Table S1 – Definition of internal symmetry coordinates used in the normal mode analysis of conformers **I** and **III** of α-furil.

	Definition[a]	Symmetry[b]	Approximate description
S_1	$\nu(C_1\text{-}C_3)$	A	ν(C-C)
S_2	$\nu(C_1{=}O_2)+\nu(C_3{=}O_4)$	A	ν(C=O) s
S_3	$\nu(C_1{=}O_2)-\nu(C_3{=}O_4)$	B	ν(C=O) as
S_4	$\nu(C_1\text{-}C_5)+\nu(C_3\text{-}C_{13})$	A	$\nu(C\text{-}C_\alpha)$ s
S_5	$\nu(C_1\text{-}C_5)-\nu(C_3\text{-}C_{13})$	B	$\nu(C\text{-}C_\alpha)$ as
S_6	$\nu(C_7\text{-}C_8)+\nu(C_8\text{-}O_9)+\nu(O_9\text{-}C_5)+\nu(C_5\text{-}C_6)+\nu(C_6\text{-}C_7)+$ $+\nu(C_{15}\text{-}C_{16})+\nu(C_{16}\text{-}O_{17})+\nu(O_{17}\text{-}C_{13})+\nu(C_{13}\text{-}C_{14})+\nu(C_{14}\text{-}C_{15})$	A	ν(ring 1) s
S_7	$\nu(C_7\text{-}C_8)+\nu(C_8\text{-}O_9)+\nu(O_9\text{-}C_5)+\nu(C_5\text{-}C_6)+\nu(C_6\text{-}C_7)-$ $-\nu(C_{15}\text{-}C_{16})-\nu(C_{16}\text{-}O_{17})-\nu(O_{17}\text{-}C_{13})-\nu(C_{13}\text{-}C_{14})-\nu(C_{14}\text{-}C_{15})$	B	ν(ring 1) as
S_8	$\nu(C_7\text{-}C_8)+\nu(C_5\text{-}C_6)+\nu(C_{15}\text{-}C_{16})+\nu(C_{13}\text{-}C_{14})$	A	ν(ring 2) s
S_9	$\nu(C_7\text{-}C_8)+\nu(C_5\text{-}C_6)-\nu(C_{15}\text{-}C_{16})-\nu(C_{13}\text{-}C_{14})$	B	ν(ring 2) as
S_{10}	$\nu(C_7\text{-}C_8)-\nu(C_5\text{-}C_6)+\nu(C_{15}\text{-}C_{16})-\nu(C_{13}\text{-}C_{14})$	A	ν(ring 3) s
S_{11}	$\nu(C_7\text{-}C_8)-\nu(C_5\text{-}C_6)-\nu(C_{15}\text{-}C_{16})+\nu(C_{13}\text{-}C_{14})$	B	ν(ring 3) as
S_{12}	$2\nu(C_6\text{-}C_7)-\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)+2\nu(C_{14}\text{-}C_{15})-\nu(C_{16}\text{-}O_{17})-\nu(O_{17}\text{-}C_{13})$	A	ν(ring 4) s
S_{13}	$2\nu(C_6\text{-}C_7)-\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)-2\nu(C_{14}\text{-}C_{15})+\nu(C_{16}\text{-}O_{17})+\nu(O_{17}\text{-}C_{13})$	B	ν(ring 4) as
S_{14}	$\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)+\nu(C_{16}\text{-}O_{17})-\nu(O_{17}\text{-}C_{13})$	A	ν(ring 5) s
S_{15}	$\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)-\nu(C_{16}\text{-}O_{17})+\nu(O_{17}\text{-}C_{13})$	B	ν(ring 5) as
S_{16}	$\nu(C_6\text{-}H_{10})+\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})+\nu(C_{14}\text{-}H_{18})+\nu(C_{15}\text{-}H_{19})+\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 1) s
S_{17}	$\nu(C_6\text{-}H_{10})+\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})-\nu(C_{14}\text{-}H_{18})-\nu(C_{15}\text{-}H_{19})-\nu(C_{16}\text{-}H_{20})$	B	ν(C-H 1) as
S_{18}	$\nu(C_6\text{-}H_{10})-\nu(C_8\text{-}H_{12})+\nu(C_{14}\text{-}H_{18})-\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 2) s
S_{19}	$\nu(C_6\text{-}H_{10})-\nu(C_8\text{-}H_{12})-\nu(C_{14}\text{-}H_{18})+\nu(C_{16}\text{-}H_{20})$	B	ν(C-H 2) as
S_{20}	$\nu(C_6\text{-}H_{10})-2\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})+\nu(C_{14}\text{-}H_{18})-2\nu(C_{15}\text{-}H_{19})+\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 3) s
