Supporting Information

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I. General Information

Organic solvents (Aldrich) were used without further purification. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63 µm). $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, $\delta$) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.
II. The General Synthetic Procedure for substrates Vinyl Iodide SI-5 and SI-6, N-Tosyl Hydrazones SI-8

General Procedure:

Vinyl iodides SI-5 were prepared through Mitsunobu reaction from vinyl iodiel alcohols SI-2 and allyl amine SI-4.

Preparation of SI-2: Compounds SI-2 were prepared as described in the literature\(^1\). To a stirred solution of propargyl alcohol SI-1 (50 mmol, 1.0 equiv) in anhydrous THF (100 mL) under N\(_2\) atmosphere was added CuI (5 mmol, 10 mol\%) and the mixture was cooled to -78°C. Grignard reagent SI-2 (125 mmol, 2.5 equiv), which had been freshly prepared in THF, was then added via constant pressure funnel maintain the temperature below -60°C for 1h. Then, the mixture was allowed to warm up to room temperature and vigorously stirred overnight. The reaction was cooled again to -78°C and treated with I\(_2\) (55 mmol, 1.1 equiv) in anhydrous THF (100 mL). After warming up to room temperature and stirring at r.t. for additional 1h, the reaction mixture was kept in refrigerator at about 0-3°C overnight. The mixture was cooled to 0°C and was quenched with saturated aqueous NH\(_4\)Cl (50 mL). The two phase mixture was poured through a separatory funnel and combined organic layers were washed extracted with saturated aqueous Na\(_2\)S\(_2\)O\(_3\) (2 x 50 mL) and saturated aqueous NaCl (100 mL), and dried over Na\(_2\)SO\(_4\). It was purified by column chromatography to give SI-2.

Preparation of SI-4: Compounds SI-4 were prepared as described in the literature\(^2\). Dropwise adding 3-Chloro-2-methylpropene SI-3(10 mmol, 1.0 equiv) to the mixture of Tosylamide (30 mmol, 3.0 equiv), K\(_2\)CO\(_3\) (25 mmol, 2.5 equiv), KI (5 mmol, 0.5
equiv) and acetone (50 mL). The mixture was stirred with reflux at 60 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na₂SO₄ and evaporated. The crude product was purified by column chromatography (PE:EA, 15:1) to give the SI-4 as a white solid.

**Preparation of SI-5:** Compounds SI-5 were prepared as described in the literature.³ To a solution of SI-4 (6.0 mmol, 1.2 equiv) in THF (15 mL) at room temperature was added PPh₃ (6.0 mmol, 1.2 equiv) and DIAD (6.0 mmol, 1.2 equiv). Then a solution of SI-2 (5.0 mmol, 1.0 equiv) in 10 mL THF was added by constant pressure funnel under moderate stirring. Then the mixture was stirred overnight. After washed with water (50 mL x 3) and 1N HCl (20 mL), then the organic layer was dried over Na₂SO₄ and purification by column chromatography to give SI-5.

![SI-2 SI-3 SI-6](image)

**Preparation of SI-6:** Compounds SI-6 were prepared through the way described in the literature.⁴ To a solution of SI-2 (10.0 mmol, 1.0 equiv) in DMF (15 mL) at 0 °C was added NaH (12 mmol, 1.2 equiv) for 50 min. Then a solution of SI-3 (12 mmol, 1.2 equiv) in 5 mL DMF was added dropwise by constant pressure funnel under vigorous stirring. Then the mixture was stirred and refluxed at r.t. for 1 h. After washed with water (50 mL x 3) and then the organic layer was dried over Na₂SO₄ and purification by column chromatography (PE:EA, 5:1) to give SI-6.

**Preparation of SI-8:**

![SI-7 SI-8](image)
To a solution of p-Toluenesulfonyl hydrazide (5.0 mmol) in 12mL MeOH, SI-7 (5.0 mmol) was added dropwise. The solution was stirred in room temperature for 3 hours, and then cooled to 0 °C. The solid in solution was filtrated and washed by a little cooled MeOH. Then N-Tosyl Hydrazones SI-8 was synthesized.
III. The General Synthetic Procedure and Analytical Data for products

General Procedure:

To the solution of vinyl iodide \textbf{SI-5} or \textbf{SI-6} (0.2 mmol, 1.0 equiv.), N-Tosyl Hydrazones \textbf{SI-8} (0.24 mmol, 1.2 equiv.), Pd(dba)$_2$ (0.01 mmol, 5 mol%), PPh$_3$ (0.02 mmol, 10 mol%) and tBuOLi (0.6 mmol, 3.0 equiv.) in 2.0 mL MeCN under N$_2$ atmosphere. The reactions were operated in sealed tube at 80 °C. After stirring for 3 hours, the mixture was evaporated and purified by flash chromatography to give product \textbf{3} or \textbf{5}. 
**Analytical Data:**

