Supplementary information

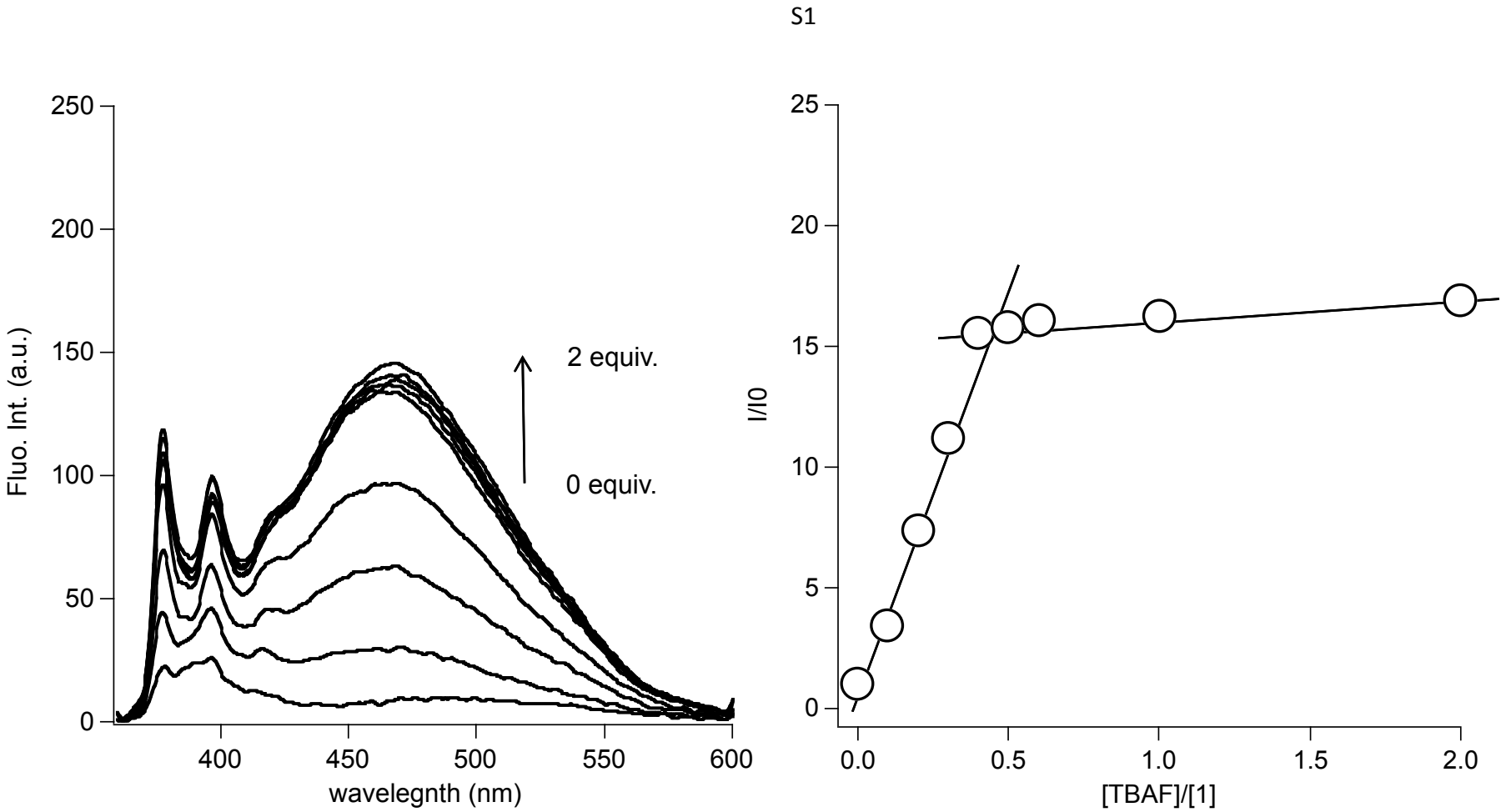


Figure S1. TBAF concentration dependence of the fluorescence profiles of **1**. the relative fluorescence intensity at 468 nm plotted against molar ratio

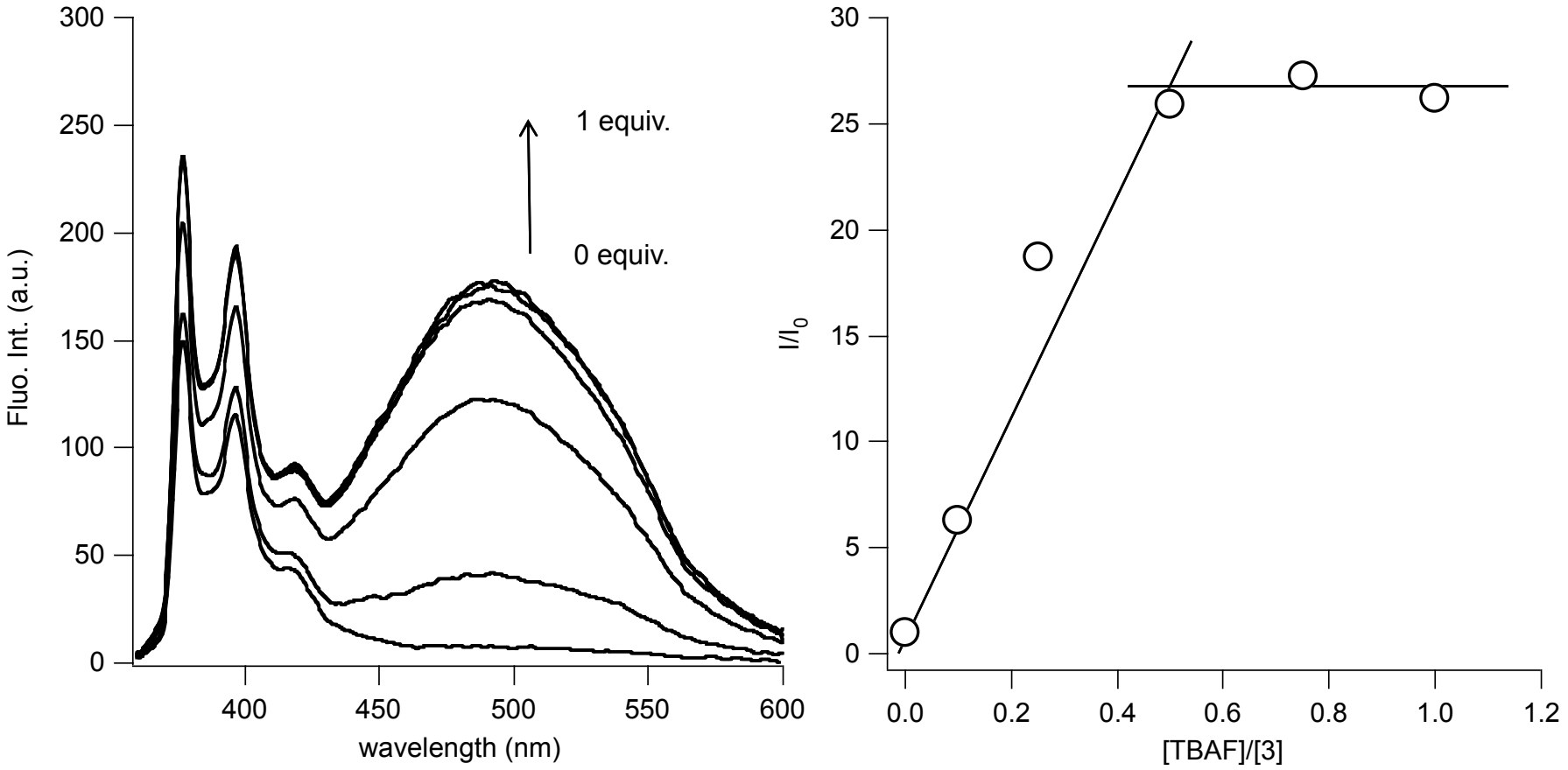


Figure S2. TBAF concentration dependence of the fluorescence profiles of **3**. The relative fluorescence intensity at 491 nm plotted against molar ratio

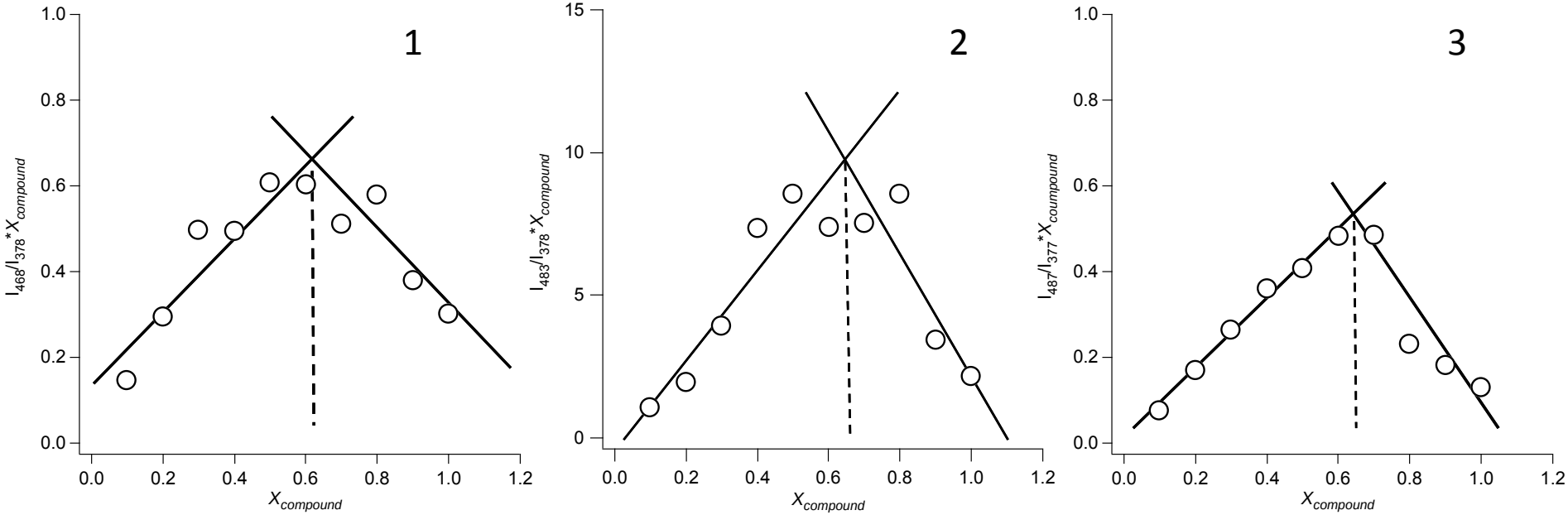


Figure S3. Job plot of a 2:1 complex of **1 – 3** and the F- ions, where the difference in Fluorescence intensity was plotted against the mole fraction of 1 at an invariant total concentration of 10 µM in DCM.

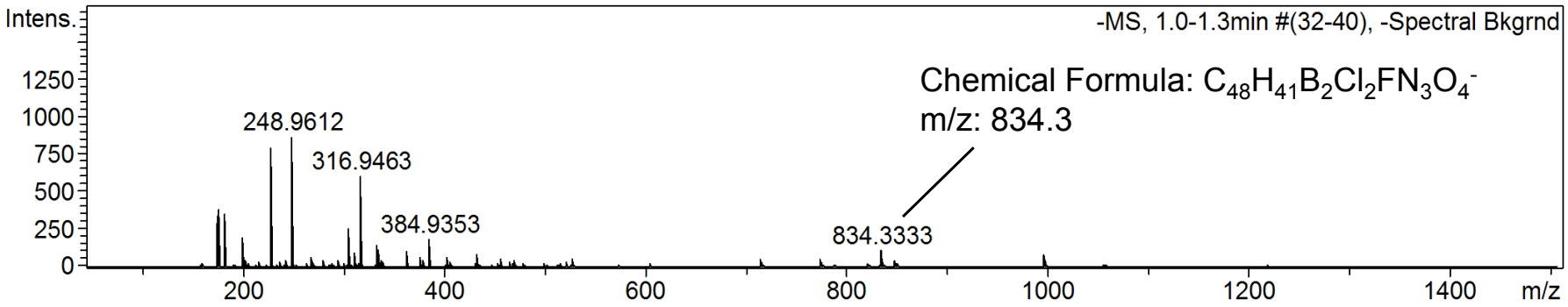


Figure S4. ESI-mass of **2** with TBAF

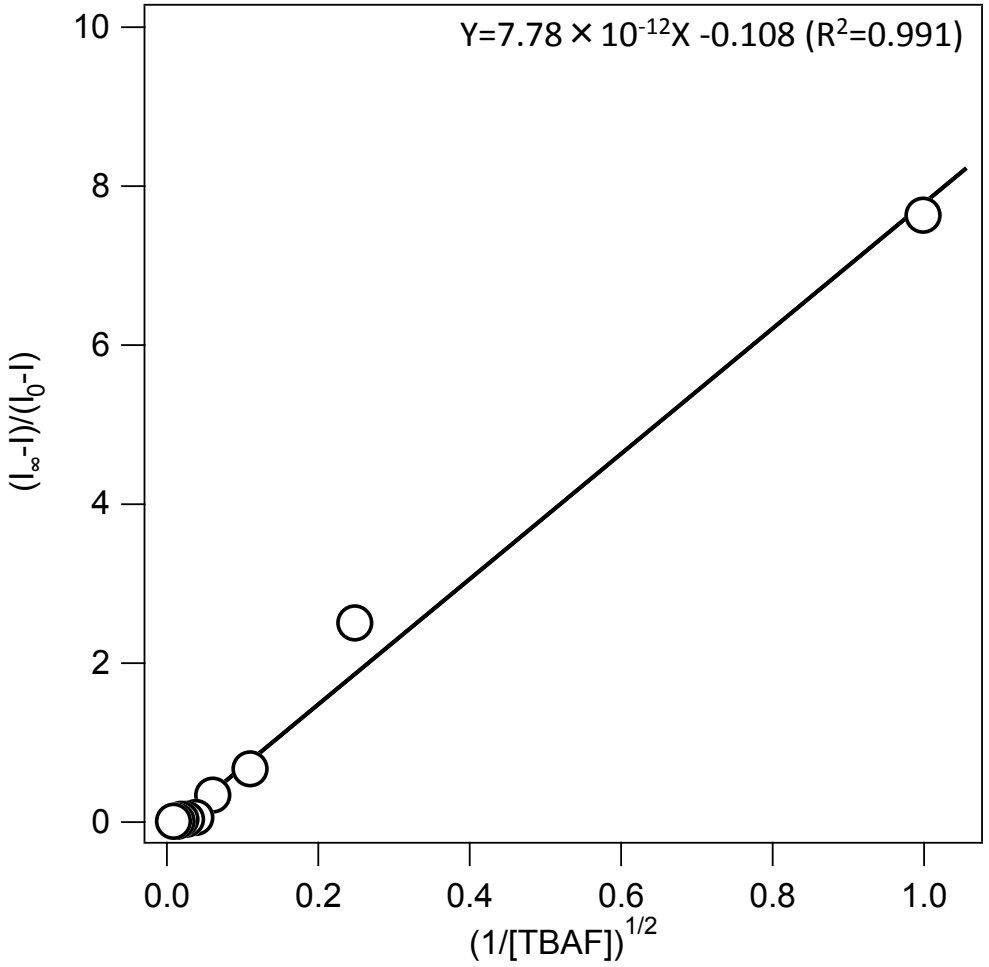


Figure S5. Benesi-Hildebrand plot of the fluorescence changes for the complexation between **2** and TBAF

