

## Supplementary Information

### Metal-Free Mizoroki-Heck Type Reaction: A Radical Oxidative Coupling Reaction of 2-Chloro-Dithiane with Substituted Olefins

Wenbin Du,<sup>a</sup> Junshan Lai,<sup>a</sup> Lixia Tian,<sup>a</sup> Xingang Xie,<sup>b</sup> Xuegong She,<sup>b</sup> Shouchu Tang<sup>\*a b</sup>

<sup>a</sup> School of Pharmacy, Lanzhou University, Lanzhou 730000, P. R. China

<sup>b</sup> State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

Email: [tangshch@lzu.edu.cn](mailto:tangshch@lzu.edu.cn)

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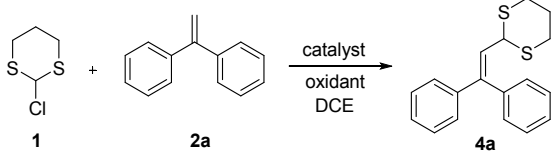
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## General Considerations

Unless otherwise noted, analytical grade solvents and commercially available reagents were used as received. Substituted olefins were all prepared following literature procedures. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were generally performed on silica gel (200-300 mesh) in petroleum (bp. 60-90 °C) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solution on the Bruker 300 and 400MHz instruments, The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (0 ppm for <sup>1</sup>H) and CDCl<sub>3</sub> (77.00 ppm for <sup>13</sup>C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion ([M+H]<sup>+</sup>). MS were measured on a HP-5988 spectrometer by direct inlet at 70 eV.

## Summary of initial studies on reaction condition optimization

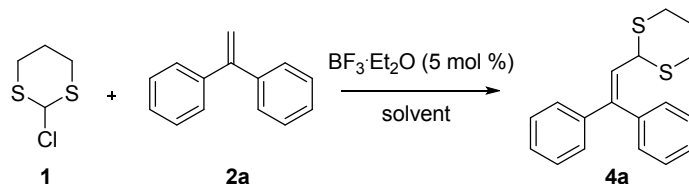
Table S1 Cross-coupling reaction between 1 and 2a under varied conditions<sup>a</sup>



entry	catalyst/mol%	oxidant	temperature/ °C	yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub> /K <sub>2</sub> CO <sub>3</sub> /PPh <sub>3</sub>	— <sup>c</sup>	80 °C	trace
2	Pd <sub>2</sub> (dba) <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> /PPh <sub>3</sub>	—	80 °C	trace
3	FeCl <sub>3</sub> (15)	Air	rt	72
4	NiCl <sub>2</sub> (10)	Air	rt	30
5	Cu(OAc) <sub>2</sub> (10)	Air	rt	24
6	CuI (10)	Air	rt	30
7	Pd(OAc) <sub>2</sub> (5)	Air	rt	35
8	MSA <sup>c</sup> (15)	Air	rt	60
9	BF <sub>3</sub> ·Et <sub>2</sub> O (15)	Air	rt	81
10	BF <sub>3</sub> ·Et <sub>2</sub> O (10)	Air	rt	80
11	BF <sub>3</sub> ·Et <sub>2</sub> O (5)	Air	rt	81
12	BF <sub>3</sub> ·Et <sub>2</sub> O (5)	—	rt	57
13	none	Air	rt	39(69 <sup>d</sup> )
14	none	—	rt	7
15	CuI (10)	—	rt	9
16	Pd(OAc) <sub>2</sub> (5)	—	rt	8
17	none	DDQ	rt	15
18	none	TBHP	rt	11
19	BF <sub>3</sub> ·Et <sub>2</sub> O (5)	DDQ	rt	30
20	BF <sub>3</sub> ·Et <sub>2</sub> O (5)	TBHP	rt	50

<sup>a</sup>Reaction conditions: entries 1 and 2 were performed with **1** (30 mg, 0.25 mmol), **2a** (40.5 mg, 0.225 mmol), 5 mol % Pd, K<sub>2</sub>CO<sub>3</sub> (69 mg, 0.5 mmol) and PPh<sub>3</sub> (9.8 mg, 0.0375 mmol) in 2 mL of DMF at 80 °C for 24 h ; entries 3-20 were performed with **1** (30 mg, 0.25 mmol), **2a** (40.5 mg, 0.225 mmol), catalyst (5~15 %) and oxidant (0.375 mmol) in 2 mL of DCE at rt for 12 h. <sup>b</sup>Yield of isolated product. <sup>c</sup>Methanesulfonic acid (MSA). <sup>d</sup>Yield of isolated product while reaction for 48 h. <sup>e</sup>Under Ar.

