Supplementary Information for

Multi-Heteroatom Doped Nanographenes: Enhancing Photosensitization Capacity by Forming an Electron Donor-Acceptor Architecture

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General Information

Solvents and chemicals were purchased from commercial sources and used directly without further purification. Molecular sieves were activated in an oven and solvents for reactions were stored with molecular sieves. Petroleum ether (PE) used had a boiling range of 60−90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was generally performed through silica gel (200−300 mesh). All reactions were run open to air unless specifically described. NMR spectra were recorded with Bruker-400, 500 or 600 MHz spectrometers. Unless specified otherwise, the NMR spectra were recorded at 22 °C; Chemical shifts were reported in parts per million (ppm). Chemical shifts were reported in ppm using TMS or deuterated solvents as internal standards standards (^{1}H NMR: $CDCl_3$, δ 7.26; DMSO-d_6 δ 2.5; MeOD δ 3.31; for ^{13}C NMR: $CDCl_3$, δ 77.0; DMSO-d_6 δ 39.6; MeOD δ 48.8). Multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (*J*) are reported in Hertz (Hz). Structural assignments were made with additional information from COSY, ROESY and NOESY experiments. UV-Vis absorption spectra were recorded using a 1-cm quartz cuvette on a Shimadzu-UV-2600 spectrometer. Fluorescence spectra were recorded using a 1-cm quartz cuvette or powder form on a Gangdong F-320 spectrofluorometer at 25 ºC. High-resolution mass spectrometry was performed on a Thermo LTQ-Orbitrap XL mass spectrometer equipped with collision cells for collision-induced dissociation or Bruker MALDI-TOF MS RapifleX with DCTB (*trans*-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix.

Computational Details

Geometry calculations of nanographenes **HBC-Bu**, **HBC-O**, **1**–**4**, and **1-Me**$^+$ were carried out by DFT methods using the Gaussian 16 program package.[S1] The optimizations of structures **HBC-Bu**, **HBC-O**, **1**–**4**, and **1-Me**$^+$ were carried out at the CAM-B3LYP/6-311+G(d,p) [S2] level of theory in the gas phase. The atomic coordinates of the calculated structures and the related energies are shown in Tables S3-S6. The isochemical shielding surface (ICSS) plots, nucleus-independent chemical shift (NICS) calculations, and NMR=GIAO[S3] was carried out at the B3LYP/6-311+G(d,p) level of theory. The responding NICS, ICSS, molecular ESP, and valence electron density, are all based on the DFT-optimized structure. Hole-electron analysis was performed by Multiwfn software[S4] based on the TD-DFT calculation at CAM-B3LYP/def2-TZVP[S5] level using the Gaussian 16 software. IGMH analysis of intermolecular interactions were performed Multiwfn software[S4] DFT calculation of crystal structures using Gaussian 16 software at B3LYP-D3(BJ)/6-311+G(d,p) level. Electronic transitions, singlet states, and triplet states energies of nanographenes were calculated by means of TD-DFT methods using the Gaussian 16 software. For the calculations, the PBE0/def2-TZVP[S5] theory level was used in gas phase. The output isosurfaces, molecular orbitals, and maps were processed by VMD software [S6].

Preparation of nanographene stock solutions.

Different NG compounds were dissolved in DMSO to make a concentrated solution (10 mM), which is then diluted in cell culture medium or methanol and PBS buffer as needed.

ROS Study by DCFH-DA in *vitro*.

2′,7′-Dichlorodihydrofluorescein diacetate (DCFH-DA) was employed for *in vitro* ROS evaluation. [S7] The ROS generation produced by different nanographenes could be evaluated by the fluorescence emission of DCF that is converted from DCFH-DA. In detail, 20 μL DCFH-DA in DMSO (10×10^{-3} M) was added to 800 μL NaOH in PBS (10×10^{-3} M) and allowed to stay at room temperature for 30 min, followed by addition of 9180 μL PBS buffer to stop the reaction, and kept in dark before use. By the time, DCFH-DA was hydrolyzed to DCFH. Subsequently, the solution of DCFH (600 μL) was mixed with 2400 μL of compound in methanol and PBS buffer mixed solvents, with the 20 μM final concentration of the compound and the final solvent is methanol and PBS buffer (v:v=1:9). Compound and indicator solution was exposed to yellow LED light (0.02 W/cm^2) or 630 nm laser (0.15 W/cm^2), 15 cm distance from the light source, fluorescence intensity of DCF at different times was measured to estimate the ROS production ability of compounds. The fluorescence intensity at 525 nm was recorded to indicate the generation rate of total ROS.

Detection of $^1O_2$ in *vitro.*

1.3-diphenylisobenzofuran (DPBF) was used as the singlet oxygen probe for *in vitro* singlet oxygen release evaluation. The DPBF was dissolve in DMSO with the concentration of 10×10^{-3} M. The solution of DPBF (24 μL) was mixed with 2976 μL of compound in the mixed solvent of methanol and PBS buffer, with the final concentration of the compound is 20 μM and the final solvent is methanol and PBS buffer (v/v = 9:1). The absorbance of DPBF after yellow LED light (0.02 W/cm^2) irradiation at different times was measured to estimate the singlet oxygen release ability.

Cell and Culture Conditions.

Hela cells were purchased from Beyotime Biotech Inc. The cell clones were cultured in DMEM medium supplemented with 10% fetal calf serum (FBS) and 1% Penicillin-Streptomycin solution at 37°C in 95% air with 5% CO_2.

Cell viability test

Briefly, Hela cells were seeded on 96 well plates (1×10^4 cells per well) and cultured for 24 h. The old medium was replaced with 100 μL fresh medium containing different concentrations of compounds (0, 2, 5, 10, 15, 20, and 25 μM) and the cells were further incubated at 37 °C for 12 h. The plates were irradiated under yellow light irradiation (0.02 W/cm^2) or 630 nm laser (0.15 W/cm^2) for 30 min or stay in dark as control groups. The cells with or without light

irradiation were cultivated for another 8h. The relative cell viability was measured by MTT assay.

Cell morphology imaging

Hela cells in exponential phase were cultured on 35 mm dishes (1×10^5 cells per well) for 24 hours, the old medium was replaced with 2 mL fresh medium containing NGs **1**–**4** and **1-Me**$^+$ (10 μM), the cells were further incubated at 37 °C for 12 h. The plates were irradiated with yellow LED light (0.02 W/cm^2) or 630 nm laser (0.15 W/cm^2, for **1-Me**$^+$) for 15 min and during this the cell images were recorded through a microscope lens.

Fluorescence Imaging of Intracellular ROS

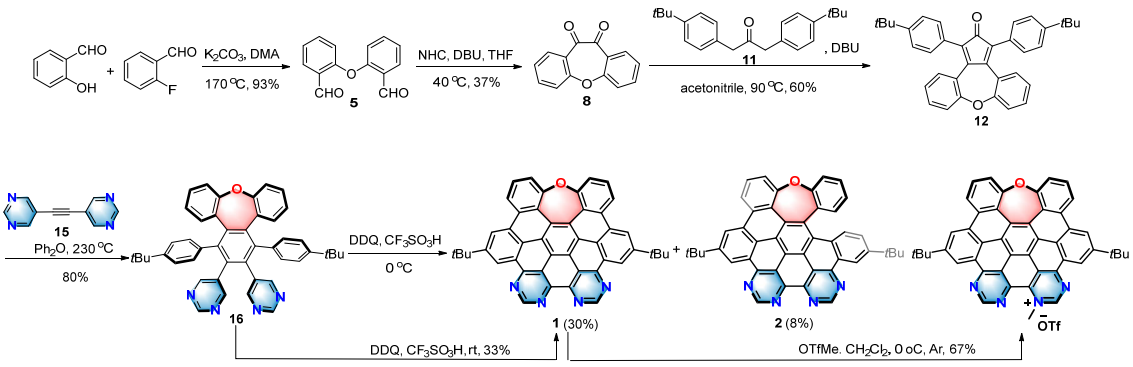
Hela cells in the exponential phase of growth were grown on 35 mm glass-bottom culture dishes (1×10^5 cells per well) for 24 h to reach about 80% confluency. The old medium was replaced with 2 mL fresh medium and the cells were incubated with or without NG **1-Me**$^+$ (10 μM) at 37 °C for 12 h. The cells were washed three times with PBS and further stained with DCFH (10 μM) in fresh medium for 30 min, then washed three times with PBS. The fluorescence images were eventually acquired via a confocal laser scanning microscope while the cells were exposed under 630 nm laser (0.02 W/cm^2). The excitation wavelength is 488 nm for DCF.

Co-staining assay by CLSM

Hela cell in exponential phase were cultured on 35 mm-glass-bottom dishes (1×10^5 cells per well) for 24 hours, the cells achieved around a confluence of 80%, the old medium was replaced with 2 mL fresh medium containing NGs **1**–**4** and **1-Me**$^+$ (10 μM). After incubated for 12 h was followed the irradiation with yellow LED light (0.02 W/cm^2) or 630 nm laser (0.15 W/cm^2 for **1-Me**$^+$) for 30 min, the cells were further incubated for 4h. The cells were washed for three times with PBS solution (1 mL), stained with Calcein (AM)/propidium iodide (PI) according to Cell Viability/Cytotoxicity Assay Kit Instruction, and then gently washed twice with PBS. The cell apoptosis was visualized by confocal laser scanning microscopy with an excitation wavelength of 494 nm for AM and excitation wavelength of 535 nm for PI.

Synthesis

Scheme S1. Synthesis of Nanographenes **1**, **2**, **and 1-Me**$^{+}$.



2,2'-oxydibenzaldehyde (**5**) and **dibenzo[b,f]oxepine-10,11-dione (8)**: Compounds **5** and **8** were synthesized by using the reported procedure.[S8]

1,3-bis(4-(tert-butyl)phenyl)-2H-dibenzo[b,f]cyclopenta[d]oxepin-2-one (12): A mixture of **11**[S9] (155 mg, 0.48 mmol) and dibenzo[b,f]oxepine-10,11-dione **8** (162 mg, 0.70 mmol) in 10 mL acetonitrile was placed in an oil bath at 90 °C for 10 min. DBU (0.07 mL, 0.48 mmol) was added to the refluxing solution and the reaction mixture was refluxed for another 3 hours. Upon complete conversion (checked by TLC), the mixture was cooled to room temperature the resulting dark violet suspension was filtered. The crude product was washed with cold acetonitrile and further purified by column chromatography on silica gel with PE/EA (20/1, v/v) as eluent to give the title product as a violet solid (221 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 14H), 6.93 (td, J = 7.5, 1.3 Hz, 2H), 1.32 (s, 18H); ^{13}C NMR (101 MHz,$CDCl_3$) δ 199.9, 157.1, 150.8, 148.5, 132.1, 131.3, 129.6, 128.1, 126.2, 125.3, 125.0, 121.7, 34.6, 31.3; IR (film) $\tilde{\upsilon}$ = 3093, 3060, 2967, 2869, 1713, 1511, 1465, 1265, 1093, 1033, 735, 708, 701 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{35}O_2$ 511.2632 $[M+H]^+$, found 511.2630.

5,15-bis(4-(tert-butyl)phenyl)dibenzo[2',3':6',7']oxepino[4',5':4,5]benzo[1,2-f]pyrimido[5,4-h]quinazoline (**16**): To a solution of compound **12** (241 mg, 0.47 mmol) in diphenyl ether (2.0 mL at room temperature) was added alkyne **15**[S9] (57 mg, 0.30 mmol). The mixture was heated to 230 °C under Ar atmosphere in the sealed tube and kept stirring for 36 hours. Then the reaction was cooled to room temperature and further purified by column chromatography on silica gel with PE/EA (2/1, v/v) as eluent to give the title compound **16** as a white solid (251 mg, 80%): ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.75 (d, J = 2.9 Hz, 2H), 8.73 (s, 2H), 7.90 (d, J = 2.9 Hz, 2H), 7.23 (dd, J = 8.1, 1.2 Hz, 2H), 7.10 – 7.07 (m, 4H), 6.99 (dd, J = 8.1, 2.0 Hz, 2H), 6.95 (dd, J = 8.2, 2.1 Hz, 2H), 6.81 (dd, J = 7.9, 1.6 Hz, 2H), 6.65 (dd, J = 8.1, 2.0 Hz, 2H), 6.57 (td, J = 7.6, 1.3 Hz, 2H), 1.16 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 157.6, 157.5, 156.2, 149.9, 141.8, 137.6, 135.7, 134.9, 134.1, 133.3, 131.9, 130.2, 129.9, 129.0, 125.1, 124.4, 123.4, 119.7, 34.3, 31.1; IR (film) $\tilde{\upsilon}$ = 3059, 3023, 2964, 2932, 1578, 1547,

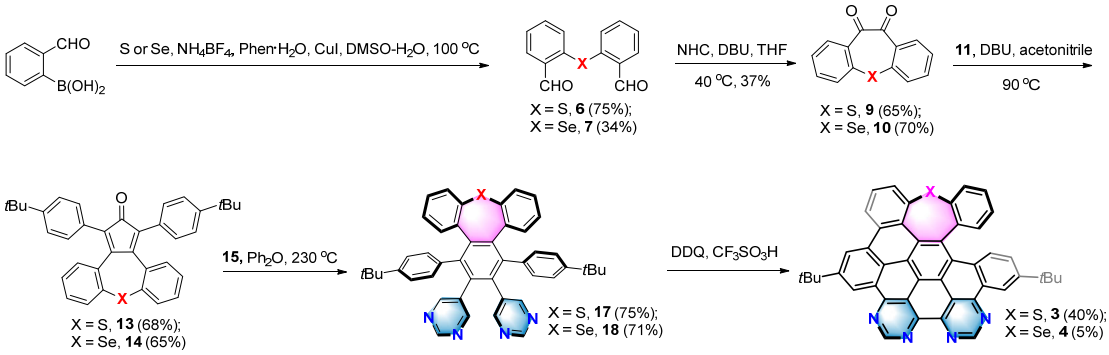
1389, 1263, 1195, 1093, 1041, 1024, 811, 801, 634, 600 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{46}H_{41}N_4O$ 665.3275, found 665.3275.

5,14-di-tert-butyl-19-oxa-7,9,10,12-tetraazabenzo[5',6']tetraceno[1',12',11',10':5,6,7,8,9]tetrapheno[10,11,12,1-nopqab]pleiadene (**1**) and **5,14-di-tert-butyl-21-oxa-7,9,10,12-tetraazadibenzo[fg,ij]benzo[6',7']cyclohepta[1',2',3',4':4,5]phenanthro[9,10,1,2,3-pqrst]pentaphene** (**2**): To a solution of compound **16** (30 mg, 0.045 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (103 mg, 0.45 mmol) in 5 mL of anhydrous CH_2Cl_2 under an atmosphere of argon cooled in an water-ice bath was added trifluoromethanesulfonic acid (0.2 mL, 2.5 mmol). The reaction was stirred for 23 minutes under argon atmosphere in water-ice bath. Then, triethyl amine (2.0 mL, 14.4 mmol) was added into the reaction solution and the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/MeOH 40/1 (V/V) as eluent to give the title compound **1** (9 mg, 30%) as orange solid together with small amount of **2** (2 mg, 8%) as yellow solid. Notably, when the reaction was set up at room temperature, only structure **1** was detected and collected with similar yield (10 mg, 33%). Structure **1**: mp: 345–347 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ 9.88 (s, 2H), 9.44 (s, 2H), 8.58 (s, 2H), 8.06 (d, J = 7.7 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 6.79 (d, J = 7.1 Hz, 1H), 1.57 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 154.6, 151.0, 150.4, 132.1, 129.3, 128.0, 128.0, 125.8, 125.0, 124.6, 123.2, 122.8, 121.9, 119.3, 118.8, 118.5, 117.4, 35.8, 31.7; IR (film) $\tilde{\upsilon}$ = 3118, 3065, 3005, 2969, 2926, 2869, 1562, 1517, 1473, 1239, 869, 783, 702 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$, calcd for $C_{46}H_{31}N_4O$ 655.2492, found 655.2496. **Structure 2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 10.11 (s, 1H), 9.78 (s, 1H), 9.51 (s, 1H), 9.07 (s, 1H), 8.61 (s, 1H), 7.83 (m, , 2H), 7.70 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.55 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.52 (d, J = 7.6Hz, 1H), 1.75 (s, 9H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 158.1, 156.8, 154.9, 154.3, 151.6, 150.9, 135.1, 134.6, 132.9, 131.7, 131.3, 130.3, 130.1, 129.6, 129.2, 128.2, 127.0, 126.7, 125.8, 124.2, 123.7, 123.4, 123.1, 121.9, 121.5, 120.7, 120.5, 120.4, 118.7, 117.9, 35.9, 35.3, 31.8, 31.4; IR (film) $\tilde{\upsilon}$ = 3116, 3036, 2964, 1617, 1547, 1517, 1393, 1264, 1073, 1035, 807 cm^{-1}; HRMS (ESI) calcd for $C_{46}H_{33}N_4O$ 657.2649 $[M+H]^+$, found 657.2645.

5,14-di-tert-butyl-10-methyl-19-oxa-7,9,10,12-tetraazabenzo[5',6']tetraceno[1',12',11',10':5,6,7,8,9]tetrapheno[10,11,12,1-nopqab]pleiaden-10-ium, trifluoromethanesulfonate (1-Me$^+$): To a solution of compound **1** (20 mg, 0.030 mmol) in anhydrous CH_2Cl_2 under an atmosphere of argon cooled in an water-ice bath was added methyl trifluoromethanesulfonate (MeOTf, 6.3 μL, 0.061 mmol). The reaction was stirred for 2h under argon atmosphere in water-ice bath. Then, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/MeOH 20/1 (V/V) as eluent to give the title compound **1** (14 mg, 67%) as dark puple solid. ^{1}H NMR (600 MHz, DMSO-d_6 and CD_3OD with trace $CDCl_3$) δ 10.35 (s, 1H), 9.98 (s, 1H), 9.36 (s, 1H), 9.30 (s, 1H), 9.04 (s, 1H), 8.93 (s, 1H), 8.66 (m, 2H), 7.85 (d, J = 8.8

Hz, 2H), 7.45 (m, 2H), 5.08 (s, 3H), 1.64 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6 and CD_3OD with trace $CDCl_3$) δ 157.7, 157.2, 156.0, 155.7, 155.4, 154.2, 152.6, 152.4, 131.5, 131.0, 128.4, 128.3, 127.7, 126.8, 126.4, 125.9, 125.3, 125.1, 124.1, 123.2, 122.8, 122.1, 121.0, 120.7, 120.1, 120.0, 119.9, 118.7, 116.9, 114.7, 36.0, 31.6, 31.4; HRMS (MALDI-TOF) calcd for $C_{47}H_{33}N_4O$ 669.2649 [M^+], found 669.2655.

Scheme S2. Synthesis of Helical Nanographenes **3** and **4**.



2,2'-thiodibenzaldehyde (**6**) and **2,2'-selenodibenzaldehyde** (**7**): Dialdehyde compounds **6** and **7** were synthesized by using the reported procedure.[S10]

Dibenzo[b,f]thiepine-10,11-dione (**9**): Dione **9** was synthesized by using the reported procedure.[S8]

Dibenzo[b,f]selenepine-10,11-dione (**10**): 2-((3-formylphenyl)selanyl)benzaldehyde **7** (300 mg, 1.03 mmol) and 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium chloride **NHC** (56 mg, 0.2 mmol) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2–3 cycles). Then dry THF were added (10 mL) to the above mixture by syringe followed by the dropwise addition of DBU (0.18 mL, 1.24 mmol) under a positive pressure of argon. Then the reaction mixture was heated to 40 °C and kept stirring for 1 hour. Then the argon protection was removed and the reaction muixture was stirred at the room temperature for another 2 hours. The water (20 mL) was added to the reaction mixture and the mixture was extracted with EtOAc (3×15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography with PE/EA 5/1 (V/V) as eluent to give title product as a yellow solid (208 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 4H), 7.47–7.40 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 140.7, 133.4, 132.7, 131.1, 129.4, 129.3; IR (film) $\tilde{\upsilon}$ = 3096, 3050, 1678, 1578, 1437, 1263, 1221, 1032, 704 cm^{-1}; HRMS (ESI) m/z: [M+H]$^+$, calcd for $C_{14}H_9O_2Se$ 288.9762, found 288.9761.

1,3-bis(4-(tert-butyl)phenyl)-2H-dibenzo[b,f]cyclopenta[d]thiepin-2-one (**13**): To a mixture of **11** (191 mg, 0.59 mmol) and dibenzo[b,f]thiepine-10,11-dione **9** (214 mg, 0.89 mmol) in acetonitrile (10 mL) at 90 °C in an oil bath was added DBU (0.08 mL, 0.59 mmol).

The reaction mixture was refluxing for around 3 hours until a complete conversion (checked by TLC). Then the mixture was cooled to room temperature and the resulting dark violet suspension was filtered. The filtrate was concentrated and purified by column chromatography on silica gel with PE/EA 20/1 (V/V) as eluent to give the title product as a violet solid (309 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.5, 1.3 Hz, 2H), 7.26 (d, J = 5.3 Hz, 4H), 7.19–7.12 (m, 8H), 7.06 (td, J = 7.5, 1.3 Hz, 2H), 1.29 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 152.4, 150.6, 137.3, 135.5, 133.5, 132.1, 129.9, 129.5, 128.9, 127.7, 125.1, 124.4, 34.6, 31.2; IR (film) $\tilde{\upsilon}$ = 3092, 3059, 2967, 2869, 2819, 1713, 1511, 1465, 1362, 1265, 1093, 1033, 736, 708 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$, calcd for $C_{37}H_{35}OS$ 527.2403 found 527.2408.

1,3-bis(4-(tert-butyl)phenyl)-2H-dibenzo[b,f]cyclopenta[d]selenepin-2-one (**14**): To a mixture of **11** (594 mg, 1.84 mmol) and dibenzo[b,f]selenepine -10,11-dione **10** (691 mg, 2.40 mmol) in acetonitrile (10 mL) at 90 ºC in an oil bath was added DBU (0.28 mL, 1.84 mmol). The reaction mixture was refluxing for around 3 hours until a complete conversion (checked by TLC). Then the mixture was cooled to room temperature and the resulting dark violet suspension was filtered. The filtrate was concentrated and purified by column chromatography on silica gel with PE/EA 20/1 (V/V) as eluent to give the title product as a violet solid (895 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.5, 1.3 Hz, 2H), 7.23 (s, 4H), 7.16–7.05 (m, 10H), 1.28 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 153.5, 150.4, 138.2, 134.9, 132.0, 131.2, 129.9, 129.2, 128.9, 127.7, 125.0, 124.1, 34.6, 31.2; IR (film) $\tilde{\upsilon}$ = 3082, 3037, 2965, 1773, 1692, 1652, 1570, 1520, 1263, 1038, 799, 744, 712 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$, calcd for $C_{37}H_{39}OSe$ 575.1848, found 575.1847.

5,5'-(1,4-bis(4-(tert-butyl)phenyl)tribenzo[b,d,f]thiepine-2,3-diyl)dipyrimidine (**17**): To a mixture of compound **13** (100 mg, 0.19 mmol) and diphenyl ether (1.0 mL at room temperature) was added alkyne **15** (23 mg, 0.12 mmol). The mixture was heated to 230 ºC under Ar atmosphere in the sealed tube and kept stirring for 36 hours. Then the reaction was cooled to room temperature and further purified by column chromatography on silica gel with PE/EA (3/1, v/v) as eluent to give the title compound **17** as a white solid (96 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 2.9 Hz, 2H), 8.74 (s, 2H), 7.97 (d, J = 2.9 Hz, 2H), 7.54 (dd, J = 7.8, 1.3 Hz, 2H), 7.03 (dd, J = 8.1, 2.1 Hz, 2H), 6.96–6.91 (m, 4H), 6.87–6.83 (m, 4H), 6.67 (td, J = 7.6, 1.3 Hz, 2H), 6.50 (dd, J = 8.1, 2.0 Hz, 2H), 1.12 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 157.6, 156.2, 149.5, 141.5, 141.3, 139.9, 135.6, 134.1, 133.1, 131.6, 131.5, 130.2, 127.1, 126.7, 124.8, 124.1, 34.2, 31.0; IR (film) $\tilde{\upsilon}$ = 3116, 3037, 2964, 2910, 1617, 1547, 1394, 1265, 1073, 1035, 832, 807, 757, 736 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$, calcd for $C_{46}H_{41}N_4S$ 681.3046, found 681.3046.

