Supplementary Information for

Truxene-cored π-Expanded Triarylborane Dyes as Single- and Two-Photon Fluorescent Probes for Fluoride

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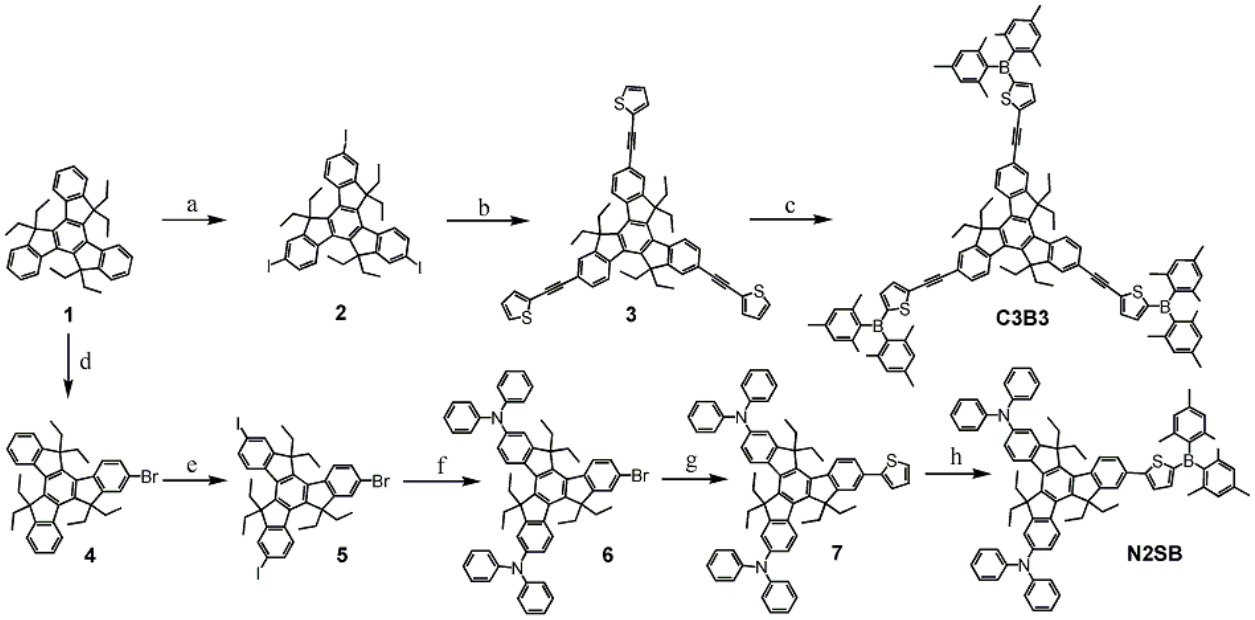
1. Synthesis



Scheme S1. Synthesis of target compounds.[1,2] (a) and (e) HIO_3, I_2, CH_3COOH-H_2SO_4-H_2O-CCl_4, 80 °C, 4 h; (b) 2-ethynylthiophene, $Pd(PPh_3)_4$, *n*-Bu_4NF, Et_3N, tetrahydrofuran (THF), reflux, 3 h; (c) and (h) dimesitylboron fluoride, *n*-BuLi, THF, −78 °C, 2 d; (d) 1,2-Propanediol carbonate, *N*-bromosuccinimide, 60 °C, 2 h; (f) diphenylamine, K_2CO_3, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h; (g) thiophen-2-yl-2-boronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF, reflux, 8 h.

2,7,12-Triiodo-5,5′,10,10′,15,15′-hexaethyltruxene (2). A mixture of compound **1** (1.33 g, 2.61 mmol), HIO_3 (0.50 g, 2.82 mmol), I_2 (1.00 g, 3.94 mmol), and 20 mL solvent (CH_3COOH:H_2SO_4:H_2O:CCl_4 = 100:5:20:8, v/v/v/v) was heated to 80 °C and stirred for 4 h at the same temperature. The mixture was then cooled to room temperature and filtered under suction. The residue was washed with water and purified by column chromatography on silica gel by using $CHCl_3$-hexane (1:5, v/v) as the eluent to obtain compound **2** (1.98 g, 85%) as a white powder [melting point (m.p.) = 334 °C to 336 °C]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.18 (s, 18 H), δ 2.04–2.11 (m, 6 H), 2.85–2.92 (m, 6 H), and 7.39–8.09 (m, 9 H). Elemental anal. calcd. for $C_{39}H_{39}I_3$: C, 52.72; and H, 4.42. Found: C, 52.92; and H, 4.33. MALDI-TOF: *m*/*z* 888.0 [M^+] and 858.9 [M-29]$^+$.

