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Switchable cascade C−H annulation to polycyclic pyryliums and pyridiniums: discovering mitochondria-targeting fluorescent probes

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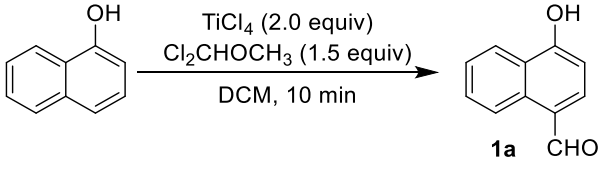
I. General remarks

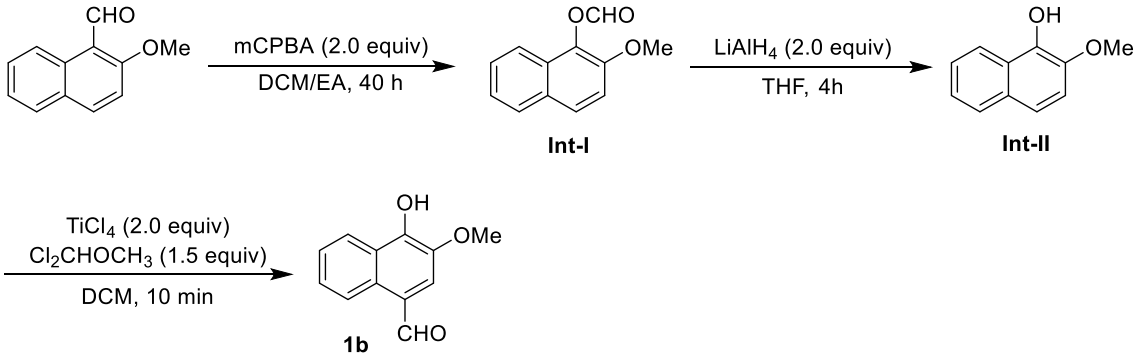
NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ =2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-ITTOF (ESI). MALDI−TOF−MS was obtained with a Bruker Autoflex III smartbeam MALDI TOF spectrometer with matrix of α-cyano-4-hydroxycinnamic acid (CCA). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. Absorption spectra were obtained on a HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. To reduce the fluctuation in the excitation intensity, the xenon lamp was kept on for 1 hour prior to the experiment. The human hepatoma cell line HepG2 was purchased from Shanghai Institute of Biochemistry and Cell Biology, Chinese Academy of Sciences. The confocal imaging experiments were performed on a Zeiss LSM 780 confocal fluorescent microscope.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $Cu(OAc)_2 \cdot H_2O$ (99% purity) was purchased from Chengdu Ke Long Chemical Engineering Reagent (China) Co., Ltd. The solvents were purified and dried using an Innovative Technology PS-MD-5 Solvent Purification System. $RhCl_3 \cdot xH_2O$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. $AgSbF_6$ was purchased from Alfa Aesar. $[Cp^*RhCl_2]_2$ was prepared according to the literature procedures.[1] Diphenylacetylene (**2a**) was purchased from Alfa Aesar. Alkynes **2b**, **2c**, **2d**, **2e**, **2f**, **2g** and **2h** were prepared according to the literature procedures.[2]

II. Synthesis of naphthalene aldehydes



4-Hydroxy-1-naphthaldehyde (1a): Titanium tetrachloride (4.4 mL, 4.0 mmol) was added dropwise to a stirred solution of 1-naphthol (2.9 g, 20.0 mmol) in CH_2Cl_2 (25.0 mL) at 0 °C. Dichloro(methoxy)methane (2.8 mL, 31.0 mmol) was then added dropwise to the resulting dark solution over 5 minutes at 0 °C. The solution was keeping stirring for additional 10 minutes, then ice water (5.6 mL) was added. The heterogeneous mixture was stirred vigorously at 0 °C until all titanium salts dissolved. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50.0 mL). The combined organic extracts were washed with brine (50.0 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5 to 50:50, v/v) to afford 4-hydroxy-1-naphthaldehyde **1a** (2.8 g, 80% yield) as a white solid.[3] ^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) = 10.32 (s, 1H, –OH), 10.18 (s, 1H), 9.34 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.73 (m, 1H), 7.62 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H). ^{13}C NMR (Acetone-d_6, 100 MHz): δ (ppm) = 192.7, 160.1, 140.9, 133.1, 130.4, 126.7, 125.6, 125.4, 125.1, 123.4, 108.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_9O_2^+$ 173.0597, found 173.0607.



4-hydroxy-3-methoxy-1-naphthaldehyde (1b): 3-Chloroperbenzoic acid (3.5 g, 20.0 mmol) was added to a solution of 2-methoxynaphthaldeyde (1.9 g, 10.0 mmol) and ethyl acetate (20.0 mL) at 0 °C. The reaction mixture was stirred at room temperature for 40 h. Then ethyl acetate was evaporated in vacuo. The residue was diluted with dichloromethane, filtrated and washed sequentially with saturated sodium bicarbonate solution and water. The organic phase was dried and concentrated to give crude product **Int-I** as violet oil.

$LiAlH_4$ (0.4 g, 10.0 mmol) was added in anhydrous THF (20.0 mL) under nitrogen and a solution of crude product **Int-I** in THF was added dropwise. After 4 h, the reaction was quenched by pouring into cold HCl (10 wt%, aq) solution (10.0 mL) and the mixture

was extracted with dichloromethane (20.0 mL). The organic phase was separated, washed with water, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to afford **Int-II** (0.8 g, 43% yield) as a green solid.[4]

Titanium tetrachloride (4.4 mL, 4.0 mmol) was added dropwise to a stirred solution of **Int-II** (3.5 g, 20.0 mmol) in CH_2Cl_2 (25.0 mL) at 0 °C. Dichloro(methoxy)methane (2.8 mL, 31.0 mmol) was then added dropwise to the resulting dark solution over 5 minutes at 0 °C. The solution was keeping stirring for additional 10 minutes, then ice water (5.6 mL) was added. The heterogeneous mixture was stirred vigorously at 0 °C until all titanium salts dissolved. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50.0 mL). The combined organic extracts were washed with brine (50.0 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5 to 50:50, v/v) to afford 4-hydroxy-3-methoxy-1-naphthaldehyde **1b** (3.5 g, 86% yield) as a gray solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 10.37 (s, 1H, –OH), 9.09-3.07 (m, 1H), 8.26-8.23 (m, 1H), 7.79 (s, 1H), 7.61-7.53 (m, 2H), 6.73 (s, 1H), 4.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 190.9, 146.5, 140.8, 128.6, 127.9, 126.5, 123.9, 123.9, 123.8, 121.9, 121.1, 57.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}O_3^+$ 203.0703, found 203.0712.

III. Optimization of the cascade C−H oxidative annulation of 4-hydroxy-1-naphthaldehyde 1a with alkyne 2a

A schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol%), oxidative, additive, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.2 mg, 0.4 mmol), and solvent (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 150 °C for 24 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was performed by column chromatography on silica gel to provide the desired product **3a** or **4a**.

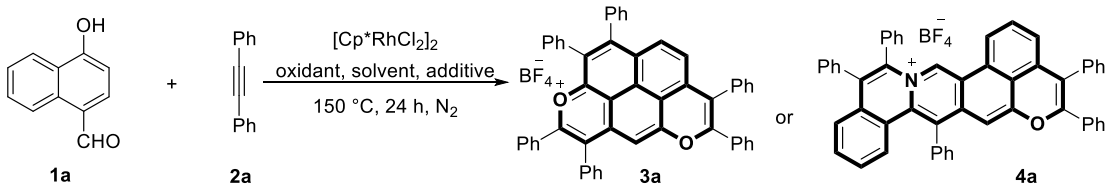


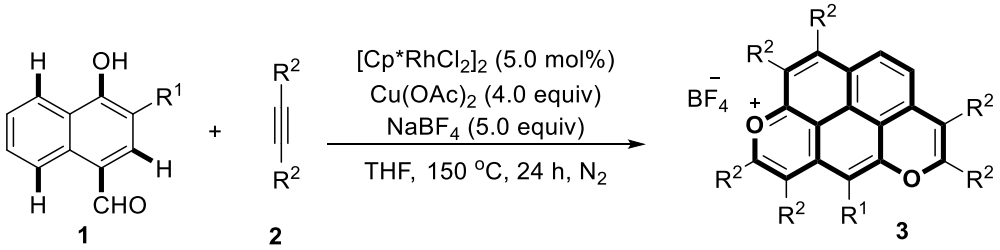
Table S1. Optimization for the synthesis of oxonium- and azanium-doped PHAs **3a** and **4a**[a)]

