Supplementary Information

Rhodium-Catalyzed Electrochemical [2+2+2] Cyclotrimerization of 1,3-Butadiynes toward Hexasubstituted Arenes

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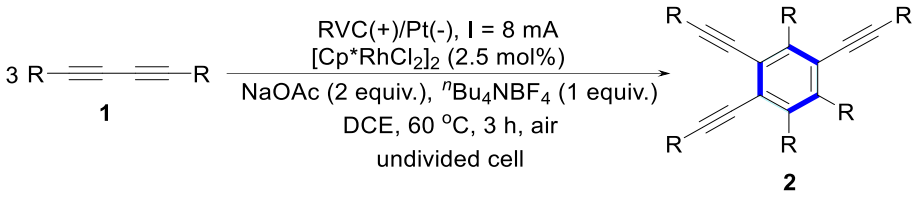
List of Contents

(A) Typical Experimental Procedure

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is RVC electrode and cathode electrode is platinum electrodes (1.0×1.0 cm^2).

(b) General procedures for electrochemical rhodium-catalyzed chemoselective [2 + 2 + 2] cyclotrimerization of 1,3-butadiynes to hexa-substituted arenes



To an undivided three-necked bottle (10 mL) were added **1** (0.3 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), NaOAc (2 equiv.), $^{n}Bu_4NBF_4$ (1 equiv.) and DCE (6 mL). The bottle was equipped with platinum plate electrodes (1.0×1.0 cm^2) as cathode and RVC electrode as anode under air. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 60 ºC for 3 h until complete consumption of **1** as monitored by TLC analysis. After the reaction was finished, added H_2O (5 mL) and the solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired arenes.

(c) Cyclic voltammogram analysis

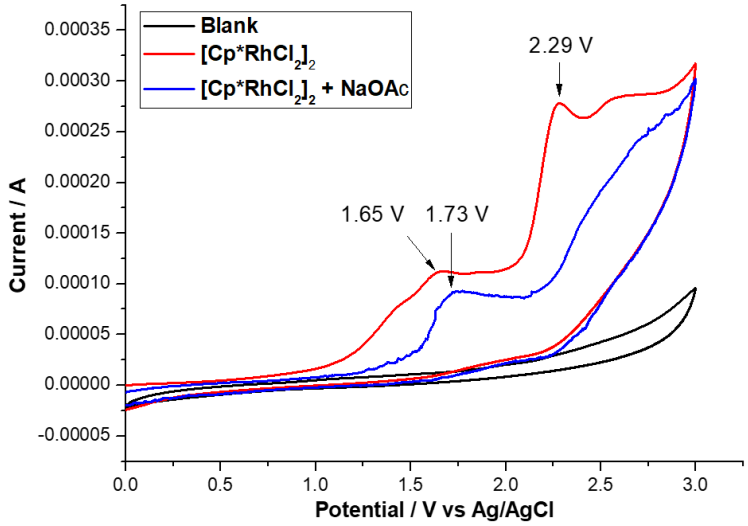


Figure S1. Cyclic voltammogram curves (0-3.0 V). Using GC disk as working electrode, Pt plate, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **Black curve**: nEt$_4$NPF$_6$ (0.1 M) and MeCN. **Curve red**: [Cp*RhCl$_2$]$_2$ (0.00125 M), nEt$_4$NPF$_6$ (0.1 M) and MeCN. **Curve blue**: [Cp*RhCl$_2$]$_2$ (0.00125 M), NaOAc (0.1 M), nEt$_4$NPF$_6$ (0.1 M) and MeCN.

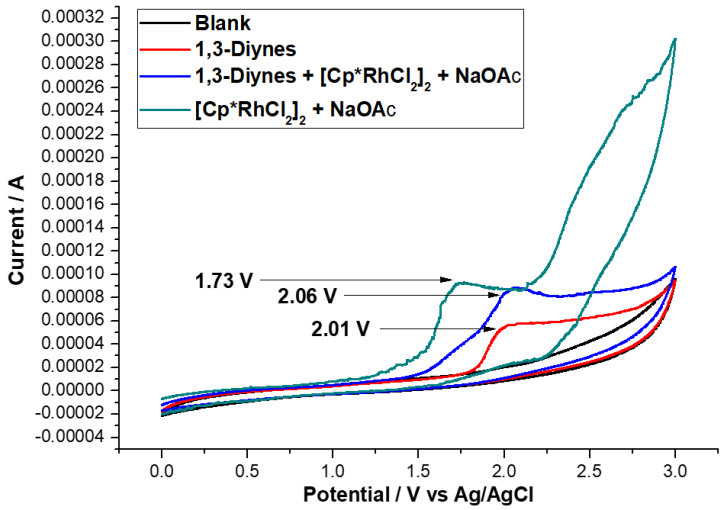
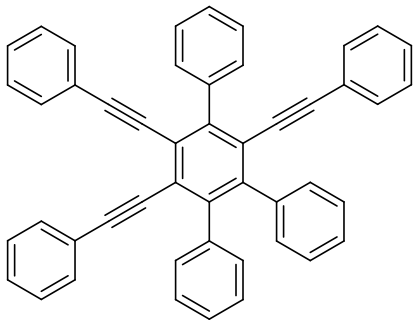


Figure S2. Cyclic voltammogram curves (0-3.0 V). Using GC disk as working electrode, Pt plate, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **Black curve**: nEt$_4$NPF$_6$ (0.1 M) and MeCN. **Curve red**: **1a** (0.05 M), nEt$_4$NPF$_6$ (0.1 M) and MeCN. **Curve blue**: **1a** (0.05 M), [Cp*RhCl$_2$]$_2$ (0.00125 M), NaOAc (0.1 M), nEt$_4$NPF$_6$ (0.1 M) and MeCN. **Curve green:** [Cp*RhCl$_2$]$_2$ (0.00125 M), NaOAc (0.1 M), nEt$_4$NPF$_6$ (0.1 M) and MeCN.

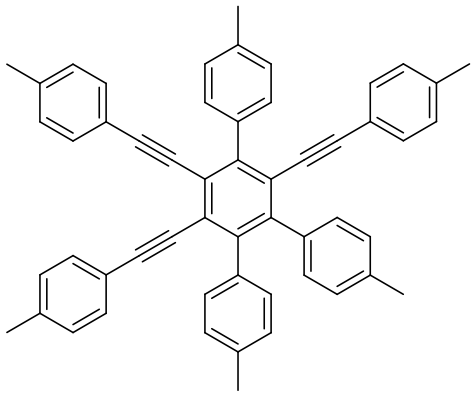
(B) Analytical data

4'-Phenyl-3',5',6'-tris(phenylethynyl)-1,1':2',1''-terphenyl (2a):



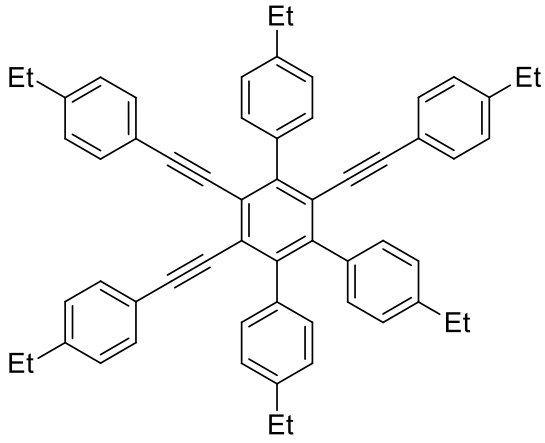
81% yield; Whilte solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.25-7.21 (m, 18H), 7.17-7.14 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 143.6, 143.1, 139.5, 139.4, 139.2, 131.5 (2C), 131.2, 130.7, 130.6, 130.4, 128.3, 128.2 (2C), 128.1, 128.0, 127.7, 127.5, 127.3, 127.2 (2C), 126. (2C), 125.6, 124.7, 123.4 (2C), 123.2, 123.1, 98.5, 98.3, 97.3, 88.9, 88.8, 88.2; HRMS *m/z* (ESI) calcd for $C_{48}H_{31}$ $[M+H]^+$ 607.2420, found 607.2431.

4,4''-Dimethyl-4'-(p-tolyl)-3',5',6'-tris(p-tolylethynyl)-1,1':2',1''-terphenyl (2b):



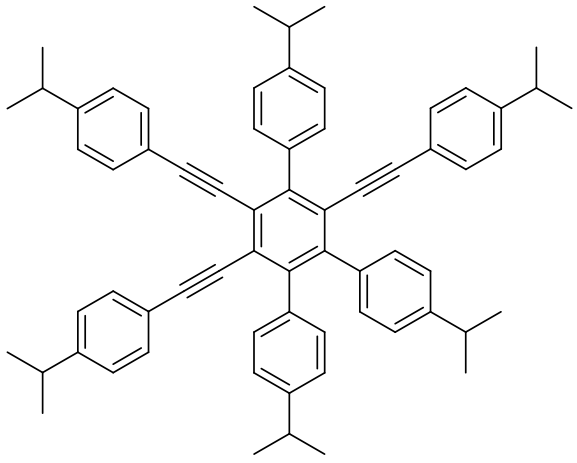
83% yield; Whilte solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.13-7.10 (m, 4H), 7.08-7.00 (m, 10H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.33-2.30 (m, 12H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 143.5, 142.8, 138.3, 138.3 (2C), 138.0, 137.0, 136.7, 136.6, 136.5, 136.0, 131.3 (2C), 131.0, 130.6, 130.5, 130.4, 128.9 (2C), 128.7, 128.0, 127.9, 127.8, 125.7, 124.6, 123.3, 120.6 (2C), 120.4, 98.4, 98.1, 97.1, 88. 7(2C), 88.0, 21.5 (2C), 21.4 (2C), 21.3 (2C); HRMS *m/z* (ESI) calcd for $C_{54}H_{43}$ $[M+H]^+$ 691.3359, found 691.3371.

4,4''-Diethyl-4'-(4-ethylphenyl)-3',5',6'-tris((4-ethylphenyl)ethynyl)-1,1':2',1''-terphenyl (2c):



79% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18-7.13 (m, 6H), 7.10-7.03 (m, 10H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 2.78 (q, *J* = 7.5 Hz, 2H), 2.65-2.58 (m, 8H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 1.25-1.18 (m, 12H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 144.6 (2C), 144.3, 143.5, 143.4, 143.0, 142.5 (2C), 137.0 (2C), 136.8, 131.5 (2C), 131.2, 130.7, 130.6, 130.5, 127.7 (2C), 127.5, 126.8, 126.7, 126.6, 125.6, 124.5, 123.3, 120.9, 120.8, 120.6, 98.4, 98.1, 97.1, 88.8 (2C), 88.0, 28.9 (2C), 28.8 (2C), 28.7 (2C), 16.1, 15.8 (2C), 15.4 (3C); HRMS *m/z* (ESI) calcd for $C_{60}H_{55}$ $[M+H]^+$ 775.4298, found 775.4306.

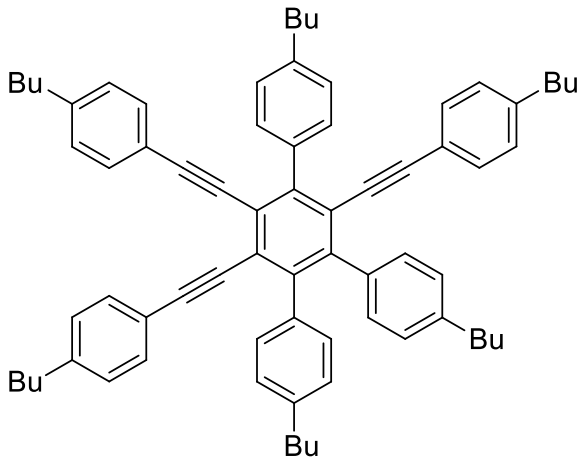
4,4''-Diisopropyl-4'-(4-isopropylphenyl)-3',5',6'-tris((4-isopropylphenyl)ethynyl)-1,1':2',1''-terphenyl (2d):



80% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.37-7.36(m, 2H), 7.16-7.04 (m, 18H), 6.96-6.94 (m, 2H), 6.65-6.63 (m, 2H), 3.07-3.03 (m, 1H), 2.9-2.84 (m, 4H), 2.81-2.77 (m, 1H), 1.40-1.37 (m, 6H), 1.26-1.19 (m, 24H), 1.16-1.14

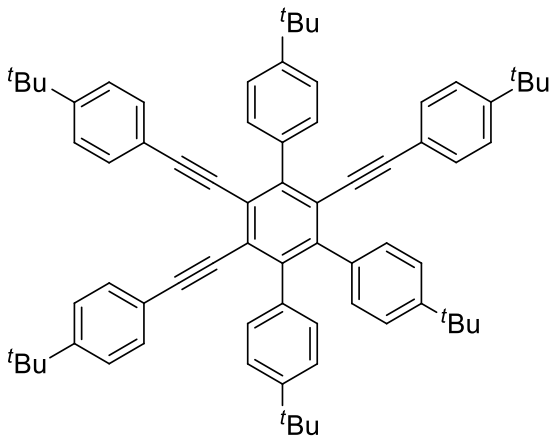
(m, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1 (2C), 148.9, 148.0, 147.0 (2C), 145.7, 143.4, 143.1, 137.3, 137.1, 137.0, 131.5, 131.2, 130.6 (2C), 130.4, 126.3, 126.2, 126.0 (2C), 125.4, 125.3, 125.2, 125.0, 124.4, 123.3, 121.0 (2C), 120.8, 98.4, 98.1, 97.1, 88.8 (2C), 88.1, 34.1 (3C), 34.0, 33.8 (2C), 24.2, 24.01, 24.0, 23.8 (2C), 23.7; HRMS *m/z* (ESI) calcd for $C_{66}H_{67}$ $[M+H]^+$ 859.5237, found 859.5252.

4,4''-Dibutyl-4'-(4-butylphenyl)-3',5',6'-tris((4-butylphenyl)ethynyl)-1,1':2',1''-terphenyl (2e):



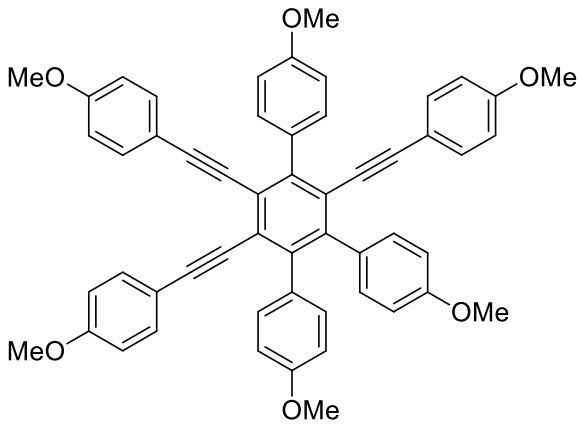
77% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.06-6.91 (m, 14H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.51-2.47 (m, 8H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.68-1.62 (m, 2H), 1.52-1.43 (m, 8H), 1.42-1.34 (m, 4H), 1.28-1.21 (m, 10H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.86-0.78 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 143.5, 143.2 (2C), 143.0, 141.9, 141.0, 137.0, 136.9, 136.8, 131.4 (2C), 131.1 (2C), 130.6 (2C), 130.4, 128.8, 128.3, 128.2, 128.0, 127.4, 127.3, 127.2, 125.4, 124.5, 123.2, 120.8 (2C), 120.6, 98.3, 98.0, 97.1, 88.8 (2C), 88.1, 35.6 (2C), 35.6, 35.5, 35.4 (2C), 34.0, 33.7 (2C), 33.4 (2C), 33.3, 22.3 (3C), 22.2 (2C), 22.1, 14.1 (2C), 14.0, 13.9 (3C); HRMS *m/z* (ESI) calcd for $C_{72}H_{79}$ $[M+H]^+$ 943.6176, found 943.6188.

4,4''-Di-*tert*-butyl-4'-(4-(*tert*-butyl)phenyl)-3',5',6'-tris((4-(*tert*-butyl)phenyl)ethynyl)-1,1':2',1''-terphenyl (2f):



74% yield; Whilte solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.27-7.22 (m, 8H), 7.17-7.09 (m, 10H), 6.64 (d, *J* = 7.5 Hz, 2H), 1.46 (s, 9H), 1.30-1.28 (m, 36H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4 (2C), 151.1, 150.1, 149.2 (2C), 145.7, 143.5, 143.1, 136.9, 136.6 (2C), 131.3, 131.2, 130.1, 130.4 (2C), 130.2, 125.3, 125.1 (2C), 124.8, 124.4, 124.2, 123.9, 123.8, 123.2, 120.7 (2C), 120.5, 98.3, 98.0, 97.1, 88.9 (2C), 88.2, 34.8, 34.7, 34.7, 34.6, 34.4 (2C), 31.5, 31.4, 31.3, 31.2, 31.1 (2C); HRMS *m/z* (ESI) calcd for $C_{72}H_{79}$ $[M+H]^+$ 943.6176, found 943.6181.

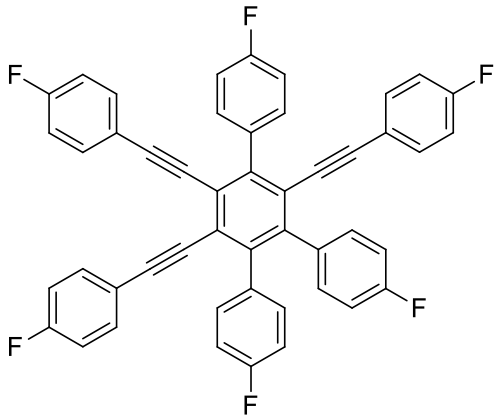
4,4''-Dimethoxy-4'-(4-methoxyphenyl)-3',5',6'-tris((4-methoxyphenyl)ethynyl)-1,1':2',1''-terphenyl (2g):



84% yield; Whilte solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.64 (m, 4H), 7.26-7.23 (m, 2H), 7.14-7.12 (m, 2H), 7.05-7.01 (m, 4H), 6.85-6.77 (m, 8H), 6.71-6.67 (m, 4H), 3.92-3.90 (m, 6H), 3.80-3.74 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 159.2 (2C), 158.9 (2C), 158.0, 145.0, 144.5, 142.7, 142.1, 132.8, 132.6, 132.2, 132.0, 131.9 (2C), 131.8, 125.4, 124.5, 123.2, 122.3, 115.6 (2C), 115.4 (2C), 113.8 (2C), 113.6,

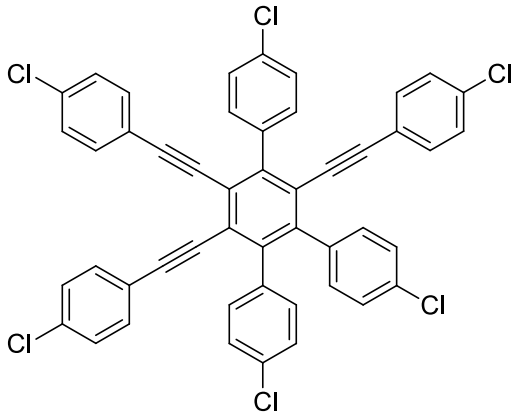
112.5 (2C), 97.7 (2C), 96.6, 88.1, 87.5, 87.4, 55.4 (2C), 55.3, 55.2 (2C), 55.1; HRMS *m/z* (ESI) calcd for $C_{54}H_{43}O_6$ $[M+H]^+$ 787.3054, found 787.3071.

