Electronic Supporting Information

Photoisomerization of the Cyanoacrylic Acid Acceptor Group –

A Potential Problem for Organic Dyes in Solar Cells

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Synthesis of L0Br

Note: Due to the light sensitive nature of the products, the entire procedure was carried out in a dark room using a yellow light bulb as the only light source.
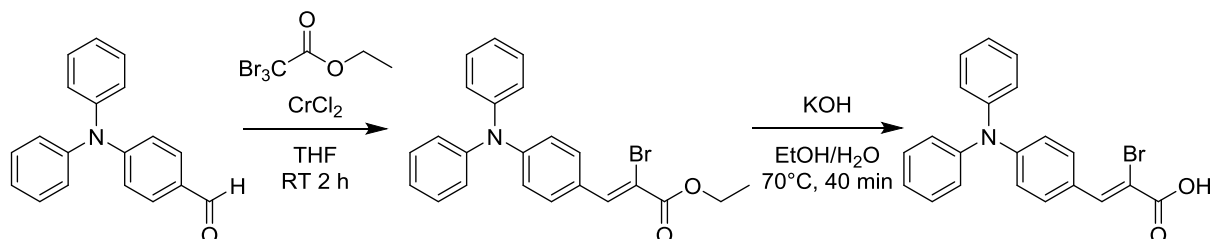
Ethyl (Z)-2-bromo-3-(4-(diphenylamino)phenyl)acrylate (**EtL0Br**). A solution of 4-(diphenylamino)benzaldehyde (273 mg, 1 mmol) and ethyl 2,2,2-tribromoacetate (147 µl, 1.1 mmol) in dry THF (8 ml) was added to a stirred suspension of $CrCl_2$ (0.737 g, 6 mmol) in dry THF (2 ml) under a nitrogen protecting atmosphere at room temperature. Heat was evolved in the reaction, causing the temperature of the solution to rise to 34°C. The mixture was stirred for 2 h and then quenched by the addition of 50 ml H_2O. The quenched reaction mixture was extracted with DCM (3 x 50 ml) and the combined extracts were washed with 30 ml H_2O + 20 ml NH_4Cl (sat). Solvent removal *in vacuo* followed by flash chromatography over SiO_2 (DCM/Pentane 1:1) gave **EtL0Br** (277 mg, 66%) as a yellow solid. ^{1}H NMR (500 MHz, Acetone-d6) δ 8.20 (s, 1H), 7.92 (d, J = 8.8 Hz, 2H), 7.39 (m, 4H), 7.19 (m, 6H), 7.00 (d, J = 8.9 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 163.93, 151.01, 147.70, 140.90, 133.06, 130.69, 126.98, 126.77, 125.56, 120.98, 110.31, 63.14, 14.60.

(Z)-2-bromo-3-(4-(diphenylamino)phenyl)acrylic acid (**L0Br**). An aqueous solution of KOH (1.3 M, 5 ml) was added to a stirred solution of **EtL0Br** (277 mg, 656 µmol) in EtOH (12 ml). The reaction mixture was heated to 70°C for 20 min and then allowed to cool. The reaction mixture was acidified by the addition of HCl (1M, 15 ml) after which the product precipitated. The suspension was filtrated and the residue was washed with a generous amount of water. The residue was finally dried *in vacuo* to yield **L0Br** (208 mg, 80%) as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d6) δ 13.39 (br, 1H), 8.13 (s, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 7.9 Hz, 4H), 7.15 (m, 6H), 6.91 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.46, 149.40, 146.25, 139.46, 132.09, 130.01, 125.78, 125.68, 124.73, 119.86, 110.88. Elemental analysis: Calculated for $C_{21}H_{16}BrNO_2$: C, 64.53; H, 4.21, N, 3.45%; Found: C, 64.58; H, 4.14; N, 3.47%.

Spectroscopy

UV/vis spectrophotometry. Absorption spectra were recorded on a Varian Cary 5000 in a 1 cm quartz cuvette with background correction.

Irradiation of L0(Br) was carried out using the light of a Xe-lamp inside the Horiba Jobin Yvon Fluorolog 3 (Model FL3-222) with 5 nm slit width. The 1 cm quartz cell was stirred during irradiation.