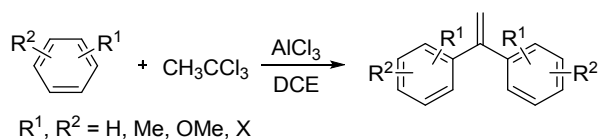
**Table S2 Cross-coupling reaction between 1 and 2a under varied solvent<sup>a</sup>**



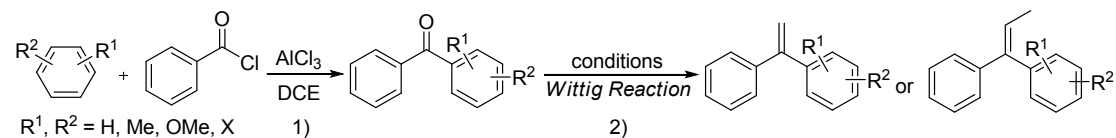
entry	solvent	yield <sup>b</sup> (%)	entry	solvent	yield <sup>b</sup> (%)
1	DCM	77	5	MeOH	trace
2	DCE	81	6	MeNO <sub>2</sub>	trace
3	toluene	26	7	DMF	0
4	DMSO	0	8	MeCN	trace

<sup>a</sup> Reaction conditions: **1** (30 mg, 0.25 mmol), **2a** (40.5 mg, 0.225 mmol), BF<sub>3</sub>·Et<sub>2</sub>O (5 mol %) in 2 mL of DCE at rt for 12 h. <sup>b</sup>Yield of isolated product.

### General procedure for synthesis of 1,1-diphenylethylene derivatives<sup>4,5</sup>



To a flame-dried 100 mL flask were sequentially added aromatic hydrocarbon (20 mmol) and AlCl<sub>3</sub> (30 mmol), DCE (40 mL), dissolved the mixture was stirred at 0 °C. Then CH<sub>3</sub>CCl<sub>3</sub> (12 mmol) were added at 0 °C in 10 minutes. Reaction mixture was stirred at 0 °C for 2-8 h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (100 mL) and dilute hydrochloric acid solution (30 mL). The organic layer was separated and washed with H<sub>2</sub>O (5×30 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by the flash chromatography (petroleum ether) to afford the desired product (70 %~80 % yield).



1). To a flame-dried 100 mL flask were sequentially added aromatic hydrocarbon (60 mmol) and phenylacetyl chloride (20 mmol), DCE (40 mL), dissolved the mixture was stirred at 0 °C. Then AlCl<sub>3</sub> (30 mmol) were added. Reaction mixture was stirred at rt for 6-12 h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (100 mL) and dilute hydrochloric acid solution (30 mL). The organic layer was separated and washed with H<sub>2</sub>O (5×30 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by the flash chromatography (petroleum ether) to afford the desired benzophenone derivatives products.

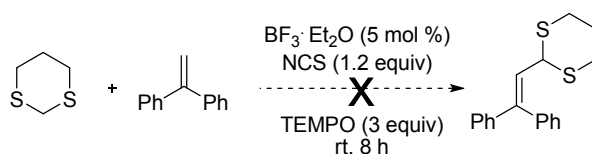
2). To a flame-dried 100 mL flask were added benzophenone derivatives (10 mmol) and THF (40 mL), dissolved the mixture was stirred at rt. Then Wittig (12 mmol) and NaH (15 mmol) were sequentially added. Reaction mixture was stirred at rt for 12-24 h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (100 mL) and dilute hydrochloric acid solution (30 mL). The organic layer was separated and washed with H<sub>2</sub>O (5×30 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by the flash chromatography (petroleum ether) to afford the desired products.

### **General procedure for the cross-coupling between 1 and Multi-substituted Alkenes**

**General BF<sub>3</sub>·Et<sub>2</sub>O as catalyst procedure:** To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (0.25 mmol) and NCS (0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 mins.<sup>6</sup> Then alkenes (0.225 mmol) and boron trifluoride-diethyl etherate (BF<sub>3</sub>·Et<sub>2</sub>O) (0.0125 mmol) were added at reaction temperature. Reaction mixture was stirred at room temperature for 8-24h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (10 mL) and H<sub>2</sub>O (1 mL). The organic layer was separated, and the aqueous phase was re-extracted with ethyl acetate (3×3 mL). The combined organic extracts were washed with brine (10 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by the flash chromatography to afford the desired product.

