Capture and Reactivity of an Elusive Carbon-Sulfur Centered Biradical

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Supporting Information – Part A: Matrix Isolation Spectra & Analytical Data

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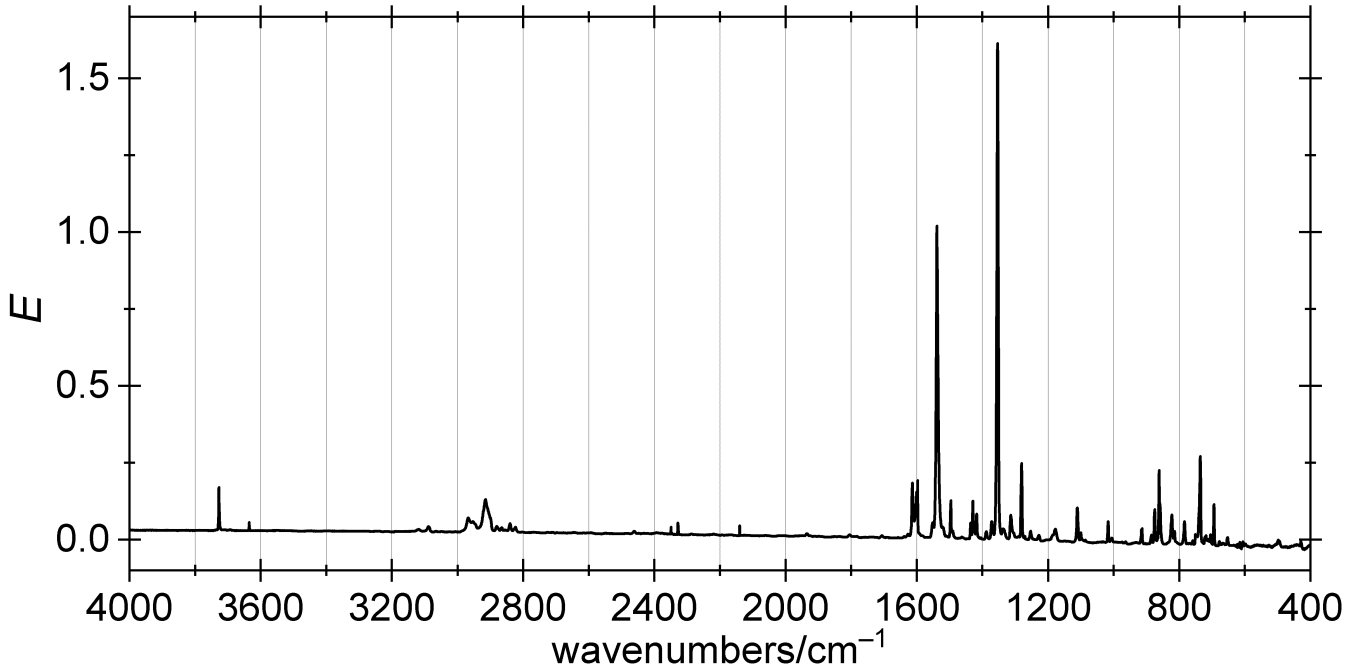


Figure S1: Matrix-isolated *p*-NBA dithiane in N_2 at 3 K.

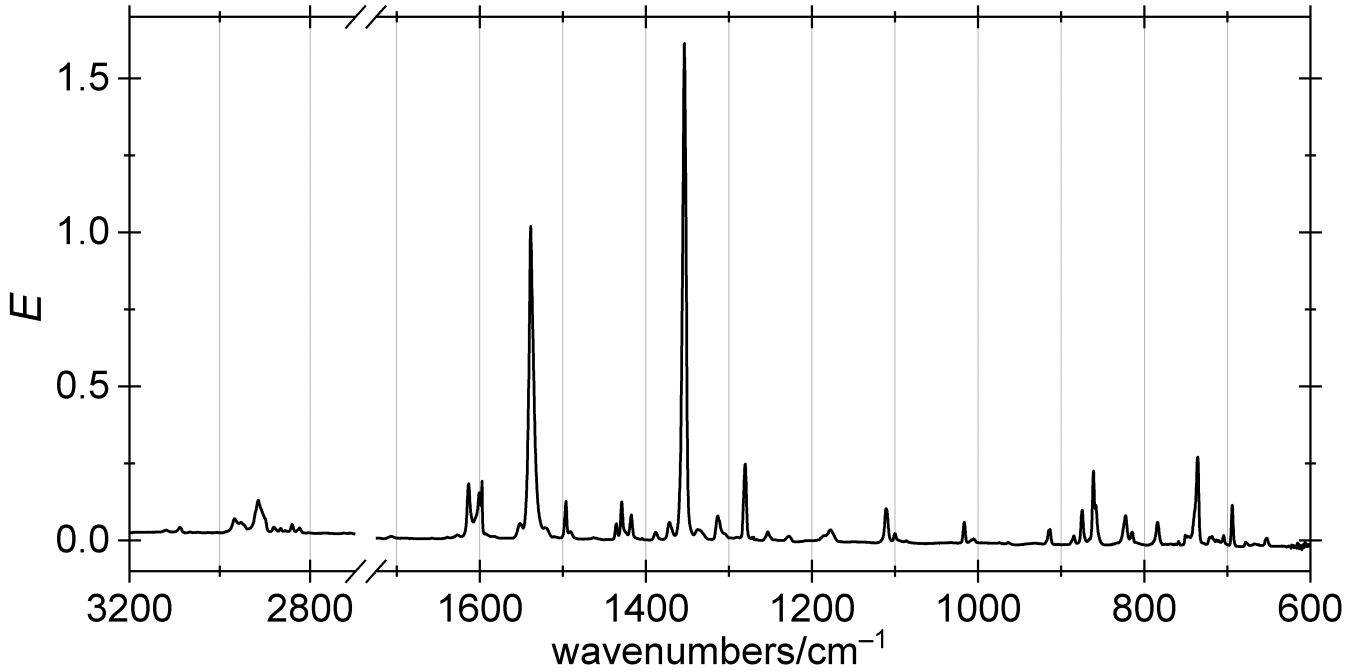


Figure S2: Matrix-isolated *p*-NBA dithiane in N_2 at 3 K (detail).

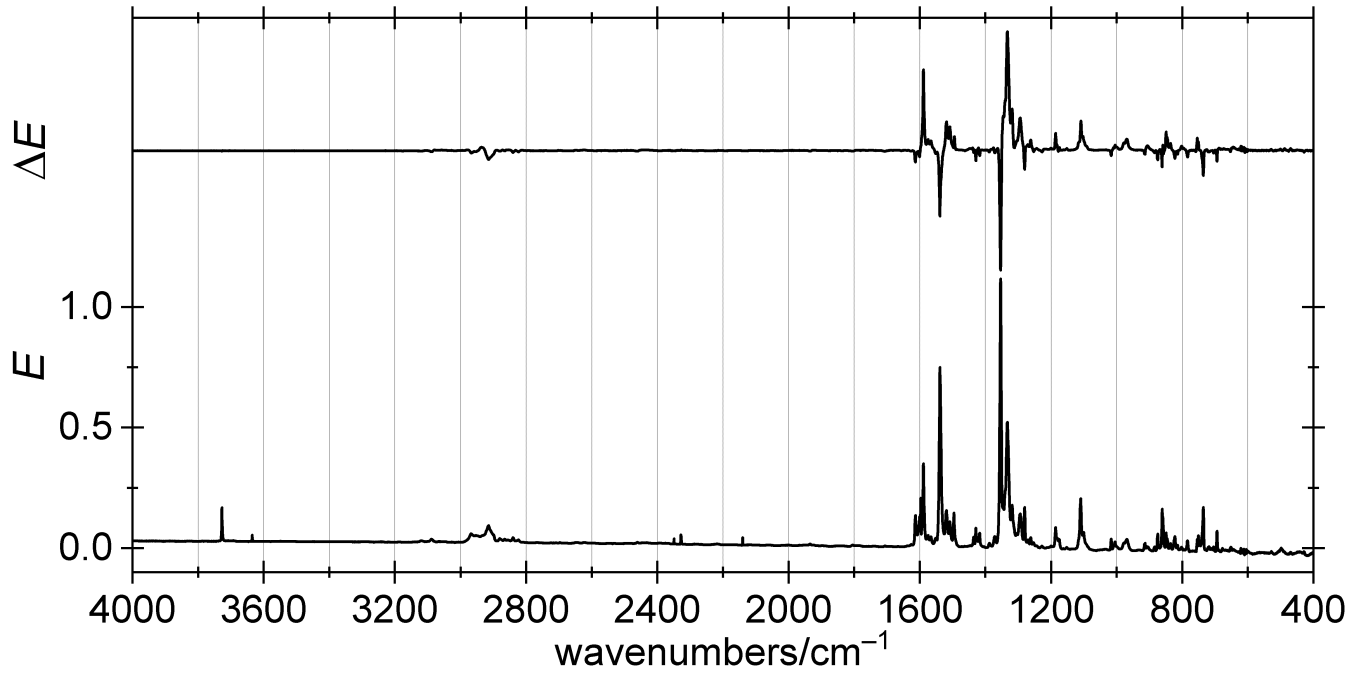


Figure S3: Matrix-isolated *p*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm; difference trace (before/after irradiation at 313 nm) on top.

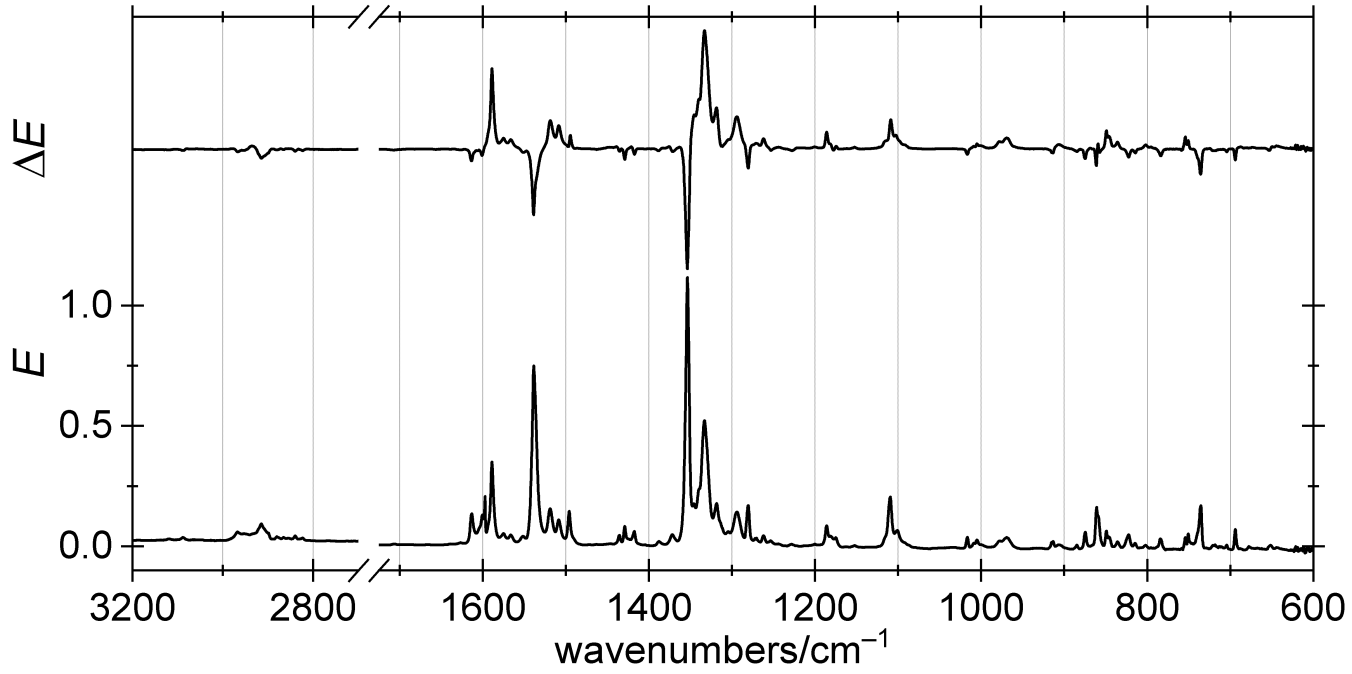
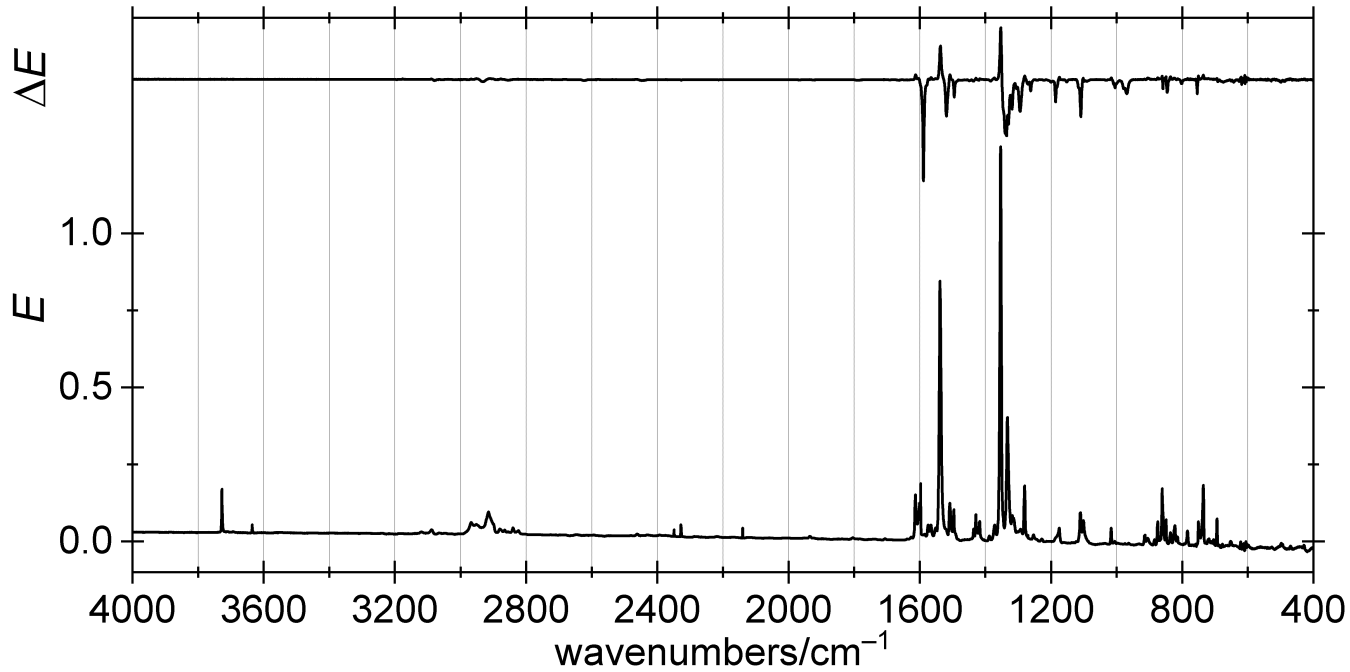


Figure S4: Matrix-isolated *p*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm (detail); difference trace (before/after irradiation at 313 nm) on top.



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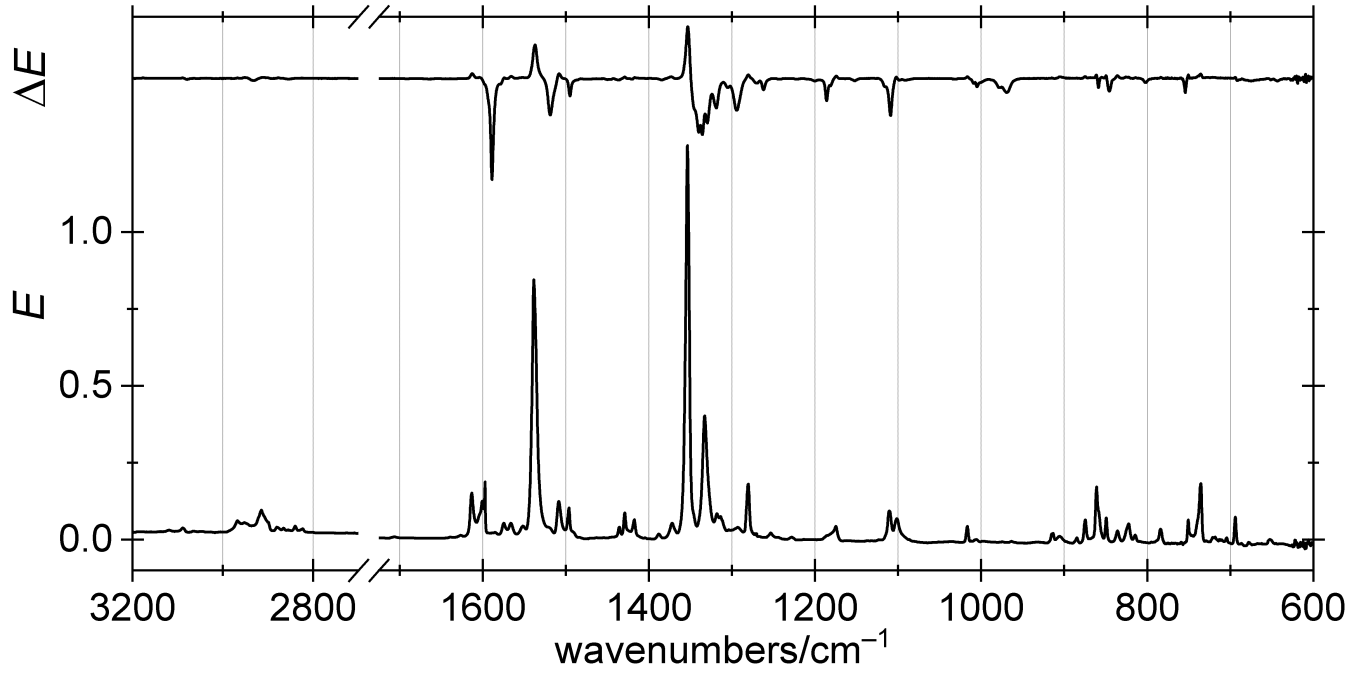

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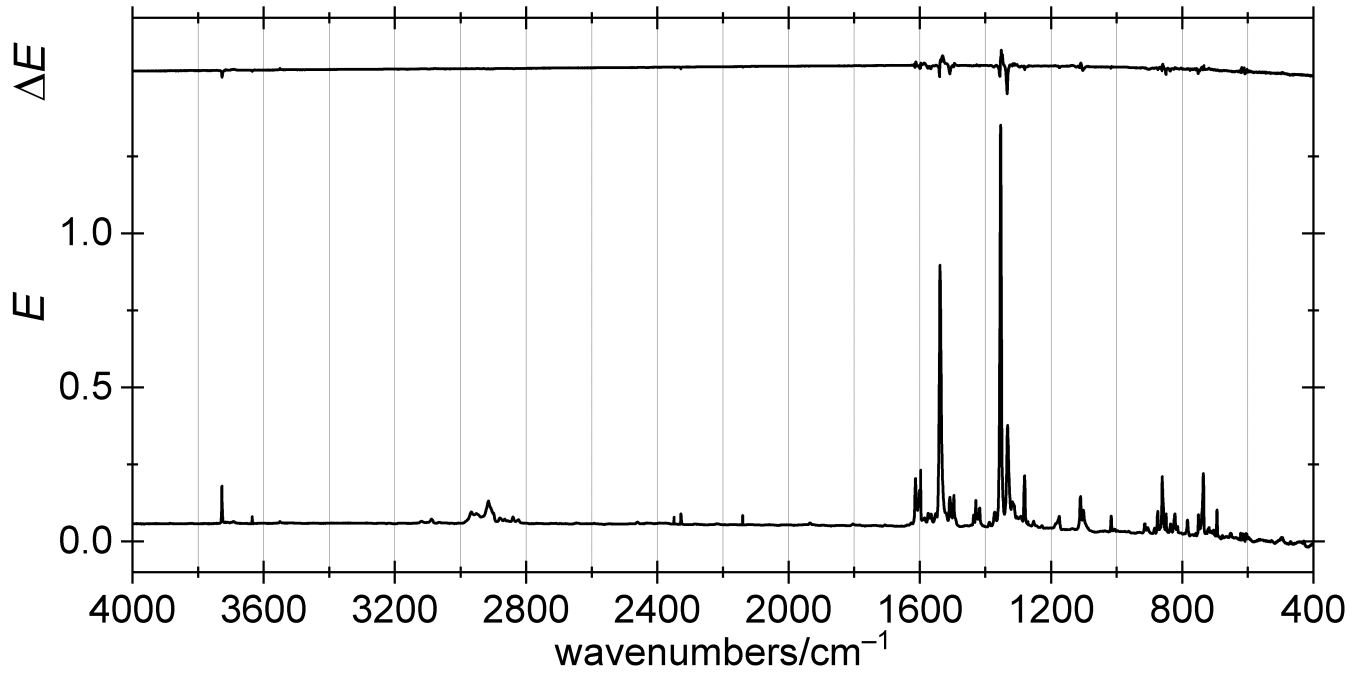

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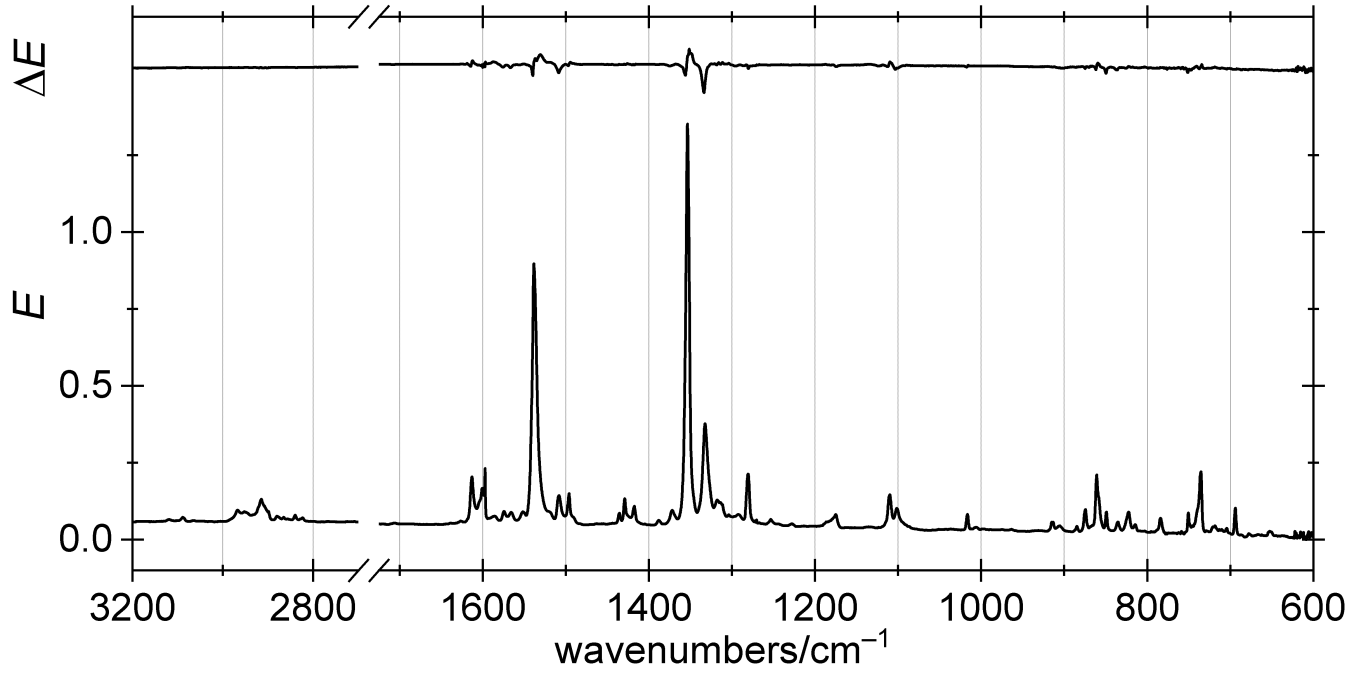

