Supporting Information for

Supramolecular construction of a cyclobutane ring system with four different substituents in the solid state

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S1. Syntheses and Photoreactions

Supplementary Methods

Triphenyl-(2,3,5,6-tetrafluorobenzyl)phosphonium bromide,\textsuperscript{1-2} 8F,\textsuperscript{1-2} and \textbf{SBZ}\textsuperscript{3} were synthesized according to literature. Triphenylphosphine (Strem) 2,3,5,6-tetrafluorobenzyl bromide (Oakwood), 2,3,4,5,6-pentafluorobenzyl bromide (Oakwood), 2,3,5,6-tetrafluorobenzaldehyde (Oakwood), 2,3,4,5,6-pentafluorobenzaldehyde (Oakwood), sodium hydride (dry, Sigma-Aldrich), \textbf{BPE} (Sigma-Aldrich), \textbf{SB} (ACROS), and solvents [toluene, chloroform, ethanol, dimethylformamide] (Fisher) were commercially available and used as received. The cross photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. All co-crystals were finely ground using a mortar and pestle, and then placed between a pair of Pyrex glass plates. Samples were irradiated in six-hour intervals.

\textit{Synthesis of trans-1-(2,3,4,5,6-pentafluorophenyl)-2-(2,3,5,6-tetrafluorophenyl)ethylene (9F):}

![Reaction Scheme]

Triphenyl-(2,3,5,6-tetrafluorobenzyl)phosphonium bromide (2.67 g, 5.3 mmol) and NaH (165 mg, 6.9 mmol) were stirred in 13 mL of DMF for 15 min. 2,3,4,5,6-pentafluorobenzaldehyde (1.1 g, 5.6 mmol) was then added to the mixture and the solution is stirred at room temperature. After 12 h, the reaction is poured on H\textsubscript{2}O and the white solid was filtered. Column chromatography using a 1:1 CH\textsubscript{2}Cl\textsubscript{2}: n-hexane system afforded \textit{trans}-1-(2,3,4,5,6-pentafluorophenyl)-2-(2,3,5,6-tetrafluorophenyl)ethylene (9F) as a white crystalline solid (1.35 g, 3.95 mmol, 75\% yield): \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_{6}) \delta 7.95 (tt, \textsuperscript{2}J\textsubscript{HF} = 10.5, \textsuperscript{3}J\textsubscript{HF} = 7.8 Hz, 1H), 7.35-7.29 (d, \textsuperscript{2}J\textsubscript{HH} = 18 Hz, 1H), 7.29-7.23 (d, \textsuperscript{2}J\textsubscript{HH} = 18 Hz, 1H).

\textit{Synthesis of the co-crystal (SB)-(8F) and the cross-photoproduct (SB-8F-cb).}

Single crystals of (SB)-(8F) were obtained by combining a solution of 8F (25 mg) in toluene (1 mL) with a solution of \textbf{SB} (14 mg, 1:1 molar ratio) in of toluene (1 mL). Single crystals suitable for X-ray diffraction studies were realized within 2 days after the slow evaporation of toluene. The photoreaction reached a quantitative yield within 30 hours of irradiation, as determined by \textsuperscript{1}H NMR spectroscopy. Single crystals of \textbf{SB-8F-cb}, suitable for X-ray diffraction, were obtained within
one day after the slow evaporation of a clear solution of the photoproduct (35 mg) in ethanol (5 mL).

**Synthesis of the co-crystal (BPE)-(8F) and the cross-photoproduct (BPE-8F-cb).**

Single crystals of (BPE)-(8F) were obtained by combining a solution of 8F (25 mg) in toluene (1 mL) with a solution of BPE (14 mg, 1:1 molar ratio) in of toluene (1 mL). Single crystals suitable for X-ray diffraction studies were realized within 1 day after the slow evaporation of toluene. The photoreaction reached a quantitative yield within 30 hours of irritation, as determined by \(^1\)H NMR spectroscopy. Single crystals of BPE-8F-cb, suitable for X-ray diffraction, were obtained within one day after the slow evaporation of a clear solution of the photoproduct (35 mg) in ethanol (3 mL).

