

## Supplementary material

### Perfluorocyclohexene Bridge in Inverse DiArylEthenes: One Step Synthesis through Pd-Catalysed C-H bond Activation, Joint Experimental and Theoretical Studies on Their Photoreactivity

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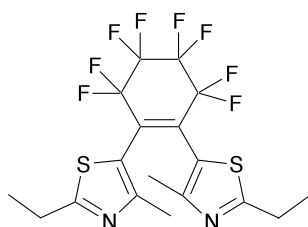
**General.** All reactions were performed in Schlenk tubes under argon. CPME analytical grade was not distilled before use. Potassium acetate 99+ was used. Commercial heteroaromatics and 1,2-dichlorooctafluorocyclohexene were used without further purification. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) and <sup>19</sup>F (376 MHz) spectra were recorded in CDCl<sub>3</sub> solutions. Chemical shifts were reported in ppm relative to CDCl<sub>3</sub> (<sup>1</sup>H: 7.26 and <sup>13</sup>C: 77.0). Flash chromatography was performed on silica gel (230-400 mesh) using pentane/ether.

## General Procedure

As a typical experiment, the reaction of the 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), thiophene or thiazole derivatives (1.5 mmol) and KOAc (1.5 mmol) at 120 °C during 20 h in CPME (3 mL) in the presence of (A): Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) and PCy<sub>3</sub> (14.0 mg, 0.05 mmol) or (B): PdCl(dppb)(C<sub>3</sub>H<sub>5</sub>) (15.3 mg, 0.025 mmol), under argon affords the corresponding coupling products **1-5** after evaporation of CPME and filtration on silica gel (pentane/ether).

## Synthesis of compounds 1-5

(1)



The reaction of 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), 2-ethyl-4-methyl-1,3-thiazole (0.191 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) and PCy<sub>3</sub> (14.0 mg, 0.05 mmol) in CPME (3 mL) at 120 °C during 20 h affords the corresponding product **1** in 46% (0.110 g) isolated yield as a yellow oil.

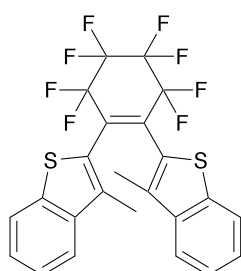
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.88 (q, *J* = 7.5 Hz, 4H), 2.10 (s, 6H), 1.27 (t, *J* = 7.5 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.6, 153.0, 116.0, 26.8, 16.4, 13.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -108.7, -134.1.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>16</sub>F<sub>8</sub>N<sub>2</sub>S<sub>2</sub> (476.45): C 45.38, H 3.38; found: C 45.67, H 3.57.

(2)



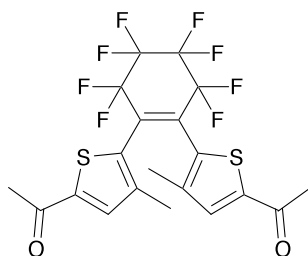
The reaction of 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), 3-methylbenzothiophene (0.222 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) and PCy<sub>3</sub> (14.0 mg, 0.05 mmol) in CPME (3 mL) at 120 °C during 20 h affords the corresponding product **2** in 40% (0.103 g) isolated yield as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 2.38 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.3, 140.1, 131.6, 129.9, 124.8, 124.3, 122.3, 122.1, 12.9.

Elemental analysis: calcd (%) for C<sub>24</sub>H<sub>14</sub>F<sub>8</sub>S<sub>2</sub> (518.49): C 55.60, H 2.72; found: C 55.41, H 3.01.

(3)



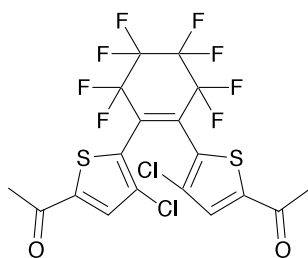
The reaction of 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), 2-acetyl-4-methylthiophene (0.210 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with PdCl(dppb)(C<sub>3</sub>H<sub>5</sub>) (15.3 mg, 0.025 mmol), in CPME (3 mL) at 120 °C during 20 h affords the corresponding product **3** in 66% (0.165 g) isolated yield as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (s, 2H), 2.55 (s, 6H), 2.26 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.5, 143.3, 138.2, 137.1, 135.1, 26.6, 15.2.

Elemental analysis: calcd (%) for C<sub>20</sub>H<sub>14</sub>F<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (502.44): C 47.81, H 2.81; found: C 47.67, H 2.96.

(4)



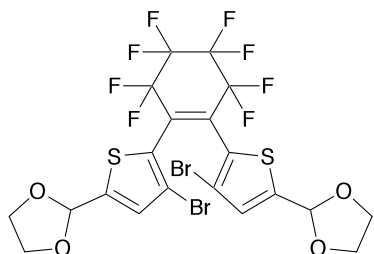
The reaction of 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), 2-acetyl-4-chlorothiophene (0.241 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with PdCl(dppb)(C<sub>3</sub>H<sub>5</sub>) (15.3 mg, 0.025 mmol), in CPME (3 mL) at 120 °C during 20 h affords the corresponding product **4** in 45% (0.122 g) isolated yield as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 (s, 2H), 2.58 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 189.6, 142.8, 133.5, 132.5, 125.8, 26.5.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>8</sub>Cl<sub>2</sub>F<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (543.28): C 39.79, H 1.48; found: C 39.97, H 1.59.

