

**Access to Fluorenones using Benzocyclopentynone  
Surrogate as Partner for the [2+2+2] Cycloaddition  
Reaction**

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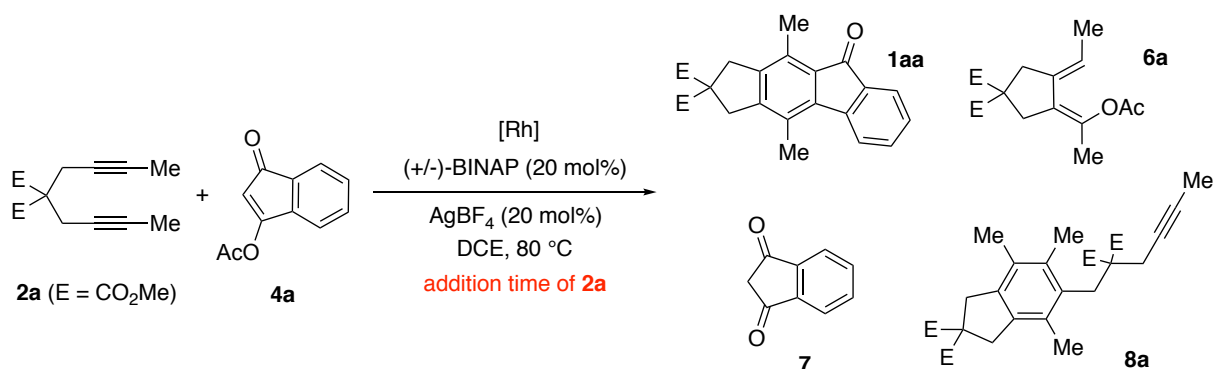
## 1. General method

All reactions were performed using standard Schlenk techniques under inert atmosphere of dry argon or in a glovebox Jacomex GP (concept)-II-P.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 400 (400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR), and Bruker AC 300 (300 MHz for  $^1\text{H}$  NMR, 75 MHz for  $^{13}\text{C}$  NMR) spectrometer. Chemical shifts were reported in ppm on the  $\delta$  scale relative to residual  $\text{CHCl}_3$  ( $\delta = 7.26$  for  $^1\text{H}$  NMR and  $\delta = 77.16$  for  $^{13}\text{C}$  NMR) as an internal reference. Coupling constant ( $J$ ) are reported in Hertz unit (Hz). Multiplicities are described with standard following abbreviations: s = singlet, br = broad, d = doublet, t = triplet, q = quadruplet, m = multiplet. Column chromatographies were performed with gel 60 (Macherey-Nagel® Si 60, 0.040-0.063 mm). Analytical thin layer chromatography (TLCs) were carried out on Merck®Kieselgel 60 F254 plates and achieved under a 254 nm UV light, visualized with a  $\text{KMnO}_4$  solution or anisaldehyde solution. High-resolution mass spectra (HRMS) were performed on a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted. Infrared spectra were recorded on a Bruker TENSOR 27 FourierTransform infrared spectrometer equipped with a single reflection diamond Attenuated Total Reflexion accessory (Bruker A222). Melting points were measured on Büchi Melting Point B-540. Anhydrous dichloromethane, toluene and tetrahydrofuran were obtained from the Solvent Purification System BRAUN MB-SPS800. Dry 1,2-dichloroethane was purchased from chemical suppliers, distilled over calcium hydride, degassed, and stored over 4 Å molecular sieves inside the glovebox. 1,3-indandione **7** was purchased from Merck.

## 2. Optimization of the reaction conditions

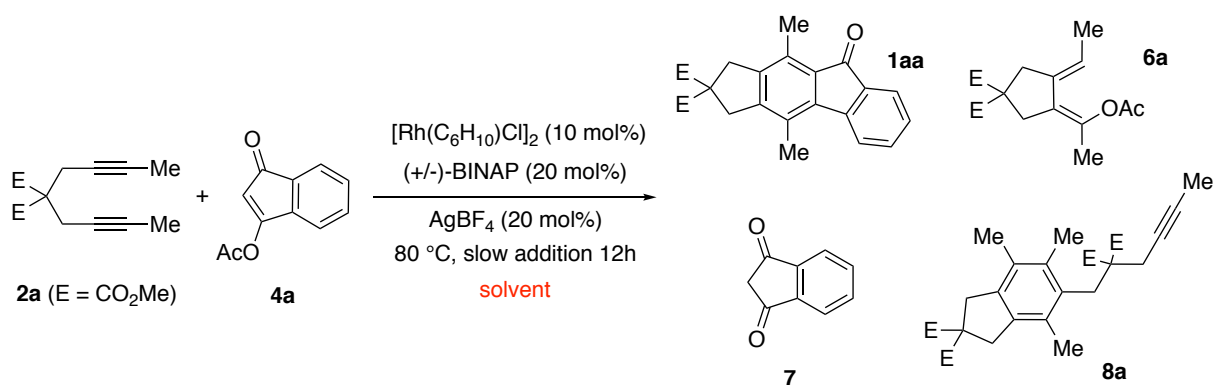
**Table S1. Optimization of the addition time**



entry	[Rh] (mol%)	addition time	time of stirring	<b>1aa</b> / <b>6a</b> / <b>7</b> / <b>8a</b>	remarks
1	[Rh(cod) <sub>2</sub> ]BF <sub>4</sub>	one-pot	12h	1 / 0,6 / 0,4 / 1 <sup>a</sup>	
2	[Rh(C <sub>6</sub> H <sub>10</sub> )Cl] <sub>2</sub> (10 mol%)	one-pot	12h	1 / 0 / 0,5 / 1 <sup>a</sup>	
3	[Rh(C <sub>6</sub> H <sub>10</sub> )Cl] <sub>2</sub> (10 mol%)	3h	1h	35 / 26 / 14 / 0 <sup>b</sup>	70% of conversion of <b>2a</b>
4	[Rh(C <sub>6</sub> H <sub>10</sub> )Cl] <sub>2</sub> (10 mol%)	12h	3h	79 / 20 / 0 / 0 <sup>b</sup>	

<sup>a</sup> The ratio was determined by <sup>1</sup>H NMR analysis of the crude mixture. <sup>b</sup> Isolated yields (%).

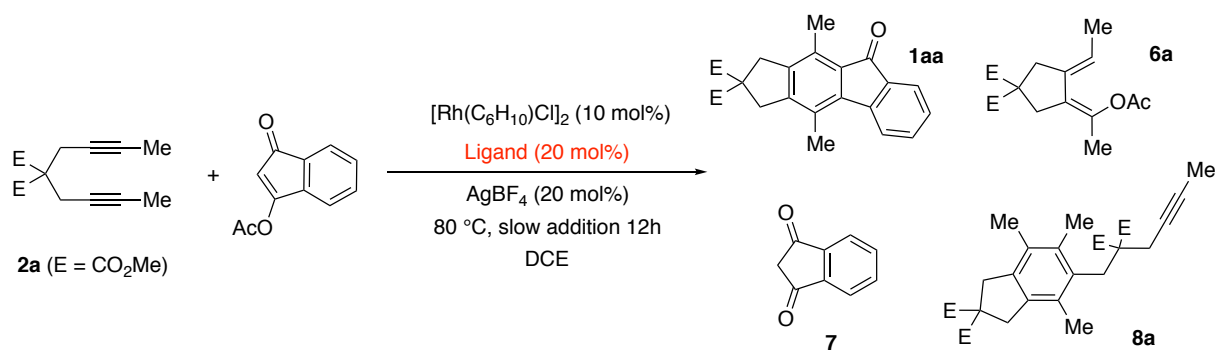
**Table S2. Optimization of the solvent**



entry	solvent	yields <b>1aa</b> / <b>6a</b> / <b>7</b> / <b>8a</b> (%)
1	DCE	79 / 20 / 0 / 0
2	Toluene	70 / 16 / 0 / 0
3	Toluene <sup>a</sup>	43 / 0 / 40 / 36
4	Trifluoroethanol	5 / 25 / 65 / traces <sup>b</sup>
5	Trifluorotoluene	14 / 15 / 62 / 0 <sup>b</sup>

<sup>a</sup> The reaction was conducted at 110 °C. <sup>b</sup> **1aa**, **6a** and **7** isolated from a complex mixture of compounds.

**Table S3. Optimization of the ligand**



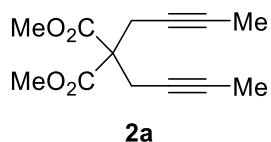
entry	Ligand	yields <b>1aa</b> / <b>6a</b> / <b>7</b> / <b>8a</b> (%)	remarks
1	dppe	11 / 11 / 38 / 0	40% of conversion of <b>2a</b>
2	dppf	36 / 48 / 12 / 0	
3	xantphos	0 / 0 / 44 / 20	60% of conversion of <b>2a</b>
4	( <i>R</i> )-Biphep	traces / 0 / 54 / 0	10% of conversion of <b>2a</b>
5	( <i>R</i> )-Segphos	9 / 13 / 52 / traces	70% of conversion of <b>2a</b>

### 3. Preparation of substrates

The diynes **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2i**, **2j**, **2k**, **2l** were synthesized using reported procedures.

4,5-dimethyl-1*H*-indene-1,3(2*H*)-dione was synthesized from 3,4-dimethylbenzoic acid using a reported procedure.<sup>1</sup>

#### Dimethyl 2,2-di(but-2-yn-1-yl)malonate (**2a**)<sup>2</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 3.74 (s, 6H), 2.90 (brq,  $J$  = 2.4 Hz, 4H), 1.75 (brt,  $J$  = 2.4 Hz, 6H).

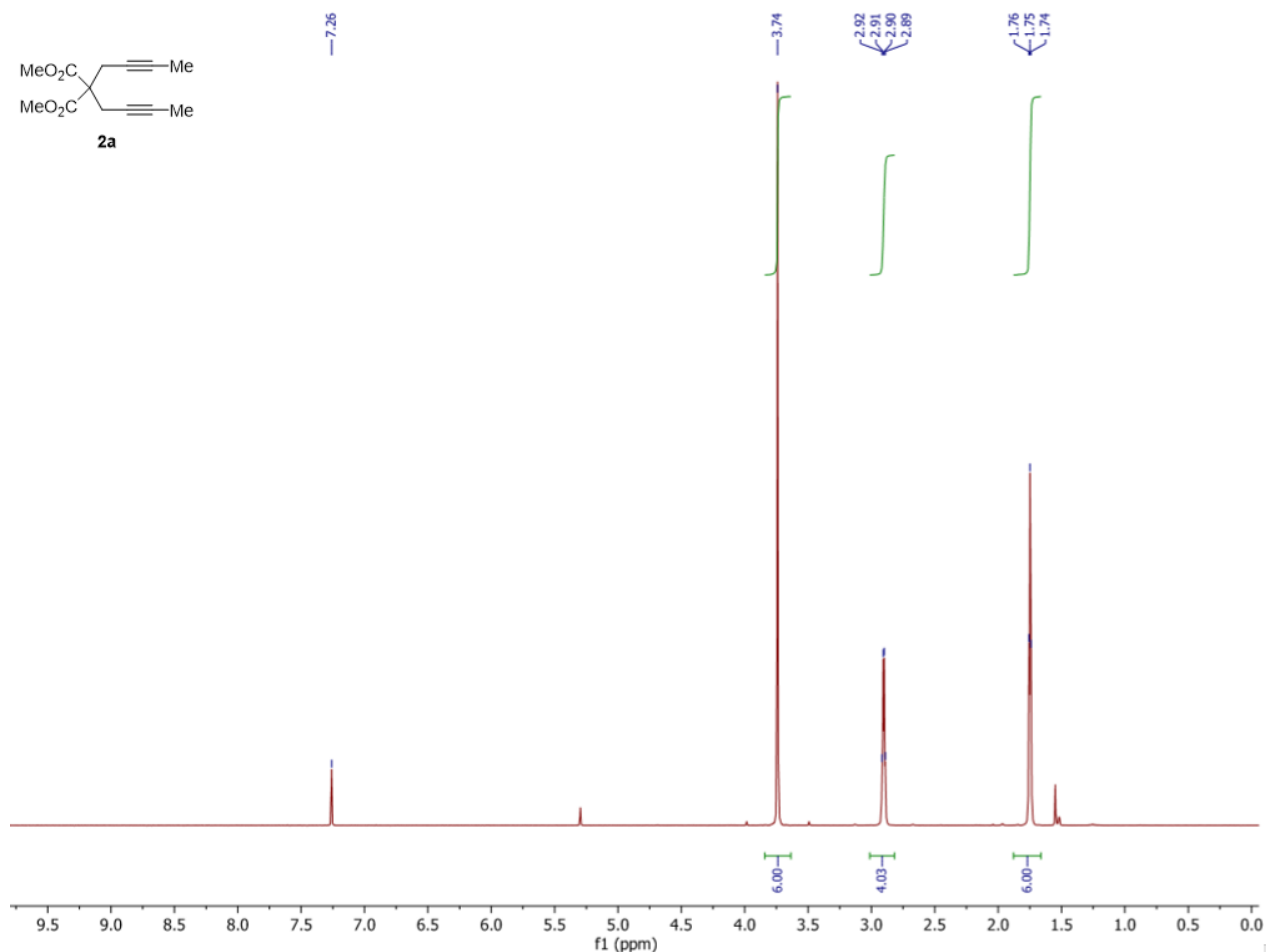
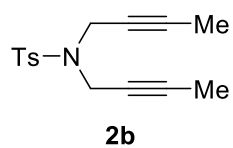


Figure S1 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

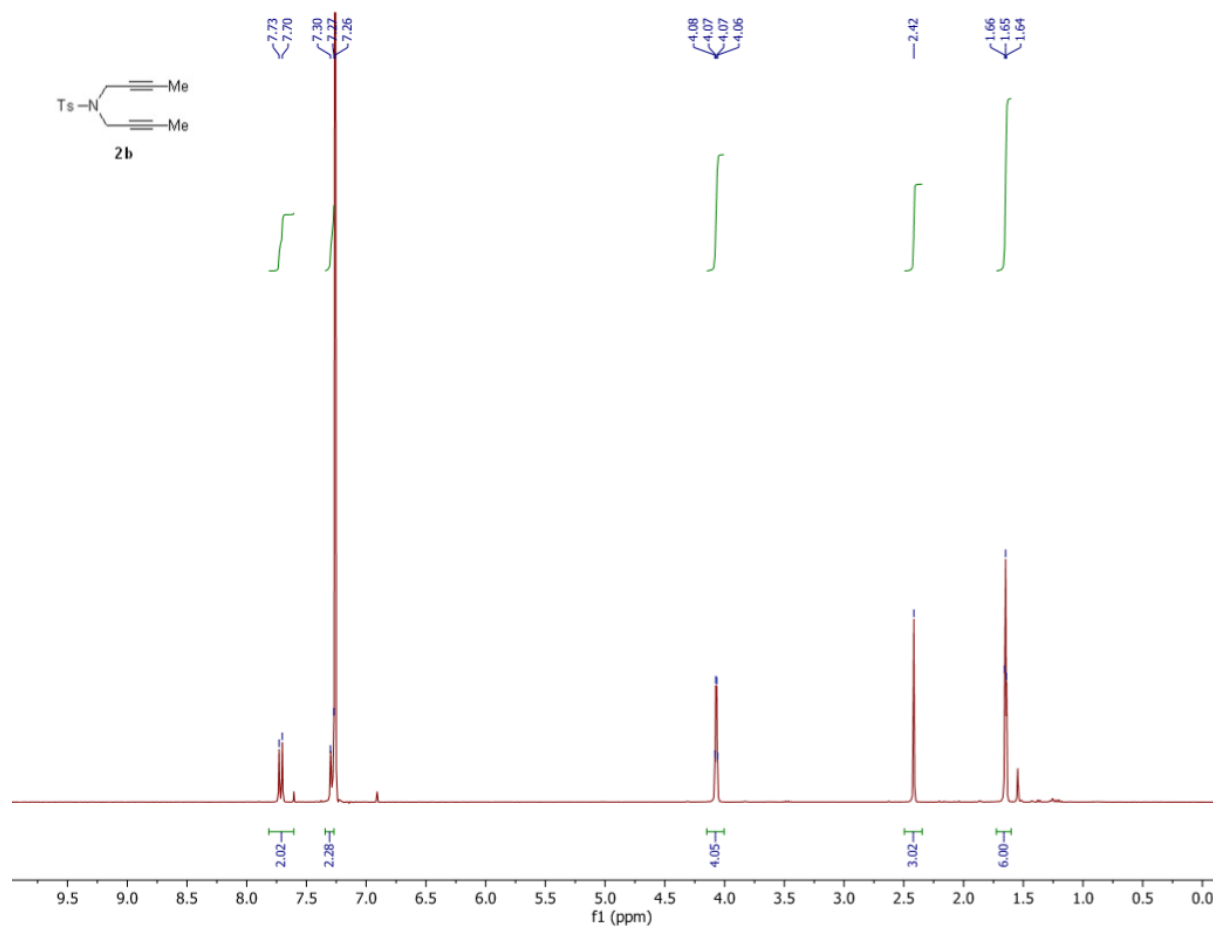
<sup>1</sup> David J. Harkin, D.J.; Broch, K.; Schreck, M.; Ceymann, H.; Stoy, A.; Yong, C.-K.; Nikolka, M.; McCulloch, I.; Stingelin, N.; Lambert, C.; Sirringhaus, H. *Advanced Materials* **2016**, *28*, 9423.

<sup>2</sup> Amatore, M.; Leboeuf, D.; Malacria, M.; Gandon, V.; Aubert, C. *J. Am. Chem. Soc.* **2013**, *135*, 4576.

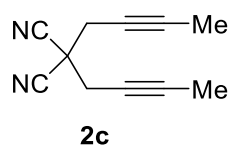
*N,N*-di(but-2-yn-1-yl)-4-methylbenzenesulfonamide (**2b**)<sup>2</sup>



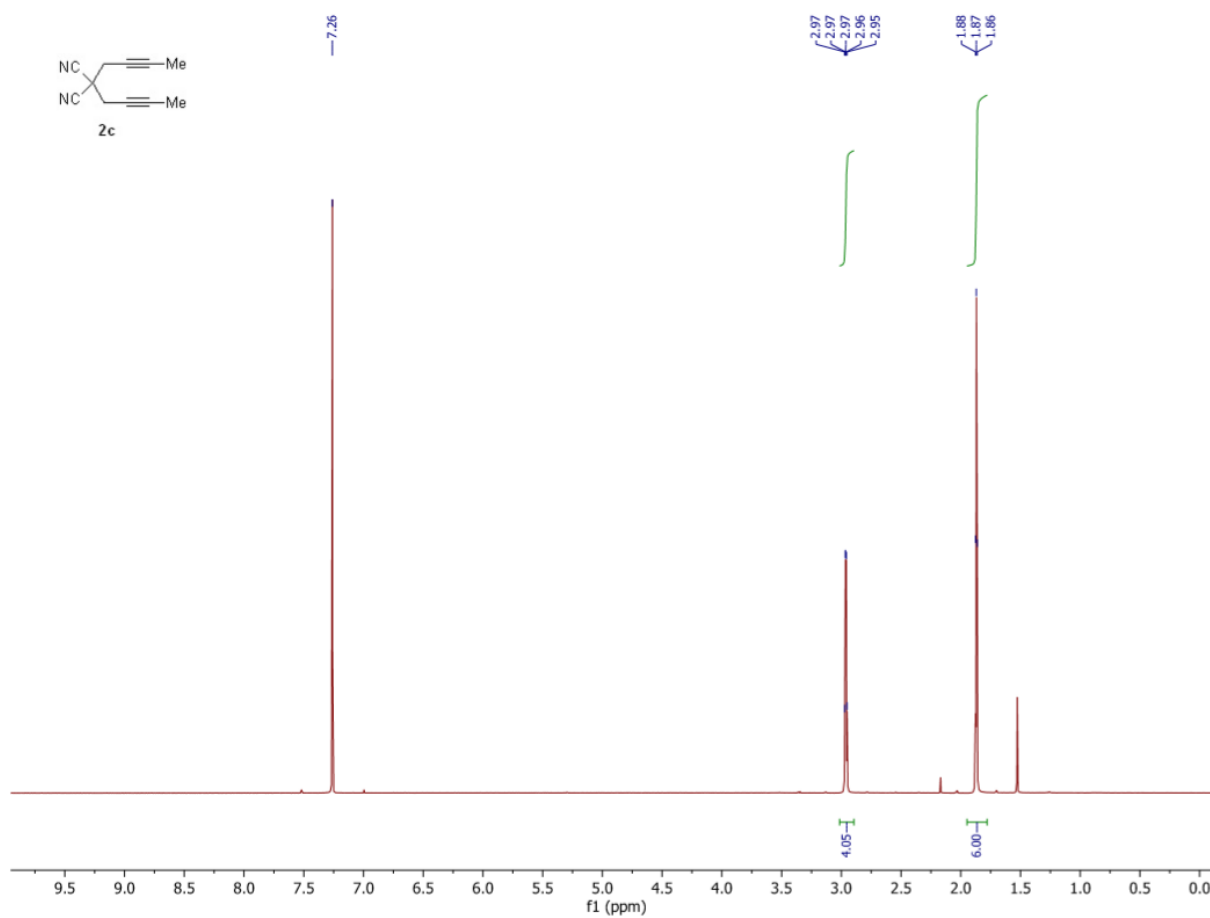
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 7.72 (d,  $J$  = 8.4 Hz, 2H), 7.30 (d,  $J$  = 8.1 Hz, 2H), 4.07 (brq,  $J$  = 2.1 Hz, 4H), 2.42 (s, 3H), 1.65 (brt,  $J$  = 2.1 Hz, 6H).



2,2-di(but-2-yn-1-yl)malononitrile (**2c**)<sup>3</sup>

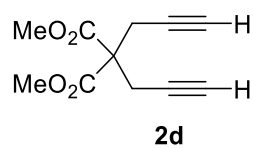


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = 2.96 (brq, *J* = 2.8 Hz, 4H), 1.87 (brt, *J* = 2.8 Hz, 6H).

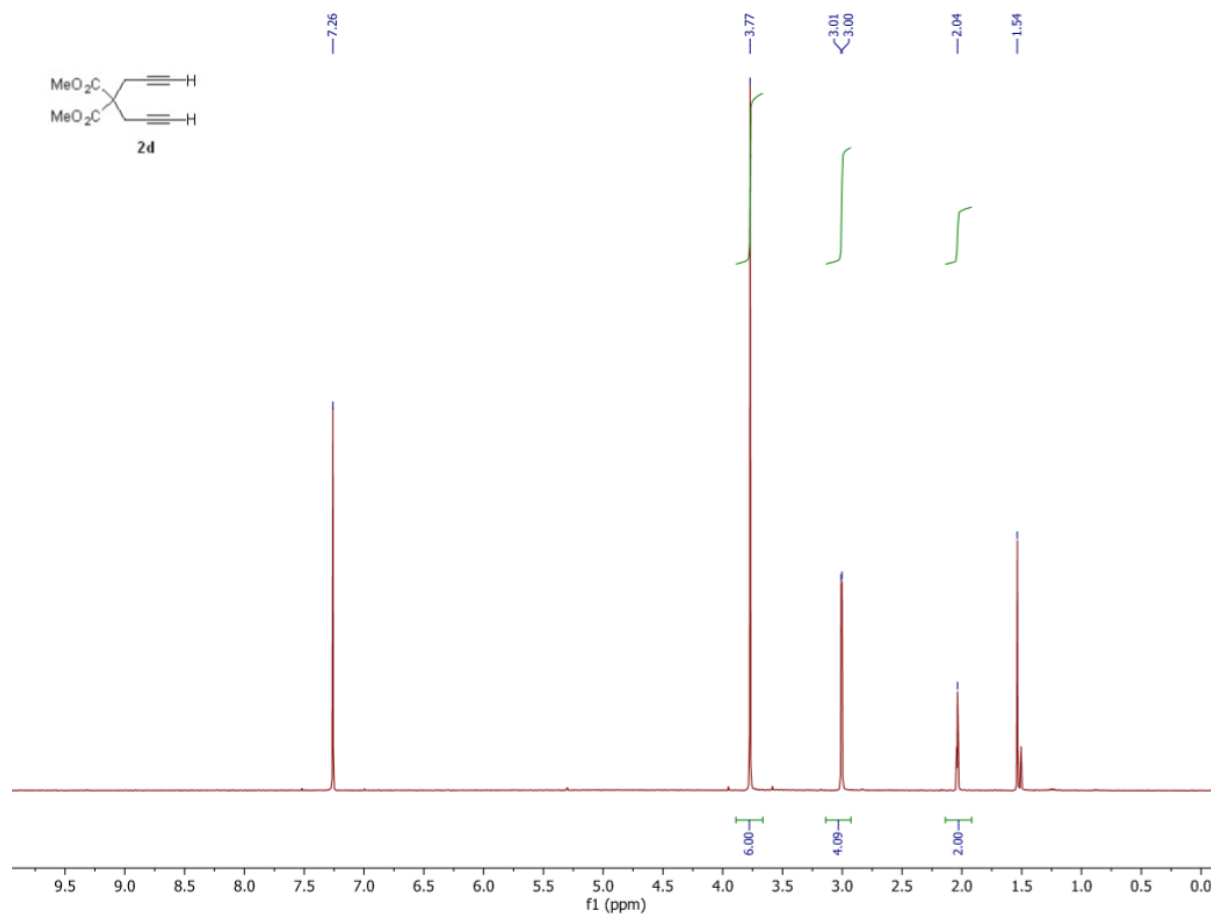


<sup>3</sup> Sugiyama, Y.-K. ; Okamoto, S. *Journal of Polymer Science, Part A : Polymer Chemistry* **2016**, 54,345.

**Dimethyl 2,2-di(prop-2-yn-1-yl)malonate (2d)**<sup>4</sup>

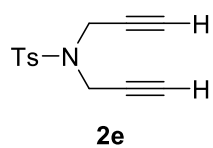


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 3.77 (s, 6H), 3.01 (brd,  $J$  = 2.8 Hz, 4H), 2.04 (brt,  $J$  = 2.8 Hz, 2H).



<sup>4</sup> Watanabe, K.; Satoh, Y.; Kamei, M.; Furukawa, H.; Fuji, M.; Obora, Y. *Org. Lett.* **2017**, *19*, 5398.

4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide (**2e**)<sup>5</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 7.72 (d,  $J$  = 8.4 Hz, 2H), 7.27 (d,  $J$  = 8.4 Hz, 2H), 4.17 (brd,  $J$  = 2.1 Hz, 4H), 2.43 (s, 3H), 2.15 (brt,  $J$  = 2.4 Hz, 2H).

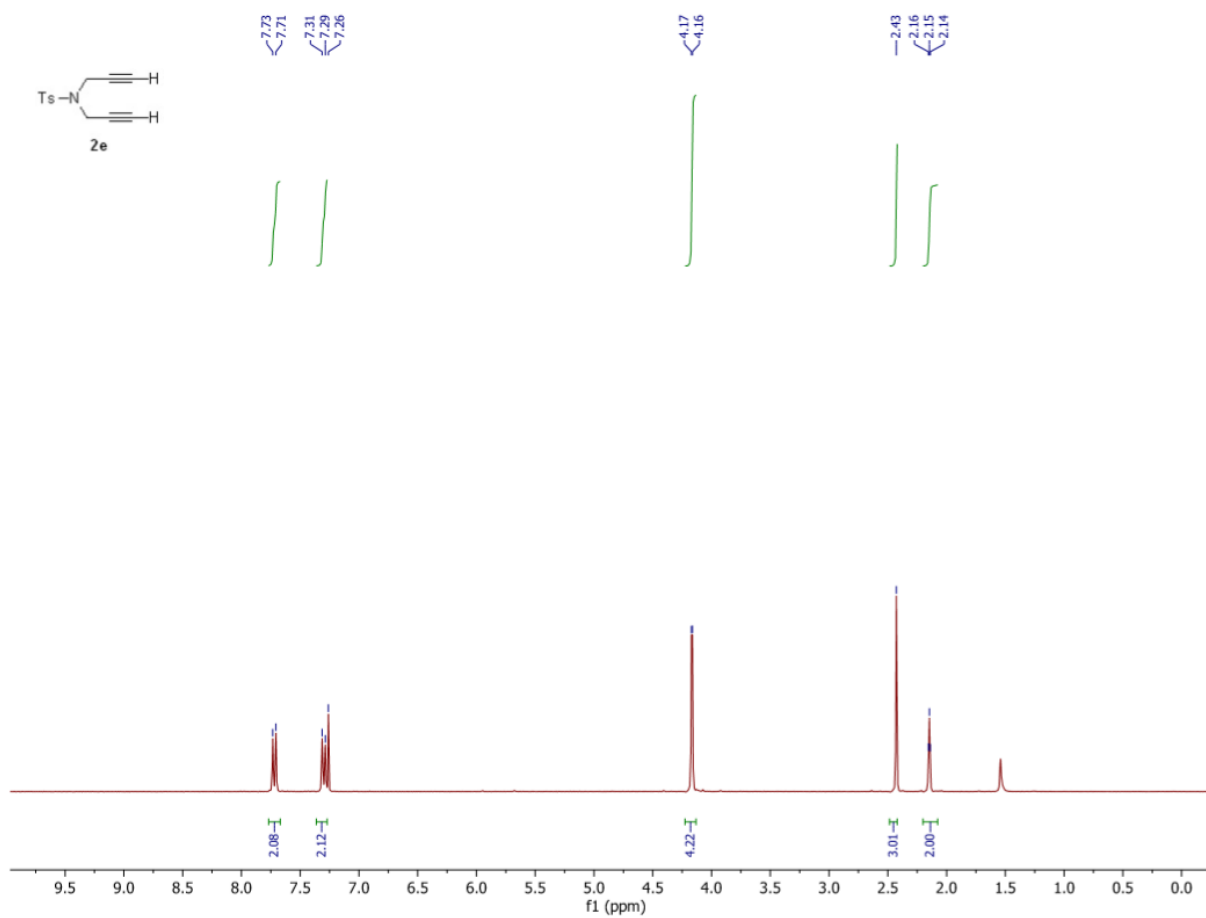
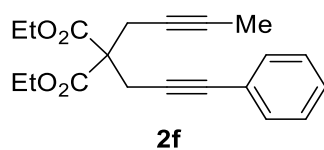


Figure 5 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

<sup>5</sup> Ghorai, S.; Lee, D. *Tetrahedron* **2017**, *73*, 4062.

Diethyl 2-(but-2-yn-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (**2f**)<sup>6</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 8.14-8.07 (m, 2H), 7.60 (td,  $J$  = 1.6 Hz, 7.6 Hz, 1H), 7.48 (td,  $J$  = 1.2 Hz, 7.6 Hz, 2H), 4.26 (q,  $J$  = 7.2 Hz, 4H), 3.29 (s, 2H), 2.99 (brq,  $J$  = 2.4 Hz, 2H), 1.77 (brt,  $J$  = 2.4 Hz, 3H), 1.27 (t,  $J$  = 7.2 Hz, 6H).

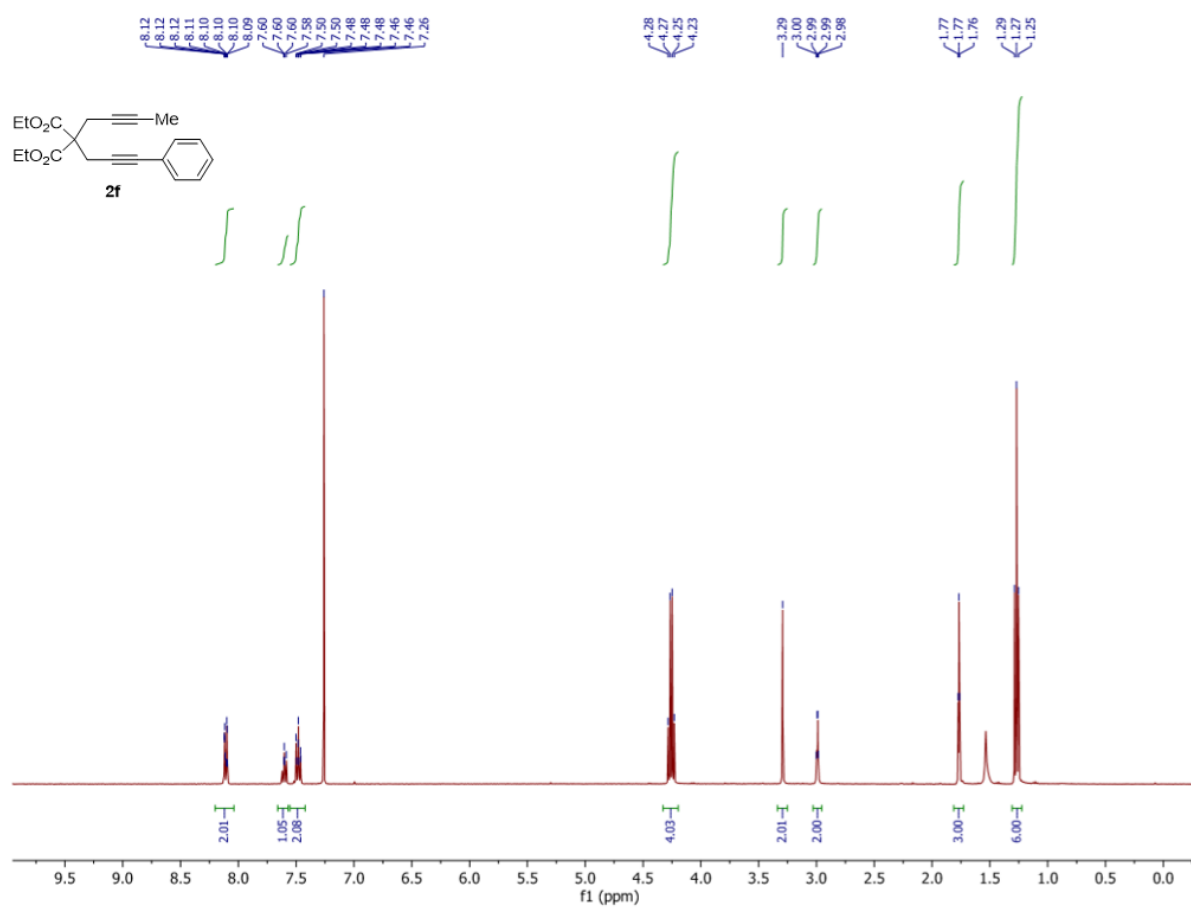
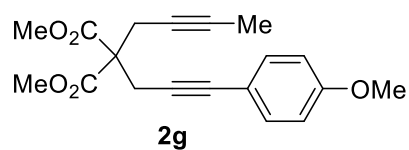


Figure S6 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

<sup>6</sup> Sato, H.; Bender, M.; Chen, W.; Krische, M. J. *J. Am. Chem. Soc.* **2016**, *138*, 16244.

Dimethyl 2-(but-2-yn-1-yl)-2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (**2g**)<sup>7</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 7.30 (d,  $J$  = 8.8 Hz, 2H), 6.79 (d,  $J$  = 8.8 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 6H), 3.16 (s, 2H), 2.98 (brq,  $J$  = 2.4 Hz, 2H), 1.76 (brt,  $J$  = 2.4 Hz, 3H).

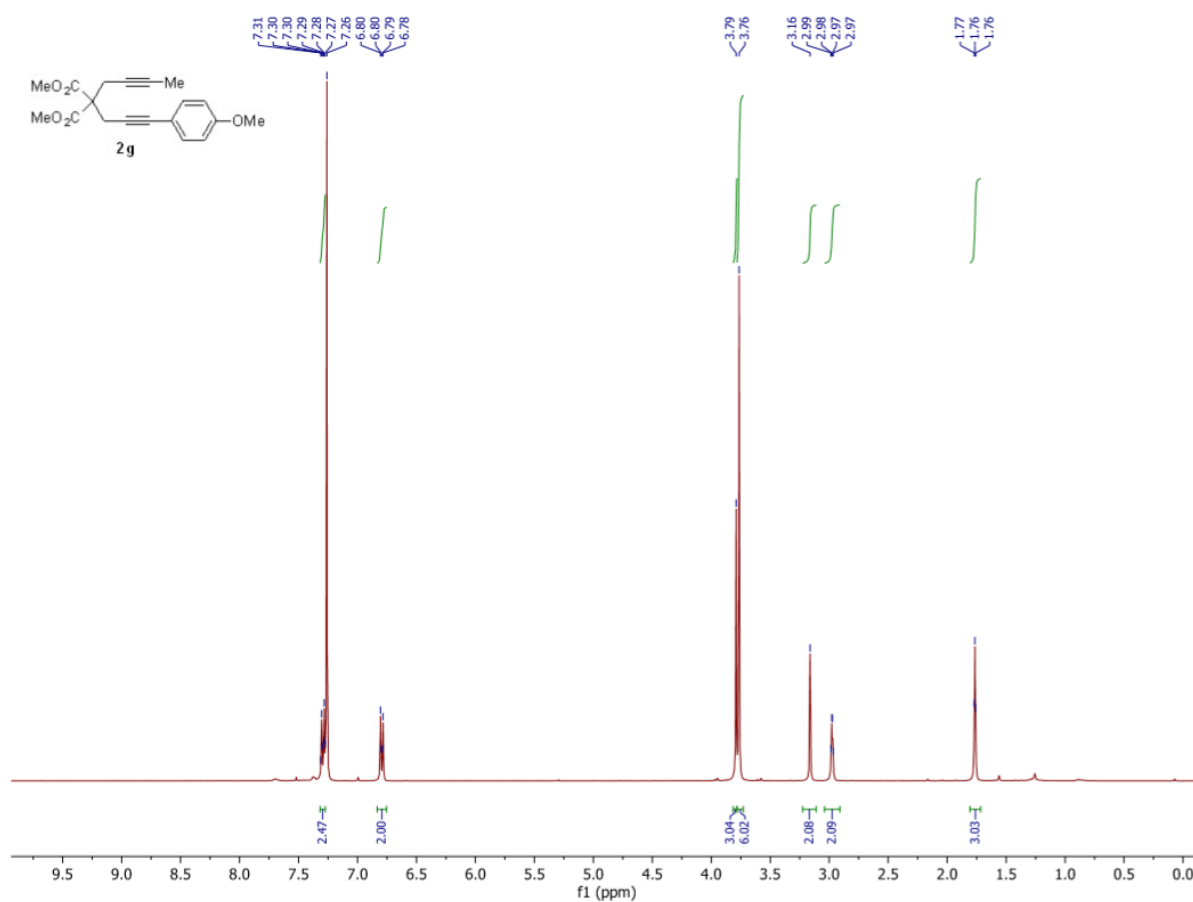
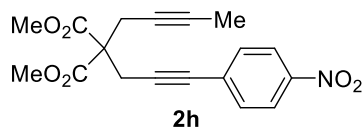


Figure S7 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

<sup>7</sup> Sperger, C.; Strand, L. H. S.; Fiksdahl, A. *Tetrahedron* **2010**, *66*, 7749.