**General no catalyst procedure:** To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (0.25 mmol) and NCS (0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 mins. Then alkenes (0.225 mmol) were added at reaction temperature. Reaction mixture was stirred in Open system at room temperature for 48h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (10 mL) and H<sub>2</sub>O (1 mL). The organic layer was separated, and the aqueous phase was re-extracted with ethyl acetate (3×3 mL). The combined organic extracts were washed with brine (10 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by the flash chromatography to afford the desired product.

### **The procedure for radical trapping experiment.**



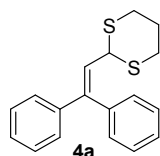
To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol) and NCS (40 mg, 0.3mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then TEMPO (124 mg, 0.65 mmol), 1,1-diphenylethylene (40.5 mg, 0.225mmol) and BF<sub>3</sub>·Et<sub>2</sub>O (1.78 mg, 0.0125 mmol) were added. Reaction mixture was stirred at rt for 12 h. Then reaction mixture was diluted with ethyl acetate (3 mL) and H<sub>2</sub>O (1 mL). The organic layer was separated, and the aqueous phase was re-extracted with ethyl acetate (3×3 mL). The combined organic

extracts were washed with H<sub>2</sub>O (10 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

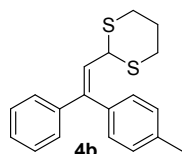
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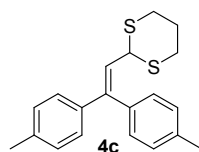
## Analytical Data of Products



The compound of **4a** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a white solid in 69% yield.  $R_f$  = 0.37 (petroleum ether: EtOAc = 50:1). Mp. 147 °C–149 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.41-7.20 (m, 10H), 6.02 (d,  $J$  = 10.8 Hz, 1H), 4.70 (d,  $J$  = 10.8 Hz, 1H), 2.78 (q,  $J$  = 3.2 Hz, 4H), 2.05-1.77 (m, 2H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 144.6, 141.1, 138.5, 129.4, 128.2, 128.0, 127.8, 127.7, 123.9, 45.1, 29.7, 24.6. **IR (KBr) cm<sup>-1</sup>**: 3402.5, 2941.1, 1598.0, 1425.2, 1299.8, 858.4, 765.1, 655.7. **HRMS (ESI)**: calculated for C<sub>18</sub>H<sub>19</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 299.0928; **found**:299.0931.

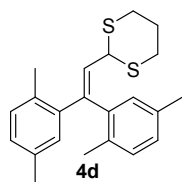


The compound of **4b** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a white solid in 73% yield.  $R_f$  = 0.35 (petroleum ether: EtOAc = 50:1). Mp. 162 °C–164 °C. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.25-7.21 (m, 9H), 5.98 (d,  $J$  = 12 Hz, 1H), 4.74 (d,  $J$  = 12 Hz, 1H), 2.87-2.76 (m, 4H), 2.40 (s, 3H), 2.08-1.82 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 144.8, 141.4, 137.4, 135.6, 129.3, 128.9, 128.7, 127.8, 123.7, 45.3, 29.8, 24.7, 21.2. **IR (KBr) cm<sup>-1</sup>**: 3433.8, 2901.7, 1618.6, 1414.5, 1274.7, 853.4, 771.8, 697.7. **HRMS (ESI)**: calculated for C<sub>19</sub>H<sub>21</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 313.1085; **found**:313.1081.

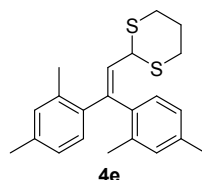


The compound of **4c** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a white solid in 78% yield.  $R_f$  = 0.40 (petroleum ether: EtOAc = 50:1). Mp. 166 °C–168 °C. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.24-7.05 (m, 8H), 5.94 (d,  $J$  = 9 Hz, 1H), 4.72 (d,  $J$  = 12 Hz, 1H), 2.79 (s, 4H), 2.40 (s, 3H), 2.32 (s, 3H), 2.01-1.84 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**:

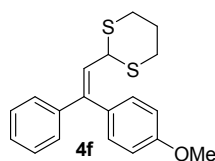
$\delta$  = 144.7, 138.6, 137.7, 137.3, 135.8, 129.3, 129.0, 128.9, 128.7, 127.6, 126.4, 122.8, 45.3, 29.8, 24.7, 21.2, 21.0. **IR (KBr)  $\text{cm}^{-1}$** : 3477.9, 2933.5, 1622.1, 1438.5, 1301.2, 866.7, 732.9, 645.8. **HRMS (ESI)**: calculated for  $\text{C}_{20}\text{H}_{23}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 327.1241; **found**: 327.1239.



