Supporting Information

Materials synthesis and characterization

2-(4-Bromophenyl)-1,4,5-triphenyl-2,5-dihydro-1H-imidazole (1): A mixture of benzil (1.5 g, 7.10 mmol), 4-bromobenzaldehyde (1.32 g, 7.10 mmol) was dissolved in acetic acid (30 mL), and stirred at room temperature. Aniline (0.98 ml, 10.70 mmol) was added dropwise and ammonium acetate (2.75 g, 35.70 mmol) was then added to the reaction mixture, followed by heat to 110ºC for 12 hours. After completion, the reaction was allowed to room temperature and pour into an ice bath. The crude solid was filtered and washed with water. The filtered solid was dissolved in dichloromethane, washed with water (4 x 30 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The product was purified by recrystallization in dichloromethane/methanol to give light brown solids (2.30 g, 74%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.60-7.55 (2H, m, Ar-*H*), 7.39-7.35 (2H, m, Ar-*H*), 7.32 - 7.17 (11H, m, Ar-*H*), 7.12 (2H, d, *J* = 6.8 Hz, Ar-*H*), 7.04(2H, d, *J* = 6.8 Hz, Ar-*H*); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 145.8, 138.5, 136.9, 134.3, 131.3, 131.2, 131.1, 130.5, 130.3, 129.5, 129.2, 128.5, 128.4, 128.2, 128.1, 127.4, 126.7, 122.6. HRMS APCI (*m/z*): calcd for $C_{48}H_{31}N_3$: 452.0711, found: 453.0672 $[MH]^+$.

1,4,5-Triphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,5-dihydro-1H-imidazole (2): A mixture of **1** (2.2 mmol), bispinacolatodiboron (1.7 g, 7 mmol), and potassium acetate (2.7g, 27.0 mmol) was suspended in dried toluene (40 mL) under a nitrogen atmosphere. Bis(triphenylphosphine)palladium(II) dichloride $Pd(PPh_3)_2Cl_2$ (77.2 mg, 0.11 mmol) was added and degassed for 10 minutes. The reaction mixture was stirred for 12 hours under reflux, cooled to room temperature and water was added. The resulting mixture was extracted with dichloromethane (4 x 70 ml), washed the organic layer with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel eluting with hexane:dichloromethane (6:4) to give white solids (1.13 g, 90%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67 (2H, d, *J* = 8.0 Hz, Ar-*H*), 7.60 (2H, d, *J* = 7.4 Hz, Ar-*H*), 7.43 (2H, d, *J* = 8.0 Hz, Ar-*H*), 7.29-7.17 (7H m, Ar-*H*), 7.14 (2H, d, *J* = 8.0 Hz, Ar-*H*), 7.04 (2H, d, *J* = 7.0 Hz, Ar-*H*), 1.32 (12H, s, (CH_3)$_4$); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 146.7, 138.5, 137.2, 134.4, 134.4, 133.0, 131.2, 131.1, 130.6, 129.1, 128.4, 128.3, 128.3, 128.1, 128.0, 127.4, 126.6, 83.9, 24.9. HRMS APCI (*m/z*): calcd for $C_{48}H_{31}N_3$: 498.2479, found: 498.2422 $[M]^+$.

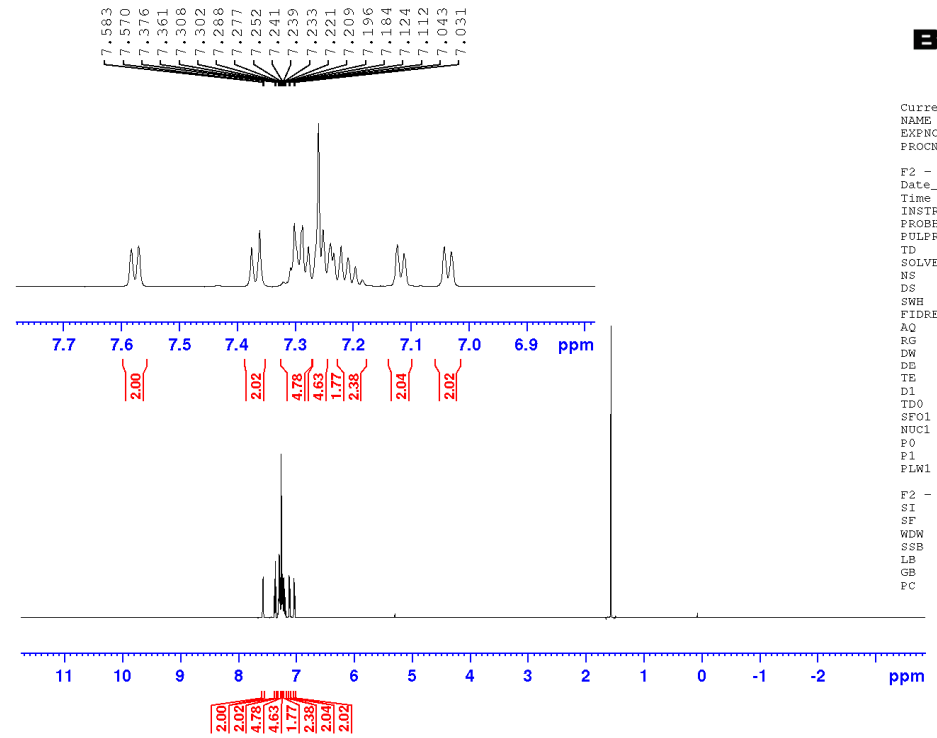
4-(10-Bromoanthracen-9-yl)benzonitrile (3): A mixture of 9,10-dibromoanthracene (200 mg, 1.36 mmol) and 4-cyanophenylboronic acid (1.4 g, 4.08 mmol) was dissolved in dried THF (30 mL) under a nitrogen atmosphere. 10% K_2CO_3 (aq) (10 mL) was added and stirred at ambient temperature. Tetrakris(triphenylphosphene)palladium(0) $Pd(PPh_3)_4$ (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% to give yellow solids (318 mg, 65%). ^{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. HRMS APCI (*m/z*): calcd for $C_{48}H_{31}N_3$: 357.0153, found: 358.0166 $[MH]^+$.

4-(12-Bromochrysen-6-yl)benzonitrile (4): A mixture of 6,12-Dibromochrysene (700 mg, 1.80 mmol) and 4-cyanophenylboronic acid (88 mg, 0.6 mmol) was dissolved in dried THF (60 mL) under a nitrogen atmosphere. 10% K_2CO_3 (aq) (10 ml) was added and 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 18h 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% to give yellow solids (147.6 mg, 60%). ^1H-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. HRMS APCI (*m/z*): calcd for $C_{48}H_{31}N_3$: 409.0289, found: 409.9745 $[MH]^+$.