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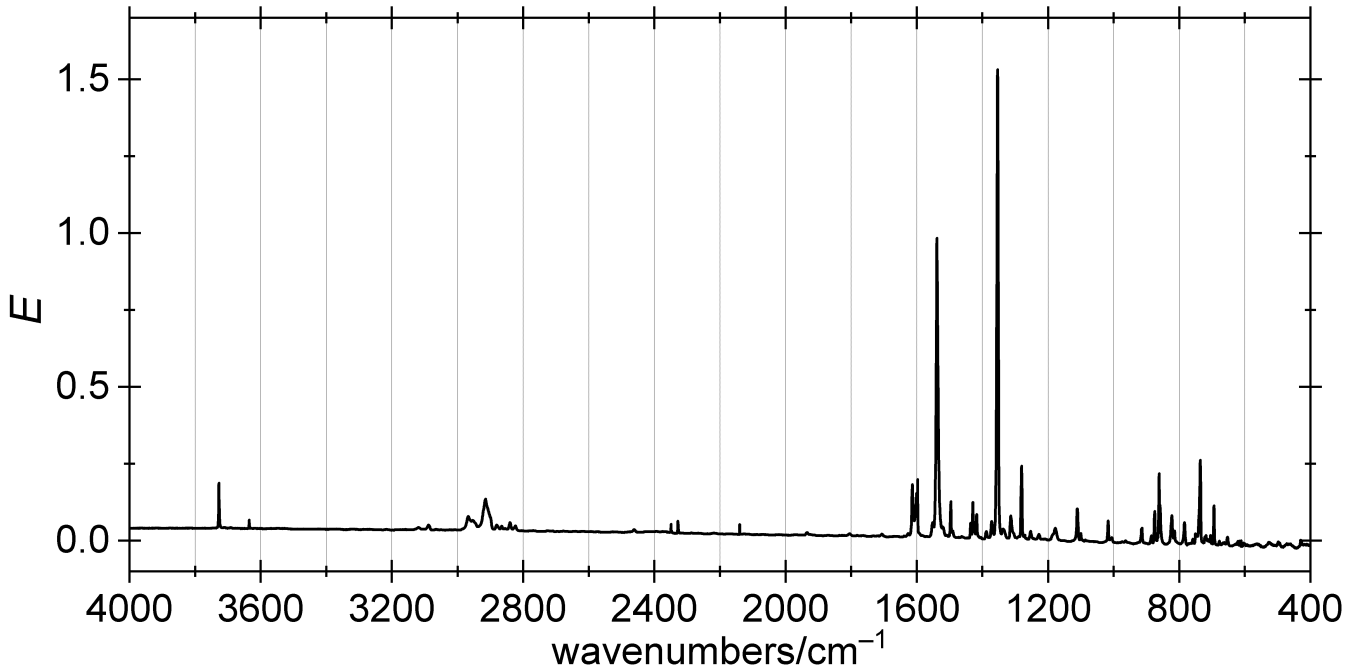
1.2. IR spectra of *p*-NBA dithiane in N_2 + 1% O_2



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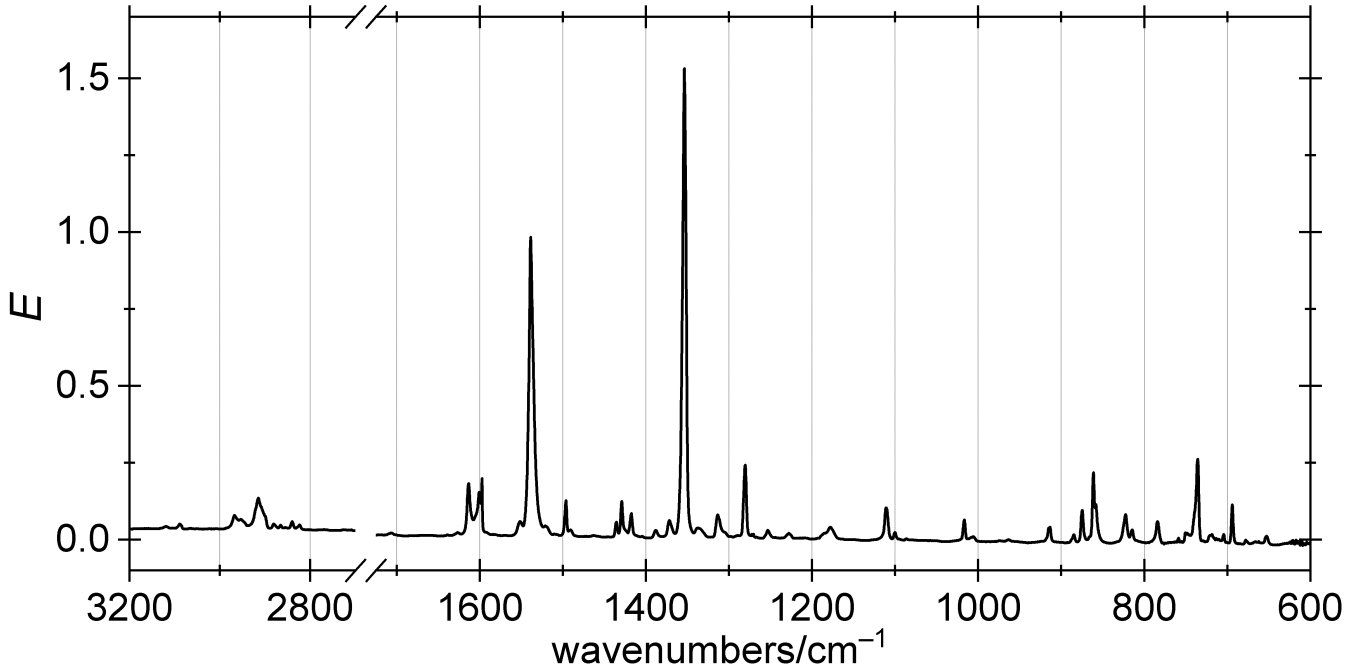

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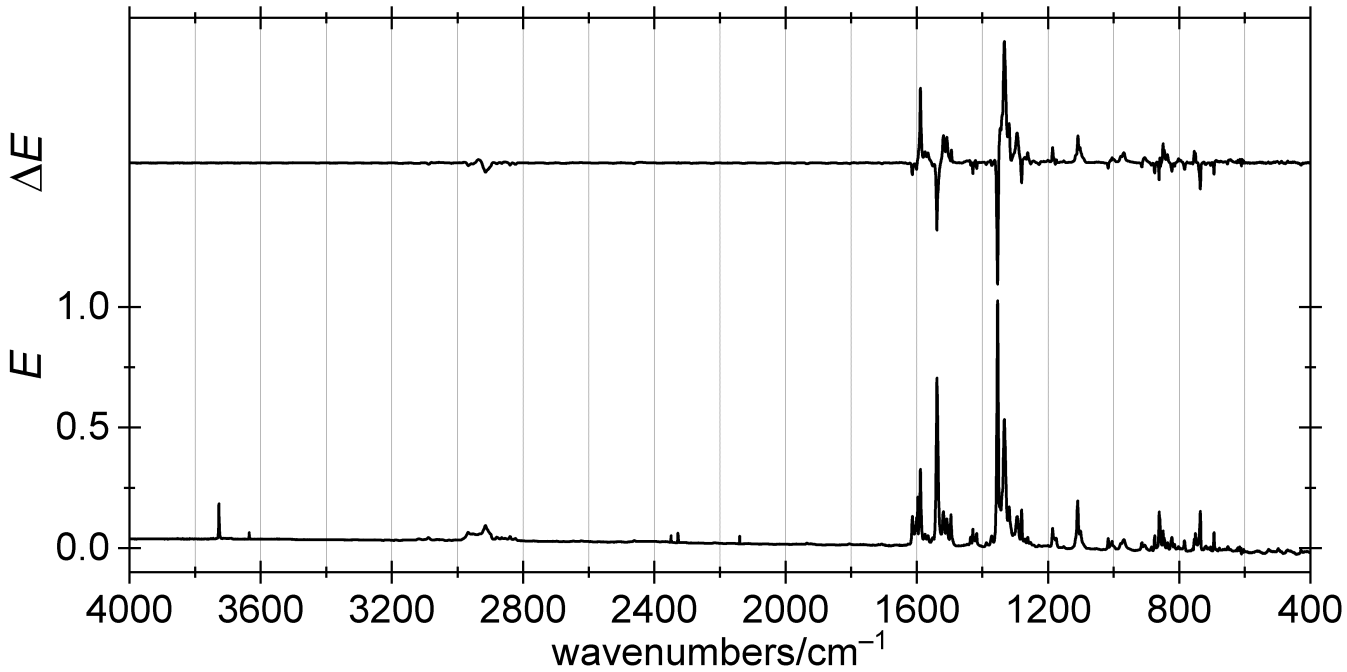

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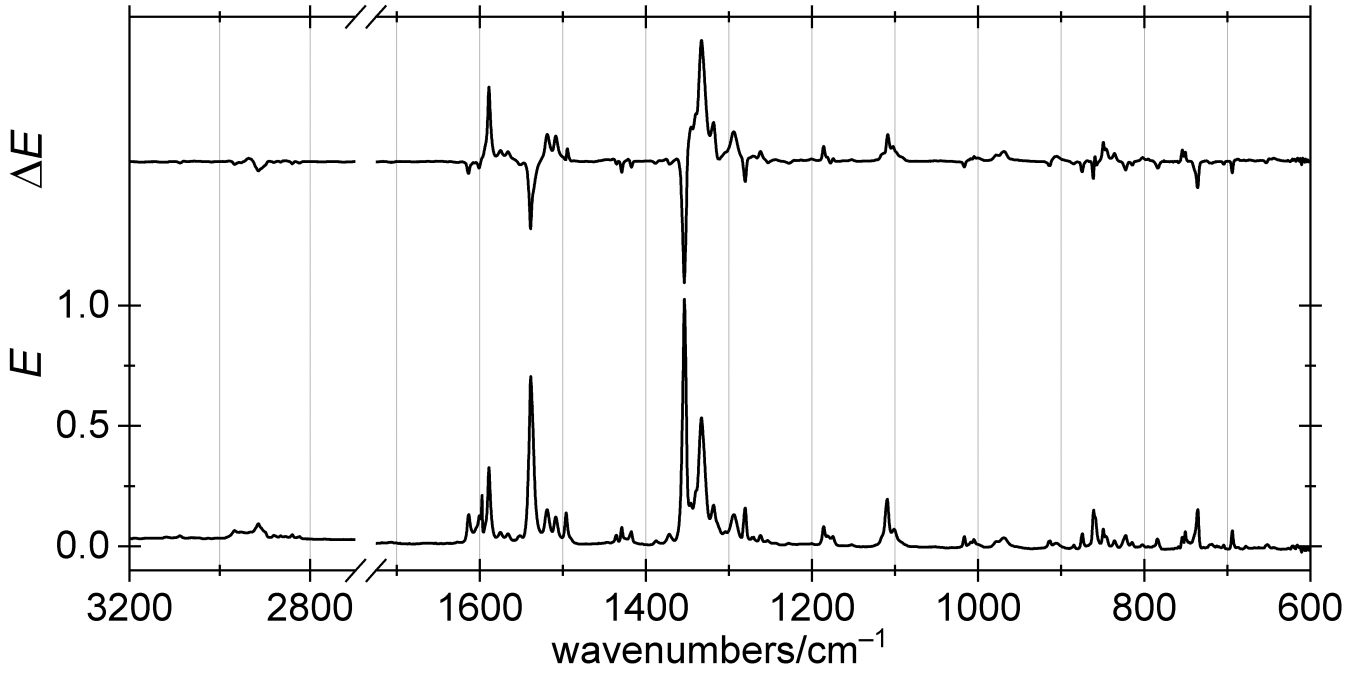

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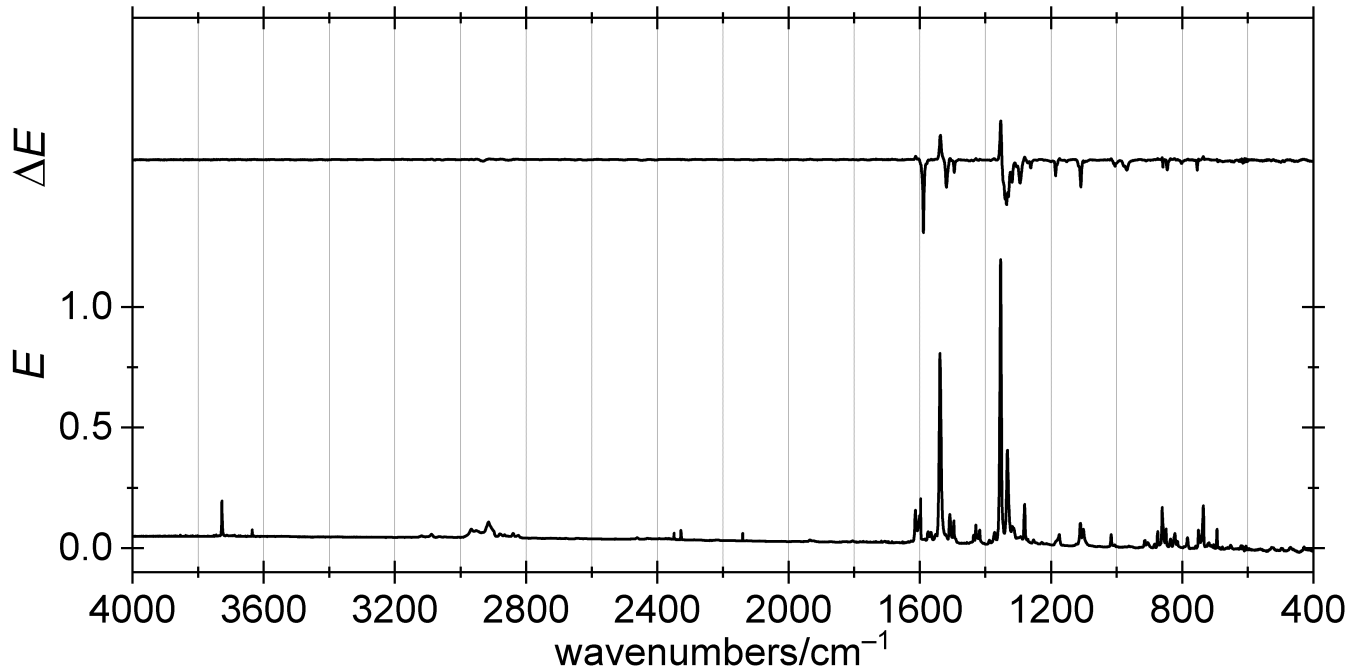

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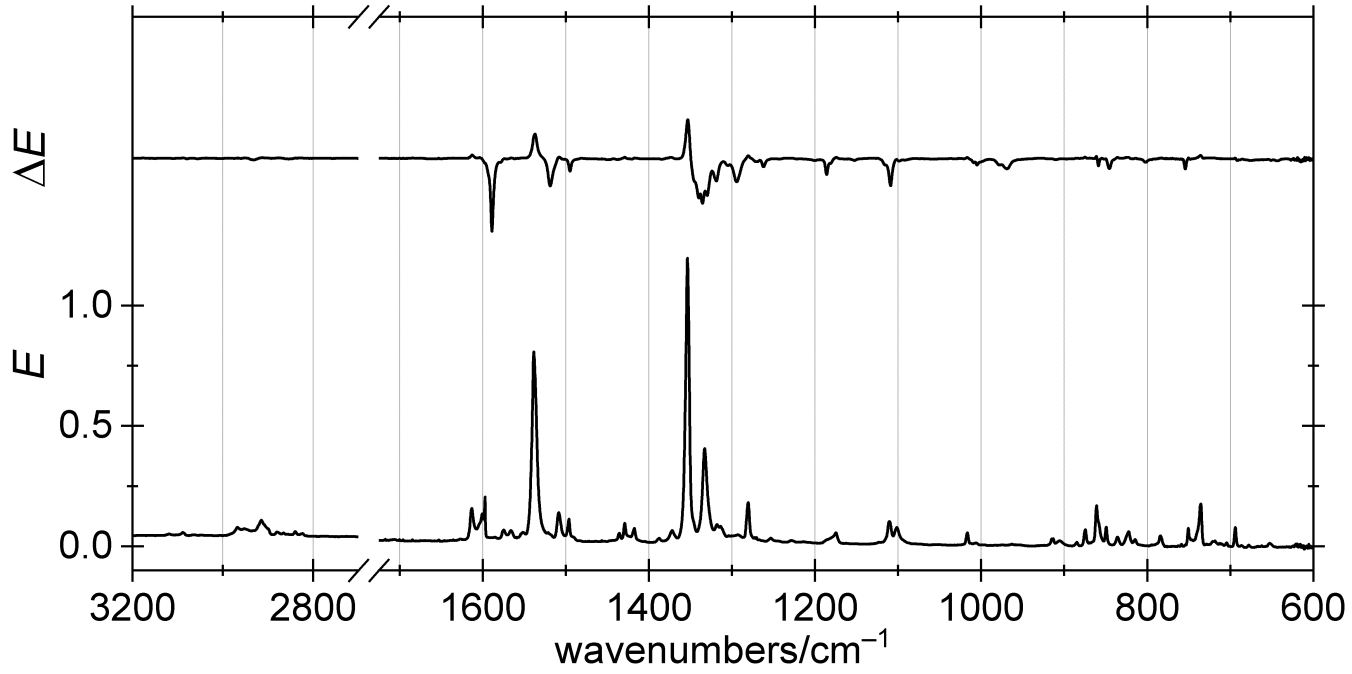

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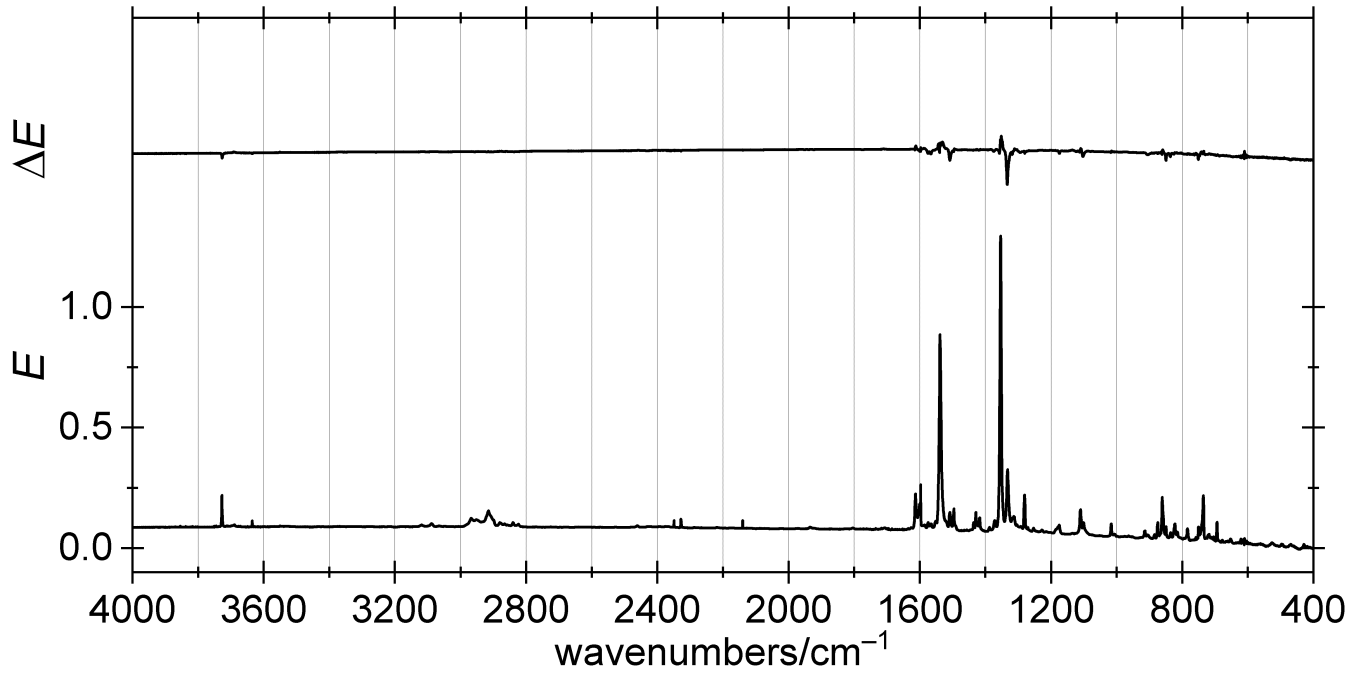

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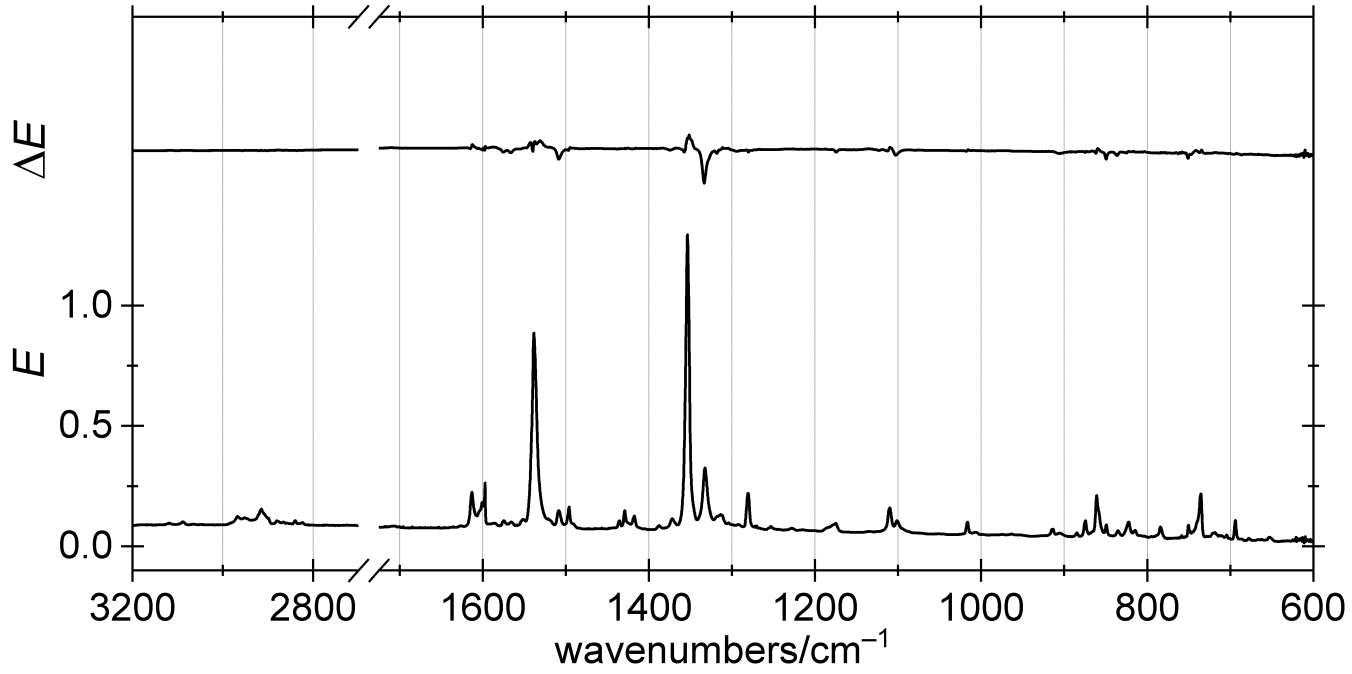

