Suporting Information

High-efficiency solution-processed triplet-triplet annihilation organic light-emitting diodes using oligocarbazole- and benzonitrile-modified polyaromatic blue fluorescent emitters

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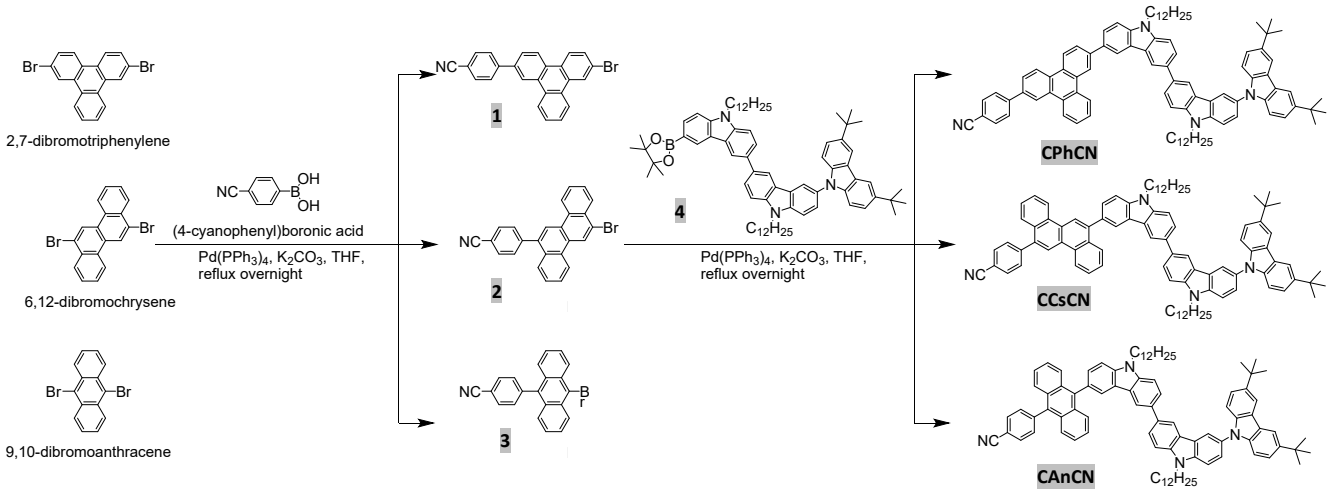
Materials synthesis and characterization



Scheme 1. Synthetic routes of **CPhCN**, **CPhCN** and **CAnCN**

4-(7-Bromotriphenylen-2-yl)benzonitrile (**1**)

2,7-Dibromotriphenylene (1.0 g, 2.6 mmol) and 4-cyanophenylboronic acid (132 mg, 0.9 mmol) were dissolved in dried THF (60 mL) under nitrogen atmosphere. 10% K_2CO_3 (aq) (10ml) was added, the mixture was stirred at ambient temperature. Tetrakris(triphenylphosphene)palladium(0), $Pd(PPh_3)_4$ (52 mg, 0.05 mmol) was then added and degassed the reaction mixture for 10 minutes. The reaction mixture was heated to reflux. After 18 h, cooled to room temperature and water was added to the reaction mixture. The resulting solution was extracted by dichloromethane (3 x 50 mL) and the organic layer was washed with brine (3 x 20 mL), dried (Na_2SO_4) and concentrated *in vacuo.* Purification by column chromatography on silica gel eluting with gradient hexane:dichloromethane from 100% to 50% gave white solids (270 mg, 74%). *m/z* APCI Found: $[M + H]^+$, 409.9523; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (1H, s, Ar-*H*), 8.79 (1H, d, *J* = 1.9 Hz, Ar-*H*), 8.73 – 8.70 (1H, m, Ar-*H*), 8.68 (1H, d, *J* = 8.5 Hz, Ar-*H*), 8.62 – 8.57 (1H, m, Ar-*H*), 8.52 (1H, d, *J* = 8.7 Hz, Ar-*H*), 7.90 – 7.87 (3H, m, Ar-*H*), 7.82 (1H, d, *J* = 8.0 Hz, Ar-*H*), 7.78 (1H, dd, *J* = 8.6, 1.9 Hz, Ar-*H*), 7.76 – 7.69 (2H, m, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 138.1, 132.8, 131.8, 130.5, 129.8, 129.3, 129.0, 128.1, 128.0, 127.9, 126.4, 126.2, 125.2, 124.2, 123.6, 123.3, 122.2, 118.9, 111.3.

4-(12-Bromochrysen-6-yl)benzonitrile (2)

6,12-Dibromochrysene (700 mg, 1.80 mmol) and 4-cyanophenylboronic acid (88 mg, 0.6 mmol) were dissolved in dried THF (60 mL) under nitrogen atmosphere. 10% K_2CO_3 (aq) (10ml) was added, the mixture was stirred at ambient temperature. Tetrakris(triphenylphosphene)palladium(0) $Pd(PPh_3)_4$ (35 mg, 5 mol%) was then added and degassed the reaction mixture for 10 minutes. The reaction mixture was heated to reflux. After 18 h the reaction was stopped, cooled to room temperature and water was added to the reaction mixture. The resulting solution was extracted by dichloromethane (3 x 50 mL) and the organic layer was washed with brine (3 x 20 mL), dried (Na_2SO_4) and concentrated *in vacuo.* Purification by column chromatography on silica gel eluting with gradient hexane:dichloromethane from 100% to 50% gave light yellow solids (147 mg, 60%). *m/z* APCI Found: $[M + H]^+$, 409.9745; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (1H, s, Ar-*H*), 8.80 (1H, d, *J* = 8.4 Hz, Ar-*H*), 8.78 – 8.73 (1H, m, Ar-*H*), 8.56 (1H, s, Ar-*H*), 8.50 – 8.45 (1H, m, Ar-*H*), 7.92 – 7.84 (m, 3H), 7.81 – 7.72 (m, 5H), 7.62 (1H, ddd, *J* = 8.1, 6.8, 1.2 Hz, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 137.8, 132.3, 131.4, 130.9, 130.8, 130.4, 130.0, 128.7, 128.3, 127.8, 127.8, 127.3, 127.2, 127.1, 126.2, 125.3, 123.6, 123.5, 123.3, 122.3, 118.8, 111.6.

4-(10-Bromoanthracen-9-yl)benzonitrile (3)

9,10-Dibromoanthracene (1.4 g, 4.08 mmol) and 4-cyanophenylboronic acid (200 mg, 1.36 mmol) were dissolved in dried THF (30 mL) under nitrogen atmosphere. 10% K_2CO_3 (aq) (10ml) was added, the mixture was stirred at ambient temperature. Tetrakris(triphenylphosphene)palladium(0) $Pd(PPh_3)_4$ (78.6 mg, 5 mol%) was then added and degassed the reaction mixture for 10 minutes. The reaction mixture was heated to reflux. After 18 h the reaction was stopped, cooled to room temperature and water was added to the reaction mixture. The resulting solution was extracted by dichloromethane (3 x 50 mL) and the organic layer was washed with brine (3 x 20 mL), dried (Na_2SO_4) and concentrated *in vacuo.* Purification by column chromatography on silica gel eluting with gradient hexane:dichloromethane from 100% to 50% gave light yellow solids (318 mg, 65%). *m/z* APCI Found: $[M + H]^+$, 358.0166; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (2H, dt, *J* = 8.9, 0.9 Hz, Ar-*H*), 7.70 – 7.64 (4H, m, Ar-*H*), 7.62 (2H, dt, *J* = 8.8, 0.9 Hz, Ar-*H*), 7.58 (2H, ddd, *J* = 8.9, 6.5, 1.2 Hz, Ar-*H*), 7.37 (2H, ddd, *J* = 8.7, 6.5, 1.1 Hz, Ar-*H*), 7.34 (3H, dd, *J* = 5.0, 1.9 Hz, Ar-*H*), 7.31 – 7.24 (8H, m, Ar-*H*), 7.23 – 7.17 (5H, m, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 138.5, 138.3, 137.2, 137.2, 134.4, 131.2, 131.0, 130.9, 130.7, 130.2, 130.1, 129.2, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.4, 127.3, 126.9, 126.7, 125.6, 122.8.