### Dimethyl 2-(but-2-yn-1-yl)-2-(3-(4-nitrophenyl)prop-2-yn-1-yl)malonate (**2h**)



In a round-bottom flask was placed, 1.0 equiv. of dimethyl 2-(but-2-yn-1-yl)-2-(prop-2-yn-1-yl)malonate **2k** (80.0 mg, 0.36 mmol) in 1.06 mL THF under argon. Then 4.0 mol % of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10.1 mg, 0.015 mmol), 8.0 mol % of CuI (5.5 mg, 0.03 mmol), 1.4 equiv. of 4-iodonitrobenzene (74.5 mg, 0.50 mmol) and 0.36 mL of Et<sub>3</sub>N were added. The mixture was stirred and heated at 40 °C (oil bath) for 20 h. Once cooled to room temperature, the reaction mixture was filtrated on celite® pad and was washed with EtOAc. The solution was dried over MgSO<sub>4</sub>, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (9:1).

Yellow solid; yield: 89% (110 mg); mp 89-90°C.

IR cm<sup>-1</sup> 3006, 2925, 1701, 1589, 1525, 1436, 1344.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 8.15 (d, *J* = 6.0 Hz, 2H), 7.50 (d, *J* = 6.0 Hz, 2H), 3.78 (s, 6H), 3.23 (s, 2H), 2.97 (brq, *J* = 3.0 Hz, 2H), 1.77 (brt, *J* = 3.0 Hz, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 169.5 (2C), 147.2, 132.6 (2C), 130.2, 123.6 (2C), 90.4, 82.2, 79.7, 72.8, 57.1, 53.2 (2C), 23.9, 23.5, 3.6.

HRMS (ESI) : *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>6</sub> 344.1129; found : 344.1135.

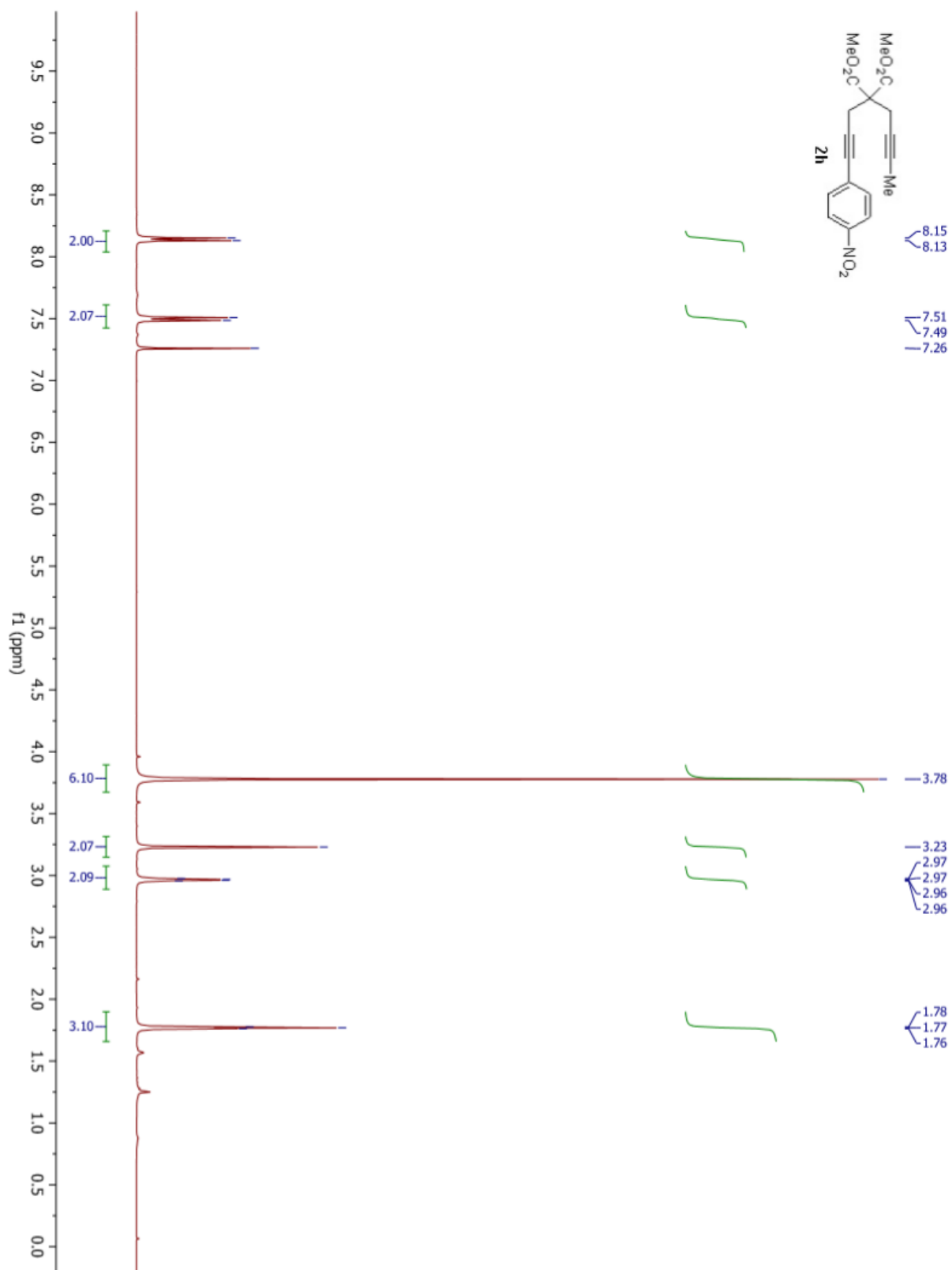


Figure S8 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

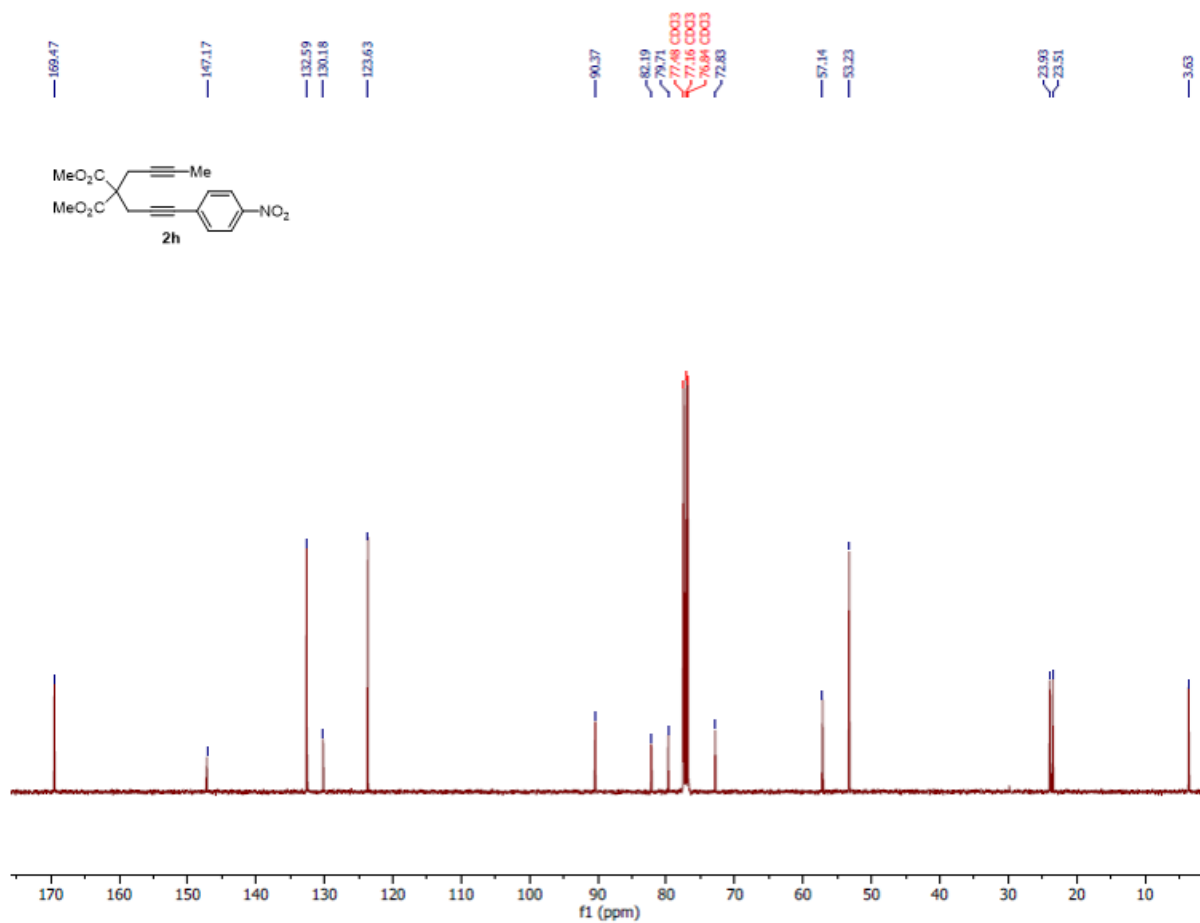


Figure S9 <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum

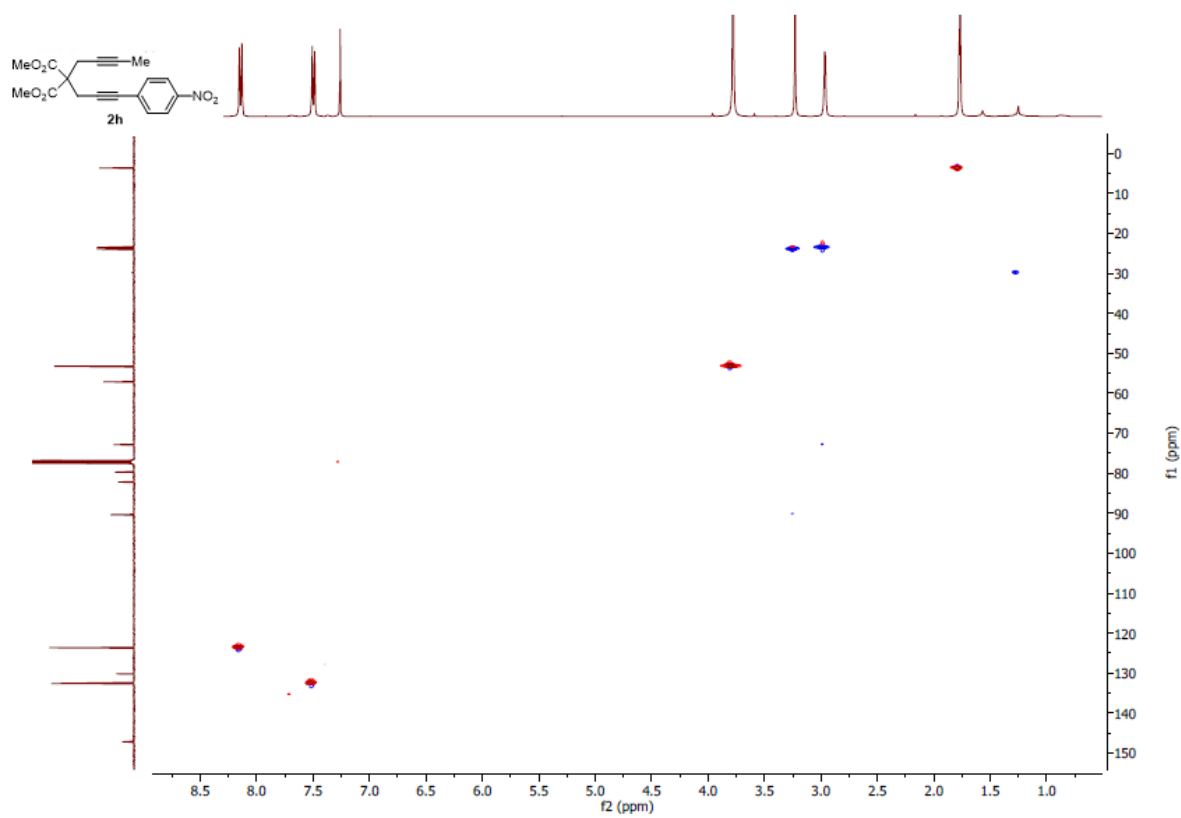
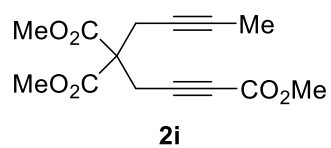
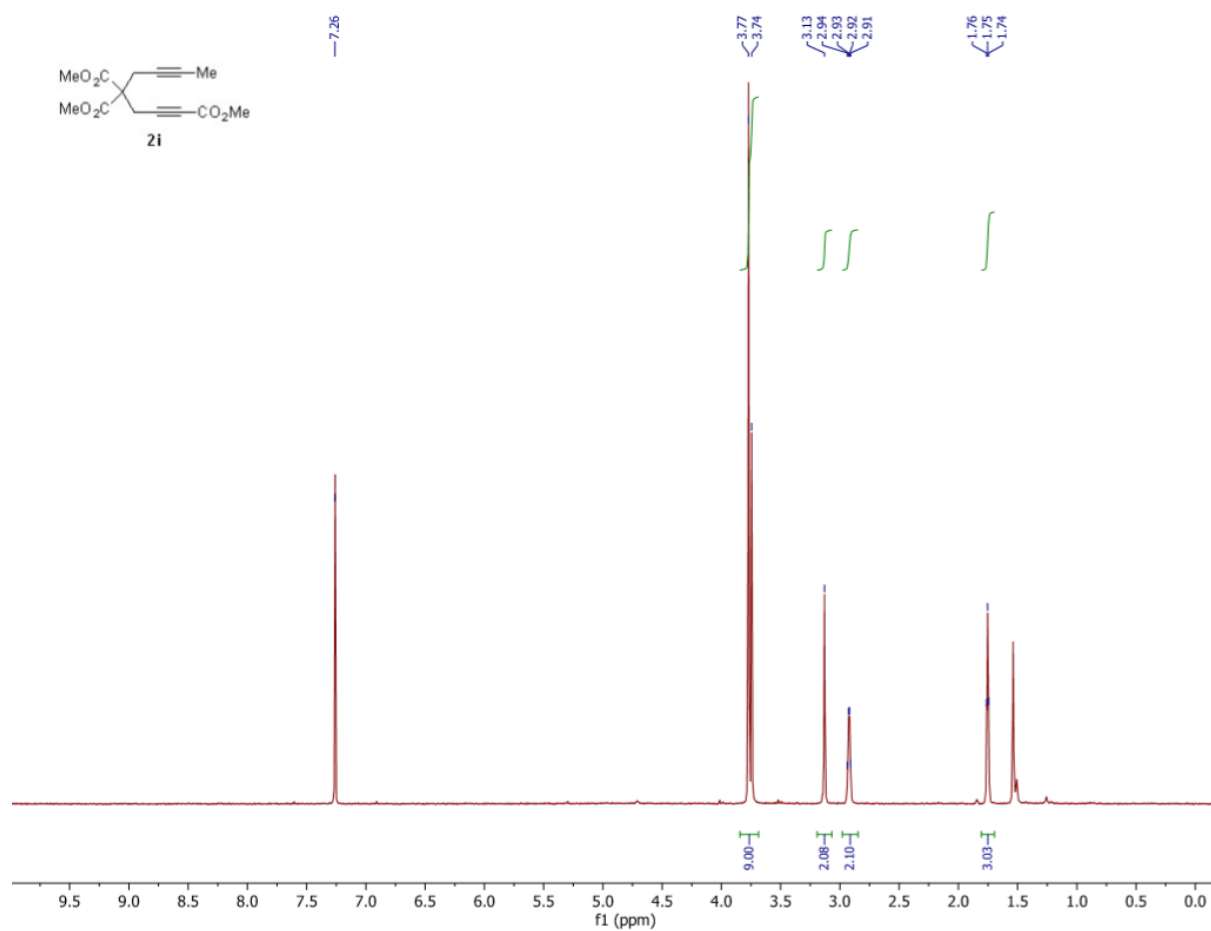


Figure S10 hsqc spectrum

Trimethyl octa-1,6-diyne-1,4,4-tricarboxylate (**2i**)<sup>8</sup>

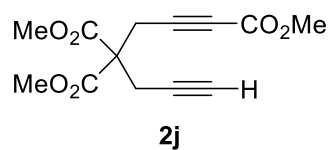


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 3.77 (s, 6H), 3.74 (s, 3H), 3.13 (s, 2H), 2.92 (brq,  $J$  = 2.4 Hz, 2H), 1.75 (brt,  $J$  = 2.4 Hz, 3H).



<sup>8</sup> Shibata, T. ; Kawachi, A. ; Ogawa, M. ; Kuwata, Y. ; Tsuchikama, K. ; Endo, K. *J. Org. Chem.* **2012**, *77*, 908.

Trimethyl hepta-1,6-diyne-1,4,4-tricarboxylate (**2j**)<sup>9</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 3.79 (s, 6H), 3.75 (s, 3H), 3.16 (s, 2H), 3.00 (brd,  $J$  = 2.7 Hz, 2H), 2.06 (brt,  $J$  = 2.7 Hz, 1H).

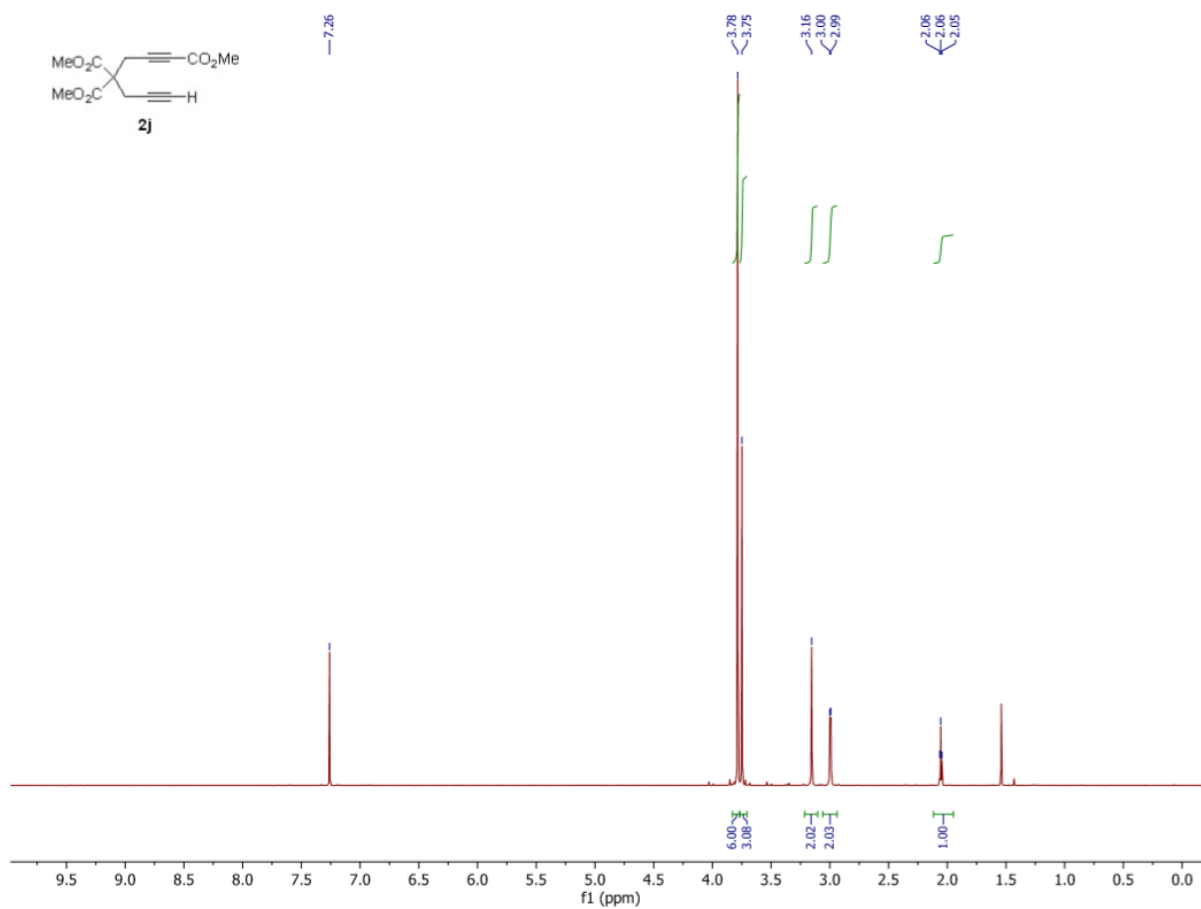
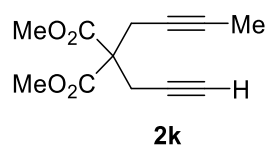


Figure S12 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

<sup>9</sup> Wang, X.; Chakrapani, H.; Madine, J. W.; Keyerleber, M. A.; Widenhoefer, R. A. *J. Org. Chem.* **2002**, *67*, 2778.

Dimethyl 2-(but-2-yn-1-yl)-2-(prop-2-yn-1-yl)malonate (**2k**)<sup>2</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 3.74 (s, 6H), 2.96 (brd,  $J$  = 2.7 Hz, 2H), 2.91 (brq,  $J$  = 2.7 Hz, 2H), 2.01 (brt,  $J$  = 2.7 Hz, 1H), 1.74 (brt,  $J$  = 2.7 Hz, 3H).

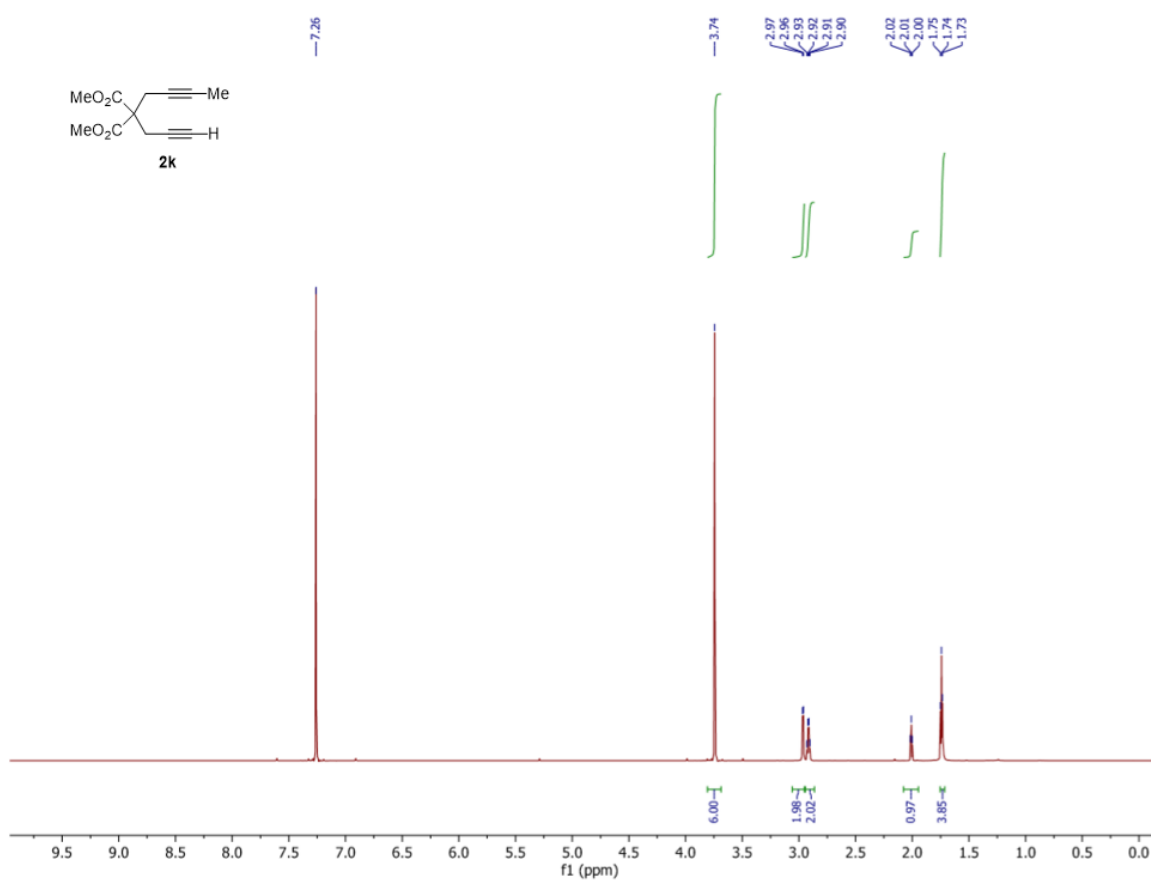
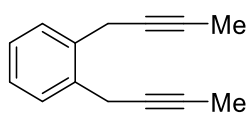


Figure S13 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

1,2-di(but-2-yn-1-yl)benzene (**2I**)<sup>10</sup>



**2I**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 7.43 (dd,  $J$  = 3.2 Hz, 5.2 Hz, 2H), 7.23 (dd,  $J$  = 3.6 Hz, 5.2 Hz, 2H), 3.55 (brq,  $J$  = 2.8 Hz, 4H), 1.84 (brt,  $J$  = 2.8 Hz, 6H).

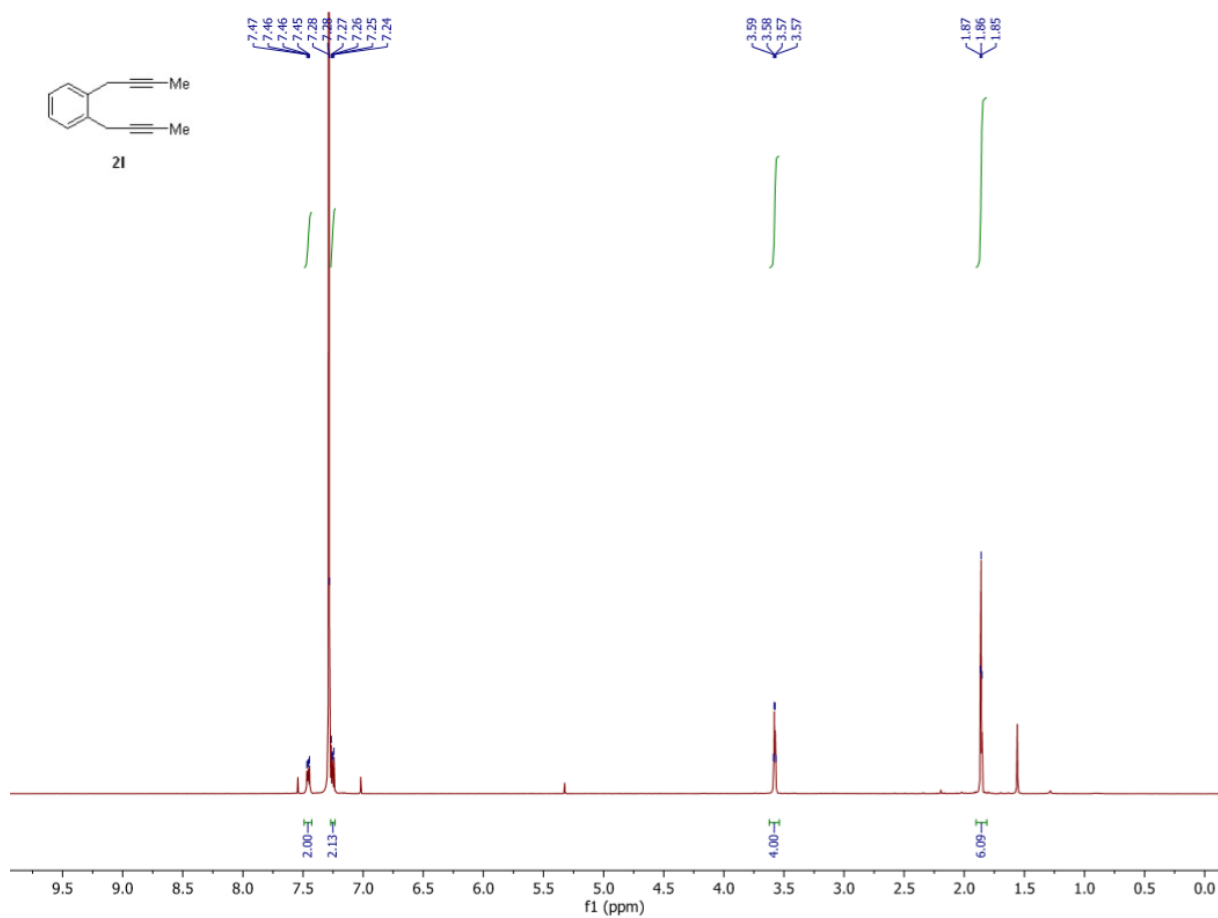
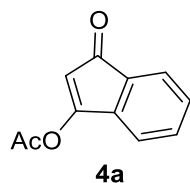


Figure S14 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

<sup>10</sup> Ogasawara, M.; Kotani, S.; Nakajima, H.; Furusho, H.; Miyasaka, M.; Shimoda, Y.; Wu, W.-Y.; Sugiura, M.; Takahashi, T.; Nakajima, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 13798.

### 1-oxo-1*H*-inden-3-yl acetate (**4a**)



The product **4a** was synthesized using a reported procedure with some modifications.<sup>11</sup>

In a Schlenk tube were placed, 1.0 equiv. of 1,3-indandione **7** (1.20 g, 8.20 mmol), 7.0 equiv. of isopropenyl acetate (5.75 g, 57.5 mmol) and 0.03 equiv. of *p*-toluenesulfonic acid (48.0 mg, 0.25 mmol) under argon. The mixture was stirred and heated at 110 °C (oil bath) for 12 h. Once cooled to room temperature, the reaction mixture was diluted with chloroform and washed successively with sat. NaHCO<sub>3</sub>aq and brine. The combined organic phases were dried over MgSO<sub>4</sub>, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (1:0 to 8:2).

Yellow solid; yield: 48% (720 mg)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 7.48 (d, *J* = 7.2 Hz, 1H), 7.39 (td, *J* = 1.2 Hz, 7.5 Hz, 1H), 7.32 (td, *J* = 1.2 Hz, 6.9 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.02 (s, 1H), 2.40 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 195.8, 167.7, 166.4, 140.3, 132.9, 130.8, 130.4, 122.2, 118.9, 108.1, 21.6.

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<sup>11</sup> Sraga, J.; Hrnčiar, P. *Chemical Papers* **1986**, *40*, 807.

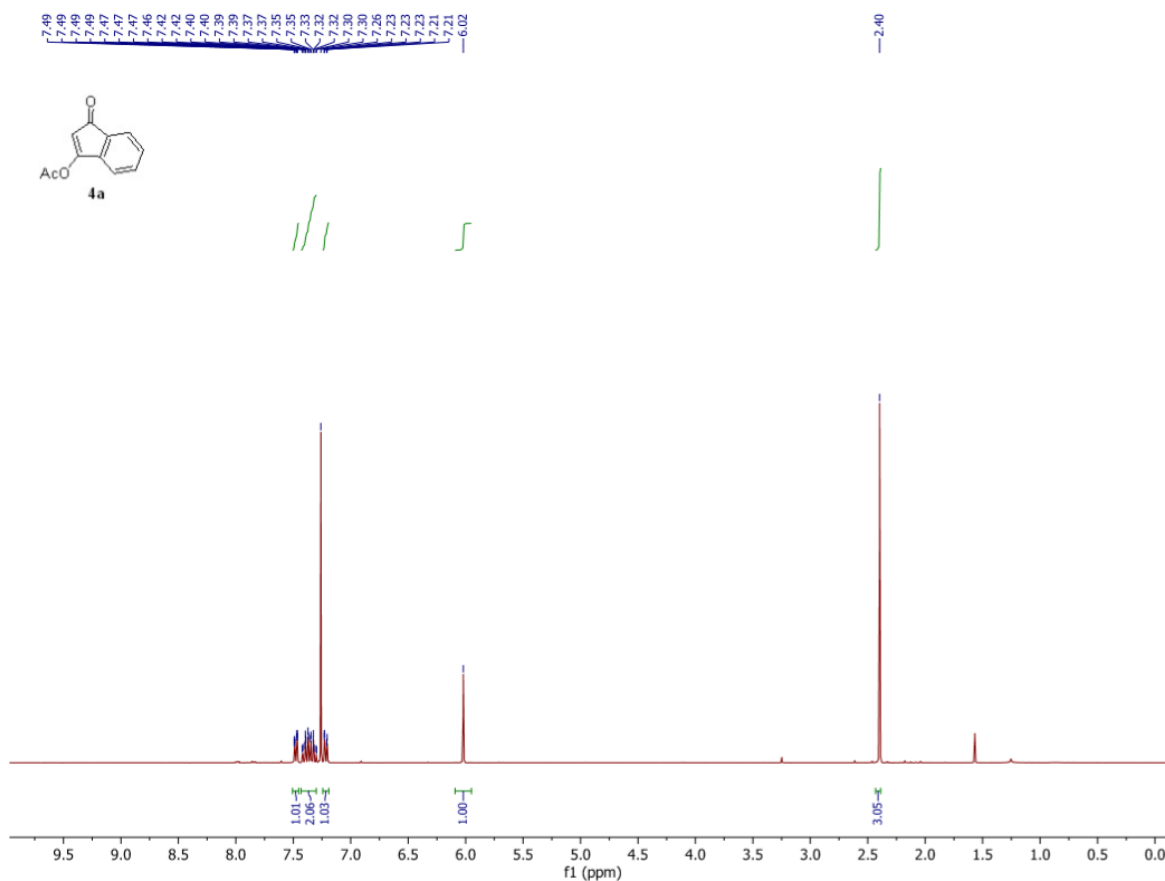


Figure S15 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

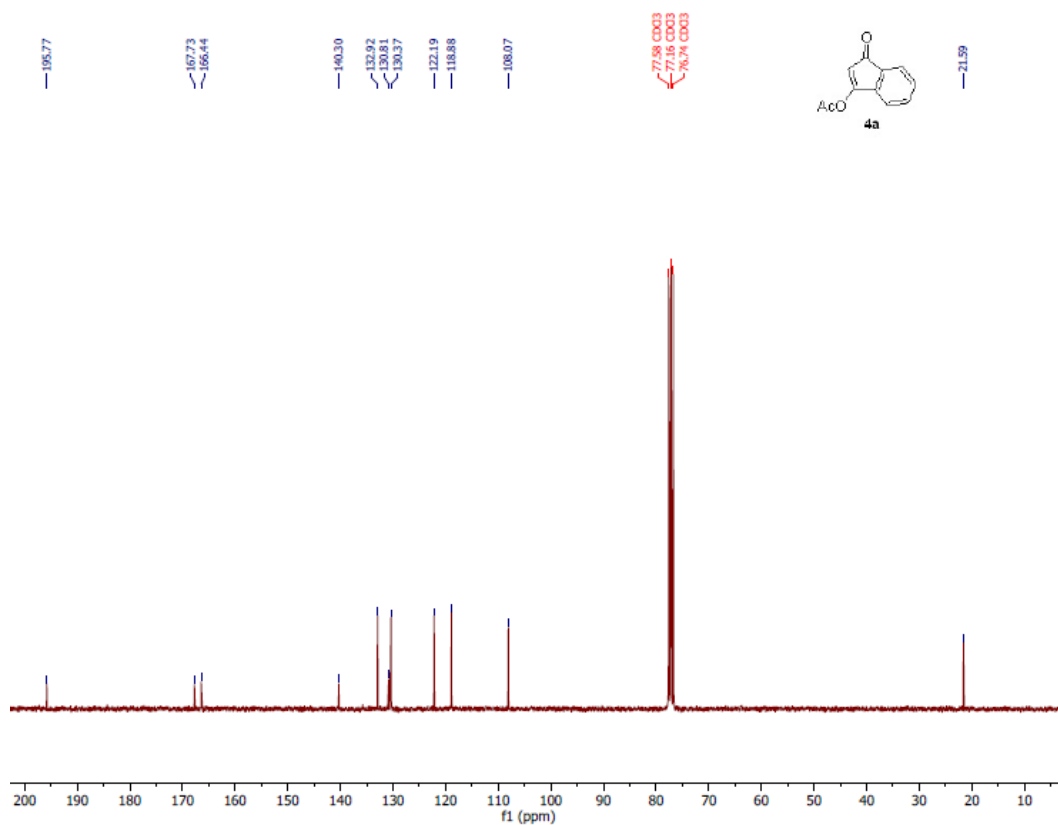
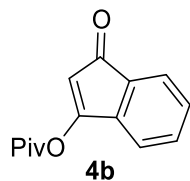


Figure S16 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

### 1-oxo-1*H*-inden-3-yl pivalate (**4b**)



In a Schlenk tube, under argon, were placed, 1.0 equiv. of 1,3-indandione **7** (150 mg, 1.02 mmol) and 2.0 equiv. of triethylamine (206 mg, 2.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.02 mL). At 0 °C 1.5 equiv. of pivaloyl chloride (185.7 mg, 1.54 mmol) was added. The mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed successively with water and sat. NH<sub>4</sub>Cl<sub>aq</sub> and brine. The combined organic phases were dried over MgSO<sub>4</sub>, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (100% to 8:2).

