

Supplementary Information

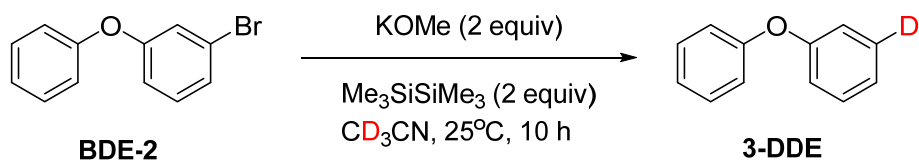
Photoexcitation Dynamics of Bromodiphenyl Ethers in Acetonitrile- d_3 by
Femtosecond Time-Resolved Infrared Spectroscopy

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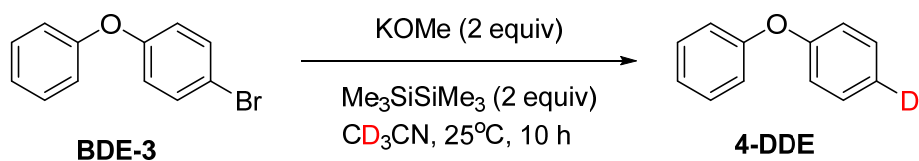
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Synthesis of 3-DDE and 4-DDE

Procedures for deuterium substitution from previous work were followed.¹



To a dry Schlenk tube equipped with a magnetic stirring bar, BDE-2 (516 mg, 2.07 mmol), KOMe (290 mg, 4.14 mmol), Me₃SiSiMe₃ (848 μL, 4.14 mmol), and CD₃CN (2.70 ml, 25 equiv) were added under argon. After stirred at 25 °C for 10 h, the mixture was diluted with water (10 mL) and extracted with Et₂O (10 mL × 3). Then the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography (100% Hexane) to provide 3-DDE (311 mg, 1.82 mmol) as a yellow oil in 88% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.31 (m, 3H), 7.10 (dddd, *J* = 7.1, 4.7, 2.3, 1.1 Hz, 2H), 7.02 (ddt, *J* = 6.4, 2.4, 1.4 Hz, 4H). Consistent with previous report.² NMR spectrum is shown in the upper panel of Fig. S7.



To a dry Schlenk tube equipped with a magnetic stirring bar, BDE-3 (507 mg, 2.04 mmol), KOMe (285 mg, 4.06 mmol), Me₃SiSiMe₃ (831 μL, 4.06 mmol), and CD₃CN (2.66 ml, 25 equiv) were added under argon. After stirred at 25 °C for 10 h, the mixture was diluted with water (10 mL) and extracted with Et₂O (10 mL × 3). Then the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography (100% Hexane) to provide 4-DDE (329 mg, 1.92 mmol) as a yellow oil in 94% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.37 (m, 3H), 7.08–7.13 (m, 1H), 6.99–7.04 (m, 4H). Consistent with previous report.³ NMR spectrum is shown in the lower panel of Fig. S8.

References

1. X. Wang, M.-H. Zhu, D. P. Schuman, D. Zhong, W.-Y. Wang, L.-Y. Wu, W. Liu, B. M. Stoltz and W.-B. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 10970-10974.
2. I. O. Shapiro, Y. I. Ranneva and A. I. Shatenshtein, *Zhurnal Obshchei Khimii*, 1979, **49**, 2030.
3. S. Vanderheiden, B. Bulat, T. Zevaco, N. Jung and S. Bräse, *ChemComm*, 2011, **47**, 9063-9065.

Substances	Experiment			Calculation	
	$\bar{\nu}$ (cm ⁻¹)	ϵ ($\times 10^3$ M ⁻¹ cm ⁻²)	FWHM (cm ⁻¹)	$\bar{\nu}$ (cm ⁻¹)	Int. (km mol ⁻¹)
BDE-2	1592	1.8	11.3	1638	5
	1582	5.4	6.6	1632	18
	1578	3.5	9.4	1618	273
	1570	0.8	16.5	1609	111
	1491	2.8	4.6		
	1489	1.4	10.7	1524	109
	1470	8.7	6.4	1501	295
	1458	0.2	3.9	1489	4
3-DDE	1590	0.7	6.9	1641	6
	1589	1.6	29.8	1630	26
	1582	4.4	8.4	1624	126
	1566	0.2	5.9	1619	75
	1542	0.1	12.7	–	–
	1492	1.0	4.4		
	1490	3.2	12.0	1523	124
	1472	6.3	5.6	1504	194
1457	0.3	7.5	1490	3	
3-CDE	1593	2.4	16.8	1645	13
				1632	13
				1630	48
	1581	5.1	11.8	1610	181
	1571	0.6	7.8		
	1491	2.3	4.4	1524	94
1483	6.4	10.7	1516	121	
1457	0.2	4.2	1488	5	
BDE-2 (R)	1588 ^a	7.1	13.7 ^a	1637	19
				1631	28
				1622	160
	1531 ^a	0.9	9.8 ^a	1565	34
	1490 ^a	4.2	6.1 ^a	1523	130
1444 ^a	10.3	4.2 ^a	1489	4	
			1476	287	
BDE-2 (RS)	1579	2.1	8.6	1643	4
				1631	18
				1629	73
	1570	5.4	13.1	1612	190
	1491	1.8	13.9	1524	107
1470	4.8	19.0	1517	114	
			1489	7	
BDE-2 (IM)	1564	13.2	35.3	–	–
	1480	2.7	17.5	–	–

Table S1 Fitted spectral parameters, vibration frequencies ($\bar{\nu}$), integrated extinction coefficients (ϵ) and full width at half maximum (FWHM) of substances and intermediates appeared during BDE-2's photodissociation from 1635 to 1435 cm⁻¹, with the calculated results using density functional theory (DFT) methods with B3LYP/cc-pVTZ. Information of BDE-2, 3-DDE, and 3-CDE was obtained from the equilibrium infrared (IR) spectra at 293 K. The others were obtained for fitting time-resolved IR (TRIR) spectra.