5,5'-(1,4-bis(4-(tert-butyl)phenyl)tribenzo[b,d,f]selenepine-2,3-diyl)dipyrimidine (**18**): To a mixture of compound **13** (342 mg, 0.59 mmol) and diphenyl ether (1.0 mL at room temperature) was added alkyne **15** (90 mg, 0.49 mmol). The mixture was heated to 230 ºC under an argon atmosphere in the sealed tube and kept stirring for 36 hours. Then the reaction was cooled to room temperature and further purified by column chromatography on silica gel with PE/EA (3/1, v/v) as eluent to give the title compound **18** as a white solid (307 mg, 71%): ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 2.9 Hz, 2H), 8.74 (s, 2H), 7.98 (d, J = 2.9 Hz, 2H), 7.65 (dd, J = 8.0, 1.3 Hz, 2H), 7.01 (dd, J = 8.1, 2.1 Hz, 2H), 6.93 (dd, J = 8.0, 2.1 Hz, 2H), 6.87 – 6.83 (m, 6H), 6.68 (td, J = 7.5, 1.3 Hz, 2H), 6.48 (dd, J = 8.1, 2.0 Hz, 2H), 1.11 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 157.6, 156.2, 149.4, 142.6, 141.1, 140.3, 137.9, 135.5, 134.0, 133.9, 133.1, 132.9, 131.4, 130.1, 126.8, 126.7, 124.7, 124.0, 34.2, 31.0; IR (film) $\tilde{\upsilon}$ = 3119, 3047, 2966, 2874, 1549, 1472, 1394, 1265, 1039, 838, 811, 798, 754, 729 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{46}H_{41}N_4Se$ 729.2491, found 729.2496.

5,14-di-tert-butyl-21-thia-7,9,10,12-tetraazadibenzo[fg,ij]benzo[6',7']cyclohepta[1',2',3',4':4,5]phenanthro[9,10,1,2,3-pqrst]pentaphene (**3**): To a solution of **17** (30 mg, 0.044 mmol) and DDQ (100 mg, 0.44 mmol) in 5 mL of anhydrous CH_2Cl_2 under an atmosphere of argon in an water-ice bath. To the was slowly added trifluoromethanesulfonic acid (0.2 mL, 2.5 mmol). The reaction mixture was stirred for 30 minutes at room temperature. Then triethyl amine (2.0 mL, 14.4 mmol) was added and the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/MeOH 40/1 (V/V) as eluent to give the title compound **3** as a yellow solid (12 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 10.08 (s, 1H), 9.78 (s, 1H), 9.59 (s, 1H), 9.08 (s, 1H), 8.78 (d, J = 7.0 Hz, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.57 – 7.55 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.16 (d, J = 7.7 Hz, 1H), 1.74 (s, 9H), 1.57 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 156.5, 155.0, 154.3, 151.3, 151.0, 146.9, 138.2, 138.1, 137.5, 133.4, 133.3, 133.2, 132.0, 131.7, 130.9, 130.3, 129.9, 129.3, 128.9, 128.7, 128.3, 124.6, 124.5, 123.6, 123.3, 122.3, 122.1, 119.2, 118.8, 117.9, 117.5, 35.9, 35.2, 31.8, 31.4; IR (film) $\tilde{\upsilon}$ = 3110, 3041, 2968, 2934, 1621, 1552, 1485, 1336, 1262, 1092, 1031, 805, 694 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{46}H_{33}N_4S$ 673.2420, found 673.2421.

5,14-di-tert-butyl-21-selena-7,9,10,12-tetraazadibenzo[fg,ij]benzo[6',7']cyclohepta[1',2',3',4':4,5]phenanthro[9,10,1,2,3-pqrst]pentaphene (**4**) To a solution of **18** (30 mg, 0.041 mmol) and DDQ (93 mg, 0.41 mmol) in 5 mL of anhydrous CH_2Cl_2 under an atmosphere of argon in a water-ice bath. To the was slowly added trifluoromethanesulfonic acid (0.2 mL, 2.5 mmol). The reaction mixture was stirred for 30 minutes at room temperature. Then triethyl amine (2.0 mL, 14.4 mmol) was added and the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/MeOH 20/1 (V/V) as eluent to give the title compound **4** as an orange solid (1.5 mg, 5%) and compound **19** as dark yellow solid (13 mg, 45%). Compound **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 10.11 (s, 1H), 9.78 (s, 1H), 9.62 (s, 1H), 9.04 (s, 1H), 8.73 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 7.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.60–7.58 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.07 (d, J = 7.7 Hz, 1H), 1.74 (s, 9H), 1.56 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 156.7, 155.0, 154.3, 151.3, 151.0, 150.9, 147.8, 138.8, 135.1, 134.5, 133.6, 133.1, 133.0, 132.1, 131.9, 130.4, 130.1, 130.0, 129.9, 129.1, 128.8, 128.7, 128.1, 127.4, 124.5, 124.5, 123.3, 123.2, 122.4, 122.1, 119.2, 118.8, 117.9, 117.3, 35.9, 35.2, 31.8, 31.3; IR (film) $\tilde{\upsilon}$ = 3238, 2966, 1691, 1645, 1609, 1514, 1263, 1130, 874, 799 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{46}H_{33}N_4Se$ 721.1865, found 721.1870.

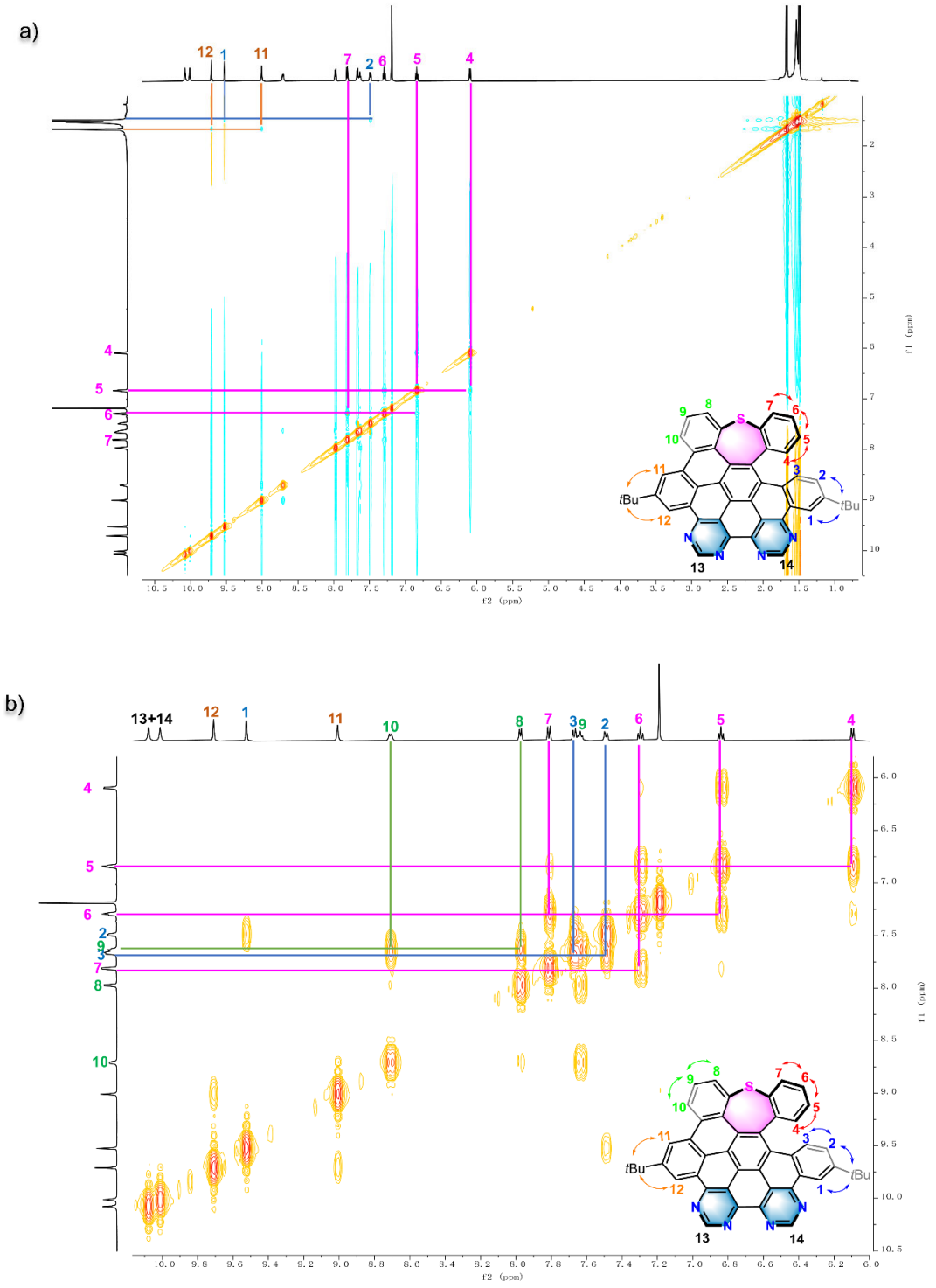


Figure S1. (a) 2D ROESY spectrum of NG **3** with structure depiction of representative NOEs by arrows. (b) 2D H-H COSY spectrum of NG **3** with different spin systems of protons marked in colors.

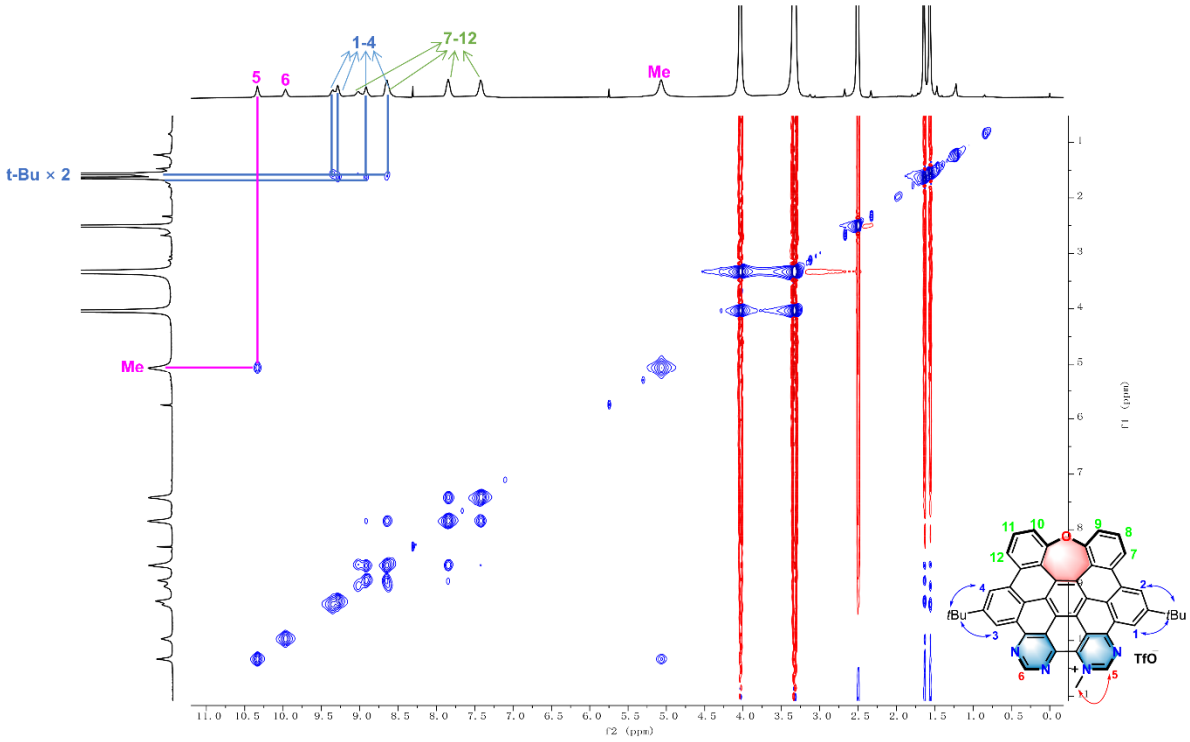
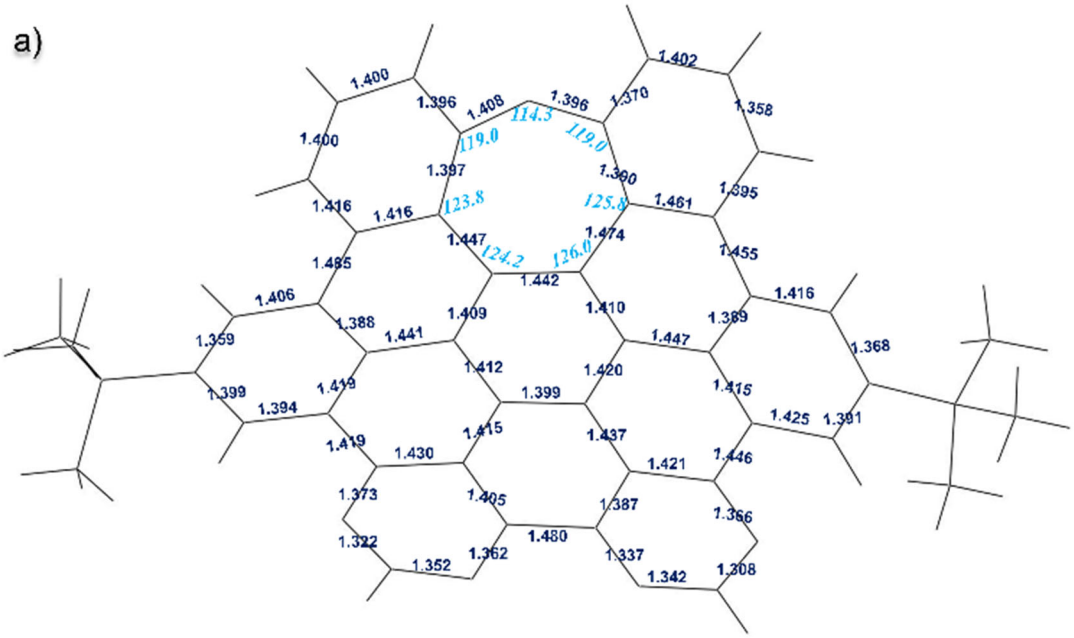


Figure S2. 2D NOESY spectrum of compound NG **1-Me**$^{+}$ with structure depiction of representative NOEs by arrows. Based on the NOE signal, protons of methyl group are spatially close to aromatic proton 5 rather than 1, suggested the methylation is selectively to the nitrogen away from proton 1.



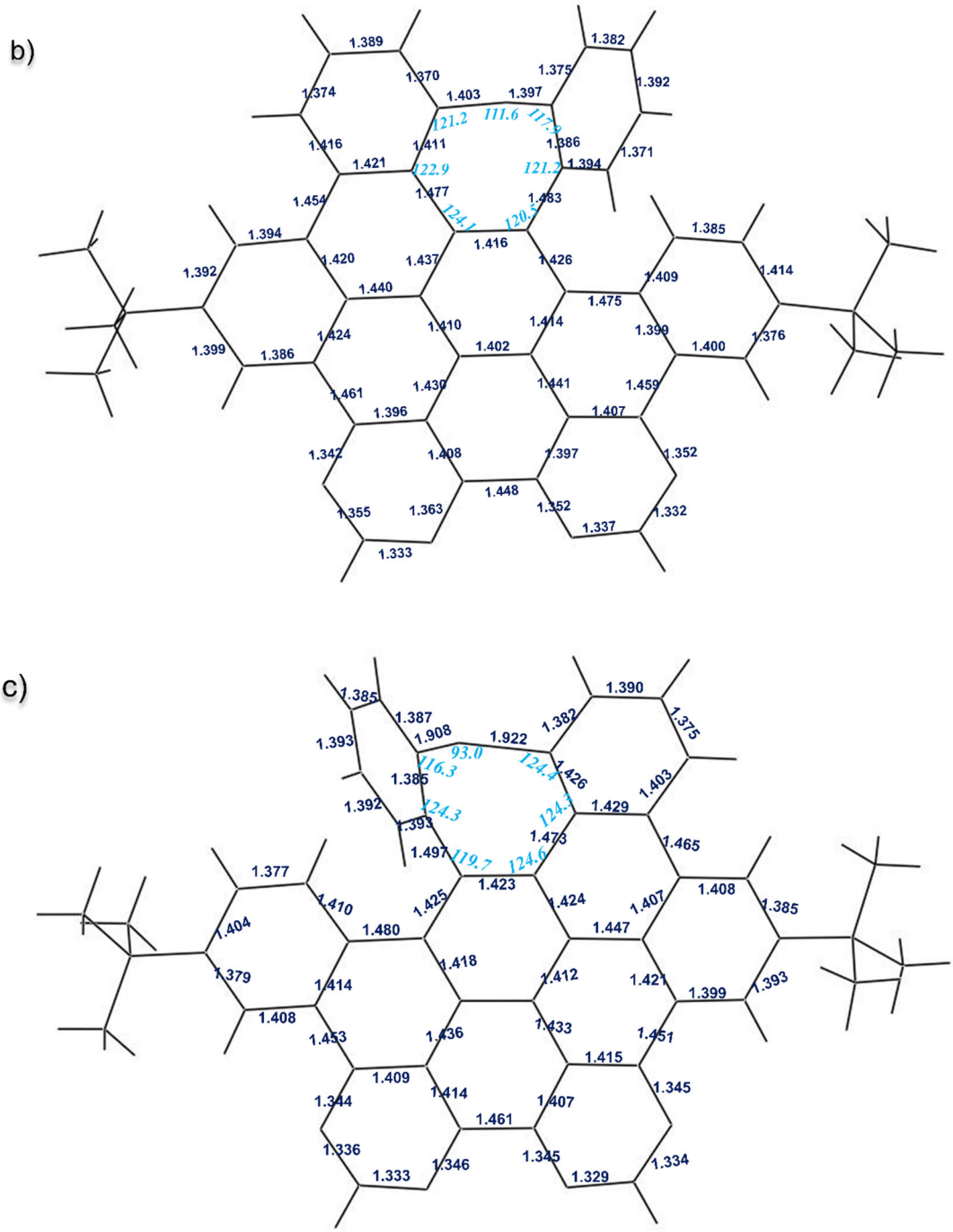


Figure S3. X-ray crystallographic structure of compounds **1**(a), **2** (b), and **4** (c) with bond lengths [Å] and angles of the seven-membered ring.

Table S1. Details of the Crystal Structure Analyses of Compounds **1**, **2** and **4**.

	1	**2**	**4**
CCDC No.	2344508	2344509	2344510
empirical formula	$C_{93}H_{61}Cl_3N_8O_2$	$C_{47}H_{34}Cl_2N_4O$	$C_{93}H_{66}Cl_2N_8Se_2$
formula wt	1428.84	741.68	1524.35
crystal system	tetragonal	Monoclinic	Triclinic
space group	P 41 21 2	P 1 n 1	P-1
T (K)	150	150	150
a (Å)	14.9010(4)	12.9051(5)	13.9675(10)
b (Å)	14.9010(4)	10.5743(5)	15.5987(11)
c (Å)	64.976(3)	25.9985(13)	17.3739(13)
α (°)	90	90	101.977(3)
β (°)	90	95.550(2)	92.500(3)
γ (°)	90	90	105.115(3)
V (Å^3)	14427.3(10)	3531.2(3)	3555.6(4)
Z	8	4	2
ρ_{calcd} (mg/m^3)	1.316	1.395	1.424
μ (mm^{-1})	1.614	0.230	2.434
θ range (°)	3.04–68.27	2.08–25.03	2.61–68.47
F (000)	5936	1544	1564
collected reflcns	70190	44182	53367
unique reflcns no.	12989	11961	12993
R [$I > 2\sigma(I)$]	0.1089	0.0630	0.0390
R (ref)	0.1378	0.1055	0.0418
wR2 [$I > 2\sigma(I)$]	0.2827	0.1392	0.0945
wR2 (ref)	0.3060	0.1632	0.0962

Table S2 Photophysical properties of NGs **1–4** and **1-Me**$^+$ in solution[a].

	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{em} (nm)[b]	Stokes shift (cm^{-1})	Φ_F[c]
1	390	2.2×10^4	502	5721	0.09
2	375	3.3×10^4	517	7325	0.13
3	375	2.1×10^4	517	7325	0.28
4	375	1.7×10^4	525	7619	0.03
1-Me$^+$	419	1.5×10^4	498, 545	5687	<0.01

[a] Measured in dichloromethane (10 μM). [b] λ_{ex1} = 335 nm; λ_{ex2-4} = 375 nm; $\lambda_{ex1\text{-}Me+}$ = 400 nm. [c] Quinine sulfate (Φ_F = 0.54 in 0.1 M H_2SO_4) as a reference.

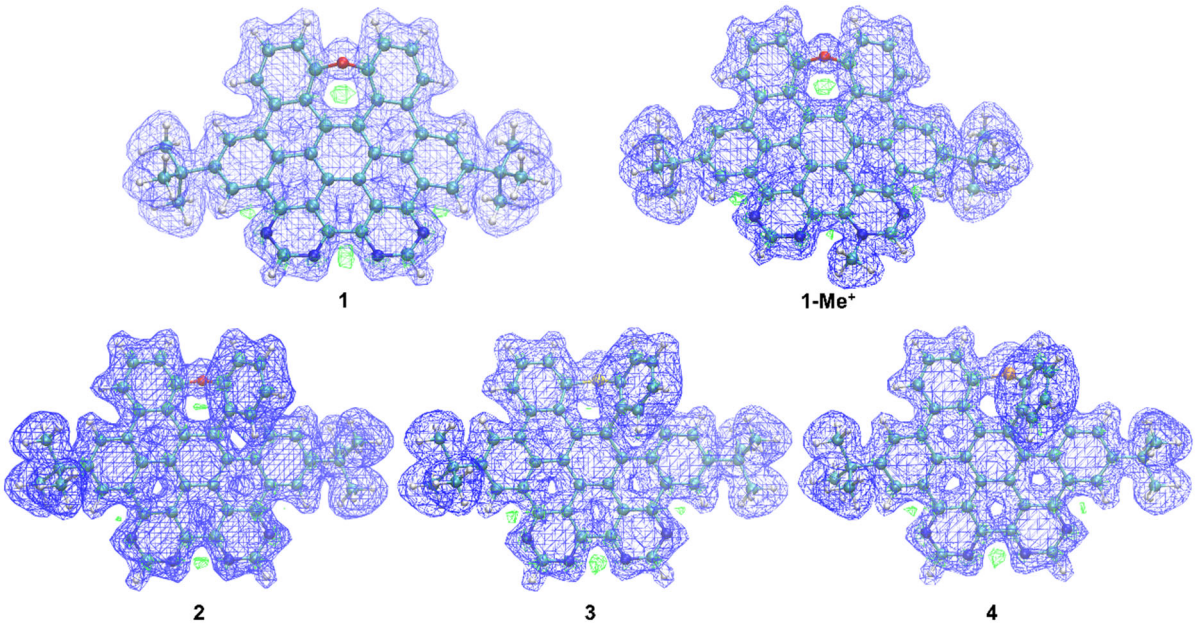


Figure S4. Calculated 3D ICSS map of NGs **1, 1-Me**$^+$**,** and **2-4**, isovalue = 5. Blue and green wireframes represent magnetically shielding and deshielding areas, respectively.

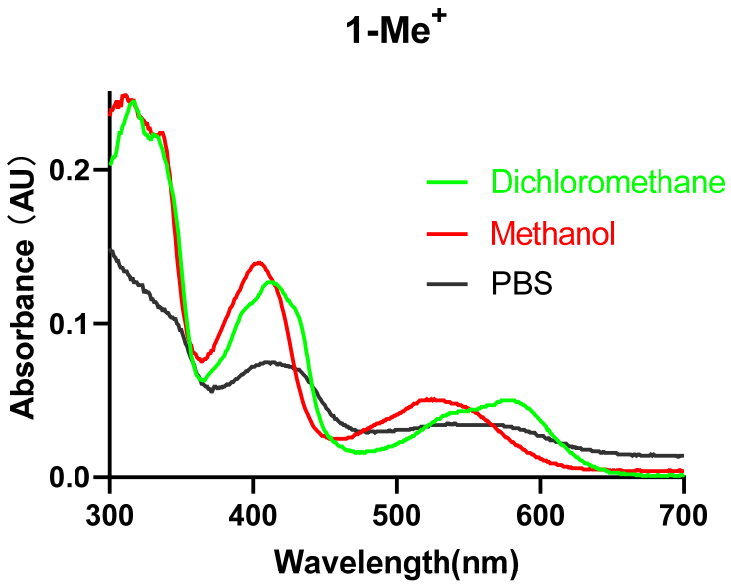


Figure S5. UV/vis absorption of NG **1-Me**$^{+}$ in different solvent at the concentration of 10 μM.