Yellow solid; yield: 34% (75 mg); mp 41 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 7.48 (d, *J* = 7.5 Hz, 1H), 7.43-7.30 (m, 2H), 7.20 (d, *J* = 6.0 Hz, 1H), 6.00 (s, 1H), 1.39 (s, 9H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 195.8, 174.0, 168.1, 140.6, 132.9, 130.9, 130.4, 122.2, 118.7, 107.9, 40.2, 27.1 (3C).

HRMS (ESI) : *m/z* [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub>O<sub>3</sub> 231.1016; found : 231.1013.



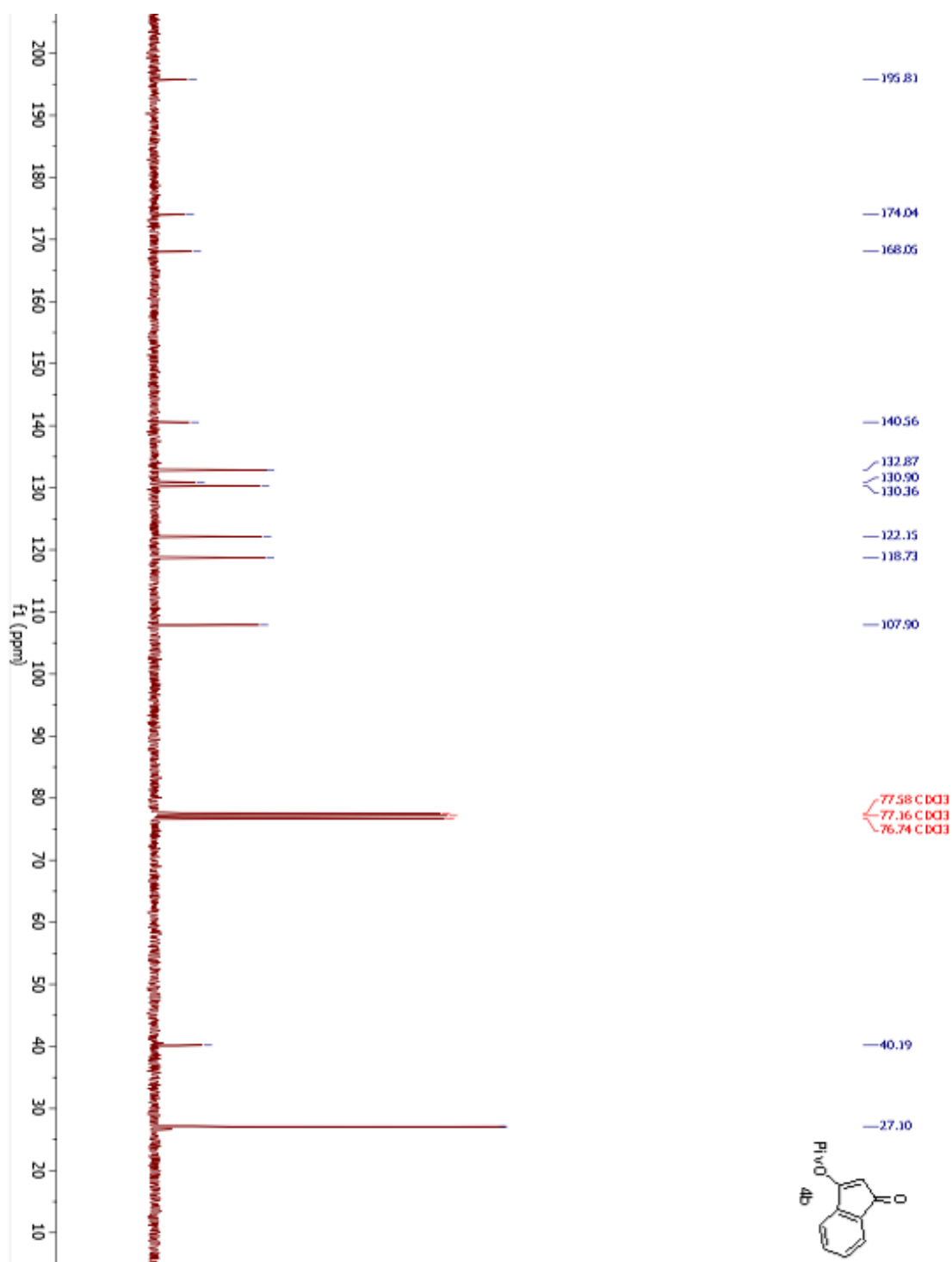
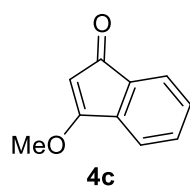


Figure S18  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) spectrum

### 3-methoxy-1H-inden-1-one (4c) (known)<sup>12</sup>



In a Schlenk tube were placed, 1.0 equiv. of 1,3-indandione **7** (500 mg, 3.42 mmol), 2.5 equiv. of  $K_2CO_3$  (1.18 g, 8.55 mmol) and 5.0 equiv. of dimethyl sulfate (2.15 g, 17.1 mmol) in 34.0 mL DMF under argon. The mixture was stirred and heated at 40 °C (oil bath) for 12 h. Once cooled to room temperature, the reaction mixture was quenched with sat.  $NH_4Cl_{aq}$  and extracted with EtOAc (three times). The combined organic phases were washed with brine. The combined organic phases were dried over  $MgSO_4$ , filtrated and the solvent was removed under vacuum. The crude residue was purified by Florisil® using pentane/EtOAc as eluent (100% to 95:5).

Orange solid; yield: 45% (246 mg).

$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  = 7.43 (d,  $J$  = 6.9 Hz, 1H), 7.36 (d,  $J$  = 7.2 Hz, 1H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.22 (d,  $J$  = 6.9 Hz, 1H), 5.07 (s, 1H), 4.00 (s, 3H).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  = 194.8, 180.1, 139.6, 133.5, 132.3, 130.4, 121.3, 118.8, 96.6, 58.8.

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<sup>12</sup> Ferreira, S. B.; Kaiser, C. R.; Ferreira, V. F. *Synlett* **2008**, 17, 2625.

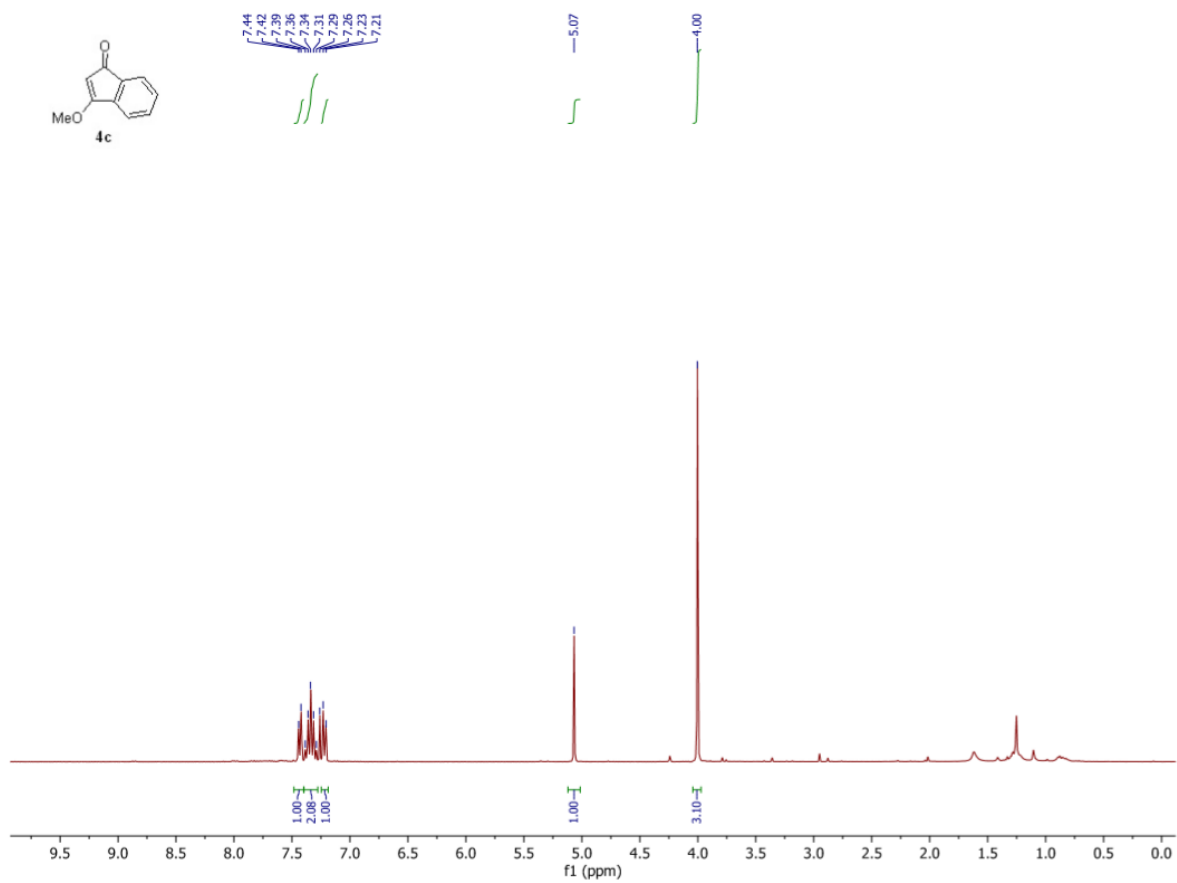


Figure S19 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

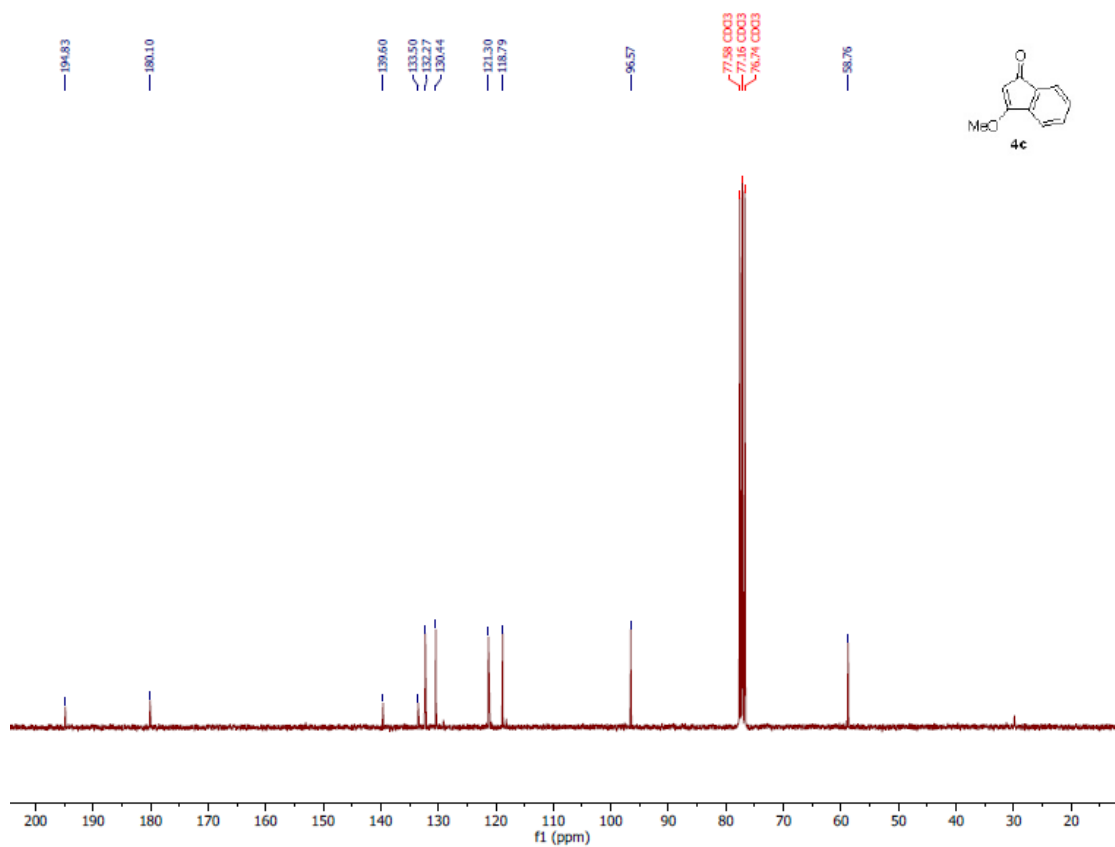
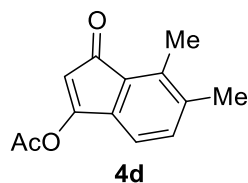


Figure S20 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

#### 6,7-dimethyl-1-oxo-1H-inden-3-yl acetate (4d)



In a Schlenk tube were placed, 1.0 equiv. of 4,5-dimethyl-1*H*-indene-1,3(2*H*)-dione (46 mg, 0.264 mmol), 7.0 equiv. of isopropenyl acetate (185 mg, 1.8 mmol) and 0.03 equiv. of *p*-toluenesulfonic acid (1.5 mg, 0.00792 mmol) under argon. The mixture was stirred and heated at 110 °C (oil bath) for 12 h. Once cooled to room temperature, the reaction mixture was diluted with chloroform and washed successively with sat. NaHCO<sub>3aq</sub> and brine. The combined organic phases were dried over MgSO<sub>4</sub>, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (1:0 to 8:2).

Yellow solid; yield: 83% (47 mg); mp 101 °C.

IR cm<sup>-1</sup> 3018, 2919, 2854, 1728, 1691, 1562.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = 7.10 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 5.89 (s, 1H), 2.48 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 197.6, 166.9, 166.6, 141.2, 138.3, 136.9, 132.6, 127.3, 116.3, 107.9, 21.6, 19.6, 13.5.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub> 217.0859; found : 217.0862.

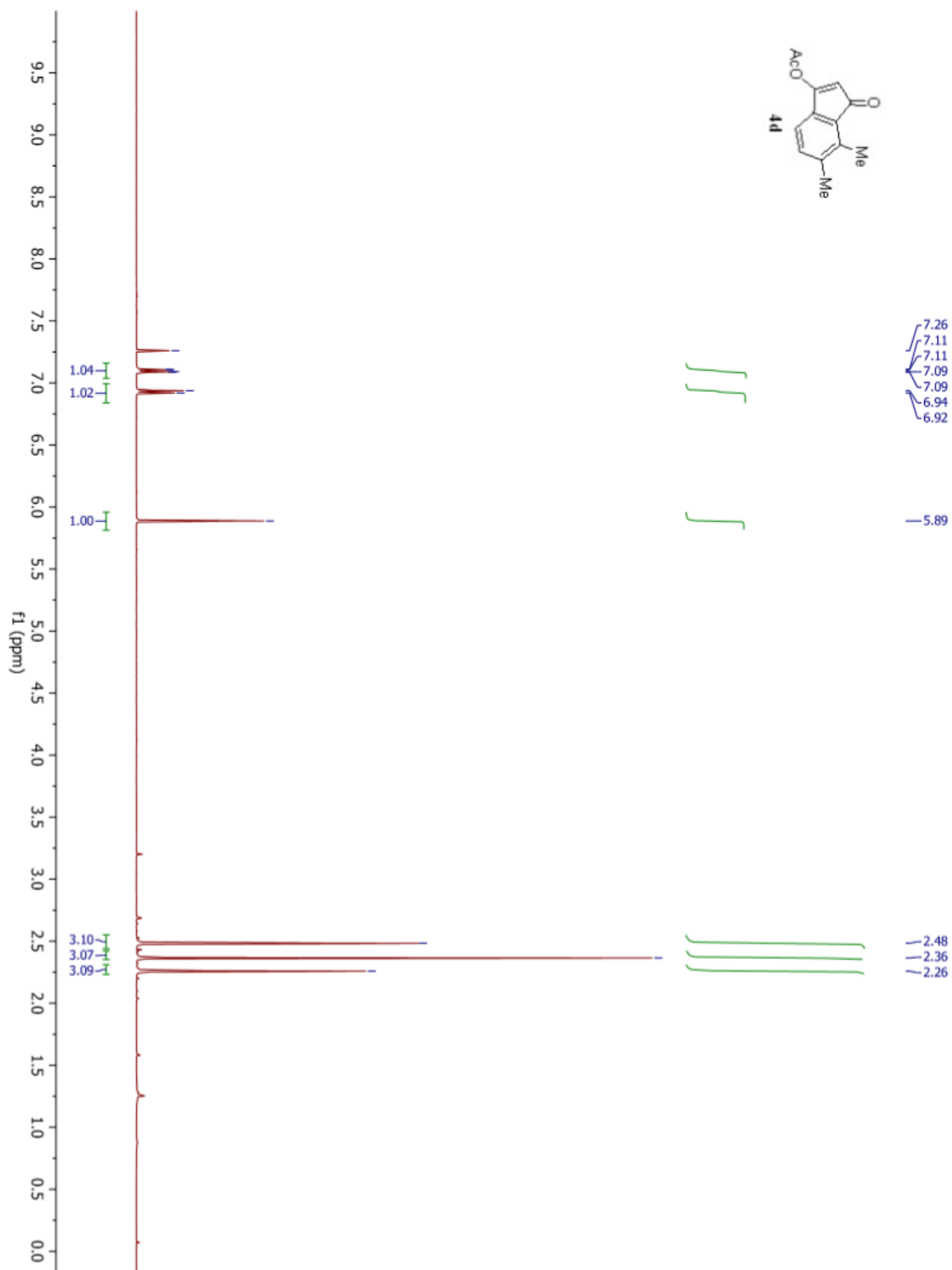


Figure S21 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

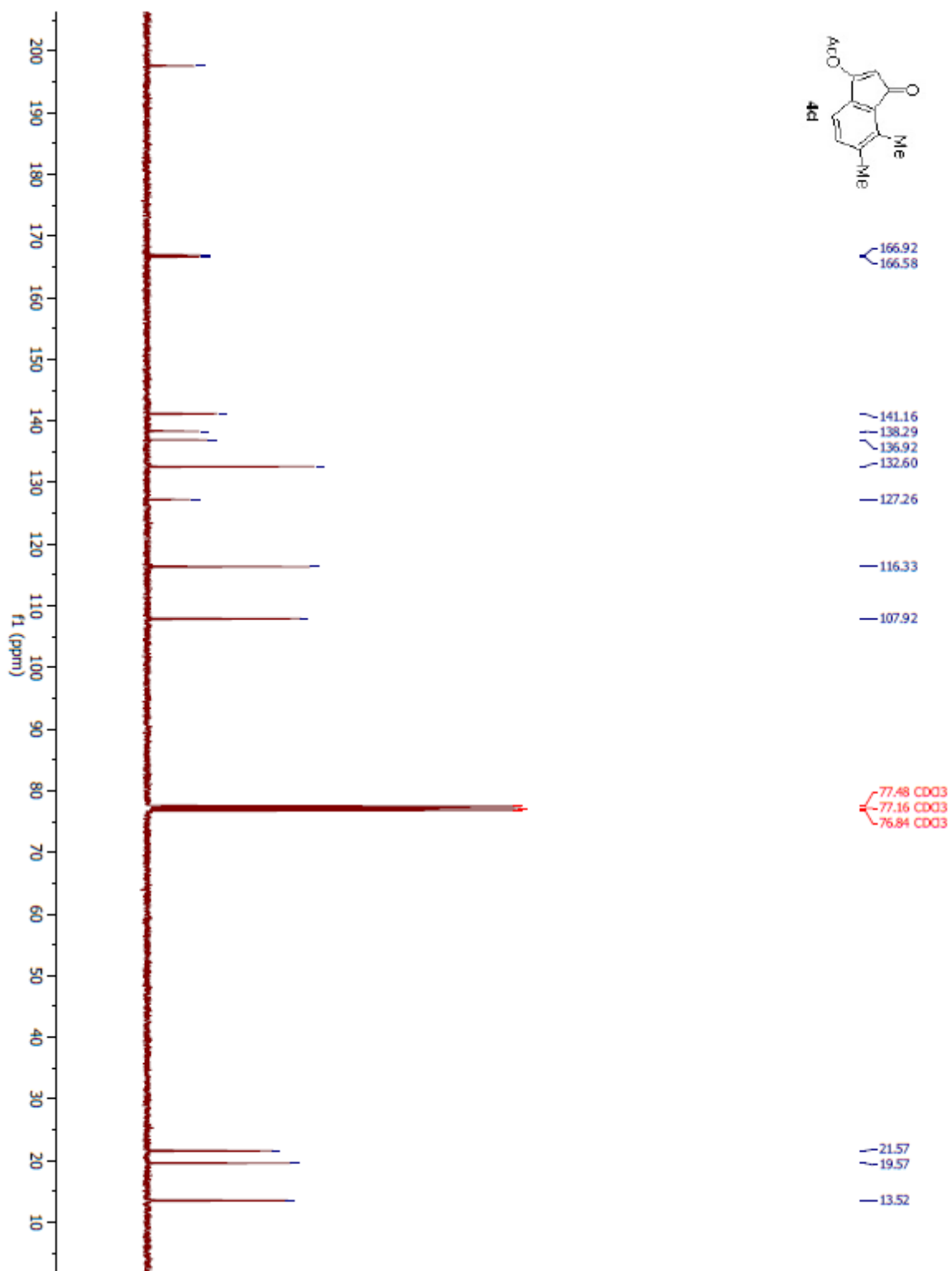
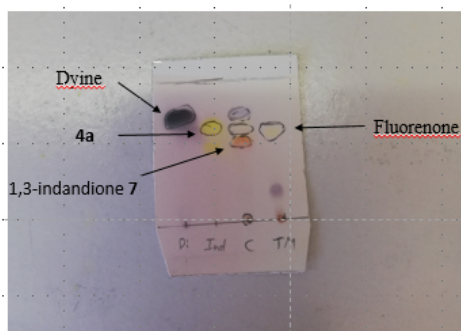
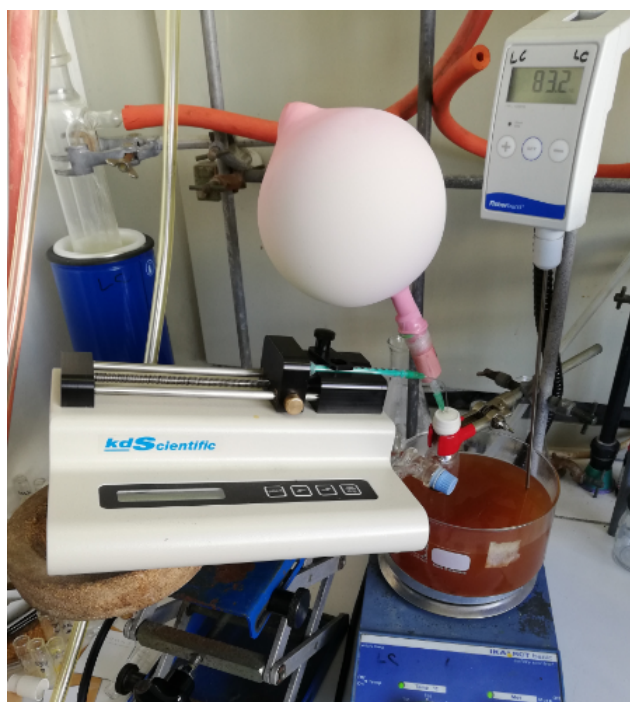


Figure S22 <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum

#### 4. General procedure for the [2+2+2] cycloaddition reaction

Inside the glove box, in a Schlenk tube were placed 10 mol% (0.0127 mmol, 5.5 mg) of  $[\text{RhCl}(\text{hexadiene})]_2$ , 20 mol% (0.025 mmol, 16.0 mg) of rac-BINAP and 20 mol% (0.025 mmol, 5.0 mg) of  $\text{AgBF}_4$  in degassed anhydrous 1,2-DCE (0.3 mL). The mixture was stirred at room temperature for 10 min. Then 1.0 equiv. (0.127 mmol) of **4a** or **4c** and 2.0 equiv. (0.254 mmol, 10.0 mg) of  $\text{CaH}_2$  were added. A solution of 1.0 equiv. of the corresponding diyne (0.127 mmol) in degassed anhydrous 1,2-dichloroethane (0.7 mL), prepared inside the glovebox, was added dropwise (rate: 0.06 mL/h - 0.0106 mmol/h - 12 h) at 80 °C (oil bath) outside the glovebox. At the end of the addition, the crude mixture was stirred 3 h more, then the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel provided the desired product (eluent  $\text{CH}_2\text{Cl}_2$  and 0.1% triethylamine). After the silica gel column chromatography, when the desired cycloadduct **1** is obtained with traces of diene **6** and diketone **7**, the resulting mixture is triturated in pentane. Diene **6** and diketone **7** are then soluble (cycloadduct **1** is not) and removed with a Pasteur pipett. The process is repeated several times.

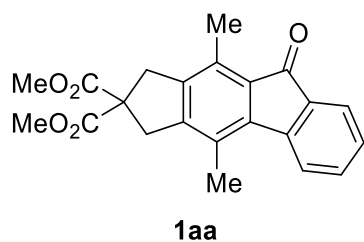


## 5. Procedure for the preparation of **1ca** on a 1 mmol scale

Inside the glove box, in a Schlenk tube were placed 10 mol% (0.10 mmol, 42.0 mg) of  $[\text{RhCl}(\text{hexadiene})]_2$ , 20 mol% (0.20 mmol, 124 mg) of rac-BINAP and 20 mol% (0.20 mmol, 39.0 mg) of  $\text{AgBF}_4$  in degassed anhydrous 1,2-DCE (2.4 mL). The mixture was stirred at room temperature for 10 min. Then 1.0 equiv. (1.0 mmol, 188 mg) of **4a** and 2.0 equiv. (2.0 mmol, 78.0 mg) of  $\text{CaH}_2$  were added. A solution of 1.0 equiv. of **2c** (1.0 mmol, 170 mg) in degassed anhydrous 1,2-dichloroethane (5.4 mL), prepared inside the glovebox, was added dropwise (rate : 0.06 mL/h - 0.0106 mmol/h – 94 h) at 80 °C (oil bath) outside the glovebox. At the end of the addition, the crude mixture was stirred 3 h more, then the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel (eluent  $\text{CH}_2\text{Cl}_2$  and 0.1% triethylamine). The desired cycloadduct **1ca** which is in mixture with traces of **7** is triturated in pentane. Diketone **7** is then soluble (cycloadduct **1ca** is not) and removed with a Pasteur pipett. The process is repeated several times provided the desired product **1ca** (112 mg, 66% yield).

## 6. Compound characterization data

### Dimethyl 4,10-dimethyl-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarboxylate (1aa)



Yellow solid; yield: 76% (35 mg); mp 259-260 °C.

IR  $\text{cm}^{-1}$  2952, 2849, 2357, 1731, 1688, 1434, 1365.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.62 (d,  $J$  = 2.4 Hz, 1H), 7.59 (d,  $J$  = 2.4 Hz, 1H), 7.43 (t,  $J$  = 7.2 Hz, 1H), 7.23 (t,  $J$  = 7.5 Hz, 1H), 3.78 (s, 6H), 3.61 (s, 2H), 3.56 (s, 2H), 2.53 (s, 3H), 2.46 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 195.2, 172.1 (2C), 146.3, 144.6, 142.6, 140.8, 135.4, 134.3, 133.1, 131.1, 128.1, 127.3, 123.9, 123.1, 59.2, 53.3 (2C), 40.3, 39.3, 16.5, 14.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{21}\text{O}_5$  365.1384; found : 365.1384.

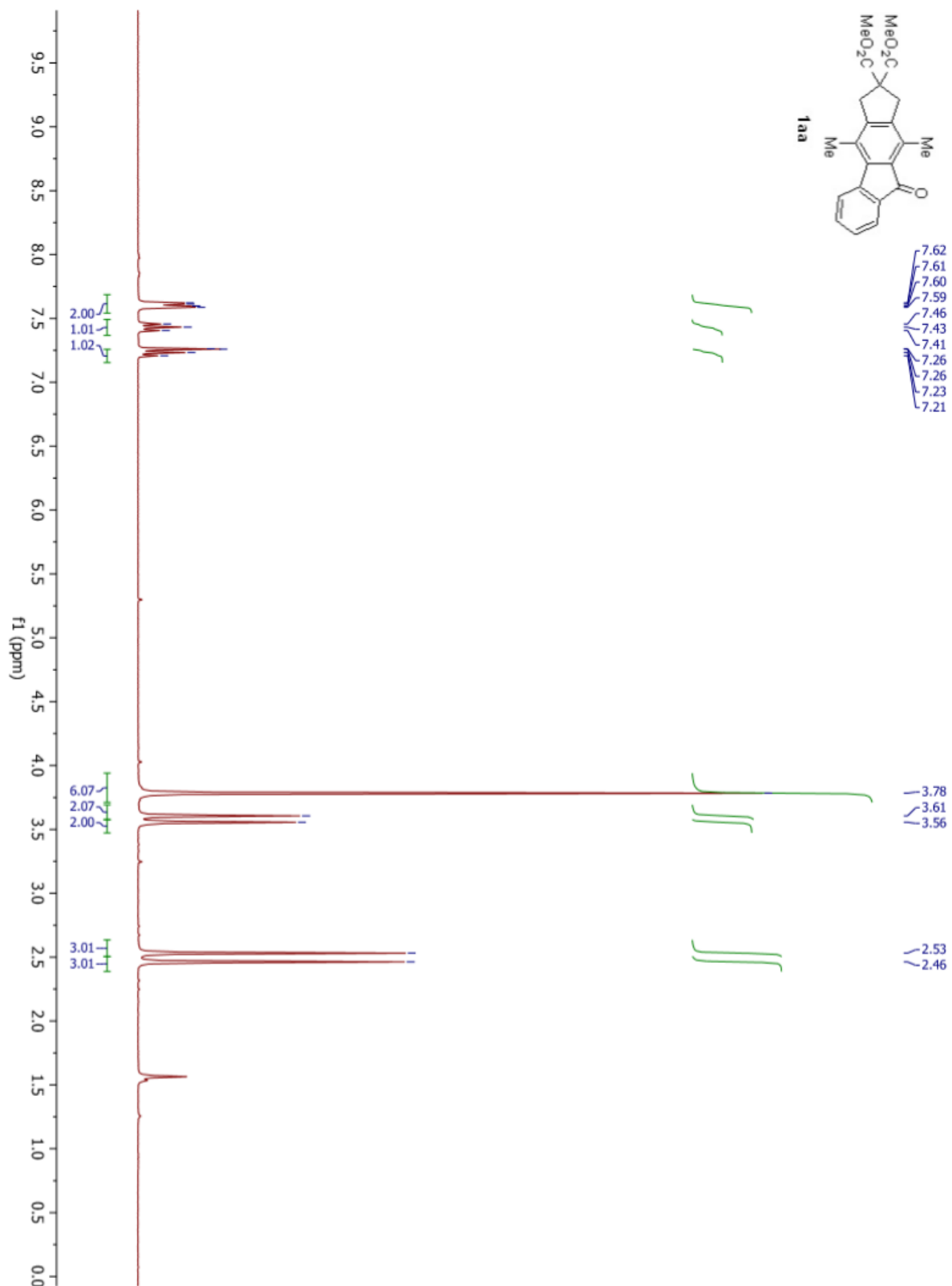


Figure S23 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

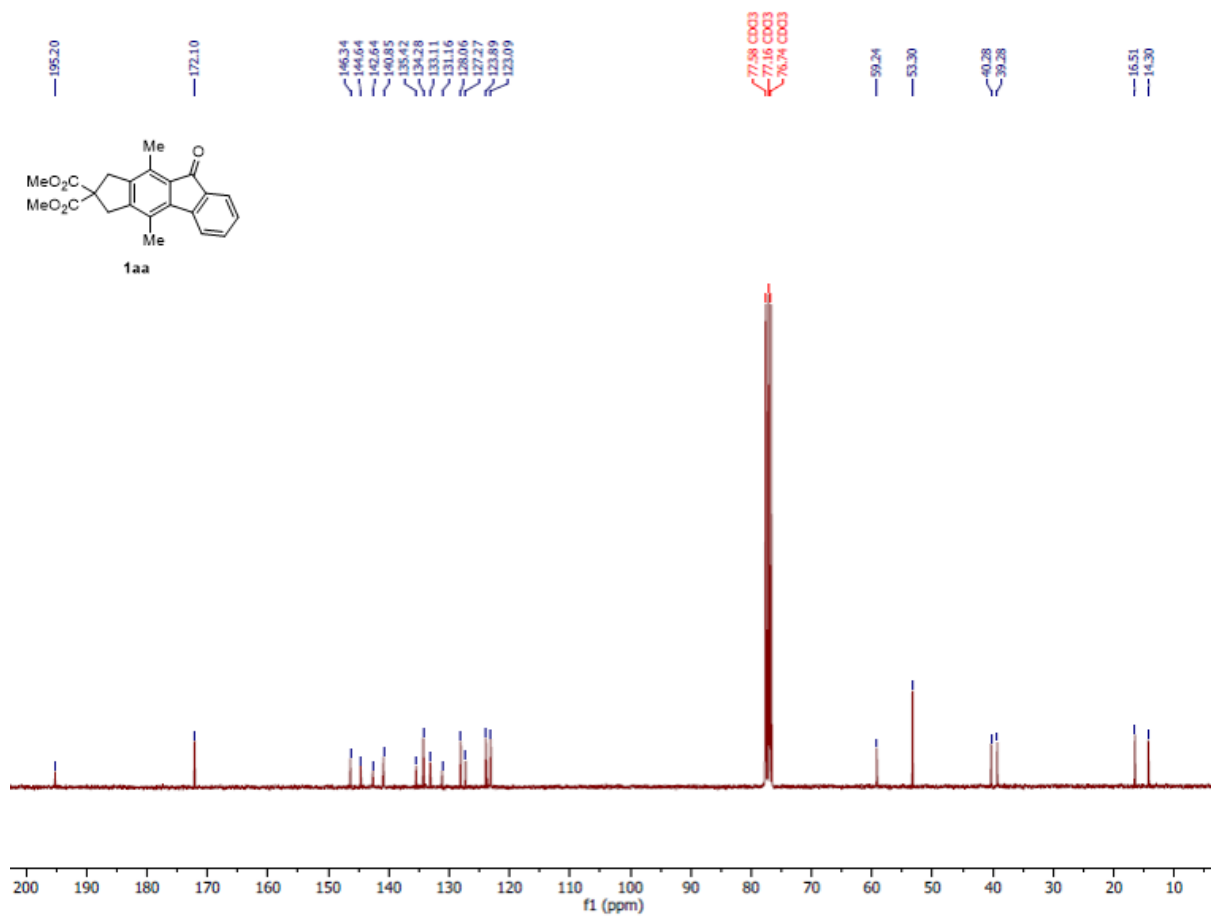


Figure S24 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectra

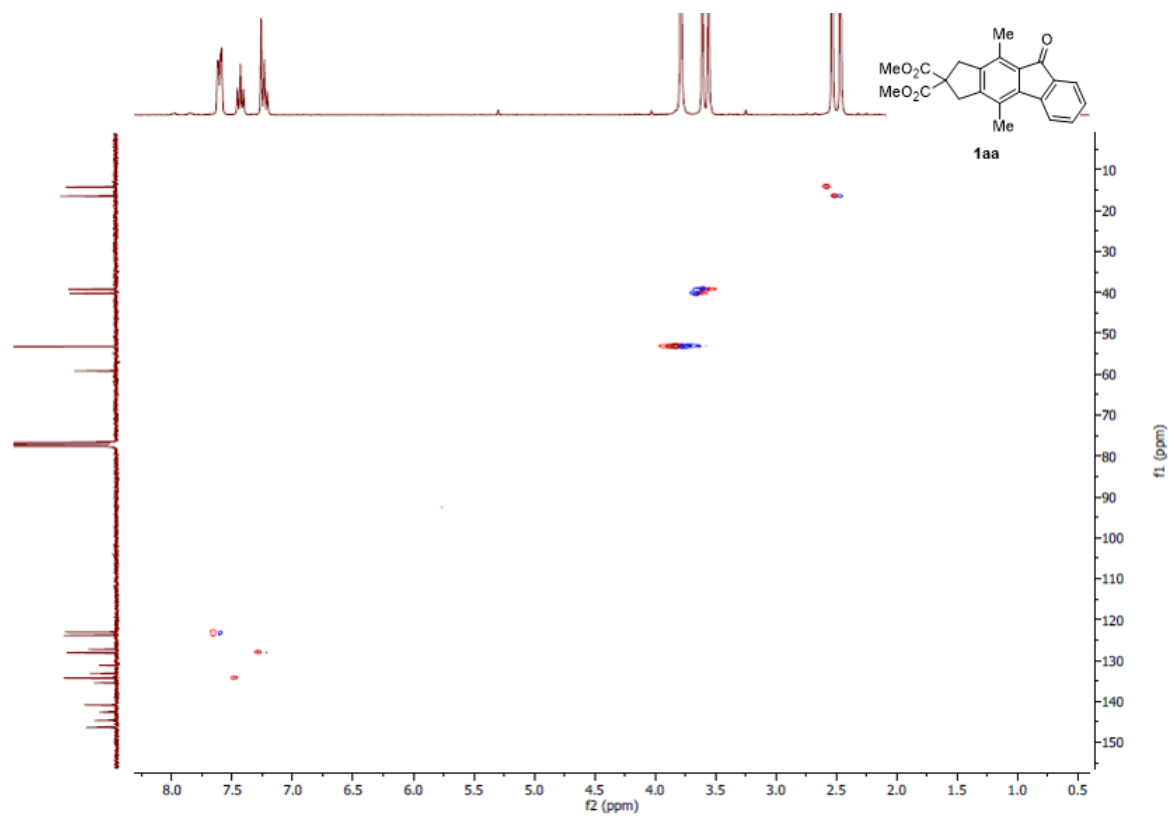
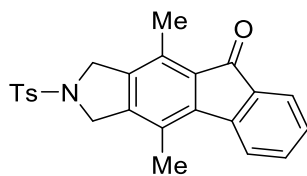


Figure S25 HSQC spectrum

**4,10-dimethyl-2-tosyl-2,3-dihydroindeno[1,2-f]isoindol-9(1H)-one (1ba)**



**1ba**

Yellow solid; yield: 54% (27 mg); mp 259-261 °C.