Figure S1. Copies of $^{1}H/^{13}C$- NMR spectra and HRMS mass spectra

2-(4-Bromophenyl)-1,4,5-triphenyl-2,5-dihydro-1H-imidazole (1)



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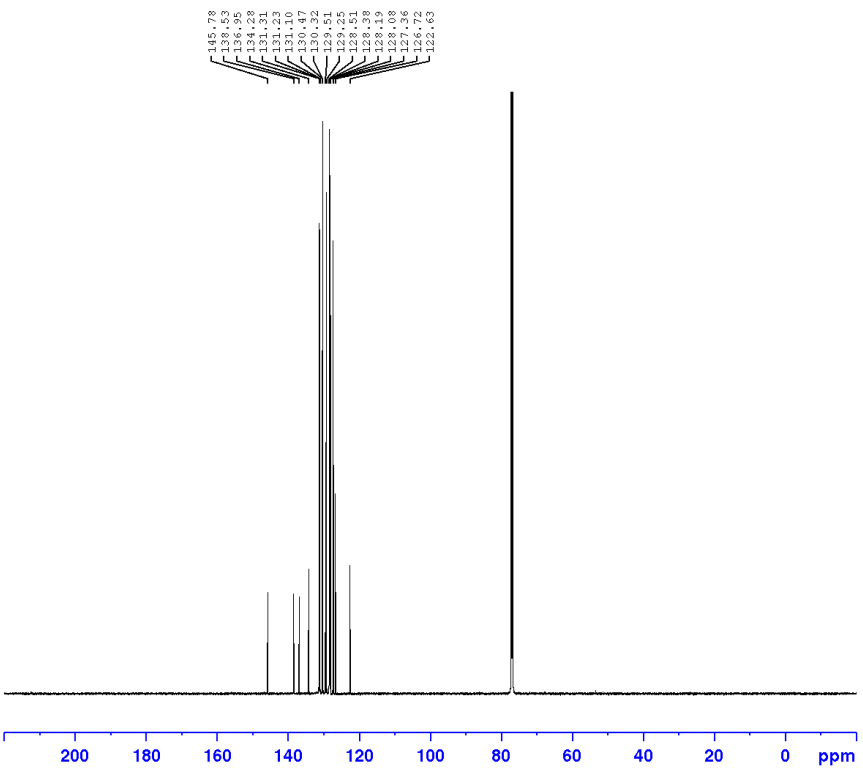

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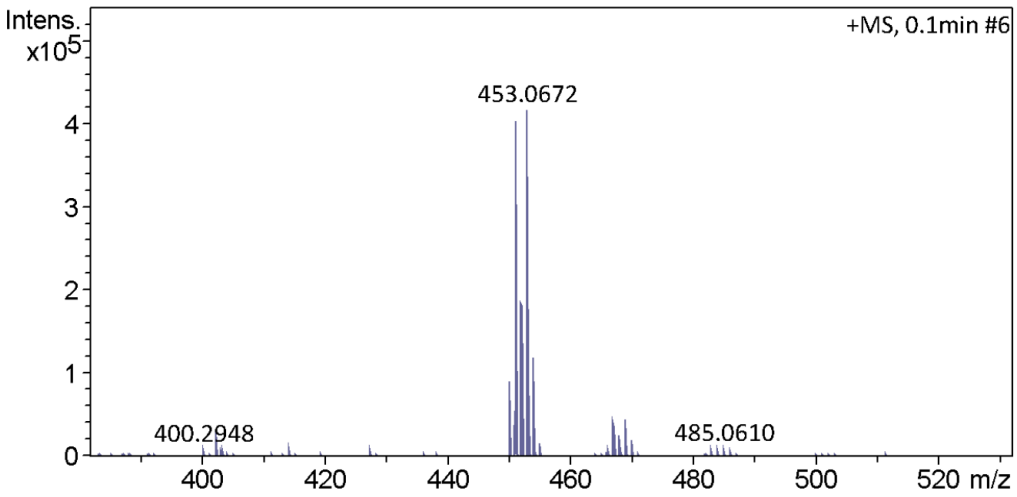
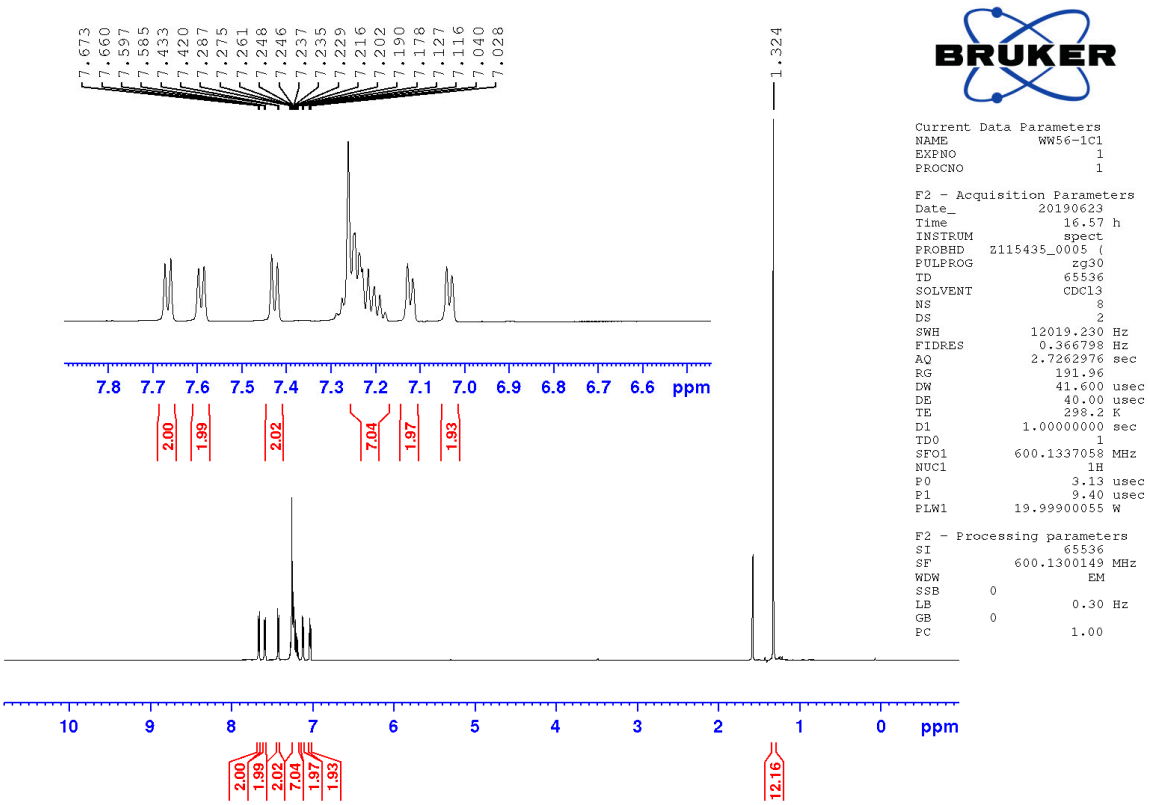
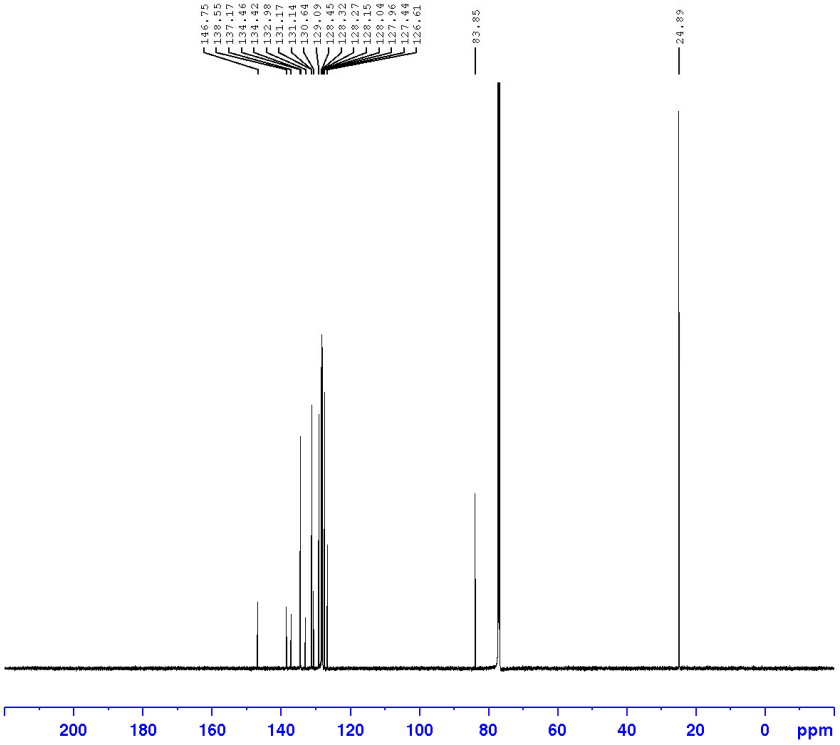


