

Supporting Information

Rhodium(III)-Catalyzed Oxidative Alkenylation of 1,3-Dithiane-Protected Arenecarbaldehydes via Regioselective C-H Bond Cleavage

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List of Contents for Experimental Section

General: S-2

Synthesis of **1v**: S-2

Reaction of 2-Phenyl-1,3-dithiane (**1a**) with n-Buthyl Acrylate (**2a**): S-3

Reaction of **3r** with Dess-Martin Periodinane: S-3

Reaction of **3r** with Raney Ni: S-3

Optimization Study for the Reaction of **1h** with **2a**: S-4

Deuterium Labelled Experiments: S-5–S-6

Characterization Data of Products: S-7 – S-13

References: S-13

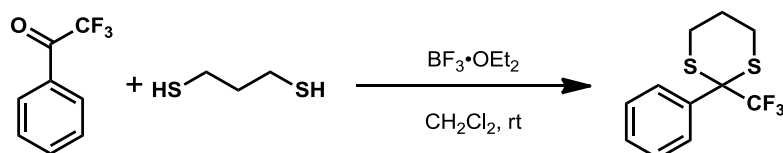
¹H and ¹³C NMR Spectra of Products: S-14 – S-40

Experimental Section

General. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded at 400, 100, 376 and 162 MHz for CDCl_3 solutions. HRMS data were obtained by CI using a TOF mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HSQC, and HMBC experiments.

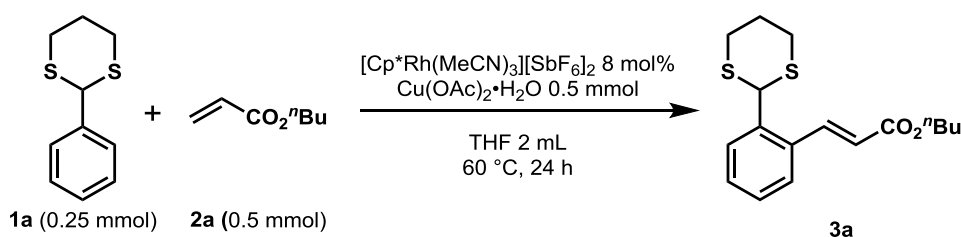
2-Aryl-1,3-dithianes and dithiolanes **1b-v** were prepared by iodine-catalyzed thioacetalization of corresponding arylaldehydes according to a published procedure.^[S1] Substrate **1v** was prepared by a $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -mediated thioacetalization as described below. Substrate **4** was prepared by a bismuth-catalyzed thia-Pictet-Spengler reaction according to a published procedure.^[S2] Other starting materials were commercially available. All dithianes were purified by recrystallization or silica gel column chromatography before use. The following experimental procedures may be regarded as typical in methodology and scale.

Synthesis of **1v**.



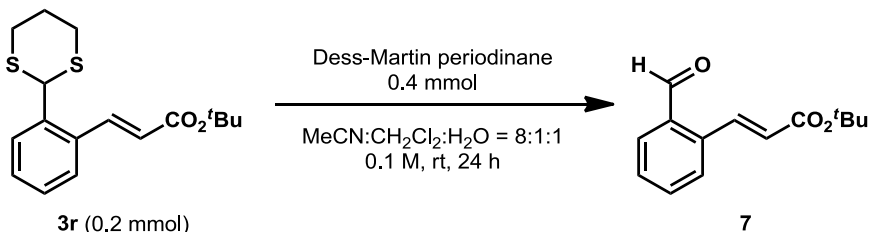
To a solution of 2,2,2-trifluoroacetophenone (5 mmol, 871 mg) and 1,3-propanedithiol (5 mmol, 0.5 mL) in CH_2Cl_2 (10 mL), $\text{BF}_3 \cdot \text{OEt}_2$ (0.6 mL) was added by a syringe at room temperature. The resulting mixture was stirred for 4 days at room temperature. The reaction was quenched by sat. NaHCO_3 aq, extracted with CH_2Cl_2 (20 mL), and washed by brine. The organic phase was dried over Na_2SO_4 , and volatiles were removed under reduced pressure. The residue was purified by recrystallization from pentane to afford dithiane **1v** (441 mg, 33%) as colorless crystals. ^1H NMR (400 MHz, CDCl_3): δ 1.92-2.02 (m, 1H), 2.13-2.21 (m, 1H), 2.17-2.78 (m, 2H), 3.17-3.25 (m, 2H), 7.34-7.42 (m, 3H), 7.85-7.88 (m, 2H).

Representative Procedure for Rh(III)-catalyzed Oxidative Coupling through C-H Bond Cleavage Directed by a 1,3-Dithiane Group.

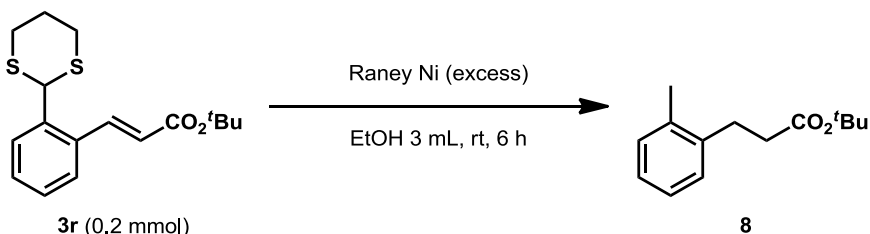


Reaction of 2-Phenyl-1,3-dithiane (1a) with *n*-Butyl Acrylate (2a) (entry 1 in Table 1).

In a schlenk tube, 2-phenyl-1,3-dithiane (49 mg, 0.25 mmol), [Cp*Rh(MeCN)₃(SbF₆)₂] (17 mg, 0.02 mmol), Cu(OAc)₂ · H₂O (100 mg, 0.5 mmol), and dibenzyl (30~40 mg; as an internal standard) were placed with a magnetic stir bar under N₂ atmosphere. Then *n*-butyl acrylate (64.1 mg, 0.5 mmol), and THF 2 mL were added by a syringe. The reaction mixture was submerged into a pre-heated 60 °C oil bath for 24 h. After cooling, the reaction mixture was diluted with 10 mL of ethyl acetate, 10 mL of water, and 1 mL of ethylenediamine. Then, insoluble solids were filtered off through a short pad of Celite. The resulting mixture was extracted three times with ethyl acetate and the combined organic layer was dried over Na₂SO₄. Volatiles were removed in vacuo and subsequent purification by column chromatography on silica gel with hexane/ethyl acetate (10:1, v/v) as an eluent gave product **3a** (70 mg, 87%).

Representative Procedure for Deprotection of a Dithiane Group.**Reaction of 3r with Dess-Martin Periodinane (eq 1).**

Oxidative deprotection of 1,3-dithiane was carried out according to the literature reported by Panek *et al.*^[S3] with some modifications as follows. In a 50 mL flask, **3r** (64 mg, 0.2 mmol), and Dess-Martin periodinane (84 mg, 0.4 mmol) were placed with a magnetic stir bar. Then, MeCN (1.6 mL), CH₂Cl₂ (0.2 mL), and H₂O (0.2 mL) were added and stirred at room temperature under air (capped by septum to prevent the vaporization of solvent). After 24 h, the reaction mixture was diluted with aq. NaHCO₃ and extracted three times with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄. Volatiles were removed in vacuo and subsequent purification by column chromatography on silica gel with hexane/ethyl acetate (20:1, v/v) as an eluent gave product **7** (44 mg, 94%).

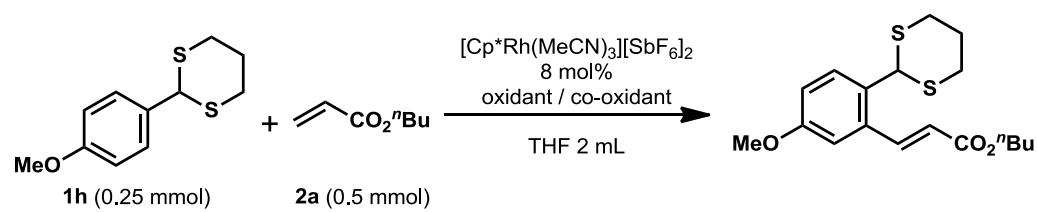
**Reaction of 3r with Raney Ni (eq 2).**

Compound **3r** (64 mg, 0.2 mmol) was dissolved to EtOH (3 mL) in a 100 mL flask. To the solution, an excess amount of Raney Ni (preactivated as water slurry, purchased from TCI) was added and the

resulting mixture was stirred at room temperature under open air for 6 h. Then, the mixture was filtered through a Celite pad, extracted with EtOAc (20 mL), and washed with brine (20 mL x 2). [Caution: Keep Ni catalyst wet during filtration to not to ignite. Dry, activated Raney Ni is pyrophoric.] The organic layer was dried over Na₂SO₄, and volatiles were removed in vacuo to give product **8** (39 mg, 88%).

Optimization Study for the Reaction of **1h** with **2a** (Table S1).

Table S1. Optimization Study.

					
entry	oxidant (mol%)	co-oxidant (mol%)	temp (°C)	time (h)	product (%) ^a
1	Cu(OAc) ₂ •H ₂ O (200)	-	60	24	16
2	Mn(OAc) ₃ •2H ₂ O (200)	-	60	24	8
3	Cu(OAc) ₂ •H ₂ O (200)	-	rt	48	trace
4	activated MnO ₂ (200)	Cu(OAc) ₂ •H ₂ O (20)	60	24	44 (42)
5	MnO ₂ (200)	Cu(OAc) ₂ •H ₂ O (20)	60	24	0
6	activated MnO ₂ (400)	Cu(OAc) ₂ •H ₂ O (20)	60	48	26
7	activated MnO ₂ (200)	-	60	24	0

^a NMR yield using CH₂Br₂ as an internal standard. Isolated yield is shown in parentheses.

Deuterium Labelled Experiments.

KIE Experiment (Side by Side)

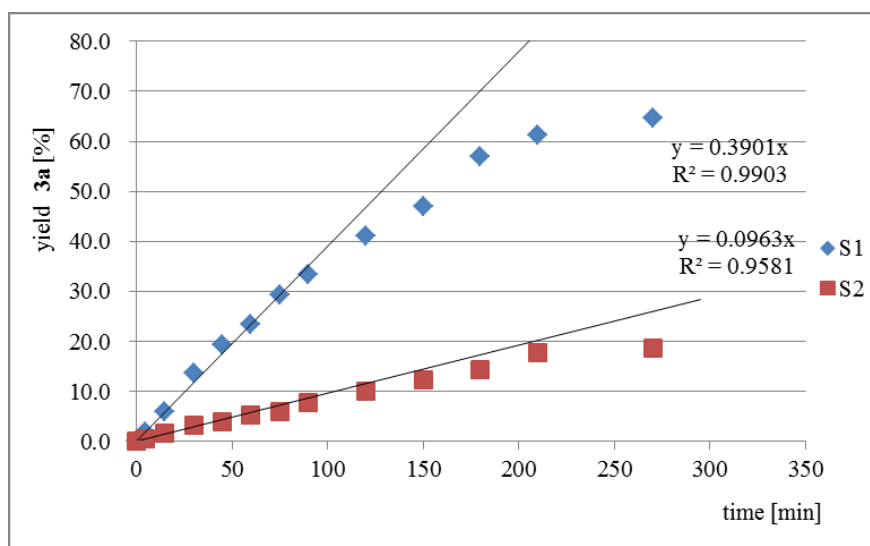
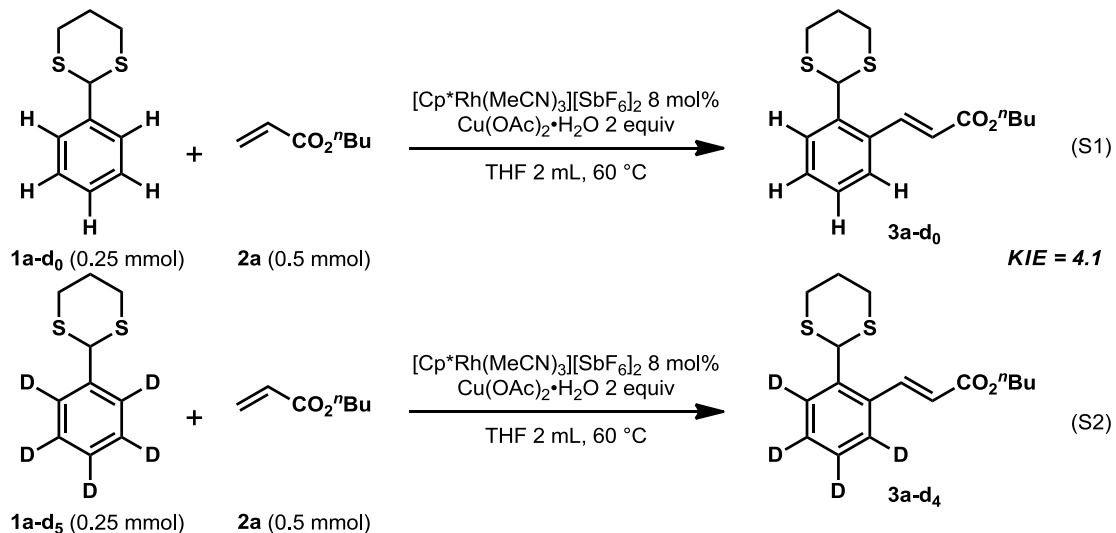
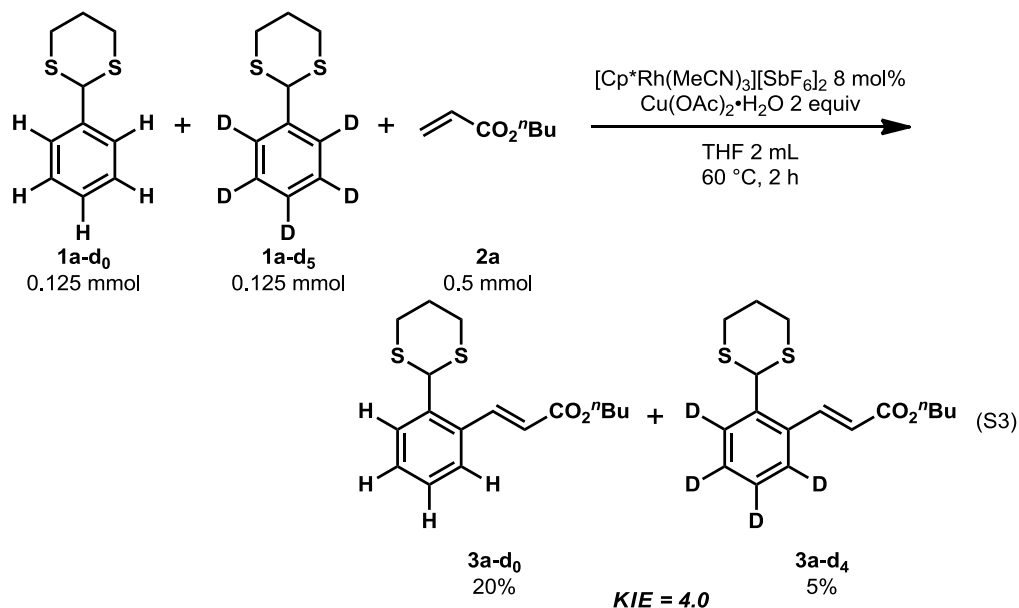


