Supporting Information for:

A palate of fluorescent corannulene derivatives: synthesis, spectroscopic properties, and bio-imaging application

Yali Wang, Haiyan Jiang, Xueling Liu, Jun Xu, Yan Gao and Nathaniel S. Finney*

School of Pharmaceutical Sciences and Technology, Health Sciences Platform,

Tianjin University. 92 Weijin Road, Nankai District, Tianjin, 300072, China.

Email: nfinney@tju.edu.cn

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1. General Experimental Details

1.1 Materials and instruments

Unless otherwise indicated, all reagents used for reactions were purchased without further purification and dry solvent was obtained by filtration of reagent-grade solvent through an Innovative Technologies solvent drying system. Cell lines (HEK 293T healthy cell line, RAW 264.7 macrophage cell line and HeLa cancerous cells) were purchased from Type Culture Collection of the Chinese Academy of Sciences, Shanghai, China. Hoechst 33342 and Thiazolyl Blue Tetrazolium Bromide (MTT) were purchased from Solarbio life sciences. All reactions were monitored by thin layer chromatography (TLC) using UV indicator and Chromatographic purifications were performed on silica gel 60 (particle size 0.040 - 0.063 mm), both of which were purchased from the Qingdao Haiyang Chemical Co., Ltd.

^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Ascend III 400 and Avance III 600 instruments at 298.6 K. ^{1}H NMR chemical shifts were recorded in parts per million (ppm) relative to $CDCl_3$ (δ = 7.26 ppm) and MSO-d_6 (δ = 2.50 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet). ^{13}C NMR chemical shifts were recorded in parts per million (ppm) relative to $CDCl_3$ (δ = 77.00 ppm), DMSO-d_6 (δ = 49.7 ppm). HRMS data were obtained with Q Exactive HF LC-MS ESI mode The UV absorption spectra were measured with Hitachi U-3900 spectrophotometer. Fluorescence measurements were carried out on Edinburgh FLS 980 spectrophotometer, using a 450 W xenon lamp. Absolute quantum yields were measured by using an integrating sphere detector from Edinburgh Instruments. Confocal fluorescence imaging was obtained under Leica TCS SP5 confocal laser scanning microscope. The average particle size at room temperature was obtained by dynamic light scattering (DLS) on Zetasizer Nanoseries (Nano ZS90). Transmission electron microscopy (TEM) pictures were obtained on a FEI Tecnai F30 transmission electron microscope at 200 kV acceleration voltage.

1.2 General procedures for the spectra measurement

All spectroscopic measurements were carried out at room temperature with HPLC grade solvents. The concentration of measured samples was 10 μM obtained by diluting the stock solution (10 mM). The UV-vis absorbance and fluorescence emission measurements were performed using a 10.0 mm path length quartz fluorescence cuvette. The slit width of excitation and emission was set as 2 nm.

1.3 X-ray crystallography

Crystals of **NI-Cor** and **BODIPY-Cor** were formed by slow evaporation of a mixture of minimal dichloromethane and an appropriate amount of hexane at room temperature. Single crystals suitable for X-ray diffraction were selected and mounted in inert oil and their X-ray diffraction intensity data was collected at 100 K on a Rigaku XtaLAB FRX diffractometer equipped with a Hypix6000HE detector, using Cu Kα

radiation (λ = 1.54184 Å) under the program CrysAlisPro. The data set was collected with redundancy factors of 10 and to a resolution of 0.79 Å. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter.

1.4 Computational method.

All calculations were performed with performed with Gaussian 09 packages[1] unless otherwise noted. The DFT method was employed using the B3LYP hybrid functional. Structures were optimized with the 6-31G(d) basis set.[2-5] The SMD implicit solvation model[6] was used to take account of the solvation effect of methanol.

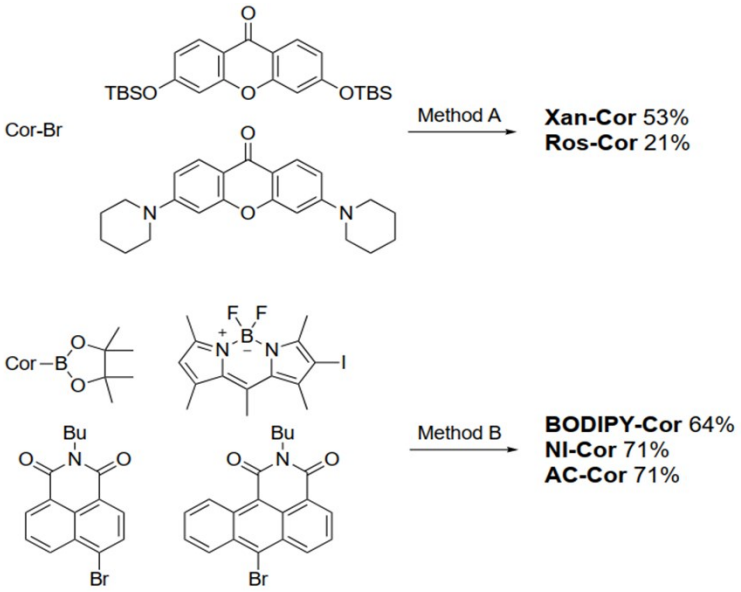
1.5 Cell culture and viability assay

Cells were incubated in Dulbeccos modified Eagles medium (DMEM) supplement with 10% (v/v) Fetal Bovine Serum (FBS, Gibco), 100 U/mL penicillin, and 100 μg/mL streptomycin at 37 ^{o}C with 5 % CO_2 in appropriate humidity. Before MTT test (MTT, a commercially available cell viability dye), three cell lines (10^4 cells/well for 24/48 h, 0.5 x 10^4 cells/well for 72 h) were dispersed in 96-well cell culture plates, and filled to 200 μL per well. 24 h after incubation, the medium was removed and the cells were supplemented with medium containing each corannulene derivative of different concentrations (5, 10, 20, 30, 50, 100 μM) containing 1% DMSO and cultured for 24, 48 and 72 h. Cells incubated with no compounds were used as blank control. Cells incubated with no compounds but 1% DMSO were used as positive control. After removal of the medium, 100 μL MTT solutions (0.5 mg/mL) were added to each well away from light. After 4 h, the MTT solutions were removed, and 200 μL of DMSO was added to each well to fully dissolve the formed formazan crystals by a shaker. Finally, a microplate reader was used to measure the absorbance at 570 nm.

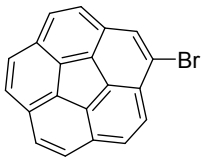
1.6 Confocal fluorescence imaging

The three cell lines were incubated for 24 h before probes loading on an uncoated 20 mm diameter glass-bottomed dish (NEST). Before loading the probes (**X-Cor** conjugates), cells were rinsed with phosphate buffered saline (PBS) for three times and then incubated with probes (5 μM) and Hoechst 33342 (1 μM) for 30 minutes at 37 °C. Then, washed twice by PBS to remove the excess dyes before confocal fluorescence imaging. To evaluate the organelle-targetable ability, cells were first incubated with probes (1 μM) for 10 min at 37 ^{o}C in a 5% CO_2/ 95% air incubator. Then 1 mL of aqueous solution of MitoTracker dye (Green or Red, final concentration, 100 nM) or 1 mL of aqueous solution of LysoTracker dye (Green or Red, final concentration, 100 nM) was added into the culture medium. The cells were incubated for another 30 minutes. After washing with PBS buffer, the co-stained cells were subjected to the confocal fluorescence imaging measurements with Leica TCS SP8 confocal laser scanning microscope.

2. Synthesis and Characterization

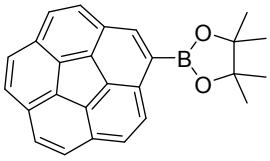


Scheme S1 Synthesis of **Xan-Cor**, **Ros-Cor**, **BODIPY-Cor**, **NI-Cor**, and **AC-Cor**.
Method A: 1. Cor-Br, *t*-BuLi, THF; ketone, THF. 2. aq. HCl.
Method B: Cor-Bpin, fluorophore-Br/I, cat. $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O.



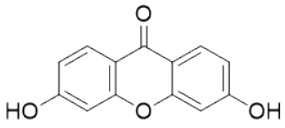
Br-Cor (1): Corannulene (500 mg, 2 mmol) and N-bromosuccinimide (390 mg, 2.2 mmol) were placed into a 25 mL flask, then, dry DCM (10 mL) was added into the mixture and stirred at room temperature (RT) for 20 h. After that, 10 mL of saturated NH_4Cl was added to quench the reaction, washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (hexane) to afford pure product as a white solid (52%). The spectroscopic data was in agree with the data reported in the literature.[7]

^1H NMR (600 MHz, $CDCl_3$) δ 8.01 (S, 1H), 7.91 (d, J = 9.9 Hz, 1H), 7.88–7.72 (m, 6H), 7.72–7.65 (m, 1H).

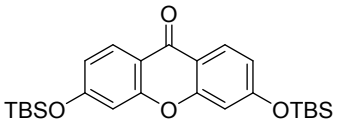


Bpin-Cor (2): **1** (329 mg, 1 mmol), bis(pinacolato)diboron （340 mg, 1.5 mmol), [$PdCl_2$(dppf)] (7.31 mg, 0.01 mmol), and AcOK (300 mg, 3 mmol) were mixed into a sealed tube and stirred at 120 °C for 12 hours, After cooled to room temperature, the mixture was concentrated under reduced pressure, and dissolved into EtOAc (20 mL), washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (hexane to hexane:EA 10:1) to afford pure product as a yellow solid (63%). The spectroscopic data was in agree with the data reported in the literature.[8]

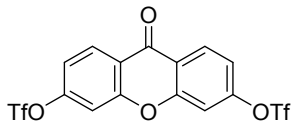
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.45 (d, J = 8.9 Hz, 1H), 7.85–7.77 (m, 7H), 1.45 (s, 12H).



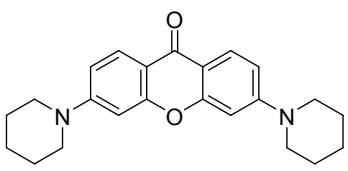
3,6-dihydroxy-9H-xanthen-9-one (3): A sealed 20-mL glass tube containing a suspension of the bis(2,4-dihydroxyphenyl)methanone (492 mg, 2 mmol) and NaOAc (16.4 mg, 0.2 mmol) in water (8 mL) was introduced in the cavity of the CEM microwave reactor and irradiated at 150 °C for 2 hours under magnetic stirring. After cooling to room temperature by air flow, the tube was removed from the rotor, and the reaction precipitate was filtered and washed with water, then dried to give a pale yellow solid product (98%). The spectroscopic data was in agree with the data reported in the literature.[9]
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.83 (s, 2H), 8.01-7.99 (d, J = 8.6 Hz 2H,), 6.90-6.87 (dd, J = 8.7, 2.2 Hz, 2H,), 6.84-6.84 (d, J = 2.2 Hz, 2H,).



3,6-bis((tert-butyldimethylsilyl)oxyl)-9H-xanthen-9-one (4): A mixture of **3** (456 mg, 2 mmol) and imidazole (1.36 g, 20 mmol) was dissolved in dry DMF (40 mL), and solid TBDMSCl (1.81 g, 12 mmol) was added. The reaction was stirred for 1 hour at room temperature (full dissolution followed by precipitation of product takes place), and water (100 mL) was then added and stirred for 15 minutes. The precipitated product was filtered and washed with water (3 x 30 mL), dried on air and in vacuum to give white powder compound, which were further purified by column chromatography (DCM:CH_3OH, 100:1) to afford pure product as a white solid (99%). The spectroscopic data was in agree with the data reported in the literature.[10]
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (d, J = 9.0 Hz, 2H,), 6.86 (m, 2H,), 6.84 (m, 2H,), 1.01 (s, 18 H), 0.29 (s, 12 H).

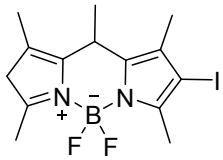


9-oxo-9H-xanthene-3,6-diyl bis(trifluoromethanesulfonate) (5): 3 (1.14 g, 5 mmol) was dissolved in 25 mL dry DCM and pyridine (4.1 mL, 50 mmol) was added slowly at 0 °C. The mixture was stirred at 0 °C for 10 min then trifluoromethanesulfonic anhydride (2.5 mL, 15 mmol) was added dropwise over 2 minutes. The reaction mixture was warmed to room temperature slowly and stirred for 12 hours, then quenched with water and the organic layer was washed with water (1 x 10 mL), 1N HCl (3 x 10 mL), brine (1 x 10 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure and the residue was purified by column chromatography (DCM:Hexane, 1:1) to afford the pure product as an white crystal (94%). The spectroscopic data was in agree with the data reported in the literature. [11]
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46-8.44 (d, J = 8.9 Hz, 2H), 7.50-7.49 (d, J= 2.3 Hz 2H), 7.37-7.34 (dd, J = 8.9, 2.3 Hz, 2H).

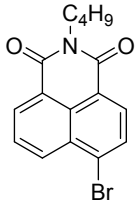


3,6-di(piperidin-1-yl)-9H-xanthen-9-one: (6) 5 (246 mg, 0.5 mmol) was dissolved in DMSO (5 mL) and piperidine (426 mg, 0.5 mL, 5 mmol) was added. The reaction

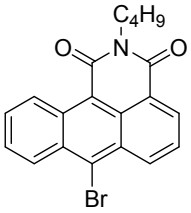
mixture was heated to 90 °C and stirred for 12 hours.
After cooling to room temperature, the reaction was quenched with water. The precipitate was filtered off, washed with saturated Na_2CO_3 (aq.) and water to give the crude product, which was purified by column chromatography (DCM:CH_3OH, 200:1) to afford the pure product as yellow solid (91%). The spectroscopic data was in agreement with the data reported in the literature.[11]
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.88-7.85 (d, 2H, *J* = 9.0 Hz), 6.99-6.96 (dd, *J* = 9.1, 2.3 Hz, 2H,), 6.74-6.73 (d, *J*= 2.4 Hz, 2H), 3.42-3.40 (m, 8H), 1.59 (br, 8H).



4,4-Difluoro-1,3,5,7,8-pentamethyl-2-iodo-6-ethyl-4-bora-3a,4a-diaza-s-indacene: (7) 4,4-Difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene (67.9 mg, 0.259 mmol) was dissolved in MeOH (15 ml), then added a MeOH solution (1.5 ml) of iodine monochloride (13 µl, 0.259 mmol). Stirred at room temperature for 40 min. Added DCM (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure and the residue was purified by column chromatography (DCM: hexane, 1:4) to afford the pure product as a yellow solid (63%). The spectroscopic data was in agreewith the data reported in the literature.[12]
^{1}H NMR (400 MHz, $CDCl_3$); δ: 6.06 (s, 1H), 2.54 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).

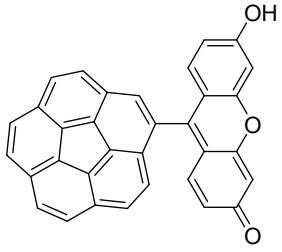


4-Bromo-N-n-butyl-1,8-naphthalimide: (8) A suspension of 4-bromo-1,8-naphthalic anhydride (1 g, 3.5 mmol) and n-butylamine (511 mg, 7 mmol) in 30 mL of ethanol was refluxed with stirring for 3 h. After the reaction was complete, the reaction mixture was cooled to room temperature and the solid phase was filtered off, washed with ethanol and dried to give pure 4-bromo-N-n-butyl-1,8-naphthalimide as a light yellow solid (93%). The spectroscopic data was in agree with the data reported in the literature.[13]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.3 Hz, 1H), 8.48 (d, *J* = 7.6 Hz, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.86–7.71 (t, *J* = 7.9 Hz, 1H), 4.20–4.03 (m, 2H), 1.70 (m, 2H), 1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).