Characterization data

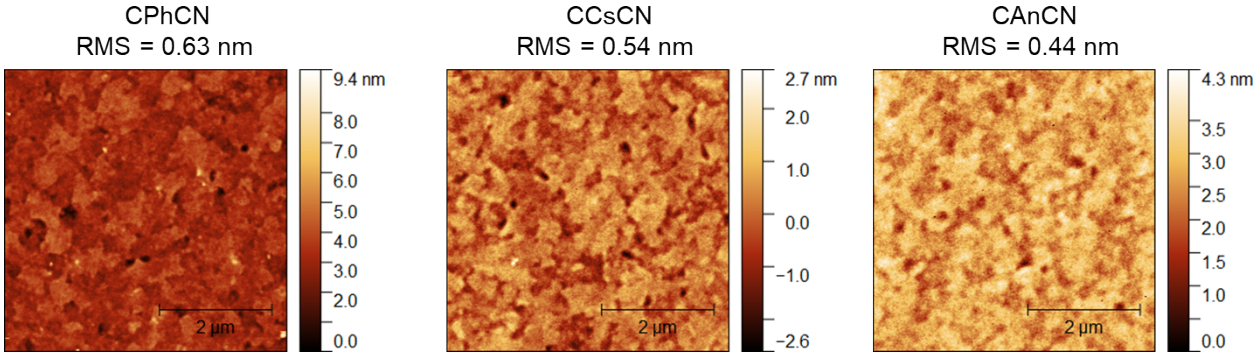


Fig. S1 AFM images of spin-coated thin films.

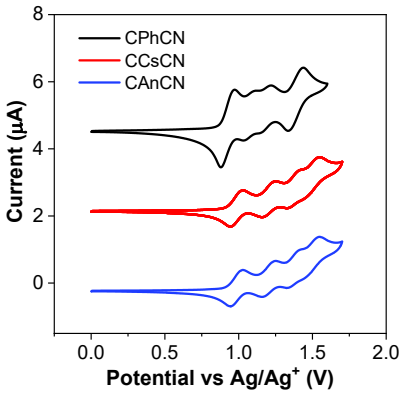


Fig. S2 CV voltammograms measured in dichloromethane solutions containing 0.1 M n-Bu_4NPF_6 at a scan rate of 50 mV s^{-1}.

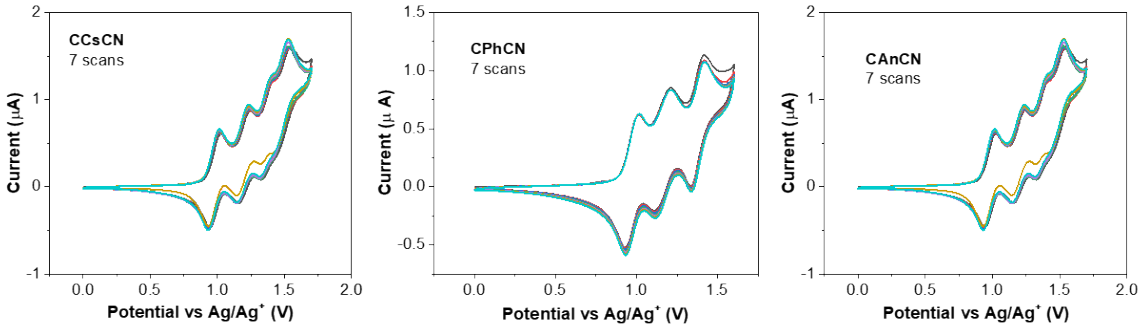


Fig. S3 Multiple scan CV plots measured in dichloromethane solutions containing 0.1 M n-Bu_4NPF_6 at a scan rate of 50 mV s^{-1}.

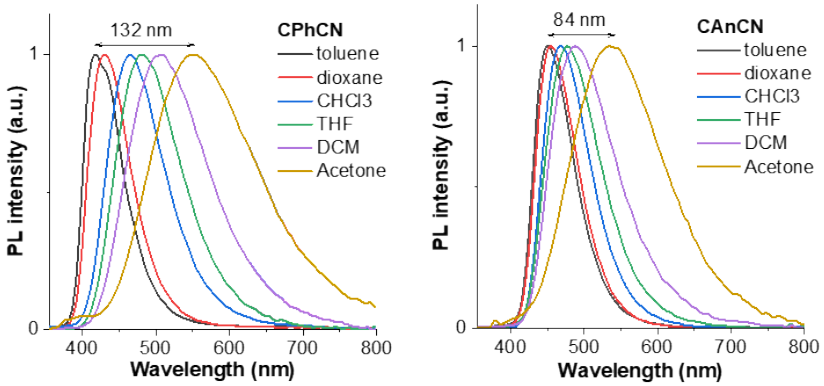


Fig. S4 PL spectra in various solvents with different polarities.

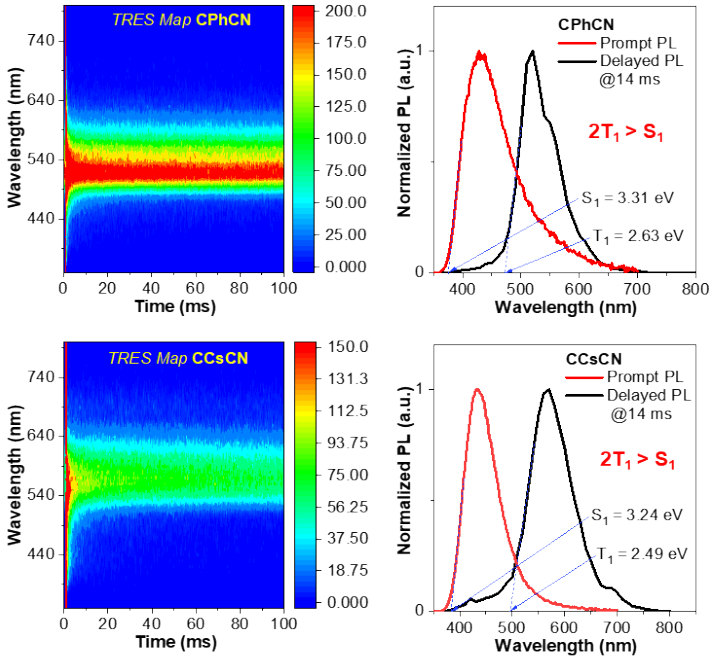


Fig. S5 a) TRES map profile and b) integrated TRES slice of prompt PL spectra and delayed PL spectra @14 ms of CPhCN/CCsCN 2 wt% doped poly(methyl methacrylate) films covered with EXCEVAL™ film.

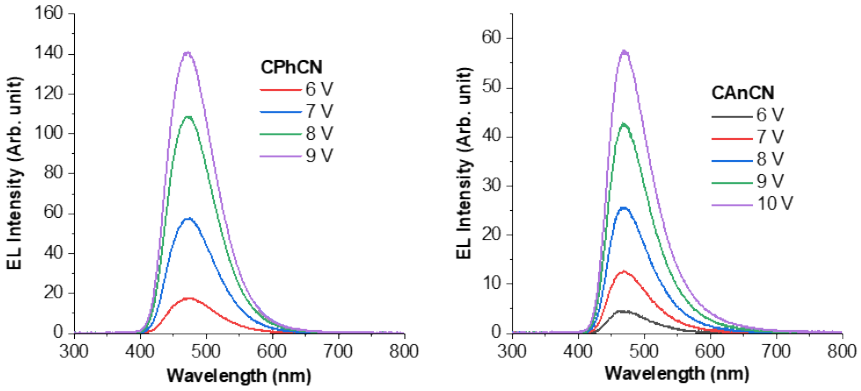


Fig. S6 EL spectra under different operating voltages of CPhCN and CAnCN-based devices.