Figure S1. Time course of the yields of **3a-d₀** (diamonds, eq S1) and **3a-d₄** (squares, eq S2) during the early stages of the reactions of **1a-d₀** and **1a-d₅** with **2a**.

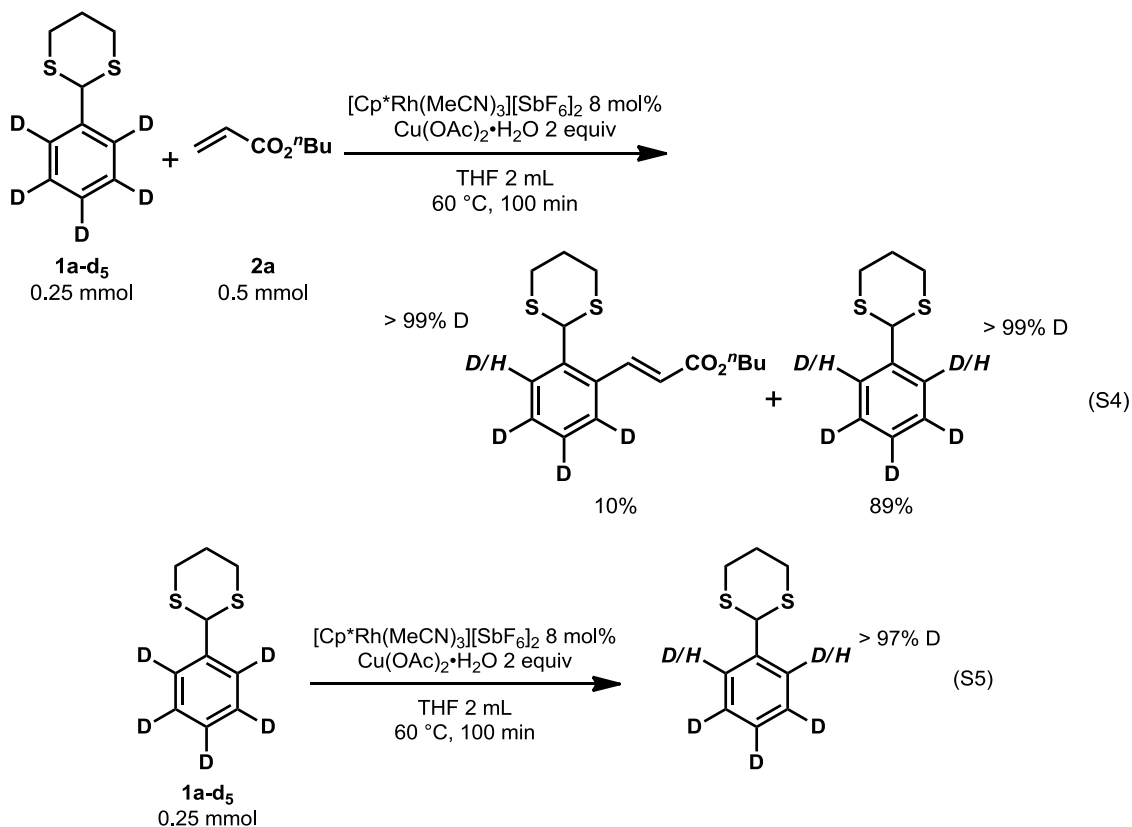
$$k_H / k_D = 0.3901/0.0963 = 4.1$$

KIE Experiment (Intermolecular Competition)



Additionally, we confirmed that the H / D exchange of **3a** was negligible at the early stage under standard conditions with or without alkene **2a** (eqs S4 and S5). Therefore, C-H bond cleavage step seems to be irreversible.

H / D Exchange Test



Characterization Data of Products

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)phenyl)acrylate (3a): colorless oil, 70.2 mg (87%); ^1H NMR (400 MHz, CDCl_3): δ 0.98 (t, $J = 7.4$ Hz, 3H), 1.46 (qt, $J = 9.3, 7.6$ Hz, 2H), 1.71 (tt, $J = 9.5, 6.9$ Hz, 2H), 1.95 (dtt, $J = 14.1, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.1, 4.3, 2.4$ Hz, 1H), 2.93 (ddd, $J = 14.5, 3.2, 3.2$ Hz, 2H), 3.09-3.16 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 5.45 (s, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 7.31 (ddd, $J = 7.4, 7.4, 1.2$ Hz, 1H), 7.38 (ddd, $J = 7.5, 7.5, 1.4$ Hz, 1H), 7.53 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.67 (dd, $J = 7.8, 1.3$ Hz, 1H), 8.19 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 25.1, 30.8, 32.3, 48.1, 64.5, 121.3, 127.2, 128.6, 128.8, 130.4, 132.7, 137.9, 141.3, 166.9; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{S}_2$: 323.1134. Found 323.1130.

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)-5-methylphenyl)acrylate (3b): colorless oil, 54.2 mg (64%); ^1H NMR (400 MHz, CDCl_3): δ 0.98 (t, $J = 7.8$ Hz, 3H), 1.46 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.70 (tt, $J = 9.6, 6.9$ Hz, 2H), 1.93 (dtt, $J = 14.3, 12.6, 3.0$ Hz, 1H), 2.19 (dtt, $J = 14.2, 4.2, 2.4$ Hz, 1H), 2.34 (s, 3H), 2.91 (ddd, $J = 14.5, 4.0, 4.0$ Hz, 2H), 3.07-3.15 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 5.42 (s, 1H), 6.39 (d, $J = 15.7$ Hz, 1H), 7.20 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.35 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 8.16 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 21.1, 25.1, 30.8, 32.3, 47.8, 64.5, 120.9, 127.7, 128.7, 131.2, 132.4, 135.1, 138.4, 141.4, 167.0; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{18}\text{H}_{25}\text{O}_2\text{S}_2$: 337.1290. Found 337.1281.

(E)-n-Butyl 3-(5-Chloro-2-(1,3-dithian-2-yl)phenyl)acrylate (3c): colorless solid, mp 79-81 $^\circ\text{C}$, 65.8 mg (74%); ^1H NMR (400 MHz, CDCl_3): δ 0.98 (t, $J = 7.4$ Hz, 3H), 1.46 (qt, $J = 9.3, 7.3$ Hz, 2H), 1.70 (tt, $J = 9.5, 6.9$ Hz, 2H), 1.93 (dtt, $J = 14.2, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.2, 4.2, 2.4$ Hz, 1H), 2.91 (ddd, $J = 14.5, 3.3, 3.3$ Hz, 2H), 3.07-3.14 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 5.38 (s, 1H), 6.40 (d, $J = 15.7$ Hz, 1H), 7.34 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 24.9, 30.7, 32.2, 47.4, 64.7, 122.5, 127.0, 130.2, 130.3, 134.48, 134.49, 136.3, 140.0, 166.5; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{17}\text{H}_{22}\text{ClO}_2\text{S}_2$: 357.0744. Found 357.0743.

(E)-n-Butyl 3-(5-Bromo-2-(1,3-dithian-2-yl)phenyl)acrylate (3d): colorless solid, mp 87-89 $^\circ\text{C}$, 73.8 mg (74%); ^1H NMR (400 MHz, CDCl_3): δ 0.98 (t, $J = 7.4$ Hz, 3H), 1.46 (qt, $J = 9.3, 7.3$ Hz, 2H), 1.70 (tt, $J = 9.4, 6.8$ Hz, 2H), 1.93 (dtt, $J = 14.1, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.2, 4.2, 2.3$ Hz, 1H), 2.91 (ddd, $J = 14.4, 3.4, 3.4$ Hz, 2H), 3.07-3.14 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 5.37 (s, 1H), 6.39 (d, $J = 15.7$ Hz, 1H), 7.49 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 2.0$ Hz, 1H), 8.08 (d, $J = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 24.9, 30.7, 32.2, 47.4, 64.7, 122.56, 122.60, 130.0, 130.5, 133.2, 134.8, 136.8, 139.9, 166.5; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{17}\text{H}_{22}\text{BrO}_2\text{S}_2$: 401.0239. Found 401.0230.

(E)-*n*-Butyl 3-(2-(1,3-Dithian-2-yl)-5-(trifluoromethyl)phenyl)acrylate (3e): colorless solid, mp 119-120 °C, 72.7 mg (75%); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.49 (qt, *J* = 9.4, 7.3 Hz, 2H), 1.71 (tt, *J* = 9.6, 6.8 Hz, 2H), 1.97 (dt, *J* = 14.2, 12.6, 3.0 Hz, 1H), 2.22 (dt, *J* = 14.2, 4.2, 2.5 Hz, 1H), 2.91-2.97 (m, 2H), 3.09-3.17 (m, 2H), 4.25 (t, *J* = 6.6 Hz, 2H), 5.44 (s, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 7.62 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76 (d, *J* = 1.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 15.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 24.9, 30.7, 32.2, 47.6, 64.8, 123.6 (q, *J* = 270.7 Hz), 123.1, 124.1 (q, *J* = 3.7 Hz), 126.7 (q, *J* = 3.7 Hz), 129.6, 131.7 (q, *J* = 32.7 Hz), 133.6, 139.9, 141.4, 166.4; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.9; HRMS *m/z* (M+H⁺) Calcd for C₁₈H₂₂F₃O₂S₂: 391.1008. Found 391.1006.

(E)-*n*-Butyl 3-(5-Acetyl-2-(1,3-dithian-2-yl)phenyl)acrylate (3f): colorless solid, mp 101-103 °C, 76.8 mg (84%); ¹H NMR (400 MHz, CDCl₃): δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.42-1.51 (m, 2H), 1.72 (tt, *J* = 9.5, 6.8 Hz, 2H), 1.97 (dt, *J* = 14.1, 12.6, 3.0 Hz, 1H), 2.19-2.26 (m, 1H), 2.62 (s, 3H), 2.94 (ddd, *J* = 14.4, 3.7, 3.7 Hz, 2H), 3.10-3.17 (m, 2H), 4.25 (t, *J* = 6.6 Hz, 2H), 5.45 (s, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 8.17 (d, *J* = 15.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 24.9, 26.7, 30.7, 32.2, 47.8, 64.7, 122.7, 127.1, 129.3, 129.8, 133.4, 137.0, 140.4, 142.4, 166.6, 197.0; HRMS *m/z* (M+H⁺) Calcd for C₁₉H₂₅O₃S₂: 365.1240. Found 365.1241.

(E)-*n*-Butyl 3-(2-(1,3-Dithian-2-yl)-5-nitrophenyl)acrylate (3g): colorless oil, 37.0 mg (40%); ¹H NMR (400 MHz, CDCl₃): δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.41-1.52 (m, 2H), 1.73 (tt, *J* = 9.4, 6.8 Hz, 2H), 1.97 (dt, *J* = 14.2, 12.7, 3.0 Hz, 1H), 2.23 (dt, *J* = 14.3, 4.4, 2.0 Hz, 1H), 2.96 (ddd, *J* = 14.4, 3.8, 3.8 Hz, 2H), 3.10-3.17 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 5.45 (s, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 15.8 Hz, 1H), 8.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.38 (d, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 24.8, 30.7, 32.1, 47.4, 64.9, 122.2, 124.1, 124.5, 130.3, 134.5, 139.0, 144.2, 147.7, 166.2; HRMS *m/z* (M+H⁺) Calcd for C₁₇H₂₂NO₄S₂: 368.0985. Found 368.0984.