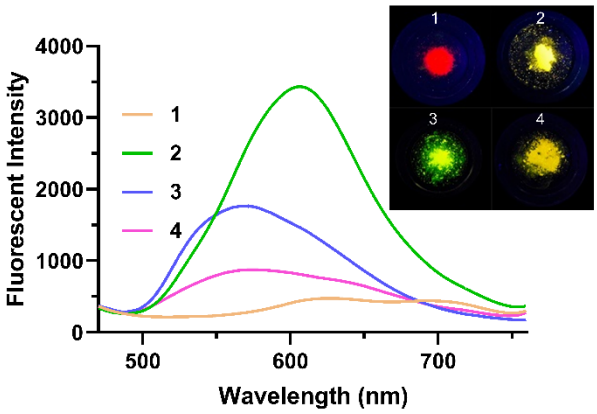


Figure S6. Solid-state fluorescence emission spectra of amorphous solid **1-4**. Inserted photographs are the solid under 365 nm UV lamp.

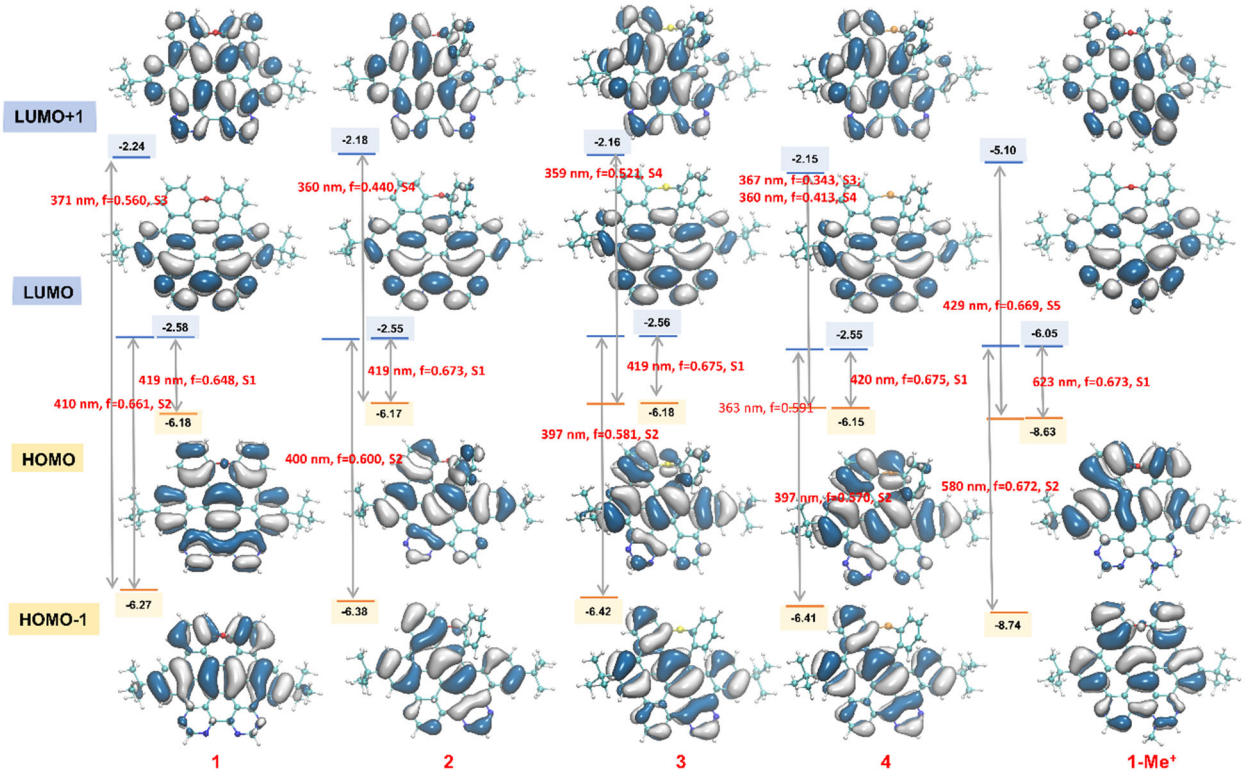


Figure S7. Molecular orbitals (HOMO-2–LUMO+2) with major transitions of compound **1**, **2**, **3**, **4**, and **1-Me**$^{+}$ calculated by DFT at the PBE0/def2-TZVP level of theory.

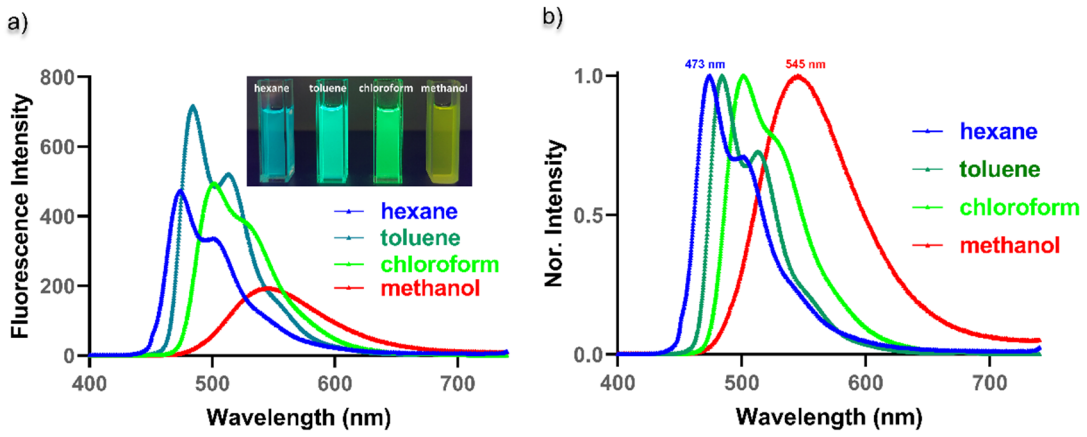


Figure S8. (a) Emission spectra of NG **1** in different solvents. (b) Solvatochromism of NG **1**. (Concentration, 10 μM; λ_{ex} = 375 nm).

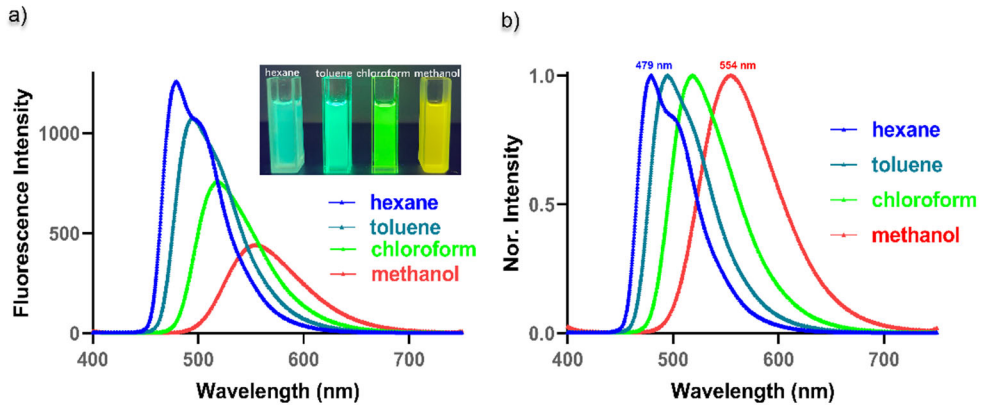


Figure S9. (a) Emission spectra of NG **2** in different solvents. (b) Solvatochromism of NG **2**. (Concentration, 10 μM; λ_{ex} = 375 nm).

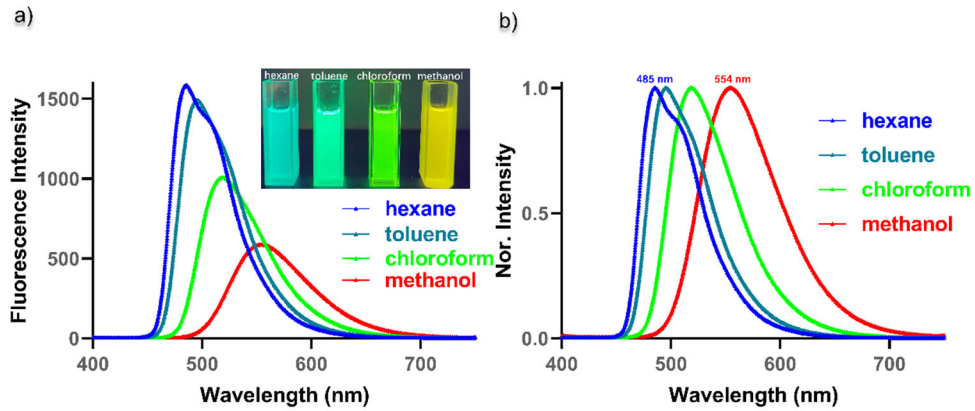


Figure S10. (a) Emission spectra of NG **3** in different solvents. (b) Solvatochromism of NG **3**. (Concentration, 10 μM; λ_{ex} = 375 nm).

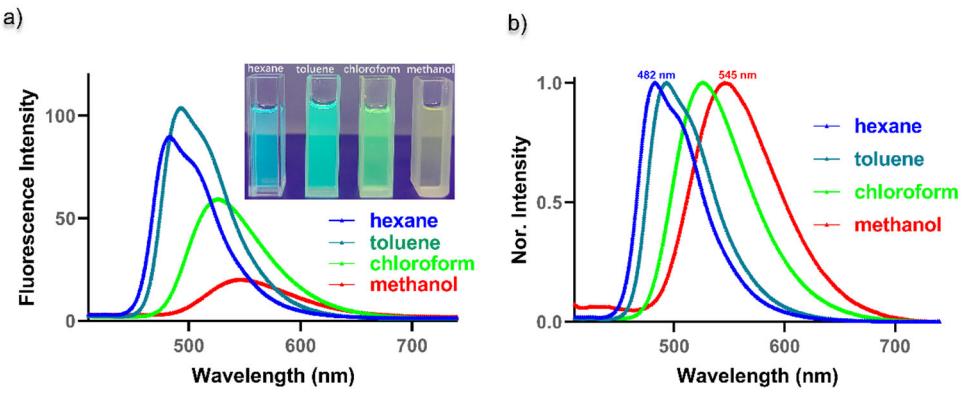


Figure S11. (a) Emission spectra of NG **4** in different solvents. (b) Solvatochromism of NG **4**. (Concentration, 10 μM; λ_{ex} = 375 nm).

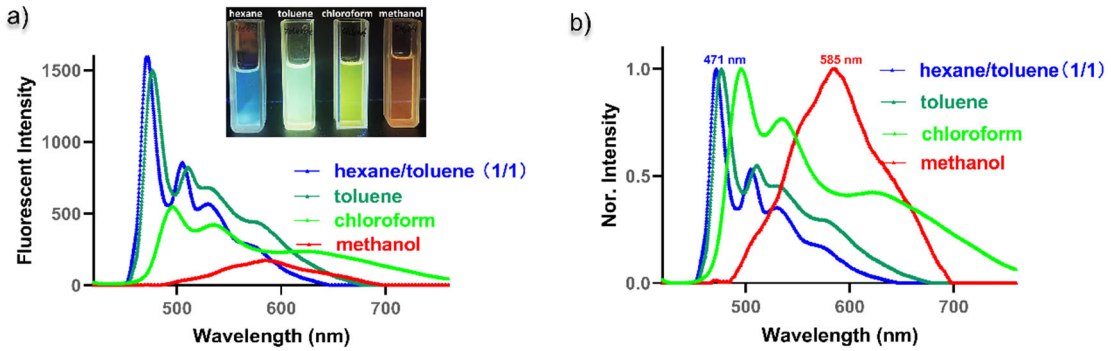


Figure S12. (a) Emission spectra of NG **1-Me**$^+$ in different solvents. (b) Solvatochromism of **1-Me**$^+$. (Concentration, 10 μM; λ_{ex} = 400 nm).

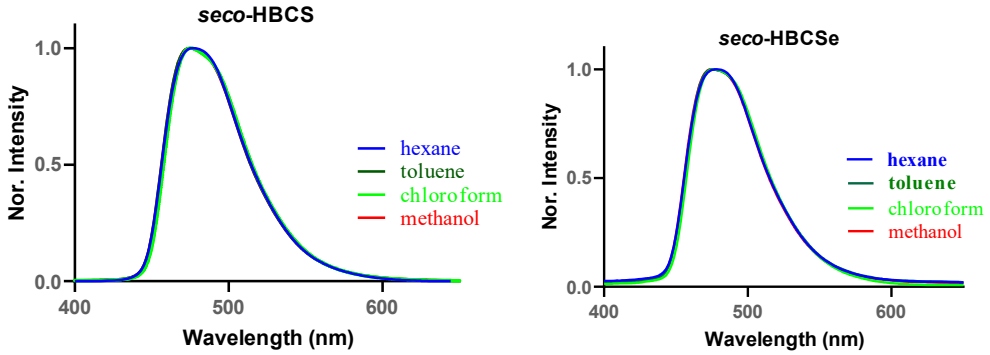


Figure S13. Solvatochromism experiment of ***seco*-HBCS** (a) and ***seco*-HBCS** (b) concentration, 5 μM, λ_{ex} = 350 nm).

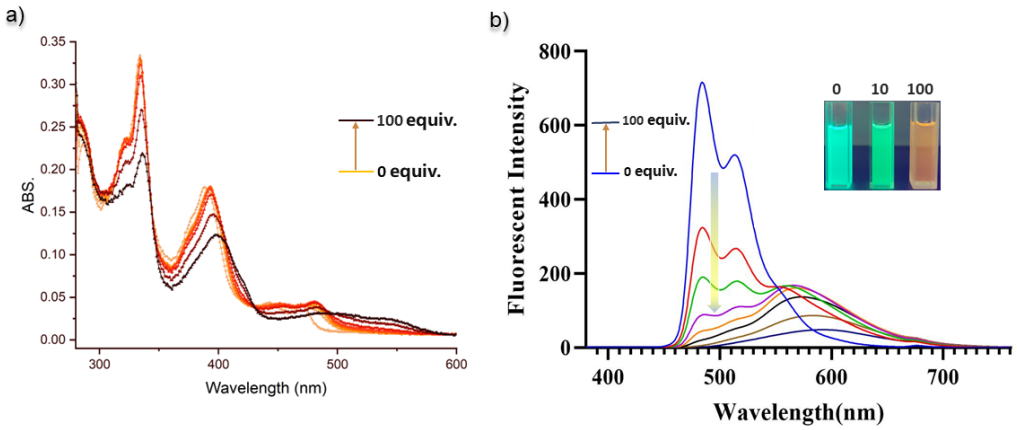


Figure S14. Changes in the UV/vis absorption (a)and emission spectra(b) of **1** on addition of trifluoroacetic acid, with the concentration of the **1** is 10 μM, and the concentration of trifluoroacetic acid is 0 to 100 times of it.

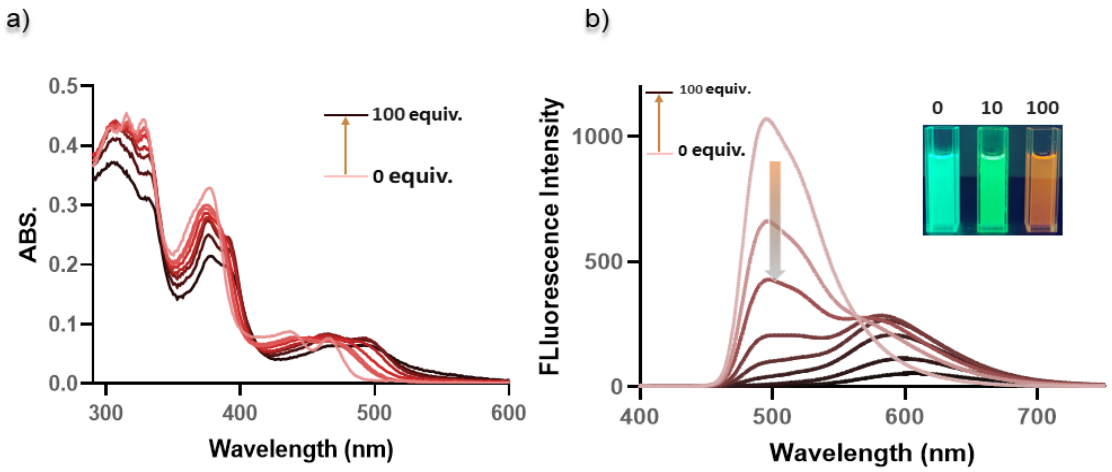


Figure S15. Changes in the UV/vis absorption (a)and emission spectra(b) of **2** on addition of trifluoroacetic acid, with the concentration of the **2** is 10 μM, and the concentration of trifluoroacetic acid is 0 to 100 times of it.

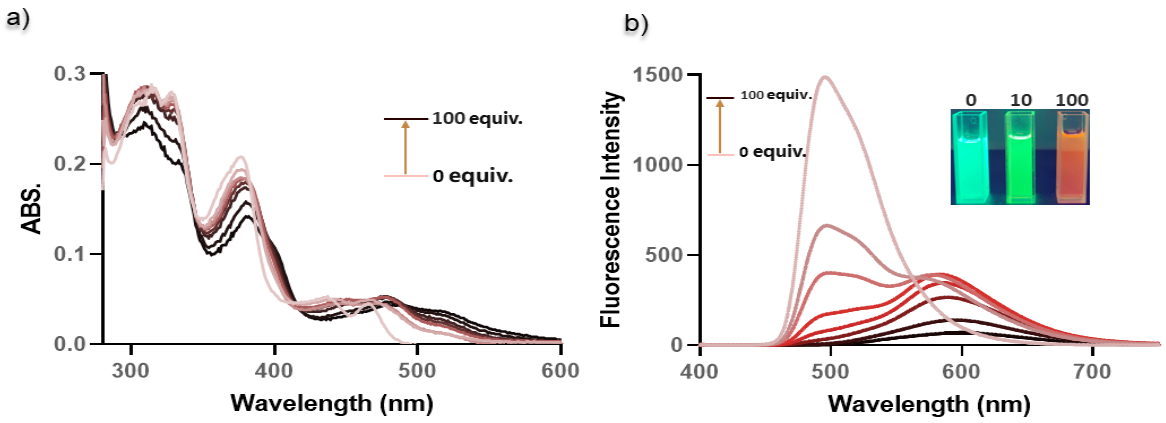


Figure S16. Changes in the UV/vis absorption (a)and emission spectra(b) of **3** on addition of trifluoroacetic acid, with the concentration of the **3** is 10 μM, and the concentration of trifluoroacetic acid is 0 to 100 times of it.

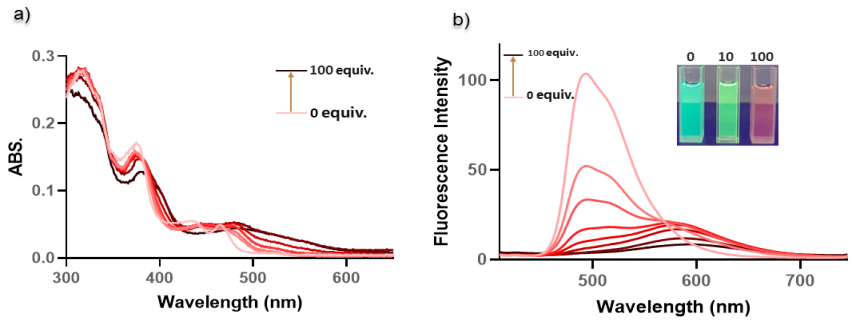


Figure S17. Changes in the UV/vis absorption (a)and emission spectra(b) of **4** on addition of Trifluoroacetic acid, with the concentration of the **4** is 10 μM, and the concentration of trifluoroacetic acid is 0 to 100 times of it.

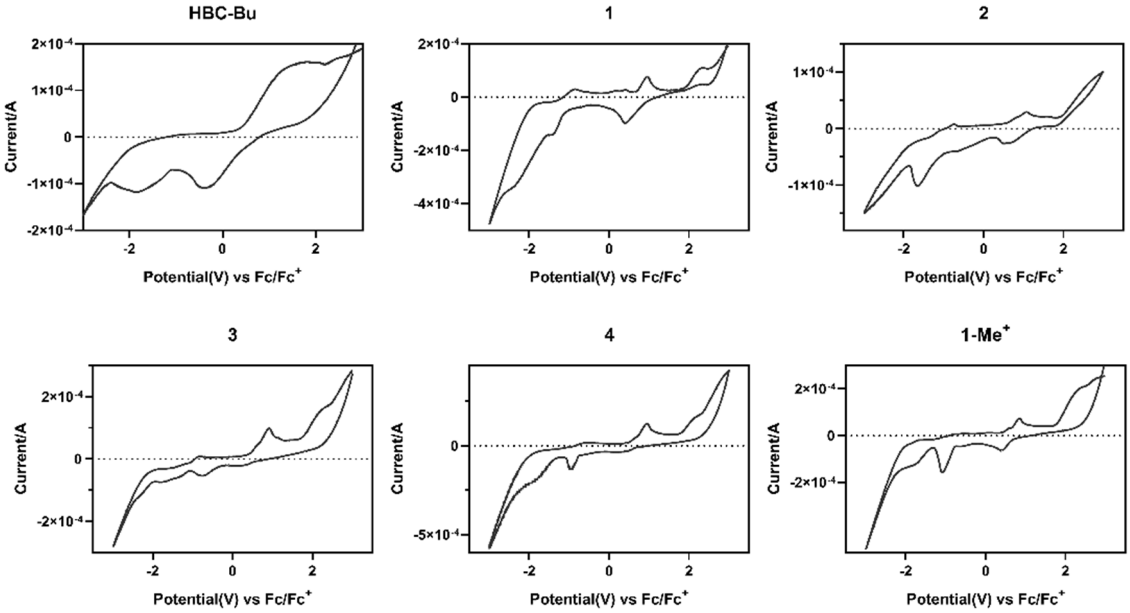


Figure S18. Cyclic voltammograms (CVs) of compounds **HBC-Bu**, **1**–**4**, and **1-Me**$^{+}$, measured in dichloromethane containing n-BuNPF_6 (0.1 M) as a supporting electrolyte.

