Electronic Supplementary Material (ESI) for RSC Advances

Peptide nanofibers decorated Pd nanoparticles to enhance the catalytic activity for C-C coupling reactions in aerobic condition.

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Contents

1. Experimental Section

NMR spectroscopy

All NMR spectra were recorded at 400 MHz Bruker AV 400 NMR. Compounds concentrations were in the range of 1-10 mmol in $(CD_3)_2SO$ and $CDCl_3$.

Mass spectrometry

Mass spectra were recorded on Bruker micrOTOF-Q II by positive and negative mode electrospray ionisations.

Polarimeter study

Specific rotations of the synthesized compounds were measured on an Autopol^R V automatic polarimeter (Rudolph research analytical). The cell (length = 100 mm, capacity = 2 mL) was used for this study at 20 °C.

FT-IR study

All the reported FT-IR spectra were taken using Bruker (Tensor 27) FT-IR spectrophotometer. The solid compounds were performed using the KBr pellet technique with a scan range between 400 to 4000 cm^{-1} over 64 scans at a resolution of 4 cm^{-1} and an interval of 1 cm^{-1}. The gel sample was prepared in D_2O and placed between crystal Zn-Se windows and scanned between 900 to 4000 cm^{-1} over 64 scans at a resolution of 4 cm^{-1} and an interval of 1 cm^{-1}.

Circular Dichroism (CD) spectroscopy

Secondary structure of peptide bolaamphiphile was analyzed with Jasco J-815 circular dischroism spectrometer. For all the case, peptide hydrogel (20 mmol L^{-1}) and the Pd nanoparticles embedded in hydrogel, were diluted to final concentration of 10 μM in ddH_2O and measured from 260 nm to 190 nm with 0.1 data pitch, 20 nm/min scanning speed, 1 nm band width and 4 s D.I.T.

Fluorescence spectroscopy

Fluorescence emission spectra of gel (20 mmol L^{-1}) were recorded on a Horiba Scientific Fluoromax-4 spectrophotometer with 1 cm path length quartz cell at room temperature. The slit width for the excitation and emission was set at 5 nm and a 1 nm data pitch. Excitation of gel sample **1** was performed at 270 nm and data range was in between 280 to 525 nm.

Time correlated single photon counting (TCSPC)

A 2 mL of gel sample was prepared in a quartz cuvette (1 cm×1 cm) and time correlated single photon counting (TCSPC) experiment was performed on Horiba Yovin (Model: Fluorocube-01-NL) instrument. Sample was excited at 376 nm using a picosecond diode laser (Model: Pico Brite-375L). The signals were collected at magic angle (54.70) polarization using a photomultiplier tube (TBX-07C) as detector, which has a dark counts less than 20 cps. The

instrument response function (IRF, FWHM~140 ps) was recorded using a very dilute scattering solution. The data analysis was performed using IBH DAS (version 6, HORIBA Scientific, Edison, NJ) decay analysis software.

The amplitude-weighted lifetime was estimated by

$$\langle\tau\rangle = \sum_{i=1}^{n} a_i \tau_i$$

where τ_i is the fluorescence lifetime of various fluorescent species and a_i are the normalized pre-exponential factors. The goodness of the fit was judged by reduced chi-squere (χ^2) value.

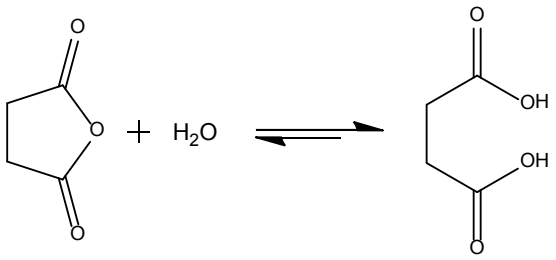
Field emission gun-scanning electron microscopy (FEG-SEM) study

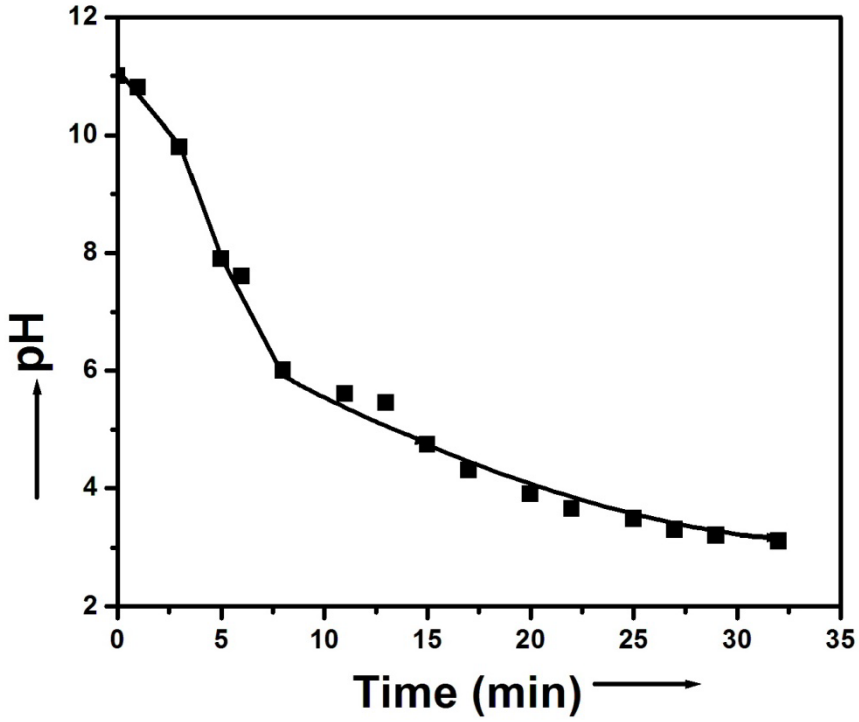
For SEM study, the hydrogel was dried on a glass slide and coated with gold. Then the micrographs were recorded in a SEM apparatus (Jeol Scanning Microscope-JSM-7600F).