10-bromo- N-(n-butyl-anthracenecarboximide: (9) A suspension of 10-bromo-1,2-dicarboxyanthracene anhydride[8] (1 g, 3 mmol) and n-butylamine (300 mg, 4 mmol) in 30 mL of ethanol was stirred at 75 °C for 12 h. After the reaction was complete, the reaction mixture was cooled to room temperature, solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (PE: DCM 3: 1) to afford compound as an orange solid (64%). The spectroscopic data was in agree with the data reported in the literature.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (d, *J* = 9.1 Hz, 1H), 8.79 (d, *J* = 8.7 Hz, 1H), 8.71 (d, *J* = 7.0 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 7.82–7.60 (m, 3H), 4.29–4.11 (t, *J* = 6.0 Hz, 2H), 1.81–1.71 (m, 2H), 1.50 (m, 2H), 1.02 (t, = 5.4 Hz, 3H).

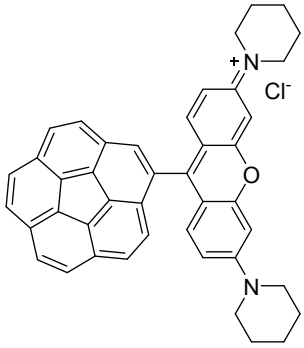


Xan-Cor: (10) 1 (100 mg, 0.3 mmol) was dissolved in dry THF (5 mL) in an overdried 25 mL flask and cooled to -78^{o} C. The mixture was degassed three times by evacuating the flask and backfilling with Ar. Then, 1.3 M *t*-BuLi (0.28 mL, 0.36 mmol) was added to the mixture over a period of 2 minutes. The mixture was stirred at -78 ^{o}C for 30 minutes, and a solution of **4** (140 mg, 0.3 mmol) in anhydrous THF (2 mL) was slowly added. Stirring was continued at room temperature for 2 hours. Then 2 N HCl aq. (1 mL) was added to it and stirred for 20 minutes, washed with water (3 x 10 mL), dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was further purified by column chromatography (DCM:CH_3OH, 100:1) to afford pure product as an orange solid (53%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (s, 1H), 8.13 (s, 2H), 8.09–7.98 (m, 4H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.52 (s, 1H), 7.37 (s, 2H), 7.20 (s, 2H), 6.89 (d, *J* = 9.5 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 157.92, 135.63, 135.32, 134.75, 134.58, 134.16, 132.47, 131.55, 131.15, 130.97, 130.40, 129.55, 129.29, 128.98, 128.58, 128.39, 128.19, 128.16, 127.83, 127.69, 127.60, 125.62, 116.90, 102.80.

HRMS (ESI) m/z calc'd for $C_{33}H_{16}O_3$ [M+H$^+$]: 461.1099; found 461.11762.

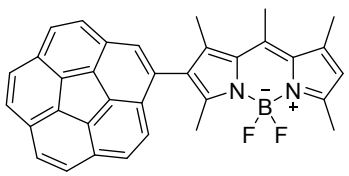


Ros-Cor: (11) 1 (100 mg, 0.3 mmol) was dissolved in dry THF (5 mL) in an overdried 25 mL flask and cooled to -78^{o} C. The mixture was degassed three times by evacuating the flask and backfilling with Ar. Then, 1.3 M *t*-BuLi (0.28 mL, 0.36 mmol) was added to the mixture over a period of 2 minutes. The mixture was stirred at -78 ℃ for 30 minutes, and a solution of **6** (110 mg, 0.3 mmol) in anhydrous THF (2 mL) was slowly added. Stirring was continued at room temperature for 2 hours. Then 2 N HCl aq. (1 mL) was added to it and stirred for 20 minutes, washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (DCM : CH_3OH, 50:1) to afford pure product as a purple solid (21%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.11-7.96 (m, 5H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.23-7.14 (m, 5H), 3.74 (t, *J* = 5.3 Hz, 8H), 1.77 – 1.55 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 158.36, 156.49, 153.90, 136.11, 135.77, 135.25, 135.11, 134.71, 132.37, 132.02, 131.67, 131.47, 130.85, 129.99, 129.85, 129.53, 129.12, 128.92, 128.72, 128.38, 128.11, 126.12, 115.50, 114.92, 97.32, 48.92, 26.22, 24.21.

HRMS (ESI) m/z calc'd for $C_{43}H_{35}N_2O^+$ [M$^+$]: 595.2749; found: 595.27512.



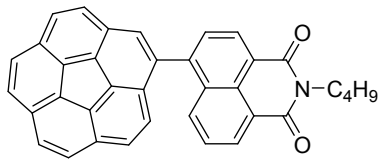
BODIPY-Cor: (12) 2 (100 mg, 0.26 mmol), **7** (80 mg, 0.2 mmol), and potassium carbonate (70 mg, 0.5 mmol) were added to a 25 mL flask, then, 5 mL THF and 0.5 mL water were added. The mixture was degassed three times by evacuating the flask and backfilling with Ar. Then, $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) was added to the mixture. The mixture was stirring

and refluxing for 12 h. After it cooled to room temperature, the reaction mixture was extracted with saturated sodium bicarbonate and DCM. Organic phase was collected and washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (DCM:PE, 1:1) to afford pure product as an orange solid (64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88–7.80 (m, 6H), 7.77 (d, J = 8.8 Hz, 1H), 7.61 (s, 1H), 7.52 (d, J = 8.6 Hz, 1H), 6.14 (s, 1H), 2.71 (s, 3H), 2.59 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.51, 152.74, 153.91, 141.78, 141.53, 138.30, 136.12, 135.92, 135.88, 135.70, 135.32, 132.83, 132.72, 131.99, 131.38, 130.98, 130.87, 130.86, 130.70, 130.56, 128.34, 127.34, 127.26, 127.20, 127.10, 127.00, 126.92, 126.52, 121.70, 17.45, 16.86, 15.90, 14.52, 13.48.

HRMS (ESI) m/z calc'd for $C_{34}H_{27}BF_2N_2$ [M+Na$^+$]: 533.1977; found: 533.19710.

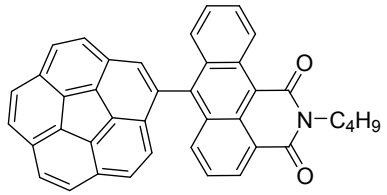


NI-Cor: (13) 2 (100 mg, 0.26 mmol), **8** (70 mg, 0.2 mmol), and potassium carbonate (70 mg, 0.5 mmol) were added to a 25 mL flask, then, 5 mL THF and 0.5 mL water was added. The mixture was degassed three times by evacuating the flask and backfilling with Ar. Then, Pd $(PPh_3)_4$ (15 mg, 0.013 mmol) was added to the mixture. The mixture was stirring and refluxing for 12 h. After it cooled to room temperature, the reaction mixture was extracted with saturated sodium bicarbonate and DCM. Organic phase was collected and washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (DCM) to afford pure product as a white solid (71%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.63 (d, J = 7.4 Hz, 1H), 8.59 (d, J = 6.9 Hz, 1H), 8.39 (s, 1H), 8.14 (s, 1H), 8.10–8.01 (m, 5H), 7.97 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 6.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 4.13 (t, J = 7.5 Hz,2H), 1.72–1.66 (m, 2H), 1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 163.46, 163.26, 143.33, 135.42, 134.95, 134.89, 134.81, 134.67, 132.62, 131.09, 130.98, 130.90, 130.74, 130.70, 130.35, 130.31, 130.10, 129.52, 128.80, 128.19, 128.02, 127.86, 127.84, 127.76, 127.66, 127.59, 127.40, 40.09, 29.68, 19.80, 13.71.

HRMS (ESI) m/z calc'd for $C_{36}H_{23}NO_2$ [M+H$^+$]: 502.1807; found: 502.17930.



AC-Cor: (14) 2 (100 mg, 0.26 mmol), **9** (77 mg, 0.2 mmol), and potassium carbonate (70 mg, 0.5 mmol) were added to a 25 mL flask, then, 5 mL THF and 0.5 mL water was added. The mixture was degassed three times by evacuating the flask and backfilling with Ar. Then, Pd $(PPh_3)_4$ (15 mg, 0.013 mmol) was added to the mixture. The mixture was stirring and refluxing for 12 h. After it cooled to room temperature, the reaction mixture was extracted with saturated sodium bicarbonate and DCM. Organic phase was collected and washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by column chromatography (DCM) to afford pure product as an orange solid (71%).

^{1}H NMR (600 MHz,$CDCl_3$) δ 10.22 (d, J = 9.2 Hz, 1H), 8.77 (d, J = 6.8 Hz, 1H), 7.96–7.85 (m, 6H), 7.85–7.79 (m, 3H), 7.77–7.63 (m, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.36 (s, 1H), 6.92 (d, J = 8.8 Hz, 1H), 4.45–4.22 (m, 2H), 1.85 (s, 2H), 1.57 (s, 2H), 1.05 (t, J = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.85, 165.30, 144.46, 136.47, 136.02, 135.90, 135.80, 135.60, 135.21, 134.36, 133.48, 133.35, 132.52, 131.27, 131.35, 130.96, 130.93, 130.80, 130.02, 129.17, 128.16, 128.65, 127.86, 127.74, 127.64, 127.56, 127.33, 127.15, 127.02, 126.92, 126.44, 125.74, 125.37, 122.67, 115.92, 76.78, 40.60, 30.36, 20.56, 13.92.
HRMS (ESI) m/z calc'd for $C_{40}H_{25}NO_2$ [M+H$^+$]: 552.1964; found: 552.19533.

3. Optical Data and Spectra

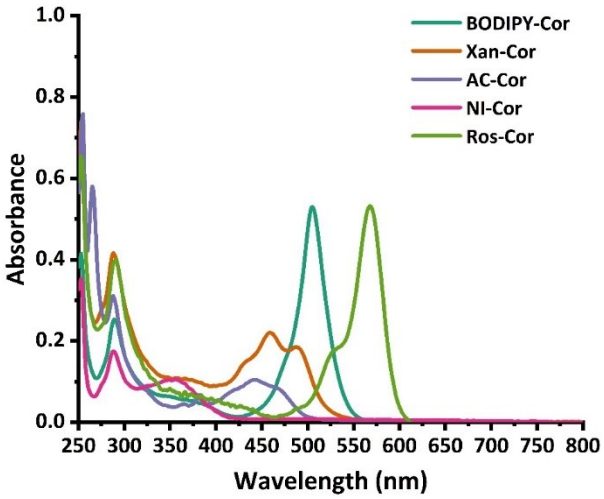


Fig. S1 Absorption spectra of the **X-Cor** conjugates (~10 μM) in MeOH.

Table S1 Comparison of the optical properties of **X-Cor** conjugates and **Ph-fluorophores**[a-d]

	λ_{max} (exc1)	ε_{max}	λ_{max}(em)	ϕ	Stokes shift
Cor	288	4.9	436	0.01	148
Xan-Ph[15]	488	1.9	518	0.3	30
Xan-Cor	490	1.84	540	0.31	50
Ros-Ph[16]	564	8.67	588	0.3	24
Ros-Cor	569	5.82	598	0.25	29
BODIPY-Ph[17]	503	8.5	529	0.71	26
BODIPY-Cor	506	5.86	542	0.73	36
NI-Ph	n.a	n.a	n.a	n.a	n.a
NI-Cor	355	1.05	502	0.63	147
AC-Ph	n.a	n.a	n.a	n.a	n.a
AC-Cor	444	1.04	542	0.94	98

[a] All measurements made at ~10^{-5} M in CH_3OH. [b] λ values in nm. [c] λ_{max}(exc) for direct excitation of the fluorophore. [d](M^{-1} cm^{-1}) × 10^4. [e] n.a. = not available.

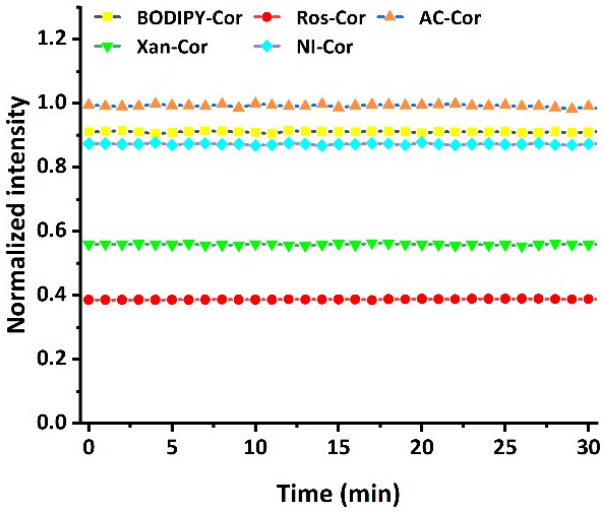


Fig. S2 Photostability examination of **X-Cor** conjugates (~10 μM) in MeOH monitored at maximum emission wavelength under continuous irradiation by a 450 W xenon lamp.

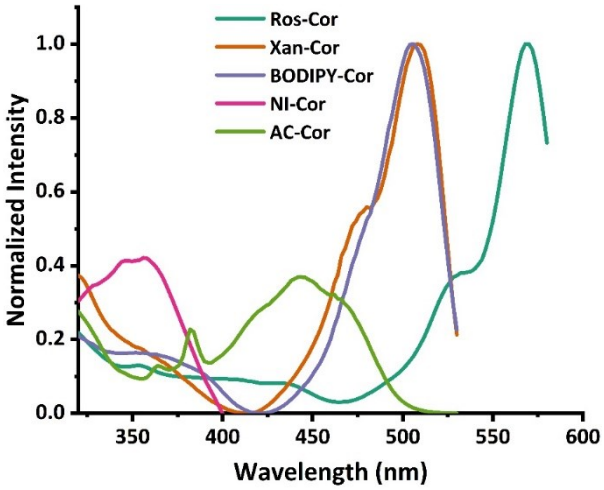


Fig. S3 Normalized excitation spectra (X-axis set so that it only shows the part of the spectrum for direct excitation of the fluorophore) of the **X-Cor** conjugates (~10 µM) in MeOH.

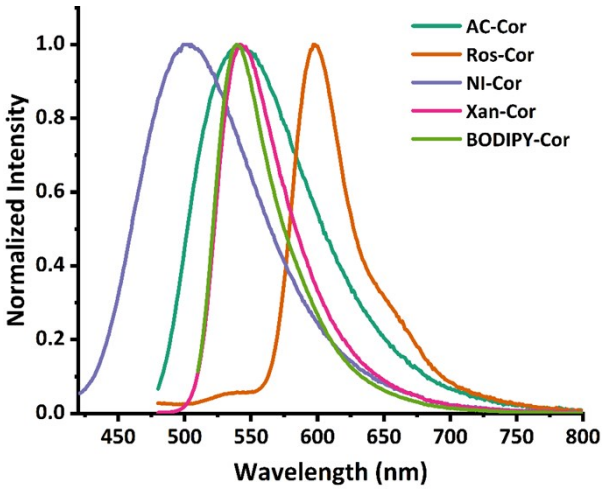


Fig. S4 Normalized emission spectra for direct fluorophore excitation of the **X-Cor** conjugates (~10 µM) in MeOH.

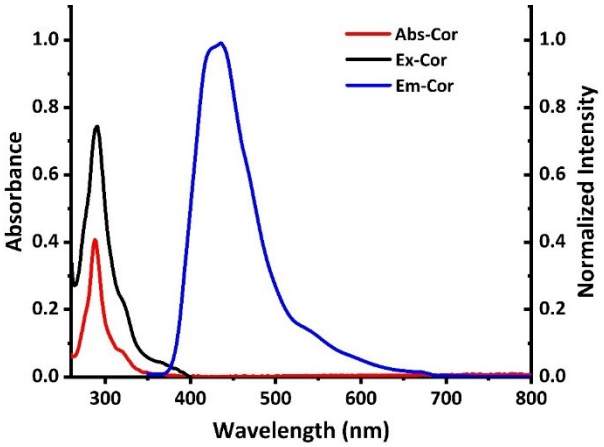


Fig. S5 Absorbance, normalized excitation and emission spectra of corannulene (~10 µM) in DCM.

