

Bottom-up approach to making larger hydrocarbon molecules capable of optical cycling

In the format provided by the
authors and unedited

Supplementary Information

Bottom-Up Approach to Larger Hydrocarbon Molecules Capable of Optical Cycling

TABLE OF CONTENTS

Synthesis of ligand precursors	p. 15
Theoretical methods	p. 16
Error analysis of VBRs	p. 17
Functionalization of diamond surfaces	p. 18
Supplementary Tables	p. 19
Supplementary Figures of vibrational displacements computation and characterization of chemicals	p. 34

I. SYNTHESIS OF LIGAND PRECURSORS

4-(1-diamantyl)-phenol (Supplementary Fig. 1)

1-bromodiamantane: 1-bromodiamantane was prepared using similar conditions published by Gund *et al.*[72] After working up the reaction, the solvent was removed under vacuum, and the resulting residue was concentrated thrice from hexanes to afford a yellow solid. The solid was dissolved in 9/1 hexane/DCM and was passed through a silica plug to afford of white crystalline solid. Yield: 1.34g (95%). Characterization data matches that of literature.[72] $R_f = 0.77$ (silica, hexanes) ^1H NMR (400 MHz, CDCl_3): δ 2.47–2.42 (m, 4H), 2.13 (m, 2H), 2.06 (m, 2H), 1.96–1.91 (m, 1H), 1.82–1.77 (m, 1H), 1.77–1.73 (m, 2H), 1.72 (m, 4H), 1.68 (m, 1H), 1.61 (m, 1H), 1.58 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 79.47, 51.69, 46.21, 41.58, 38.67, 37.31, 36.55, 34.86, 31.52, 25.25.

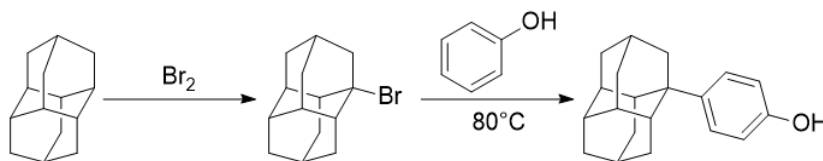
4-(1-diamantyl)-phenol: 1-bromodiamantane (100 mg, 0.37 mmol, 1 eq.) and phenol (282 mg, 3.0 mmol, 8.1 eq.) were combined and purged thrice with argon. The solids were heated at 80 °C for 40 min, at which point the reaction mixture dried up to afford a pink solid at the bottom of the flask. The solid was suspended in hot water, filtered, and washed thrice with hot water. The resulting solid was dissolved in ethyl acetate and dried over Na_2SO_4 . The solvent was removed under vacuum, and the crude mixture was purified by column chromatography on silica (10:1 hexanes/ethyl acetate) to afford 60 mg of a white crystalline solid. Yield: 58%. mp: 211–213 °C; TLC (hexanes:EtOAc, 10:1):

$R_f = 0.17$; ^1H NMR (400 MHz, CDCl_3): δ 7.23–7.18 (m, 2H), 6.82–6.76 (m, 2H), 4.59 (s, 1H), 2.32–2.26 (m, 2H), 2.00–1.95 (m, 2H), 1.89–1.84 (m, 2H), 1.84–1.81 (m, 1H), 1.81–1.75 (m, 5H), 1.69–1.63 (m, 3H), 1.56–1.50 (m, 2H), 1.45–1.37 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 152.71, 141.82, 126.55, 115.10, 49.72, 41.46, 38.50, 38.47, 38.33, 38.13, 37.17, 33.55, 28.12, 26.06; IR (neat): $\nu_{\text{max}} = 3283, 2907, 2886, 2849, 1597, 1511, 1439, 1248, 808\text{ cm}^{-1}$; HRMS (DART): m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{O}^+$ $[\text{M}+\text{H}]^+ 279.17434$, found 279.17439.

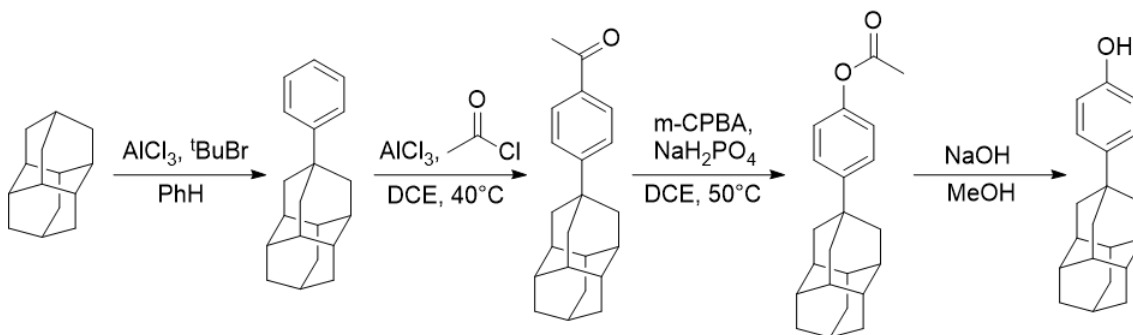
4-(4-diamantyl)-phenol (Supplementary Fig. 2)

4-phenyldiamantane: Triturated diamantane (1.88 g, 10 mmol, 1 eq.) and aluminum chloride (100 mg, 0.08 mmol, 0.008 eq.) were suspended in 50 mL benzene, and tert-butyl bromide (0.66 mL, 5.5 mmol, 0.55 eq.) was added slowly to the mixture. Gases expelled were quenched with sat. NaHCO_3 . After stirring for 30 min, a second portion of tert-butyl bromide (0.66 mL, 5.5 mmol, 0.55 eq.) was added, and the reaction was allowed to stir for an additional 30 min before being diluted with 50 mL diethyl ether. The mixture was washed sequentially with 0.5 M HCl, water, and brine, then dried over Na_2SO_4 . The filtrate was concentrated under vacuum, and the crude mixture was purified by silica gel chromatography (hexanes) to afford the crystalline product. Yield: 1.3 g (50%). Characterization data matches that of literature.[73] mp: 145–147 °C; TLC (hexanes): $R_f = 0.68$; ^1H NMR (400 MHz, CDCl_3): δ 7.45–7.38 (m, 2H), 7.37–7.31 (m, 2H), 7.23–7.17 (m, 1H), 1.99–1.93 (m, 3H), 1.93–1.89 (m, 6H), 1.89–1.83 (m, 1H), 1.83–1.77 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 150.71, 128.05, 125.47, 125.08, 43.97, 38.27, 37.78, 36.74, 34.26, 25.76; IR (neat): $\nu_{\text{max}} = 2906, 2882, 2848, 1493, 1459, 1442, 756, 696\text{ cm}^{-1}$.

4-(4-diamantyl)acetophenone: Acetyl chloride (72 μL , 1 mmol, 2 eq.) was added slowly to a stirring suspension of aluminum chloride (100 mg, 0.75 mmol, 1.5 eq.) in 2 mL DCE at room temperature. 4-phenyldiamantane (132 mg, 0.5 mmol) in 0.5 mL CHCl_3 was added dropwise to the resulting yellow solution and then the reaction was heated at 40 °C for 10 min. The reaction was then cooled down to room temperature and added into a stirring slurry of conc. HCl (1 mL) and ice (20 mL). The mixture was diluted with 20 mL CHCl_3 , and the layers were separated. The organic layer was washed with sat. NaHCO_3 , water, brine, and dried over Na_2SO_4 . Solvent was removed under vacuum and the crude material was purified on silica (95/5 hexane/ethyl acetate) to afford product. Yield: 100 mg (66%). mp: 195–203 °C; TLC (hexanes:EtOAc, 10:1 v/v): $R_f = 0.35$; ^1H NMR (400 MHz, CDCl_3): δ 7.94–7.88 (m, 2H), 7.50–7.44 (m, 2H), 2.58 (s, 3H), 1.97–1.91 (m, 3H), 1.91–1.87 (m, 6H), 1.86–1.82 (m, 1H), 1.81–1.76 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 197.87, 156.43, 134.63, 128.26, 125.35, 43.69, 38.07, 37.68, 36.62, 34.84, 26.52, 25.65; IR (neat):



Supplementary Fig. 1. Synthesis procedure of 4-(1-diamantyl)-phenol.



Supplementary Fig. 2. Synthesis procedure of 4-(4-diamantyl)-phenol.

1002 $\nu_{\max} = 2911, 2884, 2848, 1679, 1605, 1268, 1048 \text{ cm}^{-1}$;
 1003 HRMS (DART): m/z calcd. for $\text{C}_{22}\text{H}_{27}\text{O}^+ [\text{M}+\text{H}]^+$
 1004 307.20564; found, 307.20560.

1005 **4-(4-diamantyl)phenylacetate:** Under open at-
 1006 mosphere, 4-(4-diamantyl)acetophenone (176 mg,
 1007 0.58 mmol, 1 eq.), m-CPBA (296 mg, 1.73 mmol, 3 eq.),
 1008 and NaH_2PO_4 (276 mg, 2.3 mmol, 4 eq.) were suspended
 1009 in 4 mL DCE. The mixture was stirred at 50 °C for
 1010 6 h, at which point TLC (hexanes:EtOAc, 95:5) showed
 1011 complete consumption of the starting material. The
 1012 reaction mixture was cooled to room temperature
 1013 and filtered. The filtrate was diluted with DCM and
 1014 washed sequentially with saturated $\text{Na}_2\text{S}_2\text{O}_3$, saturated
 1015 NaHCO_3 , water, and brine, then dried over Na_2SO_4 .
 1016 The solvent was removed under vacuum to afford a
 1017 yellow solid. The crude material was purified by silica gel
 1018 chromatography (hexanes:EtOAc, 9:1) to give a white
 1019 crystalline solid. Yield: 169 mg (90%). mp: 137–140 °C;
 1020 TLC (hexanes:EtOAc, 10:1): $R_f = 0.40$; ^1H NMR (400
 1021 MHz, CDCl_3): δ 7.40–7.33 (m, 2H), 7.05–6.98 (m, 2H),
 1022 2.29 (s, 3H), 1.91 (m, 3H), 1.89–1.84 (m, 6H), 1.84–1.80
 1023 (m, 1H), 1.79–1.73 (m, 5H); ^{13}C NMR (101 MHz,
 1024 CDCl_3): δ 169.70, 148.34, 148.27, 126.16, 120.85, 44.04,
 1025 38.22, 37.74, 36.68, 34.10, 25.73, 21.15; IR (neat): $\nu_{\max}$
 1026 = 2908, 2872, 2848, 1763, 1508, 1367, 1208, 1171 cm^{-1} ;
 1027 HRMS (DART): m/z calcd. for $\text{C}_{22}\text{H}_{25}\text{O}_2^+ [\text{M}+\text{H}]^+$
 1028 321.18491, found 321.18491.

1029 **4-(4-diamantyl)phenol:** Under an open atmosphere,
 1030 4-(4-diamantyl)phenyl acetate (110 mg, 0.34 mmol, 1 eq.)
 1031 was suspended in 1 mL MeOH. NaOH (34 mg, 0.85 mmol,
 1032 2.5 eq.) in 50 μL water was added to the suspension, and
 1033 the reaction was stirred for 6 h at room temperature. The
 1034 solvent was removed under vacuum, and the residue was
 1035 suspended in 10 mL water and acidified with 6 M HCl.

1036 The solid was filtered, washed with water, extracted with
 1037 ethyl acetate, and the organic layer was washed with
 1038 brine. The solvent was removed under vacuum, and the
 1039 resulting solid was passed through a silica plug using a
 1040 4:1 hexanes:acetone mixture to afford a white solid in
 1041 quantitative yield. mp: sublimes ;220 °C; TLC (hex-
 1042 anes:EtOAc, 10:1): $R_f = 0.15$; ^1H NMR (400 MHz,
 1043 CDCl_3): δ 7.28–7.22 (m, 2H), 6.81–6.76 (m, 2H), 4.66
 1044 (s, 1H), 1.93–1.89 (m, 3H), 1.86–1.82 (m, 7H), 1.79–1.76
 1045 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 153.18, 143.26,
 1046 126.25, 114.79, 44.20, 38.31, 37.78, 36.73, 33.66, 25.77;
 1047 IR (neat): $\nu_{\max} = 3272, 2906, 2877, 2847, 1704, 1513,$
 1048 1439, 1244, 826 cm^{-1} ; HRMS (DART): m/z calcd. for
 1049 $\text{C}_{20}\text{H}_{23}\text{O}^+ [\text{M}+\text{H}]^+$ 279.17434, found 279.17434.

1050 II. THEORETICAL METHODS

1051 Multi-reference calculations of the vertical excitation
 1052 energies (VEEs) were performed using the Molpro soft-
 1053 ware package [59, 74, 75]. Supplementary Table 1 shows
 1054 computed VEEs for several systems investigated in this
 1055 work at the NEVPT2(9,10) level of theory with the same
 1056 basis set as the DFT/TDDFT calculations.

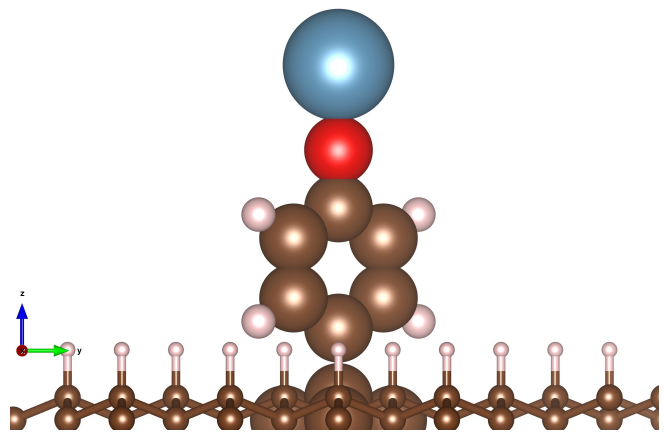
1057 Density Functional Theory calculations on periodic
 1058 structures (*i.e.* diamond surfaces) were performed with
 1059 VASP[76], version 5.4.4, using the PAW[77]-PBE[78]
 1060 method with plane-wave cutoff of 600 eV and a spin-
 1061 unrestricted (UKS) formalism. The bulk unit cell of di-
 1062 amond was optimized with a 8-8-8 k -point grid until the
 1063 components of the forces on all atoms were less than 0.01
 1064 eV/Å. A (111) surface was constructed with an in-plane
 1065 lattice parameter of 10 Å and a thickness of 3 atomic lay-
 1066 ers, and terminated with hydrogen atoms at the upper

and lower faces. The hydrogen positions of this slab were optimized, keeping the carbon atoms fixed, with a 2-1-2 k -point grid (a and c are the in-plane lattice vectors). One hydrogen atom was then replaced by a phenyl group and the structure was reoptimized, with the phenyl group and 1 carbon atom of the surface relaxed and all other atoms fixed. Finally, the uppermost hydrogen atom of the phenyl group was replaced by OCa and the optimization was repeated. The optimized C-O bond length was 1.344 Å and the optimized O-Ca bond length was 1.980 Å. Charge densities for individual orbitals were evaluated using pymatgen and visualised with VESTA. Phonons were computed for the PhOCa group and the nearest 4 C atoms of the surface at the Γ point with the finite differences method, and vibrational modes were visualised using VaspVib2XSF and VESTA.

Highly accurate wavefunction-based electronic structure calculations, particularly of excited states, are generally difficult for periodic systems due to the high scaling of the computational cost of such methods with system size. This is particularly true for defects and adsorbed molecules, of interest for optical cycling and other quantum information applications, due to large supercells being required to avoid artificial interactions between periodic images. To circumvent this, some of the authors have devised an embedding approach based on the ‘aperiodic defect model’ [58] in which a pristine non-defective crystal is used for the calculation of the embedding field, while the atoms of a fragment, subjected to this field, can be afterward manipulated to create the defect. The fragment is then treated using any appropriate quantum chemical theory including multireference.

To mimic the diamond surface we employed a pristine diamond (111) slab, 5 layers thick and terminated with hydrogen atoms (with a DFT-computed C-H bond length of 1.11 Angstroms). The defect was created by replacing one surface hydrogen with the calcium phenoxide moiety (Supplementary Fig. 3). Because forces and geometry optimizations are not yet available in the aperiodic defect model within the Cryscor code [79, 80], we used the aforementioned DFT bond lengths and angles computed in VASP. Within the aperiodic defect approach, [58] the fragment Hamiltonian, which includes the altered geometry of the defect and the Hartree-Fock embedding field from the pristine crystalline environment, was passed to a molecular program (in this case Molpro [74] or pySCF [81]) using the FCIDUMP file [82] interface, for the quantum chemical treatment. The def2-TZVPPD basis was used for Ca and O, and pob-VTZP-rev2[83] for C and H. Both used the density fitting basis set optimized for MP2/cc-pVTZ.[84]

We computed vertical excitation energies of the embedded fragment, consisting of CaOPh and its four closest diamond carbon atoms, at the second-order N-electron valence perturbation theory (NEVPT2)[59] level. The reference states were calculated using the state averaged complete active space self-consistent field (SA-CASSCF) [75] with an active space of 9 electrons in 10 orbitals.