Transmission electron microscopy (TEM) study

High-resolution transmission electron microscopic image was taken by using a PHILIPS electron microscope (model: CM 200) operated at an accelerating voltage of 200kV. The hydrogel (20 mmol L^{-1}) and the Pd nanoparticles embedded in hydrogel were diluted in double distilled water and dried on carbon-coated copper grids (300 mesh) by slow evaporation in air, then allowed to dry separately in a vacuum at room temperature. The average size of the nanoparticles was determined from the TEM images.

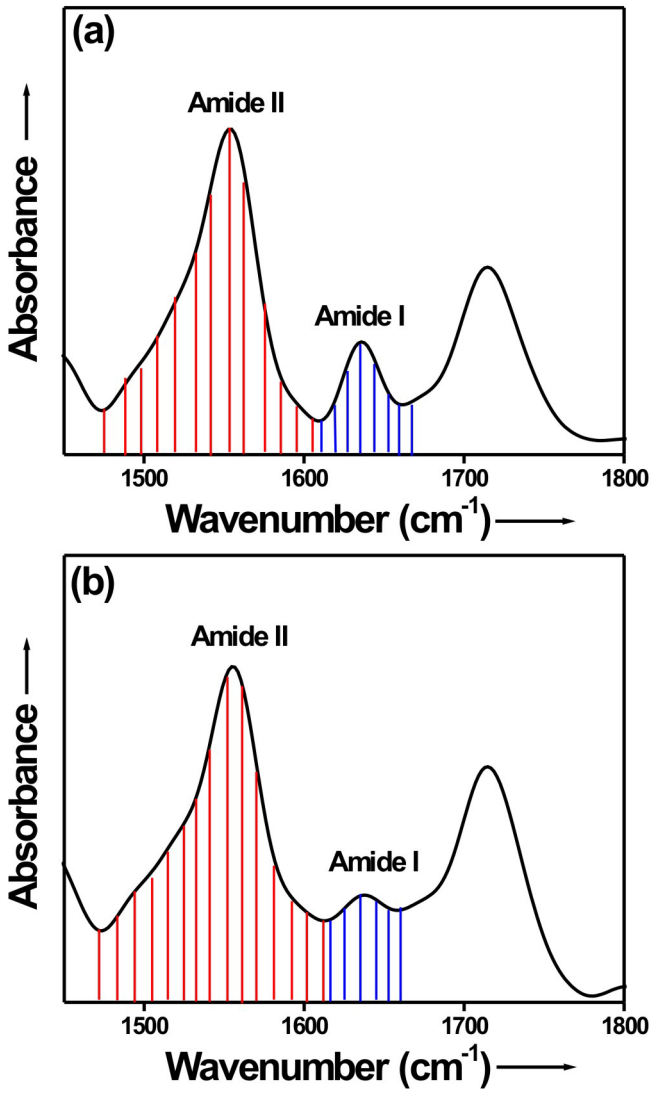
2. Change in pH over time





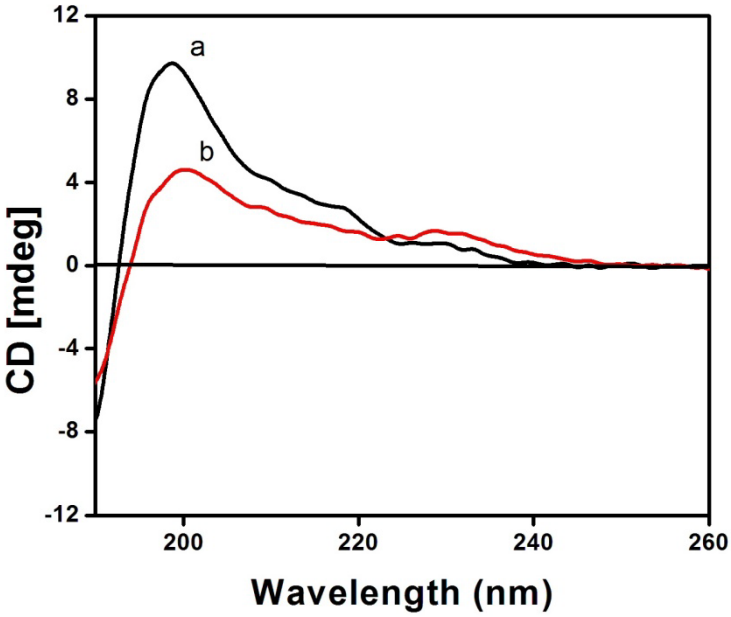
ESI Fig. 1. The pH decreases over time during the hydrolysis of succinic anhydride to succnic acid.

