Electronic Supplementary Information

Carbon-rich molecules: synthesis and isolation of aryl/heteroaryl terminal bis(butadiynes) (HC≡C–C≡C–Ar–C≡C–C≡CH) and their applications in the synthesis of oligo(arylenebutadiynylene) molecular wires

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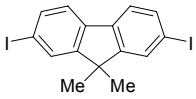
Synthetic Details

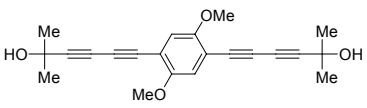
2,7-Diiodo-9,9-dimethyl-9*H*-fluorene (1c).



In a three-necked flask purged with argon and fitted with thermometer, 2,7-diiodofluorene (1.00 g, 2.39 mmol) was dissolved in anhydrous THF (40 cm^3) under argon. The reaction mixture was cooled to 0 °C and *t*-BuOK (1 M in 2-methyl-2-propanol, 3 cm^3, 3 mmol) slowly added to afford a deep red solution. MeI (0.19 cm^3, 3 mmol) was added dropwise and the reaction was stirred at 25 °C for 1 h then cooled to 0 °C and *t*-BuOK (1 M in 2-methyl-2-propanol, 3 cm^3, 3 mmol) and MeI (0.19 cm^3, 3 mmol) were added and the reaction stirred overnight at 25 °C to afford a yellow precipitate. Filtration through celite, followed by solvent removal at reduced pressure afforded **1c** as a yellow solid after recrystallisation from methanol (502 mg, 47%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 1.5 Hz, 2H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 1.46 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.2, 137.1, 136.2, 132.1, 121.8, 93.1, 47.1, 26.8; MS (EI) *m/z* 447.2 (M^+); Anal. Calcd for $C_{15}H_{12}I_2$: C, 40.39; H, 2.71. Found: C, 39.90; H, 2.64.

General procedure for the preparation of 3a-e. A mixture of the diiodoarene **1a-e**, 2-methyl-3,5-hexadiyn-2-ol **2**, $Pd(PPh_3)_2Cl_2$, CuI, triethylamine and THF was stirred at 20 °C or 50 °C. The volatile liquids were removed by vacuum evaporation and the residue was chromatographed on a silica column and/or recrystallised to afford products **3a-e**.

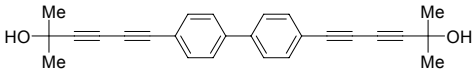
2,5-Bis(5-hydroxy-5-methyl-1,3-hexadiynyl)-1,4-dimethoxybenzene (3a).



1,4-Diiodo-2,5-dimethoxybenzene **1a**[1] (500 mg, 1.28 mmol), **2** (350 mg, 3.21 mmol), $Pd(PPh_3)_2Cl_2$ (90 mg), CuI (25 mg),

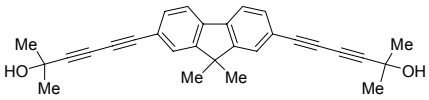
Et_3N:THF (50 cm^3, 95:5 v/v) at room temperature for 18 h and heating at 50 °C for 1 h gave **3a** as a yellow solid (292 mg, 64%) after column chromatography (silica, DCM:Et_2O, 50:50 v/v) and recrystallisation from cyclohexane: mp 163.0-163.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92 (s, 2H), 3.82 (s, 6H), 2.00 (s, 2H), 1.57 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3, 116.2, 112.8, 88.7, 79.0, 74.8, 67.1, 65.8, 56.4, 31.1; MALDI-TOF *m/z* 351.3 (M^+); Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.27; H, 6.79.

4,4-Bis(5-hydroxy-5-methyl-1,3-hexadiynyl)-biphenyl (3b).



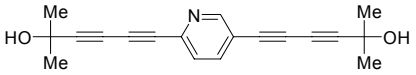
4',4-Diiodobiphenyl **1b** (300 mg, 0.74 mmol), **2** (245 mg, 2.22 mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), CuI (14 mg), triethylamine (50 cm^3) at room temperature for 18 h and heating at 50 °C for 2 h gave **3b** as a yellow solid (185 mg, 64%) after column chromatography (silica, DCM:Et_2O, 80:20 v/v): mp *ca*. 150 ^{o}C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.52 (m, 8H), 1.98 (s, 2H), 1.59 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 133.1, 127.0, 121.1, 78.7, 76.8, 74.4, 67.2, 66.0, 31.1; MS-EI *m/z* 367.2 (M^+); Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 84.70; H, 6.05.

2,7-Bis(5-hydroxy-5-methyl-1,3-hexadiynyl)-9,9-dimethyl-9*H*-fluorene (3c).



2,7-Diiodo-9,9-dimethyl-9*H*-fluorene **1c** (705 mg, 1.57 mmol), **2** (514 mg, 4.70 mmol), $Pd(PPh_3)_2Cl_2$ (110 mg), CuI (30 mg), triethylamine (70 cm^3) at room temperature for 18 h and heating at 50 °C for 1 h gave **3c** as a yellow crystalline solid (602 mg, 93%) after column chromatography (silica, DCM:Et_2O, 80:20 v/v) and recrystallisation from chloroform-hexane: mp 166.1-166.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, J = 8 Hz, 2H), 7.56, (d, J = 4 Hz, 2H), 7.47 (dd, J = 8.0, 4.0 Hz, 2H), 2.12 (s, 2H), 1.60 (s, 12H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.1, 139.5, 132.0, 127.1, 120.7, 120.6, 87.3, 79.6, 73.8, 66.0, 47.1, 31.3; MALDI-TOF *m/z* 407.2 (M^+); Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45; Found: C, 85.33; H, 6.09.

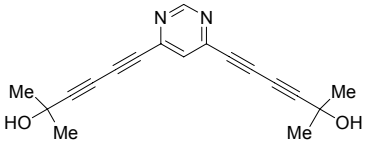
2,5-Bis(5-hydroxy-5-methyl-1,3-hexadiynyl)-pyridine (3d).



2,5-Diiodopyridine **1d** (500 mg, 1.51 mmol), **2** (410 mg, 3.77 mmol), $Pd(PPh_3)_2Cl_2$ (106 mg), CuI (30 mg), triethylamine:THF (50 cm^3, 95:5 v/v) at room temperature for 18 h and heating at 50 °C for 1 h gave **3d** as a yellow solid (263 mg, 60%) after column chromatography (silica,

dichloromethane-diethyl ether, 50:50 v/v) and recrystallisation from cyclohexane: mp 191.0-191.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66-8.65 (m, 1H), 7.71 (dd, J = 8.0, 4.0 Hz, 1H), 7.43 (dd, J = 8.0, 4.0 Hz, 1H), 2.07 (s, 1H), 2.02 (s, 1H), 1.60 (s, 6H), 1.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.7, 141.6, 139.4, 127.4, 119.0, 89.6, 89.4, 79.0, 77.3, 75.8, 75.1, 66.8, 66.7, 65.9, 31.22, 31.19; MS-(ES+) *m/z* 292.2 (M^+); Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.35; H, 5.88; N, 5.03.

4,6-Bis(5-hydroxy-5-methyl-1,3-hexadiynyl)-pyrimidine (3e).

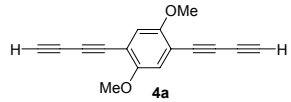


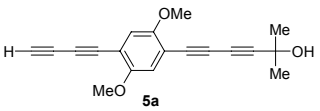
4,6-Diiodopyrimidine **1e**[2] (650 mg, 1.97 mmol), **2** (640 mg, 5.92 mmol), $Pd(PPh_3)_2Cl_2$ (138 mg), CuI (40 mg), triethylamine (50 cm^3) at room temperature for 18 h gave **3e** as a yellow solid (422 mg, 76%) after column chromatography (silica, DCM:Et_2O, 90:10 v/v) and recrystallisation from toluene: mp 158.1-158.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.11 (d, J = 1.2 Hz, 1H), 7.45 (d, J = 1.2 Hz, 1H), 2.22 (s, 2H), 1.59 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 150.1, 127.0, 91.1, 78.8, 74.7, 69.8, 65.9, 31.1; MS (ES+) *m/z* 293.3 (M^+); Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.93; H, 5.49; N, 9.51.

General Procedure for the Deprotection Reactions.

Compound **3a-e** was dissolved in either dry toluene or dry benzene. NaOH powder was added and the mixture was stirred and heated at reflux under Ar for 10 min, heating with an oil-bath at 135 ^{o}C. The reaction mixture was evaporated and the residue was purified by column chromatography on silica which separated, in order of elution, compound **4a-e**, **5a-e** and unreacted **3a-e**. ***Caution: Although no problems were experienced in the present work, care should be taken when handling solid samples of the terminal butadiynes. Explosions with analogous compounds have been reported in other laboratories, for example, terminal hexatriynes.***[3]

1,4-Bis(buta-1,3-diynyl)-2,5-dimethoxybenzene (4a) and 1-(Buta-1,3-diynyl)-4-(5-hydroxy-5-methyl-1,3-hexadiynyl)-2,5-dimethoxybenzene (5a).





Route A; Compound **3a** (175 mg, 0.48 mmol), NaOH (90 mg) and toluene (20 cm^3), column chromatography (silica, DCM) gave **4a** as a yellow solid (27 mg, 24%) and **5a** as a yellow solid (72 mg, 52% yield).

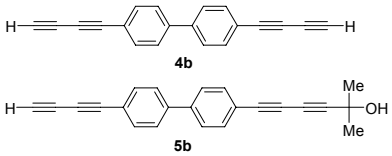
Route B; Compound **3a** (100 mg, 0.29 mmol), NaOH (50 mg)

and benzene (10 cm^3) gave **4a** as a yellow solid (43 mg, 64%).

4a: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (s, 2H), 3.85 (s, 6H), 2.62 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.7, 116.5, 112.6, 79.5, 73.4, 71.4, 68.2, 56.5; MS-MALDI-TOF *m/z* 235.1 (M^+).

Optimised synthesis of 5a. Compound **3a** (300 mg, 0.86 mmol), NaOH (150 mg) and toluene:benzene (20 cm^3, 50:50 v/v) gave **5a** as a yellow solid (154 mg, 62%) after column chromatography (silica, DCM). The single crystal (colourless) used for X-ray structural analysis was obtained by slow evaporation from deuterated chloroform. **5a:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.95 (s, 1H), 6.93 (s, 1H), 3.83 (s, 6H), 2.60 (s, 1H), 1.98 (s, 1H), 1.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.7, 155.3, 116.4, 116.3, 113.2, 112.2, 88.8, 79.4, 79.3, 74.8, 73.4, 71.5, 68.2, 67.2, 65.9, 56.54, 56.51, 31.2; MS-MALDI-TOF *m/z* 293.1 (M^+).

4-4'-Bis(buta-1,3-diynyl)-biphenyl (4b) and 4-(Buta-1,3-diynyl)-4'-(5-hydroxy-5-methyl-1,3-hexadiynyl)-biphenyl (5b).



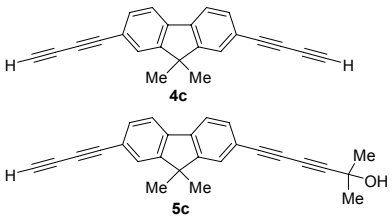
Route A; Compound **3b** (90 mg, 0.25 mmol), NaOH (45 mg) and toluene (12 cm^3), column chromatography (silica, DCM) gave **4b** as a yellow solid (40 mg, 65%) and **5b** as a yellow solid (23 mg, 0.07 mmol, 30%).

Route B; Compound **3b** (100 mg, 0.27 mmol), NaOH (50 mg) and benzene (10 mL) gave **4b** as a yellow solid (32 mg, 47%).

4b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.54 (m, 8H), 2.52 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 133.5, 127.2, 120.7, 75.2, 74.7, 72.0, 68.2; MS-MALDI-TOF *m/z* 251.1 (M^+).

5b: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61-7.55 (m, 8H), 2.52 (s, 0.8H), 2.00 (s, 0.7H), 1.61 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.2, 140.8, 133.5, 133.2, 127.2, 121.2, 120.6, 87.4, 78.6, 75.2, 74.6, 74.3, 72.0, 68.2, 67.2, 65.9, 31.3; MALDI-TOF *m/z* 309.1 (M^+).

2,7-Bis(buta-1,3-diynyl)-9,9-dimethyl-9*H*-fluorene (4c) and 2-(Buta-1,3-diynyl)-7-(5-hydroxy-5-methyl-1,3-hexadiynyl)-9,9-dimethyl-9*H*-fluorene (5c).