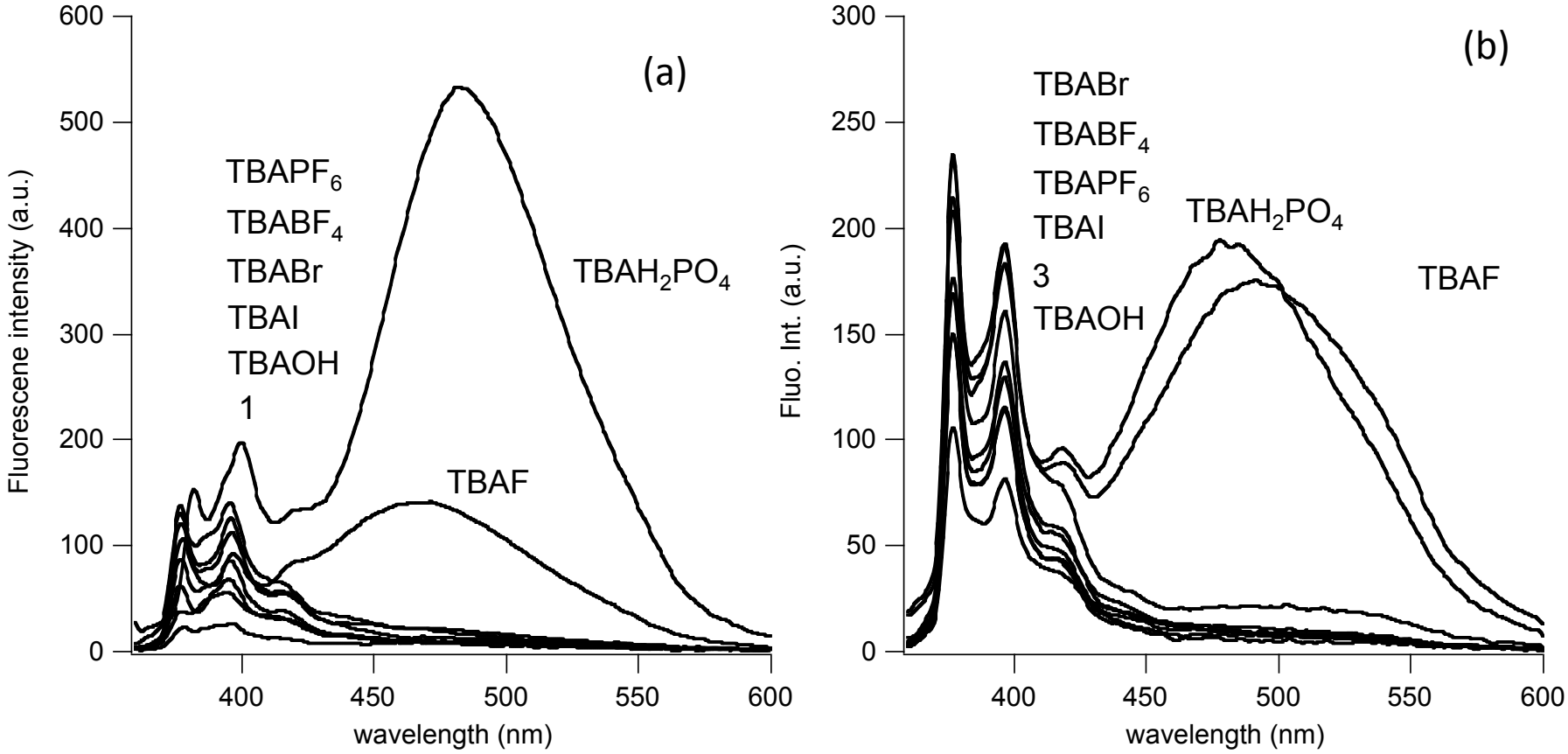


Figure S6. Fluorescence emission spectra of **1** (a) and **3** (b) (10 μM, respectively) upon addition of TBA^+ salts of F^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-,HSO_4^-, and $H_2PO_4^-$. (1.0 equiv, respectively) in DCM.

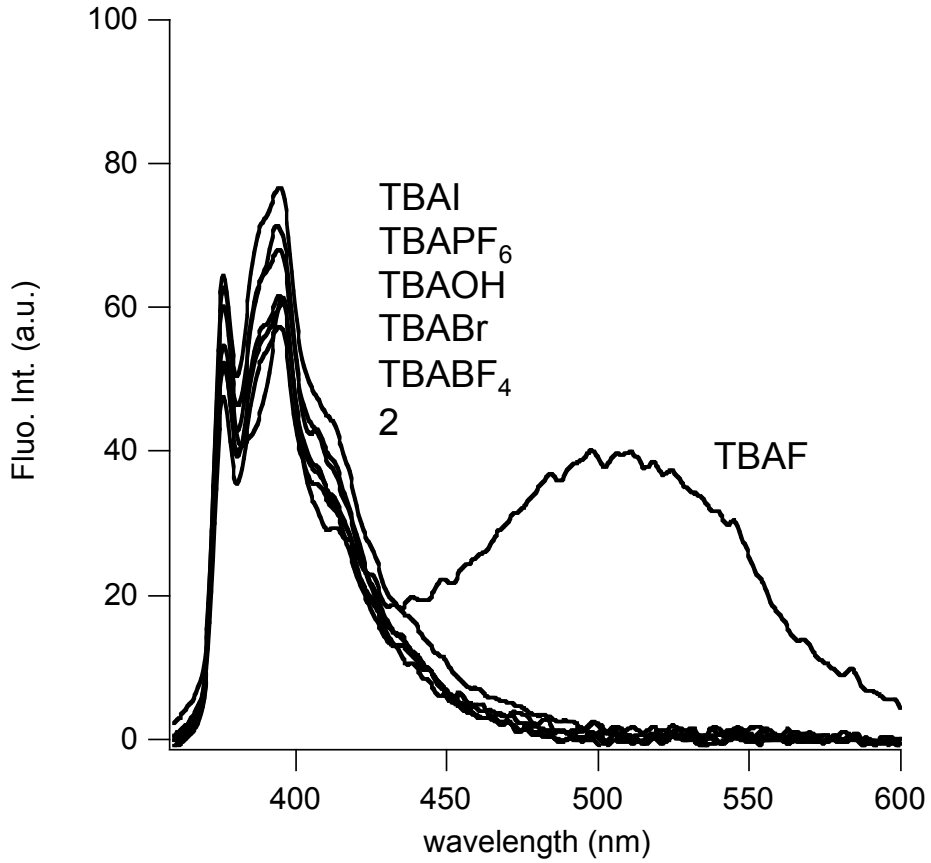


Figure S7. Fluorescence emission spectra of **2** (10 μM) upon addition of TBA^+ salts of F^-, Br^-, I^-, OH^-, BF_4^-, PF_6^- (1.0 equiv, respectively) in acetonitrile.

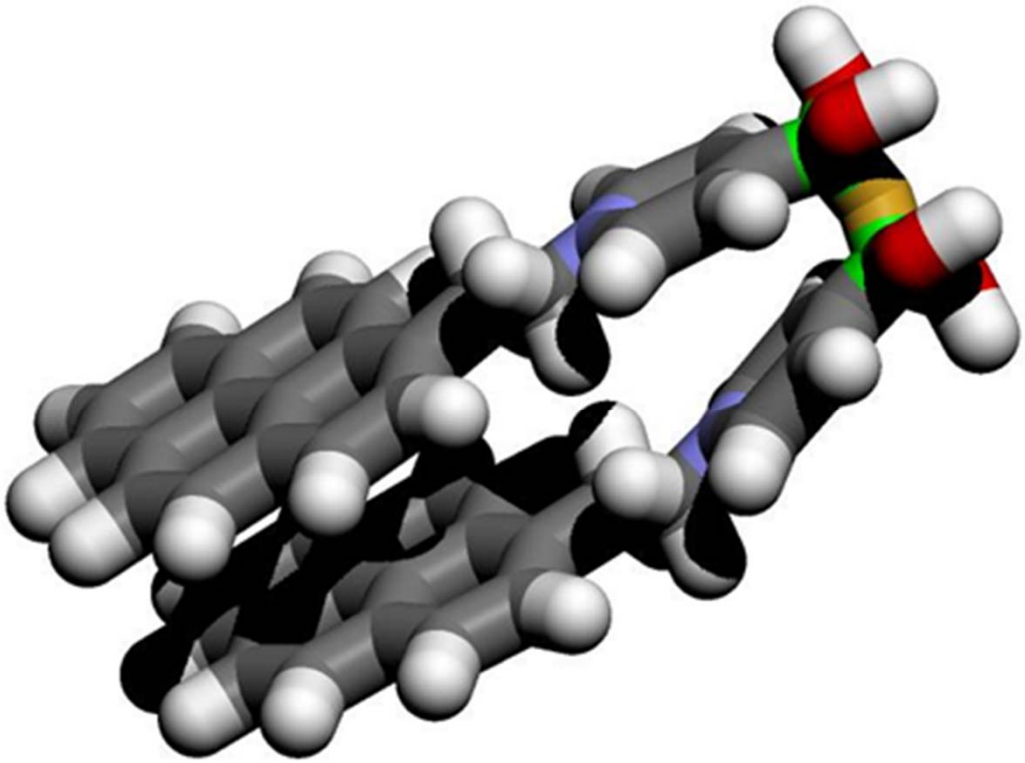


Figure S8. Schematic representation of the 2:1 complex of **2** with fluoride.

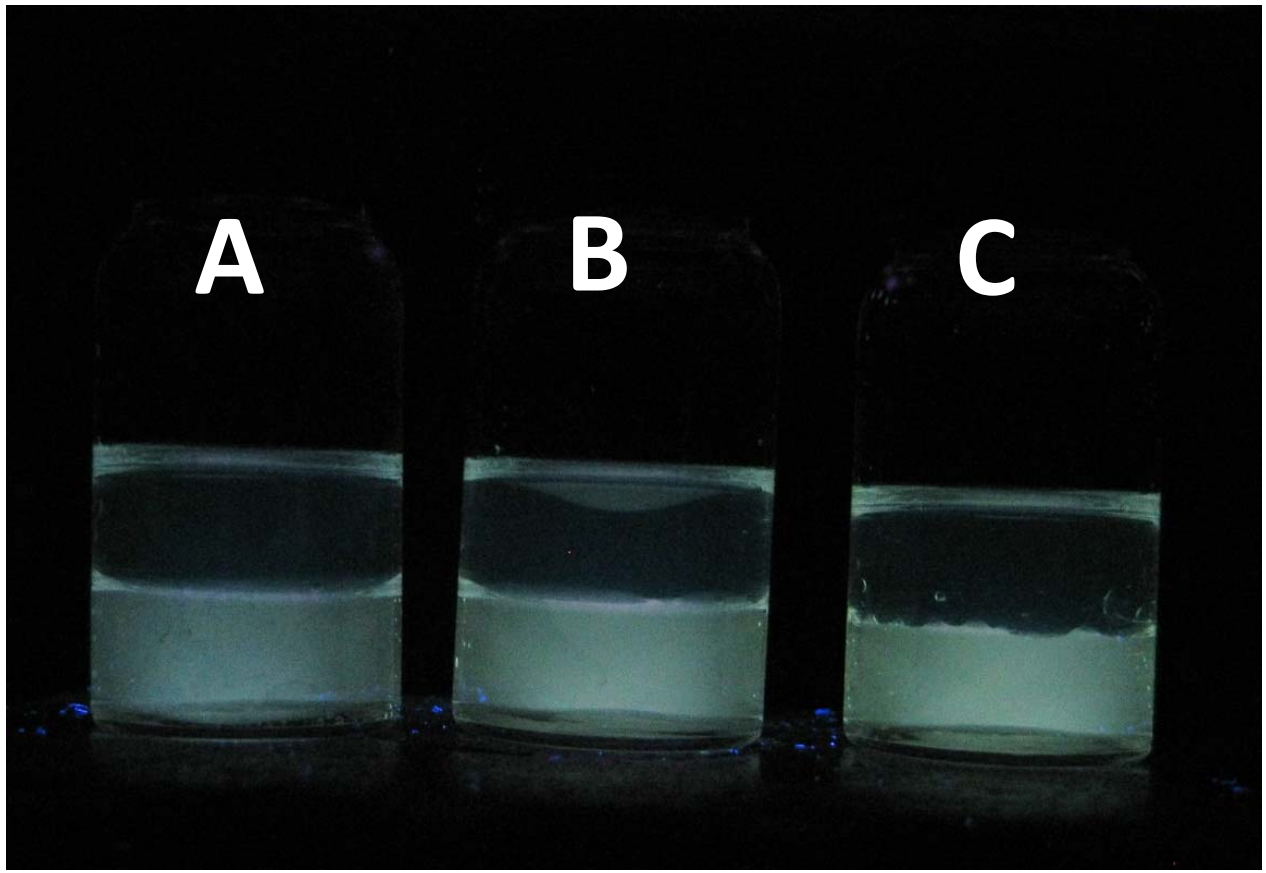
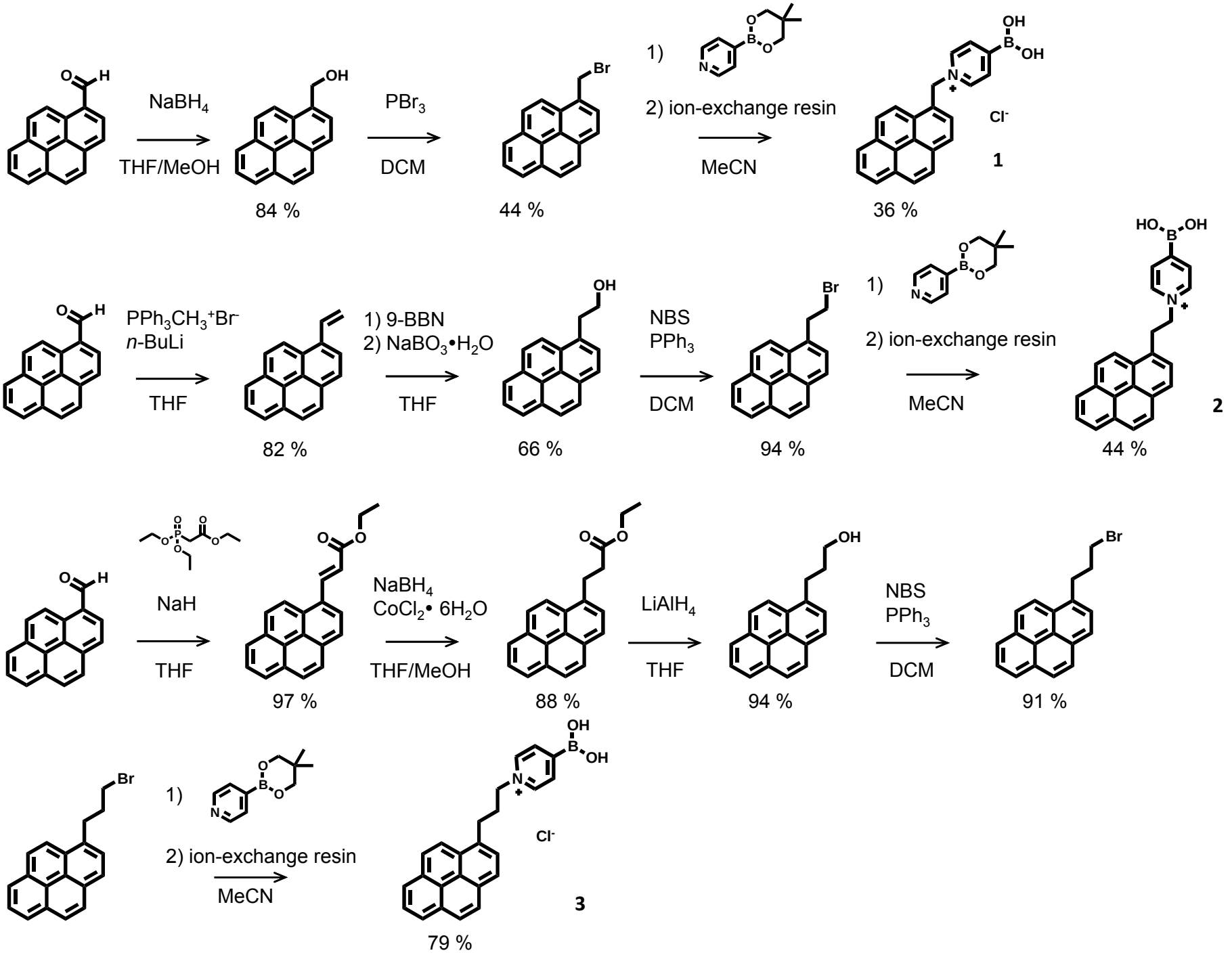


