

Supporting Information

High potential of new dyeing photoinitiators for fast curing of (meth)acrylate compositions upon UV-Vis low light intensity

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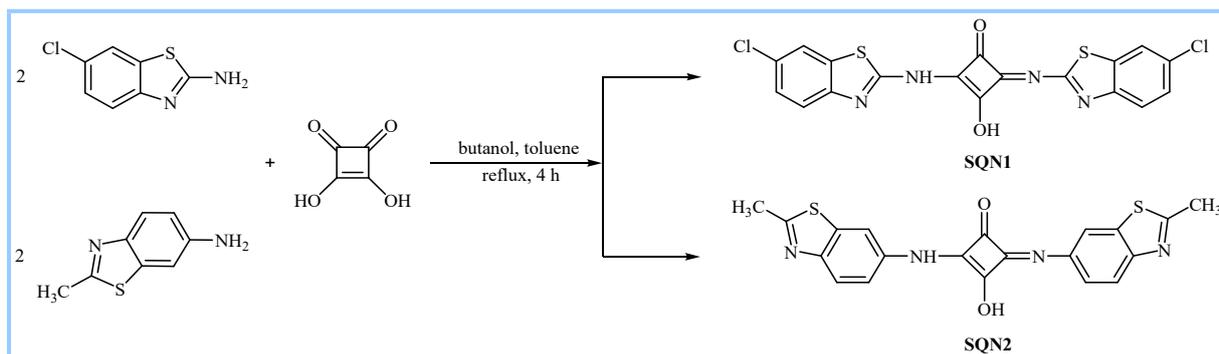
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1. Synthesis procedure

Sensitizers

Two different 1,3-bis(arylamino)squaraines used as sensitizers in photoinitiating systems under study were synthesized by the Knoevenagel condensation of two molar equivalents of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid). The general procedure for the preparation of target compounds, such as: 1,3-bis(6-chlorobenzothiazolamino)squaraine (SQN1) and 1,3-bis(2-methylbenzothiazolamino)squaraine (SQN2) is presented in Scheme S1.



Scheme S1 Preparation of squaraine derivatives.

1,3-bis(6-chlorobenzothiazolamino)squaraine (SQN1)

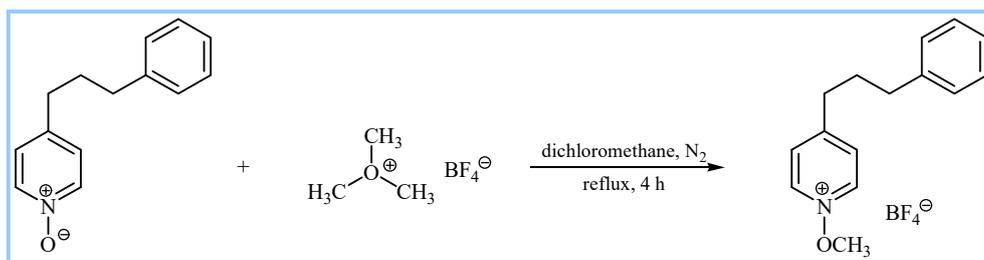
3,4-Dihydroxycyclobut-3-ene-1,2-dione (0.29 g; 2.5 mmol) was heated under reflux in a mixture of anhydrous solvents, i.e.: 1-butanol (40 ml) and toluene (20 ml). The water formed during reaction was distilled azeotropically using a Dean-Stark trap. After 1 h, 2-amine-6-chlorobenzothiazole (0.92 g; 5.0 mmol) was added and the reaction mixture was refluxed for additional 4 h. In the next step, the reaction mixture was cooled and the solvent removed under vacuum. The obtained solid was dried at ambient temperature.

1,3-bis(2-methylbenzothiazolamino)squaraine (SQN2)

3,4-Dihydroxycyclobut-3-ene-1,2-dione (0.29 g; 2.5 mmol) was heated under reflux in a mixture of anhydrous solvents, i.e.: 1-butanol (40 ml) and toluene (20 ml). The water formed during the reaction was distilled azeotropically using a Dean-Stark trap. After 1 h, 6-amine-2-methylbenzothiazole (0.82 g; 5.0 mmol) was added and the reaction mixture was refluxed for additional 4 h. In the next step, the reaction mixture was cooled and the solvent removed under vacuum. The obtained solid was dried at ambient temperature.

Co-initiator

Novel *N*-alkoxy pyridinium salt was prepared by *O*-alkylation of pyridine *N*-oxide with trimethyloxonium tetrafluoroborate. The general route of synthesis of *N*-methoxy-4-(3-phenylpropyl)pyridinium tetrafluoroborate (NO1) is shown in Scheme S2.



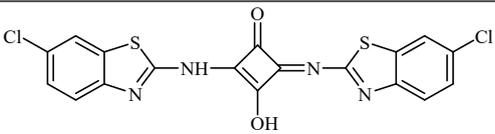
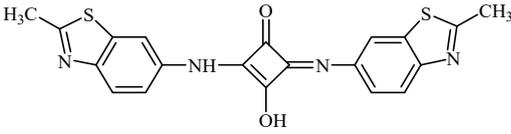
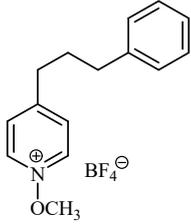
Scheme S2. Preparation of *N*-alkoxy pyridinium salt (NO1).

