A tandem elimination–cyclization–desulfitative arylation reaction of 2-(gem-dibromovinyl)phenols(thiophenols) with sodium arylsulfinates

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1. General considerations

All the tandem reactions of 2-(gem-dibromovinyl)phenols (thiophnols) with sodium arylsulfinate were carried out under a nitrogen atmosphere. $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance 400 MHz NMR spectrometer (400 MHz or 100 MHz, respectively) with CDCl$_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. The solvents and general chemicals were purchased from commercial suppliers and used without further purification. All the gem-dibromovinyl substrates were synthesized according to the reported procedures in the literature (Newman, S. G.; Aureggi, V.; Bryan, C. S.; Lautens, M. Chem. Commun. 2009, 5236–5238).

2. Typical procedure for the tandem elimination–cyclization–desulfative arylation reaction

A sealable reaction tube equipped with a magnetic stirrer bar was charged with gem-dibromovinyl substrate (0.50 mmol), TBAF (1.0 mmol) and DMF (3.0 mL). The reaction mixture was stirred for 4 h at room temperature, than sodium arylsulfinate (1.0 mmol), PdCl$_2$ (0.050 mmol), Cu(OAc)$_2$ (1.0 mmol), NEt$_3$ (1.0 mmol) were added to the reaction system. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 110 °C. After stirring the mixture at this temperature for 12 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water and brine, dried over MgSO$_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (eluant: petroleum ether) to afford the corresponding product.
3. Characterization data for all products

![Chemical structure](image)

**3a:**[^1] mp 120–121 °C.

^1^H NMR (400 MHz, CDCl₃): δ = 7.90 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.49–7.46 (m, 2H), 7.40–7.36 (m, 1H), 7.33–7.24 (m, 2H), 7.05 (s, 1H); ^13^C NMR (100 MHz, CDCl₃): δ = 155.9, 154.9, 130.5, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3.

![Chemical structure](image)

**3b:**[^1] mp 155–156 °C.

^1^H NMR (400 MHz, CDCl₃): δ = 7.83–7.81 (m, 2H), 7.51–7.50 (m, 1H), 7.45–7.33 (m, 4H), 7.22–7.19 (m, 1H), 6.91 (s, 1H); ^13^C NMR (100 MHz, CDCl₃): δ = 157.4, 153.2, 130.6, 129.9, 129.0, 128.8, 128.5, 125.0, 124.4, 120.4, 112.1, 100.8.

![Chemical structure](image)

**3c:**[^1] mp 131–132 °C.

^1^H NMR (400 MHz, CDCl₃): δ = 7.87 (d, J = 8.0 Hz, 2H), 7.48–7.42 (m, 3H), 7.37 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.98 (s, 1H), 6.92 (dd, J = 8.0, 2.8 Hz, 1H), 3.88 (s, 3H); ^13^C NMR (100 MHz, CDCl₃): δ = 156.7, 156.1, 150.0, 130.6, 129.8, 128.8, 128.5, 124.9, 113.0, 111.6, 103.3, 101.5, 55.9.
3d: \(^{[1]}\) mp 129–130 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.88 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H}), 7.48–7.34 \text{ (m, } 5\text{H}), 7.12 \text{ (d, } J = 8.0 \text{ Hz, } 1\text{H}), 6.97 \text{ (s, } 1\text{H}), 2.47 \text{ (s, } 3\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 156.0, 153.3, 132.3, 129.3, 128.8, 128.4, 125.5, 124.9, 120.7, 110.7, 101.1, 21.4.\)

3e: \(^{[1]}\) mp 103–104 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.93–7.91 \text{ (m, } 2\text{H}), 7.65 \text{ (s, } 1\text{H}), 7.52–7.48 \text{ (m, } 3\text{H}), 7.43–7.39 \text{ (m, } 2\text{H}), 7.05 \text{ (s, } 1\text{H}), 1.46 \text{ (s, } 9\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 156.0, 153.2, 146.0, 130.7, 128.9, 128.7, 128.3, 124.8, 122.2, 117.1, 110.4, 101.5, 34.7, 31.8.\)