Figure S9. Biphasic extraction experiment of **2** (50 µM) in DCM with NaF (5 mM) in water at a pH of (A) 9.0, (B) 7.0 and (C) 5.0.

Scheme S1



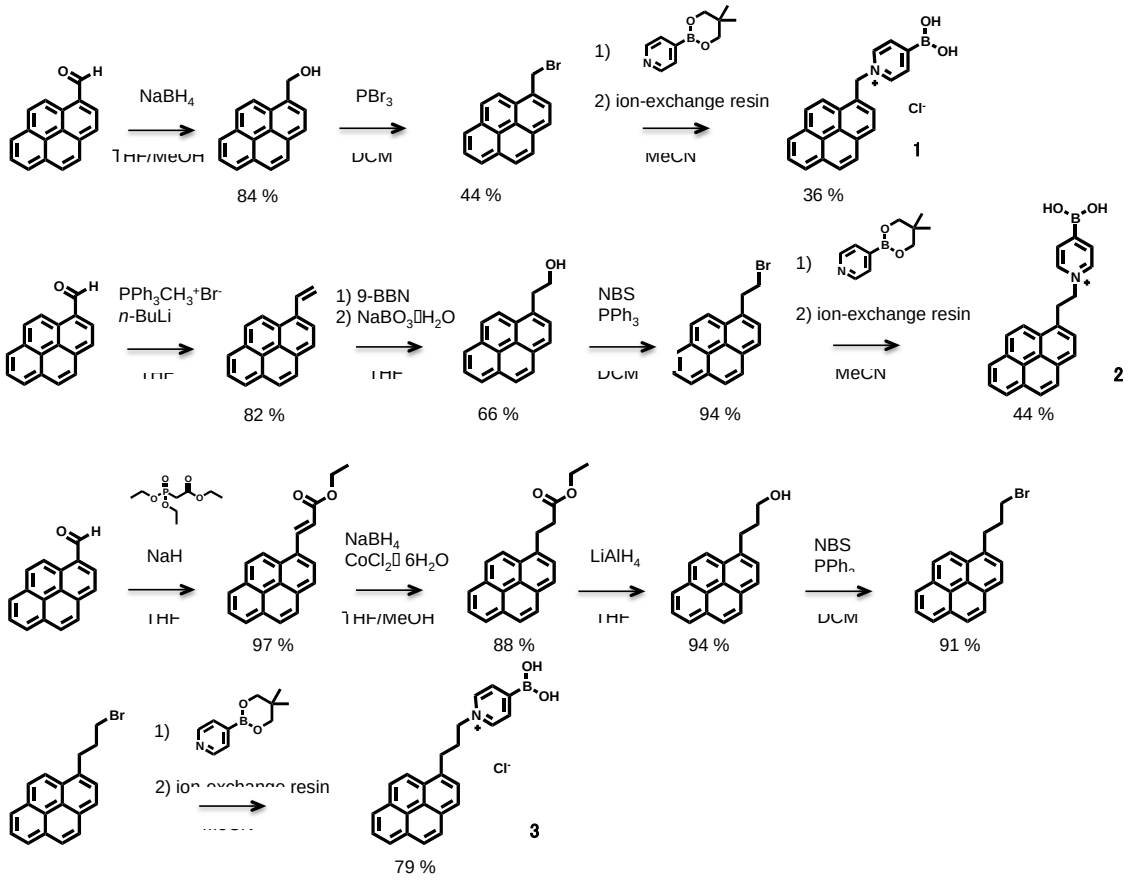
Experimental

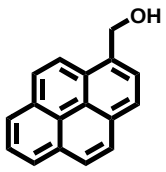
General

Solvents and reagents were reagent grade and were used without further purification. Nuclear magnetic resonance spectra were run in chloroform-*d* or methano*l*-*d* using Bruker AVANCE 250 and Bruker AVANCE 300 spectrometers to acquire 1H and 13C NMR spectra All NOSRY data were acquired using a Bruker AVANCEII 500 spectrometers. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak as an internal standard in 1H and 13C{1H} NMR spectra, with coupling constants (*J*) expressed in Hertz. All Mass spectrums were recorded on a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH) coupled to an Agilent Technologies 1200 LC system. Fluorescence measurements were performed using a Perkin-Elmer Luminescent Spectrophotometer LS50B, utilizing quartz cuvettes with 10mm path lengths.

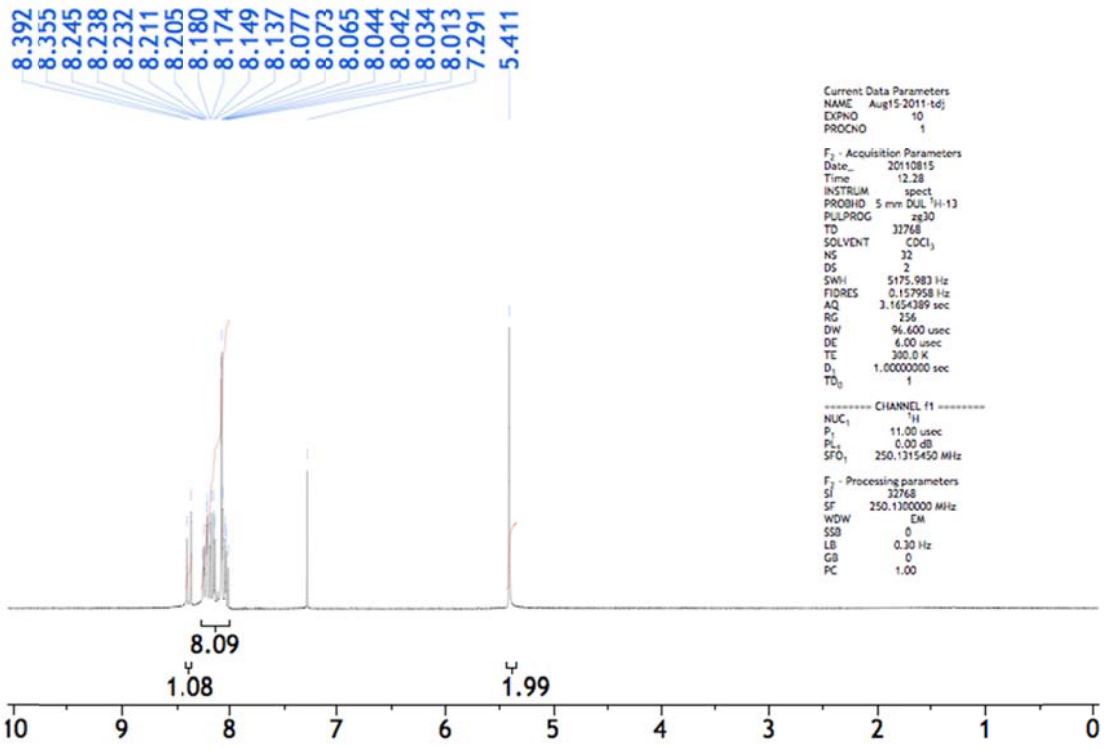
Biphasic fluoride extraction

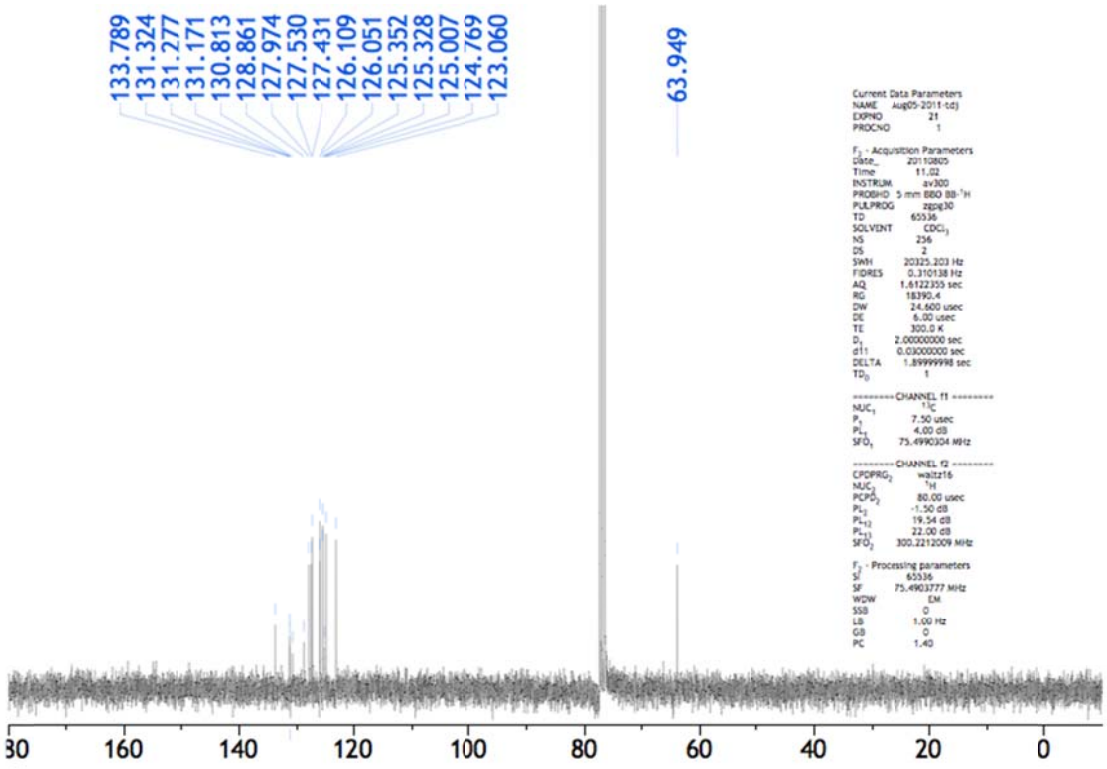
Fluorescence spectra of solutions of **2** in CH_2Cl_2 (5.0 mL, 50 μM) were collected after separating and shaking with 2.0 mL of aqueous solutions containing NaF.


NaBH4
THF/MeOH
84 %
PBr3
DCM
44 %
1)
2) ion-exchange resin
MeCN
36 %
1
PPh3CH3+Br-
n-BuLi
THF
82 %
1) 9-BBN
2) NaBO3·H2O
THF
66 %
NBS
PPh3
DCM
94 %
1)
2) ion-exchange resin
MeCN
44 %
2
NaH
THF
97 %
NaBH4
CoCl2· 6H2O
THF/MeOH
88 %
LiAlH4
THF
94 %
NBS
PPh3
DCM
91 %
1)
2) ion-exchange resin
79 %
3



1-pyrenecarboxaldehyde (0.480 g, 2.08 mmol) was dissolved in THF (15 mL) and $NaBH_4$ (0.118 g, 3.13 mmol) was added dropwise into the solution at room temperature. After stirring overnight, a few drops of 1.2 N HCl were added to the reaction mixture to quench the excess $NaBH_4$. The aqueous layer was extracted three times with dichloromethane. The combined organic fractions were washed with water, dried ($MgSO_4$), and were concentrated to give yellow solid 1-pyrenemethanol. (0.406g, 84% yield) : ^{1}H-NMR (250 MHz; $CDCl_3$): δ8.37 (d, J = 9.2 Hz, 1H), 8.24-8.01 (m, 8H), 5.41 (s, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 133.8, 131.32, 131.28, 131.17, 130.8, 128.9, 128.0, 127.53, 127.43, 126.11, 126.05, 125.35, 125.33, 125.0, 124.8, 123.1, 63.9 MS: [M+Na]+, *m/z*, (ESI, positive) found 255.0784. C17H12O1Na1 requires 255.0786.