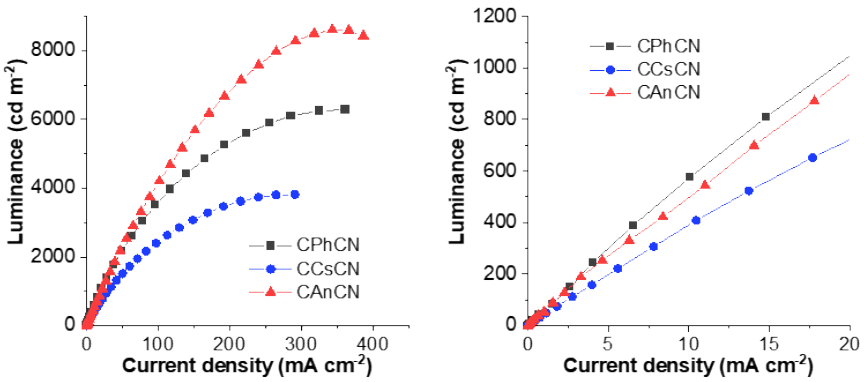
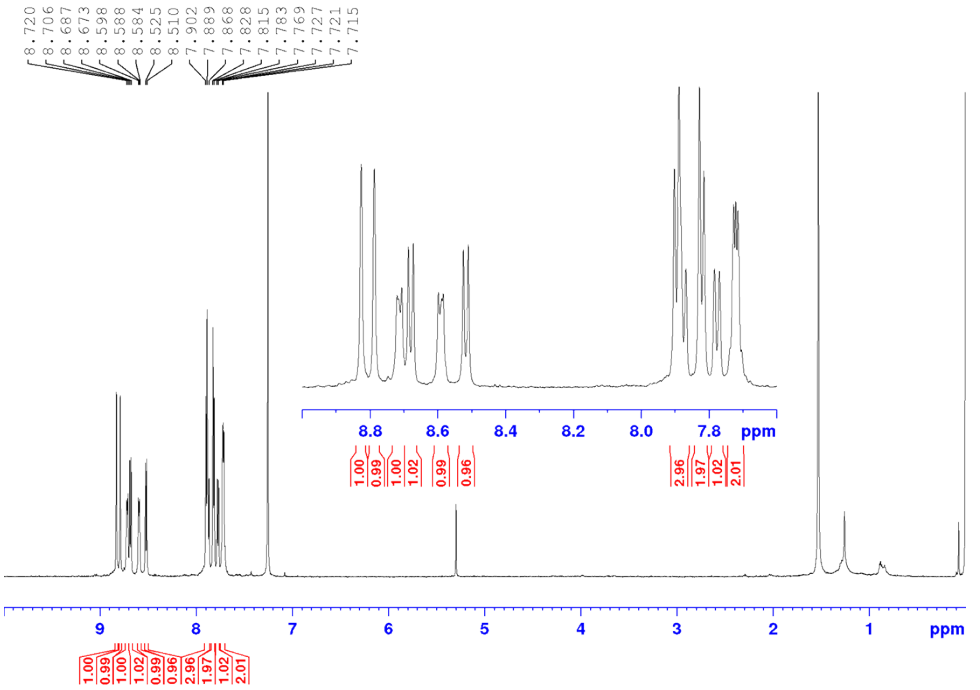
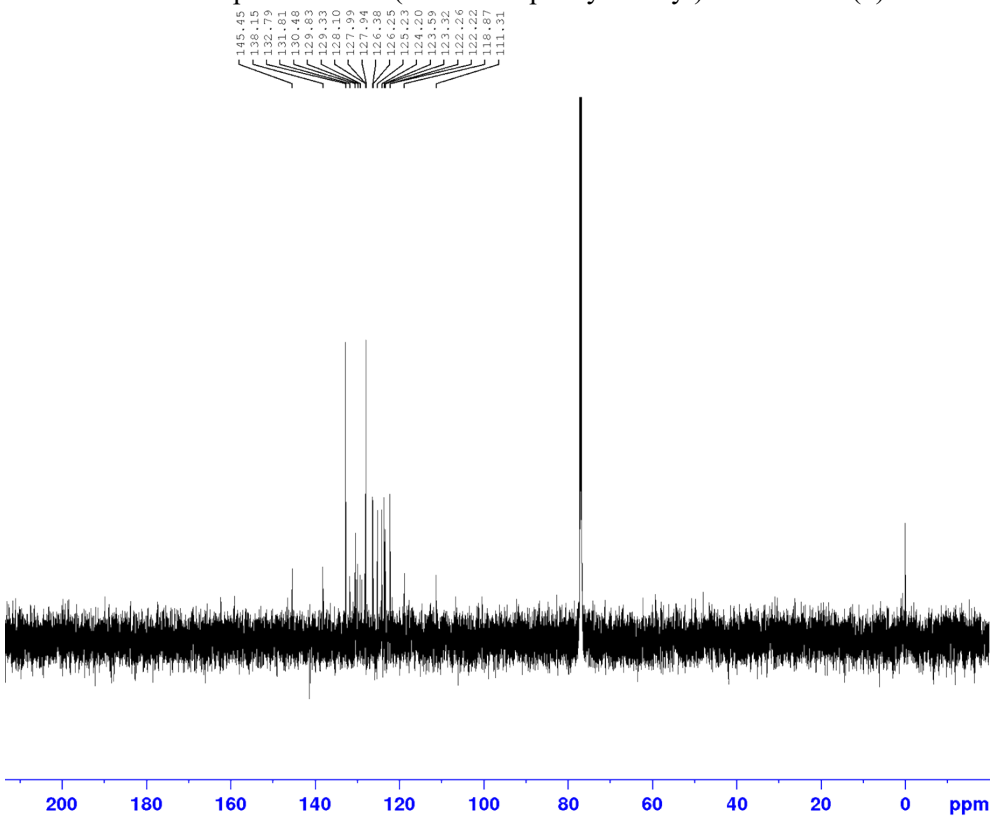


Fig. S7 Luminance–current density (*L*-*J*) characteristic of the non-doped solution-processed OLEDs.

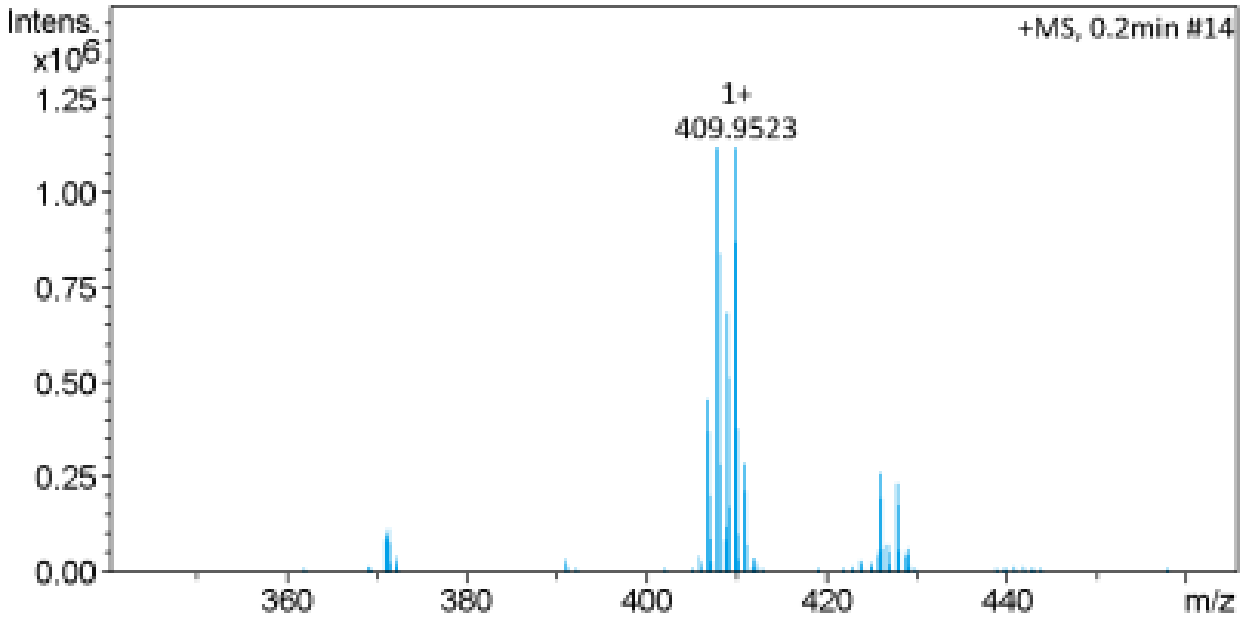
Fig. S8 Copies of ^{1}H-NMR, ^{13}C-NMR, and HRMS spectra of the synthesized compounds.