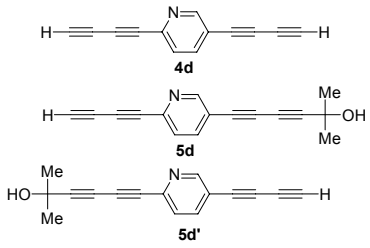
Route A; Compound **3c** (200 mg, 0.50 mmol), NaOH (100 mg) and toluene (15 cm^3), column chromatography (silica, DCM) gave **4c** as a yellow solid (88 mg, 62%) and **5c** as a dark brown oil (64 mg, 37%).

Route B; Compound **3c** (100 mg, 0.25 mmol), NaOH (50 mg) and benzene (10 cm^3) gave **4c** as a yellow solid (47 mg 0.16 mmol, 66%).

4c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8 Hz, 2H), 7.58, (d, *J* = 4 Hz, 2H), 7.50 (dd, *J* = 8.0, 4.0 Hz, 2H), 2.53 (s, 2H), 1.46 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.2, 139.7, 132.3, 127.3, 120.7, 120.3, 76.1, 74.2, 71.9, 68.3, 47.1, 26.9; MALDI-TOF *m/z* 291.1 (M^+).

5c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.64 (m, 2H), 7.58-7.55 (m, 2H), 7.52-7.46 (m, 2H), 2.52 (s, 0.9H), 2.04 (s, 0.9H), 1.60 (s, 6H), 1.45 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.14, 154.11, 139.8, 139.4, 132.3, 132.0, 127.3, 127.1, 120.9, 120.69, 120.65, 120.2, 87.3, 79.6, 76.1, 74.1,73.9, 71.9, 68.3, 67.3, 65.9, 47.1, 31.3, 26.9; MS-MALDI-TOF *m/z* 349.2 (M^+).

2,5-Bis(buta-1,3-diynyl)-pyridine (4d), 2-(Buta-1,3-diynyl)-5-(5-hydroxy-5-methyl-1,3-hexadiynyl)-pyridine (5d) and 2-(5-hydroxy-5-methyl-1,3-hexadiynyl)-5-(buta-1,3-diynyl)-pyridine (5d').



Route A; Compound **3d** (150 mg, 0.515 mmol), NaOH (100 mg) and toluene (15 cm^3), chromatography (silica, DCM) gave **4d** as a white solid (24 mg, 27%) and a mixture of isomers **5d** and **5d'** as a white solid.

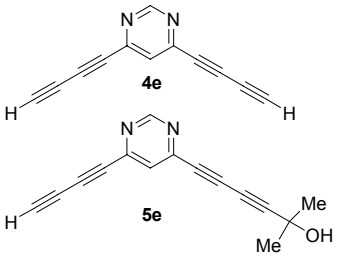
Route B; Compound **3d** (80 mg, 0.27 mmol), NaOH (40 mg) and THF (8 cm^3) gave **4d** as a white solid (24 mg, 50%). The single crystal (colourless) of **4d** used for X-ray structural analysis was obtained by slow evaporation of a dichloromethane-ether mixture.

4d: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70-8.69 (m, 1H), 7.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.48 dd, *J* = 8.0, 2.0 Hz, 1H), 2.62 (s, 1H), 2.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 141.2, 139.8, 127.7, 118.7, 79.2, 75.9, 74.0, 73.9, 73.5, 71.5, 67.6, 67.5; MS-MALDI-TOF *m/z* 176.1 (M^+).

5d and **5d':** NMR data showed the presence of these isomers in a *ca* 2:1 ratio. The peaks could not be assigned to the specific isomers.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (m, 1.40H), 7.61 (m, 1.49H), 7.37 (m, 1.44H), 2.55 (s, 0.50H), 2.52 (s, 0.88H), 2.37 (s, 0.88H), 2.18 (s, 0.46H), 1.52 (s, 8.8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.8, 153.6, 141.7, 140.8, 139.8, 139.5, 127.7, 127.4, 119.3, 118.4, 89.6, 89.4, 79.07, 79.02, 76.9, 76.0, 75.8, 74.8, 73.9, 73.8, 73.5, 71.6, 67.60, 67.56, 66.6, 66.5, 65.85, 65.83; MS-MALDI-TOF *m/z* 234.1 (M^+). The single crystal (colourless) of **5d** used for X-ray structural analysis grew on storage of a $CDCl_3$ solution of a mixture of **5d** and **5d'**.

4,6-Bis-(buta-1,3-diynyl)-pyrimidine (4e) and 4-(Buta-1,3-diynyl)-6-(5-hydroxy-5-methyl-1,3-hexadiynyl)-pyrimidine (5e).



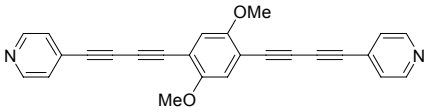
Route A; Compound **3e** (100 mg, 0.34 mmol), NaOH (50 mg) and toluene (10 cm^3), column chromatography (silica, DCM:Et_2O, 90:10 v/v) gave **4e** as a white solid (13 mg, 22%) and **5e** (12 mg, 15%).

Route B; Compound **3e** (100 mg, 0.34 mmol), NaOH (50 mg) and benzene (10 cm^3) gave **4e** as a white solid (12 mg, 20%).

4e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.15 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 2.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 149.8, 127.5, 78.8, 75.5, 71.1, 67.0; MS (DSQ) *m/z* 176.0 (M^+).

5e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.13 (d, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 1.2 Hz, 1H), 2.67 (s, 1H), 2.19 (s, 1H), 1.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 150.2, 149.6, 127.3, 91.2, 79.0, 78.6, 75.4, 74.5, 71.1, 70.0, 66.1, 65.9, 31.0; MS-MALDI-TOF *m/z* 235.2 (M^+).

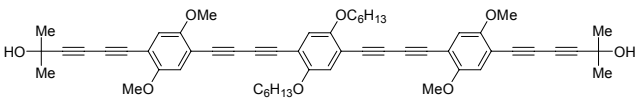
2,5-Bis[5-(4-pyridyl)-hexa-1,3-diynyl]-1,4-dimethoxybenzene (7).



Compound **4a** (86 mg, 0.367 mmol) and 4-iodopyridine **6** (225 mg, 1.10 mmol) were dissolved in anhydrous Et_3N:THF (50:50 v/v, 50 cm^3), to which CuI (6 mg) and $Pd(PPh_3)_2Cl_2$ (26 mg) were added and the reaction was stirred overnight at 25 °C followed by heating to 50 °C for 1 h. The solvent was removed and the crude residue purified by column chromatography (silica, eluent EtOAc) to give **7** (76 mg, 53 %) as a light brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (dd, *J* = 4.4, 1.6 Hz, 4H), 7.39 (dd, *J* = 4.4, 1.6 Hz, 4H), 6.96 (s, 2H), 3.81 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.6, 150.0, 129.1, 126.5, 116.4, 112.3, 77.3, 74.7, 68.3, 64.3, 55.3; MS-MALDI-TOF *m/z* 389.1 (M^+). Anal. calcd. for $C_{21}H_{16}N_2O_2$: C, 80.40; H, 4.15; N, 7.21. Found: C, 79.95; H, 4.40; N, 6.99.

Compound 9.

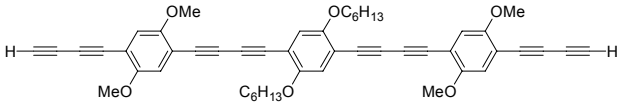


Compounds **5a** (308 mg, 1.05 mmol) and **8**[4] (223 mg, 0.42 mmol), were dissolved in THF:Et_3N (50 cm^3, 20:80 v/v) and the solution was degassed thoroughly. $Pd(PPh_3)_4$ (47 mg) and CuI (8 mg) were added in one portion and the mixture was stirred at room temperature for 18 h followed by heating at 50 °C for 1 h. Column chromatography

(silica, DCM, followed by gradual addition of Et_2O) followed by recrystallisation from cyclohexane gave **9** as a yellow solid (263 mg, 72%): mp 171.2-172.3 °C.

^{1}H NMR (C_6D_6, 200 MHz): δ 6.94 (s, 4H), 6.91 (s, 2H), 3.95 (t, *J* = 6.6 Hz, 4H), 3.83 (s, 12H), 2.24 (s, 2H), 1.80-1.76 (m, 4H), 1.56 (s, 12H), 1.50-1.33 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.2, 155.1, 154.7, 117.5, 116.0, 115.9, 113.4, 122.9, 112.6, 88.7, 80.1, 79.6, 79.3, 79.0, 74.8, 69.7, 67.0, 67.5, 56.3, 31.5, 31.0, 28.9, 25.5, 22.6, 15.2, 14.0; MALDI-TOF *m/z* 860 (M^+).

Compound 10.



Compound **9** (100 mg, 0.12 mmol), NaOH (50 mg) in refluxing benzene (10 cm^3) afforded **10** as a yellow solid (48 mg, 56%) after purification by column chromatography (silica, eluent DCM).

^{1}H NMR (C_6D_6, 500 MHz): δ 6.78 (s, 2H), 6.57 (s, 2H), 6.55 (s, 2H), 3.41 (t, *J* = 6.0 Hz, 4H), 3.03 (s, 6H), 3.02 (s, 6H), 1.90 (s, 2H), 1.52-1.13 (m, 16H), 0.86 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ 156.2, 155.8, 155.4, 117.6, 116.5, 116.1, 113.93, 113.88, 112.5, 81.8, 80.9, 80.7, 73.7, 72.3, 69.3, 68.6, 55.5, 31.7, 29.2, 25.9, 22.9, 14.2; MALDI-TOF *m/z* 743.3 (M^+).

X-Ray crystallography

In structure **5a** inversion-related molecules are linked into a dimer by a pair of O-H...O(methoxy) hydrogen bonds. The terminal butadiyne group forms a C-H...π(C≡C) bond (of optimal T-shaped geometry) with the *protected* butadiyne, thereby linking the dimers into an infinite chain, zig-zagging in the general direction [1 0 1] (Fig. S1). In structure **5a** there are no close contacts between diyne moieties. Structure **4d** contains linear arrays of molecules related by the crystallographic translation *a* (=3.79 Å), the latter forming an angle of *ca*. 75° with the diyne moieties (Fig. S2). Such packing apparently satisfies the geometrical conditions for solid-state (topotactic) polymerisation,[5] which, nevertheless, does not readily occur. Structure **5d** contains peculiar zig-zag arrays of (unprotected) diyne fragments (Fig. S2), wherein each two adjacent diynes are related via an inversion centre and hence lie in one plane, but adjacent *planes* form an angle of 89° [i.e. are mutually perpendicular].

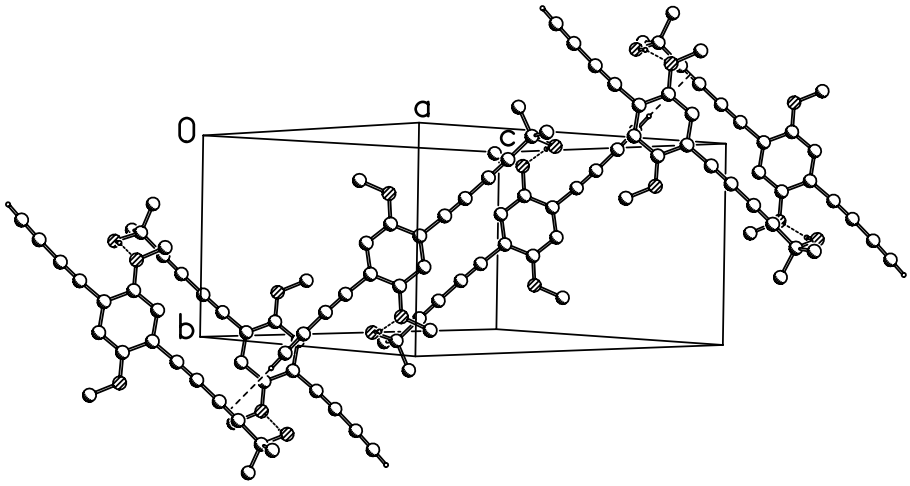


Fig. S1. Hydrogen bonds (dashed lines) in structure **5a**.