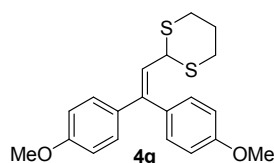
The compound of **4d** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow solid in 75% yield.  $R_f$  = 0.39 (petroleum ether: EtOAc = 50:1). Mp. 131 °C–133 °C.  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.23–6.82 (m, 6H), 5.75 (d,  $J$  = 12 Hz, 1H), 4.62 (d,  $J$  = 12 Hz, 1H), 2.78 (t,  $J$  = 6 Hz, 4H), 2.32 (d,  $J$  = 15 Hz, 6H), 2.21 (s, 3H), 2.04 (s, 3H), 1.89–1.69 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 143.7, 140.4, 138.5, 134.7, 134.7, 133.2, 132.3, 130.8, 130.5, 130.2, 130.1, 128.3, 128.1, 127.9, 44.8, 29.6, 29.4, 24.8, 20.8, 20.4, 19.7. **IR (KBr)  $\text{cm}^{-1}$** : 3411.3, 2867.7, 1614.9, 1409.5, 1224.1, 905.4, 765.1, 633.4. **HRMS (ESI)**: calculated for  $\text{C}_{22}\text{H}_{27}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 355.1554; **found**: 355.1557.



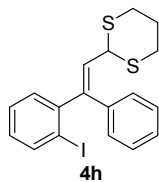
The compound of **4e** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow solid in 76% yield.  $R_f$  = 0.37 (petroleum ether: EtOAc = 50:1). Mp. 102 °C–104 °C.  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.24–6.87 (m, 6H), 5.73 (d,  $J$  = 12 Hz, 1H), 4.64 (d,  $J$  = 12 Hz, 1H), 2.77 (d,  $J$  = 6 Hz, 4H), 2.33 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.00 (s, 3H), 1.86–1.80 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 143.4, 137.4, 136.8, 136.3, 135.8, 135.7, 134.8, 131.3, 130.9, 129.5, 129.3, 127.5, 125.9, 125.8, 44.7, 29.2, 24.4, 20.8, 20.6, 19.7. **IR (KBr)  $\text{cm}^{-1}$** : 3475.1, 2967.1, 1608.6, 1427.5, 1210.3, 857.4, 751.1, 647.1. **HRMS (ESI)**: calculated for  $\text{C}_{22}\text{H}_{27}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 355.1554; **found**: 355.1556.



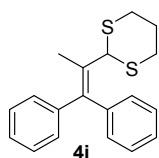
The compound of **4f** was purified by silica gel chromatography (petroleum ether: EtOAc = 80:1) to afford a thick yellow oil in 76% yield.  $R_f$  = 0.28 (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.40–6.78 (m, 9H), 5.94 (q,  $J$  = 6 Hz, 1H), 4.71 (q,  $J$  = 12 Hz, 1H), 3.81 (d,  $J$  = 21 Hz, 3H), 2.80 (d,  $J$  = 6 Hz, 4H), 2.03–1.84 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 159.2, 159.0, 144.2, 144.0, 141.4, 138.6, 130.7, 130.5, 129.2, 128.7, 128.0, 127.9, 127.6, 127.5, 122.0, 113.4, 113.3, 55.0, 45.1, 45.2, 29.6, 24.5. **IR (KBr)  $\text{cm}^{-1}$** : 3433.7, 2865.8, 1576.1, 1488.7, 1114.6, 1002.2, 817.1, 565.2. **HRMS (ESI)**: calculated for  $\text{C}_{19}\text{H}_{21}\text{OS}_2$   $[\text{M}+\text{H}]^+$ : 329.1034; **found**: 329.1033.



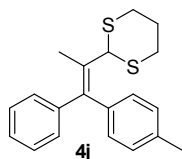
The compound of **4g** was purified by silica gel chromatography (petroleum ether: EtOAc = 80:1) to afford a thick yellow oil in 74% yield.  $R_f = 0.27$  (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**  $\delta = 7.25$  (d,  $J = 9$  Hz, 2H), 7.15 (d,  $J = 9$  Hz, 2H), 6.93 (d,  $J = 6$  Hz, 2H), 6.79 (d,  $J = 9$  Hz, 4H), 5.86 (d,  $J = 12$  Hz, 1H), 4.72 (d,  $J = 12$  Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.88-2.80 (m, 4H), 2.04-1.86 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):**  $\delta = 159.4, 159.1, 144.1, 134.2, 131.2, 130.7, 129.0, 121.8, 113.6, 113.4, 55.2, 45.6, 30.0, 24.7$ . **IR (KBr)  $\text{cm}^{-1}$ :** 3431.7, 2927.8, 1604.9, 1510.7, 1174.6, 1032.7, 834.1, 579.5. **HRMS (ESI):** calculated for  $\text{C}_{20}\text{H}_{23}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ : 359.1139; **found:** 359.1134.



