Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION:

Photochemical Reaction Dynamics of 2,2'-Dithiobis(Benzothiazole): Direct Observation of the Addition Product of an Aromatic Thiyl Radical to an Alkene with Time-Resolved Vibrational and Electronic Absorption Spectroscopy

Daisuke Koyama, and Andrew J. Orr-Ewing

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

1. Time-Resolved Electronic Absorption Spectroscopy of Pure Methanol following 300-nm Excitation

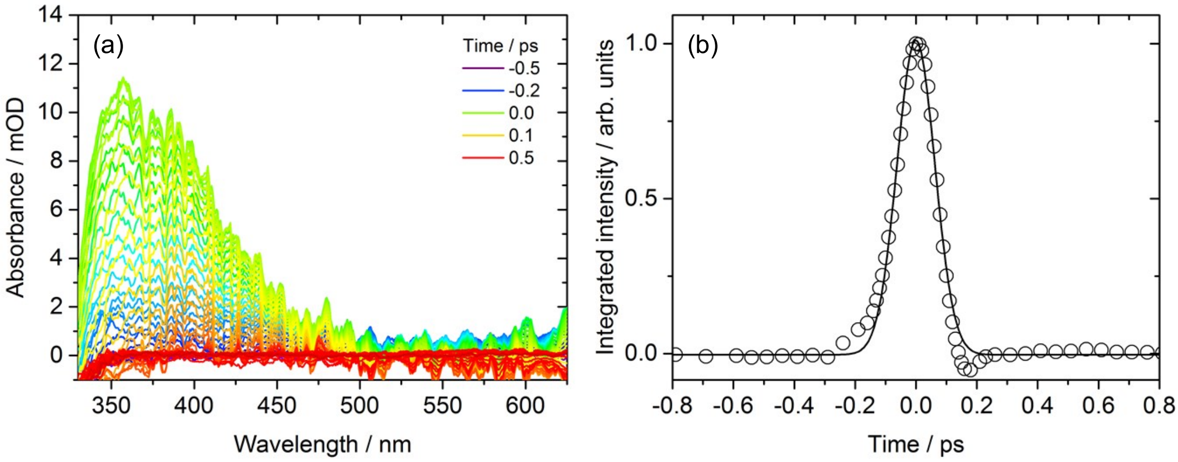

Figure S1: (a) Transient electronic absorption spectra of pure methanol following 300-nm excitation. (b) Time-dependence at 360 nm (circles). Fitting the integrated absorbance to a Gaussian function gives the instrument response function of 150 fs (solid line).