^a The values were given for spectra after thermalization.

Substances	Experiment			Calculation	
	$\bar{\nu}$ (cm ⁻¹)	ϵ ($\times 10^3$ M ⁻¹ cm ⁻²)	FWHM (cm ⁻¹)	$\bar{\nu}$ (cm ⁻¹)	Int. (km mol ⁻¹)
BDE-3	1601	0.7	8.8	1639	16
	1592	0.3	6.5	1631	16
	1581	2.7	9.9	1619	79
	1578	0.5	4.5	1614	26
	1494	0.8	4.9	1525	54
	1484	14.2	6.7	1513	439
	1457	0.1	4.3	1489	2
4-DDE	1592	0.5	9.5	1641	5
	1587	2.3	31.3	1631	23
	1584	2.3	9.5	1623	168
	1581	0.9	4.6	1619	26
	1547	0.3	13.5	–	–
	1493	0.9	5.6	1524	60
	1486	7.2	8.7	1515	291
	1479	3.6	10.1	–	–
4-CDE	1609	1.4	8.1	1646	128
	1597	0.4	9.2	1634	11
	1589	4.9	6.5	1627	189
	1580	0.4	8.3	1602	17
	1505	2.6	6.9	1535	121
	1495	5.2	16.1	1521	282
	1486	5.6	7.1	–	–
	1457	0.1	3.5	1488	3
BDE-3 (S ₁)	1582	1.4	29.4	1608	95
	1501	4.1	23.3	1538	837
	1486	8.3	11.1	1537	2670
BDE-3 (R)	1593 ^a	1.0	6.9 ^a	1638	59
	1541 ^a	5.7	13.9 ^a	1628	43
	1489 ^a	8.6	6.9 ^a	1622	6
	1443 ^a	4.6	7.2 ^a	1580	94
	–	–	–	1521	202
	–	–	–	1491	1
BDE-3 (RS)	1590	4.4	17.2	1480	89
	–	–	–	1642	67
	–	–	–	1632	11
	1570	1.4	12.2	1626	185
	1491	2.6	12.2	1607	84
BDE-3 (IM)	1476	6.0	24.0	1537	105
	1578	1.4	9.0	1522	256
–	–	–	–	–	
–	10.8	20.0	–	–	

Table S2 Fitted spectra parameters, vibration frequencies ($\bar{\nu}$), integrated extinction coefficients (ϵ) and full width at half maximum (FWHM) of substances and intermediates appeared during BDE-3's photodissociation from 1635 to 1435 cm⁻¹, and calculation results using DFT calculations with B3LYP/cc-pVTZ. Information of BDE-3, 4-DDE, 4-CDE was obtained from the equilibrium infrared IR spectra at 293 K. The others were obtained from the fitting the TRIR spectra.

^aThe values were given for spectra after thermalization.