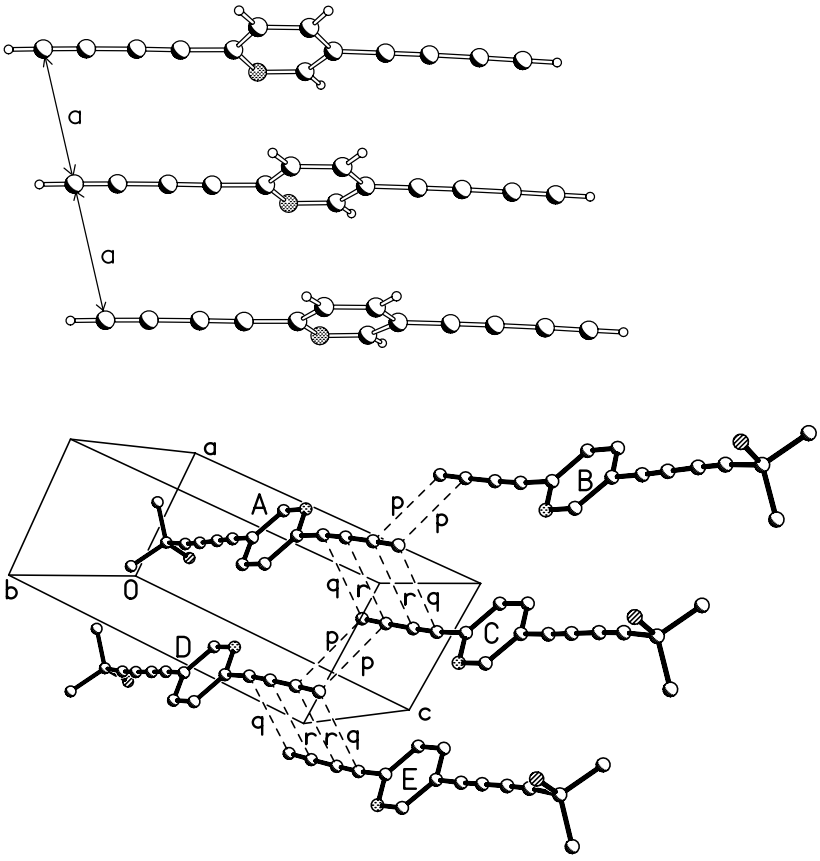


Fig. S2. Molecular arrays in solid **4d** (top) (related by the crystallographic translation a=3.79 Å) and **5d** (bottom). Symmetry transformations: (A) *x, y, z*, (B) 3−*x*, 2−*y*, 2−*z*, (C) 2−*x*, 2−*y*, 2−*z*, (D) *x*−1, *y, z*, (E) −*x*−1, 2−*y*, 2−*z*; intermolecular distances (Å): p=3.46, q=3.62, r=3.70.

Table S1. Selected bond distances (Å)

	4d	**5a**	**5d**		**4d**	**5a**	**5d**
C(2)-C(7)	1.446(7)	1.429(2)	1.4349(15)	C(5)-C(11)	1.429(7)	1.431(2)	1.4268(15)
C(7)-C(8)	1.196(7)	1.204(2)	1.2033(16)	C(11)-C(12)	1.209(7)	1.201(2)	1.2069(15)
C(8)-C(9)	1.377(7)	1.378(3)	1.3777(16)	C(12)-C(13)	1.376(8)	1.387(3)	1.3777(16)
C(9)-C(10)	1.179(7)	1.185(3)	1.1941(16)	C(13)-C(14)	1.197(7)	1.191(2)	1.1941(16)

Data collection: Bruker CCD area detector diffractometers SMART 6K (**4d**, **5a**) or 1K (**5d**), graphite-monochromated Mo-K_α radiation (λ=0.71073 Å), computations: SHELXTL version 6.12 (Bruker AXS, Madison WI, USA, 2001). *Crystal data:* $C_{13}H_5N$ **4d**, *M*=175.18, monoclinic, space group $P2_1/c$ (no. 14), *T*=120 K, *a*=3.7926(8), *b*=20.217(4), *c*= 12.385(3) Å, β=94.91(1)º, *U*= 946.2(3) Å^3, *Z*=4, D_c=1.230 g cm^{-3}, μ=0.07 mm^{-1}, 8467 reflections (2θ≤50º), R_{int}=0.151, *R(F)*=0.069 [683 data with $I\geq2\sigma(I)$], *wR*(F^2)=0.140 (1685 unique data). Weak diffraction: mean $I/\sigma(I)<3.1$. Semi-merohedral twinning by twofold rotation around the [4 0 −1] axis; component contributions were refined to 0.650(4) and 0.350(4). CCDC-??????. $C_{19}H_{16}O_3$ **5a**, *M*=292.32, monoclinic, space group *C*2/*c* (no. 15), *T*=120 K, *a*= 17.555(2), *b*= 9.126(1), *c*= 19.831(2) Å, β=101.46(1)º, *U*= 3113.7(6) Å^3, *Z*=8, D_c=1.247 g cm^{-3}, μ=0.08 mm^{-1}, 11371 reflections (2θ≤55º), R_{int}=0.068, *R(F)*=0.044 [1987 data with $I\geq2\sigma(I)$], *wR*(F^2)=0.095 (3571 unique data). CCDC-??????. $C_{16}H_{11}NO$ **5d**, *M*= 233.26, triclinic, space group *P*−1 (no. 2), *T*=120 K, *a*= 5.7609(7), *b*= 9.0756(10), *c*=12.6163(14) Å, α=87.79(1), β=77.87(1), γ=77.99(1)º, *U*=630.8(1) Å^3, *Z*=2, D_c=1.230 g cm^{-3}, μ=0.08 mm^{-1}, 7737 reflections (2θ≤60º), R_{int}=0.024, *R(F)*=0.044 [2626 data with $I\geq2\sigma(I)$], *wR*(F^2)=0.117 (3464 unique data). CCDC-??????.

UV-Vis absorption spectra.

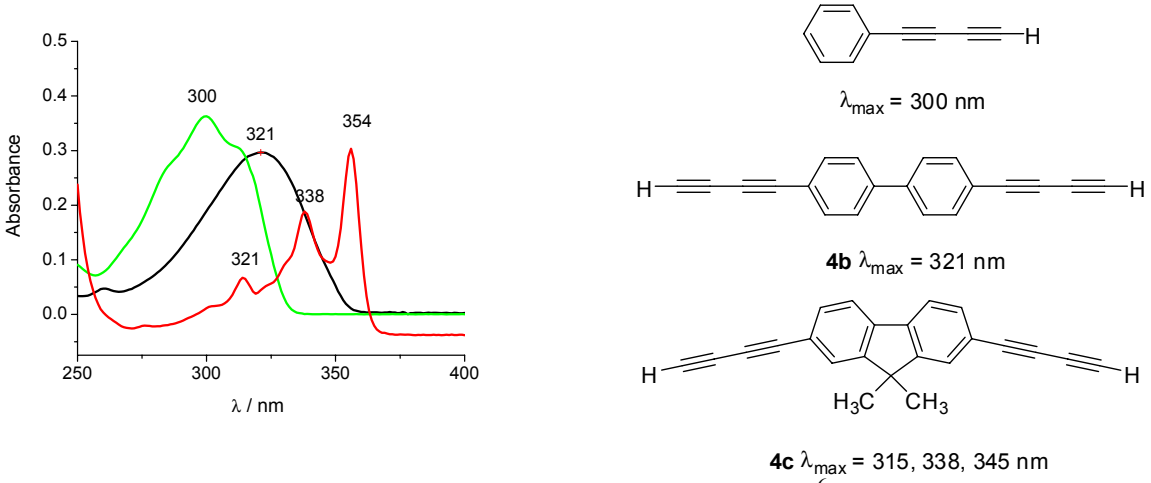


Fig. S3. UV-Vis absorption spectra of 4-(1,3-butadiynyl)biphenyl[6] (green line), **4b** (black line), and **4c** (red line) in chloroform. Note the red shifted absorption for **4c**, suggesting increased conjugation due to the planar fluorene core.

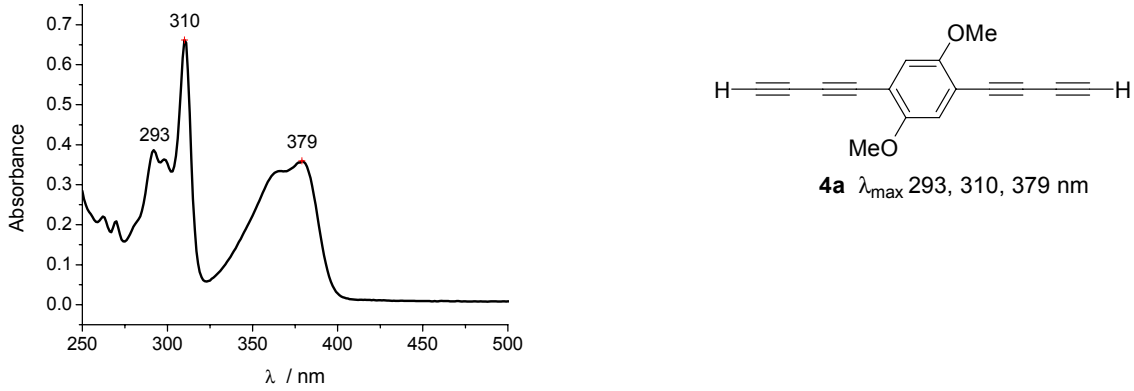


Fig. S4. UV-Vis absorption spectrum of **4a** in chloroform solution.

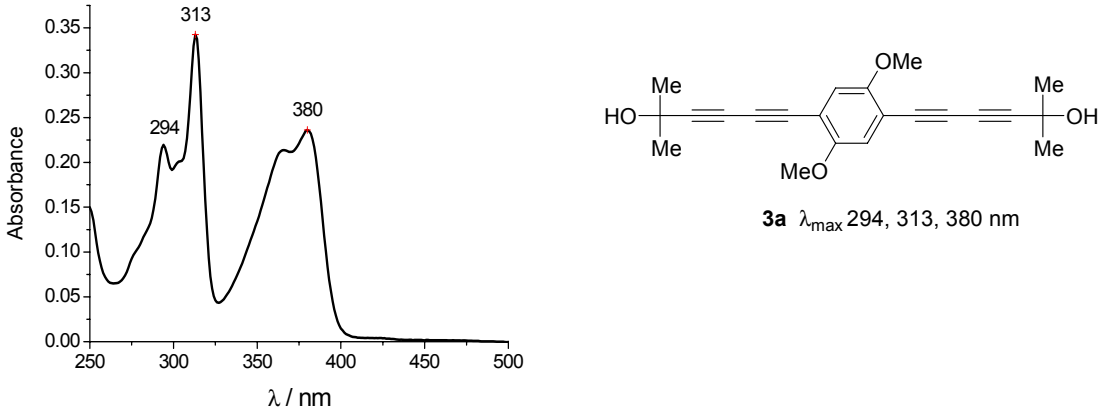
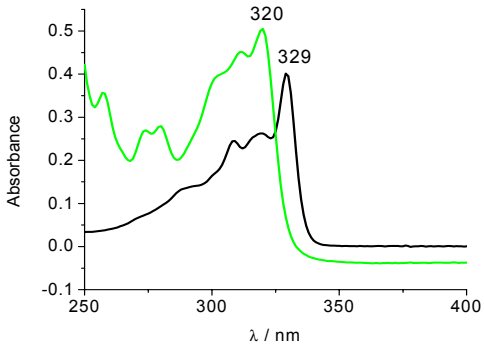


Fig. S5. UV-Vis absorption spectrum of **3a** in chloroform solution.



