

Supporting Information

Iron-Catalyzed Radical Oxidative Coupling Reaction of Aryl Olefins with 1,3-Dithiane

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Table of Contents

1.General Considerations.....	S2
2.General Procedure for the Carbolithiation Reactions between 1,3-Dithiane and Alkenes.....	S2
3.General Procedure for the Cross-couplings Between 1,3-Dithiane and Alkenes.....	S3
4.EPR Experiments.....	S3
5.General Procedure for the Gram Scale Experiment.....	S5
6.The Procedure for Radical Trapping Experiment.....	S5
7. The Procedure for Radical Trapping Experiment by NaN ₃	S6
8. The Procedure for Radical Trapping Experiment by Methanol.....	S6
9. Analytical Data of Products.....	S7
10. Copies of ¹ H and ¹³ C NMR Spectra.....	S12-S53

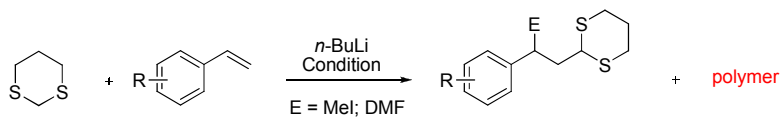
1. General Considerations

Analytical grade solvents and commercially available reagents were used as received. Substituted Styrenes 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. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution on the Bruker 300 and 400MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. MS were measured on a HP-5988 spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique.

2. General Procedure for the Carbolithiation Reactions between 1,3-Dithiane and Alkenes

A solution of the 1,3-dithiane (1 mmol) and additives (HMPA, TMEDA or (-)-sparteine) (1.65 mmol) in anhydrous THF or Et_2O (3 mL) was cooled to $-78\text{ }^\circ\text{C}$. $n\text{-BuLi}$ (2.5 M in petroleum ether, 0.9 mmol) was added dropwise via syringe, and the reaction mixture allowed to warm to $-20\text{ }^\circ\text{C}$ while stirring for 0.5 h. The mixture was re-cooled to $-78\text{ }^\circ\text{C}$ and a solution of the alkenes (0.50 mmol) in anhydrous THF or Et_2O (3 mL) was added dropwise via syringe. After the reaction was stirring for 1 h, The mixture was warmed to $-20\text{ }^\circ\text{C}$ over 1 h. After stirring an additional 4 h the reaction was quenched with saturated aqueous NH_4Cl (6 mL) and then diluted with Et_2O (20 mL). The organic layers were separated, the aqueous phase extracted with Et_2O ($3\times 5\text{ mL}$), and the combined organic layers dried over anhydrous Na_2SO_4 , filtered and concentrated.

Table 1. Carbolithiation Reaction between 1,3-Dithiane and Alkenes under Varied Conditions.

				
R	Condition	Solvent	Result	
R = Me	HMPA $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	Et_2O	NR polymer	
R = Me	HMPA $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	THF	NR polymer	
R = Me	TMEDA $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	Et_2O	NR polymer	
R = Me	TMEDA $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	THF	NR polymer	
R = Me	(-)-sparteine $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	Et_2O	NR polymer	
R = Me	(-)-sparteine $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	THF	NR polymer	
R = H	(-)-sparteine $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	Et_2O	NR polymer	
R = OMe	(-)-sparteine $-78\text{ }^\circ\text{C}$, 1 h; up to $-20\text{ }^\circ\text{C}$	Et_2O	NR polymer	

3. General Procedure for the Cross-coupling between 1,3-Dithiane and Alkenes

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) and FeCl₃ (0.025 mmol) were added at reaction temperature. Reaction mixture was stirred at -30 °C ~ room temperature for 8-24h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (10 mL) and H₂O (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 Na₂SO₄, and purified by the flash chromatography to afford the desired product.

Table 2. Cross-coupling between 1,3-Dithiane and Styrene under Varied Conditions.^a

entry	catalyst	activating agent	solvent	yield(%) ^b
1	FeCl ₃ (10 %)	DDQ	CH ₂ Cl ₂	trace
2	CuI(15 %)	DDQ	CH ₂ Cl ₂	0
3	PdCl ₂ (5 %)	DDQ	CH ₂ Cl ₂	trace
4	FeCl ₃ (10 %)	None	CH ₂ Cl ₂	0
5	FeCl ₃ (10 %)	NCS	CH ₂ Cl ₂	75
6	FeCl₃(10 %)	NCS	DCE	86
7	None	NCS	DCE	0
8	FeCl ₃ (10 %)	NBS	DCE	trace
9	FeCl ₃ (5 %)	NCS	DCE	83
10	FeCl ₃ (15 %)	NCS	DCE	84
11	FeCl ₃ (10 %)	NCS	toluene	0
12	FeCl ₃ (10 %)	NCS	DMF	0
13	FeCl ₃ (10 %)	NCS	THF	trace

^a Reaction conditions: all of the reactions were performed with **1** (30 mg, 0.25 mmol), **2a** (23.4 mg, 0.225 mmol), catalyst (5~15 %) and activating agent (0.3 mmol) in 2 mL of solvent at 0 °C for 12 h.