S_{21}	$\nu(C_6\text{-}H_{10})-2\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})-\nu(C_{14}\text{-}H_{18})+2\nu(C_{15}\text{-}H_{19})-\nu(C_{16}\text{-}H_{20})$	B	ν(C-H 3) as
S_{22}	$\delta(C_5\text{-}C_1{=}O_2)-\delta(C_3\text{-}C_1{=}O_2)+\delta(C_{13}\text{-}C_3{=}O_4)-\delta(C_1\text{-}C_3\text{-}C_4)$	A	δ(C=O) s
S_{23}	$\delta(C_5\text{-}C_1{=}O_2)-\delta(C_3\text{-}C_1{=}O_2)-\delta(C_{13}\text{-}C_3{=}O_4)+\delta(C_1\text{-}C_3\text{-}C_4)$	B	δ(C=O) as
S_{24}	$2\delta(C_5\text{-}C_1\text{-}C_3)-\delta(C_5\text{-}C_1\text{-}C_2)-\delta(C_3\text{-}C_1\text{-}C_2)+2\delta(C_{13}\text{-}C_3\text{-}C_1)-\delta(C_{13}\text{-}C_3\text{-}C_4)-\delta(C_1\text{-}C_3\text{-}C_4)$	A	$\delta(CCC_\alpha)$ s
S_{25}	$2\delta(C_5\text{-}C_1\text{-}C_3)-\delta(C_5\text{-}C_1\text{-}C_2)-\delta(C_3\text{-}C_1\text{-}C_2)-2\delta(C_{13}\text{-}C_3\text{-}C_1)+\delta(C_{13}\text{-}C_3\text{-}C_4)+\delta(C_1\text{-}C_3\text{-}C_4)$	B	$\delta(CCC_\alpha)$ as
S_{26}	$\delta(C_6\text{-}C_5\text{-}C_1)-\delta(O_9\text{-}C_5\text{-}C_1)+\delta(C_{14}\text{-}C_{13}\text{-}C_3)-\delta(O_{17}\text{-}C_{13}\text{-}C_3)$	A	ω(ring) s
S_{27}	$\delta(C_6\text{-}C_5\text{-}C_1)-\delta(O_9\text{-}C_5\text{-}C_1)-\delta(C_{14}\text{-}C_{13}\text{-}C_3)+\delta(O_{17}\text{-}C_{13}\text{-}C_3)$	B	ω(ring) as
S_{28}	$\delta(C_8\text{-}O_9\text{-}C_5)-0.809\delta(C_7\text{-}C_8\text{-}O_9)-0.809\delta(O_9\text{-}C_5\text{-}C_6)+0.309\delta(C_6\text{-}C_7\text{-}C_8)+$ $+0.309\delta(C_5\text{-}C_6\text{-}C_7)+\delta(C_{16}\text{-}O_{17}\text{-}C_{13})-0.809\delta(C_{15}\text{-}C_{16}\text{-}O_{17})-0.809\delta(O_{17}\text{-}C_{13}\text{-}C_{14})+$ $+0.309\delta(C_{14}\text{-}C_{15}\text{-}C_{16})+0.309\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	A	δ(ring 1) s
S_{29}	$\delta(C_8\text{-}O_9\text{-}C_5)-0.809\delta(C_7\text{-}C_8\text{-}O_9)-0.809\delta(O_9\text{-}C_5\text{-}C_6)+0.309\delta(C_6\text{-}C_7\text{-}C_8)+$ $+0.309\delta(C_5\text{-}C_6\text{-}C_7)-\delta(C_{16}\text{-}O_{17}\text{-}C_{13})+0.809\delta(C_{15}\text{-}C_{16}\text{-}O_{17})+0.809\delta(O_{17}\text{-}C_{13}\text{-}C_{14})-$ $-0.309\delta(C_{14}\text{-}C_{15}\text{-}C_{16})-0.309\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	B	δ(ring 1) as
S_{30}	$-1.118\delta(C_7\text{-}C_8\text{-}O_9)+1.118\delta(O_9\text{-}C_5\text{-}C_6)+1.809\delta(C_6\text{-}C_7\text{-}C_8)-1.809\delta(C_5\text{-}C_6\text{-}C_7)-$ $-1.118\delta(C_{15}\text{-}C_{16}\text{-}O_{17})+1.118\delta(O_{17}\text{-}C_{13}\text{-}C_{14})+1.809\delta(C_{14}\text{-}C_{15}\text{-}C_{16})-1.809\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	A	δ(ring 2) s
S_{31}	$-1.118\delta(C_7\text{-}C_8\text{-}O_9)+1.118\delta(O_9\text{-}C_5\text{-}C_6)+1.809\delta(C_6\text{-}C_7\text{-}C_8)-1.809\delta(C_5\text{-}C_6\text{-}C_7)+$	B	δ(ring 2) as

