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Supporting Information

# Core-Extended Nonastarazines Featuring Diverse Arm Configurations via One-Pot Sequential Reactions

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**Table of Contents**

## 1. General Methods

All reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Column chromatography was performed on silica (silica gel, 300 - 400 mesh). $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance III HD 400 or a Bruker Avance III HD 500 spectrometers operating at 500 and 101/126 MHz. Chemical shifts were reported as $\delta$ values (ppm) relative to an internal tetramethylsilane (TMS) standard. *J* values are given in Hz. The following abbreviations were used to designate multiplicities: s = singlet, t = triplet, m = multiplet. Mass spectra were obtained by electrospray ionization (ESI) or matrix-assisted laser desorption/ionization (MALDI). ESI spectra were recorded on an ESI microTOF Focus spectrometer from Bruker Daltonics. MALDI spectra were recorded on a Bruker Daltonics autoflex II LRF or a Bruker Daltonics ultrafleXtreme spectrometers.

UV/Vis spectra were recorded on a Shimadzu UV-3600 Plus spectrometer and the photoluminescence (PL) spectra were recorded by the Shimadzu RF-5301; all emission spectra were corrected for the wavelength sensitivity of the detection unit. All spectroscopy measurements were conducted with spectroscopic grade solvents. Conventional quartz cells (light path 1 cm) were used. The solvents used for spectra were toluene, o-dichlorobenzene (o-DCB), ether, chloroform (CF), tetrahydrofuran (THF) and dichloromethane (DCM). Without otherwise noted, the solutions were tested in $10^{-5}$ M, room temperature. Absolute quantum yields were determined by a calibrated integrating sphere (Hamamatsu Quantaurus-QY C11347-12).

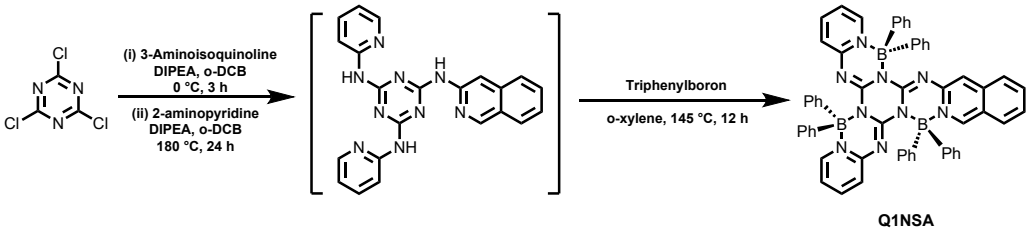
Thermo gravimetric analysis was tested by Netzsch Tg209f1, with heating range about 30 – 800$^{o}$C and heating rate about 20$^{o}$C/min.

Single crystal data for these molecules were collected on Rigaku XtaLAB P2000 FR-X at 100 K. Single crystal structure was solved by ShelXT program using Intrinsic Phasing method and refined by ShelXL refinement package using Least Squares minimization, which worked on the Olex2 program.[1]

# 2. Synthesis and Characterization

Triphenylboron were synthesized according to literature procedures.[2]

**Synthesis of Q1NSA**

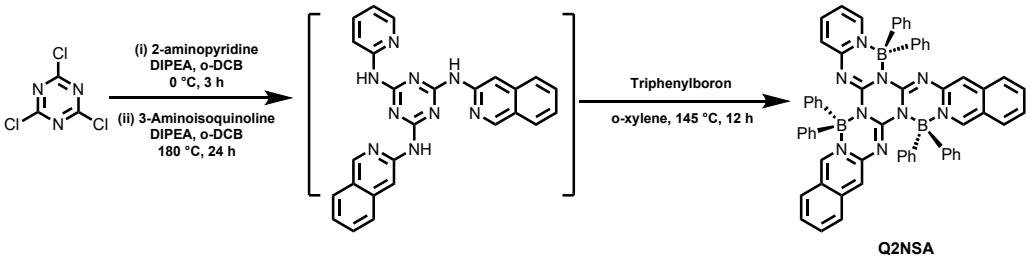



**Scheme S1.** Synthetic route of Q1NSA.

In a 100 mL round-bottomed flask equipped with a stirrer and a nitrogen inlet, cyanuric chloride (0.92 g, 5 mmol) was added. The flask was then purged with nitrogen at room temperature to ensure an inert atmosphere. Subsequently, 10 mL of ultra-dry ortho-dichlorobenzene was introduced into the flask. The mixture was stirred under nitrogen protection at 0 °C for 15 minutes. DIPEA (2.6 mL, 15 mmol) was then added dropwise to the stirred solution, maintaining the reaction temperature at 0 °C. Stirring was continued for an additional 15 minutes. Following this, another 10 mL of ultra-dry ortho-dichlorobenzene was added, and 3-aminoisoquinoline (0.72 g, 5 mmol) was introduced dropwise while keeping the reaction mixture at 0 °C. The reaction was allowed to proceed at 0 °C for 3 hours, and then it was allowed to warm to room temperature. Subsequently, 2-aminopyridine (0.94 g, 10 mmol) was added to the flask, and the mixture was heated to 180 °C for a 24-hour reaction period. After the reaction was complete, the flask was cooled to room temperature, and 50 mL of anhydrous ethanol was added. The mixture was stirred for 3 hours, and then it was filtered to remove any insoluble material. The resulting solid was dried to obtain approximately 0.77 g of the intermediate product.

In a separate 100 mL round-bottomed flask, the obtained intermediate product (0.77 g) and triphenylboron (1.60 g, 6.6 mmol) were added. The flask was purged with nitrogen at room temperature to ensure an inert atmosphere. Then, 30 mL of ultra-dry ortho-xylene was introduced into the flask. The reaction mixture was heated to 145 °C under nitrogen protection and stirred for 12 hours. After the reaction was complete, the crude product was purified by column chromatography on silica gel using a mixture of petroleum ether and dichloromethane (2:1 v/v) as the eluent. The purified product was then recrystallized to obtain Q1NSA as a yellow solid, yielding 300 mg (8%). $^1$H NMR (500 MHz, Methylene Chloride-$d_2$) δ 8.41 (s, 1H), 7.57 - 7.50 (m, 4H), 7.45 - 7.33 (m, 14H), 7.29 - 7.24 (m, 1H), 7.22 - 7.07 (m, 18H), 6.64 - 6.57 (m, 3H), 6.22 (ddd, *J* = 8.3, 6.6, 1.4 Hz, 2H), 6.17 (dd, *J* = 8.4, 1.5 Hz, 1H). $^{13}$C NMR (126 MHz, Methylene Chloride-$d_2$) δ 154.49, 154.30, 151.09, 151.05, 150.76, 148.11, 147.58, 142.63, 142.53, 141.43, 141.22, 140.62, 134.03, 133.81, 133.75, 133.72, 133.68, 129.53, 127.80, 127.71, 127.69, 126.83, 126.41, 126.27, 126.21, 126.12, 124.48, 122.21, 122.13, 117.21, 116.92, 116.85, 115.80. MALDI-TOF(m/s): calculated for $C_{58}H_{44}B_3N_9$ 899.400, found 898.174.