2. Solvent and Pump Wavelength Dependence of Time-Resolved Electronic Absorption Spectral Shapes

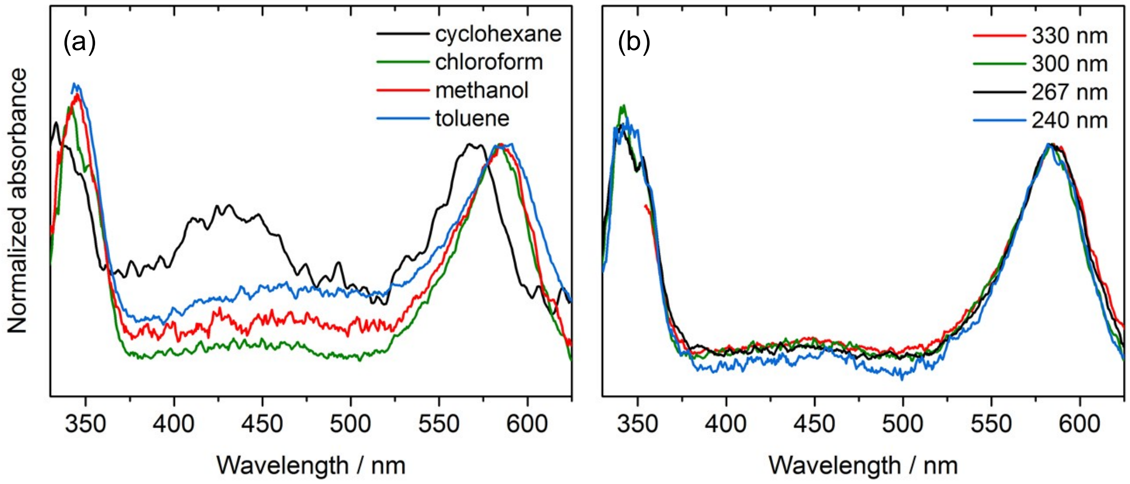

Figure S2: Normalized transient electronic absorption spectra of BSSB at a time delay of 1000 ps following: (a) 300-nm excitation in methanol, cyclohexane and chloroform solutions, and 330-nm excitation in toluene solution; (b) 330-nm (red), 300-nm (green), 267-nm (black) and 240-nm (blue) excitation in chloroform solution. The spectra are cut below ~350 nm in the toluene and chloroform solutions following 330-nm excitation because of strong interference by the pump light.

3. Spectral Decomposition of Time-Resolved Electronic Absorption Spectra of BSSB in Methanol Solution

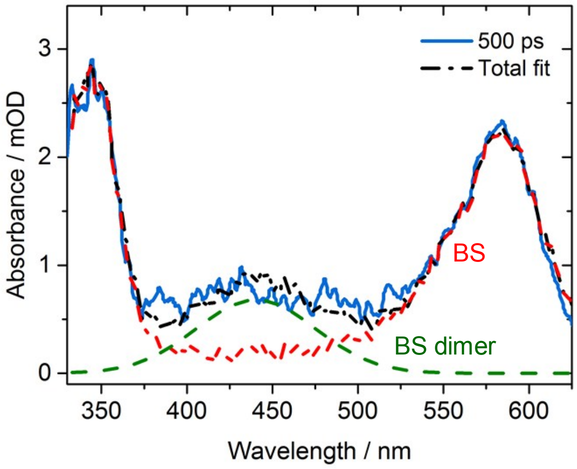

Figure S3: Example of decomposition of a TEA spectrum for 0.24 mM BSSB in methanol solution following 300-nm excitation, at a time delay of 500 ps. Red: BS radical, green: BS radical dimer, black: total fitting, blue: the spectrum at 500 ps time delay. The spectral decomposition was carried out using the absorption spectrum of BS radical at 5 ps where peak shifts of BS radical bands were complete. This method assumes that the shapes of spectra of BS radical did not change further with time.

4. Time-Resolved Electronic Absorption Spectroscopy of Pure Toluene and BSSB in Toluene Solution at a Pump Energy of 800 nJ/pulse