N-methoxy-4-(3-phenylpropyl)pyridinium tetrafluoroborate (NO1)

A mixture of 4-(3-phenylpropyl)pyridine *N*-oxide (1.35 g; 6.3 mmol) and trimethyloxonium tetrafluoroborate (1.07 g; 7.2 mmol) in 30 ml of dry dichloromethane was refluxed 4h under nitrogen. Then, the solvent was evaporated under vacuum to obtain a crude product.

2. Physicochemical data

Table S1 Physicochemical data of synthesized compounds.

Compound	Abbreviation	Physicochemical data
 1,3- <i>bis</i> (6-chlorobenzothiazolamino)squaraine	SQN1	¹H NMR: 4.19 (s, 1H, -NH), 7.28-7.30 (dd, 1H, Ar), 7.33-7.36 (d, 1H, Ar), 7.43-7.45 (dd, 1H, Ar), 7.70-7.73 (d, 1H, Ar), 7.83-7.84 (s, 1H, Ar), 8.07-8.08 (s, 1H, Ar), 8.15-8.16 (s, 1H, -OH) ¹³C NMR: 118.28, 120.76, 121.55, 122.32, 125.88, 126.54, 127.38, 128.14, 131.39, 133.22, 147.52, 148.78, 162.74, 168.20, 171.59, 186.92, 196.09 Yield: 82.7% M.p. > 305°C (decomposition)
 1,3- <i>bis</i> (2-methylbenzothiazolamino)squaraine	SQN2	¹H NMR: 2.80 (s, 6H, -CH ₃), 5.77 (s, 1H, -NH), 7.92-8.43 (s, 6H, Ar), 11.70 (s, 1H, -OH) Yield: 85.1% M.p. > 390°C (decomposition)
 <i>N</i> -methoxy-4-(3-phenylpropyl)pyridinium tetrafluoroborate	NO1	¹H NMR: 1.89-2.04 (tt, 2H, CH ₂), 2.60-2.66 (tt, 2H, CH ₂), 2.86-2.96 (tt, 2H, CH ₂), 4.40 (s, 3H, CH ₃), 7.17-7.31 (m, 5H, Ar), 7.89-7.91 (d, 1H, Ar, <i>J</i> ≈ 6.92 Hz), 8.11-8.13 (d, 1H, Ar, <i>J</i> ≈ 6.96 Hz), 8.80-9.34 (dd, 2H, Ar) ¹³C NMR: 31.16, 31.50, 34.01, 34.43, 34.79, 34.90, 69.85, 126.42, 128.08, 128.80, 129.18, 140.46, 141.69, 141.93, 162.44 Yield: 62.5%

