Electronic Supplementary Information

for

New Solvatochromic Probes: Performance Enhancement via Regulation of Excited State Structures

Huijing Liu[a,b], Xiaojie Xu[a,c], Haonan Peng[a,c], Xingmao Chang[a,b], Xuwei Fu[a,c], Qianshu Li[c], Shiwei Yin[c*], Gary J. Blanchard[d]* Yu Fang[a,c*]

[a] Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education),

[b] School of Materials Science and Engineering,

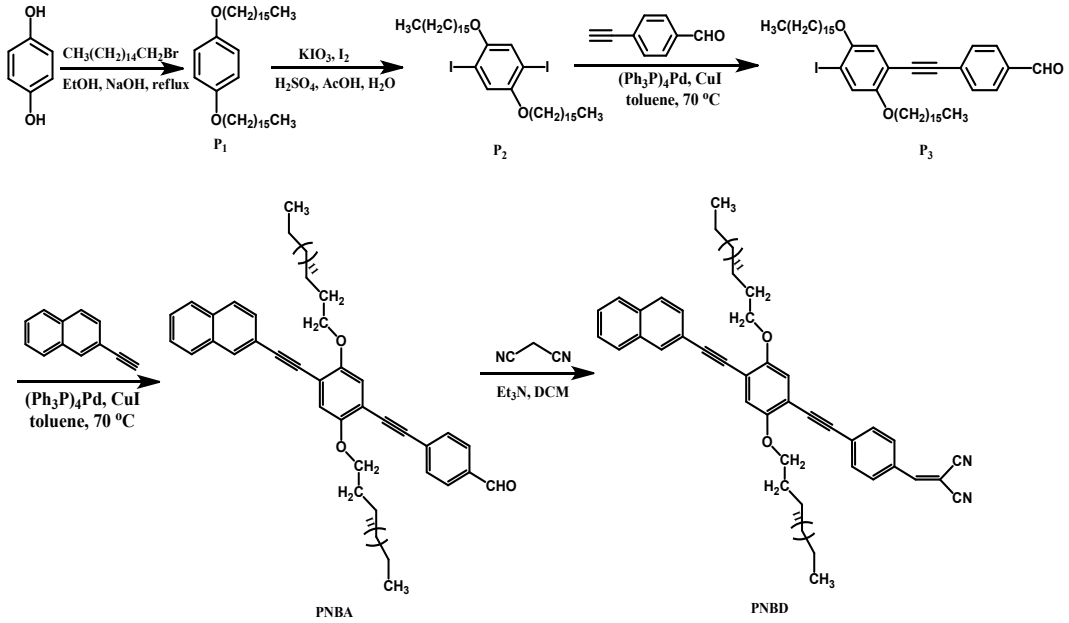
[c] School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi' an 710062, P. R. China

[d] Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States

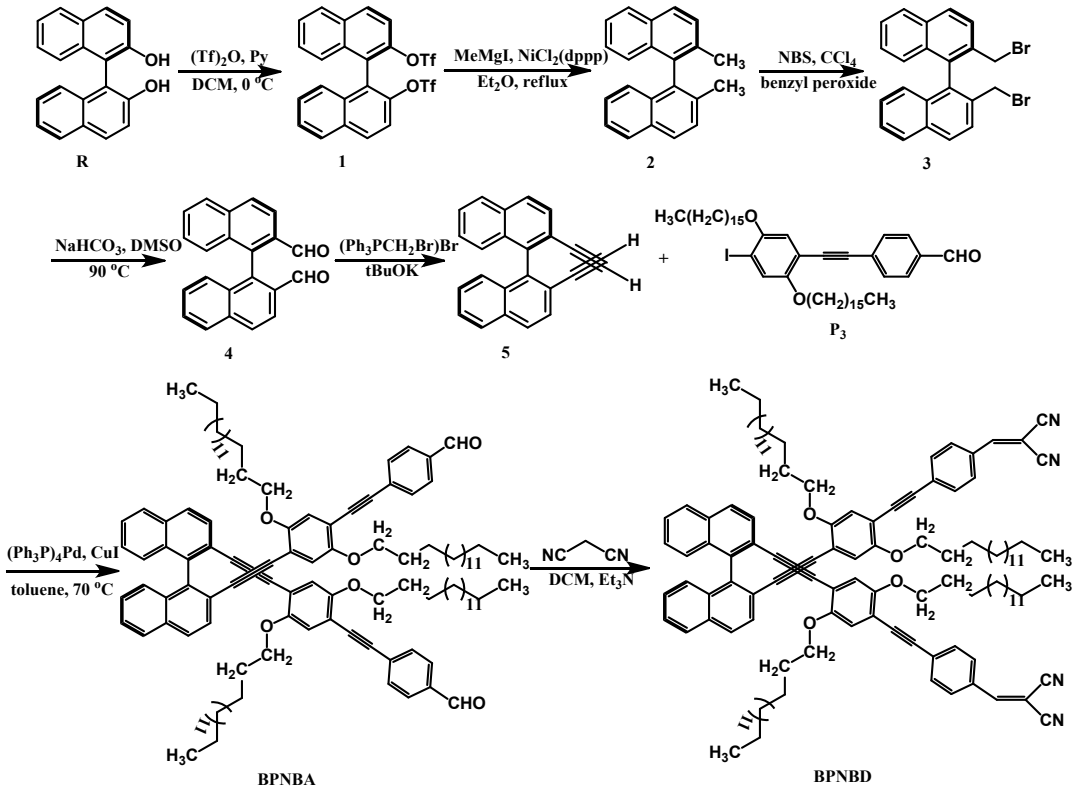
CONTENS

* Corresponding author, E-mail: yfang@snnu.edu.cn (Yu Fang); Tel: 0086-29-81530786; Fax: 0086-29-81530787.

1. Supplementary Schemes and Figures



Scheme S1 The synthesis route of PNBD



Scheme S2 The synthesis route of BPNBD

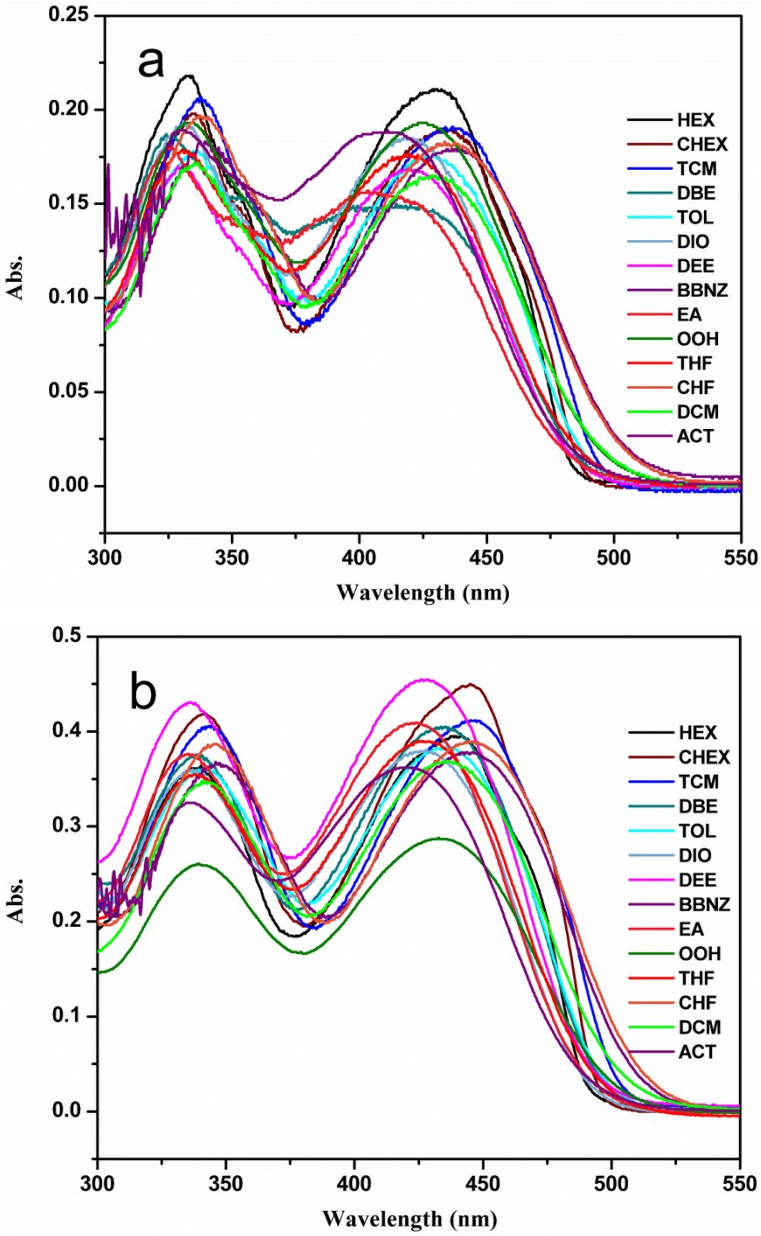


Figure S1 UV-vis absorptions of PNBD (a) and BPNBD (b) in different solvents (HEX: hexane, CHEX: cyclohexane, TCM: carbon tetrachloride, DBE: *n*- dibutyl ether, TOL: toluene, DIO: dioxane, DEE: diethyl ether, BBNZ: bromobenzene, EA: ethylacetate, OOH: *o*-octanol, THF, CHF: chloroform, DCM: dichloromethane and ACT: acetone) at a concentration of 5.0×10^{-6} mol/L.

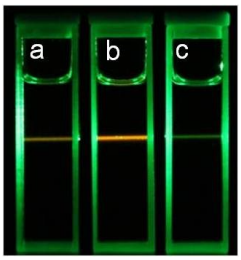


Figure S2 Tyndall test of the compound in *n*-octanol at a concentration of 5.0×10^{-6} mol/L.

Note: a-PNBD, b-BPNBD, c-blank

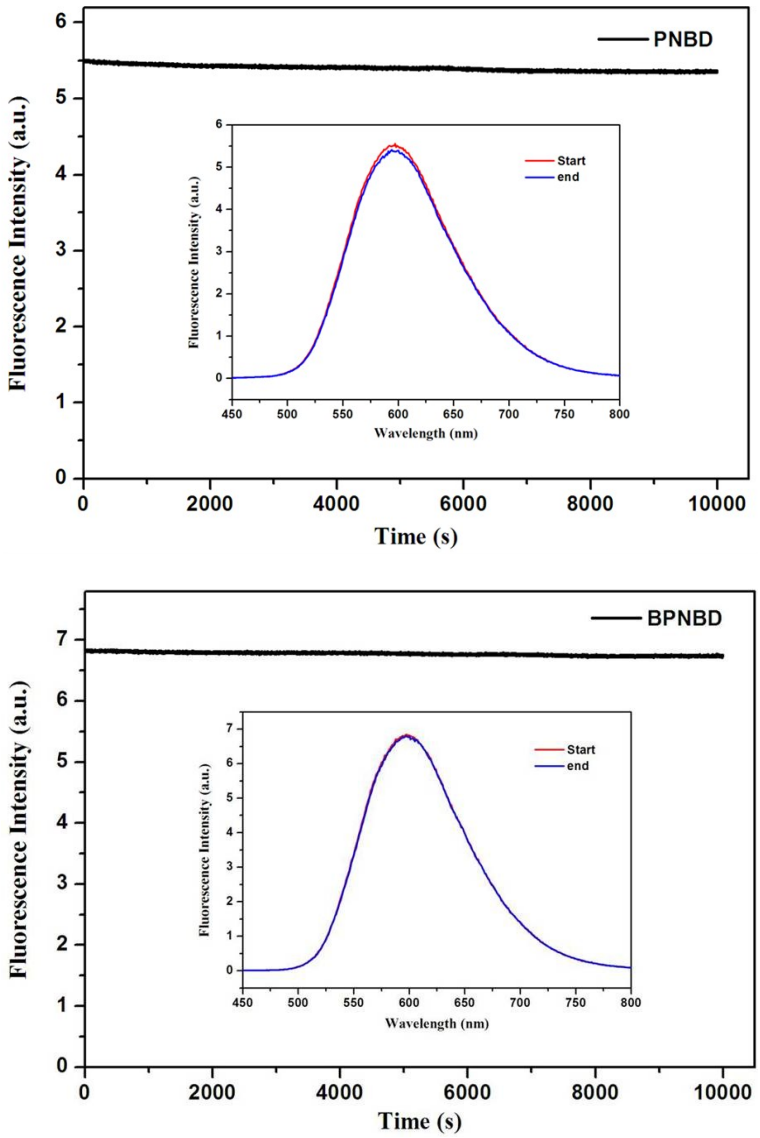
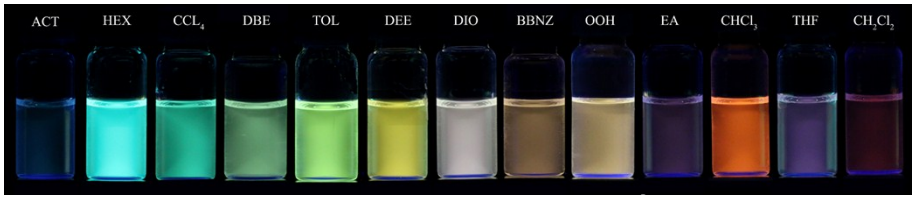


Figure S3 Photochemical stability of PNBD and BPNBD in $CHCl_3$ at a concentration of 5.0×10^{-6} mol/L，of which the emissions were monitored at the maximum emission wavelengths of them with 430 nm as the excitation wavelength. The insets of the two Figures are the emission spectra of the two investigated fluorophores recorded before and after the illumination.

PNBD



BPNBD

Figure S4 The fluorescence images of PNBD and BPNBD in fourteen different solvents.

Note: ACT: acetone, HEX: hexane, DBE: *n*- dibutyl ether, TOL: toluene, DEE: diethyl ether, DIO: dioxane, BBNZ: bromobenzene, OOH: *o*-octanol, EA: ethylacetate, and THF: tetrahydrofuran.

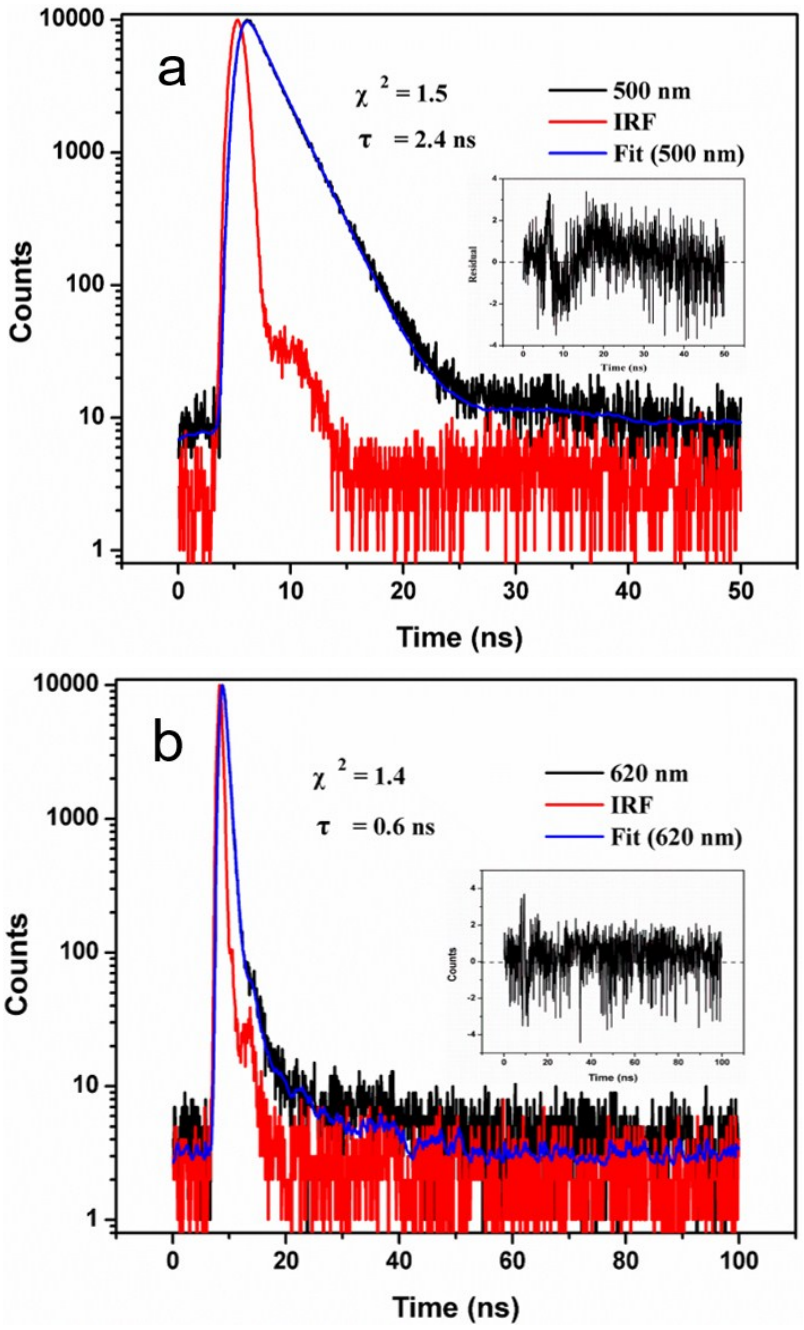


Figure S5 Fluorescence decays of PNBD in CH_2Cl_2 monitored at a concentration of 5.0×10^{-6} mol/L with 405 nm as the excitation wavelength and 500 and 620 nm as the monitoring wavelength, respectively.