Table S3. Major transitions of nanographene **1** calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description		Absolute contributions (%)
1	2.9568	419.32	0.0454	H -> L	0.64777	83.9
				H-1 -> L+1	-0.24439	12.5
2	3.0226	410.19	0.0331	H-1 -> L	0.66128	87.5
				H -> L+1	0.22563	10.2
3	3.3433	370.84	0.1242	H-1 -> L+1	0.5598	62.7
				H -> L+2	0.33093	21.9
				H -> L	0.25208	12.7
4	3.3453	370.62	0.3499	H -> L+1	0.6219	77.4
				H-1 -> L	-0.22043	9.7
				H-1 -> L+2	-0.20504	8.4
5	3.4502	359.35	0.0000	H-4 -> L	0.68052	92.6
6	3.4959	354.66	0.0028	H-5 -> L	0.6795	92.3
7	3.6640	338.38	0.0331	H-3 -> L	0.65274	85.2
8	3.6773	337.16	0.0067	H-2 -> L	0.67243	90.4
9	3.8376	323.08	0.2042	H-2 -> L+1	0.49608	49.2
				H-1 -> L+2	-0.41627	34.7
				H-3 -> L	0.20046	8.0
10	3.8396	322.91	0.2393	H -> L+2	0.55858	62.4
				H-1 -> L+1	-0.30009	18.0
				H-3 -> L+1	-0.19541	7.6

Table S4. Major transitions of nanographene **2** calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description		Absolute contributions (%)
1	2.9581	419.13	0.1016	H -> L	0.67257	91.1
				H-1 -> L+1	-0.18648	7.0
2	3.1015	399.76	0.0328	H-1 -> L	0.59936	71.8
				H -> L+1	0.33913	23.0
3	3.4246	362.04	0.1068	H-4 -> L	0.47100	44.4
				H -> L+1	-0.38081	29.0
				H-1 -> L	0.22849	10.4
				H-5 -> L	-0.17644	6.2
4	3.4412	360.29	0.1481	H -> L+1	0.43990	38.7
				H-1 -> L	0.43594	38.0
				H-5 -> L	-0.24985	12.5
5	3.4871	355.55	0.0257	H-5 -> L	0.60500	73.2
				H-1 -> L+1	-0.20647	8.5
				H-4 -> L	0.16658	5.5
6	3.5021	354.03	0.2009	H-1 -> L+1	0.54674	59.8
				H -> L+2	-0.27615	15.3
				H-5 -> L	0.21155	9.0
				H -> L	0.16157	5.2
7	3.6402	340.60	0.0012	H-2 -> L	0.67677	91.6
8	3.7970	326.53	0.0772	H-3 -> L	0.50358	50.7
				H -> L+2	0.30970	19.2
				H-2 -> L+1	0.24392	11.9
				H-1 -> L+1	0.16857	5.7
9	3.8957	318.26	0.3408	H -> L+2	0.42104	35.5
				H-2 -> L+1	-0.40777	33.3
				H-1 -> L+1	0.23169	10.7
				H-1 -> L+2	-0.19116	7.3
10	3.9163	316.59	0.0617	H-2 -> L+1	0.46952	44.1
				H-3 -> L	-0.38495	29.6
				H -> L+2	0.28257	16.0

Table S5. Major transitions of nanographene **3** calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description		Absolute contributions (%)
1	2.9618	418.61	0.1115	H -> L	0.67501	91.1
				H-1 -> L+1	0.17405	6.1
2	3.1250	396.75	0.0259	H-1 -> L	0.58072	67.4
				H -> L+1	-0.36606	26.8
3	3.4217	362.35	0.0195	H-5 -> L	0.6082	74.0
				H-6-> L	0.33093	9.2
				H -> L+1	-0.21429	5.4
4	3.4558	358.77	0.2124	H -> L+1	0.52066	54.2
				H-1 -> L	0.34289	23.5
				H-5 -> L	0.22114	9.8
5	3.4864	355.62	0.0118	H-6 -> L	0.63264	80.0
				H-5 -> L	0.17806	6.3
6	3.5307	351.16	0.1424	H-1 -> L+1	0.53986	58.3
				H -> L+2	0.35608	25.4
7	3.5658	347.70	0.0186	H-2 -> L	0.65797	86.6
8	3.7430	331.24	0.0179	H-2 -> L	0.65797	86.6
				H-3 -> L	-0.33744	22.8
				H -> L+2	0.17203	5.9
9	3.7840	327.65	0.1035	H-3 -> L	0.40372	32.6
				H-2 -> L+1	0.37992	28.9
				H -> L+2	-0.24418	11.9
				H-1 -> L+1	0.22461	10.1
10	3.8714	320.26	0.3990	H -> L+2	0.46619	43.5
				H-3 -> L	0.30505	18.6
				H-1 -> L+1	-0.26412	14.0
				H-1 -> L+2	-0.24740	12.2

Table S6. Major transitions of nanographene **4** calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description		Absolute contributions (%)
1	2.9496	420.34	0.1076	H -> L	0.67518	91.2
				H-1 -> L+1	0.16884	5.7
2	3.1254	396.70	0.0220	H-1 -> L	0.56990	65.0
				H -> L+1	-0.38123	29.1
3	3.3830	366.49	0.0856	H-2 -> L	0.48841	47.7
				H -> L+1	-0.34294	23.5
				H-1 -> L	-0.26770	14.3
				H-2 -> L+1	-0.18374	6.8
4	3.4214	362.38	0.0073	H-5 -> L	0.61489	75.6
				H-2 -> L	-0.19661	7.7
				H-6 -> L	-0.17418	6.1
5	3.4483	359.55	0.1349	H-2 -> L	0.42273	35.7
				H -> L+1	0.41342	34.2
				H-1 -> L	0.24031	11.5
6	3.4889	355.37	0.0028	H-6 -> L	0.64239	82.5
				H-5 -> L	0.19252	7.4
7	3.5318	351.05	0.1406	H-1 -> L+1	0.52731	55.6
				H -> L+2	0.38613	29.8
8	3.6240	342.12	0.0206	H-2 -> L+1	0.64596	83.5
9	3.7531	330.35	0.0952	H-3 -> L	0.54903	60.3
				H -> L+2	-0.25765	13.3
				H-1 -> L+1	0.21707	9.4
10	3.8548	321.64	0.4174	H -> L+2	0.47748	45.6
				H-1 -> L+1	-0.29889	17.9
				H-3 -> L	0.29348	17.2
				H-1 -> L+2	-0.21561	9.3

Table S7. Major transitions of nanographene **1-Me**$^{+}$ calculated by TD-DFT.

Excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	Description		Absolute contributions (%)
1	1.9896	623.16	0.0653	H -> L	0.67315	90.6
				H-1 -> L	-0.17860	6.4
2	2.1361	580.42	0.0736	H-1 -> L	0.67184	90.3
				H -> L	0.17823	6.4
3	2.4675	502.47	0.0032	H-2 -> L	0.70233	98.7
4	2.6930	460.39	0.0203	H-3 -> L	0.67962	92.4
5	2.8924	428.66	0.0943	H -> L+1	0.66903	89.5
6	3.0423	407.53	0.1790	H-1 -> L+1	0.62101	77.1
7	3.0636	404.70	0.0076	H-6 -> L	0.66060	87.3
8	3.1638	391.88	0.0158	H-4 -> L	0.66346	88.0
9	3.3272	372.64	0.0062	H-2 -> L+1	0.69187	95.7
10	3.3576	369.26	0.0394	H-5 -> L	0.66138	87.5
11	3.5597	348.30	0.0096	H-3 -> L+1	0.53367	57.0
				H -> L+2	0.33898	23.0
				H-1 -> L+2	0.20347	8.3
12	3.5813	346.20	0.0022	H-7 -> L	0.47971	46.0
				H-1 -> L+2	-0.30556	18.7
				H -> L+2	0.29957	17.9
13	3.6710	337.74	0.1141	H -> L+2	0.44859	40.2
				H-7 -> L	-0.39778	31.6
				H -> L+3	-0.17315	6.0

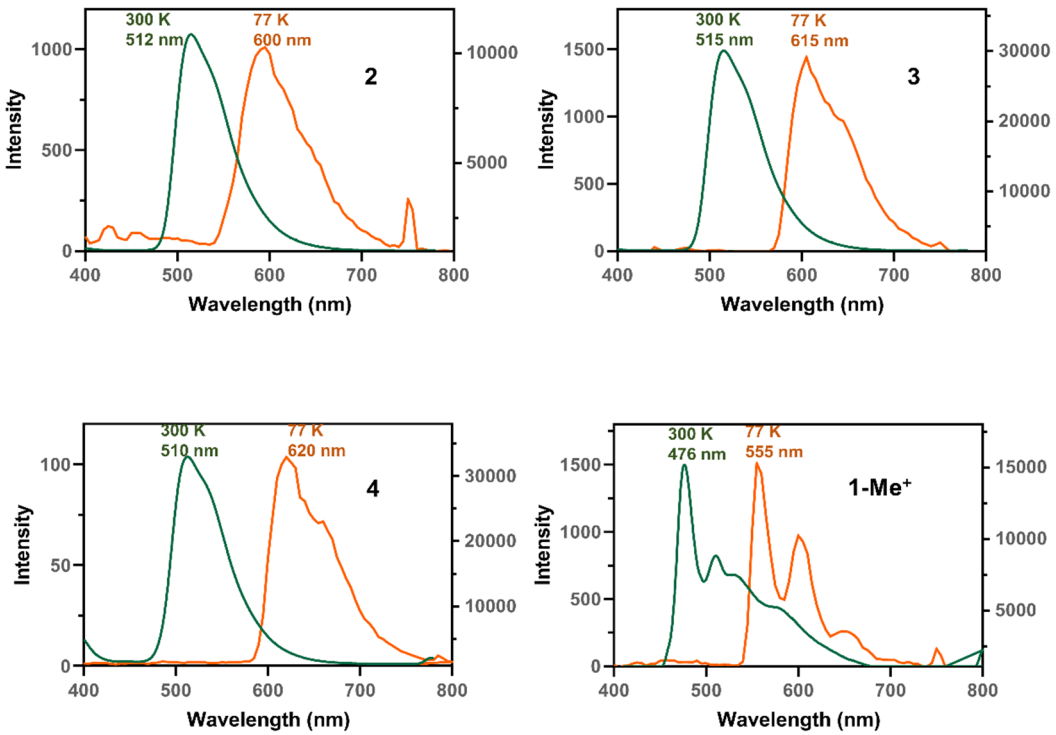
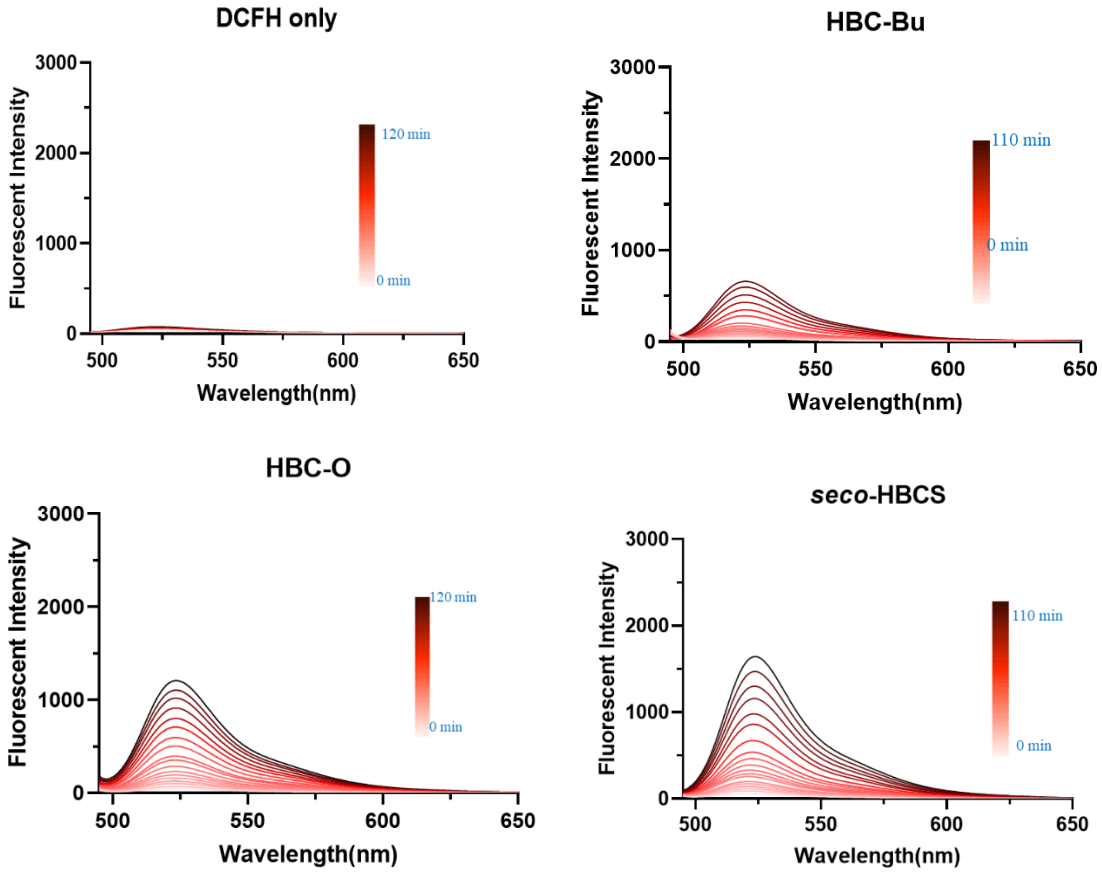


Figure S19. Photoluminescence spectra of in toluene at 300 or 77 K. λ_{ex} = 375 nm.



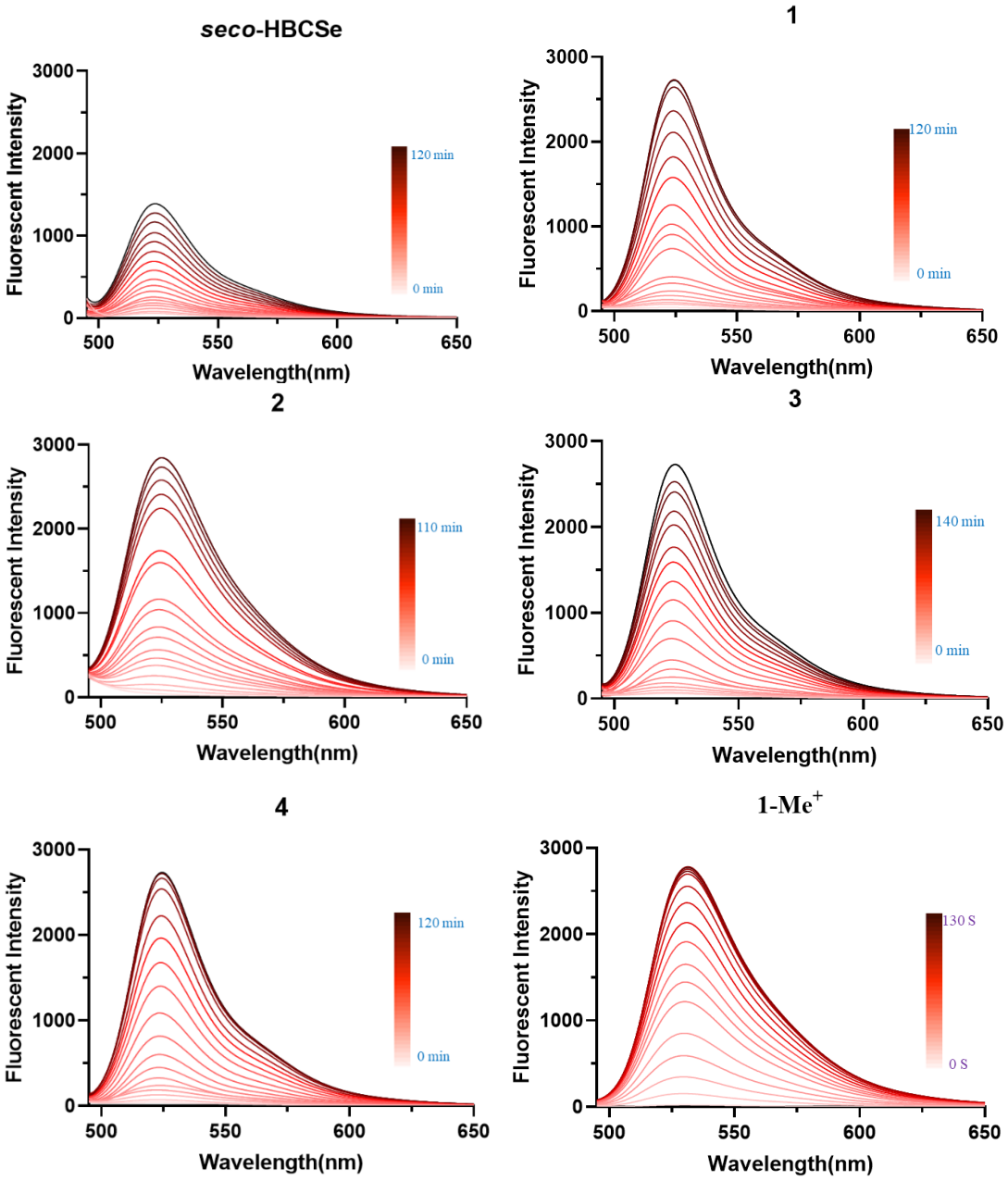


Figure S20. Emission spectra of DCFH (4 μM) in PBS buffer and methanol (v:v=9:1) in the presence of **DCFH only**, **HBC-Bu**, **HBC-O**, ***seco*-HBCS**, ***seco*-HBCSe**, **1**, **2**, **3**, **4**, and **1-Me**$^{+}$(20 μM)$^{\cdot}$, after exposure to yellow LED irradiation(0.02 W/cm^2) with different time.

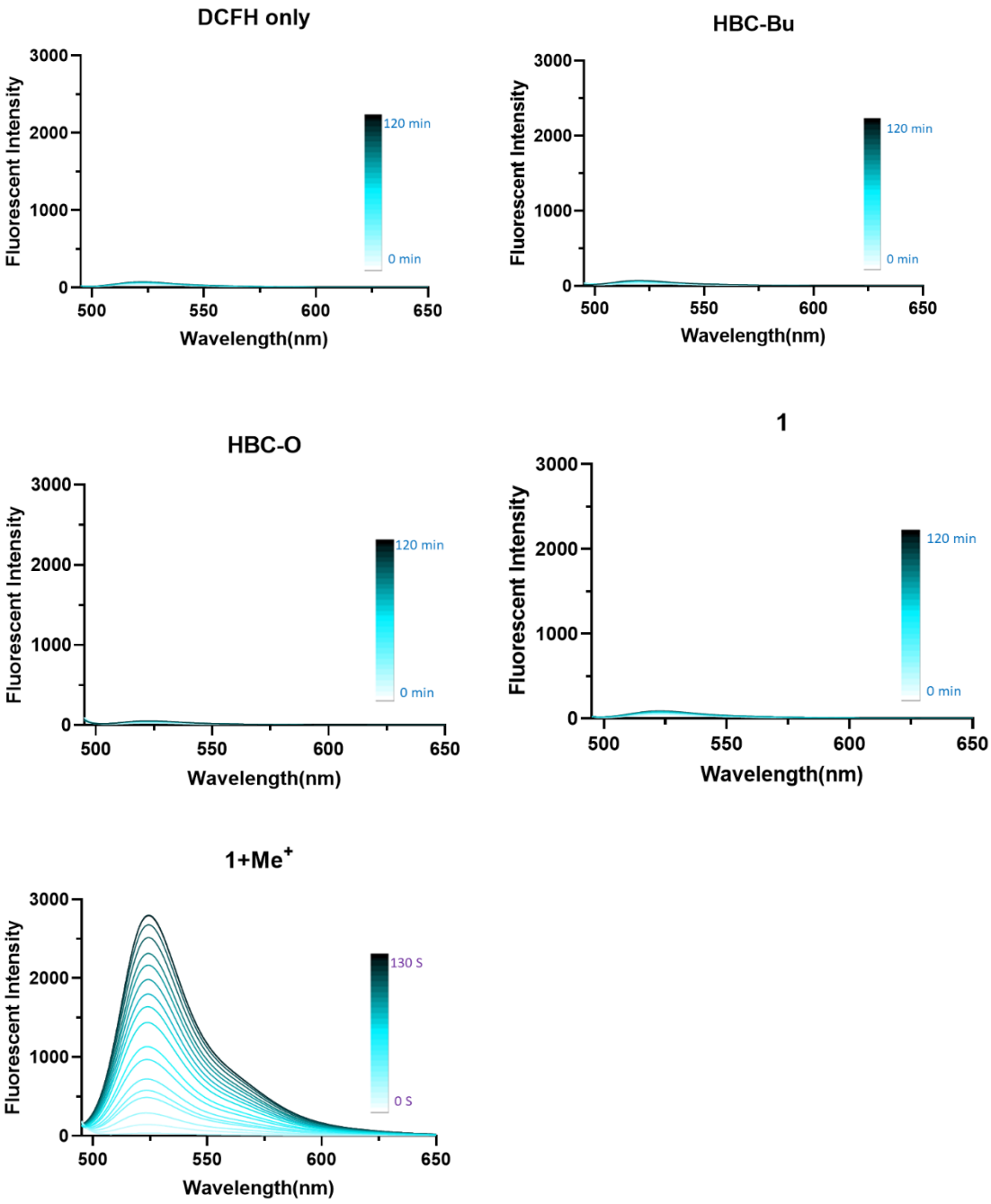
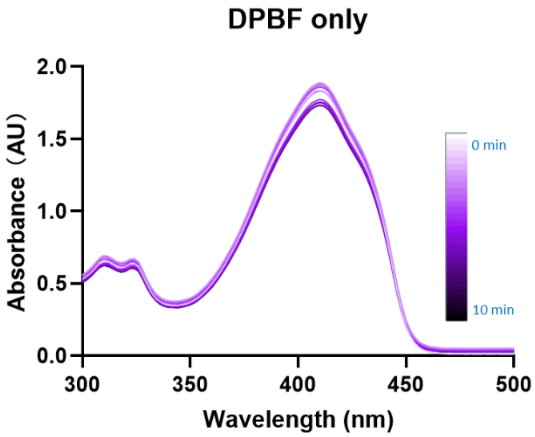
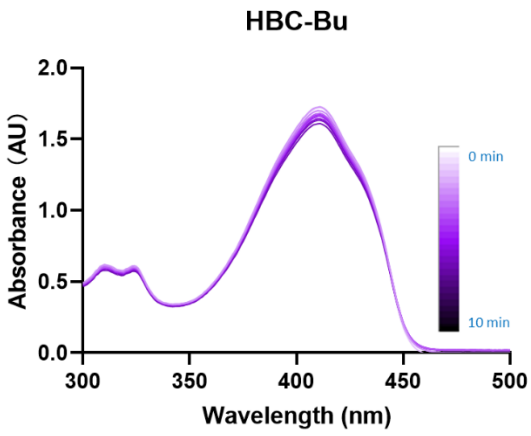
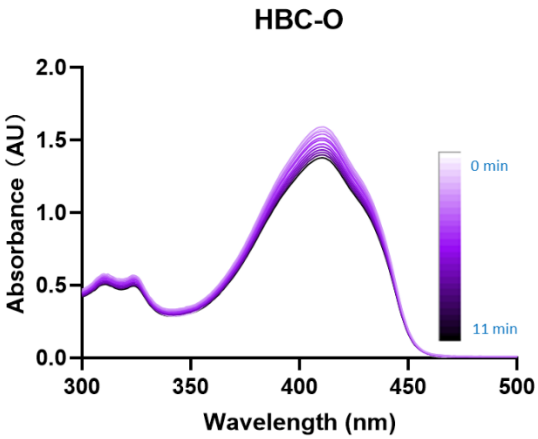
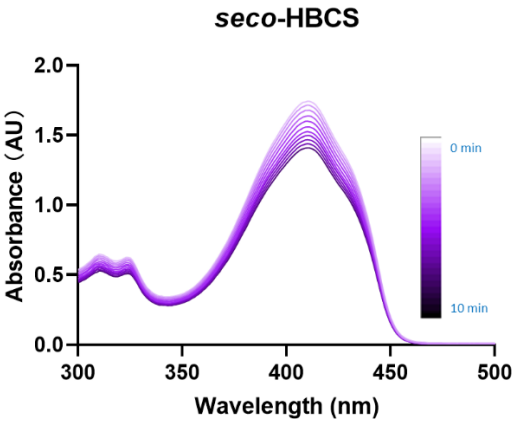


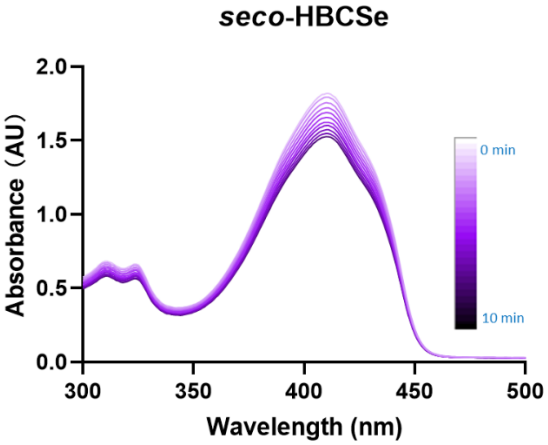
Figure S21. Emission spectra of DCFH (4 μM) in PBS buffer and methanol (v:v=9:1) in the presence of **DCFH only**, **HBC-Bu**, **HBC-O**, **1** and **1-Me**$^{+}$(20 μM) , after exposure to 630 nm laser irradiation (0.15 W/cm^{2}) with different time.