Entry	Oxidant	Additive	Solvent	Yield of **3a** (%)[b)]	Yield of **4a** (%)[b)]
1	Ag_2CO_3	$NaBF_4$	THF	trace	-
2	AgOAc	$NaBF_4$	THF	52	-
3	Ag_2O	$NaBF_4$	THF	trace	-
4	CuO	$NaBF_4$	THF	38	-
5	$Cu(NO_3)_2$	$NaBF_4$	THF	34	-
6	$Cu(acac)_2$	$NaBF_4$	THF	trace	-
7	$Cu(OAc)_2$	$NaBF_4$	THF	65	-
8	$Cu(OAc)_2$	$NaBF_4$	1,4-dioxane	34	-
9	$Cu(OAc)_2$	$NaBF_4$	DCE	n.d.	-
10	$Cu(OAc)_2$	$NaBF_4$	toluene	n.d.	-
11	$Cu(OAc)_2$	$NaBF_4$	*t*-AmylOH	52	-
12	$Cu(OAc)_2$	$NaBF_4$	HFIP	trace	-
13	$Cu(OAc)_2$	$NaBF_4$	TFE	trace	-
14	$Cu(OAc)_2$	-	THF	n.d.	-
15[c)]	$Cu(OAc)_2$	$NaBF_4$	THF	49	-
16	$Cu(OAc)_2$	NH_4BF_4	THF	-	87
17[d)]	$Cu(OAc)_2$	NH_4BF_4	THF	-	85

a) Reaction conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol%), oxidant (4.0 equiv), additive (5.0 equiv) and solvent (1.0 mL) at 150 ºC for 24 h under N_2. b) Isolated yields. c) The reaction was carried out at 120 °C. d) The reaction was carried out with 3.0 equiv of NH_4BF_4. DCE = 1,2-dichloroethane; *t*-AmylOH = *tert*-amyl alcohol; THF = tetrahydrofuran; TFE = 2,2,2-trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; n.d. = not detected.

IV. General procedure for the cascade C−H oxidative annulation of naphthol-type aldehydes 1 with alkynes 2

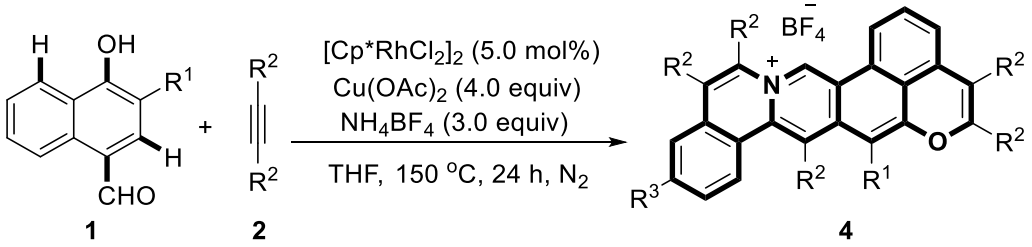
(1) General procedure for the synthesis of polycyclic pyrylium cations 3 (A)



A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol%), $Cu(OAc)_2$ (79.6 mg, 0.4 mmol), $NaBF_4$ (55.5 mg, 0.5 mmol), naphthol-type aldehyde **1** (0.1 mmol), alkyne **2** (0.4 mmol), and THF (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 150 °C for 24 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was

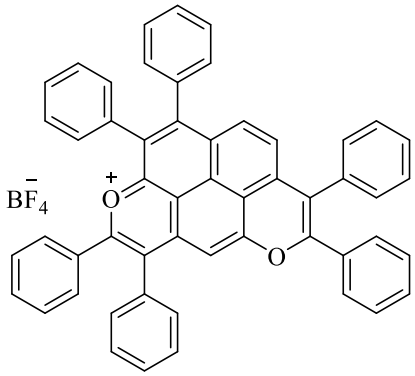
evaporated under reduced pressure and the residue was performed by column chromatography on silica gel to provide the desired product **3**.

(2) General procedure for the synthesis of polycyclic pyridinium cations 4 (B)



A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol%), $Cu(OAc)_2$ (79.6 mg, 0.4 mmol), NH_4BF_4 (31.5 mg, 0.3 mmol), naphthol-type aldehyde **1** (0.1 mmol), alkyne **2** (0.4 mmol), and THF (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 150 °C for 24 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was performed by column chromatography on silica gel to provide the desired product **4**.

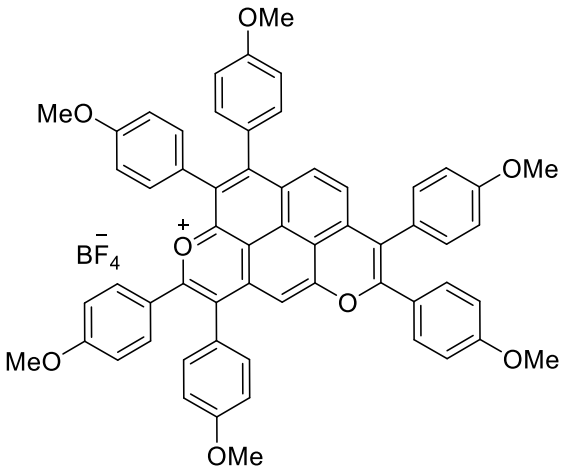
V. Experimental data of the described substances



1,2,4,5,8,9-hexaphenylpyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3a)

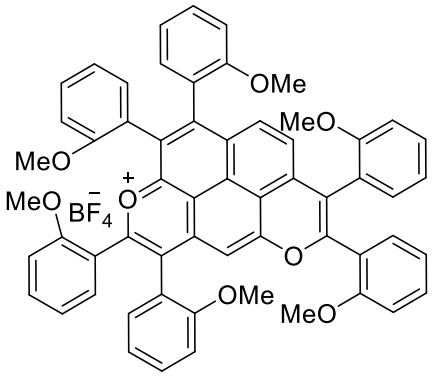
Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3a** as an orange solid (51.3 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.64 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.70 (s, 1H), 7.61-7.54 (m,

7H), 7.50-7.45 (m, 7H), 7.39-7.29 (m, 14H), 7.20-7.17 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 163.1, 158.1, 157.6, 155.4, 150.8, 146.5, 140.1, 139.2, 135.5, 133.1, 132.6, 132.3, 131.64, 131.60, 131.5, 131.3, 131.2, 131.0, 130.93, 130.85, 130.8, 130.3, 130.2, 130.1, 129.8, 129.7, 129.4, 128.8, 128.6, 128.53, 128.50, 128.3, 126.4, 123.2, 122.8, 122.6, 120.7, 117.5, 114.3, 106.4. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{53}H_{33}O_2^+$ 701.2475, found 701.2465.



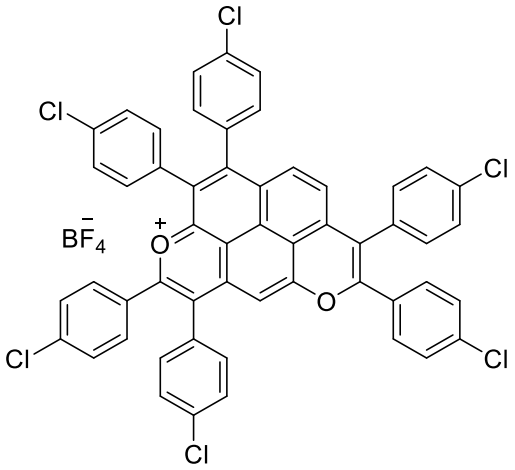
8,9-bis(3-methoxyphenyl)-1,2,4,5-tetrakis(4-methoxyphenyl)pyrano[2',3',4':4,5] naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3b)

Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (95.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3b** as a red solid (80.4 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.62 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.60 (s, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.34-7.30 (m, 4H), 7.27 (s, 1H), 7.25-7.21 (m, 3H), 7.16 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.94-6.90 (m, 4H), 6.84 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.84 (s, 6H), 3.82 (s, 3H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 162.5, 161.8, 161.6, 160.4, 160.2, 159.7, 159.4, 158.0, 157.4, 155.2, 150.3, 146.6, 140.3, 138.8, 132.7, 132.3, 132.0, 131.97, 131.89, 131.85, 131.0, 127.8, 126.4, 125.4, 124.8, 124.5, 123.9, 123.8, 122.8, 121.1, 120.9, 120.7, 117.0, 115.8, 115.4, 114.2, 114.1, 114.00, 113.96, 113.8, 105.6, 55.63, 55.59, 55.57, 55.50, 55.45. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{59}H_{45}O_8^+$ 881.3109, found 881.3101.



