

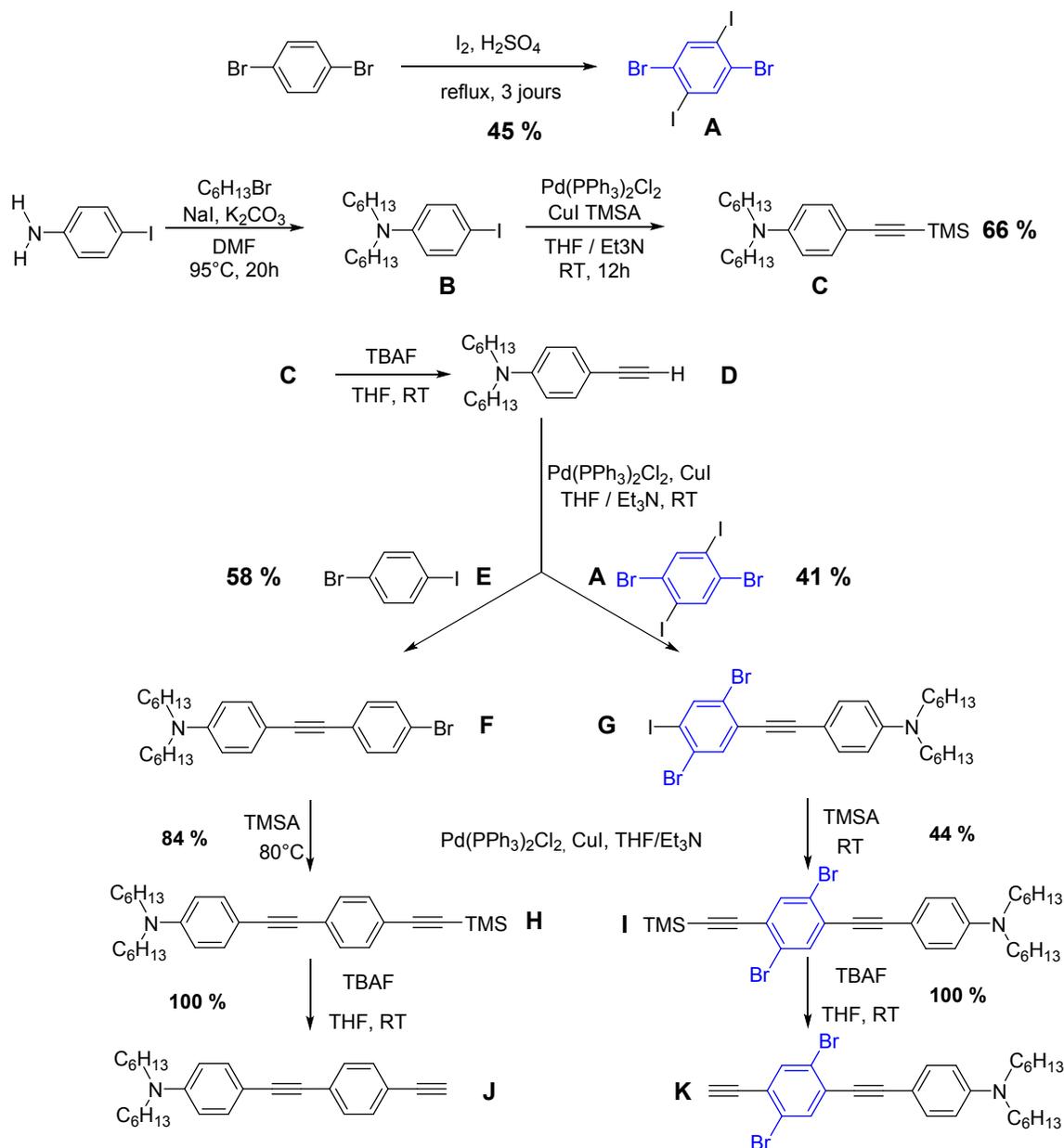
**Supporting Information for: A combined theoretical and experimental investigation on the influence of bromine substitution pattern on the photophysics of conjugated organic chromophores**

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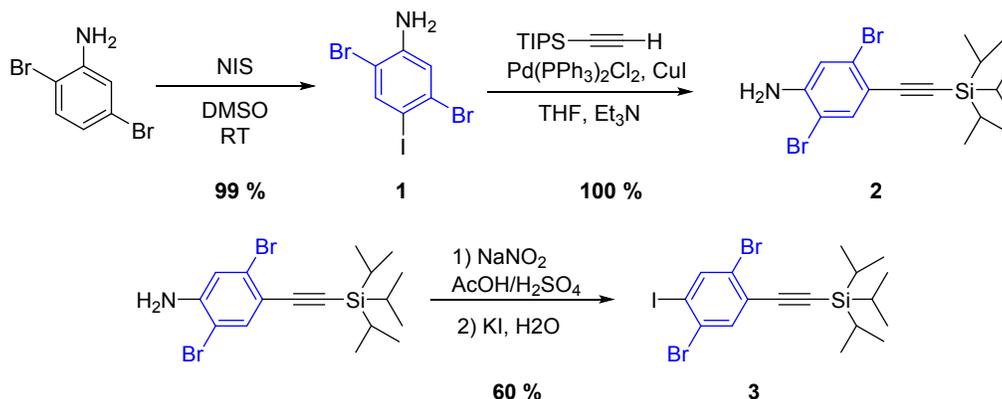
# S1-Synthesis and characterizations of all new molecules



Scheme S1. Synthesis of building block previously described in ref 1. For the sake of clarity, these building blocks are designed by letters, while all new compounds (which synthesis is described herein) are labelled with numbers

## Pentamer series

Synthesis of the centrosymmetric members of the pentameric family (**00000**, **00200**, **00200**, **02020** **02220**, **02000**) and of intermediates have been reported before.<sup>[1]</sup> Synthesis of their noncentrosymmetric analogues **02200** and **02000** required desymetrization of the central dibromophenyl moieties. This was achieved in a three steps protocol starting from the commercially available 2,5-dibromo-aniline, which was first iodinated in its *para* position, using NIS/sulfuric acid in DMSO to afford the 2,5-dibromo-4-iodoaniline **1**.<sup>[2]</sup> The resulting compound was then involved in a Sonogashira coupling with tri(isopropyl)acetylene, yielding the corresponding ethynylaniline compound **2** in nearly quantitative yield. A Sandmeyer reaction allowed substituting the arylamine moiety by iodine (Scheme S2).<sup>[3]</sup> The resulting *para*(iodinated) dibromophenylethynyl compound **3** was then involved in a Sonogashira coupling with compound **D** or **6** affording respectively, after purification, compounds **5** and **7** (Scheme S3-Scheme S4). After removal of the tris(isopropyl) protecting group upon treatment with tetrabutylammonium fluoride, the resulting acetylenes **6** and **8** were respectively involved in Sonogashira couplings with compounds **9** and **10** to yield the target **02000** and **02200** (Scheme S4).



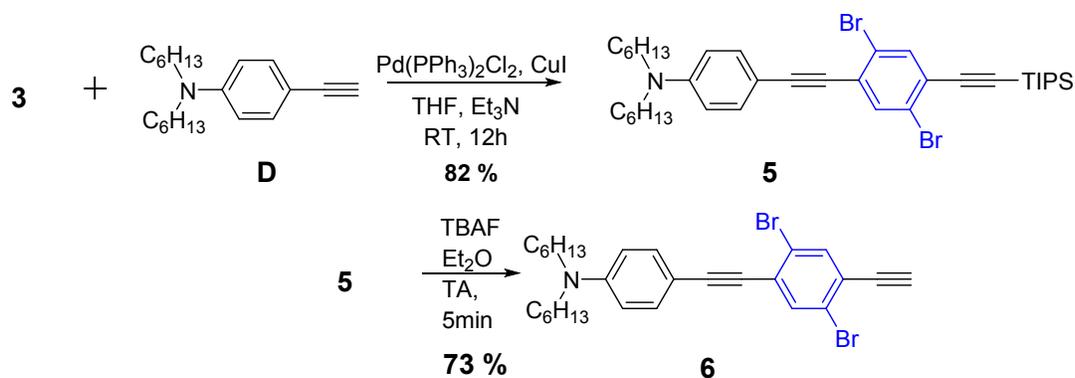
Scheme S2. Synthesis of building block **3**

**1: 2,5di-bromoaniline** (15 g, 59.8mmol) is dissolved in 200mL of DMSO. *N*-iodosuccinimide (13.45g, 60mmol) is added by portion during 20 minutes. The mixture is stirred during 3 days at room temperature. The solution is dissolved in 500mL of water and extracted three times with AcOEt (100mL). The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub> filtered and solvents are removed under reduced pressure to afford the desired compound as brown solid (22.5 mg, 99%). <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 7.76(s, 1H), 7.02 (s, 1H), 4.15 (s, 2H). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, Ppm): δ 145.31, 142.09, 129.05, 118.76, 108.67, 85.40. HRMS calcd for [C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>IN + H]<sup>+</sup> at 375.7828 found 375.7834. Elemental analysis calcd for C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>IN: C, 19.13, H, 1.07, N, 3.72 found C, 19.17, H, 1.04, N, 3.49.

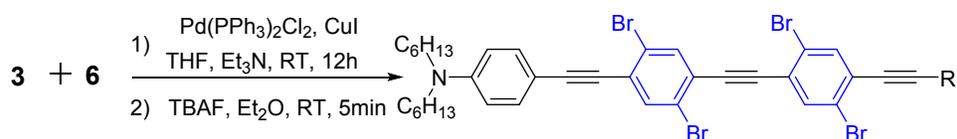
**2:** To solution of *iodo-dibromoaniline* **1** (5g, 13.27mmol) in 1:1. vol/vol dry THF/Et<sub>3</sub>N (50 mL), extensively degassed by argon bubbling, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(93mg, 0.13 mmol, 0.01 eq.) CuI (50mg, 0.27mmol, 0.02eq.) and *triisopropylsilylacetylene* (3.87mL, 17.25mmol, 1.3 eq.) are added. The tube is sealed and the mixture is stirred overnight at room temperature. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub> filtered and solvents are

removed under reduced pressure, the product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 8/1. solid deposition of the product pre-adsorbed on silica gel). to afford the desired compound as yellow solid (95%). TLC: PE / CH<sub>2</sub>Cl<sub>2</sub>: 8/1. R<sub>f</sub> = 0.15. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 7.52(s, 1H), 6.93 (s, 1H), 4.24 (s, 2H), 1.11 (s, 21H). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 144.9, 137.0, 125.5, 118.1, 116.3, 106.9, 104.0, 93.9, 18.7, 11.4.

**3:** To solution of **2** (5,68g, 13.17mmol) in acetic acid (15 mL) concentrated sulfuric acid (4 mL) is slowly added. The vial is putted in ice bath. A solution of NaNO<sub>2</sub> (2,71g, 39,25 mol) in water (6mL) is added dropwise. The color of the solution turns to orange. After 1h of stirring at 0°C, a solution of KI (6,54g, 39,38mmol) in water (6mL) is slowly added at 0°C. The solution is stirred for 1h at room temperature. 50mL of NaOH aq. Solution (5M) are added. The neutralization is completed with saturated sodium carbonate solution. The solution is extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (50mL). The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE, solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as slightly yellow oil (77%). TLC: PE. R<sub>f</sub> = 0.95. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 8.10(s, 1H), 7.74 (s, 1H), 1.19 (s, 21H). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 142.6, 136.2, 128.1, 127.1, 124.5, 102.7, 101.3, 99.5, 40.1, 11.2. HRMS calcd for [C<sub>17</sub>H<sub>23</sub>Br<sub>2</sub>ISi + H]<sup>+</sup> at 540.9053 found 540.9056. Elemental analysis calcd for C<sub>17</sub>H<sub>23</sub>Br<sub>2</sub>ISi: C, 37.66, H, 4.28 found C, 37.63, H, 4.39.

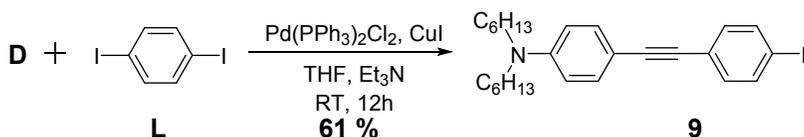


Scheme S3 synthesis of building block 6



1) R = TIPS **7 76 %**

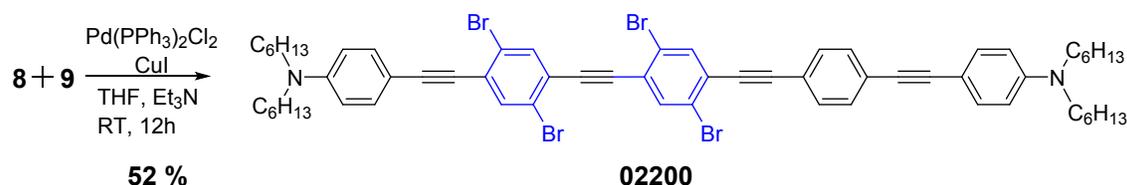
2) R = H **8 97 %**



**L**

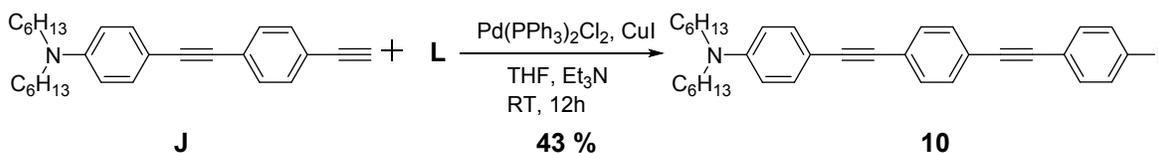
**61 %**

**9**



**52 %**

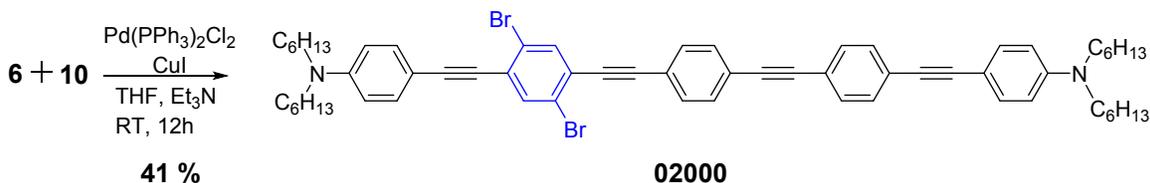
**02200**



**J**

**43 %**

**10**



**41 %**

**02000**

#### Scheme S4. Final steps in the synthesis of **02000** and **02200**

**5: 3** (1.30 g, 2.40 mmol) and **4** (1 g, 3.5 mmol) are dissolved in 1:1 vol/vol dry THF/Et<sub>3</sub>N (40 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (80 mg, 2%) and CuI (37 mg, 4%) are added. The solution is stirred overnight at room temperature. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1) to afford the desired compound as yellow oil (1.2 g, 71%). TLC: (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1) R<sub>f</sub> = 0.33. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.74 (s, 2H), 7.44 (d, 2H), 6.62 (d, 2H), 3.32 (t, 4H), 1.63 (t, 4H), 1.37 (m, 12H), 1.20 (s, 21H), 0.96 (t, 6H).

**6:** A molar solution of *TBAF* in *THF* (1.42 mL, 1.42 mmol) is added to a solution of **5** (500 mg, 0.71 mmol) in  $\text{Et}_2\text{O}$  (20mL). The mixture is stirred for 10 min at room temperature and the solution is filtered through a short pad of silica gel and eluted with  $\text{Et}_2\text{O}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$  filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil (388 mg, 86%). TLC: PE /  $\text{CH}_2\text{Cl}_2$ : 9/1.  $R_f = 0.30$ .  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.72(d, 2H), 7.41 (d, 2H), 6.58 (d, 2H), 3.47 (s, 1H), 3.30 (t, 4H), 1.60 (t, 4H), 1.34 (m, 12H), 0.93 (t, 6H).

**7:** **3** (484 mg, 0.89 mmol) and **6** (404 mg, 0.74 mmol) are dissolved in 1:1 vol/vol dry THF/ $\text{Et}_3\text{N}$  (50 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (40 mg, 2%) and  $\text{CuI}$  (18 mg, 4%) are added. The solution is stirred overnight at room temperature. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE /  $\text{CH}_2\text{Cl}_2$ : 9/1) to afford the desired compound as yellow oil (710 mg, 76%). TLC: (PE /  $\text{CH}_2\text{Cl}_2$ : 9/1)  $R_f = 0.6$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (s, 2H), 7.64 (s, 2H), 7.32 (d, 2H), 6.49 (d, 2H), 3.21 (t, 4H), 1.50 (t, 4H), 1.25 (m, 12H), 1.08 (s, 21H), 0.83 (t, 6H).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.6, 136.7, 136.4, 135.4, 133.4, 128.6, 127.2, 125.8, 124.0, 123.7, 123.5, 123.2, 111.2, 107.4, 103.3, 100.5, 100.2, 93.8, 92.8, 85.5, 51.0, 31.7, 29.8, 27.2, 22.7, 18.1, 14.1, 11.3. HRMS calcd for  $[\text{C}_{45}\text{H}_{55}\text{Br}_4\text{NSi} + \text{H}]^+$  at 954.0910 found 954.0913. Elemental analysis calcd for  $\text{C}_{45}\text{H}_{55}\text{Br}_4\text{NSi}$ : C, 56.44, H, 5.79, N, 1.46 found C, 56.37, H, 5.89, N, 1.42.

**8:** A molar solution of *TBAF* in *THF* (0.84 mL, 0.84 mmol) is added to a solution of **27** (400 mg, 0.42 mmol) in  $\text{Et}_2\text{O}$  (20mL). The mixture is stirred for 10 min at room temperature and the solution is filtered through a short pad of silica gel and eluted with  $\text{Et}_2\text{O}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$  filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil (335 mg, 100%). TLC: PE /  $\text{CH}_2\text{Cl}_2$ : 9/1.  $R_f = 0.50$ .  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.80 (m, 4H), 7.41 (d, 2H), 6.59 (d, 2H), 3.53 (s, 1H) 3.33 (t, 4H), 1.59 (t, 4H), 1.34 (m, 12H), 0.93 (t, 6H).

**9:** **4** (2.7 g, 9.46 mmol) and *1,4-iodobenzene* (9.3 g, 28.4 mmol) are dissolved in 1:1. vol/vol THF/ $\text{Et}_3\text{N}$  (100 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (133 mg, 2%) and  $\text{CuI}$  (72 mg, 4%) are added. The solution is stirred overnight at room temperature. Solvents are removed under reduced pressure and dissolve in  $\text{AcOEt}$ . The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE then PE /  $\text{CH}_2\text{Cl}_2$ : 9/1) to afford the desired compound as yellow oil (2.4, 52%). TLC: (PE /  $\text{CH}_2\text{Cl}_2$ : 9/1)  $R_f = 0.35$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 (d, 2H), 7.36 (d, 2H), 7.22 (d, 2H), 6.58 (d, 2H), 3.29 (t, 4H), 1.58 (t, 4H), 1.34 (m, 12H), 0.92 (t, 6H).

**10:** **J** (0.5 g, 1.30 mmol) and *1,4-iodobenzene* (**L**) (1.28 g, 3.89 mmol) are dissolved in 1:1. vol/vol THF/ $\text{Et}_3\text{N}$  (30 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (18 mg, 2%) and  $\text{CuI}$  (10 mg, 4%) are added. The solution is stirred overnight at room temperature. Solvents are removed under reduced pressure and dissolve in  $\text{AcOEt}$ . The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed three times with water and pre-dried by

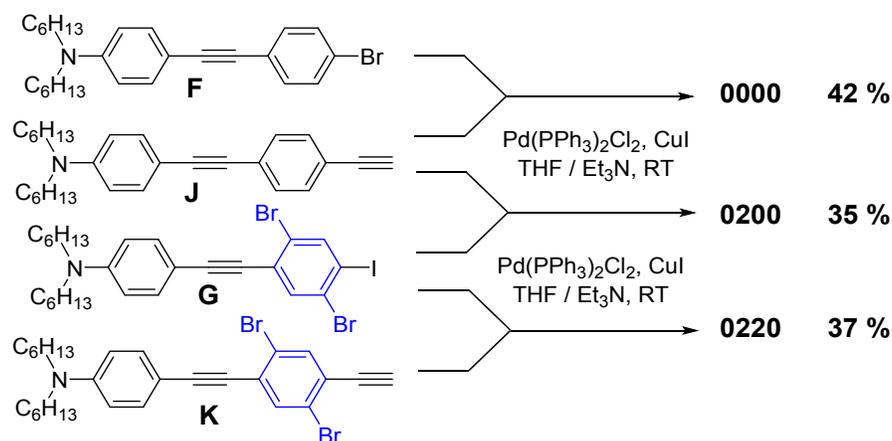
washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1) to afford the desired compound as yellow solid (213 mg, 23%). TLC: (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1) R<sub>f</sub> = 0.4. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.49 (m, 8H), 7.35 (d, 2H), 6.55 (d, 2H), 3.26 (t, 4H), 1.56 (t, 4H), 1.30 (s, 12H), 0.89 (t, 6H).

**02000:** **6** (154 mg, 0.28 mmol) and **10** (200 mg, 0.34 mmol) are dissolved in Et<sub>3</sub>N (10 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mg, 2%) and CuI (2 mg, 4%) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (228 mg, 81%). TLC: (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1) R<sub>f</sub> = 0.3. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>. ppm): δ 7.75 (s, 1H), 7.73 (s, 1H), 7.53 (m, 4H), 7.46 (m, 4H), 7.42 (d, 2H), 7.37 (d, 2H), 6.58 (d, 4H), 3.28 (m, 8H), 1.59 (m, 8H), 1.33 (m, 24H), 0.92 (t, 12H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>. ppm): δ 148.7, 148.2, 136.0, 135.4, 133.4, 133.1, 131.8, 131.7, 131.6, 131.2, 127.9, 124.9, 124.8, 123.9, 123.8, 123.3, 122.4, 121.7, 111.3, 108.4, 107.6, 99.7, 95.8, 93.5, 91.9, 90.6, 89.1, 87.2, 85.6, 51.1, 31.8, 27.3, 26.9, 22.8, 14.2. HRMS (MALDI) m/z, calcd for [M+H]<sup>+</sup>: 1001.3979, found 1001.3976. Elemental analysis calcd for C<sub>62</sub>H<sub>70</sub>Br<sub>2</sub>N<sub>2</sub>: C, 74.24, H, 7.03, N 2.79 found C, 74.33, H, 7.04, N 2.77.

**02200:** **8** (335 mg, 0.42 mmol) and **9** (300 mg, 0.63 mmol) are dissolved in Et<sub>3</sub>N/THF 1/1 vol/vol (30 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30 mg, 10%) and CuI (12 mg, 4%) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (1.7g, 51%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1) R<sub>f</sub> = 0.25. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.65 (s + d, 3H), 7.60 (s, 1H), 7.38 (m, 4H), 7.29 (m, 4H), 6.47 (m, 4H), 3.18 (t, 8H, <sup>3</sup>J = 7.8 Hz), 1.49 (t, 8H), 1.23 (m, 14H), 0.82 (t, 12H, <sup>3</sup>J = 6.5 Hz). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>. ppm): δ 147.5, 147.1, 135.3, 135.2, 135.0, 134.3, 132.3, 132.0, 130.6, 130.1, 127.4, 125.9, 124.6, 124.3, 123.0, 122.6, 122.1, 119.7, 110.1, 110.0, 107.2, 106.3, 99.1, 96.2, 92.9, 92.8, 91.8, 87.2, 86.2, 84.5, 50.0, 30.6, 26.1, 25.8, 21.1, 19.0. HRMS calcd for [C<sub>62</sub>H<sub>69</sub>Br<sub>4</sub>N<sub>2</sub> + H]<sup>+</sup> at 1157.2189 found 1157.2136. Elemental analysis calcd for C<sub>62</sub>H<sub>69</sub>Br<sub>4</sub>N<sub>2</sub>: C, 64.15, H, 5.90, N, 2.41 found C, 63.92, H, 5.85, N, 2.25.

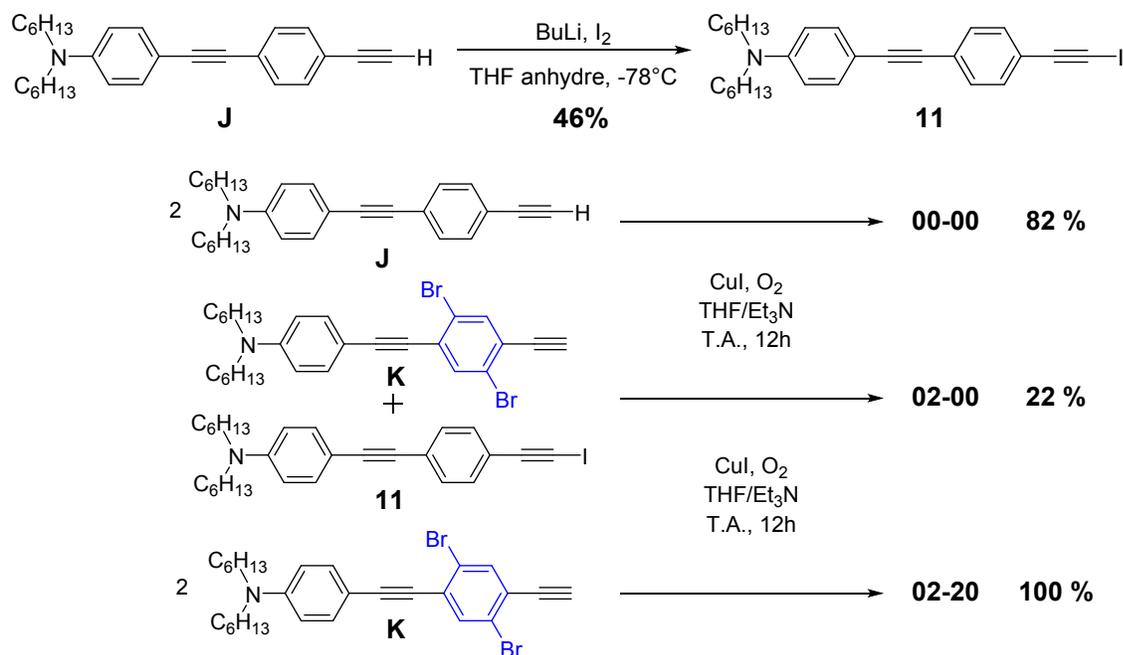
### Tetramer series

Similar building blocks and Sonogashira reactions could be used for the convergent synthesis of tetramers **0000**, **0200** and **0220**, according to the general strategy illustrated in scheme S5.



Scheme S5. General strategy towards the synthesis of **0000**, **0200** and **0220**

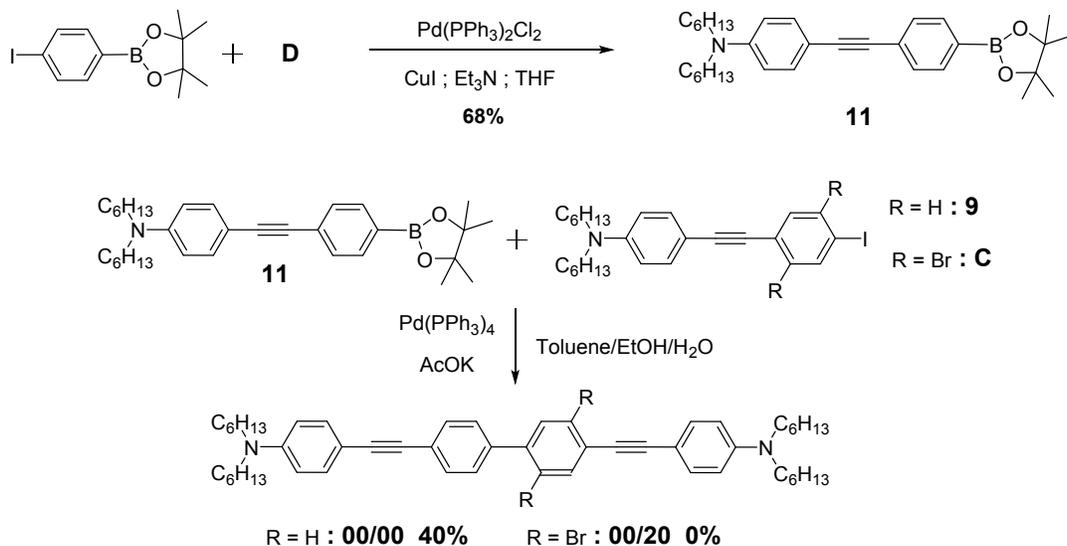
The synthesis of centrosymmetric tetrameric compounds **00-00** and **02-20** with a central diyne bridge could be achieved by simple Glaser coupling of building blocks. For the noncentro-symmetric **02-00**, Cadiot-Chodkiewicz coupling between the iodinated substituted acetylene and building block afforded exclusively the target compound **02-00**, although with low 22% yield (Scheme S6).



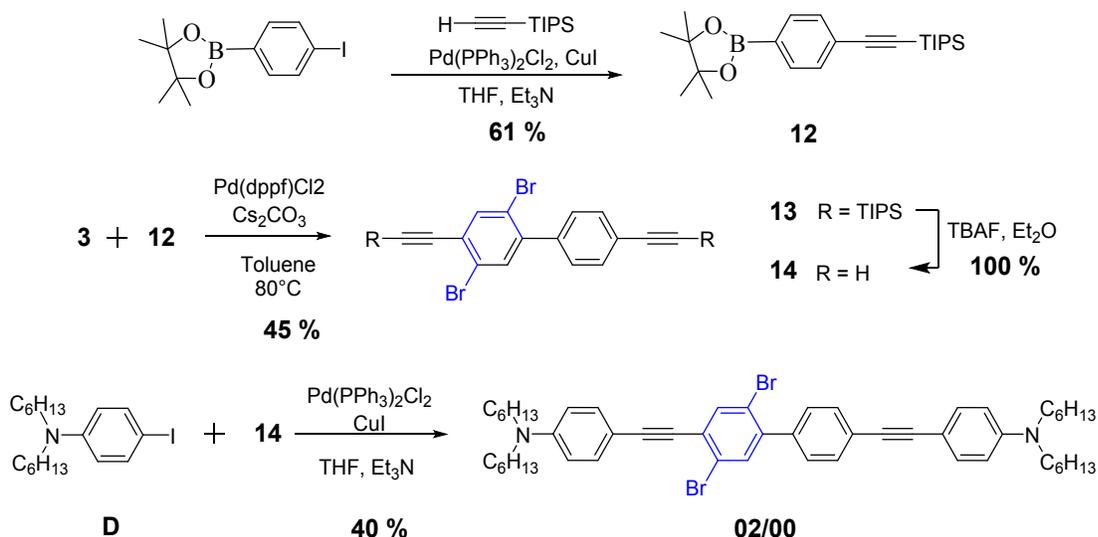
Scheme S6. Final steps in the synthesis of **00-00**, **02-00**, **02-20**

For the tetrameric compounds with a biphenyl spacer, **00/00** could be readily obtained using classical Suzuki-Miyaura coupling conditions between building block **9** and the boronic ester **11**. The latter was itself obtained by Sonogashira coupling between **4** and the commercially available 4-iodophenylboronic pinacolic ester (Scheme S7). This strategy was however inefficient in synthesizing the two other target **02/00** and **02/20** and had to be revised. For **02/00** the Suzuki coupling was carried out between the TIPS protected acetylene derivative of the iodoaryl and phenylboronic ester **12** and **3**, yielding the *bis*-TIPS protected target biphenyl intermediate **13** with a modest 45% yield. After TIPS deprotection, double

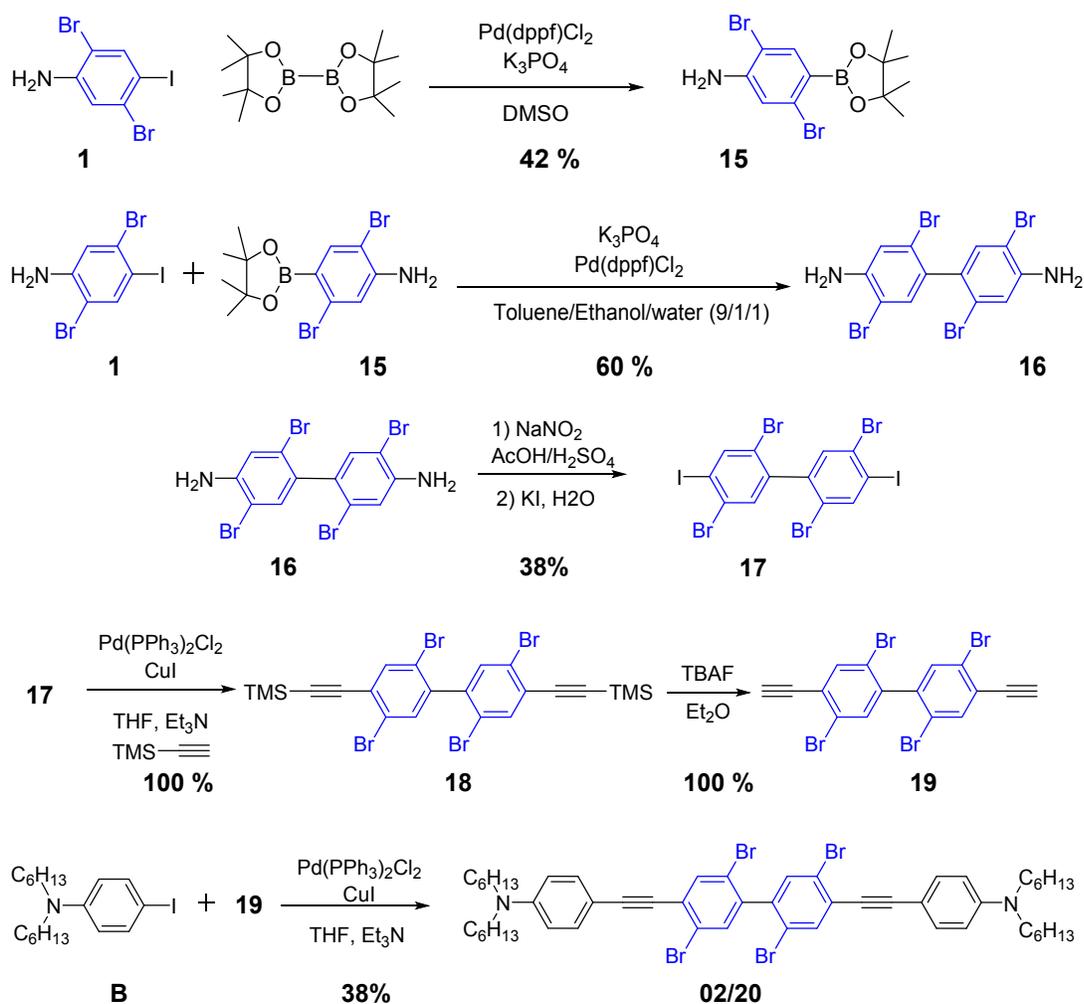
Sonogashira coupling with afforded the target **02/00** in good yields (Scheme S8). Again, use of a similar procedure did not allow to synthesize compound **02/20**, presumably because of the steric hindrance in the vicinity of the reaction center, which strongly decrease the reactivity of the intermediates. After multiple trials and errors and optimization, a new synthetic protocol involving the same 2,5-dibromo-4-iodoaniline as previously mentioned in the desymetrization step. The latter was involved in a Suzuki coupling with the corresponding boronic ester **15**, which was itself obtained by palladium catalyzed cross coupling of the same intermediate **1** with bis(pinacolato)diboron. After, iodation of amine and succession of Sonogashira cross coupling the target compound **02/20** was isolated in moderate overall yield (scheme S9).