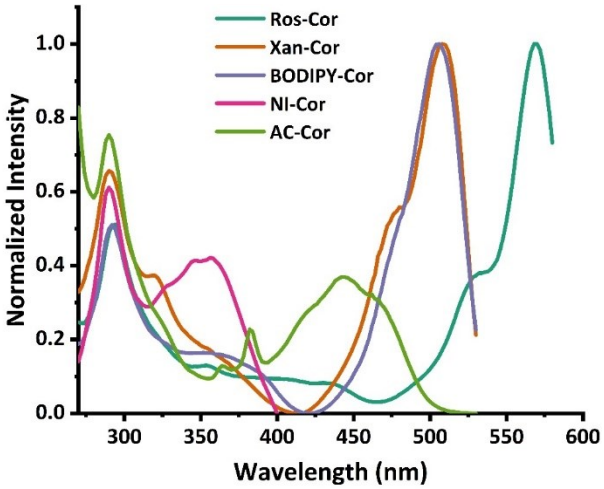


Fig. S6 Normalized excitation spectra (X-axis set so that include corannulene excitation) of the **X-Cor** conjugates (~10 µM) in MeOH.

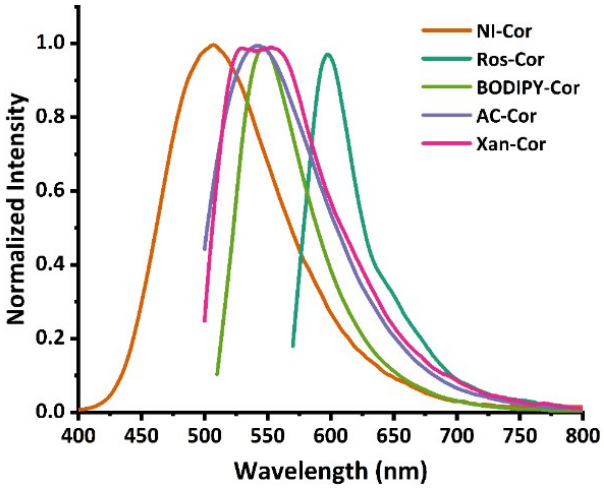


Fig. S7 Normalized emission spectra of the **X-Cor** conjugates (~10 µM) in MeOH while exciting at 292 nm (corannulene excitation).

Table S2 Optical properties of **X-Cor** conjugates at different λ(exc).[a,b]

	λ(exc)	**λ_{max}(em)**	**ϕ**	**Stokes shift**
Ros-Cor	569	598	0.25	29
	292	599	0.21	307
Xan-Cor	490	540	0.31	50
	292	540	0.25	248
BODIPY-Cor	506	542	0.73	36
	292	540	0.71	248
AC-Cor	444	542	0.94	98
	292	542	0.94	250
NI-Cor	355	502	0.63	147
	292	502	0.71	210

[a]All measurements made at ~10^{-5} M in CH_3OH. [b]λ values in nm.

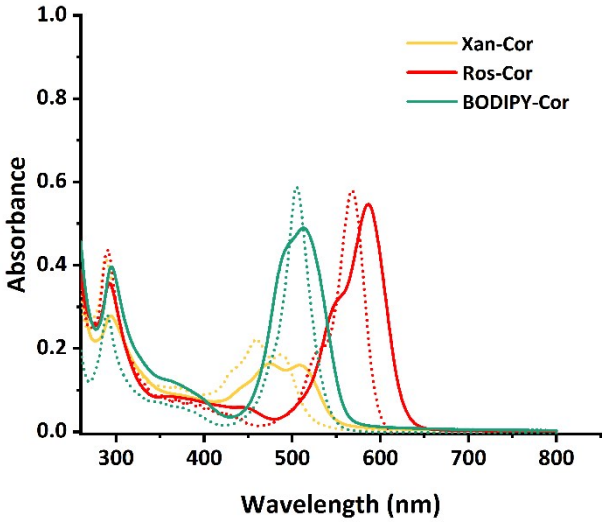


Fig. S8 UV/Vis absorption of **X-Cor** conjugates (~10 µM) in aqueous media (solid lines, water/DMSO, v/v 99:1) and in MeOH (dashed lines)

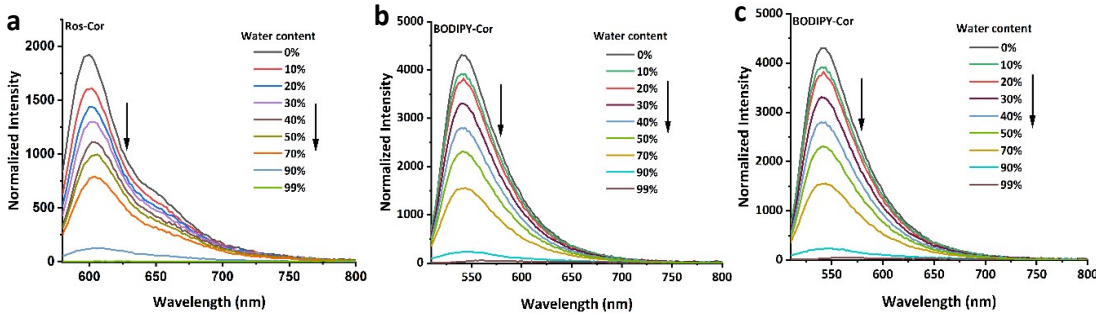


Fig. S9 Fluorescence spectra of **X-Cor** conjugates (~10 µM) in MeOH-containing water with increasing water content (0% to 99%, v/v)

Table S3 Optical properties of **X-Cor** conjugates in MeOH and water[a,b]

	Solvent	**λ_{max}(abs)**	**ε^c**	**λ_{max}(em)**	**ϕ**
Ros-Cor	MeOH	569	5.82	598	0.25
	water	583	5.46	602	0.02
Xan-Cor	MeOH	490	1.84	540	0.31
	water	502	1.66	543	0.01
BODIPY-Cor	MeOH	506	5.86	542	0.73
	water	514	5.46	548	0.06

[a]All measurements made at ~10^{-5} M. [b]λ values in nm. [c] (M^{-1} cm^{-1}) × 10^4.

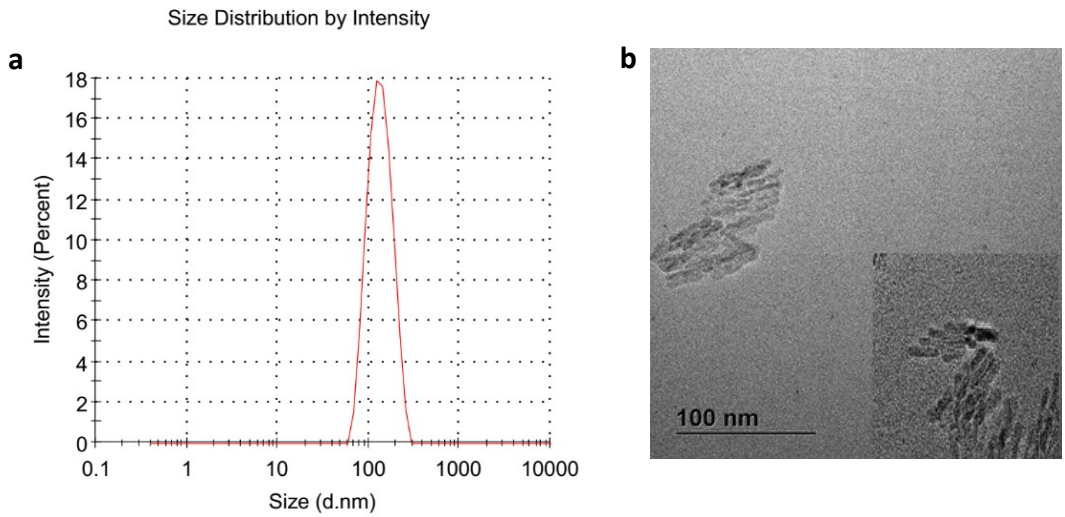


Fig. S10 DLS particle size distribution plot (a) TEM images (b) of **Ros-Cor** in aqueous solution. The nanoaggregate was prepared by injecting the concentrated solution of corresponding compounds in DMSO into water. The final concentration is $\sim 0.5 \times 10^{-4}$ M, and the proportion of DMSO in water is 1 vol %.

4. Cell Viability Assay

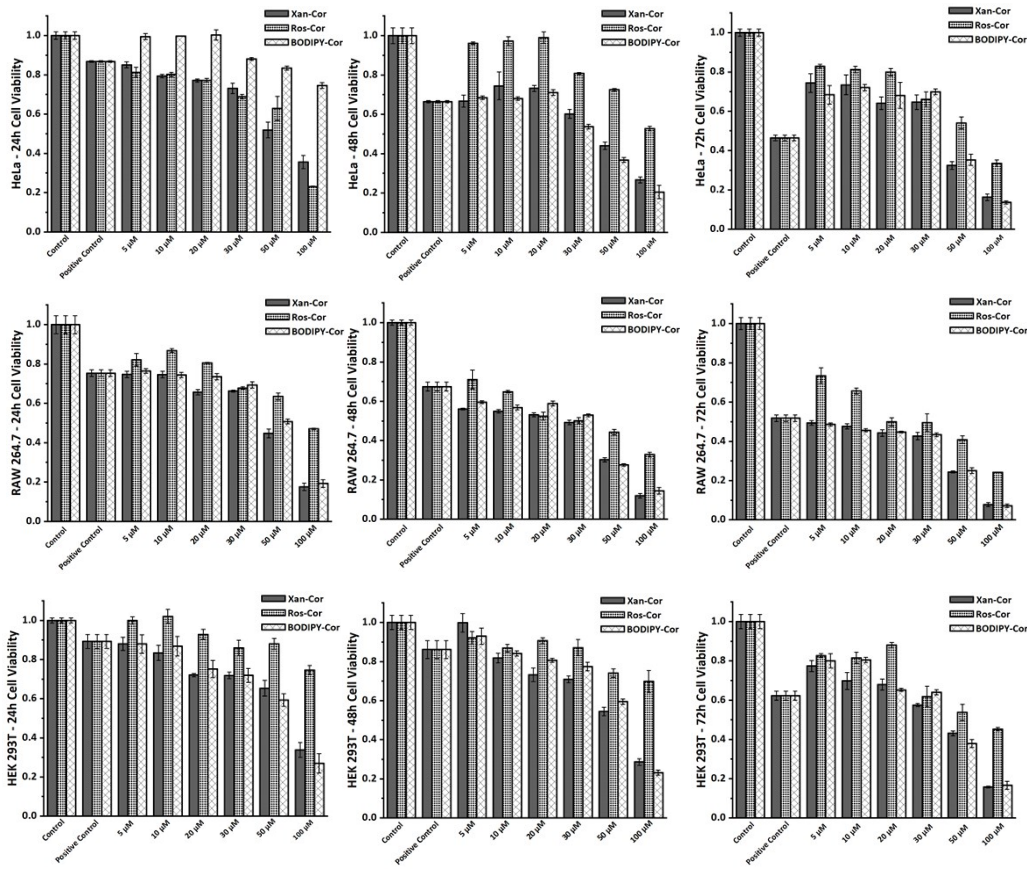


Fig. S11 Cell toxicity effect of **X-Cor** conjugates to HeLa, HEK 293T, and RAW 264.7 cell lines. Cells were incubated with these probes (0 - 100 μM) for 24 h, 48 h, 72 h respectively. Results are mean ± SD, n = 5. Control experiments were performed in the cell culture medium only. Positive Control experiments were performed in the cell culture medium contained 1% DMSO without any probes.

5. Confocal Fluorescence Imaging

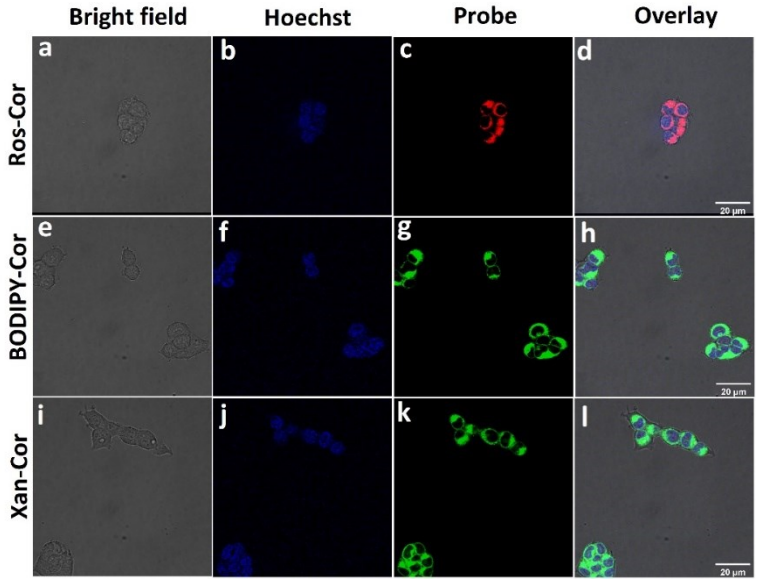


Fig. S12 Confocal fluorescence images of HEK 293T cells stained with Hoechst (1 μM) and **X-Cor** conjugates (5 μM). Column 1: Bright field images (a, e, i). Column 2: Hoechst staining (b, f, j; blue channel: λ_{ex} = 405 nm, λ_{em} = 430 - 450 nm). Column 3: **Ros-Cor** (c; red channel: λ_{ex} = 552 nm, λ_{em} = 600 - 620 nm); **BODIPY-Cor** (g; green channel: λ_{ex} = 488 nm, λ_{em} = 530 - 550 nm); **Xan-Cor** (k; green channel, λ_{ex} = 488 nm, λ_{em} = 530 - 550 nm). Column 4: Merged images (d, h, g). Scar bar: 20 μm.

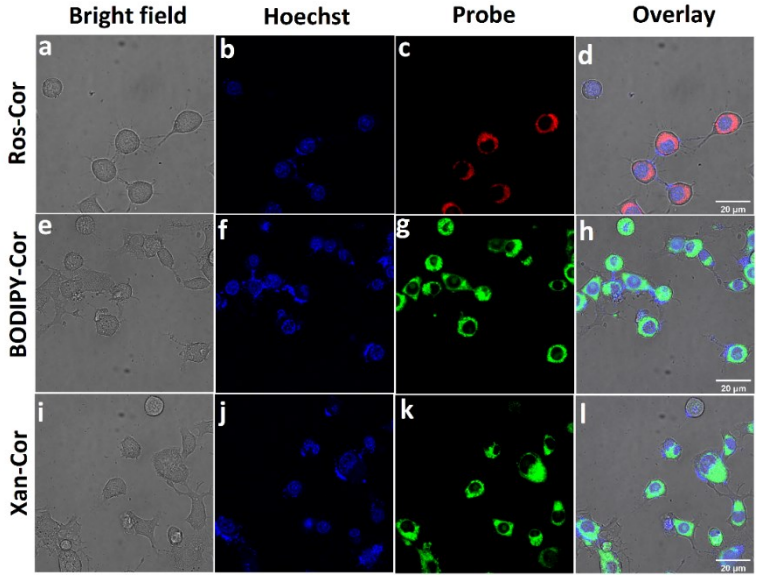


Fig. S13 Confocal fluorescence images of RAW 264.7 cells stained with Hoechst (1 μM) and **X-Cor** conjugates (5 μM). Column 1: Bright field images (a, e, i). Column 2: Hoechst staining (b, f, j; blue channel: λ_{ex} = 405 nm, λ_{em} = 430 - 450 nm). Column 3: **Ros-Cor** (c; red channel: λ_{ex} = 552 nm, λ_{em} = 600 - 620 nm); **BODIPY-Cor** (g; green channel: λ_{ex} =

488 nm, λ_{em} = 530 - 550 nm); **Xan-Cor** (k; green channel, λ_{ex} = 488 nm, λ_{em} = 530 - 550 nm). Column 4: Merged images (d, h, g). Scar bar: 20 μm.