4,4''-Difluoro-4'-(4-fluorophenyl)-3',5',6'-tris((4-fluorophenyl)ethynyl)-1,1':2',1''-terphenyl (2h):



63% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.25-7.15 (m, 10H), 7.00-6.94 (m, 8H), 6.87 (t, *J* = 7.5 Hz, 2H), 6.75-6.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 163.5, 162.8, 161.7, 161.6, 160.9, 144.8, 142.6, 142.2, 135.1 (d, *J* = 3.375 Hz), 135.0 (d, *J* = 3.25 Hz), 134.8 (d, *J* = 3.5 Hz), 133.3, 133.2, 133.0, 132.9, 132.3, 132.2 (2C), 132.1, 125.6, 125.0, 123.3, 119.1 (d, *J* = 6.75 Hz), 119.0, 118.7 (d, *J* = 3.625 Hz), 118.6 (d, *J* = 3.625 Hz), 115.9 (2C), 115.7, 115.5, 114.7, 114.6, 114.5 (2C), 114.4, 97.9, 97.8, 96.7, 88.0, 87.8, 87.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.8, -109.8, -109.9, -113.9, -114.6 (2F); HRMS *m/z* (ESI) calcd for $C_{48}H_{25}F_6$ $[M+H]^+$ 715.1855, found 715.1869.

4,4''-Dichloro-4'-(4-chlorophenyl)-3',5',6'-tris((4-chlorophenyl)ethynyl)-1,1':2',1''-terphenyl (2i):

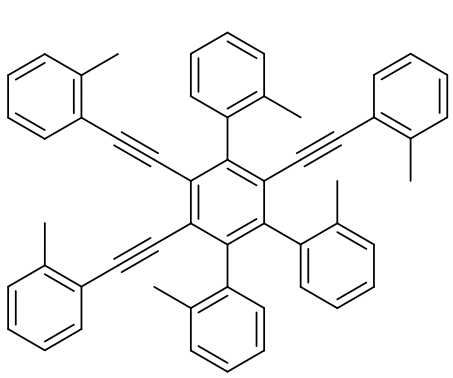


66% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.28-7.23 (m, 8H), 7.17-7.13 (m, 8H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 142.5, 142.1, 137.4, 137.2, 137.0, 134.9 (2C), 134.7,

134.1, 133.4 (2C), 132.5 (2C), 132.3, 131.8 (2C), 131.7, 128.8 (2C), 128.7, 127.9 (2C), 127.8, 125.7, 124.9, 123.1, 121.2 (2C), 120.9, 98.2 (2C), 96.9, 89.0, 88.7, 88.3; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 10), 148 (100), 120 (53), 105 (33), 93 (36); HRMS *m/z* (ESI) calcd for $C_{48}H_{25}Cl_6$ $[M+H]^+$ 811.0082, found 811.0094.

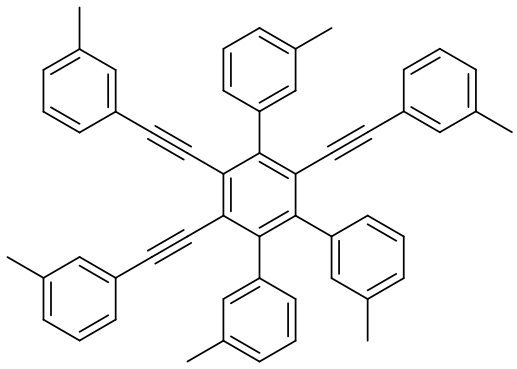
Dimethyl

2,2''-dimethyl-4'-(*o*-tolyl)-3',5',6'-tris(*o*-tolylethynyl)-1,1':2',1''-terphenyl (2j):



53% isolated yield; Light yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.41 (m, 1H), 7.33-7.31 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.15-7.10 (m, 4H), 7.08-6.96 (m, 10H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 143.2, 142.8, 140.5, 140.4, 140.0, 139.9, 138.5, 138.4, 136.5, 136.3, 136.1, 132. (3C), 132.0, 131.4, 131.3, 129.9, 129.7, 129.6 (2C), 129.2 (2C), 128.9, 128.3, 128.3, 128.1, 127.7, 127.2, 127.1, 125.7 (2C), 125.2 (2C), 125.1, 124.8, 124.6 (2C), 124.2, 123.1, 122.9, 96.9, 96.4, 95.8, 92.2, 91.7, 91.4, 20.1 (2C), 19.9 (2C), 19.8, 19.6; HRMS *m/z* (ESI) calcd for $C_{54}H_{43}$ $[M+H]^+$ 691.3359, found 691.3374.

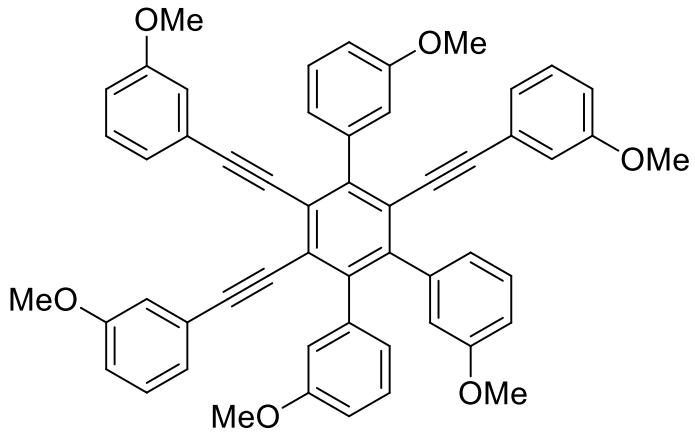
***3,3''-dimethyl-4'-(m-tolyl)-3',5',6'-tris(m-tolylethynyl)-1,1':2',1''-terphenyl* (2k):**



66% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.18-7.05 (m, 10H), 7.05-6.94 (m, 8H), 6.58 (d, *J* = 7.5 Hz, 1H),

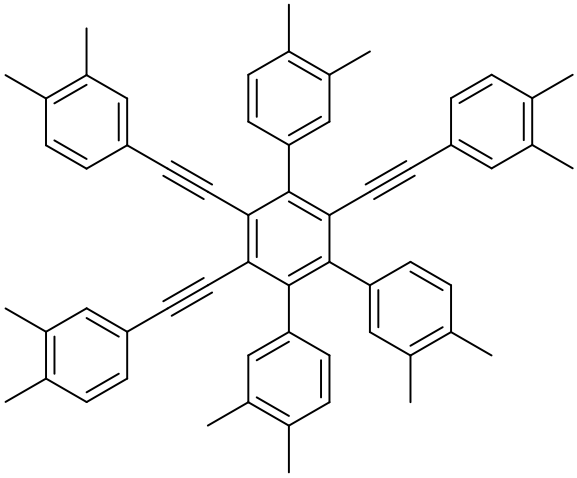
6.56 (s, 1H), 2.47 (s, 3H), 2.27 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 143.7, 143.0, 139.4, 139.3, 139.2, 137.8, 137.7, 137.5, 136.6, 136.4 (2C), 132.2, 132.1, 131.9, 131.4, 131.2, 129.1 (2C), 128.9, 128.5 (2C), 128.3, 128.1 (3C), 128.0, 127.8, 127.7 (2C), 127.6, 127.4 (2C), 127.3, 127.1, 127.0, 125.6, 124.6, 123.4, 123.3, 123.1, 123.0, 98.6, 98.4, 97.3, 88.9 (2C), 88.2, 21.6, 21.4 (2C), 21.2, 21.1 (2C); HRMS *m/z* (ESI) calcd for $C_{54}H_{43}$ $[M+H]^+$ 691.3359, found 691.3366.

3,3''-Dimethoxy-4'-(3-methoxyphenyl)-3',5',6'-tris((3-methoxyphenyl)ethynyl)-1, 1':2',1''-terphenyl (2l):



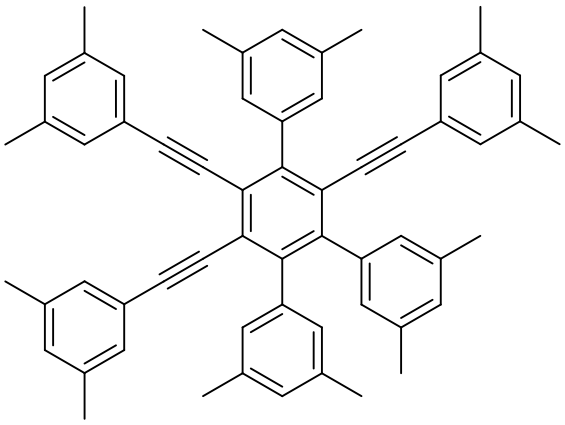
68% yield; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 (s, 1H), 7.19-7.13 (m, 4H), 7.06-7.02 (m, 2H), 6.91-6.71 (m, 13H), 6.43 (d, *J* = 7.5 Hz, 1H), 6.28 (s, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2 (2C), 159.0, 158.9, 158.7 (2C), 145.8, 143.3, 142.8, 140.6, 140.5, 140.4, 129.3 (2C), 129.1, 128.5, 128.3, 128.2, 125.5, 124.7, 124.3 (2C), 124.0, 123.9 (2C), 123.6, 123.3 (2C), 123.0, 122.9, 115.9 (2C), 115.7 (2C), 115.6, 115.4 (2C), 115.3, 115.2, 114.2, 113.4, 113.3, 98.6, 98.5, 97.4, 88.6, 88.5, 87.9, 55.32, 55.2 (2C), 55.1 (3C); HRMS *m/z* (ESI) calcd for $C_{54}H_{43}O_6$ $[M+H]^+$ 787.3054, found 787.3075.

4'-(3,4-Dimethylphenyl)-3',5',6'-tris((3,4-dimethylphenyl)ethynyl)-3,3'',4,4''-tetra methyl-1,1':2',1''-terphenyl (2m):



80% yield; Whilte solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.08-6.87 (m, 13H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.23 (s, 6H), 2.22 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 2.17 (s, 6H), 2.16 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 143.5, 142.7, 137.3, 137.0 (5C) 136.7, 136.3, 136.2, 136.0, 135.5, 134.9, 134.8, 134.7, 134.4 (2C), 132.7 (2C) 132.4, 132.1, 131.8, 129.4, 129.4, 129.2, 128.8 (2C), 128.5 (2C), 128.4 (2C), 128. (3C), 125.8, 124.4, 123.2, 121.1, 121.0, 120.1, 98.4, 98.2, 97.1, 88.9 (2C), 88.1, 19.9, 19.7 (6C) 19.5 (5C); HRMS *m/z* (ESI) calcd for $C_{60}H_{55}$ $[M+H]^+$ 775.4298, found 775.4304.

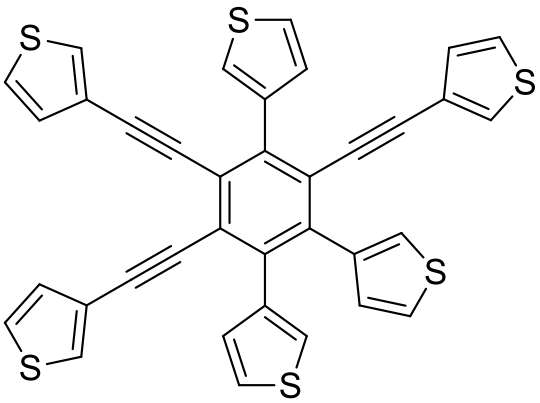
4'-(3,5-Dimethylphenyl)-3',5',6'-tris((3,5-dimethylphenyl)ethynyl)-3,3'',5,5''-tetra methyl-1,1':2',1''-terphenyl (2n):



77% isolated yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.23 (s, 1H), 7.10 (s, 1H), 6.96 (s, 2H), 6.91-6.81 (m, 10H), 6.42 (s, 2H), 2.44 (s, 6H), 2.26-2.22 (m, 24H), 2.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 143.8, 142.9, 139.4, 139.1, 139.1, 137.6, 137.5, 137.4, 136.3, 136.1 (2C), 130.0, 129.8, 129.2 (2C), 129.1, 128.9, 128.6

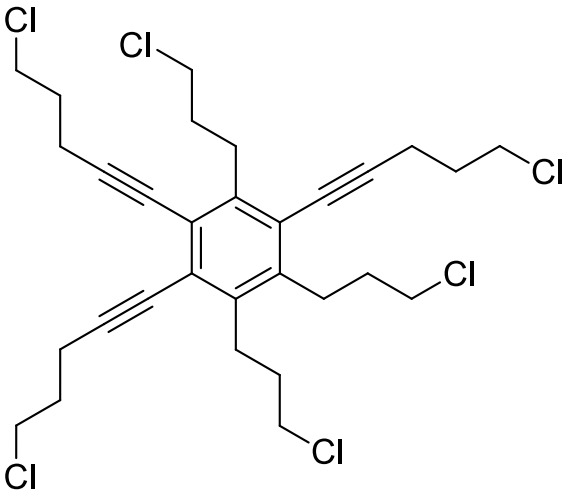
(2C), 128.5, 128.4, 128.1 (2C), 125.7, 124.4, 123.4 (2C), 123.1, 122.8, 98.7, 98.5, 97.3, 88.9 (3C), 88.3, 21.5, 21.3 (2C), 21.1, 21.0, 21.0; HRMS *m/z* (ESI) calcd for $C_{60}H_{55}$ $[M+H]^+$ 775.4298, found 775.4312.

3,3',3''-((3,5,6-Tri(thiophen-3-yl)benzene-1,2,4-triyl)tris(ethyne-2,1-diyl))trithiophene (2o):



66% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.66 (m, 1H), 7.48-7.47 (m, 1H), 7.41-7.39 (m, 1H), 7.34-7.33 (m, 1H), 7.30-7.29 (m, 1H), 7.25-7.24 (m, 1H), 7.23-7.22 (m, 1H), 7.17-7.14 (m, 5H), 7.06-7.05 (m, 1H), 7.02-7.00 (m, 1H), 6.97-6.96 (m, 1H), 6.94-6.92 (m, 2H), 6.72-6.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.0, 138.8, 138.7 (2C), 138.1, 130.1, 129.8, 129.7, 129.6, 129.4, 128.9, 128.8, 128.7, 125.8, 125.6 (2C), 125.4 (2C), 125.2, 125.1 (2C), 124.9, 123.6 (2C), 123.4, 123.3 (2C), 122.4, 122.2, 93.5, 93.4, 92.5, 88.3, 88.1, 87.7; HRMS *m/z* (ESI) calcd for $C_{36}H_{19}S_6$ $[M+H]^+$ 642.9806, found 642.9821.

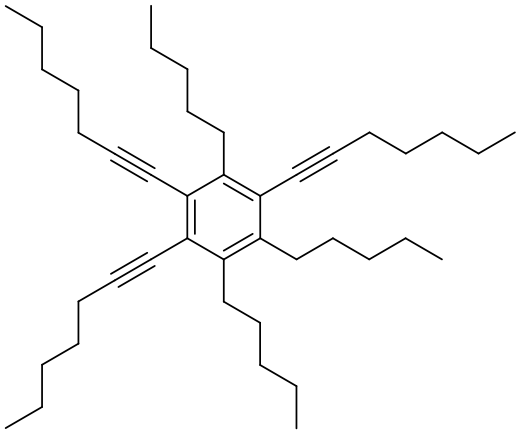
1,2,4-Tris(5-chloropent-1-yn-1-yl)-3,5,6-tris(3-chloropropyl)benzene (2p):



47% yield; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63-3.56 (m, 12H), 2.97-2.94 (m, 2H), 2.59-2.54 (m, 4H), 2.56 (dt, *J* = 6.9, 3.4 Hz, 4H), 2.02-1.97 (m, 4H), 1.90-1.86 (m, 4H), 1.83-1.79 (m, 4H), 1.72-1.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 141.5, 139.6, 125.5, 123.9, 123.0, 97.3,

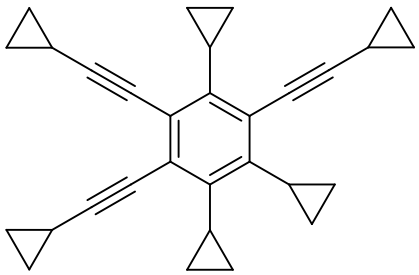
97.2, 95.9, 79.7, 79.0, 78.5, 45.0, 44.8, 44.6, 44.5, 33.0, 32.8 (2C), 32.7, 31.8, 31.7 (2C), 31.1, 30.9, 29.7, 27.6, 26.8, 26.1, 19.1; HRMS *m/z* (ESI) calcd for $C_{30}H_{37}Cl_6$ $[M+H]^+$ 607.1021, found 607.1040.

1,2,4-Tri(hept-1-yn-1-yl)-3,5,6-tripentylbenzene (2q):



43% yield; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92-2.89 (m, 2H), 2.76-2.71 (m, 4H), 2.51-2.45 (m, 6H), 1.65-1.59 (m, 8H), 1.51-1.45 (m, 10H), 1.38-1.32 (m, 20H), 0.93-0.90 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 142.1 (2C), 125.3, 123.6, 122.8, 100.0, 97.4, 96.2, 79.4, 78.8, 78.4, 33.9, 32.5, 32.4, 32.3, 32.0, 31.8, 31.2 (4C), 29.4, 28.7 (3C), 22.5 (3C), 22.3 (2C), 19.9, 19.8, 19.7, 14.1 (2C), 14.0 (2C); HRMS *m/z* (ESI) calcd for $C_{42}H_{67}$ $[M+H]^+$ 571.5237, found 571.5251.