### 3aa

**C$_{28}$H$_{29}$NO$_2$S**  
**MW:** 443.60 g.mol$^{-1}$  
Yellow liquid  
**Yield:** 88%

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ ppm):  7.73 (d, $J = 8.0$ Hz, 0.58H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.38 – 7.29 (m, 9H), 7.22-7.20 (m, 3H), 6.96 – 6.94 (m, 2H), 6.18(s, 0.14H), 5.78(s, 0.14H), 5.61 (s, 1H), 5.34 (d, $J = 1.2$ Hz, 1H), 5.18 (s, 1H), 3.75 (dd, $J = 51.6$, $15.6$ Hz, 2.4H), 2.97 – 2.87 (m, 2.4H), 2.68 (dd, $J = 14.0$, $11.6$ Hz, 2H), 2.42 (s, 3.86H), 2.06 (s, 0.7H), 1.43 (s, 0.7H), 1.03 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 145.5, 143.6, 143.0, 138.4, 133.1, 132.2, 130.7, 129.7, 128.5, 128.5, 128.3, 127.7, 127.2, 126.6, 125.2, 118.0, 53.7, 46.5, 45.5, 37.4, 24.7, 21.6.

**HRMS (ESI):** Calcd for C$_{28}$H$_{29}$NO$_2$S+H 444.1977, found 444.1980.

### 3ab

**C$_{29}$H$_{31}$NO$_3$S**  
**MW:** 473.63 g.mol$^{-1}$  
Brown liquid  
**Yield:** 86%

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ ppm):  7.5 (d, $J = 8.4$ Hz, 0.5H ), 7.52 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 4.0$ Hz, 1H) 7.23 – 7.21 (m, 5H), 7.15-7.14 (m, 2H), 6.92 -6.90 (m, 2H), 6.78 -6.75 (m, 2.5H), 6.10(s, 0.21H), 5.65(s, 0.21H), 5.54 (s, 1H), 5.20 (d, $J = 1.6$ Hz, 1H), 5.02 (d, $J =0.8$Hz, 1H), 3.80 – 3.76 (m, 1H), 3.73 (s, 3.7H), 3.62 – 3.58 (m, 1.3H), 2.81 (dd, $J = 27.3$, 12.3 Hz, 2.39H), 2.59 (dd, $J = 37.1$, 12.3 Hz, 2H), 2.35 (s, 3.6H), 1.95 (s, 0.62H), 1.35 (s, 0.65H), 0.96 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 159.0, 144.8, 143.5, 138.4, 135.4, 132.9, 132.3, 130.5, 129.7, 128.3, 127.7, 127.6, 125.2, 116.4, 113.8, 55.3, 53.7, 46.4, 45.6, 37.4, 24.7, 21.5.

**HRMS (ESI):** Calcd for C$_{29}$H$_{31}$NO$_3$S+H 474.2103, found 474.2106.
3ac
C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S
MW: 473.63 g.mol<sup>-1</sup>
Brown liquid
Yield: 77%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.72 (d, J = 7.6 Hz, 0.5H), 7.61 (d, J = 7.8 Hz, 2H), 7.34 – 7.20 (m, 8H), 7.00 – 6.95 (m, 3H), 6.9 (s, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.18 (s, 0.19H), 5.79 (s, 0.19H), 5.63 (s, 1H), 5.35 (s, 1H), 5.17 (s, 1H), 3.81 (t, J = 7.7 Hz, 1.63H), 3.76 (s, 3H), 3.70 (d, J = 15.4 Hz, 1H), 2.91 (dd, J = 44.5, 12.3 Hz, 2.52H), 2.68 (dd, J = 28.0, 12.3 Hz, 2H), 2.42 (s, 3.83H), 2.04 (s, 0.72H), 1.43 (s, 0.76H), 1.03 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 159.6, 145.4, 144.5, 143.6, 138.4, 132.8, 132.2, 130.7, 129.7, 129.4, 128.6, 128.3, 127.7, 125.2, 119.2, 118.0, 112.7, 112.4, 55.3, 53.6, 46.5, 45.5, 37.4, 24.7, 21.6.