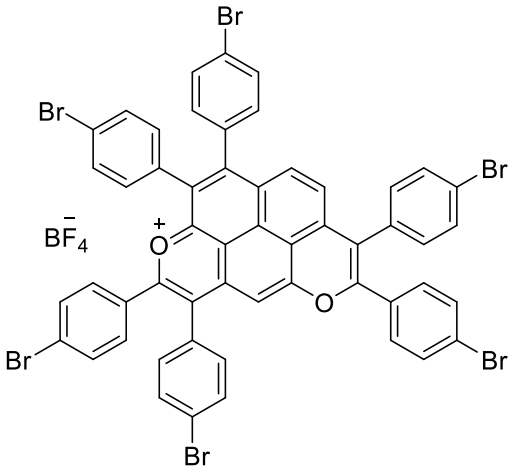
1,2,4,5,8,9-hexakis(2-methoxyphenyl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3c)

Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(2-methoxyphenyl)ethyne **2c** (95.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3c** as an orange solid (41.7 mg, 43% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.68-8.57 (m, 1H), 7.90-7.85 (m, 1H), 7.51-6.87 (m, 25H), 3.80-3.47 (m, 18H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 161.4, 160.6, 160.5, 160.2, 159.77, 159.75, 159.50, 159.47, 159.1, 150.4, 141.5, 138.4, 138.0, 135.6, 134.1, 133.8, 132.7, 132.6, 132.5, 132.31, 132.30, 132.2, 132.02, 131.95, 131.92, 131.87, 131.86, 131.6, 131.5, 130.6, 130.2, 129.7, 127.2, 126.1, 125.1, 124.0, 123.0, 121.8, 120.2, 119.5, 119.1, 116.7, 116.6, 116.2, 115.5, 115.0, 114.1, 113.5, 109.7, 101.3, 55.7, 55.64, 55.60, 55.43, 55.40, 55.3. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{59}H_{45}O_8^+$ 881.3109, found 881.3107.



1,2,4,5,8,9-hexakis(4-chlorophenyl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3d)

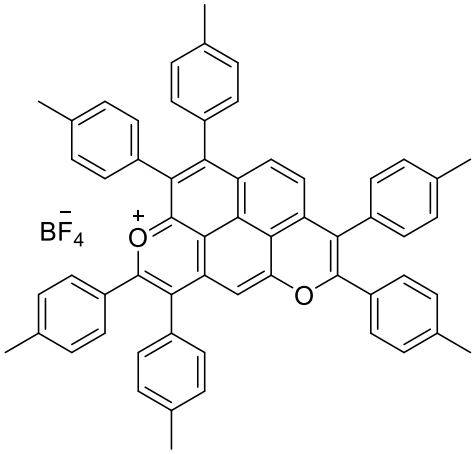
Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-chlorophenyl)ethyne **2d** (98.8 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3d** as an orange solid (47.8 mg, 48% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.61 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.66 (s, 1H), 7.59-7.53 (m, 4H), 7.46-7.41 (m, 4H), 7.34-7.27 (m, 6H), 7.22 (t, J = 8.4 Hz, 2H), 7.11-7.02 (m, 6H), 6.93 (t, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 163.0, 157.7, 156.5, 155.7, 149.4, 146.5, 139.6, 138.8, 137.8, 137.6, 136.0, 135.9, 135.3, 134.9, 133.8, 132.5, 132.43, 132.37, 132.2, 131.5, 131.43, 131.38, 130.9, 130.7, 130.63, 130.58, 130.40, 130.36, 129.8, 129.2, 129.1, 129.0, 128.8, 126.4, 122.9, 122.1, 121.7, 120.9, 117.6, 114.7, 106.5. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{53}H_{27}{}^{35}Cl_6O_2^+$ 905.0137, found 905.0135; calcd for $C_{53}H_{27}{}^{35}Cl_5{}^{37}ClO_2^+$ 907.0107, found 907.0105.



1,2,4,5,8,9-hexakis(4-bromophenyl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3e)

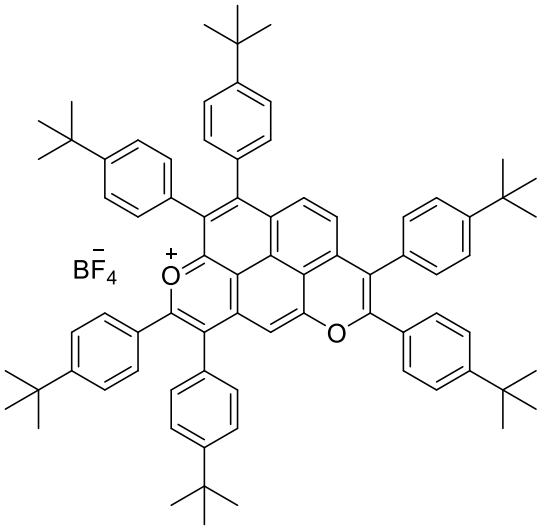
Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-bromophenyl)ethyne **2e** (134.4 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3e** as an orange solid (65.6 mg, 52% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.58 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.73-7.70 (m, 2H), 7.68-7.64 (m, 2H), 7.56-7.44 (m, 8H), 7.42-7.38 (m, 4H), 7.36-7.29 (m, 5H), 7.23-7.16 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 163.0, 157.7, 156.5, 155.6, 149.3, 146.4, 139.5, 138.8, 134.2, 133.5, 133.3, 132.8, 132.7, 132.6, 132.5, 132.2, 132.1, 131.9, 131.8, 131.7, 131.60, 131.56, 131.4, 131.3, 131.1, 130.6, 130.5, 130.3, 126.4, 126.1, 124.2, 124.1, 123.6, 123.2, 123.0, 122.1, 121.8, 120.9, 117.6, 114.6, 106.5. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{53}H_{27}{}^{79}Br_3{}^{81}Br_3O_2^+$ 1174.7044, found 1174.7050.



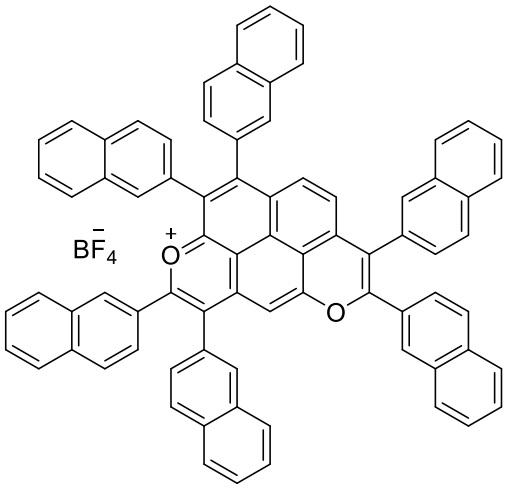
1,2,4,5,8,9-hexa-*p*-tolylpyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3f)

Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-di-*p*-tolylethyne **2f** (82.5 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3f** as an orange solid (52.4 mg, 60% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.64 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 8.8 Hz, 1H), 7.60 (s, 1H), 7.49-7.34 (m, 13H), 7.27 (s, 3H), 7.23 (d, J = 8.0 Hz, 4H), 7.20 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 159.9, 150.6, 142.4, 141.4, 140.5, 139.8, 139.6, 138.2, 138.0, 137.9, 137.6, 134.6, 134.3, 133.5, 133.1, 133.0, 132.7, 132.3, 132.0, 131.5, 131.2, 130.9, 130.8, 130.6, 130.4, 130.22, 130.19, 129.87, 129.85, 129.4, 129.2, 129.0, 128.8, 127.2, 123.23, 123.16, 122.0, 120.5, 119.8, 117.7, 101.6, 21.79, 21.78, 21.76, 21.51, 21.48. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{59}H_{45}O_2^+$ 785.3414, found 785.3409.



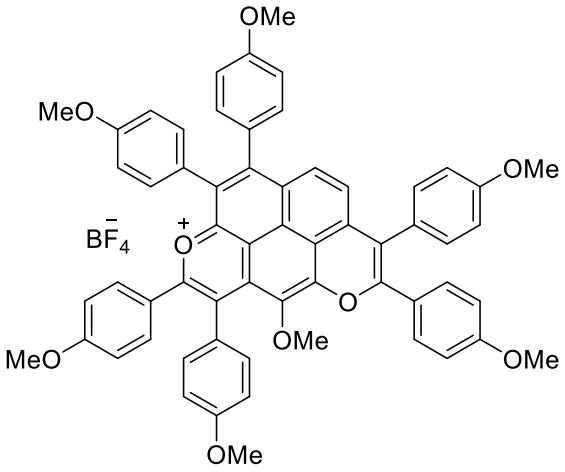
1,2,4,5,8,9-hexakis(4-(tert-butyl)phenyl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3g)

Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-(tert-butyl)phenyl)ethyne **2g** (116.2 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3g** as an orange solid (61.9 mg, 55% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.72 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.68-7.64 (m, 4H), 7.54 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.44-7.41 (m, 4H), 7.38-7.34 (m, 7H), 7.30 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.14 (s, 2H), 1.46 (s, 9H), 1.38 (s, 9H), 1.35 (s, 9H), 1.32 (s, 9H), 1.29 (s, 9H), 1.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 162.8, 157.7, 157.4, 155.2, 155.1, 154.8, 153.1, 152.7, 151.9, 151.5, 150.9, 146.6, 140.2, 139.2, 132.4, 131.6, 131.1, 131.0, 130.5, 130.3, 130.15, 130.07, 129.8, 129.5, 129.2, 128.7, 128.5, 127.4, 126.8, 126.3, 125.7, 125.5, 125.4, 125.1, 123.2, 122.2, 121.8, 120.5, 117.2, 113.9, 106.0, 35.13, 35.10, 35.02, 35.00, 34.9, 34.8, 31.5, 31.4, 31.4, 31.3, 31.1, 31.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{77}H_{81}O_2^+$ 1037.6231, found 1037.6234.