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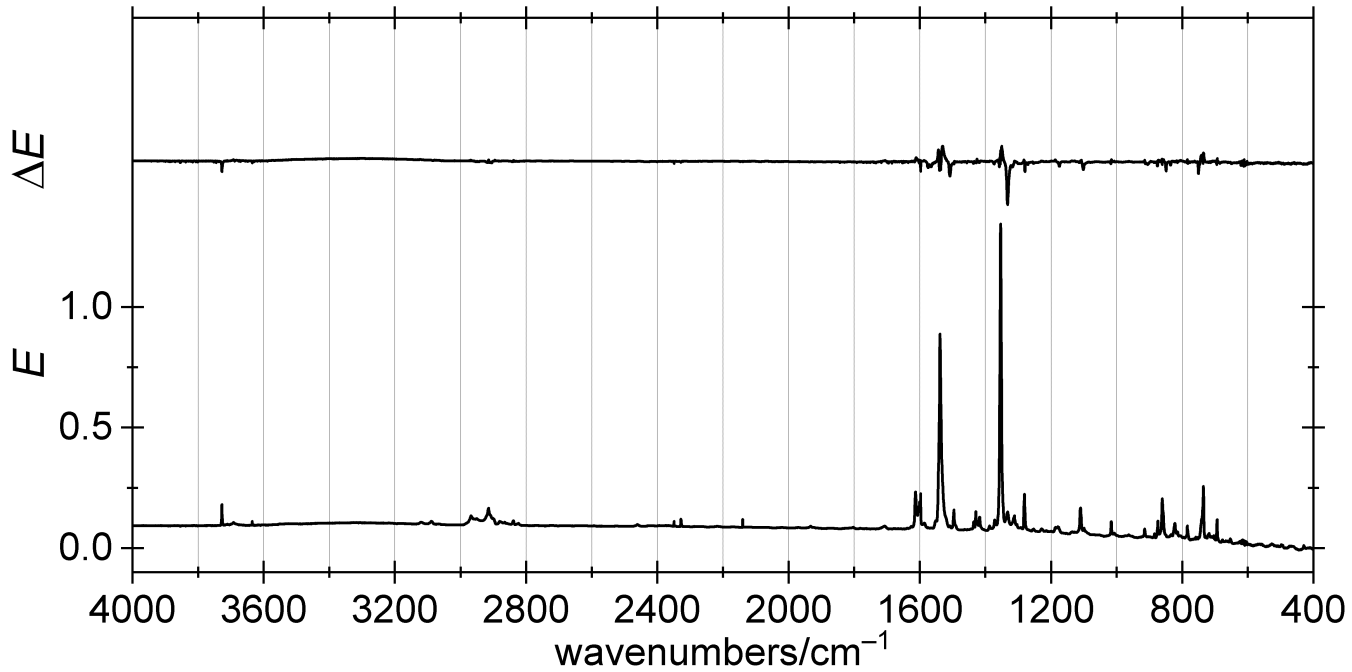

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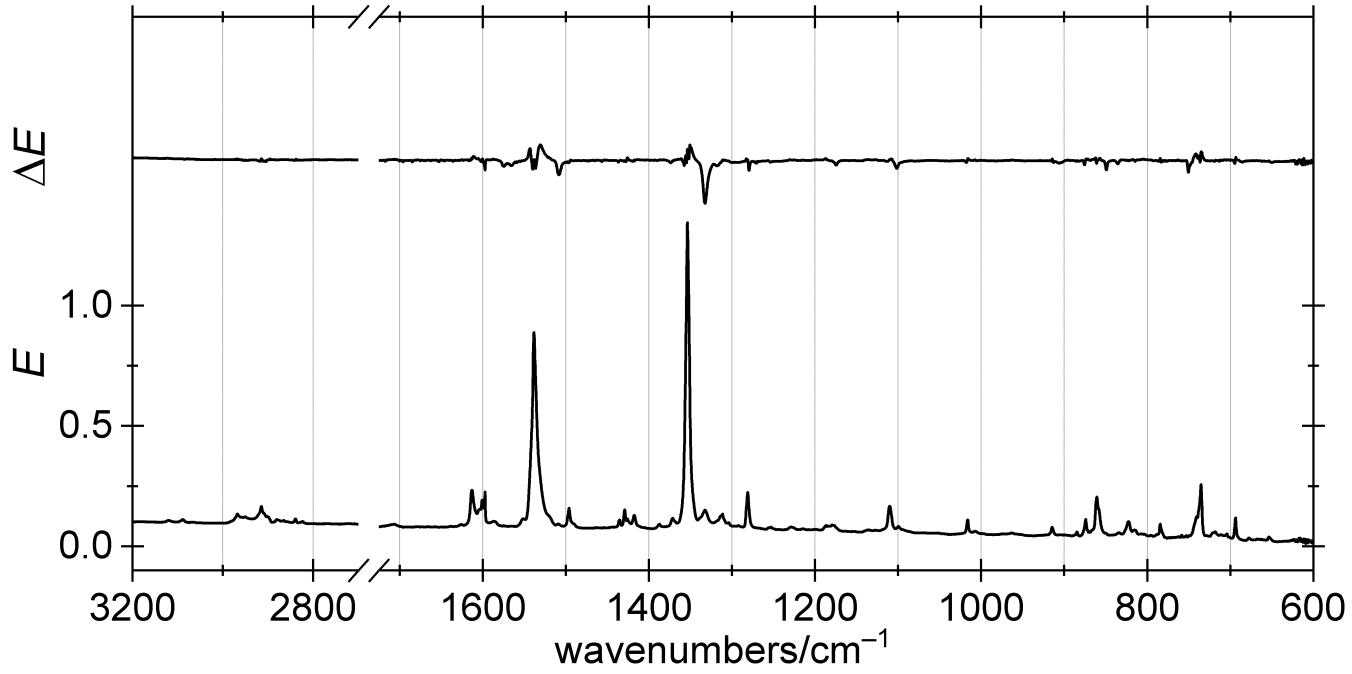

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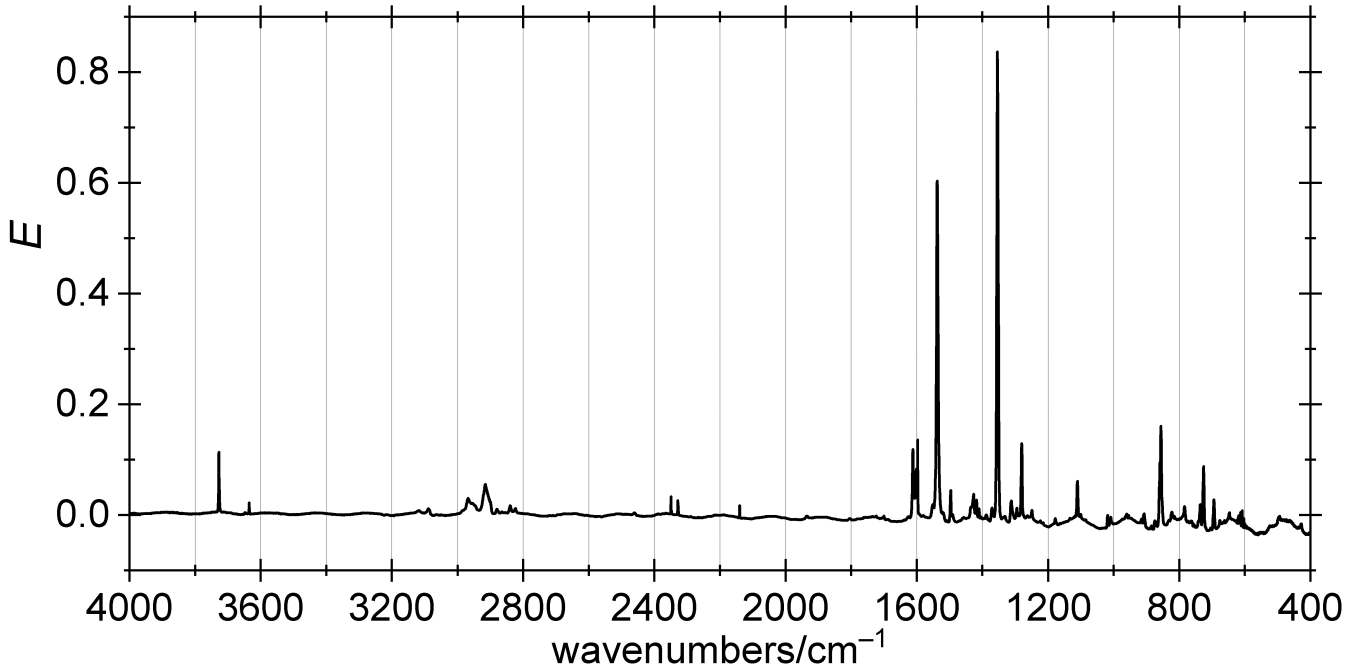
1.3. IR spectra of d_1-*p*-NBA dithiane in N_2



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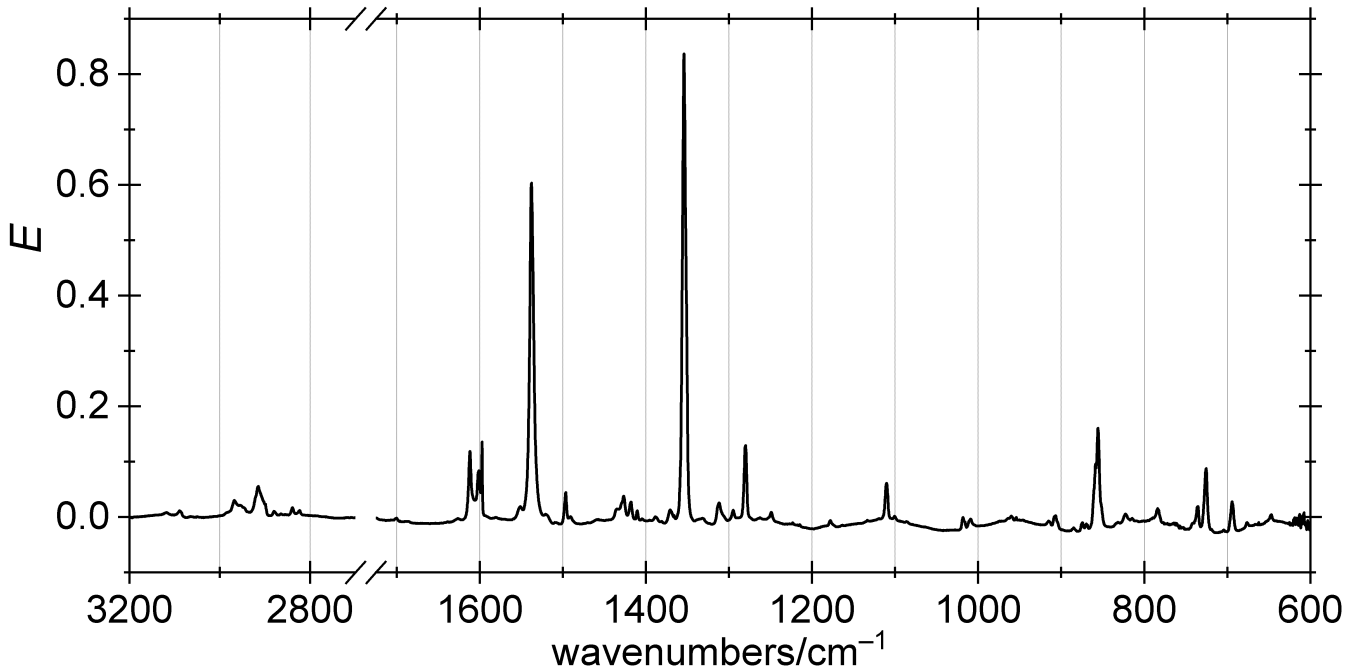

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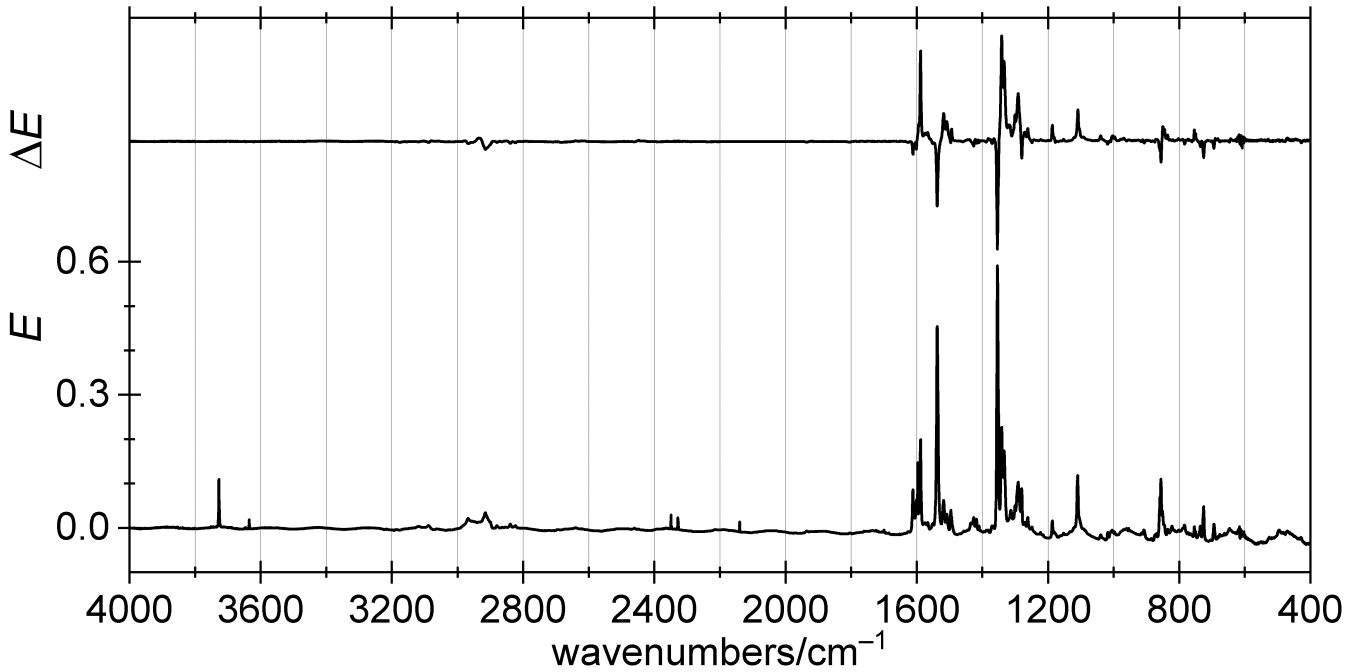

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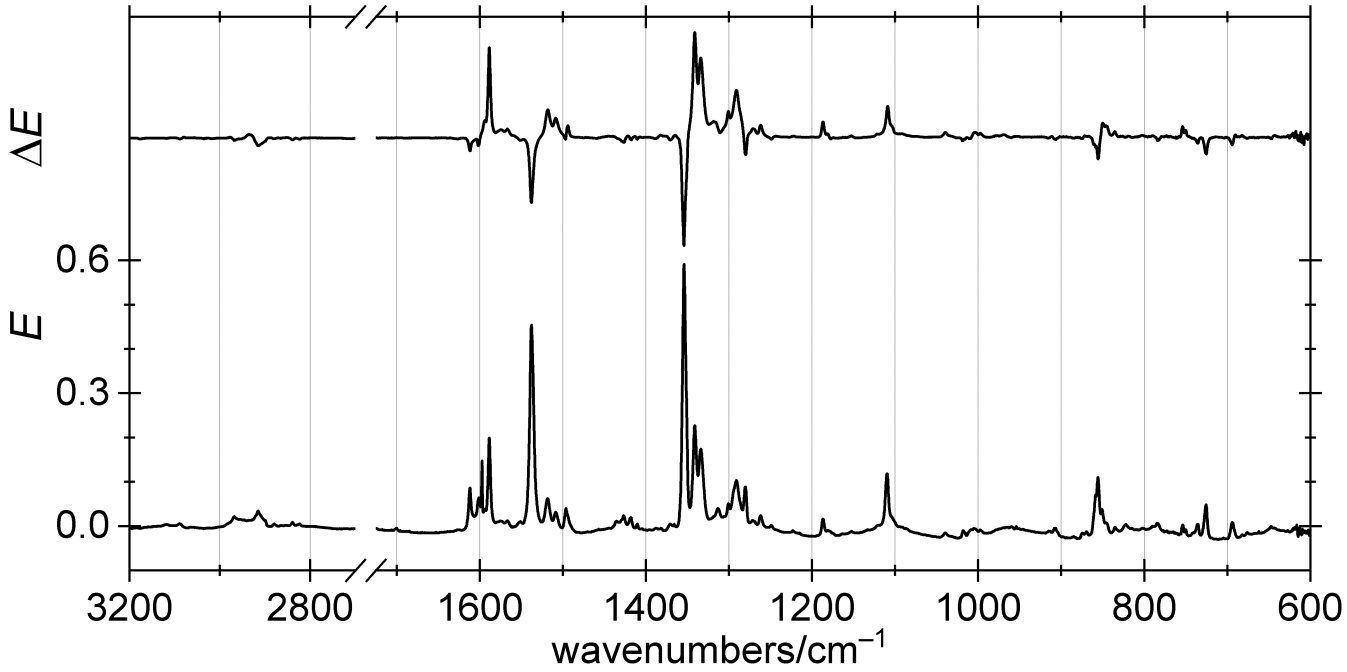
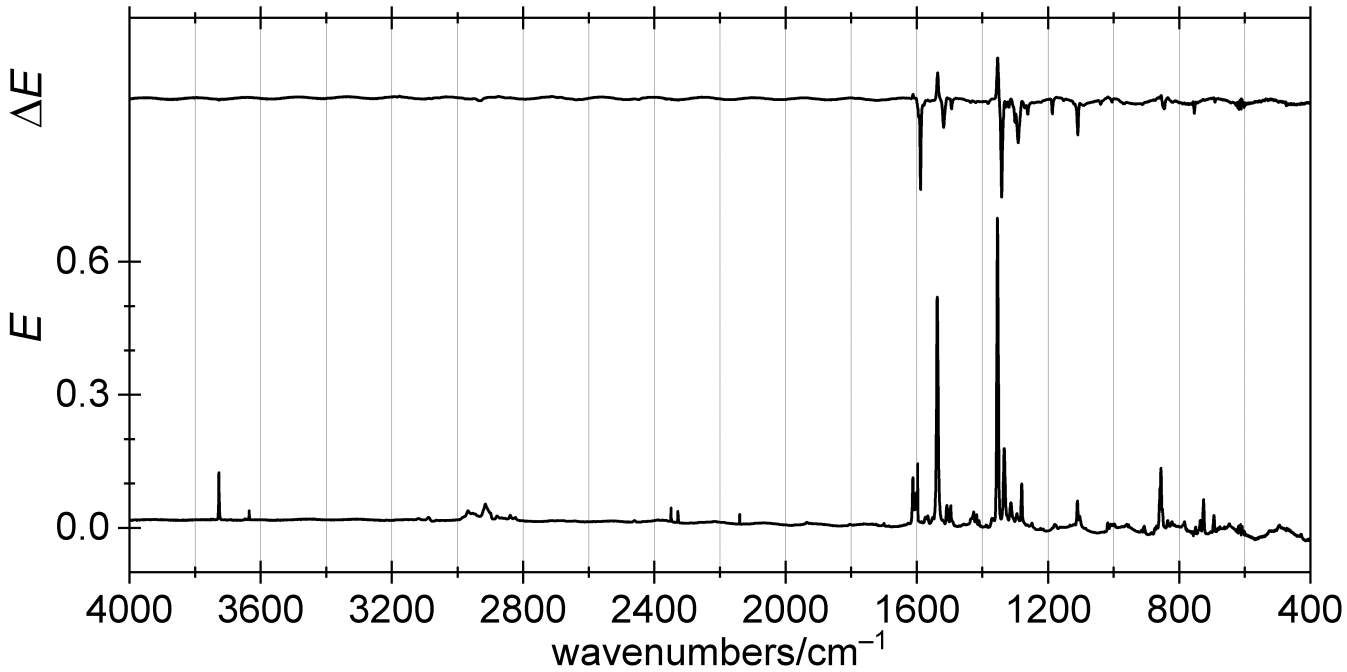


Figure S22: Matrix-isolated d_1-*p*-NBA dithiane in N_2 at 3 K after 30 s irradiation at 313 nm (detail); difference trace (before/after irradiation at 313 nm) on top.



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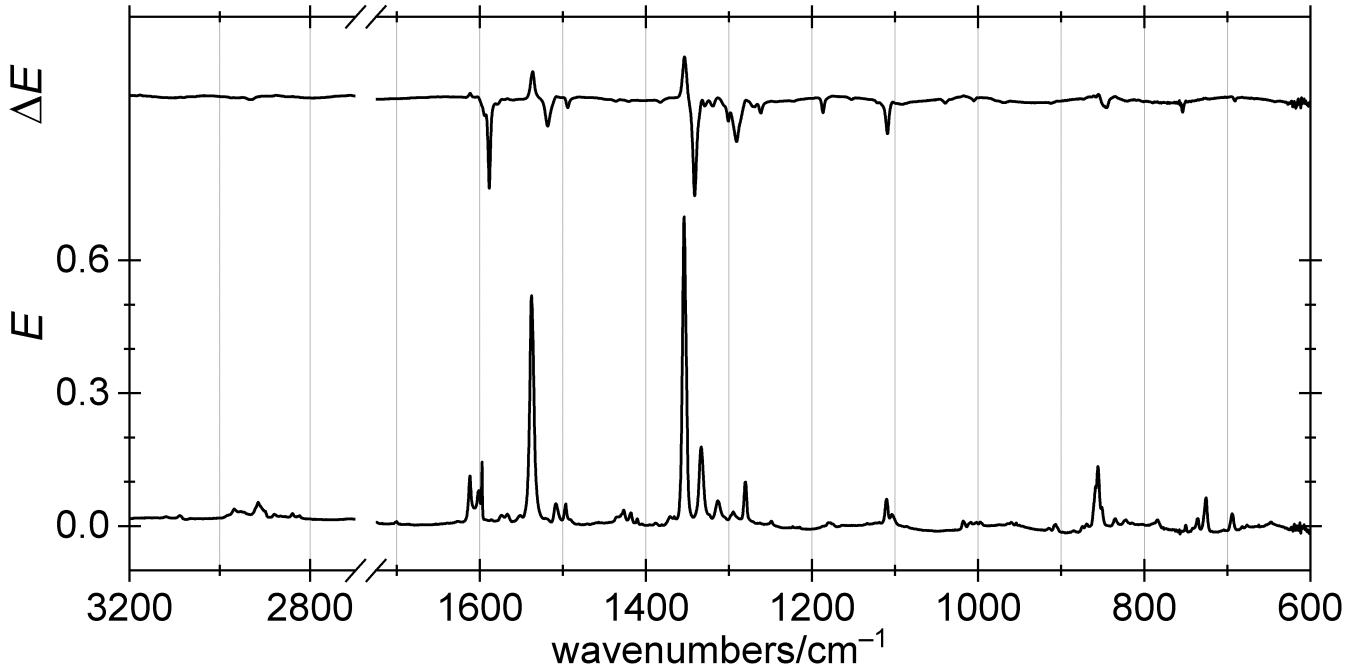

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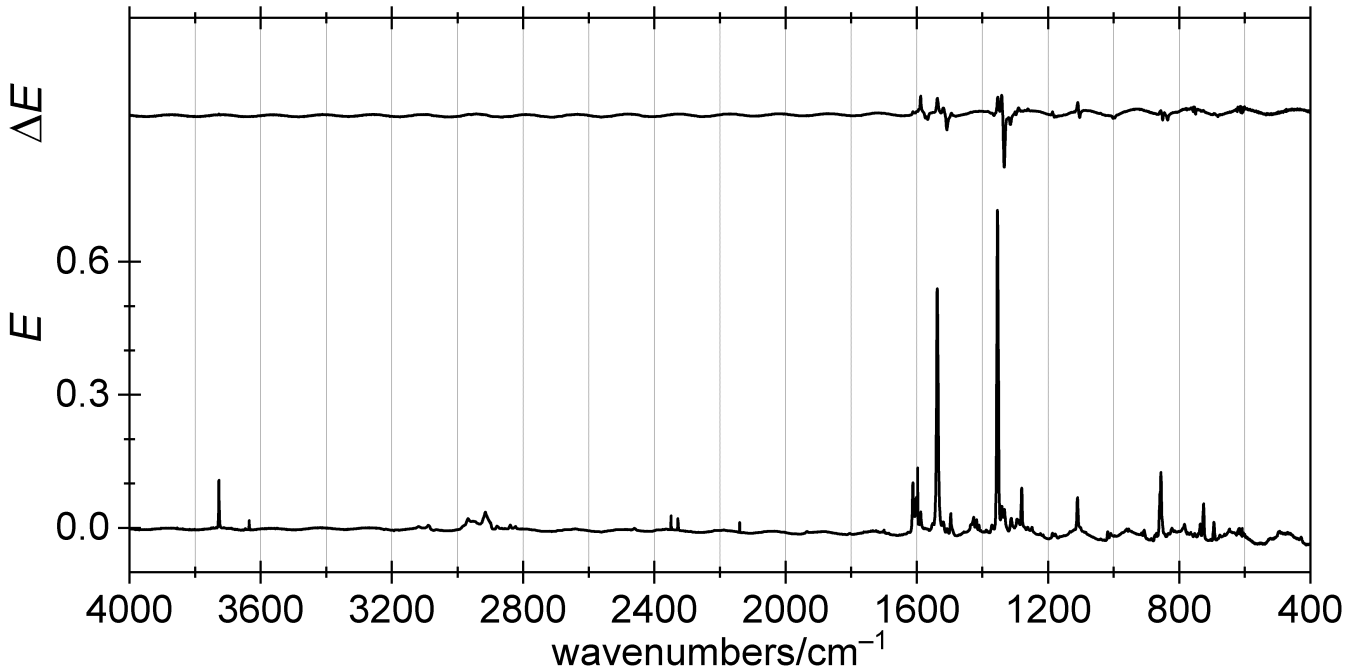