	$+1.118\delta(C_{15}\text{-}C_{16}\text{-}O_{17})\text{-}1.118\delta(O_{17}\text{-}C_{13}\text{-}C_{14})\text{-}1.809\delta(C_{14}\text{-}C_{15}\text{-}C_{16})+1.809\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$		
S_{32}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})+\delta(C_6\text{-}C_7\text{-}H_{11})\text{-}\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})$ -	A	δ(C-H 1) s
	$\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})+\delta(C_{13}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+\delta(C_{14}\text{-}C_{15}\text{-}H_{19})\text{-}\delta(C_{16}\text{-}C_{15}\text{-}H_{19})+$		
	$+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})\text{-}\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{33}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})+\delta(C_6\text{-}C_7\text{-}H_{11})\text{-}\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})$ -	B	δ(C-H 1) as
	$\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})\text{-}\delta(C_{13}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{14}\text{-}C_{15}\text{-}H_{19})+\delta(C_{16}\text{-}C_{15}\text{-}H_{19})\text{-}$		
	$\text{-}\delta(C_{15}\text{-}C_{16}\text{-}H_{20})+\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{34}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_8\text{-}H_{12})+\delta(O_9\text{-}C_8\text{-}H_{12})+$	A	δ(C-H 2) s
	$+\delta(C_{13}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{16}\text{-}H_{20})+\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{35}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_8\text{-}H_{12})+\delta(O_9\text{-}C_8\text{-}H_{12})\text{-}$	B	δ(C-H 2) as
	$\text{-}\delta(C_{13}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})\text{-}\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{36}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}2\delta(C_6\text{-}C_7\text{-}H_{11})+2\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})$ -	A	δ(C-H 3) s
	$\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})+\delta(C_{13}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{14}\text{-}H_{18})\text{-}2\delta(C_{14}\text{-}C_{15}\text{-}H_{19})+2\delta(C_{16}\text{-}C_{15}\text{-}H_{19})+$		
	$+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})\text{-}\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{37}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}2\delta(C_6\text{-}C_7\text{-}H_{11})+2\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})$ -	B	δ(C-H 3) as
	$\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})\text{-}\delta(C_{13}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+2\delta(C_{14}\text{-}C_{15}\text{-}H_{19})\text{-}2\delta(C_{16}\text{-}C_{15}\text{-}H_{19})\text{-}$		
	$\text{-}\delta(C_{15}\text{-}C_{16}\text{-}H_{20})+\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$		
S_{38}	$\tau(C_8\text{-}C_7\text{-}C_6\text{-}C_5)\text{-}0.809\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}0.809\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)+0.309\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$	A	τ(ring 1) s
	$+0.309\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)+\tau(C_{16}\text{-}C_{15}\text{-}C_{14}\text{-}C_{13})\text{-}0.809\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})\text{-}$		
	$\text{-}0.809\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})+0.309\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})+0.309\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$		
S_{39}	$\tau(C_8\text{-}C_7\text{-}C_6\text{-}C_5)\text{-}0.809\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}0.809\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)+0.309\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$	B	τ(ring 1) as
	$+0.309\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)\text{-}\tau(C_{16}\text{-}C_{15}\text{-}C_{14}\text{-}C_{13})+0.809\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})+$		
	$+0.809\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})\text{-}0.309\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})\text{-}0.309\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$		
S_{40}	$1.118\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}1.118\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)\text{-}1.809\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$	A	τ(ring 2) s
	$+1.809\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)+1.118\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})\text{-}1.118\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})\text{-}$		
	$\text{-}1.809\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})+1.809\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$		
S_{41}	$1.118\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}1.118\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)\text{-}1.809\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$	B	τ(ring 2) as
	$+1.809\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)\text{-}1.118\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})+1.118\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})+$		
	$+1.809\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})\text{-}1.809\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$		
S_{42}	$\gamma(C_1\text{-}C_6\text{-}C_5\text{-}O_9)+\gamma(C_3\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})$	A	γ(ring) s
S_{43}	$\gamma(C_1\text{-}C_6\text{-}C_5\text{-}O_9)\text{-}\gamma(C_3\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})$	B	γ(ring) as
S_{44}	$\tau(O_2{=}C_1\text{-}C_3{=}O_4)+\tau(O_2{=}C_1\text{-}C_3\text{-}C_{13})+\tau(C_5\text{-}C_1\text{-}C_3\text{-}C_{13})+\tau(C_5\text{-}C_1\text{-}C_3{=}O_4)$	A	τ(C-C)
S_{45}	$\tau(O_9\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(C_6\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(O_{17}\text{-}C_{13}\text{-}C_3\text{-}C_1)+\tau(C_{14}\text{-}C_{13}\text{-}C_3\text{-}C_1)+$	A	$\tau(C\text{-}C_\alpha)$ s
	$+\tau(O_9\text{-}C_5\text{-}C_1{=}O_2)+\tau(C_6\text{-}C_5\text{-}C_1{=}O_2)+\tau(O_{17}\text{-}C_{13}\text{-}C_3{=}O_4)+\tau(C_{14}\text{-}C_{13}\text{-}C_3{=}O_4)$		
S_{46}	$\tau(O_9\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(C_6\text{-}C_5\text{-}C_1\text{-}C_3)\text{-}\tau(O_{17}\text{-}C_{13}\text{-}C_3\text{-}C_1)\text{-}\tau(C_{14}\text{-}C_{13}\text{-}C_3\text{-}C_1)+$	B	$\tau(C\text{-}C_\alpha)$ as
	$+\tau(O_9\text{-}C_5\text{-}C_1{=}O_2)+\tau(C_6\text{-}C_5\text{-}C_1{=}O_2)\text{-}\tau(O_{17}\text{-}C_{13}\text{-}C_3{=}O_4)\text{-}\tau(C_{14}\text{-}C_{13}\text{-}C_3{=}O_4)$		
S_{47}	$\gamma(O_2{=}C_3\text{-}C_1\text{-}C_5)+\gamma(O_4{=}C_1\text{-}C_3\text{-}C_{13})$	A	γ(C=O) s
S_{48}	$\gamma(O_2{=}C_3\text{-}C_1\text{-}C_5)\text{-}\gamma(O_4{=}C_1\text{-}C_3\text{-}C_{13})$	B	γ(C=O) as
S_{49}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)+\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)+$	A	γ(C-H 1) s
	$+\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})+\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$		
S_{50}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)+\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)\text{-}$	B	γ(C-H 1) as
	$\text{-}\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})\text{-}\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})\text{-}\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$		