The compound of **4h** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a white solid in 62% yield.  $R_f = 0.38$  (petroleum ether: EtOAc = 50:1). Mp. 150 °C–152 °C.  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**  $\delta = 7.01$  (q,  $J = 3$  Hz, 1H), 7.44-7.07 (m, 8H), 6.21 (d,  $J = 12$  Hz, 1H), 4.40 (d,  $J = 9$  Hz, 1H), 2.76-2.72 (m, 4H), 2.03-1.82 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):**  $\delta = 145.8, 142.8, 139.5, 138.4, 130.3, 129.3, 129.2, 128.2, 128.0, 127.8, 126.9, 124.4, 125.9, 99.3, 44.5, 29.4, 29.3, 24.6$ . **IR (KBr)  $\text{cm}^{-1}$ :** 3424.3, 2933.5, 1612.4, 1521.7, 1214.6, 1012.7, 842.5, 545.2. **HRMS (ESI):** calculated for  $\text{C}_{18}\text{H}_{18}\text{IS}_2$   $[\text{M}+\text{H}]^+$ : 424.9895; **found:** 424.9897.

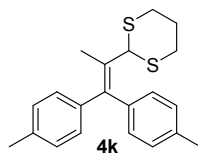


The compound of **4i** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a thick yellow oil in 70% yield.  $R_f = 0.35$  (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**  $\delta = 7.41$ -7.02 (m, 10H), 4.05 (s, 1H), 1.96 (d,  $J = 3$  Hz, 3H), 1.91-1.69 (m, 4H), 1.27-1.17 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):**  $\delta = 144.4, 144.2, 140.9, 139.1, 134.7, 128.9, 128.3, 128.1, 127.2, 127.1, 124.8, 123.8, 119.3, 53.8, 29.0, 28.9, 26.0, 12.9$ . **IR (KBr)  $\text{cm}^{-1}$ :** 3398.1, 2857.7, 1603.6, 1455.2, 1266.7, 825.4, 731.8, 674.4. **HRMS (ESI):** calculated for  $\text{C}_{19}\text{H}_{21}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 313.1085; **found:** 313.1082.

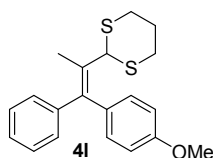


The compound of **4j** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a thick yellow oil in 72% yield.  $R_f = 0.39$  (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$**

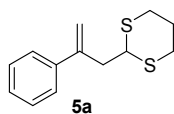
**(300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.43-6.92 (m, 9H), 4.07 (d,  $J$  = 6 Hz, 1H), 2.31 (s, 3H), 1.98 (s, 3H), 1.89-1.83 (m, 4H), 1.29-1.18 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 144.4, 141.8, 139.7, 138.9, 134.8, 134.5, 128.8, 128.2, 127.1, 119.2, 118.9, 53.7, 53.6, 29.0, 26.1, 21.3, 21.2, 12.8. **IR (KBr) cm<sup>-1</sup>:** 3430.1, 2898.3, 1635.6, 1437.4, 1251.9, 853.0, 727.4, 697.0. **HRMS (ESI):** calculated for C<sub>20</sub>H<sub>23</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 327.1241; **found:** 327.1242.



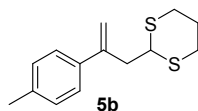
The compound of **4k** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow oil in 77% yield.  $R_f$  = 0.36 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.28-6.86 (m, 8H), 3.99 (s, 1H), 2.28 (s, 3H), 2.23 (s, 3H), 1.93 (s, 3H), 1.87-1.73 (m, 4H), 1.22-1.15 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 144.4, 141.9, 139.3, 138.8, 136.7, 134.4, 131.8, 129.0, 128.7, 127.7, 124.6, 118.9, 53.6, 29.0, 26.1, 21.3, 21.2, 12.9. **IR (KBr) cm<sup>-1</sup>:** 3433.7, 2951.6, 1615.8, 1455.0, 1232.5, 823.6, 766.8, 671.7. **HRMS (ESI):** calculated for C<sub>21</sub>H<sub>25</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 341.1398; **found:** 341.1342.