**Synthesis of Q2NSA**




**Scheme S2.** Synthetic route of Q2NSA.

The synthetic and purification procedures were the same as used for the synthesis of Q1NSA, but with a different adding sequence of the reactants 3-aminoisoquinoline and 2-aminopyridine.

In a 100 mL reaction flask, cyanuric chloride (0.92 g, 5 mmol) was added. The system was purged with nitrogen at room temperature to displace oxygen. Subsequently, 10 mL of ultra-dry ortho-dichlorobenzene was introduced into the flask. The mixture was stirred under nitrogen protection at 0 °C for 15 minutes. DIPEA (2.6 mL, 15 mmol) was then added dropwise to the stirred solution, and stirring was continued for an

additional 15 minutes. Afterward, another 10 mL of ultra-dry ortho-dichlorobenzene was added, and 2-aminopyridine (0.47 g, 5 mmol) was introduced dropwise while maintaining the reaction temperature at 0 °C. The reaction mixture was stirred at 0 °C for 3 hours before being allowed to warm to room temperature. Subsequently, 3-aminoisoquinoline (1.14 g, 10 mmol) was added to the flask, and the reaction mixture was heated to 180 °C for a 24-hour reaction period. After cooling to room temperature, 50 mL of anhydrous ethanol was added, and the mixture was stirred for 3 hours. The resulting solid was filtered and dried to obtain approximately 1.80 g of the intermediate product.

In another 100 mL reaction flask, the obtained intermediate product (1.80 g) and triphenylboron (3.30 g, 13.8 mmol) were added. The flask was purged with nitrogen at room temperature to ensure an inert atmosphere. Then, 30 mL of ultra-dry ortho-xylene was introduced into the flask. The reaction mixture was heated to 145 °C under nitrogen protection and stirred for 12 hours. After the reaction was complete, the crude product was purified by column chromatography on silica gel using a mixture of petroleum ether and dichloromethane (2:1 v/v) as the eluent. The purified product was then recrystallized to afford Q2NSA as a yellow solid, yielding 350 mg (7%). $^{1}$H NMR (500 MHz, Methylene Chloride-$d_2$) δ 8.42 (d, *J* = 11.0 Hz, 2H), 7.57 - 7.51 (m, 5H), 7.49 - 7.31 (m, 14H), 7.28 - 7.23 (m, 2H), 7.22 - 7.09 (m, 18H), 6.64 - 6.55 (m, 3H), 6.19 (dddd, *J* = 29.5, 8.1, 6.3, 1.4 Hz, 2H). $^{13}$C NMR (126 MHz, Methylene Chloride-$d_2$) δ 154.67, 154.49, 151.36, 151.05, 148.64, 148.60, 148.39, 148.10, 147.58, 147.46, 147.44, 142.53, 142.45, 141.25, 141.22, 141.04, 140.64, 140.62, 133.83, 133.82, 133.76, 133.75, 133.70, 133.68, 129.52, 127.81, 127.79, 127.68, 126.83, 126.64, 126.36, 126.18, 126.12, 126.06, 124.39, 124.33, 122.20, 122.13, 116.92, 116.85, 116.57, 115.80, 115.66, 115.59. MALDI-TOF(m/s): calculated for $C_{62}H_{46}B_3N_9$ 949.416, found 948.267.

## 3. Thermo Gravimetric Analysis

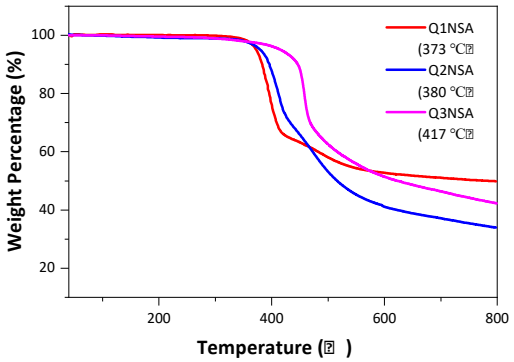



**Figure S1.** The TGA curves of Q1NSA, Q2NSA and Q3NSA.

## 4. Crystal Structure

**Table S1.** Crystal data for Q1NSA.

| Identification code | Q1NSA |
|---|---|
| CCDC number | 2356518 |
| Empirical formula | $C_{58}H_{44}B_3N_9$ |
| Formula weight | 899.40 |
| Temperature/K | 150.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.3537(3) |
| b/Å | 14.1448(4) |
| c/Å | 19.2407(5) |
| α/° | 82.035(2) |
| β/° | 75.721(2) |
| γ/° | 68.754(3) |
| Volume/Å$^3$ | 2541.39(13) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.296 |
| μ/mm$^{-1}$ | 0.595 |
| F(000) | 1040 |
| Crystal size/mm$^3$ | 0.05 × 0.04 × 0.03 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.714 to 148.016 |
| Index ranges | -12 ≤ h ≤ 12,<br>-16 ≤ k ≤ 17,<br>-17 ≤ l ≤ 23 |
| Reflections collected | 29136 |
| Independent reflections | 9823 [$R_{int}$ = 0.0270, $R_{sigma}$ = 0.0311] |
| Data/restraints/parameters | 9823/0/695 |
| Goodness-of-fit on F$^2$ | 1.076 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0696,<br>$wR_2$ = 0.1982 |
| Final R indexes [all data] | $R_1$ = 0.0777,<br>$wR_2$ = 0.2046 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.56/-0.62 |

**Table S2.** Crystal data for Q2NSA.

| Identification code | Q2NSA |
|---|---|
| CCDC number | 2356519 |
| Empirical formula | $C_{62}H_{46}B_3N_9$ |
| Formula weight | 949.42 |
| Temperature/K | 150.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.2345(3) |
| b/Å | 15.7381(4) |
| c/Å | 18.3839(4) |
| α/° | 90.259(2) |
| β/° | 95.393(2) |
| γ/° | 112.624(2) |
| Volume/Å$^3$ | 3249.74(14) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.159 |
| μ/mm$^{-1}$ | 0.526 |
| F(000) | 1192 |
| Crystal size/mm$^3$ | 0.06 × 0.04 × 0.03 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 4.832 to 148.372 |
| Index ranges | -14 ≤ h ≤ 7,<br>-16 ≤ k ≤ 19,<br>-22 ≤ l ≤ 22 |
| Reflections collected | 33919 |
| Independent reflections | 12537 [$R_{int}$ = 0.0272, $R_{sigma}$ = 0.0326] |
| Data/restraints/parameters | 12537/0/795 |
| Goodness-of-fit on $F^2$ | 1.039 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0616,<br>$wR_2$ = 0.1887 |
| Final R indexes [all data] | $R_1$ = 0.0737,<br>$wR_2$ = 0.2005 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.57/-0.33 |

**Table S3.** Planarity parameters, MPP; distance of B atom deviating from BN heterocyclic plane, $d_{dev}$; and dihedral angle between two phenyls on B atom for single crystal structures, $\vartheta$. Average values are given in parentheses.