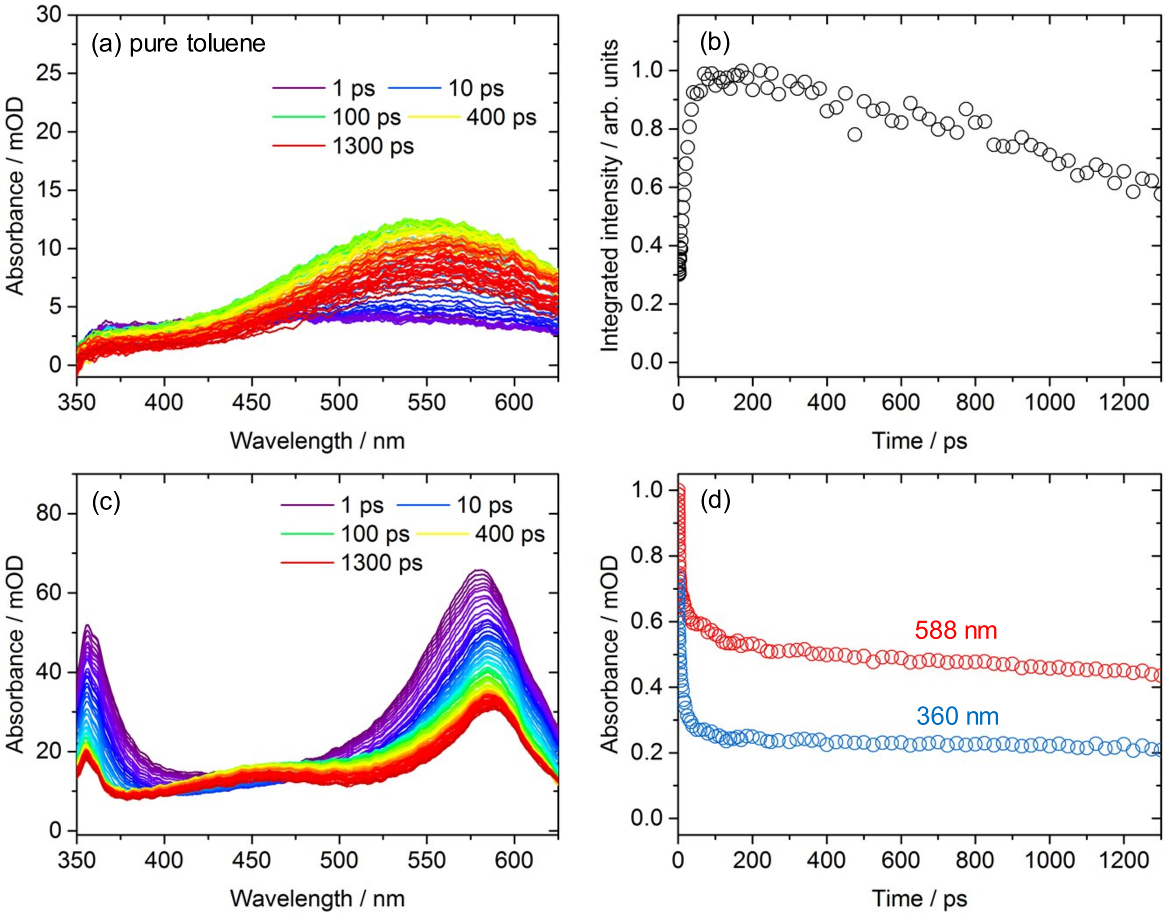

Figure S4: Transient electronic absorption spectra of pure toluene and 5.5 mM BSSB in toluene solution following 330-nm excitation at a pump energy of 800 nJ/pulse; (a) pure toluene and (b) kinetic trace at 550 nm; (c) 5.5 mM BSSB in toluene solution and (d) integrated band intensity at 360 nm (blue) and 588 nm (red).

5. Time-Resolved Electronic Absorption Spectroscopy of Pure Styrene and BSSB in Styrene Solution at a Pump Energy of 800 nJ/pulse