2,7,12-tri(2-thiophenylethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**3**). A mixture of **2** (0.50 g,

0.56 mmol), 2-ethynylthiophene (0.40 g, 3.70 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), *n*-Bu_4NF (50 mg), THF (15 mL), and triethylamine (15 mL) was heated to reflux with stirring after being flushed with nitrogen for 30 min. After reacting for 3 h under nitrogen, the mixture was cooled to room temperature and poured into water (100 mL). After several times of extraction with dichloromethane (DCM, 100 mL), the organic phase was dried over $MgSO_4$. The solvent was removed, and the residue was purified by column chromatography on silica gel by using DCM-hexane (1:5, v/v) as the eluent to obtain compound **3** (0.36 g, 78%) as a yellow powder (m.p. = 286 °C to 288 °C). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.22–0.25 (t, J = 7.3, 18 H), 2.16–2.20 (m, 6 H), 2.96–3.00 (m, 6 H), 7.04–7.06 (m, 3 H), 7.32–7.35 (m, 6 H), 7.55–7.57 (d, J = 8.0, 3 H), 7.62 (s, 3H), and 8.31–8.32 (d, J = 8.5, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 152.9, 145.1, 140.7, 138.5, 131.9, 129.8, 127.3, 127.2, 125.2, 124.5, 123.5, 121.0, 57.0, 29.5, and 8.6. MALDI-TOF: *m*/*z* 829.2 [M^+]. Elemental anal. calcd. for $C_{57}H_{48}S_3$: C, 82.56; H, 5.83; and S, 11.60. Found: C, 82.64; H, 6.13; and S, 11.32.

2-Bromo-5,5′,10,10′,15,15′-hexaethyltruxene (4). *N*-bromosuccinimide was added (0.35 g, 1.97 mmol) stepwise to a stirred solution of **1** (1.00 g, 1.96 mmol) in 1,2-propanediol carbonate (15 mL) at 60 °C. After reacting for 2 h at the same temperature, the mixture was cooled, poured into 100 mL water, extracted with DCM, and then dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography on silica gel by using DCM-hexane (1:5, v/v) as the eluent to obtain the crude product **4**. Recrystallization with ethanol yielded compound **4** (0.73 g, 63%) as a white crystal (m.p. = 232 °C to 234 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.19 (s, 18 H), 2.08 (s, 6 H), 2.86–3.03 (m, 6 H), and 7.25–8.30 (m, 11 H). TOF-MS-EI: *m*/*z* 588.0 [$M]^+$, 559.0 [$M-29]^+$, and 510.0 [$M-78]^+$.

2-Bromo-7,12-diiodo-5,5′,10,10′,15,15′-hexaethyltruxene (5). A mixture of compound **4** (0.70 g, 1.19 mmol), HIO_3 (0.11 g, 0.60 mmol), I_2 (0.30 g, 1.19 mmol), and 15 mL solvent (CH_3COOH:H_2SO_4:H_2O:CCl_4 = 100:5:20:8, v/v/v/v) was heated to 80 °C and stirred for 4 h at the same temperature. The mixture was then cooled to room temperature and filtered under suction. The

residue was washed with water and purified by column chromatography on silica gel by using $CHCl_3$-hexane (1:5, v/v) as the eluent to obtain compound **5** (0.81 g, 81%) as a white powder (m.p. = 330 °C to 332 °C). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.18 (s, 18 H), 2.04–2.10 (m, 6 H), 2.85–3.03 (m, 6 H), and 7.38–8.30 (m, 9 H). TOF-MS-EI: *m*/*z* 840.0 $[M]^+$ and 811.0 $[M-29]^+$.

2-Bromo-7,12-di(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (6). A mixture of compound **5** (0.75 g, 0.89 mmol), K_2CO_3 (1.00 g, 7.25 mmol) powder, fresh Cu (0.07 g, 1.09 mmol) powder, 18-crown-6 ether (0.15 g, 0.62 mmol), diphenylamine (0.31 g, 1.83 mmol), and 1,2-dichlorobenzene (15 mL) were heated to reflux with stirring under nitrogen atmosphere. After reacting for 8 h, the mixture was cooled to room temperature and filtered under suction. The filtrate was then condensed and purified by column chromatography on silica gel. Elution with DCM-petrol ether (1:10, v/v) yielded compound **6** (0.56 g, 69%) as a white powder (m.p. = 232 °C to 235 °C). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.20–0.28 (m, 18 H), 1.90–2.08 (m, 6 H), 2.81–2.94 (m, 6 H), 7.00–7.54 (m, 26 H), and 8.08–8.13 (m, 3 H). MALDI-TOF: *m*/*z* 924.8 $[M]^+$, 895.6 $[M-29]^+$, and 844.7 $[M-80]^+$.