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131.277
131.171
130.813
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127.431
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
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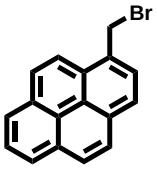
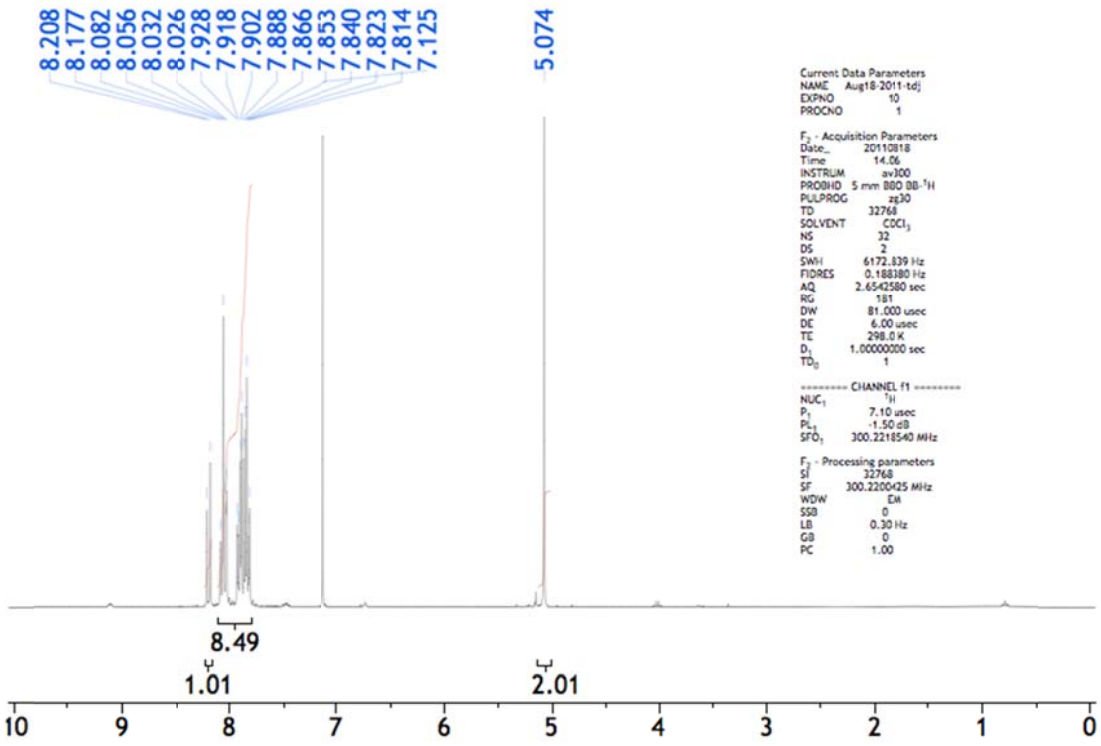
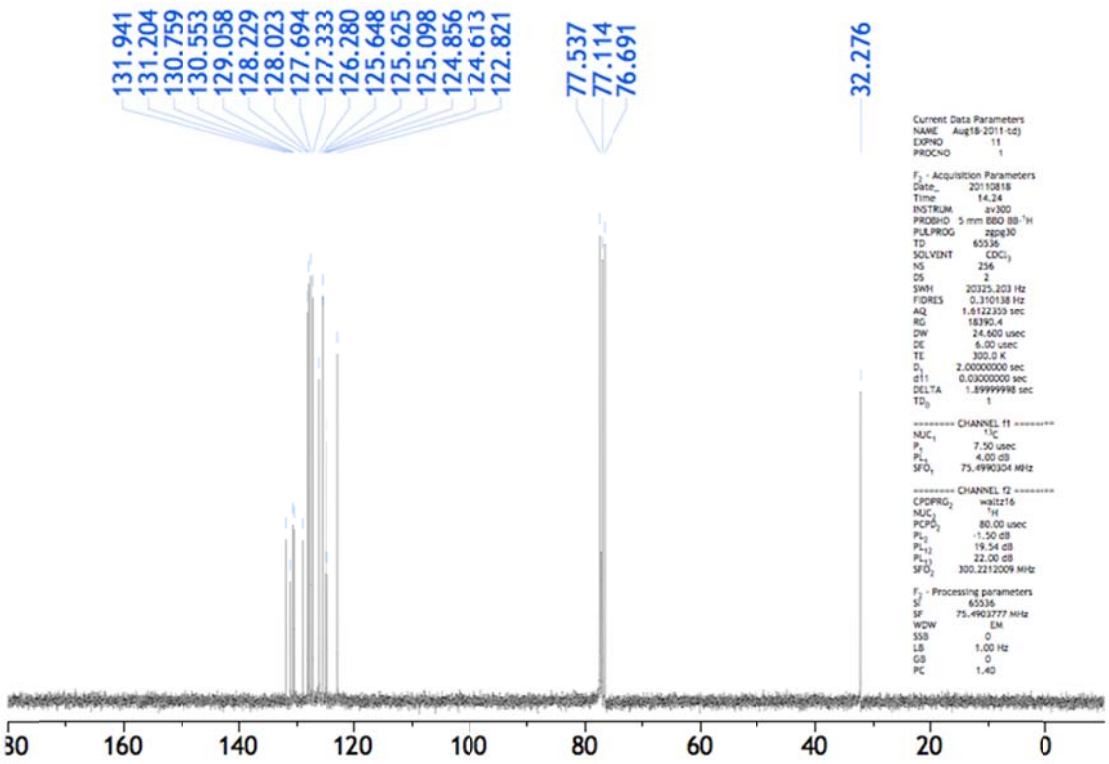


A solution of phosphorus tribromide (0.237 g, 0.88 mmol) in dichloromethane (15 mL) was added dropwise to a solution of 1-pyrenemethanol (0.406 g, 1.75 mmol) and pyridine (138 mg, 1.75 mmol) in dichloromethane (10 mL) at 0°C. After 3 hours, cracked ice and dichloromethane (20 mL) were added. The organic layer was washed with water, saturated $NaHCO_3$, and water, and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded dark yellow powder. The crude product was purified by column chromatography on silica using hexane/dichloromethane=3/1 as the eluent to yield 219 mg (42%) of 1-(bromomethyl)pyrene. :^{1}H-NMR (300 MHz; $CDCl_3$): δ 8.19 (d, J = 9.2 Hz, 1H), 8.08-7.81 (m, 8H), 5.07 (s, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 131.9, 131.2, 130.8, 130.6, 129.1, 128.2, 128.0, 127.7, 127.3, 126.3, 125.65, 125.62, 125.1, 124.9, 124.6, 122.8, 32.3

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DE 6.00 usec
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d11 0.03000000 sec
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PL1 4.00 dB
SFO1 75.4990304 MHz
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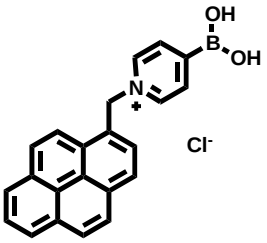
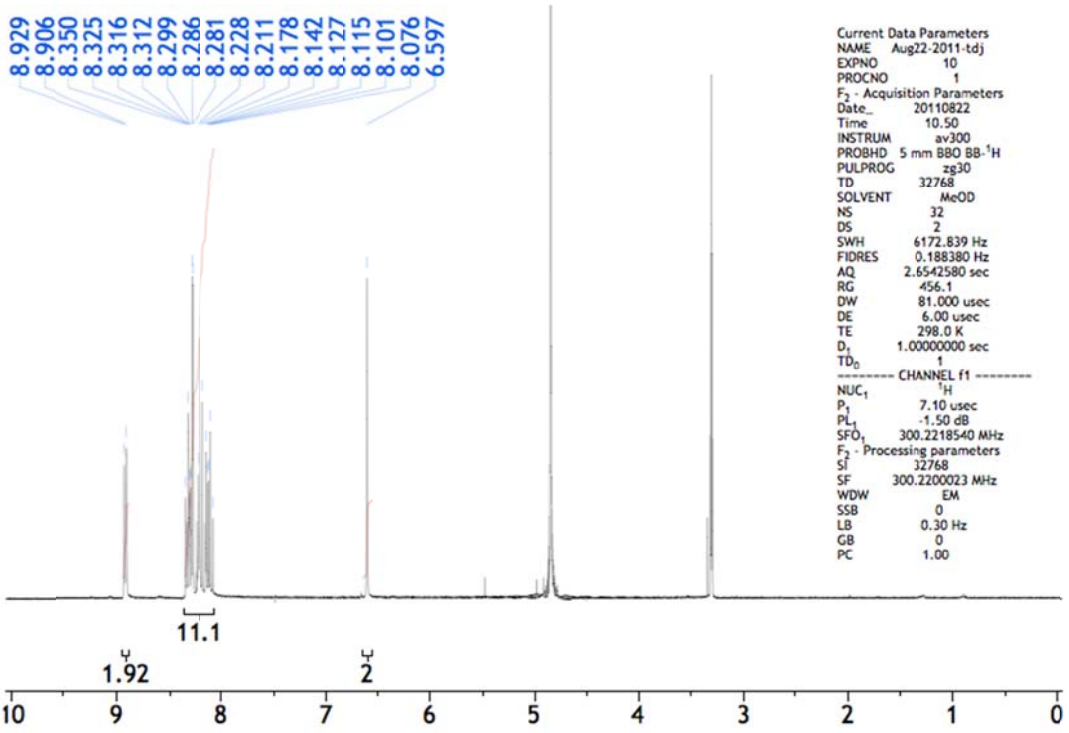
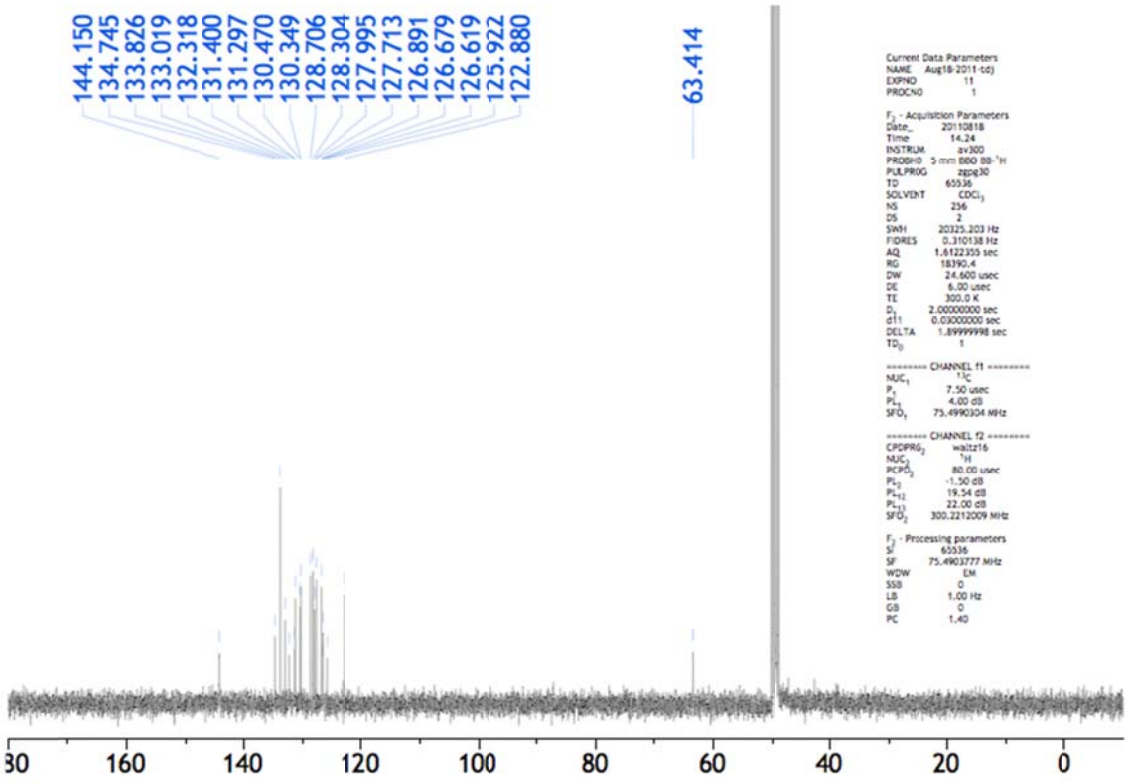


A mixture of 1-(bromomethyl)pyrene (0.218 g, 0.742 mmol) and 4-pyridineboronic acid neopentyl glycol ester (0.283 g, 1.48 mmol) in dry acetonitrile (10 mL) were heated at reflux for 48 h under N_2. After removal of acetonitrile, the mixture was stirred in mixed solvent (acetone : H_2O=9:1) for 12 hours. After deprotection of the boronic acid the mixture was purified by ion-exchange chromatography (Amberlite IRA-400 chloride form), 0.5 mol/L HCl-MeOH as eluent to give **1** as chloride salt, which was washed with water, dichloromethane to give **1** as a solid. (0.112 g, 36%). :^{1}H-NMR (300 MHz; MeOD): δ 8.92 (d, *J* = 6.7 Hz, 2H), 8.35-8.08 (m, 11H), 6.60 (s, 2H). ^{13}C-NMR (75 MHz; MeOD): δ 144.1, 134.7, 133.8, 133.0, 132.3, 131.40, 131.30, 130.47, 130.35, 128.7, 128.3, 128.0, 127.7, 126.9, 126.68, 126.62, 125.9, 122.9, 63.4 One carbon peak was not observed due to quadrupole relaxation. MS: [M+], *m/z*, (ESI, positive) found 338.1346. C22H17B1N1O2 requires 338.1347.