Note: With reference to the two decays and the fitting results shown in the insets of the figures, it is clearly seen: 1) the two decays could roughly be fitted with a mono-exponential function as evidenced by the relatively close to 1 of the χ^2 values and the randomly distributed residue distributions, suggesting that each of the decays originates from only one component; 2) the excited state of PNBD with higher energy possesses longer lifetime (~2.4 ns), in accordance with the theoretical expectation; 3) the excited state of PNBD with lower energy possesses shorter lifetime (~0.6 ns), also in accordance with the theoretical expectation.

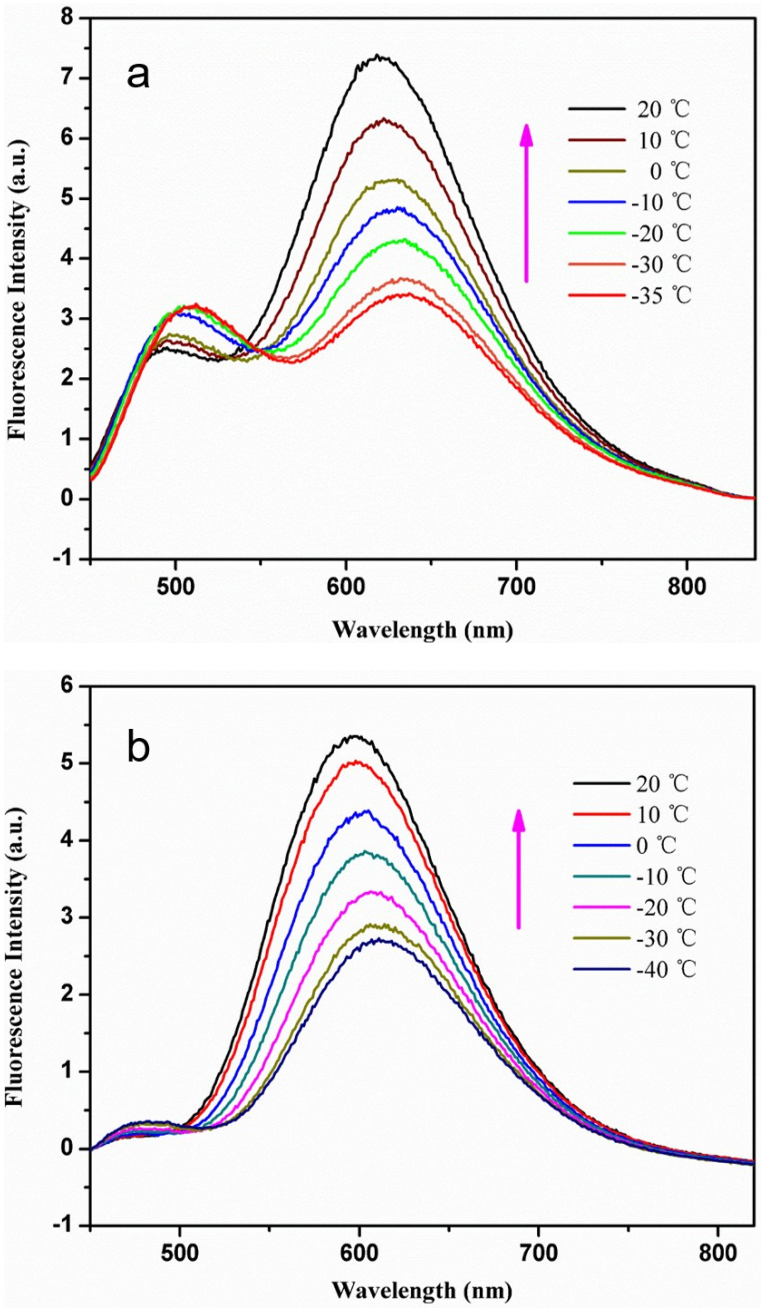


Figure S6 Temperature-dependent fluorescence emission of PNBD in CH_2Cl_2 (a) and ethyl-acetate (b) recorded at a concentration of 5.0×10^{-6} mol/L (λ_{ex}= 430 nm)

Note: With reference to the profiles of the spectra, it is seen that emission from S_3 state is inhibited upon increasing temperature, possibly due to enhanced radiationless transition to lower excited state and even ground.

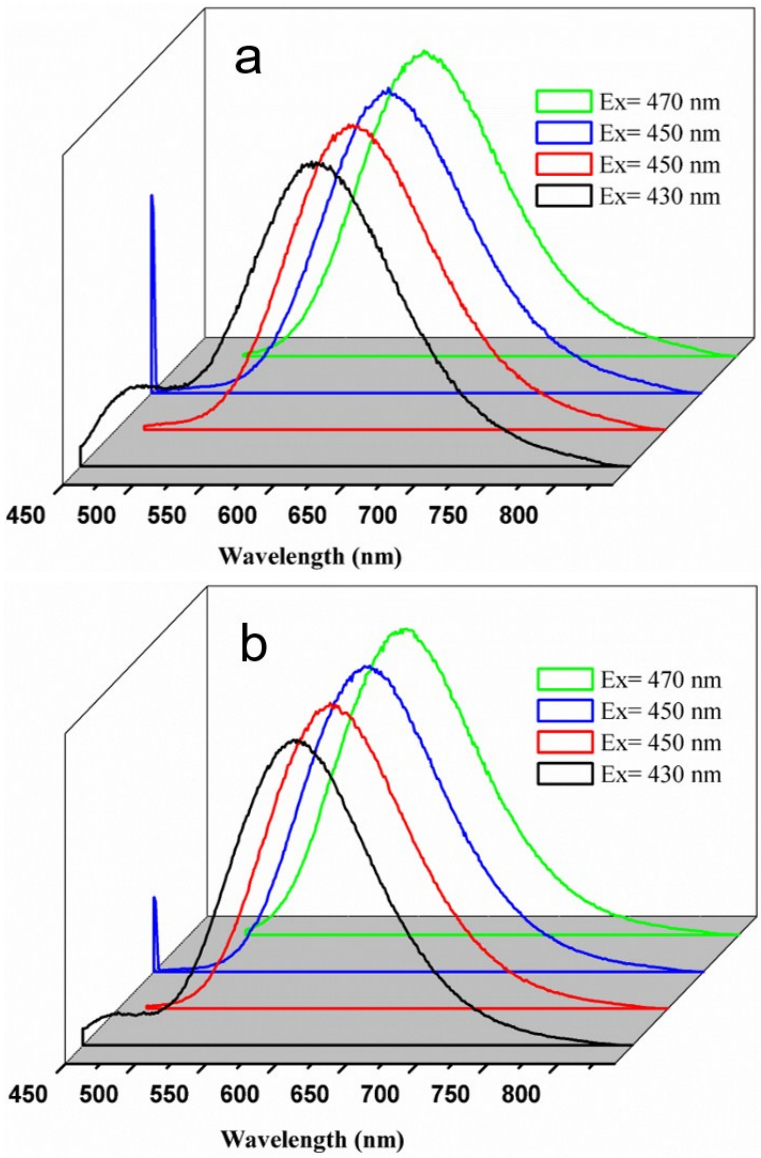


Figure S7 Fluorescence emission spectra of PNBD in CH_2Cl_2 (a) and THF (b) recorded at a concentration of 5.0×10^{-6} mol/L with different excitation wavelengths.

Note: Dual fluorescence could not be observed when a longer wavelength was adopted as the excitation wavelength due to absence of S_3 state.

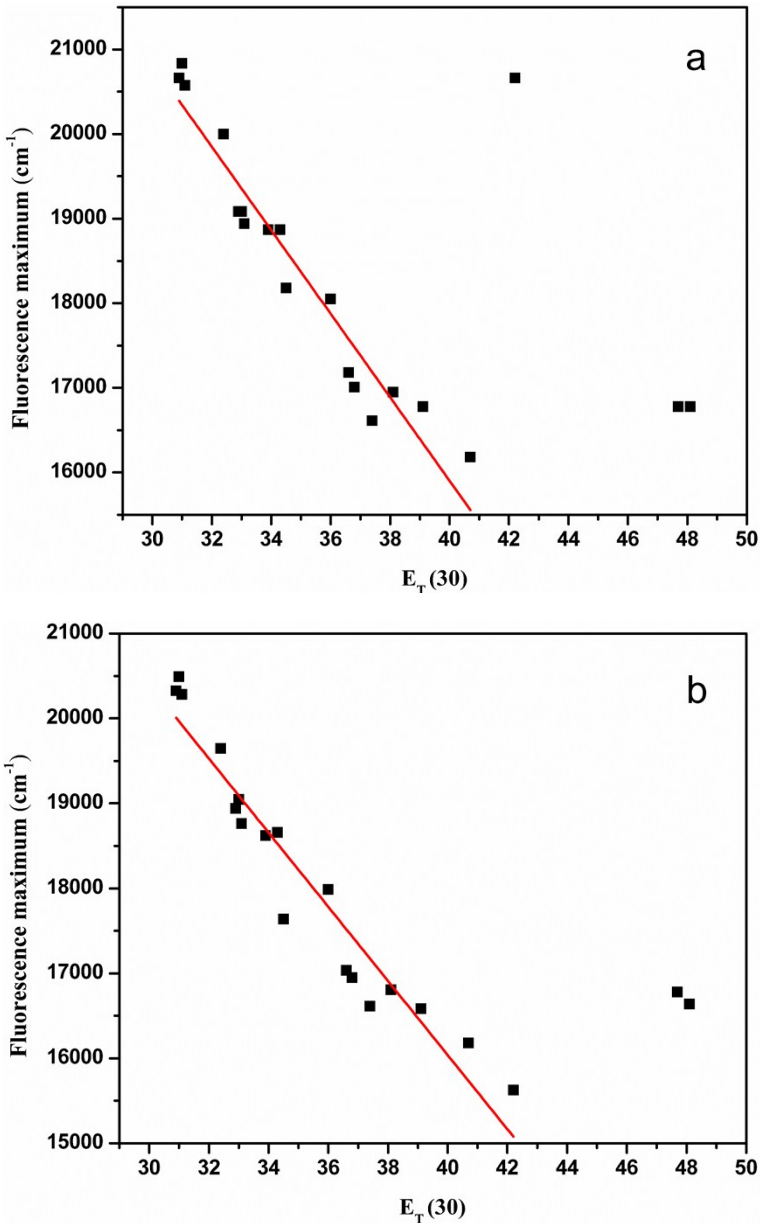


Figure S8 Plots of the wave numbers of the maximum fluorescence emissions of PNBD (a) and BPNBD (b) in different solvents *vs* the polarity indexes $E_T(30)$ of the corresponding solvents, of which the solvents from left to right are: cyclohexane, hexane, *n*-dodecane, CCl_4, 1,3,5-trimethylbenzene, di-*n*-butyl-ether, *p*-xylene, toluene, benzene, diethyl ether, 1,4-dioxane, bromobenzene, chlorobenzene, THF, EA, $CHCl_3$, CH_2Cl_2, acetone, *n* -decanol, *n*-octanol.

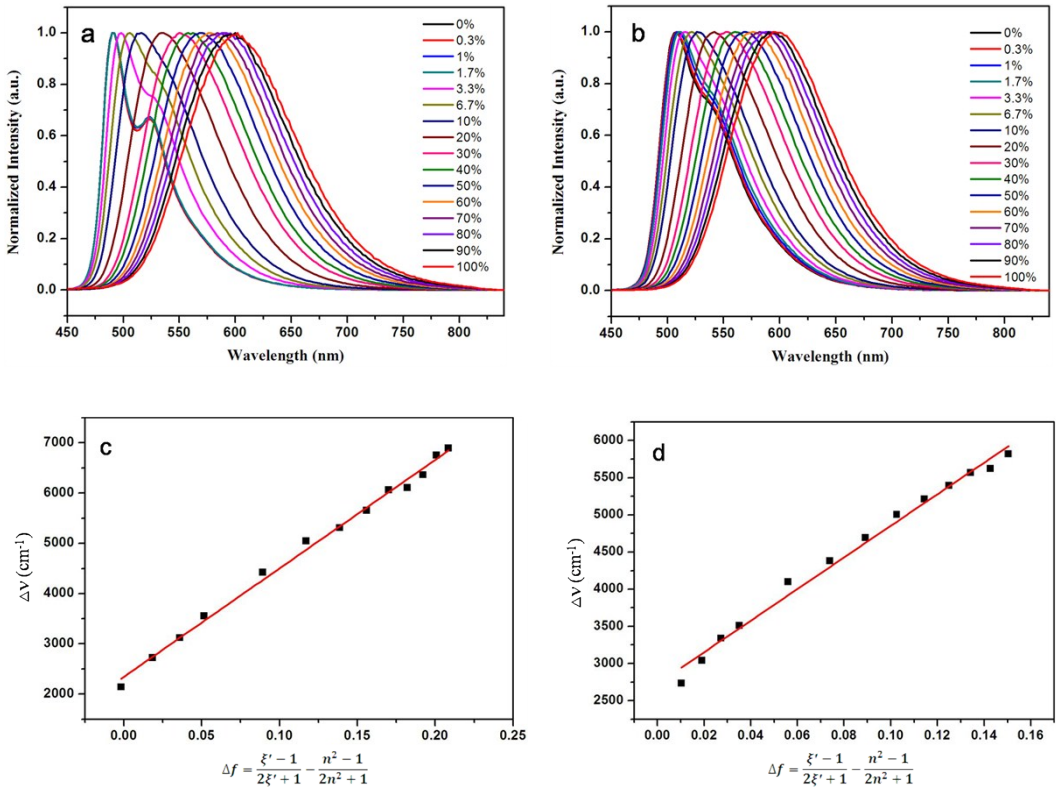


Figure S9 Fluorescence emission spectra of BPNBD in cyclohexane-THF (a), or CCl_4-$CHCl_3$ (b) of different rations at a concentration of 5.0×10^{-6} mol/L, of which both excitation wavelengths are 430 nm. Lippert plots for BPNBD in the two sets of mixture solvents (c, d).

Table S1. Fluorescence quantum yields of PNBD in two different solvents determined with different excitation wavelength (1.0×10^{-6} mol/L)

Solvent	λ_{EX} (430 nm)	λ_{EX} (460 nm)	λ_{EX} (490 nm)
1,4-Dioxane	0.50	0.64	0.75
n-Octanol	0.35	0.40	0.43

2. Experiment section

Synthesis of P_1. To a solution of 1-bromo-*n*-hexadecane (45 g, 147.4 mmol) in ethanol (75 mL) was added a mixture of 1,4-dihydroxybenzene (5.41 g, 49 mmol), NaOH (4.32 g, 108.2 mmol) and ethanol (105 mL). The reaction mixture was heated to reflux for 4 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 and the residue was removed by filtration. The solution was washed with water and the organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo. The crude sample was passed through a silica gel plug (PE/DCM = 1/10) to afford compound P_1 as white solid (17.9 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.81 (s, 4H), 3.89 (t, 4H, J = 6.6 Hz), 1.75 (m, 4H), 1.43 (m, 4H), 1.34-1.26 (m, 48H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 153.22, 115.41, 68.69, 29.69, 29.66, 29.60, 29.58, 29.42, 29.36, 26.07, 22.69, 14.10.

Synthesis of P_2. A mixture of compound P_1 (17.9 g, 31.9 mmol), potassium iodate (4.1 g, 19.1 mmol), iodine (8.6 g, 33.8 mmol), acetic acid (131.7 mL), sulfuric acid (4.1 mL), and water (8.5 mL) was stirred at 80 °C for 4 h. After cooling to room temperature, the excess iodine was destroyed with an aqueous sodium sulfite solution (10%), and then the mixture was poured into ice water. The aqueous layer was extracted with chloroform, and the combined organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo. The residue was chromatographed (PE/DCM = 5/1) to afford compound P_2 as white solid (20.7 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.17 (s, 2H), 3.93 (m, 4H), 1.79 (m, 4H), 1.49 (m, 4H), 1.26 (m, 24H), 0.88 (t, 6H, J = 6.6, 7.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 152.95, 122.90, 86.37, 70.44, 31.96, 29.73, 29.69, 29.61, 29.59, 29.39, 29.31, 29.20, 26.07, 22.72.

Synthesis of P_3. To a solution of diisopropylamine in toluene was added compound P_2 (790 mg, 0.97 mmol), 4-ethynylbenzaldehyde (48 mg, 0.37 mmol), $Pd(Ph_3P)_4$ (21.2 mg, 0.018 mmol) and CuI (3.5 mg, 0.018 mmol). The mixture was stirred at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (100 mL), and then washed with water and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug

(PE/DCM = 3/1) to afford compound P_3 as pale yellow solid (110 mg, 36.7%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.02 (s, 1H), 7.86 (d, 2H, J = 12 Hz), 7.66 (d, 2H, J = 12.6 Hz), 7.33 (s, 1H), 6.91 (s, 1H), 3.98 (m, 4H), 1.81 (m, 4H), 1.48 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6H, J = 9.6, 10.8 Hz). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 191.33, 154.55, 151.84, 135.40, 132.00, 129.57, 115.99, 112.72, 93.26, 89.88, 88.79, 70.20, 69.87, 29.71, 29.58, 29.39, 29.37, 29.32, 29.30, 29.19, 26.09, 26.05, 22.70, 14.12.