HRMS (ESI): Calcd for C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S+H 474.2103, found 474.2106

3ad
C<sub>28</sub>H<sub>28</sub>FNO<sub>2</sub>S
MW: 416.59 g.mol<sup>-1</sup>
Brown liquid
Yield: 73%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.72 (d, J = 7.6Hz, 0.5H), 7.60 (d, J = 7.6 Hz, 2H), 7.34 – 7.30 (m, 6H), 7.25 – 7.23(m, 3H), 6.99 (d, J = 7.3 Hz, 4H), 6.17 (s, 0.19H), 5.73 (s, 0.19H), 5.59 (s, 1H), 5.30 (s, 1H), 5.17 (s, 1H), 3.85 - 3.70 (m, 2.65H), 3.08 – 2.79 (m, 2.47H), 2.64 (dd, J = 11.8, 7.2 Hz, 2H), 2.42 (s, 3.83H), 2.04 (s, 0.75H), 1.42 (s, 0.73H), 1.02 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 162.2 (d, J = 197), 144.4, 143.7, 139.1, 138.3, 132.7, 132.0, 130.8, 129.7, 128.7, 128.4, 128.2, 127.7(d, J = 4Hz), 125.2, 118.0, 115.2 (d, J = 17Hz)), 53.6, 46.5, 45.7, 37.4, 24.8, 21.6, 21.6.

<sup>19</sup>F<sup>1</sup>H NMR (376 MHz, CDCl<sub>3</sub>, δ ppm): 110.0.

HRMS(ESI): Calcd for C<sub>28</sub>H<sub>28</sub>FNO<sub>2</sub>S+H 462.1903, found 412.1900.
3ae

C_{28}H_{28}ClNO_{2}S

MW: 478.05 g.mol^{-1}

Brown liquid

Yield: 76%

^{1}H NMR (400 MHz, CDCl_{3}, \delta ppm): 7.72 (d, J = 7.6 Hz, 0.5H), 7.60 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 8.4 Hz, 3.6H), 7.28 - 7.23 (m, 7H), 6.95 (d, J = 6.6 Hz, 2H), 6.17 (s, 0.18H), 5.77 (s, 0.18), 5.56 (s, 1H), 5.33 (s, 1H), 5.20 (s, 1H), 3.85 - 3.68 (m, 2.52H), 3.23-2.84 (m, 2.5H), 2.64 (dd, J = 12.0, 6.1 Hz, 2H), 2.43 (s, 3.65H), 2.04 (s, 0.84H), 1.41 (s, 0.72H), 1.02 (s, 3H).

^{13}C NMR (100 MHz, CDCl_{3}, \delta ppm): 144.4, 143.7, 141.5, 138.2, 133.1, 132.7, 132.0, 130.9, 129.7, 128.6, 128.4, 128.0, 127.7, 127.7, 125.2, 118.5, 53.6, 46.5, 45.6, 37.4, 24.7, 21.6.

HRMS(ESI): Calcd for C_{28}H_{28}ClNO_{2}S+H 478.1608, found 478.1605.

3af

C_{28}H_{28}BrNO_{2}S

MW: 522.50 g.mol^{-1}

Brown liquid

Yield: 53%

^{1}H NMR (400 MHz, CDCl_{3}, \delta ppm): 7.73 (t, J = 5.6Hz, 0.7H), 7.60 (d, J = 7.5 Hz, 2H), 7.42 (d, J = 7.7 Hz, 3H), 7.32 (d, J = 7.9 Hz, 4H), 7.26 - 7.21 (m, 5H), 6.94 (d, J = 6.6 Hz, 2H), 6.16 (s, 0.21H), 5.83 (s, 0.21H), 5.55 (s, 1H), 5.34 (s, 1H), 5.20 (s, 1H), 3.74 (q, J = 15.5 Hz, 2.58H), 3.00 - 2.85 (m, 2.52H), 2.67 - 2.61 (m, 2H), 2.43 (s, 3.89H), 2.04 (s, 0.76H), 1.41 (s, 0.86H), 1.03 (s, 3H).

^{13}C NMR (100 MHz, CDCl_{3}, \delta ppm): 144.4, 143.7, 141.9, 138.2, 132.7, 132.0, 131.5, 129.8, 128.4, 128.3, 127.7, 127.7, 125.2, 121.3, 118.5, 53.6, 46.5, 45.6, 37.4, 24.7, 21.6.

HRMS(ESI): Calcd for C_{28}H_{28}BrNO_{2}S+H 522.1102, found 522.1105.

3ag

C_{28}H_{28}BrNO_{2}S

MW: 522.50 g.mol^{-1}

Brown liquid
Yield: 57%

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.73 (d, \(J = 7.6\) Hz, 0.5H), 7.62 (d, \(J = 7.7\) Hz, 2H), 7.50 (s, 1H), 7.30 (m, 10H), 7.15 (t, \(J = 7.4\) Hz, 1H), 7.00 (d, \(J = 6.2\) Hz, 2H), 6.15 (s, 0.19H), 5.76 (s, 0.19H), 5.60 (s, 1H), 5.35 (s, 1H), 5.23 (s, 1H), 3.76-3.71 (s, 2.34H), 2.93 (dd, \(J = 62.2\), 12.3 Hz, 2.35H), 2.64 (dd, \(J = 11.9, 5.2\) Hz, 2H), 2.43 (s, 3.76H), 2.04 (s, 0.82H), 1.42 (s, 0.61H), 1.01 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\), \(\delta\) ppm): 145.2, 144.2, 143.6, 138.2, 132.7, 131.8, 131.0, 130.2, 130.0, 129.8, 129.6, 128.4, 127.7, 127.6, 125.3, 125.2, 122.6, 119.1, 53.5, 46.5, 45.3, 37.4, 24.8, 21.6.