IR  $\text{cm}^{-1}$  2924, 1703, 1597, 1491, 1446, 1343, 1289.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.84-7.77 (m, 2H), 7.60 (t,  $J$  = 8.4 Hz, 2H), 7.45 (td,  $J$  = 1.0 Hz, 7.5 Hz, 1H), 7.40-7.30 (m, 3H), 4.64 (s, 2H), 4.58 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 194.7, 144.1, 144.0, 143.1, 142.3, 137.2, 135.2, 134.5, 134.0, 131.8, 131.6, 130.1 (2C), 128.6, 127.7 (2C), 125.9, 124.1, 123.3, 53.9, 53.3, 21.7, 16.4, 14.1.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{22}\text{NO}_3\text{S}$  404.1315; found : 404.1309.

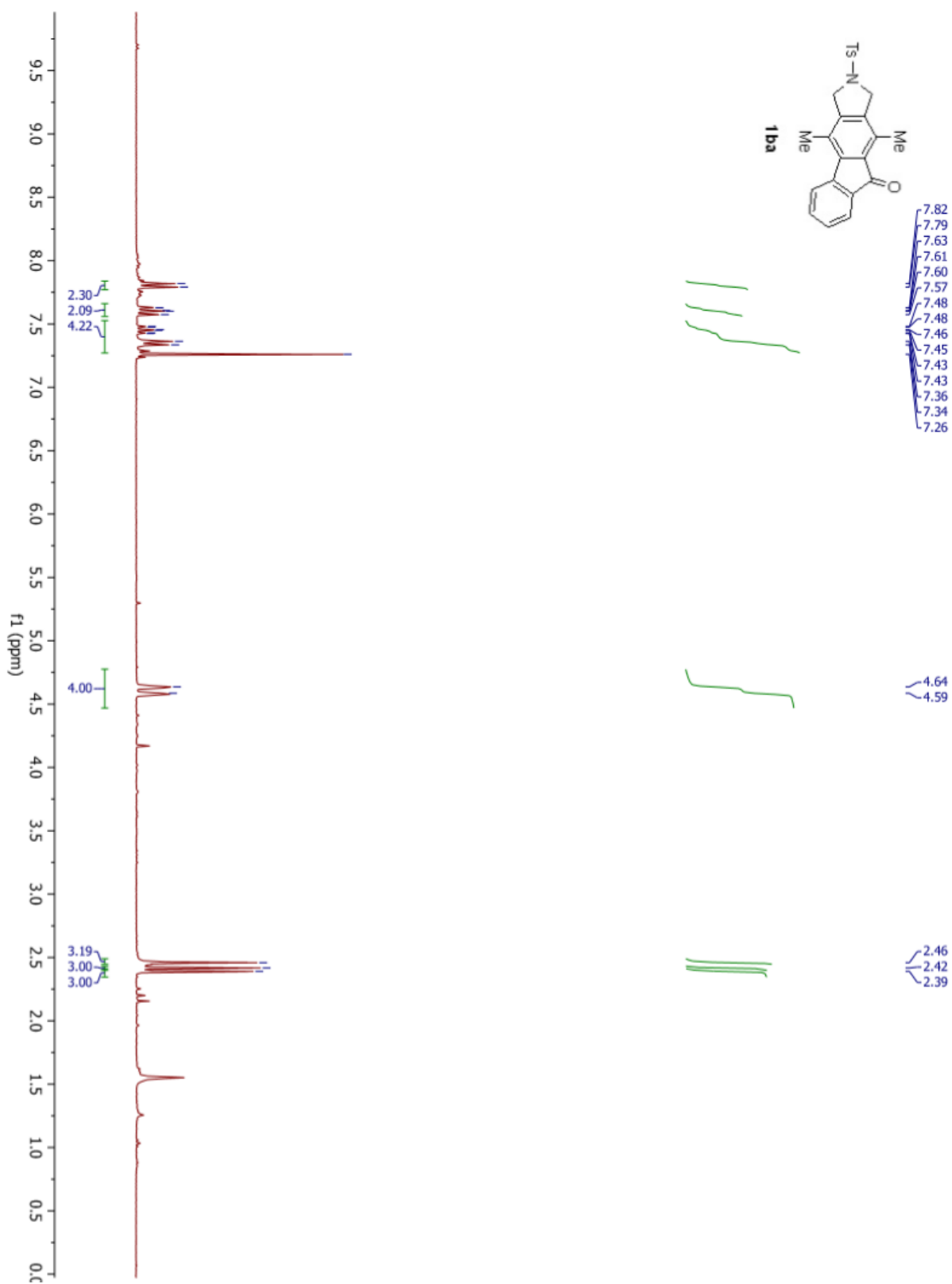


Figure S26  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) spectrum

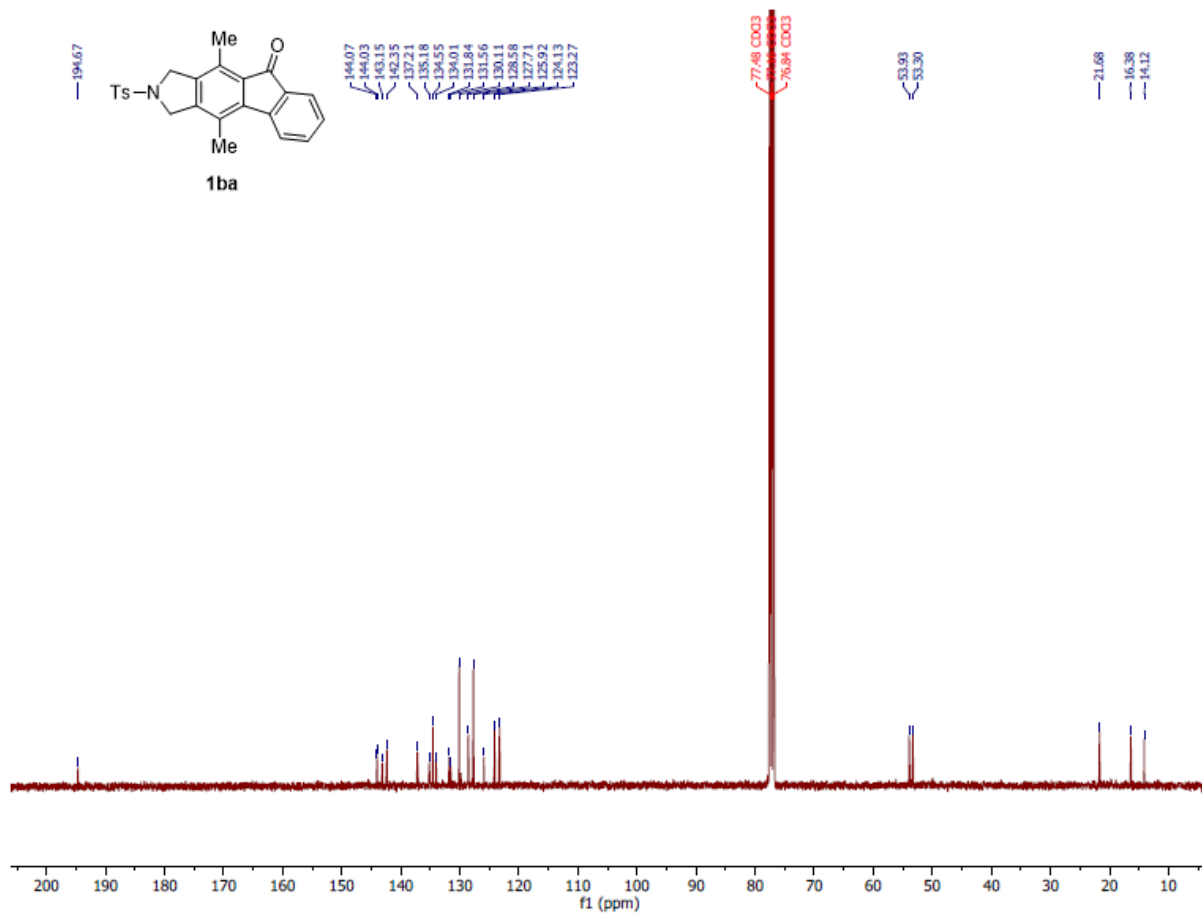


Figure S27 <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum

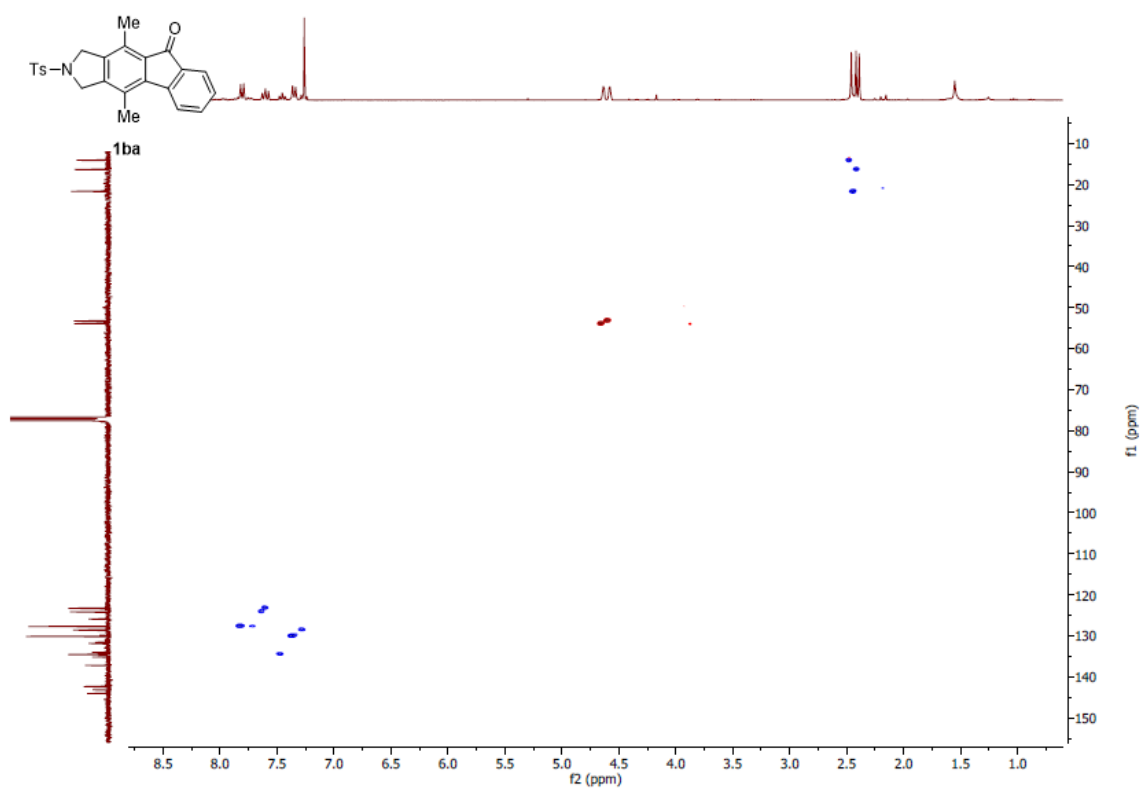
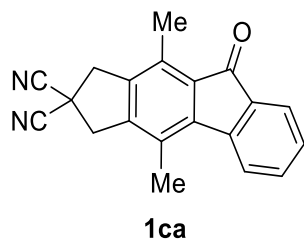


Figure S28 HSQC spectrum

**4,10-dimethyl-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarbonitrile (1ca)**



Yellow solid; yield: 81% (17 mg); mp 296-297 °C.

IR  $\text{cm}^{-1}$  2957, 2852, 2361, 1705, 1603, 1507, 1459, 1377.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.71-7.63 (m, 2H), 7.50 (td,  $J$  = 1.2 Hz, 7.8 Hz, 1H), 7.32 (td,  $J$  = 1.0 Hz, 7.5 Hz, 1H), 3.77 (s, 2H), 3.72 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 40 °C to solubilize the product)  $\delta$  = 194.7, 144.0, 142.4, 137.4, 135.4, 134.7, 133.5, 132.4, 128.9, 127.7, 124.4 (2C), 123.5, 116.3 (2C), 44.5, 43.6, 33.1, 16.7, 14.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}$  299.1179; found : 299.1179.

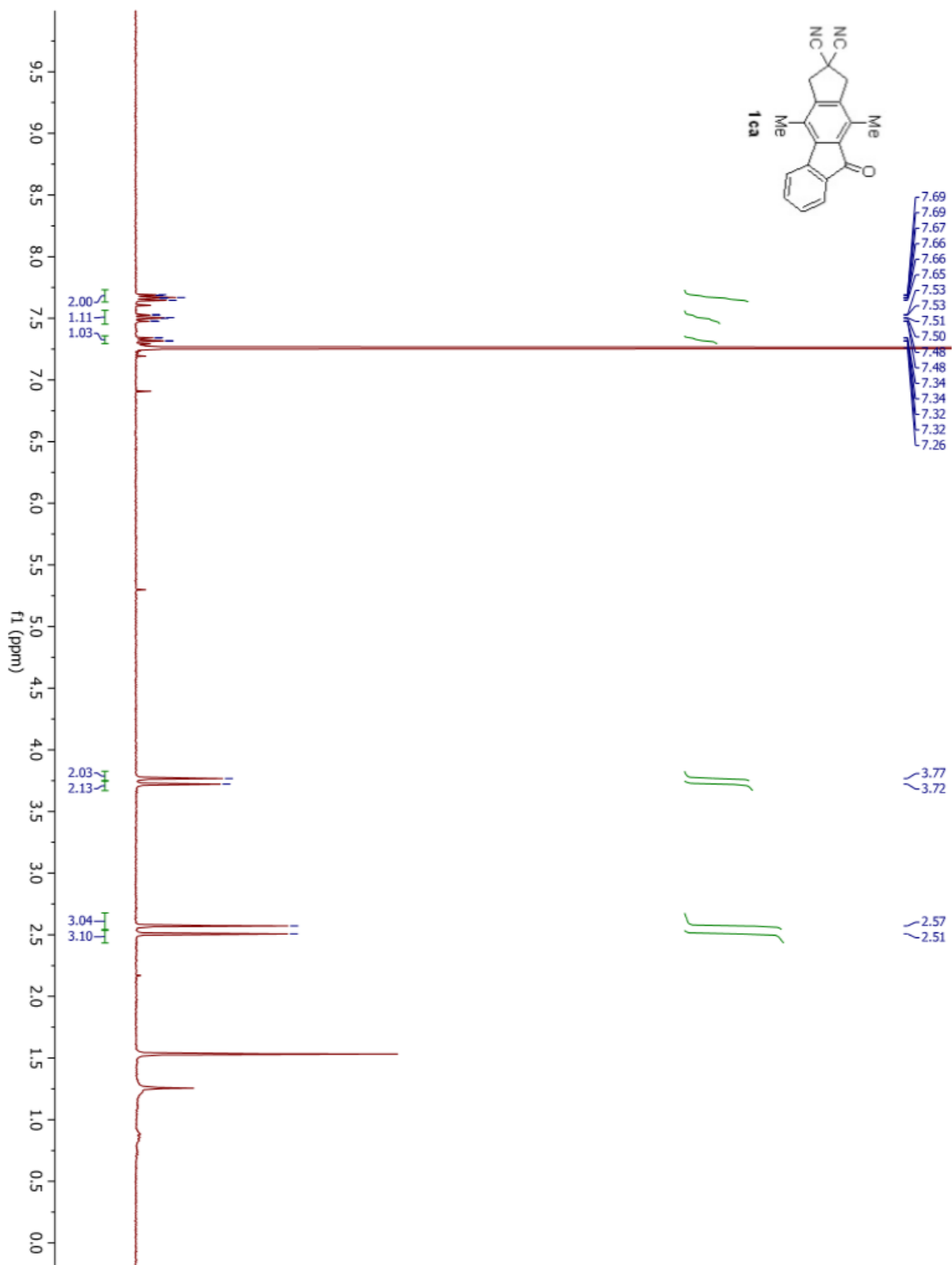


Figure S29 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

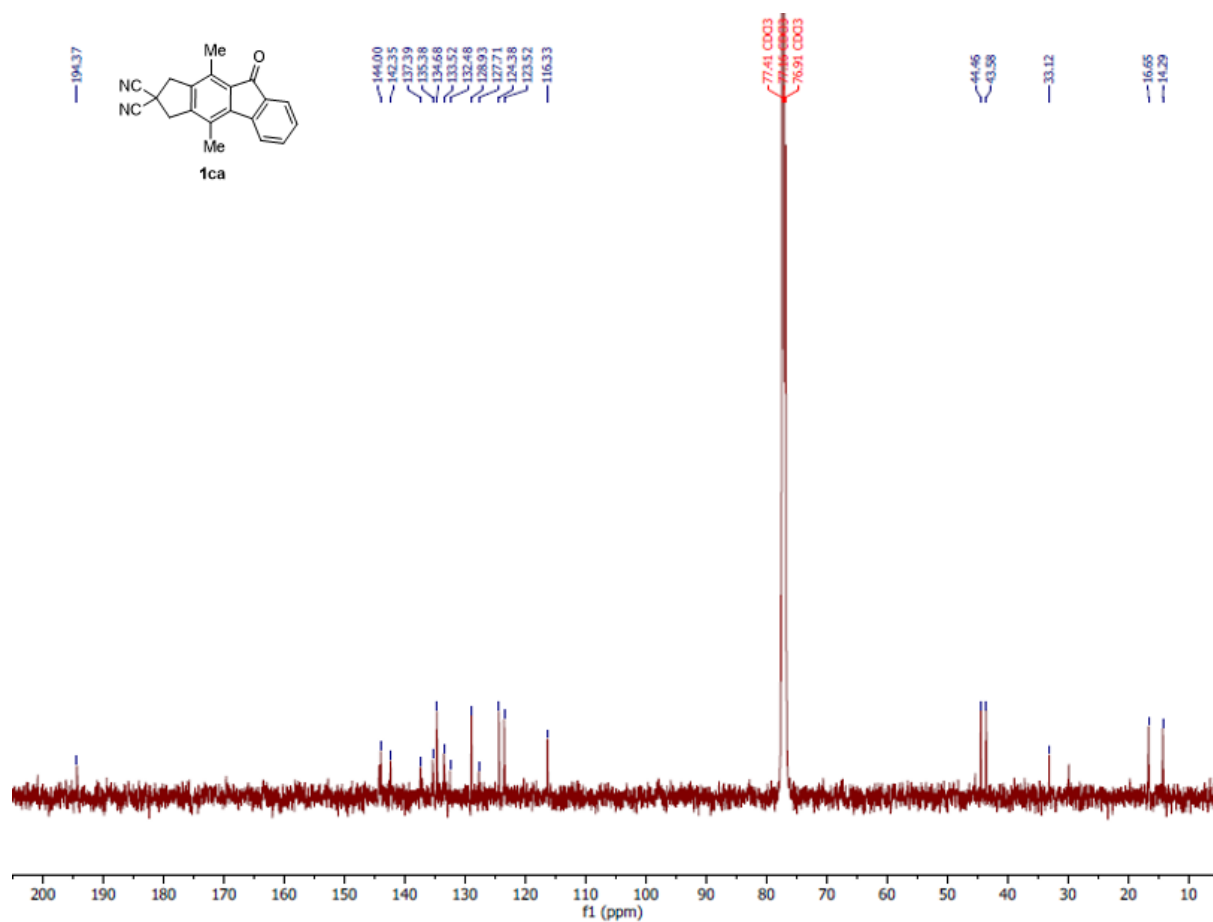


Figure S30 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum

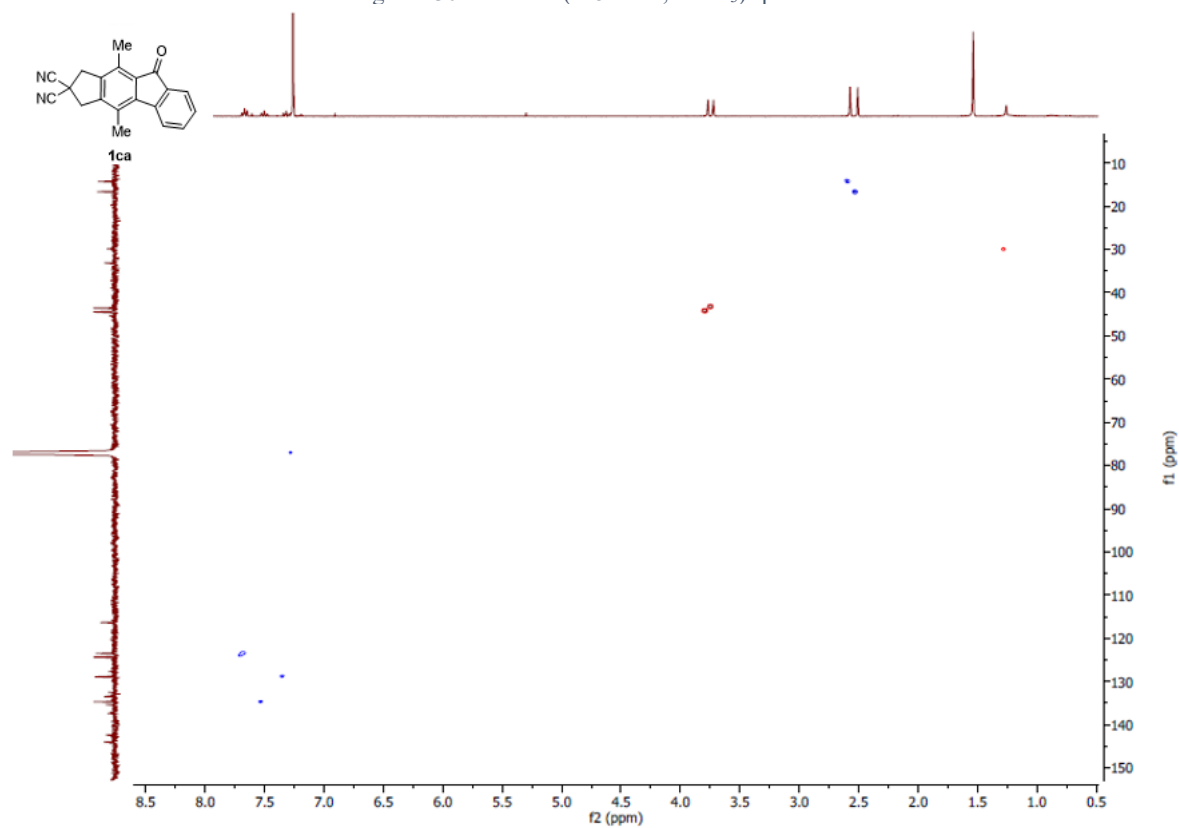
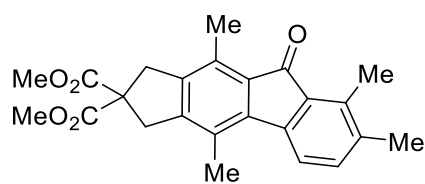


Figure S31 HSQC spectrum

**Dimethyl 4,7,8,10-tetramethyl-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarboxylate (1ad)**



**1ad**

Orange solid; yield: 51% (21 mg) ; mp 218-219 °C.

IR  $\text{cm}^{-1}$  2960, 2916, 1737, 1693, 1594, 1465, 1276, 1164.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.34 (d,  $J$  = 9.0 Hz, 1H), 7.17 (d,  $J$  = 9.0 Hz, 1H), 3.78 (s, 6H), 3.60 (s, 2H), 3.55 (s, 2H), 2.59 (s, 3H), 2.52 (s, 3H), 2.44 (s, 3H), 2.27 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 197.2, 172.2 (2C), 145.8, 143.2, 140.2, 138.4, 138.3, 134.5, 132.5, 131.9, 126.5, 120.5, 59.2, 53.3 (2C), 40.3, 39.3, 19.4, 16.6, 14.2, 13.5.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{25}\text{O}_5$  393.1697; found : 393.1691.

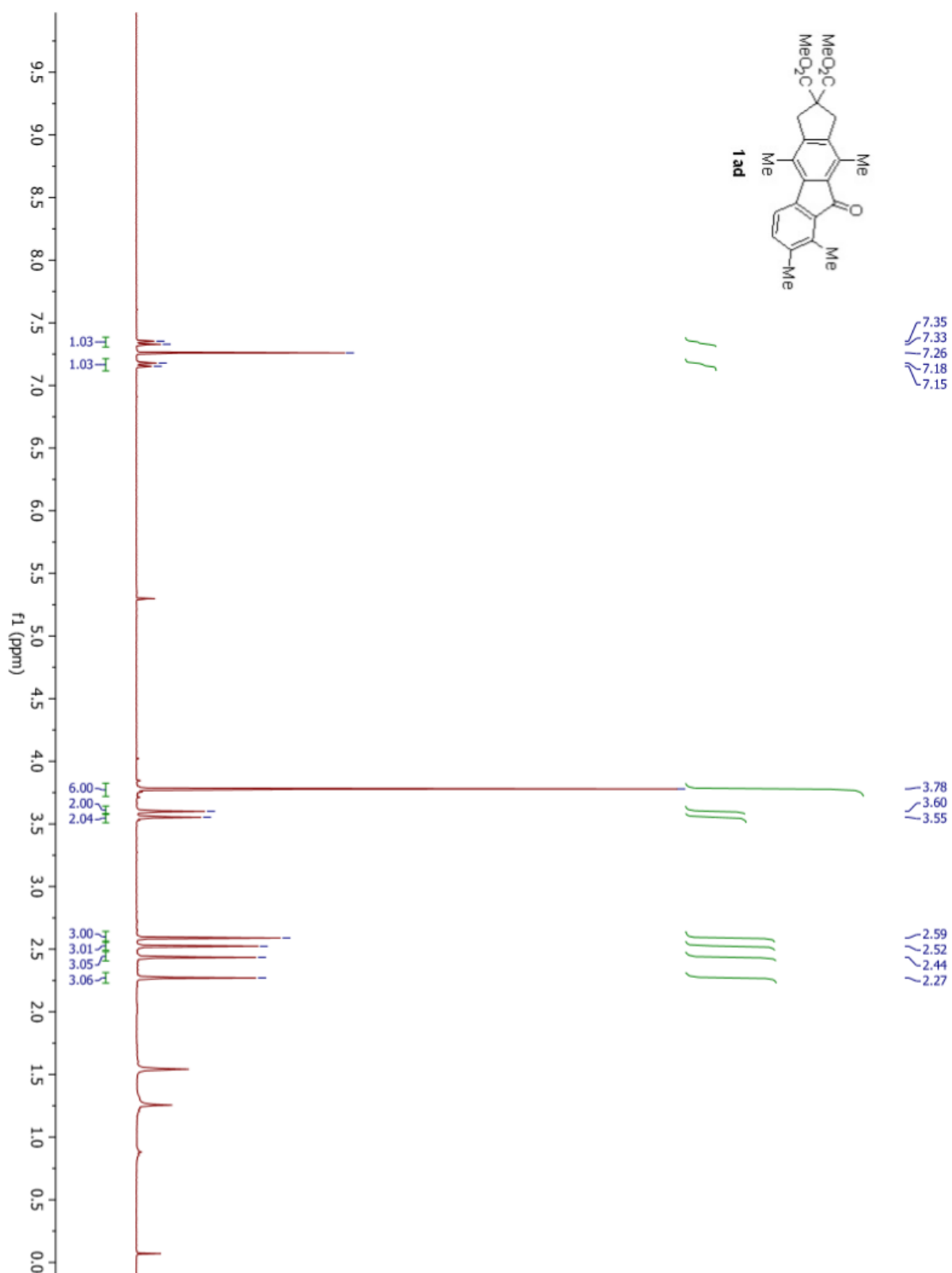


Figure S32  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum

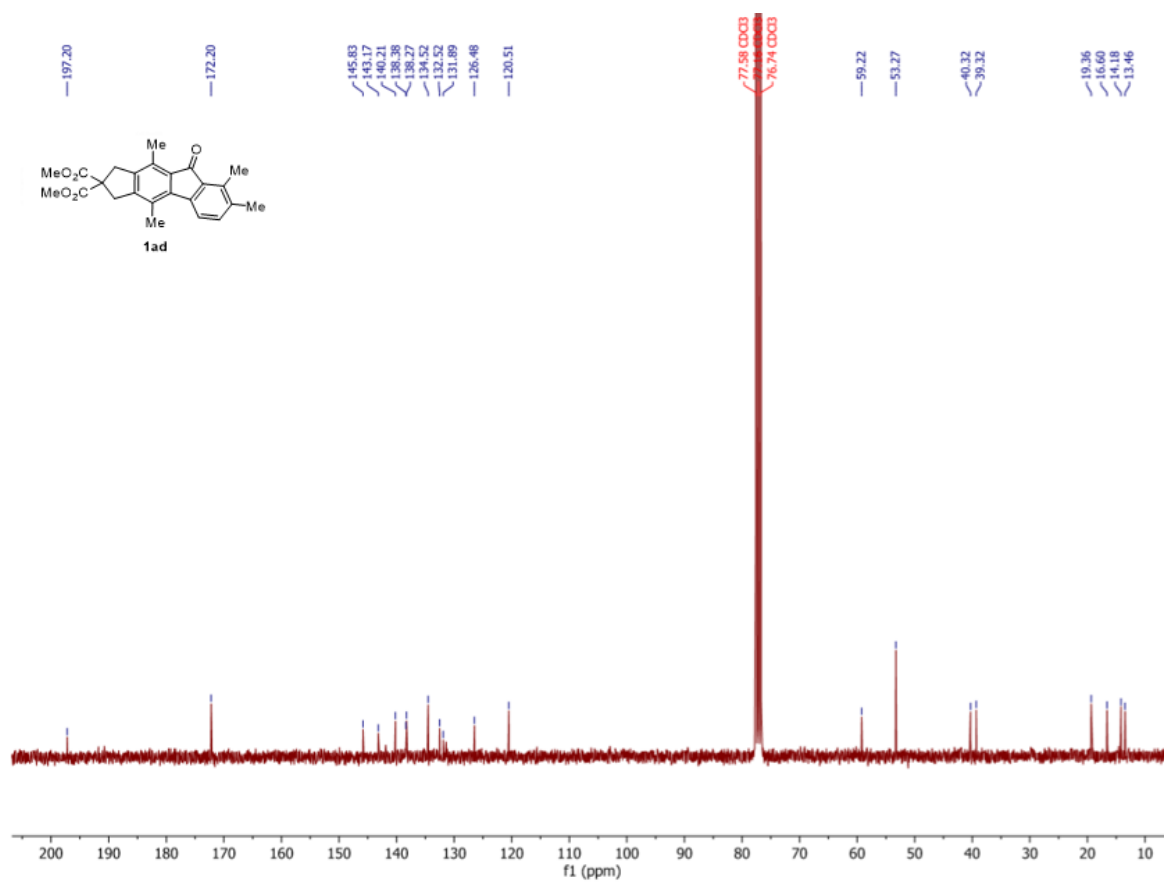


Figure S33 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

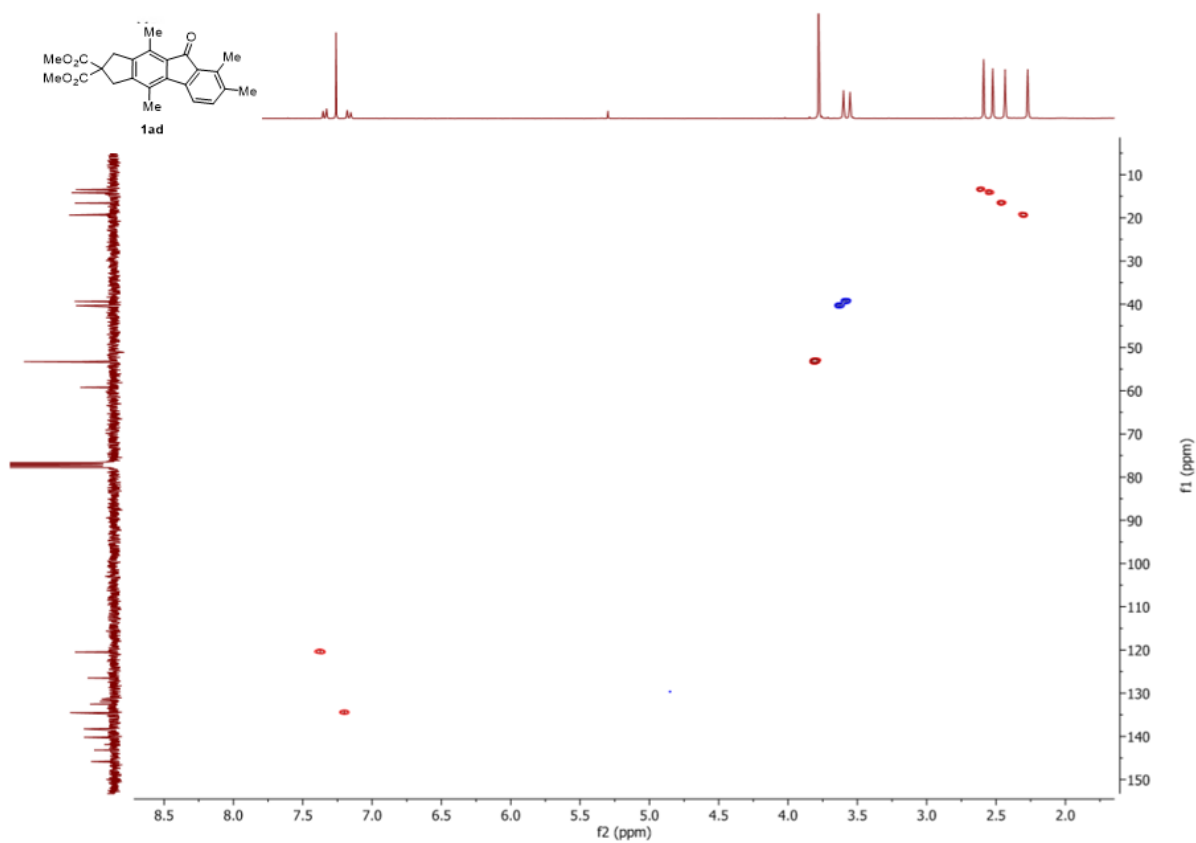
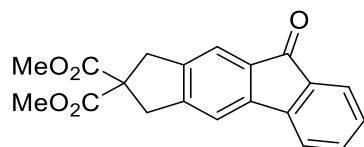


Figure S34 HSQC spectrum

**Dimethyl 9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarboxylate (1da)**



**1da**

Yellow solid; yield: 67% (28 mg); mp 163 °C.

IR  $\text{cm}^{-1}$  3751, 2953, 2359, 2343, 1728, 1654, 1558, 1507, 1488, 1314, 1255.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.61 (d,  $J$  = 7.5 Hz, 1H), 7.50-7.41 (m, 3H), 7.34 (s, 1H), 7.26-7.21 (m, 1H), 3.77 (s, 6H), 3.61 (s, 2H), 3.58 (s, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 193.5, 171.8 (2C), 147.6, 144.5 (2C), 141.1, 134.8, 134.7, 134.1, 129.0, 124.4, 120.6, 120.1, 116.6, 60.5, 53.3 (2C), 40.8, 40.2.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_5$  337.1071; found : 337.1071.