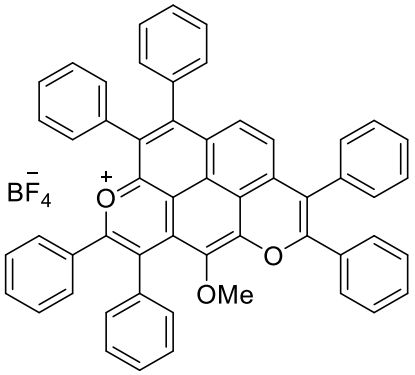
1,2,4,5,8,9-hexa(naphthalen-2-yl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3h)

Following the general procedure **A**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-di(naphthalen-2-yl)ethyne **2h** (111.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3h** as a red solid (45.7 mg, 42% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.90 (s, 1H), 8.31-8.29 (m, 1H), 8.26-8.21 (m, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.03-8.00 (m, 2H), 7.96-7.94 (m, 1H), 7.91-7.69 (m, 14H), 7.65-7.57 (m, 5H), 7.23-7.34 (m, 14H), 7.29 (d, J = 7.6 Hz, 1H), 7.19 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.02 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 160.4, 150.8, 142.2, 138.6, 136.7, 133.8, 133.5, 133.43, 133.40, 133.3, 133.29, 133.25, 132.91, 132.87, 132.8, 132.71, 132.67, 132.6, 132.5, 131.8, 131.7, 131.4, 131.2, 130.8, 130.70, 130.66, 130.2, 129.8, 129.5, 129.4, 129.23, 129.20, 129.0, 128.9, 128.80, 128.77, 128.7, 128.5, 128.4, 128.3, 128.2, 128.13, 128.10, 128.07, 128.0, 127.9, 127.84, 127.80, 127.78, 127.7, 127.62, 127.58, 127.5, 127.4, 127.3, 127.13, 127.10, 126.92, 126.88, 126.8, 126.72, 126.68, 126.6, 126.5, 126.0, 125.8, 123.3, 123.1, 122.5, 122.1, 120.8, 119.9, 118.6, 117.7, 106.7, 102.5. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{77}H_{45}O_2^+$ 1001.3414, found 1001.3417.



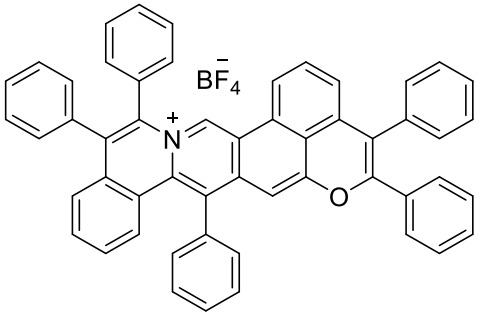
6-methoxy-1,2,4,5,8,9-hexakis(4-methoxyphenyl)pyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3i)

Following the general procedure **A**, 4-hydroxy-3-methoxy-1-naphthaldehyde **1b** (20.2 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (95.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3i** as a red solid (54.9 mg, 55% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.61-8.57 (m, 1H), 7.88-7.84 (m, 1H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.12-7.14 (m, 4H), 7.07-7.04 (m, 2H), 7.01-6.98 (m, 2H), 6.90-6.87 (m, 4H), 6.84-6.81 (m, 2H), 6.69-6.65 (m, 2H), 3.90-376 (m, 18H), 3.52-3.50 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 161.4, 161.1, 160.0, 159.5, 159.1, 158.6, 156.9, 156.5, 155.1, 149.6, 140.0, 138.9, 138.3, 137.6, 132.6, 132.4, 132.2, 132.04, 131.96, 131.6, 130.8, 127.9, 127.2, 126.0, 125.6, 124.6, 124.4, 124.1, 122.3, 121.1, 119.4, 118.0, 117.4, 115.2, 114.2, 114.1, 113.8, 113.7, 113.64, 113.61, 113.58, 61.9, 55.44, 55.41, 55.39, 55.36, 55.33, 55.29. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{60}H_{47}O_9^+$ 911.3215, found 911.3205.



6-methoxy-1,2,4,5,8,9-hexaphenylpyrano[2',3',4':4,5]naphtho[2,1,8-*def*]chromen-3-ium tetrafluoroborate (3j)

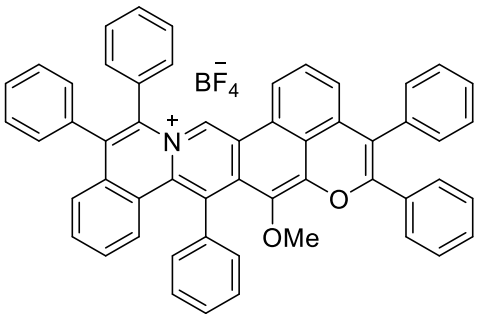
Following the general procedure **A**, 4-hydroxy-3-methoxy-1-naphthaldehyde **1b** (20.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3j** as an orange solid (43.4 mg, 53% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.62 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.60-7.57 (m, 4H), 7.51-7.49 (m, 4H), 7.44-7.41 (m, 6H), 7.37-7.31 (m, 10H), 7.24-7.22 (m, 3H), 7.16-7.12(m, 3H), 3.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 158.5, 157.2, 157.0, 155.3, 149.8, 139.8, 139.3, 138.5, 137.4, 135.6, 135.0, 133.3, 132.5, 132.0, 131.8, 131.3, 131.2, 130.84, 130.82, 130.6, 130.3, 130.2, 130.0, 129.6, 129.1, 128.5, 128.4, 128.22, 128.19, 128.05, 127.97, 128.0, 126.0, 123.6, 122.7, 122.6, 121.0, 118.5, 117.4, 114.5, 62.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{54}H_{35}O_3^+$ 731.2581, found 731.2577.



4,5,8,13,14-pentaphenylisochromeno[1,8-*gh*]isoquinolino[2,1-*b*]isoquinolin-15-ium tetrafluoroborate (4a)

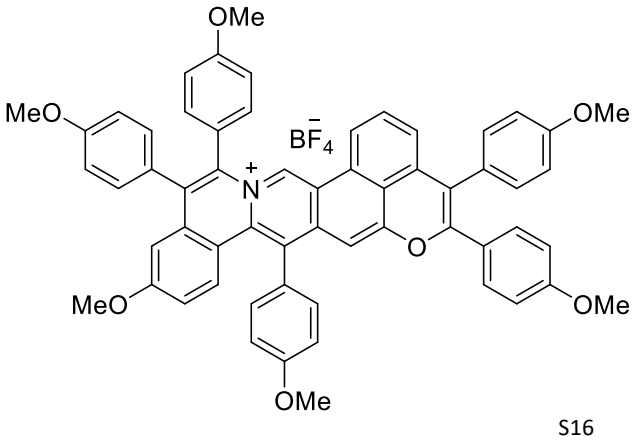
Following the general procedure **B**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **4a** as an orange solid (67.0 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.83 (s, 1H), 7.73-7.59 (m, 10H), 7.55-7.48 (m, 5H), 7.42-7.38 (m, 4H), 7.30-7.28 (m, 5H), 7.27 (s, 1H), 7.25-7.22 (m, 4H), 7.20-7.18 (m, 2H), 7.13 (d, J = 7.6 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 159.8, 150.4, 141.3, 137.7, 137.4, 137.3, 134.8, 134.1, 133.6, 133.5, 133.2, 133.0, 132.7, 132.4, 132.2, 131.8, 131.4, 131.2, 130.7, 130.63, 130.56, 130.33, 130.29, 130.2, 130.1, 129.9, 129.6, 129.4, 129.3,

129.0, 128.4, 128.11, 127.98, 128.0, 127.3, 125.4, 123.1, 122.0, 120.6, 120.0, 118.1, 101.7. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{53}H_{34}NO^+$ 700.2635, found 700.2641.



