

**ELECTRONIC SUPPLEMENTARY INFORMATION FOR:
Twisting and Piezochromism of Phenylene-Ethynylenes With
Aromatic Interactions Between Side Chains and Main Chains**

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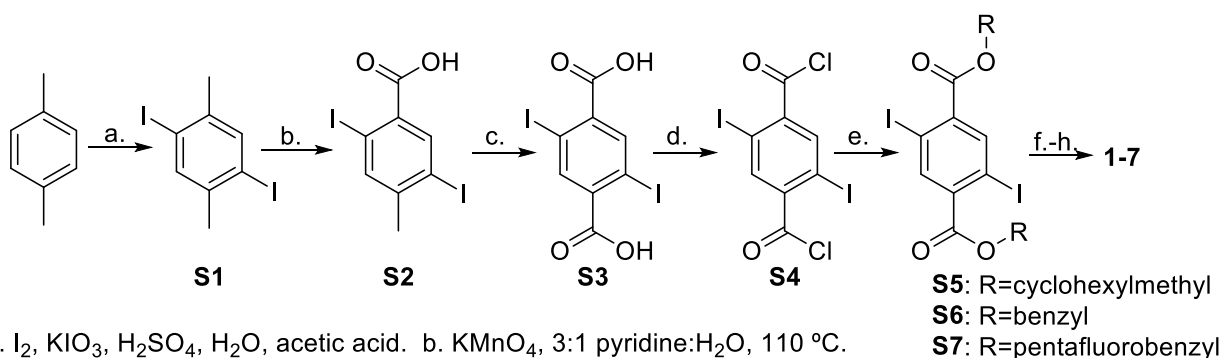
General Considerations

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Melting points were measured on an SRS Digimelt MPA190. High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. TDDFT calculations were performed using the Gaussian 09 software package at the B3LYP/6-31G(d) level.^[1]

Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired using sample absorbances less than 0.1 OD. Fluorescence quantum yields were determined relative to quinine sulfate in 0.5 M H₂SO₄. Thin films were fabricated using dichloromethane or chloroform solutions at 1–2 mg/mL that were filtered with a 0.4 μm PTFE syringe filter and drop-cast onto glass or quartz cover slips.

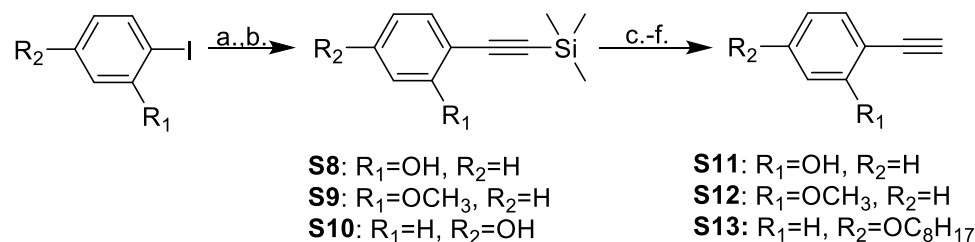
Syntheses

Scheme S1a: Preparation of **1-7** from 2,5-diiodo 1,4-terephthalate esters



- a. I₂, KIO₃, H₂SO₄, H₂O, acetic acid. b. KMnO₄, 3:1 pyridine:H₂O, 110 °C.
c. KMnO₄, 10% aq. NaOH, 100 °C. d. SOCl₂, 70 °C. e. ROH, NEt₃, CH₂Cl₂.
f. **S5**, 4-methoxyphenylacetylene, Pd(PPh₃)₂Cl₂, CuI, THF/NEt₃, 60 °C
g. **S6**, 4-methoxyphenylacetylene, Pd(PPh₃)₂Cl₂, CuI, THF/NEt₃, 60 °C
h. **S7**, **S11** or 4-methoxyphenylacetylene or **S12** or phenylacetylene or **S13**, Pd(PPh₃)₂Cl₂, CuI, THF/NEt₃, 60 °C

Scheme S1b: Preparation of 2- or 4- substituted phenylacetylenes **S11-S13**



- a. 2-iodoanisole, TMSA, Pd(PPh₃)₂Cl₂, CuI, NEt₃, RT
 b. 4-iodophenol or 2-iodophenol, TMSA, Pd(PPh₃)₂Cl₂, CuI, 1:1 dioxane:NEt₃, 45 °C
 c. **S8**, KOH, MeOH/Et₂O, RT
 d. **S9**, KOH, MeOH/THF, 2 hr, RT
 e. **S10**, C₈H₁₇Br, K₂CO₃, DMF, 50 °C, overnight. KOH, MeOH/Et₂O, 2 min, RT.

Preparation of **S1-S4**, **S6**, and **2** followed our previously reported procedures.^[2]

S5: A 20 mL scintillation vial was charged with 100 mg (0.22 mmol) **S4** and evacuated and refilled with argon three times. The reaction mixture was dissolved in 4 mL CH₂Cl₂ then 0.060 mL (55 mg, 0.48 mmol) cyclohexanemethanol and 0.3 mL NEt₃ were added to the reaction vessel and the mixture stirred 16 hours. The reaction mixture was reduced *in vacuo* and redissolved in 20 mL CH₂Cl₂, washed with 10% aqueous HCl (1x20 mL), washed with deionized water (1x20 mL), washed with brine (1x20 mL), and dried with MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by washing with methanol, yielding 52 mg (39%) of **S5** as a colorless crystalline solid. ¹H NMR (300 MHz, CDCl₃) δ: 8.26 (s, 2H) 4.16 (d, *J*=9 Hz, 2H) 1.84-1.68 (m, 11H) 1.35-0.99 (m, 11H) ¹³C NMR (125 MHz, CDCl₃) δ: 164.7, 142.6, 139.0, 92.8, 71.5, 37.0, 29.8, 26.3, 25.6; HRMS calcd for C₂₂H₂₈I₂O₄ (M+H)⁺: 611.0150, found, 611.0160.

S7: A 20 mL scintillation vial was charged with 100 mg (0.22 mmol) **S4**, 96 mg (0.49 mmol) pentafluorobenzyl alcohol. The reaction mixture was dissolved in 10 mL CH₂Cl₂, 0.3 mL NEt₃ was added and the mixture stirred 3 hours. The reaction mixture was poured into 20 mL deionized water, extracted with CH₂Cl₂ (1x15mL), washed with 10% aqueous HCl (1x15 mL), washed with deionized water (1x15 mL), washed with brine (1x15 mL), and dried with MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by recrystallization from CH₂Cl₂/hexanes, yielding 126 mg (73%) of **S7** as a colorless crystalline solid. ¹H NMR (300 MHz, CDCl₃) δ: 8.25 (s, 2H) 5.46 (s, 4H). ¹³C NMR, (125 MHz, CDCl₃) δ: 163.6, 145.8 (d, *J*=250 Hz), 143.0, 142.1 (d, *J*=256 Hz), 138.0, 137.6 (d, *J*=251 Hz), 108.6, 92.9, 54.8. ¹⁹F NMR (470 MHz, CDCl₃) δ: -141.1 (dd, *J*=19 Hz, 5 Hz, 4F) -151.3 (t, *J*=21 Hz, 2F) -160.9 (td, *J*=20, 6 Hz, 4F); HRMS calcd for C₂₂H₆F₁₀I₂O₄ (M+H)⁺, 778.8269, found, 778.8276.

S8: A round bottom flask was charged with 1.16 g (5.25 mmol) 2-iodophenol, 37 mg (0.053 mmol) Pd(PPh₃)₂Cl₂ and 28 mg (0.11 mmol) CuI and evacuated and refilled with argon three times. The reaction mixture was dissolved in 15 mL 1:1 (v:v) dioxane:triethylamine (sparged with argon 30 min) and stirred. 0.97 mL (670 mg, 6.8 mmol) trimethylsilylacetylene was added and the reaction mixture stirred at 45 °C for 16 hours. The reaction mixture was poured into 100 mL 10% aqueous HCl and extracted with diethyl ether (2x75 mL). The organic extract was washed with 5% aqueous NaHCO₃ (1x100 mL) and brine (1x75 mL) and dried with MgSO₄. The solvent was reduced *in vacuo* and purified with flash

chromatography on silica (9:1 hexanes:CH₂Cl₂) yielding 742 mg (74%) **S8** as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.30 (dd, *J*₁=2 Hz, *J*₂=8 Hz, 1H), 7.25 (dt, *J*₁=2 Hz, *J*₂=8 Hz, 1H), 6.94 (dd, *J*₁=1 Hz, *J*₂=8 Hz, 1H), 6.85 (dt, *J*₁=1 Hz, *J*₂=8 Hz, 1H), 5.83 (s, 1H), 0.28 (s, 9H), in good agreement with the same compound reported in the literature.^[3]

S9: A Schlenk tube was charged with 37 mg (0.053 mmol) Pd(PPh₃)₂Cl₂ and 28 mg (0.11 mmol) CuI and evacuated and refilled with argon three times. 720 mg (3.08 mmol) 2-iodoanisole and 0.25 mL (360 mg, 3.70 mmol) trimethylsilylacetylene were dissolved in 5 mL triethylamine, sparged with argon 30 min and added to the reaction vessel, and stirred at room temperature for 16 hours. 0.10 mL (69 mg, 0.70 mmol) trimethylsilylacetylene was added to the reaction mixture and the mixture stirred 1 additional hour. The solvent was reduced *in vacuo* and purified with flash chromatography on silica (hexanes to 7:1 hexanes:CH₂Cl₂) yielding 307 mg (49%) **S8** as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.45-7.43 (m, 1H), 7.31-7.28 (m, 1H), 6.91-6.84 (m, 2H), 3.89 (s, 3H), 0.27 (s, 9H), in good agreement with the same compound reported in the literature.^[4]

S10: A round bottom flask was charged with 2.32 g (10.5 mmol) 4-iodophenol, 74 mg (0.11 mmol) Pd(PPh₃)₂Cl₂ and 56 mg (0.21 mmol) CuI and evacuated and refilled with argon three times. The reaction mixture was dissolved in 10 mL 1:1 (v:v) dioxane:triethylamine (sparged with argon 30 min) and stirred. 1.94 mL (1.34 g, 13.7 mmol) trimethylsilylacetylene was added and the reaction mixture stirred at 45 °C for 20 hours. The reaction mixture was poured into 50 mL 10% aqueous HCl and extracted with hexanes (2x50 mL). The organic extract was washed with deionized water (2x75 mL) and brine (1x50 mL) and dried with MgSO₄. The solvent was reduced *in vacuo* and purified via flushing through a silica plug with 1:1 hexanes:CH₂Cl₂ yielding 1.66 g (82%) **S10** as a dark red solid. ¹H NMR (500 MHz, CDCl₃) δ: 7.36 (d, *J*=9 Hz, 2H), 6.75 (d, *J*=9 Hz, 2H), 0.23 (s, 9H), in good agreement with the same compound reported in the literature.^[5]

S11: 154 mg (0.7 mmol) **S8** was dissolved in 5 mL diethyl ether and added to a separatory funnel. 15 mL (30 mmol) of a 2M KOH/methanol solution was added and the mixture was vigorously shaken for 2 min, venting every 5-10 seconds. **CAUTION: Accumulation of pressure within the separatory funnel can occur during this procedure.** 10% aqueous HCl was added to the mixture until the organic layer separated. The aqueous layer was extracted with hexanes (2x10 mL), and the aqueous layer was further treated with 10% aqueous HCl until the pH was <2. The aqueous fraction was extracted with diethyl ether (2x10 mL) and all the organic fractions were combined washed with deionized water (1x20 mL), brine (1x20 mL) and dried with MgSO₄. The solvent was reduced *in vacuo* yielding 49 mg (59%) **S11** as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ: 7.38 (dd, *J*₁=2 Hz, *J*₂=8 Hz, 1H), 7.28 (dt, *J*₁=2 Hz, *J*₂=8 Hz, 1H), 6.96 (dd, *J*₁=1 Hz, *J*₂=9 Hz, 1H), 6.88 (dt, *J*₁=1 Hz, *J*₂=8 Hz, 1H), 5.78 (s, 1H), 3.47 (s, 1H), in good agreement with the same compound reported in the literature.^[6]