Supplementary Fig. 3. Visualization of the embedded fragment and the nearby atoms of its periodic surroundings. Space-filling atoms are part of the embedded fragment, while ball-and-stick atoms are part of its environment. Carbon atoms are in brown, hydrogen atoms in white, oxygen atoms in red, and calcium atoms in blue.

The NEVPT2 VEEs for the lowest two states are 1.926 eV and 1.947 eV, respectively. These values also agree up to several meV with unrestricted EOM-CCSD, calculated with pySCF [81] via the same FCIDUMP interface: 1.929 eV and 1.950 eV.

III. ERROR ANALYSIS OF VBRS

All observed peaks in DLIF spectra are fitted with the Voigt function in PGopher, with line intensities estimated from the areas under these fitted curves. The statistical uncertainties of the fitting parameters are estimated with the covariance matrix. The Jacobian conversion from wavelength and frequency is performed as a correction to the calculation of line intensities [85]. In addition, as the spectra were taken in a wide wavelength range (610-750nm) while the ICCD sensor quantum efficiency (QE) curve, > 40% in range of 600-615nm, drops to below 20% as wavelength > 710nm (the QE data was provided by the vendor, Oxford Instrument - Andor Technology), the scaling with the inverse of quantum efficiency is therefore applied to the line intensity calculation. The two corrections, denoted as Δ_J and Δ_{QE} , respectively, are calculated from the differences between the intensity ratios before and after the scaling. The corrections can be larger than the statistical uncertainties, hence, we listed these correction terms for the diagonal VBRs in the Supplementary table 14, for comparison.

The unobserved peaks which contribute to the VBRs can lead to system uncertainties [42], as the true VBRs depend on contributions of all possible decay pathways. Due to the limitations of the measurement sensitivity and the detection window, only a few vibrational decays

have been observed for each transition. Compared to a complete description of vibrational decays obtained from calculated FCFs, all unobserved vibrational decays are therefore a source of the systematic uncertainty, which is estimated by [42]:

$$S'_0 = \frac{S_0^{(c)}}{\sum_{i=0}^p S_i^{(c)} + \sum_{i=p+1}^N \frac{T_i}{C}}, \quad (1)$$

where p is the number of observed vibrational decays, T_i is the theoretical VBRs, $C = \frac{1}{p+1} \sum_{i=0}^p \frac{T_i}{S_i^{(c)}}$ is a scaling factor, and $S_i^{(c)} = S_i + \Delta_{J,i} + \Delta_{QE,i}$ denotes the intensity ratios with corrections. For a straight forward comparison between the scaled VBRs, S'_i , and the intensity ratios, $S_i^{(c)}$, we denote their differences as $\delta_{u,i} = S'_i - S_i^{(c)}$. The values of δ_u for the diagonal peaks can be found in Supplementary Table 14. As $S_0^{(c)}$ is always greater than S'_0 , it is regarded as the estimates for the upper bound of the actual diagonal VBRs, and S'_0 is the reported value for the diagonal VBRs in this work. To estimate the lower bound of the VBRs, S''_0 , we choose a smaller scaling factor $C' = C - \delta_C$ to replace C in Eq. 1, where δ_C is the uncertainty of the scaling factor:

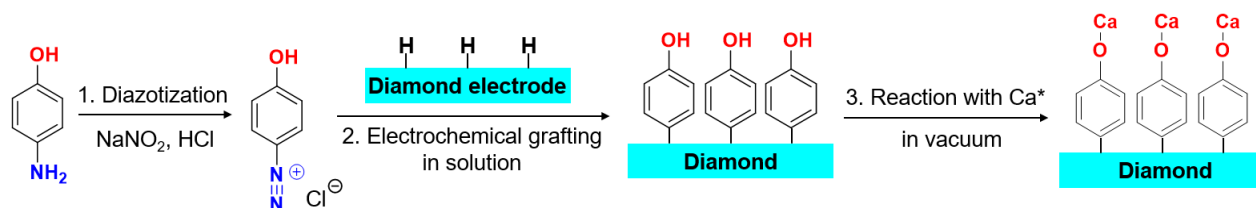
$$\begin{aligned} \delta_C &= \sqrt{\sum_{i=0}^p \left(\frac{\partial C}{\partial S_i^{(c)}} \delta S_i^{(c)} \right)^2 + \left(\frac{\partial C}{\partial p} \times 1 \right)^2} \\ &\approx \sqrt{\sum_{i=0}^p T_i^2 \left(\frac{\delta S_i^{(c)}}{(p+1)S_i^{(c)}} \right)^2 + \left(\frac{1-C}{p+2} \right)^2}, \end{aligned} \quad (2)$$

here $\delta S_i^{(c)}$ is the uncertainty of $S_i^{(c)}$. In the last step, we assumed that $\frac{T_{p+1}}{S_{p+1}^{(c)}} \approx 1$ and calculated the $\frac{\partial C}{\partial p}$ from a direct assumption that $\frac{\partial C}{\partial p} \approx \frac{1}{p+2} \sum_{i=0}^{p+1} \frac{T_i}{S_i^{(c)}} - \frac{1}{p+1} \sum_{i=0}^p \frac{T_i}{S_i^{(c)}} \approx \frac{p+1}{p+2} C + \frac{1}{p+2} - C$.

IV. FUNCTIONALIZATION OF DIAMOND SURFACES

MOPh-diamond can be synthesized through chemical functionalization on hydrogen-terminated diamond surfaces. [63, 64]. As shown in Supplementary Fig. 4, three procedures will be used to produce (CaOPh)_n-diamond complex. A crucial step, labeled as Step 2, involves chemically bonding phenol ligands onto the diamond surface, typically terminated with hydrogen atoms. This bonding process can be achieved by electrochemical grafting of freshly grown diamonds or boron-doped diamonds[86] with phenol-based diaonium salt. The diaonium salt can be synthesized via diazotization of 4-aminophenol in Step 1. Upon formation of the phenol layers on diamond surfaces, metastable calcium atoms, generated either from a hot oven or laser ablation, are introduced to react

with the phenol-diamond complex in a vacuum environment, leading to the formation of (CaOPh)_n-diamond. Using various chemical treatments, the terminated hydrogen atoms on the diamond surface can be substituted with oxygen, nitrogen and sulfur atoms. This allows for the functionalization of the diamond surface with a wide range of bond types and ligands to suit specific applications.



Supplementary Fig. 4. Procedures to synthesize (CaOPh)_n-diamond from 4-aminophenol and H-terminated diamond surface. A boron doped diamond with lower electrical resistivity can be used to improve the efficiency of the electrochemical diazonium grafting process.

Supplementary Table 1: Vertical excitation energies for several molecules calculated using NEVPT2(9,10) level of theory reported in eV.

Molecules	X $\rightarrow$ A	X $\rightarrow$ B
CaOPh-CH ₃	1.7639	1.7878
CaOPh-C(CH ₃) ₃	1.7639	1.7870
SrOPh-CH ₃	1.6832	1.7004

Supplementary Table 2: Calculated harmonic frequencies of all Ca-species. A full list of vibrational modes of CaOPh-CH₃ and the lowest fifty modes of all other molecules are presented. All vibrational modes are labeled with increasing frequency.

CaOPh-CH ₃		CaOPh-C(CH ₃) ₃		CaOPh-Ad		CaOPh-1diA		CaOPh-4diA	
Modes	Freq.	Modes	Freq.	Modes	Freq.	Modes	Freq.	Modes	Freq.
ν_1	37	ν_1	40	ν_1	30	ν_1	20	ν_1	27
ν_2	49	ν_2	50	ν_2	43	ν_2	31	ν_2	39
ν_3	56	ν_3	54	ν_3	54	ν_3	45	ν_3	52
ν_4	161	ν_4	113	ν_4	89	ν_4	78	ν_4	81
ν_5	295	ν_5	209	ν_5	129	ν_5	130	ν_5	106
ν_6	319	ν_6	228	ν_6	200	ν_6	180	ν_6	183
ν_7	341	ν_7	241	ν_7	206	ν_7	195	ν_7	189
ν_8	429	ν_8	265	ν_8	278	ν_8	248	ν_8	257
ν_9	460	ν_9	285	ν_9	317	ν_9	279	ν_9	276
ν_{10}	528	ν_{10}	328	ν_{10}	325	ν_{10}	314	ν_{10}	301
ν_{11}	561	ν_{11}	337	ν_{11}	374	ν_{11}	321	ν_{11}	340
ν_{12}	657	ν_{12}	369	ν_{12}	389	ν_{12}	365	ν_{12}	362
ν_{13}	733	ν_{13}	396	ν_{13}	408	ν_{13}	392	ν_{13}	372
ν_{14}	798	ν_{14}	430	ν_{14}	418	ν_{14}	395	ν_{14}	400
ν_{15}	832	ν_{15}	433	ν_{15}	426	ν_{15}	411	ν_{15}	403
ν_{16}	850	ν_{16}	455	ν_{16}	433	ν_{16}	421	ν_{16}	411
ν_{17}	908	ν_{17}	487	ν_{17}	449	ν_{17}	424	ν_{17}	416
ν_{18}	957	ν_{18}	557	ν_{18}	462	ν_{18}	427	ν_{18}	416
ν_{19}	982	ν_{19}	564	ν_{19}	476	ν_{19}	440	ν_{19}	431
ν_{20}	1004	ν_{20}	657	ν_{20}	479	ν_{20}	443	ν_{20}	449
ν_{21}	1031	ν_{21}	718	ν_{21}	559	ν_{21}	452	ν_{21}	463
ν_{22}	1059	ν_{22}	764	ν_{22}	643	ν_{22}	476	ν_{22}	483
ν_{23}	1129	ν_{23}	831	ν_{23}	651	ν_{23}	481	ν_{23}	526
ν_{24}	1191	ν_{24}	861	ν_{24}	659	ν_{24}	563	ν_{24}	559
ν_{25}	1247	ν_{25}	864	ν_{25}	664	ν_{25}	627	ν_{25}	640
ν_{26}	1314	ν_{26}	912	ν_{26}	720	ν_{26}	633	ν_{26}	640
ν_{27}	1341	ν_{27}	941	ν_{27}	759	ν_{27}	643	ν_{27}	647
ν_{28}	1349	ν_{28}	953	ν_{28}	795	ν_{28}	646	ν_{28}	651
ν_{29}	1406	ν_{29}	958	ν_{29}	830	ν_{29}	664	ν_{29}	662
ν_{30}	1452	ν_{30}	968	ν_{30}	836	ν_{30}	691	ν_{30}	666
ν_{31}	1480	ν_{31}	984	ν_{31}	839	ν_{31}	706	ν_{31}	726
ν_{32}	1490	ν_{32}	1029	ν_{32}	865	ν_{32}	762	ν_{32}	730
ν_{33}	1557	ν_{33}	1044	ν_{33}	880	ν_{33}	763	ν_{33}	761
ν_{34}	1625	ν_{34}	1051	ν_{34}	895	ν_{34}	827	ν_{34}	819
ν_{35}	1677	ν_{35}	1134	ν_{35}	898	ν_{35}	829	ν_{35}	819
ν_{36}	3035	ν_{36}	1143	ν_{36}	903	ν_{36}	833	ν_{36}	825
ν_{37}	3096	ν_{37}	1199	ν_{37}	912	ν_{37}	839	ν_{37}	831
ν_{38}	3124	ν_{38}	1238	ν_{38}	954	ν_{38}	858	ν_{38}	861
ν_{39}	3167	ν_{39}	1239	ν_{39}	966	ν_{39}	867	ν_{39}	876
ν_{40}	3167	ν_{40}	1304	ν_{40}	976	ν_{40}	875	ν_{40}	889
ν_{41}	3192	ν_{41}	1319	ν_{41}	983	ν_{41}	909	ν_{41}	907
ν_{42}	3195	ν_{42}	1339	ν_{42}	998	ν_{42}	910	ν_{42}	912
		ν_{43}	1353	ν_{43}	999	ν_{43}	915	ν_{43}	921
		ν_{44}	1390	ν_{44}	1002	ν_{44}	931	ν_{44}	923
		ν_{45}	1391	ν_{45}	1028	ν_{45}	955	ν_{45}	955
		ν_{46}	1422	ν_{46}	1059	ν_{46}	957	ν_{46}	956
		ν_{47}	1455	ν_{47}	1073	ν_{47}	963	ν_{47}	961
		ν_{48}	1472	ν_{48}	1074	ν_{48}	972	ν_{48}	982
		ν_{49}	1477	ν_{49}	1075	ν_{49}	981	ν_{49}	985
		ν_{50}	1482	ν_{50}	1127	ν_{50}	987	ν_{50}	987

Supplementary Table 3: Calculated harmonic frequencies of all Sr-species. A full list of vibrational modes of SrOPh-CH₃ and the lowest fifty modes of all other molecules are presented. All vibrational modes are labeled with increasing frequency.

SrOPh-CH3		SrOPh-C(CH3)3		SrOPh-Ad		SrOPh-1diA		SrOPh-4diA	
Modes	Freq.	Modes	Freq.	Modes	Freq.	Modes	Freq.	Modes	Freq.
ν_1	36	ν_1	33	ν_1	26	ν_1	20	ν_1	23
ν_2	43	ν_2	44	ν_2	36	ν_2	26	ν_2	33
ν_3	51	ν_3	54	ν_3	54	ν_3	37	ν_3	51
ν_4	158	ν_4	109	ν_4	86	ν_4	76	ν_4	77
ν_5	227	ν_5	189	ν_5	128	ν_5	130	ν_5	105
ν_6	318	ν_6	212	ν_6	160	ν_6	149	ν_6	148
ν_7	337	ν_7	226	ν_7	204	ν_7	189	ν_7	187
ν_8	428	ν_8	264	ν_8	278	ν_8	248	ν_8	257
ν_9	460	ν_9	284	ν_9	316	ν_9	279	ν_9	276
ν_{10}	526	ν_{10}	325	ν_{10}	325	ν_{10}	300	ν_{10}	300
ν_{11}	539	ν_{11}	337	ν_{11}	333	ν_{11}	320	ν_{11}	318
ν_{12}	657	ν_{12}	368	ν_{12}	388	ν_{12}	337	ν_{12}	340
ν_{13}	731	ν_{13}	372	ν_{13}	407	ν_{13}	390	ν_{13}	371
ν_{14}	792	ν_{14}	429	ν_{14}	418	ν_{14}	395	ν_{14}	399
ν_{15}	831	ν_{15}	433	ν_{15}	425	ν_{15}	411	ν_{15}	403
ν_{16}	850	ν_{16}	453	ν_{16}	432	ν_{16}	419	ν_{16}	410
ν_{17}	897	ν_{17}	487	ν_{17}	449	ν_{17}	424	ν_{17}	416
ν_{18}	954	ν_{18}	544	ν_{18}	461	ν_{18}	427	ν_{18}	416
ν_{19}	979	ν_{19}	563	ν_{19}	472	ν_{19}	438	ν_{19}	430
ν_{20}	1003	ν_{20}	657	ν_{20}	479	ν_{20}	443	ν_{20}	449
ν_{21}	1030	ν_{21}	709	ν_{21}	558	ν_{21}	447	ν_{21}	462
ν_{22}	1059	ν_{22}	761	ν_{22}	630	ν_{22}	476	ν_{22}	483
ν_{23}	1128	ν_{23}	830	ν_{23}	651	ν_{23}	480	ν_{23}	518
ν_{24}	1190	ν_{24}	859	ν_{24}	659	ν_{24}	560	ν_{24}	558
ν_{25}	1247	ν_{25}	863	ν_{25}	664	ν_{25}	622	ν_{25}	640
ν_{26}	1312	ν_{26}	901	ν_{26}	716	ν_{26}	632	ν_{26}	640
ν_{27}	1340	ν_{27}	940	ν_{27}	758	ν_{27}	636	ν_{27}	648
ν_{28}	1345	ν_{28}	953	ν_{28}	795	ν_{28}	646	ν_{28}	651
ν_{29}	1406	ν_{29}	957	ν_{29}	829	ν_{29}	664	ν_{29}	655
ν_{30}	1452	ν_{30}	965	ν_{30}	836	ν_{30}	688	ν_{30}	662
ν_{31}	1480	ν_{31}	982	ν_{31}	839	ν_{31}	705	ν_{31}	725
ν_{32}	1490	ν_{32}	1028	ν_{32}	864	ν_{32}	759	ν_{32}	728
ν_{33}	1555	ν_{33}	1043	ν_{33}	877	ν_{33}	761	ν_{33}	760
ν_{34}	1623	ν_{34}	1051	ν_{34}	895	ν_{34}	827	ν_{34}	819
ν_{35}	1677	ν_{35}	1133	ν_{35}	898	ν_{35}	828	ν_{35}	819
ν_{36}	3033	ν_{36}	1143	ν_{36}	901	ν_{36}	833	ν_{36}	825
ν_{37}	3095	ν_{37}	1198	ν_{37}	903	ν_{37}	838	ν_{37}	830
ν_{38}	3123	ν_{38}	1238	ν_{38}	953	ν_{38}	857	ν_{38}	861
ν_{39}	3165	ν_{39}	1239	ν_{39}	966	ν_{39}	864	ν_{39}	876
ν_{40}	3165	ν_{40}	1304	ν_{40}	975	ν_{40}	875	ν_{40}	885
ν_{41}	3190	ν_{41}	1318	ν_{41}	981	ν_{41}	899	ν_{41}	904
ν_{42}	3193	ν_{42}	1338	ν_{42}	998	ν_{42}	909	ν_{42}	907
		ν_{43}	1350	ν_{43}	999	ν_{43}	914	ν_{43}	921
		ν_{44}	1390	ν_{44}	1001	ν_{44}	930	ν_{44}	922
		ν_{45}	1391	ν_{45}	1027	ν_{45}	954	ν_{45}	955
		ν_{46}	1422	ν_{46}	1059	ν_{46}	957	ν_{46}	956
		ν_{47}	1455	ν_{47}	1072	ν_{47}	962	ν_{47}	959
		ν_{48}	1472	ν_{48}	1074	ν_{48}	980	ν_{48}	981
		ν_{49}	1477	ν_{49}	1075	ν_{49}	981	ν_{49}	985
		ν_{50}	1482	ν_{50}	1127	ν_{50}	987	ν_{50}	986

Supplementary Table 4: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for CaOPh-CH3 and CaOPh-tbu. VBRs are derived from calculated FCFs of corresponding vibrational decays.