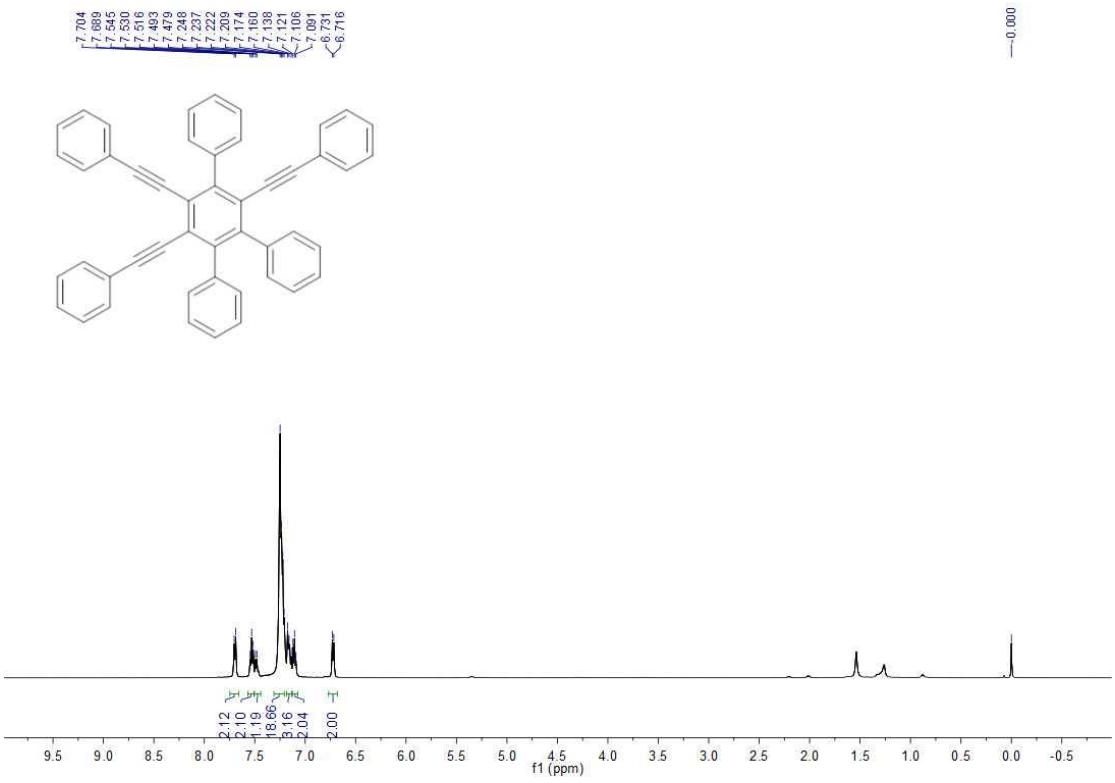
1,2,4-Tricyclopropyl-3,5,6-tris(cyclopropylethynyl)benzene (2r):



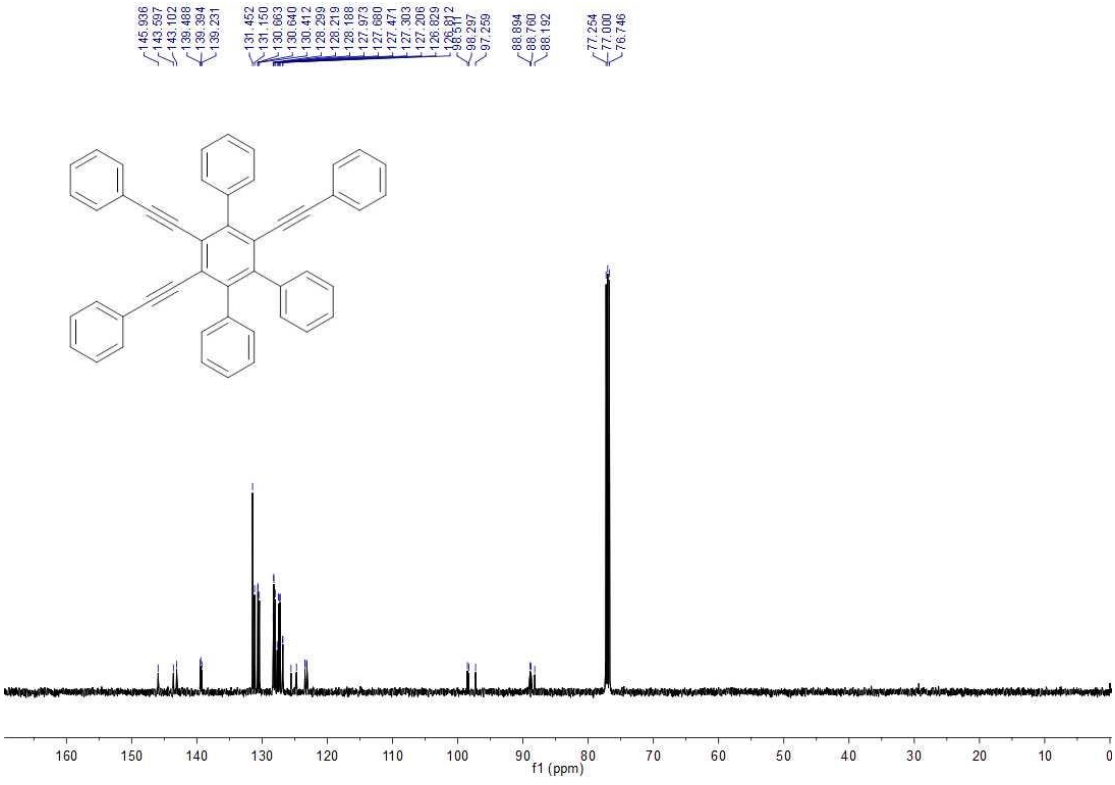
45% isolated yield; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92-1.89 (m, 2H), 1.85- 1.82 (m, 2H), 1.57- 1.52 (m, 3H), 1.00-0.59 (m, 20H), 0.63-0.59 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 143.4, 143.1, 127.4, 126.6, 125.5, 104.2, 102.7, 101.4, 74.8, 74.1, 73.8, 14.7, 14.6, 14.4, 9.2, 9.0, 8.9, 8.8, 8.7, 8.3, 0.8 (2C), 0.7; HRMS *m/z* (ESI) calcd for $C_{30}H_{31}$ $[M+H]^+$ 391.2420, found 391.2433.

(C) Spectra (NMR Spectra)

4'-Phenyl-3',5',6'-tris(phenylethynyl)-1,1':2',1''-terphenyl (2a):

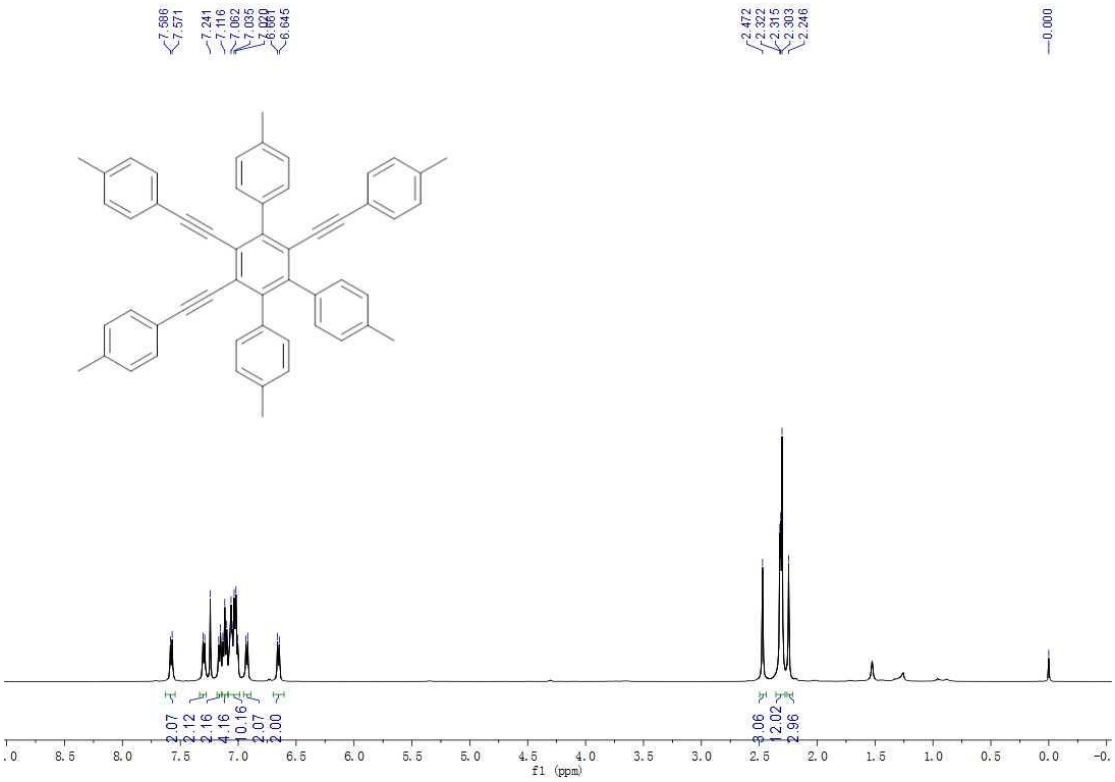


^{1}H NMR (500 MHz, $CDCl_3$)

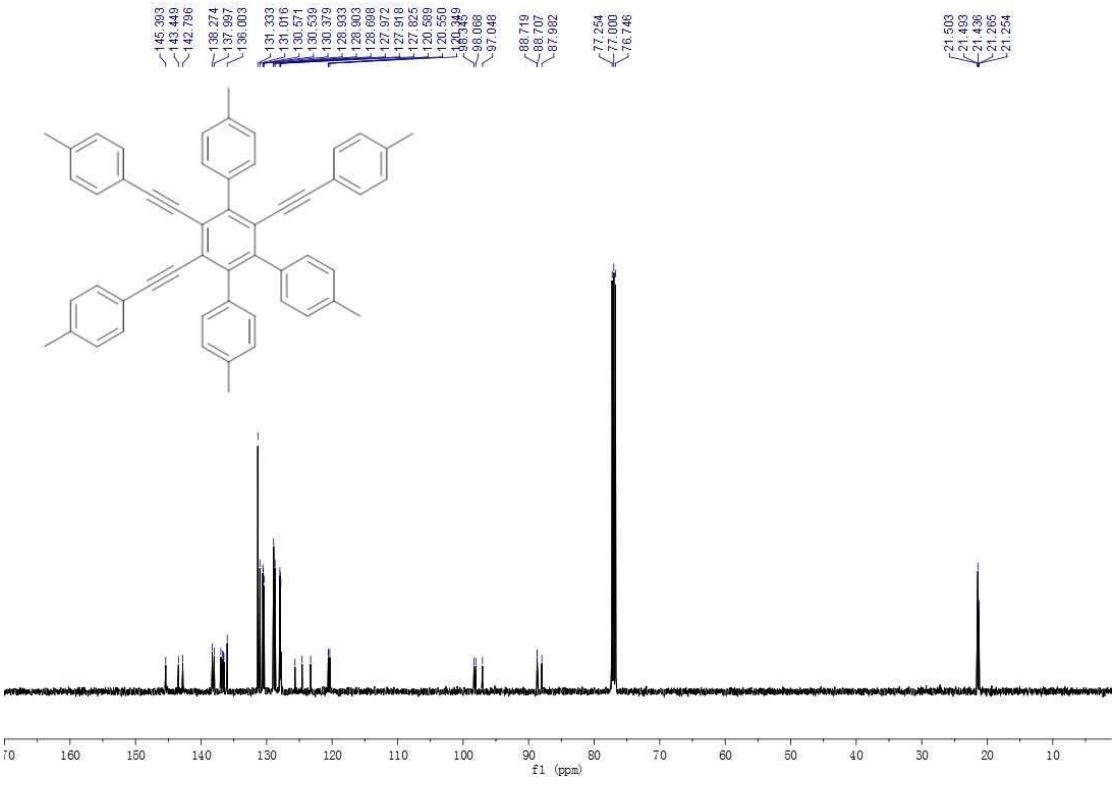


^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Dimethyl-4'-(p-tolyl)-3',5',6'-tris(p-tolylethynyl)-1,1':2',1''-terphenyl (2b):

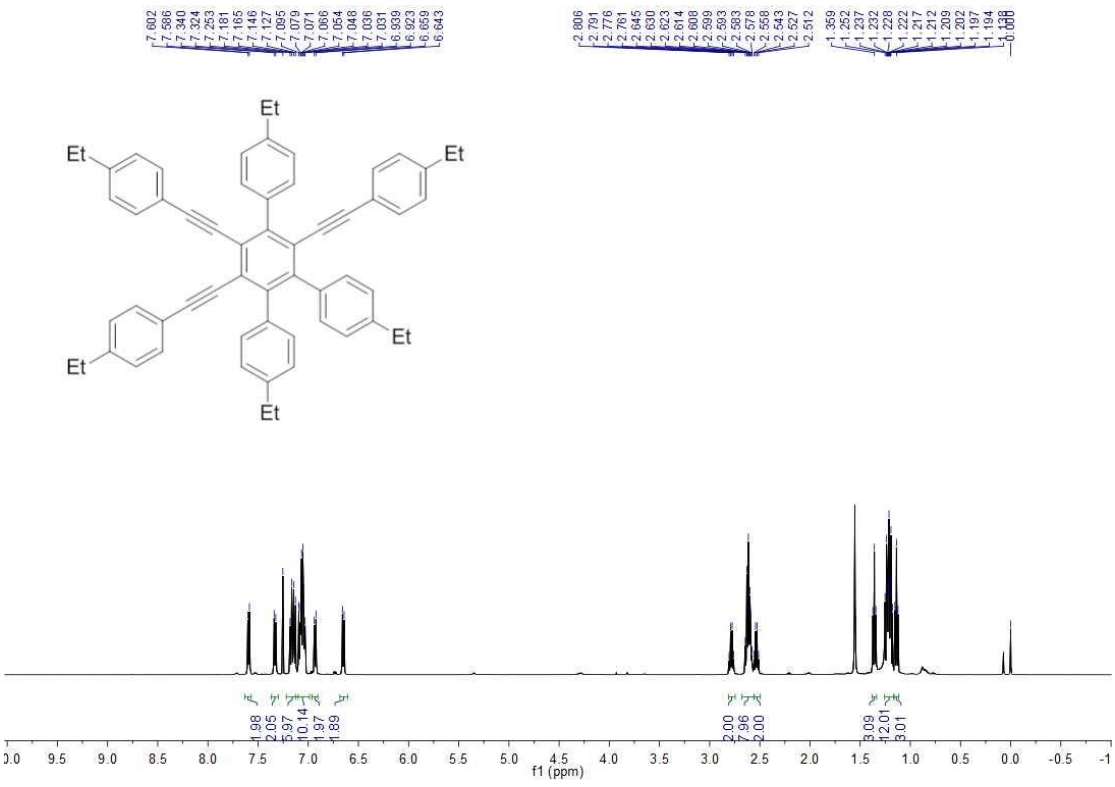


^{1}H NMR (500 MHz, $CDCl_3$)

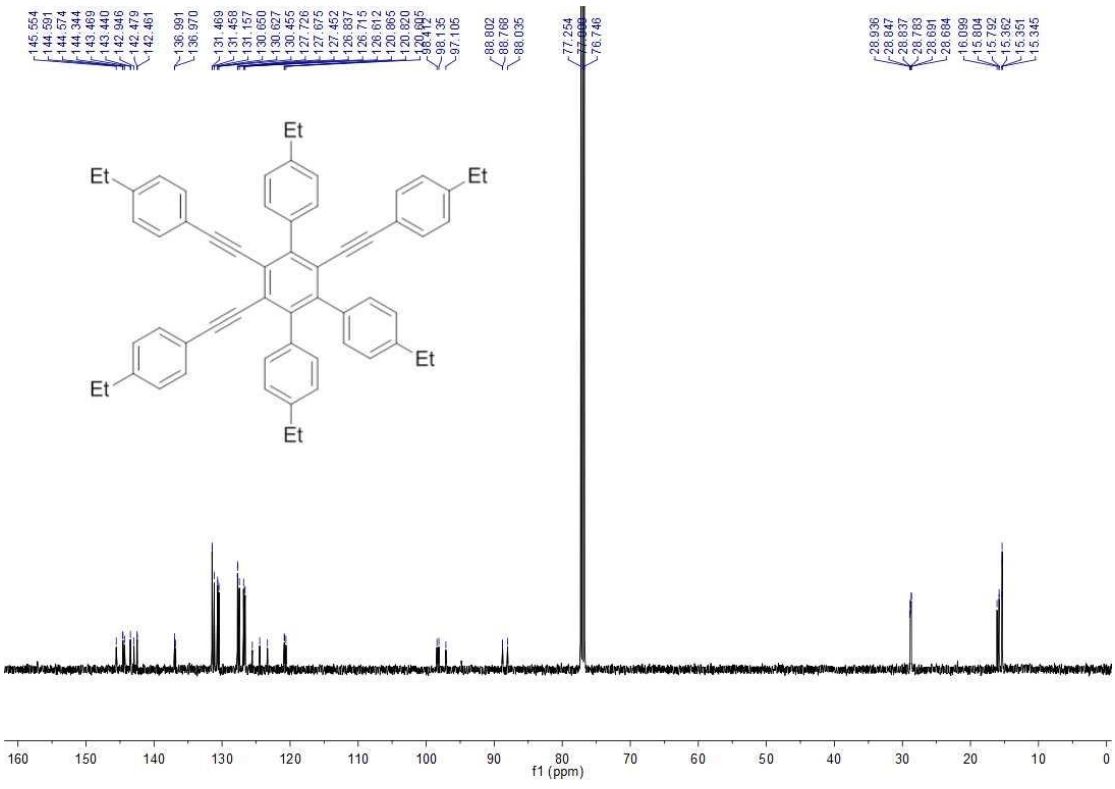


^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Diethyl-4'-(4-ethylphenyl)-3',5',6'-tris((4-ethylphenyl)ethynyl)-1,1':2',1''-ter phenyl (2c):