Scheme S7. Synthesis of **00/00**



Scheme S8. Synthesis of **02/20**



Scheme S9. Synthesis of **02/20**

**11: 4** (511 mg, 1.79 mmol) and *iodo-4-pinacolborane benzene* (394 mg, 1.19 mmol) are dissolved in 1:1. vol/vol THF/Et<sub>3</sub>N (30 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (17 mg, 2%) and CuI (9 mg, 4%) are added. The solution is stirred overnight at room temperature. Solvents are removed under reduced pressure and dissolve in AcOEt. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1) to afford the desired compound as yellow oil (355mg, 61%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1) R<sub>f</sub> = 0.7. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.75 (d, 2H), 7.47 (d, 2H), 7.36 (d, 2H), 6.56 (d, 2H), 3.26 (t, 4H), 1.57 (m, 4H), 1.34 (m, 22H), 0.90 (t, 6H).

**00/00** : **9** (90 mg, 0.19 mmol) and **11** (135 mg, 0.28 mmol) are dissolved in 9:1:1 vol/vol/vol Toluene/EtOH/saturated K<sub>2</sub>CO<sub>3</sub> (6.5 mL). The solution is extensively degassed by argon bubbling for 20

min. Pd(PPh<sub>3</sub>)<sub>4</sub> (7.1 mg, 3%) is added. The reaction mixture was stirred overnight at 85°C during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 85/15. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (1.7g, 51%). TLC: (PE / CH<sub>2</sub>Cl<sub>2</sub>: 85/15) R<sub>f</sub> = 0.4. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.54 (s, 8H), 7.35 (d, 4H, <sup>3</sup>J= 8.0 Hz), 6.55 (d, 4H, <sup>3</sup>J= 8.0 Hz), 3.26 (t, 8H, <sup>3</sup>J= 7.6 Hz), 1.56 (m, 8H), 1.30 (m, 24H), 0.88 (t, 12H, <sup>3</sup>J= 6.4 Hz). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 148.0, 139.2, 132.9, 131.7, 126.7, 123.5, 111.2, 108.7, 91.9, 87.1, 51.0, 31.7, 27.2, 26.8, 22.7, 14.1. HRMS calcd for [C<sub>52</sub>H<sub>68</sub>N<sub>2</sub> + H]<sup>+</sup> at 721.5455 found 721.5447.

**12:** To solution of *iodo-4pinacolborane benzene* (1g, 3.03 mmol) in 1:1. vol/vol dry THF/Et<sub>3</sub>N (50 mL), extensively degassed by argon bubbling, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (73 mg, 3 mol%) CuI (35 mg, 1 mol%) and *triisopropylsilylacetylene* (1.00 mL, 4.55 mmol) are added. The tube is sealed and the mixture is stirred overnight at room temperature. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub> filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE) to afford the desired compound as yellow solid (800 mg, 69%). TLC: PE. R<sub>f</sub> = 0.3. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 7.72 (d, 2H), 7.44 (d, 2H), 1.32 (s, 12H), 1.11 (s, 21H). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 134.5, 131.2, 126.2, 107.2, 92.1, 83.9, 24.9, 18.7, 11.4.

**13:** **12** (455 mg, 1.20 mmol) and **3** (500 g, 0.92 mmol) are dissolved in toluene (30 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(dppf)Cl<sub>2</sub> (100 mg, 0.12 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (600 mg, 1.84 mmol) are added. The reaction mixture is stirred overnight at 80°C. Solvents are removed under reduced pressure and dissolve in AcOEt. The mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (Pentane) to afford the desired compound as yellow oil (280 mg, 45%). TLC: (Pentane) R<sub>f</sub> = 0.85. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 1H), 7.51 (d, 2H), 7.49 (s, 1H), 7.29 (d, 2H), 1.21 (s, 42H). <sup>13</sup>H NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 143.0, 139.1, 137.6, 134.2, 131.8, 129.1, 126.3, 124.6, 123.6, 120.5, 106.6, 103.1, 98.5, 92.0, 18.5, 11.2. HRMS calcd for [C<sub>34</sub>H<sub>48</sub>Br<sub>2</sub>Si<sub>2</sub> + Na]<sup>+</sup> at 693.1554 found 693.1566. Elemental analysis calcd for C<sub>34</sub>H<sub>48</sub>Br<sub>2</sub>Si<sub>2</sub>: C, 60.70, H, 7.19 found C, 61.2, H, 7.20.

**14:** A molar solution of *TBAF* in THF (0.90 mL, 0.90 mmol) is added to a solution of **13** (200 mg, 0.30 mmol) in Et<sub>2</sub>O (20mL). The mixture is stirred for 10 min at room temperature and the solution is filtered through a short pad of silica gel and eluted with Et<sub>2</sub>O. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub> filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil (106 mg, 100%). TLC: Pentane. R<sub>f</sub> = 0.4. Used directly without any characterization: the product seems very unstable.

**02/00:** **14** (106 mg, 0.30 mmol) and **2** (345 mg, 0.89 mmol) are dissolved in Et<sub>3</sub>N (15 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (100 mg) is added. The reaction mixture

is stirred overnight at 85°C during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (185 mg, 71%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 85/15) R<sub>f</sub> = 0.45. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.78 (s, 1H), 7.53 (s+d, 3H), 7.38 (m, 6H), 6.57 (d, 4H, <sup>3</sup>J = 8.8 Hz), 3.27 (t, 8H, <sup>3</sup>J = 5.8 Hz), 1.57 (m, 8H), 1.325 (m, 24H), 0.90 (t, 12H, <sup>3</sup>J = 6.5 Hz). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 148.5, 148.1, 141.9, 138.2, 136.4, 134.2, 133.3, 133.0, 129.2, 127.1, 124.3, 123.9, 120.6, 111.2(2), 108.5, 107.7, 97.7, 92.1, 86.9, 85.5, 50.0, 30.6, 26.1, 25.8, 21.1, 19.0. HRMS calcd for [C<sub>52</sub>H<sub>66</sub>Br<sub>2</sub>N<sub>2</sub> + H]<sup>+</sup> at 877.3666 found 877.3623. Elemental analysis calcd for C<sub>52</sub>H<sub>66</sub>Br<sub>2</sub>N<sub>2</sub>: C, 71.06, H, 7.57, N, 3.19 found C, 71.08, H, 7.47, N, 3.02.

**15: 1** (2 g, 5.34 mmol) and *bispinacol-borane* (1.39 g, 5.87 mmol) are dissolved in DMSO (18 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(dppf) (90 mg, 0.11 mmol) and AcOK (1.47 g, 15 mmol) were added. The reaction mixture is stirred overnight at 90°C. Solvents are removed under reduced pressure and dissolve in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/AcOEt/Et<sub>3</sub>N: 85/10/5) to afford the desired compound as yellow oil (1.13g, 56%). TLC: (PE/AcOEt/Et<sub>3</sub>N: 85/10/5) R<sub>f</sub> = 0.3. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.75 (s, 1H), 6.96 (s, 1H), 4.33 (s, 2H), 1.38 (s, 12H). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 147.1, 140.8, 128.1, 119.1, 107.4, 84.0, 25.1, 24.8. HRMS calcd for [C<sub>12</sub>H<sub>16</sub>BBr<sub>2</sub>NO<sub>2</sub> + H]<sup>+</sup> at 375.9714 found 375.9724. Elemental analysis calcd for C<sub>12</sub>H<sub>16</sub>BBr<sub>2</sub>NO<sub>2</sub>: C, 38.24, H, 4.28, N, 3.72 found C, 38.68, H, 4.38, N, 3.68.

**16: 1** (2.55 g, 6.76 mmol) and **15** (2.55 g, 6.76 mmol) are dissolved in DMSO (35 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(dppf) (247 mg, 0.34mmol) and K<sub>3</sub>PO<sub>4</sub> (4.3 g, 20.3mmol) are added. The reaction mixture is stirred overnight at 110°C. Solvents are removed under reduced pressure and dissolve in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/AcOEt/Et<sub>3</sub>N: 75/20/5, solid deposition) to afford the desired compound as yellow oil (2.06 g, 61%). TLC: (PE/AcOEt/Et<sub>3</sub>N: 75/20/5) R<sub>f</sub> = 0.5. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.19 (s, 2H), 6.95 (s, 2H), 4.12 (s, 4H). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 147.3, 135.3, 131.2, 124.4, 118.6, 107.1.

**17:** To solution of **16** (100 mg, 0.20 mmol) in acetic acid (5 mL) concentrated sulfuric acid (1 mL) is slowly added. The vial is putted in ice bath. A solution of NaNO<sub>2</sub> (30 mg, 0.40 mmol) in water (1 mL) is added drop by drop. The color of solution turns to orangish. After 1h of stirring at 0°C, a solution of KI (73 mg, 0.44 mmol) in water (1 mL) is slowly added at 0°C. The solution is stirred 1h at room temperature. Neutralization is achieved with saturated sodium carbonate solution. The solution is extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (50mL). The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE, solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as slightly yellow oil (74 mg, 51%). TLC: PE. R<sub>f</sub> =

0.90.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.12 (s, 2H), 7.43 (s, 2H).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  143.1, 141.3, 133.7, 128.8, 122.2, 102.1. HRMS calcd for  $[\text{C}_{12}\text{H}_4\text{Br}_4\text{I}_2 + \text{H}]^+$  at 717.5130 found 717.5153. Elemental analysis calcd for  $\text{C}_{12}\text{H}_4\text{Br}_4\text{I}_2$ : C, 19.97, H, 0.56 found C, 22.01, H, 0.60.

**18:** To solution of **17** (75 mg, 0.10 mmol) in 1:1. vol/vol dry THF/ $\text{Et}_3\text{N}$  (5 mL), extensively degassed by argon bubbling,  $\text{PdCl}_2(\text{PPh}_3)_2$  (1 mg)  $\text{CuI}$  (0.5mg) and trimethylsilylacetylene (0.03 mL, 0.2 mmol) are added. The tube is sealed and the mixture is stirred overnight at room temperature. The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$  filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE) to afford the desired compound as yellow solid (69 mg, 100%). TLC: PE.  $R_f$  = 0.90.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.74(s, 2H), 7.39 (s, 4H), 0.27 (s, 18H).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  141.6, 137.2, 134.2, 127.3, 124.5, 121.8, 102.5, 101.4, 0.00.

**19:** A molar solution of *TBAF* in THF (0.20 mL, 0.2 mmol) is added to a solution of **18** (60 mg, 0.09 mmol) in  $\text{Et}_2\text{O}$  (20mL). The mixture is stirred for 10 min at room temperature and then is filtered through a short pad of silica gel and eluted with  $\text{Et}_2\text{O}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$  filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil. Use directly without any characterization: the product seems very instable.

**02/20:** **19** (50 mg, 0.10 mmol) and **D** (120 mg, 0.3 mmol) are dissolved in  $\text{Et}_3\text{N}$  (15 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (50 mg) and  $\text{CuI}$  (2 mg) are added. The reaction mixture is stirred overnight at  $85^\circ\text{C}$  during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/ $\text{CH}_2\text{Cl}_2$ : 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (75 mg, 72%). TLC: (PE/ $\text{CH}_2\text{Cl}_2$ : 9/1)  $R_f$  = 0.5.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (s, 2H), 7.43 (s, 2H), 7.40 (d, 4H,  $^3J$ = 8.8 Hz), 6.57 (d, 4H,  $^3J$ = 8.8 Hz), 3.27 (t, 8H), 1.56 (t, 7H,  $^3J$ = 7.9 Hz), 1.31 (m, 24H), 0.89 (t, 12H,  $^3J$ = 6.5 Hz).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.6, 140.2, 135.8, 134.0, 133.3, 128.2, 123.6, 121.7, 111.2, 107.6, 98.2, 84.9, 51.0, 31.8, 27.2, 26.8, 22.7, 14.1. HRMS calcd for  $[\text{C}_{52}\text{H}_{64}\text{Br}_4\text{N}_2 + \text{H}]^+$  at 1033.1835 found 1033.1876. Elemental analysis calcd for  $\text{C}_{52}\text{H}_{64}\text{Br}_4\text{N}_2$ : C, 60.25, H, 6.22, N, 2.70 found C, 59.95, H, 6.13, N, 2.48.

**0000:** **X** (100 mg, 0.21 mmol) and **Y** (100 mg, 0.26 mmol) are dissolved in 1:5:2.5 vol/vol/vol THF/Toluene/ $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (2 mg) and  $\text{CuI}$  (1 mg) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/ $\text{CH}_2\text{Cl}_2$ : 10/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (52 mg, 33%). TLC: (PE/ $\text{CH}_2\text{Cl}_2$ : 10/1)  $R_f$  = 0.3.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (s, 8H), 7.35 (d, 4H,  $^3J$ = 8.4 Hz), 6.56 (d, 4H,  $^3J$ =

8.4 Hz), 3.26 (t, 8H,  $^3J = 7.5$  Hz), 1.57 (t, 8H), 1.32 (m, 24H), 0.90 (t, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.4, 133.2, 131.7, 131.4, 124.6, 122.1, 111.4, 108.6, 93.5, 91.1, 87.3, 51.2, 31.9, 27.5, 27.1, 22.9, 14.3. HRMS calcd for  $[\text{C}_{54}\text{H}_{68}\text{N}_2 + \text{H}]^+$  at 745.5455 found 745.5445. Elemental analysis calcd for  $\text{C}_{54}\text{H}_{68}\text{N}_2 + \text{H}_2\text{O}$ : C, 84.99, H, 9.25, N, 3.67 found C, 85.53, H, 9.09, N, 3.62.

**0200:** **X** (70 mg, 0.18 mmol) and **Y** (140 mg, 0.22 mmol) are dissolved in 1:5:2.5 vol/vol/vol THF/Toluene/ $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1 mg) and  $\text{CuI}$  (2 mg) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel ( $\text{PE}/\text{CH}_2\text{Cl}_2$ : 10/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (69 mg, 36 %). TLC: ( $\text{PE} / \text{CH}_2\text{Cl}_2$ : 10/1)  $R_f = 0.3$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (s, 1H), 7.67 (s, 1H), 7.47 (m, 4H), 7.37 (m, 4H), 6.56 (d, 4H), 3.26 (t, 8H,  $^3J = 7.5$  Hz) 1.56 (m, 8H), 1.34 (m, 24H), 0.90 (t, 12H,  $^3J = 5.0$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.7, 148.3, 136.0, 135.5, 133.5, 133.1, 131.8, 131.3, 127.8, 125.3, 123.8, 123.4, 121.2, 111.5, 111.4, 108.4, 107.7, 99.6, 96.3, 93.9, 88.7, 87.3, 85.6, 51.2, 31.9, 27.4, 26.9, 22.9, 14.3. Elemental analysis calcd for  $\text{C}_{54}\text{H}_{66}\text{Br}_2\text{N}_2$ : C, 71.83, H, 7.37, N, 3.10 found C, 71.69, H, 7.43, N, 3.08.

**0220:** **X** (71 mg, 0.11 mmol) and **Y** (60 mg, 0.11 mmol) are dissolved in 1:5:2.5 vol/vol/vol THF/Toluene/ $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1 mg) and  $\text{CuI}$  (0.5 mg) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel ( $\text{PE}/\text{CH}_2\text{Cl}_2$ : 10/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (29 mg, 25%). TLC: ( $\text{PE}/\text{CH}_2\text{Cl}_2$ : 10/1)  $R_f = 0.25$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (s, 2H), 7.71 (s, 2H), 7.38 (d, 4H  $^3J = 8.4$  Hz), 6.56 (d, 4H,  $^3J = 8.4$  Hz), 3.27 (t, 8H,  $^3J = 7.5$  Hz), 1.56 (m, 8H), 1.30 (m, 24H), 0.88 (t, 12H,  $^3J = 6.4$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.0, 136.6, 135.7, 133.6, 128.6, 124.6, 123.9, 123.5, 111.5, 107.7, 100.2, 93.5, 85.8, 51.3, 32.0, 27.5, 27.1, 23.0, 14.3.

**00-00:** **X** degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1 mg) and  $\text{CuI}$  (3 mg) are **Y** (64 mg, 0.17 mmol) is dissolved in 1:1 vol/vol THF/ $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel ( $\text{PE}/\text{CH}_2\text{Cl}_2$ : 10/2. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (48 mg, 72%). TLC: ( $\text{PE}/\text{CH}_2\text{Cl}_2$ : 10/2)  $R_f = 0.15$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (m, 8H), 7.36 (d, 4H,  $^3J = 8.6$  Hz), 6.56 (d, 4H,  $^3J = 8.6$  Hz), 3.26 (t, 8H,  $^3J = 7.6$  Hz),

1.58 (m, 8H), 1.32 (m, 24H), 0.89 (t, 12H,  $^3J = 6.6$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  149. Elemental analysis calcd for  $\text{C}_{56}\text{H}_{68}\text{N}_2 + \text{H}_2\text{O}$ : C, 85.45, H, 8.96, N, 3.56 found C, 85.64, H, 8.62, N, 3.78.

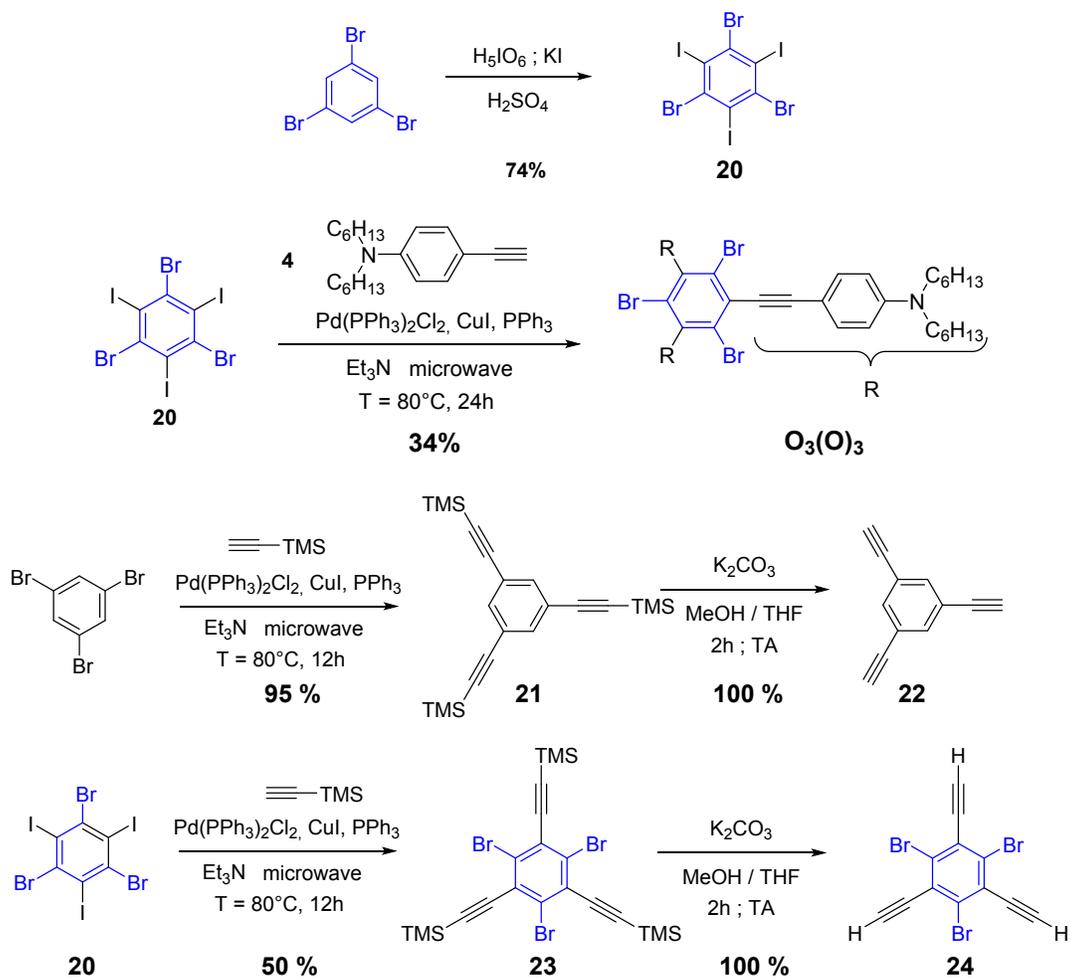
**02-00: X** (70 mg, 0.13 mmol) and **Y** (62 mg, 0.13 mmol) are dissolved in 1:1 vol/vol THF/ $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (2 mg) and  $\text{CuI}$  (0.5 mg) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/ $\text{CH}_2\text{Cl}_2$ : 10/2. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (25 mg, 23%). TLC: (PE/ $\text{CH}_2\text{Cl}_2$ : 10/2)  $R_f = 0.30$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (m, 2H), 7.41 (m, 8H,  $^3J = 8.3$  Hz), 6.56 (d, 4H,  $^3J = 8.3$  Hz), 3.27 (t, 8H,  $^3J = 8.5$  Hz), 1.55 (m, 8H), 1.30 (m, 24H), 0.89 (t, 12H,  $^3J = 6.4$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.9, 148.5, 137.3, 135.6, 133.7, 133.6, 133.3, 132.7, 131.4, 128.9, 126.1, 124.5, 123.9, 123.4, 120.1, 111.5, 108.4, 107.6, 94.7, 87.3, 85.8, 84.7, 80.5, 51.3, 31.9, 27.5, 27.1, 22.9, 14.3. HRMS calcd for  $[\text{C}_{56}\text{H}_{66}\text{Br}_2\text{N}_2 + \text{H}]^+$  at 925.3665 found 925.3661. Elemental analysis calcd for  $\text{C}_{56}\text{H}_{66}\text{Br}_2\text{N}_2 + \text{H}_2\text{O}$ : C, 71.18, H, 7.25, N, 2.96 found C, 70.59, H, 7.15, N, 2.96.

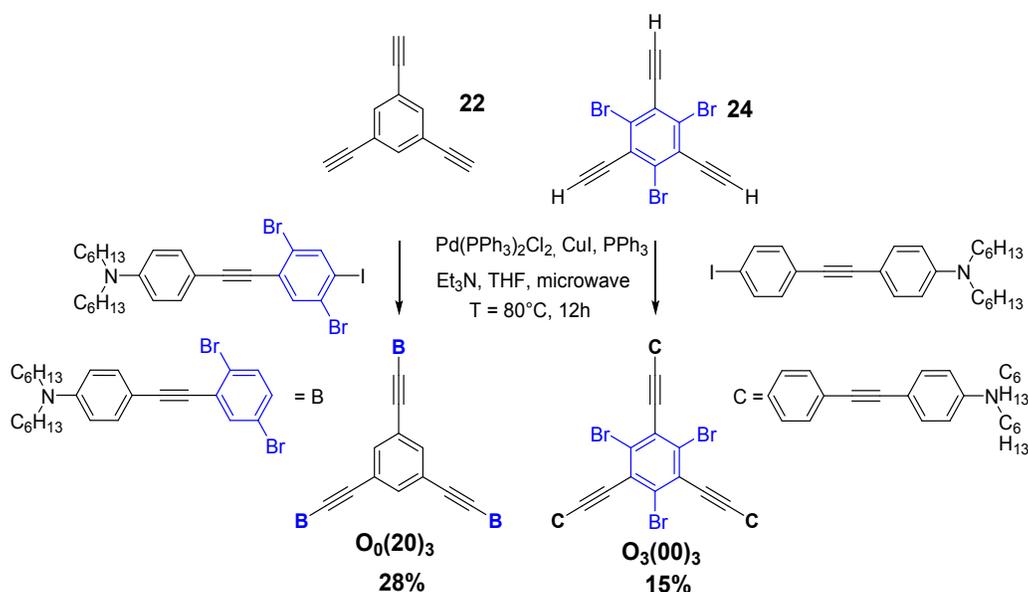
**02-20: X** (70 mg, 0.13 mmol) is dissolved in 1:1 vol/vol THF / $\text{Et}_3\text{N}$  (10 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1 mg) and  $\text{CuI}$  (1 mg) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil (70 mg, 100%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 (s, 2H), 7.67 (s, 2H), 7.37 (d, 4H,  $^3J = 8.6$  Hz), 6.55 (d, 4H,  $^3J = 8.6$  Hz), 3.27 (t, 8H,  $^3J = 7.6$  Hz), 1.57 (m, 8H), 1.31 (m, 24H), 0.88 (t, 12H,  $^3J = 6.6$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.9, 137.3, 135.5, 133.6, 129.2, 124.4, 123.4, 123.3, 111.4, 107.5, 100.9, 85.8, 81.4, 79.8, 51.2, 31.9, 27.4, 27.0, 22.9, 14.3. HRMS calcd for  $[\text{C}_{56}\text{H}_{64}\text{Br}_4\text{N}_2 + \text{H}]^+$  at 1081.1876 found 1081.1878. Elemental analysis calcd for  $\text{C}_{56}\text{H}_{64}\text{Br}_4\text{N}_2$ : C, 62.01, H, 5.95, N, 2.58 found C, 62.37, H, 5.99, N, 2.58.

## Octupole series

Synthesis of octupolar compounds **0(20)<sub>3</sub>**, **3(0)<sub>3</sub>** and **3(00)<sub>3</sub>** relied on the same general strategy, based on successive Sonogashira coupling from a tris(halogenated) central core (Scheme S10). For the synthesis of **0(20)<sub>3</sub>**, the commercially available 1,3,5-tribromobenzene was involved in Sonogashira coupling with triisopropylsilylacetylene, to afford the intermediate compound **21**. After deprotection of the acetylene groups, the resulting alkyne **22** was reacted with **C**, yielding the target **0(20)<sub>3</sub>**. Synthesis of **3(0)<sub>3</sub>** and **3(00)<sub>3</sub>** required preliminary synthesis of the 1,3,5-triiodo-2,4,6-tribromobenzene **20**, which was achieved upon treatment of 1,3,5-tribromobenzene with potassium iodide  $\text{KI}$  and periodic acid in concentrated sulfuric acid. Attempts to perform selective Sonogashira coupling on the iodide substituents using the usual mild conditions turned out unsuccessful. In contrast, the target intermediate **23** and product **3(0)<sub>3</sub>** could be

obtained in decent yield and excellent selectivity reaction upon reaction with trimethylsilyl acetylene or **4** in MW sealed tubes at 80°C. Removal of the TMS protecting group followed by Sonogashira coupling with **9**, afforded the target compounds **3(OO)<sub>3</sub>**.





Scheme S10. Synthesis of  $O_3(0)_3$ ,  $O_0(20)_3$  and  $O_3(00)_3$

**20:** Periodic acid (27.36g, 120mmol) is dissolved in concentrated sulfuric acid (410 mL) then gold to 0°C. Potassium iodine (59.7 g, 23.5 mmol) is added by portion in one hour then 1,3,5-tribromobenzene (12,59 g, 40 mmol) in 25 min. The solution is stirred during three days at room temperature. The solution is poured in an ice bath, filtered and extensively washed with water and cooled methanol. The excess of iodine is quenched by addition of sodium thiosulfate. The product is purified by recrystallization in 1:1 vol/vol pyridine/ethanol to afford the desired compound as slightly yellow solid (20.5 g, 74%). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 176.3, 145.9. T<sub>f</sub>: 267°C.

**21:** 1,3,5-tribromobenzene (500 mg, 1.6 mmol) is dissolved in Et<sub>3</sub>N (20 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (50 mg, 2%) and CuI (27 mg, 4%) are added. Then TMSA (0.8 mL, 5.8 mmol) is introduced through the septum via a syringe. The solution is stirred and heat in microwave oven at 80°C during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting solution is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, solvents are removed under reduced pressure. The product is purified on silica gel (PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow solid (mg, 95%). TLC: PE/CH<sub>2</sub>Cl<sub>2</sub>: 9/1. R<sub>f</sub> = 0.4. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 7.47(s, 1H), 0.21 (s, 27H). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 129.3, 127.7, 107.0, 102.1, 0.0. HRMS calcd for [C<sub>21</sub>H<sub>30</sub>Si<sub>3</sub> + H]<sup>+</sup> at 367.1728 found 367.1726. Elemental analysis calcd for C<sub>21</sub>H<sub>30</sub>Si<sub>3</sub>: C, 68.78, H, 8.25, found C, 68.74, H, 8.24.

**22:** **21** (150 mg, 1.09 mmol) is dissolved in 1:1 vol/vol THF/MeOH (20 mL) and K<sub>2</sub>CO<sub>3</sub> (169 mg, 3.28 mmol) is added in one portion. The mixture is stirred during two hours. The resulting solution is put into distilled water and extracted three times with AcOEt. The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure to afford the desired compound as slightly

yellow oil (62 mg, 37%).  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.55 (s, 3H), 3.09 (s, 3H). This sensitive product is involved in next step without additional characterization

**23: 20** (0.3 mg, 0.44 mmol) is dissolved in  $\text{Et}_3\text{N}$  (15 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (6 mg, 2%) and  $\text{CuI}$  (3 mg, 4%) are added. Then *TMSA* (0.18 mL, 1.32 mmol) is introduced through the septum via a syringe. The solution is stirred and heated in a microwave oven at  $80^\circ\text{C}$  during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting solution is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered, solvents are removed under reduced pressure, the product is purified on silica gel (PE. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow solid (100 mg, 42%). TLC: PE  $R_f$  = 0.25.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.27 (s, 27H).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  129.2, 127.6, 106.9, 101.9, 0.0. HRMS calcd for  $[\text{C}_{21}\text{H}_{27}\text{Br}_3\text{Si}_3 + \text{Na}]^+$  at 622.8863 found 622.8882. Elemental analysis calcd for  $\text{C}_{21}\text{H}_{27}\text{Br}_3\text{Si}_3$ : C, 41.80, H, 4.51, found C, 41.79, H, 4.52.

**24: 23** (50 mg, 0.08mmol) is dissolved in 1:1 vol/vol THF/MeOH (10 mL) and  $\text{K}_2\text{CO}_3$  (300 mg, 0.75 mmol) is added in one portion. The mixture is stirred during two hours. The resulting solution is poured into distilled water and extracted three times with  $\text{AcOEt}$ . The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE /  $\text{CH}_2\text{Cl}_2$ : 9/1) to afford the desired compound as slightly yellow oil (32 mg, 100%). TLC: PE /  $\text{CH}_2\text{Cl}_2$ : 9/1.  $R_f$  = 0.20. Used directly without another characterization.

**$\text{O}_3(\mathbf{0})_3$ : 4** (371 mg, 1.3 mmol) and **20** (300 mg, 0.43 mmol) are dissolved in  $\text{Et}_3\text{N}$  (8 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (14 mg, 4.5%),  $\text{PPh}_3$  (7 mg, 6%) and  $\text{CuI}$  (8 mg, 5%) are added. The reaction mixture is stirred and heated in microwave at  $80^\circ\text{C}$  during 24 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/ $\text{CH}_2\text{Cl}_2$ : 9/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (1.7g, 51%). TLC: (PE/ $\text{CH}_2\text{Cl}_2$ : 9/1)  $R_f$  = 0.3.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (d, 6H,  $^3J$ = 9.1 Hz), 6.58 (d, 6H,  $^3J$ = 9.1 Hz), 3.28 (t, 12H), 1.58 (t, 12H,  $^3J$ = 7.5 Hz), 1.31 (m, 36H), 0.90 (t, 18H,  $^3J$ = 6.8 Hz).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.8, 133.4, 128.3, 125.8, 111.4, 108.0, 101.5, 87.1, 51.2, 31.9, 27.4, 27.0, 22.9, 14.3. HRMS calcd for  $[\text{C}_{66}\text{H}_{90}\text{Br}_3\text{N}_3 + \text{H}]^+$  at 1162.4758 found 1162.4705. Elemental analysis calcd for  $\text{C}_{66}\text{H}_{90}\text{Br}_3\text{N}_3$ : C, 68.04, H, 7.79, N, 3.61 found C, 67.84, H, 7.72, N, 3.52.