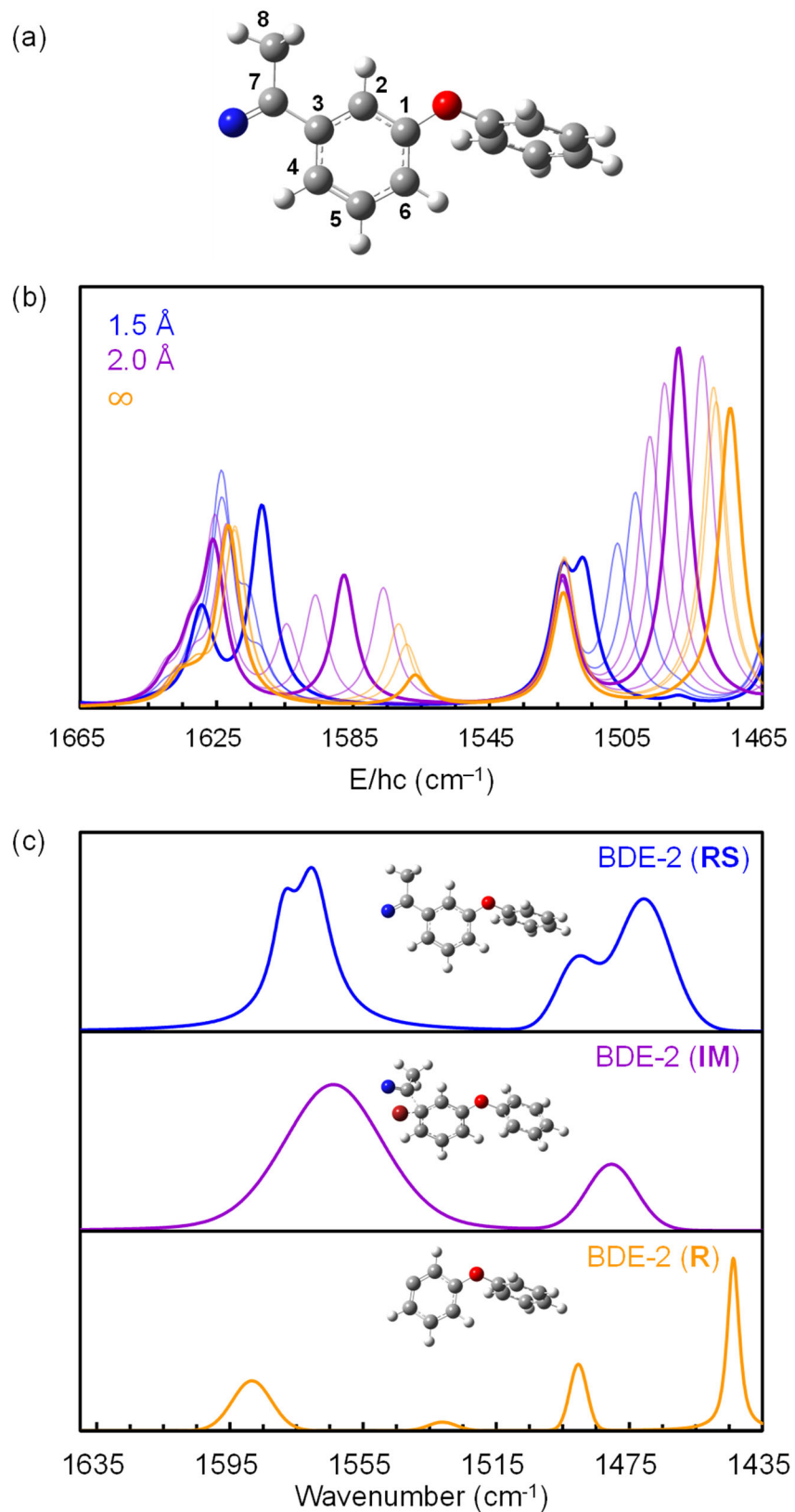


Fig. S1 (a) Optimized molecular structure of the BDE-2 (**RS**) by the DFT calculation. (b) Spectra calculated as CD_3CN approaches the BDE-2 (**R**) to the optimized distance of 1.5 Å, i.e., the distance of the $\text{C}_3\text{-C}_7$ bond of the BDE-2 (**RS**) changes from ∞ (thick orange line) to 1.5 (thick blue line) Å. Calculated spectra with FWHM of 8 cm^{-1} when the distance of the $\text{C}_3\text{-C}_7$ bond is 2 Å (thick purple line) has characteristics of the spectrum of BDE-2 (**IM**). (c) Basis spectra of **R**, **IM**, and **RS** of BDE-2 with their optimized molecular structures.