The compound of **4l** was purified by silica gel chromatography (petroleum ether: EtOAc = 80:1) to afford a thick pale brown oil in 77% yield.  $R_f$  = 0.20 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.49-6.72 (m, 9H), 4.10 (s, 1H), 3.76 (s, 3H), 2.03 (s, 3H), 1.99-1.88 (m, 4H), 1.33-1.26 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 158.0, 146.0, 144.6, 140.2, 138.4, 137.4, 134.9, 130.0, 128.8, 127.1, 124.7, 123.7, 119.6, 113.7, 110.2, 55.4, 53.7, 29.0, 26.0, 12.9, 12.8. **IR (KBr) cm<sup>-1</sup>:** 3397.2, 2874.2, 1586.9, 1500.2, 1151.5, 1042.7, 834.2, 573.3. **HRMS (ESI):** calculated for C<sub>20</sub>H<sub>23</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 343.1190; **found:** 343.1195.



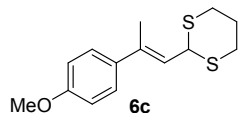
The compound of **5a** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a pale yellow oil in 77% yield.  $R_f$  = 0.34 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.44-7.25 (m, 5H), 5.40-5.38 (m, 1H), 5.20 (d,  $J$  = 3 Hz, 1H), 4.03 (d,  $J$  = 3 Hz, 1H), 2.95-2.92 (m, 2H), 2.78-2.74 (m, 4H), 2.08-1.78 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.4, 128.3, 128.1, 127.6, 127.3, 126.1, 41.3, 30.2, 25.7. **IR (KBr) cm<sup>-1</sup>:** 3034.2, 2917.3, 1617.6, 1512.3, 1283.1, 1167.8, 905.2, 823.5, 721.5, 521.3. **HRMS (ESI):** calculated for C<sub>13</sub>H<sub>17</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 237.0772; **found:** 237.0768.



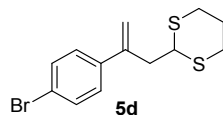
The compound of **5b** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a colorless oil in 88% yield.  $R_f$  = 0.30 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300**



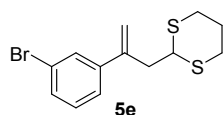
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ = 7.33-7.02 (m, 4H), 5.28 (s, 1H), 5.07 (s, 1H), 3.96 (s, 1H), 2.92 (t, *J* = 6 Hz, 2H), 2.72-2.65 (m, 4H), 2.00-1.65 (m, 2H), 1.60 (s, 3H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** δ = 143.1, 139.1, 137.3, 137.2, 129.0, 128.9, 128.8, 128.6, 126.2, 125.9, 125.7, 122.7, 114.9, 44.9, 44.7, 41.3, 30.3, 30.1, 29.9, 28.7, 25.6, 24.9, 24.5, 21.0, 20.9, 16.3. **IR (KBr) cm<sup>-1</sup>:** 3028.0, 2932.7, 1620.7, 1510.4, 1283.0, 1182.8, 895.2, 821.1, 735.1, 528.3. **HRMS (ESI):** calculated for C<sub>14</sub>H<sub>19</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 251.0928; **found:** 251.0924.



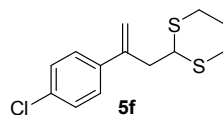
The compound of **6c** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a pale yellow oil in 82% yield. *R<sub>f</sub>* = 0.21 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ = 7.34 (d, *J* = 6 Hz, 2H), 6.85 (d, *J* = 9 Hz, 2H), 5.65 (d, *J* = 12 Hz, 1H), 5.04 (d, *J* = 9 Hz, 1H), 3.80 (s, 3H), 3.03-2.75 (m, 4H), 2.15 (s, 3H), 1.94-1.63 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** δ = 159.1, 138.8, 127.3, 127.0, 121.9, 113.5, 55.2, 44.9, 30.5, 29.6, 24.9, 16.4. **IR (KBr) cm<sup>-1</sup>:** 3346.2, 2871.4, 1521.9, 1487.2, 1210.5, 1041.4, 834.1, 563.1. **HRMS (ESI):** calculated for C<sub>14</sub>H<sub>19</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 267.0877; **found:** 267.0880.



The compound of **5d** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow oil in 65% yield. *R<sub>f</sub>* = 0.28 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ = 7.38 (d, *J* = 9 Hz, 2H), 7.20 (d, *J* = 9 Hz, 2H), 5.30 (s, 1H), 5.14 (s, 1H), 3.91 (t, *J* = 9 Hz, 1H), 2.82 (d, *J* = 6 Hz, 2H), 2.70-2.67 (m, 4H), 2.07-1.68 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** δ = 142.4, 138.5, 131.4, 127.8, 121.6, 116.3, 44.8, 41.1, 30.3, 30.2, 25.6. **IR (KBr) cm<sup>-1</sup>:** 3410.3, 2927.1, 1627.4, 1487.3, 1008.1, 833.4, 514.0. **HRMS (ESI):** calculated for C<sub>13</sub>H<sub>16</sub>BrS<sub>2</sub> [M+H]<sup>+</sup>: 314.9877; **found:** 314.9876.