S_{51}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)+\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})\text{-}\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 2) s
S_{52}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)\text{-}\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	B	γ(C-H 2) as
S_{53}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}2\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)+$ $+\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})\text{-}2\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 3) s
S_{54}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}2\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)\text{-}$ $\text{-}\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})+2\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})\text{-}\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	B	γ(C-H 3) as

[a] Normalization factors not shown. ν, bond stretching, δ, bending, γ, rocking, ω, wagging, τ, torsion, s, symmetric, as, asymmetric. See Figure 1 for atom numbering.
[b] C_2 symmetry point group.

Table S2 – Definition of internal coordinates used in the normal mode analysis of conformer **II** of α-furil.

	Definition[a]	Symmetry[b]	Approximate description
S_1	$\nu(C_1\text{-}C_3)$	A	ν(C-C)
S_2	$\nu(C_1\text{=}O_2)$	A	ν(C=O)
S_3	$\nu(C_3\text{=}O_4)$	A	ν(C=O)’
S_4	$\nu(C_1\text{-}C_5)+\nu(C_3\text{-}C_{13})$	A	$\nu(C\text{-}C_\alpha)$
S_5	$\nu(C_1\text{-}C_5)-\nu(C_3\text{-}C_{13})$	A	$\nu(C\text{-}C_\alpha)$’
S_6	$\nu(C_7\text{-}C_8)+\nu(C_8\text{-}O_9)+\nu(O_9\text{-}C_5)+\nu(C_5\text{-}C_6)+\nu(C_6\text{-}C_7)$	A	ν(ring 1)
S_7	$\nu(C_{15}\text{-}C_{16})+\nu(C_{16}\text{-}O_{17})+\nu(O_{17}\text{-}C_{13})+\nu(C_{13}\text{-}C_{14})+\nu(C_{14}\text{-}C_{15})$	A	ν(ring 1)’
S_8	$\nu(C_7\text{-}C_8)+\nu(C_5\text{-}C_6)$	A	ν(ring 2)
S_9	$\nu(C_{15}\text{-}C_{16})+\nu(C_{13}\text{-}C_{14})$	A	ν(ring 2)’
S_{10}	$\nu(C_7\text{-}C_8)-\nu(C_5\text{-}C_6)$	A	ν(ring 3)
S_{11}	$\nu(C_{15}\text{-}C_{16})-\nu(C_{13}\text{-}C_{14})$	A	ν(ring 3)’
S_{12}	$2\nu(C_6\text{-}C_7)-\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)$	A	ν(ring 4)
S_{13}	$2\nu(C_{14}\text{-}C_{15})-\nu(C_{16}\text{-}O_{17})-\nu(O_{17}\text{-}C_{13})$	A	ν(ring 4)’
S_{14}	$\nu(C_8\text{-}O_9)-\nu(O_9\text{-}C_5)$	A	ν(ring 5)
S_{15}	$\nu(C_{16}\text{-}O_{17})-\nu(O_{17}\text{-}C_{13})$	A	ν(ring 5)’
S_{16}	$\nu(C_6\text{-}H_{10})+\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})$	A	ν(C-H 1)
S_{17}	$\nu(C_{14}\text{-}H_{18})+\nu(C_{15}\text{-}H_{19})+\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 1)’
S_{18}	$\nu(C_6\text{-}H_{10})-\nu(C_8\text{-}H_{12})$	A	ν(C-H 2)
S_{19}	$\nu(C_{14}\text{-}H_{18})-\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 2)’
S_{20}	$\nu(C_6\text{-}H_{10})-2\nu(C_7\text{-}H_{11})+\nu(C_8\text{-}H_{12})$	A	ν(C-H 3)
S_{21}	$\nu(C_{14}\text{-}H_{18})-2\nu(C_{15}\text{-}H_{19})+\nu(C_{16}\text{-}H_{20})$	A	ν(C-H 3)’
S_{22}	$\delta(C_5\text{-}C_1\text{=}O_2)-\delta(C_3\text{-}C_1\text{=}O_2)+\delta(C_{13}\text{-}C_3\text{=}O_4)-\delta(C_1\text{-}C_3\text{-}C_4)$	A	δ(C=O)
S_{23}	$\delta(C_5\text{-}C_1\text{=}O_2)-\delta(C_3\text{-}C_1\text{=}O_2)-\delta(C_{13}\text{-}C_3\text{=}O_4)+\delta(C_1\text{-}C_3\text{-}C_4)$	A	δ(C=O)’
S_{24}	$2\delta(C_5\text{-}C_1\text{-}C_3)-\delta(C_5\text{-}C_1\text{-}C_2)-\delta(C_3\text{-}C_1\text{-}C_2)+2\delta(C_{13}\text{-}C_3\text{-}C_1)-\delta(C_{13}\text{-}C_3\text{-}C_4)-\delta(C_1\text{-}C_3\text{-}C_4)$	A	$\delta(CCC_\alpha)$
S_{25}	$2\delta(C_{13}\text{-}C_3\text{-}C_1)-\delta(C_{13}\text{-}C_3\text{-}C_4)-\delta(C_1\text{-}C_3\text{-}C_4)-2\delta(C_{13}\text{-}C_3\text{-}C_1)+\delta(C_{13}\text{-}C_3\text{-}C_4)+\delta(C_1\text{-}C_3\text{-}C_4)$	A	$\delta(CCC_\alpha)$’
S_{26}	$\delta(C_6\text{-}C_5\text{-}C_1)-\delta(O_9\text{-}C_5\text{-}C_1)+\delta(C_{14}\text{-}C_{13}\text{-}C_3)-\delta(O_{17}\text{-}C_{13}\text{-}C_3)$	A	ω(ring)
S_{27}	$\delta(C_6\text{-}C_5\text{-}C_1)-\delta(O_9\text{-}C_5\text{-}C_1)-\delta(C_{14}\text{-}C_{13}\text{-}C_3)+\delta(O_{17}\text{-}C_{13}\text{-}C_3)$	A	ω(ring)’
S_{28}	$\delta(C_8\text{-}O_9\text{-}C_5)-0.809\delta(C_7\text{-}C_8\text{-}O_9)-0.809\delta(O_9\text{-}C_5\text{-}C_6)+0.309\delta(C_6\text{-}C_7\text{-}C_8)+$ $+0.309\delta(C_5\text{-}C_6\text{-}C_7)+\delta(C_{16}\text{-}O_{17}\text{-}C_{13})-0.809\delta(C_{15}\text{-}C_{16}\text{-}O_{17})-0.809\delta(O_{17}\text{-}C_{13}\text{-}C_{14})+$ $+0.309\delta(C_{14}\text{-}C_{15}\text{-}C_{16})+0.309\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	A	δ(ring 1)
S_{29}	$\delta(C_8\text{-}O_9\text{-}C_5)-0.809\delta(C_7\text{-}C_8\text{-}O_9)-0.809\delta(O_9\text{-}C_5\text{-}C_6)+0.309\delta(C_6\text{-}C_7\text{-}C_8)+$ $+0.309\delta(C_5\text{-}C_6\text{-}C_7)-\delta(C_{16}\text{-}O_{17}\text{-}C_{13})+0.809\delta(C_{15}\text{-}C_{16}\text{-}O_{17})+0.809\delta(O_{17}\text{-}C_{13}\text{-}C_{14})-$ $-0.309\delta(C_{14}\text{-}C_{15}\text{-}C_{16})-0.309\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	A	δ(ring 1)’
S_{30}	$-1.118\delta(C_7\text{-}C_8\text{-}O_9)+1.118\delta(O_9\text{-}C_5\text{-}C_6)+1.809\delta(C_6\text{-}C_7\text{-}C_8)-1.809\delta(C_5\text{-}C_6\text{-}C_7)$	A	δ(ring 2)
S_{31}	$-1.118\delta(C_{15}\text{-}C_{16}\text{-}O_{17})+1.118\delta(O_{17}\text{-}C_{13}\text{-}C_{14})+1.809\delta(C_{14}\text{-}C_{15}\text{-}C_{16})-1.809\delta(C_{13}\text{-}C_{14}\text{-}C_{15})$	A	δ(ring 2)’
S_{32}	$\delta(C_5\text{-}C_6\text{-}H_{10})-\delta(C_7\text{-}C_6\text{-}H_{10})+\delta(C_6\text{-}C_7\text{-}H_{11})-\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})-\delta(O_9\text{-}C_8\text{-}H_{12})$	A	δ(C-H 1)
S_{33}	$\delta(C_{13}\text{-}C_{14}\text{-}H_{18})-\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+\delta(C_{14}\text{-}C_{15}\text{-}H_{19})-\delta(C_{16}\text{-}C_{15}\text{-}H_{19})+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})-$ $-\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$	A	δ(C-H 1)’