Synthesis of PNBA. A 25 mL flask was charged with naphthylene-2-acetylene (20 mg, 0.13 mmol), P_3 (0.1 g, 0.12 mmol), $Pd(Ph_3P)_4$ (8.5 mg, 0.074 mmol), CuI (3.4 mg, 0.018 mmol), diisopropyl-amine (3 mL) and toluene (7 mL). The reaction mixture was stirred at 75 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (100 mL), and then washed with water and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug (PE/DCM = 2/1) to afford compound PNBA (92 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.02 (s, 1H), 8.06 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.82 (t, J = 18, 10.2 Hz, 3H), 7.68 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 8.4, 1.2Hz, 1H), 7.50 (m, 2H), 7.07 (s, 1H), 7.04 (s, 1H), 4.07 (m, 4H), 1.88 (m, 4H), 1.58 (m, 4H), 1.40 (m, 4H), 1.34-1.21 (m, 44H), 0.88 (t, J = 13.8, 7.2 Hz, 6H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 191.35, 154.03, 153.77, 135.44, 131.51, 129.60, 128.03, 127.82, 126.59, 120.73, 117.13, 116.94, 115.12, 113.11, 95.83, 93.94, 90.36, 86.28, 69.83, 69.67, 29.73, 29.69, 29.66, 29.54, 29.45, 29.39, 26.20, 26.13, 22.71, 14.13. MS (MALDI-TOF): (m/z) calcd for ($C_{59}H_{80}O_3$), 836.61, found: 836.38.

Synthesis of PNBD. To a solution of compound PNBA (72 mg, 0.086 mmol) in dichloromethane was added triethylamine (12 μL, 0.086 mmol) and malononitrile (6.2 mg, 0.094 mmol). The reaction mixture was stirred at room temperature for 2 h and then removed the solvent under vacuum. The crud product was passed through a silica gel plug (PE/DCM = 2/1) to afford compound PNBD (60 mg, 84%) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.81 (m, 3H), 7.72 (s, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 9.6 Hz, 1H), 7.50 (m, 2H), 7.08 (s, 1H), 7.04 (s, 1H), 4.06 (m, 4H), 1.88 (m, 4H), 1.59 (m, 4H), 1.40 (m, 4H),

1.34-1.21 (m, 44H), 0.88 (t, J = 14.4 Hz, 6H). ^{3}C NMR (600 MHz, $CDCl_3$) δ (ppm) 158.42, 154.12, 153.69, 133.03, 132.91, 132.34, 131.52, 130.68, 130.28, 130.10, 128.35, 128.01, 127.81, 127.80, 126.77, 126.59, 120.61, 117.70, 116.76, 115.49, 113.76, 112.63 112.60, 96.08, 93.82, 92.17, 86.60, 82.53, 69.76, 69.54, 31.93, 29.71, 29.67, 29.64, 29.52, 29.42, 29.40, 29.31, 26.18, 26.07, 22.70, 14.12. MS (MALDI-TOF): (m/z) calcd for ($C_{59}H_{80}O_3$), MS (MALDI-TOF): (m/z) calcd for ($C_{124}H_{158}N_4O_4$), 884.62, found: 884.70.

Synthesis of (R)-2,2'-bistriflate-1,1'-binaphthyl (1). To a solution of (R)-BINOL (11.53 g, 40.3 mmol) in 120 mL dichloromethane was added pyridine (13.4 mL) and followed by dropwise addition of triflic anhydride (14.9 mL, 88.6 mmol) at 0 °C. The mixture was stirred at room temperature overnight. After removal of the solvent, the residue was diluted with EtOAc (300 mL) and then washed with 5% aqueous HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug (with PE/EA = 30/1) to give the (R)-bistriflate (19.95 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.14 (d, 2H, J = 9.6 Hz), 8.01 (d, 2H, J = 8.4 Hz), 7.60 (m, 4H), 7.41 (m, 2H), 7.25 (m, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 145.42, 133.19, 132.39, 131.99, 128.37, 128.00, 127.34, 126.77, 123.47, 119.34.

Synthesis of (R)-2,2'-dimethyl-1,1'-binaphthyl (2). Under nitrogen, a solution of MeI (11.3 mL, 181.7 mmol) in diethyl ether was added dropwise to a stirred suspension of Mg turnings (4.86 g, 199.8 mmol) and a little of iodine, and the solution was gently refluxed throughout the addition. The mixture was cooled to room temperature which was added dropwise to a solution of (R)-bistriflate (10 g, 18.2 mmol) in diethyl ether and $NiCl_2$(dppp) (492.4 mg, 0.9 mmol). The reaction mixture was heated to boiling and then refluxed for 24 h. The reaction was quenched by addition of saturated NH_4Cl slowly at 0 °C. The aqueous layer was extracted with ether. The combined organic layer was washed with saturated $NaHCO_3$, dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug (pure petroleum ether) to afford (R)-2,2'-dimethyl-1,1'-binaphthyl as a white solid (4.36 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.89 ~ 7.86 (m, 4H), 7.50 (d, 2H, J = 8.4

Hz), 7.37 (m, 2H), 7.19 (m, 2H), 7.04 (d, 2H, J = 8.4 Hz), 2.03 (s, 6H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 135.18, 134.32, 132.81, 132.27, 128.77, 127.97, 127.48, 126.13, 125.69, 124.94, 20.08.

Synthesis of (R)-2,2'-bis(bromomethyl-1,1'-binaphthyl (3). Under nitrogen (R)-2,2'-dimethyl-1,1'-binaphthyl (1.06 g, 3.8 mmol), *N*-bromosucc-inimde (1.47 g, 8.3 mmol) and benzyl peroxide (91.2 mg, 0.038 mmol) were stirred in CCl_4 (10 mL). The reaction mixture was heated to boiling and refluxed for 6 h. After cooling, CCl_4 was removed under vacuum and the residue was dissolved with EtOAc (100 mL). The resultant organic solution was washed with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude sample was used for the following reaction without further purification.

Synthesis of (R)-2,2'-diformyl-1,1'-binaphthyl (4). To a solution of the crude product of the former step in DMSO was added $NaHCO_3$ (1.9 g, 11.9 mmol). The reaction mixture was heated to 90 °C for 6 h. The mixture was cooled to room temperature before additional diethyl ether (150 mL) was added. This ether solution was washed with water and brine, dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug (PE/EA = 10/1) to afford (R)-2,2'- diformyl-1,1'-binaphthyl (0.48 g, 42%) (42% overall yield via 2 steps from (R)-2,2'-dimethyl-1,1'-binaphthyl. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.63 (s, 2H, -CHO), 8.21 (d, 2H, J = 8.4 Hz), 8.13 (d, 2H, J = 9.0 Hz), 8.02 (d, 2H, 7.8 Hz), 7.63 (m, 2H), 7.38 (m, 2H), 7.24 (d, 2H, J = 8.4 Hz). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 191.05, 139.64, 135.92, 133.46, 133.24, 129.77, 129.42, 128.54, 127.90, 127.28, 122.31.

Synthesis of (R)-2,2'-diethynyl-1,1'-binaphthyl (5). A 50 mL flask was charged with bromo-methyl-triphenylphosphonium (1.76 g, 4.04 mmol) and THF (10 mL), and *t*-BuOK (904 mg, 8.06 mmol) was added at -78 °C. The mixture was stirred at this temperature for 1 h, and (R)-2,2'-dimethyl-1,1'-binaphthyl (0.5 g, 1.6 mmol) in THF was added. After being stirred at -78 °C for 30 min, the mixture was stirred at 0 °C for another 2 h, and then the reaction mixture was poured into aqueous NH_4Cl solution. After usual work-up with water/EtOAc, the combined organic layer was dried over anhydrous sodium sulfate and evaporated in vacuum. The residue was

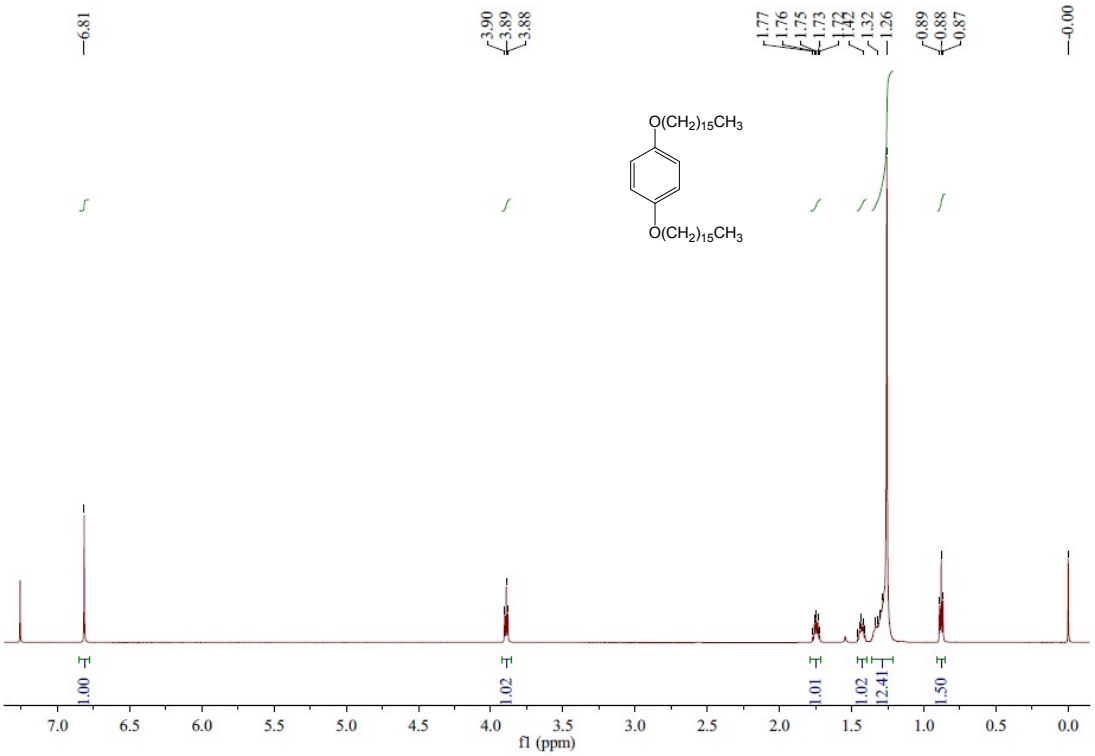
chromate-graphed (PE/EA = 20/1) to afford (R)-2,2'-diethynyl-1,1'-binaphthyl (0.2 g, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.91 (t, 2H, J = 8.4, 6.6 Hz), 7.72 (d, 2H, J = 9.0 Hz), 7.48 (m, 2H), 7.28 (m, 2H), 7.14 (d, 2H, J = 8.4 Hz), 2.78 (s, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 140.41, 133.17, 132.38, 128.94, 128.13, 128.07, 126.89, 126.76, 126.39, 120.42, 82.69, 80.66.

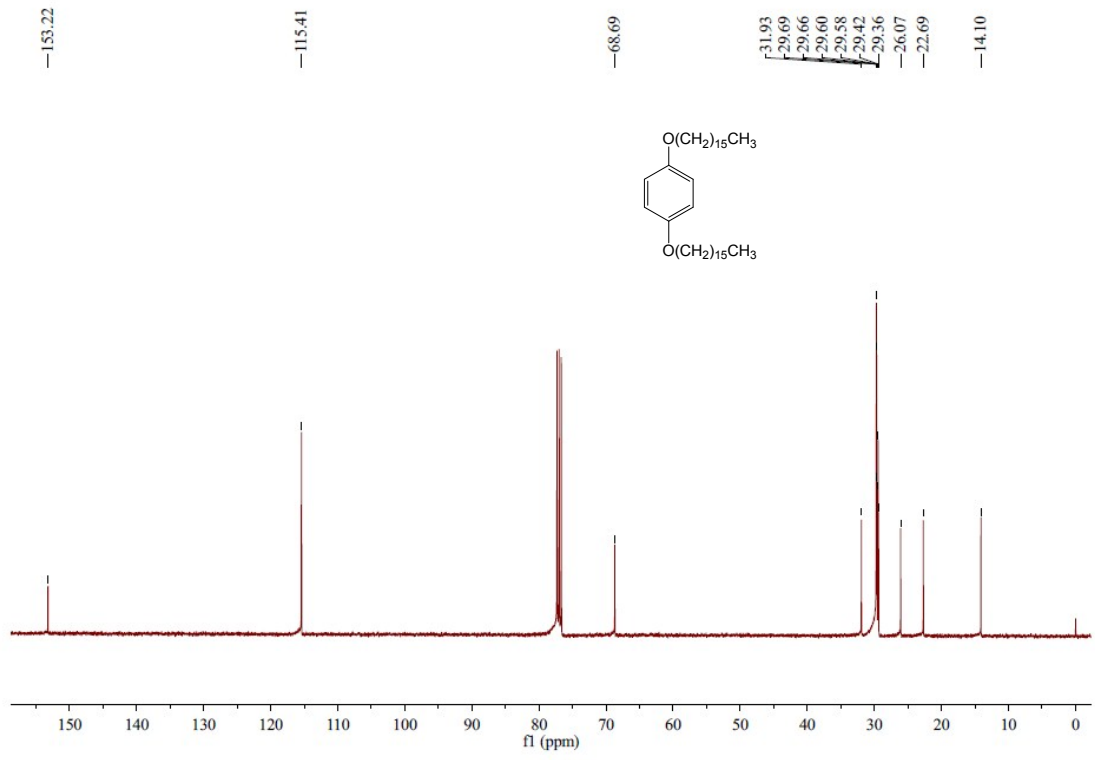
Synthesis of BPNBA. A 50 mL flask was charged with (R)-2,2'-diethynyl-1,1'-binaphthyl (93 mg, 0.31 mmol), P_3 (0.5 g, 0.62 mmol), $Pd(Ph_3P)_4$ (35.5 mg, 0.031 mmol), CuI (6 mg, 0.031 mmol), diisopropylamine (6 mL) and toluene (14 mL). The mixture was stirred at 75 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (150 mL), and then washed with water and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated and passed through a silica gel plug (PE/DCM = 1/1) to afford compound BPNBA (0.42 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.00 (s, 2H), 7.95 (d, 2H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz), 7.83 (d, 4H, J = 8.4 Hz), 7.78 (d, 2H, J = 8.4 Hz), 7.61 (d, 4H, J = 8.4 Hz), 7.49 (m, 2H), 7.40 (d, 2H, J = 8.4 Hz), 7.34 (m, 2H), 6.81 (s, 2H), 5.68 (s, 2H), 3.82 (m, 4H), 3.74 (m, 2H), 3.68 (m, 2H), 1.82 (m, 4H), 1.70 (m, 4H), 1.57 (m, 4H), 1.44 (m, 8H), 1.39-1.25 (m, 92H), 0.87 (dt, 12H, J = 9.0, 6.6, 2.4 Hz). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 191.32, 153.59, 152.70, 140.41, 131.95, 127.82, 126.65, 122.01, 117.05, 116.81, 115.04, 112.49, 95.18, 93.72, 90.54, 90.35, 69.69, 69.14, 29.75, 29.68, 29.55, 29.42, 29.38, 29.36, 29.14, 26.20, 25.95, 22.70, 14.12. MS (MALDI-TOF): (m/z) calcd for ($C_{118}H_{158}O_6$), 1671.20, found: 1671.17.