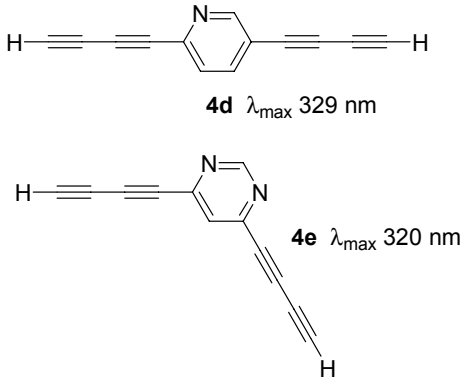


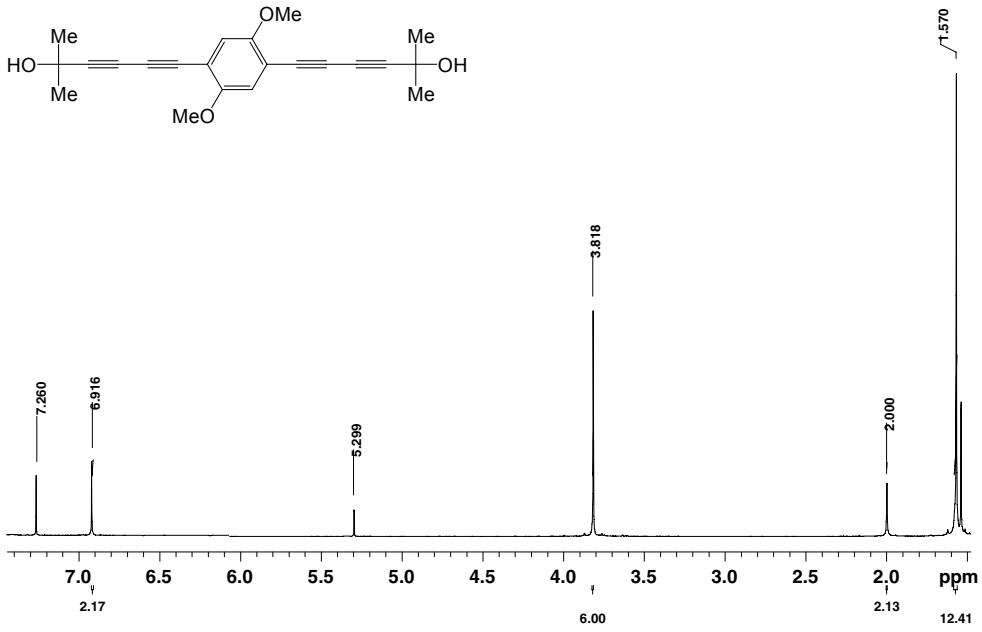
Fig. S6. UV-Vis absorption spectra of **4d** and **4e** in chloroform solution. Note the blue shifted λ_{max} value for **4e**, which could be due to decreased *meta* coupling.

Table S2. Solution absorption and emission data.

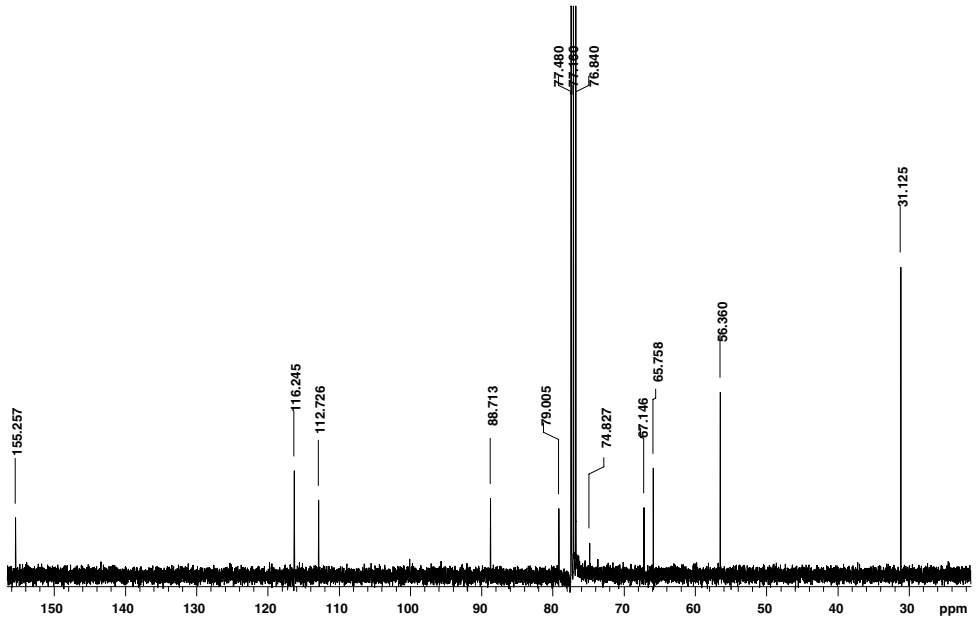
Compound	λ_{max}, abs ($CHCl_3$) / nm	λ_{max}, em ($CHCl_3$) / nm[a]
3a	294, 313, 380	402
4a	293, 310, 379	402
4b	321	369
4c	315, 338, 354	359, 378
4d	329	[b]
4e	320	[b]
7	313, 336, 400	435
9	297, 314, 335, 427	457
10	280, 313, 335, 424	457

[a] Excitation at λ_{max} abs; [b] No observable emission

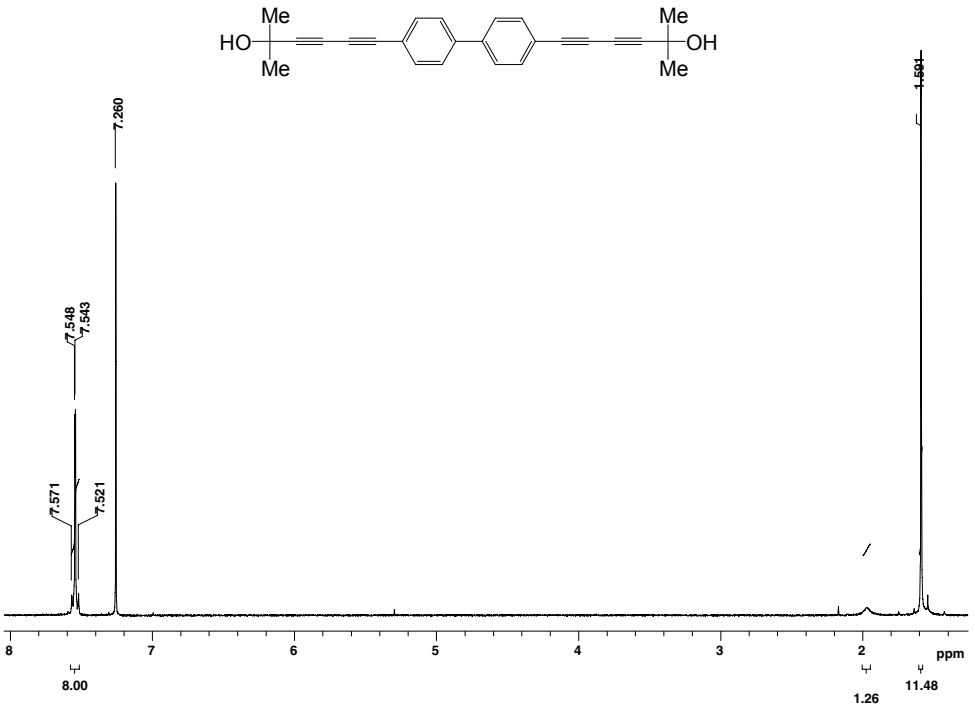
Compound **3a** ^{1}H NMR (400 MHz, $CDCl_3$)



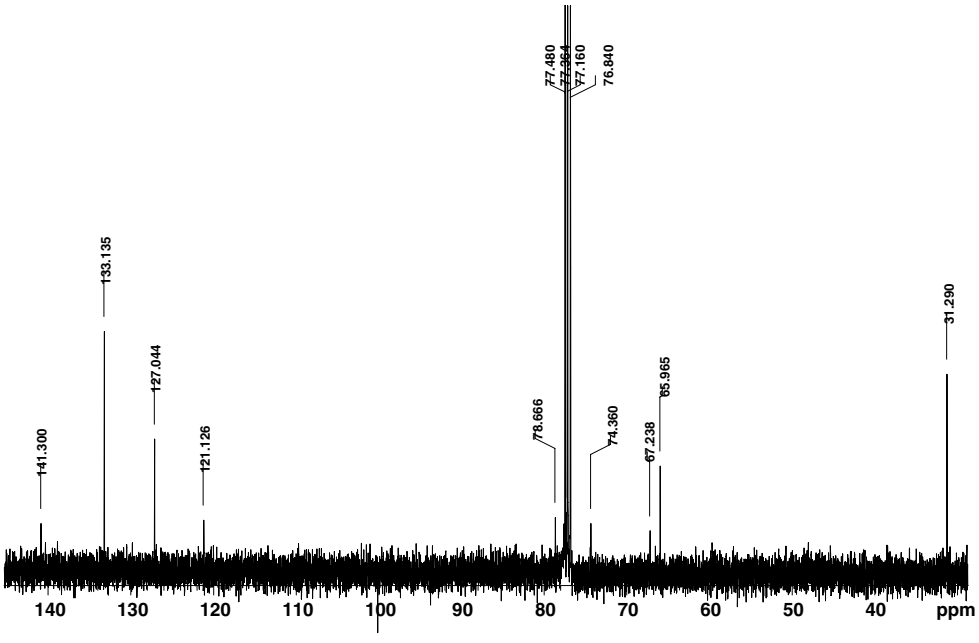
3a ^{13}C NMR (100 MHz, $CDCl_3$)



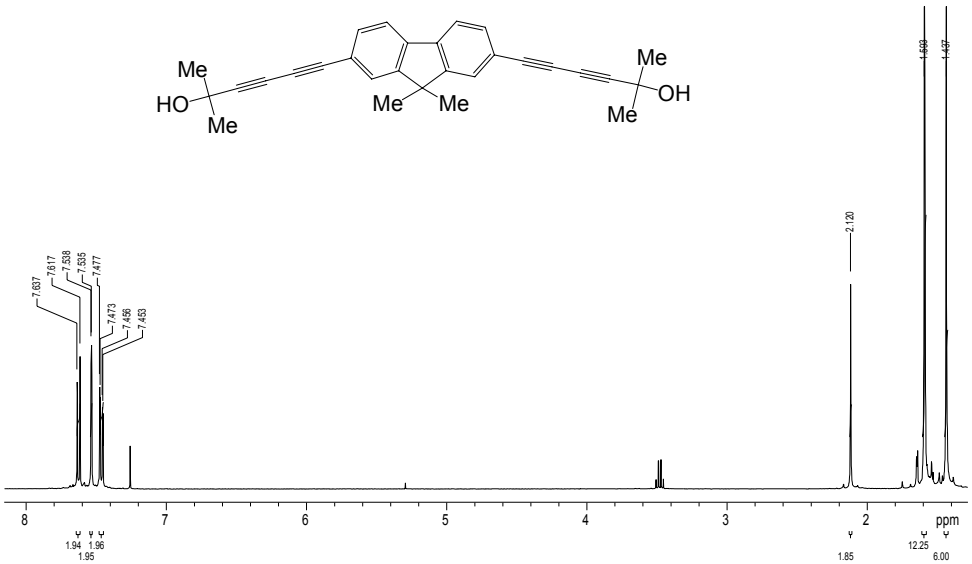
Compound **3b** ^{1}H NMR (400 MHz, $CDCl_3$)



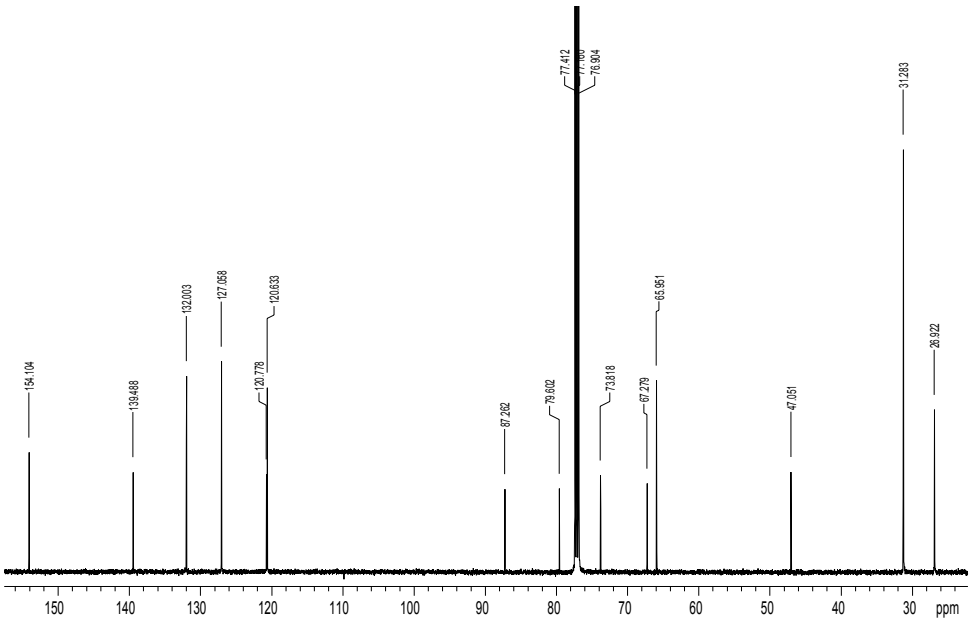
3b ^{13}C NMR (100 MHz, $CDCl_3$)



