Supplementary Information

Cis→*Trans* and *Trans*→*Cis* Isomerizations of Styrylcoumarins in the Solid State. Importance of the Location of Free Volume in Crystal Lattices

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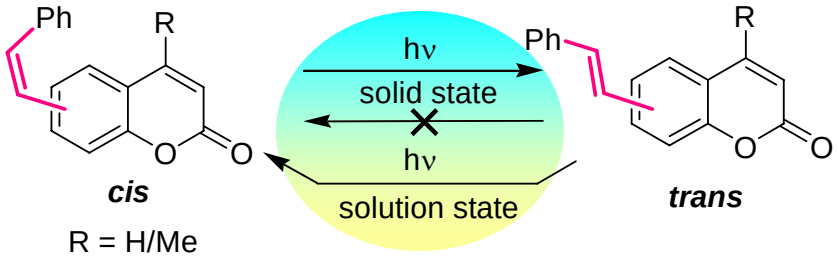

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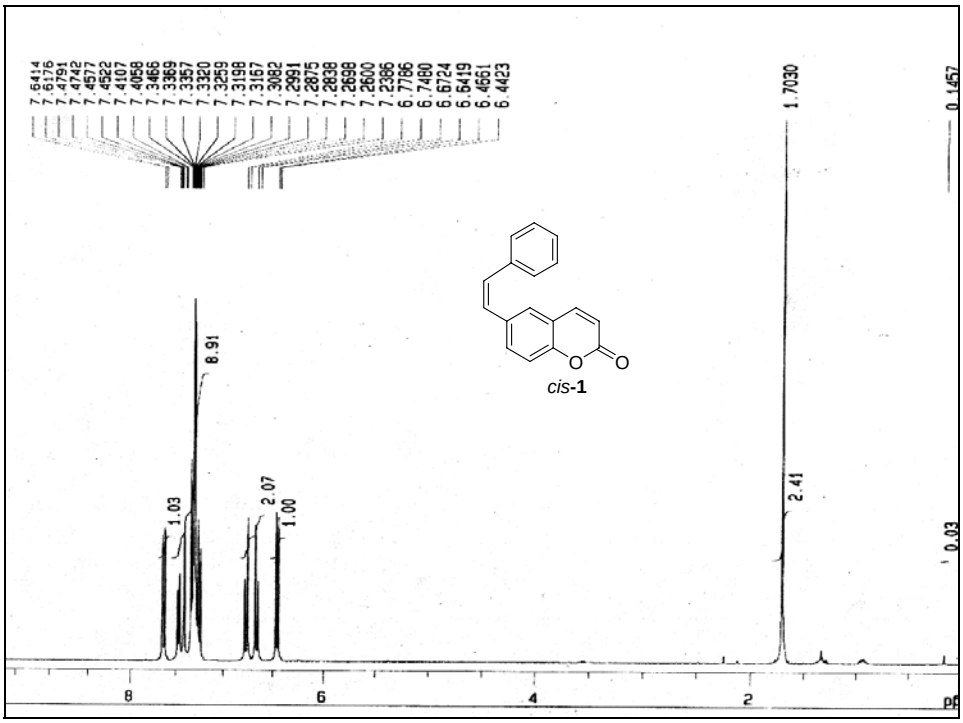


Figure S1. ^{1}H NMR spectrum of *cis*-**1**.

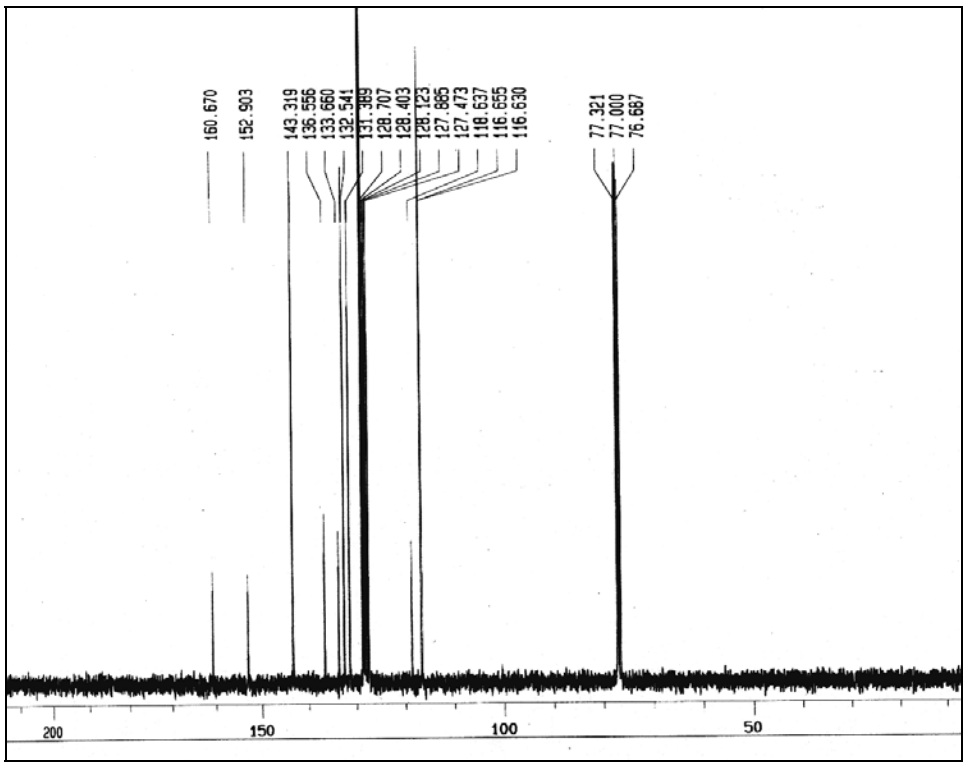


Figure S2. ^{13}C NMR spectrum of *cis*-**1**.

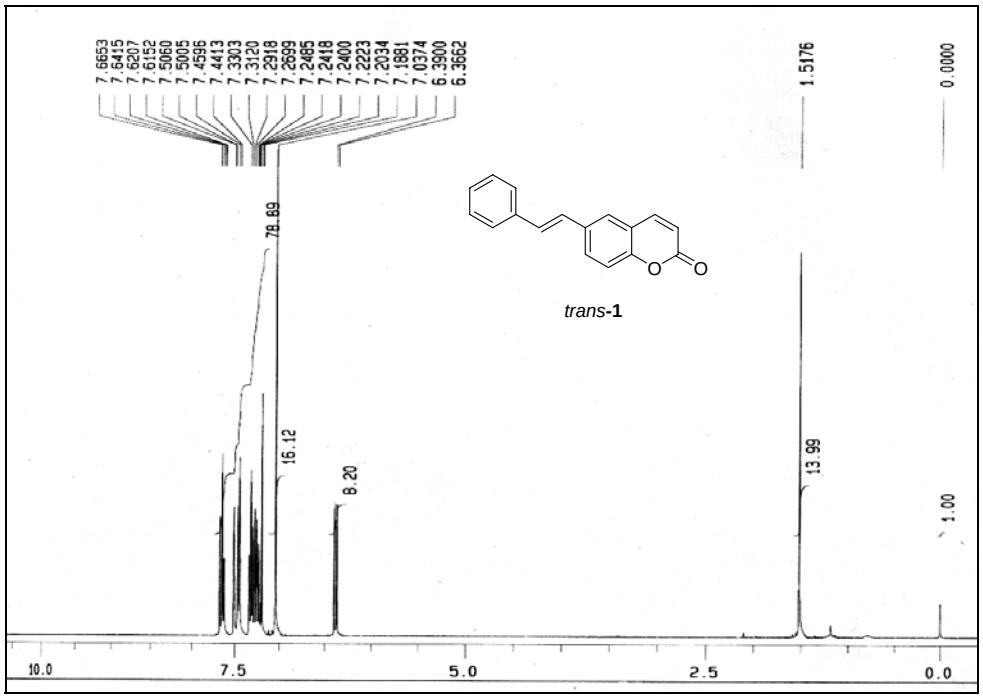


Figure S3. ^{1}H NMR spectrum of *trans*-**1**.

