Electronic Supplementary Material (ESI) for Green Chemistry.

Direct Anodic (Thio)Acetalization of Aldehydes with Alcohol(thiols) under Neutral Conditions and Computational Insight into the Electrochemical Acetals Formation

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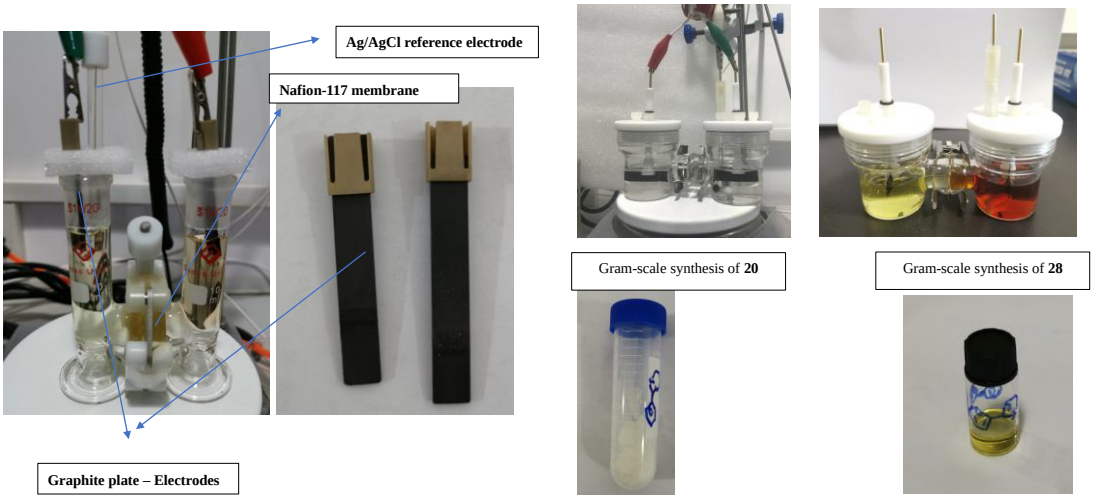
General information

Unless otherwise noted, all reactions were handled under air atmosphere, placed in a H-type electrolysis cell (10 mL, connected by Nafion-117 membrane). Graphite and platinum plates were used as electrodes for reaction optimization and substrate scope studies. HPLC grade solvents, DMF, dichloromethane (DCM), acetonitrile, methanol and ethanol were purchased from commercial sources and used without further purification. The new (thio)acetals were fully characterized by using ^{1}H NMR, ^{13}C NMR and HRMS. ^{1}H NMR spectra were recorded on a Bruker GPX 400 MHz spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for ^{1}H NMR; 77.0 ppm for ^{13}C NMR), Coupling constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. Known (thio)acetals were analyzed by GC-MS, ^{1}H NMR and verified by comparison with authentic samples of commercially available material. Mass spectra (HRMS) were conducted at Agilent Technologies 5973N (EI).

Graphical guide for the assembly of electrochemical cell

Picture 1. Typical reaction set-up and large scale electrochemical (thio)acetalization.



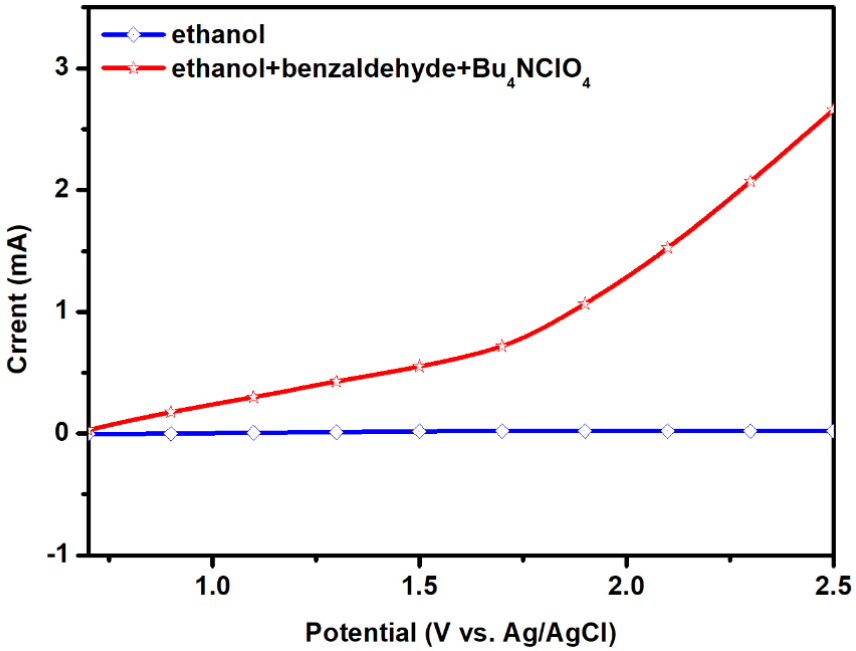


Figure S1. LSV curve of graphite anodic electrochemical acetalization (scan rate 50 mV/s). Benzaldehyde (1.0 mmol), ammonium salt (5 mol %), ethanol (5 mL) [anode], ammonium salt (5 mol %), ethanol (5 mL) [cathode] in an H-type divided cell with two graphites and a Nafion-117 membrane, under air.