(E)-*n*-Butyl 3-(2-(1,3-Dithian-2-yl)-5-methoxyphenyl)acrylate (3h): colorless oil, 37.1 mg (42%); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.46 (qt, *J* = 9.4, 7.3 Hz, 2H), 1.71 (t, *J* = 9.5, 6.9 Hz, 2H), 1.92 (dt, *J* = 14.1, 12.6, 3.0 Hz, 1H), 2.19 (dt, *J* = 14.2, 4.2, 2.3 Hz, 1H), 2.90 (ddd, *J* = 13.8, 3.8, 3.8 Hz, 2H), 3.07-3.14 (m, 2H), 3.82 (s, 3H), 4.23 (t, *J* = 6.6 Hz, 2H), 5.39 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.03 (d, *J* = 2.7 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 25.0, 30.8, 32.4, 47.5, 55.4, 64.6, 112.0, 116.2, 121.3, 130.2, 130.3, 133.9, 141.4, 159.4, 166.9; HRMS *m/z* (M+H⁺) Calcd for C₁₈H₂₅O₃S₂: 353.1240. Found 353.1241.

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)-5-(methylthio)phenyl)acrylate (3i): colorless solid, mp 95-97 °C, 52.7 mg (57%); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.46 (qt, *J* = 9.3, 7.3 Hz, 2H), 1.71 (tt, *J* = 9.5, 6.7 Hz, 2H), 1.93 (dtt, *J* = 14.1, 12.6, 3.0 Hz, 1H), 2.19 (dtt, *J* = 14.2, 4.3, 2.4 Hz, 1H), 2.50 (s, 3H), 2.91 (ddd, *J* = 14.5, 4.0, 4.0 Hz, 2H), 3.07-3.14 (m, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 5.39 (s, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 7.25 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 15.6, 19.2, 25.0, 30.8, 32.3, 47.6, 64.6, 121.7, 124.6, 128.0, 129.3, 133.2, 134.5, 139.5, 141.0, 166.8; HRMS *m/z* (M+H⁺) Calcd for C₁₈H₂₅O₂S₃: 369.1011. Found 369.1017.

(E)-n-Butyl 3-(3-(1,3-Dithian-2-yl)naphthalen-2-yl)acrylate (3j): colorless solid, mp 87-89 °C, 77.4 mg (83%); ¹H NMR (400 MHz, CDCl₃): δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.48 (qt, *J* = 9.3, 7.3 Hz, 2H), 1.73 (tt, *J* = 9.5, 6.8 Hz, 2H), 2.00 (dtt, *J* = 14.2, 12.6, 3.0 Hz, 1H), 2.24 (dtt, *J* = 14.2, 4.2, 2.4 Hz, 1H), 2.94-2.99 (m, 2H), 3.14-3.21 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 5.50 (s, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 7.47-7.52 (m, 2H), 7.80-7.84 (m, 2H), 8.02 (s, 1H), 8.13 (s, 1H), 8.30 (d, *J* = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.3, 25.2, 30.8, 32.6, 48.3, 64.5, 121.5, 127.0, 127.2, 127.3, 127.9, 128.0, 128.3, 131.1, 132.8, 133.9, 135.0, 141.9, 166.9; HRMS *m/z* (M+H⁺) Calcd for C₂₁H₂₅O₂S₂: 373.1290. Found 373.1290.

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)-4-methoxyphenyl)acrylate (3k): colorless oil, 62.3 mg (71%); ¹H NMR (400 MHz, CDCl₃): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.41-1.50 (m, 2H), 1.71 (tt, *J* = 9.4, 6.6 Hz, 2H), 1.95 (dtt, *J* = 14.1, 12.6, 2.9 Hz, 1H), 2.17-2.23 (m, 1H), 2.92 (ddd, *J* = 14.4, 3.3, 3.3 Hz, 2H), 3.09-3.17 (m, 2H), 3.85 (s, 3H), 4.22 (t, *J* = 6.7 Hz, 2H), 5.46 (s, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.20 (d, *J* = 2.7 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 25.1, 30.8, 32.3, 48.0, 55.5, 64.4, 113.6, 115.0, 118.7, 124.9, 128.6, 139.7, 140.7, 161.4, 167.3; HRMS *m/z* (M+H⁺) Calcd for C₁₈H₂₅O₃S₂: 353.1240. Found 353.1244.

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)-6-methoxyphenyl)acrylate (3k'): colorless oil, 15.4 mg (17%); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.41-1.51 (m, 2H), 1.66-1.75 (m, 2H), 1.88-2.01 (m, 1H), 2.15-2.22 (m, 1H), 2.87-2.94 (m, 2H), 3.04-3.13 (m, 2H), 3.85 (s, 3H), 4.23 (tt, *J* = 6.7 Hz, 2H), 5.40 (s, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 6.83-6.87 (m, 1H), 7.30-7.34 (m, 2H), 7.96 (d, *J* = 16.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.3, 25.1, 30.8, 32.4, 48.7, 55.7, 64.5, 110.7, 121.2, 122.1, 124.0, 130.4, 138.1, 139.1, 158.1, 167.3; HRMS *m/z* (M+H⁺) Calcd for C₁₈H₂₅O₃S₂: 353.1240. Found 353.1245.

(E)-n-Butyl 3-(2-(1,3-Dithian-2-yl)-4-phenoxyphenyl)acrylate (3l): colorless oil, 78.2 mg (75%); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.46 (qt, *J* = 9.4, 7.3 Hz, 2H), 1.70 (tt, *J* = 9.6, 6.6 Hz, 2H), 1.92 (dtt, *J* = 14.1, 12.6, 3.0 Hz, 1H), 2.18 (dtt, *J* = 14.2, 4.2, 2.4 Hz, 1H), 2.82-2.93 (m, 2H), 3.07-3.14 (m, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 5.42 (s, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.6

Hz, 1H), 7.04-7.07 (m, 2H), 7.14-7.18 (m, 1H), 7.34 (d, $J = 2.6$ Hz, 1H), 7.35-7.39 (m, 2H), 7.52 (d, $J = 8.7$ Hz, 1H), 8.14 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 25.0, 30.8, 32.3, 48.0, 64.5, 118.2, 118.6, 119.6, 119.7, 124.1, 127.2, 128.8, 129.9, 139.9, 140.6, 156.0, 159.3, 167.1; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_3\text{S}_2$: 415.1396. Found 415.1401.

(*E*)-*n*-Butyl 3-(2-(1,3-Dithian-2-yl)-6-phenoxyphenyl)acrylate (3l'): colorless oil, 18.7 mg (18%); ^1H NMR (400 MHz, CDCl_3): δ 0.95 (t, $J = 7.4$ Hz, 3H), 1.42 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.68 (tt, $J = 9.6, 6.9$ Hz, 2H), 1.96 (dtt, $J = 14.1, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.2, 4.2, 2.4$ Hz, 1H), 2.89-2.95 (m, 2H), 3.07-3.14 (m, 2H), 4.19 (t, $J = 6.7$ Hz, 2H), 5.41 (s, 1H), 6.63 (d, $J = 16.2$ Hz, 1H), 6.81 (dd, $J = 8.2, 3.0$ Hz, 1H), 6.95-6.98 (m, 2H), 7.09-7.13 (m, 2H), 7.24-7.28 (m, 1H), 7.31-7.36 (m, 2H), 7.48 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.96 (d, $J = 16.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 25.1, 30.7, 32.4, 48.5, 64.5, 118.5, 119.1, 123.7, 123.9, 124.7, 125.0, 129.9, 130.3, 137.3, 139.5, 155.7, 156.5, 167.0; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_3\text{S}_2$: 415.1396. Found 415.1399.

(*E*)-*n*-Butyl 3-(6-(1,3-Dithian-2-yl)benzo[*d*][1,3]dioxol-5-yl)acrylate (3m) + (*E*)-*n*-Butyl 3-(5-(1,3-dithian-2-yl)benzo[*d*][1,3]dioxol-4-yl)acrylate (3m') [7:1 mixture]: colorless oil, 76.1 mg (83%); **3m**: ^1H NMR (400 MHz, CDCl_3): δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.46 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.70 (tt, $J = 9.5, 6.8$ Hz, 2H), 1.86-1.98 (m, 1H), 2.16-2.22 (m, 1H), 2.91 (dd, $J = 13.8, 3.9$ Hz, 2H), 3.01-3.15 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 5.39 (s, 1H), 6.06 (s, 2H), 6.79 (d, $J = 15.9$ Hz, 1H), 6.81 (d, $J = 8.2$ Hz, 1H), 7.18 (d, $J = 8.2$ Hz, 1H), 7.99 (d, $J = 15.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 25.1, 30.8, 32.6, 47.8, 64.5, 101.6, 109.6, 115.5, 122.5, 123.5, 131.7, 135.6, 146.9, 147.6, 167.6; **3m'** (only detected peaks are noted): ^1H NMR (400 MHz, CDCl_3): δ 4.21 (t, $J = 6.6$ Hz, 2H), 5.43 (s, 1H), 5.99 (s, 2H), 6.27 (d, $J = 15.6$ Hz, 1H), 7.00 (s, 1H), 7.18 (s, 1H), 8.09 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 22.7, 25.0, 31.6, 32.3, 47.6, 101.8, 106.2, 109.0, 119.3, 140.6, 148.1; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{18}\text{H}_{23}\text{O}_4\text{S}_2$: 367.1032. Found 367.1034.

(*E*)-*n*-Butyl 3-(2-(1,3-Dithian-2-yl)-3-methylphenyl)acrylate (3n): colorless oil, 28.1 mg (33%); ^1H NMR (400 MHz, CDCl_3): δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.45-1.55 (m, 2H), 1.68-1.75 (m, 2H), 1.93-2.10 (m, 1H), 2.15-2.25 (m, 1H), 2.47 (s, 3H), 2.88-2.94 (m, 2H), 3.01-3.08 (m, 2H), 4.42 (t, $J = 6.6$ Hz, 2H), 5.62 (s, 1H), 6.28 (d, $J = 15.7$ Hz, 1H), 7.16-7.20 (m, 2H), 7.47 (s, 1H), 9.11 (d, $J = 14.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.3, 20.5, 25.4, 30.8, 30.9, 33.0, 47.8, 64.3, 117.9, 126.1, 128.3, 132.2, 135.3, 136.0, 144.9, 167.3; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{18}\text{H}_{25}\text{O}_2\text{S}_2$: 337.1290. Found 337.1283.

(*E*)-*n*-Butyl 3-(2-(1,3-Dithiolan-2-yl)-3-methylphenyl)acrylate (3o): pale yellow solid, mp 79-81 °C, 62.8 mg (78%); ^1H NMR (400 MHz, CDCl_3): δ 0.96 (t, $J = 7.4$ Hz, 3H), 1.44 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.69 (tt, $J = 9.6, 7.0$ Hz, 2H), 2.50 (s, 3H), 3.37-3.44 (m, 2H), 3.66-3.74 (m, 2H), 4.20 (t, $J = 6.7$ Hz, 2H),

6.21 (d, $J = 15.8$ Hz, 1H), 6.22 (s, 1H), 7.14-7.21 (m, 2H), 7.37 (dd, $J = 7.3, 1.3$ Hz, 1H), 8.81 (d, $J = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 20.9, 30.8, 40.6, 50.8, 64.3, 118.1, 126.7, 128.3, 132.3, 133.8, 136.0, 138.0, 144.7, 167.4; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{S}_2$: 323.1134. Found 323.1129.

(E)-*n*-Butyl 3-(2-(1,3-Dithiolan-2-yl)-3-fluorophenyl)acrylate (3p): colorless oil, 73.4 mg (90%); ^1H NMR (400 MHz, CDCl_3): δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.44 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.70 (tt, $J = 9.6, 6.6$ Hz, 2H), 3.41 (dd, $J = 11.7, 6.9$ Hz, 1H), 3.42 (dd, $J = 20.3, 9.5$ Hz, 1H), 3.706 (dd, $J = 20.3, 9.5$ Hz, 1H), 3.708 (dd, $J = 11.6, 6.9$ Hz, 1H), 4.22 (t, $J = 6.7$ Hz, 2H), 6.26 (d, $J = 2.3$ Hz, 1H), 6.27 (d, $J = 15.8$ Hz, 1H), 7.05 (ddd, $J = 10.2, 8.1, 1.4$ Hz, 1H), 7.26 (ddd, $J = 7.8, 7.8, 5.3$ Hz, 1H), 7.31 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.63 (d, $J = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 30.8, 40.9, 45.5 (d, $J = 7.0$ Hz), 64.5, 116.8 (d, $J = 23.9$ Hz), 120.0, 123.8, (d, $J = 3.2$ Hz), 124.5 (d, $J = 2.2$ Hz), 129.5 (d, $J = 9.6$ Hz), 137.2 (d, $J = 2.8$ Hz), 142.3 (d, $J = 2.8$ Hz), 161.2 (d, $J = 247.2$ Hz), 166.9; ^{19}F NMR (376 MHz, CDCl_3): δ -114.1; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{16}\text{H}_{20}\text{FO}_2\text{S}_2$: 327.0883. Found 327.0878.

(E)-*n*-Butyl 3-(4-(1,3-Dithian-2-yl)dibenzo[*b,d*]furan-3-yl)acrylate (3q): colorless solid, mp 182-183 °C, 55.0 mg (53%); ^1H NMR (400 MHz, CDCl_3): δ 0.99 (t, $J = 7.4$ Hz, 3H), 1.52 (qt, $J = 9.4, 7.3$ Hz, 2H), 1.74 (tt, $J = 9.7, 6.4$ Hz, 2H), 2.05-2.16 (m, 1H), 2.24-2.30 (m, 1H), 2.96-3.01 (m, 2H), 3.19-3.27 (m, 2H), 4.27 (t, $J = 6.5$ Hz, 2H), 6.27 (s, 1H), 6.44 (d, $J = 15.7$ Hz, 1H), 7.36 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.49 (ddd, $J = 8.4, 8.4, 1.2$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 9.05 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.3, 25.4, 30.9, 32.9, 43.9, 64.4, 112.0, 118.9, 120.6, 120.9, 122.2, 122.3, 123.2, 124.1, 125.6, 128.0, 133.5, 143.1, 153.5, 156.4, 167.1; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{23}\text{H}_{25}\text{O}_3\text{S}_2$: 413.1240. Found 413.1239.