**Synthesis of the co-crystal (SBZ)-(8F) and the cross-photoproduct (SBZ-8F-cb).**

Single crystals of (SBZ)-(8F) were obtained by combining a solution of 8F (25 mg) in toluene (1 mL) with a solution of SBZ (14 mg, 1:1 molar ratio) in of ethanol (1 mL). Single crystals suitable for X-ray diffraction studies were realized within 1 day after the slow evaporation of toluene. The photoreaction reached a quantitative yield within 30 hours of irritation, as determined by \(^1\)H NMR spectroscopy. Single crystals of SBZ-8F-cb, suitable for X-ray diffraction, were obtained within one day after the slow evaporation of a clear solution of the photoproduct (34 mg) in a toluene:ethanol mixture (2 mL, 1:1, v:v).

**Synthesis of the co-crystal (SBZ)-(9F) and the cross-photoproduct (SBZ-9F-cb).**

Single crystals of (SBZ)-(9F) were obtained by combining a solution of 9F (25 mg) in toluene (2 mL) with a solution of SBZ (13 mg, 1:1 molar ratio) in of toluene (1 mL). Single crystals suitable for X-ray diffraction studies were realized within 1 day after the slow evaporation of toluene. The photoreaction reached a quantitative yield within 30 hours of irritation, yielding SBZ-9F-cb as a light brown solid, which was determined by \(^1\)H NMR spectroscopy. Single crystals of [H-(SBZ-9F-cb)][\(p\)-TsO], suitable for X-ray diffraction, were obtained within one day after the slow evaporation of a clear solution of SBZ-9F-cb (20 mg) and \(p\)-TsOH (7.3 mg) in a dichloromethane:methanol mixture (2 mL, 1:1, v:v).
S2. $^1$H NMR Spectral Data.

$^1$H-NMR spectra were recorded using a Bruker AVANCE-400 NMR spectrometer operating at 400 MHz using DMSO-$d_6$ as the NMR solvent. All data were processed with MestReNova suite of software programs.

Figure S1. $^1$H NMR spectra of (SB·(8F)).
Figure S2. $^1$H NMR spectra of SB-8F-cb.
Figure S3. $^1$H NMR spectra of (BPE)$\cdot$(8F).
Figure S4. $^1$H NMR spectra of (BPE-8F-cb).
Figure S5. $^1$H NMR spectra of (SBZ)-(8F).
Figure S6. $^1$H NMR spectra of SBZ-8F-cb.
Figure S7. $^1$H NMR spectra of (SBZ)·(9F).
Figure S8. $^1$H NMR spectra of SBZ-9F-cb.
S3. Powder X-ray Diffraction Data

PXRD data were collected from samples mounted on glass slides by a Bruker D8 DaVinci powder X-ray diffraction (XRD) system using CuKα1 radiation (λ = 1.54056 Å) (scan type: locked coupled; scan mode: continuous; step size: 0.02°).

Figure S9. Powder X-ray diffraction of powder of (SB)·(8F) and simulated pattern from single-crystal X-ray diffraction data.
**Figure S10.** Powder X-ray diffraction of powder of (BPE)-(8F) and simulated pattern from single-crystal X-ray diffraction data.
Figure S11. Powder X-ray diffraction of powder of \((\text{SBZ})\cdot(\text{8F})\) and simulated pattern from single-crystal X-ray diffraction data.
**Figure S12.** Powder X-ray diffraction of powder of (SBZ)-(9F) and simulated pattern from single-crystal X-ray diffraction data.
Figure S13. Powder X-ray diffraction of powder of [H-SBZ-9F-cb][p-TsO] and simulated pattern from single-crystal X-ray diffraction data.
S4. Single Crystal X-ray Diffraction Data

Single crystal data was collected with a Bruker APEX II Kappa Diffractometer equipped with an Oxford Cryostream low temperature device using MoKα radiation (λ = 0.71073 Å) after having been secured to Mitegen magnetic mounts using Paratone oil. Data collection strategies to ensure maximum data redundancy and completeness were calculated using Apex2. All calculation dealing with data collection, initial indexing, frame integration, Lorentz- polarization corrections and final cell parameter were again carried out by Apex2. All structures were solved using ShelXT and refined using ShelXL in the Olex2 graphical user interface. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained positions with isotropic thermal parameter $U_{iso}(H) = 1.2 \times U_{eq}(C_H)$. 
Table S1. Crystal data and structure refinement for (SB)-(8F) and SB-8F-cb.