1,4,5-Triphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,5-dihydro-1H-imidazole (2)



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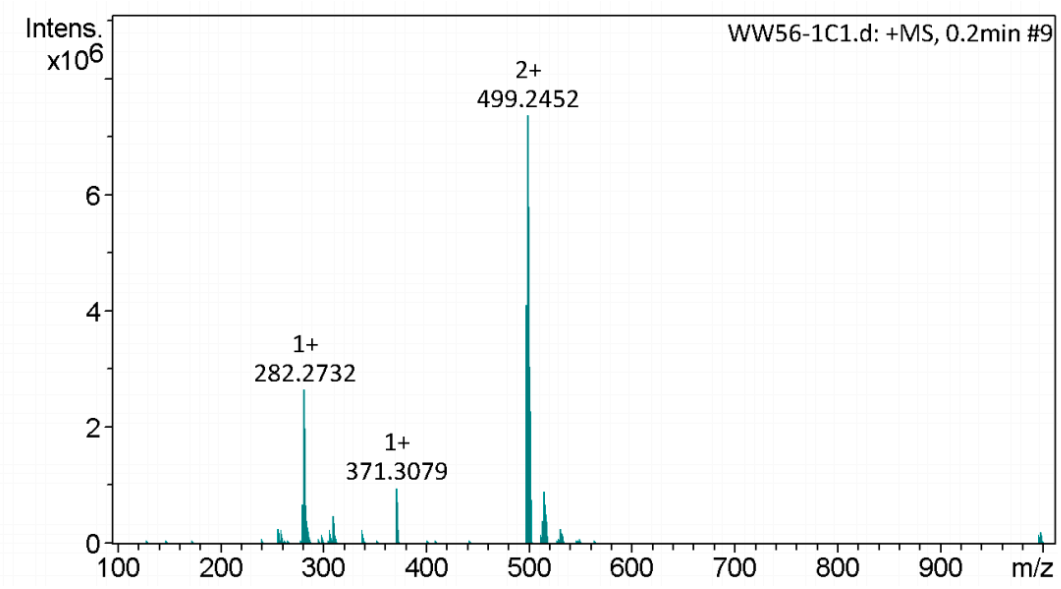
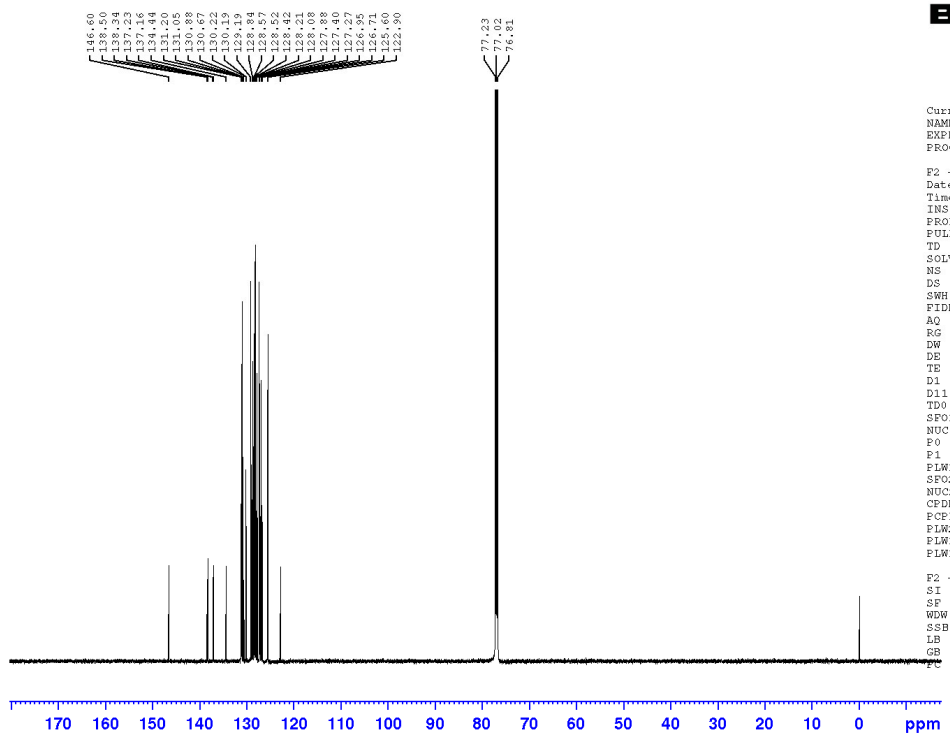


4-(10-Bromoanthracen-9-yl)benzonitrile (3)



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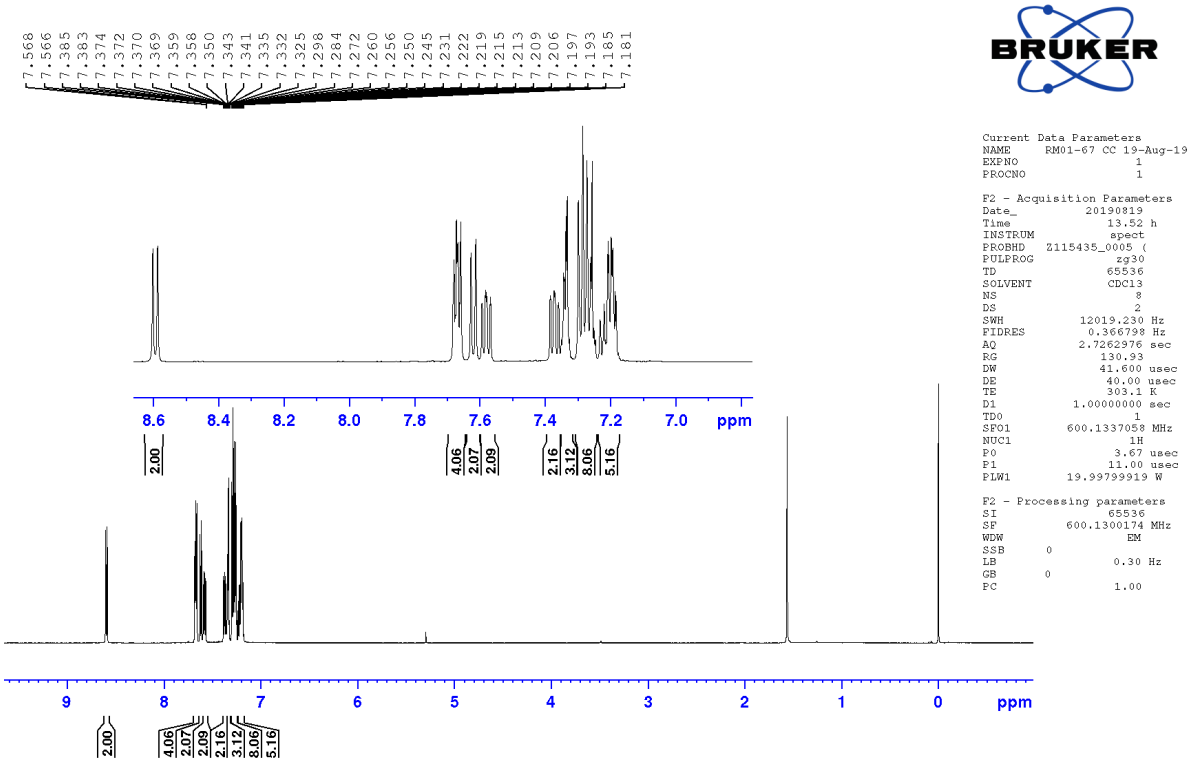