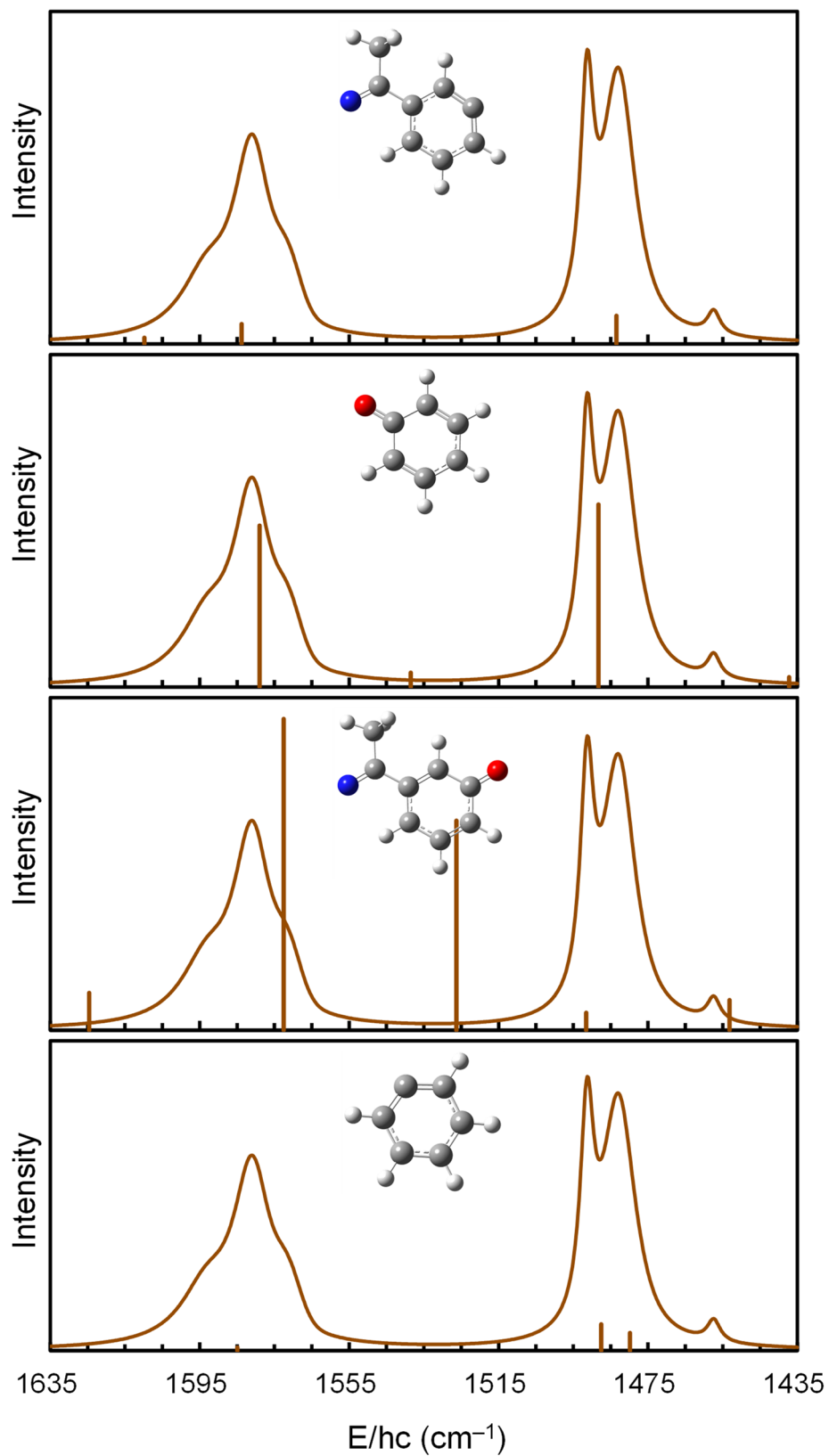


Fig. S2 Calculated spectra (sticks) and optimized molecular structures of anticipated fragments produced upon dissociation of the C-O bond of BDE-2 by the DFT methods (B3LYP/cc-pVTZ) in the basis spectrum of BDE-2 (X).

