Supporting Information

In Situ Preparation of Highly Fluorescent Pyrene-Dyes from Non-luminous Precursors Upon Photoirradiation

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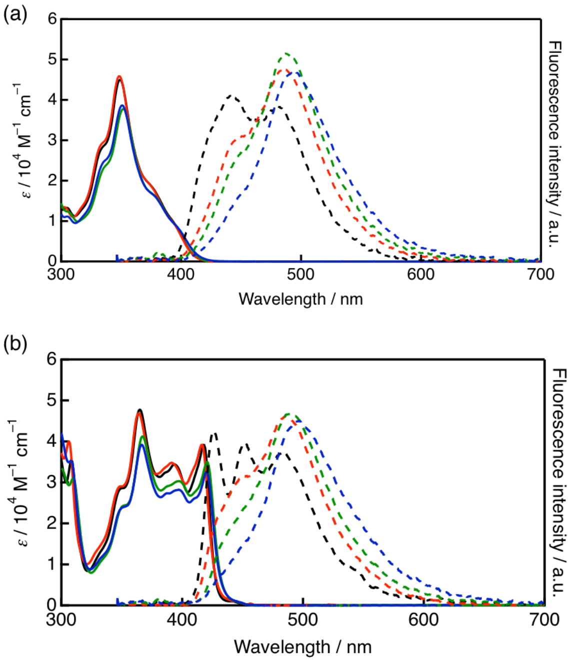

Figure S1. The absorption (solid lines) and fluorescence (dotted lines) spectra of (a) **PyAnt** and (b) **Py-3-Ant** in toluene (black), dichloromethane (red), benzonitrile (green), and DMSO (blue). Fluorescence spectra were excited at 380 nm. (Concentration; 10^{-6} M)

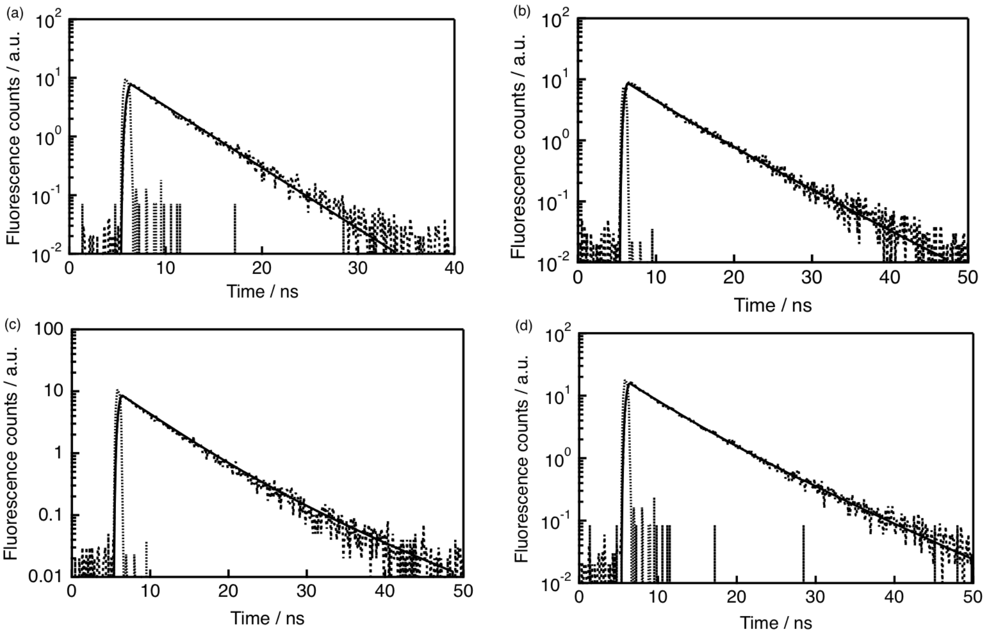

Figure S4. Fluorescence decays of **PyAnt** in (a) toluene at 440 nm, (b) CH_2Cl_2 at 450 nm, (c) PhCN at 450 nm and (d) DMSO at 470 nm; excited at 366 nm.

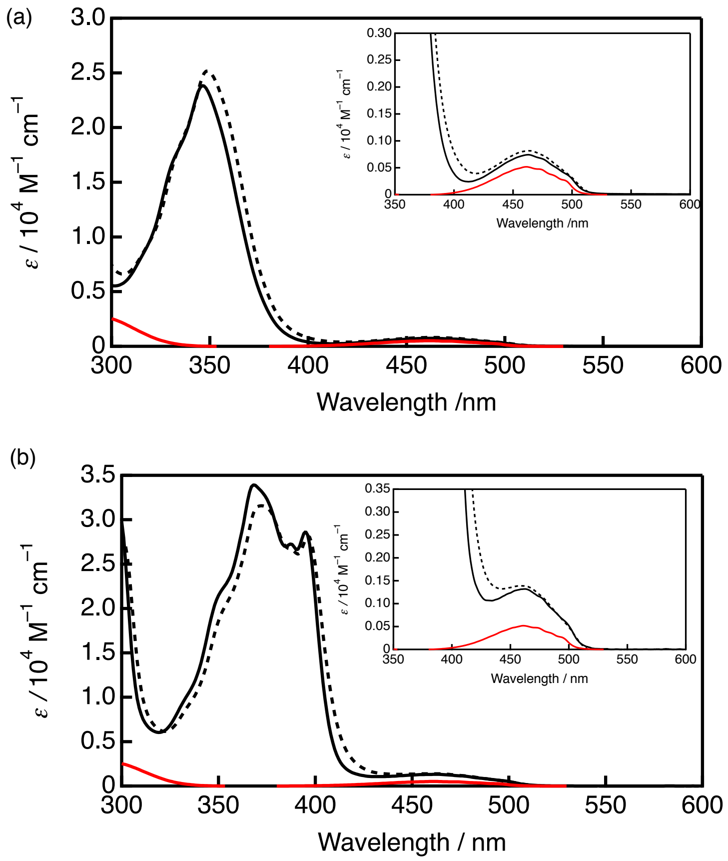

Figure S3. The absorption spectra of **PyDK** (a) and **Py-3-DK** (b) in toluene (solid lines) and PhCN (dashed lines) with **DK** (red) in toluene as a reference.

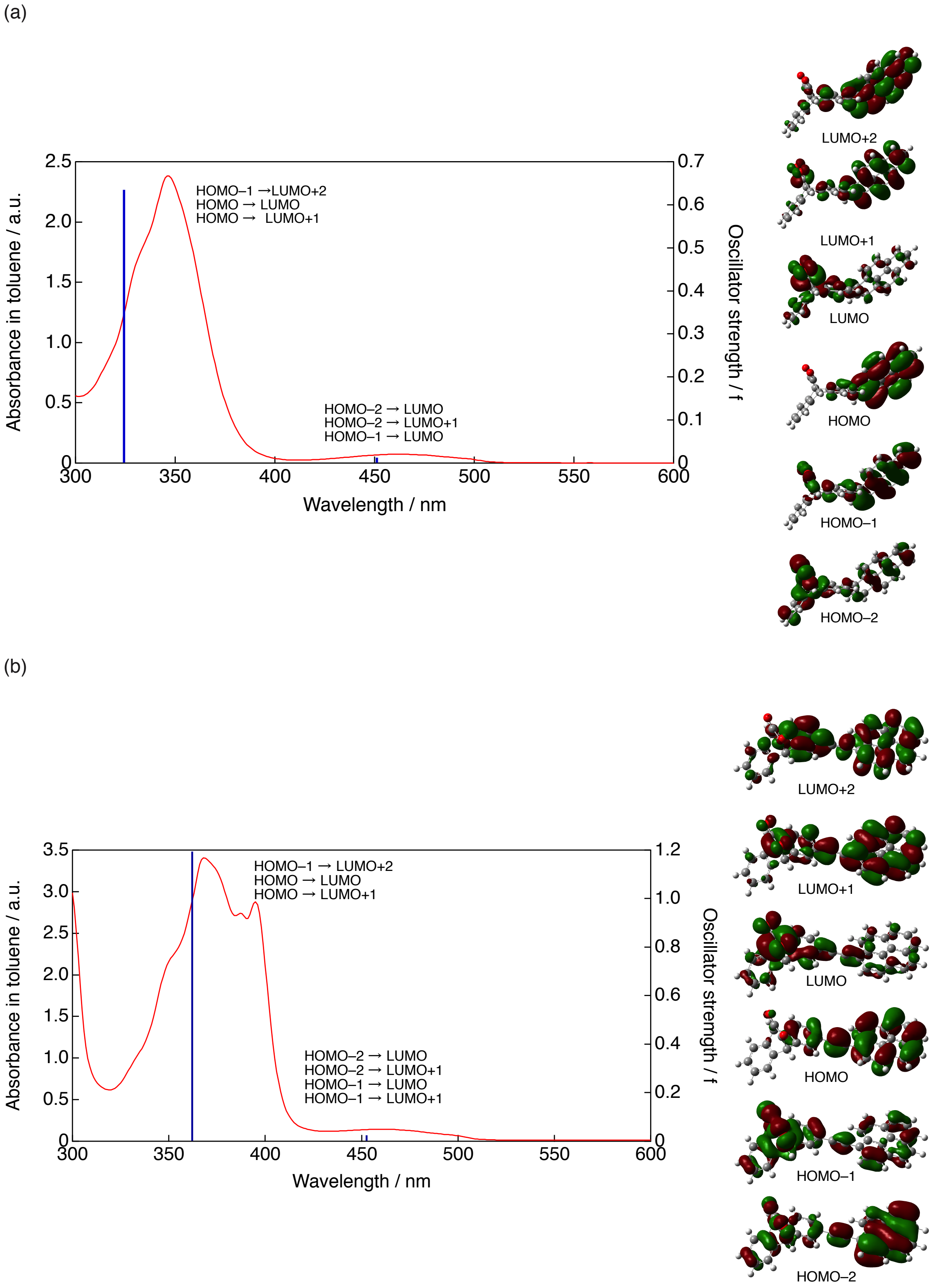

Figure S4. TD-DFT calculation of **PyDK** (a) and **Py-3-DK** (b) at B3LYP/6-31G(d)//CAM-B3LPY/6-31G(d). In toluene (red) and TD-DFT calculation (blue bar).

Cartesian coordinates and vibrational frequencies for the optimized structure of PyDK

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E(RB3LYP) =    -1380.56401243        A.U.

Stoichiometry       C32H18O2
 Framework group    C1[X(C32H18O2)]
 Deg. of freedom     150
 Full point group                 C1          NOp     1
 Largest Abelian subgroup         C1          NOp     1
 Largest concise Abelian subgroup C1          NOp     1
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -3.977988   -1.324669   -0.635152
      2          6           0       -4.752025   -0.043236   -0.859875
      3          6           0       -4.544152    0.886580    0.088471
      4          6           0       -3.581503    0.447116    1.171529
      5          6           0       -4.379120   -1.803300    0.771548
      6          6           0       -4.166925   -0.861625    1.732183
      7          6           0       -2.323236    0.043788    0.430698
      8          6           0       -2.534667   -0.889234   -0.508881
      9          6           0       -1.504061   -1.328736   -1.239336
     10          6           0       -0.276734   -0.836040   -1.004541
     11          6           0       -0.018953    0.081917   -0.045771
     12          6           0       -1.090730    0.524627    0.649498
     13          6           0       -5.165816    2.072915    0.024766
     14          6           0       -5.998026    2.320836   -0.999748
     15          6           0       -6.205898    1.391275   -1.947557
     16          6           0       -5.584029    0.202715   -1.882185
     17          6           0        1.228472    0.581162    0.160281
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     19          6           0        3.592793    0.532922    0.083832
     20          6           0        3.643207    1.852640    0.349389
     21          6           0        2.502383    2.518866    0.574270
     22          6           0        1.325678    1.887298    0.486241
     23          6           0        2.445168   -1.440112   -0.120735
     24          6           0        3.592340   -2.110508   -0.291856
     25          6           0        4.763233   -1.458011   -0.296806
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     28          6           0        5.964566    1.842341    0.197482
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     46          1           0        1.548241   -2.074889   -0.055038
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      52          1           0         8.068055    0.371974   -0.192576
 ---------------------------------------------------------------------
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities
(A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses
(AMU), force constants (mDyne/A), and normal coordinates:
                      1                      2                      3
                      A                      A                      A
 Frequencies --     18.6045                28.8102                37.7810
 Red. masses --      6.5602                 6.2155                 5.7302
 Frc consts  --      0.0013                 0.0030                 0.0048
 IR Inten    --      0.4916                 0.4716                 0.0687
```

Cartesian coordinates and vibrational frequencies for the optimized structure of Py-3-DK

```
E(RB3LYP) =   -1456.88445095       A.U.