(E)-*t*-Butyl 3-(2-(1,3-Dithian-2-yl)phenyl)acrylate (3r): colorless solid, mp 106-108 °C, 69.3 mg (86%); ^1H NMR (400 MHz, CDCl_3): δ 1.55 (s, 9H), 1.95 (dtt, $J = 14.2, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.1, 4.3, 2.4$ Hz, 1H), 2.91 (ddd, $J = 14.5, 4.0, 3.1$ Hz, 2H), 3.09-3.16 (m, 2H), 5.46 (s, 1H), 6.33 (d, $J = 15.7$ Hz, 1H), 7.27-7.31 (m, 1H), 7.37 (ddd, $J = 7.6, 7.6, 1.4$ Hz, 1H), 7.53 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.67 (dd, $J = 7.8, 1.3$ Hz, 1H), 8.09 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 25.1, 28.3, 32.3, 48.0, 80.7, 123.1, 127.1, 128.6, 128.8, 130.2, 132.8, 137.8, 140.1, 166.2; HRMS m/z ($\text{M}+\text{H}^+$) Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{S}_2$: 323.1134. Found 323.1132.

(E)-Phenyl 3-(2-(1,3-Dithian-2-yl)phenyl)acrylate (3s): colorless solid, mp 96-98 °C, 71.3 mg (83%); ^1H NMR (400 MHz, CDCl_3): δ 1.95 (dtt, $J = 14.2, 12.6, 3.0$ Hz, 1H), 2.20 (dtt, $J = 14.2, 4.3, 2.4$ Hz, 1H), 2.93 (ddd, $J = 14.5, 4.0, 3.1$ Hz, 2H), 3.10-3.17 (m, 2H), 5.48 (s, 1H), 6.60 (d, $J = 15.7$ Hz, 1H), 7.18-7.45 (m, 7H), 7.62 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.70 (dd, $J = 7.8, 1.3$ Hz, 1H), 8.38 (d, $J = 15.7$ Hz, 1H); ^{13}C

NMR (100 MHz, CDCl₃): δ 25.0, 32.3, 48.1, 120.2, 121.7, 125.9, 127.3, 128.8, 129.0, 129.5, 130.9, 132.4, 138.1, 143.3, 150.8, 165.3; HRMS m/z (M+H⁺) Calcd for C₁₉H₁₉O₂S₂: 343.0821. Found 343.0828.

(E)-Diethyl 2-(1,3-Dithian-2-yl)styrylphosphonate (3t): pale yellow oil, 83.2 mg (93%); ¹H NMR (400 MHz, CDCl₃): δ 1.38 (t, J = 7.1 Hz, 6H), 1.94 (dt, J = 14.1, 12.7, 3.0 Hz, 1H), 2.20 (dt, J = 14.2, 4.2, 2.4 Hz, 1H), 2.88-2.93 (m, 2H), 3.09-3.16 (m, 2H), 4.17 (qd, J = 7.2, 7.2 Hz, 4H), 5.45 (s, 1H), 6.24 (dd, J = 18.4, 17.3 Hz, 1H), 7.31 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 7.38 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.51 (dd, J = 7.8, 1.2 Hz, 1H), 7.67 (dd, J = 7.8, 1.2 Hz, 1H), 7.99 (dd, J = 22.5, 17.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 16.5 (d, J = 6.4 Hz), 25.0, 32.2, 47.9, 62.0 (d, J = 5.4 Hz), 117.6 (d, J = 188.2 Hz), 126.9 (d, J = 1.0 Hz), 128.6, 128.8, 130.4, 133.3 (d, J = 22.9 Hz), 137.5, 145.4 (d, J = 7.4 Hz); ³¹P {¹H} NMR (CDCl₃, 162 MHz): δ 18.6; HRMS m/z (M+H⁺) Calcd for C₁₆H₂₄O₃PS₂: 359.0899. Found 359.0908.

(E)-n-Butyl 3-(2-(2-(Trifluoromethyl)-1,3-dithian-2-yl)phenyl)acrylate (3v): colorless oil, 77.6 mg (79%); ¹H NMR (400 MHz, CDCl₃): δ 0.97 (t, J = 7.4 Hz, 3H), 1.41-1.50 (m, 2H), 1.71 (tt, J = 9.5, 6.8 Hz, 2H), 2.20-2.29 (m, 2H), 2.74-2.78 (m, 2H), 3.20-3.25 (m, 2H), 4.23 (t, J = 6.7 Hz, 2H), 6.12 (d, J = 15.7 Hz, 1H), 7.32-7.40 (m, 2H), 7.55 (dd, J = 7.1, 2.1 Hz, 1H), 7.69-7.71 (m, 1H), 9.35 (d, J = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 22.1, 29.0, 30.8, 56.6 (d, J = 28.0 Hz), 64.4, 117.0, 127.4 (q, J = 282.0 Hz), 129.1 (br, m), 129.2, 129.6, 130.5, 132.6, 136.6, 147.2, 167.4; ¹⁹F NMR (376 MHz, CDCl₃): δ -65.1; HRMS m/z (M+H⁺) Calcd for C₁₈H₂₂F₃O₂S₂: 391.1008. Found 391.1005.

(E)-n-Butyl 3-(2-(Isothiochroman-1-yl)phenyl)acrylate (5): colorless oil, 64.1 mg (73%); ¹H NMR (400 MHz, CDCl₃): δ 0.96 (t, J = 7.4 Hz, 3H), 1.37-1.46 (m, 2H), 1.67 (tt, J = 9.4, 6.8 Hz, 2H), 2.87 (ddd, J = 13.1, 8.8, 4.6 Hz, 1H), 2.98 (ddd, J = 13.1, 6.4, 4.8 Hz, 1H), 3.16 (ddd, J = 16.3, 8.8, 4.8 Hz, 1H), 3.25-3.32 (m, 1H), 4.19 (t, J = 6.6 Hz, 2H), 5.52 (s, 1H), 6.36 (d, J = 15.7 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 7.00-7.09 (m, 2H), 7.16-7.30 (m, 4H), 7.59-7.61 (m, 1H), 8.13 (d, J = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 25.0, 30.8, 31.1, 42.5, 64.5, 120.5, 126.3, 127.0, 127.4, 127.6, 128.8, 129.5, 129.9, 130.2, 133.7, 136.4, 136.8, 141.7, 141.9, 166.8; HRMS m/z (M+H⁺) Calcd for C₂₂H₂₅O₂S: 353.1570. Found 353.1571.

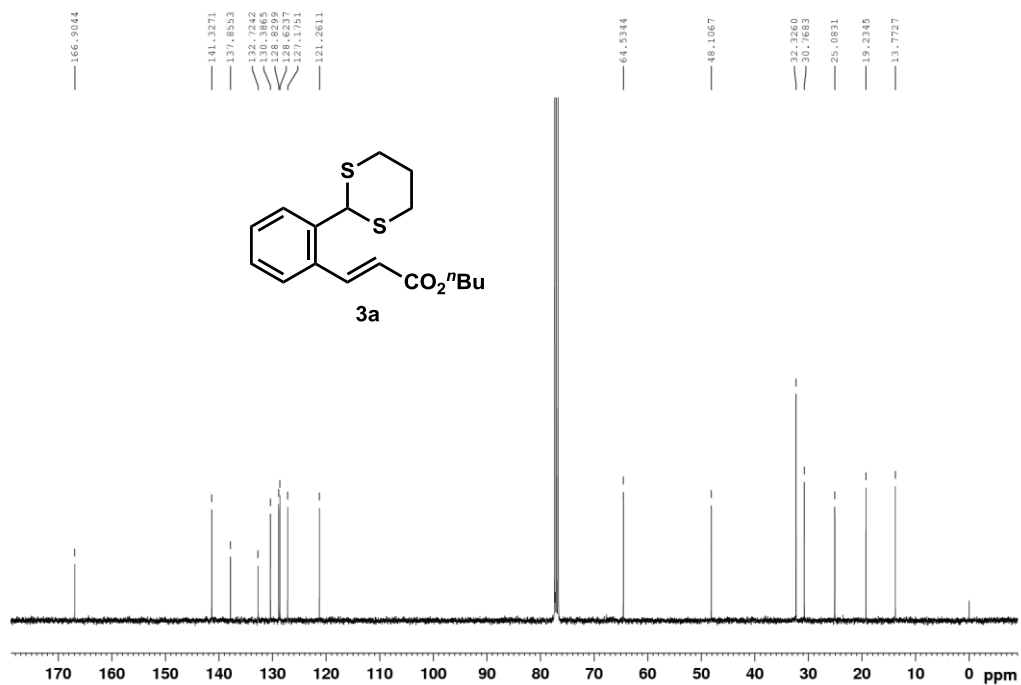
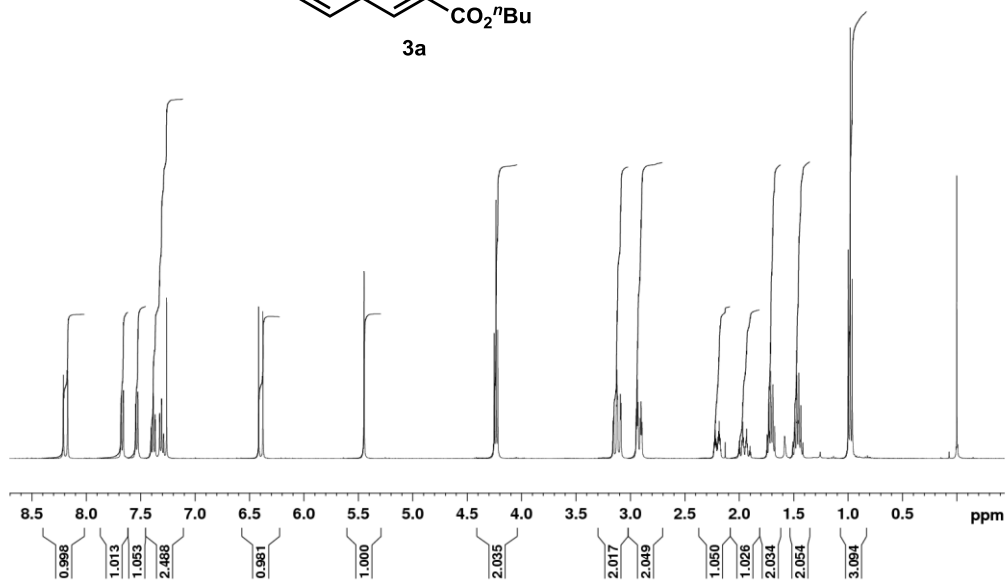
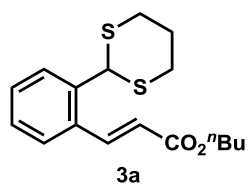
(2E,2'E)-dibutyl 3,3'-(2-(Isothiochroman-1-yl)-1,3-phenylene)diacrylate (6): colorless oil, 112.0 mg (94%); ¹H NMR (400 MHz, CDCl₃): δ 0.94 (t, J = 7.4 Hz, 6H), 1.33-1.42 (m, 4H), 1.59-1.66 (m, 4H), 2.92-2.98 (m, 1H), 3.14-3.25 (m, 2H), 3.48-3.55 (m, 1H), 4.13 (t, J = 6.6 Hz, 4H), 5.91 (s, 1H), 6.19 (d(br), J = 14.4 Hz, 2H), 6.59 (d, J = 7.8 Hz, 1H), 6.96-7.15 (m, 1H), 7.08-7.15 (m, 2H), 7.35 (dd, J = 7.7, 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 2H), 8.06 (d, J = 15.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 19.2, 27.7, 30.7, 31.9, 41.4, 64.4, 126.57, 126.64, 127.9, 128.3, 129.3 (2C, overlapped), 130.2, 135.8, 136.1, 136.4, 139.2, 143.2, 166.5; HRMS m/z (M+H⁺) Calcd for C₂₉H₃₅O₄S: 479.2251. Found 479.2253.