CaOPh-CH3						CaOPh-tbu					
A-X			B-X			A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9524	0	0	0.9695	0	0	0.9099	0	0	0.9683
5 ₁	295	0.0342	5 ₁	295	0.0213	2 ₂	100	0.0321	7 ₁	241	0.0139
11 ₁	561	0.0052	11 ₁	561	0.0047	7 ₁	241	0.0213	13 ₁	396	0.0075
17 ₁	908	0.0023	17 ₁	908	0.0014	13 ₁	396	0.0111	18 ₁	557	0.0027
28 ₁	1349	0.0023	14 ₁	798	0.0010	18 ₁	557	0.0029	21 ₁	718	0.0015
5 ₂	590	0.0007	28 ₁	1349	0.0010	26 ₁	912	0.0021	26 ₁	912	0.0013
3 ₂	112	0.0006	5 ₂	590	0.0003	43 ₁	1353	0.0020	10 ₁	328	0.0010
14 ₁	798	0.0006	33 ₁	1557	0.0003	3 ₁ 2 ₁	104	0.0018	43 ₁	1353	0.0009
33 ₁	1557	0.0004	2 ₂	99	0.0001	2 ₄	199	0.0017	5 ₁	209	0.0007
11 ₁ 5 ₁	856	0.0002	3 ₂	112	0.0001	10 ₁	328	0.0015	9 ₁	285	0.0005
35 ₁	1677	0.0002	7 ₁	341	0.0001	15 ₁ 2 ₁	483	0.0012	24 ₁	861	0.0002
2 ₂	99	0.0001	11 ₁ 5 ₁	856	0.0001	5 ₁	209	0.0010	54 ₁	1556	0.0002
7 ₁	341	0.0001	28 ₁ 5 ₁	1644	0.0001	21 ₁	718	0.0010	1 ₂	79	0.0001
						17 ₁ 2 ₁	537	0.0009	2 ₂	100	0.0001
						7 ₁ 2 ₂	341	0.0007	7 ₂	483	0.0001
						5 ₁ 2 ₁	259	0.0006	13 ₁ 7 ₁	637	0.0001
						9 ₁	285	0.0006	42 ₁	1339	0.0001
						2 ₁ 1 ₁	89	0.0005	56 ₁	1675	0.0001
						7 ₁ 2 ₁	291	0.0005			
						13 ₁ 2 ₂	496	0.0004			
						54 ₁	1556	0.0004			
						2 ₁	50	0.0003			
						7 ₂	483	0.0003			
						13 ₁ 7 ₁	637	0.0003			
						3 ₁ 2 ₃	204	0.0002			
						24 ₁	861	0.0002			
						35 ₁ 2 ₁	1183	0.0002			
						42 ₁	1339	0.0002			
						56 ₁	1675	0.0002			
						2 ₃ 1 ₁	189	0.0001			
						2 ₆	299	0.0001			

Supplementary Table 5: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for CaOPh-Ad and CaOPh-1diA. VBRs are derived from calculated FCFs of corresponding vibrational decays.

CaOPh-ad						caoph-1diA					
A-X			B-X			A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9272	0	0	0.9457	0	0	0.9260	0	0	0.9516
6 ₁	200	0.0208	6 ₁	200	0.0130	12 ₁	365	0.0181	12 ₁	365	0.0120
11 ₁	374	0.0167	3 ₂	109	0.0112	6 ₁	180	0.0129	6 ₁	180	0.0085
3 ₁ 2 ₁	97	0.0068	11 ₁	374	0.0107	7 ₁	195	0.0096	7 ₁	195	0.0060
3 ₂	109	0.0053	3 ₁ 1 ₁	85	0.0040	1 ₂	40	0.0051	1 ₁	20	0.0042
22 ₁	643	0.0022	22 ₁	643	0.0023	1 ₁	20	0.0040	10 ₁	314	0.0027
37 ₁	912	0.0022	37 ₁	912	0.0014	10 ₁	314	0.0040	21 ₁	452	0.0020
5 ₁ 3 ₁	183	0.0017	19 ₁	476	0.0009	21 ₁	452	0.0029	27 ₁	643	0.0018
19 ₁	476	0.0013	4 ₁ 3 ₁	143	0.0008	42 ₁	910	0.0023	42 ₁	910	0.0015
70 ₁	1353	0.0013	3 ₁	54	0.0007	27 ₁	643	0.0018	84 ₁	1351	0.0009
4 ₁ 3 ₁	143	0.0007	70 ₁	1353	0.0007	84 ₁	1351	0.0016	1 ₂	40	0.0008
12 ₁	389	0.0007	12 ₁	389	0.0005	3 ₂	90	0.0008	19 ₁	440	0.0005
69 ₁	1352	0.0007	29 ₁ 3 ₁	884	0.0005	19 ₁	440	0.0007	25 ₁	627	0.0005
8 ₁ 3 ₁	332	0.0006	15 ₁ 3 ₁	480	0.0004	25 ₁	627	0.0005	30 ₁	691	0.0005
3 ₁ 1 ₁	85	0.0005	26 ₁	720	0.0004	13 ₁	392	0.0004	104 ₁	1556	0.0004
11 ₁ 6 ₁	574	0.0004	69 ₁	1352	0.0004	30 ₁	691	0.0004	2 ₂	61	0.0003
26 ₁	720	0.0004	84 ₁	1556	0.0004	42 ₁ 1 ₁	930	0.0004	13 ₁	392	0.0003
84 ₁	1556	0.0004	7 ₁ 3 ₁	260	0.0003	87 ₁	1359	0.0004	42 ₁ 1 ₁	930	0.0003
3 ₁	54	0.0003	16 ₁ 3 ₁	488	0.0003	104 ₁	1556	0.0004	16 ₁	421	0.0002
2 ₁ 1 ₁	73	0.0003	1 ₁	30	0.0002	12 ₁ 6 ₁	545	0.0003	23 ₁	481	0.0002
6 ₂	399	0.0003	1 ₂	61	0.0002	27 ₁ 1 ₁	663	0.0003	27 ₁ 1 ₁	663	0.0002
20 ₁	479	0.0003	4 ₁ 1 ₁	119	0.0002	70 ₁ 1 ₁	1216	0.0003	32 ₁	762	0.0002
29 ₁ 3 ₁	884	0.0003	3 ₄	218	0.0002	7 ₁ 6 ₁	375	0.0002	38 ₁	858	0.0002
6 ₁ 3 ₁	254	0.0002	6 ₁ 3 ₂	309	0.0002	16 ₁	421	0.0002	70 ₁ 1 ₁	1216	0.0002
6 ₁ 3 ₁ 2 ₁	297	0.0002	20 ₁	479	0.0002	23 ₁	481	0.0002	87 ₁	1359	0.0002
12 ₁ 3 ₁	443	0.0002	11 ₁ 6 ₁	574	0.0002	12 ₁ 7 ₁	561	0.0002	2 ₁ 1 ₁	51	0.0001
22 ₁ 3 ₁	697	0.0002	33 ₁	880	0.0002	12 ₂	730	0.0002	4 ₁	78	0.0001
11 ₂	748	0.0002	2 ₂	86	0.0001	44 ₁	931	0.0002	4 ₁ 2 ₁	109	0.0001
29 ₁ 2 ₁	873	0.0002	4 ₁	89	0.0001	106 ₁	1674	0.0002	7 ₁ 1 ₁	216	0.0001
33 ₁	880	0.0002	4 ₂	177	0.0001	129 ₁ 1 ₁	3223	0.0002	7 ₁ 6 ₁	375	0.0001
29 ₁ 5 ₁	959	0.0002	3 ₃ 1 ₁	194	0.0001	2 ₁	31	0.0001	12 ₁ 6 ₁	545	0.0001
86 ₁	1675	0.0002	6 ₁ 3 ₁ 1 ₁	284	0.0001	1 ₃	60	0.0001	12 ₁ 7 ₁	561	0.0001
2 ₂	86	0.0001	6 ₂	399	0.0001	2 ₂	61	0.0001	31 ₁	706	0.0001
						7 ₁ 1 ₁	216	0.0001	30 ₁ 1 ₁	711	0.0001
						6 ₁ 1 ₂	220	0.0001	12 ₂	730	0.0001
						7 ₁ 1 ₂	236	0.0001	32 ₁ 1 ₁	782	0.0001

Supplementary Table 6: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for CaOPh-4diA. VBRs are derived from calculated FCFs of corresponding vibrational decays.

CaOPh-4diA					
A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9438	0	0	0.9584
6 ₁	183	0.0195	12 ₁	62	0.0122
12 ₁	362	0.0191	6 ₁	83	0.0120
23 ₁	526	0.0024	3 ₁	2	0.0023
42 ₁	912	0.0021	30 ₁	66	0.0019
3 ₁	52	0.0020	23 ₁	26	0.0018
86 ₁	1352	0.0020	3 ₂	04	0.0017
30 ₁	666	0.0018	42 ₁	12	0.0013
13 ₁	372	0.0010	86 ₁	352	0.0011
3 ₁ 2 ₁	91	0.0005	3 ₁ 1 ₁	9	0.0009
12 ₁ 6 ₁	545	0.0004	1 ₂	4	0.0007
104 ₁	1556	0.0004	13 ₁	72	0.0006
4 ₁	81	0.0003	2 ₂	9	0.0005
5 ₁	106	0.0003	4 ₁	1	0.0004
40 ₁	889	0.0003	40 ₁	89	0.0004
1 ₁	27	0.0002	104 ₁	556	0.0004
3 ₂	104	0.0002	2 ₁ 1 ₁	6	0.0003
4 ₁ 3 ₁	133	0.0002	32 ₁	30	0.0003
6 ₂	367	0.0002	1 ₁	7	0.0002
12 ₂	724	0.0002	5 ₁	06	0.0002
32 ₁	730	0.0002	12 ₁ 6 ₁	45	0.0002
81 ₁	1339	0.0002	4 ₁ 1 ₁	08	0.0001
106 ₁	1675	0.0002	7 ₁ 3 ₁	41	0.0001
2 ₁ 1 ₁	66	0.0001	11 ₁	40	0.0001
5 ₁ 3 ₁	158	0.0001	6 ₂	67	0.0001
8 ₁ 3 ₁	309	0.0001	19 ₁ 3 ₁	83	0.0001

Supplementary Table 7: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for SrOPh-CH₃ and SrOPh-tbu. VBRs are derived from calculated FCFs of corresponding vibrational decays.

SrOPh-CH ₃						SrOPh-tbu					
A-X			B-X			A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9221	0	0	0.9399	0	0	0.9138	0	0	0.9383
5 ₁	227	0.0595	5 ₁	227	0.0441	5 ₁	189	0.0496	5 ₁	189	0.0368
1 ₂	72	0.0044	1 ₂	72	0.0045	13 ₁	372	0.0075	13 ₁	372	0.0064
11 ₁	539	0.0041	11 ₁	539	0.0041	6 ₁	212	0.0055	6 ₁	212	0.0037
28 ₁	1345	0.0027	28 ₁	1345	0.0019	3 ₂	108	0.0051	18 ₁	544	0.0022
17 ₁	897	0.0020	17 ₁	897	0.0014	43 ₁	1350	0.0024	43 ₁	1350	0.0016
5 ₂	453	0.0017	14 ₁	792	0.0010	18 ₁	544	0.0023	10 ₁	325	0.0015
14 ₁	792	0.0008	5 ₂	453	0.0009	26 ₁	901	0.0019	21 ₁	709	0.0013
33 ₁	1555	0.0007	33 ₁	1555	0.0006	10 ₁	325	0.0018	26 ₁	901	0.0013
5 ₁ 1 ₂	299	0.0003	3 ₂	103	0.0004	5 ₂	378	0.0013	4 ₁ 1 ₁	143	0.0010
35 ₁	1677	0.0003	5 ₁ 1 ₂	299	0.0002	21 ₁	709	0.0011	5 ₂	378	0.0006
2 ₂	87	0.0002	35 ₁	1677	0.0002	54 ₁	1555	0.0006	54 ₁	1555	0.0005
11 ₁ 5 ₁	765	0.0002	2 ₂	87	0.0001	3 ₁ 1 ₁	87	0.0004	24 ₁	859	0.0004
28 ₁ 5 ₁	1572	0.0002	11 ₁ 5 ₁	765	0.0001	24 ₁	859	0.0004	2 ₂	87	0.0003
3 ₂	103	0.0001	28 ₁ 5 ₁	1572	0.0001	2 ₁	44	0.0003	2 ₁	44	0.0002
4 ₁ 2 ₁	201	0.0001				3 ₁ 2 ₁	98	0.0003	2 ₁ 1 ₁	77	0.0002
						4 ₁ 3 ₁	164	0.0003	4 ₂	219	0.0002
						9 ₁	284	0.0003	9 ₁	284	0.0002
						5 ₁ 3 ₂	297	0.0003	13 ₁ 5 ₁	561	0.0002
						13 ₁ 5 ₁	561	0.0003	23 ₁ 1 ₁	863	0.0002
						23 ₁ 3 ₁	884	0.0003	42 ₁	1338	0.0002
						42 ₁	1338	0.0003	56 ₁	1674	0.0002
						56 ₁	1674	0.0003	3 ₁	54	0.0001
						6 ₁ 3 ₁	266	0.0002	7 ₁ 1 ₁	260	0.0001
						6 ₁ 5 ₁	402	0.0002	8 ₁ 1 ₁	297	0.0001
						14 ₁ 3 ₁	483	0.0002	6 ₁ 5 ₁	402	0.0001
						1 ₂	66	0.0001	14 ₁ 1 ₁	462	0.0001
						5 ₁ 2 ₁	233	0.0001	19 ₁ 3 ₁	617	0.0001
						14 ₁ 2 ₁	472	0.0001	18 ₁ 5 ₁	734	0.0001
						10 ₁ 5 ₁	514	0.0001	23 ₁ 4 ₁	939	0.0001
						20 ₁ 3 ₁	711	0.0001	23 ₁ 19 ₁	1393	0.0001
						18 ₁ 5 ₁	734	0.0001	43 ₁ 5 ₁	1539	0.0001

Supplementary Table 8: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for SrOPh-Ad and SrOPh-1diA. VBRs are derived from calculated FCFs of corresponding vibrational decays.

