Electronic Supporting Information

Trace Water in BF$_3$·OEt$_2$ System: A Facile Access to Sulfinyl Alkenylsulfone from Alkynes and Sodium Sulfinates

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Contents

General Information..................................................................................................................................................[2]
Preparation of Sodium Sulfinates and Isosorbide Derived Alkyne...................................................................[2]
Experimental Procedure for Compounds 3a-3u, 4a-4l.....................................................................................[4]
Gram-scale Experimental Procedure for Compound 3a..................................................................................[5]
Experimental Procedure for Compounds 7a-7c............................................................................................[5]
Data of Single-crystal X-ray Analysis (Figures S1-S2, Tables S1-S2).................................................................[8]
Characterization Data for All Products 3a-3u, 4a-4l, 5a and 7a-7c.................................................................[10]
Experimental Spectra Used in Discussions (Figure S3)......................................................................................[28]
NMR Spectra and HRMS for All Compounds 3a-3u, 4a-4l, 5a and 7a-7c.........................................................[30]
References..............................................................................................................................................................[90]
General Information

$^1$H and $^{13}$C NMR spectra were collected on an AVANCE NEO-600 in CDCl$_3$ using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. High-resolution mass spectra (HR-MS) were obtained with a MAT 95XP mass spectrometer. Single-crystal X-ray analysis was obtained using Agilent Gemini E. Reactions were monitored using thin-layer chromatography (TLC) and visualized with UV light at 254 nm.

All reagents and solvents, including various alkyne compounds 1 (including 1u), were purchased from commercial sources and used without further purification. Different sodium sulfinites 2 and isosorbide derived alkyne (1t) were synthesized according to the literature procedure.\[^1\]

Preparation of Sodium Sulfinites and Isosorbide Derived Alkyne

\[
\text{Ar-SO$_2$Cl} \xrightarrow{\text{Na$_2$SO$_3$, NaHCO$_3$}} \xrightarrow{\text{H$_2$O, 80 °C, 4 h}} \text{Ar-SO$_2$Na}
\]

According to the literature,$^{[1a,1b]}$ the mixture of arylsulfonyl chloride (10 mmol), sodium sulfite (20 mmol), sodium bicarbonate (20 mmol) in H$_2$O (15 mL) was stirred at 80 °C for 4 h. Water was removed by rotary evaporator. Then, the remaining solid was extracted and recrystallized by ethanol to get the required compound 2.

According to the literature,$^{[1c]}$ isosorbide (1.00 g, 6.8 mmol) was dissolved in KOH solution (4.6 g, 82.0 mmol KOH in 16 mL water), and propargyl bromide (4.7 mL, 54.6 mmol
in 16 mL toluene) was dissolved in 20 mL of DCM. Then, their solution mixture with tetrabutylammonium bromide (220 mg, 0.7 mmol) was stirred at 55 °C for 24 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated NH₄Cl (2 × 15 mL) and NaCl (2 × 15 mL). After the organic layer was dried over anhydrous Na₂SO₄, the filtration and the evaporation of the solvents under reduced pressure gave the crude product, which was purified by column chromatography on silica gel to afford the required isosorbide derivative 1t.
Experimental Procedure for Compounds 3a-3u

The mixture of alkyne compound 1 (0.30 mmol, 1.0 equiv.), sodium 4-methylbenzenesulfinate 2a (1.20 mmol, 4.0 equiv.) and BF$_3$·OEt$_2$ (0.84 mmol, 2.8 equiv.) in undried DCM (4 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product 3.

Experimental Procedure for Compounds 4a-4l

4a: Ar = C$_6$H$_5$; 4b: Ar = 4-OMeC$_6$H$_4$; 4c: Ar = 4-PhC$_6$H$_4$; 4d: Ar = 4-FC$_6$H$_4$; 4e: Ar = 4-ClC$_6$H$_4$; 4f: Ar = 4-BrC$_6$H$_4$; 4g: Ar = 4-Ic$_6$H$_4$; 4h: Ar = 4-FC$_6$H$_4$; 4i: Ar = 3-BrC$_6$H$_4$; 4j: Ar = 3-MeC$_6$H$_4$; 4k: Ar = 2-Naphthyl; 4l: Ar = 2-Thienyl.
The mixture of phenylacetylene 1a (0.30 mmol, 1.0 equiv.), sodium sulfinate compound 2 (1.20 mmol, 4.0 equiv.) and BF$_3$·OEt$_2$ (0.84 mmol, 2.8 equiv.) in undried DCM (4 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product 4.

**Gram-scale Experimental Procedure for Compound 3a**

![Chemical structure of 3a](image)

The mixture of phenylacetylene 1a (3.0 mmol, 0.33 mL), sodium 4-methylbenzene-sulfinate 2a (12.0 mmol, 2.136 g) and BF$_3$·OEt$_2$ (8.4 mmol, 2.2 mL) in undried DCM (10 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (45 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 20 mL). Then, the organic extracts were dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to afford the desired product of 3a (yield 95%, 1.13 g).

**Experimental Procedure for Compounds 7a-7c**
According to the literature,[2, 3] the mixture of compound 3a (0.30 mmol, 1.0 equiv.), NaH (0.45 mmol, 1.5 equiv.) in anhydrous CH$_3$CN (4 mL) was stirred at room temperature for 6 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product 7a.

According to the literature,[2, 3] the mixture of compound 3a (0.30 mmol, 1.0 equiv.), DBU (3.0 mmol, 10.0 equiv.) in toluene (4 mL) was stirred at 100 °C for 6 h. After the completion of reaction, the saturated ammonium chloride solution (10 mL) was added to the reaction system to quench the reaction. Then, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product 7b.
According to the literature,[2, 3] the mixture of compound 3a (0.30 mmol, 1.0 equiv.), m-CPBA (0.45 mmol, 1.5 equiv.) in DCM (4 mL) was stirred at room temperature for 24 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product 7c.
Data of Single-crystal X-ray Analysis

**Table S1.** Crystal data and structure refinement for 3a.

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<th>Compound</th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{20}O_{3}S_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>Temperature (K)</td>
<td>297</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
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</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2_{1}/c</td>
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<tr>
<td>Unit cell dimensions (Å, °)</td>
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<td></td>
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<tr>
<td>Volume (Å³)</td>
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<td>Z</td>
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</tr>
<tr>
<td>Density (calculated) (g/cm³)</td>
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<td>F(000)</td>
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<tr>
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<tr>
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<tr>
<td>Independent reflections</td>
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<tr>
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<td>Least Squares minimisation</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
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</tbody>
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![The molecular structure of 3a.](image)

**Fig. S1.** The molecular structure of 3a.
Table S2. Crystal data and structure refinement for 3f.

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<th>Compound</th>
<th>3f</th>
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<td>Empirical formula</td>
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<tr>
<td>Temperature (K)</td>
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<tr>
<td>Wavelength (Å)</td>
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</tr>
<tr>
<td>Crystal system</td>
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<td>Space group</td>
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<td>(\alpha = 101.895(6), \beta = 92.033(7), \gamma = 91.343(7))</td>
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<tr>
<td>Volume (Å³)</td>
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<tr>
<td>Z</td>
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</tr>
<tr>
<td>Density (calculated) (g/cm³)</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<tr>
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<td>Absorption correction</td>
<td>Multi-Scan</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Least Squares minimisation</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0999, wR_2 = 0.1330)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.19 and -0.34 e.Å⁻³</td>
</tr>
</tbody>
</table>