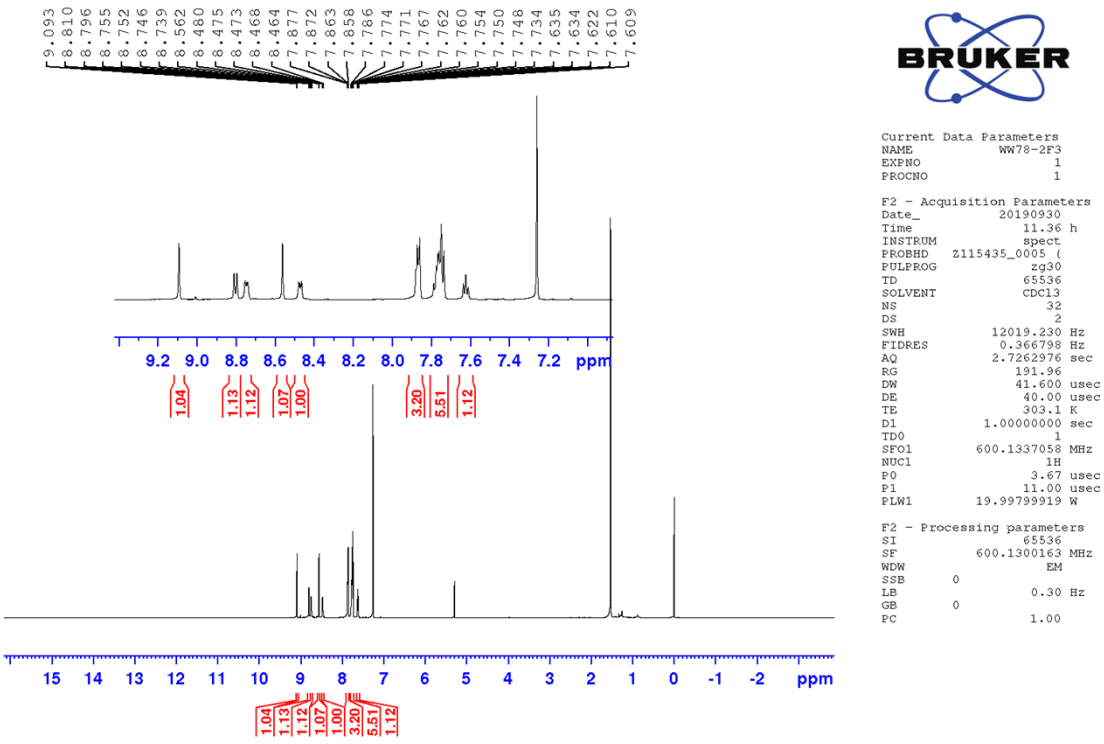
^{1}H NMR spectrum of 4-(7-bromotriphenylen-2-yl)benzonitrile (**1**)



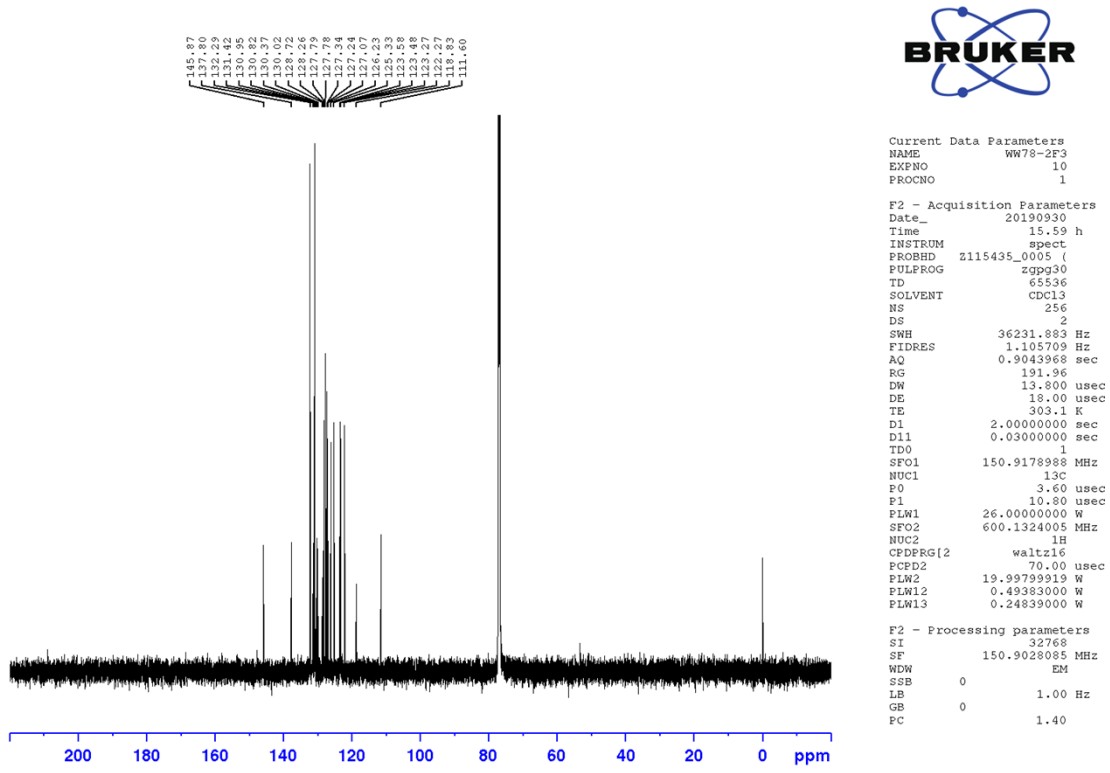
^{13}C NMR spectrum of 4-(7-bromotriphenylen-2-yl)benzonitrile (**1**)



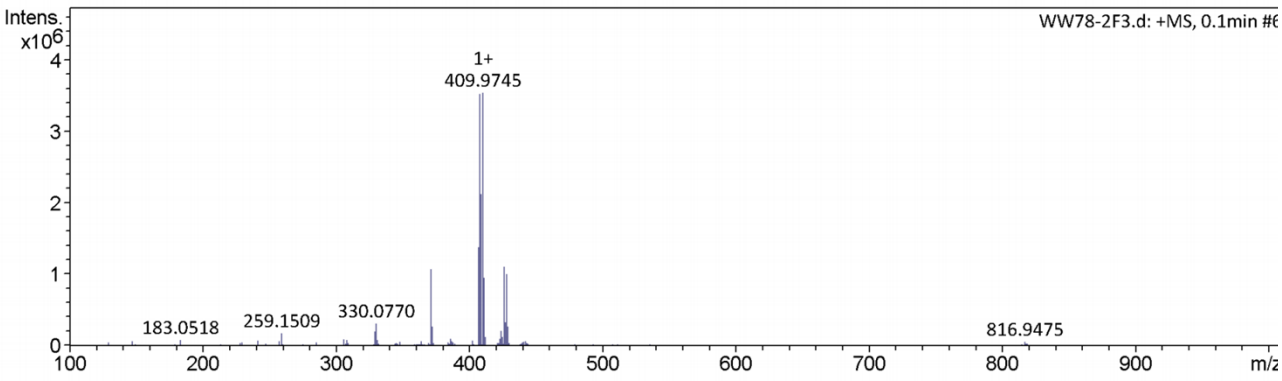
Mass spectrum of 4-(7-bromotriphenylen-2-yl)benzonitrile (**1**)