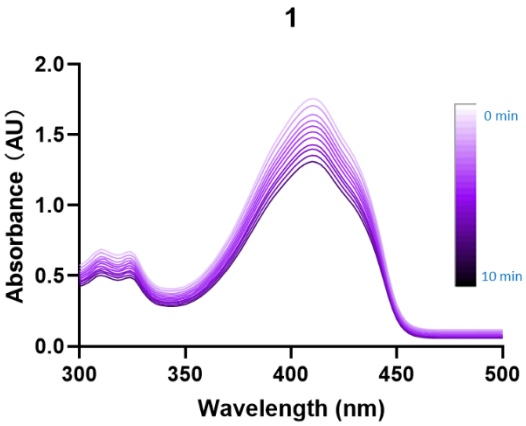

DPBF only
Absorbance (AU)
Wavelength (nm)
0 min
10 min


HBC-Bu
Absorbance (AU)
Wavelength (nm)
0 min
10 min


HBC-O
Absorbance (AU)
Wavelength (nm)
0 min
11 min


seco-HBCS
Absorbance (AU)
Wavelength (nm)
0 min
10 min


seco-HBCSe
Absorbance (AU)
Wavelength (nm)
0 min
10 min


1
Absorbance (AU)
Wavelength (nm)
0 min
10 min

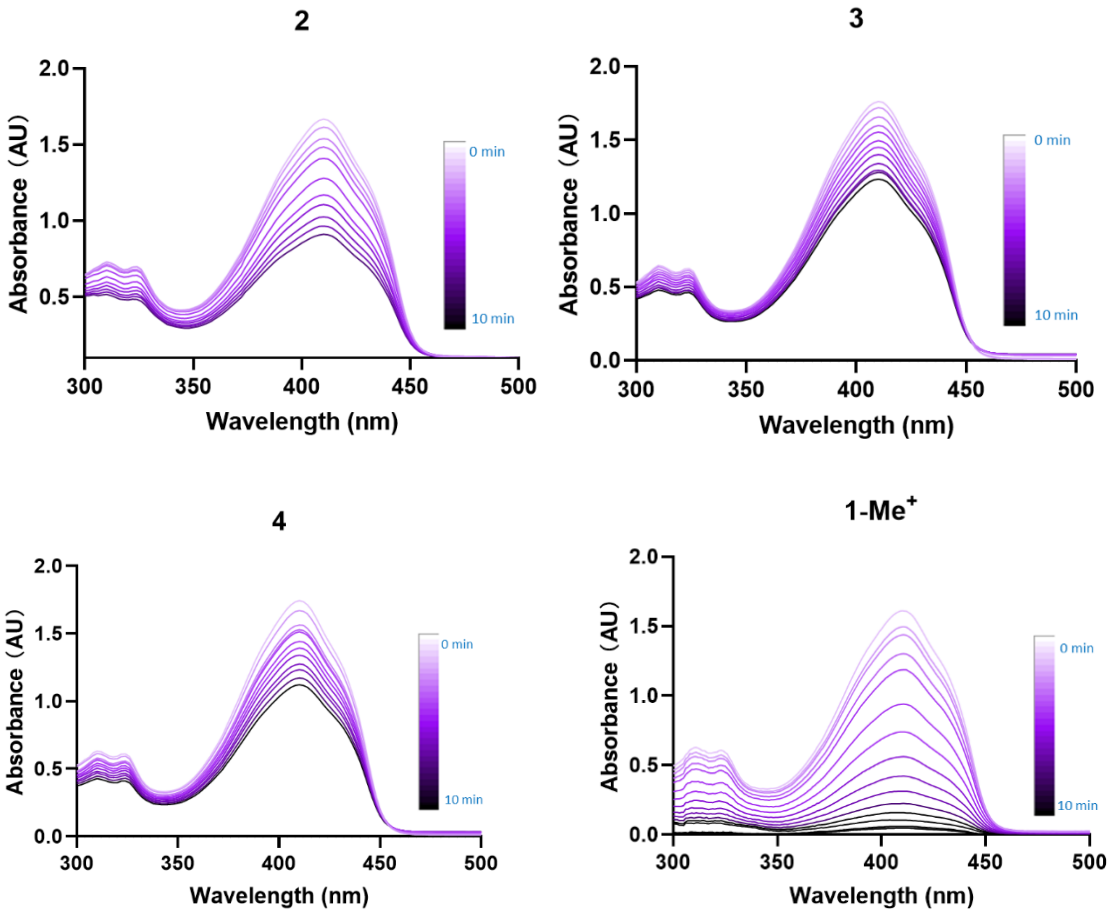
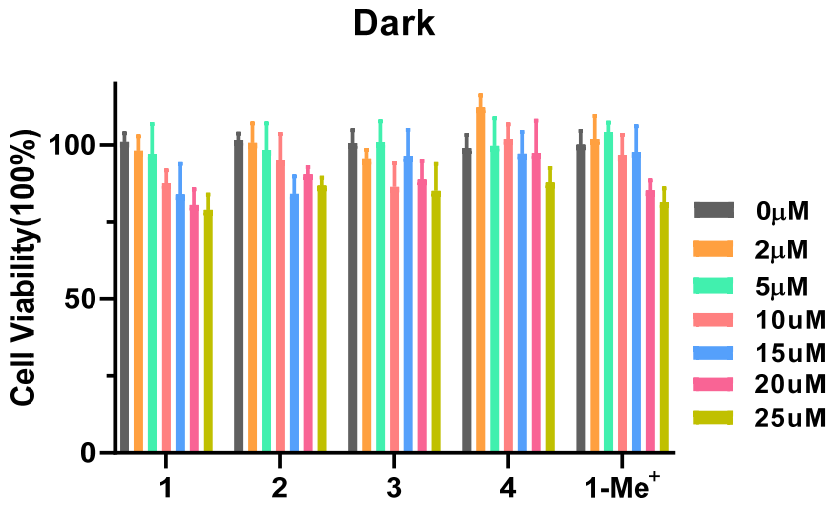


Figure S22. Absorption spectra of DPBF (80 μM) in PBS buffer and methanol (v:v=1:9) in the presence of **DPBF only**, **HBC-Bu**, **HBC-O**, **HBC-S**, **HBC-Se**, **1**, **2**, **3**, **4**, and **1-Me**$^{+}$(20 μM) , after exposure to yellow LED irradiation(0.02 W/cm^{2}) with different time.

a)



b)

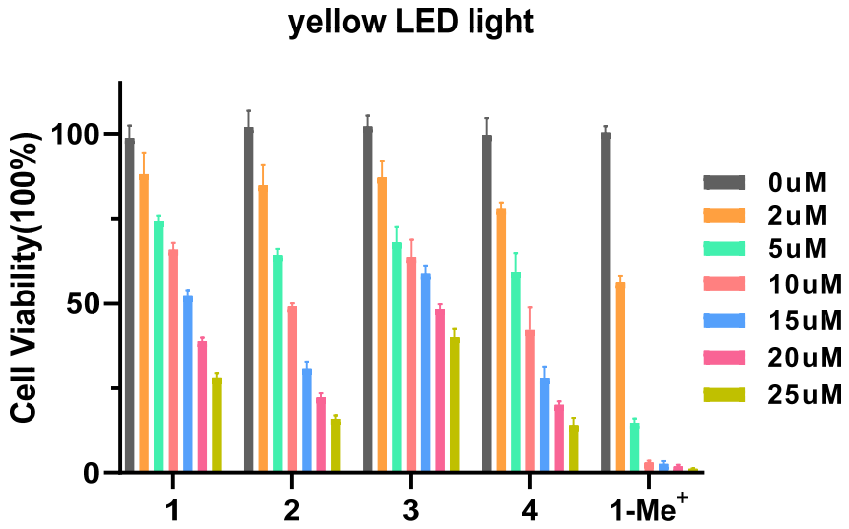


Figure S23. Cell viability of Hela cells after incubation of **1**–**4** and **1-Me**$^{+}$ with or without yellow LED light irradiation for 30min (0.02 W/cm^2, n = 4, mean ± SD).

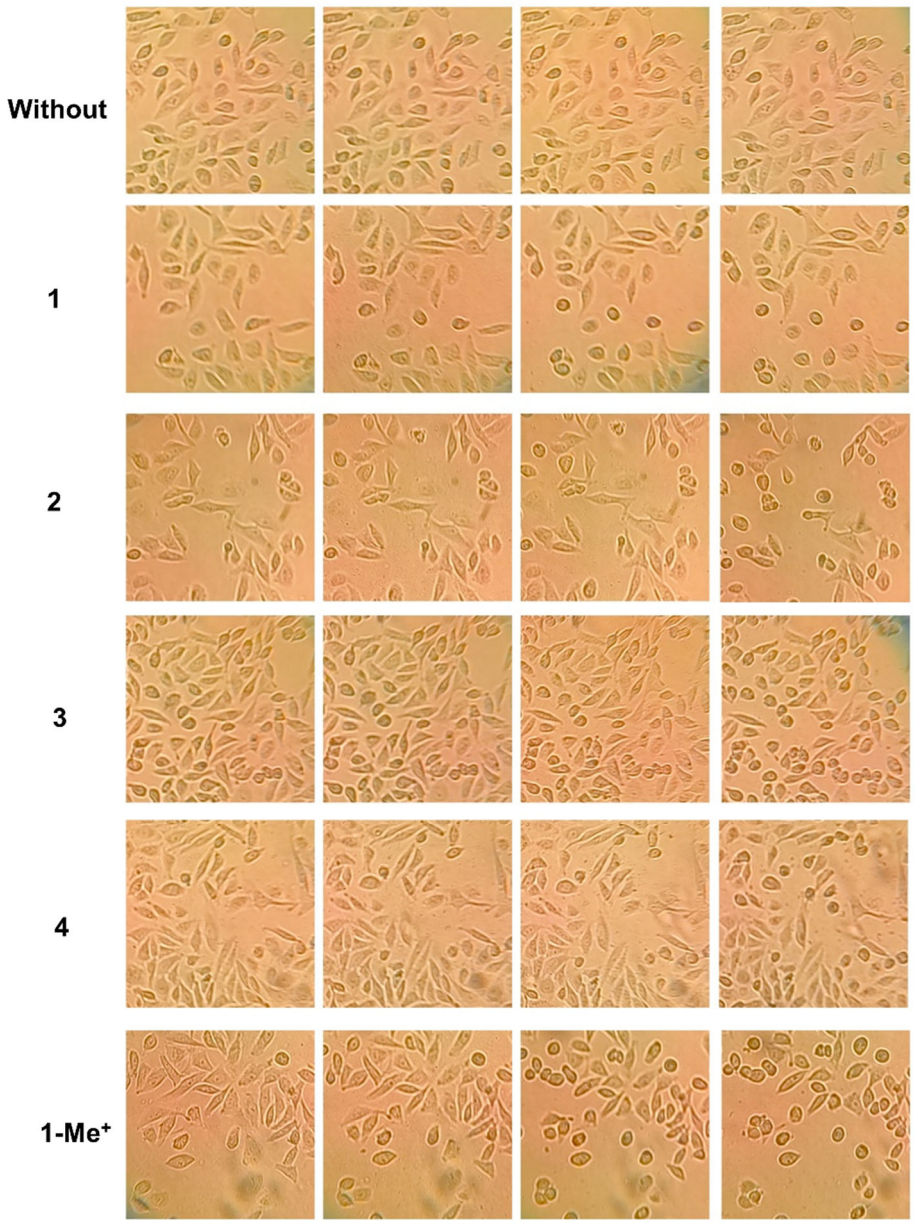


Figure S24. Hela cell morphological changes incubated with different compounds (10 μM) under yellow LED light irradiation monitored during 5 mins (0.02 W/cm^2).

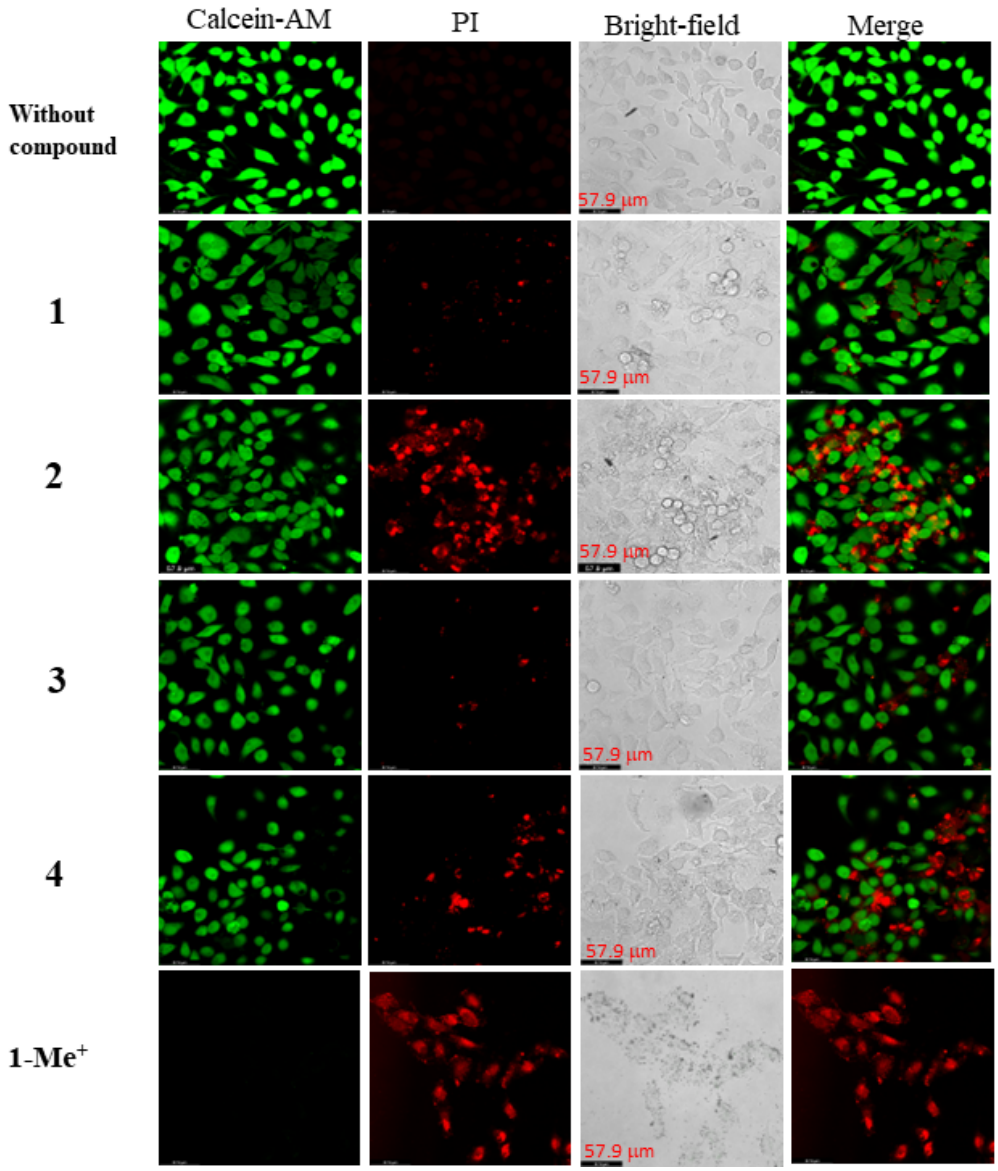


Figure S25. Confocal laser scanning microscopy evaluation of tumor killing effect by calcein AM /propidium iodide (PI) dyes in Hela cells treated with NGs**1-4** and **1-Me**$^{+}$ (10 μM) under yellow LED light treatment (0.02 W/cm^{2}).

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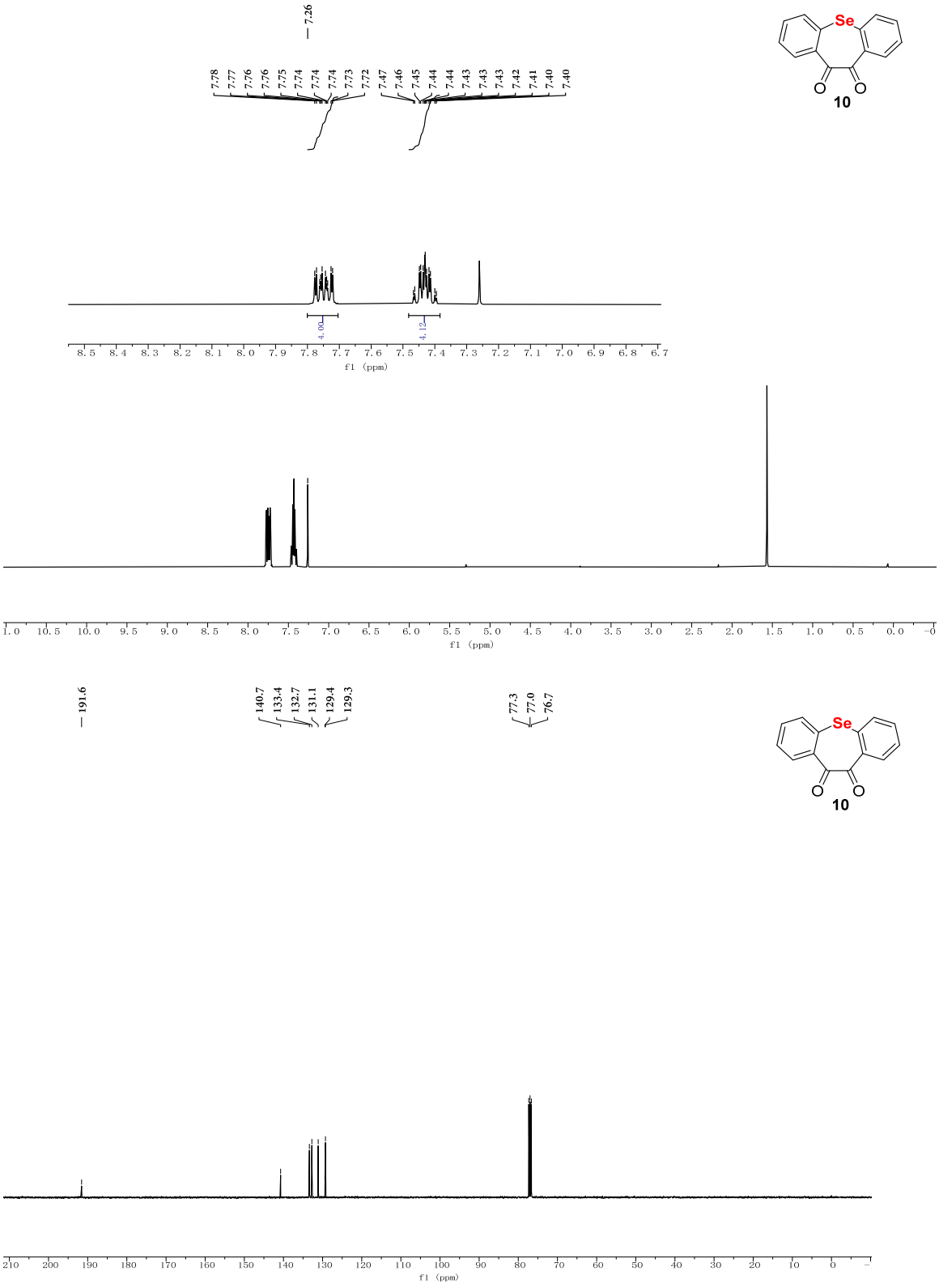
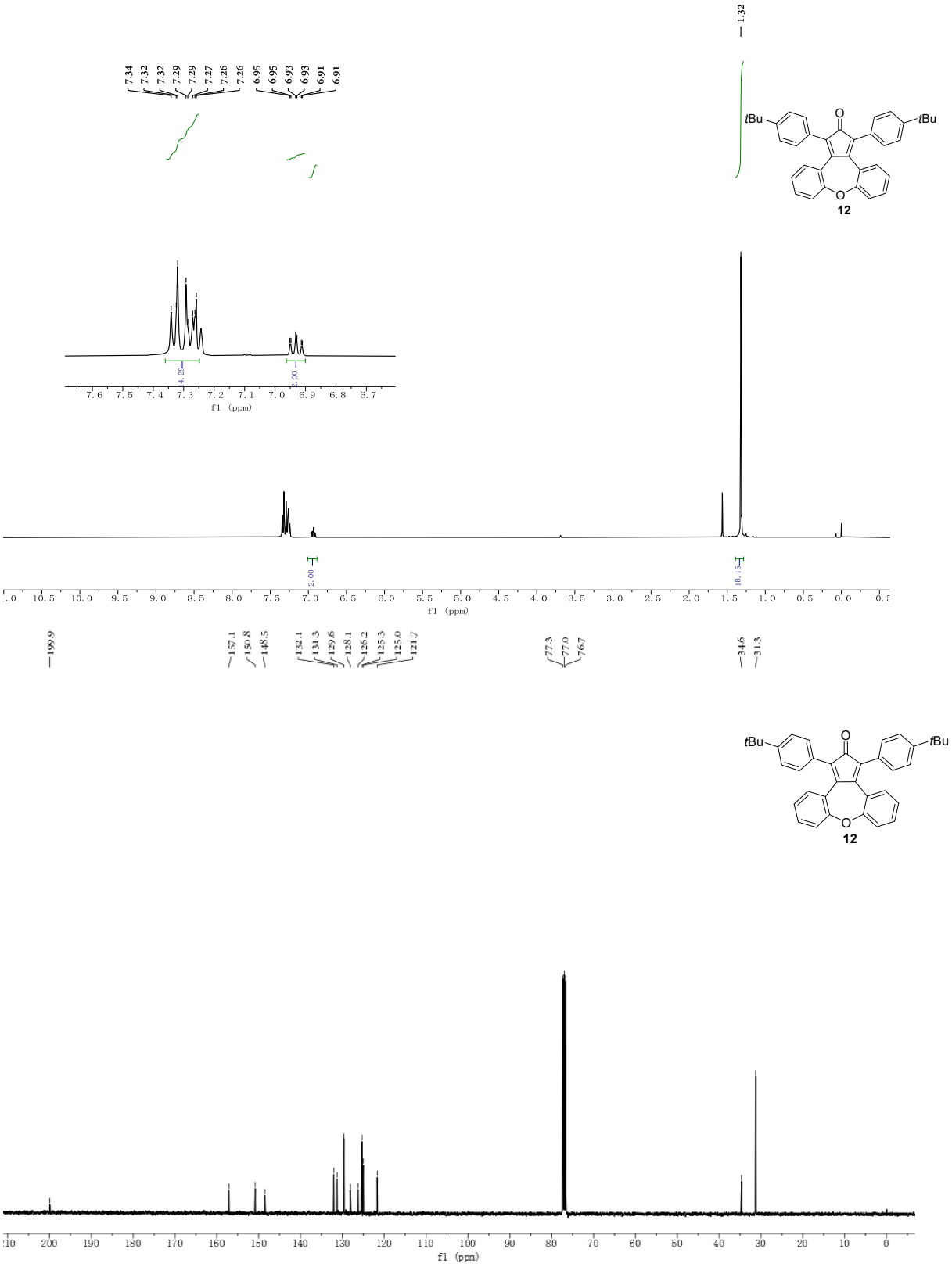
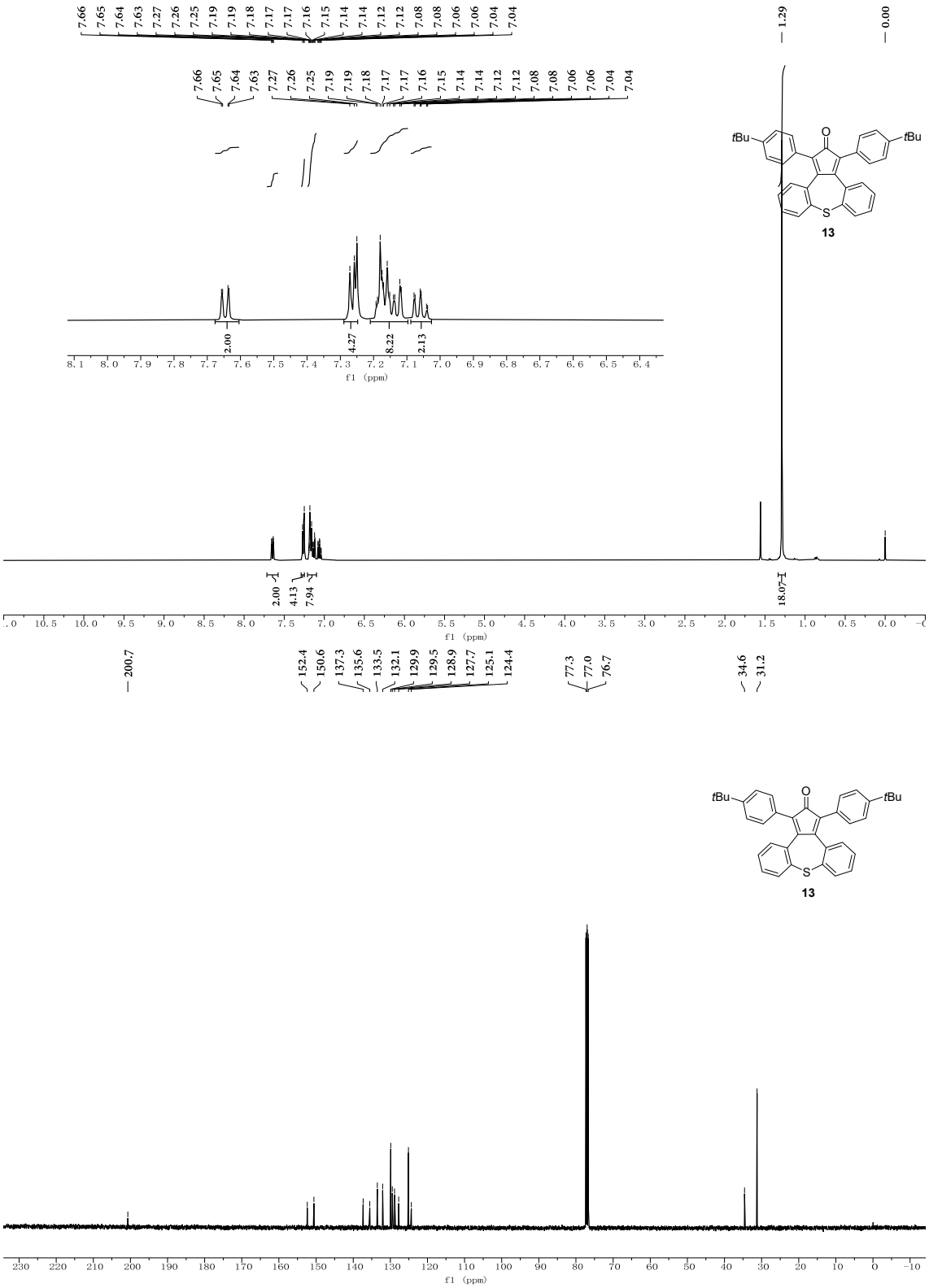
Spectra (^{1}H NMR and ^{13}C NMR**)**