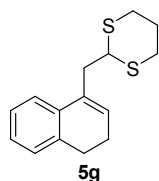


The compound of **5e** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a pale yellow solid in 66% yield. *R<sub>f</sub>* = 0.27 (petroleum ether: EtOAc = 50:1). Mp. 43 °C–45 °C. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ = 7.56-7.19 (m, 4H), 5.38 (s, 1H), 5.24 (s, 1H), 4.00 (t, *J* = 6 Hz, 1H), 2.90 (d, *J* = 9 Hz, 2H), 2.80-1.77 (m, 4H), 2.14-2.04 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** δ = 142.2, 130.5, 129.8, 129.3, 124.8, 117.0, 52.0, 44.7, 41.1, 30.1, 25.6. **IR (KBr) cm<sup>-1</sup>:** 3421.5, 2988.1, 1656.1, 1487.0, 1021.3, 834.4, 523.9. **HRMS (ESI):** calculated for C<sub>13</sub>H<sub>16</sub>BrS<sub>2</sub> [M+H]<sup>+</sup>: 314.9877; **found:** 314.9875.

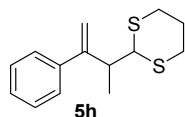


The compound of **5f** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow oil in 60% yield. *R<sub>f</sub>* = 0.25 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ = 7.46-7.23 (m, 4H), 5.36 (s, 1H), 5.20 (s, 1H), 3.99 (t, *J* = 9 Hz, 1H), 2.89 (d, *J* = 6 Hz, 2H), 2.77-2.73 (m, 4H), 2.09-1.71 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** δ = 142.3, 137.9,

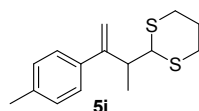
133.2, 128.3, 127.4, 116.2, 44.7, 41.1, 30.1, 25.5. **IR (KBr)  $\text{cm}^{-1}$** : 3447.3, 2897.0, 1644.2, 1455.7, 1032.1, 837.5, 514.7. **HRMS (ESI)**: calculated for  $\text{C}_{13}\text{H}_{16}\text{ClS}_2$   $[\text{M}+\text{H}]^+$ : 271.0382; **found**: 271.0386.



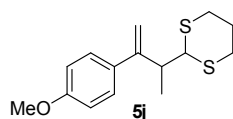
The compound of **5g** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow oil in 80% yield.  $R_f$  = 0.34 (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.23-7.13 (m, 4H), 5.96 (t,  $J$  = 3 Hz, 1H), 4.23 (t,  $J$  = 3 Hz, 1H), 2.78 (d,  $J$  = 3 Hz, 2H), 2.78-2.73 (m, 6H), 2.29-2.24 (m, 2H), 2.09-1.80 (m, 2H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 136.9, 134.0, 131.8, 128.5, 127.8, 126.9, 126.4, 122.3, 45.5, 39.2, 30.5, 28.9, 28.1, 25.9, 23.2. **IR (KBr)  $\text{cm}^{-1}$** : 3032.2, 2862.7, 1559.3, 1226.4, 725.3. **HRMS (ESI)**: calculated for  $\text{C}_{15}\text{H}_{19}\text{S}_2$   $[\text{M}+\text{Na}]^+$ : 263.0928; **found**: 263.0929.



The compound of **5h** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a pale yellow oil in 80% yield.  $R_f$  = 0.32 (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.39-7.26 (m, 5H), 5.32 (s, 1H), 5.19 (s, 1H), 4.07 (d,  $J$  = 6 Hz, 1H), 3.12 (t,  $J$  = 9 Hz, 1H), 2.82-2.76 (m, 4H), 2.06-1.76 (m, 2H), 1.38(d,  $J$  = 9 Hz, 3H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 150.0, 141.6, 128.1, 127.3, 126.8, 114.2, 52.5, 42.9, 42.8, 31.0, 30.4, 25.8, 15.9. **IR (KBr)  $\text{cm}^{-1}$** : 3122.5, 2924.6, 1607.1, 1500.3, 1262.3, 1185.2, 900.2, 824.7, 721.1, 522.9. **HRMS (ESI)**: calculated for  $\text{C}_{14}\text{H}_{19}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 251.0928; **found**: 251.0926.