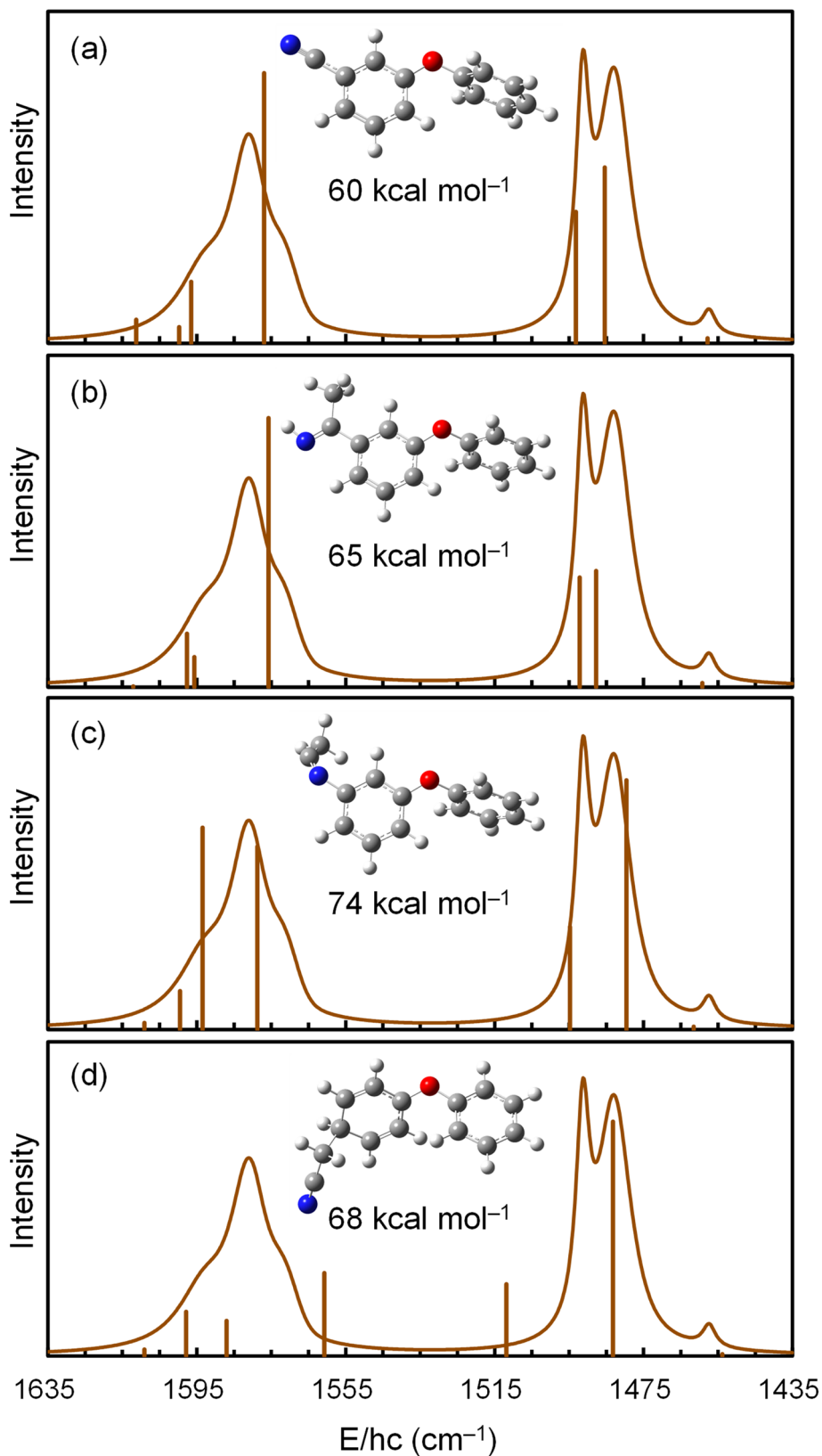


Fig. S3 Calculated spectra (sticks) and optimized molecular structures of various candidates for BDE-2 (**X**) by the DFT methods (B3LYP/cc-pVTZ). (a) 3-CDE. (b) D attached to N of BDE-2 (**RS**). (c) BDE-2 (**RS**) attached with N of CD_3CN . (d) BDE-2 (**RS**) with C of CD_3 attached. The calculated frequencies were scaled using scale factors of 0.975–0.981 to best match with the observed bands. The energy values are calculated relative Gibbs free energies for the corresponding compounds from BDE-2 in the ground state.

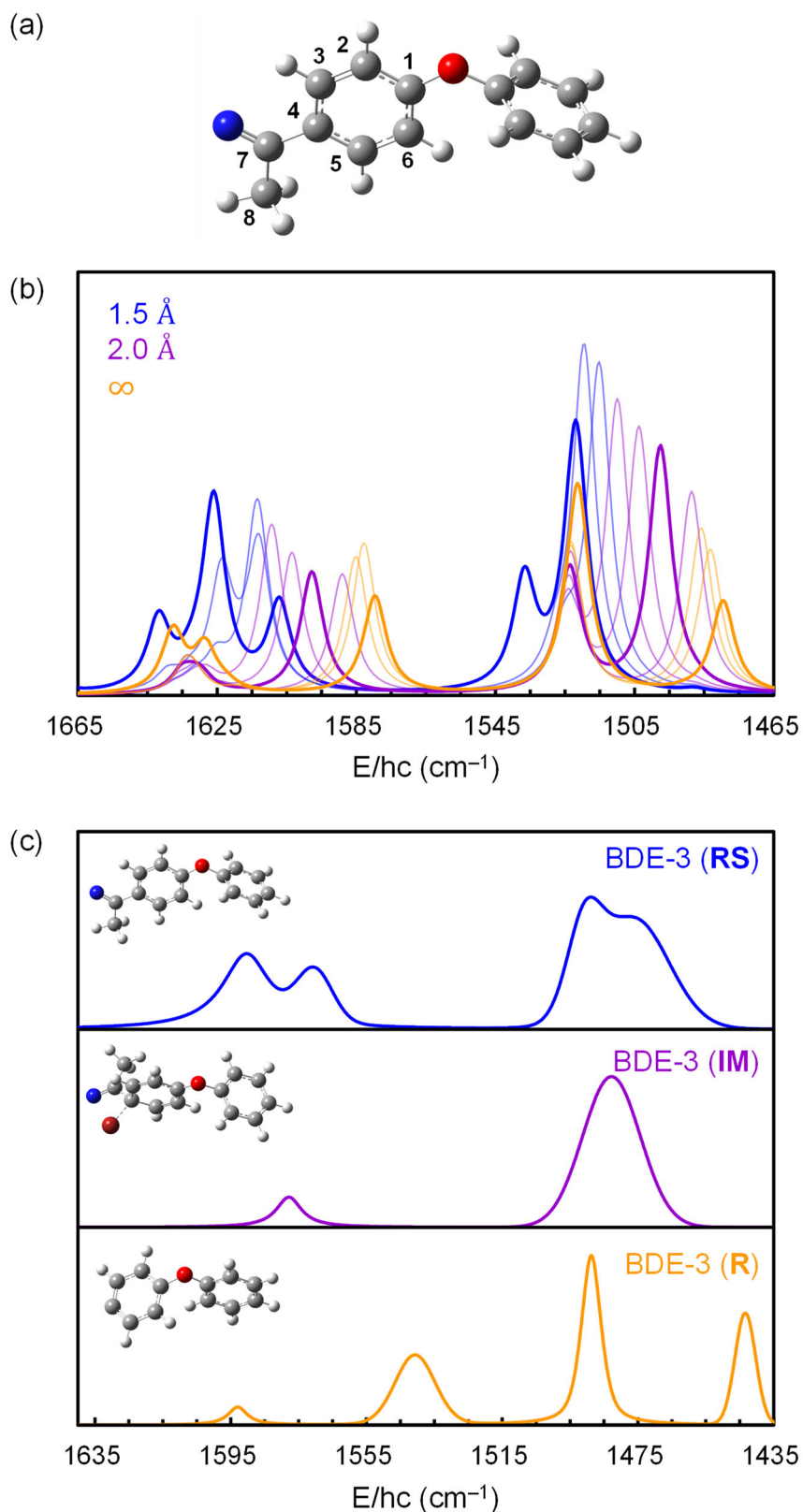


Fig. S4 (a) Optimized molecular structure of the BDE-3 (**RS**) by the DFT calculation (B3LYP/cc-pVTZ). (b) Spectra calculated as CD₃CN approaches the BDE-3 (**R**) to the optimized distance of 1.5 Å, i.e., the distance of the C₄–C₇ bond of the BDE-3 (**RS**) changes from ∞ (thick orange line) to 1.5 (thick blue line) Å. Calculated spectra with FWHM of 8 cm⁻¹ when the distance of the C₄–C₇ bond is 2 Å (thick purple line) has characteristics of the spectrum of BDE-3 (**IM**). (c) Basis spectra of **R**, **IM**, and **RS** of BDE-3 with their optimized molecular structures.