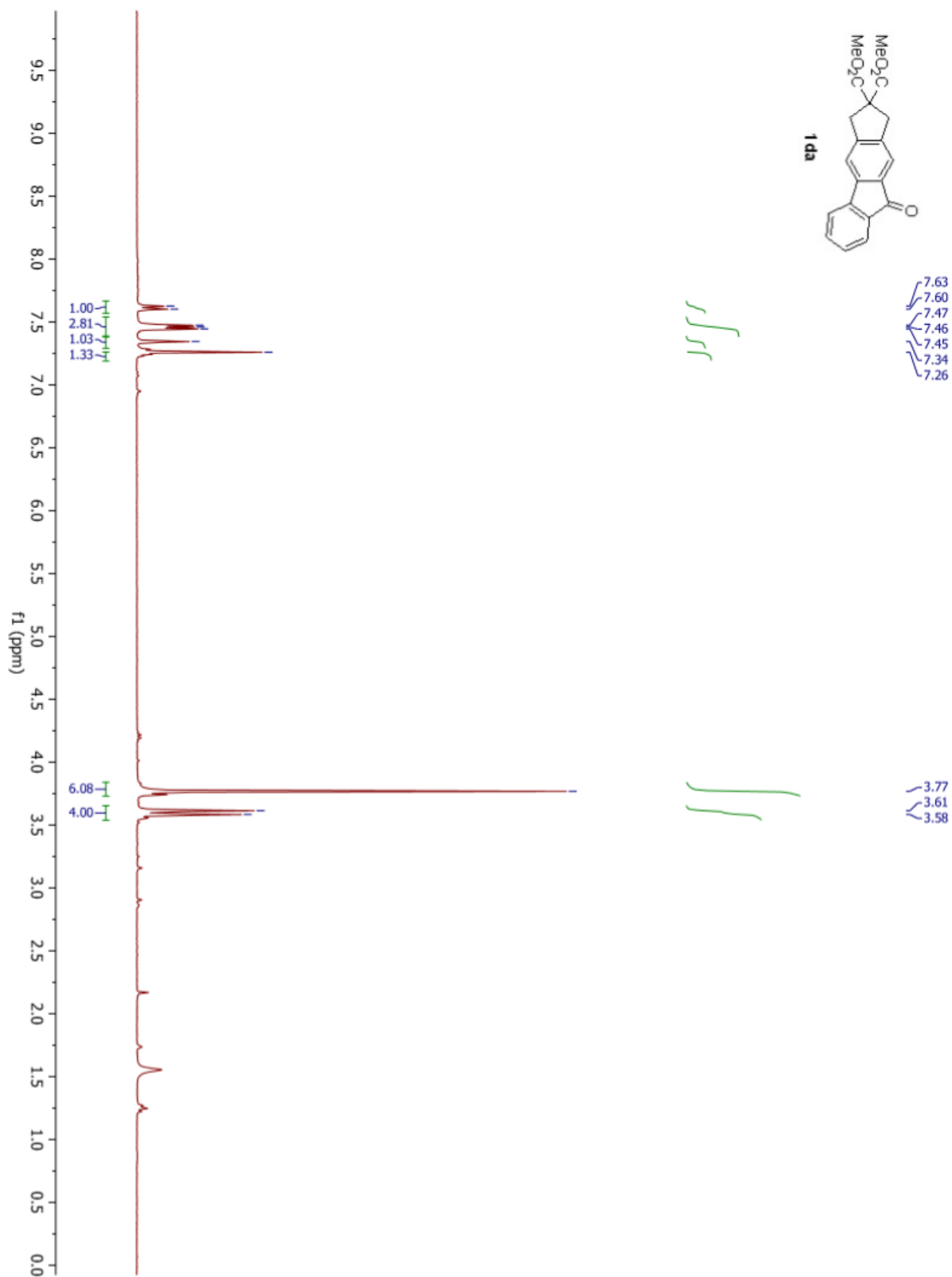


Figure S35 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

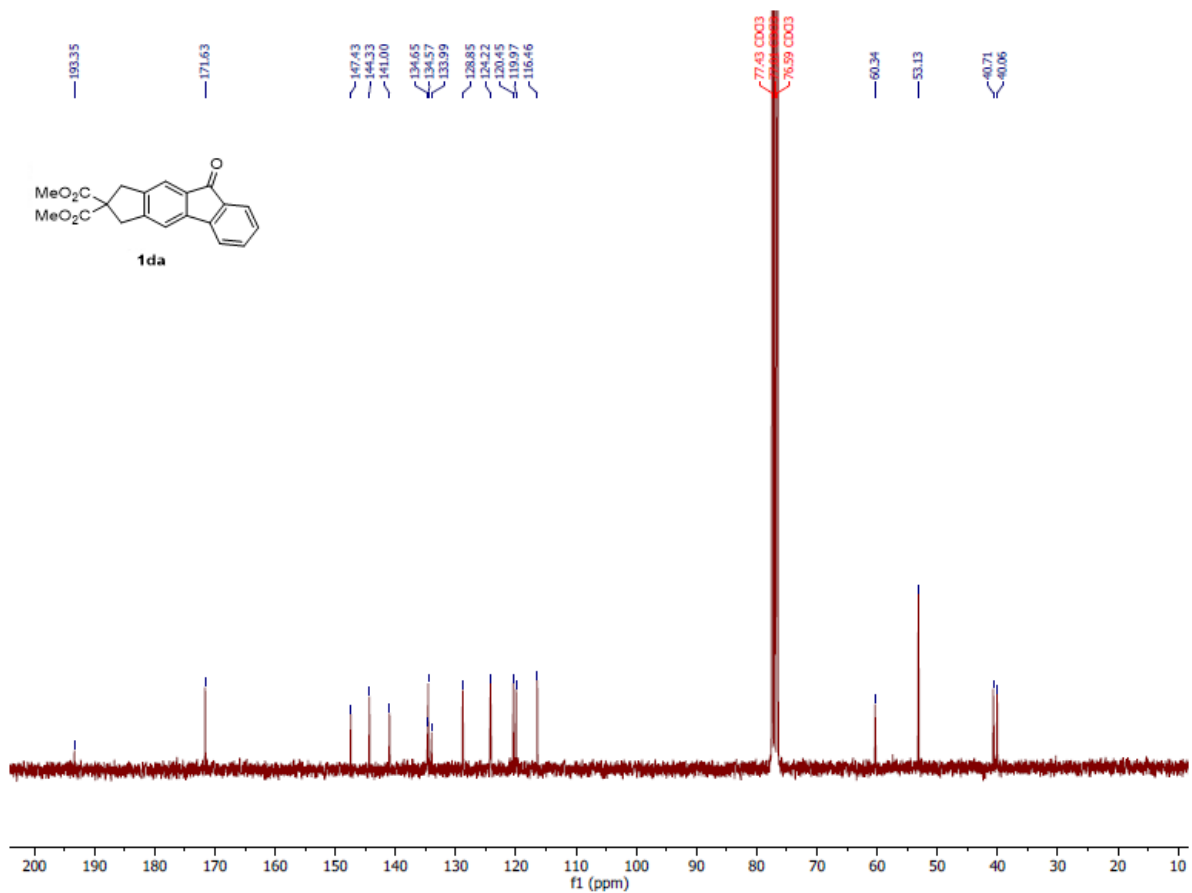


Figure S36 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

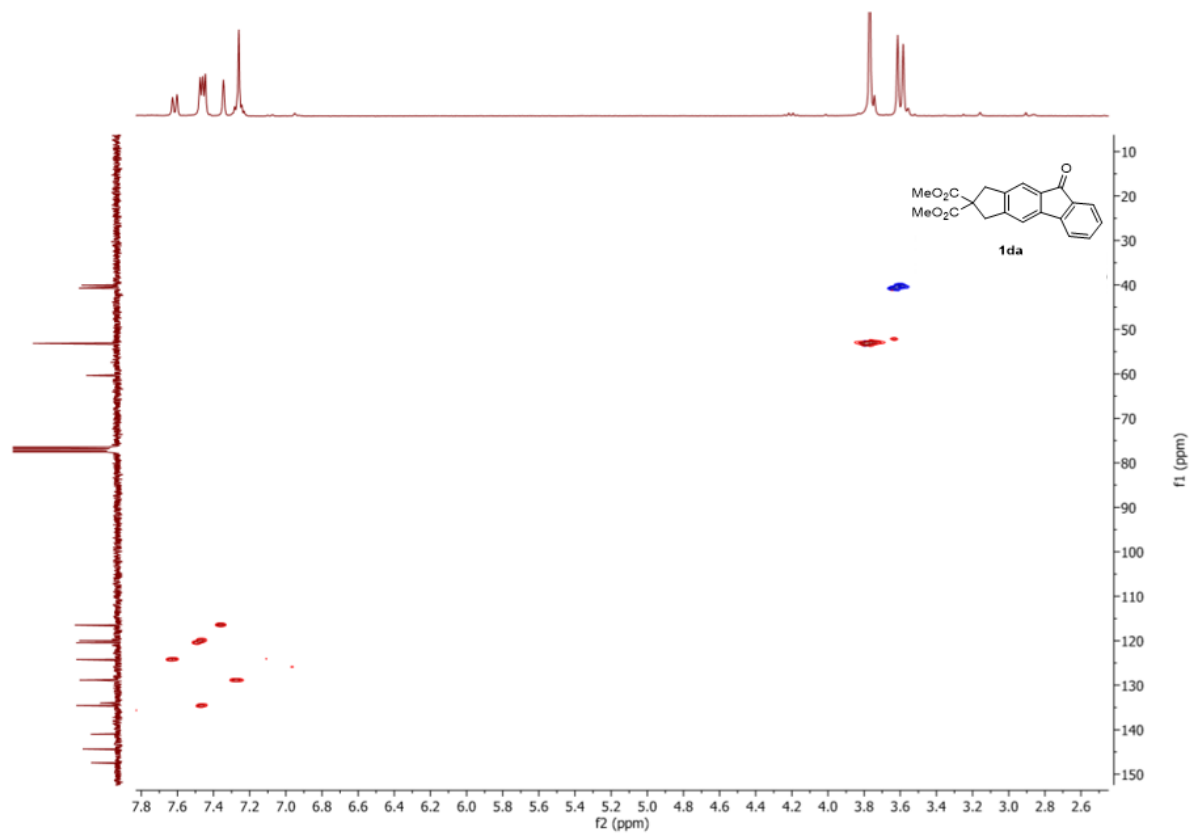
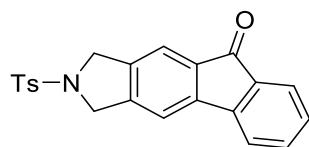


Figure S37 HSQC spectrum

**2-tosyl-2,3-dihydroindeno[1,2-f]isoindol-9(1H)-one (1ea)**



**1ea**

Orange solid; yield: 62% (29 mg); mp 190-191 °C.

IR  $\text{cm}^{-1}$  2919, 2850, 1710, 1618, 1598, 1495, 1338, 1290, 1152.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.78 (dt,  $J$  = 2.1 Hz, 8.1 Hz, 2H), 7.64 (dt,  $J$  = 0.9 Hz, 7.5 Hz, 1H), 7.50-7.42 (m, 3H), 7.37-7.27 (m, 4H), 4.65 (s, 2H), 4.60 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 193.1, 144.9 (2C), 144.1, 143.2 (2C), 137.3, 135.0, 134.6, 133.7, 130.1 (2C), 129.5, 127.8 (2C), 124.6, 120.4, 119.0, 114.9, 53.8, 53.5, 21.7.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{18}\text{NO}_3\text{S}$  376.1002; found : 376.1001.

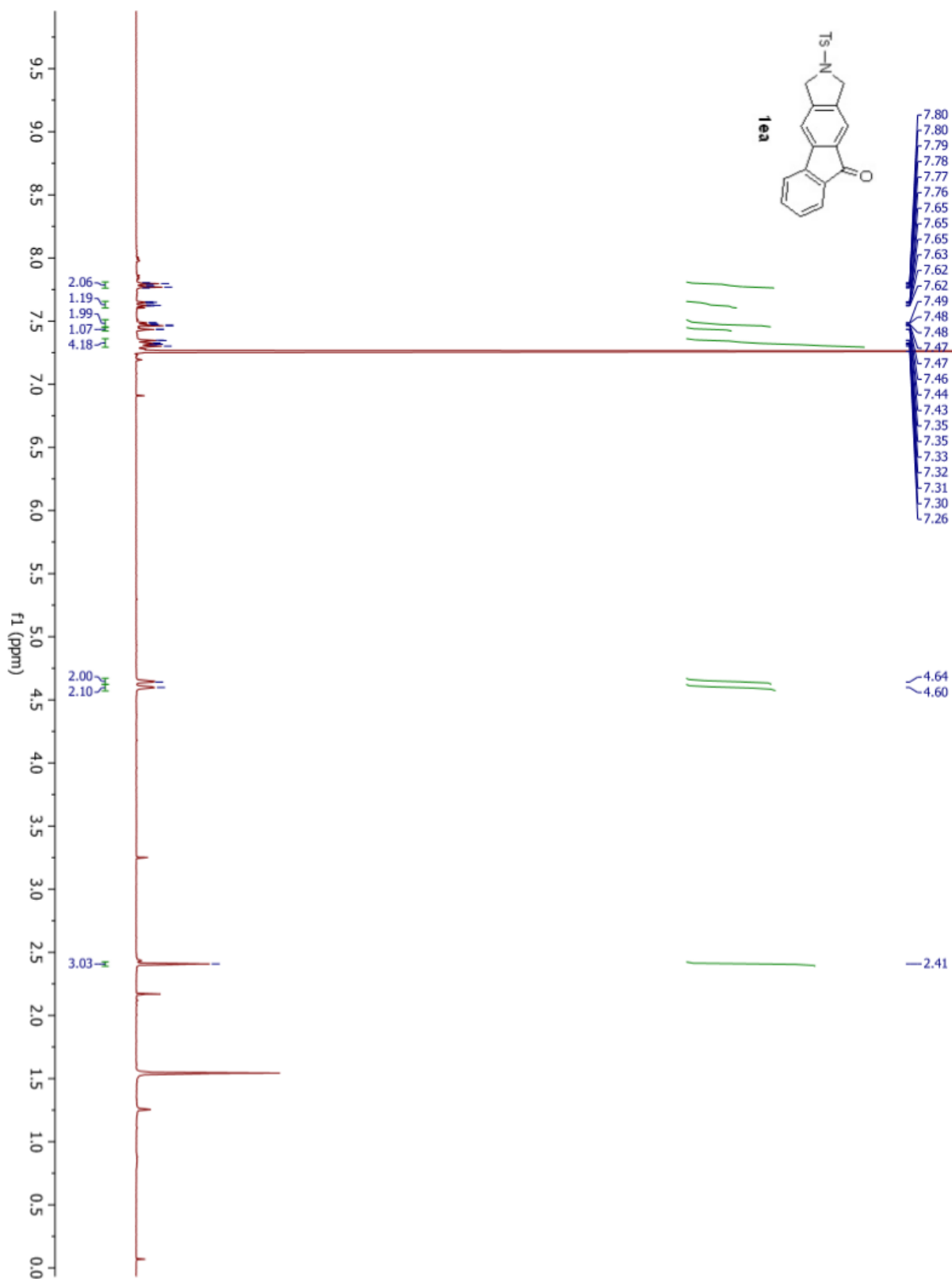


Figure S38  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum

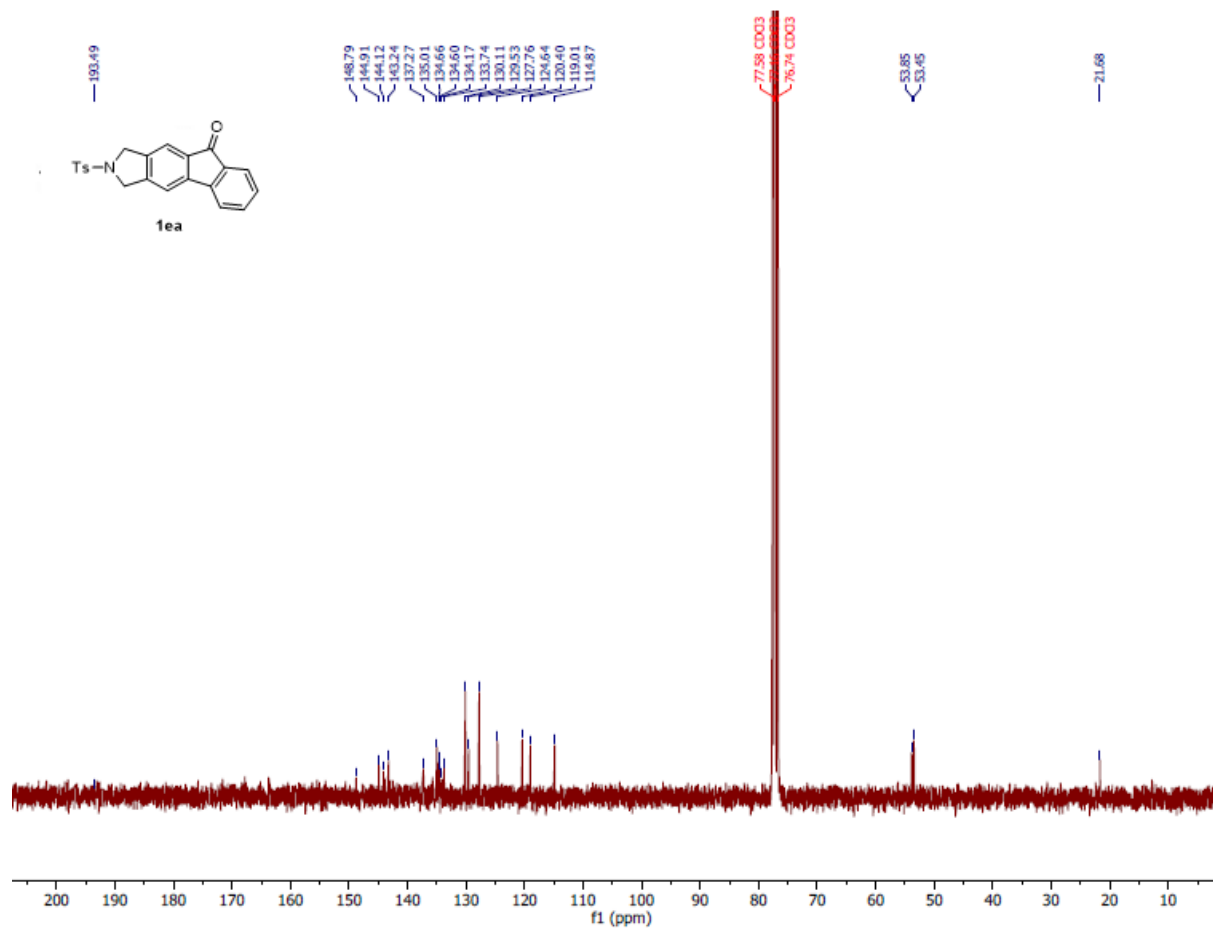


Figure S39 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

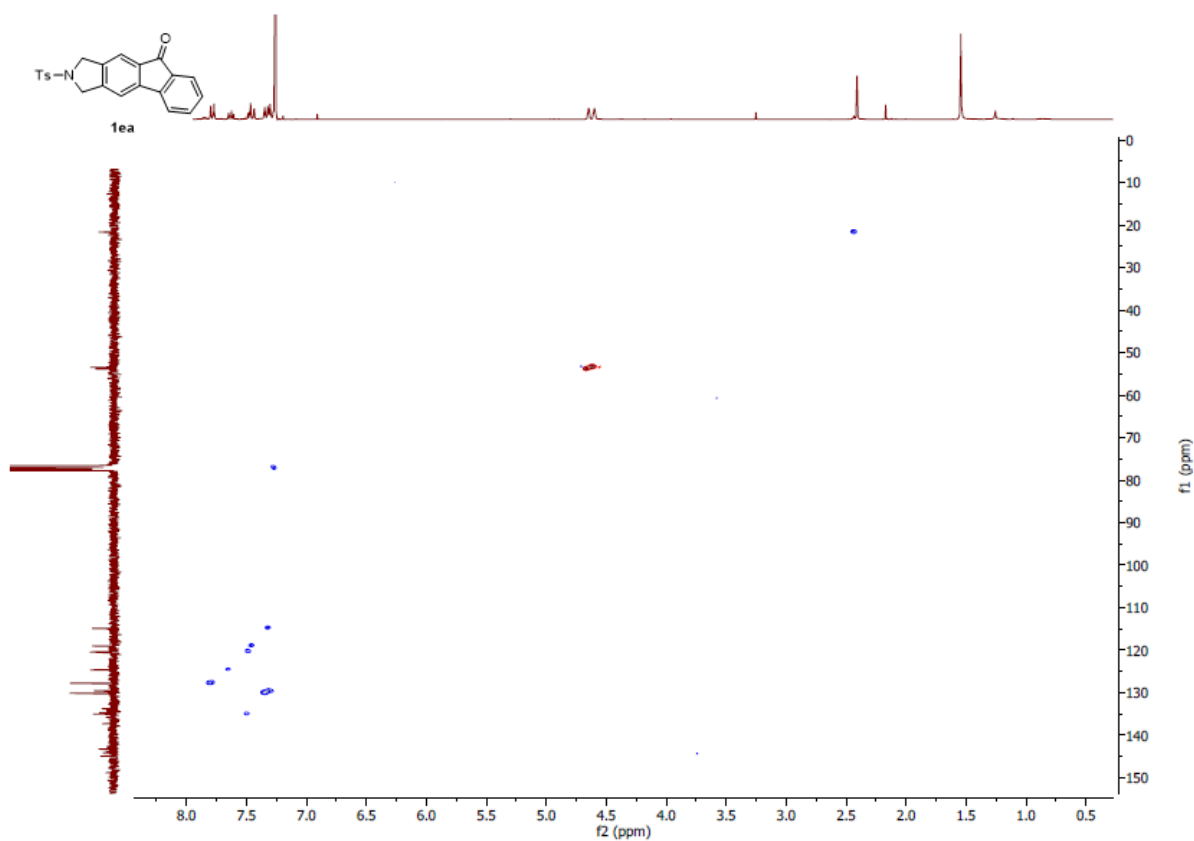
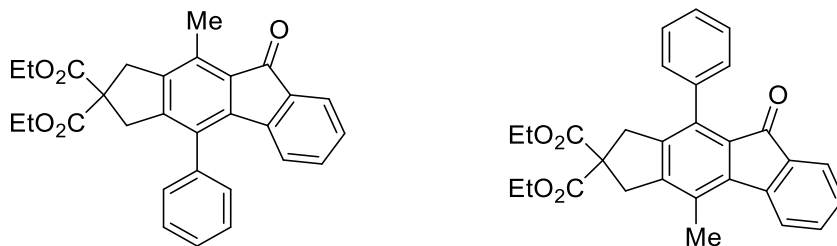


Figure S40 HSQC spectrum

**Diethyl 10-methyl-9-oxo-4-phenyl-3,9-dihydrocyclopenta[b]fluorene-2,2(1*H*)-dicarboxylate (1fa)**



Mixture of regioisomers (ratio 1:1, determined by  $^1\text{H}$  NMR analysis of the crude).

Yellow solid; yield: 41% (23 mg); mp 156 °C.

IR  $\text{cm}^{-1}$  3052, 2977, 2360, 1729, 1698, 1570, 1520, 1458, 1440, 1365, 1272, 1186, 1067.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 7.67 (d,  $J$  = 7.6 Hz, 1H, regio B), 7.58-7.36 (m, 8H, regio A and B), 7.35-7.27 (m, 4H, regio A and B), 7.26-7.20 (m, 2H, regio B), 7.12 (td,  $J$  = 1.2 Hz, 7.6 Hz, 1H, regio A), 7.06 (td,  $J$  = 1.6 Hz, 7.6 Hz, 1H, regio A), 6.28 (d,  $J$  = 7.6 Hz, 1H, regio A), 4.19 (q,  $J$  = 7.2 Hz, 4H), 3.66 (s, 2H, regio B), 3.59 (s, 2H, regio A), 3.38 (s, 2H, regio B), 3.30 (s, 2H, regio A), 2.62 (s, 3H, regio A), 2.56 (s, 3H, regio B), 1.24 (t,  $J$  = 7.2 Hz, 6H, regio A and B).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 194.9, 193.0, 171.5, 171.5, 147.1, 146.1, 144.6, 143.8, 141.9, 141.1, 140.5, 138.0, 136.5, 136.0, 135.4, 135.3, 134.9, 134.4, 133.9, 132.2, 130.9, 129.3, 129.1, 128.9, 128.8, 128.3, 128.2, 128.2, 127.8, 124.1, 123.7, 123.2, 122.7, 62.0, 59.7, 40.3, 40.2, 39.7, 39.2, 16.7, 14.5, 14.2.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{29}\text{H}_{27}\text{O}_5$  455.1853; found : 455.1851.

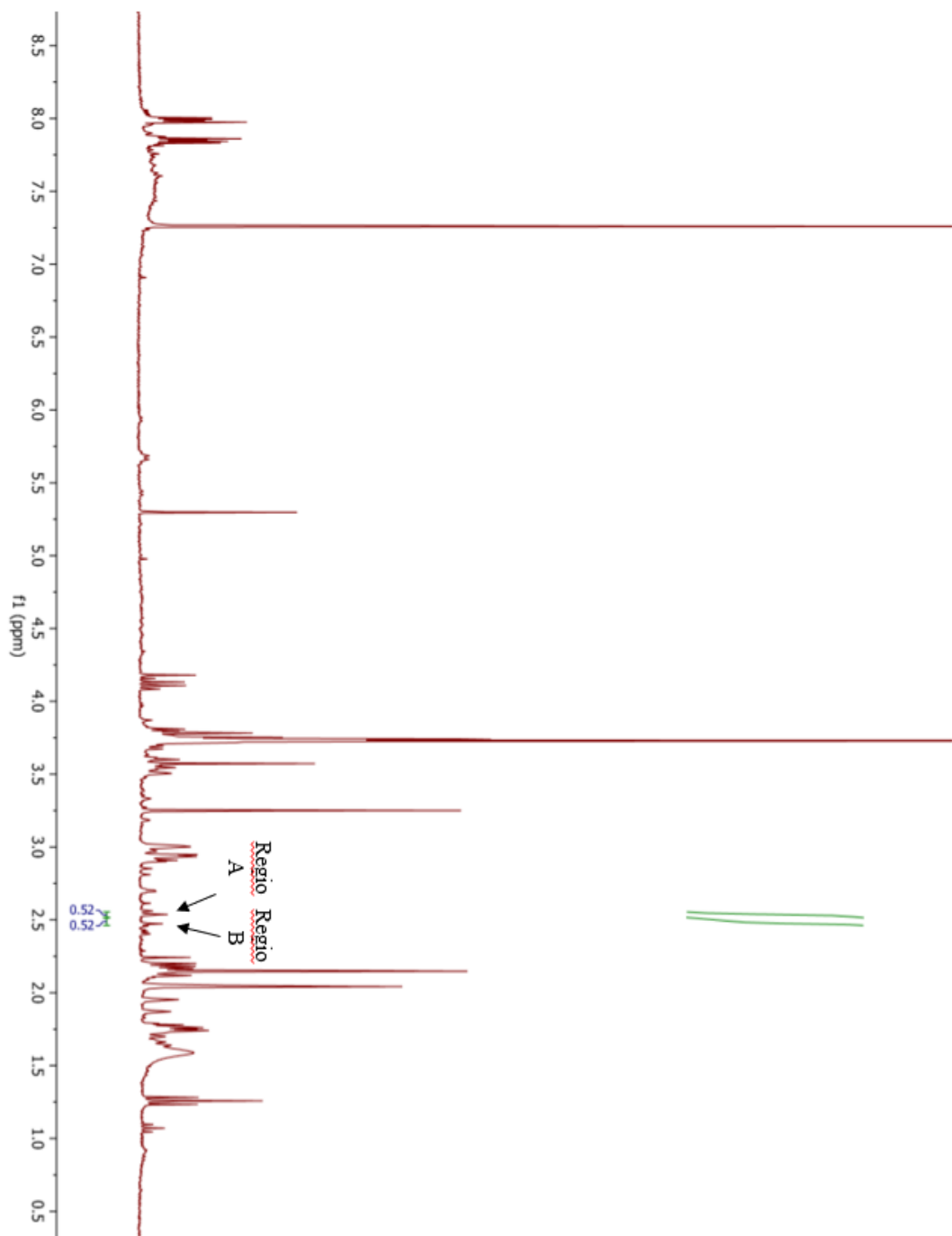


Figure S41  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of the crude mixture

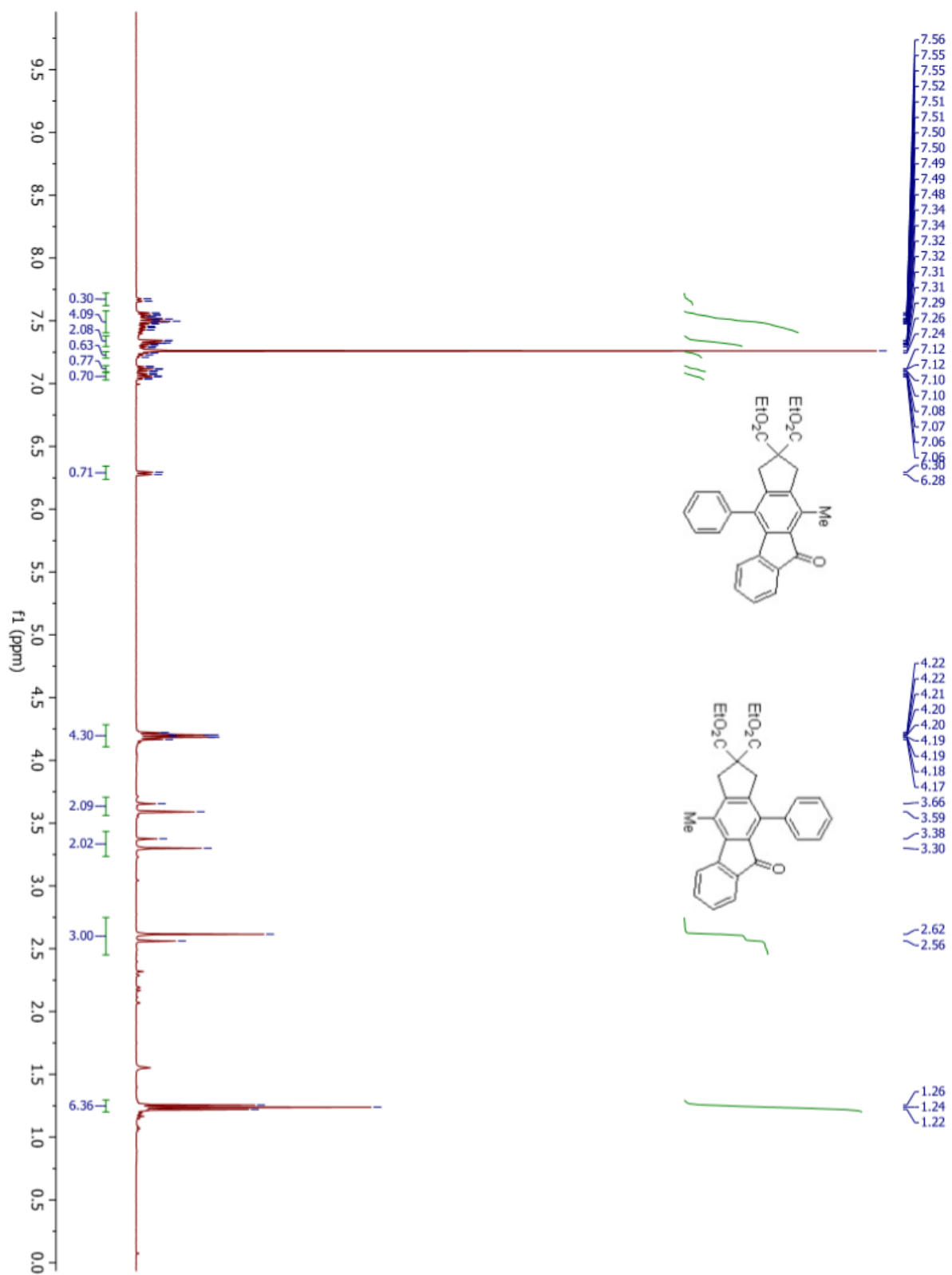


Figure S42  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum

Mixture of regioisomers **1fa**

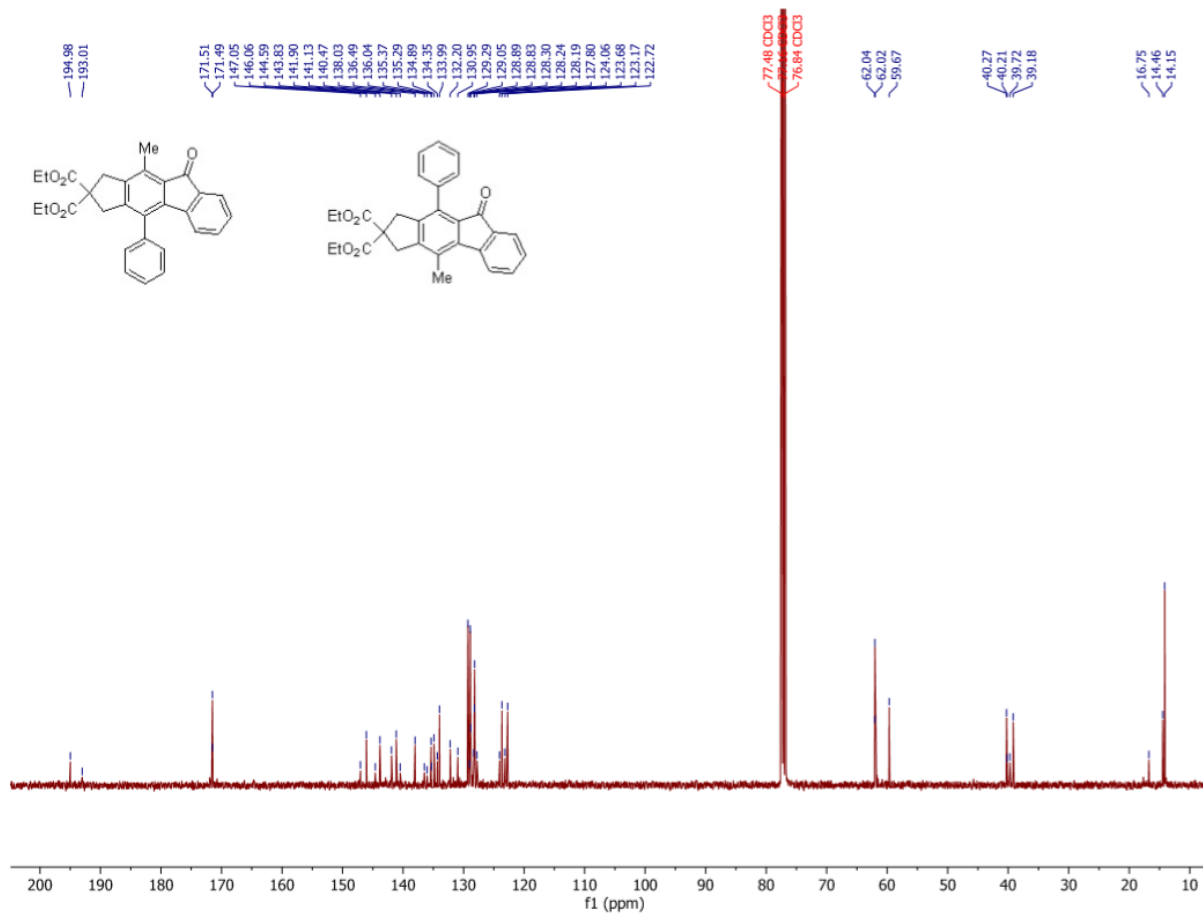


Figure S43  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum

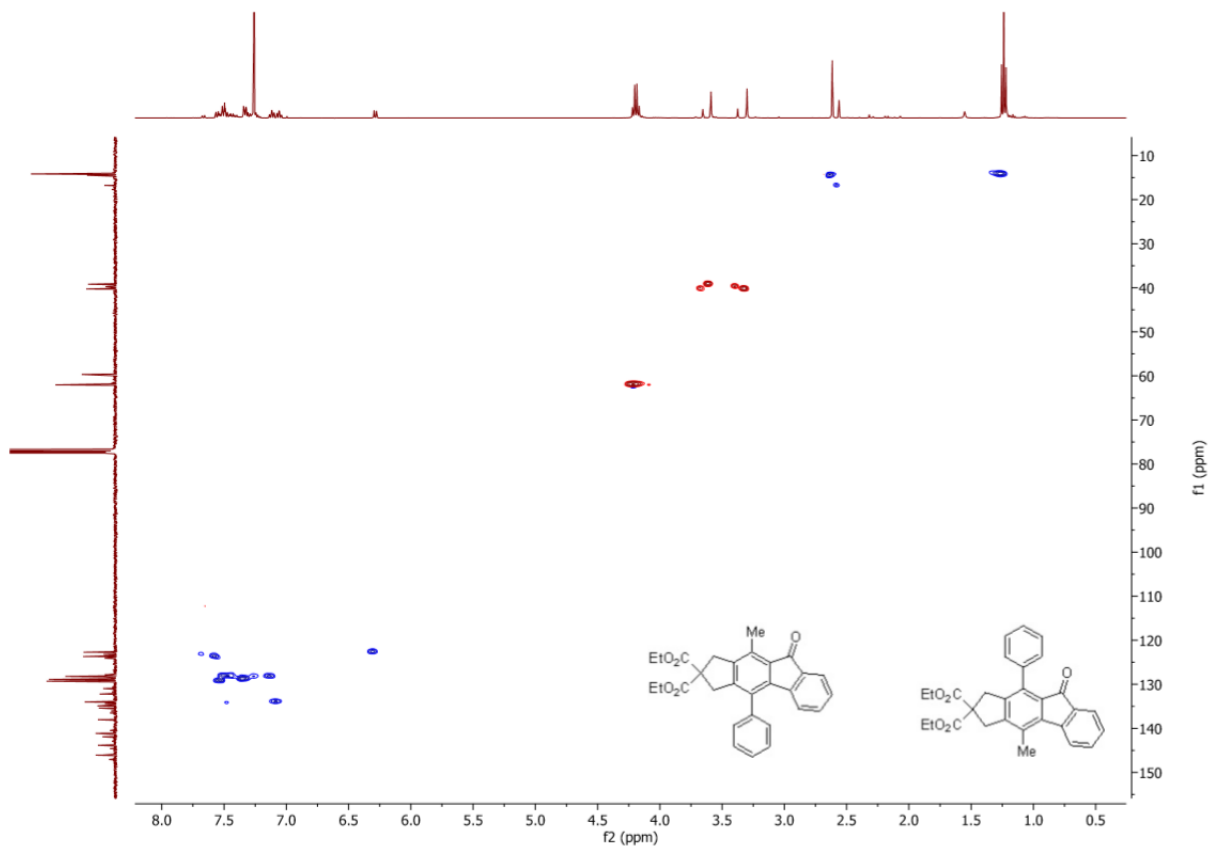
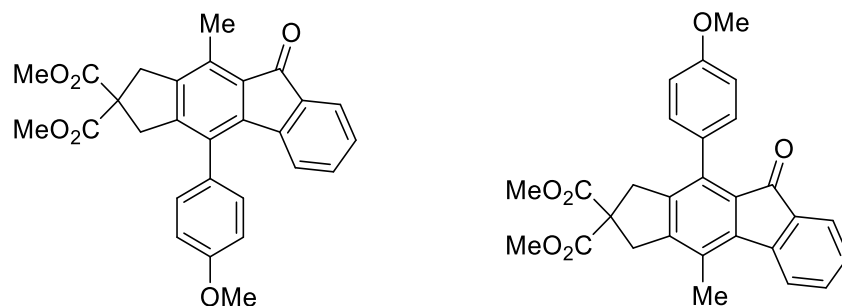


Figure S44 HSQC spectrum

**Dimethyl 4-(4-methoxyphenyl)-10-methyl-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarboxylate (1ga)**



Mixture of regioisomers (ratio 1:1, determined by  $^1\text{H}$  NMR analysis of the crude).

Yellow solid; yield: 65% (37 mg); mp 193 °C.