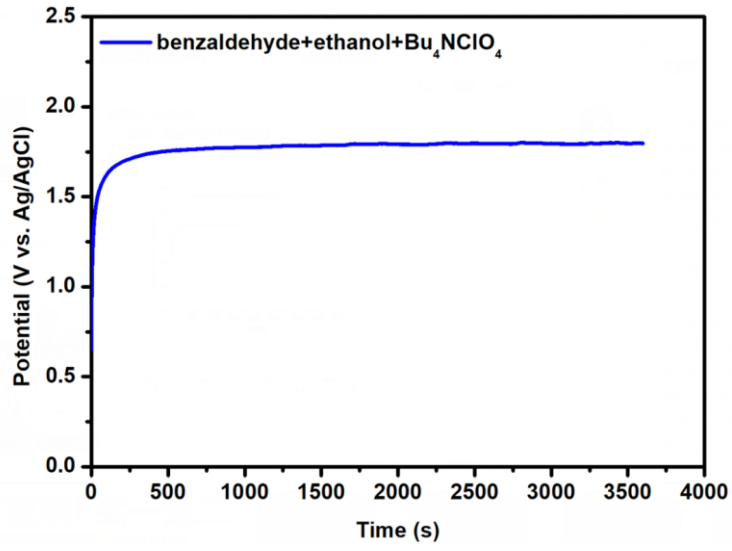
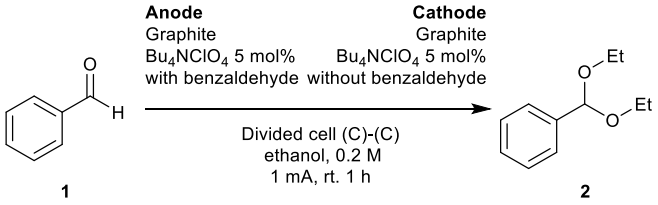


Figure S2. Chronopotentiometry plot at a constant current of 1 mA.

Optimization conditions of (thio)acetalization

Table S1. Summary of acetalization reaction optimization [a]

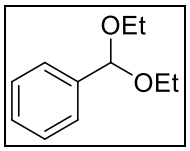


Entry	Anode	Electrolyte	Temp (°C)	Current (mA)	Time (h)	Yield (%) [b]
1	Graphite	Bu_4NBF_4	25	1	0.5	44.1
2	RVC	Bu_4NBF_4	25	1	0.5	11.7
3	glassy carbon	Bu_4NBF_4	25	1	0.5	7.3
4	Pt	Bu_4NBF_4	25	1	0.5	14.1
5	Au	Bu_4NBF_4	25	1	0.5	38.5
6	Graphite	Bu_4NBF_4	25	0.1	0.5	12.9
7	Graphite	Bu_4NBF_4	25	5	0.5	54.3
8	Graphite	Bu_4NBF_4	25	1	1	69.6
9	Graphite	Bu_4NBF_4	25	1	1.5	79.9
10	Graphite	Bu_4NBF_4	25	1	2	91.0
11	Graphite	Bu_4NBF_4	25	1	3	91.7(90)
12	Graphite	Bu_4NI	25	1	0.5	8.6
13	Graphite	Bu_4NBr	25	1	0.5	85.8
14	Graphite	Bu_4NPF_6	25	1	0.5	89.0
15	Graphite	Bu_4NCl	25	1	0.5	86.3
16	Graphite	Bu_4NClO_4	25	1	0.5	89.1
17	Graphite	Bu_4NClO_4	25	1	1	92.8(91)
18	Graphite	Bu_4NClO_4	25	1	1.5	90.0
19	Graphite	Bu_4NClO_4	50	1	0.5	84.7
20	Graphite	Bu_4NClO_4 [a]	25	1	0.5	87.5
21 [c]	Graphite	Bu_4NClO_4	25	1	0.5	65.6
22	Graphite	Bu_4NClO_4	25	3.5 V [c]	0.5	84.7
23 [e]	Graphite	Bu_4NClO_4	25	1	0.5	10.7
24	Graphite	Bu_4NClO_4	25	0	0.5	0
25 [f]	Graphite	Bu_4NBF_4	25	1	0.5	13.0

[a] Conditions: **1** (1.0 mmol), ammonium salt (5 mol %), ethanol (5 mL) [anode], ammonium salt (5 mol %), ethanol (5 mL) [cathode] in an H-type divided cell with two electrodes and a Nafion-117 membrane, under air. [b] Yields were determined by GC with dodecane as the internal standard, isolated yield was given in the parentheses. No side products were observed. [c] 1.0 mol/L of benzaldehyde; [d] Constant voltage; [e] 10 vol% of water/ethanol as solvent; [f] Reaction in undivided cell.

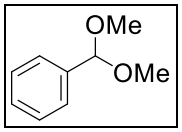
General procedure for the synthesis of (thio)acetals

A divided H-type cell was equipped with a pair of graphite electrodes and connected to an electrochemical workstation regulated power supply. To the anodic chamber was added aldehydes (1.0 mmol, 1.0 equiv.), Bu_4NClO_4 (17.1 mg, 0.0500 mmol) and 5 mL alcohol solvent (Methanol and Ethanol, in other cases, MeCN was used as solvent, 0.2 M). The cathodic chamber was added Bu_4NClO_4 (17.1 mg, 0.0500 mmol) and 5 mL alcohol solvent (methanol or ethanol, in other cases, MeCN was used as solvent, 0.2 M). The mixture was electrolyzed under constant current (1-2 mA) at room temperature with magnetic stirring for 1 hour. Then, 50 μL dodecane was added to the reaction solution as internal standard and a partial solution was filtered through a short silica gel column for GC and GC-MS analysis. The combined solution was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford the desired (thio)acetals.



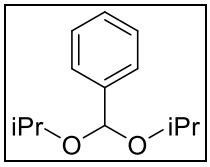
(Diethoxymethyl)benzene(2)[1,3]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **2** as a colorless oil, 164 mg, 91% yield. **2** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with authentic sample of commercially available material.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* =7.6 Hz, 2H), 7.41–7.30 (m, 3H), 5.51 (s, 1H), 3.69–3.48 (m, 4H), 1.24 (t, *J* =7.1 Hz, 6H).



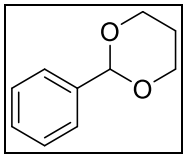
(Dimethoxymethyl)benzene (3)[2]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **3** as a colorless oil, 138 mg, 91% yield. **3** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with authentic sample of commercially available material.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 4.0 Hz, 2H), 7.46–7.33 (m, 3H), 5.45 (s, 1H), 3.38 (s, 6H).