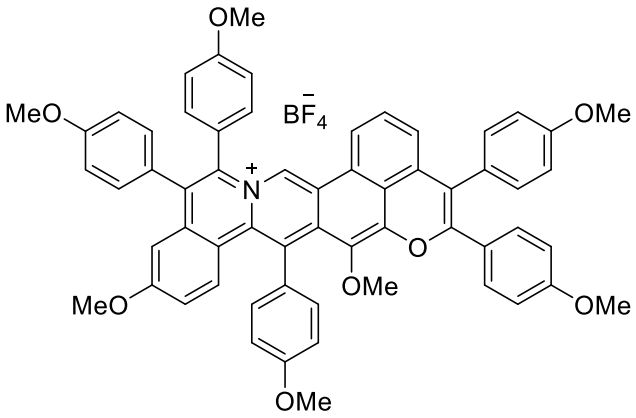
7-methoxy-4,5,8,13,14-pentaphenylisochromeno[1,8-*gh*]isoquinolino[2,1-*b*]isoquinolin-15-ium tetrafluoroborate (4b)

Following the general procedure **B**, 4-hydroxy-3-methoxy-1-naphthaldehyde **1b** (20.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **4b** as an orange solid (45.0 mg, 55% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.73 (s, 1H), 7.76-7.74 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 6.8 Hz, 2H), 7.58-7.57 (m, 3H), 7.54-7.52 (m, 1H), 7.50-7.49 (m, 1H), 7.47-7.45 (m, 2H), 7.44-7.41 (m, 5H), 7.40-7.39 (m, 1H), 7.31-7.29 (m, 5H), 7.28-7.27 (m, 2H), 7.25-7.23 (m, 2H), 7.204-7.201 (m, 1H), 7.189-7.185 (m, 1H), 7.14-7.10 (m, 2H), 7.07 (d, J = 7.6 Hz, 1H), 6.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 152.6, 150.1, 139.1, 138.4, 137.0, 135.4, 134.9, 134.8, 134.0, 133.8, 133.2, 132.9, 132.5, 132.4, 131.7, 131.5, 131.00, 130.98, 130.9, 130.7, 130.42, 130.40, 130.2, 129.8, 129.5, 129.3, 128.92, 128.87, 128.70, 128.66, 128.4, 128.3, 128.03, 127.99, 127.36, 127.35, 126.8, 125.6, 123.1, 122.8, 120.5, 120.0, 118.1, 61.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{54}H_{36}NO_2^+$ 730.2741, found 730.2736.



11-methoxy-4,5,8,13,14-pentakis(4-methoxyphenyl)isochromeno[1,8-*gh*]isoquinolino[2,1-*b*]isoquinolin-15-ium tetrafluoroborate (4c)

Following the general procedure **B**, 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (95.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **4c** as a red solid (89.0 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.78 (s, 1H), 7.70-7.61 (m, 4H), 7.51-7.45 (m, 4H), 7.23(bs, 1H), 7.18-7.14 (m, 5H), 7.05 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.4 Hz, 3H), 6.86-6.81 (m, 6H), 6.74 (d, J = 8.4 Hz, 2H), 4.00 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 161.4, 160.6, 160.54, 160.48, 160.2, 159.8, 159.5, 159.2, 159.1, 135.7, 134.1, 134.0, 133.78, 133.75, 133.7, 132.8, 132.7, 132.23, 132.21, 132.1, 132.0, 131.9, 131.60, 131.58, 131.5, 130.6, 127.3, 124.1, 122.9, 120.3, 119.5, 119.1, 116.7, 116.2, 115.5, 115.0, 114.1, 113.6, 109.7, 101.3, 55.72, 55.65, 55.6, 55.5, 55.42, 55.37. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{59}H_{46}NO_7^+$ 880.3269, found 880.3260.



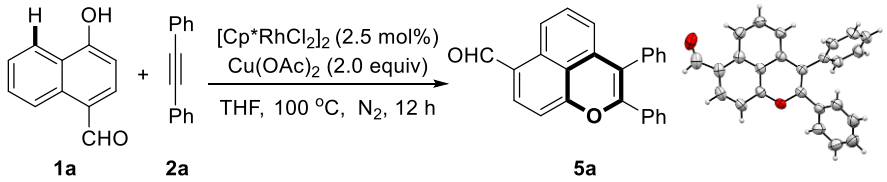
7,10-dimethoxy-4,5,8,13,14-pentakis(4-methoxyphenyl)isochromeno[1,8-*gh*]isoquinolino[2,1-*b*]isoquinolin-15-ium tetrafluoroborate (4d)

Following the general procedure **B**, 4-hydroxy-3-methoxy-1-naphthaldehyde **1b** (20.2 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (95.3 mg, 0.4 mmol) were used. The mixture was heated at 150 ℃ for 24 h. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **4d** as a red solid (59.9 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.67 (s, 1H), 7.65-7.59 (m, 3H), 7.52 (t, J = 8.0 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 9.2 Hz, 1H), 7.28-7.27 (m, 1H), 7.20-7.16 (m, 4H), 7.11-7.10 (m, 2H),

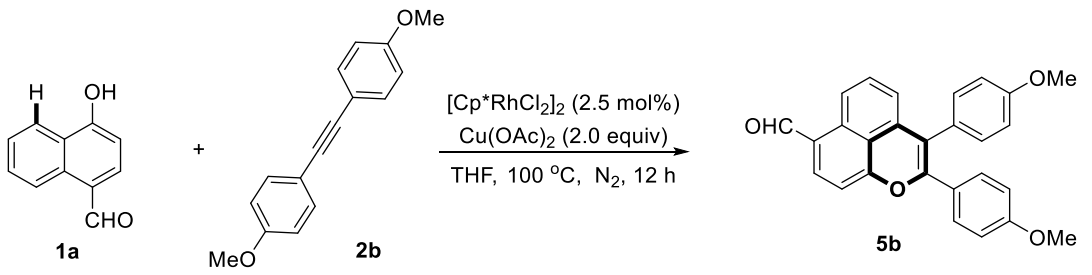
7.07 (d, *J* = 7.6 Hz, 1H), 7.02-6.97 (m, 5H), 6.85-6.83 (m, 2H), 6.80 (d, *J* = 2.8 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.73-6.72 (m, 1H), 6.713-6.708 (m, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 3.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 161.0, 160.4, 160.0, 159.9, 159.8, 159.4, 159.0, 152.2, 149.9, 139.2, 137.6, 135.8, 135.1, 134.9, 133.8, 133.0, 132.8, 132.4, 132.3, 132.2, 131.9, 131.5, 130.9, 130.7, 130.3, 127.3, 127.1, 126.1, 125.1, 123.9, 122.6, 122.4, 120.1, 119.4, 119.3, 116.3, 116.0, 115.3, 114.9, 114.3, 113.8, 113.4, 108.9, 60.8, 55.5, 55.4, 55.31, 55.28, 55.24, 55.20. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{60}H_{48}NO_8^+$ 910.3374, found 910.3365.

VI. Mechanistic study

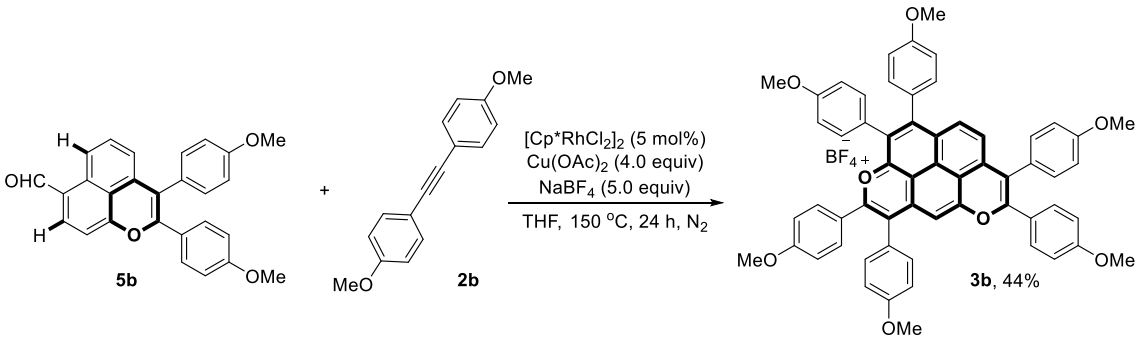
(1) Control experiments



A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), $Cu(OAc)_2$ (39.8 mg, 0.2 mmol), 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (35.7 mg, 0.2 mmol), and THF (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 100 °C for 12 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was performed by column chromatography on silica (petroleum ether/dichloromethane = 20:1, v/v) gel to provide the desired product **5a** as a green solid (32.1 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 10.14 (s, 1H), 9.07-8.98 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.44-7.36 (m, 3H), 7.33-7.30 (m, 2H), 7.28-7.27 (m, 1H), 7.26-7.25 (m, 1H), 7.24-7.19 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.77-6.75 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 191.6, 157.9, 149.0, 140.3, 134.6, 133.2, 132.7, 131.8, 131.2, 130.8, 129.2, 128.9, 128.8, 128.0, 127.8, 124.0, 122.4, 121.8, 118.5, 117.8, 106.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{17}O_2^+$ 349.1223, found 349.1215.