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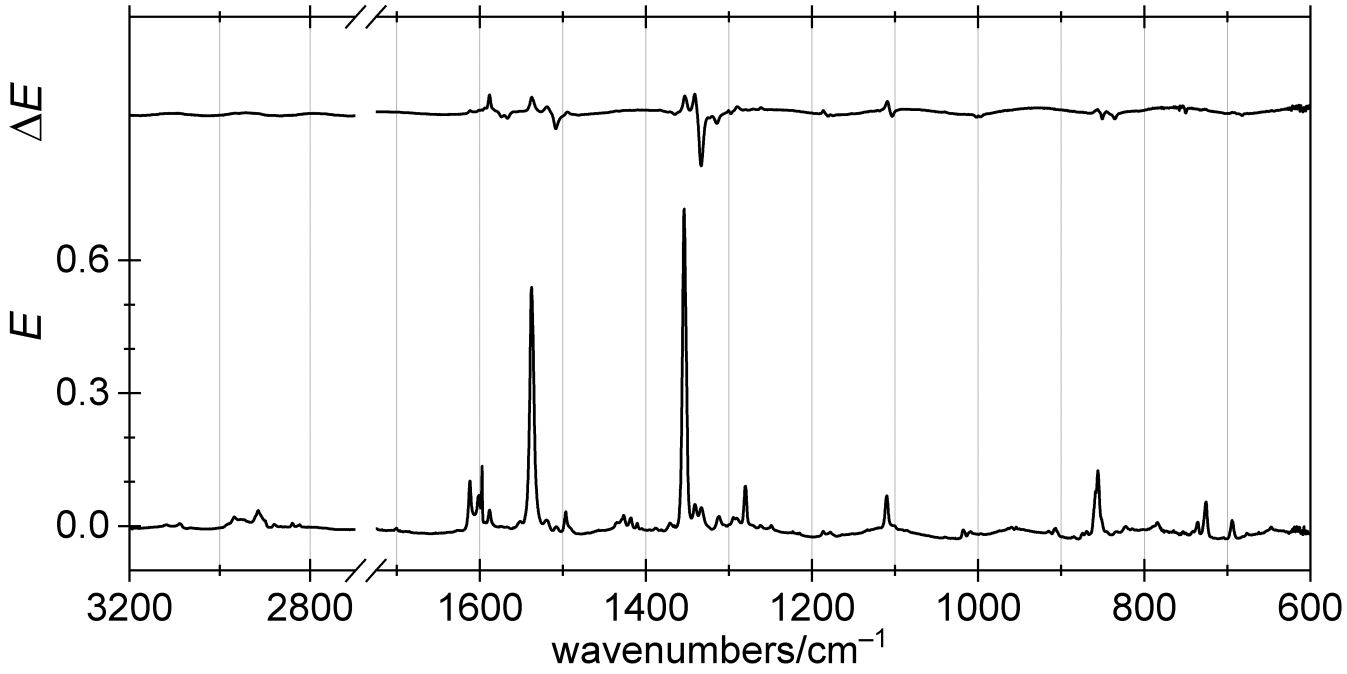

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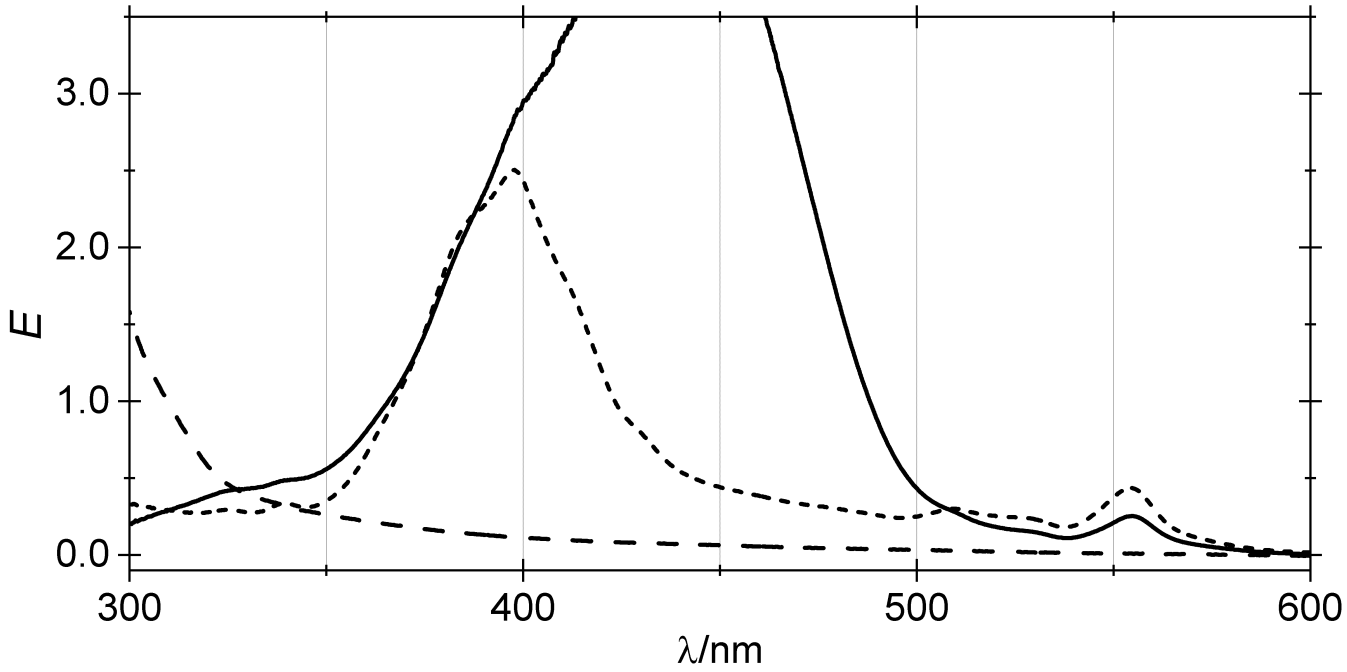
1.4. UV/Vis spectra of *p*-NBA dithiane in N_2



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1.5. UV/Vis spectra of d_1-*p*-NBA dithiane in N_2

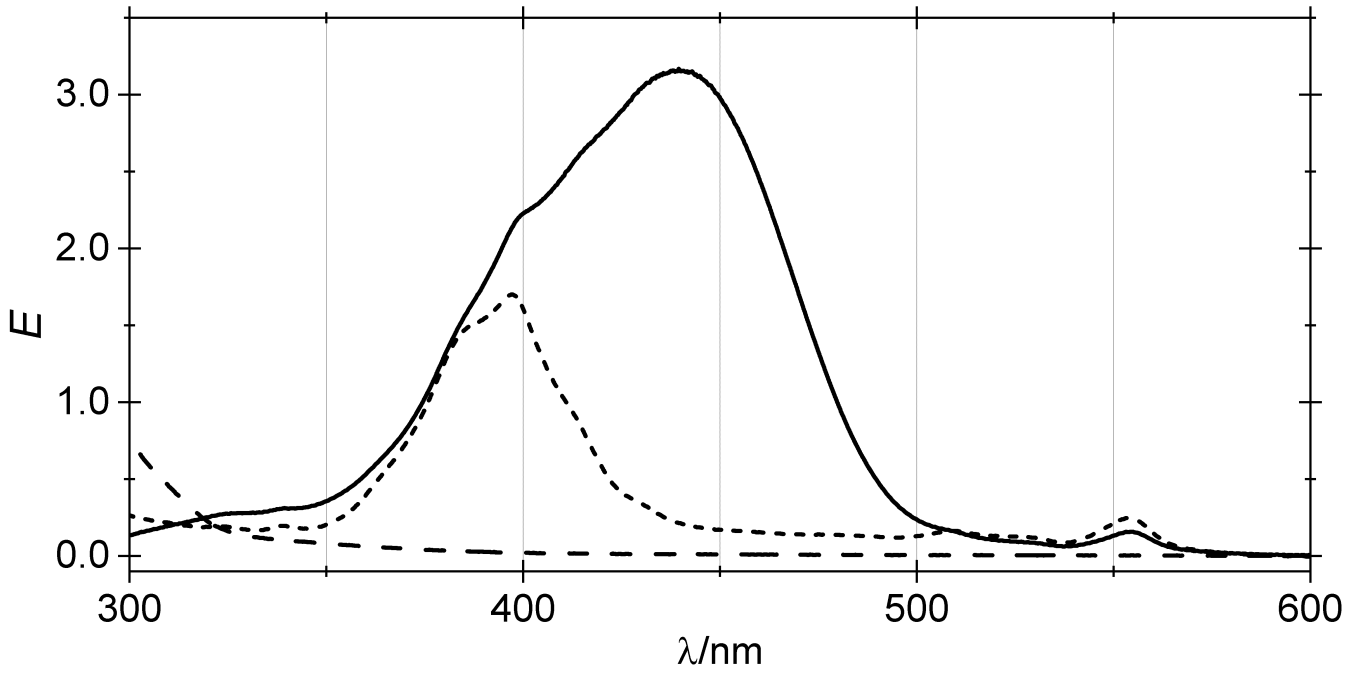


Figure S28: Matrix-isolated d_1-*p*-NBA dithiane in N_2 at 3 K after deposition (dashed trace), after 30 s irradiation at 313 nm (solid trace), and after 60 s irradiation at 436 nm (short-dashed trace).

2. Matrix isolation experiments on *p*-nitrobenzaldehyde dimethyl bisthioacetal (*p*-NBA-DMTA)

2.1. IR spectra of *p*-NBA-DMTA in N_2

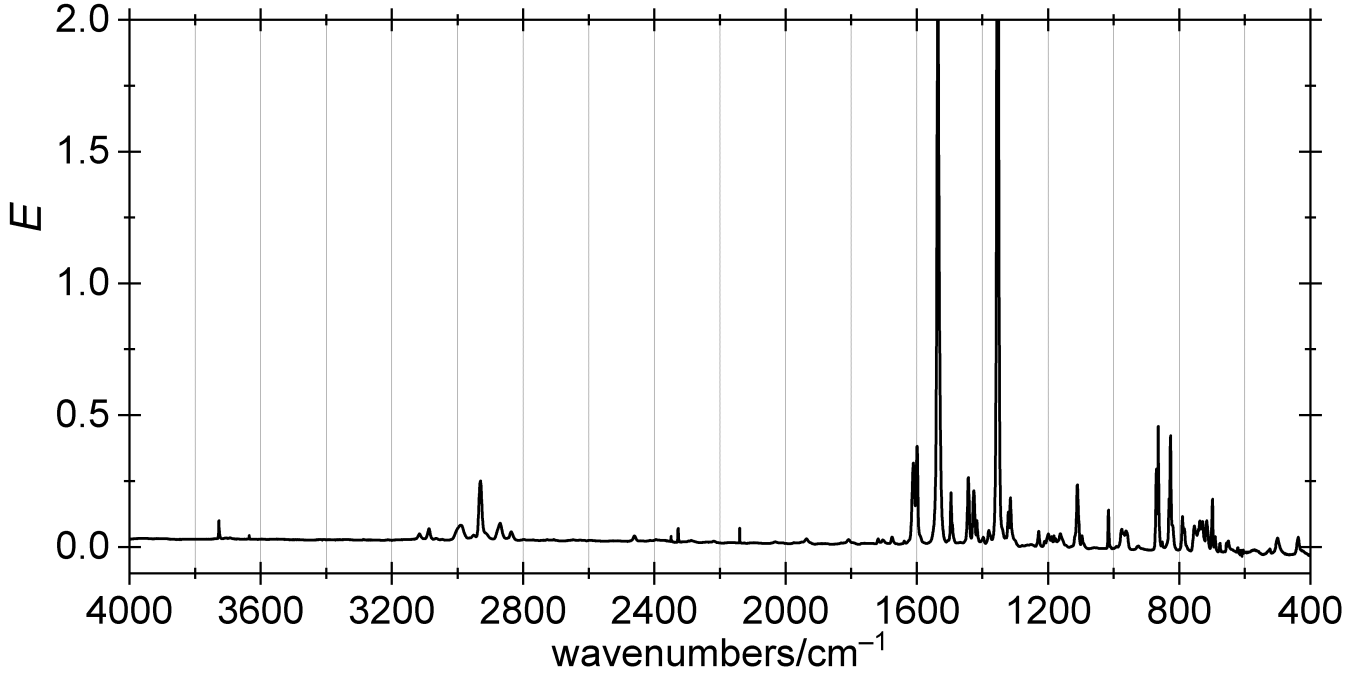


Figure S29: Matrix-isolated *p*-NBA-DMTA in N_2 at 3 K.

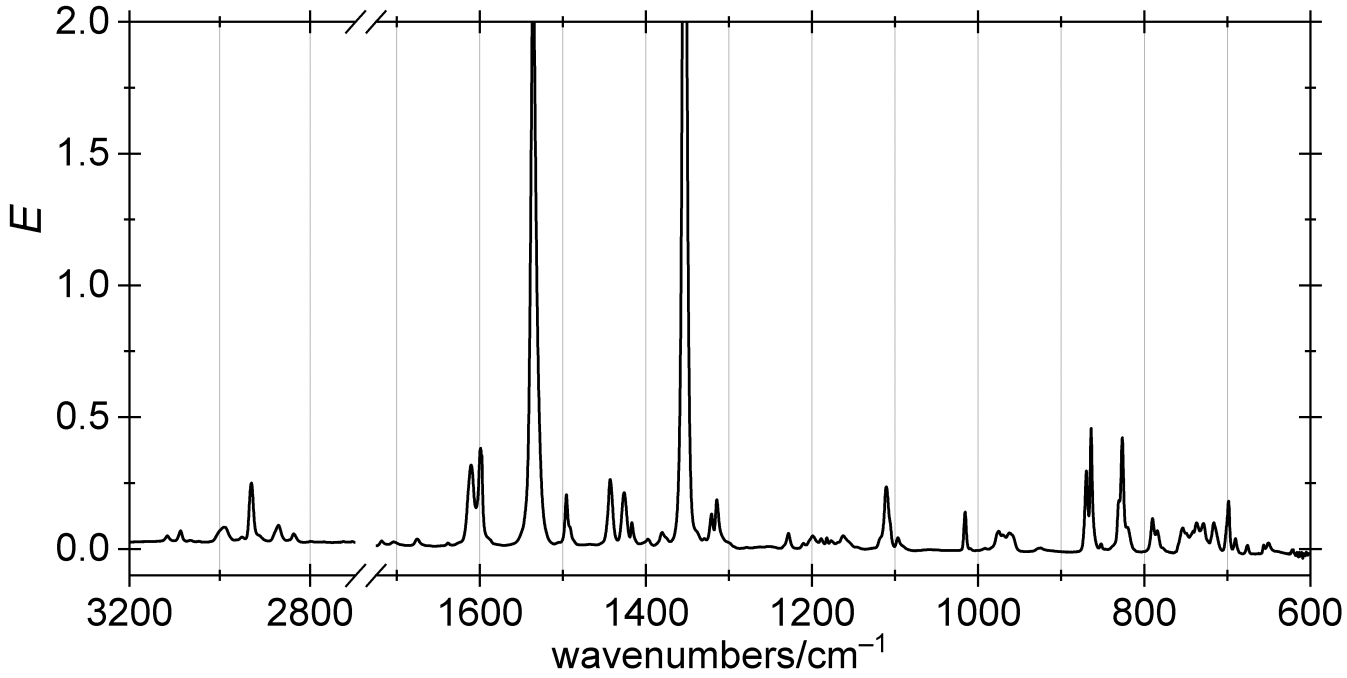


Figure S30: Matrix-isolated *p*-NBA-DMTA in N_2 at 3 K (detail).

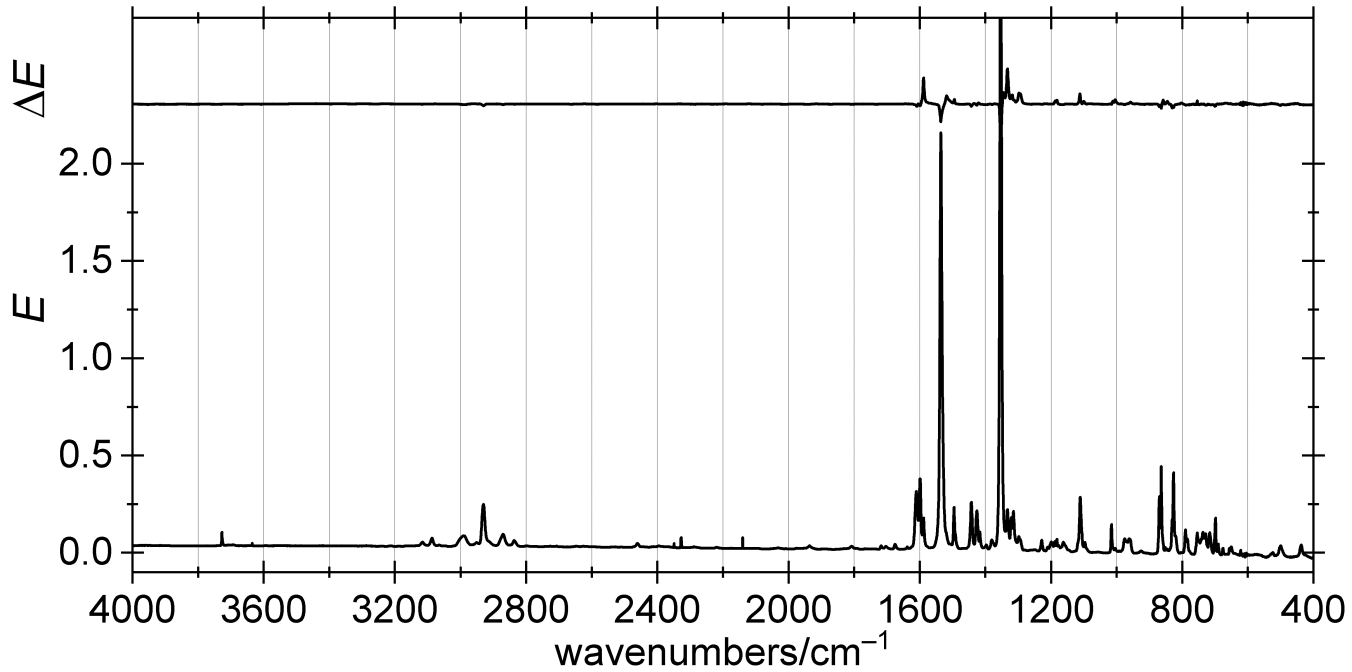


Figure S31: Matrix-isolated *p*-NBA-DMTA in N_2 at 3 K after 60 s irradiation at 313 nm; difference trace (before/after irradiation at 313 nm) on top.

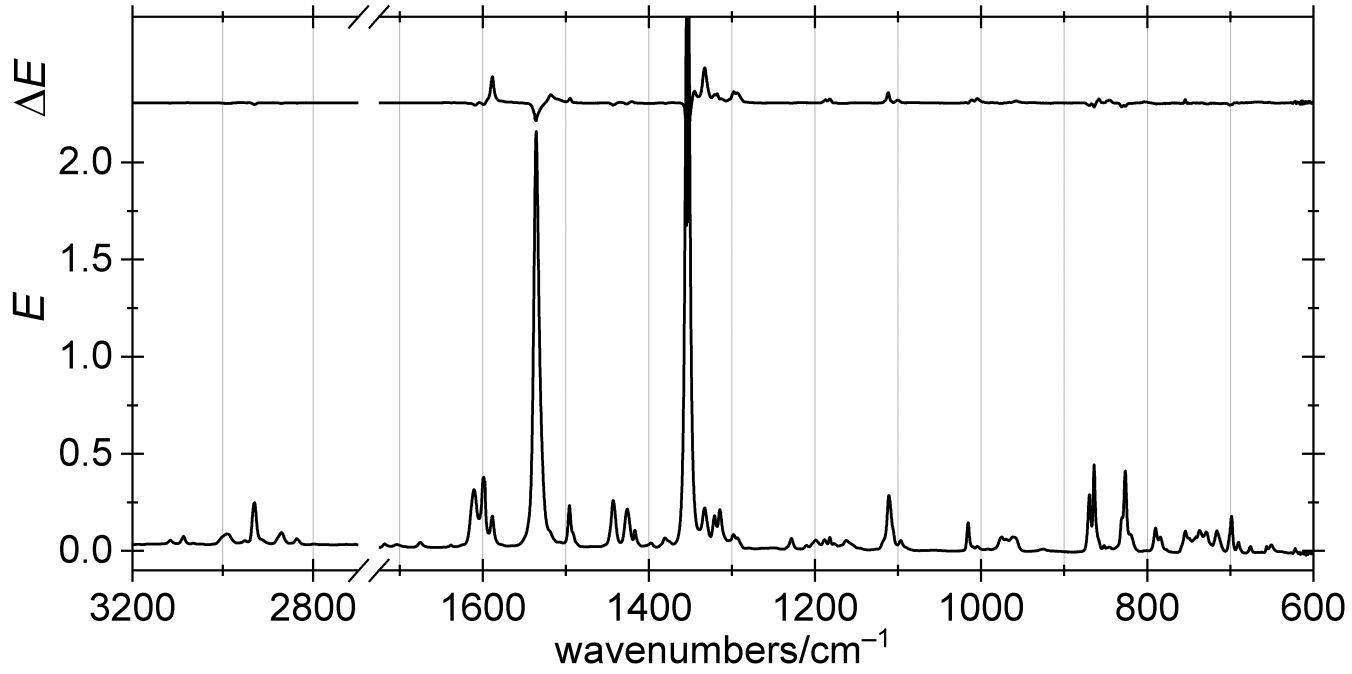


Figure S32: Matrix-isolated *p*-NBA-DMTA in N_2 at 3 K after 60 s irradiation at 313 nm (detail); difference trace (before/after irradiation at 313 nm) on top.