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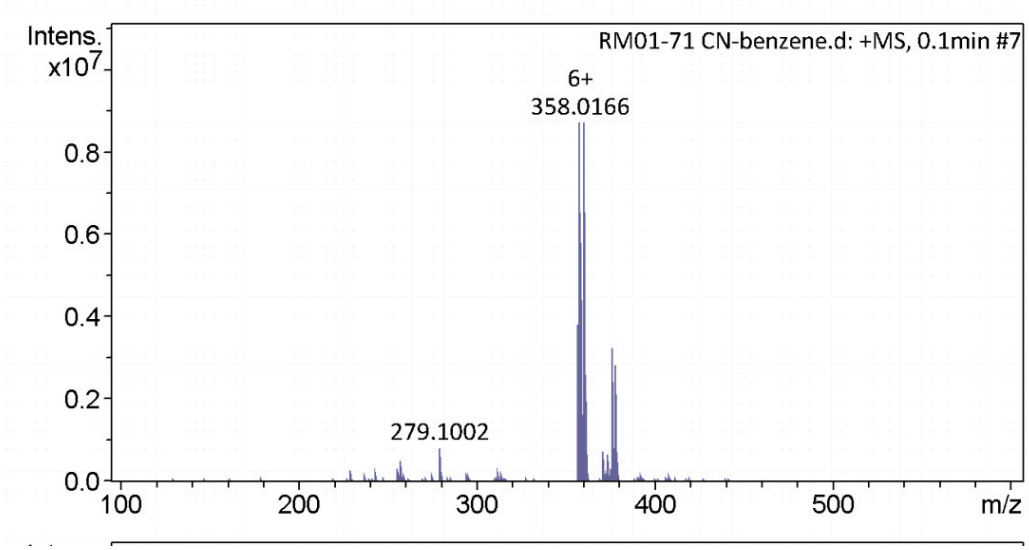
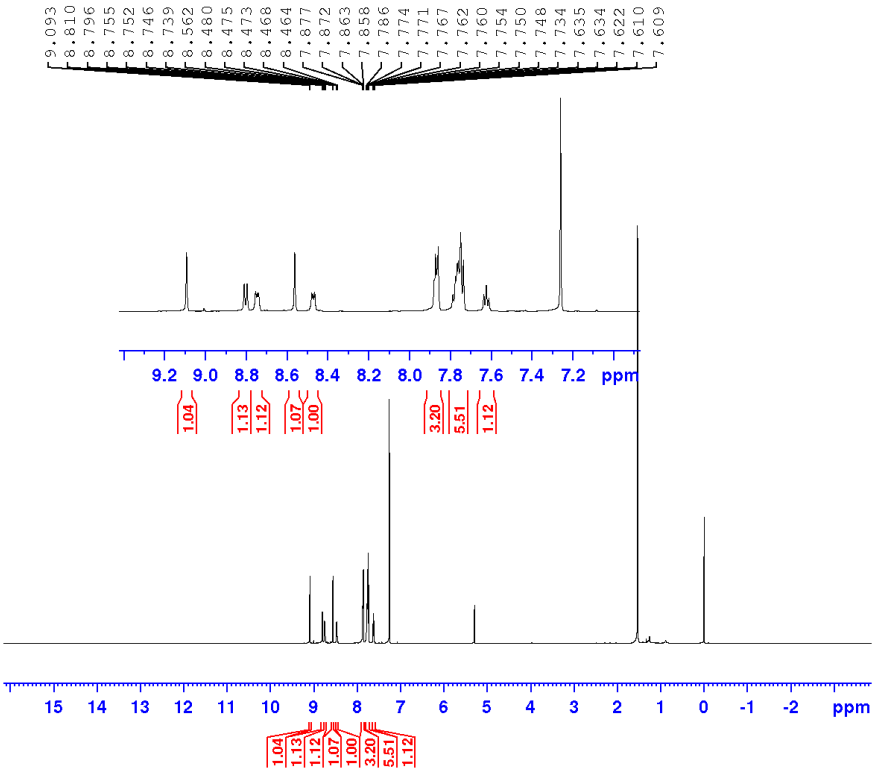


4-(12-Bromochrysen-6-yl)benzonitrile (4)

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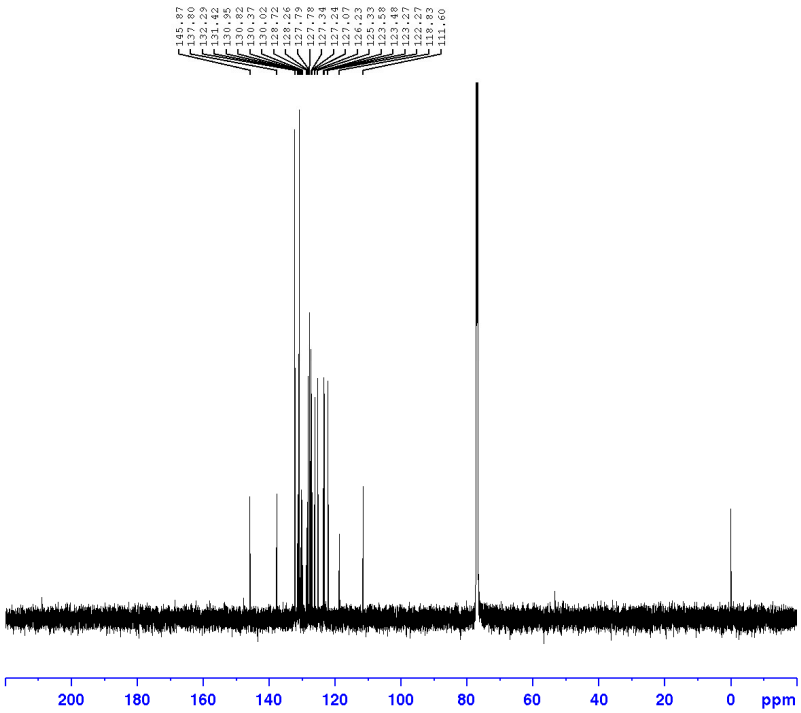