3. ^1H NMR and ^{13}C NMR spectra

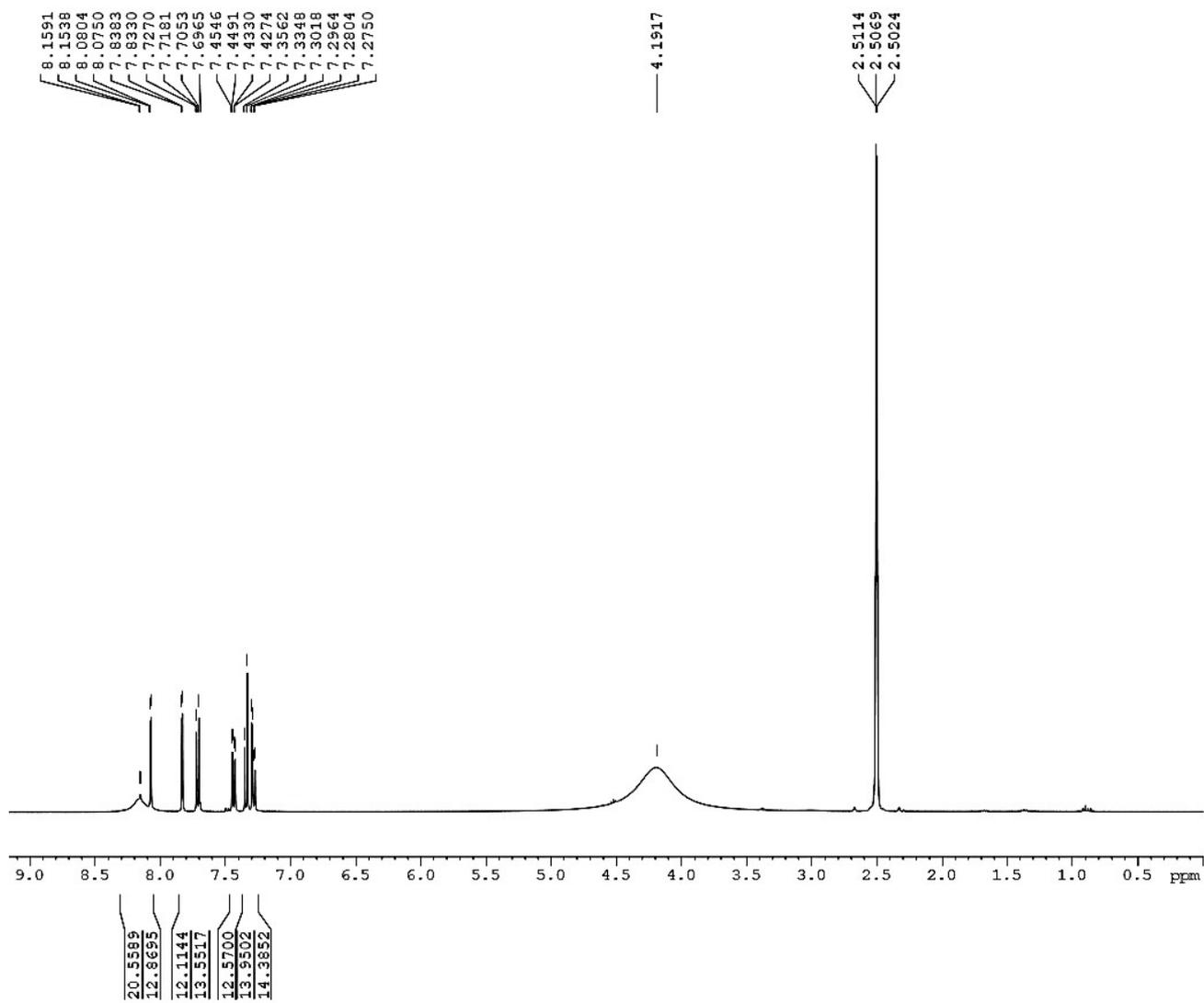


Fig. S1 ^1H NMR spectrum of 1,3-bis(6-chlorobenzothiazolamino)squaraine, SQN1.

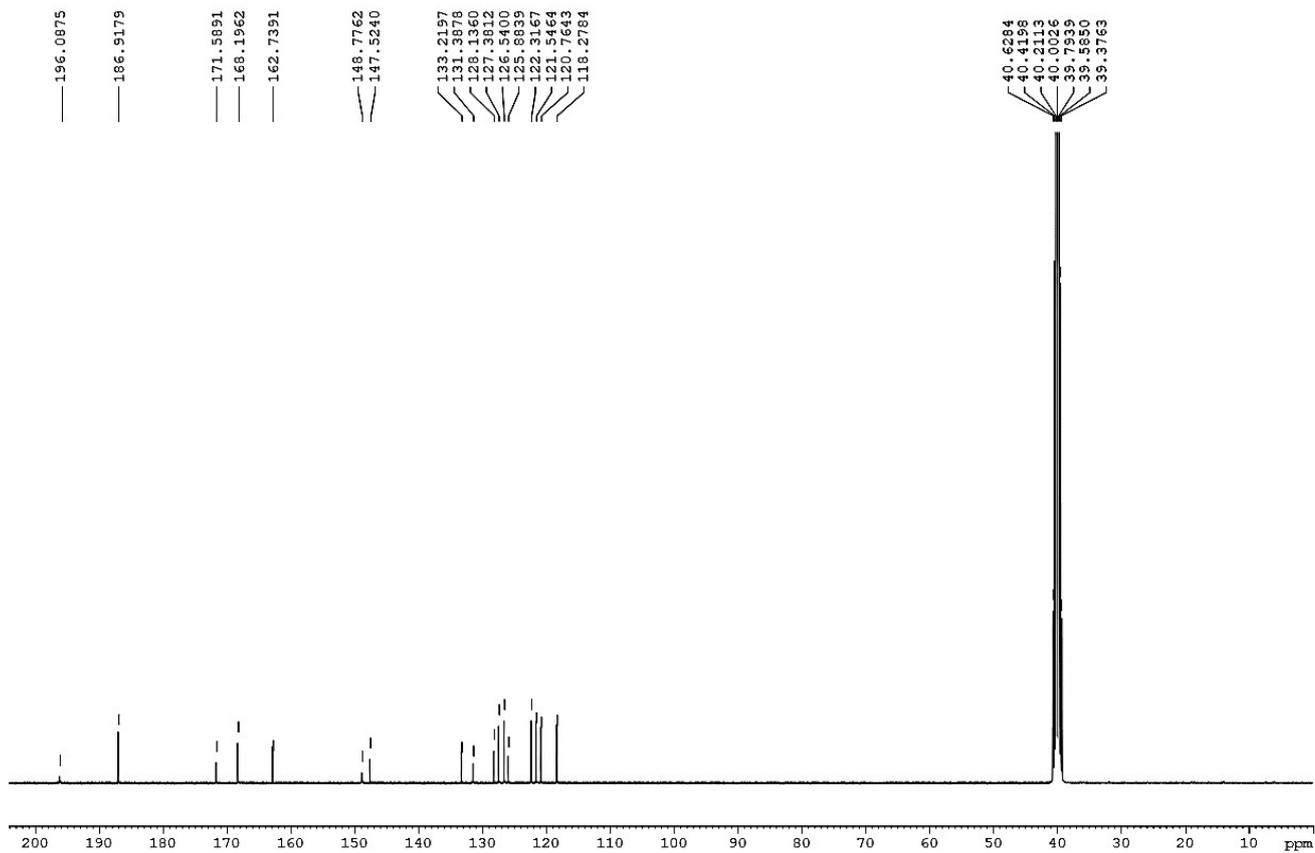


Fig. S2 ^{13}C NMR spectrum of 1,3-*bis*(6-chlorobenzothiazolamino)squaraine, SQN1.