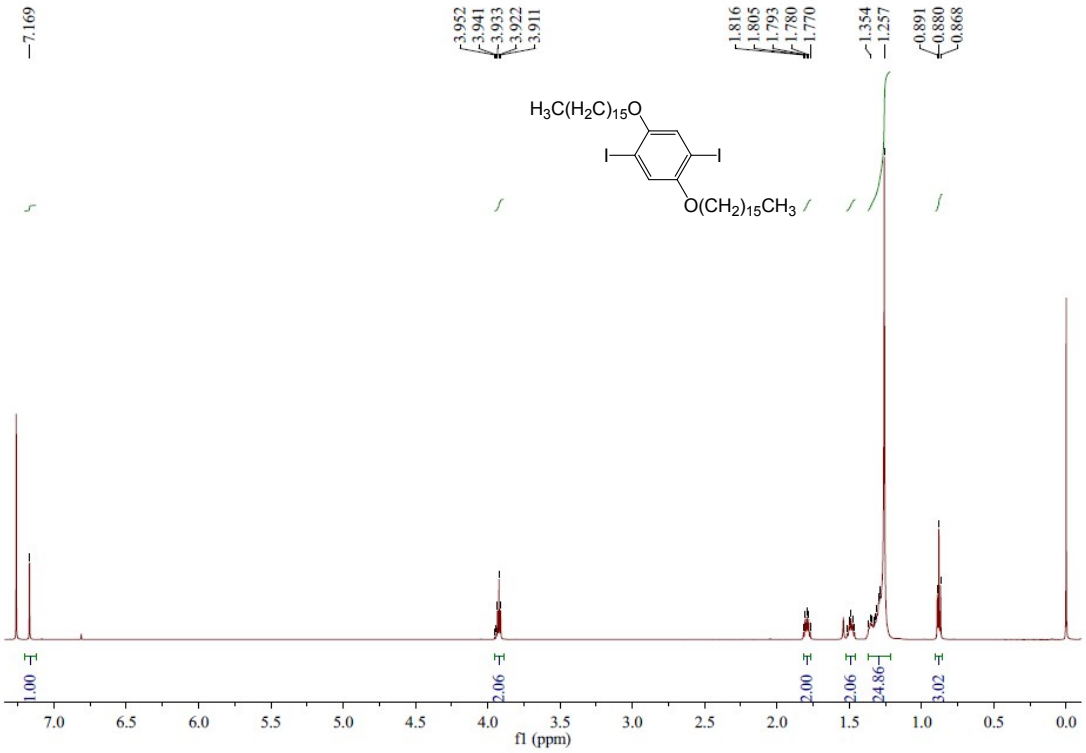
Synthesis of BPNBD. To a solution of compound BNPA (94 mg, 0.056 mmol) in dichloromethane was added triethylamine (16 μL, 0.11 mmol) and malononitrile (8.2 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for 2 h and then removed the solvent under vacuum. The crud product was passed through a silica gel plug (PE/DCM = 1/1) to afford compound BPNBD (81 mg, 84%) as an orange red foam. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.95 (d, 2H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz), 7.87 (d, 4H, J = 8.4 Hz), 7.78 (d, 2H, J = 8.4 Hz), 7.70 (s, 2H), 7.58 (d, 4H, J = 8.4 Hz), 7.49 (m, 2H), 7.40 (d, 2H, J = 8.4 Hz), 7.34 (m, 2H), 6.81 (s, 2H), 5.67 (s, 2H), 3.82 (m, 4H), 3.73 (m, 2H), 3.68 (m, 2H), 1.82 (m, 4H), 1.69 (m, 4H), 1.57 (m,

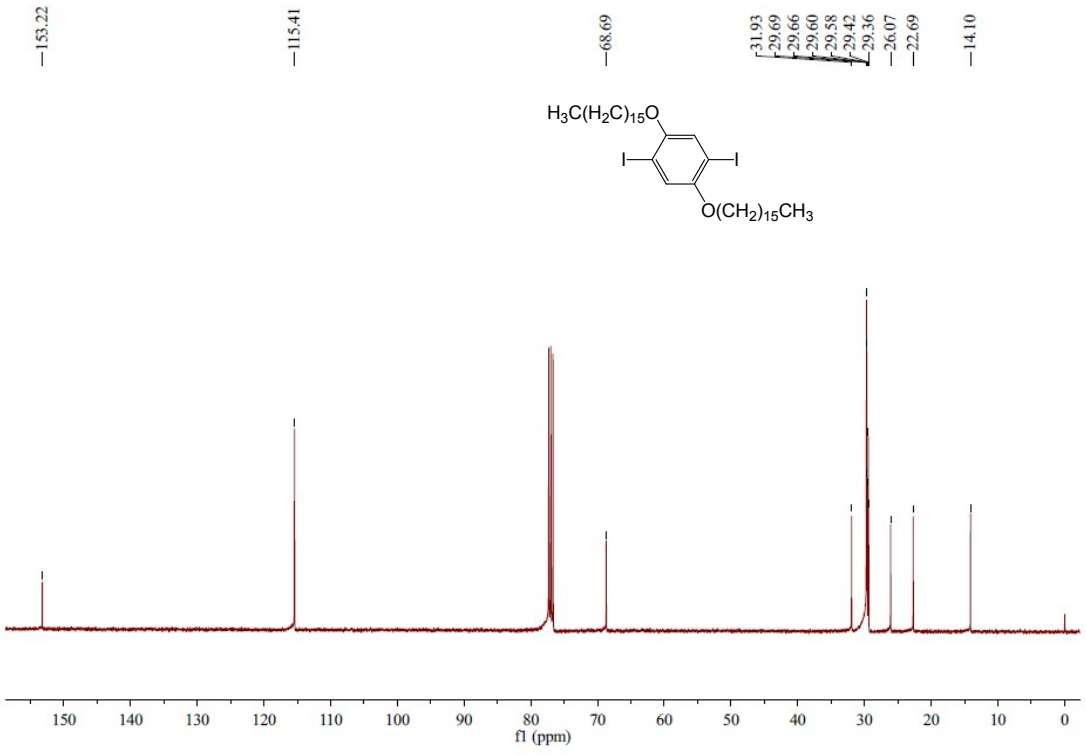
4H), 1.44 (m, 8H), 1.38-1.25 (m, 92H), 0.87 (td, 12H, J = 9.6, 6.6, 2.4 Hz). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 158.43, 153.79, 152.73, 140.50, 132.31, 130.07, 127.76, 126.73, 121.99, 117.09, 115.52, 113.79, 112.65, 112.15, 95.46, 93.69, 92.24, 90.54, 82.53, 69.75, 69.16, 31.96, 29.77, 29.71, 29.54, 29.44, 29.40, 29.35, 29.17, 25.98, 22.72, 14.14. MS (MALDI-TOF): (m/z) calcd for ($C_{124}H_{158}N_4O_4$), 1767.23, found: 1767.04.

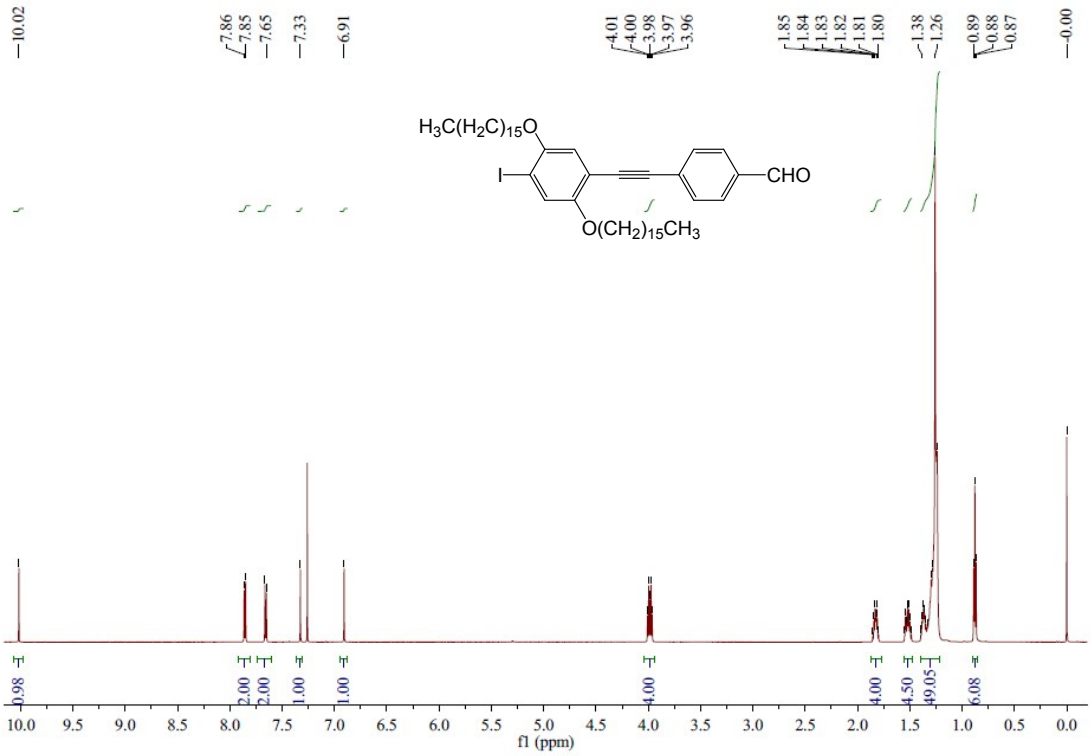
3. ^{1}H and ^{13}C NMR spectra for all compounds

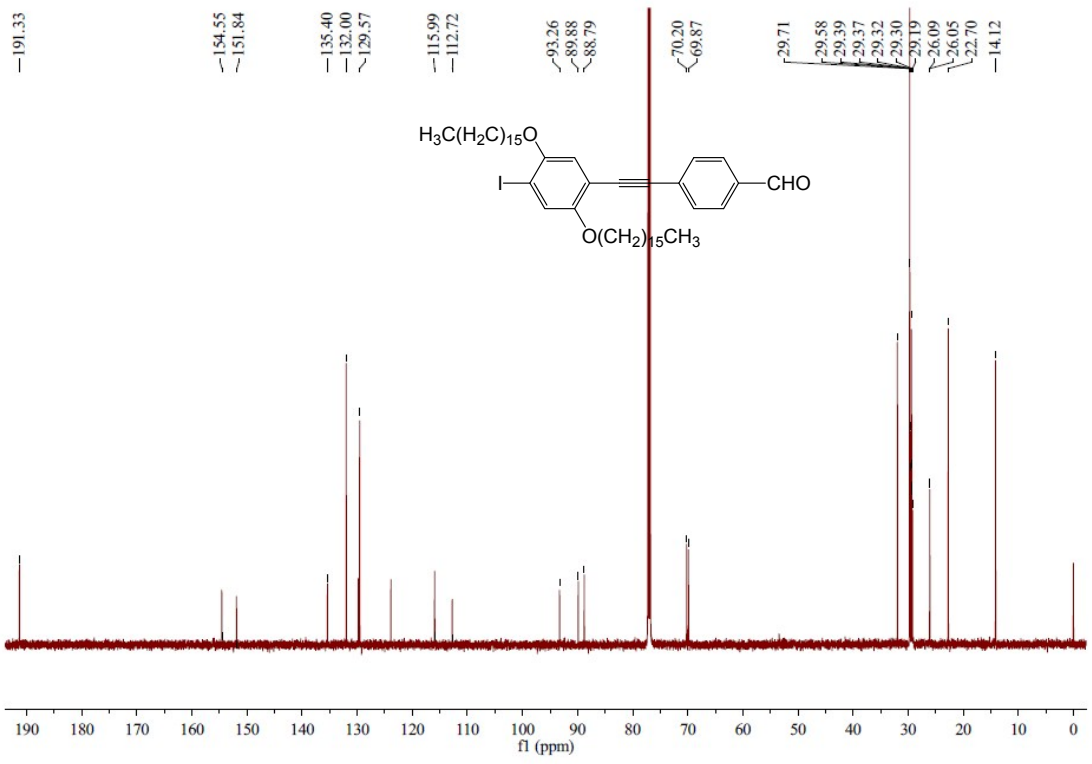

6.81
3.90
3.89
3.88
1.77
1.76
1.75
1.73
1.72
1.42
1.32
1.26
0.89
0.88
0.87
0.00
O(CH2)15CH3
O(CH2)15CH3
1.00
1.02
1.01
1.02
12.41
1.50
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

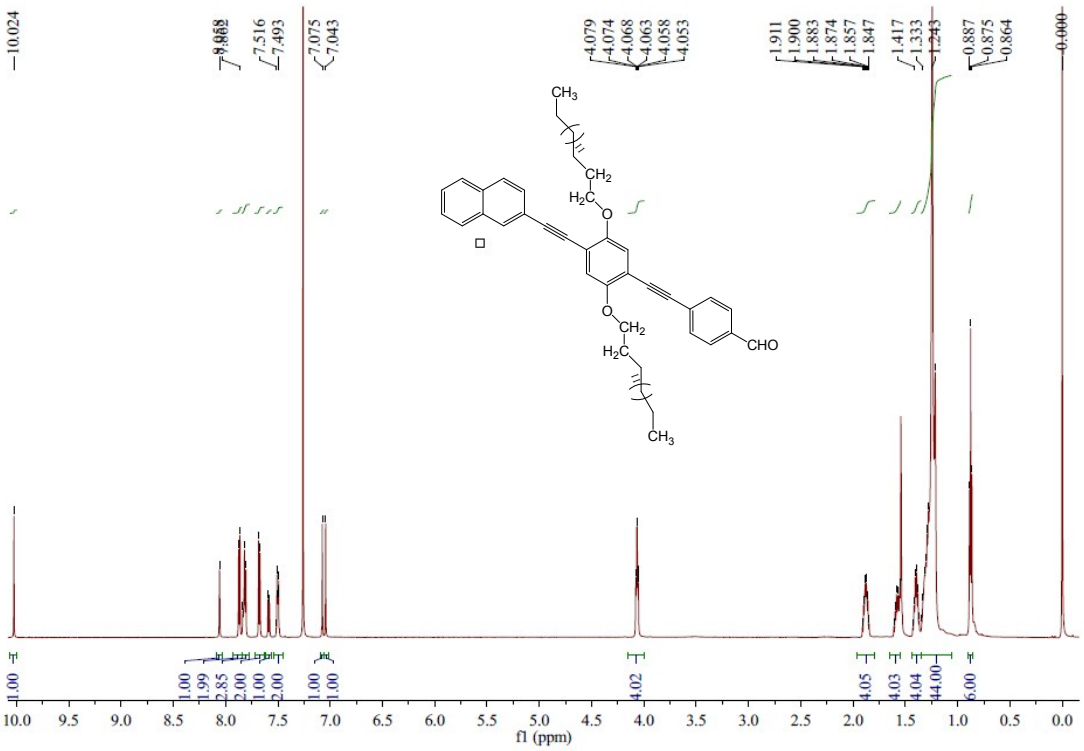

153.22
115.41
68.69
31.93
29.69
29.66
29.60
29.58
29.42
29.36
26.07
22.69
14.10
O(CH2)15CH3
O(CH2)15CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

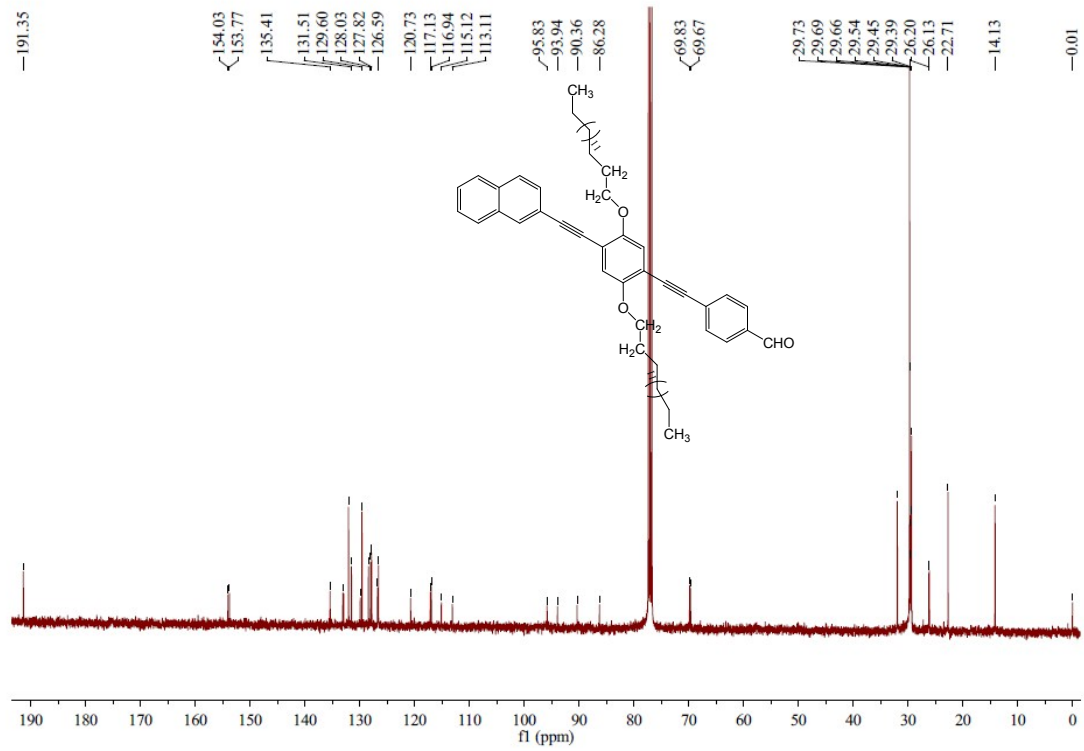

7.169
3.952
3.941
3.933
3.922
3.911
1.816
1.805
1.793
1.780
1.770
1.354
1.257
0.891
0.880
0.868
H3C(H2C)15O
I
I
O(CH2)15CH3
1.00
2.06
2.00
2.06
24.86
3.02
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