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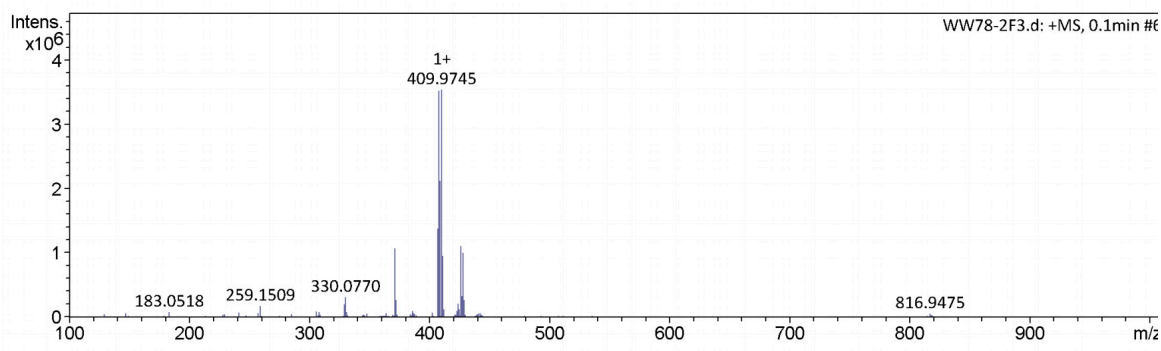
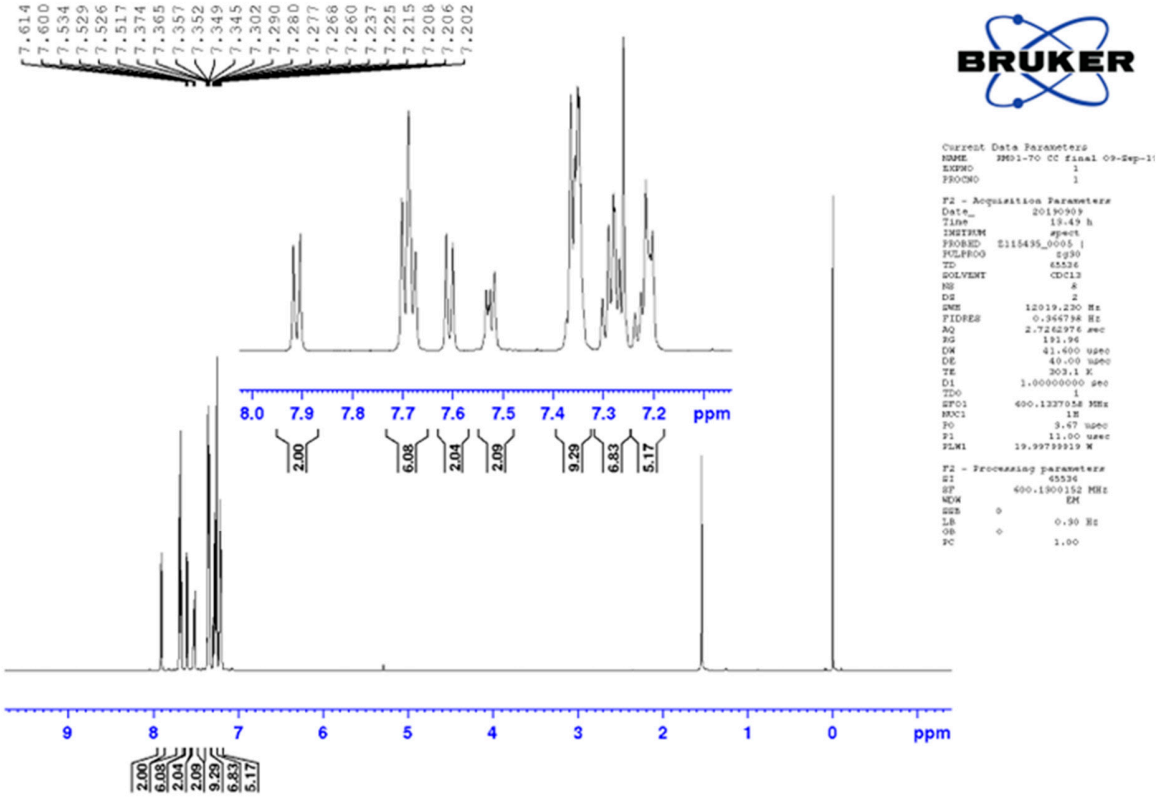


Compound TPIAnCN



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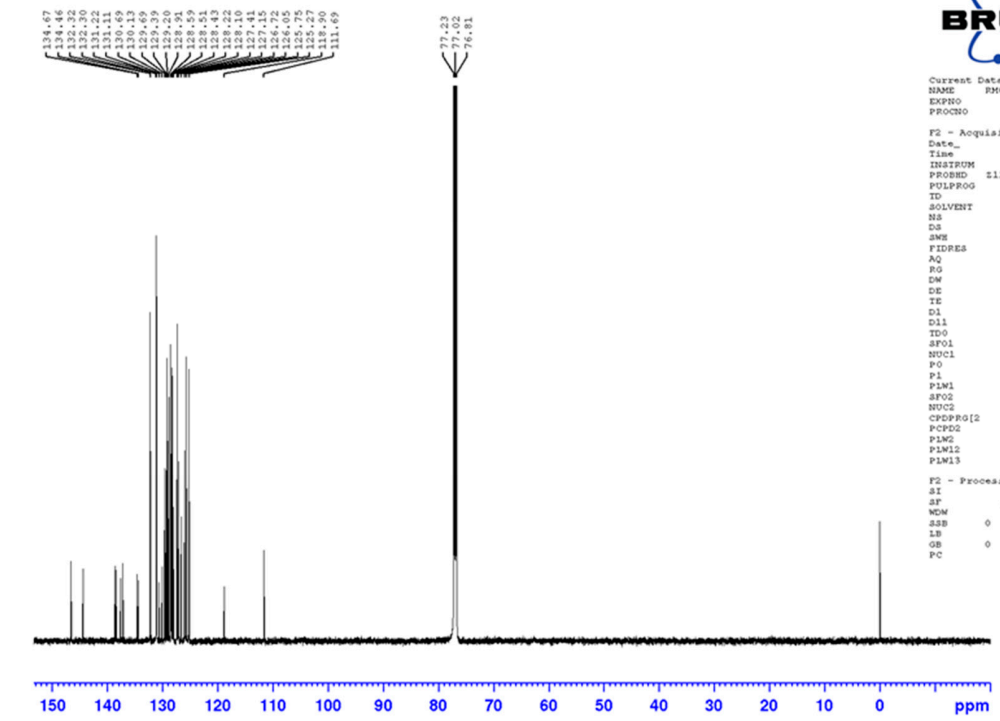

