

Electronic Supplementary Information (ESI)

Minimalist Columnar Liquid Crystals: Influence of fluorination on the mesogenic behavior of tetramethoxytriphenylene derivatives

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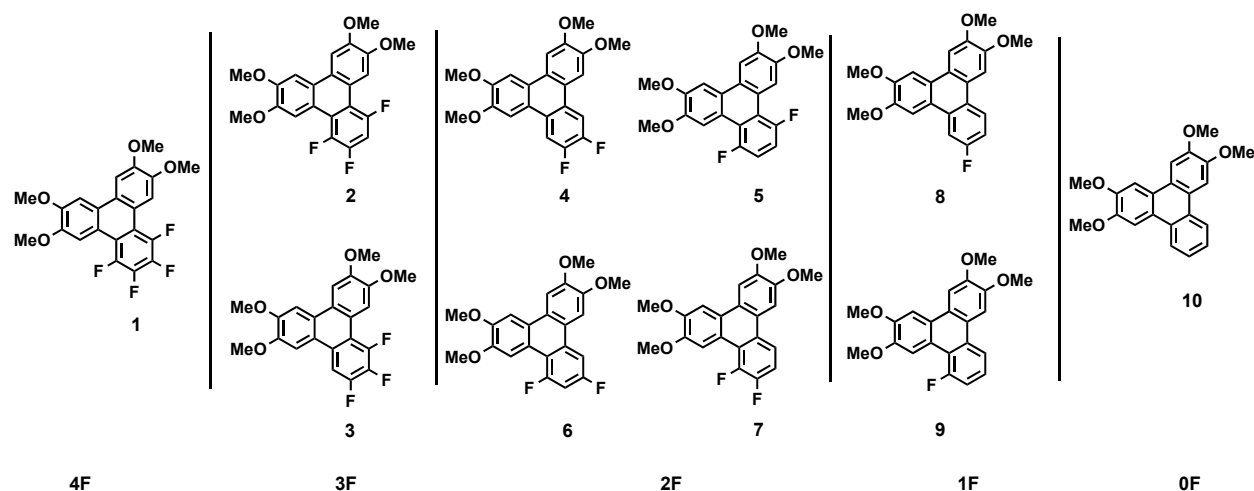
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List of the target compounds

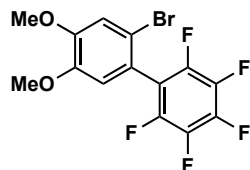


SII. The structure of the targeted tetramethoxy triphenylene compounds with varying extent of fluorination in different location

Synthesis of intermediates

a. Synthesis of biphenyl intermediates

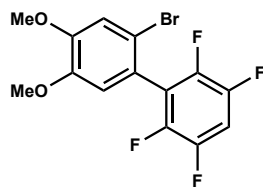
2,3,4,5,6-pentafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl¹



In a 200 ml round bottom flask was placed potassium pentafluorobenzoate (7.5 g, 30.0 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene (6.84 g, 20.0 mmol), CuI (1.14 g, 30 mol%) and dry diglyme (35.0 ml). The mixture was refluxed at 160 °C for five hours and monitored by TLC to observe complete transformation of the starting material to a new product which was confirmed by GCMS. The reaction mixture was cooled to room temperature and ethyl acetate was added to bring the volume up to 200 ml. The mixture was vacuum filtered through a sintered glass funnel and the filtrate was washed with water and brine. The organic extract was dried over anhydrous magnesium sulfate and vacuum filtered. Some silica gel was added to the filtrate and solvent was removed under reduced pressure and the silica powder thus obtained was placed at the top of a column and eluted with a mixture of ethyl acetate and hexanes (10% EtOAc in hexane). Fractions containing the desired product were combined and concentrated to obtain a viscous colorless liquid product which crystallized on long standing. Yield – 6.25 g (82 %)

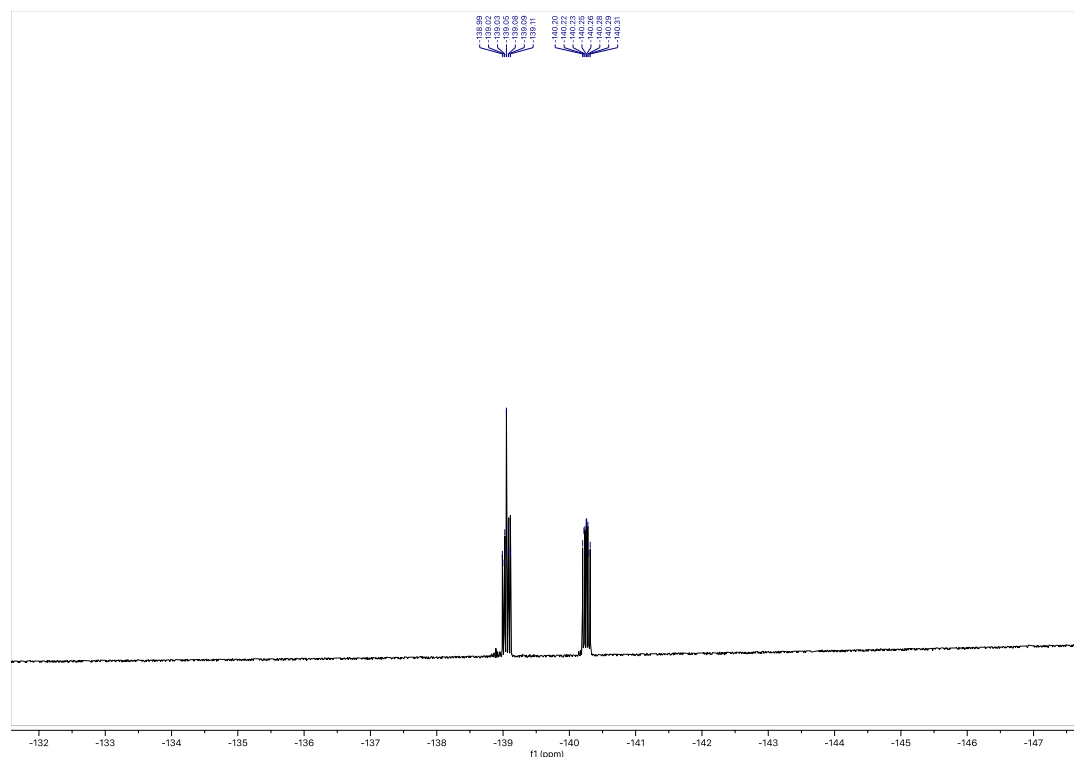
¹⁹F NMR (376 MHz, CDCl₃) δ -137.89 – -140.86 (m, 2F), -154.39 (td, *J* = 21.2, 7.0 Hz, 1F), -162.16 (tdd, *J* = 21.2, 8.9, 4.8 Hz, 2F). ¹H NMR (400 MHz, CDCl₃) δ 7.19 (s, 1H), 6.76 (s, 1H), 3.96 (d, *J* = 0.8 Hz, 3H), 3.89 (d, *J* = 1.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.58, 148.54, 145.55, 145.51, 143.09, 143.05, 142.37, 139.84, 136.38, 119.45, 119.43, 115.69, 115.66, 114.84, 114.08, 56.27, 56.26, 56.21.

2,3,5,6-tetrafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl

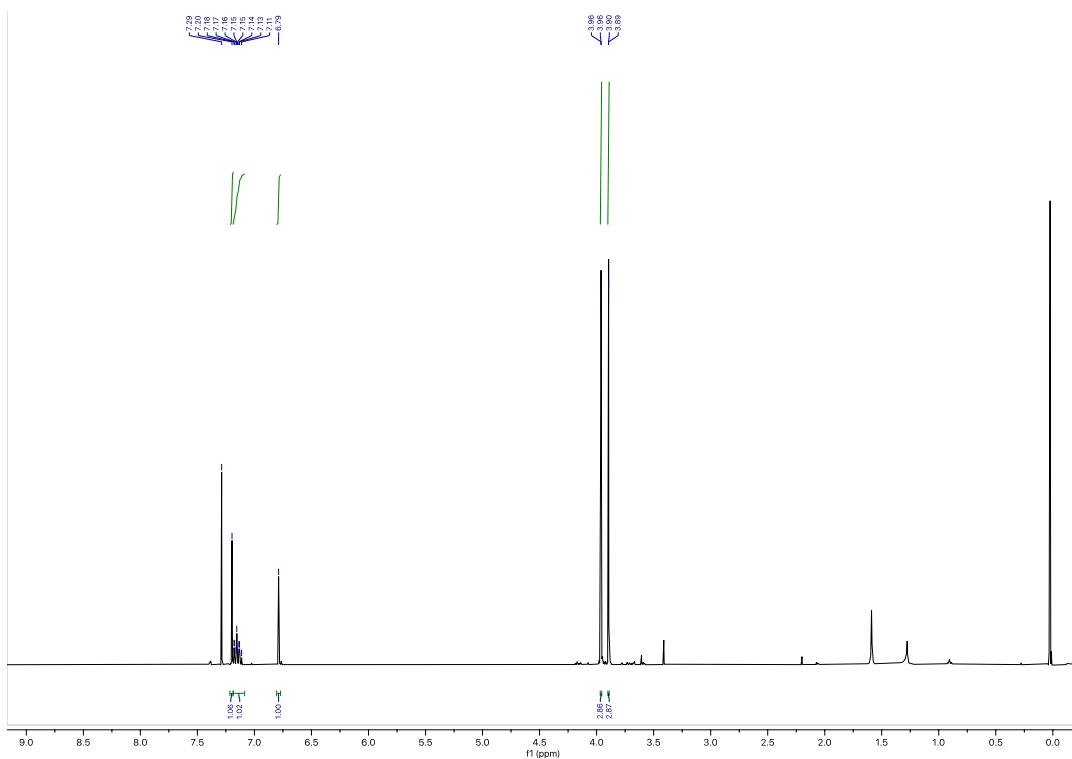


In a 250 ml round bottom flask was placed 1-bromo-2-iodo-4,5-dimethoxybenzene (3.41 g, 10.0 mmol), potassium-2,3,5,6-tetrafluorobenzoate (4.18 g, 18.5 mmol), CuI (0.58 g, 30.0 mol%) and dry diglyme (40.0 ml) under a nitrogen atmosphere. The mixture was refluxed at 160 °C and left stirring until CO₂ gas evolution ceased. After six hours the reaction was monitored by TLC which indicated the formation of a new more polar product and the disappearance of the starting material. The reaction mixture was allowed to cool to room temperature and ethyl acetate was added with stirring to make the volume up to 200 ml. The mixture was filtered through a short silica pad and the filtrate was washed with water and brine. The organic portion thus obtained was dried over anhydrous magnesium sulfate and vacuum filtered. Some silica gel was added to the filtrate and the solvent was removed under reduced pressure and the powder thus obtained was placed at the top of a column and eluted with a mixture of ethyl acetate and hexanes (10% EtOAc). Fractions containing the pure product were combined and concentrated to get a viscous colorless oily product that crystallized on long standing. In later fractions, some uncharacterized byproducts were also eluted from the column mixed with the desired product. Yield – 1.61 g (42 %)

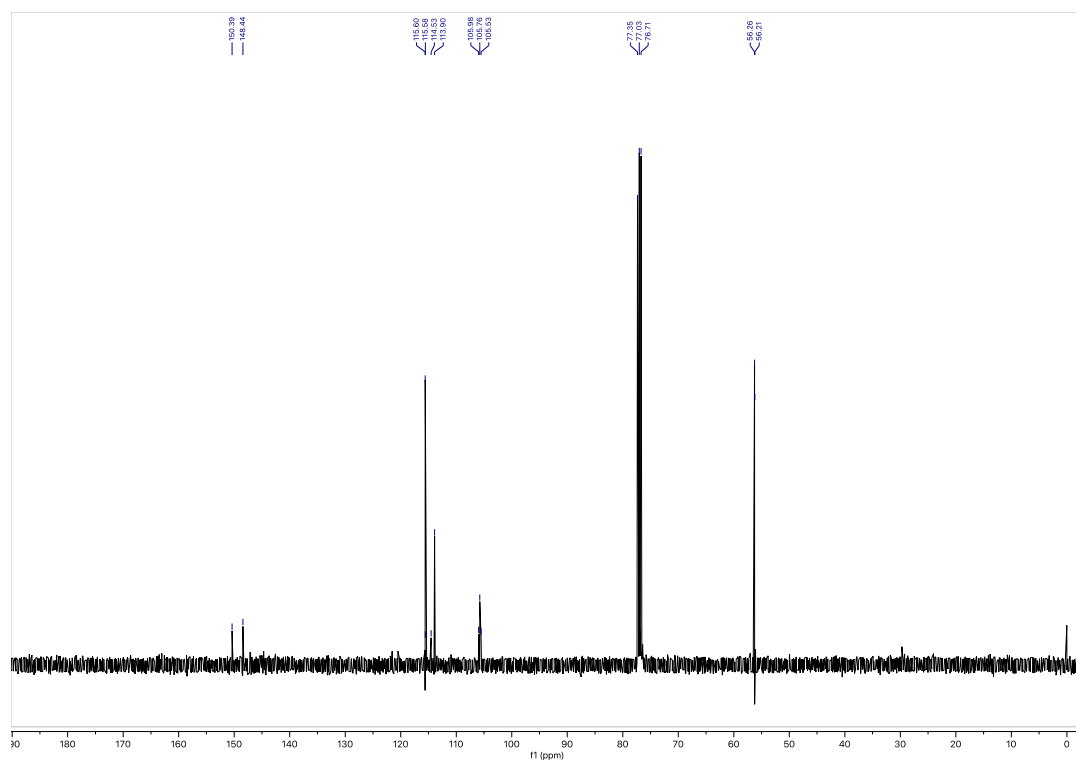
¹⁹F NMR (376 MHz, CDCl₃) δ -139.05 (ddd, *J* = 22.7, 12.8, 9.8 Hz), -140.26 (ddd, *J* = 23.0, 12.9, 7.4 Hz).
¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 7.19 – 7.10 (m, 1H), 6.79 (s, 1H), 3.96 (d, *J* = 0.3 Hz, 3H), 3.89 (d, *J* = 0.3 Hz, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 150.39, 148.44, 115.60, 115.58, 114.53, 113.90, 105.98, 105.76, 105.53, 56.26, 56.21.



SI2. ¹⁹F NMR for 2,3,5,6-tetrafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl

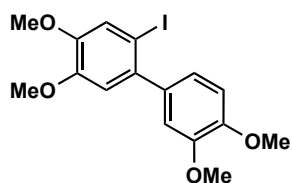


SI3. ^1H NMR for 2,3,5,6-tetrafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl



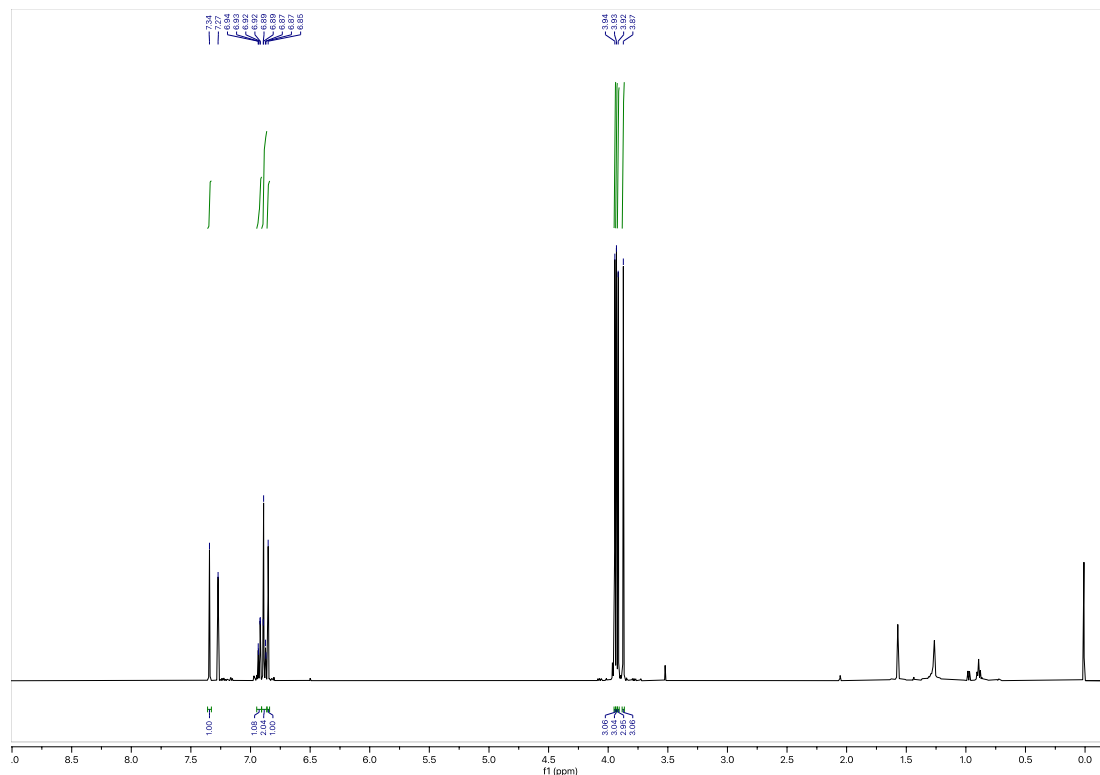
SI4. ^{13}C NMR for 2,3,5,6-tetrafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl

2-iodo-4,5,3',4'-tetramethoxybiphenyl

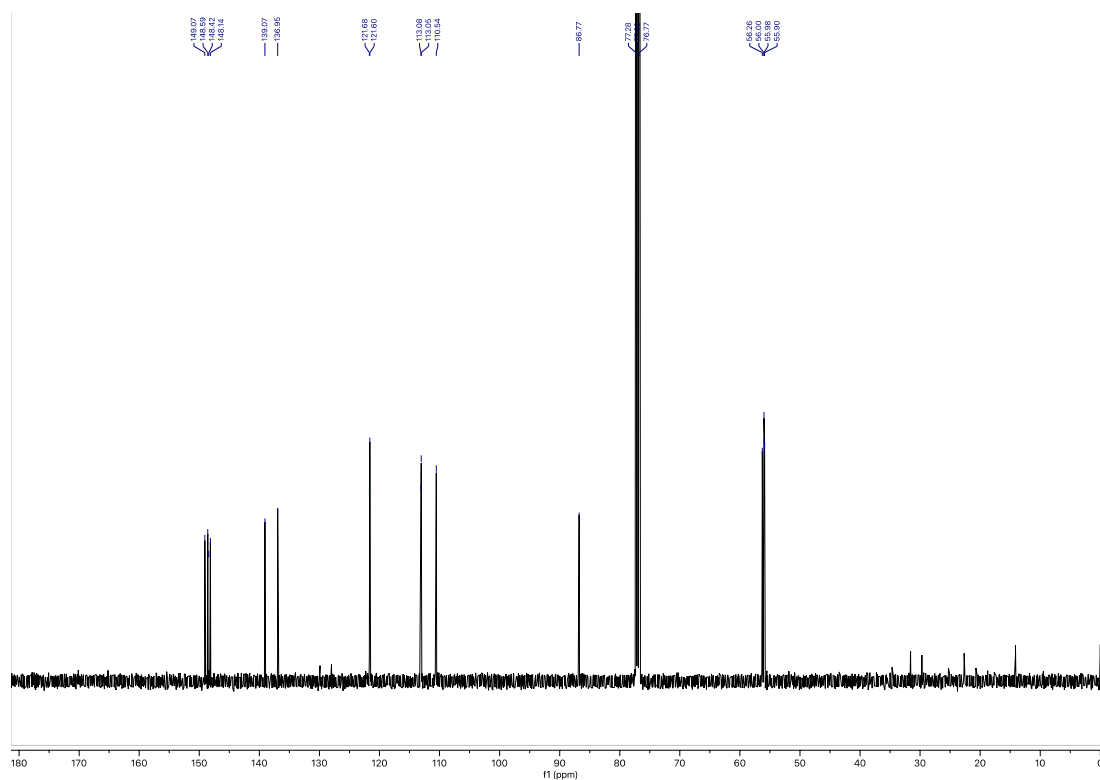


In a 200 ml round bottom flask was placed 1,2-diiodo-4,5-dimethoxybenzene (3.89 g, 10.0 mmol), 3,4-dimethoxyphenylboronic acid (1.62 g, 9.0 mmol), dioxane (30.0 ml) and water (10.0 ml). The mixture was stirred while potassium carbonate (2.80 g, 20.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, PdCl₂(PPh₃)₂ (0.14 g, 2.0 mol%) was added and the temperature was gradually raised to 95 °C. The reaction was terminated after three hours when the amount of starting material was significantly reduced, and a couple of polar spots were observed in TLC and later monitored by GCMS. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was isolated by vacuum filtration and then dissolved in ethyl acetate and adsorbed on some silica gel and Montmorillonite clay. This silica gel was placed at the top of a column and then eluted with 10% EtOAc in hexanes. Fractions containing the pure product were combined and concentrated to provide a white solid product. Some diadduct was also isolated from the column. Yield – 2.10 g (52 %)

¹H NMR (500 MHz, CDCl₃) δ 7.34 (s, 1H), 6.93 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.85 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.07, 148.59, 148.42, 148.14, 139.07, 136.95, 121.68, 121.60, 113.08, 113.05, 110.54, 86.77, 56.26, 56.00, 55.98, 55.90.

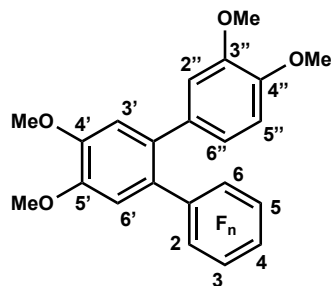


S15. ¹H NMR for 2-iodo-4,5,3',4'-tetramethoxybiphenyl



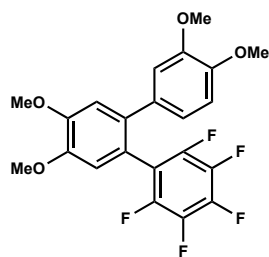
SI6. ^{13}C NMR for 2-iodo-4,5,3',4'-tetramethoxybiphenyl

b. Synthesis of *o*-terphenyl intermediates



General structure of o-terphenyl intermediates

2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl¹

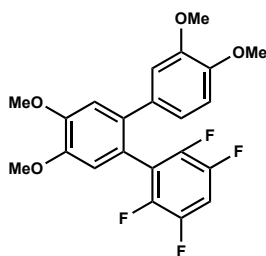


In a 200 ml round bottom flask was placed 2,3,4,5,6-pentafluoro-2'-bromo-4',5'-dimethoxy-1,1'-biphenyl (3.82 g, 10.0 mmol), 3,4-dimethoxyphenylboronic acid (2.73 g, 15.0 mmol), dioxane (30.0 ml) and water

(10.0 ml). The mixture was stirred while potassium carbonate (2.12 g, 15.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, PdCl₂(PPh₃)₂ (0.15 g, 2.0 mol%) was added and the temperature was gradually raised to 95 °C. The reaction was complete after four hours as indicated by the new spot in TLC. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was isolated by vacuum filtration and then dissolved in ethyl acetate and some silica gel and Montmorillonite clay was added and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column packed with silica made up of 10% EtOAc in hexanes and then eluted with the same solvent. Fractions containing the pure product were combined and concentrated to provide a cream-colored solid product. Yield – 3.17 g (72 %)

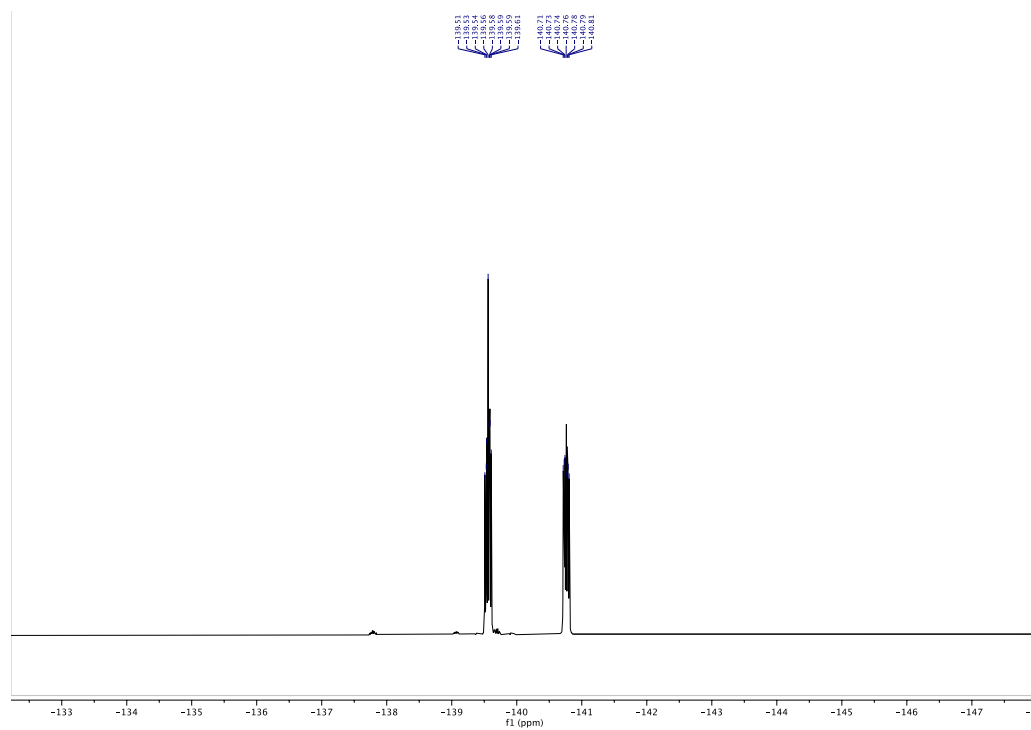
¹⁹F NMR (376 MHz, CDCl₃) δ -138.94 – -140.87 (m, 2F), -155.52 (t, *J* = 21.0 Hz, 1F), -162.55 (ddd, *J* = 23.7, 20.8, 8.3 Hz, 2F). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 1H), 6.82 – 6.75 (m, 2H), 6.74 – 6.65 (m, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H), 3.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.75, 148.33, 148.24, 148.12, 135.88, 133.03, 120.92, 113.50, 113.11, 111.83, 110.76, 56.19, 56.04, 55.81, 55.78.

2,3,5,6-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

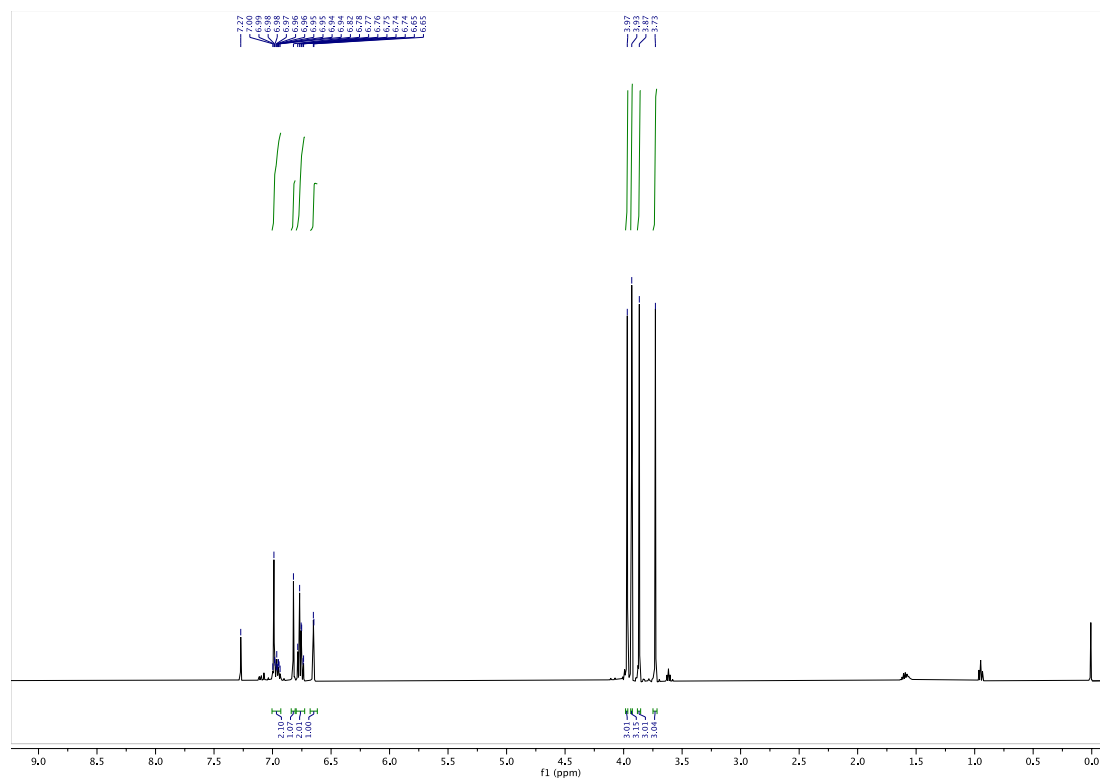


In a 100 ml round bottom flask was placed 2,3,5,6-tetrafluoro-2'-iodo-4',5'-dimethoxy-1,1'-biphenyl (1.42 g, 4.0 mmol), 3,4-dimethoxyphenylboronic acid (1.26 g, 8.0 mmol), dioxane (20.0 ml) and water (8.0 ml). The mixture was stirred while potassium carbonate (2.26 g, 16.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst PdCl₂(PPh₃)₂ (0.07 g) was added, and the mixture was slowly warmed up to 95 °C. The reaction was run overnight, and a new product was indicated by a new spot in TLC, however, some starting material persisted. The reaction was terminated and after cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black sticky crude product obtained was extracted with ethyl acetate, dried over anhydrous MgSO₄ and then vacuum filtered. Some silica gel and Montmorillonite clay were added to the filtrate and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column packed with silica made up of 10% EtOAc in hexanes and then eluted with the same solvent. Fractions containing pure product were combined and concentrated to get a cream-colored solid product. Some biphenyl starting material of the reaction was recovered. Yield – 0.49 g (30 %); MP- 145-147 °C

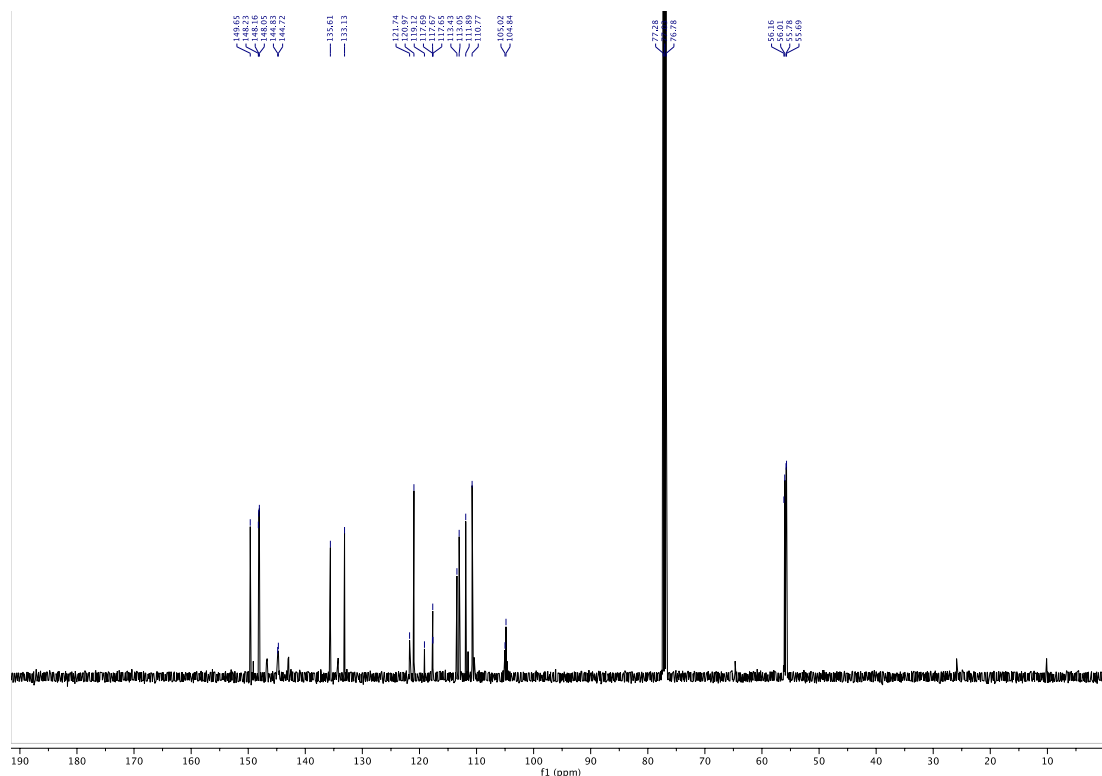
¹⁹F NMR (470 MHz, CDCl₃) δ -139.56 (ddd, *J* = 22.4, 12.8, 9.5 Hz), -140.76 (ddd, *J* = 21.3, 12.7, 7.2 Hz). ¹H NMR (500 MHz, CDCl₃) δ 7.01 – 6.91 (m, 2H), 6.82 (s, 1H), 6.80 – 6.72 (m, 2H), 6.65 (d, *J* = 1.9 Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 3.73 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.65, 148.23, 148.16, 148.05, 144.83, 144.72, 135.61, 133.13, 121.74, 120.97, 119.12, 117.69, 117.67, 117.65, 113.43, 113.05, 111.89, 110.77, 105.02, 104.84, 56.16, 56.01, 55.78, 55.69.



