Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regiodivergent Radical Oxidative Coupling of Vinyl Ethers with Dithiane by Copper or Iron Catalysis

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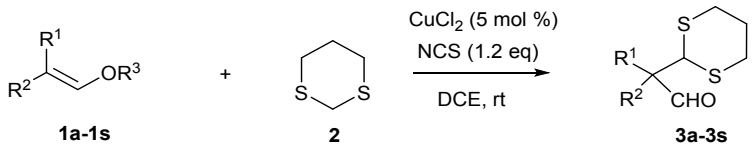
1. General information

Analytical grade solvents and commercially available reagents were used as received. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. 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. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, HRMS. ^{1}H and ^{13}C NMR data were recorded with Bruker 300 MHz with tetramethylsilane as internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane (0 ppm for ^{1}H) and $CDCl_3$ (77.00 ppm for ^{13}C). IR spectra were obtained with neat thin films on a sodium chloride disk and were recorded on an FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak). High-resolution mass spectra were recorded using electrospray ionization (ESI).

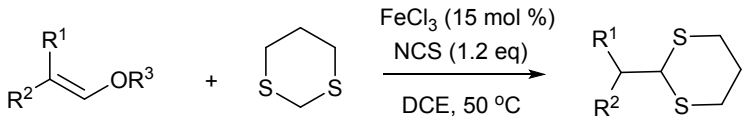
2. Experimental section

2.1 General procedure for α-dithianyl aldehydes 3a-3s



To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then **1a-1s** (0.3 mmol) and $CuCl_2$ (1.3 mg, 0.01 mmol) were added at room temperature. Reaction mixture was stirred at rt for 1-8 h until the reaction was complete (as determined by TLC analysis). Reaction mixture was diluted with ethyl acetate (10 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 brine (10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate (EA/PE = 1: 50～2: 50) to yield the product **3a-3s**.

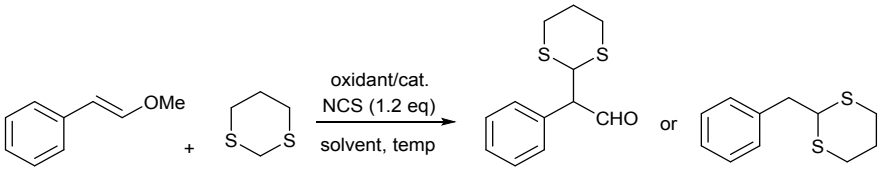
2.2 General procedure for 2-substituted dithiane derivatives 4



1 **2** **4**

To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then **1** (0.3 mmol) and $FeCl_3$ (4.9 mg, 0.03 mmol) were added at reaction temperature. Reaction mixture was stirred at 50 °C for 8 h until the reaction was complete (as determined by TLC analysis). Reaction mixture was diluted with ethyl acetate (10 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 brine (10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate (EA/PE = 1: 100～1: 50) to yield the product **4**.

3. Optimization of the Reaction Conditions[a]



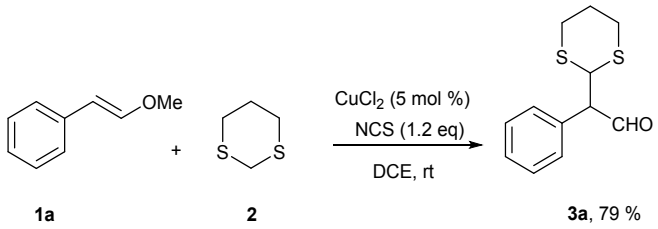
1a **2** **3a** **4a**

Entry	Oxidant/Cat (*x* mol %)	Temp (°C)	Solvent	3a (%)[b]	4a (%)
1	none	rt	DCE	38	-[c]
2	none	rt	THF	-	-
3	CuCl (5)	rt	DCE	43	-
4	CuI (5)	rt	DCE	60	-
5	CuBr (5)	rt	DCE	73	-
6	$Cu(OAc)_2$ (5)	rt	DCE	51	-
7	$CuBr_2$ (5)	rt	DCE	47	-
8	$Cu(OTf)_2$ (5)	rt	DCE	55	-
9	$CuCl_2$ (5)	rt	DCE	90	-
10	$CuCl_2$ (15)	rt	DCE	88	-
11	CuO (5)	rt	DCE	64	-
12	$CuCl_2$ (5)	rt	THF	-	-
13	$CuCl_2$ (5)	rt	toluene	32	-
14	$CuCl_2$ (5)	rt	$CHCl_3$	84	-
15	$CuCl_2$ (5)	rt	CCl_4	43	-

16	$CuCl_2$ (5)	rt	DMF	-	-
17	DTBP (200)	rt	DCE	44	-
18	TBHP (200)	rt	DCE	trace	-
19	$FeCl_3$ (15)	50	DCE	-	89
20	$FeCl_2{\cdot}4H_2O$ (15)	50	DCE	-	43
21	$Fe(acac)_3$ (15)	50	DCE	-	52
22	MsOH (80)	50	DCE	-	75
23	TsOH (80)	50	DCE	-	63
24	BF_3 Et_2O (20)	50	DCE	-	55

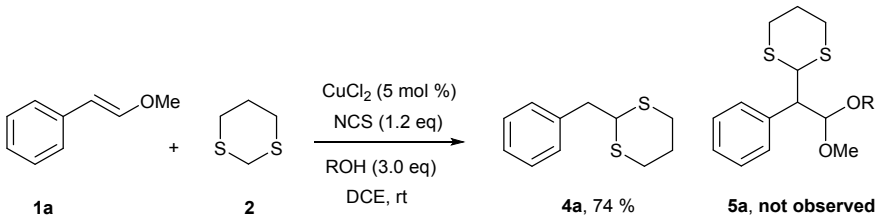
[a]Reaction conditions: 1,3-dithiane (**2**, 0.2 mmol), NCS (0.24 mmol), vinyl ether (**1a**, 0.3 mmol) and Oxidant/Cat (*x* mol %) in 2 mL of solvent at 50 °C or room temperature for 1-8 h. [b]Isolated yield. [c]Not detected or isolated.

4. General Procedure for the Gram Scale Experiment



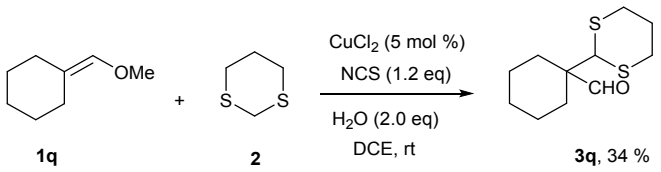
To a flame-dried 100 mL flask were sequentially added 1,3-dithiane (1.2 g, 10 mmol) and NCS (1.6 g, 12 mmol), DCE (60 mL), after dissolved the mixture was stirred at 0 °C for 40 mins. Then 1a (2.0 g, 15 mmol) and $CuCl_2$ (67.2 mg, 0.5 mmol) were added at room temperature. Reaction mixture was stirred at rt for 12 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 brine (30 mL), and dried over anhydrous Na_2SO_4, and purified by the flash chromatography to afford the desired product in 79% yield.

5. Mechanistic Experiments



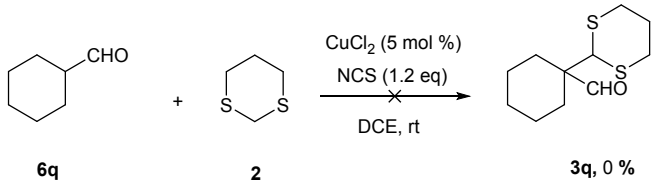
To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then ROH (R = Me, *t*-Bu;

0.6 mmol), **1a** (40 mg, 0.3 mmol) and $CuCl_2$ (1.3 mg, 0.01 mmol) were added at room temperature. Reaction mixture was stirred at rt 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 H_2O (10 mL), and dried over anhydrous Na_2SO_4, and purified by the flash chromatography to afford **4a** product (R = Me, 74% yield; R = *t*-Bu, 65% yield).



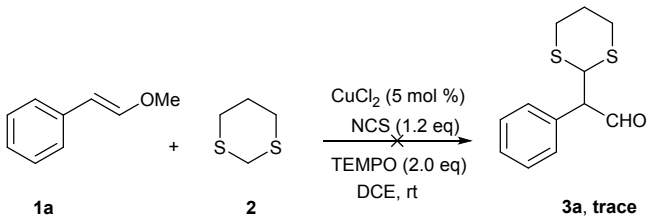
1q **2** **3q**, 34 %

To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then H_2O (7.2 μL, 0.4 mmol), **1q** (38 mg, 0.3 mmol) and $CuCl_2$ (1.3 mg, 0.01 mmol) were added at room temperature. Reaction mixture was stirred at rt 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 H_2O (10 mL), and dried over anhydrous Na_2SO_4, and purified by the flash chromatography to afford **3q** product in 34% yield.

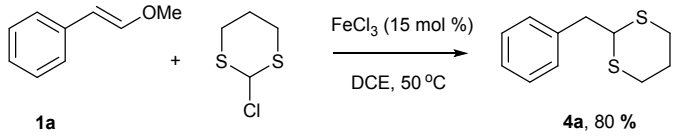


6q **2** **3q**, 0 %

To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then **6q** (34 mg, 0.3 mmol) and $CuCl_2$ (1.3 mg, 0.01 mmol) were added at room temperature. Reaction mixture was stirred at rt 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 H_2O (10 mL), and dried over anhydrous Na_2SO_4.

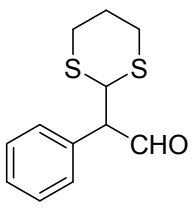


To a flame-dried 10 mL flask 1,3-dithiane **2** (24 mg, 0.2 mmol) and NCS (32 mg, 0.24 mmol), DCE (2 mL), after dissolved the mixture was stirred at 0 °C for 40 min. Then TEMPO (62 mg, 0.4 mmol), **1a** (40 mg, 0.3 mmol) and $CuCl_2$ (1.3 mg, 0.01 mmol) were added at room temperature. Reaction mixture was stirred at rt 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 H_2O (10 mL), and dried over anhydrous Na_2SO_4.



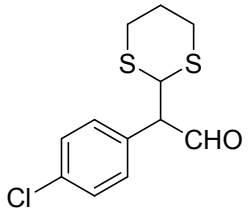
To a flame-dried 10 mL flask 2-chloro-1,3-dithiane (31 mg, 0.2 mmol), **1a** (40 mg, 0.3 mmol) and $FeCl_3$ (4.9 mg, 0.03 mmol) were added at reaction temperature in solvent (2 mL). Reaction mixture was stirred at 50 °C for 8 h until the reaction was complete (as determined by TLC analysis). Reaction mixture was diluted with ethyl acetate (10 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 brine (10 mL), and dried over anhydrous Na_2SO_4, and purified by the flash chromatography to afford the desired product in 80% yield.

6. Characterization of synthesized compounds



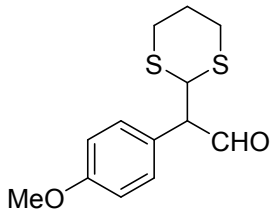
3a

2-(1,3-Dithian-2-yl)-2-phenylacetaldehyde (3a): Yellow solid; R_f = 0.25 (EA/PE = 1:10); mp (°C) 125-126; isolated yield 90% (43 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.7 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.31 – 7.23 (m, 2H), 4.69 (d, *J* = 9.6 Hz, 1H), 3.91 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.94 – 2.77 (m, 4H), 2.19 – 1.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 132.7, 129.2, 128.8, 128.3, 62.3, 45.7, 29.4, 29.3, 25.1; IR (neat, cm^{-1}) 3055 (w), 2927 (m), 2853 (w), 1673 (s), 1598 (w), 1579 (w), 1558 (m), 1443 (m), 1421 (m), 1355 (w), 1265 (s), 1195 (w), 1027 (w), 895 (w), 871 (w), 736 (m), 704 (w); HRMS (ESI): *m/z*: calcd for $C_{12}H_{15}OS_2$ $[M+H]^+$: 239.0564, found: 239.0565.



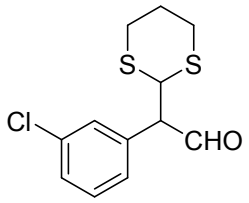
3b

2-(4-Chlorophenyl)-2-(1,3-dithian-2-yl)acetaldehyde (3b): Yellow oil; R_f = 0.21 (EA/PE = 1:10); isolated yield 87% (47 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (d, *J* = 2.7 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.67 (d, *J* = 8.4 Hz, 1H), 3.89 (dd, *J* = 9.3, 2.4 Hz, 1H), 2.96 – 2.79 (m, 4H), 2.14 – 1.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 134.5, 131.2, 130.7, 129.2, 61.6, 46.0, 29.7, 29.6, 25.2; IR (neat, cm^{-1}) 3054 (w), 2928 (m), 2720 (w), 1722 (m), 1678 (s), 1572 (w), 1552 (w), 1489 (s), 1421 (w), 1357 (w), 1264 (w), 1197 (w), 1093 (m), 1014 (m), 909 (w), 872 (m), 838 (m), 759 (w), 737 (m), 569 (w); HRMS (ESI): *m/z*: calcd for $C_{12}H_{14}ClOS_2$ $[M+H]^+$: 273.0175, found: 273.0179.



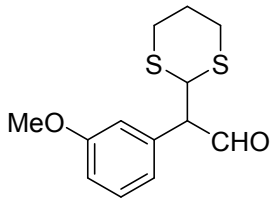
3c

2-(1,3-Dithian-2-yl)-2-(4-methoxyphenyl)acetaldehyde (3c): Green solid; R_f = 0.16 (EA/PE = 1:10); mp (°C) 127-128; isolated yield 89% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.7 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.67 (d, *J* = 9.6 Hz, 1H), 3.85 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.79 (s, 3H), 2.92 – 2.79 (m, 4H), 2.11 – 1.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 159.5, 130.4, 124.4, 114.3, 61.6, 55.1, 46.0, 29.6, 29.5, 25.2; IR (neat, cm^{-1}) 3035 (w), 3001 (w), 2934 (m), 2904 (s), 2835 (m), 2720 (w), 1717 (s), 1669 (m), 1582 (w), 1510 (s), 1422 (m), 1304 (m), 1180 (m), 1030 (m), 907 (w), 830 (m), 735 (m), 656 (w), 607 (w), 543 (m); HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}O_2S_2$ $[M+H]^+$: 269.0670, found: 269.0673.



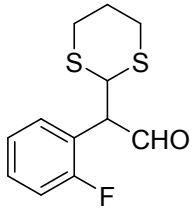
3d

2-(3-Chlorophenyl)-2-(1,3-dithian-2-yl)acetaldehyde (3d): Yellow oil; R_f = 0.19 (EA/PE = 1:10); isolated yield 84% (46 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (d, *J* = 2.7 Hz, 1H), 7.35 – 7.24 (m, 3H), 7.18 – 7.10 (m, 1H), 4.64 (d, *J* = 9.6 Hz, 1H), 3.88 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.93 – 2.78 (m, 4H), 2.11 – 1.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 134.8, 134.7, 130.1, 129.3, 128.6, 127.5, 61.8, 45.7, 29.5, 29.3, 25.1; IR (neat, cm^{-1}) 3056 (w), 2904 (m), 2828 (m), 2721 (w), 1723 (m), 1668 (s), 1594 (m), 1421 (m), 1298 (w), 1264 (m), 1196 (w), 1082 (w), 999 (w), 876 (m), 792 (m), 735 (s), 692 (m), 480 (w); HRMS (ESI): *m/z*: calcd for $C_{12}H_{14}ClOS_2$ $[M+H]^+$: 273.0175, found: 273.0180.



3e

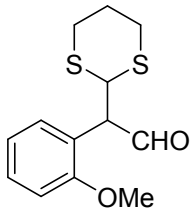
2-(1,3-Dithian-2-yl)-2-(3-methoxyphenyl)acetaldehyde (3e): Yellow oil; R_f = 0.15 (EA/PE = 1:10); isolated yield 87% (47 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (d, *J* = 2.4 Hz, 1H), 7.35 – 7.27 (m, 1H), 6.90 – 6.78 (m, 3H), 4.68 (d, *J* = 9.9 Hz, 1H), 3.87 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.80 (s, 3H), 2.93 – 2.77 (m, 4H), 2.11 – 1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 159.8, 134.1, 129.9, 121.4, 115.1, 113.6, 62.3, 55.2, 45.7, 29.5, 29.3, 25.2; IR (neat, cm^{-1}) 3052 (w), 3001 (w), 2935 (s), 2834 (m), 1721 (m), 1672 (s), 1487 (m), 1429 (m), 1317 (w), 1257 (m), 1167 (m), 1099 (w), 995 (w), 908 (w), 858 (m), 783 (w), 736 (m), 698 (w); HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}O_2S_2$ $[M+H]^+$: 269.0670, found: 269.0674.



3f

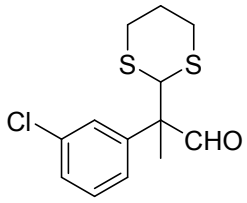
2-(1,3-Dithian-2-yl)-2-(2-fluorophenyl)acetaldehyde (3f): Yellow oil; R_f = 0.22 (EA/PE = 1:10); isolated yield 85% (44 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.29 – 7.22 (m, 1H), 7.20 – 7.07 (m, 2H), 4.70

(d, J = 9.9 Hz, 1H), 4.21 (dd, J = 9.9, 2.4 Hz, 1H), 2.95 – 2.73 (m, 4H), 2.13 – 1.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 130.9, 130.2, 130.1, 124.5, 116.0, 115.7, 56.1, 44.7, 28.9, 28.7, 25.2; IR (neat, cm^{-1}) 3055 (w), 2916 (m), 2829 (w), 1723 (m), 1673 (s), 1568 (m), 1487 (m), 1450 (m), 1354 (w), 1265 (m), 1225 (m), 1187 (w), 1082 (m), 910 (w), 872 (m), 825 (m), 757 (m), 736 (s), 702 (m), 680 (w); HRMS (ESI): *m/z*: calcd for $C_{12}H_{14}FOS_2$ $[M+H]^+$: 257.0470, found: 257.0472.



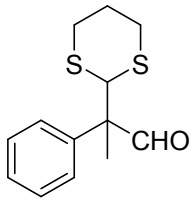
3g

2-(1,3-Dithian-2-yl)-2-(2-methoxyphenyl)acetaldehyde (3g): Yellow oil; R_f = 0.18 (EA/PE = 1:10); isolated yield 88% (47 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (d, J = 2.1 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.17 (dd, J = 7.5, 1.8 Hz, 1H), 6.98 – 6.88 (m, 2H), 4.80 (d, J = 9.9 Hz, 1H), 4.12 (dd, J = 9.9, 2.1 Hz, 1H), 3.82 (s, 3H), 2.91 – 2.76 (m, 4H), 2.10 – 1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 157.1, 130.9, 129.5, 122.6, 120.6, 110.9, 57.2, 55.4, 44.6, 29.0, 28.8, 25.2; IR (neat, cm^{-1}) 3049 (w), 3004 (w), 2936 (s), 2902 (m), 2836 (m), 2724 (w), 1721 (s), 1672 (m), 1598 (m), 1422 (w), 1333 (w), 1247 (m), 1026 (m), 938 (w), 908 (m), 870 (w), 752 (m), 702 (w), 508 (w); HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}O_2S_2$ $[M+H]^+$: 269.0670, found: 269.0675.



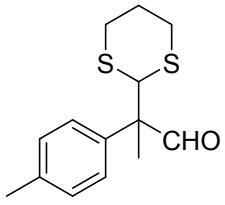
3h

2-(3-Chlorophenyl)-2-(1,3-dithian-2-yl)propanal (3h): Colorless oil; R_f = 0.24 (EA/PE = 1:10); isolated yield 81% (46 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.50 – 7.11 (m, 4H), 4.82 (s, 1H), 3.10 – 2.70 (m, 4H), 2.17 – 1.76 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 139.2, 134.8, 129.9, 128.1, 127.7, 125.6, 57.3, 54.4, 31.3, 25.5, 16.0; IR (neat, cm^{-1}) 3075 (w), 2983 (w), 2937 (w), 2902 (m), 2828 (w), 1729 (s), 1593 (m), 1570 (m), 1479 (m), 1421 (m), 1266 (m), 1196 (w), 1100 (w), 998 (w), 933 (w), 907 (m), 788 (m), 737 (s), 691 (m), 668 (w), 441 (w); HRMS (ESI): *m/z*: calcd for $C_{13}H_{16}ClOS_2$ $[M+H]^+$: 287.0331, found: 287.0333.