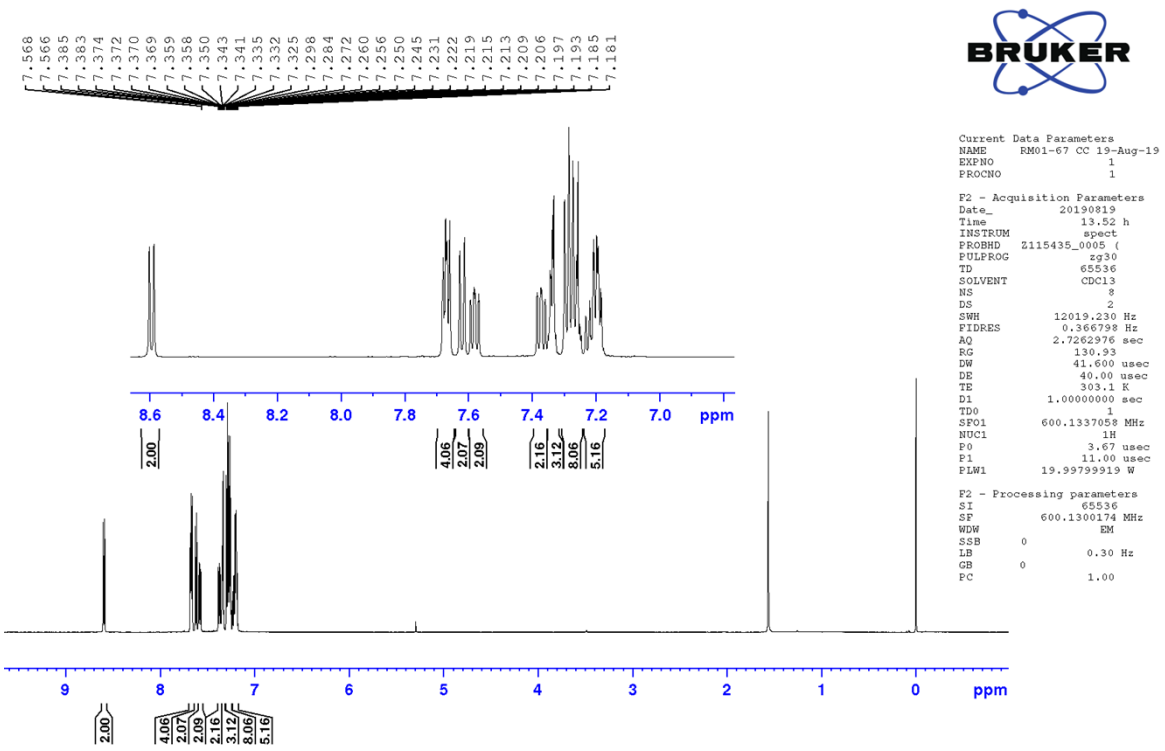
^{1}H NMR spectrum of **4-(12-Bromochrysen-6-yl)benzonitrile** (**2**)



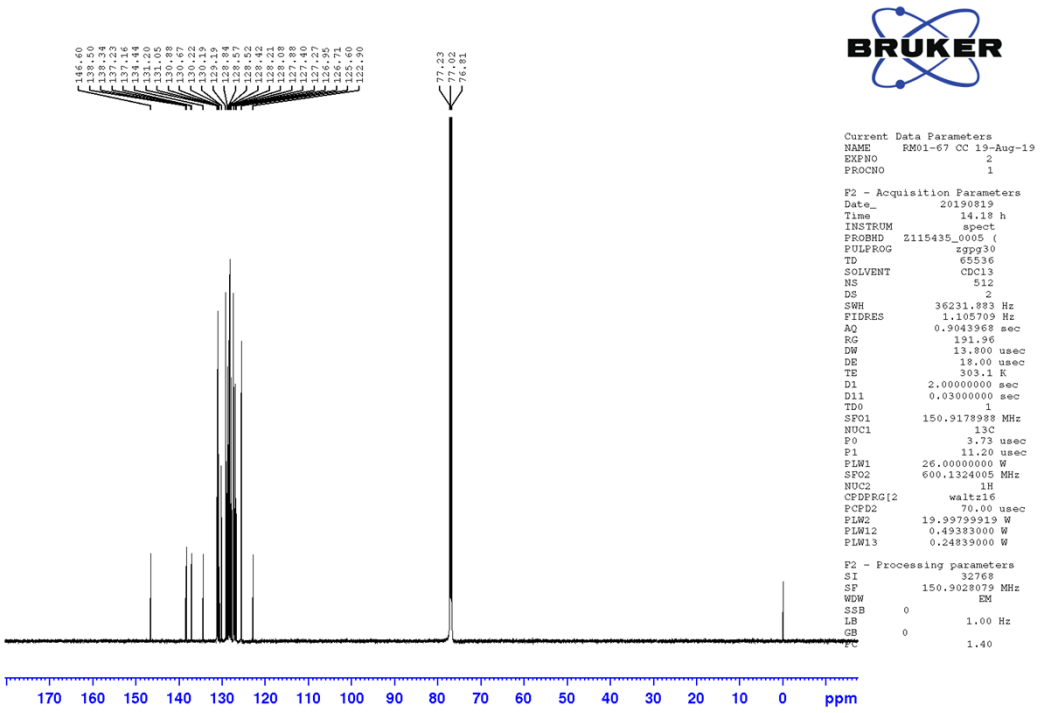
^{13}C NMR spectrum of **4-(12-Bromochrysen-6-yl)benzonitrile** (**2**)



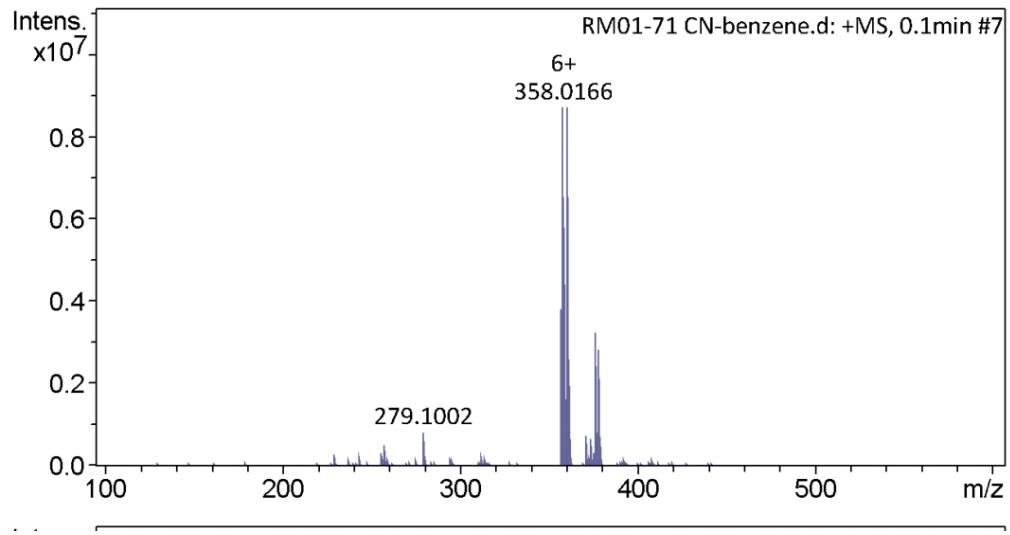
Mass spectrum of **4-(12-Bromochrysen-6-yl)benzonitrile** (**2**)



