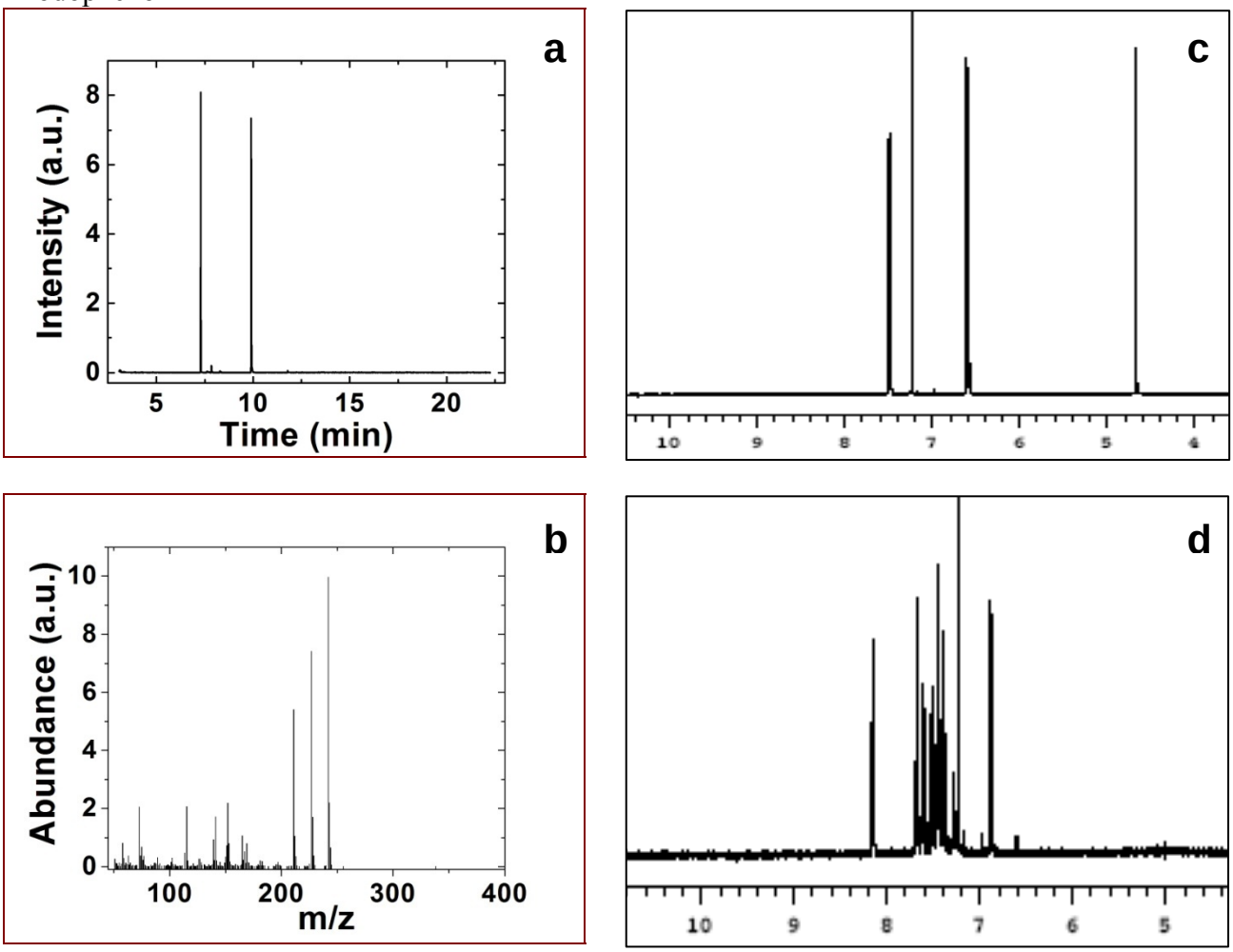


Figure S10. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-iodophenol and $PhSnCl_3$ (0.05 mol% Pd, 24 h) after derivatization with MSTFA. The mass spectrum (b) of the peak at 9.90 min corresponds to the 4-phenylphenol trimethylsilyl ester derivative (m/z = 242). ^1H NMR spectrum of 4-iodophenol (c) and the crude product of the Stille reaction added with 0.5 mmols of biphenylcarboxylic acid (BPCA) (d). The integration of the peak at δ 6.88 ppm (product) was compared with the integration of the peak at δ 8.15 ppm (BPCA) to obtain the percent yield of the reaction.