Stoichiometry     C34H18O2
 Framework group   C1[X(C34H18O2)]
 Deg. of freedom    156
 Full point group                 C1        NOp    1
 Largest Abelian subgroup         C1        NOp    1
 Largest concise Abelian subgroup C1        NOp    1
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0         7.350170    2.410774   -1.167777
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      6          6           0         6.373252    2.264074   -0.179891
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      8          6           0         3.959910   -1.103836   -0.446706
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     24          6           0        -5.180044    2.001217    0.236947
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     52          1           0       -6.582059    3.640858    0.562353
     53          1           0       -9.433197   -2.434368   -0.227467
     54          1           0       -9.645783    0.000252    0.168431
 ---------------------------------------------------------------------
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities
(A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses
(AMU), force constants (mDyne/A), and normal coordinates:
                      1                      2                      3
                      A                      A                      A
 Frequencies --     7.7116                17.6945                19.0457
 Red. masses --     6.0888                 6.5110                 6.3785
 Frc consts  --     0.0002                 0.0012                 0.0014
 IR Inten    --     0.3867                 0.4452                 0.0021
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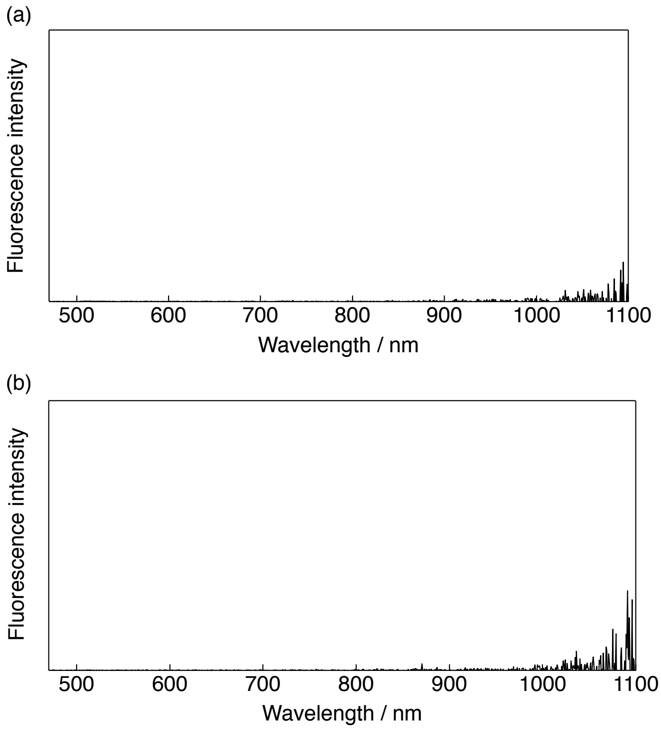


Figure S5. The fluorescence spectra of (a) **PyDK** and (b) **Py-3-DK** in toluene (λ_{ex} = 460 nm, Concentration; 10^{-4} M).

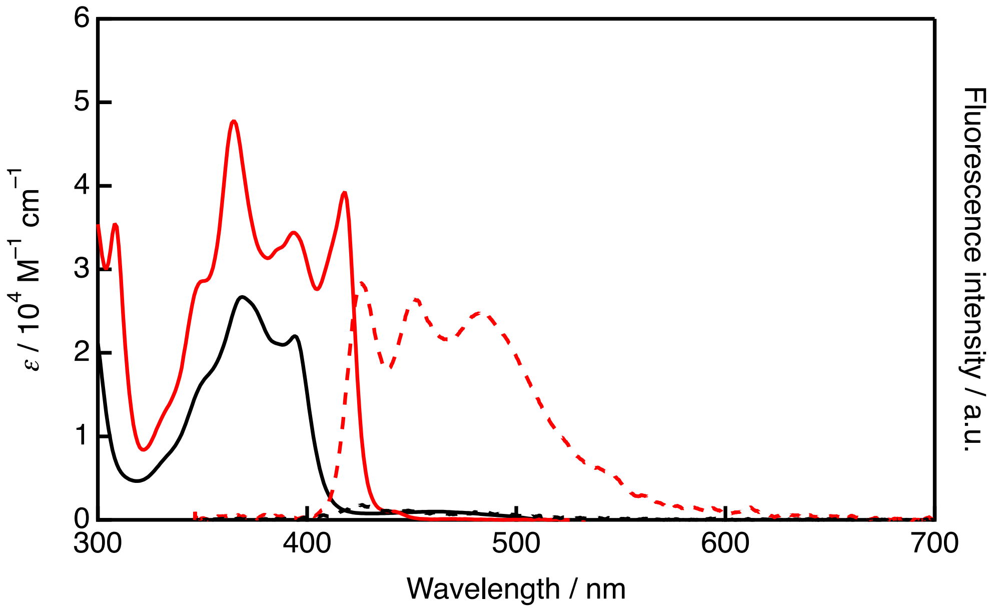


Figure S6. The absorption spectra (solid lines) and fluorescence (dotted lines) spectra in toluene: **Py-3-DK** (black) and **Py-3-Ant** (red). (λ_{ex} = 380 nm).

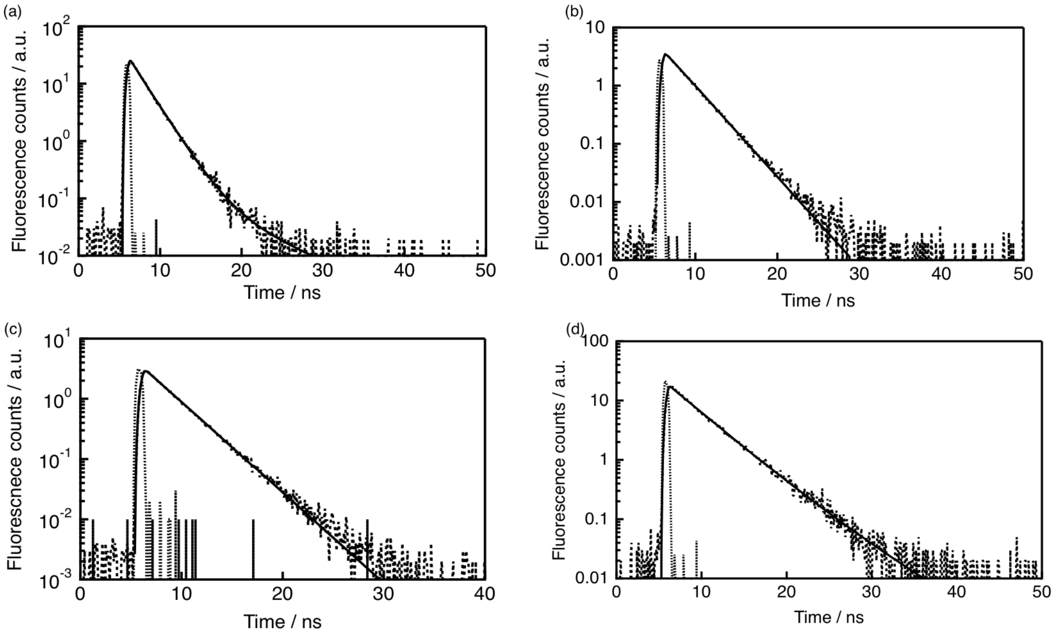


Figure S7. Fluorescence decays of **Py-3-Ant** in (a) toluene at 450 nm, (b) CH_2Cl_2 at 450 nm, (c) PhCN at 460 nm and (d) DMSO at 470 nm; excited at 366 nm.

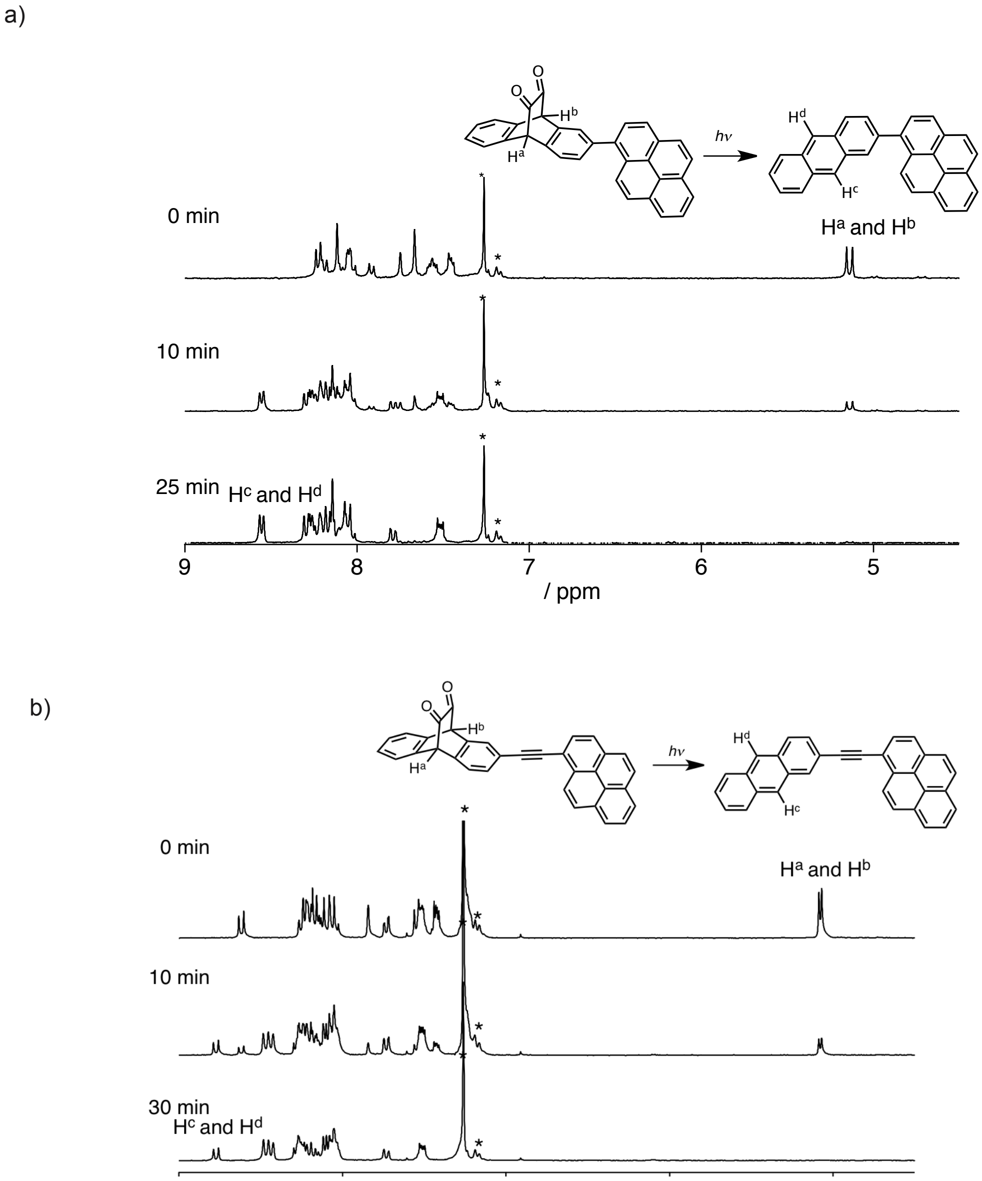


Figure S8 The change in ^{1}H-NMR spectra during photolysis (λ_{ex} = 470 nm) of a) **PyDK** and b) **Py-3-DK** in $CDCl_3$.