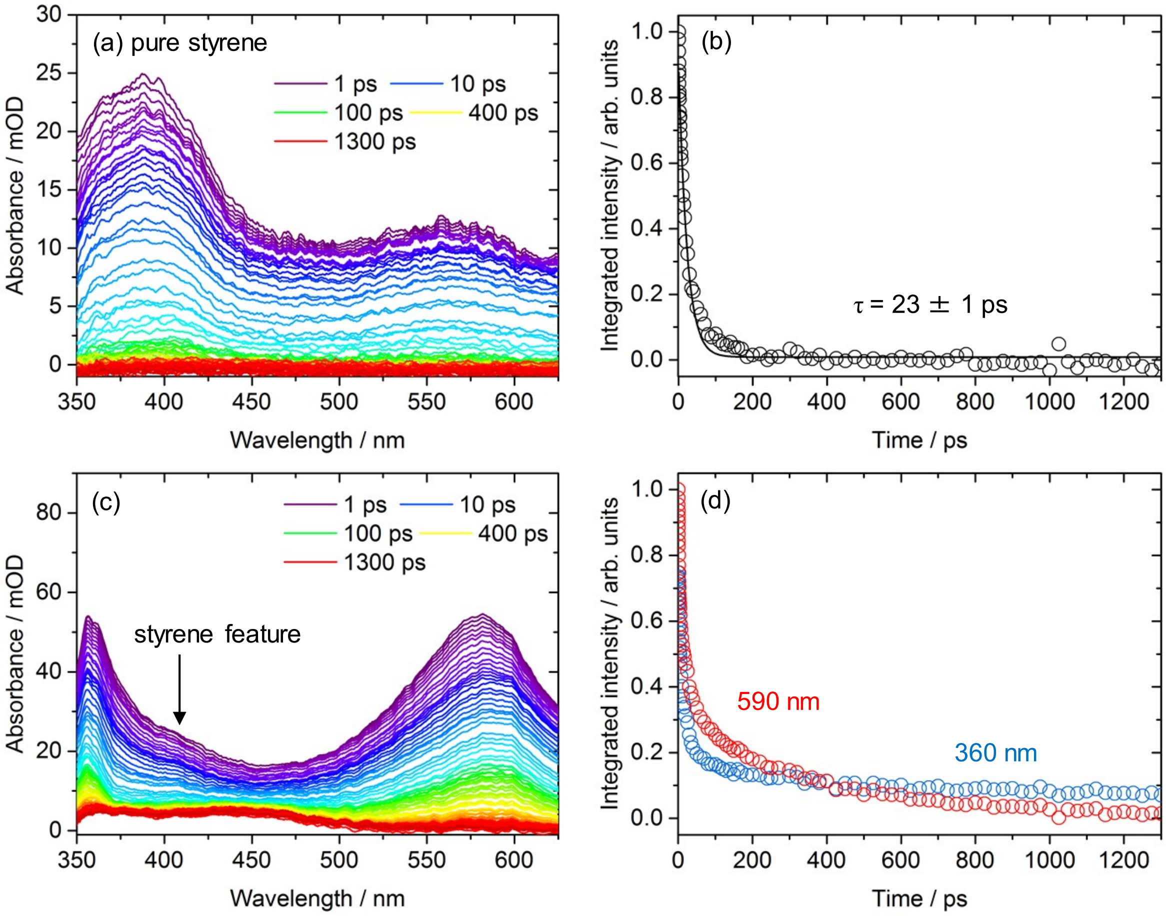

Figure S5: Transient electronic absorption spectra of pure styrene and 5.5 mM BSSB in styrene solution following 330-nm excitation at a pump power of 800 nJ/pulse; (a) pure styrene and (b) kinetic trace at 390 nm and a fitting to a single exponential function (solid line); (c) 5.5 mM BSSB in styrene solution and (d) integrated band intensity at 360 nm (blue) and 590 nm (red).

6. Spectral Decomposition of Time-Resolved Electronic Absorption Spectra of BSSB in Styrene Solution

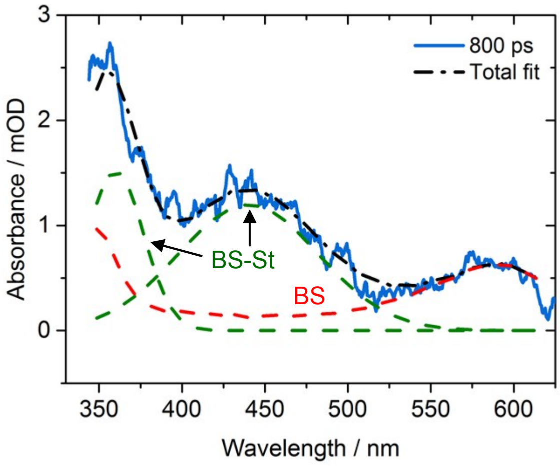

Figure S6: Example of decomposition of a TEA spectrum for 5.5 mM BSSB in styrene solution following 330-nm excitation, obtained at a time delay of 800 ps. Red: BS radical, green: addition product, black: total fitting, blue: the spectrum at 800 ps time delay. The spectral decomposition was carried out in the same way as Figure S3.