3i

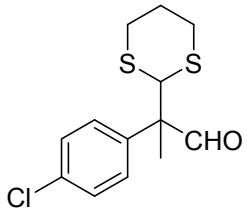
2-(1,3-Dithian-2-yl)-2-phenylpropanal (3i):[1] White solid; R_f = 0.28 (EA/PE = 1:10); mp (°C) 107-108; isolated yield 95% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.47 – 7.24 (m, 5H), 4.87 (s, 1H), 3.05 – 2.75 (m, 4H), 2.15 – 1.77 (m, 2H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 136.9, 128.7, 127.9, 127.3, 57.4, 54.5, 31.3, 31.2, 25.6, 15.8; IR (neat, cm^{-1}) 3067 (w), 2979 (m), 2951 (m), 2885 (s), 2825 (m), 2723 (w), 1727 (s), 1493 (m), 1443 (m), 1391 (w), 1279 (m), 1246 (w), 935 (m), 904 (m), 879 (m), 781 (w), 698 (m); HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}OS_2$ $[M+H]^+$: 253.0721, found: 253.0726.



3j

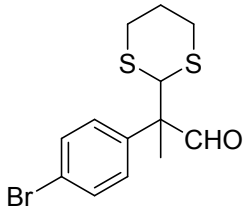
2-(1,3-Dithian-2-yl)-2-(p-tolyl)propanal (3j): White solid; R_f = 0.27 (EA/PE = 1:10); mp (°C) 88-89; isolated yield 90% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.49 – 7.33 (m, 4H), 5.01 (s, 1H), 3.28 – 2.83 (m, 4H), 2.49 (s, 3H), 2.33 – 1.87 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 137.6, 133.7, 129.4, 127.1, 57.0, 54.5, 31.2, 31.2, 25.5, 20.9, 15.6; IR (neat, cm^{-1}) 3025 (w), 2981 (m), 2900 (m), 2826 (m), 2715 (w), 1723 (s), 1670 (w), 1512 (m), 1421 (m), 1372 (m), 1276 (m), 1186 (w), 1068 (w), 906 (m), 812 (m), 779 (w), 701 (w), 634 (w), 544 (w), 514 (m); HRMS (ESI): *m/z*: calcd for $C_{14}H_{19}OS_2$ $[M+H]^+$: 267.0877,

found: 267.0872.



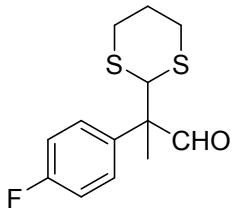
3k

2-(4-Chlorophenyl)-2-(1,3-dithian-2-yl)propanal (3k): White solid; R_f = 0.28 (EA/PE = 1:10); mp (°C) 112-113; isolated yield 87% (50 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.49 – 7.19 (m, 4H), 4.82 (s, 1H), 3.08 – 2.71 (m, 4H), 2.22 – 1.73 (m, 2H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 135.5, 133.9, 128.8, 128.7, 57.0, 54.3, 31.2, 25.4, 16.0; IR (neat, cm^{-1}) 3020 (w), 2935 (w), 2900 (w), 2825 (w), 1726 (s), 1669 (w), 1493 (m), 1421 (w), 1276 (w), 1097 (m), 1011 (m), 928 (w), 906 (w), 822 (w), 723 (w), 517 (w); HRMS (ESI): *m/z*: calcd for $C_{13}H_{16}ClOS_2$ $[M+H]^+$: 287.0331, found: 287.0334.



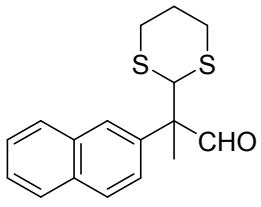
3l

2-(4-Bromophenyl)-2-(1,3-dithian-2-yl)propanal (3l): White solid; R_f = 0.25 (EA/PE = 1:10); mp (°C) 116-117; isolated yield 85% (56 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 4.81 (s, 1H), 3.21 – 2.73 (m, 4H), 2.17 – 1.76 (m, 2H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 136.0, 131.8, 129.1, 122.3, 57.1, 54.4, 31.2, 25.5, 16.1; IR (neat, cm^{-1}) 3014 (w), 2987 (w), 2948 (w), 2902 (s), 2817 (m), 2710 (w), 1724 (s), 1491 (m), 1458 (w), 1399 (m), 1277 (m), 1083 (m), 1008 (m), 904 (m), 814 (m), 703 (w), 654 (m), 522 (m); HRMS (ESI): *m/z*: calcd for $C_{13}H_{16}BrOS_2$ $[M+H]^+$: 330.9826, found: 330.9831.



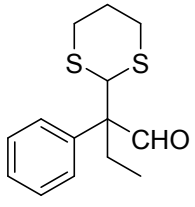
3m

2-(1,3-Dithian-2-yl)-2-(4-fluorophenyl)propanal (3m): White solid; R_f = 0.26 (EA/PE = 1:10); mp (°C) 89-90; isolated yield 84% (45 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.58 – 7.19 (m, 2H), 7.19 – 7.02 (m, 2H), 4.82 (s, 1H), 3.03 – 2.75 (m, 4H), 2.14 – 1.79 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 163.8, 160.5, 132.7, 129.2, 115.8, 115.5, 56.9, 54.5, 31.2, 31.2, 25.5, 16.2; IR (neat, cm^{-1}) 3071 (w), 2980 (w), 2896 (m), 2833 (w), 1725 (s), 1598 (m), 1509 (s), 1455 (w), 1410 (m), 1373 (w), 1277 (m), 1200 (m), 1167 (m), 946 (w), 832 (m), 778 (w), 737 (m), 703 (w), 532 (m); HRMS (ESI): *m/z*: calcd for $C_{13}H_{16}FOS_2$ $[M+H]^+$: 271.0627, found: 271.0630.



3n

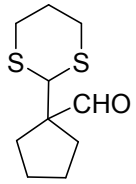
2-(1,3-Dithian-2-yl)-2-(naphthalen-2-yl)propanal (3n): White solid; R_f = 0.24 (EA/PE = 1:10); mp (°C) 138-139; isolated yield 91% (55 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.92 – 7.75 (m, 4H), 7.55 – 7.43 (m, 3H), 4.99 (s, 1H), 3.11 – 2.76 (m, 4H), 2.23 – 1.84 (m, 2H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 134.4, 133.1, 132.6, 128.5, 128.2, 127.5, 127.1, 126.6, 126.4, 124.6, 57.6, 54.5, 31.3, 25.6, 16.2; IR (neat, cm^{-1}) 3056 (w), 2982 (w), 2935 (w), 2899 (w), 2825 (w), 1725 (s), 1597 (w), 1506 (w), 1421 (w), 1276 (m), 1183 (w), 947 (w), 908 (w), 748 (m), 658 (w), 477 (m); HRMS (ESI): *m/z*: calcd for $C_{17}H_{19}OS_2$ $[M+H]^+$: 303.0877, found: 303.0880.



3o

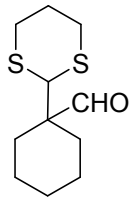
2-(1,3-Dithian-2-yl)-2-phenylbutanal (3o): Colorless oil; R_f = 0.38 (EA/PE = 1:10); isolated yield 84% (45 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.62 – 6.92 (m, 5H), 4.70 (s, 1H), 3.20 – 2.63 (m, 4H), 2.31 – 2.04 (m, 2H), 2.02 – 1.52

(m, 2H), 0.83 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 135.7, 128.7, 128.3, 127.8, 61.1, 52.5, 31.3, 31.1, 26.0, 25.5, 8.4; IR (neat, cm^{-1}) 3057 (w), 3025 (w), 2968 (m), 2935 (s), 2829 (m), 1724 (s), 1668 (m), 1495 (m), 1421 (m), 1276 (m), 1181 (w), 1002 (w), 909 (m), 758 (m), 700 (s), 555 (m); HRMS (ESI): *m/z*: calcd for $C_{14}H_{19}OS_2$ $[M+H]^+$: 267.0877, found: 267.0875.



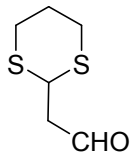
3p

1-(1,3-Dithian-2-yl)cyclopentane-1-carbaldehyde (3p): Yellow oil; R_f = 0.32 (EA/PE = 1:10); isolated yield 83% (36 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 4.44 (s, 1H), 2.99 – 2.83 (m, 4H), 2.22 – 2.00 (m, 2H), 1.97 – 1.77 (m, 4H), 1.69 – 1.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 61.4, 54.4, 31.1, 30.4, 25.8, 25.7; IR (neat, cm^{-1}) 2952 (s), 2902 (m), 2868 (m), 2827 (w), 2726 (w), 1722 (s), 1449 (m), 1422 (m), 1390 (w), 1276 (m), 1183 (w), 1001 (w), 909 (m), 882 (w), 866 (w), 778 (m); HRMS (ESI): *m/z*: calcd for $C_{10}H_{17}OS_2$ $[M+H]^+$: 217.0721, found: 217.0724.



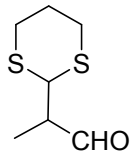
3q

1-(1,3-Dithian-2-yl)cyclohexane-1-carbaldehyde (3q):[2] Colorless oil; R_f = 0.45 (EA/PE = 1:10); isolated yield 86% (40 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 4.26 (s, 1H), 3.11 – 2.69 (m, 4H), 2.17 – 2.00 (m, 2H), 1.95 – 1.49 (m, 6H), 1.46 – 1.05 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.5, 55.3, 53.1, 31.4, 29.0, 25.9, 25.2, 22.3; IR (neat, cm^{-1}) 3053 (w), 2936 (s), 2857 (m), 2711 (w), 1724 (s), 1671 (w), 1451 (m), 1423 (m), 1348 (w), 1265 (s), 1192 (w), 963 (w), 907 (m), 832 (w), 737 (s), 704 (m), 660 (w); HRMS (ESI): *m/z*: calcd for $C_{11}H_{19}OS_2$ $[M+H]^+$: 231.0877, found: 231.0872.



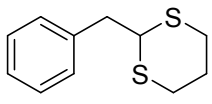
3r

2-(1,3-Dithian-2-yl)acetaldehyde (3r):[3] Yellow oil; R_f = 0.21 (EA/PE = 1:10); isolated yield 93% (30 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.8 Hz, 1H), 4.52 (t, J = 6.9 Hz, 1H), 3.02 – 2.92 (m, 2H), 2.90 – 2.80 (m, 4H), 2.21 – 1.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 48.1, 40.0, 29.9, 24.9; IR (neat, cm^{-1}) 2900 (m), 2828 (m), 2731 (w), 1722 (s), 1422 (m), 1336 (w), 1277 (w), 1244 (w), 1175 (w), 1029 (w), 908 (m), 772 (w), 659 (w), 534 (w); HRMS (ESI): *m/z*: calcd for $C_6H_{11}OS_2$ $[M+H]^+$: 163.0251, found: 163.0254.



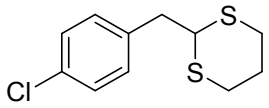
3s

2-(1,3-Dithian-2-yl)propanal (3s):[4] Colorless oil; R_f = 0.34 (EA/PE = 1:10); isolated yield 85% (30 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (d, J = 1.8 Hz, 1H), 4.41 (d, J = 5.7 Hz, 1H), 3.05 – 2.80 (m, 4H), 2.79 – 2.66 (m, 1H), 2.24 – 1.77 (m, 2H), 1.27 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 50.2, 48.0, 30.1, 30.0, 25.3, 11.3; IR (neat, cm^{-1}) 3052 (w), 2935 (m), 2904 (m), 2830 (m), 2727 (w), 1724 (s), 1670 (w), 1423 (m), 1375 (w), 1266 (w), 1185 (w), 946 (w), 908 (m), 736 (s), 703 (m), 658 (w); HRMS (ESI): *m/z*: calcd for $C_7H_{13}OS_2$ $[M+H]^+$: 177.0408, found: 177.0405.



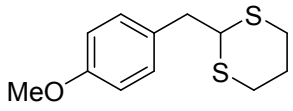
4a

2-Benzyl-1,3-dithiane (4a):[5] Yellow oil; R_f = 0.53 (EA/PE = 1:10); isolated yield 89% (37 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 4.24 (t, J = 7.5 Hz, 1H), 3.02 (d, J = 7.5 Hz, 2H), 2.91 – 2.72 (m, 4H), 2.18 – 1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 129.1, 128.3, 126.9, 48.6, 41.7, 30.5, 25.7; IR (neat, cm^{-1}) 3061 (w), 3027 (w), 2932 (m), 2899 (s), 2847 (w), 2826 (w), 1603 (w), 1496 (m), 1453 (m), 1421 (m), 1275 (m), 1242 (w), 1075 (w), 1029 (w), 941 (w), 907 (m), 740 (m), 698 (s), 663 (w), 510 (w); HRMS (ESI): *m/z*: calcd for $C_{11}H_{15}S_2$ $[M+H]^+$: 211.0615, found: 211.0611.



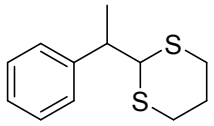
4b

2-(4-Chlorobenzyl)-1,3-dithiane (4b):[6] Yellow solid; R_f = 0.48 (EA/PE = 1:10); mp (°C) 65-66; isolated yield 86% (42 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 1H), 2.99 (d, *J* = 7.2 Hz, 2H), 2.90 – 2.77 (m, 4H), 2.14 – 1.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 130.5, 128.5, 48.4, 41.0, 30.5, 25.6; IR (neat, cm^{-1}) 3077 (w), 2933 (m), 2899 (s), 2852 (w), 2827 (w), 1491 (s), 1422 (m), 1241 (w), 1177 (w), 1092 (m), 1015 (m), 907 (m), 867 (w), 803 (w), 765 (w), 519 (m); HRMS (ESI): *m/z*: calcd for $C_{11}H_{14}ClS_2$ $[M+H]^+$: 245.0225, found: 245.0222.



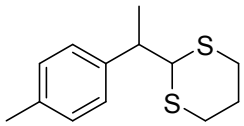
4c

2-(4-Methoxybenzyl)-1,3-dithiane (4c):[7] White solid; R_f = 0.43 (EA/PE = 1:10); mp (°C) 71-72; isolated yield 87% (42 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 2.96 (d, *J* = 7.2 Hz, 2H), 2.88 – 2.75 (m, 4H), 2.16 – 1.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 130.1, 129.2, 113.6, 55.1, 48.9, 40.8, 30.5, 25.7; IR (neat, cm^{-1}) 3030 (w), 2996 (w), 2931 (m), 2901 (m), 2932 (w), 1611 (m), 1512 (s), 1437 (m), 1276 (s), 1246 (s), 1178 (m), 907 (w), 868 (m), 822 (m), 782 (w), 729 (w), 545 (m); HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}OS_2$ $[M+H]^+$: 241.0721, found: 241.0722.



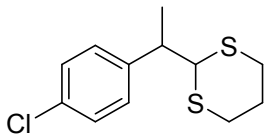
4i

2-(1-Phenylethyl)-1,3-dithiane (4i):[8] Colorless oil; R_f = 0.53 (EA/PE = 1:10); isolated yield 91% (41 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 4.24 (d, *J* = 7.5 Hz, 1H), 3.17 – 3.03 (m, 1H), 2.88 – 2.69 (m, 4H), 2.12 – 1.71 (m, 2H), 1.47 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 128.1, 127.6, 126.9, 54.8, 44.8, 30.9, 30.5, 25.7, 18.6; IR (neat, cm^{-1}) 3059 (w), 3026 (m), 2968 (m), 2896 (s), 2827 (w), 1601 (w), 1421 (m), 1276 (m), 1179 (w), 1014 (w), 905 (w), 797 (w), 754 (m), 698 (m); HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}S_2$ $[M+H]^+$: 225.0772, found: 225.0775.



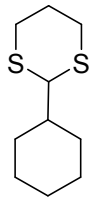
4j

2-(1-(p-tolyl)ethyl)-1,3-dithiane (4j):[9] Colorless oil; R_f = 0.57 (EA/PE = 1:10); isolated yield 90% (43 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 4H), 4.23 (d, *J* = 7.5 Hz, 1H), 3.13 – 2.99 (m, 1H), 2.86 – 2.71 (m, 4H), 2.32 (s, 3H), 2.13 – 1.70 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 136.5, 128.9, 127.4, 55.0, 44.3, 30.9, 30.5, 25.8, 21.1, 18.6; IR (neat, cm^{-1}) 3020 (m), 2968 (m), 2896 (s), 2826 (w), 1514 (m), 1421 (m), 1276 (m), 1183 (w), 1046 (w), 904 (w), 816 (m), 719 (w); HRMS (ESI): *m/z*: calcd for $C_{13}H_{19}S_2$ $[M+H]^+$: 239.0928, found: 239.0933.



4k

2-(1-(4-Chlorophenyl)ethyl)-1,3-dithiane (4k): Colorless oil; R_f = 0.49 (EA/PE = 1:10); isolated yield 87% (45 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.21 (d, *J* = 7.2 Hz, 1H), 3.18 – 3.00 (m, 1H), 2.92 – 2.73 (m, 4H), 2.09 – 1.71 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 132.7, 129.0, 128.3, 54.7, 44.2, 30.9, 30.6, 25.7, 18.6; IR (neat, cm^{-1}) 3031 (w), 2969 (m), 2931 (m), 2898 (m), 2827 (w), 1713 (w), 1492 (s), 1451 (m), 1421 (m), 1376 (w), 1275 (m), 1178 (m), 1094 (m), 1012 (m), 904 (w), 823 (m), 772 (w), 724 (w), 568 (w), 536 (m); HRMS (ESI): *m/z*: calcd for $C_{12}H_{16}ClS_2$ $[M+H]^+$: 259.0382, found: 259.0380.



4q

2-Cyclohexyl-1,3-dithiane (4q):[10] White solid; R_f = 0.59 (EA/PE = 1:10); mp (°C) 46-47; isolated yield 84% (34 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (d, *J* = 5.4 Hz, 1H), 2.99 – 2.80 (m, 4H), 2.19 – 2.04 (m, 1H), 1.95 – 1.87 (m, 2H), 1.86 – 1.56 (m, 6H), 1.23 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 43.1, 30.9, 30.4, 26.4, 26.2, 26.1; IR (neat, cm^{-1}) 2926 (s), 2851 (s), 2662 (w), 1709 (w), 1687 (w), 1448 (s), 1421 (m), 1348 (w), 1276 (m), 1183 (m), 1112 (w), 1040 (w), 964 (w), 909 (m), 870 (w), 790 (w), 760 (m), 684 (w), 606 (w); HRMS (ESI): *m/z*: calcd for $C_{10}H_{19}S_2$ $[M+H]^+$: 203.0928, found: 203.0931.