| Molecules | MPP (Å) | $d_{dev}$ (Å) | $\vartheta$ (°) |
|---|---|---|---|
| Q1NSA | 0.514 | 0.590/0.535/0.518 (0.548) | 86.14/78.09/69.00 (77.74) |
| Q2NSA | 0.466 | 0.551/0.543/0.373 (0.489) | 69.96/69.11/58.22 (65.76) |
| Q3NSA | 0.242 | 0.580/0.047/0.159 (0.262) | 74.28/46.72/43.84 (54.95) |

**Table S4.** The bond lengths from single crystal structures. (The values in parentheses are the average bond length values.)

| Molecule | C1-N1 (Å) | C2-N1 (Å) | C2-N2 (Å) | B1-N2 (Å) | B1-N3 (Å) | C1-N3 (Å) | N3-C1' (Å) |
|---|---|---|---|---|---|---|---|
| Q1NSA | 1.294 | 1.353 | 1.372 | 1.602 | 1.617 | 1.373 | 1.378 |
| | 1.301 | 1.359 | 1.347 | 1.602 | 1.612 | 1.369 | 1.383 |
| | 1.301 | 1.346 | 1.350 | 1.606 | 1.617 | 1.365 | 1.385 |
| | (1.299) | (1.353) | (1.356) | (1.603) | (1.615) | (1.369) | (1.382) |
| Q2NSA | 1.303 | 1.365 | 1.379 | 1.614 | 1.600 | 1.362 | 1.386 |
| | 1.294 | 1.363 | 1.376 | 1.611 | 1.602 | 1.375 | 1.378 |
| | 1.307 | 1.359 | 1.357 | 1.597 | 1.623 | 1.371 | 1.388 |
| | (1.301) | (1.362) | (1.371) | (1.607) | (1.608) | (1.369) | (1.384) |
| Q3NSA | 1.306 | 1.361 | 1.384 | 1.593 | 1.604 | 1.371 | 1.386 |
| | 1.300 | 1.362 | 1.368 | 1.621 | 1.595 | 1.362 | 1.384 |
| | 1.295 | 1.366 | 1.378 | 1.621 | 1.594 | 1.370 | 1.375 |
| | (1.300) | (1.363) | (1.377) | (1.612) | (1.598) | (1.368) | (1.382) |

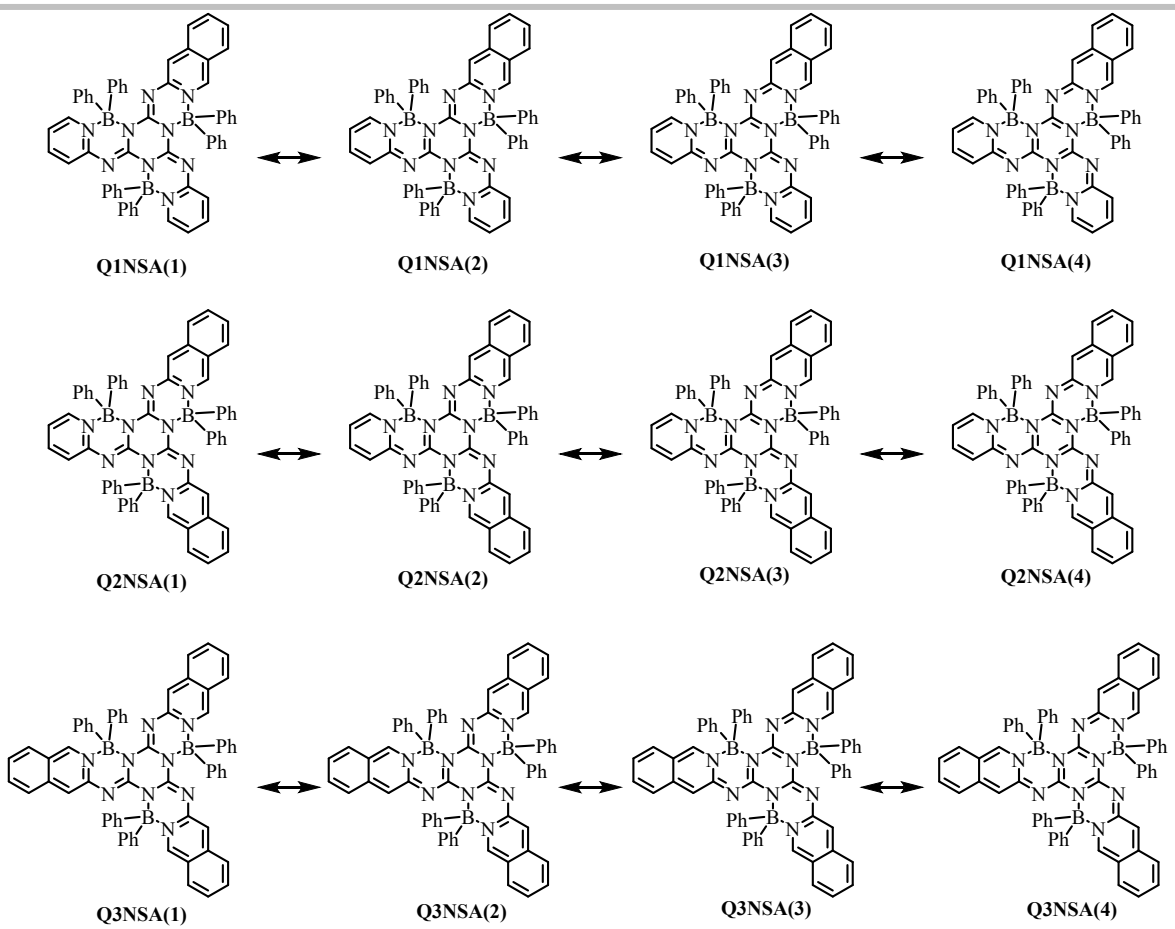



**Figure S2.** Possible resonance structures of Q1NSA, Q2NSA and Q3NSA.

## 5. Photophysical Properties

The steady-state absorption and PL spectra at room temperature for Q1NSA, Q2NSA and Q3NSA were tested in solvents of different polarities, as shown in Figure S3. All molecules were tested in$10^{-5}$ M solution.