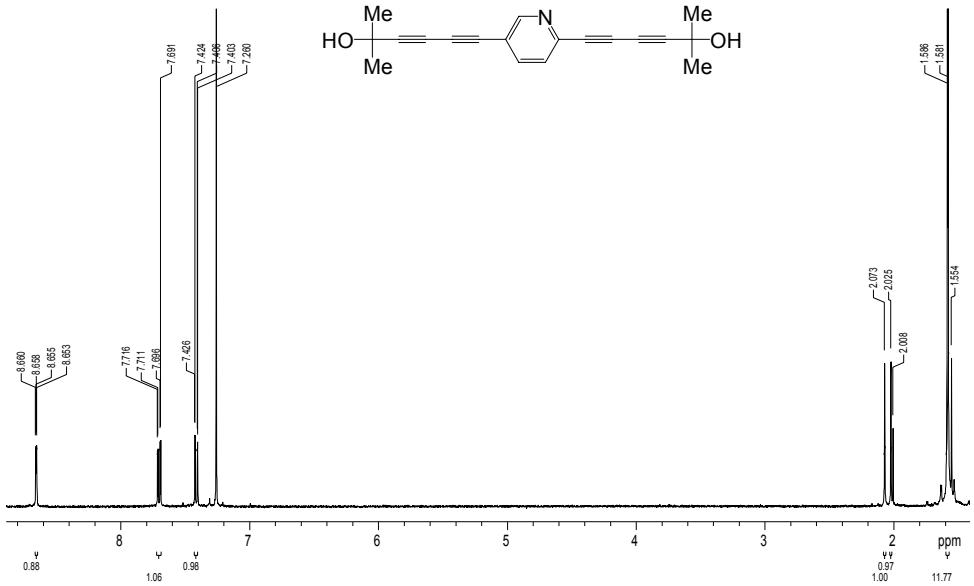
Compound **3c** ^{1}H NMR (400 MHz, $CDCl_3$)



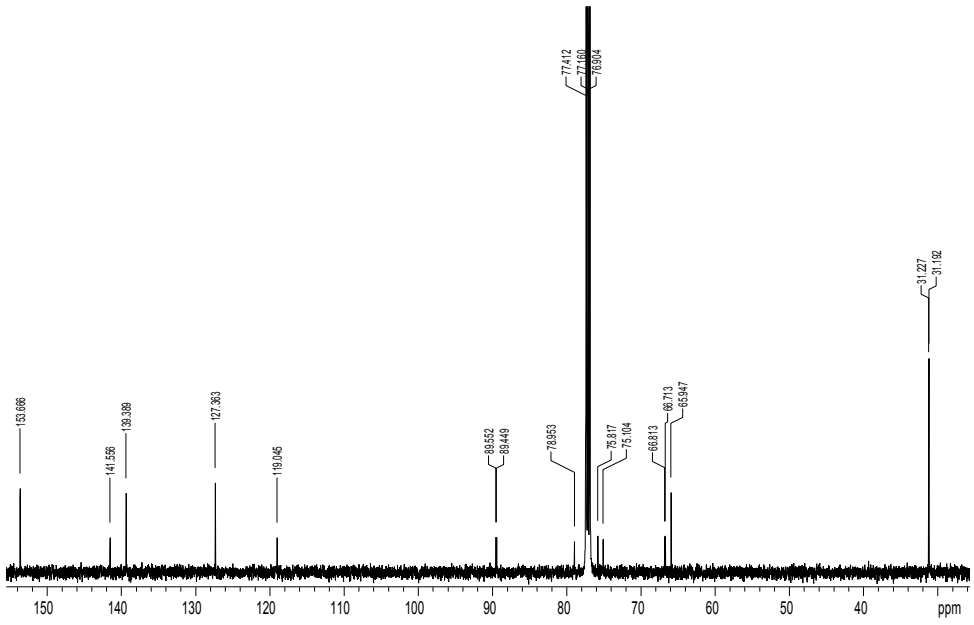
3c ^{13}C NMR (400 MHz, $CDCl_3$)



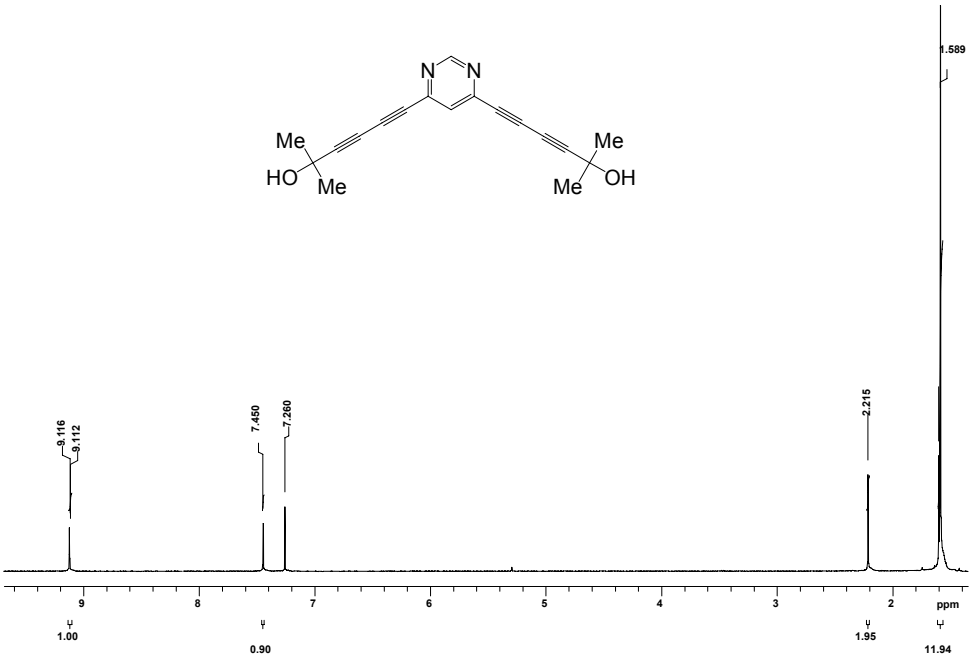
Compound **3d** ^{1}H NMR ($CDCl_3$, 400 MHz)



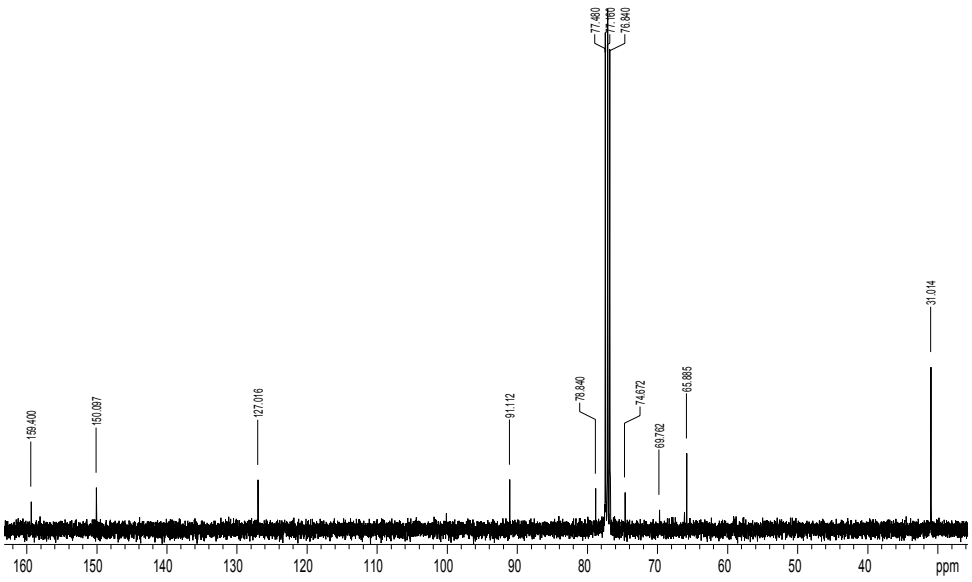
3d ^{13}C NMR ($CDCl_3$, 100 MHz)



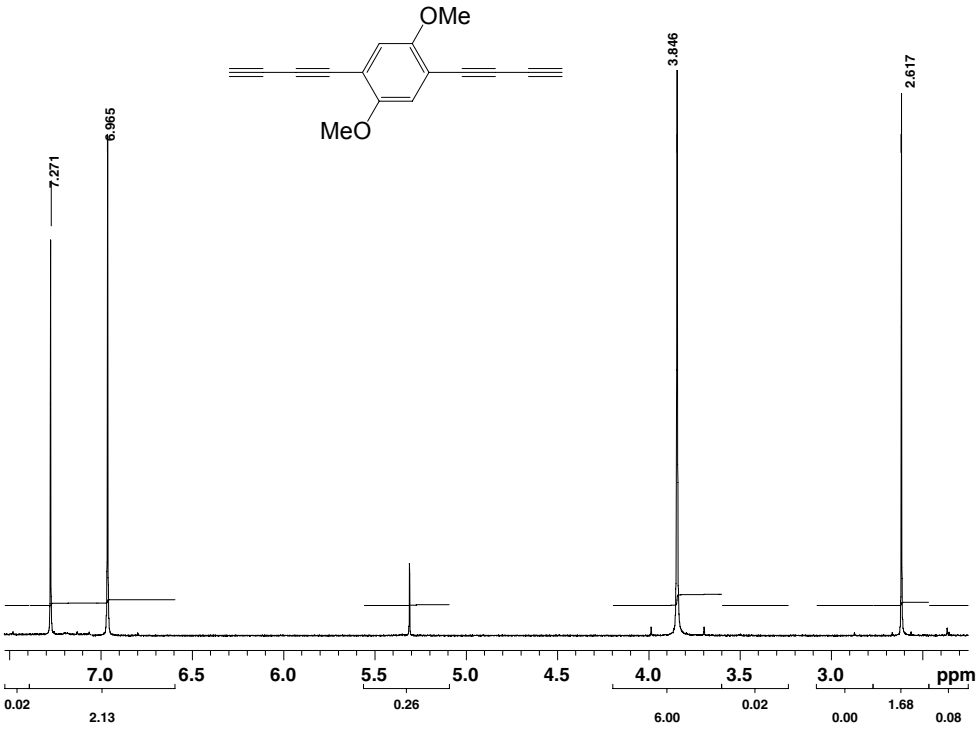
Compound **3d** ^{1}H NMR ($CDCl_3$, 400 MHz)



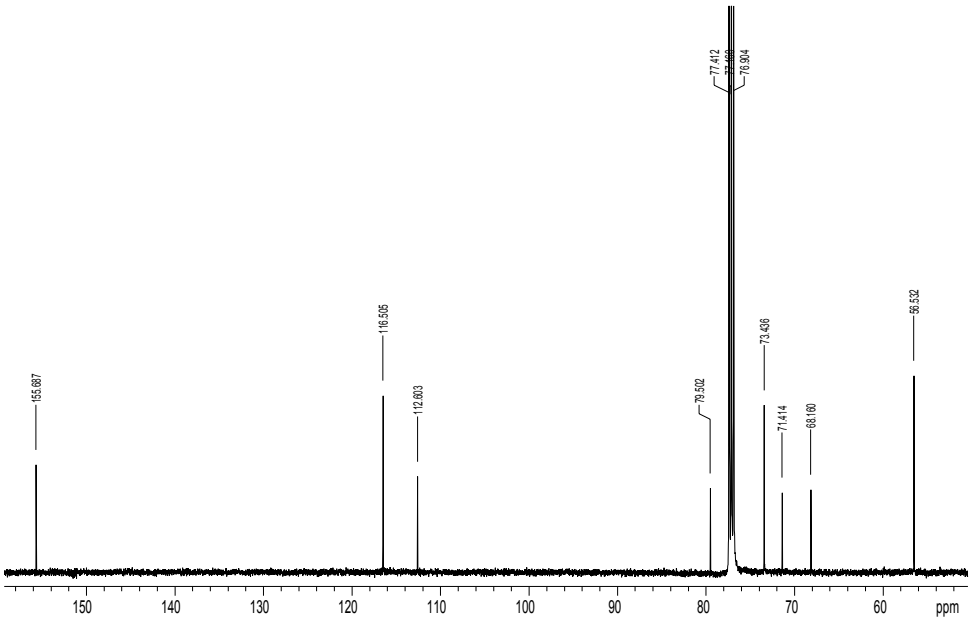
3d ^{13}C NMR ($CDCl_3$, 100 MHz)



