

New insights about structure/optical waveguide behavior relationships in linear bisethynylbenzenes

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1. Experimental section

1.1. General techniques

All reagents were used as purchased. Reaction with air-sensitive materials were carried out under an argon atmosphere. Microwave irradiations were performed in a Discover® (CEM) focused microwave reactor. Flash chromatography was carried out using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates.

¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance Neo NMR spectrometers operating at 399.77 and 500.16 MHz for ¹H and 100.53 and 125.75 MHz for ¹³C, respectively. All spectra were performed at 298 K using partially deuterated solvents as internal reference. Coupling constants (J) are denoted in hertz (Hz) and chemical shifts (δ) in ppm. Multiplicities are denoted as: s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sext = sextet and m = multiplet.

UV–visible and fluorescence spectroscopy studies in solution state were conducted on a Jasco V-750 spectrophotometer and Jasco FP-8300 spectrofluorometer, respectively. The absorption and emission spectra were recorded in chloroform at concentration of 10⁻⁵ M at room temperature using standard quart cells of 1 cm width and solvents of spectroscopic grade.

The melting points of the solid products were determined using a Büchi model M-569 melting point meter.

MALDI-TOF mass spectra were obtained on a Bruker Autoflex II TOF/TOF spectrometer employing dithranol as matrix. Samples, co-crystallized with the matrix on the probe, were ionized with a nitrogen laser pulse (337 nm) and accelerated under 20 kV with time-delayed extraction before entering the time-of-flight mass spectrometer. Matrix (10 mg/mL) and sample (1 mg/mL) were separately dissolved in tetrahydrofuran and mixed in a matrix/sample ratio ranging from 100:1 to 50:1. Typically, a 5 μL mixture of matrix and sample was applied to a MALDI-TOF MS probe and air-dried. MALDI-TOF MS in positive reflector mode was used for all samples. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700–3200 Da) from Care (Bruker). The applied peak (m/z determination) detection method was the threshold centroid at 50% height of the peak maximum.

SEM images were obtained by a HRSEM Zeiss GeminiSEM 500 operating at 3 kV. The corresponding crystal, obtained by slow diffusion, was deposited onto a glass substrate and the remaining solvent was slowly evaporated.

X-ray diffraction data were collected on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromated MoK α radiation source ($\lambda = 0.71073 \text{ \AA}$). Data were integrated using SAINT¹ and an absorption correction was performed with the program SADABS.² The structure was solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F2 with the WINGX and OLEX2 software packages.³⁻⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.

PL microscopy images were acquired with a Nikon Eclipse Ti inverted microscope with dry objectives (100X N.A. 0.8 and 20X N.A. 0.45) coupled to a Shamrock spectrometer from Andor Technology with a thermoelectrically cooled Newton EM (Andor) CCD. The excitation was obtained by appropriate filtering of the lines from a Xe lamp.

Loss coefficients in fibres were obtained upon exciting the fibres with a pulsed Nd:YAG laser (355 nm, 300 ps, 1 KHz, 30 $\mu\text{J/pulse}$). A set of filters were employed to attenuate the photoexcitation. Detection from the fibre edge was focused in free space on to a 0.5 m length SP2558 Princeton Instruments (Acton Research) spectrometer equipped with a 600 lines/mm grating and a liquid nitrogen cooled CCD.

1.2 Experimental procedures

3b-e, **4a** and **6** are commercially available and were used without further purification. Dibromobenzene **5** was synthesized as described by Devic and col.⁶ From **3b-e**, the arylethynylstannanes **4b-e** were synthesized as previously reported.⁷

- General procedure for the synthesis of derivatives **4**

n-BuLi was added dropwise to a solution of the corresponding acetylene derivative (**3b-e**) in dry THF (-78 °C) under inert atmosphere. The mixture was stirred for 30 min. and then Bu₃SnCl was added dropwise. The reaction mixture was carried out to room temperature and stirred for 2 h. Then water (30 mL) was added to the crude reaction, neutralized with HCl 1M and the organic layers were extracted with dichloromethane

(3x30 mL). The organic layers were dried with MgSO₄, the solvent was removed in vacuo and the product was employed in the next step without previous purification.

- Tributyl((2-(trifluoromethyl)phenyl)ethynyl)stannane (**4b**)

From 1-ethynyl-2-(trifluoromethyl)benzene (**3b**) (0.5 g, 2.94 mmol), n-BuLi (2.75 mL, 4.41 mmol) and Bu₃SnCl (0.96 mL, 3.52 mmol), a brown liquid was obtained (1.28 g, 95%). ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.59 (t, *J* = 7.6 Hz, 2H) 7.43 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 1.62 (quint, *J* = 7.0 Hz, 6H), 1.37 (sext, *J* = 7.2 Hz, 6H), 1.07 (t, *J* = 8.0 Hz, 6H), 0.92 (t, *J* = 7.2 Hz, 9H).

- Tributyl((2-methoxyphenyl)ethynyl)stannane (**4c**)

From 1-ethynyl-2-methoxybenzene (**3c**) (0.5 g, 3.78 mmol), n-BuLi (3.55 mL, 5.67 mmol) and Bu₃SnCl (1.23 mL, 4.54 mmol), a yellow liquid was obtained (1.40 g, 88%). ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (td, *J* = 8.4, 1.6 Hz, 1H), 6.84 (m, 2H), 3.86 (s, 3H), 1.63 (quint, *J* = 7.6 Hz, 6H), 1.38 (sext, *J* = 7.6 Hz, 6H), 1.06 (t, *J* = 8 Hz, 6H), 0.92 (t, *J* = 7.6 Hz, 9H).

- Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (**4d**)

From 1-ethynyl-4-(trifluoromethyl)benzene (**3d**) (0.5 g, 2.94 mmol), n-BuLi (2.75 mL, 4.41 mmol) and Bu₃SnCl (0.96 mL, 3.52 mmol), a yellow liquid was obtained (1.24 g, 92%). ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.53 (bs, 4H), 1.61 (quint, *J* = 7.6 Hz, 6H), 1.37 (sext, *J* = 7.6 Hz, 6H), 1.05 (t, *J* = 7.6 Hz, 6H), 0.92 (t, *J* = 7.6 Hz, 9H).

- Tributyl((4-methoxyphenyl)ethynyl)stannane (**4e**)

From 1-ethynyl-4-methoxybenzene (**3e**) (0.5 g, 3.78 mmol), n-BuLi (3.55 mL, 5.67 mmol) and Bu₃SnCl (1.23 mL, 4.54 mmol), a yellow liquid was obtained (1.35 g, 85%). ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.38 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 1.62 (quint, *J* = 7.6 Hz, 6H), 1.37 (sext, *J* = 7.2 Hz, 6H), 1.05 (t, *J* = 7.6 Hz, 6H), 0.92 (t, *J* = 7.2 Hz, 9H).

- General procedure for the synthesis of derivatives **1a-e**

A mixture of 1,4-dibromo-2,5-bis(trifluoromethyl)benzene (**5**) (0.100 g, 0.27 mmol), the corresponding ethynylstannane **4** (0.69 mmol), PdCl₂(PPh₃)₂ (0.007 g, 0.01 mmol) and

LiCl (0.035 g, 0.08 mmol) was charged under inert atmosphere to a microwave vessel. CH₃CN (1 mL) was added, and the vessel was closed and irradiated at 110 °C for 20 min. The crude reaction was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate to afford the pure products **1a-e**.

- 1,4-bis(phenylethynyl)-2,5-bis(trifluoromethyl)benzene (**1a**)

From tributyl(phenylethynyl)stannane (**4a**) (0.274 g, 0.69 mmol), **1a** was obtained as white solid (0.080 g, 72%) by chromatography, eluting with hexane. M. p.: 145-147 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.96 (s, 2H), 7.57 (m, 4H), 7.40 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, ppm) δ: 134.2 (q, *J*_{C-F}= 31.32 Hz), 132.5, 131.9, 131.3 (q, *J*_{C-F}= 5.2 Hz), 129.5, 128.5, 122.6 (q, *J*_{C-F}= 272.3 Hz), 122.0, 98.4, 84.3. MS calcd for (C₂₄H₁₂F₆) M⁺ 414.0843, found 414.2806.

- 1,4-bis(2-trifluoromethylphenylethynyl)-2,5-bis(trifluoromethyl)benzene (**1b**)

From tributyl(2-trifluoromethylphenylethynyl)stannane (**4b**) (0.322 g, 0.69 mmol), **1b** was obtained as pale yellow solid (0.064 g, 43%) by chromatography, eluting with hexane/ethyl acetate 20:1. M. p.: 176-178 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.98 (s, 2H), 7.73 (d, *J*= 8.1 Hz, 4H), 7.58 (t, *J*= 7.6 Hz, 2H), 7.50 (t, *J*= 7.6 Hz, 2H). ¹³C-NMR (CDCl₃, 100 MHz, ppm) δ: 134.5, 134.3 (q, *J*_{C-F}= 31.3 Hz), 131.9 (q, *J*_{C-F}= 5.1 Hz), 131.8 (q, *J*_{C-F}= 31.0 Hz), 131.6, 129.3, 126.1 (q, *J*_{C-F}= 5.0 Hz), 123.3 (q, *J*_{C-F}= 273.5 Hz), 122.3 (q, *J*_{C-F}= 271.3 Hz), 121.6, 120.0, 94.0, 89.1. MS calcd for (C₂₆H₁₀F₁₂) M⁺ 550.0590, found 550.2815.

- 1,4-bis(2-methoxyphenylethynyl)-2,5-bis(trifluoromethyl)benzene (**1c**)

From tributyl(2-methoxyphenylethynyl)stannane (**4c**) (0.295 g, 0.69 mmol), **1c** was obtained as yellow solid (0.090 g, 70%) by chromatography, eluting with hexane/ethyl acetate 20:1. M. p.: 178-180 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.97 (s, 2H), 7.51 (dd, *J*= 7.6, 1.6 Hz, 2H), 7.37 (td, *J*= 8.4, 1.6 Hz, 2H), 6.97 (td, *J*= 7.2, 1.2 Hz, 2H), 6.93 (d, *J*= 8.4 Hz, 2H), 3.93 (s, 6H). ¹³C-NMR (CDCl₃, 100 MHz, ppm) δ: 160.5, 133.9 (q, *J*_{C-F}= 30.0 Hz), 133.8, 131.3 (q, *J*_{C-F}= 5.2 Hz), 131.0, 122.7 (q, *J*_{C-F}= 270.0 Hz), 121.3, 120.6, 111.4, 110.9, 95.1, 88.3, 55.9. MS calcd for (C₂₆H₁₆F₆O₂) M⁺ 474.1054, found 474.3297.

- 1,4-bis(4-trifluoromethylphenylethynyl)-2,5-bis(trifluoromethyl)benzene (**1d**)

From tributyl(4-trifluoromethylphenylethynyl)stannane (**4d**) (0.322 g, 0.69 mmol), **1d** was obtained as white solid (0.070 g, 47%) by chromatography, eluting with hexane. M. p.: 197-199 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 8.00 (s, 2H), 7.67 (AA'BB' *J*= 8.8 Hz, 8H). ¹³C-NMR (CDCl₃, 125 MHz, ppm) δ: 134.5 (q, *J*_{C-F}= 31.6 Hz), 132.1, 131.5 (q, *J*_{C-F}= 5.2 Hz), 131.2 (q, *J*_{C-F}= 32.3 Hz), 125.5 (q, *J*_{C-F}= 4.0 Hz), 123.7 (q, *J*_{C-F}= 270.5 Hz), 122.4 (q, *J*_{C-F}= 272.4 Hz), 121.1, 96.8, 86.1. MS calcd for (C₂₆H₁₀F₁₂) M⁺ 550.0590, found 550.2367.

- 1,4-bis(4-methoxyphenylethynyl)-2,5-bis(trifluoromethyl)benzene (**1e**)

From tributyl(4-methoxyphenylethynyl)stannane (**4e**) (0.295 g, 0.69 mmol), **1e** was obtained as yellow solid (0.085 g, 63%) by chromatography, eluting with hexane/ethyl acetate 20:1. M. p.: 180-181 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm) δ: 7.91 (s, 2H), 7.51 (d, *J*= 8.5 Hz, 4H), 6.91 (d, *J*= 8.5 Hz, 4H), 3.85 (s, 6H). ¹³C-NMR (CDCl₃, 125 MHz, ppm) δ: 160.6, 133.7 (q, *J*_{C-F}= 31.1 Hz), 133.5, 131.0 (q, *J*_{C-F}= 5.2 Hz), 122.7 (q, *J*_{C-F}= 272.7 Hz), 121.1, 114.2, 114.1, 98.6, 83.5, 55.4. MS calcd for (C₂₆H₁₆F₆O₂) M⁺ 474.1054, found 474.3210.

- General procedure for the synthesis of derivatives **2a-e**

A mixture of 1,4-dibromo-2,5-bis(methoxy)benzene (**6**) (0.100 g, 0.34 mmol), the corresponding ethynylstannane **4a-e** (0.87 mmol), PdCl₂(PPh₃)₂ (0.010 g, 0.013 mmol) and LiCl (0.043 g, 1.01 mmol) was charged under an inert atmosphere to a microwave vessel. CH₃CN (1 mL) was added, and the vessel was closed and irradiated at 110 °C for 20 min. The crude reaction was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate to afford the pure products **2a-e**.

- 1,4-bis(phenylethynyl)-2,5-dimethoxybenzene (**2a**)

From tributyl(phenylethynyl)stannane (**4a**) (0.343 g, 0.87 mmol), **2a** was obtained as yellow solid (0.080 g, 70%) by chromatography, eluting with hexane/ethyl acetate 20:1. M. p.: 175-177 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm) δ: 7.57 (dd, *J*= 7.9, 2.4, 4H), 7.35 (m, 6H), 7.04 (s, 2H), 3.91 (s, 6H). ¹³C-NMR (CDCl₃, 100 MHz, ppm) δ: 153.9, 131.7, 128.4, 128.3, 123.2, 115.7, 113.4, 95.0, 85.6, 56.5. MS calcd for (C₂₄H₁₈O₂) M⁺ 338.1307, found 338.3123.

- 1,4-bis(2-trifluoromethylphenylethynyl)-2,5-dimethoxybenzene (**2b**)

From tributyl(2-trifluoromethylphenylethynyl)stannane (**4b**) (0.404 g, 0.87 mmol), **2b** was obtained as white solid (0.092 g, 60%) by chromatography, eluting with hexane/ethyl acetate 9:1. M. p.: 123-124 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.70 (t, *J* = 8.6 Hz, 4H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.03 (s, 2H), 3.91 (s, 6H). ¹³C-NMR (CDCl₃, 125 MHz, ppm) δ: 154.3, 133.9, 131.4 (q, *J*_{C-F} = 30.3 Hz) 131.3, 128.1, 125.9 (q, *J*_{C-F} = 5.2 Hz), 123.6 (q, *J*_{C-F} = 271.9 Hz), 121.5, 115.9, 113.7, 91.3, 91.0, 56.3. MS calcd for (C₂₆H₁₆F₆O₂) M⁺ 474.1054, found 474.2917.

- 1,4-bis(2-methoxyphenylethynyl)-2,5-dimethoxybenzene (**2c**)

From tributyl(2-methoxyphenylethynyl)stannane (**4c**) (0.370 g, 0.87 mmol), **2c** was obtained as white solid (0.103 g, 77%) by chromatography, eluting with hexane/ethyl acetate 6:1. M. p.: 125-127 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.53 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.31 (td, *J* = 7.5, 1.7 Hz, 2H), 7.06 (s, 2H), 6.94 (td *J* = 7.6, 0.8 Hz, 2H), 6.91 (d *J* = 8.4 Hz, 2H), 3.94 (s, 6H), 3.91 (s, 6H). ¹³C-NMR (CDCl₃, 125 MHz, ppm) δ: 159.9, 153.9, 133.6, 129.9, 120.4, 115.6, 113.5, 112.4, 110.6, 91.4, 89.8, 56.6, 55.9. MS calcd for (C₂₆H₂₂O₄) M⁺ 398.1518, found 398.4101.

- 1,4-bis(4-trifluoromethylphenylethynyl)-2,5-dimethoxybenzene (**2d**)

From tributyl(4-(trifluoromethyl)phenylethynyl)stannane (**4d**) (0.404 g, 0.87 mmol), **2d** was obtained as yellow solid (0.093 g, 63%) by chromatography, eluting with hexane/ethyl acetate 20:1. M. p.: 172-174 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.64 (AA'BB', *J* = 8.2 Hz, 8H), 7.06 (s, 2H), 3.92 (s, 6H). ¹³C-NMR (CDCl₃, 100 MHz, ppm) δ: 154.1, 131.9, 130.1 (q, *J*_{C-F} = 32.5 Hz), 127.0, 125.3 (q, *J*_{C-F} = 3.9 Hz), 123.9 (q, *J*_{C-F} = 270.6 Hz) 115.7, 113.3, 93.8, 87.9, 56.5. MS calcd for (C₂₆H₁₆F₆O₂) M⁺ 474.1054, found 474.3445.

- 1,4-bis(4-methoxyphenylethynyl)-2,5-dimethoxybenzene (**2e**)

From tributyl(4-methoxyphenylethynyl)stannane (**4e**) (0.370 g, 0.87 mmol), **2e** was obtained as yellow solid (0.085 g, 63%) by chromatography, eluting with hexane/ethyl acetate 6:1. M. p.: 165-166 °C. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ: 7.51 (d, *J* = 8.8 Hz, 4H), 7.01 (s, 2H), 6.88 (d, *J* = 8.8 Hz, 4H), 3.90 (s, 6H), 3.84 (s, 6H). ¹³C-NMR (CDCl₃, 125 MHz, ppm) δ: 159.7, 153.8, 133.2, 115.5, 115.4, 114.0, 113.3, 95.0, 84.4, 56.5, 55.3. MS calcd for (C₂₆H₂₂O₄) M⁺ 398.1518, found 398.5129.

2. PL in solid state

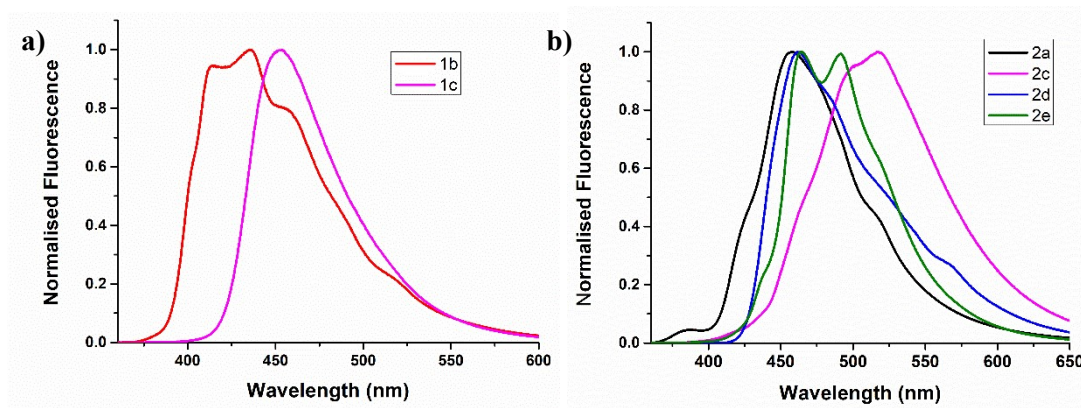
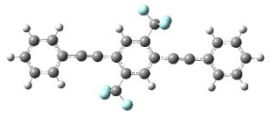
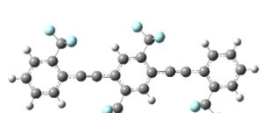
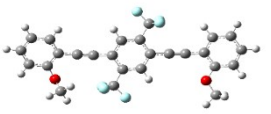


Figure S1: PL spectra of derivatives a) **1** and b) **2** in solid state.

3. Computational study

Computational calculations were carried out by means of Gaussian 16 software.⁸ The calculations were performed within the Density Functional Theory (DFT) framework.⁹ Geometry optimizations were carried out using the B3LYP¹⁰ functional and the medium-sized 6-31G (d,p) basis set as implemented in the Gaussian 16 program. Solvent effects were estimated using the polarizable continuum model¹¹ (PCM) within the self-consistent reaction field (SCRF) approach using chloroform ($\epsilon = 4.7113$) as solvent.

Table S1: Topologies of the HOMO-LUMO molecular orbitals and the HOMO-LUMO gap value calculated at B3LYP/6-31G(d,p) according to the CPCM method employing chloroform as solvent for derivatives **1** and **2**.