SI7. ^{19}F NMR for 2,3,5,6-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

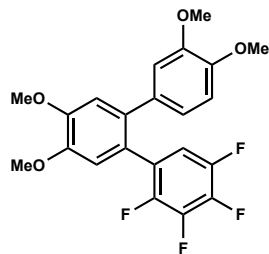


SI8. ^1H NMR for 2,3,5,6-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



SI9. ^{13}C NMR for 2,3,5,6-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

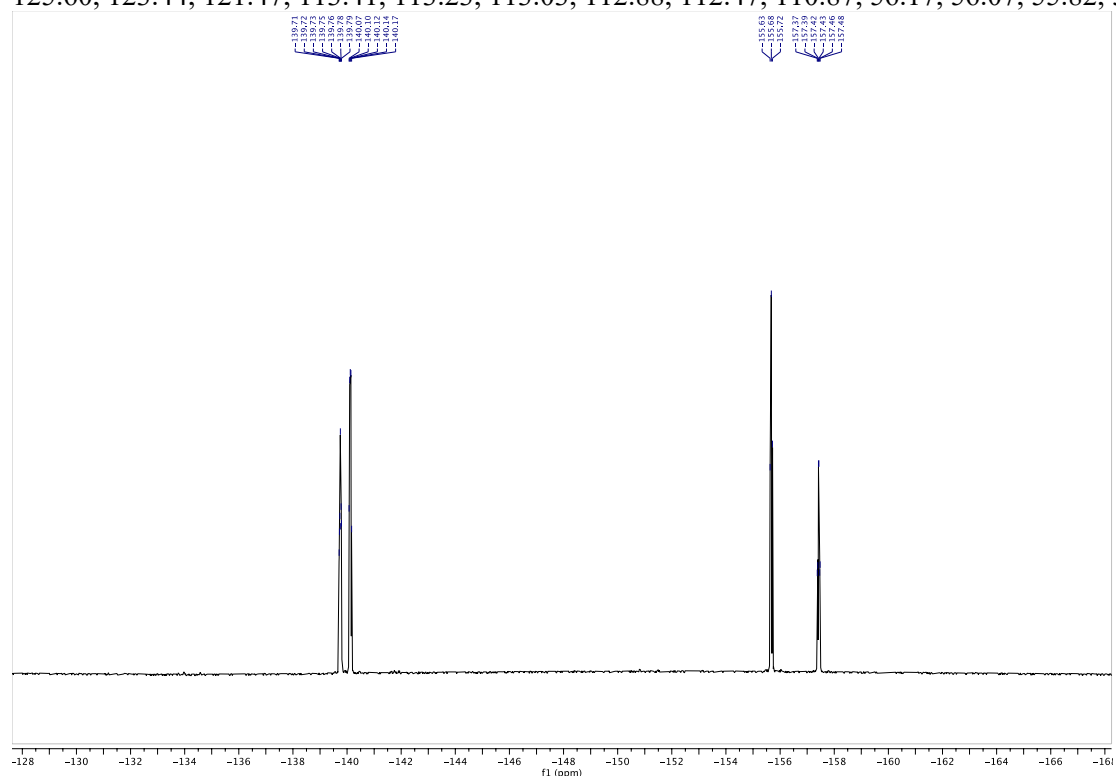
2,3,4,5-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



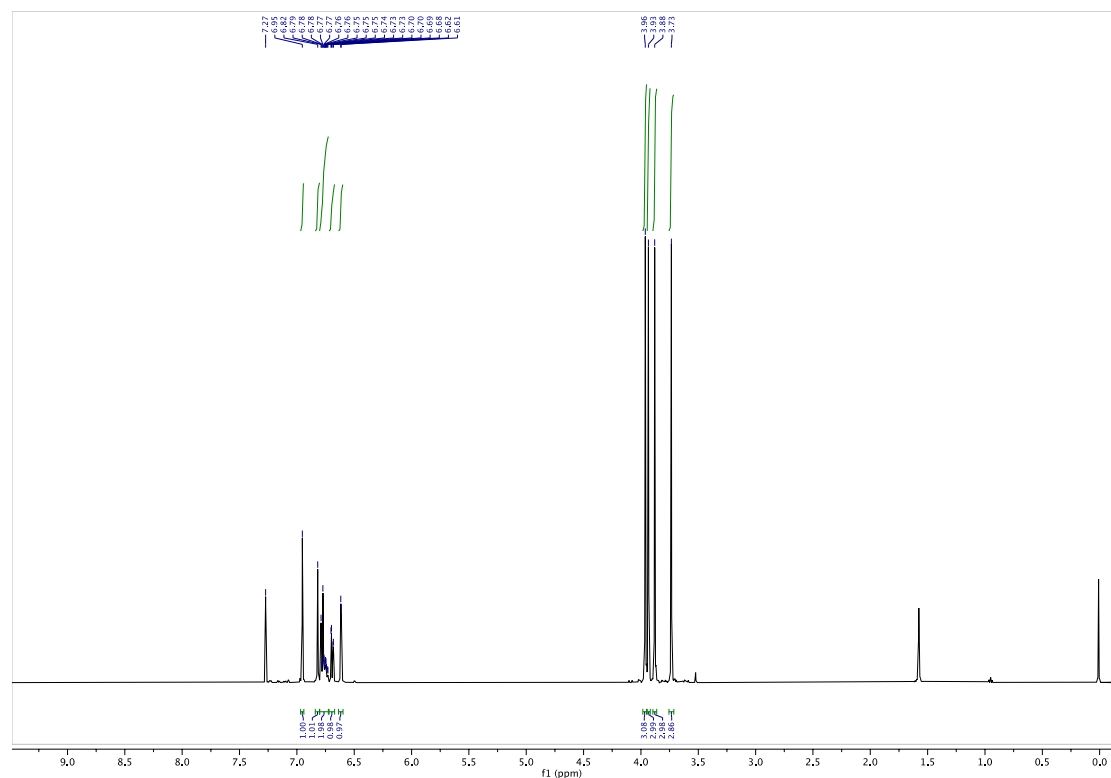
In a 100 ml round bottom flask was placed 2-iodo-4,5,3',4'-tetramethoxybiphenyl (0.60 g, 1.5 mmol), potassium 2,3,4,5-tetrafluorobenzoate (0.92 g, 4.0 mmol) and DMAc (15.0 ml). The mixture was stirred with gentle heating in an oil bath under a nitrogen atmosphere. CuI (0.08 g, 20.0 mol %) and TDA-1 (0.50 g, 1.5 mmol) were added to the mixture and the mixture was heated at 160 °C overnight. A product peak was evident in GCMS with some other byproduct peaks and the disappearance of the starting material peak. The mixture was cooled to room temperature and ethyl acetate was added to fill the reaction vessel. The mixture was filtered through a short pad of silica gel and the solvent was evaporated under vacuum. Ethyl acetate and silica gel were added to the residue and concentrated to dryness by rotary evaporation. This material was placed at the top of a column made up of a mixture of hexanes and ethyl acetate. The column was eluted with 10-20 % EtOAc in hexanes and fractions containing the product were combined and concentrated to get a viscous liquid product which slowly crystallized to a white solid which was recrystallized from 1-propanol. Yield- 0.46 g (73%); MP- 142-144 °C

^{19}F NMR (470 MHz, CDCl_3) δ -139.75 (ddd, $J = 19.8, 13.2, 6.3$ Hz), -140.12 (dt, $J = 22.0, 11.3$ Hz), -155.68 (t, $J = 20.6$ Hz), -157.43 (td, $J = 20.1, 7.8$ Hz). ^1H NMR (500 MHz, CDCl_3) δ 6.95 (s, 1H), 6.82 (s, 1H), 6.80 – 6.72 (m, 2H), 6.69 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.62 (d, $J = 2.1$ Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H),

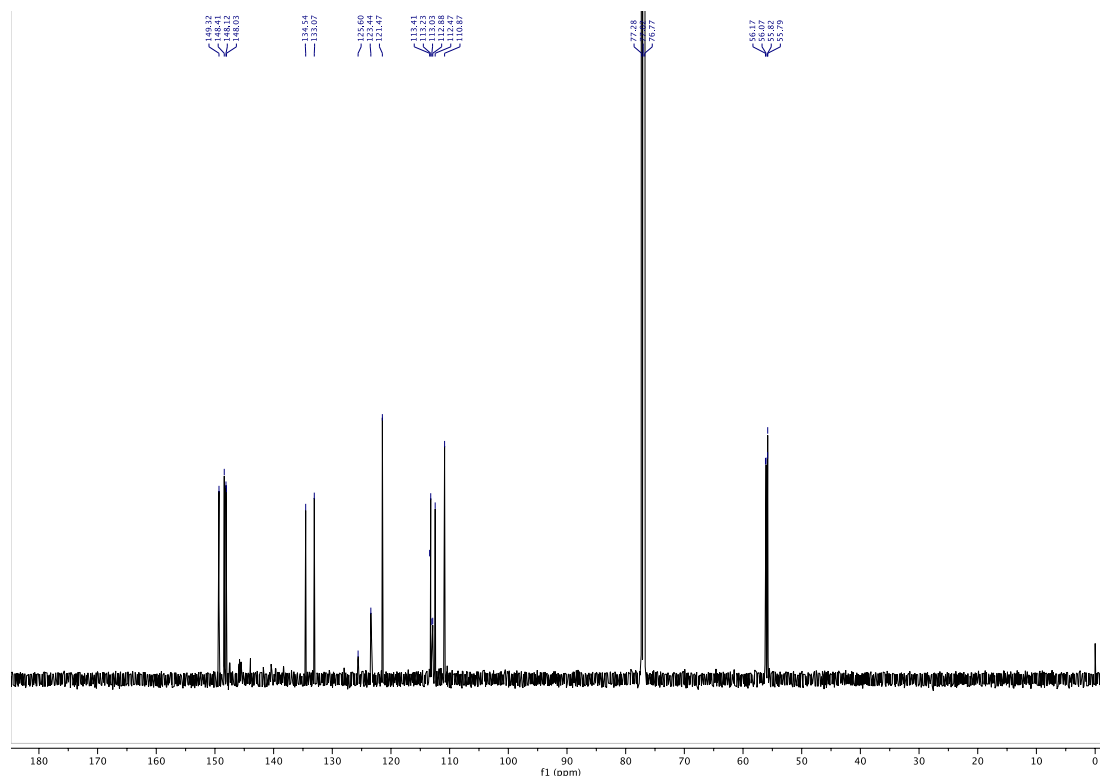
3.88 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.32, 148.41, 148.12, 148.03, 134.54, 133.07, 125.60, 123.44, 121.47, 113.41, 113.23, 113.03, 112.88, 112.47, 110.87, 56.17, 56.07, 55.82, 55.79.



SI10. ^{19}F NMR for 2,3,4,5-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

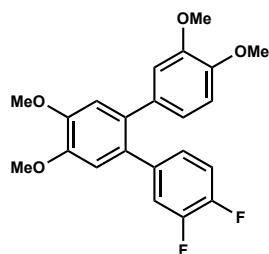


SI11. ^1H NMR for 2,3,4,5-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



SI12. ^{13}C NMR for 2,3,4,5-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

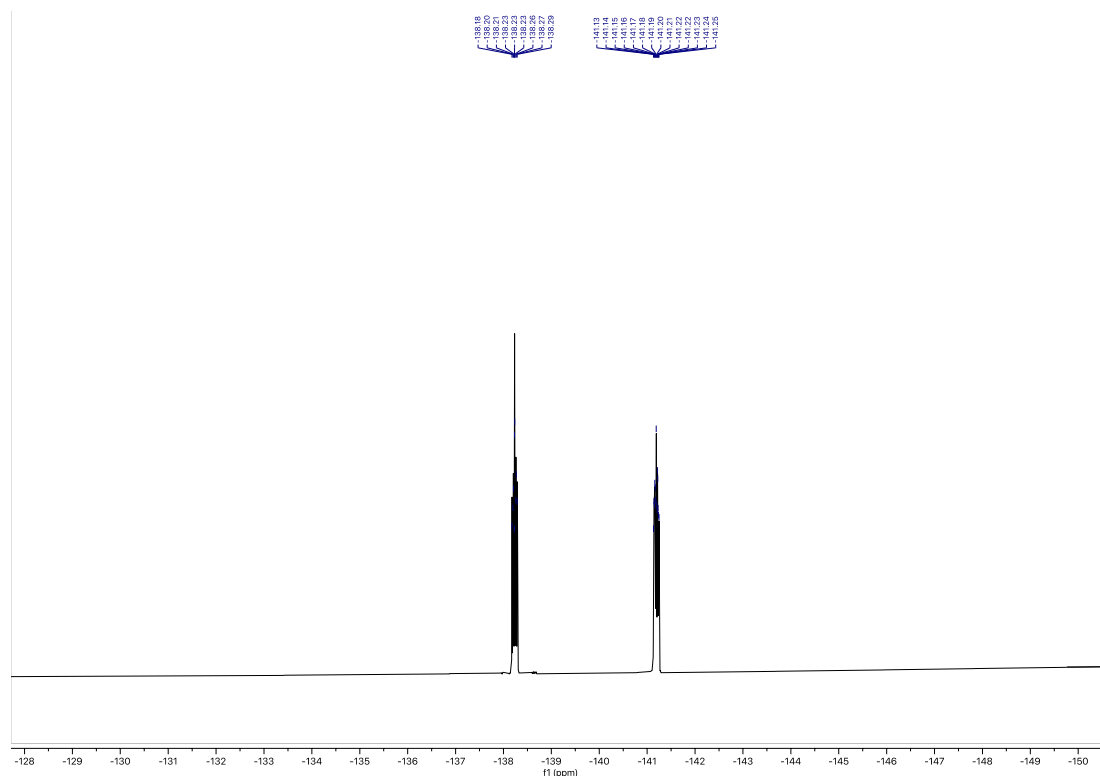
3,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



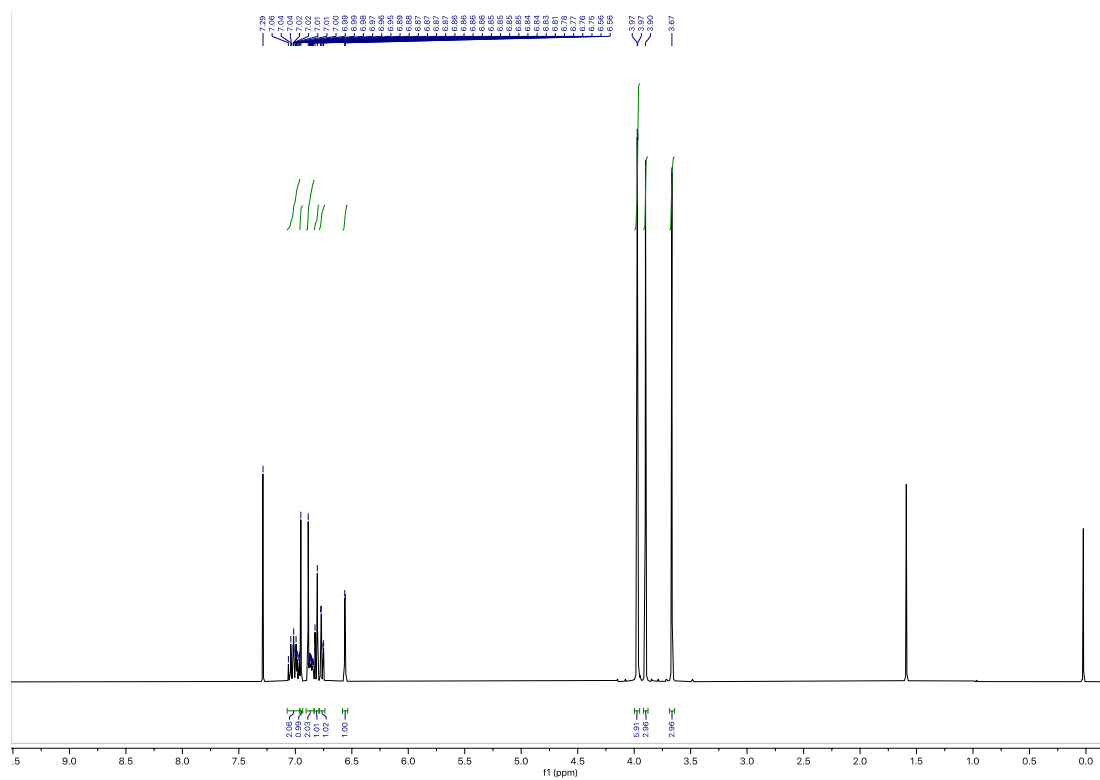
In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.70 g, 2.0 mmol), 3,4-difluorophenylboronic acid (0.48 g, 3.0 mmol), dioxane (15.0 ml) and water (7.0 ml). The mixture was stirred while potassium carbonate (0.88 g, 6.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ (0.035 g, 2.0 mol%) was added and the mixture temperature was slowly raised to 100°C. The reaction was completed after four hours as indicated by the new spot in TLC and GCMS confirmed the mass of the product formed to be that of the desired product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black sticky crude product was extracted with ethyl acetate and dried over anhydrous MgSO_4 then vacuum filtered. Some silica gel and Montmorillonite clay were added to the filtrate and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column made up of hexanes and then the column was eluted with 20-30% EtOAc in hexanes and fractions containing the product were combined and concentrated to get a viscous liquid product which slowly crystallized on standing. Yield- 0.49 g (64%); MP- 135-137 °C

^{19}F NMR (376 MHz, CDCl_3) δ -138.23 (ddd, $J = 21.3, 11.4, 8.1$ Hz), -140.68 – -142.10 (m).

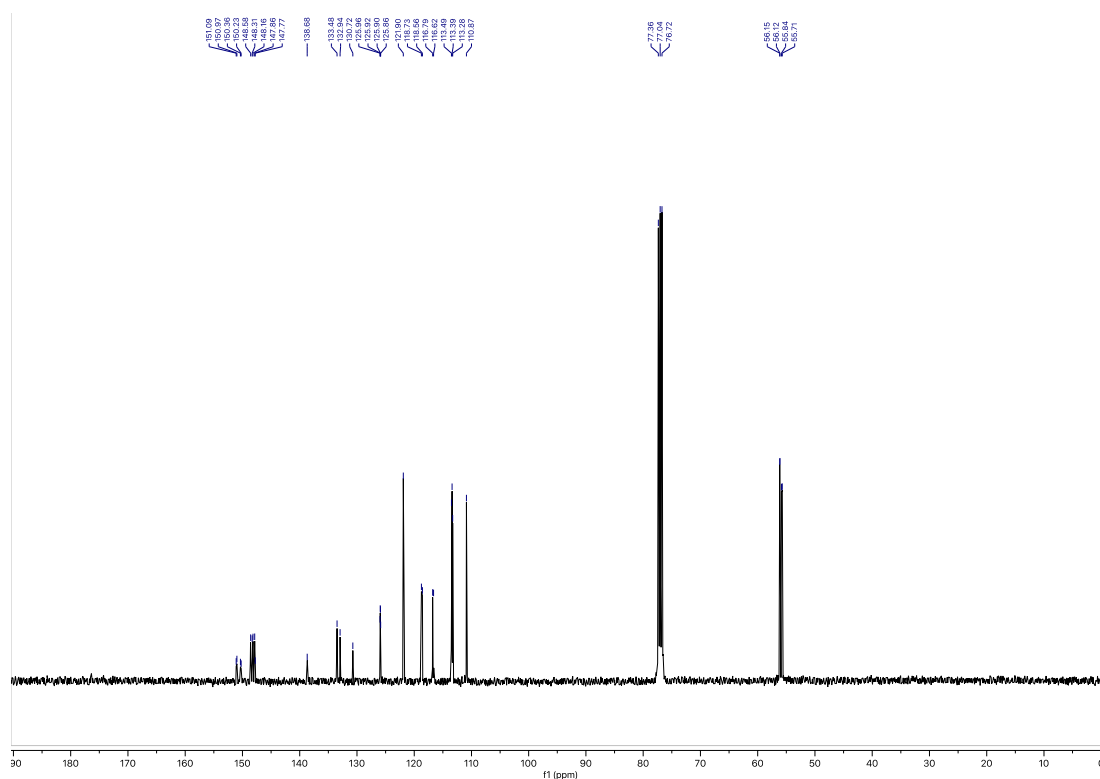
^1H NMR (400 MHz, CDCl_3) δ 7.08 – 6.96 (m, 2H), 6.95 (s, 1H), 6.89 – 6.83 (m, 2H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.76 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.56 (d, $J = 2.0$ Hz, 1H), 3.97 (d, $J = 1.6$ Hz, 6H), 3.90 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.09, 150.97, 150.36, 150.23, 148.58, 148.31, 148.16, 147.86, 147.77, 138.68, 133.48, 132.94, 130.72, 125.96, 125.92, 125.90, 125.86, 121.90, 118.73, 118.56, 116.79, 116.62, 113.49, 113.39, 113.28, 110.87, 56.15, 56.12, 55.84, 55.71.



SI12. ^{13}C NMR for 3,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

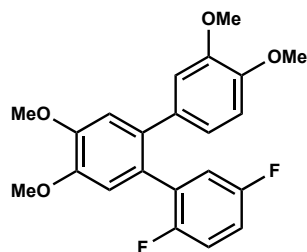


SI13. ^1H NMR for 3,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



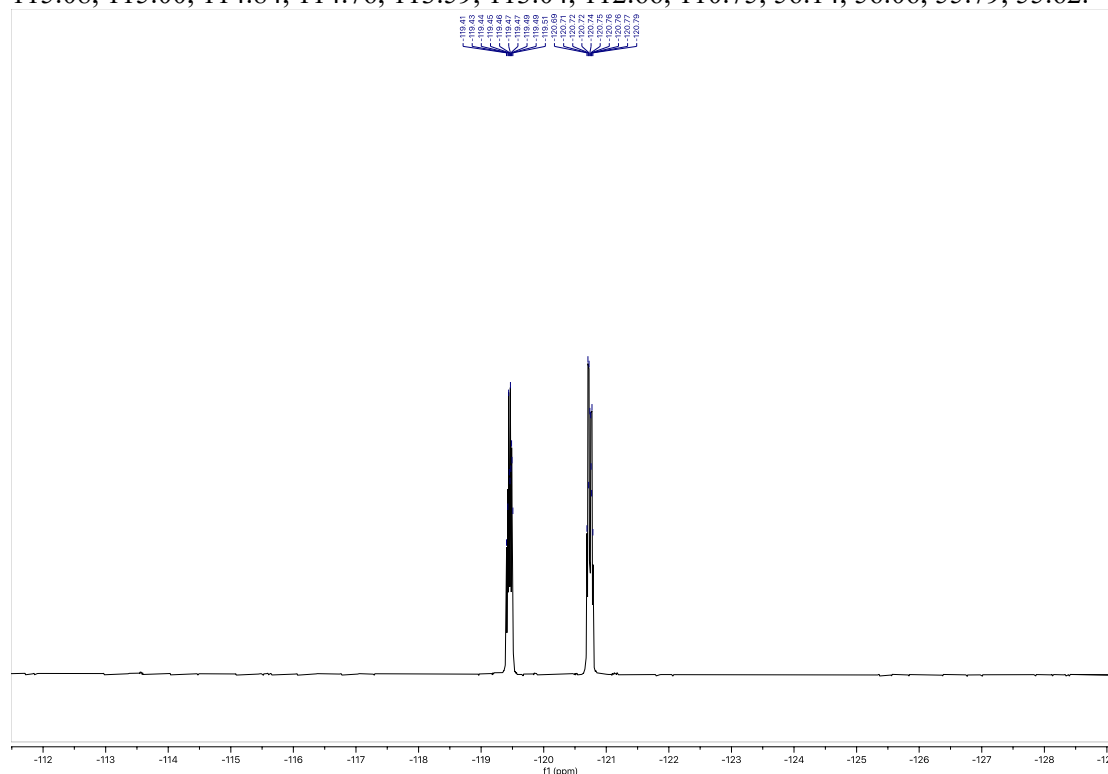
SI14. ^{13}C NMR for 3,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

2,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

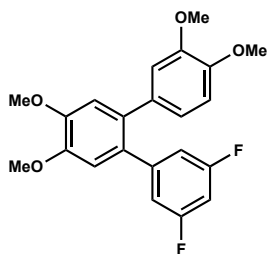


In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.60 g, 1.70 mmol), 2,5-difluorophenylboronic acid (0.42 g, 2.5 mmol), dioxane (15.0 ml) and water (7.0 ml) under a nitrogen atmosphere. The mixture was stirred while potassium carbonate (0.70 g, 5.0 mmol) was added, and the mixture temperature was raised. At 70 °C, the catalyst PdCl₂(PPh₃)₂ (0.030 g, 2.0 mol%) was added the mixture temperature was slowly raised to 100°C. The reaction was completed after seven hours as indicated by the new spot in TLC and GCMS confirmed the mass of the product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was dissolved with ethyl acetate, some silica gel, and Montmorillonite clay was added to the filtrate, and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column made up of hexanes. The column was eluted with 20-30% EtOAc in hexanes. The fractions containing the pure product were combined and concentrated to get a viscous liquid product which slowly crystallized on standing. Yield- 0.40 g (64%); MP- 155-157 °C

¹⁹F NMR (376 MHz, CDCl₃) δ -119.27 – -119.79 (m), -120.42 – -121.06 (m). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 1H), 6.95 – 6.85 (m, 4H), 6.83 – 6.77 (m, 2H), 6.59 (t, *J* = 1.1 Hz, 1H), 3.97 (d, *J* = 10.2 Hz, 6H), 3.89 (s, 3H), 3.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.47, 157.05, 154.62, 148.94, 148.11, 147.89, 147.83, 134.15, 133.55, 125.34, 121.32, 118.62, 118.59, 118.39, 118.35, 116.60, 116.51, 116.35, 116.26, 115.08, 115.00, 114.84, 114.76, 113.59, 113.04, 112.66, 110.75, 56.14, 56.06, 55.79, 55.62.

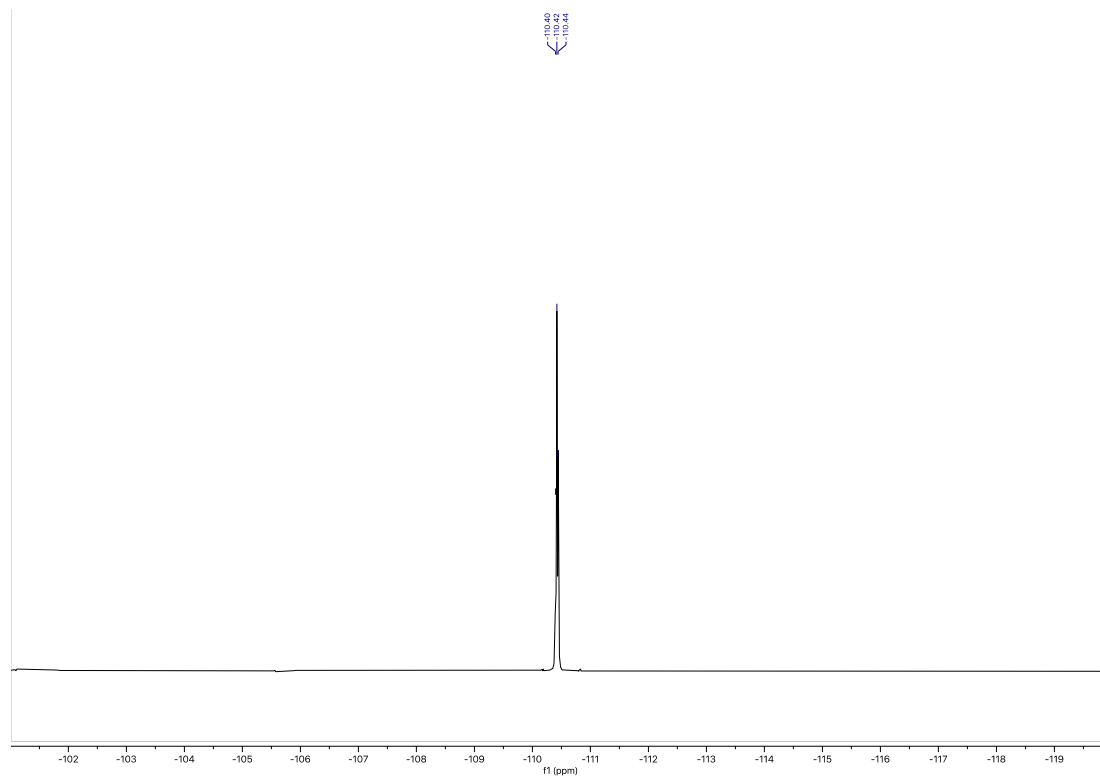


SI15. ¹⁹F NMR for 2,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

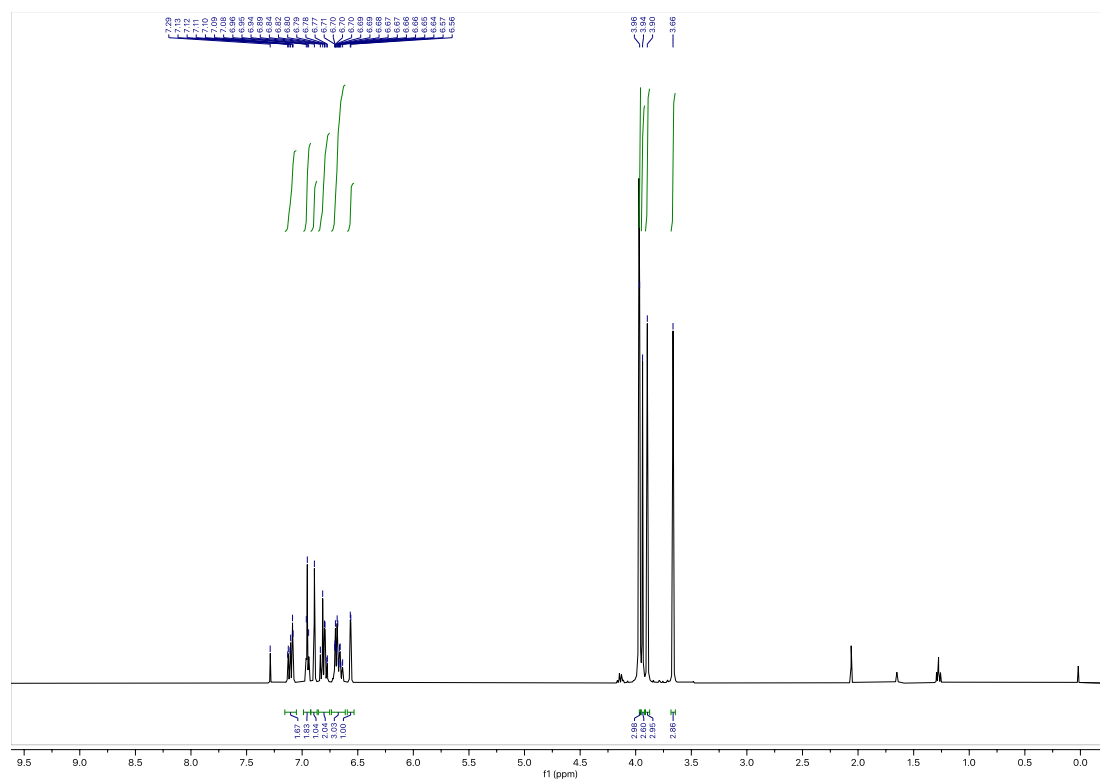


In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.71 g, 2.0 mmol), 3,5-difluorophenylboronic acid (0.48 g, 3.0 mmol), dioxane (15.0 ml) and water (7.0 ml). The mixture was stirred while potassium carbonate (0.88 g, 6.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst PdCl₂(PPh₃)₂ (0.035 g, 2.0 mol%) was added and the temperature was slowly raised to 100°C. The reaction was completed after four hours as indicated by a new spot in TLC and GCMS confirmed the mass of the product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The crude product was isolated by vacuum filtration from the mixture. The black solid crude product was then dissolved in ethyl acetate; some silica gel and Montmorillonite clay was added to the filtrate and the solvent was evaporated by rotary evaporation. This material was placed at the top of a column and was eluted with 20% EtOAc in hexanes. Fractions containing the pure product were combined and concentrated to give a viscous liquid product which slowly crystallized on standing. Yield- 0.56 g (73%); MP- 141-143 °C

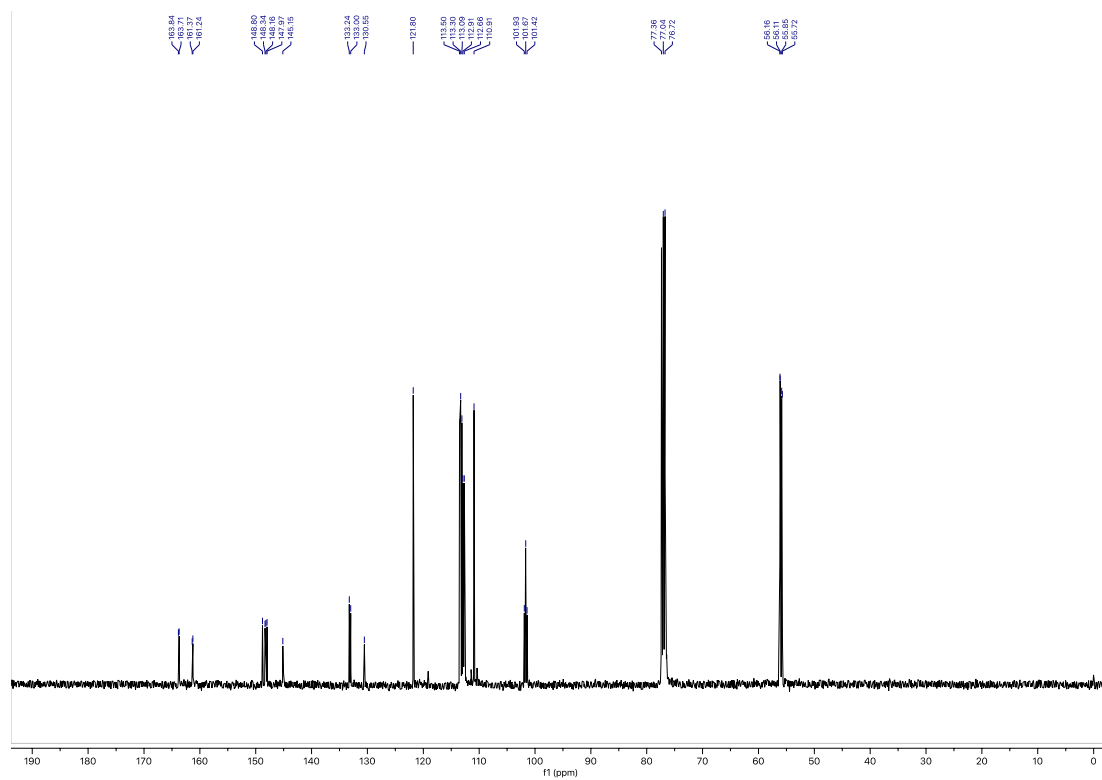
¹⁹F NMR (376 MHz, CDCl₃) δ -110.42 (t, *J* = 8.3 Hz). ¹H NMR (400 MHz, CDCl₃) δ 7.12 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 6.95 (t, *J* = 4.1 Hz, 2H), 6.89 (s, 1H), 6.85 – 6.76 (m, 2H), 6.73 – 6.59 (m, 3H), 6.57 (d, *J* = 1.9 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 2H), 3.90 (s, 3H), 3.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.84, 163.71, 161.37, 161.24, 148.80, 148.34, 148.16, 147.97, 145.15, 133.24, 133.00, 130.55, 121.80, 113.50, 113.30, 113.09, 112.91, 112.66, 110.91, 101.93, 101.67, 101.42, 56.16, 56.11, 55.85, 55.72.