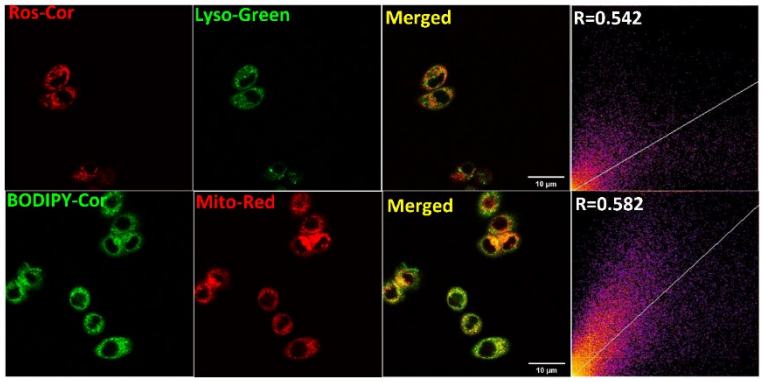


Fig. S14 Confocal fluorescence images of HeLa cells stained with **Ros-Cor** (1 μM, Red channel: λ_{ex} = 552 nm, λ_{em} = 610 - 620 nm); LysoTracker Green (100 nm, green channel: λ_{ex} = 488 nm, λ_{em} = 500 – 510 nm). BODIPY-Cor (1 μM, Green channel: λ_{ex} = 488 nm, λem = 530 - 540 nm); MitoTracker Red (100 nM, red channel: λ_{ex} = 552 nm, λ_{em} = 600 – 610 nm). Scale bar: 10 μm.

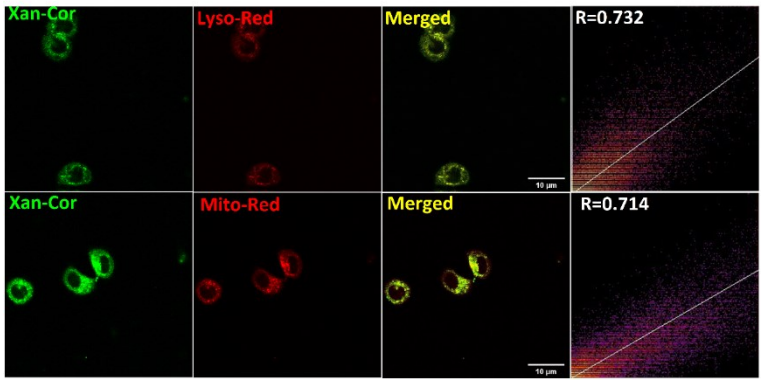


Fig. S15 Confocal fluorescence images of HeLa cells stained with **Xan-Cor** (1 μM, green channel: λ_{ex} = 488 nm, λ_{em} = 530–540nm); MitoTracker Red (100 nm, λ_{ex} = 552 nm, λ_{em} = 600–610 nm). LysoTracker Red (100 nm, Red channel: λ_{ex} = 552 nm, λ_{em} = 600-610 nm). Scale bar: 10 μm.

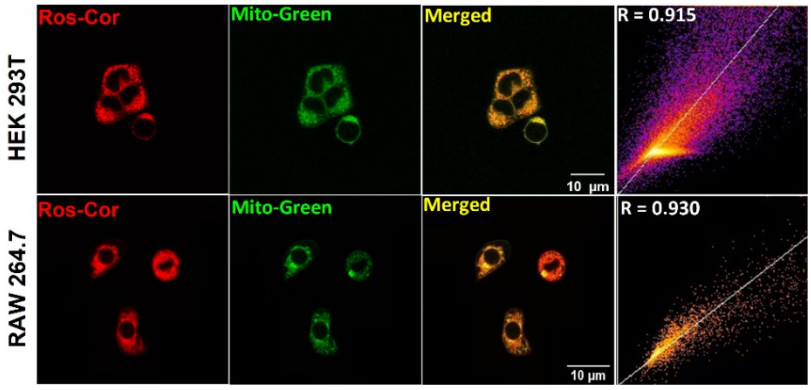


Fig. 16 Confocal fluorescence images of **Ros-Cor** (1 μM, Red channel: λ_{ex} = 552 nm, λ_{em} = 610 -620 nm); MitoTracker Green (100 nM, green channel: λ_{ex} = 488 nm, λ_{em} = 500–510 nm) in HEK 293T and RAW 267.4 cells. Scale bar: 10 μm.

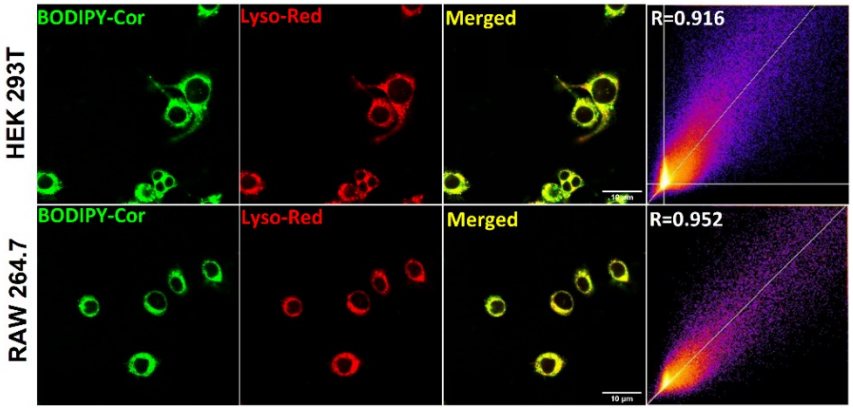
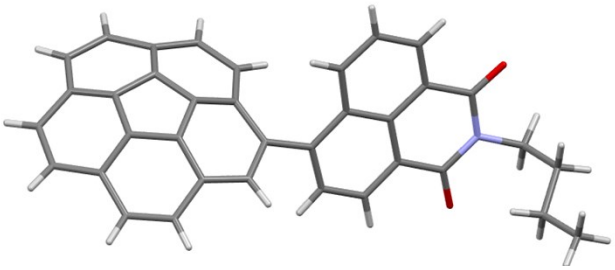


Fig. S17 Confocal fluorescence images of **BODIPY-Cor** (1 μM, Green channel: λ_{ex} = 488 nm, λ_{em} = 530-540 nm); LysoTracker Red (100 nM, red channel: λ_{ex} = 552 nm, λ_{em} = 600–610 nm) in HEK 293T and RAW 267.4 cells. Scale bar: 10 μm.

6. X-Ray Crystal Data



Fg. S18 Single-crystal X-ray diffraction structures of **NI-Cor**. Thermal ellipsoids set to 50 % probability.

Table S4 Crystal data and structure refinement for **NI-Cor**

Identification code	**NI-Cor**
Empirical formula	$C_{36}H_{23}NO_2$
Formula weight	501.55
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	17.1874(5)
b/Å	7.5058(3)
c/Å	37.0743(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4782.8(3)
Z	8
ρcalcg/cm^3	1.393
μ/mm^{-1}	0.674
F(000)	2096
Crystal size/mm^3	0.3 × 0.2 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.014 to 153.044
Index ranges	-21 ≤ h ≤ 14, -9 ≤ k ≤ 9, -42 ≤ l ≤ 46
Reflections collected	15372
Independent reflections	4783 [Rint = 0.0601, Rsigma = 0.0575]
Data/restraints/parameters	4783/0/353
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0573, wR_2 = 0.1464

Final R indexes [all data]	R_1 = 0.0770, wR_2 = 0.1606
Largest diff. peak/hole / e Å^{-3}	0.36/-0.31

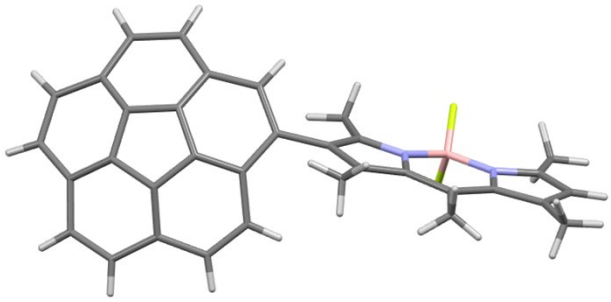


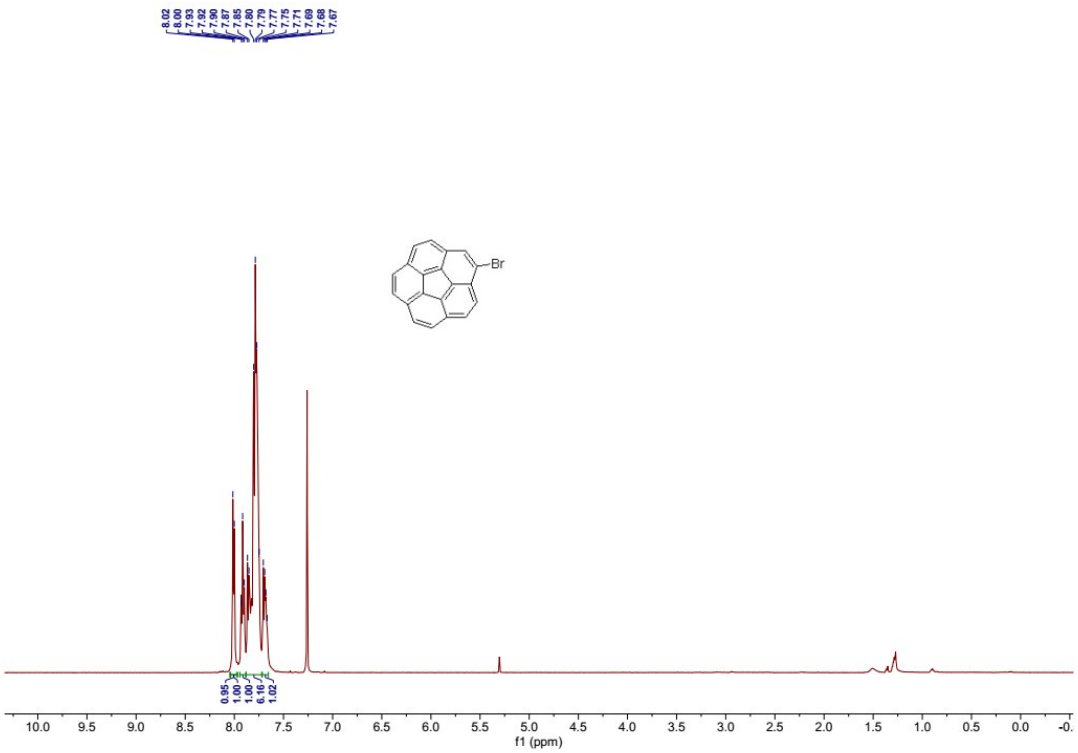
Fig. S19 Single-crystal X-ray diffraction structures of **BODIPY-Cor**. Thermal ellipsoids set to 50 % probability.

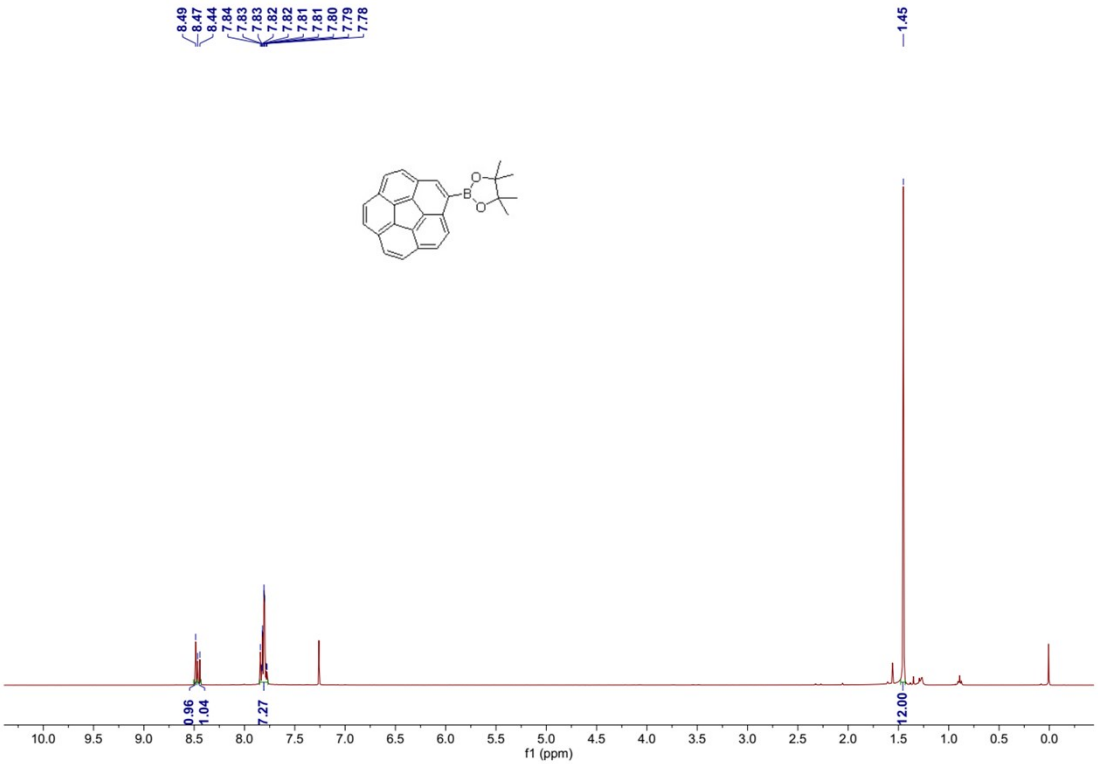
Table S5 Crystal data and structure refinement for **BODIPY-Cor**

Identification code	**BODIPY-Cor**
Empirical formula	$C_{34}H_{25}BF_2N_2$
Formula weight	510.37
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.15670(10)
b/Å	7.75280(10)
c/Å	34.6394(3)
α/°	90
β/°	91.1160(10)
γ/°	90
Volume/Å^3	2458.59(5)
Z	4
ρ_{calc}g/cm^3	1.379
μ/mm^{-1}	0.725
F(000)	1064.0
Crystal size/mm^3	0.15 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.104 to 149.61
Index ranges	-10 ≤ h ≤ 11, -9 ≤ k ≤ 9, -42 ≤ l ≤ 43
Reflections collected	24826
Independent reflections	4897 [R_{int} = 0.0376, R_{sigma} = 0.0280]
Data/restraints/parameters	4897/0/357
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.1074
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1096