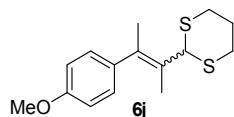


The compound of **5i** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a yellow solid in 88% yield.  $R_f$  = 0.30 (petroleum ether: EtOAc = 50:1). Mp. 61 °C–63 °C.  **$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 7.20 (d,  $J$  = 9 Hz, 2H), 7.06 (d,  $J$  = 6 Hz, 2H), 5.22 (s, 1H), 5.07 (s, 1H), 4.00 (d,  $J$  = 6 Hz, 1H), 3.03 (t,  $J$  = 6 Hz, 1H), 2.73-2.68 (m, 4H), 2.27 (s, 3H), 1.97-1.68 (m, 2H), 1.29 (d,  $J$  = 9 Hz, 3H).  **$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**:  $\delta$  = 149.8, 138.6, 137.0, 128.8, 126.7, 113.6, 52.6, 42.8, 31.0, 30.3, 25.8, 21.0, 15.9. **IR (KBr)  $\text{cm}^{-1}$** : 3036.1, 2932.0, 1621.0, 1525.4, 1275.2, 1082.8, 896.3, 839.5, 744.1, 504.4. **HRMS (ESI)**: calculated for  $\text{C}_{15}\text{H}_{21}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 265.1085; **found**: 265.1089.

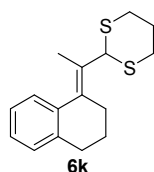


The compound of **5j** was purified by silica gel chromatography (petroleum ether: EtOAc = 80:1) to afford a colorless oil in 55% yield.  $R_f$  = 0.24 (petroleum ether: EtOAc = 50:1).  **$^1\text{H NMR}$  (300**

**MHz, CDCl<sub>3</sub>**:  $\delta$  = 7.24 (d,  $J$  = 6 Hz, 2H), 6.80 (d,  $J$  = 9 Hz, 2H), 5.19 (s, 1H), 5.04 (s, 1H), 4.00 (d,  $J$  = 6 Hz, 1H), 3.74 (s, 3H), 3.02 (t,  $J$  = 6 Hz, 1H), 2.74-2.66 (m, 4H), 1.98-1.68 (m, 2H), 1.29 (d,  $J$  = 6 Hz, 3H). **IR (KBr) cm<sup>-1</sup>**: 3342.3, 2874.2, 1535.1, 1505.2, 1138.5, 1072.1, 841.2, 560.3. **HRMS (ESI)**: calculated for C<sub>15</sub>H<sub>21</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 281.1034; **found**: 281.1033.



The compound of **6j** was purified by silica gel chromatography (petroleum ether: EtOAc = 80:1) to afford a colorless oil in 26% yield.  $R_f$  = 0.22 (petroleum ether: EtOAc = 50:1). **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.12 (t,  $J$  = 6 Hz, 2H), 6.80 (d,  $J$  = 6 Hz, 2H), 4.83 (s, 1H), 3.74 (d,  $J$  = 3 Hz, 3H), 2.95-2.91 (m, 3H), 2.81-2.65 (m, 4H), 2.01-1.94 (m, 2H), 1.87 (s, 3H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 158.1, 135.4, 134.6, 129.0, 128.3, 127.4, 113.3, 113.2, 55.0, 52.8, 30.4, 28.6, 24.9, 24.5, 21.3, 14.8. **IR (KBr) cm<sup>-1</sup>**: 3345.4, 2874.7, 1541.2, 1507.7, 1138.2, 1088.1, 822.5, 563.1. **HRMS (ESI)**: calculated for C<sub>15</sub>H<sub>21</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 281.1034; **found**: 281.1030.



The compound of **6k** was purified by silica gel chromatography (petroleum ether: EtOAc = 100:1) to afford a white solid in 79% yield.  $R_f$  = 0.34 (petroleum ether: EtOAc = 50:1). Mp. 140 °C–142 °C. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.46-6.98 (m, 8H), 6.59 (d,  $J$  = 9 Hz, 1H), 4.89 (s, 1H), 2.91-2.63 (m, 8H), 2.02-1.75 (m, 2H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 135.9, 135.8, 133.3, 129.4, 128.4, 127.3, 127.0, 126.6, 126.1, 51.7, 30.5, 28.8, 28.4, 24.9, 24.2. **IR (KBr) cm<sup>-1</sup>**: 3033.7, 2884.0, 1623.8, 1261.3, 759.3. **HRMS (ESI)**: calculated for C<sub>16</sub>H<sub>21</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 277.1085; **found**: 277.1088.

## Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