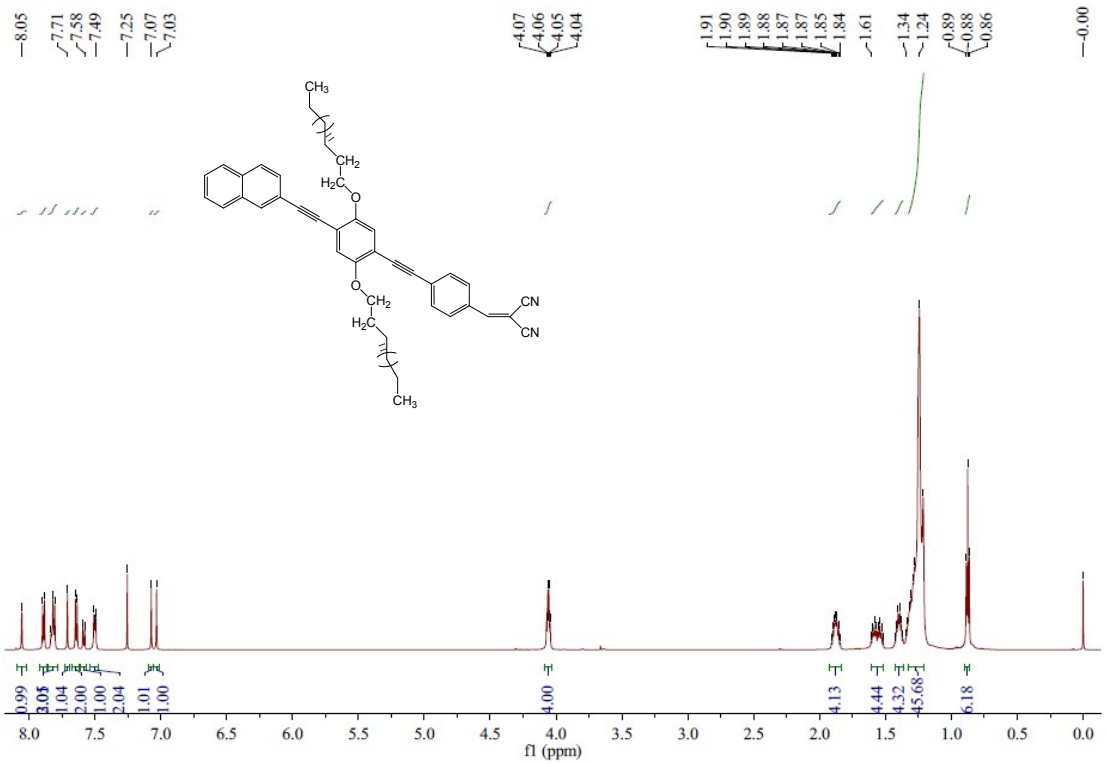

153.22
115.41
68.69
31.93
29.69
29.66
29.60
29.58
29.42
29.36
26.07
22.69
14.10
H3C(H2C)15O
I
I
O(CH2)15CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

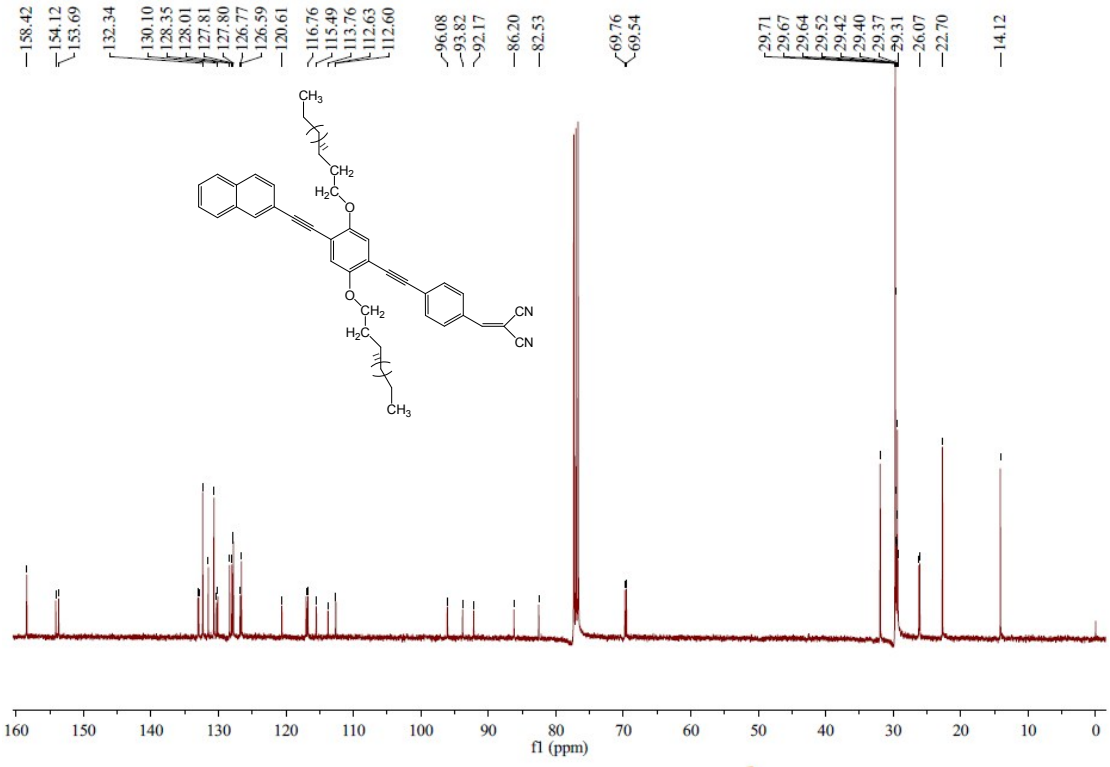

10.02
7.86
7.85
7.65
7.33
6.91
4.01
4.00
3.98
3.97
3.96
1.85
1.84
1.83
1.82
1.81
1.80
1.38
1.26
0.89
0.88
0.87
0.00
H3C(H2C)15O
I
CHO
O(CH2)15CH3
0.98
2.00
2.00
1.00
1.00
4.00
4.00
4.50
49.05
6.08
f1 (ppm)

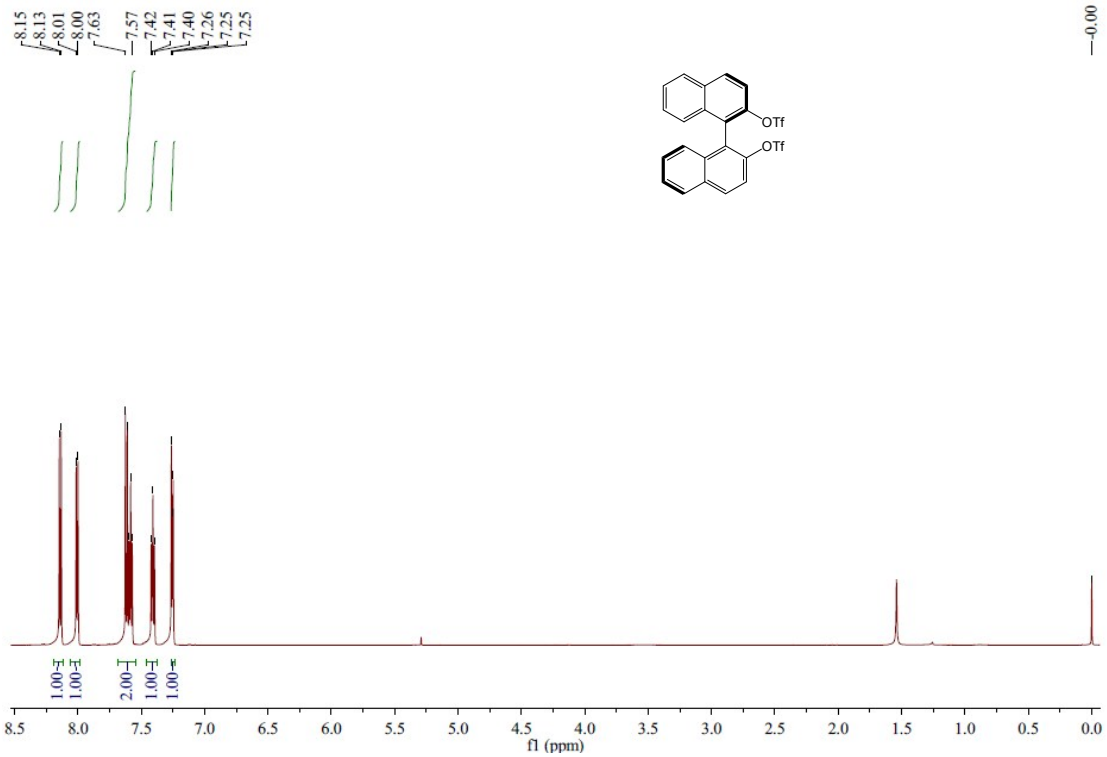

191.33
154.55
151.84
135.40
132.00
129.57
115.99
112.72
93.26
89.88
88.79
70.20
69.87
29.71
29.58
29.39
29.37
29.32
29.30
29.19
26.09
26.05
22.70
14.12
H3C(H2C)15O
I
CHO
O(CH2)15CH3
f1 (ppm)

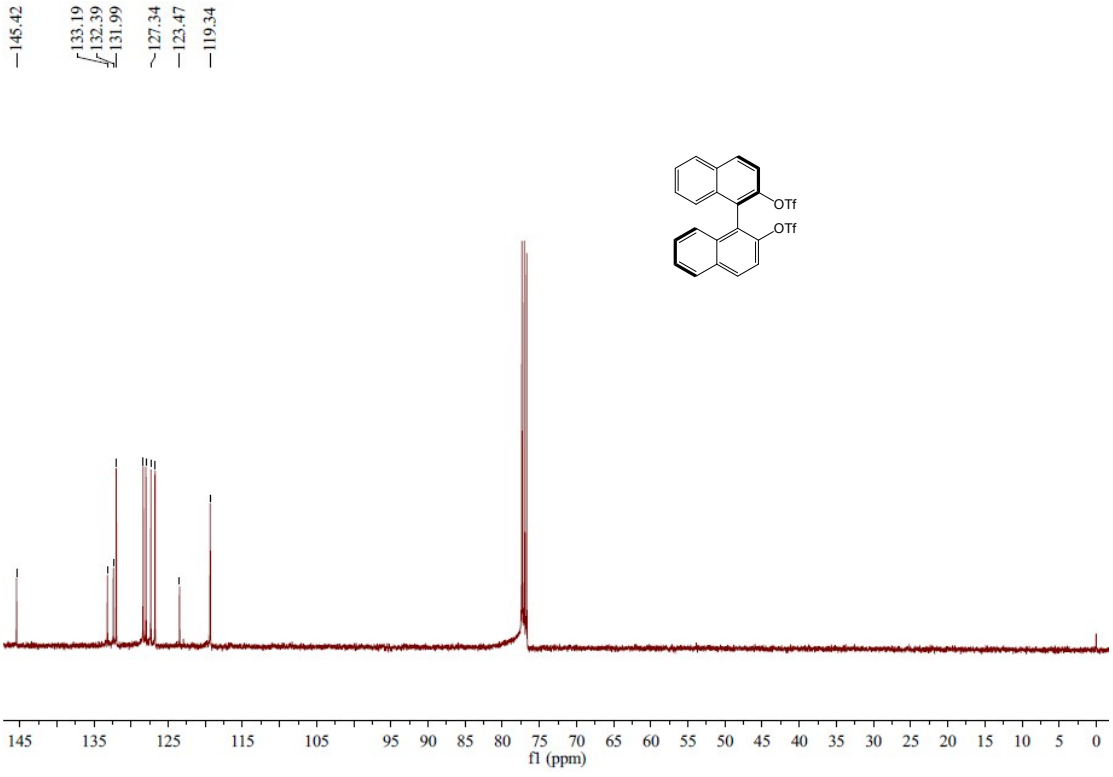

10.024
8.068
8.052
7.516
7.493
7.075
7.043
4.079
4.074
4.068
4.063
4.058
4.053
1.911
1.900
1.883
1.874
1.857
1.847
1.417
1.333
1.243
0.887
0.875
0.864
0.000
CH3
CH2
H2C
O
CH2
H2C
CH3
CHO
1.00
1.00
1.99
2.85
2.00
1.00
2.00
1.00
1.00
4.02
4.05
4.03
4.04
14.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

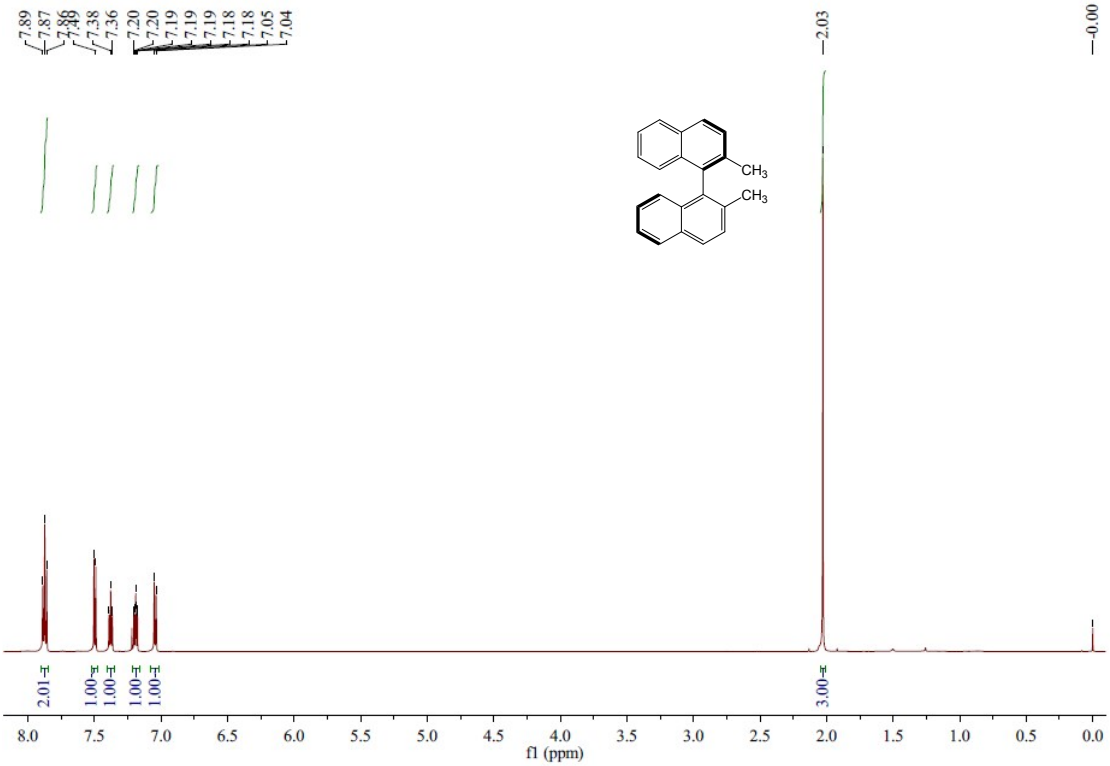

191.35
154.03
153.77
135.41
131.51
129.60
128.03
127.82
126.59
120.73
117.13
116.94
115.12
113.11
95.83
93.94
90.36
86.28
69.83
69.67
29.73
29.69
29.66
29.54
29.45
29.39
26.20
26.13
22.71
14.13
0.01
CH3
CH2
H2C
O
CH2
H2C
CH3
CHO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

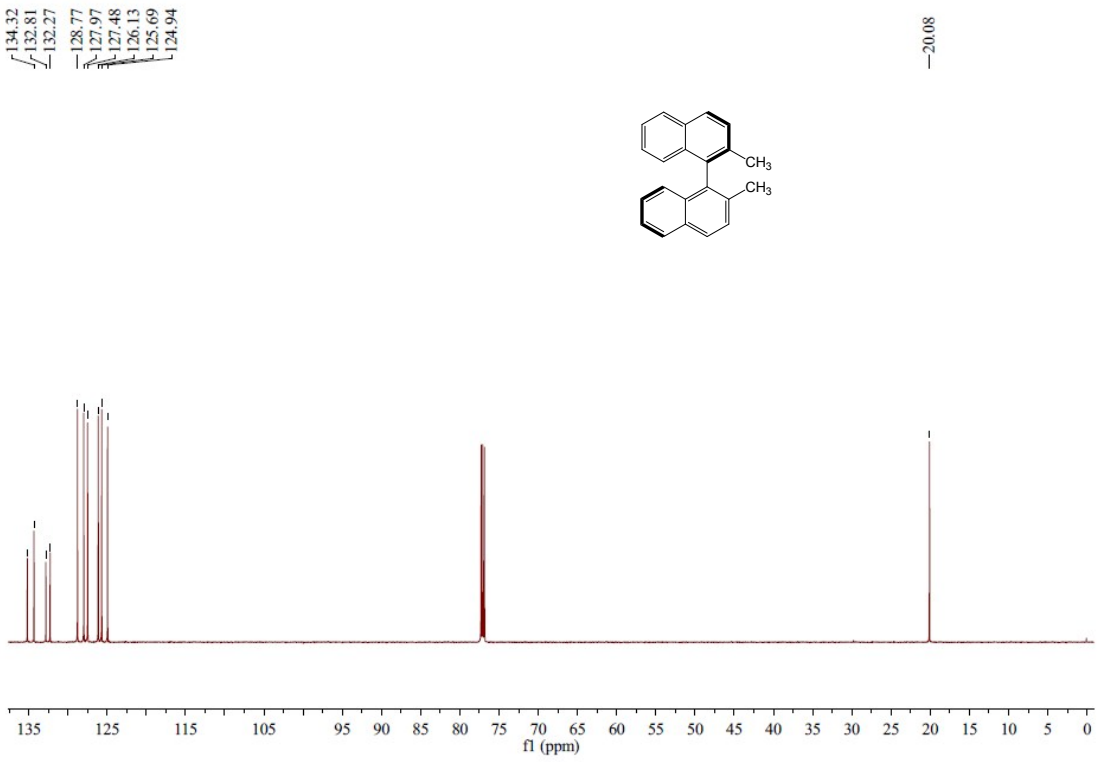

8.05
7.71
7.58
7.49
7.25
7.07
7.03
4.07
4.06
4.05
4.04
1.91
1.90
1.89
1.88
1.87
1.87
1.85
1.84
1.61
1.34
1.24
0.89
0.88
0.86
0.00
CH3
CH2
H2C
O
CN
CN
0.99
3.05
1.04
2.00
1.00
2.04
1.01
1.00
4.00
4.13
4.44
4.32
45.68
6.18
f1 (ppm)