Fig. S2. The molecular structure of 3f.
Characterization Data for All Products 3a-3u, 4a-4l, 5a and 7a-7c

\[(E)-1\text{-Methyl}-4-((2\text{-phenyl}-2-(p\text{-tolylsulfinyl}vinyl)sulfonyl)benzene \ (3a). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3a as a white solid (116.4 mg, 98%); m.p.: 166-168 °C (166-167 °C\textsuperscript{[2]}); }^{1}\text{H NMR (600 MHz, CDCl}_3\text{)}, \delta, \text{ppm: } 2.33 \text{ (s, 3H, CH}_3\text{)}, 2.40 \text{ (s, 3H, CH}_3\text{)}, 6.92 \text{ (d, } J = 7.2 \text{ Hz, 2H, ArH}, 7.08-7.13 \text{ (m, 4H, ArH)}, 7.22 \text{ (d, } J = 7.8 \text{ Hz, 2H, ArH}), 7.23-7.27 \text{ (m, 2H, ArH)}, 7.32 \text{ (s, 1H, =CH)}, 7.36 \text{ (t, } J = 7.8 \text{ Hz, 1H, ArH}), 7.55 \text{ (d, } J = 8.4 \text{ Hz, 2H, ArH}); }^{13}\text{C NMR (150 MHz, CDCl}_3\text{)}, \delta, \text{ppm: 21.6, 21.8, 125.6, 128.0, 128.2, 128.3, 129.4, 129.6, 129.8, 130.0, 130.2, 137.0, 137.6, 142.9, 144.9, 160.7; ESI-HRMS, } m/z: \text{ Calcd for C}_{22}\text{H}_{21}\text{O}_3\text{S}_2\text{ [M+H]}^+: 397.0927, \text{ Found: 397.0920.}

The data are in agreement with those previously reported in the literature.\textsuperscript{[2]}

\[(E)-1\text{-Methyl}-4-((2-(p\text{-tolyl})-2-(p\text{-tolylsulfinyl})vinyl)sulfonyl)benzene \ (3b). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3b as a white solid (115.6 mg, 94%); m.p.: 165-166 °C (166-167 °C\textsuperscript{[2]}); }^{1}\text{H NMR (600 MHz, CDCl}_3\text{)}, \delta, \text{ppm: } 2.34 \text{ (s, 3H, CH}_3\text{)}, 2.35 \text{ (s, 3H, CH}_3\text{)}, 2.41 \text{ (s, 3H, CH}_3\text{)}, 6.85 \text{ (d, } J = 7.8 \text{ Hz, 2H, ArH}), 7.07 \text{ (d, } J = 8.4 \text{ Hz, 2H, ArH}), 7.10-7.15 \text{ (m, 4H, ArH)}, 7.23 \text{ (d, } J = 7.8 \text{ Hz, 2H, ArH}), 7.28 \text{ (s, 1H, =CH)}, 7.58 \text{ (d, } J = 7.8 \text{ Hz, 2H, ArH}); }^{13}\text{C NMR (150 MHz, CDCl}_3\text{)}, \delta, \text{ppm: 21.6, 21.7, 21.8, 125.3, 125.6, 128.1, 129.0, 129.1, 129.3, 129.9, 130.0, 137.2, 137.7, 140.6, 142.8, 144.9, 160.8.}

The data are in agreement with those previously reported in the literature.\textsuperscript{[2]}

10
(E)-1-Ethyl-4-(1-(p-tolylsulfanyl)-2-tosylviny)benzene (3c). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3c as a white solid (117.1 mg, 92%); m.p.: 161-163 °C; ¹H NMR (600 MHz, CDCl₃), δ, ppm: 1.23 (t, J = 7.2 Hz, 3H, CH₃), 2.33 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.64 (q, J = 7.2 Hz, 2H, CH₂), 6.85 (d, J = 8.4 Hz, 2H, ArH), 7.07 (d, J = 8.4 Hz, 2H, ArH), 7.09-7.12 (m, 4H, ArH), 7.20 (d, J = 9.0 Hz, 2H, ArH), 7.30 (s, 1H, =CH), 7.55 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 15.4, 21.6, 21.8, 28.8, 125.4, 125.5, 127.7, 128.1, 129.2, 129.4, 129.8, 129.9, 137.2, 137.7, 142.7, 144.8, 146.8, 160.9; ESI-HRMS, m/z: Calcd for C₂₄H₂₅O₂S₂ [M+H]⁺: 425.1240, Found: 425.1230.

(E)-1-Methoxy-4-(1-(p-tolylsulfanyl)-2-tosylviny)benzene (3d). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3d as a white solid (121.4 mg, 95%); m.p.: 149-151 °C (150-151 °C[²]); ¹H NMR (600 MHz, CDCl₃), δ, ppm: 2.34 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 3.82 (s, 3H, OCH₃), 6.80 (d, J = 9.0 Hz, 2H, ArH), 6.94 (d, J = 9.0 Hz, 2H, ArH), 7.11-7.13 (m, 4H, ArH), 7.24 (d, J = 7.8 Hz, 2H, ArH), 7.27 (s, 1H, =CH), 7.58 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 21.6, 21.8, 55.4, 113.8, 120.4, 125.5, 128.0, 128.8, 129.9, 130.0, 131.0, 137.5, 137.8, 142.7, 144.9, 160.5, 161.3.

The data are in agreement with those previously reported in the literature.[²]
**(E)-4-(1-(p-tolylsulfinyl)-2-tosylvinyl)-1,1′-biphenyl (3e).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3e as a white solid (120.4 mg, 85%); m.p.: 172-173 °C (162-163 °C[2]); 

$^1$H NMR (600 MHz, CDCl$_3$), δ, ppm: 2.34 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 7.01 (d, $J = 8.4$ Hz, 2H, ArH), 7.12-7.16 (m, 4H, ArH), 7.22 (d, $J = 7.8$ Hz, 2H, ArH), 7.36 (s, 1H, =CH), 7.38 (t, $J = 7.8$ Hz, 1H, ArH), 7.44-4.47 (m, 2H, ArH), 7.49 (d, $J = 8.4$ Hz, 2H, ArH), 7.58-7.60 (m, 4H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), δ, ppm: 21.6, 21.8, 125.6, 126.7, 127.2, 128.0, 128.1, 129.0, 129.6, 129.8, 130.0, 130.1, 131.3, 131.6, 133.9, 142.8, 145.0, 160.5.

The data are in agreement with those previously reported in the literature.[2]

**(E)-1-Fluoro-4-(1-(p-tolylsulfinyl)-2-tosylvinyl)benzene (3f).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3f as a white solid (110.6 mg, 89%); m.p.: 149-150 °C (148-149 °C[2]); $^1$H NMR (600 MHz, CDCl$_3$), δ, ppm: 2.35 (s, 1H, CH$_3$), 2.42 (s, 1H, CH$_3$), 6.91-6.98 (m, 4H, ArH), 7.11-7.15 (m, 4H, ArH), 7.26 (d, 2H, $J = 7.2$ Hz, ArH), 7.33 (s, 1H, =CH), 7.58 (d, $J = 8.4$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), δ, ppm: 21.6, 21.8, 115.6 (d, $J = 22.5$ Hz), 124.3 (d, $J = 3.0$ Hz), 125.6, 128.0, 129.9, 130.0, 130.1, 131.5 (d, $J = 9.0$ Hz), 136.9, 137.5, 143.1, 145.2, 159.7, 163.8 (d, $J = 249.0$ Hz); $^{19}$F NMR (564 MHz, CDCl$_3$), δ, ppm: -109.3.