HRMS(ESI): Calcd for C\(_{28}\)H\(_{28}\)BrNO\(_2\)S+H 522.1102, found 522.1105.

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3ah

C\(_{28}\)H\(_{28}\)INO\(_2\)S

MW: 569.50 g.mol\(^{-1}\)

Brown liquid

Yield: 42%

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.73 (dd, \(J = 8.4\) Hz, \(J = 6.0\) Hz, 0.8H), 7.61 (t, \(J = 8.4\) Hz, 4.5Hz), 7.34 – 7.31 (m, 5H), 7.25 – 7.23 (m, 2H), 7.10 (dt, \(J = 8.4\) Hz, \(J = 2.4\) Hz, 2H), 6.91 (dt, \(J = 6.4, J = 1.6\) Hz, 2H), 6.16 (s, 0.2H), 5.77 (s, 0.2H), 5.53 (s, 1H), 5.34 (d, \(J = 1.6\) Hz, 1H), 5.20 (s, 1H), 3.74 (q, \(J = 16.0\) Hz, 2.6Hz), 2.52 (dd, \(J = 28.0, 9.6\) Hz, 0.45H), 2.92 (dd, \(J = 38.4, 11.2\) Hz, 2H), 2.63 (t, \(J = 12.4\) Hz, 2H), 2.44 (s, 3H), 2.42 (s, 0.8H), 2.03 (d, \(J = 1.2\) Hz, 0.62H), 1.41 (s, 0.61H), 1.02 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\), \(\delta\) ppm): 144.5, 143.7, 142.6, 138.3, 137.5, 132.7, 131.9, 130.9, 129.8, 128.6, 128.5, 127.8, 127.7, 125.1, 118.4, 92.73, 53.60, 46.5, 45.5, 37.4, 24.7, 21.6.

HRMS(ESI): Calcd for C\(_{28}\)H\(_{28}\)INO\(_2\)S+H 570.0964, found 570.0961

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3ai

C\(_{28}\)H\(_{28}\)N\(_2\)O\(_2\)S

MW: 468.61 g.mol\(^{-1}\)

Brown liquid

Yield: 45%

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.72 (d, \(J = 8.0\)Hz, 0.5H), 7.64 (d, \(J = 8.2\) Hz, 2H), 7.58 (d, \(J = 8.4\) Hz, 2H), 7.48 (d, \(J = 8.4\) Hz, 2H), 7.36 – 7.31 (m, 4H), 7.26 –
7.20 (m, 3H), 6.91 (dd, J = 6.4, 3.1 Hz, 2H), 6.18 (s, 0.18), 5.67 (s, 0.18), 5.49 (s, 1H), 5.45 (s, 1H), 5.36 (s, 1H), 3.92 – 3.86 (m, 1.56H), 3.61 (dd, J = 15.6, 1.7 Hz, 1H), 3.19 (d, J = 11.3 Hz, 1H), 3.10 (q, J = 11.3 Hz, 0.63H), 2.96 (d, J = 13.5 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.44 (s, 3.76H), 2.09 (s, 0.61H), 1.42 (s, 0.61H), 0.98 (s, 3H).

**13C NMR (100 MHz, CDCl₃, δ ppm):** 147.6, 144.2, 143.8, 138.0, 132.8, 131.56, 131.3, 129.8, 128.4, 127.9, 127.7, 127.3, 125.0, 120.6, 118.8, 110.7, 53.3, 46.4, 45.1, 37.4, 24.8, 21.6.

**HRMS(ESI):** Calcd for C₂₉H₂₈N₂O₂S+H 469.1950, found 469.1953

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**3aj**

C₂₇H₂₇NO₂S

**MW:** 429.57 g.mol⁻¹

Brown liquid

**Yield:** 87%

**1H NMR (400 MHz, CDCl₃, δ ppm):** 7.71 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 3.6 Hz, 4H), 7.32 – 7.27 (m, 6H), 7.02 (dd, J = 8.6, 2.9 Hz, 2H), 6.42 (d, J = 16.2 Hz, 1H), 6.24 (d, J = 16.2 Hz, 1H), 5.93 (s, 1H), 3.94 (dd, J = 5.6, 1.9 Hz, 2H), 3.09 (dd, J = 74.2, 11.3 Hz, 2H), 2.40 (s, 3H), 1.35 (s, 3H).