|                           | (SB)-(8F)          | SB-8F-cb         |
|---------------------------|--------------------|------------------|
| CCDC                      | 2042036            | 2042037          |
| Empirical formula         | C_{28}H_{16}F_{8}  | C_{28}H_{16}F_{8}|
| Formula weight            | 504.41             | 504.41           |
| Temperature/K             | 296.15             | 100.04           |
| Crystal system            | triclinic          | triclinic        |
| Space group               | P-1                | P-1              |
| a/Å                       | 6.2588(4)          | 8.0657(3)        |
| b/Å                       | 7.6417(6)          | 10.9450(4)       |
| c/Å                       | 11.6953(8)         | 12.9478(5)       |
| α/°                       | 87.276(4)          | 68.754(2)        |
| β/°                       | 89.359(4)          | 87.400(2)        |
| γ/°                       | 82.433(4)          | 78.137(2)        |
| Volume/Å³                 | 553.86(7)          | 1042.05(7)       |
| Z                         | 1                  | 2                |
| ρ_{calc}/g/cm³            | 1.512              | 1.608            |
| μ/mm⁻¹                    | 0.134              | 0.143            |
| F(000)                    | 256.0              | 512.0            |
| Crystal size/mm³          | 0.547 × 0.529 × 0.053 | 0.584 × 0.316 × 0.253 |
| Radiation                 | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.486 to 50.894   | 3.376 to 61.366  |
| Index ranges              | -7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -14 ≤ l | -11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -18 ≤ l ≤ 14 |
| Reflections collected     | 8790               | 16630            |
| Independent reflections   | 2034 [R\text{int} = 0.0252, R\text{sigma} = 0.0260] | 6175 [R\text{int} = 0.0245, R\text{sigma} = 0.0362] |
| Data/restraints/parameters | 2034/0/163         | 6175/0/325       |
| Goodness-of-fit on F²     | 1.024              | 1.057            |
| Final R indexes [I>=2σ (I)] | R_1 = 0.0522, wR_2 = 0.1378 | R_1 = 0.0617, wR_2 = 0.1568 |
| Final R indexes [all data] | R_1 = 0.0858, wR_2 = 0.1733 | R_1 = 0.0851, wR_2 = 0.1741 |
| Largest diff. peak/hole / e Å⁻³ | 0.29/-0.23       | 0.63/-0.26       |
Table S2. Crystal data and structure refinement for (BPE)-(8F) and BPE-8F-cb.

|                          | (BPE)-(8F)            | BPE-8F-cb               |
|--------------------------|-----------------------|-------------------------|
| CCDC                     | 2042038               | 2042039                 |
| Empirical formula        | C_{26}H_{14}F_{8}N_{2} | C_{26}H_{14}F_{8}N_{2}  |
| Formula weight           | 506.39                | 506.39                  |
| Temperature/K            | 273.15                | 293(2)                  |
| Crystal system           | triclinic             | triclinic               |
| Space group              | P-1                   | P-1                     |
| a/Å                      | 6.286(3)              | 8.1788(6)               |
| b/Å                      | 7.690(4)              | 10.5773(8)              |
| c/Å                      | 11.654(7)             | 12.7786(10)             |
| α/°                      | 81.58(4)              | 108.775(4)              |
| β/°                      | 81.41(4)              | 99.388(4)               |
| γ/°                      | 81.23(4)              | 99.387(4)               |
| Volume/Å³                | 546.1(5)              | 1004.75(13)             |
| Z                        | 1                     | 2                       |
| ρ_{calc}/g/cm³           | 1.540                 | 1.674                   |
| μ/mm⁻¹                   | 0.139                 | 0.151                   |
| F(000)                   | 256.0                 | 512.0                   |
| Crystal size/mm³         | 0.369 × 0.217 × 0.054 | 0.271 × 0.164 × 0.142   |
| Radiation                | MoKα (λ = 0.71073)    | MoKα (λ = 0.71073)      |
| 2Θ range for data collection/° | 3.564 to 52.43       | 3.46 to 55.07           |
| Index ranges             | -7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14 | -10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16 |
| Reflections collected    | 11212                 | 15472                   |
| Independent reflections  | 2147 [R_{int} = 0.0527, R_{sigma} = 0.0424] | 4521 [R_{int} = 0.0375, R_{sigma} = 0.0501] |
| Data/restraints/parameters | 2147/0/163         | 4521/0/325              |
| Goodness-of-fit on F²    | 0.935                 | 1.057                   |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0529, wR₂ = 0.1492 | R₁ = 0.0498, wR₂ = 0.1239 |
| Final R indexes [all data] | R₁ = 0.1116, wR₂ = 0.1965 | R₁ = 0.0852, wR₂ = 0.1423 |
| Largest diff. peak/hole / e Å⁻³ | 0.26/-0.20         | 0.38/-0.27              |
Table S3. Crystal data and structure refinement for (SBZ)-(8F) and SBZ-8F-cb.