Compound	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
 1a	-5.87	-2.35	3.52
 1b	-6.10	-2.59	3.51
 1c	-5.72	-2.29	3.43

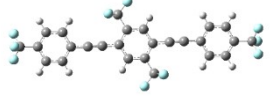
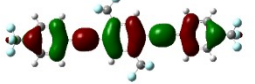
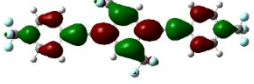
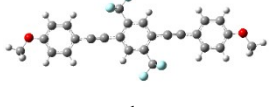
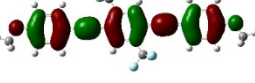

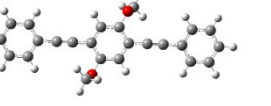
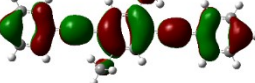
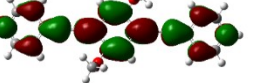
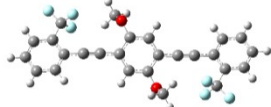
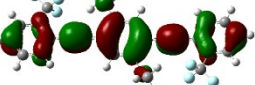
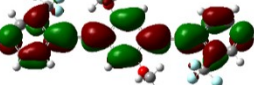
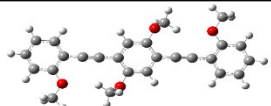
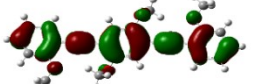
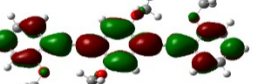
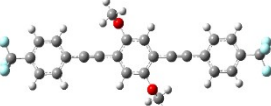

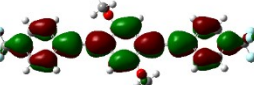
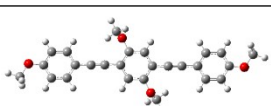
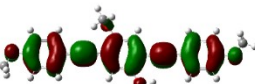
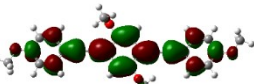
 1d	 -6.15	 -2.62	3.53
 1e	 -5.48	 -2.18	3.30
 2a	 5.58	 1.92	3.66
 2b	 -5.81	 -2.15	3.66
 2c	 -5.36	 -1.82	3.54
 2d	 -5.83	 -2.24	3.59
 2e	 5.26	 1.74	3.52

Table S2: Cartesian coordinates for optimized geometry of **1a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.770332	1.168735	-0.000136
2	6	0	-0.614601	1.247077	-0.000136
3	6	0	-1.418841	0.090944	-0.000044
4	6	0	-0.770310	-1.168372	0.000049
5	6	0	0.614623	-1.246714	0.000049
6	6	0	1.418862	-0.090581	-0.000043
7	1	0	-1.096465	2.216144	-0.000208
8	1	0	1.096487	-2.215782	0.000120
9	6	0	2.832056	-0.219167	-0.000044
10	6	0	-2.832035	0.219537	-0.000048
11	6	0	-4.043129	0.335305	-0.000050
12	6	0	4.043146	-0.334984	-0.000039
13	6	0	5.463761	-0.424969	0.000021
14	6	0	6.109087	-1.678207	0.000197

15	6	0	6.241861	0.751442	-0.000101
16	6	0	7.499500	-1.747470	0.000250
17	6	0	7.631198	0.670061	-0.000046
18	1	0	5.742968	1.714961	-0.000238
19	6	0	8.263378	-0.576837	0.000129
20	1	0	7.988928	-2.716513	0.000386
21	1	0	8.222827	1.580302	-0.000142
22	6	0	-5.463773	0.424853	0.000004
23	6	0	-6.241517	-0.751794	0.000152
24	6	0	-6.109477	1.677895	-0.000091
25	6	0	-7.630879	-0.670834	0.000204
26	1	0	-5.742334	-1.715163	0.000225
27	6	0	-7.499911	1.746737	-0.000038
28	6	0	-8.263435	0.575873	0.000109
29	1	0	-8.222233	-1.581254	0.000319
30	1	0	-7.989632	2.715631	-0.000112
31	6	0	1.585036	2.440222	-0.000232
32	6	0	-1.585013	-2.439860	0.000146
33	9	0	0.803246	3.541291	-0.000324
34	9	0	2.385323	2.522076	1.086186
35	9	0	2.385338	2.521905	-1.086653
36	9	0	-2.385310	-2.521545	1.086569
37	9	0	-0.803220	-3.540927	0.000235
38	9	0	-2.385302	-2.521715	-1.086271
39	1	0	-5.512782	2.584051	-0.000205
40	1	0	5.512118	-2.584182	0.000290
41	1	0	-9.347506	0.634682	0.000150
42	1	0	9.347431	-0.635974	0.000171

Table S3: Cartesian coordinates for optimized geometry of **1b**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.469041	1.319936	0.000012
2	6	0	-0.894435	1.066294	0.000015
3	6	0	-1.395357	-0.249857	0.000018
4	6	0	-0.469049	-1.319946	0.000015
5	6	0	0.894426	-1.066304	0.000011
6	6	0	1.395348	0.249847	0.000010
7	1	0	-1.597556	1.889216	0.000017
8	1	0	1.597548	-1.889225	0.000010
9	6	0	2.799890	0.450240	0.000007
10	6	0	-2.799898	-0.450255	0.000021
11	6	0	-4.009550	-0.566927	0.000034
12	6	0	4.009544	0.566899	0.000013
13	6	0	5.420455	0.745997	-0.000017
14	6	0	6.318656	-0.349433	-0.000020
15	6	0	5.945647	2.052079	-0.000041
16	6	0	7.693069	-0.124207	-0.000047
17	6	0	7.321491	2.264066	-0.000069
18	1	0	5.256748	2.889602	-0.000038

19	6	0	8.197179	1.177946	-0.000072
20	1	0	8.369849	-0.969977	-0.000049
21	1	0	7.708401	3.277946	-0.000088
22	1	0	9.270031	1.339135	-0.000093
23	6	0	-5.420464	-0.745999	0.000010
24	6	0	-5.945676	-2.052073	0.000009
25	6	0	-6.318650	0.349444	-0.000009
26	6	0	-7.321522	-2.264042	-0.000011
27	1	0	-5.256787	-2.889606	0.000025
28	6	0	-7.693066	0.124237	-0.000029
29	6	0	-8.197195	-1.177908	-0.000031
30	1	0	-7.708446	-3.277916	-0.000012
31	1	0	-8.369834	0.970016	-0.000043
32	1	0	-9.270049	-1.339083	-0.000047
33	6	0	5.788657	-1.760754	0.000009
34	6	0	-5.788630	1.760756	-0.000007
35	9	0	6.782639	-2.675091	-0.000001
36	9	0	5.020004	-2.012306	1.085824
37	9	0	5.019956	-2.012334	-1.085765
38	9	0	-5.019963	2.012314	1.085796
39	9	0	-5.019935	2.012306	-1.085792
40	9	0	-6.782598	2.675109	-0.000022
41	6	0	0.962175	2.747317	0.000012
42	6	0	-0.962184	-2.747326	0.000017
43	9	0	-0.055651	3.632824	0.000011
44	9	0	1.721869	3.011698	1.086310
45	9	0	1.721871	3.011697	-1.086285
46	9	0	-1.721878	-3.011706	1.086315
47	9	0	0.055642	-3.632834	0.000015
48	9	0	-1.721881	-3.011707	-1.086279

Table S4: Cartesian coordinates for optimized geometry of **1c**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.699986	1.518871	-0.010887
2	6	0	-0.686993	1.537293	0.000118
3	6	0	-1.442404	0.348919	0.036669
4	6	0	-0.739013	-0.880211	0.068590
5	6	0	0.648043	-0.899369	0.057286
6	6	0	1.403056	0.289124	0.015058
7	1	0	-1.209854	2.484603	-0.023119
8	1	0	1.171441	-1.846273	0.082676
9	6	0	2.819076	0.220608	0.001801
10	6	0	-2.860434	0.429447	0.037628
11	6	0	-4.071922	0.542810	0.026318
12	6	0	4.034170	0.153664	-0.010530
13	6	0	5.453491	0.150759	-0.028029
14	6	0	6.159726	1.367684	-0.072708
15	6	0	7.579118	-1.041866	-0.020229

16	6	0	7.550650	1.387579	-0.091098
17	1	0	5.590426	2.291201	-0.092669
18	6	0	8.252765	0.181016	-0.064664
19	1	0	8.147067	-1.963563	-0.000586
20	1	0	8.081523	2.332951	-0.125715
21	1	0	9.338478	0.183249	-0.078634
22	6	0	-5.487511	0.684969	0.030852
23	6	0	-6.085770	1.891759	0.449439
24	6	0	-7.469131	2.037047	0.448721
25	1	0	-5.446757	2.706744	0.773044
26	6	0	-7.708102	-0.217919	-0.399658
27	6	0	-8.281611	0.981959	0.022882
28	1	0	-7.913444	2.972020	0.774401
29	1	0	-8.322585	-1.042879	-0.745524
30	1	0	-9.361430	1.093898	0.015813
31	6	0	-6.322181	-0.373336	-0.400948
32	6	0	6.180869	-1.069176	-0.001661
33	8	0	-5.769584	-1.535293	-0.881766
34	8	0	5.433499	-2.201017	0.040716
35	6	0	-5.511038	-2.542186	0.108411
36	6	0	6.103831	-3.460582	0.069008
37	1	0	-5.097383	-3.397641	-0.427033
38	1	0	-4.781516	-2.194888	0.845712
39	1	0	-6.437278	-2.837868	0.614901
40	1	0	6.735072	-3.556629	0.959375
41	1	0	5.316838	-4.213995	0.099953
42	1	0	6.713986	-3.607996	-0.828983
43	6	0	1.458830	2.823445	-0.052759
44	6	0	-1.493717	-2.185393	0.139091
45	9	0	0.630331	3.889868	-0.073734
46	9	0	2.264901	2.968968	1.022945
47	9	0	2.245427	2.911172	-1.148881
48	9	0	-2.242168	-2.263545	1.266111
49	9	0	-2.336710	-2.340828	-0.905344
50	9	0	-0.666072	-3.251631	0.142523

Table S5: Cartesian coordinates for optimized geometry of **1d**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.724134	1.198443	-0.000494
2	6	0	-0.662648	1.222871	0.006460
3	6	0	-1.419071	0.035232	0.007152
4	6	0	-0.724135	-1.198526	0.000521
5	6	0	0.662646	-1.222954	-0.006433
6	6	0	1.419070	-0.035315	-0.007126
7	1	0	-1.182370	2.172131	0.011512
8	1	0	1.182369	-2.172214	-0.011485
9	6	0	2.836569	-0.107753	-0.014207
10	6	0	-2.836570	0.107669	0.014229

11	6	0	-4.050786	0.173403	0.020161
12	6	0	4.050785	-0.173483	-0.020144
13	6	0	5.473322	-0.201635	-0.025854
14	6	0	6.172791	-1.424828	-0.028939
15	6	0	6.198851	1.007404	-0.031994
16	6	0	7.562577	-1.435967	-0.035000
17	6	0	7.588031	0.990117	-0.038264
18	1	0	5.661227	1.949130	-0.034367
19	6	0	8.271389	-0.230449	-0.039687
20	1	0	8.097102	-2.379123	-0.043011
21	1	0	8.141906	1.922099	-0.048975
22	6	0	-5.473322	0.201606	0.025861
23	6	0	-6.198893	-1.007407	0.031990
24	6	0	-6.172749	1.424824	0.028943
25	6	0	-7.588073	-0.990072	0.038246
26	1	0	-5.661302	-1.949151	0.034364
27	6	0	-7.562535	1.436011	0.034990
28	6	0	-8.271388	0.230517	0.039666
29	1	0	-8.141980	-1.922035	0.048948
30	1	0	-8.097027	2.379186	0.042998
31	6	0	1.490152	2.500630	-0.000602
32	6	0	-1.490154	-2.500713	0.000629
33	9	0	0.666580	3.569873	0.005853
34	9	0	2.291193	2.608191	1.082535
35	9	0	2.281491	2.613836	-1.090290
36	9	0	-2.281495	-2.613918	1.090315
37	9	0	-0.666581	-3.569956	-0.005825
38	9	0	-2.291192	-2.608274	-1.082509
39	1	0	-5.619410	2.357326	0.028982
40	1	0	5.619484	-2.357349	-0.028971
41	6	0	-9.774347	0.245101	-0.012922
42	6	0	9.774349	-0.244979	0.012886
43	9	0	-10.291328	1.349866	0.569903
44	9	0	-10.312783	-0.829229	0.606542
45	9	0	-10.231512	0.227773	-1.289199
46	9	0	10.312741	0.829362	-0.606595
47	9	0	10.231525	-0.227622	1.289158
48	9	0	10.291363	-1.349733	-0.569931

Table S6: Cartesian coordinates for optimized geometry of **1e**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.730627	-1.117379	0.000053
2	6	0	-0.655991	-1.151380	0.000057
3	6	0	-1.425012	0.029161	0.000046
4	6	0	-0.734285	1.266826	0.000033
5	6	0	0.652285	1.300819	0.000030
6	6	0	1.421351	0.120262	0.000041
7	1	0	-1.167892	-2.104973	0.000067

8	1	0	1.164188	2.254411	0.000019
9	6	0	2.836728	0.204332	0.000041
10	6	0	-2.840434	-0.054143	0.000052
11	6	0	-4.055546	-0.131966	0.000055
12	6	0	4.051767	0.283328	0.000039
13	6	0	5.471292	0.335338	0.000002
14	6	0	6.159390	1.569786	0.000048
15	6	0	6.226474	-0.852773	-0.000082
16	6	0	7.543099	1.606469	0.000015
17	6	0	7.617963	-0.822296	-0.000118
18	1	0	5.709979	-1.807045	-0.000121
19	6	0	8.285309	0.411905	-0.000068
20	1	0	8.078009	2.550254	0.000052
21	1	0	8.168353	-1.754870	-0.000186
22	6	0	-5.475382	-0.174691	0.000018
23	6	0	-6.224029	1.024982	0.000061
24	6	0	-6.170475	-1.397978	-0.000056
25	6	0	-7.607488	0.994079	0.000030
26	1	0	-5.700656	1.975385	0.000121
27	6	0	-7.562210	-1.435432	-0.000088
28	6	0	-8.289710	-0.235897	-0.000045
29	1	0	-8.188121	1.910447	0.000064
30	1	0	-8.066282	-2.393803	-0.000145
31	6	0	1.503170	-2.414043	0.000079
32	6	0	-1.506859	2.563579	0.000008
33	9	0	0.686661	-3.490287	0.000055
34	9	0	2.301100	-2.523231	-1.086254
35	9	0	2.301025	-2.523223	1.086469
36	9	0	-2.304657	2.672618	-1.086386
37	9	0	-0.690276	3.639693	0.000023
38	9	0	-2.304713	2.672632	1.086359
39	1	0	-5.611073	-2.327701	-0.000089
40	1	0	5.593488	2.495448	0.000113
41	8	0	-9.645661	-0.156172	-0.000069
42	8	0	9.635629	0.558749	-0.000099
43	6	0	-10.400099	-1.367488	-0.000154
44	6	0	10.449239	-0.613719	-0.000112
45	1	0	-10.194143	-1.966165	0.894212
46	1	0	-11.447499	-1.065792	-0.000167
47	1	0	-10.194093	-1.966071	-0.894571
48	1	0	11.480374	-0.260412	-0.000077
49	1	0	10.273140	-1.221841	0.894224
50	1	0	10.273185	-1.221791	-0.894491

Table S7: Cartesian coordinates for optimized geometry of **2a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.719098	-1.187166	0.196684
2	6	0	0.669591	-1.205051	0.201656

3	6	0	1.419071	-0.027106	0.009614
4	6	0	0.719091	1.187000	-0.196811
5	6	0	-0.669598	1.204886	-0.201784
6	6	0	-1.419078	0.026941	-0.009739
7	1	0	1.179220	-2.148663	0.361615
8	1	0	-1.179228	2.148498	-0.361746
9	6	0	-2.839560	0.067376	0.001439
10	6	0	2.839552	-0.067542	-0.001570
11	6	0	4.055669	-0.126382	-0.006585
12	6	0	-4.055675	0.126240	0.006468
13	6	0	-5.479197	0.190207	0.018036
14	6	0	-6.143268	1.409240	-0.230838
15	6	0	-6.245396	-0.964943	0.278258
16	6	0	-7.534328	1.465901	-0.218769
17	6	0	-7.635930	-0.897237	0.288005
18	1	0	-5.739005	-1.904896	0.471526
19	6	0	-8.284922	0.315592	0.039992
20	1	0	-8.034550	2.410066	-0.411781
21	1	0	-8.215343	-1.793035	0.489903
22	6	0	5.479199	-0.190185	-0.018018
23	6	0	6.245290	0.965051	-0.278174
24	6	0	6.143386	-1.409141	0.230918
25	6	0	7.635833	0.897504	-0.287796
26	1	0	5.738810	1.904947	-0.471491
27	6	0	7.534454	-1.465645	0.218974
28	6	0	8.284940	-0.315251	-0.039721
29	1	0	8.215162	1.793366	-0.489646
30	1	0	8.034765	-2.409753	0.412033
31	8	0	1.403255	2.355110	-0.440285
32	8	0	-1.403262	-2.355276	0.440154
33	6	0	1.868731	3.035738	0.734190
34	6	0	-1.868745	-3.035897	-0.734322
35	1	0	2.569023	2.414052	1.302007
36	1	0	2.381512	3.933567	0.385534
37	1	0	1.029006	3.321446	1.378591
38	1	0	-2.569048	-2.414211	-1.302126
39	1	0	-1.029026	-3.321594	-1.378734
40	1	0	-2.381516	-3.933733	-0.385669
41	1	0	5.558514	-2.300783	0.431644
42	1	0	-5.558313	2.300815	-0.431615
43	1	0	9.369519	-0.363613	-0.048178
44	1	0	-9.369495	0.364077	0.048545

Table S8: Cartesian coordinates for optimized geometry of **2b**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.881513	1.016970	0.399749
2	6	0	-0.488253	1.248207	0.383275
3	6	0	-1.395599	0.244255	-0.008751

4	6	0	-0.881687	-1.016173	-0.401099
5	6	0	0.488075	-1.247440	-0.384568
6	6	0	1.395426	-0.243512	0.007536
7	1	0	-0.857990	2.219907	0.691122
8	1	0	0.857846	-2.219116	-0.692454
9	6	0	2.792632	-0.503920	0.026364
10	6	0	-2.792844	0.504462	-0.027282
11	6	0	-3.986912	0.737271	-0.029688
12	6	0	3.986649	-0.737008	0.029164
13	6	0	5.371344	-1.071049	0.046919
14	6	0	6.394923	-0.092353	-0.004202
15	6	0	5.745949	-2.427028	0.119977
16	6	0	7.734520	-0.476212	0.022293
17	6	0	7.087189	-2.798427	0.146223
18	1	0	4.966810	-3.180340	0.158610
19	6	0	8.085181	-1.824681	0.099232
20	1	0	8.504829	0.284276	-0.018796
21	1	0	7.351259	-3.849569	0.204390
22	1	0	9.131941	-2.109059	0.120196
23	6	0	-5.371687	1.070977	-0.047022
24	6	0	-5.746691	2.426812	-0.120644
25	6	0	-6.394969	0.092019	0.005044
26	6	0	-7.088046	2.797822	-0.146555
27	1	0	-4.967776	3.180319	-0.159995
28	6	0	-7.734684	0.475488	-0.021142
29	6	0	-8.085746	1.823821	-0.098657
30	1	0	-7.352434	3.848859	-0.205178
31	1	0	-8.504767	-0.285189	0.020668
32	1	0	-9.132594	2.107898	-0.119353
33	6	0	6.043385	1.368495	-0.112407
34	6	0	-6.042963	-1.368676	0.113851
35	9	0	7.140366	2.156790	-0.126895
36	9	0	5.355037	1.635697	-1.251349
37	9	0	5.270550	1.788838	0.915803
38	9	0	-5.270585	-1.789355	-0.914563
39	9	0	-5.353919	-1.635084	1.252553
40	9	0	-7.139725	-2.157263	0.129373
41	8	0	-1.724166	-2.000641	-0.854731
42	8	0	1.723842	2.001635	0.853193
43	6	0	-2.292617	-2.835127	0.167158
44	6	0	2.293594	2.834865	-0.169003
45	1	0	-2.908937	-2.253167	0.857772
46	1	0	-2.922946	-3.560508	-0.348539
47	1	0	-1.505911	-3.359085	0.722361
48	1	0	2.909805	2.251920	-0.858867
49	1	0	1.507608	3.359066	-0.725002
50	1	0	2.924246	3.560095	0.346506

Table S9: Cartesian coordinates for optimized geometry of **2c**

Standard orientation:

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.840668	-1.101371	0.226871
2	6	0	0.539205	-1.260069	0.234947
3	6	0	1.410286	-0.174065	0.013660
4	6	0	0.840670	1.101353	-0.226843
5	6	0	-0.539203	1.260051	-0.234919
6	6	0	-1.410285	0.174047	-0.013632
7	1	0	0.946892	-2.247430	0.420962
8	1	0	-0.946890	2.247412	-0.420934
9	6	0	-2.816781	0.372749	-0.001592
10	6	0	2.816783	-0.372765	0.001619
11	6	0	4.019709	-0.562250	0.002545
12	6	0	-4.019706	0.562240	-0.002521
13	6	0	-5.420983	0.801683	-0.001852
14	6	0	-6.338829	-0.282816	0.029533
15	6	0	-5.925177	2.114858	-0.033817
16	6	0	-7.714165	-0.030737	0.032192
17	6	0	-7.295707	2.360107	-0.031876
18	1	0	-5.218461	2.937883	-0.058779
19	6	0	-8.184153	1.284795	0.002070
20	1	0	-8.422307	-0.849622	0.056683
21	1	0	-7.665775	3.379721	-0.055840
22	1	0	-9.255377	1.462214	0.004481
23	6	0	5.420988	-0.801680	0.001872
24	6	0	5.925195	-2.114849	0.033886
25	6	0	6.338823	0.282826	-0.029569
26	6	0	7.295727	-2.360085	0.031941
27	1	0	5.218487	-2.937880	0.058890
28	6	0	7.714161	0.030761	-0.032232
29	6	0	8.184162	-1.284766	-0.002061
30	1	0	7.665806	-3.379694	0.055943
31	1	0	8.422295	0.849651	-0.056765
32	1	0	9.255388	-1.462174	-0.004476
33	8	0	1.625965	2.193277	-0.512451
34	8	0	-1.625964	-2.193295	0.512478
35	6	0	2.294085	2.784714	0.612379
36	6	0	-2.294080	-2.784733	-0.612353
37	1	0	3.032496	2.102068	1.042526
38	1	0	2.803166	3.671143	0.229955
39	1	0	1.570865	3.083656	1.380149
40	1	0	-3.032489	-2.102088	-1.042504
41	1	0	-1.570858	-3.083678	-1.380119
42	1	0	-2.803163	-3.671161	-0.229929
43	8	0	5.785914	1.524243	-0.052548
44	8	0	-5.785933	-1.524239	0.052466
45	6	0	6.653543	2.655512	-0.091012
46	6	0	-6.653573	-2.655502	0.090874
47	1	0	6.001353	3.528678	-0.108021
48	1	0	7.295307	2.698005	0.796319
49	1	0	7.277622	2.650204	-0.991736
50	1	0	-7.295329	-2.697950	-0.796466
51	1	0	-6.001392	-3.528674	0.107852
52	1	0	-7.277661	-2.650225	0.991591

Table S10: Cartesian coordinates for optimized geometry of **2d**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.691066	-1.206061	-0.188768
2	6	0	-0.697548	-1.190011	-0.204570
3	6	0	-1.416876	0.007586	-0.020655
4	6	0	-0.691067	1.206004	0.188826
5	6	0	0.697546	1.189954	0.204630
6	6	0	1.416875	-0.007642	0.020712
7	1	0	-1.229924	-2.120491	-0.366808
8	1	0	1.229923	2.120434	0.366869
9	6	0	2.837683	-0.003746	0.021355
10	6	0	-2.837684	0.003695	-0.021302
11	6	0	-4.054540	-0.022737	-0.025883
12	6	0	4.054539	0.022695	0.025928
13	6	0	5.477919	0.049766	0.024394
14	6	0	6.171549	1.244760	0.306185
15	6	0	6.215854	-1.118847	-0.255192
16	6	0	7.560904	1.268248	0.305402
17	6	0	7.605264	-1.090021	-0.255392
18	1	0	5.689856	-2.042574	-0.469423
19	6	0	8.280558	0.102137	0.025071
20	1	0	8.087185	2.189483	0.529211
21	1	0	8.165881	-1.993791	-0.466395
22	6	0	-5.477920	-0.049794	-0.024378
23	6	0	-6.215848	1.118877	0.254989
24	6	0	-6.171559	-1.244827	-0.305978
25	6	0	-7.605257	1.090069	0.255159
26	1	0	-5.689842	2.042635	0.469072
27	6	0	-7.560916	-1.268299	-0.305221
28	6	0	-8.280560	-0.102131	-0.025112
29	1	0	-8.165867	1.993884	0.465988
30	1	0	-8.087203	-2.189566	-0.528879
31	8	0	-1.351431	2.387928	0.423835
32	8	0	1.351427	-2.387986	-0.423779
33	6	0	-1.766632	3.091535	-0.756831
34	6	0	1.766665	-3.091575	0.756886
35	1	0	-2.467657	2.493341	-1.348573
36	1	0	-2.264286	3.999511	-0.413107
37	1	0	-0.902552	3.359694	-1.375761
38	1	0	2.467706	-2.493371	1.348598
39	1	0	0.902604	-3.359728	1.375844
40	1	0	2.264312	-3.999554	0.413158
41	1	0	-5.611552	-2.146846	-0.526593
42	1	0	5.611535	2.146733	0.526969
43	6	0	-9.781695	-0.145718	0.032857
44	6	0	9.781690	0.145780	-0.032919
45	9	0	-10.295341	-1.064834	-0.816004
46	9	0	-10.228561	-0.470222	1.271744
47	9	0	-10.336981	1.047207	-0.278773

48	9	0	10.295332	1.064531	0.816343
49	9	0	10.228516	0.470862	-1.271669
50	9	0	10.337018	-1.047267	0.278161

Table S11: Cartesian coordinates for optimized geometry of **2e**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.663486	1.220105	0.184457
2	6	0	-0.724409	1.174803	0.184051
3	6	0	-1.420819	-0.037645	0.003967
4	6	0	-0.663484	-1.220064	-0.184443
5	6	0	0.724411	-1.174762	-0.184037
6	6	0	1.420821	0.037686	-0.003954
7	1	0	-1.276139	2.096856	0.329953
8	1	0	1.276141	-2.096816	-0.329940
9	6	0	2.841182	0.061304	0.013394
10	6	0	-2.841180	-0.061263	-0.013380
11	6	0	-4.059397	-0.055683	-0.022685
12	6	0	4.059399	0.055719	0.022698
13	6	0	5.482235	0.056266	0.038843
14	6	0	6.209370	-1.123743	-0.204327
15	6	0	6.203991	1.243561	0.299021
16	6	0	7.602200	-1.131221	-0.191363
17	6	0	7.588680	1.243008	0.313668
18	1	0	5.662092	2.163894	0.490191
19	6	0	8.301103	0.056268	0.068596
20	1	0	8.128304	-2.058126	-0.383433
21	1	0	8.146215	2.152076	0.513430
22	6	0	-5.482233	-0.056256	-0.038839
23	6	0	-6.203965	-1.243565	-0.299020
24	6	0	-6.209391	1.123740	0.204326
25	6	0	-7.588654	-1.243038	-0.313675
26	1	0	-5.662048	-2.163888	-0.490185
27	6	0	-7.602222	1.131191	0.191353
28	6	0	-8.301100	-0.056311	-0.068609
29	1	0	-8.146171	-2.152117	-0.513440
30	1	0	-8.128344	2.058087	0.383419
31	8	0	-1.290824	-2.423236	-0.415574
32	8	0	1.290826	2.423277	0.415587
33	6	0	-1.744298	-3.100977	0.764664
34	6	0	1.744298	3.101019	-0.764651
35	1	0	-2.480147	-2.500542	1.309889
36	1	0	-2.211614	-4.027356	0.426572
37	1	0	-0.903049	-3.337103	1.427117
38	1	0	2.480154	2.500589	-1.309871
39	1	0	0.903049	3.337135	-1.427108
40	1	0	2.211604	4.027403	-0.426560
41	1	0	-5.673326	2.045354	0.406231
42	1	0	5.673286	-2.045347	-0.406231

43	8	0	-9.656586	-0.163656	-0.105608
44	8	0	9.656591	0.163588	0.105588
45	6	0	-10.437610	1.005219	0.135207
46	6	0	10.437592	-1.005300	-0.135239
47	1	0	-10.236219	1.781870	-0.611367
48	1	0	-11.478236	0.690071	0.056895
49	1	0	-10.254917	1.409052	1.137532
50	1	0	11.478224	-0.690170	-0.056936
51	1	0	10.236194	-1.781950	0.611335
52	1	0	10.254882	-1.409127	-1.137563

Table S12: Total energies for optimized derivatives **1**

Compound	1a	1b	1c	1d	1e
Energy (Hartrees)	1520.47689	2194.53351	1794.46026	2194.53797	1749.46774

Table S13: Total energies for optimized derivatives **2**

Compound	2a	2b	2c	2d	2e
Energy (Hartrees)	1075.39827	1749.45727	1304.38520	1749.46057	1304.38807

4. SEM Images

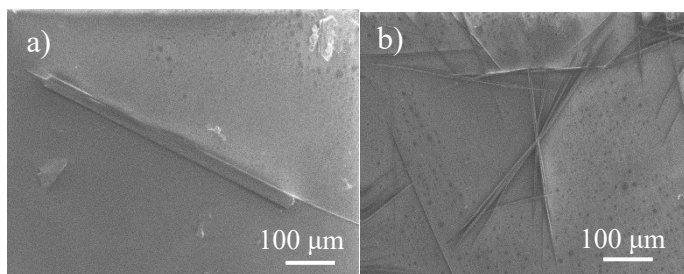


Figure S2: SEM images for supramolecular aggregates **1b,c** using the mixture of solvents a) **1b**, (THF/ethanol) and b) **1c**, (THF/methanol).

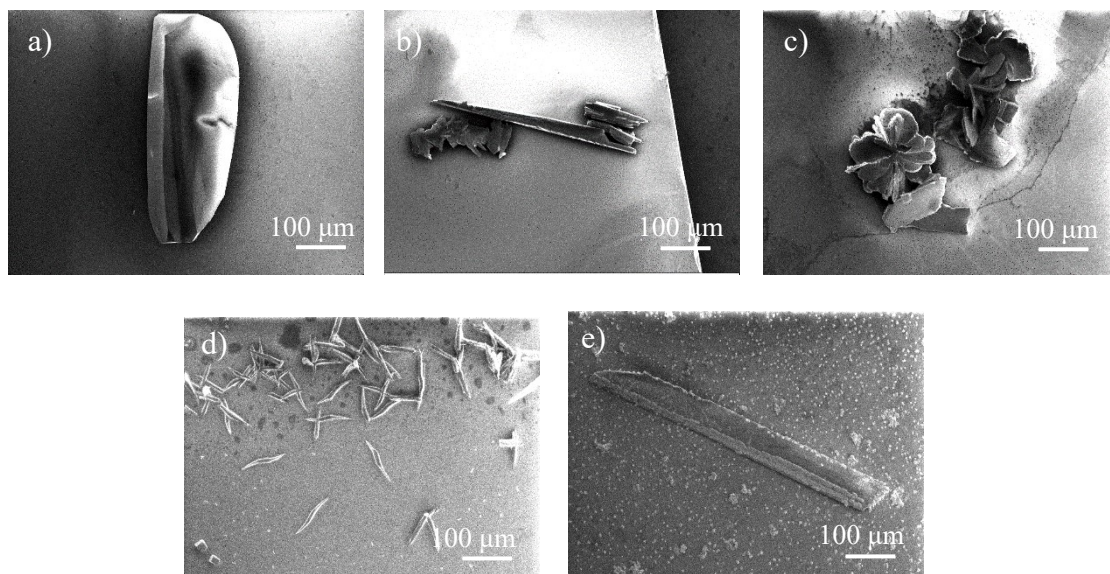


Figure S3: SEM images for supramolecular aggregates of **2a-e** using the mixture of solvents a) **2a**, (THF/methanol) b) **2b**, (CHCl₃/ethanol), c) **2c**, (THF/methanol), d) **2d** (CHCl₃/ethanol) and e) **2e** (THF/ethanol).

5. X-Ray diffraction studies

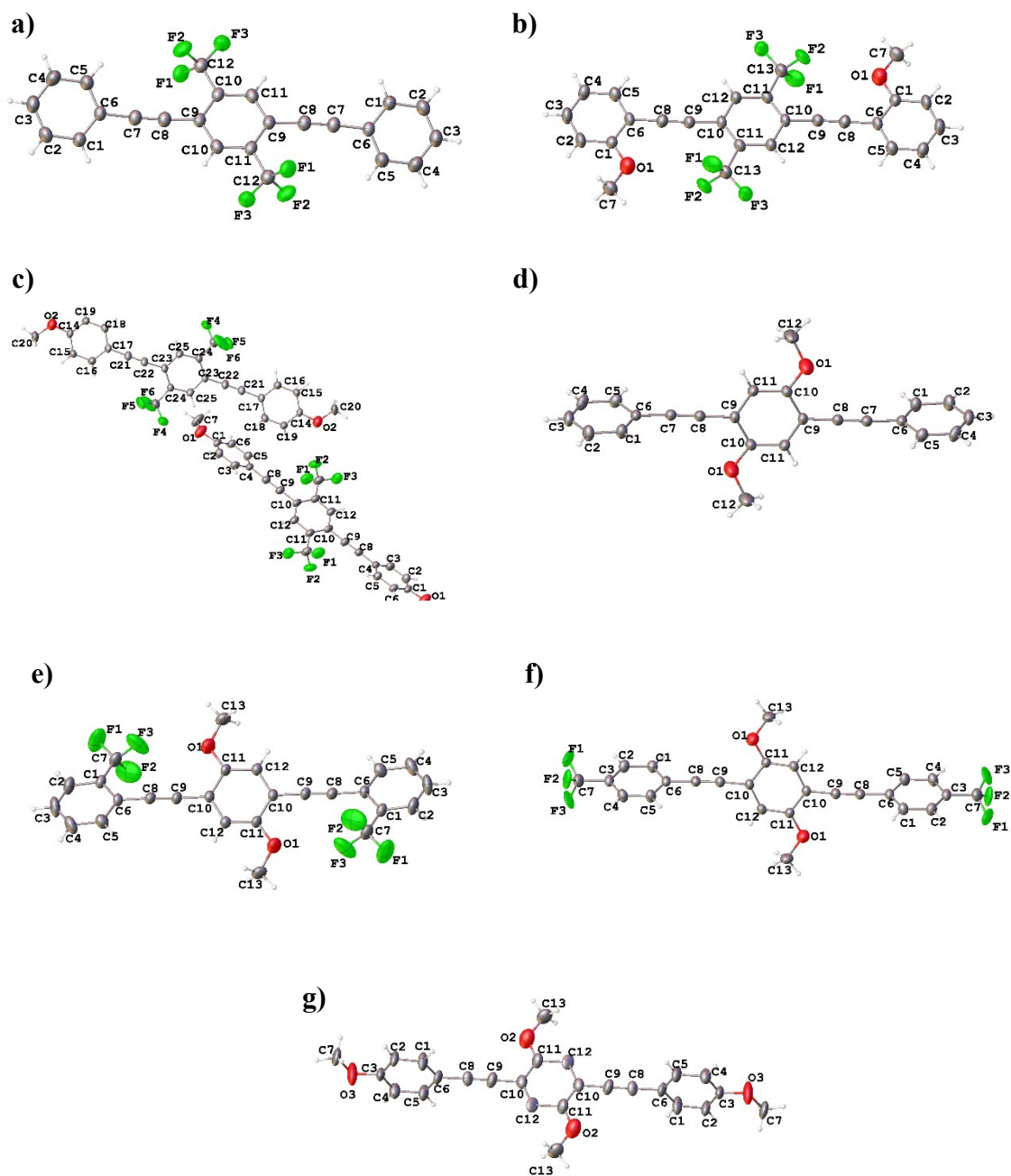


Figure S4: Ortep drawing of compounds a) 1a, b) 1c, c) 1e, d) 2a, e) 2b, f) 2d, y g) 2e. Ellipsoids are given at the 30 % probability level.

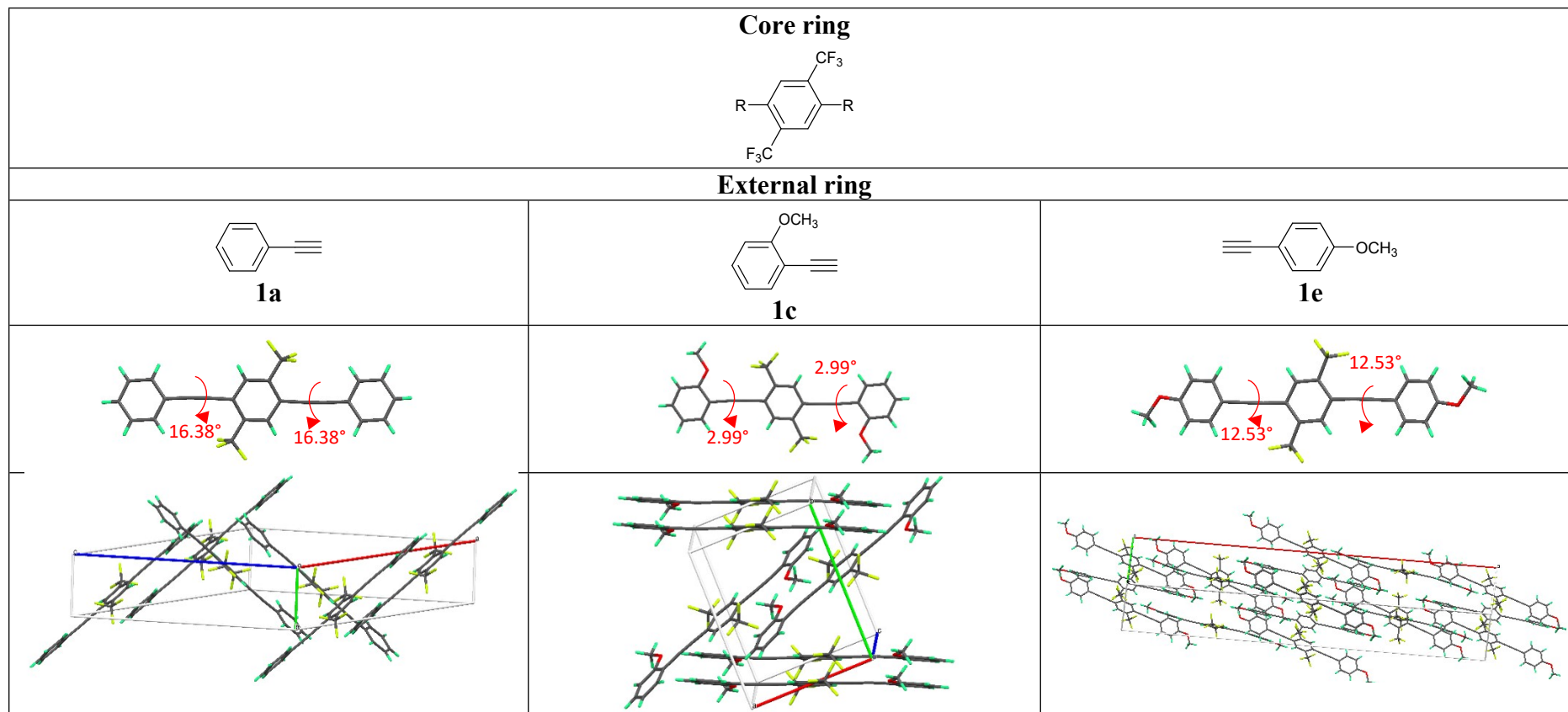


Figure S5: X-Ray structure of compounds **1a**, **1c** and **1e**

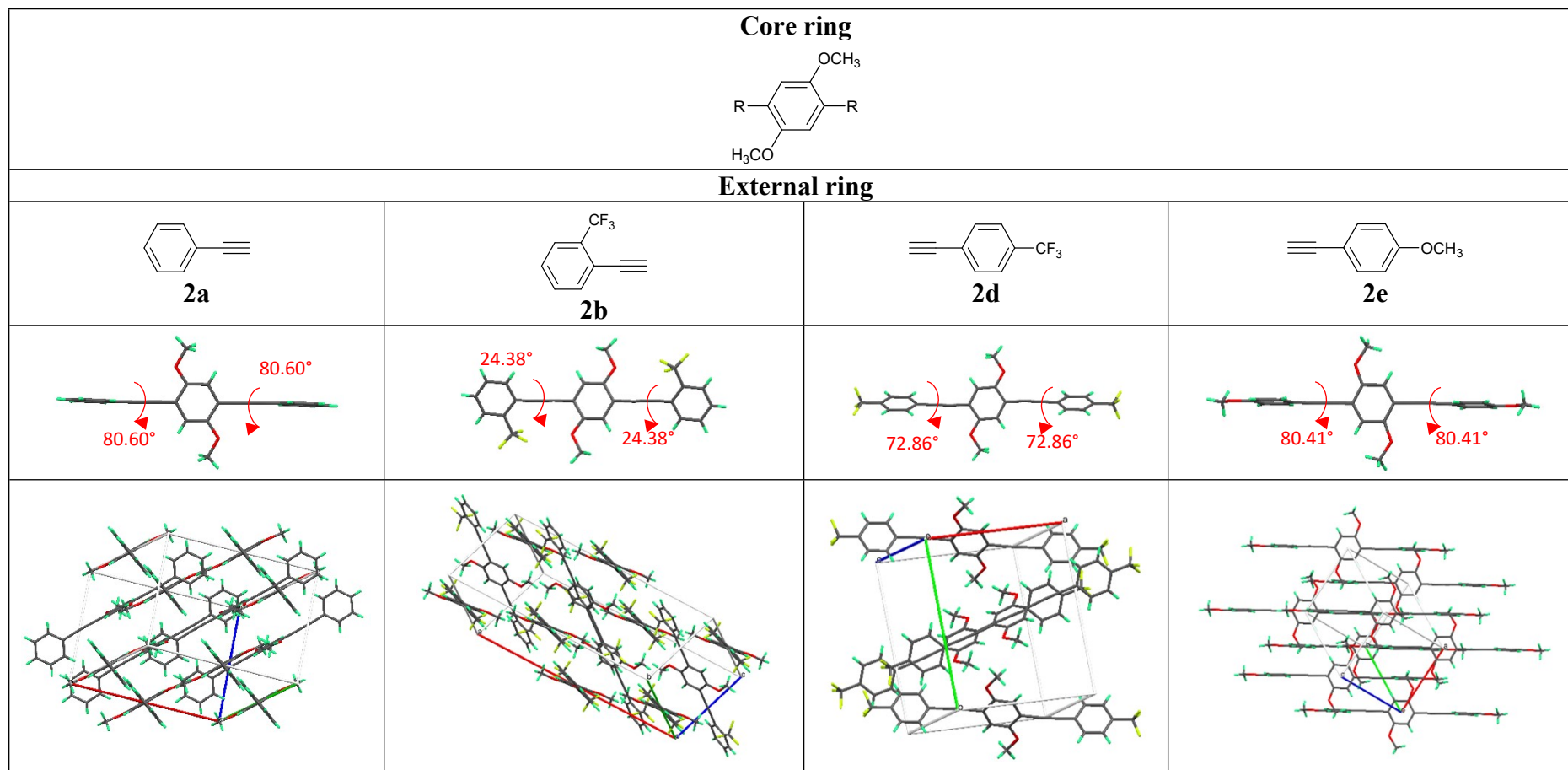


Figure S6: X-Ray structure of compounds **2a**, **2b**, **2d** and **2e**

Table S14. Crystal data and structure refinement for **1a**, **1c** and **1e**.