Time-Correlated Single Photon Counting (TCSPC). The setup has been described in detail earlier.[12]

ZrO_2 films on glass were prepared as described previously.[12]

NMR spectroscopy. ^{1}H and ^{13}C NMR were recorded on a Bruker spectrometer at 500 and 125 MHz, respectively using the residual solvent signals as internal standards.

Quantum Chemical Calculations

Calculations were made using the Gaussian09 program, version A.02. All calculations were made using the hybrid

density functional B3LYP with the Cambridge long-range correction (cam-B3LYP) and basis sets of 6-311G type with amended diffuse and polarization functions. The L0 and L0Br molecules were geometrically optimized and the *trans* configuration of formal C_1 symmetry found to represent the global energy minimum. The data for the S_0 state were obtained as the singlet ground state. The data for the S_1 and T_1 states were obtained from time-dependent calculations. The dihedral angle of the cyano (bromo) acrylic acid group in the *trans* configuration of the S_0 state was found to be essentially planar, deviating by <0.1° for both dye molecules. Optimization of the *cis* configuration rendered optimal dihedral angles very close to 180°, deviating by <1°.

The potential energy map (PEM) of rotation around the cyano (bromo) acrylic acid double bond was made without relaxation. The reason is that *intra*-molecular hydrogen bonding gives a sling-shot effect making estimates of the rotational barrier heights less reliable and the results would also be directionally dependent. The main features of the PEM are expected to be properly modelled also using a non-relaxed calculational strategy. The PEMs for L0 and L0Br are given in Fig. S1. The apparent barriers at 180° are the results of the non-relaxed calculational strategy rendering a steric obstruction between a hydrogen atom of the phenyl group and an oxygen atom of the carboxylic group. The optimized structures of the *cis* configurations mentioned above clearly show that such a steric hindrance would be absent in a relaxed PEM.

The full Gaussian09 reference is as follows:

Gaussian09 (v. A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc., Wallingford CT, **2009**.
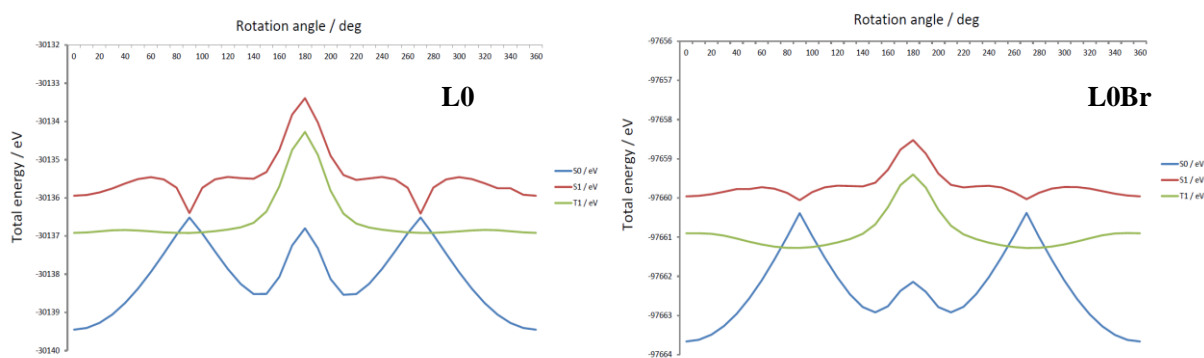