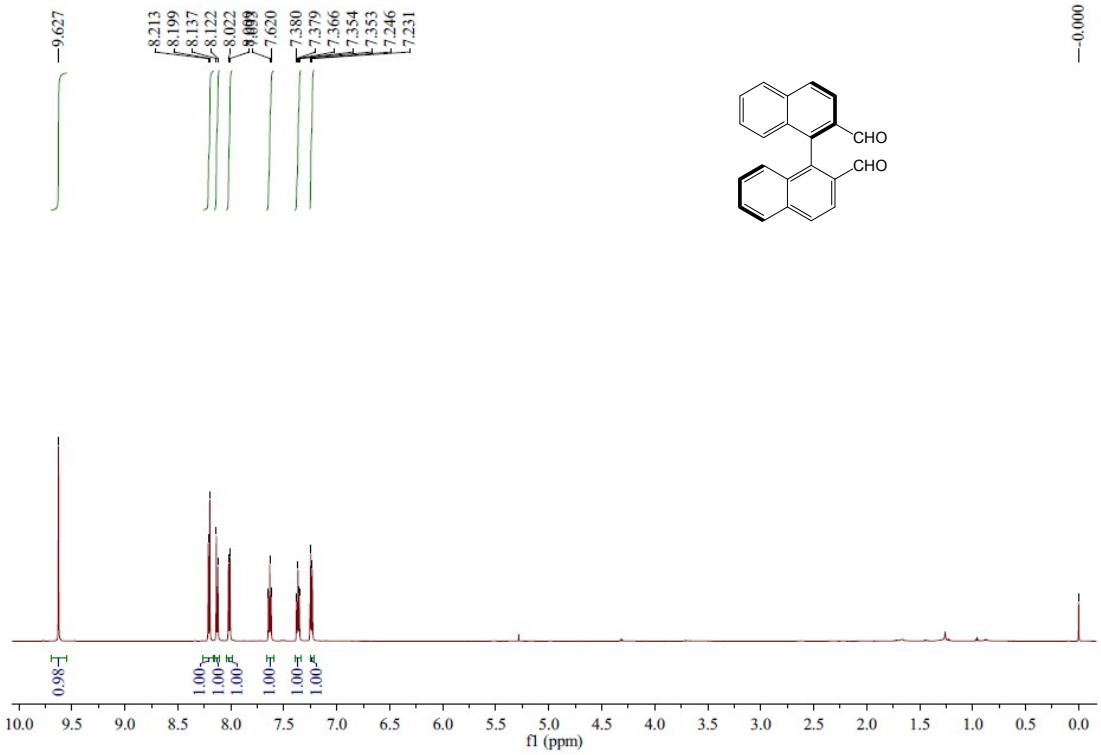

158.42
154.12
153.69
132.34
130.10
128.35
128.01
127.81
127.80
126.77
126.59
120.61
116.76
115.49
113.76
112.63
112.60
96.08
93.82
92.17
86.20
82.53
69.76
69.54
29.71
29.67
29.64
29.52
29.42
29.40
29.37
29.31
26.07
22.70
14.12
CH3
CH2
H2C
O
CN
CN
f1 (ppm)

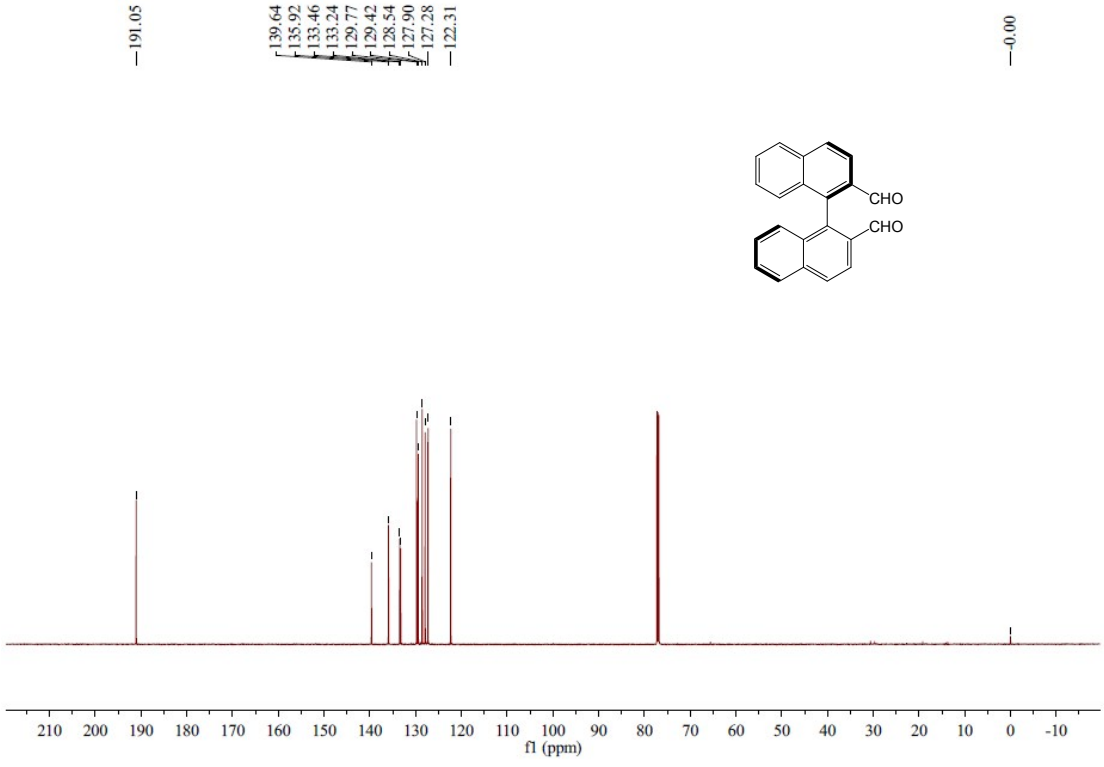

8.15
8.13
8.01
8.00
7.63
7.57
7.42
7.41
7.40
7.26
7.25
7.25
0.00
OTf
OTf
1.00
1.00
2.00
1.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

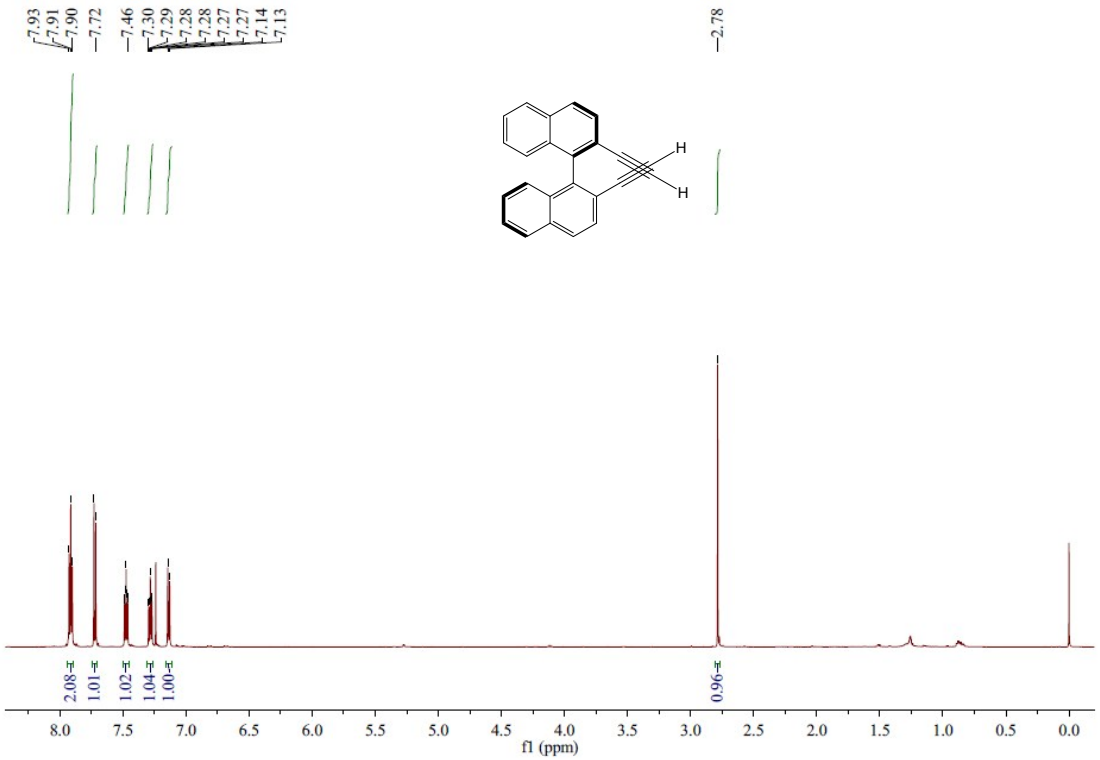

145.42
133.19
132.39
131.99
127.34
123.47
119.34
OTf
OTf
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

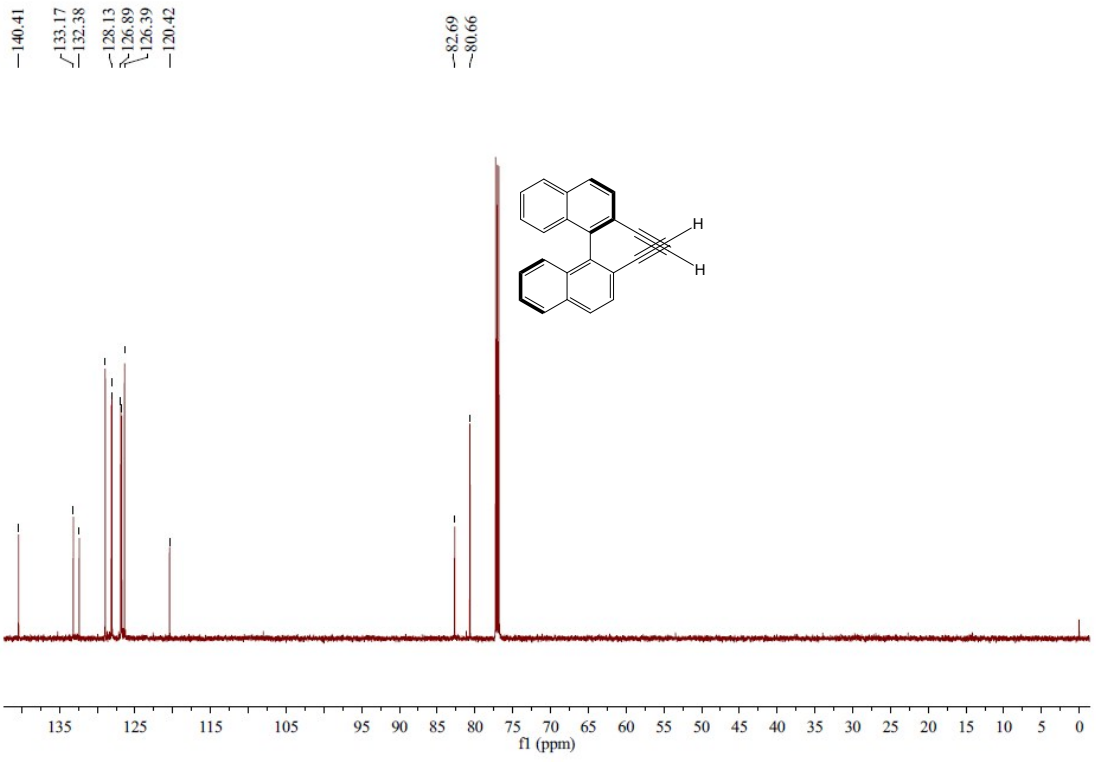

7.89
7.87
7.38
7.36
7.20
7.19
7.19
7.19
7.18
7.05
7.04
2.03
0.00
CH3
CH3
2.01
1.00
1.00
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

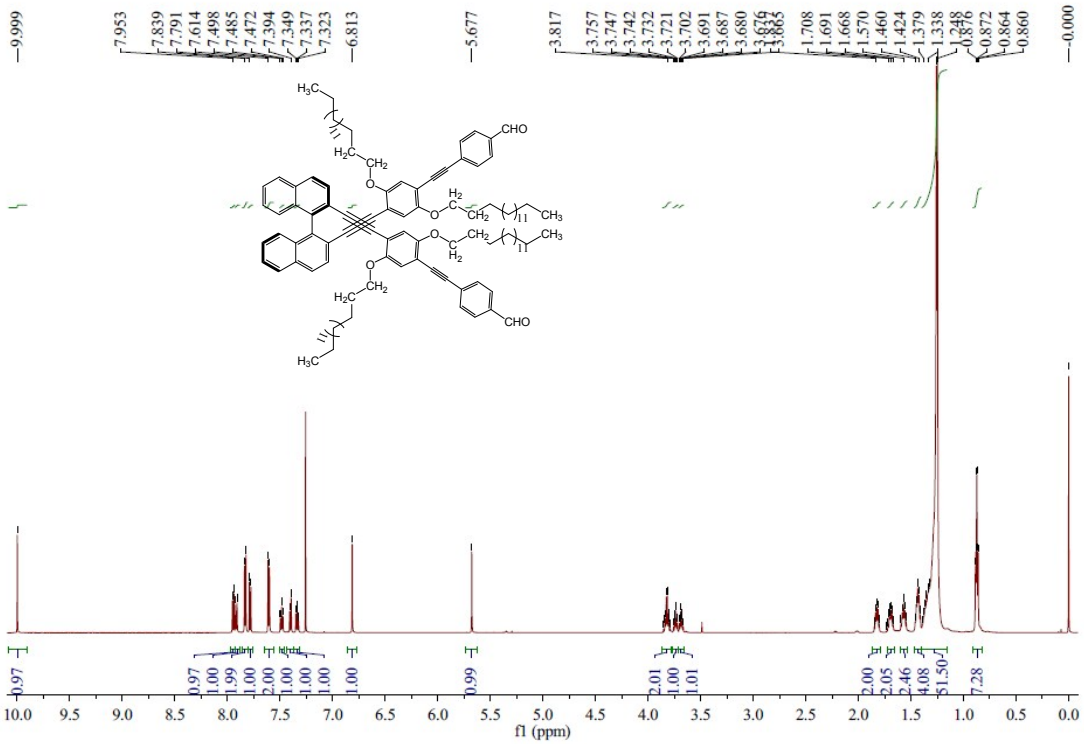

134.32
132.81
132.27
128.77
127.97
127.48
126.13
125.69
124.94
20.08
CH3
CH3
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

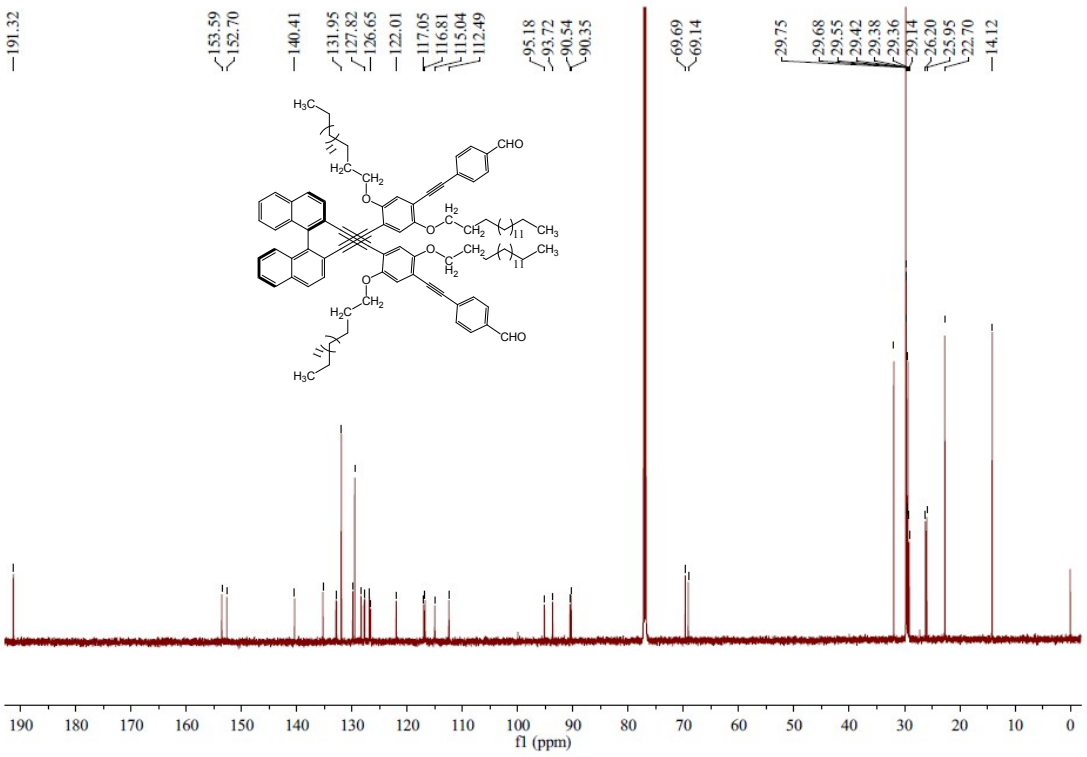

9.627
8.213
8.199
8.137
8.122
8.022
7.620
7.380
7.379
7.366
7.354
7.353
7.246
7.231
0.000
CHO
CHO
0.98
1.00
1.00
1.00
1.00
1.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