The data are in agreement with those previously reported in the literature.[2]
(E)-1-Chloro-4-(1-(p-tolylsulfinyl)-2-tosylvinyl)benzene (3g). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3g as a white solid (120.0 mg, 93%); m.p.: 184-185 °C (185-186 °C\textsuperscript{[2]}; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}), δ, ppm: 2.35 (s, 3H, CH\textsubscript{3}), 2.43 (s, 3H, CH\textsubscript{3}), 6.86 (d, J = 8.4 Hz, 2H, ArH), 7.12-7.16 (m, 4H, ArH), 7.23-7.27 (m, 4H, ArH), 7.32 (s, 1H, =CH), 7.58 (d, J = 8.4 Hz, 2H, ArH); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}), δ, ppm: 21.7, 21.8, 125.7, 126.8, 128.1, 128.6, 130.0, 130.2, 130.6, 136.6, 136.7, 137.4, 143.2, 145.3, 159.4.

The data are in agreement with those previously reported in the literature.\textsuperscript{[2]}

(1Bromo-4-(1-(p-tolylsulfinyl)-2-tosylvinyl)benzene (3h). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3h as a white solid (129.4 mg, 91%); m.p.: 188-190 °C (189-190 °C\textsuperscript{[2]}; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}), δ, ppm: 2.36 (s, 3H, CH\textsubscript{3}), 2.43 (s, 3H, CH\textsubscript{3}), 6.79 (d, J = 9.0 Hz, 2H, ArH), 7.13-7.17 (m, 4H, ArH), 7.26 (d, J = 7.8 Hz, 2H, ArH), 7.33 (s, 1H, =CH), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.58 (d, J = 8.4 Hz, 2H, ArH); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}), δ, ppm: 21.7, 21.8, 125.0, 125.7, 127.3, 128.1, 130.0, 130.1, 130.8, 131.5, 136.7, 137.4, 143.3, 145.3, 159.4.

The data are in agreement with those previously reported in the literature.\textsuperscript{[2]}
(E)-1-Methyl-4-((2-(4-nitrophenyl)-2-(p-tolylsulfanyl)vinyl)sulfonyl)benzene (3i). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3i as a white solid (115.1 mg, 87%); m.p.: 180-182 °C (180-181 °C[2]); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 2.37 (s, 3H, CH\(_3\)), 2.45 (s, 3H, CH\(_3\)), 7.09 (d, \(J = 9.0\) Hz, 1H, ArH), 7.14-7.18 (m, 4H, ArH), 7.30 (d, \(J = 7.8\) Hz, 2H, ArH), 7.37 (s, 1H, =CH), 7.62 (d, \(J = 8.4\) Hz, 2H, ArH), 8.12 (d, \(J = 9.0\) Hz, 2H, ArH); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 21.7, 21.9, 123.3, 125.8, 128.1, 130.2, 130.3, 130.4, 131.2, 135.2, 136.1, 137.0, 143.8, 145.7, 148.6, 158.3.

The data are in agreement with those previously reported in the literature.[2]

\(\text{F}_3\text{C}-\text{O}=\text{S}-\text{O}\)

(E)-1-Methyl-4-((2-(p-tolylsulfanyl)-2-(4-trifluoromethylphenyl)vinyl)sulfonyl)benzene (3j). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3j as a white solid (122.5 mg, 88%); m.p.: 172-174 °C (174-175 °C[2]); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 2.36 (s, 3H, CH\(_3\)), 2.42 (s, 3H, CH\(_3\)), 7.00 (d, \(J = 7.8\) Hz, 2H, ArH), 7.12-7.17 (m, 4H, ArH), 7.25 (d, \(J = 8.4\) Hz, 2H, ArH), 7.38 (s, 1H, =CH), 7.50 (d, \(J = 8.4\) Hz, 2H, ArH), 7.56 (d, \(J = 8.4\) Hz, 2H, ArH); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 21.7, 21.8, 123.7 (q, \(J = 271.5\) Hz), 125.1 (q, \(J = 3.0\) Hz), 125.7, 128.1, 129.7, 130.0, 130.2, 130.9, 132.0 (q, \(J = 33.0\) Hz), 132.2, 136.4, 137.1, 143.5, 145.4, 159.0; \(^19\)F NMR (564 MHz, CDCl\(_3\)), \(\delta\) ppm: -62.9.

The data are in agreement with those previously reported in the literature.[2]

\(\text{O}=\text{S}-\text{O}\)

(E)-1-Methyl-3-(1-(p-tolylsulfanyl)-2-tosylvinyl)benzene (3k). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3k as a white solid (113.2 mg, 92%); m.p.: 161-162 °C (157-158 °C[2]);
$^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 2.24 (s, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 6.65 (s, 1H, ArH), 6.68 ($d$, $J = 7.8$ Hz, 1H, ArH), 7.08-7.15 ($m$, 6H, ArH), 7.21 ($d$, $J = 7.8$ Hz, 2H, ArH), 7.30 (s, 1H, =CH), 7.54 ($d$, $J = 8.4$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.4, 21.6, 21.8, 125.6, 126.7, 128.0, 128.1, 129.5, 129.6, 129.8, 129.9, 130.9, 137.1, 137.6, 137.8, 142.8, 144.8, 160.9.

The data are in agreement with those previously reported in the literature.$^{[2]}$

(E)-1-Methoxy-3-(1-(p-tolylsulfanyl)-2-tosylviny1)benzene (3l). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3l as a white solid (115.0 mg, 90%); m.p.: 157-159 ºC (153-154 ºC$^{[2]}$); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 2.34 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 3.66 (s, 3H, OCH$_3$), 6.35-6.36 ($m$, 1H, ArH), 6.50 ($d$, $J = 7.8$ Hz, 1H, ArH), 6.87-6.88 ($dd$, $J = 2.4$ Hz, $J = 8.4$ Hz, 1H, ArH), 7.11-7.13 ($m$, 4H, ArH), 7.14-7.17 ($m$, 1H, ArH), 7.22 ($d$, $J = 7.8$ Hz, 2H, ArH), 7.32 (s, 1H, =CH), 7.56 ($d$, $J = 7.8$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.6, 21.8, 55.4, 114.3, 116.4, 121.7, 125.7, 128.1, 129.3, 129.4, 129.7, 129.8, 130.0, 137.1, 137.6, 142.9, 144.9, 159.1, 160.5.