Synthesis of 2,7-di(N,N-diphenylamino)-12-(2-thiophenyl)- hexaethyltruxene (7). A mixture of compound **6** (0.50 g, 0.54 mmol), 2-thiophene-boronic acid (0.10 g, 0.78 mmol), $Pd(PPh_3)_4$ (30 mg, 0.03 mmol), toluene (30 mL), ethanol (8 mL), and 2 M aqueous K_2CO_3 solution (2 mL) was heated to reflux with stirring under a nitrogen atmosphere for 24 h. The mixture was cooled to room temperature and poured into water (100 mL). After extraction with DCM, the organic phase was dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography on silica gel by using DCM-hexane (1:20, v/v) as the eluent to obtain compound **7** (0.16 g, 32%) (m.p. = 156 °C to 158 °C). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.28 (m, 18 H), 1.89–2.15 (m, 6 H), 2.84–2.99 (m, 6 H), 7.02–7.67 (m, 29 H), and 8.09–8.27 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ154.22, 153.67, 152.67, 147.96, 129.24, 129.05, 128.24, 128.09, 126.35, 126.04, 125.31, 124.92, 124.59, 124.21, 122.95, 122.88, 122.69, 122.27, 121.98, 119.47, 117.66, 67.98, 56.65, 29.40, 29.19, 25.63, 21.46, 8.69, 8.65, and 8.61. MALDI-TOF: *m*/*z* 927.1 $[M^+]$ and 898.0 $[M-29]^+$.

2. Theoretical Calculation

Table S1. The graphic representations of the frontier molecular orbits of **N2SB**.

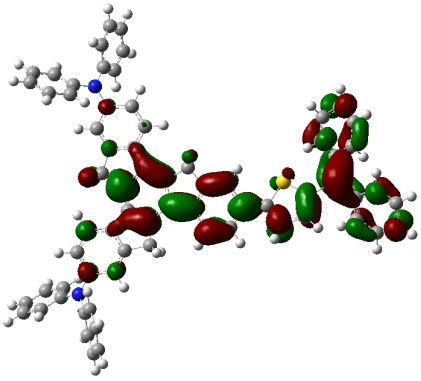
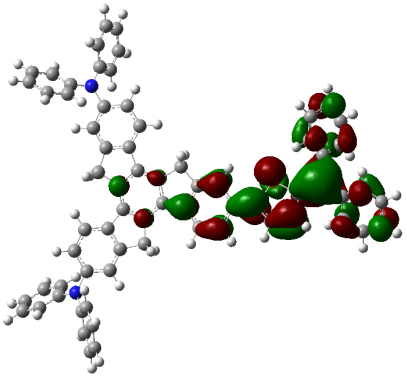
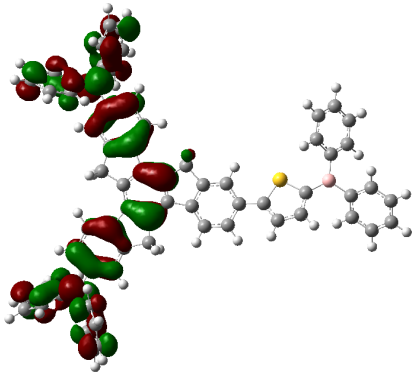
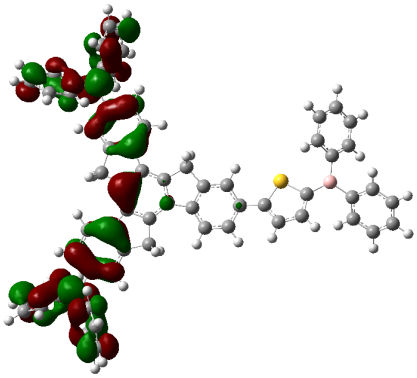
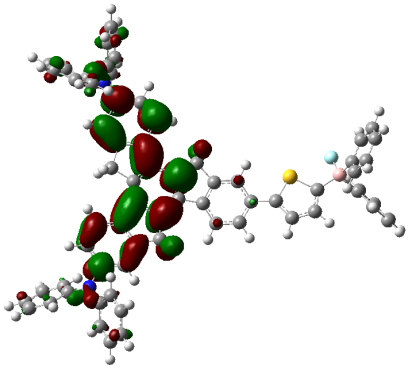
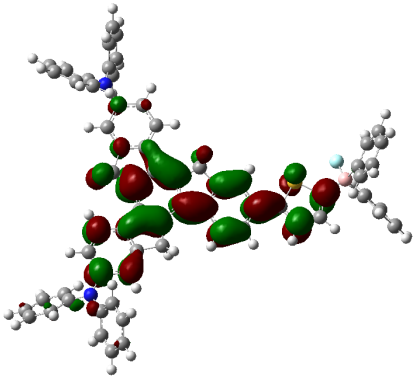
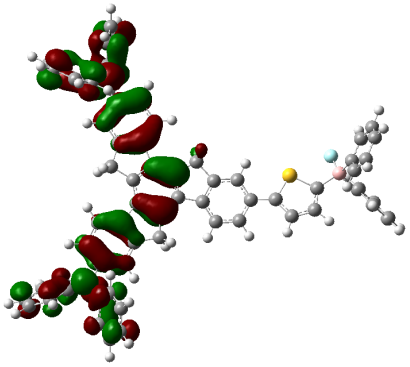
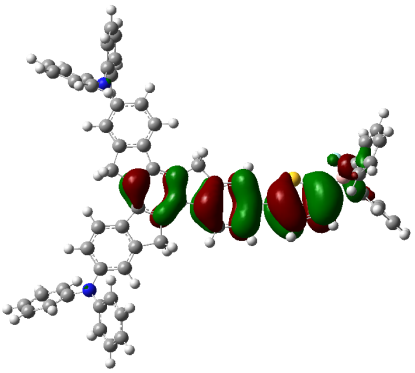
N2SB **LUMO+1** No.244 -1.109 eV		Excited State 1: Singlet-A 2.5887 eV 478.94 nm f=0.0106 242 -> 243 0.70286 Excited State 2: Singlet-A 2.6828 eV 462.14 nm f=0.0825 241 -> 243 0.70240 Excited State 3: Singlet-A 3.0487 eV 406.68 nm f=1.4054 240 -> 243 0.68328 242 -> 245 -0.12504
N2SB **LUMO** No.243 -2.047 eV		
N2SB **HOMO** No.242 -4.893 eV		
N2SB **HOMO-1** No.241 -4.969eV		