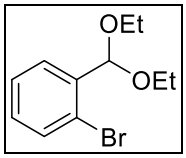


(Diisopropoxymethyl)benzene(4)[3]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **4** as a colorless oil, 116 mg, 56% yield.

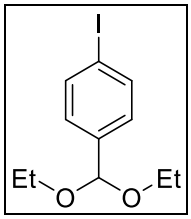
^{1}H NMR (400 MHz, $CDCl_3$):7.53–7.31(m, 5H), 5.59 (s, 1H), 3.94 (septet, *J* = 6.27 Hz, 2H), 1.23 (d, *J* = 6.27 Hz, 6H), 1.20 (d, *J* = 6.27 Hz, 6H).



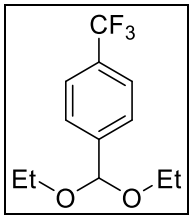
2-Phenyl-1,3-dioxane(5)[3]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **5** as a colorless solid, 141 mg, 86% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.40–7.33 (m, 3H), 5.51 (s, 1H), 4.31–4.25 (m, 2H), 4.04–3.96 (m, 2H), 2.24 (dtt, *J* = 13.4, 12.4, 5.0 Hz, 1H), 1.45 (dtt, *J* = 13.5, 2.6, 1.4 Hz, 1H).



1-Bromo-2-(diethoxymethyl)benzene(6)[4]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **6** as a colorless oil, 241 mg, 93% yield. **6** was analyzed by GC-MS, ^{1}H NMR and authentic sample of commercially available material.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.14 (m, 4H), 5.27 (s, 1H), 3.71-3.54 (m, 4H), 1.27–1.23(t, *J* = 7.2 MHz, 6H).

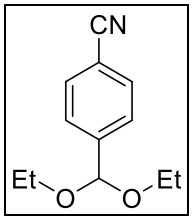


1-(Diethoxymethyl)-4-iodobenzene(7)[23]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **7** as a colorless oil, 278 mg, 91% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.22 (m, 2H), 5.45 (s, 1H), 3.64–3.46 (m, 4H), 1.23 (t, *J* = 7.0, 6H).



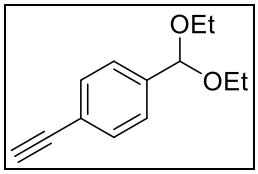
1-(Diethoxymethyl)-4-(trifluoromethyl)benzene(8)[2]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **8** as a colorless oil, 223 mg, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.55 (m, 4H), 5.55 (s, 1H), 3.64–3.52 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).



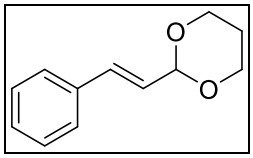
4-(Diethoxymethyl)benzonitrile(9)[2]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether/ethyl acetate to afford **9** as a colorless oil, 168 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 2H), 5.55 (s, 1H), 3.65–3.52 (m, 4H), 1.25 (t, *J* = 7.0 Hz, 6H).



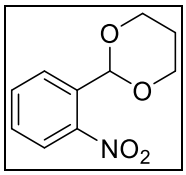
1-(Diethoxymethyl)-4-ethynylbenzene(10)[5]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **10** as a yellow solid, 153 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 5.49 (s, 1H), 3.62–3.49 (m, 4H), 3.08 (s, 1H), 1.23 (t, *J* = 7.1 Hz, 6H).



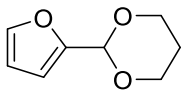
(*E*)-2-styryl-1,3-dioxane(11)[6, 8]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **11** as a brown oil, 129 mg, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.74 (m, 5 H), 6.72–6.77 (d, *J* = 16 Hz, 1 H), 6.17–6.24 (m, 1 H), 5.11–5.14 (m, 1 H), 4.06–4.12 (m, 2 H), 3.80–3.90 (m, 2 H), 1.92–2.09 (m, 1 H), d = 1.32–1.40 (m, 1 H).

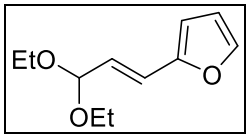


2-(2-Nitrophenyl)-1,3-dioxane(12)[7]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **12** as a colorless oil, 199 mg, 95% yield.

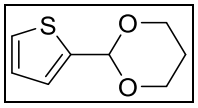
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.88 (m, 2H), 7.62 (m, 1H), 7.44 (m, 1H), 5.89 (s, 1H), 3.13 (m, 2H), 2.93 (m, 2H), 2.20 (m, 1H), 1.99 (m, 1H).



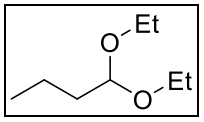
2-(Furan-2-yl)-1,3-dioxane(13)[8]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **13** as a yellow oil, 125 mg, 81% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 1.8-0.9, 1 H,), 6.39 (m, 2 H), 5.92 (s, 1H), 4.06 (m, 4 H).



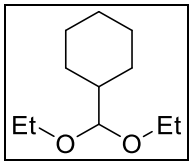
(*E*)-2-(3,3-diethoxyprop-1-en-1-yl)furan(14)[22]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **14** as a brown oil, 163 mg, 83% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 6.62-5.44 (m, 3H), 6.31 (d, *J* =15.8 Hz, 1H), 5.70 (m, 1H), 3.68 (q, *J* =7.0 Hz, 4H), 1.23 (t, *J* =7.0 Hz, 6H).



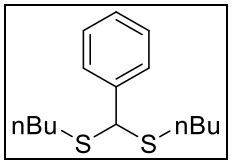
2-(Thiophen-2-yl)-1,3-dioxane(15)[10]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **15** as a colorless oil, 143 mg, 84% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.75 (s, 1H), 4.26 (ddd, *J* = 11.9, 4.9, 1.2 Hz, 2H), 3.99 (ddd, *J* = 12.2, 3.8, 2.5 Hz, 2H), 2.32–2.12 (m, 1H), 1.44 (m, 1H).