^bYield of isolated product.

4. EPR Experiments.

a) Procedure for EPR Investigation of NCS, FeCl₃, and 1,3-Dithiane.

NCS (13.3 mg, 0.1 mmol), FeCl₃ (16.3 mg, 0.1 mmol), and 1,3-dithiane (12 mg, 0.1 mmol) was dissolved in 1 mL DCE, the mixture was stirred at room temperature for few minutes, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure S1).

b) Procedure for EPR Investigation of the Reaction between NCS and FeCl₃ or 1,3-Dithiane.

To a flame-dried 10 mL flask were sequentially added NCS (13.3 mg, 0.1 mmol) and 1 mL DCE

were combined. Then 1,3-dithiane (12 mg, 0.1 mmol) or FeCl_3 (16.3 mg, 0.1 mmol) was added. After the mixture was stirred for few minutes, few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature.

c) Procedure for EPR Investigation of the Reaction between 1,3-Dithiane, NCS and FeCl_3 .

To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (12 mg, 0.1 mmol), NCS (13.3 mg, 0.1 mmol), FeCl_3 (16.3 mg, 0.1 mmol) and 1 mL DCE were combined. After the mixture was stirred for few minutes, few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature.

d) Procedure for EPR Investigation of the Radical Cross-Coupling between 1,3-Dithiane and Styrene.

To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol), NCS (40 mg, 0.3 mmol), and styrene **2a** (23.4 mg, 0.225 mmol), DCE (2 mL), at room temperature. After the mixture was stirred for few minutes, few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature. (Figure S2, 0 min). Then FeCl_3 (0.025 mmol) was added in the mixture, and after 25 mins and 50 mins, few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature. (Figure S2, 25 min and 50 min).

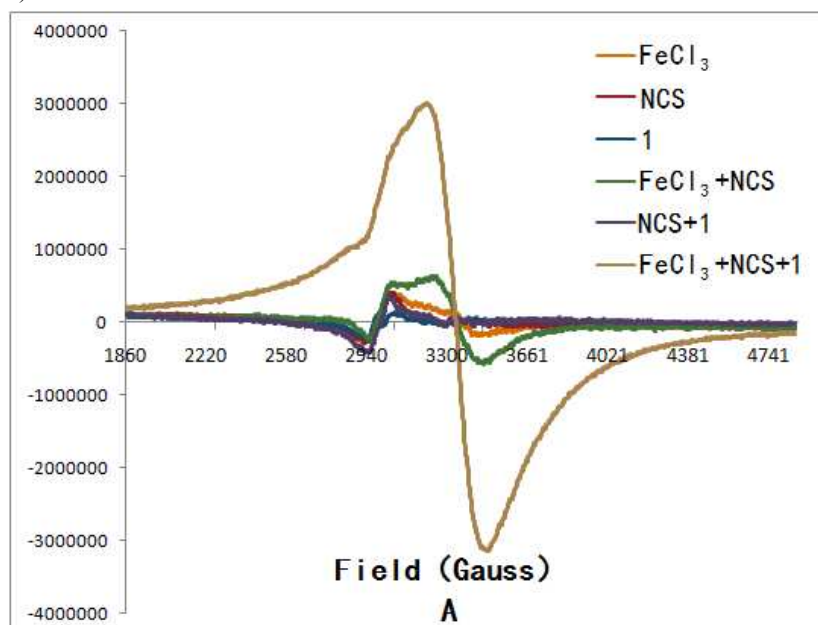


Figure S1. EPR spectra from the reaction between 1) FeCl_3 , **1**, NCS; 2) NCS and **1** or FeCl_3 ; 3) the mixture of FeCl_3 , **1** and NCS in DCE at room temperature.