4-bromophenol, 0.10 mol% Pd, 3.0 d

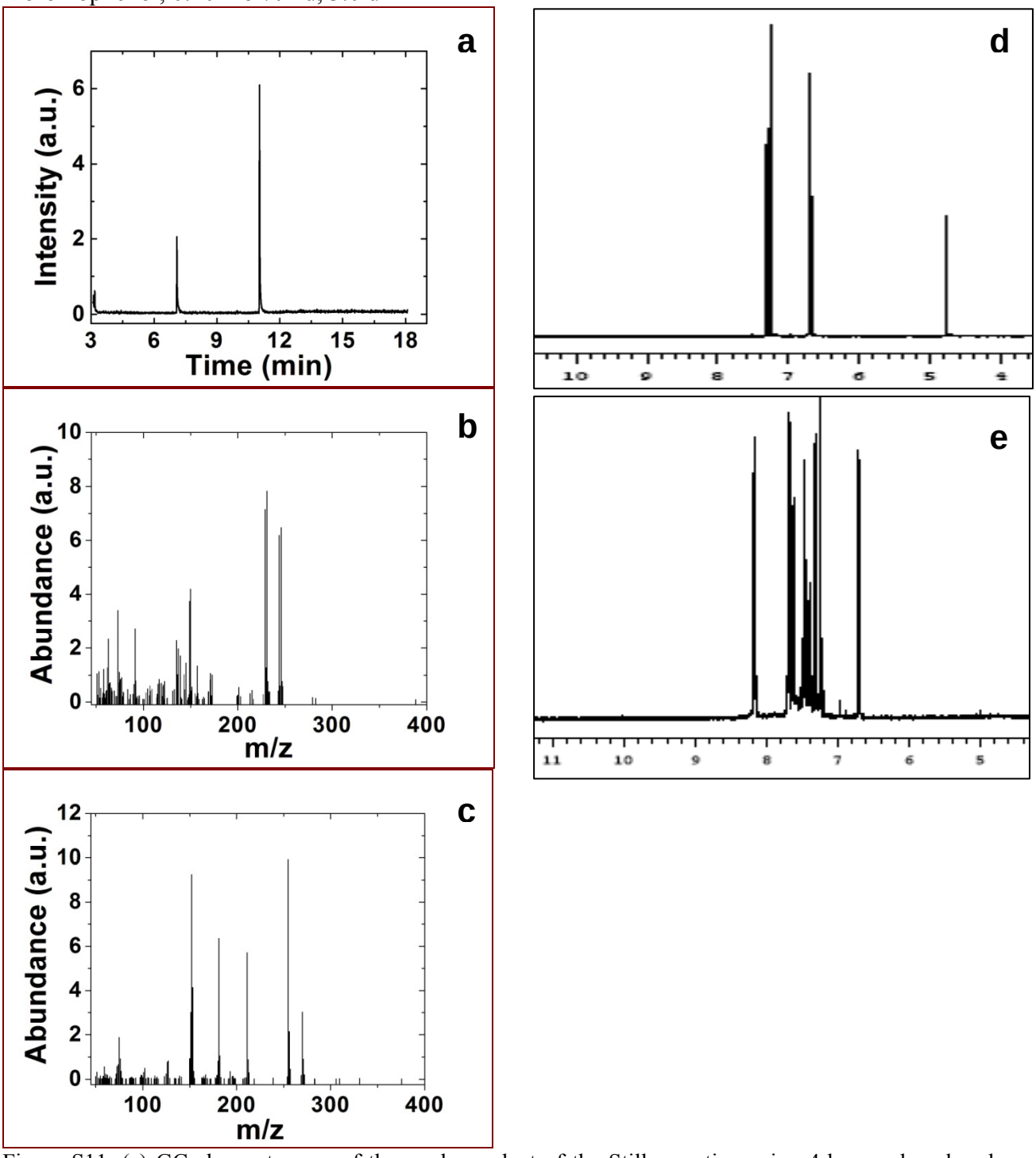


Figure S11. (a) GC chromatogram of the crude product of the Stille reaction using 4-bromophenol and $PhSnCl_3$ (0.10nmol% Pd, 3.0 d) after derivatization with MSTFA. The mass spectrum (b) of the peak at 7.09 min corresponds to the 4-bromophenol trimethylsilyl ester derivative (m/z = 246). The mass spectrum (c) of the peak at 11.03 min, corresponds to the internal standard biphenylcarboxylic acid (BPCA). ^{1}H NMR spectrum of 4-bromophenol (d) and the crude product of the Stille reaction added with 0.5 mmols of BPCA (e). The integration of the peak at δ 6.88 ppm (product) was compared with the integration of the peak at δ 8.15 ppm (BPCA) to obtain the percent yield of the reaction.