The data are in agreement with those previously reported in the literature.$^{[2]}$

(E)-1-Chloro-3-(1-(p-tolylsulfanyl)-2-tosylviny1)benzene (3m). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3m as a white solid (113.5 mg, 88%); m.p.: 184-186 ºC (180-181 ºC$^{[3]}$); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 2.36 (s, 3H, CH$_3$), 2.42 (s, 3H, CH$_3$), 6.74-6.76 ($m$, 2H, ArH), 7.12-7.19 ($m$, 5H, ArH), 7.24 ($d$, $J = 7.8$ Hz, 2H, ArH), 7.30-7.32 ($m$, 1H, ArH), 7.35 (s, 1H, =CH), 7.55 ($d$, $J = 8.4$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.7, 21.8,
The data are in agreement with those previously reported in the literature.\[^{[3]}\]

\[\text{(E)-1-Methoxy-2-(1-(p-tolylsulfanyl)-2-tosylvinyl)benzene (3n).} \]

The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3n as a white solid (109.9 mg, 86%); m.p.: 137-139 °C (138-139 °C\[^{[2]}\]); \[^{1}\text{H NMR (600 MHz, CDCl}\_3\]), \(\delta\), ppm: 2.34 (s, 3H, CH\_3), 2.40 (s, 3H, CH\_3), 3.47 (s, 3H, OCH\_3), 6.47-6.61 (m, 1H, ArH), 6.68 (d, \(J = 8.4\) Hz, 1H, ArH), 6.77-6.82 (m, 1H, ArH), 7.11-7.14 (m, 4H, ArH), 7.19 (d, \(J = 8.4\) Hz, 2H, ArH), 7.28-7.31 (m, 1H, ArH), 7.39 (s, 1H, =CH), 7.53 (d, \(J = 8.4\) Hz, 2H, ArH); \[^{13}\text{C NMR (150 MHz, CDCl}\_3\]), \(\delta\), ppm: 21.6, 21.8, 55.2, 110.4, 117.0, 120.0, 125.8, 128.2, 129.5, 129.6, 129.9, 131.3, 131.8, 137.5, 142.6, 144.5, 156.5.

The data are in agreement with those previously reported in the literature.\[^{[2]}\]

\[\text{(E)-1-Fluo-ro-2-(1-(p-tolylsulfanyl)-2-tosylvinyl)benzene (3o).} \]

The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3o as a white solid (99.3 mg, 80%); m.p.: 157-158 °C (156-157 °C\[^{[3]}\)); \[^{1}\text{H NMR (600 MHz, CDCl}\_3\]), \(\delta\), ppm: 2.35 (s, 3H, CH\_3), 2.43 (s, 3H, CH\_3), 6.75-6.82 (m, 1H, ArH), 6.93-6.97 (m, 1H, ArH), 7.03-7.07 (m, 1H, ArH), 7.13-7.16 (m, 4H, ArH), 7.28 (d, \(J = 7.8\) Hz, 2H, ArH), 7.33-7.37 (m, 1H, ArH), 7.41 (s, 1H, =CH), 7.64 (d, \(J = 7.8\) Hz, 2H, ArH); \[^{13}\text{C NMR (150 MHz, CDCl}\_3\]), \(\delta\), ppm: 21.7, 21.8, 115.6 (d, \(J = 21.0\) Hz), 116.5 (d, \(J = 16.5\) Hz), 123.8 (d, \(J = 3.0\) Hz), 125.8, 128.2, 129.9, 130.0, 131.0 (d, \(J = 12.0\) Hz), 131.1, 132.3 (d, \(J = 7.5\) Hz), 136.6, 137.1, 143.2, 145.2, 155.0, 159.1 (d, \(J = 250.5\) Hz); \[^{19}\text{F NMR (564 MHz, CDCl}\_3\]), \(\delta\), ppm: -110.74.
The data are in agreement with those previously reported in the literature.[3]

(E)-2-(1-(p-Tolylsulfinyl)-2-tosylvinylnaphthalene (3p). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3p as a white solid (108.4 mg, 81%); m.p.: 172-174 °C (168-169 °C[2]); ¹H NMR (600 MHz, CDCl₃), δ, ppm: 2.31 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 6.93-6.95 (dd, J = 8.4 Hz, 1.8 Hz, 1H, ArH), 7.07 (d, J = 7.8 Hz, 2H, ArH), 7.10-7.12 (m, 4H, ArH), 7.40-7.43 (m, 2H, =CH, ArH), 7.50-7.56 (m, 4H, ArH), 7.67 (d, J = 8.4 Hz, 1H, ArH), 7.73 (d, J = 7.8 Hz, 1H, ArH), 7.81 (d, J = 7.8 Hz, 1H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 21.6, 21.7, 125.6, 125.9, 126.6, 126.9, 127.6, 127.92, 127.93, 128.1, 128.5, 129.0, 129.7, 129.9, 130.0, 132.3, 133.7, 137.0, 137.5, 142.9, 145.0, 160.6.

The data are in agreement with those previously reported in the literature.[2]

(E)-2-(1-(p-Tolylsulfinyl)-2-tosylvinyl)thiophene (3q). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3q as a white solid (69.9 mg, 58%); m.p.: 156-158 °C (156-157 °C[2]); ¹H NMR (600 MHz, CDCl₃), δ, ppm: 2.34 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 7.02-7.04 (m, 1H, ArH), 7.14-7.15 (m, 3H, ArH), 7.21 (d, J = 7.8 Hz, 2H, ArH), 7.26 (d, J = 7.8 Hz, 2H, ArH), 7.33 (s, 1H, =CH), 7.48 (d, J = 5.4 Hz, 1H, ArH), 7.65 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 21.6, 21.8, 125.5, 127.6, 127.8, 128.0, 129.6, 129.9, 130.1, 130.7, 132.2, 137.4, 137.9, 143.0, 145.1, 154.0.

The data are in agreement with those previously reported in the literature.[2]
(E)-1-Methyl-4-((2-(p-tolylsulfinyl)hex-1-en-1-yl)sulfonyl)benzene (3r). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3r as a white solid (57.5 mg, 51%); m.p.: 151-153 °C (152-153 °C[2]); 1H NMR (600 MHz, CDCl₃), δ, ppm: 0.85 (t, J = 7.2 Hz, 3H, CH₃), 1.25-1.33 (m, 2H, CH₂), 1.49-1.57 (m, 2H, CH₂), 1.97-2.02 (m, 1H, CH₂a), 2.42 (s, 3H, CH₃), 2.47 (s, 3H, CH₃), 2.96-3.01 (m, 1H, CH₂b), 7.13 (s, 1H, =CH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.37 (d, J = 7.8 Hz, 2H, ArH), 7.47 (d, J = 7.8 Hz, 2H, ArH), 7.82 (d, J = 8.4 Hz, 2H, ArH); 13C NMR (150 MHz, CDCl₃), δ, ppm: 13.7, 21.7, 21.8, 22.9, 26.7, 31.5, 126.7, 127.7, 127.8, 130.2, 130.5, 137.9, 138.0, 143.7, 145.2, 162.3.

The data are in agreement with those previously reported in the literature.[2]

(E)-1-Methyl-4-((1-phenyl-1-(p-tolylsulfinyl)prop-1-en-2-yl)sulfonyl)benzene (3s). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3s as a white solid (105.8 mg, 86%); m.p.: 143-145 °C (143-144 °C[3]); 1H NMR (600 MHz, CDCl₃), δ, ppm: 2.37 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.72 (s, 3H, CH₃), 6.21 (d, J = 6.0 Hz, 1H, ArH), 6.76 (d, J = 6.0 Hz, 1H, ArH), 6.99-7.02 (m, 3H, ArH), 7.10 (d, J = 7.8 Hz, 2H, ArH), 7.15 (d, J = 8.4 Hz, 2H, ArH), 7.24-7.28 (m, 4H, ArH); 13C NMR (150 MHz, CDCl₃), δ, ppm: 15.8, 21.6, 21.7, 124.4, 126.6, 126.8, 128.1, 128.9, 129.6, 129.8, 131.0, 136.6, 137.9, 142.1, 144.2, 144.6, 153.4.