	1a	1c	1e
Empirical formula	C ₂₄ H ₁₂ F ₆	C ₂₆ H ₁₆ F ₆ O ₂	C ₂₆ H ₁₆ F ₆ O ₂
Formula weight	414.34	474.39	474.39
Temperature (K)	290(2)	290(2)	290(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c	P 2 ₁ /n	C 2/c
a(Å)	23.127(13)	8.656(6)	50.82(4)
b(Å)	4.957(3)	11.264(8)	11.076(9)
c(Å)	18.228(10)	11.003(8)	8.019(7)
α(°)	90	90	90
β(°)	115.632(7)	96.45(3)	92.988(14)
γ(°)	90	90	90
Volume(Å ³)	1884.0(19)	1066.1(13)	4508(7)
Z	4	2	8
Density (calculated) (g/cm ³)	1.461	1.478	1.398
Absorption coefficient (mm ⁻¹)	0.126	0.128	0.121
F(000)	840	484	1936
Crystal size (mm ³)	0.36 x 0.09 x 0.03	0.17 x 0.09 x 0.03	0.25 x 0.09 x 0.07
Index ranges	-27 ≤ h ≤ 28 -6 ≤ k ≤ 6 -21 ≤ l ≤ 22	-10 ≤ h ≤ 10 -13 ≤ k ≤ 13 -13 ≤ l ≤ 12	-63 ≤ h ≤ 62 -13 ≤ k ≤ 13 -10 ≤ l ≤ 9
Reflections collected	6273	5990	12348
Independent reflections	1903 [R(int) = 0.0581]	1863 [R(int) = 0.0915]	4558 [R(int) = 0.0856]
Data / restraints / parameters	1903 / 0 / 137	1863 / 0 / 156	4558 / 0 / 310
Goodness-of-fit on F ²	0.999	0.971	0.999
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0498 wR2 = 0.1015	R1 = 0.0808 wR2 = 0.1923	R1 = 0.0687 wR2 = 0.1451
Extinction coefficient	0.0037(8)	0.083(13)	0.0012(2)
Largest diff. peak / hole, e.Å ⁻³	0.173 and -0.219	0.291 and -0.332	0.336 and -0.311

Table S15: Crystal data and structure refinement for **2a**, **2b**, **2d** and **2e**.

	2a	2b	2d	2e
Empirical formula	C ₂₄ H ₁₈ O ₂	C ₂₆ H ₁₆ F ₆ O ₂	C ₂₆ H ₁₆ F ₆ O ₂	C ₂₆ H ₂₀ O ₄
Formula weight	338.38	474.39	474.39	396.42
Temperature (K)	290(2)	290(2)	290(2)	290(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C 2/c	C 2/c	P 2 ₁ /c	P $\bar{1}$
a(Å)	15.569(5)	23.880(19)	11.1094(18)	8.14(8)
b(Å)	11.084(3)	10.813(8)	13.026(2)	8.41(9)
c(Å)	10.773(3)	8.582(7)	7.5574(12)	9.10(9)
α (°)	90	90	90	64.74(9)
β (°)	101.868(4)	100.551(8)	97.468(2)	89.93(11)
γ (°)	90	90	90	66.50(10)
Volume(Å ³)	1819.5(10)	2178(3)	1084.4(3)	506(9)
Z	4	4	2	1
Density (calc) (g/cm ³)	1.235	1.446	1.453	1.301
Absorp. Coeff. (mm ⁻¹)	0.077	0.125	0.126	0.087
F(000)	712	968	484	208
Crystal size (mm ³)	0.34x0.25x0.21	0.40x0.32x0.31	0.36x0.28x0.22	0.36x0.28x0.22
Index ranges	-15 ≤ h ≤ 19 -13 ≤ k ≤ 13 -13 ≤ l ≤ 13	-28 ≤ h ≤ 28 -12 ≤ k ≤ 11 -10 ≤ l ≤ 10	-12 ≤ h ≤ 13 -13 ≤ k ≤ 15 -8 ≤ l ≤ 8	-9 ≤ h ≤ 9 -9 ≤ k ≤ 9 -10 ≤ l ≤ 10
Reflections collected	6625	6198	6176	2921
Independent reflections	1854 [R(int)=0.0225]	1904 [R(int)=0.0425]	1880 [R(int)=0.0940]	1705 [R(int)=0.3633]
Data/restraints/parameters	1854/0/119	1904 / 0 / 156	1880/12/180	1705/117/158
Goodness-of-fit on F ²	1.050	1.119	1.087	0.653
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0455 wR2 = 0.1123	R1 = 0.0965 wR2 = 0.2323	R1 = 0.0688 wR2 = 0.1568	R1 = 0.0732 wR2 = 0.0892
Larg. diff. peak/hole, e.Å ⁻³	0.126 / -0.167	0.531 / -0.278	0.271 / -0.315	0.176 / -0.211

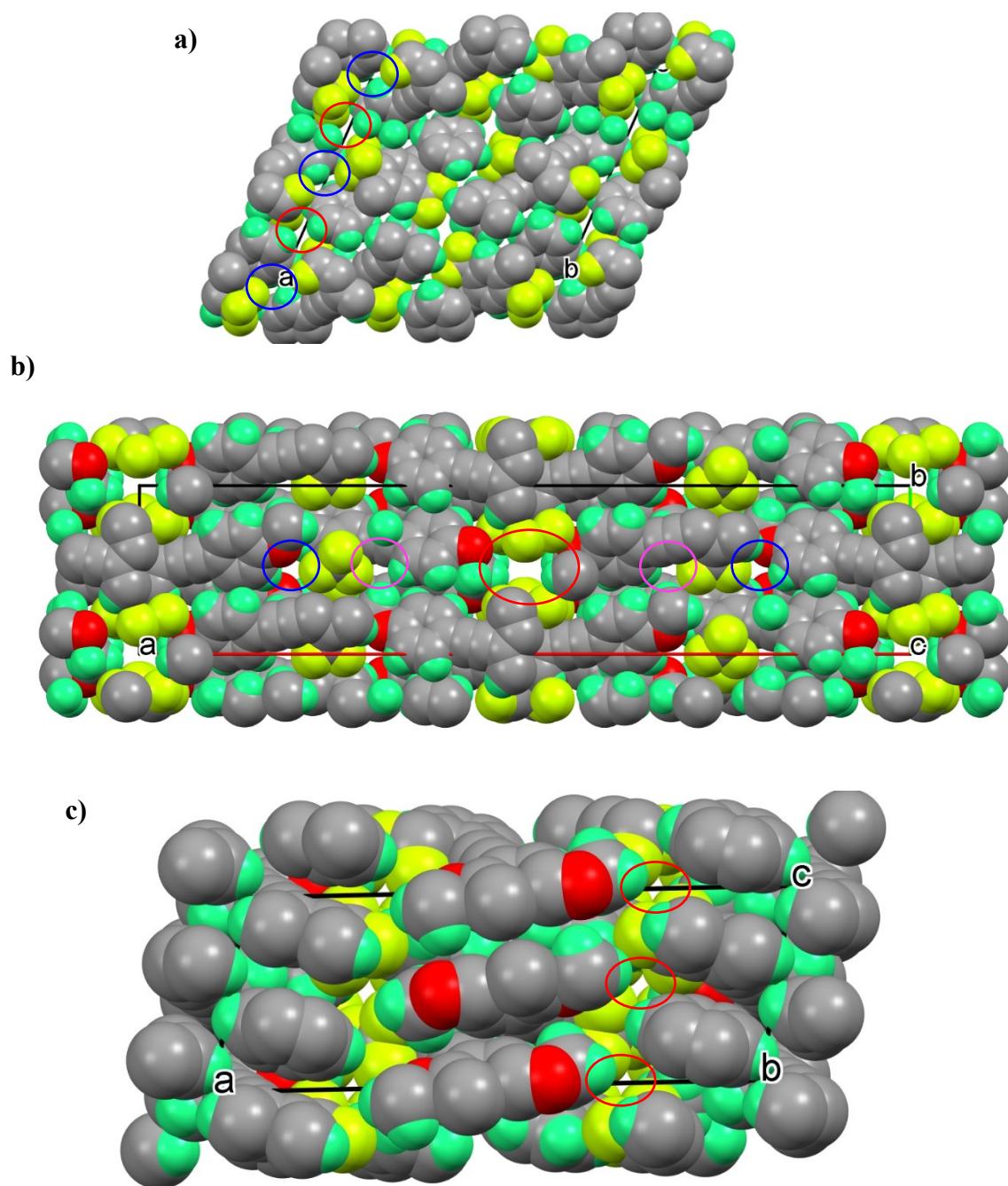


Figure S7: a) View down b axis of channels in the packing of compound **1a**. Representatives channels A and B are marked in red and blue circles, respectively. The longest axis of the unit cell is a axis. b) View down c axis of channels in the packing of compound **1e**. Representatives channels A, B and C are marked in red, blue and pink circles, respectively. The longest axis of the unit cell is a axis. c) View down b axis of channels in packing of compound **2b**. Representatives channels are marked in red. The longest axis of the unit cell is a axis.

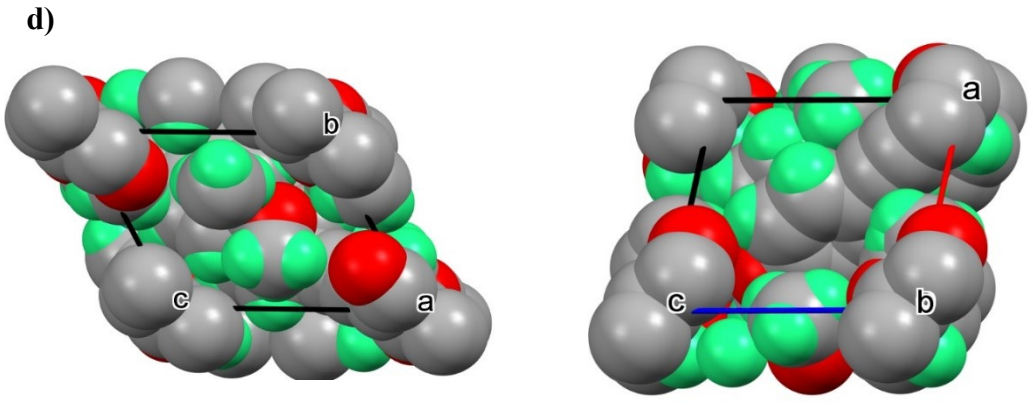
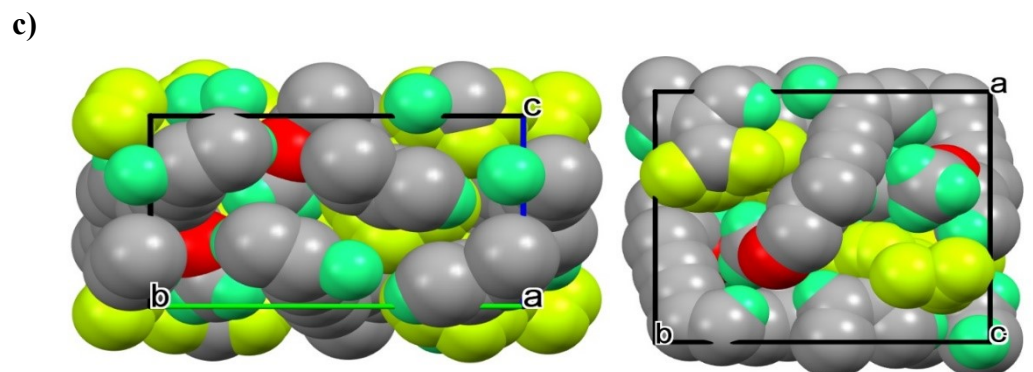
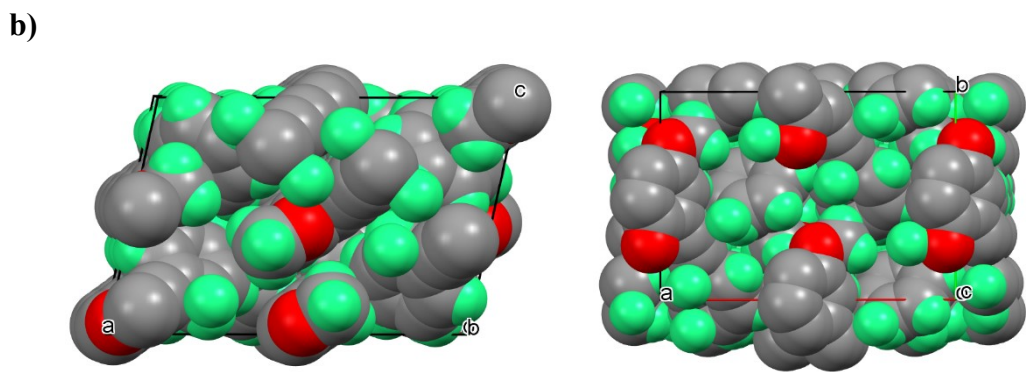
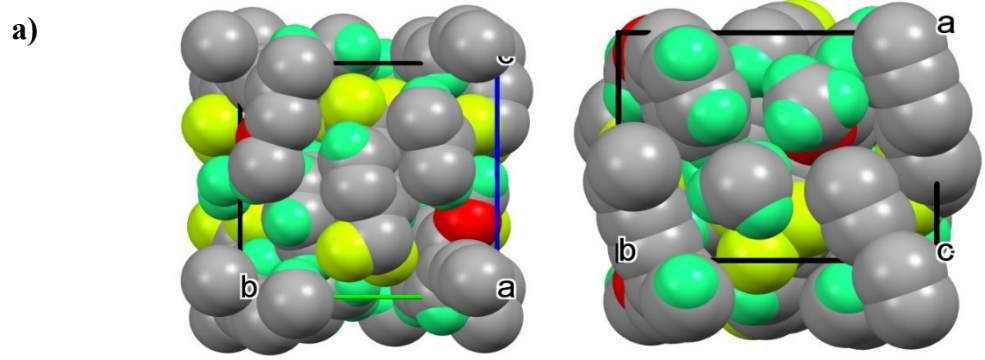


Figure S8. Packings without internal channels of a) **1c**. View down *a* and *c* axis. The longest axis of the unit cell is the *b* axis. b) **2a**. View down *b* and *c* axis. The longest axis of the unit cell is the *a* axis. c) **2d**. View down *a* and *c* axis. The longest axis of the unit cell is the *b* axis. d) **2e**. View down *a* and *b* axis. The longest axis of the unit cell is the *c* axis.

Table S16: Intermolecular contacts and channel size of compounds **1a**, **1e** y **2b**.

Channel	Distance (Å)		Size (Å)	
<i>Compound 1a</i>				
A	F1···H4	2.70	Plane(F1-H4)-plane(F1-H4)	4.64
	F3···H3	2.77	Plane(F3-H4)-plane(F3-H4)	3.73
B	F2···H4	2.82	Plane(F2-H4)-plane(F2-H4)	3.96
	F2···H5	3.33	Plane(H4-H5)-plane(H4-H5)	2.50
<i>Compound 1e</i>				
A	F3···H20B	2.67	Plane H20B-plane H20B	4.48
			Plane F3-plane F3	3.38
B	O1···H25	2.53	Plane(O1-H25)-Plane (O1-H25)	3.29
	F4···H25	2.35	Plane (H2)-Plane(F4)	3.74
C	F6···H7C	2.62	Plane (H16)-Plane(F5)	3.61
	C21...H7A	2.81	Plane(C21-C22)-Plane(C21-C22)	3.70
<i>Compound 2b</i>				
	F3···H13C	3.54	Plane(F1-H13C)-plane (F1-H13C)	3.00
	F1···H13C	2.67	Plane (F1-F3)-Plane(F1-F3)	3.66

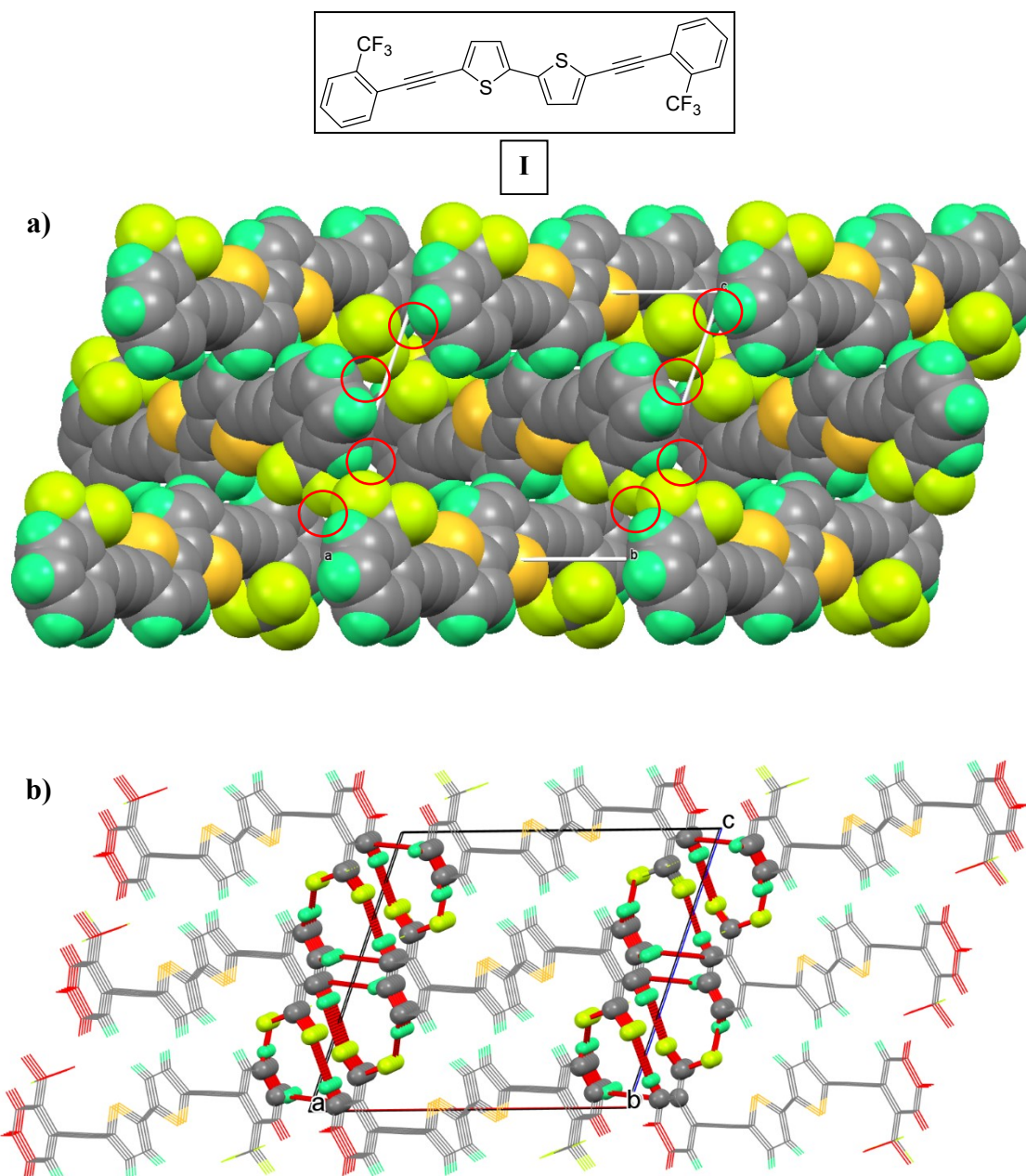
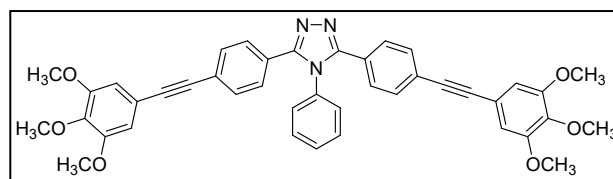


Figure S9: Packing molecular of compound **I** with the internal channels view down *b* axis a) with the atoms in their Van der Waals radii and b) with the atoms in wireframe style. The channels are marked in colour red. The longest axis of the unit cell is the *a* axis. Reference 49 in the manuscript. CCDC: DEBJED



