Supplementary Information

Direct difunctionalization of alkynes with sulfinic acids and molecular iodine: a simple and convenient approach to (E)-β-iodovinyl sulfones

Wei Wei, Jiangwei Wen, Daoshan Yang, Huijun Jing, Jinmao You, Hua Wang*

a The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China.
*Phone: +86 537 4458317; Fax: +86 537 4458317. E-mail: huawang_qfnu@126.com

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz $^1$H, 100 MHz $^{13}$C) at room temperature, the chemical shifts ($\delta$) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).
2. General procedure for direct synthesis of \((E)\)-\(\beta\)-iodovinyl sulfones via difunctionalization of alkynes with sulfinic acids and molecular iodine.

\[
\begin{align*}
R^1&=\text{alkyne} \\
R^2&=\text{sulfinic acid} \\
I_2&=\text{molecular iodine} \\
DMEM&=\text{DME}
\end{align*}
\]

In a sealed tube, alkynes (0.5 mmol), sulfinic acids (1.0 mmol), molecular iodine (0.5 mmol), and DME (2 mL) were added. The mixture was allowed to stir at 100°C for 12-24h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3. The procedure (A) for the reaction of \((E)\)-\(\beta\)-iodovinyl sulfone with alkynes leading to alkynylation products.

\[
\begin{align*}
\text{I} & \quad \text{S} \\
\text{O} & \quad \text{O} \\
\text{PdCl}_2(\text{PPh}_3)_2 & \quad \text{CuI} \quad \text{Et}_3\text{N} \quad \text{THF} \quad \text{1h}
\end{align*}
\]

To a mixture of \((E)\)-\(\beta\)-iodovinyl sulfone 3aa (0.25 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (3 mol%), CuI (5 mol%), Et\(_3\)N (0.25 mmol), and alkyne (0.75 mmol) in a 25 mL round-bottomed flask at room temperature, was added the THF (2 mL). The reaction vessel was allowed to stir at room temperature for 1 h. After the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products.

4. The procedure (B) for the synthesis of acetylenic sulfone (5aa).
In a sealed tube, phenylacetylene \( 1a \) (0.5 mmol), benzenesulfinic acid \( 2a \) (1.0 mmol), molecular iodine (0.5 mmol), \( K_2CO_3 \) (1 mmol), and DME (2 mL) were added. The mixture was allowed to stir at 100°C for 12h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product \( 5aa \) (78%).

5. The procedure (C) for the synthesis of (E)-vinyl sulfones.

In a sealed tube, alkenes (0.5 mmol), sulfinic acids (1.0 mmol), molecular iodine (0.5 mmol), and DCE (2 mL) were added. The mixture was allowed to stir at 60°C for 12h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired (E)-vinyl sulfones.

6. Characterization data of products 3aa-6af

(E)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene\(^{[1]}\)

Compound \( 3aa \) was obtained in 88% yield according to the general procedure (12h). \(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \( \delta 7.61-7.55 \) (m, 3H), \( 7.41 \) (s, 1H), \( 7.40 \) (t, \( J = 7.8 \) Hz, 2H), \( 7.34-7.28 \) (m, 3H), \( 7.25-7.23 \) (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): \( \delta 141.1, 140.3, 139.6, 133.5, 129.8, 129.0, 128.0, 127.8, 127.7, 114.7 \); HRMS calc. for \( C_{14}H_{11}IO_2SNa \) (M+Na\(^+\)), 392.9422; found, 392.9424.

(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methoxybenzene\(^{[1]}\)

\( (E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4\)methoxybenzene
Compound **3ba** was obtained in 88% yield according to the general procedure (12h).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.63 (d, $J = 7.3$ Hz, 2H), 7.56 (d, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.9$ Hz, 2H), 7.33 (s, 1H), 7.27 (t, $J = 6.6$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 160.9, 140.5, 140.2, 133.5, 131.8, 130.0, 129.0, 127.8, 115.5, 113.3, 55.4; HRMS calc. for C$_{15}$H$_{13}$I$_2$SNa (M+Na)$^+$, 422.9528; found, 422.9529.

\[(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methylbenzene\]

Compound **3ca** was obtained in 75% yield according to the general procedure (12h).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.64-7.62 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.41 (t, $J = 8.1$ Hz, 2H), 7.37 (s, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 140.6, 140.4, 140.3, 136.8, 133.5, 129.0, 128.6, 127.8, 115.4, 21.5; HRMS calc. for C$_{15}$H$_{13}$I$_2$SNa (M+Na)$^+$, 406.9579; found, 406.9577.