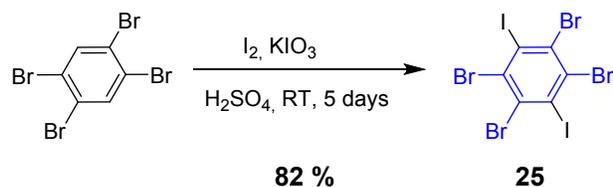
**$\text{O}_6(\mathbf{20})_3$ : C** (150 mg, 1.00 mmol) and **22** (2.58 g, 4.00 mmol) are dissolved in  $\text{Et}_3\text{N}$  (40 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (42 mg, 6%) and  $\text{CuI}$  (6 mg, 3%) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the

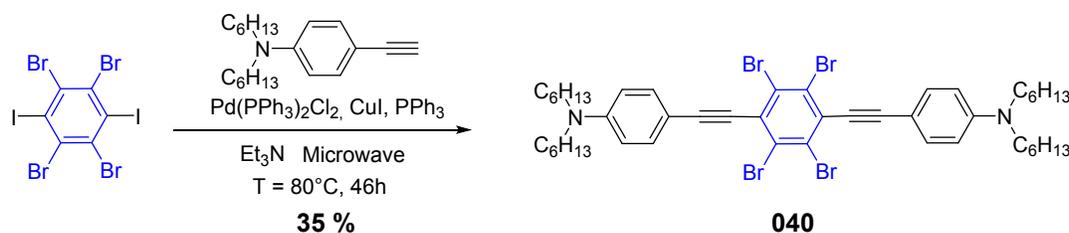
product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 8/2. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (250 mg, 14%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 8/2) R<sub>f</sub> = 0.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.70 (s, 3H), 7.67 (s, 3H), 7.33 (d, 6H, <sup>3</sup>J= 8.9 Hz), 6.51 (d, 6H, <sup>3</sup>J= 8.9 Hz), 3.22 (t, 12H, <sup>3</sup>J= 7.9 Hz), 1.51 (t, 12H), 1.25 (m, 36H), 0.84 (t, 18H, <sup>3</sup>J= 6.5 Hz). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 148.8, 136.3, 135.6, 134.9, 133.5, 128.4, 124.5, 124.0, 123.9, 123.8, 123.4, 111.4, 107.6, 100.0, 95.2, 85.6, 51.2, 31.9, 27.4, 27.0, 22.9, 14.2. Elemental analysis calcd for C<sub>66</sub>H<sub>90</sub>Br<sub>3</sub>N<sub>3</sub>: C, 68.04, H, 7.79, N, 3.61 found C, 67.84, H, 7.72, N, 3.51.

**O<sub>3</sub>(00)<sub>3</sub>: 9** (150 mg, 0.10 mmol) and **24** (33 mg, 0.03 mmol) are dissolved in Et<sub>3</sub>N/THF 8/5 vol/vol (13 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3.6 mg, 8%) and CuI (2 mg, 4%) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 8/2. solid deposition of the product pre-adsorbed on silica gel). to afford the desired compound as yellow brown oil (1.7g, 51%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 8/2) R<sub>f</sub> = 0.20. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.51 (d, 6H, <sup>3</sup>J= 8.4Hz), 7.46 (d, 6H, <sup>3</sup>J= 8.4 Hz), 7.42 (d, 6H, <sup>3</sup>J= 9.0 Hz), 6.55 (d, 6H, <sup>3</sup>J= 9.0Hz), 3.24 (t, 12H, <sup>3</sup>J= 7.5 Hz), 1.54 (m, 12H), 1.30 (m, 36H), 0.86 (t, 18H, <sup>3</sup>J= 6.5 Hz). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 148.4, 133.2, 131.9, 131.1, 128.2, 127.9, 125.7, 121.0, 111.4, 108.4, 99.8, 94.1, 89.3, 87.3, 51.2, 31.9, 27.4, 27.0, 22.9, 14.3. HRMS calcd for [C<sub>90</sub>H<sub>102</sub>Br<sub>3</sub>N<sub>3</sub> + 2H]<sup>+</sup> at 731.7856 found 731.7885. Elemental analysis calcd for C<sub>90</sub>H<sub>102</sub>Br<sub>3</sub>N<sub>3</sub>: C, 73.76, H, 7.04, N, 2.87 found C, 74.01, H, 7.08, N, 2.86.

### Tetrabrominated isomers

Similar reactivity issues were faced in the synthesis of compound **040**. The perhalogenated 1,4-diiodo-2,3,5,6-tetrabromobenzene core **25** was first synthesized by iodination of the commercially available 1,2,3,5-tetrabromobenzene, in similar conditions as mentioned above for **20**, and selective Sonogashira coupling on the iodinated position also required the reaction between **25** and **D** to be performed at 80°C upon microwave activation (Scheme S11).<sup>[4]</sup>



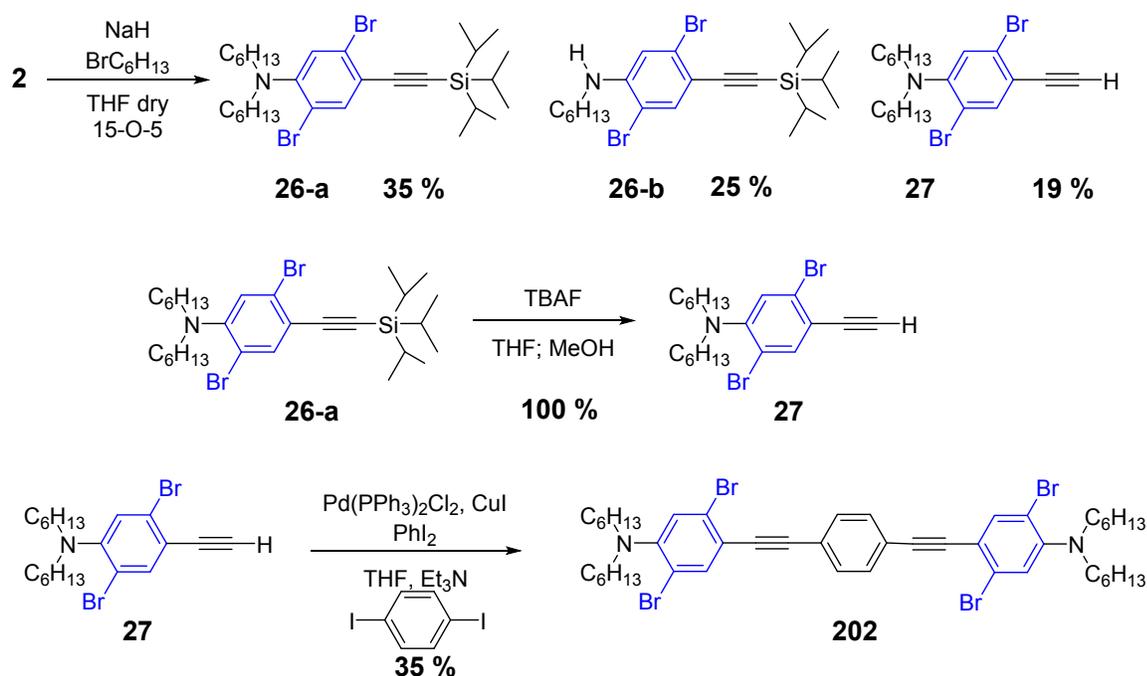


Scheme S11. synthesis of **040**

**25:** 1,2,4,5-tetrabromobenzene (6 g, 15.2 mmol) is dissolved in concentrated sulfuric acid (35mL). In a RB flask iodine (21.3 g, 84 mmol) and potassium iodate (2.55 g, 12 mmol) are mixed in sulfuric acid (30mL). The two solution are combined and stirred during five days. The reaction is stopped and neutralized by adding 200mL of caustic soda (5M). The neutralization is completed with saturated sodium carbonate solution. The excess of iodine is quenched by addition of sodium thiosulfate. The disappearance of iodine is controlled by potassium iodide starch paper. A solid is obtained, filtered and washed several times with water. The solid is dried in oven (100°C). The product is purified by recrystallization in toluene to afford the desired compound as white solid (8.08 g, 82%).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.9, 150.9. Tf: 330°C.

**040:** **4** (354 mg, 1.24 mmol) and **25** (400 mg, 0.62 mmol) are dissolved in  $\text{Et}_3\text{N}$  (8 mL). The solution is extensively degassed by argon bubbling for 20 min.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (20 mg, 4.5%),  $\text{PPh}_3$  (10mg, 6%) and  $\text{CuI}$  (8 mg, 5%) are added. The reaction mixture is stirred and heated in microwave at 80°C during 46 hours. Solvents are removed under reduced pressure and the crude product is dissolved in  $\text{AcOEt}$ . The resulting mixture is filtered through a short pad of silica gel and eluted with  $\text{AcOEt}$ . The resulting solution is washed one time with saturated  $\text{NH}_4\text{Cl}$  solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel ( $\text{PE}/\text{CH}_2\text{Cl}_2/\text{Toluene}$ : 8/1/1. solid deposition of the product pre-adsorbed on silica gel) to afford the desired compound as yellow brown oil (184 mg, 31%). TLC: ( $\text{PE}/\text{CH}_2\text{Cl}_2/\text{Toluene}$ : 8/1/1)  $R_f$  = 0.6.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 (d, 4H,  $^3J$ = 9.0 Hz), 6.56 (d, 4H,  $^3J$ = 9.0 Hz), 3.27 (t, 8H,  $^3J$ = 7.8 Hz), 1.56 (t, 8H), 1.30 (m, 24H), 0.89 (t, 12H,  $^3J$ = 6.9 Hz).  $^{13}\text{H}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.8, 133.4, 128.6, 126.7, 111.2, 111.1, 107.4, 103.1, 88.7, 51.0, 31.7, 27.2, 26.8, 14.1. HRMS calcd for  $[\text{C}_{46}\text{H}_{60}\text{Br}_4\text{N}_2 + \text{H}]^+$  at 961.1 found 961.1. Elemental analysis calcd for  $\text{C}_{46}\text{H}_{60}\text{Br}_4\text{N}_2 + \text{C}_7\text{H}_{16}$ : C, 60.01, H, 7.22, N, 2.73 found C, 60.53, H, 6.93, N, 2.67.

Synthesis of its position isomer **202** required the key intermediate **2**. The latter was obtained from the already mentioned 2,5-dibromo-4-iodoaniline intermediate. Attempts to perform bisalkylation of the aniline group were poised by the occurrence of unexpected side reactions, including nucleophilic substitution of the para iodine substituents by the hydride used as a base in the reaction. Insertion of a protected alkyne group by Sonogashira coupling between **1** and triisopropylsilyl acetylene was thus performed first to obtain **2** (as already depicted in scheme S2), followed by bisalkylation of the aniline moiety with hexyl chains and *in situ* removal of the silylprotecting group to afford intermediate **27** along with side products **26a** (which was subsequently deprotected by TBAF treatment to quantitatively generate **27**) and **26b**. **27** was then readily coupled with the commercially available 1,4-diiodobenzene.



Scheme S12. Synthesis of **202**

**26-a**, **26-b**, **27**: **2** (1.1 g, 2.55 mmol), 1-bromohexane (0.90 mL, 6.38 mmol), and of 15-crown-5 (0.25 mL, 1.41 mmol) are dissolved in dry THF (25 mL). Oil-free NaH, washed by petroleum ether, (127 mg, 5.10 mmol) is added gradually over several minutes as a solid. The purple reaction mixture is refluxed for 20 hours. The reaction is cooled to room temperature and quenched slowly with water. The resulting solution is extracted three times with  $\text{CH}_2\text{Cl}_2$ . The resulting organic phase is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$ , filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE /  $\text{CH}_2\text{Cl}_2$ : 9/1) to afford the desired compounds as colorless oil **26-a**, (535 mg, 35%) **26-b**(330 mg, 25%) **27**(215 mg, 19%).

**27**: A molar solution of *TBAF* in THF (1.25 mL, 1.25 mmol) is added to a solution of **26-a** (500 mg, 0.83 mmol) in  $\text{Et}_2\text{O}$  (20mL). The mixture is stirred for 10 min at room temperature and the solution is filtered through a short pad of silica gel and eluted with  $\text{Et}_2\text{O}$ . The resulting solution is washed three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with  $\text{Na}_2\text{SO}_4$  filtered and solvents are removed under reduced pressure to afford the desired compound as yellow brown oil (370 mg, 100%).

**26-a**: TLC: PE /  $\text{CH}_2\text{Cl}_2$ : 9/1.  $R_f$  = 0.45.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.64 (s, 1H), 7.17 (s, 1H), 3.14 (t, 4H), 1.41 (t, 4H), 1.26 (m, 12H), 1.12 (s, 21H), 0.85 (t, 6H).  $^{13}\text{C}$  NMR (126.3MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  150.8, 138.1, 127.0, 124.6, 120.6, 118.9, 103.8, 95.7, 52.8, 31.6, 26.8.1, 26.7, 22.6, 18.7, 14.1, 11.3. HRMS calcd for  $[\text{C}_{29}\text{H}_{49}\text{Br}_2\text{NSi} + \text{H}]^+$  at 589.2074 found 598.2069. Elemental analysis calcd for  $\text{C}_{29}\text{H}_{49}\text{Br}_2\text{NSi}$ : C, 58.09, H, 8.24, N, 2.34 found C, 58.38, H, 8.15, N, 2.31.

**26-b**: TLC: PE /  $\text{CH}_2\text{Cl}_2$ : 9/1.  $R_f$  = 0.30.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.57 (s, 1H), 6.19 (s, 1H), 4.47 (t, 1H), 3.03 (t, 3H), 2.99 (t, 4H), 1.41 (t, 4H), 1.22 (m, 12H), 0.85 (t, 6H).

**27:** TLC: PE / CH<sub>2</sub>Cl<sub>2</sub>: 9/1. R<sub>f</sub> = 0.15. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, ppm): δ 7.66 (s, 1H), 7.16 (s, 1H), 3.30 (s, 1H), 3.03 (t, 3H), 2.99 (t, 4H), 1.41 (t, 4H), 1.22 (m, 12H), 0.85 (t, 6H).

**202: 27** (168 mg, 0.38 mmol) and *1,4-diiodobenzene* (60 mg, 0.19 mmol) are dissolved in Et<sub>3</sub>N/THF 1/1 vol/vol (10 mL). The solution is extensively degassed by argon bubbling for 20 min. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (11 mg, 4%) and CuI (5 mg, 3%) are added. The reaction mixture is stirred overnight at room temperature during 12 hours. Solvents are removed under reduced pressure and the crude product is dissolved in AcOEt. The resulting mixture is filtered through a short pad of silica gel and eluted with AcOEt. The resulting solution is washed one time with saturated NH<sub>4</sub>Cl solution, three times with water and pre-dried by washing with saturated sodium chloride solution. The solution is dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and solvents are removed under reduced pressure, the product is purified on silica gel (PE/CH<sub>2</sub>Cl<sub>2</sub>: 95/5. solid deposition of the product pre-adsorbed on silica gel). to afford the desired compound as yellow brown oil (120 mg, 34%). TLC: (PE/CH<sub>2</sub>Cl<sub>2</sub>: 95/5) R<sub>f</sub> = 0.15. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.71 (s, 2H), 7.50 (s, 4H), 7.22 (s, 2H), 3.05 (t, 8H, <sup>3</sup>J= 7.5 Hz), 1.44 (m, 8H), 1.23 (m, 24H), 0.85 (t, 12H, <sup>3</sup>J= 6.6 Hz). <sup>13</sup>C NMR (126.3MHz, CDCl<sub>3</sub>, ppm): δ 151.1, 137.6, 131.6, 126.9, 124.5, 123.0, 119.9, 118.8, 93.2, 89.2, 52.7, 31.6, 26.9, 26.7, 22.7, 14.1. HRMS calcd for [C<sub>46</sub>H<sub>60</sub>Br<sub>4</sub>N<sub>2</sub> + H]<sup>+</sup> at 957.1503 found 957.1500.

# S2-Spectroscopy

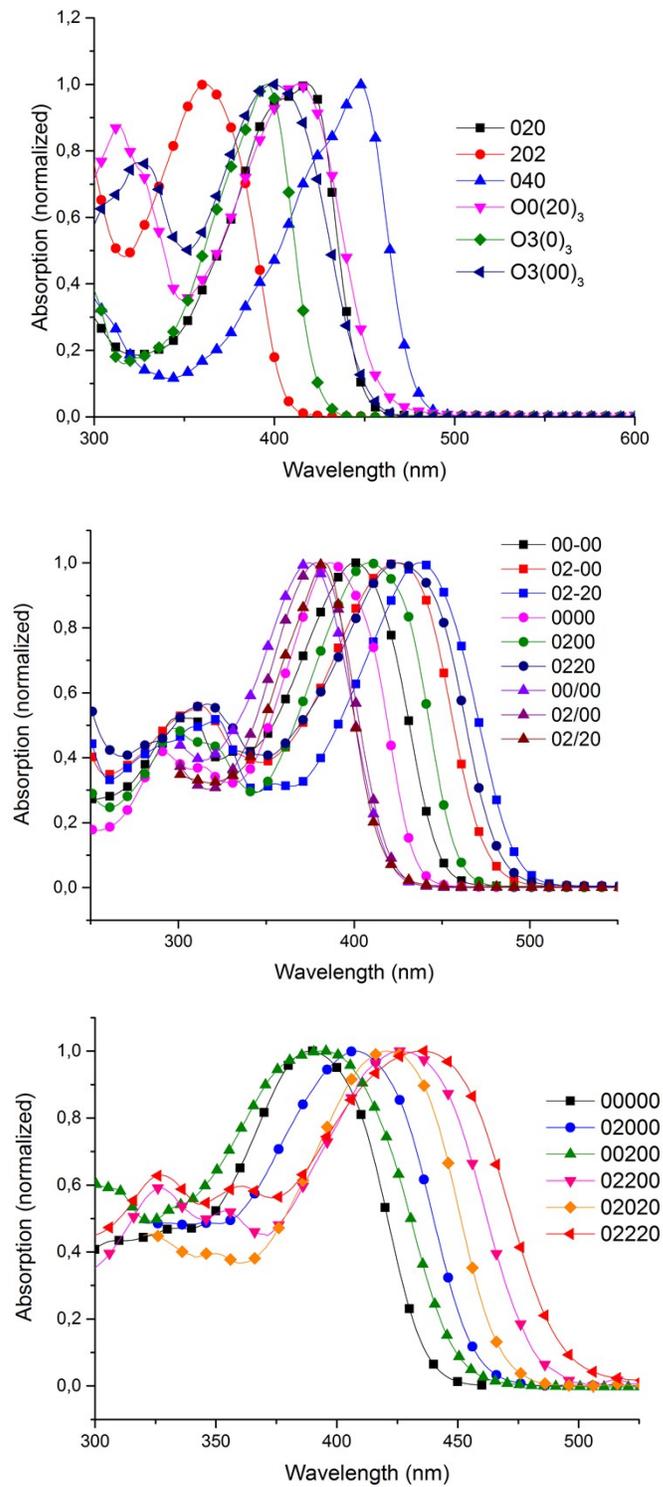


Figure S1- normalized absorptions of all studied compounds in  $CHCl_3$

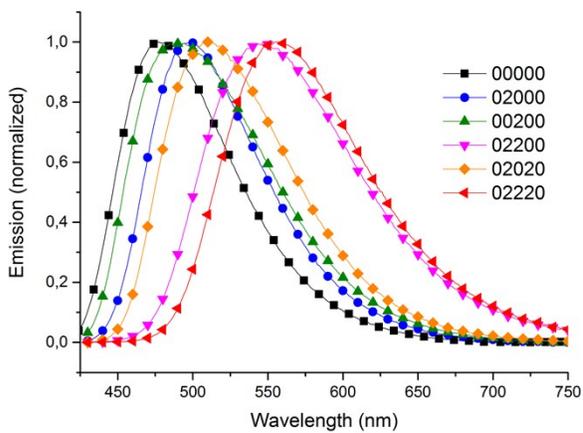
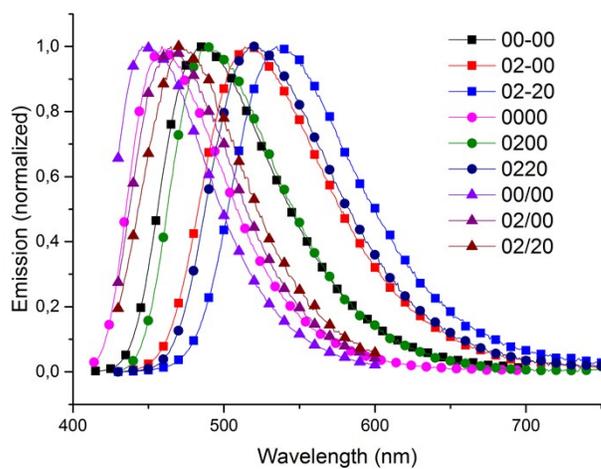
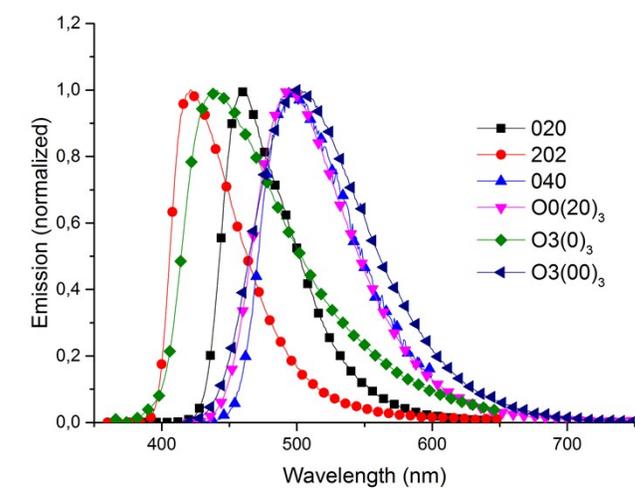


Figure S2- Normalized emissions of all studied compounds in CHCl<sub>3</sub>

Table S1- Spectroscopic data of 020, 040 and tetrameric series

	<b>020</b>	<b>040</b>	<b>0000</b>	<b>0200</b>	<b>0220</b>	<b>00-00</b>	<b>02-00</b>	<b>02-20</b>	<b>00/00</b>	<b>02/00</b>	<b>02/20</b>
$\lambda_{\text{abs}}^{\text{max}}$ (nm)	421	447	387	409	425	401	424	437	374	379	383
$\epsilon$ (L.cm <sup>-1</sup> .mol <sup>-1</sup> )	91500	78865	86066	88611	42064	56549	80950	77718	79796	64762	66163
$\lambda_{\text{em}}^{\text{max}}$ (nm)	458	492	459	489	522	484	518	535	449	465	470
$\phi_f$	0.25	0.09	0.8	0.39	0.31	0.79	0.27	0.29	0.9	0.39	0.16
$\phi_{\Delta}$	0.53	0.33	0	0.44	0.53	0	0.54	0.55	0	0.26	0.34
$\phi_f + \phi_{\Delta}$	0.78	0.42	0.8	0.83	0.84	0.79	0.81	0.84	0.9	0.65	0.5
Stokes shift (cm <sup>-1</sup> )	1919	2046	4053	4000	4372	4276	4280	4192	4466	4880	4833
$\lambda_{\text{TPA}}^{\text{max}}$ (nm)	730	780	< 710	760	810	750	800	840	< 720	< 720	< 730
$\sigma_{\text{TPA}}^{\text{max}}$ (GM)	689	376	1451	998	404	600	805	1221	>249	>997	>314
$\sigma_{\text{TPA}, 800}$ (GM)	75	182	313	667	400	373	805	939	33	142	70
$\sigma_{\text{TPA}, 800} * \phi_{\Delta}$	40	60	0	293	212	0	435	516	0	37	24
$\tau_F$ (ns)	0.26	<0.3	1.11	0.71	0.65	1.20	0.70	0.74	1.07	0.43	0.30
$kr$ (s <sup>-1</sup> )	9.6.10 <sup>8</sup>	-	7.2.10 <sup>8</sup>	5.5.10 <sup>8</sup>	4.8.10 <sup>8</sup>	6.6.10 <sup>8</sup>	3.9.10 <sup>8</sup>	3.9.10 <sup>8</sup>	8.4.10 <sup>8</sup>	9.1.10 <sup>8</sup>	5.3.10 <sup>8</sup>
$k_{\text{ISC}}$ (s <sup>-1</sup> )	2.0 10 <sup>9</sup>	-	≈0	6.2 10 <sup>8</sup>	8.1 10 <sup>8</sup>	≈0	7.7 10 <sup>8</sup>	7.4 10 <sup>8</sup>	≈0	-	-
$knr$ (s <sup>-1</sup> )	8.4 10 <sup>8</sup>	-	1.8.10 <sup>8</sup>	2.4 10 <sup>8</sup>	2.4 10 <sup>8</sup>	1.8.10 <sup>8</sup>	2.7 10 <sup>8</sup>	2.2.10 <sup>8</sup>	9.4.10 <sup>7</sup>	-	-

Table S2- Spectroscopic data of pentameric series and octupoles

	<b>202</b>	<b>00000</b>	<b>02000</b>	<b>00200</b>	<b>02200</b>	<b>02020</b>	<b>02220</b>	<b>O<sub>0</sub>(20)<sub>3</sub></b>	<b>O<sub>3</sub>(0)<sub>3</sub></b>	<b>O<sub>3</sub>(00)<sub>3</sub></b>
$\lambda_{\text{abs}}^{\text{max}}$ (nm)	362	389	408	394	425	421	435	413	396	400
$\epsilon$ (L.cm <sup>-1</sup> .mol <sup>-1</sup> )	65806	97131	92021	40454	87394	98127	62653	92227	139941	133096
$\lambda_{\text{em}}^{\text{max}}$ (nm)	420	477	499	491	548	510	557	494	420	502
$\phi_f$	0.09	0.82	0.41	0.74	0.41	0.44	0.40	0.16	0.01	0.18
$\phi_{\Delta}$	0.04	0.00	0.43	0.11	0.46	0.44	0.48	0.39	0.17	0.48
$\phi_f + \phi_{\Delta}$	0.13	0.82	0.84	0.85	0.87	0.88	0.88	0.55	0.18	0.66
Stokes shift(cm <sup>-1</sup> )	4422	4743	4470	5014	5281	4145	5035	3970	1443	5080
$\lambda_{\text{TPA}}^{\text{max}}$ (nm)	750	730	770	750	820	810	850	810	< 730	760
$\sigma_{\text{TPA}}^{\text{max}}$ (GM)	32	832	432	460	745	690	489	214	> 69	725
$\sigma_{\text{TPA}, 800}$ (GM)	6	406	381	250	680	652	308	205	36	652
$\sigma_{\text{TPA}, 800} * \phi_{\Delta}$	0	0	164	28	313	287	148	80	6	313
$\tau_F$ (ns)	<0.3	1.35	0.74	1.25	0.68	0.82	1.17	0.51	<0.3	>0.3
$k_r$ (s <sup>-1</sup> )	-	6.1 10 <sup>8</sup>	5.5 10 <sup>8</sup>	5.9 10 <sup>8</sup>	6.0.10 <sup>8</sup>	5.4.10 <sup>8</sup>	3.4.10 <sup>8</sup>	3.1.10 <sup>8</sup>	-	-
$k_{\text{ISC}}$ (s <sup>-1</sup> )	-	0	5.8 10 <sup>8</sup>	8.8 10 <sup>7</sup>	6.7 10 <sup>8</sup>	5.4 10 <sup>8</sup>	4.1 10 <sup>8</sup>	7.6 10 <sup>8</sup>	-	-
$k_{\text{nr}}$ (s <sup>-1</sup> )	-	1.3 10 <sup>8</sup>	2.1 10 <sup>8</sup>	1.2 10 <sup>8</sup>	1.9 10 <sup>8</sup>	1.5 10 <sup>8</sup>	1.1 10 <sup>8</sup>	1.6 10 <sup>9</sup>	-	-

## S2-Discussion: Influence on Stokes shift

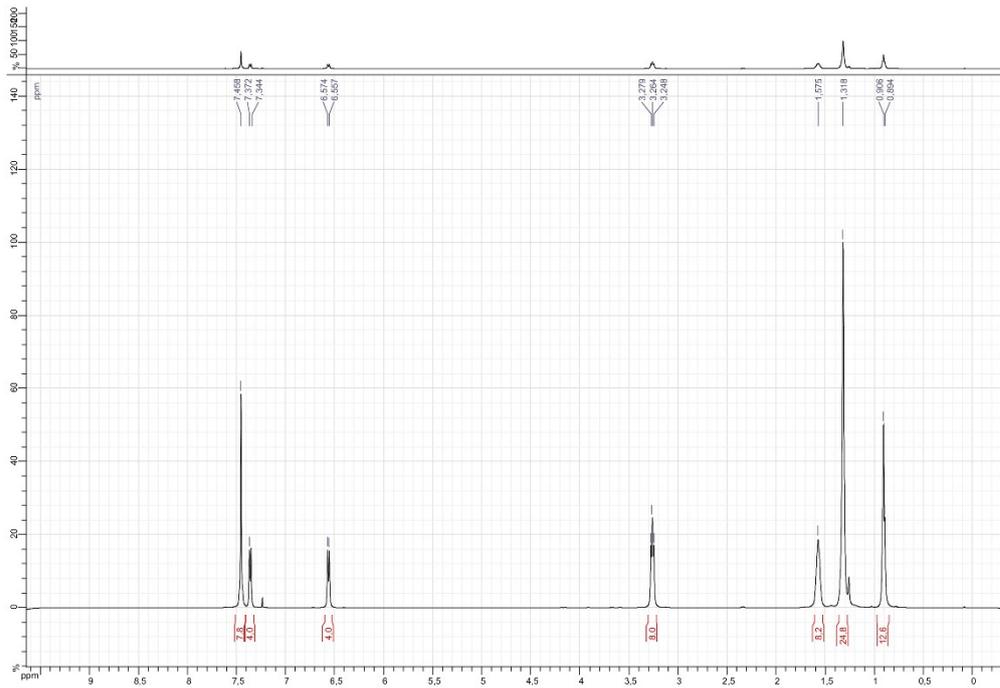
As a first approximation, the length of the  $\pi$ -conjugated backbone is the main factor of influence. While an average Stokes shift of 2000  $\text{cm}^{-1}$  is measured for the trimer series (**020** and **040**), it is close to 4000  $\text{cm}^{-1}$  for the tetramer series, raises to 4250  $\text{cm}^{-1}$  for the tetramer with a diyne central bridge and exceeds 4500  $\text{cm}^{-1}$  in the case of the pentamer series. Distortion of the  $\pi$ -conjugated backbone in the latter series, as previously mentioned as an explanation the saturation of the bathochromic effect, could also play a role in the increased Stokes shift in this series. Indeed, the nature of the  $\pi$ -conjugated bridge in all synthesized molecules implies that the excited state has a cumulenic/quinoidal nature: in the case of molecules with a ground state distorted geometry, large reorganization processes are required to reach a planar geometry. This effect can also be noticed in the tetramer series with a biphenyl central bridge (**00/00**, **02/00** and **02/20**). In spite of a shorter conjugation length and a decreased bathochromic shift in the latter as compared to the other tetrameric and pentameric series, the observed Stokes shift is comparable to that measured for the pentamer series ( $>4500 \text{ cm}^{-1}$ ).

Octupolar compounds follow the general trend, and exhibit a clear increase of their Stokes shifts upon increasing peripheral substituents length.