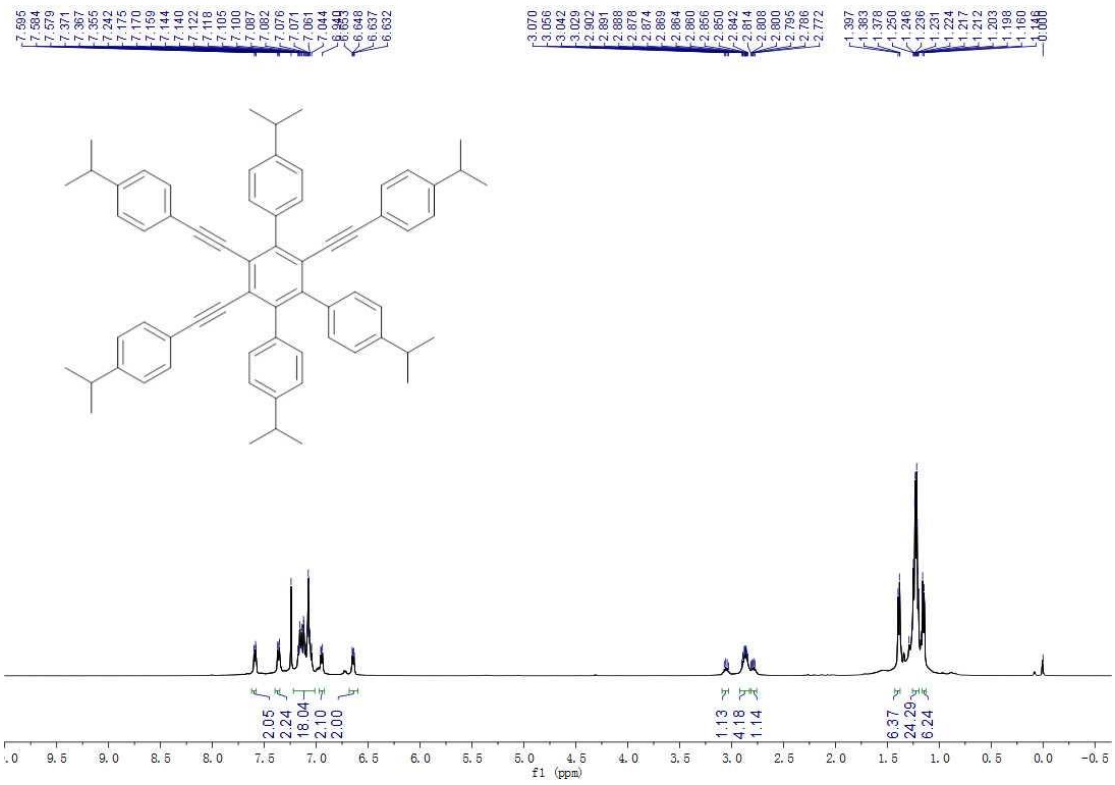


^{1}H NMR (500 MHz, $CDCl_3$)

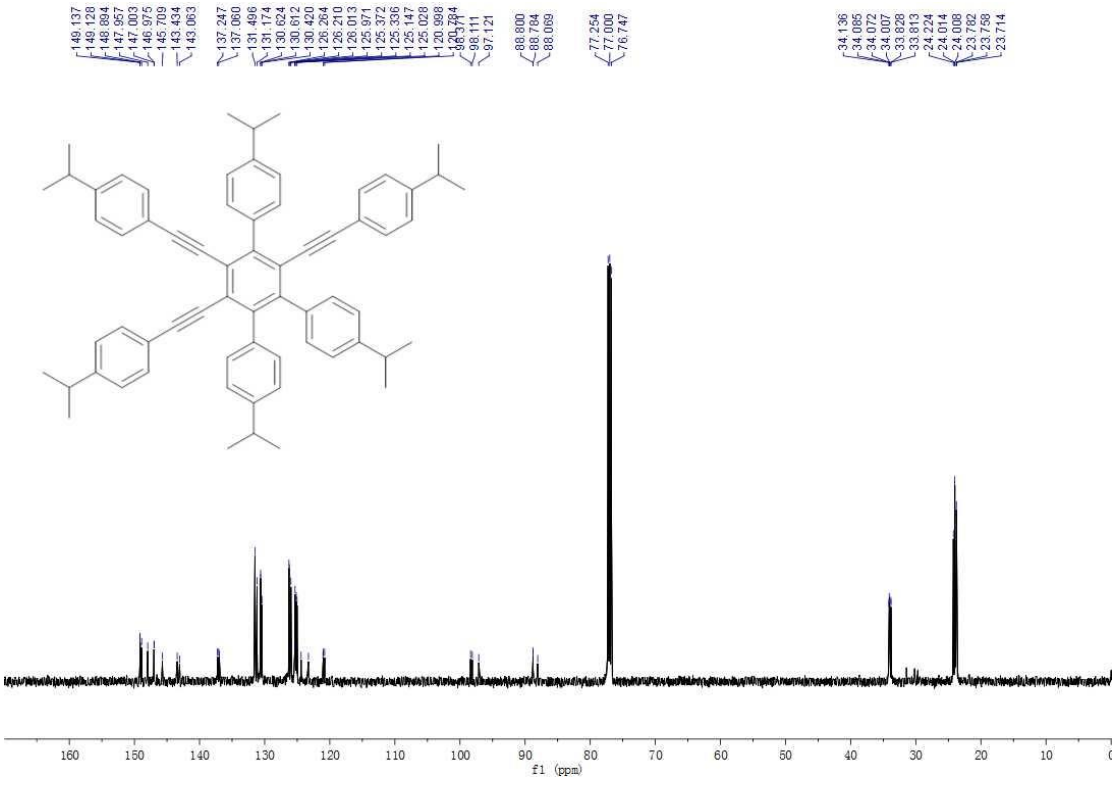


^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Diisopropyl-4'-(4-isopropylphenyl)-3',5',6'-tris((4-isopropylphenyl)ethynyl)-1,1':2',1''-terphenyl (2d):



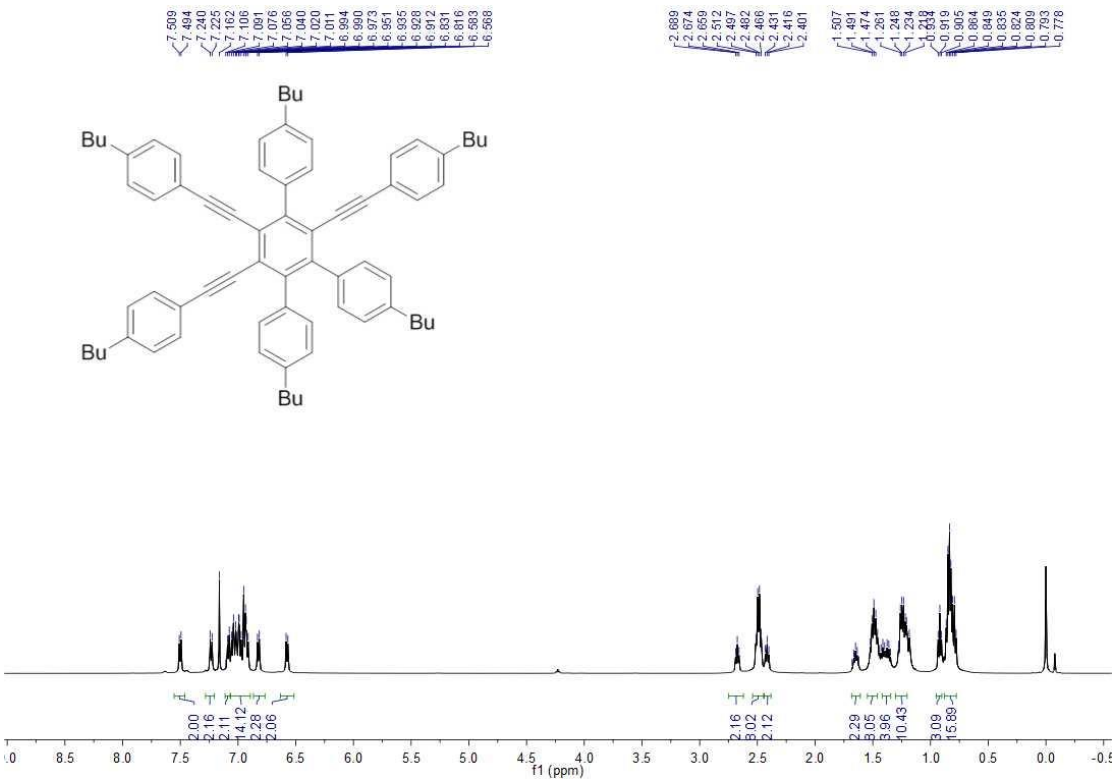
^{1}H NMR (500 MHz, $CDCl_3$)



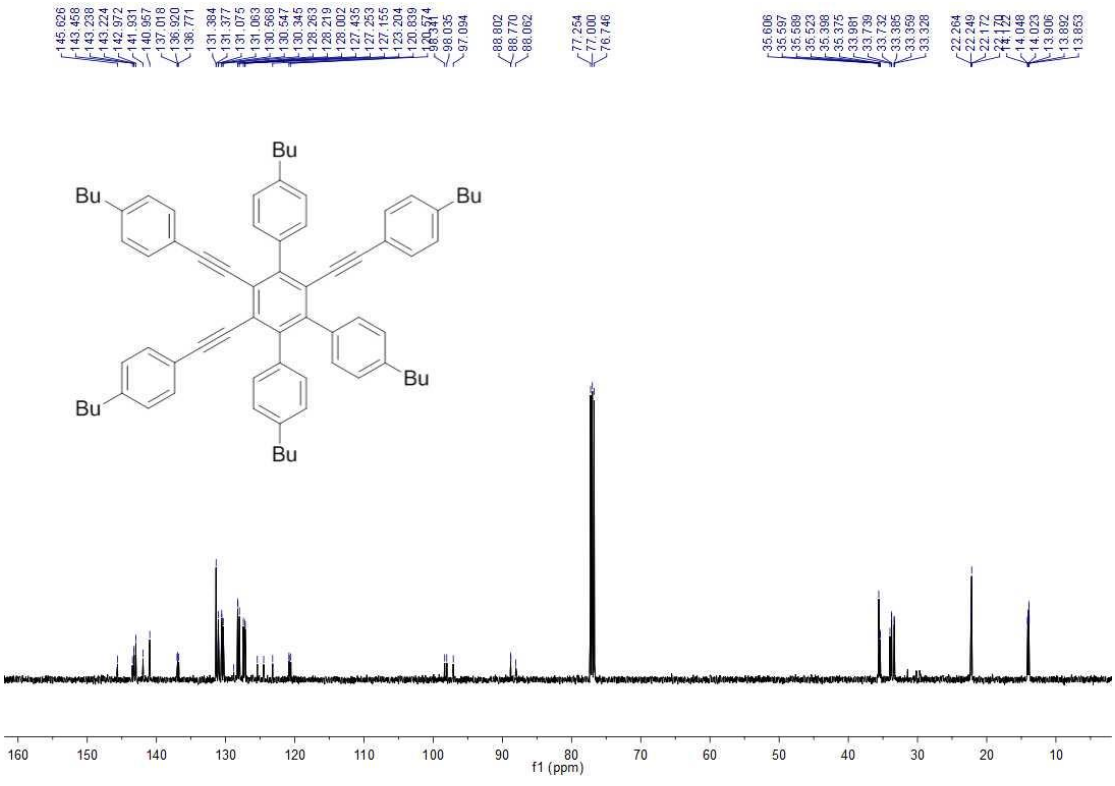
^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Dibutyl-4'-(4-butylphenyl)-3',5',6'-tris((4-butylphenyl)ethynyl)-1,1':2',1''-te

rphenyl (2e):

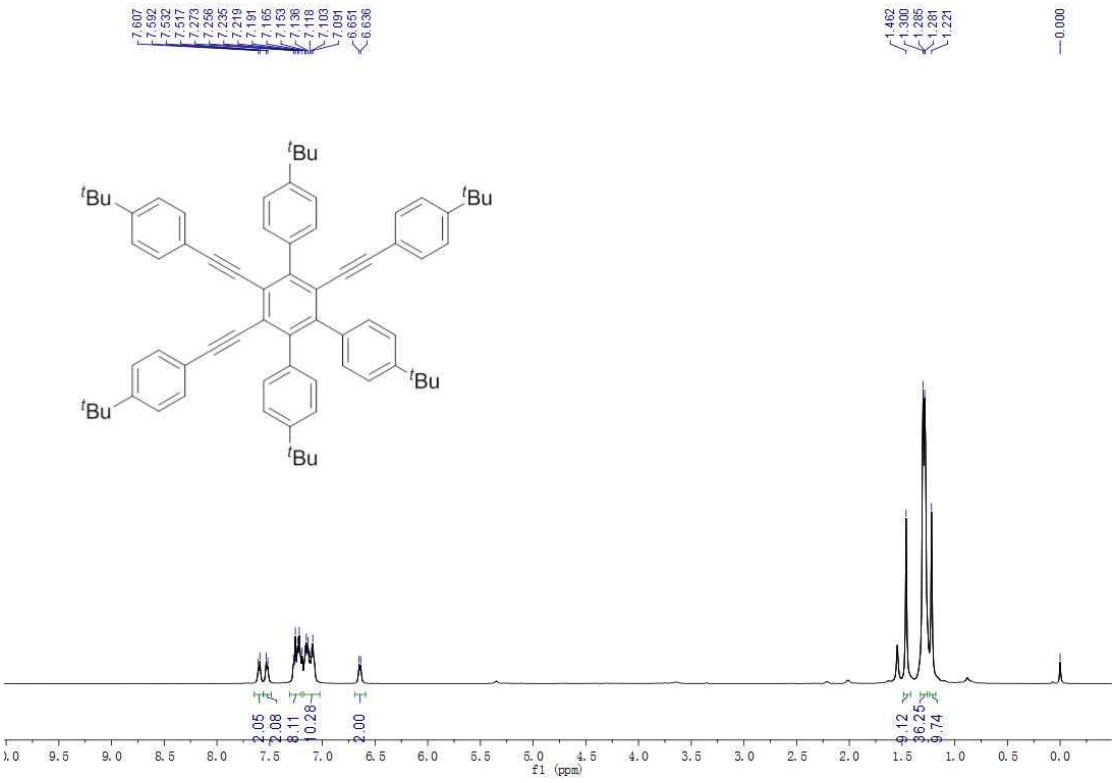


^{1}H NMR (500 MHz, $CDCl_3$)

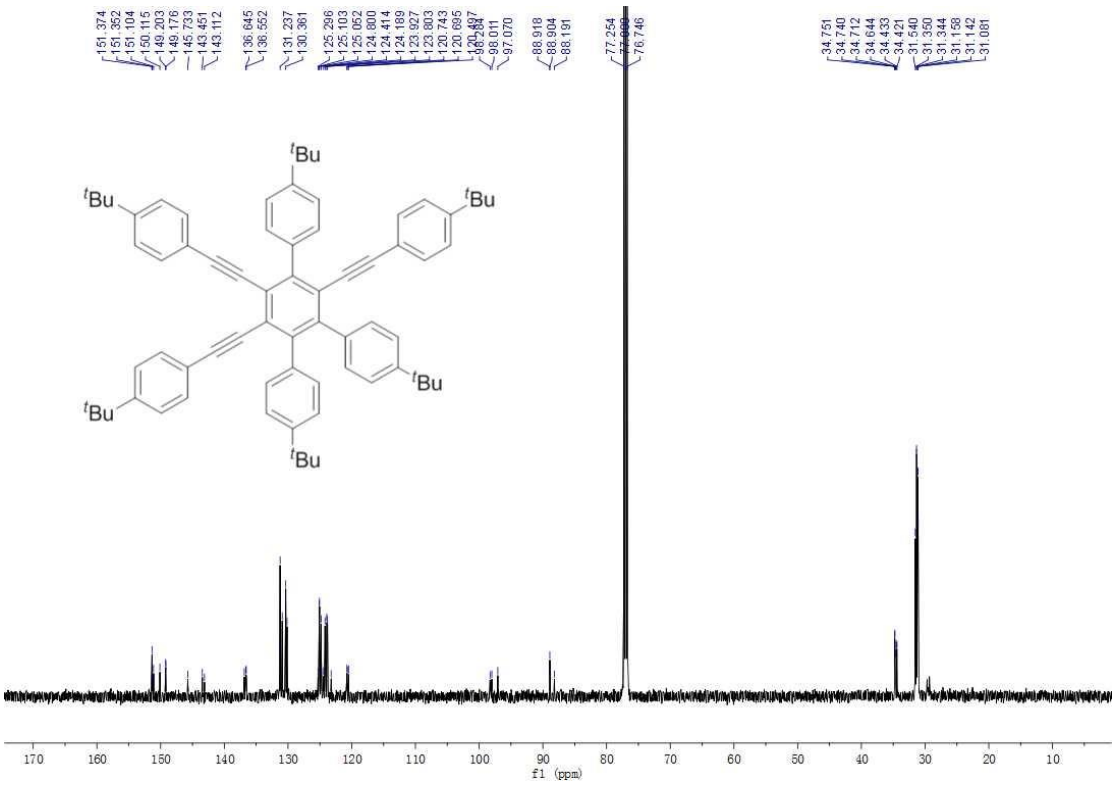


^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Di-tert-butyl-4'-(4-(tert-butyl)phenyl)-3',5',6'-tris((4-(tert-butyl)phenyl)ethynyl)-1,1':2',1''-terphenyl (2f):