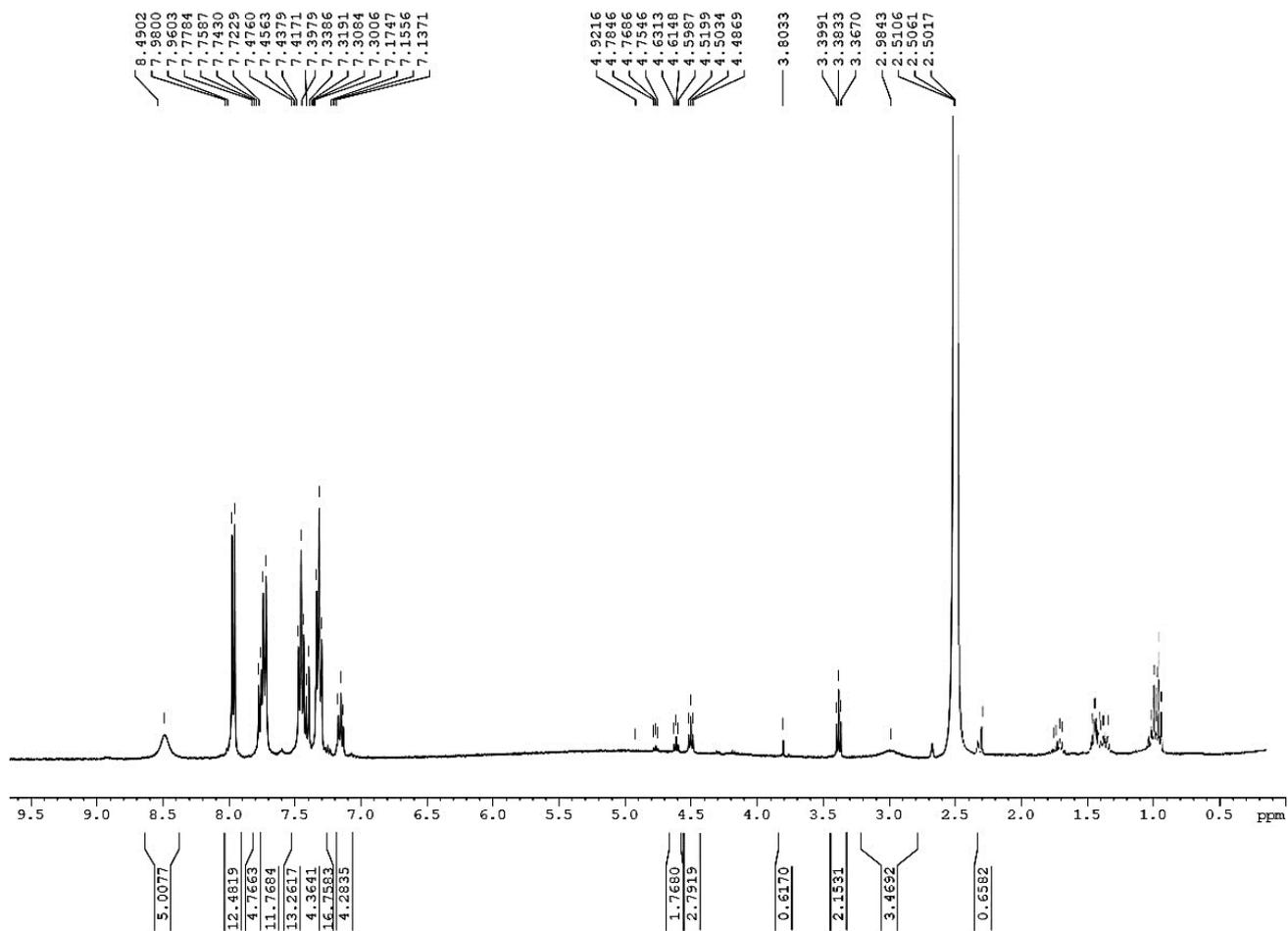


Fig. S3 ¹H NMR spectrum of 1,3-bis(2-methylbenzothiazolamino)squaraine, SQN2.