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DE 6.00 usec
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D1 2.00000000 sec
d11 0.03000000 sec
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PL13 22.00 dB
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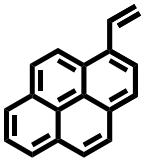
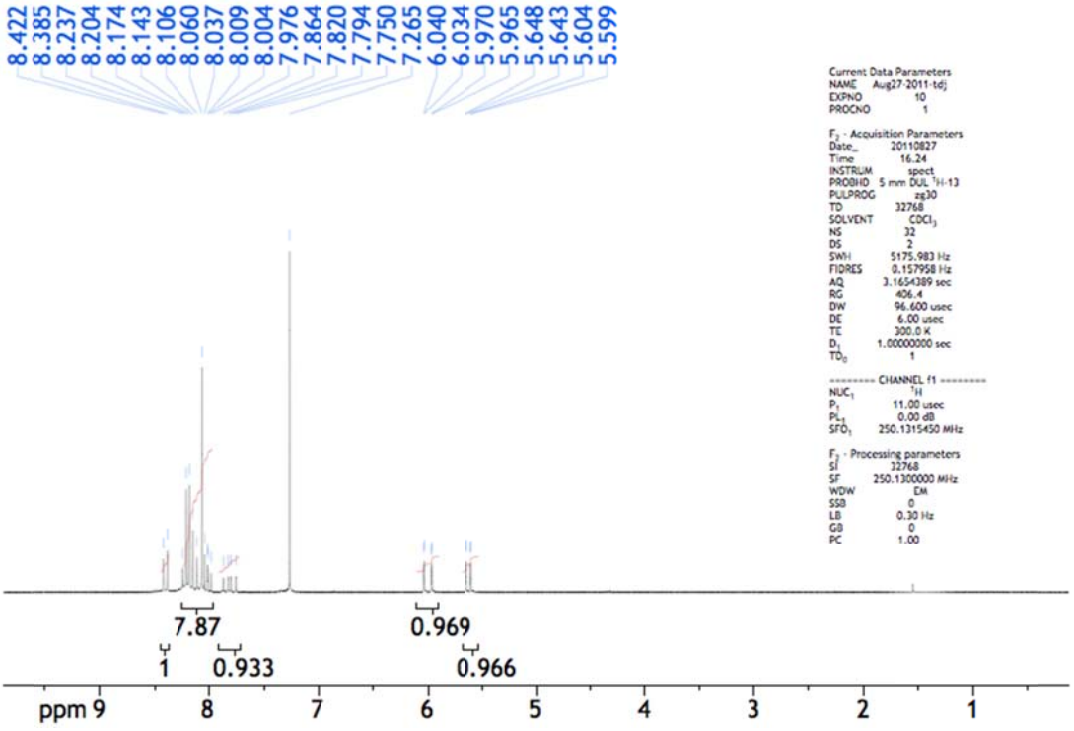
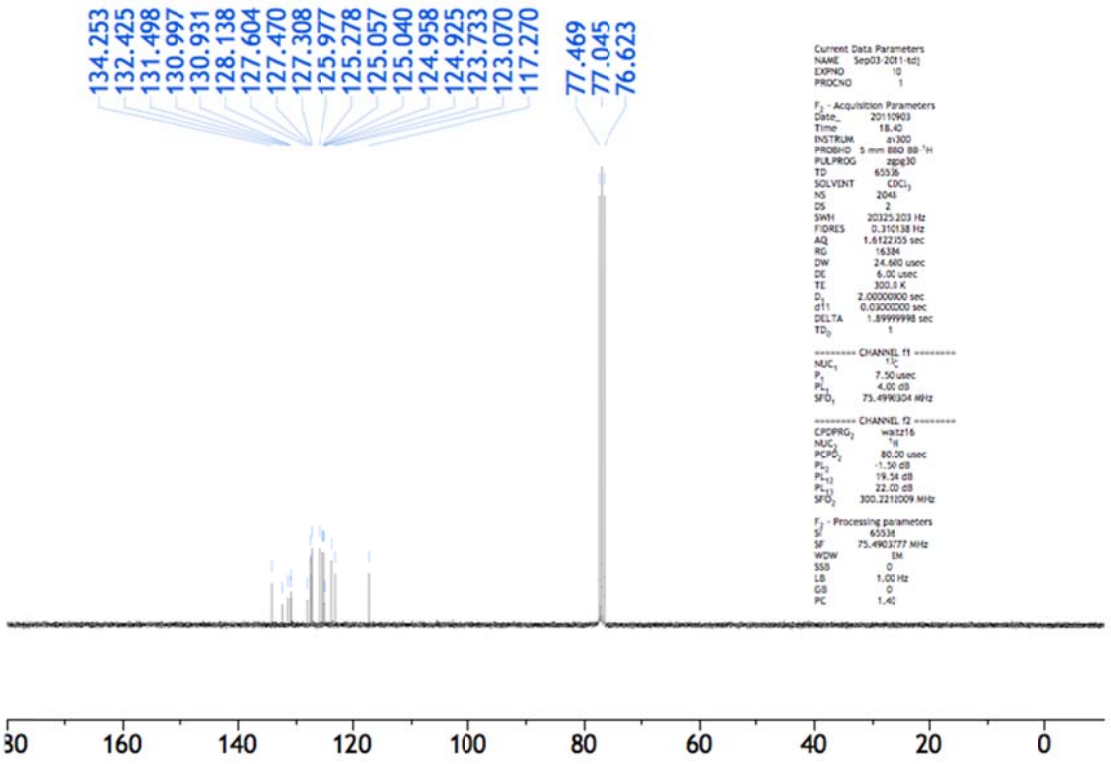


To a suspension of triphenylphosphonium bromide (1.97 g, 5.33 mmol) in 10 mL of dry THF at 0 °C under N_2 was added dropwise (2.21 mL, 5.53 mmol) of n-butyllithium solution (2.5 M in hexanes). The resulting solution was allowed to warm to room temperature and stirred for an additional 10 min. 1-Pyrenecarboxaldehyde (0.85 g, 3.69 mmol) in 10 mL of THF was added to the reaction mixture dropwise over 10 min. The resulting yellow suspension was stirred at room temperature overnight. The reaction mixture was then filtered, and the filtrate was poured into 30 mL of water. The aqueous layer was back-extracted with of diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica using Hexane/dichloromethane=10/1 as the eluent to yield 692 mg (82%) of 1-vinylpyrene as a yellow solid. :^{1}H-NMR (250 MHz; $CDCl_3$): δ 8.40 (d, J = 9.3 Hz, 1H), 8.24-7.98 (m, 8H), 7.81 (dd, J = 17.3, 11.0 Hz, 1H), 6.00 (dd, J = 17.3, 1.3 Hz, 1H), 5.62 (dd, J = 11.0, 1.3 Hz, 1H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 134.3, 132.4, 131.5, 131.00, 130.93, 128.1, 127.60, 127.47, 127.31, 126.0, 125.3, 125.06, 125.04, 124.96, 124.93, 123.7, 123.1, 117.3

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DW 24.600 usec
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d11 0.03000000 sec
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NUC2 1H
PCPD2 80.00 usec
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PL12 19.34 dB
PL13 22.00 dB
SFO2 300.2211009 MHz
F2 - Processing parameters
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SF 75.4903777 MHz
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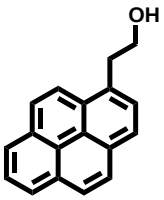
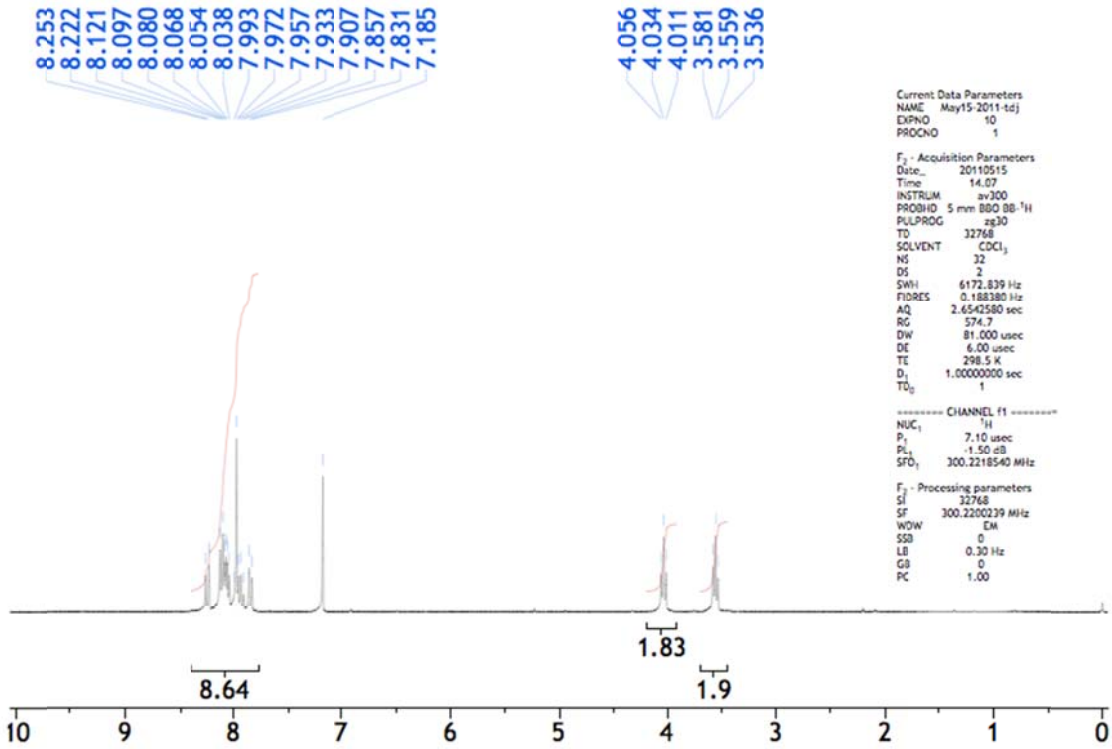
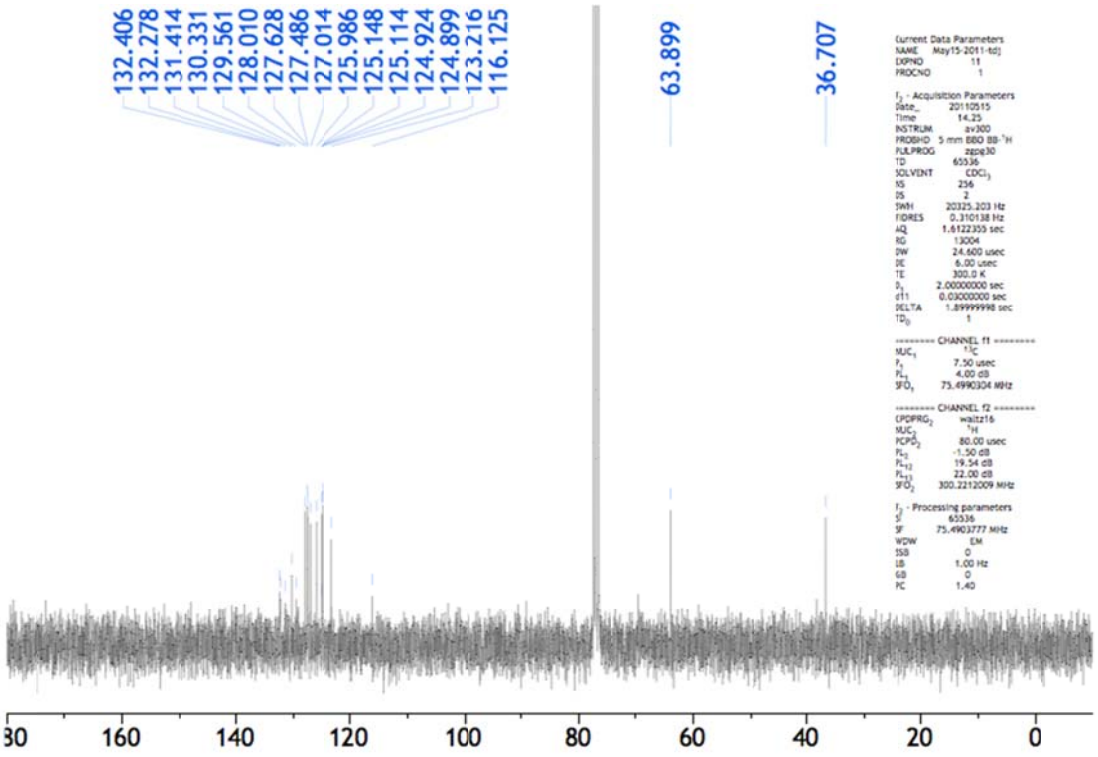


To a solution of 1-vinylpyrene (348 mg, 1.52 mmol) in 10 mL of dry THF at 0 °C under N_2 was added dropwise (9.14 mL, 4.57 mmol) of 9-BBN solution (0.5 M in THF). The mixture solution was stirred at 50 °C for 1h. The mixture solution was cooled to rt. Water (3 mL) and sodium perborate (703 mg, 4.57 mmol) was added sequentially to the flask, and the mixture was stirred at room temperature for overnight. The two phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography on silica using dichloromethane as the eluent to yield 250 mg (66%) of 2-(pyren-1-yl)ethanol. :^{1}H-NMR (300 MHz; $CDCl_3$): δ8.25-7.83 (m, 9H), 4.03 (t, *J* = 6.7 Hz, 2H), 3.56 (t, *J* = 6.7 Hz, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 132.41, 132.28, 131.4, 130.3, 129.6, 128.0, 127.63, 127.49, 127.0, 126.0, 125.15, 125.11, 124.92, 124.90, 123.2, 116.1, 63.9, 36.7 MS: [M+H]+, *m/z*, (ESI, positive) found 247.1126. C18H15O1 requires 247.1123.

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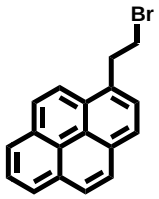
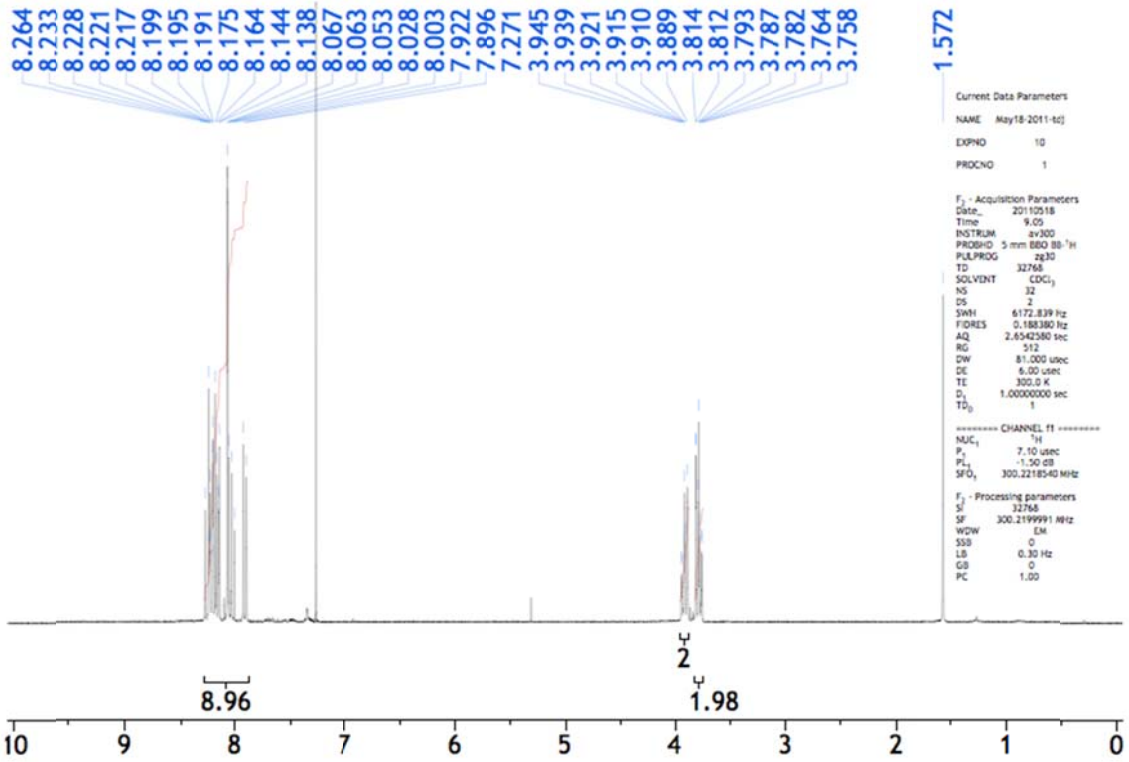
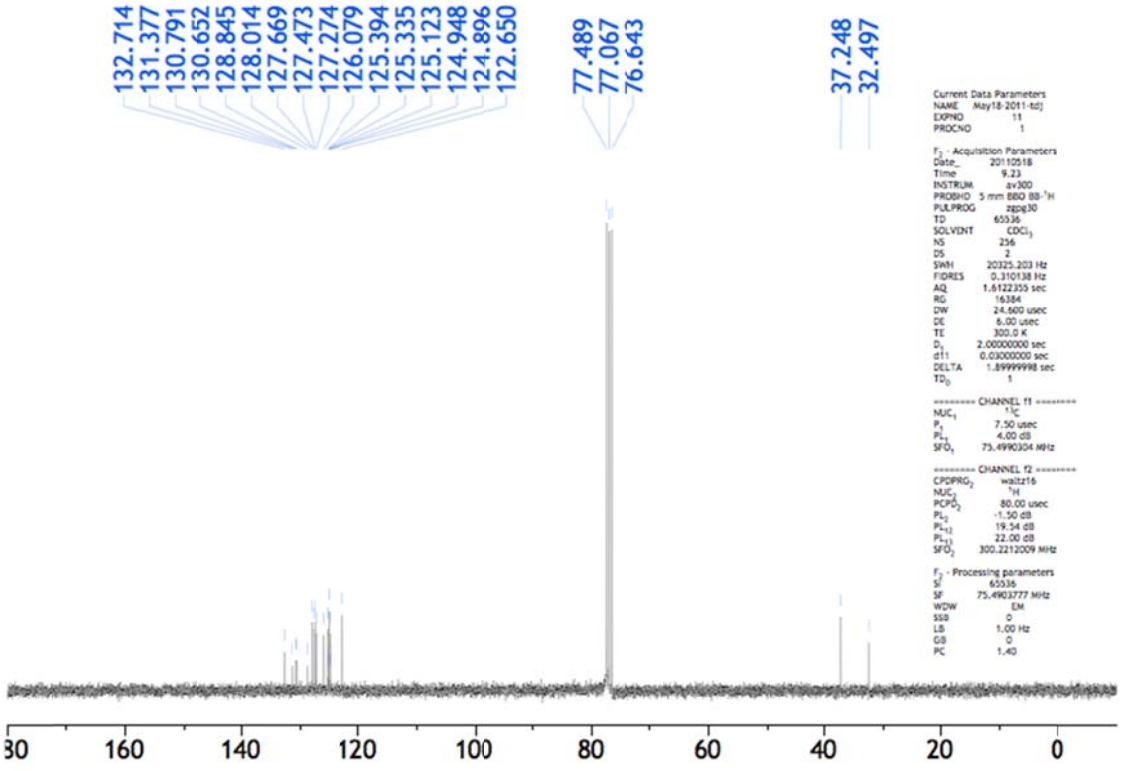