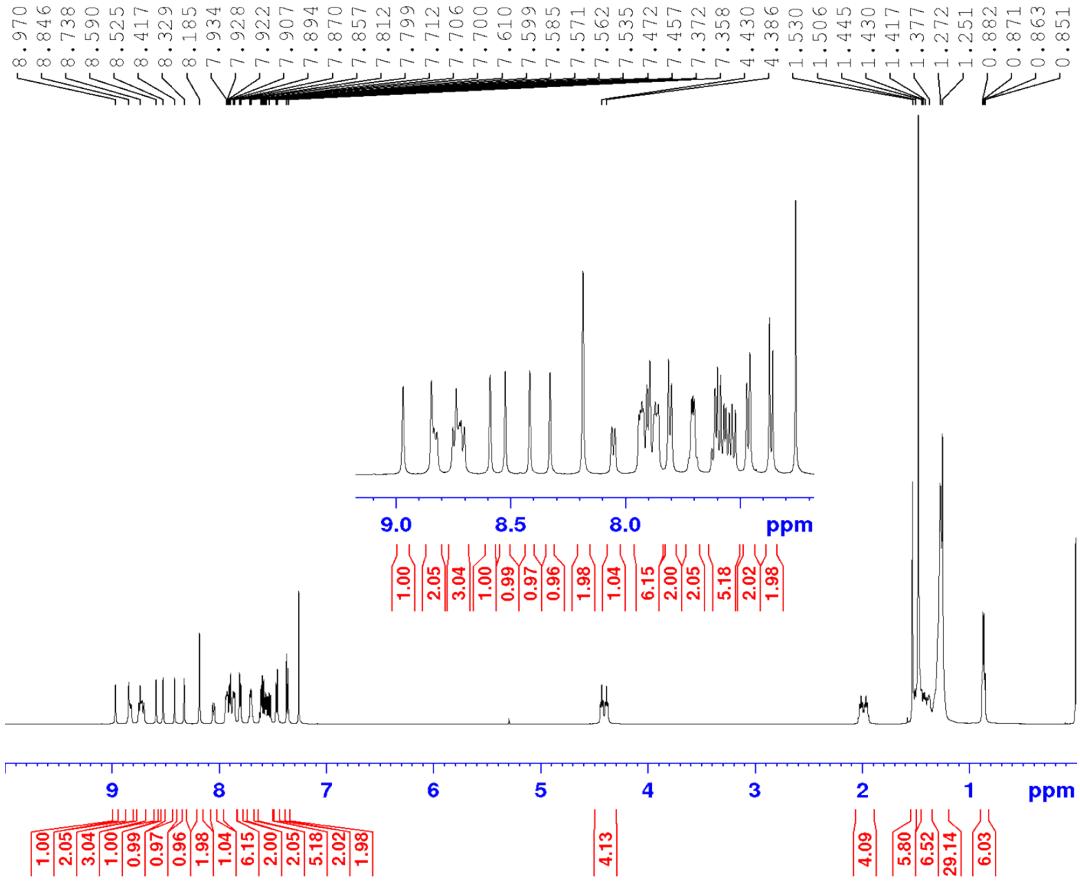
^{1}H NMR spectrum of **4-(10-bromoanthracen-9-yl)benzonitrile** (**3**)



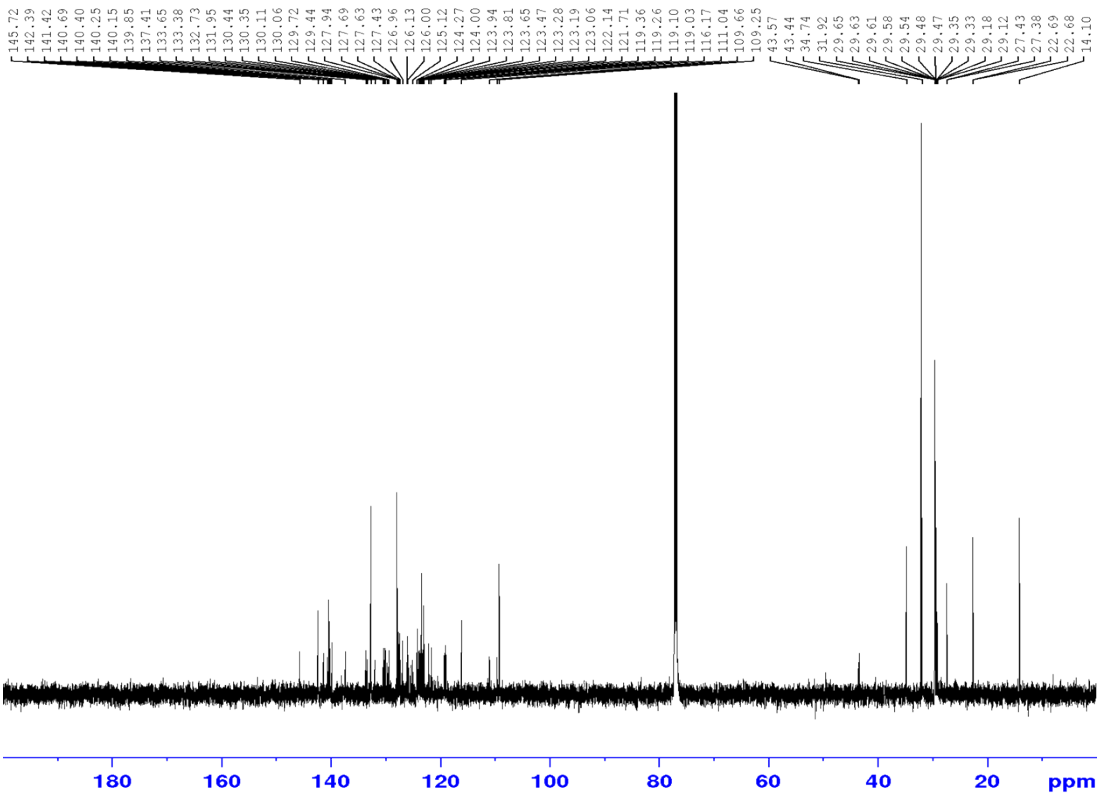
^{13}C NMR spectrum of **4-(10-bromoanthracen-9-yl)benzonitrile** (**AnCN**)



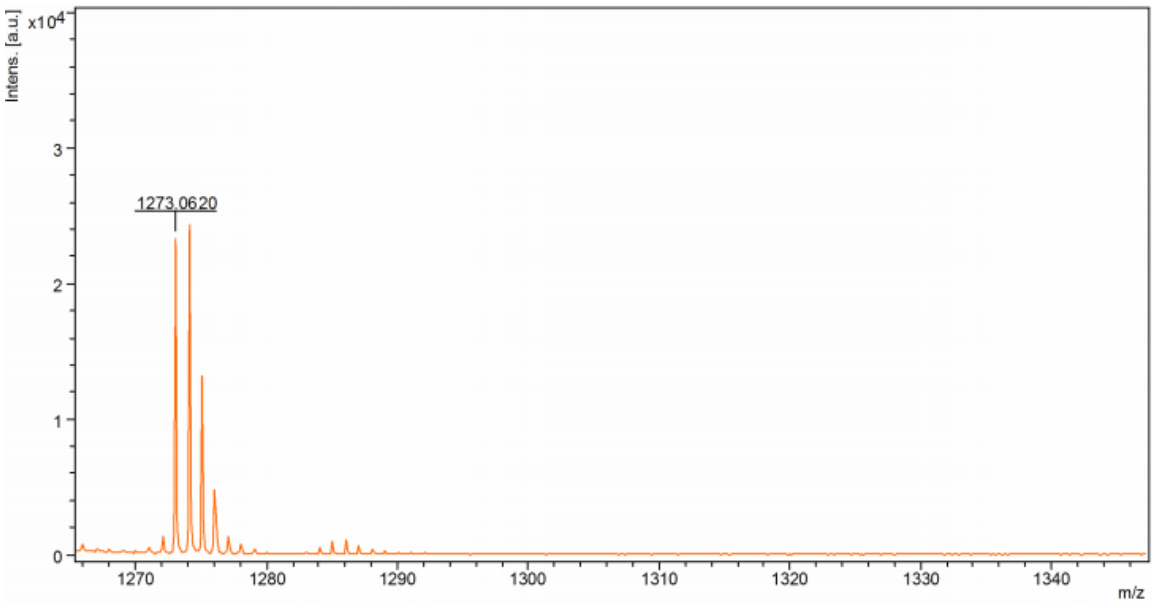
Mass spectrum of **4-(10-bromoanthracen-9-yl)benzonitrile** (**3**)



^{1}H NMR spectrum of 4-(7-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,92'H-[3,3':6',9"-tercarbazol]-6-yl)triphenylen-2-yl)benzonitrile (**CPhCN**)