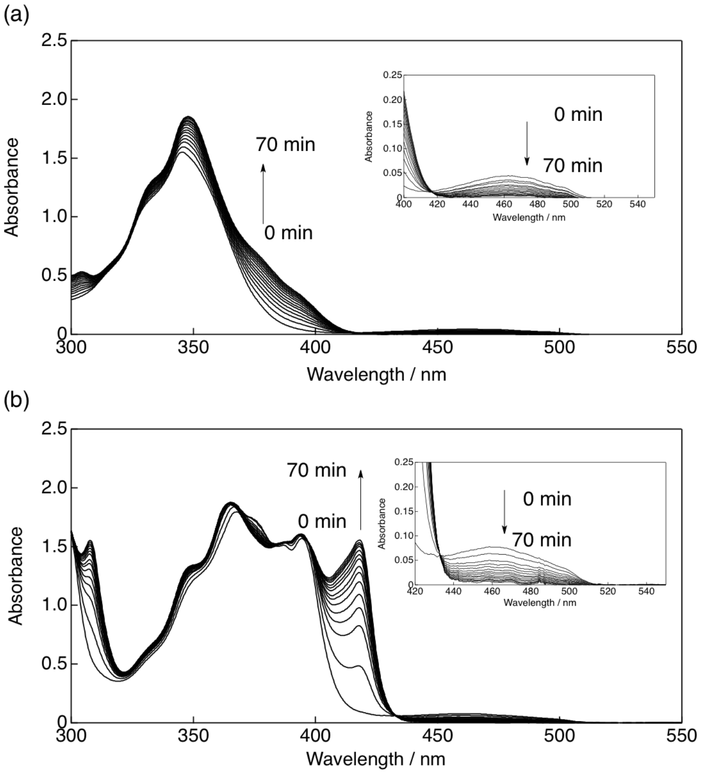


Figure S9. Change the absorption spectra during photolysis (λ_{ex} = 468 nm) in toluene. (a) **PyDK** (7.6×10^{-5} M). (b) **Py-3-DK** (5.6×10^{-5} M).

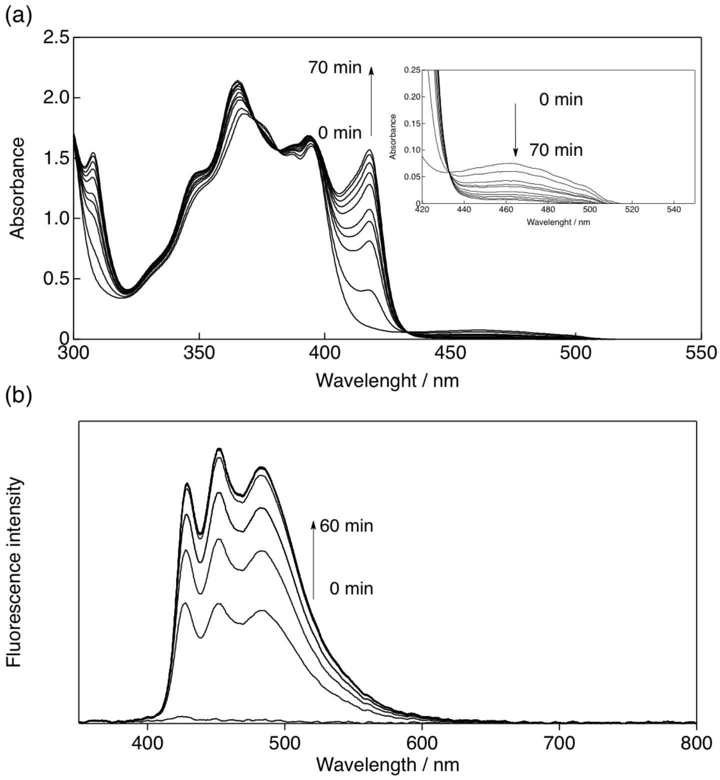


Figure S10. The change in (a) the absorption spectra (6.0 × 10^{-5} M) and (b) fluorescence spectra (3.8 × 10^{-5} M) during photolysis of **Py-3-DK** in toluene (λ_{ex} = 370 nm).

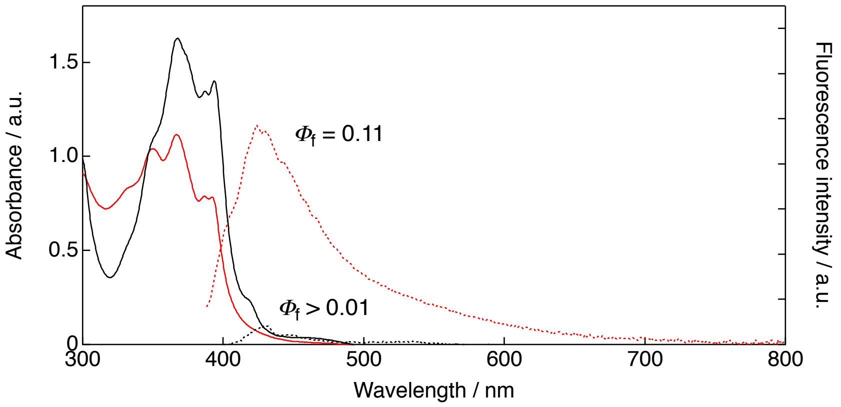


Figure S11. Absorption and emission spectra of **Py-3-DK** and **Py-3-Ant** in PMMA film; excited at 380 nm.

Experimental conditions

General ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 and AL 300 spectrometers at ambient temperature using tetramethylsilane as an internal standard. FAB, EI and ESI mass spectra were measured on a JEOL JMS-700 spectrometer. UV-vis spectra were measured on a JASCO UV/VIS/NIR Spectro-photometer V-570. Steady-state fluorescence spectra were measured on USB4000 (Ocean Optics, Inc.) in the range of 345-1100 nm with an irradiation light through a monochromator (Ritsu MC-10N) using a 500W Xenon lamp (Ushio XB-50102AA-A). Fluorescence quantum yields were measured on an Absolute PL Quantum Yield Measurement System C9920-02. Elemental analyses were performed on a Yanaco MT-5 elemental analyzer.

Materials Thin-layer chromatography (TLC) and gravity column chromatography were performed on Art. 5554 (Merck KGaA), and Silica Gel 60N (Kanto Chemical Co.), respectively. Benzonitrile was distilled from P_2O_5 *in vacuo*. All other solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For spectral measurements, spectral grade toluene, dichloromethane and DMSO were purchased from Nacalai tesque Inc.

Photochemical reactions The photocleavage reactions were carried out in a quartz UV cell which was irradiated by monochromatic excitation light through a monochrometor (Ritsu MC-10N) by a 500 W xenon lamp (Ushio XB-50102AA-A) and monitored by an OCEAN OPTICS high resolution spectrometer system HR-4000 with light source DH-2000-BAL.

Measurement of quantum yields of the photoreaction The quantum yield of the photochemical reactions of 9,10-diketoanthracene was determined as 0.37±0.06 with a standard actinometer (potassium ferrioxalate; $K_3[Fe(C_2O_4)_3]$).[1] A square quartz cuvette (10 mm i.d.) which contained a deaerated solution (3.0 cm^3) of 9,10-diketoanthracene was irradiated with monochromatized light of $\lambda = 468$ nm by a light through a monochromator (Ritsu MC-10N) using a 500W Xenon lamp (Ushio XB-50102AA-A). Under the conditions of actinometry experiments, the actinometer, 9,10-diketoanthracene absorbed essentially all incident light. The photochemical reaction was monitored using a JASCO UV/VIS/NIR Spectrophotometer V-570. The quantum yields were determined from the increase in absorbance due to the anthracene (378 nm) at the beginning of the reaction. The quantum yield was the average value of 8 measurements. The relative quantum yields of **PyDK** and **Py-3-DK** were determined based on the quantum yield of 9,10-diketoanthracene.

Photochemical reactions in film PMMA (470 mg) was dissolved with toluene (10 mL). The solution was stirred overnight and filtrated. **PyDK** or **Py-3-DK** (1 mg) was dissolved in CH_2Cl_2 (200 μL). PMMA solution

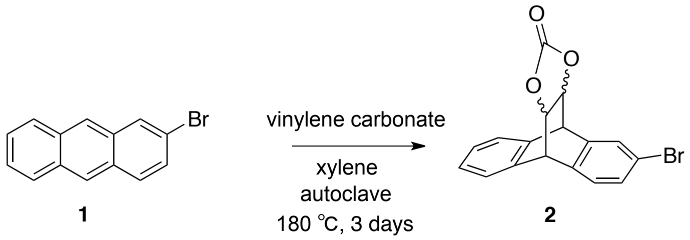
(200 μL) and diketone solution (10 μL) were mixed. The mixture solution (50 μL) was dropped on glass substrate (1 cm × 1 cm) and dried under vacuum condition. The substrate was converted upon photo-irradiation for 10 min using a metal-halide lamp (Nippon P. I. PCS-UMX375RC, 375W) over 390 nm under vacuum condition. Steady-state absorption spectra were measured on USB4000 by a light through a monochromator (Ritsu MC-10N) using a 500W Xenon lamp (Ushio XB-50102AA-A). Fluorescence quantum yields were measured on Absolute PL Quantum Yield Measurement System (Hamamatsu Photonics C9920-02).

Theoretical calculations All density functional theory calculations were achieved with the Gaussian09[1] program package. The geometry was fully optimized at the Becke's three-parameter hybrid functional combined with the Lee-Yang-Parr correlation functional abbreviated as the B3LYP level of density functional theory with 6-31G(d) basis set. Equilibrium geometries were verified by the frequency calculations, where no imaginary frequency was found. Based on the B3LYP/6-31G(d) optimized geometry, time dependent density functional theory (TDDFT) was conducted at the CAM-B3LYP/6-31G(d) level of theory.

1) M. J. Frisch, G. W. Trucks, H.s B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Cossi, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, . Ö, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, et al. Gaussian 09 revision A.2, Gaussian, Inc.: Wallingford, CT, 2009.

Synthesis

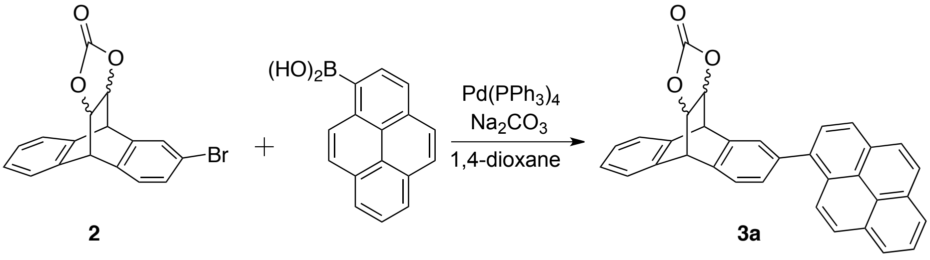
2-brome-9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diyl carbonate(2)



A solution of 2-bromoanthracene **1** (0.72 g, 2.8 mmol) and vinylene carbonate (0.28 mL, 4.4 mmol) in xylene (12 mL) was heated at 180 °C in an autoclave for 3 d. After removal of the solvent *in vacuo*, the residue was rinsed with hexane to give **2** as white crystals (0.73 g, 76%).

^{1}H NMR (400 MHz; $CDCl_3$) ［mixture of isomers］: δ = 7.55 (m, 1H), 7.39-7.37 (m, 3H), 7.28-7.25 (m, 3H), 4.88 (m, 2H), 4.68 (m, 2H); ^{13}C NMR (100 MHz; $CDCl_3$: Mixture of isomers): δ = 153.67, 140.00, 139.83, 136.70, 136.65, 135.37, 134.47, 130.69, 128.76, 127.88, 127.86, 127.30, 126.66, 126.60, 126.58, 121.41, 75.86, 75.79, 75.75, 47.50, 47.38, 47.29; MS (DI-EI) *m*/*z*: 344 [M$^+$]; Anal. Calcd. for $C_{17}H_{11}BrO_3$•1/6 $CHCl_3$: C, 56.79; H, 3.10.; Found: C, 56.80; H, 3.20.

2-(1-Pyrenyl)-9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diyl carbonate (3a)

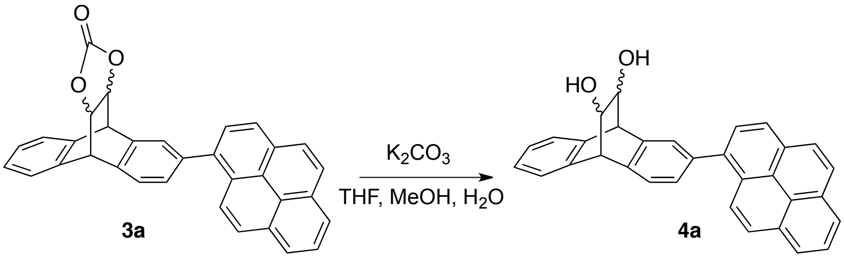


The compound **2** (0.638 g, 1.86 mmol), pyrenylboronic acid (0.586 g, 2.42 mmol), and Na_2CO_3 (3.08 g) were added to 1,4-dioxane (50 mL) and the suspension was degassed by freeze-pump-thaw cycling. Then $Pd(PPh_3)_4$ (0.229 g, 0.198 mmol) was added and the solution was refluxed for 18 h under argon atmosphere, then cooled to rt. The solution was poured into aqueous NH_4Cl, filtrated with Celite, and extracted with EtOAc. The organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography ($CHCl_3$) and recrystallized from $CHCl_3$/hexane to give **3a** as white powder

(0.441 g, 51%).