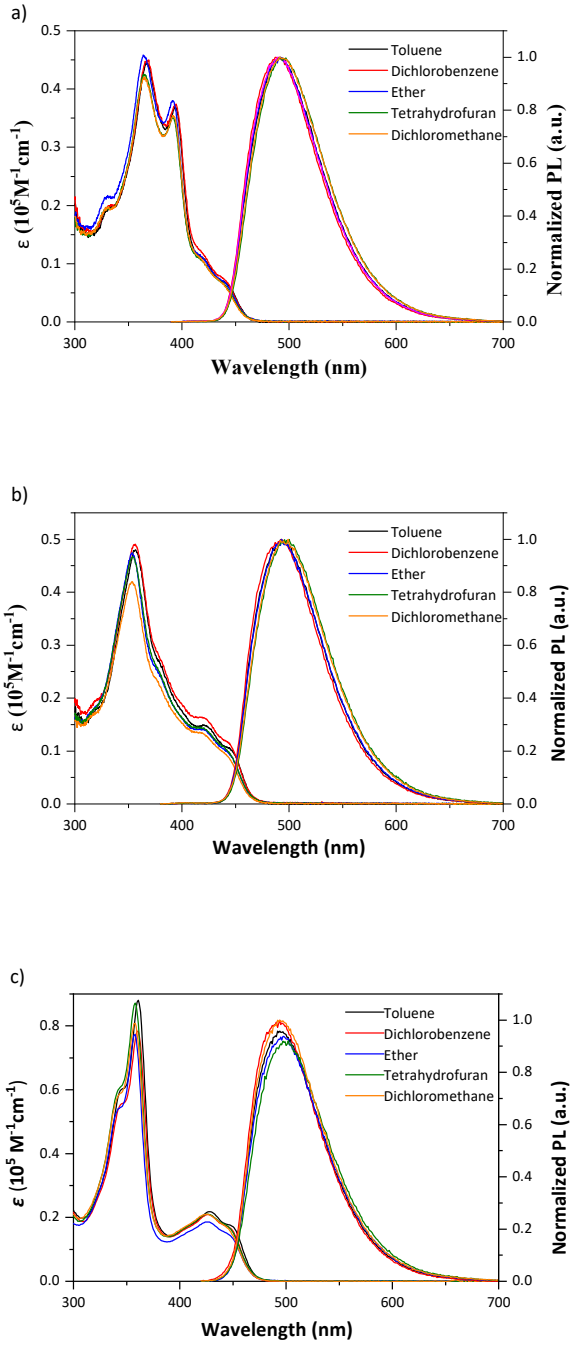



**Figure S3.** Absorption and normalized fluorescence spectra of a) Q1NSA, b) Q2NSA and c) Q3NSA.

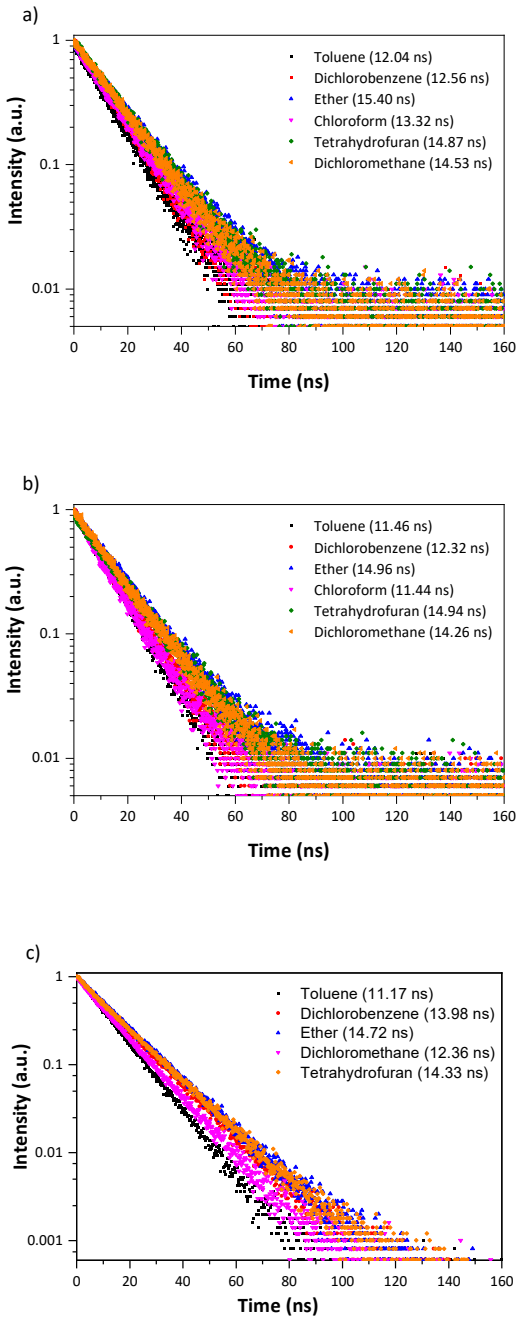



**Figure S4.** Fluorescence decay curves of a) Q1NSA, b) Q2NSA and c) Q3NSA.

# 6. Electrochemical Characterization

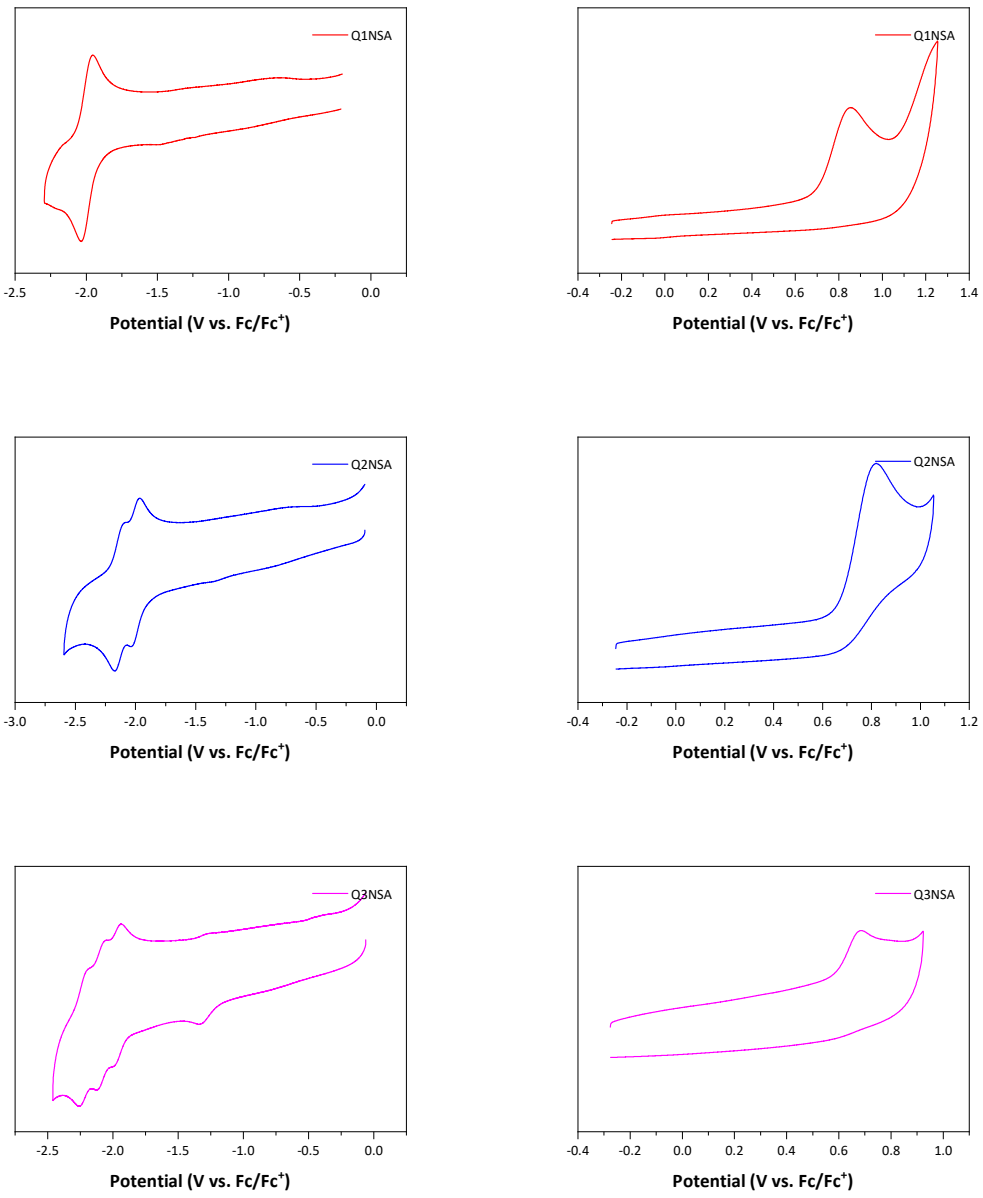
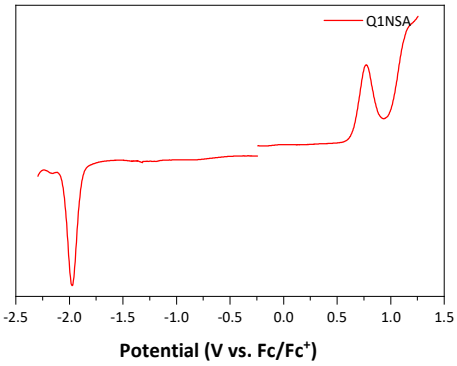
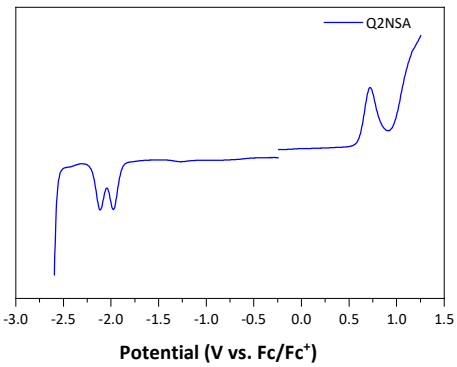