7. Steady State FT-IR spectra of BSSB in Styrene, Pure Styrene and Pure Toluene

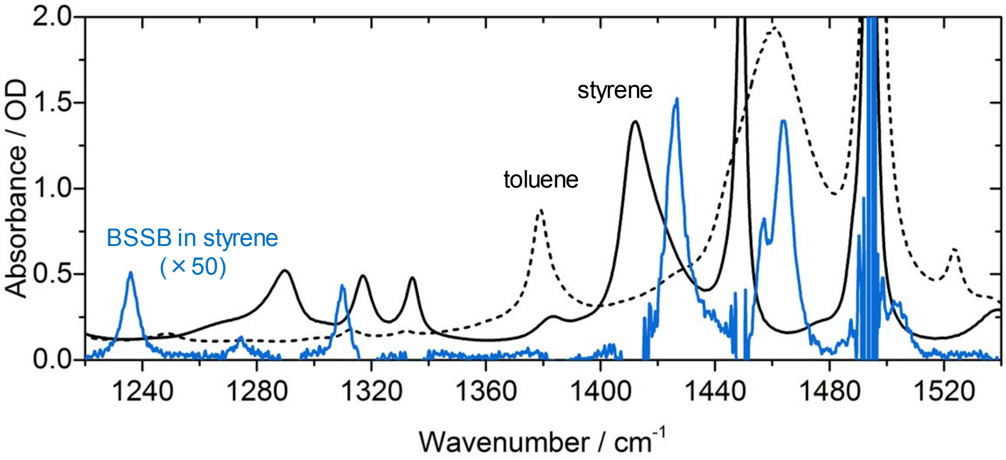

Figure S7: Steady state FTIR spectra of styrene (black), toluene (dashed black) and 6.9 mM of BSSB in styrene (blue). The spectrum for BSSB is multiplied by a factor of 50 for clarity and was obtained by taking the difference between spectra before and after adding BSSB to the styrene. Each spectrum was obtained in a Harrick cell with a 50 µm thick spacer and CaF_2 windows.

8. Time-Resolved Vibrational Absorption Spectroscopy of BSSB in Deuterated Chloroform Solution

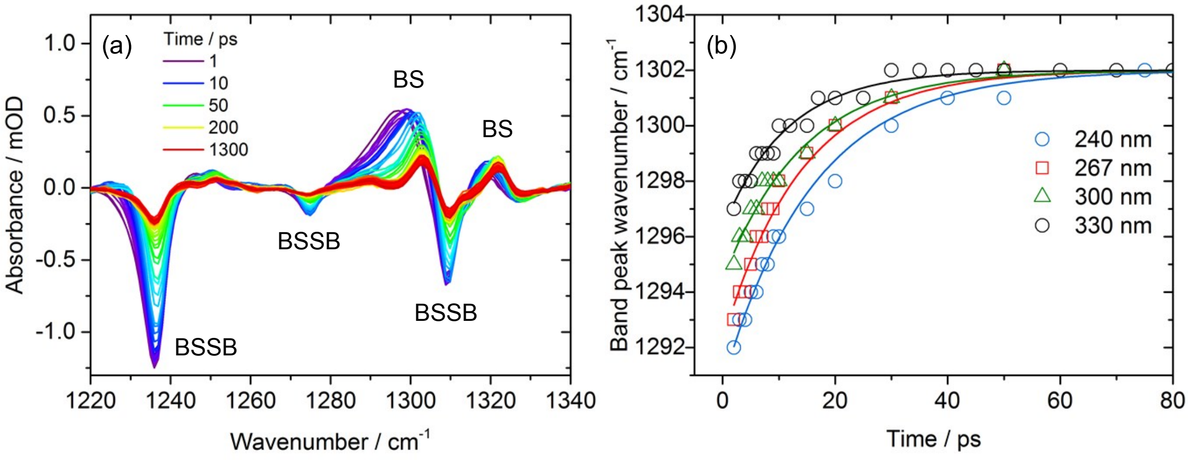

Figure S8: (a) Transient vibrational absorption spectra of BSSB in deuterated chloroform solution following 330-nm excitation. (b) Temporal band position shift for the BS radical at 1302 cm^{-1} in deuterated chloroform solutions following 240-nm (blue), 267-nm (red), 300-nm (green) and 330-nm (black) excitation.

9. Linear Correction for Computed Infrared Frequencies

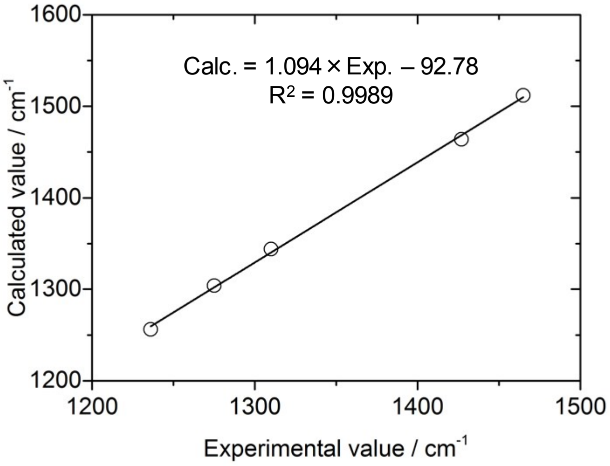

Figure S9: Linear correlation between experimental infrared frequencies of BSSB in styrene solution and computed infrared band positions for BSSB obtained at the B3LYP/6-311++G(3df,3pd) level.