^{1}H NMR (400 MHz; $CDCl_3$): δ = 8.21 (d, J = 7.6 Hz, 2H), 8.17 (d, J = 7.6 Hz, 1H), 8.10 (s, 2H), 8.06-7.99 (m, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.66 (m, 1H), 7.57 (m, 1H), 7.51-7.44 (m, 3H), 7.43-7.30 (m, 2H), 5.05 (m, 2H), 4.83 (m, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) ［Two peaks are lacked.］: δ = 153.95, 140.96, 137.84, 136.54, 136.24, 136.18, 131.38, 130.80, 130.71, 129.97, 128.25, 127.78, 127.43, 127.65, 127.58, 127.43, 127.27, 126.71, 126.64, 126.06, 125.52, 125.24, 124.90, 124.86, 124.80, 124.76, 124.58, 76.33, 76.32, 47.94, 47.65; MS (FAB) m/z: 464 [M$^+$]; Anal. Calcd. for $C_{33}H_{20}O_3$•$CHCl_3$•1/2 H_2O: C, 68.88; H, 3.74.; Found: C, 68.58; H, 3.77.

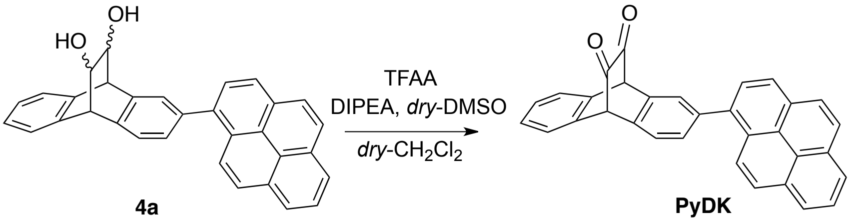
2-(1-Pyreno)-9,10-dihydro-11,12-dihydroxy-9,10-ethanoanthracene (**4a**)



To a solution of **3a** (0.250 g, 0.538 mmol) in THF (21 mL), MeOH (20 mL) and water (10 mL), K_2CO_3 (3.60 g) was added. The solution was refluxed for 1 h and cooled to rt. The product was extracted with $CHCl_3$ and washed with water and brine and the organic layer was dried over Na_2SO_4. The organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3$/EtOAc = 1/1) and recrystallized from $CHCl_3$/hexane to give **4a** as white powder (0.175 g, 74%).

^{1}H NMR (400 MHz; $CDCl_3$): δ = 8.19 (d, J = 7.6 Hz, 2H), 8.14 (m, 2H), 8.08 (s, 2H), 8.00 (m, 2H), 7.91 (d, J = 7.6 Hz, 1H), 7.58 (m, 1H), 7.51-7.43 (m, 4H), 7.28 (m, 2H), 4.56 (2, 1H), 4.53 (s, 1H), 4.23 (m, 2H), 2.17 (m, 2H, -OH); ^{13}C NMR (100 MHz; $CDCl_3$)［Two peaks are lacked.］: δ = 139.90, 139.66, 138.69, 138.48, 137.24, 131.32, 130.79, 130.40, 128.88, 128.31, 127.49, 127.31, 127.28, 127.23, 126.76, 126.73, 126.56, 126.49, 125.86, 125.09, 124.96, 124.78, 124.72, 124.67, 124.56, 124.46, 68.21, 68.18, 51.43, 51.14; MS (ESI) m/z: 461 [M+Na]; (HR-ESI-TOF) m/z = 461.15170, calcd for $C_{32}H_{22}NaO_2$ = 461.15175 [M+Na]$^+$.

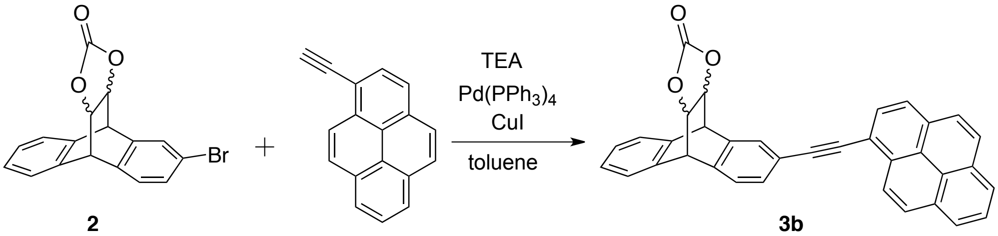
2-(1-Pyreno)-9,10-dihydro-9,10-ethanoanthracene-11,12-dione (**PyDK**)



Under argon atmosphere, *dry*-DMSO (1.0 mL, 14 mmol) and *dry*-CH_2Cl_2 (8.0 mL) were cooled to −60 °C. Trifluoroacetic anhydride (1.8 mL, 13 mmol) was added dropwise over 10 min. After the solution was stirred for 10min, **4a** (0.175 g, 0.399 mmol) in *dry*-DMSO (4.4 mL) and *dry*-CH_2Cl_2 (4.4 mL) was added dropwise over 10 min. After the solution was stirred for 90 min, *N*,*N*-(*iso*-Pro)$_2$EtN (4.0 mL, 23 mmol) was added dropwise over 5 min. The solution was stirred for 60 min and left to warm up to rt. 3 M HCl (50 mL) was added to the solution, the product was extracted with CH_2Cl_2, and the organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography (CH_2Cl_2), recrystallized from CH_2Cl_2/hexane, and rinsed with (Et_2O/hexane = 1/1) to give **PyDK** as yellow powder (0.024 g, 14%).

^{1}H NMR (400 MHz; $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.11 (m, 2H), 8.03 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.65 (m, 2H), 7.55 (m, 2H), 7.44 (m, 2H), 5.15 (s, 1H), 5.11 (s, 1H); ^{13}C NMR (100 MHz; $CDCl_3$): δ = 183.67, 183.47, 142.77, 136.05, 134.97, 134.84, 134.79, 133.62, 131.68, 131.36, 130.88, 130.79, 129.49, 129.46, 128.35, 128.18, 127.85, 127.70, 127.37, 127.26, 126.42, 126.36, 126.23, 126.09, 125.33, 125.01, 124.84, 124.72, 124.65, 124.60, 60.11, 59.84; MS (ESI) m/z: 457 [M+Na]; (HR-ESI-TOF) *m/z* = 457.12038, calcd for $C_{32}H_{18}NaO_2$ = 457.12045 $[M+Na]^+$.

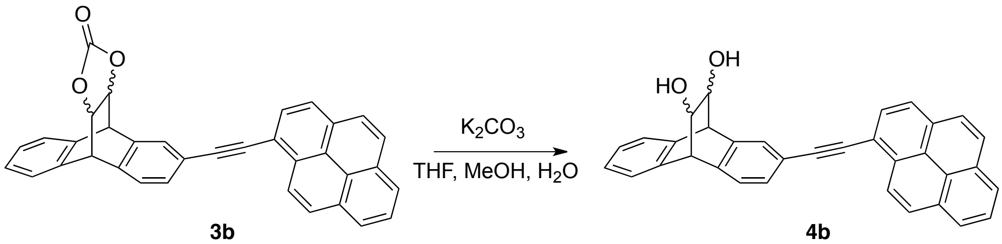
2-(1-Pyreno-ethynyl)-9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diyl carbonate(**3b**)



The compound **2** (0.682 g, 1.99 mmol), 1-ethynylpyrene (0.678 g, 3.00 mmol) and CuI (0.020 mg) were added to a mixture of toluene (10 mL) and Et_3N (10 mL). The solution was bubbled with argon gas for 20 min and dried by freeze-pump-thaw cycling. $Pd(PPh_3)_4$ (0.116 g, 0.100 mmol) was added to the solution. The solution was warmed to 70 °C for 18 h and cooled to rt. The solution was filtered with Celite, washed with $CHCl_3$ and the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography (1st. CH_2Cl_2, 2nd. EtOAc/hexane = 3/7) to give **3b** as yellow powder (0.331 g, 34%).

^{1}H NMR (300 MHz; $CDCl_3$): δ = 8.64 (d, *J* = 9.0 Hz, 1H), 8.25-8.03 (m, 9H), 7.76 (m, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.47-7.41 (m, 3H), 7.28 (m, 1H), 4.95 (m, 2H), 4.78 (m, 2H); ^{13}C NMR (75 MHz; $CDCl_3$)［Two peaks are lacked.］: *δ* = 154.02, 137.29, 136.71, 136.62, 131.93, 131.29, 131.24, 131.10, 131.08, 129.73, 129.62, 128.37, 128.19, 128.04, 127.26, 127.23, 126.78, 126.24, 125.79, 125.74, 125.65, 125.57, 124.54, 124.47, 124.31, 122.94, 117.62, 94.67 88.96, 76.18, 76.11, 47.66, 47.59; MS (FAB) m/z: 488 $[M]^+$; HR-FAB *m/z* = 488.1412, calcd for $C_{35}H_{20}O_3$ = 488.1412 $[M]^+$.

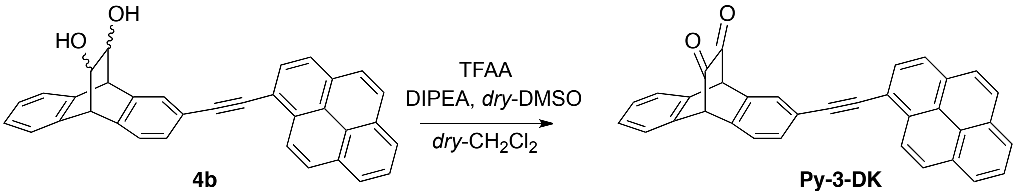
2-(1-Pyreno-ethynyl)-9,10-dihydro-11,12-dihydroxy-9,10-ethanoanthracene carbonate(**4b**)



3b **4b**

To the solution of compound **3b** (0.310 g, 0.635 mmol) in a mixture of THF (25 mL), MeOH (25 mL) and water (4 mL), K_2CO_3 (4.03 g) was added. The solution was stirred overnight and quenched with water. The organic solvent was removed under reduced pressure and the product was extracted with EtOAc. The organic layer was washed with water and brine, and dried over Na_2SO_4. The organic solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography (EtOAc/ hexane = 1/1) to give **4b** as yellow powder (0.178 g, 61%). ^{1}H NMR (300 MHz; $CDCl_3$): δ = 8.65 (d, *J* = 9.0 Hz, 1H), 8.24-8.03 (m, 8H), 7.76 (s, 1H), 7.59 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.44 (d, *J* = 10 Hz, 1H), 7.35 (m, 2H), 7.19 (m, 2H), 4.50 (m, 2H), 4.13 (m, 2H), 2.25 (m, 2H); ^{13}C NMR (75 MHz; $CDCl_3$)［Three peaks are lacked.］: *δ* = 139.46, 139.30, 138.98, 131.88, 131.24, 131.19, 131.07, 130.20, 129.60, 129.56, 128.31, 128.12, 127.27, 126.98, 126.70, 126.23, 125.60, 125.57, 124.90, 124.53, 124.49, 124.49, 124.32, 121.85, 121.84, 95.15, 88.46, 68.12, 68.03, 51.33, 51.22; MS (FAB) m/z: 462 $[M]^+$; HR-FAB *m/z* = 462.1623, calcd for $C_{34}H_{22}O_2$ = 461.1620 $[M]^+$.