7. Refrences

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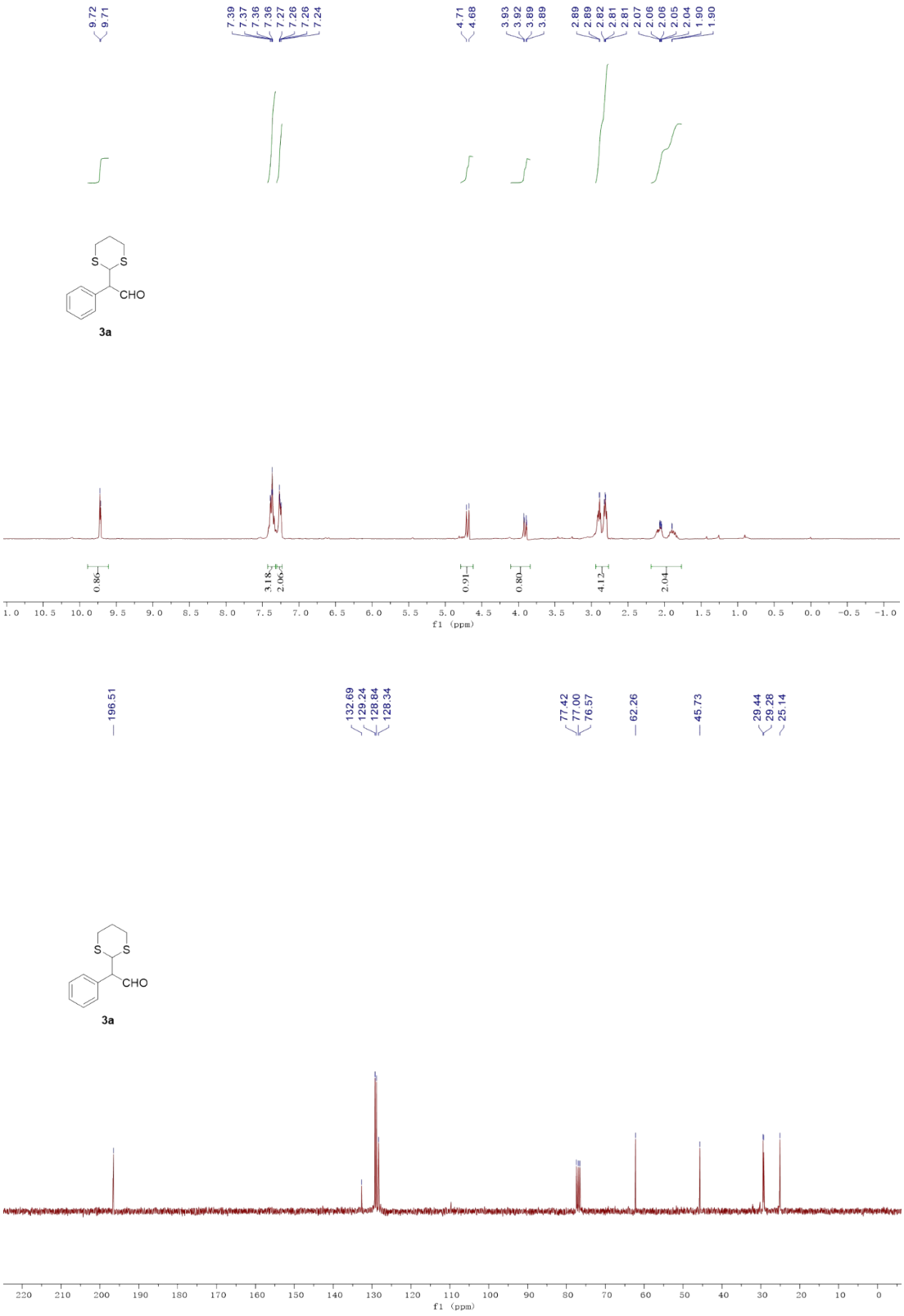
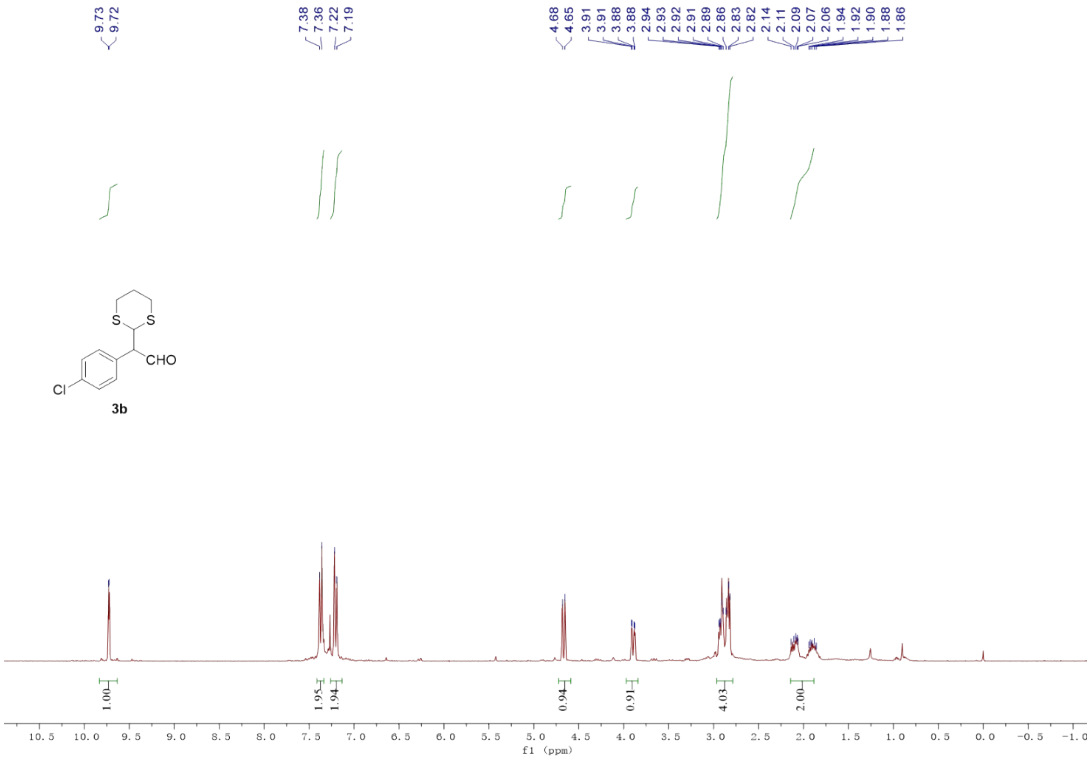
8. ^{1}H NMR and ^{13}C NMR spectra data of products

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1.94
1.92
1.90
1.88
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Cl
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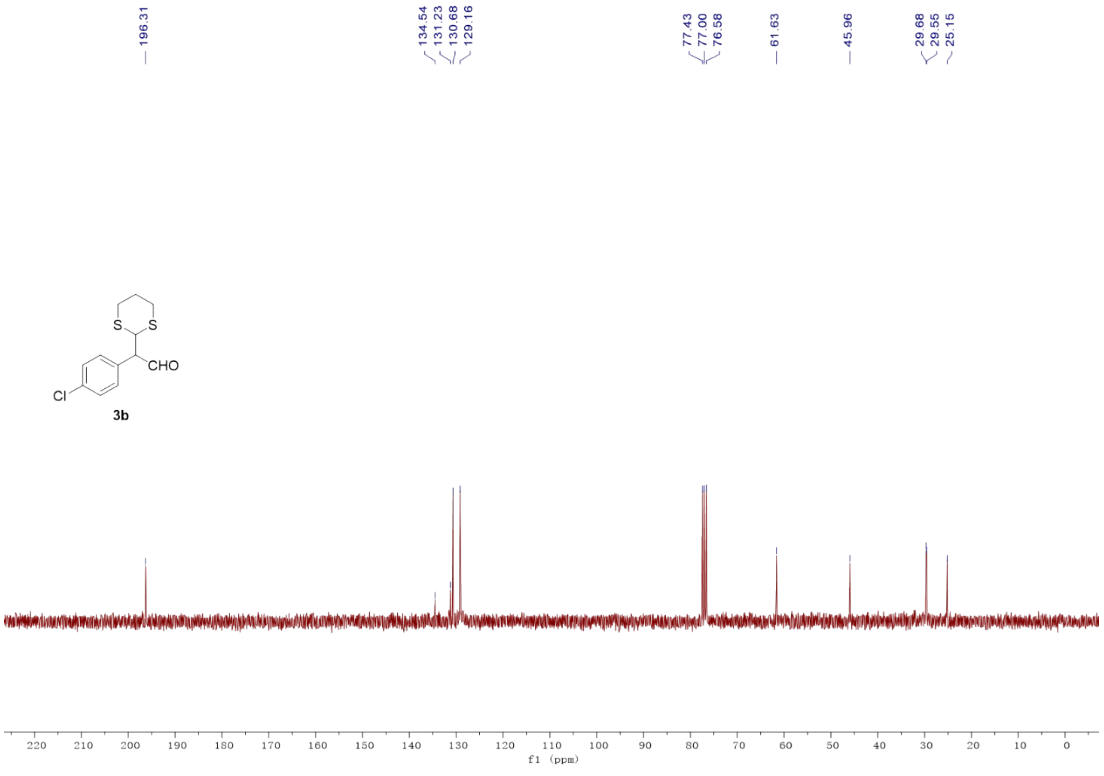
f1 (ppm)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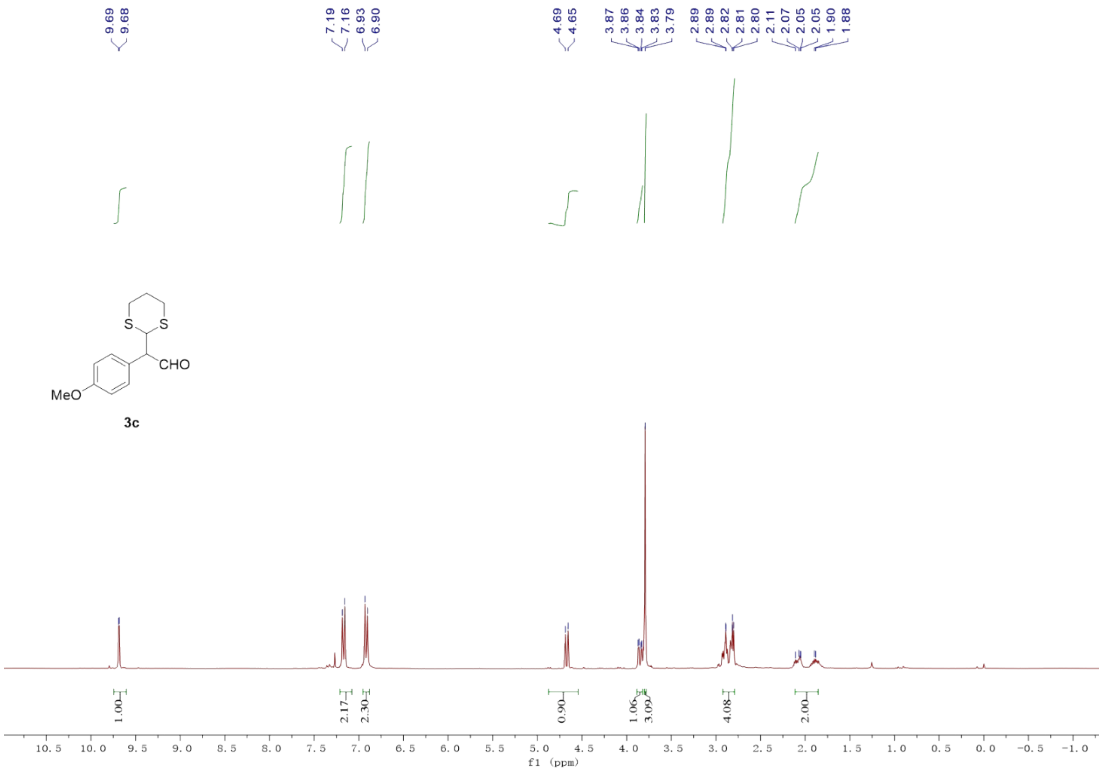
f1 (ppm)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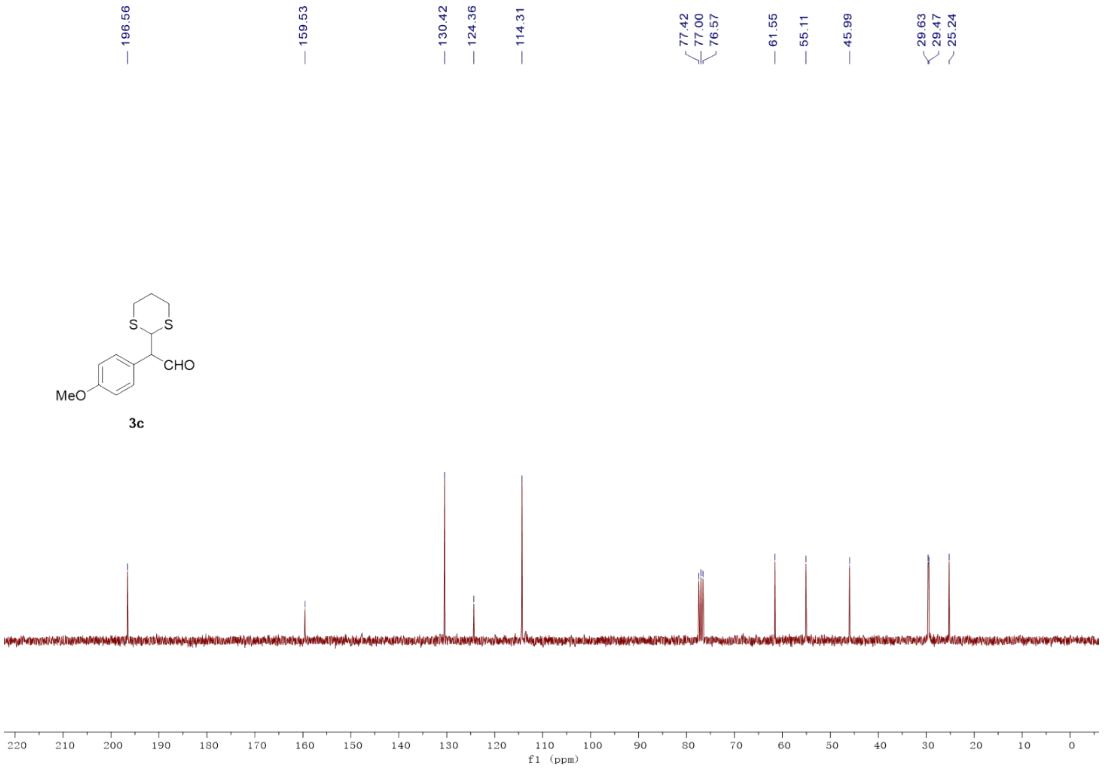
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3c
f1 (ppm)


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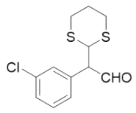
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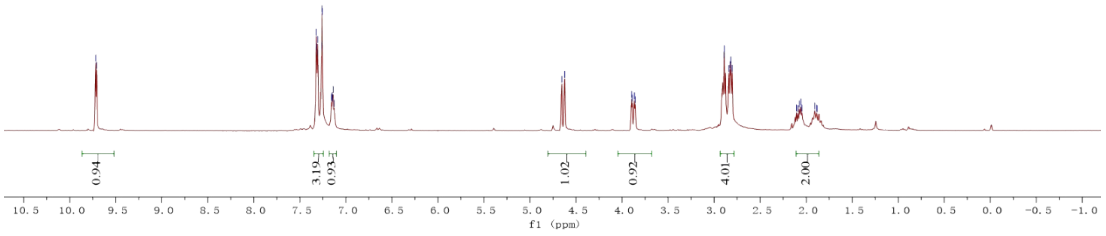
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f1 (ppm)


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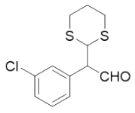
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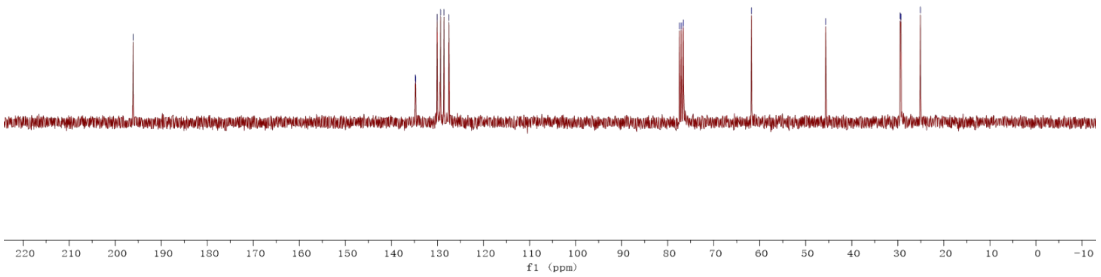
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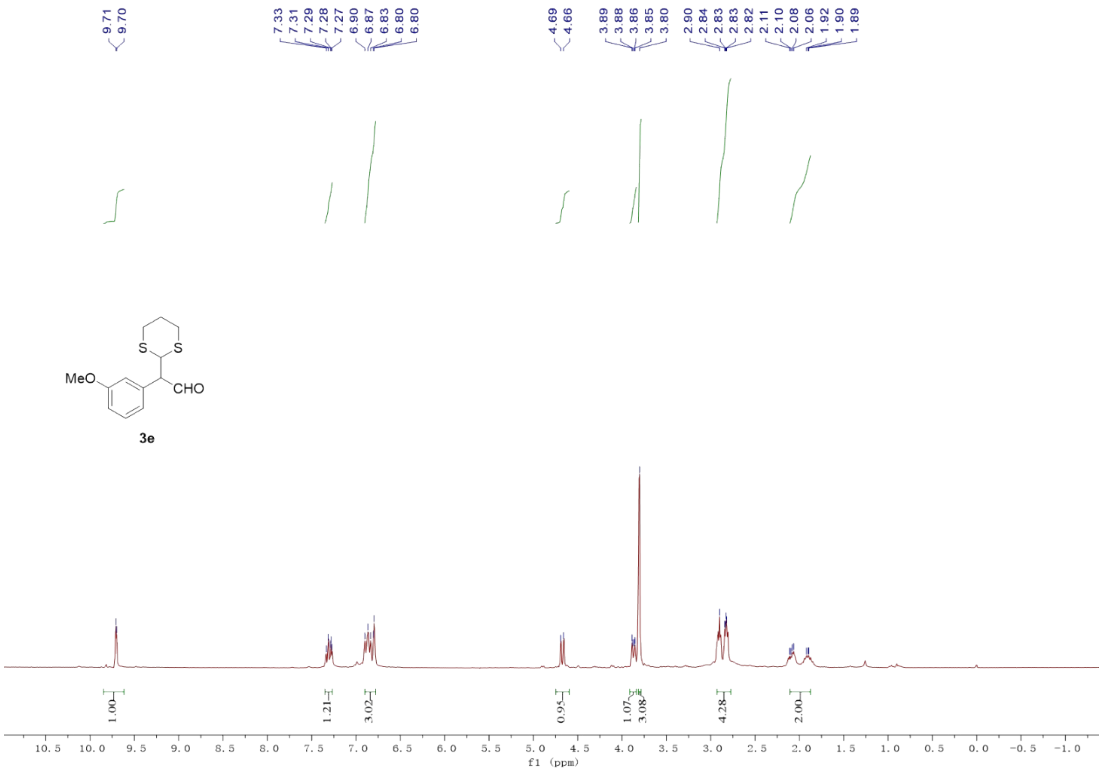
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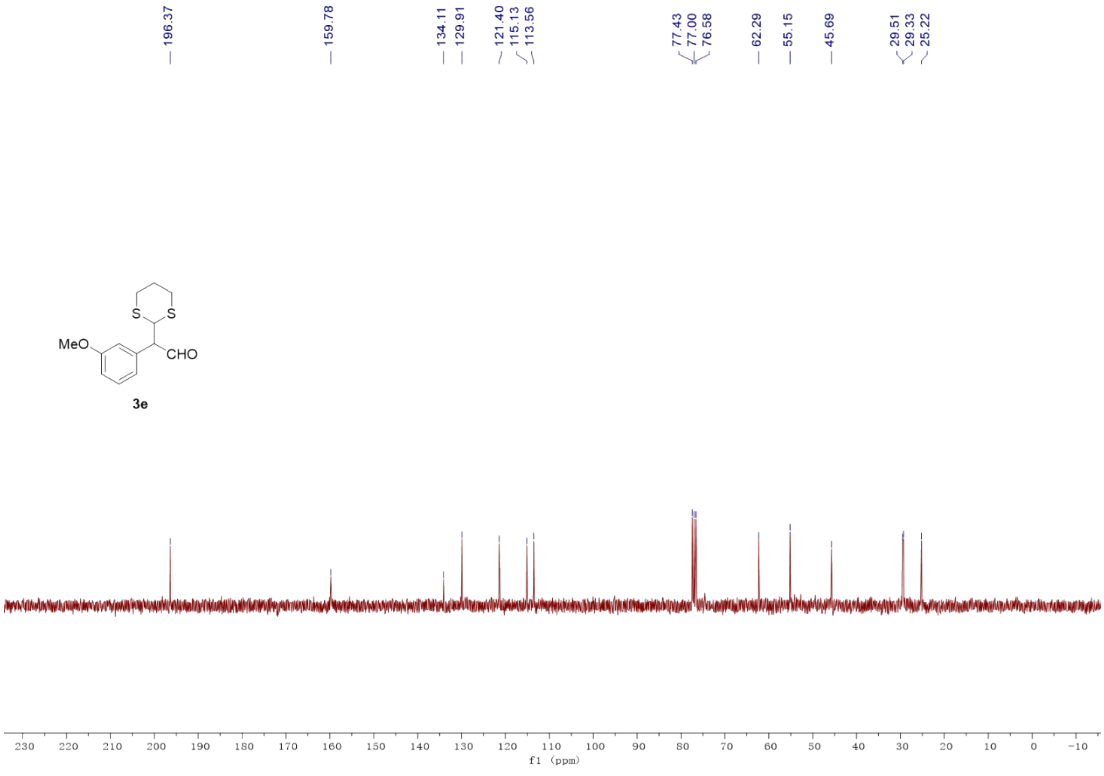
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CHO
3e
f1 (ppm)