3. FT-IR study



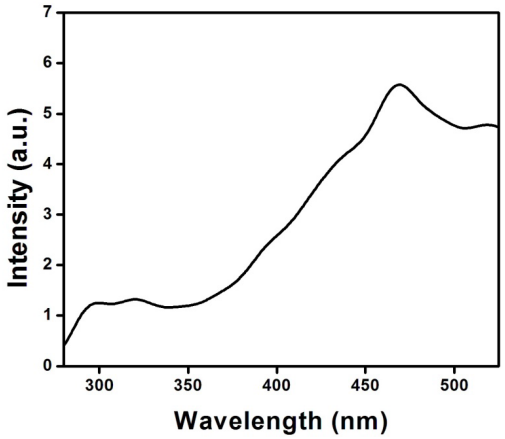
ESI Fig. 2. FT-IR spectra of hydrogel show (a) an amide **I** band at 1629 cm^{-1} and the blue lines area indicates area of amide **I** while red lines area indicates the area of amide **II** with a band at 1554 cm^{-1}. (b) The amide **I** band appeared at 1635 cm^{-1} with the area filled by blue lines while red lines area indicates the area of amide **II** with a band at 1556 cm^{-1} for peptide nanofibers decorated with Pd nanoparticles.

4. Circular dichroism (CD) spectroscopy



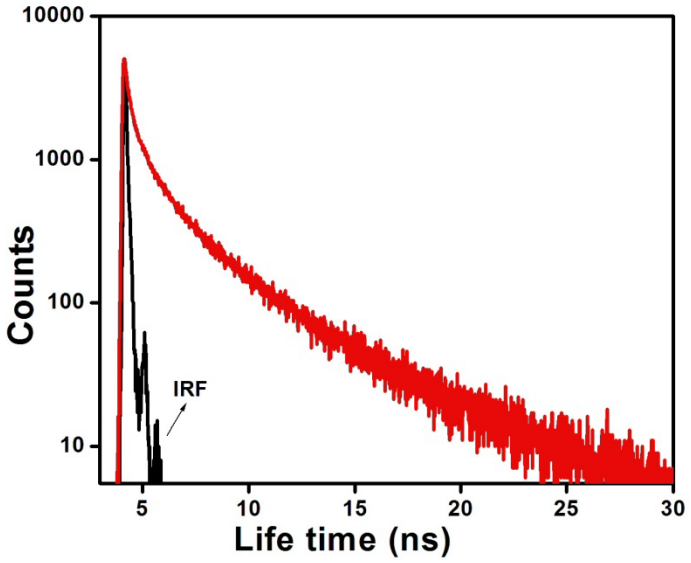
ESI Fig. 3. (a) The CD spectra of (a) hydrogel **1** and (b) peptide nanofibers decorated with Pd nanoparticles.

5. Fluorescence spectroscopy



ESI Fig. 4. Emission spectroscopy of hydrogel **1** reveals the π-π stacking interaction and self-assembly towards higher ordered aggregated structures. Concentration of the sample is 20 mmol L^{-1} and λ_{ex} = 270 nm.

6. Time correlated single photon counting (TCSPC)

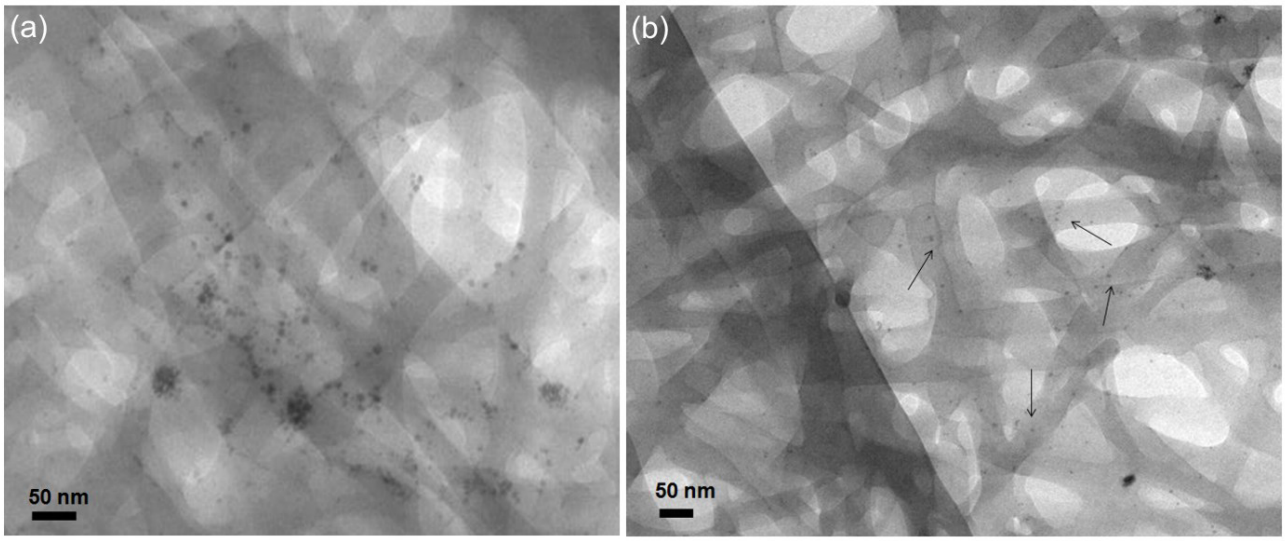


ESI Fig. 5. Time resolved spectroscopy for the hydrogel.