SI18. ^{19}F NMR for 3,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

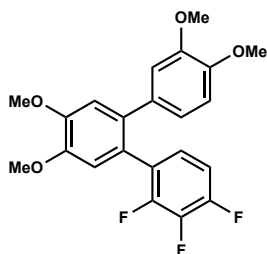


SI19. ^1H NMR for 3,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



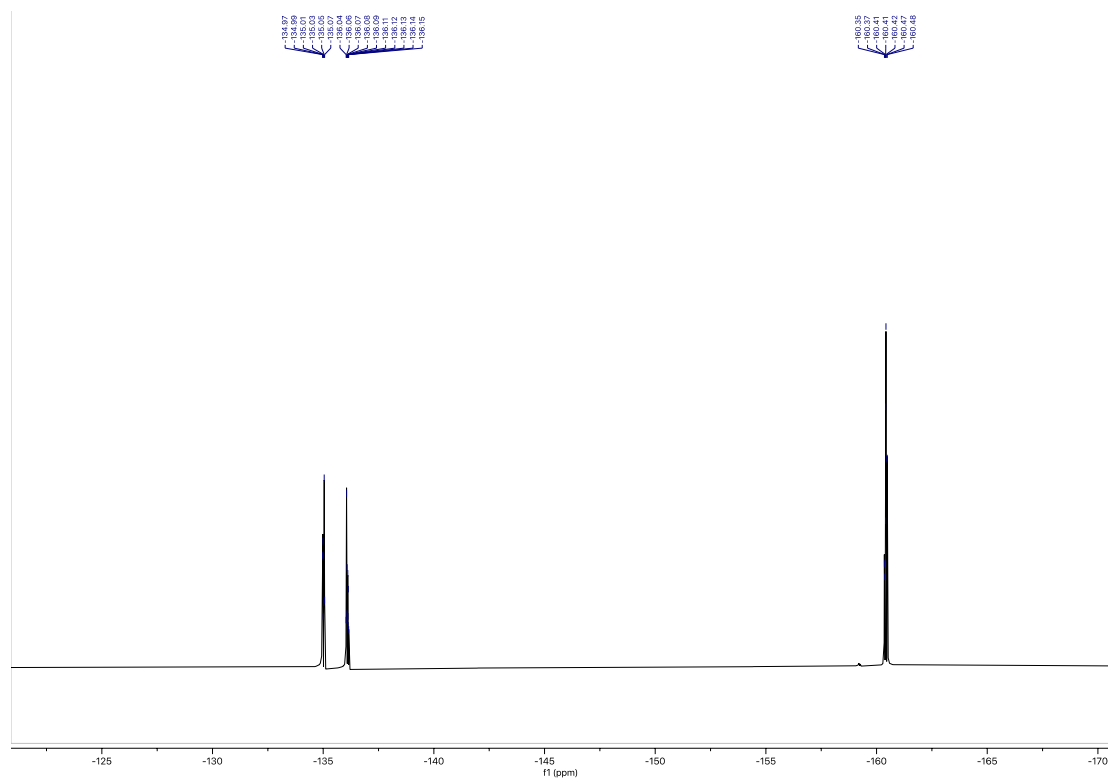
SI20. ^{13}C NMR for 3,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

2,3,4-trifluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

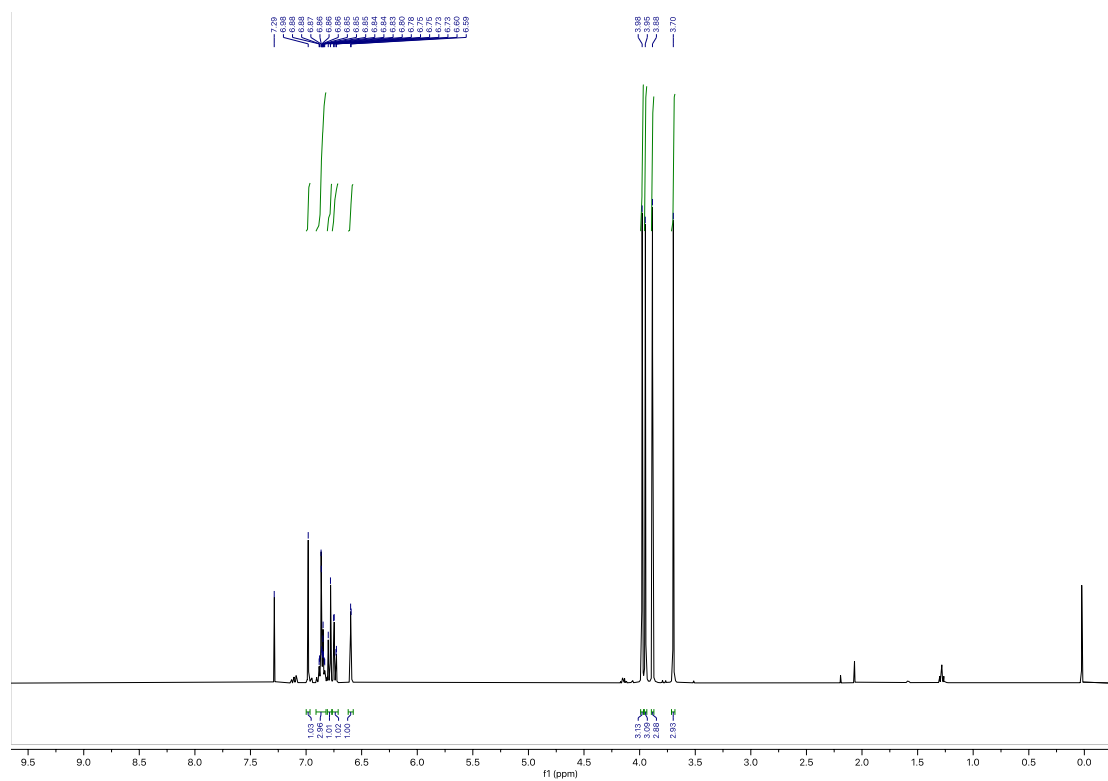


In a 100 ml round bottom flask was placed 2-iodo-4,5,3',4'-tetramethoxybiphenyl (0.60 g, 1.50 mmol), 2,3,4-trifluorophenylboronic acid (0.56 g, 3.0 mmol), dioxane (12.0 ml) and water (5.0 ml). The mixture was stirred while potassium carbonate (0.88 g, 6.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst PdCl₂(PPh₃)₂ (2.0 mol%) was added, and the temperature was slowly raised to 95°C. The reaction was completed after seven hours as indicated by the new spot in TLC. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black sticky crude product was extracted with ethyl acetate, dried over anhydrous MgSO₄ then vacuum filtered. Some silica gel and Montmorillonite clay were added to the filtrate and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column made up of hexanes. The column was eluted with 25% EtOAc in hexanes. The fractions containing the pure product were combined and concentrated to get a viscous liquid product which slowly crystallized on standing and was used in the subsequent reaction without further purification. Yield: 0.47 g (77 %); MP- 133-135 °C

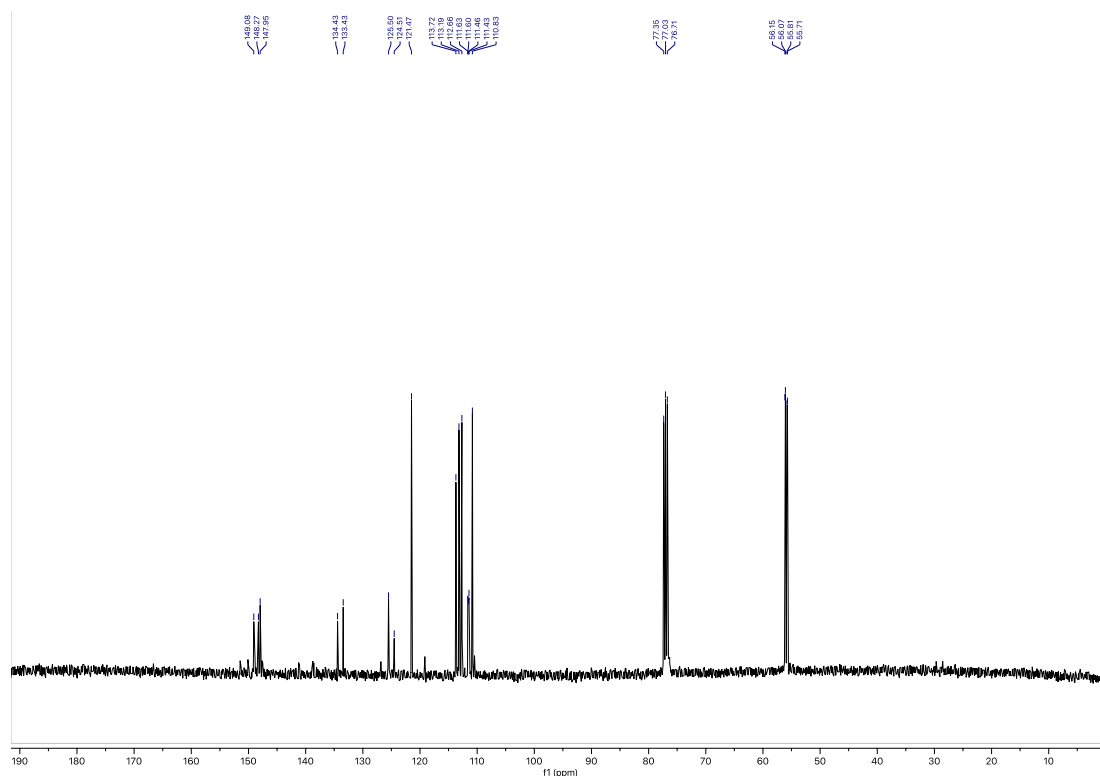
¹⁹F NMR (376 MHz, CDCl₃) δ -135.02 (dt, *J* = 22.6, 6.3 Hz), -135.71 – -136.86 (m), -160.42 (td, *J* = 21.6, 5.6 Hz). ¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 1H), 6.91 – 6.82 (m, 3H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.88 (s, 3H), 3.70 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.08, 148.27, 147.95, 134.43, 133.43, 125.50, 124.51, 121.47, 113.72, 113.19, 112.66, 111.63, 111.60, 111.46, 111.43, 110.83, 56.15, 56.07, 55.81, 55.71.



SI21. ^{19}F NMR for 2,3,4-trifluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

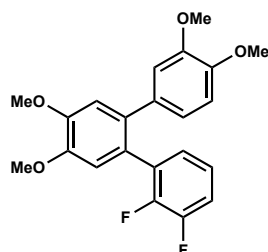


SI22. ^1H NMR for 2,3,4-trifluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



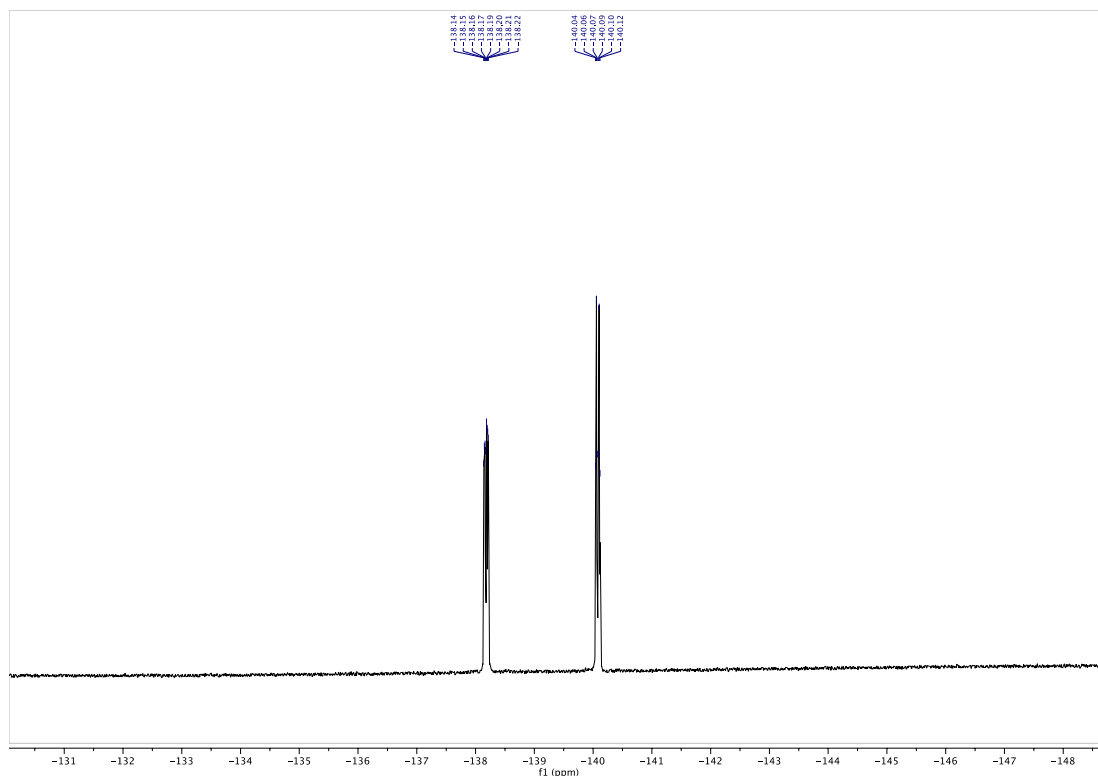
SI23. ^{13}C NMR for 2,3,4-trifluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

2,3-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

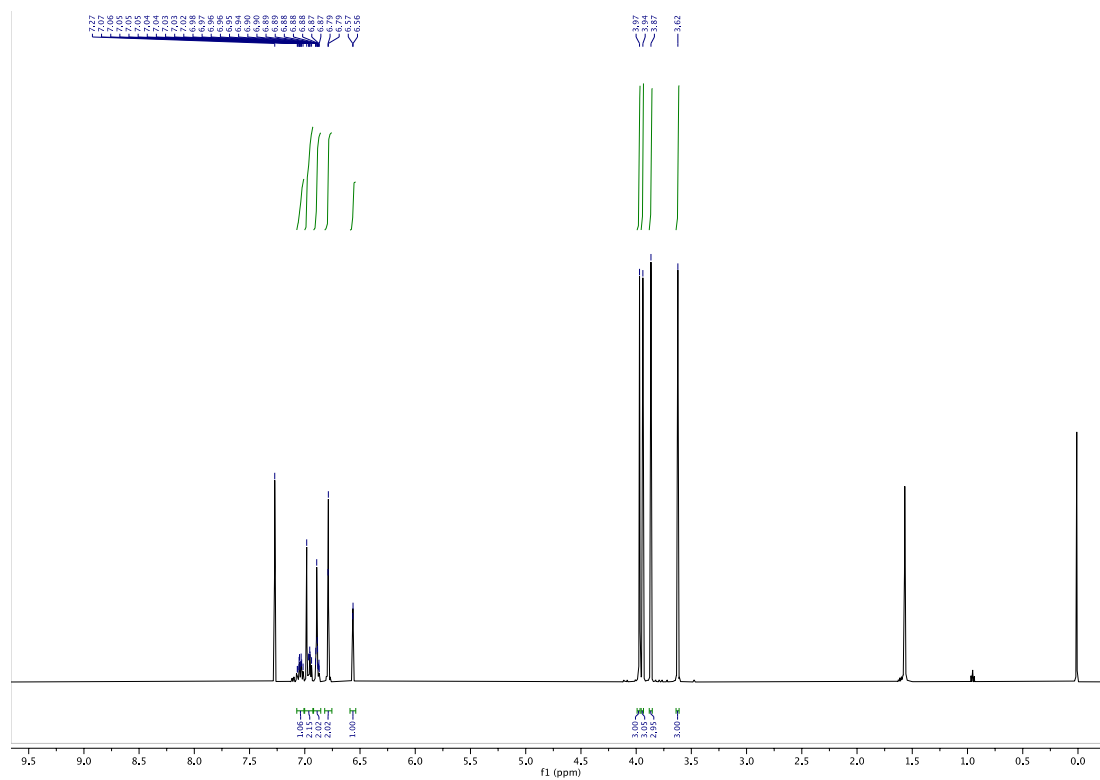


In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.71 g, 2.0 mmol), 2,3-difluorophenylboronic acid (0.48 g, 3.0 mmol), dioxane (15.0 ml) and water (6.0 ml). The mixture was stirred while potassium carbonate (0.88 g, 6.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ (2 mol%) was added and temperature was slowly raised to 100 °C. The reaction was completed after four hours as indicated by the new spot in TLC and GCMS confirmed the mass of the product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was dissolved in ethyl acetate then some silica gel and Montmorillonite clay were added, and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column and then eluted with 20% EtOAc in hexanes. Fractions containing the product were combined and concentrated to obtain the white solid product which was used for the subsequent reaction without further purification. Yield: 0.36 g (48%); MP- 148-151 °C ^{19}F NMR (470 MHz, CDCl_3) δ -138.18 (ddd, $J = 21.3, 10.1, 5.0$ Hz), -140.08 (dt, $J = 21.7, 6.8$ Hz). ^1H NMR (500 MHz, CDCl_3) δ 7.07 – 7.01 (m, 1H), 6.99 – 6.92 (m, 2H), 6.90 – 6.85 (m, 2H), 6.79 (d, $J = 1.4$ Hz, 2H), 6.56 (d, $J = 1.3$ Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 3.87 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (126 MHz,

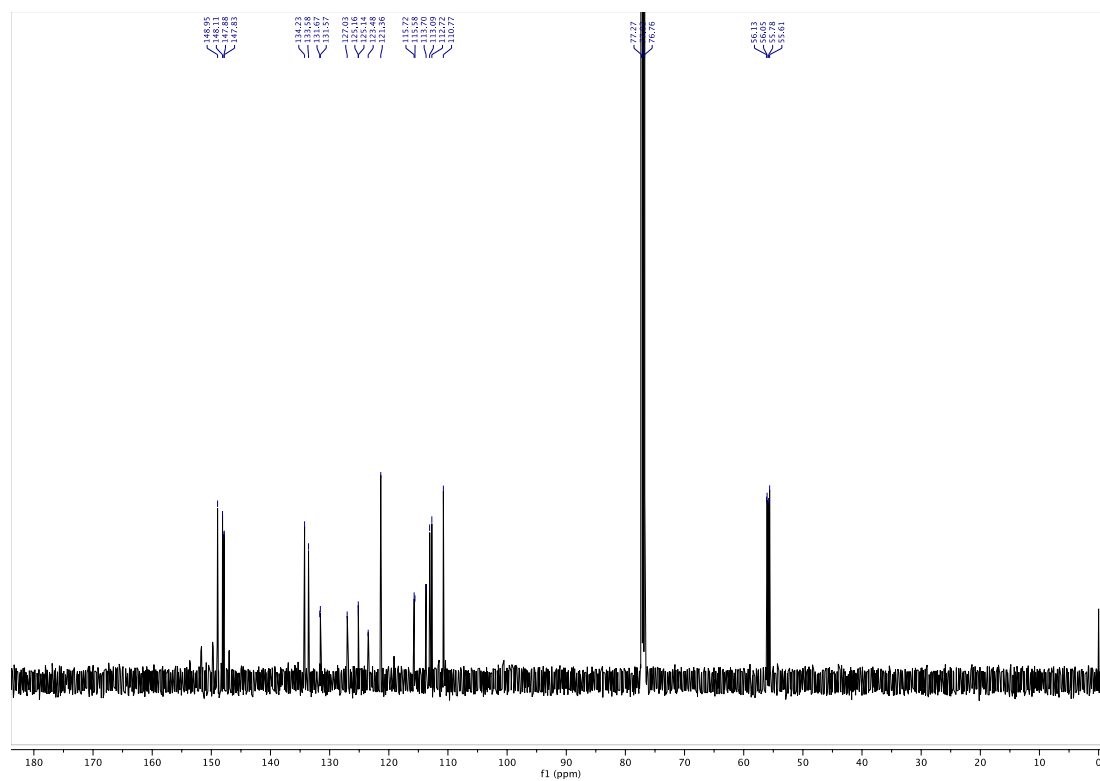
CDCl₃) δ 148.95, 148.11, 147.88, 147.83, 134.23, 133.58, 131.67, 131.57, 127.03, 125.16, 125.14, 123.48, 121.36, 115.72, 115.58, 113.70, 113.09, 112.72, 110.77, 56.13, 56.05, 55.78, 55.61.



SI24. ¹⁹F NMR for 2,3-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

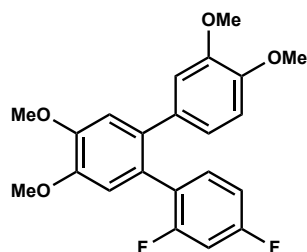


SI25. ^1H NMR for 2,3-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

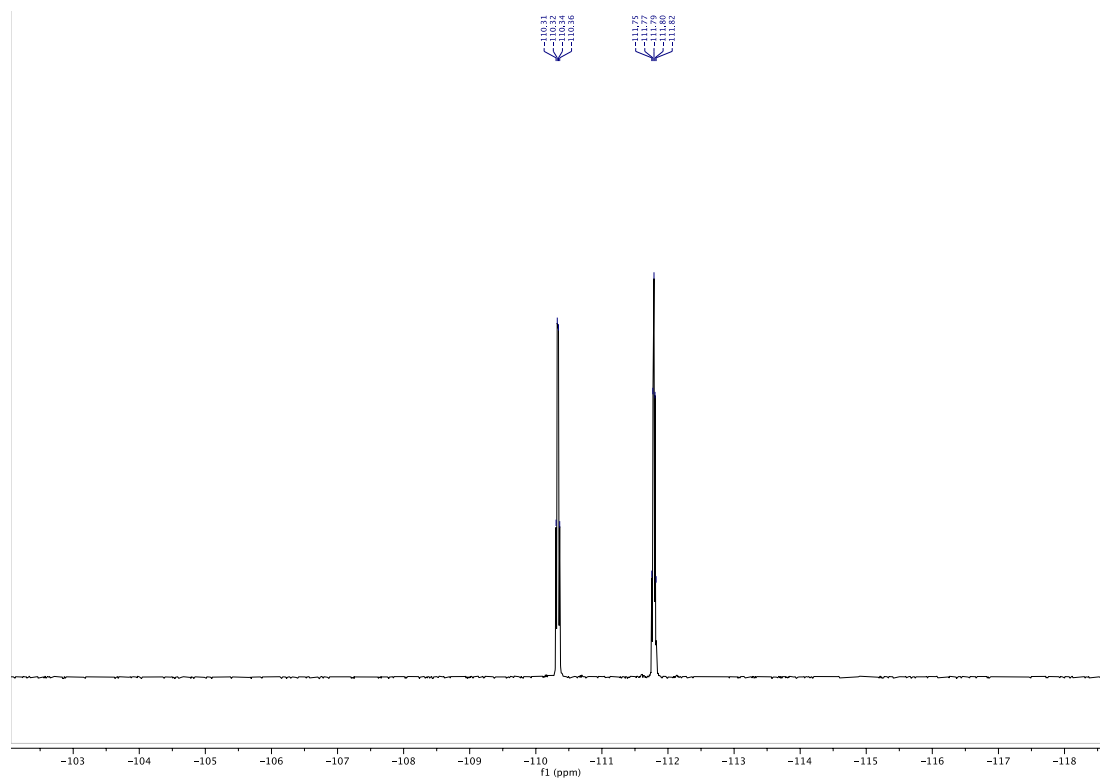


SI26. ^{13}C NMR for 2,3-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

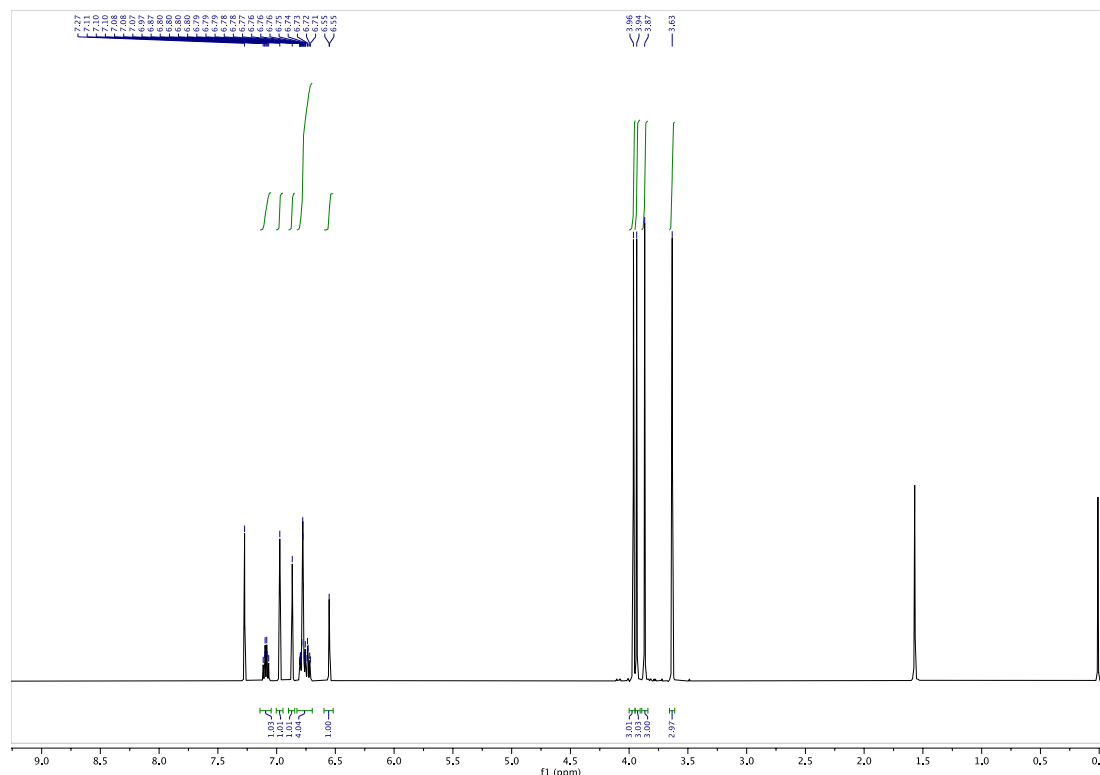
2,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



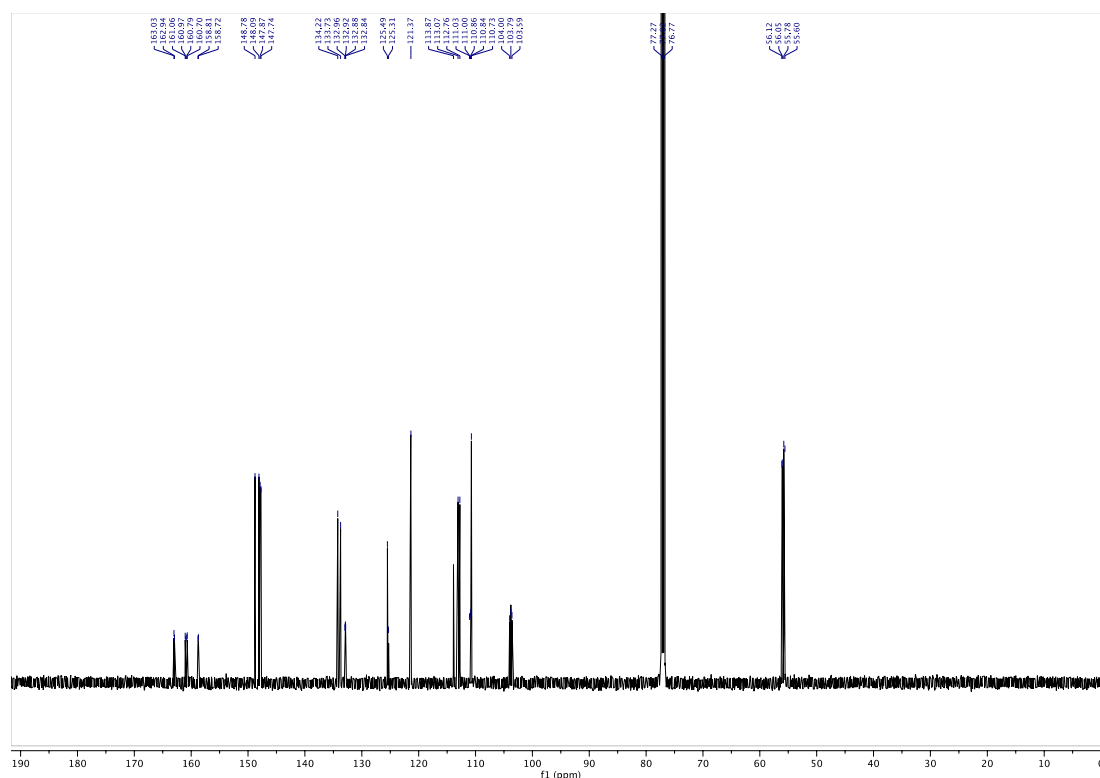
In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.71 g, 2.0 mmol), 2,4-difluorophenylboronic acid (0.63 g, 4.0 mmol), dioxane (15.0 ml) and water (6.0 ml). The mixture was stirred while potassium carbonate (1.14 g, 8.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst PdCl₂(PPh₃)₂ (2 mol%) was added and the temperature was slowly raised to 100 °C. The reaction was completed after three hours as indicated by the new spot in TLC and GCMS confirmed the mass of the product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was dissolved in ethyl acetate then some silica gel and Montmorillonite clay were added, and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column and then eluted with 20% EtOAc in hexanes. Fractions containing the product were combined and concentrated to get the white solid product which was used in the subsequent reaction without further purification. Yield: 0.62 g (81%); MP- 154-156 °C (POM)
¹⁹F NMR (470 MHz, CDCl₃) δ -110.33 (q, *J* = 8.7 Hz), -111.79 (p, *J* = 8.0 Hz).
¹H NMR (500 MHz, CDCl₃) δ 7.09 (td, *J* = 8.5, 6.5 Hz, 1H), 6.97 (s, 1H), 6.87 (s, 1H), 6.82 – 6.69 (m, 4H), 6.55 (d, *J* = 1.6 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.87 (s, 3H), 3.63 (s, 3H).
¹³C NMR (126 MHz, CDCl₃) δ 163.03, 162.94, 161.06, 160.97, 160.79, 160.70, 158.81, 158.72, 148.78, 148.09, 147.87, 147.74, 134.22, 133.73, 132.96, 132.92, 132.88, 132.84, 125.49, 125.31, 121.37, 113.87, 113.07, 112.76, 111.03, 111.00, 110.86, 110.84, 110.73, 104.00, 103.79, 103.59, 56.12, 56.05, 55.78, 55.60.