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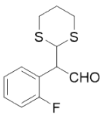
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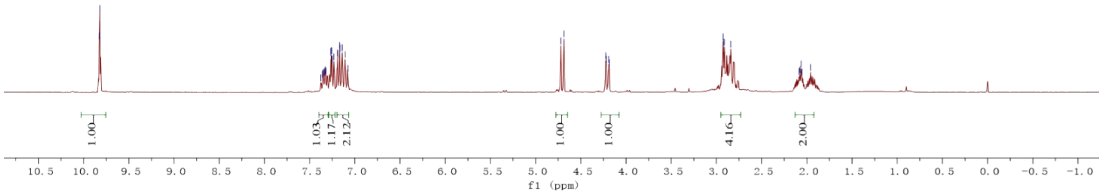
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f1 (ppm)


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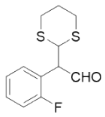
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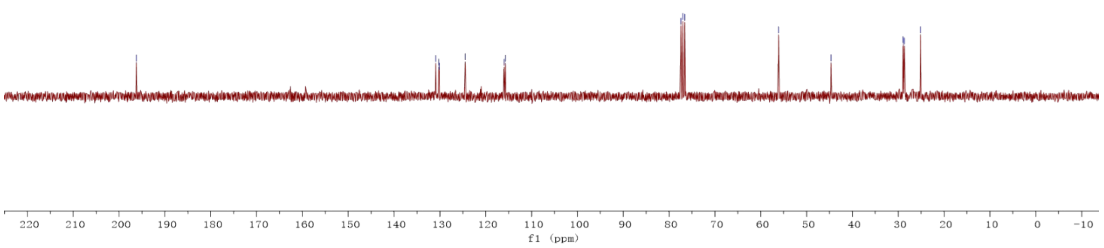
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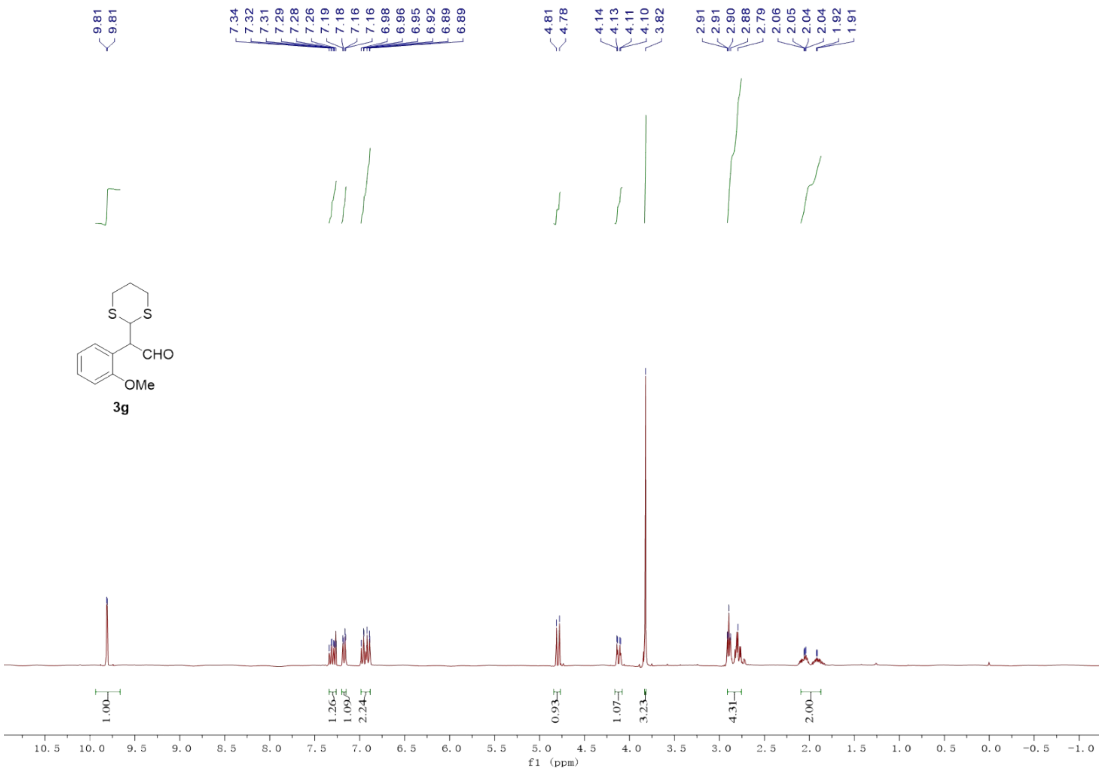
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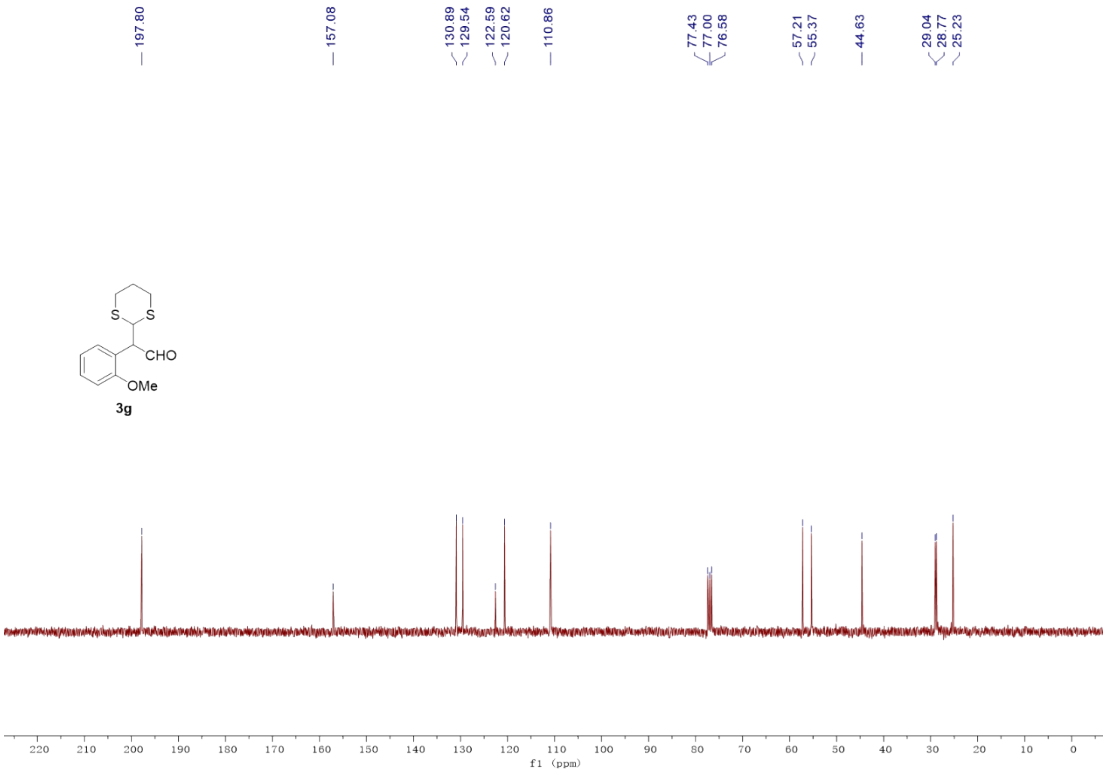
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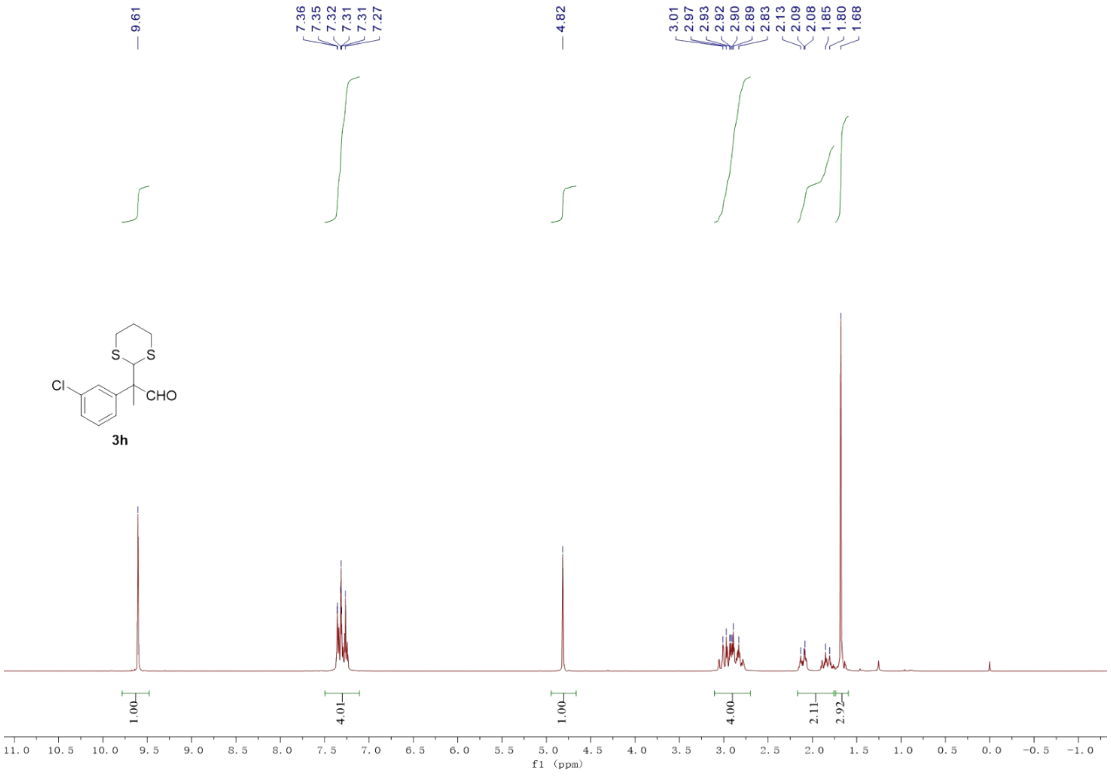
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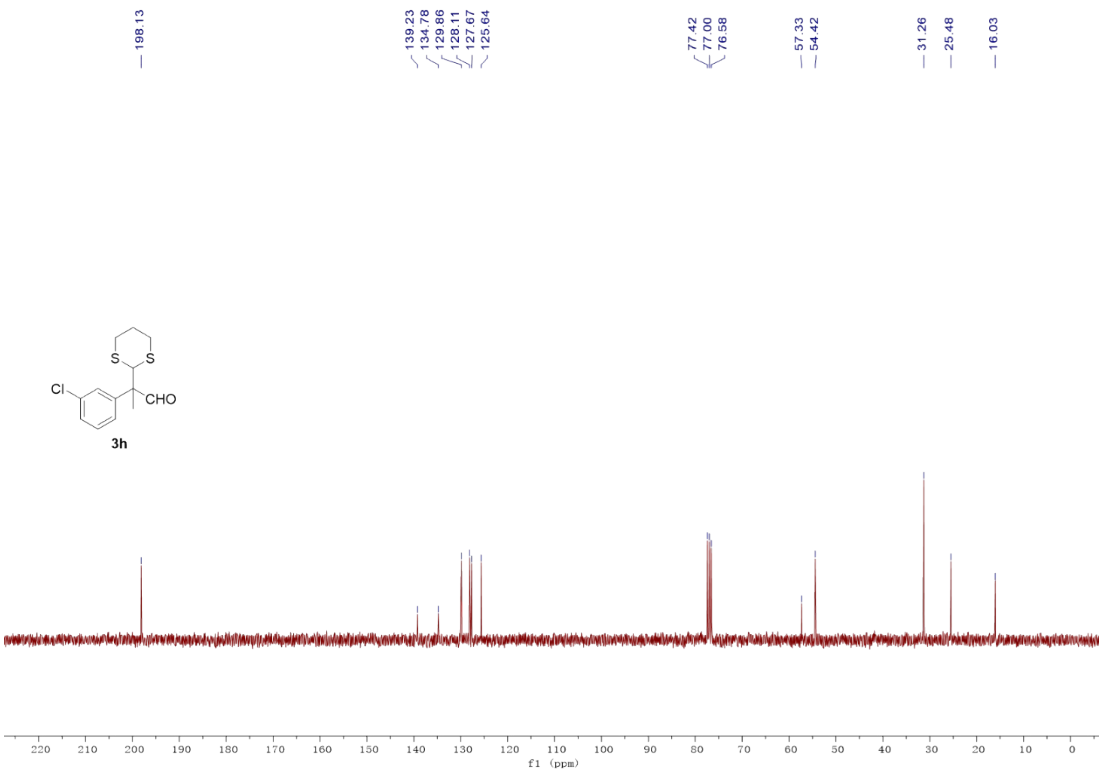