S12: A 20 mL scintillation vial was charged with 298 mg (1.46 mmol) **S9** and evacuated and refilled with argon three times. 5 mL (10 mmol) of a 2M KOH/methanol solution was added and the reaction stirred. Anhydrous tetrahydrofuran was added until the reaction mixture became homogenous (3 mL) and the reaction stirred 2 hours. The reaction mixture was poured into 40 mL 10% aqueous HCl and extracted with diethyl ether (1x30 mL). The organic extract was washed with brine (1x20 mL) and dried with MgSO₄. The solvent was reduced *in vacuo* yielding 129 mg (67%) **S12** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ: 7.47-7.46 (m, 1H), 7.34-7.31 (m, 1H), 6.93-6.88 (m, 2H), 3.91 (s, 3H), 3.31 (s, 1H), in good agreement with the same compound reported in the literature.^[7]

S13: A round bottom flask was charged with 435 mg (3.15 mmol) potassium carbonate and evacuated and refilled with argon three times. 200 mg (1.05 mmol) **S10** was dissolved in 9 mL DMF in argon

atmosphere and added to the reaction vessel. 0.22 mL (240 mg, 1.3 mmol) 1-bromooctane was added to the reaction vessel and the mixture was stirred at 50 °C for 16 hours. The reaction mixture was poured into 50 mL deionized water and extracted with diethyl ether (3x10 mL). The organic fraction was washed with 10% aqueous HCl (1x20 mL) and deionized water (2x20mL). 20 mL 2M KOH/methanol solution was added to the organic fraction and the mixture was shaken vigorously for 3 minutes, venting every 5-10 seconds. **CAUTION: Pressure can accumulate within the separatory funnel during this procedure.** 10% aqueous HCl was added until the organic layer separated. The aqueous fraction was extracted with hexanes (2x10 mL) and the organic fractions were combined and washed with brine (1x20 mL) and dried with MgSO₄. The solvent was reduced *in vacuo* and the crude product was purified with flash chromatography on silica (hexanes) yielding 120 mg (50%) **S13** as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ: 7.41 (d, *J*=9 Hz, 2H), 6.83 (d, *J*=9 Hz, 2H), 3.95 (t, *J*=7 Hz, 2H), 2.99 (s, 1H), 1.78 (quin, *J*=7 Hz, 2H), 1.47-1.25 (m, 10H), 0.89 (t, *J*=7 Hz, 3H), in good agreement with the same compound reported in the literature.^[8]

1: A Schlenk tube was charged with 4 mg (0.006 mmol) Pd(PPh₃)₄ and 2 mg (0.006 mmol) CuI, and evacuated and refilled with argon three times. 38 mg (0.062 mmol) **S5** and 18 mg (0.136 mmol) 4-ethynylanisole were dissolved in 10 mL 1:1 THF:NEt₃, sparged with argon 30 minutes and added to the reaction vessel and the mixture was stirred at 60 °C for 16 hours. The solvent was reduced *in vacuo* and the crude product immobilized on silica and purified with flash chromatography on silica (3:1 CH₂Cl₂:hexanes) and further purified by recrystallization from CH₂Cl₂/hexanes yielding 33 mg (87%) of **1** as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ: 8.16 (s, 2H) 7.52 (d, *J*=9 Hz, 4H) 6.90 (d, *J*=9 Hz, 4H) 4.19 (d, *J*=6 Hz, 4H) 3.85 (s, 6H), 1.87-1.69 (m, 12H), 1.25-1.02 (m, 10H). ¹³C NMR (125 MHz, CDCl₃) δ: 165.4, 160.1, 135.8 134.3, 133.4, 122.8, 115.1, 114.1, 96.8, 86.6, 70.9, 55.4, 37.1, 29.8, 26.3, 25.6. HRMS calcd for C₄₀H₄₂O₆ (M+H)⁺, 619.3054, found, 619.3143. Melting point: 162-164 °C.

3: A Schlenk tube was charged with 30 mg (0.039 mmol) **S7**, < 1 mg Pd(PPh₃)₂Cl₂ and <1 mg CuI, and evacuated and refilled with argon three times. 14 mg (0.12 mmol) **S11** was dissolved in 10 mL 1:1 THF:NEt₃ and sparged with argon for 20 minutes and added to the reaction vessel. The mixture heated to 60 °C, allowed to return to room temperature and stirred for 16 hours. The mixture was poured into 25 mL 10 % aqueous HCl, extracted with CH₂Cl₂ (3x15 mL), washed with deionized water (1x15 mL), washed with brine (1x15 mL) and dried with MgSO₄. The mixture was reduced *in vacuo* and the crude product was purified by flash chromatography (3:1 hexanes:CH₂Cl₂ eluent) followed by recrystallization from CH₂Cl₂:hexanes yielding 12 mg (42%) of **3** as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ: 8.26 (s, 2H) 7.88 (s, 2H), 7.44 (dd, *J*₁=1 Hz, *J*₂=8 Hz, 2H) 7.35 (dt, *J*₁=2 Hz, *J*₂=7 Hz, 2H) 7.04 (d, *J*=8 Hz, 2H) 6.91 (dt, *J*₁=1 Hz, *J*₂=8 Hz, 2H), 5.56 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ: 163.9, 159.4, 146.9 (d, *J*=251 Hz), 142.3 (d, *J*=256 Hz), 137.7 (d, *J*=246 Hz) 135.5 132.0, 131.3, 123.6, 120.0, 115.6, 108.5, 94.4, 93.9, 55.1. ¹⁹F NMR (470 MHz, CDCl₃) δ: -141.1 (dd, *J*₁=5 Hz, *J*₂=19 Hz, 4F), -151.1 (t, *J*=21 Hz, 2H), -160.7 (dt, *J*₁=5 Hz, *J*₂=19 Hz); HRMS calcd for C₃₈H₁₆F₁₀O₆ (M+H)⁺, 759.0860, found 759.0870. Melting point: 234-235 °C.

4: A Schlenk tube was charged with 4 mg (0.006 mmol) Pd(PPh₃)₄ and 2 mg (0.006 mmol) CuI, and evacuated and refilled with argon three times. 50 mg (0.064 mmol) **S7** and 19 mg (0.141 mmol) 4-ethynylanisole were dissolved in 10 mL 1:1 THF:NEt₃, sparged with argon 30 minutes and added to the reaction vessel and the mixture was stirred at 60 °C for 16 hours. The solvent was reduced *in vacuo* and the crude product immobilized on silica and purified with flash chromatography on silica (1:1 CH₂Cl₂:hexanes) and further purified by recrystallization from CH₂Cl₂/hexanes yielding 40 mg (80%) of **4** as a white solid ¹H NMR (500 MHz, CDCl₃) δ: 8.15 (s, 2H) 7.38 (d, *J*=8.5 Hz, 4H) 6.88 (d, *J*=8.5 Hz,

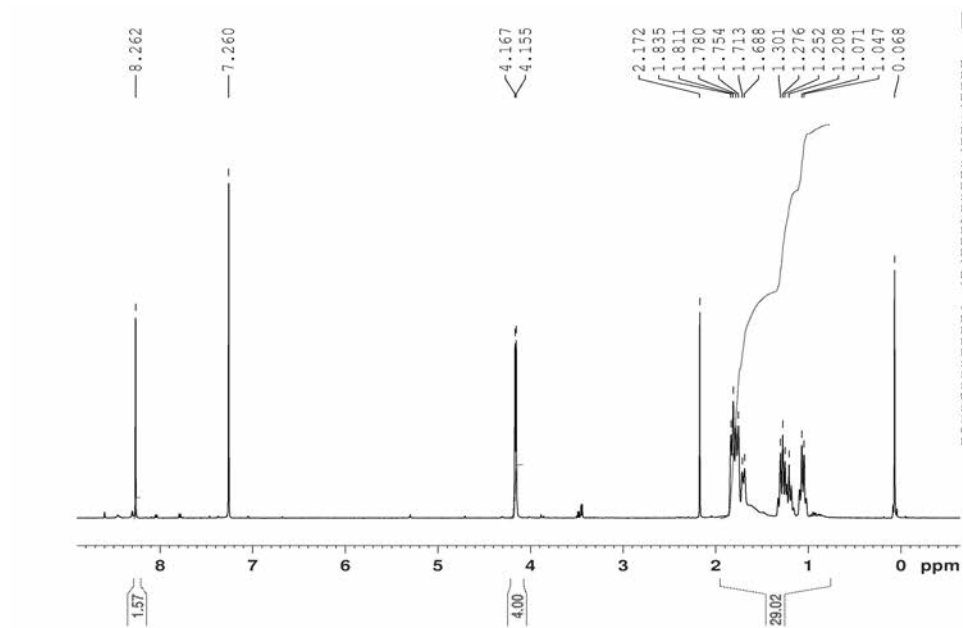
4H) 5.47 (s, 4H) 3.85 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ : 164.3, 160.3, 145.8 (d, $J=249$ Hz), 141.9 (d, $J=254$ Hz), 137.5 (d, $J=251$ Hz) 136.2, 133.1, 133.0, 123.3, 114.5, 114.1, 109.0 (t, $j=17.5$ Hz) 97.5, 85.8, 55.4, 54.3. ^{19}F NMR (470 MHz, CDCl_3) δ : -141.5 (dd), -152.0 (t), -161.3 (td); HRMS calcd for $\text{C}_{40}\text{H}_{20}\text{F}_{10}\text{O}_6(\text{M}+\text{H})^+$, 787.1173, found, 787.1181. Melting point: 232-234 °C.

5: A Schlenk tube was charged with 43 mg (0.055 mmol) **S7**, 16 mg (0.12 mmol) **S12**, 4 mg (0.006 mmol) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 2 mg (0.006 mmol) CuI , and evacuated and refilled with argon three times. The reaction mixture was dissolved in 10 mL 1:1 THF: NEt_3 (sparged with argon for 30 minutes). The mixture was heated to 65 °C and stirred for 16 hours. The mixture was reduced *in vacuo* and the crude product immobilized on silica and purified with flash chromatography on silica (gradient elution, 3:1 hexanes: CH_2Cl_2 to 1:1 hexanes: CH_2Cl_2) followed by recrystallization from CH_2Cl_2 :hexanes, yielding 28 mg (64%) of **5** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ : 8.23 (s, 2H) 7.39-7.34 (m, 4H) 6.95-6.89 (m, 4H) 5.46 (s, 4H) 3.91 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ : 164.3, 160.0, 145.8 (d, $J=254$ Hz), 141.7 (d, $J=254$ Hz), 139.7 (d, $J=250$ Hz) 138.4, 138.3, 136.4, 133.4, 133.2, 130.6, 123.4, 120.5, 111.6, 110.6, 108.9, 93.9, 90.7, 55.8, 54.2. ^{19}F NMR (470 MHz, CDCl_3) δ : -141.5 (dd), -151.9 (t), -161.5 (td); HRMS calcd for $\text{C}_{40}\text{H}_{20}\text{F}_{10}\text{O}_6(\text{M}+\text{H})^+$, 787.1173, found, 787.1170. Melting point: 211-212 °C.