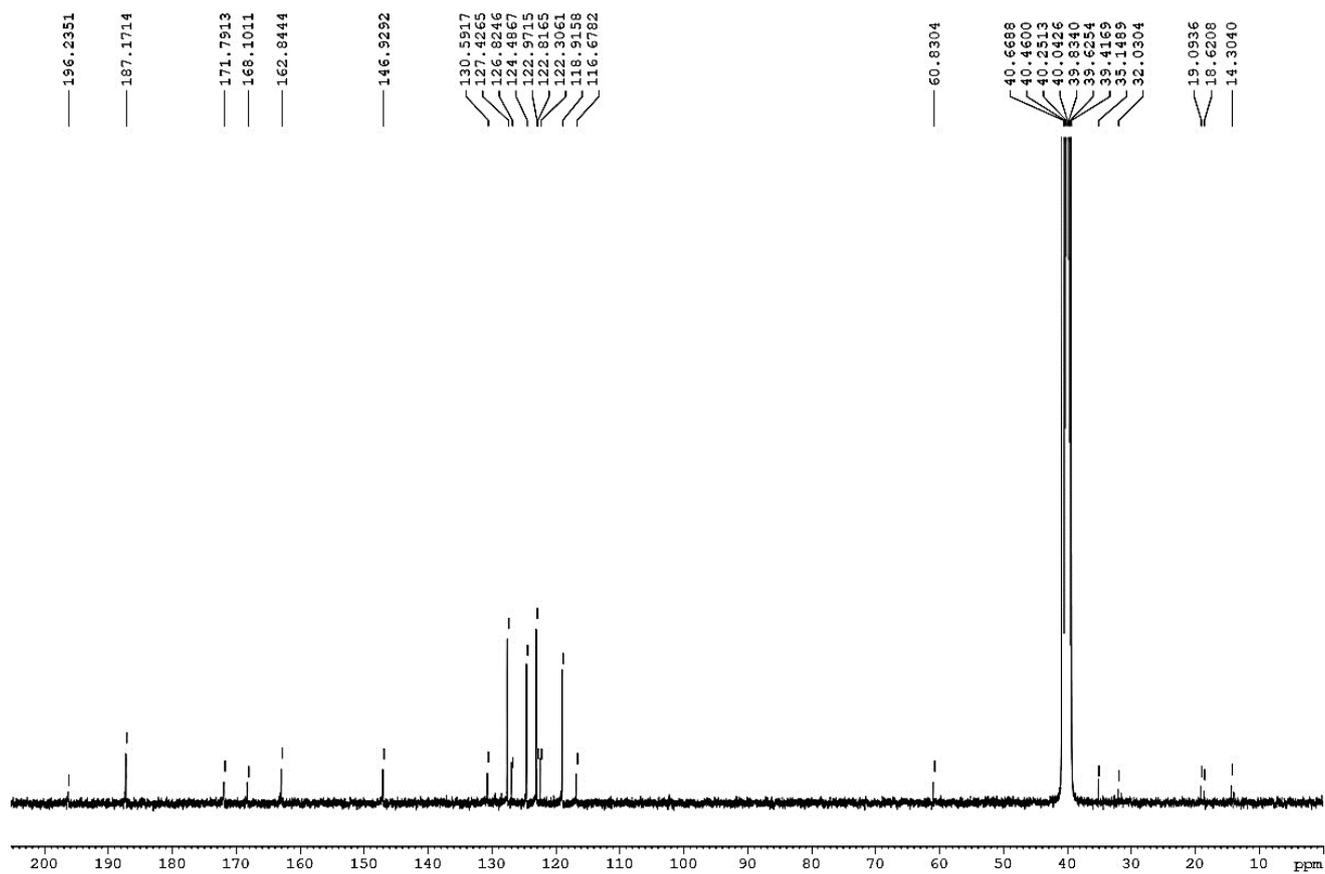


Fig. S4 ^{13}C NMR spectrum of 1,3-*bis*(2-methylbenzothiazolamino)squaraine, SQN2.