SI27. ^{19}F NMR for 2,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

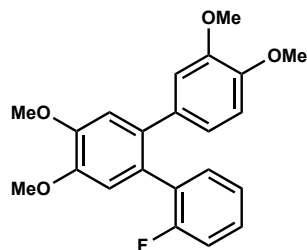


SI28. ^1H NMR for 2,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



SI29. ^{13}C for 2,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

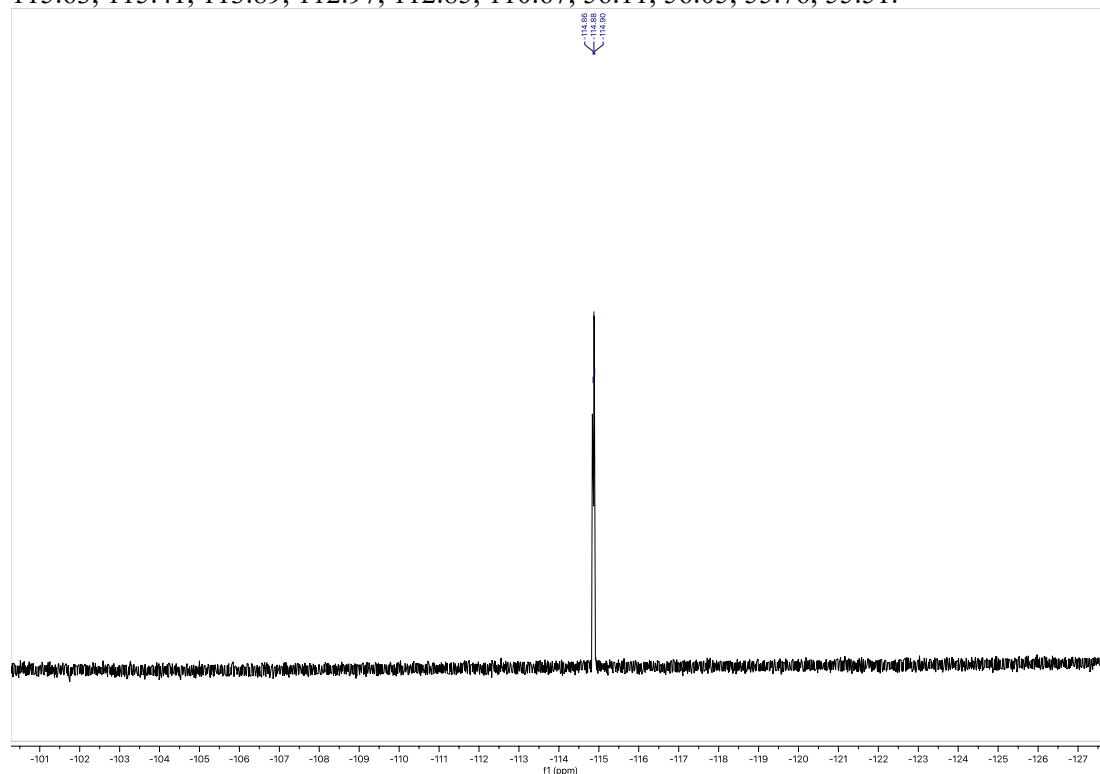
2-fluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



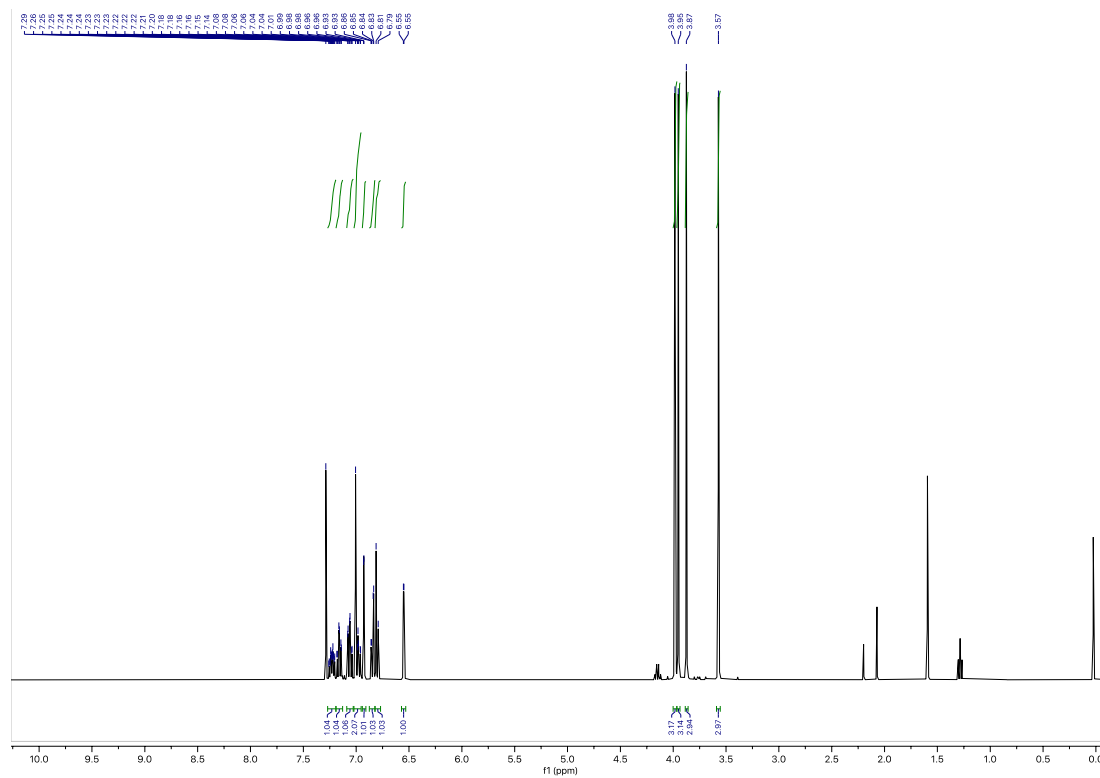
In a 100 ml round bottom flask was placed 2-bromo-4,5,3',4'-tetramethoxybiphenyl (0.71 g, 2.0 mmol), 2-fluorophenylboronic acid (0.43 g, 3.0 mmol), dioxane (15.0 ml) and water (6.0 ml). The mixture was stirred while potassium carbonate (0.88 g, 6.0 mmol) was added, and the mixture was heated in an oil bath under a nitrogen atmosphere. At 70 °C, the catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ (0.035 g, 2 mol%) was added, and the temperature was slowly raised to 100°C. The reaction was completed after three hours as indicated by the new spot in TLC and GCMS confirmed the mass of the product. After cooling to room temperature ice water was added dropwise with stirring to fill the flask. The black solid crude product was dissolved in ethyl acetate then some silica gel and Montmorillonite clay were added, and the mixture was concentrated by rotary evaporation. This material was placed at the top of a column and then eluted with 20% EtOAc in hexanes. Fractions containing the product were combined and concentrated to get the white solid product which was used in the subsequent reaction without further purification. Yield: 0.60 g (81%); MP- 137-139 °C (POM)

^{19}F NMR (376 MHz, CDCl_3) δ -113.67 – -115.74 (m). ^1H NMR (400 MHz, CDCl_3) δ 7.23 (dddd, J = 8.2, 7.1, 5.1, 1.9 Hz, 1H), 7.16 (td, J = 7.5, 1.8 Hz, 1H), 7.06 (td, J = 7.5, 1.2 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.93

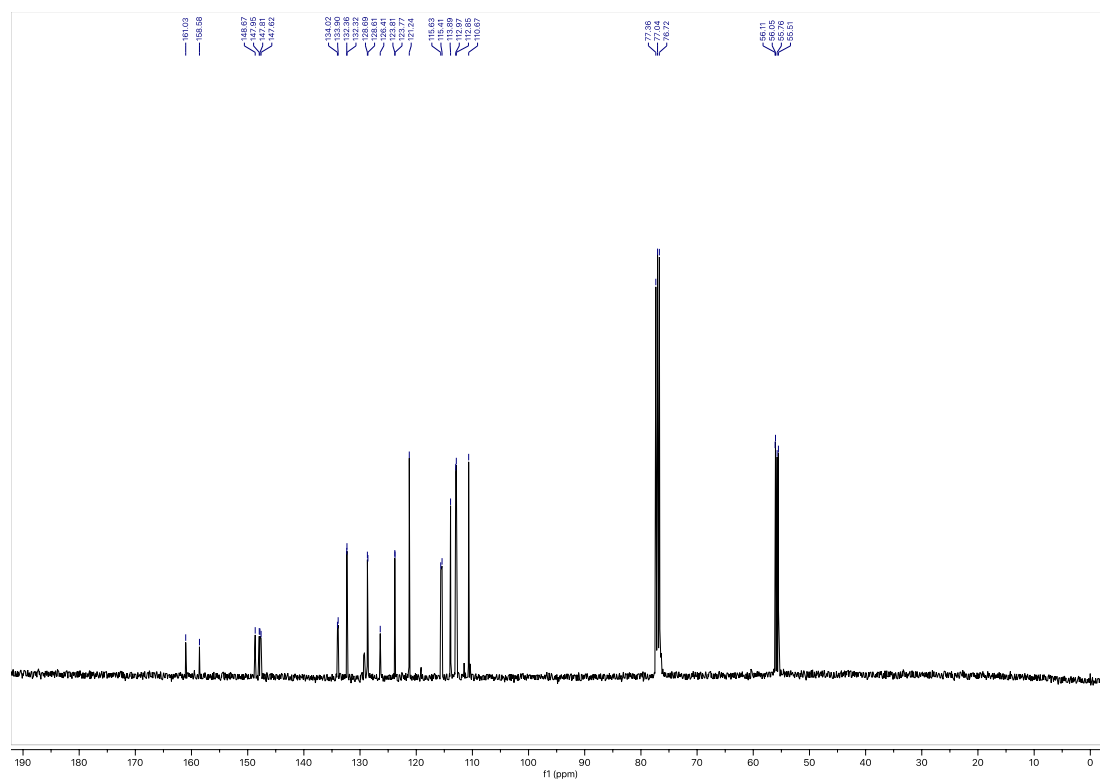
(d, $J = 0.9$ Hz, 1H), 6.85 (dd, $J = 8.3, 2.0$ Hz, 1H), 6.80 (d, $J = 8.3$ Hz, 1H), 6.55 (d, $J = 2.0$ Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.87 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.03, 158.58, 148.67, 147.95, 147.81, 147.62, 134.02, 133.90, 132.36, 132.32, 128.69, 128.61, 126.41, 123.81, 123.77, 121.24, 115.63, 115.41, 113.89, 112.97, 112.85, 110.67, 56.11, 56.05, 55.76, 55.51.



SI30. ^{13}C NMR for 2-fluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

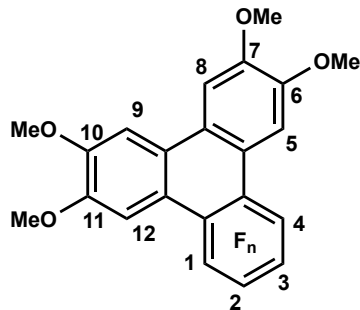


SI31. ^1H NMR for 2-fluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl



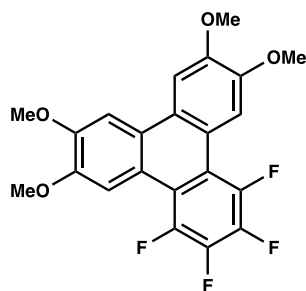
SI32. ^{13}C for 2-fluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl

Synthesis of target compounds



General structure of 6,7,10,11-tetramethoxytriphenylenes

*1,2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene*¹



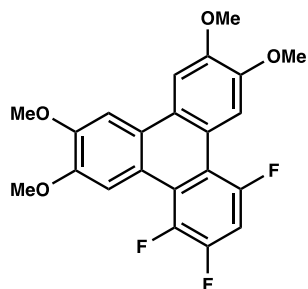
In a (100 cm x 10 cm) quartz tube was placed 2,3,4,5,6-pentafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.57 g, 1.31 mmol) and acetonitrile (60.0 ml). The mixture was irradiated with 16x254 nm lamps for twelve hours in a Rayonet. The solution turned from colorless to dark brown and some white crystalline precipitate appeared at the bottom of the tube. The photoreaction was monitored by GCMS which indicated the complete transformation of the starting material and so the reaction was terminated after a total of twenty hours. The precipitate was vacuum-filtered and washed with acetonitrile. The filtrate was concentrated and redissolved in ethyl acetate and adsorbed on some silica gel. The yellow silica gel powder was placed at the top of a column and eluted with a mixture of ethyl acetate and hexanes (10% EtOAc in hexanes). The fractions containing the product were combined and concentrated to get a solid white product which was combined with the previously filtered off product. Yield – 0.40 g (73 %)

¹⁹F NMR (376 MHz, CDCl₃) δ -139.74 – -139.94 (m, 2F), -159.30 – -159.43 (m, 2F).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (dd, *J* = 4.1, 2.3 Hz, 2H), 7.65 (s, 2H), 4.14 (s, 6H), 4.06 (s, 6H).

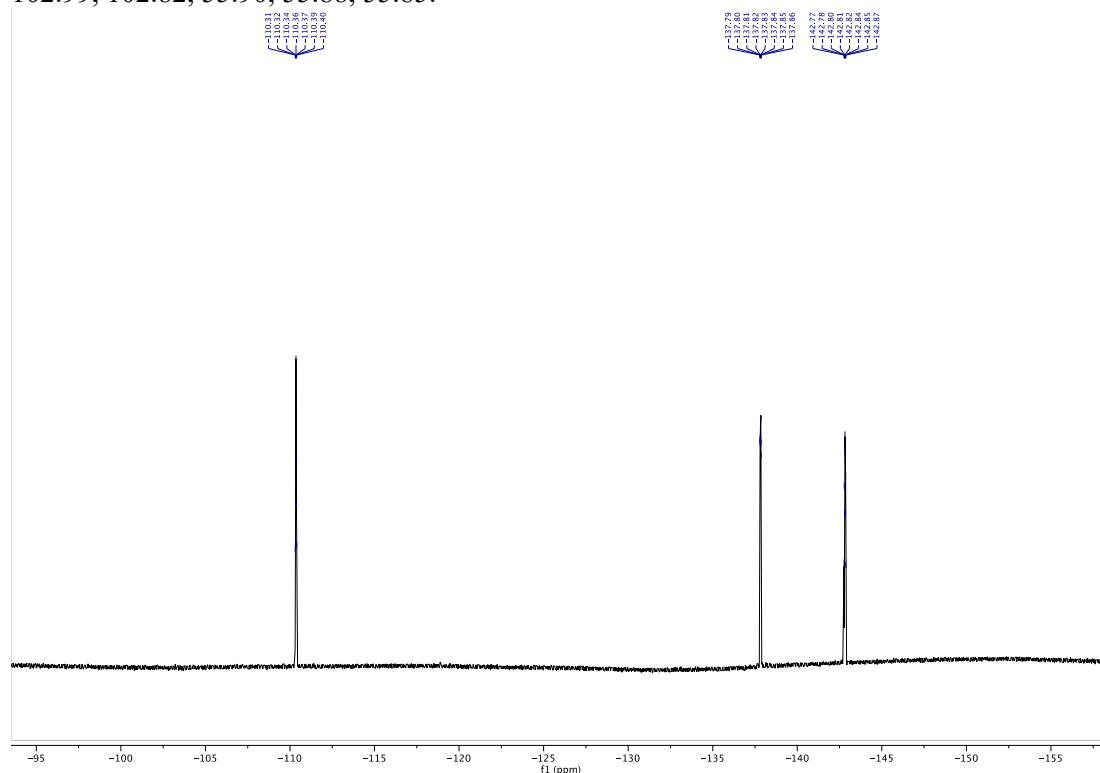
¹³C NMR (101 MHz, CDCl₃) δ 149.68, 148.56, 124.80, 119.41, 115.19, 108.92, 108.77, 108.61, 103.61, 55.84, 55.81.

1,2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene

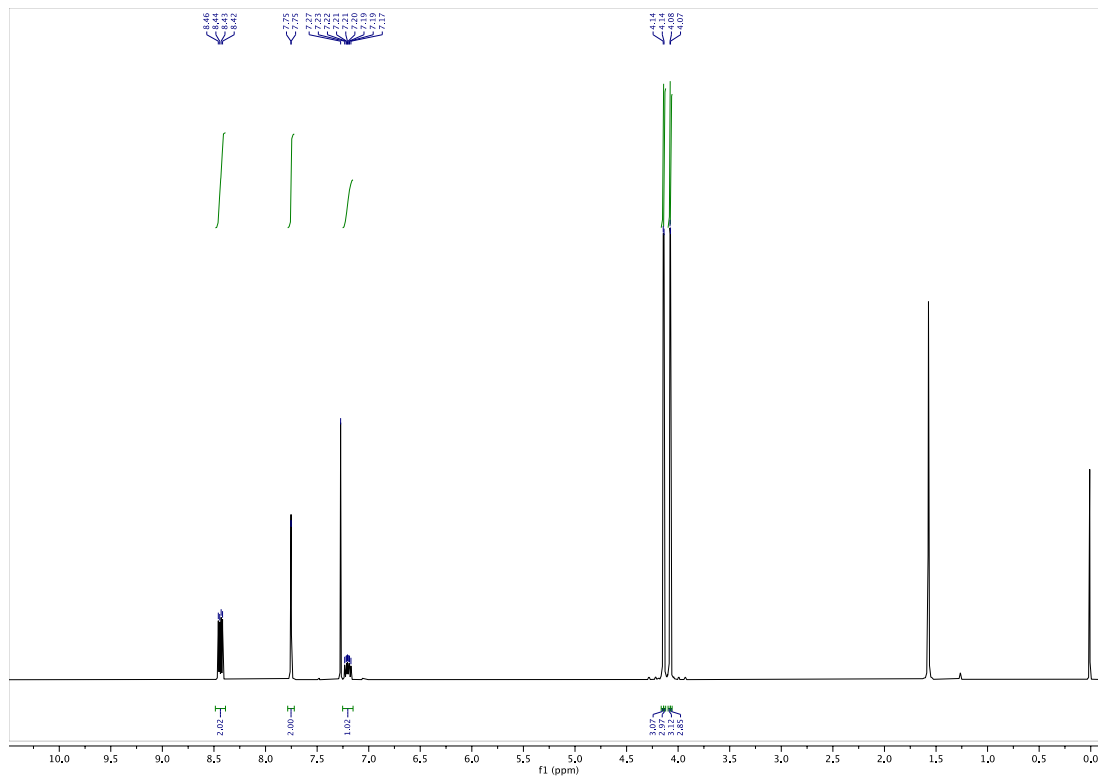


In a (100 cm x 10 cm) quartz tube was placed 2,3,5,6-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.18 g, 0.4 mmol) and acetonitrile (30.0 ml). The mixture was irradiated with 16x254nm lamps for fifteen hours in a Rayonet. The solution turned from colorless to yellow. The photoreaction was monitored by TLC which indicated the complete transformation of the starting material and so the reaction was terminated. After cooling the mixture to room temperature, a white precipitate appeared and after some time all the precipitate settled at the bottom of the tube. The precipitate was vacuum filtered and then washed with acetonitrile to get the tan solid product which was recrystallized with acetonitrile. Yield – 0.12 g (71 %)

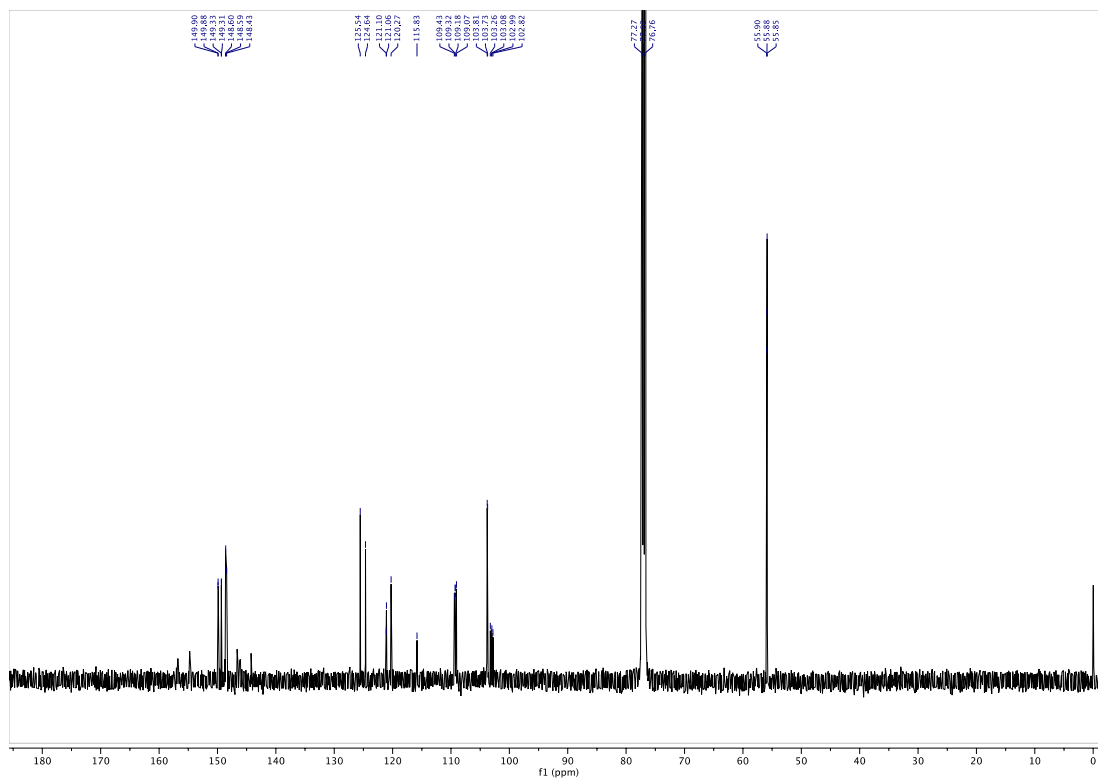
^{19}F NMR (470 MHz, CDCl_3) δ -110.35 (ddd, $J = 20.4, 13.7, 5.8$ Hz), -137.83 (ddd, $J = 19.3, 9.6, 4.8$ Hz), -142.82 (ddd, $J = 26.7, 14.7, 6.8$ Hz). ^1H NMR (500 MHz, CDCl_3) δ 8.44 (dd, $J = 14.1, 6.8$ Hz, 2H), 7.75 (d, $J = 1.2$ Hz, 2H), 7.20 (ddd, $J = 13.8, 9.7, 6.8$ Hz, 1H), 4.14 (s, 3H), 4.14 (s, 3H), 4.08 (s, 3H), 4.07 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.90, 149.88, 149.33, 149.31, 148.60, 148.59, 148.43, 125.54, 124.64, 121.10, 121.06, 120.27, 115.83, 109.43, 109.32, 109.18, 109.07, 103.81, 103.73, 103.26, 103.08, 102.99, 102.82, 55.90, 55.88, 55.85.



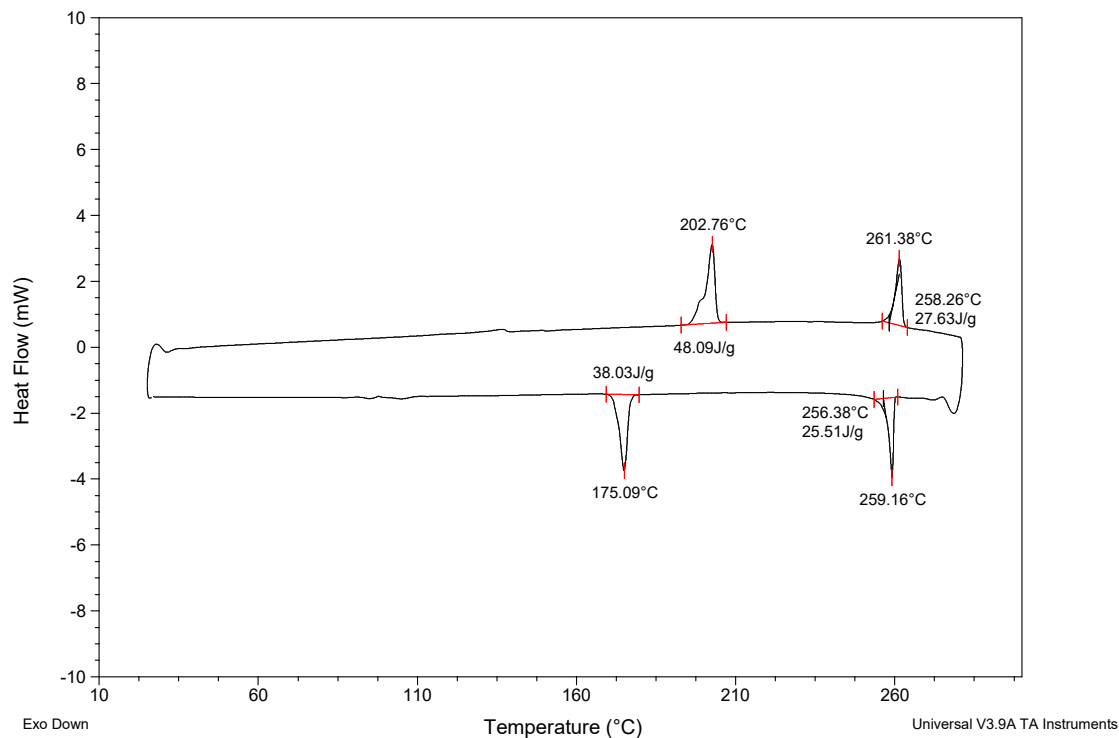
SI33. ^{19}F NMR for 1,2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene



SI34. ¹H NMR for 1,2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene

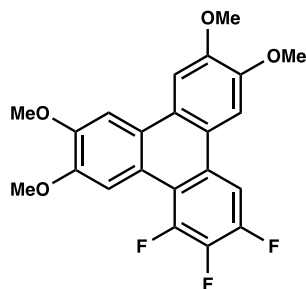


SI35. ¹³C NMR for 1,2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene



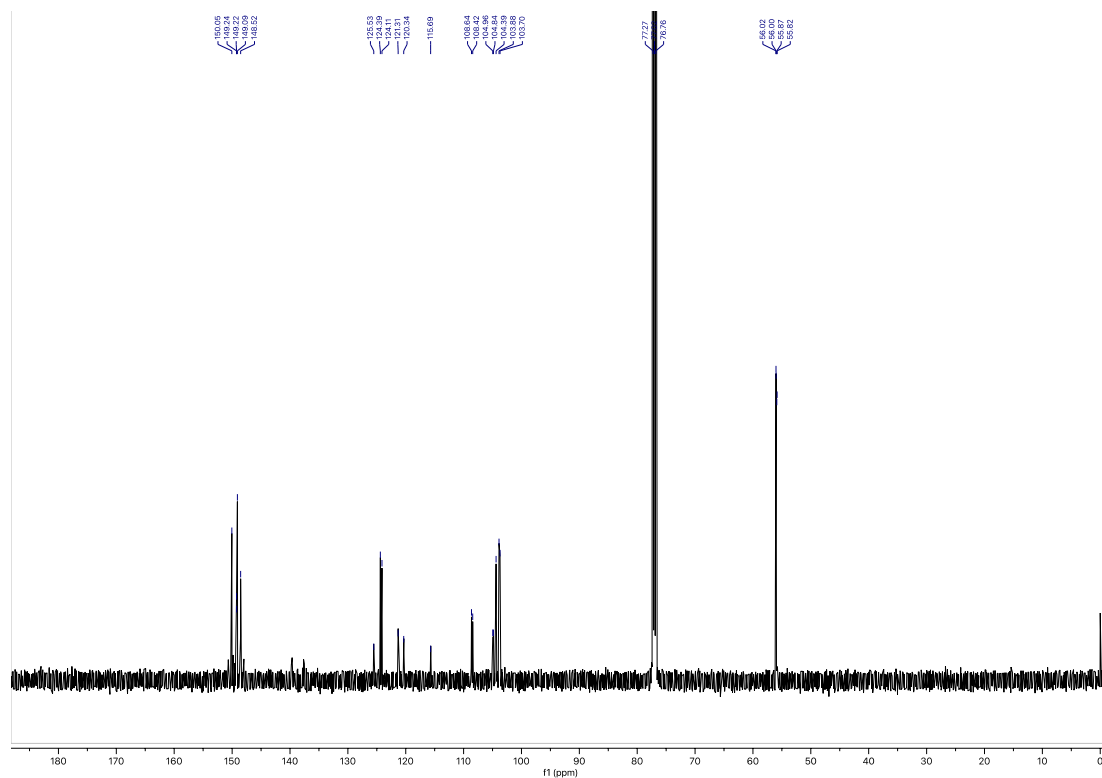
SI36. A DSC scan for 1,2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene

1,2,3-trifluoro-6,7,10,11-tetramethoxytriphenylene

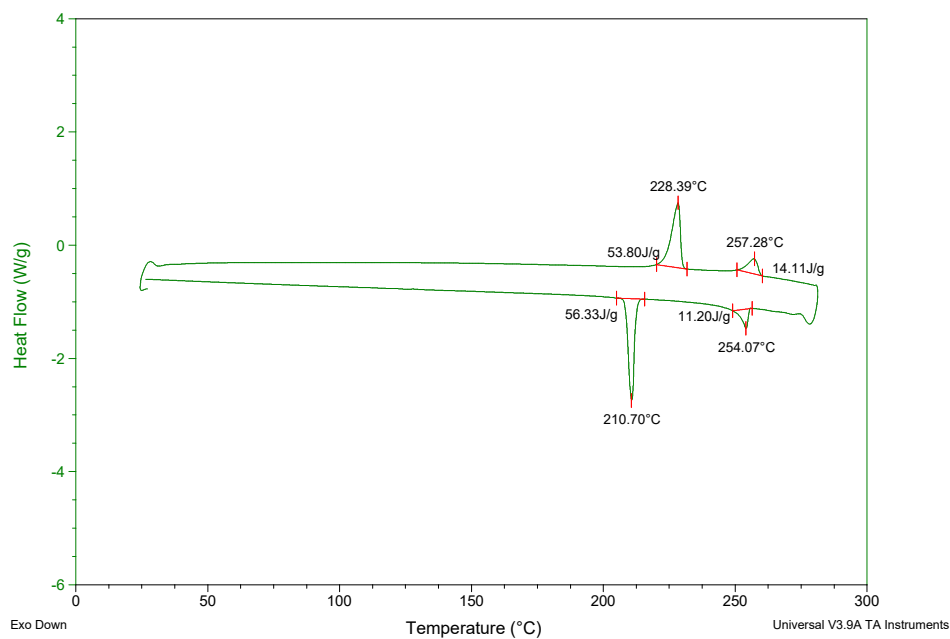


In a (100 cm x 10 cm) quartz tube was placed 2,3,4,5-tetrafluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.37 g, 0.9 mmol) and acetonitrile (50.0 ml). The mixture was irradiated with 16x254nm lamps in a Rayonet. The solution turned from colorless to yellow. The photoreaction was monitored by TLC which indicated the complete transformation of the starting material and so the reaction was terminated after a total of twenty-four hours. The reaction mixture was allowed to cool down and the mixture was transferred to a recovery flask and concentrated under reduced pressure to get a brownish residue. The residue was redissolved in ethyl acetate and adsorbed on some silica gel. The yellow silica gel powder was placed at the top of a column and eluted with a gradient of 20% to 40 % EtOAc in hexanes. Fractions containing the product were combined and concentrated to get a brownish solid product which was recrystallized from 1-propanol to get pale brown crystals. Yield- 0.13 g (37 %)

¹⁹F NMR (470 MHz, CDCl₃) δ -134.28 (ddd, *J* = 17.6, 10.7, 4.2 Hz), -136.91 (ddd, *J* = 20.5, 12.2, 8.0 Hz), -162.21 (ddd, *J* = 21.9, 17.5, 7.2 Hz). ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 6.2 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.69 (s, 1H), 7.65 (s, 1H), 7.56 (s, 1H), 4.13 (s, 6H), 4.10 (s, 3H), 4.07 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 150.05, 149.24, 149.22, 149.09, 148.52, 125.53, 124.39, 124.11, 121.31, 120.34, 115.69, 108.64, 108.42, 104.96, 104.84, 104.39, 103.88, 103.70, 56.02, 56.00, 55.87, 55.82.