4-bromophenol, 0.10 mol% Pd, 7.0 d

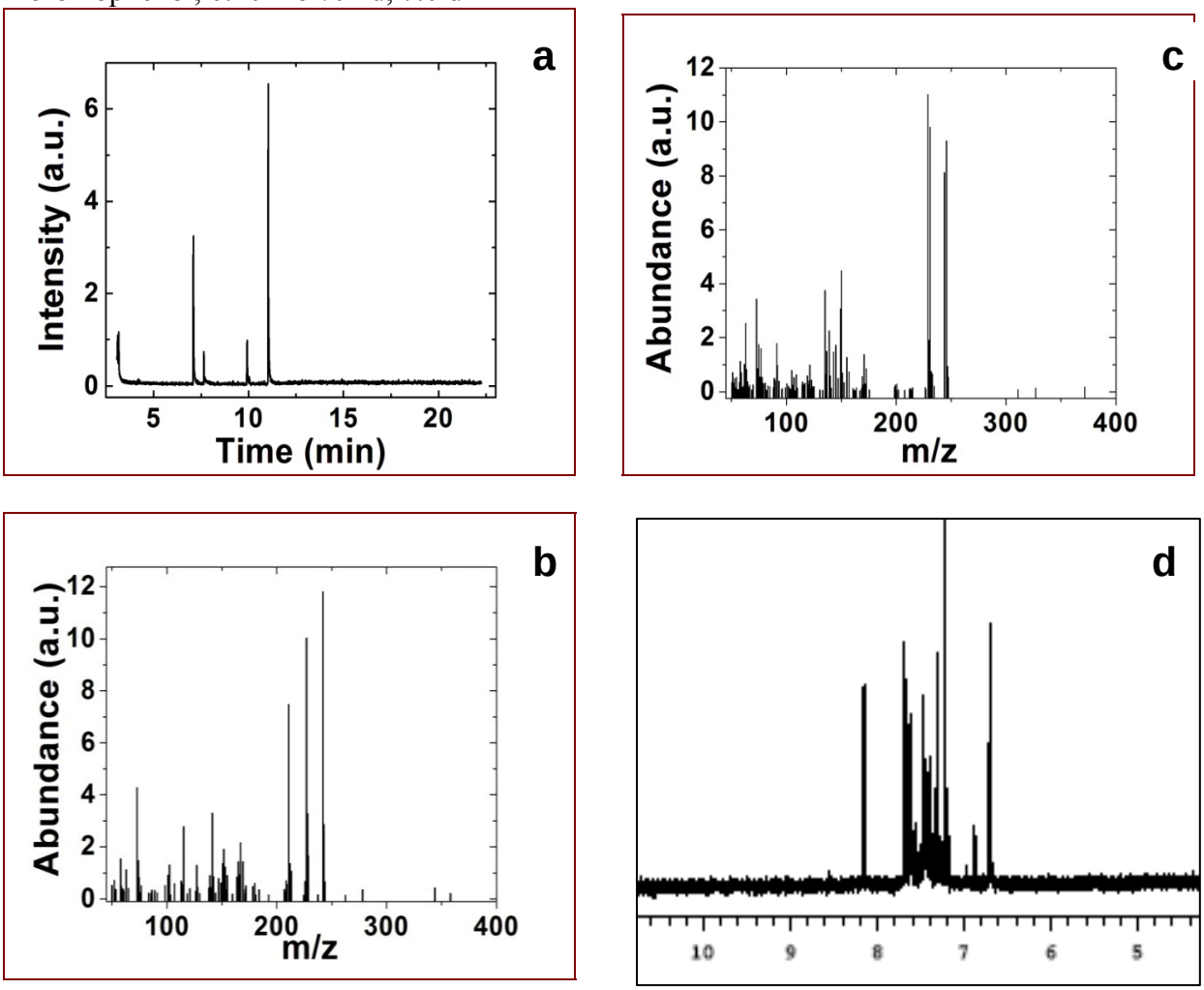
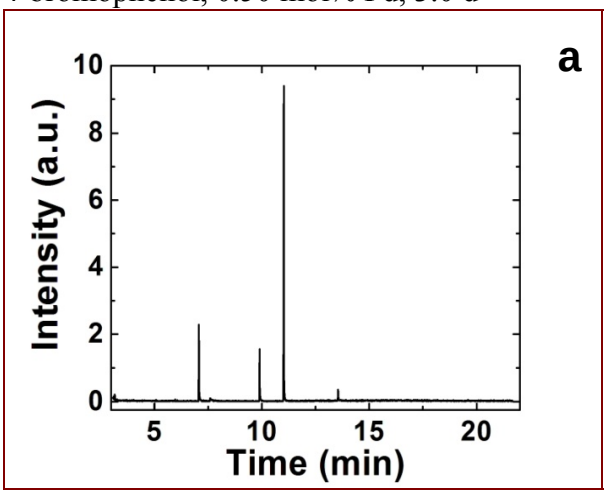
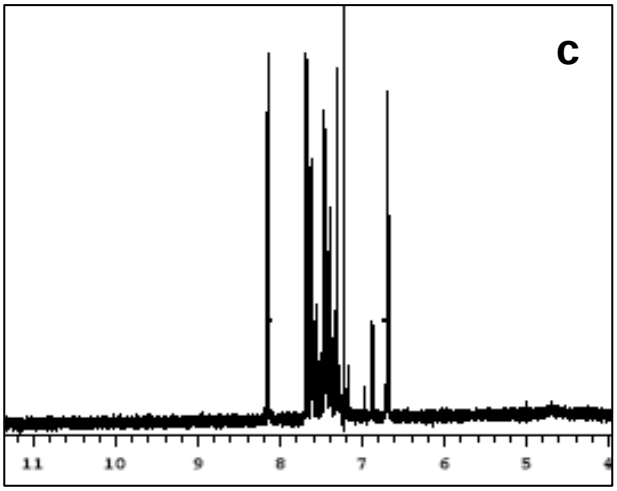