2.2. UV/Vis spectra of *p*-NBA-DMTA in N_2

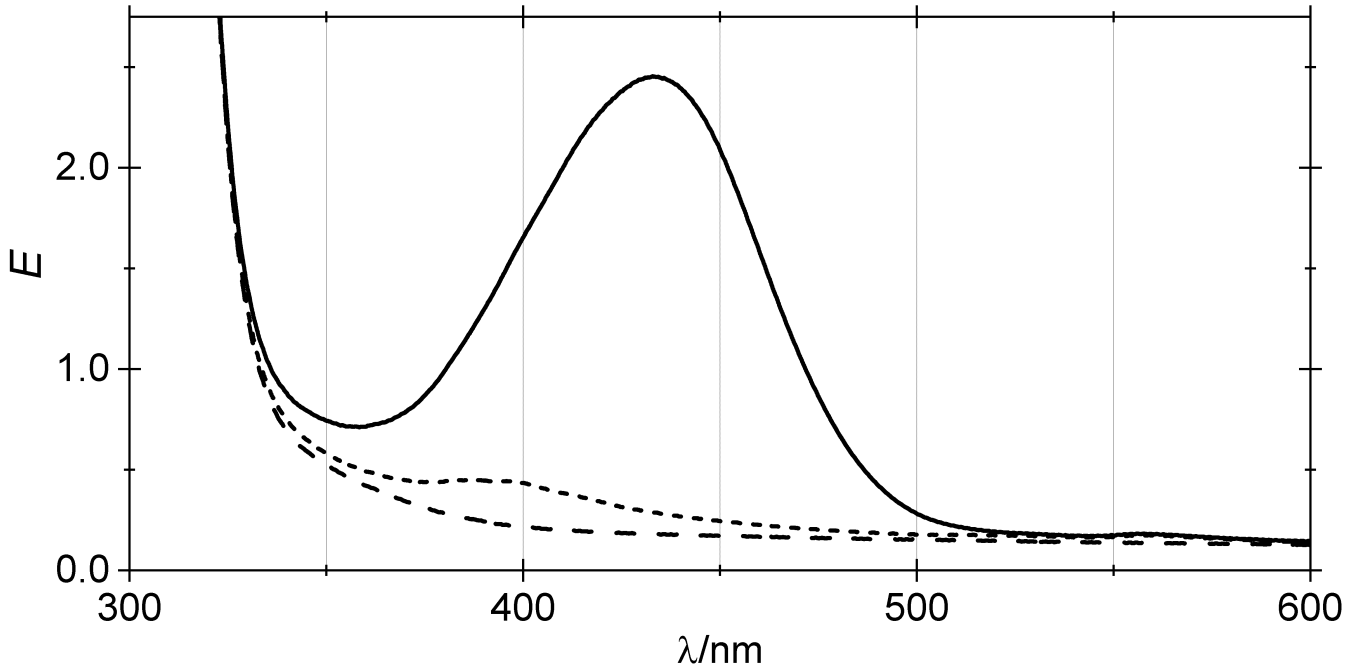


Figure S33: Matrix-isolated *p*-NBA-DMTA in N_2 at 3 K after deposition (dashed trace), after 60 s irradiation at 313 nm (solid trace), and after 90 s irradiation at 436 nm (short-dashed trace).

3. Matrix isolation experiments on *o*-nitrobenzaldehyde (*o*-NBA) dithiane

3.1. IR spectra of *o*-NBA dithiane in N_2

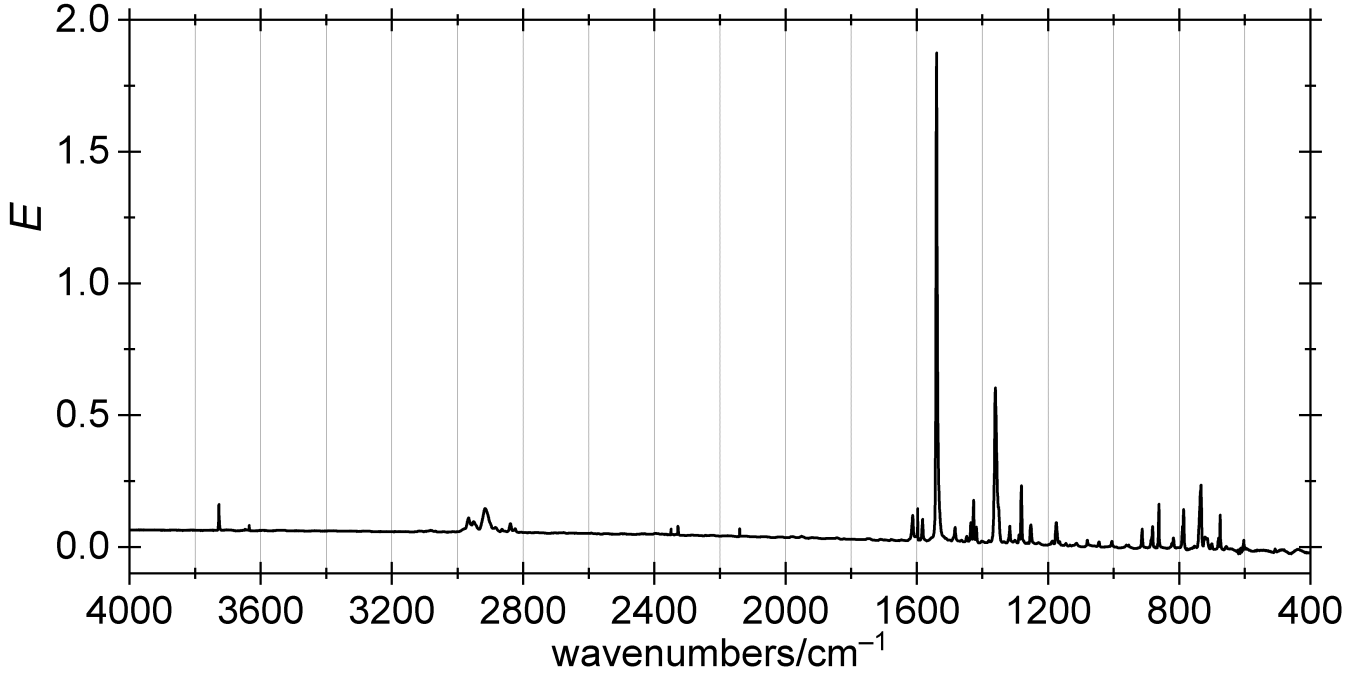


Figure S34: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K.

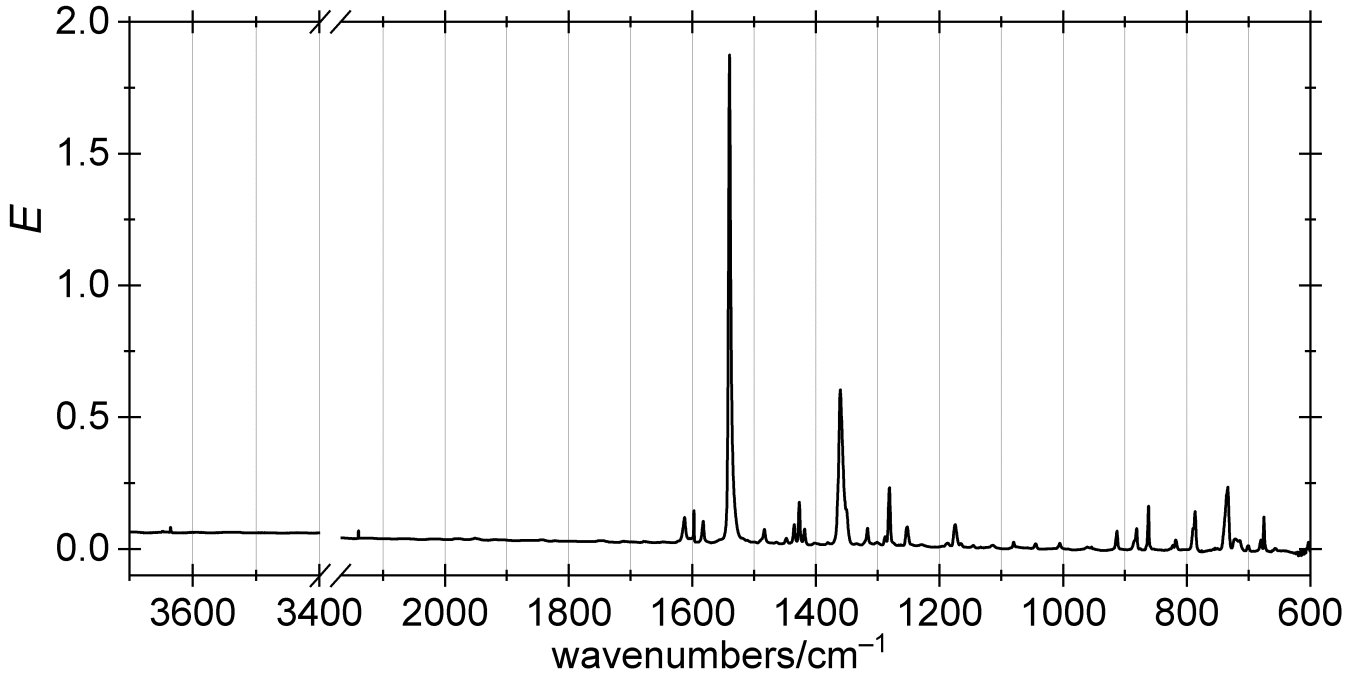


Figure S35: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K (detail).

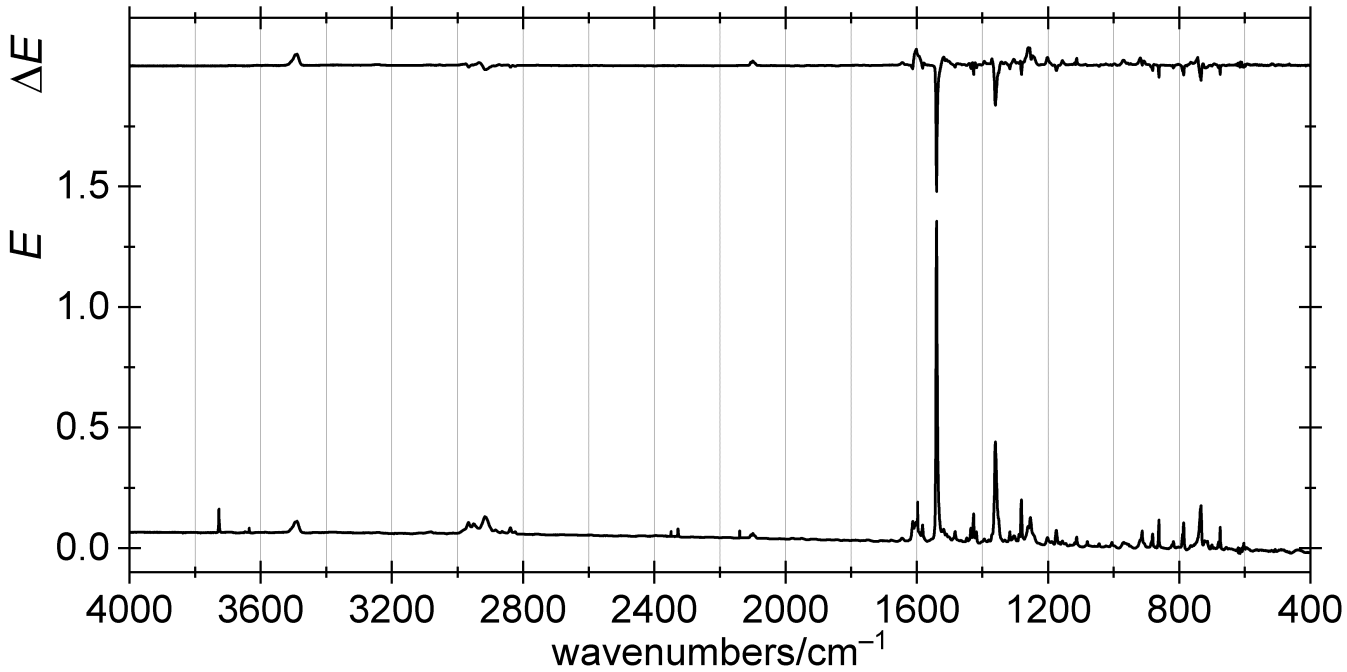


Figure S36: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm; difference trace (before/after irradiation at 313 nm) on top.

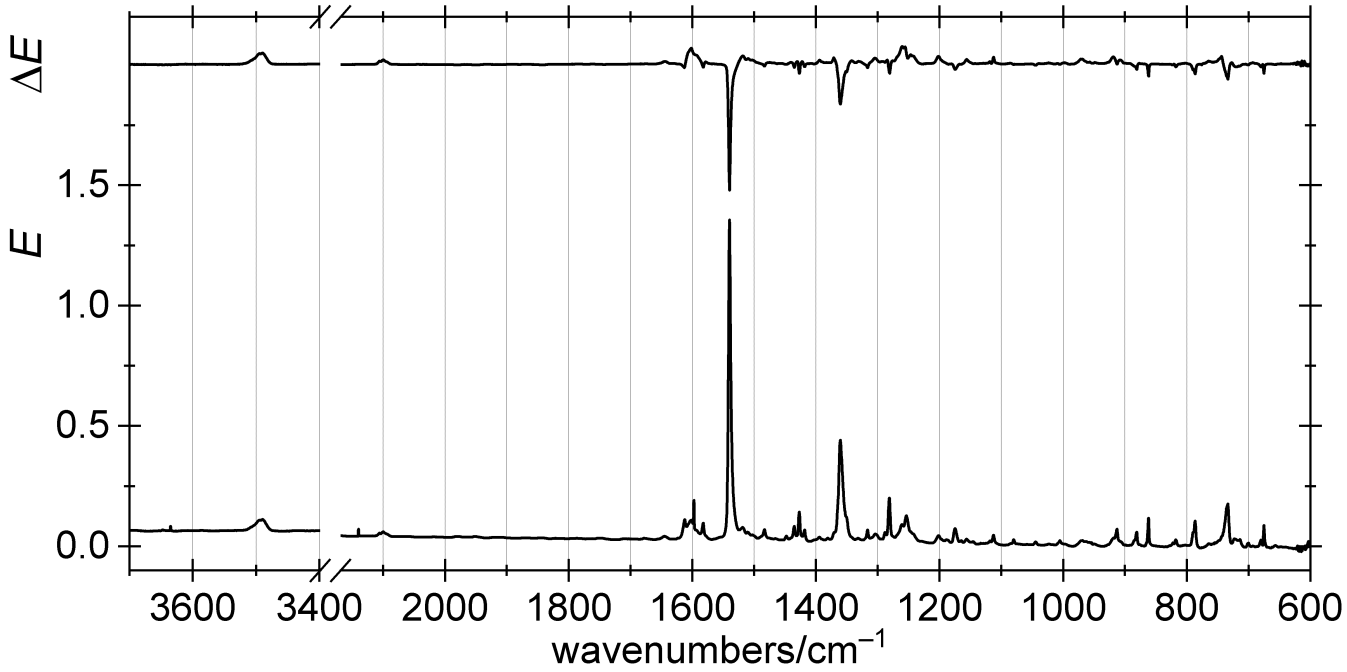


Figure S37: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm (detail) ; difference trace (before/after irradiation at 313 nm) on top.

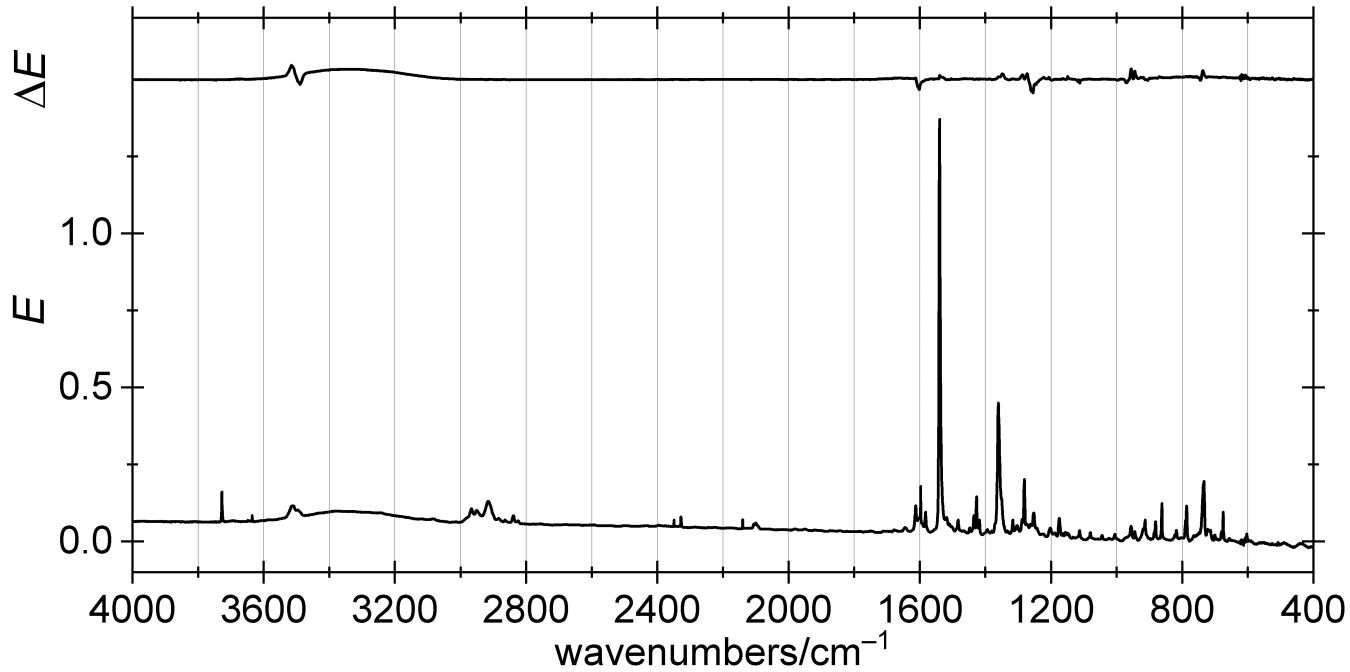


Figure S38: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm and 19 h in the dark; difference trace (before/after 19 h in the dark) on top.

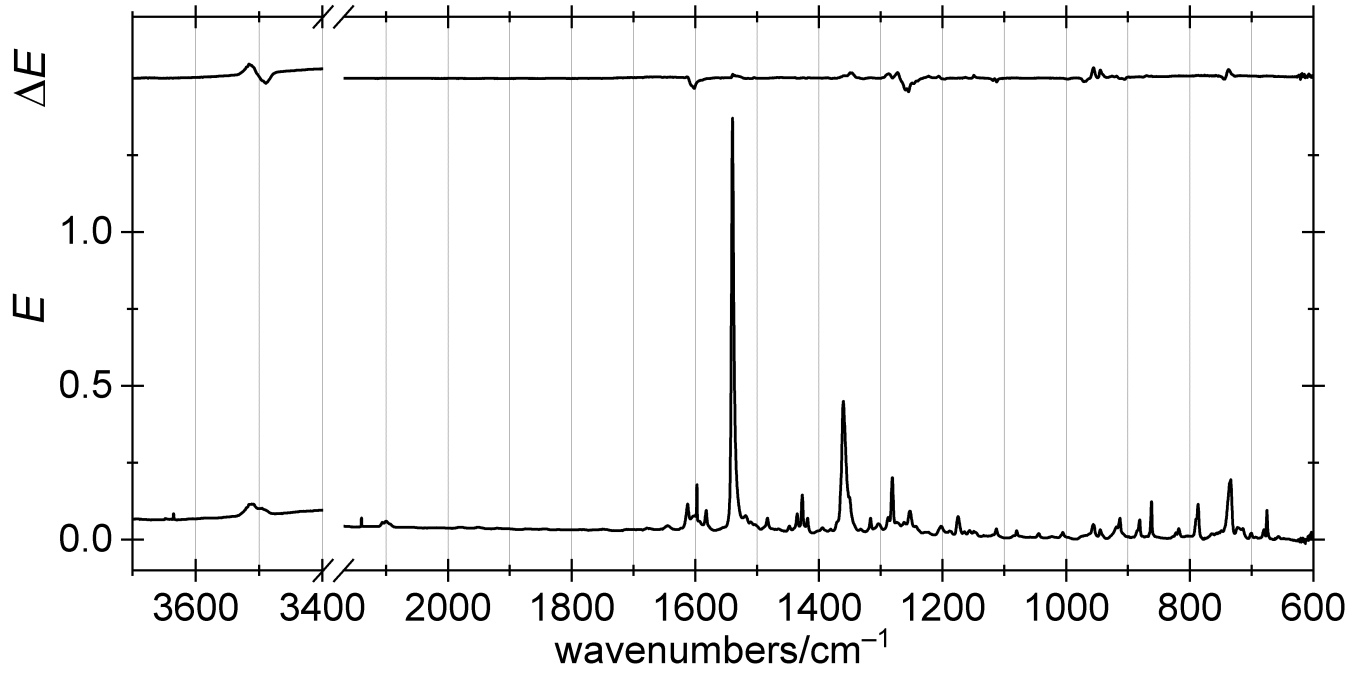


Figure S39: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm and 19 h in the dark (detail); difference trace (before/after 19 h in the dark) on top.

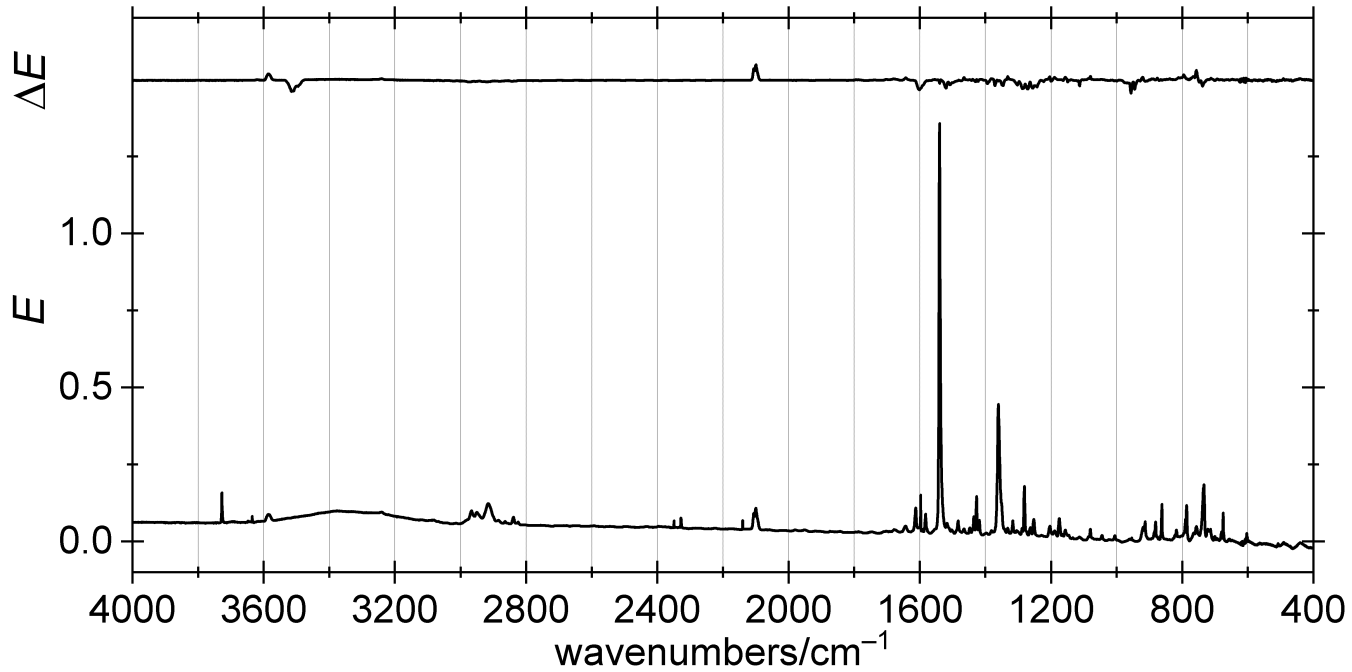


Figure S40: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 19 h in the dark, and 6 min irradiation at 436 nm; difference trace (before/after irradiation at 436 nm) on top.