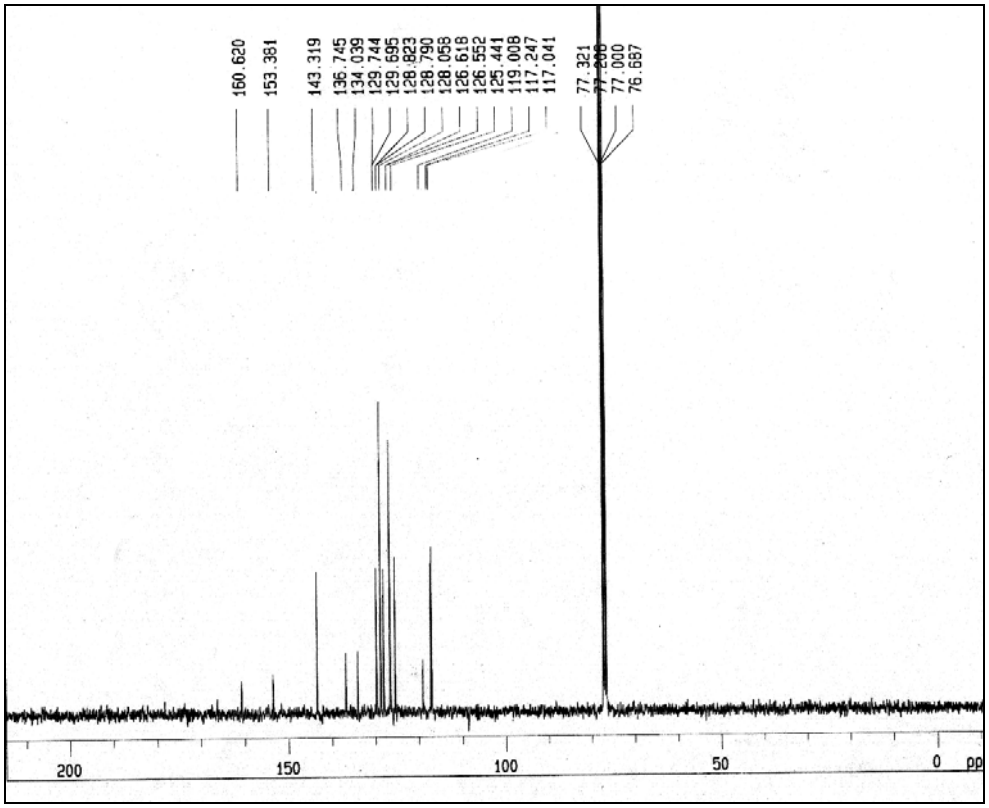


Figure S4. ^{13}C NMR spectrum of *trans*-**1**.

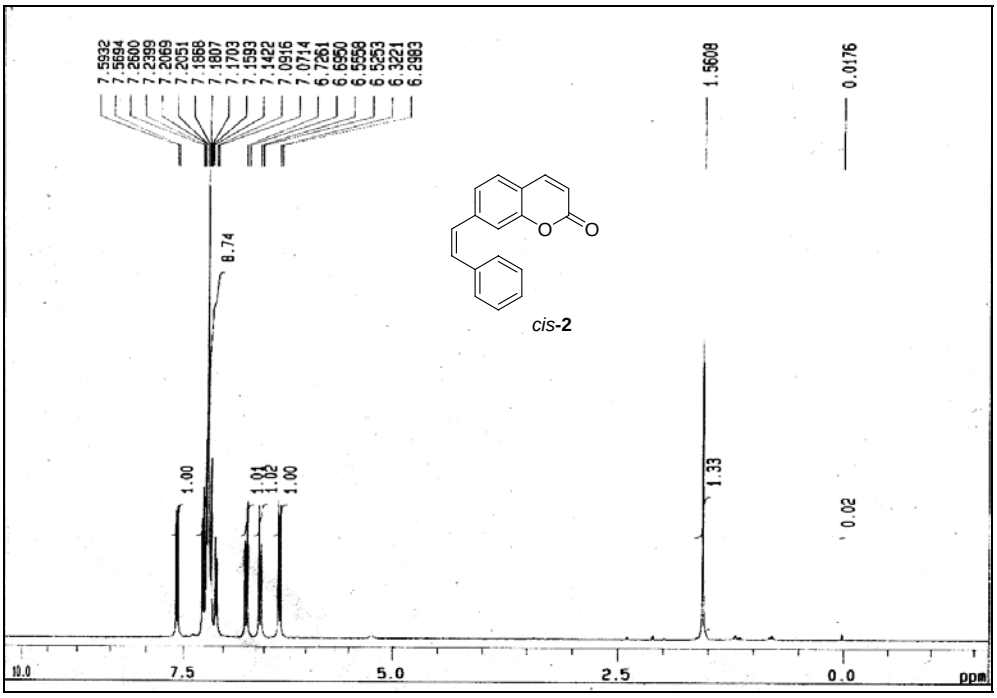


Figure S5. ^{1}H NMR spectrum of *cis*-**2**.

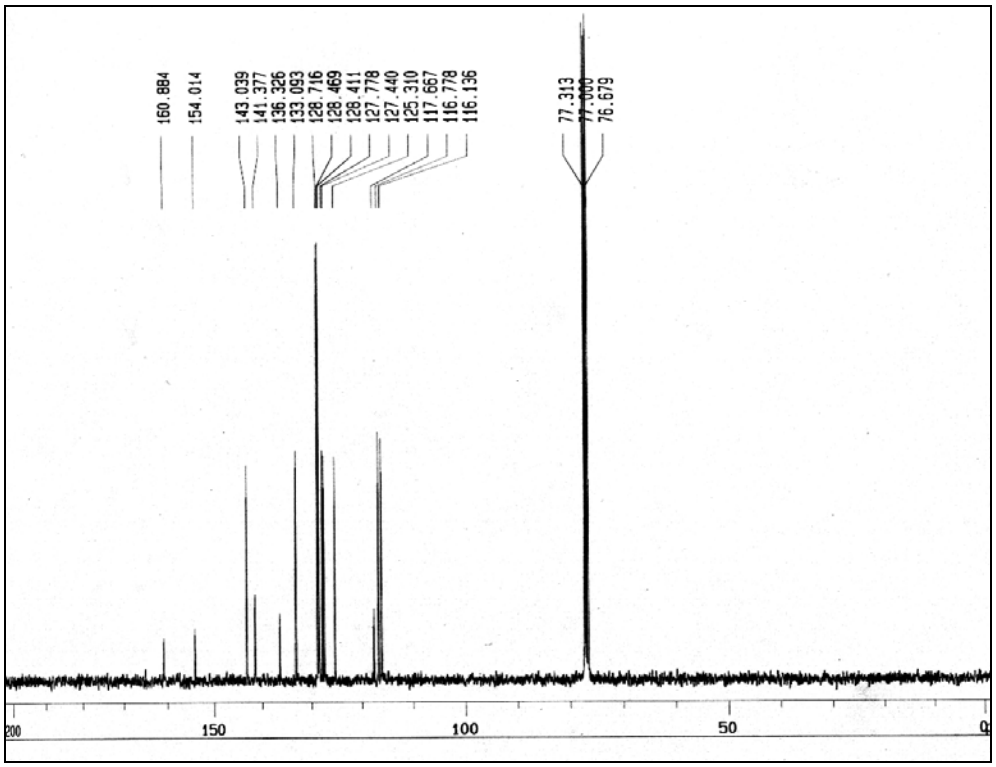


Figure S6. ^{13}C NMR spectrum of *cis*-**2**.