N-bromosuccinimide (233 mg, 1.31 mmol) was added to a solution of triphenylphosphine (427 mg, 1.63 mmol) in dichloromethane (10 mL) at -15 °C. After 20 min stirring, 2-(pyren-1-yl)ethanol (250 mg, 1.01 mmol) dissolved in dichloromethane (10 mL) was added. The resulting solution was stirred for 3 h at room temperature, diluted with water, washed with water and brine, and then dried over $MgSO_4$. The solvent was removed in vacuo, and The crude product was purified by column chromatography on silica using hexane/dichloromethane=3/1 as the eluent to yield 293 mg (94%) of 1-(2-bromoethyl) pyrene. :^{1}H-NMR (300 MHz; $CDCl_3$): δ8.26-7.90 (m, 9H), 3.94-3.89 (m, 2H), 3.81-3.76 (m, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 132.7, 131.4, 130.79, 130.65, 128.8, 128.0, 127.67, 127.47, 127.27, 126.1, 125.39, 125.34, 125.12, 124.95, 124.90, 122.6, 37.2, 32.5

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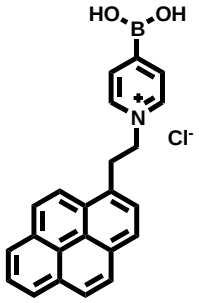
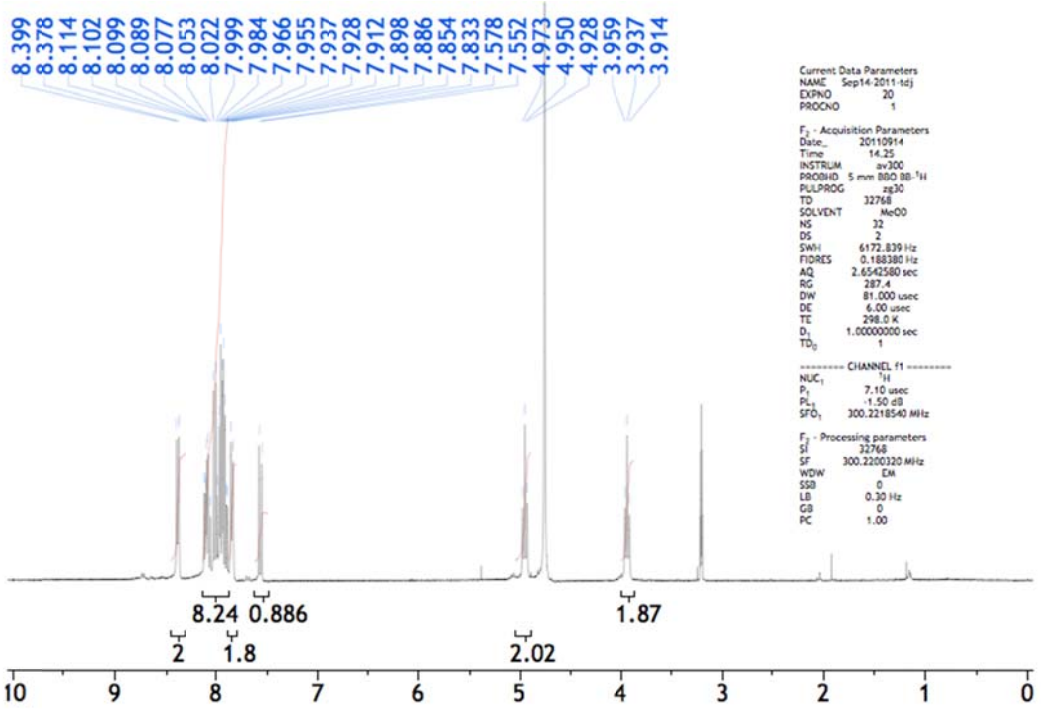
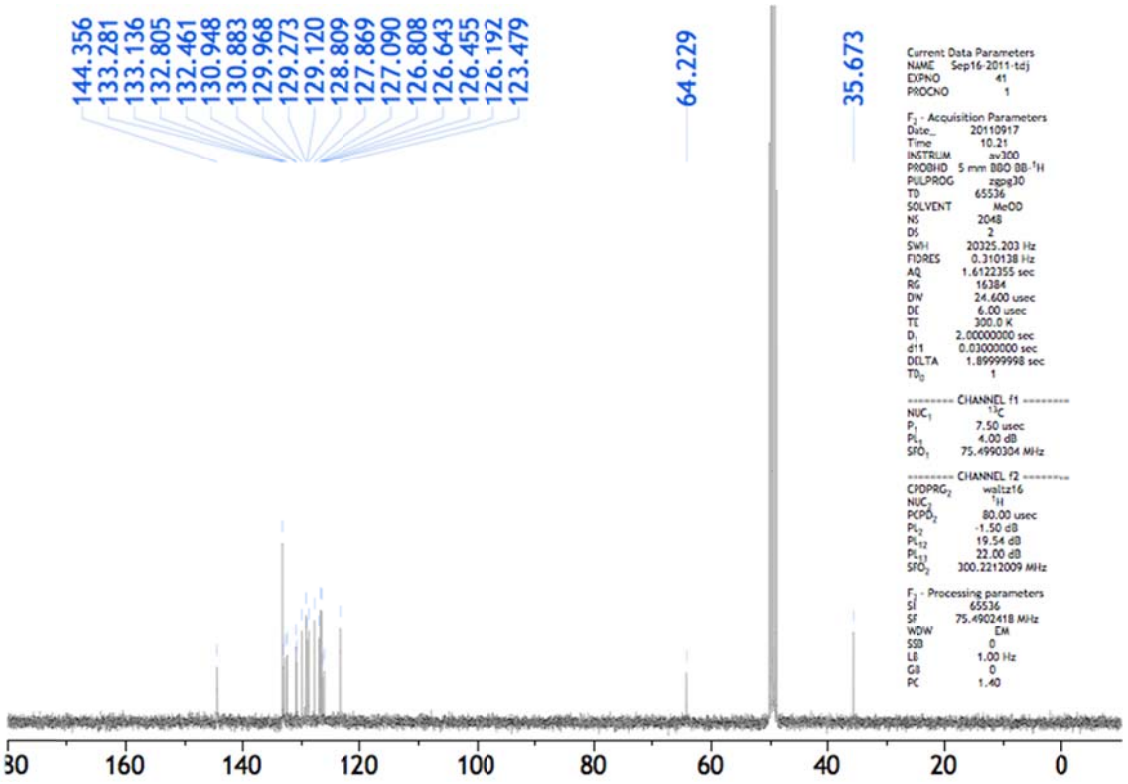


A mixture of 1-(2-bromoethyl) pyrene (60 mg, 0.195 mmol) and 4-pyridineboronic acid neopentyl glycol ester (75 mg, 0.390 mmol) in dry acetonitrile (10 mL) were heated at reflux for 48 h under N_2. After removal of acetonitrile, the mixture was stirred in mixed solvent (acetone:H_2O=9:1) for 12 hours. After deprotection of the boronic acid the mixture was purified by ion-exchange chromatography (Amberlite IRA-400 chloride form), 0.5 mol/L HCl-MeOH as eluent to give **2** as chloride salt, which was washed with water, dichloromethane to give **2** as a solid. (34 mg, 44%). :^{1}H-NMR (300 MHz; MeOD): δ8.39 (d, *J* = 6.4 Hz, 2H), 8.11-7.89 (m, 8H), 7.84 (d, *J* = 6.3 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 4.95 (t, *J* = 6.7 Hz, 2H), 3.94 (t, *J* = 6.7 Hz, 2H). ^{13}C-NMR (75 MHz; MeOD): δ 144.4, 133.28, 133.14, 132.8, 132.5, 130.95, 130.88, 130.0, 129.27, 129.12, 128.8, 127.9, 127.1, 126.81, 126.64, 126.45, 126.2, 123.5, 64.2, 35.7 One carbon peak was not observed due to quadrupole relaxation. MS: [M+], *m/z*, (ESI, positive) found 352.1506. C23H19B1N1O2 requires 352.1504.

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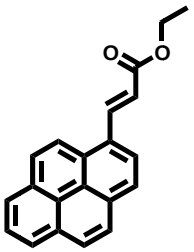
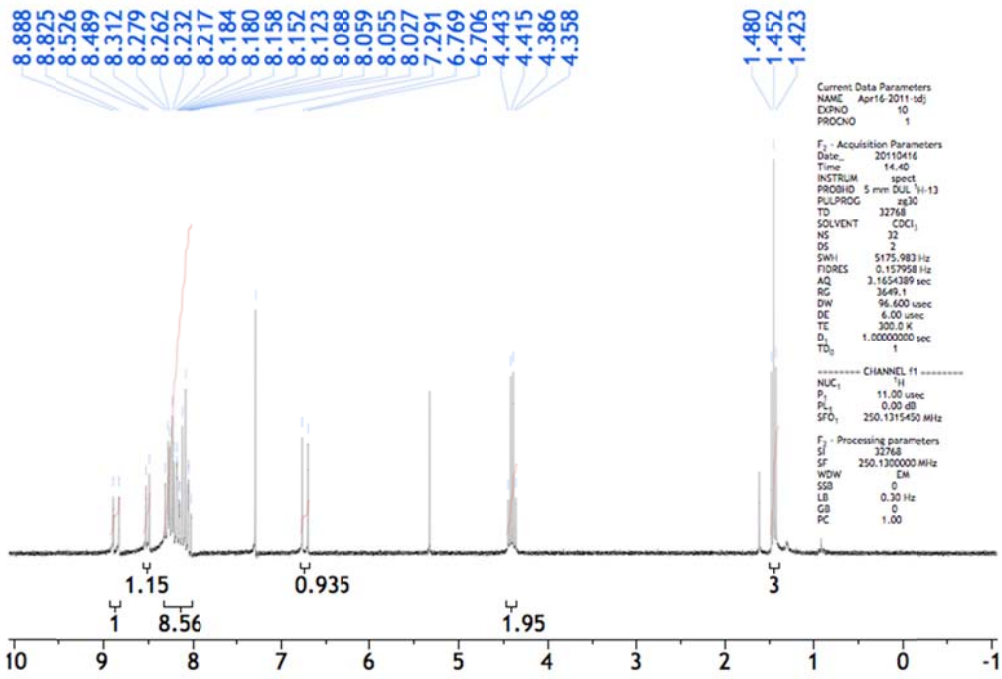
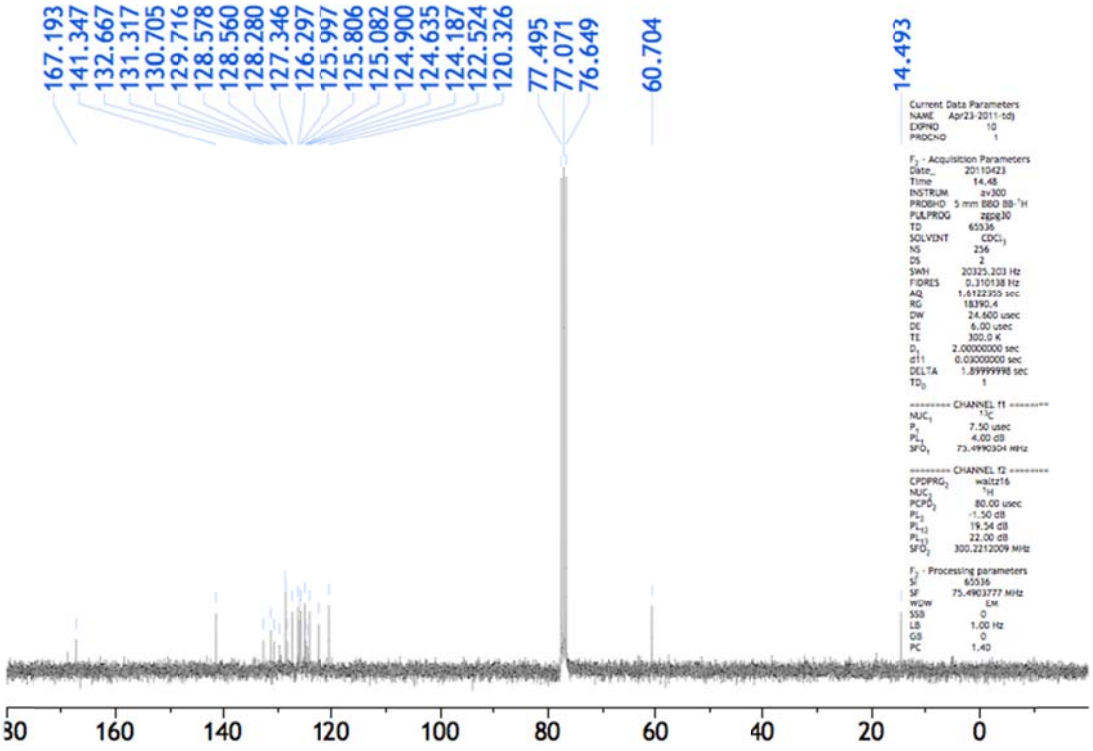


Sodium hydride (0.286g, 7.16 mmol) was added portionwise to a solution of triethylphosphonoacetate (1.360 g, 6.08 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. 1-Pyrenecarboxaldehyde (1.000 g, 4.34 mmol) in THF (25 mL) was slowly added. The resulting solution was stirred for one night at room temperature. The mixture was diluted with a 1.2 N HCl solution, extracted three times with toluene, washed with brine and water, dried over $MgSO_4$, and concentrated. The desired ethyl 3-(pyren-1-yl)acrylate (1.27 g, 97% yield) precipitated upon trituration of the crude mixture in Methanol. :^{1}H-NMR (250 MHz; $CDCl_3$): δ 8.86 (d, J = 15.7, 1H), 8.51 (d, J = 9.4, 1H), 8.31-8.03 (m, 9H), 6.74 (d, J = 15.7, 1H), 4.40 (q, J = 7.1, 2H), 1.45 (t, J = 7.1, 3H) ^{13}C-NMR (75 MHz; $CDCl_3$): δ 167.2, 141.3, 132.7, 131.3, 130.7, 129.7, 128.58, 128.56, 128.3, 127.3, 126.3, 126.00, 125.81, 125.08, 124.90, 124.6, 124.2, 122.5, 120.3, 60.7, 14.5 MS: [M+H]+, *m/z*, (ESI, positive) found 301.1224. C21H17O2 requires 301.1229.