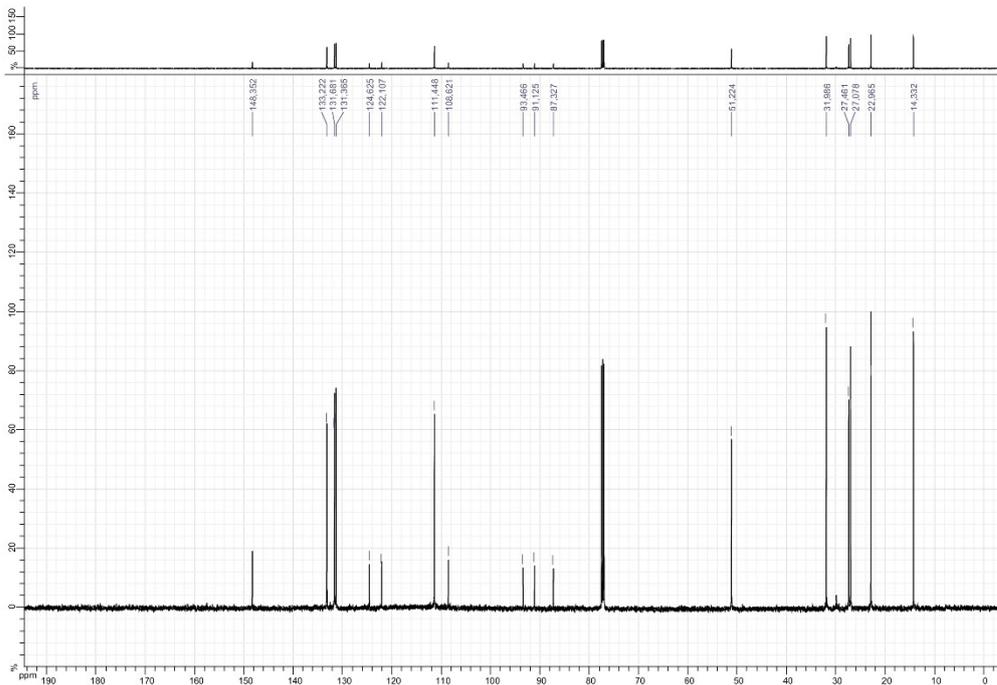
For a given series, it is hard to extract a general trend for the observed Stokes shift evolution that accompanies the modifications in bromine substitution pattern. On average, only little increase in the Stokes shift is observed upon increasing number of bromine substituents. These conclusions must however be balanced for the pentamer series and the extended octupoles (**O0(20)<sub>3</sub>** and **O3(00)<sub>3</sub>**). For both series, the amplitude of the Stokes shift is strongly correlated to the position of the bromine substituents: in the absence of bromine on the central ring (**02000**, **02020** and **O0(20)<sub>3</sub>**) the observed Stokes shift is close to 4000  $\text{cm}^{-1}$ , and never exceeds 4400  $\text{cm}^{-1}$ . When the central position is occupied [**00200**, **02220**, **02200**, **O3(00)<sub>3</sub>**], the Stokes shift reaches or exceeds 5000  $\text{cm}^{-1}$ . This difference can be attributed to the increased distance between the peripheral aniline donor group and the central bromine substituted aryl, which contributes in increasing the charge transfer extent

## S3- $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of all studied compounds and of their main intermediates

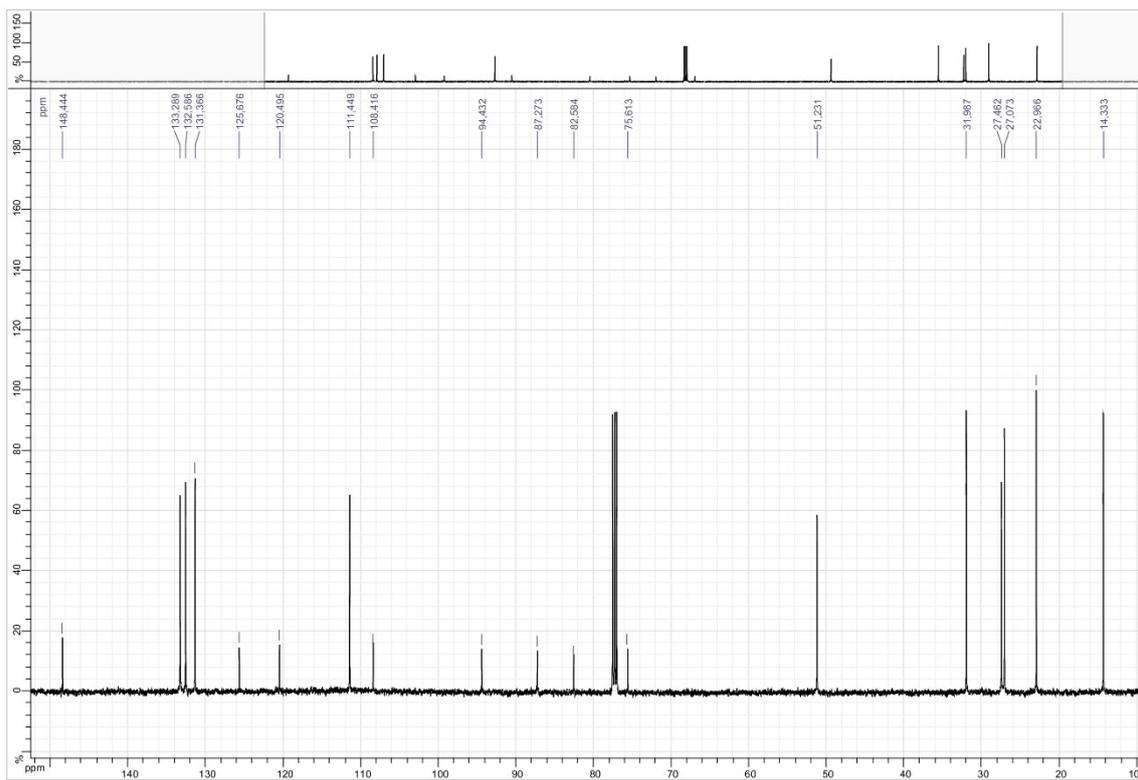
0000 ( $^1\text{H}$ )



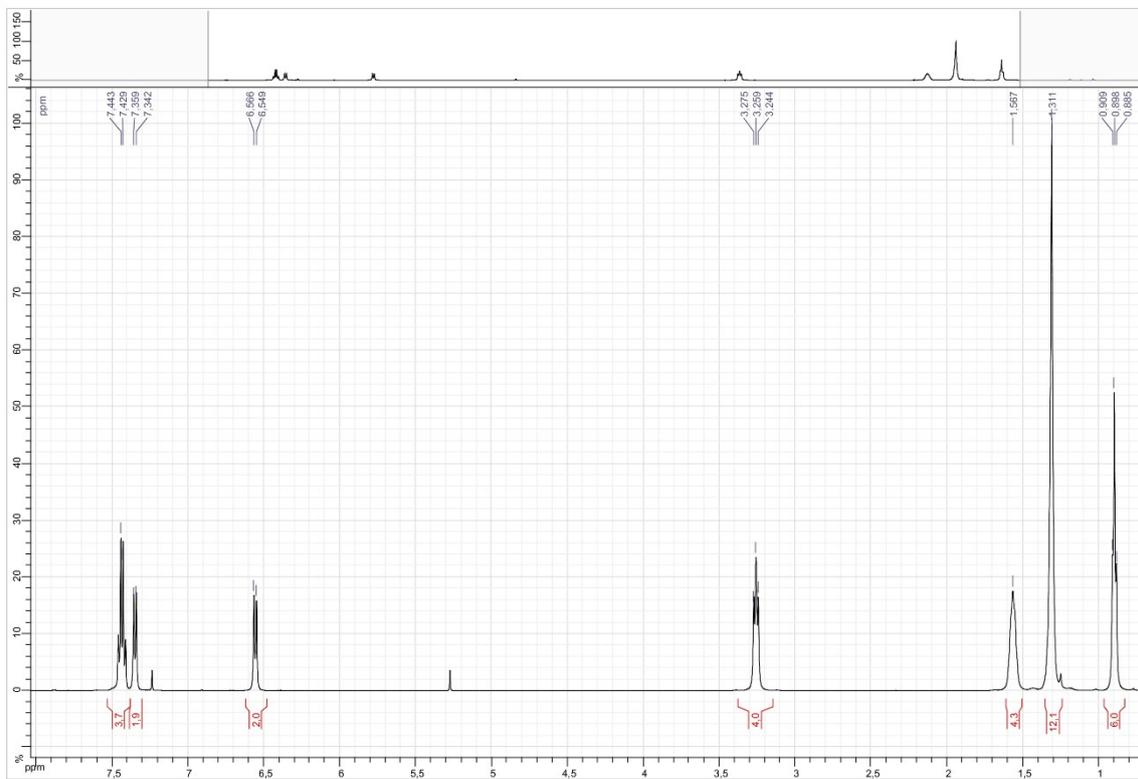
0000 (<sup>13</sup>C)



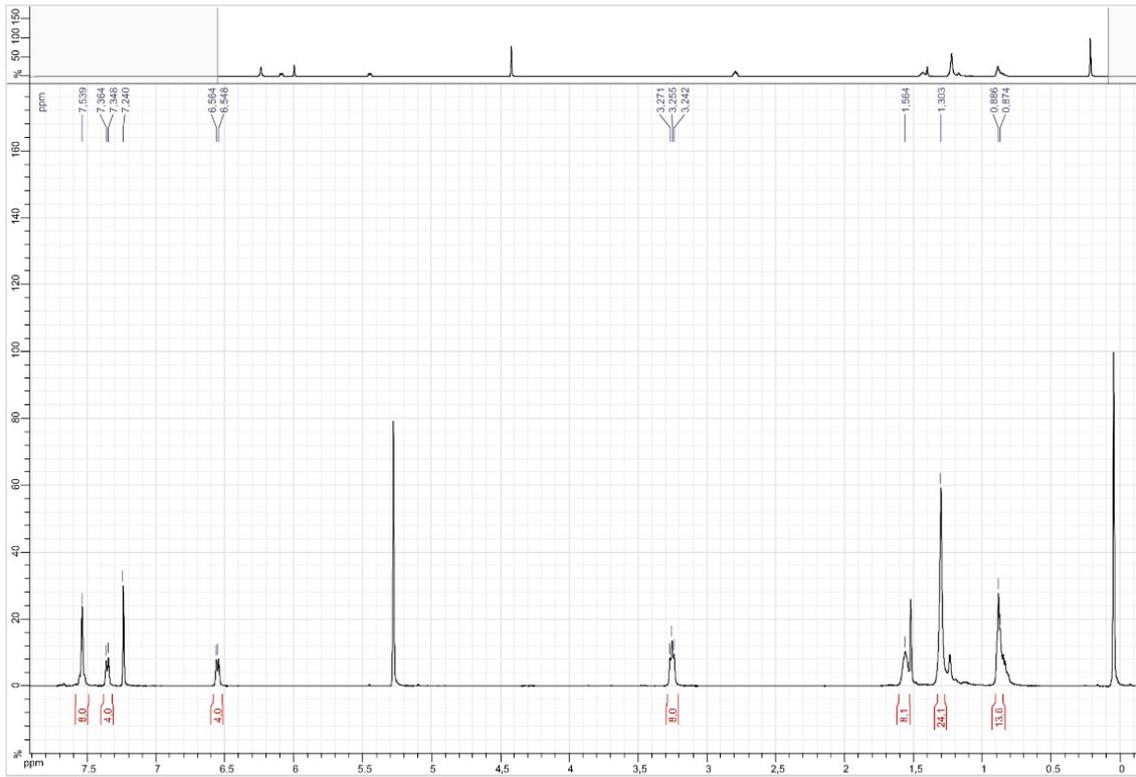
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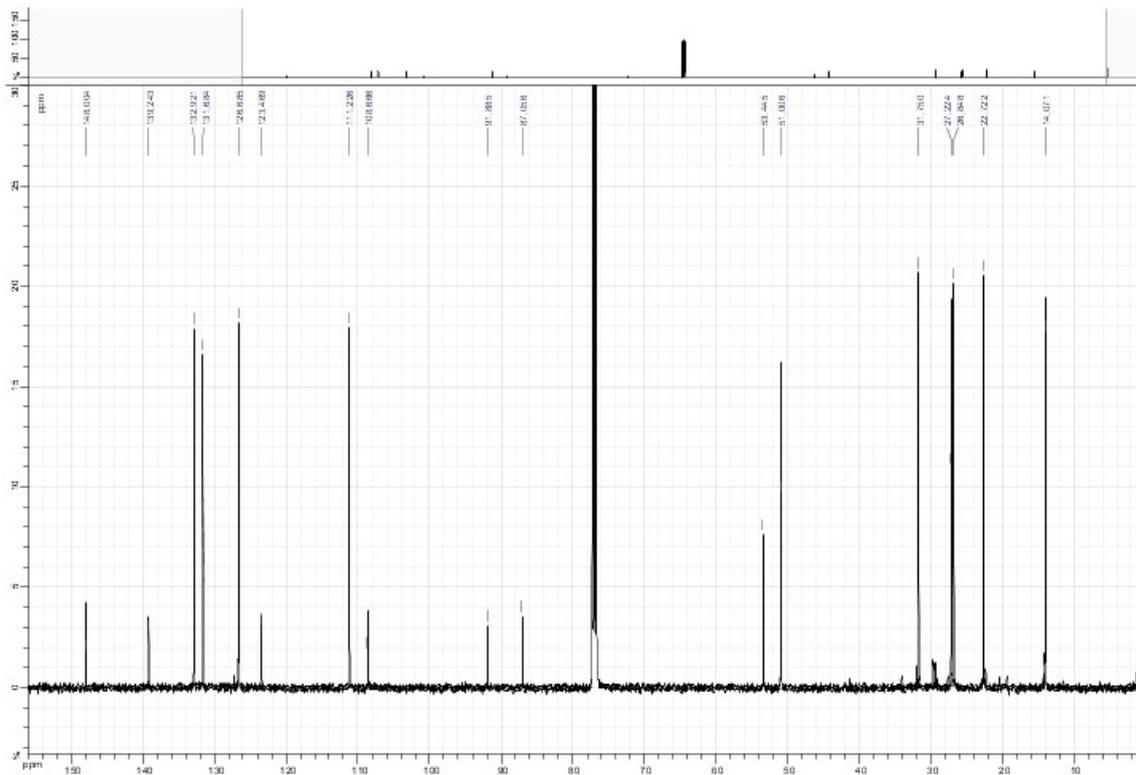
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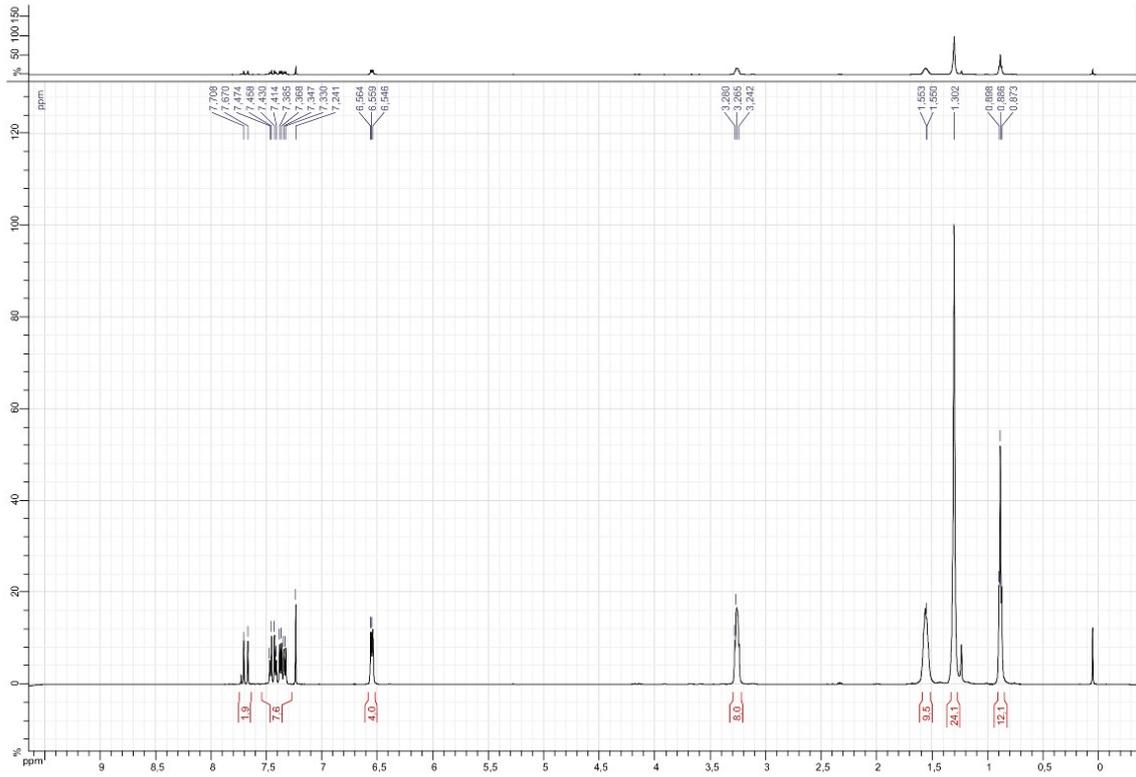
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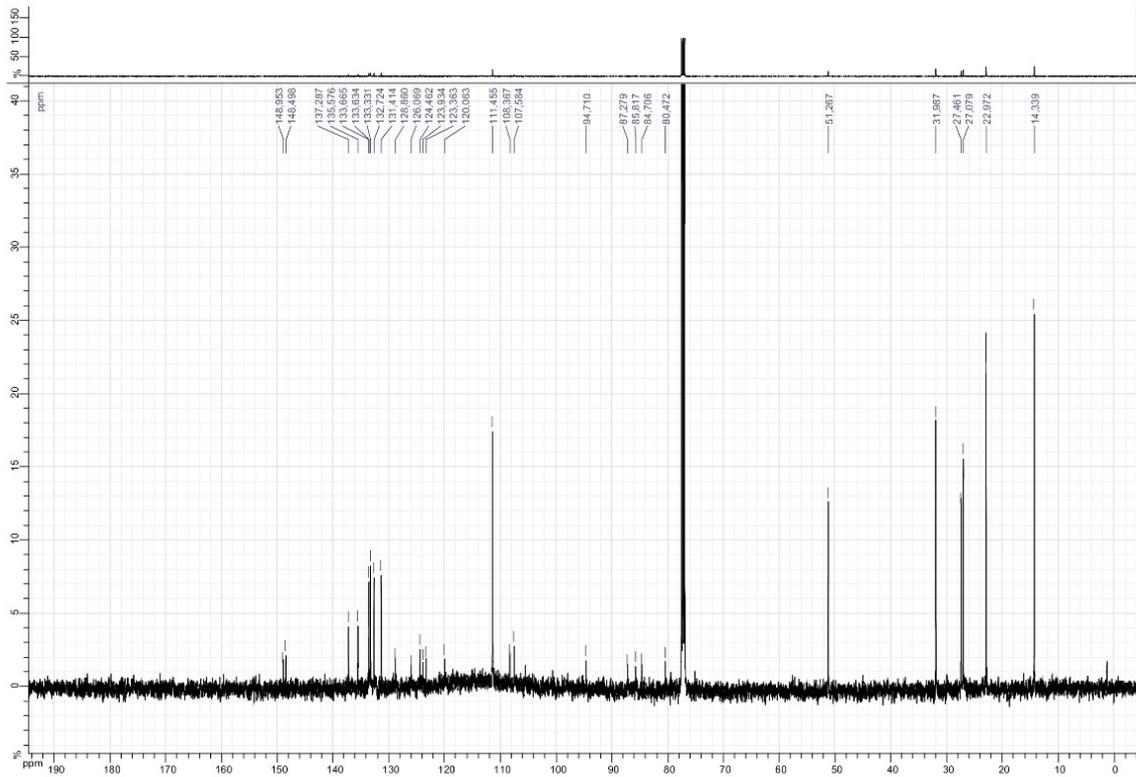
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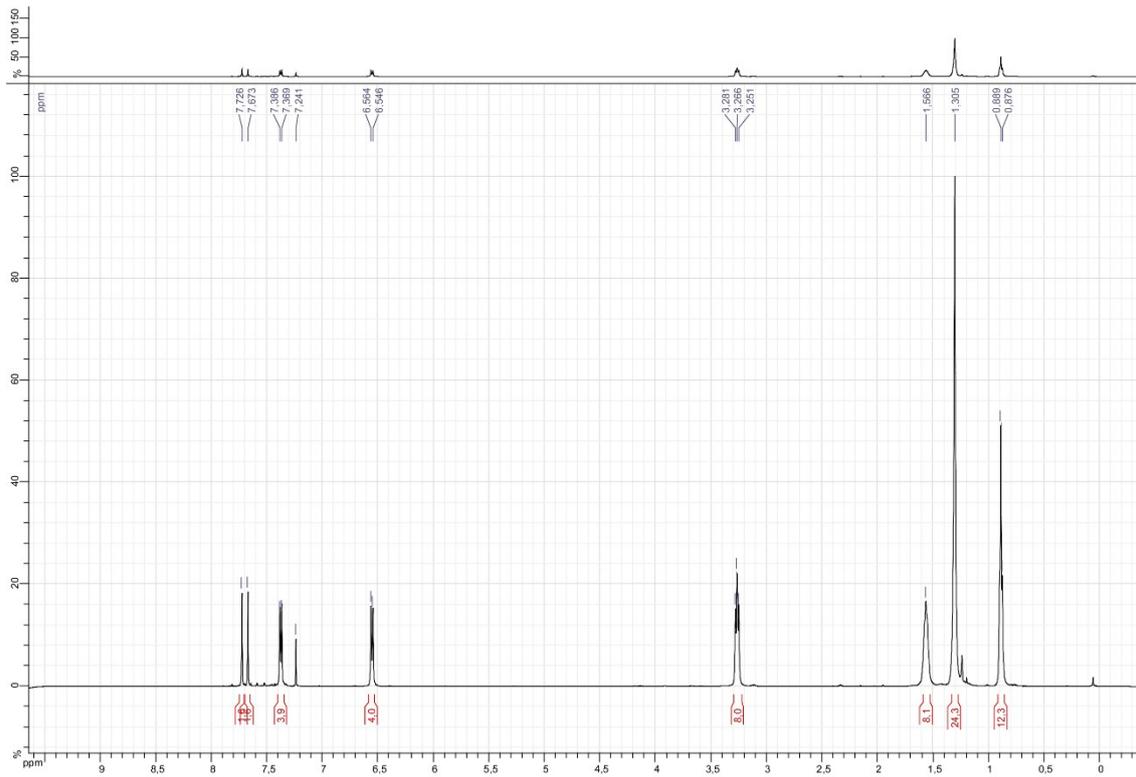
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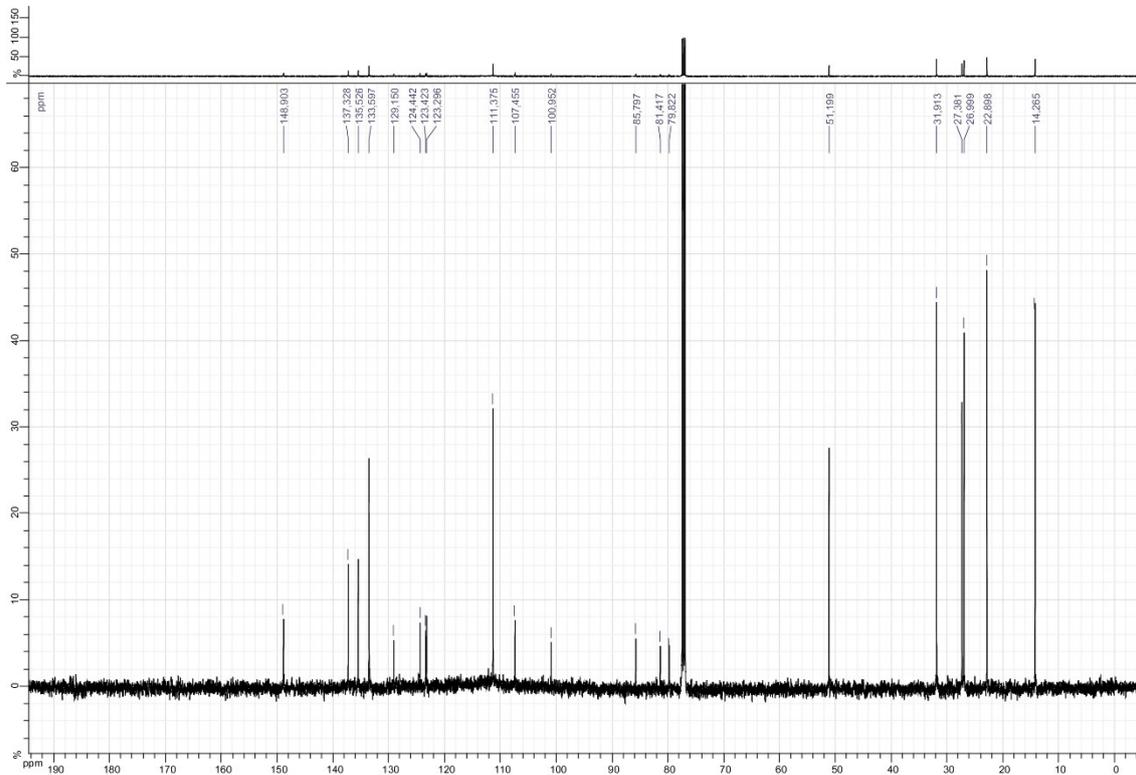
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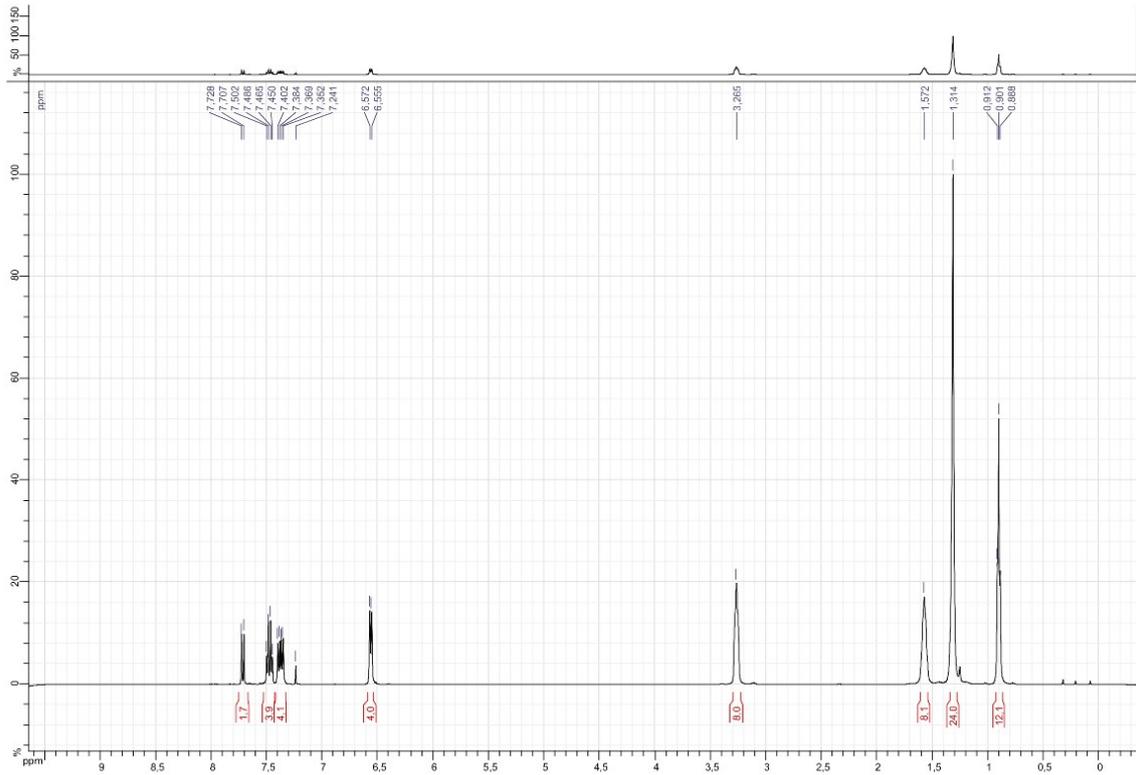
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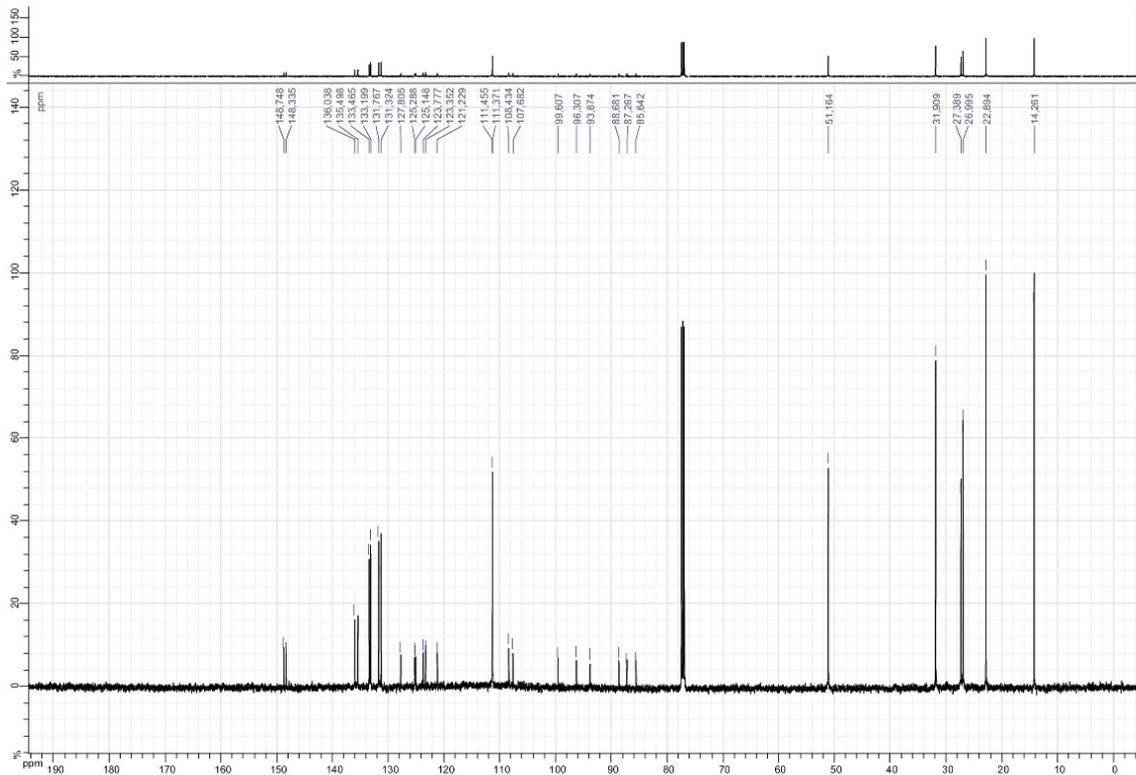
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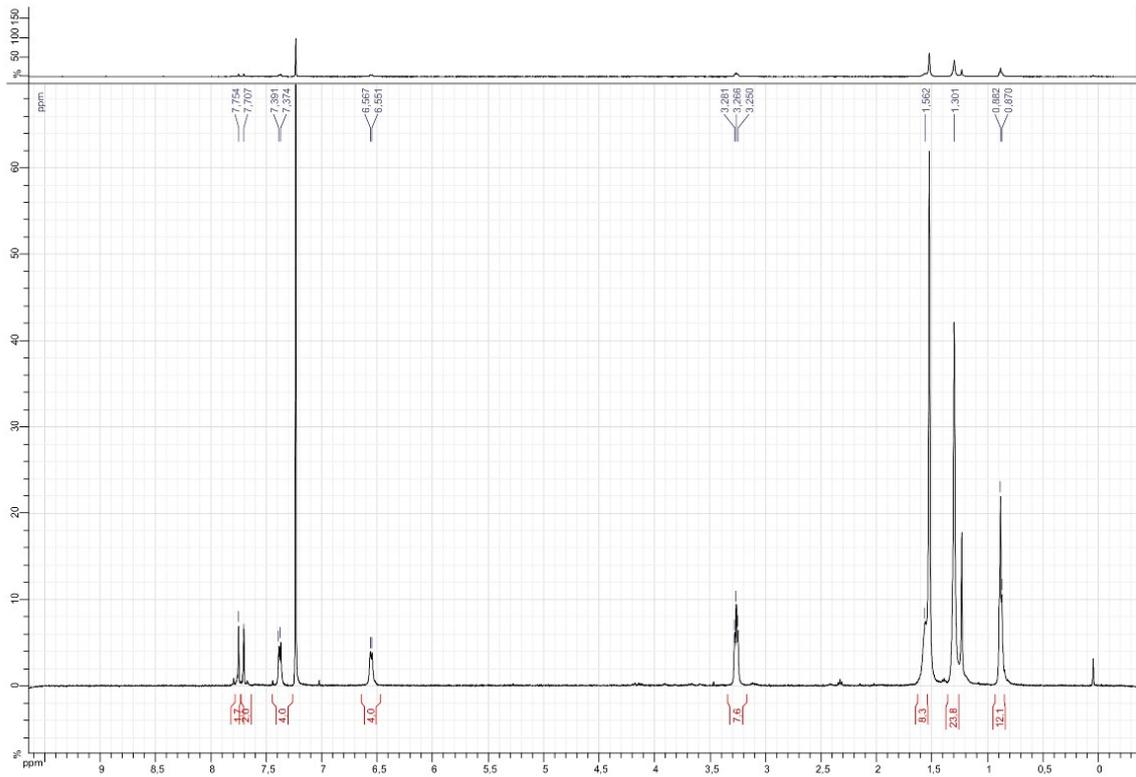
0200 (<sup>1</sup>H)