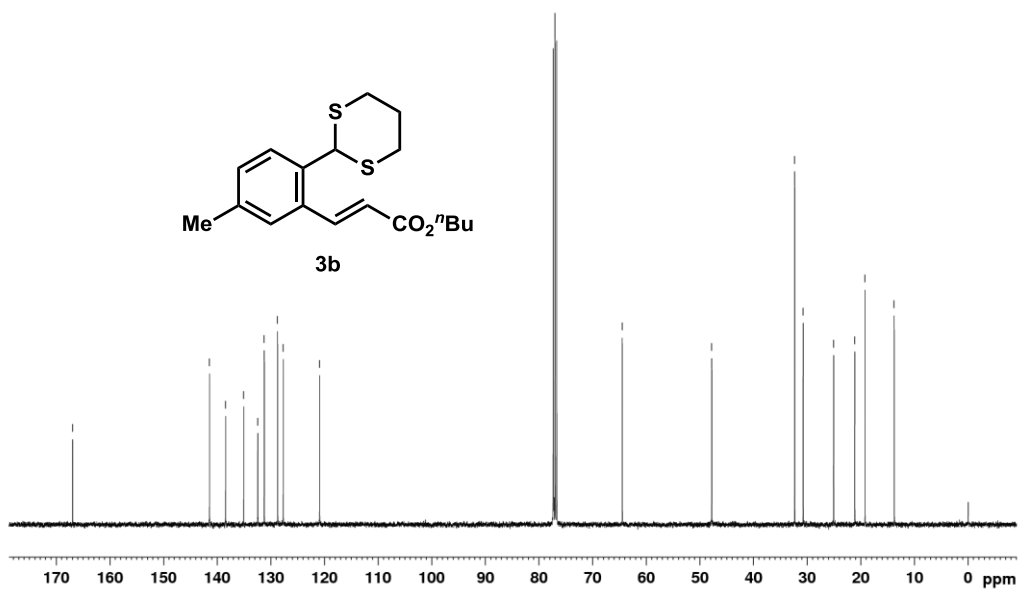
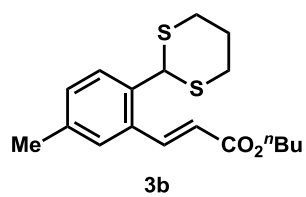
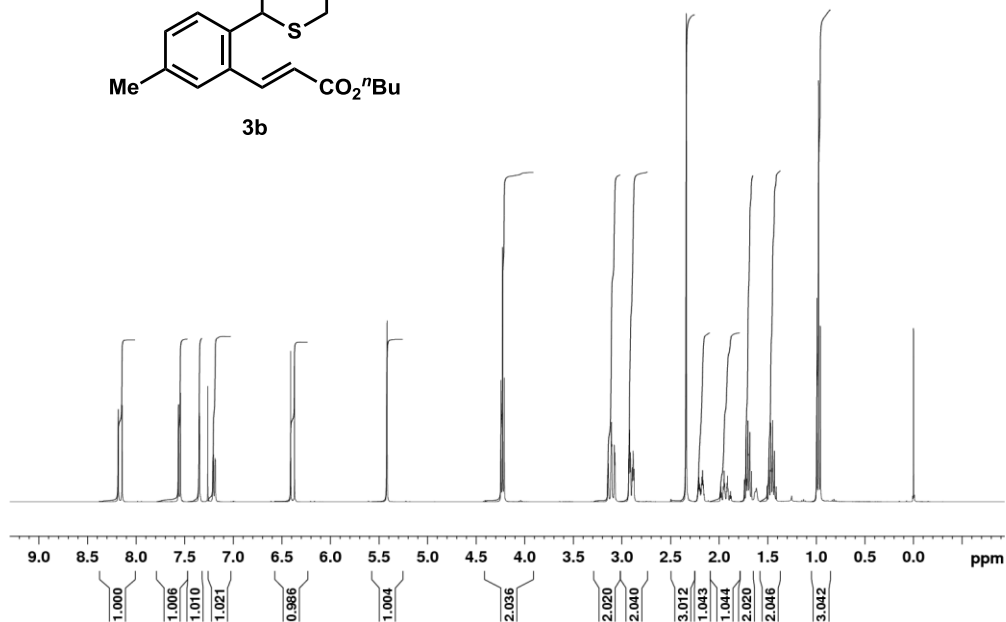
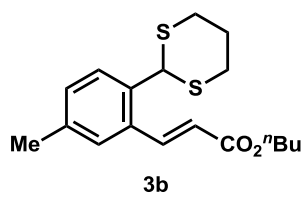
(E)-*t*-Butyl 3-(2-Formylphenyl)acrylate (7):^[S4] colorless oil, 43.5 mg (94%); ¹H NMR (400 MHz, CDCl₃): δ 1.55 (s, 9H), 6.31 (d, J = 15.8 Hz, 1H), 7.53 (ddd, J = 7.2, 7.2, 1.8 Hz, 1H), 7.58-7.64 (m, 2H), 7.87-7.89 (m, 1H), 8.42 (d, J = 15.8 Hz, 1H), 10.33 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 28.2, 81.0, 125.3, 128.0, 129.6, 131.7, 133.8, 133.9, 137.0, 139.6, 165.5, 191.7; HRMS m/z (M+H⁺) Calcd for C₁₄H₁₇O₃: 233.1178. Found 233.1176.

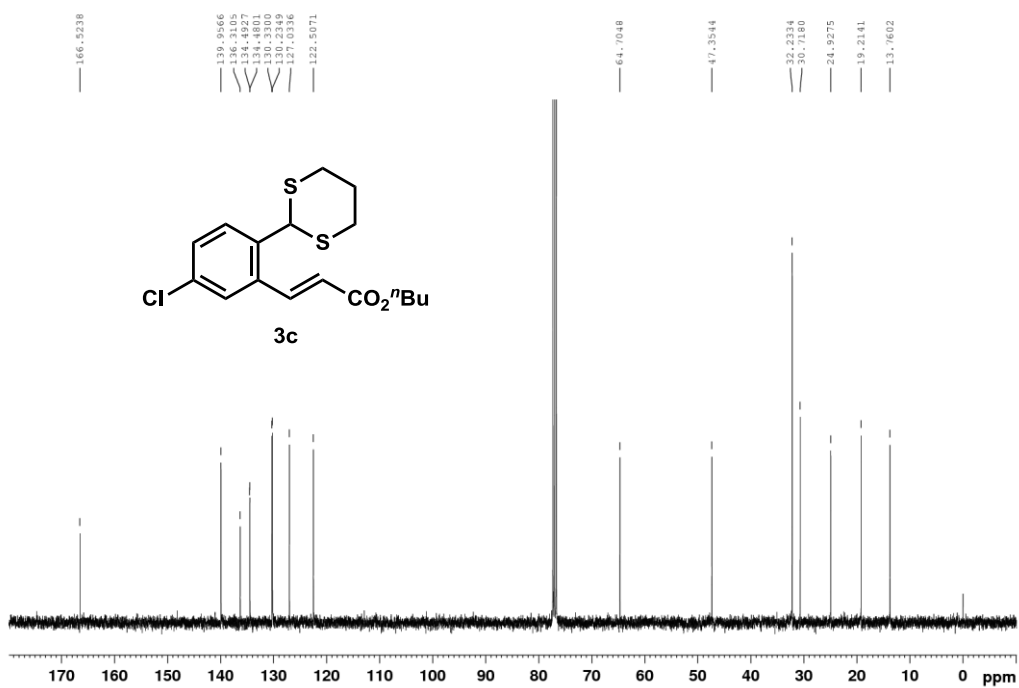
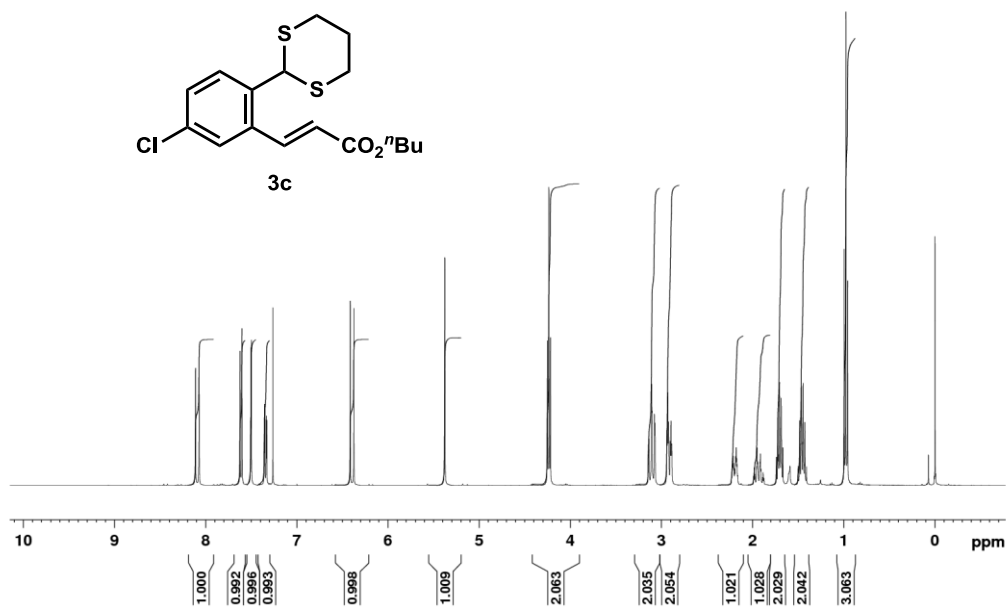
***t*-Butyl 3-(4-Methylphenyl)propanoate (8):** colorless oil, 38.9 mg (88%); ¹H NMR (400 MHz, CDCl₃): δ 1.44 (s, 9H), 2.32 (s, 3H), 2.48-2.52 (m, 2H), 2.88-2.92 (m, 2H), 7.09-7.15 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 19.3, 28.1, 28.4, 35.7, 80.4, 126.0, 126.3, 128.5, 130.2, 136.0, 138.9, 172.5; HRMS (EI) m/z (M⁺) Calcd for C₁₄H₂₀O₂: 220.1463. Found 220.1465.

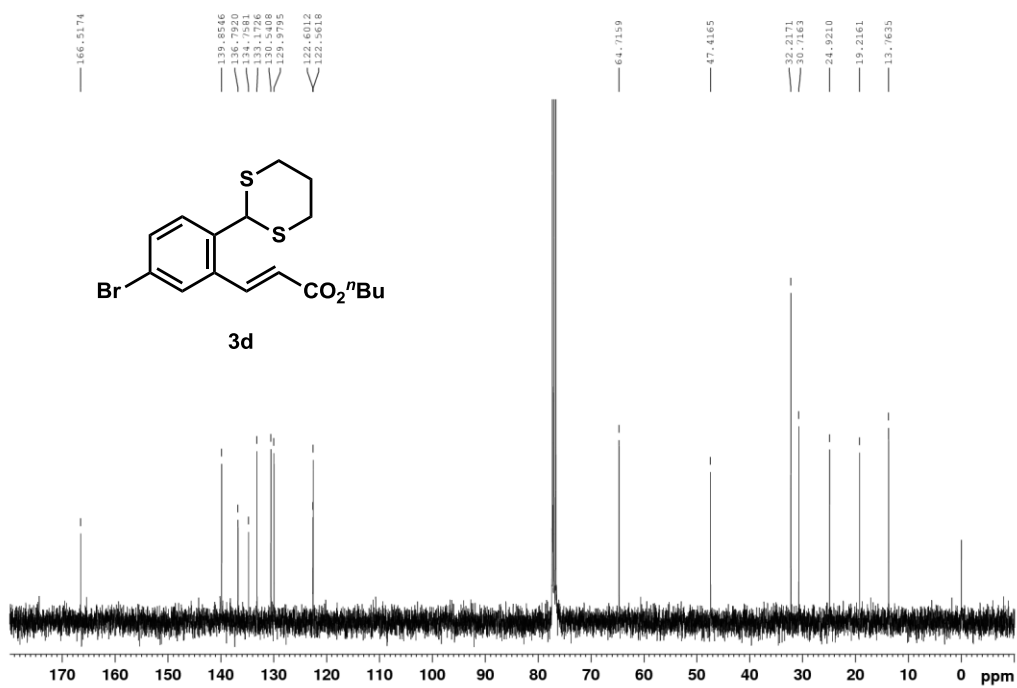
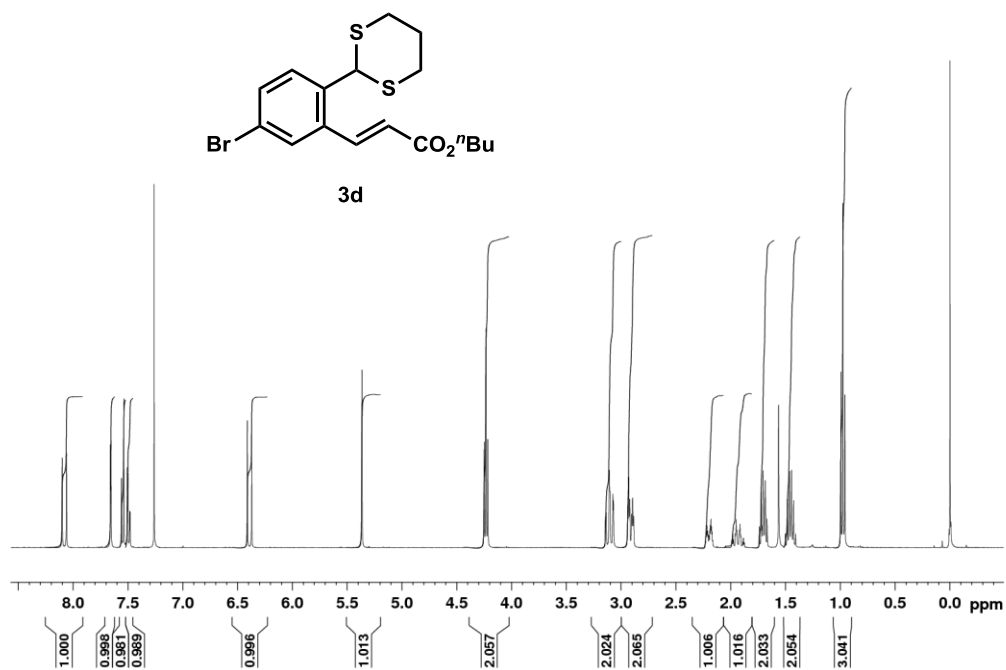
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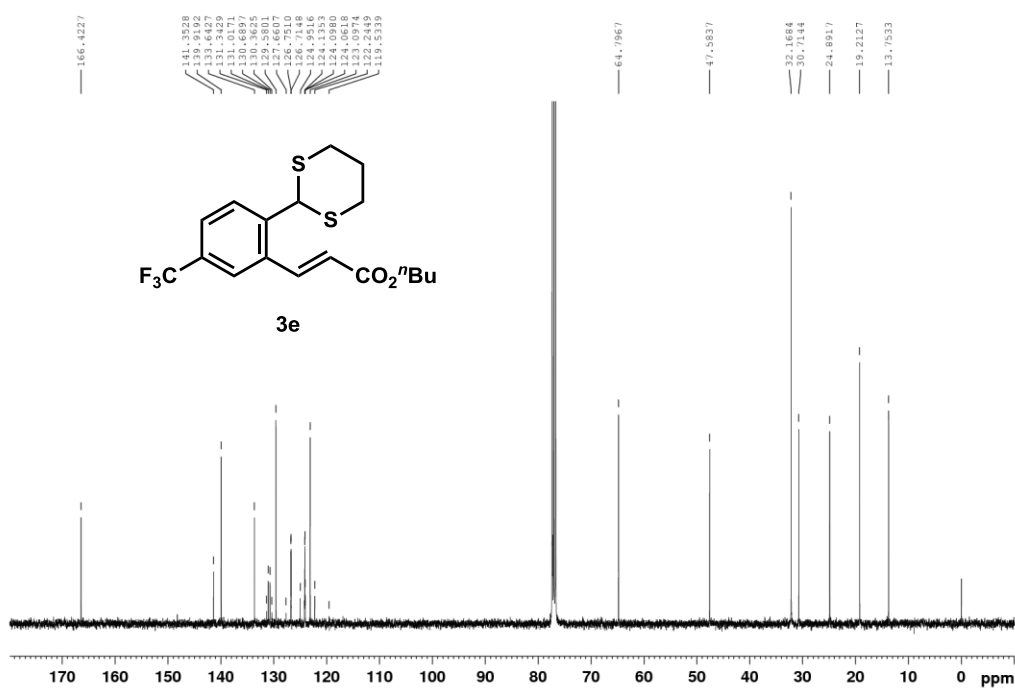
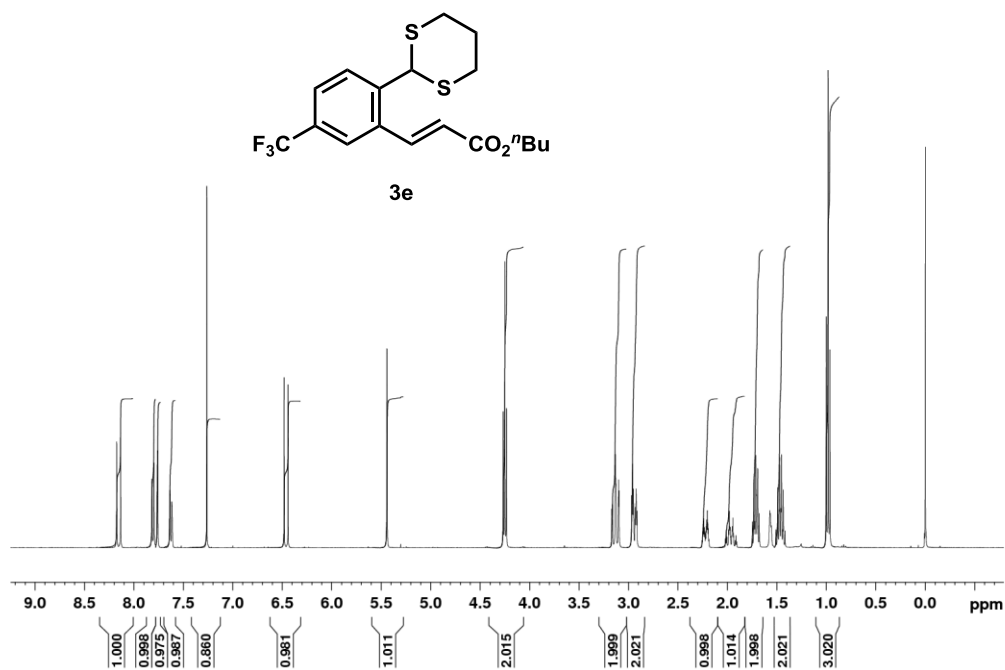
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[S2] Lherbet, C.; Soupaya, D.; Baudoin-Dehoux, C.; André, C.; Blonski, C.; Hoffmann, P. *Tetrahedron Lett.* **2008**, *49*, 5449-5451.
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[S4] Zhang, T.; Wu, L.; Li, X. *Org. Lett.* **2013**, *15*, 6294-6297.