ESI Table 1. Decay parameters for hydrogel **1**.

Concentration of Hydrogel **1**	α_1	α_2	α_3	τ_1 (ns)	τ_2(ns)	τ_3(ns)	τ_a (ns)	$\chi 2$
20 mmol L^{-1}	0.26	0.09	0.65	0.96	3.81	0.18	0.69	1.09

7. TEM images of decorated Pd nanoparticles



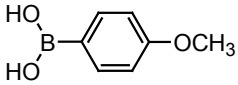
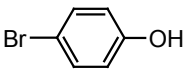
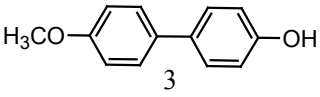
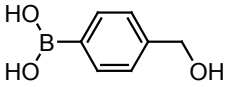
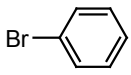
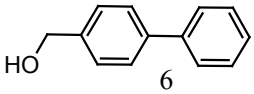
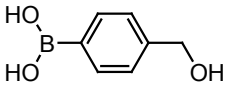
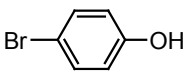
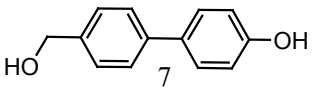
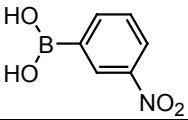
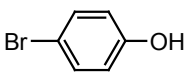
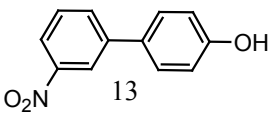
ESI Fig. 6. TEM images of Pd nanoparticles decorated peptide nanofibers.

8. Recovery of Pd nanoparticles after Suzuki coupling reactions and the recyclability of the catalyst

After the 1st batch of reaction, methanol was evaporated and 1M Na_2CO_3 was added to the reaction mixture for the removal of peptide nanofibers decorated Pd nanoparticles. The reaction mixture was extracted with chloroform (3 × 20 mL). The organic layer was evaporated to isolate the coupling products and the aqueous layer was centrifuged for five times by using a high-speed centrifuge (10000 rpm). After centrifugation, the Pd nanoparticles were precipitated out at the bottom of centrifuge tube. The Pd nanoparticles decorated on peptide nanofibers (~ 60%) were recovered after the 1st batch of reaction.

To test the recyclability, several experiments were set up. The recovered Pd nanoparticles were used further for Suzuki coupling reactions. In the 2nd batch, the mixture of 0.08 mmol aryl halide and 0.12 mmol of aryl boronic acid were dissolved in 2 mL of water-methanol (1:1) solvent. The recovered Pd nanoparticles (0.0024 mmol,) were added to the reaction mixture. Potassium carbonate (6 equiv., 0.48 mmol) was used as a base for the coupling reactions. We observed that 87-90% C-C coupling products were synthesized after 4 hours of reaction at 50 °C without loss in catalytic activity during 2nd batch of reaction.

ESI Table 2. Suzuki coupling reactions by using the recovered Pd nanoparticles after the 1st batch of reaction.

Entry	Boronic acids	Aryl halides	Products	Time (h)	Yield [b] (%)
1			 3	4	89
2			 6	4	87
3			 7	4	90
4			 13	4	87

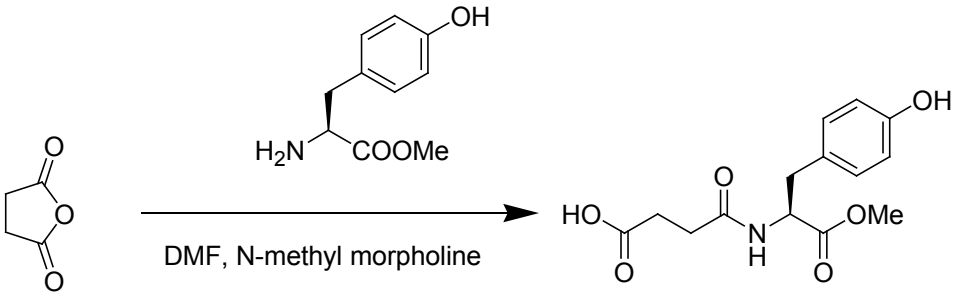
[b] Isolated yield

9. Synthesis of peptide bolaamphiphile

Peptide bolaamphiphile **1** employed in this report was synthesized by conventional solution phase methodology. The C-terminus of amino acid was protected as methyl ester. Couplings were mediated by dicyclohexylcarbodiimide-1-hydroxybenzotriazole (DCC-HOBt). The final compounds were purified and fully characterized by ^{1}H NMR and mass spectral studies.