**Figure S5**. The cyclic voltammetry curve of Q1NSA, Q2NSA and Q3NSA.



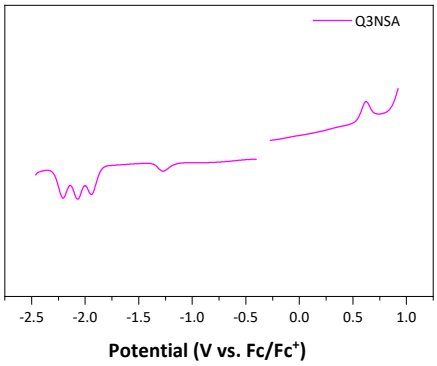




**Figure S6**. The DPV curve of Q1NSA, Q2NSA and Q3NSA.

# 7. Theoretical Calculation

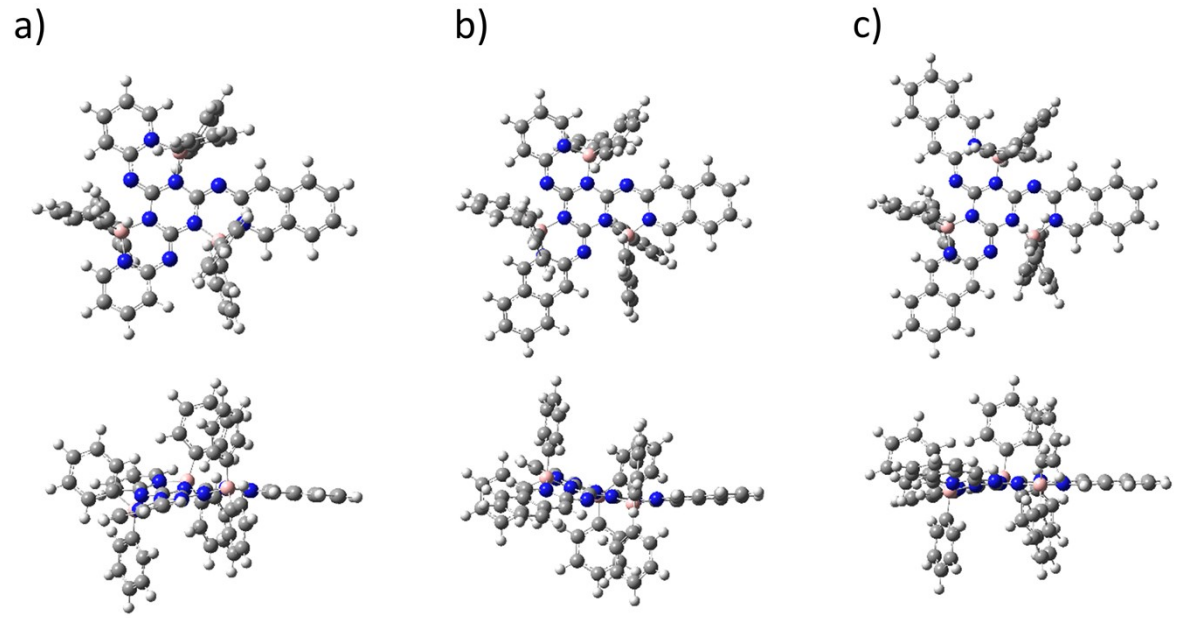



**Figure S7.** The optimal configuration of a) Q1NSA, b) Q2NSA and c) Q3NSA.

**Table S5.** Planarity parameters MPP, distance of B atom from BN heterocyclic plane $d_{dev}$, and dihedral angle between two phenyls on B atom for the optimized configuration. (Average value is given in parentheses.)

| Molecules | MPP (Å) | $d_{dev}$ (Å) | $\vartheta$ (°) |
|---|---|---|---|
| Q1NSA | 0.249 | 0.318/0.161/0.034 | 52.45/48.94/44.87 |
| | | (0.171) | (48.75) |
| Q2NSA | 0.343 | 0.412/0.338/0.145 | 49.88/55.82/50.20 |
| | | (0.255) | (51.97) |
| Q3NSA | 0.221 | 0.327/0.241/0.003 | 53.32/51.92/45.26 |
| | | (0.190) | (50.17) |

**Table S6.** The bond lengths of obtained from optimal configuration. (The values in parentheses are the average bond length values.)

