Supporting Information

A dimethyl ketal-protected benzoin-based linker suitable for photolytic release of unprotected peptides

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Assignment of the signals in $^1$H- and $^{13}$C-NMR spectra of compounds 3, 5-10 was accomplished using additional COSY, HSQC and HMBC experiments for each compound. For convenience in assigning resonances in NMR spectra, the numbering of atoms listed below does not coincide with IUPAC nomenclature.

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Compound 5
Compound 5

gCOSY
Compound 5

$^{13}$C NMR
Compound 5

gHSQC, multiplicity-edited
Red= CH/CH₃, Blue=CH₂
Compound 5

gHMBC
Compound 5
Compound 6
Compound 6

gCOSY
Compound 6

$^{13}$C NMR

C6, C5, C7, C4, C3 and C2
Compound 6

gHSQC, multiplicity-edited
Red=CH/CH₃, Blue=CH₂
Compound 6

gHMBC
Compound 6

gHMBC - expansion
Compound 7

**1H NMR**

- TBSO: 5.00 ppm
- OTBS: 3.54 ppm
- Four Si-Me: 0.56 ppm, 0.48 ppm, 0.35 ppm, 0.09 ppm
- Two tBu: 1.96 ppm, 1.36 ppm

- H7: 1.00 ppm
- H5: 2.07 ppm
- H3: 1.06 ppm
- H4: 1.08 ppm
- H16: 7.81 ppm
- H14: 7.81 ppm
- H18: 7.81 ppm
- H12: 7.81 ppm
- Two OMe: 6.32 ppm
- Two H9: 2.12 ppm
- Two H11: 2.12 ppm
- Two H10: 3.00 ppm
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Compound 7

[Chemical structure and NMR spectrum]
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Compound 7
Compound 7

gHSQC, multiplicity edited
Red=CH/CH₃, Blue=CH₂

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Compound 7

gHMBC
Compound 7

gHMBC - expansion
Compound 8
Compound 8

2D-gCOSY
Compound 8
Compound 8

gHSQC phase-edited
Red=CH/CH$_3$, Blue=CH$_2$
Compound 8

2D- gHMBC
Compound 3
Compound 3
Compound 3
Compound 3

2D-gHSQC phase-edited
Red=CH/CH₃, Blue=CH₂
Compound 3

2D-gHMBC
Compound 3

2D-gHMBC - expansion
Compound 9

HRMAS, 1H NMR
HRMAS 1H NMR of TYR on Linker (Compound 10)
Table 1, Entry 4

1H NMR of VAL-TYR after photo-cleavage from solid-phase support

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<table>
<thead>
<tr>
<th>2H4</th>
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<tbody>
<tr>
<td>H2</td>
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<tr>
<td>H7</td>
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</tbody>
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Water

MeOH

PEG

3H9
3H8
```
Table 1, Entry 4

2D-NOESY NMR of VAL-TYR after photo-cleavage from solid-phase support
500MHz 1H NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, WET solvent suppression.
500MHz 1H NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, WET solvent suppression.
500MHz 1H NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, WET solvent suppression.
500MHz 2D DQF-COSY of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, WET solvent suppression.
500MHz 2D DQF-COSY of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, WET solvent suppression.

KTRRRPRRSQRKRG
2D-DQF-COSY, Amide to alpha H correlations
500MHz TOCSY NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, with solvent suppression.

TOCSY, 80 ms
Relaxation delay 1.2000
Pulse width 9.2500
500MHz TOCSY NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, with solvent suppression.

TOCSY, 80 ms
Relaxation delay 1.2000
Pulse width 9.2500
500MHz TOCSY NMR of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, with solvent suppression.

TOCSY, 80 ms
Relaxation delay 1.2000
Pulse width 9.2500
500 MHz 1H-15N gHSQC (natural abundance) of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, with solvent suppression.

Concentrated sample KTRRRPRRSQRKRG; gNhsqc-Amides
500 MHz 1H-13C gHSQC (natural abundance) of Lys-Tyr-Arg-Arg-Arg-Pro-Arg-Arg-Ser-Gln-Arg-Lys-Arg-Gly after cleavage from solid-phase support, with no further purification. Solvent is 90%/10% H2O/D2O, with solvent suppression

Concentrated sample KTRRRPRRSQRKRG; gHSQC
Figure 1. Top view of the photoreactor.