|                          | (SBZ)-(8F)       | SBZ-8F-cb       |
|--------------------------|------------------|-----------------|
| CCDC                     | 2042040          | 2042041         |
| Empirical formula        | C$_{27}$H$_{15}$F$_8$N | C$_{27}$H$_{15}$F$_8$N |
| Formula weight           | 505.40           | 505.40          |
| Temperature/K            | 299.79           | 99.97           |
| Crystal system           | triclinic        | triclinic       |
| Space group              | P-1              | P-1             |
| a/Å                      | 6.2524(8)        | 8.0271(8)       |
| b/Å                      | 7.6581(12)       | 10.9328(12)     |
| c/Å                      | 23.133(3)        | 12.7798(13)     |
| α/°                      | 87.316(9)        | 68.901(6)       |
| β/°                      | 85.878(9)        | 87.057(6)       |
| γ/°                      | 81.898(9)        | 78.538(6)       |
| Volume/Å$^3$             | 1093.0(3)        | 1025.23(19)     |
| Z                        | 2                | 2               |
| ρ$_{calc}$/cm$^3$         | 1.536            | 1.637           |
| μ/mm$^{-1}$              | 0.138            | 0.147           |
| F(000)                   | 512.0            | 512.0           |
| Crystal size/mm$^3$      | 0.432 × 0.343 × 0.153 | 0.234 × 0.171 × 0.079 |
| Radiation                | MoKα (k = 0.71073) | MoKα (k = 0.71073) |
| 2θ range for data        | 3.532 to 54.204  | 3.416 to 54.35  |
| collection/°             |                  |                 |
| Index ranges             | -8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -29 ≤ l | -10 ≤ h ≤ 10, -14 ≤ k ≤ 11, -16 ≤ l ≤ 16 |
| Reflections collected    | 20678            | 14002           |
| Independent reflections  | 4748 [R$_{int}$ = 0.0293, R$_{sigma}$ = 0.0266] | 4499 [R$_{int}$ = 0.0405, R$_{sigma}$ = 0.0650] |
| Data/restraints/parameters | 4748/0/325       | 4499/0/325      |
| Goodness-of-fit on F$^2$ | 1.024            | 0.995           |
| Final R indexes [I≥2σ (I)] | R$_1$ = 0.0517, wR$_2$ = 0.1495 | R$_1$ = 0.0600, wR$_2$ = 0.1385 |
| Final R indexes [all data] | R$_1$ = 0.0968, wR$_2$ = 0.1862 | R$_1$ = 0.1098, wR$_2$ = 0.1649 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.28/-0.18 | 0.60/-0.29 |
Table S4. Crystal data and structure refinement for (SBZ·(9F) and [H-(SBZ-9F-cb)][p-TsO].

|                         | (SBZ)·(9F) | [H-(SBZ-9F-cb)][p-TsO] |
|-------------------------|------------|------------------------|
| CCDC                    | 2042042    | 2042043                |
| Empirical formula       | C_{27}H_{14}F_{9}N | C_{34}H_{22}F_{9}NO_{3}S |
| Formula weight          | 523.39     | 695.58                 |
| Temperature/K           | 296.15     | 99.99                  |
| Crystal system          | triclinic  | monoclinic             |
| Space group             | P-1        | P_{21}/n                |
| a/Å                     | 6.2122(8)  | 5.8302(3)              |
| b/Å                     | 7.6774(8)  | 23.7785(12)            |
| c/Å                     | 23.672(3)  | 22.0776(11)            |
| α/°                     | 85.610(7)  | 90                     |
| β/°                     | 87.631(5)  | 96.947(2)              |
| γ/°                     | 82.946(7)  | 90                     |
| Volume/Å³               | 1116.6(2)  | 3038.2(3)              |
| Z                       | 2          | 4                      |
| ρ_calc/g/cm³            | 1.557      | 1.521                  |
| μ/mm⁻¹                  | 0.144      | 0.2                    |
| F(000)                  | 528        | 1416                   |
| Crystal size/mm³        | 0.34 × 0.3 × 0.025 | 0.1 × 0.03 × 0.01 |
| Radiation               | Mo Kα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data       | 5.18 to 50.798 | 5.466 to 53.732 |
| collection/°            |            |                        |
| Index ranges            | -7 ≤ h ≤ 7, -9 ≤ k ≤ 8, -27 ≤ l ≤ 28 | -7 ≤ h ≤ 6, -30 ≤ k ≤ 30, -28 ≤ l ≤ 28 |
| Reflections collected   | 3871       | 97040                  |
| Independent reflections | 3871 [R_{int} = 0.0525, R_{sigma} = 0.1477] | 6532 [R_{int} = 0.0858, R_{sigma} = 0.0289] |
| Data/restraints/parameters | 3871/0/334 | 6532/0/434             |
| Goodness-of-fit on F²   | 0.972      | 1.037                  |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0639, wR₂ = 0.1110 | R₁ = 0.0399, wR₂ = 0.0866 |
| Final R indexes [all data] | R₁ = 0.2505, wR₂ = 0.1696 | R₁ = 0.0608, wR₂ = 0.0944 |
| Largest diff. peak/hole / e Å⁻³ | 0.18/-0.19 | 0.29/-0.37            |
S5. Molecular Modeling