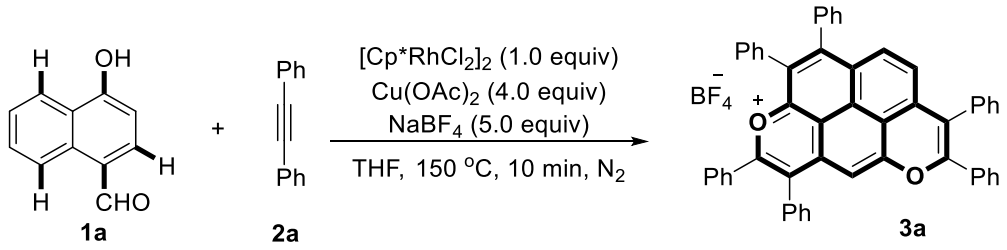
A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), $Cu(OAc)_2$ (39.8 mg, 0.2 mmol), 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (47.7 mg, 0.2 mmol), and THF (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 100 °C for 12 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was performed by column chromatography on silica (petroleum ether/dichloromethane = 20:1, v/v) gel to provide the mono-annulated product **5b** as a green solid (38.8 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 10.13 (s, 1H), 8.96 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.17 (m, 2H), 7.08-6.96 (m, 4H), 6.76 (s, 4H), 3.86 (s, 3H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 191.8, 159.8, 159.3, 158.2, 149.0, 140.4, 132.9, 132.6, 132.1, 131.4, 130.4, 127.1, 125.9, 124.0, 121.5, 117.6, 117.2, 114.9, 113.4, 107.0, 55.42, 55.38. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}O_4^+$ 409.1434, found 409.1433.



Then, a Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol%), $Cu(OAc)_2$ (79.6 mg, 0.4 mmol), the mono-annulated product **5b** (34.8 mg, 0.1 mmol), 1,2-bis(4-methoxyphenyl)ethyne **2b** (71.5 mg, 0.3 mmol), $NaBF_4$ (55.5 mg, 0.5 mmol) and THF (1.0 mL) under N_2. The resulting mixture was stirred at room temperature for 10 min and then at 150 °C for 24 h. Subsequently, it was diluted with 5.0 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was performed by column chromatography on silica gel (dichloromethane/ethyl

acetate = 1:1, v/v, then dichloromethane/methanol = 20:1, v/v) to provide the desired product **3b** as a red solid (42.3 mg, 44% yield), which was confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra and high resolution mass spectrometry (HRMS).

(2) Spectra of MAIDL-TOF-MS



A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol), $Cu(OAc)_2$ (79.6 mg, 0.4 mmol), $NaBF_4$ (55.5 mg, 0.5 mmol), 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) and THF (1.0 mL) under N_2. The resulting mixture was stirred at 150 °C for 10 min. The MALDI−TOF−MS analysis of the reaction mixture was then performed immediately (Figure S1-S3).

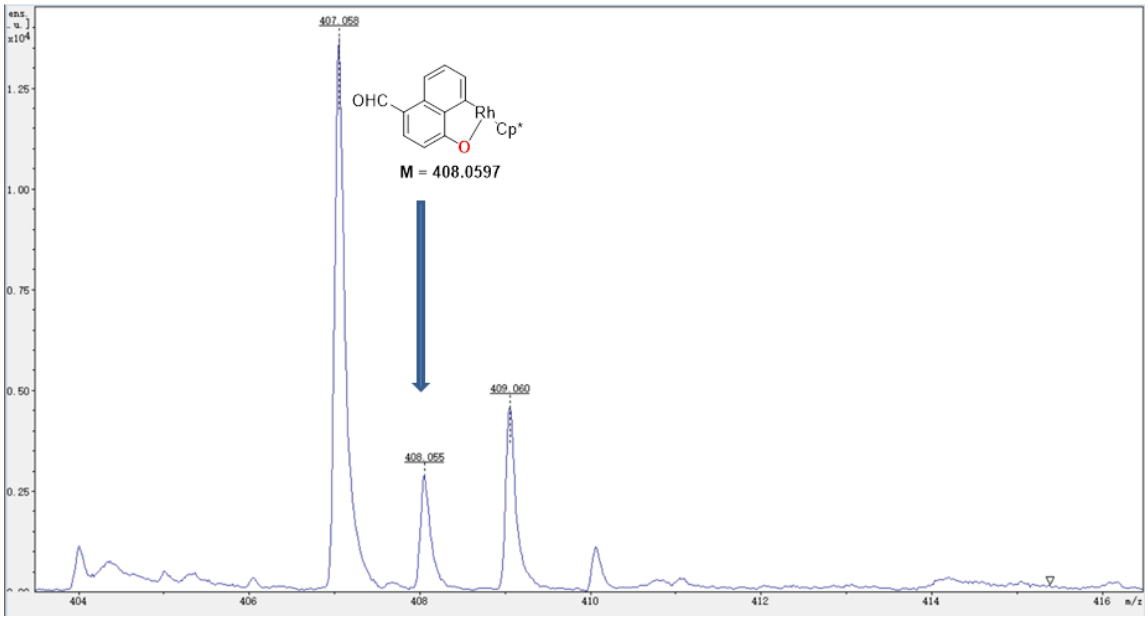


Figure S1. MAIDL-TOF-MS spectrum of the possible intermediate **A**.

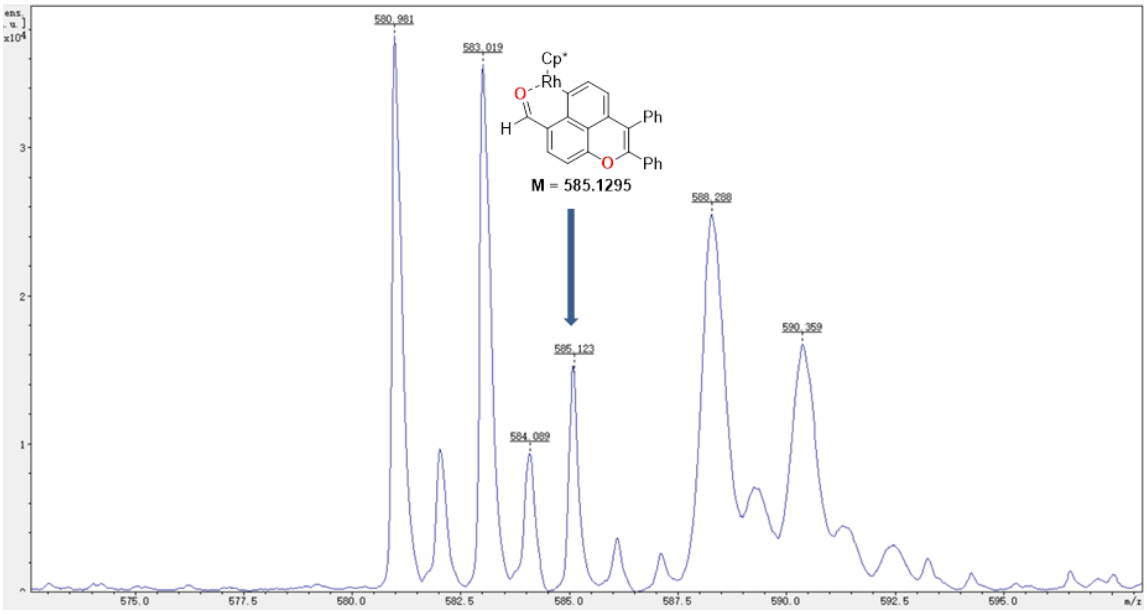


Figure S2. MAIDL-TOF-MS spectrum of the possible intermediate **C**.

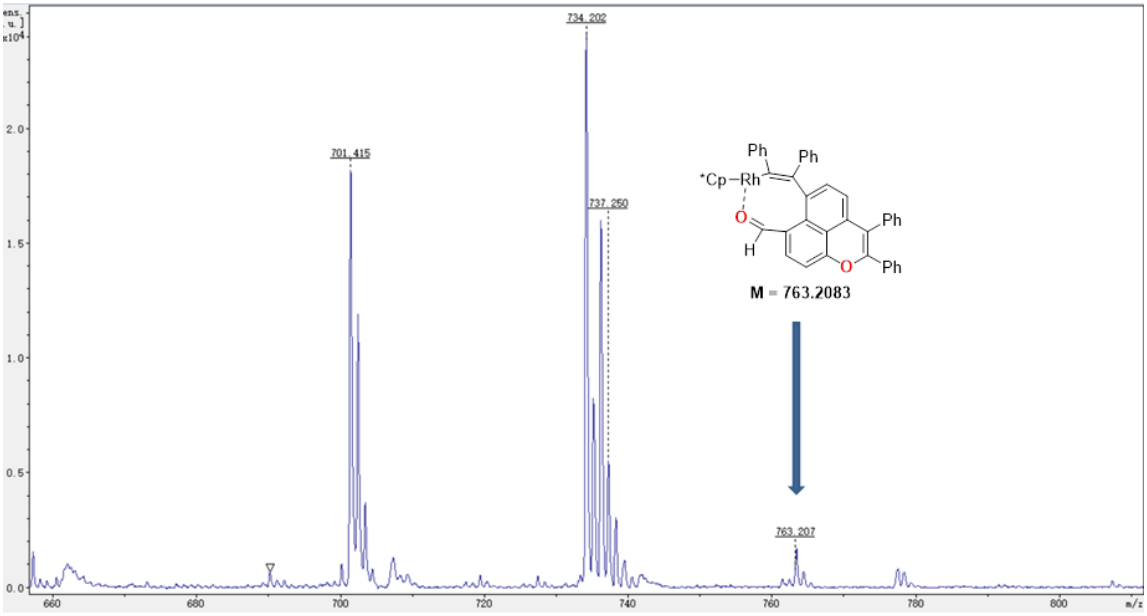
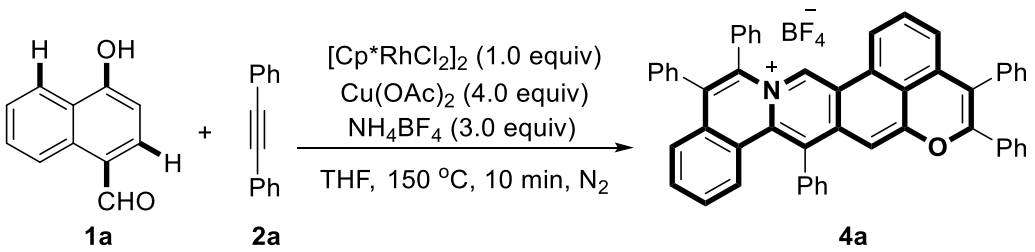


Figure S3. MAIDL-TOF-MS spectrum of the possible intermediate **D**.