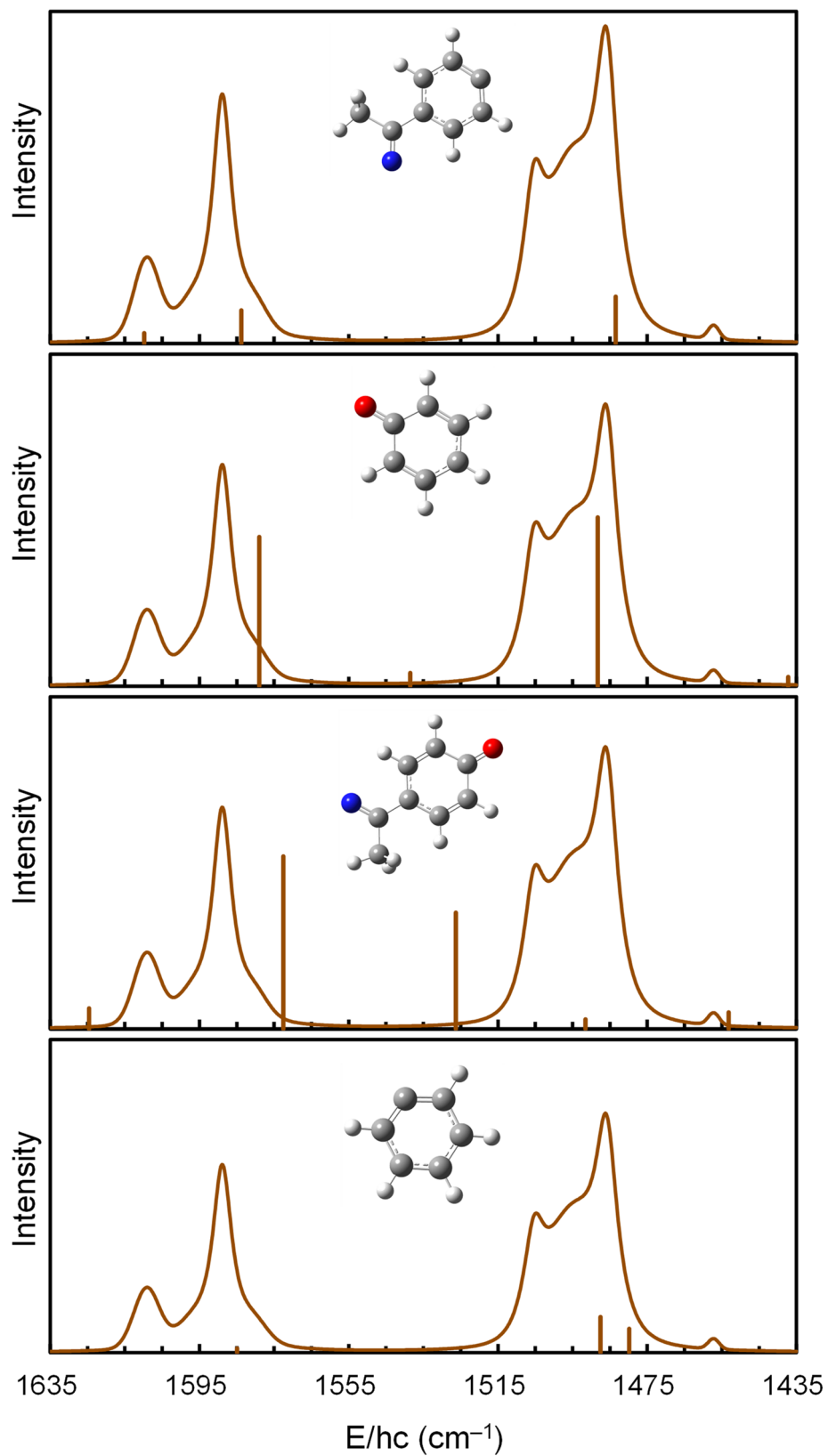


Fig. S5 Calculated spectra (sticks) and optimized molecular structures of anticipated fragments produced upon dissociation of the C–O bond of BDE-3 by the DFT methods (B3LYP/cc-pVTZ) in the basis spectrum of BDE-3 (X).