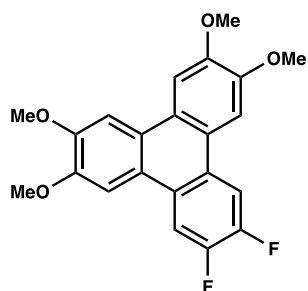


SI39. ^{13}C NMR for 1,2,3-trifluoro-6,7,10,11-tetramethoxytriphenylene

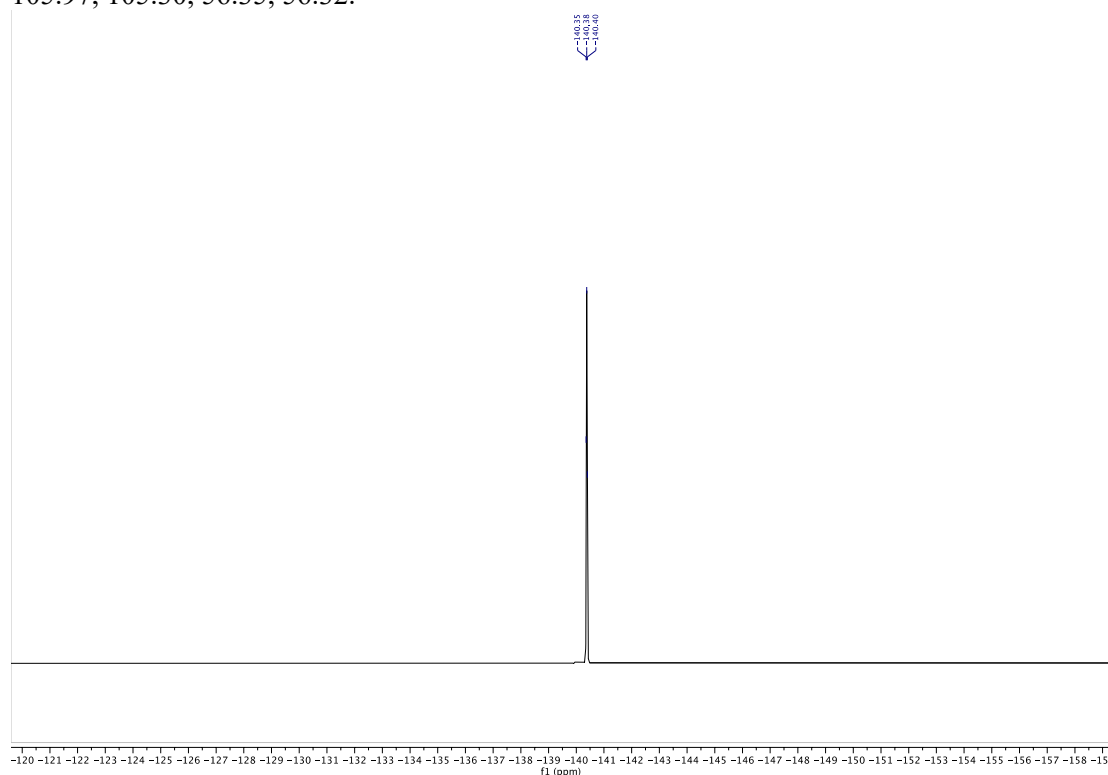


SI40. A DSC scan for 1,2,3-trifluoro-6,7,10,11-tetramethoxytriphenylene

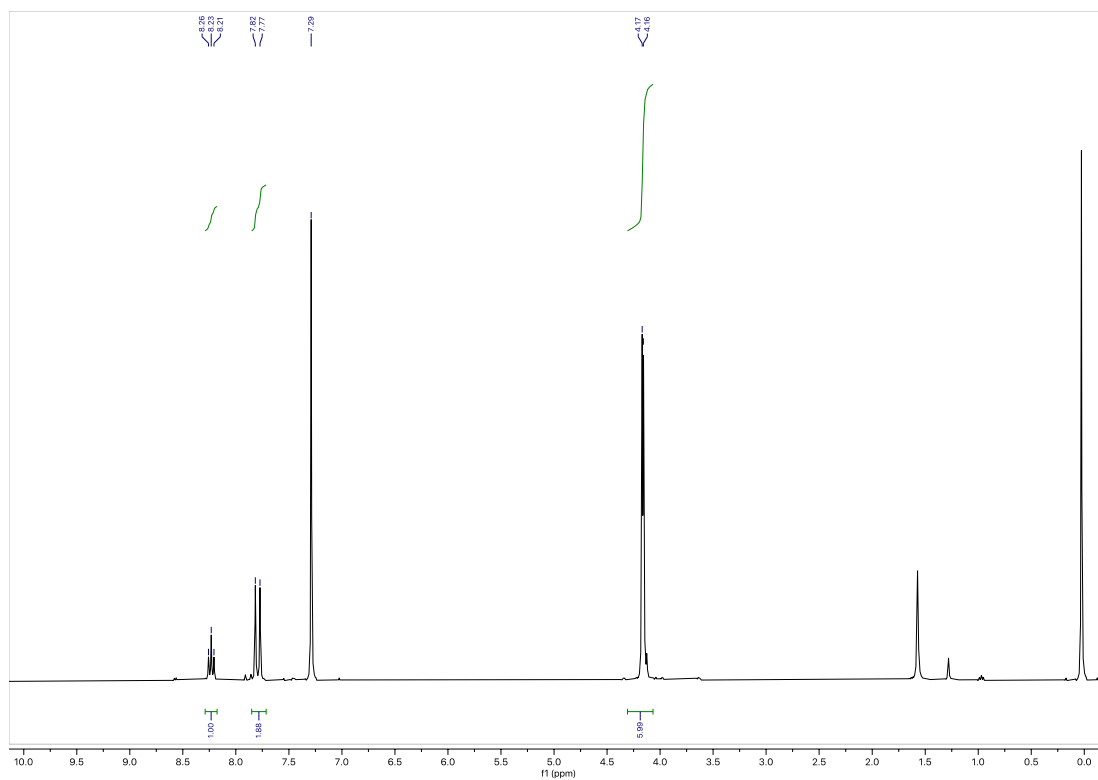
2,3-difluoro-6,7,10,11-tetramethoxytriphenylene ²



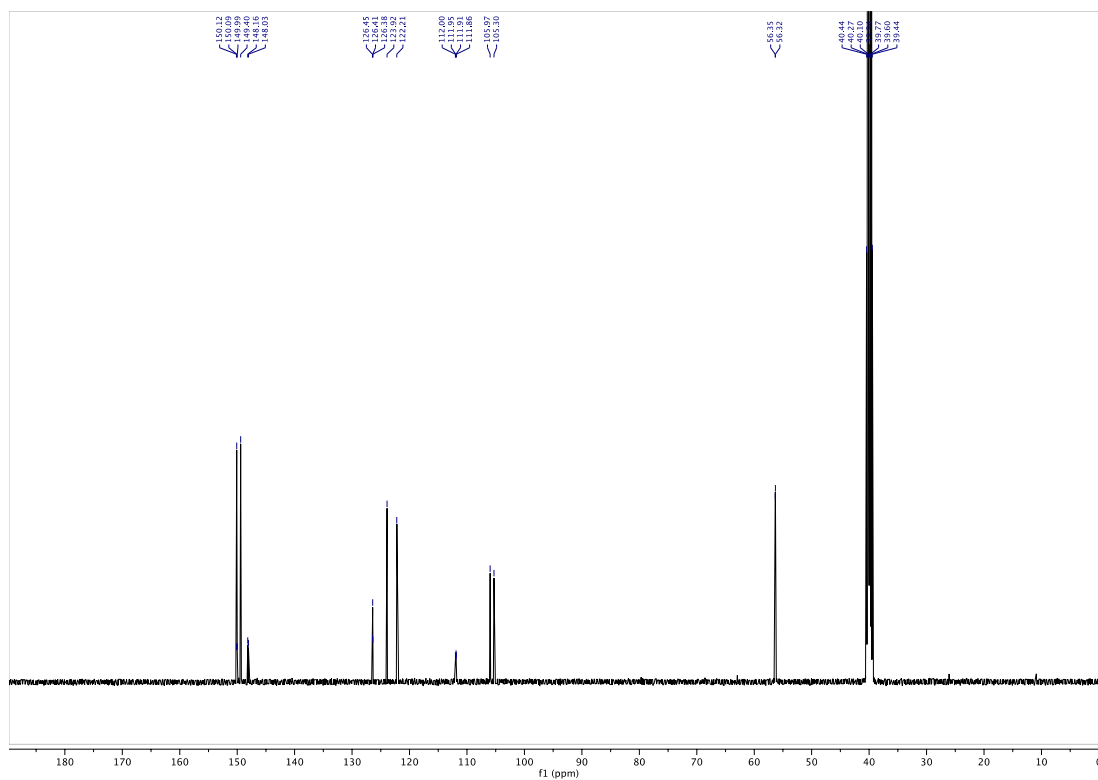
In a 100 ml round bottom flask was placed 3,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.19 g, 0.5 mmol) and DCM (25.0 ml) was added under a nitrogen atmosphere. FeCl₃ (0.24 g, 1.5 mmol) dissolved in nitromethane (4.0 ml) was added dropwise to the mixture while stirring and left for an hour at room temperature. A polar product spot was observed, however the starting material remained. More FeCl₃ (0.08 g, 0.5 mmol) was added to the reaction mixture and after four hours the reaction was found to be complete. A mixture of methanol and water (4 ml + 4 ml) was added to quench the reaction. The mixture was extracted with DCM and the organic portion was dried over anhydrous Na₂SO₄ and vacuum filtered. Some silica gel was added to the filtrate, and the solvent was removed under reduced pressure. This material was placed at the top of a column made up of 10% EtOAc in hexanes and eluted with a gradient of up to 25% EtOAc in hexanes. Fractions containing the product were combined and concentrated to get a cream-colored solid which was recrystallized with 1-propanol to give a white solid product. Yield- 0.16 g (85%)
¹⁹F NMR (470 MHz, DMSO) δ -140.38 (t, J = 11.0 Hz). ¹H NMR (400 MHz, CDCl₃) δ 8.23 (t, J = 10.3 Hz, 1H), 7.79 (d, J = 17.6 Hz, 2H), 4.16 (d, J = 4.7 Hz, 6H). ¹³C NMR (126 MHz, DMSO) δ 150.12, 150.09, 149.99, 149.40, 148.16, 148.03, 126.45, 126.41, 126.38, 123.92, 122.21, 112.00, 111.95, 111.91, 111.86, 105.97, 105.30, 56.35, 56.32.



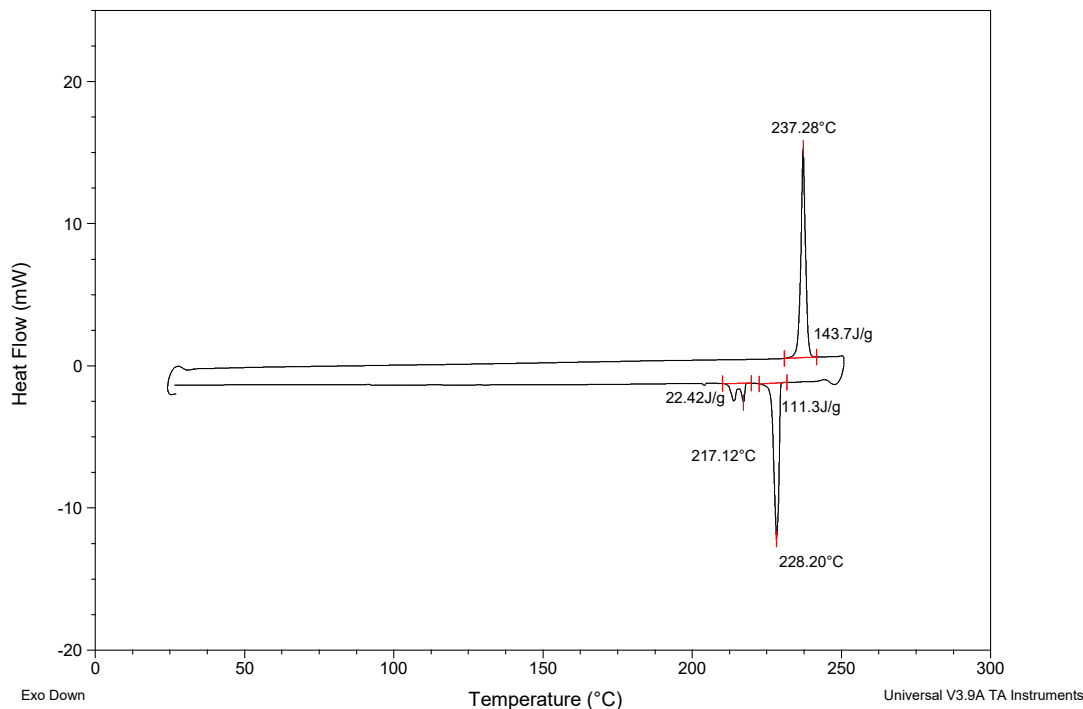
SI41. ¹⁹F NMR for 2,3-difluoro-6,7,10,11-tetramethoxytriphenylene



SI42. ^1H NMR for 2,3-difluoro-6,7,10,11-tetramethoxytriphenylene

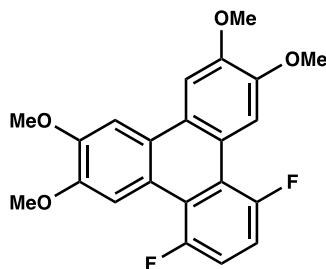


SI43. ^{13}C NMR for 2,3-difluoro-6,7,10,11-tetramethoxytriphenylene



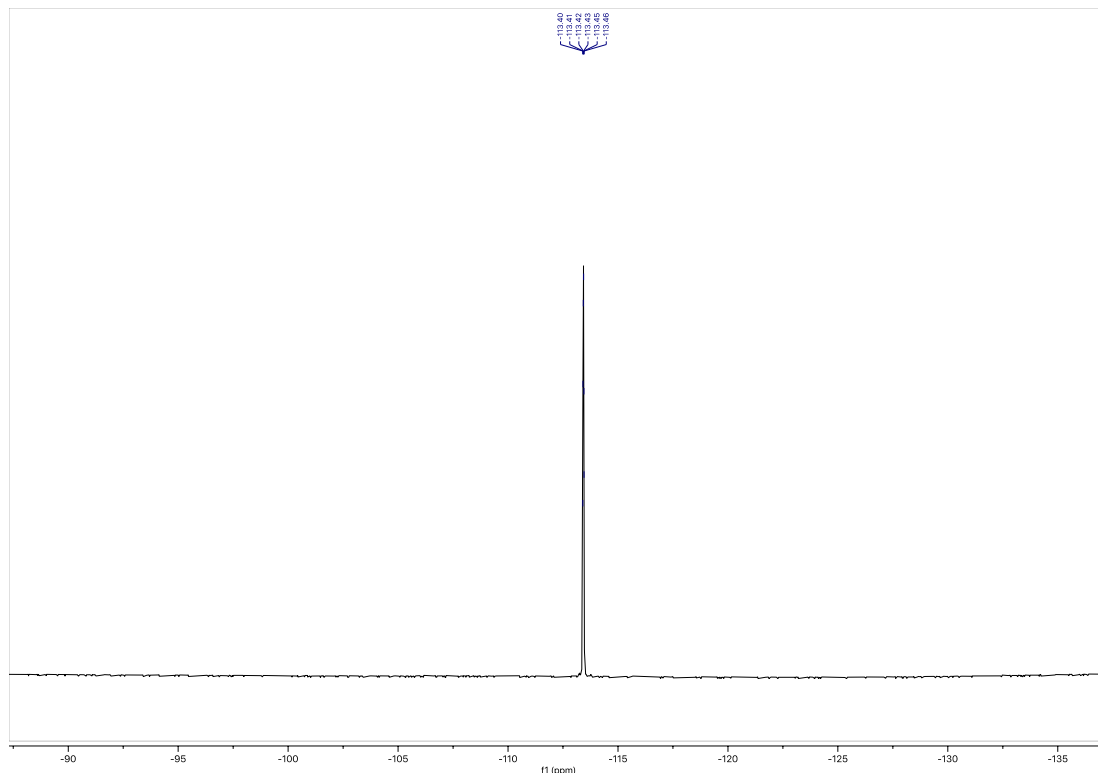
SI44. A DSC scan for 2,3-difluoro-6,7,10,11-tetramethoxytriphenylene

1,4-difluoro-6,7,10,11-tetramethoxytriphenylene

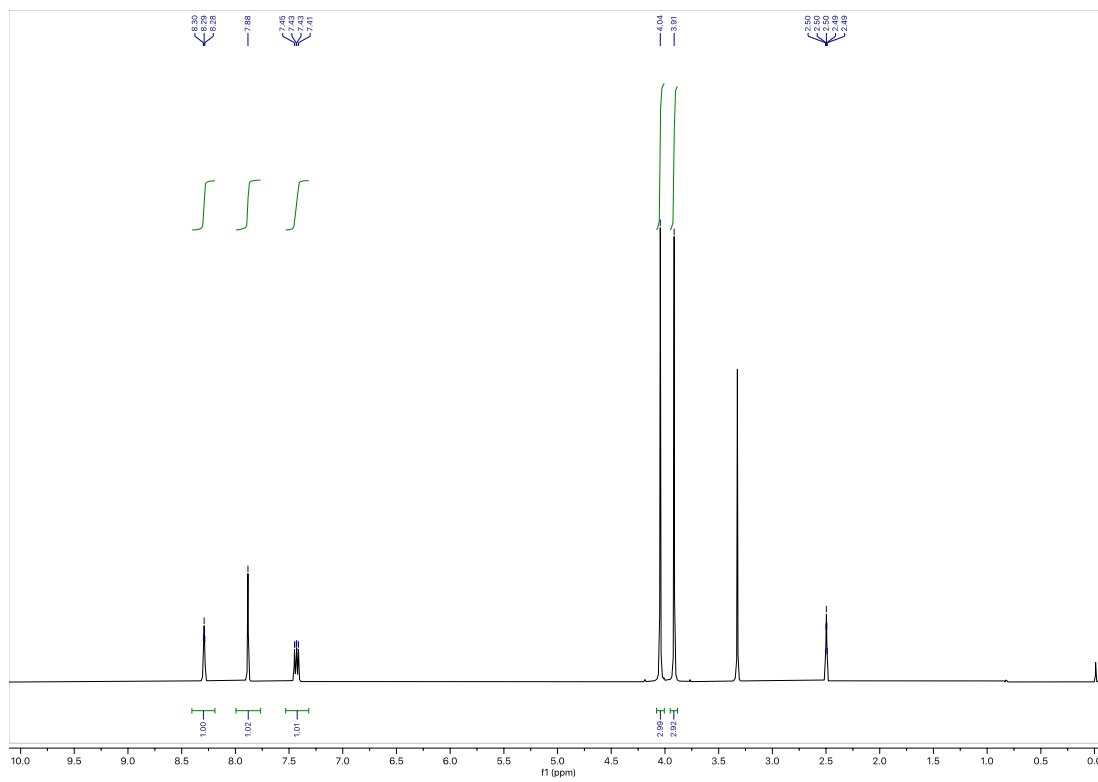


In a 100 ml round bottom flask was placed 2,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.19 g, 0.5 mmol) and DCM (25.0 ml) was added under a nitrogen atmosphere. FeCl₃ (0.32 g, 2.0 mmol) dissolved in nitromethane (4.0 ml) was added dropwise to the mixture while stirring and left for an hour at room temperature. A polar product spot was observed, however some starting material remained. The reaction was left stirring at room temperature for overnight and the next day on monitoring by TLC, almost all starting material was found to be transformed. A mixture of methanol and water (4 ml + 4 ml) was added to quench the reaction. The mixture was extracted with DCM and the organic portion was dried over anhydrous Na₂SO₄ and vacuum filtered. Some silica gel was added to the filtrate and the solvent was removed under reduced pressure. This material was placed at the top of a column made up of 10% EtOAc in hexanes and eluted with a gradient of up to 25% EtOAc in hexanes. Fractions containing the product were combined and concentrated to obtain a crude solid which was recrystallized from 1-propanol to get a white solid product. Yield- 0.11 g (60 %)

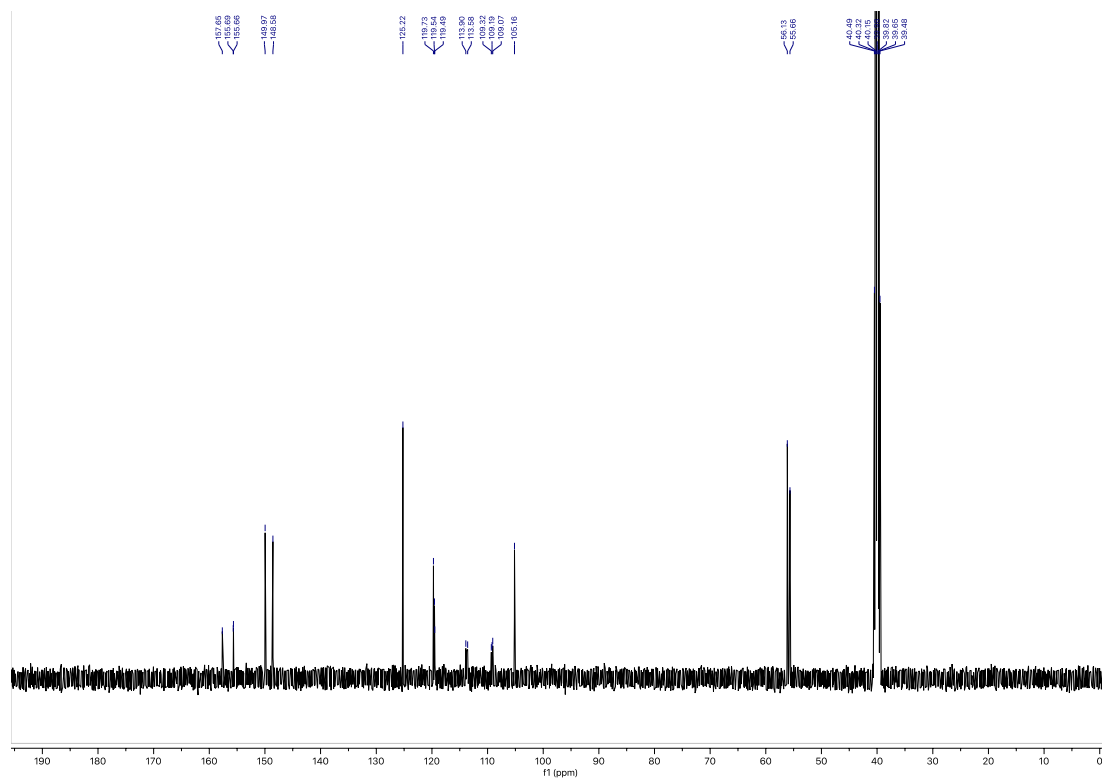
¹⁹F NMR (470 MHz, DMSO) δ -113.43 (dt, *J* = 10.4, 5.3 Hz). ¹H NMR (500 MHz, DMSO) δ 8.29 (t, *J* = 3.3 Hz, 1H), 7.88 (s, 1H), 7.43 (dd, *J* = 10.4, 7.8 Hz, 1H), 4.04 (s, 3H), 3.91 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 157.65, 155.69, 155.66, 149.97, 148.58, 125.22, 119.73, 119.54, 119.49, 113.90, 113.58, 109.32, 109.19, 109.07, 105.16, 56.13, 55.66.



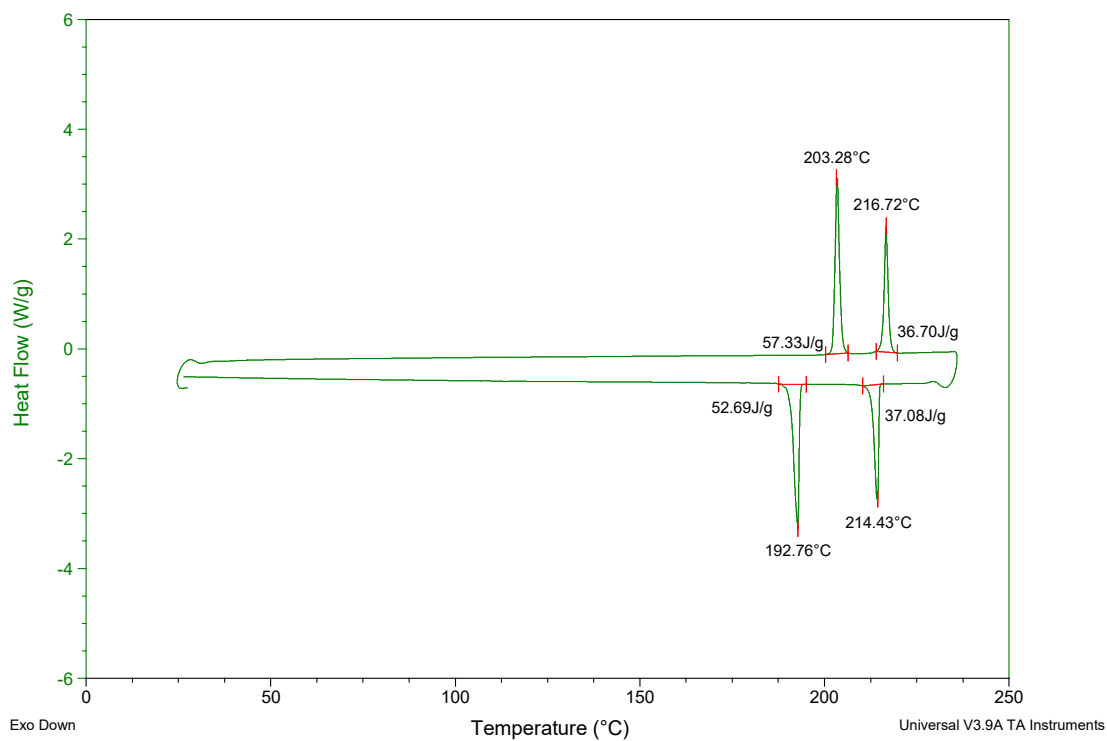
SI45. ^{19}F NMR for 1,4-difluoro-6,7,10,11-tetramethoxytriphenylene



SI46. ^1H NMR for 1,4-difluoro-6,7,10,11-tetramethoxytriphenylene

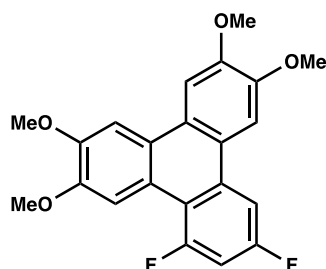


SI47. ^{13}C NMR for 1,4-difluoro-6,7,10,11-tetramethoxytriphenylene



SI48. A DSC scan for 1,4-difluoro-6,7,10,11-tetramethoxytriphenylene

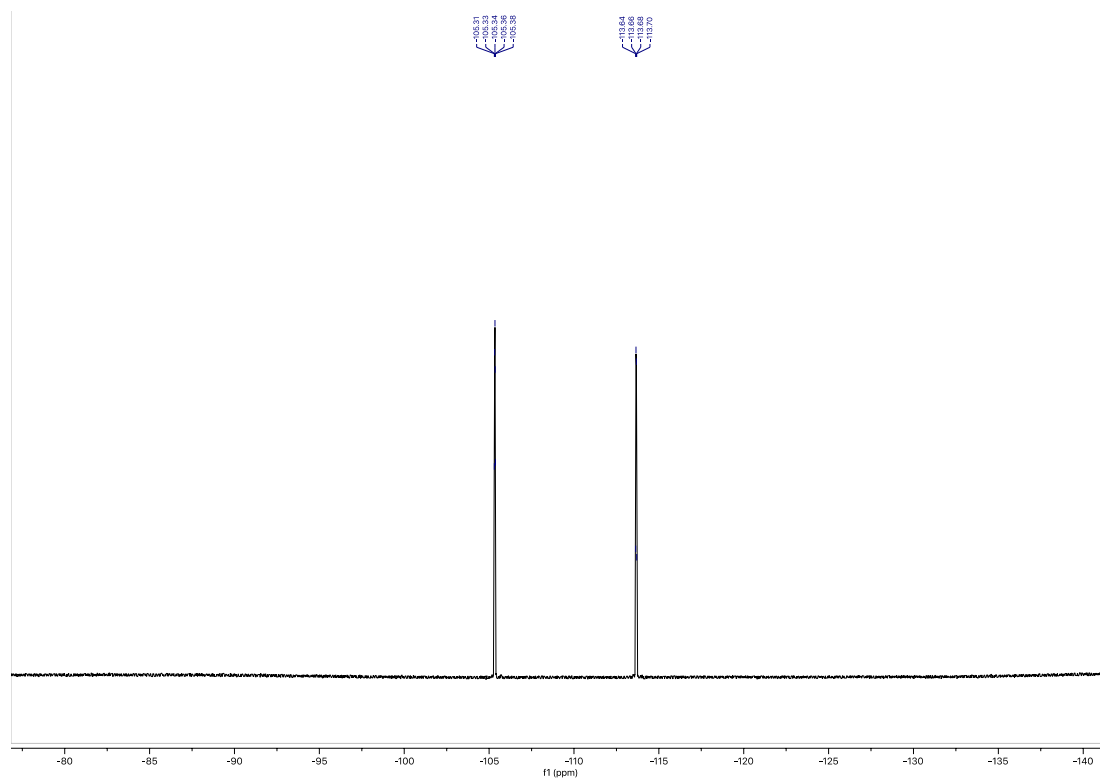
1,3-difluoro-6,7,10,11-tetramethoxytriphenylene



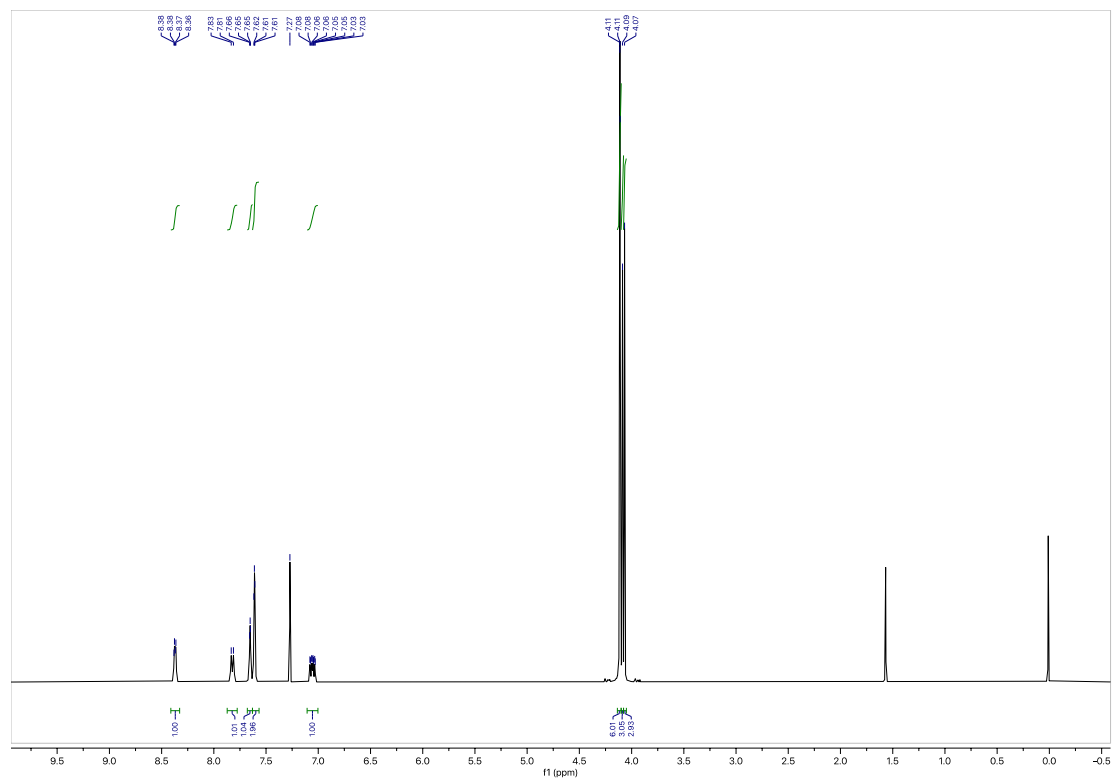
In a 100 ml round bottom flask was placed 3,5-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.19 g, 0.5 mmol) and DCM (25.0 ml) was added under a nitrogen atmosphere. FeCl₃ (0.17 g, 1.0 mmol) dissolved in nitromethane (4.0 ml) was added dropwise to the mixture while stirring and left for an hour at room temperature. A polar product spot was observed in TLC, however some starting material remained. More FeCl₃ (0.10 g, 0.6 mmol) was added to the reaction mixture and after four hours the reaction was found to be complete. A mixture of methanol and water (4 ml+4 ml) was added to quench the reaction. The mixture was extracted with DCM and the organic portion was dried over anhydrous Na₂SO₄ and vacuum filtered. To the filtrate, some silica gel was added, and the solvent was removed under reduced pressure. This material was placed at the top of a column made up of 10% EtOAc in hexanes and eluted with a gradient of up to 25% EtOAc in hexanes. Fractions containing the product were combined and concentrated to get a cream-colored solid which was recrystallized with 1-propanol. Yield- 0.13 g (68%)

¹⁹F NMR (470 MHz, CDCl₃) δ -105.34 (dt, *J* = 15.1, 8.1 Hz), -113.67 (q, *J* = 9.5 Hz).