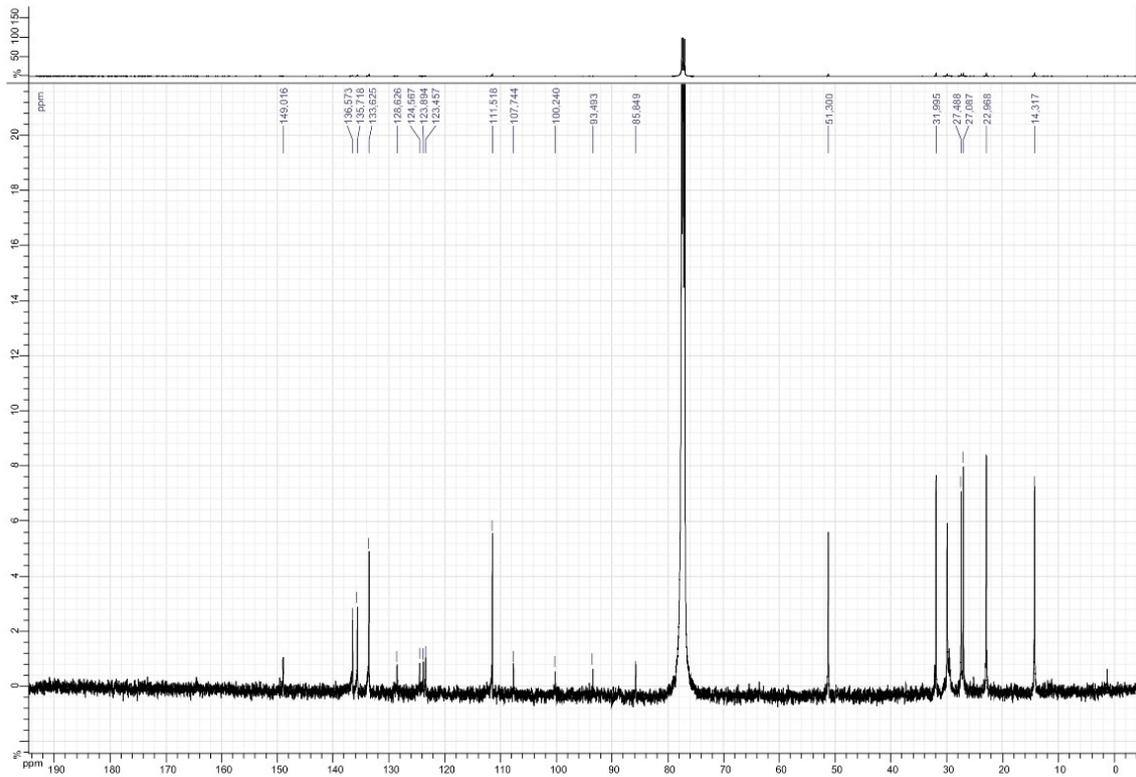
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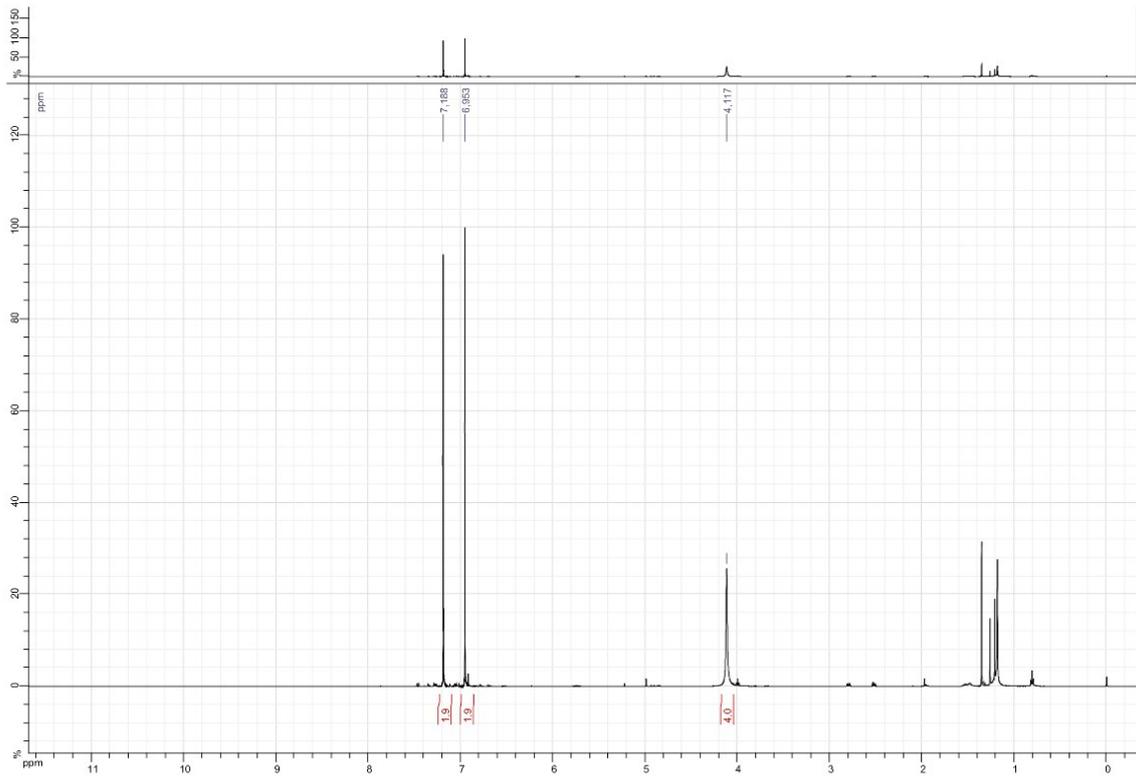
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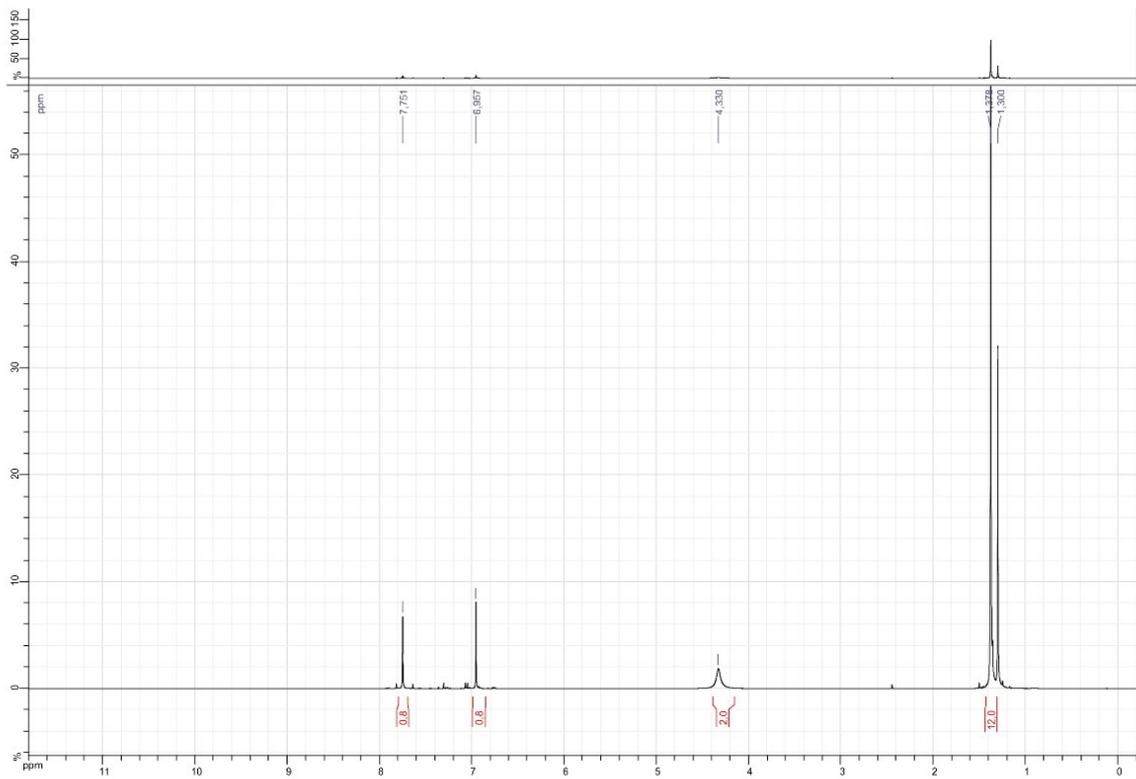
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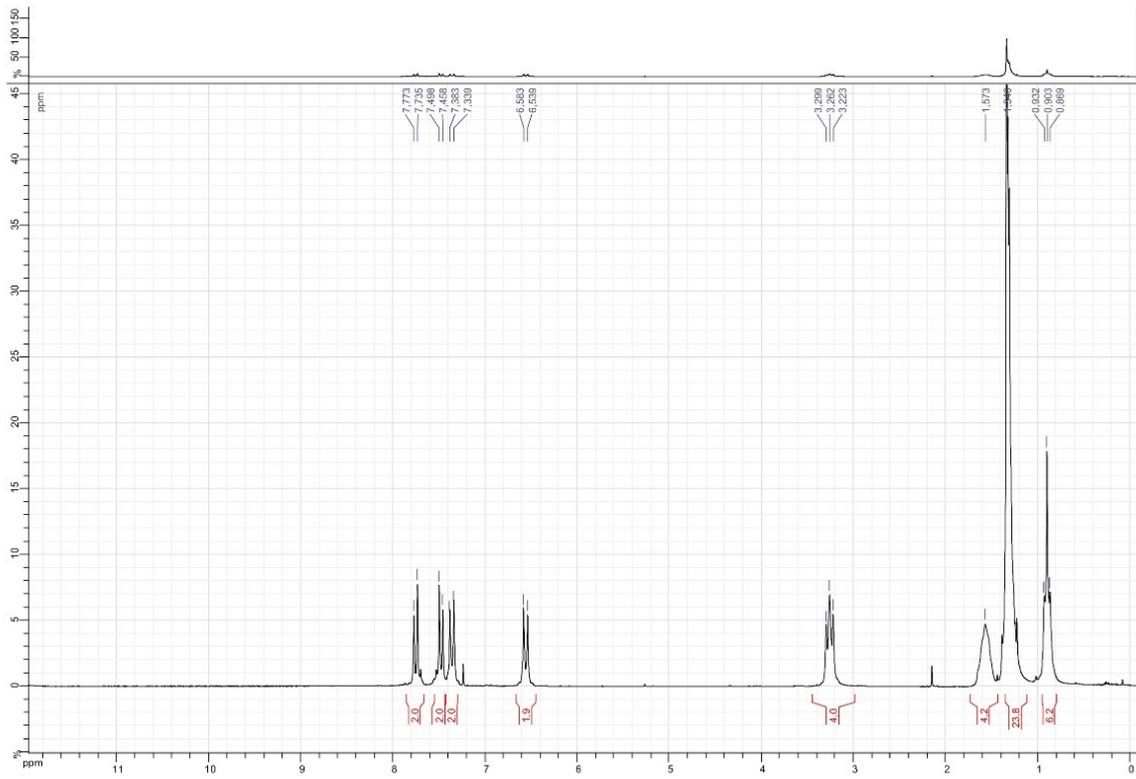
16 (<sup>1</sup>H)



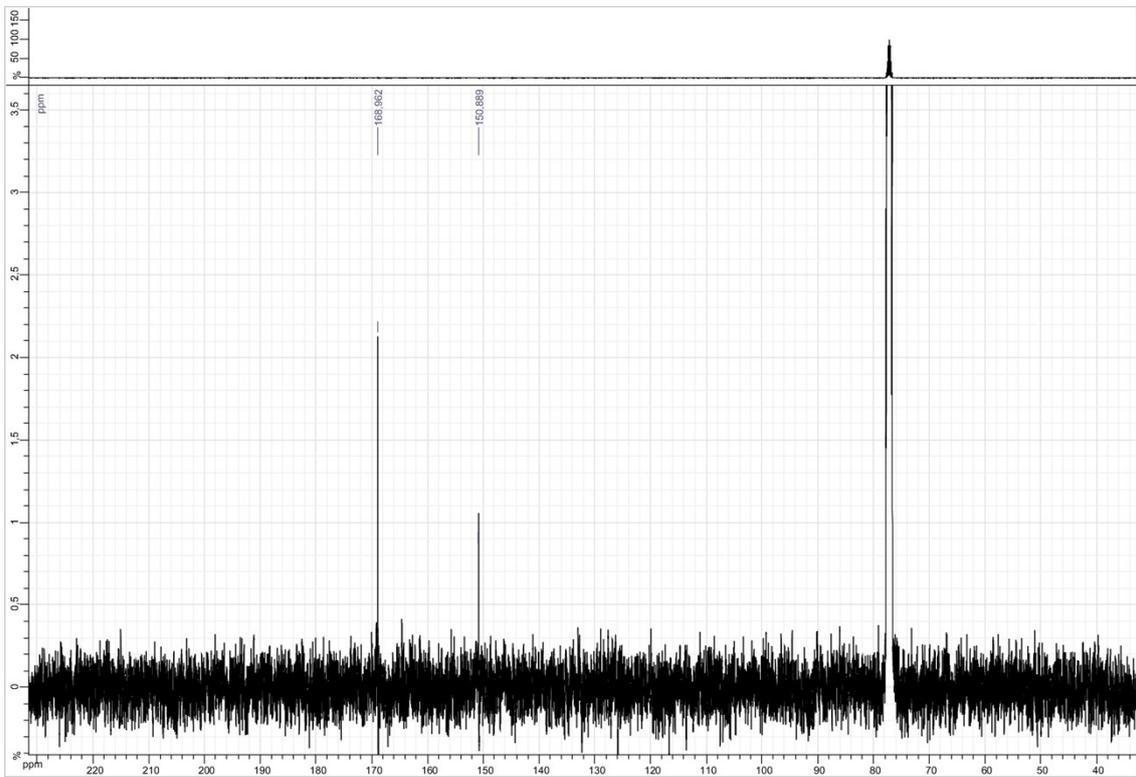
**16 (<sup>13</sup>C)**



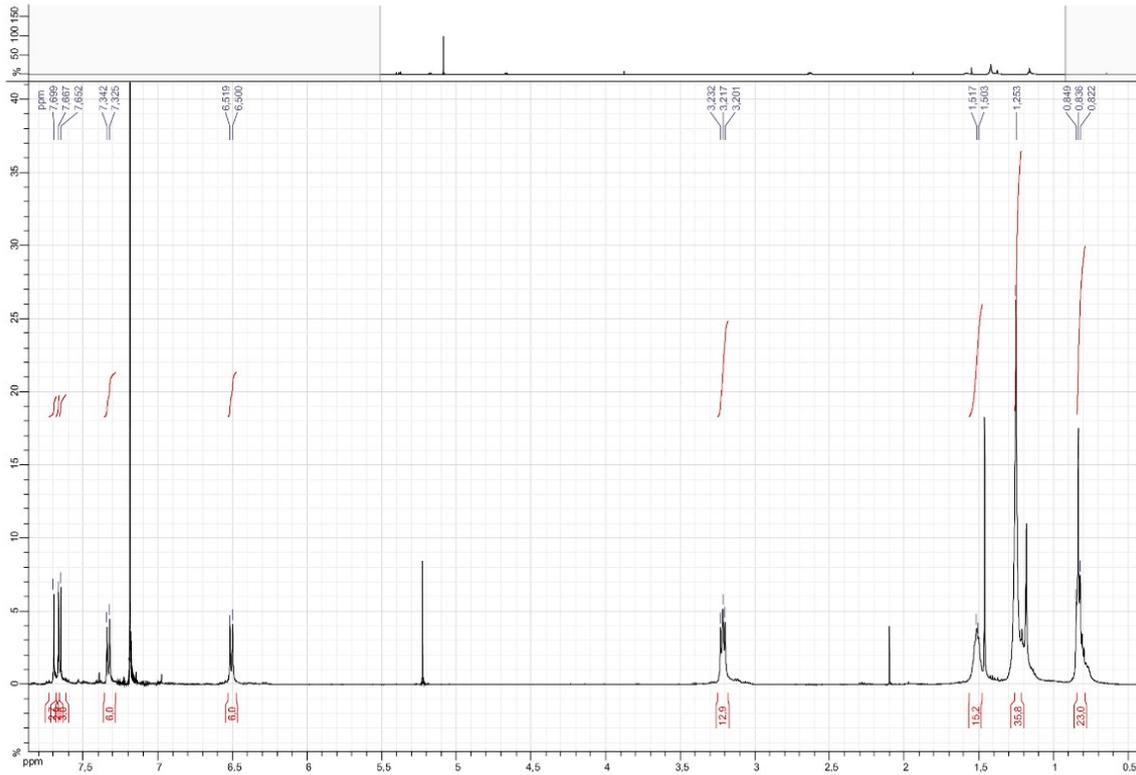
**11 (<sup>1</sup>H)**



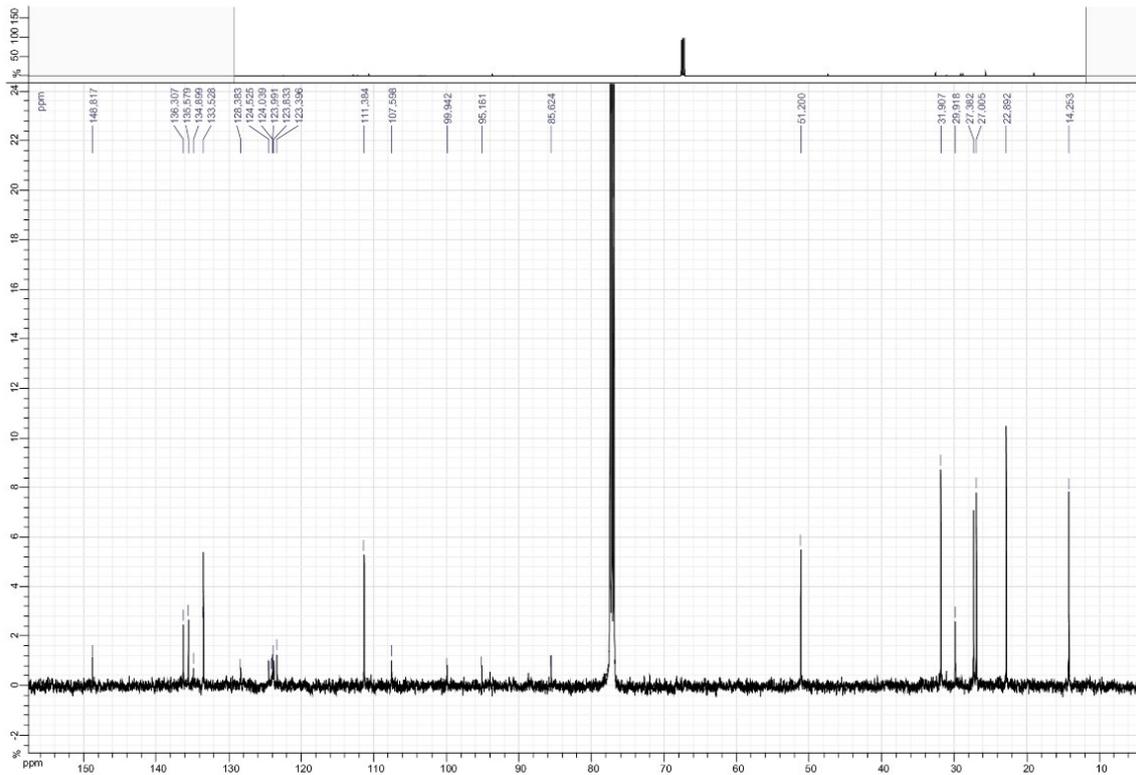
25 (<sup>13</sup>C)



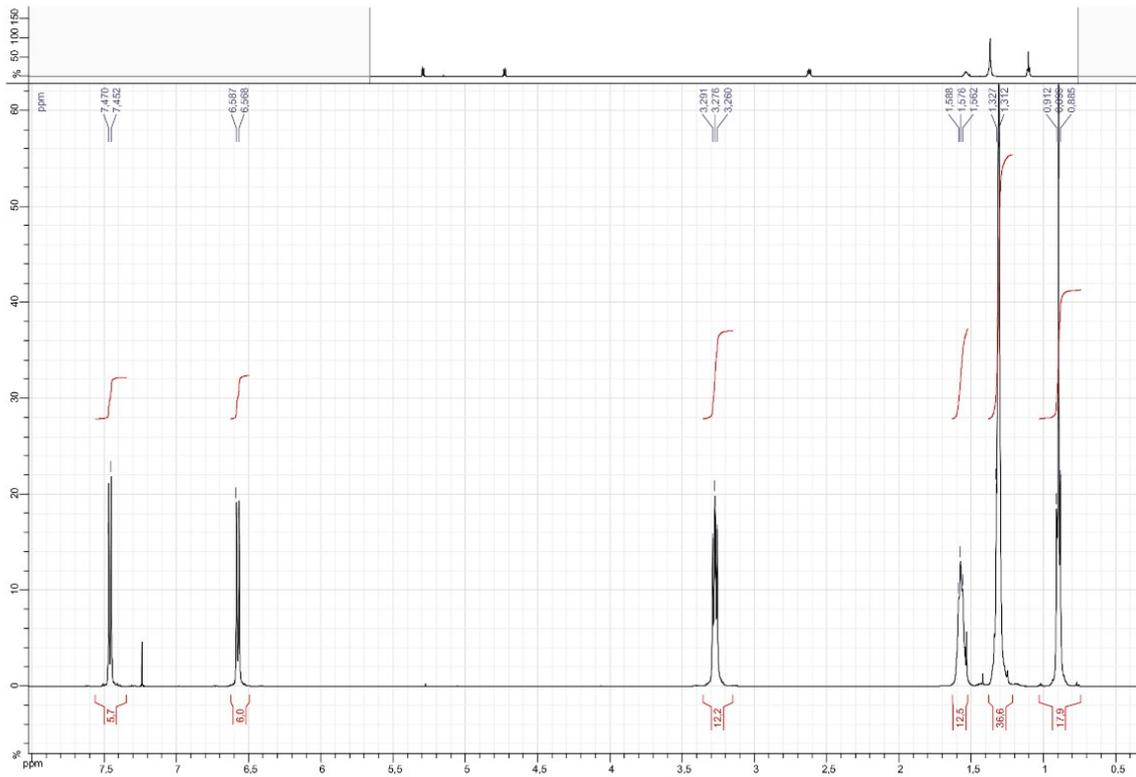
Oo(2O)<sub>3</sub> (<sup>1</sup>H)



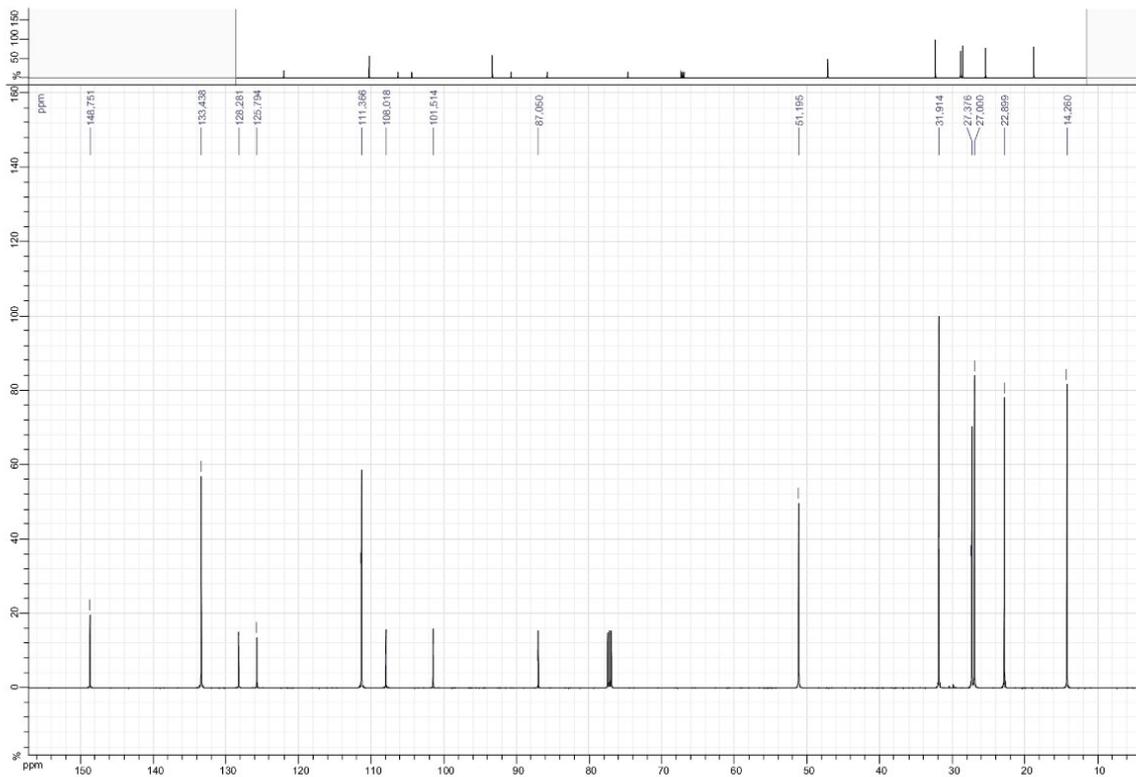
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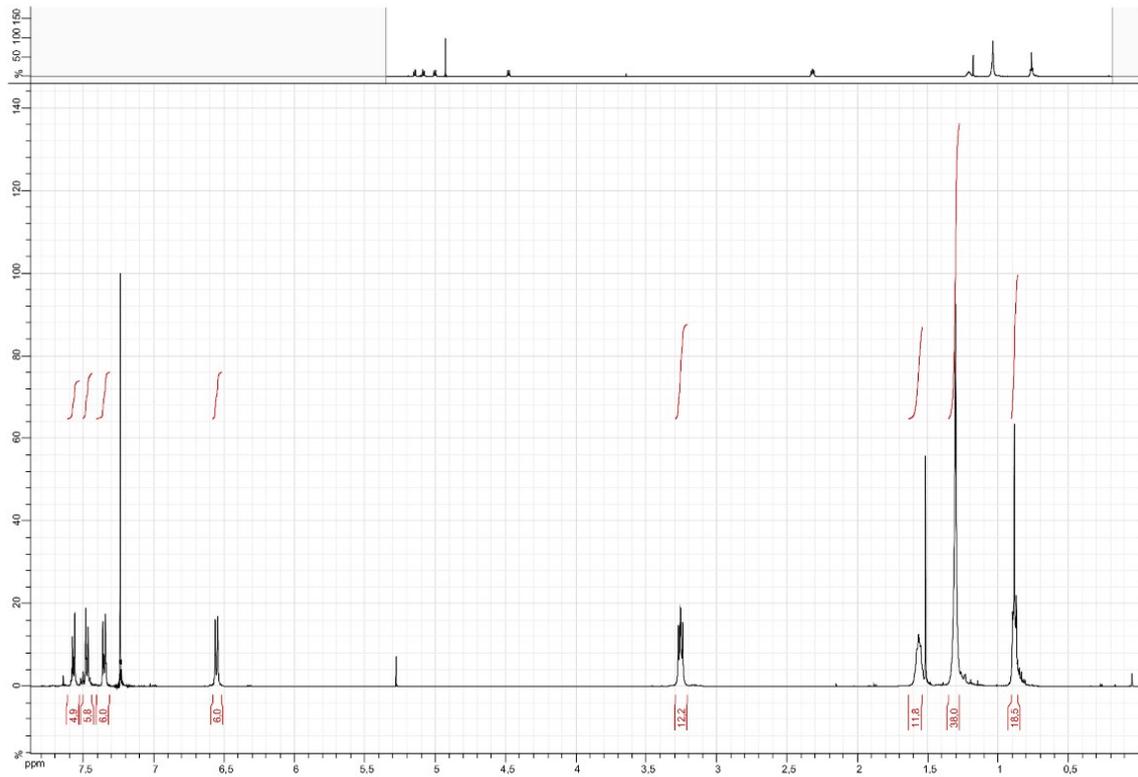
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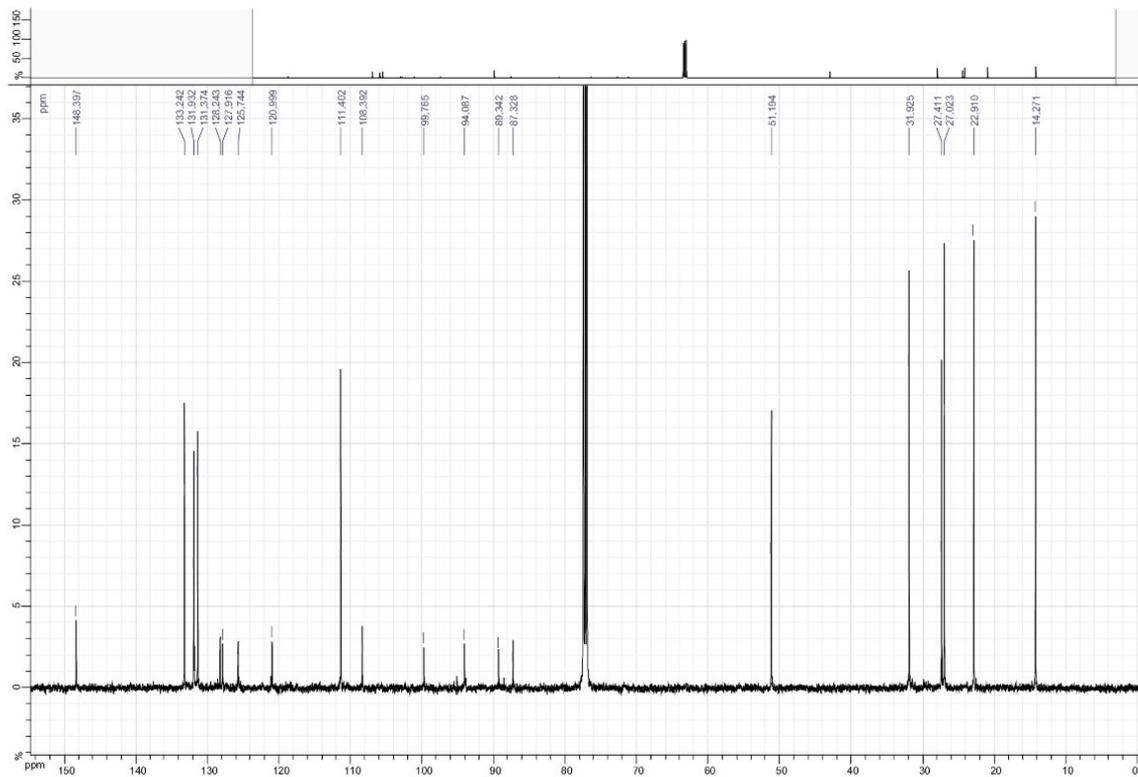
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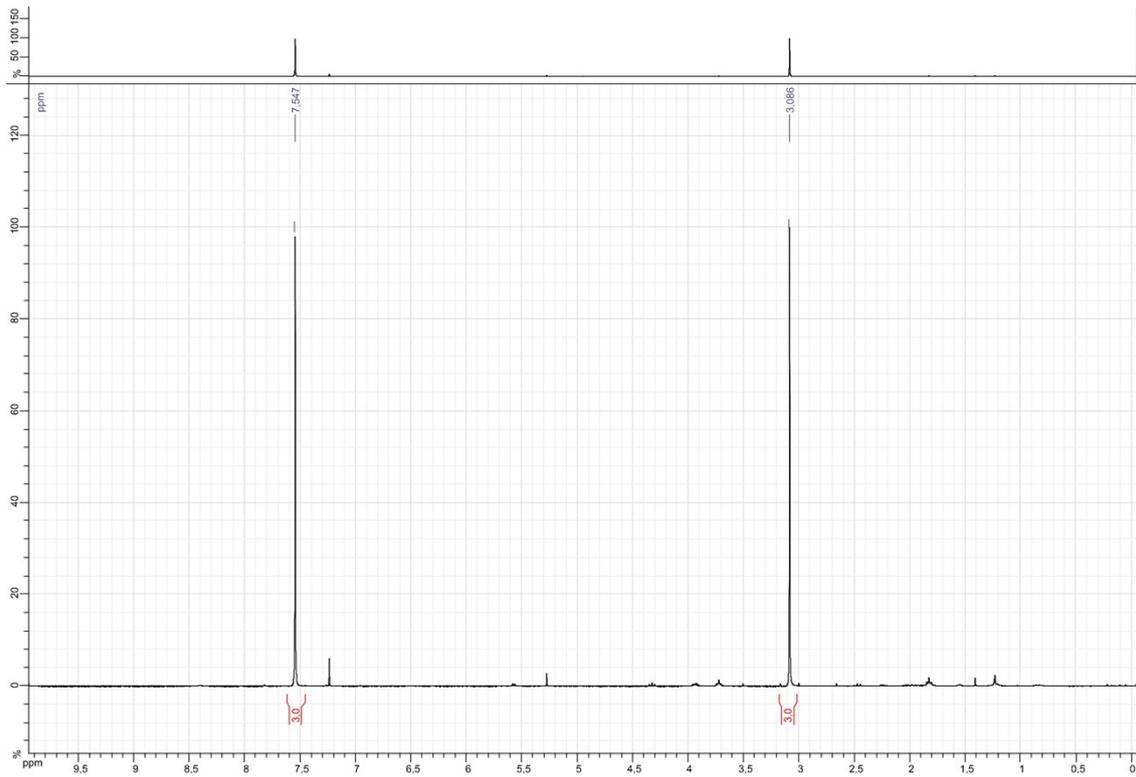
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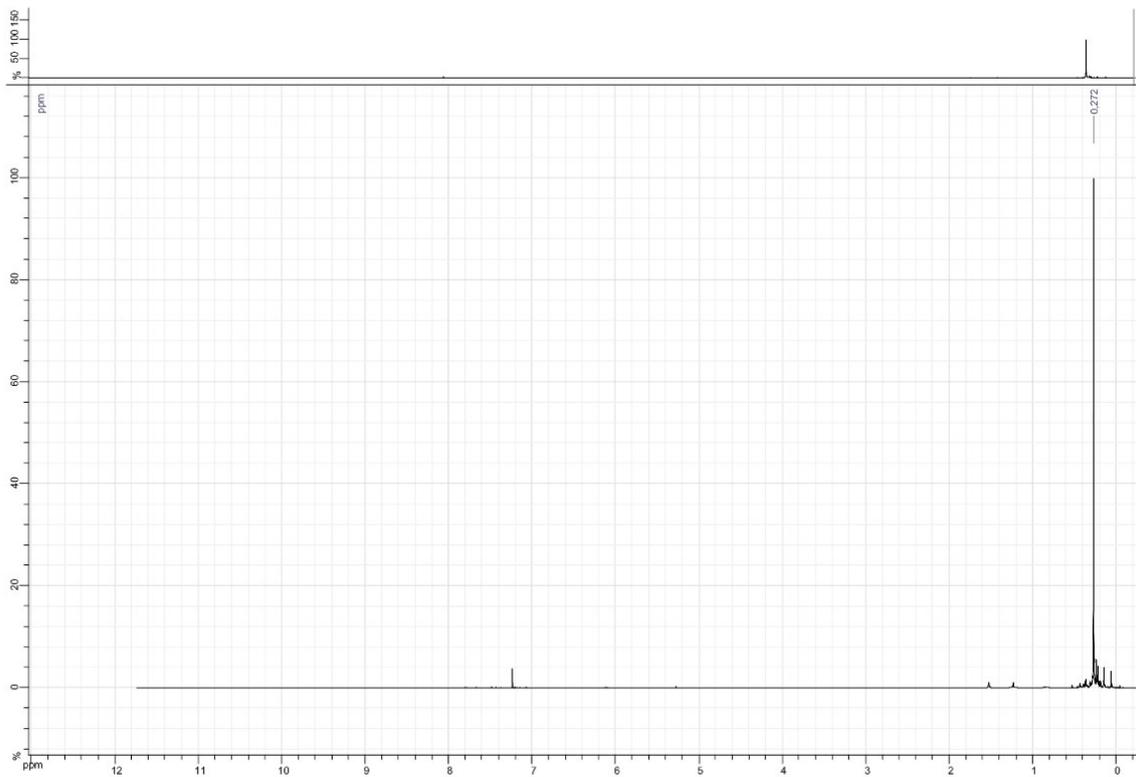
03(00)<sub>3</sub> ( $^{13}\text{C}$ )