(5)



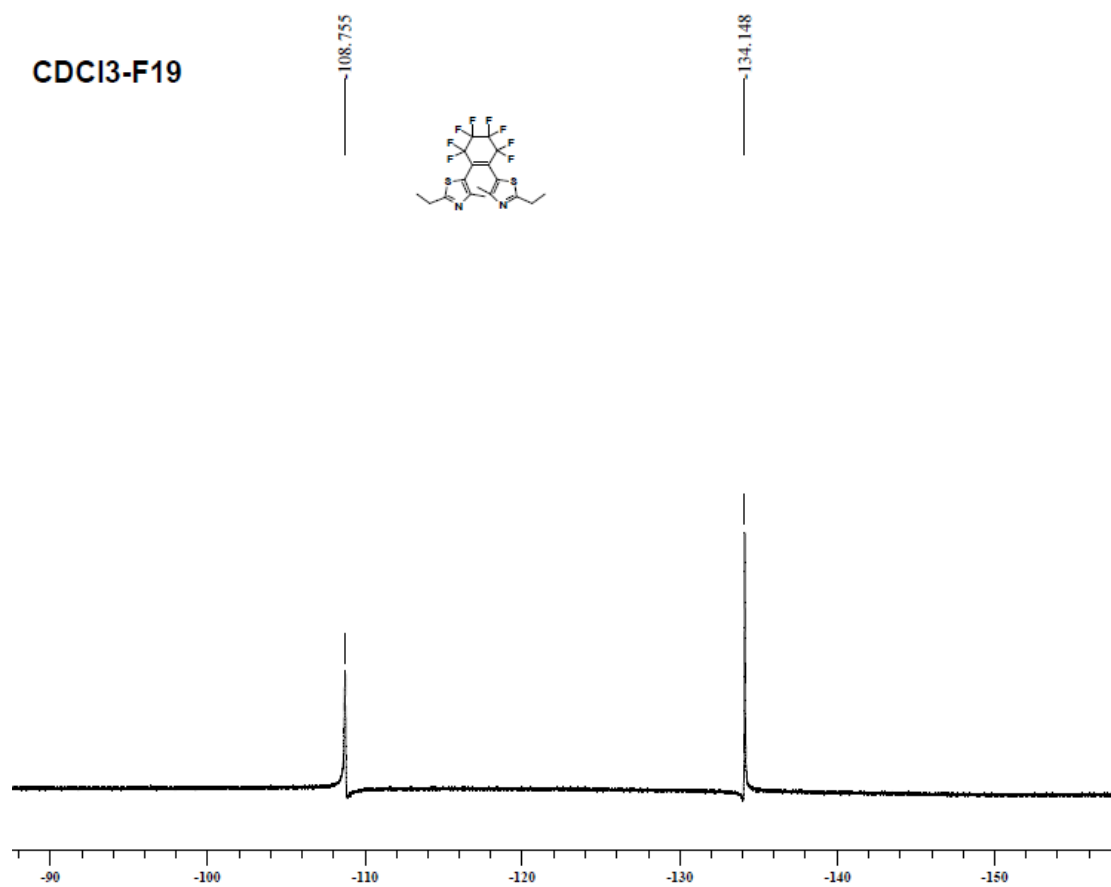
The reaction of 1,2-dichlorooctafluorocyclohexene (0.148 g, 0.5 mmol), 2-(4-bromothiophen-2-yl)-[1,3]dioxolane (0.352 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) and PCy<sub>3</sub> (14.0 mg, 0.05 mmol), in CPME (3 mL) at 120 °C during 20 h affords the corresponding product **5** in 80% (0.277 g) isolated yield as a yellow solid.