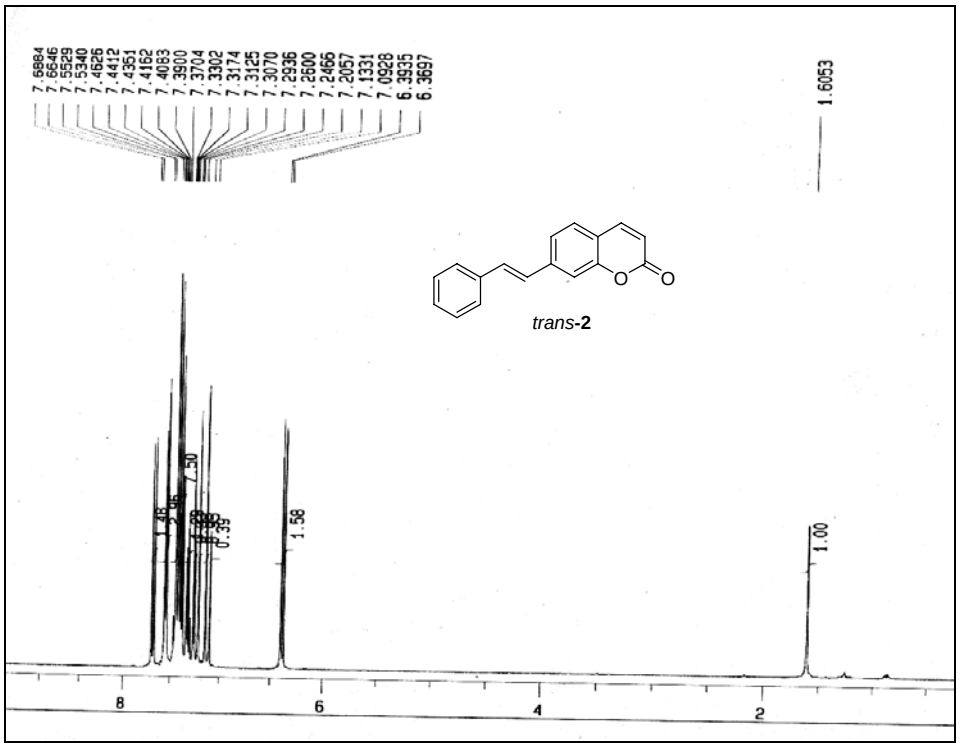


Figure S7. ^{1}H NMR spectrum of *trans*-**2**.

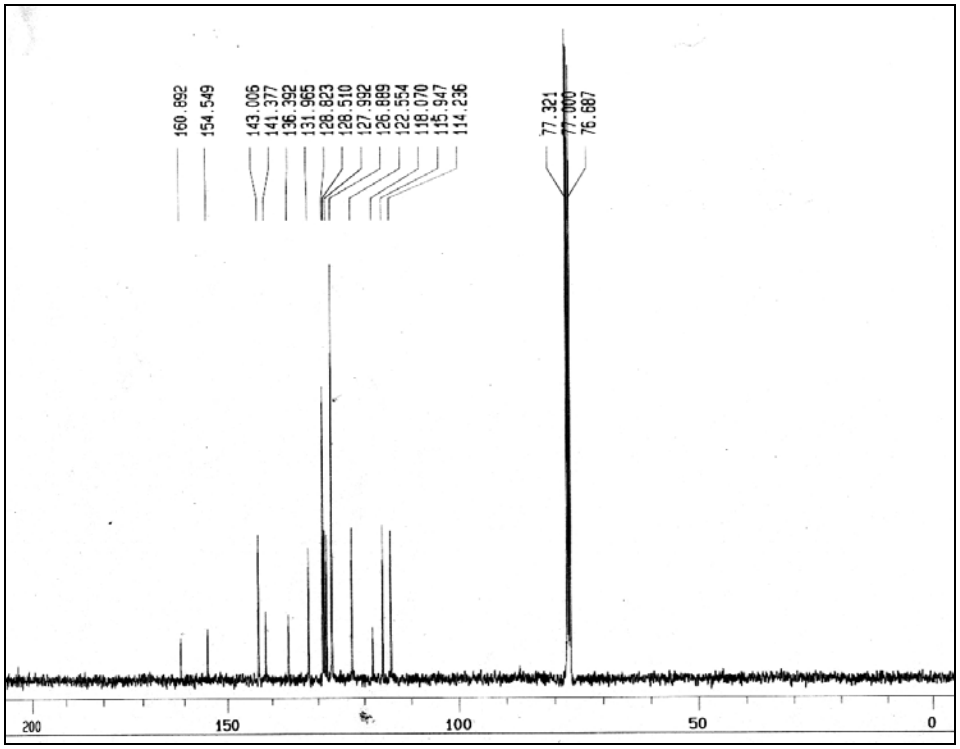


Figure S8. ^{13}C NMR spectrum of *trans*-**2**.

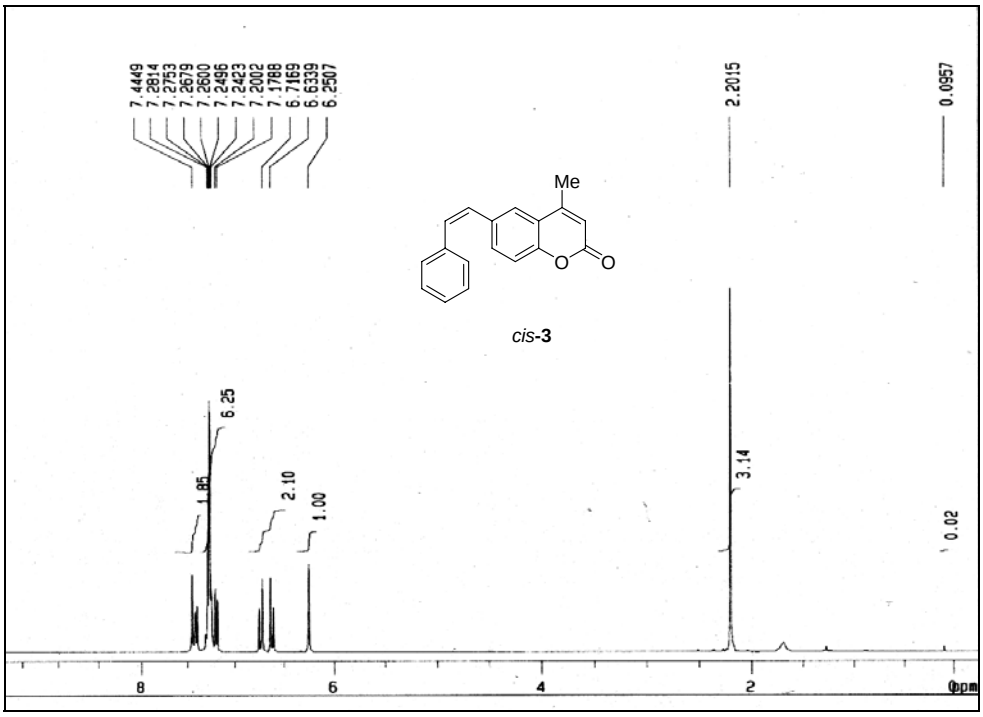


Figure S9. ^{1}H NMR spectrum of *cis*-**3**.