Fig. S1 PEMs for L0 (left) and L0Br (right) obtained through non-relaxed scans in steps of 10° for the S_0, S_1 and T_1 states.
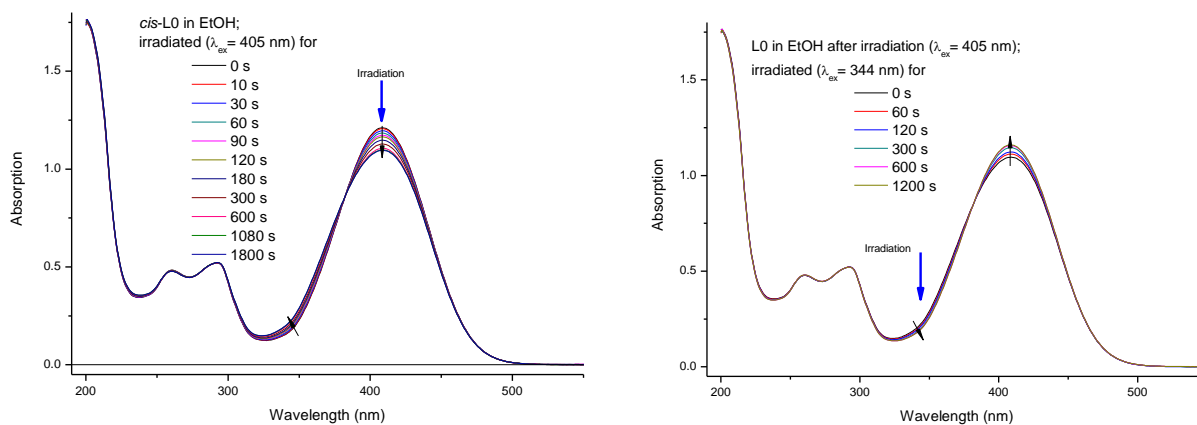
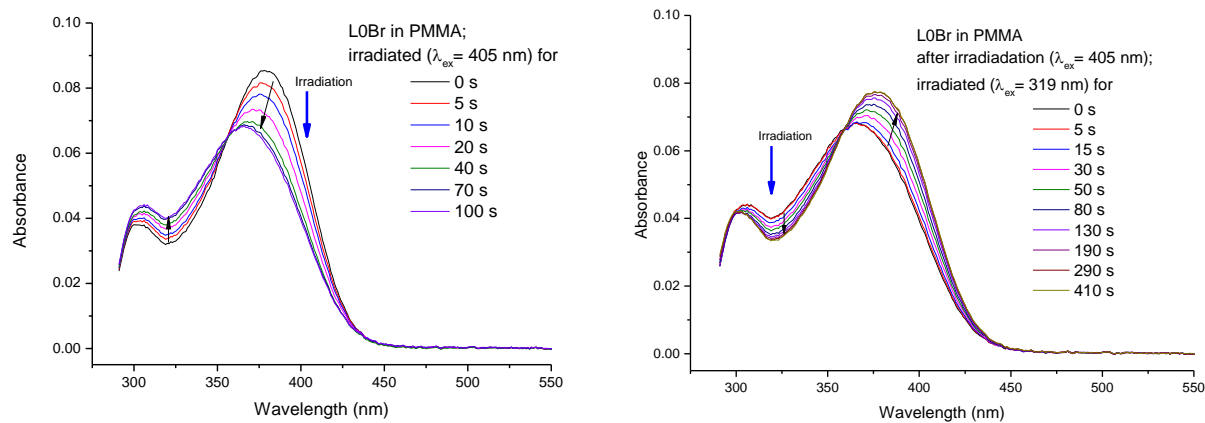**Fig. S2** UV/vis-spectra of L0 in ethanol upon irradiation at 405 nm (left) and 344 nm (right)

Fig. S3 UV/vis-spectra of L0Br in solid PMMA matrix upon irradiation at 405 nm (left) and 319 nm (right)
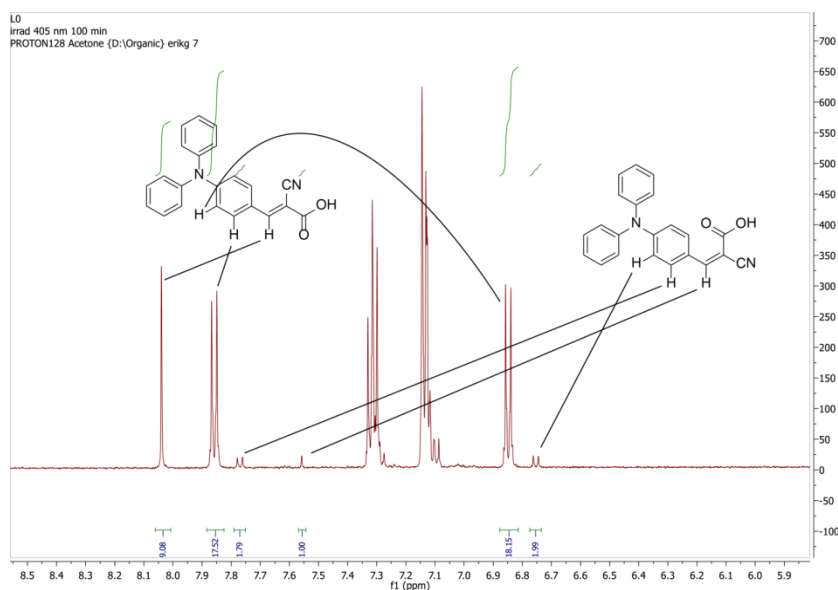