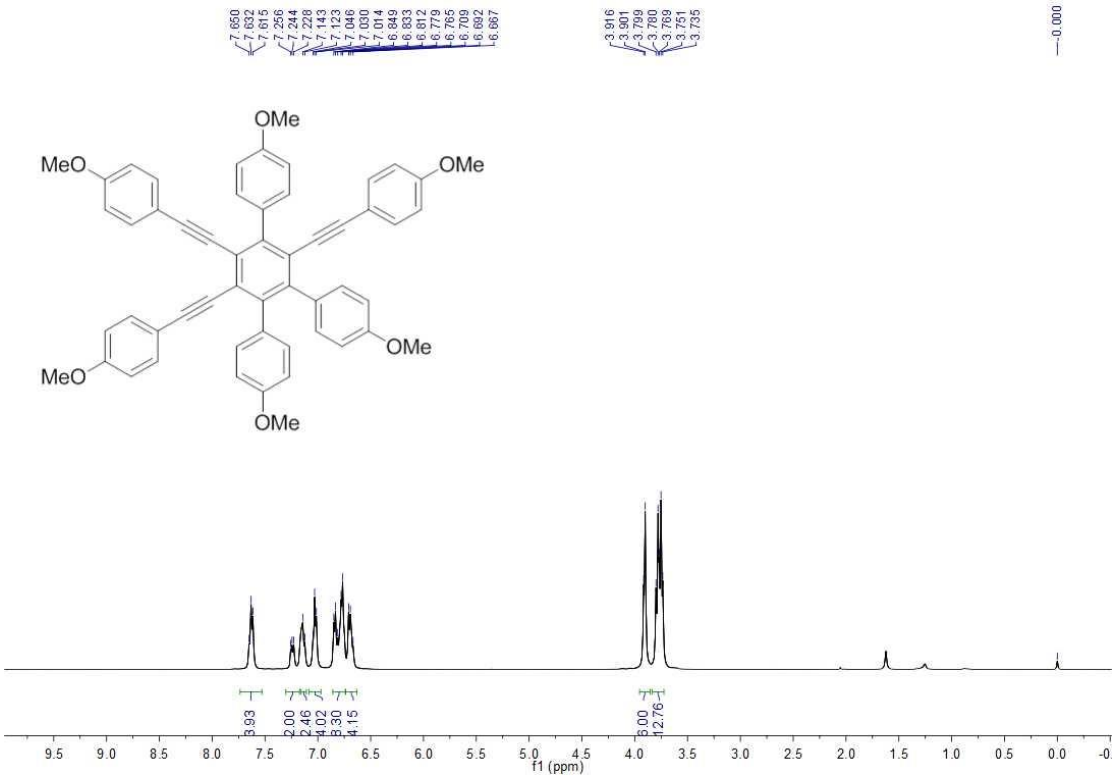


^{1}H NMR (500 MHz, $CDCl_3$)

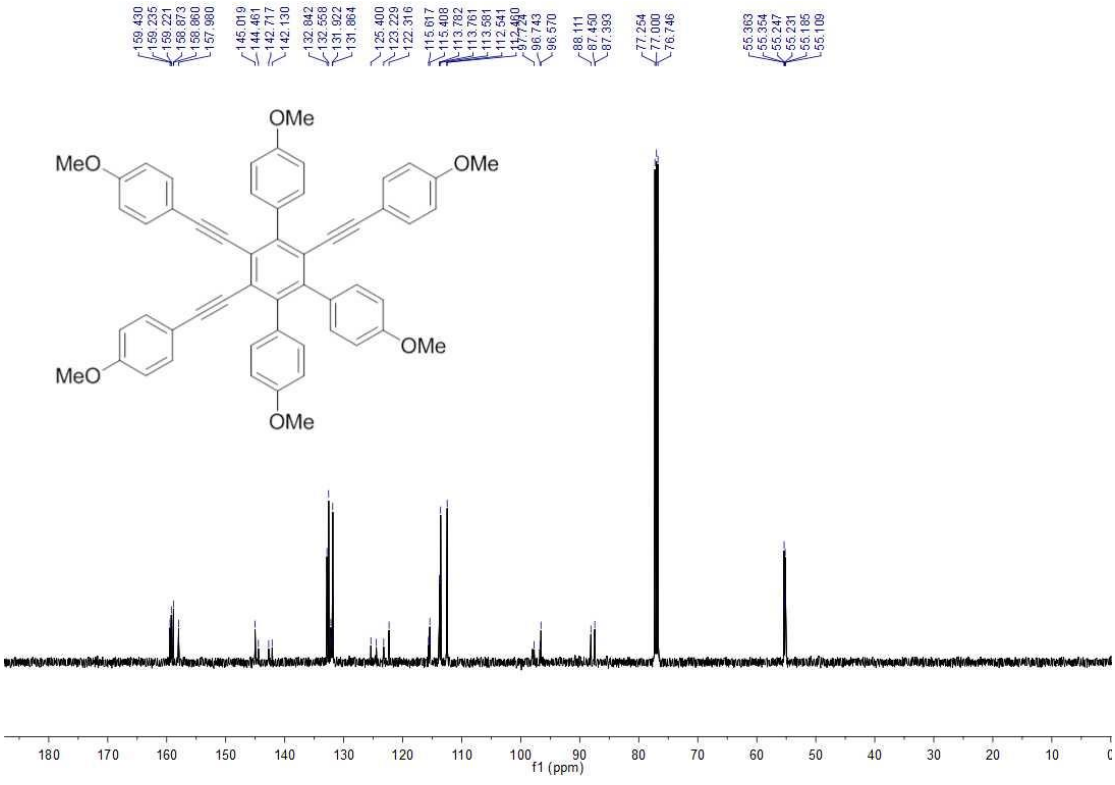


^{13}C NMR (125 MHz, $CDCl_3$)

4,4''-Dimethoxy-4'-(4-methoxyphenyl)-3',5',6'-tris((4-methoxyphenyl)ethynyl)-1, 1':2',1''-terphenyl (2g):

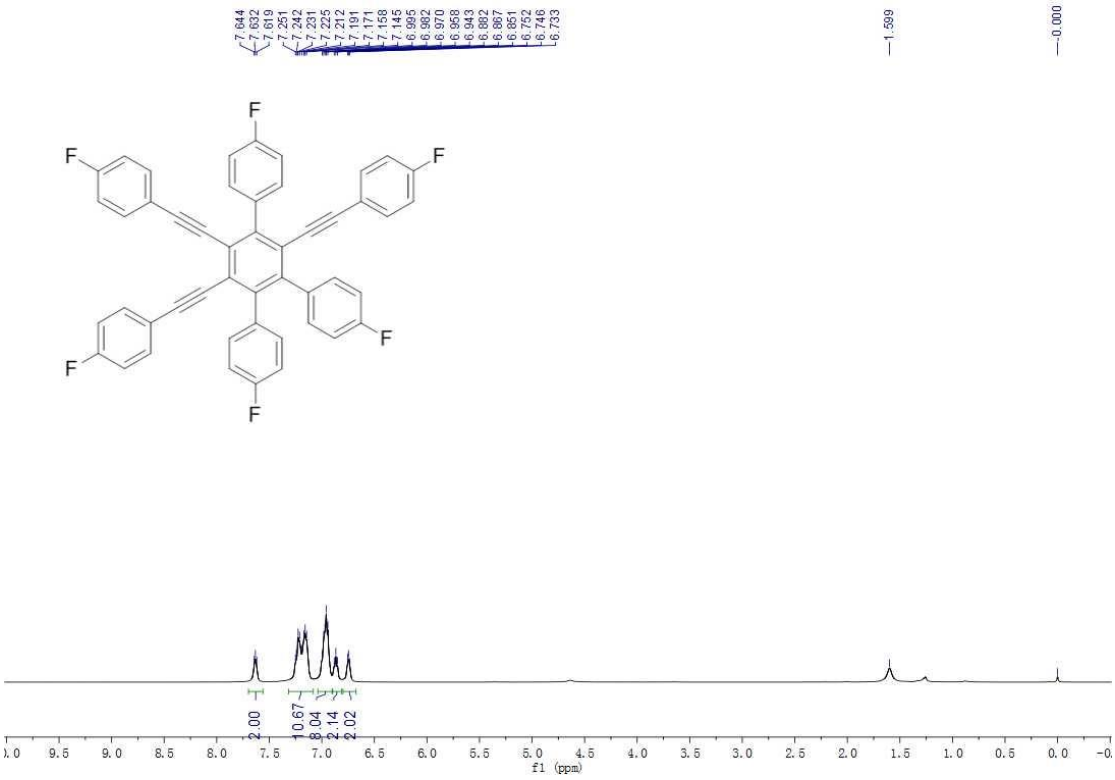


^{1}H NMR (500 MHz, $CDCl_3$)

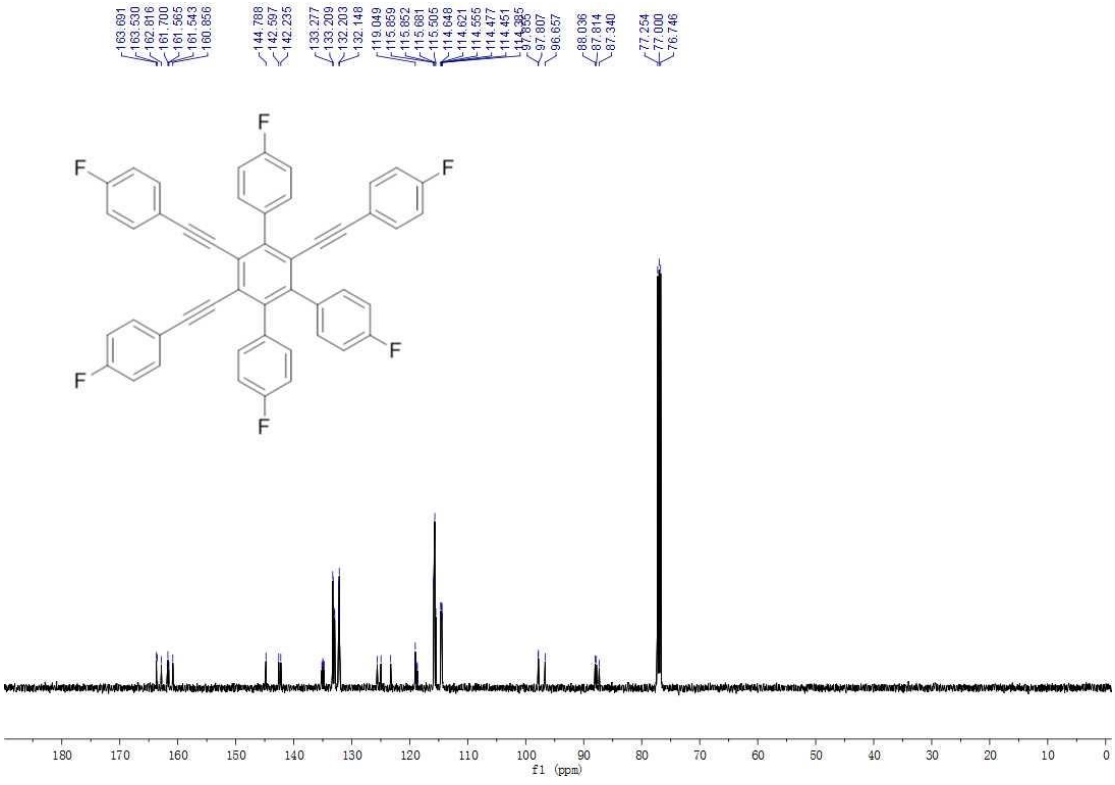


^{13}C NMR (125 MHz, $CDCl_3$)

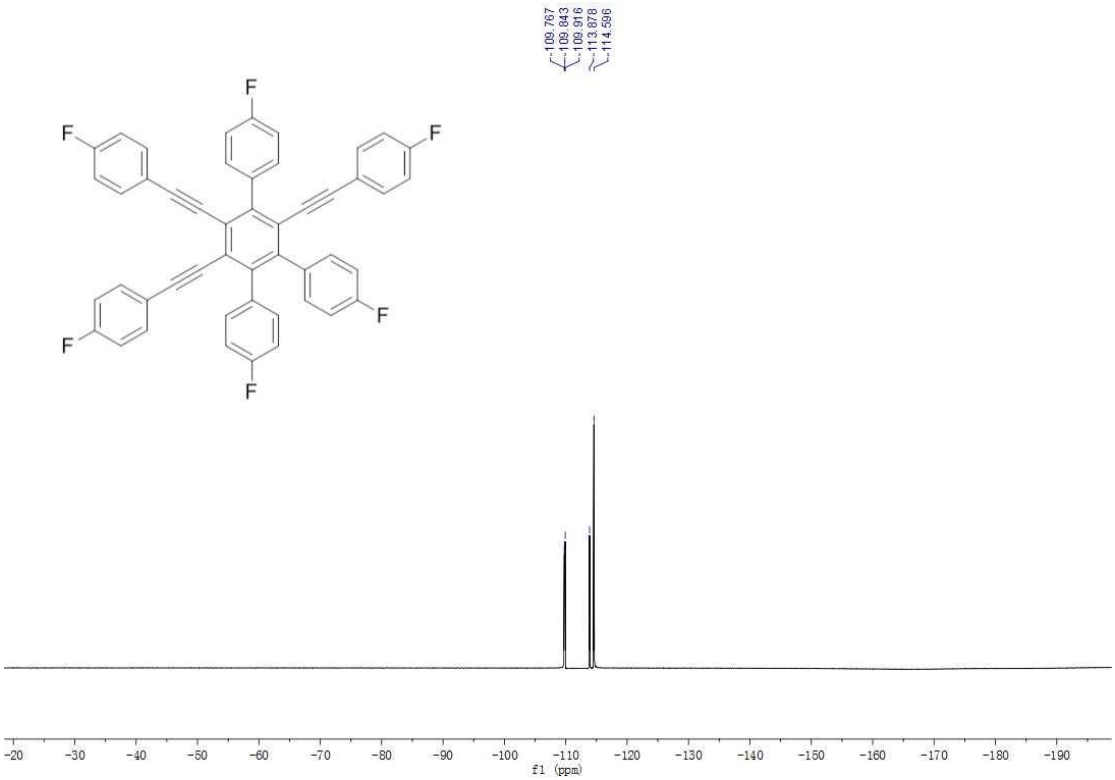
4,4''-Difluoro-4'-(4-fluorophenyl)-3',5',6'-tris((4-fluorophenyl)ethynyl)-1,1':2',1''-terphenyl (2h):



^{1}H NMR (500 MHz, $CDCl_3$)

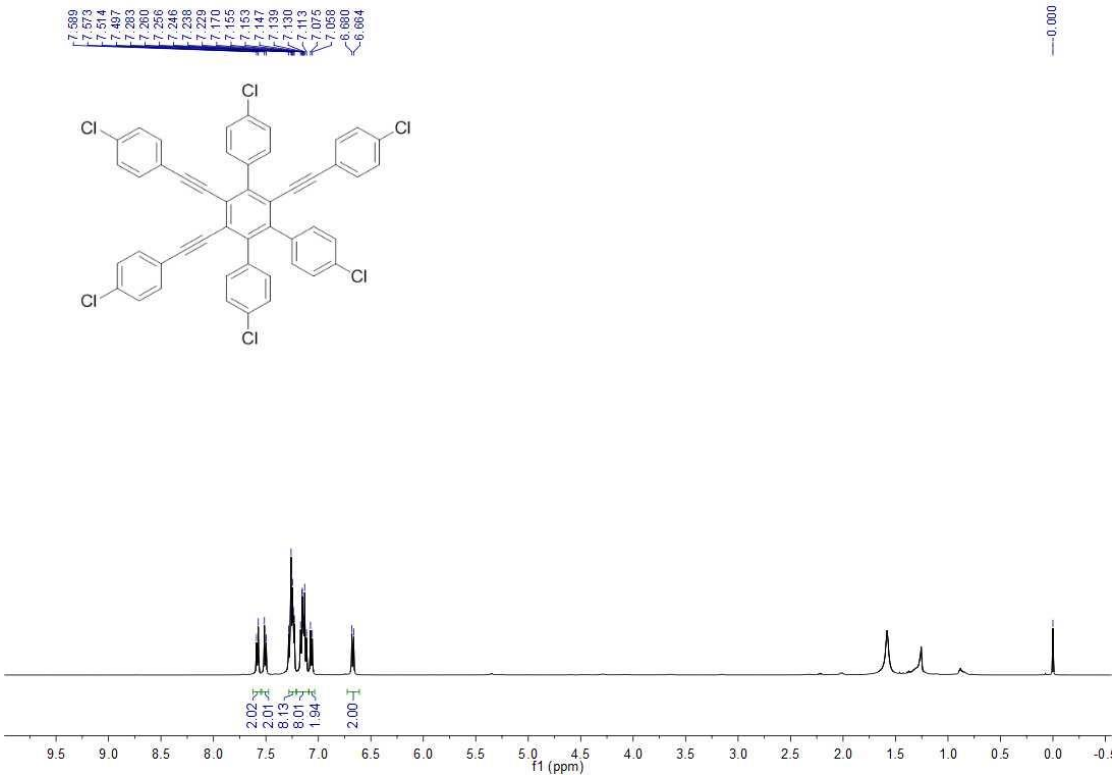


^{13}C NMR (125 MHz, $CDCl_3$)