The data are in agreement with those previously reported in the literature.[3]
(3R,3aR,6S,6aR)-3-(Prop-2-yn-1-yloxy)-6-((E)-2-(p-tolylsulfinyl)-3-tosylallyl)oxy-hexahydrofuro[3,2-b]furan (3t). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3t as a white waxy solid (94.4 mg, 61 %); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 2.40-2.49 (m, 6H, CH\(_3\)), 3.48-4.04 (m, 6H, =CH, CH, CH\(_2\)), 4.10-4.36 (m, 4H, CH\(_2\)), 4.50-4.69 (m, 2H, CH), 5.22-5.40 (m, 1H, CH), 7.17-7.38 (m, 5H, =CH, ArH), 7.47-7.55 (m, 2H, ArH), 7.79-7.83 (m, 2H, ArH); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 21.7, 21.9, 56.9, 57.8, 57.9, 63.0, 63.1, 63.7, 64.7, 69.9, 70.3, 70.4, 72.7, 73.2, 73.3, 75.2, 75.3, 75.4, 78.6, 78.9, 79.2, 79.3, 80.26, 80.28, 80.5, 80.58, 80.60, 83.11, 83.12, 84.6, 84.8, 85.3, 85.6, 86.3, 86.33, 126.3, 126.4, 126.44, 126.5, 127.8, 127.93, 127.95, 128.0, 128.3, 128.9, 129.2, 130.3, 130.33, 130.34, 130.36, 130.4, 130.44, 130.5, 137.0, 137.1, 137.14, 137.22, 137.9, 138.0, 138.4, 143.1, 143.2, 143.4, 143.5, 145.5, 145.6, 145.65, 145.7, 158.8, 158.9, 159.5; ESI-HRMS, \textit{m/z}: Calcd for C\(_{25}\)H\(_{29}\)O\(_7\)S\(_2\) [M+H]\(^+\): 517.1349, Found: 517.1346.

(E)-2-(p-Tolylsulfonyl)-3-tosylallyl-2-(4-(5-chloro-3-fluoropyridin-2-yl)oxyphenoxy)-propanoate (3u). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product 3u as a white waxy solid (108.0 mg, 56 %, dr = 1:1), (76 %, dr = 1:1\(^{[2]}\)); \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 1.58 (d, \(J = 6.6\) Hz, 3H, CH\(_3\)), 1.63 (d, \(J = 7.2\) Hz, 3H, CH\(_3\)), 2.40 (s, 3H, CH\(_3\)), 2.41 (s, 3H, CH\(_3\)), 2.47 (s, 3H, CH\(_3\)), 2.48 (s, 3H, CH\(_3\)), 4.49 (d, \(J = 14.4\) Hz, 1H, CH), 4.59 (d, \(J = 14.4\) Hz, 1H, CH), 4.72-4.76 (m, 2H, CH), 5.80-5.83 (m, 1H, CH), 5.86-5.89 (m, 1H, CH), 6.90 (d, \(J = 7.2\) Hz, 2H, ArH), 6.91 (d, \(J = 7.2\) Hz, 2H, ArH), 7.08-7.10 (m, 4H, ArH), 7.25 (d, \(J = 9.6\) Hz, 2H, ArH), 7.27 (s, 1H, =CH), 7.28 (s, 1H, =CH), 7.30 (d, \(J = 8.4\) Hz, 2H, ArH), 7.39 (d, \(J = 8.4\) Hz, 4H,
ArH), 7.44-7.50 (m, 6H, ArH), 7.80-7.87 (m, 6H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 18.6, 18.7, 21.7, 21.9, 57.5, 57.8, 72.9, 73.1, 116.2, 116.3, 122.6, 122.7, 125.04 (d, $J = 15.0$ Hz), 125.05 (d, $J = 4.5$ Hz), 125.16 (d, $J = 18.0$ Hz), 125.17 (d, $J = 4.5$ Hz), 126.4, 126.5, 128.16, 128.19, 130.4, 130.6, 130.7, 130.8, 136.69, 136.72, 137.0, 137.1, 140.26 (d, $J = 6.0$ Hz), 140.27 (d, $J = 10.5$ Hz), 150.7, 154.7, 154.8, 155.6, 155.7, 171.2; ESI-HRMS, m/z: Calcd for C$_{31}$H$_{28}$CIFNO$_7$S$_2$ [M+H]$^+$: 644.0974, Found: 644.0966.

The data are in agreement with those previously reported in the literature.$^{[2]}$

$^{(E)}$-((2-Phenyl-2-phenylsulfinylvinyl)sulfonyl)benzene (4a). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4a as a white solid (102.7 mg, 93%); m.p.: 183-184 °C; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 6.90 (d, $J = 7.2$ Hz, 2H, ArH), 7.20 (d, $J = 7.2$ Hz, 2H, ArH), 7.24-7.27 (m, 2H, ArH), 7.31-7.33 (m, 2H, ArH), 7.35 (s, 1H, =CH), 7.37 (t, $J = 7.8$ Hz, 1H, ArH), 7.41-7.45 (m, 3H, ArH), 7.58 (t, $J = 7.2$ Hz, 1H, ArH), 7.68 (d, $J = 7.2$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 125.5, 128.0, 128.1, 128.3, 129.2, 129.3, 129.4, 129.5, 130.4, 132.2, 133.9, 140.3, 140.5, 161.3; ESI-HRMS, m/z: Calcd for C$_{20}$H$_17$O$_3$S$_2$ [M+H]$^+$: 369.0614, Found: 369.0609.

$^{(E)}$-1-Methoxy-4-(2-(4-methoxyphenylsulfinyl)-2-phenylvinyl)sulfonylbenzene (4b). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4b as a white solid (120.7 mg, 94%); m.p.: 154-156 °C; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 3.77 (s, 1H, OCH$_3$), 3.83 (s, 1H, OCH$_3$), 6.80 (d, $J = 9.0$ Hz, 2H, ArH), 6.86 (d, $J = 9.0$ Hz, 2H, ArH), 6.89 (d, $J = 8.4$ Hz, 2H, ArH), 7.16 (d, $J = 9.0$ Hz, 2H, ArH), 7.20 (d, $J = 7.2$ Hz, 2H, ArH), 7.24-7.27 (m, 2H, ArH), 7.35 (s, 1H, =CH), 7.37 (t, $J = 7.8$ Hz, 1H, ArH), 7.41-7.45 (m, 3H, ArH), 7.58 (t, $J = 7.2$ Hz, 1H, ArH), 7.68 (d, $J = 7.2$ Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 125.5, 128.0, 128.1, 128.3, 129.2, 129.3, 129.4, 129.5, 130.4, 132.2, 133.9, 140.3, 140.5, 161.3; ESI-HRMS, m/z: Calcd for C$_{20}$H$_17$O$_3$S$_2$ [M+H]$^+$: 369.0614, Found: 369.0609.
Hz, 2H, ArH), 7.21-7.25 (m, 2H, ArH), 7.31-7.34 (m, 2H, =CH, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 55.6, 55.8, 114.4, 114.7, 127.7, 128.1, 128.4, 129.3, 129.9, 130.0, 130.2, 130.9, 160.3, 162.7, 163.9; ESI-HRMS, m/z: Calcd for C$_{22}$H$_{21}$O$_5$S$_2$ [M+H]$^+$: 429.0825, Found: 429.0820.