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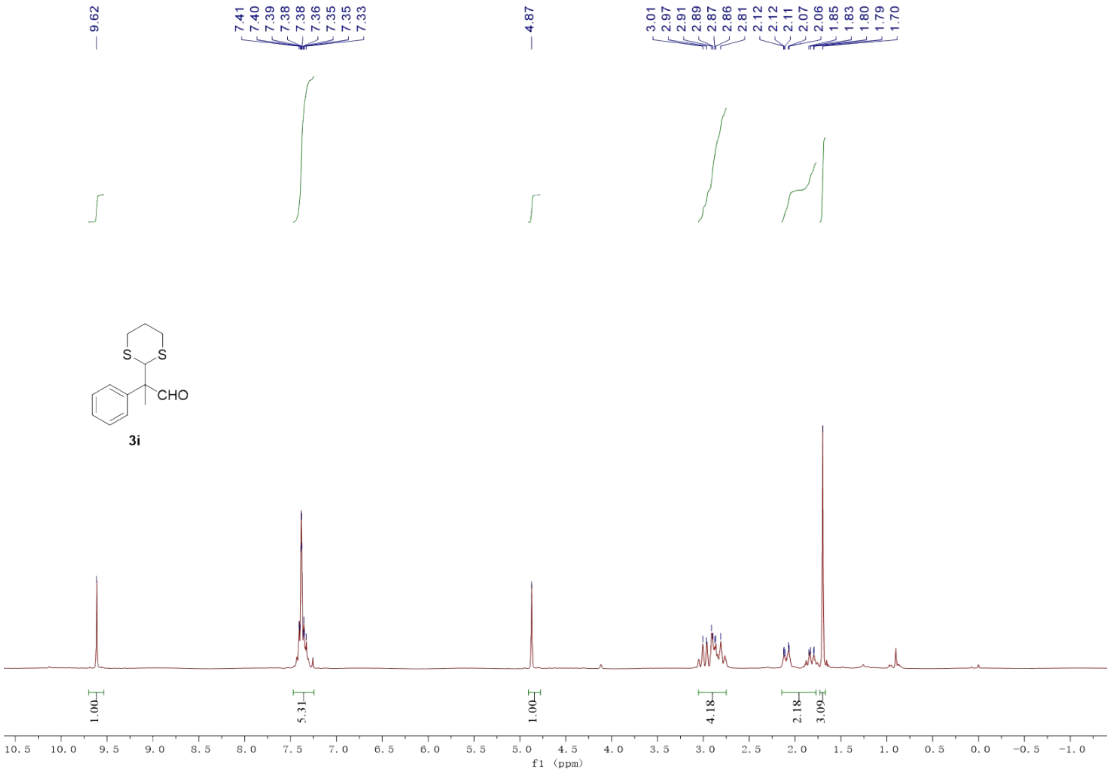
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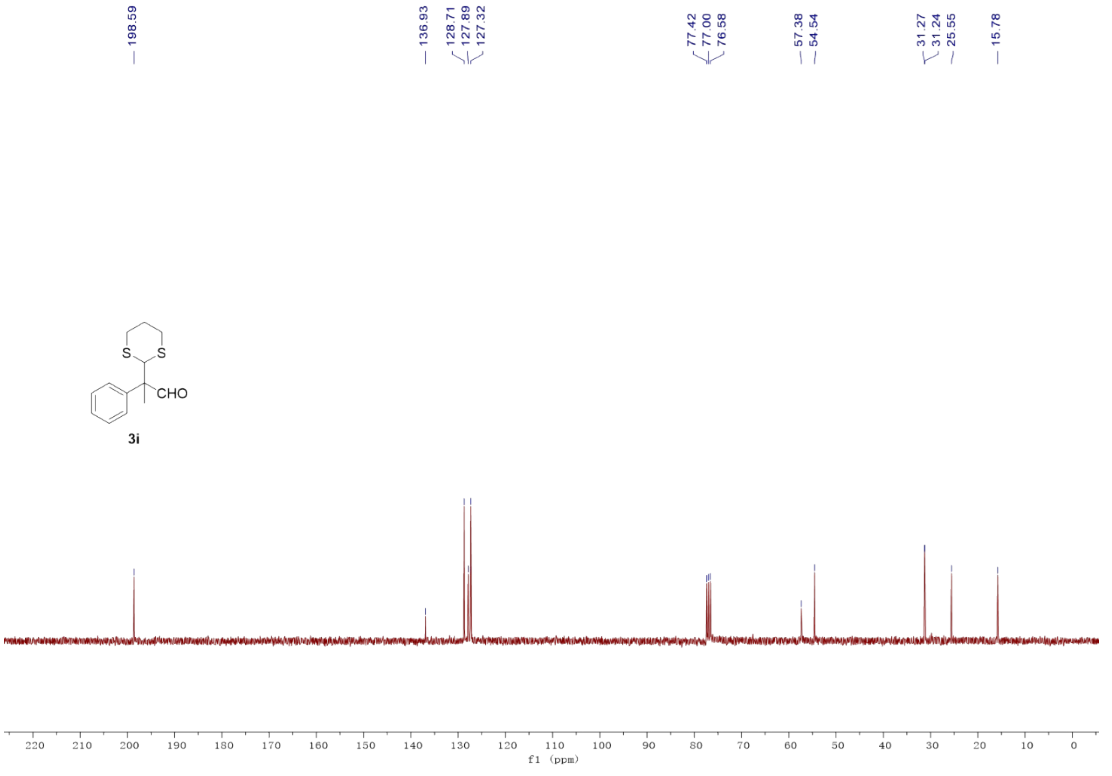
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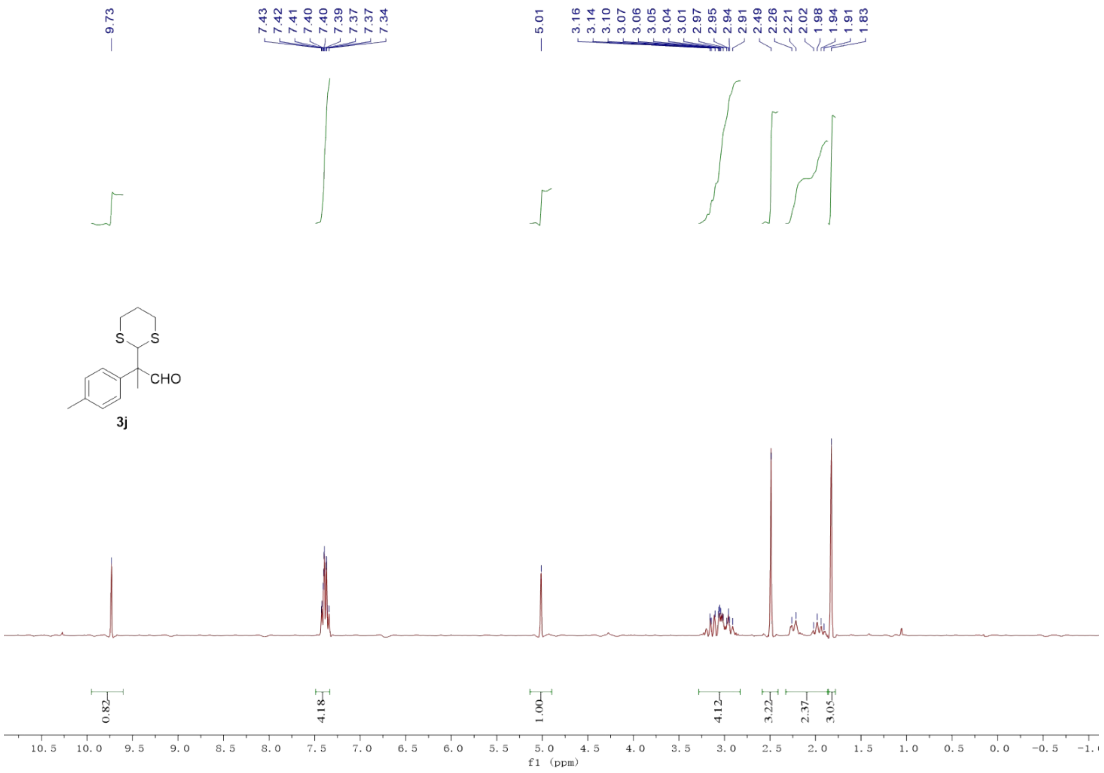
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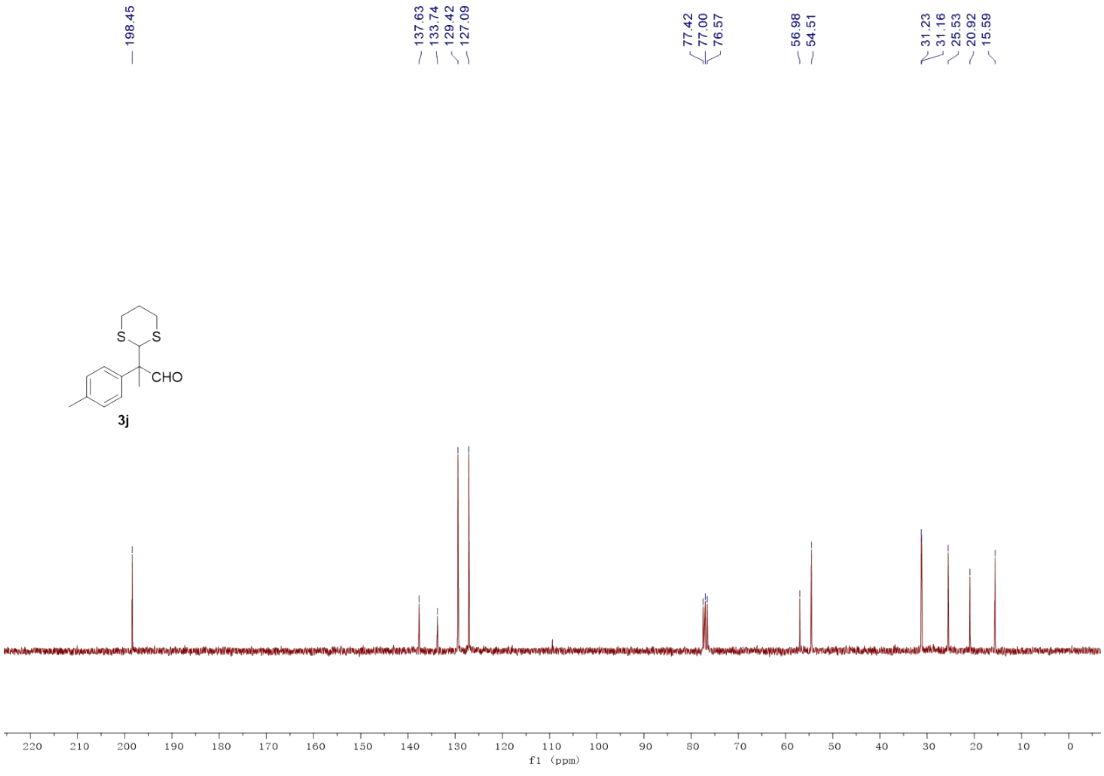
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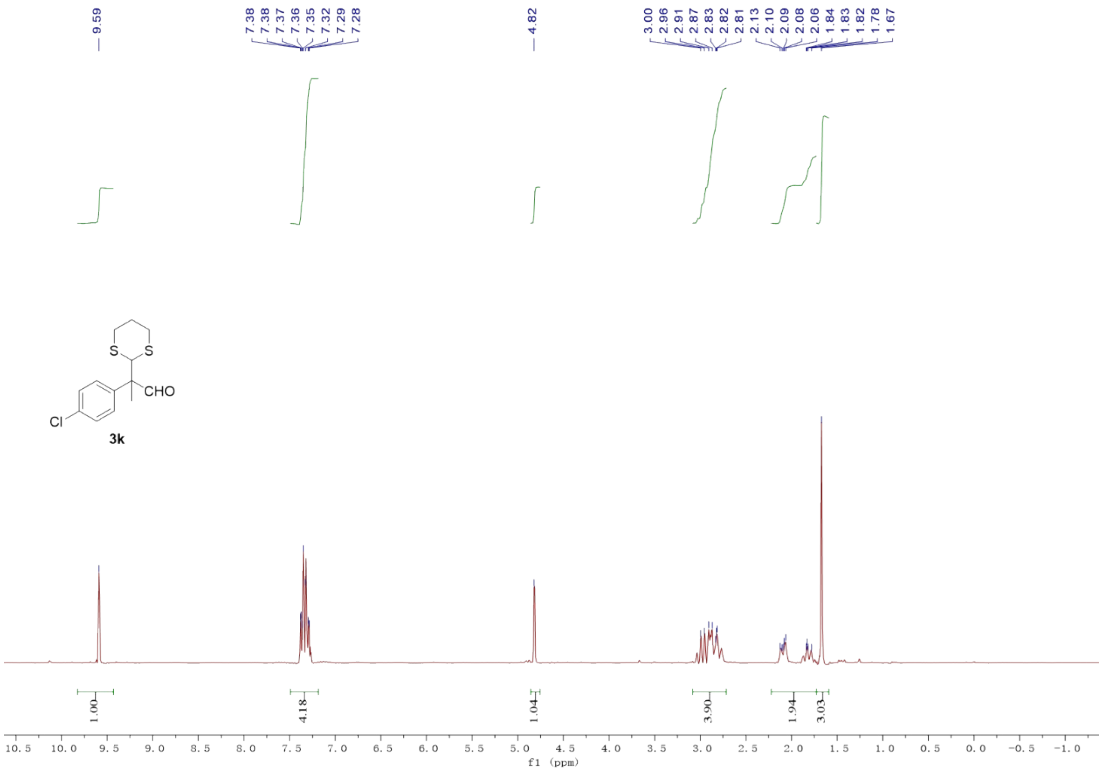
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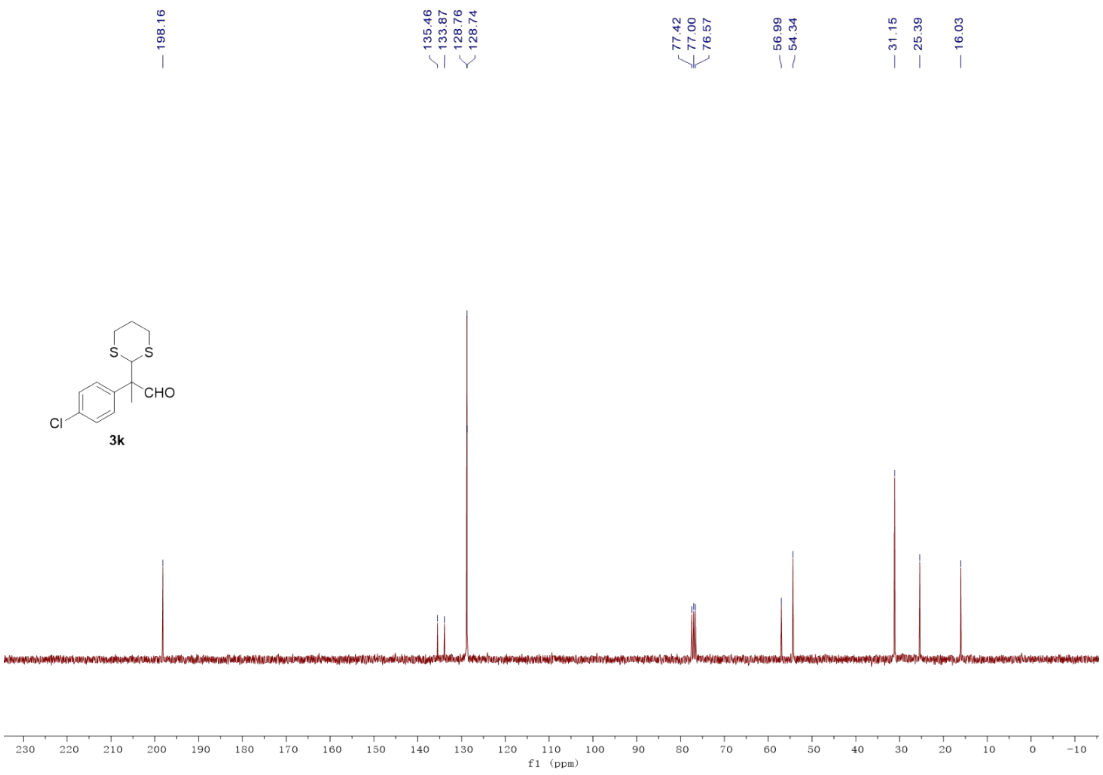
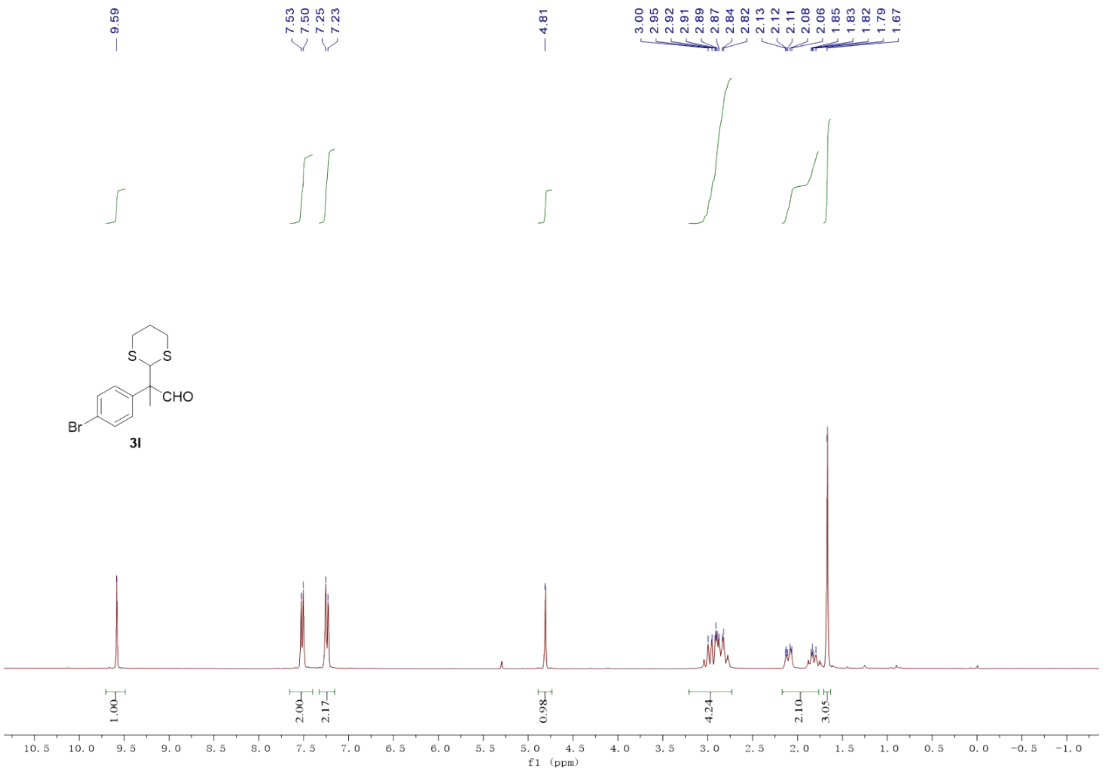
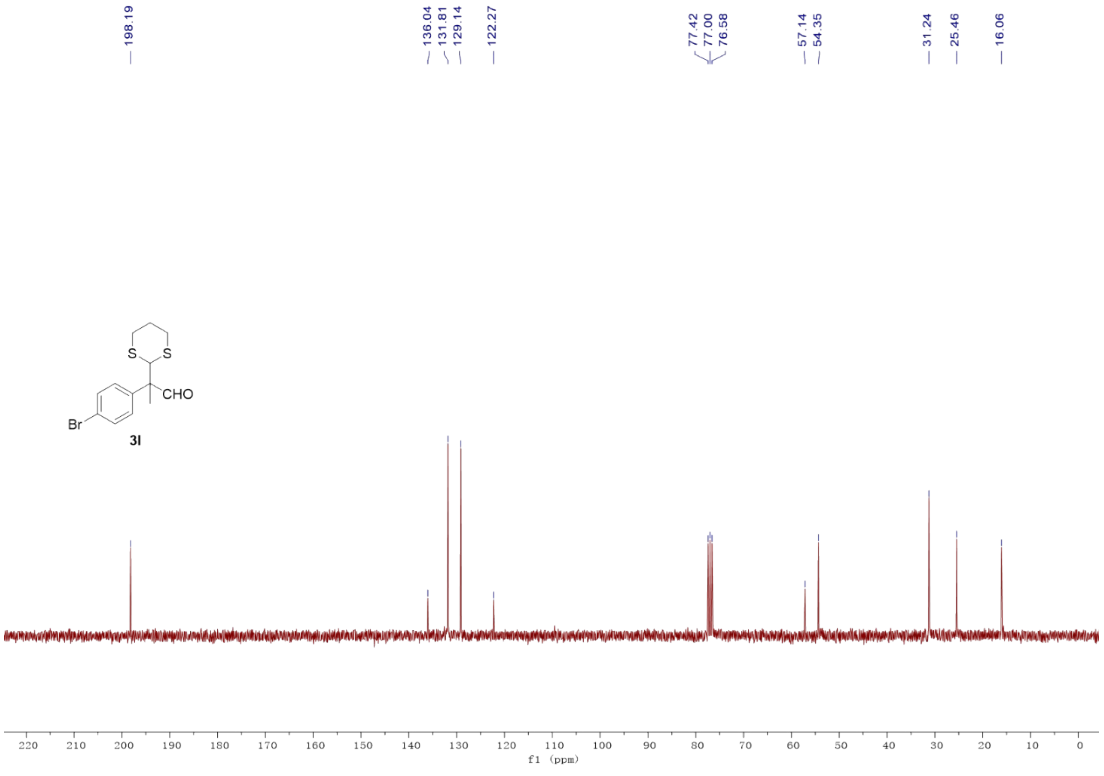
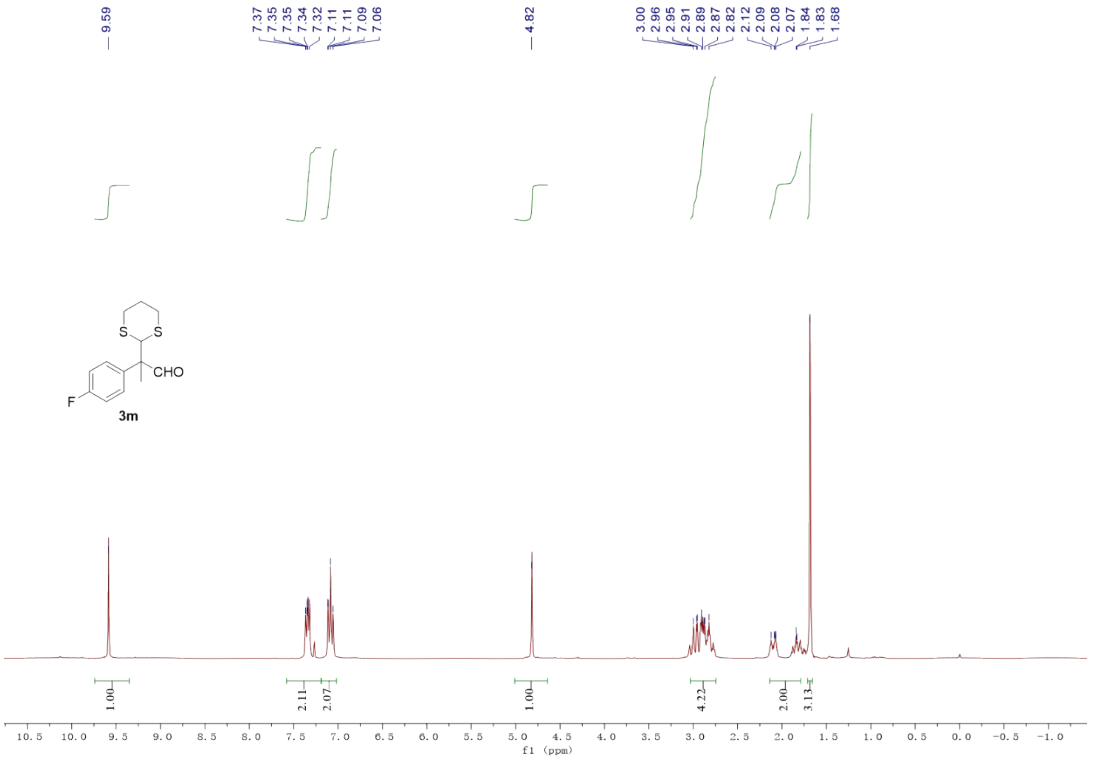
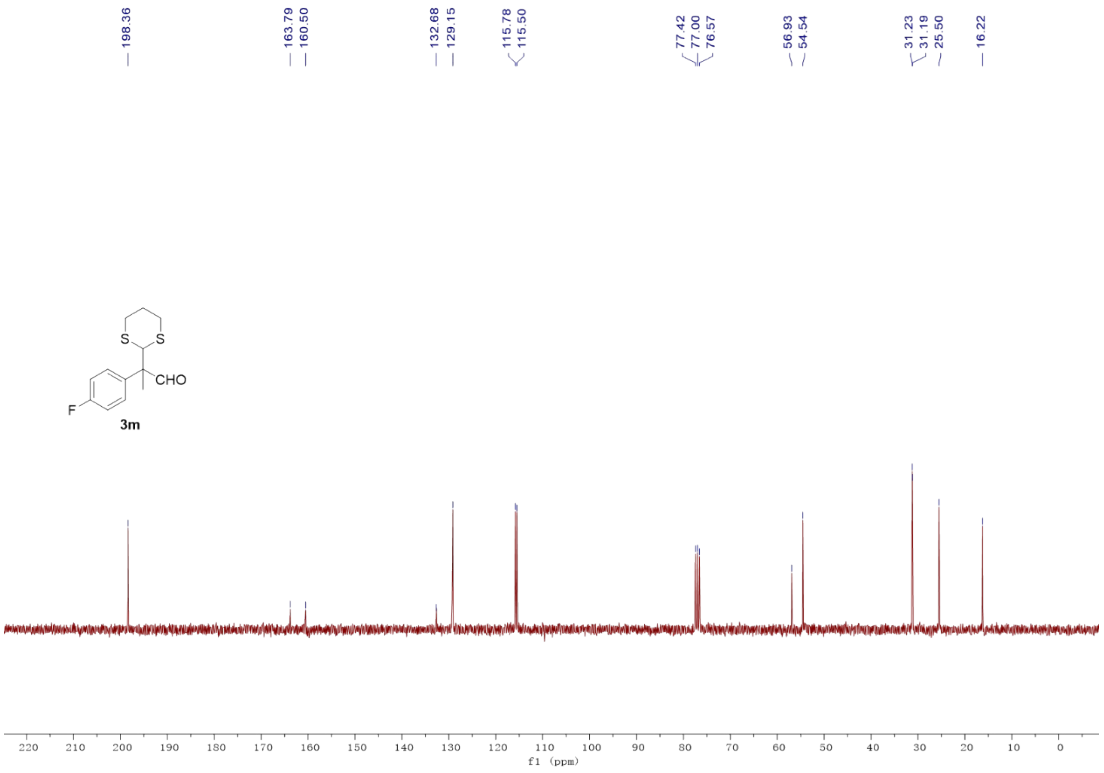
3.03
f1 (ppm)

