Efficient pseudo-five-component coupling-Fiesselmann synthesis of luminescent oligothiophenes and their modification

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Supporting Information

Table of Contents

1 GENERAL CONSIDERATIONS 1
2 1H AND 13C NMR SPECTRA 2
3 UV-VIS AND FLUORESCENCE SPECTRA 33
1 GENERAL CONSIDERATIONS

All cross-coupling reactions were carried out in oven-dried *Schlenk* glassware using septa and syringes under nitrogen or argon atmosphere. THF was dried using MBraun system MB-SPS-800, and triethylamine was refluxed under argon over ketyl sodium, distilled and stored in a *Schlenk* flask over potassium hydroxide pellets under argon atmosphere.

Commercial grade reagents were used as supplied without further purification and were purchased from Sigma-Aldrich Chemie GmbH, Fluka AG, ABCR GmBH & Co. KG, Alfa Aesar GmbH & Co. KG and Riedel-de Haën. Some of the alkynes and the catalysts were prepared according to literature.

The purification of products was performed on silica gel 60 (0.04-0.063 mm) from Macherey-Nagel GmbH & Co. KG using flash technique and under pressure of 2 bar or using the automatic chromatography system Biotage SP4.

The crude mixtures were adsorbed on Celite® 545 (0.02-0.10 mm) from Merck KGaA Darmstadt or silica gel 60 (0.2-0.5 mm) from Merck Darmstadt prior to chromatographic purification.

The reaction progress was monitored qualitatively using TLC Silica gel 60 F254 5 x 7.5 cm aluminium sheets obtained by Merck KGaA Darmstadt. The spots were detected with UV light at 254 nm and using aqueous potassium permanganate solution.

$^1$H, $^{13}$C, and 135-DEPT NMR spectra were recorded on Bruker DRX 500 spectrometer. CDCl$_3$ and DMSO-d$_6$ were used as deuterated solvents. TMS was used as reference ($\delta = 0.0$) or the resonances of the solvents were locked as internal standards (CDCl$_3$: $^1$H $\delta$ 7.24, $^{13}$C $\delta$ 77.2). The multiplicities of signals were abbreviated as follows: s: singlet; d: doublet; t: triplet; dd: doublet of doublets, m: multiplet and br: broad signal. The type of carbon nuclei was determined on the basis of 135-DEPT NMR spectra. EI mass spectra were measured on Finnigan MAT 8200 spectrometer. IR spectra were obtained on Bruker Vector 22 FT-IR. The solids were measured as KBr pellets and oils as films on KBr plates. The intensity of signals is abbreviated as follows: s (strong), m (medium) and w (weak). The melting points (uncorrected) were measured on Reichert-Jung Thermovar. Combustion analyses were carried out on Perkin Elmer Series II Analyser 2400 in the microanalytical laboratory of Institut für Pharmazeutische und Medizinische Chemie at the Heinrich-Heine-Universität Düsseldorf.
2 \textbf{\textsuperscript{1}H AND \textsuperscript{13}C NMR SPECTRA}

\textsuperscript{1}H-NMR of 6a (CDCl\textsubscript{3}, 500 MHz, 298 K)

\textsuperscript{13}C-NMR of 6a (CDCl\textsubscript{3}, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 6a (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 6b (CDCl$_3$, 500 MHz, 298 K)
$^{1}H$ and $^{13}C$ NMR SPECTRA

$^{13}C$-NMR of 6b (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 6b (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 6c (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 6c (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 6c (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 6d (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 6d (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 6d (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$DEPT of 6e (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 6f (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 6f (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 6f (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 6g (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 6g (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 8a (CDCl$_3$, 500 MHz, 298 K)

$^{13}$S-DEPT of 6g (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 8a (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 8a (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 8b (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 8b (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 8b (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 8c (CDCl$_3$, 500 MHz, 298 K)
1H and 13C NMR SPECTRA

13C-NMR of 8c (CDCl₃, 125 MHz, 298 K)

135-DEPT of 8c (CDCl₃, 125 MHz, 298 K)

1H-NMR of 8d (CDCl₃, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 8d (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 8d (CDCl$_3$, 125 MHz, 298 K)
$^1H$ and $^{13}C$ NMR SPECTRA

$^1H$-NMR of 8e (CDCl$_3$, 500 MHz, 298 K)

$^{13}C$-NMR of 8e (CDCl$_3$, 125 MHz, 298 K)
$^{1}H$ and $^{13}C$ NMR SPECTRA

$^{13}$-DEPT of 8e (CDCl$_3$, 125 MHz, 298 K)

$^{1}$H-NMR of 8f (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 8f (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 8f (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 10a (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 10a (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 10a (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 10b (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 10b (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 10b (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 12a (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 12a (CDCl$_3$, 125 MHz, 298 K)
\(^1\text{H}\) and \(^{13}\text{C}\) NMR SPECTRA

135-DEPT of \textit{12a} (CDCl\(_3\), 125 MHz, 298 K)

\(^1\text{H}\)-NMR of \textit{12b} (CDCl\(_3\), 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 12b (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 12b (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 13 (CDCl$_3$, 500 MHz, 298 K)

- 1H-NMR of 13 (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 13 (CDCl$_3$, 125 MHz, 298 K)

- $^{13}$C-NMR of 13 (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 13 (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 14 (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 14 (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 14 (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^1$H-NMR of 15 (CDCl$_3$, 500 MHz, 298 K)

$^{13}$C-NMR of 15 (CDCl$_3$, 125 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

135-DEPT of 15 (CDCl$_3$, 125 MHz, 298 K)

$^1$H-NMR of 16 (CDCl$_3$, 500 MHz, 298 K)
$^1$H and $^{13}$C NMR SPECTRA

$^{13}$C-NMR of 16 (CDCl$_3$, 125 MHz, 298 K)

135-DEPT of 16 (CDCl$_3$, 125 MHz, 298 K)
3 UV-VIS AND FLUORESCENCE SPECTRA

Figure 1: Absorption (solid line) and emission (dashed line) spectra of compounds 6 in CH$_2$Cl$_2$, T = 293 K.

Figure 2: Absorption (solid line) and emission (dashed line) spectra of compounds 8 in CH$_2$Cl$_2$, T = 293 K.
Figure 3: Absorption (solid line) and emission (dashed line) spectra of compounds 10 in CH$_2$Cl$_2$, T = 293 K.

Figure 4: Absorption (solid line) and emission (dashed line) spectra of compounds 12 in CH$_2$Cl$_2$, T = 293 K.
Figure 5: Absorption (solid line) and emission (dashed line) spectra of compounds 13 and 14 in CH₂Cl₂, T= 293 K.

Figure 6: Absorption (solid line) and emission (dashed line) spectra of compounds 15 and 16 in CH₂Cl₂, T= 293 K.