Figure S12. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromophenol and $PhSnCl_3$ (0.10 mol% Pd, 7.0 d) after derivatization with MSTFA. The mass spectrum (b) of the peak at 9.90 min, corresponds to the 4-phenylphenol trimethylsilyl derivative (m/z = 242). The mass spectrum (c) of the peak at 7.09 min, corresponds to the 4-bromophenol trimethylsilyl derivative (m/z = 246). (d) ^1H NMR spectrum of the crude product of the Stille reaction added with 0.5 mmols of BPCA. The integration of the peak at δ 6.88 ppm (product) was compared with the integration of the peak at δ 8.15 ppm (BPCA) to obtain the percent yield of the reaction.

4-bromophenol, 0.50 mol% Pd, 3.0 d





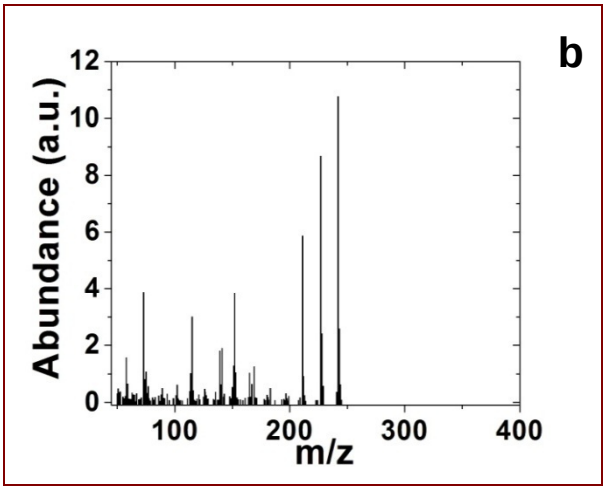


Figure S13. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromophenol and $PhSnCl_3$ (0.50 mol% Pd, 3.0 d) after derivatization with MSTFA. The mass spectrum (b) of the peak at 9.90 min, corresponds to the 4-phenylphenol trimethylsilyl derivative (m/z = 242). (c) ^1H NMR spectrum of the crude product of the Stille reaction added with 0.5 mmols of BPCA. The integration of the peak at δ 6.88 ppm (product) was compared with the integration of the peak at δ 8.15 ppm (BPCA) to obtain the percent yield of the reaction.