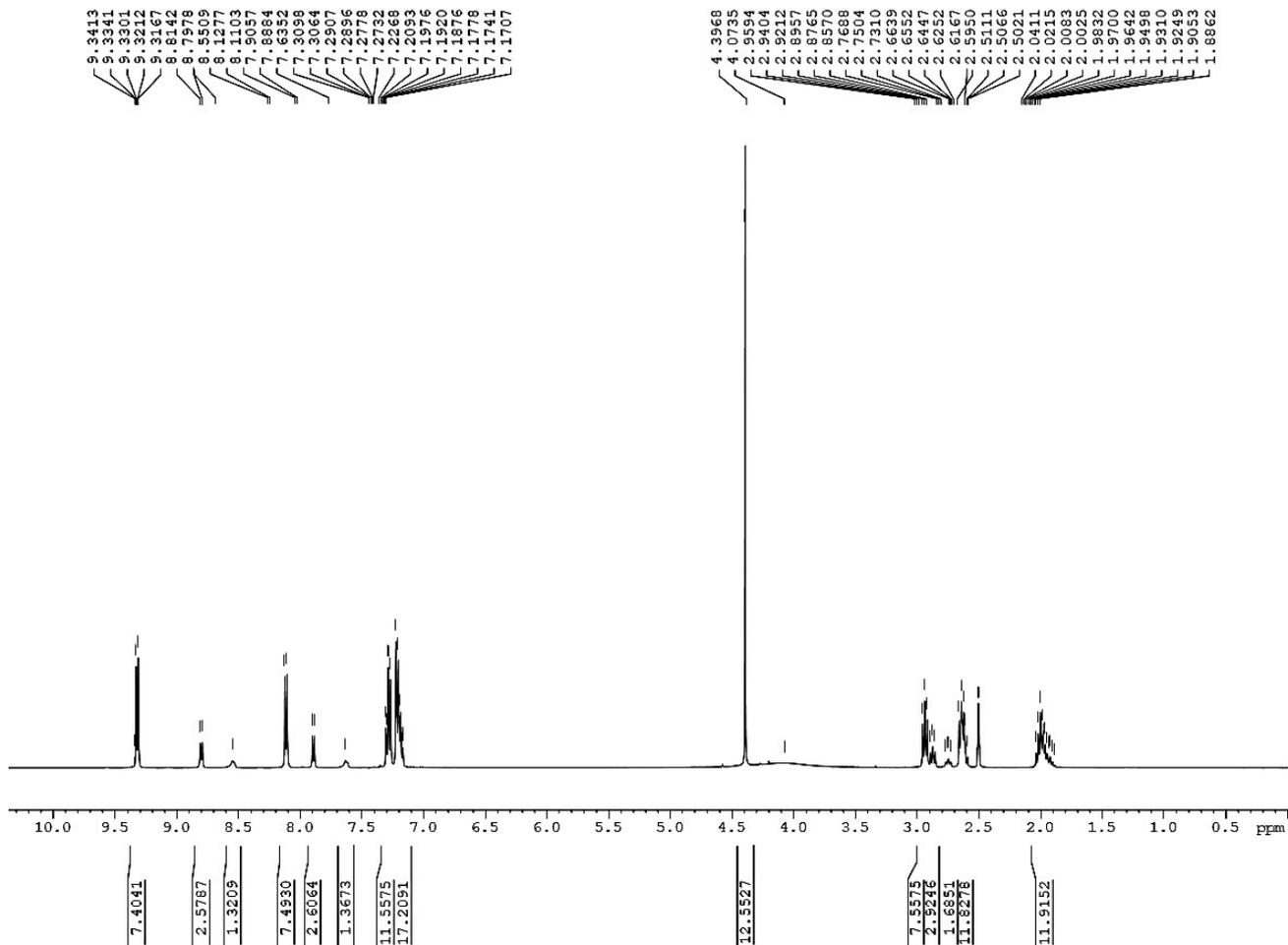


Fig. S5 ¹H NMR spectrum of *N*-methoxy-4-(3-phenylpropyl)pyridinium tetrafluoroborate, NO1.