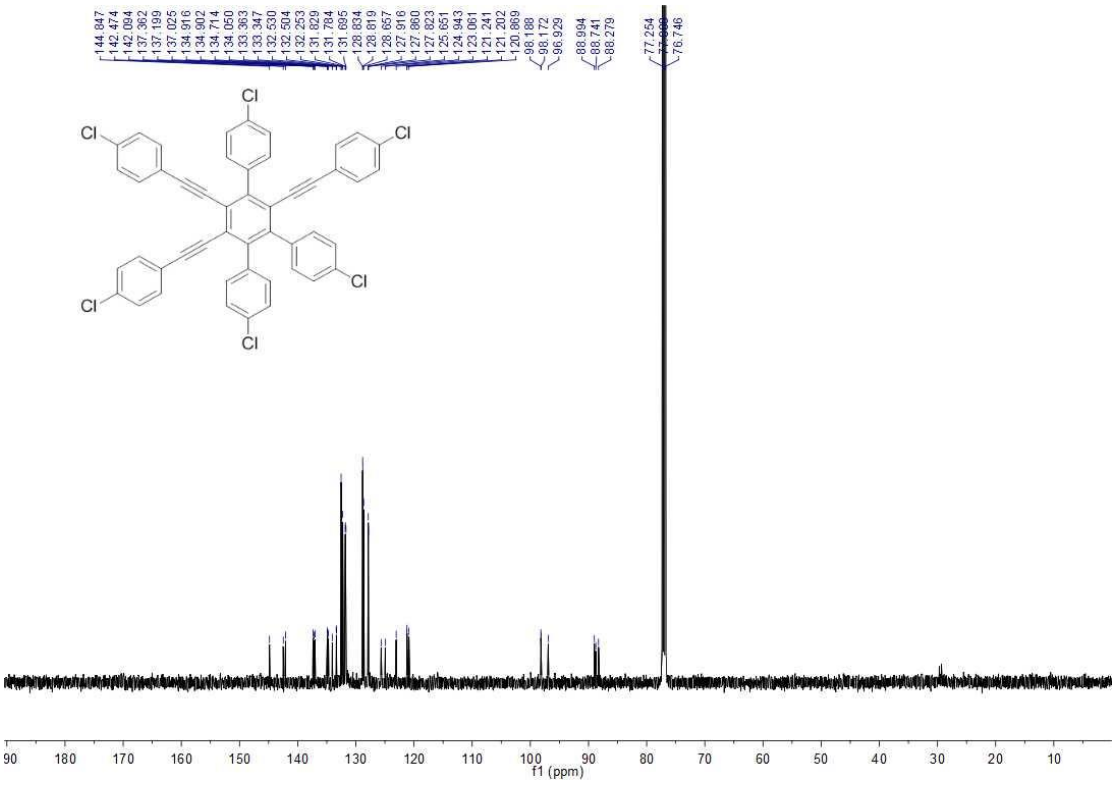


^{19}F NMR (471 MHz, $CDCl_3$)

4,4''-Dichloro-4'-(4-chlorophenyl)-3',5',6'-tris((4-chlorophenyl)ethynyl)-1,1':2',1''-terphenyl (2i):



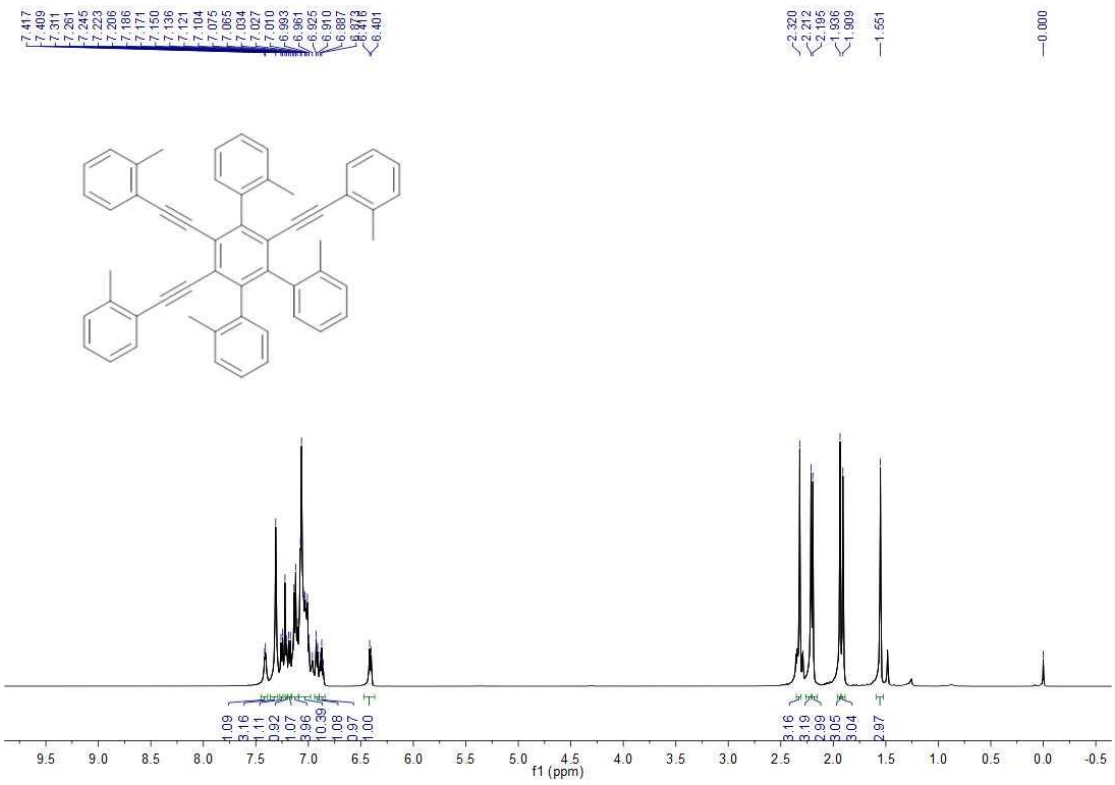
^{1}H NMR (500 MHz, $CDCl_3$)



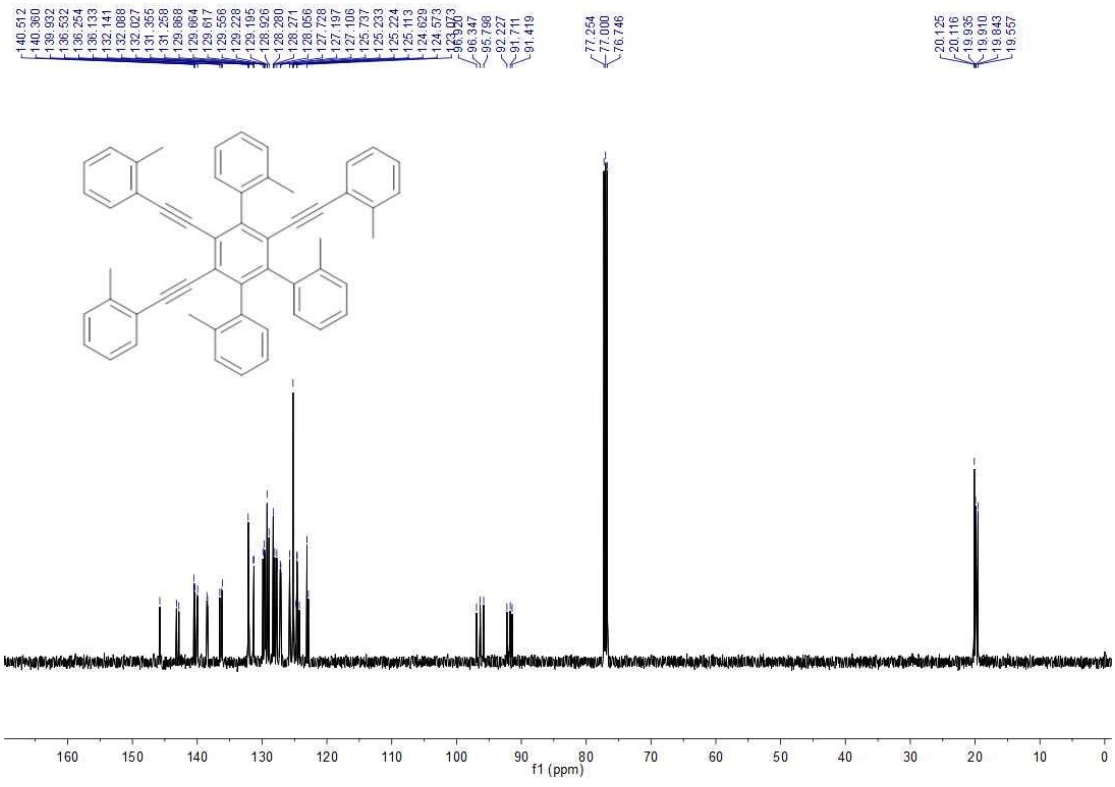
^{13}C NMR (125 MHz, $CDCl_3$)

Dimethyl

2,2''-dimethyl-4'-(o-tolyl)-3',5',6'-tris(o-tolylethynyl)-1,1':2',1''-terphenyl (2j):

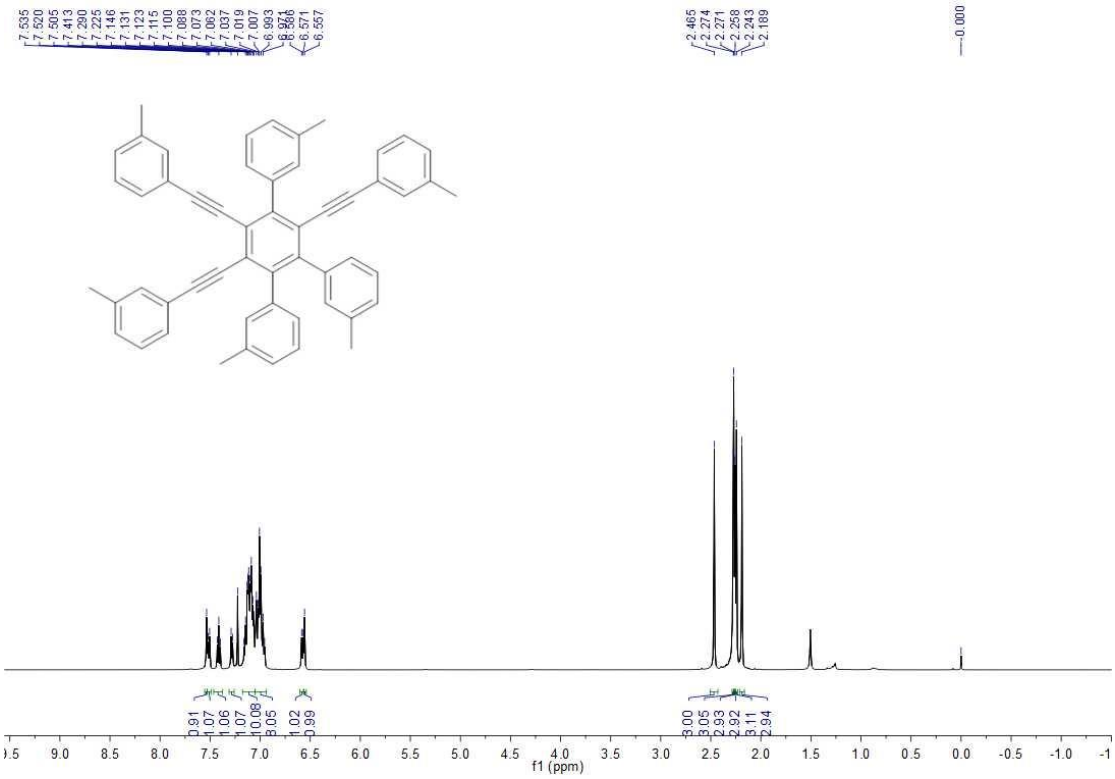


^{1}H NMR (500 MHz, $CDCl_3$)

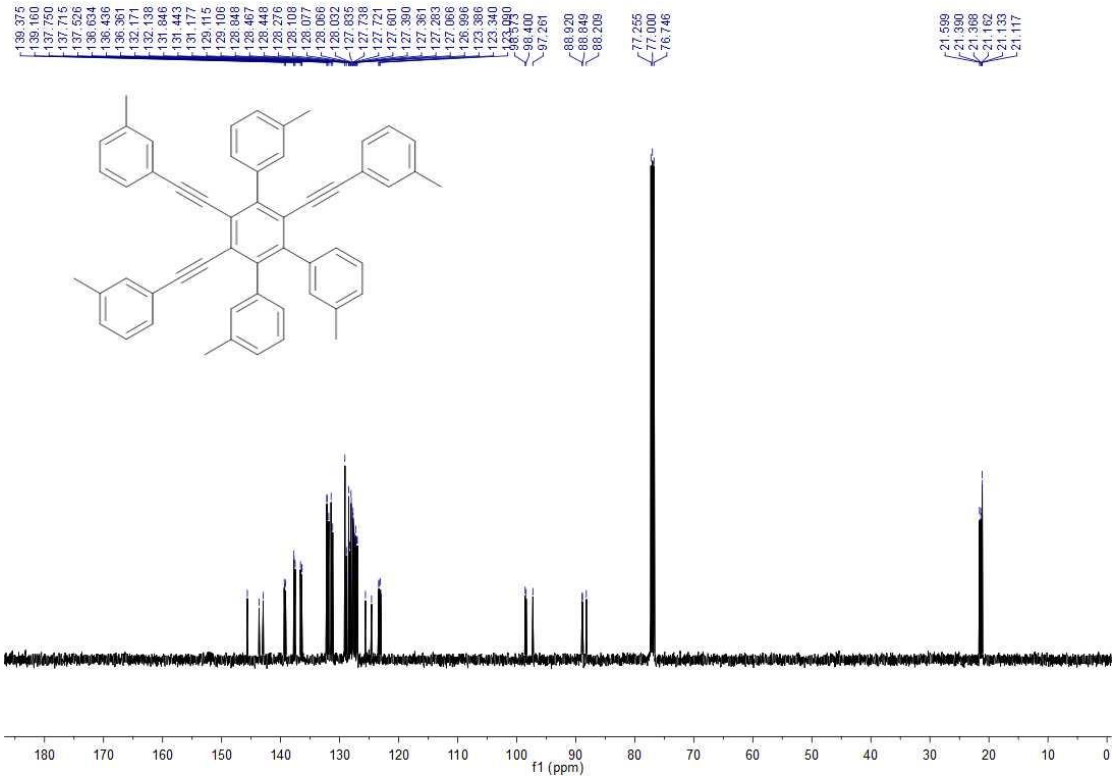


^{13}C NMR (125 MHz, $CDCl_3$)

3,3''-Dimethyl-4'-(m-tolyl)-3',5',6'-tris(m-tolylethynyl)-1,1':2',1''-terphenyl (2k):

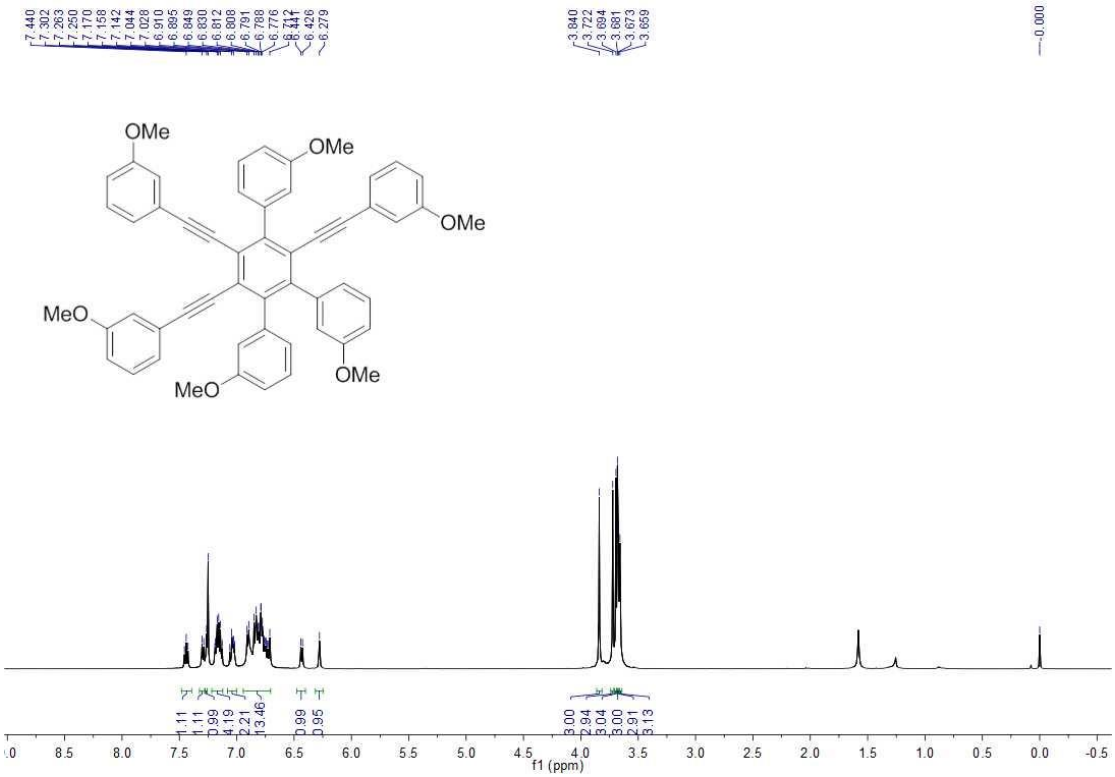


^{1}H NMR (500 MHz, $CDCl_3$)

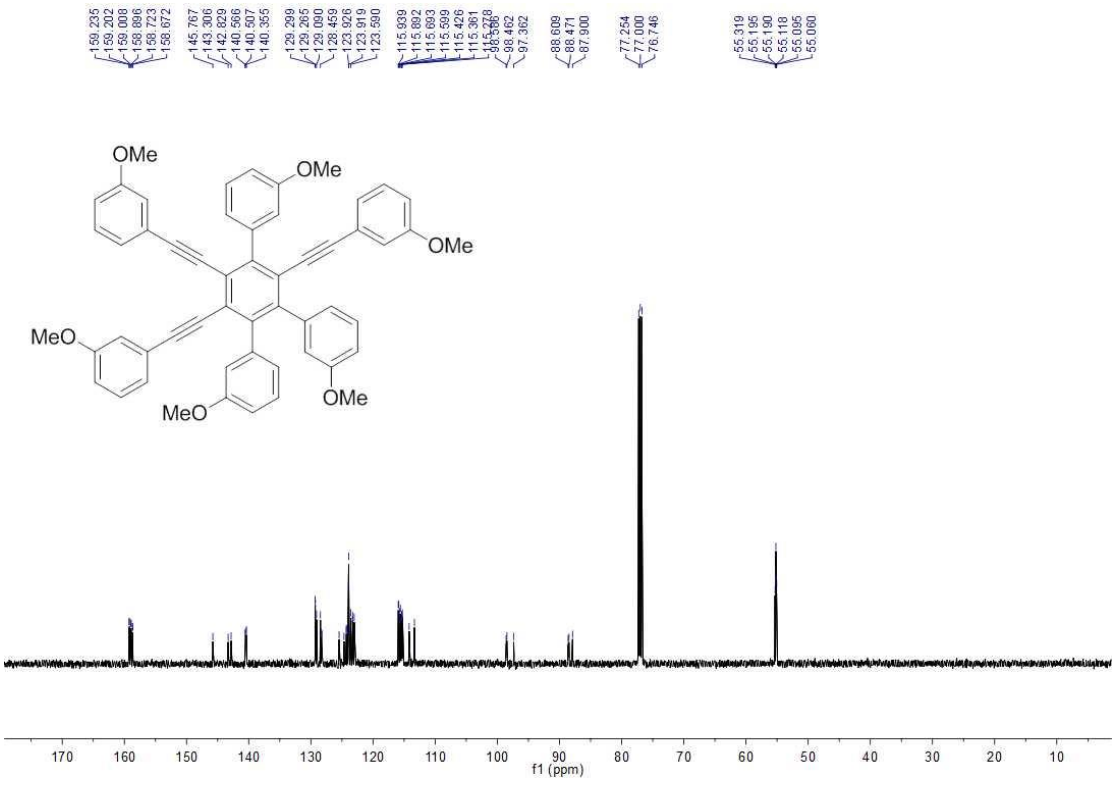


^{13}C NMR (125 MHz, $CDCl_3$)