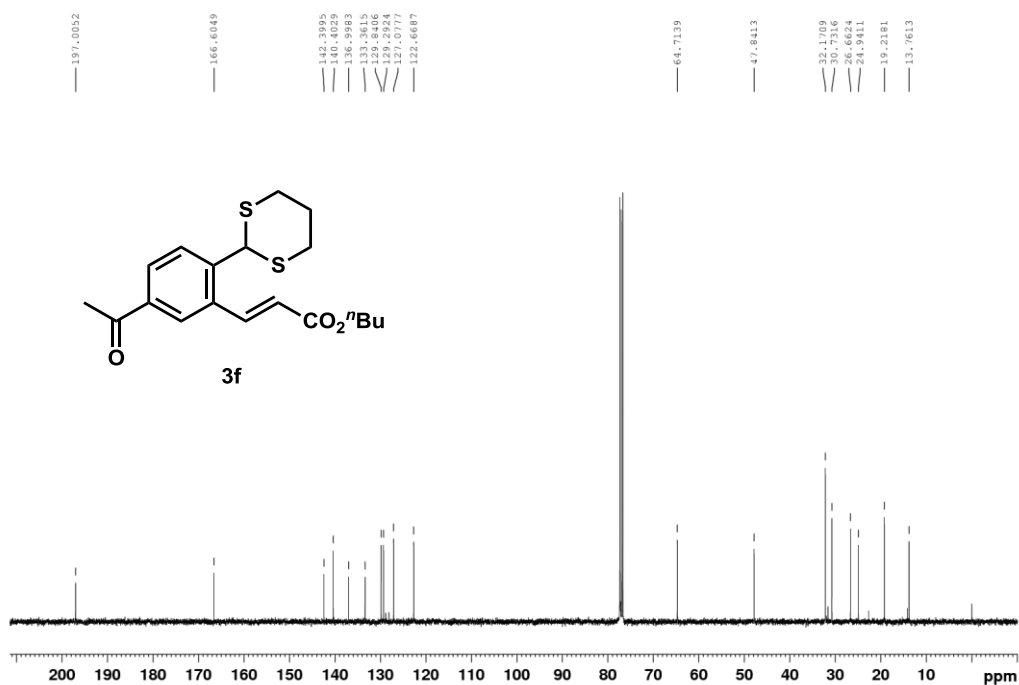
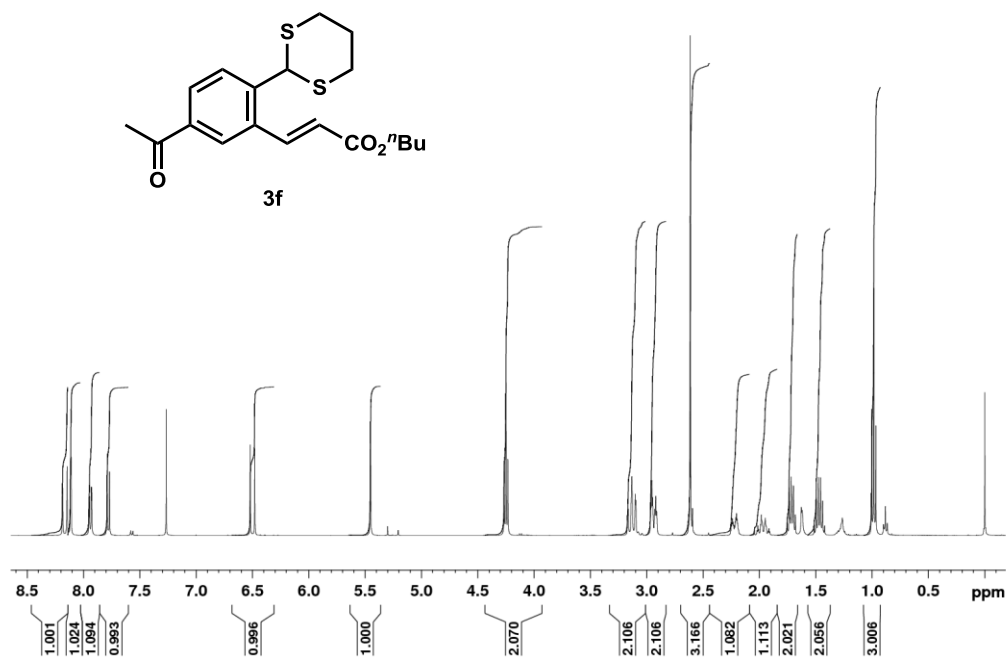


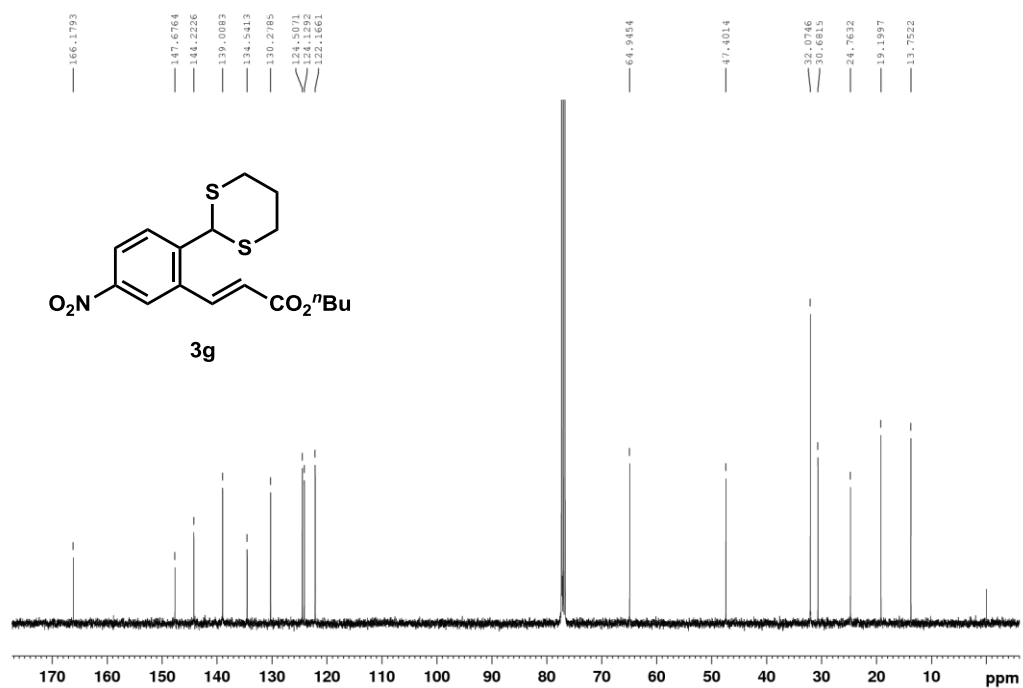
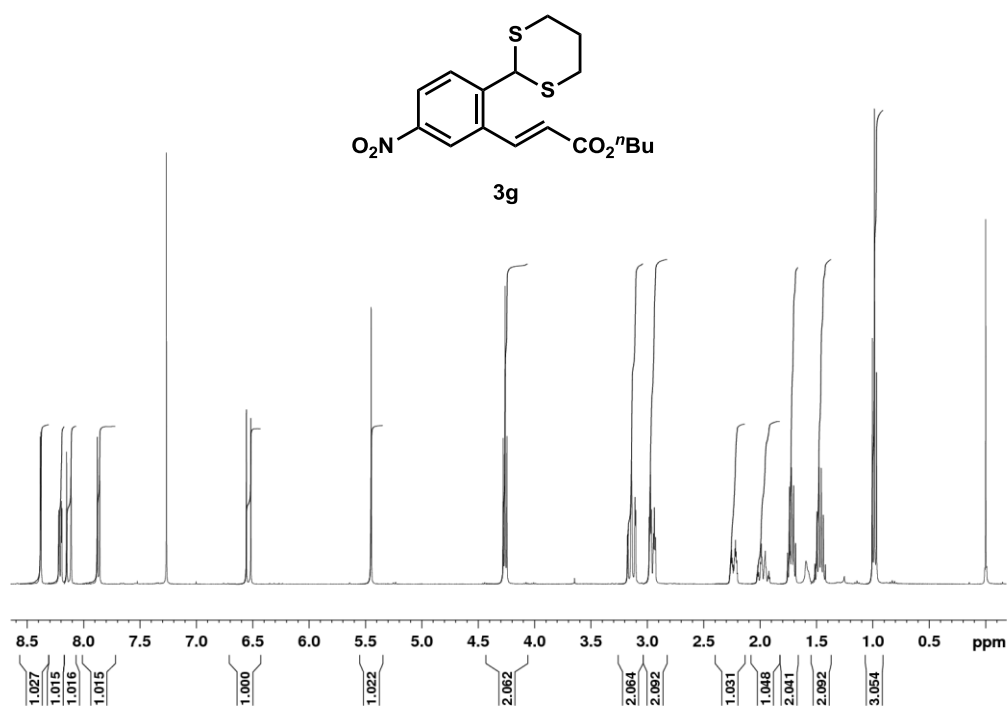