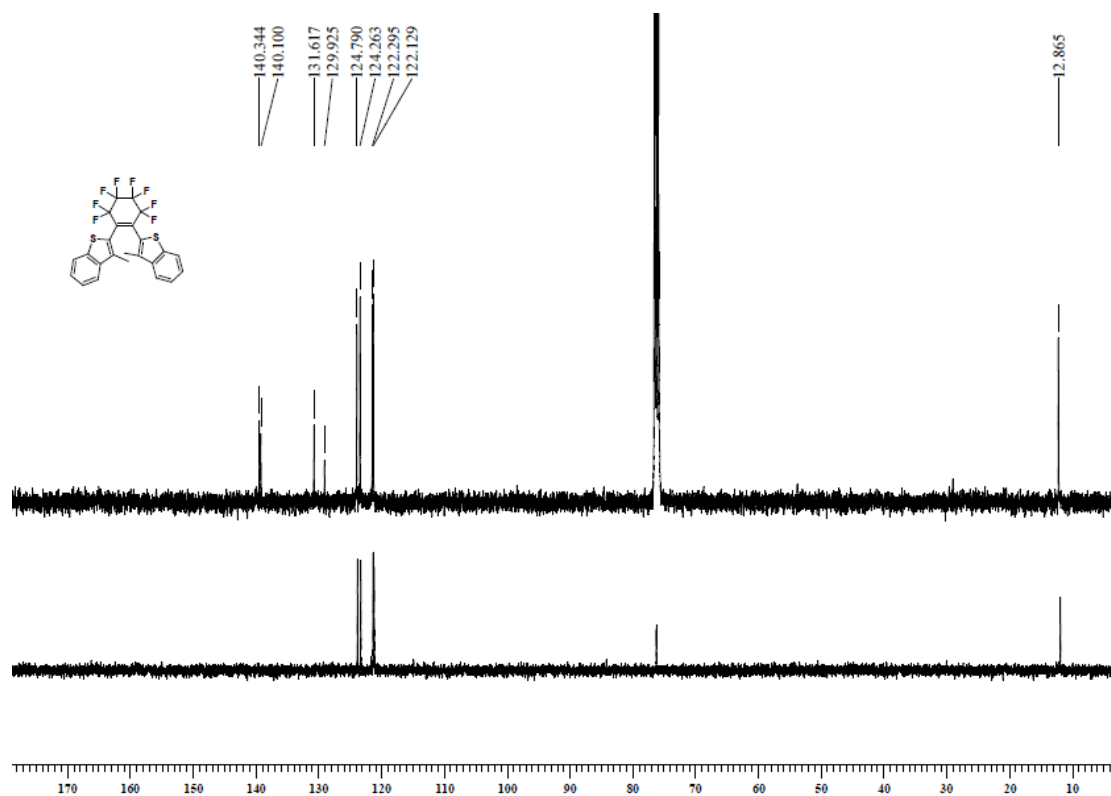
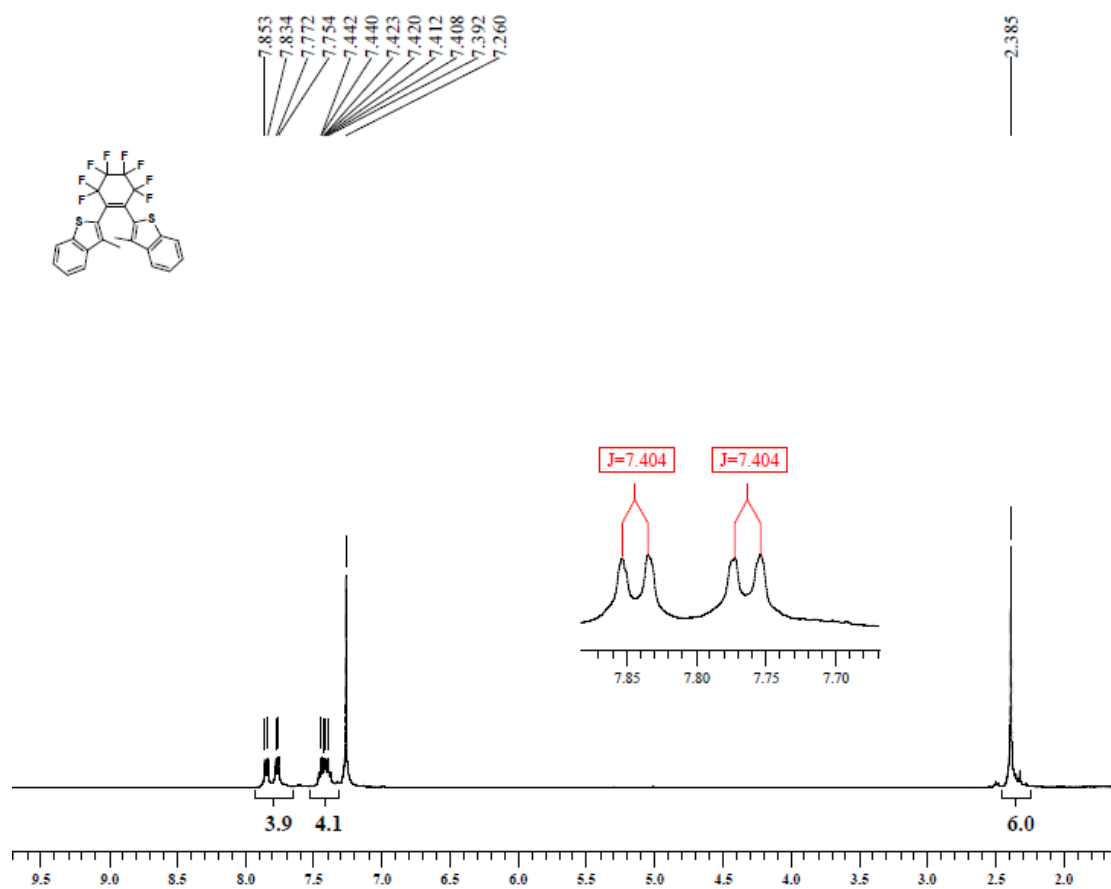
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35 (s, 2H), 6.08 (s, 2H), 4.15-4.03 (m, 8H).