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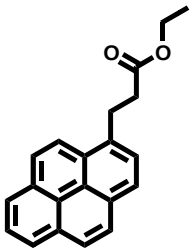
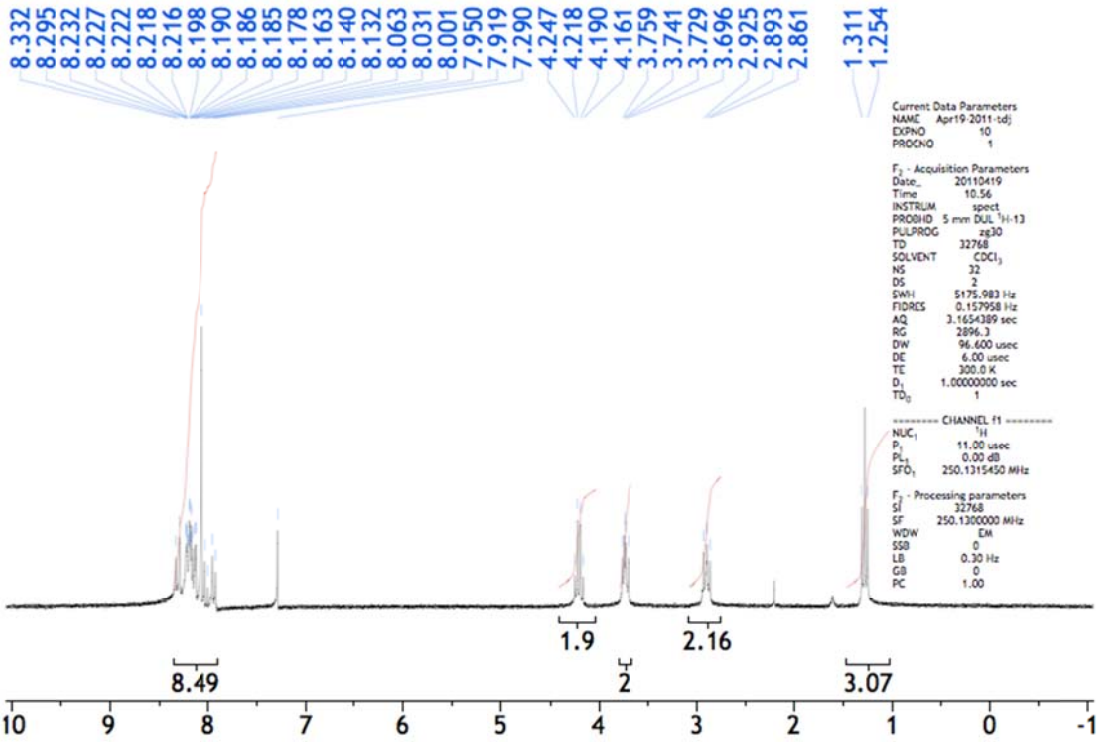
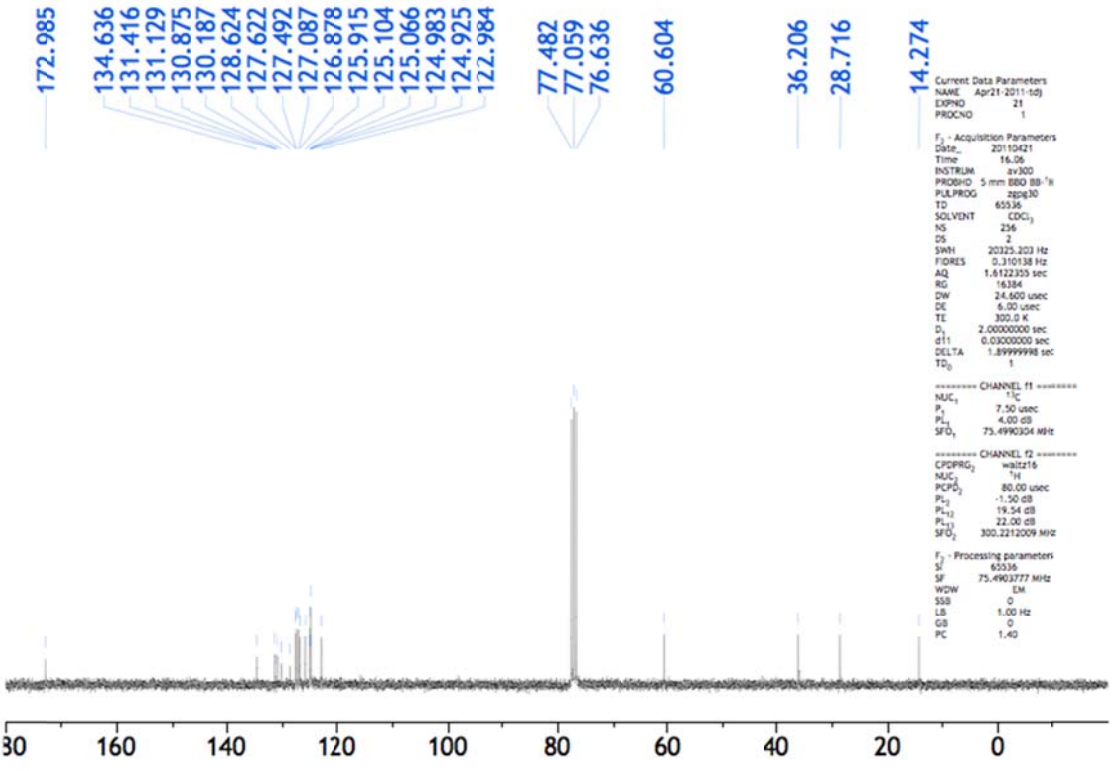


Sodium borohydride (0.151 g, 3.98 mmol) was added to a solution of (E)-ethyl 3-(pyren-1-yl)acrylate (0.500 g, 1.66 mmol) and cobalt chloride hexahydrate (0.118 g, 0.50 mol) dissolved in a mixture of MeOH and THF 7/4 (33 mL). The solution was stirred for 48 h at room temperature. After concentration, the residue was diluted with a 1.2 N aqueous HCl, and the aqueous layer was extracted three times with toluene. The combined organic fractions were washed with water, dried over $MgSO_4$, and concentrated. ethyl 3-(pyren-1-yl)propanoate (0.443 g, 88% yield) was precipitated by trituration of the crude residue in MeOH. :^{1}H-NMR (250 MHz; $CDCl_3$): δ 8.33-7.92 (m, 8H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.73 (dd, *J* = 9.4, 6.3 Hz, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 1.28 (d, *J* = 14.3 Hz, 3H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 173.0, 134.6, 131.4, 131.1, 130.9, 130.2, 128.6, 127.62, 127.49, 127.1, 126.9, 125.9, 125.10, 125.07, 124.98, 124.92, 123.0, 60.6, 36.2, 28.7, 14.3 MS: [M+Na]+, *m/z*, (ESI, positive) found 325.1173. C21H18O2Na1 requires 325.1204.

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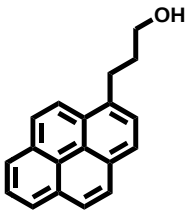
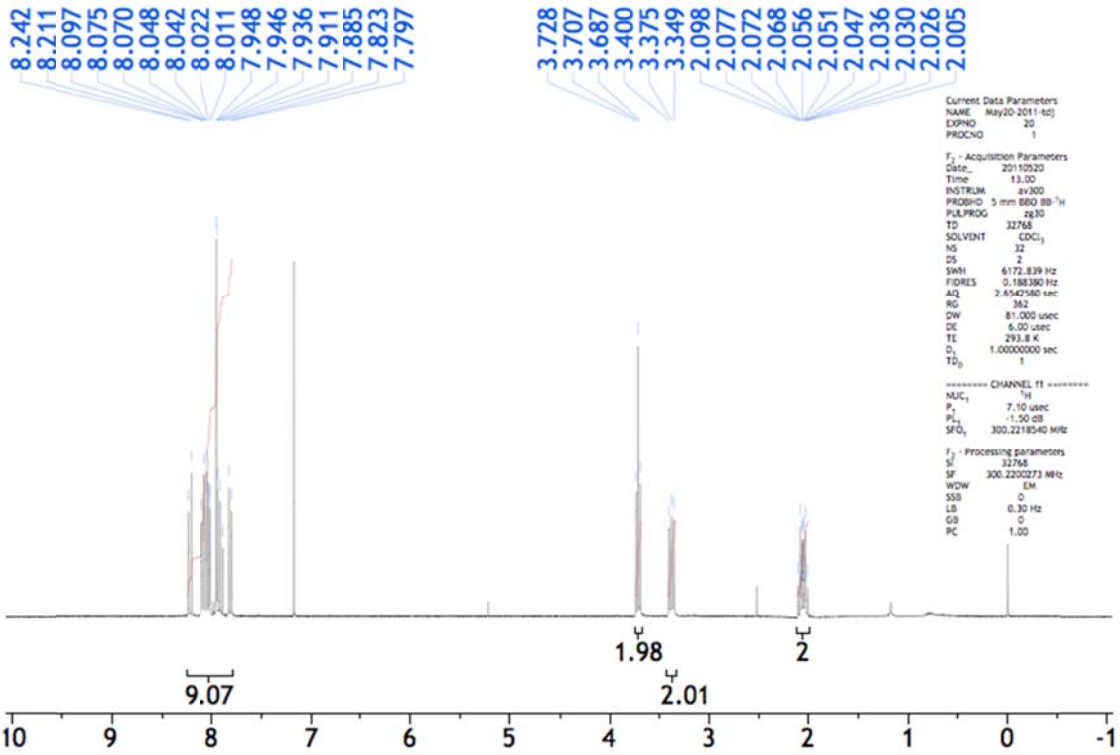
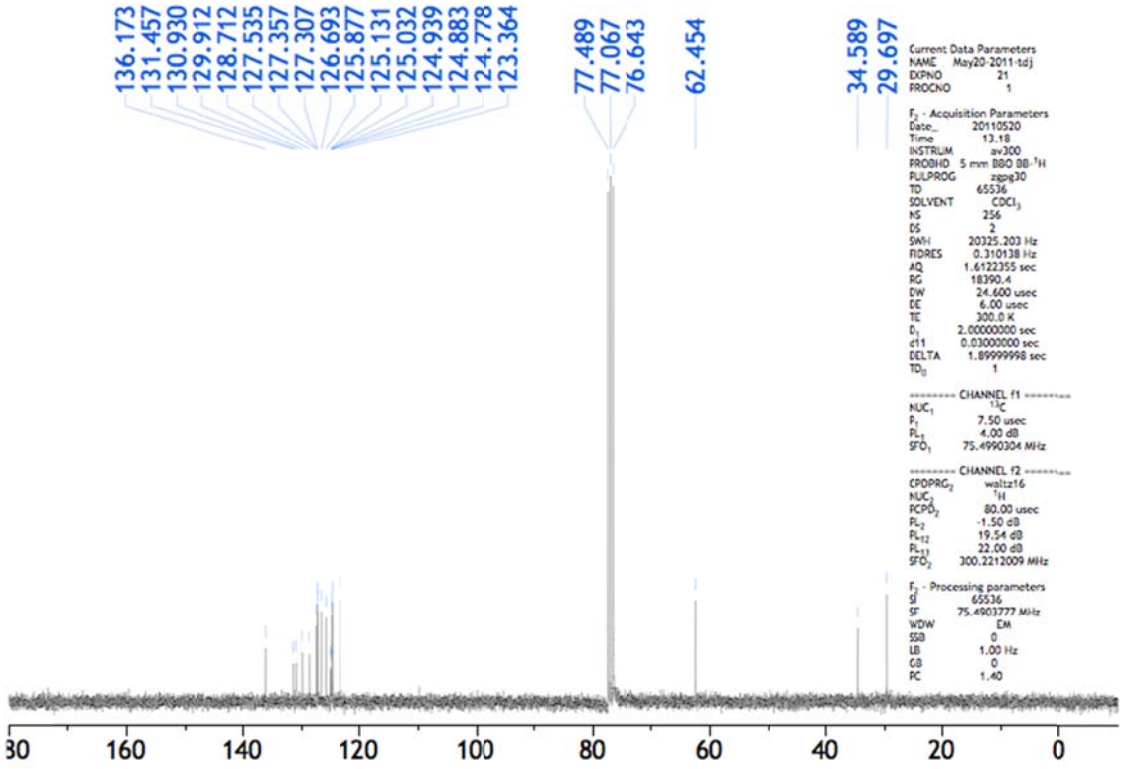


To a solution of ethyl 3-(pyren-1-yl)propanoate (425 mg, 1.41 mmol) in THF (5 mL) was added $LiAlH_4$ (75 mg, 1.97 mmol). The solution was stirred for 2 h at room temperature. The reaction mixture was quenched by the sequential addition of 1 mL of H_2O, 1 mL of 15 wt% NaOHaq and 3 mL of water. The insoluble materials were removed by filtration through Celite. After dilution with toluene, aqueous phase was extracted twice with toluene, and the combined organic layers were washed with brine and dried over $MgSO_4$. The solution was concentrated to give the desired primary alcohol (343 mg, 94% yield). :^{1}H-NMR (300 MHz; $CDCl_3$): δ 8.24-7.80 (m, 9H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.37 (t, *J* = 7.7 Hz, 2H), 2.10-2.00 (m, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 136.2, 131.5, 130.9, 129.9, 128.7, 127.54, 127.36, 127.31, 126.7, 125.9, 125.13, 125.03, 124.94, 124.88, 124.78, 123.4, 62.5, 34.6, 29.7 MS: [M+H]+, *m/z*, (ESI, positive) found 261.1262. C19H17O1 requires 261.1279.