\[(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-3-methylbenzene\]

Compound **3da** was obtained in 90% yield according to the general procedure (12h).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.59-7.53 (m, 3H), 7.41 (s, 1H), 7.39 (t, $J = 8.3$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 6.93 (s, 1H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.1, 140.3, 139.5, 137.7, 133.4, 130.7, 128.9, 128.0, 127.9, 124.8, 115.2, 21.3; HRMS calc. for C$_{15}$H$_{14}$I$_2$S (M+H)$^+$, 384.9759; found, 384.9759.

\[(E)-1-fluoro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene\]

Compound **3ea** was obtained in 71% yield according to the general procedure (12h).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.64-7.58 (m, 3H), 7.45 (t, $J = 8.1$ Hz, 2H), 7.40 (s, 1H), 7.28-7.25 (m, 2H), 6.99 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 163.2 (d, $J = 250.1$ Hz), 141.5, 140.2, 135.6 (d, $J = 14.1$ Hz), 133.7, 130.0 (d, $J = 34.6$ Hz), 129.1, 127.8, 115.1 (d, $J = 22.0$ Hz), 113.1; HRMS calc. for C$_{14}$H$_{10}$FIO$_2$SNa (M+Na)$^+$, 410.9328; found, 410.9324.
(E)-1-chloro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene[1] Cl

Compound 3fa was obtained in 73% yield according to the general procedure (12h). 1H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.59 (m, 3H), 7.45 (t, J = 8.0 Hz, 2H), 7.39 (s, 1H), 7.28 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 141.6, 140.1, 138.0, 136.0, 133.7, 129.2, 129.1, 128.3, 127.8, 112.7; HRMS calc. for C₁₄H₁₀ClIO₂SNa (M+Na)^+, 426.9032; found, 426.9033.

(E)-1-bromo-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene[1] Br

Compound 3ga was obtained in 83% yield according to the general procedure (12h). 1H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.60 (m, 3H), 7.48-7.43 (m, 4H), 7.40 (s, 1H), 7.12 (d, J = 8.5 Hz, 2H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 141.6, 140.1, 138.5, 133.7, 131.2, 129.3, 129.2, 127.8, 124.3, 112.6; HRMS calc. for C₁₄H₁₀BrIO₂SNa (M+Na)^+, 470.8527; found, 470.8529.

(E)-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzonitrile NC

Compound 3ha was obtained in 78% yield according to the general procedure (16h). 1H NMR (CDCl₃, 400 MHz, ppm): δ 7.67-7.62 (m, 5H), 7.50 (t, J = 7.4 Hz, 2H), 7.41 (s, 1H), 7.36 (d, J = 8.5 Hz, 2H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 144.1, 142.1, 139.9, 134.1, 131.8, 129.4, 128.2, 127.8, 118.0, 113.4, 110.4; HRMS calc. for C₁₅H₁₀INO₂SNa (M+Na)^+, 417.9375; found, 417.9370.

(E)-4-(1-iodo-2-(phenylsulfonyl)vinyl)biphenyl Ph

Compound 3ia was obtained in 90% yield according to the general procedure (12h). 1H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.59 (m, 4H), 7.57 (t, J = 7.5 Hz, 1H), 7.52-7.48 (m, 4H), 7.45 (s, 1H), 7.44-7.38 (m, 3H), 7.32 (d, J = 8.3 Hz, 2H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 142.7, 141.3, 140.3, 140.0, 138.4, 133.5, 129.0, 128.9, 128.4, 128.0, 127.9, 127.1, 126.6, 114.4; HRMS calc. for C₂₀H₁₅IO₂SNa (M+Na)^+, 468.9735; found, 468.9729.
(E)-3-(1-iodo-2-(phenylsulfonyl)vinyl)thiophene

Compound 3ja was obtained in 62% yield according to the general procedure (12h).
1H NMR (CDCl₃, 400 MHz, ppm): δ 7.66-7.63 (m, 2H), 7.60 (dd, J₁ = 1.3 Hz, J₂ = 3.0 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 8.1 Hz, 2H), 7.39 (s, 1H), 7.21 (dd, J₁ = 1.3 Hz, J₂ = 5.0 Hz, 1H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 141.3, 140.2, 138.8, 133.5, 129.0, 128.4, 127.6, 125.5, 108.0; HRMS calc. for C₁₂H₉IO₂S₂Na (M+Na)⁺, 398.8986; found, 398.8983.