II

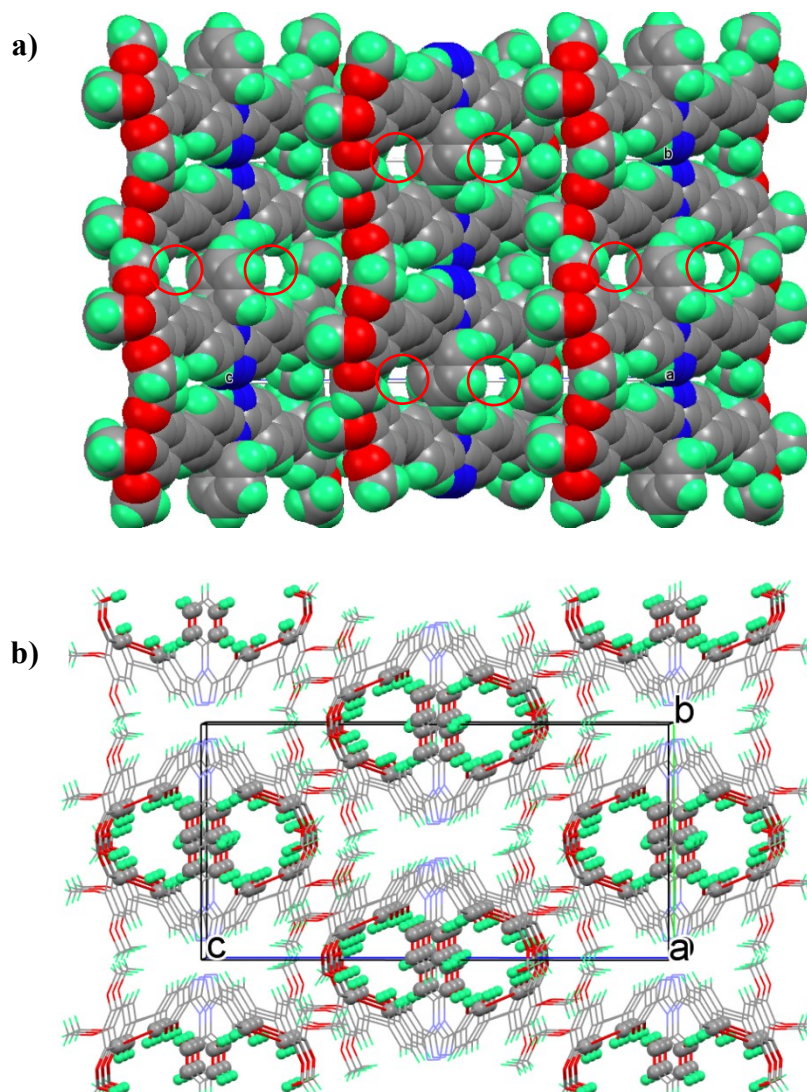


Figure S10: Packing molecular of compound **II** with the internal channels view down a axis a) with the atoms in their Van der Waals radii and b) with the atoms in wireframe style. The channels are marked in colour red. The longest axis of the unit cell is the c axis. Reference 43 in the manuscript. CCDC: XOWDIY

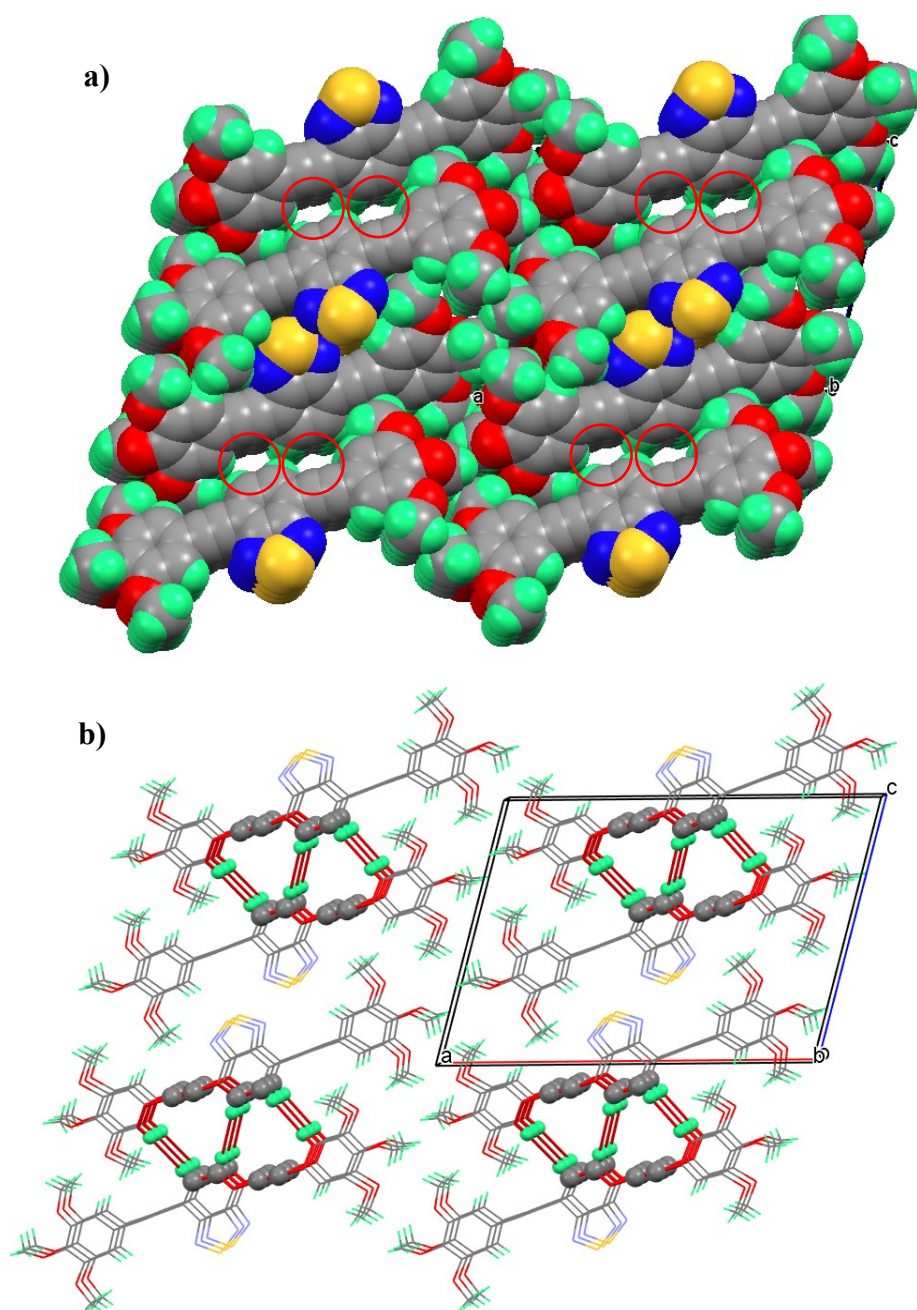
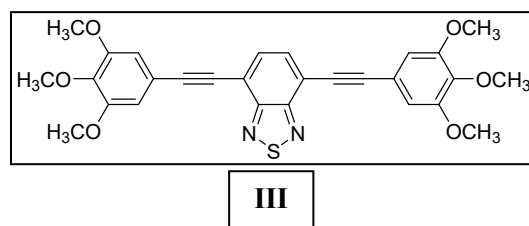


Figure S11: Packing molecular of compound **III** with the internal channels view down *b* axis a) with the atoms in their Van der Waals radii and b) with the atoms in wireframe

style. The channels are marked in colour red. The longest axis of the unit cell is the a axis. Reference 44 in the manuscript. CCDC: DEBMAC

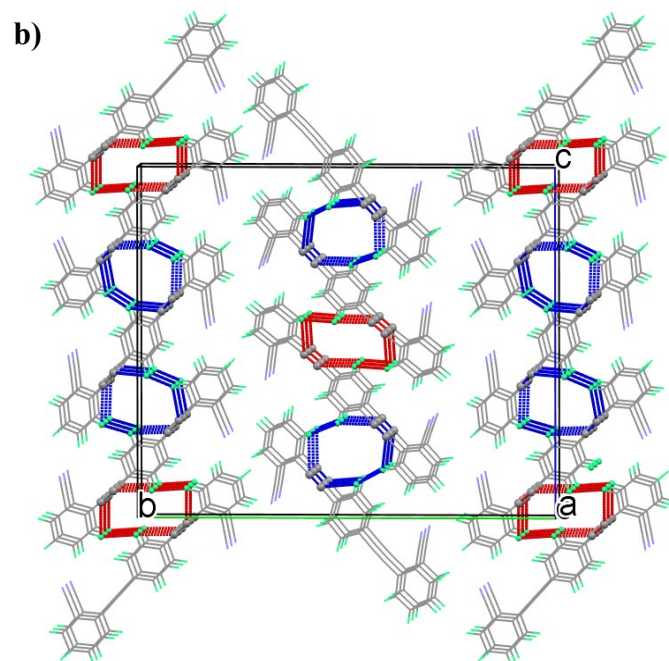
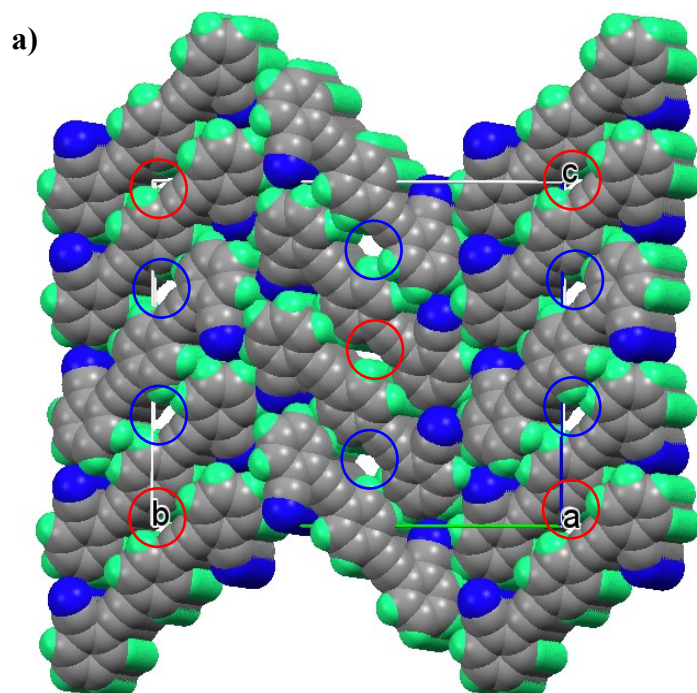
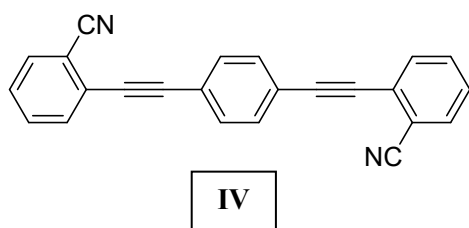


Figure S12: Packing molecular of compound IV with the internal channels view down a

axis a) with the atoms in their Van der Waals radii and b) with the atoms in wireframe style. The channels are marked red and blue. The longest axis of the unit cell is the *b* axis. Reference 49 in the manuscript. CCDC: DAZXUB

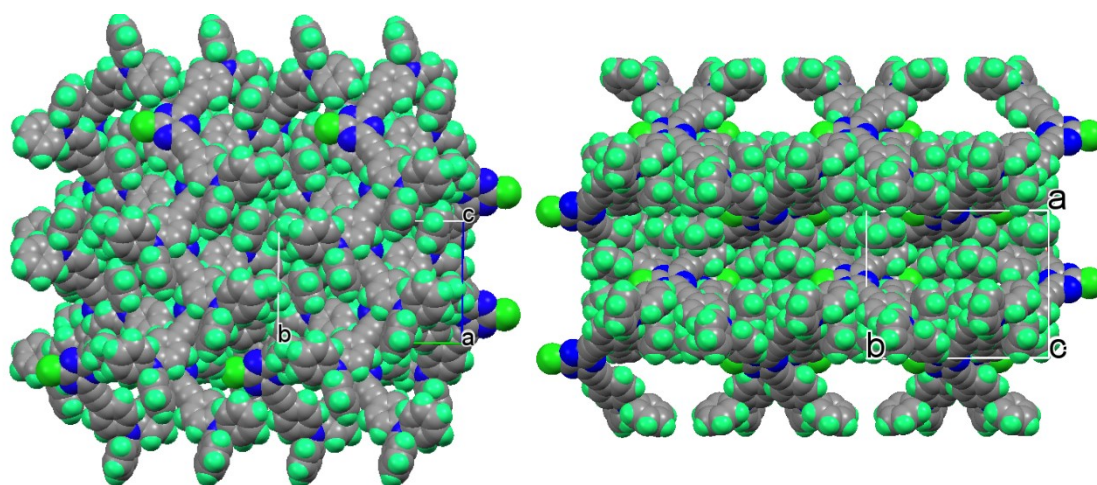
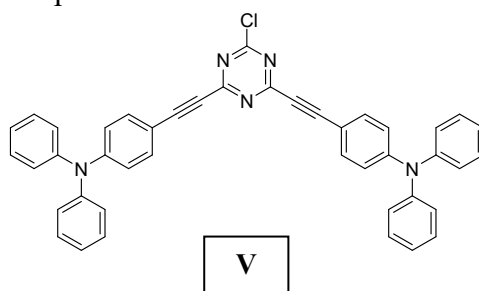


Figure S13: Packing molecular of compound V without internal channels view down *a* and *c* axis. The longest axis of the unit cell is the *b* axis. Reference 61 in the manuscript.

6. NMR spectra

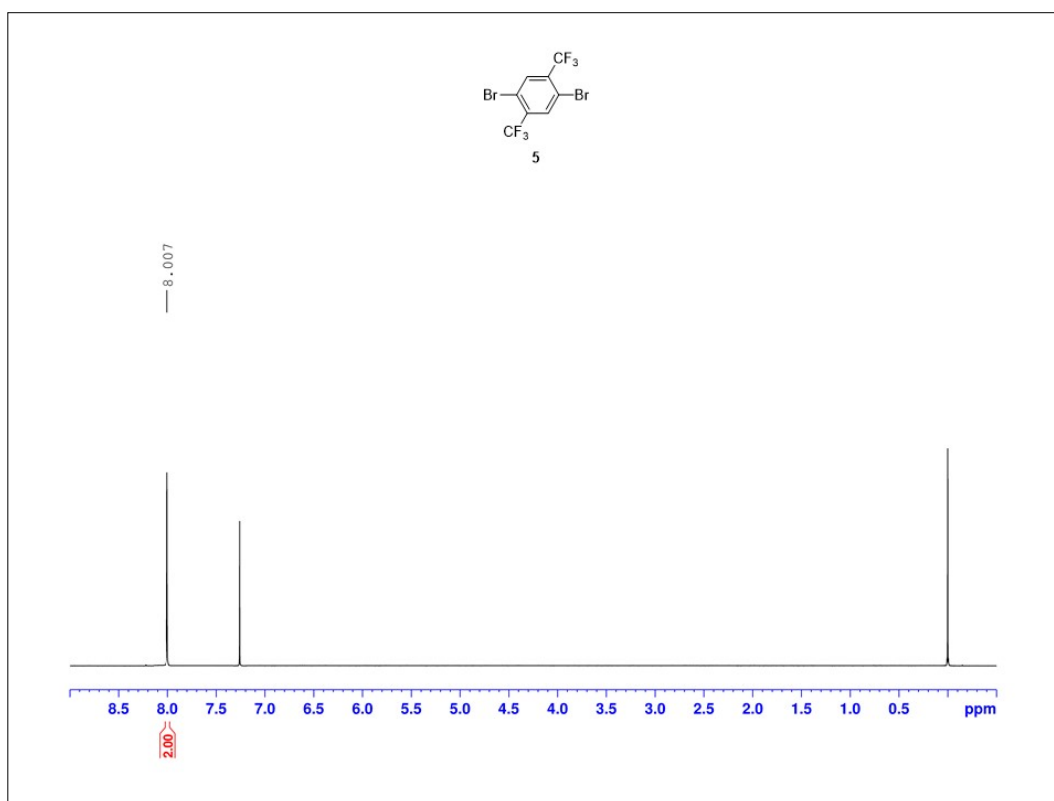


Figure S14: $^1\text{H NMR}$ spectrum of compound **5** in CDCl_3 .

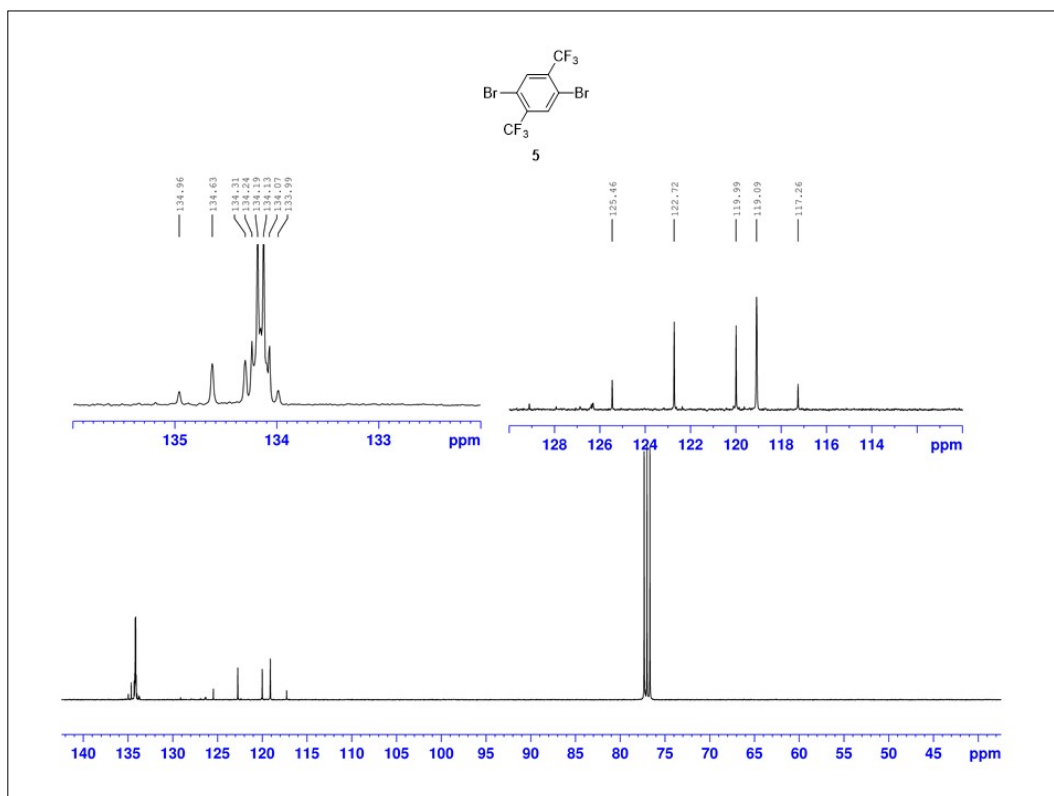


Figure S15: $^{13}\text{C NMR}$ spectrum of compound **5** in CDCl_3 .

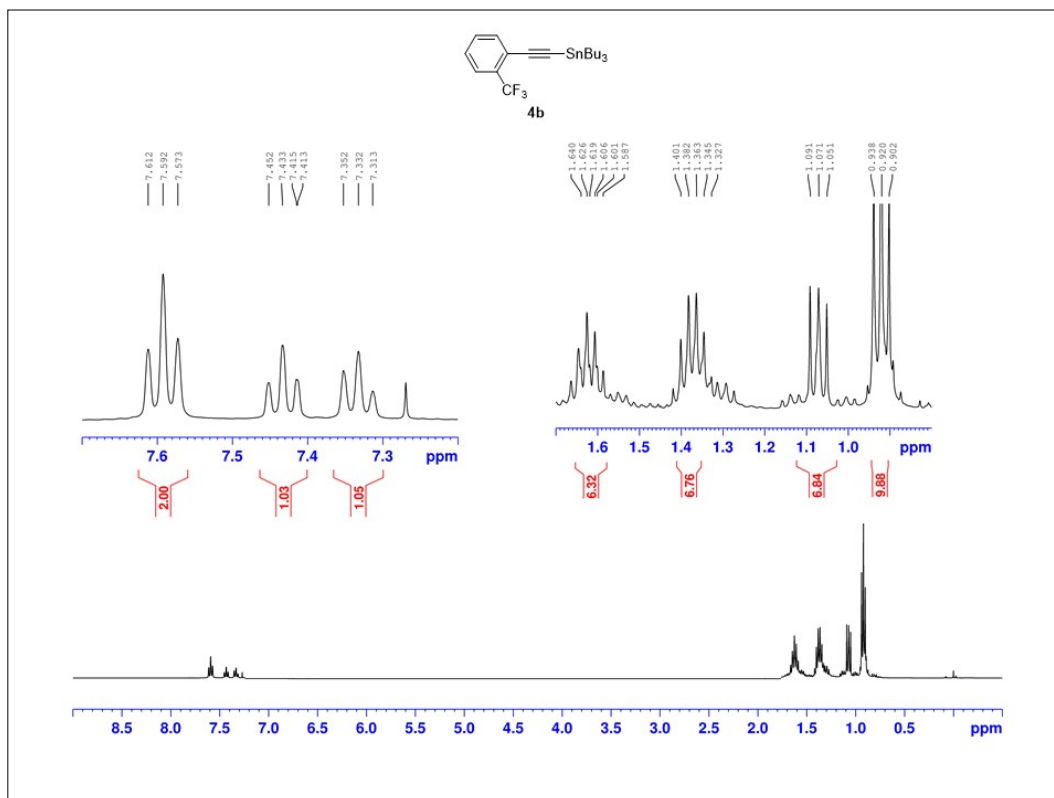


Figure S16: $^1\text{H NMR}$ spectrum of compound **4b** in CDCl_3 .