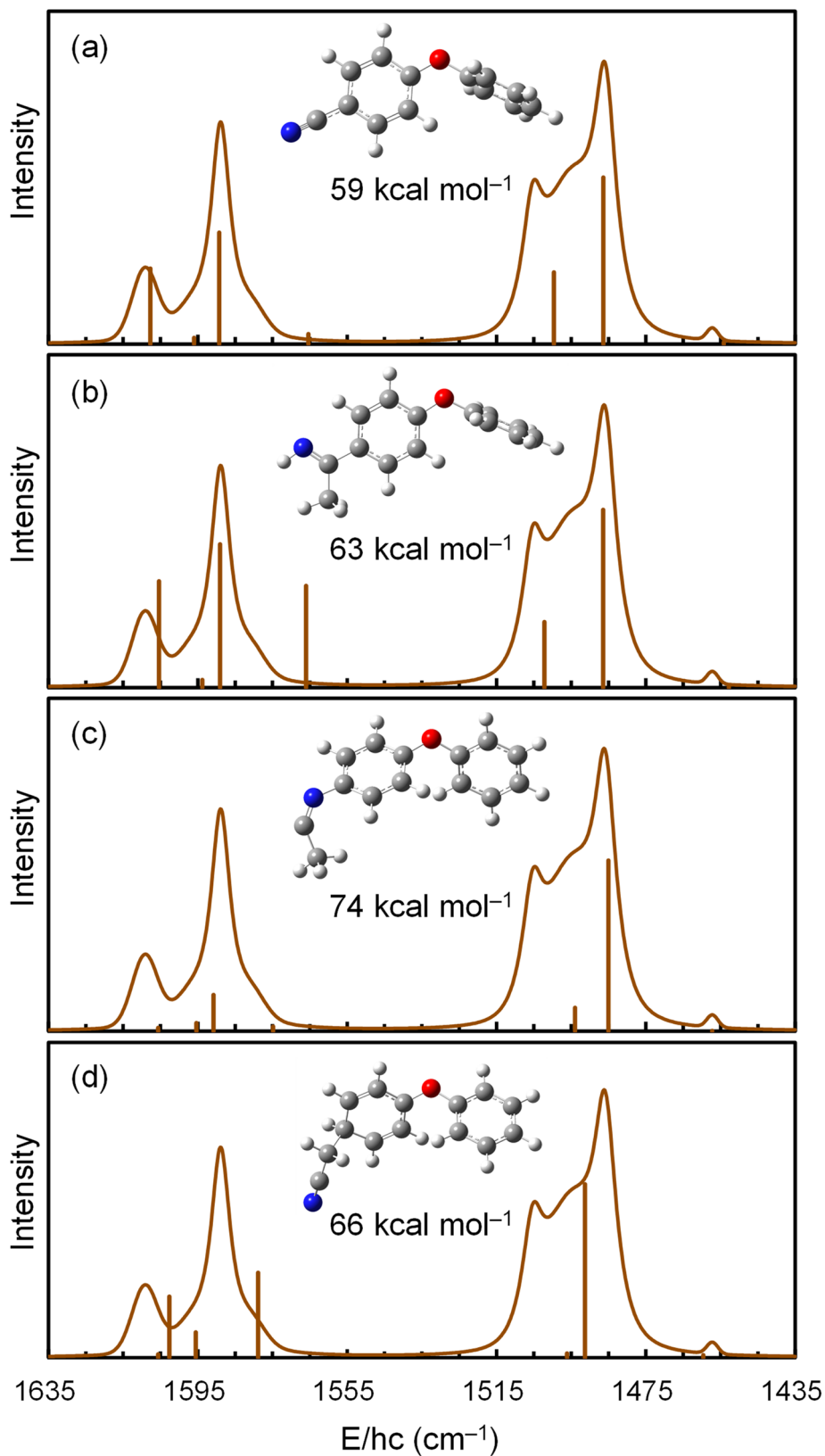


Fig. S6 Calculated spectra (sticks) and optimized molecular structures of various candidates for BDE-3 (X) by the DFT methods (B3LYP/cc-pVTZ). (a) 4-CDE. (b) D attached to N of BDE-3 (RS). (c) BDE-3 (RS) attached with N of CD_3CN . (d) BDE-3 (RS) with C of CD_3 attached. The calculated frequencies were scaled using scale factors of 0.977–0.980 to best match with the observed bands. The energy values are calculated relative Gibbs free energies for the corresponding compounds from BDE-3 in the ground state.