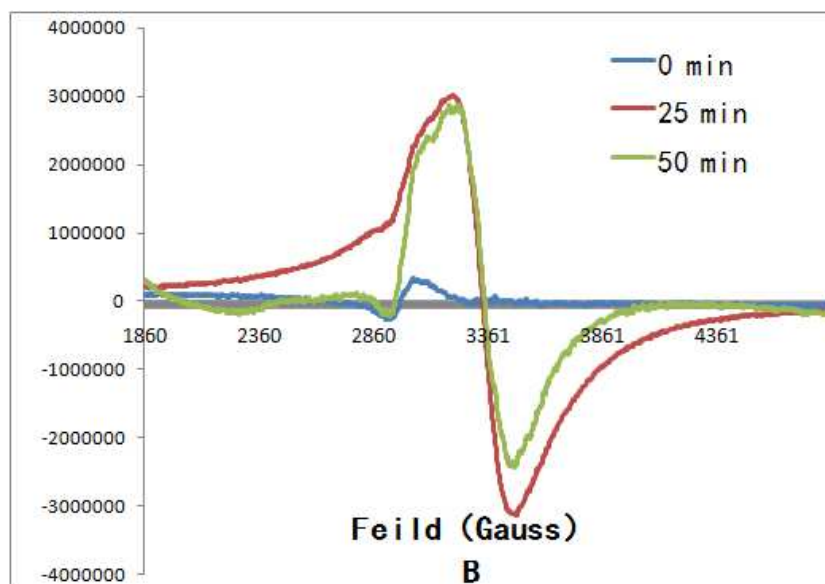
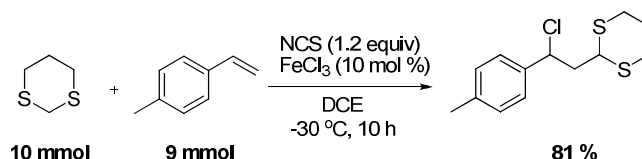


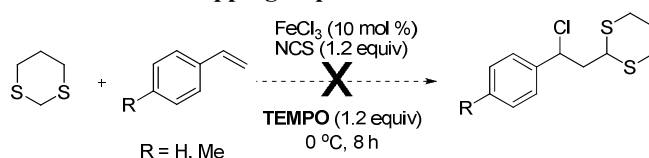
Figure S2. EPR spectra acquired during the cross-coupling reaction time course between 1 and 2a.

5. General Procedure for the Gram Scale Experiment



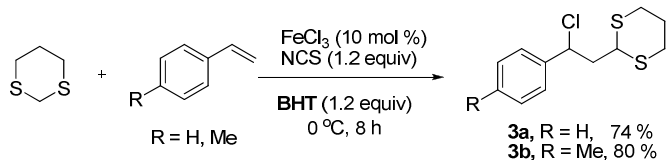
To a flame-dried 100 mL flask were sequentially added 1,3-dithiane (1.2 g, 10 mmol) and NCS (1.6 g, 12 mmol), DCE (60 mL), after dissolved the mixture was stirred at 0 °C for 40 mins. Then 4-methylphenylene (1.06 g, 9 mmol) and FeCl_3 (162.5 mg, 1 mmol) were added. Reaction mixture was stirred at -30 °C for 10 h until TLC analysis showed the reaction was completed. Reaction mixture was diluted with ethyl acetate (120 mL) and H_2O (40 mL). The organic layer was separated, and the aqueous phase was re-extracted with ethyl acetate (3×50 mL). The combined organic extracts were washed with H_2O (30 mL), and dried over anhydrous Na_2SO_4 , and purified by the flash chromatography to afford the desired product.

6. The Procedure for Radical Trapping Experiment.



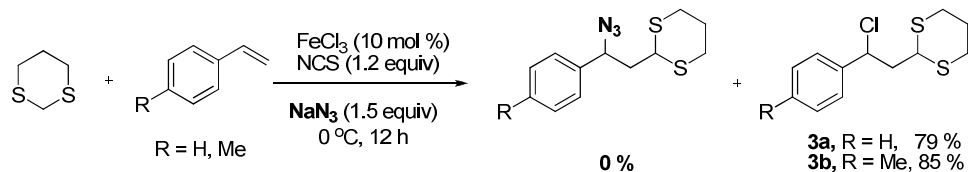
To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol) and NCS (40 mg, 0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then TEMPO (46.9 mg, 0.3 mmol), styrene (23.4 mg, 0.225 mmol) or 4-methylphenylene (26.5 mg, 0.225 mmol) and FeCl_3 (4.1 mg, 0.025 mmol) were added. Reaction mixture was stirred at 0 °C for 8 h. Then reaction mixture was diluted with ethyl acetate (3 mL) and H_2O (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 H₂O (10 mL), and dried over anhydrous Na₂SO₄.



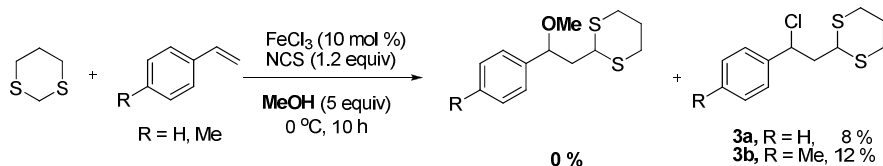
To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol) and NCS (40 mg, 0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then BHT (66.1 mg, 0.3 mmol), styrene (23.4 mg, 0.225 mmol) or 4-methylphenylene (26.5 mg, 0.225 mmol) and FeCl₃ (4.1 mg, 0.025 mmol) were added. Reaction mixture was stirred at 0 °C for 8 h. Then reaction mixture was diluted with ethyl acetate (3 mL) and H₂O (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 H₂O (10 mL), and dried over anhydrous Na₂SO₄, and purified by the flash chromatography to afford the desired product.