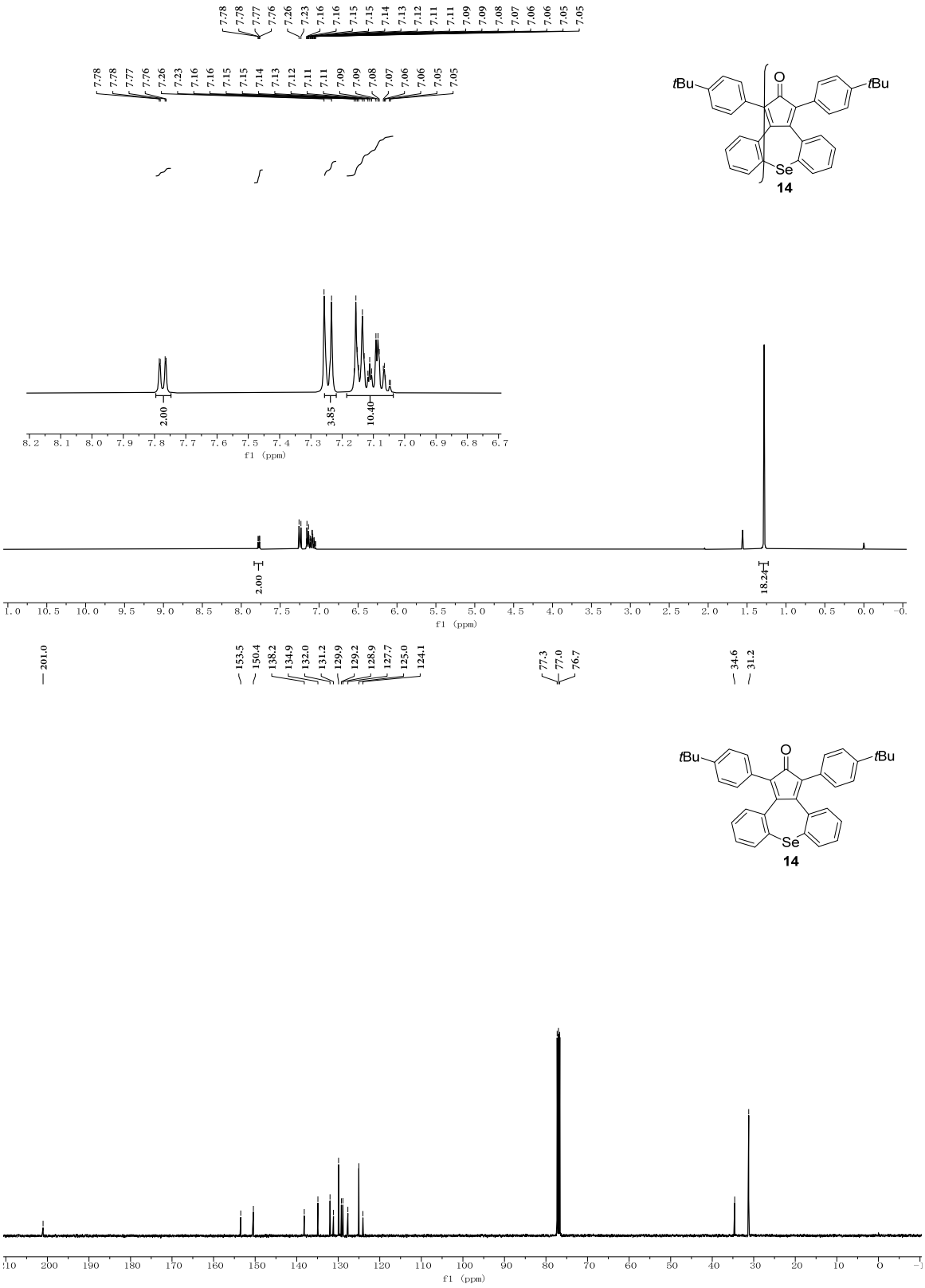
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **10** in $CDCl_3$.



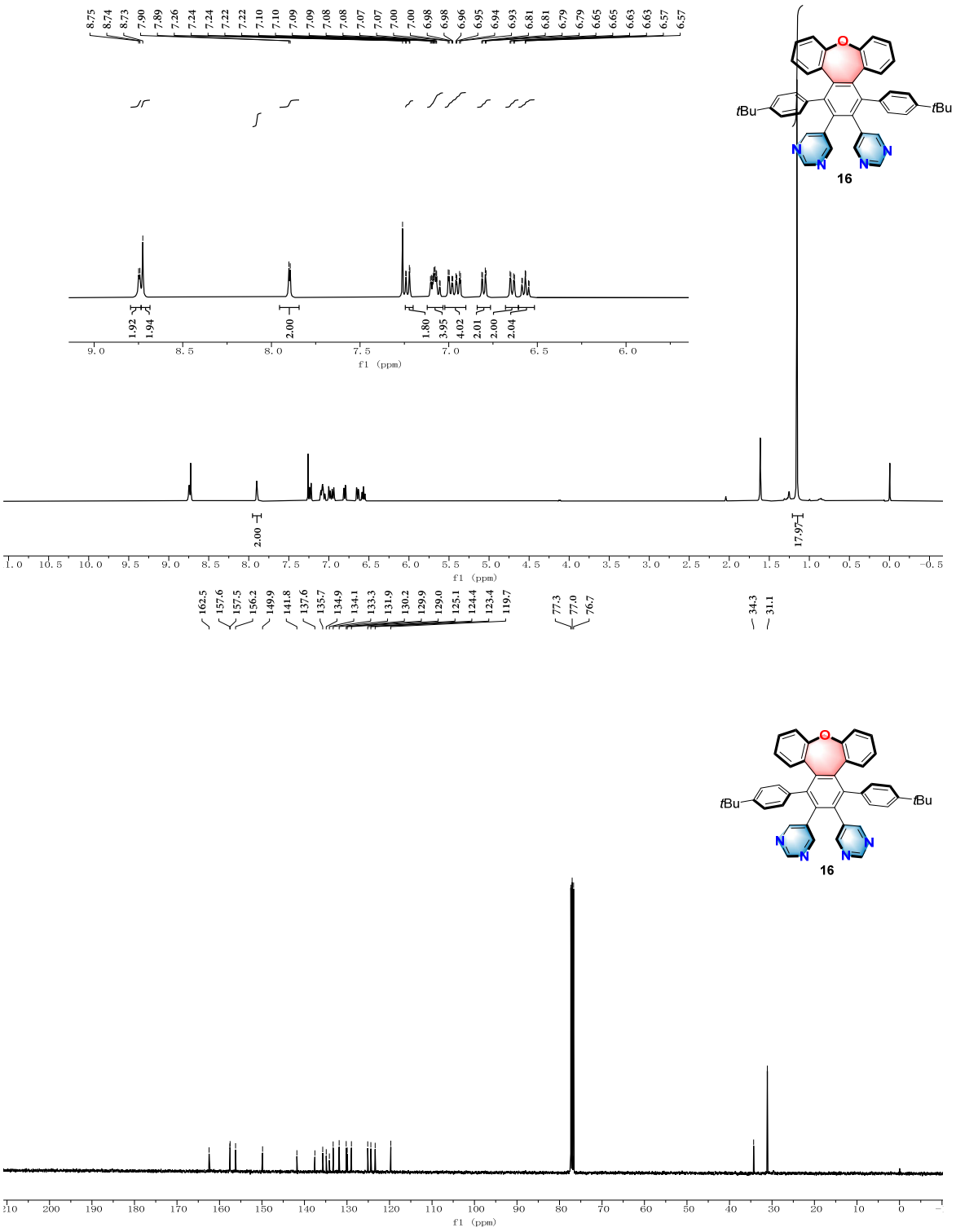
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **12** in $CDCl_3$.



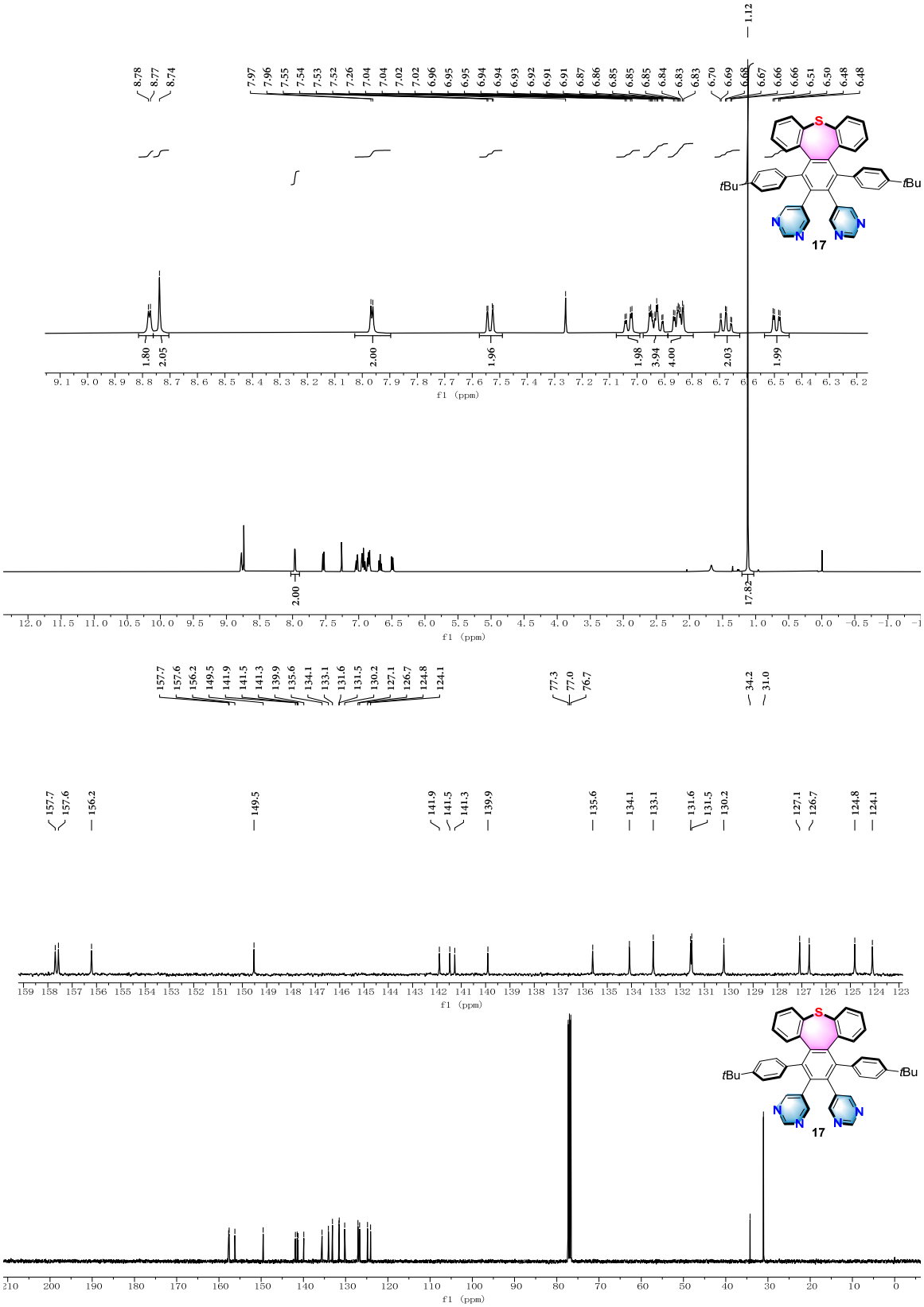
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **13** in $CDCl_3$.



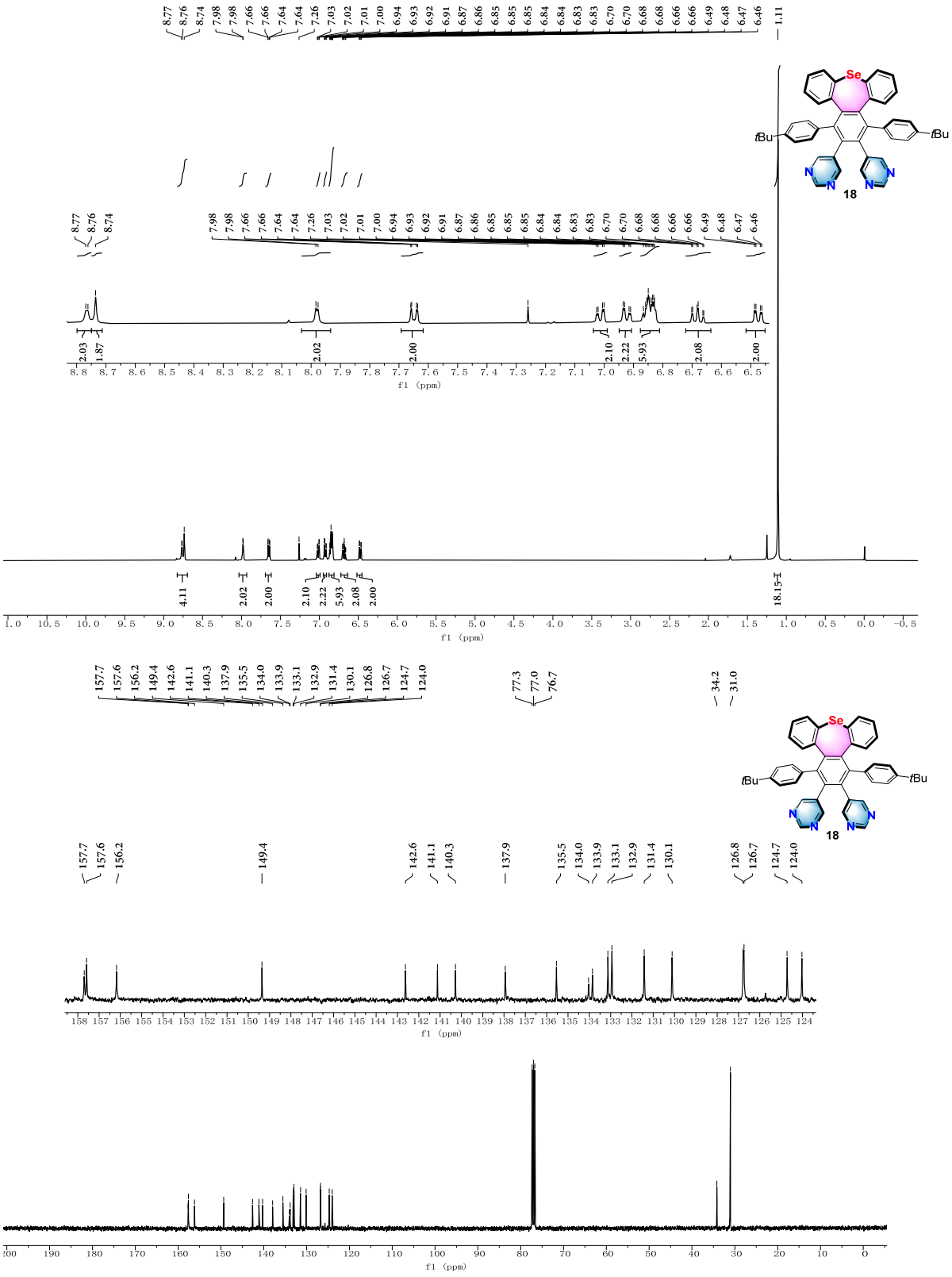
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **14** in $CDCl_3$.



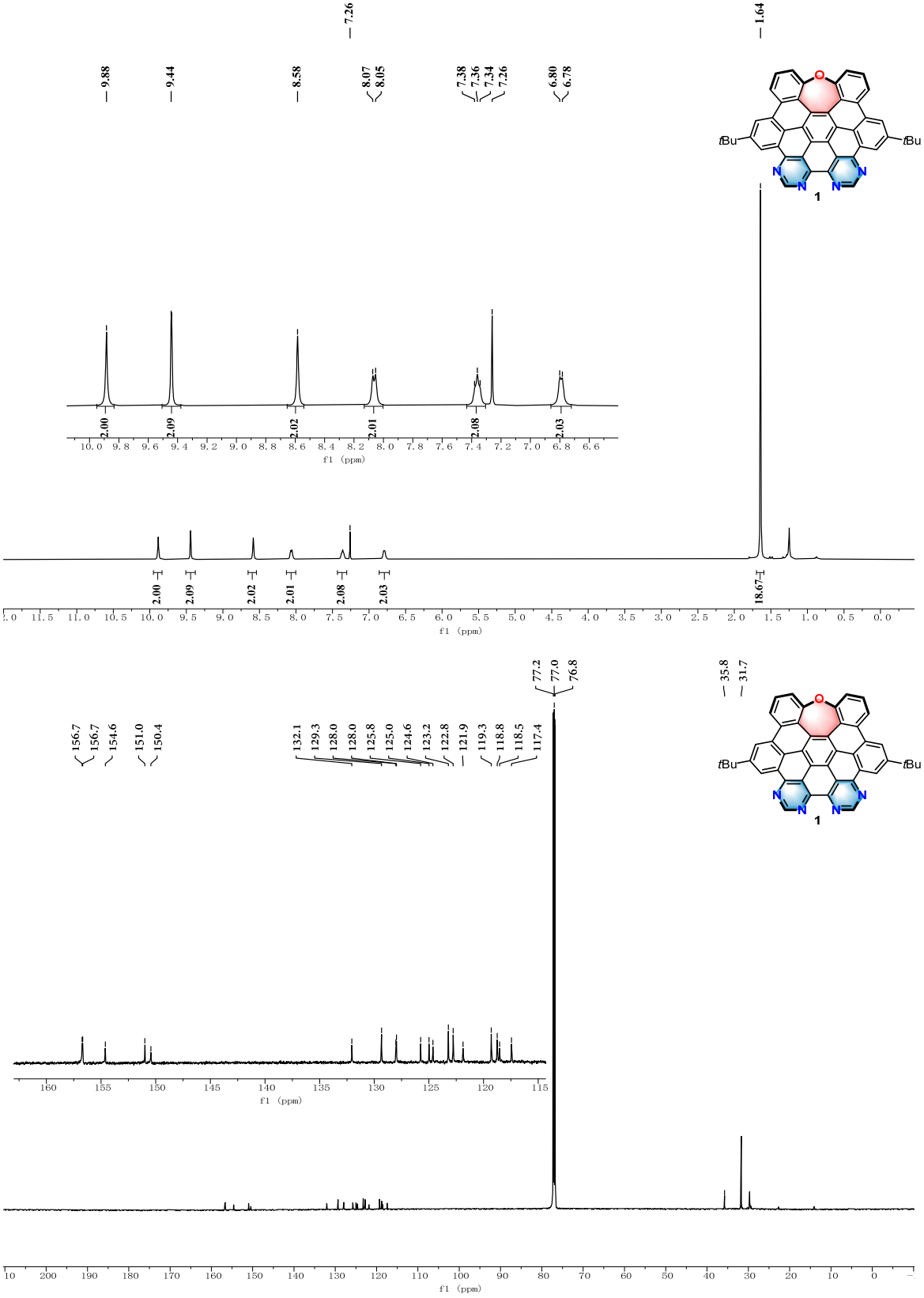
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **16** in $CDCl_3$.



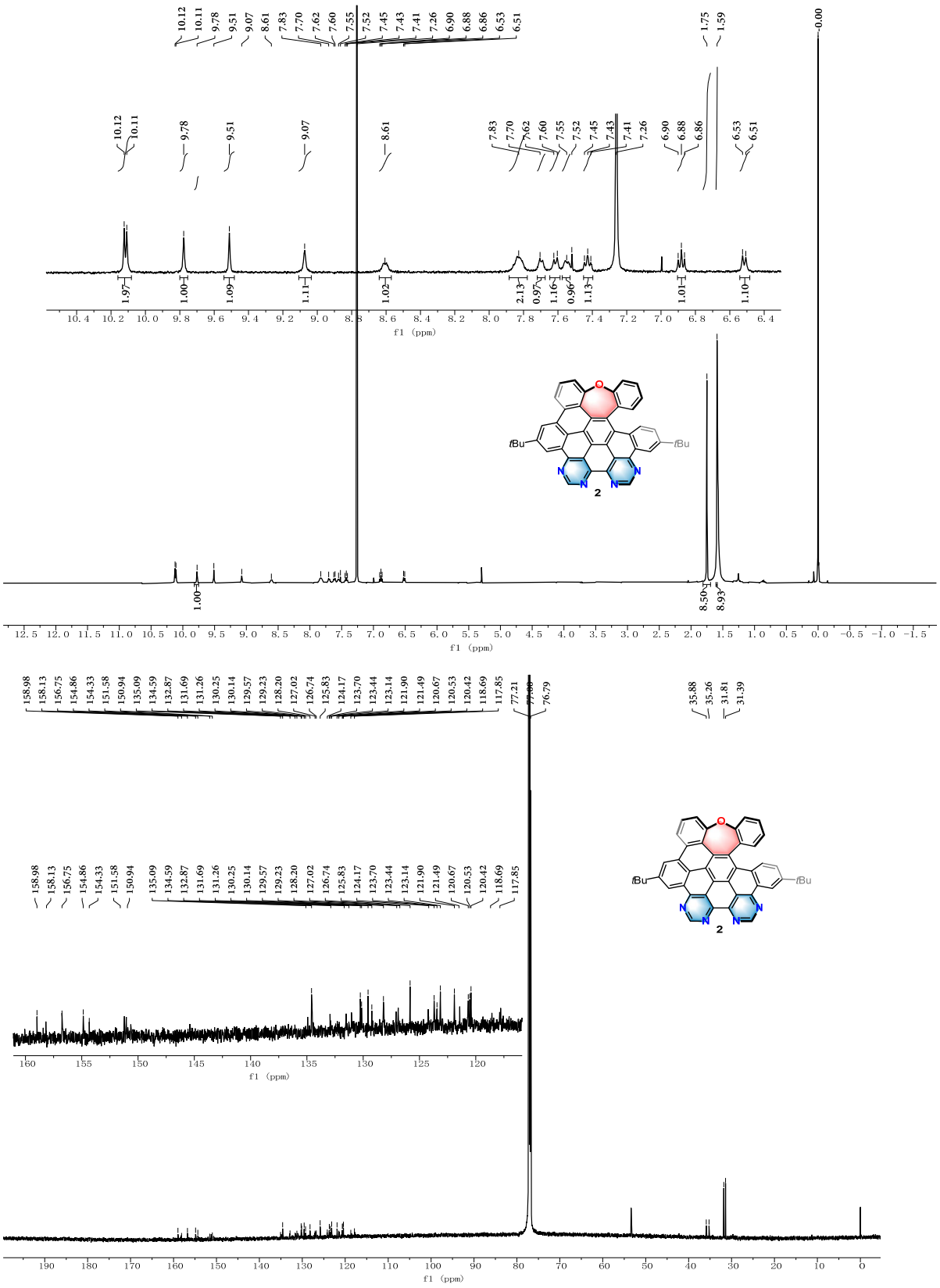
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **17** in $CDCl_3$.