3f: \(^{[1]}\) mp 78–79 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.84 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H}), 7.47–7.43 \text{ (m, } 3\text{H}), 7.36–7.32 \text{ (m, } 1\text{H}), 7.00 \text{ (d, } J = 1.6 \text{ Hz, } 1\text{H}), 6.97 \text{ (s, } 1\text{H}), 6.90 \text{ (dd, } J = 8.0, 2.4 \text{ Hz, } 1\text{H}), 3.89 \text{ (s, } 3\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 158.1, 155.9, 155.1, 130.7, 128.7, 128.0, 124.4, 122.6, 121.0, 112.0, 101.1, 95.9, 55.7.\)
3g. \(^{[1]}\) mp 151–152 °C.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.51\) (d, \(J = 2.4\) Hz, 1H), 8.22 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.90–7.88 (m, 2H), 7.60 (d, \(J = 9.2\) Hz, 1H), 7.52–7.48 (m, 2H), 7.46–7.42 (m, 1H), 7.13 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 159.3, 157.6, 144.3, 129.7, 129.6, 129.2, 129.0, 125.3, 120.1, 117.2, 111.4, 101.6.\)

3h. \(^{[1]}\) mp 78–79 °C.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.94–7.92\) (m, 2H), 7.49–7.45 (m, 2H), 7.39–7.36 (m, 1H), 7.23–7.16 (m, 2H), 7.04 (s, 1H), 6.84 (d, \(J = 8.0\) Hz, 1H), 4.08 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 156.1, 145.4, 144.2, 131.0, 130.4, 128.7, 128.6, 125.1, 123.6, 113.4, 106.7, 101.7, 56.2.\)

3i. \(^{[2]}\) mp 128–129 °C.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.89\) (d, \(J = 8.0\) Hz, 2H), 7.50–7.40 (m, 4H), 7.28 (d, \(J = 1.6\) Hz, 1H), 6.98 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 158.1, 149.2, 131.5, 129.4, 129.3, 128.9, 128.7, 125.2, 124.3, 119.0, 117.1, 101.2.\)
3j: mp 60–61 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85–7.83 (m, 2H), 7.43–7.39 (m, 2H), 7.33–7.29 (m, 1H), 7.16 (s, 1H), 6.90–6.88 (m, 2H), 2.52 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.6, 152.4, 132.3, 130.8, 128.8, 128.7, 128.2, 126.6, 124.8, 120.8, 118.1, 101.3, 21.3, 15.0.

3k: mp 142–143 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.20 (d, $J$ = 8.0 Hz, 1H), 7.98–7.94 (m, 3H), 7.76–7.70 (m, 2H), 7.64–7.60 (m, 1H), 7.55 (s, 1H), 7.53–7.48 (m, 3H), 7.39–7.36 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.4, 152.4, 130.7, 130.4, 128.9, 128.8, 128.3, 127.6, 126.3, 125.2, 124.7, 124.6, 124.5, 123.5, 112.3, 100.5.

3l: mp 174–176 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.87–7.85 (m, 1H), 7.81–7.79 (m, 1H), 7.76–7.74 (m, 2H), 7.58 (s, 1H), 7.47–7.44 (m, 2H), 7.40–7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 144.2, 140.7, 139.5, 134.3, 128.9, 128.2, 126.5, 124.5, 124.3, 123.5,
122.2, 119.4.

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3m: \([1]\) mp 111–112 °C.

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3\text{)}: \delta = 7.77–7.71 \text{ (m, 4H), 7.48–7.45 \text{ (m, 2H), 7.41–7.37 (m, 2H), 7.27–7.23 \text{ (m, 1H);} \ \text{^1\text{C NMR (100 MHz, CDCl}_3\text{)}:} \ \delta = 145.2, 140.4, 138.9, 133.7, 129.0, 128.6, 128.4, 126.5, 124.8, 124.4, 120.7, 117.6.}
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4a: \([3]\) mp 126–127 °C.