Largest diff. peak/hole / e Å^{-3} 0.28/-0.20

7. NMR and HRMS Spectra

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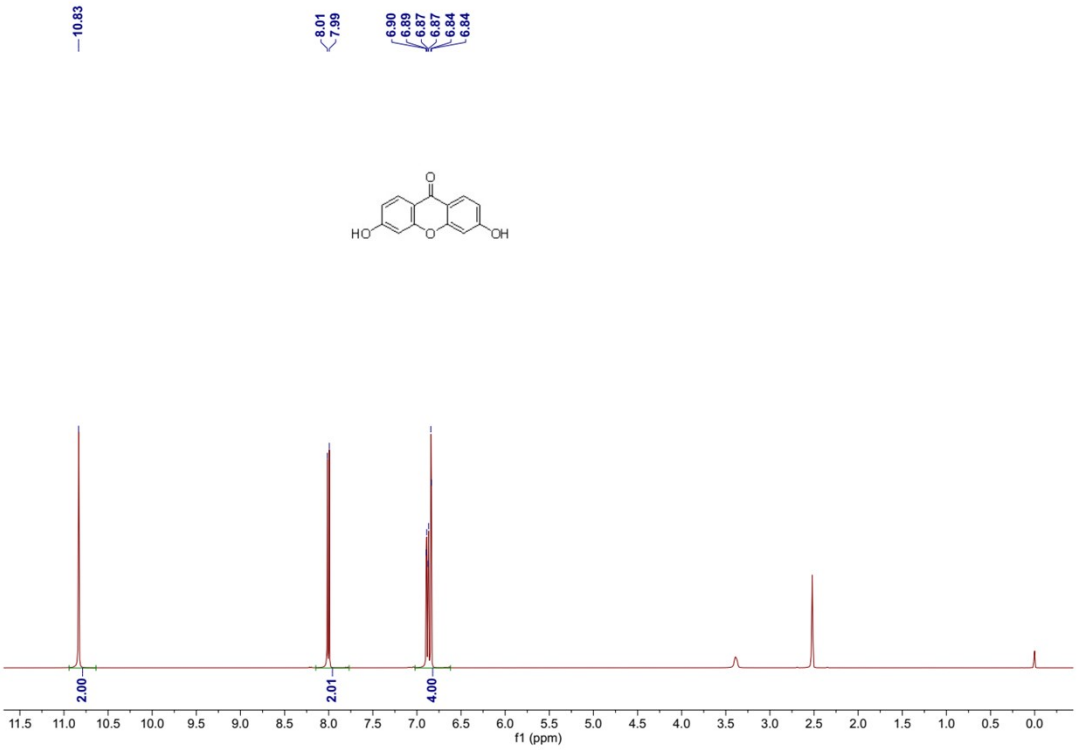
8.44
7.84
7.83
7.83
7.82
7.82
7.81
7.81
7.80
7.79
7.78
1.45
O
B
O
0.96
1.04
7.27
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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6.84
HO
OH
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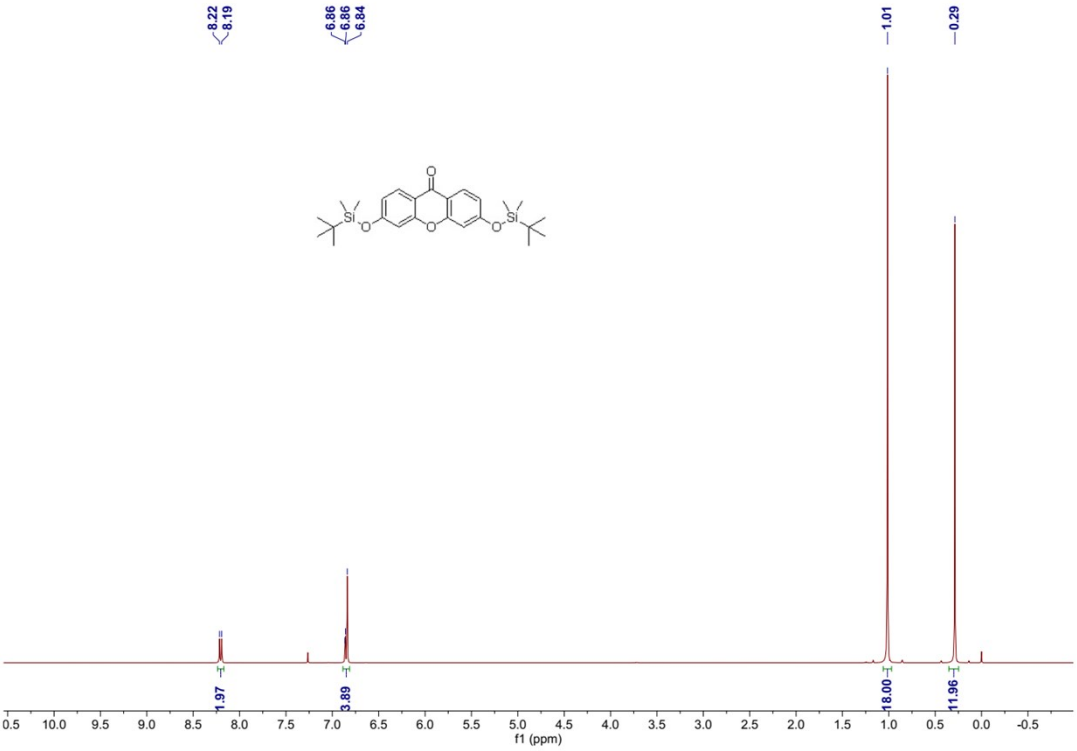
4.00
f1 (ppm)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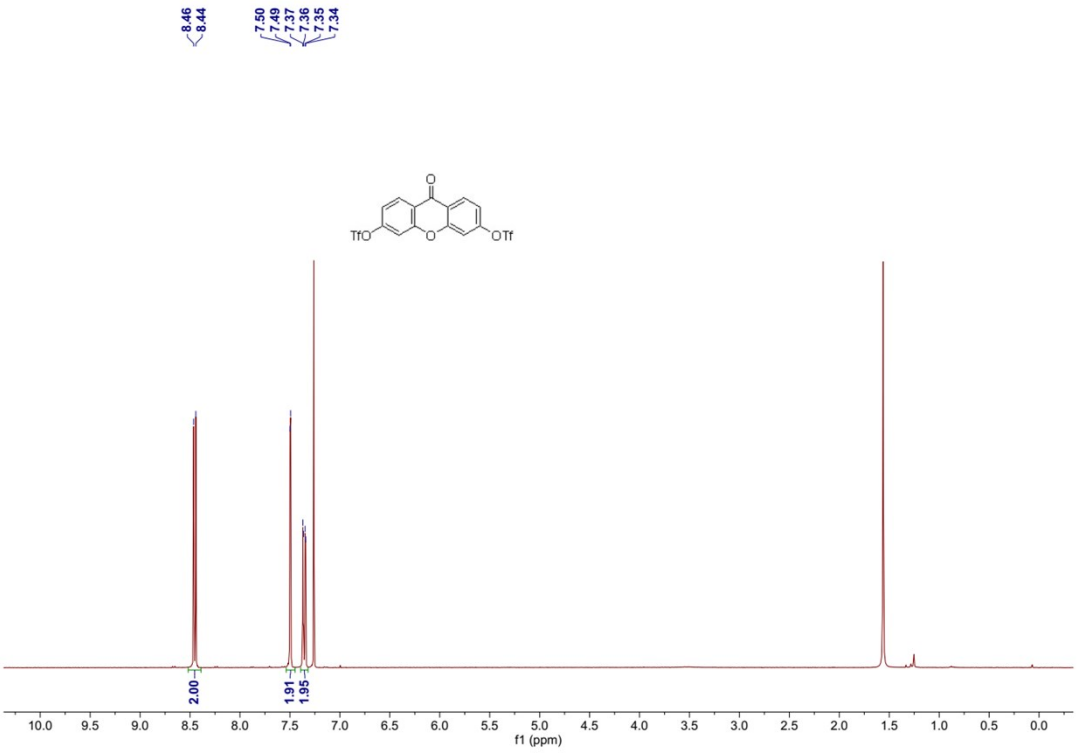
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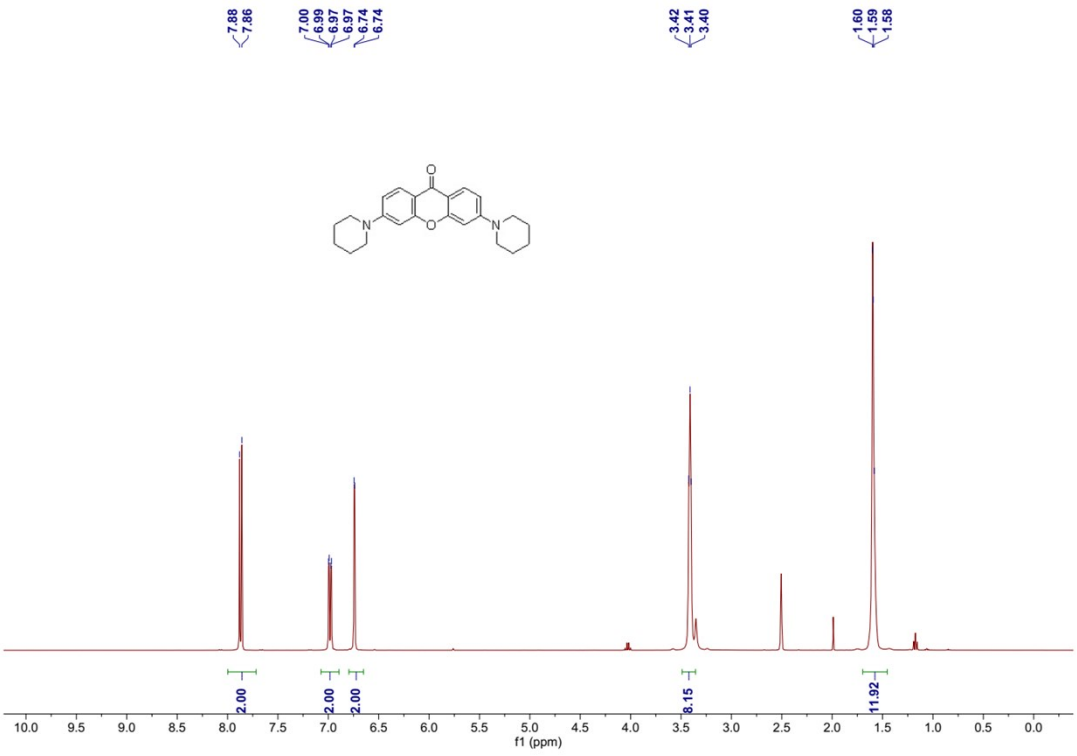
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6.97
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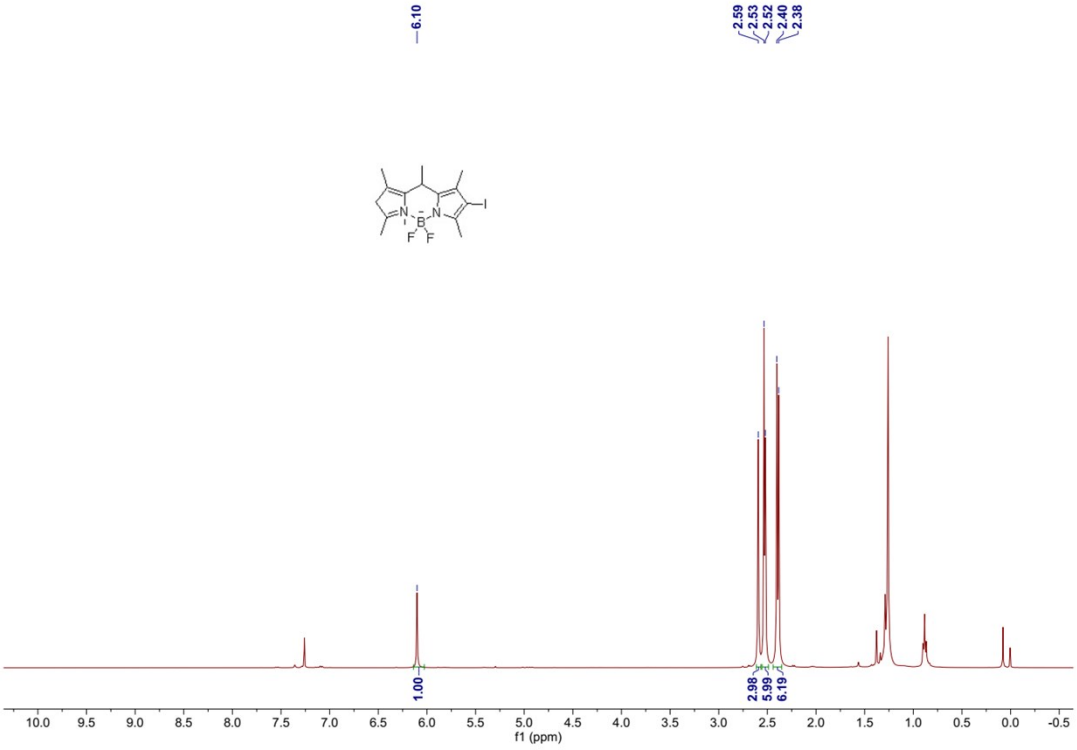
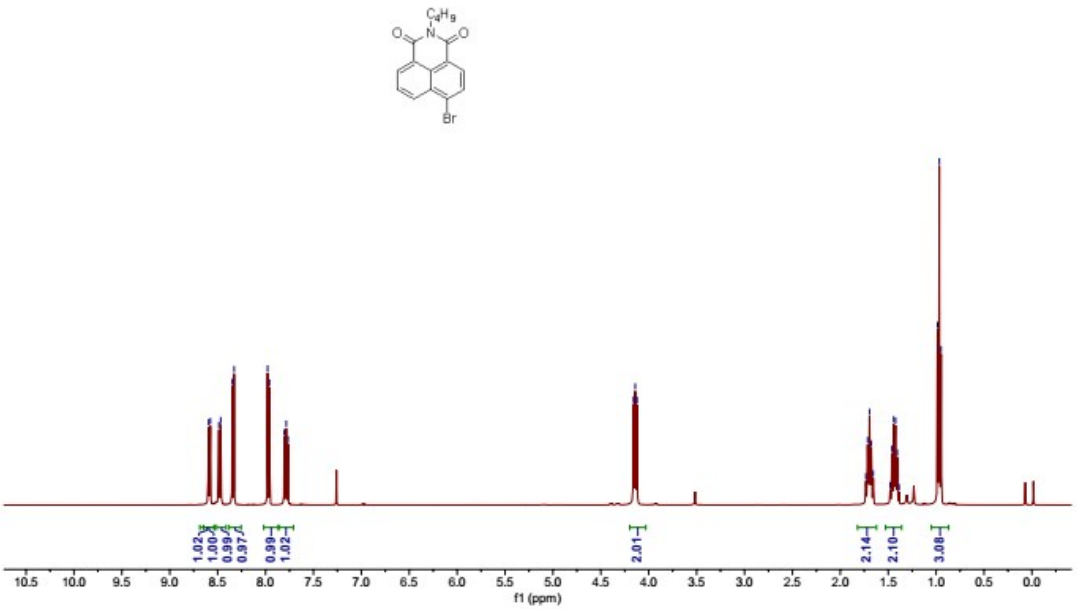
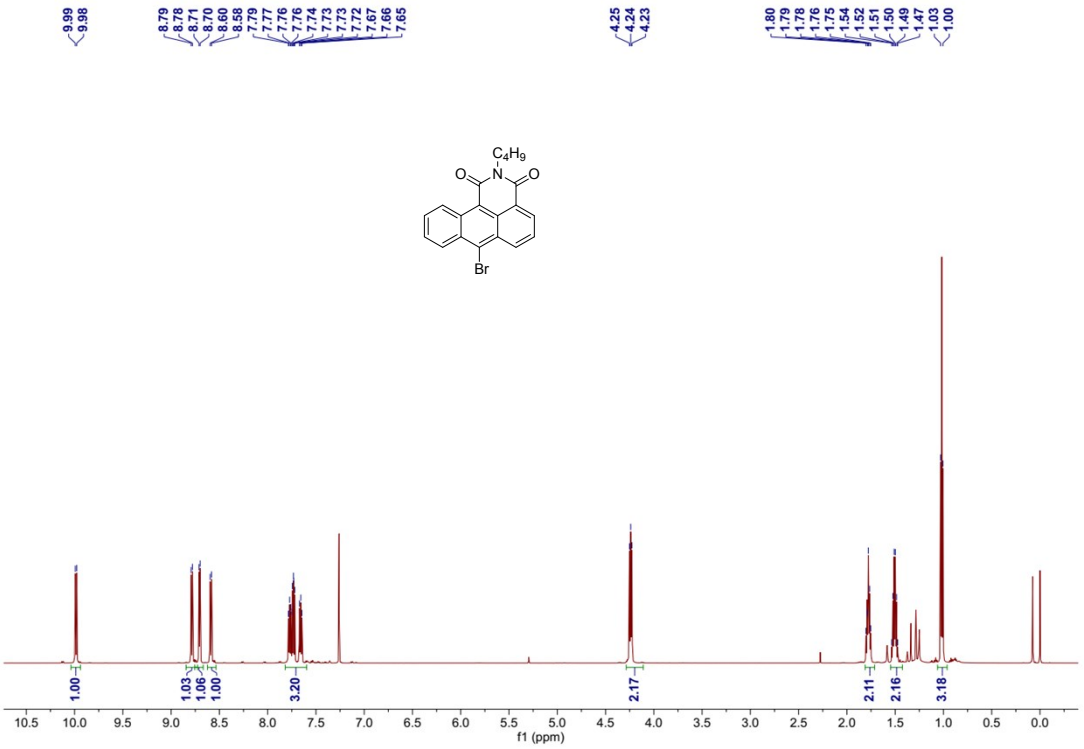
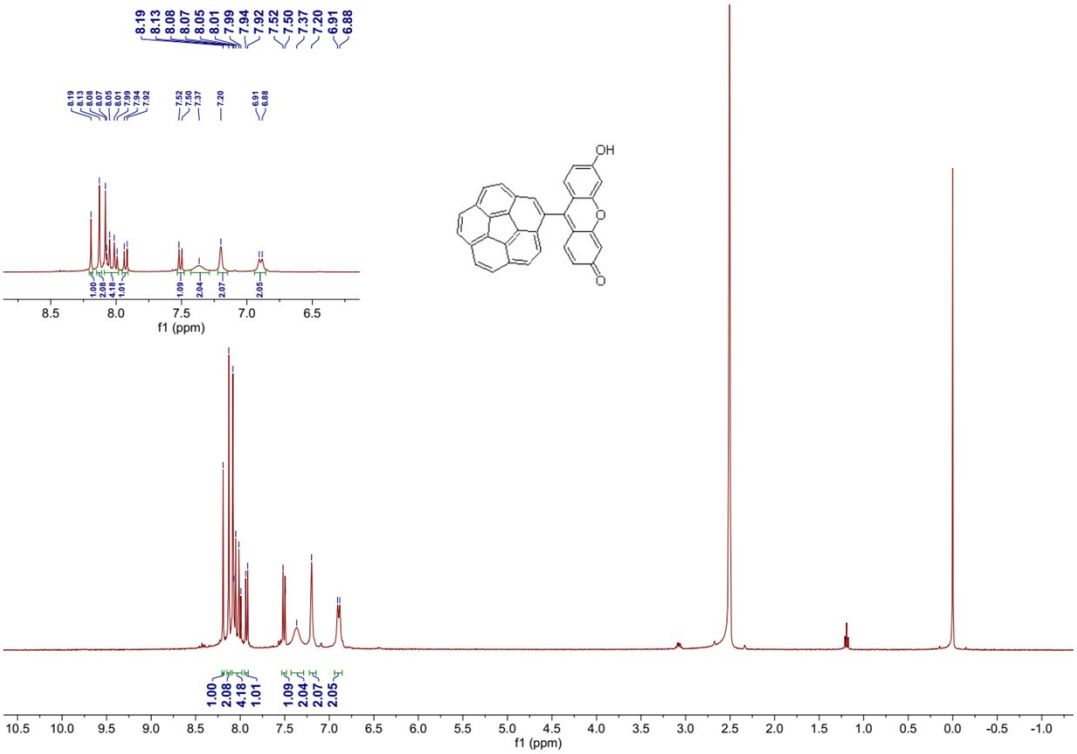
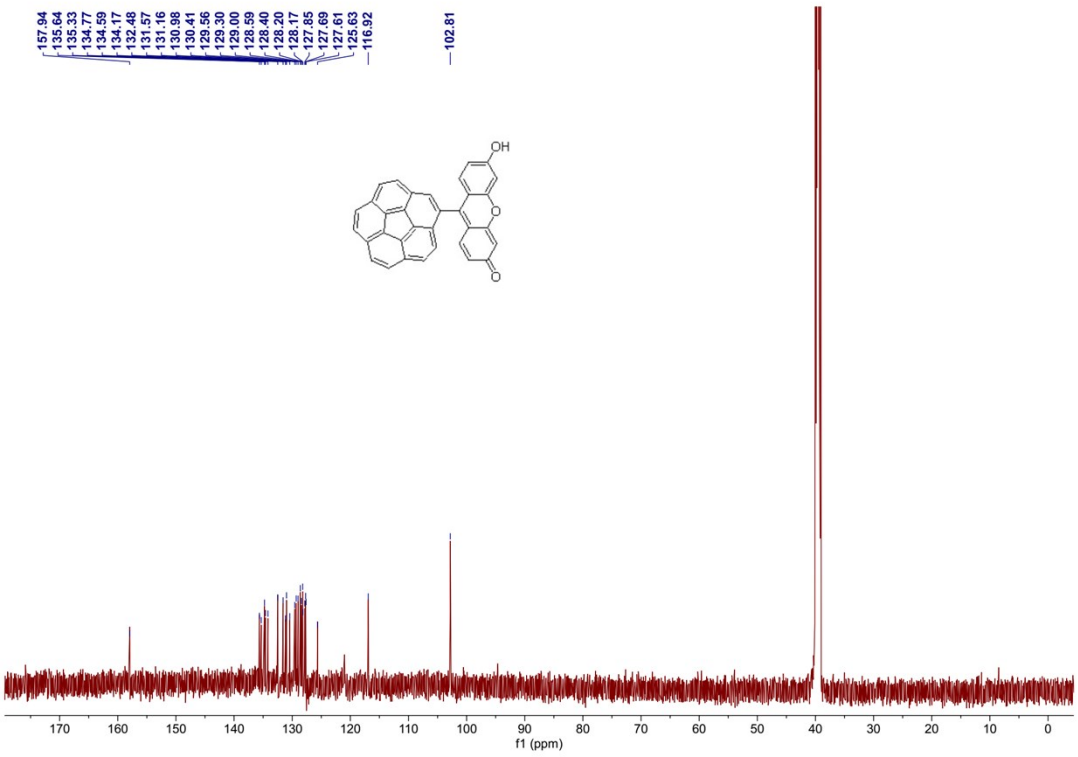
1.59
1.58
2.00
2.00
2.00
8.15
11.92
f1 (ppm)