1,1-Diethoxybutane(16)[4]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **16** as a colorless oil, 111 mg, 76% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.47-4.44 (t, *J* = 5.6 MHz, 1H), 3.64–3.41 (m, 4H), 1.58-1.32 (m, 4H), 1.16 (t, *J* = 7.2 MHz, 6H), 0.90 (t, *J* = 7.2MHz, 3H)

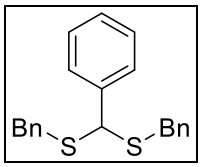


(Diethoxymethyl)cyclohexane(17)[4]: compound **17** was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **17** as a colorless oil, 193 mg, 93% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (d, *J* = 7.2 Hz, 1H), 3.66–3.43 (m, 4H), 1.80–1.43 (m, 8H), 1.37–1.11 (m, 7H), 1.00 (t, *J* = 7.3 Hz, 2H).



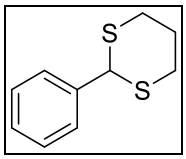
(Phenylmethylene)bis(butylsulfane)(18)[16]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **18** as a colorless oil, 11.6 g, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.34–7.29 (m, 2H), 7.27–7.22 (m, 1H), 4.87 (s, 1H), 2.54 (ddt, *J* = 29.3, 12.5, 7.4 Hz, 4H), 1.58–1.48 (m, 4H), 1.41–1.31 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H).



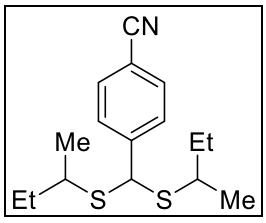
(Phenylmethylene)bis(benzylsulfane)(19)[12]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **19** as a colorless solid, 309 mg, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 4H), 7.26–7.22 (m, 7H), 7.17–7.12 (m, 4H), 4.45 (s, 1H), 3.77 (d, *J* = 13.4 Hz, 2H), 3.55 (d, *J* = 13.4 Hz, 2H).



2-Phenyl-1,3-dithiane(20)[9]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **20** as a colorless solid, 184 mg, 94% yield.

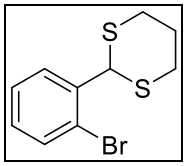
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.37–7.27 (m, 3H), 5.17 (s, 1H), 3.13–3.02 (m, 2H), 2.92 (ddd, *J* = 14.6, 4.2, 3.2 Hz, 2H), 2.22–2.13 (m, 1H), 1.94 (dtt, *J* = 14.2, 12.4, 3.1 Hz, 1H).



4-(Bis(sec-butylthio)methyl)benzonitrile(21): was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **21** as a yellow oil, 223 mg, 76% yield.

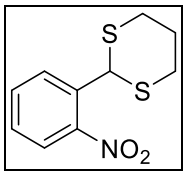
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 –7.56 (m, 4H), 4.91 (s, 1H), 2.73 (dddd, *J* = 46.5, 16.0, 13.2, 6.7 Hz, 2H), 1.64 –1.38 (m, 4H), 1.22 (dd, *J* = 6.9, 1.4 Hz, 6H), 0.97–0.87 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 132.3, 128.6, 118.6, 111.3, 50.1, 42.8, 29.4, 20.6, 11.1.

HRMS: calculated for $C_{16}H_{24}S_2N^+$: $[M+H]^+$ 294.1350, found 294.1368.



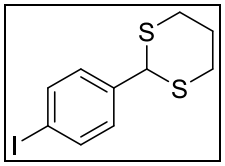
2-(2-Bromophenyl)-1,3-dithiane(22)[9]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **22** as a colorless solid, 253 mg, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.33 (td, *J* = 7.7, 1.1 Hz, 1H), 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 5.60 (s, 1H), 3.18–3.08 (m, 2H), 2.93 (dt, *J* = 7.3, 3.9 Hz, 2H), 2.19 (dtd, *J* = 13.6, 4.3, 2.2 Hz, 1H), 1.95 (ddd, *J* = 6.0, 4.5, 3.0 Hz, 1H).



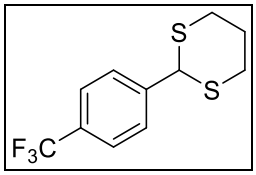
2-(2-Nitrophenyl)-1,3-dithiane(23)[11]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether/ethyl acetate to afford **23** as a colorless solid, 236 mg, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.86 (m, 2H), 7.64–7.59 (m, 1H), 7.47–7.41 (m, 1H), 5.88 (s, 1H), 3.17–3.06 (m, 2H), 2.93 (dt, *J* = 7.4, 4.0 Hz, 2H), 2.24–2.16 (m, 1H), 1.94 (dt, *J* = 4.7, 2.9 Hz, 1H).



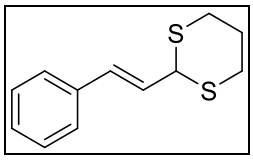
2-(4-Iodophenyl)-1,3-dithiane(24)[9]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **24** as a colorless solid, 270 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.21 (t, *J* = 5.3 Hz, 2H), 5.10 (s, 1H), 3.10–3.00 (m, 2H), 2.91 (dt, *J* = 7.5, 4.1 Hz, 2H), 2.17 (dtt, *J* = 14.0, 4.6, 2.5 Hz, 1H), 1.97–1.85 (m, 1H).

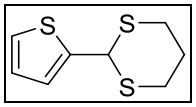


2-(4-(Trifluoromethyl)phenyl)-1,3-dithiane(25)[9]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **25** as a colorless solid, 256 mg, 97% yield.

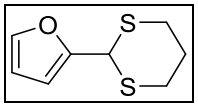
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 4H), 5.20 (s, 1H), 3.14–3.02 (m, 2H), 2.99–2.88 (m, 2H), 2.26–2.12 (m, 1H), 2.03–1.87 (m, 1H).