Table S2. The graphic representations of the frontier molecular orbits of **[N2SB-F]**$^-$.

[N2SB-F]$^-$ **LUMO+1** No.249 -1.109 eV		Excited State 1: Singlet-A 3.2324 eV 383.56 nm f=0.5702 246 -> 248 -0.13755 246 -> 249 -0.11871 247 -> 248 0.49949 247 -> 249 0.44033 Excited State 2: Singlet-A 3.2426 eV 382.36 nm f=0.9099 246 -> 248 -0.10531 246 -> 249 0.15449 247 -> 248 -0.43456 247 -> 249 0.50212 Excited State 3: Singlet-A 3.4037 eV 364.26 nm f=0.9199 245 -> 249 -0.30815 246 -> 248 0.58344 246 -> 250 -0.16608 247 -> 249 0.10871
[N2SB-F]$^-$ **LUMO** No.248 -2.047 eV		
[N2SB-F]$^-$ **HOMO** No.247 -4.893 eV		
[N2SB-F]$^-$ **HOMO-1** No.246 -4.969eV		

3. Calculation of association constants

The association constants of **C3B3** and **N2SB** were calculated according to a previously reported method.[5]

C3B3

A THF solution of **C3B3** (2 mL, 10 μM) was placed in the cell and titrated with incremental amounts of F^- by adding a 5 μL THF solution of *n*-Bu_4NF (1.8 mM), which represents a 0.45 equivalent of **C3B3**. The absorption at 405 nm was monitored.

Fitting was conducted according to the following equations:

$$C3B3 + 3F^- \leftrightarrow C3B3F3$$

$$A = k_s[C3B3] + k_p[C3B3F3]$$

$$A_0 = k_s[C3B3]_0$$

$$[C3B3]_0 = [C3B3] + [C3B3F3]$$

$$K = [C3B3F3] / [C3B3][F]^3$$

$$A/A_0 = (1 + (k_p/k_s)K[F]^3)/(1 + K[F]^3) \longrightarrow (1 - A/A_0)/[F]^3 = K(A/A_0) - K(k_p/k_s)$$

The slope of the plot of $(1 - A/A_0)/[F^-]^3$ vs A/A_0 indicates that the total binding constant $K_{(total)}$ of the three F^- was 1.3×10^{14} M^{-3} (Figure S1).

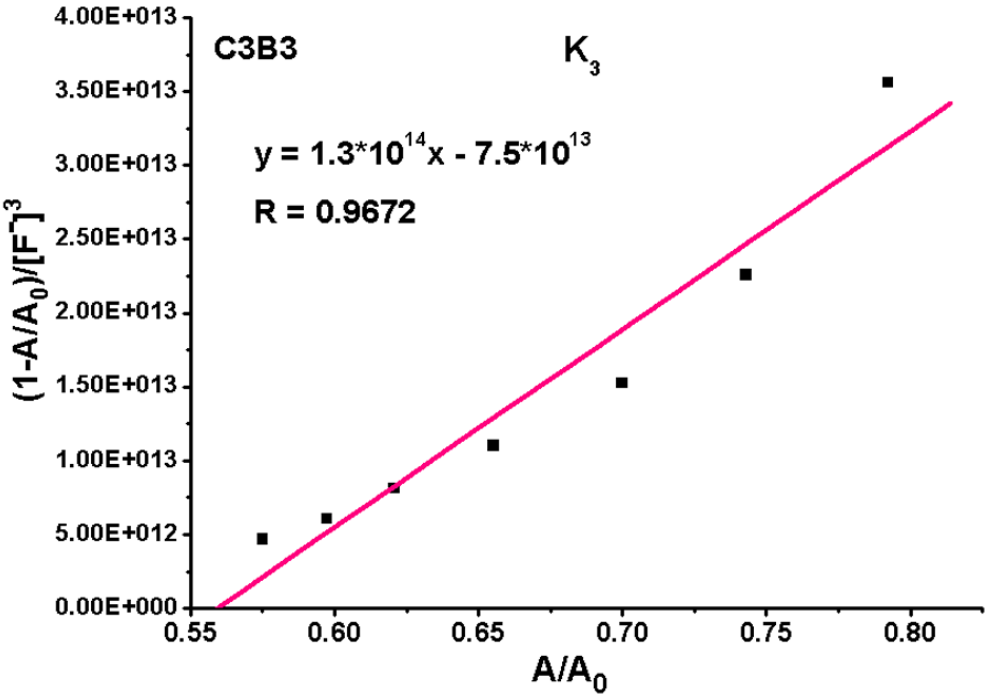


Figure S1. Results of fitting of absorption titration data of **C3B3** with F^-.