IR  $\text{cm}^{-1}$  2952, 1734, 1697, 1576, 1433, 1375, 1308, 1237, 1110.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.70-7.40 (m, 2H, regio A), 7.26-7.19 (m, 2H, regio A), 7.16-6.90 (m, 11H, regio A and B), 6.43-6.37 (m, 1H; regio A), 3.91 (s, 3H, regio A), 3.87 (s, 3H, regio B), 3.74 (s, 12H, regio A and B), 3.66 (s, 2H, regio B), 3.59 (s, 2H, regio A), 3.42 (s, 2H, regio B), 3.33 (s, 2H, regio A), 2.60 (s, 3H, regio A), 2.55 (s, 3H, regio B).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 195.1, 172.0 (2C), 159.3, 146.4, 143.9, 142.2, 140.8, 135.6, 134.7, 134.0, 131.9, 131.0, 130.2, 130.1, 128.3, 128.2, 123.7, 122.8, 114.7, 113.6, 59.4, 55.5, 53.2 (2C), 40.5, 39.3, 14.5.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{28}\text{H}_{25}\text{O}_6$  457.1646; found : 457.1647.

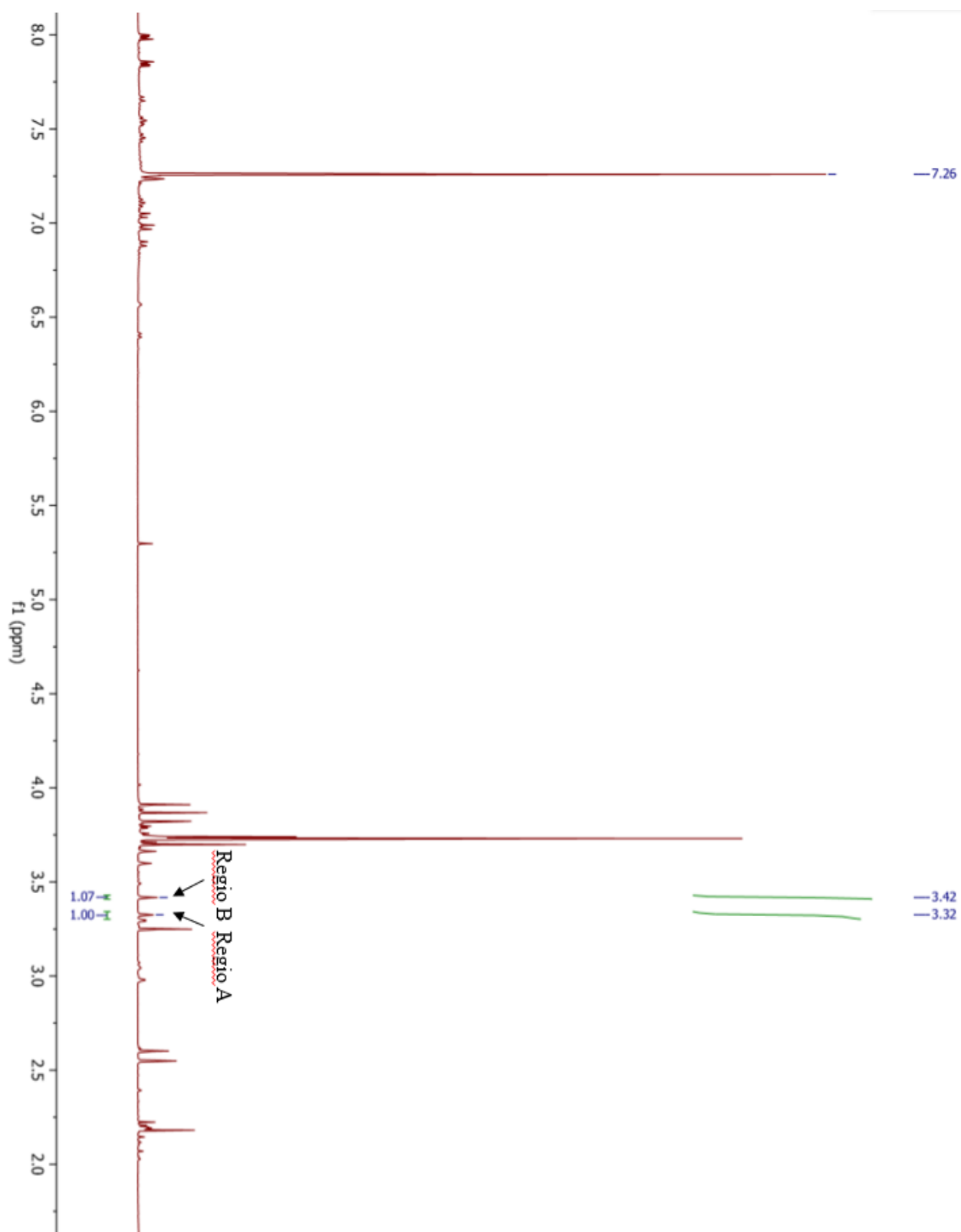


Figure S45  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of the crude mixture

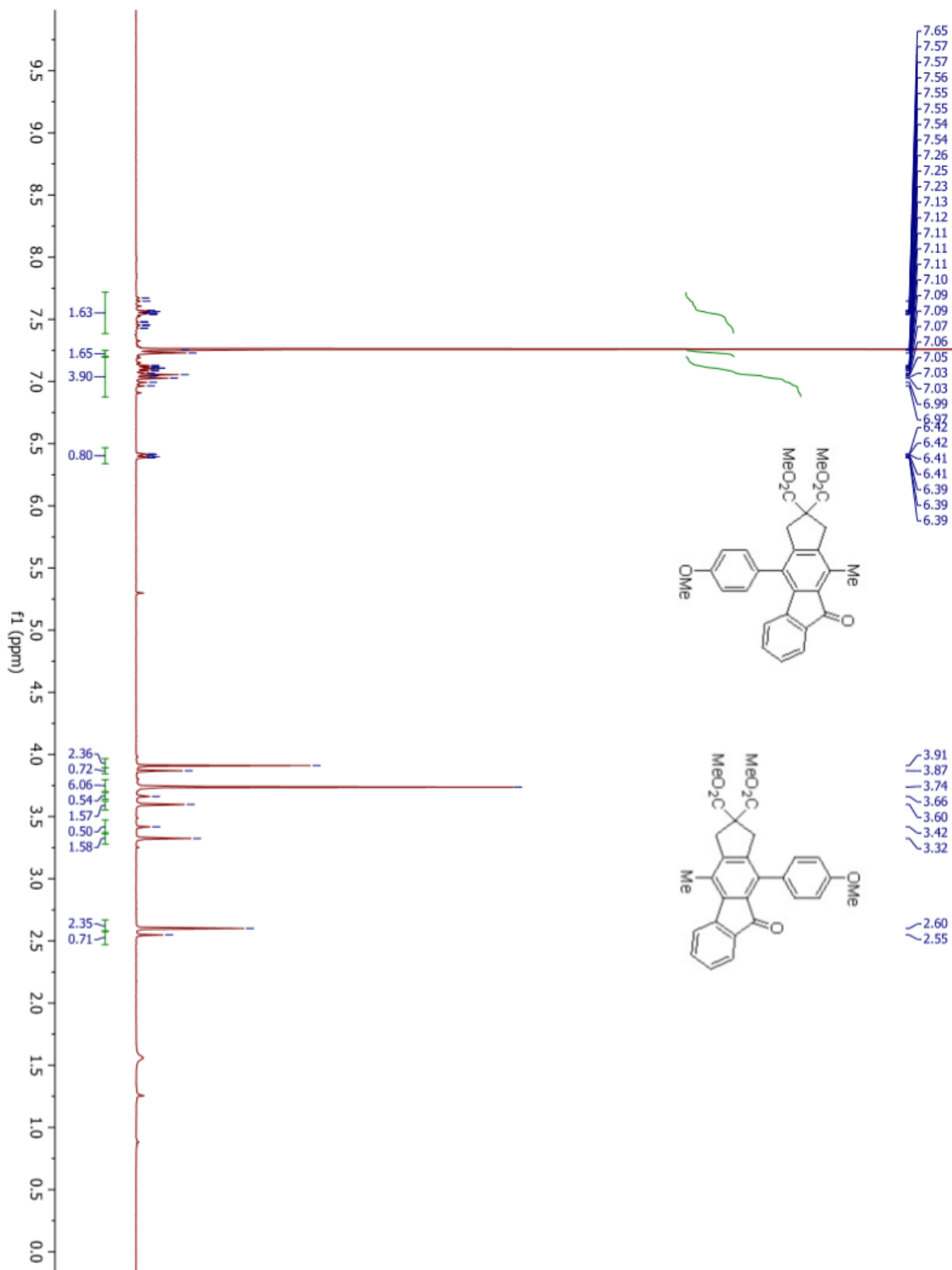


Figure S46  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum

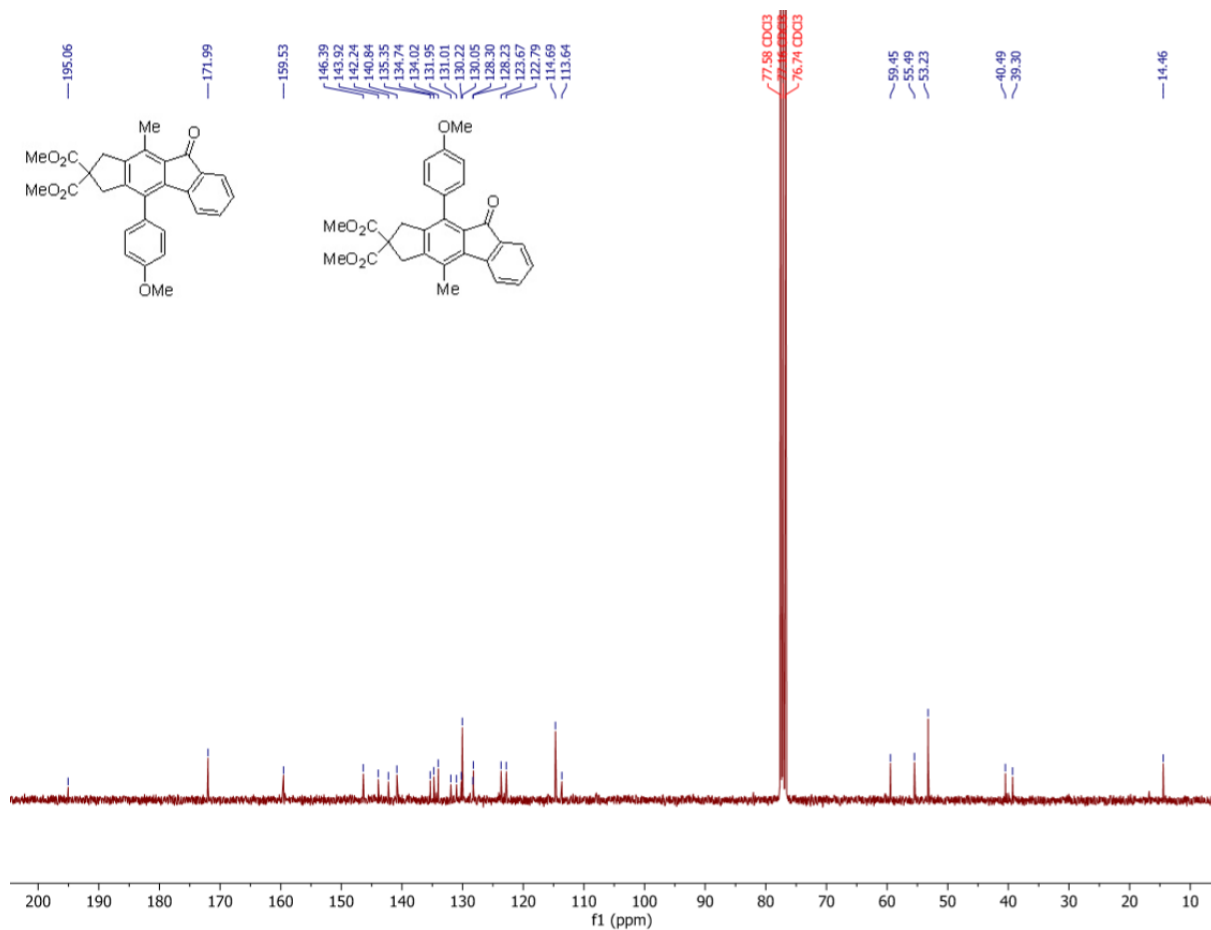


Figure S47  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) spectrum

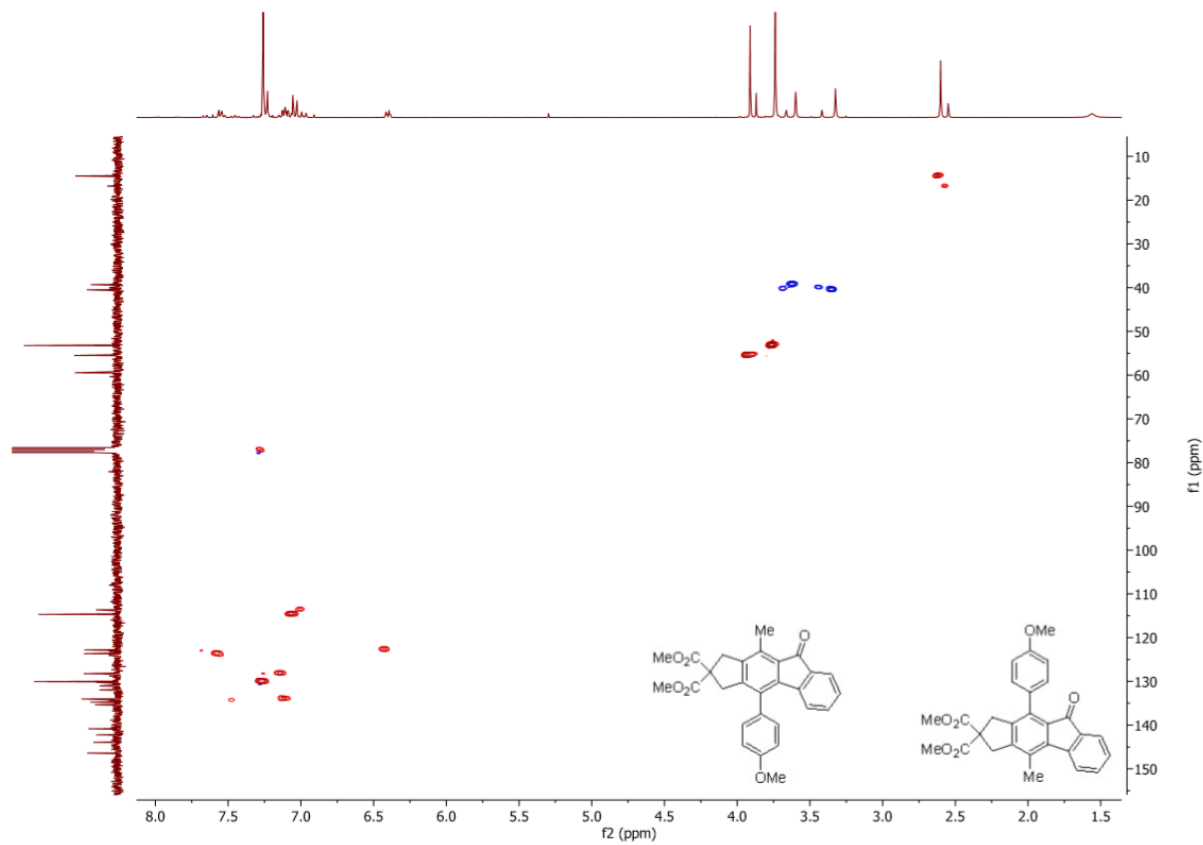
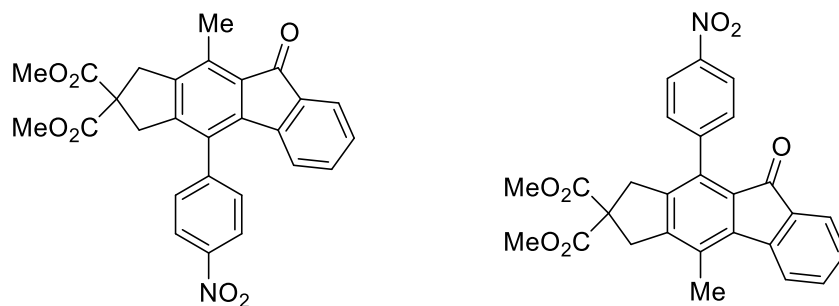


Figure S48 HSQC spectrum

**Dimethyl 10-methyl-4-(4-nitrophenyl)-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2(1*H*)-dicarboxylate (1ha)**



Mixture of regioisomers (ratio 1:1, determined by  $^1\text{H}$  NMR analysis of the crude).

Yellow solid; yield: 54% (31 mg); mp 155 °C.

IR  $\text{cm}^{-1}$  2955, 2323, 1731, 1697, 1571, 1541, 1347, 1252.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 8.40 (td,  $J$  = 2.1 Hz, 8.7 Hz, 2H, regio A), 8.31 (td,  $J$  = 1.8 Hz, 8.9 Hz, 2H, regio B), 7.68 (d,  $J$  = 7.8 Hz, 1H, regio B), 7.62-7.45 (m, 7H, regio A and B), 7.31-7.26 (m, 1H, regio B), 7.17 (td,  $J$  = 0.9 Hz, 7.2 Hz, 1H, regio B), 7.10 (td,  $J$  = 1.5 Hz, 7.5 Hz, 1H, regio A), 6.27 (d,  $J$  = 7.2 Hz, 1H, regio A), 3.75 (s, 6H, regio B), 3.75 (s, 6H, regio A), 3.69 (s, 2H, regio B), 3.62 (s, 2H, regio A), 3.33 (s, 2H, regio B), 3.26 (s, 2H, regio A), 2.62 (s, 3H, regio A), 2.58 (s, 3H, regio B).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 194.3, 192.8, 171.7, 171.7, 148.0, 147.6, 147.4, 145.1, 145.0, 144.4, 143.5, 143.2, 142.9, 141.6, 141.5, 139.6, 136.0, 135.7, 135.2, 134.9, 134.8, 134.2, 133.3, 131.2, 130.6, 130.2, 130.1, 129.6, 128.9, 128.7, 124.6, 124.3, 124.1, 123.6, 123.4, 123.4, 122.3, 59.5, 53.4, 40.2, 39.6, 39.2, 16.8, 14.5.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{22}\text{O}_7\text{N}$  472.1391; found : 472.1391.

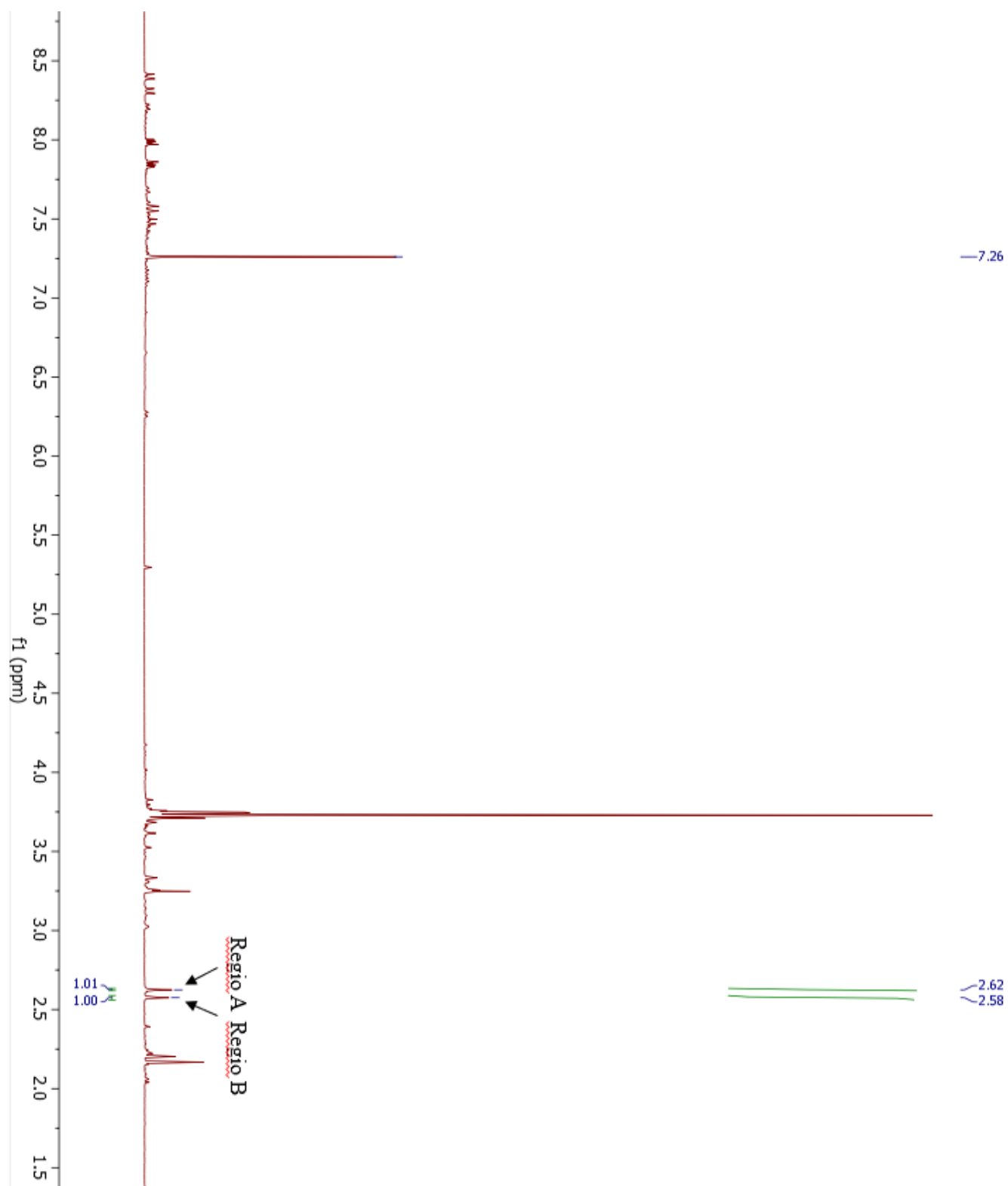


Figure S49 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of the crude mixture

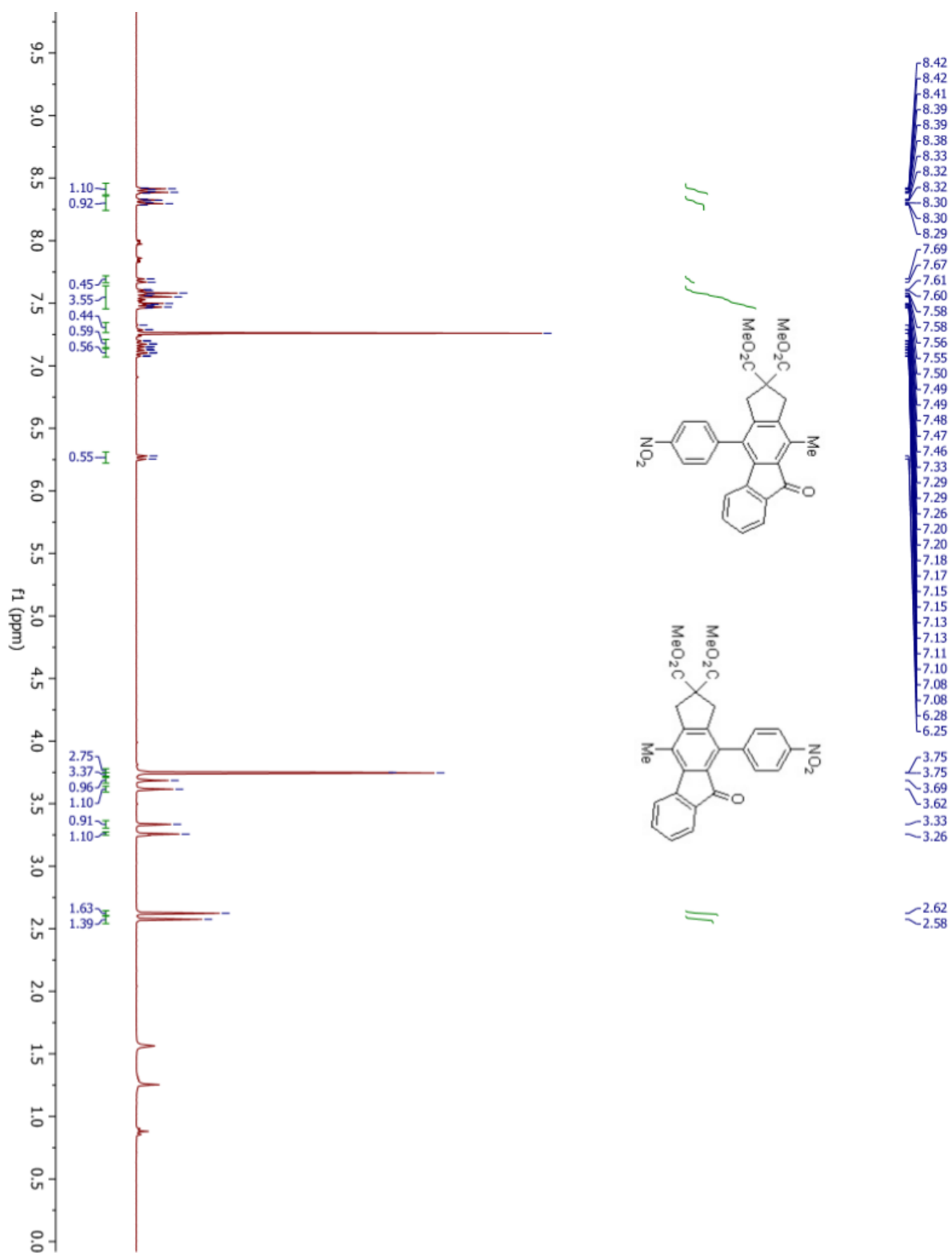


Figure S50 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

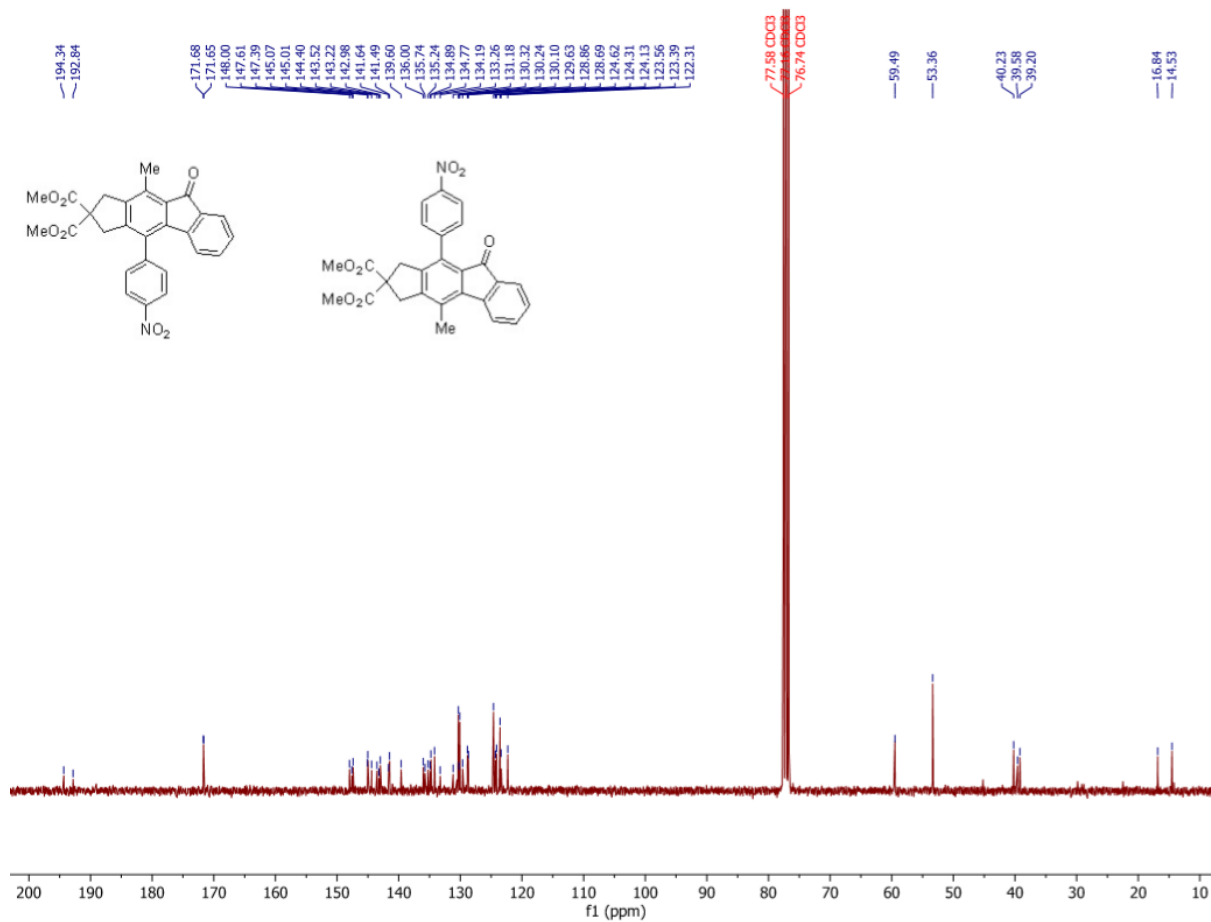


Figure S51  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) spectrum

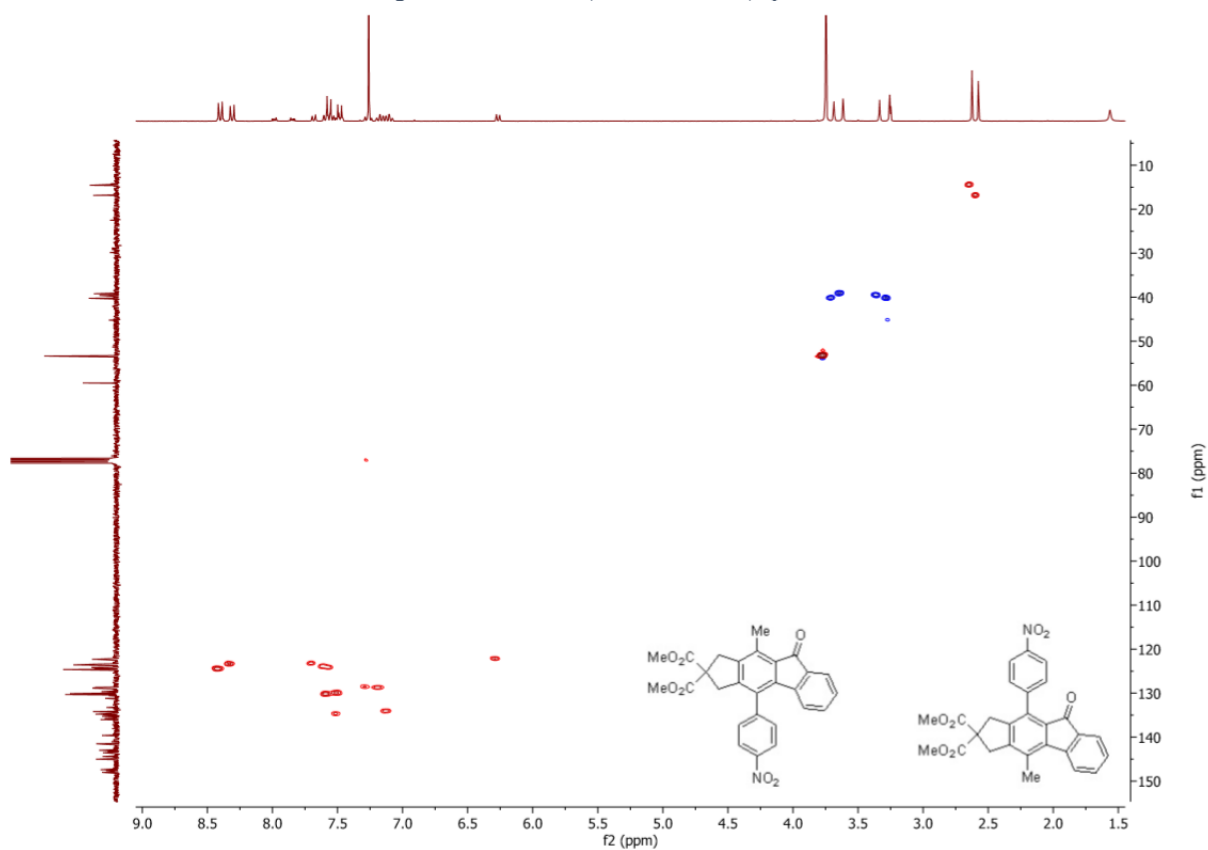
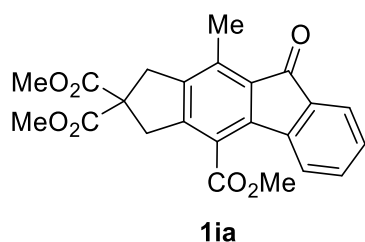


Figure S52 HSQC spectrum

**Trimethyl 10-methyl-9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2,4(1*H*)-tricarboxylate (1ia)**



Yellow solid; yield: 73% (37 mg); mp 196-197 °C.

IR cm<sup>-1</sup> 2991, 2359, 1732, 1706, 1578, 1462, 1376, 1278, 1241, 1201.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 7.65-7.57 (m, 2H), 7.42 (td, *J* = 1.2 Hz, 7.5 Hz, 1H), 7.29 (dd, *J* = 0.6 Hz, 7.2 Hz, 1H), 4.02 (s, 3H), 3.78 (s, 6H), 3.71 (s, 2H), 3.55 (s, 2H), 2.60 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 193.9, 171.7 (2C), 167.9, 144.9, 142.9, 142.1, 138.0, 135.7, 135.1, 134.6, 131.2, 129.3, 123.9, 123.4, 121.9, 59.3, 53.4 (2C), 52.6, 41.0, 38.8, 14.7.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>21</sub>O<sub>7</sub> 409.1282; found : 409.1275.

X-Ray: the product was crystallized from CH<sub>3</sub>CN.

CCDC 1977637 contains the supplementary crystallographic data for this paper.

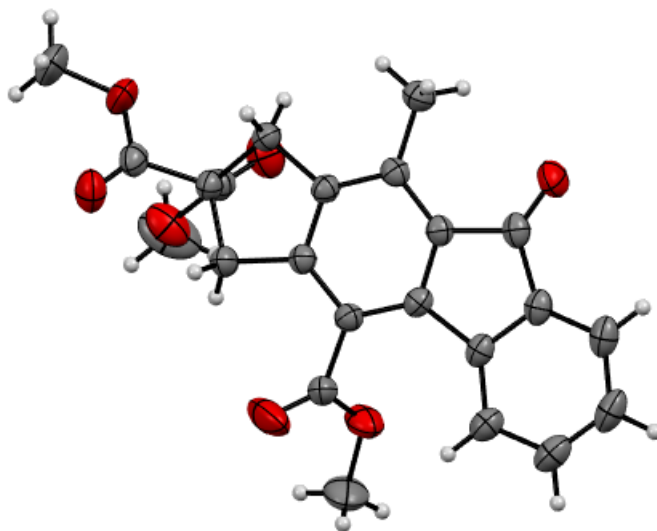


Figure S53 Crystallographically-derived molecular structure of the regioisomer 1ia.