Synthesis of HO-Phe(4)-Tyr(3)-Suc-Tyr(1)-Phe(2)-OH 1

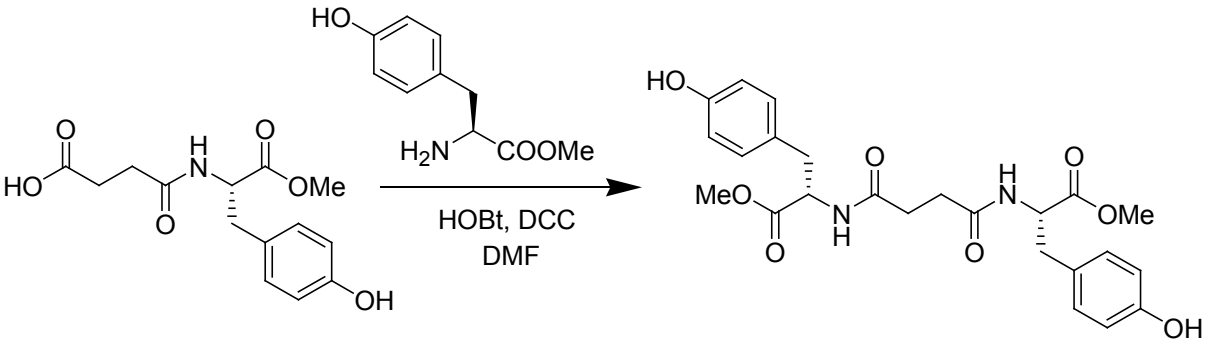
HO-Suc-Tyr(1)-OMe 1a:



0.5 g (5 mmol) succinic anhydride in 3 mL of DMF was cooled in an ice-water bath and H-Tyr-OMe was isolated from 1.16 g (5 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction by ethyl acetate. The ethyl acetate extract was concentrated to 8 mL. It was then added to the reaction mixture, followed immediately by 0.5 g (5 mmol, 550 µL) N-methyl morpholine. The reaction mixture was stirred for overnight. 50 mL ethyl acetate was added to the reaction mixture and the organic layer was washed with 1M HCl (3 X 50 mL). The ethyl acetate part was dried over anhydrous Na_2SO_4 and filtered. It was evaporated in vacuum to yield **1a** as sticky compound. Purification was done by silica gel column (100-200 mesh) using chloroform-methanol as eluent.

Yield: 1.32 g (4.5 mmol, 90 %); ϑ̃ = 3294 (s), 1721 (s), 1646 (s), 1543 (s) cm^{-1} ; ^{1}H NMR (400 MHz, DMSO-d_6, δ_{ppm}): 12.06 (s, 1H, -COO<u>H</u>), 8.29 (d, *J* = 7.6 Hz, 1H, NH of Tyr(1)), 7.00 (d, *J* = 8 Hz, 2H, ring protons of Tyr(1)), 6.67 (d, *J* = 8 Hz, 2H, ring protons of Tyr(1)), 4.36 (m, 1H, C$^{\alpha}$ H of Tyr(1)), 3.57 (s, 3H, COOC<u>H</u>$_3$), 2.86 (d, *J* = 6 Hz, 1H, C$^{\beta}$ Hs of Tyr(1)), 2.80 (d, *J* = 8.8 Hz, 1H, C$^{\beta}$ Hs of Tyr(1)), 2.35 (m, 4H, -C<u>H</u>$_2$- of Suc); $[\alpha]_D^{20}$ = +15.53 (*c* = 1.03 in CH_3OH); HRMS (ESI, *m/z*): $(M + Na)^+$ Calcd. for $C_{14}H_{17}NO_6Na$, 318.0948; found 318.0934.

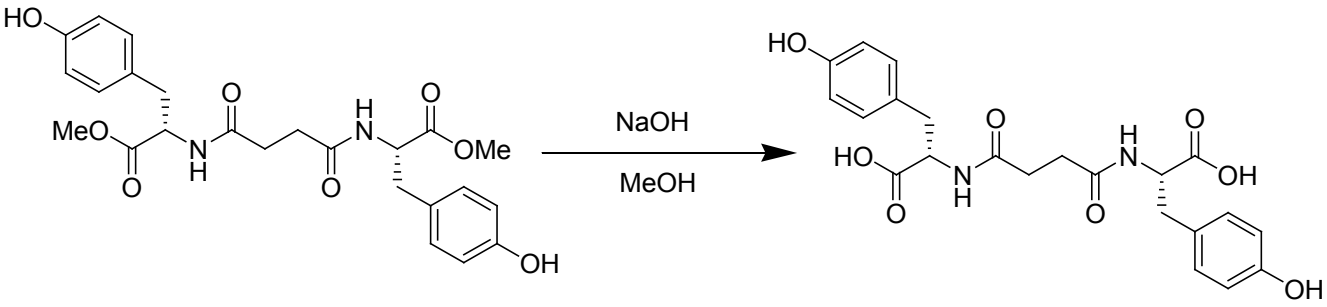
Meo-Tyr(2)-Suc-Tyr(1)-OMe 1b:



1.03 g (3.5 mmol) of HO-Suc-Tyr(1)-OMe **1a** in 3 mL of DMF was cooled in an ice-water bath and H-Tyr-OMe was isolated from 1.62 g (7 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 mL. It was then added to the reaction mixture, followed immediately by 0.68 g (3.85 mmol) DCC and 0.520 g (3.85 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 mL) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 50 mL), brine (2 × 50 mL), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **1b** as a white solid. Purification was done by silica gel column (100-200 mesh) using chloroform-methanol as eluent.