(E)-4-(2-([1,1'-biphenyl]-4-ylsulfinyl)-2-phenylvinyl)sulfonyl-1,1'-biphenyl (4c). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4c as a white solid (109.2 mg, 70%); m.p.: 176-178 °C; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 6.97 (d, J = 7.2 Hz, 2H, ArH), 7.27-7.29 (m, 3H, ArH), 7.37-7.40 (m, 2H, ArH), 7.43 (s, 1H, =CH), 7.44-7.46 (m, 3H, ArH), 7.47-7.50 (m, 3H, ArH), 7.53-7.55 (m, 4H, ArH), 7.56-7.58 (m, 2H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH), 7.73 (d, J = 8.4 Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 125.9, 127.3, 127.5, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.8, 129.1, 129.2, 129.4, 129.8, 130.4, 138.8, 138.9, 139.3, 139.4, 145.1, 146.9, 161.0; ESI-HRMS, m/z: Calcd for C$_{32}$H$_{23}$O$_3$S$_2$ [M-H]$^-$: 519.1094, Found: 519.1093.

(E)-1-Fluoro-4-((2-(4-fluorophenylsulfinyl)-2-phenylvinyl)sulfonyl)benzene (4d). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4d as a white solid (71.5 mg, 59%); m.p.: 144-146 ºC; $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 6.90 (d, J = 7.2 Hz, 2H, ArH), 7.00-7.04 (m, 2H, ArH), 7.07-7.11 (m, 2H, ArH), 7.19-7.21 (m, 2H, ArH), 7.27-7.30 (m, 2H, ArH), 7.34 (s, 1H, =CH), 7.39 (t, J = 7.8 Hz, 1H, ArH), 7.65-7.67 (m, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 116.5 (d, J = 22.5 Hz), 116.7 (d, J = 22.5 Hz), 127.8 (d, J = 9.0 Hz), 127.9, 128.5, 129.2,
129.7, 130.6, 131.0 \((d, J = 9.0 \text{ Hz})\), 135.6 \((d, J = 3.0 \text{ Hz})\), 136.3 \((d, J = 3.0 \text{ Hz})\), 161.3, 164.9 \((d, J = 253.0 \text{ Hz})\), 166.0 \((d, J = 255.0 \text{ Hz})\); \(^1^9\)F NMR \((564 \text{ MHz, CDCl}_3\), \(\delta\), ppm: -102.8, -105.9; ESI-HRMS, \(m/z\): Calcd for C\(_{20}\)H\(_{15}\)F\(_2\)O\(_3\)S\(_2\) \([M+H]^+\): 405.0425, Found: 405.0419.

\[(E)-1\text{-Chloro-4-}((2\text{-}(4\text{-chlorophenylsulfinyl})\text{-2-phenylvinyl})\text{sulfonyl})\text{benzene } \text{(4e)}\].

The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product \(4e\) as a white solid \((117.7 \text{ mg, 90\%})\); m.p.: 187-189 °C; \(^1\)H NMR \((600 \text{ MHz, CDCl}_3\), \(\delta\), ppm: 6.91 \((d, J = 7.2 \text{ Hz}, 2\text{H, ArH})\), 7.10 \((d, J = 8.4 \text{ Hz, 2H, ArH})\), 7.29-7.31 \((m, 4\text{H, ArH})\), 7.32 \((s, 1\text{H, -CH})\), 7.38-7.43 \((m, 3\text{H, ArH})\), 7.57 \((d, J = 9.0 \text{ Hz, 2H, ArH})\); \(^{13}\)C NMR \((150 \text{ MHz, CDCl}_3\), \(\delta\), ppm: 126.6, 127.7, 128.5, 129.3, 129.4, 129.5, 129.6, 130.7, 138.5, 138.6, 138.7, 140.8, 161.4; ESI-HRMS, \(m/z\): Calcd for C\(_{20}\)H\(_{15}\)Cl\(_2\)O\(_3\)S\(_2\) \([M+H]^+\): 436.9834, Found: 436.9826.

\[(E)-1\text{-Bromo-4-}((2\text{-}(4\text{-bromophenylsulfinyl})\text{-2-phenylvinyl})\text{sulfonyl})\text{benzene } \text{(4f)}\].

The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product \(4f\) as a yellow solid \((136.7 \text{ mg, 87\%})\); m.p.: 190-192 °C; \(^1\)H NMR \((600 \text{ MHz, CDCl}_3\), \(\delta\), ppm: 6.91 \((d, J = 7.2 \text{ Hz, 2H, ArH})\), 7.03 \((d, J = 9.0 \text{ Hz, 2H, ArH})\), 7.29-7.32 \((m, 3\text{H, -CH, ArH})\), 7.42 \((t, J = 7.8 \text{ Hz, 1H, ArH})\), 7.46 \((d, J = 8.4 \text{ Hz, 2H, ArH})\), 7.49 \((d, J = 8.4 \text{ Hz, 2H, ArH})\), 7.56 \((d, J = 9.0 \text{ Hz, 2H, ArH})\); \(^{13}\)C NMR \((150 \text{ MHz, CDCl}_3\), \(\delta\), ppm: 126.7, 127.0, 127.7, 128.6, 129.3, 129.4, 129.5, 129.6, 130.8, 132.5, 132.6, 139.2, 139.3, 161.3; ESI-HRMS, \(m/z\): Calcd for C\(_{20}\)H\(_{15}\)Br\(_2\)O\(_3\)S\(_2\) \([M+H]^+\): 526.8803, Found: 526.8795.
(E)-1-Iodo-4-(2-(4-iodophenylsulfinyl)-2-phenylvinyl)sulfonylbenzene (4g). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4g as a yellow solid (150.7 mg, 81%); m.p.: 187-189 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 6.87 \((d, J = 8.4\) Hz, 2H, ArH), 6.91 \((d, J = 7.2\) Hz, 2H, ArH), 7.29-7.32 \((m, 4H, ArH), 7.34 \((s, 1H, =CH), 7.42 \((t, J = 7.8\) Hz, 1H, ArH), 7.66 \((d, J = 8.4\) Hz, 2H, ArH), 7.77 \((d, J = 9.0\) Hz, 2H, ArH); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 99.1, 102.1, 126.6, 127.7, 128.5, 129.3, 129.4, 129.5, 130.8, 138.4, 138.5, 139.9, 140.1, 161.3; ESI-HRMS, \(m/z\): Calcd for C\(_{20}\)H\(_{15}\)I\(_2\)O\(_3\)S\(_2\) [M+H]\(^+\): 620.8547, Found: 620.8536.