SrOPh-Ad						SrOPh-1diA					
A-X			B-X			A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9097	0	0	0.9186	0	0	0.8610	0	0	0.8475
6 ₁	160	0.0515	6 ₁	160	0.0377	6 ₁	149	0.0450	1 ₂	40	0.0541
11 ₁	333	0.0170	11 ₁	333	0.0132	3 ₂	75	0.0281	6 ₁	149	0.0319
3 ₁ 2 ₁	90	0.0028	22 ₁	630	0.0023	1 ₂	40	0.0206	10 ₁	300	0.0078
69 ₁	1349	0.0023	69 ₁	1349	0.0015	10 ₁	300	0.0105	2 ₁ 1 ₁	46	0.0071
22 ₁	630	0.0021	36 ₁	901	0.0012	12 ₁	337	0.0080	12 ₁	337	0.0060
2 ₂	73	0.0019	3 ₁ 2 ₁	90	0.0009	7 ₁	189	0.0021	1 ₄	80	0.0052
36 ₁	901	0.0017	19 ₁	472	0.0008	41 ₁	899	0.0019	4 ₁ 2 ₁	103	0.0050
6 ₂	321	0.0014	6 ₂	321	0.0007	84 ₁	1349	0.0018	2 ₂	53	0.0047
5 ₁	128	0.0010	1 ₂	51	0.0006	6 ₁ 3 ₂	224	0.0015	4 ₁ 1 ₁	96	0.0026
3 ₂	108	0.0009	3 ₂	108	0.0006	3 ₄	150	0.0014	6 ₁ 1 ₂	189	0.0020
19 ₁	472	0.0009	5 ₁	128	0.0006	3 ₁ 1 ₁	58	0.0012	3 ₁ 1 ₁	58	0.0014
11 ₁ 6 ₁	494	0.0008	84 ₁	1554	0.0006	6 ₁ 1 ₂	189	0.0011	2 ₁ 1 ₃	86	0.0014
84 ₁	1554	0.0006	11 ₁ 6 ₁	494	0.0005	6 ₂	297	0.0011	4 ₂	152	0.0014
33 ₁	877	0.0005	33 ₁	877	0.0005	25 ₁	622	0.0011	7 ₁	189	0.0014
26 ₁	716	0.0003	26 ₁	716	0.0003	27 ₁	636	0.0008	41 ₁	899	0.0014
86 ₁	1674	0.0003	3 ₁	54	0.0002	1 ₄	80	0.0007	84 ₁	1349	0.0012
3 ₁	54	0.0002	4 ₁ 1 ₁	111	0.0002	3 ₂ 1 ₂	115	0.0007	25 ₁	622	0.0011
6 ₁ 3 ₁ 2 ₁	251	0.0002	86 ₁	1674	0.0002	5 ₁ 3 ₁	167	0.0007	27 ₁	636	0.0008
66 ₁	1339	0.0002	3 ₁ 1 ₁	80	0.0001	21 ₁	447	0.0007	1 ₆	120	0.0006
1 ₂	51	0.0001	4 ₁ 3 ₁	140	0.0001	19 ₁	438	0.0006	6 ₂	297	0.0006
3 ₁ 1 ₁	80	0.0001	5 ₁ 3 ₁	182	0.0001	104 ₁	1554	0.0006	21 ₁	447	0.0006
4 ₁ 1 ₁	111	0.0001	12 ₁	388	0.0001	10 ₁ 6 ₁	449	0.0005	4 ₁ 1 ₃	136	0.0005
4 ₁ 2 ₁	122	0.0001	11 ₂	667	0.0001	12 ₁ 6 ₁	485	0.0004	10 ₁ 1 ₂	340	0.0005
4 ₁ 3 ₁	140	0.0001	22 ₁ 6 ₁	791	0.0001	5 ₁ 1 ₁	150	0.0003	19 ₁	438	0.0005
5 ₁ 3 ₁	182	0.0001	29 ₁ 3 ₁	883	0.0001	10 ₁ 1 ₂	340	0.0003	104 ₁	1554	0.0005
6 ₁ 2 ₂	233	0.0001	66 ₁	1339	0.0001	10 ₁ 3 ₂	375	0.0003	3 ₂	75	0.0004
6 ₁ 3 ₂	268	0.0001	70 ₁	1352	0.0001	12 ₁ 3 ₂	412	0.0003	7 ₁ 2 ₁	216	0.0004
6 ₁ 5 ₁	288	0.0001	69 ₁ 6 ₁	1509	0.0001	106 ₁	1673	0.0003	12 ₁ 1 ₂	377	0.0004
						12 ₁ 1 ₂	377	0.0002	3 ₁ 1 ₃	98	0.0003
						30 ₁	688	0.0002	6 ₁ 2 ₁ 1 ₁	195	0.0003
						38 ₁	857	0.0002	7 ₁ 4 ₁	266	0.0003
						80 ₁	1331	0.0002	10 ₁ 6 ₁	449	0.0003
						87 ₁	1358	0.0002	30 ₁	688	0.0003
						2 ₁ 1 ₁	46	0.0001	35 ₁ 1 ₁	848	0.0003
						3 ₁ 3 ₁	98	0.0001	2 ₁ 1 ₅	126	0.0002
						4 ₁ 2 ₁	103	0.0001	4 ₁ 2 ₂ 1 ₁	149	0.0002
						3 ₃ 1 ₁	132	0.0001	6 ₁ 2 ₂	201	0.0002
						6 ₁ 1 ₁	169	0.0001	6 ₁ 1 ₄	229	0.0002
						6 ₁ 3 ₁ 1 ₁	206	0.0001	6 ₁ 4 ₂ 1 ₁	251	0.0002
						3 ₆	225	0.0001	17 ₁ 1 ₁	444	0.0002
						5 ₁ 3 ₃	242	0.0001	12 ₁ 6 ₁	485	0.0002
						7 ₁ 3 ₂	264	0.0001	34 ₁ 1 ₁	847	0.0002
						6 ₁ 3 ₄	299	0.0001	38 ₁	857	0.0002
						7 ₁ 6 ₁	338	0.0001	87 ₁	1358	0.0002
						13 ₁	390	0.0001	106 ₁	1673	0.0002
						16 ₁	419	0.0001	1 ₁	20	0.0001
						23 ₁	480	0.0001	3 ₁ 2 ₁	64	0.0001
						12 ₁ 10 ₁	637	0.0001	2 ₂ 1 ₂	93	0.0001
						31 ₁	705	0.0001	2 ₃ 1 ₁	99	0.0001
						33 ₁	761	0.0001	3 ₁ 2 ₁ 1 ₂	104	0.0001

Supplementary Table 9: Theoretical harmonic frequencies and FCFs ($\gtrsim 10^{-4}$) of vibrational decays from A-X and B-X transitions for SrOPh-4diA. VBRs are derived from calculated FCFs of corresponding vibrational decays.

SrOPh-4diA					
A-X			B-X		
Final states	Harm. freq.	FCFs	Final states	Harm. freq.	FCFs
0	0	0.9144	0	0	0.9327
6 ₁	148	0.0502	6 ₁	148	0.0376
11 ₁	318	0.0209	11 ₁	318	0.0160
85 ₁	1349	0.0018	3 ₁ 1 ₁	74	0.0019
23 ₁	518	0.0017	29 ₁	655	0.0018
29 ₁	655	0.0016	23 ₁	518	0.0016
6 ₂	295	0.0013	85 ₁	1349	0.0012
41 ₁	904	0.0013	40 ₁	885	0.0009
11 ₁ 6 ₁	465	0.0010	41 ₁	904	0.0009
40 ₁	885	0.0010	6 ₂	295	0.0007
83 ₁	1348	0.0007	104 ₁	1554	0.0006
104 ₁	1554	0.0007	11 ₁ 6 ₁	465	0.0005
5 ₁	105	0.0006	83 ₁	1348	0.0005
81 ₁	1338	0.0003	2 ₂	66	0.0002
106 ₁	1674	0.0003	3 ₂	103	0.0002
2 ₂	66	0.0002	5 ₁	105	0.0002
11 ₂	635	0.0002	4 ₁ 3 ₁	129	0.0002
1 ₂	45	0.0001	32 ₁	728	0.0002
4 ₁ 1 ₁	100	0.0001	81 ₁	1338	0.0002
23 ₁ 6 ₁	666	0.0001	106 ₁	1674	0.0002
31 ₁	725	0.0001	1 ₂	45	0.0001
32 ₁	728	0.0001	5 ₁ 2 ₁	138	0.0001
29 ₁ 6 ₁	803	0.0001	6 ₁ 3 ₁ 1 ₁	222	0.0001
41 ₁ 6 ₁	1051	0.0001	19 ₁ 1 ₁	452	0.0001
68 ₁	1197	0.0001	11 ₂	635	0.0001
93 ₁	1389	0.0001	23 ₁ 6 ₁	666	0.0001
85 ₁ 6 ₁	1497	0.0001	31 ₁	725	0.0001

Supplementary Table 10: The observed frequencies of all resolved vibrational modes in the electronic ground states of all the molecular species involved in this work (unit: cm^{-1}). The calculated harmonic frequencies of the fundamental modes are given for comparison. Related vibrational displacements of fundamental modes are presented in Supplementary Figs. 5-9. The uncertainties of observed frequencies are within 5 cm^{-1} .

CaOPh-CH3			CaOPh-C(CH3)3			SrOPh-CH3			SrOPh-C(CH3)3		
Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.
2 ₁	47	49	1 ₁	38	39	2 ₁ 4 ₁	197		1 ₁	30	30
3 ₂	113		2 ₁	38	39	5 ₁	226	227	3 ₂	109	
4 ₁	165	161	1 ₂	78		4 ₂	313		5 ₁	187	189
5 ₁	290	295	5 ₁	212	209	5 ₂	451		6 ₁	217	212
6 ₁	320	319	7 ₁	240	241	11 ₁	530	539	10 ₁	321	325
3 ₁ 6 ₁	365		9 ₁	275	285	14 ₁	777	792	5 ₂	375	
11 ₁	553	561	10 ₁	327	328				5 ₁ 6 ₁	400	
5 ₂	581		10 ₁ 2 ₁	374					5 ₁ 10 ₁	502	
5 ₁ 9 ₁	758		13 ₁	393	396				13 ₁	362	372
14 ₁	779	798	15 ₁ 2 ₁	480					18 ₁	539	544
17 ₁	884	908	18 ₁	548	557				21 ₁	694	709
			7 ₁ 13 ₁	631					26 ₁	876	901
			21 ₁	701	718						
			26 ₁	886	912						
CaOPh-Ad			CaOPh-1diA			SrOPh-Ad			SrOPh-1diA		
Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.
2 ₁	41	43	2 ₁	28	31	5 ₁	128	128	6 ₁	141	149
3 ₁	49	54	1 ₂	42		6 ₁	155	160	4 ₂	152	
1 ₁ 3 ₁	81		1 ₁ 3 ₁	61		2 ₁ 5 ₁	170		10 ₁	293	300
2 ₁ 4 ₁	86		3 ₂	79		11 ₁	329	333	12 ₁	330	337
6 ₁	198	200	6 ₁	177	180						
11 ₁	368	374	7 ₁	193	196						
19 ₁	471	476	10 ₁	307	314						
22 ₁	632	643	12 ₁	358	365						
37 ₁	887	912	6 ₁ 7 ₁	374							
			21 ₁	442	452						
			6 ₁ 12 ₁	523							
			25 ₁	614	626						
			27 ₁	631	643						
			42 ₁	886	910						
CaOPh-4diA			SrOPh-4diA			SrOPh-4diA			SrOPh-4diA		
Vib. modes	Exp.	Theo.				Vib. modes	Exp.	Theo.	Vib. modes	Exp.	Theo.
2 ₁	39	39				2 ₁	31	33	2 ₁	31	33
3 ₁	47	52				2 ₂	64		2 ₂	64	
1 ₁ 3 ₁	77					2 ₁ 5 ₁	136		2 ₁ 5 ₁	136	
2 ₁ 3 ₁	93					6 ₁	145	148	6 ₁	145	148
6 ₁	178	183				4 ₂	154		4 ₂	154	
12 ₁	349	362				2 ₁ 6 ₁	181		2 ₁ 6 ₁	181	
23 ₁	527	526				11 ₁	312	318	11 ₁	312	318
30 ₁	659	666				23 ₁	512	518	23 ₁	512	518
40 ₁	892	889				29 ₁	644	655	29 ₁	644	655
42 ₁	907	912									

Supplementary Table 11: The intensity ratios of all observed vibrational decays for Ca-containing molecules. These are measured from the relative peak areas from the Voigt fits with corrections of ICCD quantum efficiency. The errors indicate the combined statistical uncertainties from the Voigt fits and the ICCD quantum efficiency. The theoretical VBRs are also added for comparison.

CaOPh-CH₃					CaOPh-Ad				
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)	Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)
0	0.9562	0.9421(13)	0.9718	0.9393(19)	0	0.9345	0.9247(26)	0.9503	0.9268(19)
2 ₁			< 10 ⁻⁴	0.0013(4)	2 ₁	< 10 ⁻⁴	0.0043(3)		
3 ₂			< 10 ⁻⁴	0.0032(3)	3 ₁			0.0007	0.0042(5)
4 ₁			< 10 ⁻⁴	0.0076(15)	1 ₁ 3 ₁	0.0005	0.0030(3)	0.0040	0.0029(3)
5 ₁	0.0325	0.0425(12)	0.0202	0.0344(11)	2 ₁ 4 ₁	< 10 ⁻⁴	0.0027(2)		
6 ₁	< 10 ⁻⁴	0.0027(3)	< 10 ⁻⁴	0.0016(3)	6 ₁	0.0202	0.0307(19)	0.0126	0.0277(15)
3 ₁ 6 ₁	< 10 ⁻⁴	0.0026(1)	< 10 ⁻⁴	0.0031(6)	11 ₁	0.0157	0.0247(13)	0.0100	0.0306(9)
11 ₁	0.0047	0.0050(3)	0.0042	0.0016(2)	19 ₁	0.0012	0.0018(4)	0.0008	0.0019(5)
5 ₂	0.0006	0.0019(1)	0.0003	0.0009(1)	22 ₁	0.0020	0.0037(3)	0.0020	0.0030(2)
5 ₁ 9 ₁			< 10 ⁻⁴	0.0023(1)	37 ₁	0.0019	0.0044(4)	0.0012	0.0030(2)
14 ₁	0.0005	0.0004(1)	0.0009	0.0008(2)					
17 ₁	0.0020	0.0028(3)	0.0012	0.0038(2)					
CaOPh-C(CH₃)₃					CaOPh-1diA				
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)	Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)
0	0.9159	0.9447(12)	0.9711	0.9389(16)	0	0.9341	0.8890(18)	0.9564	0.9243(23)
1 ₁			< 10 ⁻⁴	0.0168(9)	2 ₁			< 10 ⁻⁴	0.0124(18)
2 ₁	0.0003	0.0027(7)			1 ₂	0.0051	0.0048(7)		
1 ₂	< 10 ⁻⁴	0.0043(6)	< 10 ⁻⁴	0.0053(10)	1 ₁ 3 ₁	0.0015	0.0018(2)		
5 ₁	0.0010	0.0042(4)	0.0007	0.0028(6)	3 ₂	0.0067	0.0067(13)	< 10 ⁻⁴	0.0160(6)
7 ₁	0.0205	0.0248(6)	0.0133	0.0203(8)	6 ₁	0.0126	0.0357(5)	0.0083	0.0164(9)
9 ₁	0.0006	0.0009(3)	0.0005	0.0009(2)	7 ₁	0.0093	0.0121(4)	0.0058	0.0093(7)
10 ₁	0.0014	0.0014(1)	0.0009	0.0014(1)	10 ₁	0.0038	0.0038(2)		
10 ₁ 2 ₁	< 10 ⁻⁴	0.0010(2)			12 ₁	0.0171	0.0314(7)	0.0113	0.0141(5)
13 ₁	0.0104	0.0085(2)	0.0070	0.0075(2)	6 ₁ 7 ₁	0.0002	0.0014(4)		
15 ₁ 2 ₁	0.0011	0.0005(0)			21 ₁	0.0027	0.0051(2)	0.0019	0.0048(7)
18 ₁	0.0026	0.0030(1)	0.0024	0.0025(1)	6 ₁ 12 ₁	0.0003	0.0029(2)		
7 ₁ 13 ₁	0.0003	0.0005(0)			25 ₁	0.0004	0.0010(2)		
21 ₁	0.0009	0.0013(0)	0.0013	0.0018(2)	27 ₁	0.0016	0.0018(2)	0.0016	0.0027(6)
26 ₁	0.0018	0.0022(1)	0.0011	0.0018(1)	42 ₁	0.0020	0.0024(4)		
CaOPh-4diA									
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)					
0	0.9490	0.8895(31)	0.9621	0.9239(31)					
2 ₁	< 10 ⁻⁴	0.0033(3)							
3 ₁			0.0023	0.0035(11)					
1 ₁ 3 ₁	< 10 ⁻⁴	0.0211(9)	0.0009	0.0052(11)					
2 ₁ 3 ₁	0.0005	0.0092(8)		0.0163(5)					
6 ₁	0.0189	0.0337(14)	0.0117	0.0196(5)					
12 ₁	0.0179	0.0319(9)	0.0114	0.0276(28)					
23 ₁	0.0022	0.0046(2)	0.0016	0.0013(2)					
30 ₁	0.0016	0.0033(2)	0.0017	0.0016(3)					
40 ₁	0.0003	0.0020(3)	0.0003	0.0011(2)					
42 ₁	0.0018	0.0014(2)							

Supplementary Table 12: The intensity ratios of all observed vibrational decays for Sr-containing molecules. These are measured from the relative peak areas from the Voigt fits with corrections of ICCD quantum efficiency. The errors indicate the combined statistical uncertainties from the Voigt fits and the ICCD quantum efficiency. The theoretical VBRs are also added for comparison.