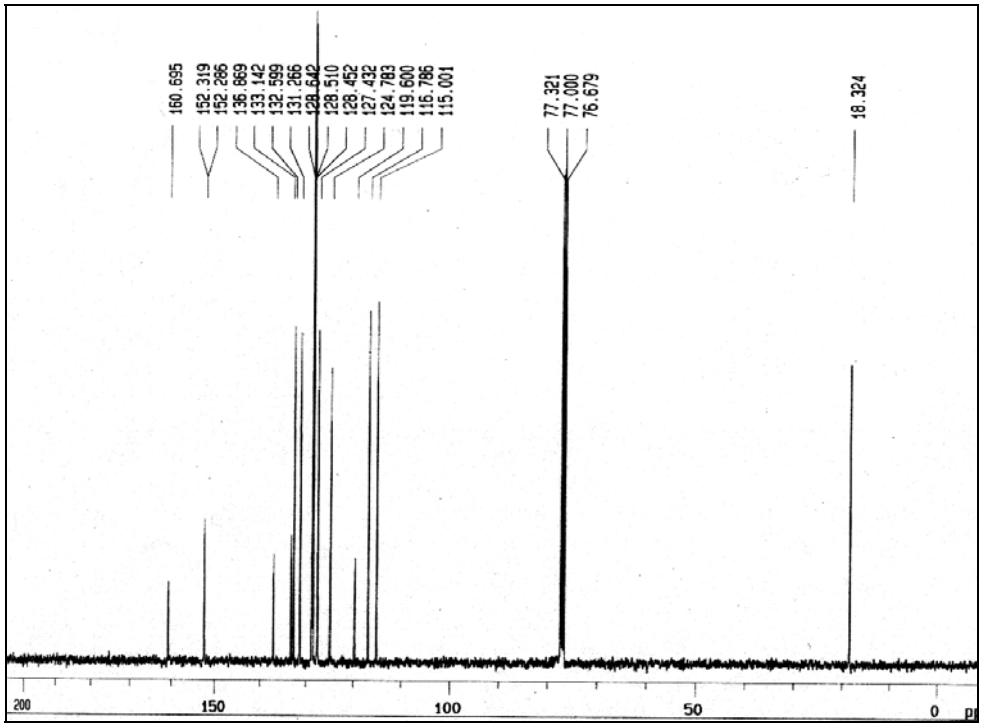


Figure S10. ^{13}C NMR spectrum of *cis*-**3**.

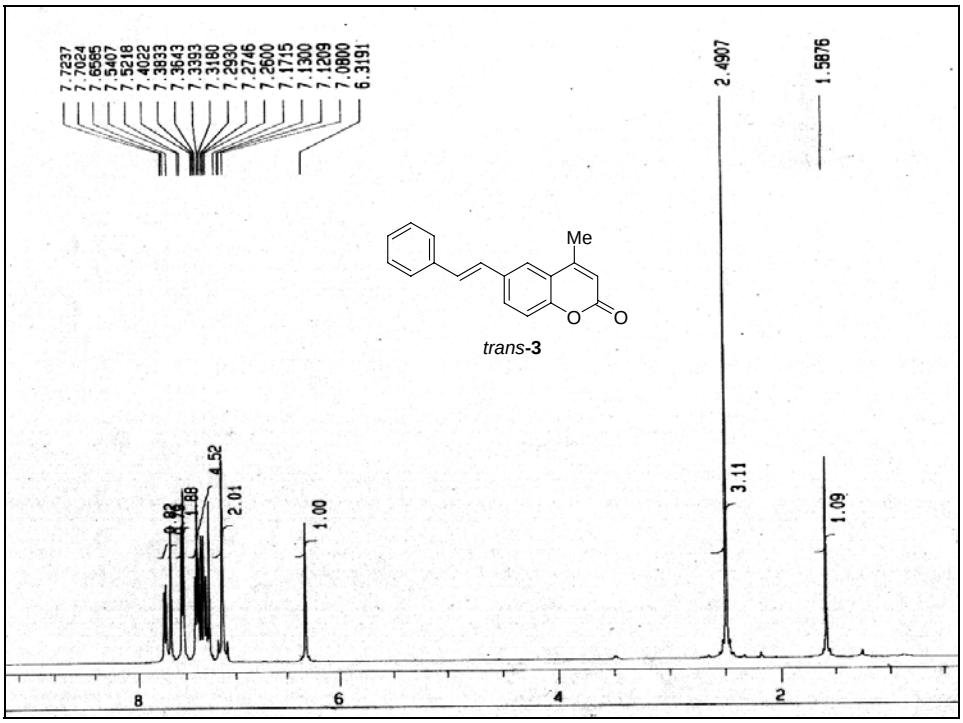


Figure S11. ^{1}H NMR spectrum of *trans*-**3**.

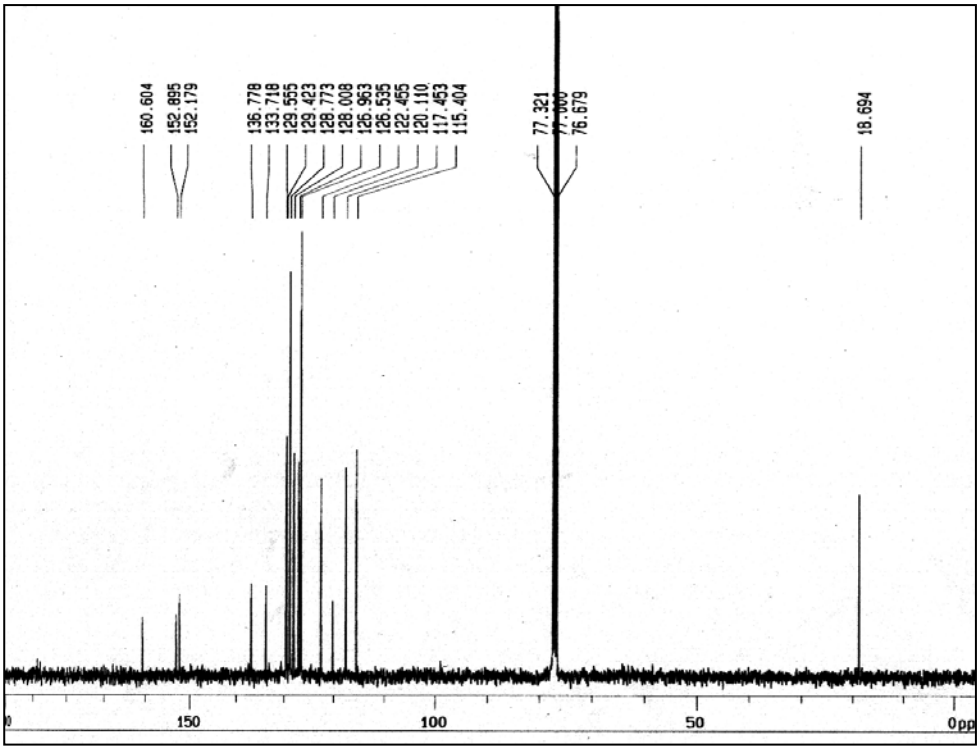


Figure S12. ^{13}C NMR spectrum of *trans*-**3**.