**13C NMR (100 MHz, CDCl₃, δ ppm):** 143.7, 138.2, 137.1, 134.8, 133.2, 132.4, 130.2, 129.8, 129.2, 128.6, 128.5, 128.0, 127.8, 127.5, 126.4, 125.4, 53.5, 46.3, 39.4, 24.7, 21.6.

**HRMS(ESI):** Calcd for C₂₇H₂₇NO₂S+H 430.1841, found 430.1844.

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**3ak**

C₂₉H₃₁NO₂S

**MW:** 457.62 g.mol⁻¹

Brown liquid

**Yield:** 83%

**1H NMR (400 MHz, CDCl₃, δ ppm):** 7.73 (t, J = 6.8 Hz, 0.35H), 7.57 (d, J = 7.6 Hz, 2H), 7.30 – 7.19 (m, 11H), 6.89 (d, J = 5.1 Hz, 2H), 5.79 (q, J = 7.4 Hz, 1H), 5.59 (d, J = 2.4 Hz, 1H), 5.59 (s, 0.09H), 3.73 (dd, J = 138.1, 15.4 Hz, 2.4H), 2.79 (dd, J = 30.4, 11.2 Hz, 2.2H), 2.79 (dd, J = 112.8, 13.6 Hz, 2H), 2.42 (s, 3.4H), 2.03 (s, 0.46H), 1.80 (d, J = 6.8 Hz, 3H), 1.59 (s, 0.30H), 1.05 (s, 3H).
**13C NMR (100 MHz, CDCl₃, δ ppm):** 145.5, 143.5, 138.4, 137.9, 132.9, 132.5, 132.3, 130.4, 129.7, 129.6, 128.4, 127.7, 126.7, 125.3, 125.1, 54.3, 46.3, 39.4, 38.5, 25.0, 21.5, 15.2.

**HRMS(ESI):** Calcd for C₂₉H₃₁NO₂S+H 458.2154, found 458.2151.

**3ba**

C₂₄H₂₉NO₂S  
MW: 395.56 g.mol⁻¹  
Yellow liquid  
**Yield:** 91%

**1H NMR (400 MHz, CDCl₃, δ ppm):** 7.69 (d, J = 7.6 Hz, 0.5H), 7.55 (d, J = 7.8 Hz, 2H), 7.34 – 7.26 (m, 9H), 5.70 (s, 0.20H), 5.55 (s, 0.19H), 5.30 (s, 1H), 5.13 (s, 1H), 4.96 (s, 1H), 3.33 – 3.12 (m, 2.54H), 2.81 (dd, J = 42.4, 12.2 Hz, 2.46H), 2.58 – 2.50 (m, 2H), 2.43 (s, 3.8H), 2.01 (s, 0.76H), 1.74 (p, J = 7.2 Hz, 2H), 1.56 (s, 0.78H), 0.89 (s, 3H), 0.76 (t, J = 7.4 Hz, 3H).

**13C NMR (100 MHz, CDCl₃, δ ppm):** 145.7, 143.3, 143.1, 132.9, 132.6, 129.5, 128.2, 127.8, 127.7, 126.6, 117.5, 53.9, 47.4, 45.4, 36.7, 26.9, 24.8, 21.5, 11.7.


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**3ca**

C₂₆H₃₃NO₂S  
MW: 423.61 g.mol⁻¹  
Yellow liquid  
**Yield:** 82%

**1H NMR (400 MHz, CDCl₃, δ ppm):** 7.67 – 7.59 (m, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.26 – 7.19 (m, 8H), 5.63 (s, J = 1.2H, 0.17H), 5.48 (s, 0.18H), 5.23 (d, J = 1.8 Hz, 1H), 5.06 (d, J = 1.7 Hz, 1H), 4.92 (s, 1H), 3.23 – 3.09 (m, 2.42H), 2.78 – 2.65 (m, 2.41H), 2.47 (dd, J = 12.2, 8.0 Hz, 2H), 2.36 (s, 3.9H), 1.94 (d, J = 1.1 Hz, 0.66H), 1.64 (dd, J = 12.4, 6.6 Hz, 2.2H), 1.54 (s, 0.45H) 1.24 – 1.21 (m, 2.3H), 1.10 – 1.06 (m, 2H), 0.81 (s, 3H), 0.76 (t, J = 6.9 Hz, 3.2H).

**13C NMR (100 MHz, CDCl₃, δ ppm):** 145.7, 143.3, 143.2, 132.9, 131.4, 129.6, 128.2, 127.7, 127.1, 126.6, 125.9, 117.6, 53.9, 47.4, 45.3, 36.8, 34.0, 29.5, 24.7, 22.3, 21.5, 13.9.