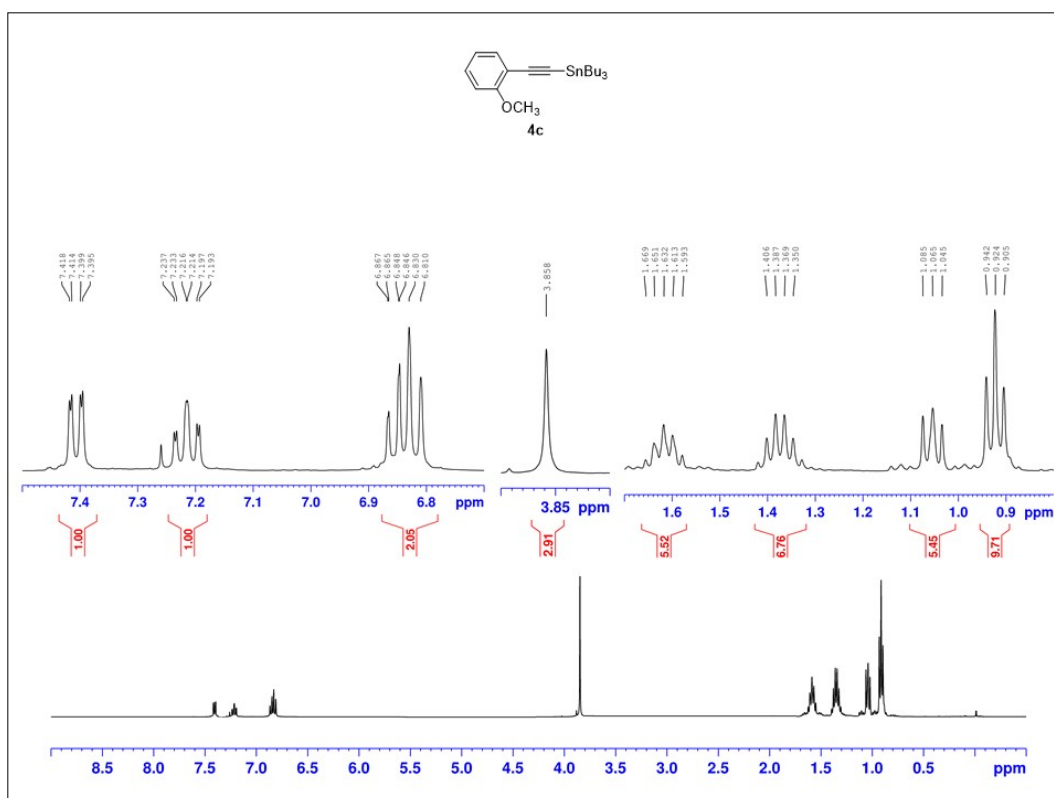


Figure S17: $^1\text{H NMR}$ spectrum of compound **4c** in CDCl_3 .

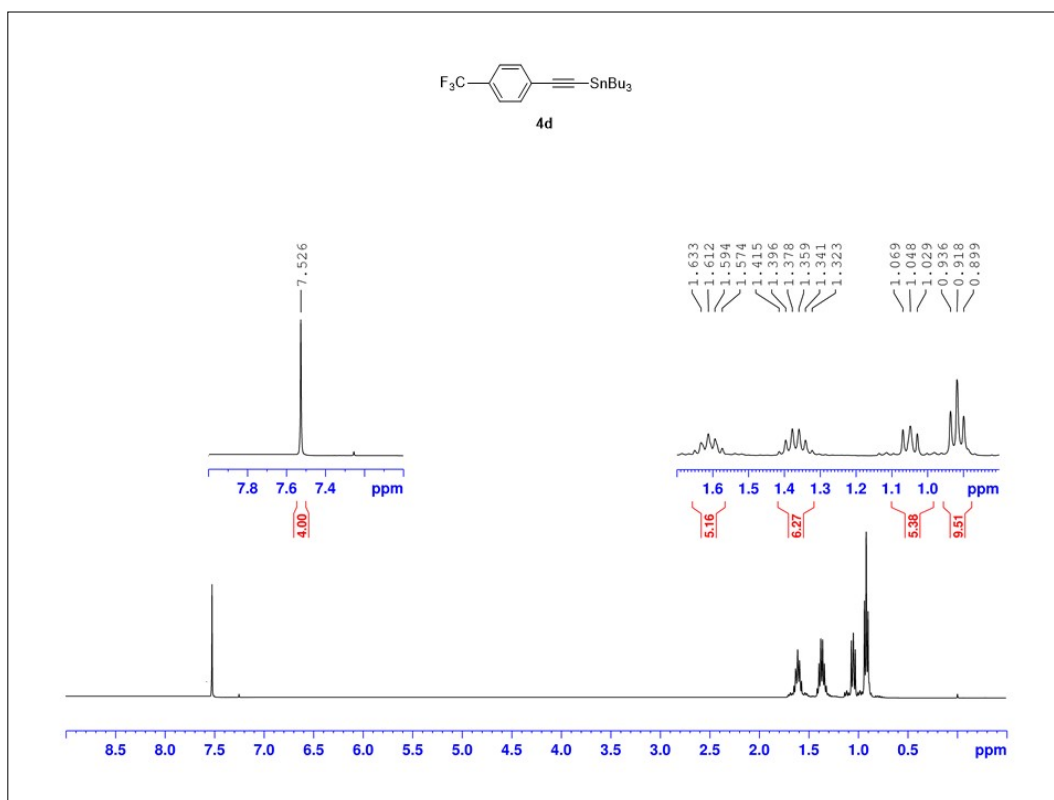


Figure S18: ^1H NMR spectrum of compound **4d** in CDCl_3 .

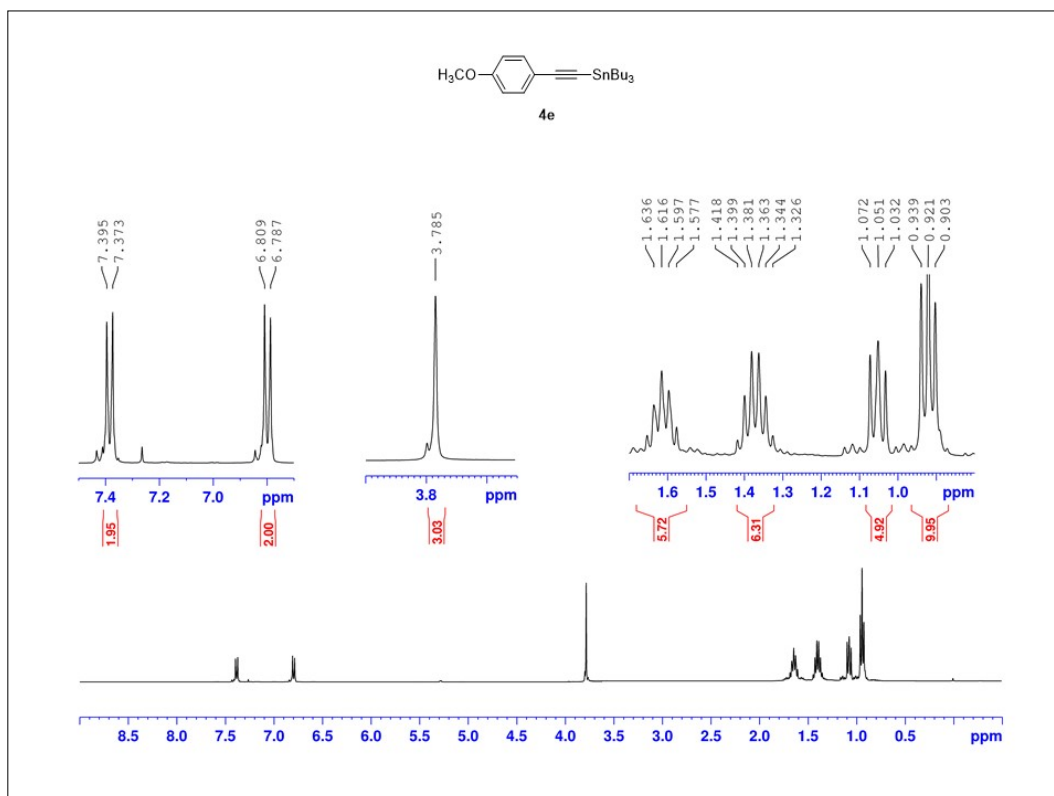


Figure S19: ^1H NMR spectrum of compound **4e** in CDCl_3 .

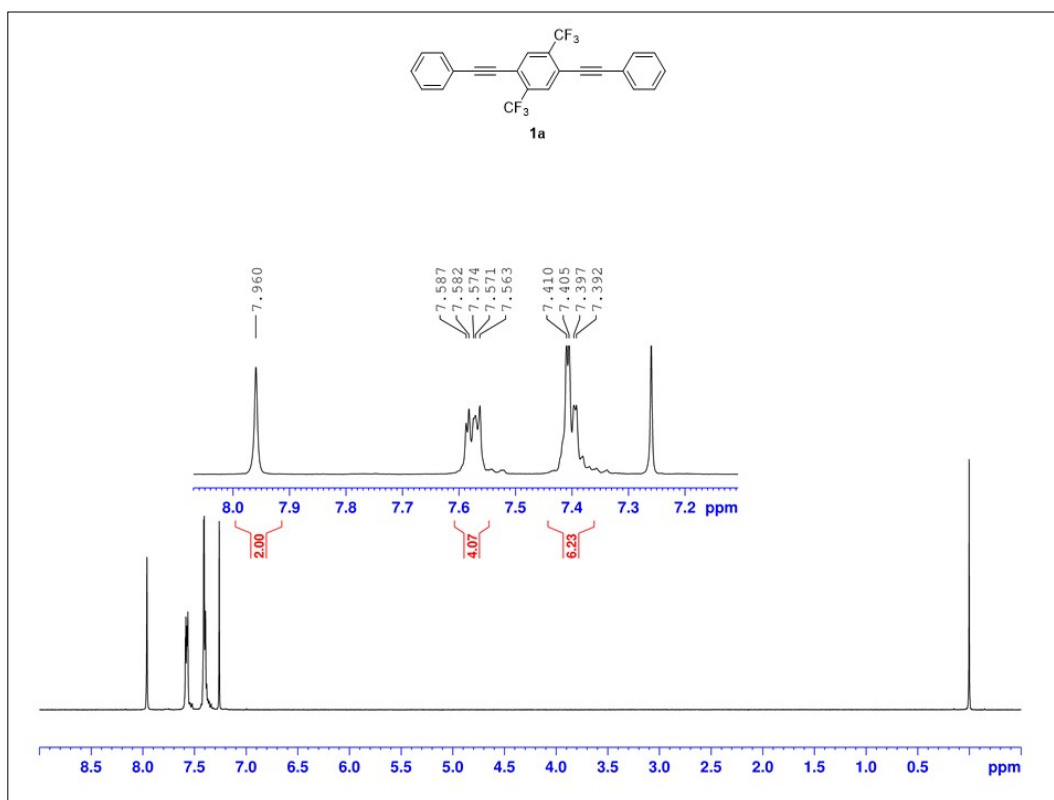


Figure S20: ¹H NMR spectrum of compound **1a** in CDCl₃.

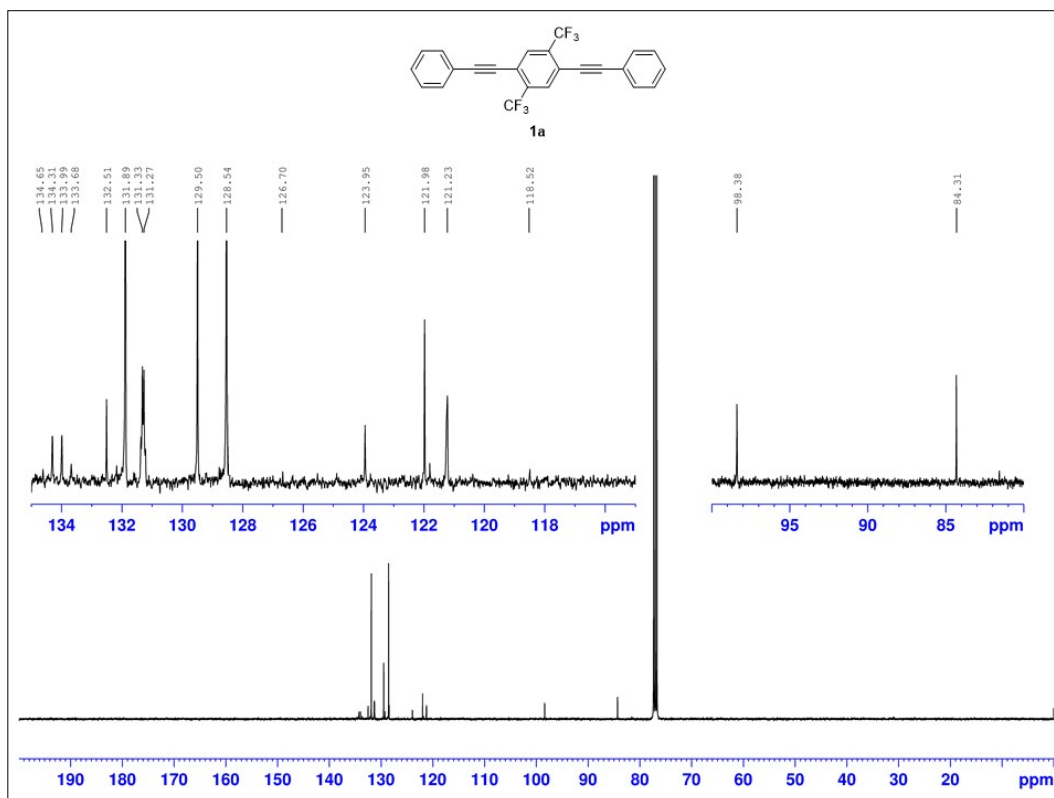


Figure S21: ¹³C NMR spectrum of compound **1a** in CDCl₃.

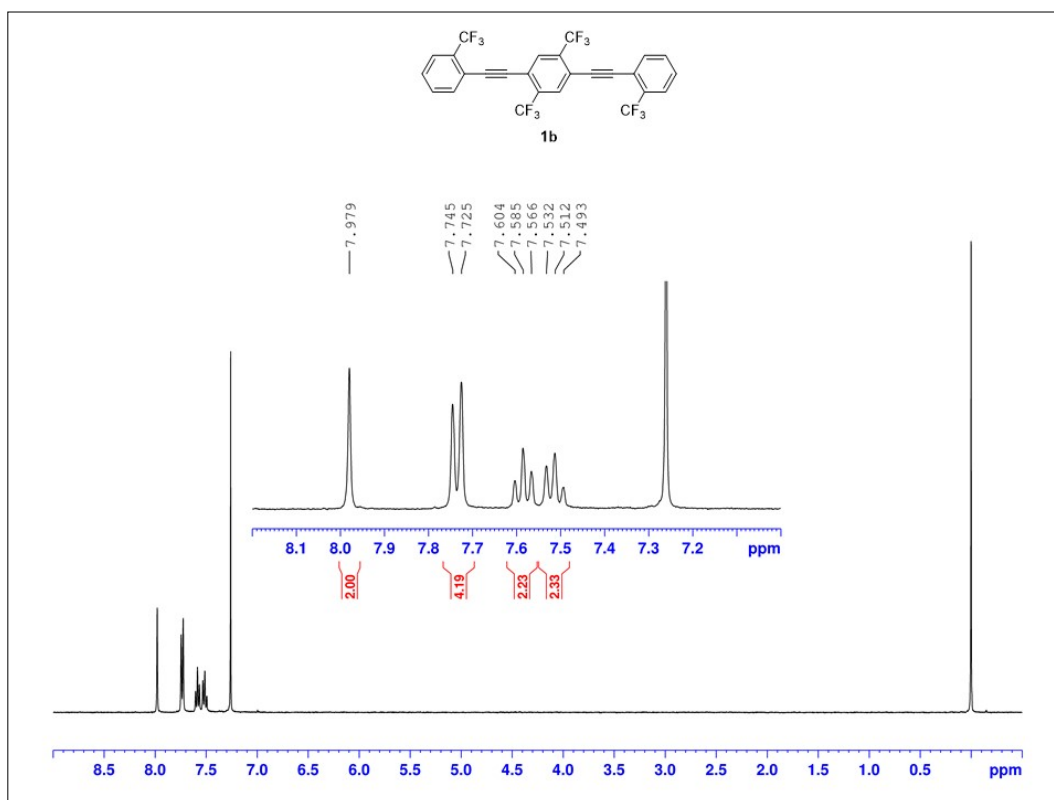


Figure S22: ^1H NMR spectrum of compound **1b** in CDCl_3 .

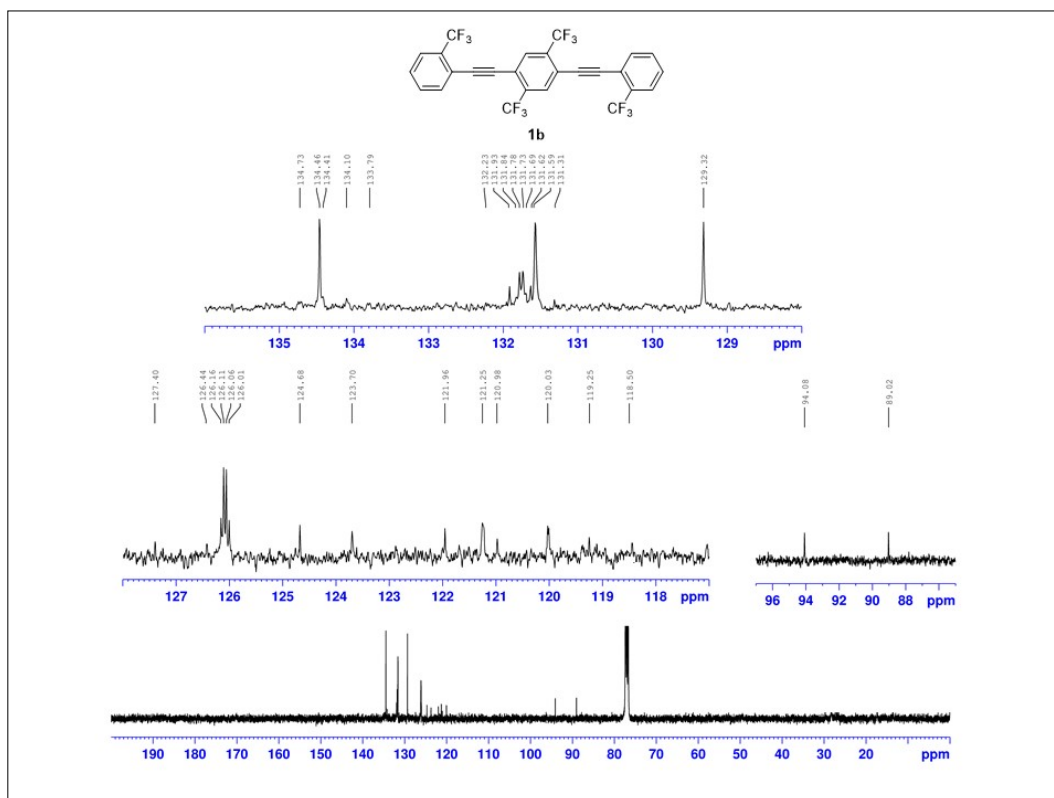


Figure S23: ^{13}C NMR spectrum of compound **1b** in CDCl_3 .

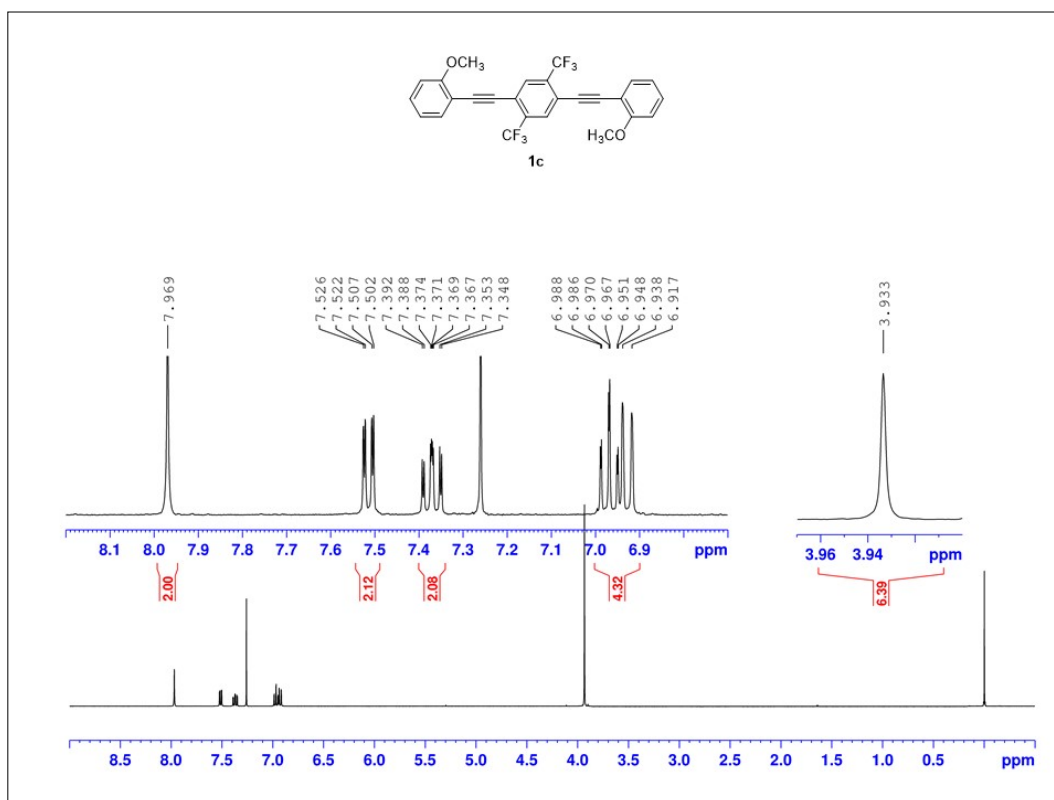


Figure S24: ¹H NMR spectrum of compound **1c** in CDCl₃.