| Molecule | C1-N1 (Å) | C2-N1 (Å) | C2-N2 (Å) | B1-N2 (Å) | B1-N3 (Å) | C1-N3 (Å) | N3-C1' (Å) |
|---|---|---|---|---|---|---|---|
| Q1NSA | 1.301 | 1.353 | 1.384 | 1.631 | 1.628 | 1.376 | 1.380 |
| | 1.310 | 1.347 | 1.362 | 1.623 | 1.630 | 1.372 | 1.384 |
| | 1.309 | 1.348 | 1.362 | 1.627 | 1.623 | 1.366 | 1.386 |
| | (1.307) | (1.349) | (1.369) | (1.627) | (1.627) | (1.371) | (1.383) |
| Q2NSA | 1.303 | 1.354 | 1.386 | 1.635 | 1.607 | 1.373 | 1.384 |
| | 1.302 | 1.353 | 1.384 | 1.629 | 1.626 | 1.377 | 1.381 |
| | 1.311 | 1.347 | 1.363 | 1.623 | 1.628 | 1.370 | 1.387 |
| | (1.305) | (1.351) | (1.378) | (1.629) | (1.620) | (1.373) | (1.384) |
| Q3NSA | 1.305 | 1.350 | 1.384 | 1.629 | 1.624 | 1.374 | 1.386 |
| | 1.305 | 1.351 | 1.383 | 1.634 | 1.617 | 1.371 | 1.384 |
| | 1.304 | 1.352 | 1.384 | 1.631 | 1.626 | 1.373 | 1.385 |
| | (1.305) | (1.351) | (1.384) | (1.631) | (1.622) | (1.373) | (1.385) |

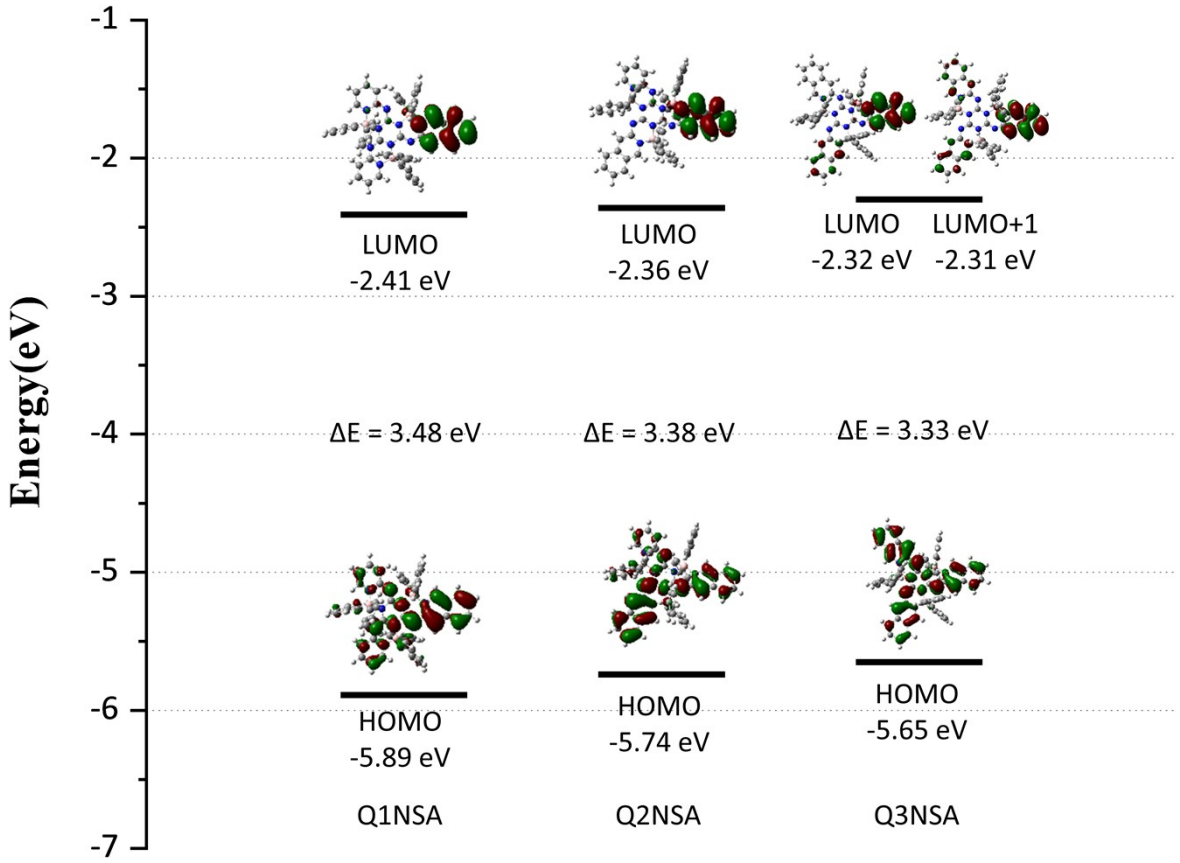



**Figure S8.** Frontier orbital distribution and energy levels of Q1NSA, Q2NSA and Q3NSA were calculated using the B3PW91 functional with the def2-TZVP basis set at an isosurface value of 0.02 a.u.

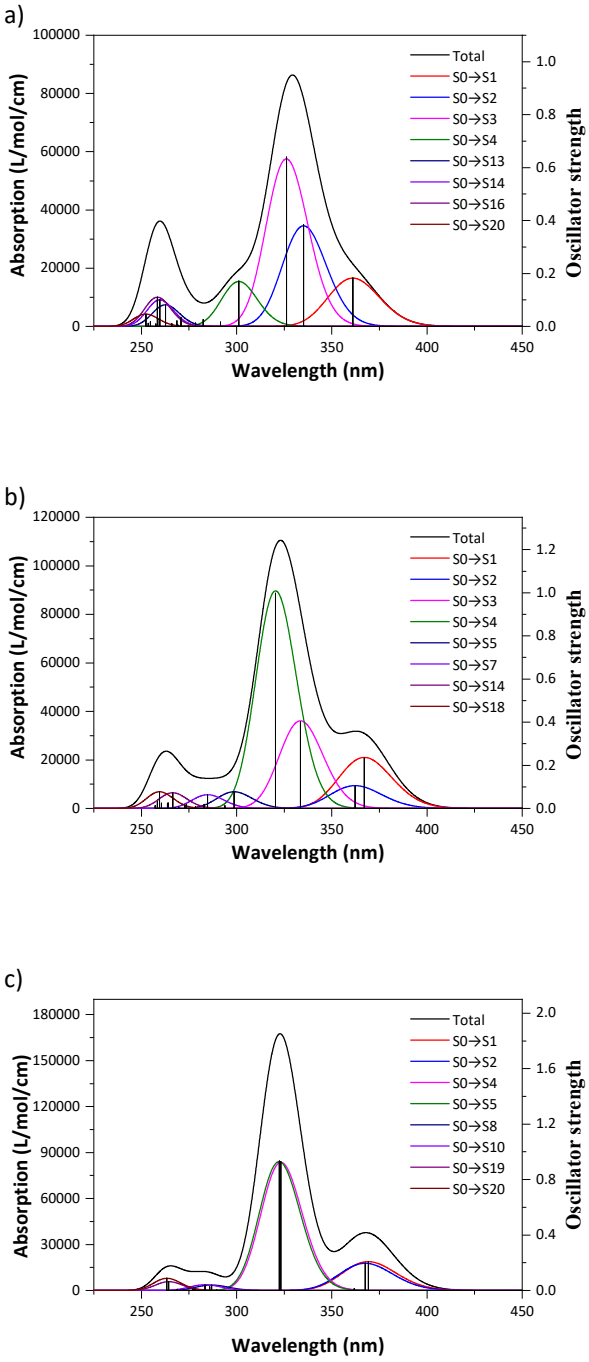



**Figure S9**. The UV-visible absorption spectra of a) Q1NSA, b) Q2NSA and c) Q3NSA obtained from theoretical calculations.