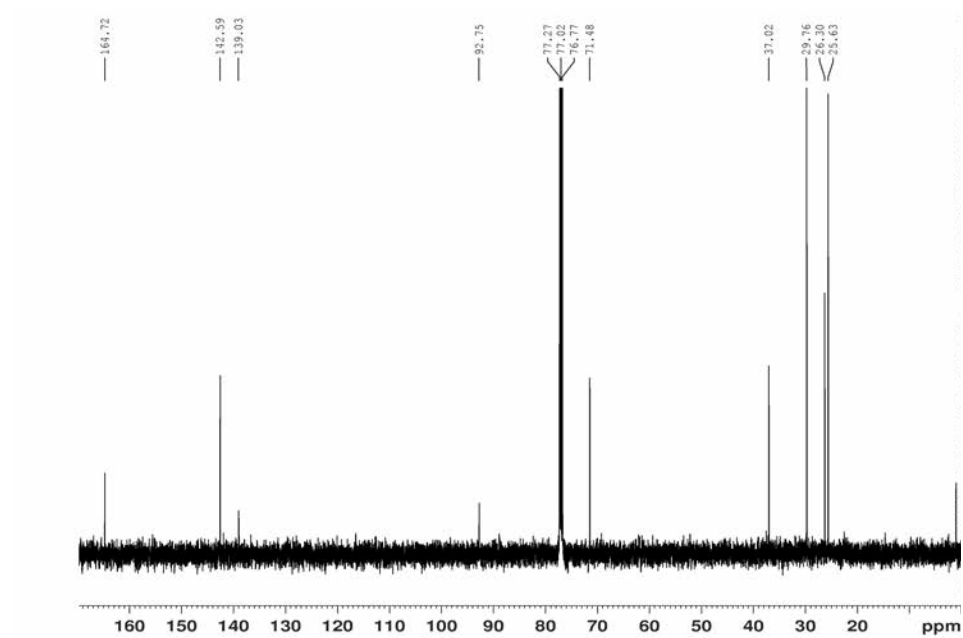
6: A Schlenk tube was charged with 30 mg (0.039 mmol) **S7**, 3 mg (0.004 mmol) $\text{Pd}(\text{PPh}_3)\text{Cl}_2$, and 1 mg (0.004 mmol) CuI and evacuated and refilled with argon three times. 10 mg (0.094 mmol) phenylacetylene and was dissolved in 10 mL 1:1 (v:v) THF: NEt_3 and the solution was sparged with argon 30 minutes and added to the reaction vessel. The reaction mixture was stirred 16 hours at 65 °C, then reduced *in vacuo* and immobilized on silica. The crude product was purified by flash chromatography on silica (gradient elution, 7:1 hexanes: CH_2Cl_2 to 3:1 hexanes: CH_2Cl_2). The product was further purified by recrystallization from hexanes: CH_2Cl_2 yielding 16 mg (55%) **6**, a white solid. ^1H NMR (500 MHz, CDCl_3) δ : 8.19 (s, 2H), 7.45-7.34 (m, 10H), 5.48 (s, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ : 164.1, 145.8 (d, $J=246$ Hz), 141.9 (d, $J=251$ Hz), 138.5, 136.4, 133.4, 131.4, 129.1, 128.4, 123.3, 122.4, 108.9, 97.3, 86.7, 54.4. ^{19}F NMR (475 MHz, CDCl_3) δ : -141.5 (dd, $J_1=9$ Hz, $J_2=24$ Hz) -151.7 (t, $J=19$ Hz), -161.2 (td, $J_1=10$ Hz, $J_2=23$ Hz). HRMS calcd for $\text{C}_{38}\text{H}_{16}\text{F}_{10}\text{O}_4(\text{M}+\text{H})^+$, 727.0962, found, 727.0945. Melting point: 227-228 °C.

7: A Schlenk tube was charged with 31 mg (0.04 mmol) **S7**, 3.5 mg (0.005 mmol) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and 1 mg (0.005 mmol) CuI , and evacuated and refilled with argon three times. 25.2 mg (0.11 mmol) **S13** was dissolved in 10 mL 1:1 THF: NEt_3 and sparged with argon for 30 minutes and added to the reaction vessel. The mixture heated to 60 °C and stirred for 16 hours. The mixture was poured into 20 mL 10 % aqueous HCl, extracted with hexanes (1x20 mL), washed with deionized water (1x20 mL), washed with brine (1x20 mL) and dried with MgSO_4 . The mixture was reduced *in vacuo* and purified with flash chromatography on silica (3:1 hexanes: CH_2Cl_2) followed by recrystallization from hexanes yielding 21 mg (52%) of **7** as a waxy, pale yellow solid. ^1H NMR (500 MHz, CDCl_3) δ : 8.14 (s, 2H) 7.37 (d, $J=8.5$ Hz, 4H) 6.86 (d, $J=8.5$ Hz, 4H) 5.47 (s, 4H) 3.85 (t, 4H), 1.81 (quin, $J=7$ Hz, 4 H) 1.47 (quin, $J=7$ Hz, 4H), 1.38-1.25 (m, 16H), 0.89 (t, $J=7$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ : 164.3, 159.9, 144.7 (d, $J=248$ Hz), 141.8 (d, $J=270$ Hz), 137.5 (d, $J=249$ Hz) 136.2, 133.0, 123.3, 114.6, 114.2, 108.9, 97.7, 85.8, 68.2, 54.2, 31.8, 29.3, 29.2, 29.2, 26.0, 22.7, 14.1. ^{19}F NMR (470 MHz, CDCl_3) δ : -141.5 (dd, $J_1=7$ Hz, $J_2=21$ Hz), -152.0 (t, $J=19$ Hz), -161.3 (td, $J_1=10$ Hz, $J_2=23$ Hz); HRMS calcd for $\text{C}_{54}\text{H}_{48}\text{F}_{10}\text{O}_6(\text{M}+\text{H})^+$, 983.3364, found, 983.3362. Melting point: 144-145 °C.

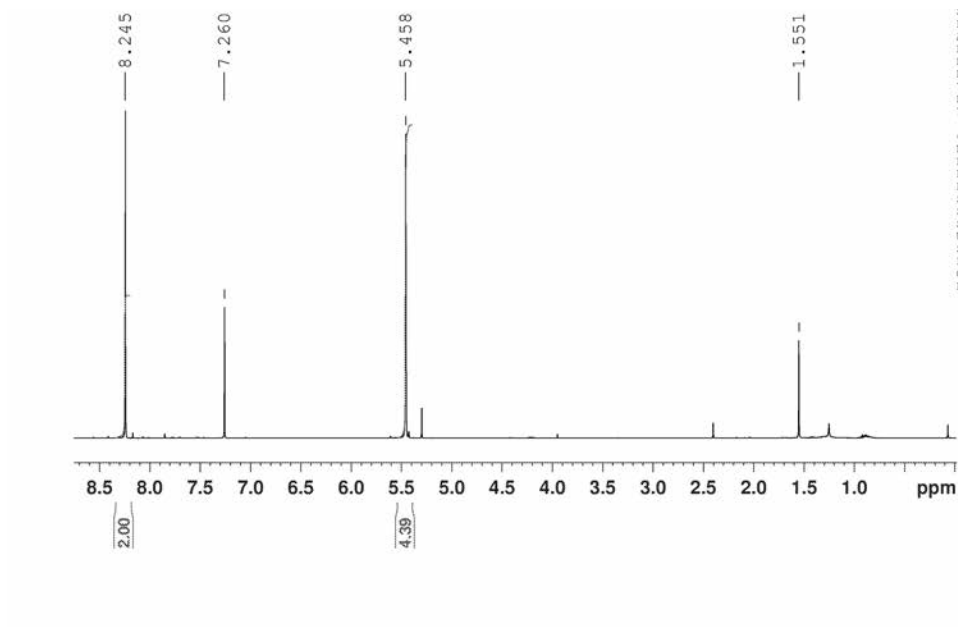
S5, ^1H NMR, (500 MHz, CDCl_3)



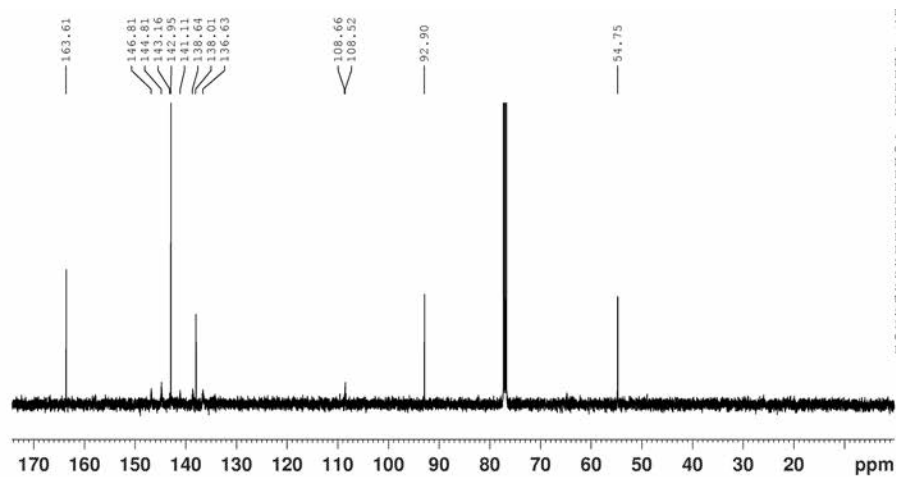
S5, ^{13}C NMR, (125 MHz, CDCl_3)



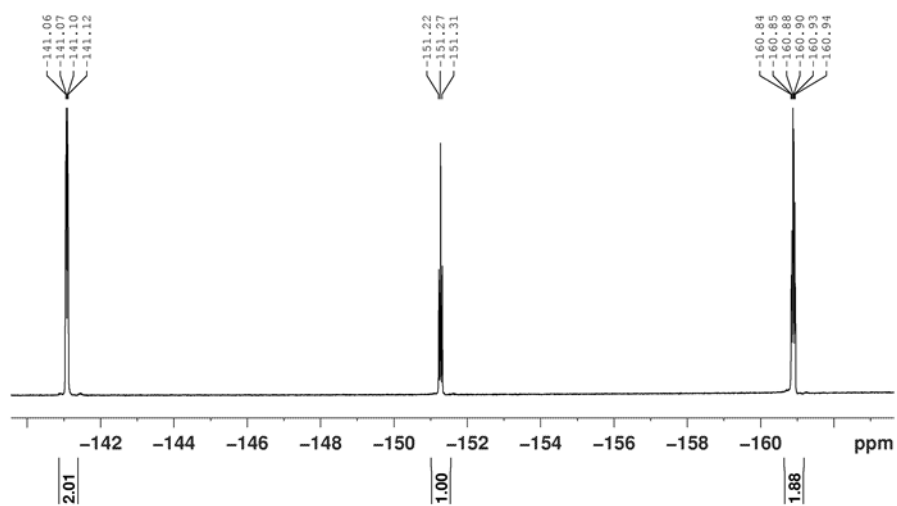
S7, ^1H NMR (500 MHz, CDCl_3)