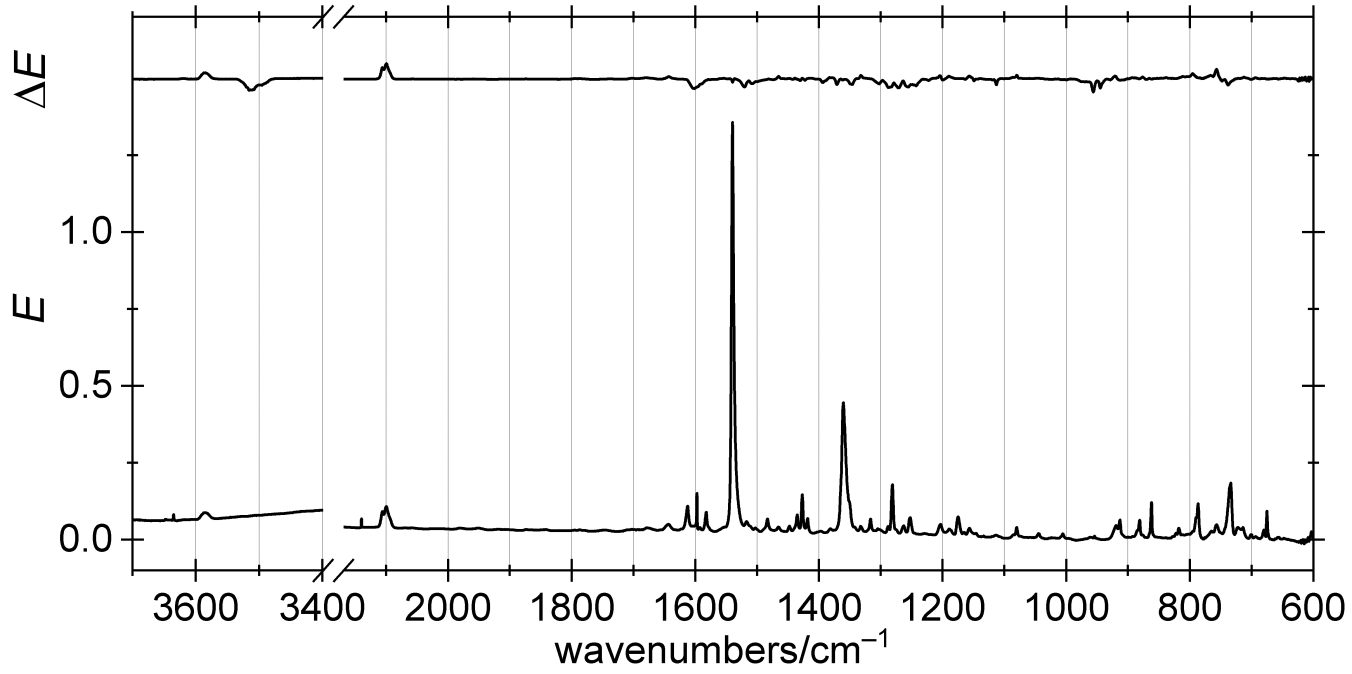


Figure S41: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 19 h in the dark, and 6 min irradiation at 436 nm (detail); difference trace (before/after irradiation at 436 nm) on top.

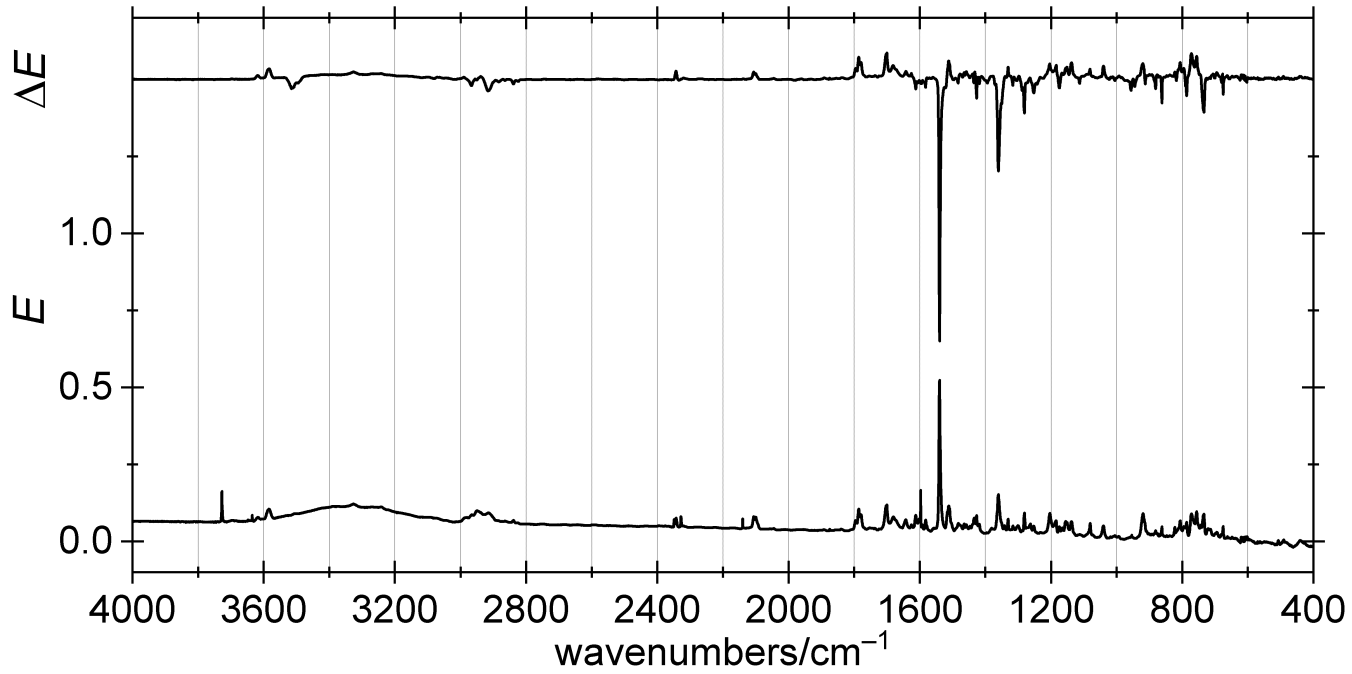


Figure S42: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 19 h in the dark, and 4 h irradiation at 436 nm; difference trace (before/after irradiation at 436 nm) on top.

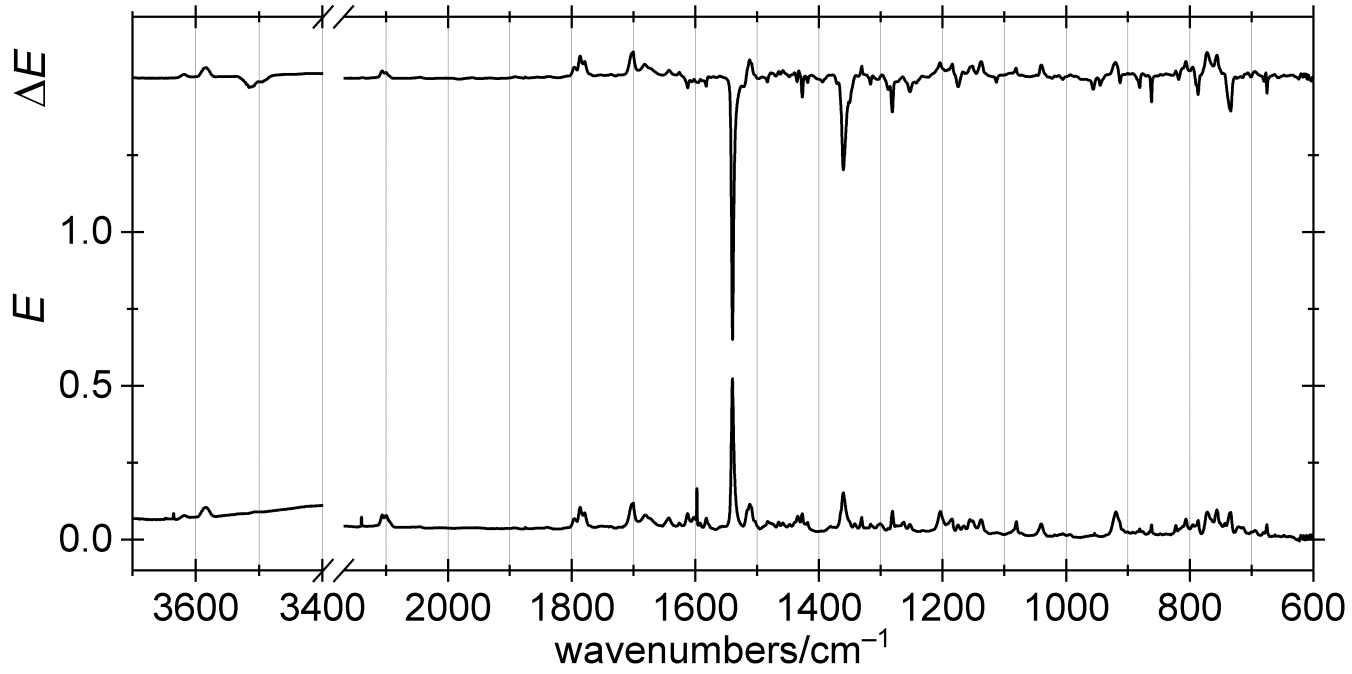


Figure S43: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 19 h in the dark, and 4 h irradiation at 436 nm (detail); difference trace (before/after irradiation at 436 nm) on top.

3.2. IR spectra of d_1-*o*-NBA dithiane in N_2

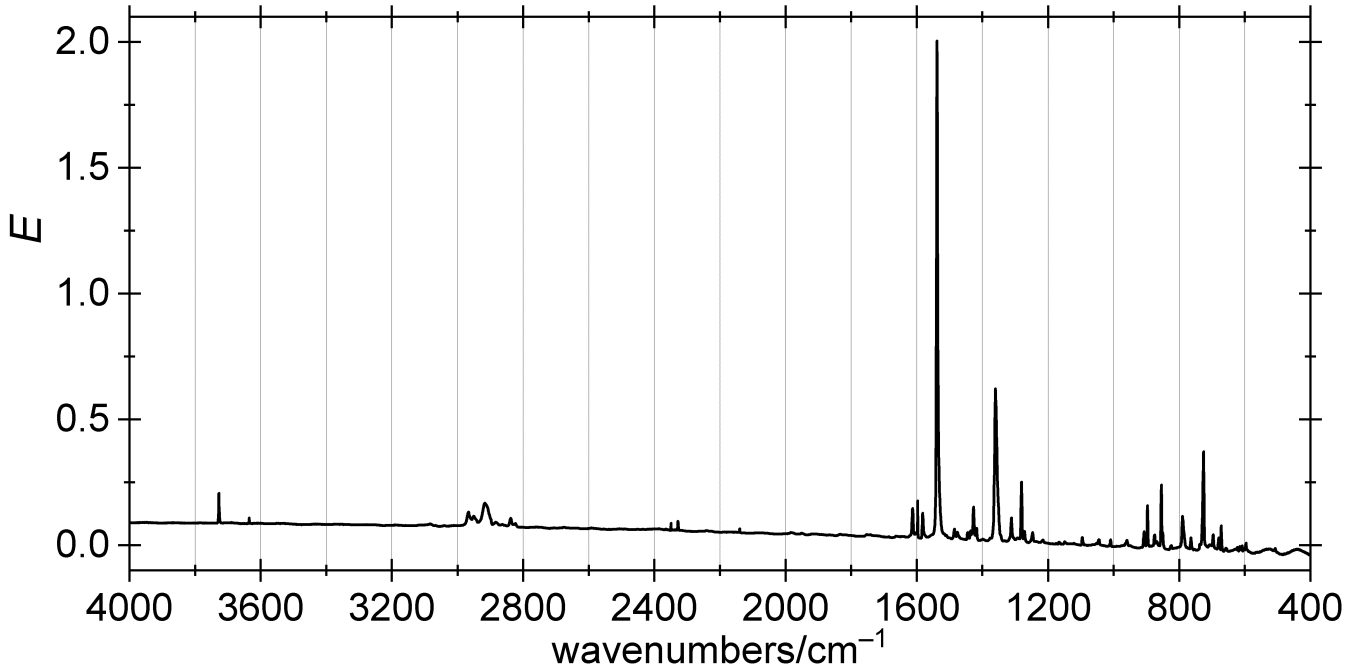


Figure S44: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K.

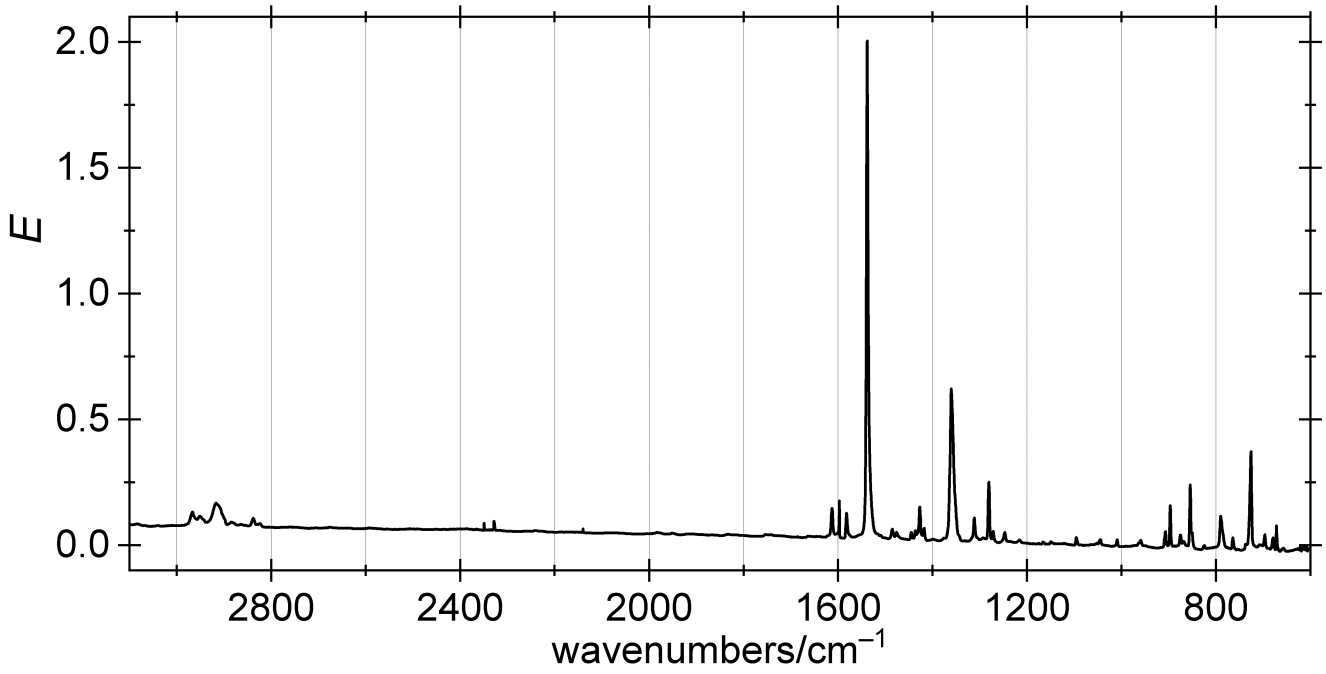


Figure S45: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K (detail).

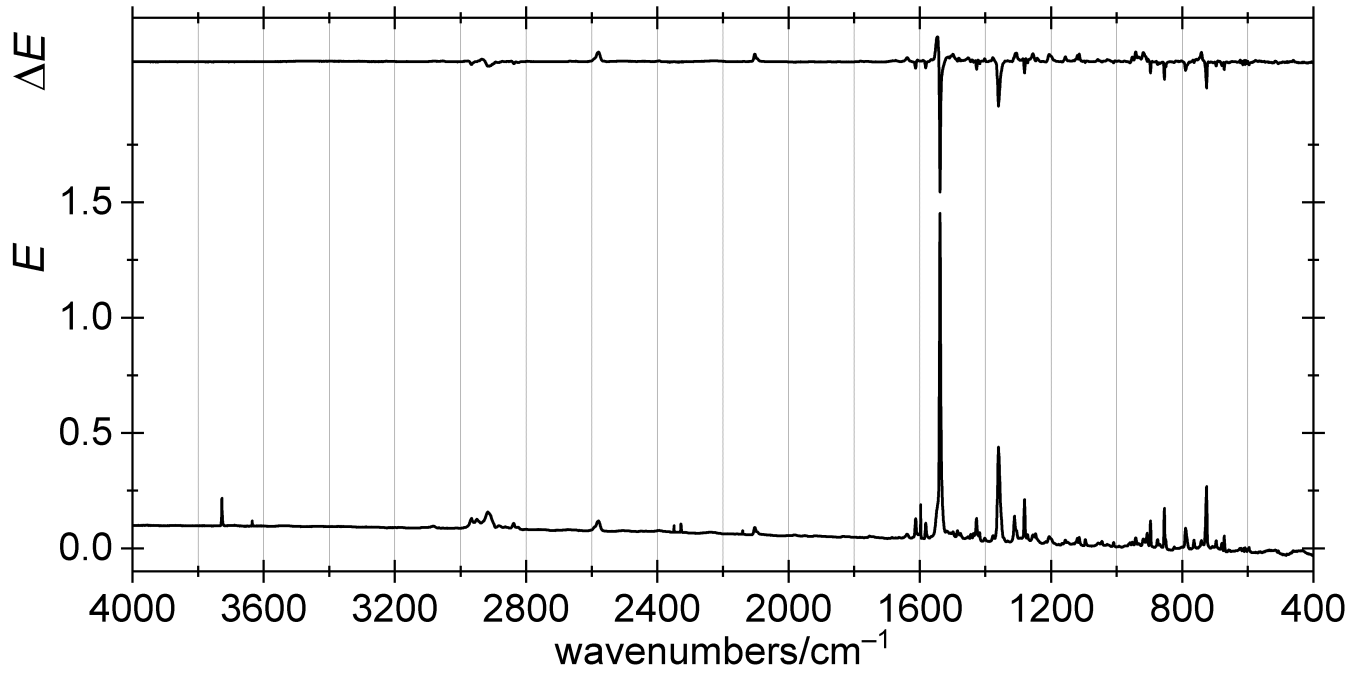


Figure S46: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm; difference trace (before/after irradiation at 313 nm) on top.

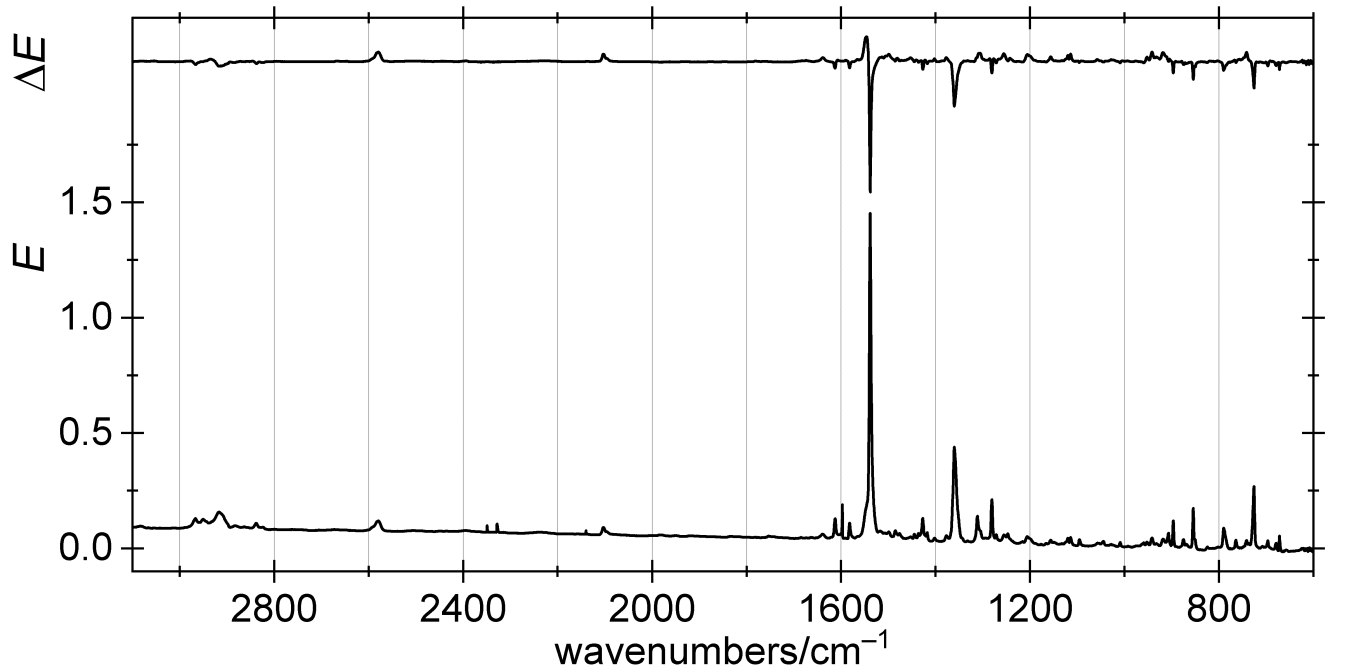


Figure S47: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm (detail); difference trace (before/after irradiation at 313 nm) on top.

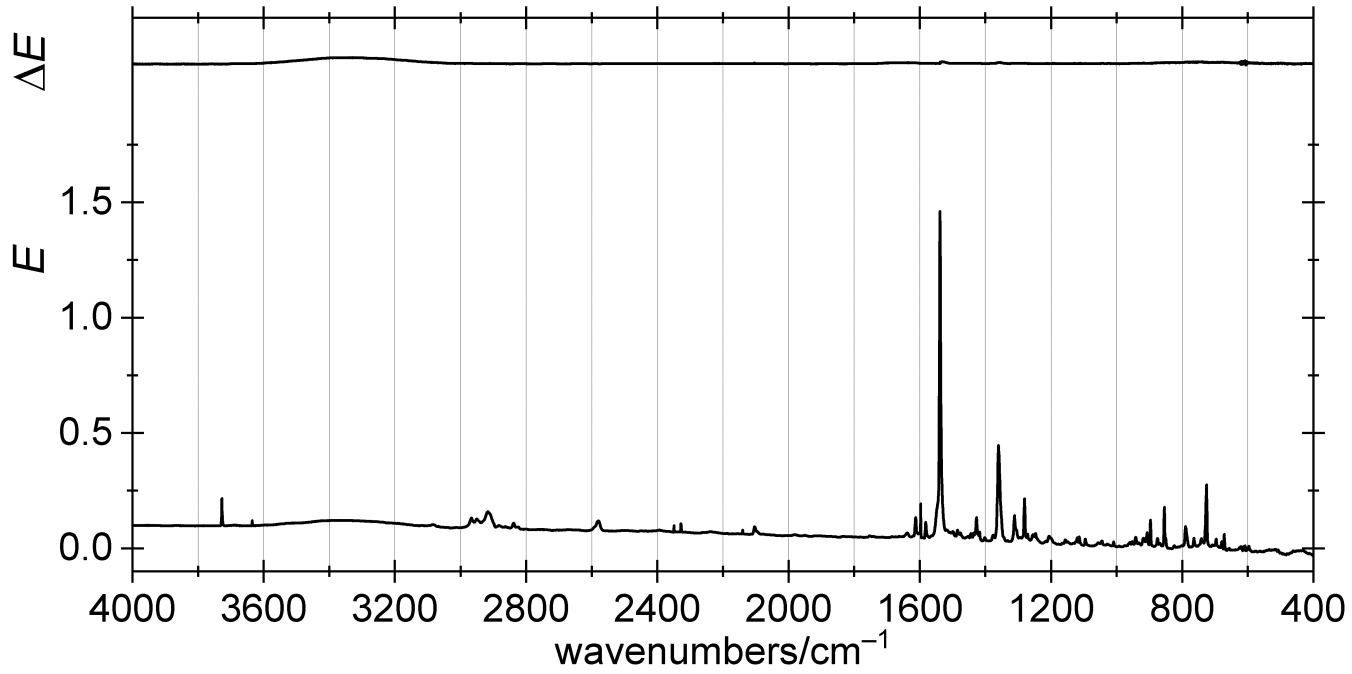


Figure S48: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm and 16 h in the dark; difference trace (before/after 16 h in the dark) on top.