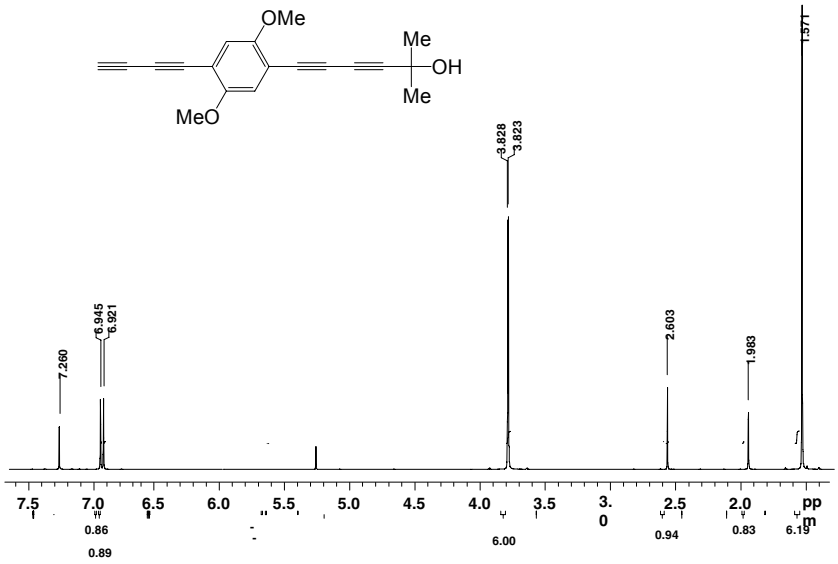
Compound **4a** ^{1}H NMR (400 MHz, $CDCl_3$)



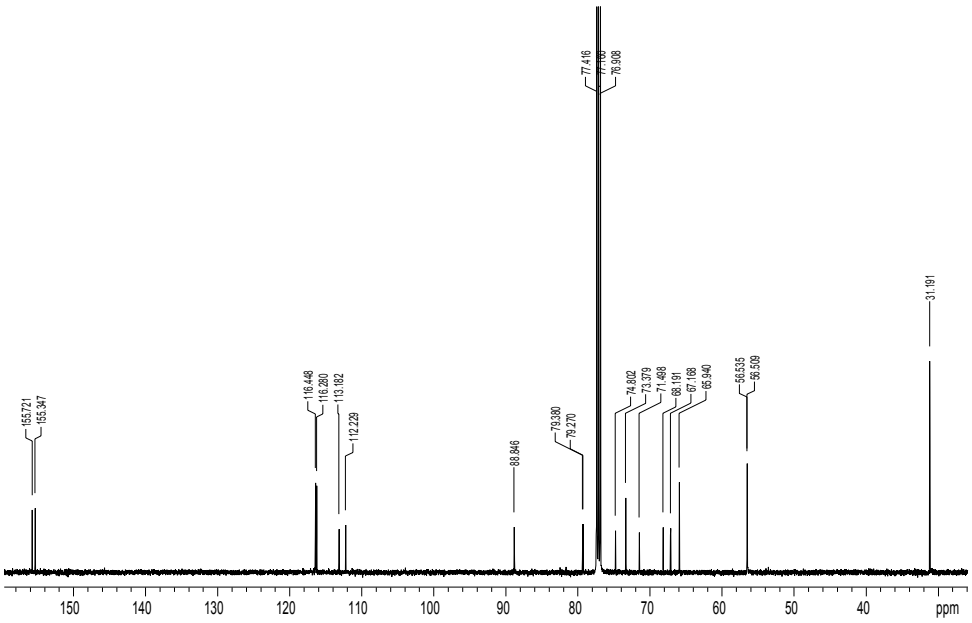
4a ^{13}C NMR (100 MHz, $CDCl_3$)



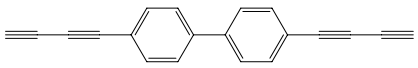
Compound **5a** ^{1}H NMR (400 MHz, $CDCl_3$)

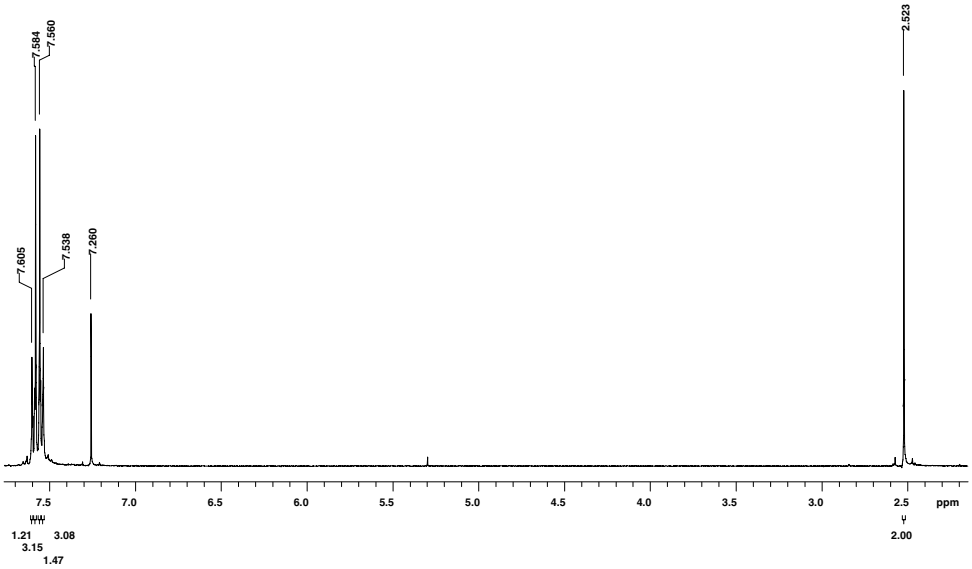


5a ^{13}C NMR (400 MHz, $CDCl_3$)

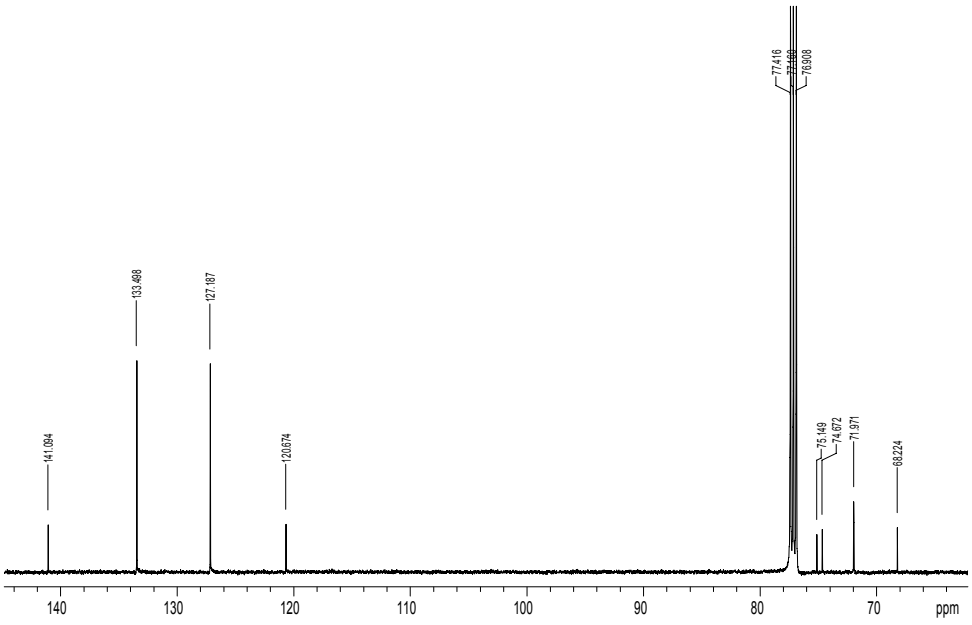


Compound **4b** ^{1}H NMR (400 MHz, $CDCl_3$)

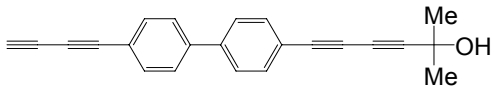


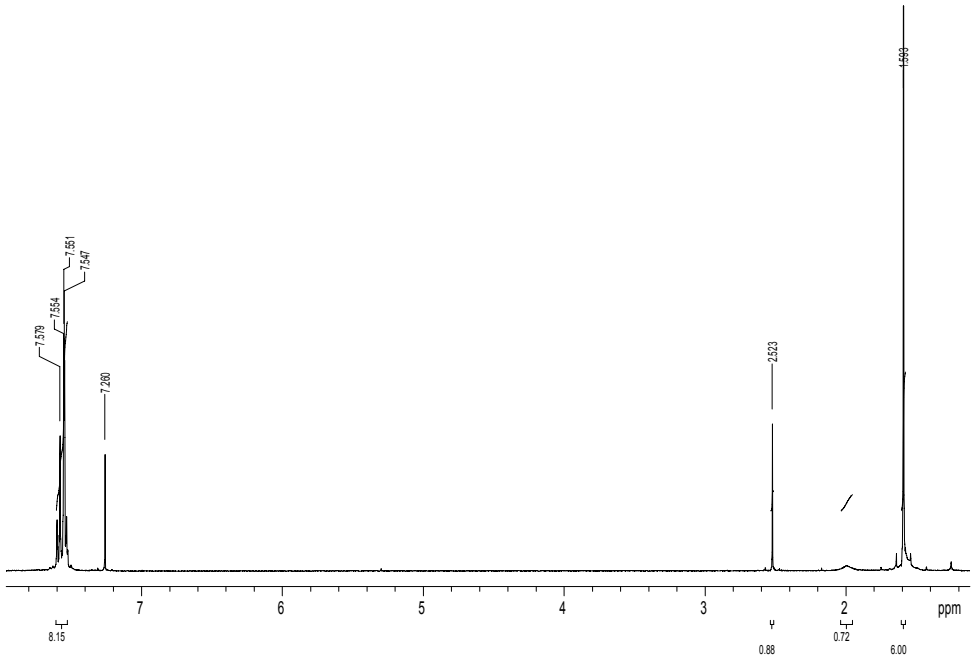


4b ^{13}C NMR (100 MHz, $CDCl_3$)

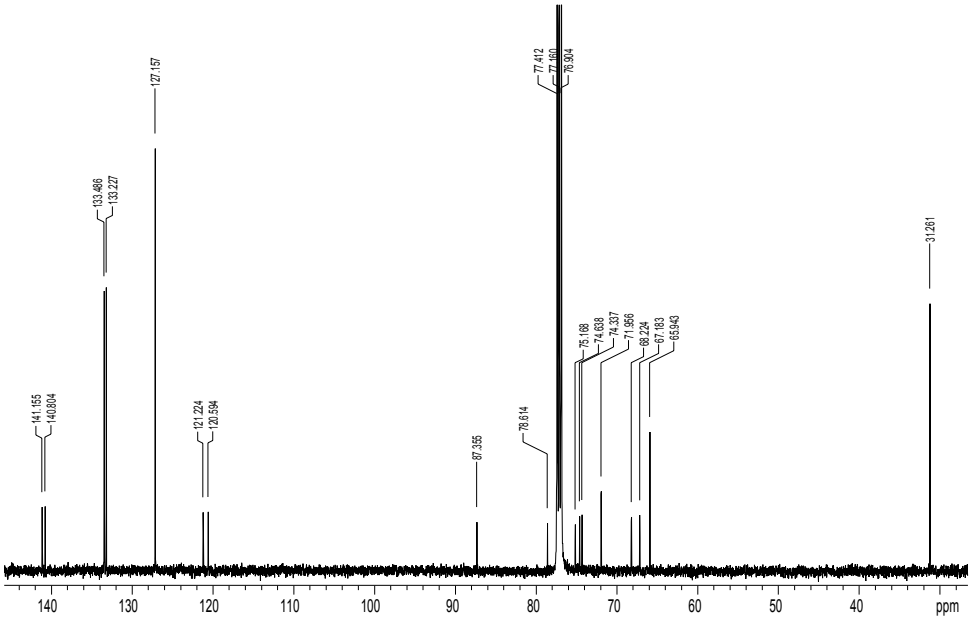


Compound **5b** ^{1}H NMR (400 MHz, $CDCl_3$)