4-bromophenol, 0.50 mol% Pd, 7.0 d

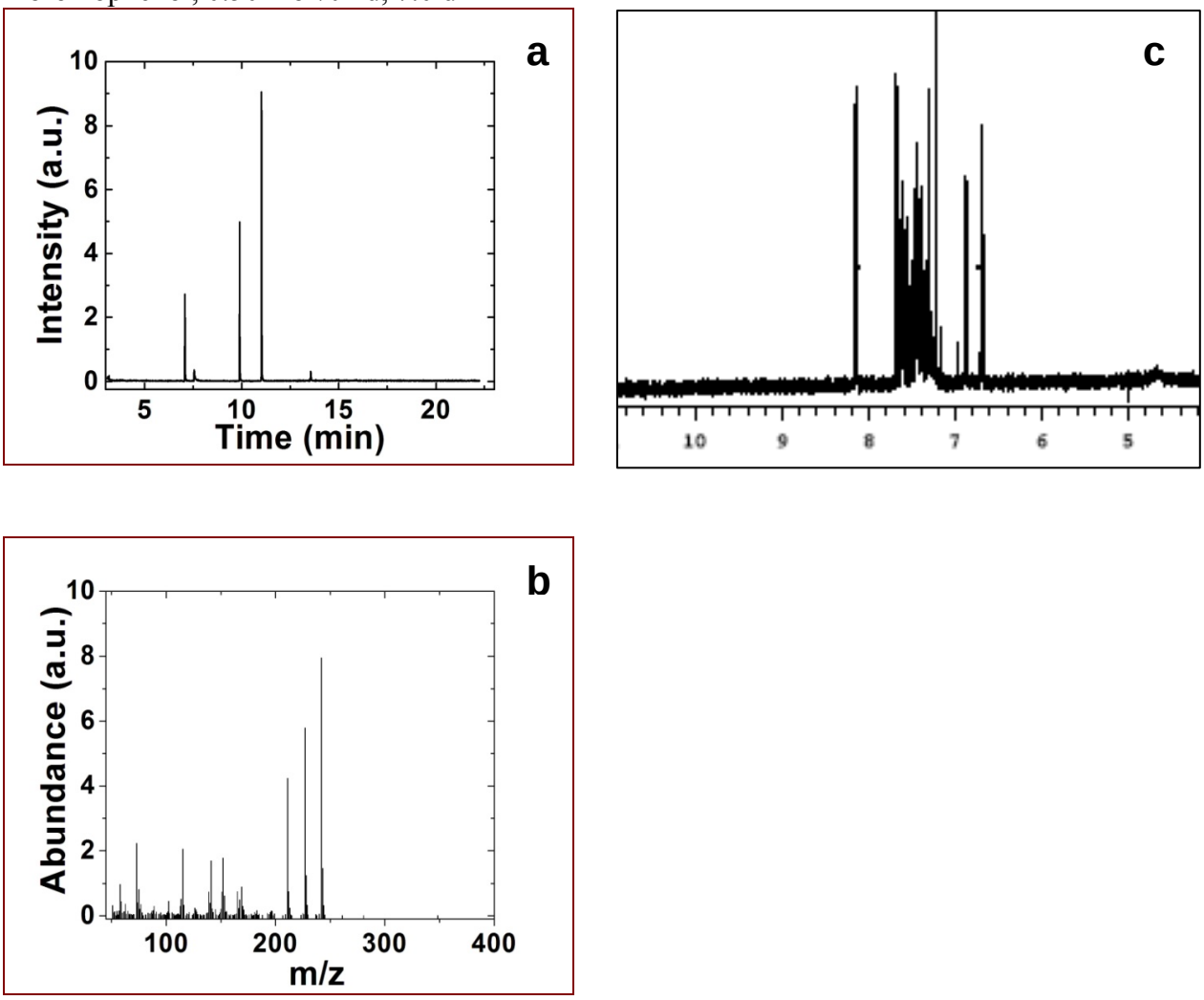


Figure S14. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-bromophenol and $PhSnCl_3$ (0.50 mol% Pd, 7.0 d) after derivatization with MSTFA. The mass spectrum (b) of the peak at 9.90 min, corresponds to the 4-phenylphenol trimethylsilyl derivative (m/z = 242). (c) ^1H NMR spectrum of the crude product of the Stille reaction added with 0.50 mmols of BPCA. The integration of the peak at δ 6.88 ppm (product) was compared with the integration of the peak at δ 8.15 ppm (BPCA) to obtain the percent yield of the reaction.