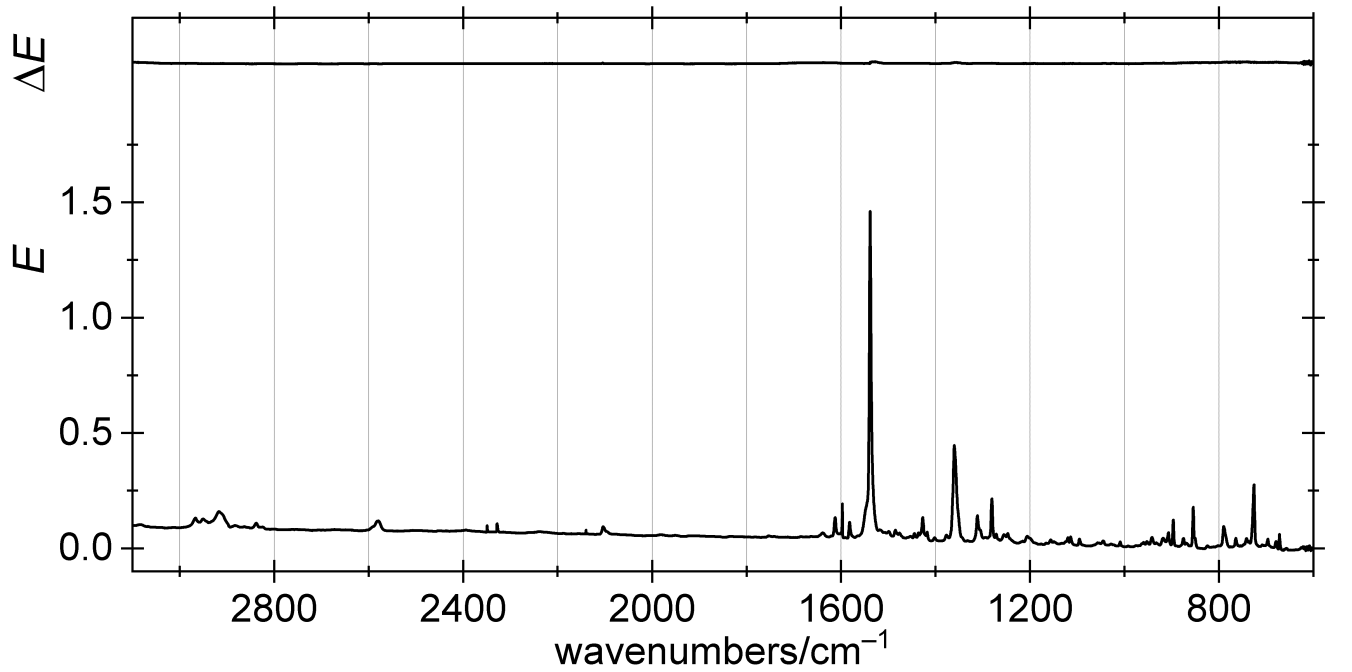


Figure S49: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm and 16 h in the dark (detail); difference trace (before/after 16 h in the dark) on top.

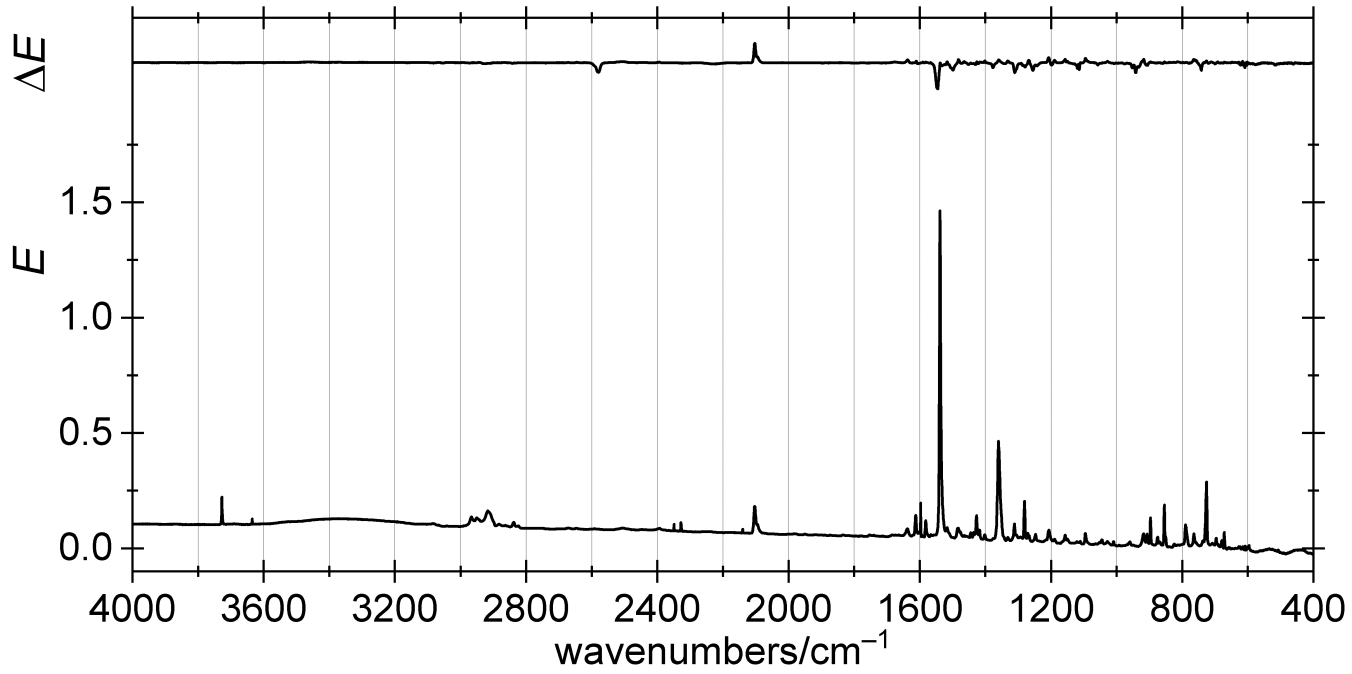


Figure S50: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, and 4 min irradiation at 436 nm; difference trace (before/after irradiation at 436 nm) on top.

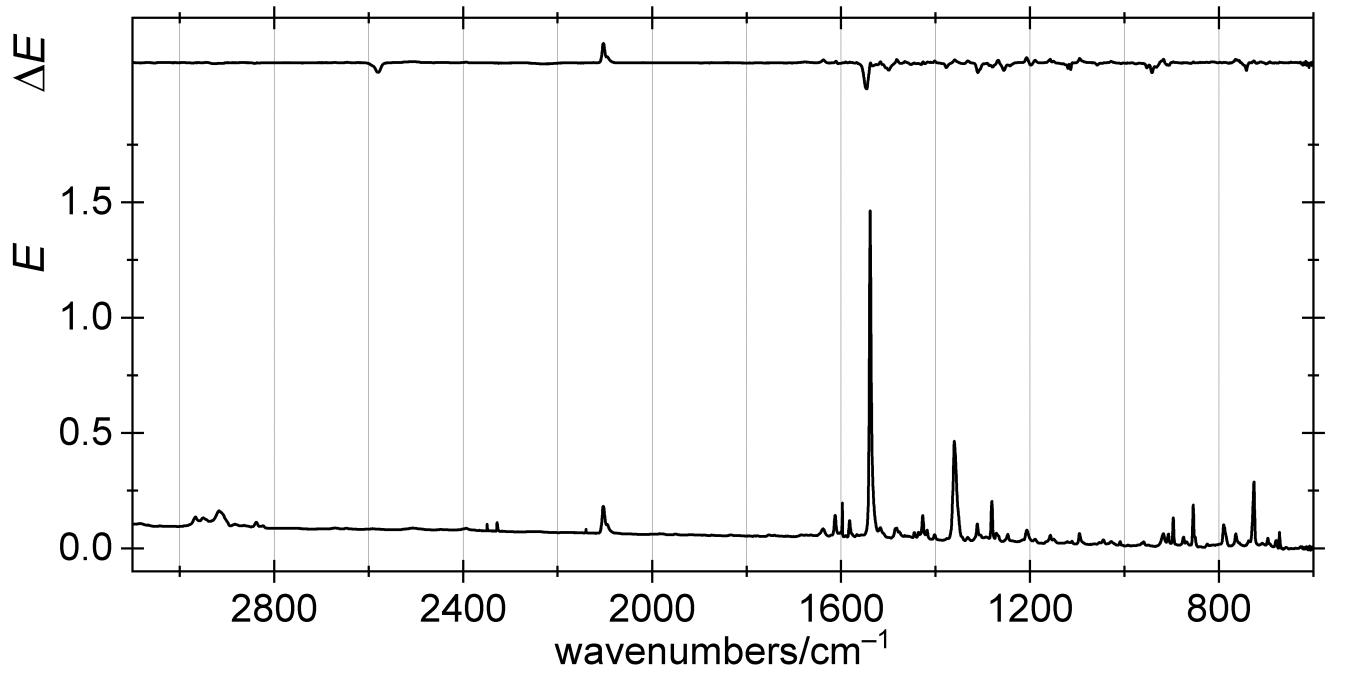


Figure S51: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, and 4 min irradiation at 436 nm (detail); difference trace (before/after irradiation at 436 nm) on top.

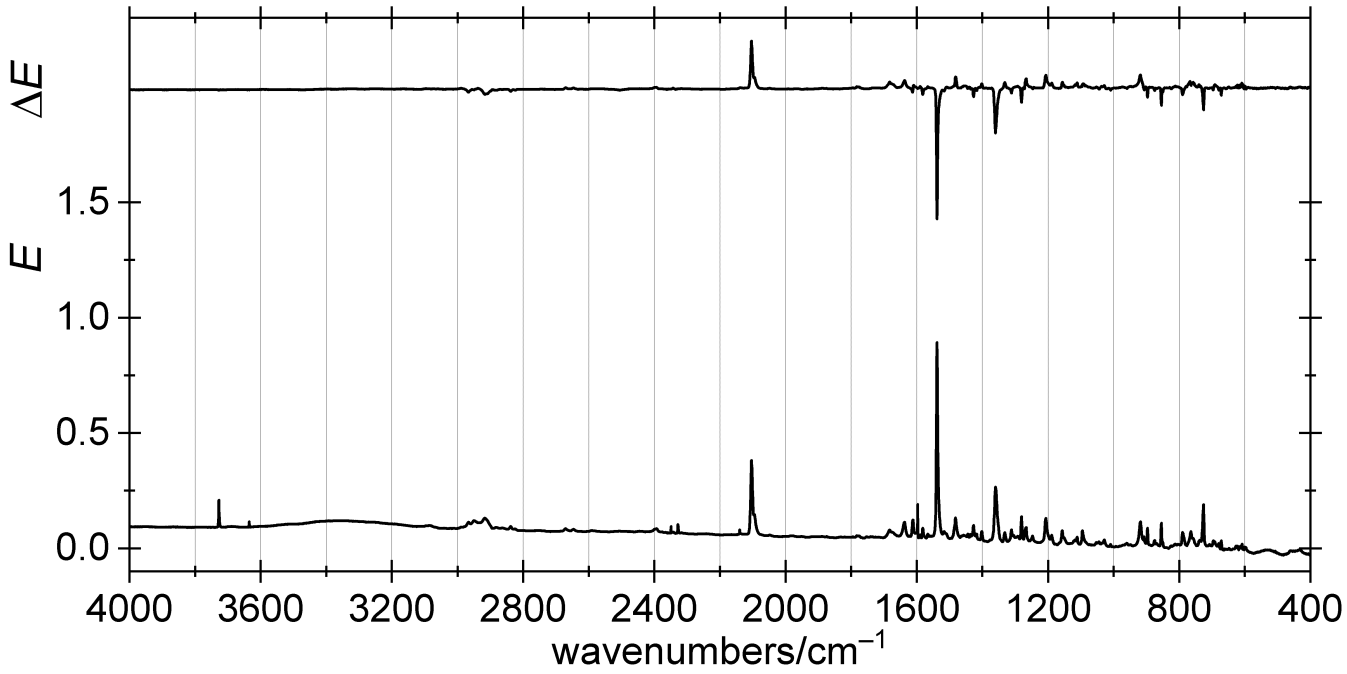


Figure S52: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, and 20 min irradiation at 405 nm; difference trace (before/after irradiation at 405 nm) on top.

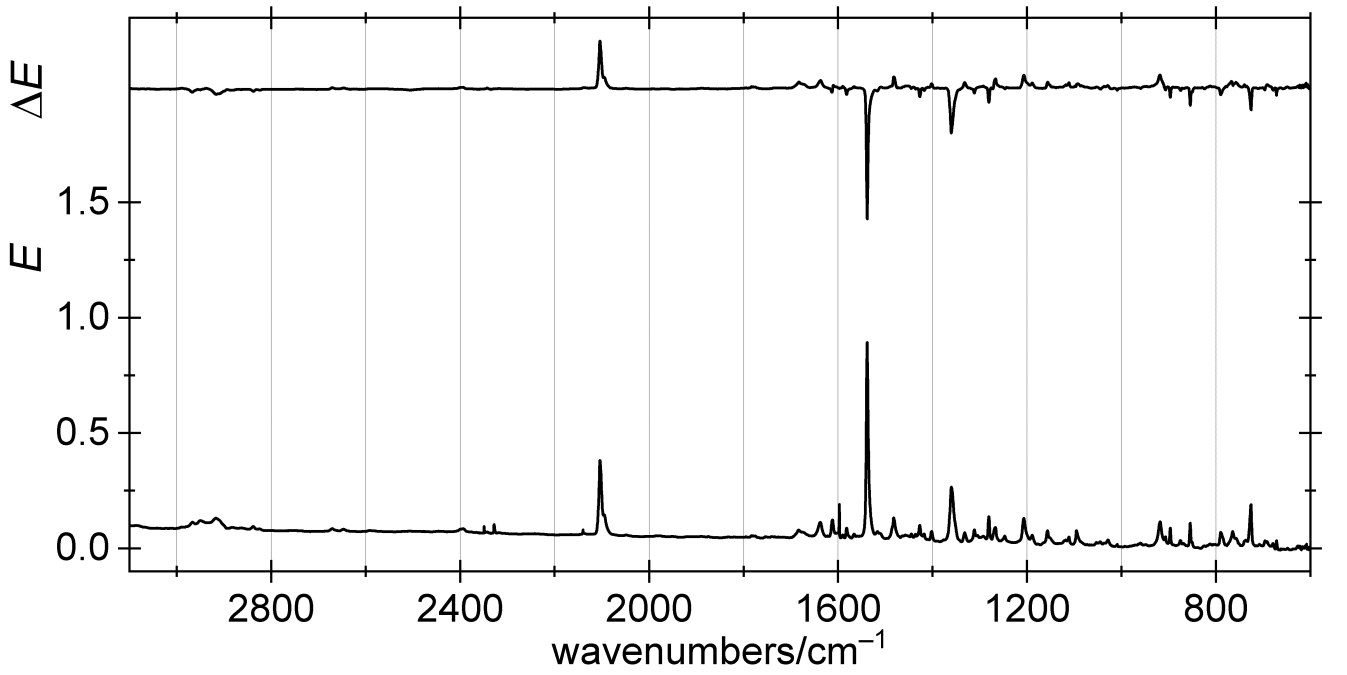


Figure S53: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, and 20 min irradiation at 405 nm (detail); difference trace (before/after irradiation at 405 nm) on top.

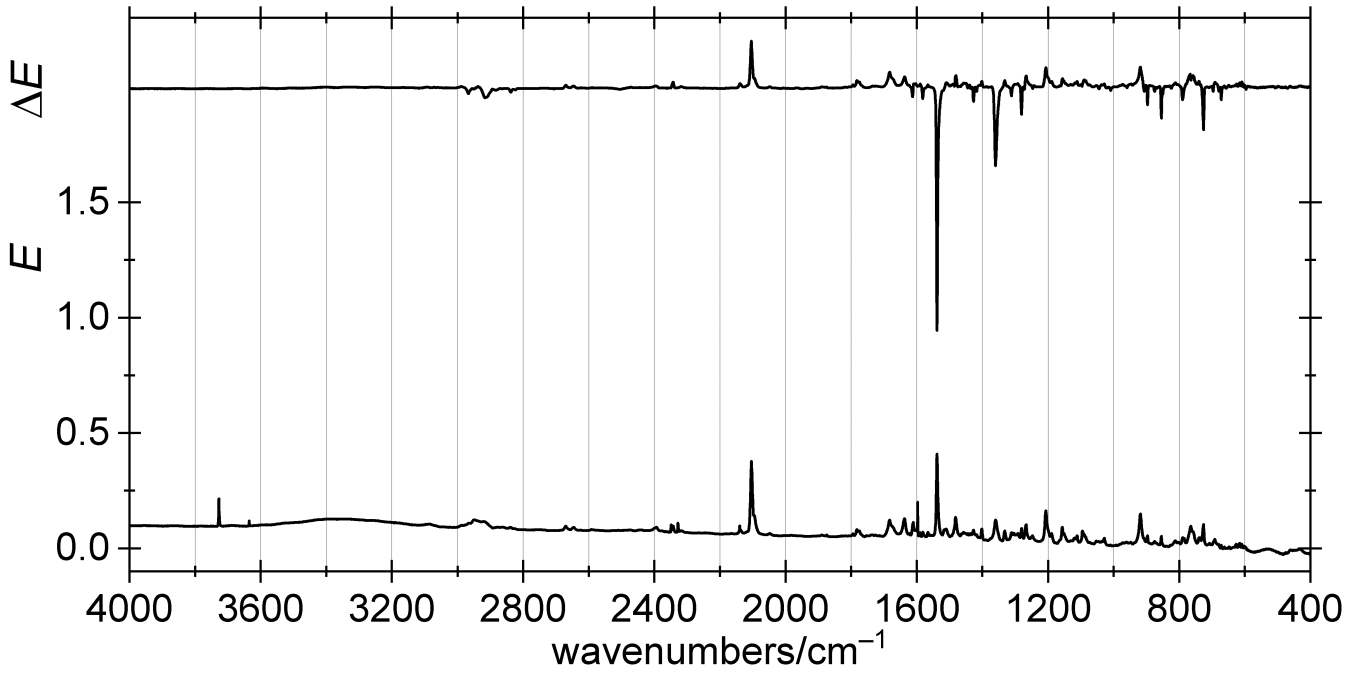


Figure S54: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, and 60 min irradiation at 405 nm; difference trace (before/after irradiation at 405 nm) on top.

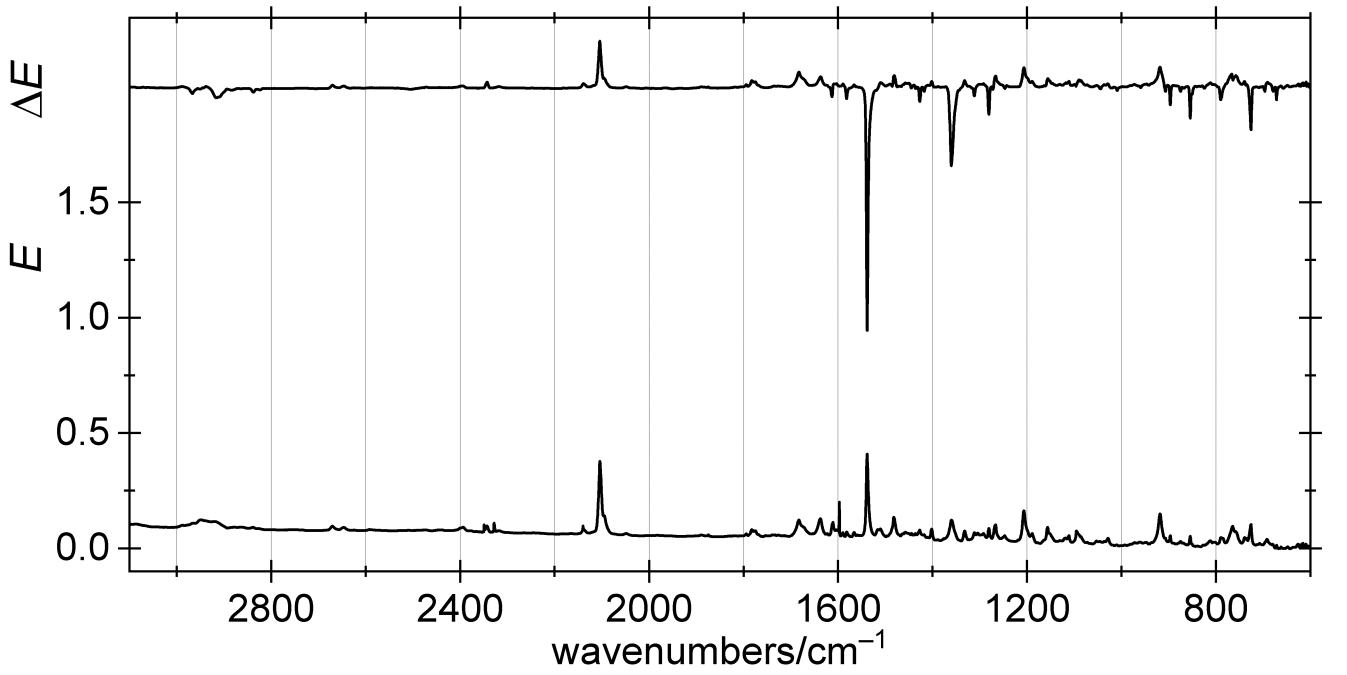


Figure S55: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, and 60 min irradiation at 405 nm (detail); difference trace (before/after irradiation at 405 nm) on top.

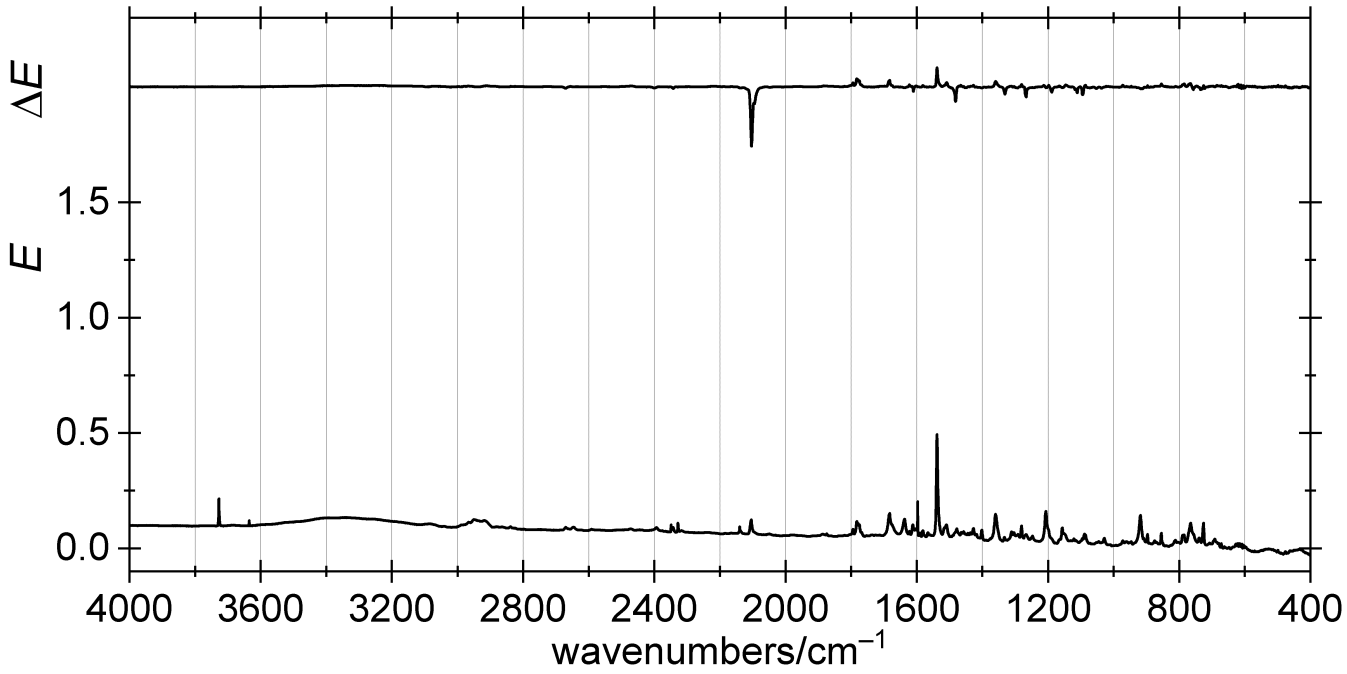


Figure S56: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, 60 min irradiation at 405 nm, and 125 min irradiation at 546 nm; difference trace (before/after irradiation at 546 nm) on top.