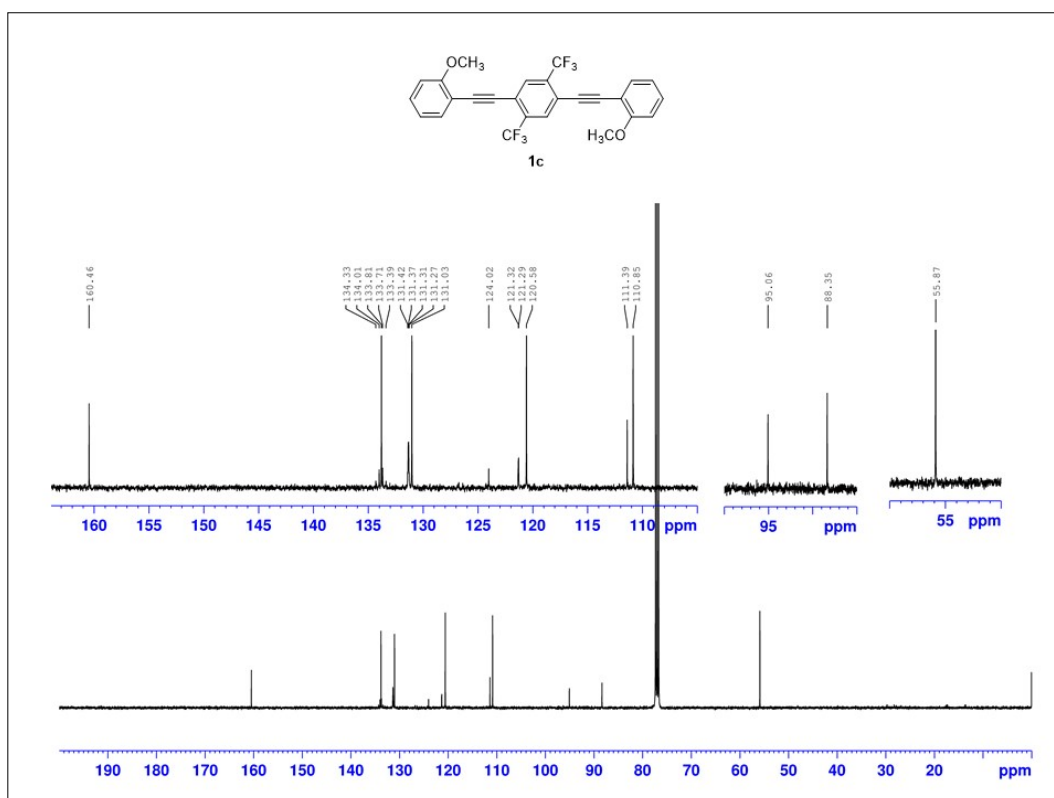


Figure S25: ¹³C NMR spectrum of compound **1c** in CDCl₃.

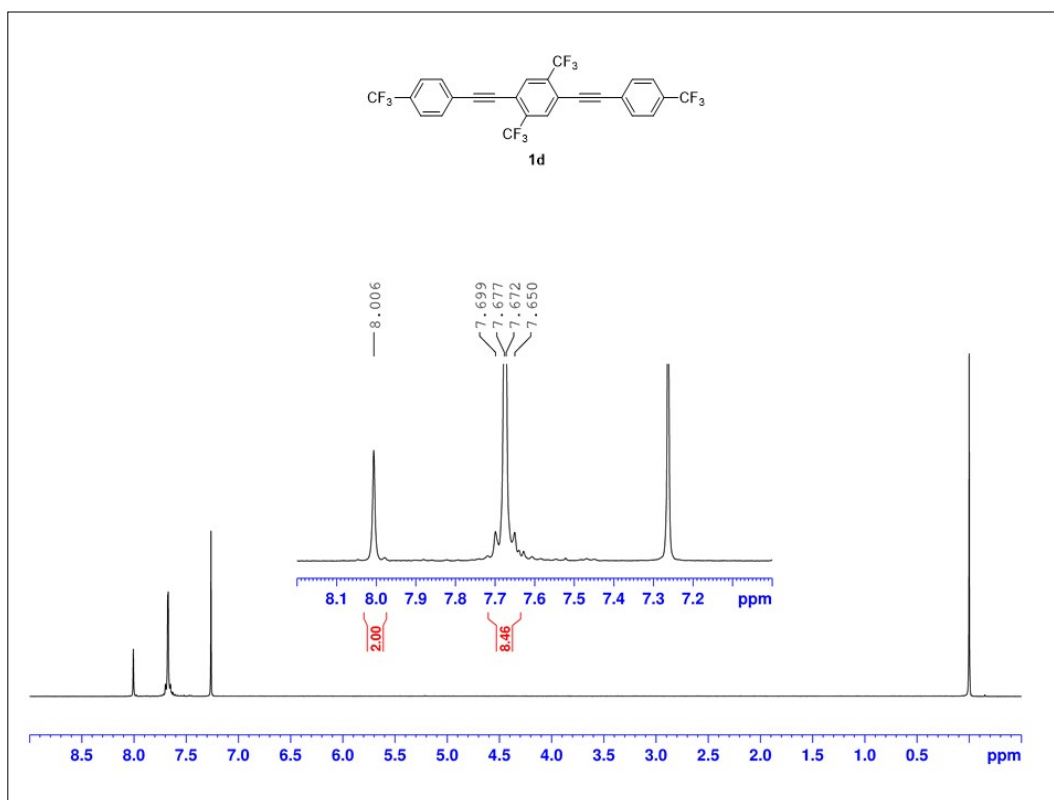


Figure S26: ¹H NMR spectrum of compound **1d** in CDCl₃.

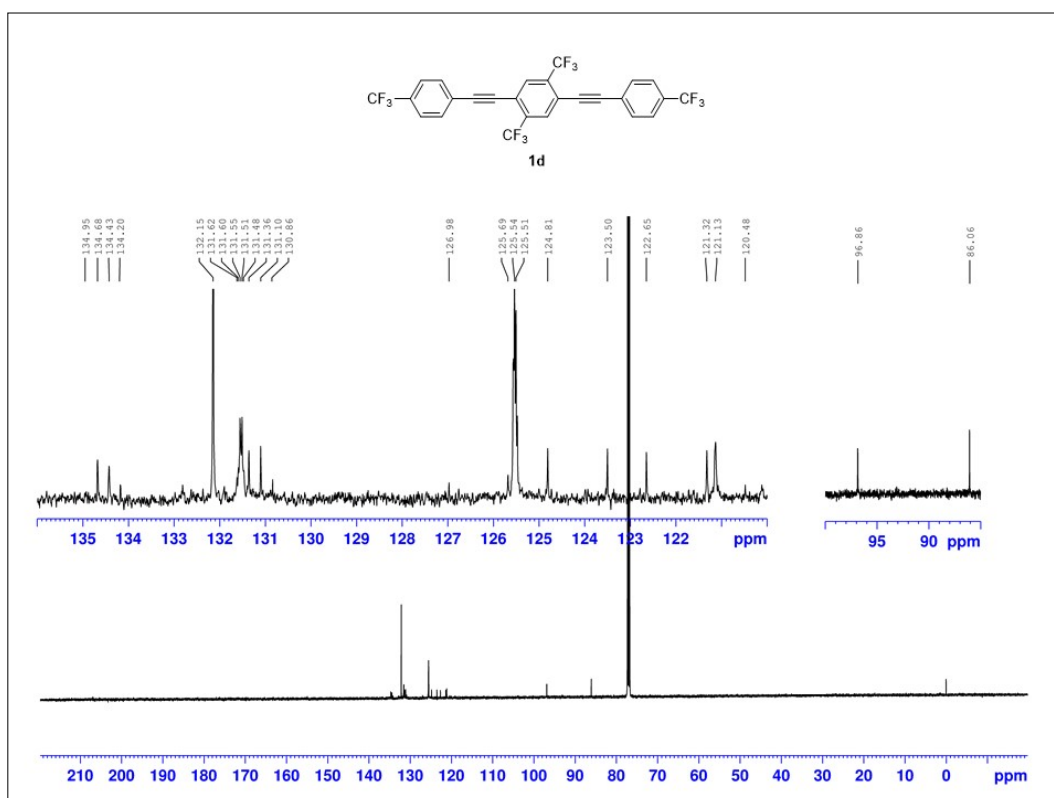


Figure S27: ¹³C NMR spectrum of compound **1d** in CDCl₃.

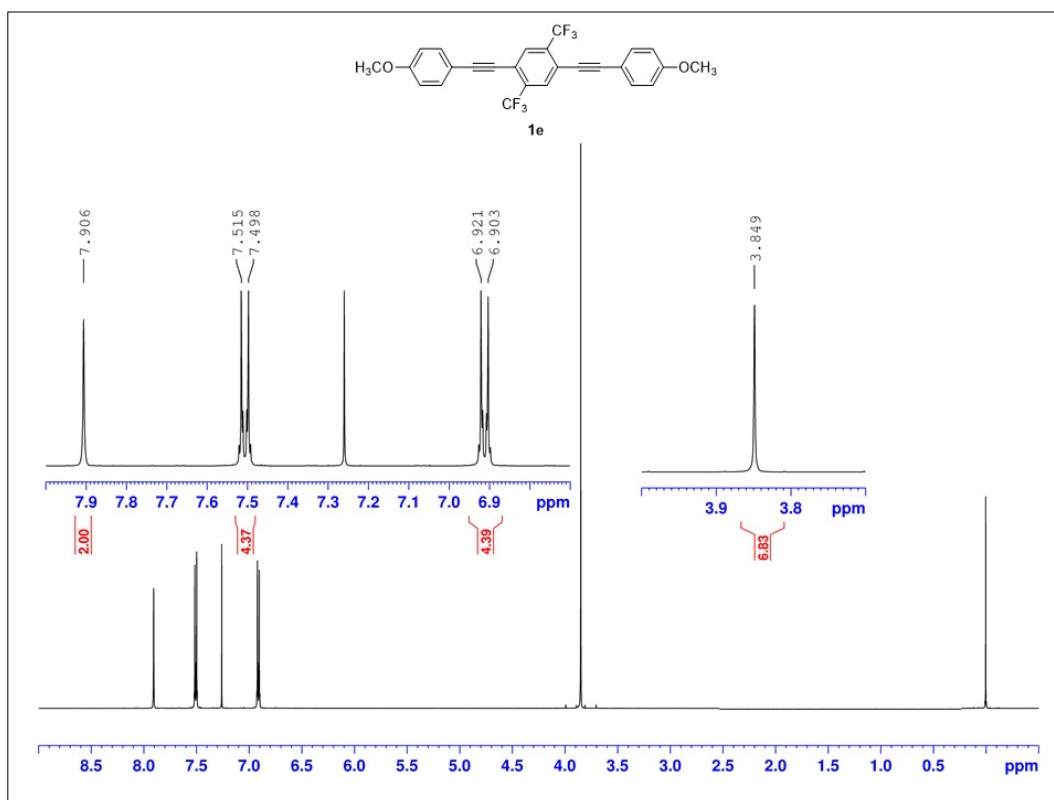


Figure S28: ¹H NMR spectrum of compound **1e** in CDCl₃.

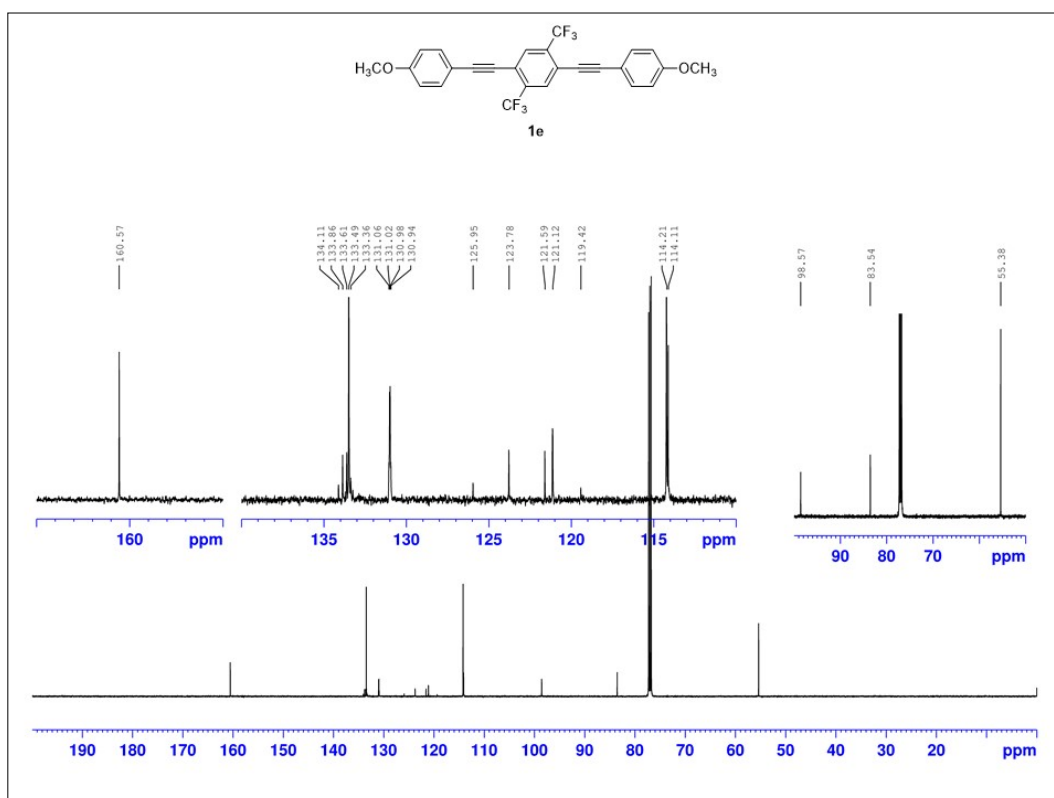


Figure S29: ¹³C NMR spectrum of compound **1e** in CDCl₃.

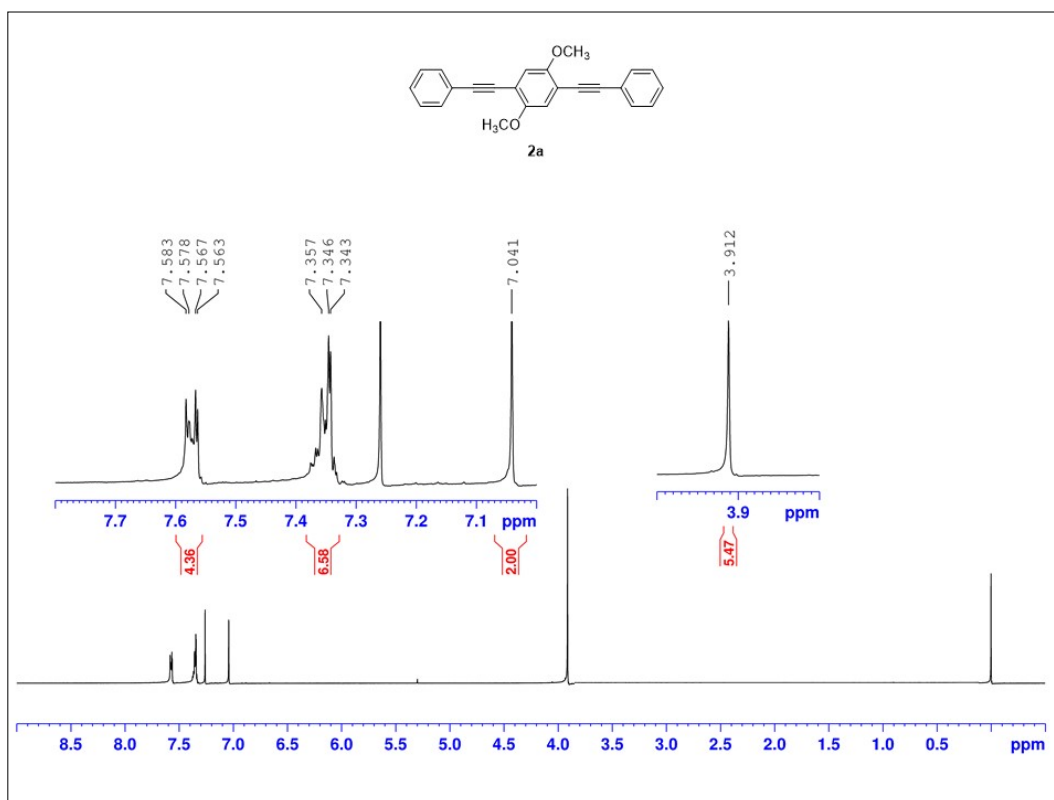


Figure S30: ¹H NMR spectrum of compound **2a** in CDCl₃.

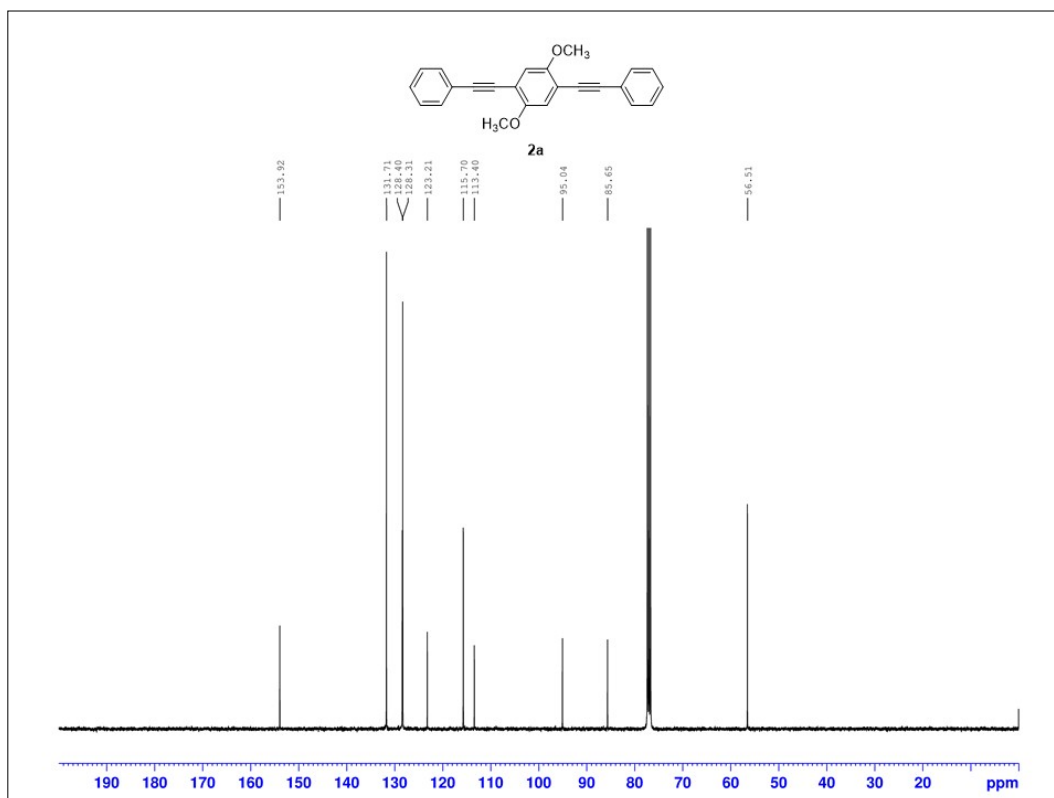


Figure S31: ¹³C NMR spectrum of compound **2a** in CDCl₃.