4-chlorophenol

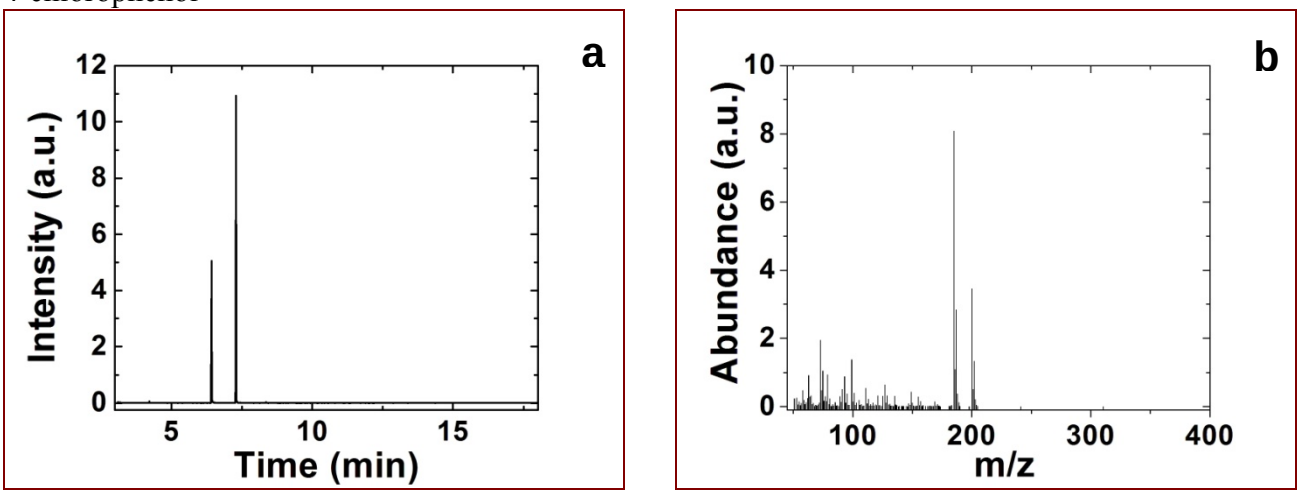


Figure S15. (a) GC chromatogram and (b) mass spectrum of the crude product of the Stille reaction using 4-chlorophenol and $PhSnCl_3$ (0.05 mol% Pd, 24 h), after derivatization with MSTFA. The mass spectrum (b) of the peak at 6.42 min corresponds to the 4-chlorophenol trimethylsilyl derivative (m/z = 200). No product is formed in this reaction.

Stille Coupling Reaction in Ethanol/water

4-iodobenzoic acid, 0.05mol% Pd, 24 h

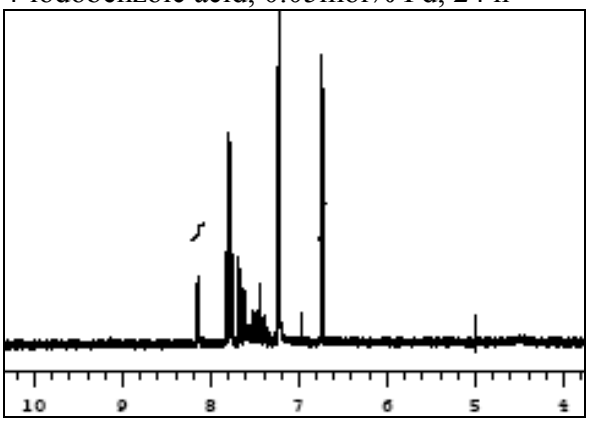


Figure S16. ^{1}H NMR spectrum of the extracted product of the Stille reaction in ethanol/water solvent added with 0.50 mmols of TBP. The integration of the peak at δ 8.15 ppm (BPCA) was compared with the integration of the peak at δ 6.74 ppm (TBP) to obtain the percent yield of the reaction.