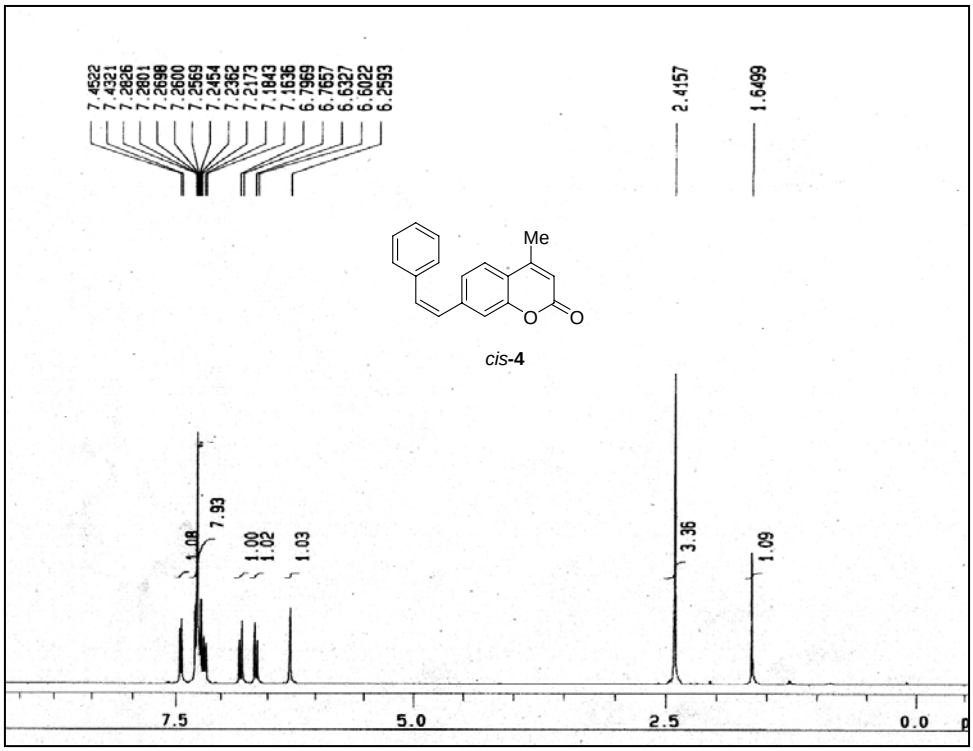


Figure S13. ^{1}H NMR spectrum of *cis*-**4**.

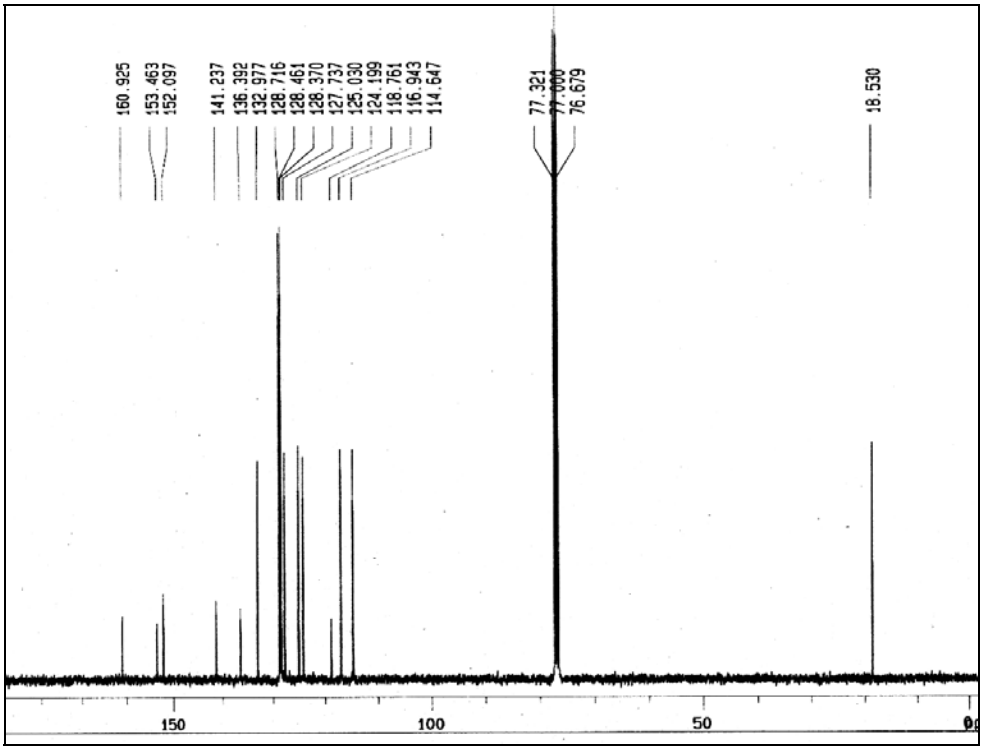


Figure S14. ^{13}C NMR spectrum of *cis*-**4**.

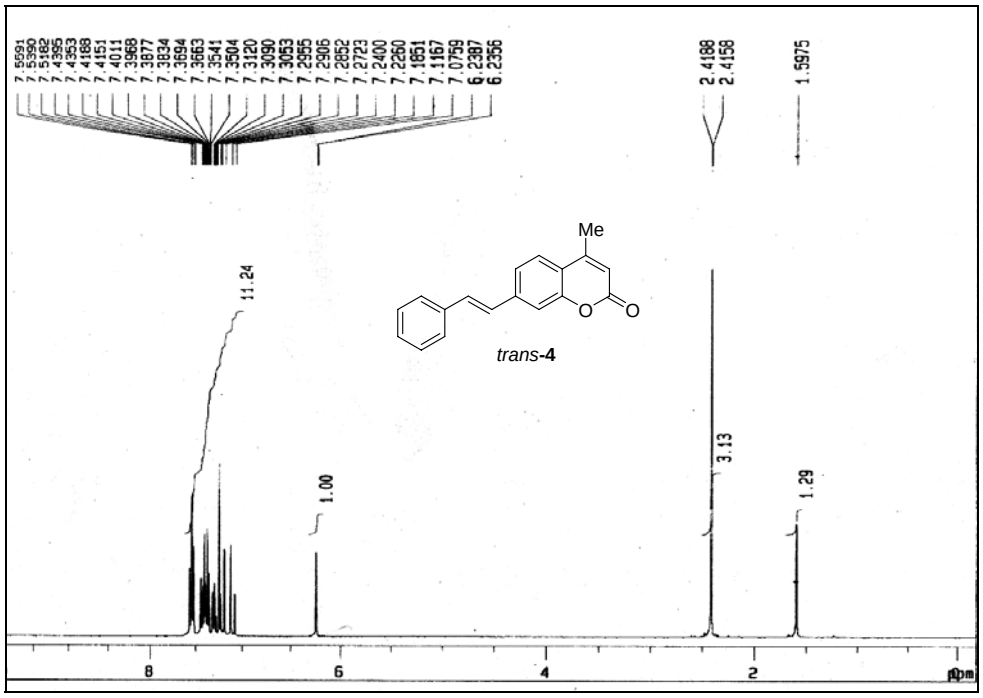


Figure S15. ^{1}H NMR spectrum of *trans*-**4**.