SrOPh-CH₃					SrOPh-Ad				
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)	Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)
0	0.9269	0.9578(6)	0.9438	0.9161(13)	0	0.9156	0.9310(12)	0.9387	0.9162(11)
2 ₁ 4 ₁	< 10 ⁻⁴	0.0008(1)	0.0000	0.0039(3)	5 ₁			0.0006	0.0023(7)
5 ₁	0.0571	0.0347(5)	0.0423	0.0701(10)	6 ₁	0.0502	0.0380(9)	0.0374	0.0360(4)
4 ₂	< 10 ⁻⁴	0.0008(1)			2 ₁ 5 ₁	0.0000	0.0142(6)	< 10 ⁻⁴	0.0123(4)
5 ₂	0.0016	0.0014(1)	0.0008	0.0009(2)	11 ₁	0.0160	0.0168(5)	0.0126	0.0332(7)
11 ₁	0.0037	0.0041(2)	0.0037	0.0077(2)					
14 ₁	0.0007	0.0005(1)	0.0009	0.0012(1)					
SrOPh-C(CH₃)₃					SrOPh-1diA				
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)	final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)
0	0.9200	0.9451(9)	0.9431	0.9068(31)	0	0.8865	0.9308(9)	0.9031	0.9054(16)
1 ₁			< 10 ⁻⁴	0.0019(3)	6 ₁	0.0450	0.0245(4)	0.0330	0.0255(6)
3 ₂			< 10 ⁻⁴	0.0040(3)	4 ₂	< 10 ⁻⁴	0.0247(4)	0.0014	0.0253(6)
5 ₁	0.0481	0.0382(6)	0.0357	0.0652(20)	10 ₁	0.0102	0.0105(4)		
6 ₁	0.0053	0.0041(2)	0.0036	0.0057(4)	12 ₁	0.0077	0.0095(6)	0.0060	0.0437(15)
10 ₁	0.0017	0.0018(1)							
13 ₁	0.0070	0.0033(1)	0.0060	0.0065(4)					
5 ₂	0.0012	0.0040(1)	0.0006	0.0054(4)					
5 ₁ 6 ₁	0.0002	0.0009(1)							
5 ₁ 10 ₁	< 10 ⁻⁴	0.0005(1)							
18 ₁	0.0021	0.0015(5)							
21 ₁	0.0010	0.0006(1)	0.0011	0.0027(3)					
26 ₁			0.0011	0.0018(3)					
SrOPh-4diA					SrOPh-4diA				
Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)	Final states	Theo. (A)	Exp. (A)	Theo. (B)	Exp. (B)
0	0.9196	0.9396(22)	0.9368	0.9315(85)	0	0.9196	0.9396(22)	0.9368	0.9315(85)
2 ₁	< 10 ⁻⁴	0.0080(9)			2 ₁	< 10 ⁻⁴	0.0080(9)		
2 ₂			0.0002	0.0145(20)	2 ₂			0.0002	0.0145(20)
2 ₁ 5 ₁	< 10 ⁻⁴	0.0039(11)			2 ₁ 5 ₁	< 10 ⁻⁴	0.0039(11)		
6 ₁	0.0490	0.0157(8)	0.0367	0.0170(17)	6 ₁	0.0490	0.0157(8)	0.0367	0.0170(17)
4 ₂	< 10 ⁻⁴	0.0130(9)	< 10 ⁻⁴	0.0188(31)	4 ₂	< 10 ⁻⁴	0.0130(9)	< 10 ⁻⁴	0.0188(31)
2 ₁ 6 ₁			< 10 ⁻⁴	0.0041(10)	2 ₁ 6 ₁			< 10 ⁻⁴	0.0041(10)
11 ₁	0.0197	0.0159(8)			11 ₁	0.0197	0.0159(8)		
23 ₁	0.0015	0.0016(3)	0.0014	0.0140(9)	23 ₁	0.0015	0.0016(3)	0.0014	0.0140(9)
29 ₁	0.0016	0.0022(9)			29 ₁	0.0016	0.0022(9)		

Supplementary Table 13: Measured intensity ratios and scaled VBRs of the diagonal 0-0 decay of all molecules. The scaling process considering contributions of unobserved vibrational decays is detailed in the section of error analysis of VBRs. The values of CaOPh and SrOPh are obtained from references [42, 43, 53].

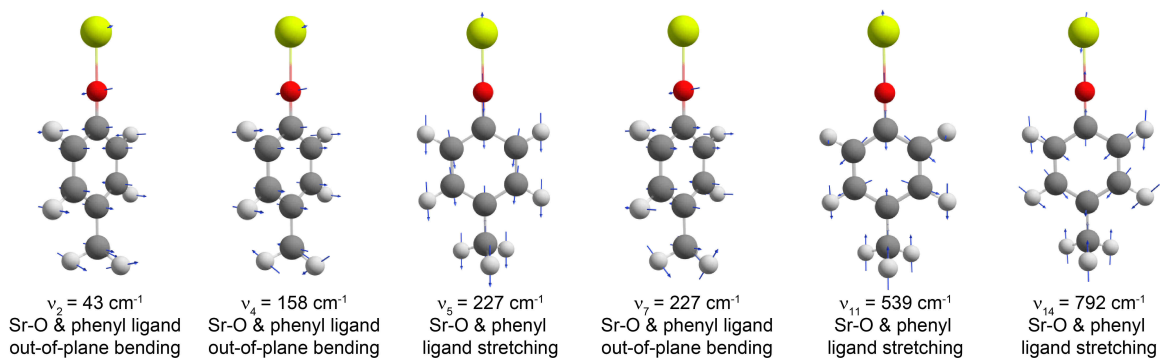
Species	Transitions	Theo.VBR	Exp. VBR	Exp.VBR errs	Scaled VBR	Scaled VBR	Scaled VBR
						upper errs	lower errs
CaOPh	X-A	0.9611	0.9339	0.0029	0.9286	0.0053	0.0012
	X-B	0.9758	0.9446	0.0068	0.9339	0.0048	0.0016
CaOPh-CH ₃	X-A	0.9562	0.9421	0.0013	0.9357	0.0040	0.0013
	X-B	0.9718	0.9393	0.0019	0.9381	0.0020	0.0019
CaOPh-tBU	X-A	0.9159	0.9447	0.0012	0.9288	0.0139	0.0020
	X-B	0.9711	0.9389	0.0016	0.9350	0.0027	0.0016
CaOPh-Ad	X-A	0.9345	0.9247	0.0026	0.8855	0.0365	0.0180
	X-B	0.9503	0.9268	0.0019	0.8969	0.0272	0.0034
CaOPh-1diA	X-A	0.9341	0.8890	0.0018	0.8822	0.0038	0.0018
	X-B	0.9564	0.9243	0.0023	0.9024	0.0203	0.0034
CaOPh-4diA	X-A	0.9490	0.8895	0.0031	0.8745	0.0123	0.0031
	X-B	0.9621	0.9239	0.0031	0.9105	0.0107	0.0032
SrOPh	X-A	0.9284	0.888	0.011	0.888	0.011	0.011
	X-B	0.9453	0.872	0.013	0.872	0.013	0.013
SrOPh-CH ₃	X-A	0.9269	0.9578	0.0006	0.9486	0.0077	0.0013
	X-B	0.9438	0.9161	0.0013	0.9034	0.0101	0.0016
SrOPh-tBU	X-A	0.9200	0.9451	0.0009	0.9312	0.0122	0.0009
	X-B	0.9431	0.9068	0.0031	0.8937	0.0109	0.0043
SrOPh-Ad	X-A	0.9156	0.9310	0.0012	0.9120	0.0173	0.0012
	X-B	0.9387	0.9162	0.0011	0.8996	0.0144	0.0013
SrOPh-1diA	X-A	0.8865	0.9308	0.0009	0.8802	0.0489	0.0012
	X-B	0.9031	0.9054	0.0016	0.8603	0.0425	0.0302
SrOPh-4diA	X-A	0.9196	0.9396	0.0022	0.9306	0.0077	0.0023
	X-B	0.9368	0.9315	0.0085	0.9080	0.0233	0.0310

Supplementary Table 14: Measured intensity ratios and scaled VBRs of the diagonal 0-0 decay of all molecules. The scaling process considering contributions of unobserved vibrational decays is detailed in the section of error analysis of VBRs.

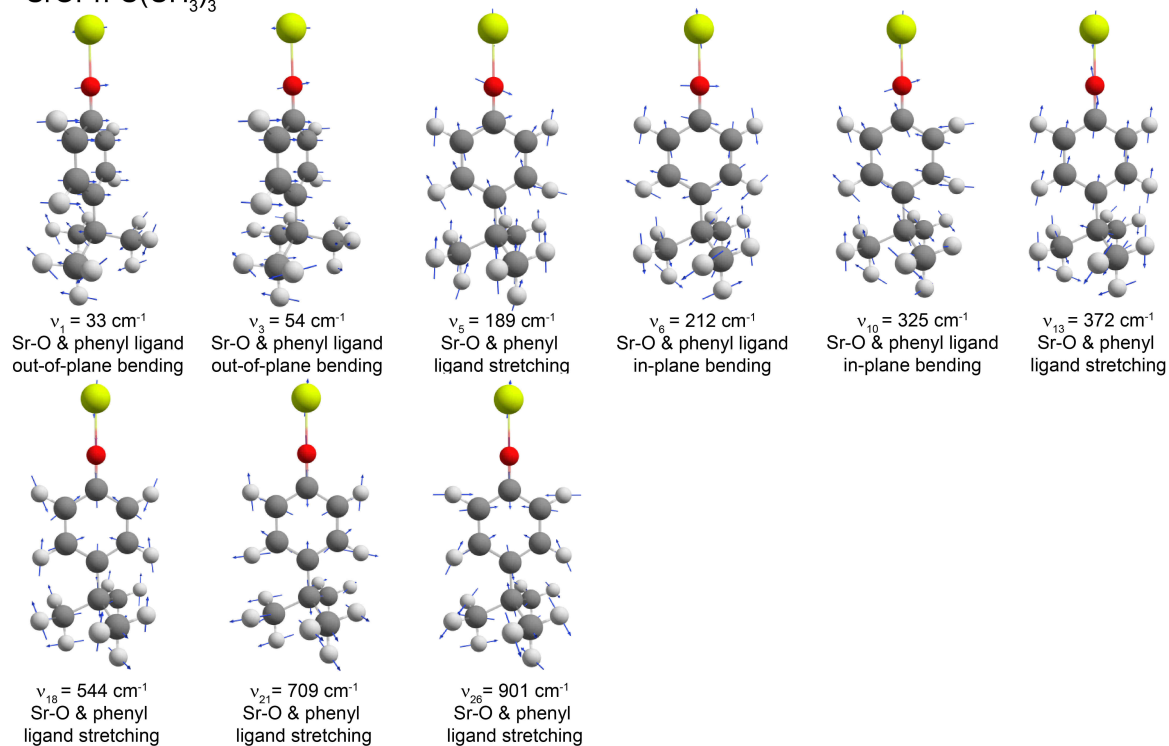
Molecule	CaOPh-CH3		SrOPh-CH3		CaOPh-C(CH ₃) ₃		SrOPh-C(CH ₃) ₃		CaOPh-Ad		SrOPh-Ad	
Transition	A - X	B - X	A - X	B - X	A - X	B - X	A - X	B - X	A - X	B - X	A - X	B - X
0-0 Intensity ratios (S_0)	0.9421	0.9418	0.9556	0.9009	0.9447	0.9383	0.9445	0.9042	0.9293	0.9308	0.9341	0.9200
Curve fitting uncertainty (δS_0)	0.0012	0.0019	0.0005	0.0012	0.0012	0.0016	0.0008	0.0030	0.0025	0.0018	0.0011	0.0010
Jacobian correction (Δ_J)	-0.0029	-0.0026	-0.0023	-0.0044	-0.0024	-0.0020	-0.0019	-0.0032	-0.0028	-0.0027	-0.0018	-0.0023
Sensitivity correction (Δ_{QE})	-0.0024	-0.0017	-0.0027	-0.0049	-0.0019	-0.0013	-0.0021	-0.0036	-0.0046	-0.0041	-0.0032	-0.0038
Uncertainty from unobserved decays (δ_u)	-0.0019	-0.0006	-0.0065	-0.0067	-0.0117	-0.0011	-0.0098	-0.0097	-0.0414	-0.0227	-0.0178	-0.0119
Scaled diagonal VBRs $S'_0 = S_0 + \Delta_J + \Delta_{QE} + \delta_u$	0.9350	0.9369	0.9442	0.8850	0.9288	0.9339	0.9329	0.8877	0.8805	0.9015	0.9114	0.9020
Lower estimates of scaled VBRs (S''_0)	0.9349	0.9369	0.9438	0.8845	0.9287	0.9338	0.9319	0.8865	0.8752	0.8990	0.9113	0.9002
Upper error bar $\sqrt{(\delta S_0)^2 + \delta_u^2}$	0.0023	0.0020	0.0065	0.0068	0.0118	0.0020	0.0098	0.0102	0.0415	0.0228	0.0178	0.0120
Lower error bar $\sqrt{(\delta S_0)^2 + (S'_0 - S''_0)^2}$	0.0013	0.0019	0.0007	0.0013	0.0012	0.0016	0.0013	0.0033	0.0060	0.0031	0.0012	0.0021
Molecule	CaOPh-1diA		CaOPh-4diA		SrOPh-1diA		SrOPh-4diA					
Transition	A - X	B - X	A - X	B - X	A - X	B - X	A - X	B - X				
0-0 Intensity ratios (S_0)	0.8947	0.9270	0.8903	0.9243	0.9339	0.9098	0.9413	0.9079				
Curve fitting uncertainty (δS_0)	0.0018	0.0022	0.0030	0.0031	0.0009	0.0015	0.0021	0.0082				
Jacobian correction (Δ_J)	-0.0034	-0.0018	-0.0032	-0.0023	-0.0017	-0.0027	-0.0016	-0.0028				
Sensitivity correction (Δ_{QE})	-0.0057	-0.0026	-0.0025	-0.0013	-0.0030	-0.0044	-0.0017	-0.0030				
Uncertainty from unobserved decays (δ_u)	-0.0034	-0.0202	-0.0078	-0.0084	-0.0219	-0.0504	-0.0074	-0.0159				
Scaled diagonal VBRs $S'_0 = S_0 + \Delta_J + \Delta_{QE} + \delta_u$	0.8822	0.9023	0.8768	0.9123	0.9072	0.8524	0.9306	0.8862				
Lower estimates of scaled VBRs (S''_0)	0.8821	0.8998	0.8762	0.9117	0.9069	0.8397	0.9299	0.8817				
Upper error bar $\sqrt{(\delta S_0)^2 + \delta_u^2}$	0.0038	0.0203	0.0084	0.0089	0.0220	0.0504	0.0077	0.0180				
Lower error bar $\sqrt{(\delta S_0)^2 + (S'_0 - S''_0)^2}$	0.0018	0.0034	0.0031	0.0032	0.0010	0.0128	0.0023	0.0096				

1204 **SUPPLEMENTARY FIGURES OF**
1205 **VIBRATIONAL DISPLACEMENTS**
1206 **COMPUTATION AND CHARACTERIZATION**
1207 **OF CHEMICALS**