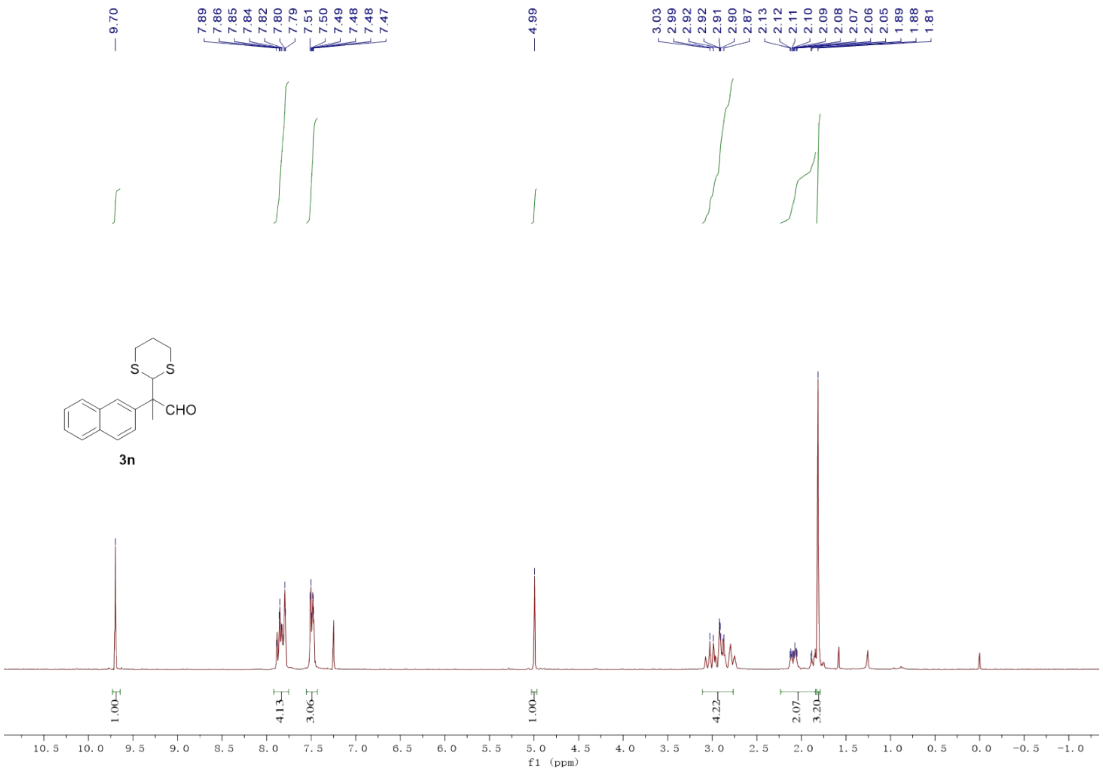

198.16
135.46
133.87
128.76
128.74
77.42
77.00
76.57
56.99
54.34
31.15
25.39
16.03
S
S
CHO
Cl
3k
f1 (ppm)

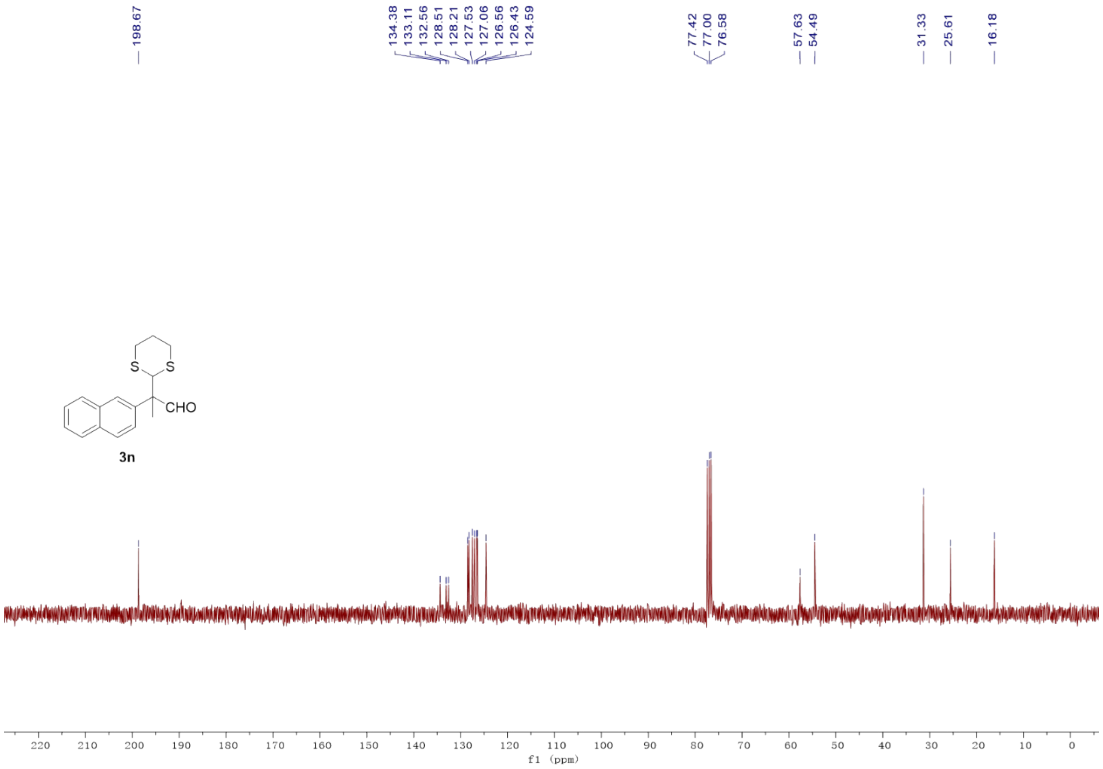

9.59
7.53
7.50
7.25
7.23
4.81
3.00
2.95
2.92
2.91
2.89
2.87
2.84
2.82
2.13
2.12
2.11
2.08
2.06
1.85
1.83
1.82
1.79
1.67
S
S
CHO
Br
3l
1.00
2.00
2.17
0.98
4.24
2.10
3.05
f1 (ppm)

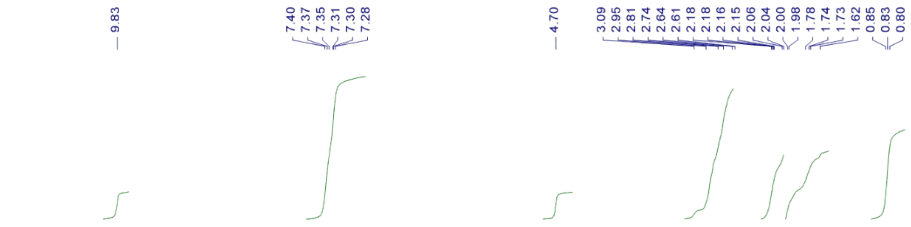

198.19
136.04
131.81
129.14
122.27
77.42
77.00
76.58
57.14
54.35
31.24
25.46
16.06
S
S
CHO
Br
3l
f1 (ppm)

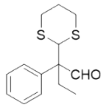

9.59
7.37
7.35
7.35
7.34
7.32
7.11
7.11
7.09
7.06
4.82
3.00
2.96
2.95
2.91
2.89
2.87
2.82
2.12
2.09
2.08
2.07
1.84
1.83
1.68
S
S
CHO
F
3m
1.00
2.11
2.07
1.00
4.22
2.00
3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


198.36
163.79
160.50
132.68
129.15
115.78
115.50
77.42
77.00
76.57
56.93
54.54
31.23
31.19
25.50
16.22
S
S
CHO
F
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

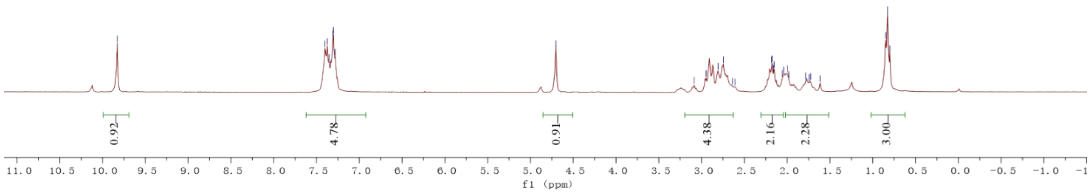

9.70
7.89
7.86
7.85
7.84
7.82
7.80
7.79
7.51
7.50
7.49
7.48
7.48
7.47
4.99
3.03
2.99
2.92
2.92
2.91
2.90
2.87
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.05
1.89
1.88
1.81
S
S
CHO
3n
1.00
4.13
3.06
1.00
4.22
2.07
3.20
f1 (ppm)


198.67
134.38
133.11
132.56
128.51
128.21
127.53
127.06
126.56
126.43
124.59
77.42
77.00
76.58
57.63
54.49
31.33
25.61
16.18
S
S
CHO
3n
f1 (ppm)

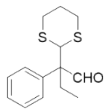

9.83
7.40
7.37
7.35
7.31
7.30
7.28
4.70
3.09
2.95
2.81
2.74
2.64
2.61
2.18
2.18
2.16
2.15
2.06
2.04
2.00
1.98
1.78
1.74
1.73
1.62
0.85
0.83
0.80


S
S
CHO

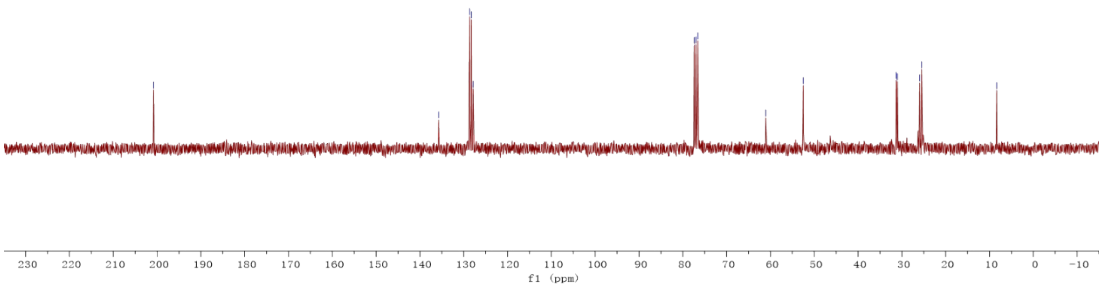
3o

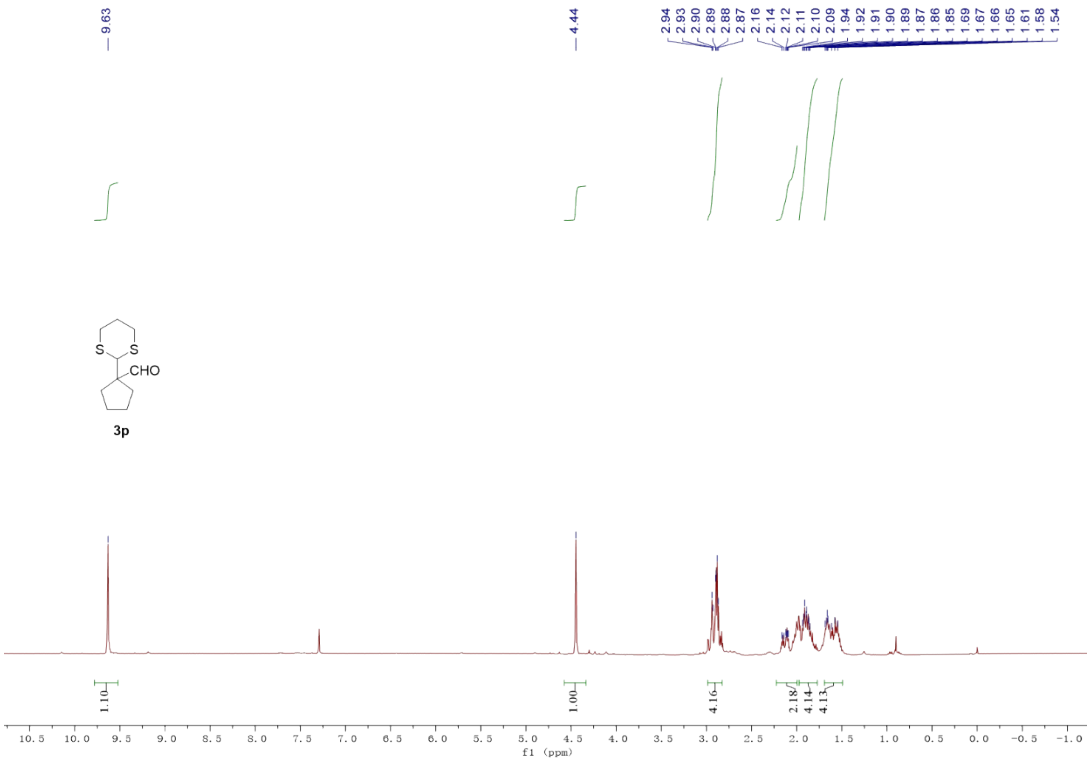

0.92
4.78
0.91
4.38
2.16
2.28
3.00
f1 (ppm)

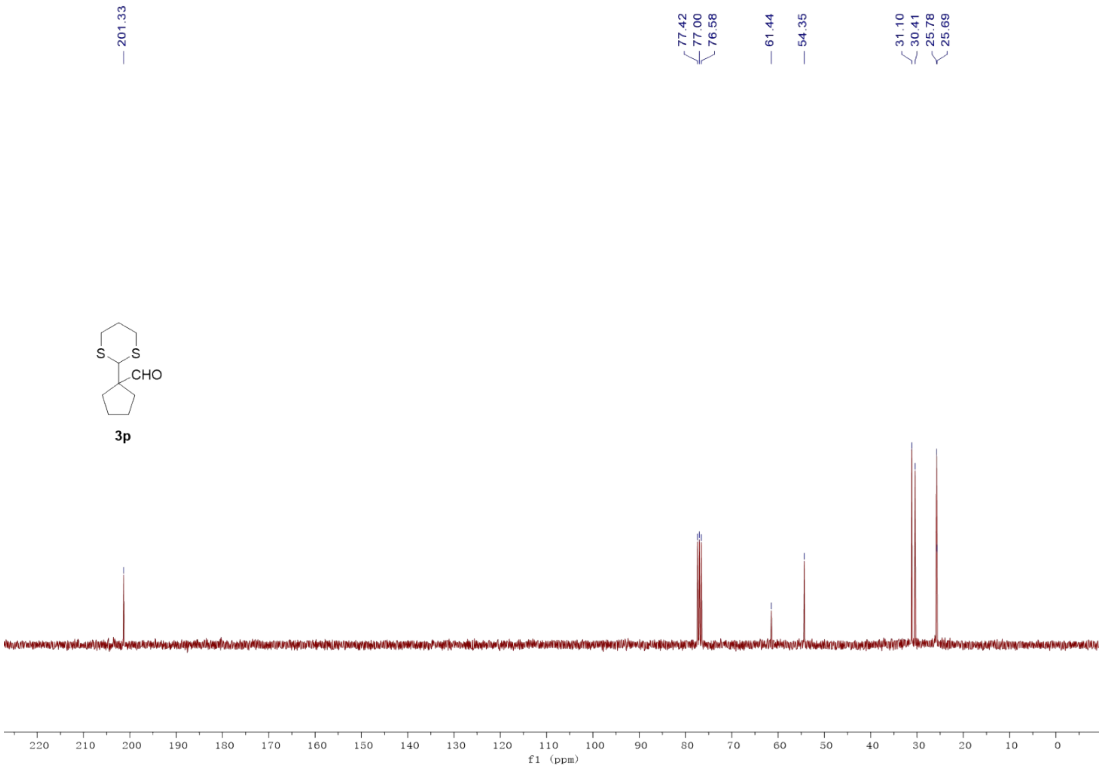

200.79
135.71
128.65
128.27
127.84
77.42
77.00
76.58
61.07
52.51
31.29
31.05
25.97
25.49
8.35

