Supporting Information

Nr.	Atom	X	Y	Z
1	C	-1.199125	0.195487	0.007724
2	C	-1.204282	-1.197737	0.007724
3	C	-0.000000	-1.898098	0.006451
4	C	1.204282	-1.197737	0.007724
5	C	1.199125	0.195487	0.007724
6	C	-0.000000	0.912818	0.005155
7	H	-2.139587	0.735525	0.012573
8	H	-2.145145	-1.733580	0.012494
9	H	-0.000000	-2.980597	0.009400
10	H	2.145145	-1.733580	0.012494
11	H	2.139587	0.735525	0.012573
12	C	-0.000000	2.415831	-0.030217
13	H	0.882490	2.820789	0.462959
14	H	-0.000000	2.778826	-1.059173
15	H	-0.882490	2.820789	0.462959

Table S1. Optimized geometry data of toluene by MP2/6-311++G(3df,2p) in Cartesian coordinates are shown in unit of angstrom. Number of atoms and Cartesian coordinates are shown in Fig. S1.
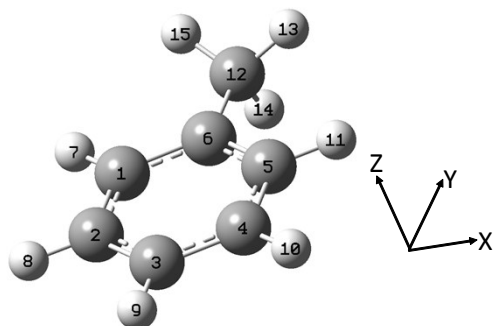

Fig. S1. Geometrical structure of toluene (C_S).

27 (A') 0.055 a.u.   26 (A") 0.052 a.u.

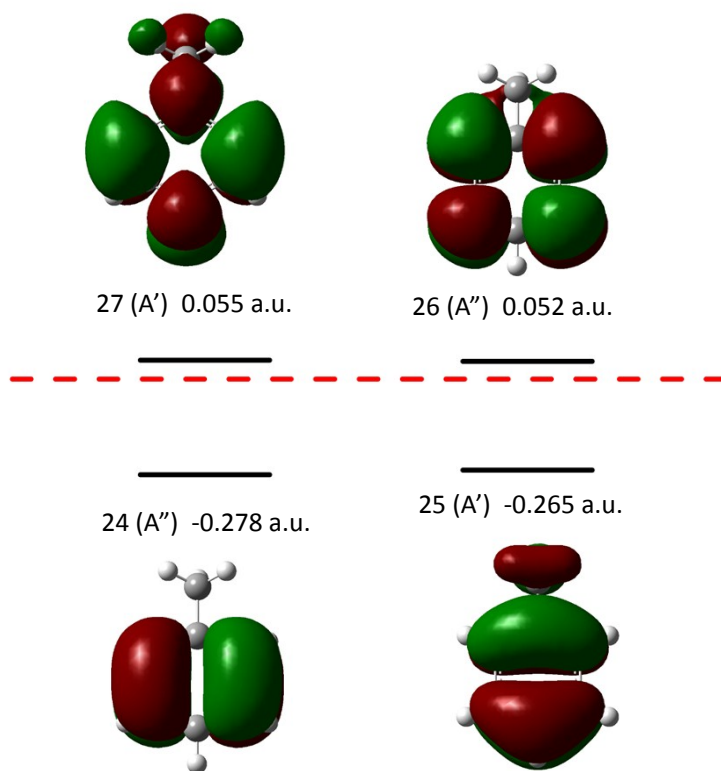24 (A") -0.278 a.u.   25 (A') -0.265 a.u.

Fig. S2. Active orbitals with orbital energies, which were obtained by the CASSCF calculation, are shown.

CASSCF wavefunctions:

$\Phi_{S_0}(A') \equiv |\phi_{24}\bar{\phi}_{24}\phi_{25}\bar{\phi}_{25}|$ for the ground state configuration. $\Psi_{S_0}(A') = 0.975\Phi_{S_0(A')} + L$ for the ground state.