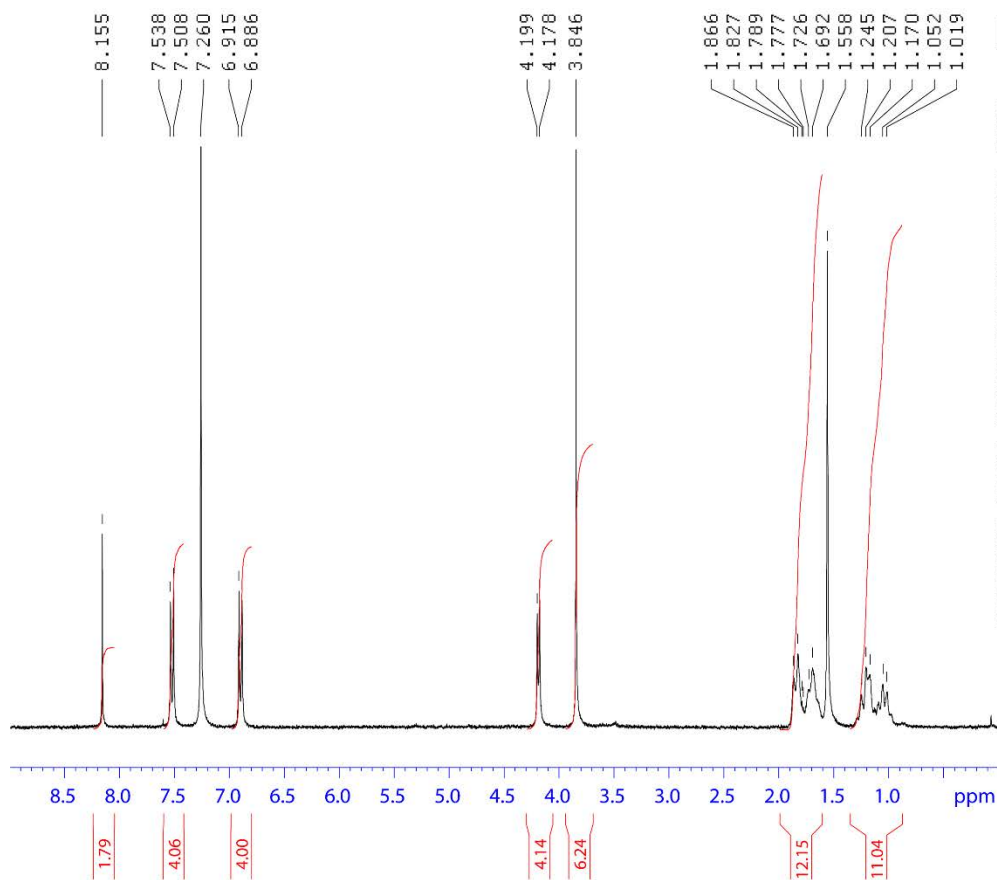
S7, ^{13}C NMR, 125 MHz, CDCl_3



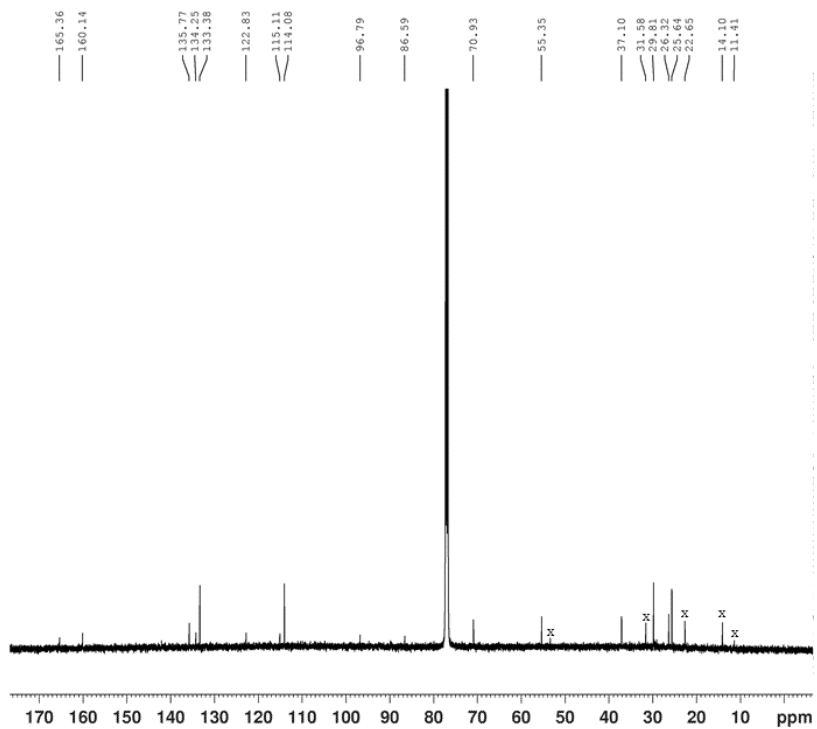
S7, ^{19}F NMR, 470 MHz, CDCl_3



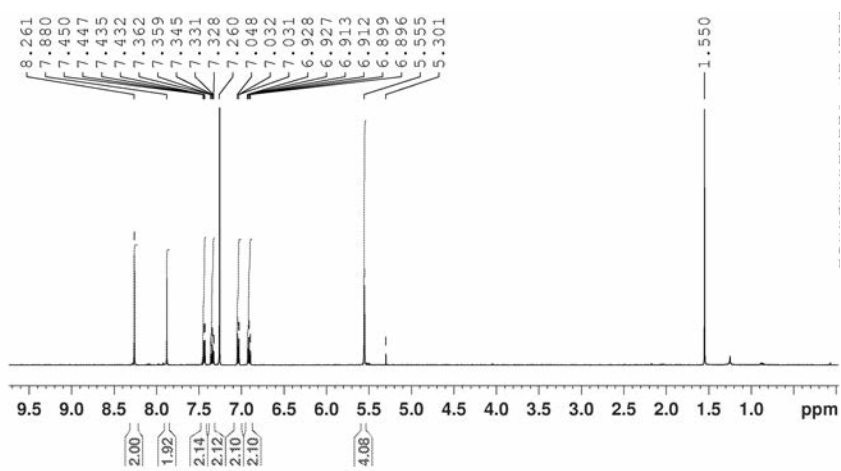
1, ^1H NMR, 300 MHz, CDCl_3



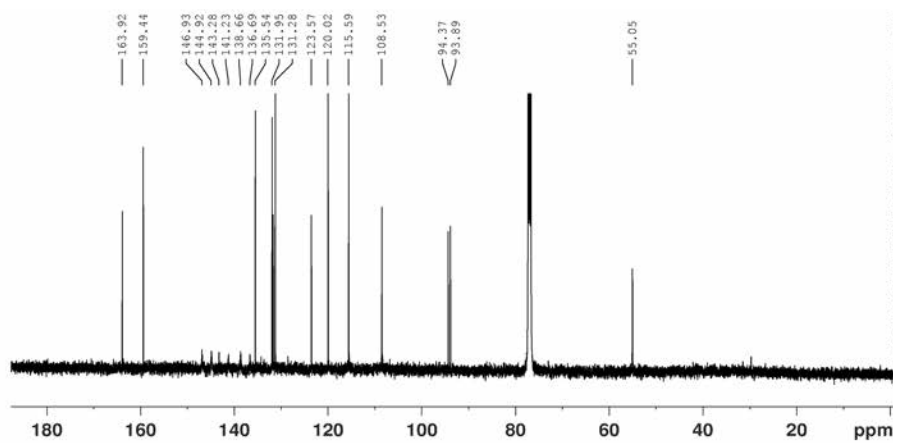
1, ^{13}C NMR, 125 MHz, CDCl_3 (X=residual solvent)