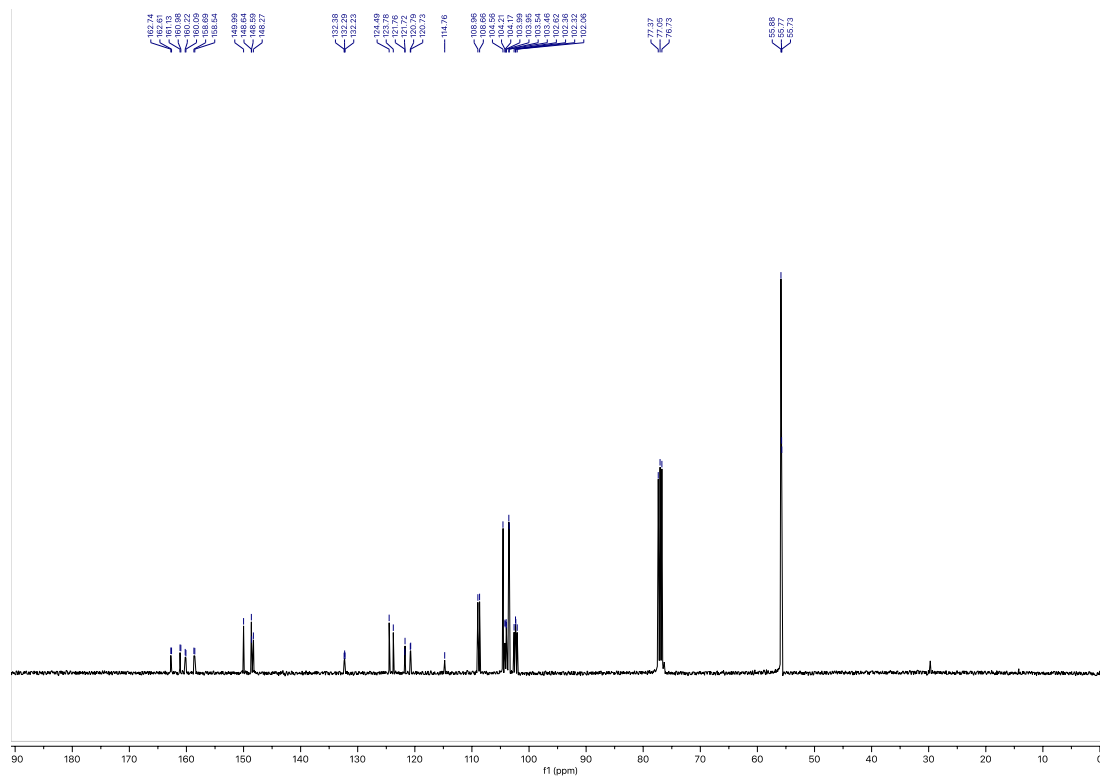
¹H NMR (500 MHz, CDCl₃) δ 8.37 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.82 (d, *J* = 10.7 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.62 – 7.60 (m, 2H), 7.05 (ddd, *J* = 14.6, 8.2, 2.5 Hz, 1H), 4.11 (d, *J* = 1.3 Hz, 6H), 4.09 (s, 3H), 4.07 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.74, 162.61, 161.13, 160.98, 160.22, 160.09, 158.69, 158.54, 149.99, 148.64, 148.59, 148.27, 132.38, 132.29, 132.23, 124.49, 123.78, 121.76, 121.72, 120.79, 120.73, 114.76, 108.96, 108.66, 104.56, 104.21, 104.17, 103.99, 103.95, 103.54, 103.46, 102.62, 102.36, 102.32, 102.06, 55.88, 55.77, 55.73.



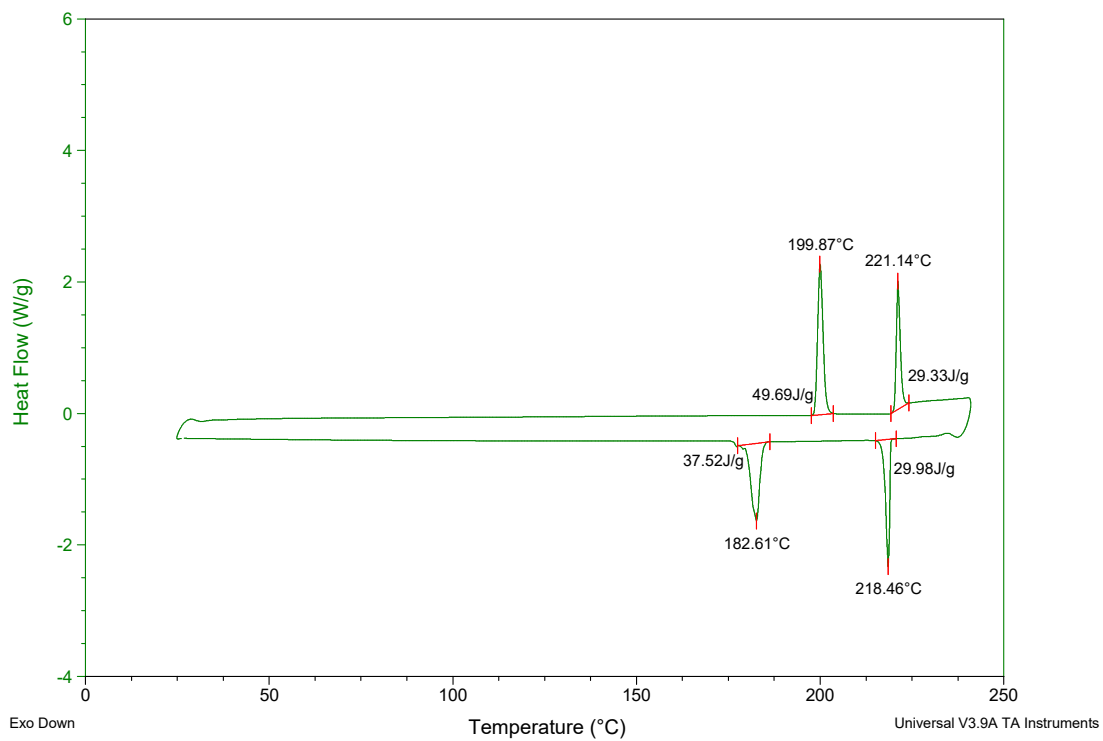
SI49. ^{19}F NMR for 1,3-difluoro-6,7,10,11-tetramethoxytriphenylene



SI50. ^1H NMR for 1,3-difluoro-6,7,10,11-tetramethoxytriphenylene

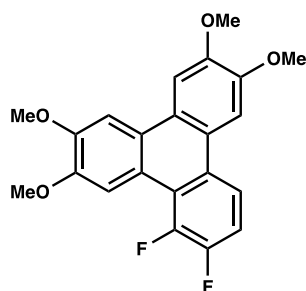


S151. ^{13}C NMR for 1,3-difluoro-6,7,10,11-tetramethoxytriphenylene



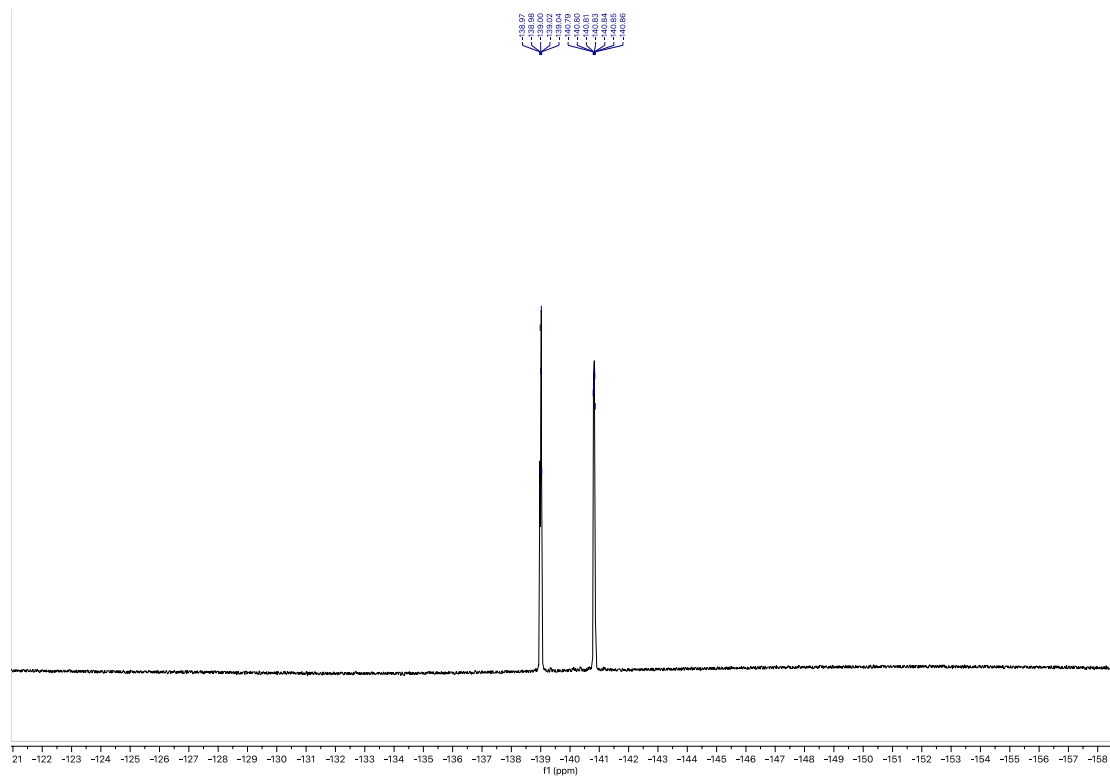
S152. A DSC scan for 1,3-difluoro-6,7,10,11-tetramethoxytriphenylene

1,2-difluoro-6,7,10,11-tetramethoxytriphenylene

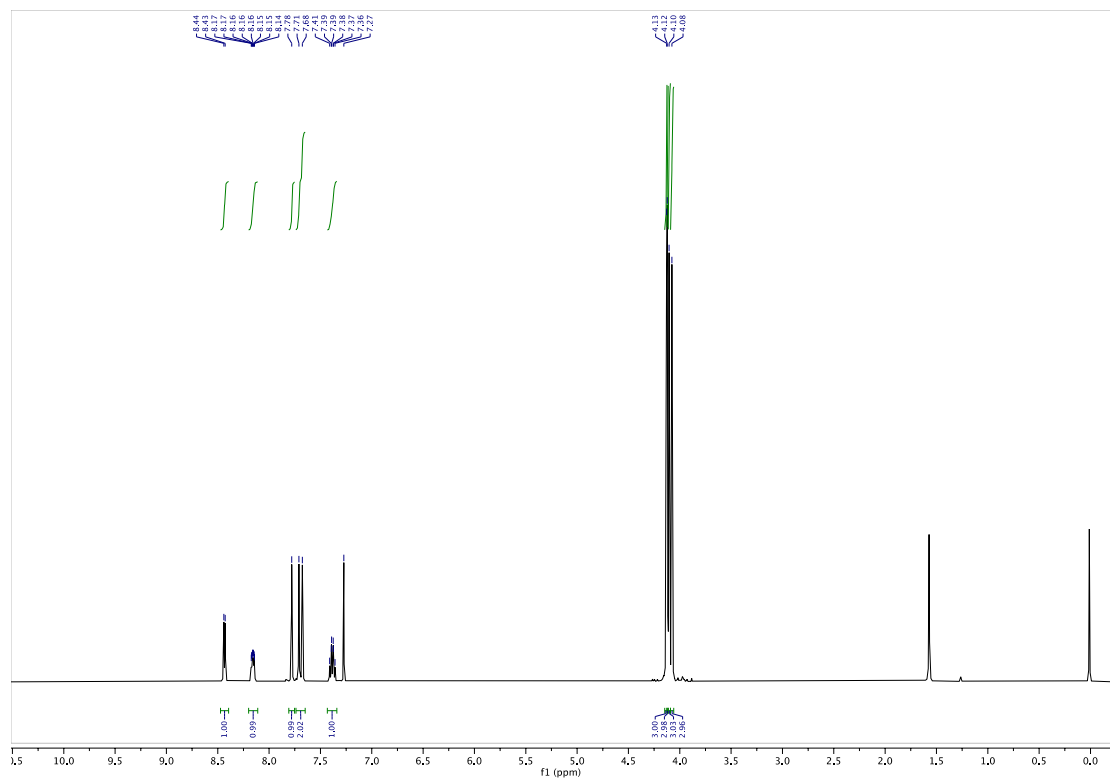


In a (100 cm x 10 cm) quartz tube was placed 2,3,4-trifluoro-4',5',3'',4''-tetramethoxy-1,1': 2',1''-terphenyl (0.40 g, 1.0 mmol) and acetonitrile (50.0 ml). The mixture was irradiated with 16x254nm lamps in a Rayonet. The solution turned from colorless to deep yellow. The photoreaction was monitored by TLC which indicated a new polar spot and a trace of starting material spot, so the reaction was terminated after a total of thirty hours. The reaction mixture was allowed to cool and transferred to a recovery flask then concentrated under reduced pressure to get a brownish residue. This residue was redissolved in ethyl acetate and adsorbed on some silica gel. This material was placed at the top of a column and eluted with a gradient of 20% EtOAc in hexanes up to 40% EtOAc in hexanes. Fractions containing the product were combined and concentrated to get a light-yellow product which was recrystallized from 1-propanol. Yield- 0.15 g (40 %)

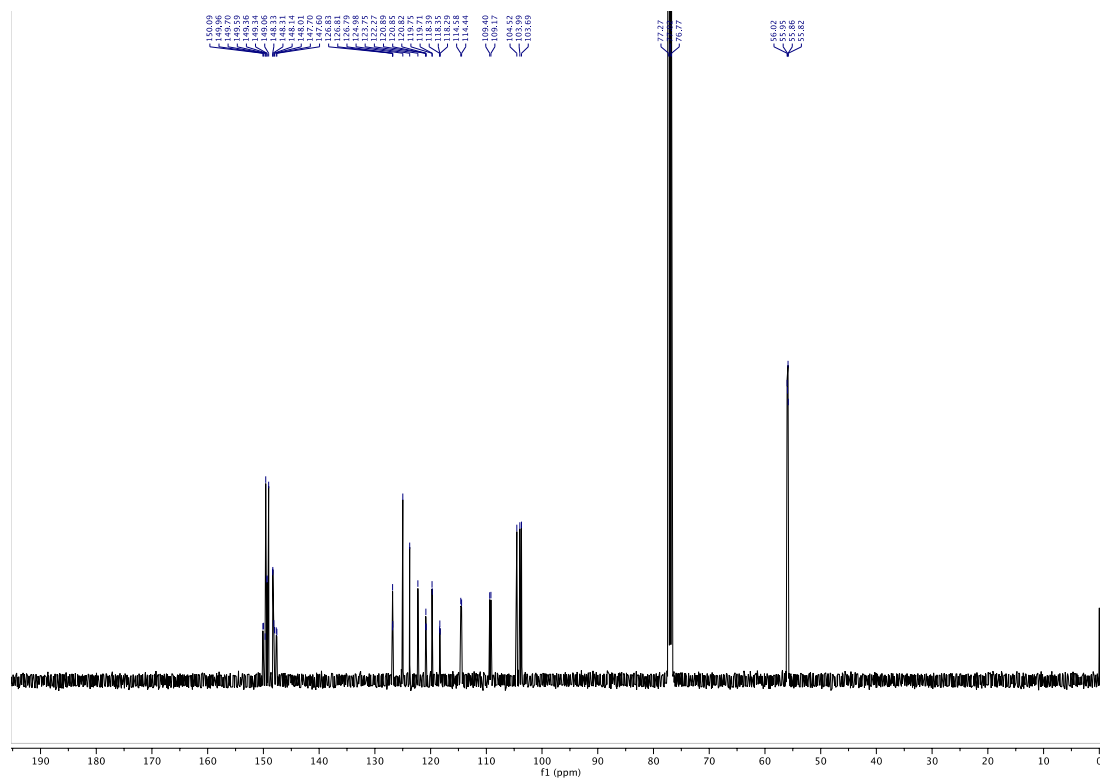
^{19}F NMR (470 MHz, CDCl_3) δ -139.00 (dt, $J = 16.1, 7.4$ Hz), -140.76 – -140.88 (ddd, $J = 17.6, 9.1, 5.0$ Hz). ^1H NMR (500 MHz, CDCl_3) δ 8.43 (d, $J = 6.7$ Hz, 1H), 8.16 (ddd, $J = 9.4, 5.1, 1.8$ Hz, 1H), 7.78 (s, 1H), 7.69 (d, $J = 16.9$ Hz, 2H), 7.38 (td, $J = 9.1, 7.9$ Hz, 1H), 4.13 (s, 3H), 4.12 (s, 3H), 4.10 (s, 3H), 4.08 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.09, 149.96, 149.70, 149.59, 149.36, 149.34, 149.06, 148.33, 148.31, 148.14, 148.01, 147.70, 147.60, 126.83, 126.81, 126.79, 124.98, 123.75, 122.27, 120.89, 120.85, 120.82, 119.75, 119.71, 118.39, 118.35, 118.29, 114.58, 114.44, 109.40, 109.17, 104.52, 103.99, 103.69, 56.02, 55.95, 55.86, 55.82.



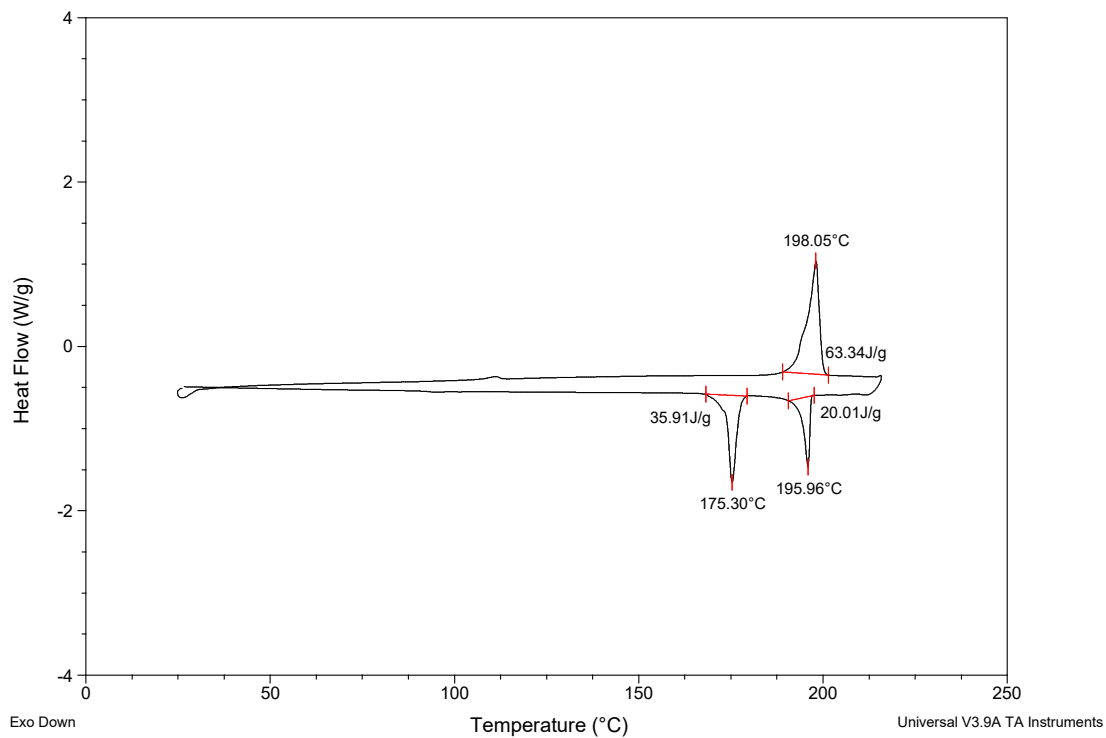
SI53. ^{19}F NMR for 1,2-difluoro-6,7,10,11-tetramethoxytriphenylene



SI54. ^1H NMR for 1,2-difluoro-6,7,10,11-tetramethoxytriphenylene

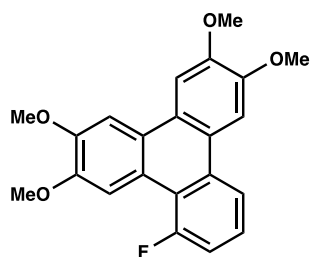


SI55. ^{13}C NMR for 1,2-difluoro-6,7,10,11-tetramethoxytriphenylene



SI56. A DSC scan for 1,2-difluoro-6,7,10,11-tetramethoxytriphenylene

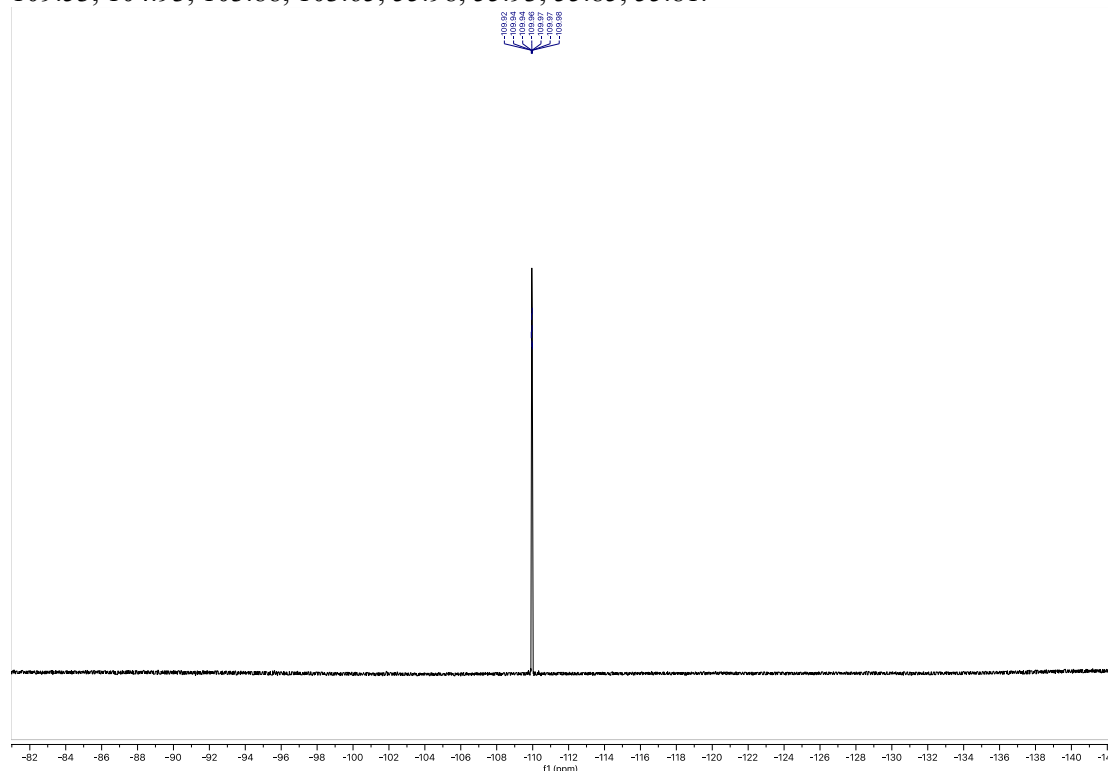
1-fluoro-6,7,10,11-tetramethoxytriphenylene



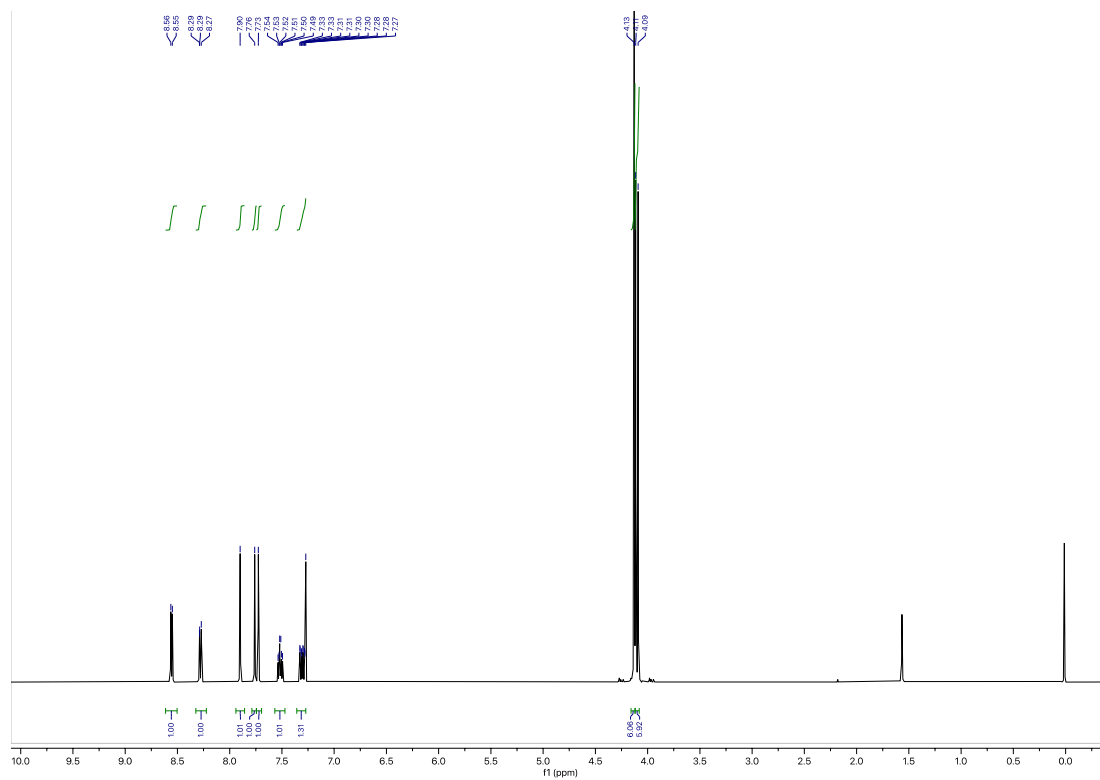
In a (100 cm x 10 cm) quartz tube was placed 2,3-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.30 g, 0.8 mmol) and acetonitrile (50.0 ml). The mixture was irradiated with 16x254nm lamps in a Rayonet. The solution turned from colorless to yellow. The photoreaction was monitored by TLC which indicated the complete transformation of the starting material and so the reaction was terminated after a total of twenty hours. The reaction mixture was allowed to cool to room temperature. The mixture was transferred to a recovery flask and concentrated under reduced pressure to give a brownish residue. This residue was redissolved in ethyl acetate and adsorbed on some silica gel. The yellow silica gel was placed at the top of a column and eluted with a gradient of 20% EtOAc in hexanes up to 40% EtOAc in hexanes. Fractions containing the product were combined and concentrated to obtain a pale-yellow solid product which was recrystallized from 1-propanol to obtain a white product. Yield: 0.15 g (52%)

^{19}F NMR (470 MHz, CDCl_3) δ -108.68 – -112.73 (m).

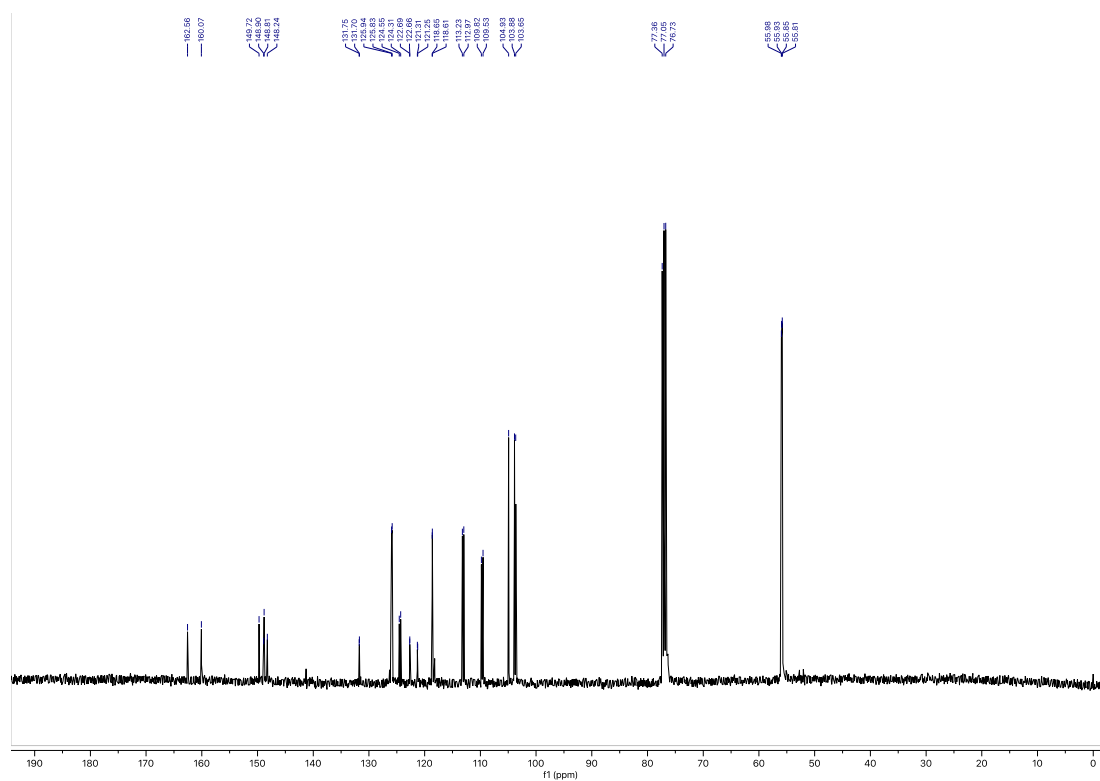
^1H NMR (500 MHz, CDCl_3) δ 8.56 (d, J = 7.4 Hz, 1H), 8.34 – 8.24 (m, 1H), 7.90 (s, 1H), 7.76 (s, 1H), 7.73 (s, 1H), 7.52 (td, J = 8.0, 5.2 Hz, 1H), 7.30 (ddd, J = 14.8, 7.8, 1.1 Hz, 1H), 4.13 (s, 5H), 4.10 (d, J = 11.6 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.56, 160.07, 149.72, 148.90, 148.81, 148.24, 131.75, 131.70, 125.94, 125.83, 124.55, 124.31, 122.69, 122.66, 121.31, 121.25, 118.65, 118.61, 113.23, 112.97, 109.82, 109.53, 104.93, 103.88, 103.65, 55.98, 55.93, 55.85, 55.81.