The lower four singlet excited states are approximately expressed as a linear combination of the one-electron excited configurations as

$$\Psi_{S_1(A'')} = 0.524\left(\left|\phi_{24}\bar{\phi}_{24}\phi_{25}\bar{\phi}_{26}\right| - \left|\phi_{24}\bar{\phi}_{24}\bar{\phi}_{25}\phi_{26}\right|\right) + 0.469\left(\left|\phi_{24}\bar{\phi}_{27}\phi_{25}\bar{\phi}_{25}\right| - \left|\bar{\phi}_{24}\phi_{27}\phi_{25}\bar{\phi}_{25}\right|\right)$$

$$\Psi_{S_2(A')} = 0.511\left(\left|\phi_{24}\bar{\phi}_{24}\phi_{25}\bar{\phi}_{27}\right| - \left|\phi_{24}\bar{\phi}_{24}\bar{\phi}_{25}\phi_{27}\right|\right) + 0.487\left(\left|\phi_{24}\bar{\phi}_{26}\phi_{25}\bar{\phi}_{25}\right| - \left|\bar{\phi}_{24}\phi_{26}\phi_{25}\bar{\phi}_{25}\right|\right)$$

$$\Psi_{S_3(A'')} = -0.458\left(\left|\phi_{24}\bar{\phi}_{24}\phi_{25}\bar{\phi}_{26}\right| - \left|\phi_{24}\bar{\phi}_{24}\bar{\phi}_{25}\phi_{26}\right|\right) + 0.513\left(\left|\phi_{24}\bar{\phi}_{27}\phi_{25}\bar{\phi}_{25}\right| - \left|\bar{\phi}_{24}\phi_{27}\phi_{25}\bar{\phi}_{25}\right|\right)$$

$$\Psi_{S_4(A')} = -0.473\left(\left|\phi_{24}\bar{\phi}_{24}\phi_{25}\bar{\phi}_{27}\right| - \left|\phi_{24}\bar{\phi}_{24}\bar{\phi}_{25}\phi_{27}\right|\right) + 0.498\left(\left|\phi_{24}\bar{\phi}_{26}\phi_{25}\bar{\phi}_{25}\right| - \left|\bar{\phi}_{24}\phi_{26}\phi_{25}\bar{\phi}_{25}\right|\right)$$
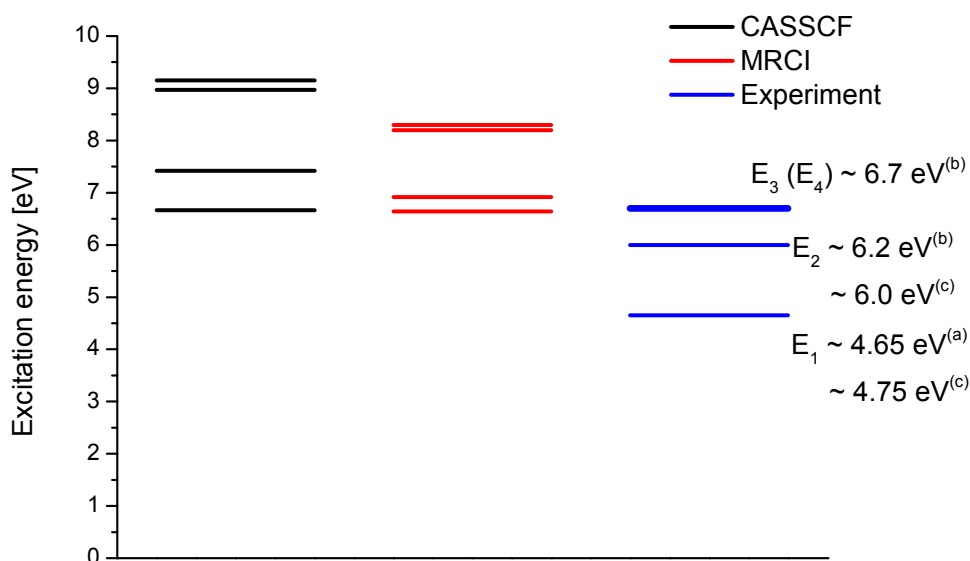
Fig. S3. Comparison of the excitation energies between the computational levels: CASSCF/6-311++G(3df,2p), MRCI/6-311++G(3df,2p) and experimental data[a], [b], [c].

Table S2. Data of the excitation energies calculated by CASSCF/6-311++G(3df,2p), MRCI/6-311++G(3df,2p) and experimental data[a], [b], [c].

	E_1 [eV]	E_2 [eV]	E_3 [eV]	E_4 [eV]
CASSCF(4, 4)	6.63	7.42	8.97	9.15
MRCI	6.64	6.91	8.20	8.30
Exp.	4.65[a]	6.2[b]	6.7[b]	6.7[b]
	4.75[c]	6.0[c]		

References

(a) N. Ginsburg, W.W. Robertson, and F.A. Matsen, J. Chem. Phys., 9, 511 (1946).

(b) M.B. Robin, Higher Excited states of Polyatomic Molecules. (Academia New York, 1975), Vol. 2.

(c) B.D. Mistry, A Handbook of Spectroscopic Data Chemistry (UV, IR, PMR, 13CNMR and Mass Spectroscopy), Oxford Book Company, Jaipur, India, 2009). On pp. 16-17 4.75 eV for S_1, and 6.0 eV for S_2 in Methanol (2%). There is no data for S_3 and S_4.