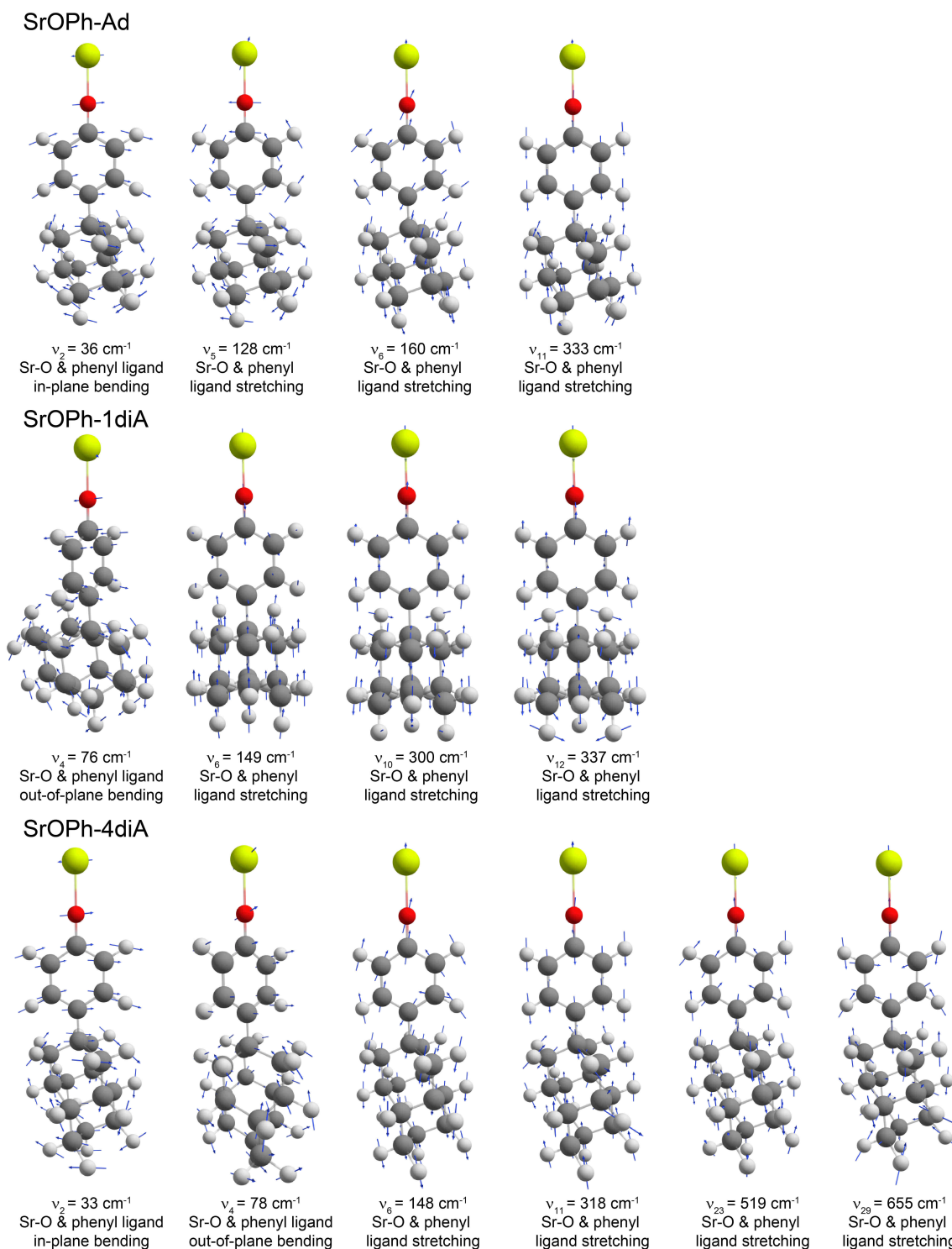
SrOPh-CH₃



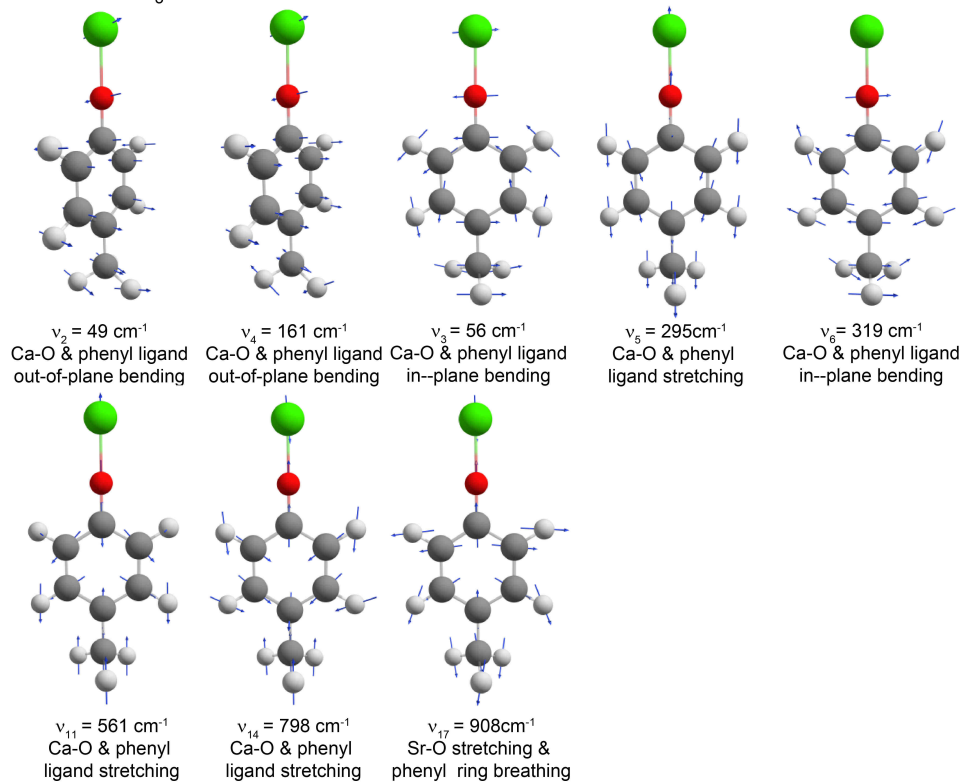
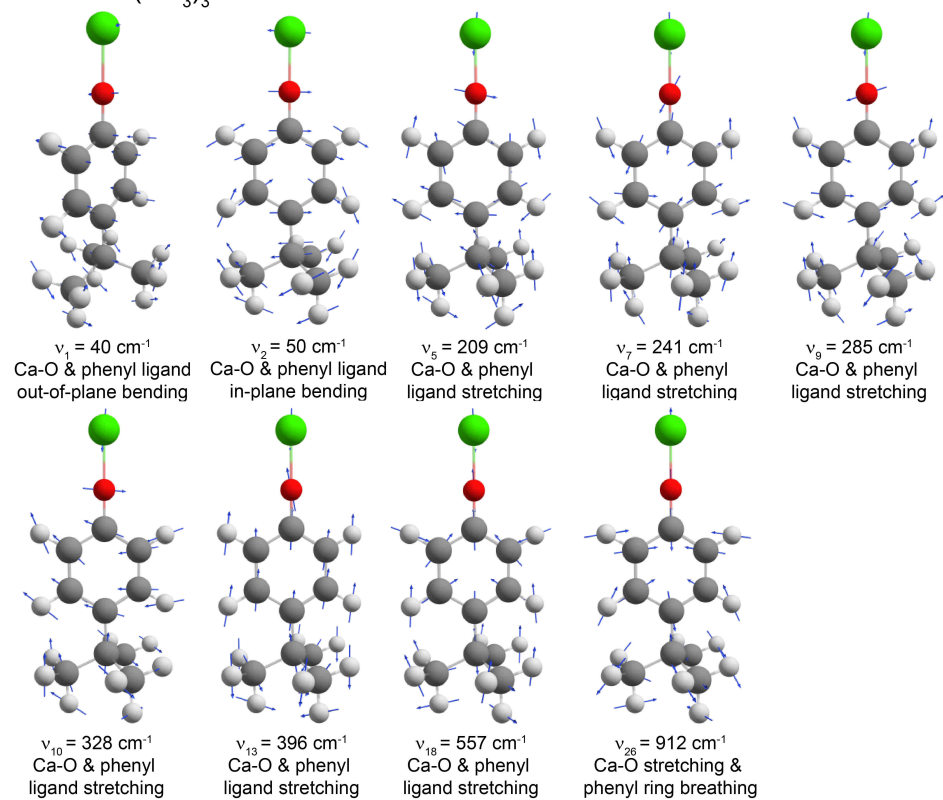
SrOPh-C(CH₃)₃



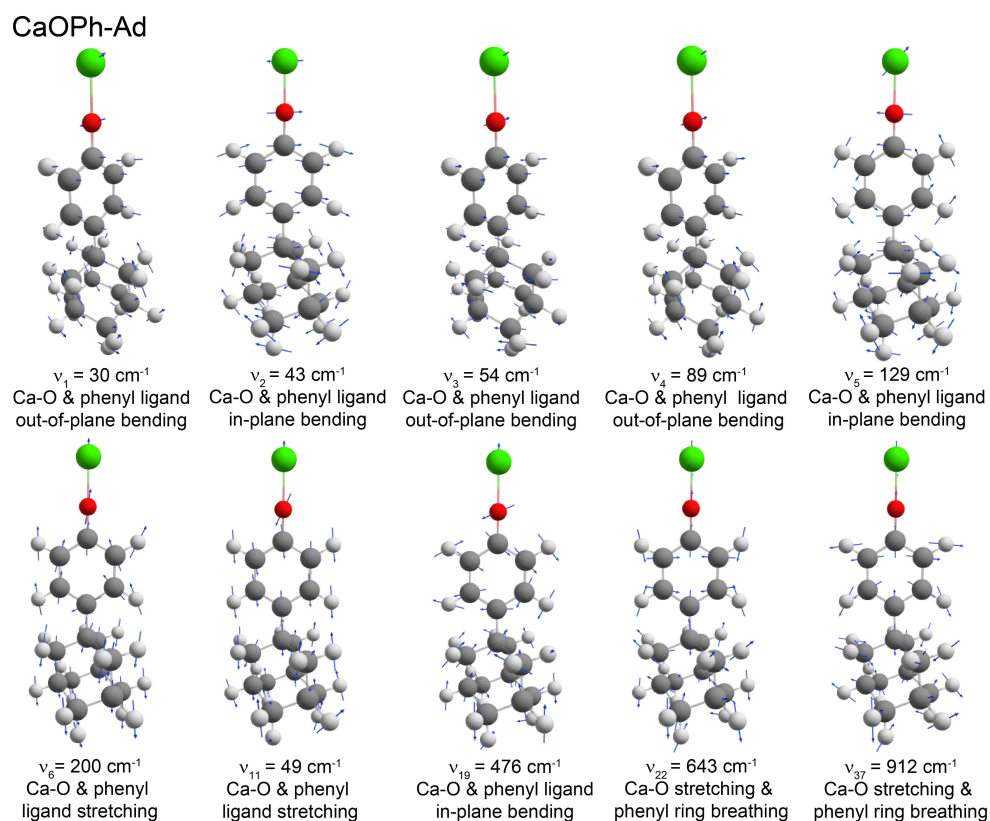
Supplementary Fig. 5. Vibrational displacements of related fundamental vibrational modes for SrOPh-CH₃ and SrOPh-C(CH₃)₃. The calculated harmonic frequencies are given.



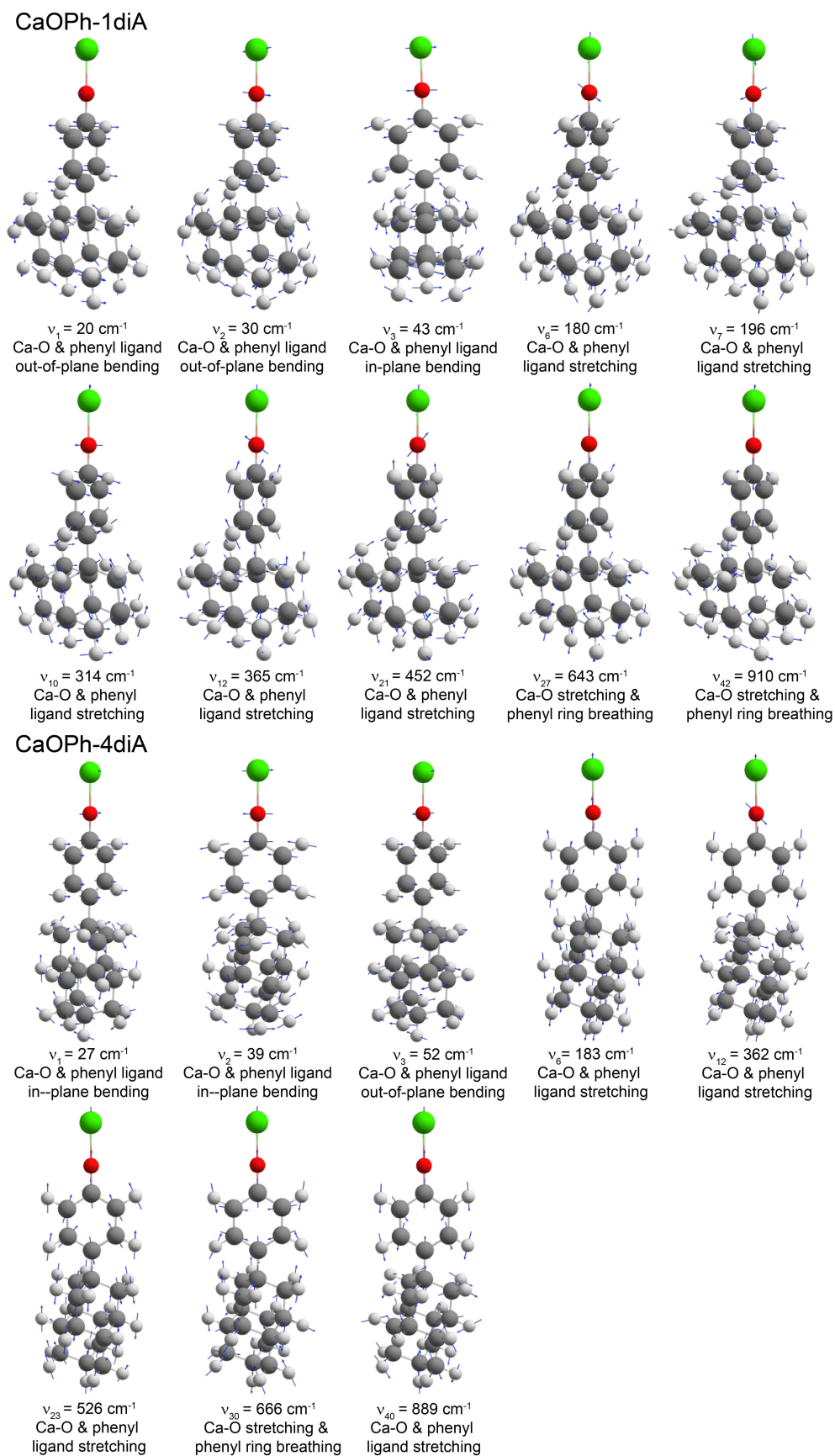
Supplementary Fig. 6. Vibrational displacements of related fundamental vibrational modes for SrOPh-Ad, SrOPh-1diA and SrOPh-4diA. The calculated harmonic frequencies are given.

CaOPh-CH₃CaOPh-C(CH₃)₃

Supplementary Fig. 7. Vibrational displacements of related fundamental vibrational modes for CaOPh-CH₃ and CaOPh-C(CH₃)₃. The calculated harmonic frequencies are given.



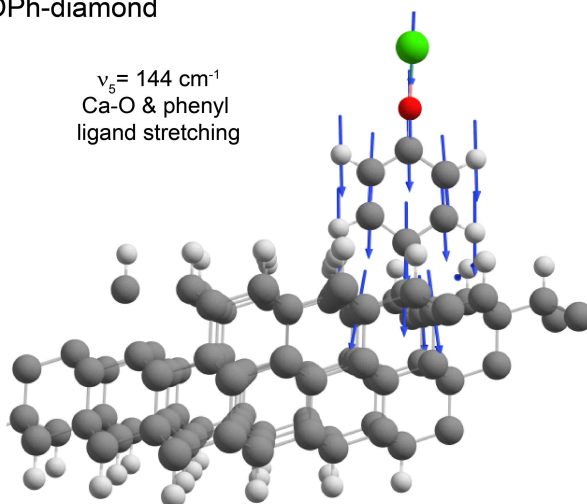
Supplementary Fig. 8. Vibrational displacements of related fundamental vibrational modes for CaOPh-Ad. The calculated harmonic frequencies are given.