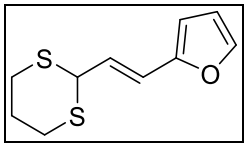
(*E*)-2-Styryl-1,3-dithiane(26)[17]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **26** as a brown oil, 211 mg, 95% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.40 (5H, m), 6.76 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.82 (d, *J* = 7.6Hz, 1H), 2.83–2.99 (4H, m), 2.11–2.16 (1H, m), 1.89–1.95 (1H, m).



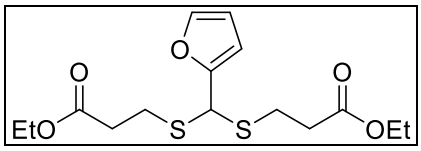
2-(Thiophen-2-yl)-1,3-dithiane(27)[17]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **27** as a yellow solid, 180 mg, 89% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.17–7.15 (m, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.41 (s, 1H), 3.00 (t, *J* = 3.5 Hz, 1H), 2.96 (dd, *J* = 4.1, 2.4 Hz, 2H), 2.94 (t, *J* = 4.3 Hz, 1H), 2.19–2.12 (m, 1H), 1.97 (ddd, *J* = 10.2, 5.0, 2.6 Hz, 1H).



2-(1,3-Dithian-2-yl)furan(28)[18]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **28** as a yellow oil, 158 mg, 85% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 1H), 6.38 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 5.21 (s, 1H), 2.94 (dd, *J* = 7.4, 3.3 Hz, 4H), 2.16–2.07 (m, 1H), 2.02–1.91 (m, 1H).

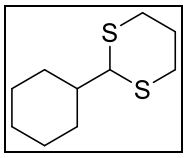


(*E*)-2-(2-(1,3-dithian-2-yl)vinyl)furan(29)[19]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **29** as a yellow oil, 11.6 g, 91% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 1H), 6.38 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 5.21 (s, 1H), 2.94 (dd, *J* = 7.4, 3.3 Hz, 4H), 2.16–2.07 (m, 1H), 2.02–1.91 (m, 1H).

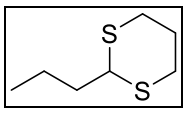


Diethyl 3,3'-((furan-2-ylmethylene)bis(sulfanediyl))dipropionate(30): was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **30** as a yellow oil, 304 mg, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 –7.33 (m, 1H), 6.36 (d, *J* = 3.3 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.03 (s, 1H), 4.14 (t, *J* = 7.1 Hz, 4H), 2.98 – 2.74 (m, 4H), 2.56 (t, *J* = 7.3 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 151.3, 142.5, 110.5, 108.1, 60.71, 46.20, 34.51, 26.39, 14.16. **HRMS** calculated for $C_{15}H_{22}O_5S_2Na^+$: $[M+Na]^+$ 369.0806, found 369.0816.



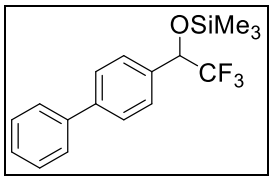
2-Cyclohexyl-1,3-dithiane(31)[9]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **31** as a colorless oil, 182 mg, 90% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (d, *J* = 5.4 Hz, 1H), 2.90–2.84 (m, 4H), 2.14–2.06 (m, 1H), 1.93–1.86 (m, 2H), 1.78–1.71 (m, 2H), 1.69–1.60 (m, 3H), 1.28–1.19 (m, 4H), 1.01 (t, *J* = 7.3 Hz, 1H).



2-Propyl-1,3-dithiane(32)[10]: was prepared on a 1 mmol scale following the general procedure, and purified by petroleum ether to afford **32** as a colorless oil, 133 mg, 82% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.9 Hz, 1H), 2.94–2.73 (m, 4H), 2.19–2.06 (m, 1H), 1.93–1.86 (m, 1H), 1.72 (dt, *J* = 12.8, 6.1 Hz, 2H), 1.55 (dt, *J* = 15.1, 4.4 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

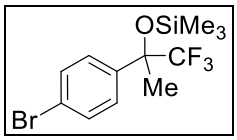
General procedure for trifluoromethylation of aldehyde and ketone

A divided H-type cell was equipped with a pair of graphite electrodes and connected to an electrochemical workstation regulated power supply. To the anodic chamber was added aldehydes (1 mmol), Bu_4NClO_4 (17.1 mg, 0.0500 mmol), CF_3SiMe_3 (0.30 g, 1.5 mmol) and 5 mL MeCN solvent. The cathodic chamber was added Bu_4NClO_4 (17.1 mg, 0.0500 mmol) and 5 mL MeCN. The mixture was electrolyzed under constant current (2 mA) at room temperature with magnetic stirring for 1 hour, and then a partial solution was filtered through a short silica gel column for GC and GC-MS analysis. The combined solution was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford the trifluoromethylated products.



(1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethoxy)trimethylsilane(33)[20, 21]: was prepared on a 1 mmol scale following the general procedure described above, and purified by petroleum ether to afford **33** as a colorless oil, 230 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.67 (m, 9H), 4.99 (q, J = 6.5 Hz, 1H), 0.17 (s, 9H).



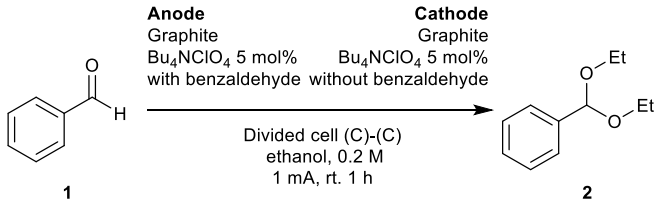
((2-(4-Bromophenyl)-1,1,1-trifluoropropan-2-yl)oxy)trimethylsilane(34)[21]: was prepared on a 1 mmol scale following the general procedure described above. Purification by using petroleum ether as eluent afforded **34** as a colorless oil, 11.6 g, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.53 (m, 2H), 7.38-7.44 (m, 2H), 1.80 (d, J =1.1 Hz, 3H), 0.16 (s, 9H).