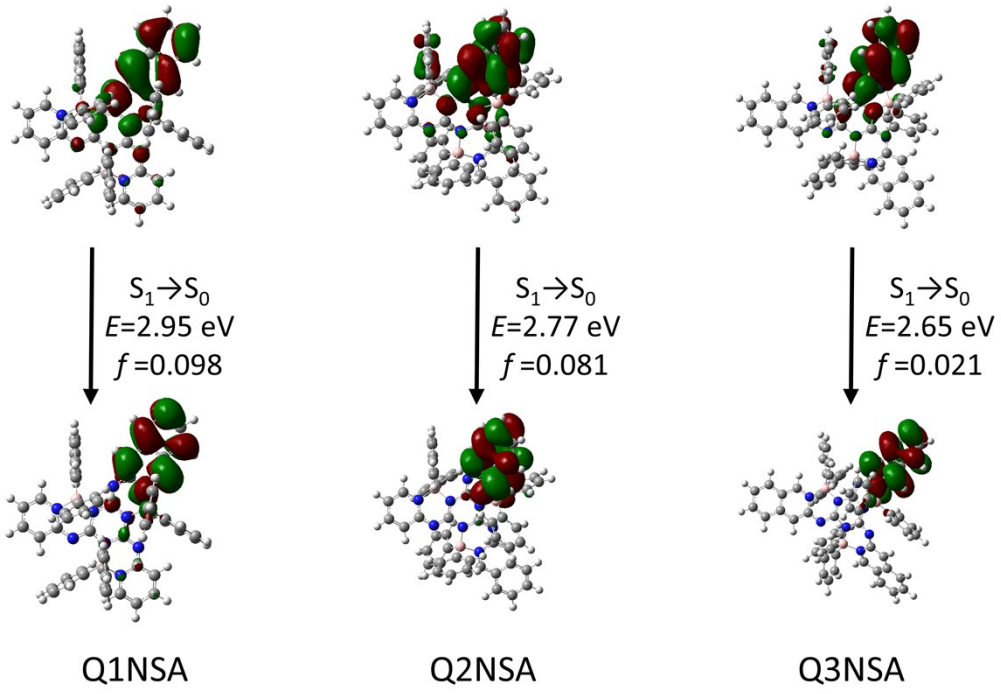



**Figure S10**. Oscillator strength, energy levels and electronic distribution in the $S_1 \rightarrow S_0$ transitions of Q1NSA, Q2NSA and Q3NSA were calculated at the level of M06-2X/6-311g(d,p).

## 8. Reference

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

[2] J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2016**, *55*, 613.