(E)-1-(2-Phenyl-2-(4-trifluoromethylphenylsulfinyl)vinyl)sulfonyl-4-trifluoromethylbenzene (4h). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4h as a white solid (80.1 mg, 53 %); m.p.: 145-146 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 6.92 \((d, J = 7.8\) Hz, 2H, ArH), 7.26 \((d, J = 8.4\) Hz, 2H, ArH), 7.29-7.33 \((m, 2H, ArH), 7.36 \((s, 1H, =CH), 7.44 \((t, J = 7.8\) Hz, 1H, ArH), 7.58 \((d, J = 8.4\) Hz, 2H, ArH), 7.68 \((d, J = 8.4\) Hz, 2H, ArH), 7.78 \((d, J = 8.4\) Hz, 2H, ArH); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 123.1 \((q, J = 271.5\) Hz), 123.3 \((q, J = 271.5\) Hz), 125.5, 126.2 \((q, J = 3.0\) Hz), 126.3 \((q, J = 3.0\) Hz), 127.3, 128.7, 129.3, 129.5, 131.1, 134.0 \((q, J = 33.0\) Hz), 135.0 \((q, J = 33.0\) Hz), 143.5, 144.5, 161.8; \(^19\)F NMR (564 MHz, CDCl\(_3\)), \(\delta\) ppm: -63.0, -63.3; ESI-HRMS, \(m/z\): Calcd for C\(_{22}\)H\(_{15}\)F\(_6\)O\(_3\)S\(_2\) [M+H]\(^+\): 505.0361, Found: 505.0355.
(E)-1-Bromo-3-((3-bromophenyl)sulfinyl)-2-phenylvinyl)sulfonylbenzene (4i). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4i as a white solid (114.7 mg, 73%); m.p.: 122-124 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 6.90 (\(d, J = 7.8\) Hz, 2H, ArH), 7.04 (\(d, J = 7.8\) Hz, 1H, ArH), 7.18 (\(t, J = 7.8\) Hz, 1H, ArH), 7.26-7.27 (\(m, 1H, ArH\)), 7.30-7.34 (\(m, 4H, =CH, ArH\)), 7.44-7.46 (\(m, 1H, ArH\)), 7.55 (\(d, J = 7.2\) Hz, 1H, ArH), 7.62 (\(d, J = 7.2\) Hz, 1H, ArH), 7.68-7.69 (\(m, 2H, ArH\)); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 123.2, 123.4, 123.7, 126.6, 127.4, 127.9, 128.6, 129.3, 129.7, 130.6, 130.8, 131.0, 131.1, 135.2, 137.0, 142.0, 142.2, 161.8; ESI-HRMS, \(m/z\): Calcd for C\(_{20}\)H\(_{15}\)Br\(_2\)O\(_3\)S\(_2\) [M+H]\(^+\): 524.8658, Found: 524.8650.

(E)-1-Methyl-3-((2-phenyl-2-(m-tolylsulfinyl)vinyl)sulfonyl)benzene (4j). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4j as a white solid (97.4 mg, 82%); m.p.: 87-89 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)), \(\delta\) ppm: 2.27 (\(s, 3H, CH_3\)), 2.34 (\(s, 3H, CH_3\)), 6.89 (\(d, J = 7.2\) Hz, 2H, ArH), 6.91 (\(d, J = 7.8\) Hz, 1H, ArH), 7.02 (\(s, 1H, ArH\)), 7.17 (\(t, J = 7.8\) Hz, 1H, ArH), 7.21 (\(d, J = 7.2\) Hz, 1H, ArH), 7.25-7.27 (\(m, 2H, ArH\)), 7.30-7.34 (\(m, 1H, ArH\)), 7.34 (\(s, 1H, =CH\)), 7.35-7.38 (\(m, 2H, ArH\)), 7.43 (\(s, 1H, ArH\)), 7.48 (\(d, J = 7.8\) Hz, 1H, ArH); \(^13\)C NMR (150 MHz, CDCl\(_3\)), \(\delta\) ppm: 21.3, 21.4, 122.7, 125.1, 125.5, 128.1, 128.2, 128.4, 128.9, 129.1, 129.4, 129.6, 130.2, 133.0, 134.6, 139.5, 139.6, 139.9, 140.3, 161.1; ESI-HRMS, \(m/z\): Calcd for C\(_{22}\)H\(_{19}\)O\(_3\)S\(_2\) [M-H]\(^-\): 395.0781, Found: 395.0777.
(E)-2-(2-(Naphthalen-2-ylsulfinyl)-2-phenylvinyl)sulfonylnaphthalene (4k). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4k as a white solid (108.1 mg, 77%); m.p.: 172-174 °C; $^1$H NMR (600 MHz, CDCl$_3$), δ, ppm: 6.86 ($d$, $J = 7.2$ Hz, 2H, ArH), 7.13-7.16 ($m$, 2H, ArH), 7.25-7.27 ($m$, 1H, ArH), 7.28 ($t$, $J = 7.8$ Hz, 1H, ArH), 7.50-7.52 ($m$, 2H, =CH, ArH), 7.55-7.60 ($m$, 2H, ArH), 7.64-7.70 ($m$, 4H, ArH), 7.80-7.83 ($m$, 2H, ArH), 7.87-7.89 ($m$, 2H, ArH), 8.15 ($s$, 1H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), δ, ppm: 120.4, 122.6, 127.0, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 129.3, 129.4 129.5, 129.6, 129.7, 130.0, 130.1, 130.4, 132.1, 132.5, 134.8, 135.4, 137.0, 137.1, 161.2; ESI-HRMS, m/z: Calcd for C$_{28}$H$_{21}$O$_3$S$_2$ [M+H]$^+$: 469.0926, Found: 469.0920.

(E)-2-(2-Phenyl-2-(thiophen-2-ylsulfinyl)vinyl)sulfonylthiophene (4l). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product 4l as a yellow solid (78.6 mg, 69%); m.p.: 133-134 °C; $^1$H NMR (600 MHz, CDCl$_3$), δ, ppm: 6.91-6.92 ($m$, 1H, ArH), 7.05-7.06 ($m$, 1H, ArH), 7.07-7.08 ($m$, 3H, ArH), 7.29-7.31 ($m$, 2H, ArH), 7.38 ($t$, $J = 7.2$ Hz, 1H, ArH), 7.48-7.49 ($dd$, $J = 3.6$ Hz, 1.2 Hz, 1H, ArH), 7.49 ($s$, 1H, =CH), 7.61-7.62 ($dd$, $J = 5.4$ Hz, 1.2 Hz, 1H, ArH), 7.67-7.68 ($dd$, $J = 4.8$ Hz, 1.2 Hz, 1H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), δ, ppm: 127.4, 127.9, 128.1, 128.4, 129.1, 130.3, 130.5, 132.8, 133.2, 134.6, 134.9, 141.47, 141.49, 160.2; ESI-HRMS, m/z: Calcd for C$_{16}$H$_{13}$O$_3$S$_4$ [M+H]$^+$: 380.9742, Found: 380.9734.

S-(p-Tolyl) 4-methylbenzenesulphonothioate (5a). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 15:1) to provide the product 5a as a white solid (10 mg); m.p.: 73-75 °C (74-75 °C$^4$); $^1$H NMR (600 MHz,
CDCl$_3$, $\delta$, ppm: 2.38 (s, 3H, CH$_3$), 2.42 (s, 3H, CH$_3$), 7.14 ($d$, $J$ = 7.8 Hz 2H, ArH), 7.21 ($d$, $J$ = 8.4 Hz, 2H, ArH), 7.24 ($d$, $J$ = 7.8 Hz, 2H, ArH), 7.46 ($d$, $J$ = 8.4 Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.6, 21.8, 124.7, 127.7, 129.5, 130.3, 136.6, 140.6, 142.2, 144.7.

The data are in agreement with those previously reported in the literature.[4]

1-Methyl-4-(phenylethynylsulfonyl)benzene (7a). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 20:1) to provide the product 7a as a white solid (46.1 mg, 60%); m.p.: 79-81 °C; (73-74 °C$^{[2]}$); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 2.47 (s, 3H, CH$_3$), 7.35-7.40 (m, 4H, ArH), 7.47 (t, $J$ = 7.8 Hz, 1H, ArH), 7.51-7.53 (m, 2H, ArH), 7.96 ($d$, $J$ = 8.4 Hz, 2H, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.9, 85.7, 93.1, 118.2, 127.7, 128.8, 130.1, 131.6, 132.9, 139.1, 145.5; ESI-HRMS, m/z: Calcd for C$_{15}$H$_{13}$O$_2$S [M+H]$^+$: 257.0631, Found: 257.0629.