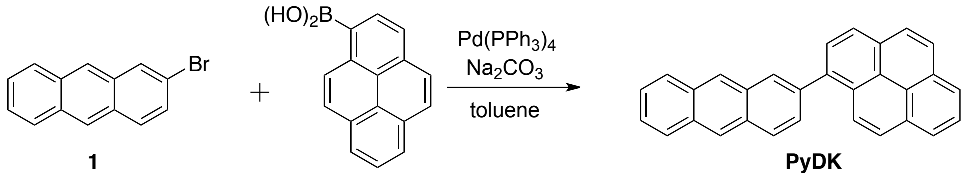
2-(1-Pyreno-ethynyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dione (**Py-3-DK**)



Under argon atmosphere, *dry*-DMSO (1.0 mL, 14 mmol) and *dry*-CH_2CL_2 (4.0 mL) were cooled to -60 °C. Trifluoroacetic anhydride (1.0 mL, 0.72 mmol) was added dropwise over 10 min. After the solution was stirred for 10min, **4b** (0.181 g, 0.391 mmol) in a mixture of *dry*-DMSO (1.0 mL) and *dry*-CH_2Cl_2 (2.0 mL) was added dropwise over 10 min. After the solution was stirred for 60 min, *N*, *N*-(*iso*-Pro)$_2$EtN (2.7 mL, 16 mmol) was added dropwise over 5 min. The solution was stirred for 60 min and warmed to rt. The product was extracted with CH_2Cl_2 and washed with 1 M HCl, water, and brine. The organic layer was dried over Na_2SO_4 and removed under reduced pressure. The crude product was purified on silica gel column chromatography (CH_2Cl_2) and recrystallized from toluene/hexane to give **Py-3-DK** as yellow powder (0.107 g, 60%).

^{1}H NMR (300 MHz; $CDCl_3$): δ = 8.62 (d, *J* = 9.1 Hz, 1H), 8.25-8.04 (m, 8H), 7.83 (m, 1H), 7.71 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.54-7.50 (m, 3H), 7.42 (m, 2H), 5.08 (s, 1H), 5.06 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$)[One peak is lacked.]: δ = 183.42, 183.25, 135.18, 134.70, 134.51,134.45, 132.61, 131.97, 131.51, 131.17, 130.96, 129.61, 129.19, 129.02, 128.53, 128.40, 128.21, 127.20, 126.49, 126.45, 126.41, 126.31, 125.77, 125.27, 124.87, 124.54, 124.42, 124.22, 117.02, 93.86, 90.37, 59.91, 59.78 ; MS (FAB) m/z: 458 $[M]^+$; HR-FAB *m/z* = 458.1305, calcd for $C_{34}H_{18}O_2$ = 458.1307 $[M]^+$.

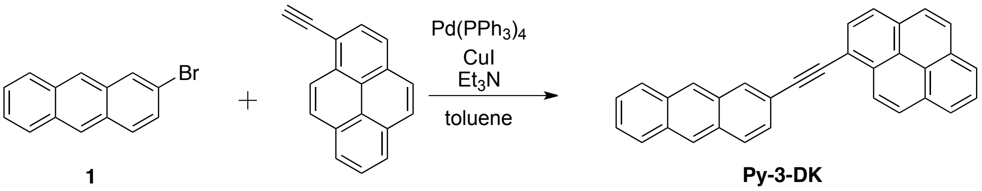
2-(1-Pyreno)anthracene (PyAnt)



2-Bromoanthracene **1** (0.193 g, 0.749 mmol), pyrenylboronic acid (0.2773 g, 1.17 mmol), and Na_2CO_3 (0.240 g) were added to toluene (10.0 mL) and water (1.1 mL). The suspension was degassed by freeze-pump-thaw cycling. Then $Pd(PPh_3)_4$ (0.045 g, 0.039 mmol) was added and the solution was refluxed for 24 h under argon atmosphere, then cooled to rt. The solution was filtrated with Celite, and extracted with $CHCl_3$. The organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was washed with $CHCl_3$ and recrystallized from toluene to give **PyAnt** as pale yellow solids (0.0100 g, 3%).

^{1}H NMR (400 MHz; $CDCl_3$): δ = 8.54 (d, *J* = 7.2 Hz, 1H), 8.30-8.03 (m, 13H), 7.78 (d, *J* = 6.6 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): *δ* = 138.05, 137.53, 132.04, 131.86, 131.60, 131.43, 130.94, 130.71, 130.65, 129.25, 128.72, 128.61, 128.19, 128.13, 128.01, 127.73, 127.55, 127.44, 127.38, 126.45, 126.10, 125.99, 125.50, 125.42, 125.26, 125.12, 124.98, 124.86, 124.85, 124.67; MS (EI) m/z: 378 $[M]^+$; HR-EI *m/z* = 378.1409, calcd for $C_{30}H_{18}$ = 378.1409 $[M]^+$.

2-(1-Pyreno-ethynyl)anthracene (Py-3-Ant)

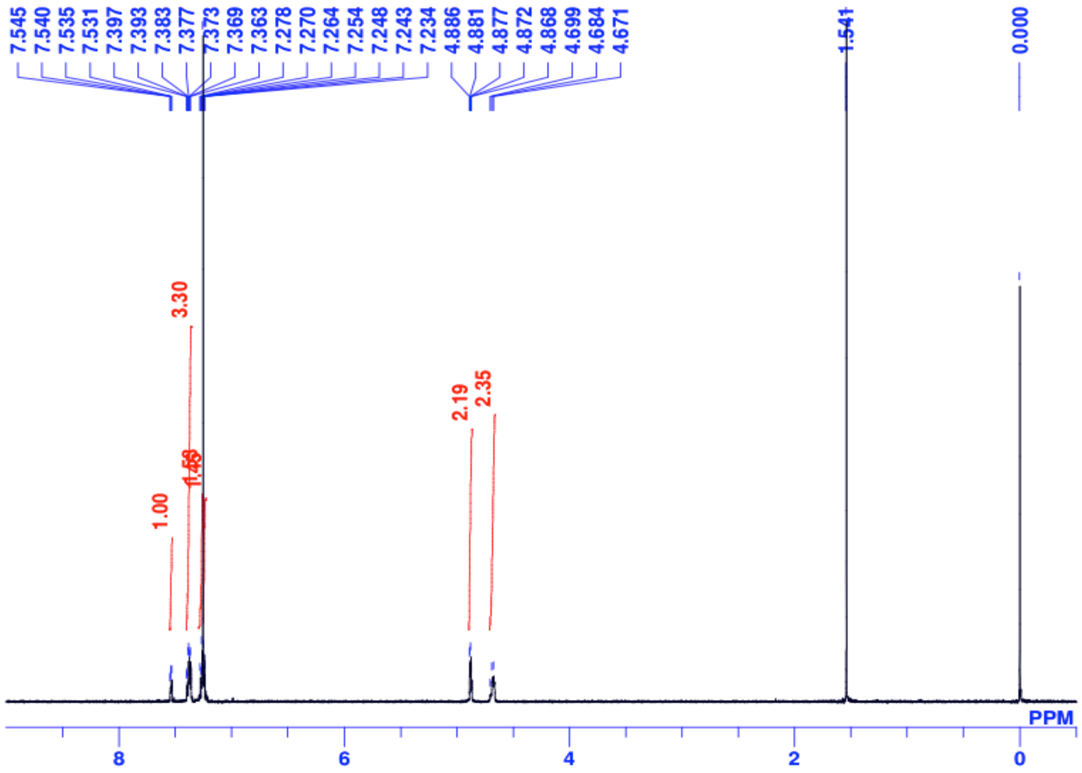


2-bromoanthracene (0.205 g, 0.797 mmol), 1-ethynylpyrene (0.276 g, 1.22 mmol), and CuI (0.018 mg) were added to a mixture of toluene (7.0 mL) and Et_3N (4.0 mL). The solution was bubbled with argon gas for 20 min and dried by freeze-pump-thaw cycling. $Pd(PPh_3)_4$ (0.044 g, 0.0380 mmol) was added to the solution. The solution was refluxed for 17 h under argon atmosphere then cooled to rt. The solution was filtered with Celite, washed with $CHCl_3$ and the solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography ($CHCl_3$/hexane = 1/4) and recrystallized from toluene to give **Py-3-DK** as yellow solids (0.040 g, 12%).

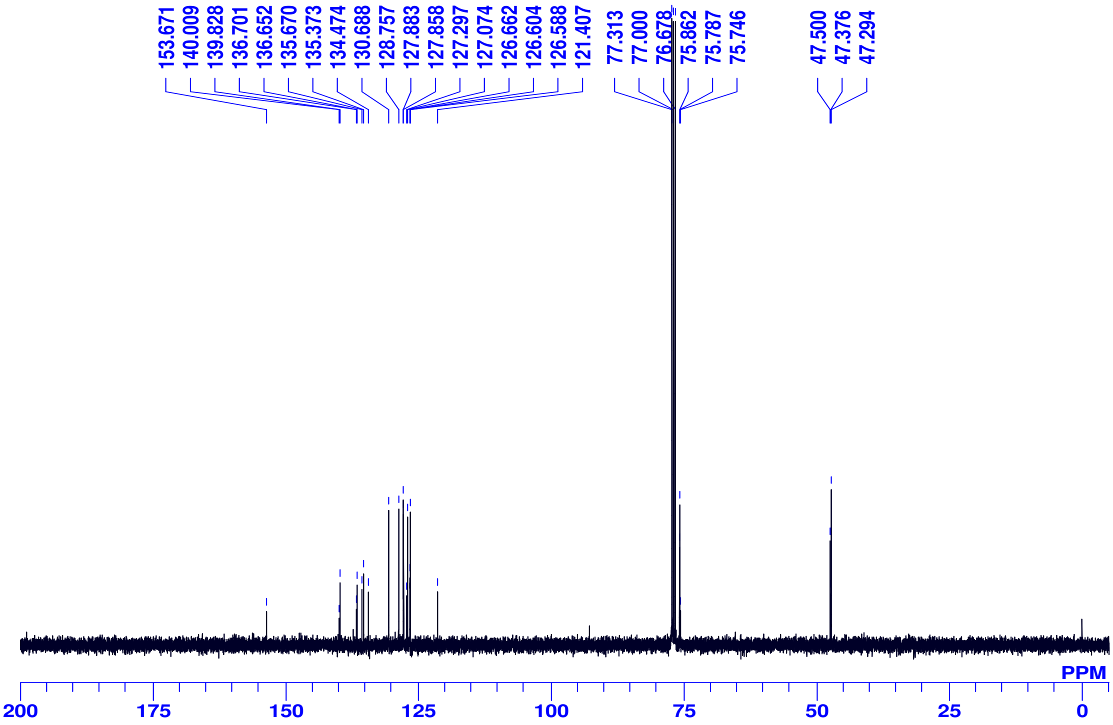
^{1}H NMR (300 MHz; $CDCl_3$): δ = 8.78 (d, *J* = 9.0 Hz, 1H), 8.48 (s, 1H), 8.45 (s, 1H), 8.42 (s, 1H), 8.30-8.03 (m, 11H), 7.72 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.51 (m, 2H); MS (EI) m/z: 402 $[M^+]$; HR-EI *m/z* =402.1409, calcd for $C_{32}H_{18}$ = 402.1409 $[M^+]$; ^{13}C NMR spectrum was not recorded because of poor solubility.

Characterization of compound

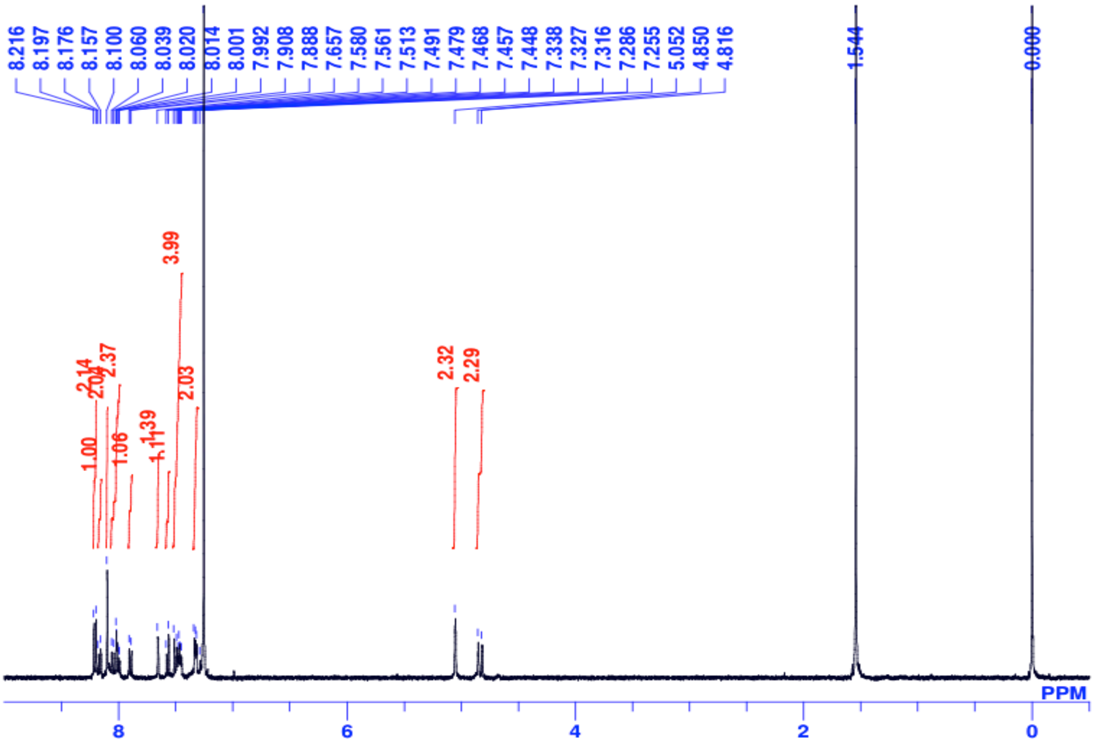
^{1}H NMR spectrum (CDCl$_3$) of **2**.