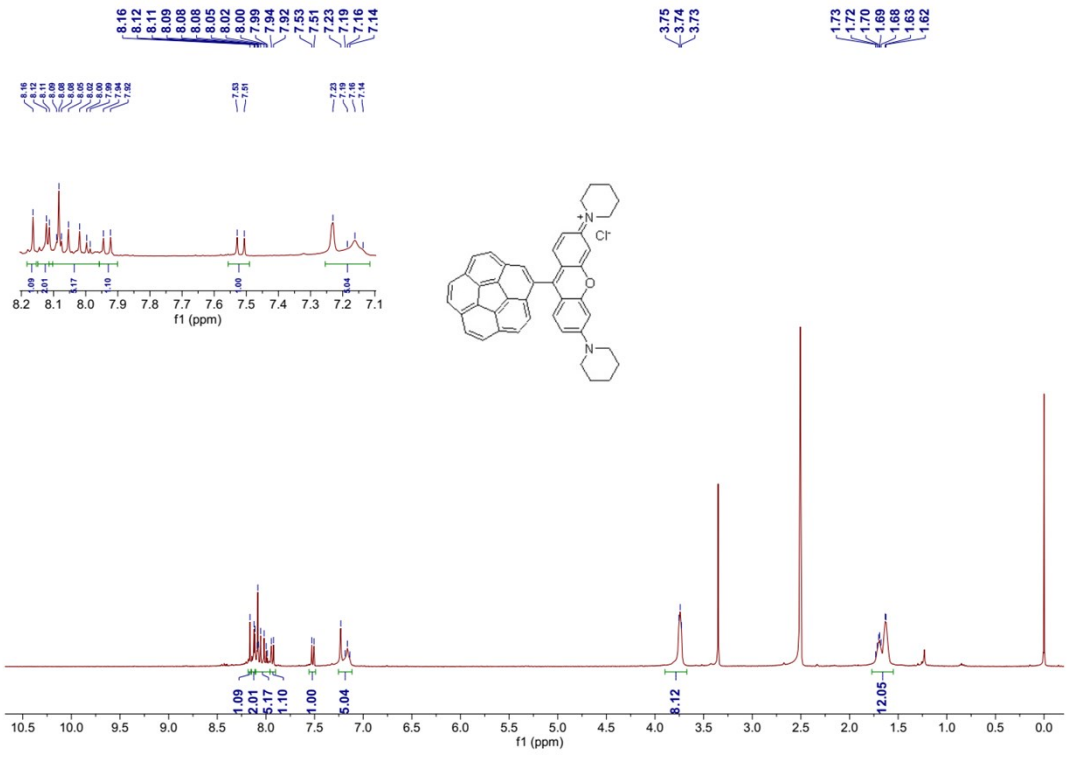

6.10
2.59
2.53
2.52
2.40
2.38
1.00
2.98
5.99
6.19
f1 (ppm)

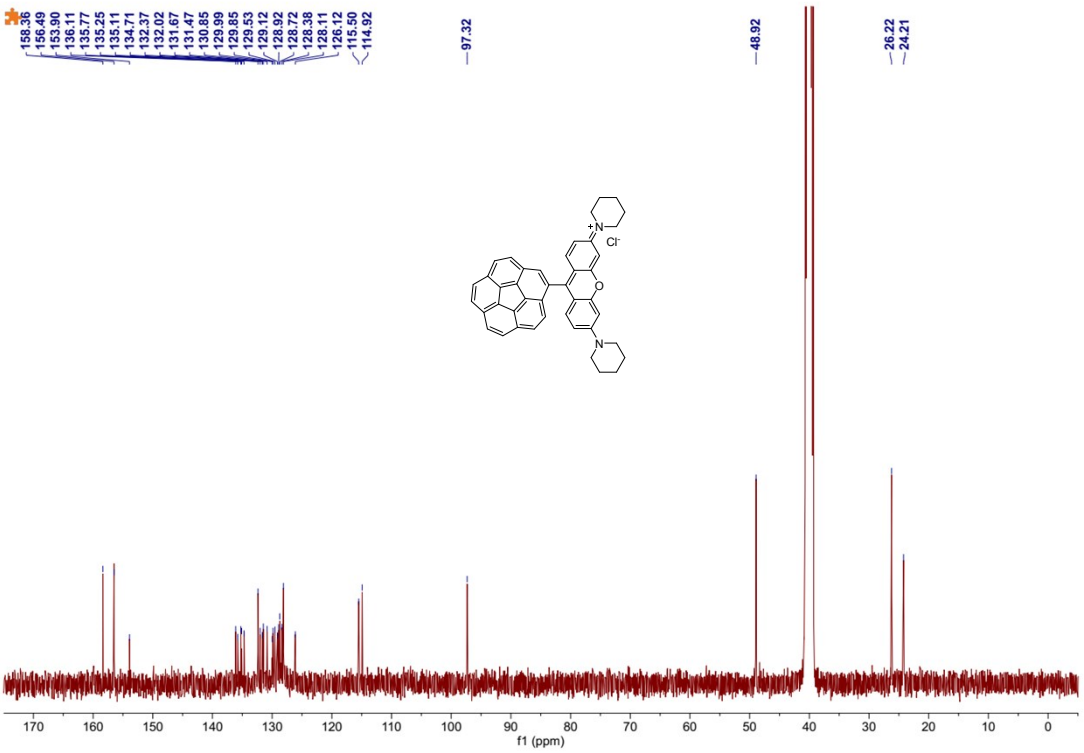

8.59
8.58
8.49
8.47
8.35
8.33
7.98
7.96
7.80
7.78
7.77
4.16
4.14
4.12
1.73
1.71
1.70
1.68
1.66
1.48
1.46
1.44
1.42
1.40
1.39
0.98
0.97
0.95
1.02
1.00
0.99
0.97
0.99
1.02
2.01
2.14
2.10
3.08
f1 (ppm)


9.99
9.98
8.79
8.78
8.71
8.70
8.60
8.58
7.79
7.77
7.76
7.76
7.74
7.73
7.72
7.67
7.66
7.65
4.25
4.24
4.23
1.80
1.79
1.78
1.76
1.75
1.54
1.52
1.51
1.50
1.49
1.47
1.03
1.00
C4H9
O
N
O
Br
1.00
1.03
1.06
1.00
3.20
2.17
2.11
2.16
3.18
f1 (ppm)


8.19
8.13
8.08
8.07
8.05
8.01
7.99
7.94
7.92
7.52
7.50
7.37
7.20
6.91
6.88
OH
O
O
1.00
2.08
4.18
1.01
1.09
2.04
2.07
2.05
f1 (ppm)