S_{34}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_8\text{-}H_{12})+\delta(O_9\text{-}C_8\text{-}H_{12})+$ $+\delta(C_{13}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{16}\text{-}H_{20})+\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$	A	δ(C-H 2)
S_{35}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_8\text{-}H_{12})+\delta(O_9\text{-}C_8\text{-}H_{12})\text{-}$ $\text{-}\delta(C_{13}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})\text{-}\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$	A	δ(C-H 2)’
S_{36}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}2\delta(C_6\text{-}C_7\text{-}H_{11})+2\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})\text{ -}$ $\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})+\delta(C_{13}\text{-}C_{14}\text{-}H_{18})\text{-}\delta(C_{15}\text{-}C_{14}\text{-}H_{18})\text{-}2\delta(C_{14}\text{-}C_{15}\text{-}H_{19})+2\delta(C_{16}\text{-}C_{15}\text{-}H_{19})+$ $+\delta(C_{15}\text{-}C_{16}\text{-}H_{20})\text{-}\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$	A	δ(C-H 3)
S_{37}	$\delta(C_5\text{-}C_6\text{-}H_{10})\text{-}\delta(C_7\text{-}C_6\text{-}H_{10})\text{-}2\delta(C_6\text{-}C_7\text{-}H_{11})+2\delta(C_8\text{-}C_7\text{-}H_{11})+\delta(C_7\text{-}C_8\text{-}H_{12})\text{ -}$ $\text{-}\delta(O_9\text{-}C_8\text{-}H_{12})\text{-}\delta(C_{13}\text{-}C_{14}\text{-}H_{18})+\delta(C_{15}\text{-}C_{14}\text{-}H_{18})+2\delta(C_{14}\text{-}C_{15}\text{-}H_{19})\text{-}2\delta(C_{16}\text{-}C_{15}\text{-}H_{19})\text{-}$ $\text{-}\delta(C_{15}\text{-}C_{16}\text{-}H_{20})+\delta(O_{17}\text{-}C_{16}\text{-}H_{20})$	A	δ(C-H 3)’
S_{38}	$\tau(C_8\text{-}C_7\text{-}C_6\text{-}C_5)\text{-}0.809\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}0.809\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)+0.309\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$ $+0.309\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)+\tau(C_{16}\text{-}C_{15}\text{-}C_{14}\text{-}C_{13})\text{-}0.809\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})\text{-}$ $\text{-}0.809\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})+0.309\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})+0.309\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$	A	τ(ring 1)
S_{39}	$\tau(C_8\text{-}C_7\text{-}C_6\text{-}C_5)\text{-}0.809\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}0.809\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)+0.309\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$ $+0.309\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)\text{-}\tau(C_{16}\text{-}C_{15}\text{-}C_{14}\text{-}C_{13})+0.809\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})+$ $+0.809\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})\text{-}0.309\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})\text{-}0.309\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$	A	τ(ring 1)’
S_{40}	$1.118\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}1.118\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)\text{-}1.809\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$ $+1.809\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)+1.118\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})\text{-}1.118\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})\text{-}$ $\text{-}1.809\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})+1.809\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$	A	τ(ring 2)
S_{41}	$1.118\tau(O_9\text{-}C_8\text{-}C_7\text{-}C_6)\text{-}1.118\tau(C_7\text{-}C_6\text{-}C_5\text{-}O_9)\text{-}1.809\tau(C_5\text{-}O_9\text{-}C_8\text{-}C_7)+$ $+1.809\tau(C_6\text{-}C_5\text{-}O_9\text{-}C_8)\text{-}1.118\tau(O_{17}\text{-}C_{16}\text{-}C_{15}\text{-}C_{14})+1.118\tau(C_{15}\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})+$ $+1.809\tau(C_{13}\text{-}O_{17}\text{-}C_{16}\text{-}C_{15})\text{-}1.809\tau(C_{14}\text{-}C_{13}\text{-}O_{17}\text{-}C_{16})$	A	τ(ring 2)’
S_{42}	$\gamma(C_1\text{-}C_6\text{-}C_5\text{-}O_9)$	A	γ(ring)
S_{43}	$\gamma(C_3\text{-}C_{14}\text{-}C_{13}\text{-}O_{17})$	A	γ(ring)’
S_{44}	$\tau(O_2{=}C_1\text{-}C_3{=}O_4)+\tau(O_2{=}C_1\text{-}C_3\text{-}C_{13})+\tau(C_5\text{-}C_1\text{-}C_3\text{-}C_{13})+\tau(C_5\text{-}C_1\text{-}C_3{=}O_4)$	A	τ(C-C)
S_{45}	$\tau(O_9\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(C_6\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(O_9\text{-}C_5\text{-}C_1{=}O_2)+\tau(C_6\text{-}C_5\text{-}C_1{=}O_2)+$ $+\tau(O_9\text{-}C_5\text{-}C_1{=}O_2)+\tau(C_6\text{-}C_5\text{-}C_1{=}O_2)+\tau(O_{17}\text{-}C_{13}\text{-}C_3{=}O_4)+\tau(C_{14}\text{-}C_{13}\text{-}C_3{=}O_4)$	A	$\tau(C\text{-}C_\alpha)$
S_{46}	$\tau(O_9\text{-}C_5\text{-}C_1\text{-}C_3)+\tau(C_6\text{-}C_5\text{-}C_1\text{-}C_3)\text{-}\tau(O_{17}\text{-}C_{13}\text{-}C_3\text{-}C_1)\text{-}\tau(C_{14}\text{-}C_{13}\text{-}C_3\text{-}C_1)+$ $+\tau(O_9\text{-}C_5\text{-}C_1{=}O_2)+\tau(C_6\text{-}C_5\text{-}C_1{=}O_2)\text{-}\tau(O_{17}\text{-}C_{13}\text{-}C_3{=}O_4)\text{-}\tau(C_{14}\text{-}C_{13}\text{-}C_3{=}O_4)$	A	$\tau(C\text{-}C_\alpha)$’
S_{47}	$\gamma(O_2{=}C_3\text{-}C_1\text{-}C_5)+\gamma(O_4{=}C_1\text{-}C_3\text{-}C_{13})$	A	γ(C=O)
S_{48}	$\gamma(O_2{=}C_3\text{-}C_1\text{-}C_5)\text{-}\gamma(O_4{=}C_1\text{-}C_3\text{-}C_{13})$	A	γ(C=O)’
S_{49}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)+\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)$	A	γ(C-H 1)
S_{50}	$\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})+\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 1)’
S_{51}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)+\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})\text{-}\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 2)
S_{52}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)\text{-}\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 2)’
S_{53}	$\gamma(H_{10}\text{-}C_5\text{-}C_6\text{-}C_7)\text{-}2\gamma(H_{11}\text{-}C_6\text{-}C_7\text{-}C_8)+\gamma(H_{12}\text{-}C_7\text{-}C_8\text{-}O_9)$	A	γ(C-H 3)
S_{54}	$\gamma(H_{19}\text{-}C_{13}\text{-}C_{14}\text{-}C_{15})\text{-}2\gamma(H_{19}\text{-}C_{14}\text{-}C_{15}\text{-}C_{16})+\gamma(H_{20}\text{-}C_{15}\text{-}C_{16}\text{-}O_{17})$	A	γ(C-H 3)’

[a] Normalization factors not shown. ν, bond stretching, δ, bending, γ, rocking, ω, wagging, τ, torsion. See Figure 1 for atom numbering.
[b] C_1 symmetry point group.