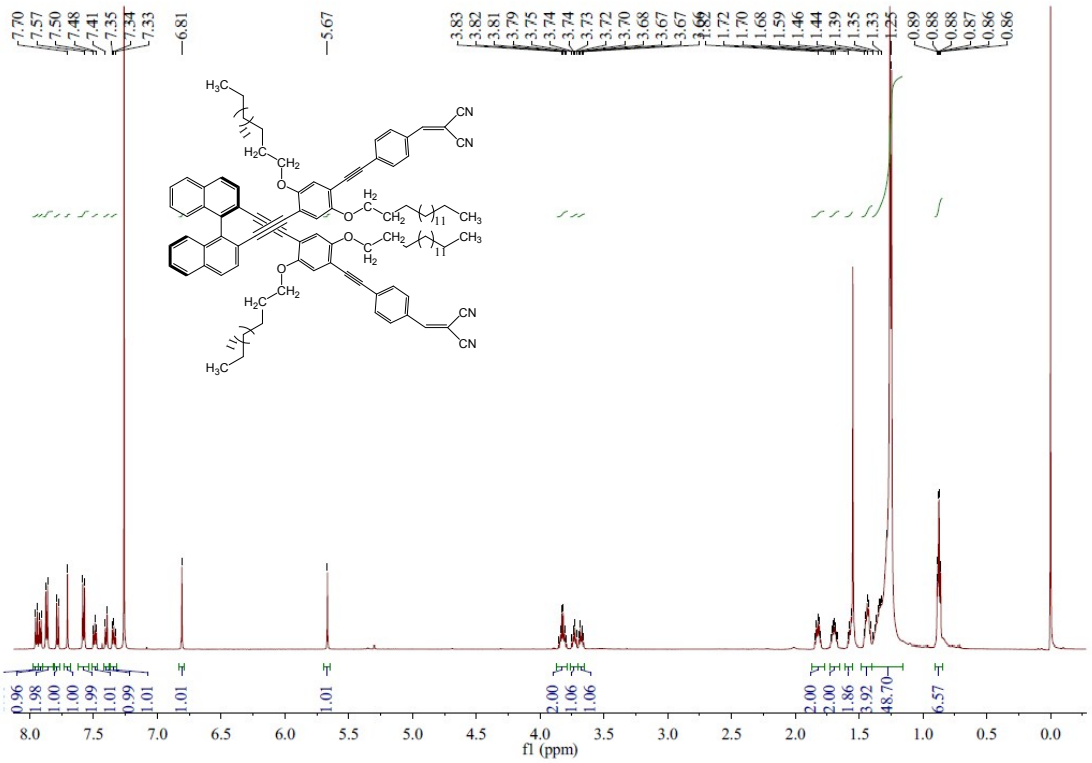

191.05
139.64
135.92
133.46
133.24
129.77
129.42
128.54
127.90
127.28
122.31
0.00
CHO
CHO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

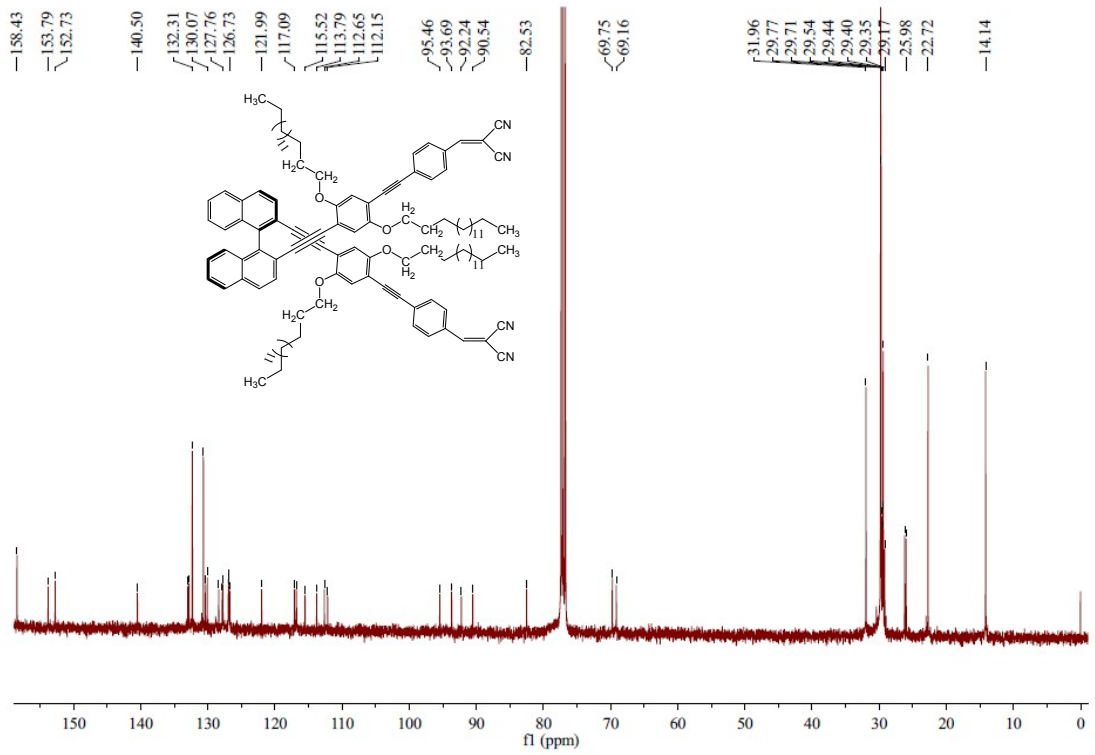

7.93
7.91
7.90
7.72
7.46
7.30
7.29
7.28
7.28
7.27
7.27
7.14
7.13
2.78
H
H
2.08
1.01
1.02
1.04
1.00
0.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.41
133.17
132.38
128.13
126.89
126.39
120.42
82.69
80.66
H
H
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

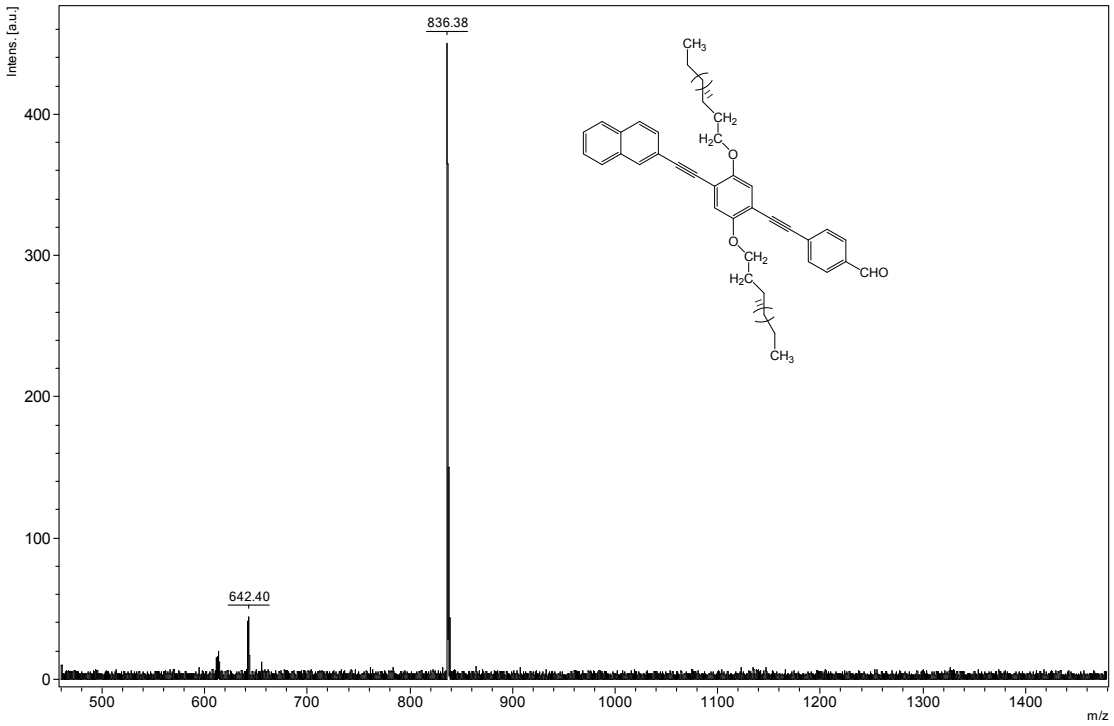

9.999
7.953
7.839
7.791
7.614
7.498
7.485
7.472
7.394
7.349
7.337
7.323
6.813
5.677
3.817
3.757
3.747
3.742
3.732
3.721
3.702
3.691
3.687
3.680
1.708
1.691
1.668
1.570
1.460
1.424
1.379
1.338
0.872
0.864
0.860
0.000
0.97
1.00
1.99
1.00
2.00
1.00
1.00
1.00
0.99
2.01
1.00
1.01
2.00
2.05
2.46
4.08
51.50
7.28
f1 (ppm)

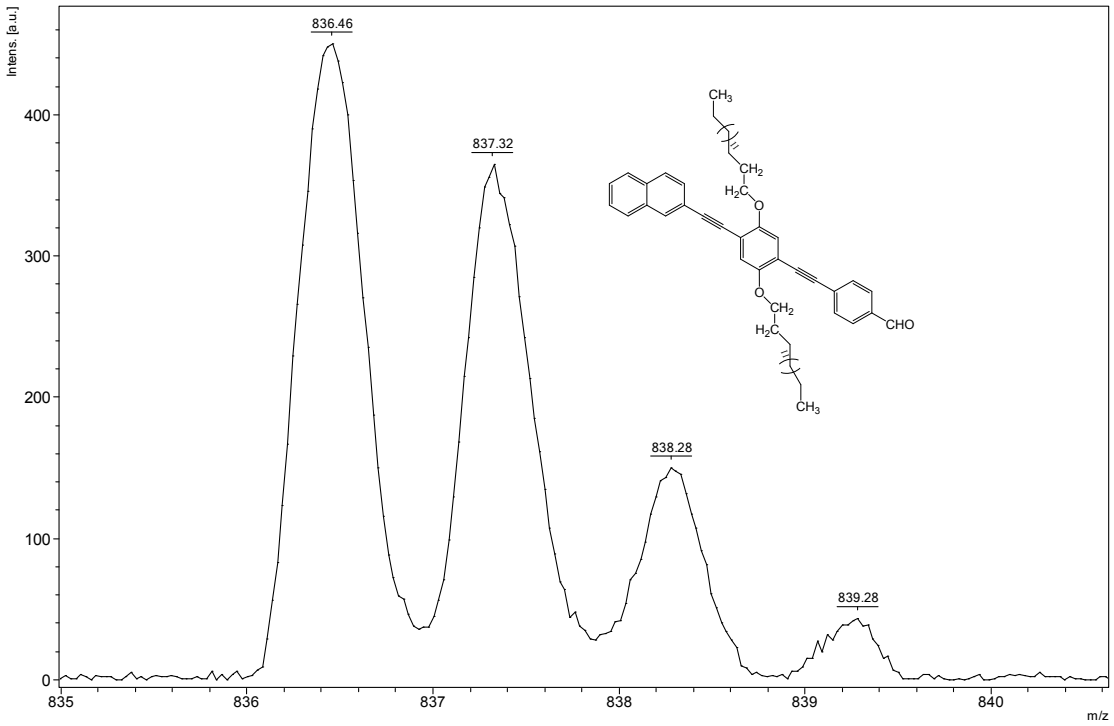

191.32
153.59
152.70
140.41
131.95
127.82
126.65
122.01
117.05
116.81
115.04
112.49
95.18
93.72
90.54
90.35
69.69
69.14
29.75
29.68
29.55
29.42
29.38
29.36
29.14
26.20
25.95
22.70
14.12
f1 (ppm)

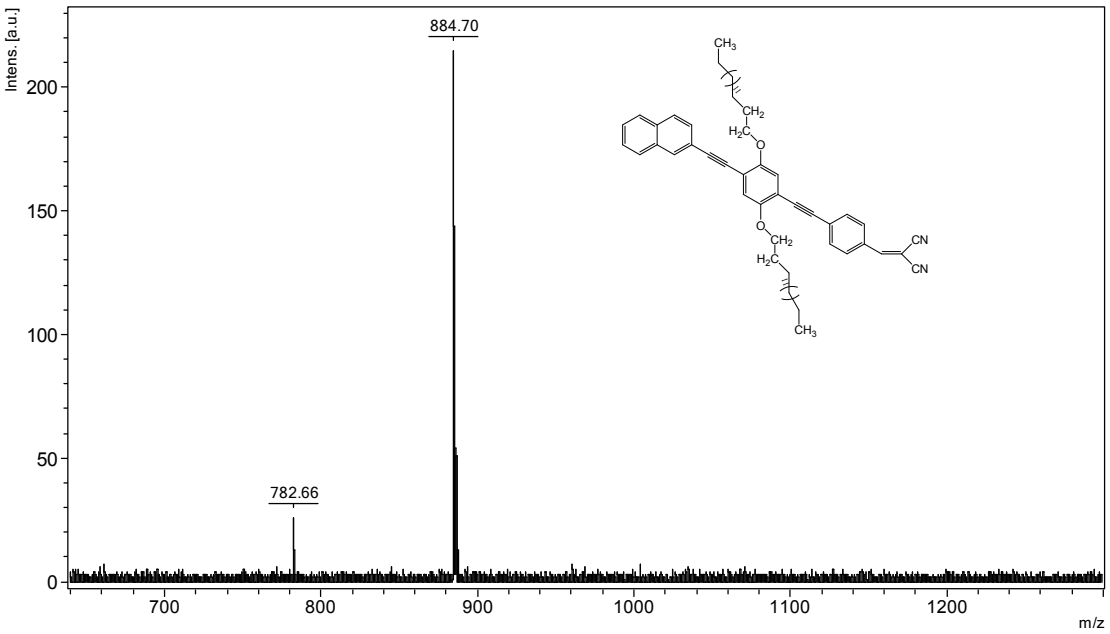

7.70
7.57
7.50
7.48
7.41
7.35
7.34
7.33
6.81
5.67
3.83
3.82
3.81
3.79
3.75
3.74
3.74
3.73
3.72
3.70
3.68
3.67
3.67
1.72
1.70
1.68
1.59
1.46
1.44
1.39
1.35
1.33
1.25
0.89
0.88
0.88
0.87
0.86
0.86
0.96
1.98
1.00
1.00
1.99
1.01
0.99
1.01
1.01
1.01
2.00
1.06
1.06
2.00
2.00
1.86
3.92
48.70
6.57
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

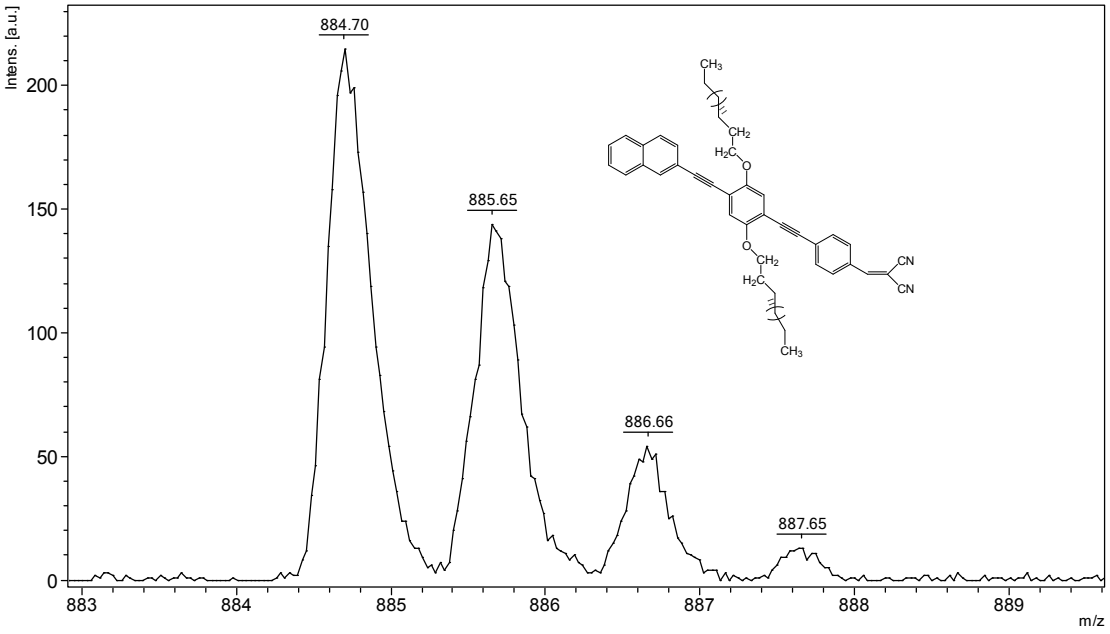

158.43
153.79
152.73
140.50
132.31
130.07
127.76
126.73
121.99
117.09
115.52
113.79
112.65
112.15
95.46
93.69
92.24
90.54
82.53
69.75
69.16
31.96
29.77
29.71
29.54
29.44
29.40
29.35
29.17
25.98
22.72
14.14
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