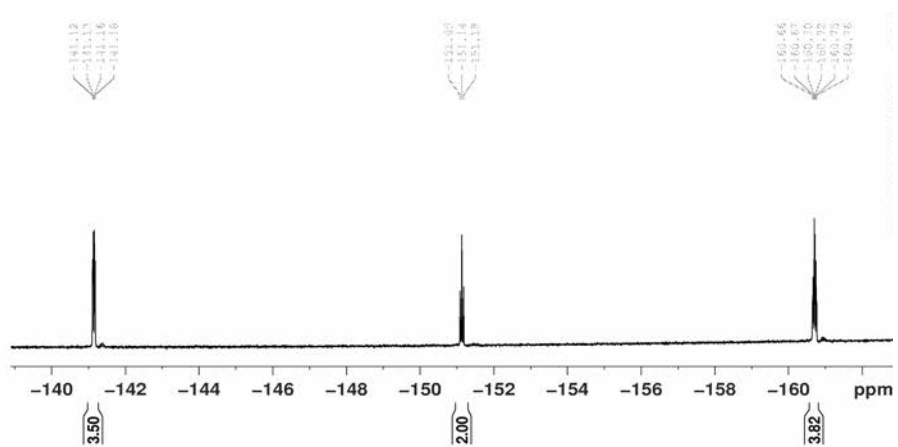
3, ^1H NMR, 500 MHz, CDCl_3



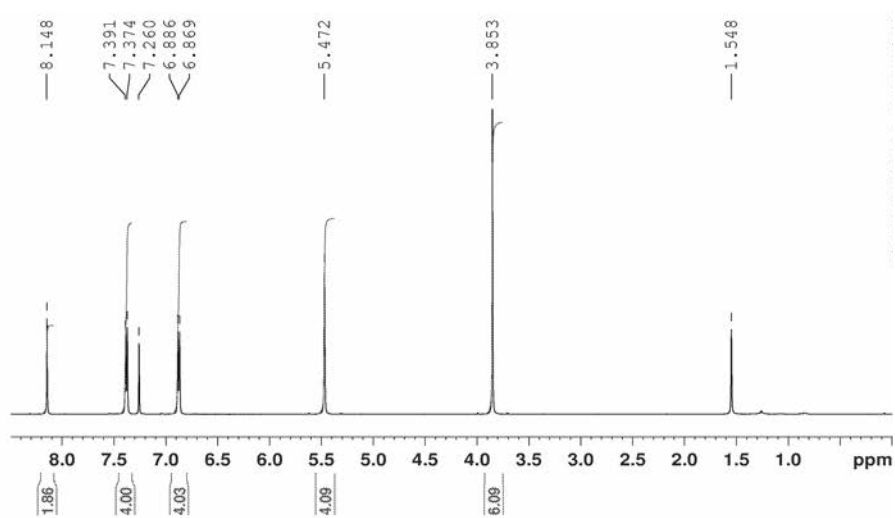
3, ^{13}C NMR, 125 MHz, CDCl_3



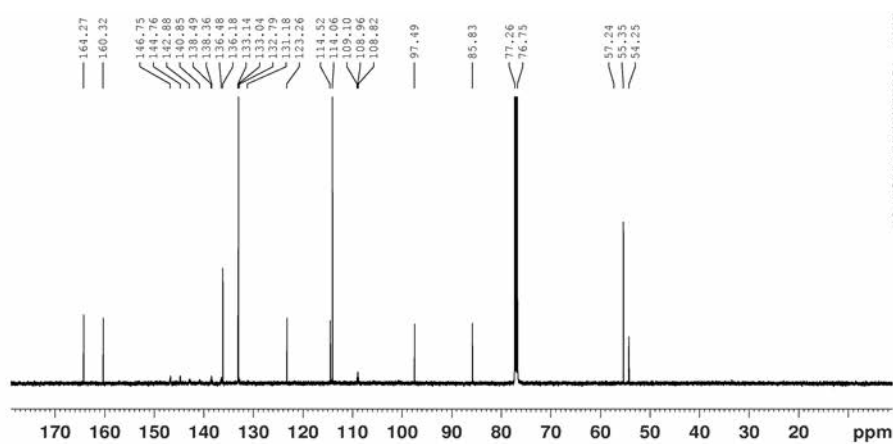
3, ^{19}F NMR, 470 MHz, CDCl_3



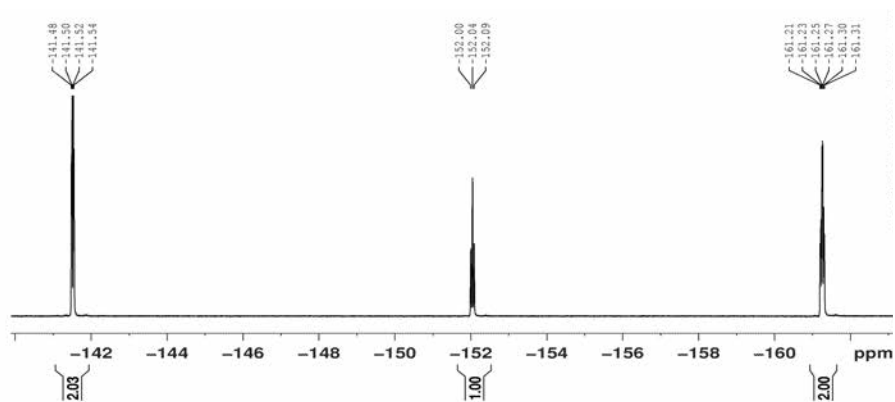
4, ^1H NMR, 500 MHz, CDCl_3



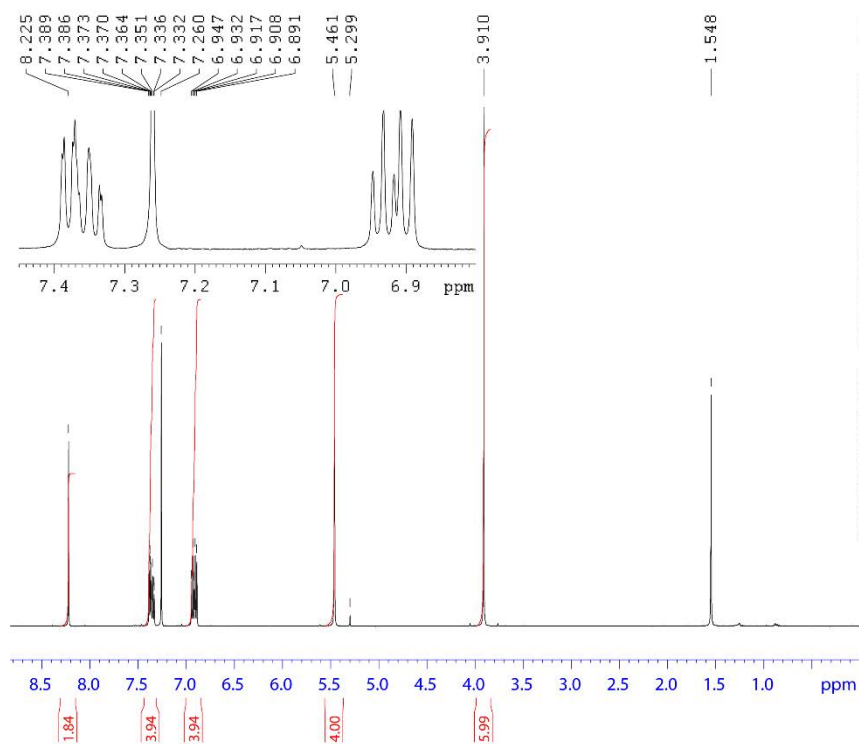
4, ^{13}C NMR, 125 MHz, CDCl_3



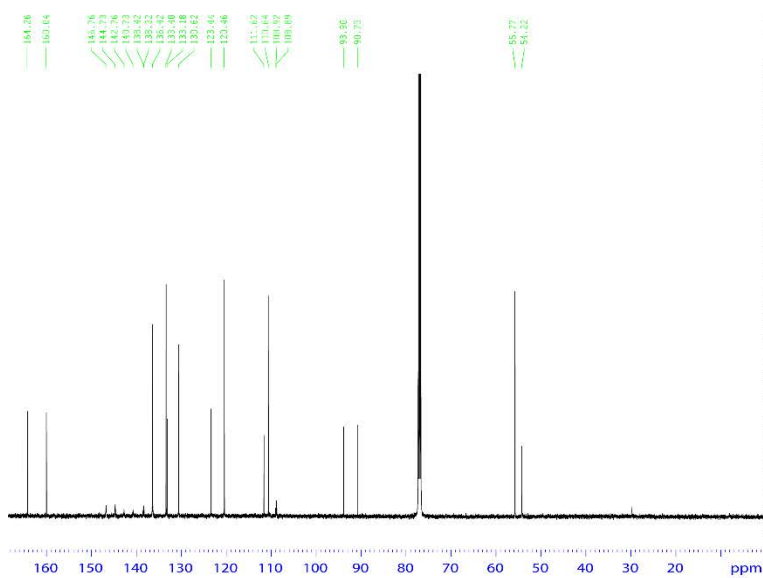
4, ^{19}F NMR, 470 MHz, CDCl_3



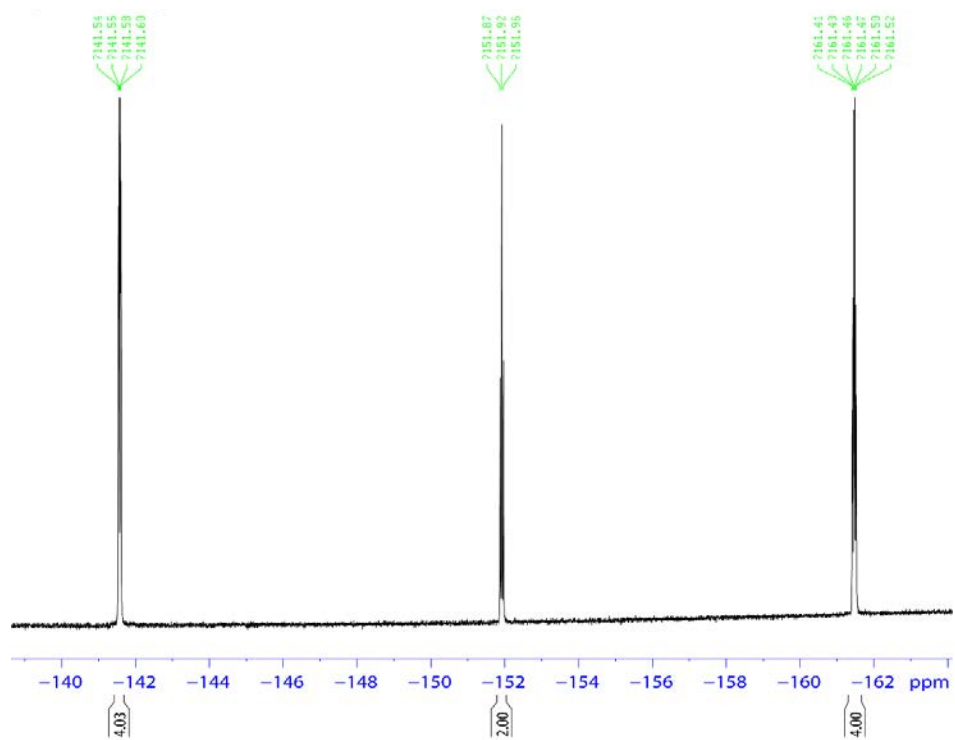
5, ^1H NMR, 500 MHz, CDCl_3



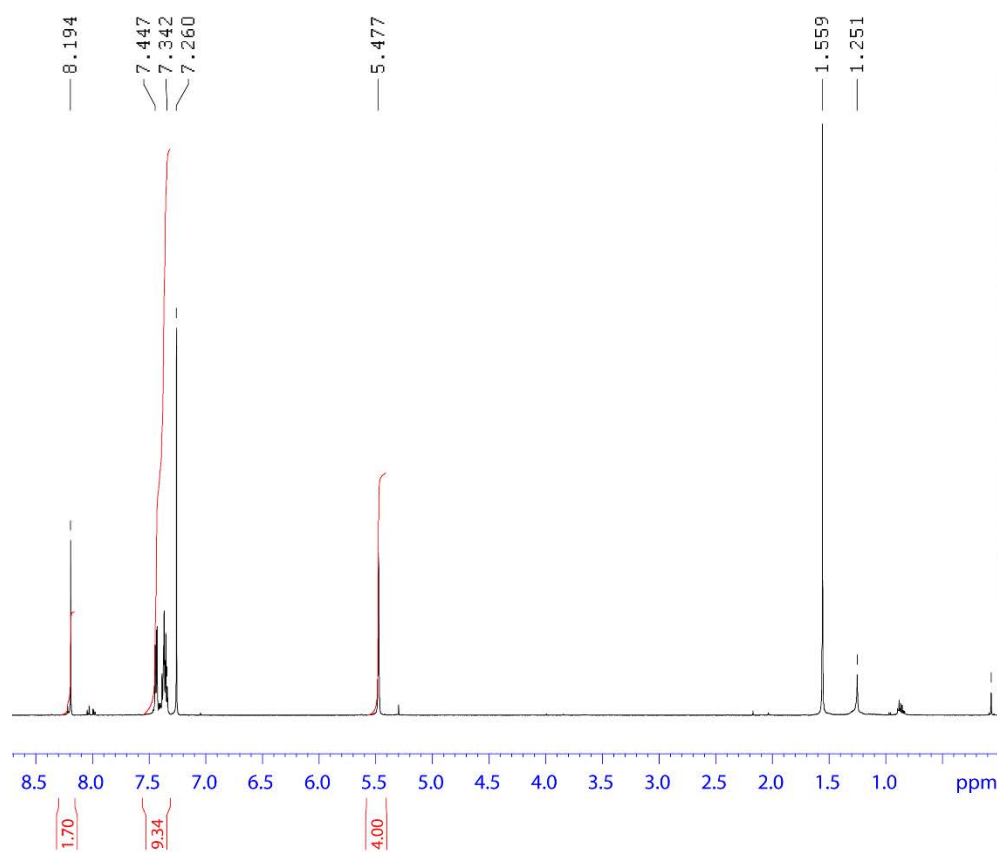
5, ^{13}C NMR, 125 MHz, CDCl_3