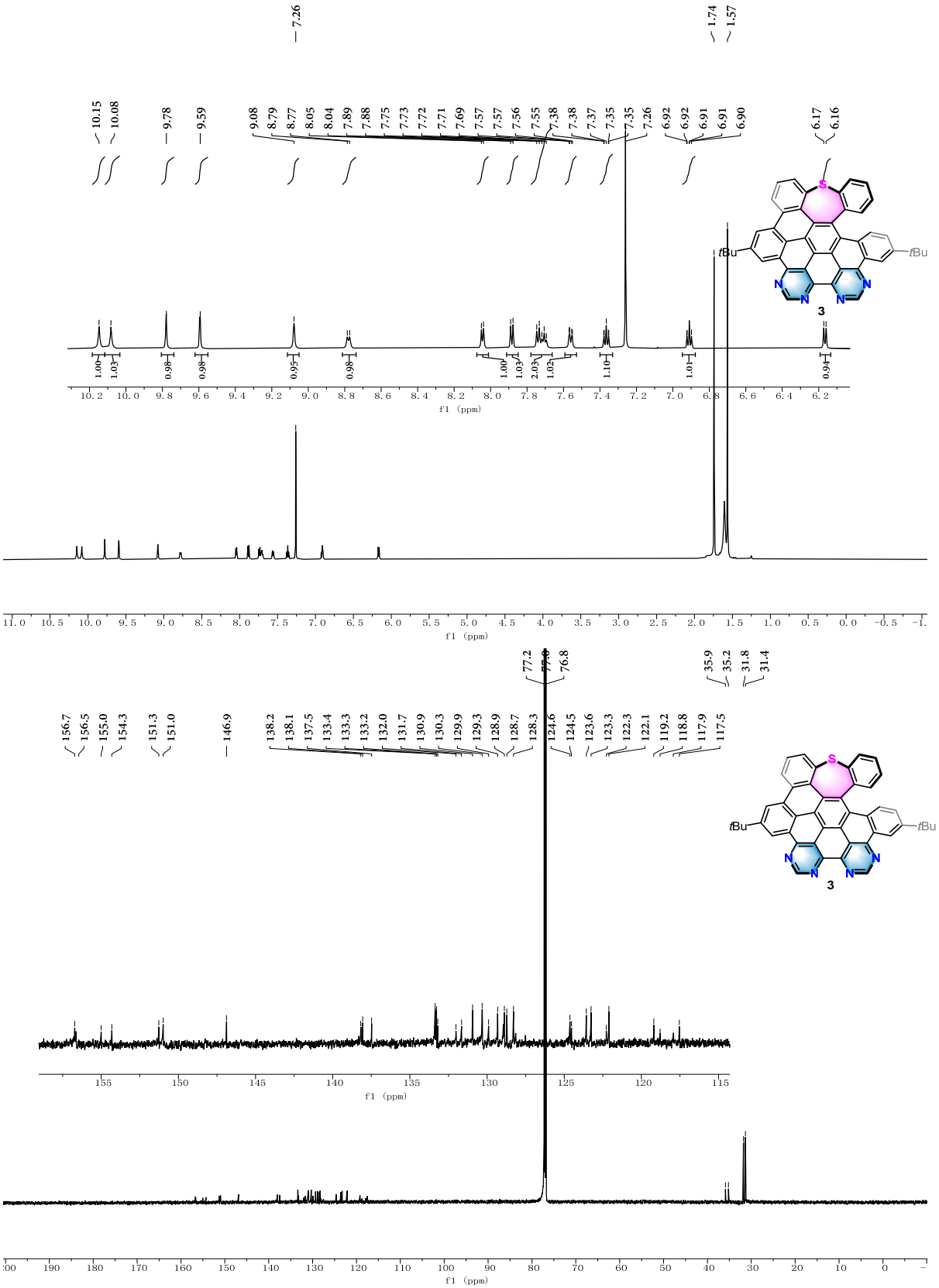
^{1}H NMR (400 MHz, up) and ^{13}C NMR (101 MHz, down) of **18** in $CDCl_3$.



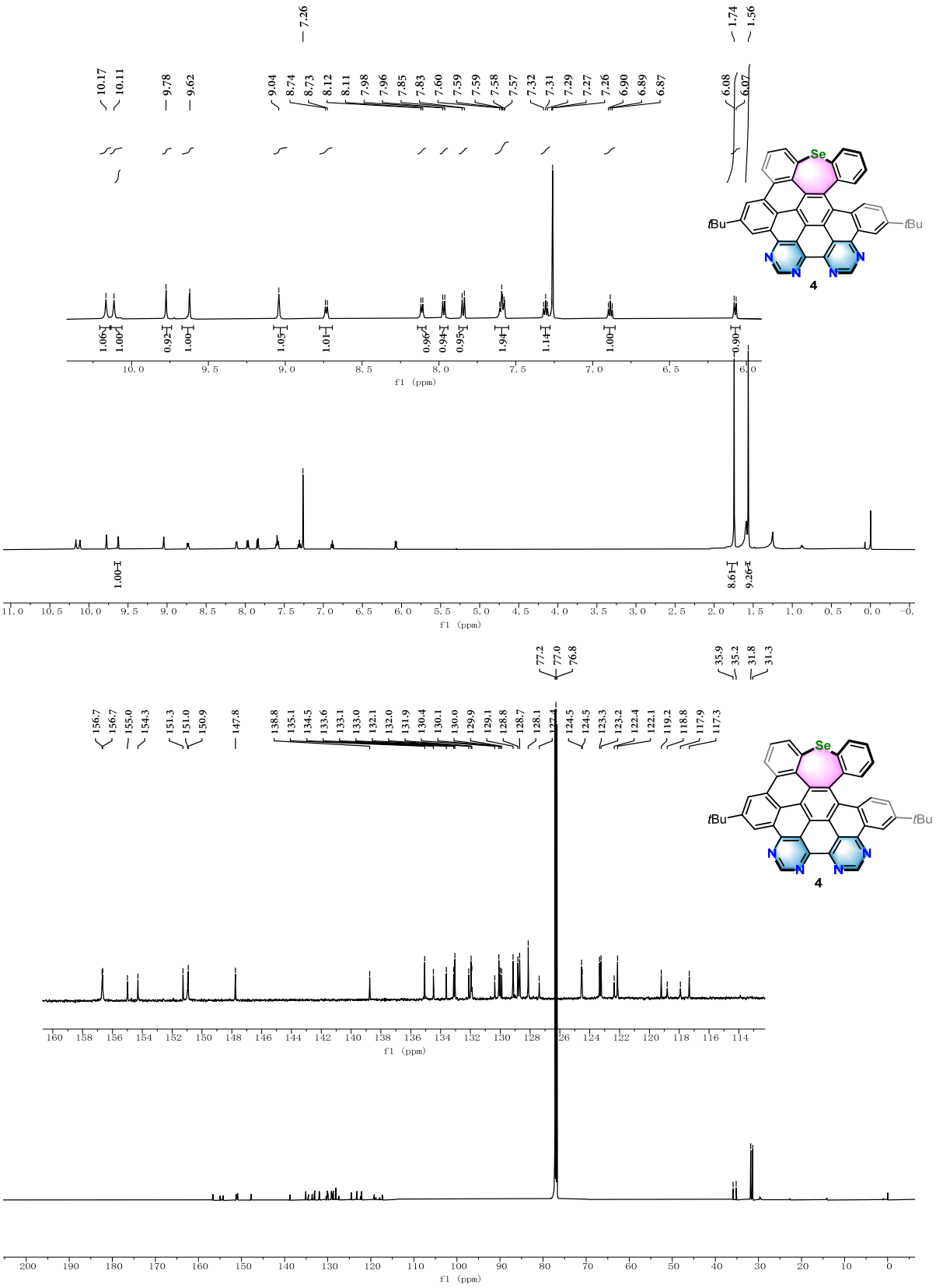
^{1}H NMR (400 MHz, up) and ^{13}C NMR (151 MHz, down) of **1** in $CDCl_3$.



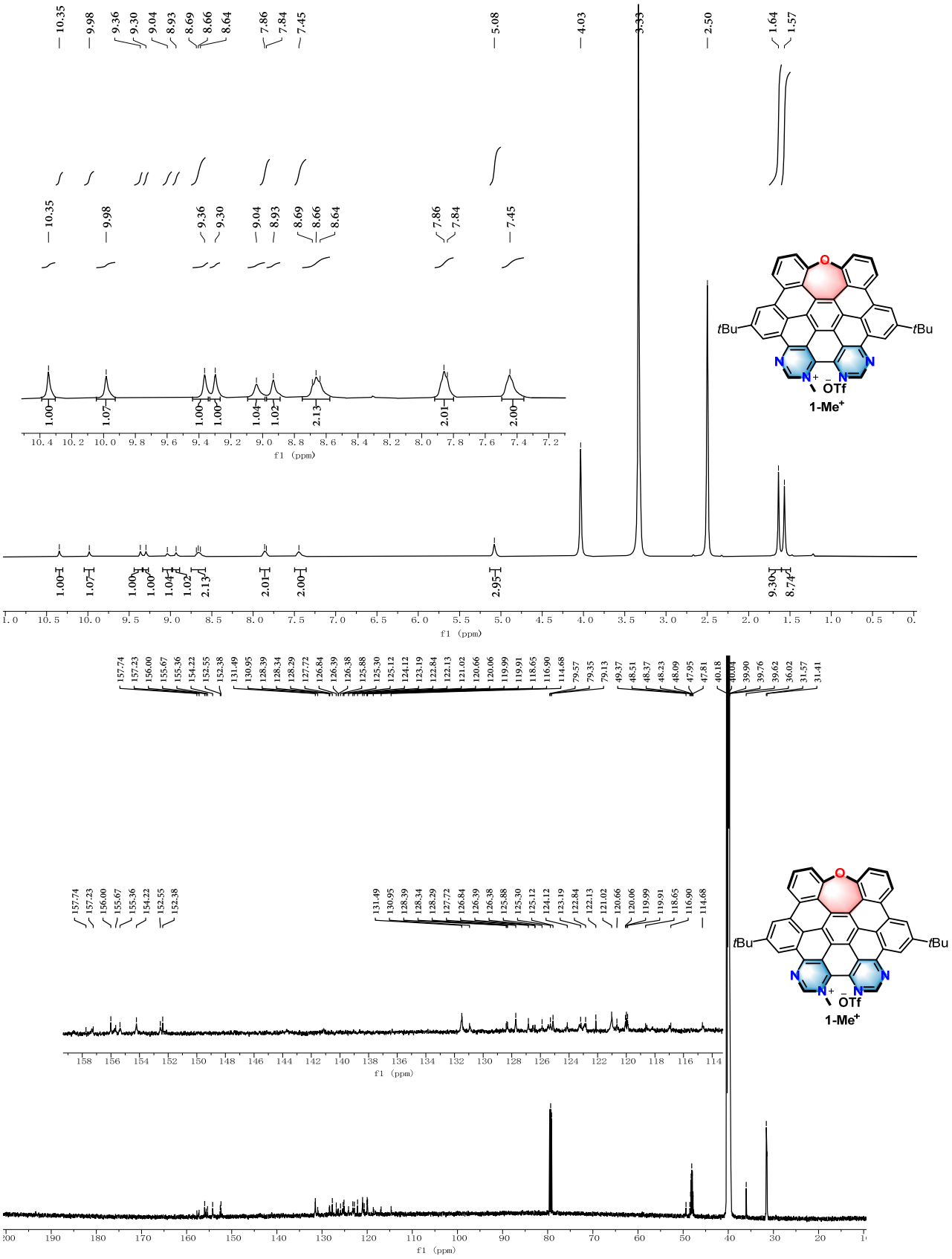
^{1}H NMR (400 MHz, up) and ^{13}C NMR (151 MHz, down) of **2** in $CDCl_3$.



^{1}H NMR (400 MHz, up) and ^{13}C NMR (151 MHz, down) of **3** in $CDCl_3$.



^{1}H NMR (400 MHz, up) and ^{13}C NMR (151 MHz, down) of **4** in $CDCl_3$.



^{1}H NMR (600 MHz, up) and ^{13}C NMR (151 MHz, down) of **1-Me**$^{+}$ in DMSO-d6–CD_3OD–$CDCl_3$ mixed solvents.

Table S8. Atomic coordinates and energies of NG **1.**

Zero-point correction=	0.642158 (Hartree/Particle)
Thermal correction to Energy=	0.678526
Thermal correction to Enthalpy=	0.679470
Thermal correction to Gibbs Free Energy=	0.576457
Sum of electronic and zero-point Energies=	-2064.071855
Sum of electronic and thermal Energies=	-2064.035487
Sum of electronic and thermal Enthalpies=	-2064.034543
Sum of electronic and thermal Free Energies=	-2064.137556

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000003	3.770437	-1.704125
2	6	0	6.992449	-0.338978	1.165395
3	6	0	5.535973	-0.206925	0.711305
4	6	0	4.865883	1.005569	0.669039
5	1	0	5.398466	1.895819	0.960599
6	6	0	3.536995	1.123747	0.246732
7	6	0	2.820636	-0.032581	-0.092991
8	6	0	1.402829	0.038278	-0.383151
9	6	0	0.695235	-1.176426	-0.494573
10	6	0	-0.695236	-1.176426	-0.494550
11	6	0	-1.392257	-2.430289	-0.562479
12	6	0	-2.784809	-2.491689	-0.407638
13	6	0	-3.503462	-1.270497	-0.070020
14	6	0	-4.833166	-1.339712	0.309703
15	1	0	-5.298091	-2.315958	0.301208
16	6	0	-5.535969	-0.206923	0.711315
17	6	0	-6.992445	-0.338978	1.165406
18	6	0	2.897715	2.420288	0.039262
19	6	0	3.633182	3.607279	0.175549
20	1	0	4.634961	3.576065	0.576237
21	6	0	3.134150	4.819310	-0.239950
22	1	0	3.727402	5.719273	-0.136270
23	6	0	1.891267	4.864326	-0.856373
24	1	0	1.495741	5.775039	-1.286255
25	6	0	1.152886	3.709038	-0.961155
26	6	0	-1.152884	3.709038	-0.961162
27	6	0	-1.891269	4.864324	-0.856392
28	1	0	-1.495743	5.775036	-1.286278
29	6	0	-3.134155	4.819309	-0.239975
30	1	0	-3.727410	5.719271	-0.136305

31	6	0	-3.633186	3.607280	0.175530
32	1	0	-4.634967	3.576066	0.576213
33	6	0	-2.897715	2.420290	0.039256
34	6	0	-3.536994	1.123749	0.246727
35	6	0	-4.865880	1.005572	0.669043
36	1	0	-5.398461	1.895822	0.960605
37	6	0	-2.715094	-4.728899	-0.764684
38	6	0	-0.731149	-3.653915	-0.747254
39	6	0	0.731145	-3.653917	-0.747250
40	6	0	1.392254	-2.430291	-0.562471
41	6	0	2.784806	-2.491692	-0.407629
42	6	0	2.715089	-4.728905	-0.764657
43	6	0	3.503461	-1.270500	-0.070016
44	6	0	0.719540	1.271831	-0.474265
45	6	0	1.570287	2.473655	-0.447013
46	6	0	-0.719536	1.271833	-0.474242
47	6	0	-1.402833	0.038280	-0.383179
48	6	0	-2.820634	-0.032580	-0.092988
49	6	0	-1.570286	2.473656	-0.447017
50	6	0	4.833167	-1.339715	0.309700
51	1	0	5.298091	-2.315962	0.301208
52	6	0	-7.830229	-0.925693	0.016521
53	1	0	-8.872447	-1.033649	0.327796
54	1	0	-7.802838	-0.273484	-0.859449
55	1	0	-7.469585	-1.909634	-0.287331
56	6	0	-7.603469	1.006766	1.567805
57	1	0	-7.618501	1.713279	0.734459
58	1	0	-8.636770	0.855720	1.887004
59	1	0	-7.066634	1.465420	2.401636
60	6	0	-7.059634	-1.281403	2.379411
61	1	0	-6.474011	-0.886945	3.213071
62	1	0	-8.094526	-1.392285	2.713276
63	1	0	-6.677556	-2.275529	2.142226
64	6	0	7.830245	-0.925655	0.016497
65	1	0	7.802842	-0.273428	-0.859459
66	1	0	8.872464	-1.033597	0.327772
67	1	0	7.469620	-1.909596	-0.287375
68	6	0	7.603456	1.006763	1.567828
69	1	0	8.636763	0.855724	1.887011
70	1	0	7.618466	1.713302	0.734504
71	1	0	7.066623	1.465383	2.401680
72	6	0	7.059643	-1.281432	2.379377
73	1	0	8.094535	-1.392317	2.713239

74	1	0	6.474018	-0.886997	3.213047
75	1	0	6.677569	-2.275554	2.142166
76	1	0	3.261944	-5.659232	-0.881678
77	1	0	-3.261950	-5.659225	-0.881706
78	7	0	3.441499	-3.644369	-0.514182
79	7	0	1.398322	-4.800515	-0.866500
80	7	0	-1.398327	-4.800511	-0.866515
81	7	0	-3.441504	-3.644364	-0.514203

Table S9. Atomic coordinates and energies of NG **2.**

Zero-point correction= 0.666401 (Hartree/Particle)
Thermal correction to Energy= 0.703750
Thermal correction to Enthalpy= 0.704695
Thermal correction to Gibbs Free Energy= 0.599107
Sum of electronic and zero-point Energies= -2065.226012
Sum of electronic and thermal Energies= -2065.188663
Sum of electronic and thermal Enthalpies= -2065.187719
Sum of electronic and thermal Free Energies= -2065.293306

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.403192	0.039591	-0.200407
2	6	0	0.672043	1.234921	-0.100563
3	6	0	-0.729468	1.209451	-0.062374
4	6	0	-1.269827	-2.403471	0.740719
5	6	0	0.670433	3.721192	0.012326
6	6	0	-1.419032	-0.017259	-0.004049
7	6	0	-0.661881	-1.203834	0.110012
8	6	0	0.723201	-1.199410	-0.174175
9	6	0	1.354041	2.497484	-0.059432
10	6	0	-1.443820	2.453763	0.026771
11	6	0	2.846451	0.092712	-0.189639
12	6	0	-0.792285	3.696473	0.076030
13	6	0	1.504959	-2.415815	-0.440924
14	6	0	3.603295	-1.089360	-0.211819
15	6	0	-2.845633	2.478722	0.117571
16	6	0	-3.585771	1.229529	0.003219
17	6	0	3.525500	1.326916	-0.088689
18	6	0	-2.890235	0.013266	-0.104485
19	6	0	2.756882	2.564009	-0.065695
20	6	0	2.637501	4.827385	0.008737

21	6	0	4.907023	1.364730	0.019588
22	1	0	5.369282	2.339165	0.097099
23	6	0	-2.781172	4.740586	0.286978
24	6	0	2.919116	-2.362772	-0.449617
25	6	0	4.990637	-1.008067	-0.063429
26	1	0	5.561678	-1.921879	-0.031968
27	6	0	-1.943989	-2.301849	1.959387
28	1	0	-2.034879	-1.332499	2.433499
29	6	0	5.665852	0.199276	0.054547
30	6	0	-5.735765	0.143650	-0.337125
31	6	0	-4.984730	1.272765	-0.087791
32	1	0	-5.444568	2.243236	0.022772
33	6	0	0.914679	-3.630952	-0.851899
34	6	0	-5.028602	-1.053730	-0.533128
35	1	0	-5.563389	-1.960783	-0.787751
36	6	0	-3.660218	-1.119164	-0.423143
37	1	0	-3.178369	-2.065564	-0.609725
38	6	0	7.186151	0.289168	0.218444
39	6	0	3.657802	-3.504811	-0.786884
40	1	0	4.736116	-3.459316	-0.813512
41	6	0	-1.144327	-3.659484	0.176242
42	6	0	3.041842	-4.681903	-1.143256
43	1	0	3.633490	-5.547461	-1.414488
44	6	0	1.656813	-4.740585	-1.188467
45	1	0	1.131625	-5.632374	-1.503908
46	6	0	-2.507633	-3.419321	2.551962
47	1	0	-3.032011	-3.320658	3.494307
48	6	0	-1.711327	-4.787553	0.743948
49	1	0	-1.600475	-5.742559	0.246358
50	6	0	-7.261768	0.158290	-0.438502
51	6	0	-2.405996	-4.662244	1.937274
52	1	0	-2.856430	-5.535196	2.393583
53	6	0	7.854993	-1.088802	0.237953
54	1	0	8.933378	-0.967382	0.359457
55	1	0	7.690237	-1.635272	-0.693778
56	1	0	7.499035	-1.703666	1.068004
57	6	0	7.511541	1.001542	1.542473
58	1	0	7.106474	0.448703	2.393254
59	1	0	7.098531	2.011027	1.571569
60	1	0	8.594087	1.079615	1.672074
61	6	0	-7.686314	-0.306807	-1.842015
62	1	0	-7.283292	0.356388	-2.610702
63	1	0	-8.776143	-0.302358	-1.926399

64	1	0	-7.340809	-1.319342	-2.058109
65	6	0	7.774552	1.094563	-0.952552
66	1	0	8.859566	1.174431	-0.846932
67	1	0	7.368261	2.106354	-0.993553
68	1	0	7.560781	0.608598	-1.907351
69	6	0	-7.847099	-0.798240	0.614574
70	1	0	-7.498858	-1.822781	0.471326
71	1	0	-8.938423	-0.805070	0.552574
72	1	0	-7.566121	-0.486386	1.623129
73	6	0	-7.842464	1.554651	-0.197069
74	1	0	-7.586832	1.934360	0.794529
75	1	0	-8.931772	1.513609	-0.265933
76	1	0	-7.491371	2.274820	-0.939143
77	7	0	3.391069	3.735151	-0.032544
78	7	0	1.315447	4.884825	0.040261
79	7	0	-1.464231	4.838442	0.203006
80	7	0	-3.505290	3.628720	0.251658
81	1	0	3.163824	5.776649	0.023640
82	1	0	-3.329879	5.670766	0.397199
83	8	0	-0.450823	-3.760293	-1.012192

Table S10. Atomic coordinates and energies of NG **3.**

Zero-point correction=	0.663553 (Hartree/Particle)
Thermal correction to Energy=	0.701546
Thermal correction to Enthalpy=	0.702490
Thermal correction to Gibbs Free Energy=	0.595287
Sum of electronic and zero-point Energies=	-2388.213020
Sum of electronic and thermal Energies=	-2388.175027
Sum of electronic and thermal Enthalpies=	-2388.174083
Sum of electronic and thermal Free Energies=	-2388.281287

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.757773	-3.735997	-1.457523
2	6	0	1.430852	0.098943	-0.261510
3	6	0	0.706015	1.299801	-0.195222
4	6	0	-0.696071	1.283308	-0.147111
5	6	0	-1.245361	-2.299727	0.775424
6	6	0	0.722479	3.789544	-0.171541
7	6	0	-1.390547	0.062171	-0.034359
8	6	0	-0.636497	-1.130892	0.072631
9	6	0	0.745071	-1.139455	-0.237041
10	6	0	1.396958	2.559433	-0.187881

11	6	0	-1.399147	2.537055	-0.091730
12	6	0	2.873590	0.146840	-0.199247
13	6	0	-0.739448	3.776802	-0.105026
14	6	0	1.529314	-2.356534	-0.517513
15	6	0	3.619513	-1.039500	-0.138114
16	6	0	-2.797359	2.577976	0.031115
17	6	0	-3.547959	1.331414	0.011800
18	6	0	3.557929	1.377842	-0.106038
19	6	0	-2.866868	0.103409	-0.064390
20	6	0	2.799766	2.618710	-0.167495
21	6	0	2.696180	4.883335	-0.199189
22	6	0	4.931050	1.410045	0.082340
23	1	0	5.397368	2.383407	0.148039
24	6	0	-2.717195	4.845162	0.083616
25	6	0	2.941282	-2.308545	-0.413540
26	6	0	4.994538	-0.964315	0.099946
27	1	0	5.553672	-1.880237	0.202673
28	6	0	-1.679883	-2.129573	2.090215
29	1	0	-1.560687	-1.164273	2.566902
30	6	0	5.673505	0.241389	0.215074
31	6	0	-5.724971	0.257642	-0.156298
32	6	0	-4.949154	1.387769	-0.011378
33	1	0	-5.391599	2.369222	0.067639
34	6	0	0.965187	-3.553660	-1.029705
35	6	0	-5.040100	-0.956751	-0.316369
36	1	0	-5.594960	-1.871465	-0.487150
37	6	0	-3.668236	-1.032734	-0.274542
38	1	0	-3.212843	-1.995314	-0.429995
39	6	0	7.180467	0.325633	0.476099
40	6	0	3.703446	-3.448062	-0.701670
41	1	0	4.780051	-3.404327	-0.632588
42	6	0	-1.389203	-3.551245	0.189943
43	6	0	3.121494	-4.617077	-1.127912
44	1	0	3.730537	-5.484076	-1.352151
45	6	0	1.747981	-4.659308	-1.312267
46	1	0	1.271328	-5.553778	-1.690706
47	6	0	-2.279232	-3.173163	2.777809
48	1	0	-2.618478	-3.020412	3.795116
49	6	0	-1.991150	-4.601751	0.869902
50	1	0	-2.090649	-5.564511	0.384388
51	6	0	-7.253736	0.287200	-0.180068
52	6	0	-2.449567	-4.407535	2.164564
53	1	0	-2.923977	-5.222122	2.698194