3,3''-Dimethoxy-4'-(3-methoxyphenyl)-3',5',6'-tris((3-methoxyphenyl)ethynyl)-1,1':2',1''-terphenyl (2l):

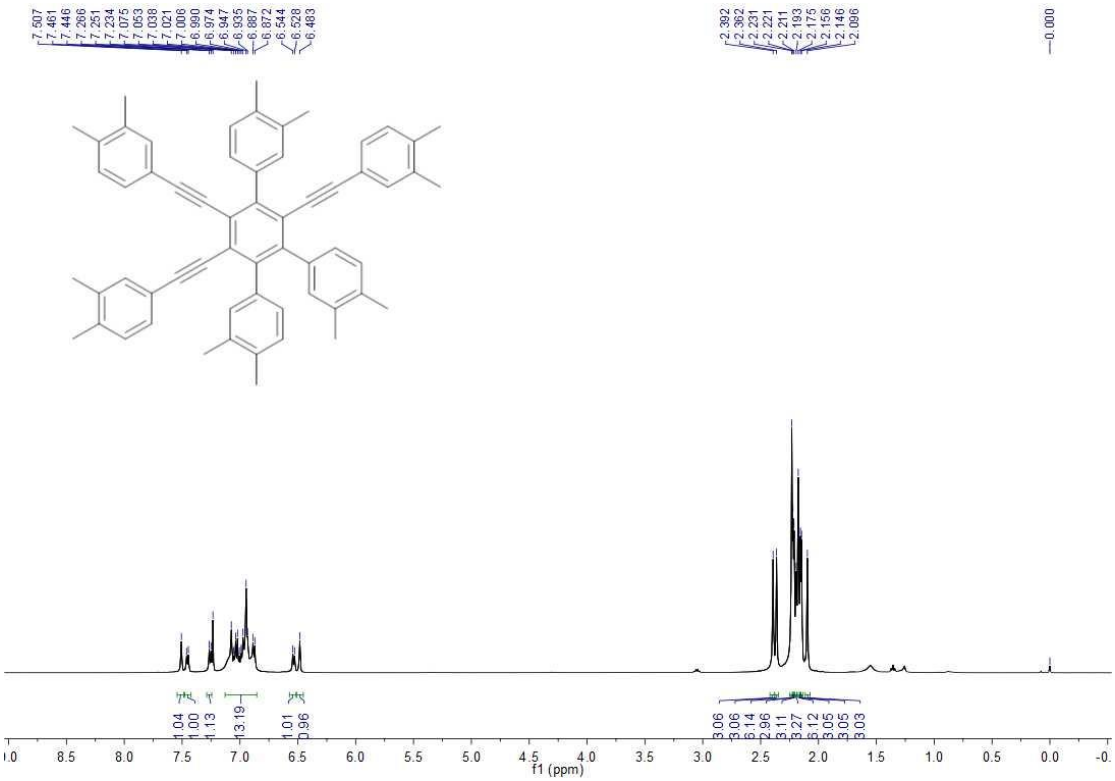


^{1}H NMR (500 MHz, $CDCl_3$)

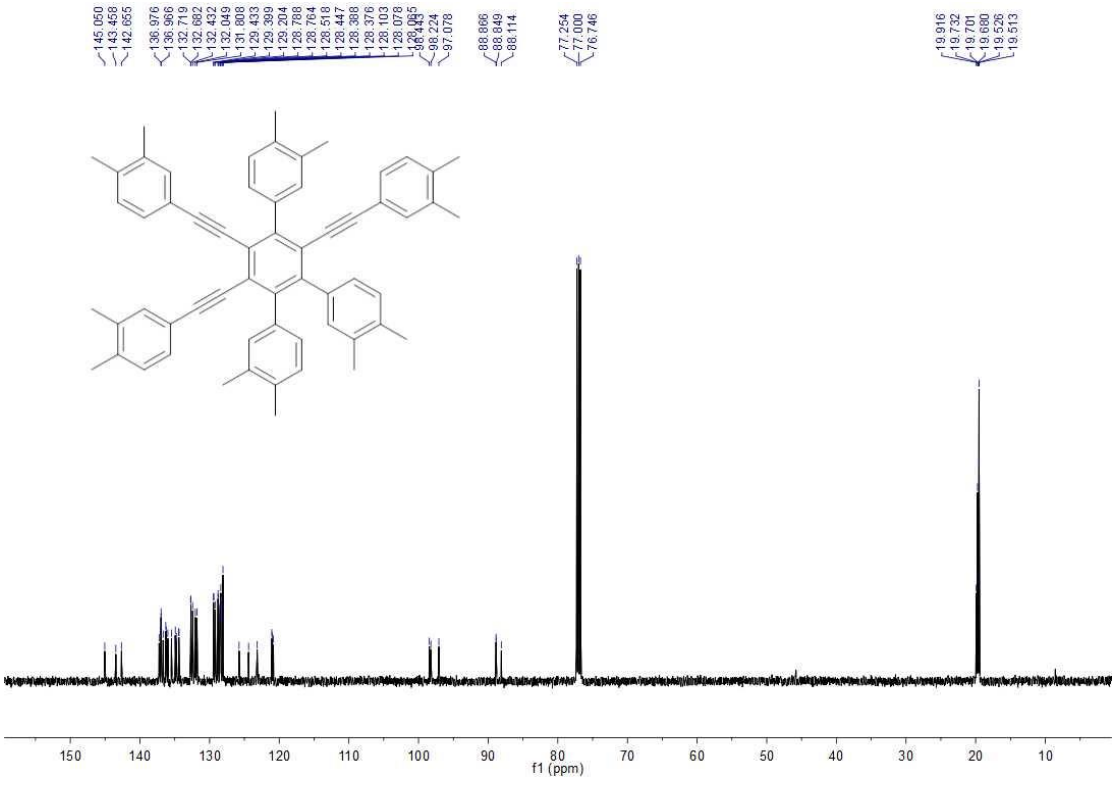


^{13}C NMR (125 MHz, $CDCl_3$)

4'-(3,4-Dimethylphenyl)-3',5',6'-tris((3,4-dimethylphenyl)ethynyl)-3,3'',4,4''-tetra methyl-1,1':2',1''-terphenyl (2m):

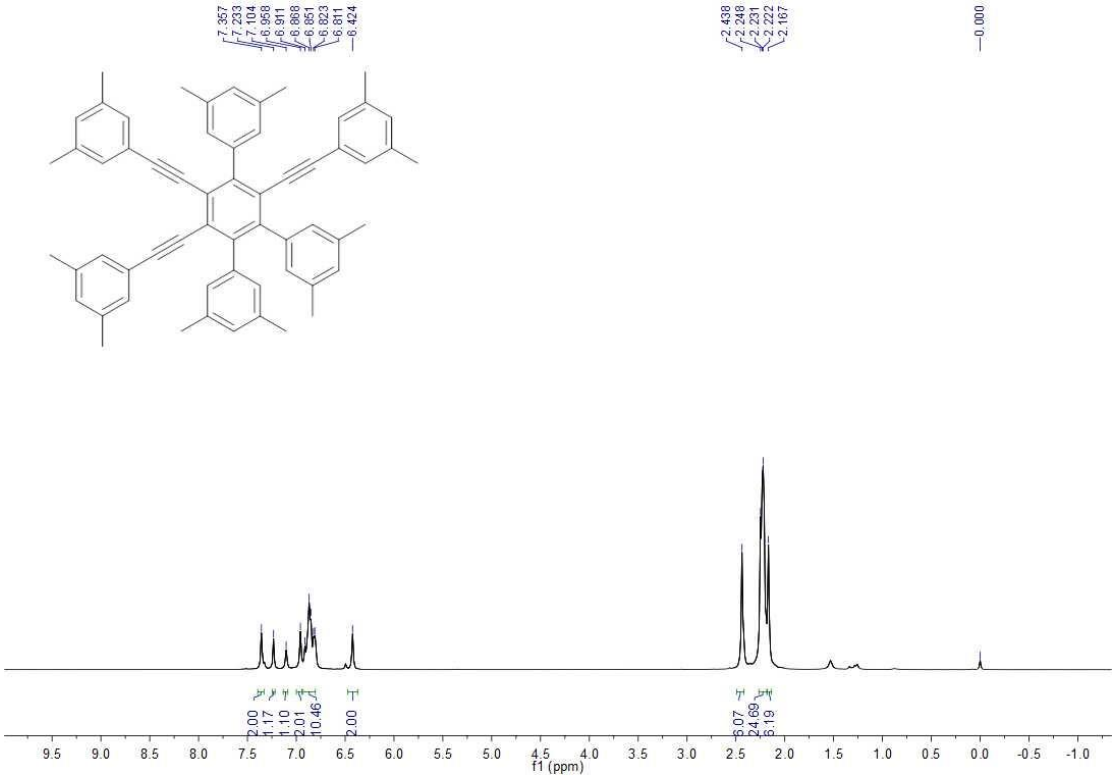


^{1}H NMR (500 MHz, $CDCl_3$)

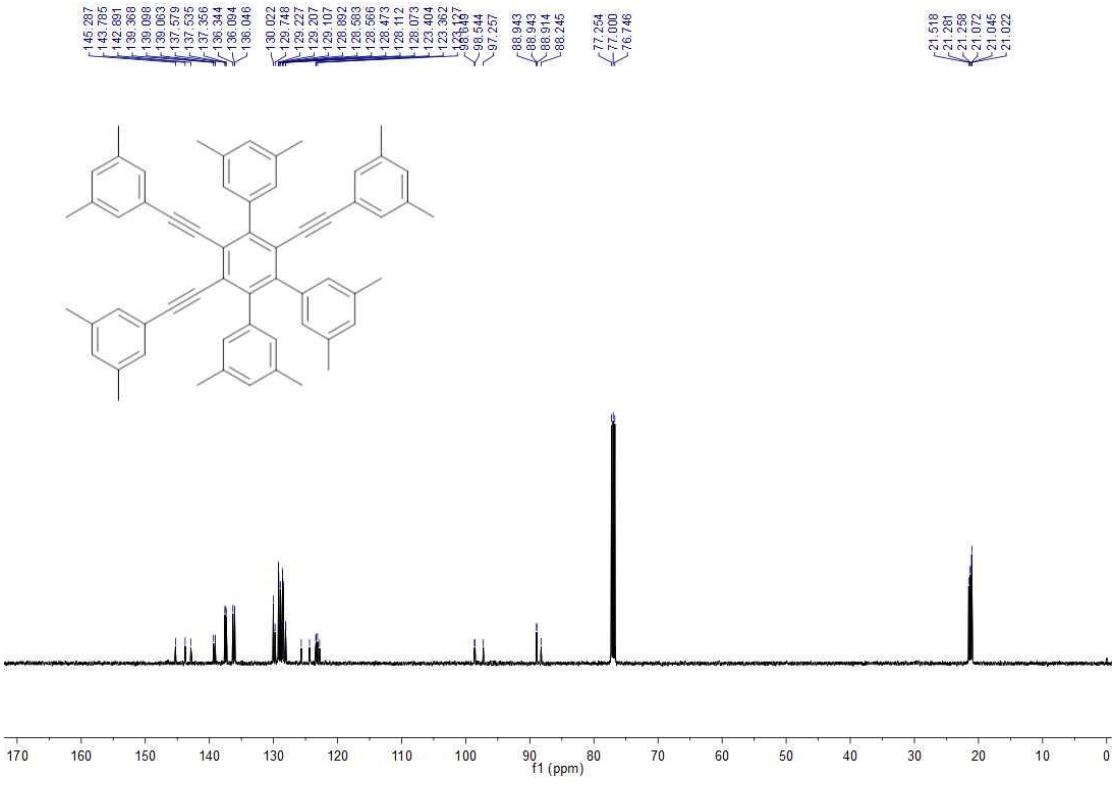


^{13}C NMR (125 MHz, $CDCl_3$)

4'-(3,5-Dimethylphenyl)-3',5',6'-tris((3,5-dimethylphenyl)ethynyl)-3,3'',5,5''-tetra methyl-1,1':2',1''-terphenyl (2n):

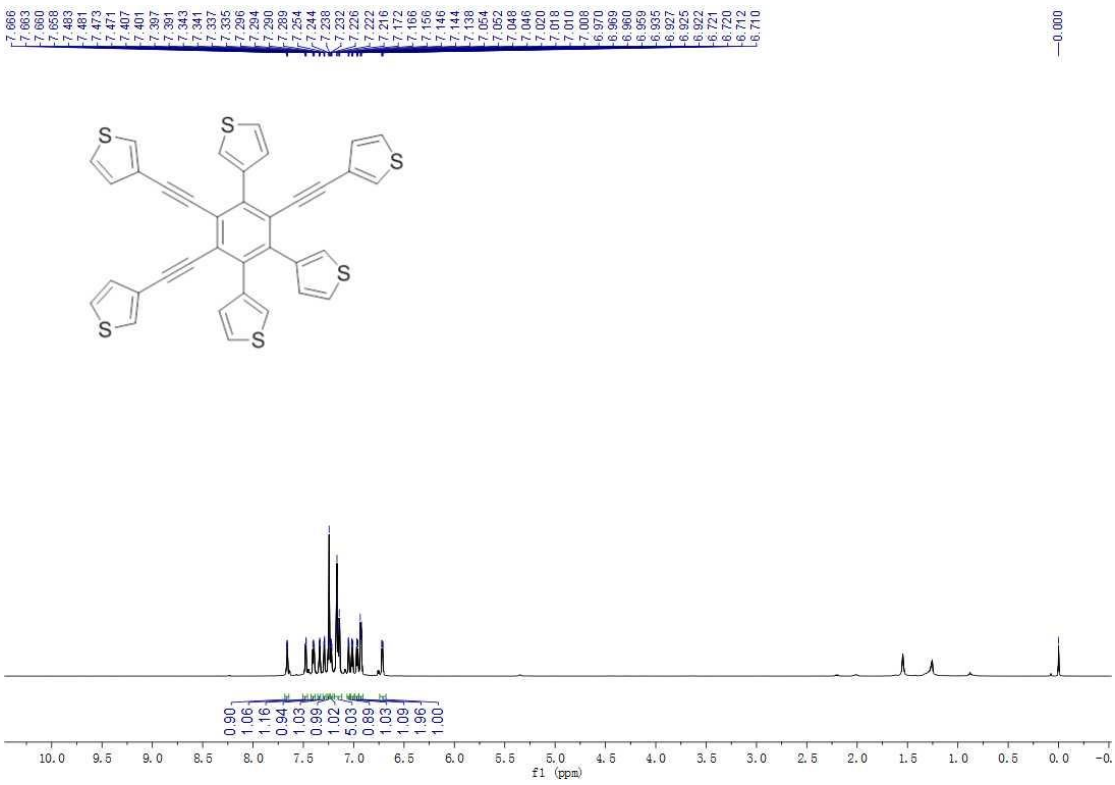


^{1}H NMR (500 MHz, $CDCl_3$)

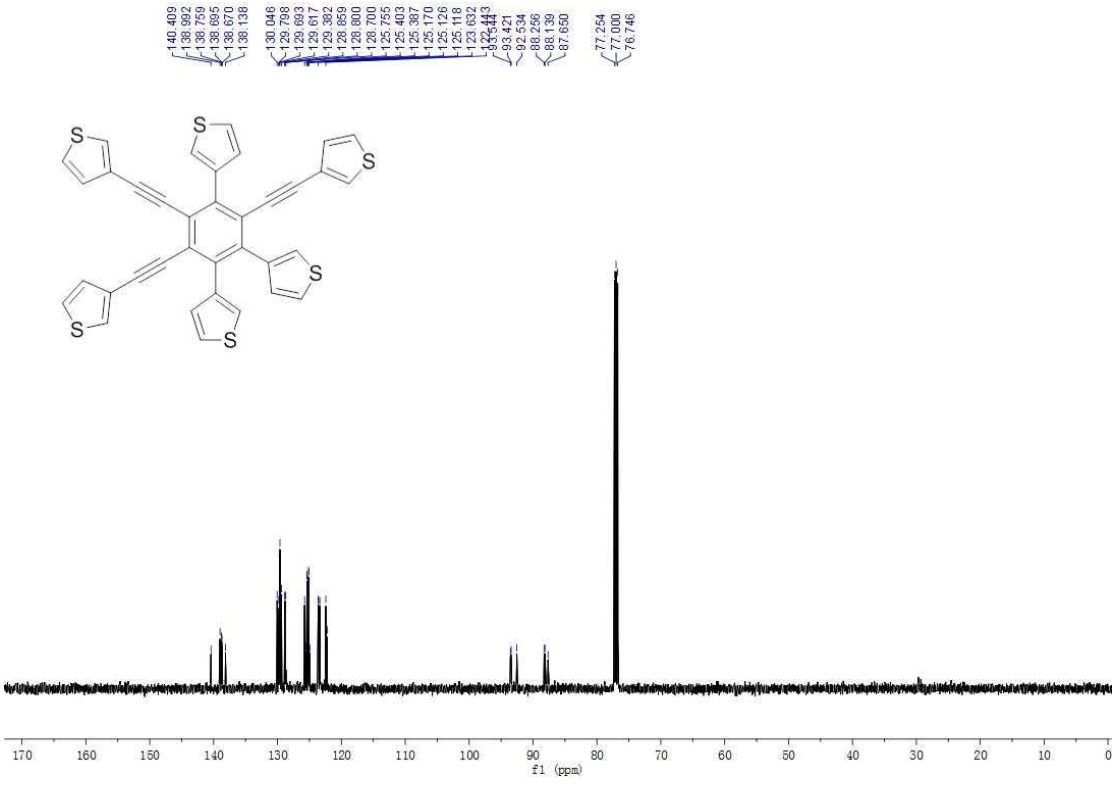


^{13}C NMR (125 MHz, $CDCl_3$)