7. The Procedure for Radical Trapping Experiment by NaN₃.



To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol) and NCS (40 mg, 0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then NaN₃ (24.4 mg, 0.375 mmol) was added. After 1h styrene (23.4 mg, 0.225 mmol) or 4-methylphenylene (26.5 mg, 0.225 mmol) and FeCl₃ (4.1 mg, 0.025 mmol) were added. Reaction mixture was stirred at 0 °C for 12 h. Then reaction mixture was diluted with ethyl acetate (3 mL) and H₂O (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 H₂O (10 mL), and dried over anhydrous Na₂SO₄, and purified by the flash chromatography to afford the desired product.

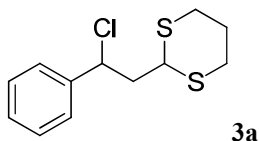
8. The Procedure for Radical Trapping Experiment by methanol.



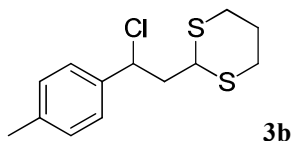
To a flame-dried 10 mL flask were sequentially added 1,3-dithiane (30 mg, 0.25 mmol) and NCS (40 mg, 0.3 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then methanol (40 mg, 1.25 mmol) was added. After 1h styrene (23.4 mg, 0.225 mmol) or 4-methylphenylene (26.5 mg, 0.225 mmol) and FeCl₃ (4.1 mg, 0.025 mmol) were added. Reaction

mixture was stirred at 0 °C for 10 h. Then reaction mixture was diluted with ethyl acetate (3 mL) and H₂O (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 H₂O (10 mL), and dried over anhydrous Na₂SO₄, and purified by the flash chromatography to afford the desired product.

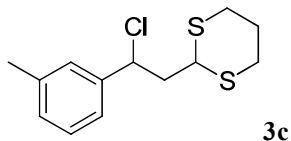
9. Analytical Data of Products



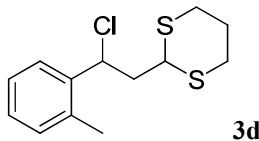
¹H NMR (400 MHz, CDCl₃): δ = 7.33-7.22 (m, 5H), 5.12 (dd, J = 4.0, 8.0 Hz, 1H), 3.95 (dd, J = 8.0, 16.0 Hz, 1H), 2.76-2.70 (m, 4H), 2.51-2.33 (m, 2H), 2.00-1.76 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 140.3, 128.6, 128.4, 126.8, 59.7, 44.8, 43.6, 29.2, 29.1, 25.6. **IR (KBr) cm⁻¹:** 3043.2, 2905.7, 1602.3, 1266.5, 737.3. **HRMS (ESI):** calculated for C₁₂H₁₅ClNaS₂ [M+Na]⁺: 281.0201; **found:** 281.0202.



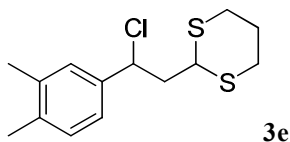
¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, J = 8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.17 (dd, J = 6.0, 8.8 Hz, 1H), 4.02 (dd, J = 6.4, 8.4 Hz, 1H), 2.83-2.79 (m, 4H), 2.60-2.38 (m, 2H), 2.35 (d, J = 9.2, 3H), 2.12-1.85 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 138.4, 137.5, 129.3, 126.8, 59.7, 44.8, 43.7, 29.3, 29.2, 25.7, 21.1. **IR (KBr) cm⁻¹:** 3057.5, 2911.2, 1601.7, 1477.3, 142.6, 1281.4, 908.8, 790.2, 736.4. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaS₂ [M+Na]⁺: 295.0358; **found:** 295.0356.



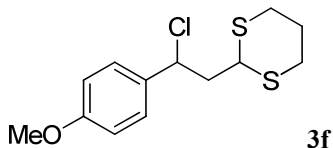
¹H NMR (400 MHz, CDCl₃): δ = 7.25-7.10 (m, 4H), 5.16 (dd, J = 8.0, 16.0 Hz, 1H), 4.04 (dd, J = 8.0, 16.0 Hz, 1H), 2.82-2.78 (m, 4H), 2.55 (t, J = 4 Hz, 2H), 2.43-2.34 (m, 3H), 2.09-1.84 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 140.3, 138.2, 129.2, 128.4, 127.5, 123.9, 59.8, 44.7, 43.5, 29.2, 29.0, 25.6, 21.2. **IR (KBr) cm⁻¹:** 3053.6, 2902.4, 1606.8, 1489.1, 1423.0, 1265.1, 906.4, 784.4, 737.9. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaS₂ [M+Na]⁺: 295.0358; **found:** 295.0362.