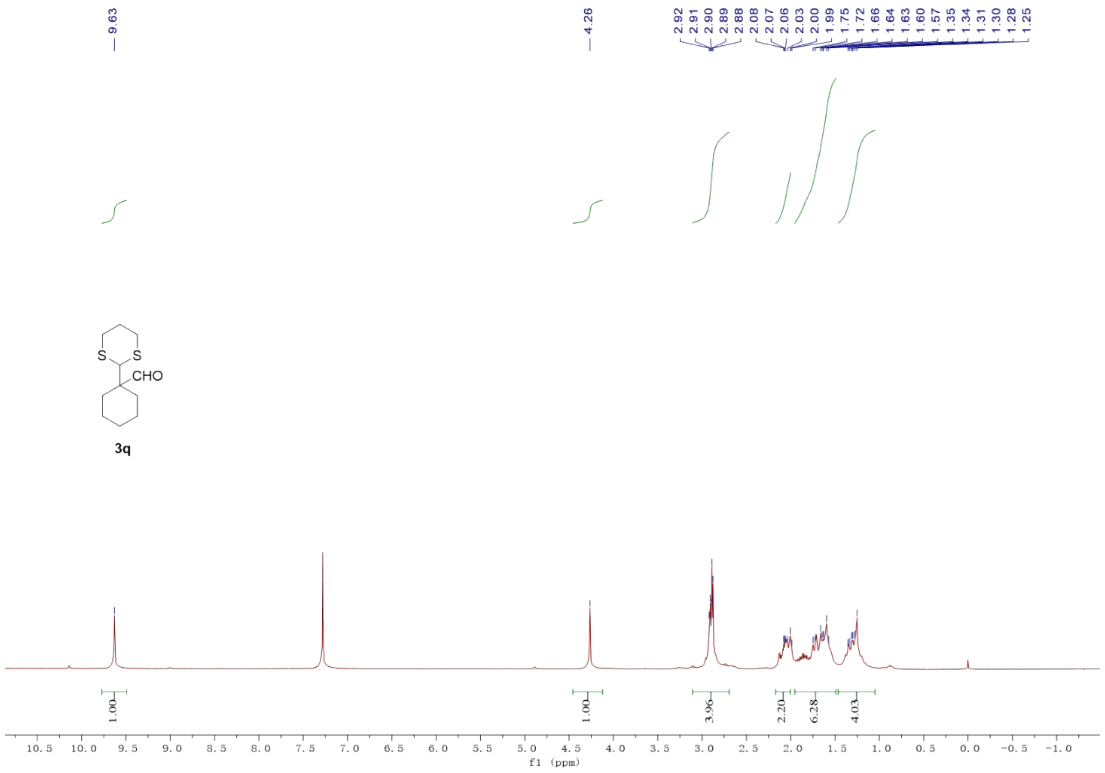

S
S
CHO

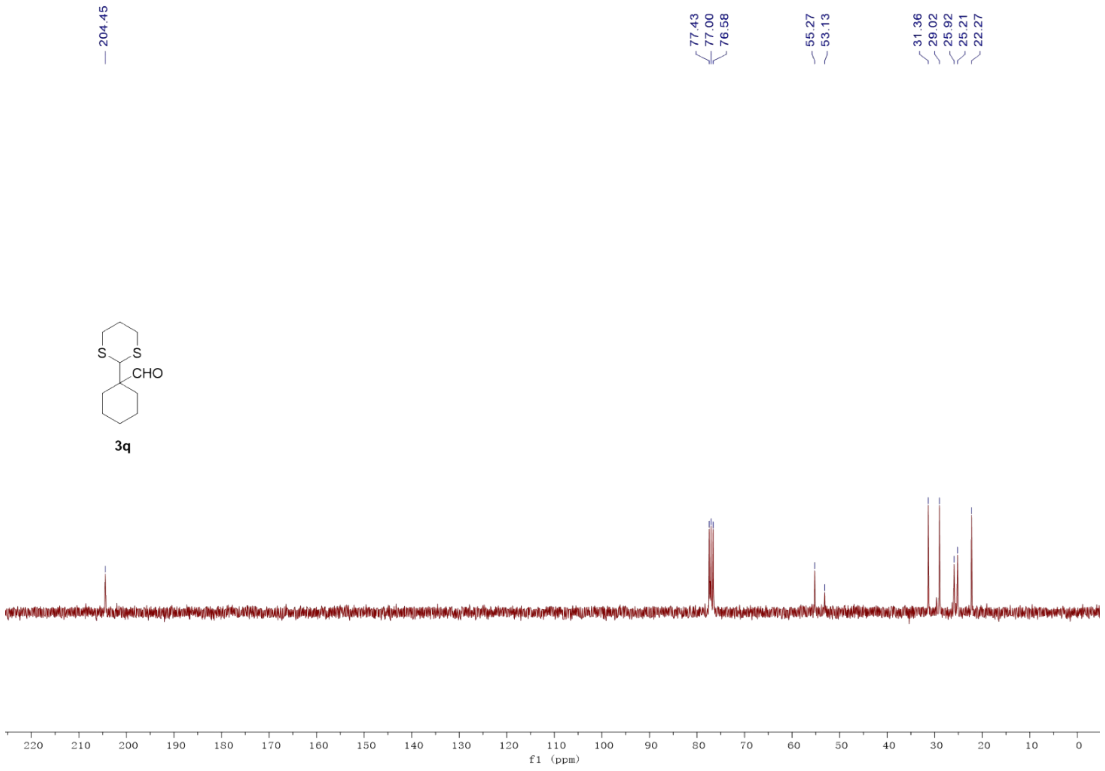
3o

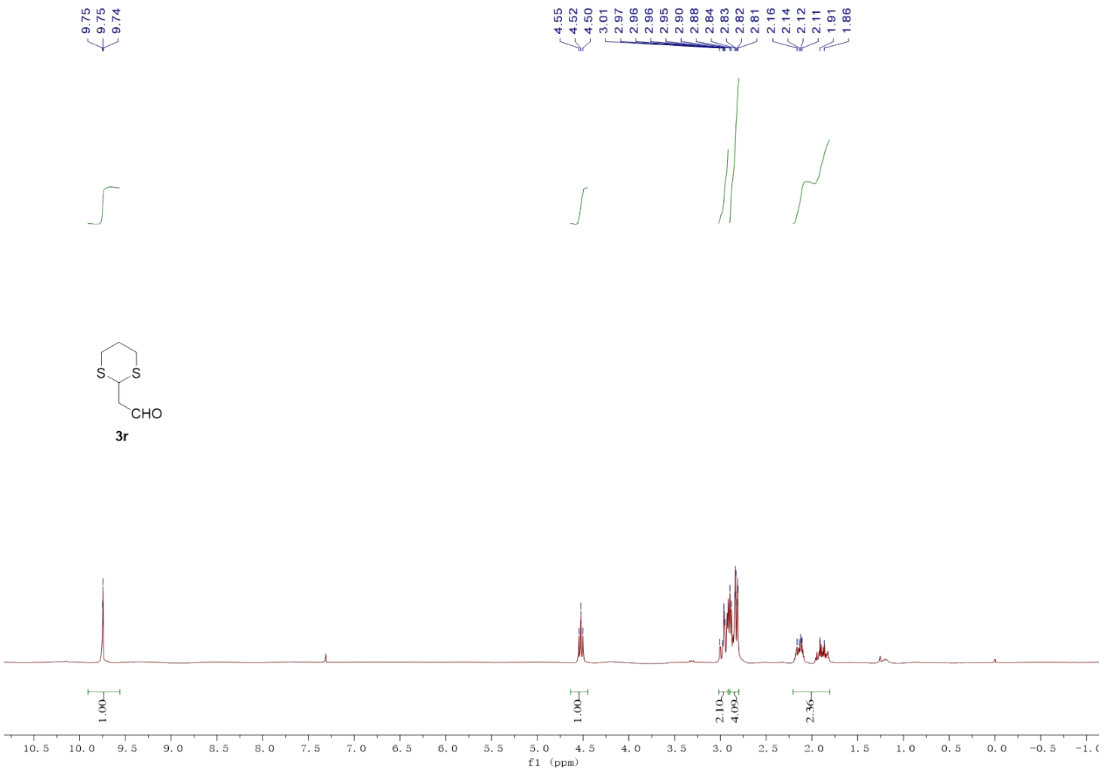

f1 (ppm)

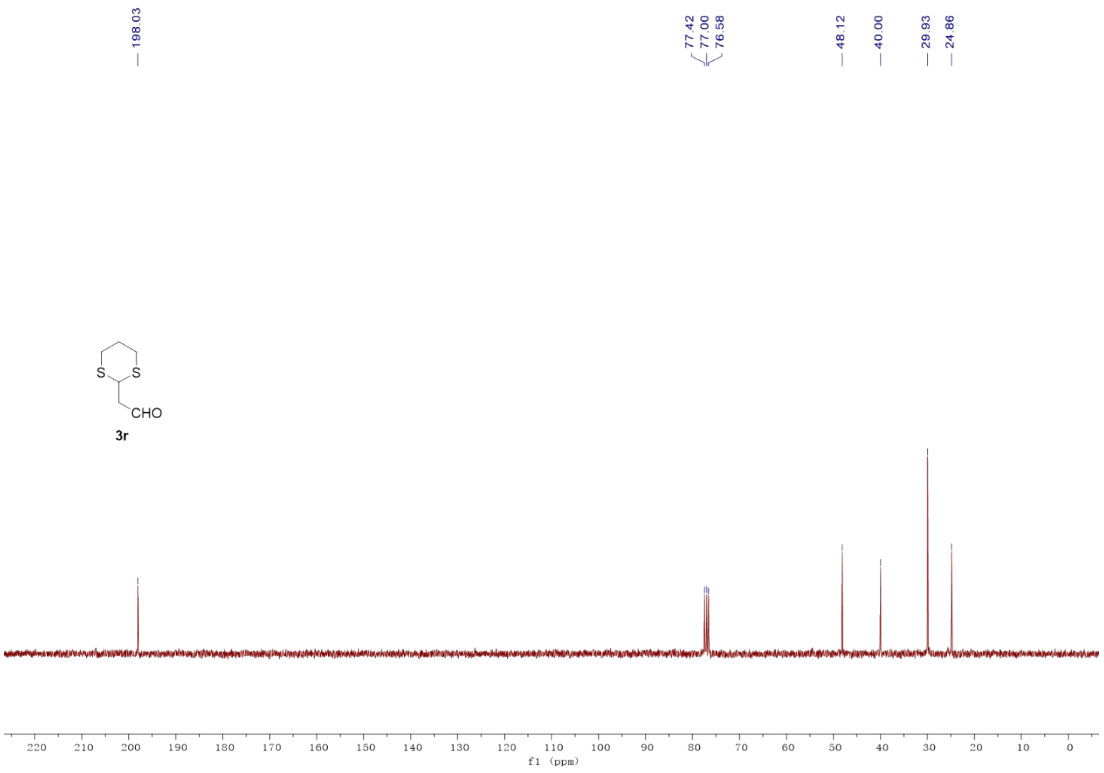

9.63
4.44
2.94
2.93
2.90
2.89
2.88
2.87
2.16
2.14
2.12
2.11
2.10
2.09
1.94
1.92
1.91
1.90
1.89
1.87
1.86
1.85
1.69
1.67
1.66
1.65
1.61
1.58
1.54
S
S
CHO
3p
1.10
1.00
4.16
2.18
4.14
4.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

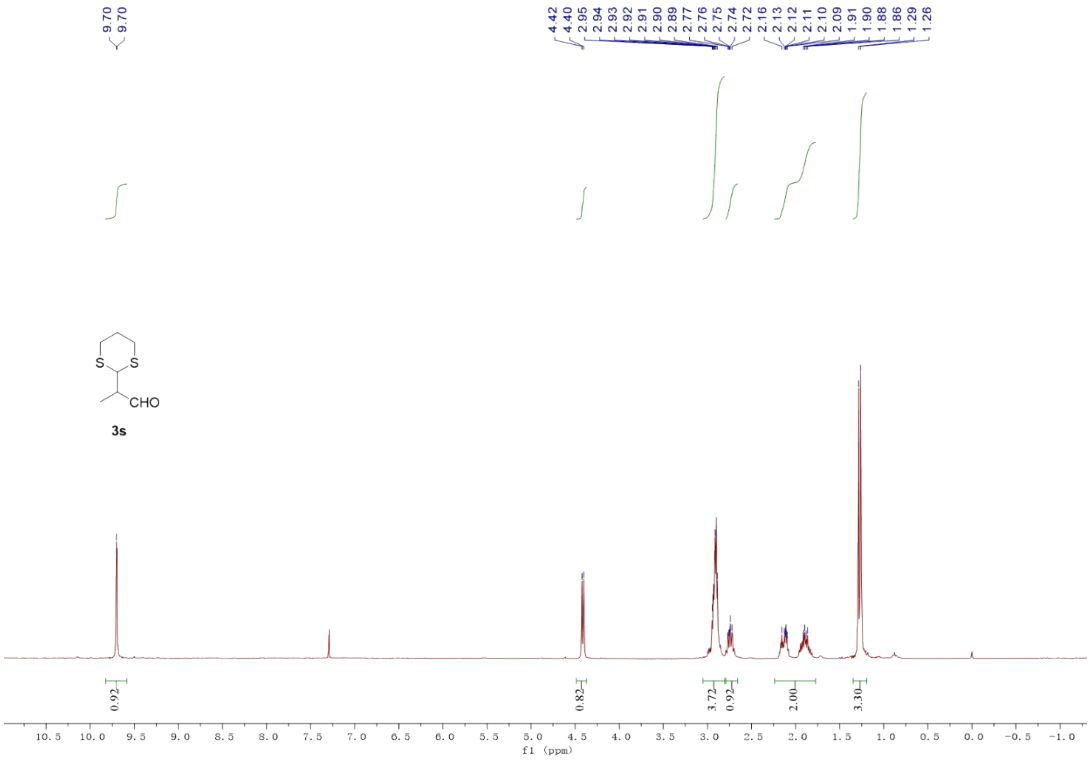

201.33
77.42
77.00
76.58
61.44
54.35
31.10
30.41
25.78
25.69
S
S
CHO
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

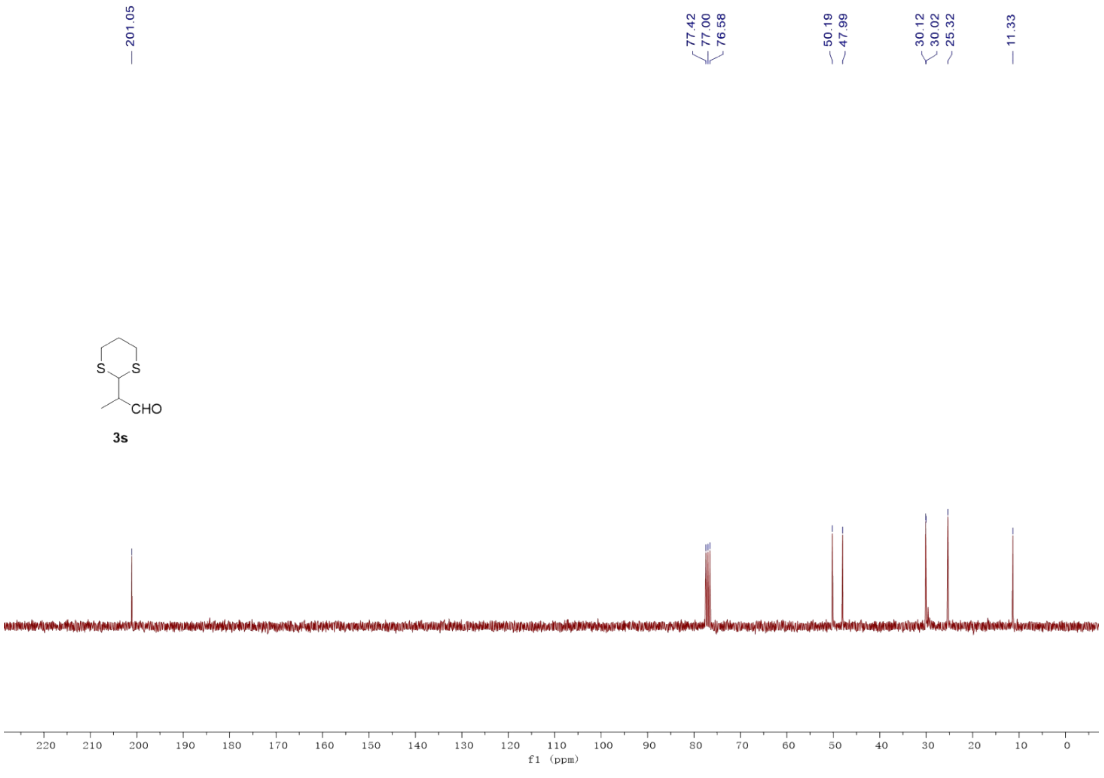

9.63
4.26
2.92
2.91
2.90
2.89
2.88
2.08
2.07
2.06
2.03
2.00
1.99
1.75
1.72
1.66
1.64
1.63
1.60
1.57
1.35
1.34
1.31
1.30
1.28
1.25
S
S
CHO
3q
1.00
1.00
3.96
2.20
6.28
4.03
f1 (ppm)

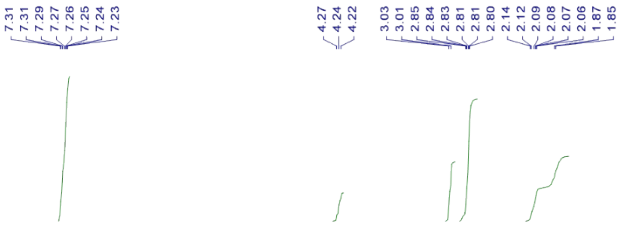

204.45
77.43
77.00
76.58
55.27
53.13
31.36
29.02
25.92
25.21
22.27
S
S
CHO
3q
f1 (ppm)


9.75
9.75
9.74
4.55
4.52
4.50
3.01
2.97
2.96
2.96
2.95
2.90
2.88
2.84
2.83
2.82
2.81
2.16
2.14
2.12
2.11
1.91
1.86
S
S
CHO
3r
1.00
1.00
2.10
4.09
2.36
f1 (ppm)


198.03
77.42
77.00
76.58
48.12
40.00
29.93
24.86
S
S
CHO
3r
f1 (ppm)


9.70
9.70
4.42
4.40
2.95
2.94
2.93
2.92
2.91
2.90
2.89
2.77
2.76
2.75
2.74
2.72
2.16
2.13
2.12
2.11
2.10
2.09
1.91
1.90
1.88
1.86
1.29
1.26
S
S
CHO
3s
0.92
0.82
3.72
0.92
2.00
3.30
f1 (ppm)


201.05
77.42
77.00
76.58
50.19
47.99
30.12
30.02
25.32
11.33
S
S
CHO
3s
f1 (ppm)


7.31
7.31
7.29
7.27
7.26
7.25
7.24
7.23
4.27
4.24
4.22
3.03
3.01
2.85
2.84
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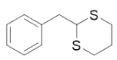
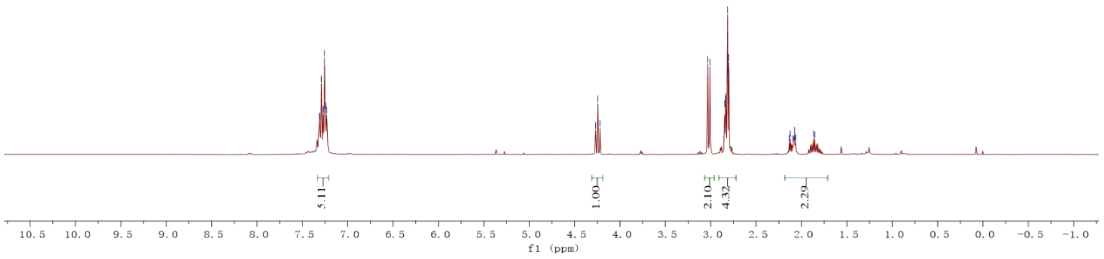
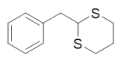
2.09
2.08
2.07
2.06
1.87
1.85



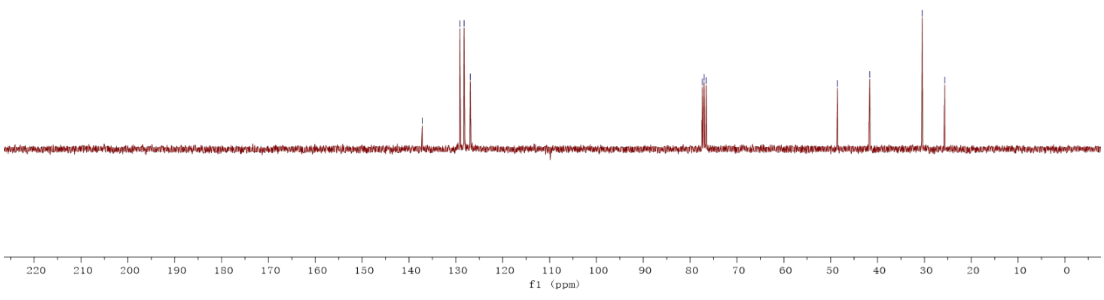
4a

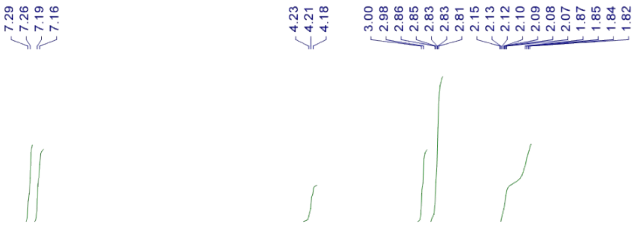

5.11
1.00
2.10
4.32
2.29
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


137.20
129.12
128.25
126.92
77.42
77.00
76.57
48.57
41.67
30.46
25.67



4a


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.29
7.26
7.19
7.16
4.23
4.21
4.18
3.00
2.98
2.86
2.85
2.83
2.83
2.81
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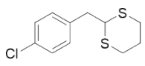
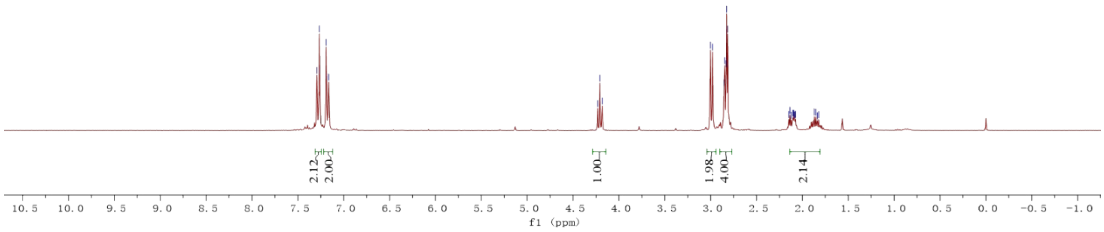
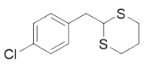
2.08
2.07
1.87
1.85
1.84
1.82