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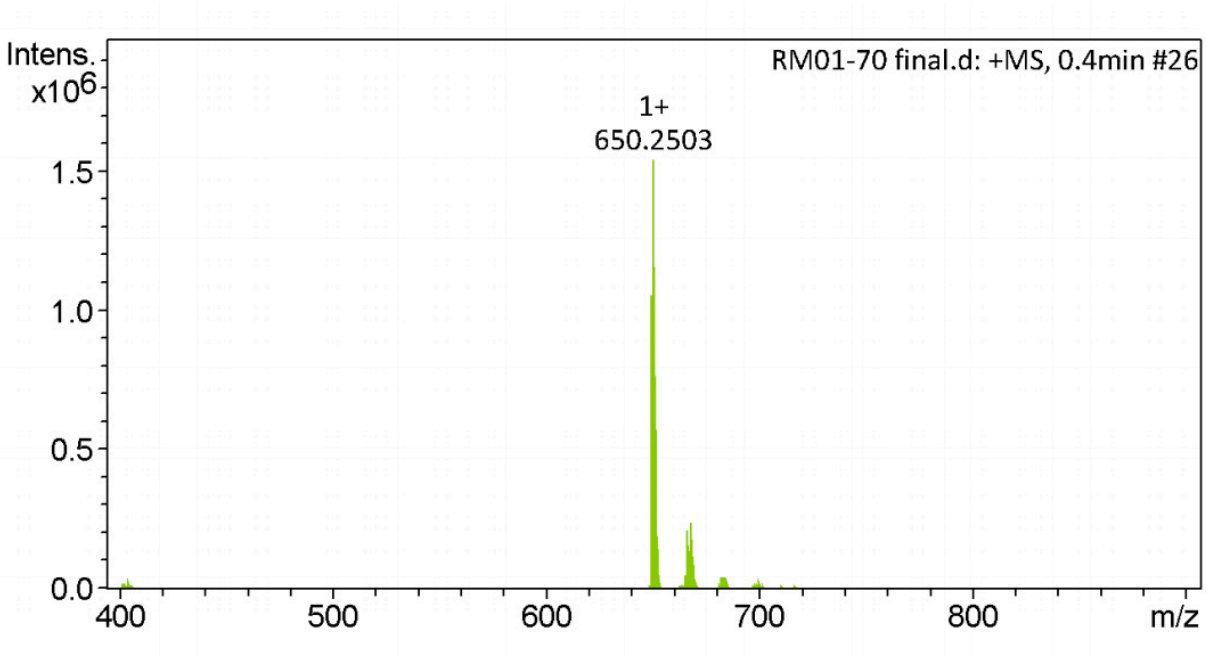
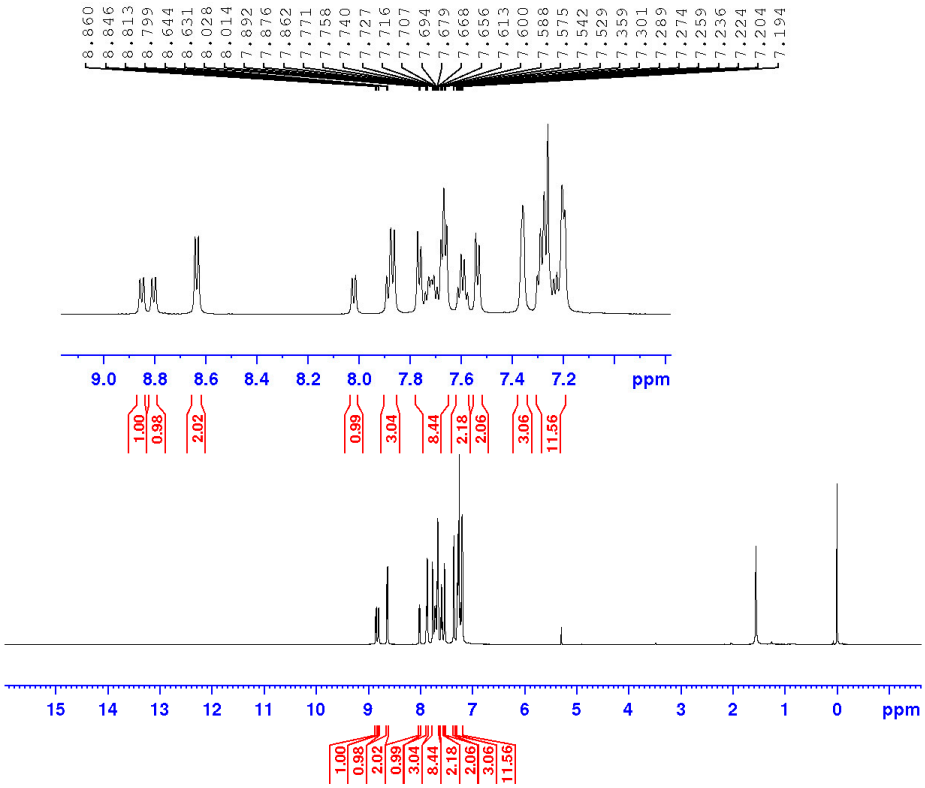


Compound TPIChCN

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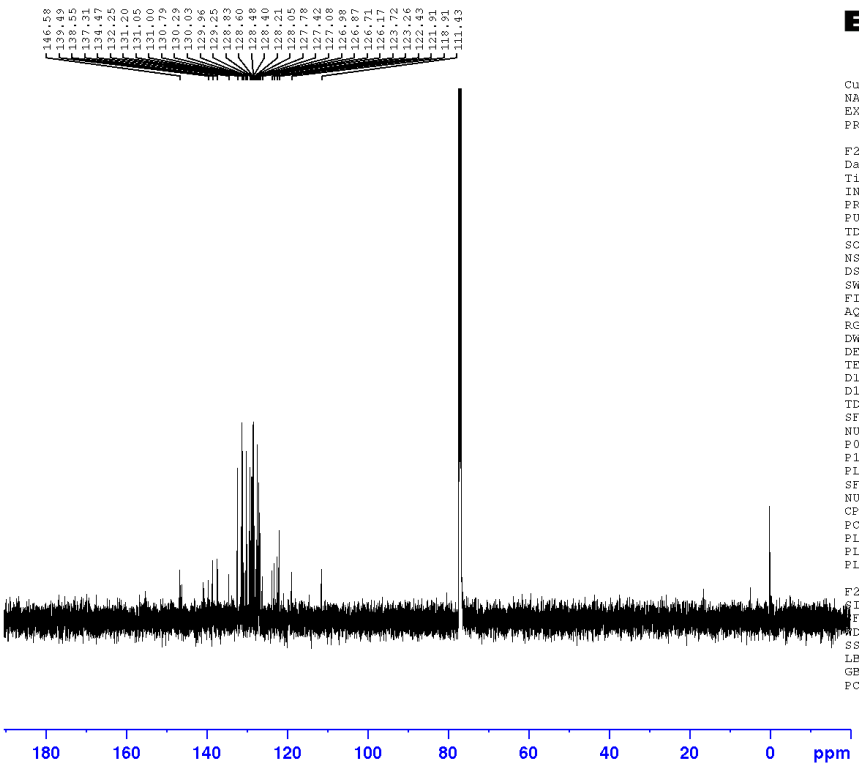

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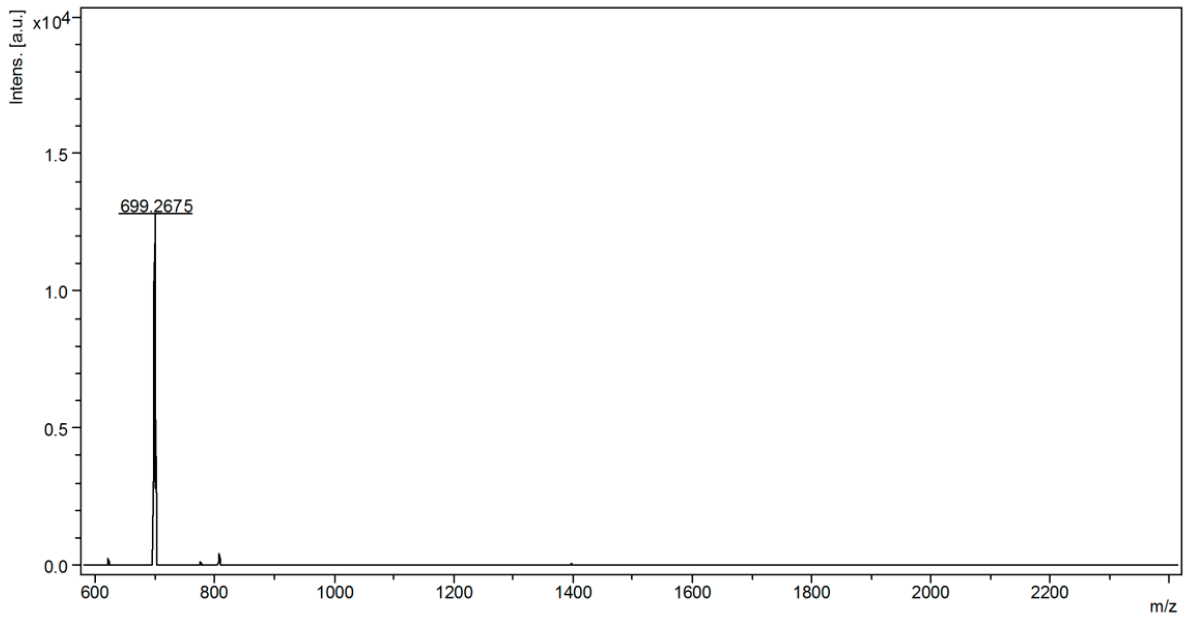
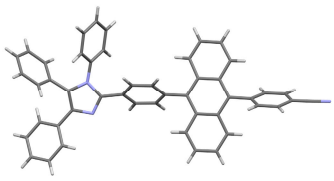
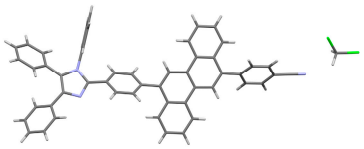
TD0                         1
SFO1            150.9178988 MHz
NUC1                      13C
P0                       3.27 usec
P1                       9.80 usec
PLW1           100.69000244 W
SFO2            600.1324005 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                   70.00 usec
PLW2           23.00000000 W
PLW12           0.44165000 W
PLW13           0.22215000 W