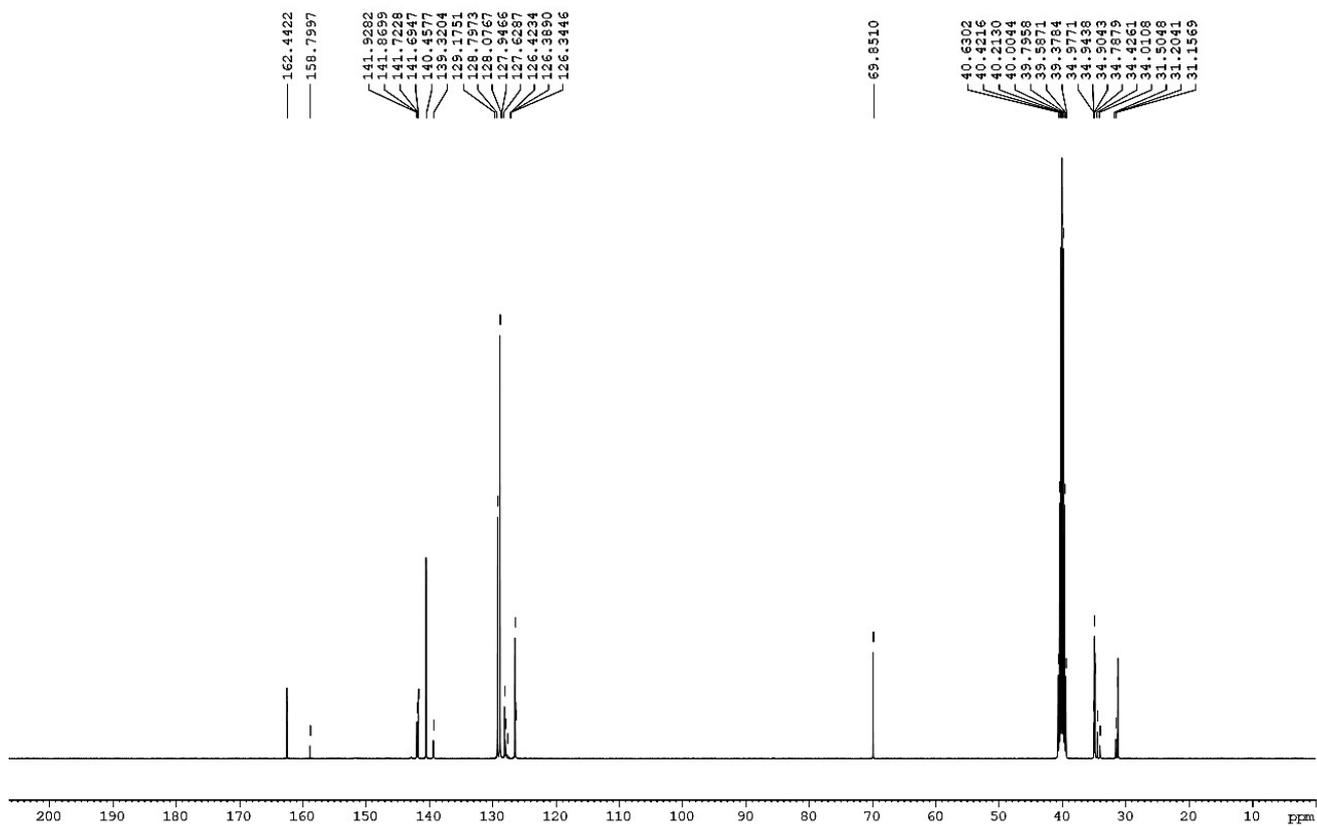


Fig. S6 ^{13}C NMR spectrum of *N*-methoxy-4-(3-phenylpropyl)pyridinium tetrafluoroborate, NO1.

4. Steady state photolysis

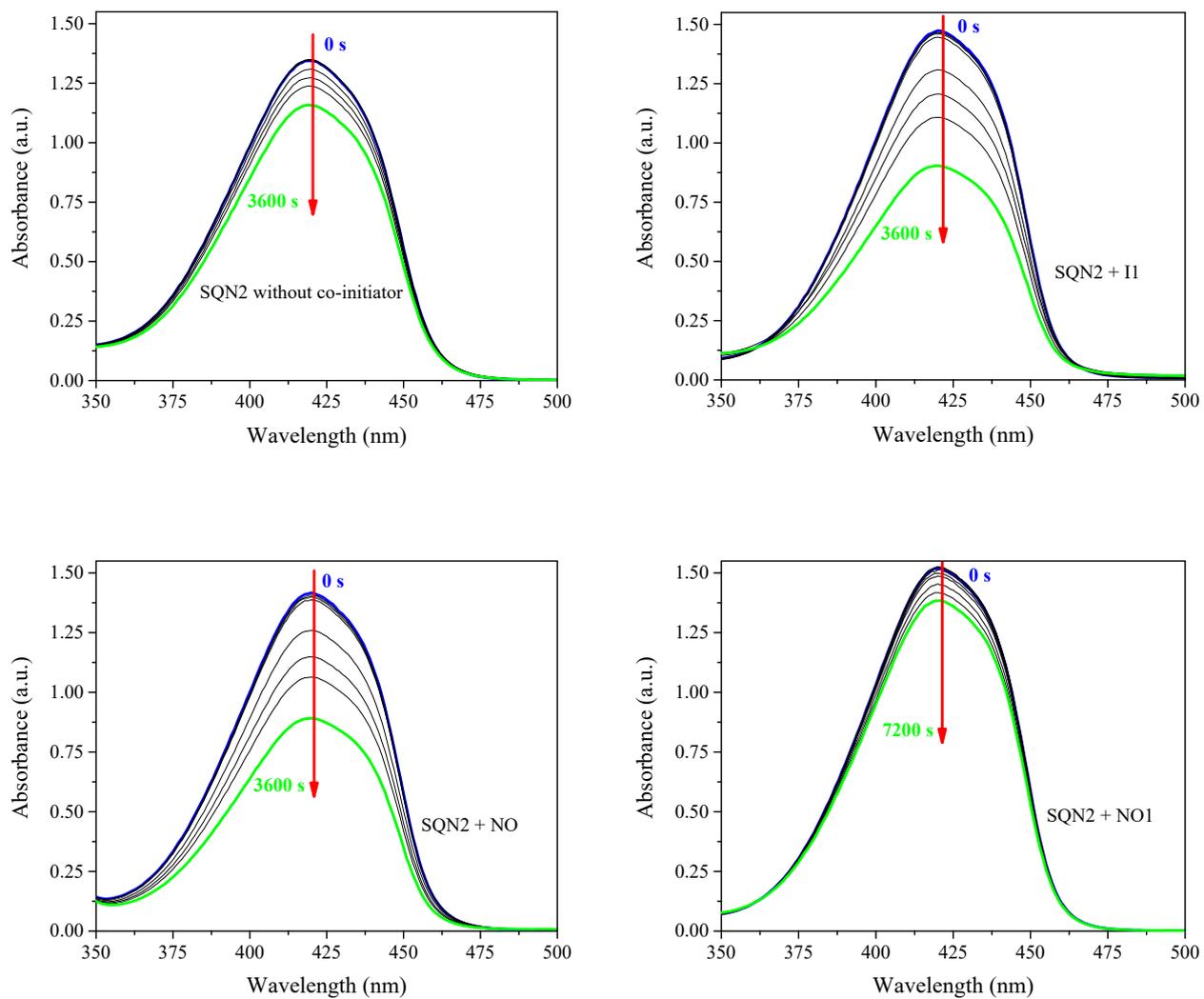


Fig. S7 The steady-state photolysis curves of SQN2 (alone and combined with onium salts) in *N,N*-dimethylformamide under irradiation at 518 nm; light intensity: 30 mW cm⁻², concentration of co-initiator: 1 × 10⁻³ M. The type of co-initiator was marked on the figure.