N2SB:

A THF solution of **N2SB** (2 mL, 10 μM) was placed in the cell and titrated with incremental amounts of F^- by adding a 5 μL THF solution of *n*-Bu_4NF (1.0 mM), which represents a 0.25 equivalent of **N2SB.** The absorption at 362 nm was monitored.

Fitting was conducted according to the following equations:

N2SB + F^- ↔ N2SBF

$A = k_s[\text{N2SB}] + k_p[\text{N2SBF}]$

$A_0 = k_s[\text{N2SB}]_0$

$[\text{N2SB}]_0 = [\text{N2SB}] + [\text{N2SBF}]$

$K = [\text{N2SBF}]/ [\text{N2SB}][\text{F}]$

$A/A_0 = (1 + (k_p/k_s)K[\text{F}])/(1 + K[\text{F}]) \longrightarrow (1 - A/A_0)/[\text{F}] = K(A/A_0) - K(k_p/k_s)$

The slope of the plot of $(1 - A/A_0)/[F^-]$ vs A/A_0 indicates that the binding constant K of **N2SB** for F^- was $3.5 \times 10^5\ M^{-1}$ (Figure S2).

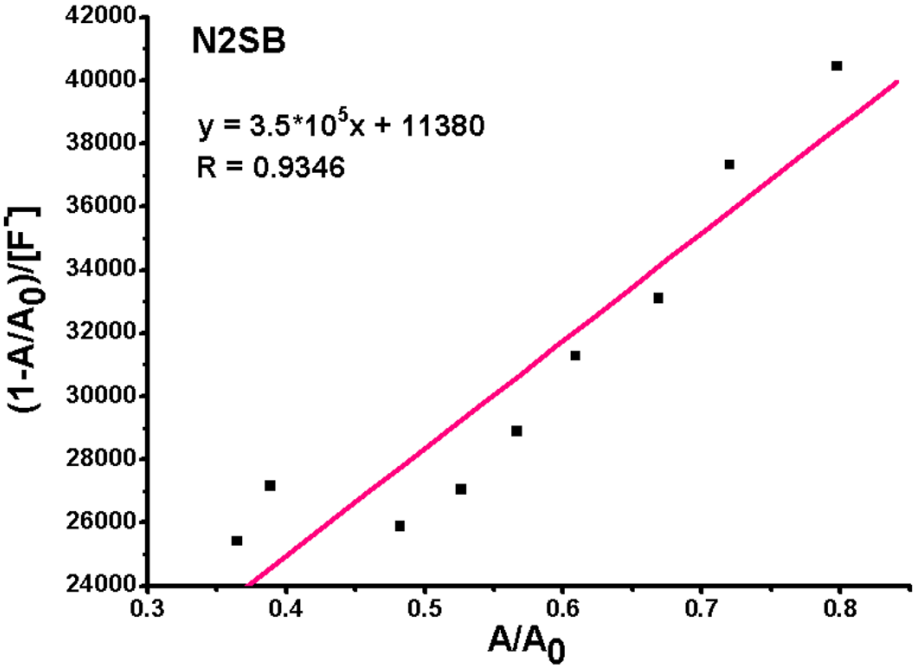


Figure S2. Results of fitting of absorption titration data of **N2SB** with F^-.