The data are in agreement with those previously reported in the literature.[2]

$^{(E)}$-(2-Phenyl-2-(p-tolylsulfinyl)vinyl)(p-tolyl)sulfane (7b). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 10:1) to provide the product 7b as a white solid (45.7 mg, 42%); m.p.: 114-116 °C; (117-118 °C$^{[2]}$); $^1$H NMR (600 MHz, CDCl$_3$), $\delta$, ppm: 2.32 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 7.12 ($d$, $J$ = 7.8 Hz, 2H, ArH), 7.15-7.18 (m, 4H, ArH), 7.25-7.27 (m, 2H, ArH), 7.29-7.32 (m, 3H, ArH), 7.37 ($d$, $J$ = 8.4 Hz, 2H, ArH), 7.41 (s, 1H, =CH); $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$, ppm: 21.3, 21.5, 125.2, 128.7, 129.0, 129.1, 129.7, 130.3, 130.6, 131.1, 131.7, 132.3, 138.3, 139.3, 140.0, 141.6; ESI-HRMS, m/z: Calcd for C$_{22}$H$_{21}$O$_2$S [M+H]$^+$: 365.1028, Found: 365.1025.

The data are in agreement with those previously reported in the literature.[2]
(E)-4,4’-(1-Phenylethene-1,2-diyldisulfonyl)bis(methylbenzene) (7c). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate/ DCM = 8:1:1) to provide the product 7c as a white solid (112.5 mg, 91%); m.p.: 148-150 °C (152-153 °C[2]); 1H NMR (600 MHz, CDCl₃), δ, ppm: 2.39 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 6.91 (d, J = 7.2 Hz, 2H, ArH), 7.17-7.20 (m, 6H, ArH), 7.34-7.37 (m, 3H, ArH), 7.45 (d, J = 8.4 Hz, 2H, ArH), 7.75 (s, 1H, =CH); 13C NMR (150 MHz, CDCl₃), δ, ppm: 21.7, 21.8, 127.8, 128.3, 129.3, 129.8, 129.9, 130.1, 130.3, 133.3, 133.9, 136.4, 137.7, 145.5, 145.8, 152.9; ESI-HRMS, m/z: Calcd for C₂₂H₂₄O₄S₂ [M+H]⁺: 413.0876, Found: 413.0873.

The data are in agreement with those previously reported in the literature.[2]
Experimental Spectra Used in Discussions
Fig. S3. The HRMS and GC-MS of control experiments.
NMR Spectra and HRMS for All Compounds 3a-3u, 4a-4l, 5a and 7a-7c

$^1$H NMR spectrum of compound 3a

$^{13}$C NMR spectrum of compound 3a
HRMS spectrum of compound 3a
$^1$H NMR spectrum of compound 3b

$^{13}$C NMR spectrum of compound 3b
$^1$H NMR spectrum of compound 3c

$^{13}$C NMR spectrum of compound 3c
HRMS spectrum of compound 3c
$^1$H NMR spectrum of compound 3d

$^{13}$C NMR spectrum of compound 3d
1H NMR spectrum of compound 3e

13C NMR spectrum of compound 3e
$^1$H NMR spectrum of compound 3f

$^{13}$C NMR spectrum of compound 3f
$^{19}$F NMR spectrum of compound 3f

$^1$H NMR spectrum of compound 3g
$^{13}$C NMR spectrum of compound 3g

$^1$H NMR spectrum of compound 3h
$^{13}$C NMR spectrum of compound 3h

$^1$H NMR spectrum of compound 3i
$^{13}$C NMR spectrum of compound 3i

$^1$H NMR spectrum of compound 3j
$^{13}$C NMR spectrum of compound 3j

$^{19}$F NMR spectrum of compound 3j
$^{1}$H NMR spectrum of compound 3k

$^{13}$C NMR spectrum of compound 3k
$^1$H NMR spectrum of compound 3l

$^{13}$C NMR spectrum of compound 3l
$^1\text{H NMR spectrum of compound 3m}$

$^{13}\text{C NMR spectrum of compound 3m}$
$^1$H NMR spectrum of compound 3n

$^{13}$C NMR spectrum of compound 3n
$^1$H NMR spectrum of compound 3o

$^{13}$C NMR spectrum of compound 3o
$^{19}$F NMR spectrum of compound $3o$

$^1$H NMR spectrum of compound $3p$
$^1$H NMR spectrum of compound 3q

$^{13}$C NMR spectrum of compound 3p
$^{13}$C NMR spectrum of compound 3q

$^1$H NMR spectrum of compound 3r
$^{13}$C NMR spectrum of compound 3r

$^1$H NMR spectrum of compound 3s
$^{13}$C NMR spectrum of compound 3s

$^1$H NMR spectrum of compound 3t
$^{13}$C NMR spectrum of compound 3t
HRMS of compound 3t
$^1$H NMR spectrum of compound 3u

$^{13}$C NMR spectrum of compound 3u
HRMS of compound 3u
\( \text{\(^1H\) NMR spectrum of compound 4a} \)

\( \text{\(^13C\) NMR spectrum of compound 4a} \)
HRMS spectrum of compound 4a

NL:
1.04E9
17#17 RT: 0.18
AV: 1 T: FTMS + c
APCI corona Full
ms
[50.0000-750.0000]

C_{20}H_{17}O_{3}S_{2}^+ + H
C_{20}H_{10}O_{3}S_{2}
pa Chrg 1
$^1$H NMR spectrum of compound 4b

$^{13}$C NMR spectrum of compound 4b
HRMS of compound 4b
\(^1\)H NMR spectrum of compound 4c

\(^{13}\)C NMR spectrum of compound 4c
HRMS of compound 4c
$^1$H NMR spectrum of compound 4d

$^{13}$C NMR spectrum of compound 4d
$^{19}$F NMR spectrum of compound 4d
HRMS of compound 4d
\( ^1 \)H NMR spectrum of compound 4e

\( ^{13} \)C NMR spectrum of compound 4e
HRMS of compound 4e
$^1$H NMR spectrum of compound 4f

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

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

$^{13}$C NMR spectrum of compound 4h
$^{19}$F NMR spectrum of compound $4h$
HRMS of compound 4h
$^1$H NMR spectrum of compound 4i

$^{13}$C NMR spectrum of compound 4i
HRMS of compound 4i
$^1$H NMR spectrum of compound 4j

$^{13}$C NMR spectrum of compound 4j
HRMS of compound 4j
$^1$H NMR spectrum of compound 4k

$^{13}$C NMR spectrum of compound 4k
HRMS of compound 4k
$^1$H NMR spectrum of compound 4l

$^{13}$C NMR spectrum of compound 4l
HRMS of compound 4l
$^1$H NMR spectrum of compound 5a

$^{13}$C NMR spectrum of compound 5a
$^1$H NMR spectrum of compound 7a

$^{13}$C NMR spectrum of compound 7a
HRMS of compound 7a
$^1$H NMR spectrum of compound 7b

$^{13}$C NMR spectrum of compound 7b
NL: 1.26E8
2#20 RT: 0.21
AV: 1 T: FTMS + c
APCI corona Full
ms
[50.0000-750.0000]

NL: 7.08E5
C_{22}H_{20}O_2S_2 +H:
C_{22}H_{21}O_1S_2
pa Chrg 1

HRMS of compound 7b
$^1$H NMR spectrum of compound 7c

$^{13}$C NMR spectrum of compound 7c
HRMS of compound 7c
References