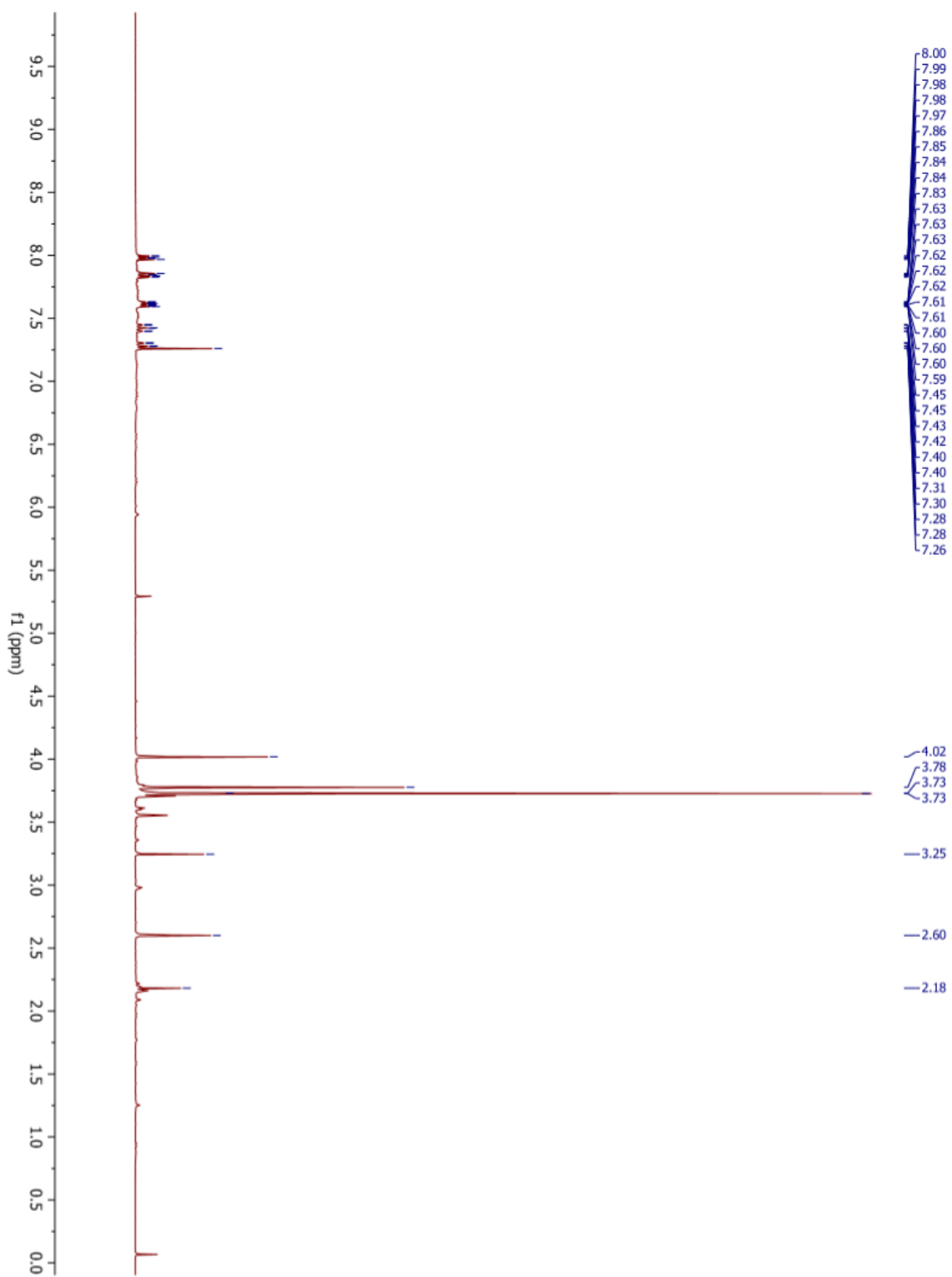


Figure S54 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of the crude mixture

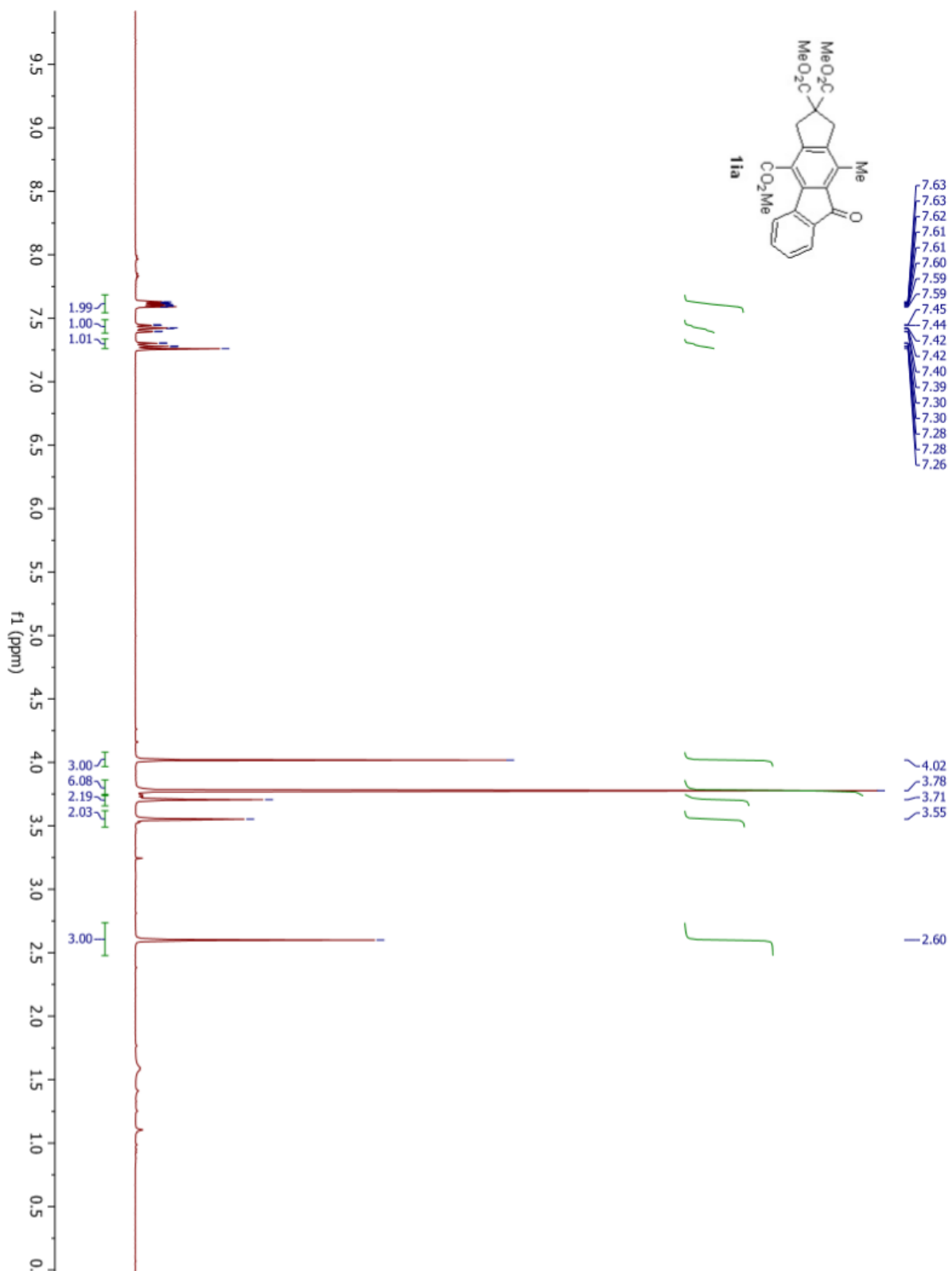


Figure S55 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

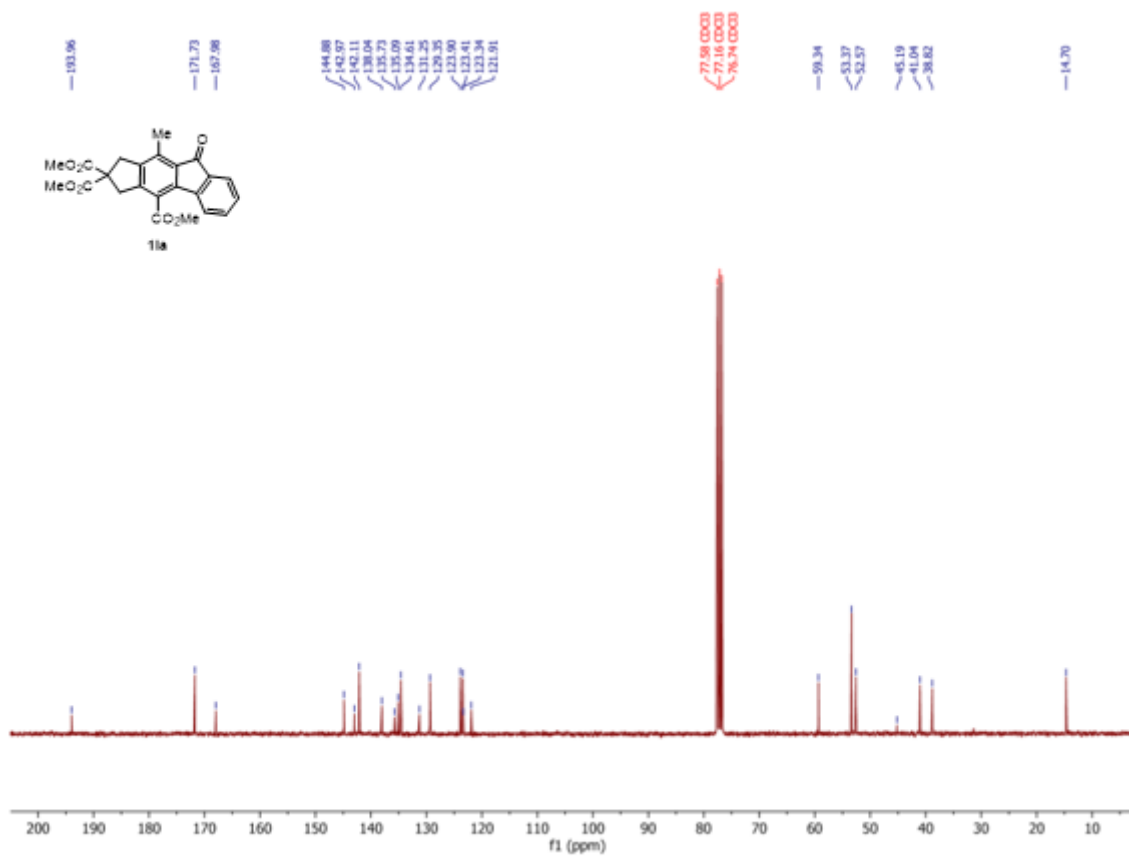


Figure S56 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum

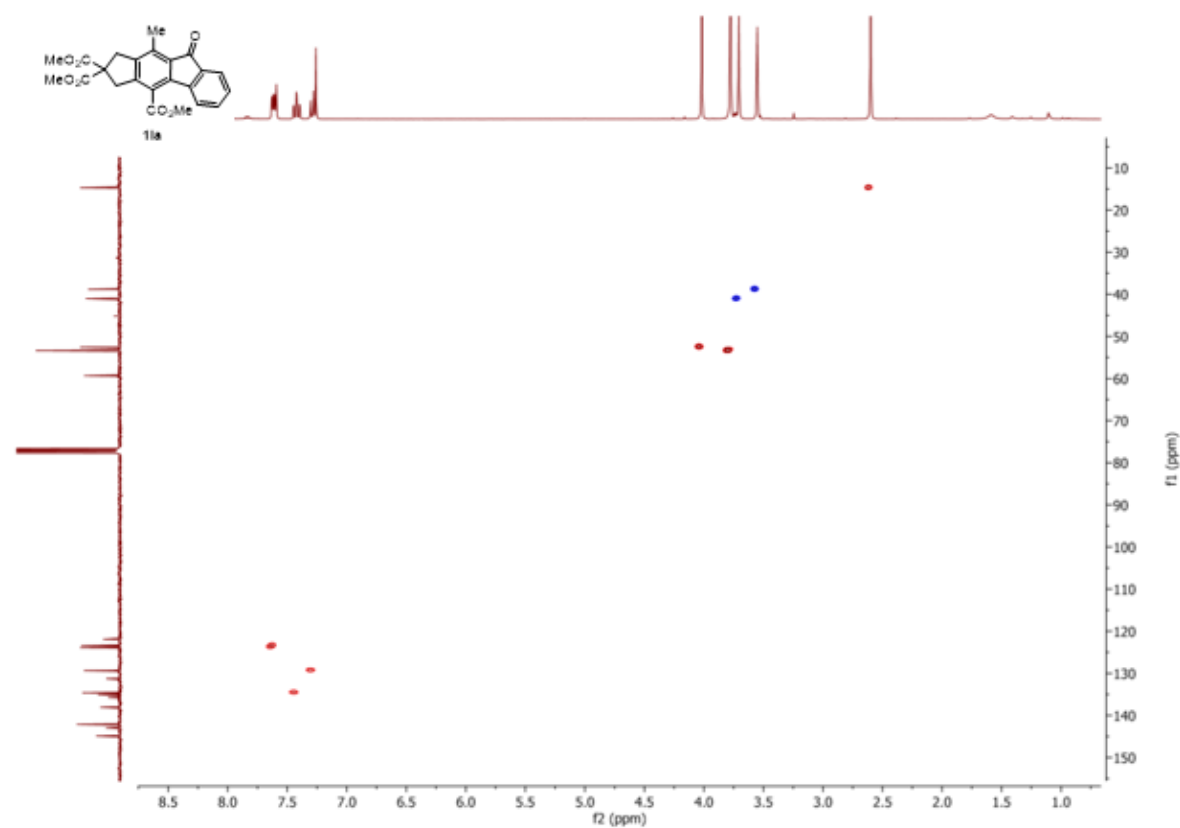
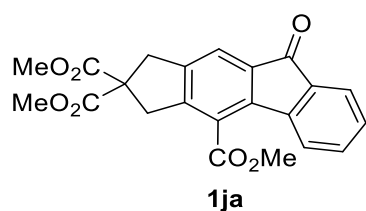


Figure S57 HSQC spectrum

**Trimethyl 9-oxo-3,9-dihydrocyclopenta[*b*]fluorene-2,2,4(1*H*)-tricarboxylate (1ja)**



Mixture of regioisomers (ratio 9:1, determined by <sup>1</sup>H NMR analysis of the crude).

Orange solid; yield: 56% (28 mg)

mp 139-140 °C.

Only the major regioisomer was described.

IR cm<sup>-1</sup> 2955, 2851, 1715, 1605, 1575, 1433, 1371, 1280.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 7.71-7.63 (m, 2H), 7.60 (s, 1H), 7.46 (td, *J* = 1.2 Hz, 7.5 Hz, 1H), 7.32 (dd, *J* = 0.9 Hz, 7.5 Hz, 1H), 4.04 (s, 3H), 3.77 (s, 6H), 3.72 (s, 2H), 3.61 (s, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 194.6, 171.6 (2C), 166.8, 146.4, 143.1, 141.9 (2C), 135.2, 135.0, 134.9, 129.5, 124.4, 124.2, 123.8, 122.4, 59.9, 53.4 (2C), 52.7, 40.9, 40.1.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>19</sub>O<sub>7</sub> 395.1125; found : 395.1131.

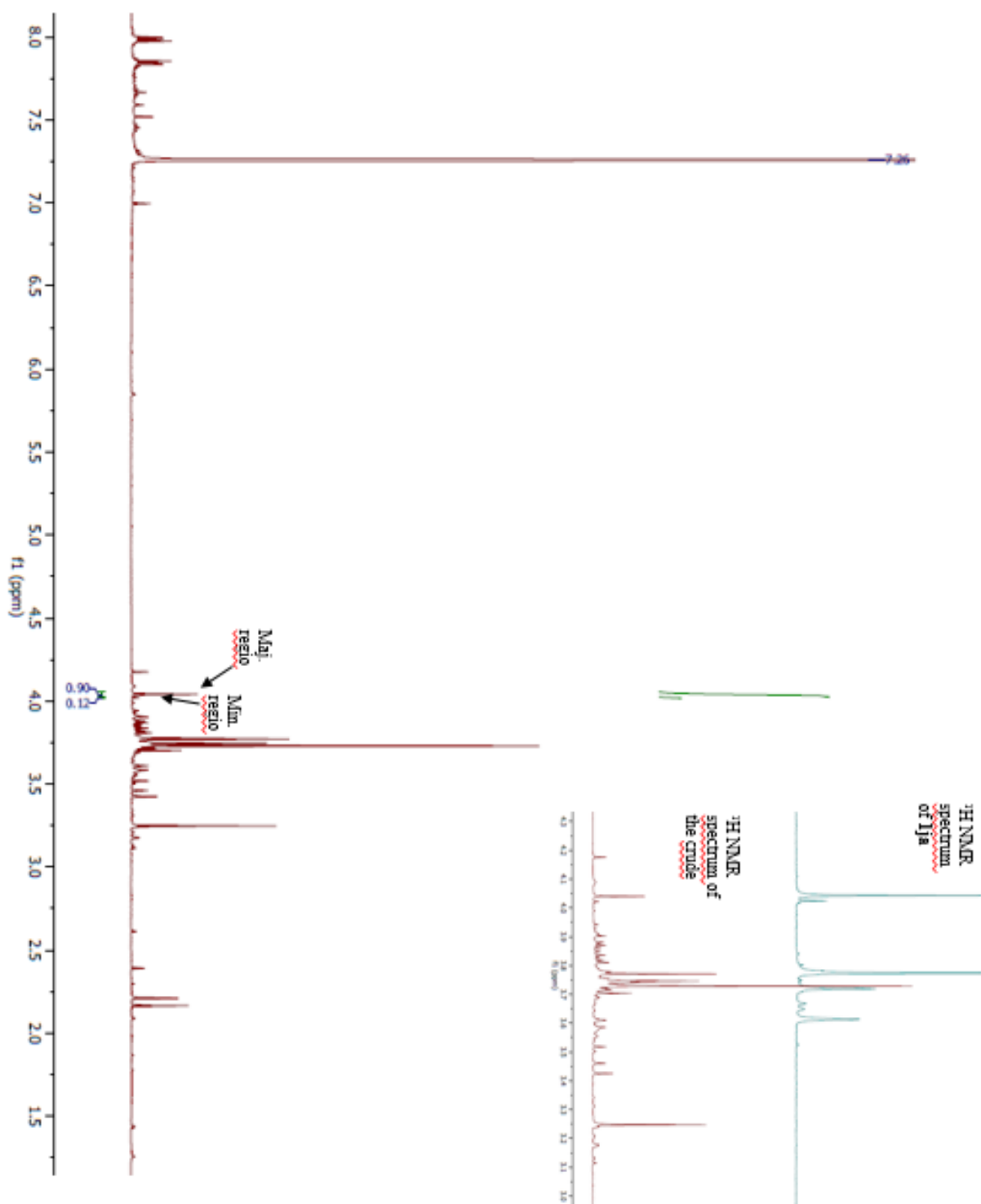


Figure S58 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of the crude mixture

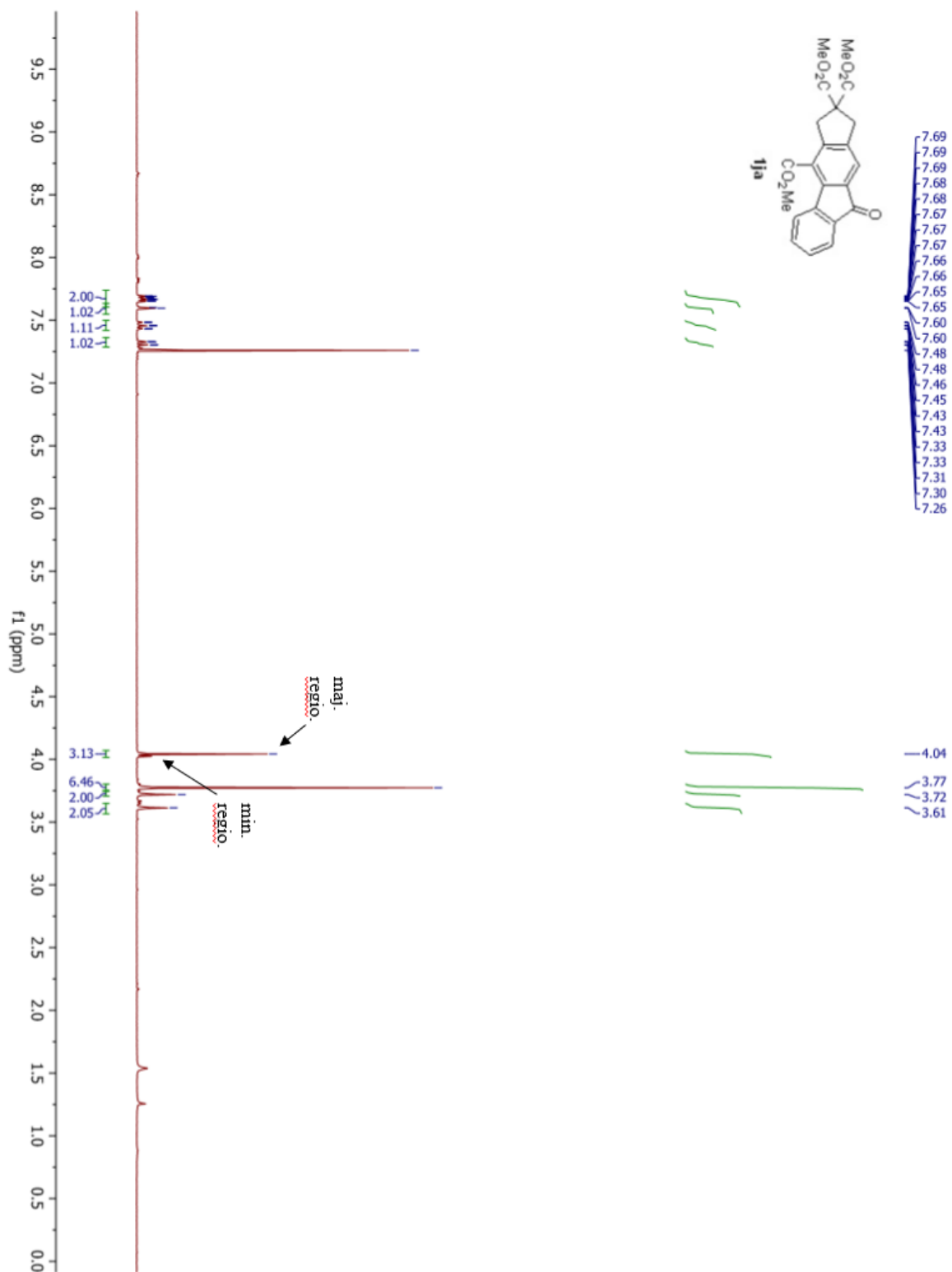


Figure S59  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum

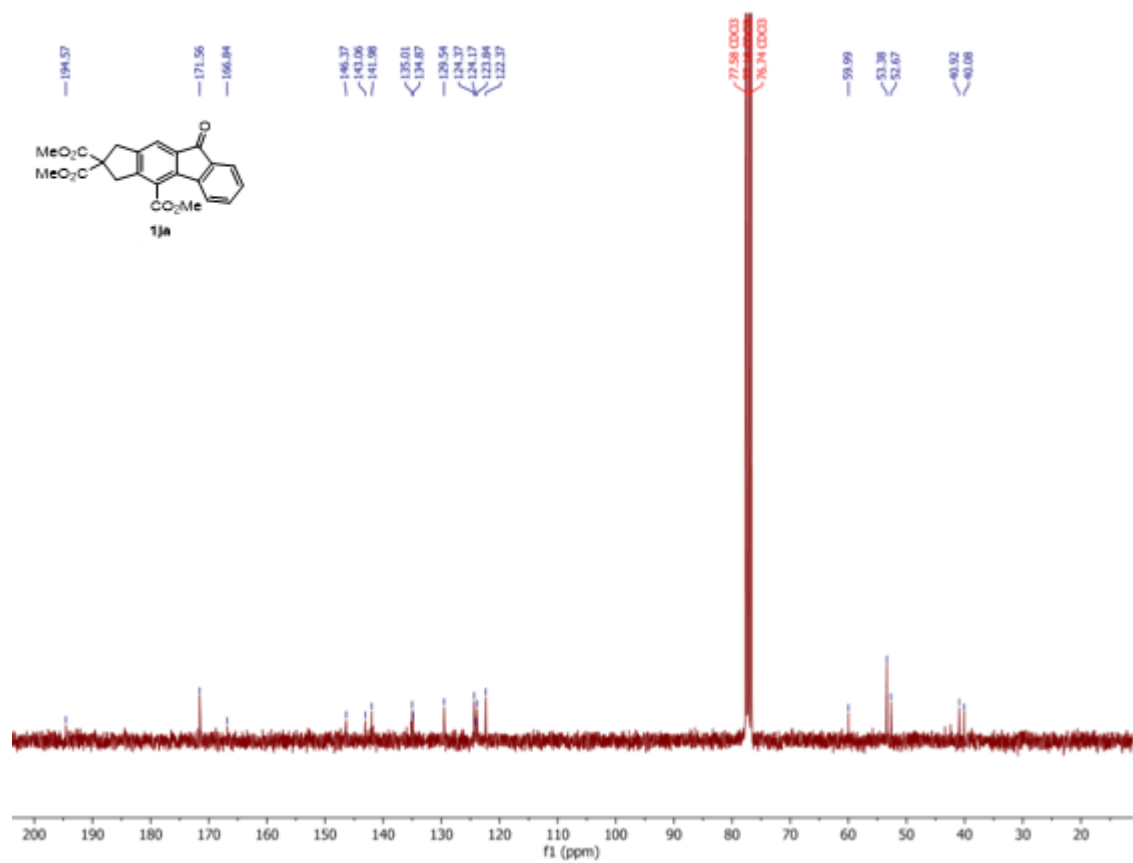


Figure S60  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) spectrum

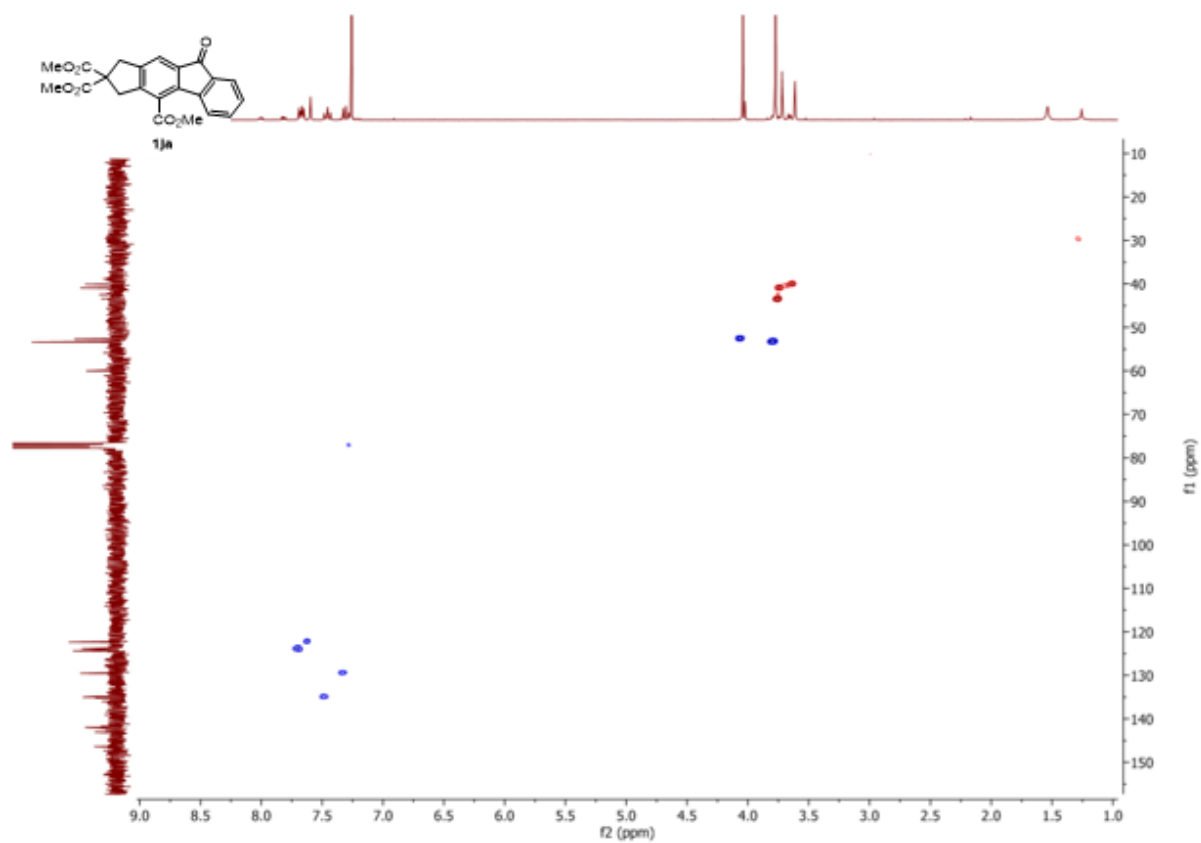
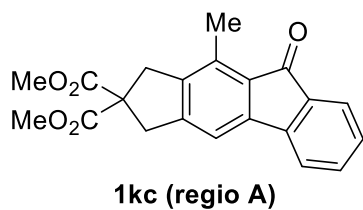


Figure S61 HSQC spectrum

**Dimethyl 10-methyl-9-oxo-3,9-dihydrocyclopenta[b]fluorene-2,2(1H)-dicarboxylate (1kc)**



Mixture of regioisomers (ratio 1:1, determined by <sup>1</sup>H NMR analysis of the crude).

Yellow solid; yield: 36% (16 mg, only the regioisomer A was isolated as a pure form); mp 217 °C.

IR cm<sup>-1</sup> 3050, 2917, 2341, 1729, 1699, 1595, 1488, 1255.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = 7.62-7.55 (m, 1H), 7.47-7.41 (m, 2H), 7.26-7.21 (m, 1H), 7.19 (s, 1H), 3.78 (s, 6H), 3.62 (s, 2H), 3.53 (s, 2H), 2.56 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 194.8, 171.9 (2C), 146.5, 145.2, 143.8, 141.3, 135.9, 135.1, 134.3, 130.5, 128.8, 123.9, 119.8, 114.1, 59.9, 53.3 (2C), 41.2, 38.9, 14.4.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>19</sub>O<sub>5</sub> 351.1227; found : 351.1227.

X-Ray: the product **1kc** (regio. A) was crystallized from CH<sub>3</sub>CN.

CCDC 1977638 contains the supplementary crystallographic data for this paper.

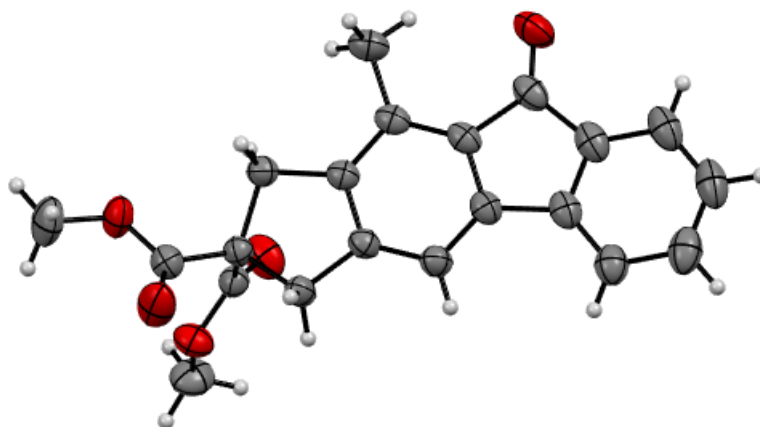


Figure S62 Crystallographically-derived molecular structure of the regioisomer A **1kc**.

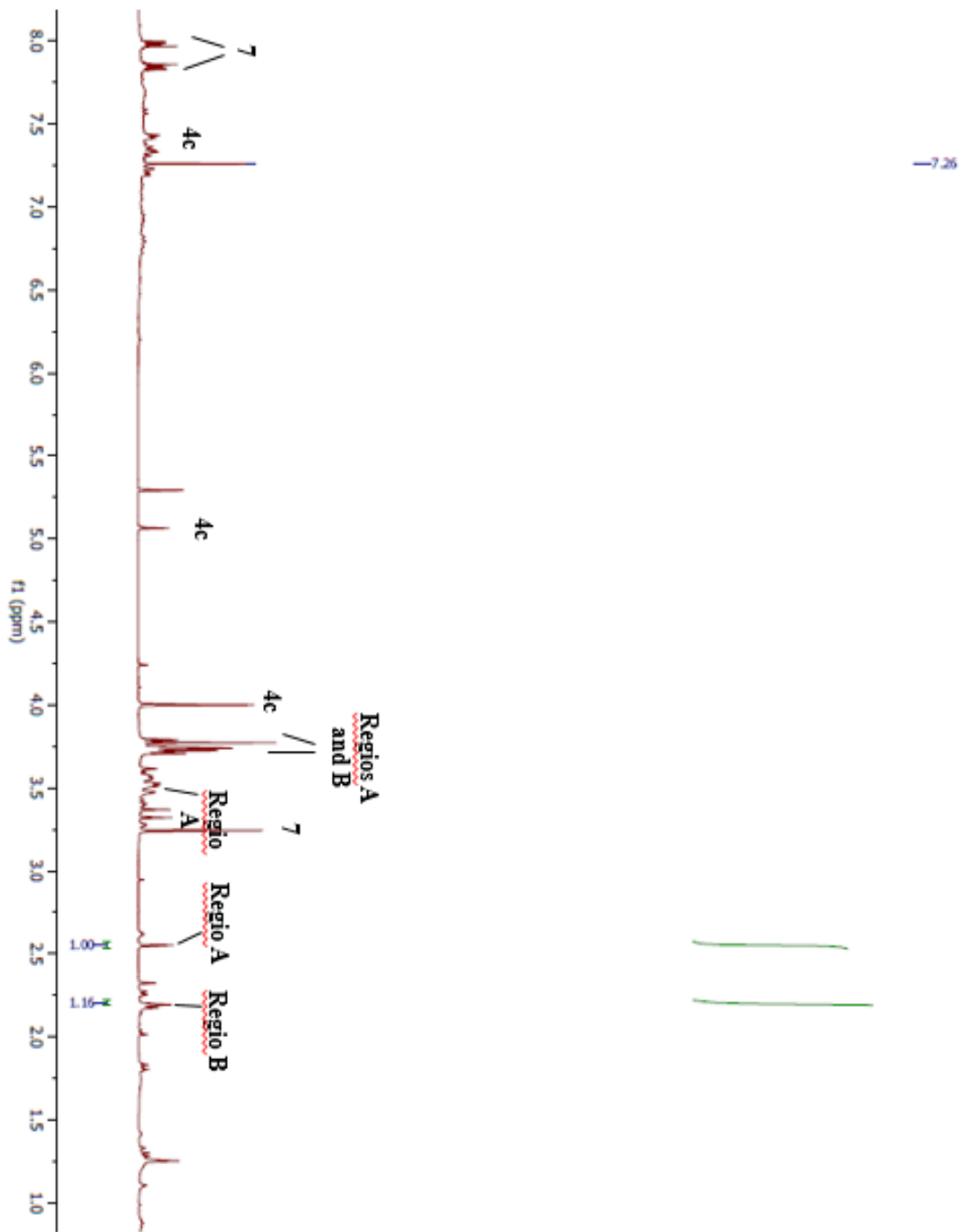


Figure S63  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of the crude mixture (ratio regioisomers A and B 1:1)

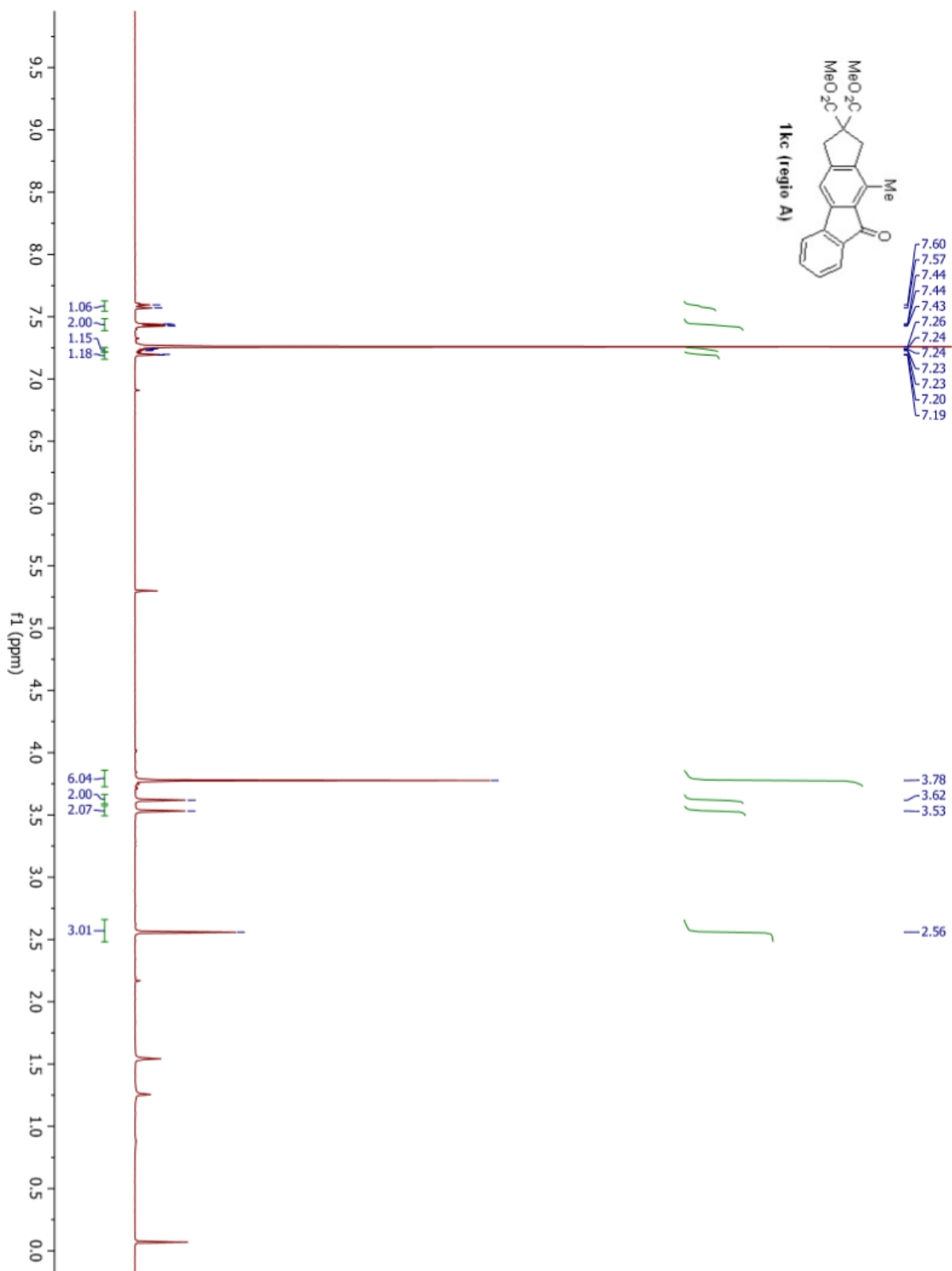


Figure S64 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

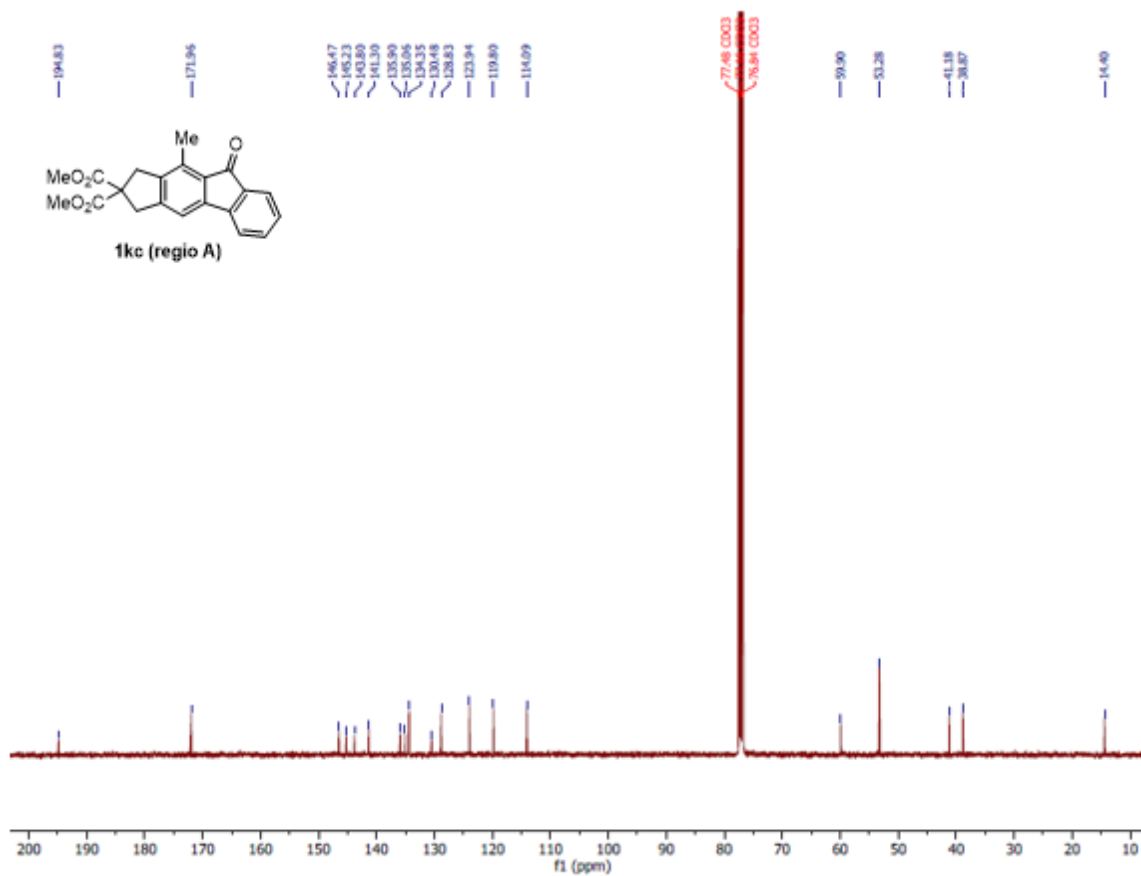


Figure S65 <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum

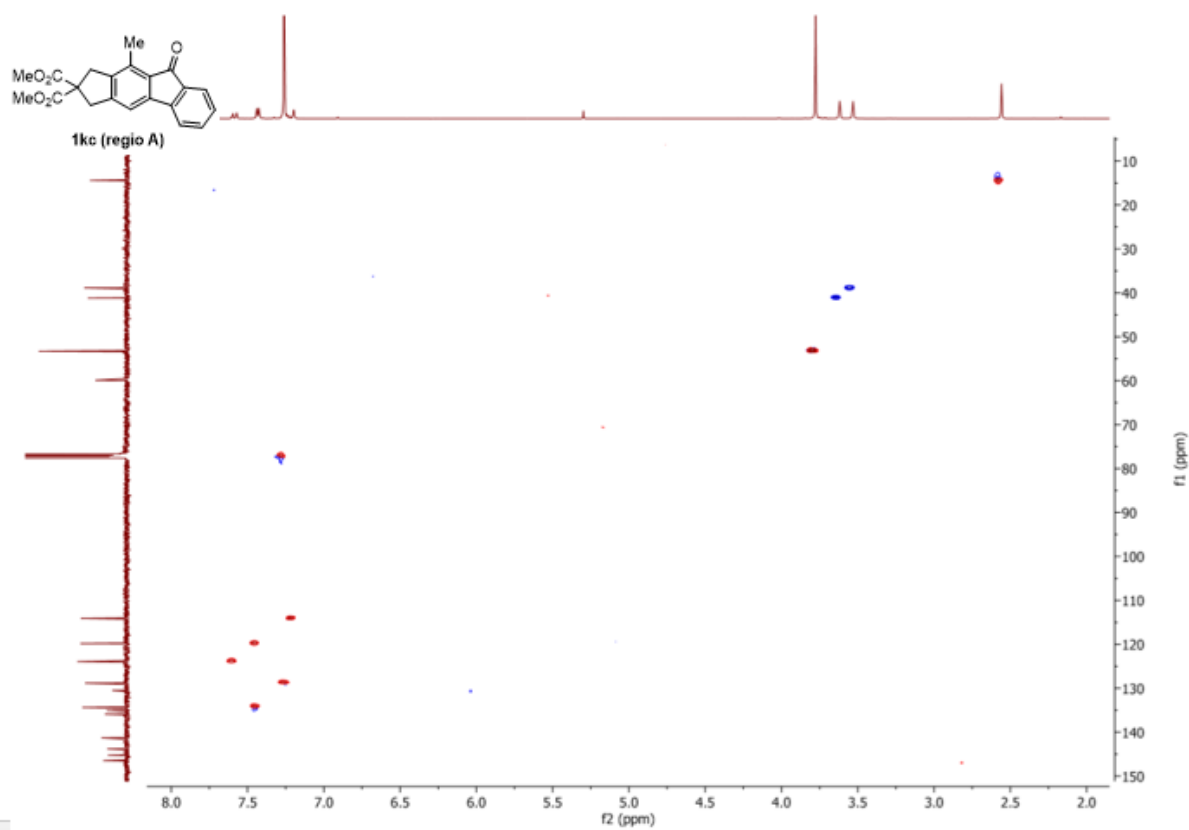
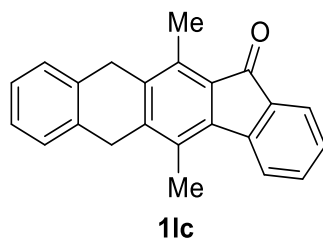


Figure S66 HSQC spectrum

**5,12-dimethyl-6,11-dihydro-13H-indeno[1,2-b]anthracen-13-one (11c)**



Yellow solid; yield: 41% (17 mg); mp 135-136 °C.