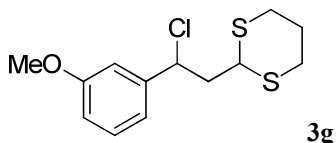
¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.14 (m, 4H), 5.49 (dd, J = 8.0, 12.0 Hz, 1H), 4.16 (dd, J = 4.0, 8.0 Hz, 1H), 2.85-2.80 (m, 4H), 2.56 (dd, J = 4.0, 8.0 Hz, 2H), 2.46-2.40 (m, 3H), 2.12-1.85 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 138.4, 135.3, 130.5, 128.2, 126.5, 126.2, 55.9, 43.8, 43.7, 29.4, 29.2, 25.7, 19.0. **IR (KBr) cm⁻¹:** 3044.6, 2899.1, 1611.4, 1490.3, 1422.8, 1259.8, 901.2, 792.4, 739.2. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaS₂ [M+Na]⁺: 295.0358; **found:** 295.0360.



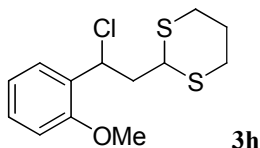
¹H NMR (300 MHz, CDCl₃): δ = 7.10-7.05 (m, 3H), 5.08 (dd, J = 6.0, 9.0 Hz, 1H), 3.98 (dd, J = 6.0, 9.0 Hz, 1H), 2.79-2.74 (m, 4H), 2.55-2.28 (m, 2H), 2.19 (d, J = 6 Hz, 6H), 2.07-1.79 (m, 2H). **¹³C NMR (75 MHz, CDCl₃):** δ = 137.9, 137.2, 137.0, 129.9, 128.2, 124.3, 59.9, 44.7, 43.8, 29.4, 29.2, 25.8, 19.8, 19.5. **IR (KBr) cm⁻¹:** 3036.9, 2910.2, 1609.4, 1474.3, 1417.6, 1260.9, 906.4, 789.4, 733.1. **HRMS (ESI):** calculated for C₁₄H₁₉ClNaS₂ [M+Na]⁺: 309.0514; **found:** 309.0517.



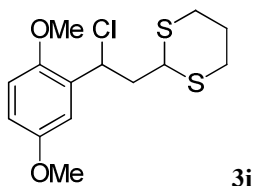
¹H NMR (400 MHz, CDCl₃): δ = 7.30-6.85 (m, 4H), 5.16 (dd, J = 6.0, 9.2 Hz, 1H), 4.04 (dd, J = 6.0, 8.4 Hz, 1H), 3.82 (s, 3H), 2.86-2.82 (m, 4H), 2.59-2.37 (m, 2H), 2.14-1.86 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 159.8, 142.0, 129.8, 119.2, 114.1, 112.6, 59.7, 55.3, 44.9, 43.7, 29.4, 29.2, 25.8. **IR (KBr) cm⁻¹:** 3327.9, 2915.2, 2898.4, 1597.4, 1493.7, 1452.0, 1258.9, 1042.0, 741.5, 698.2. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaOS₂ [M+Na]⁺: 311.0307; **found:** 311.0304.



¹H NMR (400 MHz, CDCl₃): δ = 7.29-6.84 (m, 4H), 5.16 (dd, J = 6.0, 8.4 Hz, 1H), 4.03 (dd, J = 6.4, 8.4 Hz, 1H), 3.81 (s, 3H), 2.87-2.77 (m, 4H), 2.60-2.37 (m, 2H), 2.13-1.86 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 159.7, 142.0, 129.7, 119.2, 114.0, 112.6, 59.6, 55.2, 44.8, 43.6, 29.3, 29.2, 25.7. **IR (KBr) cm⁻¹:** 3336.8, 2935.5, 2907.5, 1600.5, 1491.3, 1434.5, 1266.7, 1047.8, 737.3, 700.5. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaOS₂ [M+Na]⁺: 311.0307; **found:** 311.0302.

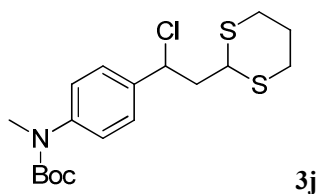


¹H NMR (300 MHz, CDCl₃): δ = 7.43-6.85 (m, 4H), 5.71 (dd, J = 3.0, 9.0 Hz, 1H), 4.21 (dd, J = 6.0, 9.0 Hz, 1H), 3.82 (d, J = 3.0 Hz, 3H), 2.86-2.81 (m, 4H), 2.50-2.42 (m, 2H), 2.12-1.85 (m, 2H). **¹³C NMR (75 MHz, CDCl₃):** δ = 154.8, 128.3, 127.5, 126.4, 119.6, 109.6, 54.4, 53.2, 42.8, 42.5, 28.4, 27.9, 25.7, 24.7. **IR (KBr) cm⁻¹:** 3339.1, 2946.8, 2909.1, 1605.8, 1499.4, 1447.0, 1256.3, 1050.7, 736.3, 706.4. **HRMS (ESI):** calculated for C₁₃H₁₇ClNaOS₂ [M+Na]⁺: 311.0307; **found:** 311.0310.

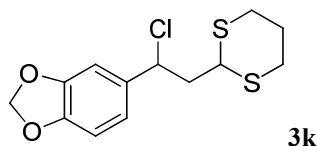


¹H NMR (300 MHz, CDCl₃): δ = 7.05-6.80 (m, 3H), 5.78 (dd, J = 6.0, 9.0 Hz, 1H), 4.21 (dd, J = 6.0, 9.0 Hz, 1H), 3.78 (d, J = 9.0 Hz, 6H), 2.90-2.78 (m, 4H), 2.44 (t, J = 6 Hz, 2H), 2.13-1.85 (m,

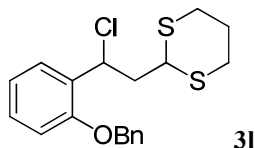
2H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 153.4, 150.0, 129.5, 113.8, 113.4, 111.7, 56.0, 55.5, 54.1, 43.6, 43.5, 29.3, 28.7, 25.6. **IR (KBr) cm⁻¹**: 3341.7, 2951.8, 2915.3, 1611.2, 1503.0, 1428.6, 1273.8, 1050.2, 744.3, 703.1. **HRMS (ESI)**: calculated for C₁₄H₁₉ClNaO₂S₂ [M+Na]⁺: 341.0413; **found**: 341.0416.



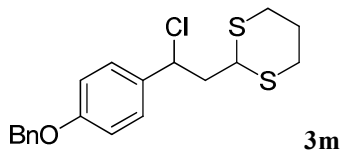
¹H NMR (300 MHz, CDCl₃): δ = 7.38-7.24 (m, 4H), 5.19 (t, *J* = 6.0 Hz, 1H), 4.15-4.00 (m, 1H), 3.27 (s, 3H), 2.84 (t, *J* = 6.0 Hz, 4H), 2.56-2.40 (m, 2H), 2.10-1.88 (m, 2H), 1.47 (s, 9H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 154.4, 143.8, 137.0, 127.2, 125.3, 80.5, 59.2, 44.7, 43.6, 37.0, 29.6, 29.3, 29.2, 28.2, 25.7. **IR (KBr) cm⁻¹**: 3355.2, 2915.2, 1597.4, 1493.7, 1421.7, 1258.9, 1042.0, 741.5. **HRMS (ESI)**: calculated for C₁₈H₂₆ClNNaO₂S₂ [M+Na]⁺: 410.0991; **found**: 410.0995.



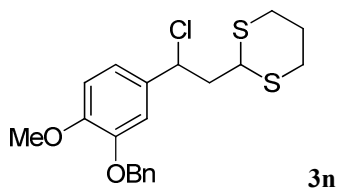
¹H NMR (300 MHz, CDCl₃): δ = 6.91-6.75 (m, 3H), 5.98 (s, 2H), 5.13 (t, *J* = 9.0 Hz, 1H), 3.99 (t, *J* = 6.0 Hz, 1H), 2.88-2.77 (m, 4H), 2.59-2.33 (m, 2H), 2.12-1.84 (m, 2H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 147.9, 147.7, 134.1, 120.7, 107.9, 107.2, 101.2, 59.8, 44.8, 43.6, 29.3, 29.2, 25.7. **IR (KBr) cm⁻¹**: 3348.0, 2953.2, 2915.0, 1608.2, 1487.3, 1431.8, 1394.3, 1364.3, 1261.0, 1052.6, 744.1, 694.8. **HRMS (ESI)**: calculated for C₁₃H₁₅ClNaO₂S₂ [M+Na]⁺: 325.0100; **found**: 325.0099.



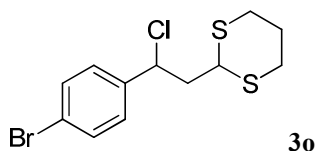
¹H NMR (300 MHz, CDCl₃): δ = 7.52-6.91 (m, 9H), 5.81 (t, *J* = 6 Hz, 1H), 5.12 (s, 2H), 4.17 (t, *J* = 6 Hz, 1H), 2.81-2.78 (m, 4H), 2.76-2.49 (m, 2H), 2.07-1.83 (m, 2H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 154.9, 136.6, 129.4, 129.1, 128.4, 127.9, 127.8, 127.2, 121.1, 112.1, 70.1, 54.5, 43.7, 43.5, 29.1, 28.5, 25.8. **IR (KBr) cm⁻¹**: 3354.2, 3078.4, 2920.4, 2872.0, 1614.2, 1491.3, 1422.5, 1272.2, 1062.7, 749.2. **HRMS (ESI)**: calculated for C₁₉H₂₁ClNaO₂S₂ [M+Na]⁺: 387.0620; **found**: 387.0624.



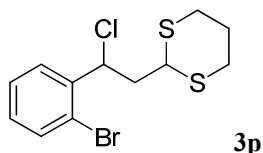
¹H NMR (300 MHz, CDCl₃): δ = 7.42-6.92 (m, 9H), 5.17 (t, *J* = 9.0 Hz, 1H), 5.03 (s, 2H), 4.00 (t, *J* = 9.0 Hz, 1H), 2.84-2.78 (m, 4H), 2.62-2.34 (m, 2H), 2.07-1.81 (m, 2H). **¹³C NMR (75 MHz, CDCl₃)**: δ = 158.7, 136.5, 132.7, 128.5, 128.2, 127.9, 127.3, 114.8, 69.8, 59.6, 44.7, 43.7, 29.3, 29.2, 25.7. **IR (KBr) cm⁻¹**: 3361.7, 3057.4, 2933.6, 2889.5, 1594.2, 1498.0, 1398.5, 1262.1, 1049.8, 740.9. **HRMS (ESI)**: calculated for C₁₉H₂₁ClNaO₂S₂ [M+Na]⁺: 387.0620; **found**: 387.0617.



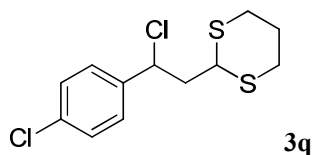
¹H NMR (300 MHz, CDCl₃): δ = 7.46-6.83 (m, 8H), 5.17 (s, 2H), 5.11 (dd, J = 6.0, 9.0 Hz, 1H), 3.94 (dd, J = 6.0, 9.0 Hz, 1H), 3.87 (s, 3H), 2.85-2.73 (m, 4H), 2.57-2.29 (m, 2H), 2.12-1.84 (m, 2H). **¹³C NMR (75 MHz, CDCl₃):** δ = 149.7, 147.7, 136.6, 132.6, 128.4, 127.8, 127.4, 119.9, 112.6, 111.3, 70.9, 59.9, 44.7, 43.6, 29.3, 29.2, 26.8, 25.7. **IR (KBr) cm⁻¹:** 3328.5, 2922.3, 2899.4, 1617.6, 1493.8, 1412.9, 1283.2, 1061.0, 751.4, 712.7. **HRMS (ESI):** calculated for C₂₀H₂₃ClNaO₂S₂ [M+Na]⁺: 417.0726; **found:** 417.0727.



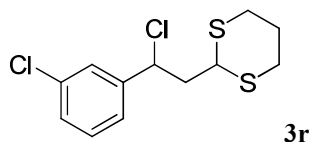
¹H NMR (400 MHz, CDCl₃): δ = 7.49 (q, J = 1.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.15 (dd, J = 6.0, 8.4 Hz, 1H), 3.99 (dd, J = 6.8, 8.4 Hz, 1H), 2.87-2.78 (m, 4H), 2.57-2.34 (m, 2H), 2.13-1.85 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 139.5, 131.8, 128.7, 122.4, 58.8, 44.7, 43.6, 29.4, 29.2, 25.7. **IR (KBr) cm⁻¹:** 3354.5, 2909.9, 2374.0, 1489.1, 1422.5, 1264.8, 1073.1, 1011.2, 738.0, 704.5. **HRMS (ESI):** calculated for C₁₂H₁₄BrClNaS₂ [M+Na]⁺: 358.9307; **found:** 358.9310.



¹H NMR (400 MHz, CDCl₃): δ = 7.54-7.06 (m, 4H), 5.63 (dd, J = 4.0, 12.0 Hz, 1H), 4.15 (dd, J = 8.0, 12.0 Hz, 1H), 2.81-2.70 (m, 4H), 2.38-1.95 (m, 2H), 1.86-1.80 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 139.4, 132.7, 129.6, 128.4, 127.8, 122.4, 58.6, 43.9, 31.7, 29.4, 29.1, 26.3. **IR (KBr) cm⁻¹:** 3347.2, 2915.2, 3405.9, 1497.6, 1403.8, 1255.7, 1088.0, 988.5, 745.6, 705.1. **HRMS (ESI):** calculated for C₁₂H₁₄BrClNaS₂ [M+Na]⁺: 358.9307; **found:** 358.9308.