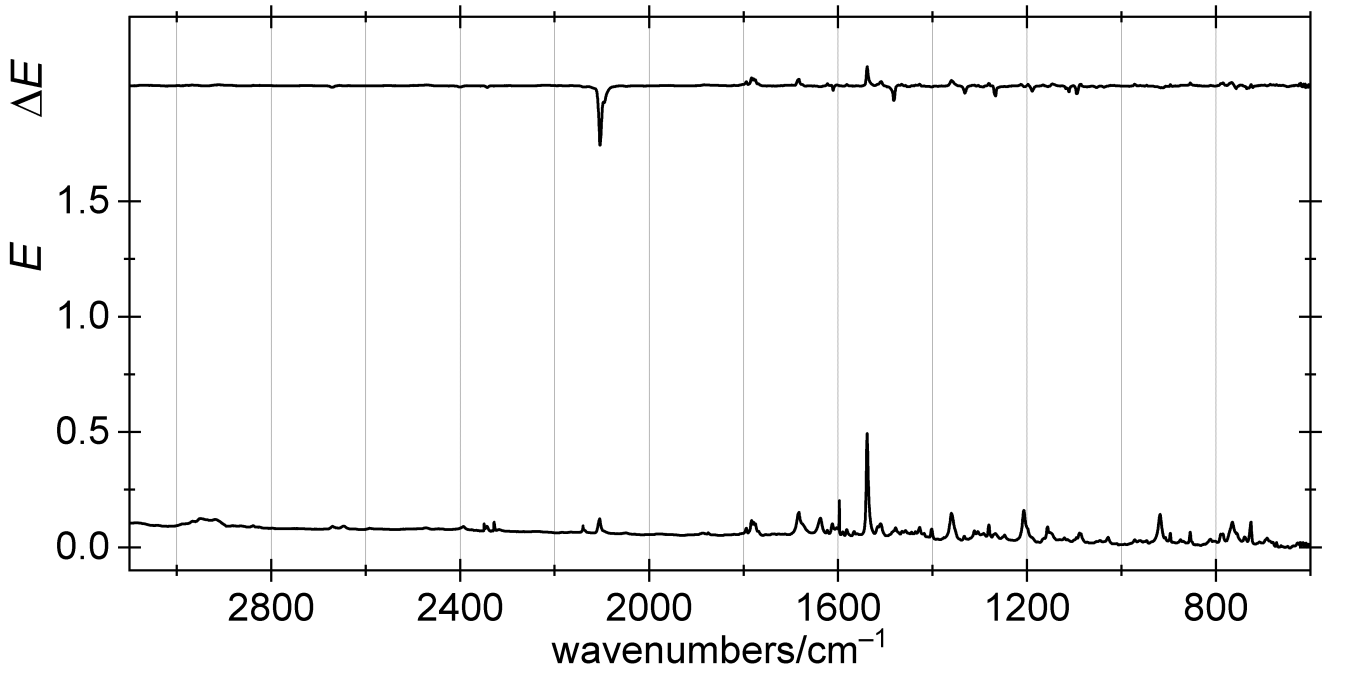


Figure S57: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after 60 s irradiation at 313 nm, 16 h in the dark, 4 min irradiation at 436 nm, 60 min irradiation at 405 nm, and 125 min irradiation at 546 nm (detail); difference trace (before/after irradiation at 546 nm) on top.

3.3. UV/Vis spectra of *o*-NBA dithiane in N_2

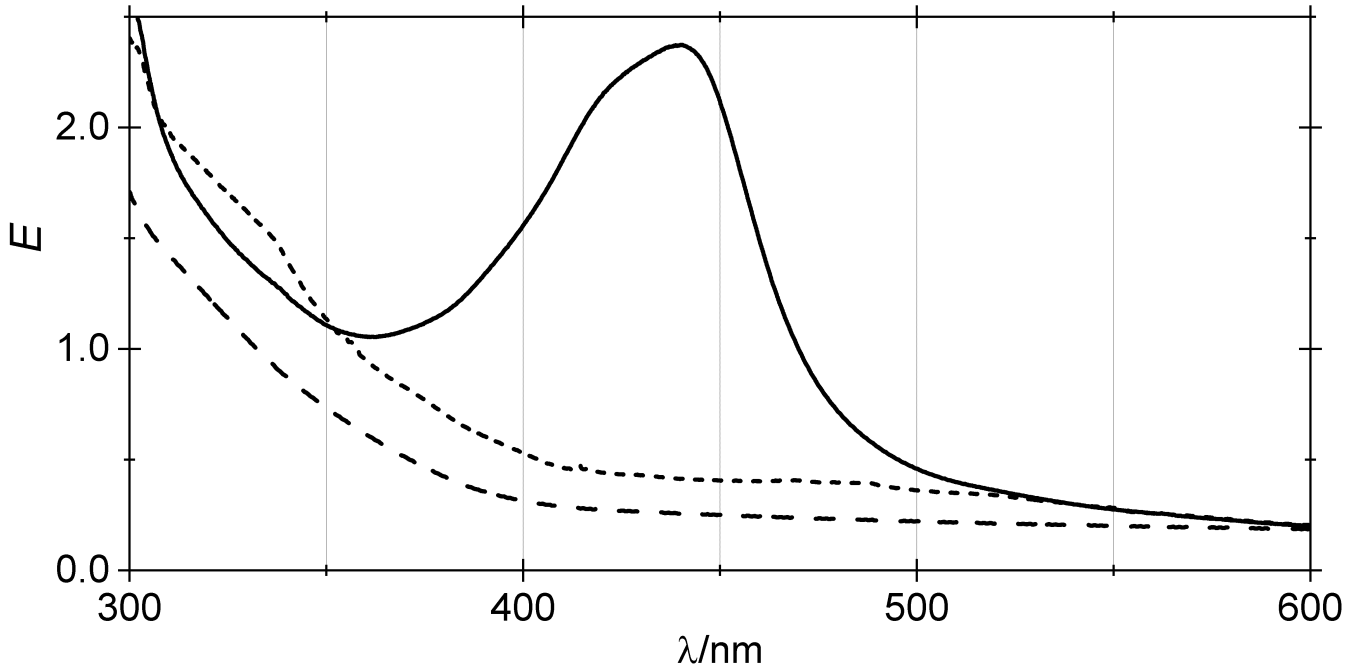


Figure S58: Matrix-isolated *o*-NBA dithiane in N_2 at 3 K after deposition (dashed trace), after 60 s irradiation at 313 nm (solid trace), and 6 min irradiation at 436 nm (short-dashed trace).

3.4. UV/Vis spectra of d_1-*o*-NBA dithiane in N_2

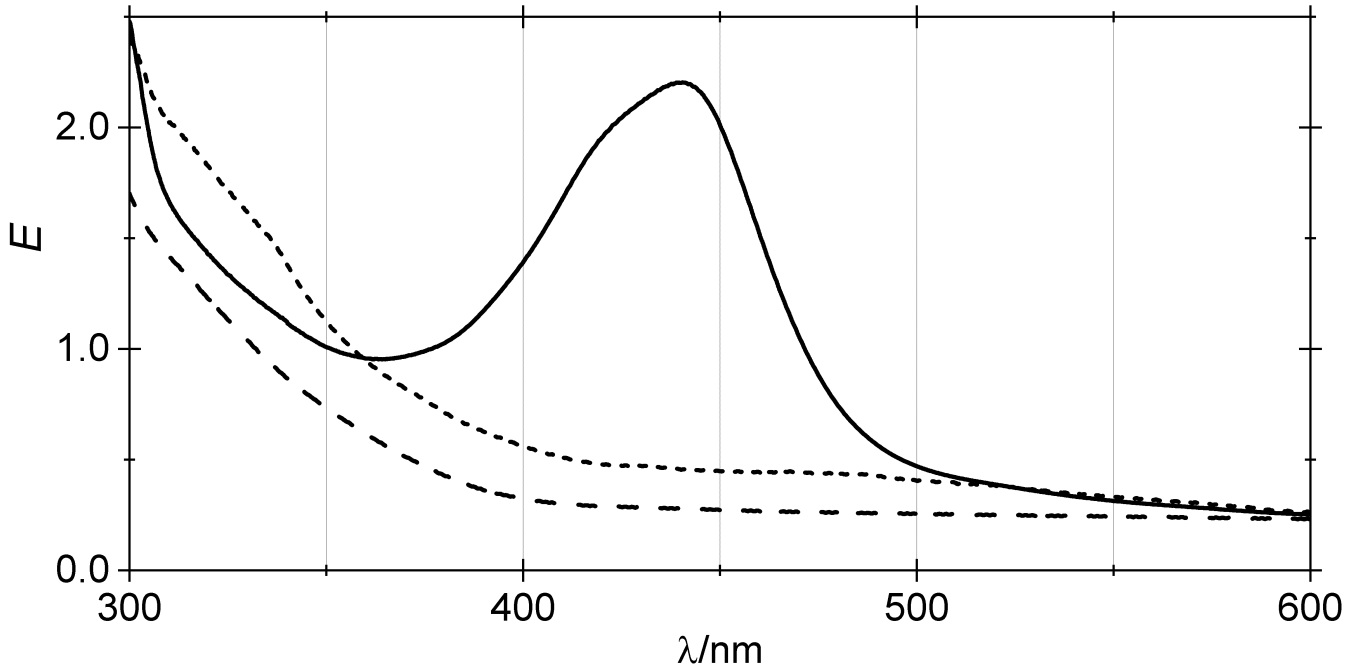
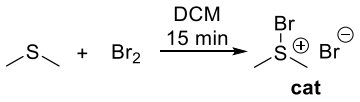


Figure S59: Matrix-isolated d_1-*o*-NBA dithiane in N_2 at 3 K after deposition (dashed trace), after 60 s irradiation at 313 nm (solid trace), and 4 min irradiation at 436 nm (short-dashed trace).

4. Compound syntheses and characterization

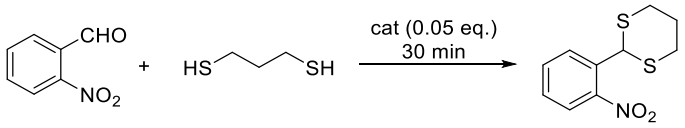
All starting materials were purchased from commercial suppliers and used for synthesis without further purification. Solvents for column chromatography, extractions, and filtrations were distilled prior to use. All NMR spectra were recorded on Bruker AV 400 or AV 400HD spectrometers. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS (δ = 0.00 ppm) as internal standard or to the respective solvent residual peak of D_2O (δ = 4.79 ppm). ^{13}C {^1H} NMR spectra in D_2O are calibrated to 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSPA).

4.1. (Bromodimethyl)sulfonium bromide



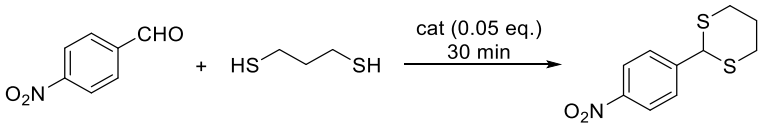
10 mL (200 mmol) bromine were diluted in 40 mL dry dichloromethane (DCM). A mixture of 15 mL (200 mmol) dimethyl sulfide in 40 mL DCM was added dropwise over 15 min at r. t. The resulting orange powder was washed with hexane and dried in vacuo over P_4O_{10} (0.18 mol, 40.3 g, 92%). ^1H NMR (400 MHz, D_2O): δ = 3.56 (s, 6H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 38.7 ppm.

4.2. 2-(2-Nitrophenyl)-1,3-dithiane



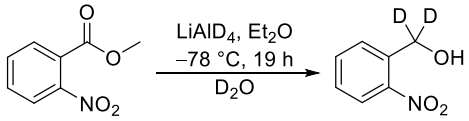
1.81 g (12 mmol) 2-nitrobenzaldehyde were dissolved in 1.3 mL (13.2 mmol) 1,3-propane dithiol. 138.9 mg (0.60 mmol, 0.05 eq.) **cat** were added to the yellow-green solution. After 30 min, a yellow gel formed, which was heated to 100 °C in 10 mL isopropanol after the addition of two drops of saturated aqueous $NaHCO_3$. During cooling, light-yellow crystals formed, which were separated from the gel and washed with isopropanol. This procedure was repeated until no more crystals could be separated from the gel. The product was purified by column chromatography (ethyl acetate/*n*-pentane 1:2; R_f = 0.63) and dried in vacuo over P_4O_{10} (2.07 mmol, 0.50 g, 17%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 2H), 7.55 (m, 1H), 7.37 (m, 1H), 5.82 (s, 1H), 3.10-2.84 (m, 4H), 2.17-1.83 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 130.7, 129.0, 124.7, 46.0, 32.3, 25.1 ppm. Note that quaternary carbon signals were not detected. HRMS (ESI): calcd m/z for $C_{10}H_{11}NO_2S_2Na$ $[M + Na]^+$ 264.0123, found 264.0120.

4.3. 2-(4-Nitrophenyl)-1,3-dithiane



1.81 g (12 mmol) 4-nitrobenzaldehyde were dissolved in 1.3 mL (13.2 mmol) 1,3-propane dithiol. 139.5 mg (0.63 mmol, 0.05 eq.) **cat** were added to the yellow-green solution. After 30 min, a yellow gel formed, which was heated to 100 °C in 10 mL isopropanol after addition of two drops of saturated aqueous $NaHCO_3$. During cooling, light-yellow crystals formed, which were separated from the gel and washed with isopropanol. This procedure was repeated until no more crystals could be separated from the gel. The product was purified by column chromatography (DCM; $R_f = 0.73$) and dried in vacuo over P_4O_{10} (3.36 mmol, 0.81 g, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (m, 2H), 7.67 (m, 2H), 5.23 (s, 1H), 3.12-2.92 (m, 4H), 2.25-1.91 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 146.1, 128.9, 124.0, 50.4, 31.8, 24.8 ppm. Chemical shifts agree with a reference spectrum.[1] HRMS (ESI): calcd m/z for $C_{10}H_{11}NO_2S_2Na$ $[M + Na]^+$ 264.0123, found 264.0126.

4.4. 2-Nitrobenzyl-α,α-d_2-methanol

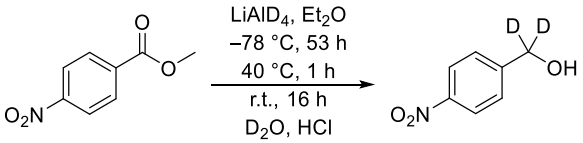


0.30 g (7.15 mmol) lithium aluminium deuteride ($LiAlD_4$) were dissolved in 15 mL diethyl ether (Et_2O) and cooled to −78 °C with acetone/CO_2 dry ice. A mixture of 1.75 mL (12.5 mmol) methyl-2-nitrobenzoate in 5 mL Et_2O was added dropwise and stirred for 19 h while slowly reaching r. t. D_2O was added until gas formation had stopped. Diluted aqueous HCl was added until the precipitate had dissolved. The phases were separated and the aqueous layer was extracted twice with 20 mL Et_2O. The combined organic phases were washed with 40 mL brine. After evaporation of the solvent, the remaining brown solid was purified by column chromatography (DCM; $R_f = 0.33$) and dried in vacuo over P_4O_{10} (3.93 mmol, 0.61 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (m, 1H), 7.66 (m, 2H), 7.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 136.6, 134.2, 130.1, 128.6, 125.0 ppm. Note that the CD_2 carbon signal was not detected. Chemical shifts agree with a reference spectrum.[2] HRMS (ESI): calcd m/z for $C_7H_5D_2NO_3Na$ $[M + Na]^+$ 178.0443, found 178.0445.

[1] Ong, B. S. *Tetrahedron Lett.* **1980**, *21*, 4225-4228.

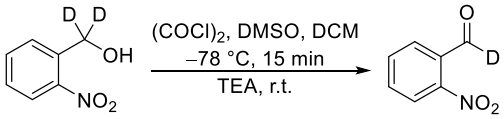
[2] Blanc, A.; Bochet, C. G. *Org. Lett.* **2007**, *9*, 2649-2651.

4.5. 4-Nitrobenzyl-α,α-d_2-methanol



0.30 g (7.15 mmol) lithium aluminium deuteride ($LiAlD_4$) were dissolved in 15 mL diethyl ether (Et_2O) and cooled to −78 °C with acetone/CO_2 dry ice. A mixture of 2.27 g (12.5 mmol) methyl-4-nitrobenzoate in 20 mL Et_2O was added dropwise. The mixture was stirred for 53 h while slowly reaching r. t., subsequently heated to 40 °C for 1 h, and stirred at r. t. for 16 h. D_2O was added until gas formation had stopped. Diluted aqueous HCl was added until the precipitate had dissolved. The phases were separated and the aqueous layer was extracted twice with 20 mL Et_2O. The combined organic phases were washed with 40 mL of brine. After evaporation of the solvent, the remaining yellow solid was purified by column chromatography (*tert*-butyl methyl ether; $R_f = 0.28$) and dried in vacuo over P_4O_{10} (6.97 mmol, 1.08 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.15$ (m, 2 H), 7.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.0$, 147.4, 127.1, 123.8 ppm. Note that the *C*D_2 carbon signal was not detected. Chemical shifts agree with a reference spectrum.[3] HRMS (ESI): calcd m/z for $C_7H_5D_2NO_3Na$ $[M + Na]^+$ 178.0443, found 178.0446.

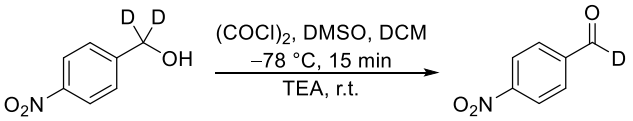
4.6. 2-Nitrobenzyl-α-*d*-aldehyde



0.5 mL (5.83 mmol) oxalyl chloride [$(COCl)_2$] were dissolved in 10 mL DCM and cooled to −78 °C with acetone/CO_2 dry ice. A mixture of ca. 0.7 mL (9.86 mmol) dimethyl sulfoxide (DMSO) in 2 mL DCM was added. After 5 min, a mixture of 0.6 g (3.87 mmol) 2-nitrobenzyl-α,α-d_2-methanol in 9 mL DCM was added. After another 15 min, 3 mL (21.64 mmol) triethyl amine (TEA) were added to the brown solution. After warming the reaction mixture to r. t., 15 mL water were added. The phases were separated and the aqueous phase was extracted with 15 mL DCM. The combined organic phases were subsequently washed with 45 mL brine, 15 mL diluted H_2SO_4, 15 mL water, and 15 mL saturated aqueous $NaHCO_3$. After evaporation of the solvent, the remaining brown-yellow solid was purified by column chromatography (ethyl acetate; $R_f = 0.75$) and dried in vacuo over P_4O_{10} (3.03 mmol, 0.46 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (m, 1H), 7.89 (m, 1H), 7.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.1$, 133.7, 129.7, 124.5 ppm. Note that quaternary and *C*O carbon signals were not detected. HRMS (ESI): calcd m/z for $C_8H_8DNO_4Na$ $[M + MeOH + Na]^+$ 207.0486, found 207.0490.

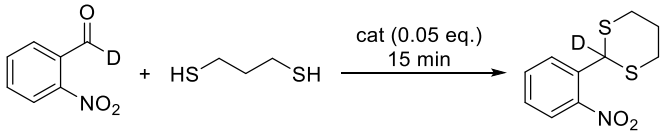
[3] Price, K. E.; Broadwater, S. J.; Walker, B. J.; McQuade, D. T. *J. Org. Chem.* **2005**, *70*, 3980-3987.

4.7. 4-Nitrobenzyl-α-*d*-aldehyde



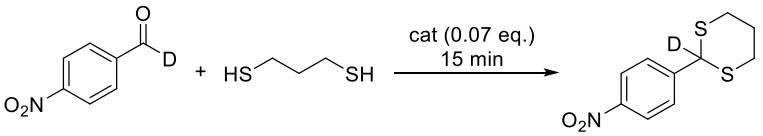
0.6 mL (7.00 mmol) oxalyl chloride [$(COCl)_2$] were dissolved in 15 mL DCM and cooled to −78 °C with acetone/CO_2 dry ice. A mixture of 1 mL (14.1 mmol) dimethyl sulfoxide (DMSO) in 3 mL DCM was added. After 5 min, a mixture of 1.0 g (6.45 mmol) 4-nitrobenzyl-α,α-d_2-methanol in 15 mL DCM was added. After another 15 min, 4.5 mL (32.51 mmol) triethyl amine (TEA) were added to the yellow solution. After warming the reaction mixture to r. t., 30 mL water were added. The phases were separated and the aqueous phase was extracted with 30 mL DCM. The combined organic phases were subsequently washed with 70 mL brine, 30 mL diluted H_2SO_4, 30 mL water, and 30 mL saturated aqueous $NaHCO_3$. After evaporation of the solvent, the remaining yellow solid was purified by column chromatography (ethyl acetate; $R_f = 0.78$) and dried in vacuo over P_4O_{10} (5.06 mmol, 0.77 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (m, 2H), 8.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.5, 124.3 ppm. Note that quaternary and *C*O carbon signals were not detected. HRMS (ESI): calcd m/z for $C_8H_8DNO_4Na$ [M + MeOH + Na]$^+$ 207.0486, found 207.0490.

4.8. 2-Deutero-2-(2-nitrophenyl)-1,3-dithiane



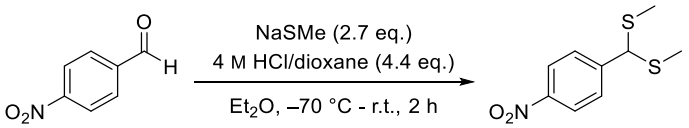
0.21 g (1.38 mmol) 2-nitrobenzyl-α-*d*-aldehyde were dissolved in 0.15 mL (1.49 mmol) 1,3-propane dithiol. 16.5 mg (0.07 mmol, 0.05 eq.) **cat** were added to the brown solution. After 15 min, a brown gel formed, which was heated to 100 °C in ca. 3 mL isopropanol after addition of two drops of saturated aqueous $NaHCO_3$. During cooling, light-yellow crystals formed, which were separated from the gel and washed with isopropanol. This procedure was repeated until no more crystals could be separated from the gel. The product was purified by column chromatography (ethyl acetate/*n*-pentane 1:2; $R_f = 0.60$) and dried in vacuo over P_4O_{10} (0.62 mmol, 0.15 g, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (m, 2H), 7.62 (m, 1H), 7.44 (m, 1H), 3.17-2.90 (m, 4H), 2.23-1.94 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.5, 130.8, 129.1, 124.8, 32.3, 25.0 ppm. Note that quaternary and *C*D carbon signals were not detected. HRMS (ESI): calcd m/z for $C_{10}H_{10}DNO_2S_2Na$ [M + Na]$^+$ 265.0186, found 265.0183.

4.9. 2-Deutero-2-(4-nitrophenyl)-1,3-dithiane



0.20 g (1.31 mmol) 4-nitrobenzyl-α-*d*-aldehyde were dissolved in 0.15 mL (1.49 mmol) 1,3-propane dithiol. 19.0 mg (0.09 mmol, 0.07 eq.) **cat** were added to the brown solution. After 15 min, a yellow gel formed, which was heated to 100 °C in ca. 3 mL isopropanol after addition of two drops of saturated aqueous $NaHCO_3$. During cooling, light-yellow crystals formed, which were separated from the gel and washed with isopropanol. This procedure was repeated until no more crystals could be separated from the gel. The product was purified by column chromatography (ethyl acetate/*n*-pentane 1:2; $R_f = 0.49$) and the crystals were dried in vacuo over P_4O_{10} (1.53 mmol, 0.37 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (m, 2H), 7.66 (m, 2H), 3.12-2.92 (m, 4H), 2.25-1.92 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 146.1, 128.9, 124.1, 31.7, 24.8 ppm. Note that the *C*D carbon signal was not detected. HRMS (ESI): calcd m/z for $C_{10}H_{10}DNO_2S_2Na$ $[M + Na]^+$ 265.0186, found 265.0184.

4.10. 4-Nitrobenzaldehyde dimethyl bisthioacetal



Sodium methanethiolate (372.0 mg, 5.3 mmol) was suspended in Et_2O (5 mL) and cooled to –70 °C. HCl in dioxane (4 M, 2.2 mL, 8.8 mmol) was added dropwise with stirring followed by a solution of *p*-nitrobenzaldehyde (302.0 mg, 2.0 mmol) in Et_2O (15 mL). The reaction mixture was allowed to slowly warm to r. t. and stirred for further 2 h. Saturated aqueous $NaHCO_3$ (10 mL) was then added and the reaction mixture was diluted with Et_2O. The phases were separated and the organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL). Drying over Na_2SO_4, removal of the solvent under reduced pressure, and column chromatography (hexane/EtOAc 2:1; $R_f = 0.59$) afforded 74.0 mg (0.32 mmol, 16%) of the desired product as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (m, 2H), 7.59 (m, 2H), 4.83 (s, 1H), 2.12 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.5, 147.3, 128.7, 124.0, 55.8, 15.0 ppm. HRMS (ESI): calcd m/z for $C_9H_{11}NO_2S_2Na$ $[M + Na]^+$ 252.0123, found 252.0125.