^{13}C NMR spectrum of 4-(7-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,92'H-[3,3':6',9"-tercarbazol]-6-yl)triphenylen-2-yl)benzonitrile (**CPhCN**)



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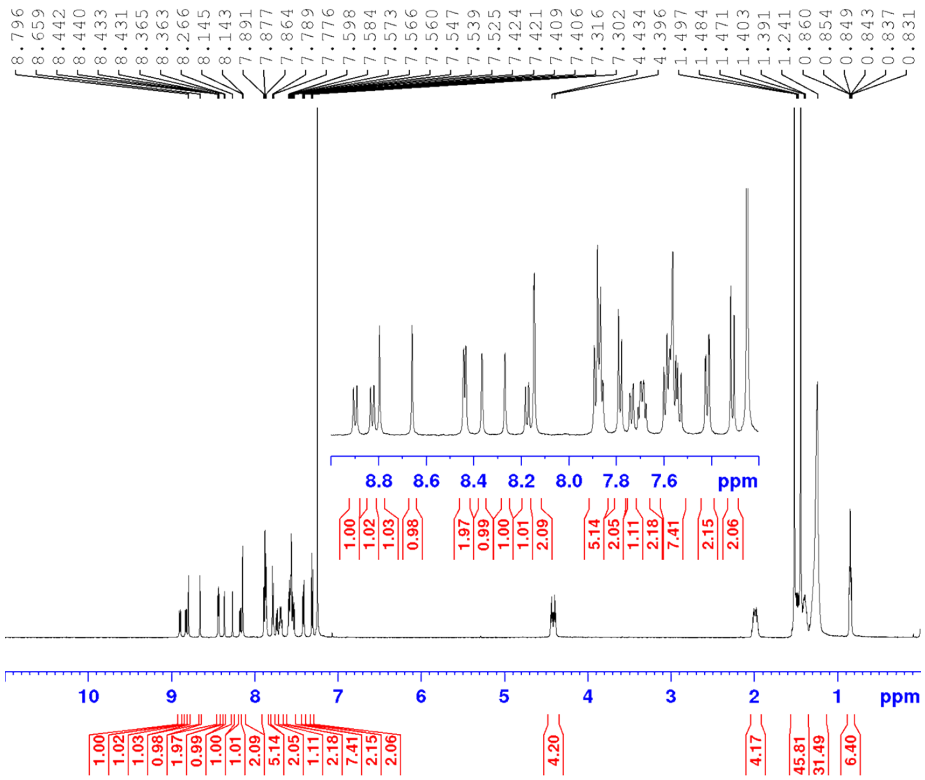
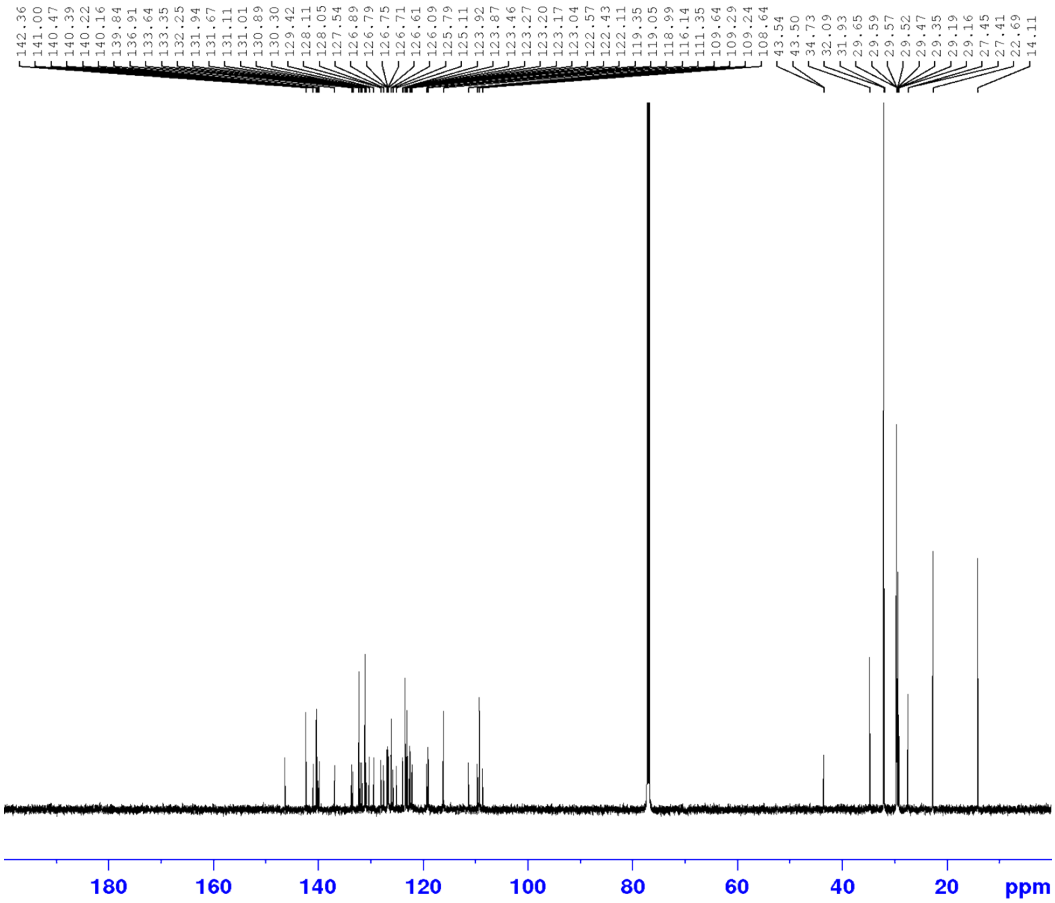
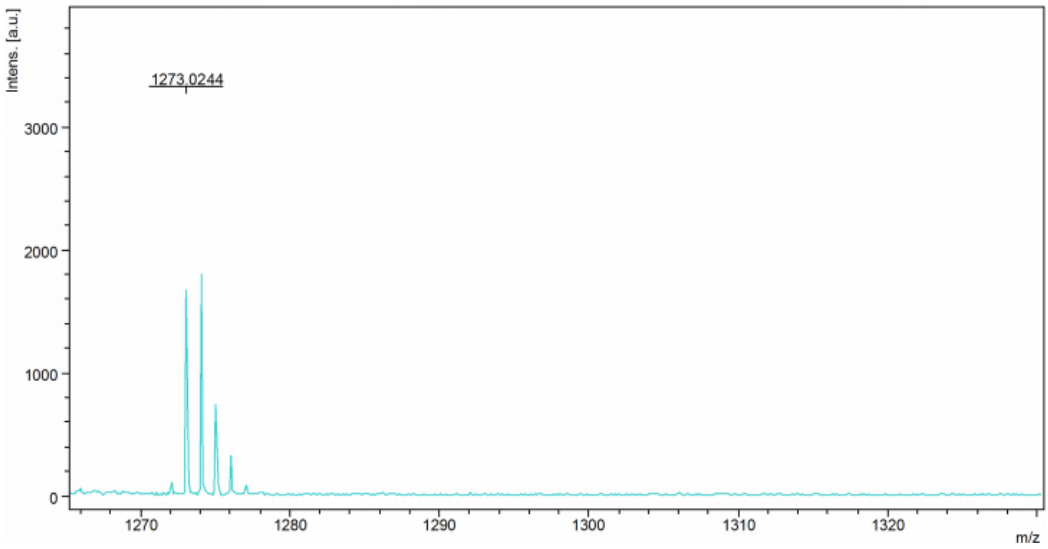


^{1}H NMR spectrum of 4-(12-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,9'H-[3,3':6',9"-tercarbazol]-6-yl)chrysen-6-yl)benzonitrile (**CCsCN**)



^{13}C NMR spectrum of 4-(12-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,9'H-[3,3':6',9"-tercarbazol]-6-yl)chrysen-6-yl)benzonitrile (**CCsCN**)