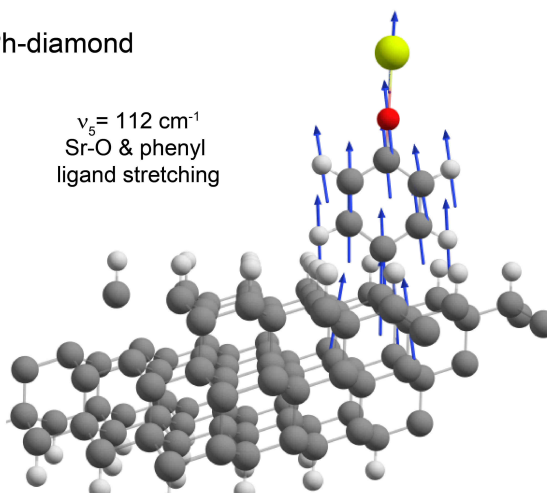
Supplementary Fig. 9. Vibrational displacements of related fundamental vibrational modes for CaOPh-1diA and CaOPh-4diA. The calculated harmonic frequencies are given.

CaOPh-diamond

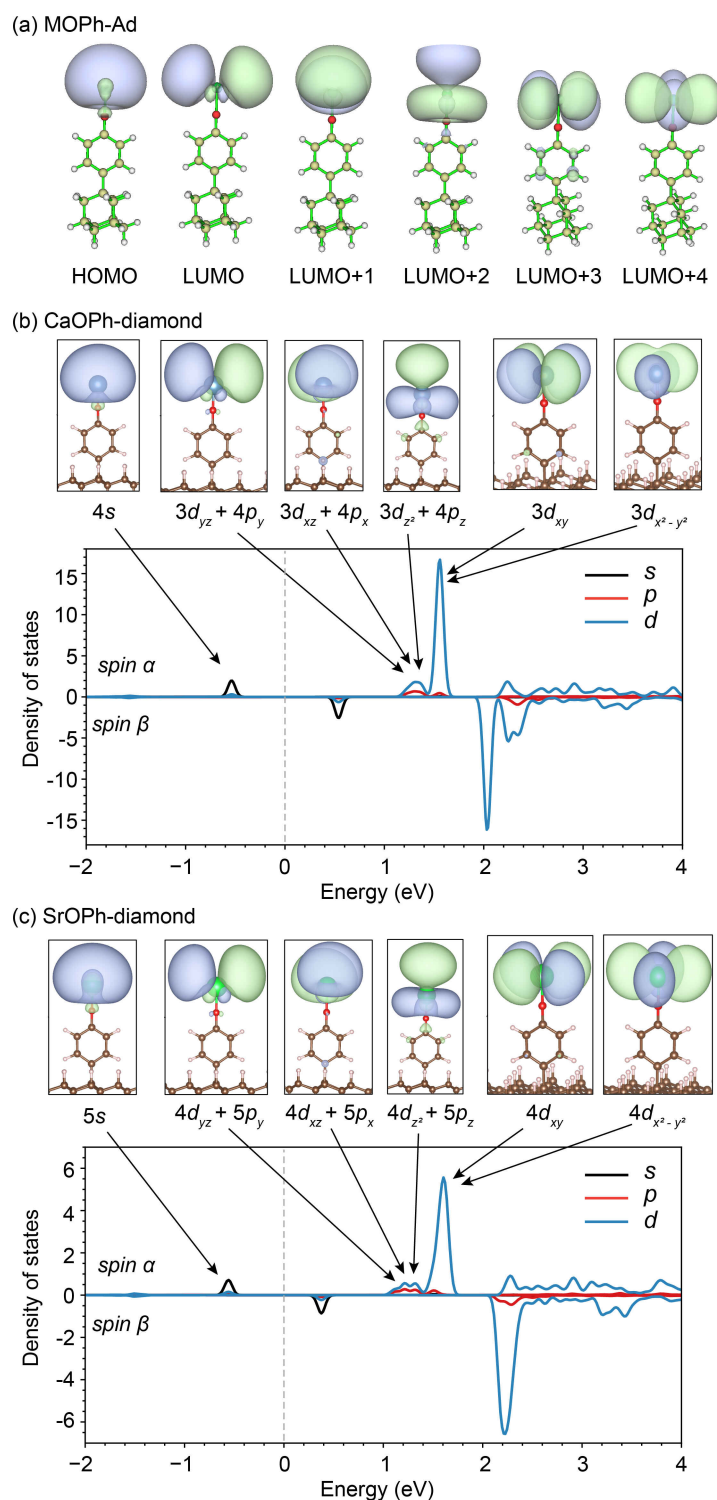
$\nu_5 = 144 \text{ cm}^{-1}$
Ca-O & phenyl
ligand stretching

**SrOPh-diamond**

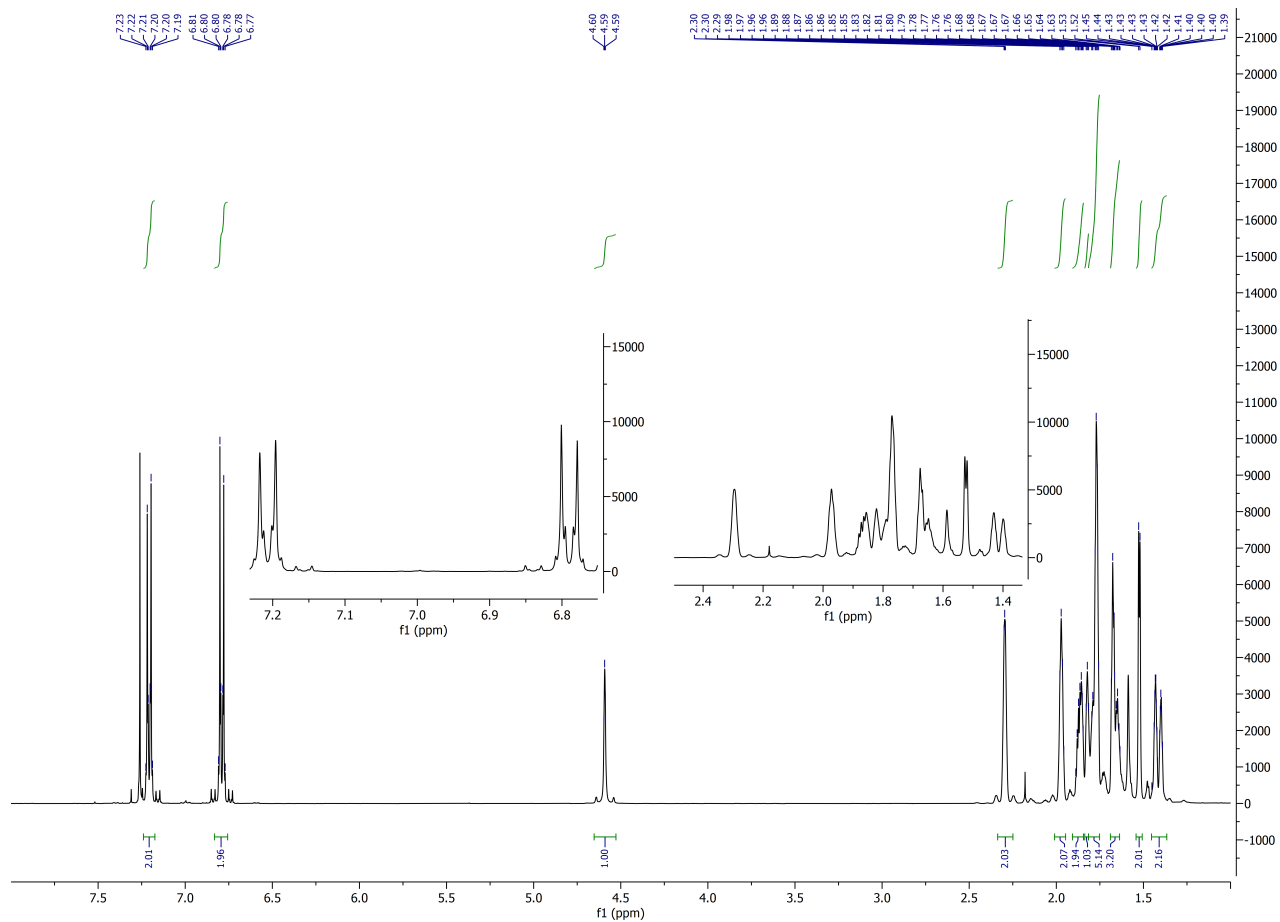
$\nu_5 = 112 \text{ cm}^{-1}$
Sr-O & phenyl
ligand stretching



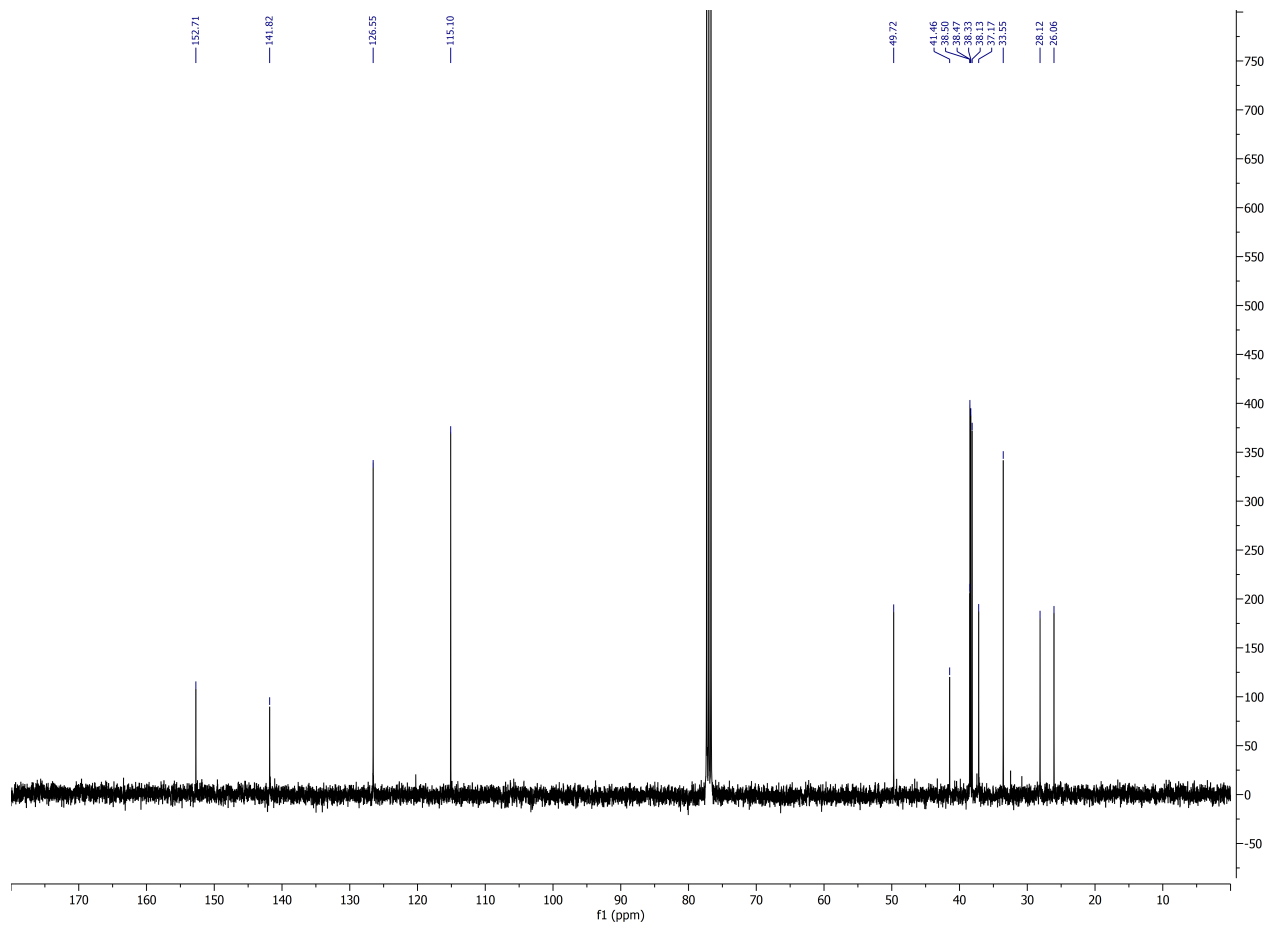
Supplementary Fig. 10. Vibrational displacements of the lowest-frequency stretching vibrational modes for CaOPh-diamond and SrOPh-diamond. The calculated harmonic frequencies are given.



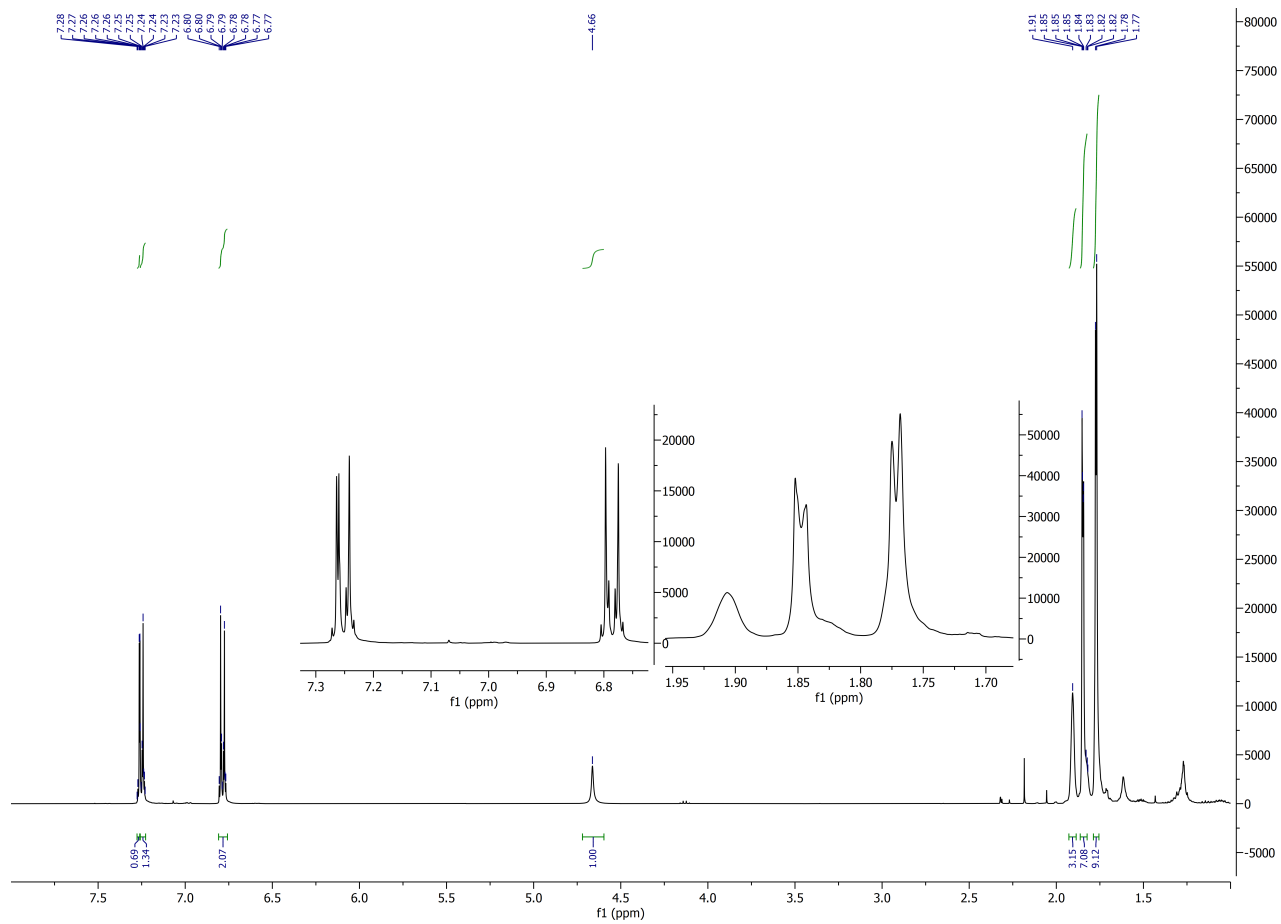
Supplementary Fig. 11. (a) Molecular orbitals of HOMO and LUMOs of MOPh-Ad. (b) PDOS and OCC orbitals for CaOPh-diamond. (c) PDOS and OCC orbitals for SrOPh-diamond. The PDOS plots show the contributions from s , p , d orbitals of the metal atom.