IR  $\text{cm}^{-1}$  3056, 1695, 1598, 1541, 1455, 1350, 1252.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 7.73 (d,  $J$  = 7.6 Hz, 1H), 7.65 (dq,  $J$  = 0.7 Hz, 7.4 Hz, 1H), 7.46 (td,  $J$  = 1.2 Hz, 7.6 Hz, 1H), 7.35-7.29 (m, 2H), 7.28-7.25 (m, 1H), 7.25-7.22 (m, 2H), 4.04 (s, 2H), 3.97 (s, 2H), 2.74 (s, 3H), 2.64 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 195.6, 144.7, 141.8, 140.8, 136.8, 135.6, 135.2, 134.9, 134.9, 134.2, 129.5, 129.1, 127.9, 127.7, 127.6, 126.6, 126.5, 123.9, 123.4, 33.4, 32.1, 15.9, 13.4.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{19}\text{O}$  311.1430; found : 311.1428.

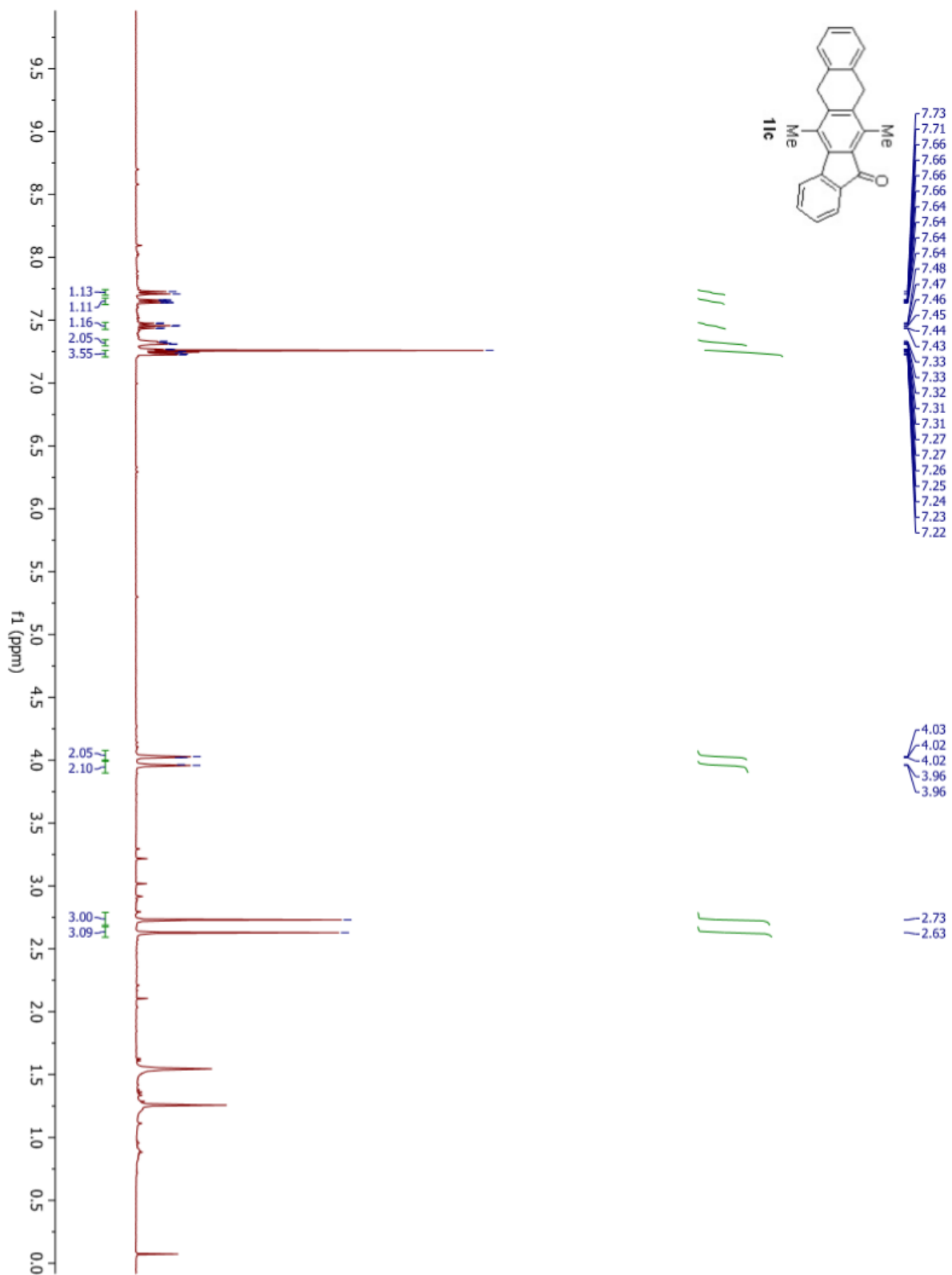


Figure S67 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum

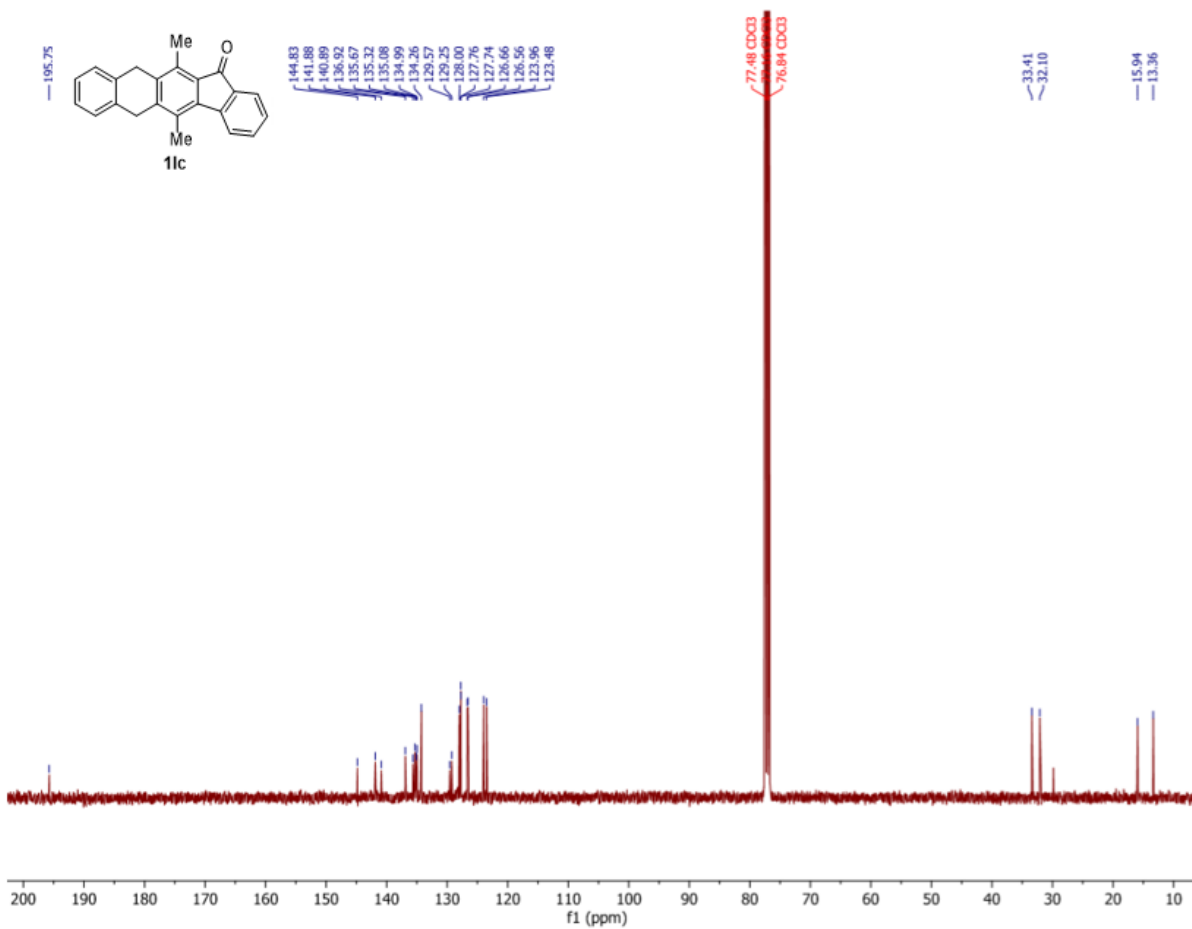


Figure S68 <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

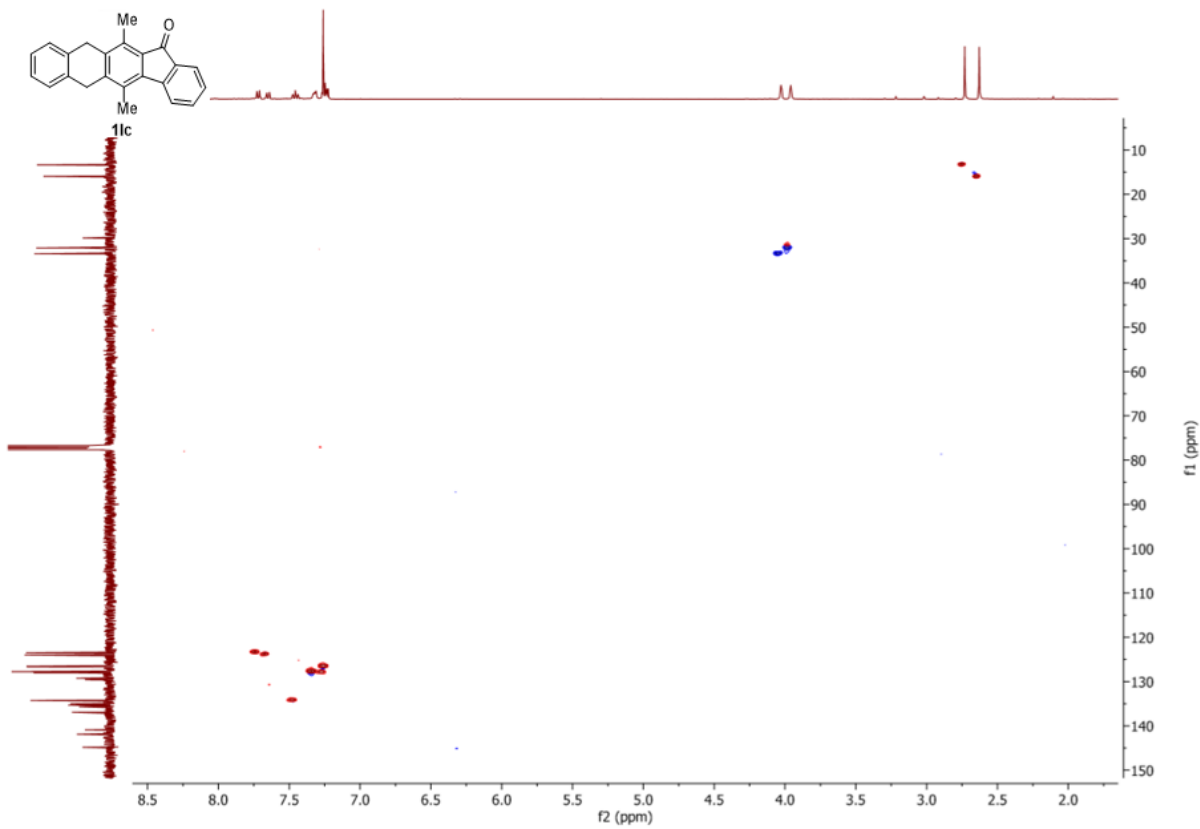
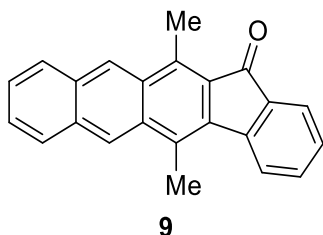


Figure S69 HSQC spectrum

### Synthesis of 5,12-dimethyl-13*H*-indeno[1,2-*b*]anthracen-13-one (9)



In a round-bottom flask was placed, 1.0 equiv. of 5,12-dimethyl-6,11-dihydro-13*H*-indeno[1,2-*b*]anthracen-13-one **11c** (11.0 mg, 0.035 mmol) in 1.5 mL DCE under argon. Then 2.4 equiv. of DDQ (19.0 mg, 0.085 mmol) was added. The mixture was stirred and heated at 80 °C for 3 h. Once cooled to room temperature, the solvent was removed under vacuum. The reaction mixture was diluted in 0.25 mL of Et<sub>3</sub>N and 0.25 mL of toluene. The mixture was stirred and heated at 80 °C for 24 h. Then the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel provided the desired product (eluent CH<sub>2</sub>Cl<sub>2</sub> and 0.1% triethylamine).

Yellow solid; yield: 91% (10 mg) ; mp 176-177 °C.

IR cm<sup>-1</sup> 3065, 2921, 2858, 1691, 1594, 1468.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 8.70 (s, 1H), 8.59 (s, 1H), 8.07-7.99 (m, 3H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.60 (td, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.58-7.49 (m, 2H), 7.37 (td, *J* = 0.4 Hz, 7.6 Hz, 1H), 3.22 (s, 3H), 3.03 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ = 194.6, 145.1, 138.3, 138.0, 134.7, 133.9, 133.5, 133.3, 132.4, 131.8, 128.7, 128.5, 128.4, 127.3, 126.9, 126.5, 124.9, 124.4, 124.1, 123.9, 123.7, 15.4, 12.9.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>17</sub>O 309.1274; found : 309.1274.

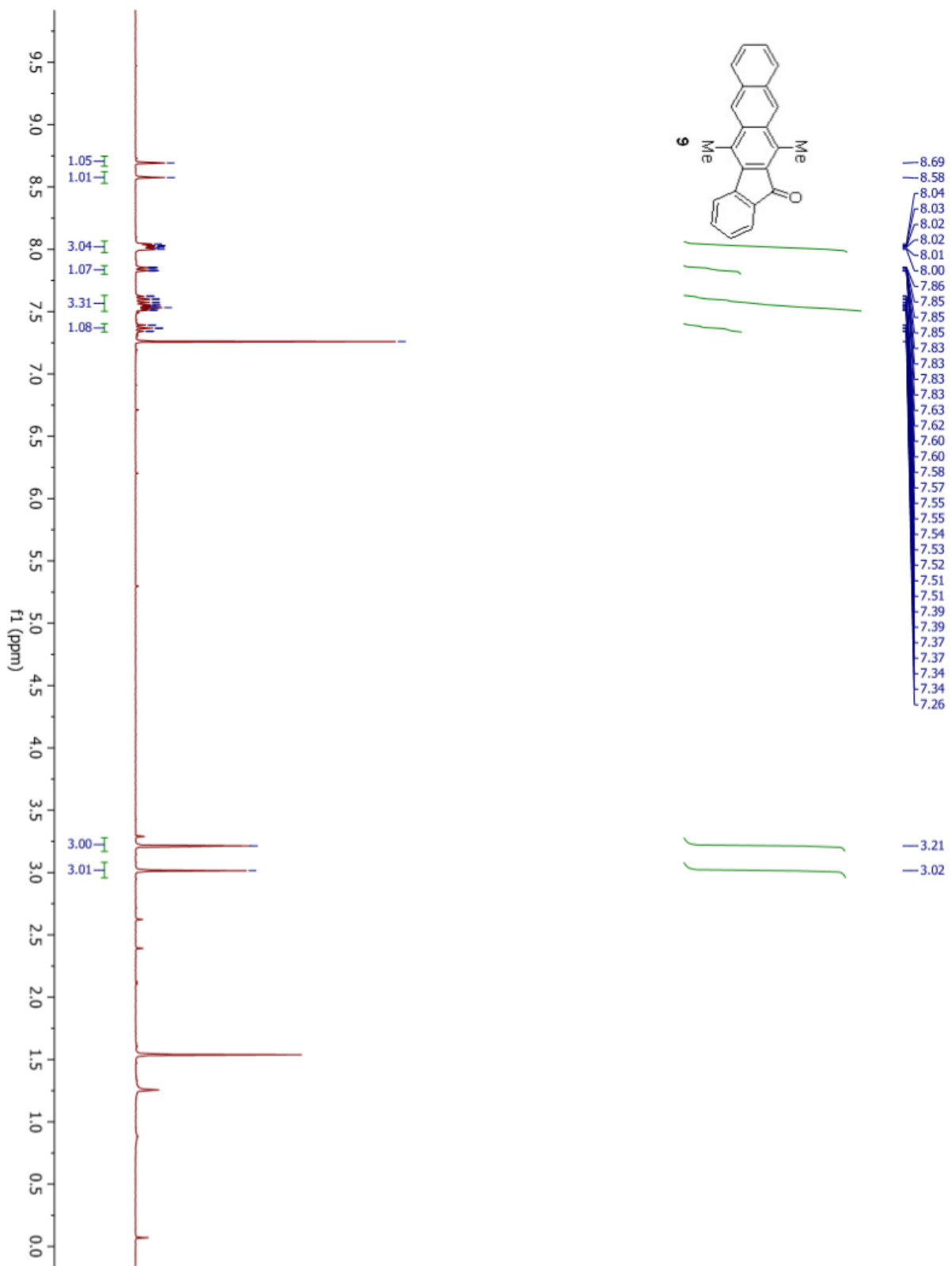


Figure S70 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

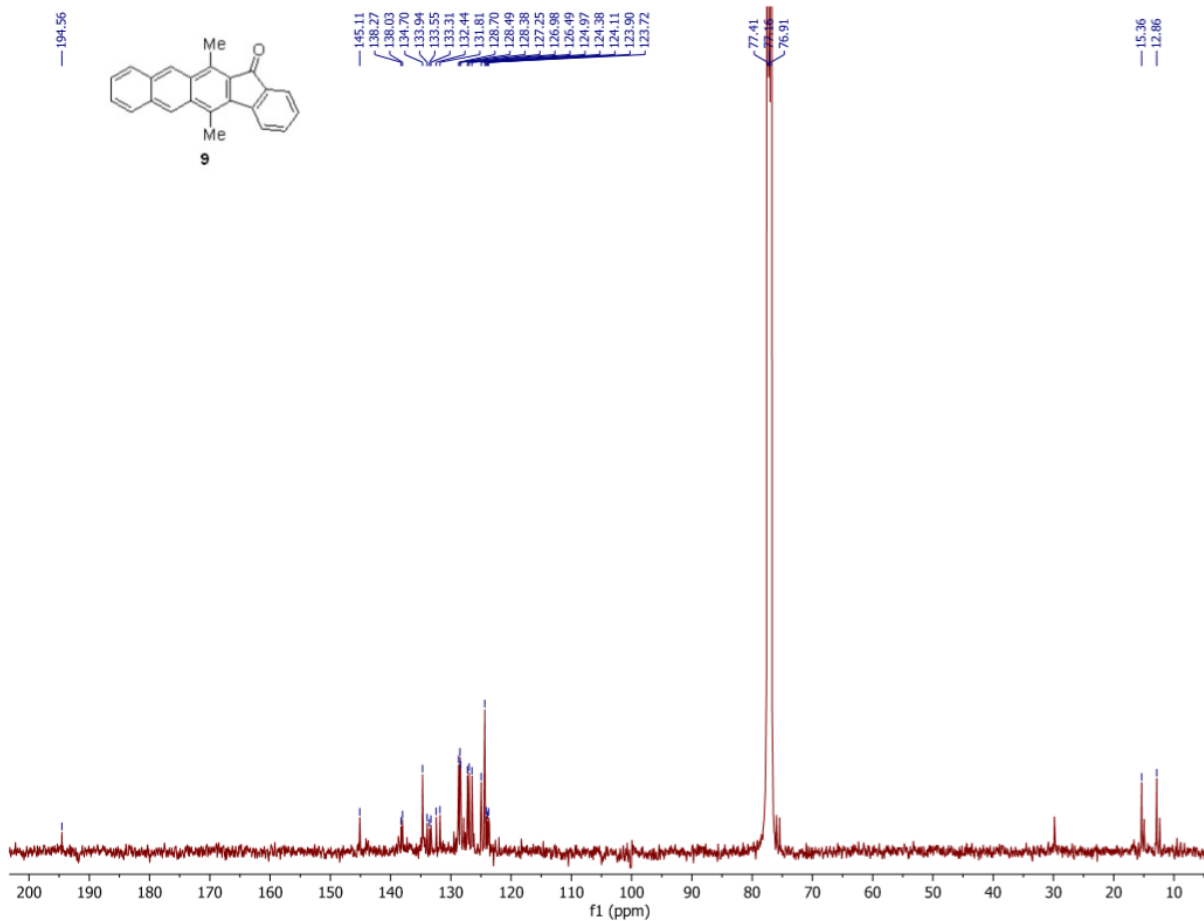


Figure 71 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum

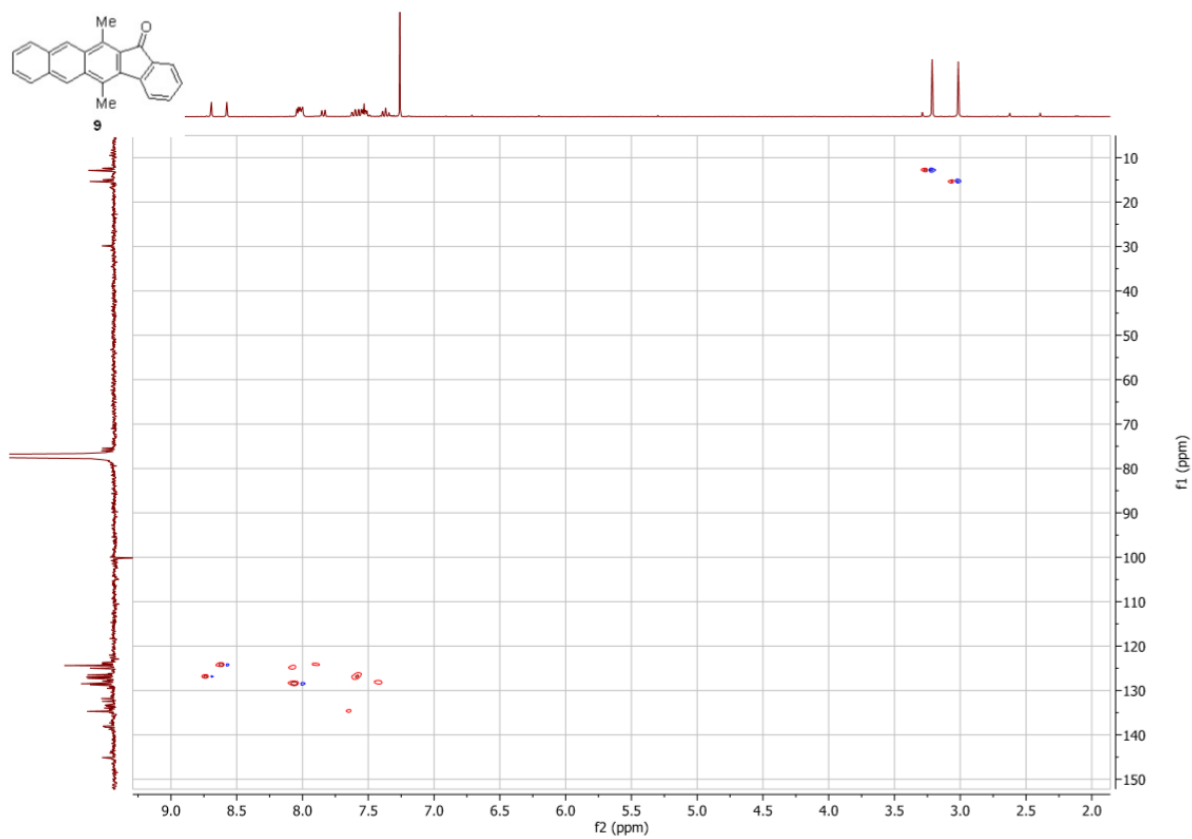
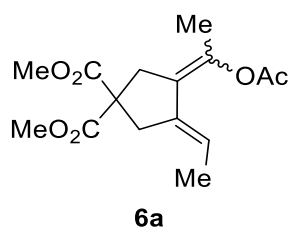


Figure S72 HSQC spectrum

**Dimethyl-3-(1-acetoxyethylidene)-4-ethylidenecyclopentane-1,1-dicarboxylate (6a)**



Yellow solid; mp 247-248 °C.

IR  $\text{cm}^{-1}$  2954, 1728, 1431, 1253, 1201.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 5.68 (q,  $J$  = 6.0 Hz, 1H), 3.73 (s, 6H), 3.00 (s, 2H), 2.94 (s, 2H), 2.15 (s, 3H), 2.06 (s, 3H), 1.75 (d,  $J$  = 6.0 Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 171.9 (2C), 168.9, 140.2, 135.6, 125.5, 121.7, 57.1, 53.0 (2C), 38.3, 37.6, 21.0, 18.9, 15.6.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_6\text{Na}$  319.1158; found : 319.1152.

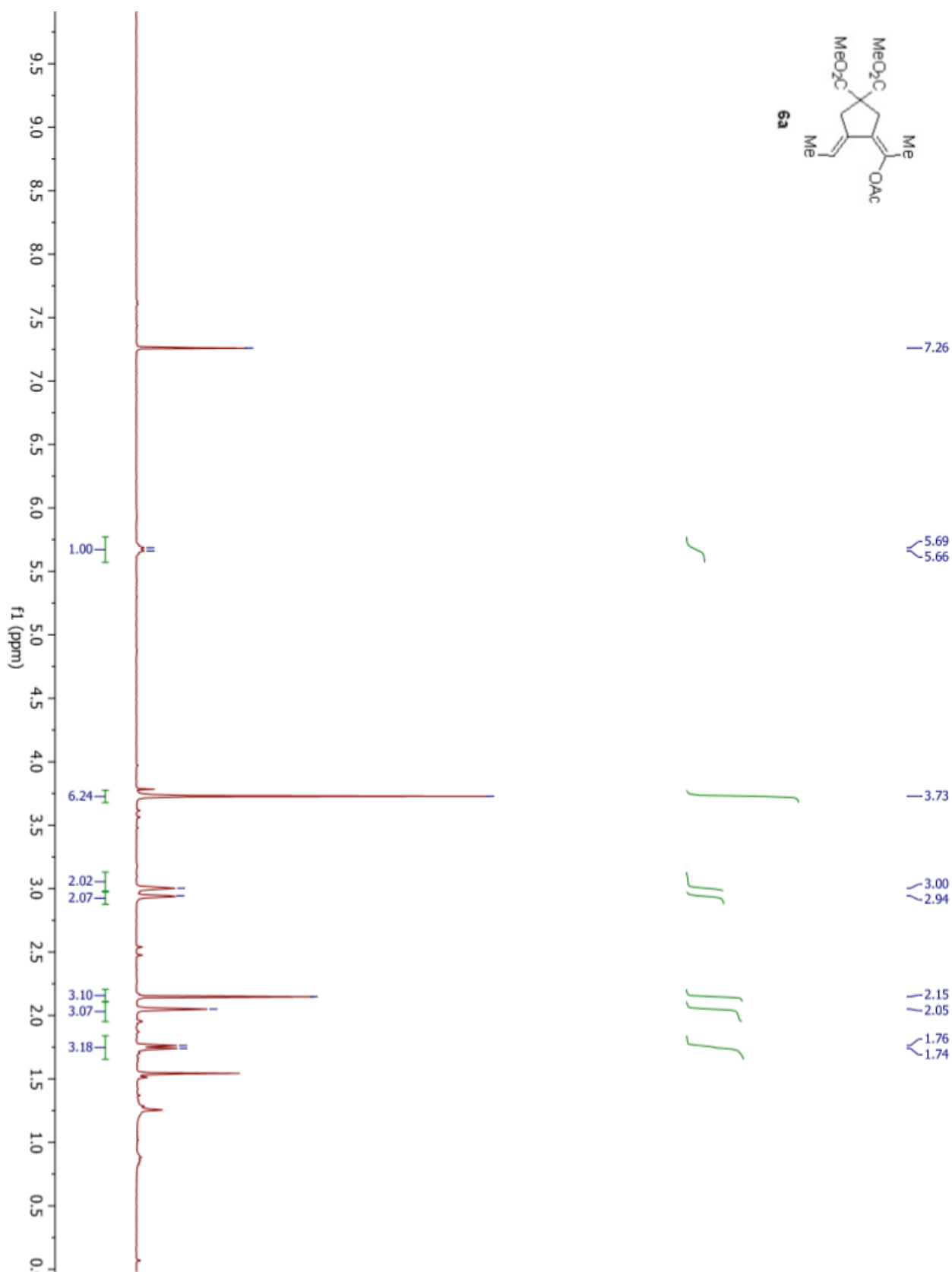


Figure S73 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum

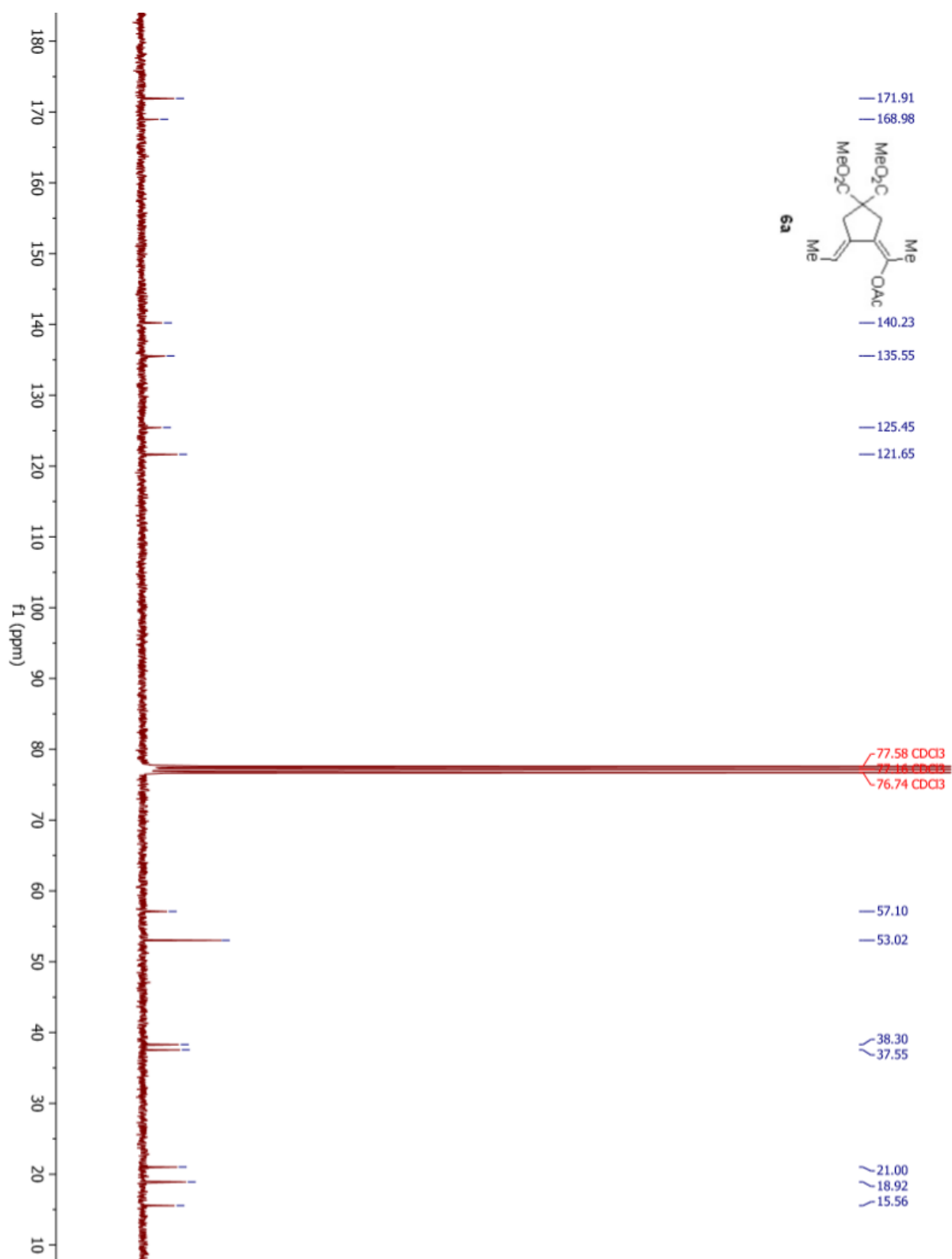


Figure S74 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum