Supporting information

Computational Details

6-311G** Basis set in Gaussian 09 program package was employed to perform the geometry optimization and energies computation. By using HF (Hartree-Fock) method, the geometry optimization of enol and keto forms of the phototautomers in the ground state (S_0) was obtained. While single-excitation configuration interaction (CIS) method was employed to optimize the geometries in the first singlet excited state (S_1) of the target molecules. The energies of the optimized geometries of S_0 and S_1 states were computed by DFT and TD-DFT (time-dependence DFT) method with B3LYP function at HF and CIS levels respectively such as DFT//HF or TDDFT//CIS (represented the single-point calculation//optimization method). The organic solvent DMF were used as the medium in the theoretical computation.

Synthesis and characterization of C1~C18

General Synthesis Procedue of C1~C6

In a three-necked flask equipped with a magnetic stirrer, coumarin derivatives and 3-(2H-benzotriazol-2-yl)-4-hydroxybenzaldehyde were added into 10 mL ethanol with the molar ratio of 1.2:1. A few drops of piperidine were added into to the above solution. The mixture was heated to 110 °C for overnight, and then the solvent was removed under vacuum. The target molecules were purified by column chromatography using equivoluminal of cyclohexane and dichloromethane as the eluents, which were further recrystallized in dichloromethane.

General Synthesis Procedue of C7~C12

The synthesis of **C7~C12** basically followed the same procedures as described those of **C1~C6**, where 3-(2H-benzotriazol-2-yl)-4-hydroxybenzaldehyde was replaced by 3-(2H-benzotriazol-2-yl)-4-acetoxybenzaldehyde.

General Synthesis Procedue of C13~C18

The synthesis of **C13~C18** basically followed the same procedures as described those of **C1~C6**, where 3-(2H-benzotriazol-2-yl)-4-hydroxybenzaldehyde was replaced by *p*-hydroxybenzaldehyde.

C1, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-6-cyano-2H-chromen-2-one, yellow solid, (yield 45.2%): m.p. 298.1-299.2 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.256-7.273 (d, 1H, Ar-H, J=7.2 Hz), 7.479-7.510 (d, 1H, -CH=, J=12.4 Hz), 7.548-7.573 (m, 2H, Ar-H), 7.840-7.873 (m, 2H, Ar-H), 7.899-7.920 (m, 1H, Ar-H), 8.047-8.070 (m, 2H, Ar-H), 8.083-8.099 (d, J=6.4 Hz, 1H, -CH=), 8.135 (s, 3H, Ar-H), 8.218-8.222 (d, J=1.6 Hz, 1H, Ar-H), 8.630 (s, 1H, -CH=), 11.240 (s, 1H, -OH). IR(cm^{-1}): 3432.0, 3127.7, 3010.3, 2229.9, 1737.9, 1657.9, 1607.0, 1572.2, 1514.0, 1400.4, 1301.1, 1183.3, 975.3, 740.8. Elementary analysis, Anal. Calcd (Found) for $C_{25}H_{14}N_4O_4$, C, 69.12 (69.21), H, 3.25 (3.17), N, 12.90 (12.98).

C2, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-6-chloro-2H-chromen-2-one, saffron yellow powder, (yield 30.3%): m.p. 312.2-313.8 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.247-7.264 (d, 1H, -CH=, J=6.8 Hz), 7.515-7.567 (m, 4H, Ar-H), 7.781-7.799 (m, 1H, Ar-H), 7.820-7.852 (d, 1H, -CH=, J= 12.8 Hz), 7.888-7.909 (m, 1H, Ar-H), 8.050-8.069 (m, 3H, Ar-H), 8.207-8.210 (d, 1H, Ar-H, J=1.2 Hz), 8.571 (s, 1H, -CH=), 11.227 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 116.622, 118.261, 118.891, 119.134, 123.885, 125.346, 126.235, 127.003, 127.653, 127.956, 128.890, 130.112, 131.158, 132.036, 134.546, 143.897, 144.555,

145.987, 146.916, 154.015, 154.800, 158.340, 187.097. IR(cm^{-1}): 3423.2, 3128.2, 2920.6, 2850.5, 1738.7, 1666.1, 1607.7, 1578.2, 1514.2, 1400.1, 1326.7, 1292.5, 1181.7, 1134.5, 1092.6, 983.6, 739.5, Elementary analysis, Anal. Calcd (Found) for $C_{24}H_{14}ClN_3O_4$, C, 64.95 (65.06), H, 3.18 (3.11), N, 9.47 (9.52).

C3, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, pale yellow needle solid, (yield 25.7%): m.p. 256.3-258.0 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.262 (s, 1H, -CH=), 7.373-7.400 (t, 2H, Ar-H), 7.430-7.446 (d, 2H, Ar-H, J=14.4 Hz), 7.528-7.547 (m, 2H, Ar-H), 7.675-7.721 (m, 3H, Ar-H), 7.960-7.981 (m, 3H, Ar-H), 7.988-7.994 (d, 1H, -CH=, J=2.4 Hz), 8.626(s, 1H, -CH=), 8.749 (s, 1H, Ar-H), 11.201 (s, 1H, -OH).^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 116.620, 118.340, 118.701, 119.937, 124.031, 125.897, 126.142, 127.987, 127.046, 127.866, 127.941, 128.445, 130.732, 132.021, 134.456, 143.755, 144.203, 144.253, 146.872, 153.988, 154.791, 158.196, 187.782. IR(cm^{-1}): 3431.6, 3131.4, 3108.7, 2920.6, 2850.5, 1729.1, 1661.2, 1607.8, 1579.5, 1515.0, 1432.2, 1400.1, 1301.5, 1260.4, 1179.7, 973.3, 751.6. Elementary analysis, Anal. Calcd (Found) for $C_{24}H_{15}N_3O_4$, C, 70.41 (70.49), H, 3.69 (3.61), N, 10.26 (10.32).