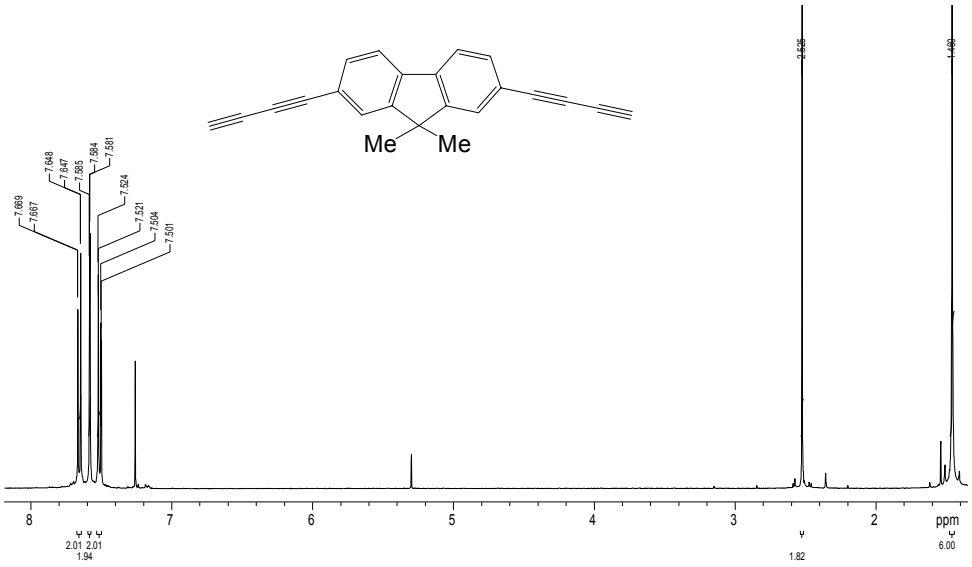




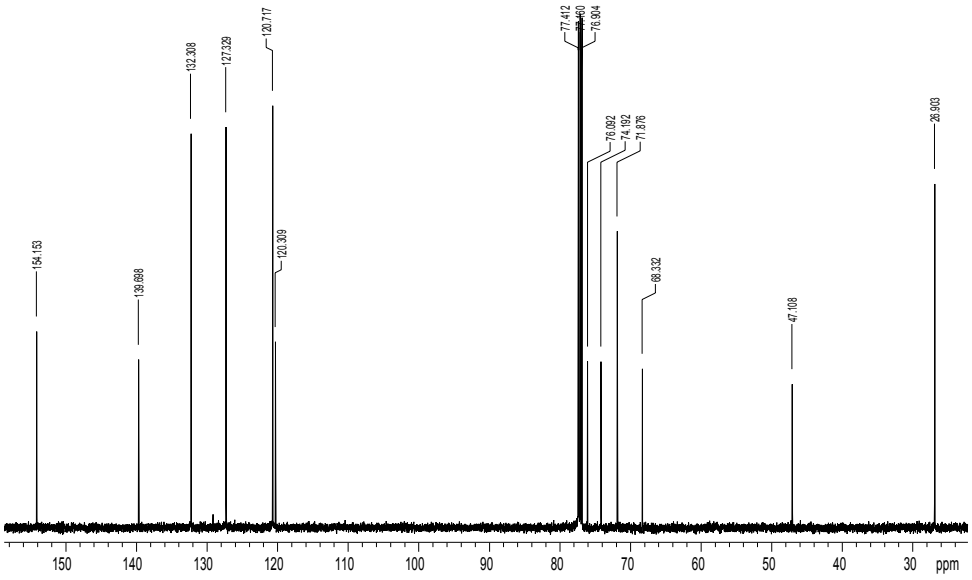
5b ^{13}C NMR (100 MHz, $CDCl_3$)



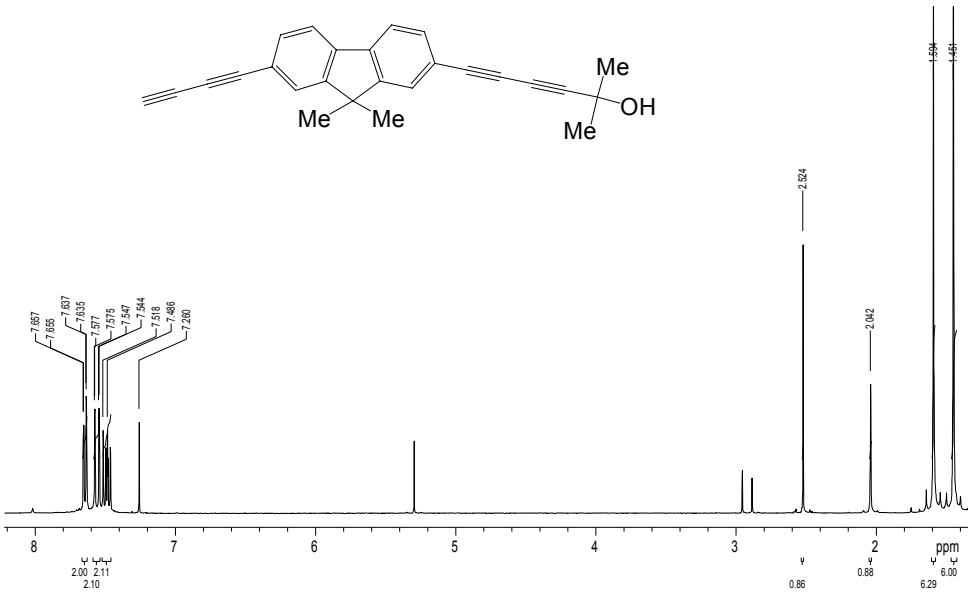
Compound **4c** ^{1}H NMR (400 MHz, $CDCl_3$)



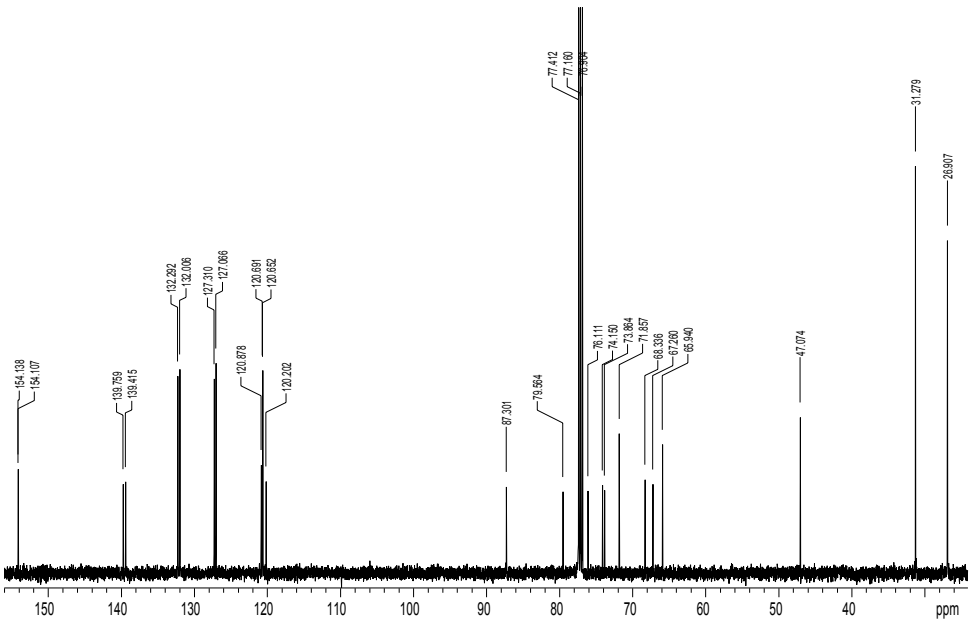
4d ^{13}C NMR (100 MHz, $CDCl_3$)



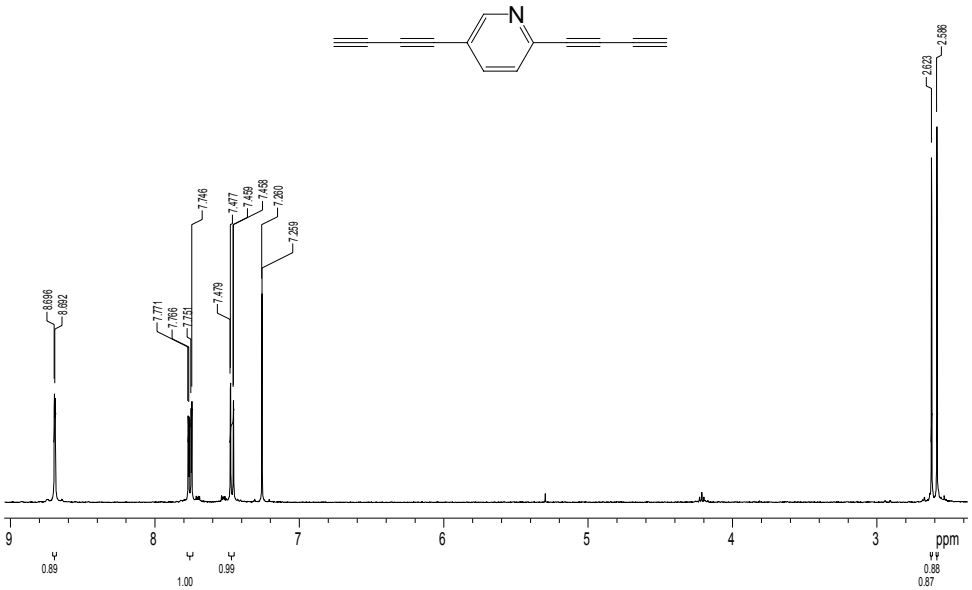
Compound **5c** ^{1}H NMR (400 MHz, $CDCl_3$)



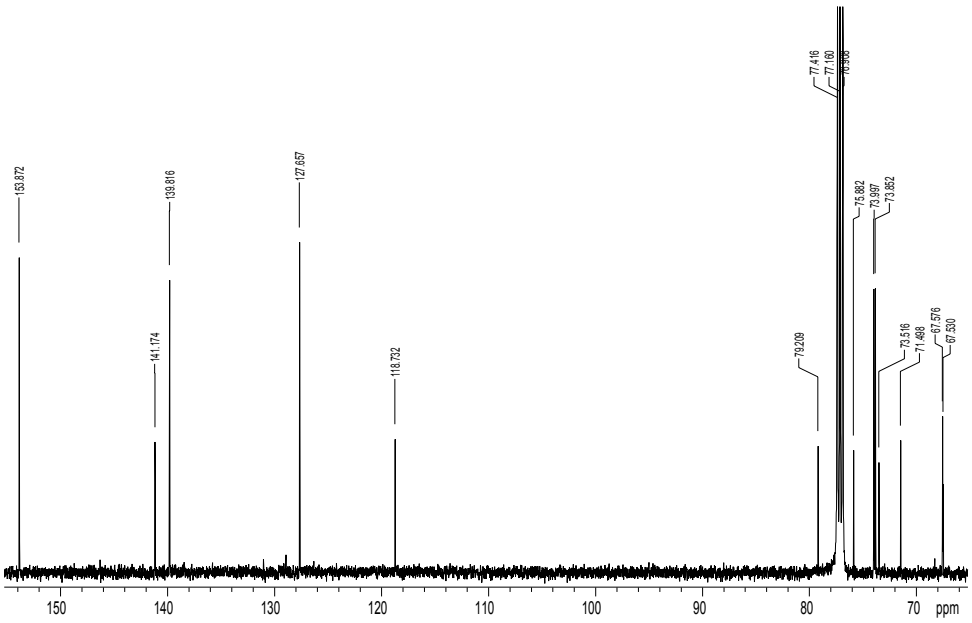
5c ^{13}C NMR (100 MHz, $CDCl_3$)