Control experiments of electrolysis time and yield of acetal

The electrochemical acetalization reaction of **1** in ethanol was carried out on 1 mmol scale according to the general reaction set-up. The reaction mixture was electrolysed for a short period (2 min, 5 min and 10 min entry 1-3), followed by rigid stirring, gave acetal product **2** in good yield. For entries 4-10, we analyzed the yield of acetal **2** in reaction mixture after electrolysis for 5 min (entry 4, measured immediately, 13% yield), then we measured the yield of product **2** every 30 min (entries 5-10), during which the current was off. These results suggest that the initial anodic activation produced some reactive catalytic species in the reaction, which promoted the acetalization reaction. There was no reaction without anodic activation (entry 11).

Table S2. Control-experiments of electrolysis time and yield of 2 [a]



Entry	Anode	Electrolysis time	Temp.(°C)	Current (mA)	Time	Yield (%) [b]
1	Graphite	2 min	25	1	2 h	77
2	Graphite	5 min	25	1	2 h	72
3	Graphite	10 min	25	1	2 h	82
4 [c]	Graphite	5 min	25	1	5 min	13
5 [c]	Graphite	5 min	25	1	0.5 h	43
6 [c]	Graphite	5 min	25	1	1.0 h	57
7 [c]	Graphite	5 min	25	1	1.5 h	61
8 [c]	Graphite	5 min	25	1	2.0 h	63
9 [c]	Graphite	5 min	25	1	2.5 h	62
10 [c]	Graphite	5 min	25	1	3.0 h	64
11	Graphite	0	25	0	2 h	0

[a] Conditions: **1** (1.0 mmol), ammonium salt (5 mol %), ethanol (5 mL) [anode], ammonium salt (5 mol %), ethanol (5 mL) [cathode] in an H-type divided cell with two electrodes and a Nafion-117 membrane, under air. [b] After the stirring, dodecane was added and the reaction solution passed through a short silica column for GC analysis. [c] For entries 4-10, dodecane was added at the beginning of reaction set-up, a small portion of reaction solution was measured at 5 min and then every 30 min.

Computational details

All calculations presented in this work are performed using the generalized gradient approximation (GGA)-Perdew, Burke and Ernzerhof (PBE)[24] as implemented in the all-electron DMol3 code[25, 26]. Double numerical plus polarization (DNP) basis set was used throughout the calculation. The convergence criteria were set to be $2x10^{-5}$ Ha, 0.004 HaÅ^{-1}, and 0.005 Å for energy, force, and displacement convergence, respectively. A self-consistent field (SCF) density convergence with a threshold value of $1x10^{-6}$ Ha was specified. All electronic property analyses

are deal with Multiwfn software, a program for realizing electronic wavefunction analysis[27]. single point energy calculation also carried out for all stationary points using Gaussian09 software[28], with the aim of getting wave function files needed for the qualitative analysis the electronic character of all intermediates using Multiwfn.

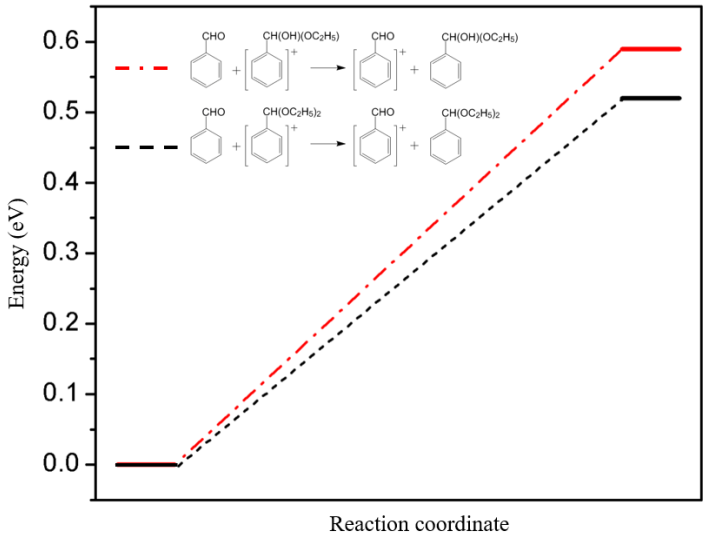


Figure S3. Cation ion exchange of benzaldehyde with [hemiacetal]$^+$ or [acetal]$^+$.

$$\Delta E_{trans}(\text{black}) = E(\text{benzaldehyde})^+ + E(\text{acetal}) - [E(\text{benzaldehyde}) + E(\text{acetal})^+] = 0.52 \text{ eV}$$

$$\Delta E_{trans}(\text{red}) = E(\text{benzaldehyde})^+ + E(\text{hemiacetal}) - [E(\text{benzaldehyde}) + E(\text{hemiacetal})^+] = 0.59 \text{ eV}$$

The above DFT calculation suggests that cation ion exchange between benzaldehyde and [acetal]$^+$ is the more favorable pathway than benzaldehyde with [hemiacetal]$^+$.

The electron transfer energy (ΔE_{trans}) have been calculated by the following formula:

$$\Delta E_{trans} = E(\text{benzaldehyde})^+ + E(\text{hemiacetal or acetal}) - [E(\text{benzaldehyde}) + E(\text{hemiacetal or acetal})^+]$$

Where $E(\text{benzaldehyde})^+$ represents the energy of benzaldehyde with a positive charge, E(hemiacetal or acetal) represents the energy of hemiacetal or acetal, E(benzaldehyde) represents the energy of benzaldehyde and $E(\text{hemiacetal or acetal})^+$ represents the energy of hemiacetal or acetal with a positive charge. Calculated ΔE_{trans} for cation ion exchange between benzaldehyde with positive charged hemiacetal or acetal indicates that the benzaldehyde is more prone to transfer an electron to the positive charged acetal than the positive charged hemiacetal, thereby providing the essential reactant (positive charged benzaldehyde) for this reaction, ensuring the smooth progress of the reaction.