C4, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-6-methyl-2H-chromen-2-one, yellow powder, (yield 45.4%): m.p. 320.1-321.7 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.215-7.232 (d, 1H , Ar-H, J=6.8 Hz), 7.449-7.481 (s, 1H, -CH=), 7.533-7.545 (m, 2H, Ar-H), 7.700-7.719 (d, 1H, Ar-H, J=7.6 Hz), 7.823-7.890 (m, 2H, Ar-H) 8.031-8.043 (m, 2H, Ar-H), 8.178 (s, 1H, -CH=), 8.498-8.517 (m, 1H, Ar-H), 8.733 (s, 1H, -CH=), 8.892 (s, 1H, Ar-H), 11.190 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 55.334, 115.312, 117.381, 119.800, 119.998, 126.025, 126.874, 127.821, 128.096, 128.974, 130.051, 130.945, 131.912,

133.874, 136.071, 142.98887, 143.921, 145.001, 147.128, 148.912, 157.144, 159.762, 163.208, 186.934. IR(cm^{-1}): 3432.8, 3145.9, 3041.1, 2920.6, 1728.8, 1660.6, 1606.5, 1584.7, 1557.9, 1513.5, 1399.3, 1302.3, 1185.5, 981.7, 834.8, 738.4. Elementary analysis, Anal. Calcd (Found) for $C_{25}H_{17}N_3O_4$, C, 70.91 (71.02), H, 4.05 (3.95), N, 9.92 (9.98).

C5, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-6-oxymethyl-2H-chromen-2-one, deep yellow solid, (yield 40.1%): m.p. 325.6-326.5 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): (s, 3H, -OMe), 7.224-7.245 (d, 1H, -CH=, J=8.4 Hz), 7.304-7.344 (m, 1H, Ar-H), 7.412-7.435 (d, 1H, Ar-H, J=9.6 Hz), 7.469-7.476 (d, 1H, Ar-H, J=2.8 Hz), 7.518-7.584 (m, 3H, Ar-H), 7.767-7.807 (d, 1H, Ar-H, J=16.0 Hz), 7.857-7.879 (d, 1H, Ar-H, J=8.8 Hz), 8.020-8.044 (m, 2H, Ar-H), 8.189-8.191 (d, 1H, -CH=, J=0.8 Hz), 8.560 (s, 1H, -CH=), 11.140 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 187.822， 158.963, 156.215, 154.092, 149.312, 146.731, 144.218, 143.731, 132.026, 127.865, 127.051, 126.405, 123.855, 122.299, 119.261, 118.919, 118.495, 117.758, 112.363, 56.250. IR(cm^{-1}): 3415.1, 3126.5, 3015.9, 2842.1, 1728.2, 1659.0, 1605.7, 1583.3, 1514.9, 1400.3, 1281.3, 1187.1, 1039.4, 956.0, 742.7. Elementary analysis, Anal. Calcd (Found) for $C_{25}H_{17}N_3O_5$, C, 68.33 (68.45), H, 3.90 (3.83), N, 9.56 (9.67).

C6, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl)acryloyl)-7-oxymethyl-2H-chromen-2-one, deep yellow solid, (yield 35.6%): m.p. 327.8-328.4 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 3.879 (s, 3H, -OMe), 7.000-7.018 (m, 1H, Ar-H), 7.074 (s, 1H, Ar-H), 7.215-7.230 (d, 1H, -CH=, J=6.0 Hz), 7.518-7.532 (m, 2H, Ar-H), 7.659-7.686 (d, 1H, Ar-H, J=6.8 Hz), 7.740-7.766 (d, 1H, Ar-H, J=10.4 Hz), 7.839-7.854 (m, 2H, -CH=), 8.021-8.037 (m, 2H, Ar-H), 8.163 (s, 1H, -CH=), 8.644 (s, 1H, Ar-H), 11.157 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 186.910, 165.091, 159.272, 157.345, 148.064, 144.221, 142.765, 132.026, 128.484, 127.861, 126.756,

123.768, 121.931, 118.893, 118.506, 113.903, 112.502, 100.810, 56.733. IR(cm^{-1}): 3426.9, 3129.2, 3027.1, 1728.3, 1656.2, 1604.5, 1504.8, 1400.2, 1247.4, 1190.2, 1165.0, 1070.2, 1023.0, 974.4, 740.8. Elementary analysis, Anal. Calcd (Found) for $C_{25}H_{17}N_3O_5$, C, 68.33 (68.41), H, 3.90 (3.82), N, 9.56 (9.61).