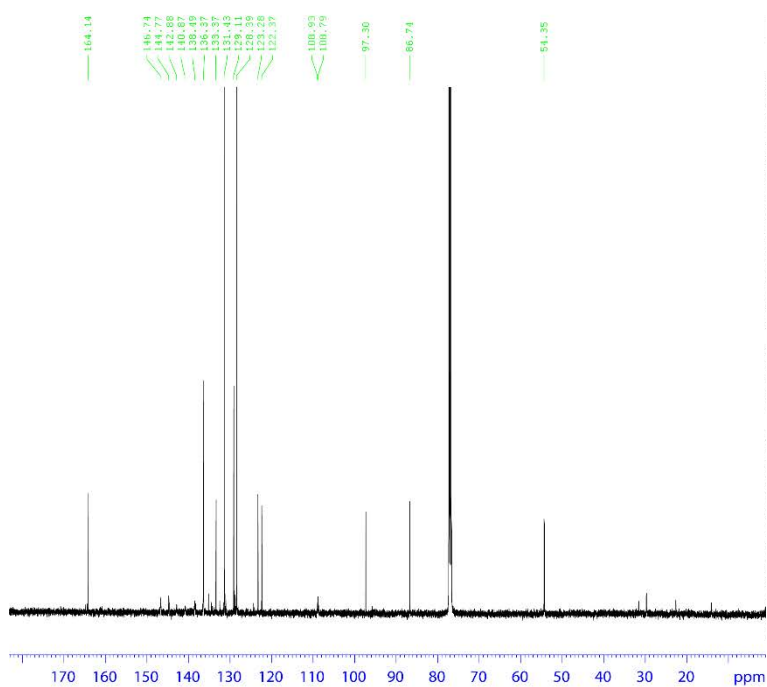
5, ^{19}F NMR, 470 MHz, CDCl_3



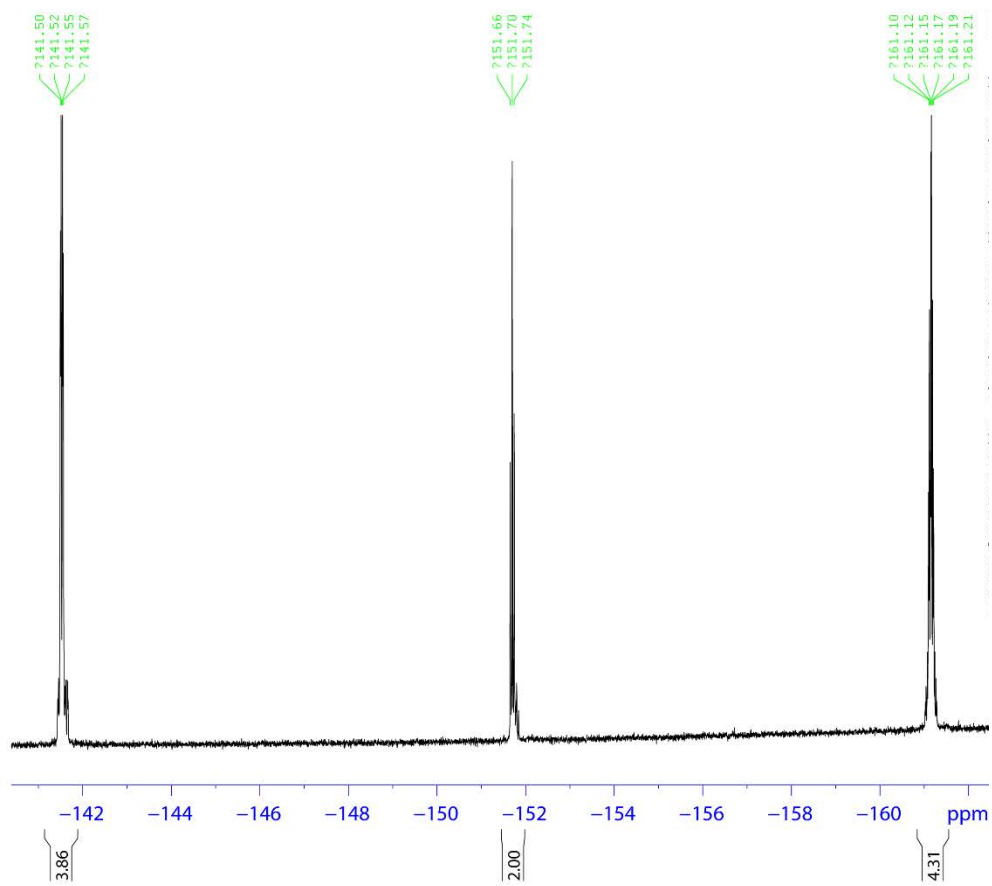
6, ^1H NMR, 500 MHz, CDCl_3



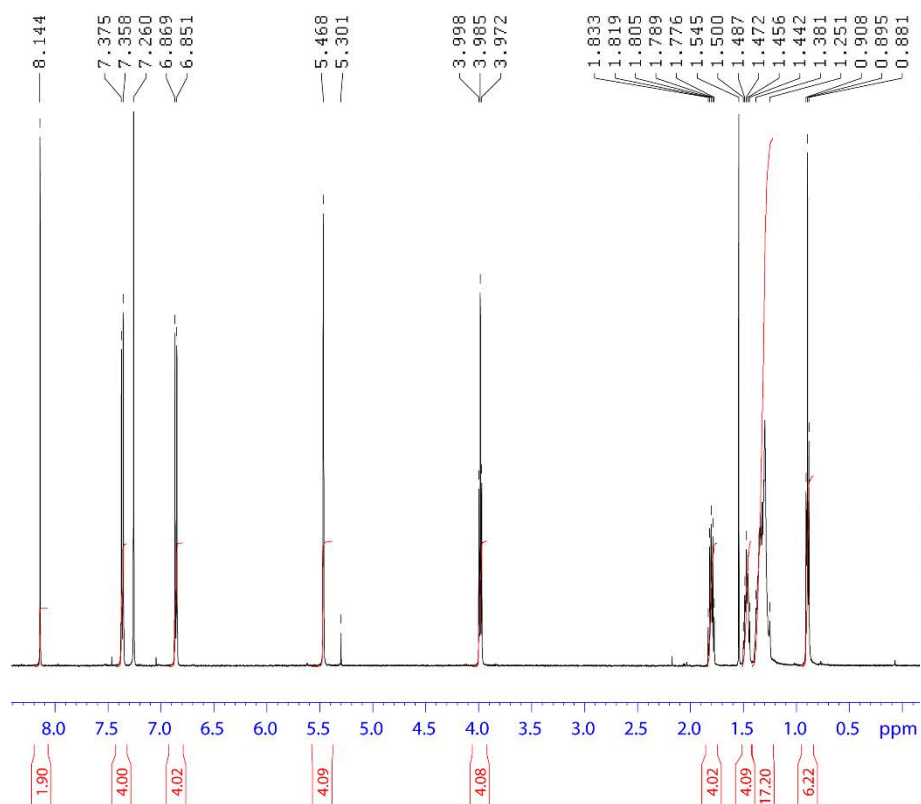
6, ^{13}C NMR, 125 MHz, CDCl_3



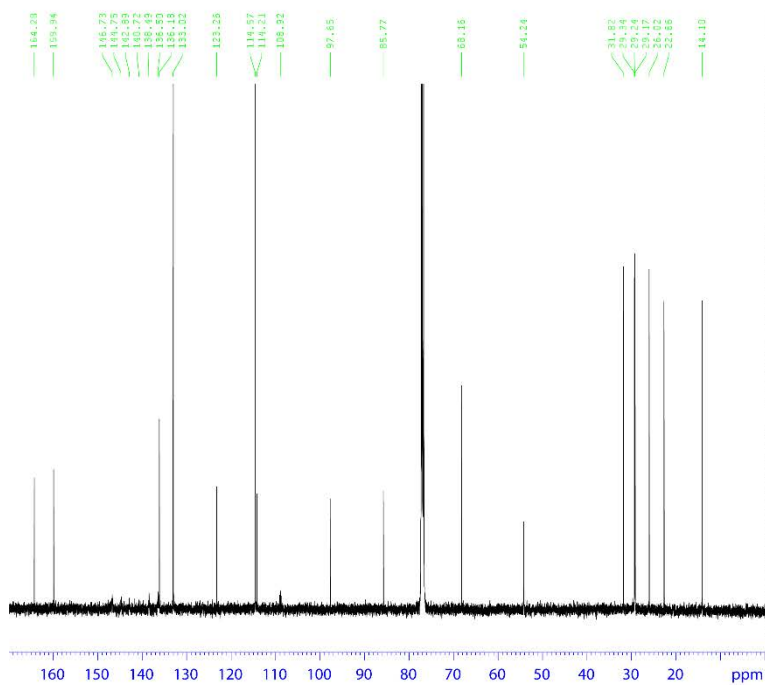
6, ^{19}F NMR, 470 MHz, CDCl_3



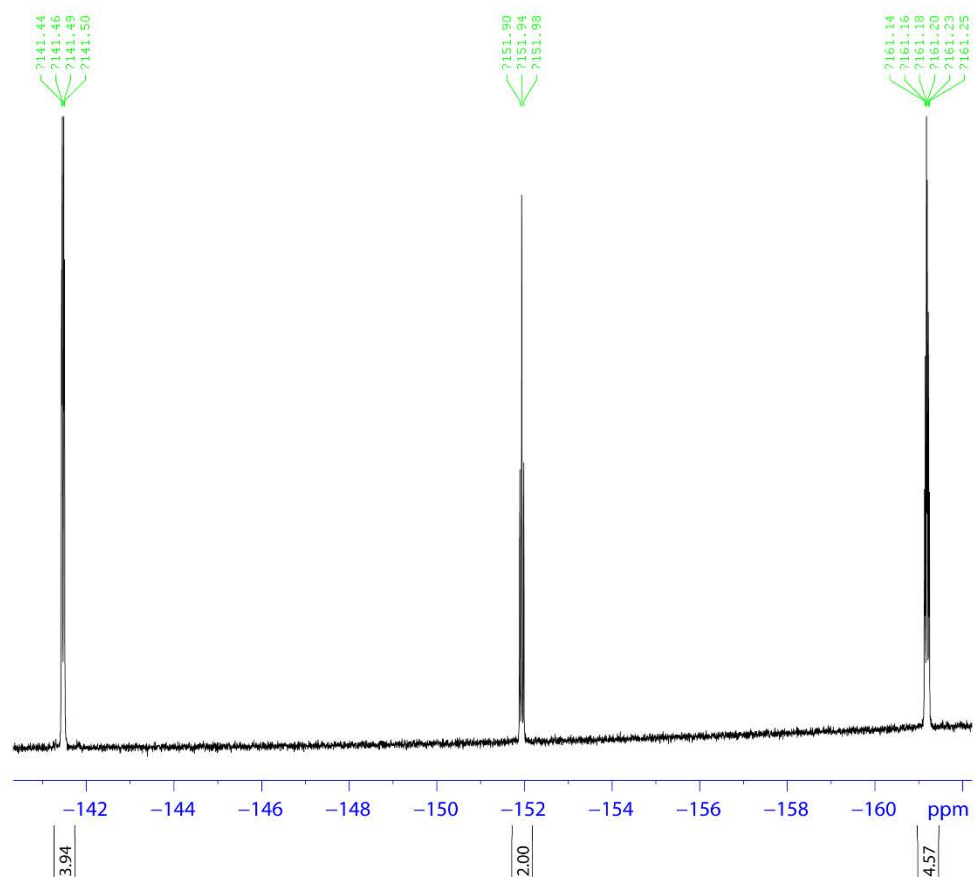
7, ^1H NMR, 500 MHz, CDCl_3



7, ^{13}C NMR, 125 MHz, CDCl_3



7, ^{19}F NMR, 470 MHz, CDCl_3



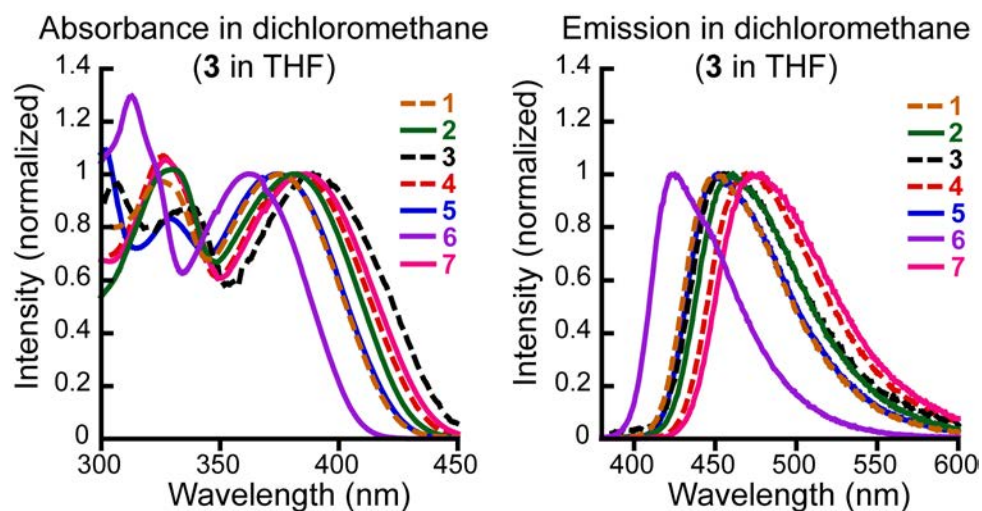


Figure S1: Absorbance and emission spectra of **1**, **2** and **4-7** in CH_2Cl_2 , **3** in THF