A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol), $Cu(OAc)_2$ (79.6 mg, 0.4 mmol), NH_4BF_4 (31.5 mg, 0.3 mmol), 4-hydroxy-1-naphthaldehyde **1a** (17.2 mg, 0.1 mmol), diphenylacetylene **2a** (71.3 mg, 0.4 mmol) and THF (1.0 mL) under N_2. The resulting mixture was stirred at 150 °C for 10 min. The

MALDI−TOF−MS analysis of the reaction mixture was then performed immediately (Figure S4 and S5).

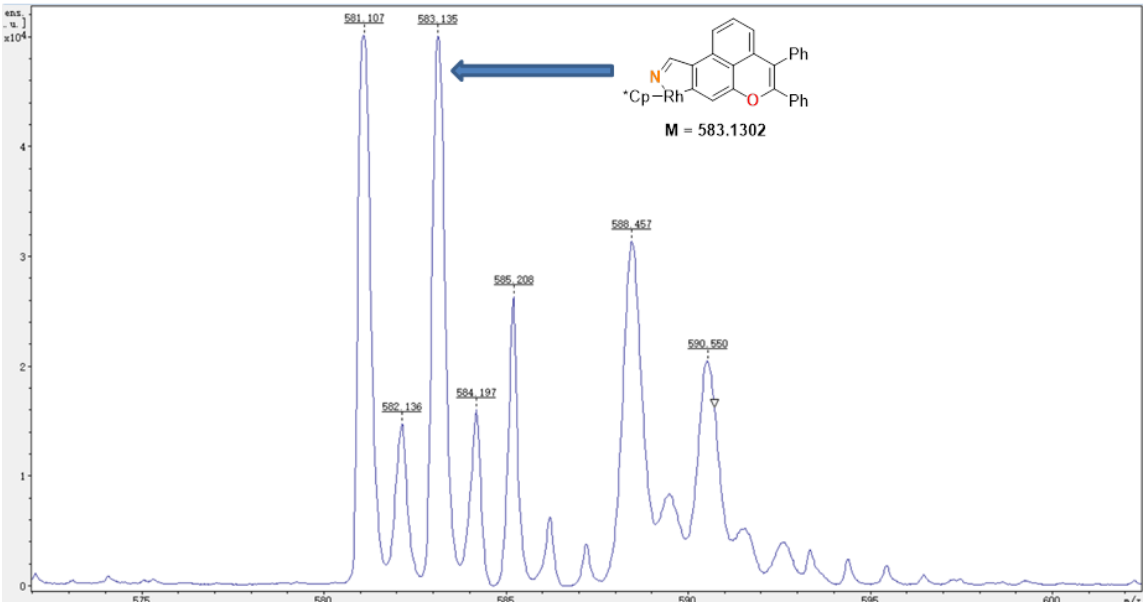


Figure S4. MAIDL-TOF-MS spectrum of the possible intermediate **I**.

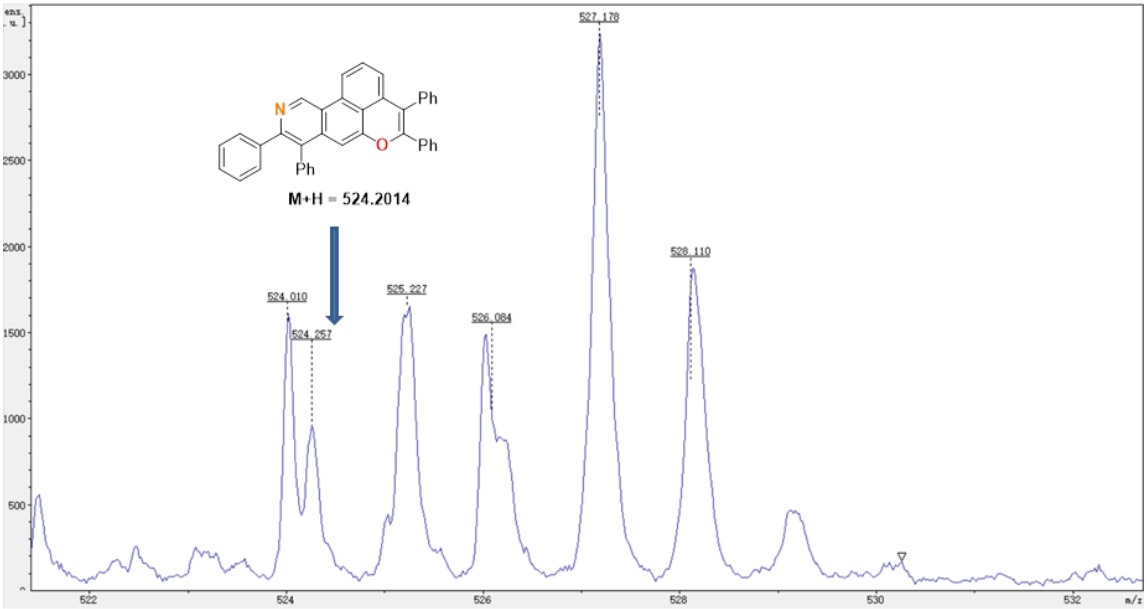


Figure S5. MAIDL-TOF-MS spectrum of the possible intermediate **K**.

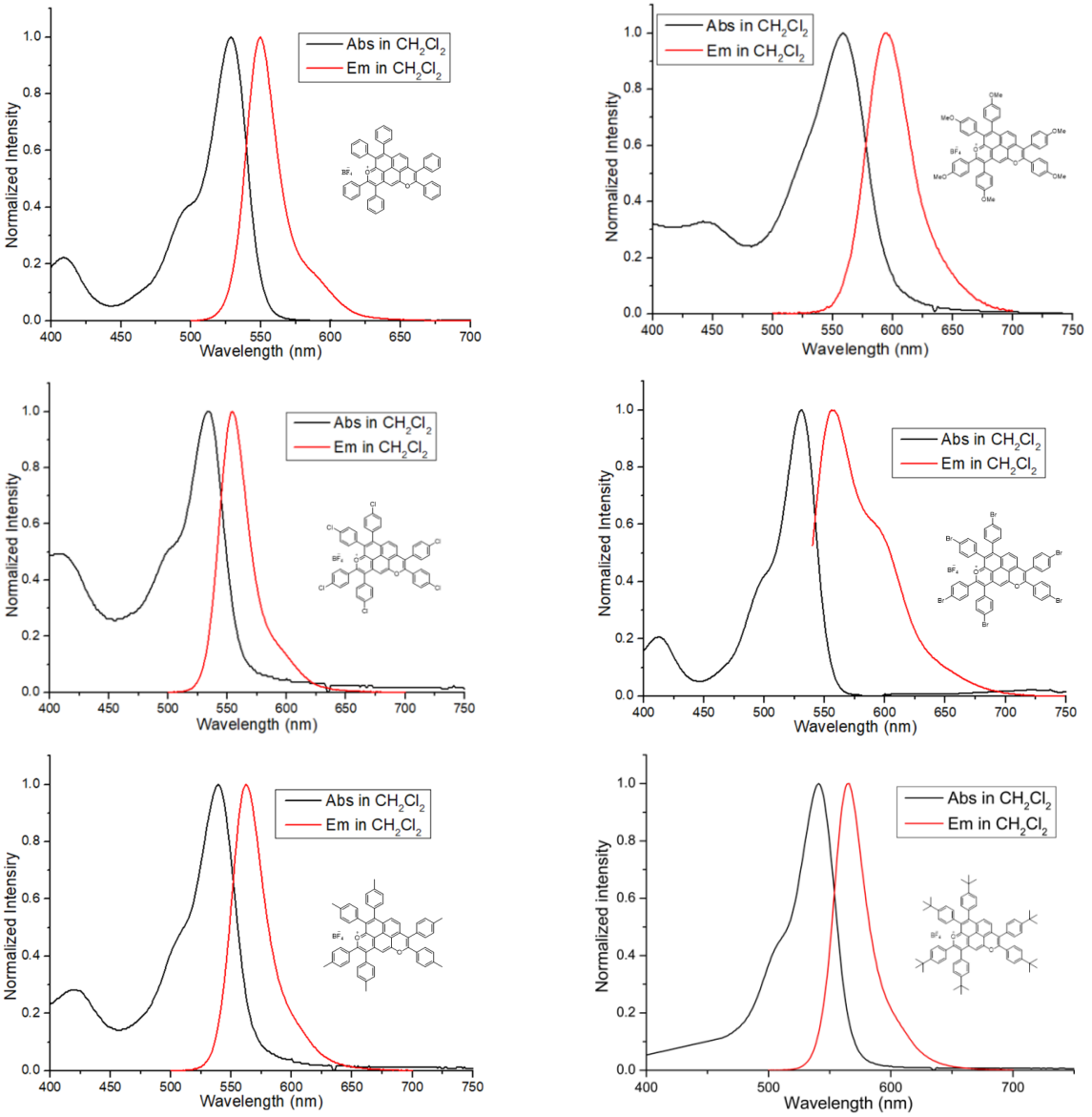
VII. Photophysical properties of Pyrylium-Fluors and Pyrydinium-Fluors