10. Spectral Decomposition of Time-Resolved Vibrational Absorption Spectra of BSSB in Styrene Solution

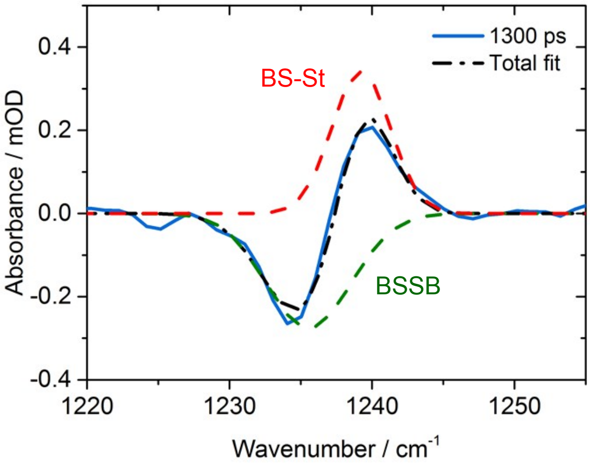

Figure S10: Example of decomposition of a TVA spectrum for 7.2 mM BSSB in styrene solution following 330-nm excitation, obtained at a time delay of 1300 p. Red: BS-St, green: BSSB bleach, black: total fitting, blue: the spectrum at 1300 ps time delay.

11. Time-Resolved Vibrational Absorption Spectroscopy of Pure Styrene following 330 nm Excitation

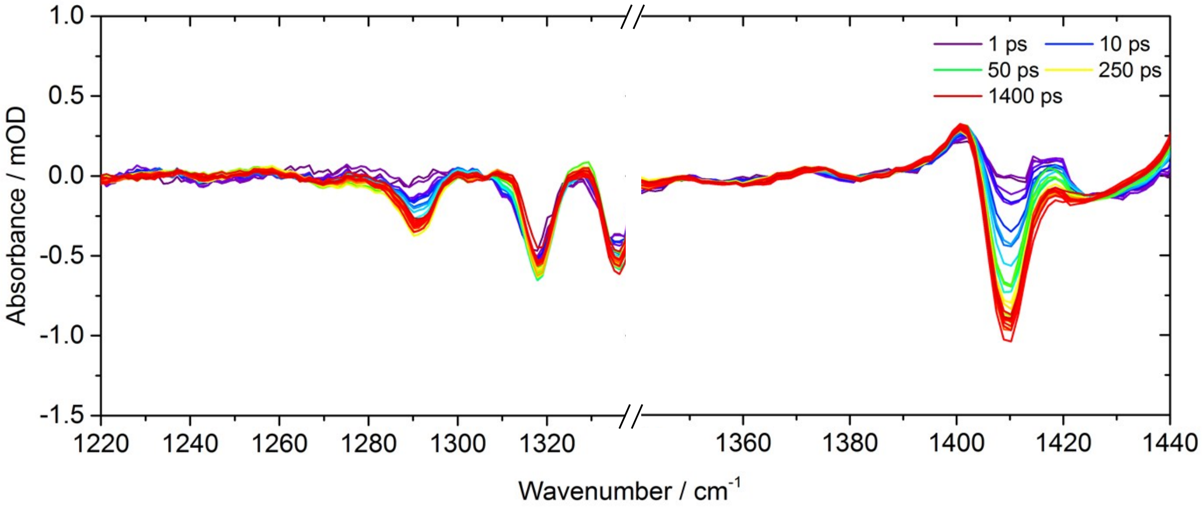

Figure S11: Transient vibrational absorption spectra of pure styrene following 330-nm excitation.