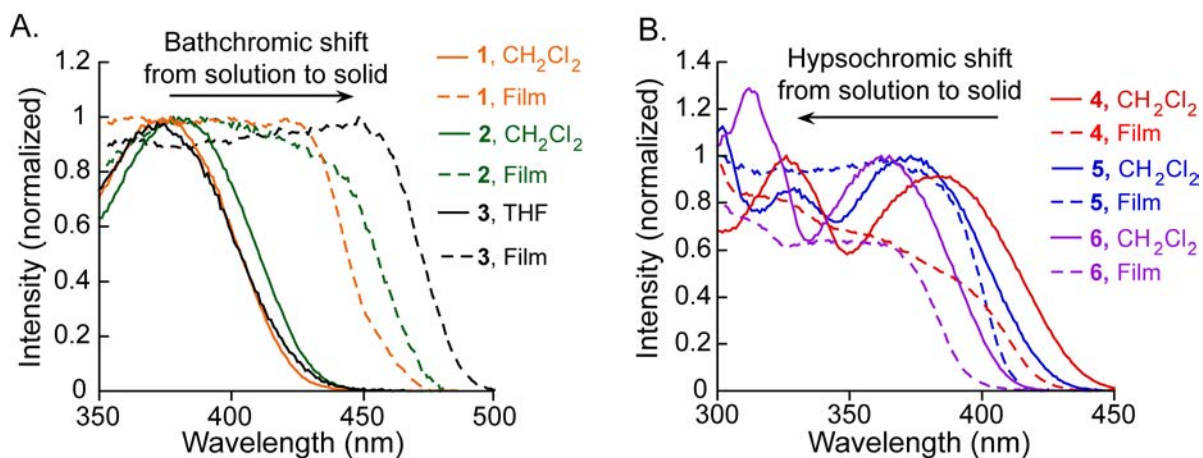


Figure S2: Excitation spectra of **1-3** (A) and **4-6** (B) in solution and in films

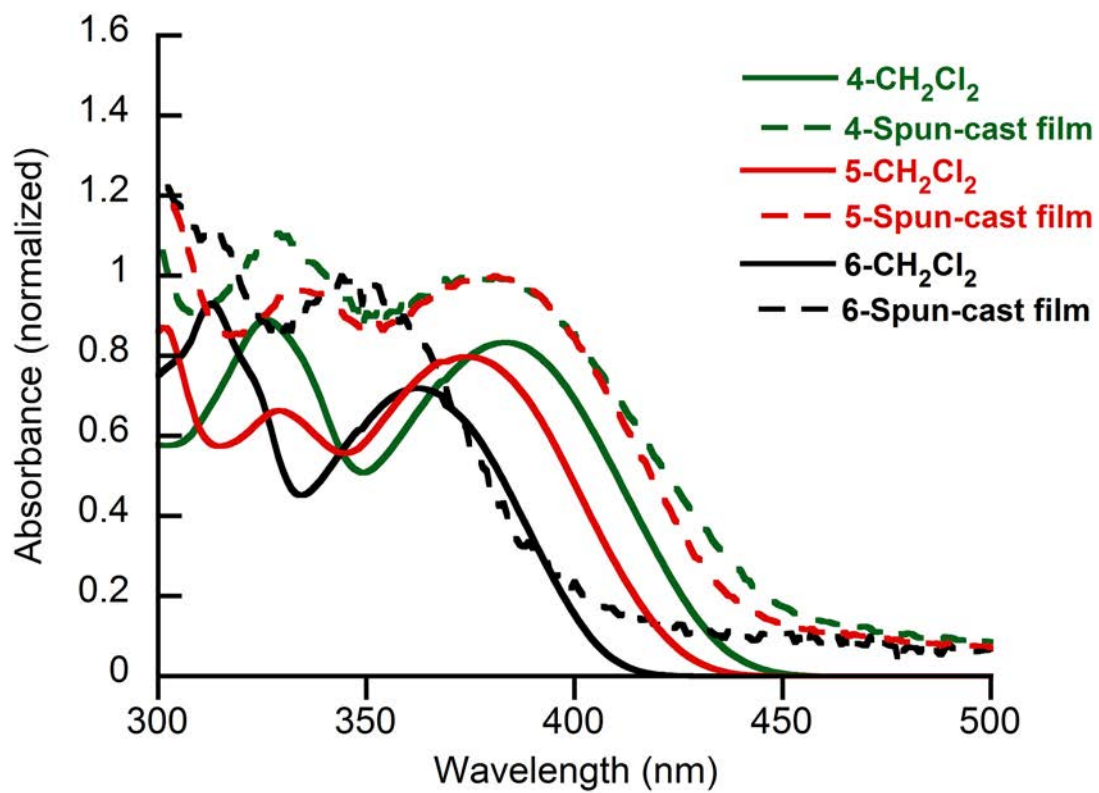


Figure S3: Absorbance spectra of 4-6 in CH_2Cl_2 (smooth lines) and spun-cast films (dashed lines)

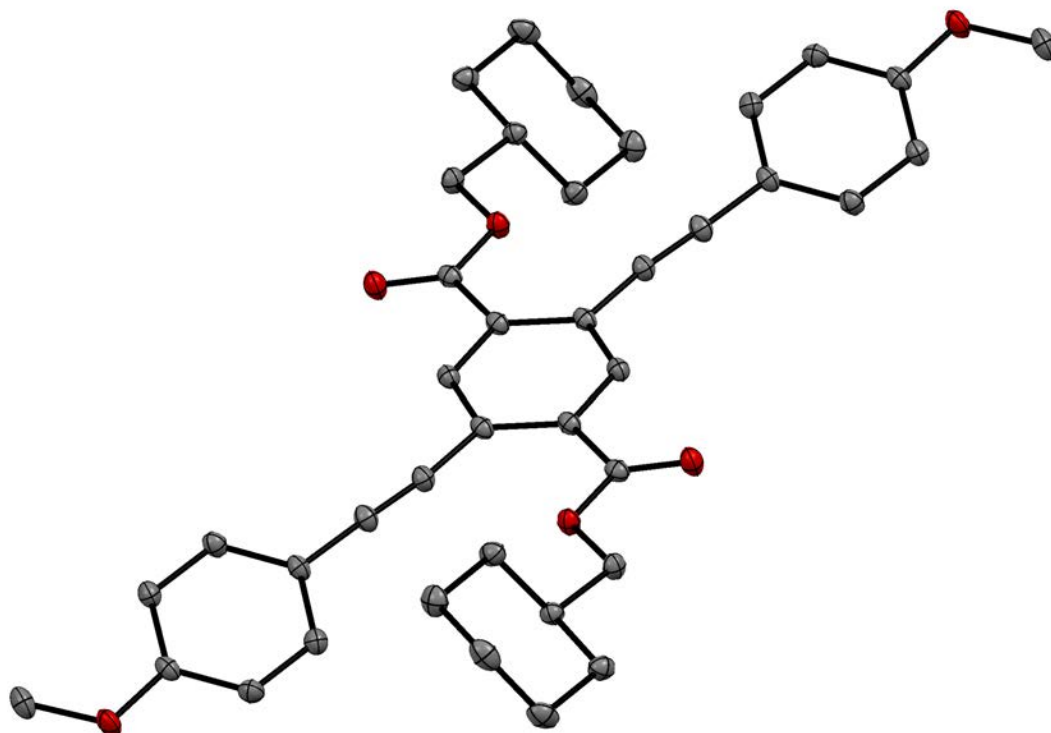


Figure S4. X-Ray crystal structure of **1**, hydrogens not shown for clarity. Ellipsoids shown at 50% probability.

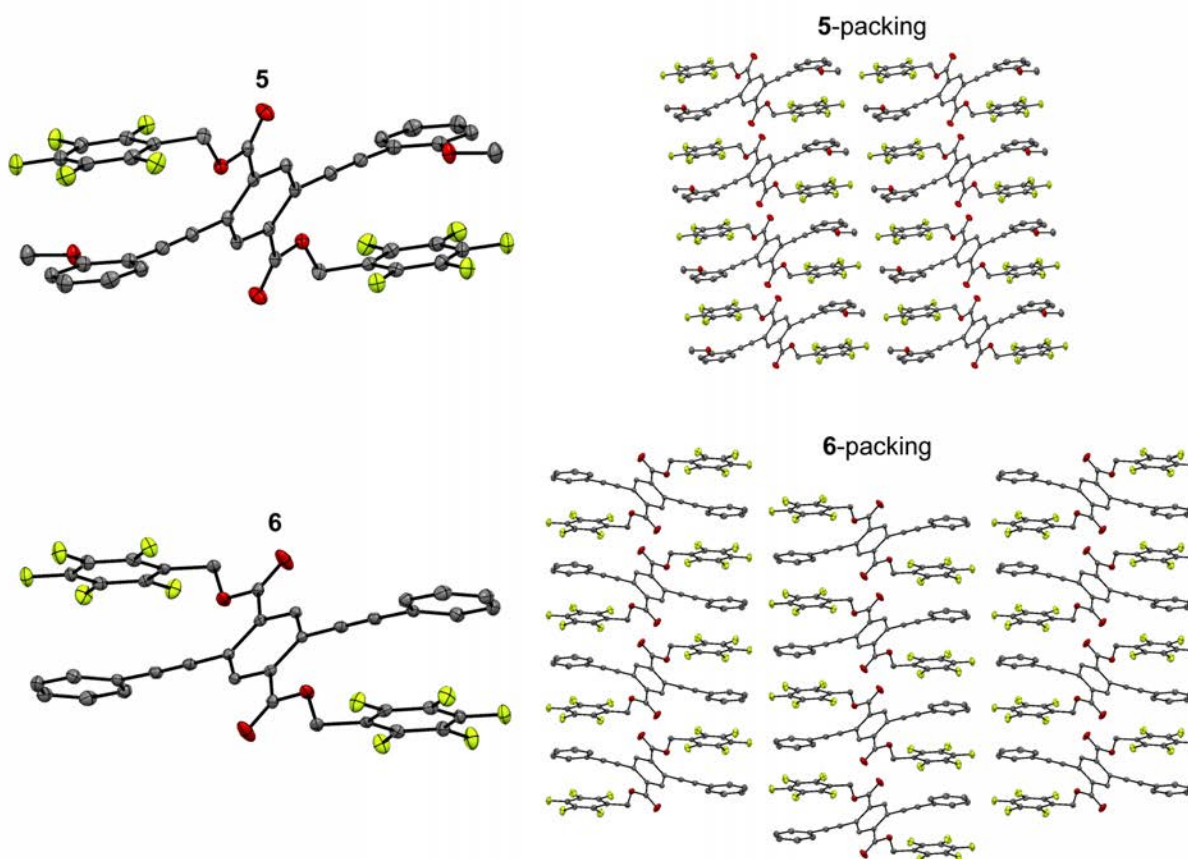


Figure S5. X-Ray crystal structure and packing of **5-6**, hydrogen atoms not shown for clarity. Thermal ellipsoids shown at 50% probability.