4. ^{1}H NMR and ^{13}C NMR of C3B3 and N2SB

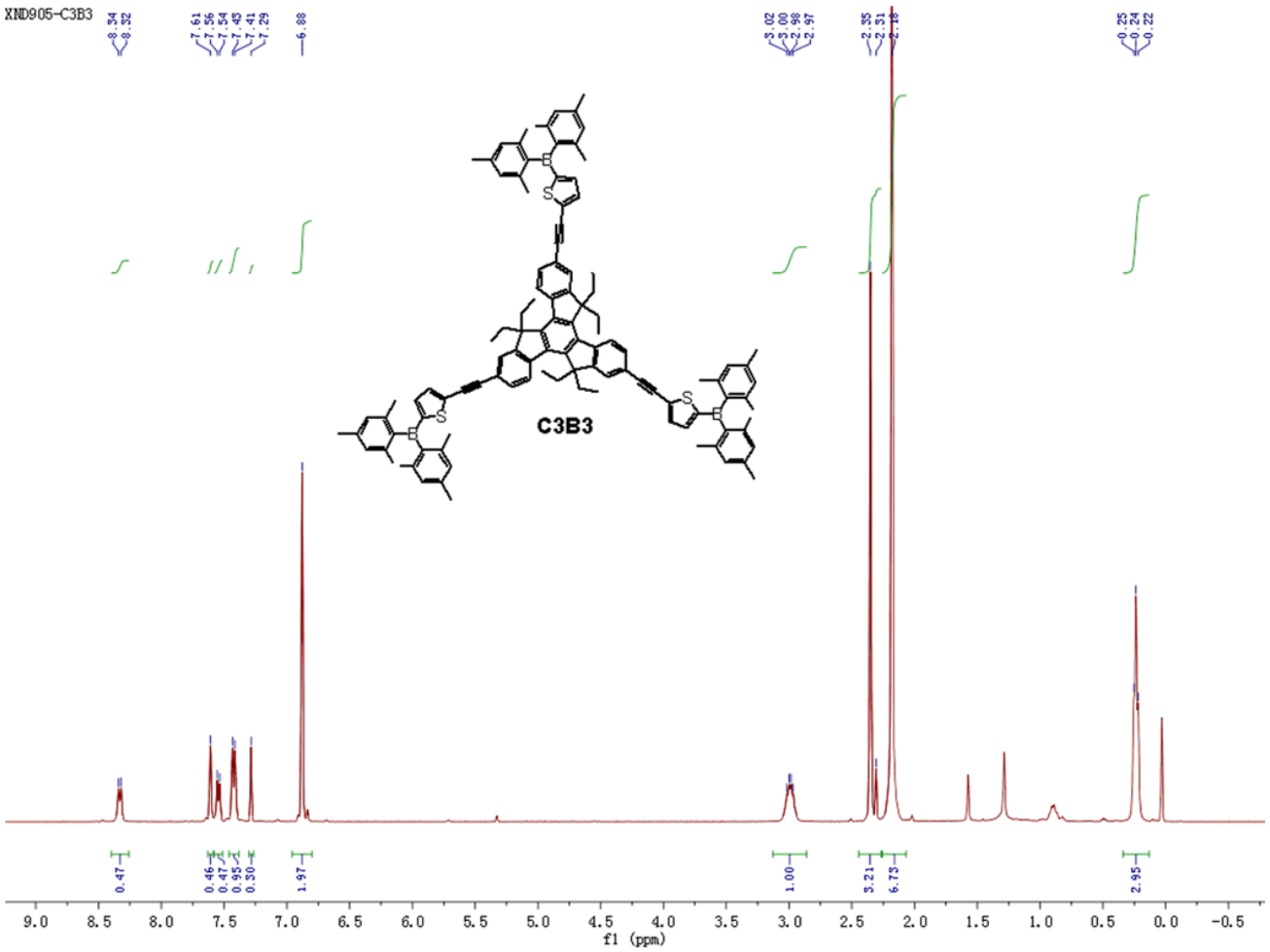


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **C3B3**.