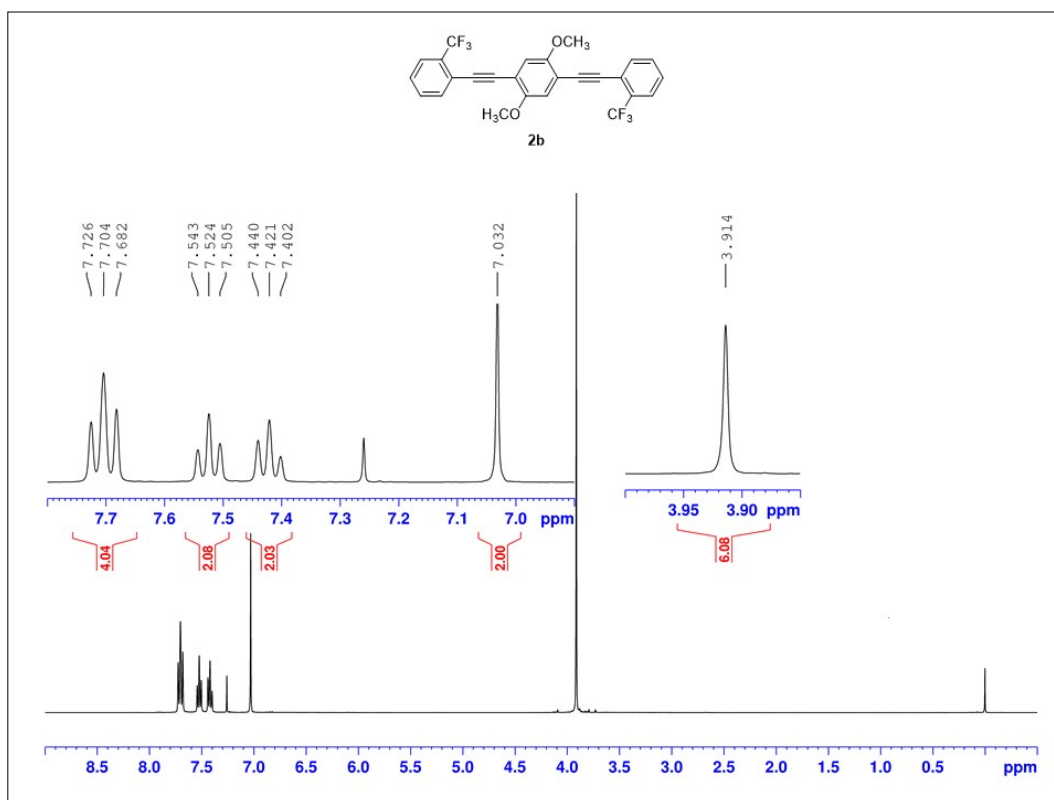


Figure S32: ¹H NMR spectrum of compound **2b** in CDCl₃.

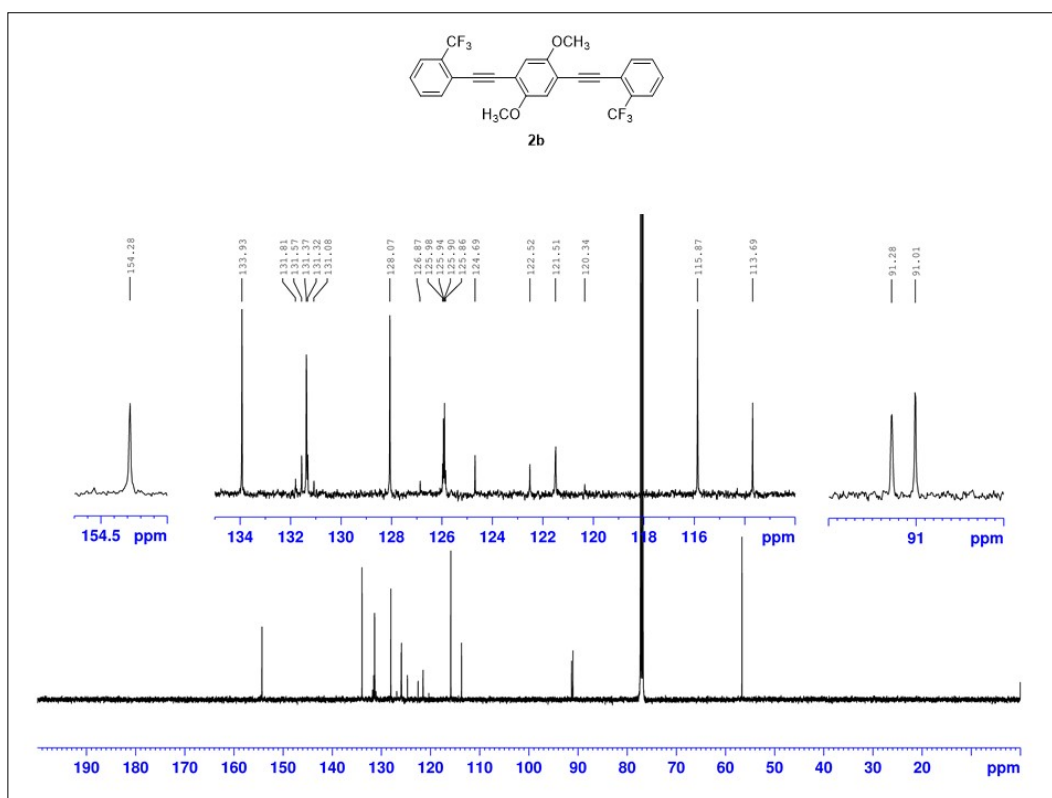


Figure S33: ¹³C NMR spectrum of compound **2b** in CDCl₃.

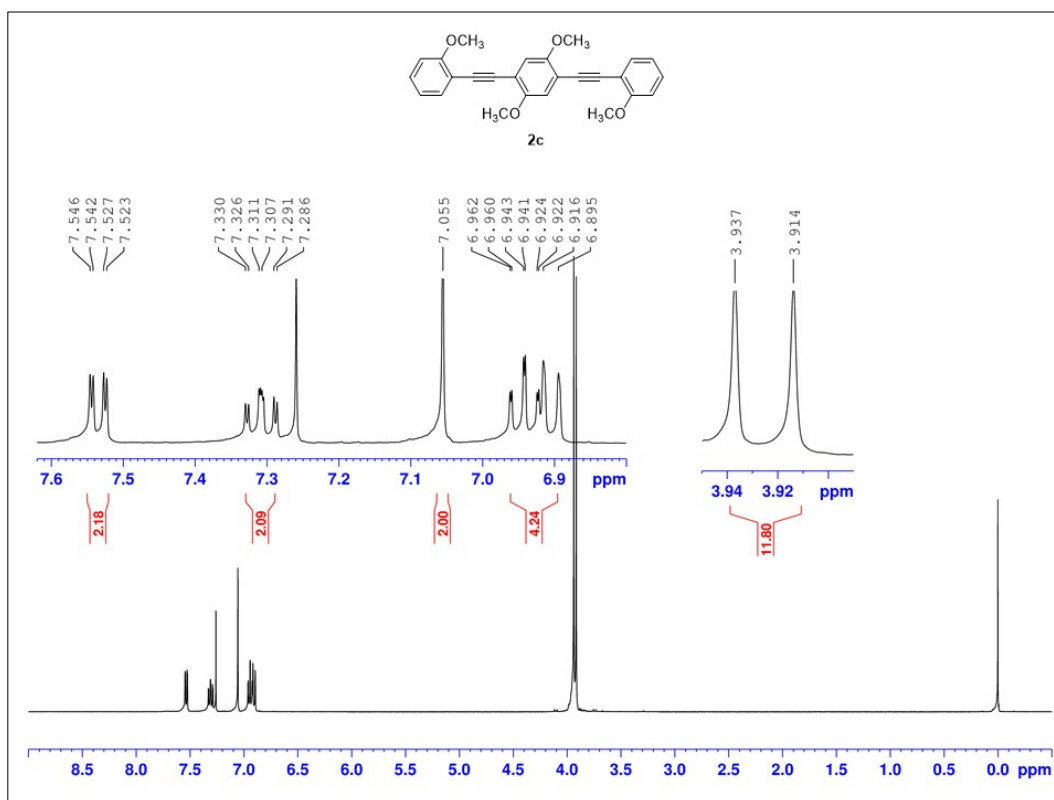


Figure S34: $^1\text{H NMR}$ spectrum of compound **2c** in CDCl_3 .

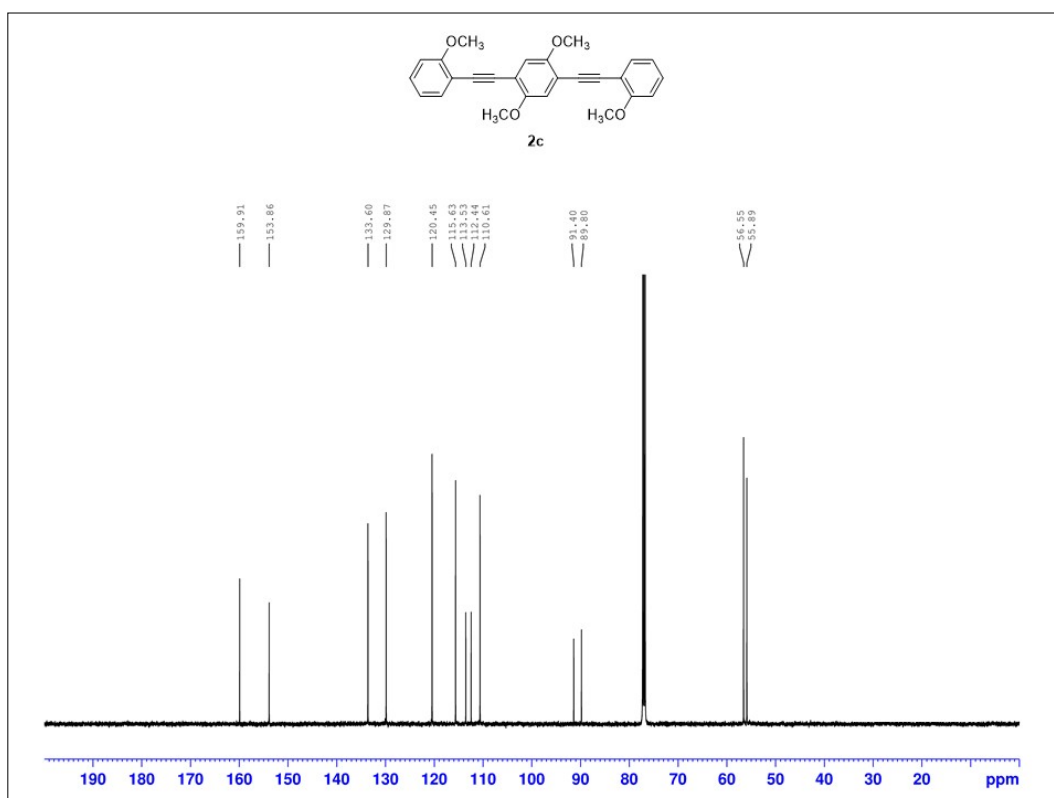


Figure S35: $^{13}\text{C NMR}$ spectrum of compound **2c** in CDCl_3 .

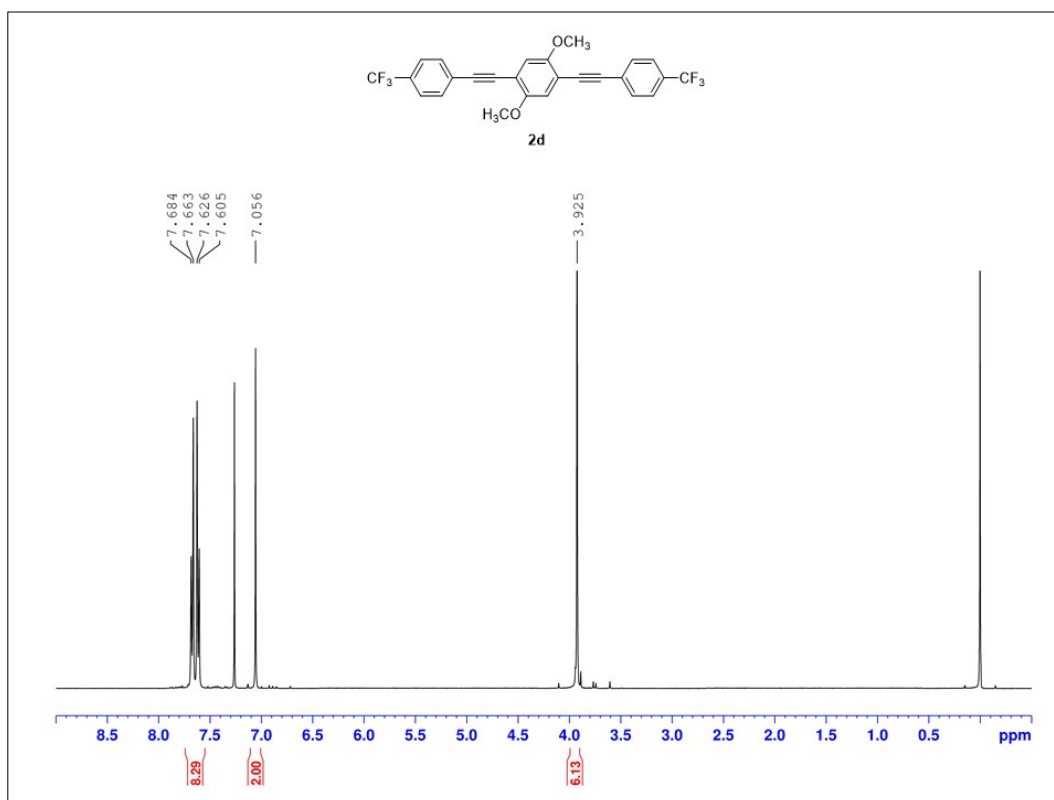


Figure S36: ¹H NMR spectrum of compound **2d** in CDCl₃.

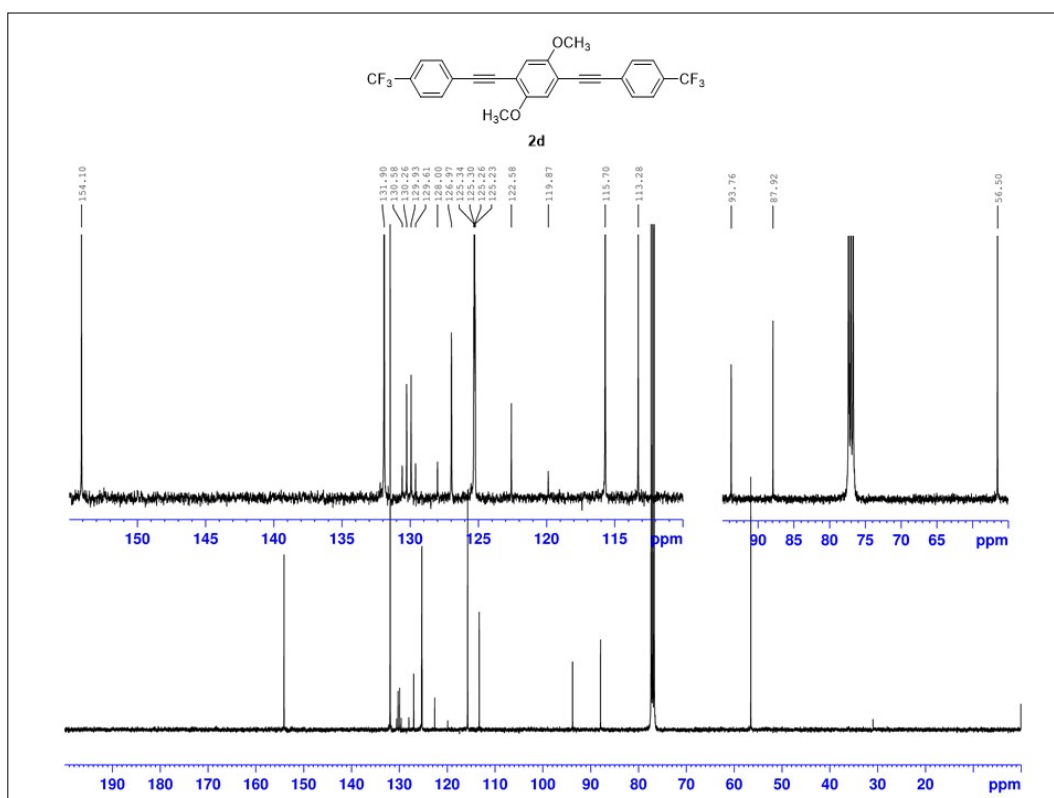


Figure S37: ¹³C NMR spectrum of compound **2d** in CDCl₃.

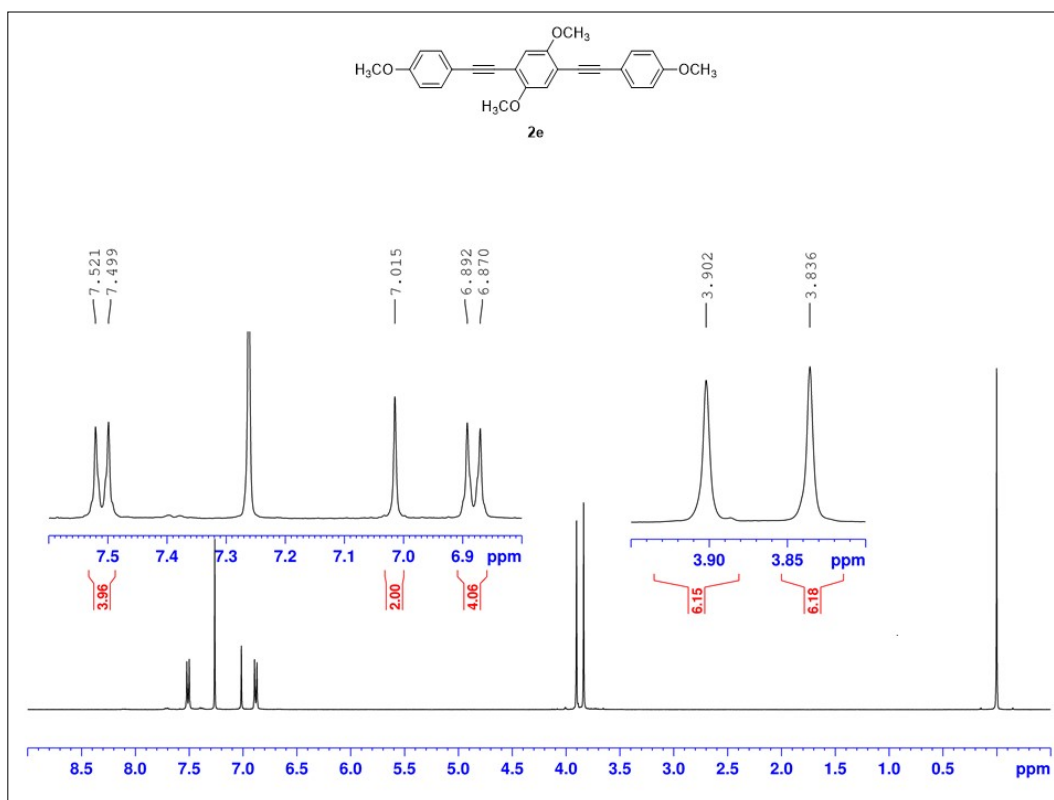


Figure S38: ¹H NMR spectrum of compound **2e** in CDCl₃.

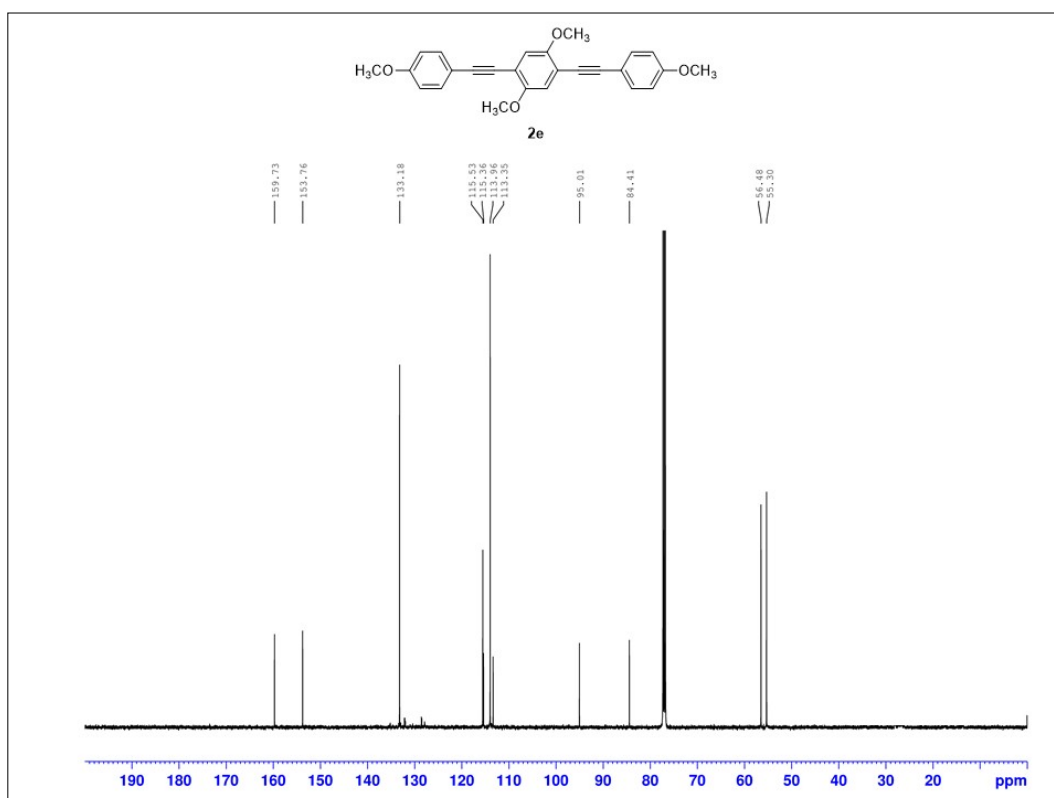


Figure S39: ¹³C NMR spectrum of compound **2e** in CDCl₃.

7. References

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