(E)-(1-iodo-1-phenylprop-1-en-2-ylsulfonyl)benzene

Compound 3ka was obtained in 70% yield according to the general procedure (12h).
1H NMR (CDCl₃, 400 MHz, ppm): δ 7.53-7.50 (m, 3H), 7.37 (t, J = 6.5 Hz, 2H), 7.25-7.22 (m, 3H), 7.12-7.10 (m, 2H), 2.56 (s, 3H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 144.0, 142.8, 140.4, 133.1, 128.9, 128.7, 127.7, 127.6, 116.1, 27.0; HRMS calc. for C₁₅H₁₄IO₂S (M+H)⁺, 384.9759; found, 384.9757.

(E)-1-(1-iodo-2-(phenylsulfonyl)prop-1-enyl)naphthalene

Compound 3la was obtained in 82% yield according to the general procedure (12h).
1H NMR (CDCl₃, 400 MHz, ppm): δ 7.86-7.80 (m, 2H), 7.71 (s, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.47-7.38 (m, 4H), 7.32 (d, J = 7.3 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 8.0 Hz, 2H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 143.7, 139.2, 136.1, 133.4, 133.1, 130.2, 128.5, 128.3, 127.8, 126.6, 126.3, 125.2, 125.0, 124.9, 112.4; HRMS calc. for C₁₈H₁₃IO₂SNa (M+Na)⁺, 442.9579; found, 442.9578.

(E)-ethyl 2-iodo-3-(phenylsulfonyl)acrylate

Compound 3ma was obtained in 36% yield according to the general procedure (12h).
1H NMR (CDCl₃, 400 MHz, ppm): δ 8.00-7.98 (m, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 8.0 Hz, 2H), 6.98 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); 13C NMR (CDCl₃, 100 MHz, ppm): δ 164.6, 139.7, 139.0, 134.3, 129.6, 128.2, 100.4, 63.4, 13.8; HRMS calc. for C₁₁H₁₁IO₄SNa (M+Na)⁺, 388.9320; found, 388.9319.
Compound 3na was obtained in 12% yield according to the general procedure (12h). 
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.95-7.92 (m, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.9 Hz, 2H), 7.04 (s, 1H), 3.06 (t, $J = 7.4$ Hz, 2H), 1.56-1.51 (m, 2H), 1.42-1.37 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.0, 138.6, 133.7, 129.5, 127.5, 126.2, 39.9, 32.0, 21.7, 13.8; HRMS calc. for C$_{12}$H$_{15}$IO$_2$SNa (M+Na)$^+$, 372.9735; found, 372.9733.

Compound 3ab was obtained in 88% yield according to the general procedure (12h). 
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.48 (d, $J = 8.3$ Hz, 2H), 7.38 (s, 1H), 7.34-7.28 (m, 3H), 7.26-7.24 (m, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 144.6, 141.3, 139.7, 137.4, 129.8, 129.7, 127.9, 127.7, 114.2, 21.6; HRMS calc. for C$_{13}$H$_{13}$IO$_2$SNa (M+Na)$^+$, 406.9579; found, 406.9577.

Compound 3bb was obtained in 74% yield according to the general procedure (12h). 
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.52 (d, $J = 8.3$ Hz, 2H), 7.33 (s, 1H), 7.24-7.18 (m, 4H), 7.12 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 144.5, 140.7, 140.2, 137.5, 136.9, 129.7, 128.6, 127.9, 127.8, 114.8, 21.6, 21.5; HRMS calc. for C$_{16}$H$_{15}$IO$_2$SNa (M+Na)$^+$, 420.9735; found, 420.9736.