Yield: 1.37 g (2.9 mmol, 82.8 %); $\tilde{\upsilon}$ = 3322 (w), 3264(w), 1725 (s), 1639 (s), 1617 (s), 1568 (s) cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$, δ_{ppm}): 6.89 (d, *J* = 8.8 Hz, 4H, ring protons of Tyr(1) and Tyr(2)), 6.68 (d, *J* = 8.4 Hz, 4H, ring protons of Tyr(1) and Tyr(2)), 6.25 (d, *J* = 8.0 Hz, 2H, NH of Tyr(1) and Tyr(2)), 4.73 (m, 2H, $C^{\alpha}H$ of Tyr(1) and Tyr(2)), 3.66 (s, 6H, -COOC$\underline{H}_3$), 2.99 and 2.91 (d, *J* = 5.2 Hz, *J* = 6.8 Hz, 4H, $C^{\beta}Hs$ of Tyr(1) and Tyr(2)), 2.37 (m, 4H,-C$\underline{H}_2$- of Suc); $[\alpha]_D^{20}$ = + 12.67 (*c* = 0.31 in $CHCl_3$); HRMS (ESI, *m/z*): $(M + Na)^+$ Calcd. for $C_{24}H_{28}N_2O_8Na$, 473.1918; found 495.2321.

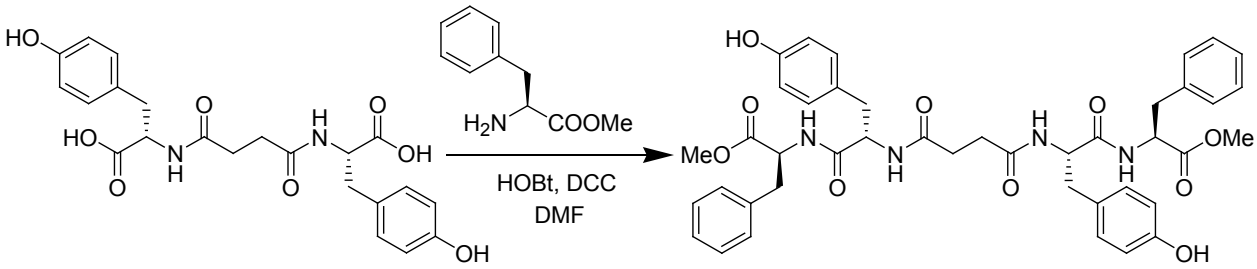
HO-Tyr-(2)-Suc-Tyr(1)-OH 1c:



1.27 g (2.7 mmol) of MeO-Tyr(2)-Suc-Tyr(1)-OMe **1b** in 6 mL MeOH was taken in a round bottom flask and 2M NaOH was added dropwise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 mL of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 mL). Then it was cooled down under ice water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1 M HCl. It was extracted with ethyl acetate (3 x 50 mL) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **1c** as a white solid.

Yield: 1.15 g (2.6 mmol, 96.29 %); $\tilde{\upsilon}$ = 3297 (m), 1711 (s), 1649 (s), 1614 (s), 1537 (s) cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6, δ_{ppm}): 12.57 (s, 1H, -COO<u>H</u>), 8.16(d, *J* = 8 Hz, 2H, NH of Tyr(1) and Tyr(2)), 7.06 (d, *J* = 8 Hz, 4H, ring protons of Tyr(1) and Tyr (2)), 6.71 (d, *J* = 8 Hz, 4H, ring protons of Tyr(1) and Tyr (2)), 4.34 (m, 2H, C^{α} H of Tyr(1) and Tyr (2)), 2.97 and 2.93 (d, *J* = 4.8 Hz, 2H, C^{β}Hs of Tyr(1) and Tyr(2)), 2.80 and 2.76 (d, *J* = 9.2 Hz, 2H, C^{β}Hs of Tyr(1) and Tyr(2)), 2.29 (m, 4H, -C<u>H</u>$_2$- of Suc); $[\alpha]_D^{20}$ = +35.34 (*c* = 0.43 in CH_3OH); HRMS (ESI, *m/z*): $(M + H)^+$ Calcd. for $C_{22}H_{25}N_2O_6$, 445.1611; found 445.1639.