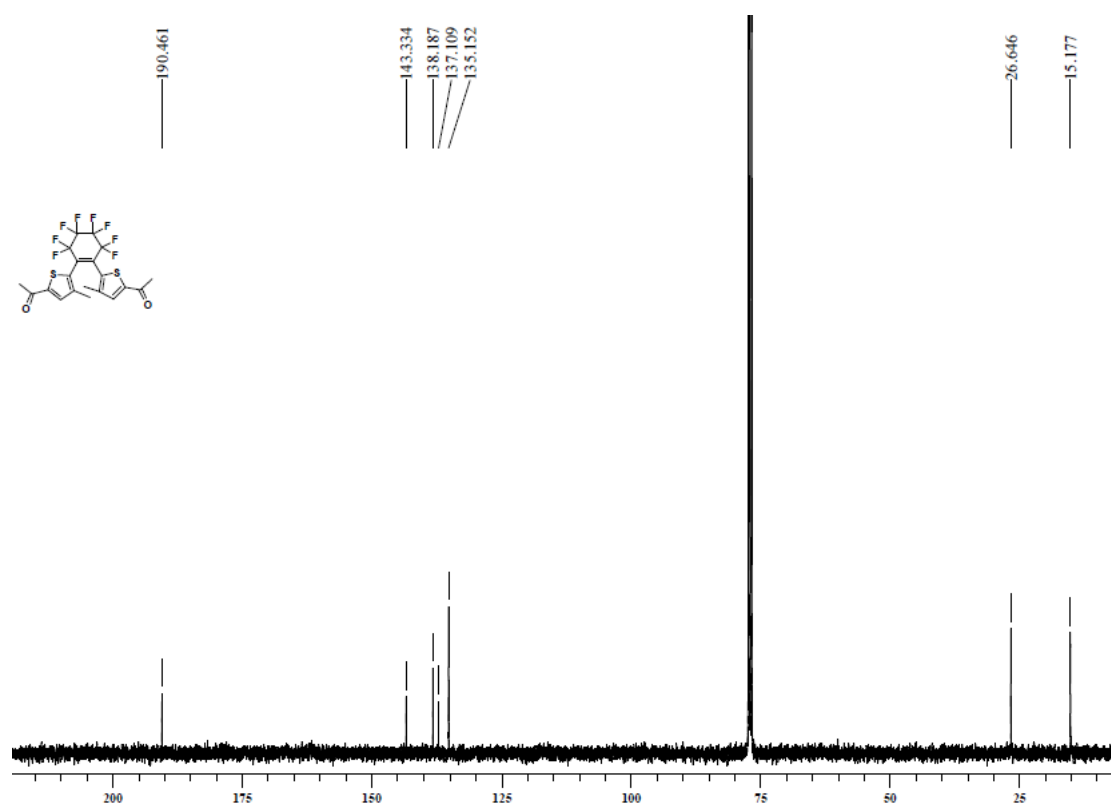
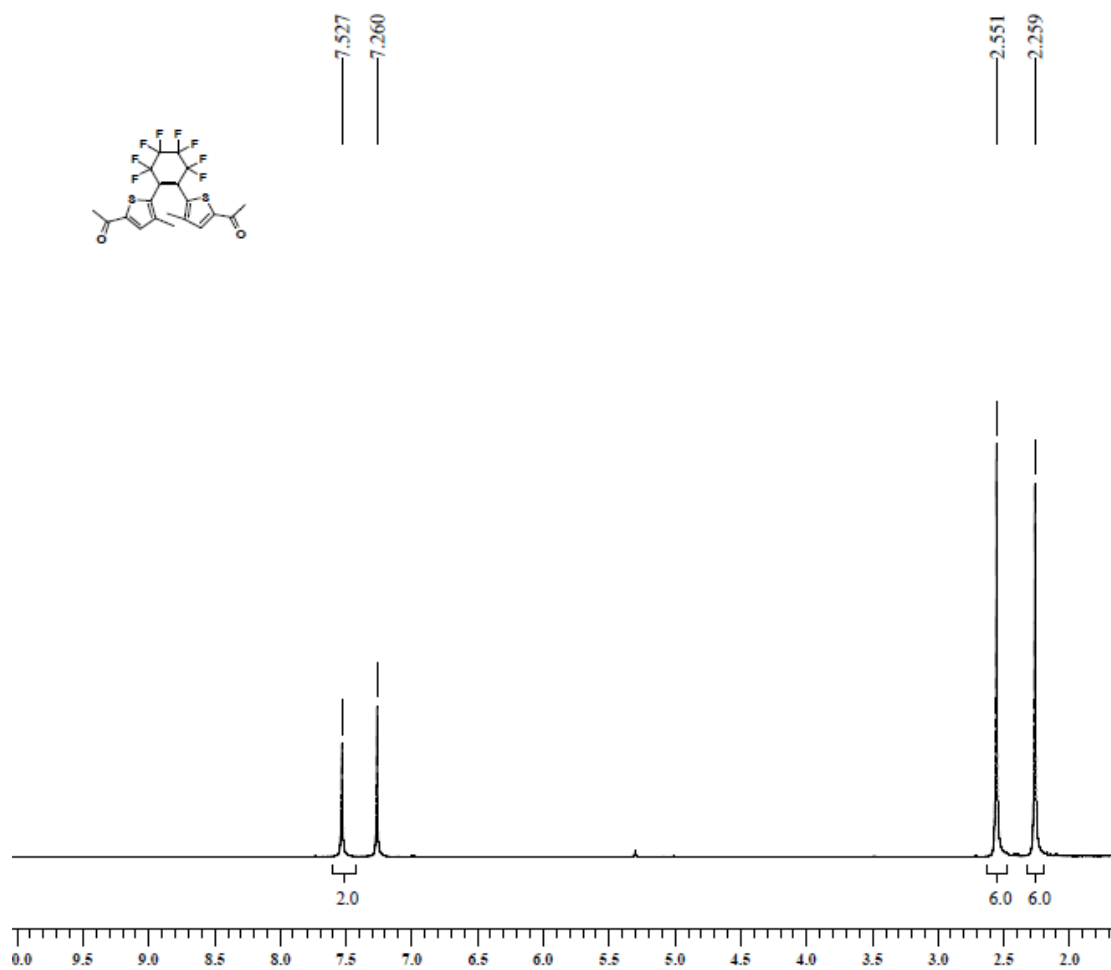
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.0, 141.2, 128.3, 114.2, 109.5, 98.9, 65.5.