F2 - Processing parameters
SI                       32768
SF                150.9028085 MHz
WDW                         EM
SSB                  0
LB                      1.00 Hz
GB                   0
PC                      1.40
```



m/z	S/N	Quality Fac.	Res.	Intens.	Area
699.2675				2544	

Table S1 Crystallographic data of **TPIAnCN** and **TPIChCN**.

Chemical structure		
CCDC Deposit Number	**2048655**	**2011495**
Empirical formula	$C_{48}H_{31}N_3$	$C_{53}H_{35}Cl_2N_3$
Formula weight	649.76	784.74
Temperature/K	100.0	110.0
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a/Å b/Å c/Å	6.0526(4) 14.6484(9) 38.294(3)	10.0312(6) 10.7769(7) 18.8593(11)
α/° β/° γ/°	90 93.888(3) 90	90.123(2) 101.607(2) 107.107(2)
Volume/$Å^3$	3387.4(4)	1904.6(2)
Z	4	2
$\rho_{calc}g/cm^3$	1.274	1.368
μ/mm^{-1}	0.573	0.215
F(000)	1360.0	816.0
Crystal size/mm^3	0.25 × 0.12 × 0.03	0.554 × 0.284 × 0.058
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.626 to 99.484	3.962 to 52.744
Index ranges	$-5 \le h \le 5$, $-13 \le k \le 14$, $-37 \le l \le 37$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-23 \le l \le 23$
Reflections collected	35796	74150
Independent reflections	3420 [R_{int} = 0.1802, R_{sigma} = 0.1039]	7800 [R_{int} = 0.0510, R_{sigma} = 0.0259]