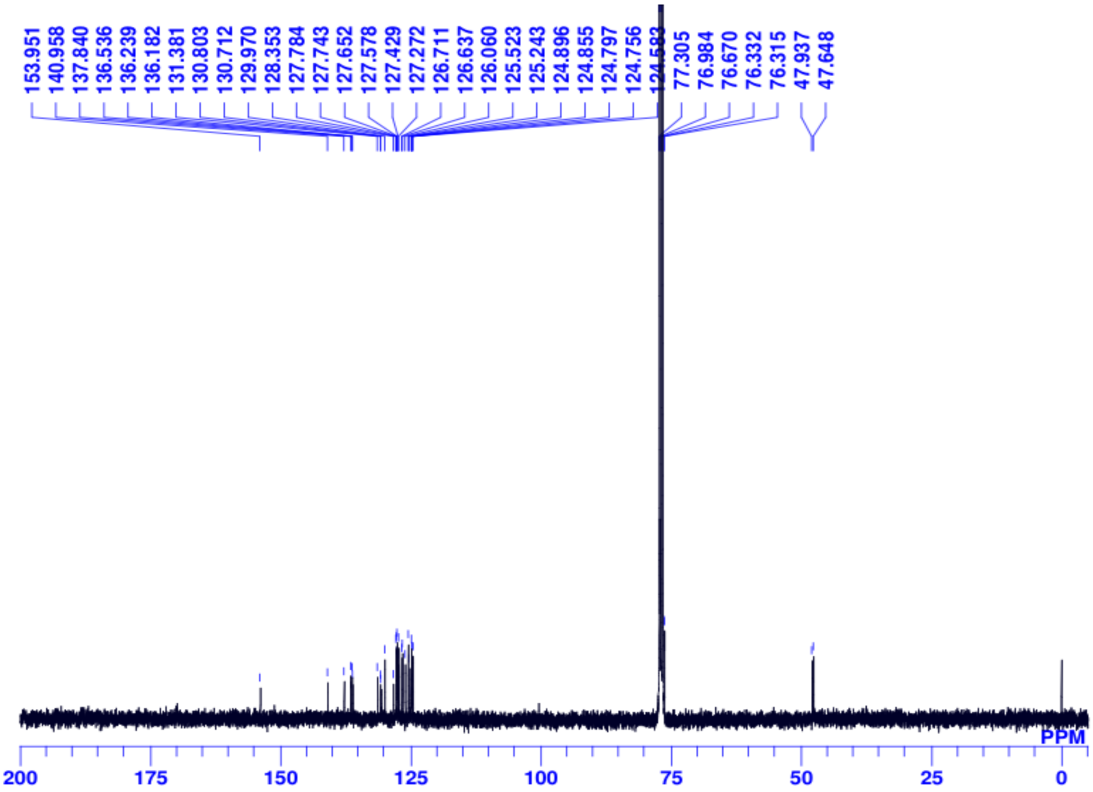
^{13}C NMR spectrum (CDCl$_3$) of **2**.



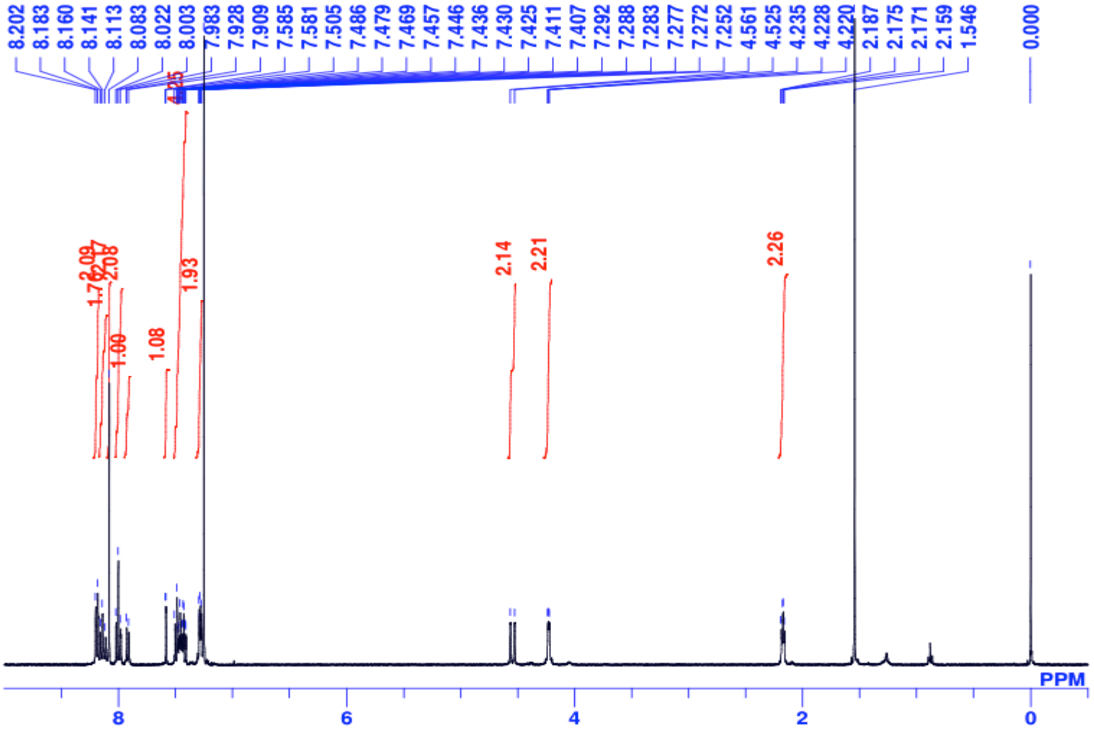
^{1}H NMR spectrum ($CDCl_3$) of **3a**.



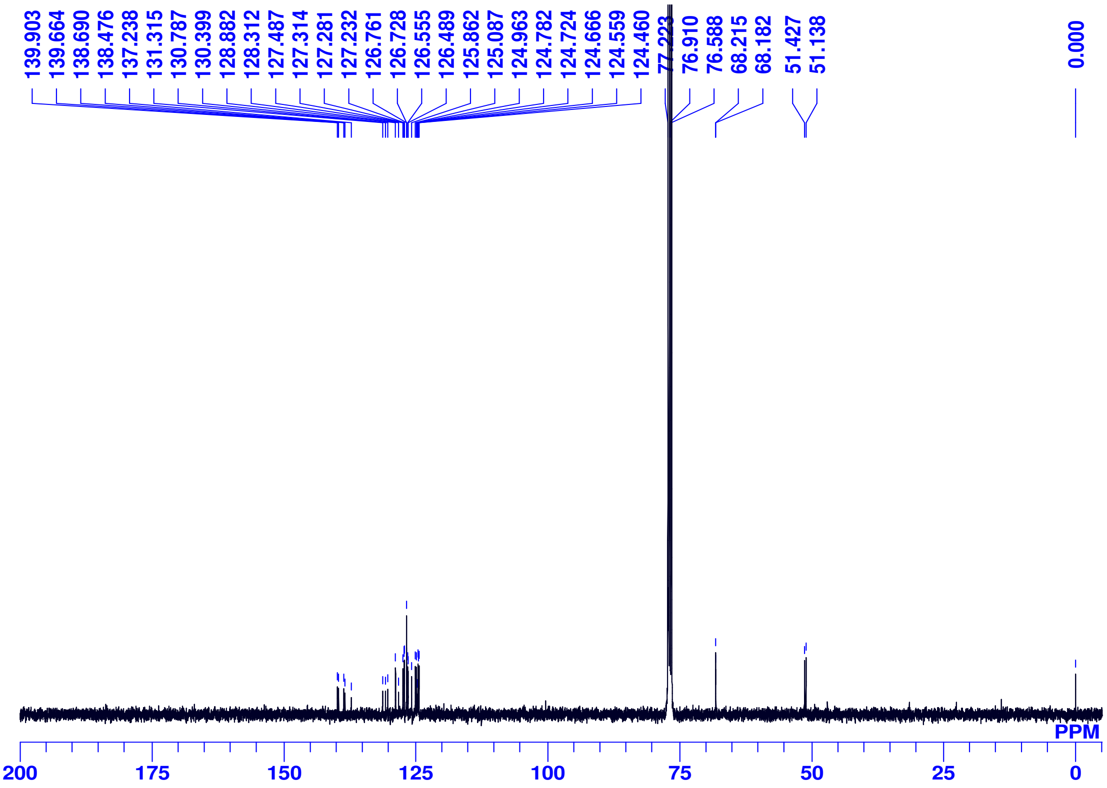
^{13}C NMR spectrum ($CDCl_3$) of **3a**.



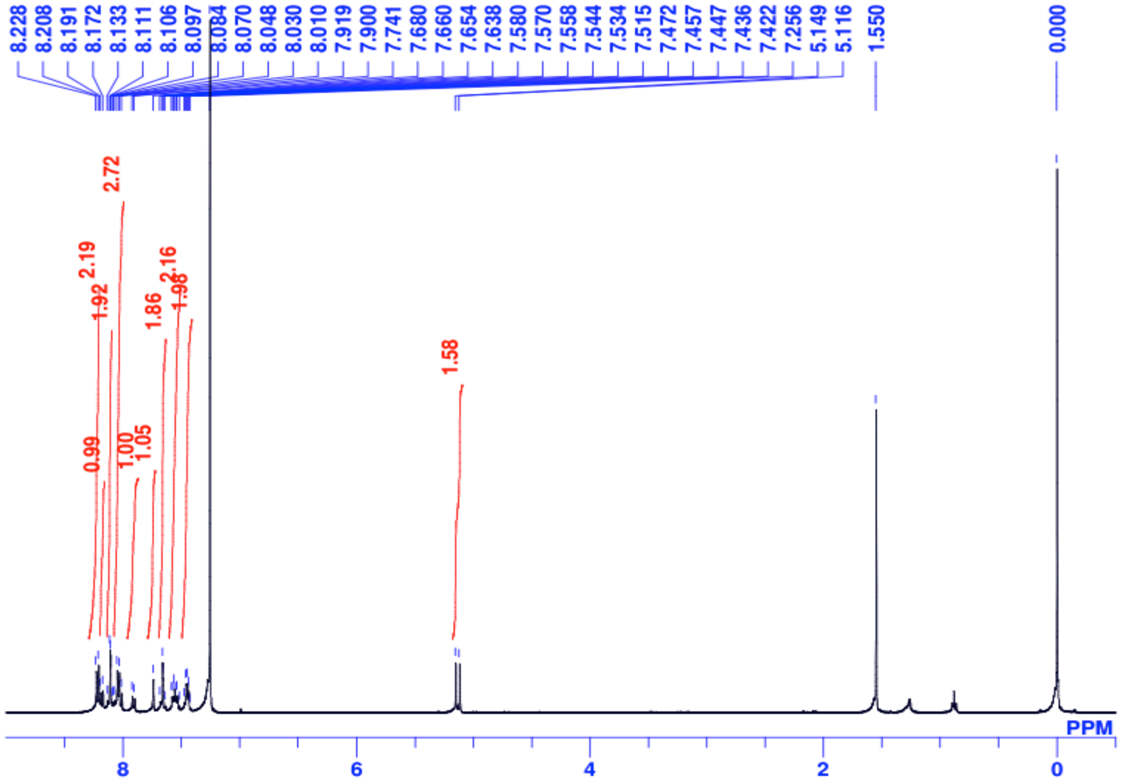
^{1}H NMR spectrum ($CDCl_3$) of **4a**.