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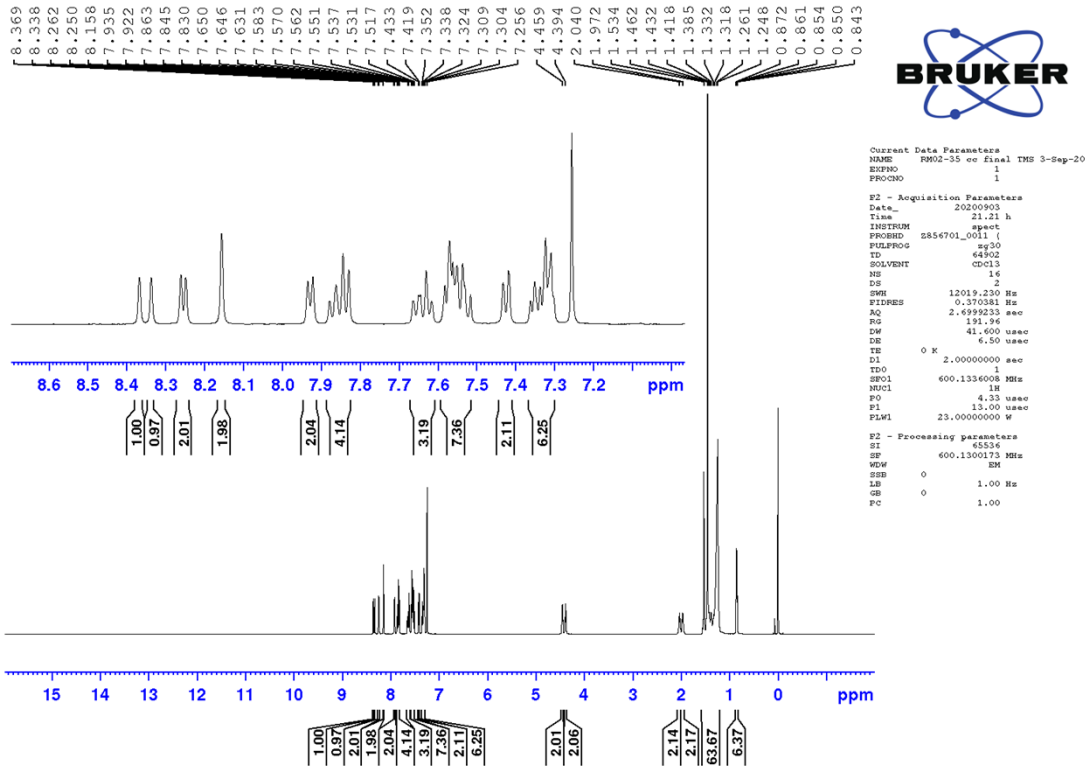
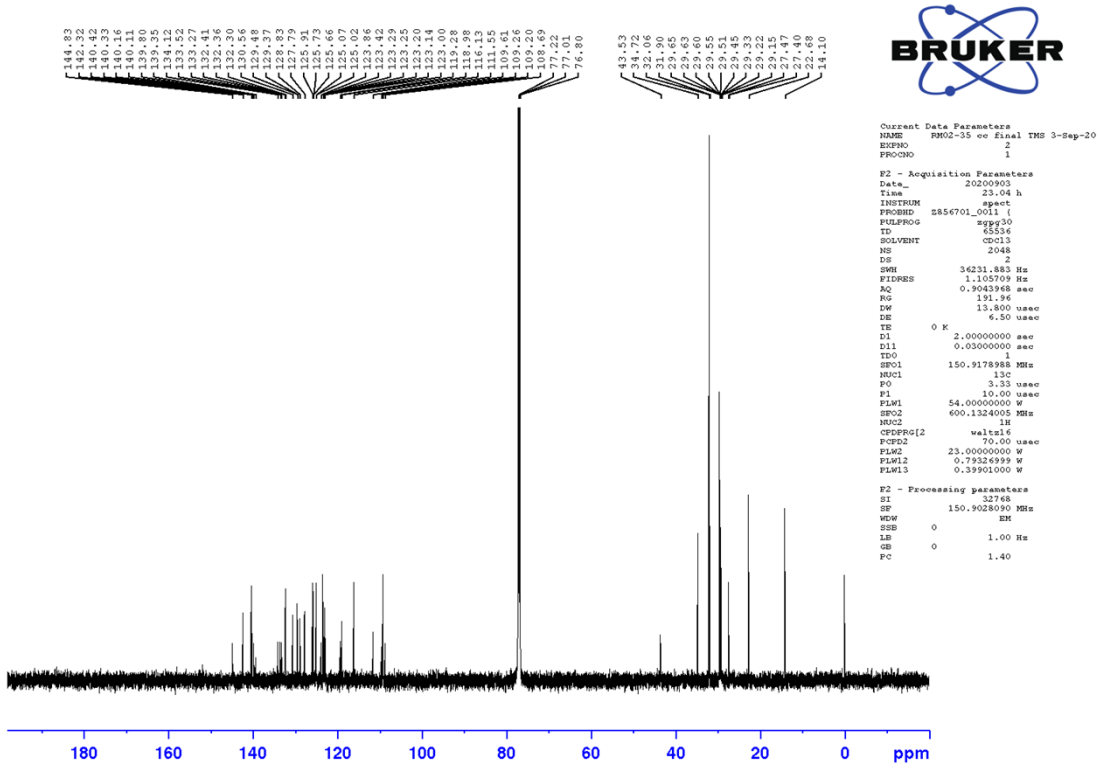
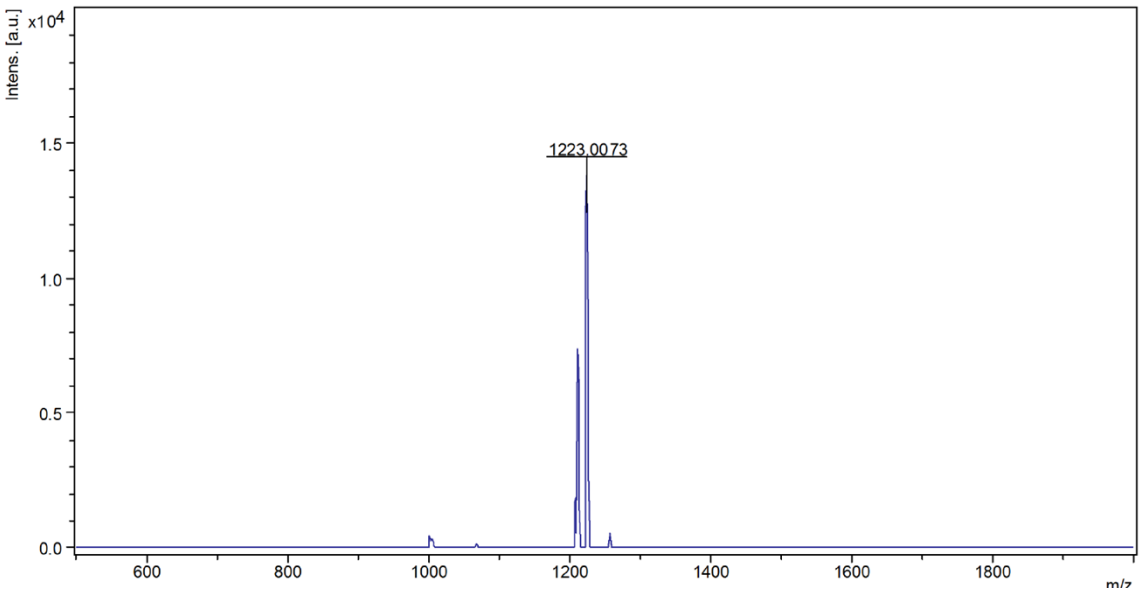


^{1}H NMR spectrum of 4-(10-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,9'H-[3,3':6',9"-tercarbazol]-6-yl)anthracen-9-yl)benzonitrile (**CAnCN**)



^{13}C NMR spectrum of 4-(10-(3",6"-di-tert-butyl-9,9'-didodecyl-9H,9'H-[3,3':6',9"-tercarbazol]-6-yl)anthracen-9-yl)benzonitrile (**CAnCN**)



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