3,3',3''-((3,5,6-Tri(thiophen-3-yl)benzene-1,2,4-triyl)tris(ethyne-2,1-diyl))trithiophene (2o):

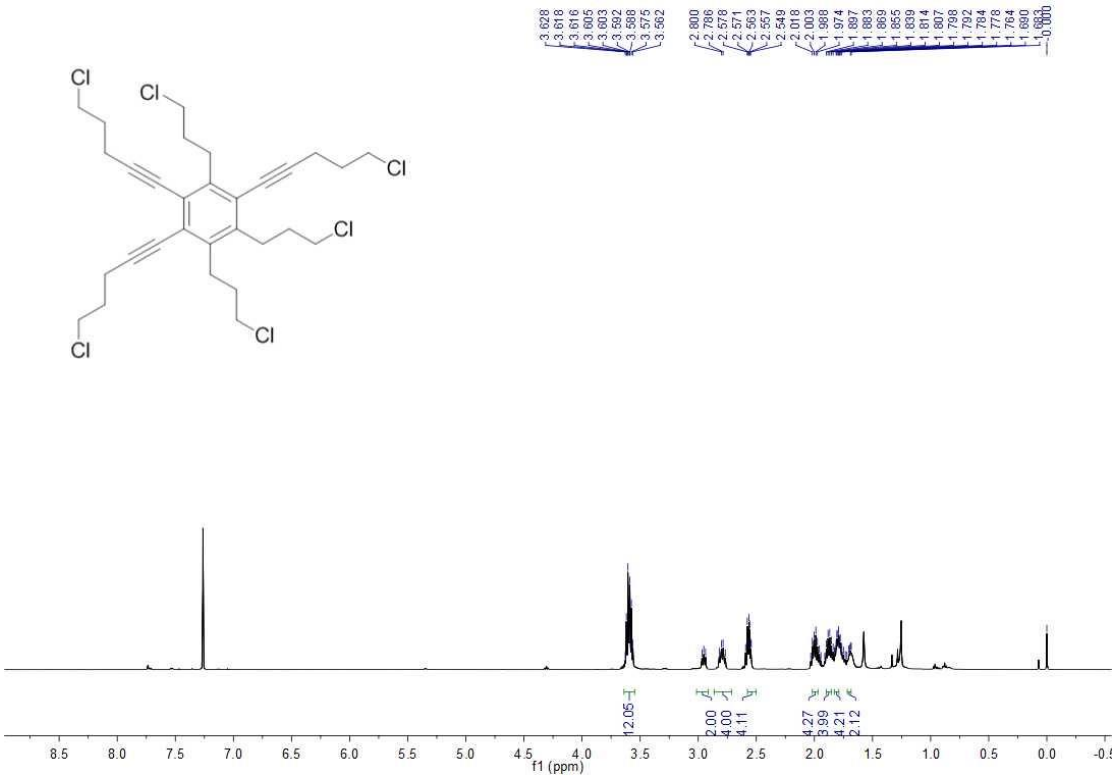


^{1}H NMR (500 MHz, $CDCl_3$)

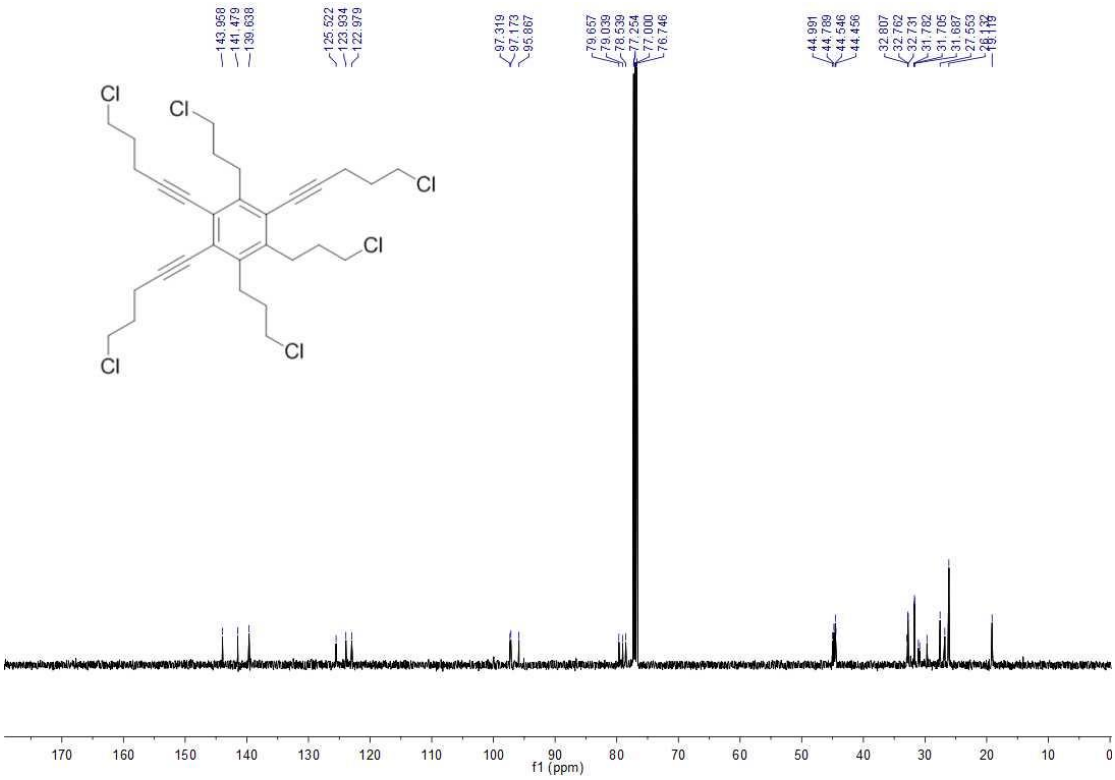


^{13}C NMR (125 MHz, $CDCl_3$)

1,2,4-Tris(5-chloropent-1-yn-1-yl)-3,5,6-tris(3-chloropropyl)benzene (2p):

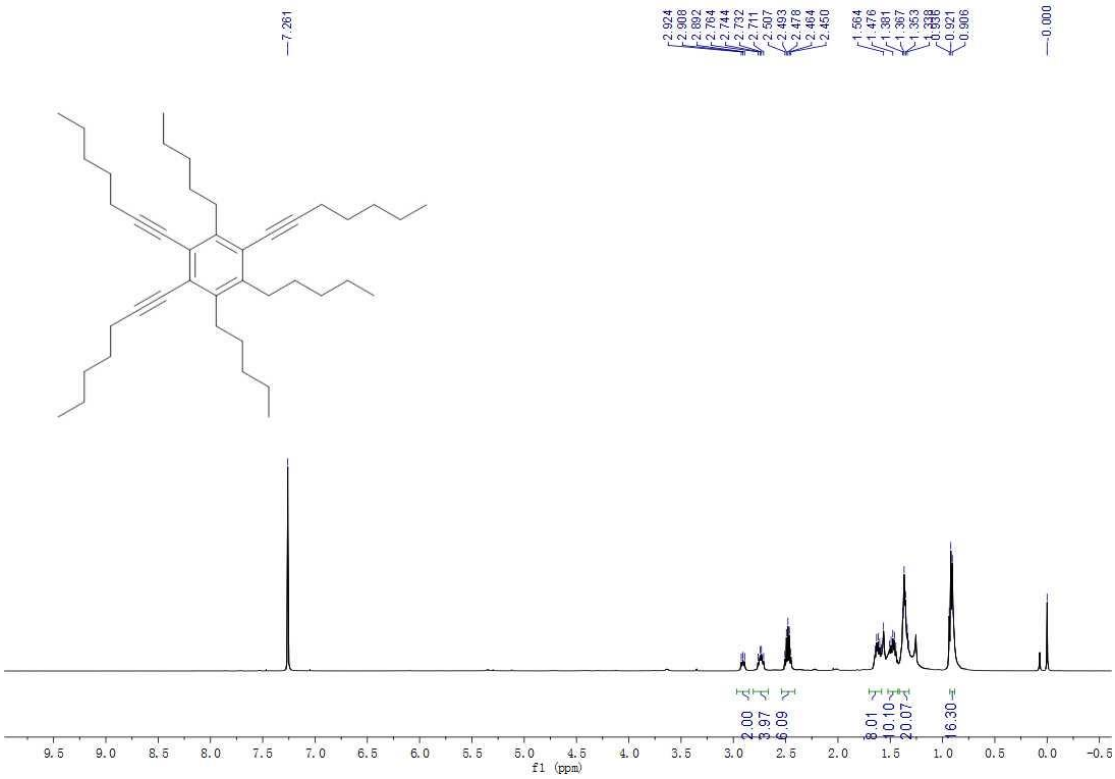


^{1}H NMR (500 MHz, $CDCl_3$)

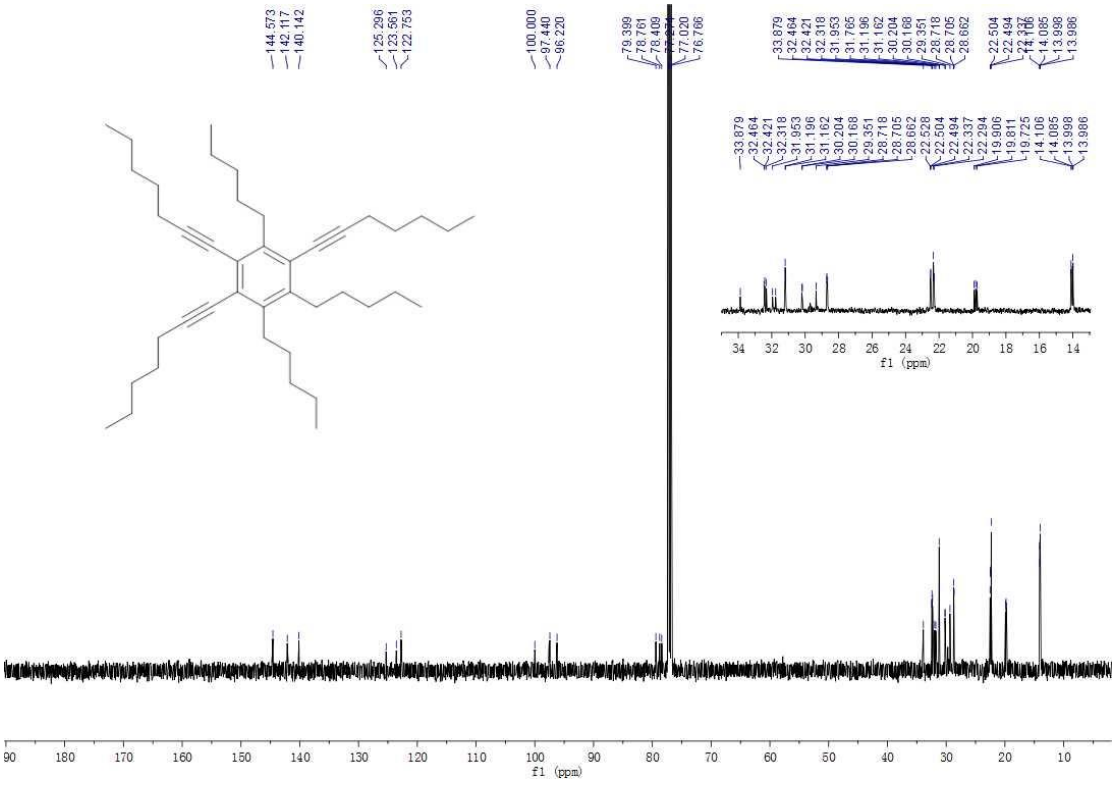


^{13}C NMR (125 MHz, $CDCl_3$)

1,2,4-Tri(hept-1-yn-1-yl)-3,5,6-tripentylbenzene (2q):

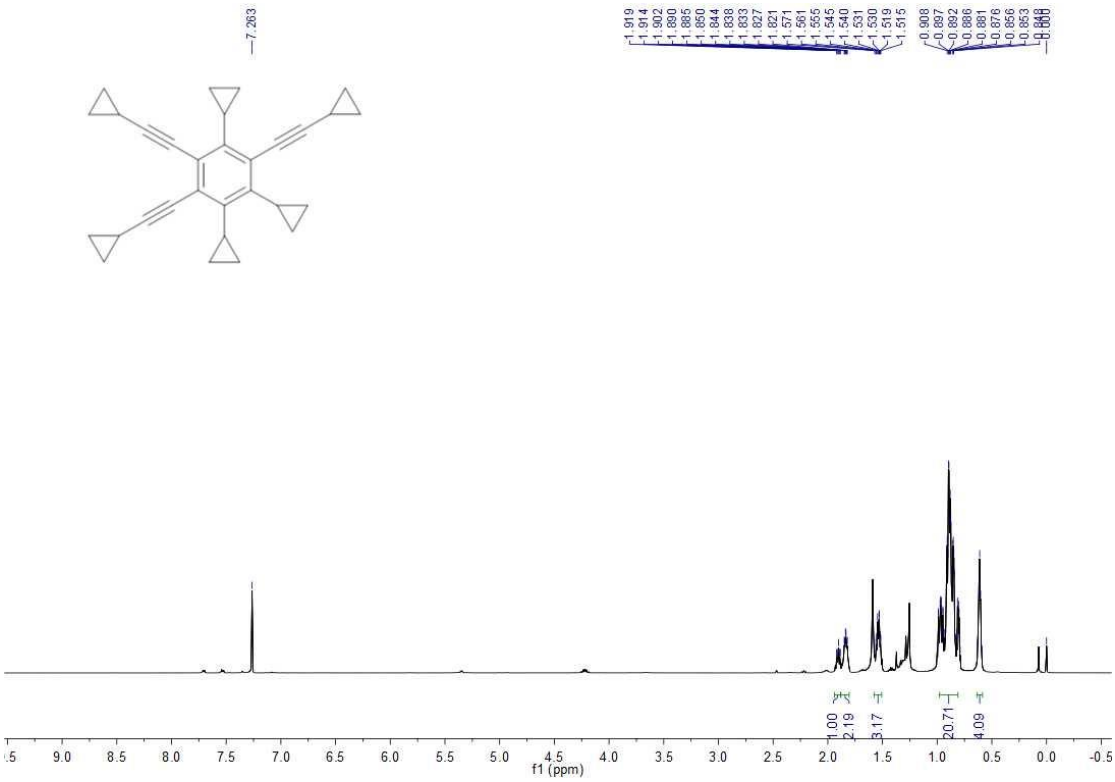


^{1}H NMR (500 MHz, $CDCl_3$)

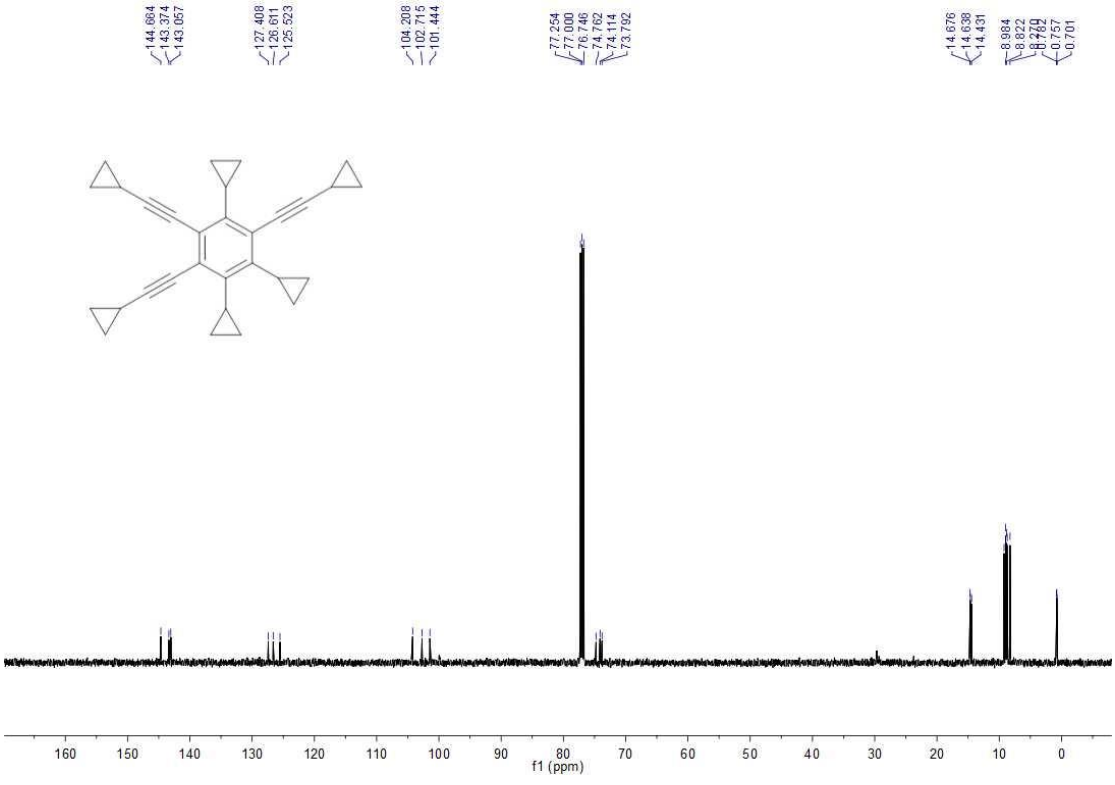


^{13}C NMR (125 MHz, $CDCl_3$)

1,2,4-Tricyclopropyl-3,5,6-tris(cyclopropylethynyl)benzene (2r):



^{1}H NMR (500 MHz, $CDCl_3$)



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