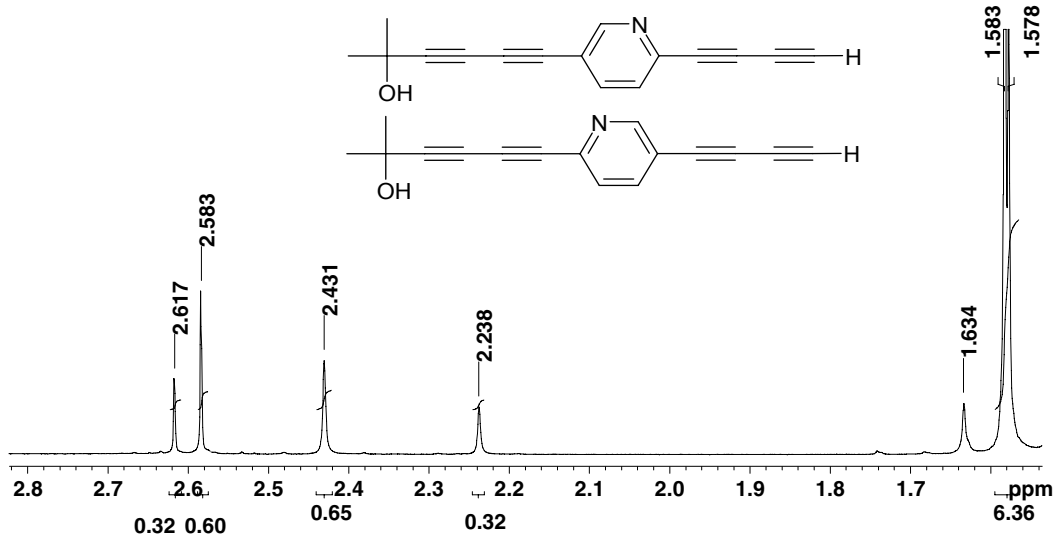
Compound **4d** ^{1}H NMR (400 MHz, $CDCl_3$)



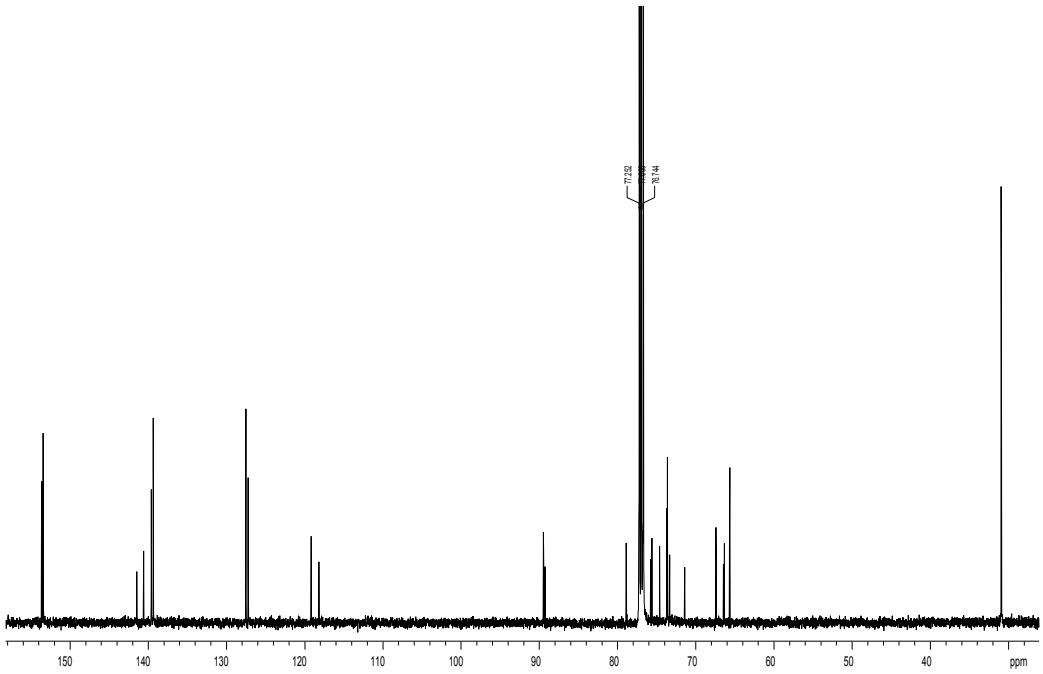
4d ^{13}C NMR (100 MHz, $CDCl_3$)



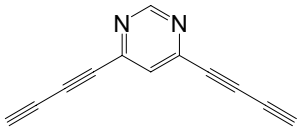
Compounds **5d** and **5d'** ^{1}H NMR (400 MHz, $CDCl_3$): part of the spectrum



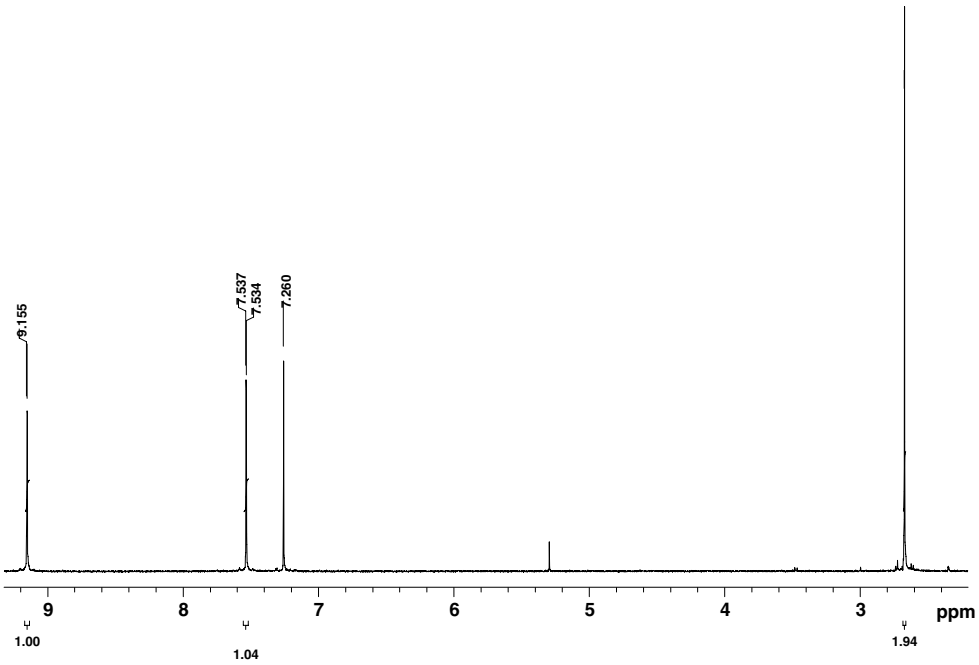
Compounds **5d** and **5d'** ^{13}C NMR (125 MHz, $CDCl_3$)



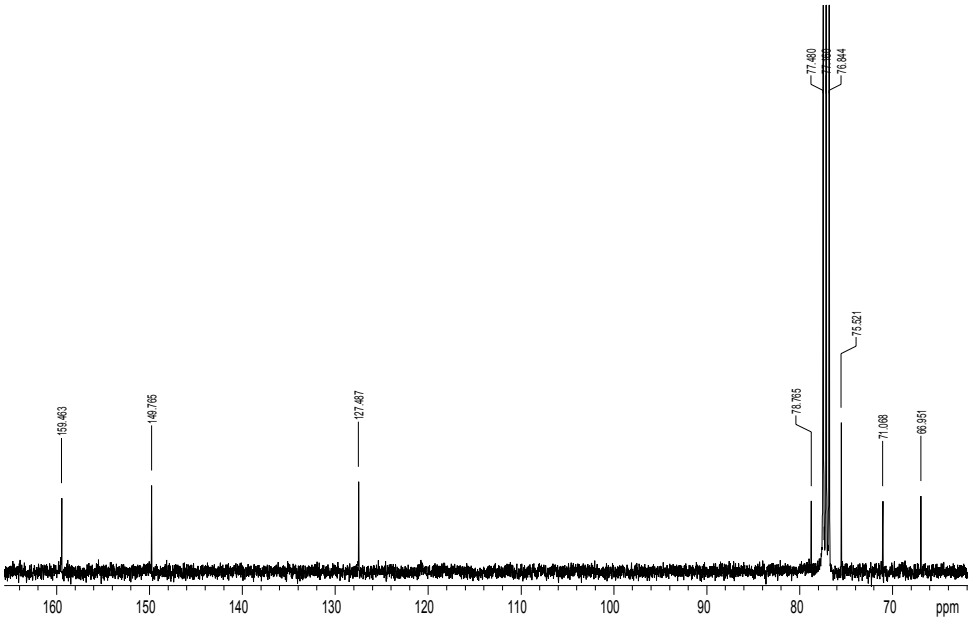
Compound **4e** ^{1}H NMR (400 MHz, $CDCl_3$)



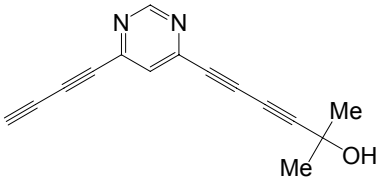
2.674

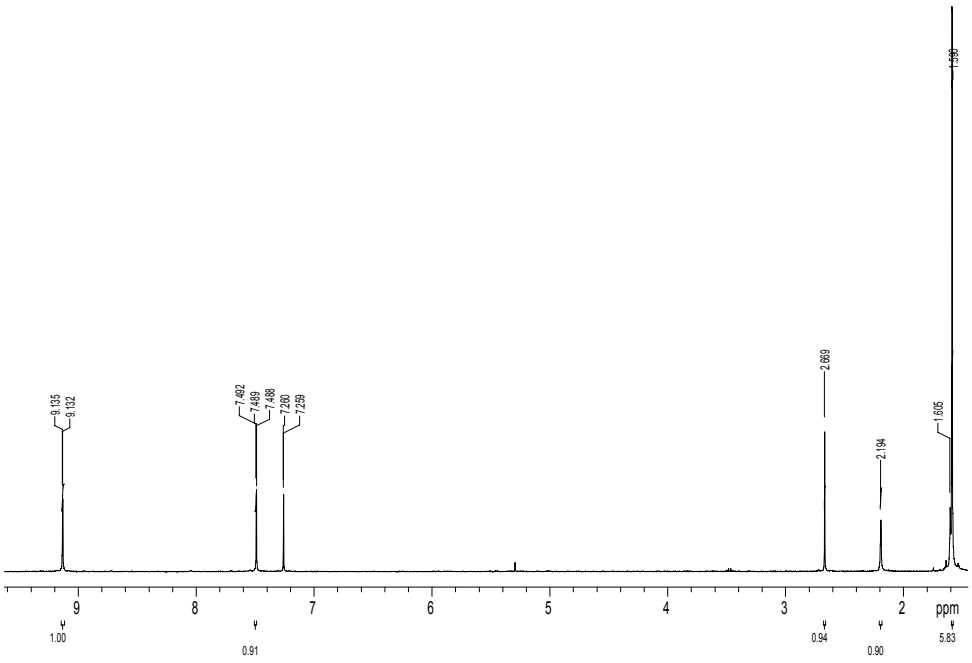


4e ^{13}C NMR (100 MHz, $CDCl_3$)

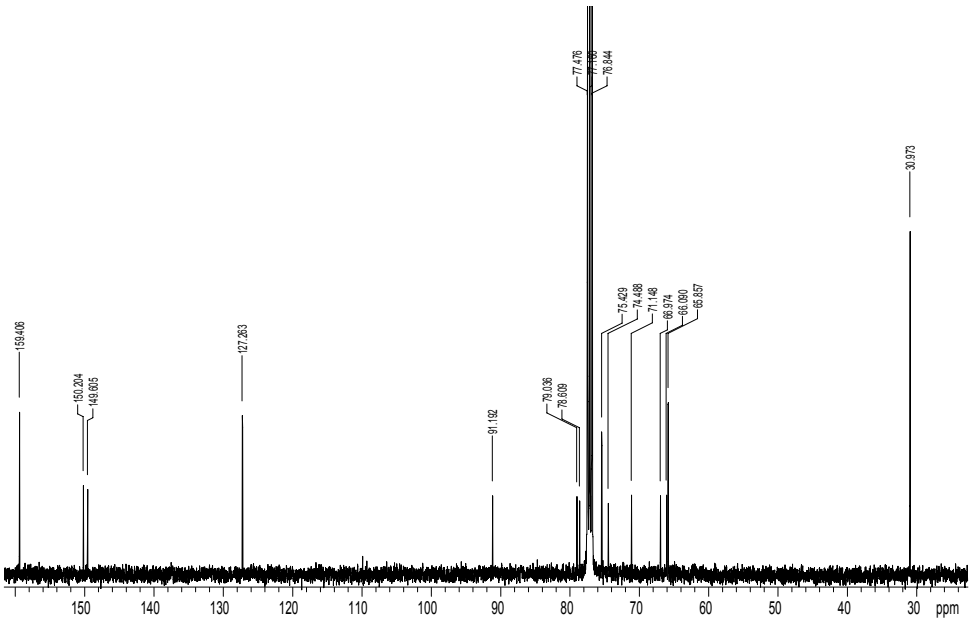


Compound **5e** ^{1}H NMR (400 MHz, $CDCl_3$)





5e ^{13}C NMR (100 MHz, $CDCl_3$)



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