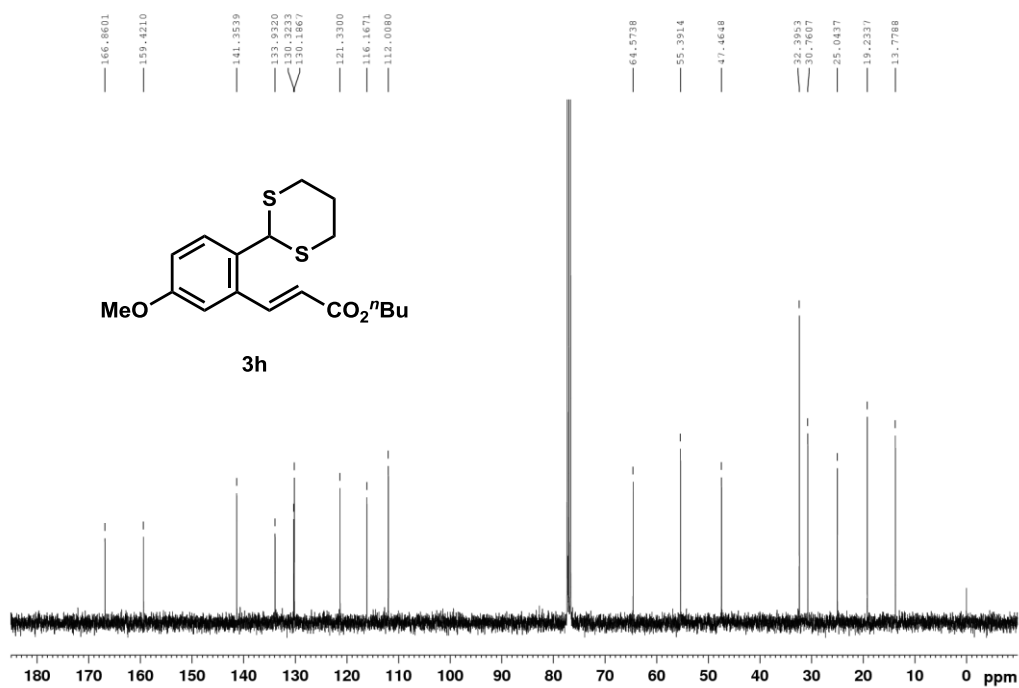
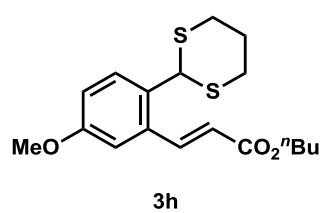
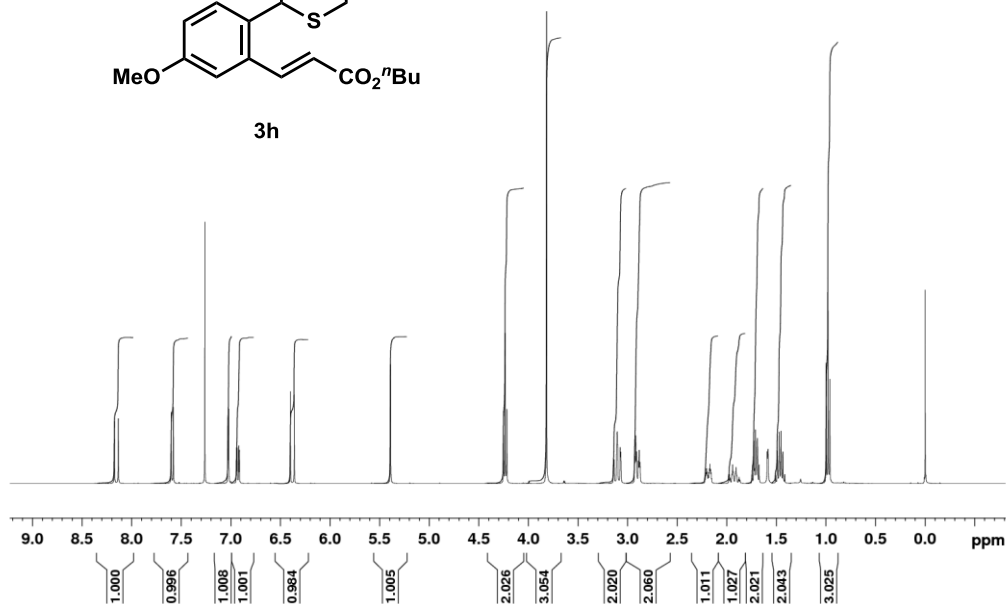
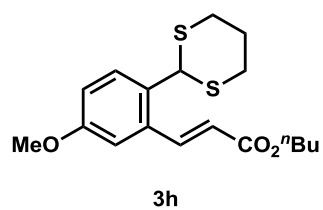


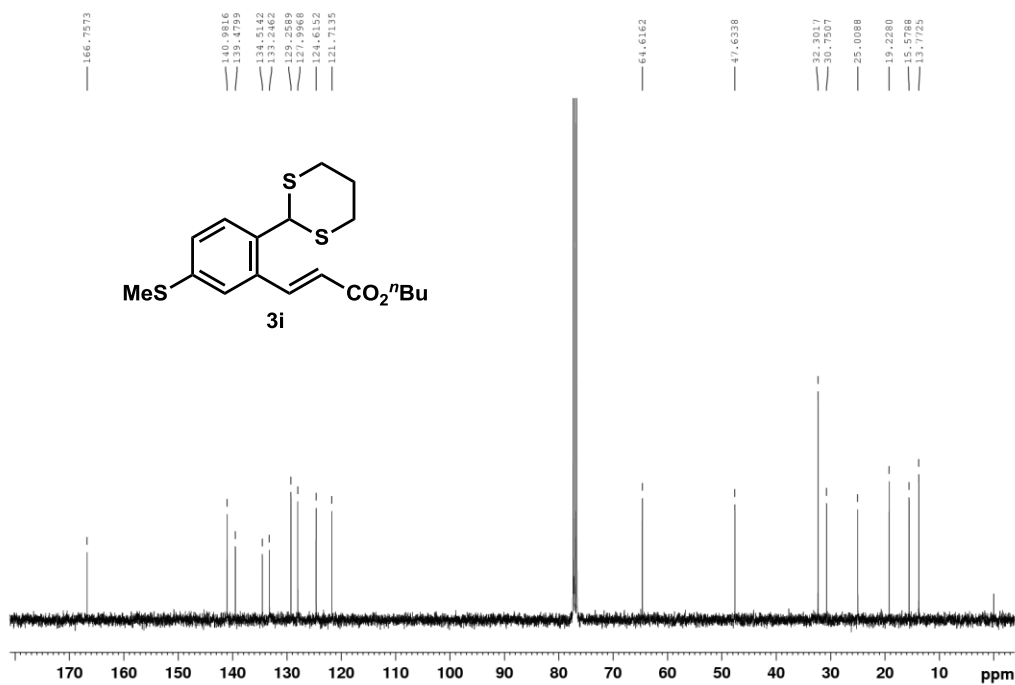
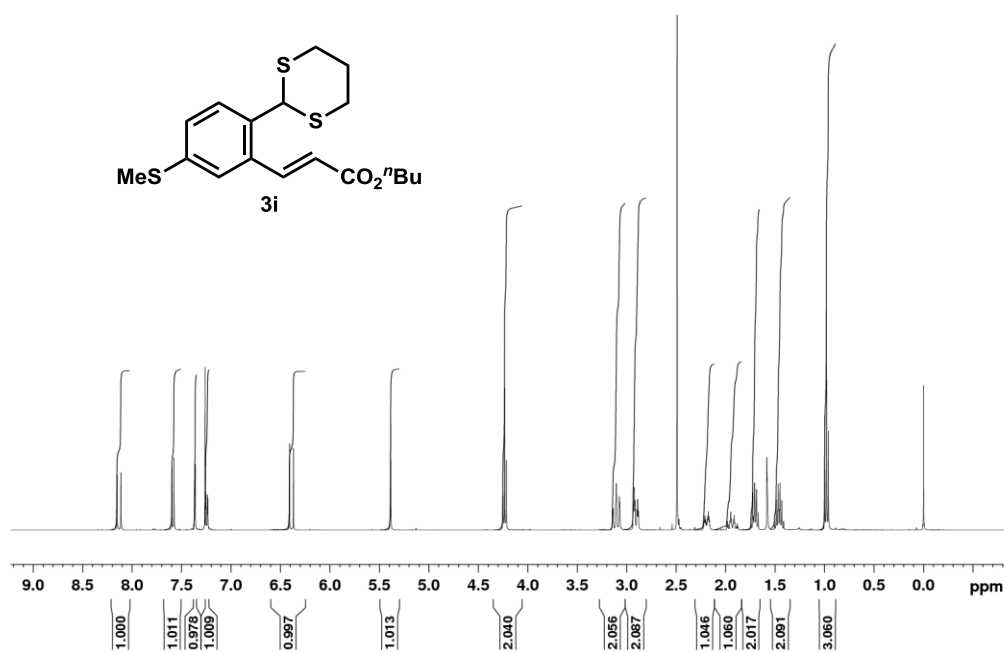


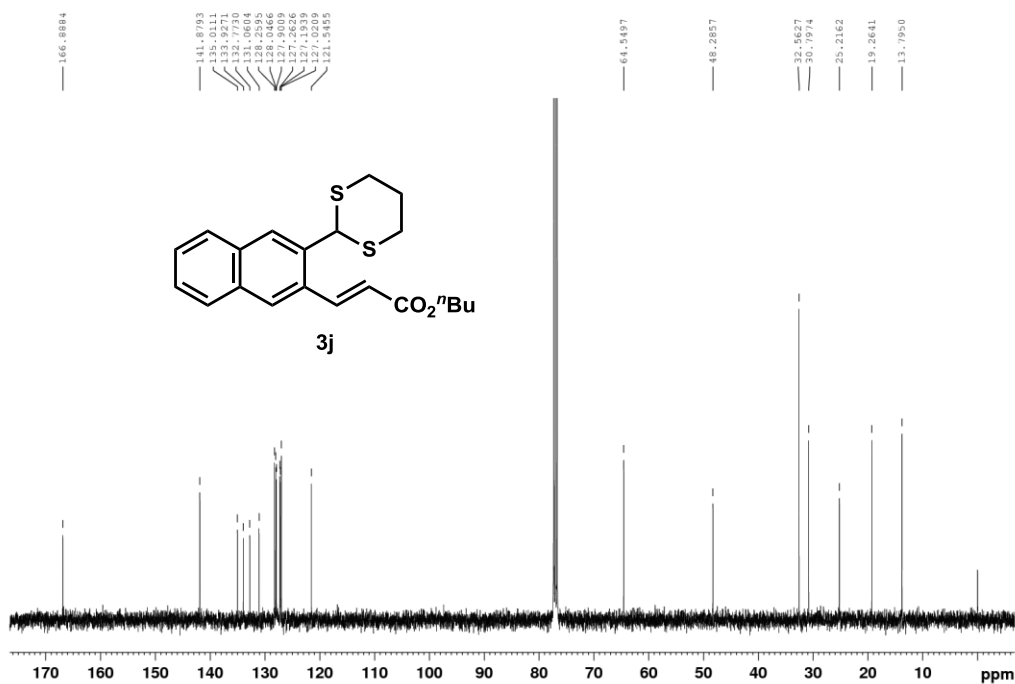
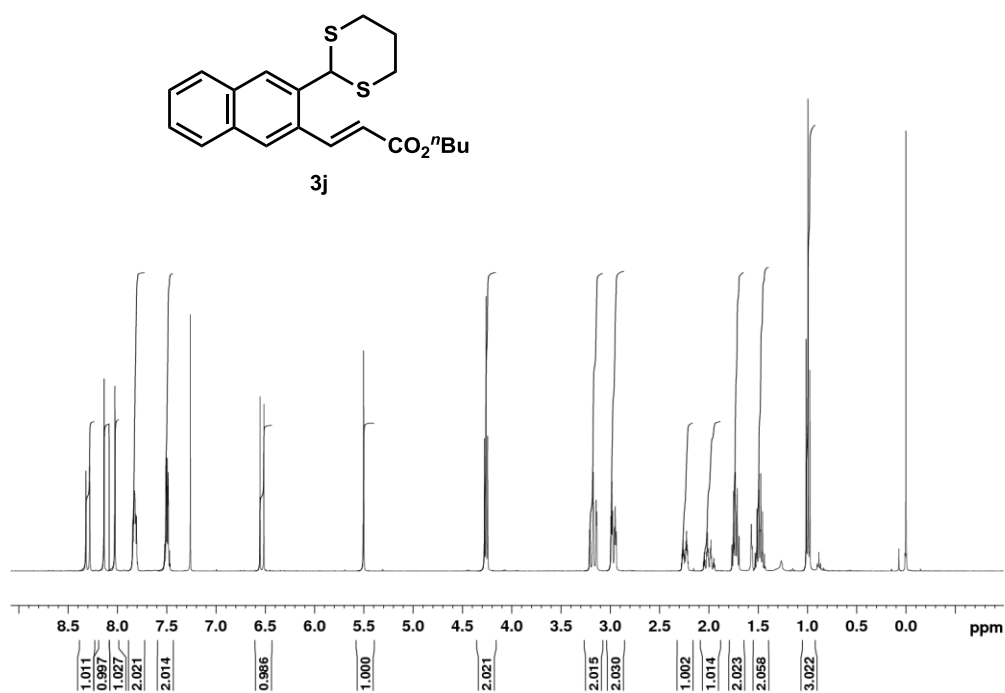