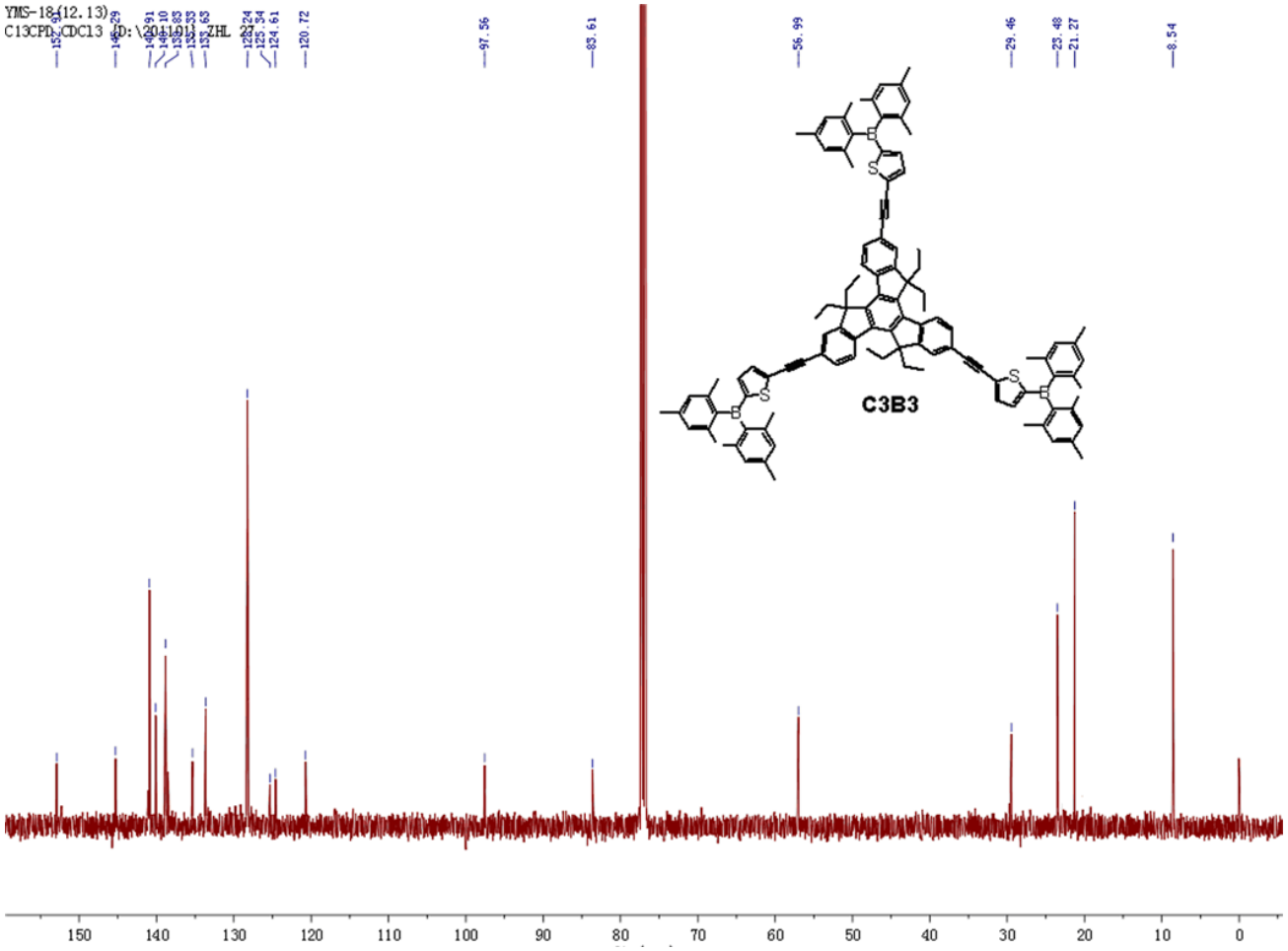


Figure S4. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **C3B3**.