Elemental analysis: calcd (%) for C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>F<sub>8</sub>O<sub>4</sub>S<sub>2</sub> (692.23): C 34.70, H 1.75; found: C 34.57, H 1.89.

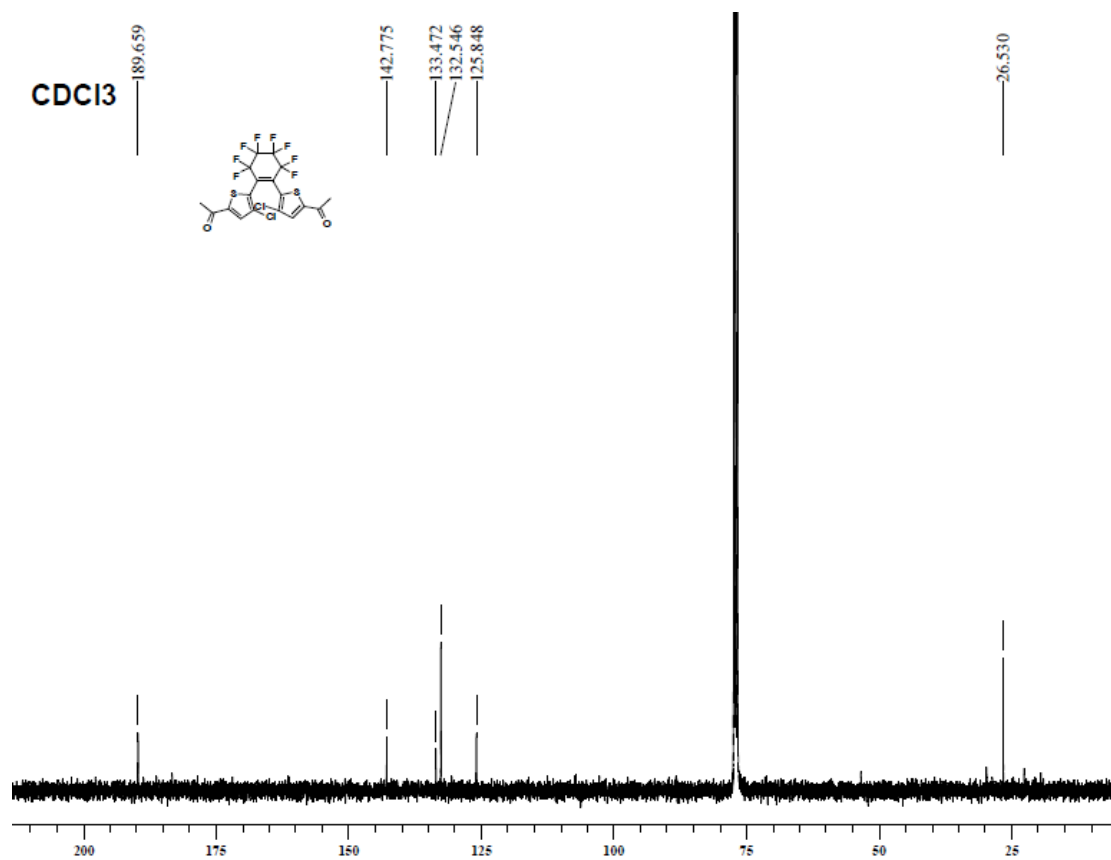
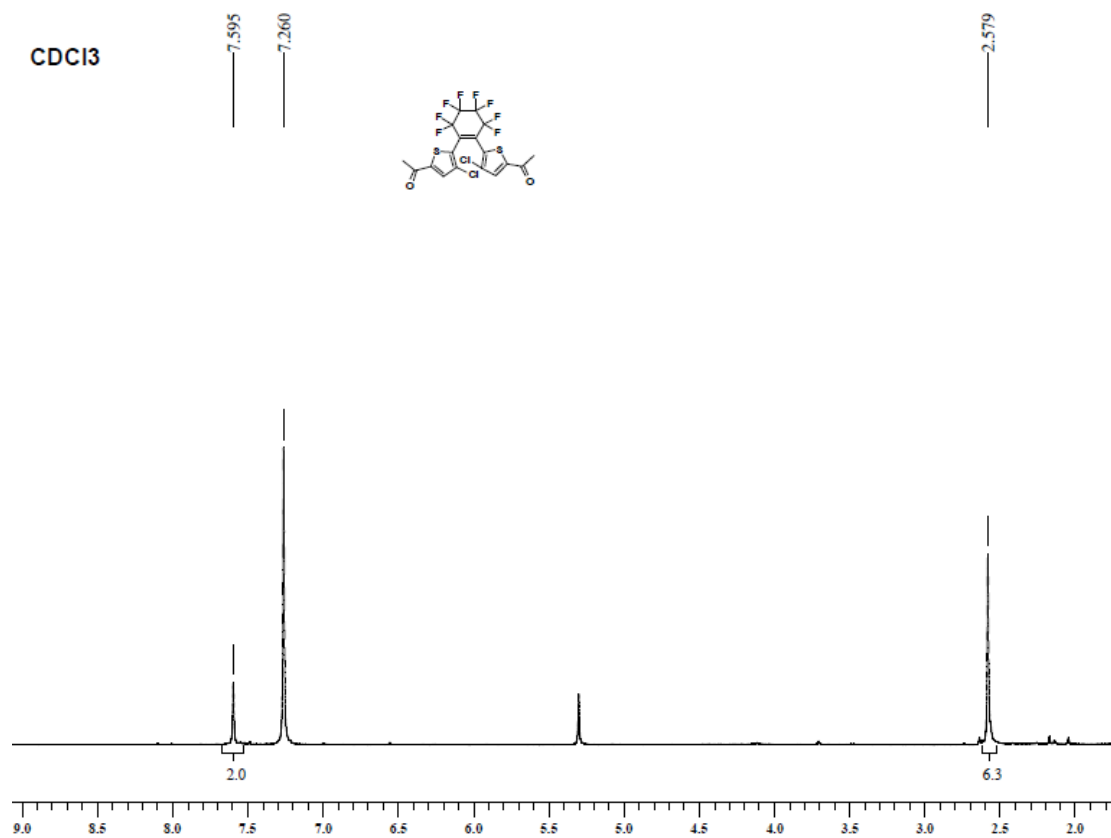