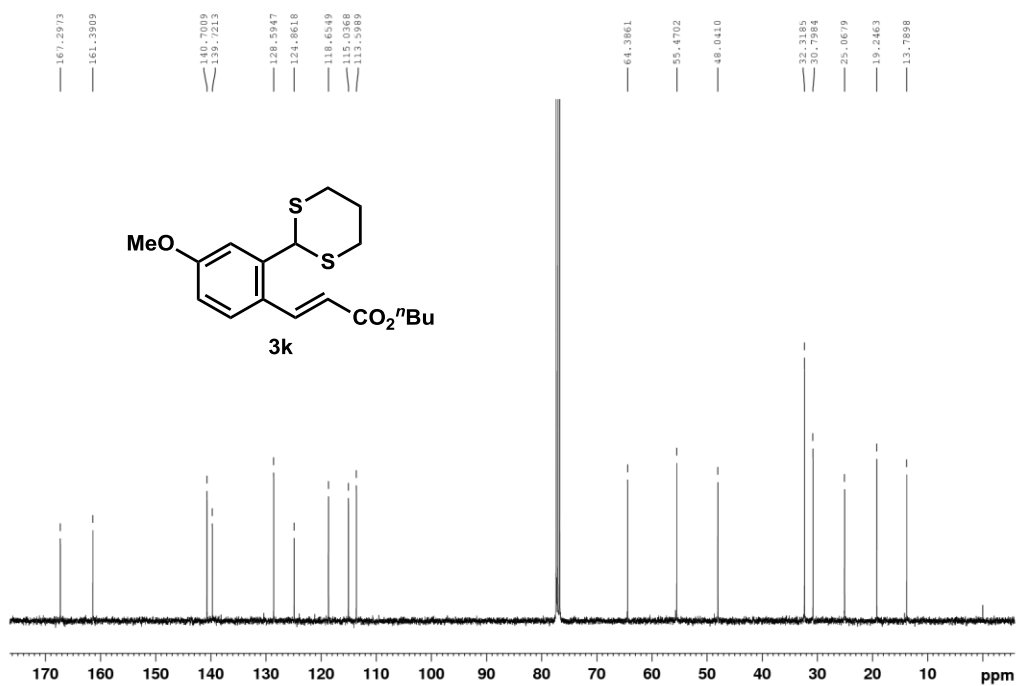
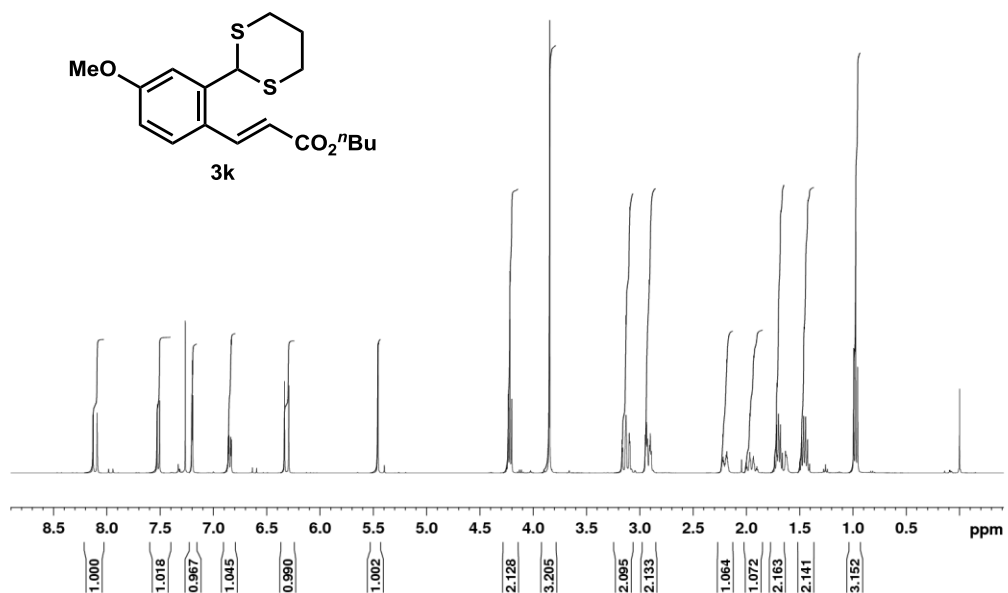


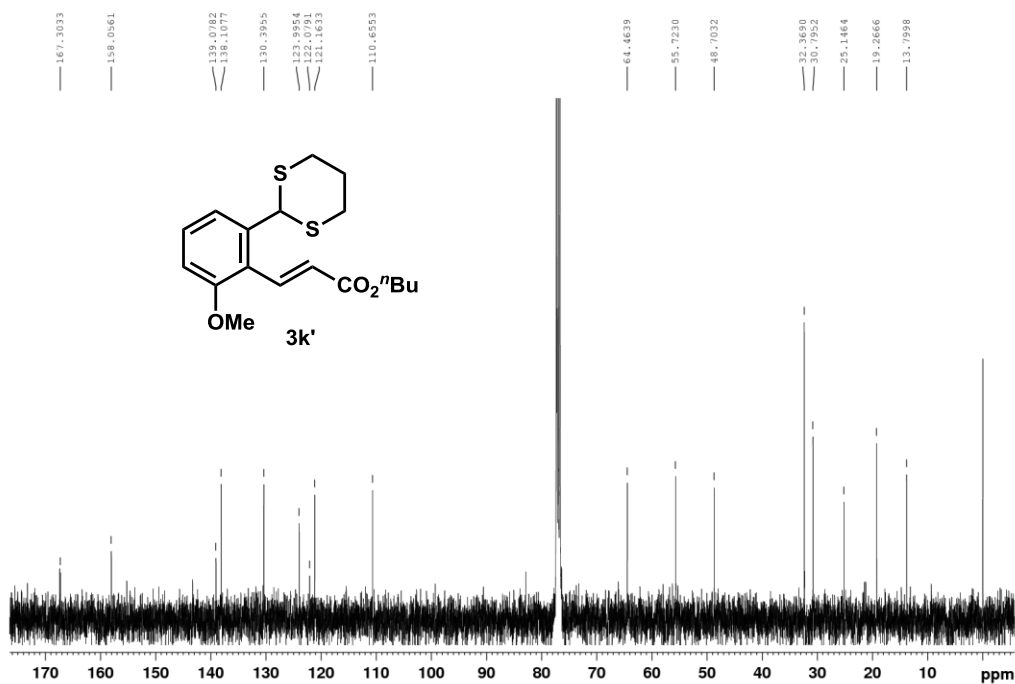
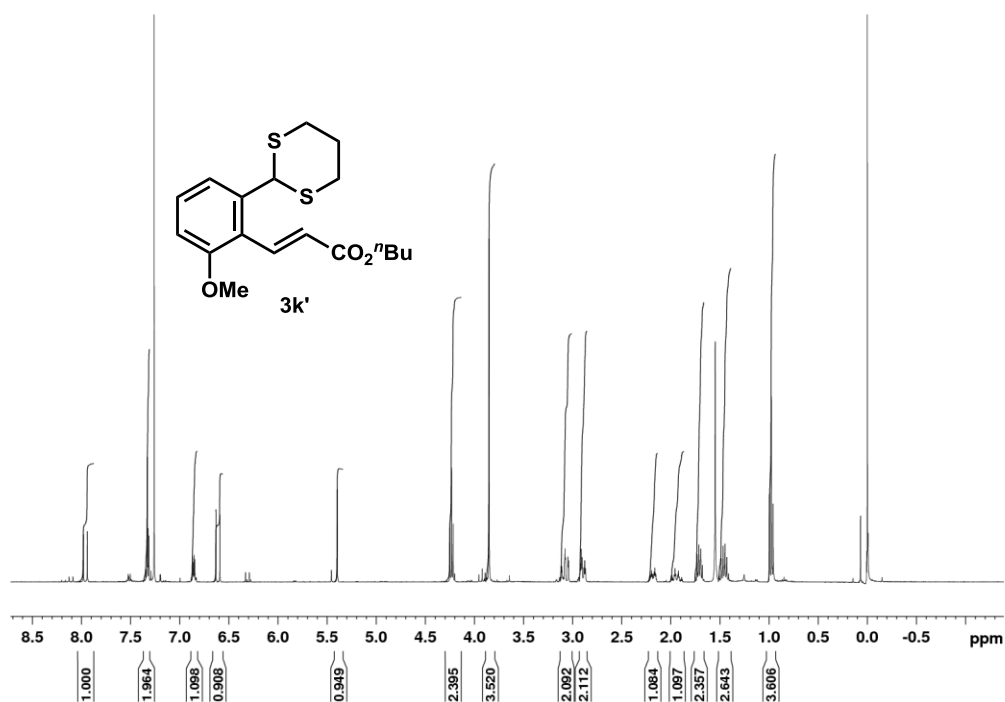


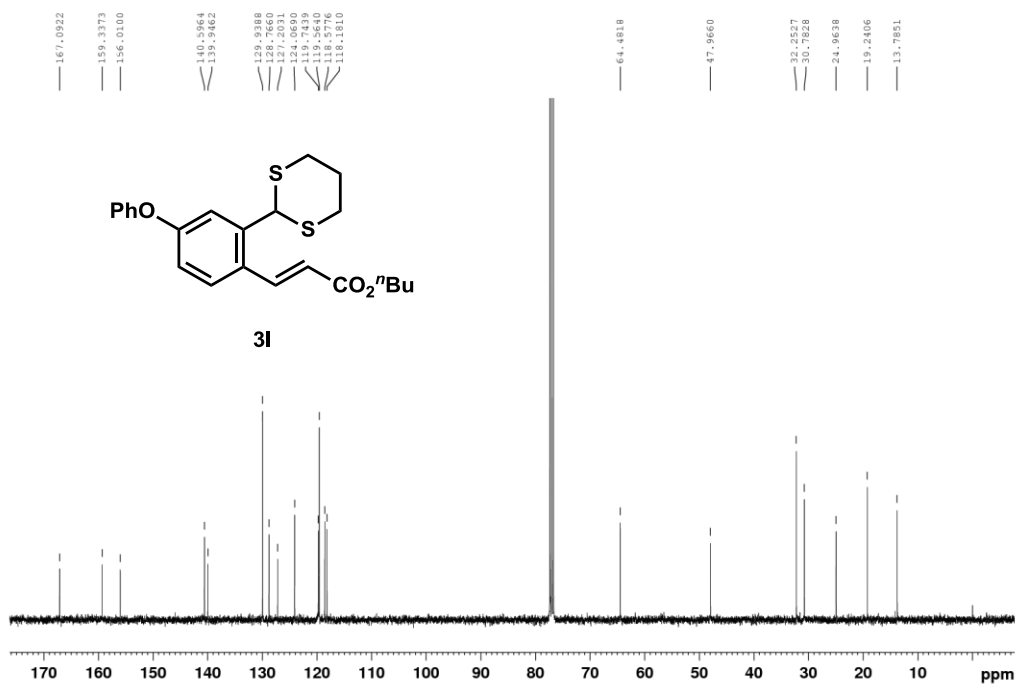
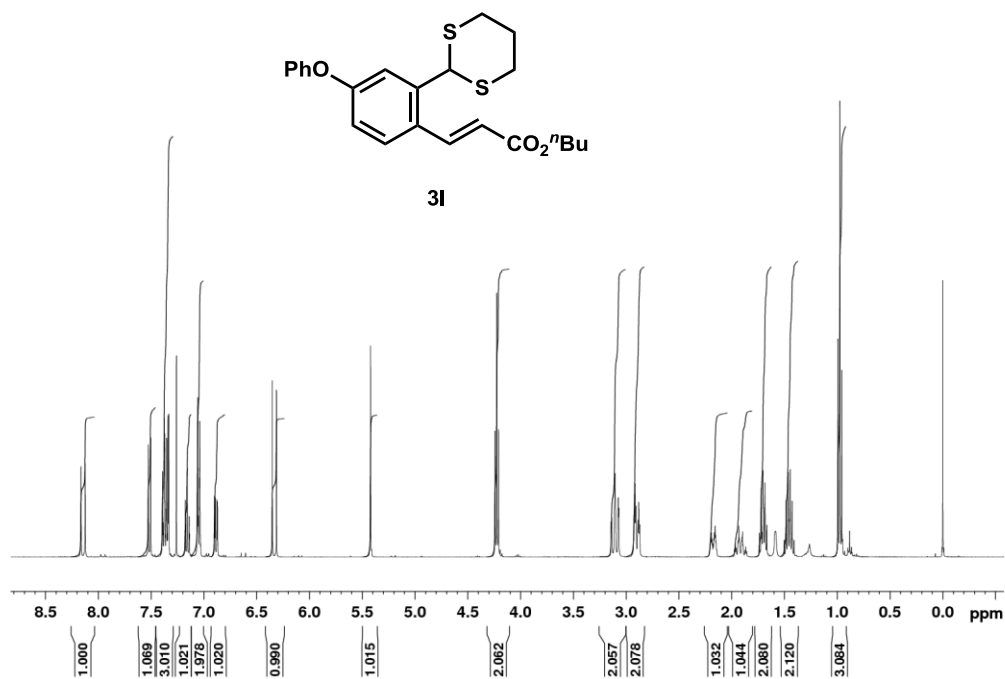


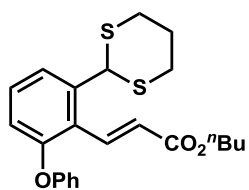












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