# 9. $^{1}$H and $^{13}$C NMR Spectra

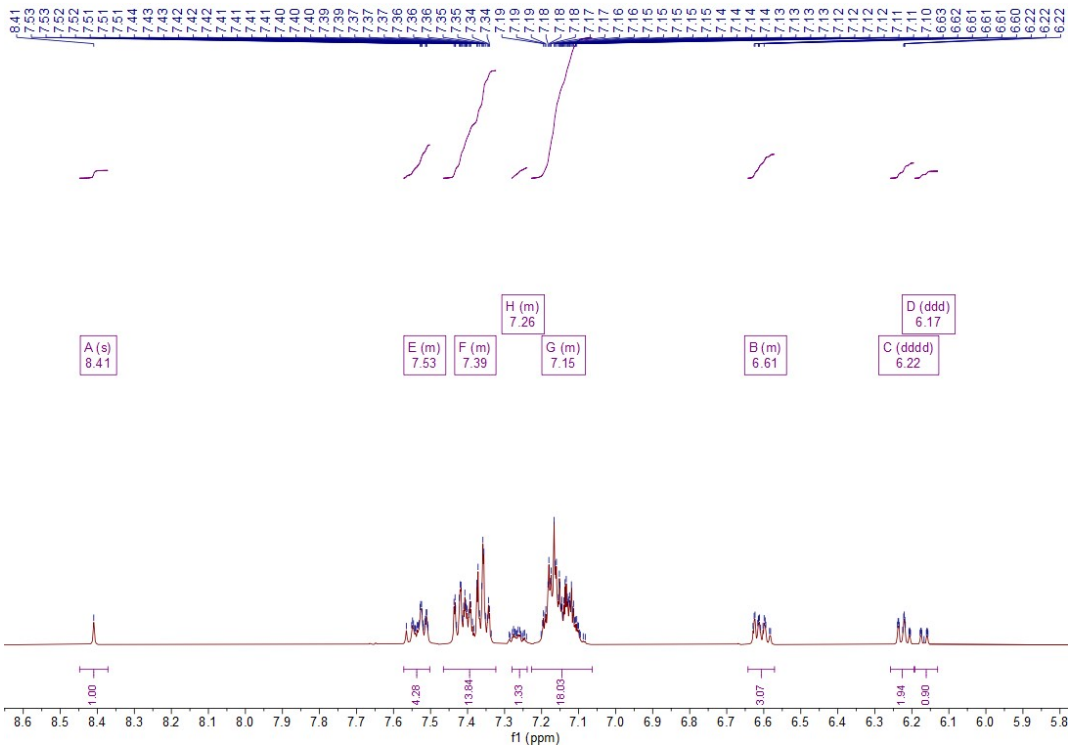



**Figure S11**. $^{1}$H NMR spectra of Q1NSA (500 MHz, $CD_2Cl_2$)

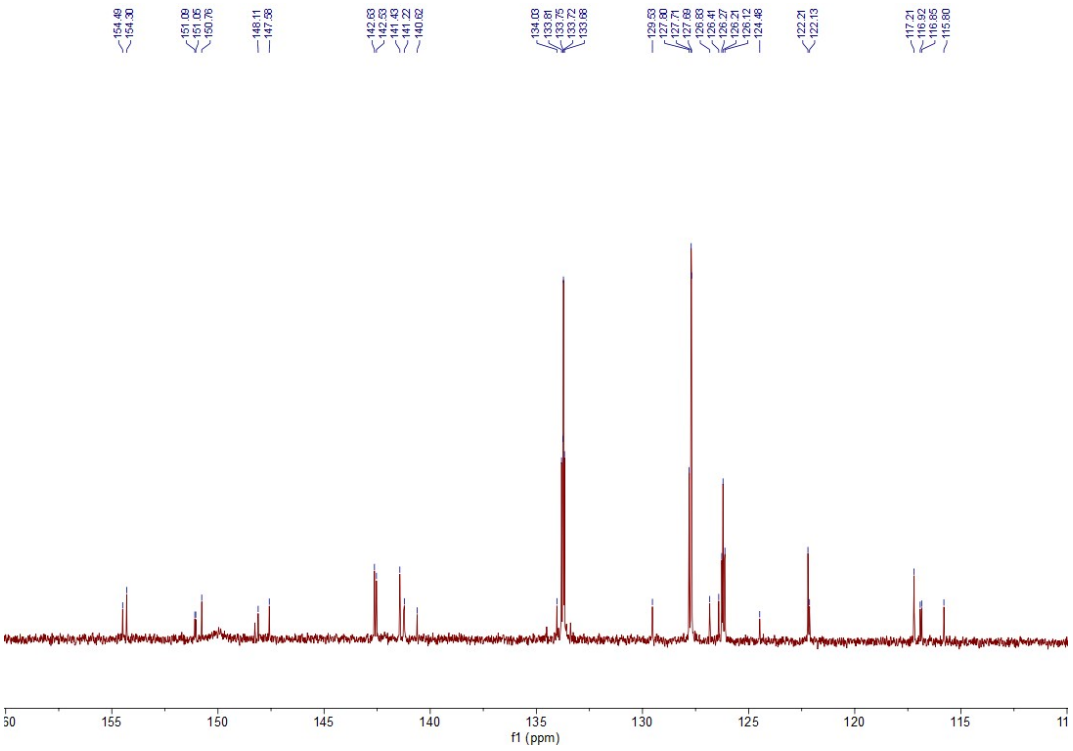



**Figure S12**. $^{13}$C NMR spectra of Q1NSA (126 MHz, $CD_2Cl_2$)

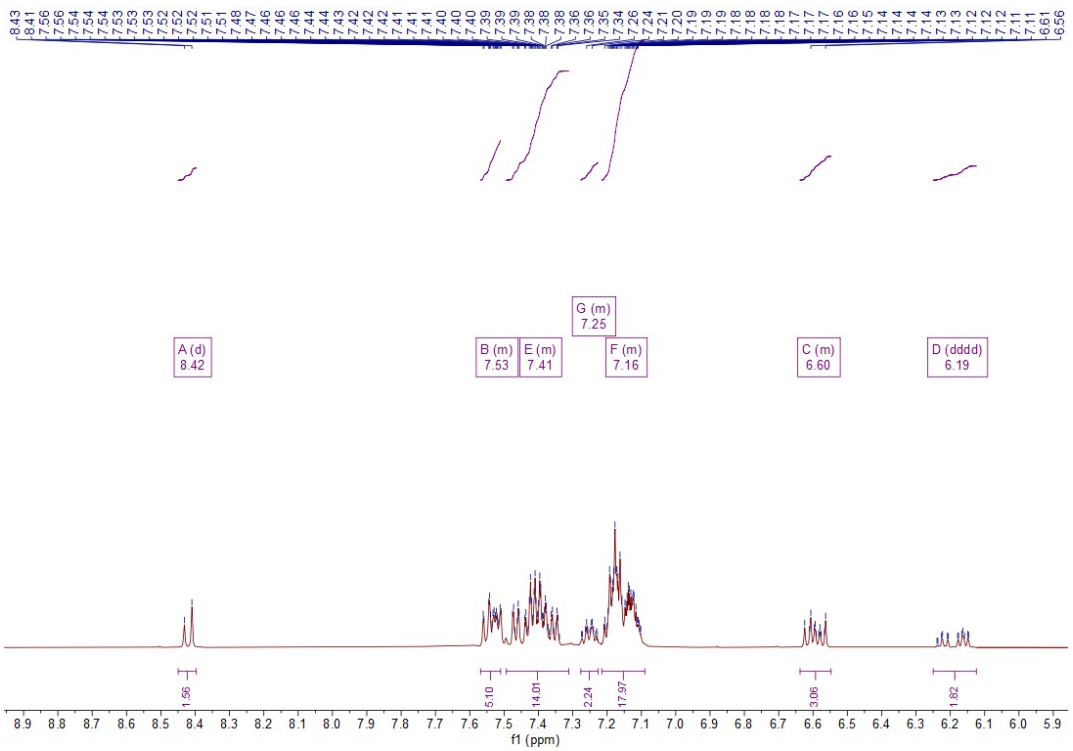



**Figure S13**. $^{1}$H NMR spectra of Q2NSA (500 MHz, $CD_2Cl_2$)

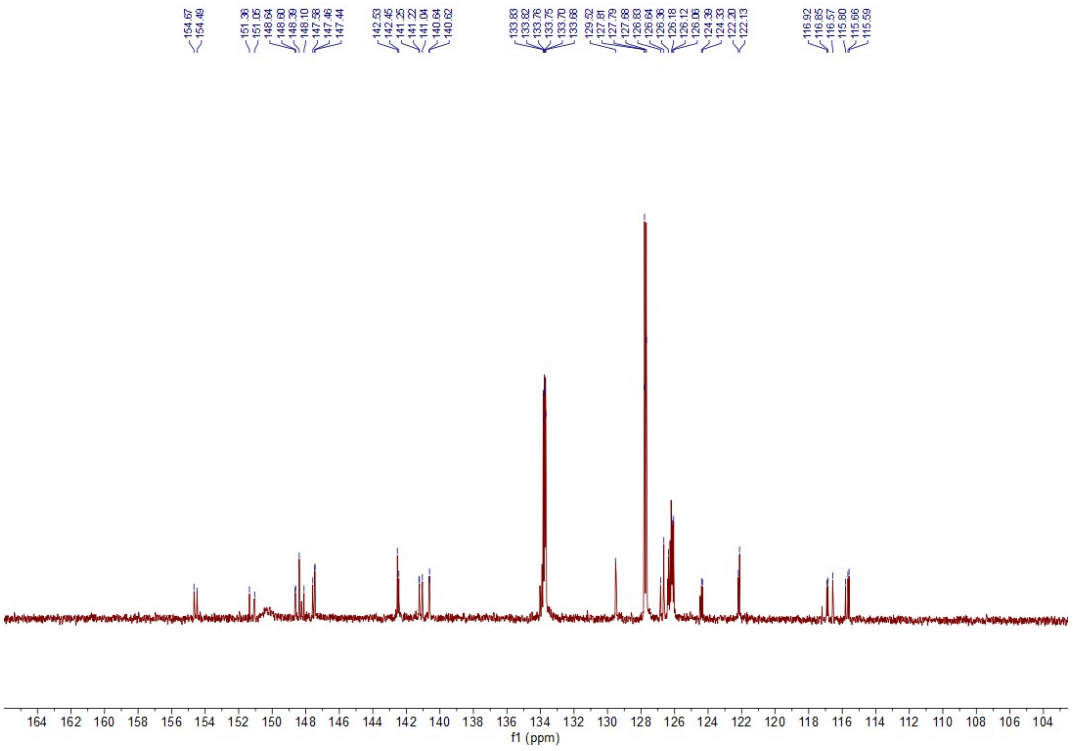



**Figure S14**. $^{13}$C NMR spectra of Q2NSA (126 MHz, $CD_2Cl_2$)