Table S3 - Calculated [scaled, DFT(B3LYP)/6-311++G(d,p)] wavenumbers, IR intensities and Potential Energy Distributions (PED) for conformer **I** of α-furil.[a]

Approximate description	Wavenumber[b]	Intensity	PED[c]
ν(C-H 1) as	3209.0	6.5	$S_{17}(69)$, $S_{19}(24)$
ν(C-H 1) s	3209.0	<0.1	$S_{16}(69)$, $S_{18}(24)$
ν(C-H 2) s	3199.9	<0.1	$S_{16}(27)$, $S_{18}(71)$
ν(C-H 2) as	3199.9	0.8	$S_{17}(27)$, $S_{19}(71)$
ν(C-H 3) s	3177.3	<0.1	$S_{20}(93)$
ν(C-H 3) as	3177.2	2.3	$S_{21}(93)$
ν(C=O) s	1681.7	48.6	$S_{2}(86)$
ν(C=O) as	1675.2	560.2	$S_{3}(96)$
ν(ring 3) s	1554.9	2.1	$S_{4}(10)$, $S_{10}(65)$, $S_{34}(13)$
ν(ring 3) as	1550.8	51.3	$S_{11}(67)$, $S_{35}(14)$
ν(ring 2) s	1456.9	2.0	$S_{8}(55)$, $S_{28}(10)$
ν(ring 2) as	1448.1	214.2	$S_{9}(59)$, $S_{29}(10)$
ν(ring 4) s	1396.1	3.3	$S_{12}(39)$, $S_{32}(18)$, $S_{34}(14)$, $S_{36}(10)$
ν(ring 4) as	1393.2	85.5	$S_{13}(42)$, $S_{33}(15)$, $S_{35}(16)$, $S_{37}(12)$
ν(C-C_α) s	1299.6	3.2	$S_{1}(13)$, $S_{4}(24)$, $S_{6}(11)$, $S_{8}(14)$, $S_{22}(15)$
ν(C-C_α) as	1248.3	160.4	$S_{5}(30)$, $S_{7}(33)$
δ(C-H 1) s	1219.8	0.3	$S_{32}(67)$
δ(C-H 1) as	1219.2	1.7	$S_{33}(64)$
ν(ring 5) s	1164.7	0.1	$S_{14}(57)$, $S_{34}(19)$
ν(ring 5) as	1162.3	12.7	$S_{9}(14)$, $S_{15}(50)$, $S_{35}(20)$
ν(ring 1) s	1098.9	<0.1	$S_{6}(64)$
δ(C-H 2) as	1088.6	48.9	$S_{7}(30)$, $S_{11}(11)$, $S_{15}(14)$, $S_{35}(15)$, $S_{37}(12)$
δ(C-H 3) s	1063.2	0.1	$S_{1}(12)$, $S_{8}(11)$, $S_{14}(10)$, $S_{36}(32)$
δ(C-H 3) as	1021.2	161.7	$S_{13}(28)$, $S_{35}(16)$, $S_{37}(47)$
δ(C-H 2) s	1008.8	3.8	$S_{12}(35)$, $S_{34}(24)$, $S_{36}(24)$
ν(ring 1) as	928.2	39.3	$S_{7}(19)$, $S_{13}(11)$, $S_{15}(20)$, $S_{29}(17)$
δ(ring 1) s	906.7	2.2	$S_{14}(10)$, $S_{28}(41)$, $S_{30}(11)$
γ(C-H 3) as	898.8	1.4	$S_{52}(14)$, $S_{54}(89)$
γ(C-H 3) s	898.0	3.6	$S_{51}(12)$, $S_{53}(93)$
δ(ring 2) as	884.3	26.5	$S_{29}(38)$, $S_{31}(51)$
δ(ring 2) s	883.2	0.8	$S_{28}(25)$, $S_{30}(64)$
γ(C-H 2) as	853.1	<0.1	$S_{48}(10)$, $S_{52}(67)$, $S_{54}(22)$
γ(C-H 2) s	847.2	7.1	$S_{51}(83)$, $S_{53}(18)$
γ(C=O) as	809.0	27.1	$S_{48}(58)$, $S_{52}(14)$
γ(C-H 1) s	764.2	121.2	$S_{49}(86)$
γ(C-H 1) as	763.7	3.7	$S_{50}(87)$
δ(ring 1) as	758.2	243.6	$S_{23}(28)$, $S_{29}(11)$, $S_{31}(13)$, $S_{48}(12)$
ν(C-C)	687.8	2.4	$S_{24}(14)$, $S_{40}(25)$, $S_{42}(17)$, $S_{47}(19)$, $S_{1}(10)$
τ(ring 2) s	634.6	1.5	$S_{24}(24)$, $S_{40}(31)$
τ(ring 2) as	617.2	2.8	$S_{39}(12)$, $S_{41}(76)$
τ(ring 1) s	590.0	18.9	$S_{38}(87)$, $S_{40}(23)$
τ(ring 1) as	589.5	0.4	$S_{39}(95)$, $S_{41}(15)$
ω(ring) as	502.3	4.8	$S_{5}(32)$, $S_{23}(19)$, $S_{27}(13)$, $S_{29}(12)$
γ(C=O) s	466.1	14.7	$S_{4}(12)$, $S_{40}(17)$, $S_{47}(43)$
δ(C=O) s	375.5	2.5	$S_{1}(21)$, $S_{22}(55)$
ω(ring) s	280.6	0.2	$S_{1}(22)$, $S_{4}(18)$, $S_{26}(37)$
δ(C=O) as	278.8	21.5	$S_{23}(37)$, $S_{25}(24)$, $S_{27}(34)$
δ(CCC_α) s	193.0	0.6	$S_{24}(41)$, $S_{26}(38)$
γ(ring) as	171.2	0.1	$S_{43}(80)$
γ(ring) s	156.8	0.2	$S_{42}(67)$, $S_{47}(19)$
δ(CCC_α) as	126.0	2.5	$S_{25}(45)$, $S_{27}(26)$, $S_{46}(24)$
τ(C-C_α) as	74.0	1.5	$S_{25}(17)$, $S_{46}(77)$
τ(C-C_α) s	60.7	0.5	$S_{45}(97)$
τ(C-C)	21.7	6.5	$S_{44}(91)$

[a] Wavenumbers in cm^{-1}, calculated intensities in km mol^{-1}, ν, bond stretching, δ, bending, γ, rocking, ω,

wagging, τ, torsion, s, symmetric, as, asymmetric. See Table S1 for definition of internal coordinates and Figure 1 for atom numbering. [b] Scaled (0.978). [c] Only PED values greater than 10 % are given.