Compound 3ac was obtained in 81% yield according to the general procedure (12h). 
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.48 (d, $J = 8.7$ Hz, 2H), 7.41 (s, 1H), 7.37-7.28 (m, 5H), 7.22-7.20 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.0, 140.2, 139.5, 138.7, 130.0, 129.3, 129.3, 128.1, 127.7, 115.3; HRMS calc. for C$_{14}$H$_{10}$ClIO$_2$SNa (M+Na)$^+$, 426.9032; found, 426.9037.
(E)-1-chloro-4-(2-iodo-2-p-tolylvinylsulfonyl)benzene

Compound 3bc was obtained in 70% yield according to the general procedure (12h).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 7.51 (d, J = 8.3 \text{ Hz, } 2H), 7.37 (s, 1H), 7.29-7.24 (m, 4H), 7.00 (t, J = 8.6 \text{ Hz, } 2H), 2.43 (s, 3H); \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta 164.5, 162.0, 144.8, 141.7, 137.3, 135.7, 130.1, 130.0, 129.8, 127.8, 115.2, 115.0, 112.6, 21.6; \]

HRMS calc. for C_{15}H_{12}ClIO_2SNa (M+Na)^+, 440.9189; found, 440.9187.

(E)-1-(2-iodo-2-phenylvinylsulfonyl)-4-(trifluoromethyl)benzene

Compound 3ad was obtained in 77% yield according to the general procedure (12h).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 7.69-7.62 (m, 4H), 7.45 (s, 1H), 7.34 (t, J = 7.3 \text{ Hz, } 1H), 7.30-7.26 (m, 2H), 7.18 (d, J = 7.1 \text{ Hz, } 2H); \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta 143.7, 140.7, 139.4, 135.0 (d, J = 32.9 \text{ Hz}), 130.1, 128.4, 128.1, 127.6, 126.0 (q, J = 3.6 \text{ Hz}), 123.0 (q, J = 256.1 \text{ Hz}), 116.0; \]

HRMS calc. for C_{15}H_{10}F_3IO_2SNa (M+Na)^+, 460.9296; found, 460.9299.

(E)-1-(2-iodo-2-phenylvinylsulfonyl)-2-(trifluoromethyl)benzene

Compound 3ae was obtained in 86% yield according to the general procedure (16h).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 7.82 (d, J = 7.8 \text{ Hz, } 1H), 7.64 (t, J = 7.6 \text{ Hz, } 1H), 7.57 (d, J = 7.9 \text{ Hz, } 1H), 7.51 (d, J = 1.4 \text{ Hz, } 1H), 7.40 (t, J = 7.4 \text{ Hz, } 1H), 7.28 (t, J = 7.2 \text{ Hz, } 1H), 7.22 (t, J = 7.6 \text{ Hz, } 2H), 7.16-7.14 (m, 2H); \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta 141.7 (q, J = 22.4 \text{ Hz}), 139.5, 138.7, 133.5, 132.0, 129.8, 128.5 (d, J = 33.3 \text{ Hz}), 128.2 (q, J = 6.0 \text{ Hz}), 128.0, 127.5, 122.6 (q, J = 272.7 \text{ Hz}), 114.5; \]

HRMS calc. for C_{15}H_{10}F_3IO_2SNa (M+Na)^+, 460.9296; found, 460.9297.

(E)-1-bromo-2-(2-iodo-2-phenylvinylsulfonyl)benzene

Compound 3af was obtained in 87% yield according to the general procedure (12h).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta 7.65 (dd, J_1 = 1.1 \text{ Hz, } J_2 = 8.0 \text{ Hz, } 1H), 7.62 (s, 1H), 7.48 (dd, J_1 = 1.6 \text{ Hz, } J_2 = 7.9 \text{ Hz, } 1H), 7.32-7.28 (m, 1H), 7.20-7.17 (m, 1H), \]
7.15-7.10 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 140.4, 139.8, 139.3, 134.9, 134.2, 131.2, 129.8, 127.8, 127.4, 127.4, 120.6, 114.7; $^1$HRMS calc. for C$_{14}$H$_{10}$BrI$_2$O$_2$SNa (M+Na)$^+$, 470.8527; found, 470.8529.

(E)-2-(2-iodo-2-phenylvinylsulfonyl)naphthalene

Compound 3ag was obtained in 74% yield according to the general procedure (12h). $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.03 (d, $J$ = 1.5 Hz, 1H), 7.89 (t, $J$ = 8.8 Hz, 2H), 7.81 (t, $J$ = 8.1 Hz, 1H), 7.69-7.58 (m, 3H), 7.49 (s, 1H), 7.26-7.23 (m, 1H), 7.21 (d, $J$ = 4.3 Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.3, 139.5, 136.9, 135.1, 132.0, 130.0, 129.9, 129.4, 129.3, 127.9, 127.7, 127.6, 122.4, 114.8; HRMS calc. for C$_{18}$H$_{13}$IO$_2$SNa (M+Na)$^+$, 442.9579; found, 442.9578.