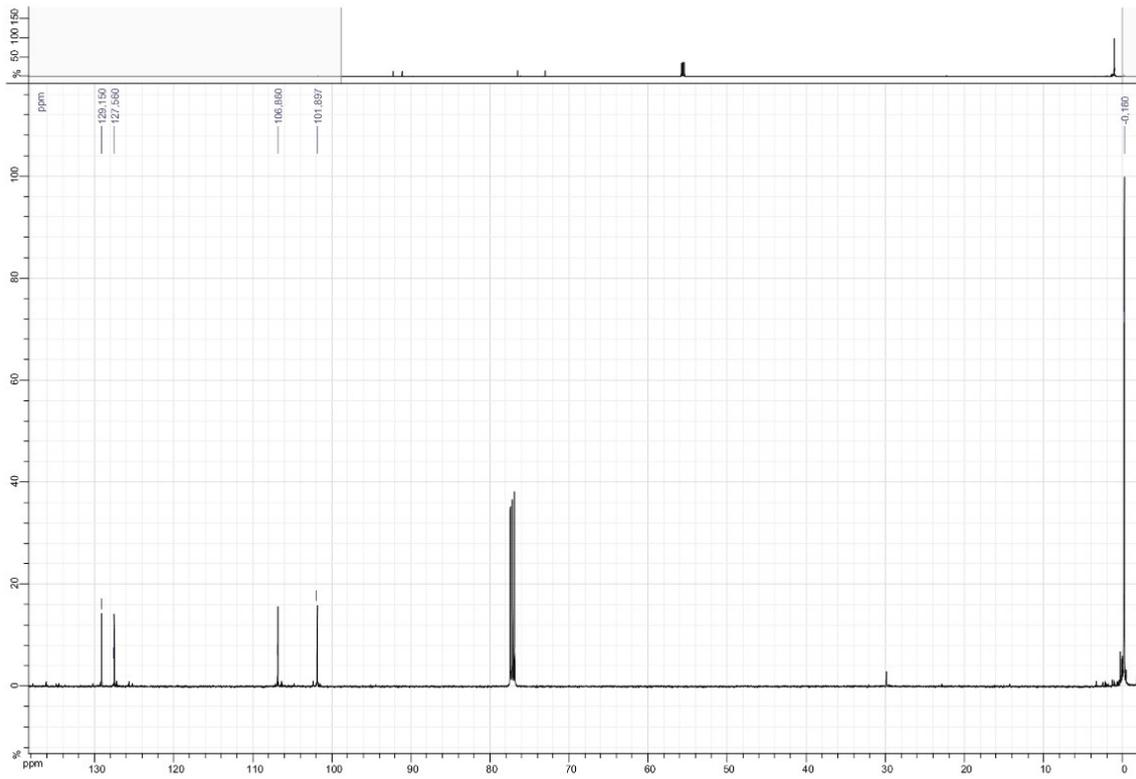
22 ( $^1\text{H}$ )



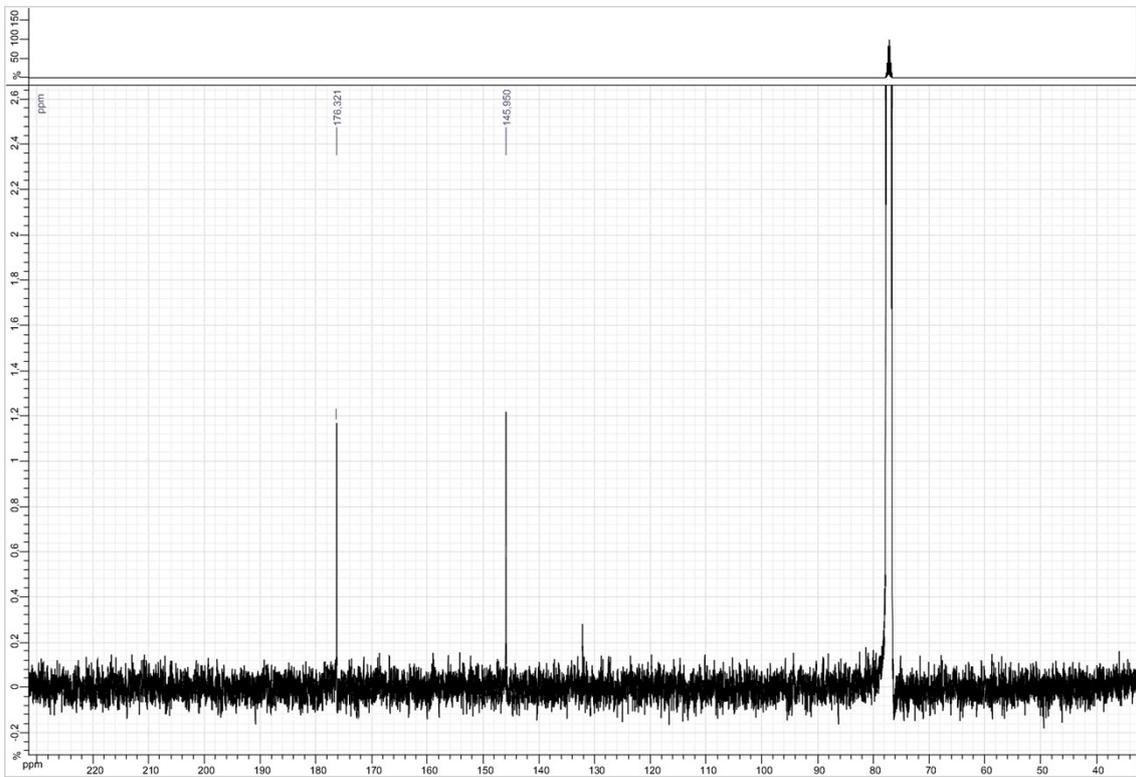
23 ( $^1\text{H}$ )



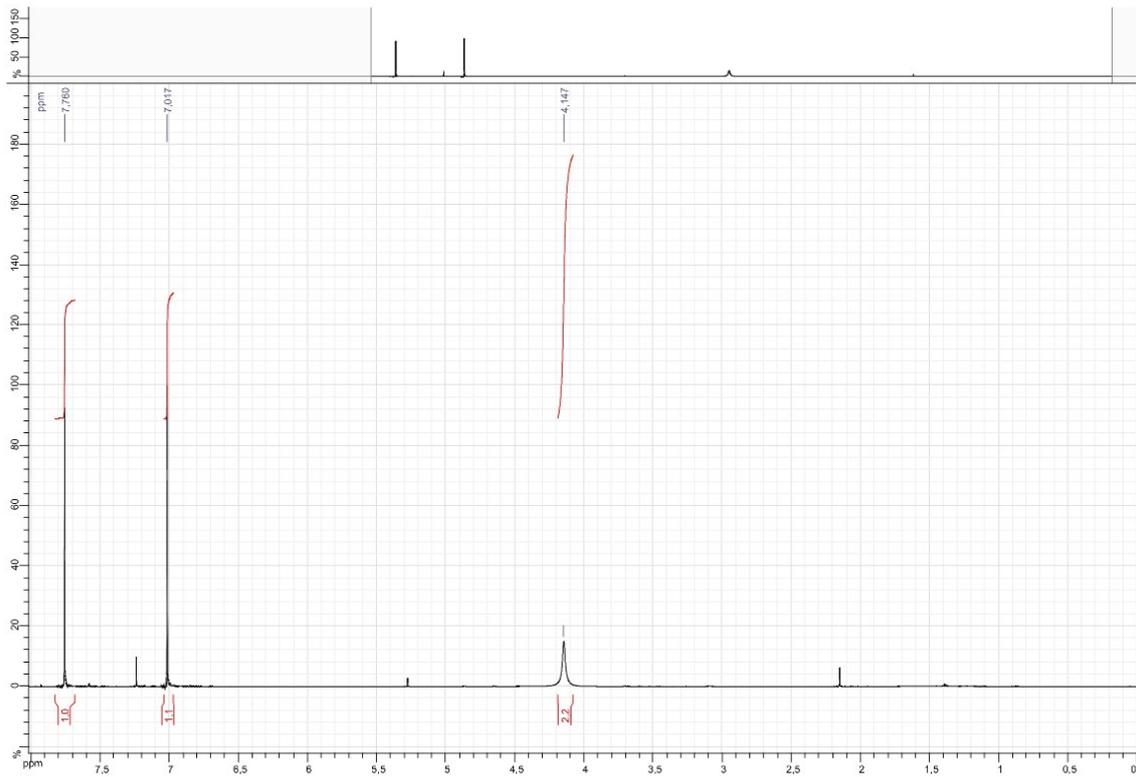
23 ( $^{13}\text{C}$ )



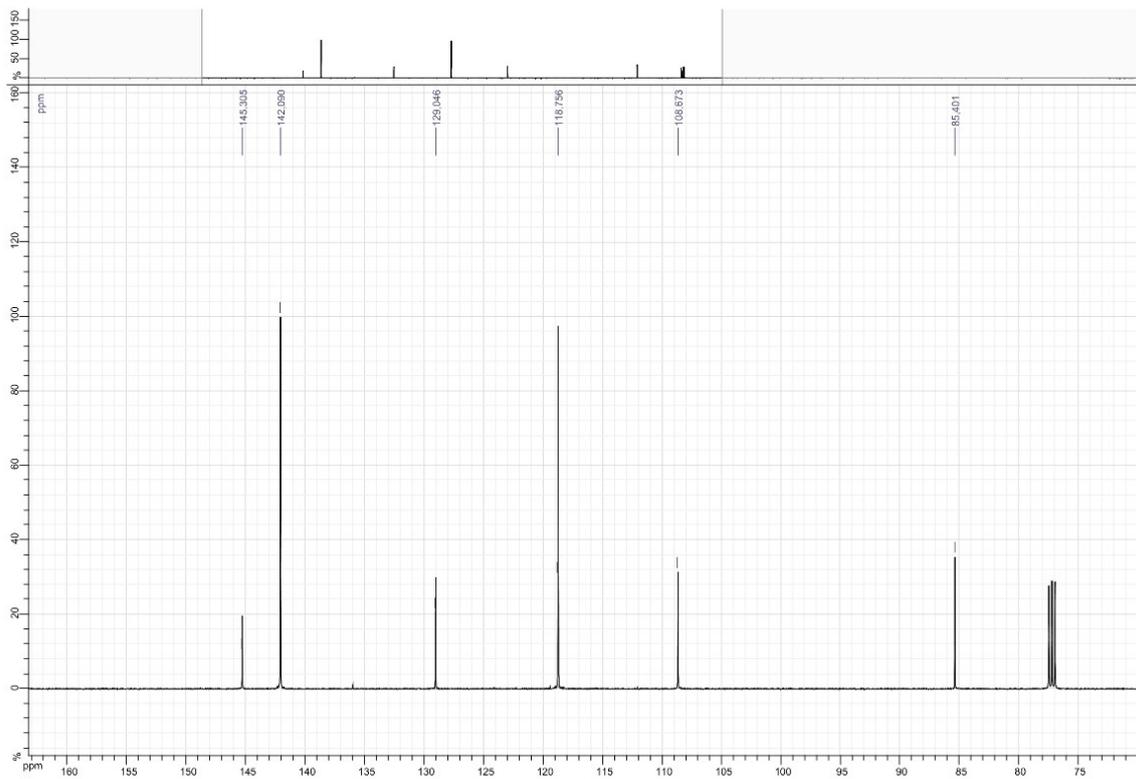
20 ( $^{13}\text{C}$ )



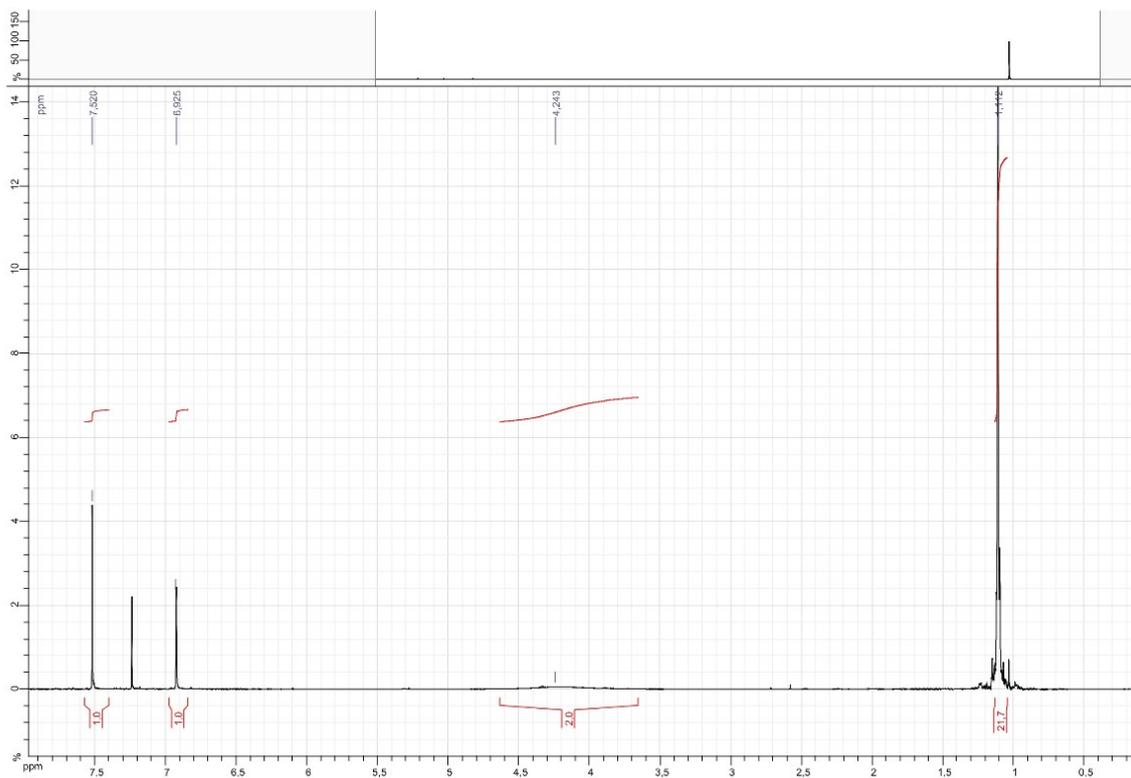
1 ( $^1\text{H}$ )



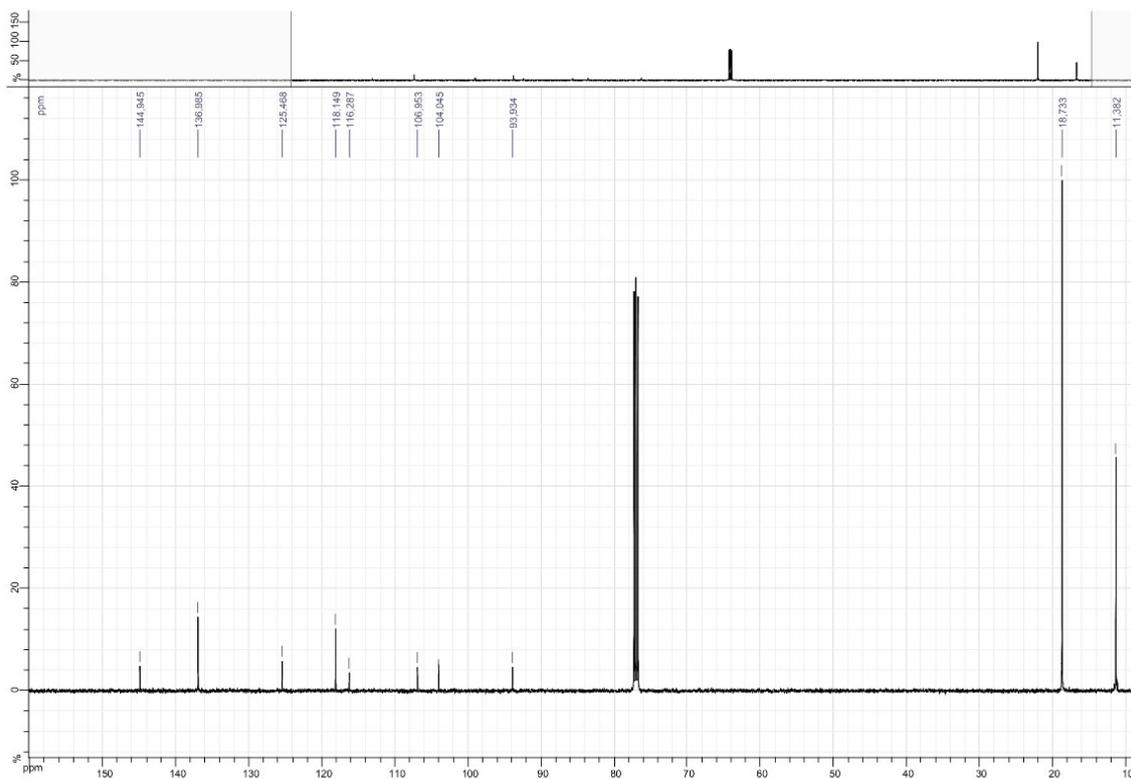
**1** (<sup>13</sup>C)



**2** (<sup>1</sup>H)



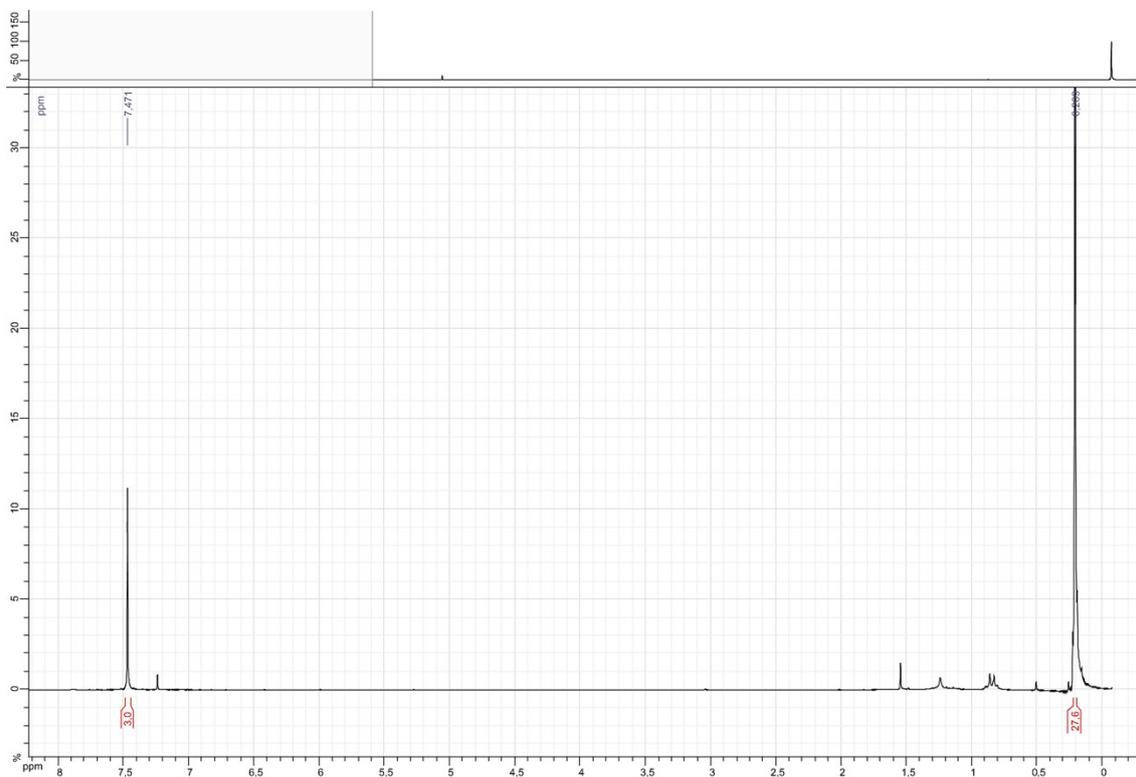
**2 (<sup>13</sup>C)**



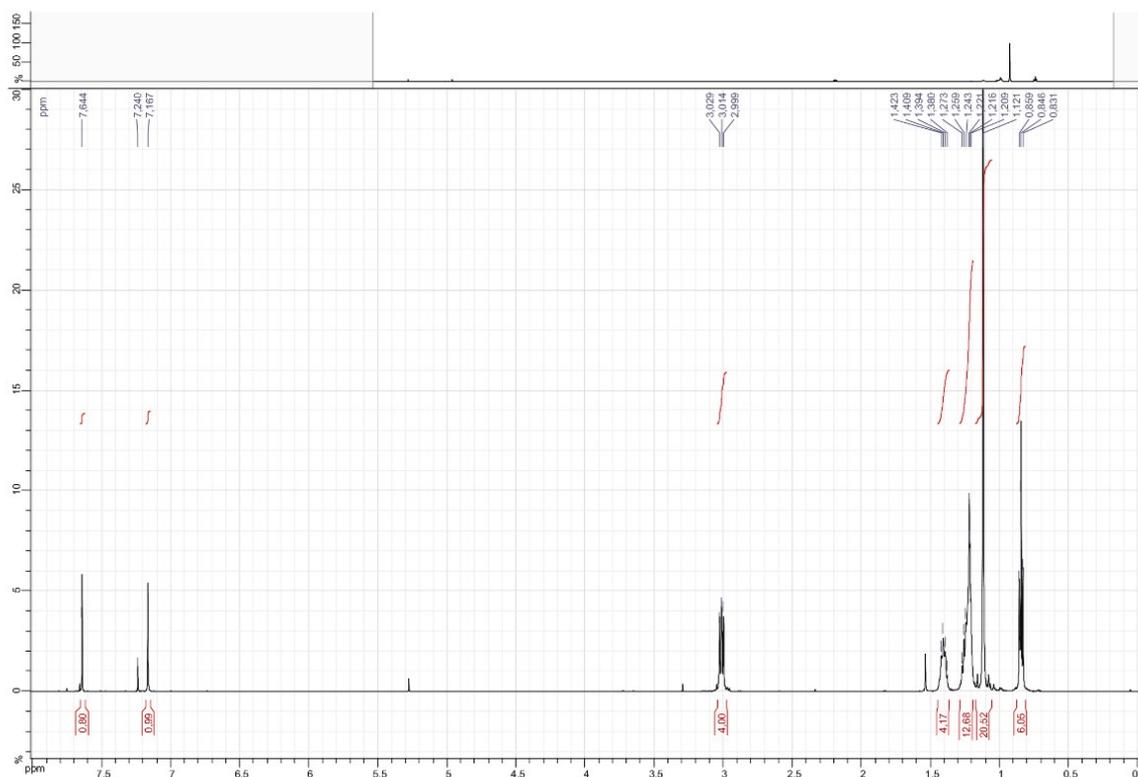
**12 (<sup>1</sup>H)**



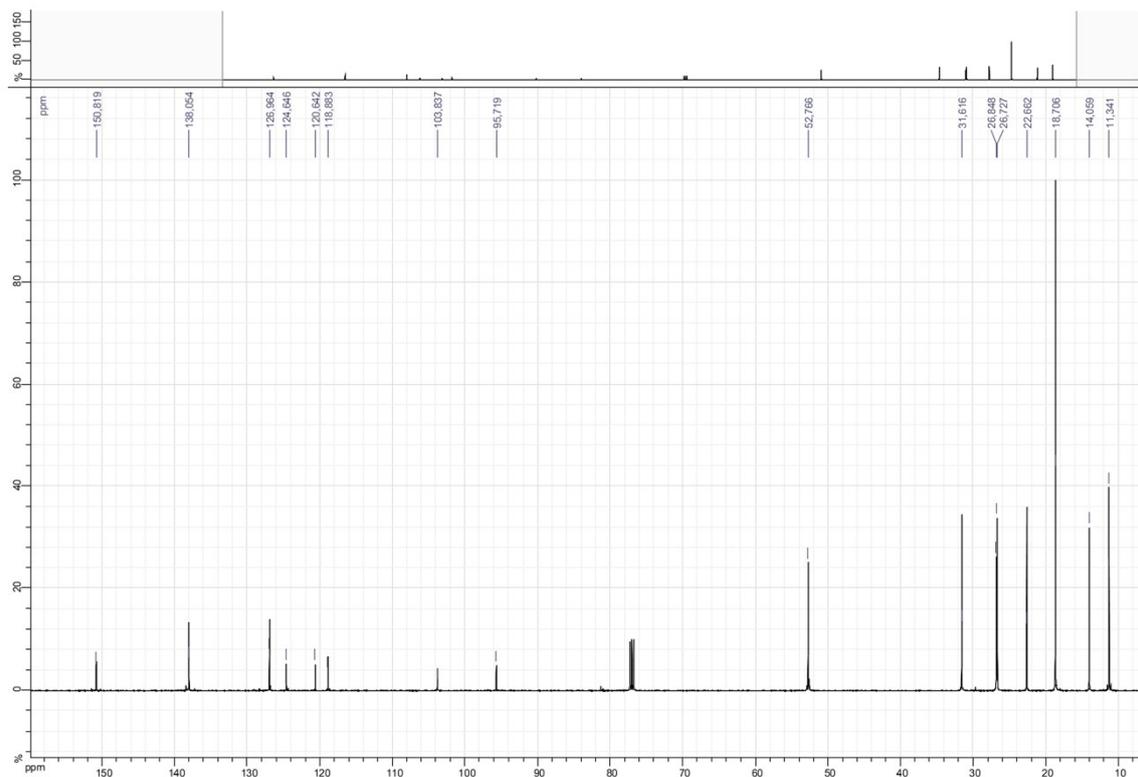
21 ( $^1\text{H}$ )



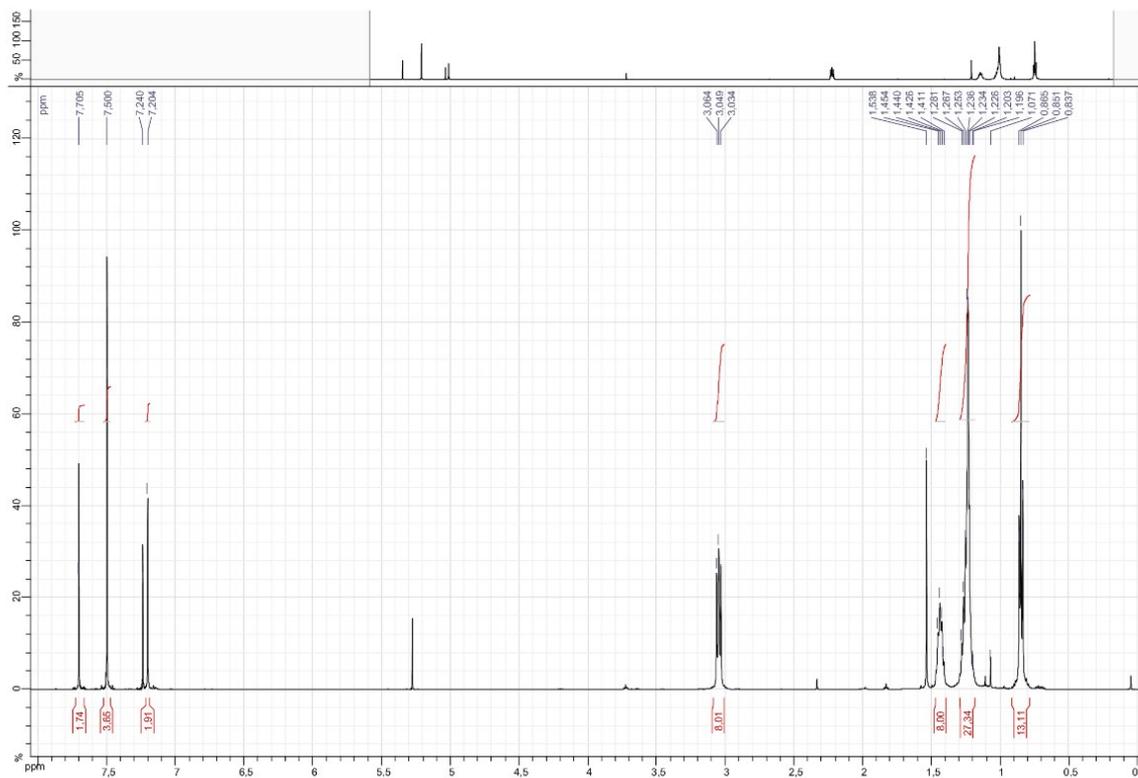
26-a ( $^1\text{H}$ )



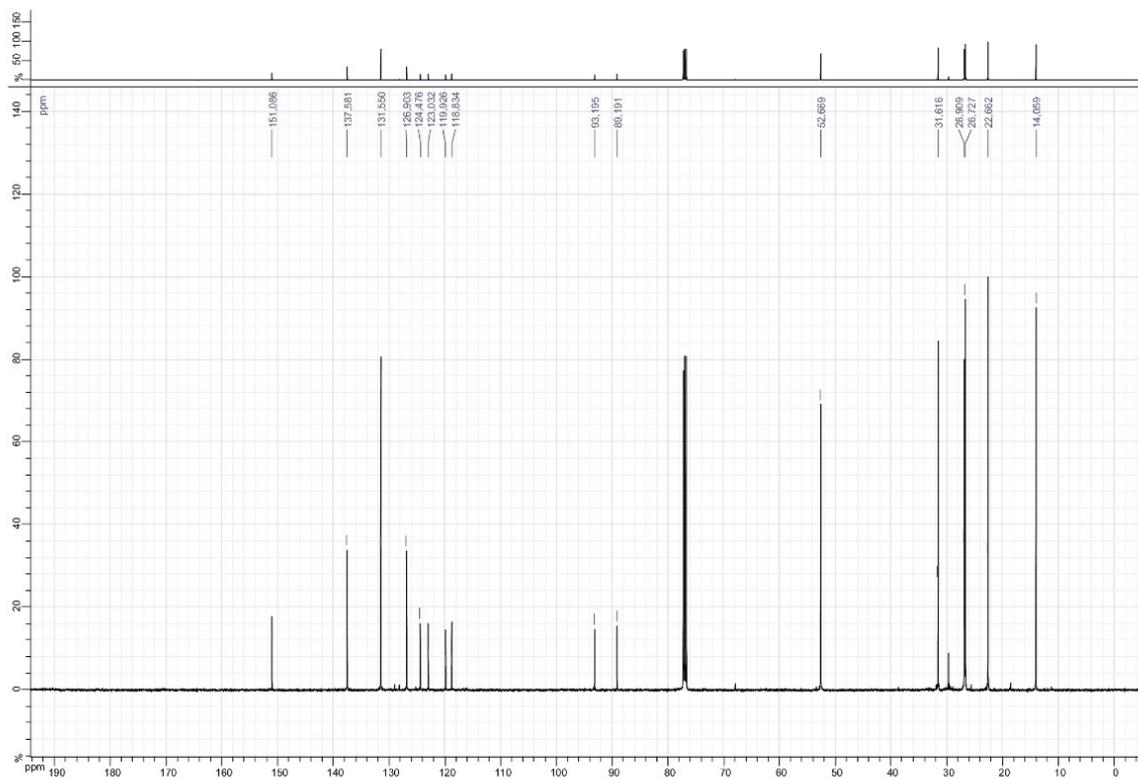
26-a (<sup>13</sup>C)



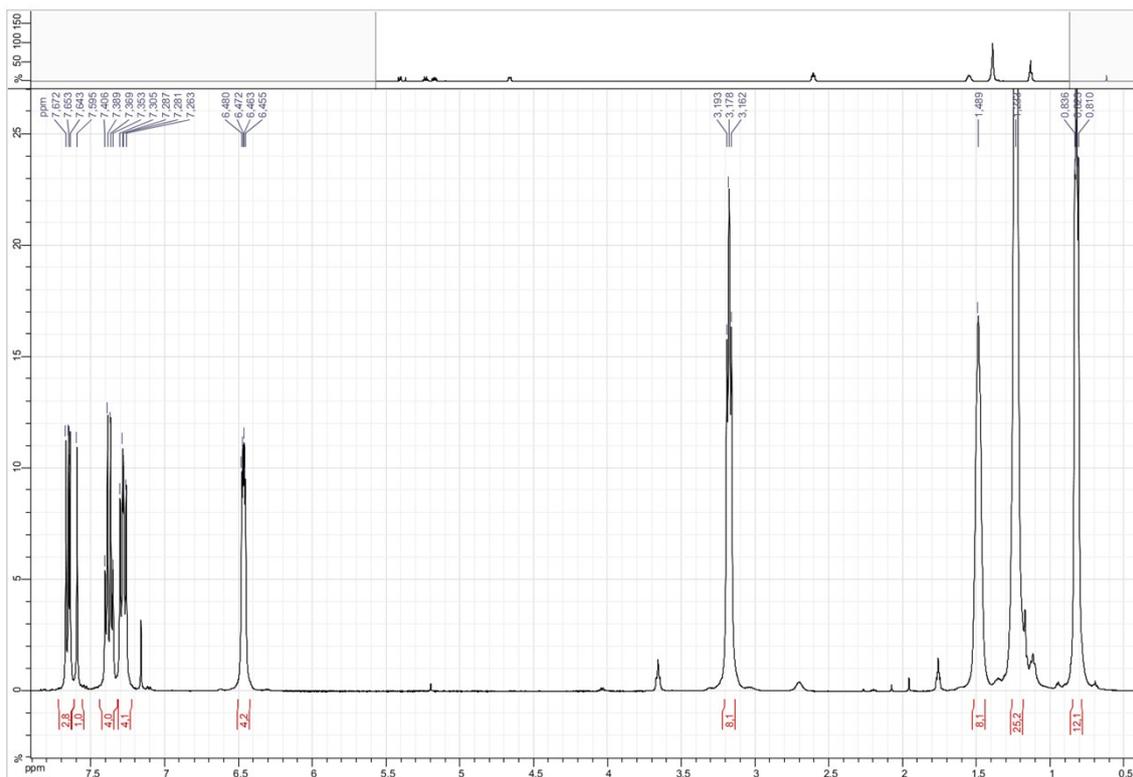
202 (<sup>13</sup>C)