Table S4- Calculated [scaled, DFT(B3LYP)/6-311++G(d,p)] wavenumbers, IR intensities and Potential Energy Distributions (PED) for conformer **II** of α-furil.[a]

Approximate description	Wavenumber[b]	Intensity	PED[c]
ν(C-H 1)	3203.5	<0.1	$S_{16}(77)$, $S_{18}(21)$
ν(C-H 1)'	3202.9	0.2	$S_{17}(94)$
ν(C-H 2)'	3195.9	1.1	$S_{19}(94)$
ν(C-H 2)	3191.3	1.1	$S_{16}(21)$, $S_{18}(78)$
ν(C-H 3)'	3177.2	1.4	$S_{21}(97)$
ν(C-H 3)	3176.2	0.8	$S_{20}(99)$
ν(C=O)'	1692.3	265.3	$S_{3}(88)$
ν(C=O)	1673.2	302.6	$S_{2}(89)$
ν(ring 3)	1562.3	63.4	$S_{4}(10)$, $S_{10}(55)$
ν(ring 3)'	1554.9	54.7	$S_{11}(58)$, $S_{35}(12)$
ν(ring 2)'	1456.9	60.2	$S_{8}(22)$, $S_{9}(30)$, $S_{34}(10)$
ν(ring 2)	1450.2	181.6	$S_{8}(27)$, $S_{9}(29)$
ν(ring 4)'	1394.5	37.1	$S_{13}(40)$, $S_{33}(15)$, $S_{34}(10)$
ν(ring 4)	1390.2	19.5	$S_{12}(44)$, $S_{32}(14)$, $S_{35}(10)$
ν(C-C_α)	1298.5	21.8	$S_{1}(12)$, $S_{4}(24)$, $S_{22}(10)$
ν(C-C_α)'	1248.9	116.3	$S_{5}(26)$, $S_{6}(17)$, $S_{7}(14)$, $S_{32}(15)$
δ(C-H 1)'	1223.6	2.2	$S_{33}(66)$
δ(C-H 1)	1216.3	3.4	$S_{14}(25)$, $S_{32}(43)$
ν(ring 5)'	1163.1	4.5	$S_{9}(10)$, $S_{15}(49)$, $S_{34}(13)$
ν(ring 5)	1155.5	10.1	$S_{8}(23)$, $S_{14}(33)$, $S_{35}(13)$
ν(ring 1)	1105.9	24.7	$S_{6}(50)$, $S_{7}(19)$
δ(C-H 2)'	1088.4	26.5	$S_{7}(28)$, $S_{15}(13)$, $S_{35}(11)$
δ(C-H 3)	1058.9	3.7	$S_{1}(12)$, $S_{36}(27)$
δ(C-H 3)'	1018.5	83.1	$S_{13}(28)$, $S_{35}(11)$, $S_{37}(39)$
δ(C-H 2)	1008.9	40.5	$S_{12}(27)$, $S_{34}(21)$, $S_{36}(24)$
ν(ring 1)'	938.3	11.5	$S_{7}(11)$, $S_{15}(10)$, $S_{29}(16)$
δ(ring 1)	905.9	13.2	$S_{28}(40)$
γ(C-H 3)	894.0	1.7	$S_{53}(93)$
γ(C-H 3)'	888.9	1.4	$S_{54}(98)$
δ(ring 2)	884.1	4.8	$S_{28}(23)$, $S_{30}(56)$
δ(ring 2)'	883.3	14.9	$S_{29}(27)$, $S_{31}(56)$
γ(C-H 2)	849.2	7.4	$S_{48}(15)$, $S_{51}(57)$, $S_{53}(12)$
γ(C-H 2)'	840.7	6.5	$S_{52}(84)$
γ(C=O)'	811.9	51.3	$S_{23}(15)$, $S_{48}(36)$, $S_{51}(26)$
γ(C-H 1)'	760.8	76.7	$S_{50}(82)$
γ(C-H 1)	759.3	45.3	$S_{49}(81)$
δ(ring 1)'	738.3	224.2	$S_{23}(19)$, $S_{29}(12)$, $S_{48}(22)$
ν(C-C)	718.2	9.9	$S_{1}(10)$, $S_{24}(22)$, $S_{47}(29)$
τ(ring 2)'	626.0	5.4	$S_{24}(10)$, $S_{39}(11)$, $S_{41}(53)$
τ(ring 2)	618.5	2.1	$S_{40}(75)$
τ(ring 1)'	590.4	14.7	$S_{39}(85)$, $S_{41}(18)$
τ(ring 1)	588.9	2.3	$S_{38}(93)$, $S_{40}(11)$
δ(C=O)'	489.5	2.8	$S_{5}(29)$, $S_{23}(16)$, $S_{26}(13)$, $S_{29}(10)$
γ(C=O)	475.8	8.0	$S_{4}(23)$, $S_{47}(24)$
δ(C=O)	342.9	3.5	$S_{1}(29)$, $S_{22}(52)$
ω(ring)'	285.5	3.1	$S_{1}(13)$, $S_{4}(17)$, $S_{27}(32)$
ω(ring)	264.7	24.3	$S_{23}(36)$, $S_{25}(14)$, $S_{26}(33)$
γ(ring)	174.1	0.2	$S_{42}(63)$, $S_{43}(12)$
γ(ring)'	162.5	0.1	$S_{27}(16)$, $S_{43}(50)$
δ(CCC_α)	149.8	1.3	$S_{24}(34)$, $S_{27}(21)$, $S_{43}(11)$, $S_{44}(12)$, $S_{47}(12)$
δ(CCC_α)'	125.3	0.7	$S_{25}(36)$, $S_{26}(21)$, $S_{46}(37)$
τ(C-C_α)'	62.3	2.0	$S_{25}(21)$, $S_{46}(59)$
τ(C-C_α)	55.5	0.4	$S_{45}(82)$
τ(C-C)	25.7	5.0	$S_{44}(87)$

[a] Wavenumbers in cm^{-1}, calculated intensities in km mol^{-1}, ν, bond stretching, δ, bending, γ, rocking, ω,

wagging, τ, torsion. See Table S2 for definition of internal coordinates and Figure 1 for atom numbering. [b] Scaled (0.978). [c] Only PED values greater than 10 % are given.

Table S5- Calculated [scaled, DFT(B3LYP)/6-311++G(d,p)] wavenumbers, IR intensities and Potential Energy Distributions (PED) for conformer **III** of α-furil.[a]

Approximate description	Wavenumber[b]	Intensity	PED[c]
ν(C-H 1) as	3203.5	<0.1	$S_{17}(76)$, $S_{19}(22)$
ν(C-H 1) s	3203.5	<0.1	$S_{16}(76)$, $S_{18}(22)$
ν(C-H 2) s	3190.8	0.6	$S_{16}(22)$, $S_{18}(77)$
ν(C-H 2) as	3190.7	1.8	$S_{17}(22)$, $S_{19}(77)$
ν(C-H 3) s	3175.9	0.3	$S_{20}(99)$
ν(C-H 3) as	3175.9	1.2	$S_{21}(99)$
ν(C=O) s	1692.5	183.9	$S_{2}(90)$
ν(C=O) as	1683.1	345.9	$S_{3}(95)$
ν(ring 3) s	1568.2	36.6	$S_{4}(14)$, $S_{10}(62)$, $S_{34}(10)$
ν(ring 3) as	1562.8	146.3	$S_{5}(10)$, $S_{11}(66)$, $S_{35}(12)$
ν(ring 2) s	1459.1	90.3	$S_{4}(10)$, $S_{8}(47)$, $S_{34}(12)$
ν(ring 2) as	1452.6	185.9	$S_{9}(54)$, $S_{35}(11)$
ν(ring 4) s	1388.7	4.5	$S_{12}(44)$, $S_{32}(15)$, $S_{34}(18)$, $S_{36}(11)$
ν(ring 4) as	1387.5	17.8	$S_{13}(44)$, $S_{33}(14)$, $S_{35}(18)$, $S_{37}(12)$
ν(C-$C_α$) s	1286.3	2.6	$S_{1}(12)$, $S_{4}(23)$, $S_{6}(11)$, $S_{8}(16)$, $S_{32}(18)$
ν(C-$C_α$) as	1243.1	123.1	$S_{5}(21)$, $S_{7}(28)$, $S_{33}(34)$
δ(C-H 1) s	1216.5	3.0	$S_{14}(23)$, $S_{32}(48)$
δ(C-H 1) as	1211.2	10.1	$S_{15}(28)$, $S_{33}(32)$
ν(ring 5) s	1155.4	0.1	$S_{8}(22)$, $S_{14}(35)$, $S_{34}(18)$, $S_{36}(13)$
ν(ring 5) as	1153.6	25.3	$S_{9}(24)$, $S_{15}(33)$, $S_{35}(18)$, $S_{37}(13)$
ν(ring 1) s	1109.5	19.6	$S_{6}(71)$
ν(ring 1) as	1088.3	33.2	$S_{7}(40)$, $S_{15}(15)$, $S_{35}(10)$, $S_{37}(11)$
δ(C-H 3) s	1052.4	0.1	$S_{1}(13)$, $S_{10}(14)$, $S_{14}(15)$, $S_{36}(24)$
δ(C-H 3) as	1011.8	104.0	$S_{13}(31)$, $S_{35}(18)$, $S_{37}(45)$
δ(C-H 2) s	1008.2	1.5	$S_{12}(30)$, $S_{34}(28)$, $S_{36}(30)$
δ(C-H 2) as	946.6	9.4	$S_{7}(15)$, $S_{11}(10)$, $S_{15}(15)$, $S_{29}(15)$, $S_{35}(11)$
δ(ring 1) s	900.5	0.1	$S_{14}(12)$, $S_{28}(33)$, $S_{30}(21)$
γ(C-H 3) as	892.7	1.3	$S_{52}(11)$, $S_{54}(95)$
γ(C-H 3) s	891.9	1.4	$S_{51}(10)$, $S_{53}(97)$
δ(ring 2) as	883.4	12.7	$S_{29}(28)$, $S_{31}(61)$
δ(ring 2) s	883.1	1.3	$S_{28}(36)$, $S_{30}(53)$
γ(C-H 2) as	847.4	20.5	$S_{48}(13)$, $S_{52}(54)$, $S_{54}(18)$
γ(C-H 2) s	840.4	4.4	$S_{51}(78)$, $S_{53}(16)$
γ(C=O) as	813.4	76.4	$S_{23}(20)$, $S_{29}(12)$, $S_{48}(25)$, $S_{52}(27)$
γ(C-H 1) s	758.3	74.1	$S_{49}(84)$, $S_{51}(12)$
γ(C-H 1) as	757.8	45.3	$S_{50}(86)$, $S_{52}(11)$
ν(C-C)	739.8	16.3	$S_{1}(10)$, $S_{24}(22)$, $S_{47}(38)$
δ(ring 1) as	717.3	203.6	$S_{23}(13)$, $S_{25}(11)$, $S_{29}(11)$, $S_{48}(27)$
τ(ring 2) as	619.1	3.6	$S_{41}(82)$
τ(ring 2) s	618.9	4.9	$S_{40}(79)$
τ(ring 1) s	590.8	9.9	$S_{38}(95)$, $S_{40}(12)$
τ(ring 1) as	589.3	3.7	$S_{39}(99)$
γ(C=O) s	483.1	4.1	$S_{4}(30)$, $S_{47}(16)$
δ(C=O) as	481.9	1.4	$S_{5}(29)$, $S_{23}(15)$, $S_{27}(13)$
δ(C=O) s	329.8	2.9	$S_{1}(39)$, $S_{22}(43)$
ω(ring) s	283.0	2.4	$S_{4}(13)$, $S_{22}(17)$, $S_{26}(32)$
ω(ring) as	261.8	30.4	$S_{23}(35)$, $S_{25}(11)$, $S_{27}(31)$
γ(ring) as	173.9	0.3	$S_{43}(73)$
γ(ring) s	167.6	0.1	$S_{42}(75)$
δ(CC$C_α$) s	126.2	0.9	$S_{24}(44)$, $S_{26}(34)$
δ(CC$C_α$) as	122.1	0.1	$S_{25}(36)$, $S_{27}(24)$, $S_{46}(36)$
τ(C-$C_α$) s	58.2	0.6	$S_{45}(86)$
τ(C-$C_α$) as	56.3	2.2	$S_{25}(21)$, $S_{46}(60)$
τ(C-C)	21.8	3.6	$S_{44}(90)$

[a] Wavenumbers in cm^{-1}, calculated intensities in km mol^{-1}, ν, bond stretching, δ, bending, γ, rocking, ω,

wagging, τ, torsion, s, symmetric, as, asymmetric. See Table S1 for definition of internal coordinates and Figure 1 for atom numbering. [b] Scaled (0.978). [c] Only PED values greater than 10 % are given.