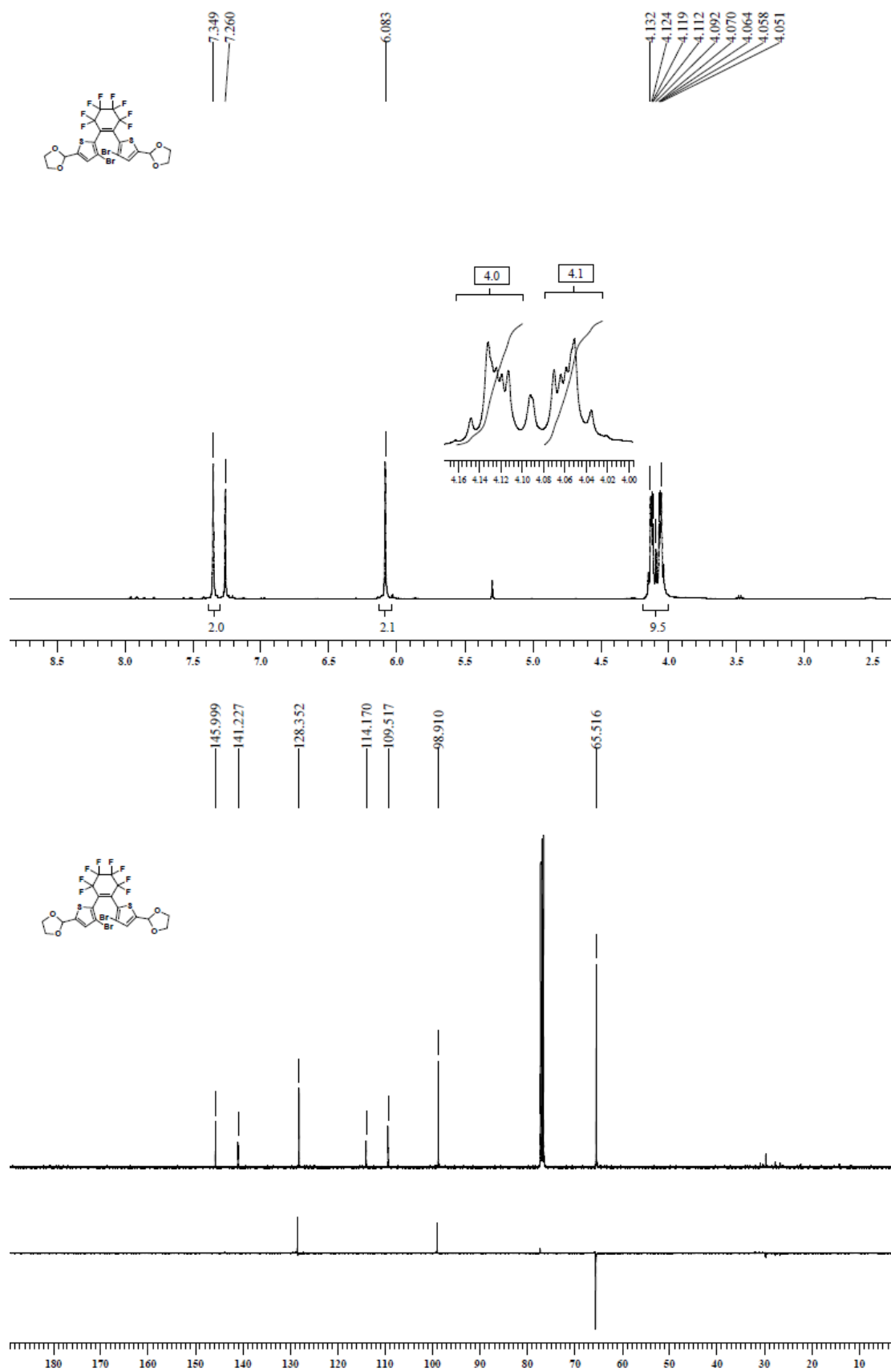












### UV-Visible absorption and emission data.

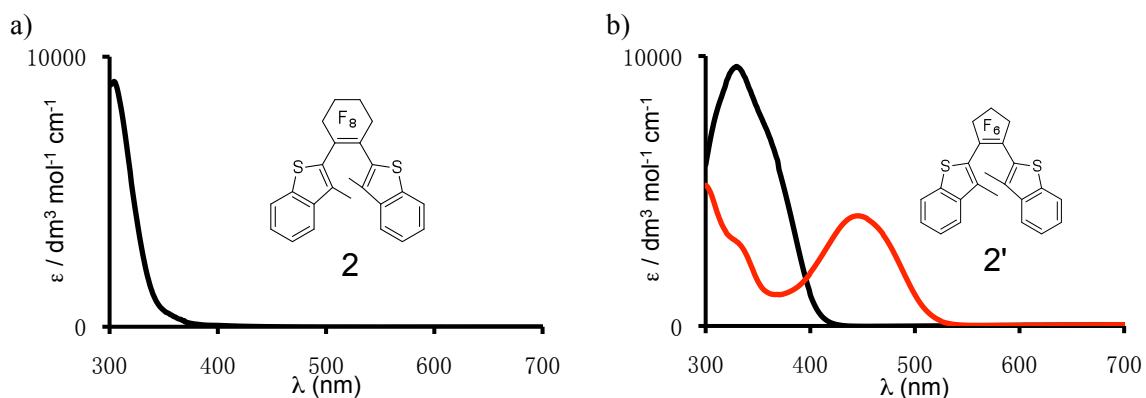
Compound **2**<sup>1</sup> (C5) was prepared following the reported procedure.<sup>2</sup> UV/vis absorption spectra were recorded using a Specord 205 UV-Vis-NIR spectrophotometer using quartz cuvettes of 1 cm pathlength. Irradiations of solutions have been made using a LS series Light Source of ABET technologies, Inc (150 W xenon lamp) with 350 nm single wavelength light filter. Steady-state luminescence spectra were measured using an Edinburgh FS920 Steady State Fluorimeter. The spectra were corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using anthracene ( $\Phi = 0.27$ ) as standard and correcting for the refractive index.