Electrostatic potentials for each functionalized alkene were calculated at ground state in gas phase using Spartan '18 V1.2.0 software. Equilibrium geometry was used for calculation without further constraints. All calculations were performed using the B3LYP/6-31G* density functional model.

**Table S5.** Mulliken charge distribution values along with the designated number system.

| Template | Energy (a.u.) | Mulliken Charges |
|----------|---------------|------------------|
| SB       | -540.71       | C1(C14): -0.129; H1(H14): 0.130  |
|          |               | C2(C13): -0.131; H2(H13): 0.130  |
|          |               | C3(C12): -0.129; H3(H12): 0.130  |
|          |               | C4(C11): -0.180; H4(H11): 0.130  |
|          |               | C5(C10): -0.198; H5(H10): 0.127  |
|          |               | C6(C9): 0.182    |
|          |               | C7(C8): -0.189; H7(H8): 0.127    |
| BPE      | -572.78       | N1(N14): -0.407  |
|          |               | C2(C13): 0.036; H2(H13): 0.144  |
|          |               | C3(C12): 0.040; H3(H12): 0.137  |
|          |               | C4(C11): -0.185; H4(H11): 0.137 |
|          |               | C5(C10): -0.203; H5(H10): 0.137 |
|          |               | C6(C9): 0.193    |
|          |               | C7(C8): -0.174; H7(H8): 0.138   |
| SBZ      | -556.75       | N1: -0.411       |
|          |               | C2: 0.039; H2: 0.140  |
|          |               | C3: 0.034; H3: 0.140  |
|          |               | C4: -0.205; H4: 0.132  |
|          |               | C5: -0.187; H5: 0.134  |
|          |               | C6: 0.196        |
|          |               | C7: -0.183; H7: 0.132  |
|          |               | C8: -0.180; H8: 0.133  |
|          |               | C9: 0.179        |
|          |               | C10: -0.177; H10: 0.133 |
|          |               | C11: -0.195; H11: 0.131 |
|          |               | C12: -0.131; H12: 0.134 |
|          |               | C13: -0.130; H13: 0.135 |
|          |               | C14: -0.127; H14: 0.134 |
| 8F   | -1334.54 | C1(C14): -0.293; H1(H14): 0.182 |
|      |          | C2(C13): 0.346; F2(F13): -0.279 |
|      |          | C3(C12): 0.344; F3(F12): -0.279 |
|      |          | C4(C11): 0.262; F4(F11): -0.273 |
|      |          | C5(C10): 0.235; F5(F10): 0.272  |
|      |          | C6(C9): 0.039                     |
|      |          | C7(C8): -0.190; H7(H8): 0.178    |
| 9F   | -1433.76 | C1: -0.293; H1: 0.243             |
|      |          | C2: 0.344; F2: -0.278             |
|      |          | C3: 0.346; F3: -0.279             |
|      |          | C4: 0.235; F4: -0.272             |
|      |          | C5: 0.261; F5: -0.273             |
|      |          | C6: 0.039                         |
|      |          | C7: -0.191; H7: 0.176             |
|      |          | C8: -0.189; H8: 0.178             |
|      |          | C9: 0.040                         |
|      |          | C10: 0.240; F10: -0.269           |
|      |          | C11: 0.270; F11: -0.270           |
|      |          | C12: 0.263; F12: -0.264           |
|      |          | C13: 0.265; F13: -0.265           |
|      |          | C14: 0.262; F14: -0.259           |
S6. Supplementary References

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