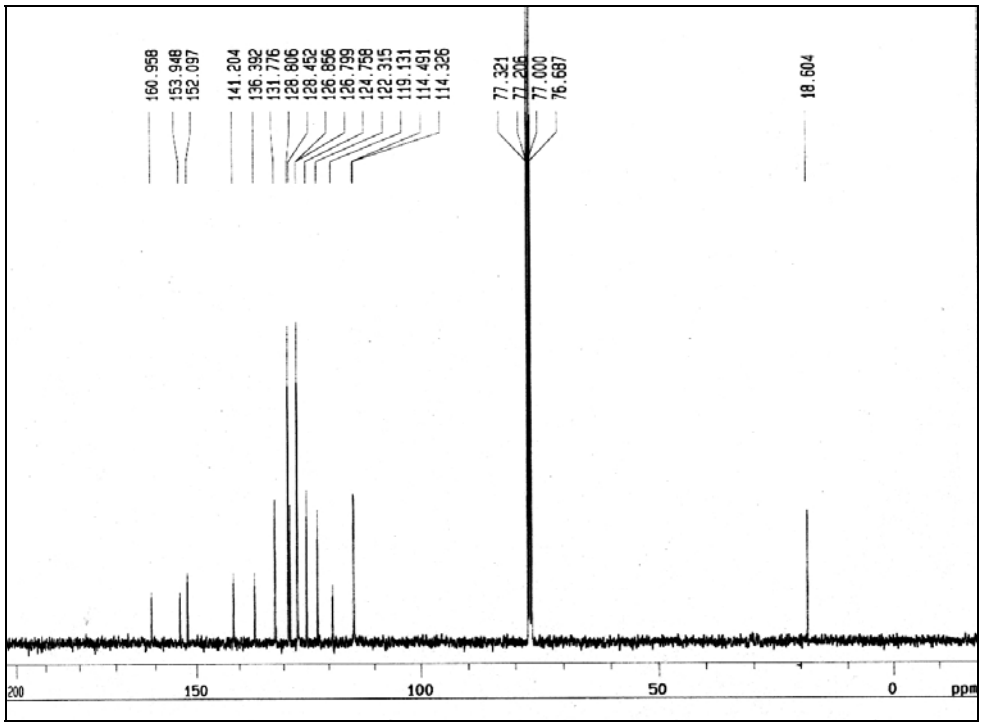
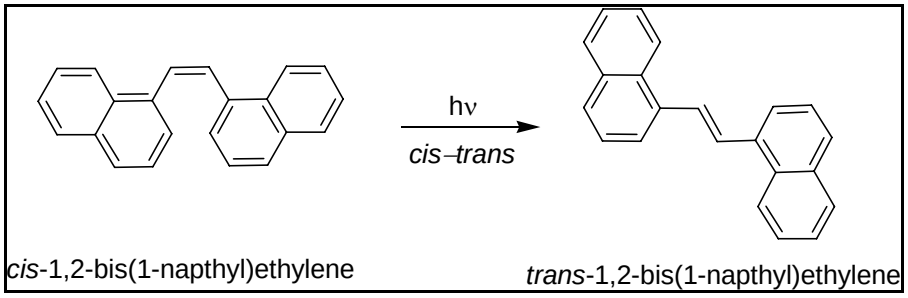


Figure S16. ^{13}C NMR spectrum of *trans*-**4**.

***cis-trans* isomerization of *cis*-1,2-bis(1-naphthyl)ethylene**



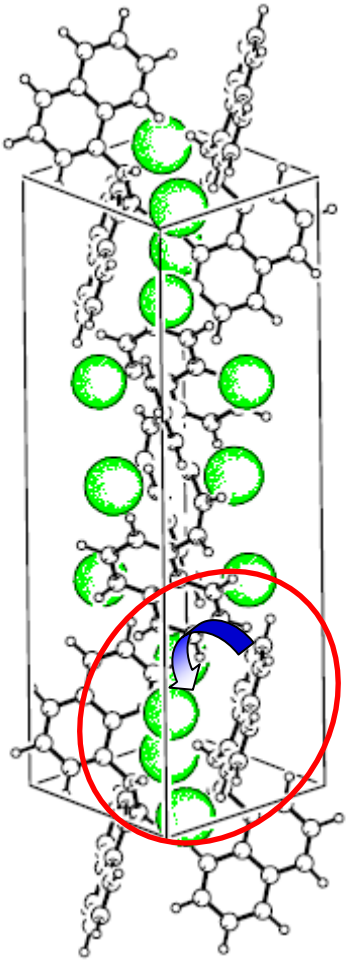
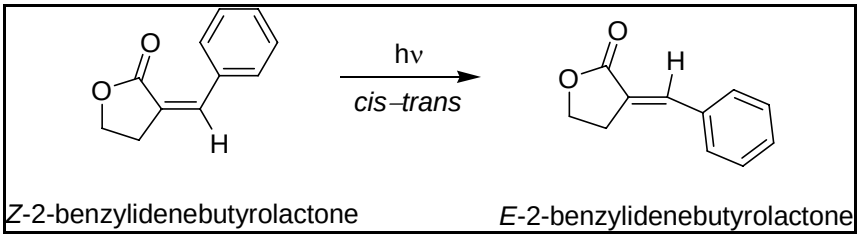


Figure S17. The cavity plot for *cis*-1,2-bis(1-naphthyl)ethylene. The voids of radius 1.0 Å can be identified over the napthyl ring in the direction along which *cis*→*trans* isomerization may occur. The direction for the motion of the ring is indicated by an arrow. (ref: Aldoshin, S. M.; Alfimov, M. V.; Atovmyan, L. O.; Kaminsky, V. F.; Razumov, V. F.; Rachinsky, A. G. *Mol. Cryst. Liq. Cryst.* **1984**, *108*, 1).

***cis-trans* isomerization of *Z*-2-benzylidenebutyrolactone**



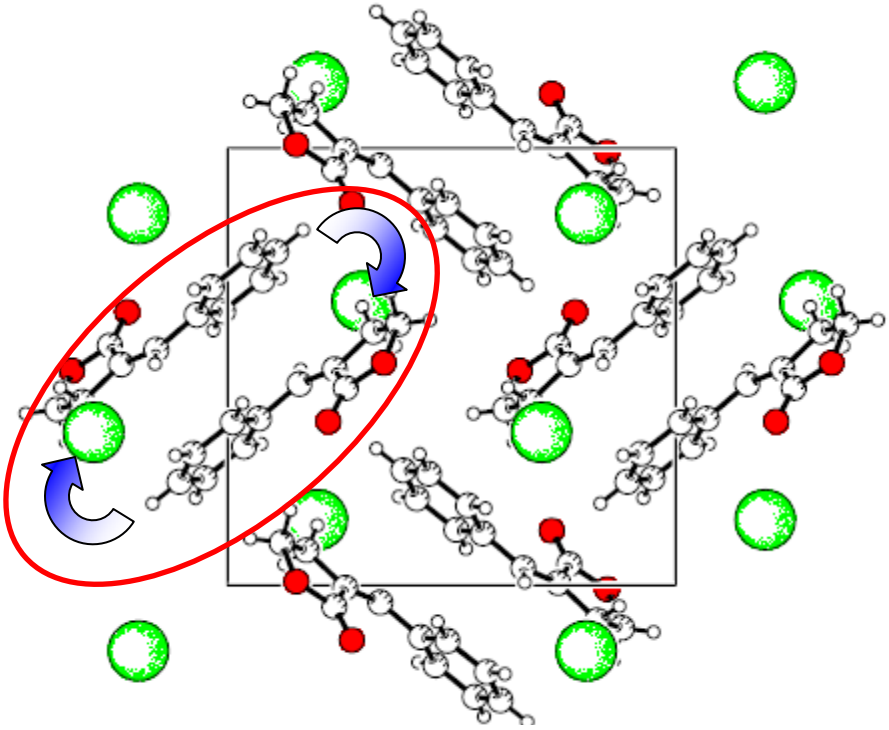
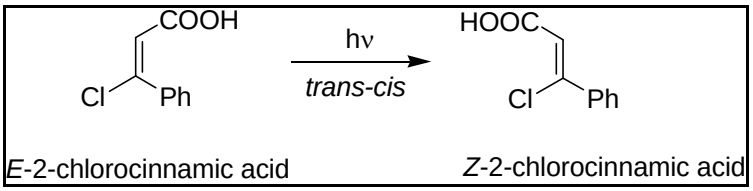


Figure S18. The cavity plot for *Z*-2-benzylidenebutyrolactone. Notice that the location of the empty spaces for the motions of the phenyl ring may permit *Z*→*E* isomerization (ref: Kaupp, G.; Haak, M. *Angew.Chem., Int. Ed.* **1996**, *35*, 2774).