**HRMS(ESI):** Calcd for C₂₆H₃₃NO₂S+H 424.2310, found 424.2313.
Yellow liquid

Yield: 79%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.68 (d, $J = 7.6$ Hz, 0.38H), 7.54 (d, $J = 7.6$ Hz, 2H), 7.29 (m, 9H), 5.70 (s, 0.12H), 5.55 (s, 0.13H), 5.29 (s, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 3.32 – 3.11 (m, 2.32H), 2.79 (dd, $J = 42.0$, 12.2 Hz, 2.30H), 2.54 (dd, $J = 11.8$, 5.4 Hz, 2H), 2.42 (s, 3.41H), 2.01 (s, 0.39H), 1.71 (d, $J = 4.8$ Hz, 2H), 1.58 (s, 0.40H), 1.24 (d, $J = 17.1$ Hz, 20H), 1.14 (s, 3H), 0.88 (s, 3.3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 145.6, 143.3, 143.2, 132.7, 131.4, 129.6, 128.9, 128.2, 127.7, 127.1, 126.6, 117.7, 53.9, 47.4, 45.3, 36.8, 34.3, 32.0, 29.7, 29.7, 29.6, 29.4, 29.3, 27.3, 24.7, 22.8, 21.6, 14.2.

HRMS(ESI): Calcd for C$_{34}$H$_{49}$NO$_2$S+H 536.3562, found 536.3565.

Yellow liquid

Yield: 68%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.68 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.31 (m, 2H), 7.29 – 7.24 (m, 7.2H), 5.67 (s, 0.24H), 5.60 (s, 0.24H), 5.24 (d, $J = 2.0$ Hz, 1H), 5.08 (d, $J = 1.6$ Hz, 1H), 4.93 (s, 1H), 3.26 – 3.23 (m, 2.75H), 2.86 – 2.70 (m, 2.55H), 2.66 – 2.53 (m, 2H), 2.42 (s, 4.2H), 1.98 (d, $J = 1.2$ Hz, 2H), 1.78 – 1.66 (m, 2.78H), 1.30 – 1.23 (m, 2.7H), 1.14 – 1.11 (m, 2.77H), 1.03 (t, $J = 7.6$ Hz, 1H), 0.91 – 0.87 (m, 2.3H), 0.81 (t, $J = 6.4$ Hz, 3H), 0.74 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 146.0, 143.3, 143.2, 138.1, 132.9, 129.6, 128.1, 127.7, 127.0, 126.7, 125.9, 117.5, 52.4, 47.4, 42.9, 41.5, 39.3, 37.1, 27.0, 25.9, 23.3, 21.6, 14.1, 11.7.

HRMS(ESI): Calcd for C$_{27}$H$_{35}$NO$_2$S+H 438.2467, found 438.2470.

Yellow liquid

Yield: 58%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.64 (d, $J = 8.4$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 5.67 (s, 0.24H), 5.60 (s, 0.24H), 5.24 (d, $J = 2.0$ Hz, 1H), 5.08 (d, $J = 1.6$ Hz, 1H), 4.93 (s, 1H), 3.26 – 3.23 (m, 2.75H), 2.86 – 2.70 (m, 2.55H), 2.66 – 2.53 (m, 2H), 2.42 (s, 4.2H), 1.98 (d, $J = 1.2$ Hz, 2H), 1.78 – 1.66 (m, 2.78H), 1.30 – 1.23 (m, 2.7H), 1.14 – 1.11 (m, 2.77H), 1.03 (t, $J = 7.6$ Hz, 1H), 0.91 – 0.87 (m, 2.3H), 0.81 (t, $J = 6.4$ Hz, 3H), 0.74 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 146.0, 143.3, 143.2, 138.1, 132.9, 129.6, 128.1, 127.7, 127.0, 126.7, 125.9, 117.5, 52.4, 47.4, 42.9, 41.5, 39.3, 37.1, 27.0, 25.9, 23.3, 21.6, 14.1, 11.7.

HRMS(ESI): Calcd for C$_{33}$H$_{31}$NO$_2$S+H 538.2467, found 538.2470.
Yellow liquid

**Yield:** 24%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.51 (d, $J = 8.4$ Hz, 2H), 7.32 – 7.16 (m, 16.6H), 6.96 (dd, $J = 6.4$, 2.8Hz, 2H), 6.14 (s, 1H), 5.29 (s, 0.13H), 5.14 (d, $J = 1.2$ Hz, 1H), 4.86 (s, 1H), 3.80 (t, $J = 2.4$ Hz, 2.16H), 3.26 (s, 2H), 3.26 (dd, $J = 52.8$, 14Hz, 2H), 2.39 (s, 3.25H), 1.57 (s, 0.87H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 144.9, 143.9, 143.5, 143.0 138.4, 132.9, 132.4, 129.8, 129.7, 128.4, 128.4, 128.3, 127.8, 127.7, 127.1, 126.9, 126.6, 126.5, 125.3, 118.1, 53.5, 46.4, 45.8, 45.0, 21.5.