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3\text{)}: \delta = 7.79 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.61–7.53 \text{ (m, 2H), 7.32–7.23 \text{ (m, 4H), 6.99 (s, 1H), 2.43 (s, 3H);} \ \text{^1\text{C NMR (100 MHz, CDCl}_3\text{)}:} \ \delta = 156.2, 154.8, 138.6, 129.5, 129.4, 127.8, 124.9, 124.0, 122.9, 120.7, 111.1, 100.6, 21.4.}
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4b: \([4]\) mp 148–149 °C.

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3\text{)}: \delta = 7.80 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.61 (d, } J = 7.2 \text{ Hz, 1H), 7.54 (d, } J = 8.0 \text{ Hz, 1H), 7.43 (d, } J = 8.0 \text{ Hz, 2H), 7.35–7.25 \text{ (m, 2H), 7.01 (s, 1H);} \ \text{^1\text{C NMR (100 MHz, CDCl}_3\text{)}:} \ \delta = 154.9, 154.8, 134.3, 129.1, 129.0, 129.0, 126.1, 124.6, 123.1, 121.0, 111.2, 101.8.}
\]
$4c^{[5]}$ mp 148–149 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.74$ (d, $J = 8.0$ Hz, 2H), 7.61–7.53 (m, 4H), 7.34–7.24 (m, 2H), 7.03 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 154.9$, 154.7, 131.9, 129.4, 129.0, 126.3, 124.6, 123.1, 122.5, 121.0, 111.2, 101.8.

$4d^{[6]}$ mp 128–129 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.34–7.25 (m, 2H), 7.02 (s, 1H), 1.41 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 156.2$, 154.9, 151.8, 129.4, 127.8, 125.8, 124.8, 124.0, 122.9, 120.8, 111.2, 100.7, 34.8, 31.3.

$4e^{[3]}$ mp 149–150 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.8$ Hz, 2H), 7.58–7.57 (m, 1H), 7.53–7.51 (m, 1H), 7.29–7.22 (m, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 6.91 (s, 1H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 160.0$, 156.1, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.4.
4f: \([17]\) mp 183–184 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.31 (d, J = 8.4 \text{ Hz}, 2\text{H}), 8.01 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.66–7.64 (m, 1\text{H}), 7.58–7.56 (m, 1\text{H}), 7.40–7.36 (m, 1\text{H}), 7.31–7.27 (m, 1\text{H}), 7.24 (s, 1\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.4, 153.2, 147.2, 136.3, 128.6, 125.8, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1.\)

4g: \([3]\) mp 119–120 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.87–7.84 (m, 2\text{H}), 7.61–7.60 (m, 1\text{H}), 7.56–7.54 (m, 1\text{H}), 7.34–7.27 (m, 2\text{H}), 7.19–7.14 (m, 2\text{H}), 6.97 (s, 1\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 162.8 (d, J = 247.2 \text{ Hz}), 155.0, 154.8, 129.1, 126.7 (d, J = 8.1 \text{ Hz}), 124.3, 123.0, 120.9, 115.8 (d, J = 21.8 \text{ Hz}), 111.1, 101.0, 100.9.\)

4h: \([8]\) mp 77–78 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.74–7.70 (m, 2\text{H}), 7.61 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.56 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.39–7.24 (m, 3\text{H}), 7.21–7.19 (m, 1\text{H}), 7.04 (s, 1\text{H}), 2.46 (s, 3\text{H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 156.1, 154.9, 138.4, 130.4, 129.4, 129.3, 128.7, 125.5, 124.2, 122.9, 122.1, 120.8, 111.1, 101.2, 21.5.\)
4i: mp 98–99 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.86–7.84 (m, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.32–7.28 (m, 4H), 7.26–7.24 (m, 1H), 6.90 (s, 1H), 2.59 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 155.7, 154.4, 135.9, 131.2, 130.0, 129.2, 128.5, 128.2, 126.1, 124.2, 122.8, 120.9, 111.1, 105.1, 21.9.
4. $^1$H and $^{13}$C NMR spectra of the products

![NMR spectra of 3a](image)

![NMR spectra of 3a](image)
5. References