(E)-(4-(phenylsulfonyl)but-3-en-1-yne-1,3-diyl)dibenzene

Compound 4aa was obtained in 92% yield according to the procedure A (1h). $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.70-7.67 (m, 2H), 7.54 (t, $J$ = 7.5 Hz, 1H), 7.49-7.43 (m, 5H), 7.42-7.34 (m, 7H), 7.00 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.0, 137.4, 135.3, 134.2, 133.3, 132.0, 129.7, 129.6, 129.1, 128.9, 128.5, 128.0, 127.8, 121.6, 97.7, 88.3; HRMS calc. for C$_{22}$H$_{17}$O$_2$S (M+H)$^+$, 345.0949; found, 345.0943.

(E)-1-chloro-4-(3-phenyl-4-(phenylsulfonyl)but-3-en-1-ynyl)benzene

Compound 4af was obtained in 84% yield according to the procedure A (1h). $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.69-7.67 (m, 2H), 7.55 (t, $J$ = 7.5 Hz, 1H), 7.47-7.45 (m, 3H), 7.43-7.36 (m, 6H), 7.35-7.31 (m, 2H), 6.99 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 140.8, 137.0, 135.9, 135.7, 134.0, 133.3, 133.2, 129.7, 129.0, 128.9, 128.9, 128.1, 127.8, 120.0, 96.3, 89.1; HRMS calc. for C$_{22}$H$_{15}$ClO$_2$SNa (M+Na)$^+$, 401.0379; found, 401.0383.

(phenylethynylsulfonyl)benzene 5aa$^{[3]}$
Compound 5aa was obtained in 78% yield according to the procedure B (12h). $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.12-8.10 (m, 2H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.65-7.61 (t, $J = 7.9$ Hz, 2H), 7.56-7.54 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.8, 134.2, 132.8, 131.6, 129.4, 128.7, 127.4, 117.9, 93.5, 85.4; HRMS calc. for C$_{14}$H$_{10}$O$_2$SNa (M+Na)$^+$, 265.0299; found, 265.0293.

(E)-1-fluoro-4-(2-(phenylsulfonyl)vinylibenzene (6ea)$^{[4]}$

Compound 6ea was obtained in 73% yield according to the procedure C. $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.97 (d, $J = 7.7$ Hz, 2H), 7.69-7.63 (m, 2H), 7.57 (t, $J = 7.9$ Hz, 2H), 7.52-7.49 (m, 2H), 7.10 (t, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 165.6 (d, $J = 251.5$Hz), 141.2, 140.7, 133.5, 130.6 (d, $J = 8.7$ Hz), 129.4, 128.7, 127.7, 127.1 (d, $J = 2.4$ Hz), 116.3 (d, $J = 22.0$ Hz); HRMS calc. for C$_{14}$H$_{11}$FO$_2$SNa (M+Na)$^+$, 285.0361; found, 285.0366.

(E)-1-chloro-4-(2-(phenylsulfonyl)vinylibenzene (6fa)$^{[4]}$

Compound 6fa was obtained in 74% yield according to the procedure C. $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.97 (d, $J = 7.2$ Hz, 2H), 7.68-7.63 (m, 2H), 7.57 (t, $J = 7.8$ Hz, 2H), 7.45-7.37 (m, 4H), 6.87 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 141.0, 140.5, 137.3, 133.5, 130.9, 129.8, 129.4, 128.0, 127.7; HRMS calc. for C$_{14}$H$_{11}$ClO$_2$SNa (M+Na)$^+$, 301.0066; found, 301.0065.

(E)-1-bromo-2-(styrylsulfonyl)benzene (6af)

Compound 6af was obtained in 77% yield according to the procedure C. $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.28 (dd, $J_1 = 1.7$ Hz, $J_2 = 7.9$ Hz, 1H), 7.81 (d, $J = 15.4$ Hz, 1H), 7.71 (d, $J_1 = 1.1$ Hz, $J_2 = 7.9$ Hz, 1H), 7.55-7.53 (m, 3H), 7.49-7.43 (m, 4H), 7.14 (d, $J = 15.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 145.5, 139.9, 135.5, 134.5, 132.4, 131.5, 131.1, 129.2, 128.7, 128.1, 125.0, 121.0; HRMS calc. for C$_{14}$H$_{11}$O$_2$BrSNa (M+Na)$^+$, 344.9561; found, 344.9563.
7. Reference