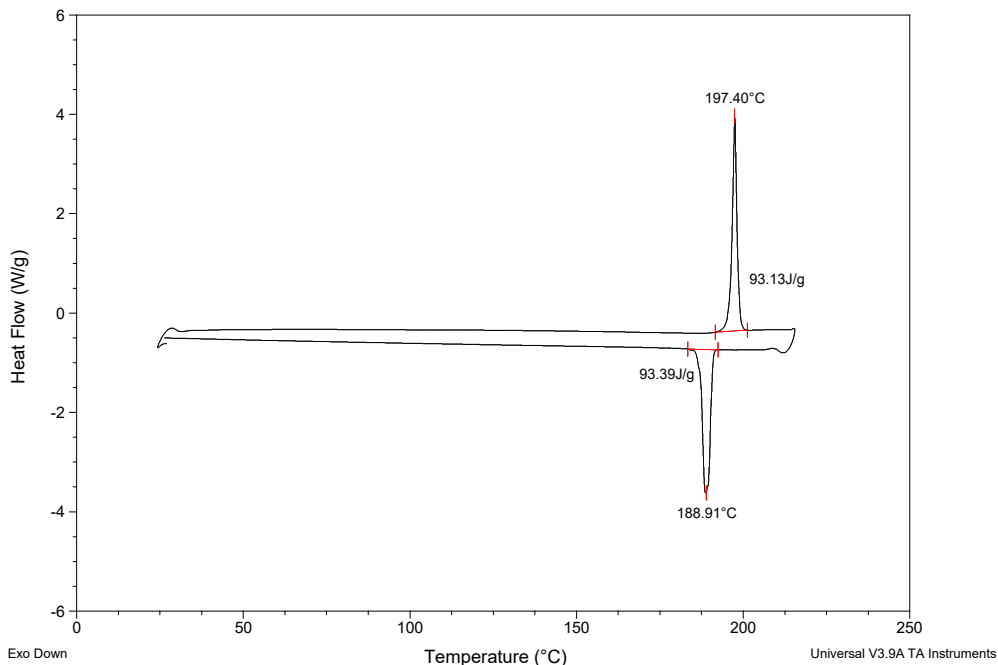
S157. ^{19}F NMR for 1-fluoro-6,7,10,11-tetramethoxytriphenylene



S158. ^1H NMR for 1-fluoro-6,7,10,11-tetramethoxytriphenylene

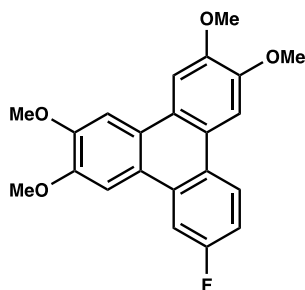


S159. ^{13}C NMR for 1-fluoro-6,7,10,11-tetramethoxytriphenylene



SI60. A DSC scan for 1-fluoro-6,7,10,11-tetramethoxytriphenylene

2-fluoro-6,7,10,11-tetramethoxytriphenylene²

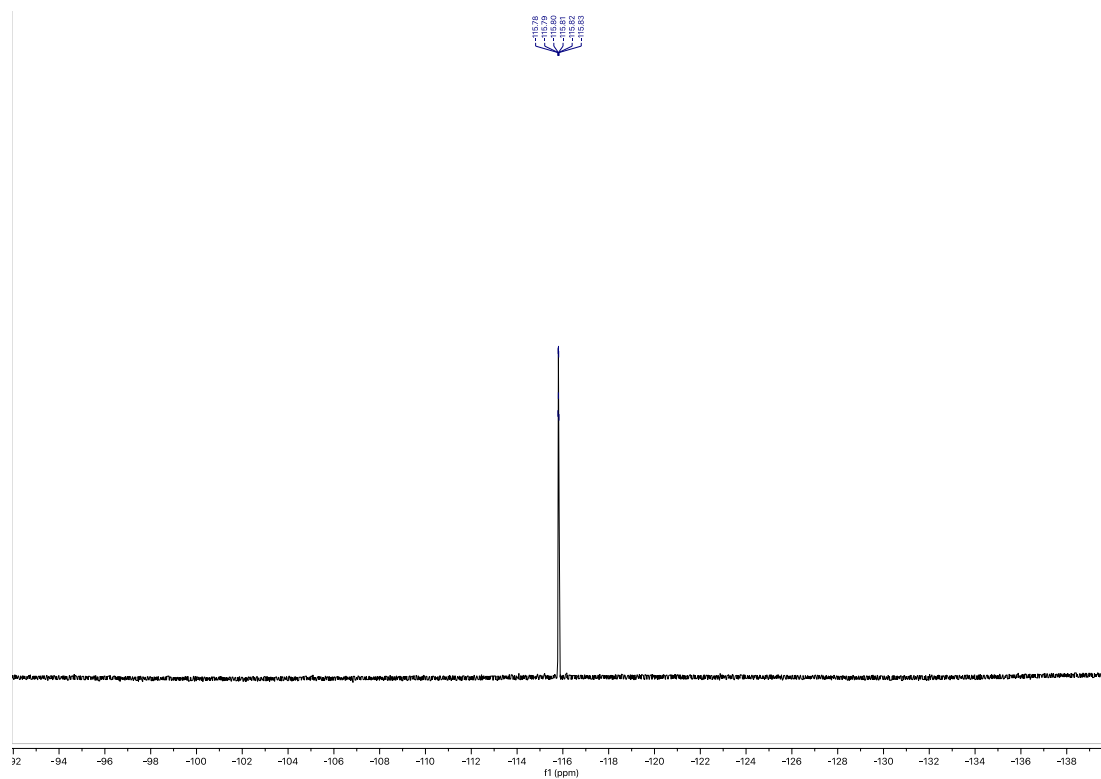


In a (100 cm x 10 cm) quartz tube was placed 2,4-difluoro-4',5',3'',4''-tetramethoxy-1,1':2',1''-terphenyl (0.42 g, 1.1 mmol) and acetonitrile (50.0 ml). The mixture was irradiated with 16x254nm lamps in a Rayonet. The solution turned from colorless to yellow. The photoreaction was monitored by TLC which indicated only a minor product spot and a significant remaining starting material spot after twenty-four hours of irradiation. After a couple more hours, the irradiation was terminated, and the reaction mixture was allowed to cool to room temperature and transferred into a recovery flask. The solvent was removed under reduced pressure, redissolved with ethyl acetate then adsorbed on some silica gel. This material was placed at the top of a column made up of hexanes and eluted with a gradient of up to 45 % EtOAc in hexanes. Fractions containing the pure product were combined and concentrated to get a pale-yellow solid product which was recrystallized with 1-propanol. Yield: 0.11 g (28 %). Some starting material was also recovered.

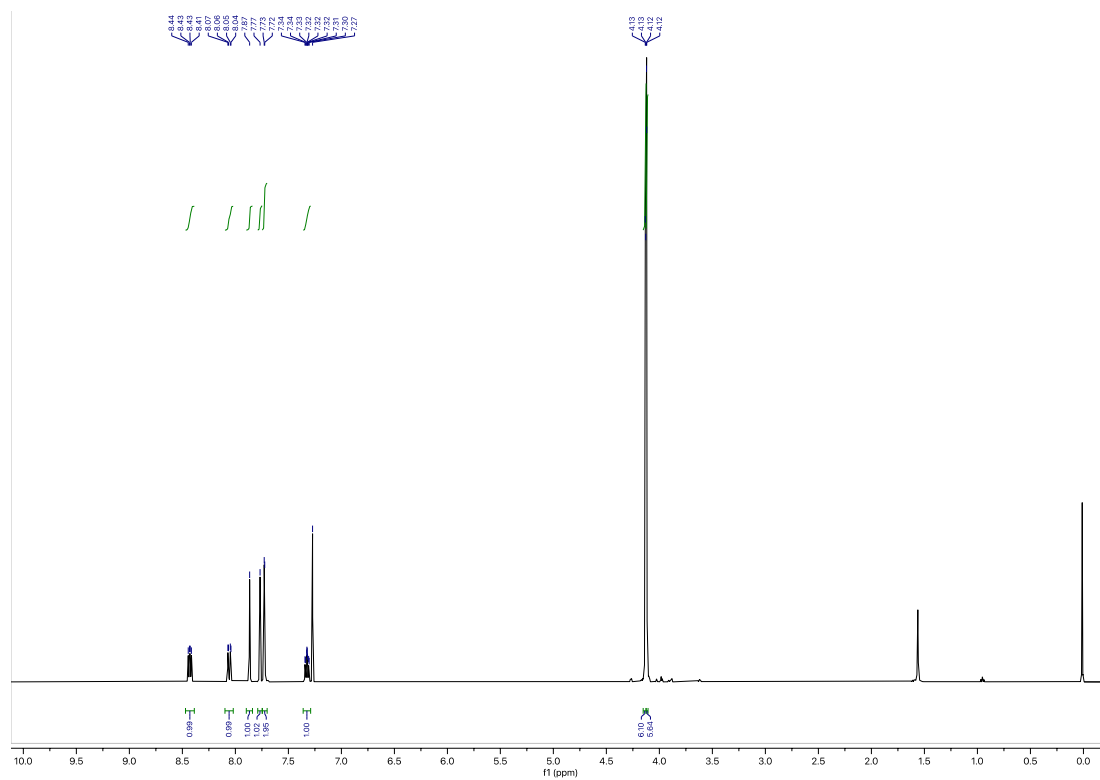
¹⁹F NMR (470 MHz, CDCl₃) δ -115.81 (dt, *J* = 11.3, 6.6 Hz).

¹H NMR (500 MHz, CDCl₃) δ 8.43 (dd, *J* = 9.1, 5.7 Hz, 1H), 8.06 (dd, *J* = 11.3, 2.6 Hz, 1H), 7.87 (s, 1H), 7.77 (s, 1H), 7.73 (d, *J* = 2.3 Hz, 2H), 7.32 (ddd, *J* = 9.0, 7.7, 2.6 Hz, 1H), 4.13 (d, *J* = 2.0 Hz, 6H), 4.12 – 4.12 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.57, 160.14, 149.58, 148.99, 148.77, 148.61, 142.48,

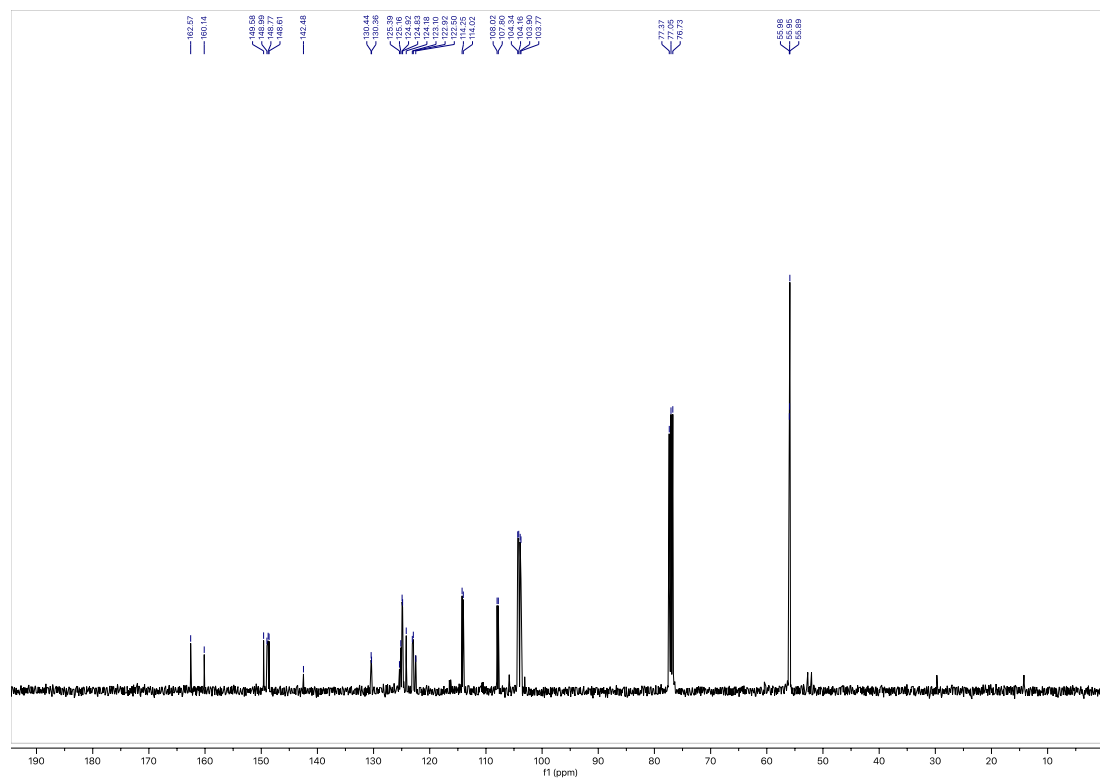
130.44, 130.36, 125.39, 125.16, 124.92, 124.83, 124.18, 123.10, 122.92, 122.50, 114.25, 114.02, 108.02, 107.80, 104.34, 104.16, 103.90, 103.77, 55.98, 55.95, 55.89.



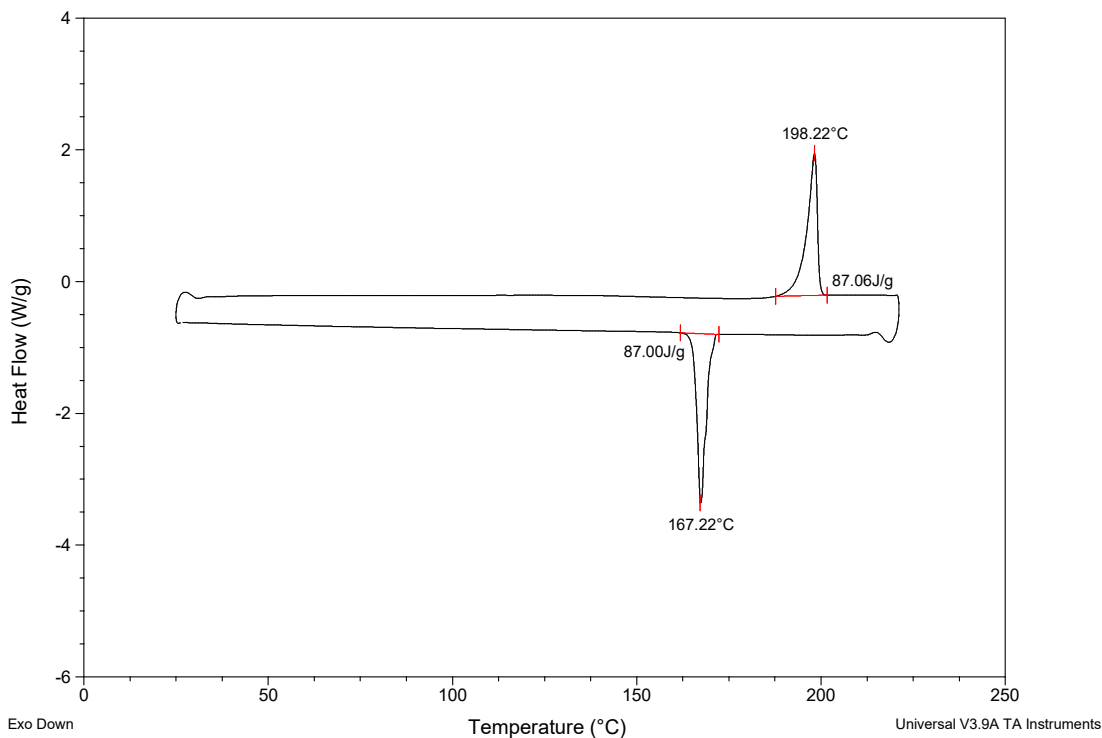
SI161. ^{19}F NMR for 2-fluoro-6,7,10,11-tetramethoxytriphenylene



SI62. ^1H NMR for 2-fluoro-6,7,10,11-tetramethoxytriphenylene

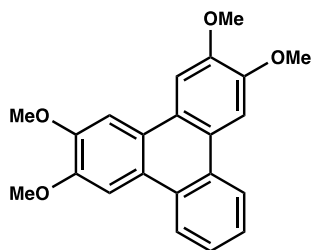


SI63. ^{13}C NMR for 2-fluoro-6,7,10,11-tetramethoxytriphenylene



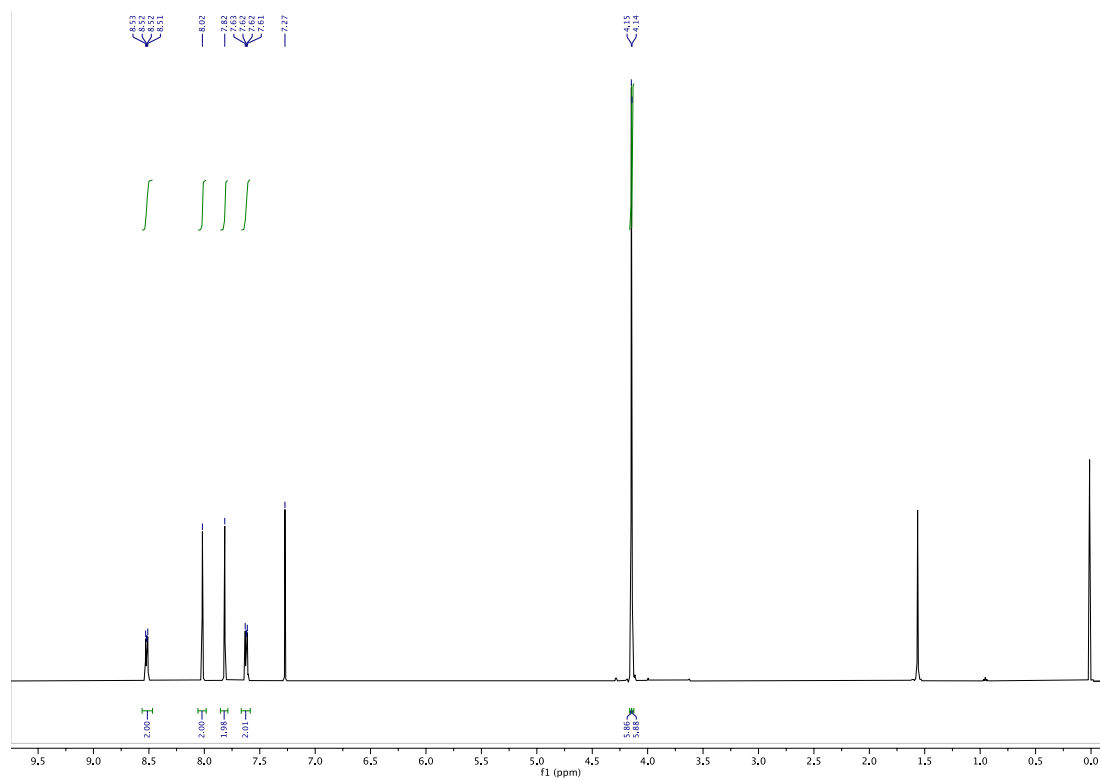
SI64. A DSC scan for 1-fluoro-6,7,10,11-tetramethoxytriphenylene

6,7,10,11-tetramethoxytriphenylene³

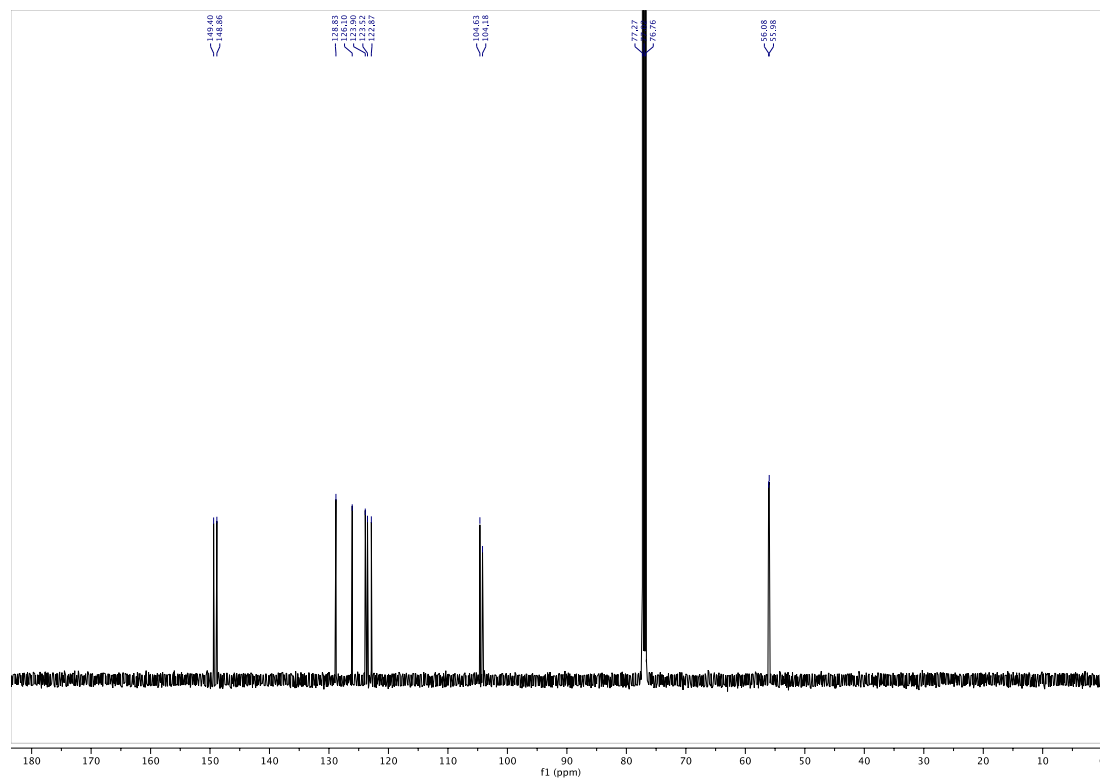


In a (100 cm x 10 cm) quartz tube was placed 2-fluoro-4',5',3'',4''-tetramethoxy-1,1': 2',1''-terphenyl (0.44 g, 1.2 mmol) and acetonitrile (50.0 ml). The mixture was irradiated with 16x254nm lamps in the Rayonet. The solution turned from colorless to yellow. The photoreaction was monitored by TLC which indicated the complete transformation of the starting material after twenty-four hours. The reaction was terminated, and the reaction mixture was allowed to cool. The mixture was transferred to a recovery flask and concentrated under reduced pressure to get a yellowish residue. The residue was redissolved in ethyl acetate and adsorbed on some silica gel. The yellow silica gel was placed at the top of a column and eluted with a gradient of 20% EtOAc up to 40% EtOAc in hexanes. Fractions containing the product were combined and concentrated to obtain a pale yellowish solid product which was recrystallized from 1-propanol to get white crystals. Yield: 0.21 g (50 %)

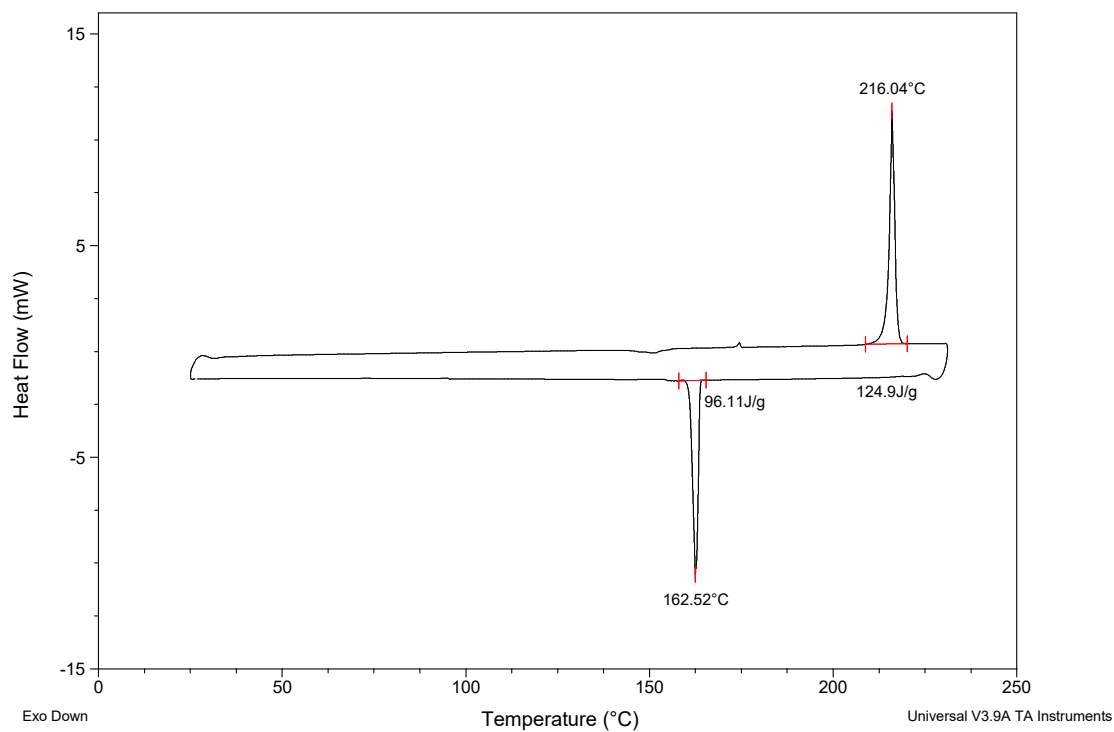
¹H NMR (500 MHz, CDCl₃) δ 8.52 (dd, *J* = 6.3, 3.4 Hz, 2H), 8.02 (s, 2H), 7.82 (s, 2H), 7.62 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.15 (s, 6H), 4.14 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 149.40, 148.86, 128.83, 126.10, 123.90, 123.52, 122.87, 104.63, 104.18, 56.08, 55.98.



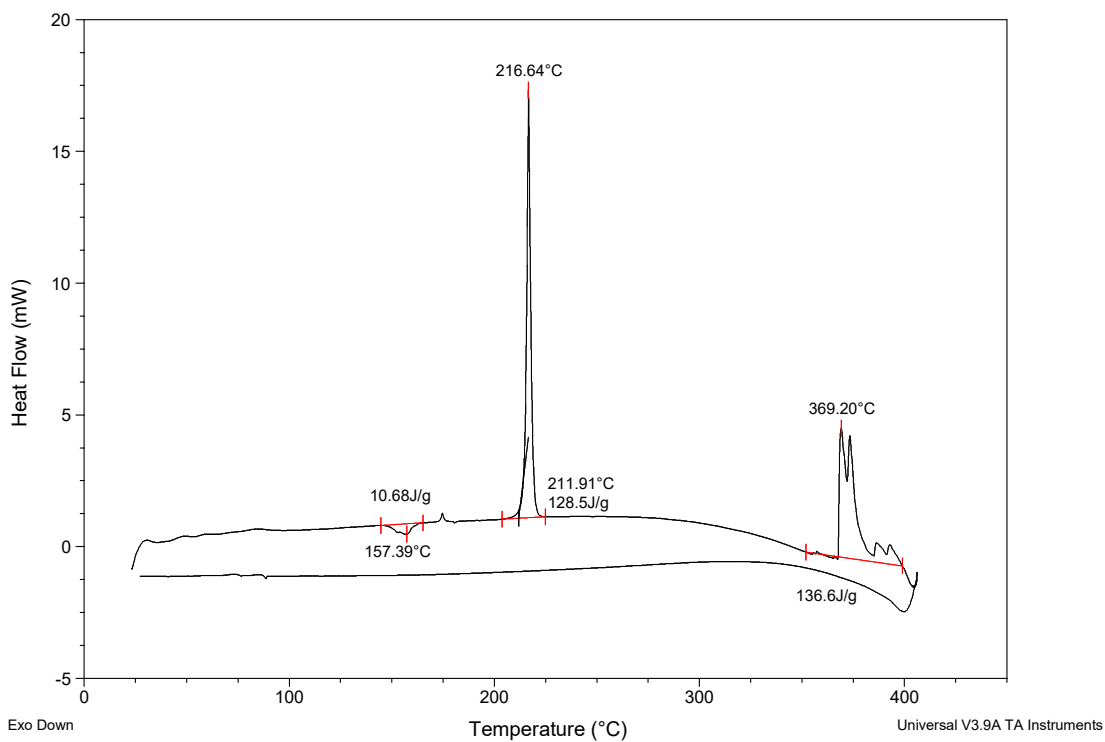
SI65. ^1H NMR for 6,7,10,11-tetramethoxytriphenylene



SI66. ^{13}C NMR for 6,7,10,11-tetramethoxytriphenylene



SI67. A DSC scan for 6,7,10,11-tetramethoxytriphenylene



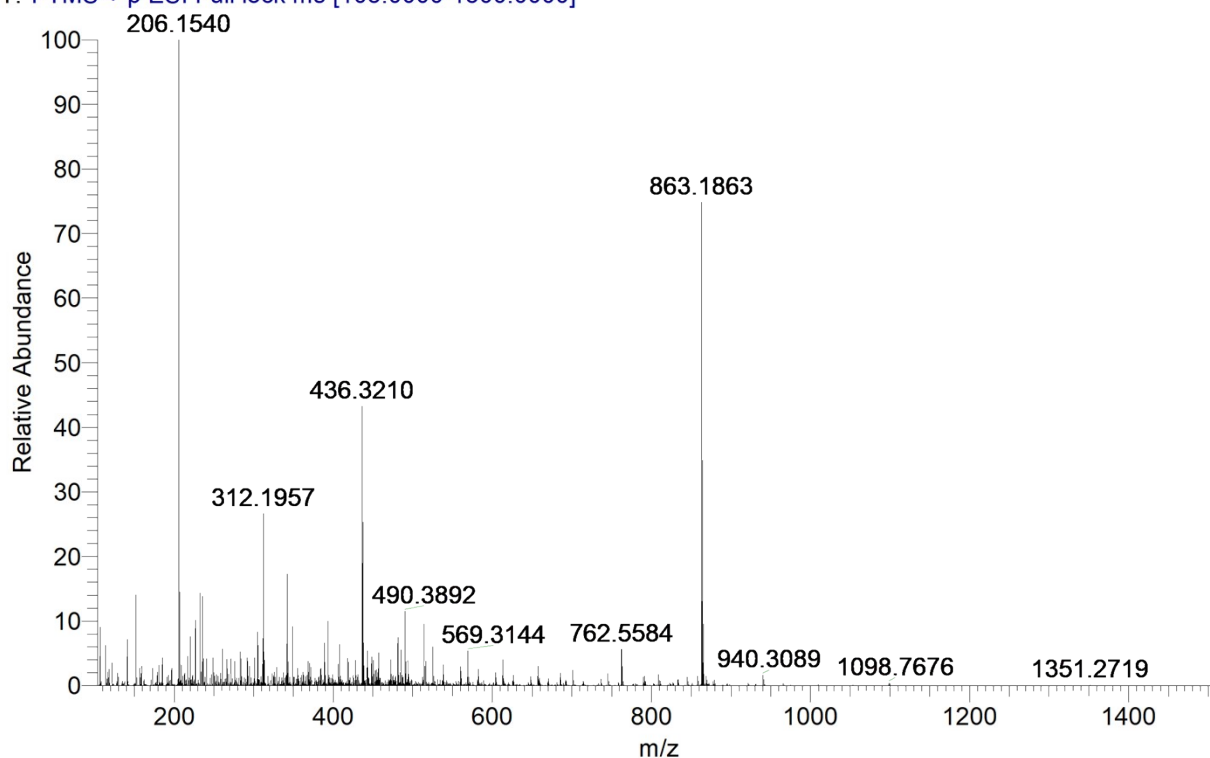
SI68. A DSC scan to check the decomposition temperature of 6,7,10,11-tetramethoxytriphenylene.

HRMS measurement of the target compounds

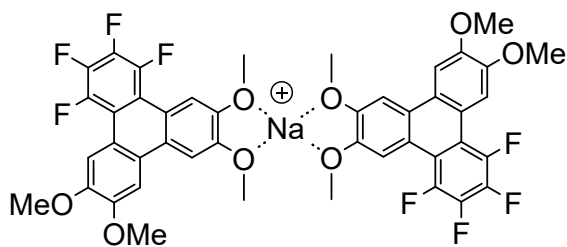
- Stock solutions were prepared by dissolution in MeCN.
- Samples were further diluted in solvent mixture designated as Na-Blank2 (80:20 = MeCN: H₂O with 0.1 mM NaHCOO)
- ESI-HRMS measurements were performed via flow injection into 15 μ L/min Na-Blank2.

1. 1, 2,3,4-tetrafluoro-6,7,10,11-tetramethoxytriphenylene

PG01178_Dil2_NaBlank2_mz105to1500_ESI HRMS_positive #103-143 RT: 0.90-1.25 AV: 41 NL: 1.13E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI69. HRMS spectra of compound **1**. Only weak signal at 443.0875 for $[C_{22}H_{16}F_4O_4+Na]^+$ was observed and second strongest peak at 863.1863 is for $[(C_{22}H_{16}F_4O_4)_2+Na]^+$.

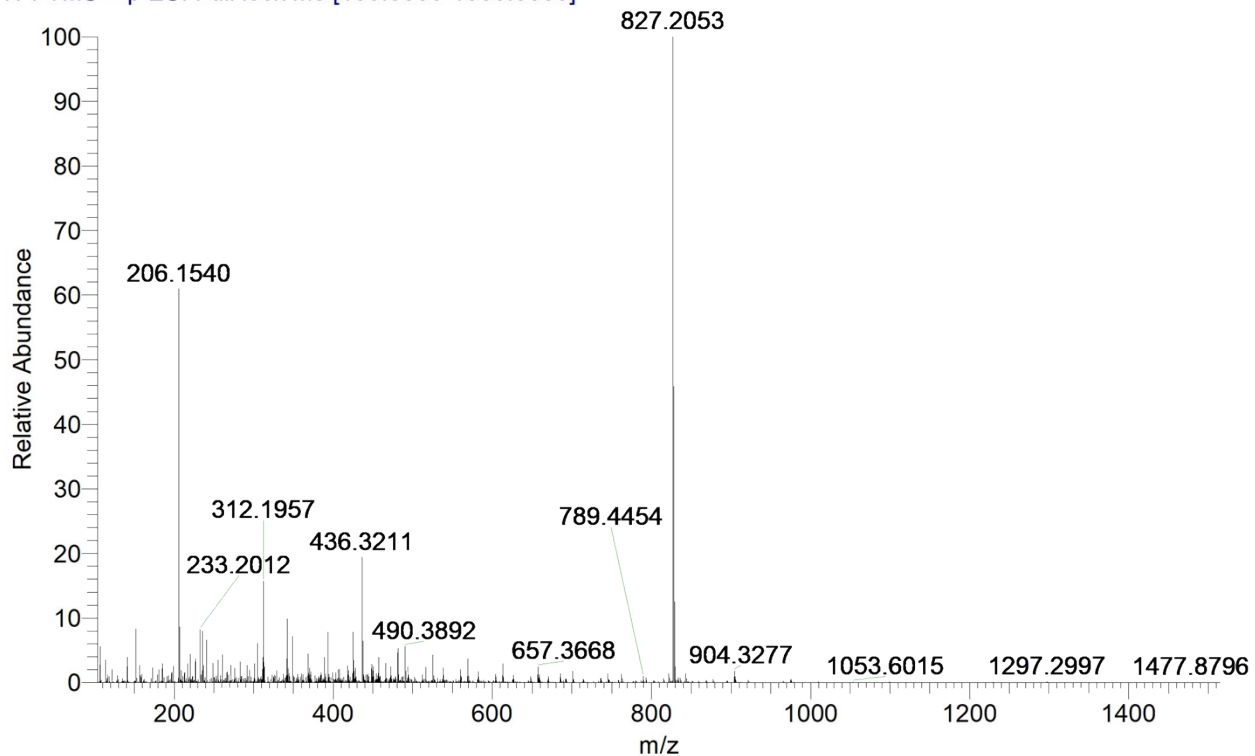


Chemical Formula: $C_{44}H_{32}F_8NaO_8^+$

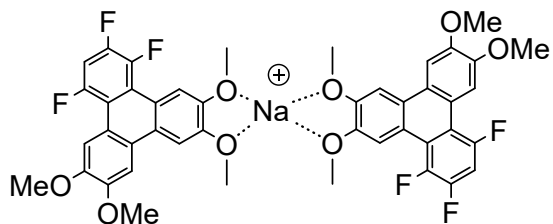
Exact Mass: 863.1862

2. 1, 2,4-trifluoro-6,7,10,11-tetramethoxytriphenylene

PG02087_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #103-118 RT: 0.90-1.03 AV: 16 NL: 1.96E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI70. HRMS spectra of compound 2. Only weak peak at 425.0969 for $[C_{22}H_{17}F_3O_4+Na]^+$ was observed and base peak at 827.2055 is for $[(C_{22}H_{17}F_3O_4)_2+Na]^+$.