Fig. S4 ^{1}H-NMR peak assigment of L0 in acetone solution after 100 min irradiation by a 405 nm LED, clearly identifying both the initial *trans* isomer and the converted *cis* isomer.
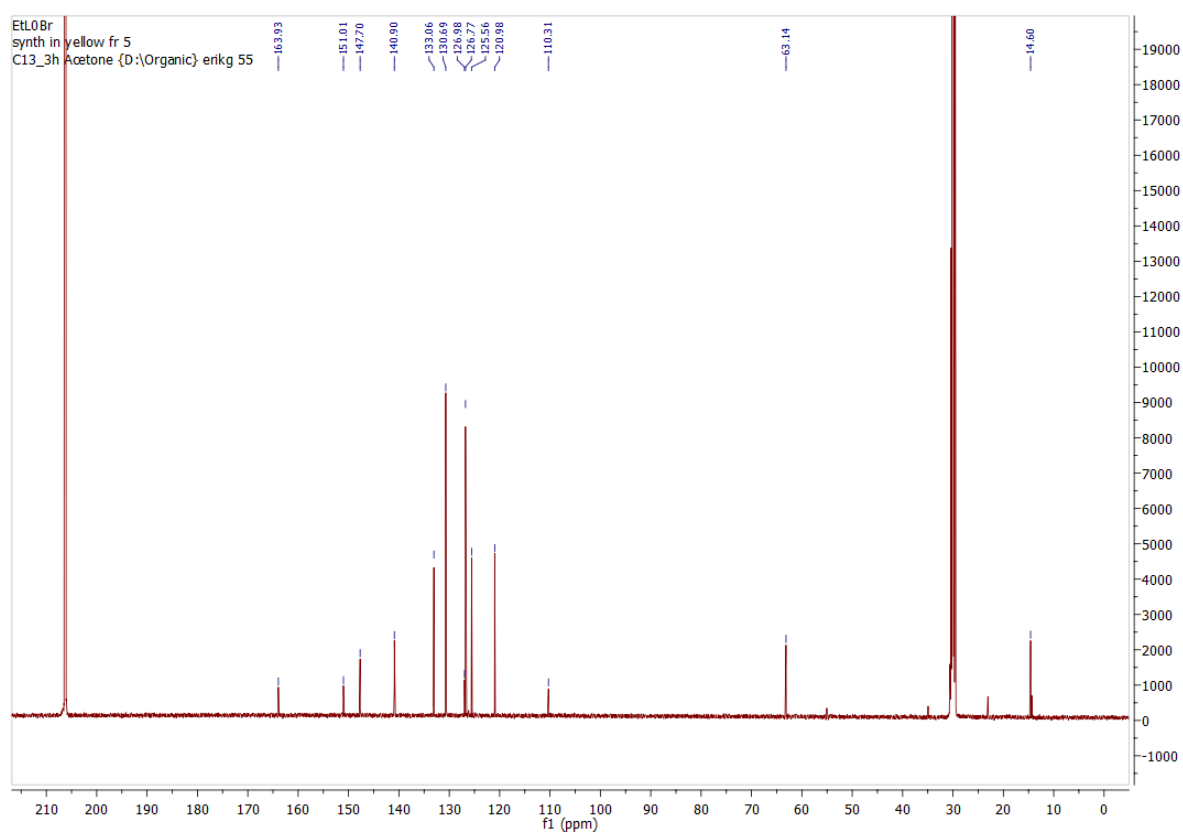