**HRMS(ESI):** Calcd for C$_{33}$H$_{31}$NO$_2$S+H 506.2154, found 506.2151.

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Yellow liquid

**Yield:** 90%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.93 - 7.90 (m, 0.35H), 7.42 – 7.39 (m, 2H), 7.36 – 7.27 (m, 5H), 7.22 (d, $J = 7.6$ Hz, 3H), 6.96 (dd, $J = 7.7$, 1.7 Hz, 2H), 6.26 (s, 0.29H), 5.74 (d, $J = 0.8$Hz, 0.29H), 5.70 (s, 1H), 5.33 (d, $J = 1.8$ Hz, 1H), 5.12 (s, 1H), 4.54 (dd, $J = 24.0$, 1.2 Hz, 0.43H), 4.49 – 4.30 (m, 2.0H), 3.70 (d, $J = 4.4$, 10.8 Hz, 0.65H), 3.46 (dd, $J = 104.8$, 10.8 Hz, 2H), 2.74 (dd, $J = 70.8$, 13.2 Hz, 2H), 2.17 (dd, $J = 1.2$ Hz, 0.88H), 1.38 (s, 0.86H), 0.95 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 146.1, 143.0, 138.1, 133.3, 131.2, 128.3, 128.2, 127.3, 126.6, 125.9, 124.8, 117.1, 74.3, 66.9, 44.8, 35.6, 23.7.

**HRMS(ESI):** Calcd for C$_{21}$H$_{22}$O+H 291.1749, found 291.1752.

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Yellow liquid

**Yield:** 80%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.41 – 7.36 (m, 3H), 7.32 – 7.25 (m, 5H), 6.90 (d, $J = 6.9$ Hz, 2H), 6.76 (d, $J = 7.8$ Hz, 2H), 6.16 (s, 0.31H), 5.74 (s, 0.31H), 5.60 (s, 1H), 5.32 (s, 1H), 5.11 (s, 1H), 4.36 (dd, $J = 44.0$, 16.0Hz, 2.4H), 3.81 (s, 0.86H), 3.78 (s, 3H), 3.63 (d, $J = 10.8$ Hz, 0.53H), 3.57 (d, $J = 12$Hz, 1H), 3.31 (d, $J = 12$ Hz, 1H), 2.72 (dd, $J = 64$, 16 Hz, 2H), 2.16 (s, 0.86H), 1.37 (s, 0.86H), 0.94 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 158.9, 146.1, 143.1, 132.7, 130.7, 129.8, 129.6, 128.4, 126.6, 12.6, 117.1, 113.8, 74.3, 67.0, 55.2, 44.9, 35.6, 23.9.

HRMS: Calcd for C$_{22}$H$_{24}$O$_2$+H 321.1855, found 321.1852.

5ca

![Structure of 5ca](image)

C$_{21}$H$_{21}$FO

MW: 308.39 g.mol$^{-1}$

Yellow liquid

Yield: 89%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.40 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.26 (s, 1.5H), 6.92 - 6.88 (m, 4H), 6.19 (s, 0.09H), 5.73 (s, 0.09H), 5.60 (s, 1H), 5.32 (s, 1H), 5.11 (s, 1H), 4.34 (dd, J = 48.0, 16.0 Hz, 2.2H), 3.46 (dd, J = 104.0, 12.0 Hz, 2.2H), 2.74 (dd, J = 80.0, 12.0 Hz, 2H), 2.16 (s, 0.21H), 1.55 (s, 0.44H), 0.95 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 163.1, 161.1, 146.0, 143.0, 132.4, 131.2, 128.4, 127.2, 126.5 (d, J = 22.0 Hz), 126.3, 117.2, 115.1 (d, J = 17.0 Hz), 74.3, 66.9, 44.9, 35.6, 23.7.

$^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$, δ ppm): 115.7.

HRMS(ESI): Calcd for C$_{21}$H$_{21}$FO+H 309.1655, found 309.1658.