Cl
S
S

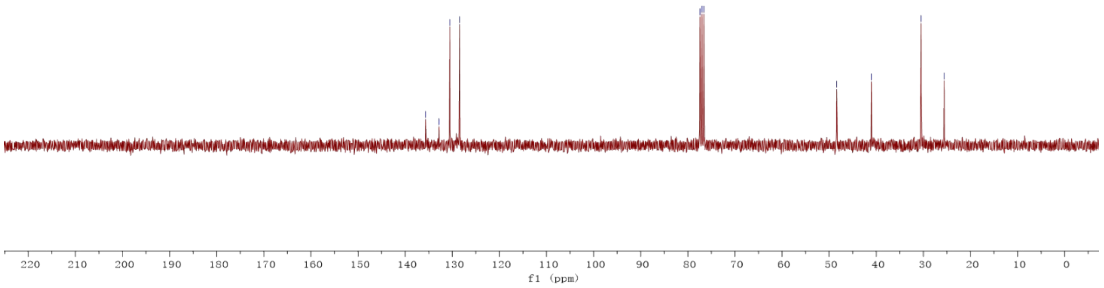
4b

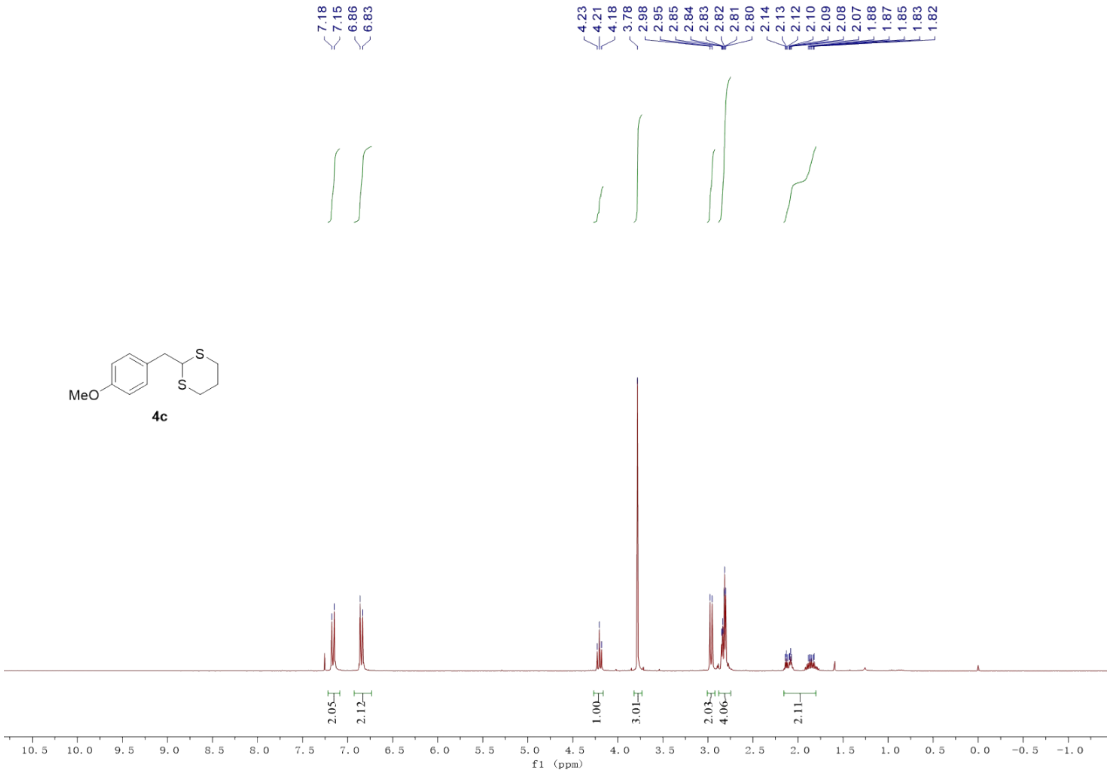

2.12
2.00
1.00
1.98
4.00
2.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

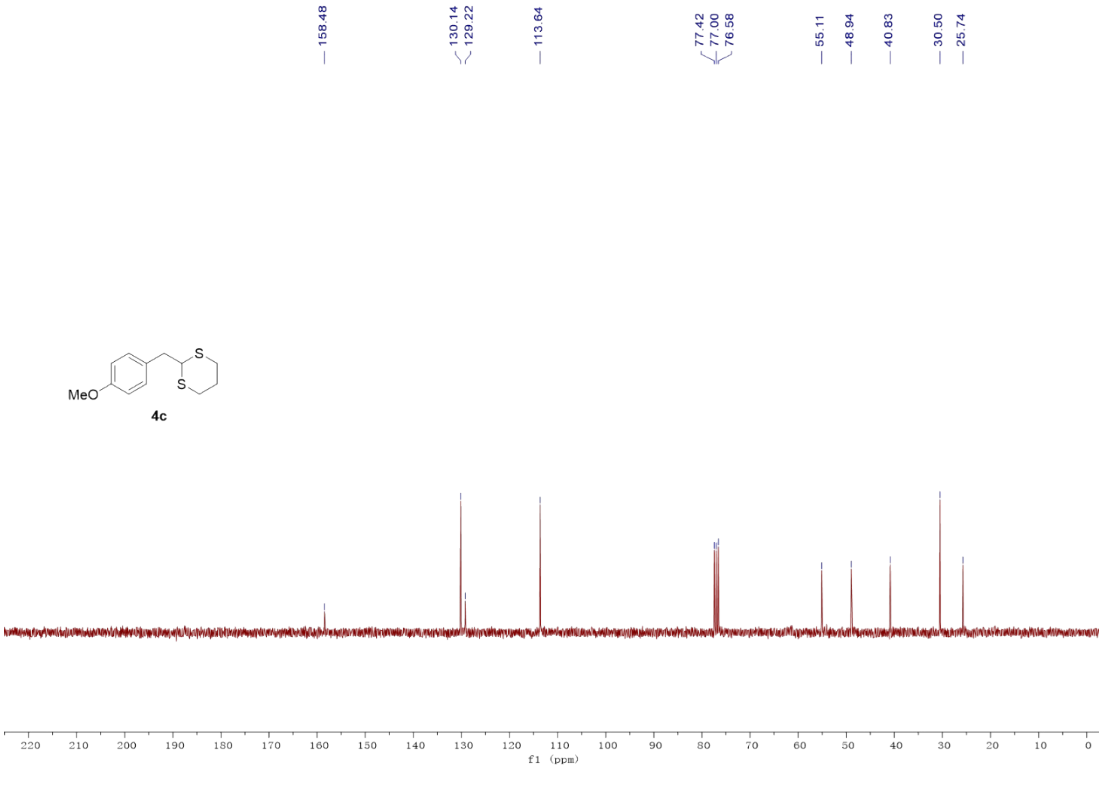

135.67
132.82
130.52
128.45
77.42
77.00
76.58
48.39
41.02
30.48
25.61

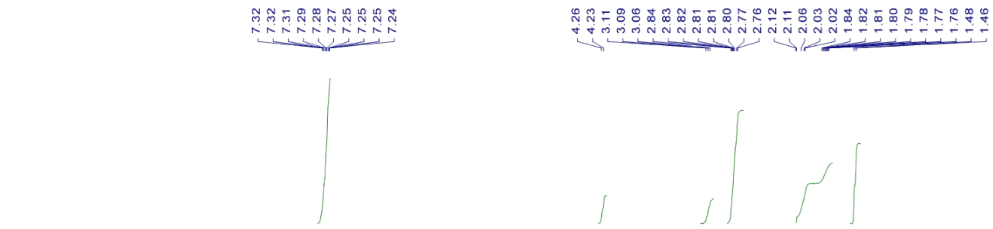

Cl
S
S

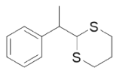
4b


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

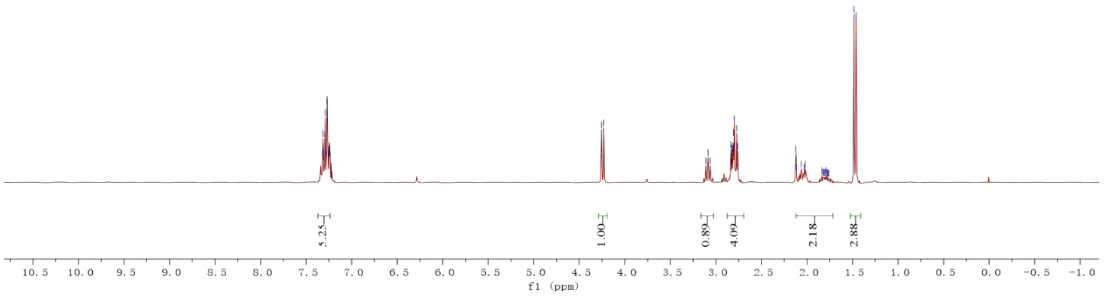

7.18
7.15
6.86
6.83
4.23
4.21
4.18
3.78
2.98
2.95
2.85
2.84
2.83
2.82
2.81
2.80
2.14
2.13
2.12
2.10
2.09
2.08
2.07
1.88
1.87
1.85
1.83
1.82
MeO
S
S
4c
2.05
2.12
1.00
3.01
2.03
4.06
2.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.48
130.14
129.22
113.64
77.42
77.00
76.58
55.11
48.94
40.83
30.50
25.74
MeO
S
S
4c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

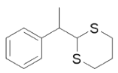

7.32
7.32
7.31
7.29
7.28
7.27
7.25
7.25
7.25
7.24
4.26
4.23
3.11
3.09
3.06
2.84
2.83
2.82
2.81
2.81
2.80
2.77
2.76
2.12
2.11
2.06
2.03
2.02
1.84
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.48
1.46



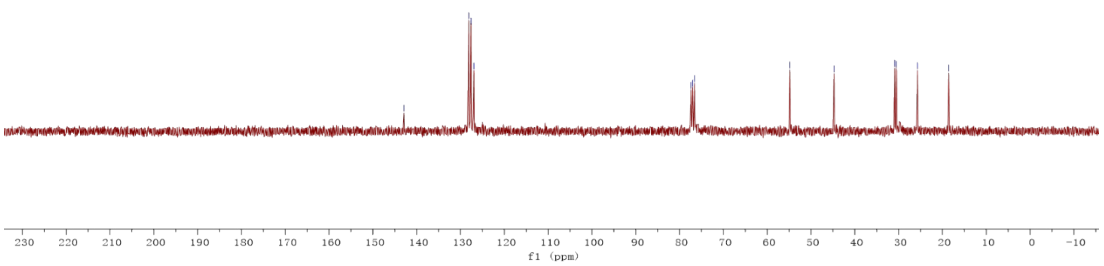
4i

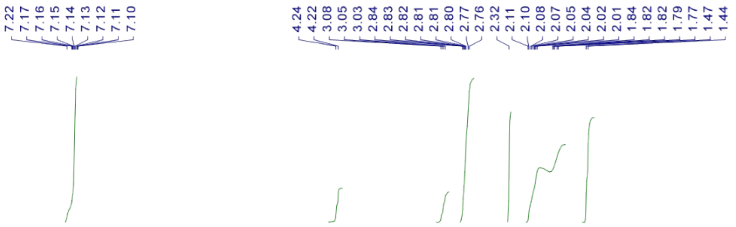

5.25
1.00
0.89
4.09
2.18
2.88
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

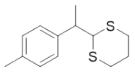

142.90
128.13
127.59
126.94
77.43
77.01
76.58
54.82
44.75
30.90
30.50
25.74
18.56



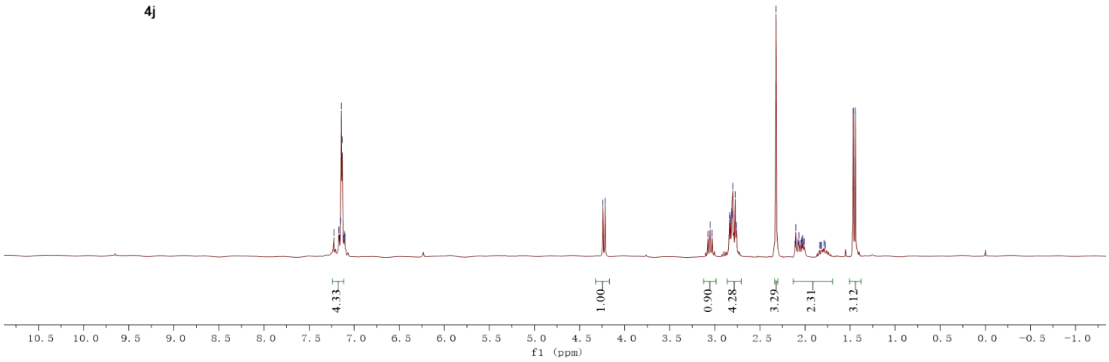
4i


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

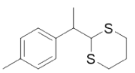

7.22
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.10
4.24
4.22
3.08
3.05
3.03
2.84
2.83
2.82
2.81
2.81
2.80
2.77
2.76
2.32
2.11
2.10
2.08
2.07
2.05
2.04
2.02
2.01
1.84
1.82
1.82
1.79
1.77
1.47
1.44



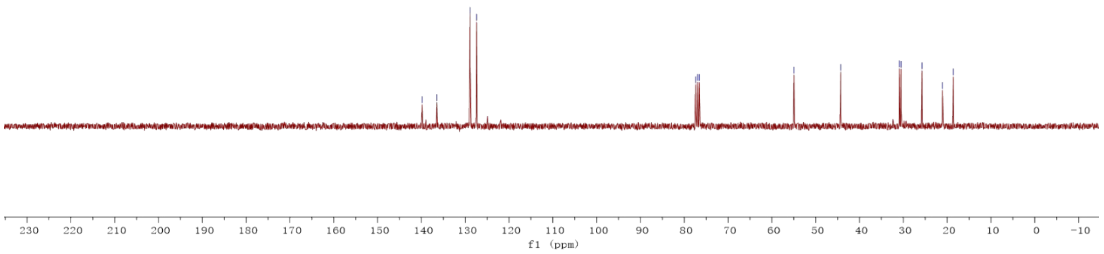
4j

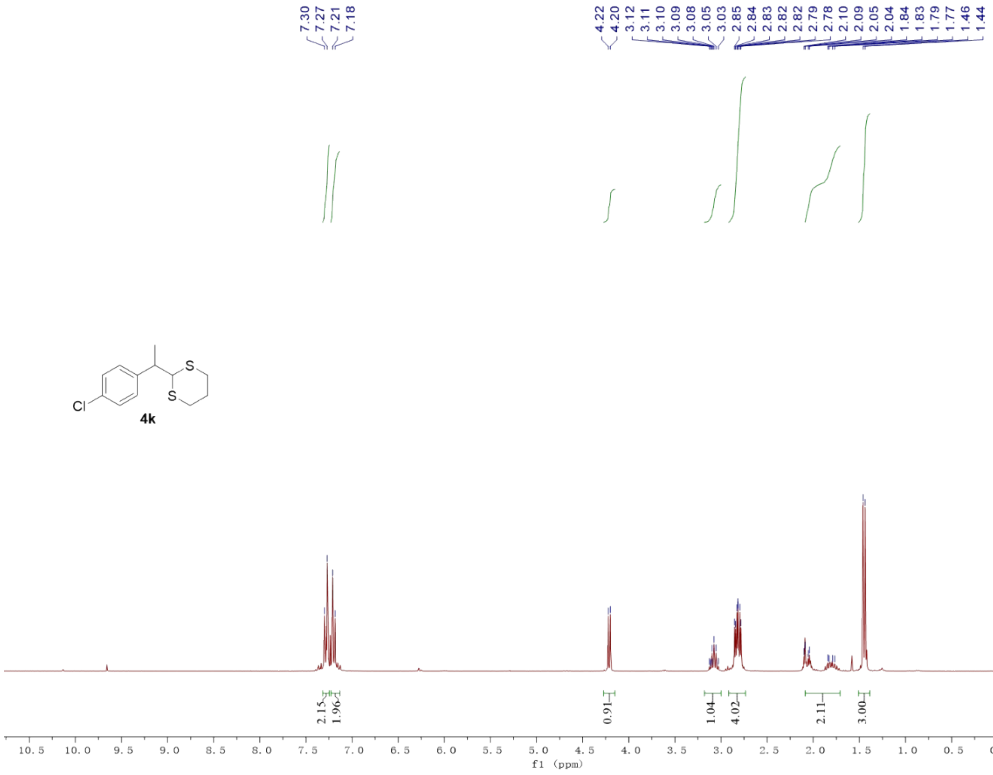

4.33
1.00
0.90
4.28
3.29
2.31
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

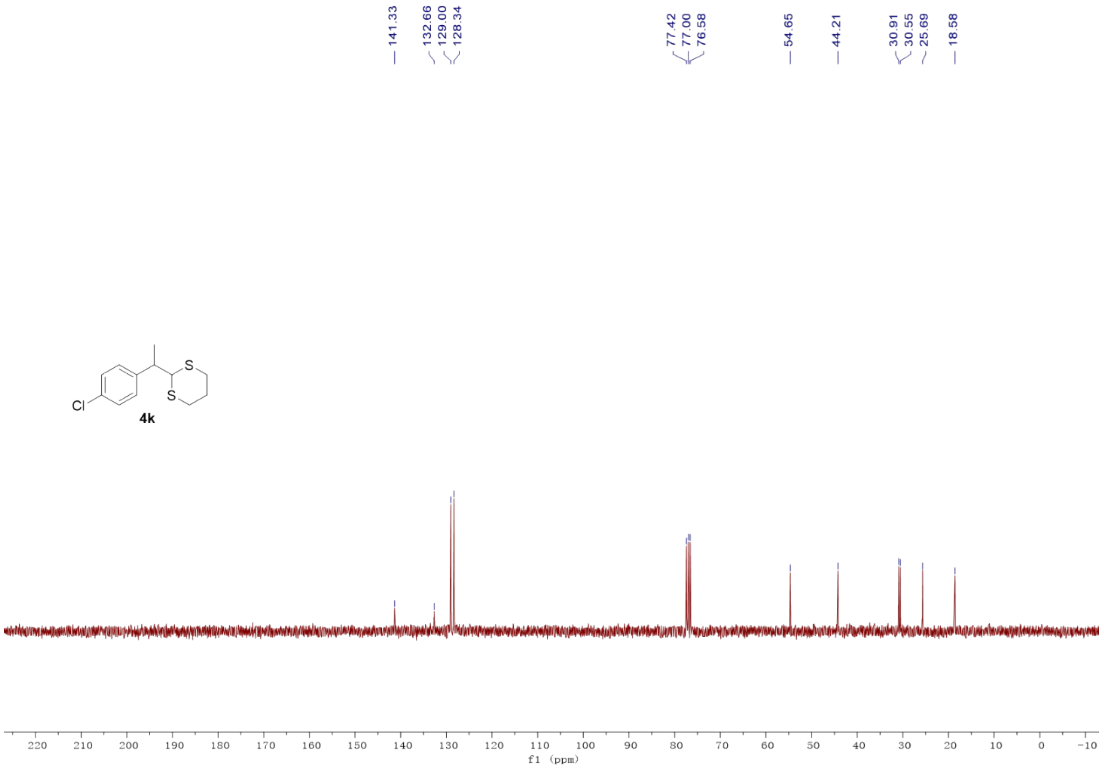

139.84
136.47
128.88
127.42
77.42
77.00
76.58
54.96
44.33
30.92
30.53
25.75
21.06
18.61

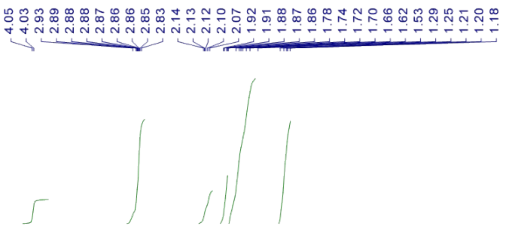


4j


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.30
7.27
7.21
7.18
4.22
4.20
3.12
3.11
3.10
3.09
3.08
3.05
3.03
2.85
2.84
2.83
2.82
2.82
2.79
2.78
2.10
2.09
2.05
2.04
1.84
1.83
1.79
1.77
1.46
1.44
S
S
Cl
4k
2.15
1.96
0.91
1.04
4.02
2.11
3.00
f1 (ppm)


141.33
132.66
129.00
128.34
77.42
77.06
76.58
54.65
44.21
30.91
30.55
25.69
18.58
S
S
Cl
4k
f1 (ppm)


4.05
4.03
2.93
2.89
2.88
2.88
2.87
2.86
2.86
2.85
2.83
2.14
2.13
2.12
2.10
2.07
1.92
1.91
1.88
1.87
1.86
1.78
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1.70
1.66
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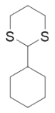
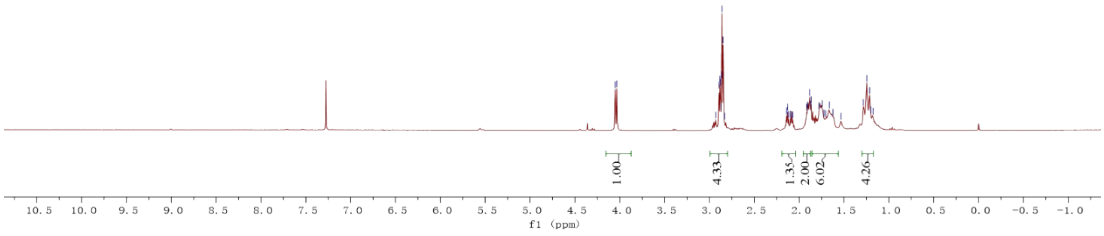
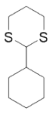
1.53
1.29
1.25
1.21
1.20
1.18



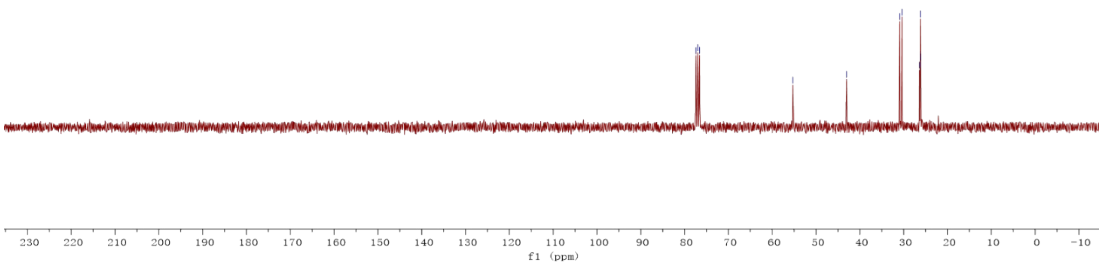
4q


1.00
4.33
1.35
2.00
6.02
4.26
f1 (ppm)


77.42
77.00
76.58
55.29
43.06
30.90
30.39
26.40
26.19
26.13



4q


f1 (ppm)