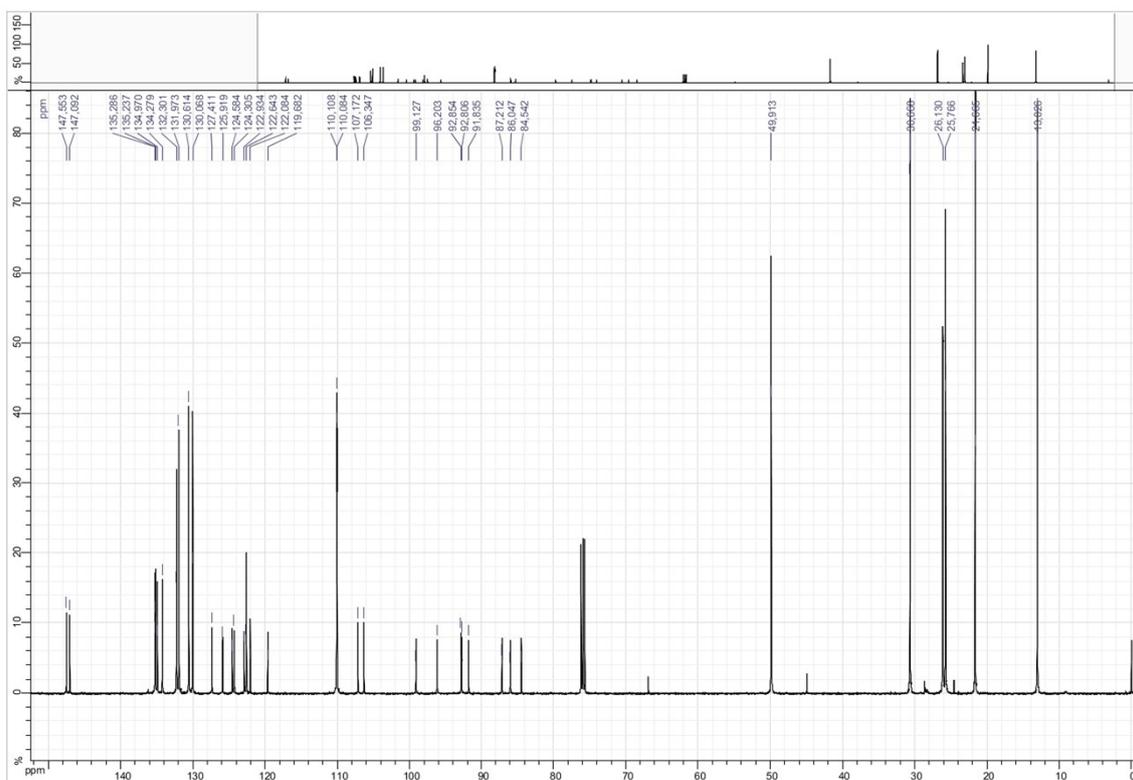
202 (<sup>13</sup>C)



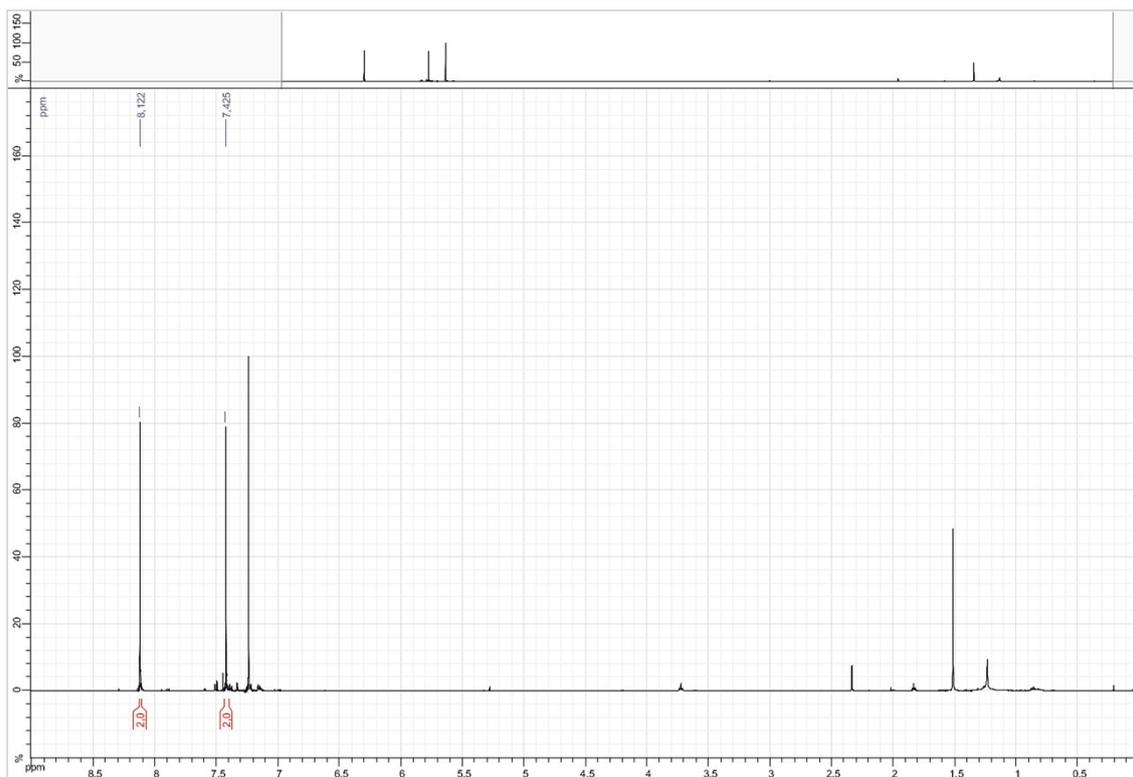
02200 (<sup>1</sup>H)



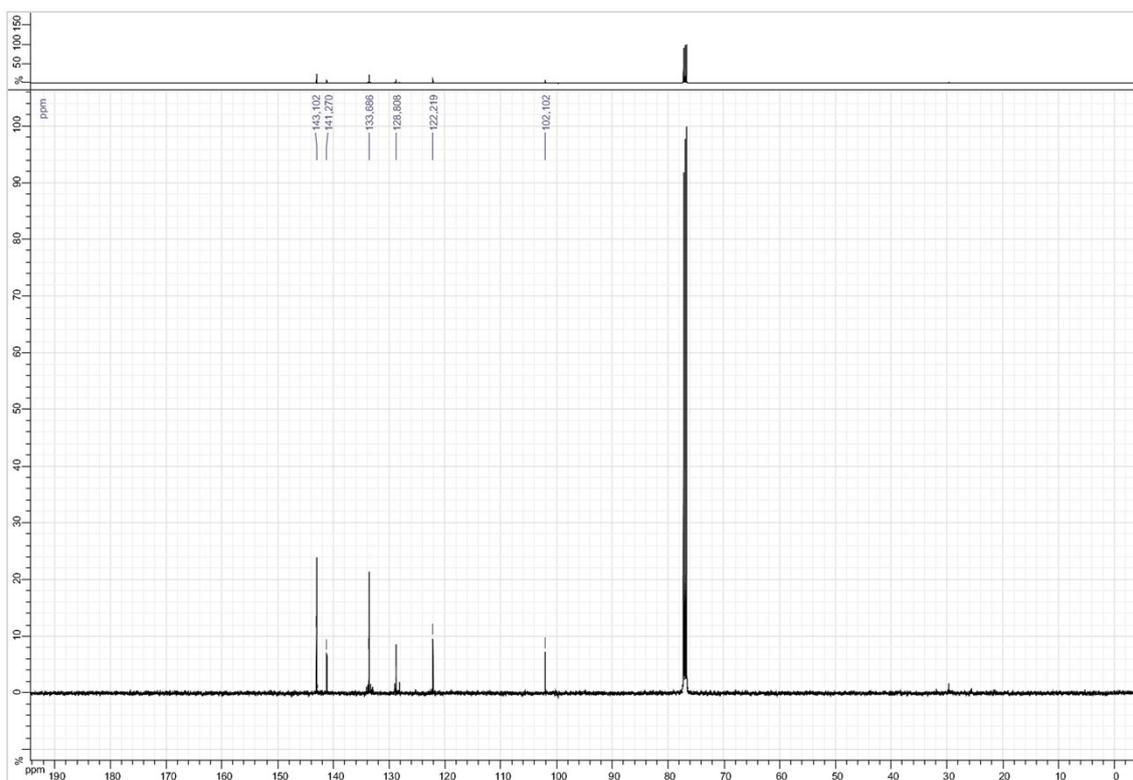
02200 (<sup>13</sup>C)



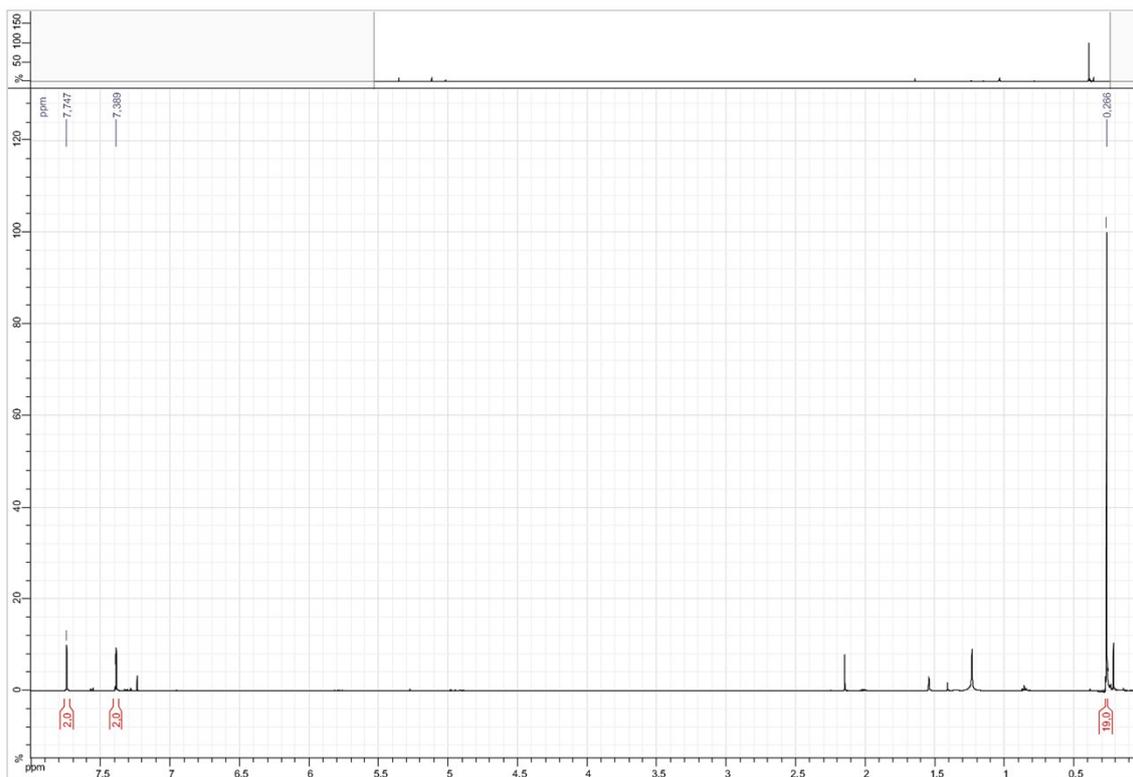
17 (<sup>1</sup>H)



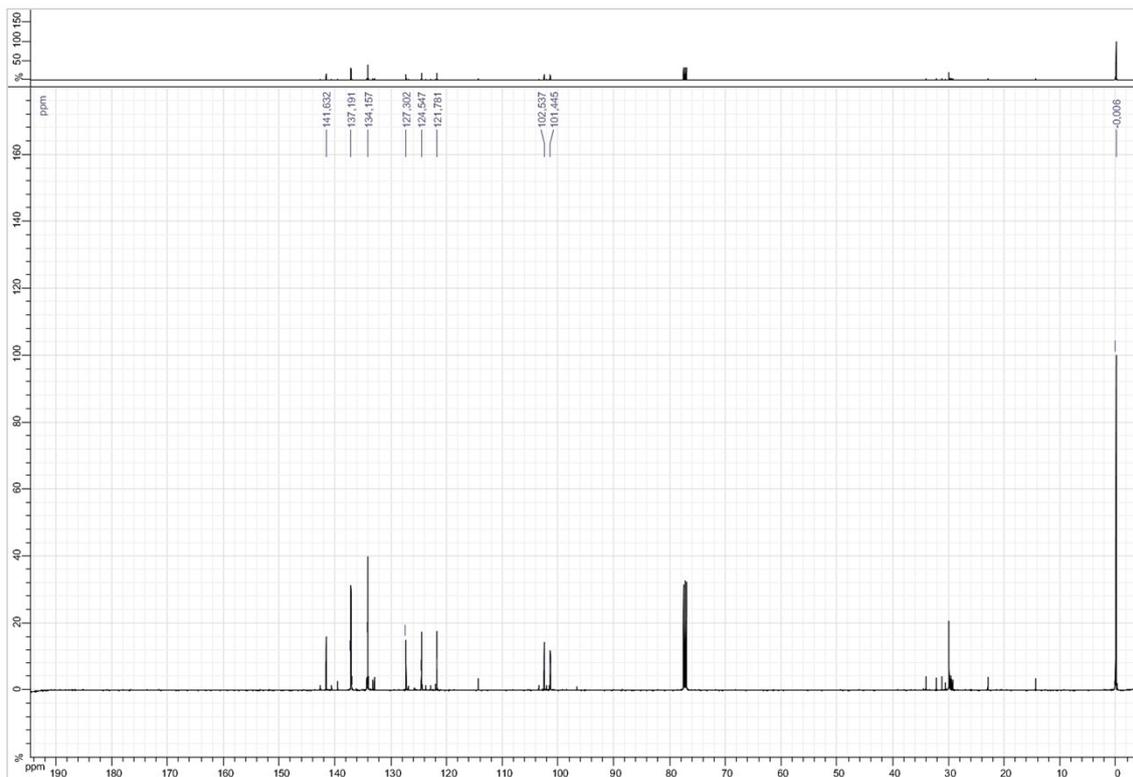
**17 (<sup>13</sup>C)**



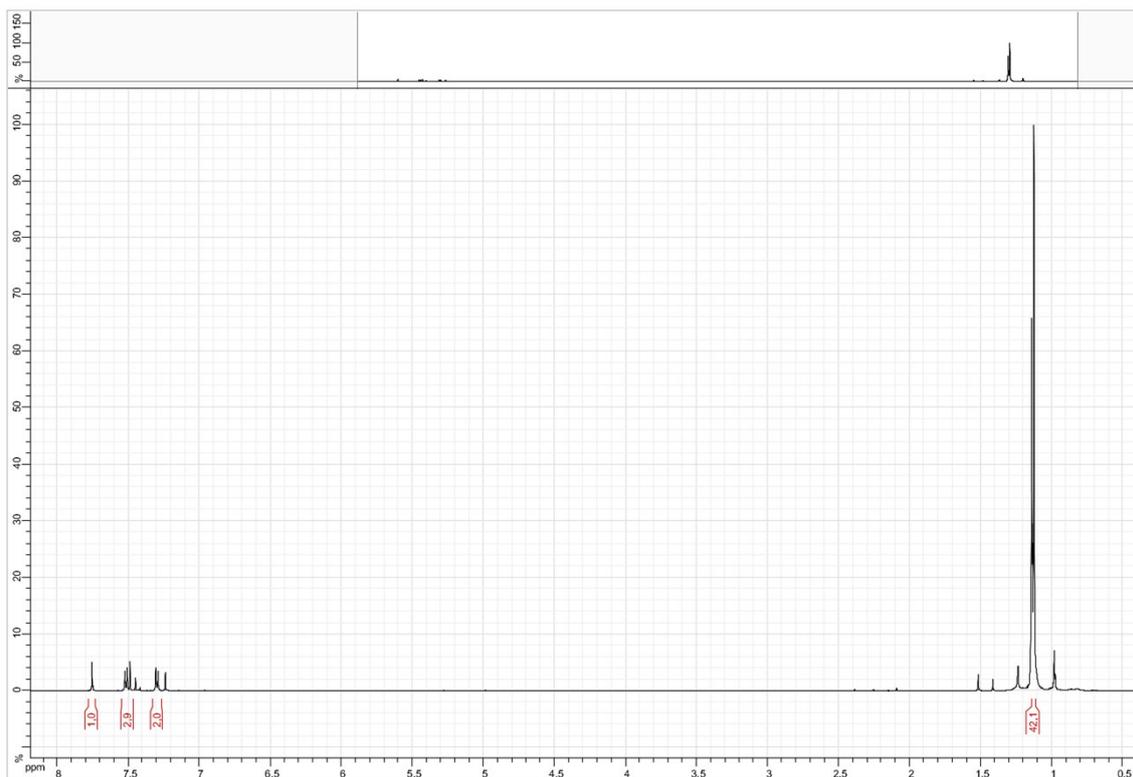
**18 (<sup>1</sup>H)**



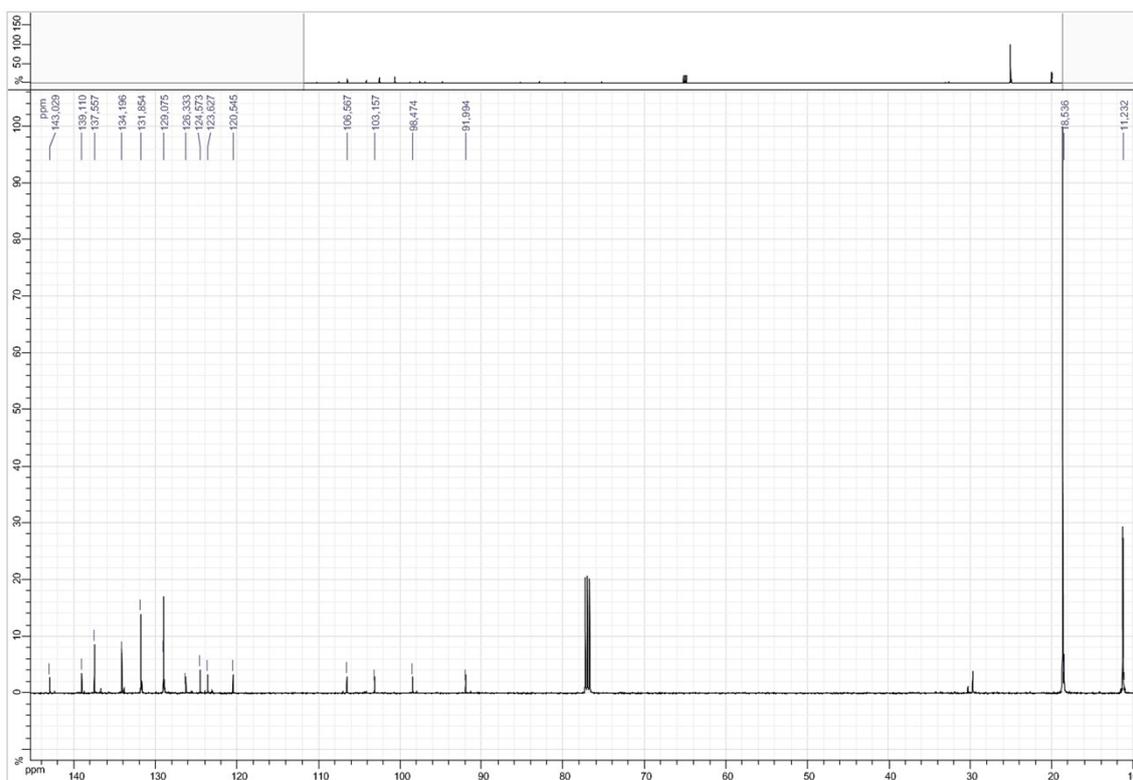
18 (<sup>13</sup>C)



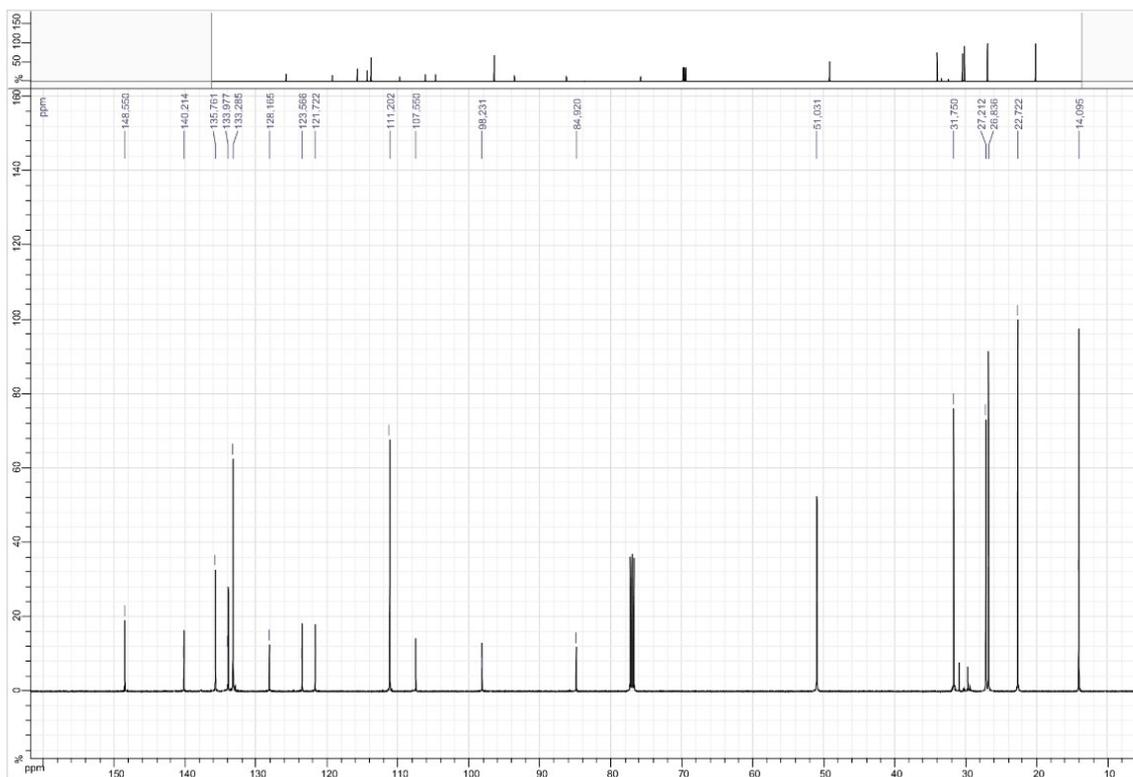
13 (<sup>1</sup>H)



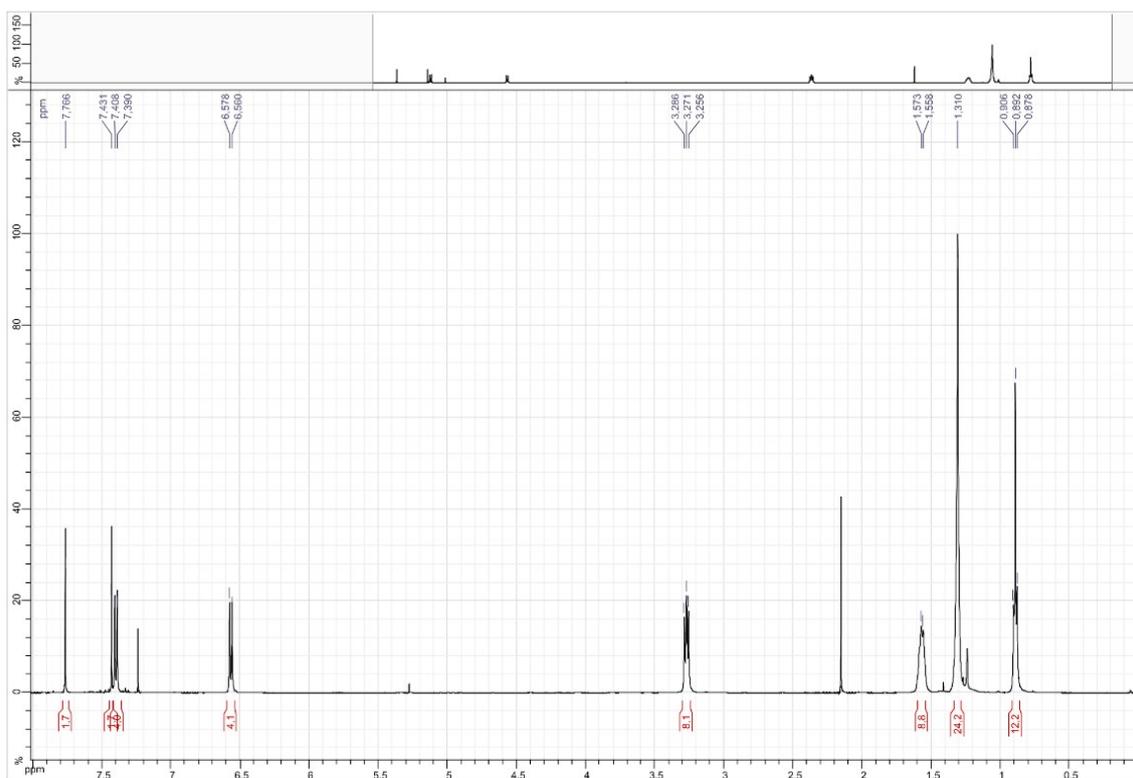
13 (<sup>13</sup>C)



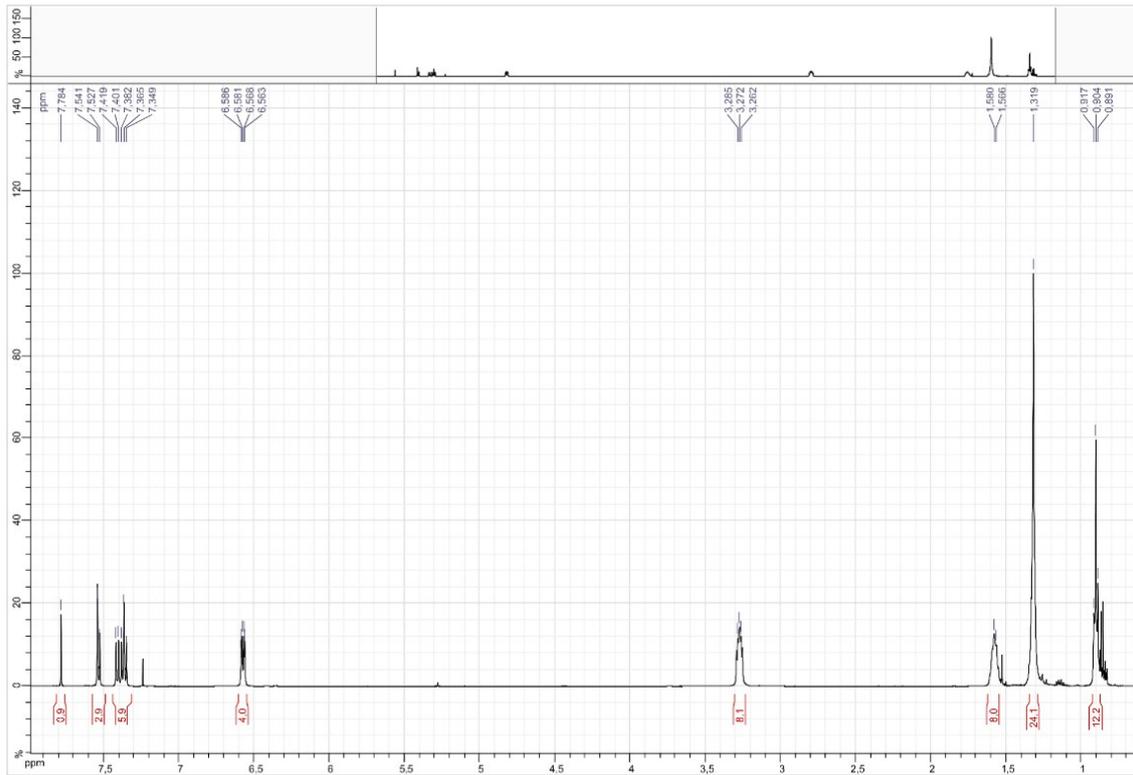
02/20 (<sup>13</sup>C)



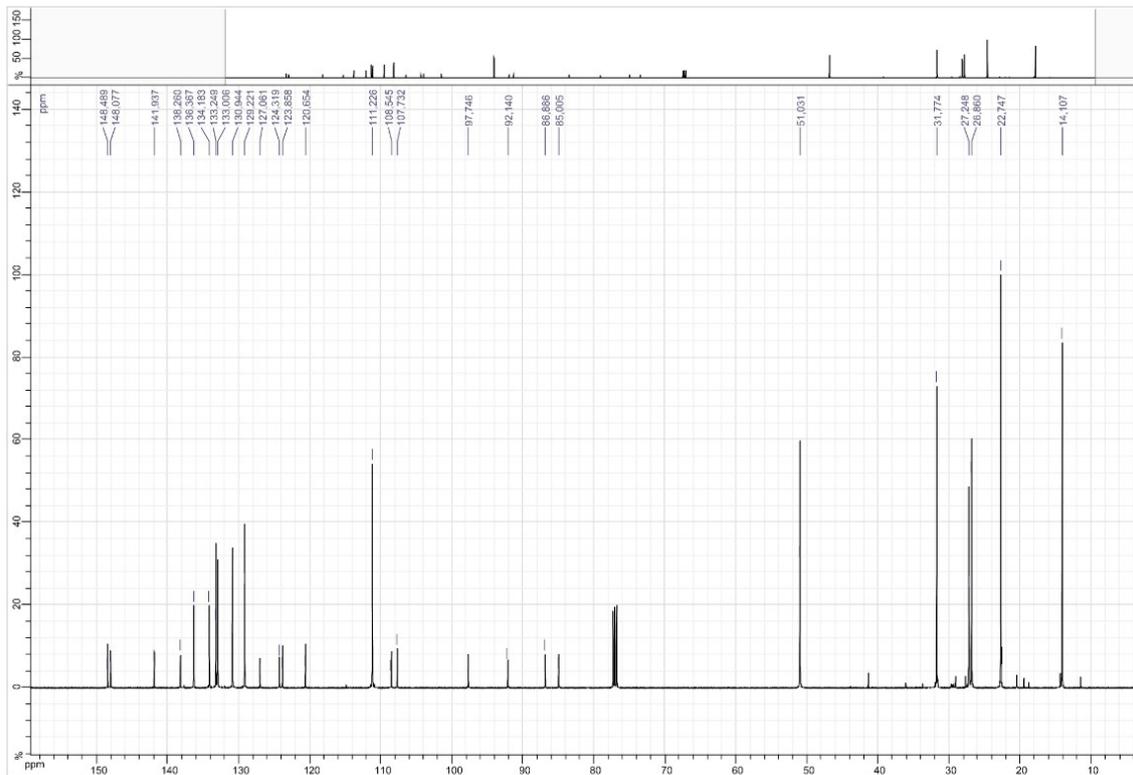
02/20 (<sup>1</sup>H)



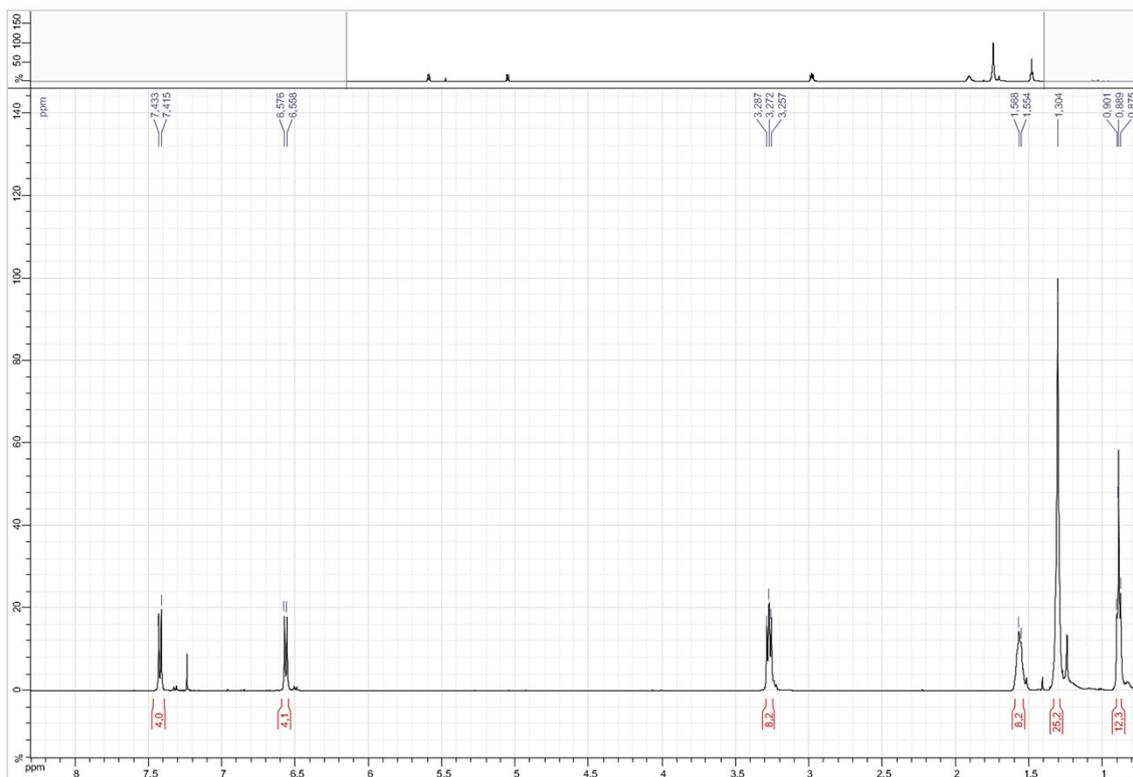
02/00 (<sup>1</sup>H)