MeO-Phe(4)-Tyr(3)-Suc-Tyr(1)-Phe(2)-OMe 1d:

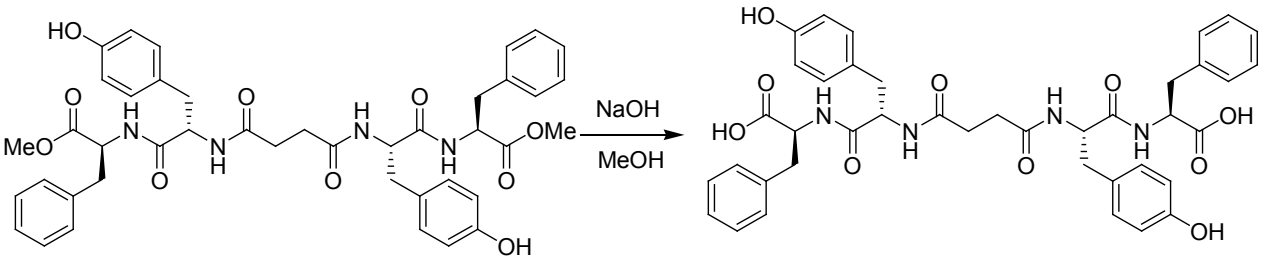


1.07 g (2.42 mmol) of HO-Tyr(2)-Suc-Tyr(1)-OH **1c** in 3 mL of DMF was cooled in an ice-water bath and H-Phe-OMe was isolated from 2.09 g (9.7 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 mL. It was then added to the reaction mixture, followed immediately by 1.09 g (5.32 mmol) DCC and 0.718 g (5.32 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 mL) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 50 mL), brine (2 × 50 mL), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **1d** as a white solid. Purification was done by silica gel column (100-200 mesh) using chloroform-methanol as eluent.

Yield: 1.53 g (2.0 mmol, 82.64 %); ^1H NMR (400 MHz, DMSO-d_6, δ_{ppm}): 8.36 (d, *J* = 7.6 Hz, 2H, NH of Phe(2) and Phe(4)), 7.98 (d, *J* = 8.8 Hz, 2H, NH of Tyr(1) and Tyr(3)), 7.25(d, *J* = 6.8 Hz, 4H, ring protons of Phe(2) and Phe(4)), 7.21(t, *J* = 7.6 Hz, 6H, ring protons of Phe(2) and

Phe(4)), 6.99 (d, J = 8.4, Hz, 4H, ring protons of Tyr(1) and Tyr(3)), 6.63(d, J = 8.8, Hz, 4H of Tyr(1) and Tyr(3)), 4.46 (m, 2H, $C^{\alpha}H$ of Phe(2) and Phe(4)), 4.40 (m, 2H, $C^{\alpha}Hs$ of Tyr(1) and Tyr(3)), 3.56 (s, 6H, -COOC$\underline{H}_3$), 2.99 and 2.97 (d, J = 6 Hz, 2H, d, J = 4.8 Hz, 2H, $C^{\beta}Hs$ of Phe(2) and Phe(4)), 2.86 and 2.82 (d, J = 4.8 Hz, 2H, d, J = 4.0 Hz, 2H, $C^{\beta}Hs$ of Tyr(1) and Tyr(3)), 2.50 (m, 4H, -C$\underline{H}_2$- of Suc); $[\alpha]_D^{20}$ = - 23.18 (c = 0.2 in CH_3OH); HRMS (ESI, *m/z*): $(M + Na)^+$ Calcd. for $C_{42}H_{46}N_4O_{10}Na$, 789.3112; found 789.3184.

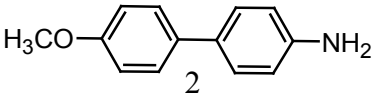
HO-Phe(4)-Tyr(3)-Suc-Tyr(1)-Phe(2)-OH 1:



1.38 g (1.8 mmol) of MeO-Phe(4)-Tyr(3)-Suc-Tyr(1)-Phe(2)-OMe **1d** in 10 mL MeOH was taken in a round bottom flask and 2M NaOH was added to it drop-wise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 mL of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 mL). Then it was cooled under ice water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1M HCl. It was extracted by ethyl acetate (3 x 50 mL) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **1** as a white solid.

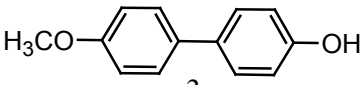
Yield: 1.25 g (1.7 mmol, 94.4%); $\tilde{\upsilon}$ = 3391 (s), 1708 (m), 1636 (s), 1559 (s), 1513 (m) cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6, δ_{ppm}): 12.72 (s, 2H, -COO$\underline{H}$), 8.23 (d, J = 7.6 Hz, 2H, NH of Phe(2) and Phe(4)), 8.00 (d, J = 8.4 Hz, 2H, NH of Tyr(1) and Tyr(3)), 7.32-7.27 (m, 10H, ring protons of Phe(2) and Phe(4)), 7.05 (d, J = 8.0, Hz, 4H, ring protons of Tyr(1) and Tyr(3)), 6.68 (d, J = 8.4, Hz, 4H of Tyr(1) and Tyr(3)), 4.46 (m, 4H, $C^{\alpha}H$ of Tyr (1), Phe(2), Tyr(3) and Phe(4)), 3.10 and 2.98 (d, J = 5.2 Hz, J = 8.8 Hz, 4H, $C^{\beta}Hs$ of Phe(2) and Phe(4)), 2.89 and 2.61 (d, J = 10.8 Hz, J = 10.0 Hz, 4H, $C^{\beta}Hs$ of Tyr(1) and Tyr(3)), 2.25 (m, 4H, -C$\underline{H}_2$- of Suc); ^{13}C NMR (100 MHz, DMSO-d_6, δ_{ppm}): 173.13, 172.82, 172.69, 171.38, 171.08, 169.19, 155.63, 137.68, 137.41, 130.02, 129.10, 129.00, 128.15, 127.97, 126.40, 114.75, 53.93, 53.44, 36.73, 36.58, 30.73, 23.26, 22.29; $[\alpha]_D^{20}$ = -23.75 (c = 0.12 in CH_3OH); HRMS (ESI, *m/z*): $(M + Na)^+$ Calcd. for $C_{40}H_{42}N_4O_{10}Na$, 761.2693; found 761.2622.

10. Characterizations of Suzuki coupling products



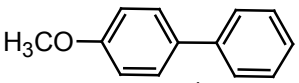
2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 (d, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.95 (d, 2H), 6.75 (d, *J* = 8 Hz, 2H), 3.84 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 157.39, 144.26, 132.87, 130.37, 126.71, 126.58, 126.38, 114.41, 113.14, 113.08, 54.31; HRMS (ESI, *m/z*): $(M + H)^+$ Calcd for $C_{13}H_{14}NO$, 200.1070; found 200.1069.



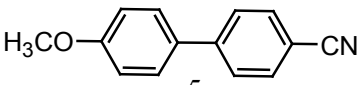
3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47(d, *J* = 8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 6.4 Hz, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 126.92, 126.69, 126.64, 118.72, 114.57, 113.14, 111.25, 59.47.



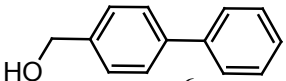
4

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (dd, *J* = 8.4 Hz, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 158.12, 139.80, 132.76, 127.68, 127.12, 126.71, 125.71, 113.12, 54.31.



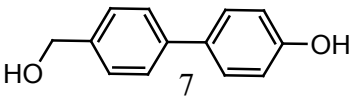
5

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.68 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 159.19, 144.21, 131.56, 130.51, 127.34, 126.71, 126.10, 118.07, 113.53, 113.14, 109.11, 54.38; HRMS (ESI, *m/z*): $(M)^+$ Calcd. for $C_{14}H_{11}NO$, 200.0841; found 200.0961



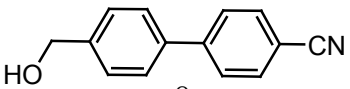
6

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 4.72 (s, 2H), 3.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 129.35, 129.25, 127.99, 127.02, 126.68, 126.35, 126.17, 125.48, 28.67;



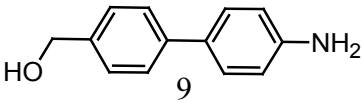
7

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8 Hz, 2H), 4.75 (s, 2H), 3.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 131.43, 130.83, 127.78, 126.61, 126.49, 126.26,126.01, 122.71, 116.16, 63.61; HRMS (ESI, *m/z*): $(M\text{-H})^-$ Calcd. for $C_{13}H_{11}O_2$, 199.0754; found 199.0769.



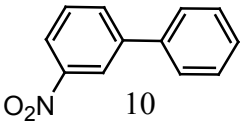
8

HRMS (ESI, *m/z*): $(M + K)^+$ Calcd. for $C_{14}H_{11}NOK$, 248.0478; found 248.0158.



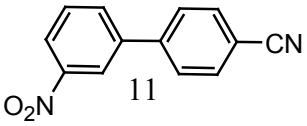
9

HRMS (ESI, *m/z*): $(M + H)^+$ Calcd. for $C_{13}H_{14}NO$, 200.1075; found 200.1051.



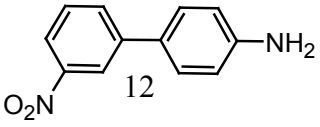
10

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (s,1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 8 Hz, 3H), 7.43 (t, *J* = 6.8 Hz, 1H); HRMS (ESI, *m/z*): $(M + 2Na)^+$ Calcd for $C_{12}H_9Na_2NO_2$, 245.0429; found 245.0709.



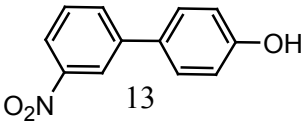
11

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (s,1H), 8.24 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.63 (m, 1H), 7.53 (d, *J* = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 132.16, 132.03, 131.95, 129.27, 129.19, 126.87, 126.40, 122.29, 121.11, 120.63, 109.94.



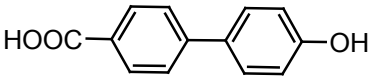
12

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (s,1H), 8.10 (d, *J* = 6.8 Hz, 1H), 7.85 (d, *J* = 6.4 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 6 Hz, 2H), 6.79 (d, *J* = 6 Hz, 2H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_{ppm}): 132.16, 132.03, 131.95, 129.27, 129.19, 126.87, 126.40, 122.29, 121.11, 120.63, 109.94; HRMS (ESI, *m/z*): $(M+H)^+$ Calcd. for $C_{12}H_{11}N_2O_2$, 215.0815; found 215.0819.



13

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50 (s, 1H), 8.31 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6 Hz, 1H), 7.70 (t, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.25 (s, 1H).



14

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.26 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 5.6 Hz, 2H), 6.66 (m, 4H), 6.06 (broad, 1H).