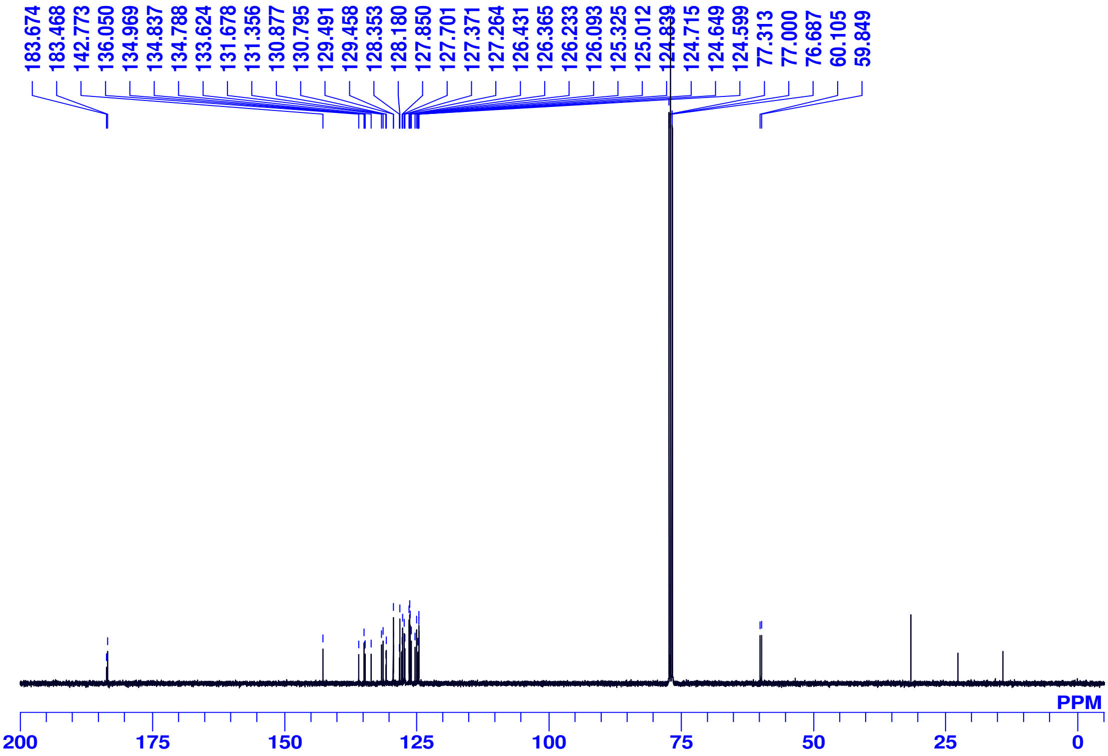
^{13}C NMR spectrum ($CDCl_3$) of **4a**.



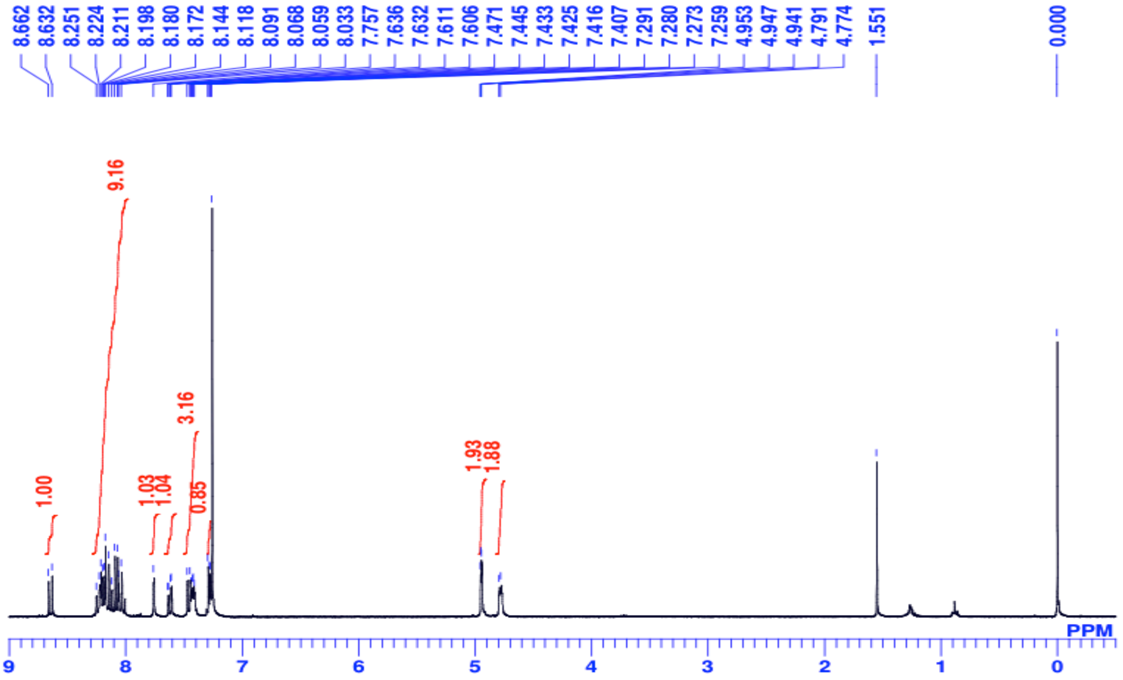
^{1}H NMR spectrum ($CDCl_3$) of **PyDK**.



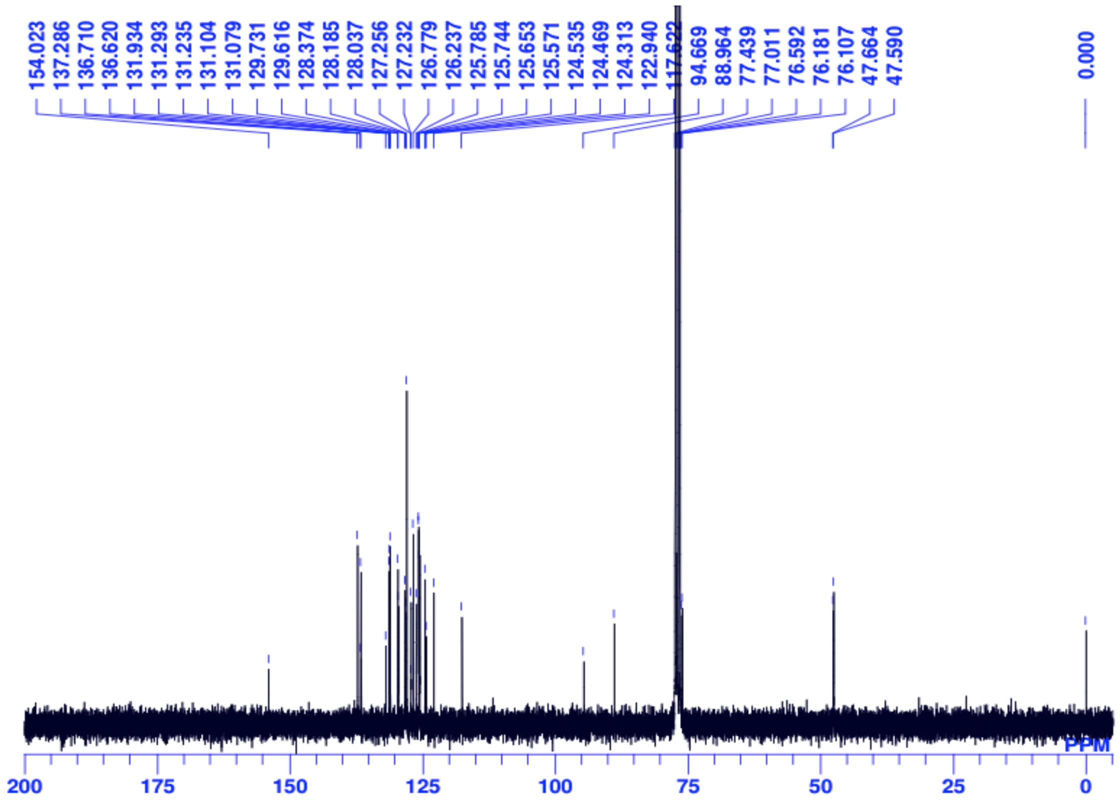
^{13}C NMR spectrum ($CDCl_3$) of **PyDK**.



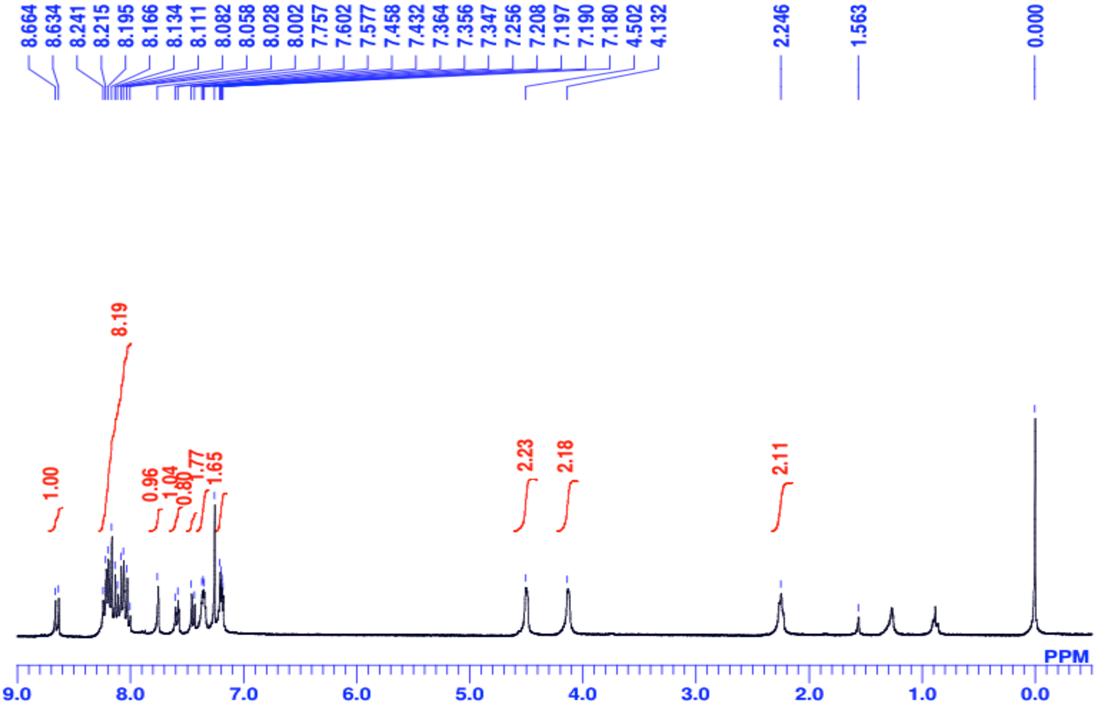
^{1}H NMR spectrum ($CDCl_3$) of **3b**.