157.94
135.64
135.33
134.77
134.59
134.17
132.48
131.57
131.16
130.98
130.41
129.56
129.30
129.00
128.59
128.40
128.20
128.17
127.85
127.69
127.61
125.63
116.92
102.81
OH
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.16
8.12
8.11
8.09
8.08
8.08
8.05
8.02
8.00
7.99
7.94
7.92
7.53
7.51
7.23
7.19
7.16
7.14
3.75
3.74
3.73
1.73
1.72
1.70
1.69
1.68
1.63
1.62
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
N
Cl-
O
N
1.09
2.01
5.17
1.10
1.00
5.04
8.12
12.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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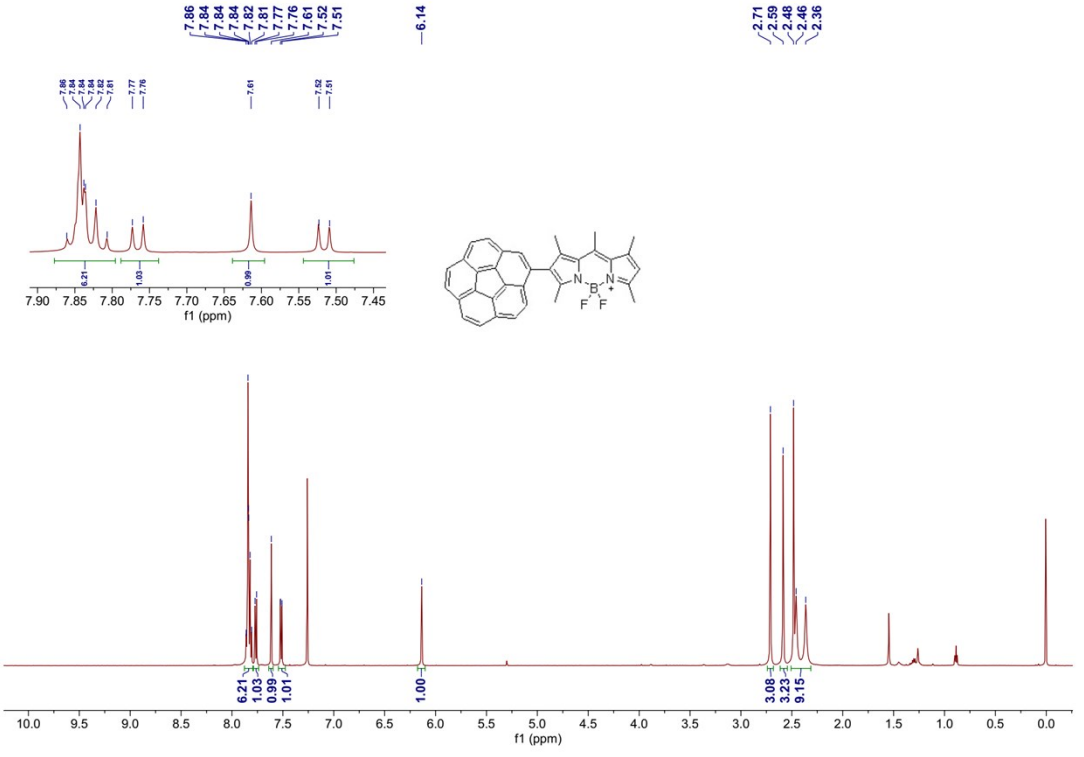
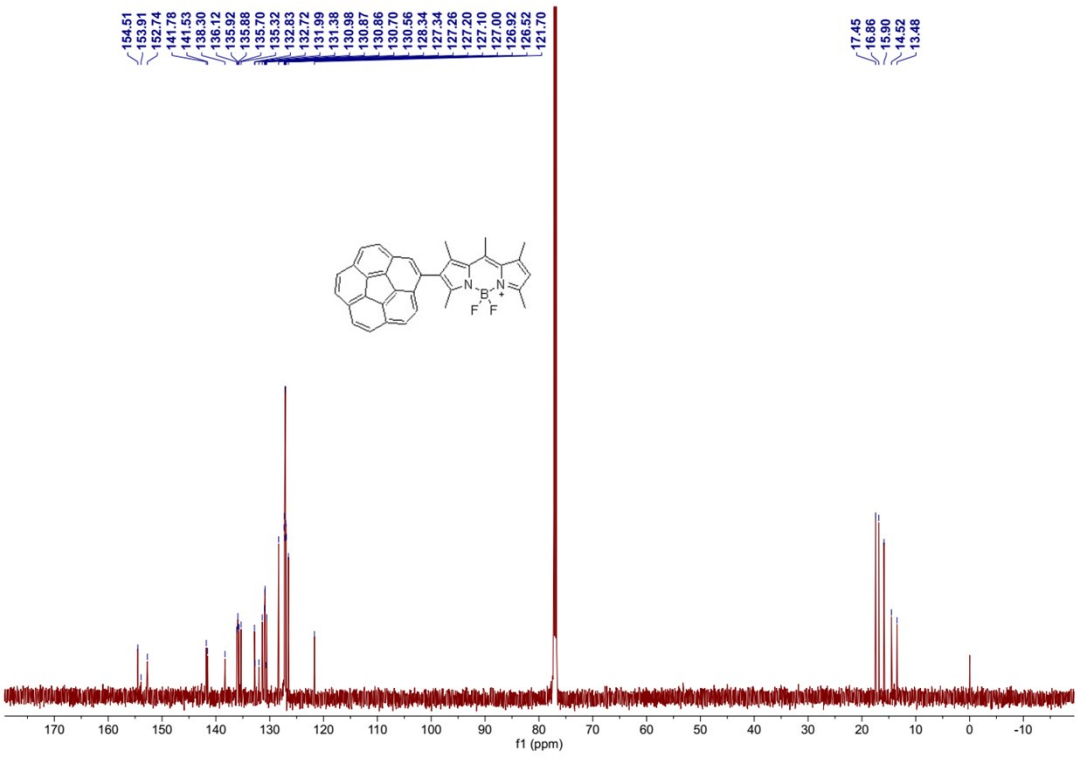
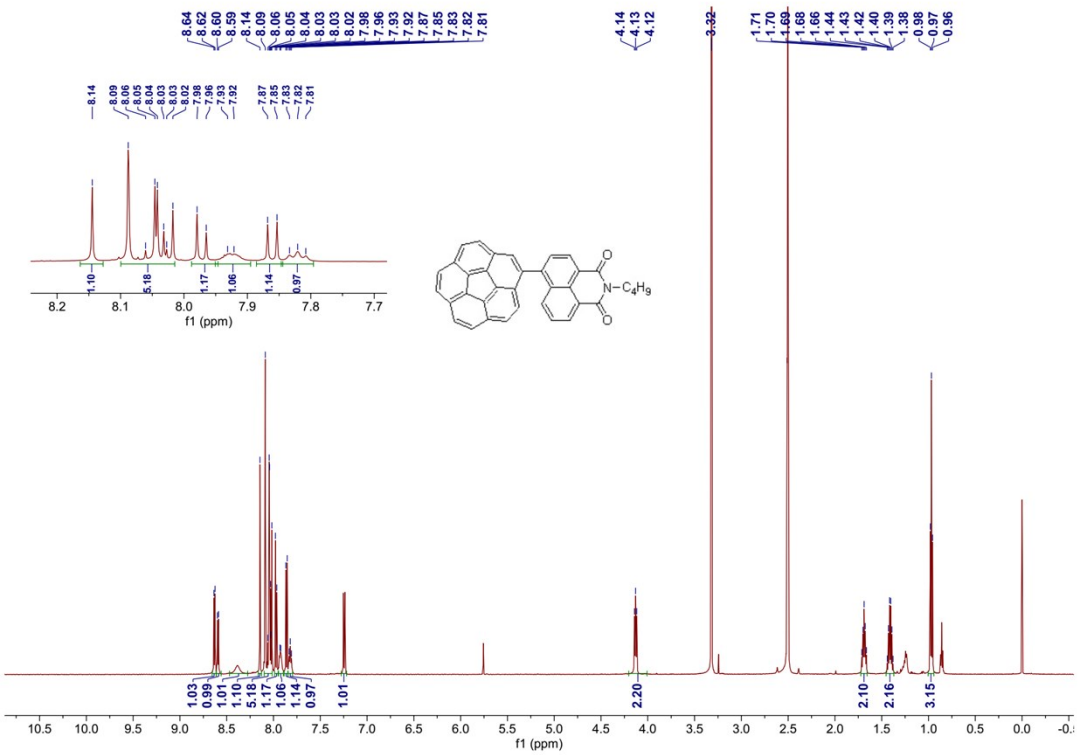
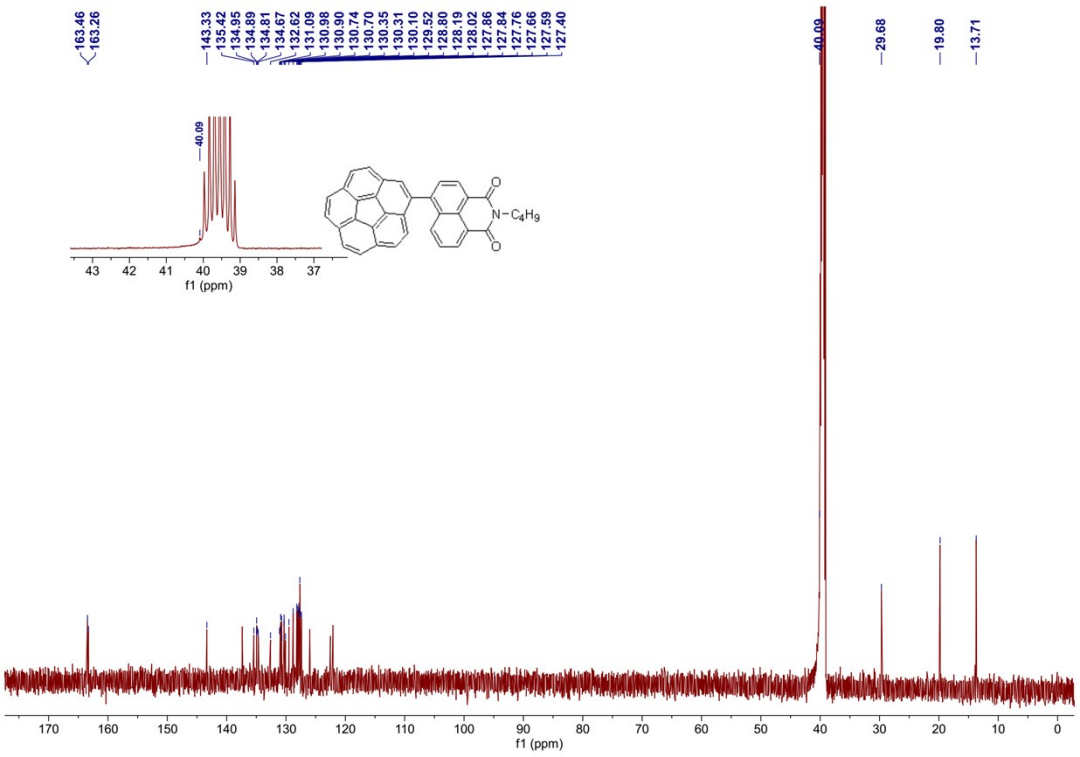
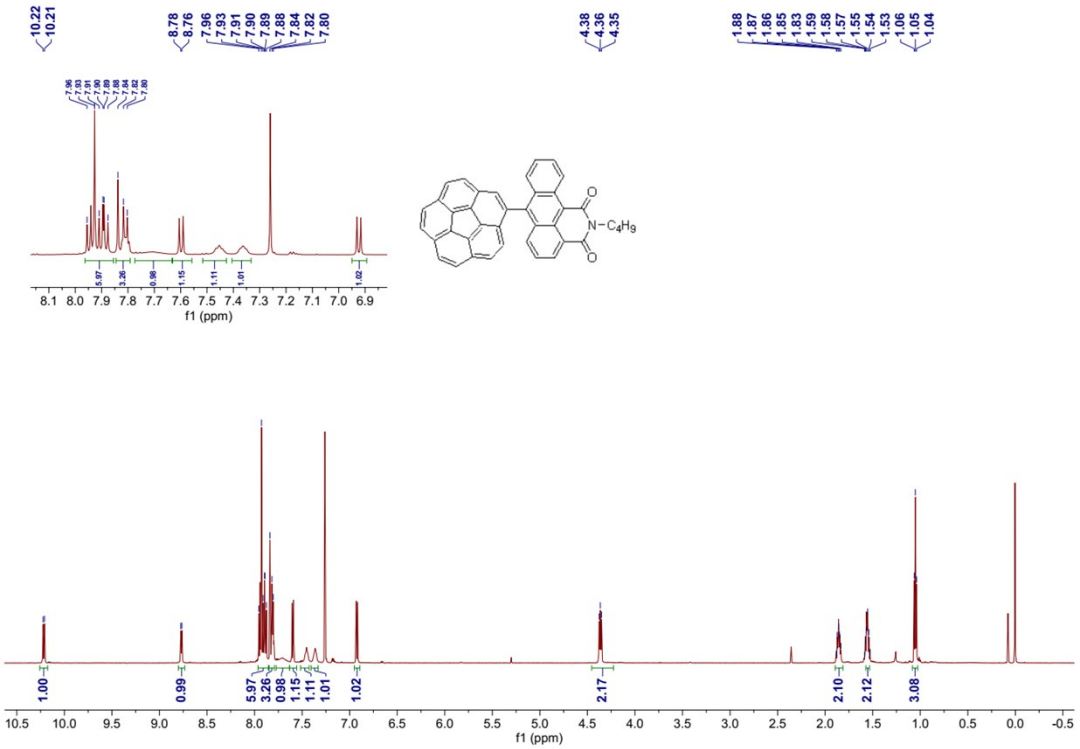
156.49
153.90
136.11
135.77
135.25
135.11
134.71
132.37
132.02
131.67
131.47
130.85
129.99
129.85
129.53
129.12
128.92
128.72
128.38
128.11
126.12
115.50
114.92
97.32
48.92
26.22
24.21
Cl-
f1 (ppm)

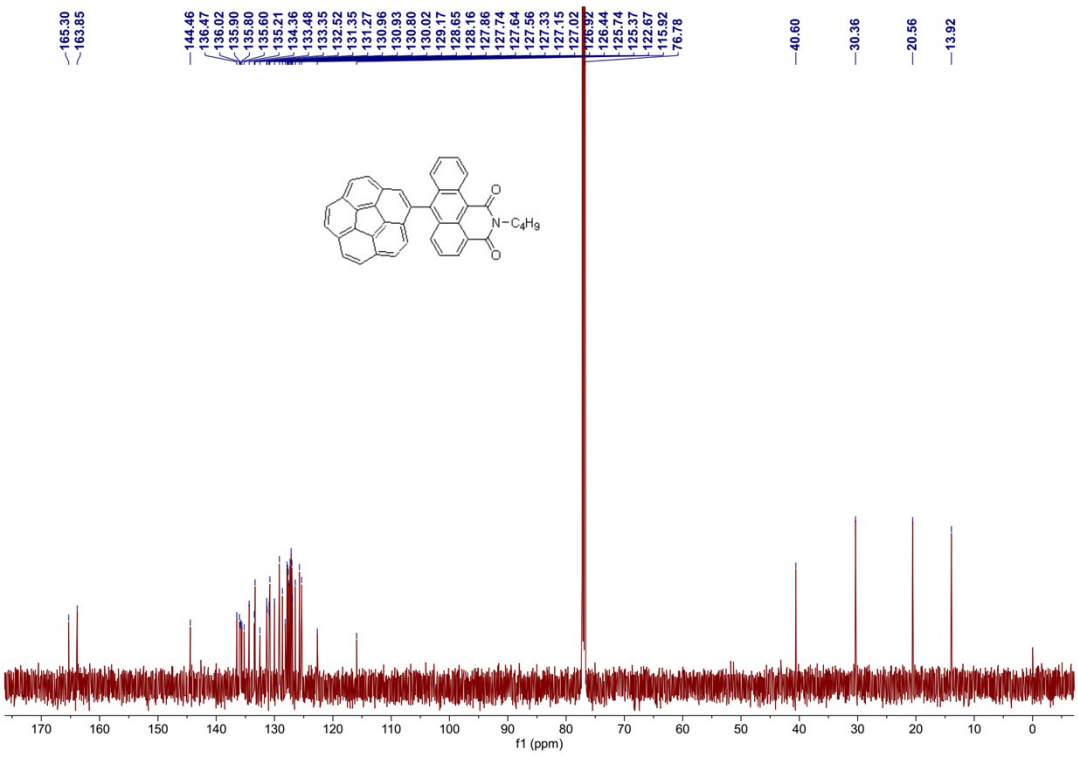

7.86
7.84
7.84
7.84
7.82
7.61
7.77
7.76
7.61
7.52
7.51
6.14
2.71
2.59
2.48
2.46
2.36
6.21
1.03
0.99
1.01
1.00
3.08
3.23
9.15
f1 (ppm)

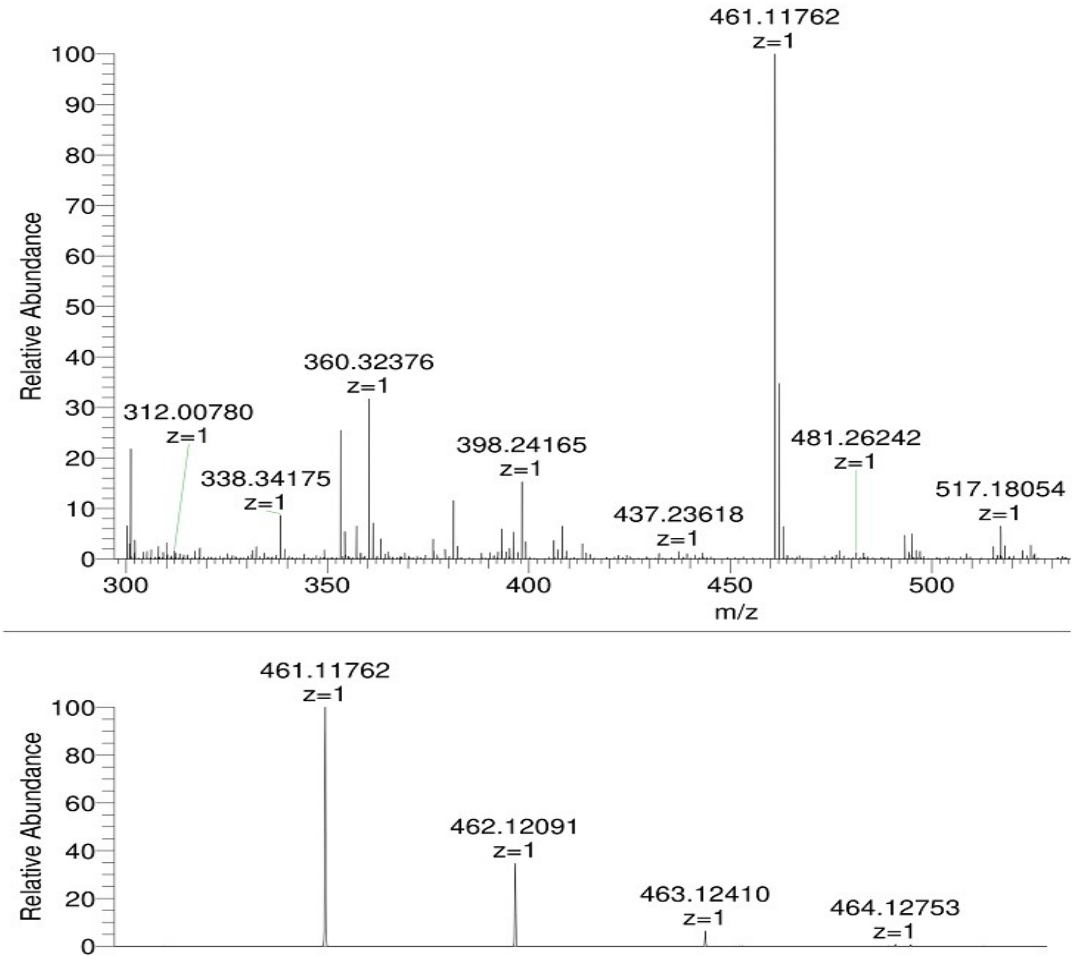

154.51
153.91
152.74
141.78
141.53
138.30
136.12
135.92
135.88
135.70
135.32
132.83
132.72
131.99
131.38
130.98
130.87
130.66
130.70
130.56
128.34
127.34
127.26
127.20
127.10
127.00
126.92
126.52
121.70
17.45
16.86
15.90
14.52
13.48
f1 (ppm)


8.64
8.62
8.60
8.59
8.14
8.09
8.06
8.05
8.04
8.03
8.02
7.98
7.96
7.93
7.92
7.87
7.85
7.83
7.82
7.81
4.14
4.13
4.12
3.32
1.71
1.70
1.69
1.68
1.66
1.44
1.43
1.42
1.40
1.39
1.38
0.98
0.97
0.96
1.10
5.18
1.17
1.06
1.14
0.97
f1 (ppm)
1.03
0.99
1.01
1.10
5.18
1.17
1.06
1.14
0.97
1.01
2.20
2.10
2.16
3.15
f1 (ppm)