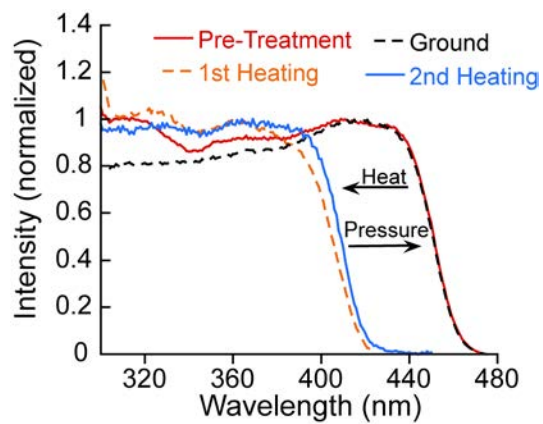


Figure S6: Film excitation spectra of **7**

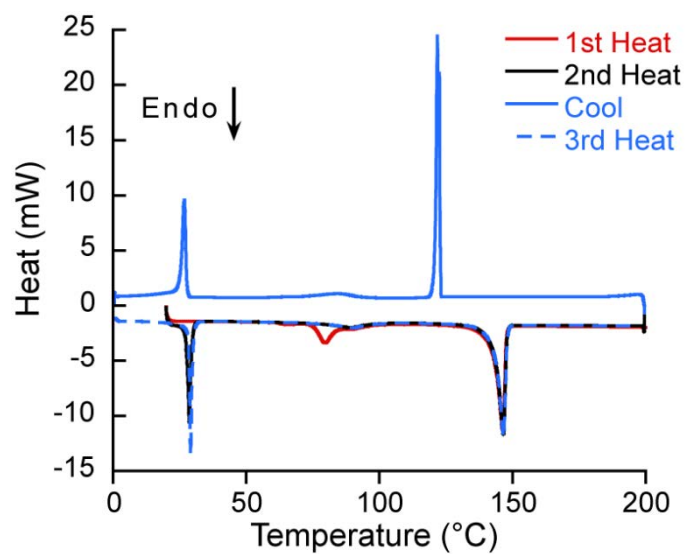


Figure S7: DSC traces of 7

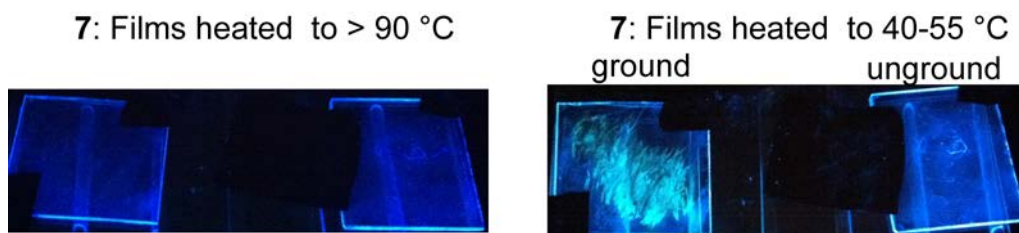


Figure S8: Films of 7 after heating to 90 °C, then grinding and heating to below the transition temperature of 80 °C

Crystallographic Details

X-ray Crystallography.

Single crystals suitable from X-Ray crystallography were prepared by slow evaporation of CH₂Cl₂ from a CH₂Cl₂/hexanes mixture (for **1**, **5** and **6**), diffusion of hexanes into a CH₂Cl₂ solution (**2**) or CHCl₃ solution (**4**) and slow evaporation of CDCl₃ from an NMR tube (**3**). Low-temperature diffraction data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from an *I μ S* micro-source, (for **1**, **2** and **4**) or on a Bruker-D8 Quest diffractometer coupled to a Photon CMOS detector with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focused sealed tube source (for **3**, **5**, and **6**), both performing φ - and ω -scans. The structures were solved by direct methods using SHELXS^[9] and refined against F^2 on all data by full-matrix least squares with SHELXL-97^[10] or SHELXL-13 following established refinement strategies.^[11] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality, and refinement statistics are listed in Tables S1 to S6.

Table S1. Crystal data and structure refinement for **1**

Identification code	mo_x8_12160_0m	
Empirical formula	C ₄₀ H ₄₂ O ₆	
Formula weight	618.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	$a = 6.6014(4) \text{ \AA}$	$\alpha = 90.00^\circ$
	$b = 17.3786(11) \text{ \AA}$	$\beta = 97.042(4)^\circ$
	$c = 13.6759(9) \text{ \AA}$	$\gamma = 90.00^\circ$
Volume	1557.11(17) Å ³	
Z	2	
Density (calculated)	1.320 Mg/m ³	
Absorption coefficient	0.087 mm ⁻¹	
<i>F</i> (000)	660	
Crystal size	0.30 x 0.20 x 0.01 mm ³	
Theta range for data collection	1.90 to 30.51°.	
Index ranges	-9 ≤ <i>h</i> ≤ 8, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 18	
Reflections collected	44002	
Independent reflections	4772 [<i>R</i> _{int} = 0.0434]	
Completeness to theta = 30.55°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9996 and 0.9772	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4772/ 0 / 209	
Goodness-of-fit on <i>F</i> ²	1.052	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0423, <i>wR</i> 2 = 0.1101	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0579, <i>wR</i> 2 = 0.1197	
Largest diff. peak and hole	0.474 and -0.207 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **2**

Identification code	mo_x8_12116_0m	
Empirical formula	C ₄₀ H ₃₀ O ₆	
Formula weight	606.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	$a = 12.8251(95) \text{ \AA}$	$\alpha = 90.00^\circ$.
	$b = 17.633(3) \text{ \AA}$	$\beta = 93.491(3)^\circ$.
	$c = 13.242(2) \text{ \AA}$	$\gamma = 90.00^\circ$.
Volume	3011.7(8) Å ³	
Z	4	
Density (calculated)	1.338 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
<i>F</i> (000)	1272	
Crystal size	0.30 x 0.20 x 0.06 mm ³	
Theta range for data collection	1.92 to 31.62°.	
Index ranges	$-18 \leq h \leq 18, -25 \leq k \leq 25, -19 \leq l \leq 19$	
Reflections collected	90592	
Independent reflections	10090 [$R_{int} = 0.0370$]	
Completeness to theta = 31.62°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9947 and 0.9737	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10090 / 0 / 417	
Goodness-of-fit on F^2	1.031	
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0452, wR2 = 0.1263$	
<i>R</i> indices (all data)	$R1 = 0.0549, wR2 = 0.1361$	
Largest diff. peak and hole	0.690 and -0.221 e.Å ⁻³	

Table S3. Crystal data and structure refinement for **3**

Identification code	RP-3-30-14_a	
Empirical formula	C38H16F10O6	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.2523 (6) Å	$\alpha = 73.9040 (17)^\circ$
	b = 12.5862 (10) Å	$\beta = 86.2990 (18)^\circ$
	c = 15.2850 (12) Å	$\gamma = 83.5410 (18)^\circ$
Volume	1514.7 (2) Å ³	
Z	2	
Density	1.663 Mg/m ³	
Absorption coefficient	0.153 mm ⁻¹	
F(000)	764	
Crystal size	0.28 x 0.17 x 0.09 mm	
Theta range for data collection	2.80° to 29.13°	
Index ranges	$-11 \leq h \leq 11, -17 \leq k \leq 17, -20 \leq l \leq 20$	
Reflections collected	30543	
Independent reflections	8146 [$R_{\text{int}} = 0.0267$]	
Completeness to theta = 29.13°	99.8%	
Absorbance correction	Semi-empirical from equivalents (SADABS)	
Max and Min Transmission	0.986, 0.970	
Refinement method	Full matrix least squares on F ²	
Data / restraints / parameters	8146/0/489	
Goodness-of-fit on F2	1.02	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0386$ $wR2 = 0.0933$	
R indices [all data]	$R1 = 0.0549$, $wR2 = 0.1013$	
Largest diff, peak and hole	0.467 Å ⁻³ and -0.221 Å ⁻³	

Table S4. Crystal data and structure refinement for **4**

Identification code	mo_x8_12144_0m	
Empirical formula	C ₄₀ H ₂₀ F ₁₀ O ₆	
Formula weight	786.56	
Temperature	190(2)K	
Wavelength	0.7103	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9613(5)	α = 91.6740(10)
	b = 7.1312(5)	β = 90.0290(10)
	c = 17.3912(13)	γ = 106.6190(10)
Volume	826.89	
Z	1	
Density(calculated)	1.580 Mg/m ³	
Absorption coefficient	0.143 mm ⁻¹	
F(000)	398	
Crystal size	0.20 x 0.15 x 0.05 mm ³	
Theta range for data collection	1.17° to 30.51°	
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, 0 ≤ l ≤ 24	
Reflections collected	23776	
Independent reflections	5012 [R _{int} = 0.0256]	
Completeness to theta=		
Absorption correction	Semi-empirical from equivalents (SADABS)	
Max. and min. transmission	0.9929 and 0.9720	
Refinement method	Full-matrix least squares on F ²	
Data / restraints / parameters	5012 / 0 / 255	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0500, wR2 = 0.1353	
R indices [all data]	R1 = 0.0601, wR2 = 0.1437	
Largest diff. peak and hole	0.553 and -0.278 e Å ³	

Table S5. Crystal data and structure refinement for **5**

Identification code	RP100913
Empirical formula	C ₄₀ H ₂₀ F ₁₀ O ₆
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.816 (2) Å α = 79.881 (7)° b = 7.448 (3) Å β = 81.961 (7)° c = 16.417 (6) Å γ = 75.475 (7)°
Volume	790.2 (7) Å ³
Z	1
Density	1.653 Mg/m ³
Absorption coefficient	0.15 mm ⁻¹
F(000)	398
Crystal size	0.48 x 0.12 x 0.10 mm
Theta range for data collection	2.86° to 26.37°
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	11514
Independent reflections	3224 [R _{int} = 0.0706]
Completeness to theta = 26.37°	99.5%
Absorbance correction	Semi-empirical from equivalents (SADABS)
Max and Min Transmission	0.985, 0.979
Refinement method	Full matrix least squares on F ²
Data / restraints / parameters	3224/0/254
Goodness-of-fit on F ²	1.07
Final R indices [I > 2σ(I)]	R1 = 0.0751 wR2 = 0.2009
R indices (all data)	R1 = 0.0908, wR2 = 0.2180
Largest difference, peak and hole	0.555 Å ⁻³ and -0.423 Å ⁻³

Table S6. Crystal data and structure refinement for **6**

Identification code	Rp_a
Empirical formula	C38H16F10O4
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P-1
Unit cell dimensions	a = 6.8870 (7) Å $\alpha = 90^\circ$ b = 31.518 (3) Å $\beta = 107.6540 (7)^\circ$ c = 7.1384 (7) Å $\gamma = 90^\circ$
Volume	1476.5 (2) Å ³
Z	2
Density	1.634 Mg/m ³
Absorption coefficient	0.148 mm ⁻¹
F(000)	732
Crystal size	0.72 x 0.27 x 0.22 mm
Theta range for data collection	3.06° to 26.37°
Index ranges	-8 < h < 8, -39 < k < 39, -8 < l < 8
Reflections collected	22257
Independent reflections	3013 [R _{int} = 0.0249]
Completeness to theta = 26.37°	99.9%
Absorbance correction	Semi-empirical from equivalents (SADABS)
Max and Min Transmission	0.968, 0.953
Refinement method	Full matrix least squares on F ²
Data / restraints / parameters	3013/63/235
Goodness-of-fit on F2	1.20
Final R indices [I > 2σ(I)]	R1 = 0.0432 wR2 = 0.1000
R indices (all data)	R1 = 0.0458, wR2 = 0.1014
Largest difference, peak and hole	0.308 Å ⁻³ and -0.213 Å ⁻³

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