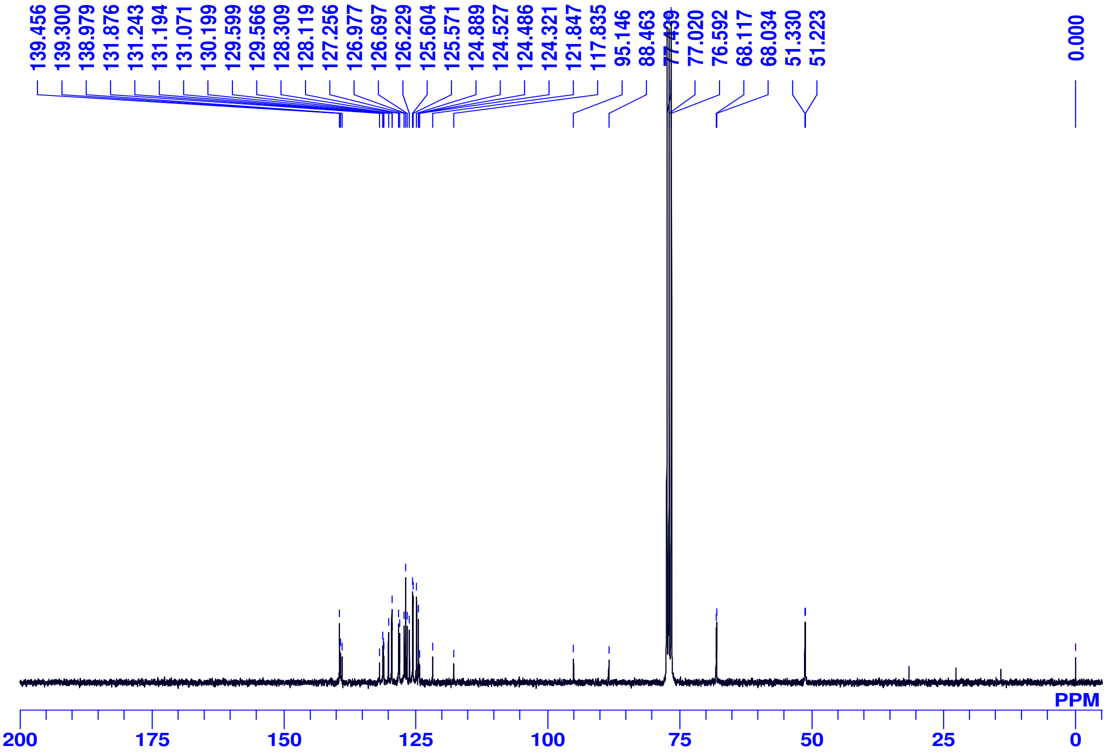
^{13}C NMR spectrum ($CDCl_3$) of **3b**.



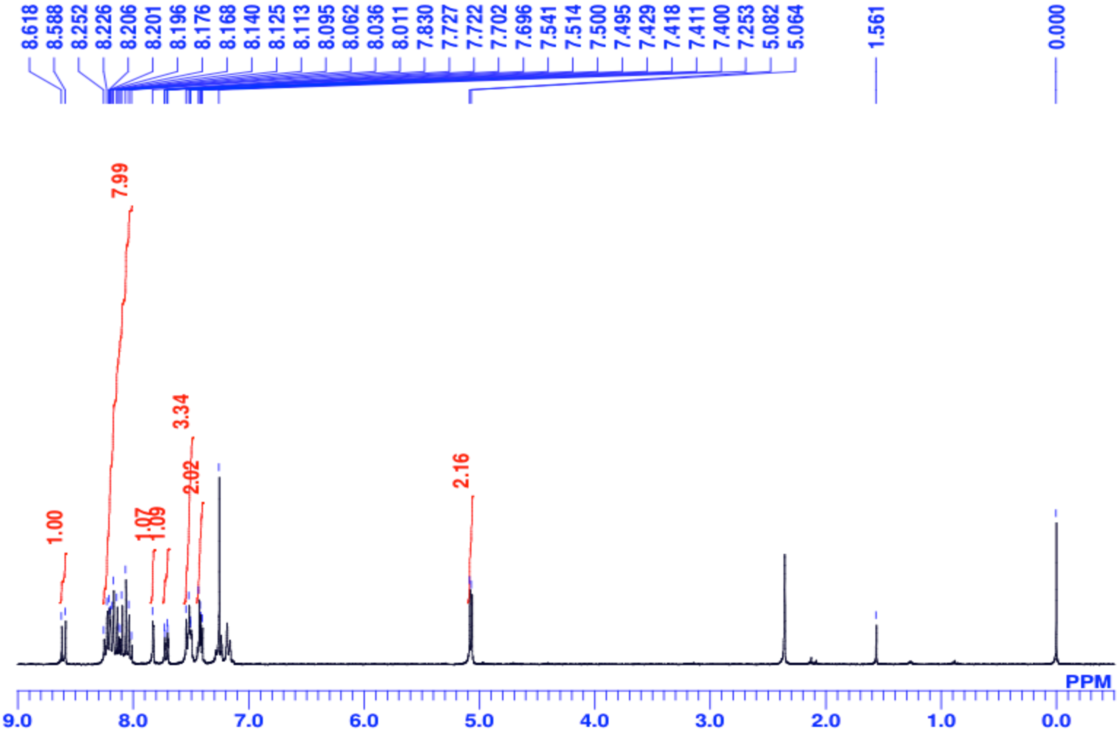
^{1}H NMR spectrum ($CDCl_3$) of **4b**.



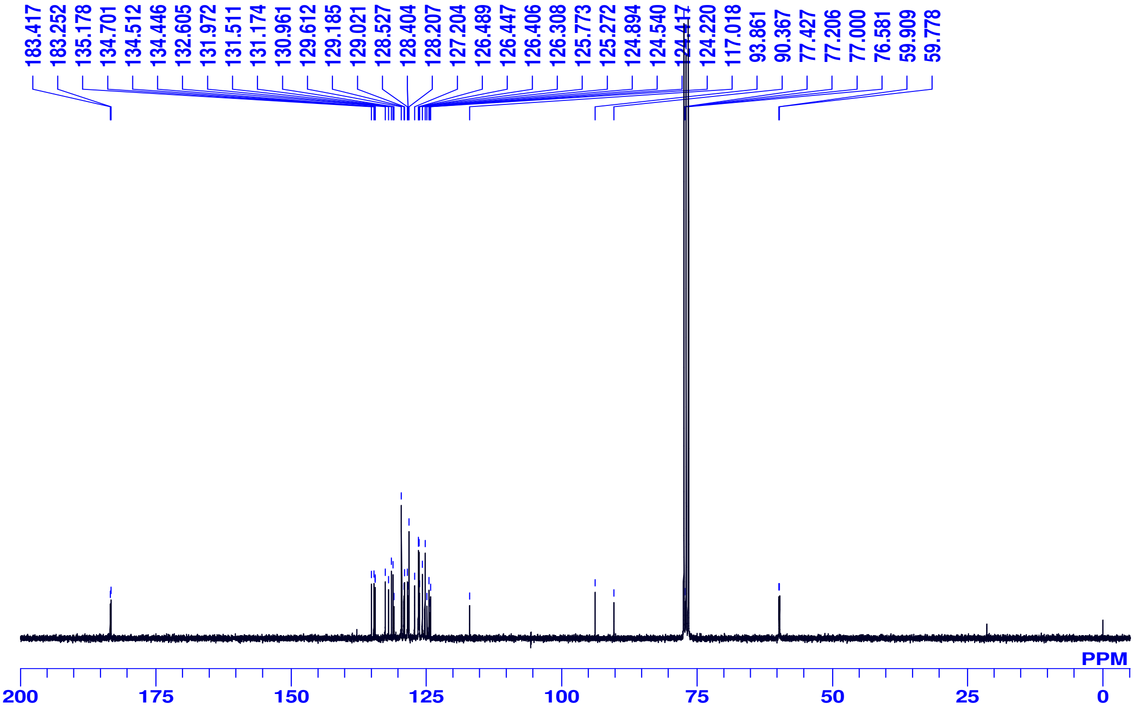
^{13}C NMR spectrum ($CDCl_3$) of **4b**.



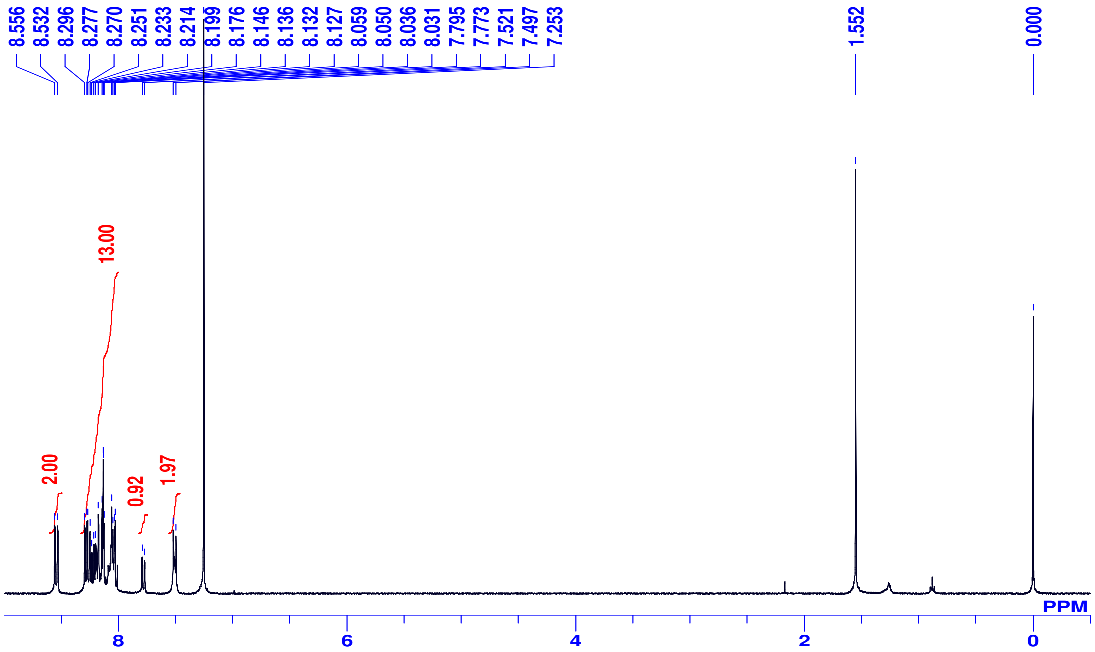
^{1}H NMR spectrum ($CDCl_3$) of **Py-3-DK**.



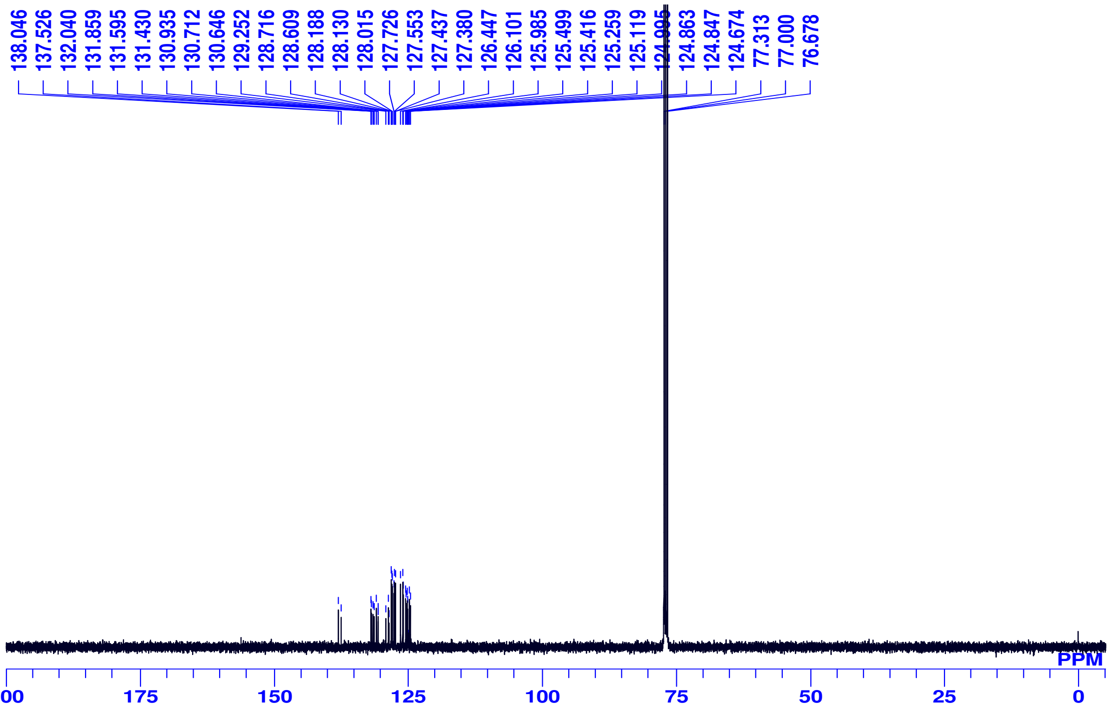
^{13}C NMR spectrum ($CDCl_3$) of **Py-3-DK**.



^{1}H NMR spectrum ($CDCl_3$) of **PyAnt**.



^{13}C NMR spectrum ($CDCl_3$) of **PyAnt**.



^{1}H NMR spectrum ($CDCl_3$) of **Py-3-Ant**.