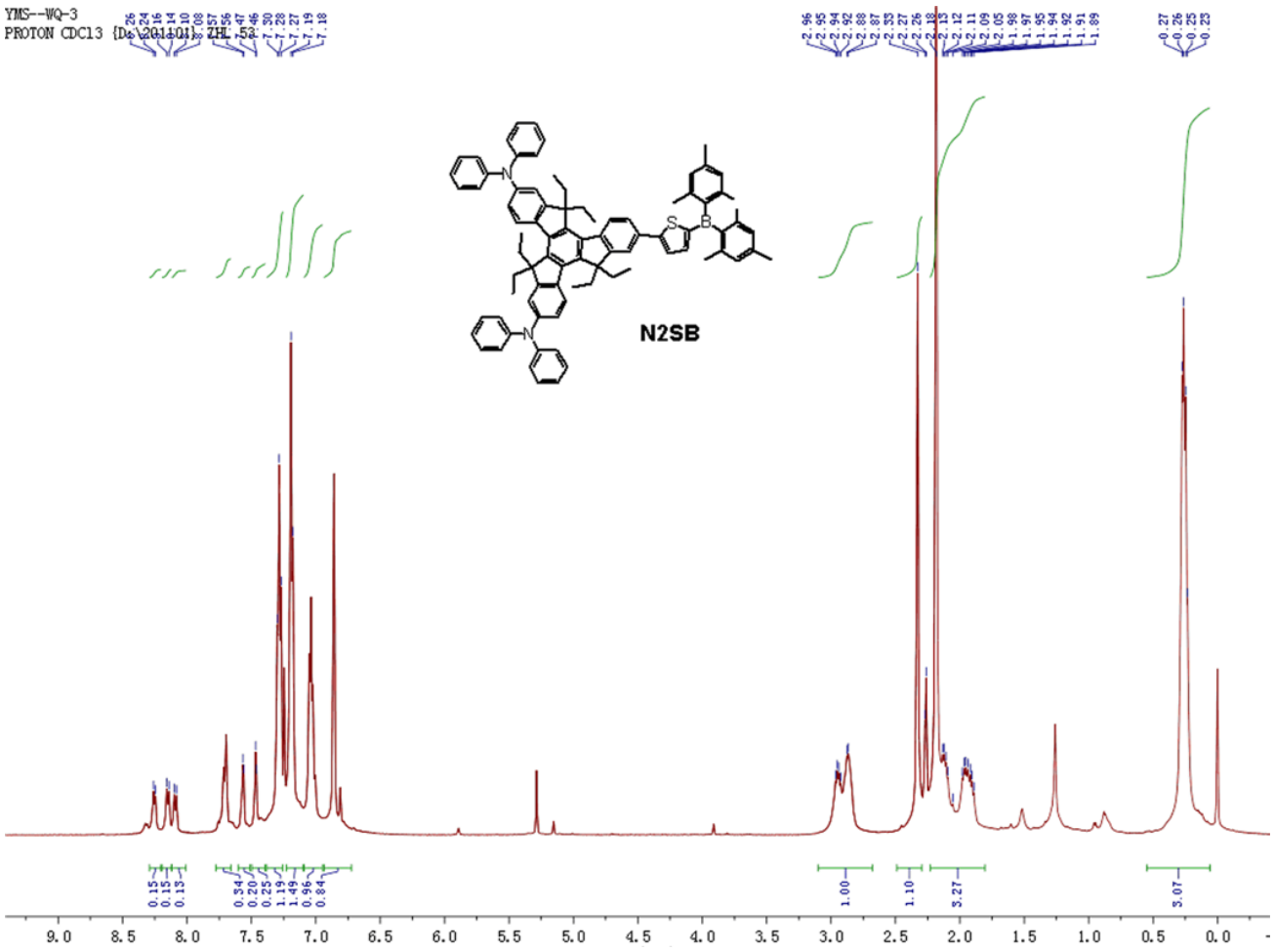


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **N2SB**.

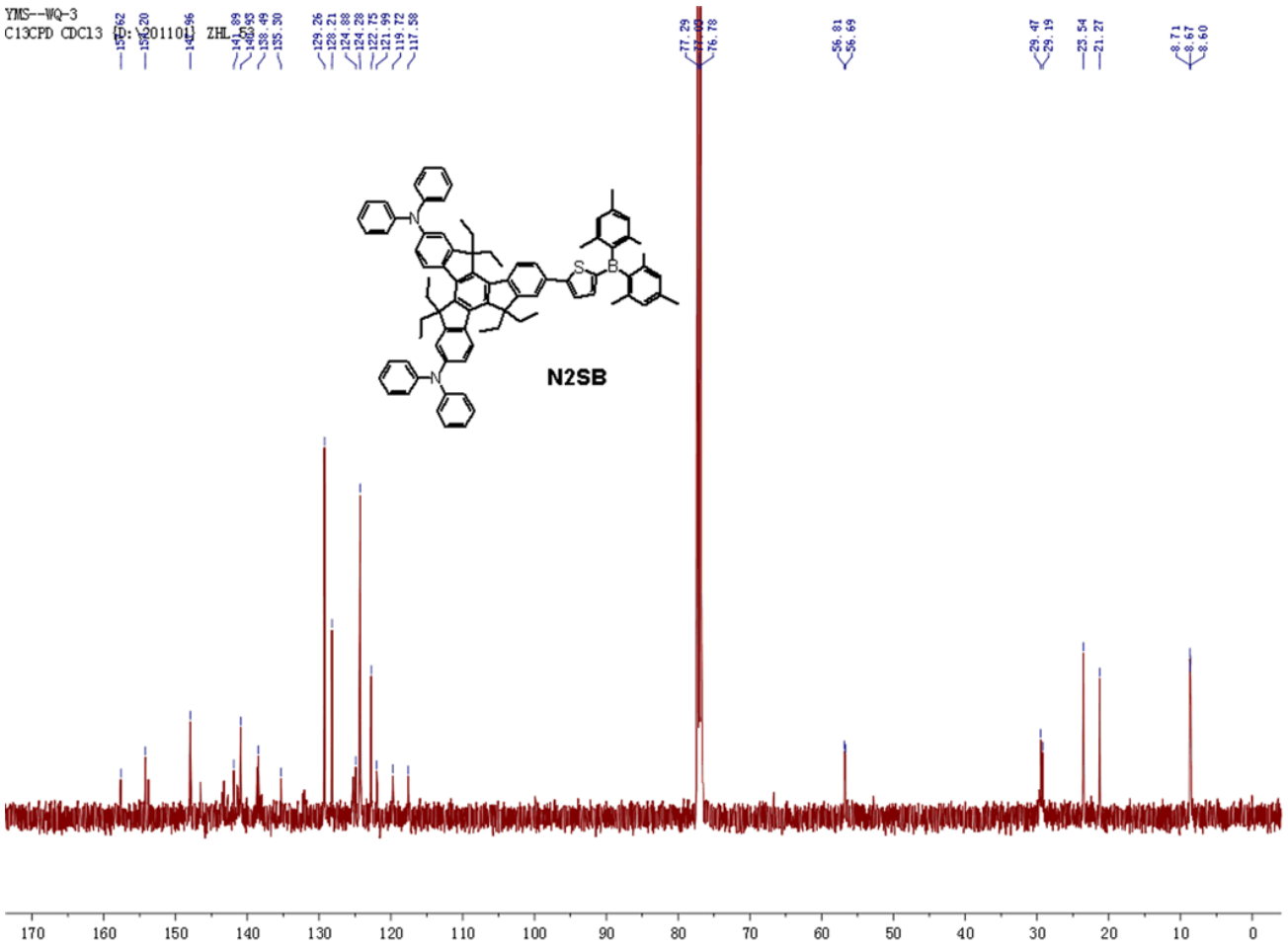


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **N2SB**.

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