***trans-cis* isomerization of *E*-2-chlorocinnamic acid**



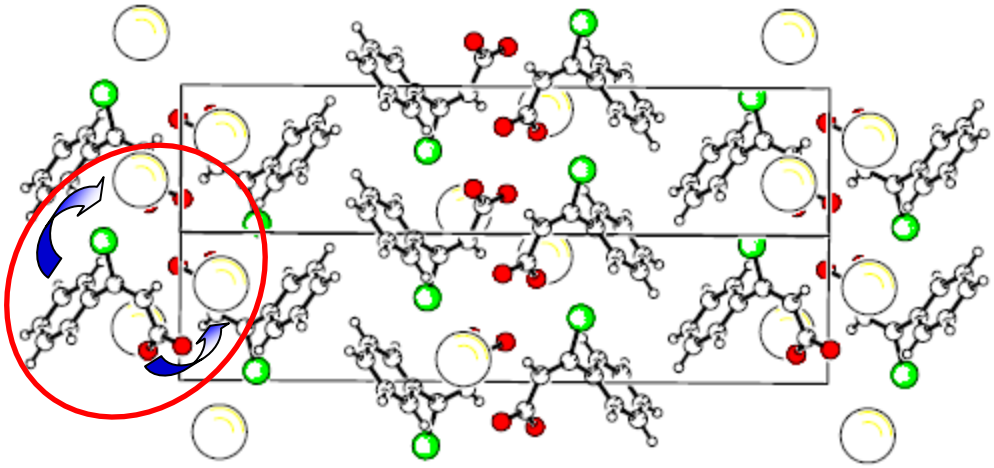
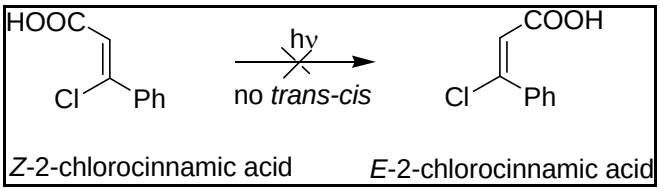


Figure S19. The cavity plot for the *E*-2-chlorocinnamic acid. There are no spaces between the aryl rings, but the cages above and below the carboxy moiety can be identified suggesting the possibility of the motion of the latter as being responsible for the initial course of the isomerization. In this case, *E*→*Z* isomerization is observed. (ref: (a) James, T. C. *J. Chem. Soc.* **1911**, *99*, 1620. (b) Filippakis, S. E.; Leiserowitz, L.; Rabinovich, D.; Schmidt, G. M. J. *J. Chem. Soc., Perkin Trans. 2*. **1972**, 1750).

The case of *Z*-2-chlorocinnamic acid. No *cis-trans* isomerization!



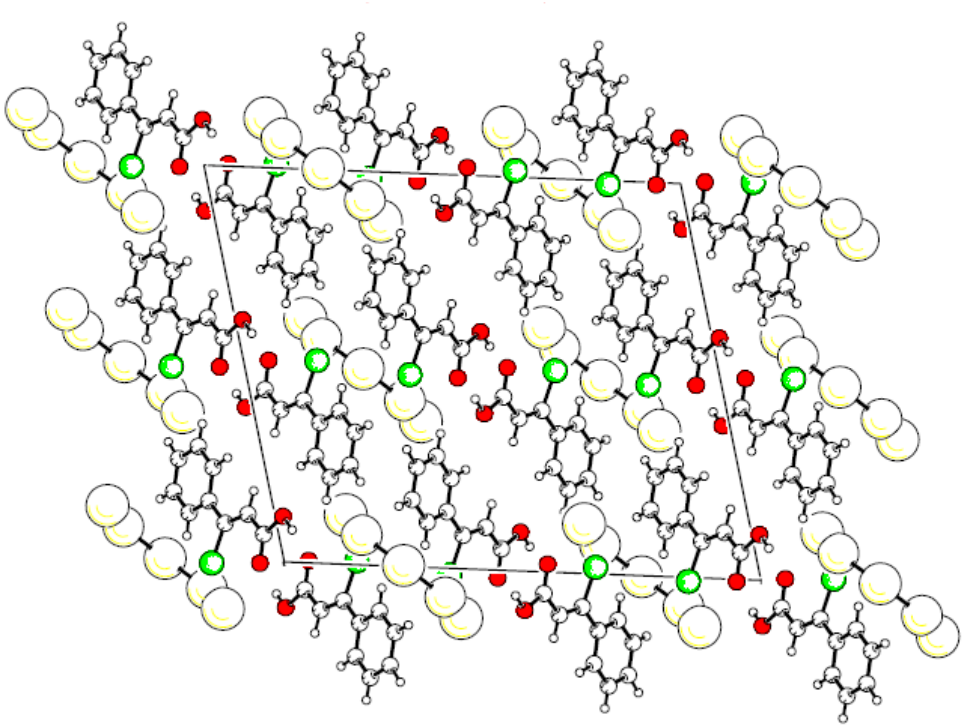
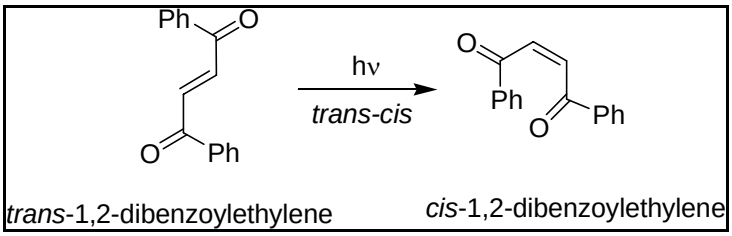


Figure S20. The cavity plot for the *Z*-2-chlorocinnamic acid. There are no voids between the aryl rings, but they can be found in the region close to Cl atoms. In this instance, no *Z*→*E* isomerization is observed. (ref: Filippakis, S. E.; Leiserowitz, L.; Rabinovich, D.; Schmidt, G. M. J. *J. Chem. Soc., Perkin Trans. 2*. **1972**, 1750).

***trans-cis* isomerization of *trans*-1,2-dibenzoylethylene**



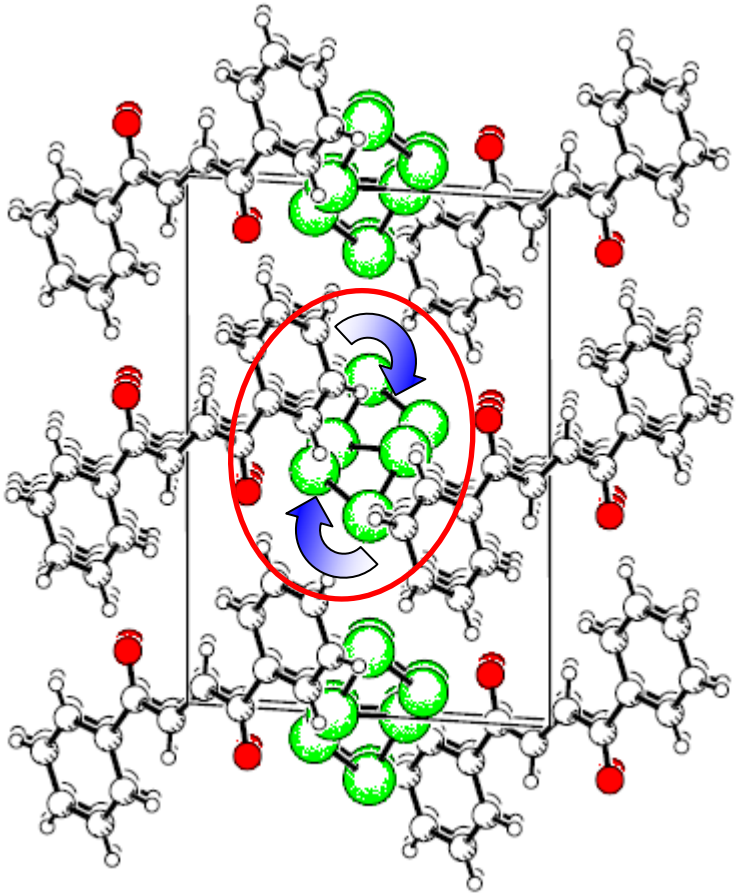
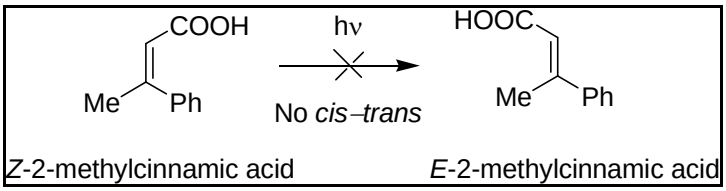