Data/restraints/parameters	3420/0/460	7800/0/524
Goodness-of-fit on F^2	1.046	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1071	R_1 = 0.0630, wR_2 = 0.1710
Final R indexes [all data]	R_1 = 0.1255, wR_2 = 0.1253	R_1 = 0.0749, wR_2 = 0.1788
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.24	0.82/-1.34

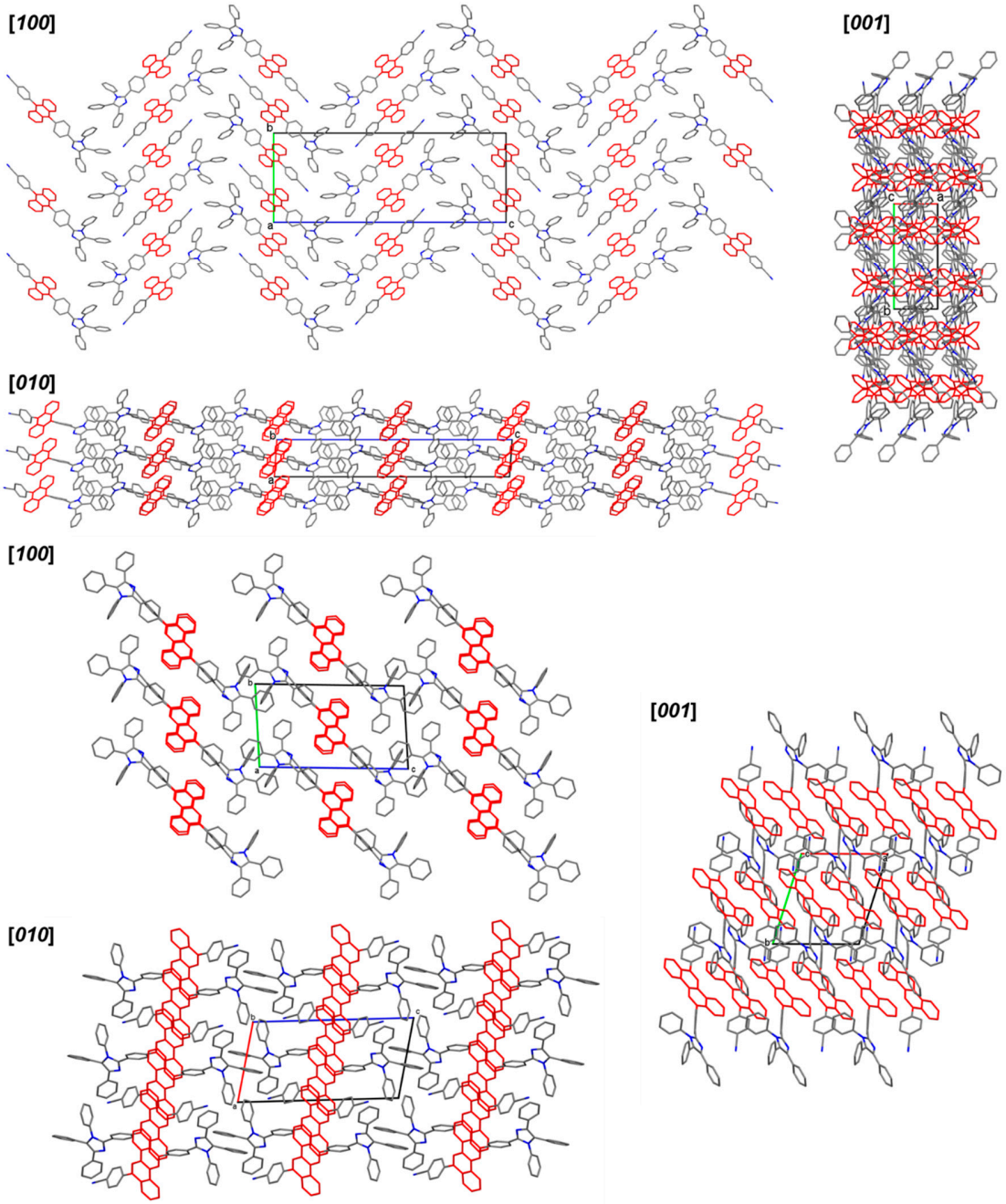


Figure S2. Crystal packing of (top) **TPIAnCN** and (bottom) **TPIChCN** along [*100*], [*010*] and [*001*] directions with red-highlighted structures of anthracene and chrysene cores, respectively. All hydrogen atoms and solvent residues were omitted for clarity.

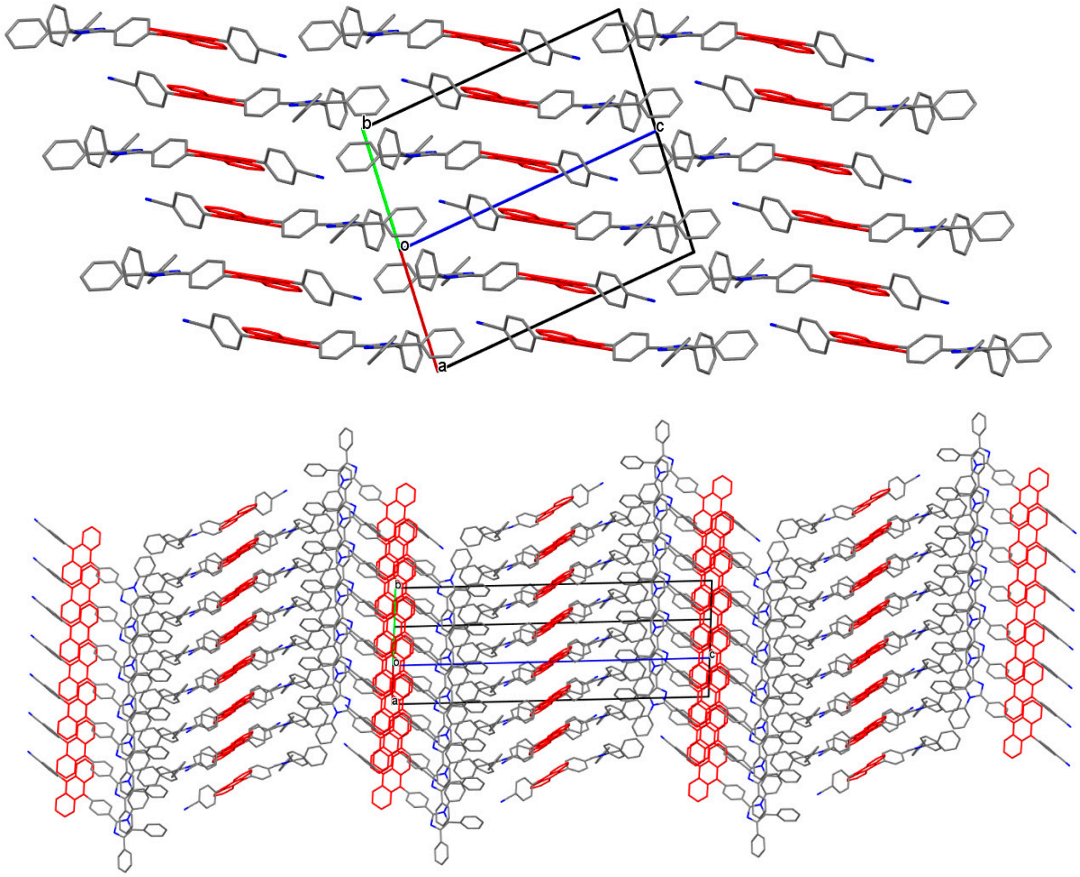


Figure S3. Packing structure of (top) **TPIAnCN** and (bottom) **TPIChCN** along [*110*] and [*210*] directions, respectively, with red-highlighted structures of anthracene and chrysene moieties. All hydrogen atoms and solvent residues were omitted for clarity.

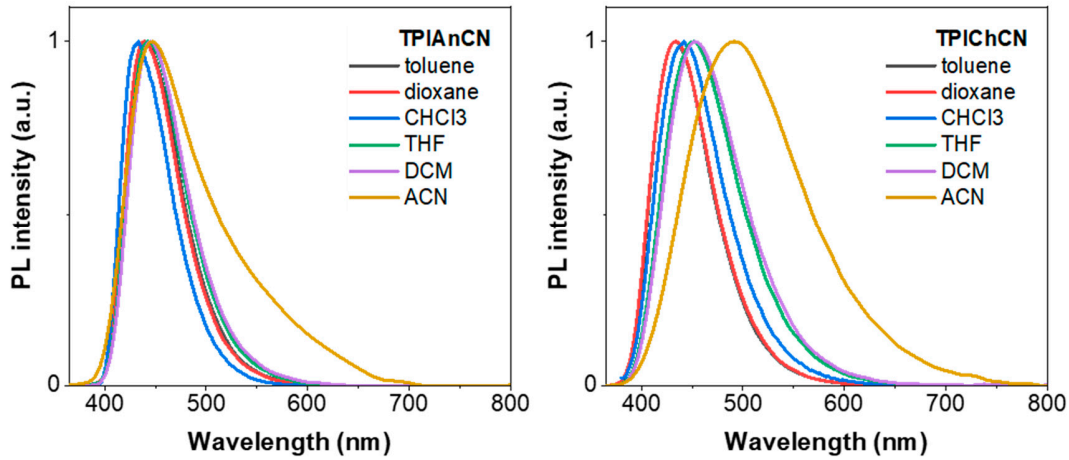


Figure S4. PL spectra in different solvents.

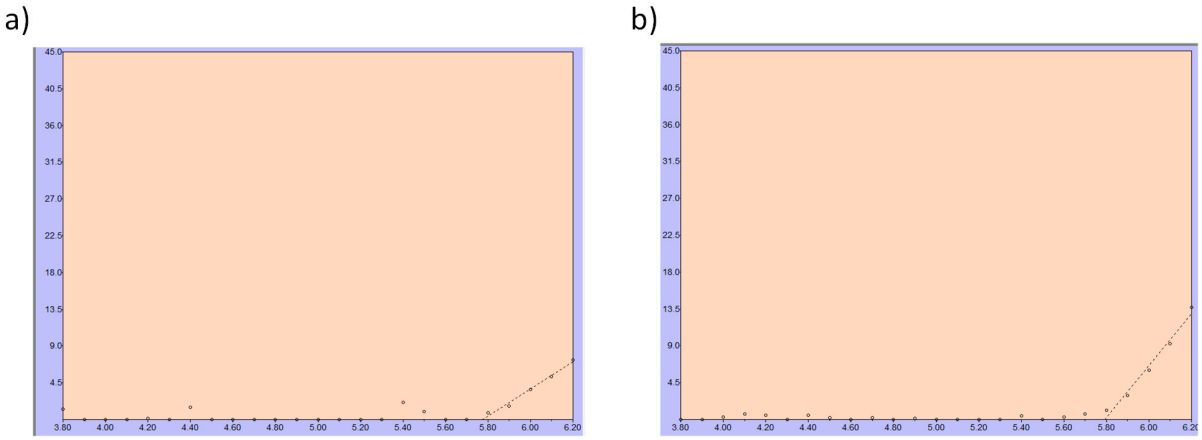


Figure S5. AC-2 plots of a) **TPIAnCN** and b) **TPIChCN**.

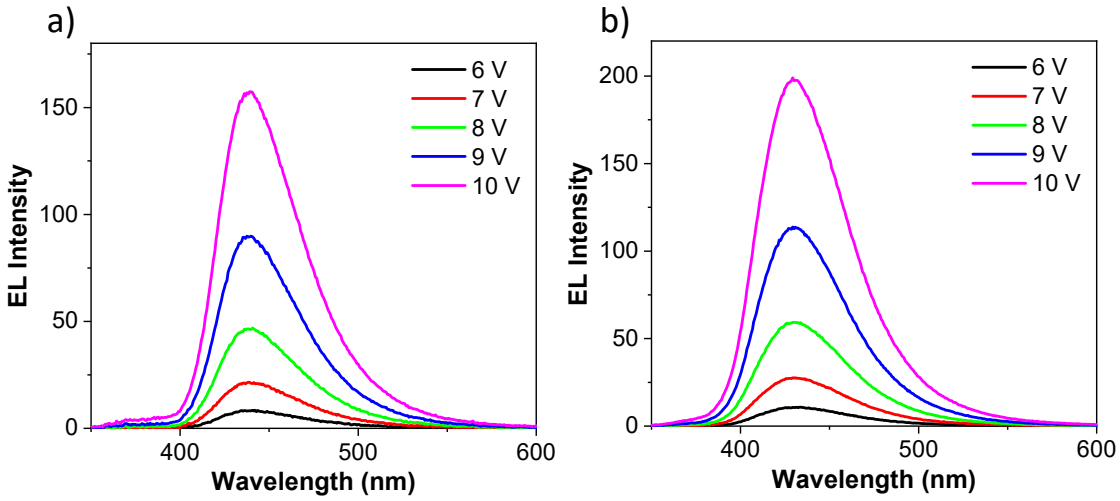


Figure S6. EL spectra under different applied voltages.