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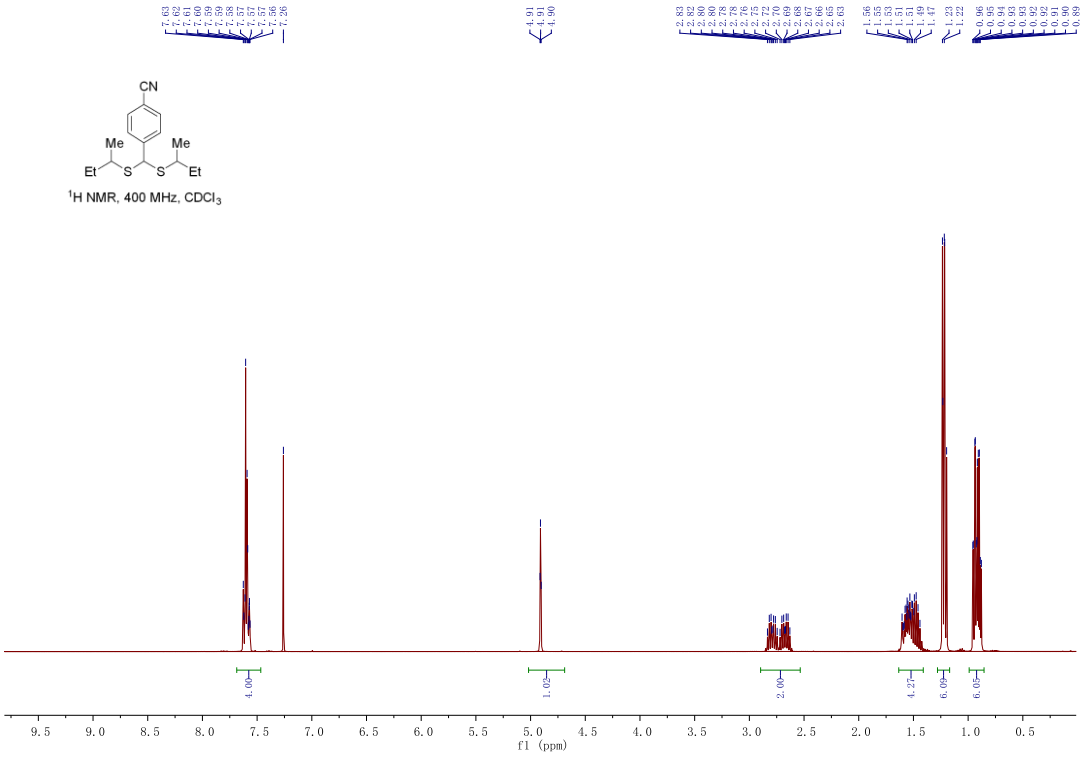
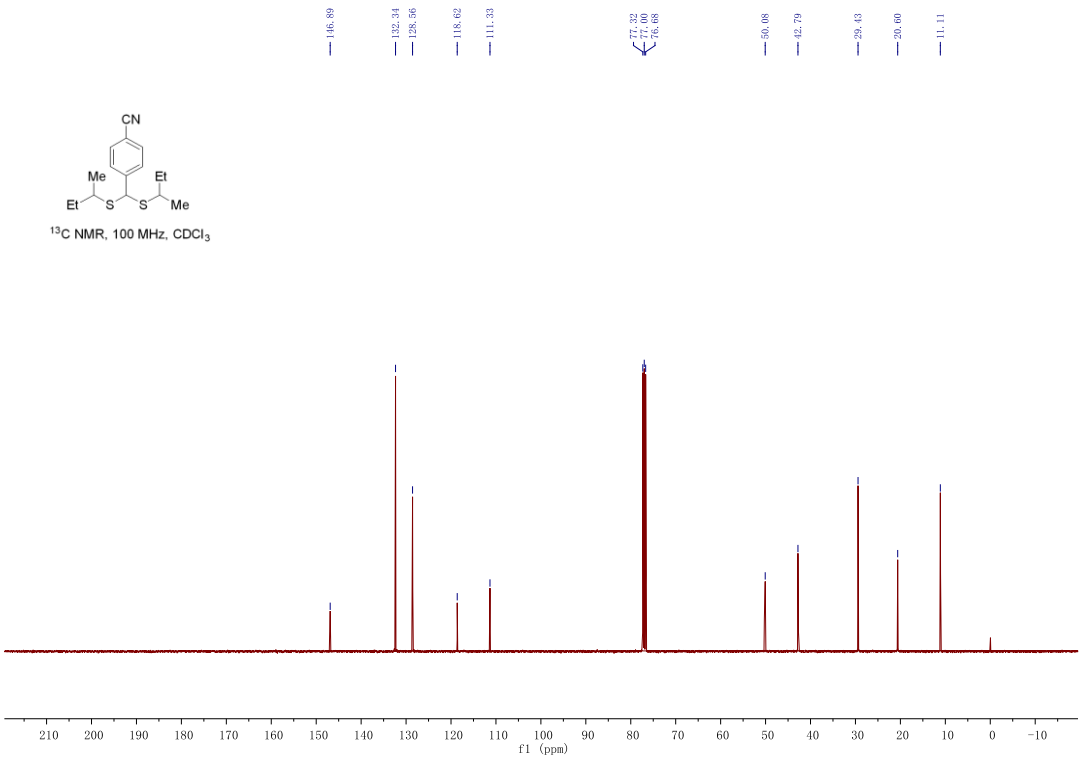
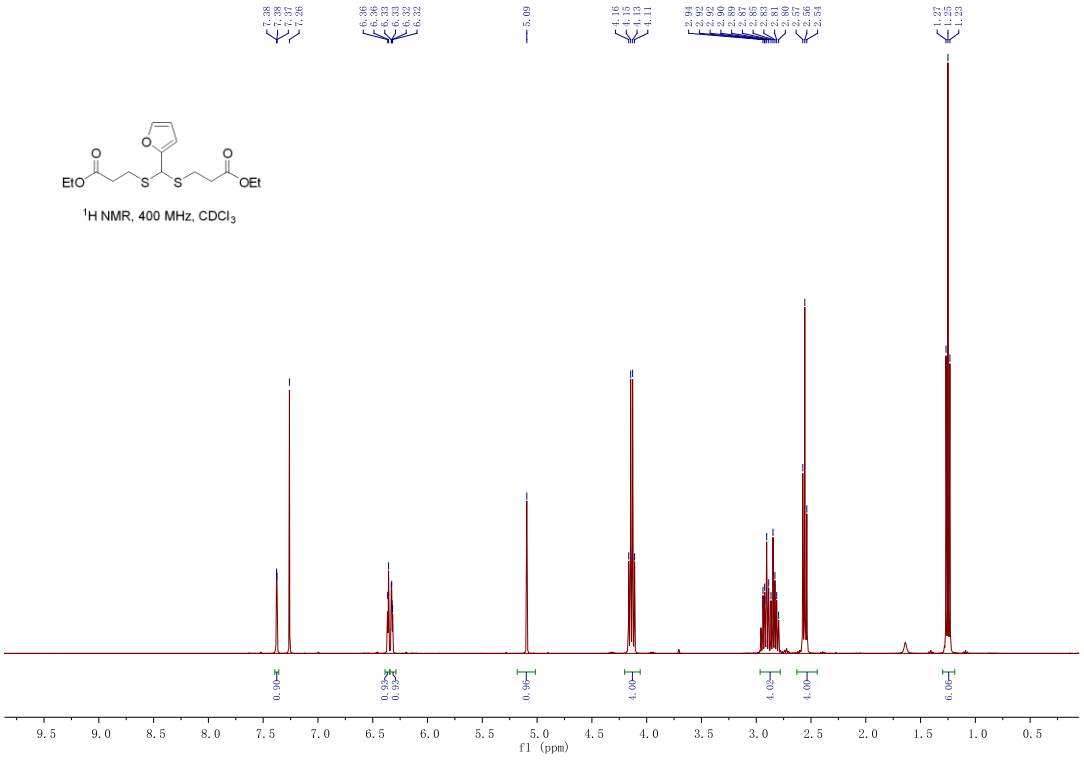
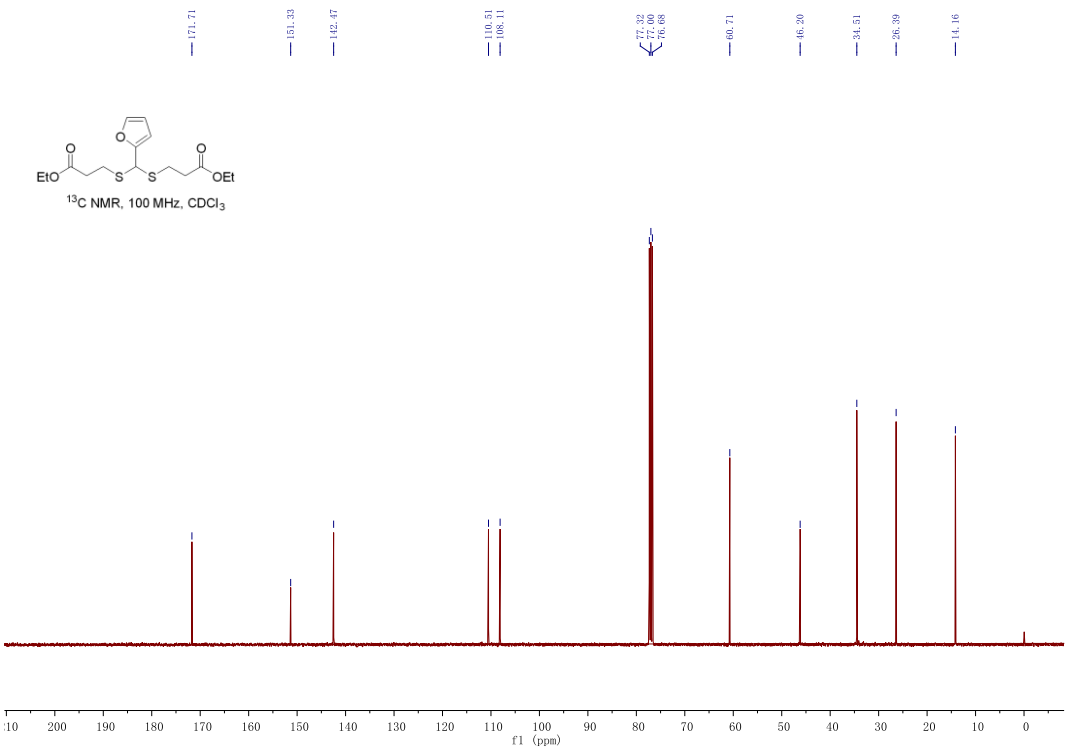
Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

NMR Spectra




146.89
132.34
128.56
118.62
111.33
77.32
77.00
76.68
50.08
42.79
29.43
20.60
11.11
CN
Me
Et
Et
S
S
Me
13C NMR, 100 MHz, CDCl3
f1 (ppm)


7.38
7.38
7.37
7.26
6.36
6.36
6.33
6.33
6.32
6.32
5.09
4.16
4.15
4.13
4.11
2.94
2.92
2.92
2.90
2.89
2.87
2.85
2.83
2.81
2.80
2.57
2.56
2.54
1.27
1.25
1.23
O
EtO
S
S
O
OEt
1H NMR, 400 MHz, CDCl3
0.90
0.95
0.95
0.96
4.00
4.02
4.00
6.06
f1 (ppm)


171.71
151.33
142.47
110.51
108.11
77.32
77.00
76.68
60.71
46.20
34.51
26.39
14.16
EtO
OEt
^{13}C NMR, 100 MHz, CDCl$_3$
f1 (ppm)