5. Cyclic voltammetry

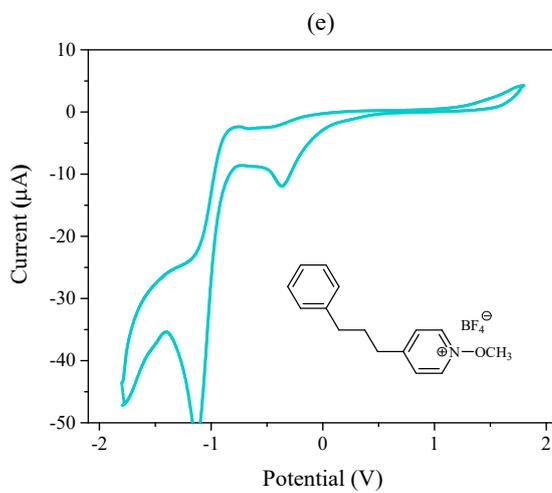
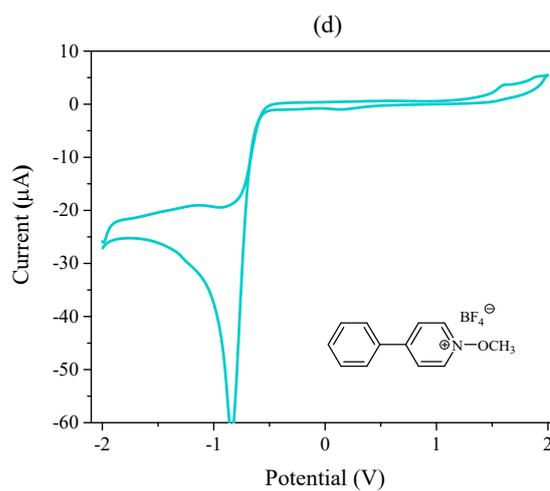
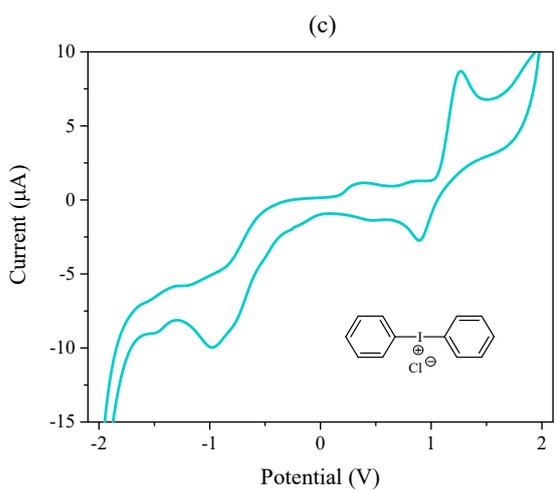
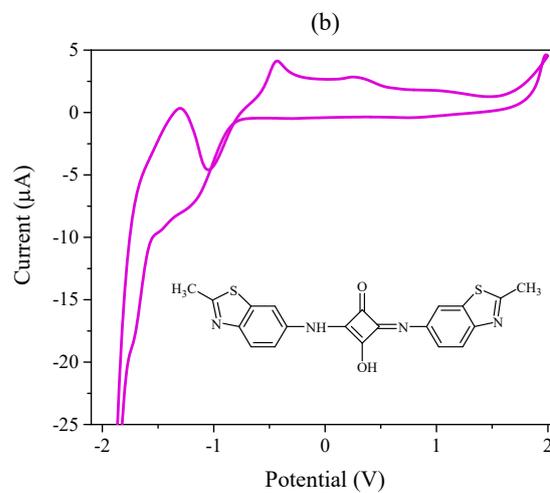
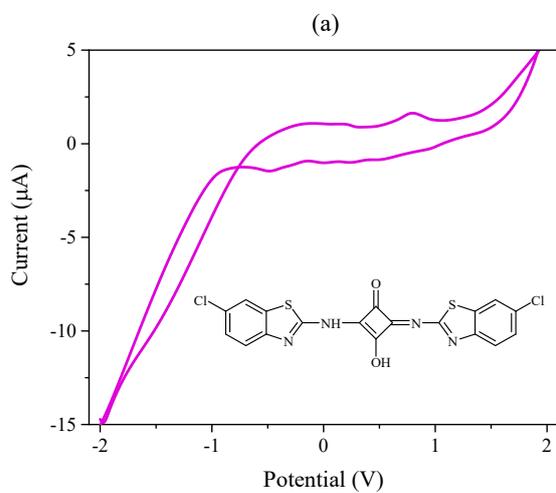


Fig. S8 Cyclic voltammograms of squaraines: (a) SQN1, (b) SQN2, and onium salts: (c) I1, (d) NO, (e) NO1, registered in 0.1 M tetrabutylammonium perchlorate in dry acetonitrile as the supporting electrolyte.