Figure S21. The cavity plot for the *trans*-1,2-dibenzoylethylene. The cages lie in the direction in which the phenyl rings may undergo in-plane motion to afford *cis* product. In this case, facile *trans-cis* isomerization is observed. (ref: (a) Bart, J. C. J.; Schmidt, G. M. J. *Recl. Trav. Chim. Pays-Bas*. **1978**, *97*, 231. (b) Kaupp, G.; Schmeyers, J. *J. Photochem. Photobiol. B: Biol.* **2000**, *59*, 15).

The case of *Z*-2-methylcinnamic acid. No *cis-trans* isomerization!



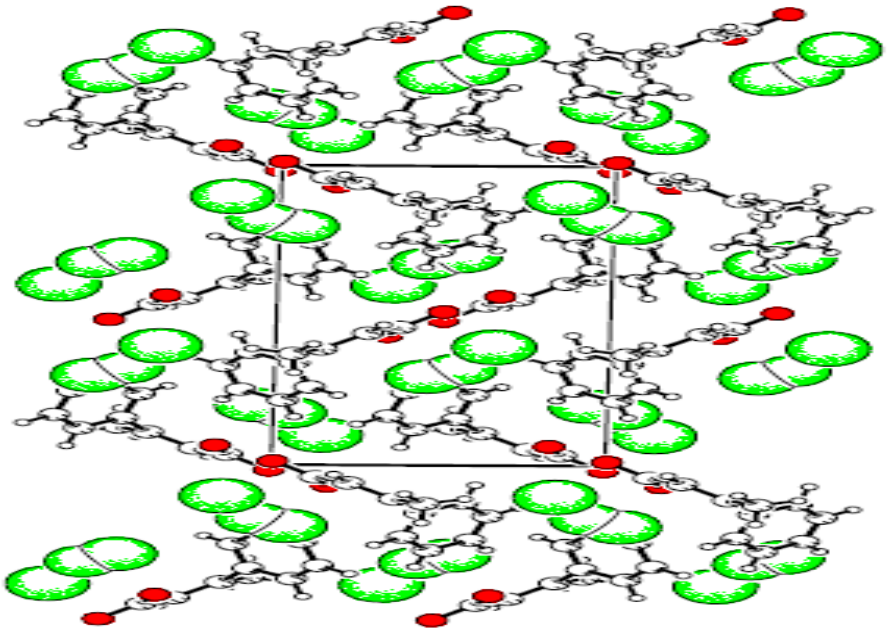
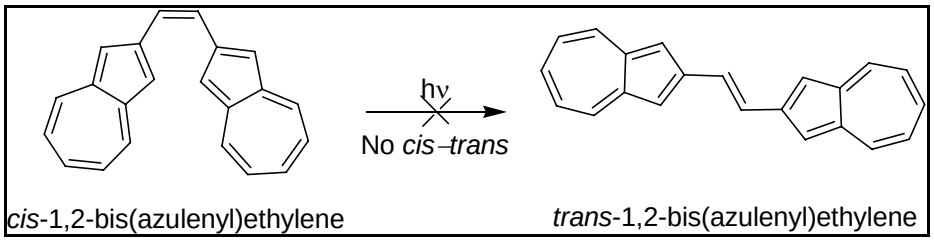


Figure S22. The cavity plot for the *Z*-2-methylcinnamic acid. The cages lie over the edges of the phenyl rings, but their location is in the direction opposite to the axis about which the motion of atom may facilitate the isomerization. Hence no *Z*→*E* isomerization is observed. (ref: Filippakis, S. E.; Leiserowitz, L.; Rabinovich, D.; Schmidt, G. M. J. *J. Chem. Soc., Perkin Trans. 2*. **1972**, 1750).

The case of *cis*-1,2-bis(azulenyl)ethylene. No *cis-trans* isomerization!



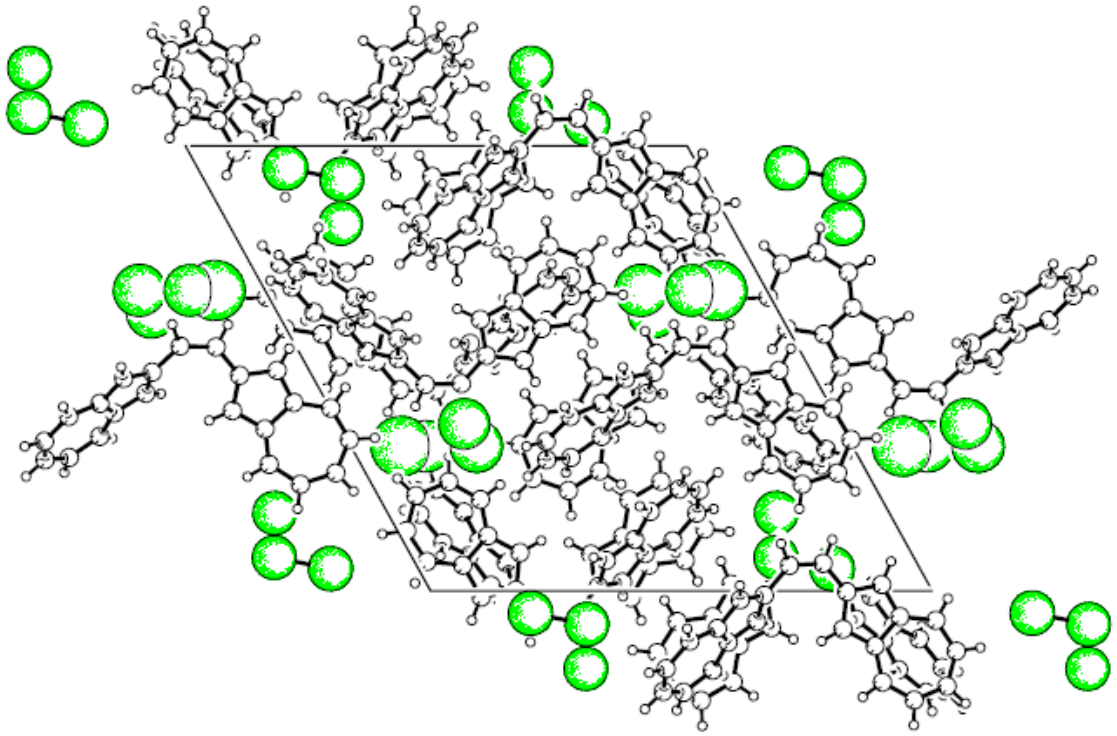


Figure S23. The cavity plot for the *cis*-1,2-bis(azulenyl)ethylene is shown above. The sites of location of empty cages may not permit isomerization (ref: Natarajan, A.; Mague, J. T.; Venkatesan, K.; Arai, T. ; Ramamurthy, V. *J. Org. Chem.* **2006**, *71*, 1055).