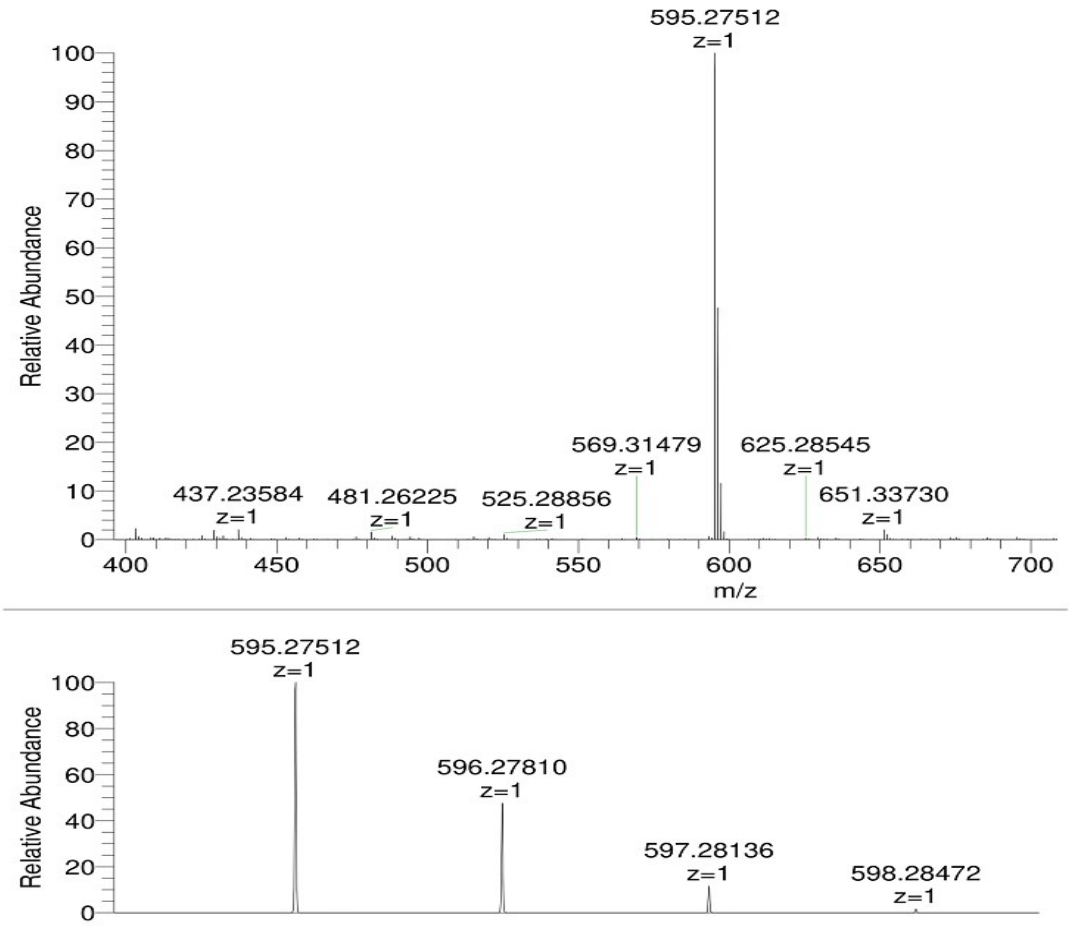

163.46
163.26
143.33
135.42
134.95
134.89
134.81
134.67
132.62
131.09
130.98
130.90
130.74
130.70
130.35
130.31
130.10
129.52
128.80
128.19
128.02
127.86
127.84
127.76
127.66
127.59
127.40
40.09
29.68
19.80
13.71
40.09
43 42 41 40 39 38 37
f1 (ppm)
N−C4H9
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.22
10.21
8.78
8.76
7.96
7.93
7.91
7.90
7.89
7.88
7.84
7.82
7.80
4.38
4.36
4.35
1.88
1.87
1.86
1.85
1.83
1.59
1.58
1.57
1.55
1.54
1.53
1.06
1.05
1.04
5.97
3.26
0.98
1.15
1.11
1.01
1.02
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
N−C4H9
O
O
1.00
0.99
5.97
3.26
0.98
1.15
1.11
1.01
1.02
2.17
2.10
2.12
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

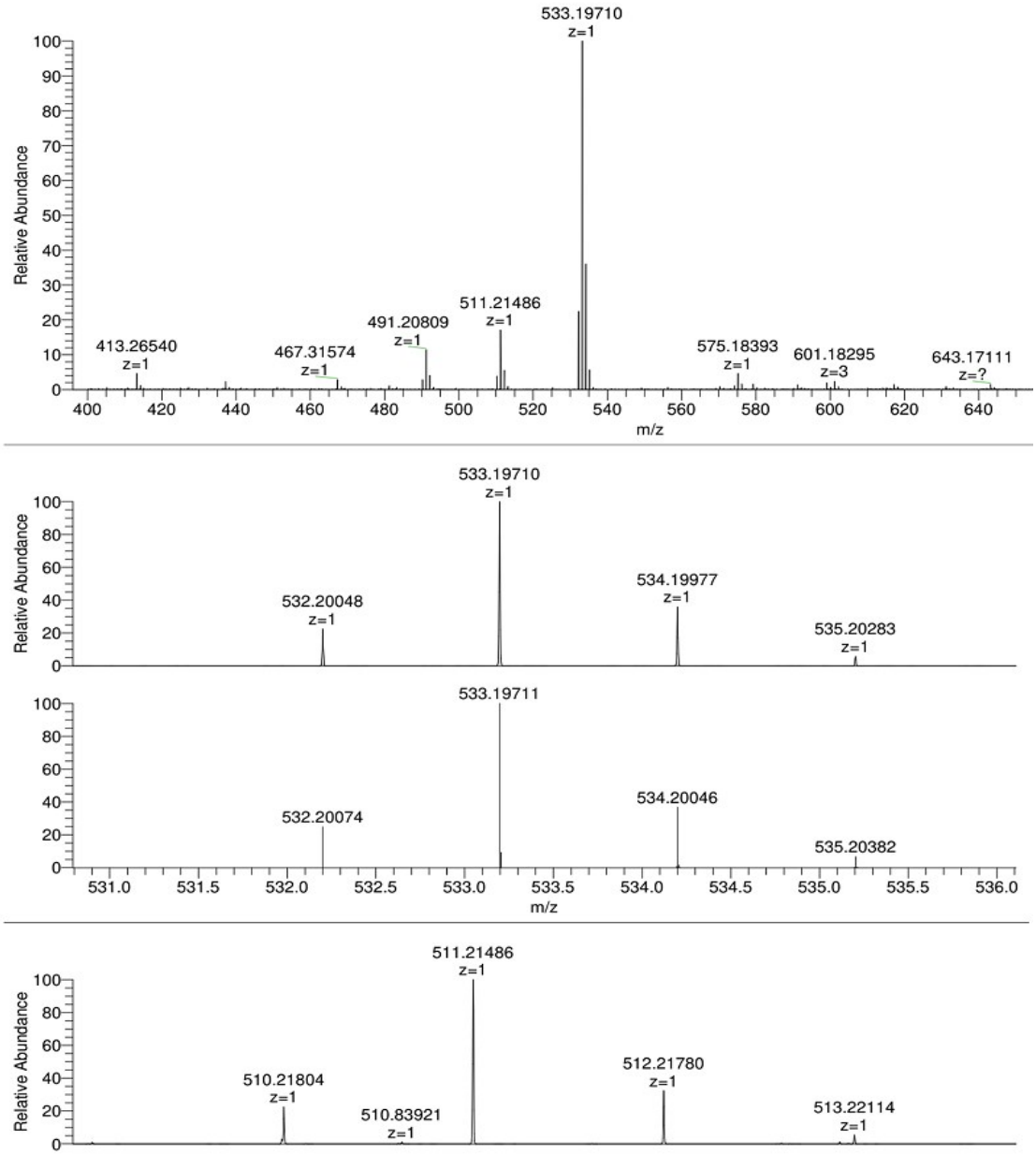

165.30
163.85
144.46
136.47
136.02
135.90
135.80
135.60
135.21
134.36
133.48
133.35
132.52
131.35
131.27
130.96
130.93
130.80
130.02
129.17
128.65
128.16
127.86
127.74
127.64
127.56
127.33
127.15
127.02
126.92
126.44
125.74
125.37
122.67
115.92
76.78
40.60
30.36
20.56
13.92
O
N−C4H9
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



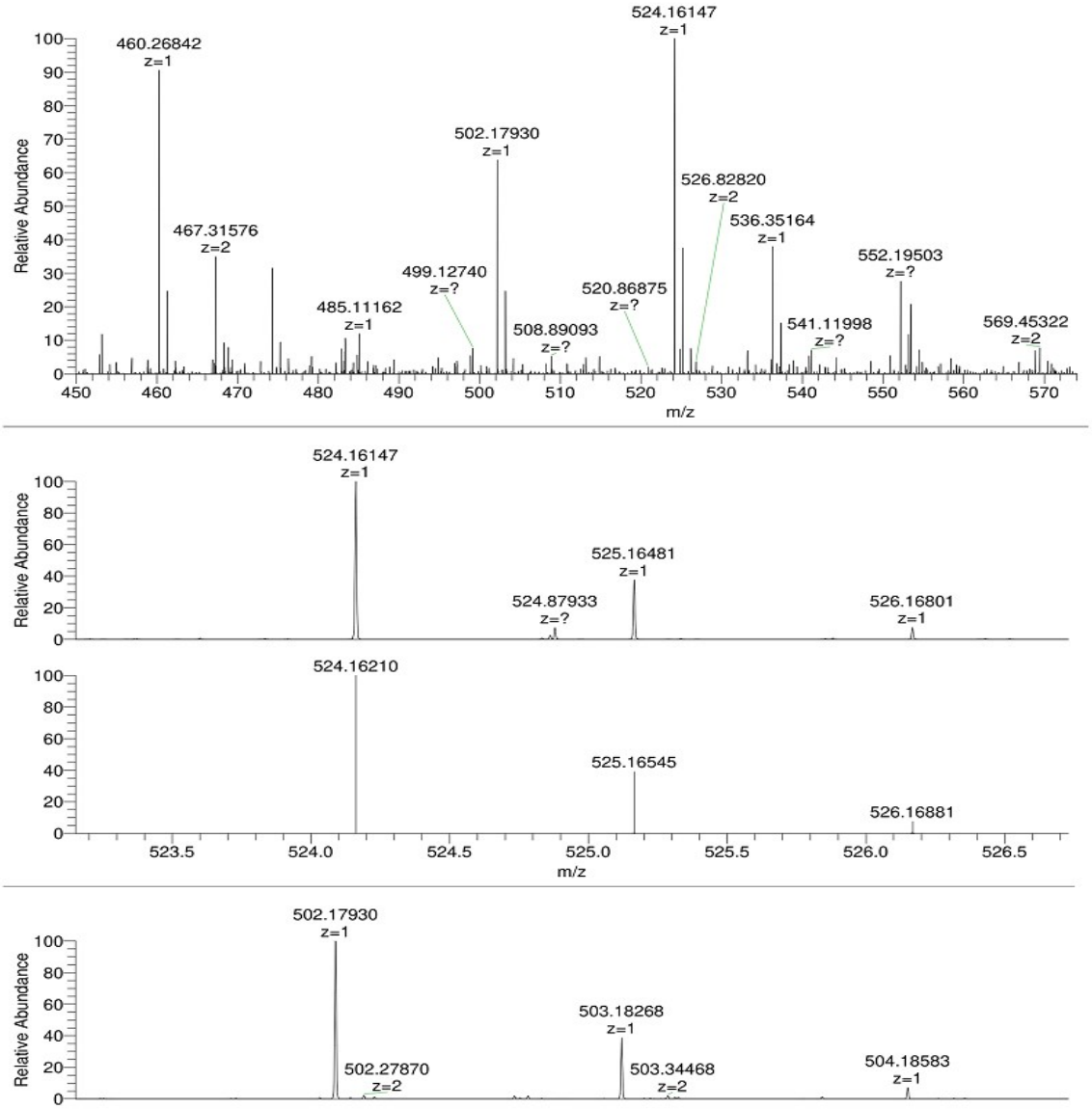
HRMS-ESI spectrum of **10** (**Xan-Cor**)



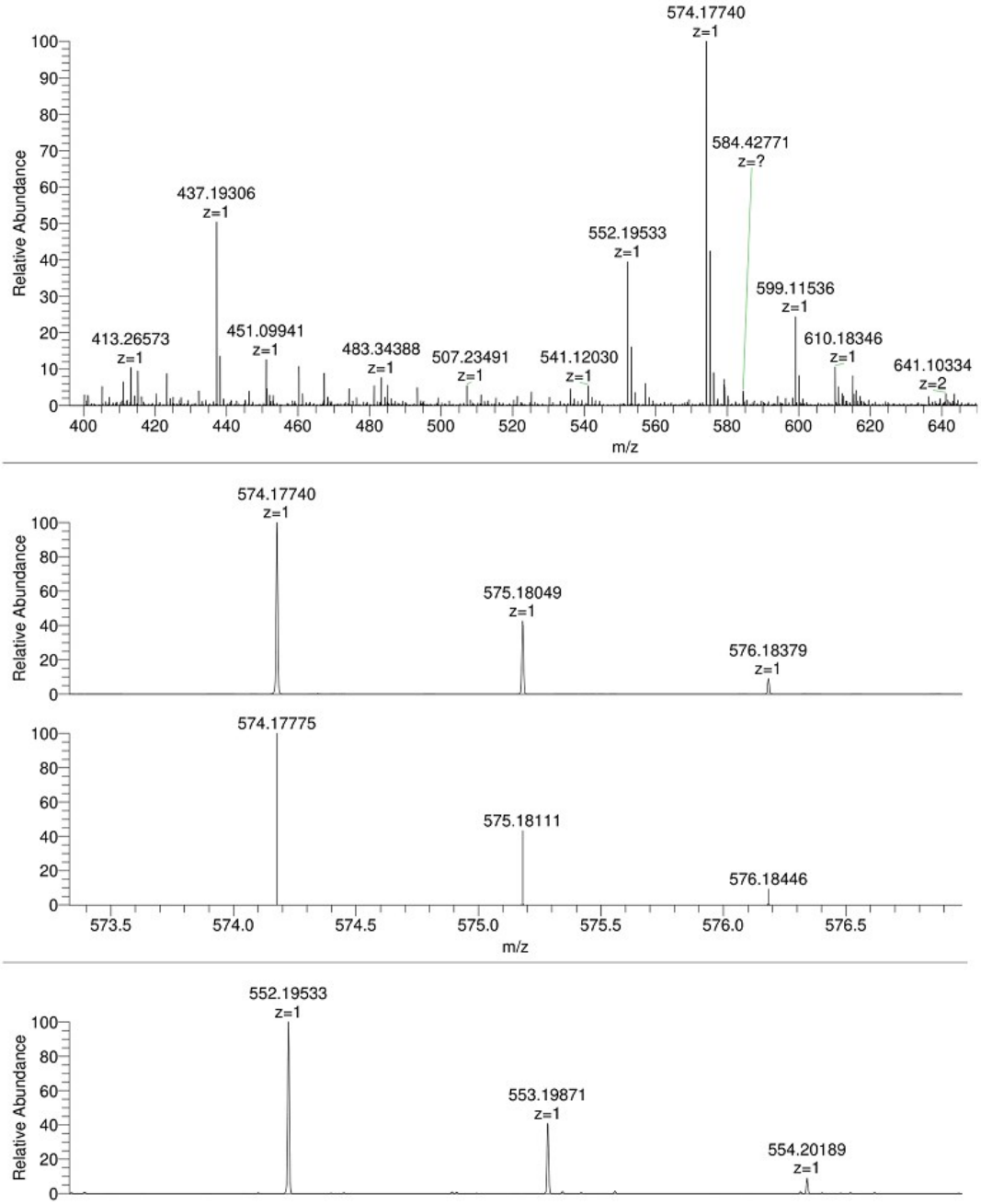
HRMS-ESI spectrum of **11** (**Ros-Cor**)



HRMS-ESI spectrum of **12** (**BODIPY-Cor**)



HRMS-ESI spectrum of **13** (**NI-Cor**)



HRMS-ESI spectrum of **14** (**AC-Cor)**

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