C7, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-6-cyano-2H-chromen-2-one, deep yellow solid (yeild: 35.3%): m.p. 252.3-253.0 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.349 (s, 3H, -$COCH_3$), 7.373-7.394 (d, 1H, -CH=, J=8.4 Hz), 7.446-7.467 (m, 2H, Ar-H), 7.607-7.627 (d, 1H, Ar-H, J=8.0 Hz), 7.689 (s, 1H, Ar-H), 7.792-7.823 (t, 2H, Ar-H, J=6.2 Hz), 7.937 (s, 3H, Ar-H), 8.460 (s, 1H, Ar-H), 8.563 (s, 1H, -CH=). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 195.932, 188.147, 169.109, 157.926, 154.127, 145.184, 144.778, 144.653, 143.253, 133.989, 133.222, 131.633, 130.900, 128.673, 128.450, 128.021, 126.936, 126.461, 125.982, 122.697, 120.777, 118.687, 118.126, 115.319, 21.143. IR(cm^{-1}): 3127.9, 3015.9, 2231.3, 1740.6, 1662.8, 1616.5, 1508.4, 1400.6, 1221.2, 1178.8, 1146.4, 1067.0, 960.7, 741.6. Elementary analysis, Anal. Calcd (Found) for $C_{27}H_{16}N_4O_5$, C, 68.07 (68.12), H, 3.38 (3.31), N, 11.76 (11.83).

C8, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-6-chloro-2H-chromen-2-one, pale yellow (yield: 20.6%): m.p. 300.3-301.9 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.375 (s, 3H, -$COCH_3$), 7.381-7.395 (d, 1H, -CH=, J=1.6 Hz), 7.395-7.411 (d, 1H, Ar-H, J=6.4 Hz), 7.472-7.491 (m, 2H, Ar-H), 7.630-7.652 (m, 1H, Ar-H), 7.691-7.695 (d, 1H, Ar-H, J=1.6 Hz), 7.837-7.857 (m, 1H, Ar-H), 7.927-7.968 (d, 1H, -CH=, J=16.4 Hz), 7.974-8.028 (m, 3H, Ar-H), 8.479-8.482 (d, 1H, Ar-H, J=1.6 Hz), 8.544 (s, 1H, -CH=). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 187.995, 169.114, 158.418, 153.492, 145.870, 144.785, 144.607, 142.711, 134.053, 133.989, 130.910, 129.615, 129.023, 128.443, 127.052, 126.973, 126.445, 125.873, 120.208,

118.733, 118.694. 21.141. IR(cm^{-1}): 3127.4, 3015.9, 2853.5, 1768.7, 1724.2, 1660.2, 1610.4, 1551.9, 1506.6 1401.2, 1297.5, 1203.2, 1180.9, 1067.9, 988.1, 744.6. Elementary analysis, Anal. Calcd (Found) for $C_{26}H_{16}ClN_3O_5$, C, 64.27 (64.35), H, 3.32 (3.27), N, 8.65(8.73).

C9, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-2H-chromen-2-one, pale yellow powder (yield 30.2%): m.p. 287.1-282.2 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.374(s, 3H, -$COCH_3$), 7.287-7.408(m, 2H, Ar-H), 7.430-7.447 (d, 1H, -CH=, J=6.8 Hz), 7.464-7.494 (m, 2H, Ar-H), 4.686-7.727 (m, 2H, Ar-H), 7.843-7.864 (m, 1H, Ar-H), 7.923-7.980 (m, 3H, Ar-H), 8.043-8.074 (d, 1H, -CH=, J=12.0 Hz), 8.478-8.482 (d, 1H, -CH=, J=1.6 Hz), 8.645 (s, 1H, -CH=). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 187.954, 169.120, 158.822, 154.902, 147.387, 144.786, 144.553, 142.196, 134.690, 134.139, 133.234, 130.938, 130.882, 128.430, 127.054, 126.409, 125.793, 125.423, 118.820, 228.696, 116.683, 26.775, 21.177. IR(cm^{-1}): 3126.2, 2927.4, 1765.5, 1720.7, 1664.8, 1560.8, 1506.8, 1400.7, 1296.3, 1205.3, 1187.8, 1069.8, 987.1, 759.5, 746.2. Elementary analysis, Anal. Calcd (Found) for $C_{26}H_{17}N_3O_5$, C, 69.18 (69.23), H, 3.80 (3.72), N, 9.31(9.39).

C10, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-6-methyl-2H-chromen-2-one, yellow powder (yield 20.1%): m.p. 305.3-306.8 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.281 (s, 3H, -$COCH_3$), 2.399 (s, 3H, -ArCH3), 7.406-7.422 (d, 1H, Ar-H, J=6.4 Hz), 7.555-7.560 (d, 1H, -CH=, J=2.0 Hz), 7.568-7.605 (m, 3H, Ar-H), 7.735-7.787 (t, 2H, Ar-H, J=20.8 Hz), 7.884-7.916 (d, 1H, Ar-H, J=12.8 Hz), 8.056-8.066 (d, 2H, Ar-H, J=4.0 Hz), 8.072 (s, 1H, -CH=), 8.525 (s, 1H, -CH=), 8.623 (s, 1H, Ar-H). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 7.957, 169.114, 158.978, 153.104, 147.350, 144.783, 144.536, 142.054, 135.642, 134.723, 134.142, 133.227, 130.920, 130.329, 128.422, 127.081, 126.400, 125.845, 125.767, 118.694, 118.666,

118.547, 116.458, 21.135, 20.655. IR(cm^{-1}): 3126.5, 2923.1, 2852.3, 1763.9, 1730.6, 1661.9, 1617.1, 1579.4, 1508.6, 1400.4,1325.5, 1277.6, 1182.5, 1137.7, 2067.0, 985.6, 742.9. Elementary analysis, Anal. Calcd (Found) for $C_{27}H_{19}N_3O_5$, C, 69.67 (69.77), H, 4.11 (4.05), Cl, N, 9.03(9.11).

C11, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-6-oxymethyl-2H-chromen-2-one, pale yellow powder (yield 25.3%): m.p. 285.9-287.4 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.337 (s, 3H, -$COCH_3$), 3.925 (s, 3H, -OMe), 6.683(s, 1H, Ar-H) 6.906-6.933 (d, 1H, -CH=, J=10.0 Hz), 7.349-7.370 (d, 1H, Ar-H, J=8.4 Hz), 7.433-7.457 (m, 2H, Ar-H), 7.568-7.590 (d, 1H, Ar-H, J=8.8 Hz), 7.813-7.870 (t, 1H, Ar-H, J=11.4 Hz), 7.910-7.947 (m, 3H, Ar-H), 8.076-8.115 (d, 1H, -CH=, J=15.6 Hz), 8.443 (s, 1H, -CH=), 8.610 (s, 1H, Ar-H). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 187.052, 169.123, 165.270, 159.289, 157.476, 148.517, 144.788, 144.710, 144.455, 141.229, 138.348, 134.270, 132.617, 132.430, 130.952, 128.411, 128.299, 127.006, 126.387, 125.535, 118.705, 118.663, 113.995, 100.842, 100.780, 56.764, 21.133. IR(cm^{-1}): 3126.5, 3015.9, 2926.2, 2850.5, 1763.1, 1730.4, 1608.4, 1578.4, 1506.7, 1400.6, 1279.9, 1182.4, 1130.6, 1068.4, 1036.5, 993.2, 743.4. Elementary analysis, Anal. Calcd (Found) for $C_{27}H_{19}N_3O_6$, C, 67.36 (67.46), H, 3.98 (3.89), N, 8.73 (8.79)

C12, 3-(3-(3-(2H-Benzotriazol-2-yl)-4-acetoxyphenyl)acryloyl)-7-oxymethyl -2H-chromen-2-one, pale yellow powder (yield 20.8%): m.p. 290.1-290.9 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.341 (s, 3H, -$COCH_3$), 3.878 (s, 3H, -OMe), 7.066-7.073 (d, 1H, Ar-H, J=2.8 Hz), 7.237-7.267 (d, 1H, -CH=, J=12.0 Hz), 7.327-7.377 (m, 2H, Ar-H), 7.435-7.459 (m, 2H, Ar-H), 7.807-7.833 (m, 1H, Ar-H), 7.881-7.946 (m, 3H, Ar-H), 8.016-8.056 (d, 1H, -CH=, J=16.0 Hz), 8.445-8.450 (d, 1H, Ar-H, J=2.0 Hz), 8.561 (s, 1H, -CH=). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 188.668, 187.049, 169.120, 165.269, 159.288, 157.477, 148.514, 144.789, 141.226, 132.429, 130.948,

128.409, 128.299, 127.006, 126.387, 125.535, 118.704, 118.661, 118.523, 113.994, 112.488, 100.843, 56.764, 21.133. IR(cm^{-1}): 3126.6, 3015.9, 2926.2, 2856.1, 1783.9, 1736.4, 1656.9, 1615.3, 1578.5, 1508.3, 1400.9, 1293.3, 1220.6, 1185.4, 1160.0, 1066.6, 1028.5, 982.1, 737.0. Elementary analysis, Anal. Calcd (Found) for $C_{27}H_{19}N_3O_6$, C, 67.36 (67.43), H, 3.98 (3.92), N, 8.73 (8.84).

C13, 6-Cyano-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, deep yellow solid (yield 20.7%): m.p. 237.3-238.1 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 6.835-6.855 (d, 1H, Ar-H, J=8.0 Hz), 7.245-7.267 (d, 2H, Ar-H, J=8.8 Hz), 7.411-7.743 (d, 1H, -CH=, J=12.8 Hz), 7.621-7.654 (m, 2H, Ar-H), 7.664-7.695 (d, 1H, -CH=, J=12.4 Hz), 7.801-7.823 (m, 1H, Ar-H), 8.554 (s, 1H, -CH=), 10.219 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 185.434 162.575, 160.434, 158.964, 143.549, 131.109, 128.459, 127.544, 121.247, 115.465, 114.867, 102.477. Elementary analysis, Anal. Calcd (Found) for $C_{19}H_{11}NO_4$, C, 71.92 (72.03), H, 3.49 (3.41), N, 4.41 (4.50).

C14, 6-Chloro-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, saffron yellow powder, (yield 36.5%): m.p. 232.1-232.5 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 6.841-6.859 (d, 1H, Ar-H, J=7.2 Hz), 7.397-7.429 (d, 1H, -CH=, J=12.8 Hz), 7.528-7.546 (d, 1H, Ar-H, J=7.2 Hz), 7.612-7.629 (d, 2H, Ar-H, J=6.8 Hz), 7.698-7.730 (d, 1H, -CH=, J=12.8 HZ), 7.767-7.784 (m, 1H, Ar-H), 8.050-8.055 (d, 1H, Ar-H, J=2.0 Hz), 8.553 (s, 1H, -CH=), 10.203 (s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 186.375, 158.575, 156.486, 144.576, 130.756, 129.001, 128.343, 127.876, 122.965, 118.436, 115.383, 110.874. Elementary analysis, Anal. Calcd (Found) for $C_{18}H_{11}ClO_4$, C, 66.17 (66.28), H, 3.39 (3.30).

C15, 3-(3-(4-Hydroxyphenyl)acryloyl)-2H-chromen-2-one, yellow powder (yield 18.6%): m.p.

233.9-235.1°C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 6.837-6.857 (s, 1H, Ar-H), 7.434-7.487 (m, 2H, Ar-H), 7.485-7.502 (d, 1H, -CH=, J=6.8 Hz), 7.613-7.630 (d, 2H, Ar-H, J=6.8 Hz), 7.688-7.719 (d, 1H, -CH=, J=12.4 Hz), 7.928-7.946 (m, 1H, Ar-H), 8.625 (s, 1H, -CH=), 10.133(s, 1H, -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 186.024, 159.746, 155.912, 143.193, 129.943, 128.873, 128.124, 127.013, 123.012, 118.049, 114.847. Elementary analysis, Anal. Calcd (Found) for $C_{18}H_{12}O_4$, C, 73.97 (74.08), H, 4.14 (4.05).

C16, 6-Methyl-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, deep yellow powder (yield 40.1%): m.p. 238.3-240.0 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 2.390 (s, 3H. Ar-CH3), 6.836-6.853 (d, 1H, Ar-H, J=6.8 Hz), 7.381-7.398 (d, 1H, Ar-H, J=6.8 Hz), 7.442-7.474 (d, 1H, -CH=, J=12.8 Hz), 7.553-7.573 (m, 1H, Ar-H), 7.605-7.622 (d, 2H, Ar-H, J=6.8 Hz), 7.670-7.702 (d, 1H, -CH=, J=12.8 Hz), 7.710 (s, 1H, Ar-H) 8.543 (s, 1H, -CH=), 10.163 (s, 1H -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 186.603, 160.367, 143.193, 132.955, 130.764, 127.984, 127.013, 120.984, 118.283, 114.932, 110.83, 56.038. Elementary analysis, Anal. Calcd (Found) for $C_{19}H_{14}O_4$, C, 74.50 (74.59), H, 4.61 (4.52).

C17, 6-Oxymethyl-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, yellow solid (yield 45.2%): m.p. 245.7-245.5 °C. ^{1}H-NMR (400 MHz, DMSO-*d6*) δ (ppm): 3.871 (s, 3H, -OMe), 6.812-6.825 (d, 1H, Ar-H, J=5.2 Hz), 7.412-7.445 (d, 1H, -CH=, J=12.8 Hz), 7.486-7.501 (m, 2H, Ar-H), 7.532-7.545 (d, 2H, Ar-H, J=5.2 Hz), 7.634-7.661 (d, 1H, -CH=, J=10.8 Hz), 7.712-7.730 (d, 2H, Ar-H, J=7.2 Hz), 8.550 (s, 1H, -CH=), 10.151 (s, 1H -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 185.484, 158.443, 144.586, 131.293, 130.484, 129.002, 127.983, 120.938, 118.484, 115.938, 113.938, 57.001. Elementary analysis, Anal. Calcd (Found) for $C_{19}H_{14}O_5$, C, 70.80 (70.89), H, 4.38 (4.29).

C18, 7-Methyl-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one, yellow solid (yield 45.6%): m.p. 244.1-244.9°C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 3.839 (s, 3H, -OMe), 6.766-6.778 (d, 1H, Ar-H, J=4.8 Hz), 7.239-7.265 (m, 2H, Ar-H), 7.498-7.530(d, 1H, -CH=, J=12.8 Hz), 7.552-7.570 (d, 1H, Ar-H, J=7.8 Hz), 7.601-7.633 (d, 1H, -CH=, J=12.8 Hz), 7.721-7.740 (m, 2H, Ar-H), 8.496 (s, 1H, -CH=), 10.146 (s, 1H -OH). ^{13}C-NMR (101-MHz, DMSO-d_6) δ (ppm): 18.038, 159.98, 143.938, 130.937, 129.026, 128.837, 128.132, 125.238, 120.736, 118.836, 118.238, 115.938, 57.541. Elementary analysis, Anal. Calcd (Found) for $C_{19}H_{14}O_5$, C, 70.80 (70.87), H, 4.38 (4.30).

Figures S1~S9

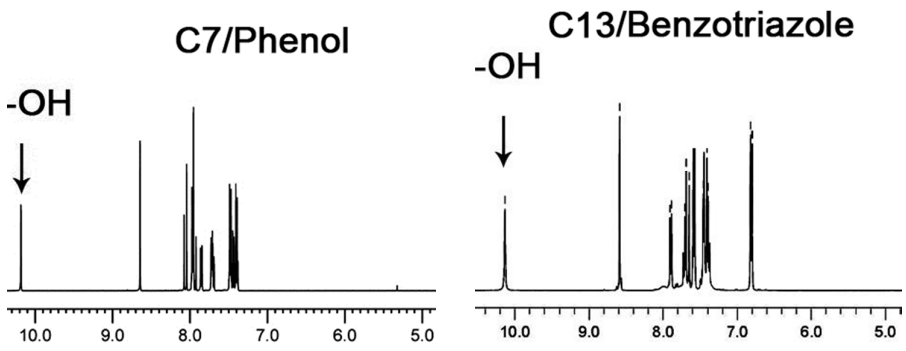


Figure S1 ^{1}H-NMR spectra of equal molar mixture of **C7**/phenol and **C13**/benzotriazole in DMSO-D_6 (500 MHz)

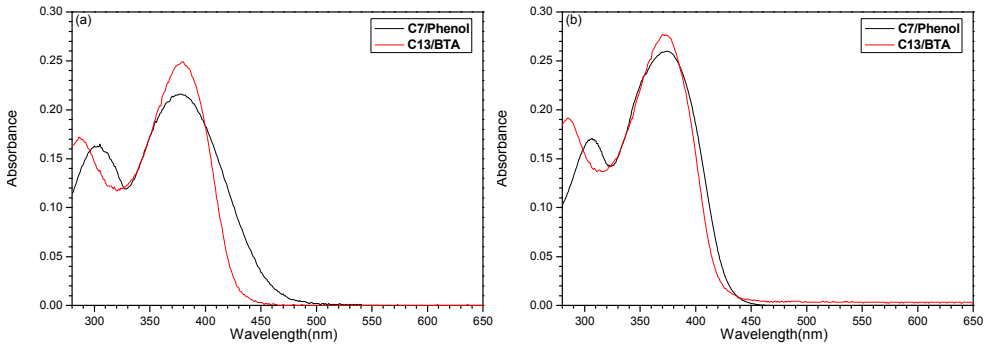


Figure S2 Linear UV/visible absorption of equal molar mixture of **C7**/phenol and **C13**/benzotriazole in 1, 4-diaxane (a) and DMF (b), the concentrations are 1×10^{-5} mol/L

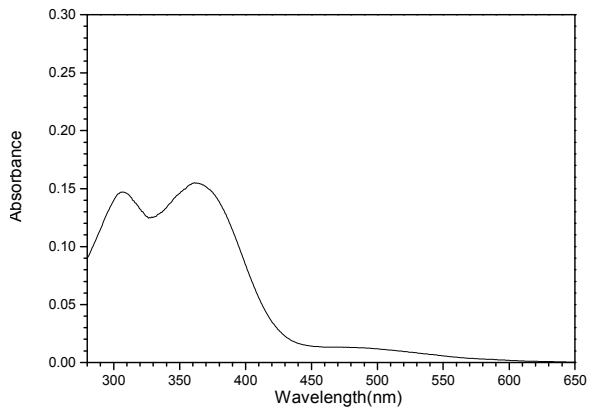


Figure S3 Linear UV/visible absorption of **C1** in methanol, the concentration of **C1** is 1×10^{-5} mol/L

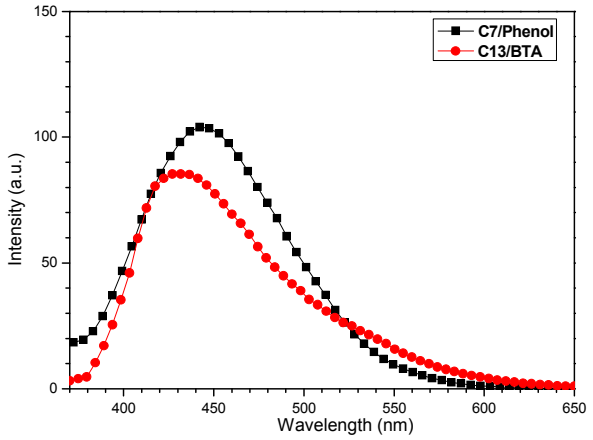


Figure S4 Linear fluorescence emission spectra of equal molar of **C7**/phenol and **C13**/benzotriazole in DMF, the concentrations are 1×10^{-5} mol/L

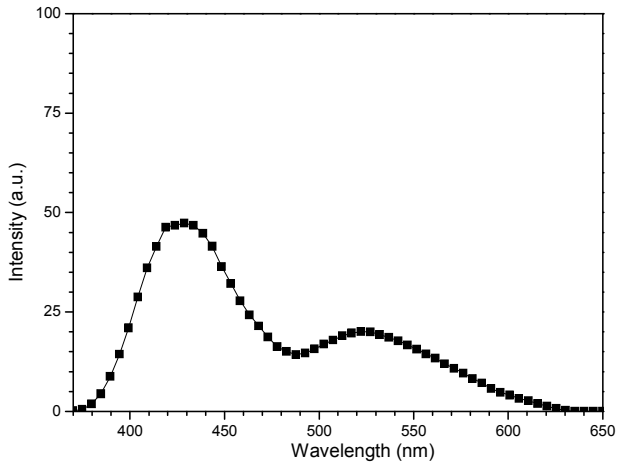


Figure S5 Linear fluorescence emission spectra of **C1** in methanol, the concentration of **C1** is 1×10^{-5} mol/L, excited wavelength: 350 nm

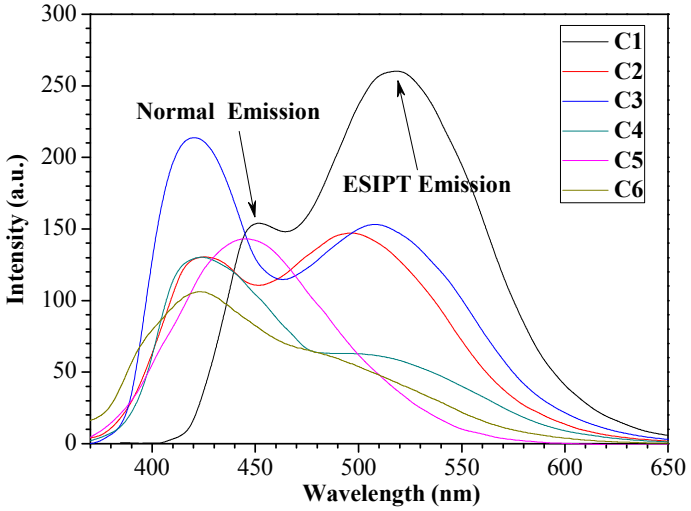


Figure S6. Linear fluorescence emission spectra of **C1**~**C6** in DMF, the concentration is 1×10^{-5} mol/L, excited wavelength: 350 nm

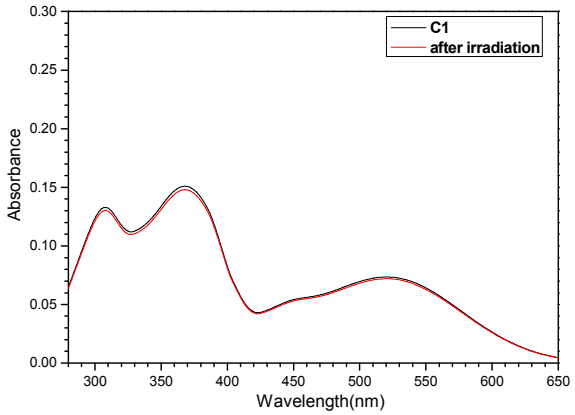


Figure S7 UV/visible absorption spectra of **C1** and after 2 hours of UV irradiation in DMF

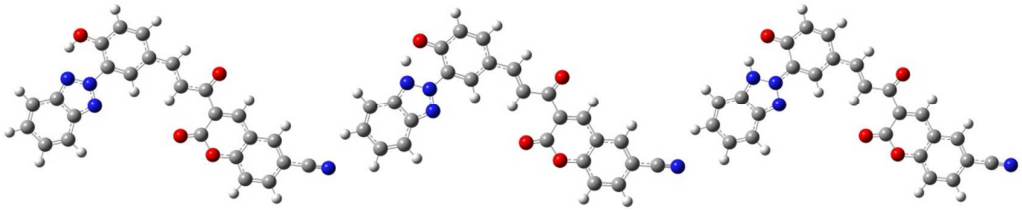
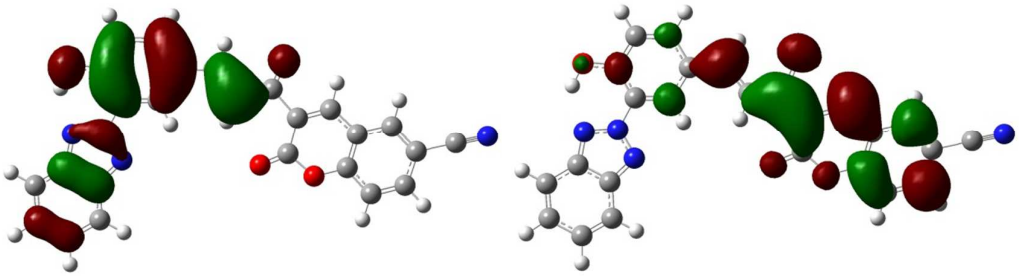
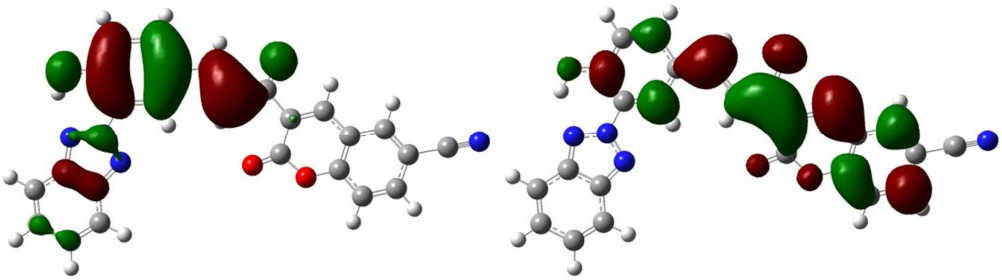


Figure S8 Optimized molecular geometries of enol, TS and keto forms in excited state of **C1**



C1 HOMO LUMO



C1* HOMO LUMO

Figure S9. HOMO and LUMO orbitals in the ground and excited states of **C1**

Tables S1~S10

Table S1 The UV spectral parameters of **C1**, **C7**and **C13** in various solvents, $\lambda_{a,max}$: the absorption maximum (nm), ε_{max}: the maximal molar extinction coefficient (10^4 cm^{-1}●mol^{-1}●L)

Solvents	C1		C7		C13	
	$\lambda_{a,max}$	ε_{max}	$\lambda_{a,max}$	ε_{max}	$\lambda_{a,max}$	ε_{max}
1,4-Dioxane	352	1.464	357	1.050	365	2.753
THF	346	1.662	355	0.905	368	2.061
EtOAc	355	1.723	365	1.234	359	1.878
DCM	359	1.215	358	1.059	360	2.757
Acetone	355	1.758	355	1.694	359	3.384
MeCN	349	1.375	363	1.701	350	2.148
DMSO	346	1.512	353	1.512	359	2.374
DMF	365	1.652	360	1.445	366	2.414
MeOH	362	1.550	368	1.254	362	1.972
EtOH	359	1.311	366	1.127	370	1.951
PrOH	359	1.618	367	1.253	372	2.514
BuOH	362	1.267	365	1.081	373	2.280

Table S2 The fluorescence spectral parameters of **C1**, **C7**and **C13** in various solvents, $\lambda_{f,max}$: the emission maximum (nm), Φ: the fluorescence quantum yield

Solvents	C1		C7		C13	
	$\lambda_{f,max}$	Φ	$\lambda_{f,max}$	Φ	$\lambda_{f,max}$	Φ
1,4-Dioxane	441	0.0528	433	0.0624	439	0.0536
THF	429	0.0131	383	0.0651	442	0.0692
EtOAc	424	0.0524	404	0.0589	441	0.0843
DCM	428	0.0194	398	0.0290	442	0.0612
Acetone	432	0.0442	430	0.0814	442	0.0418
MeCN	436	0.0096	431	0.0235	442	0.0487
DMSO	405, 515	0.0361	423	0.1249	434	0.0624
DMF	450, 519	0.0503	431	0.1038	445	0.0299
MeOH	436, 523	0.0195	432	0.0171	445	0.0205
EtOH	427, 522	0.0675	425	0.0812	441	0.0495
PrOH	429, 522	0.0437	417	0.0531	442	0.0478
BuOH	426, 520	0.0372	407	0.0497	442	0.0338

Table S3 Two-photon cross-sections (GM, 1GM=10^{-50}●cm●s^{-1}●$photon^{-1}$) of the dyads under 730 nm femtosecond laser irradiation in DMF solution

Target Dyads	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Two-photon Cross-sections	139.6	127.1	110.7	105.0	89.6	97.2
Reference Dyads	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
Two-photon Cross-sections	12.8	10.0	11.9	9.0	9.1	5.8

Table S4 Photobleaching rates (ν/h^{-1}) of reference molecules studied in this work in various solvents with saturated air under UV light irradiation

ν	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
DMF	9.76	10.83	11.87	13.79	13.61	11.98
1,4-dioxane	10.22	11.21	12.32	13.12	13.19	12.65
Methanol	10.28	9.98	10.65	12.76	12.19	12.98
ν	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**
DMF	13.44	13.87	13.79	14.54	14.31	14.32
1,4-dioxane	13.43	13.76	13.89	14.01	14.11	14.00
Methanol	13.76	13.98	12.97	13.87	14.09	14.76

Table S5 Photobleaching rates (*v*/h^{-1}) of target dyads in various solvents with saturated oxygen under UV light irradiation

v	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
DMF	6.54	6.94	7.01	8.96	13.87	9.17
1, 4-dioxane	18.12	18.96	19.06	20.65	24.86	21.43
Methanol	13.58	14.04	14.76	15.87	19.76	16.08

Table S6 Photobleaching rates (ν/h^{-1}) of reference molecules studied in this work in various solvents with saturated oxygen under UV light irradiation

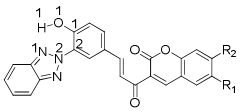
ν	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
DMF	26.68	27.97	30.18	34.25	33.87	30.41
1,4-dioxane	25.70	28.78	31.13	32.83	32.98	31.83
Methanol	26.81	26.17	27.59	32.07	30.86	32.53
ν	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**
DMF	30.36	31.13	30.99	32.35	31.93	31.95
1,4-dioxane	30.34	30.93	31.17	31.39	31.57	31.37
Methanol	30.93	31.33	29.50	31.13	31.53	32.75

Table S7 Photobleaching rates (ν/h^{-1}) of reference molecules studied in this work in various solvents under 730 nmnear-IR laser

ν	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**

DMF	19.34	19.97	19.56	19.16	20.18	20.29
1,4-dioxane	19.45	20.01	19.81	18.92	20.17	19.59
Methanol	18.09	19.26	19.89	20.15	20.65	20.43
ν	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**
DMF	21.89	22.93	22.95	23.76	23.91	22.35
1,4-dioxane	22.09	23.65	22.97	23.83	24.01	22.79
Methanol	23.01	23.31	23.52	23.97	23.91	23.12

Table S8 Important bond lengths (Å) and dihedral angel (°) associated with ESIPT of **C1** and **C4** (enol, enol*, keto* and transition state) in the ground and excited states



Structural parameters	C1				C4			
	E	E*	TS*	K*	E	E*	TS	K*
O-H(Å)	0.9509	0.9563	1.1960	1.8459	0.9509	0.9558	1.2064	1.8430
N-H(Å)	1.8691	1.8313	1.2417	1.0021	1.8693	1.8333	1.2513	1.0023
O-N(Å)	2.6673	2.6384	2.3575	2.5952	2.6678	2.6401	2.3654	2.5943
∠C1O1H1N1(°)	-0.1548	-0.0270	-0.0004	0.0329	0.0142	0.1104	0.0043	0.0483
∠C1C2N2N1(°)	-0.3996	-0.0451	-0.0027	0.4573	0.0104	-0.2043	0.0063	0.4257

Table S9 The energy barriers (kJ/mol) of phototautomerization of the target dyads **C1~C6** in the excited states

Target Dyads	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Energy Barrier	8.34	9.23	9.56	14.98	23.23	16.85

Table S10 Mulliken charge of N and O atom in enol forms of target dyads in the ground state and the excited state

Compounds	Mulliken charge in S_0		Mulliken charge in S_1	
	N	O	N	O
C1	-0.462	-0.667	-0.476	-0.651
C2	-0.462	-0.668	-0.474	-0.654
C3	-0.463	-0.669	-0.473	-0.656
C4	-0.463	-0.666	-0.472	-0.655
C5	-0.463	-0.669	-0.473	-0.658
C6	-0.463	-0.669	-0.471	-0.660