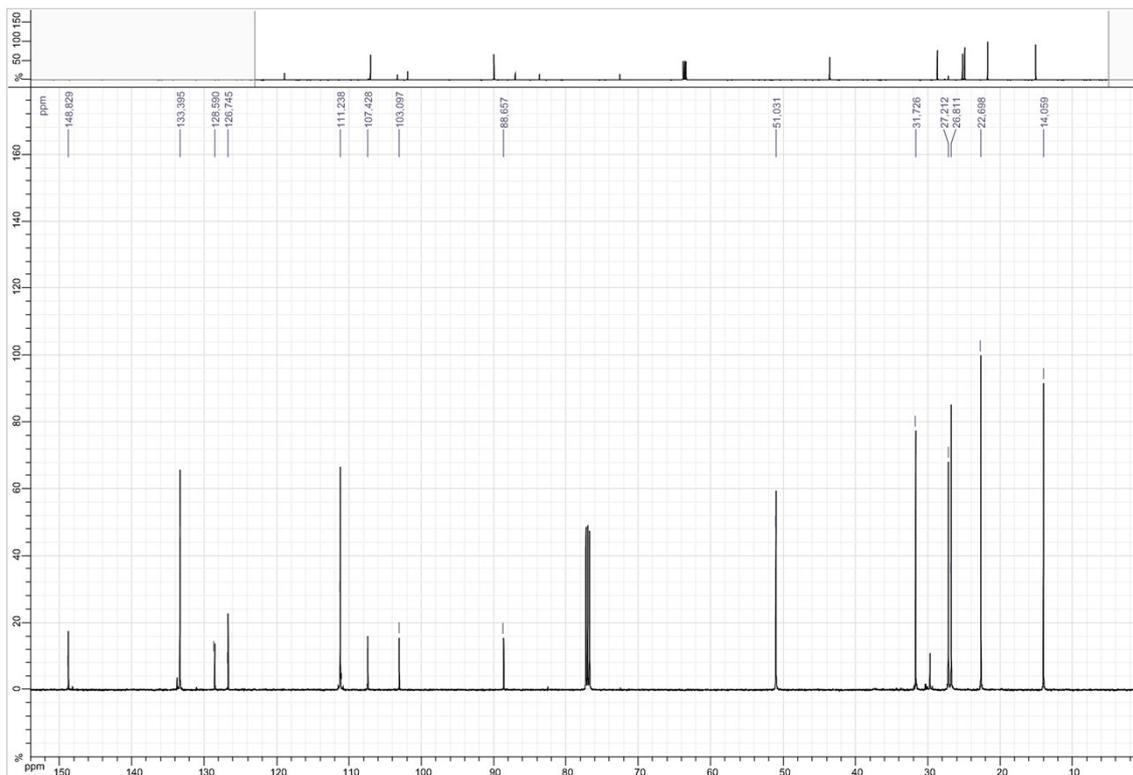
02/00 (<sup>13</sup>C)



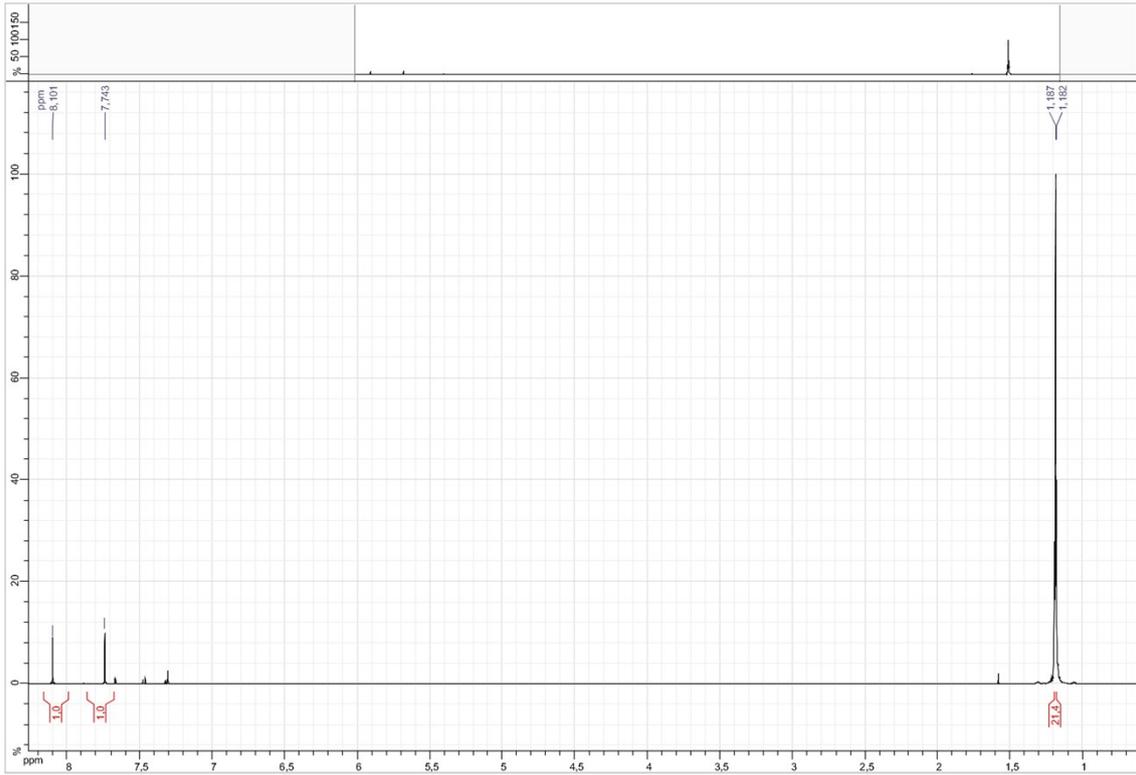
040 (<sup>1</sup>H)



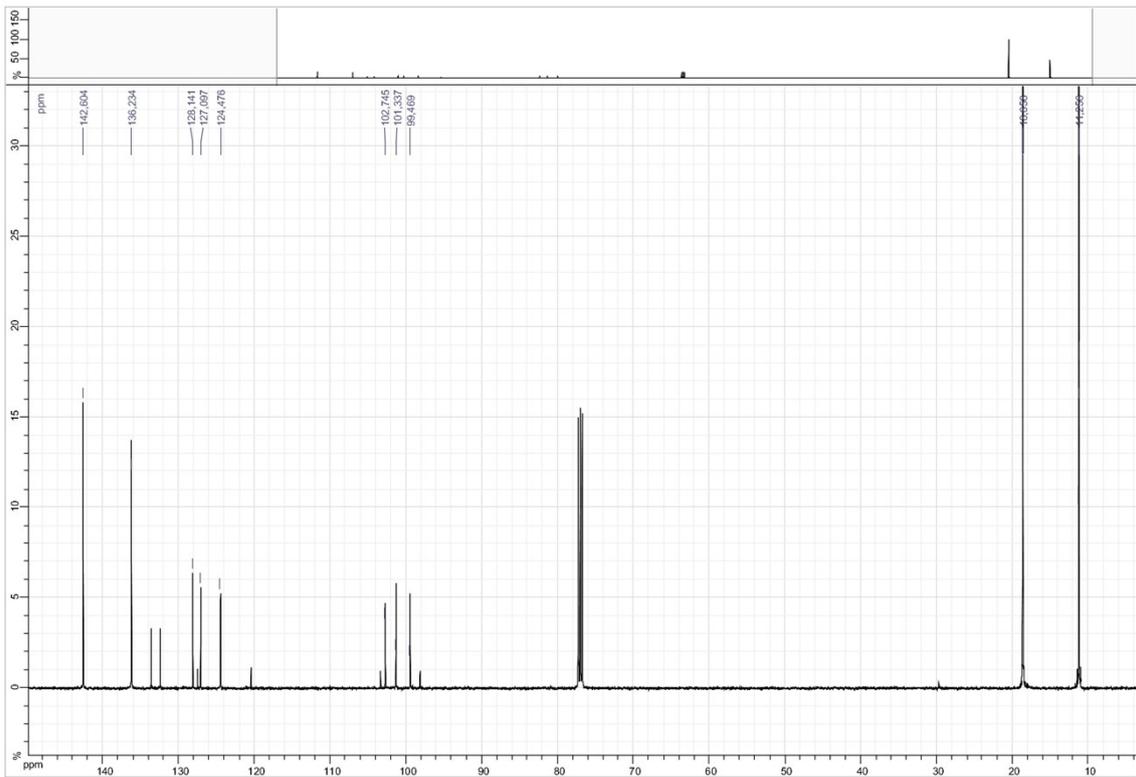
**040 (<sup>13</sup>C)**



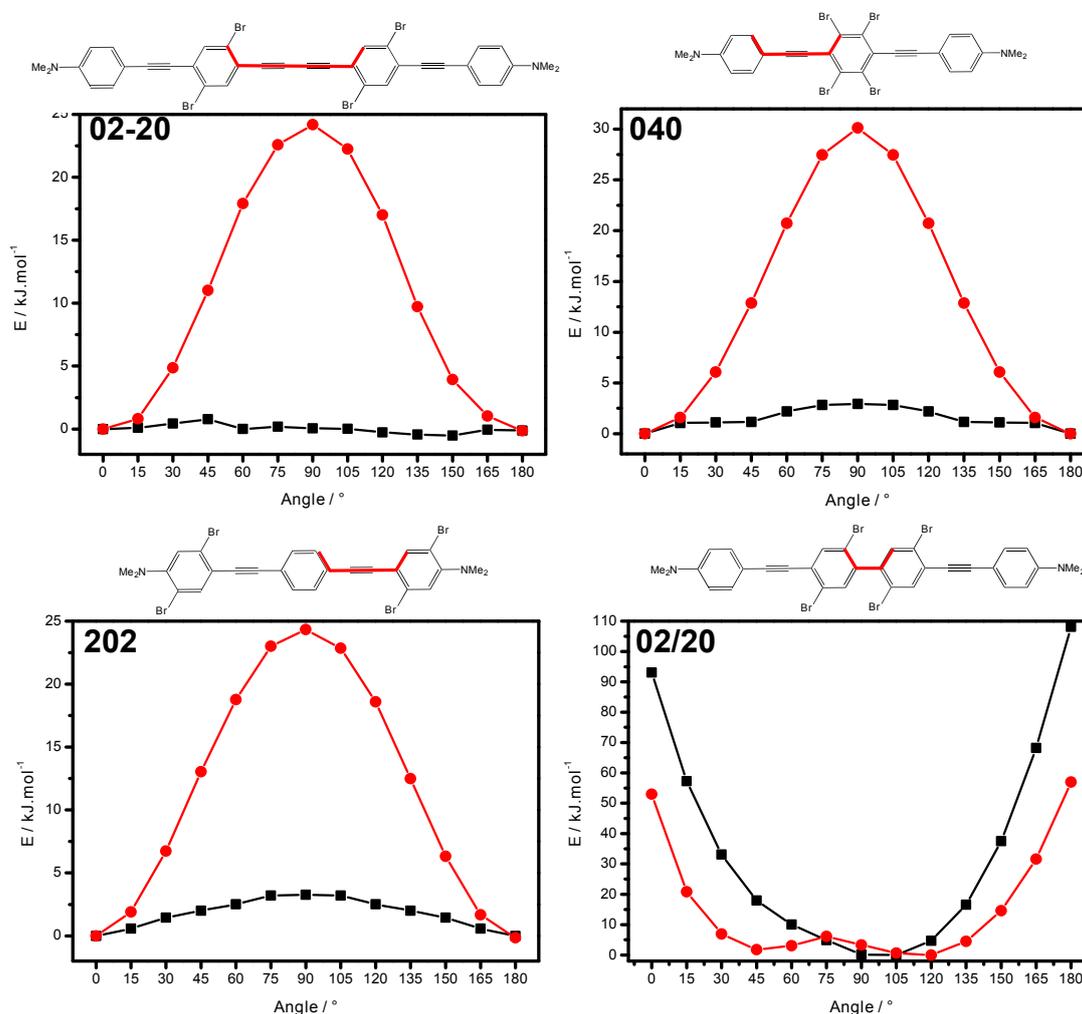
**3 (<sup>1</sup>H)**



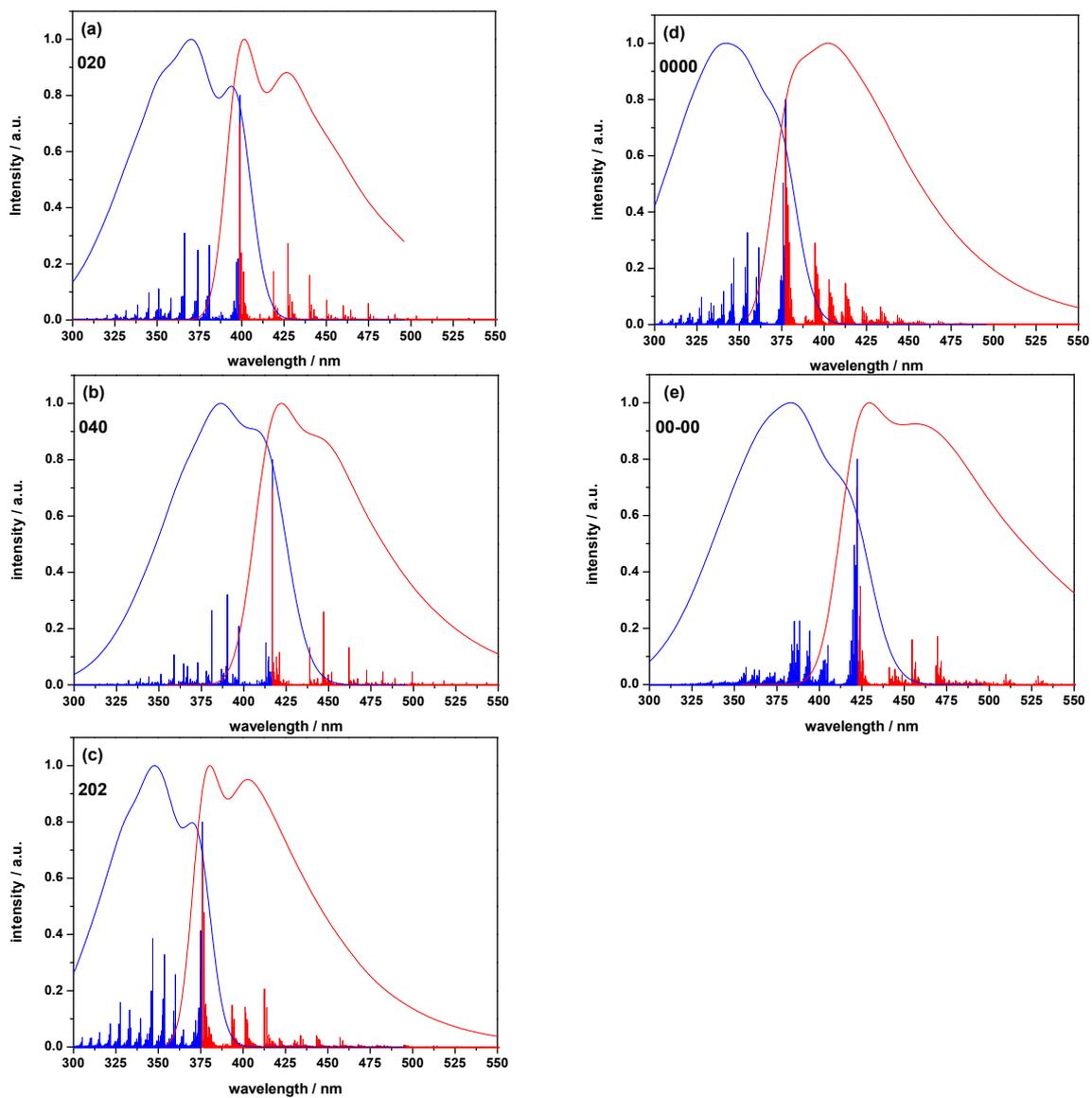
3 (<sup>13</sup>C)



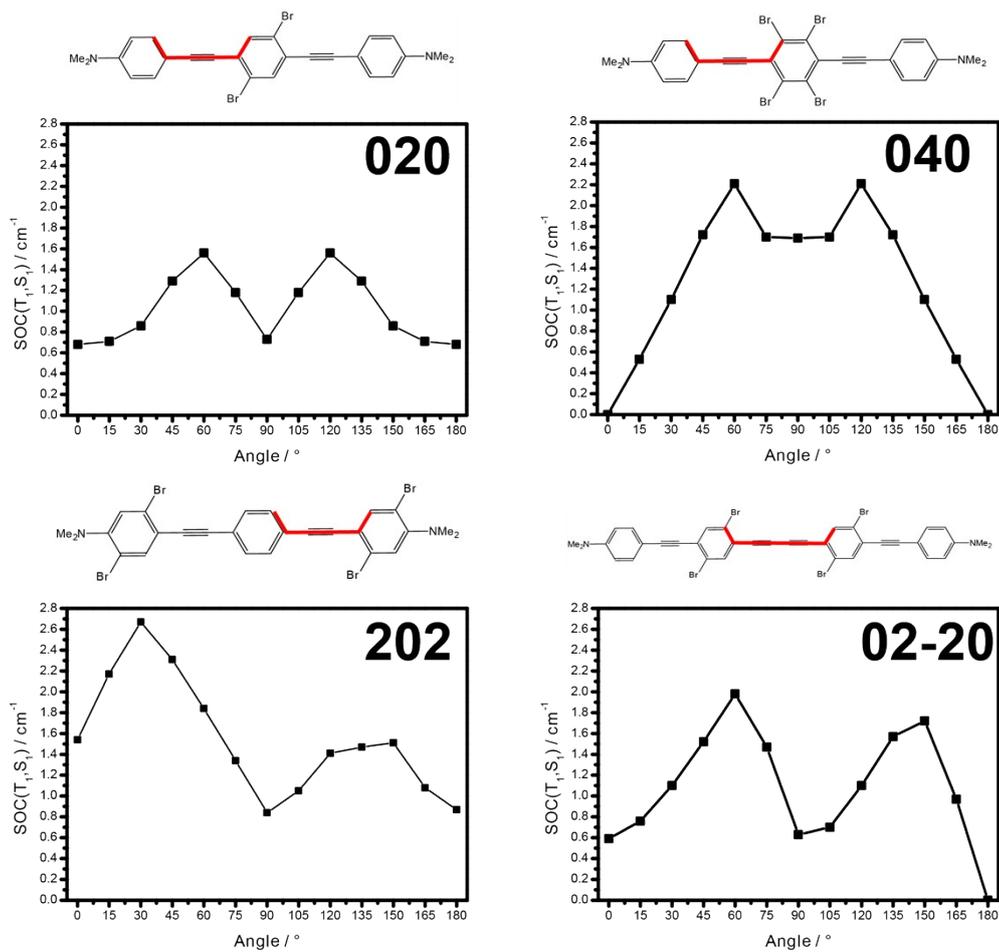
# S4- Computational results



**Figure S3: Potential energy surface scan along the dihedral angle indicated in red both for  $S_0$  (black curve) and  $S_1$  states (red curve).**



**Figure S4 Computed vibrationaly resolved absorption and fluorescence spectra for molecules 020 (a), 040 (b), 202 (c), 0000 (d) and 00-00 (e).**



**Figure S5. Variation of the spin-orbit interaction between  $T_1$  and  $S_1$  as a function of a dihedral angle for 020, 040, 202 and 02-20.**

	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
000	H $\rightarrow$ L 0.66 H-1 $\rightarrow$ L+1 0.19 H-2 $\rightarrow$ L -0.14	H-1 $\rightarrow$ L 0.60 H $\rightarrow$ L+1 0.31
020	H $\rightarrow$ L 0.66 H-1 $\rightarrow$ L+2 0.17 H-2 $\rightarrow$ L -0.13	H-1 $\rightarrow$ L 0.63 H $\rightarrow$ L+2 0.26
040	H $\rightarrow$ L 0.66 H-1 $\rightarrow$ L+3 0.16 H-2 $\rightarrow$ L -0.14	H-1 $\rightarrow$ L 0.64 H $\rightarrow$ L+3 0.24
202	H $\rightarrow$ L 0.65 H-1 $\rightarrow$ L+1 0.19	H-1 $\rightarrow$ L 0.54 H $\rightarrow$ L+1 0.38
00/00	H $\rightarrow$ L 0.61 H-1 $\rightarrow$ L+1 0.26	H-1 $\rightarrow$ L 0.54 H $\rightarrow$ L+1 0.39
02/00	H $\rightarrow$ L 0.53 H-1 $\rightarrow$ L+1 0.28 H-1 $\rightarrow$ L 0.26	H-1 $\rightarrow$ L 0.49 H $\rightarrow$ L+1 0.42
02/20	H $\rightarrow$ L 0.50 H-1 $\rightarrow$ L+1 -0.43	H-1 $\rightarrow$ L 0.49 H $\rightarrow$ L+1 -0.45
0000	H $\rightarrow$ L 0.61 H-1 $\rightarrow$ L+1 0.23 H-2 $\rightarrow$ L -0.21	H-1 $\rightarrow$ L 0.55 H $\rightarrow$ L+1 0.38
0200	H $\rightarrow$ L 0.59 H-1 $\rightarrow$ L+1 0.22 H-2 $\rightarrow$ L -0.22	H-1 $\rightarrow$ L 0.55 H $\rightarrow$ L+1 0.36
0220	H $\rightarrow$ L 0.61 H-1 $\rightarrow$ L+1 0.23 H-2 $\rightarrow$ L -0.22	H-1 $\rightarrow$ L 0.58 H $\rightarrow$ L+1 0.34
00-00	H $\rightarrow$ L 0.59 H-1 $\rightarrow$ L+1 -0.23 H-2 $\rightarrow$ L -0.26	H-1 $\rightarrow$ L 0.54 H $\rightarrow$ L+1 -0.39
02-00	H $\rightarrow$ L 0.55 H-1 $\rightarrow$ L+1 -0.20 H-2 $\rightarrow$ L -0.26	H-1 $\rightarrow$ L 0.53 H $\rightarrow$ L+1 0.36
02-20	H $\rightarrow$ L 0.58 H-1 $\rightarrow$ L+1 -0.24 H-2 $\rightarrow$ L 0.26	H-1 $\rightarrow$ L 0.56 H $\rightarrow$ L+1 -0.36
00000	H $\rightarrow$ L 0.55 H-1 $\rightarrow$ L+1 0.29 H-2 $\rightarrow$ L -0.27	H-1 $\rightarrow$ L 0.45 H $\rightarrow$ L+1 0.41
02000	H $\rightarrow$ L 0.47 H-1 $\rightarrow$ L -0.30 H-2 $\rightarrow$ L 0.27 H-1 $\rightarrow$ L+1 0.24	H-1 $\rightarrow$ L 0.45 H $\rightarrow$ L+1 0.41

00200	H → L	0.54	H-1 → L	0.51
	H-1 → L+1	-0.25	H → L+1	-0.39
	H-2 → L	0.31		
02200	H → L	0.46	H-1 → L	0.46
	H-1 → L+1	-0.23	H → L+1	-0.36
	H-2 → L	0.30	H → L	0.22
	H-1 → L	-0.29		
02020	H → L	0.54	H-1 → L	0.49
	H-1 → L+1	0.28	H → L+1	0.42
	H-2 → L	-0.28		
02220	H → L	0.54	H-1 → L	0.51
	H-1 → L+1	-0.27	H → L+1	-0.39
	H-2 → L	0.30		

**Table S3: Monoelectronic decomposition of the electronic transitions (TD-DFT; cam-B3LYP/6-31+G(d)).**

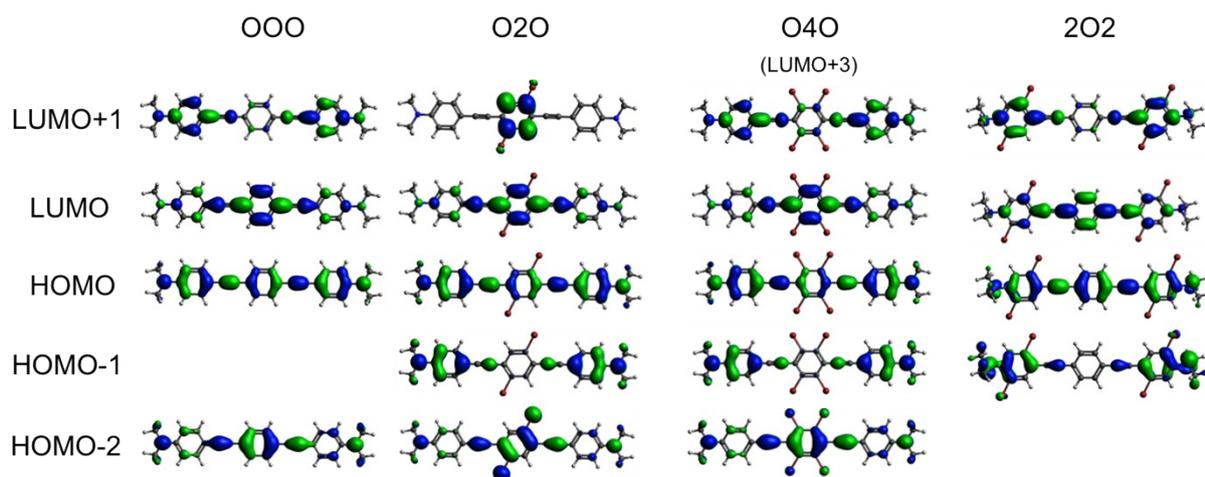


Figure S6. Computed orbitals of the trimer series (cam-B3LYP/6-31+G(d), isosurface 0.03 a.u.)

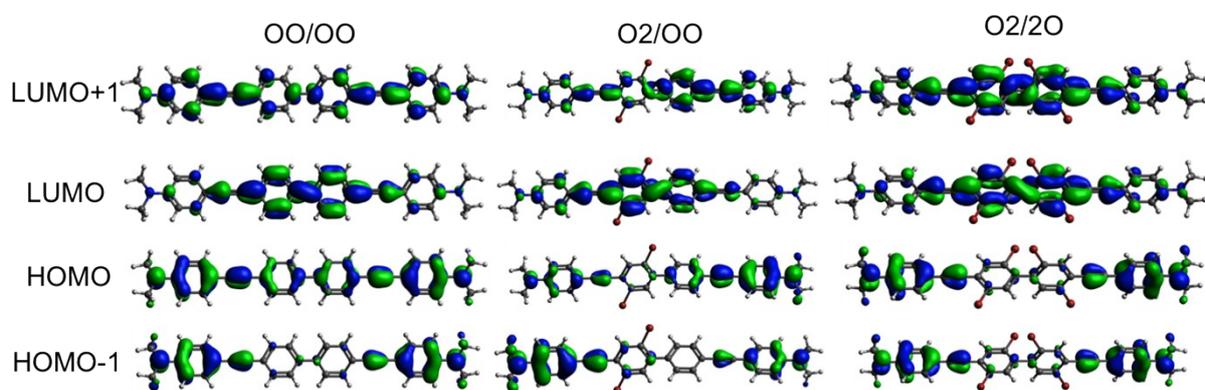


Figure S7. Computed orbitals of the diphenyl series (cam-B3LYP/6-31+G(d), isosurface 0.03 a.u.)

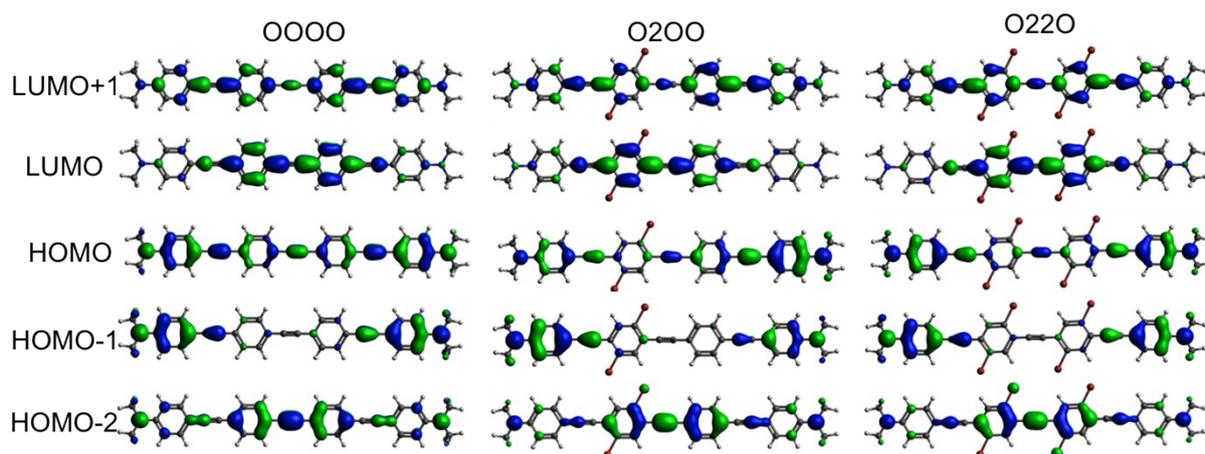


Figure S8. Computed orbitals of the tetramer series (cam-B3LYP/6-31+G(d), isosurface 0.03 a.u.)

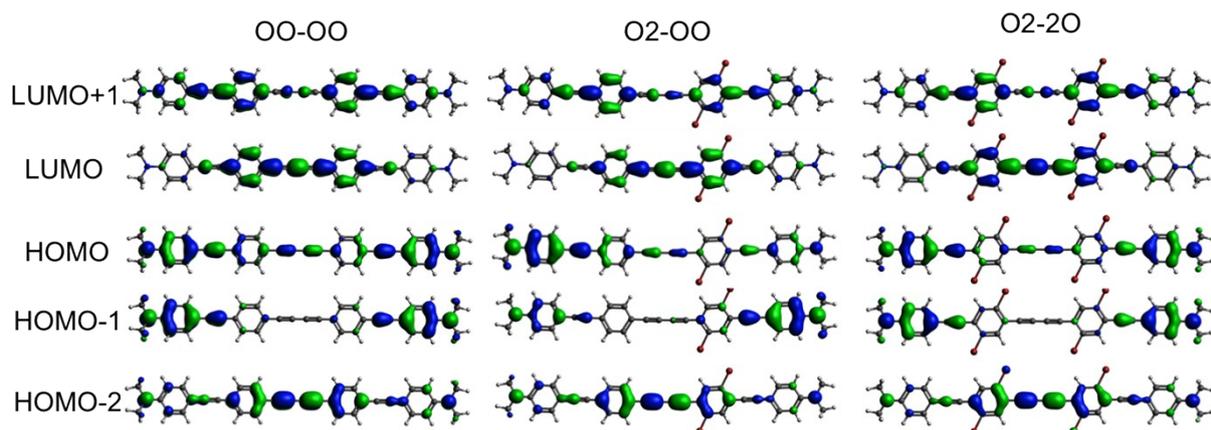


Figure S9. Computed orbitals of the diyne series (cam-B3LYP/6-31+G(d), isosurface 0.03 a.u.)

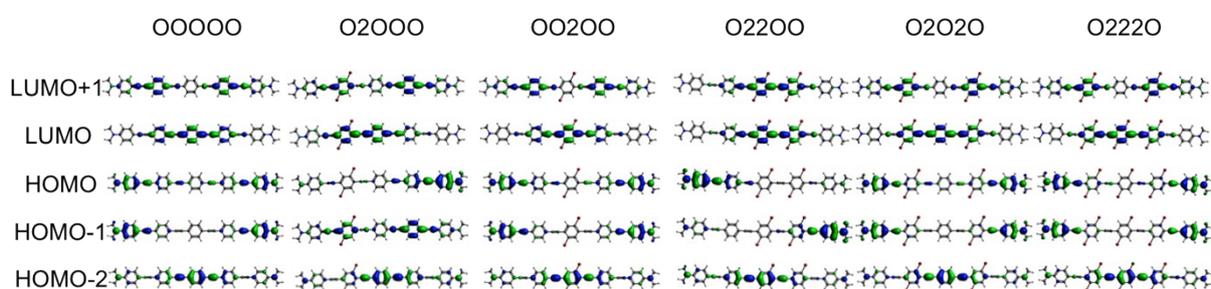


Figure S10. Computed orbitals of the pentamer series (cam-B3LYP/6-31+G(d), isosurface 0.03 a.u.)

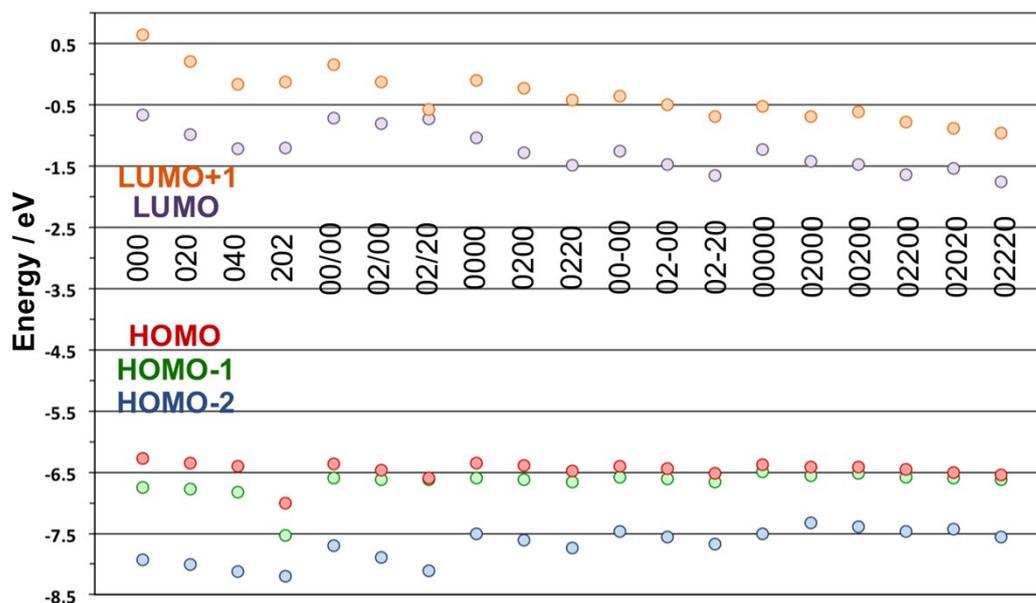


Figure S11. Computed orbital positions (cam-B3LYP/6-31+G(d)).

- [1] P.-H. Lanoe, T. Gallavardin, A. Dupin, O. Maury, P. L. Baldeck, M. Lindgren, C. Monnereau, C. Andraud, *Organic & Biomolecular Chemistry* **2012**, *10*, 6275-6278.
- [2] H. Shen, K. P. C. Vollhardt, *Synlett* **2012**, *2012*, 208-214.
- [3] Y. Kubo, M. Ikeda, A. Sugasaki, M. Takeuchi, S. Shinkai, *Tetrahedron Letters* **2001**, *42*, 7435-7438.
- [4] aJ. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, R. A. Pascal, *Journal of the American Chemical Society* **2004**, *126*, 11168-11169; bJ. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, S. Bernhard, N. Byrne, L. R. Kim, R. A. Pascal, *Journal of the American Chemical Society* **2006**, *128*, 17043-17050.