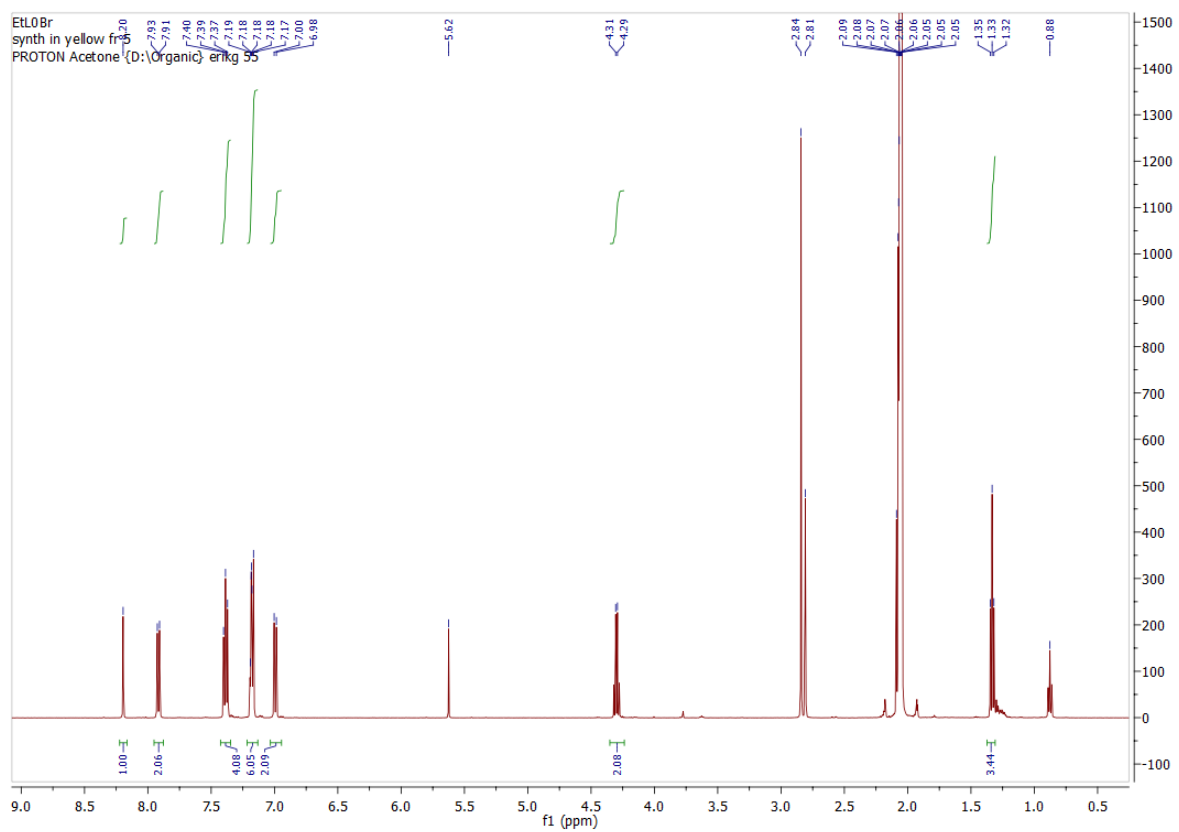
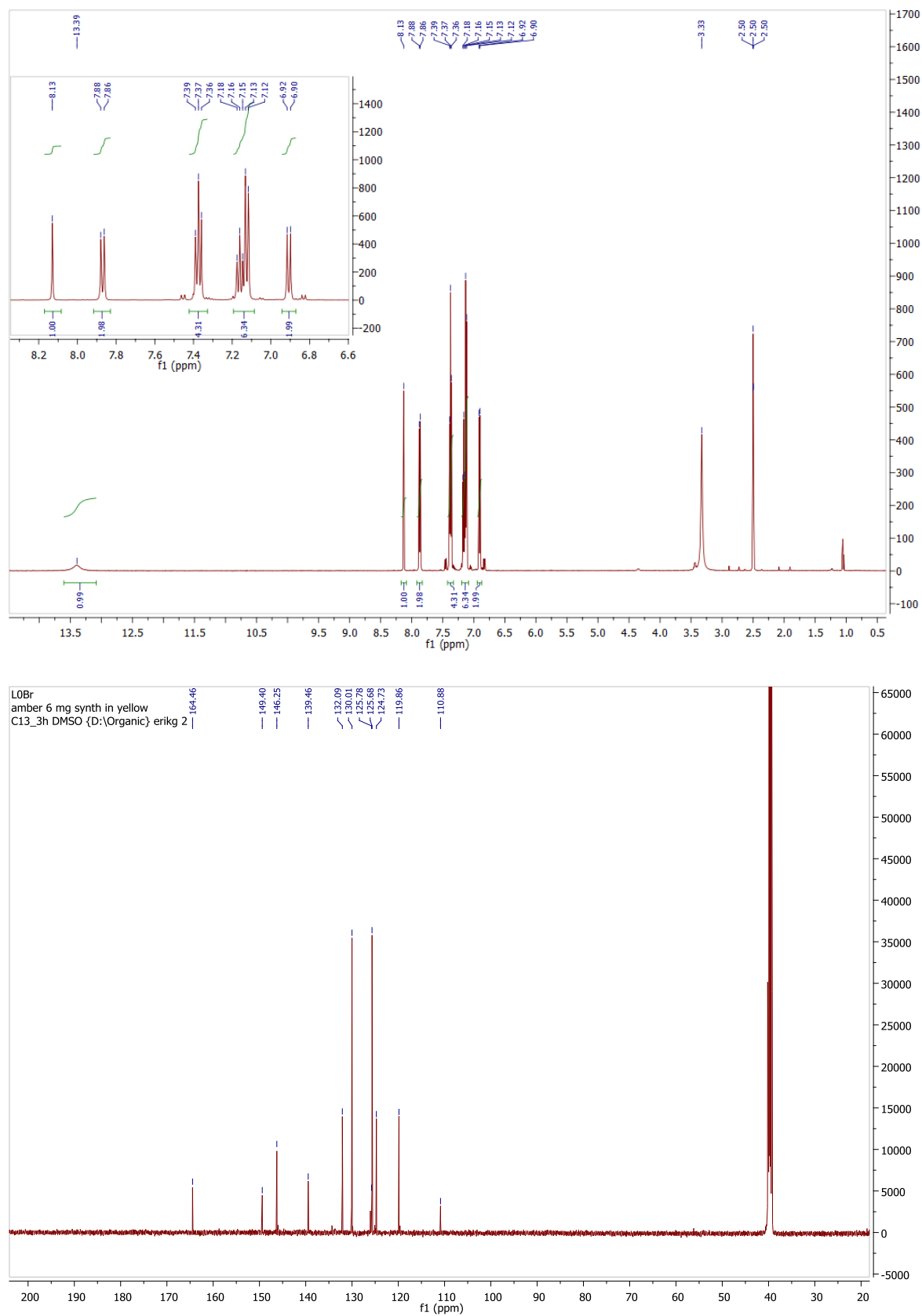**Fig. S5.** ¹H- and ¹³C-NMR spectra of EtL0Br in Acetone-d_6.

Fig. S6 ^{1}H- and ^{13}C-NMR spectra of L0Br in DMSO-d_6. Some isomerization can be seen even though care is taken not to expose the sample to light and the solution is kept in an amber NMR tube.
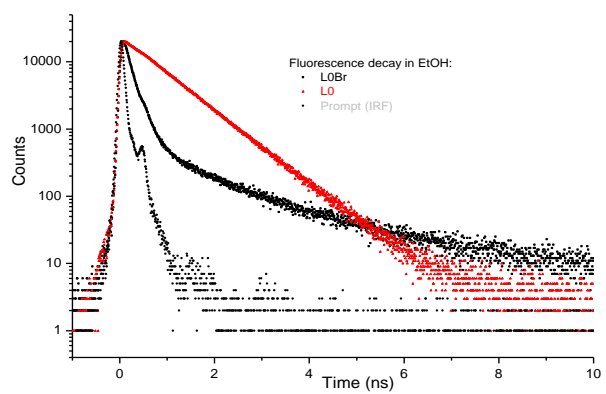
Fig. S7 Fluorescence decay of L0Br and L0 in ethanol.