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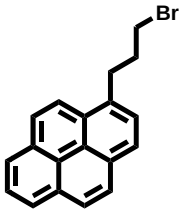
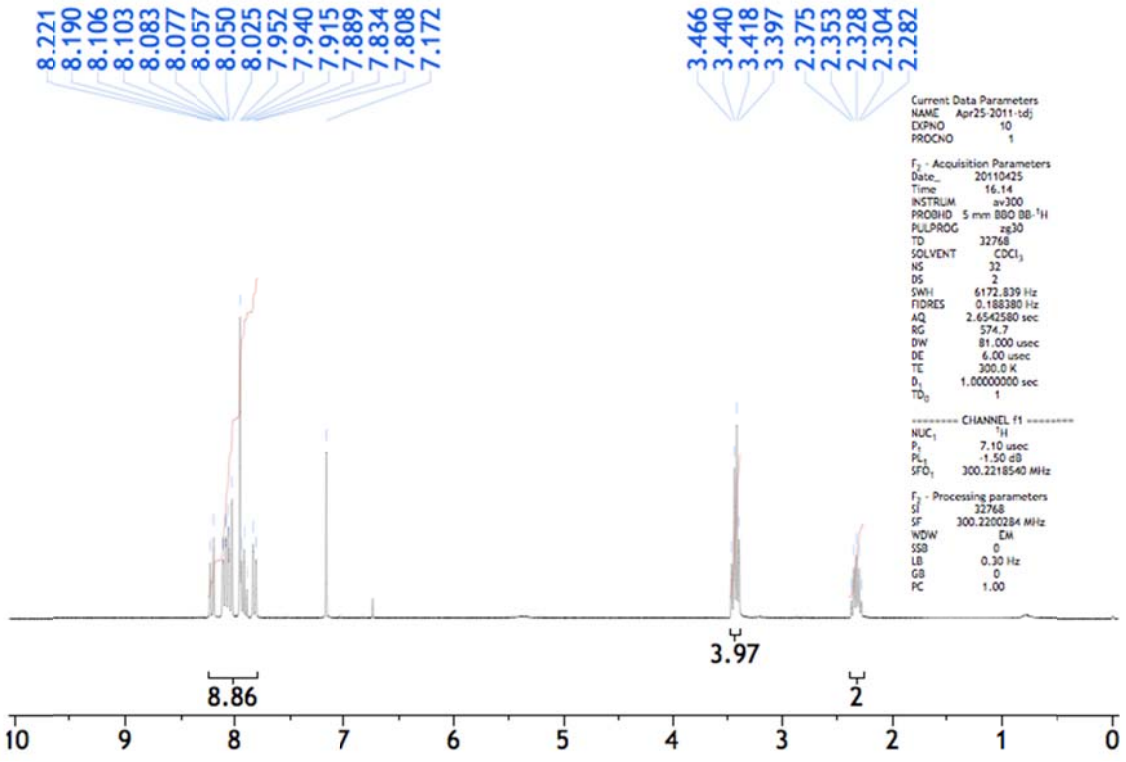
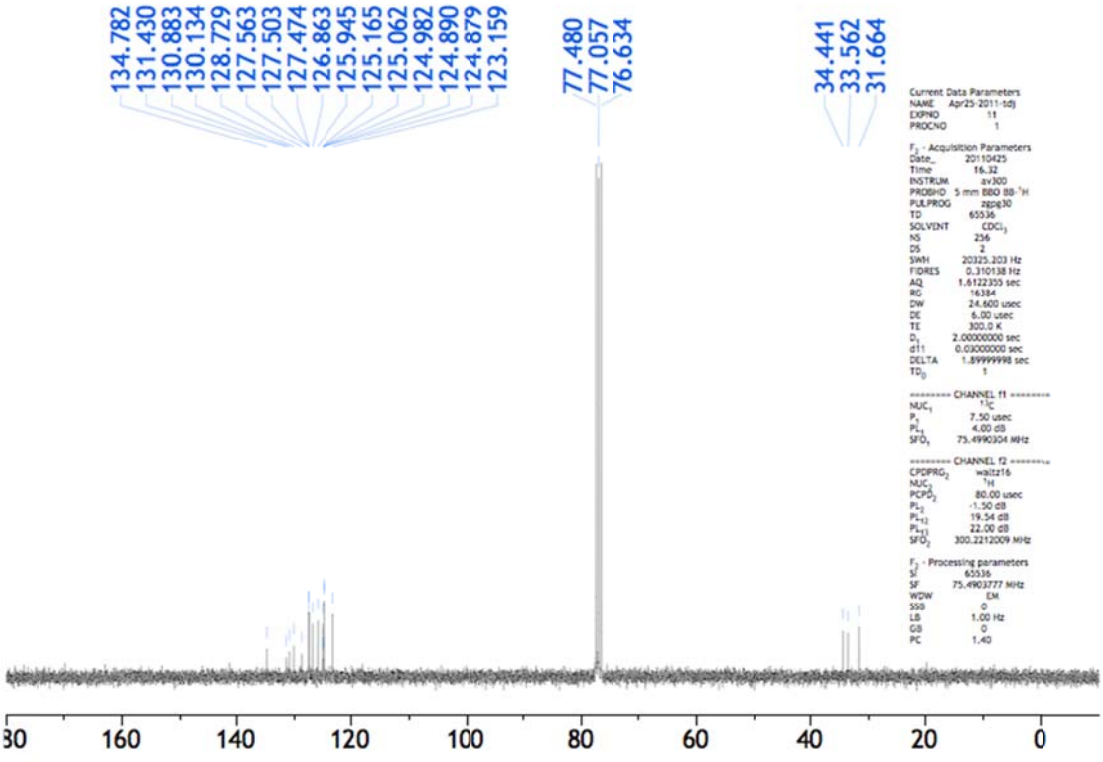


N-bromosuccinimide (262 mg, 1.47 mmol) was added to a solution of triphenylphosphine (474 mg, 1.81mmol) in dichloromethane (10 mL) at -10 °C. After 20 min stirring, 3-(pyren-1-yl)propan-1-ol (343 mg, 1.13mmol) dissolved in dichloromethane (10 mL) was added. The resulting solution was stirred for 3 h at room temperature, diluted with dichloromethane, washed with sat. $NaHCO_3$ solution and brine, and then dried over $MgSO_4$. The solvent was removed in vacuo, and The crude product was purified by column chromatography on silica using dichloromethane/Hexane = 3/1 as the eluent to yield 343 mg (94%) of 1-(3-bromopropyl)pyrene. :^{1}H-NMR (300 MHz; $CDCl_3$): δ 8.22-7.81 (m, 9H), 3.43 (m, 4H), 2.33 (quintet, J = 7.1 Hz, 2H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 134.8, 131.4, 130.9, 130.1, 128.7, 127.56, 127.50, 127.47, 126.9, 125.9, 125.17, 125.06, 124.98, 124.89, 124.88, 123.2, 34.4, 33.6, 31.7

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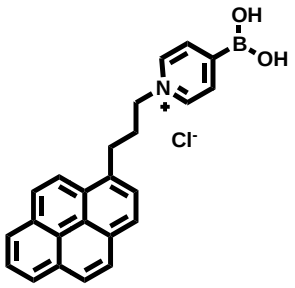
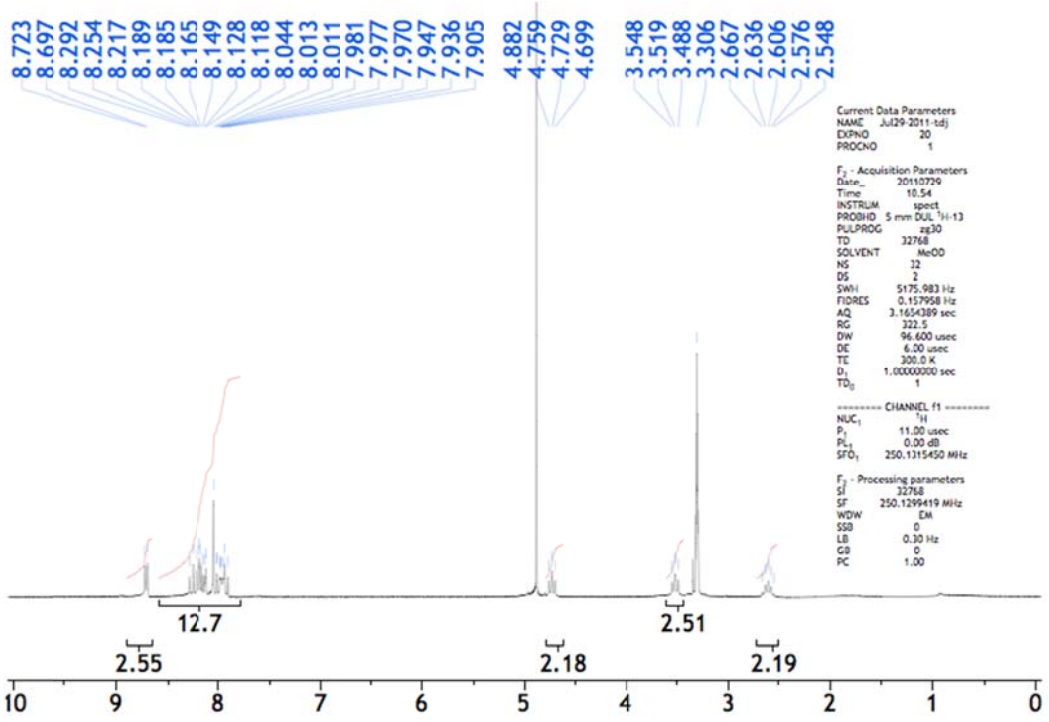
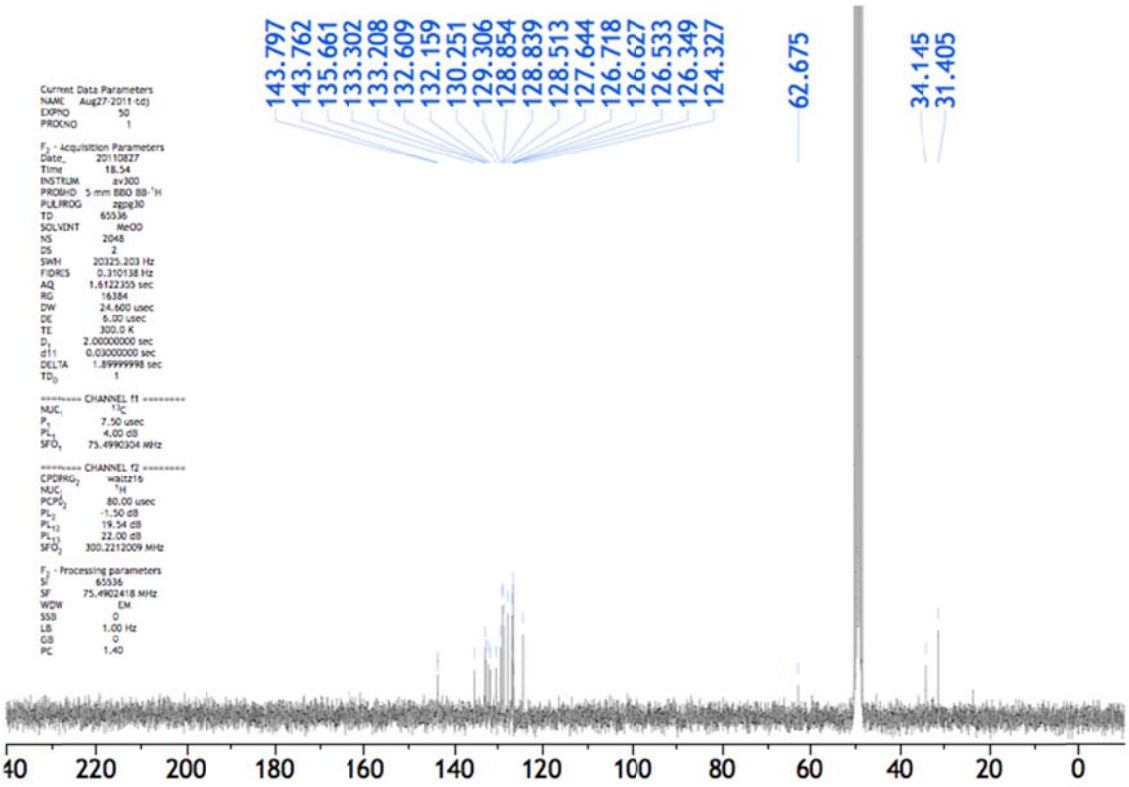


A mixture of 1-(3-bromopropyl)pyrene (193 mg, 0.60 mmol) and 4-pyridineboronic acid neopentyl glycol ester (229 mg, 1.20 mmol) in dry acetonitrile (15 mL) were heated at reflux for 48 h under N_2. After removal of acetonitrile, the mixture was stirred in mixed solvent (acetone : H_2O=9:1) for 12 hours. After deprotection of the boronic acid the mixture was purified by ion-exchange chromatography (Amberlite IRA-400 chloride form), 0.5 mol/L HCl-MeOH as eluent to give **3** as chloride salt, which was washed with water, dichloromethane to give **3** as a solid. (189 mg, 79 % yield). : ^{1}H-NMR (250 MHz; MeOD): δ 8.71 (d, J = 6.6 Hz, 2H), 8.29-7.90 (m, 11H), 4.73 (t, J = 7.4 Hz, 2H), 3.52 (t, J = 7.6 Hz, 2H), 2.61 (dt, J = 14.9, 7.4 Hz, 2H). ^{13}C-NMR (75 MHz; MeOD): δ 143.80, 143.76, 135.7, 133.30, 133.21, 132.6, 132.2, 130.3, 129.3, 128.85, 128.84, 128.5, 127.6, 126.72, 126.63, 126.53, 126.35, 124.3, 62.7, 34.1, 31.4 One carbon peak was not observed due to quadrupole relaxation. MS: [M+], *m/z*, (ESI, positive) found 366.1784. C24H21N1O2B1 requires 366.1660.

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128.513
127.644
126.718
126.627
126.533
126.349
124.327
62.675
34.145
31.405
Current Data Parameters
NAME Aug27-2011-cdj
EXPNO 50
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110827
Time 18.54
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2048
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6122355 sec
RG 16384
DW 24.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 4.00 dB
SFO1 75.4990304 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.50 dB
PL12 19.54 dB
PL13 22.00 dB
SFO2 300.2212009 MHz
F2 - Processing parameters
SI 65536
SF 75.4902418 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
40
220
200
180
160
140
120
100
80
60
40
20
0