**Table S1** Absorption and emission data of compounds **1-5** in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K.

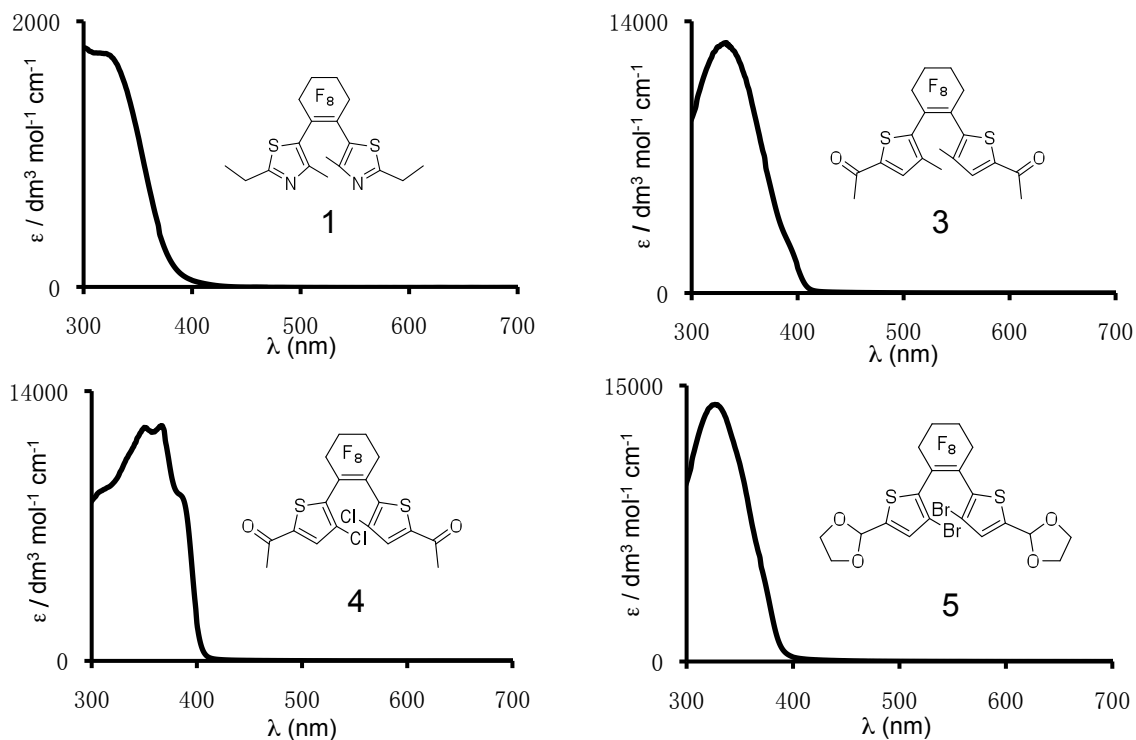
Compound	$\lambda_{\text{max}} / \text{nm}$ ( $\epsilon \times 10^3 / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{em}}^{\text{a}} / \text{nm}$	$\Phi^{\text{a, b}}$
<b>1</b>	329 (1.7)	380 <sup>c</sup> , 400	0.03
<b>2</b>	304 (9.0)	385 <sup>c</sup> , 405	0.81
<b>3</b>	330 (12.9)	410, 430 <sup>c</sup>	0.26
<b>4</b>	305sh (8.6), 350 (12.1), 366 (12.1), 385sh (8.6)	405, 425 <sup>c</sup>	0.12
<b>5</b>	327 (14.0), 335 (9.4)	512	0.43

<sup>a</sup> $\lambda_{\text{exc}} = 340 \text{ nm}$ , <sup>b</sup> ref : anthracene, <sup>c</sup> $\lambda_{\text{max}}$ .

**Photochromic studies:** No modification of the UV-visible absorption spectra of compounds **1-5** were observed upon UV irradiation at 350 nm, in CH<sub>2</sub>Cl<sub>2</sub> solution.



**Fig. S1** UV-visible absorption spectra of a) **2** (C6) and b) **2'** (C5) in the open (black line) and closed forms (red line) upon light irradiation at 350 nm, in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



**Fig. S2** UV-visible absorption spectra of **1**, **3-5** in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

### Theoretical calculations: Models.

All calculations were carried out with the Gaussian09 program<sup>3</sup> tightening both self-consistent field ( $10^{-9}$  a.u.) and geometry optimization ( $10^{-5}$  a.u.) convergence thresholds. We have first optimized the ground-state geometries of several conformers using the PBE0 hybrid functional,<sup>4</sup> and the 6-311G(d,p) atomic basis set. This combination has been shown to be very adequate for evaluating the ground-state structures of DTE compounds.<sup>5</sup> In a second step, we have used the same level of theory to determine the vibrational spectra of the optimized structures. This also allowed to compute Gibbs energies ( $G$ ) for all compounds. In a last step, the total DFT energies have been corrected thanks to single-point MP4(SDQ)/6-311++g(d,p) calculations, which allowed accurately determine relative free energies with

$$G = G_{\text{PBE0}}^{6-311\text{G(d,p)}} + E_{\text{MP4(SDQ)}}^{6-311++\text{G(d,p)}} - E_{\text{PBE0}}^{6-311\text{G(d,p)}}$$

All calculations have been performed with the Polarizable Continuum Model (PCM) using dichloromethane as a solvent.<sup>6</sup> Molecular orbitals and transition energies have been computed at the CAM-B3LYP/6-311+G(2d,p) level,<sup>7</sup> following recent works demonstrating the adequacy of that level for the electronic properties of DAE.<sup>8</sup>

1. T. Yamaguchi, K. Uchida and M. Irie, *Mol. Cryst. Liq. Cryst.*, 2007, **474**, 111-118.
2. K. Beydoun, J. Roger, J. Boixel, H. Le Bozec, V. Guerchais and H. Doucet, *Chem. Commun.*, 2012, **48**, 11951-11953.
3. 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 and D. J. Fox, *Gaussian 09 Revision C.01*, 2009, Gaussian Inc. Wallingford CT.
4. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
5. D. Jacquemin and E.A. Perpète, *Chem. Phys.Lett.*, 2006, **429**, 147-152.
6. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.
7. T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys.Lett.*, 2006, **393**, 51-57.
8. A. Perrier, F. Maurel and D. Jacquemin, *Acc. Chem. Res.*, 2012, **45**, 1173-1182 and refs therein.