Supporting Information

One-pot synthesis of monodisperse dual-functionalized polyethylene glycols through macrocyclic sulfates

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Table S1 Optimization of reaction conditions

![Chemical structure of compounds 2a and 3a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>NaClO (equiv.)</th>
<th>RuCl₃·3H₂O (equiv.)</th>
<th>Concentration (mmol/mL)</th>
<th>Yield (%)</th>
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<td>0.001</td>
<td>0.20</td>
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<td>90</td>
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<td>0.08</td>
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<tr>
<td>11</td>
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<td>0.005</td>
<td>0.06</td>
<td>82</td>
</tr>
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</table>

¹H NMR of compound 3a

![NMR spectrum of compound 3a]
$^1$H NMR of compound 3b

$^1$H NMR of compound 3c
$^1$H NMR of compound 3d

$^1$H NMR of compound 3e

S4
$^1$H NMR of compound 4a

$^1$H NMR of compound 4b
$^1$H NMR of compound 4c

$^{13}$C NMR of compound 4c
\textbf{19F NMR of compound 4c}

\includegraphics{19F_NMR.png}

\textbf{HRMS of compound 4c}

\includegraphics{HRMS.png}
$^1$H NMR of compound 4d

$^{13}$C NMR of compound 4d
HRMS of compound 4d

$^{1}$H NMR of compound 4e
$^1$H NMR of compound 4f

$^{13}$C NMR of compound 4f
HRMS of compound 4f

1H NMR of compound 4g
$^{13}$C NMR of compound 4g

HRMS of compound 4g
$^1$H NMR of compound 4h

$^{13}$C NMR of compound 4h
HRMS of compound 4h

^1^H NMR of compound 5a
$^1$H NMR of compound 5b

$^{13}$C NMR of compound 5b
HRMS of compound 5b

\[ \text{HRMS of compound } 5b \]

\[ \text{1H NMR of compound } 5c \]
$^{13}$C NMR of compound 5c

$^{19}$F NMR of compound 5c
HRMS of compound 5c

\[ \text{HRMS of compound 5c} \]

\[ \text{5c} \]

\[ \text{F}_3\text{C} \longrightarrow \text{O} \longrightarrow \text{CF}_3 \]

\[ \text{446.1395} \]

\[ \text{444.1025} \]

\[ \text{441.0339} \]

\[ \text{441.2615} \]

\[ \text{440.1374} \]

\[ \text{438.1233} \]

\[ \text{435.0473} \]

\[ \text{434.0074} \]

\[ \text{464.2576} \]

\[ \text{460.0351} \]

\[ \text{470.1683} \]

\[ \text{471.9472} \]

\[ \text{471.8906} \]

\[ \text{471.7337} \]

\[ \text{471.5769} \]

\[ \text{470.4148} \]

\[ \text{470.9128} \]

\[ \text{1H NMR of compound 5d} \]

\[ \text{1H NMR of compound 5d} \]

\[ \text{5d} \]

\[ \text{H NMR (400 MHz, CDCl\textsubscript{3})} \]
$^{13}$C NMR of compound 5d

HRMS of compound 5d
$^1$H NMR of compound 5e

$^{13}$C NMR of compound 5e
HRMS of compound 5e

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hrms.png}
\end{figure}

\textsuperscript{1}H NMR of compound 5f

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hnmr.png}
\end{figure}
$^{13}$C NMR of compound 5f

HRMS of compound 5f
$^1$H NMR of compound 5g

$^{13}$C NMR of compound 5g
HRMS of compound 5g

1H NMR of compound 5h
$^{13}$C NMR of compound 5h

HRMS of compound 5h
$^1$H NMR of compound 6a

$^{13}$C NMR of compound 6a
$^{19}$F NMR of compound 6a

HRMS of compound 6a
$^1$H NMR of compound 6b

$^{13}$C NMR of compound 6b
HRMS of compound 6b

1H NMR of compound 6c
\[ ^{13}\text{C} \text{NMR of compound 6c} \]

\[ \text{HRMS of compound 6c} \]
$^1$H NMR of compound 6d

$^{13}$C NMR of compound 6d
$^{19}$F NMR of compound 6d

HRMS of compound 6d
$^1$H NMR of compound 6e

$^{13}$C NMR of compound 6e
HRMS of compound 6e

$^{1}$H NMR of compound 6f
$^{13}$C NMR of compound 6f

HRMS of compound 6f
$^1$H NMR of compound 6g

$^{13}$C NMR of compound 6g
HRMS of compound 6g

\[ \text{RT: 12.03 mAU, 1 NL, 3.4760} \]
\[ \text{F1000 = c 0.3 Sum F1000 (535/000-3600/000)} \]

\[ \text{6g} \]

\[ \text{605.3093} \]

\[ 610.0754, 615.1591 \]

\[ \text{1H NMR of compound 6h} \]

\[ \text{f1 NMR (400 MHz, CDCl3)} \]
$^{13}$C NMR of compound 6h

HRMS of compound 6h
$^1$H NMR of compound 6i

$^{13}$C NMR of compound 6i
HRMS of compound 6i

1H NMR of compound 6j
$^{13}$C NMR of compound 6j

HRMS of compound 6j
$^1$H NMR of compound 7a

$^{13}$C NMR of compound 7a
$^{19}\text{F} \text{ NMR of compound 7a}$

$\text{HRMS of compound 7a}$
$^1$H NMR of compound 7b

$^{13}$C NMR of compound 7b
HRMS of compound 7b

1H NMR of compound 7c
$^{13}$C NMR of compound 7c

HRMS of compound 7c
$^1$H NMR of compound 7d

$^{13}$C NMR of compound 7d
$^{19}$F NMR of compound 7d

HRMS of compound 7d
$^1$H NMR of compound 7e

$^{13}$C NMR of compound 7e
HRMS of compound 7e

\[ \text{HRMS of compound 7e} \]

1H NMR of compound 7f

\[ \text{1H NMR of compound 7f} \]
$^{13}$C NMR of compound 7f

[Image of the $^{13}$C NMR spectrum of compound 7f]

HRMS of compound 7f

[Image of the HRMS spectrum of compound 7f]
$^1$H NMR of compound 7g

$^{13}$C NMR of compound 7g
HRMS of compound 7g

1H NMR of compound 7h
$^{13}$C NMR of compound 7h

HRMS of compound 7h
$^1$H NMR of compound 7i

$^{13}$C NMR of compound 7i
HRMS of compound 7i

1H NMR of compound 7j
$^{13}$C NMR of compound 7j

HRMS of compound 7j
$^1$H NMR of compound 8a

$^{13}$C NMR of compound 8a
HRMS of compound 8a

+ESI Scan (#17) Frag=70.0V 2018101701.1.d Subtract (3)

Counts vs. Mass-to-Charge (m/z)

520 525 530 535 540 545 550 555 560 565 570 575

568.34994

573.30364

H NMR of compound 8b

^H NMR (400 MHz, CDCl3)
$^{13}$C NMR of compound 8b

HRMS of compound 8b