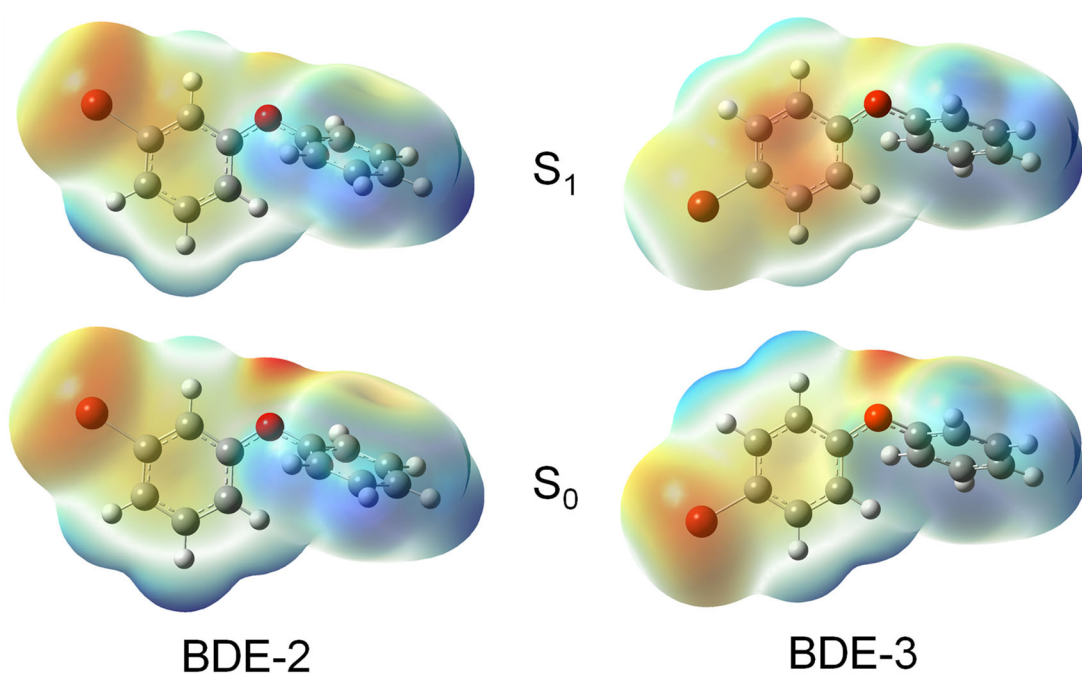


Fig. S7 Charge density maps of the S_0 and S_1 states of BDE-2 and BDE-3.

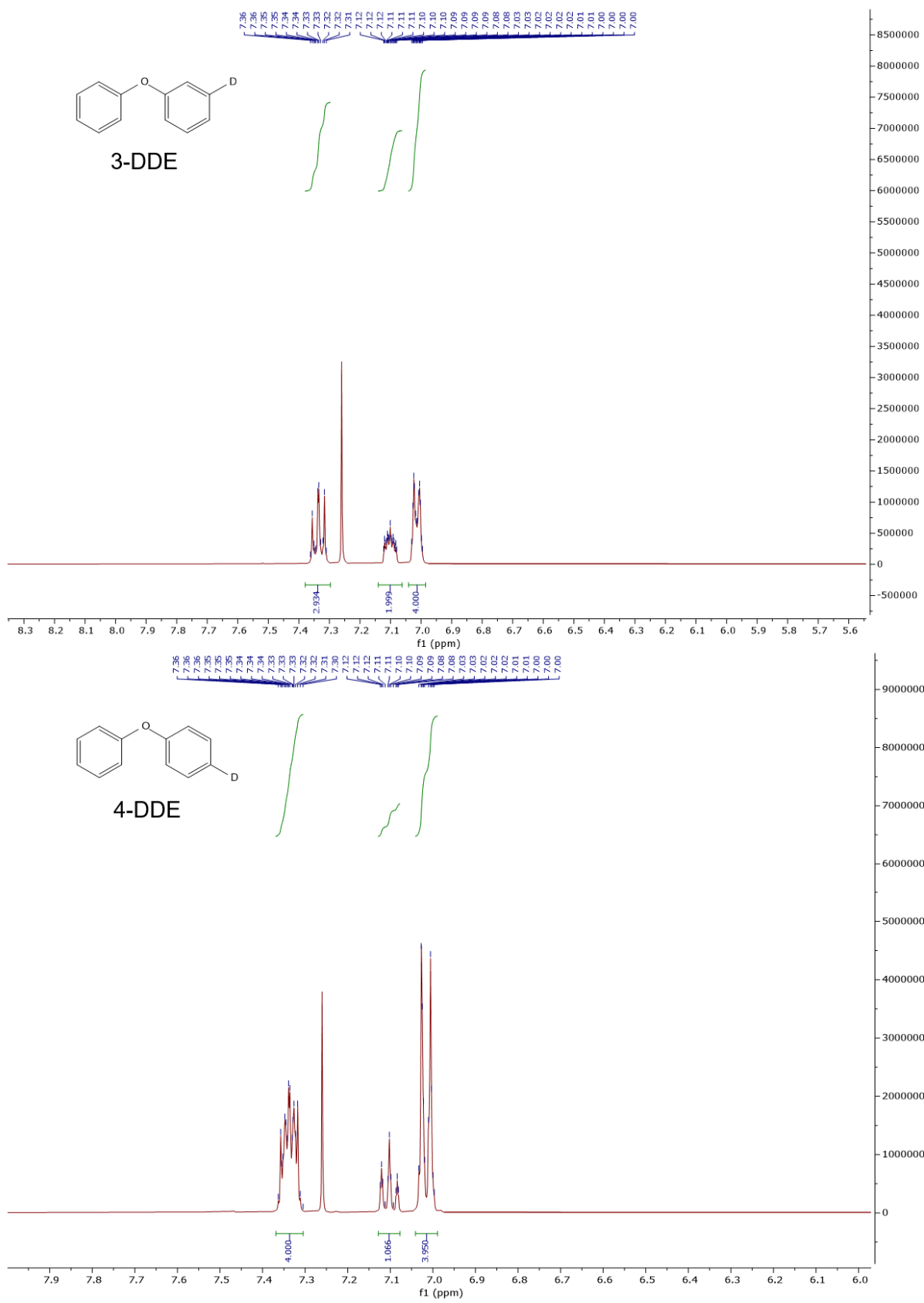


Fig. S8 ^1H NMR (400 MHz, CDCl_3) of 3-DDE and 4-DDE.