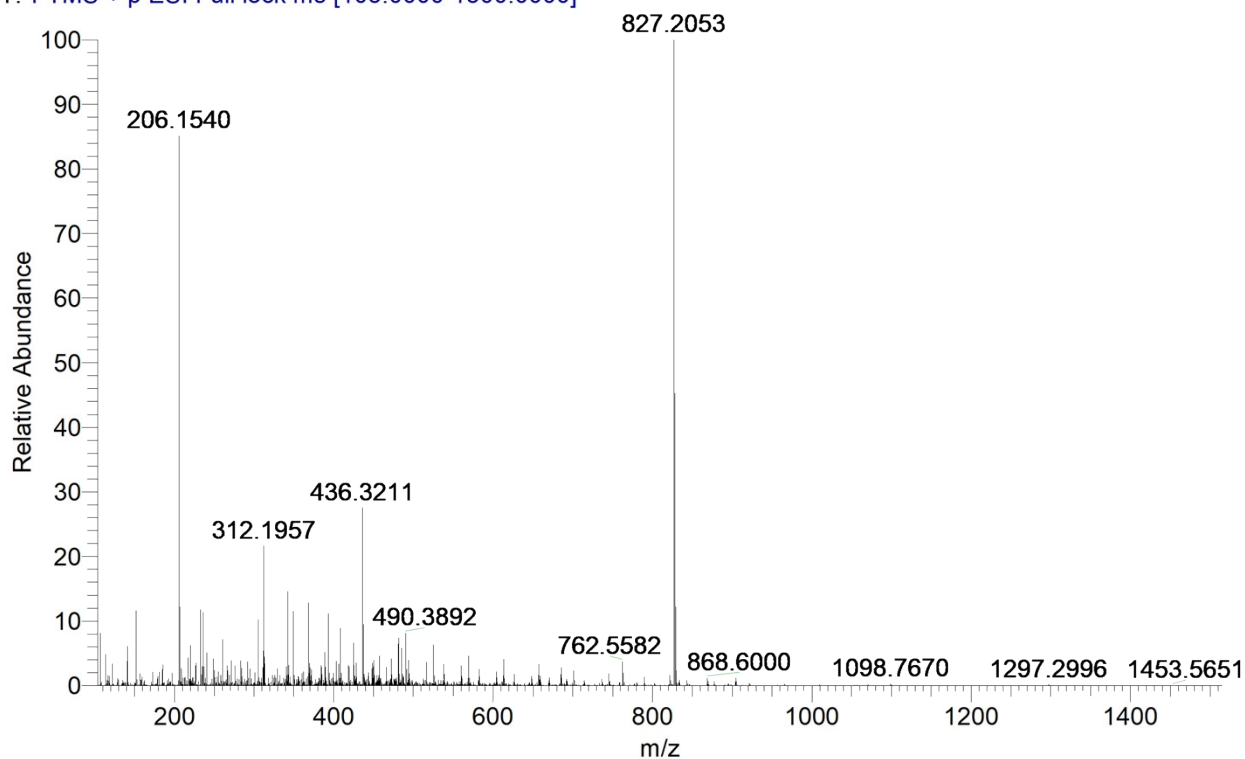


Chemical Formula: $C_{44}H_{34}F_6NaO_8^+$

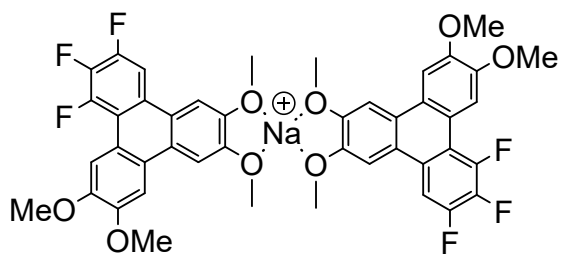
Exact Mass: 827.2050

3. 1, 2,3-trifluoro-6,7,10,11-tetramethoxytriphenylene

PG03017_Dil3_NaBlank2_mz105to1500_ESI HRMS_positive #100-115 RT: 0.87-1.00 AV: 16 NL: 1.42E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI71. HRMS spectra of compound 3. Only weak peak at 425.0970 for $[C_{22}H_{17}F_3O_4+Na]^+$ was observed and base peak at 827.2053 is for $[(C_{22}H_{17}F_3O_4)_2+Na]^+$.

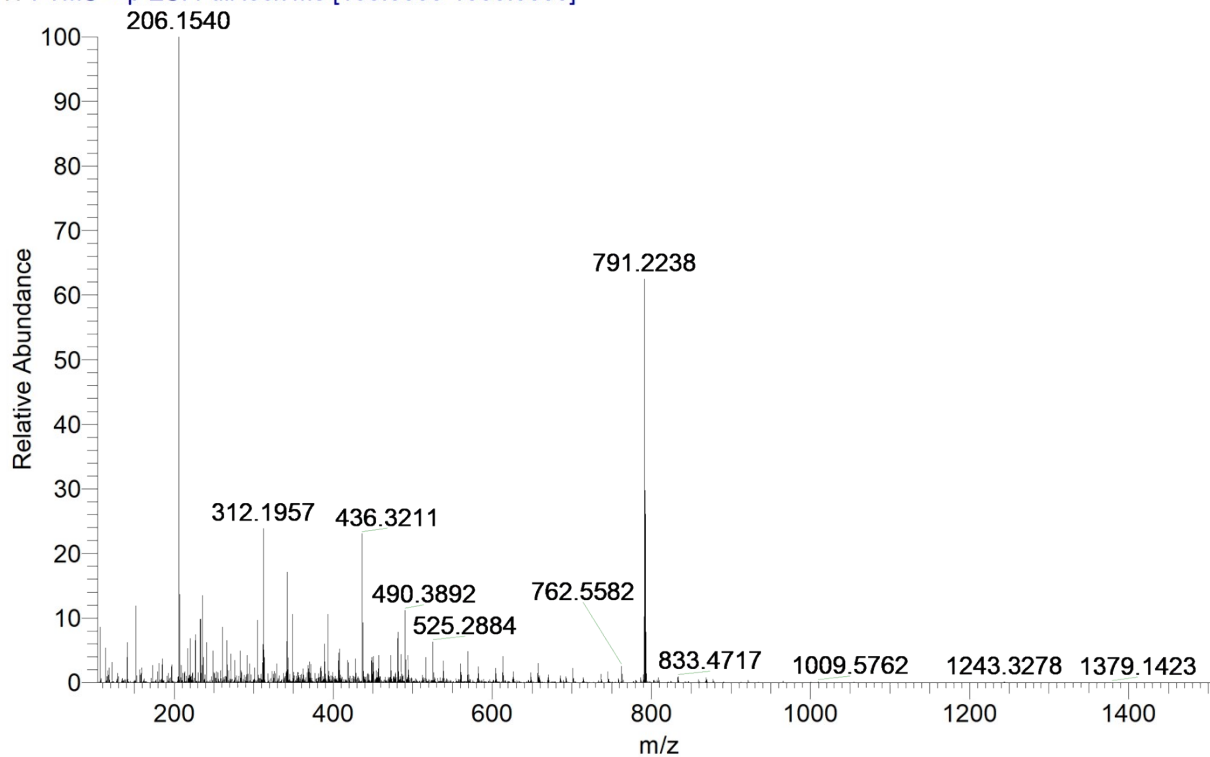


Chemical Formula: $C_{44}H_{34}F_6NaO_8^+$

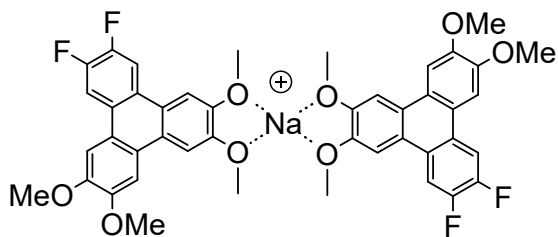
Exact Mass: 827.2050

4. 2,3-difluoro-6,7,10,11-tetramethoxytriphenylene

PG03032_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #99-127 RT: 0.86-1.11 AV: 29 NL: 1.34E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI72. HRMS spectra of compound 4. Only weak peak at 407.1063 for $[C_{22}H_{18}F_2O_4+Na]^+$ was observed and second strongest peak at 791.2241 is for $[(C_{22}H_{18}F_2O_4)_2+Na]^+$.

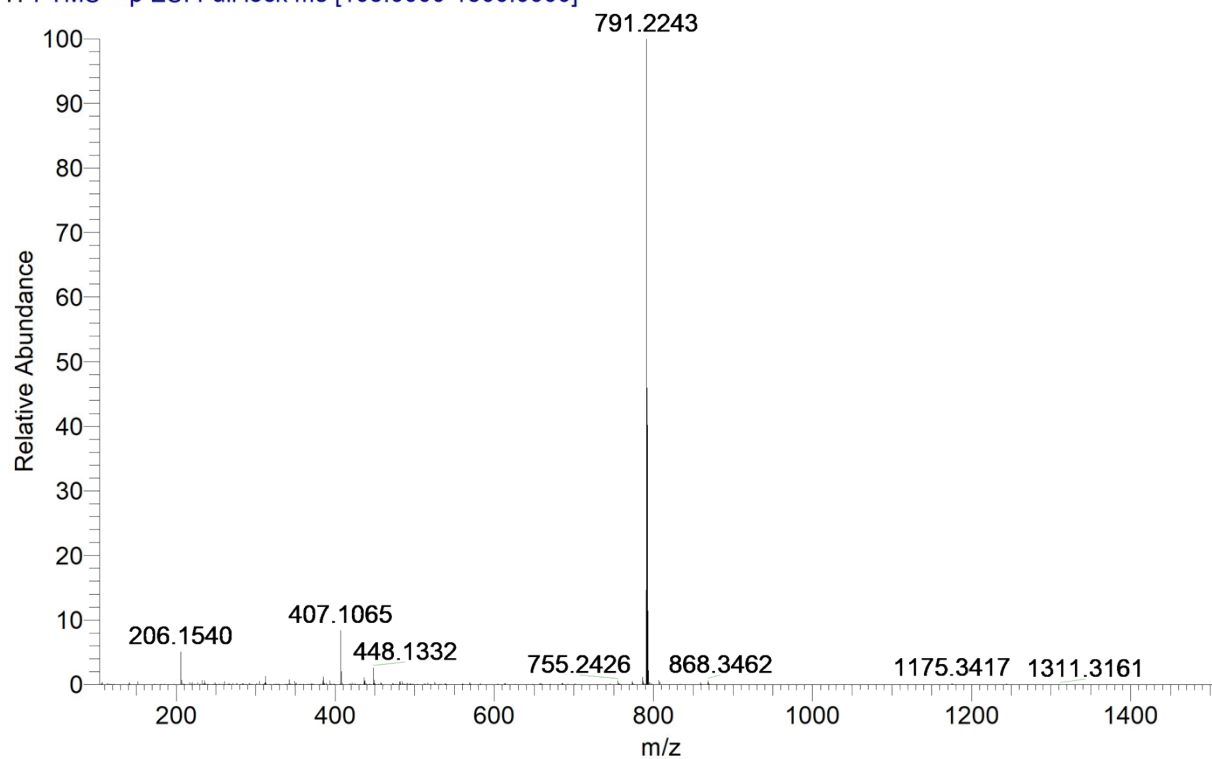


Chemical Formula: $C_{44}H_{36}F_4NaO_8^+$

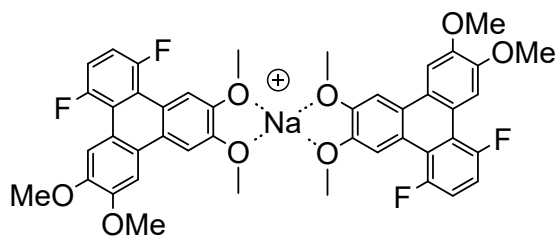
Exact Mass: 791.2239

5. 1, 4-difluoro-6,7,10,11-tetramethoxytriphenylene

PG03034_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #101-117 RT: 0.88-1.02 AV: 17 NL: 2.08E9
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI73. HRMS spectra of compound 5. Peak observed at 407.1065 is for $[C_{22}H_{18}F_2O_4+Na]^+$ and base peak at 791.2242 is for $[(C_{22}H_{18}F_2O_4)_2+Na]^+$.

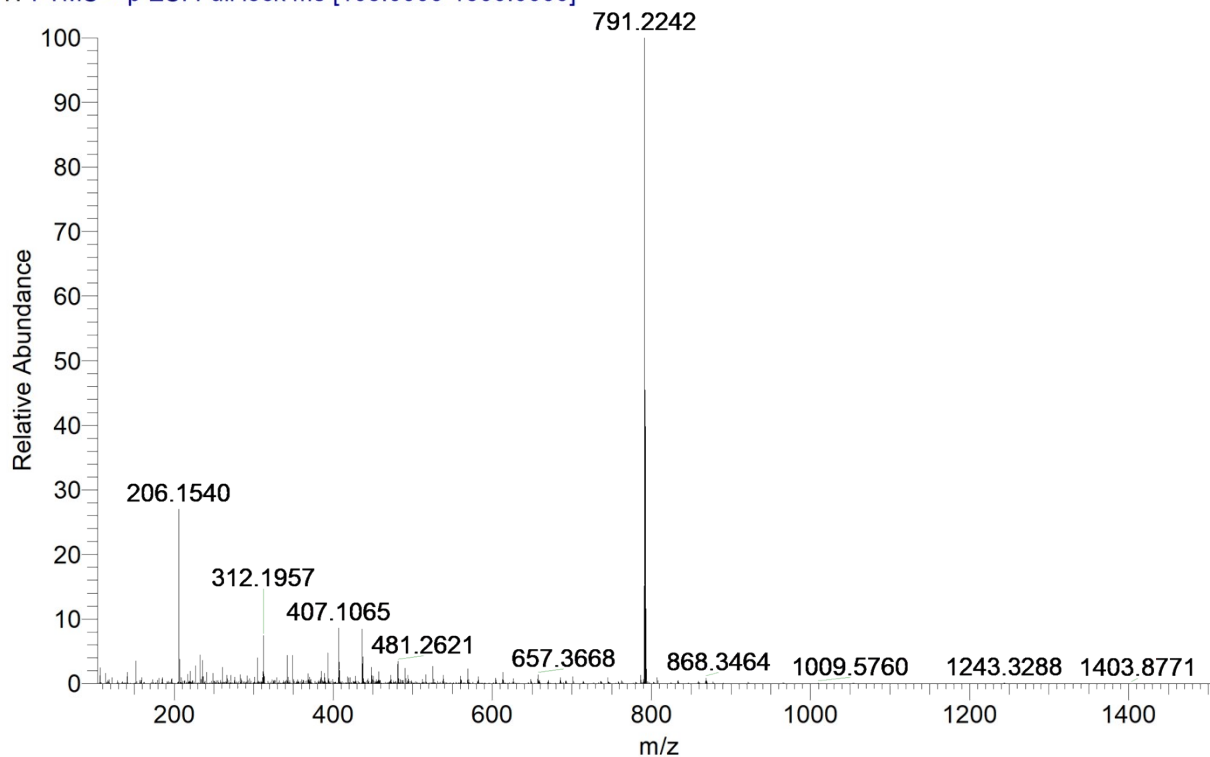


Chemical Formula: $C_{44}H_{36}F_4NaO_8^+$

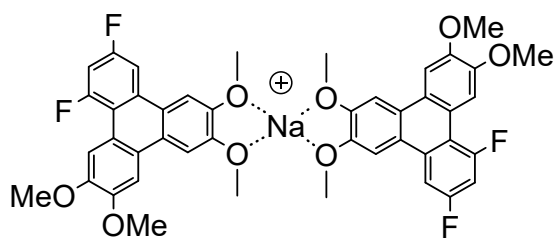
Exact Mass: 791.2239

6. 1, 3-difluoro-6,7,10,11-tetramethoxytriphenylene

PG03030_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #99-118 RT: 0.86-1.03 AV: 20 NL: 4.36E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI74. HRMS spectra of compound **6**. Small peak observed at 407.1065 is for $[C_{22}H_{18}F_2O_4+Na]^+$ and base peak at 791.2243 is for $[(C_{22}H_{18}F_2O_4)_2+Na]^+$.

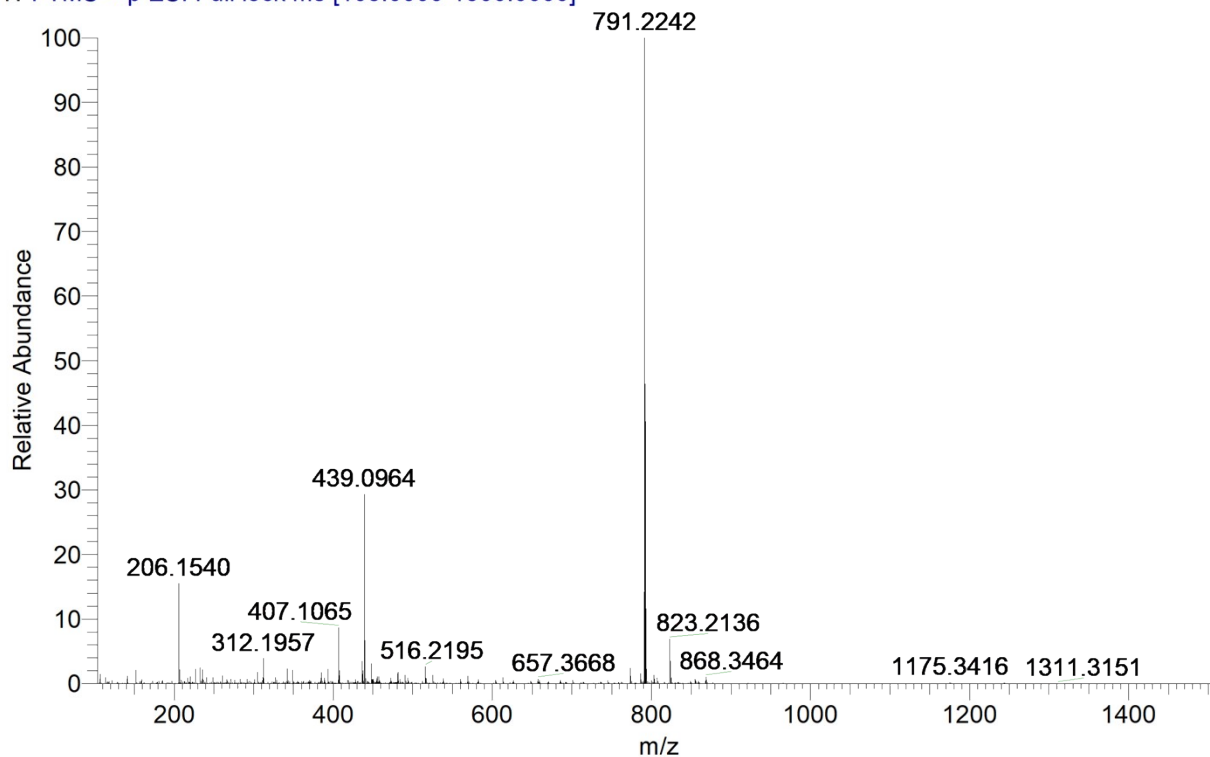


Chemical Formula: $C_{44}H_{36}F_4NaO_8^+$

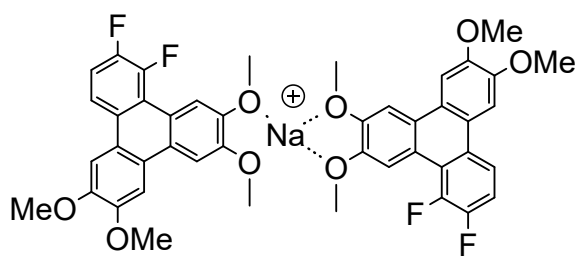
Exact Mass: 791.2239

7. 1, 2-difluoro-6,7,10,11-tetramethoxytriphenylene

PG02116_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #105-126 RT: 0.92-1.10 AV: 22 NL: 6.49E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI75. HRMS spectra of compound 7. Small peak observed at 407.1065 is for $[C_{22}H_{18}F_2O_4+Na]^+$ and base peak at 791.2272 is for $[(C_{22}H_{18}F_2O_4)_2+Na]^+$.

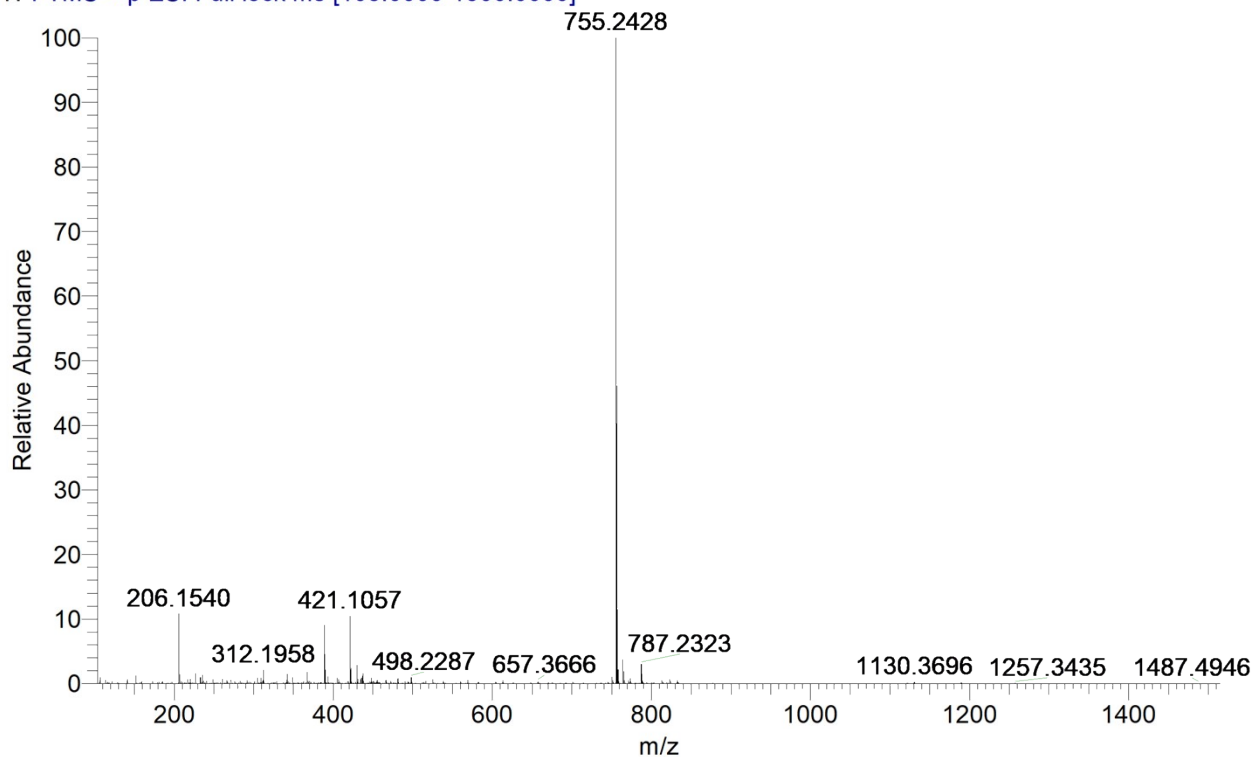


Chemical Formula: $C_{44}H_{36}F_4NaO_8^+$

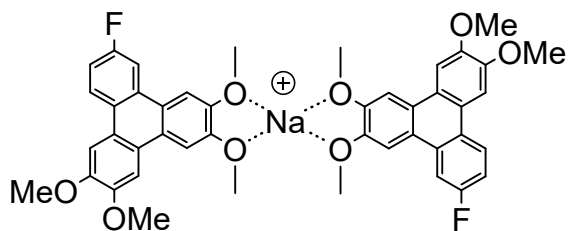
Exact Mass: 791.2239

8. 2-fluoro-6,7,10,11-tetramethoxytriphenylene

PG02153_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #108-124 RT: 0.94-1.08 AV: 17 NL: 9.70E8
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI76. HRMS spectra of compound **8**. Small peak observed at 389.1158 is for $[C_{22}H_{19}FO_4+Na]^+$ and base peak at 755.2429 is for $[(C_{22}H_{19}FO_4)_2+Na]^+$.

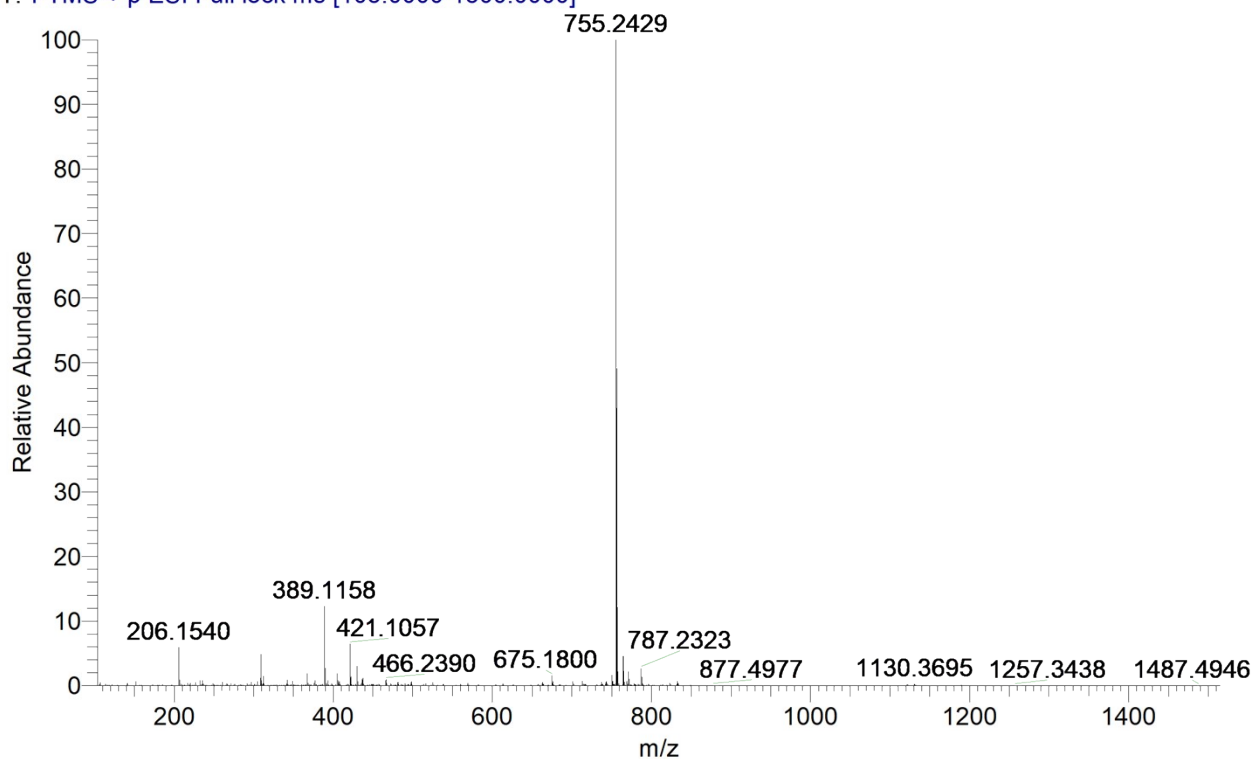


Chemical Formula: $C_{44}H_{38}F_2NaO_8^+$

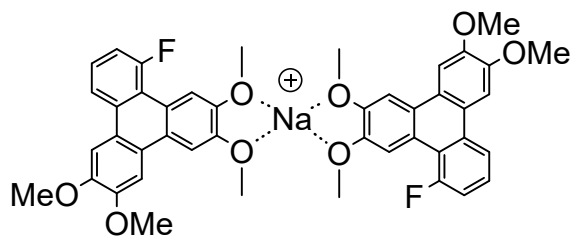
Exact Mass: 755.2427

9. 1-fluoro-6,7,10,11-tetramethoxytriphenylene

PG02151_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #95-114 RT: 0.83-0.99 AV: 20 NL: 1.75E9
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI77. HRMS spectra of compound **9**. Small peak observed at 389.1157 is for $[C_{22}H_{19}FO_4+Na]^+$ and base peak at 755.2428 is for $[(C_{22}H_{19}FO_4)_2+Na]^+$.

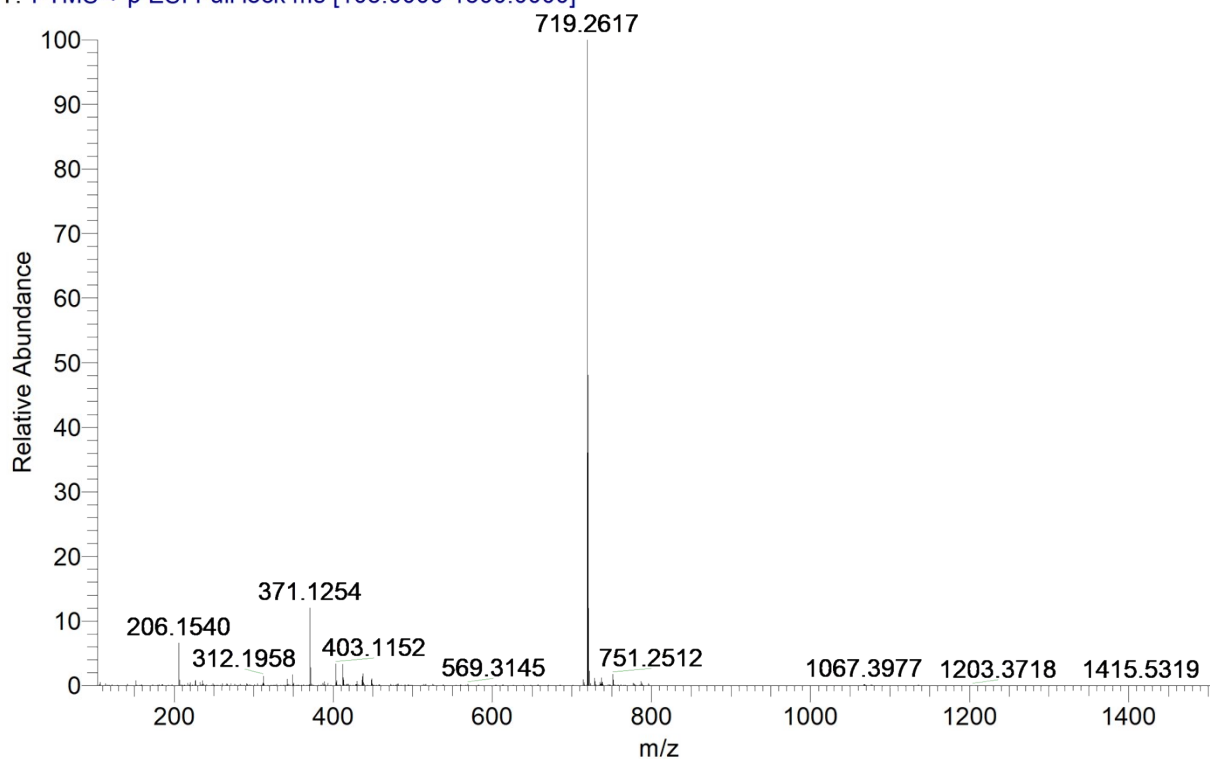


Chemical Formula: $C_{44}H_{38}F_2NaO_8^+$

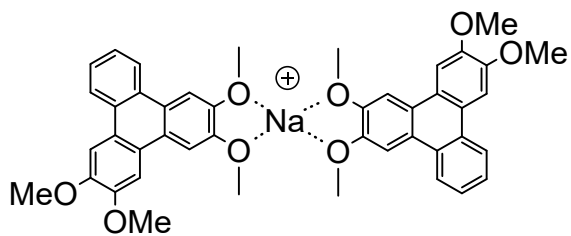
Exact Mass: 755.2427

10. 6,7,10,11-tetramethoxytriphenylene

PG03004_Dil1_NaBlank2_mz105to1500_ESI HRMS_positive #99-109 RT: 0.86-0.95 AV: 11 NL: 1.69E9
T: FTMS + p ESI Full lock ms [105.0000-1500.0000]



SI78. HRMS spectra of compound **10**. Smaller peak observed at 371.1254 is for $[C_{22}H_{20}O_4+Na]^+$ and base peak at 719.2618 is for $[(C_{22}H_{20}O_4)_2+Na]^+$.



Chemical Formula: $C_{44}H_{40}NaO_8^+$

Exact Mass: 719.2615

References

1. P. Guragain et.al. Mater. Adv. 2023,4,4129-4137.
2. Y. Wu et. al., Org. Lett., 2018, 20, 2278-2281.
3. M. Ichihara et. al. Liq. Cryst. 2007, 34, 401-410.