54	6	0	7.832087	-1.055719	0.593621
55	1	0	8.901181	-0.938133	0.782374
56	1	0	7.724301	-1.637014	-0.325298
57	1	0	7.415193	-1.634775	1.421066
58	6	0	7.424619	1.086925	1.790340
59	1	0	6.958349	0.571036	2.632953
60	1	0	7.020798	2.099836	1.752611
61	1	0	8.496904	1.161865	1.988792
62	6	0	-7.755271	-0.253608	-1.530009
63	1	0	-7.385854	0.357932	-2.356248
64	1	0	-8.847920	-0.239672	-1.558654
65	1	0	-7.431682	-1.281547	-1.703086
66	6	0	7.853718	1.079739	-0.683256
67	1	0	8.930025	1.155563	-0.508343
68	1	0	7.461358	2.092146	-0.790744
69	1	0	7.699165	0.558148	-1.630648
70	6	0	-7.793877	-0.597907	0.956281
71	1	0	-7.464776	-1.633815	0.855880
72	1	0	-8.886977	-0.593045	0.950954
73	1	0	-7.457186	-0.231837	1.928902
74	6	0	-7.805957	1.703233	0.007485
75	1	0	-7.495970	2.136439	0.960917
76	1	0	-8.897762	1.673657	-0.004182
77	1	0	-7.484869	2.373877	-0.792340
78	7	0	3.442297	3.785691	-0.174487
79	7	0	1.374414	4.949540	-0.187153
80	7	0	-1.400964	4.928583	-0.023760
81	7	0	-3.447387	3.738300	0.121020
82	1	0	3.228566	5.829024	-0.223260
83	1	0	-3.258269	5.783808	0.152300

Table S11. Atomic coordinates and energies of NG **4.**

Zero-point correction=	0.662325 (Hartree/Particle)
Thermal correction to Energy=	0.700809
Thermal correction to Enthalpy=	0.701753
Thermal correction to Gibbs Free Energy=	0.593014
Sum of electronic and zero-point Energies=	-4391.635447
Sum of electronic and thermal Energies=	-4391.596964
Sum of electronic and thermal Enthalpies=	-4391.596020
Sum of electronic and thermal Free Energies=	-4391.704758

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.479660	0.243662	-0.220078
2	6	0	0.773824	1.457362	-0.204749
3	6	0	-0.628215	1.464981	-0.149772
4	6	0	-1.225519	-2.067646	0.934488
5	6	0	0.831862	3.944999	-0.297730
6	6	0	-1.341424	0.260857	0.023754
7	6	0	-0.604961	-0.940655	0.168943
8	6	0	0.774893	-0.982095	-0.149231
9	6	0	1.485609	2.704689	-0.255131
10	6	0	-1.309173	2.732575	-0.147849
11	6	0	2.923022	0.272097	-0.149915
12	6	0	-0.629394	3.959243	-0.226436
13	6	0	1.543447	-2.219387	-0.391230
14	6	0	3.649083	-0.921439	-0.026241
15	6	0	-2.704819	2.804320	-0.014215
16	6	0	-3.476126	1.572126	0.041680
17	6	0	3.626530	1.494682	-0.106231
18	6	0	-2.818120	0.329034	0.016985
19	6	0	2.889172	2.742712	-0.233569
20	6	0	2.822777	5.004283	-0.377419
21	6	0	4.997788	1.514194	0.097413
22	1	0	5.479051	2.482162	0.122753
23	6	0	-2.587343	5.069535	-0.079334
24	6	0	2.954705	-2.189576	-0.262678
25	6	0	5.021773	-0.857230	0.227480
26	1	0	5.564387	-1.776219	0.379540
27	6	0	-1.579080	-1.831732	2.263639
28	1	0	-1.385501	-0.858555	2.698298
29	6	0	5.719077	0.341634	0.295625
30	6	0	-5.676515	0.535053	-0.029455
31	6	0	-4.876187	1.654964	0.040933
32	1	0	-5.297935	2.647946	0.076550
33	6	0	0.974572	-3.419662	-0.887574
34	6	0	-5.017465	-0.698784	-0.136947
35	1	0	-5.592057	-1.610663	-0.247164
36	6	0	-3.646571	-0.799165	-0.116997
37	1	0	-3.214775	-1.777594	-0.228302
38	6	0	7.223753	0.413921	0.572901
39	6	0	3.704266	-3.349416	-0.497120
40	1	0	4.779655	-3.320128	-0.405174
41	6	0	-1.469143	-3.328548	0.404378
42	6	0	3.113142	-4.521793	-0.900133

43	1	0	3.712236	-5.405559	-1.081944
44	6	0	1.743992	-4.545799	-1.120231
45	1	0	1.266162	-5.445624	-1.484052
46	6	0	-2.191939	-2.818625	3.020356
47	1	0	-2.466420	-2.613472	4.047947
48	6	0	-2.082380	-4.323145	1.152755
49	1	0	-2.256191	-5.297101	0.712617
50	6	0	-7.204537	0.594027	-0.025988
51	6	0	-2.457137	-4.062256	2.463287
52	1	0	-2.940454	-4.833116	3.051240
53	6	0	7.850367	-0.970528	0.765744
54	1	0	8.918617	-0.861328	0.964090
55	1	0	7.745433	-1.593523	-0.125770
56	1	0	7.412470	-1.502325	1.613804
57	6	0	7.463931	1.233798	1.852179
58	1	0	6.977858	0.767207	2.712165
59	1	0	7.078345	2.250311	1.760074
60	1	0	8.534687	1.300287	2.061620
61	6	0	-7.742963	-0.007776	-1.335262
62	1	0	-7.378520	0.551433	-2.199895
63	1	0	-8.835514	0.026349	-1.344068
64	1	0	-7.442299	-1.049728	-1.458948
65	6	0	7.924529	1.100035	-0.612079
66	1	0	8.999682	1.166379	-0.426505
67	1	0	7.550966	2.112413	-0.773244
68	1	0	7.773049	0.536041	-1.535365
69	6	0	-7.738759	-0.218158	1.166226
70	1	0	-7.431668	-1.264392	1.115385
71	1	0	-8.831457	-0.191440	1.181393
72	1	0	-7.375655	0.192328	2.111215
73	6	0	-7.725778	2.028887	0.095628
74	1	0	-7.389052	2.505803	1.018642
75	1	0	-8.817981	2.020781	0.105652
76	1	0	-7.407450	2.649493	-0.744670
77	7	0	3.550793	3.897215	-0.296294
78	7	0	1.502396	5.092277	-0.369818
79	7	0	-1.270822	5.124787	-0.199425
80	7	0	-3.334883	3.978635	0.021565
81	1	0	3.370528	5.938783	-0.448310
82	1	0	-3.112321	6.019491	-0.056132
83	34	0	-0.872635	-3.612305	-1.387366

Table S12. Atomic coordinates and energies of NG **1-Me$^+$.**

Zero-point correction=	0.686363 (Hartree/Particle)
Thermal correction to Energy=	0.724381
Thermal correction to Enthalpy=	0.725325
Thermal correction to Gibbs Free Energy=	0.618746
Sum of electronic and zero-point Energies=	-2103.707810
Sum of electronic and thermal Energies=	-2103.669793
Sum of electronic and thermal Enthalpies=	-2103.668849
Sum of electronic and thermal Free Energies=	-2103.775427

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.083193	-3.857041	-1.809915
2	6	0	-7.000681	0.266781	1.238356
3	6	0	-5.551337	0.126036	0.767343
4	6	0	-4.903509	-1.095214	0.672011
5	1	0	-5.451197	-1.984608	0.936715
6	6	0	-3.579906	-1.225368	0.233038
7	6	0	-2.845623	-0.071470	-0.068004
8	6	0	-1.432519	-0.158485	-0.359201
9	6	0	-0.701598	1.046792	-0.452828
10	6	0	0.689294	1.026219	-0.447010
11	6	0	1.409312	2.262534	-0.503506
12	6	0	2.813791	2.265949	-0.327441
13	6	0	3.492704	1.046976	0.002891
14	6	0	4.827459	1.085026	0.397938
15	1	0	5.321942	2.045895	0.410056
16	6	0	5.497047	-0.066337	0.790703
17	6	0	6.949084	0.018498	1.268689
18	6	0	-2.969863	-2.523408	-0.031819
19	6	0	-3.729331	-3.699201	0.052880
20	1	0	-4.731995	-3.666830	0.450677
21	6	0	-3.251876	-4.901345	-0.413366
22	1	0	-3.863936	-5.792143	-0.351608
23	6	0	-2.006736	-4.948022	-1.026040
24	1	0	-1.631268	-5.849176	-1.492189
25	6	0	-1.243717	-3.806777	-1.078160
26	6	0	1.056932	-3.850379	-1.048648
27	6	0	1.771157	-5.021661	-0.965762
28	1	0	1.368487	-5.911878	-1.430261
29	6	0	3.002700	-5.021179	-0.324752
30	1	0	3.573614	-5.936803	-0.237847
31	6	0	3.522062	-3.834186	0.136316
32	1	0	4.516830	-3.839739	0.555348

33	6	0	2.813436	-2.630175	0.020903
34	6	0	3.470839	-1.352528	0.268609
35	6	0	4.794780	-1.262744	0.712728
36	1	0	5.305295	-2.169041	0.994994
37	6	0	2.875486	4.501186	-0.693170
38	6	0	0.758827	3.492857	-0.677043
39	6	0	-0.689939	3.524062	-0.642865
40	6	0	-1.366202	2.306852	-0.476678
41	6	0	-2.767074	2.390887	-0.295681
42	6	0	-2.661084	4.641299	-0.575464
43	6	0	-3.503633	1.178231	0.009904
44	6	0	-0.774059	-1.398985	-0.504529
45	6	0	-1.642468	-2.584637	-0.518891
46	6	0	0.669273	-1.424247	-0.489892
47	6	0	1.374137	-0.206601	-0.361476
48	6	0	2.781018	-0.176470	-0.049858
49	6	0	1.494369	-2.640832	-0.491030
50	6	0	-4.829383	1.260579	0.401636
51	1	0	-5.280702	2.242340	0.434170
52	6	0	7.817886	0.600918	0.140617
53	1	0	8.857255	0.670785	0.468563
54	1	0	7.786122	-0.033240	-0.748143
55	1	0	7.495565	1.602948	-0.148501
56	6	0	7.513725	-1.351326	1.656762
57	1	0	7.527197	-2.043758	0.811641
58	1	0	8.544446	-1.234715	1.995399
59	1	0	6.953149	-1.809174	2.475317
60	6	0	7.019484	0.938848	2.499526
61	1	0	6.409834	0.549240	3.317923
62	1	0	8.050453	1.012453	2.852188
63	1	0	6.675430	1.949887	2.273604
64	6	0	-7.834671	0.908764	0.116239
65	1	0	-7.825721	0.289521	-0.783547
66	1	0	-8.872012	1.020324	0.439517
67	1	0	-7.464143	1.899391	-0.152977
68	6	0	-7.629772	-1.082632	1.597547
69	1	0	-8.656727	-0.925693	1.931720
70	1	0	-7.667664	-1.758144	0.739578
71	1	0	-7.095739	-1.580159	2.410679
72	6	0	-7.038498	1.166909	2.485578
73	1	0	-8.067854	1.280904	2.832605
74	1	0	-6.453231	0.734454	3.300329
75	1	0	-6.646498	2.164690	2.280829

76	1	0	-3.193861	5.583906	-0.642769
77	1	0	3.440834	5.415966	-0.822188
78	7	0	-3.396585	3.556671	-0.352870
79	7	0	-1.348618	4.688957	-0.704167
80	7	0	1.536799	4.617582	-0.817878
81	7	0	3.515595	3.405315	-0.429483
82	6	0	1.019711	5.970934	-1.126677
83	1	0	0.379750	5.931334	-2.001372
84	1	0	0.444481	6.355016	-0.291251
85	1	0	1.880857	6.605139	-1.321629

Table S13. Atomic coordinates of NG **HBC-Bu.**

Zero-point correction=	0.907748 (Hartree/Particle)
Thermal correction to Energy=	0.954953
Thermal correction to Enthalpy=	0.955897
Thermal correction to Gibbs Free Energy=	0.826396
Sum of electronic and zero-point Energies=	-2238.835571
Sum of electronic and thermal Energies=	-2238.788366
Sum of electronic and thermal Enthalpies=	-2238.787422
Sum of electronic and thermal Free Energies=	-2238.916923

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.707484	0.127511	-0.000439
2	6	0	1.397238	-1.102413	-0.000336
3	6	0	0.677129	-2.317682	-0.000912
4	6	0	-0.734162	-2.300310	-0.001139
5	6	0	-1.423631	-1.067833	-0.000393
6	6	0	-0.703266	0.144896	-0.000339
7	6	0	-1.410732	1.404649	0.000114
8	6	0	-2.867622	-1.045399	-0.000387
9	6	0	-1.475327	-3.542473	-0.001623
10	6	0	1.387825	-3.576747	-0.001258
11	6	0	2.841369	-1.117187	-0.000128
12	6	0	1.445486	1.370469	-0.000328
13	6	0	-2.819769	1.435650	0.000627
14	6	0	-3.477783	2.667793	0.001270
15	6	0	-2.797790	3.872672	0.001425
16	6	0	-1.409064	3.822529	0.000773
17	6	0	-0.700573	2.626805	0.000008
18	6	0	-3.602970	-2.251683	-0.000600
19	6	0	-4.992224	-2.201315	0.000034
20	6	0	-5.698765	-1.005128	0.000973

21	6	0	-4.964020	0.167671	0.001184
22	6	0	-3.567453	0.178265	0.000580
23	6	0	-0.789490	-4.778624	-0.002500
24	6	0	-2.903708	-5.946170	-0.003605
25	6	0	-2.889883	-3.529934	-0.001720
26	6	0	2.802575	-3.597672	-0.000794
27	6	0	2.758293	-6.013754	-0.002524
28	6	0	0.672480	-4.796316	-0.002217
29	6	0	3.572902	0.092477	0.000599
30	6	0	4.962853	0.043749	0.002180
31	6	0	5.672574	-1.150393	0.002950
32	6	0	4.940979	-2.325303	0.001895
33	6	0	3.545085	-2.337549	0.000422
34	6	0	0.764915	2.609085	-0.000895
35	6	0	1.502004	3.787762	-0.002106
36	6	0	2.891191	3.804725	-0.002825
37	6	0	3.541874	2.583416	-0.001982
38	6	0	2.854537	1.368111	-0.000679
39	6	0	-7.231394	-1.026844	0.001722
40	6	0	-7.834950	0.381403	0.002740
41	6	0	-7.731904	-1.761709	1.257017
42	6	0	-7.733150	-1.760427	-1.253826
43	6	0	7.205169	-1.125262	0.004945
44	6	0	7.811223	-2.532473	0.005559
45	6	0	7.703270	-0.390295	1.261130
46	6	0	7.706578	-0.389983	-1.249740
47	6	0	3.635777	5.144504	-0.004521
48	6	0	5.157588	4.966511	-0.005172
49	6	0	3.249554	5.946087	1.250309
50	6	0	3.248196	5.943658	-1.260481
51	6	0	-3.509640	5.230114	0.002288
52	6	0	-5.035315	5.089205	0.002917
53	6	0	-3.103905	6.021325	-1.252967
54	6	0	-3.102769	6.020303	1.257817
55	1	0	-4.554366	2.685736	0.001683
56	1	0	-0.867780	4.756018	0.000972
57	1	0	-5.552791	-3.123351	-0.000100
58	1	0	-5.493797	1.105044	0.001910
59	1	0	-3.457566	-6.877161	-0.004413
60	1	0	3.289594	-6.957809	-0.003091
61	1	0	5.522364	0.966401	0.003123
62	1	0	5.471817	-3.262120	0.002452
63	1	0	0.983116	4.733875	-0.002759

64	1	0	4.618617	2.575103	-0.002646
65	1	0	-7.543286	0.949781	-0.883431
66	1	0	-8.924843	0.310392	0.003250
67	1	0	-7.542396	0.948882	0.889192
68	1	0	-7.376720	-2.792961	1.293514
69	1	0	-8.824838	-1.785210	1.270944
70	1	0	-7.390393	-1.259147	2.164790
71	1	0	-8.826097	-1.783912	-1.266696
72	1	0	-7.392535	-1.256943	-2.161424
73	1	0	-7.378008	-2.791642	-1.291724
74	1	0	7.521177	-3.100768	-0.881198
75	1	0	8.900991	-2.459591	0.006955
76	1	0	7.518922	-3.100974	0.891441
77	1	0	7.346613	0.640463	1.297549
78	1	0	8.796156	-0.365282	1.276255
79	1	0	7.361505	-0.893802	2.168274
80	1	0	8.799501	-0.365032	-1.262013
81	1	0	7.367146	-0.893223	-2.157908
82	1	0	7.350091	0.640810	-1.286808
83	1	0	5.503969	4.429569	-0.891263
84	1	0	5.638892	5.946938	-0.006408
85	1	0	5.504934	4.431333	0.881609
86	1	0	2.178409	6.151641	1.287910
87	1	0	3.773426	6.905600	1.262396
88	1	0	3.516389	5.400769	2.158409
89	1	0	3.772023	6.903163	-1.274973
90	1	0	3.514089	5.396601	-2.167811
91	1	0	2.177004	6.149100	-1.297345
92	1	0	-5.394844	4.561263	0.889145
93	1	0	-5.492590	6.081084	0.003516
94	1	0	-5.395642	4.561967	-0.883406
95	1	0	-2.028063	6.200680	-1.290691
96	1	0	-3.604238	6.993315	-1.265636
97	1	0	-3.383965	5.482141	-2.160748
98	1	0	-3.603056	6.992300	1.271709
99	1	0	-3.382047	5.480398	2.165411
100	1	0	-2.026886	6.199586	1.294739
101	6	0	-3.578225	-4.741601	-0.002711
102	1	0	-4.657605	-4.760050	-0.002876
103	6	0	-1.524146	-5.963776	-0.003456
104	1	0	-1.023596	-6.920148	-0.004139
105	6	0	1.378394	-5.998458	-0.002834
106	1	0	0.855250	-6.942660	-0.003592

107	6	0	3.461705	-4.826172	-0.001492
108	1	0	4.540268	-4.870924	-0.001332

Table S14. Atomic coordinates of NG **HBC-O.**

Zero-point correction= 0.914626 (Hartree/Particle)
Thermal correction to Energy= 0.963000
Thermal correction to Enthalpy= 0.963944
Thermal correction to Gibbs Free Energy= 0.835689
Sum of electronic and zero-point Energies= -2314.001516
Sum of electronic and thermal Energies= -2313.953141
Sum of electronic and thermal Enthalpies= -2313.952197
Sum of electronic and thermal Free Energies= -2314.080452

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000014	-4.482600	-2.246598
2	6	0	-6.796701	-0.953239	1.742304
3	6	0	-5.412070	-1.000007	1.087453
4	6	0	-4.761024	-2.185320	0.790064
5	1	0	-5.252161	-3.119251	1.009384
6	6	0	-3.485024	-2.211018	0.221281
7	6	0	-2.803257	-1.005155	-0.006940
8	6	0	-1.396471	-1.013478	-0.349329
9	6	0	-0.697406	0.214954	-0.307870
10	6	0	0.697429	0.214976	-0.308217
11	6	0	1.412895	1.465553	-0.257155
12	6	0	2.812273	1.474347	-0.091757
13	6	0	3.483369	0.211643	0.219964
14	6	0	4.760181	0.187598	0.764310
15	1	0	5.248437	1.126858	0.982709
16	6	0	5.412129	-0.999982	1.087335
17	6	0	6.796787	-0.953205	1.742130
18	6	0	-2.869663	-3.448566	-0.249160
19	6	0	-3.618142	-4.632514	-0.326009
20	1	0	-4.617844	-4.662909	0.080782
21	6	0	-3.137354	-5.750080	-0.967809
22	1	0	-3.740340	-6.647660	-1.028328
23	6	0	-1.899418	-5.692724	-1.593708
24	1	0	-1.514859	-6.515283	-2.182235
25	6	0	-1.152047	-4.541597	-1.499982
26	6	0	1.152052	-4.541604	-1.499945
27	6	0	1.899403	-5.692746	-1.593630
28	1	0	1.514843	-6.515312	-2.182145

29	6	0	3.137327	-5.750108	-0.967706
30	1	0	3.740296	-6.647702	-1.028185
31	6	0	3.618130	-4.632528	-0.325941
32	1	0	4.617826	-4.662930	0.080862
33	6	0	2.869676	-3.448560	-0.249150
34	6	0	3.485047	-2.211004	0.221257
35	6	0	4.761075	-2.185298	0.789974
36	1	0	5.252227	-3.119225	1.009274
37	6	0	3.504119	2.671885	-0.200542
38	1	0	4.582489	2.660706	-0.125274
39	6	0	2.856278	3.884810	-0.427954
40	6	0	3.680967	5.168892	-0.570852
41	6	0	1.473375	3.869243	-0.504620
42	1	0	0.951310	4.801831	-0.643775
43	6	0	0.731219	2.687734	-0.410612
44	6	0	-0.731242	2.687729	-0.410587
45	6	0	-1.412914	1.465529	-0.257279
46	6	0	-2.812280	1.474326	-0.091773
47	6	0	-3.504148	2.671842	-0.200647
48	1	0	-4.582519	2.660647	-0.125387
49	6	0	-2.856323	3.884769	-0.428096
50	6	0	-3.681046	5.168821	-0.571086
51	6	0	-1.473416	3.869219	-0.504719
52	1	0	-0.951358	4.801807	-0.643896
53	6	0	-3.483365	0.211621	0.219969
54	6	0	-0.716066	-2.217959	-0.624138
55	6	0	-1.558177	-3.414681	-0.772817
56	6	0	0.716084	-2.217941	-0.624216
57	6	0	1.396454	-1.013493	-0.349169
58	6	0	2.803286	-1.005140	-0.006998
59	6	0	1.558177	-3.414687	-0.772778
60	6	0	-4.760146	0.187576	0.764385
61	1	0	-5.248402	1.126837	0.982788
62	6	0	7.778462	-0.214334	0.816717
63	1	0	7.461654	0.812106	0.624069
64	1	0	8.771251	-0.175499	1.272798
65	1	0	7.865542	-0.723619	-0.145729
66	6	0	6.699231	-0.206534	3.083595
67	1	0	7.680296	-0.162121	3.564016
68	1	0	6.345009	0.817512	2.953748
69	1	0	6.010273	-0.714124	3.762480
70	6	0	7.360199	-2.351551	2.014775
71	1	0	6.721234	-2.922625	2.692137

72	1	0	7.487704	-2.925429	1.093948
73	1	0	8.341955	-2.263298	2.485150
74	6	0	-4.636537	5.026976	-1.768318
75	1	0	-5.322949	4.187869	-1.643082
76	1	0	-5.235660	5.934176	-1.883700
77	1	0	-4.079488	4.866578	-2.694144
78	6	0	-4.499514	5.400799	0.710529
79	1	0	-5.090797	6.315976	0.621031
80	1	0	-5.189415	4.578362	0.907001
81	1	0	-3.844189	5.502344	1.578599
82	6	0	-2.804251	6.403234	-0.805013
83	1	0	-2.122279	6.582326	0.029449
84	1	0	-2.214737	6.315641	-1.720460
85	1	0	-3.438671	7.286555	-0.905771
86	6	0	4.636495	5.027151	-1.768069
87	1	0	5.235572	5.934387	-1.883397
88	1	0	5.322951	4.188077	-1.642858
89	1	0	4.079475	4.866765	-2.693915
90	6	0	4.499384	5.400844	0.710800
91	1	0	3.844027	5.502331	1.578853
92	1	0	5.189306	4.578422	0.907263
93	1	0	5.090639	6.316044	0.621363
94	6	0	2.804118	6.403270	-0.804745
95	1	0	2.214624	6.315681	-1.720206
96	1	0	2.122120	6.582293	0.029711
97	1	0	3.438497	7.286626	-0.905455
98	6	0	-7.778417	-0.214379	0.816922
99	1	0	-8.771191	-0.175556	1.273036
100	1	0	-7.461629	0.812068	0.624273
101	1	0	-7.865519	-0.723661	-0.145522
102	6	0	-7.360086	-2.351592	2.014965
103	1	0	-7.487638	-2.925462	1.094140
104	1	0	-6.721078	-2.922669	2.692285
105	1	0	-8.341816	-2.263352	2.485397
106	6	0	-6.699109	-0.206567	3.083764
107	1	0	-6.010121	-0.714149	3.762626
108	1	0	-6.344905	0.817482	2.953908
109	1	0	-7.680158	-0.162172	3.564220