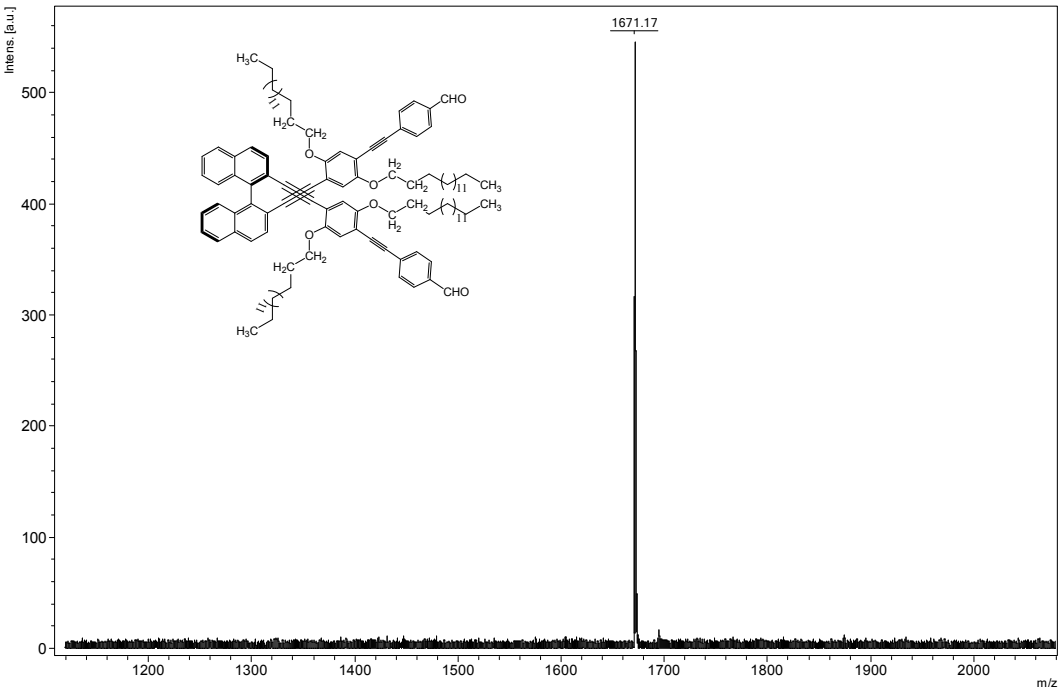
4. MS spectra for PNBA, PNBD, BPNBA and BPNBD

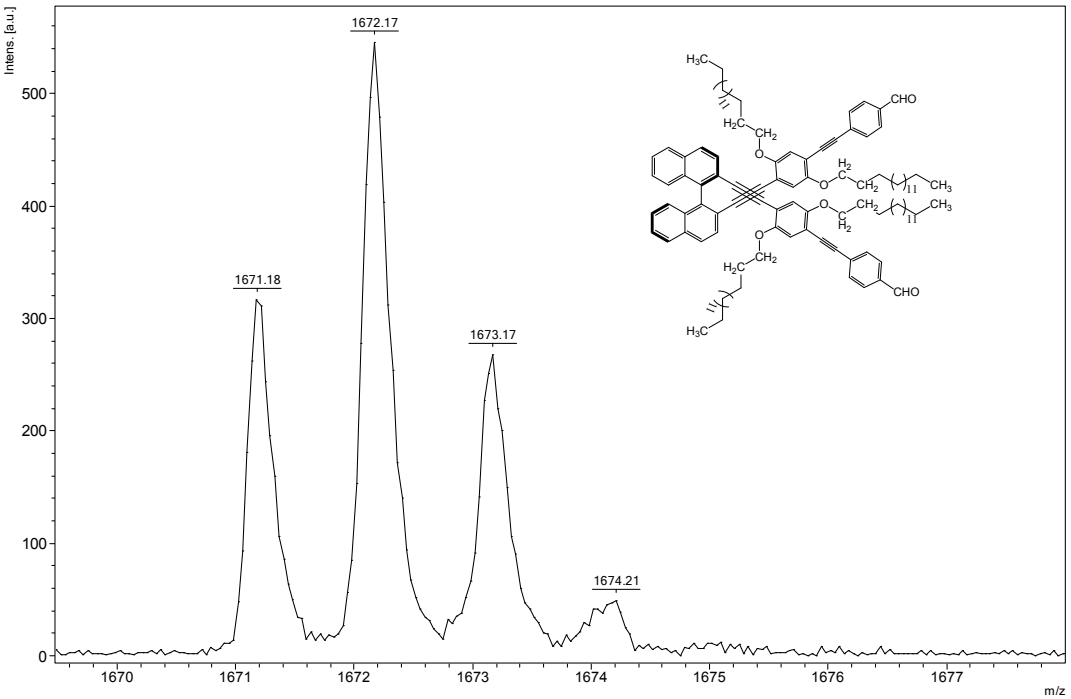


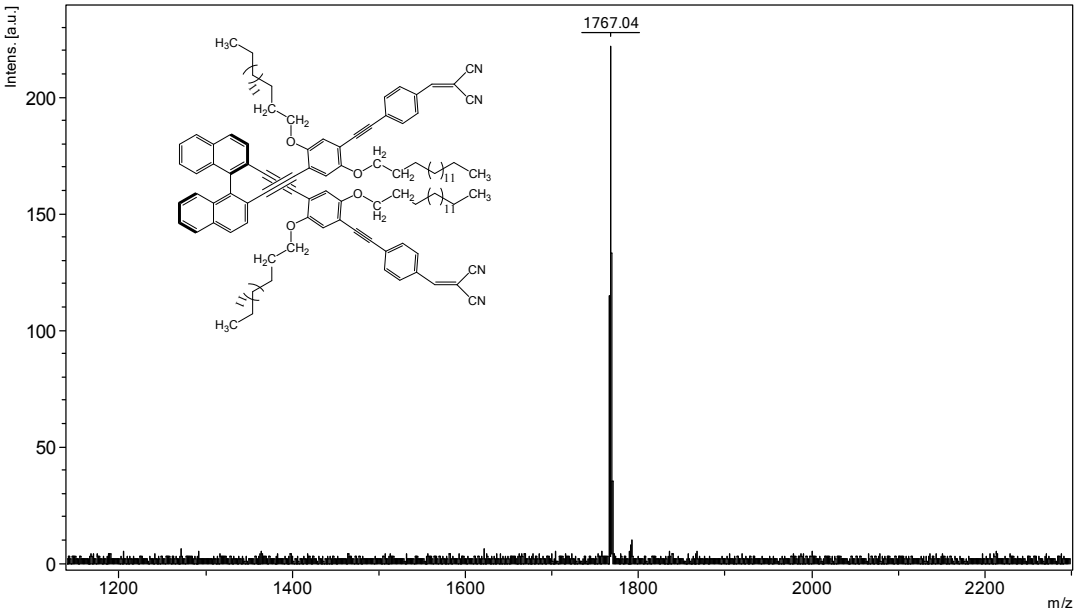


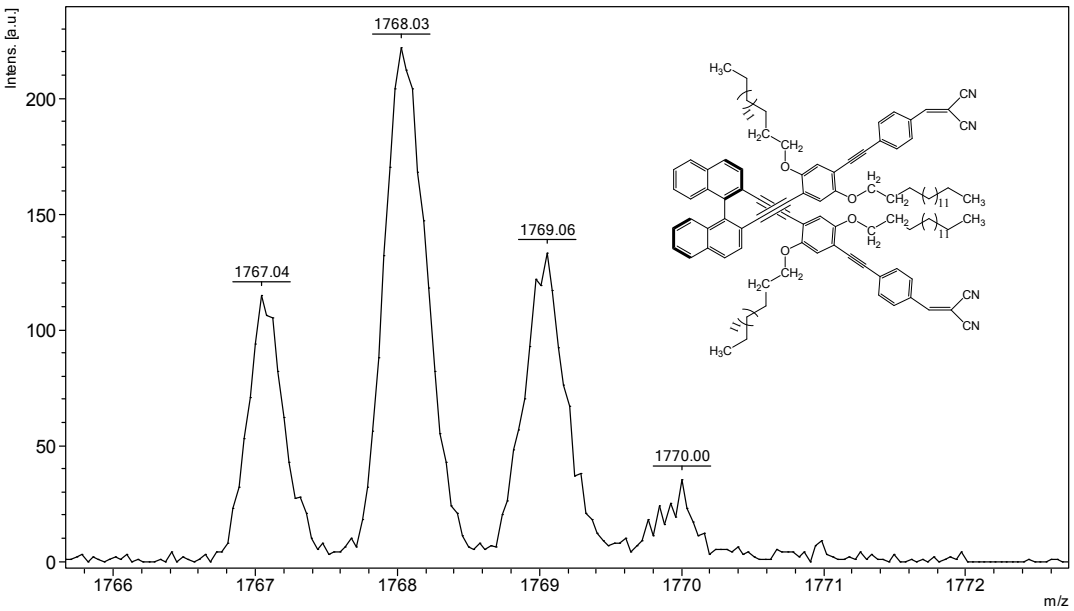

Intens. [a.u.]
884.70
782.66
m/z


Intens. [a.u.]
884.70
885.65
886.66
887.65
m/z


Intens. [a.u.]
1671.17
m/z


Intens. [a.u.]
1672.17
1671.18
1673.17
1674.21
m/z


Intens. [a.u.]
1767.04
200
150
100
50
0
1200
1400
1600
1800
2000
2200
m/z


Intens. [a.u.]
1768.03
1769.06
1767.04
1770.00
200
150
100
50
0
1766
1767
1768
1769
1770
1771
1772
m/z

5. The optimized structures for PNBD and BPNBD

Ground state structure for **PNBD**:

	x	y	z
C	-8.97651	0.44863	-0.06627
C	-8.29197	-0.80418	-0.20103
C	-6.87673	-0.82308	-0.17238
C	-6.14223	0.34695	-0.01663
C	-6.83463	1.59159	0.1163
C	-8.20547	1.6335	0.09144
C	-10.395	0.46269	-0.0953
C	-11.1087	-0.70532	-0.2504
C	-10.4337	-1.94376	-0.3842
C	-9.05851	-1.9916	-0.36014
H	-6.35618	-1.77068	-0.27834
C	-4.72018	0.31654	0.01141
H	-6.25486	2.50123	0.23728
H	-8.72306	2.58433	0.19343
H	-10.9114	1.41421	0.0072
H	-12.1948	-0.68095	-0.2712
H	-11.0081	-2.85783	-0.5066
H	-8.53742	-2.94031	-0.4636
C	-3.50304	0.2927	0.03105
C	-2.08384	0.2856	0.05331
C	-1.37274	1.50502	0.07481
C	0.01888	1.52774	0.0673
C	0.74547	0.30588	0.03319
C	0.02883	-0.9046	0.02002
C	-1.35936	-0.92936	0.03057
H	-1.94285	2.4253	0.08853
O	0.76894	2.66024	0.0846
H	0.56819	-1.84508	-0.01197
O	-2.00715	-2.13933	-0.03695
C	2.16119	0.30652	0.01462
C	3.37909	0.28508	-0.00162
C	4.79475	0.28136	-0.0212
C	5.51798	1.49452	-0.0062
C	6.9013	1.4818	-0.02556
C	7.63146	0.27036	-0.06017
C	6.90158	-0.94168	-0.07539
C	5.51785	-0.93362	-0.05637
H	4.97552	2.43372	0.02041

H	7.44294	2.42438	-0.01376
C	9.07407	0.37758	-0.07727
H	7.41761	-1.89326	-0.10262
H	4.97157	-1.87113	-0.069
C	10.05858	-0.57501	-0.1072
H	9.44666	1.39952	-0.06352
C	11.43075	-0.15935	-0.1176
N	12.54243	0.18518	-0.1258
C	9.84328	-1.98921	-0.12922
N	9.68788	-3.14288	-0.14718
C	0.10162	3.91426	0.1097
C	-2.50203	-2.62976	1.21192
H	-0.52338	4.0541	-0.78146
H	0.88982	4.66865	0.12119
H	-0.51792	4.02121	1.0093
H	-2.97389	-3.59074	0.99552
H	-3.24399	-1.94804	1.64371
H	-1.68279	-2.77864	1.92788

Ground state structure for **BPNBD**:

	x	y	z
C	-2.25516	-5.88315	1.49765
C	-2.00275	-4.98031	2.56457
C	-0.92981	-4.06776	2.44541
C	-0.13467	-4.03425	1.31985
C	-0.39485	-4.93782	0.23684
C	-1.42695	-5.83087	0.34789
C	-3.32673	-6.80252	1.61423
C	-4.10983	-6.82366	2.7375
C	-3.85903	-5.92463	3.80004
C	-2.83087	-5.02514	3.71551
H	-0.72732	-3.37787	3.25869
C	0.94859	-3.10945	1.23117
H	-1.62782	-6.51664	-0.47052
H	-3.51639	-7.49095	0.79557
H	-4.928	-7.53251	2.8173
H	-4.48696	-5.95238	4.685
H	-2.63349	-4.33235	4.52857
C	1.86745	-2.32969	1.14273
C	2.958	-1.42847	0.97957
C	3.57937	-1.29908	-0.26865
C	4.62044	-0.40692	-0.45845
C	5.07134	0.39137	0.60773

C	4.45761	0.25381	1.85867
C	3.41905	-0.6409	2.05018
H	3.23226	-1.88967	-1.10903
O	5.17486	-0.27927	-1.70327
H	4.78066	0.86427	2.69391
O	2.82191	-0.70624	3.27907
C	6.12022	1.33532	0.41538
C	7.01143	2.13959	0.27065
C	8.05453	3.09006	0.08384
C	8.5181	3.39358	-1.20402
C	9.53145	4.31598	-1.37528
C	10.12197	4.96704	-0.2793
C	9.65137	4.66025	1.00878
C	8.63666	3.73946	1.18362
H	8.07066	2.90134	-2.06
H	9.88032	4.54389	-2.3783
C	11.18145	5.91446	-0.57725
H	10.07521	5.14066	1.88059
H	8.28037	3.5106	2.18164
C	11.95954	6.67517	0.23224
H	11.38875	6.03223	-1.63766
C	12.9466	7.53554	-0.35502
N	13.73943	8.22468	-0.83919
C	11.8901	6.69924	1.66259
N	11.84514	6.72749	2.81834
C	6.37129	-1.02115	-1.8942
C	3.20113	-1.82552	4.06877
H	7.15733	-0.69336	-1.20497
H	6.68966	-0.83495	-2.92094
H	6.19347	-2.09462	-1.75722
H	2.65497	-1.73705	5.00891
H	4.27889	-1.81327	4.2719
H	2.93318	-2.7679	3.58017
C	2.29771	-5.7226	-2.37572
C	1.51794	-5.79851	-1.1877
C	0.4381	-4.88577	-0.99973
C	0.16325	-3.93623	-1.97207
C	0.95398	-3.86794	-3.15314
C	1.98795	-4.73538	-3.34541
C	3.36771	-6.63181	-2.56221
C	3.66224	-7.57479	-1.6149
C	2.89554	-7.64849	-0.43112
C	1.85329	-6.7855	-0.22285

C	-0.9145	-3.01539	-1.80477
H	0.7145	-3.11196	-3.89286
H	2.58864	-4.68158	-4.2488
H	3.95211	-6.56478	-3.47566
H	4.48455	-8.26639	-1.7689
H	3.1364	-8.39557	0.31865
H	1.26905	-6.84812	0.68791
C	-1.82245	-2.23022	-1.66394
C	-2.90306	-1.33424	-1.42333
C	-3.50153	-1.28642	-0.15819
C	-4.53238	-0.40311	0.11097
C	-4.99705	0.46808	-0.89013
C	-4.40559	0.4136	-2.15812
C	-3.37649	-0.47169	-2.42886
H	-3.14331	-1.9347	0.63354
O	-5.06439	-0.35542	1.37108
H	-4.73874	1.08161	-2.94389
O	-2.80039	-0.4543	-3.66936
C	-6.03814	1.3994	-0.61301
C	-6.9236	2.19236	-0.39123
C	-7.95947	3.12676	-0.10833
C	-8.40004	3.32098	1.20847
C	-9.40639	4.2282	1.47491
C	-10.0124	4.97197	0.44854
C	-9.56499	4.77438	-0.86886
C	-8.55739	3.86884	-1.13882
H	-7.94023	2.75636	2.01157
H	-9.73739	4.37087	2.49951
C	-11.0623	5.89378	0.84429
H	-10.0016	5.32831	-1.68925
H	-8.21911	3.7246	-2.15869
C	-11.8486	6.72544	0.1166
H	-11.2528	5.91945	1.91405
C	-12.8221	7.53496	0.79216
N	-13.6038	8.18222	1.34705
C	-11.8005	6.87461	-1.30702
N	-11.7726	7.00401	-2.4564
C	-6.24599	-1.12584	1.54038
C	-3.19259	-1.51794	-4.52666
H	-7.04849	-0.77224	0.88343
H	-6.54916	-1.00202	2.58103
H	-6.05483	-2.18716	1.34134
H	-2.6623	-1.36516	-5.4676

H	-4.27363	-1.49334	-4.71036
H	-2.91609	-2.49095	-4.10786

6. References

1. An, D. L.; Nakano, T.; Orita, A.; Otera, J. *Angew. Chem. Int. Ed*. 2002, 41, 171-173.
2. Ooi, T.; Kameda, M.; Maruoka, K. *J. Am. Chem. Soc*. 2003, 125, 5139-5151.
3. Cui, H.; He, G.; Wang, H. Y.; Sun, X. H. Ding, L. P.; Fang Y. *ACS Appl. Mater. Interfaces*, 2012, 4, 6935-6941.