5da

![Structure of 5da](image)

C$_{27}$H$_{42}$O

MW: 382.6218 g.mol$^{-1}$

Yellow liquid

Yield: 82%

$^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 7.37 - 7.26 (m, 5H), 7.23 (d, J = 6.3 Hz, 1H), 5.67 (s, 0.19H), 5.59 (s, 0.19H), 5.27 (s, 1H), 5.06 (s, 1H), 5.05 (s, 1H), 4.04 (s, 0.39H), 3.89 (s, 2H), 3.58 (dd, J = 50.4, 10.9 Hz, 0.52H), 3.31 (dd, J = 115.6, 10.8 Hz, 2H), 2.61 (dd, J = 37.2, 13.2 Hz, 2H), 2.13 (s, 0.63H), 1.93 (t, J = 8.0 Hz, 0.43H), 1.70 (d, J = 4.0 Hz, 2H), 1.42 (s, 0.66H), 1.26 (s, 20H), 0.88 (t, J = 6.0 Hz, 3.7H), 0.81 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 146.3, 143.2, 134.6, 128.1, 127.1, 126.6, 125.9, 116.8, 74.3, 68.0, 44.6, 35.2, 32.7, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 27.3, 23.8, 22.8, 14.2.

HRMS(ESI): Calcd for C$_{27}$H$_{42}$O+H 383.3314, found 383.3311.
5ea

C_{17}H_{22}O

MW: 242.36 g.mol\(^{-1}\)

Yellow liquid

Yield: 86%

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.91 (d, \(J = 6.0\) Hz, 0.45H), 7.36 (d, \(J = 7.3\) Hz, 2H), 7.30 – 7.22 (m, 4H), 5.67 (s, 0.23H), 5.59 (s, 0.23H), 5.27 (s, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 4.05 (s, 0.5H), 3.89 (s, 2H), 3.66 – 3.50 (m, 0.66H), 3.33 (dd, \(J = 115.4\), 10.8 Hz, 2H), 2.73 – 2.51 (m, 2H), 2.12 (s, 0.76H), 1.96 – 1.93 (m, 0.64H), 1.71 (p, \(J = 7.2\) Hz, 2H), 1.33 (s, 0.59H), 1.05 (t, \(J = 7.2\) Hz, 0.86H), 0.82 (s, 3H), 0.79 (t, \(J = 7.4\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\) ppm): 146.4, 143.2, 135.8, 128.1, 127.0, 126.6, 116.7, 74.4, 68.0, 44.7, 35.0, 25.2, 23.7, 11.5.

HRMS(ESI): Calcd for C_{17}H_{22}O+H 243.1749, found 243.1746.

5eb

C_{17}H_{21}BrO

MW: 321.25 g.mol\(^{-1}\)

Yellow liquid

Yield: 75%

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.91 (d, \(J = 5.2\) Hz, 0.41H), 7.36 (d, \(J = 7.2\) Hz, 2H), 7.28 (t, \(J = 7.3\) Hz, 2H), 7.23 (d, \(J = 7.2\) Hz, 1H), 5.67(s, 0.25H), 5.59(s, 0.25H), 5.27 (s, 1H), 5.05 (s, 1H), 5.04 (s, 1H), 4.05 (s, 0.52H), 3.89 (s, 2H), 3.67 – 3.50 (m, 0.71H), 3.33 (dd, \(J = 115.8\), 10.8 Hz, 2H), 2.62 (dd, \(J = 48.4\), 13.2 Hz, 2H), 2.12 (s, 0.83H), 2.00 – 1.92 (m, 0.56H), 1.71 (p, \(J = 7.3\) Hz, 2H), 1.35 (s, 0.46H), 1.05 (t, \(J = 7.4\) Hz, 0.87H), 0.82 (s, 3H), 0.78 (t, \(J = 7.4\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\) ppm): 146.4, 143.2, 135.8, 128.1, 127.0, 126.6, 116.7, 74.4, 68.0, 44.7, 35.0, 25.2, 23.9, 11.6.

HRMS(ESI): Calcd for C_{17}H_{21}BrO+H 321.0854, found 321.0851.
IV Copies of the $^1$H NMR, $^{13}$C NMR

3aa
5ea

5eb
V. Copies of the NOESY for Product 3ak

From the view of the spectrum \(3ak\), there was signal between protons of the allyl (\(H^a, 5.79\)) and phenyl (7.30). There were signals between protons of methyl (\(Me^a, 1.80\)) and methylene (\(x, \text{ dd, } 2.96 \text{ and } 2.68\)). On the contrast, there were no signals between \(H^a\) and methylene hydrogen (\(x\)), or methyl hydrogen (\(Me^a\)) and phenyl. So, the isomer of product \(3ak\) should be in E configuration as below.

\[
\begin{align*}
\text{N} & \quad \text{M} \\
\text{Me}^b & \quad \text{Me}^a \\
\text{O=S=O} & \quad 3ak \\
\text{H}^b & \quad \text{H}^a \\
\end{align*}
\]

3 Hui Liu, Chaolong Li, Dong Qiu, Xiaofeng Tong, *Journal of the American Chemical Society*, 2011, 133, 6187 – 6193.
5 Abadh Kishor Jha, Nidhi Jain, *Chemical Communications*, 2016, 52, 1831 – 1834.