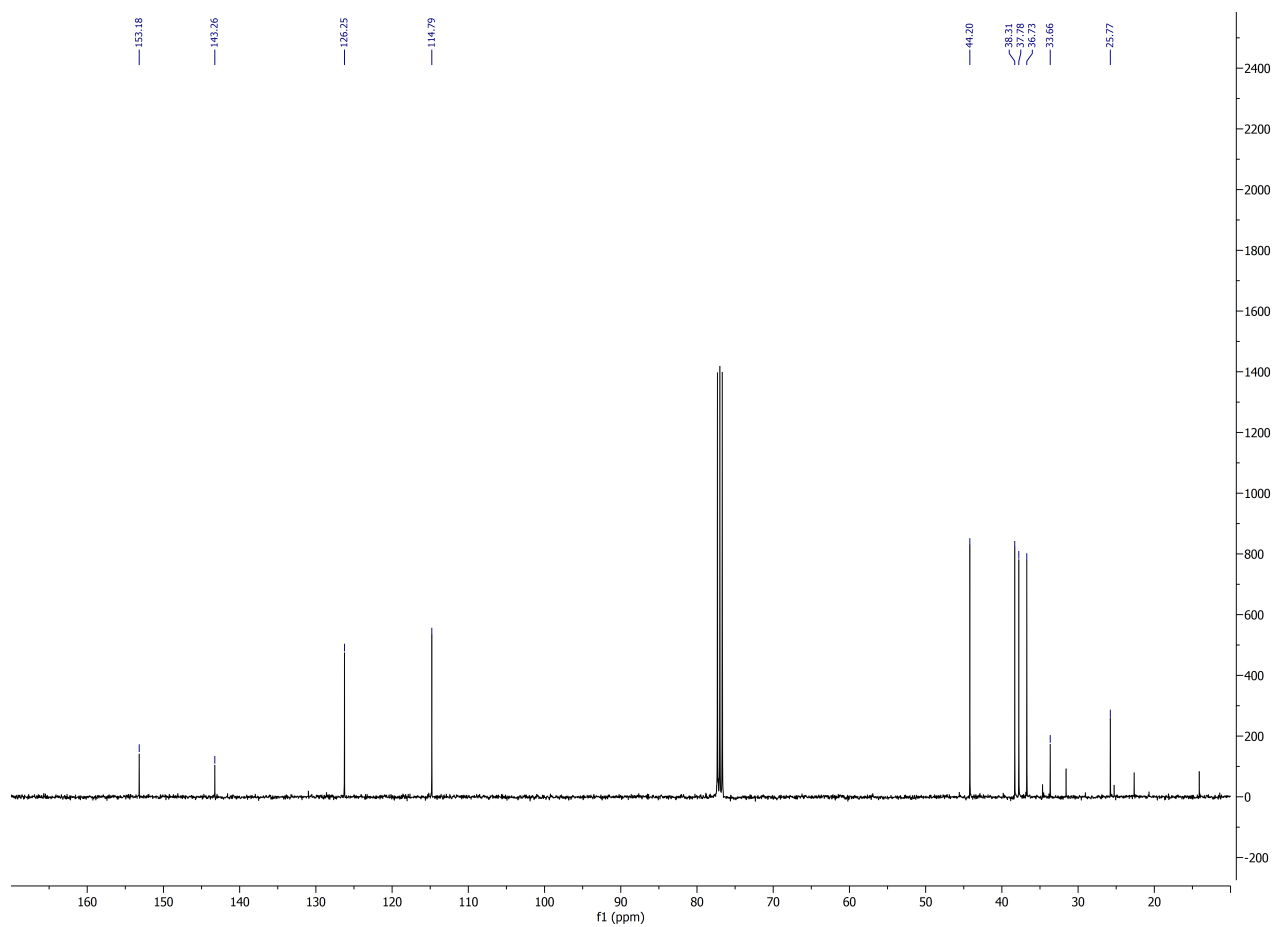
Supplementary Fig. 12. ^1H NMR spectrum of 4-(1-diamantyl)-phenol.



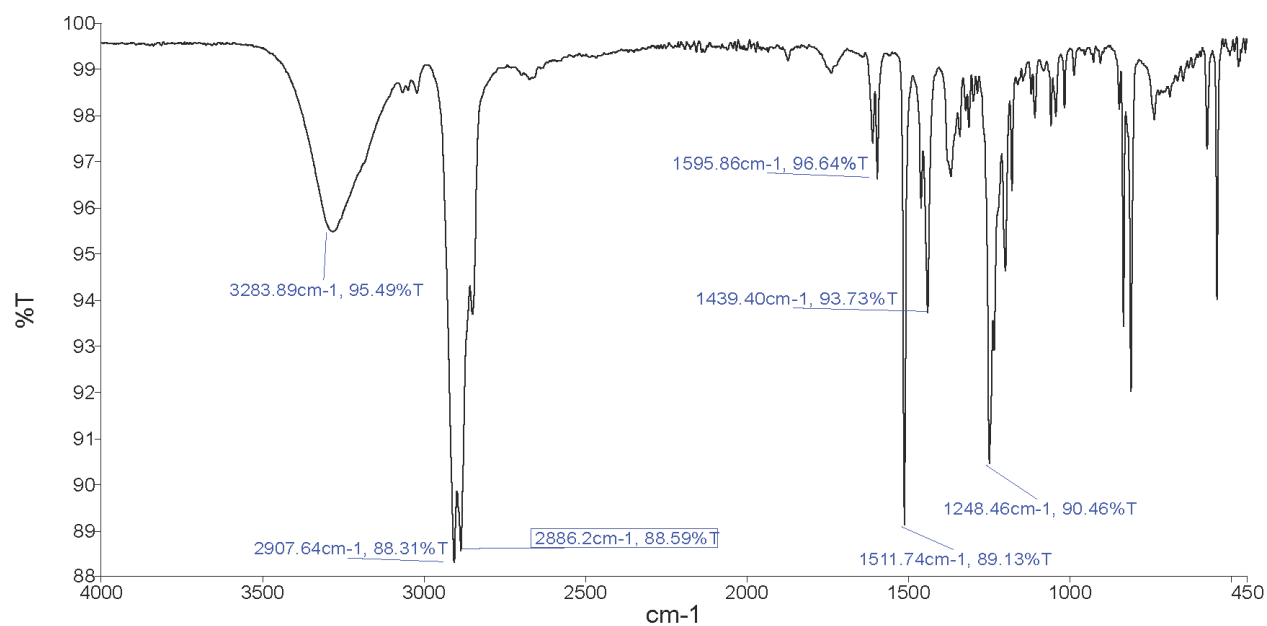
Supplementary Fig. 13. ^{13}C NMR spectrum of 4-(1-diamantyl)-phenol.



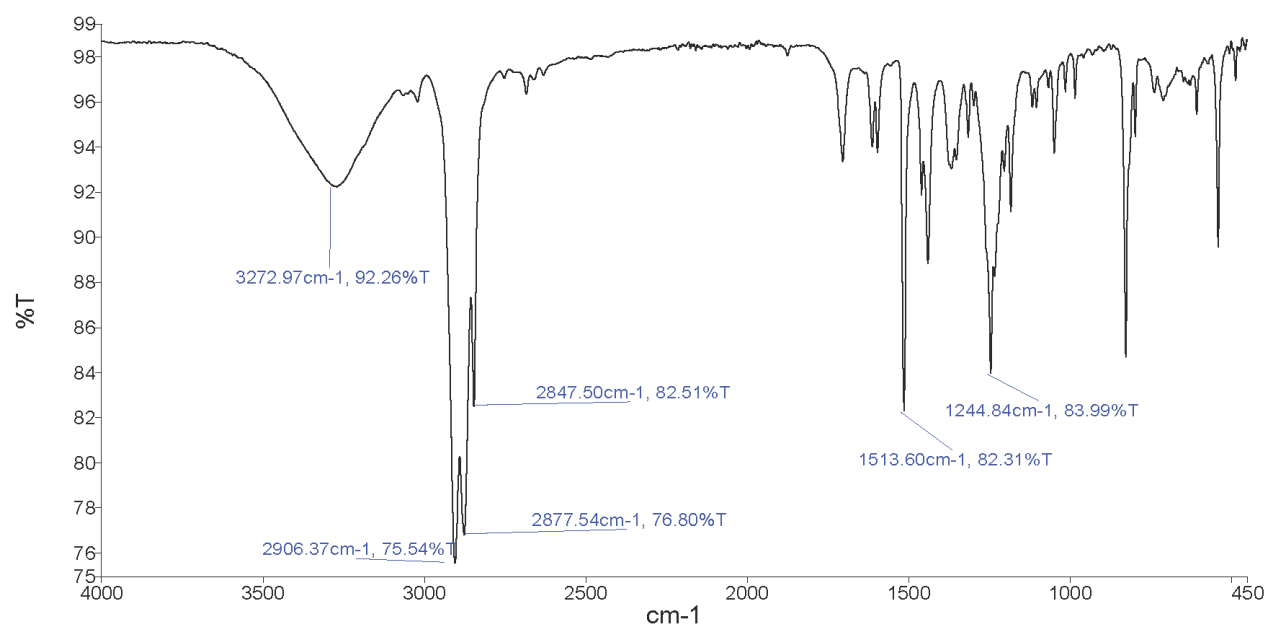
Supplementary Fig. 14. ¹H NMR spectrum of 4-(4-diamantyl)-phenol.



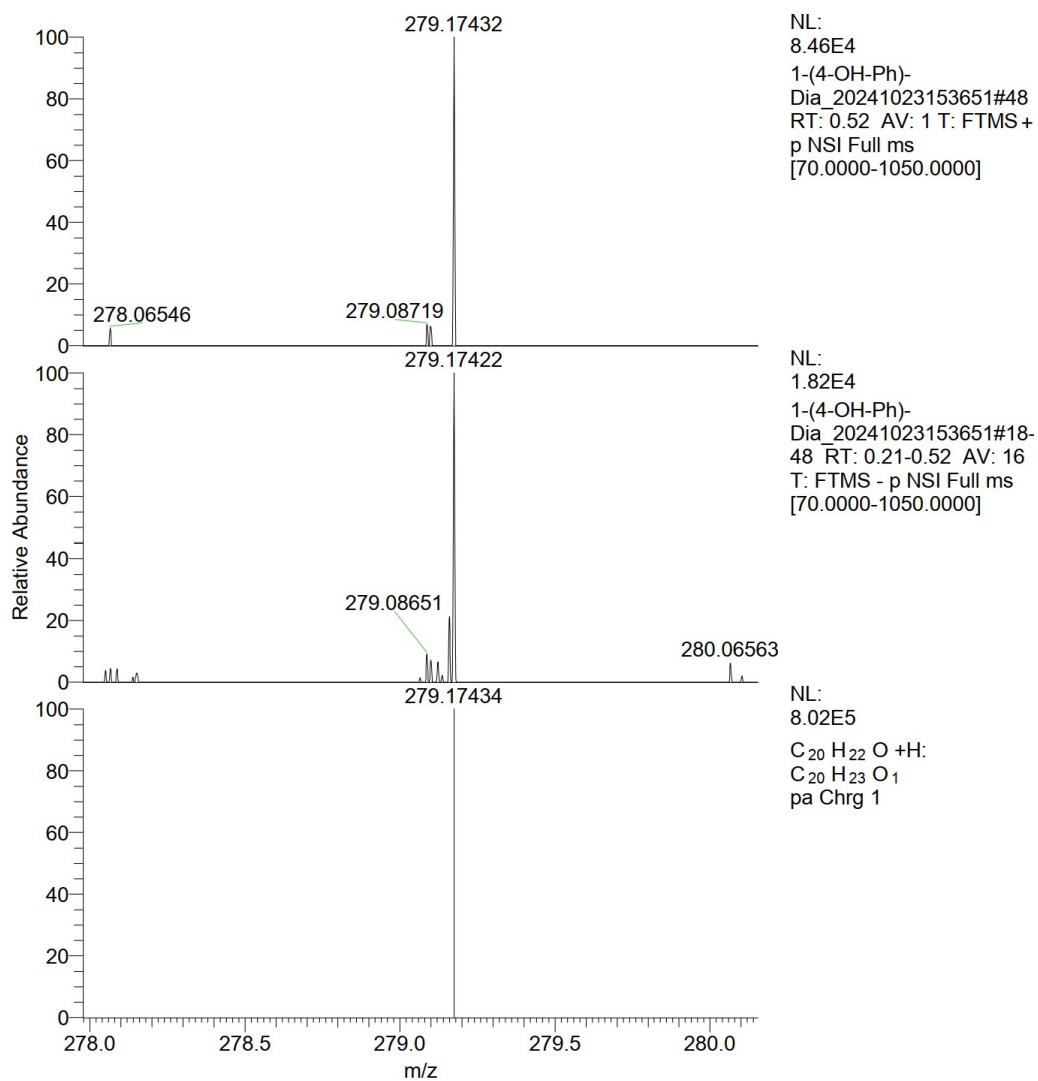
Supplementary Fig. 15. ¹³C NMR spectrum of 4-(4-diamantyl)-phenol.



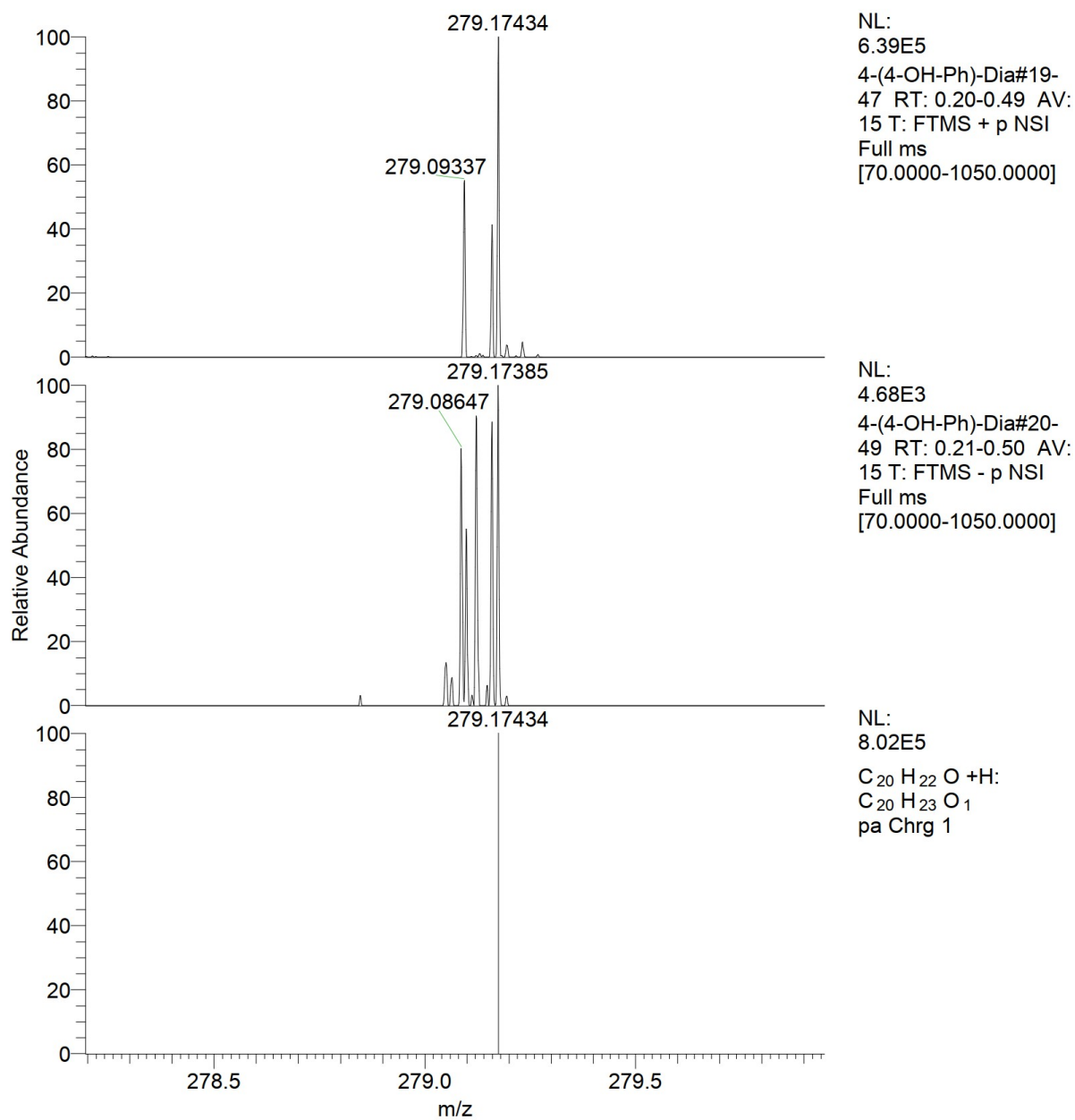
Supplementary Fig. 16. FT-IR spectrum of 4-(1-diamantyl)-phenol.



Supplementary Fig. 17. FT-IR spectrum of 4-(4-diamantyl)-phenol.



Supplementary Fig. 18. High resolution mass spectrum of 4-(1-diamantyl)-phenol.



Supplementary Fig. 19. High resolution mass spectrum of 4-(4-diamantyl)-phenol.