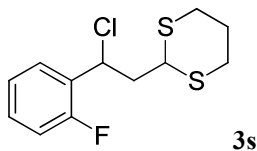


¹H NMR (400 MHz, CDCl₃): δ = 7.345 (s, 4H), 5.16 (dd, J = 6.0, 8.8 Hz, 1H), 4.00 (dd, J = 6.8, 8.4 Hz, 1H), 2.85-2.82 (m, 4H), 2.58-2.34 (m, 2H), 2.14-1.85 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ = 139.0, 134.3, 128.9, 128.4, 58.8, 44.8, 43.6, 29.5, 29.3, 25.7. **IR (KBr) cm⁻¹:** 3386.6, 2907.7, 1596.4, 1492.7, 1422.7, 1264.6, 1092.2, 738.3, 703.8. **HRMS (ESI):** calculated for C₁₂H₁₄Cl₂NaS₂ [M+Na]⁺: 314.9812; **found:** 314.9810.

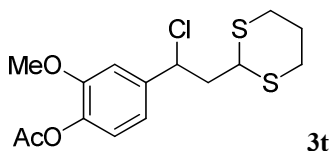


¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.28 (m, 4H), 5.15 (dd, J = 4.0, 8.0 Hz, 1H), 4.03 (dd, J = 8.0, 12.0 Hz, 1H), 2.88-2.79 (m, 4H), 2.57-2.50 (m, 2H), 2.42-1.86 (m, 2H). **¹³C NMR (100 MHz,**

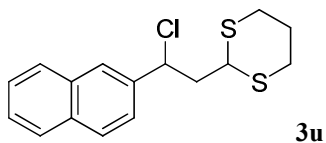
CDCl₃): δ = 142.4, 134.4, 129.9, 128.7, 127.2, 125.2, 58.7, 44.7, 43.5, 29.4, 29.2, 25.7. **IR (KBr) cm⁻¹**: 3415.7, 2909.7, 1607.0, 1488.4, 1417.5, 1270.9, 1096.3, 738.9, 722.6. **HRMS (ESI)**: calculated for C₁₂H₁₄Cl₂NaS₂ [M+Na]⁺: 314.9812; **found**: 314.9813.



¹H NMR (400 MHz, CDCl₃): δ = 7.52-7.05 (m, 4H), 5.54 (dd, J = 8.0, 12.0 Hz, 1H), 4.15 (dd, J = 8.0, 12.0 Hz, 1H), 2.92-2.81 (m, 4H), 2.58-2.47 (m, 2H), 2.14-1.90 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ = 160.7, 130.1, 128.3, 127.7, 124.5, 115.8, 52.8, 48.1, 43.5, 28.9, 28.8, 25.7. **IR (KBr) cm⁻¹**: 3327.3, 2892.4, 2438.7, 1500.3, 1464.5, 1276.2, 1099.1, 735.2, 684.2. **HRMS (ESI)**: calculated for C₁₂H₁₄ClFNaS₂ [M+Na]⁺: 299.0107; **found**: 299.0109.



¹H NMR (400 MHz, CDCl₃): δ = 7.02-6.97 (m, 3H), 5.18 (dd, J = 4.0, 8.0 Hz, 1H), 4.05, (t, J = 4.0 Hz, 1H), 3.83 (s, 3H), 2.82 (d, J = 4.0 Hz, 4H), 2.55-2.42 (m, 2H), 2.30 (s, 3H), 2.10-1.87 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ = 168.6, 150.9, 139.5, 139.1, 122.6, 119.0, 110.9, 59.3, 55.7, 44.7, 43.3, 29.1, 28.9, 25.5, 20.4. **IR (KBr) cm⁻¹**: 3356.2, 2917.2, 1613.6, 1508.1, 1472.5, 1270.2, 1049.9, 736.7. **HRMS (ESI)**: calculated for C₁₅H₁₉ClNaO₃S₂ [M+Na]⁺: 369.0362; **found**: 369.0359.



¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.46 (m, 7H), 5.37 (t, J = 12.0 Hz, 1H), 4.03 (t, J = 8.0 Hz, 1H), 2.82 (d, J = 20.0 Hz, 4H), 2.72-2.47 (m, 2H), 2.06-1.84 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ = 137.5, 133.1, 132.8, 128.8, 128.0, 127.6, 126.5, 126.4, 126.1, 124.4, 60.0, 44.6, 43.7, 29.3, 29.2, 25.7. **IR(KBr)cm⁻¹**: 3055.3, 1647.9, 1589.6, 1469.1, 1451.7, 1404.9, 1318.3, 1293.3, 1238.4, 1179.1, 1158.1, 1116.6, 737.3. **HRMS (ESI)**: calculated for C₁₆H₁₇ClNaS₂ [M+Na]⁺: 331.0358; **found**: 331.0357.

10. Copies of ¹H and ¹³C NMR Spectra