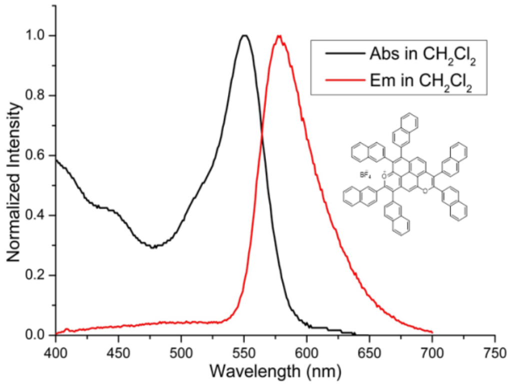
Table S2. Photophysical data of **Pyrylium-Fluor** and **Pyrydinium-Fluor** in CH_2Cl_2[a)]

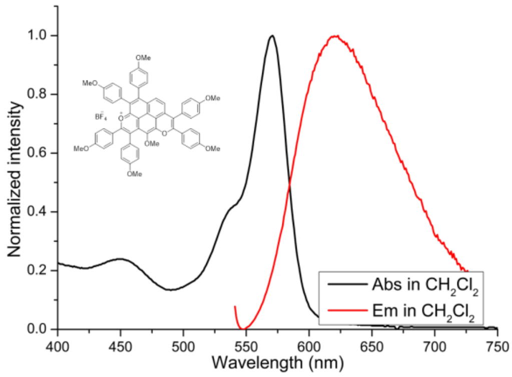
Compd	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)[b)]	Stokes Shift (cm^{-1})	Φ_F[c)]
3a	529	529	550	722	0.57
3b	559	560	595	1082	0.47
3d	533	535	554	711	0.35
3e	531	533	556	847	0.36

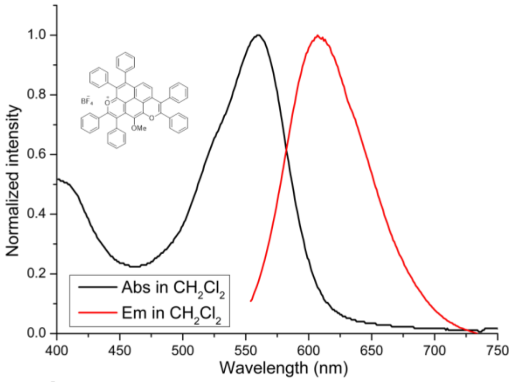
3f	539	538	562	759	0.43
3g	541	539	566	816	0.51
3h	550	551	579	911	0.55
3i	570	571	623	1492	0.42
3j	560	562	607	1383	0.45
4a	499	500	552	1924	0.69
4c	519	521	581	2056	0.60
5a	401	402	470	3661	0.44
5b	402	403	485	4257	0.36

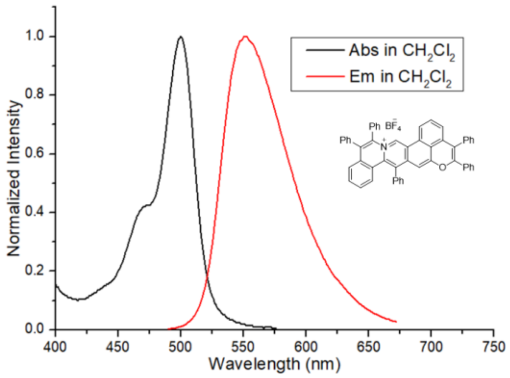
a) Photophysical properties at 10.0 μM; b) Emission maximum excited at the maximum excitation wavelength; c) Absolute quantum yield determined with an integrating sphere system.

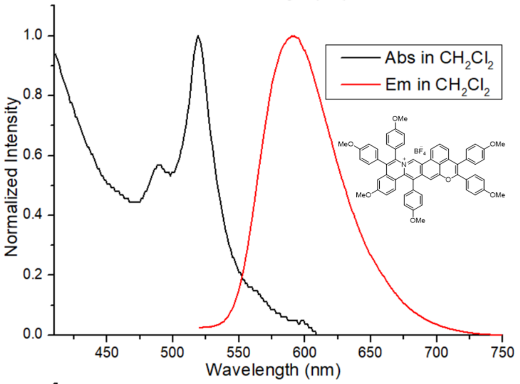


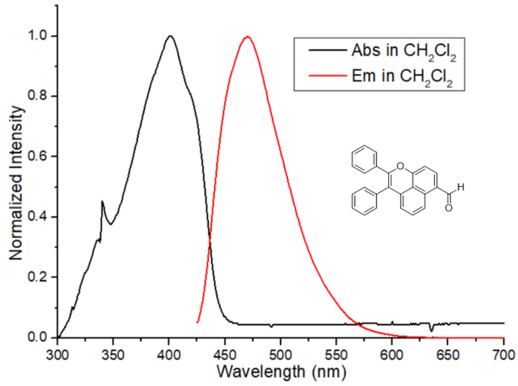


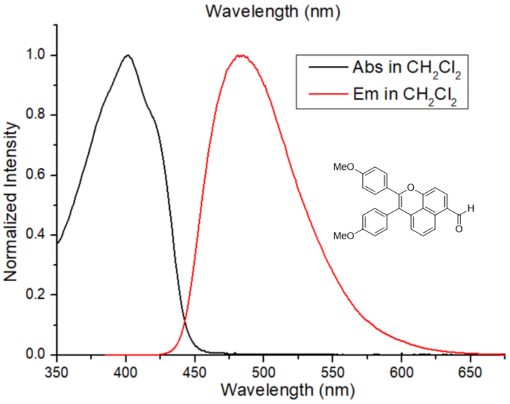




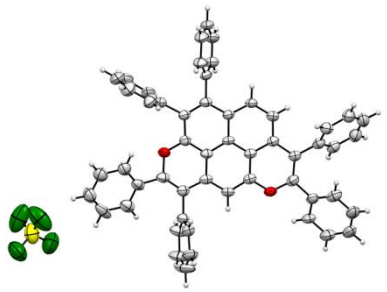








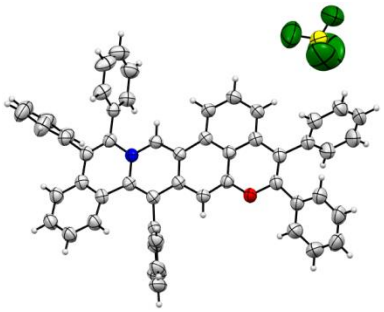
VIII. Single crystal X-ray structures of 3a, 4a and 5a



CCDC **2027223** (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data request/cif.

Table S3. Crystal Data and Structure Refinement for **3a**

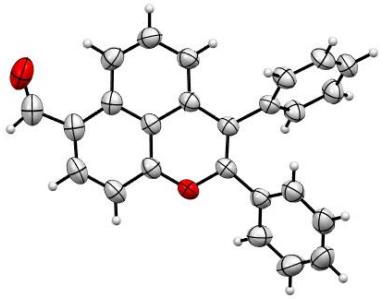
Identification code	**3a**
Empirical formula	$C_{55}H_{33}BF_4O_2$
Formula weight	788.25
Temperature/K	150
Crystal system	tetragonal
Space group	P42/n
a/Å	19.1081(4)
b/Å	19.1081(4)
c/Å	24.3996(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8908.8(4)
Z	8
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	1.223
F(000)	3612
Crystal size/mm^3	0.4 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.768 to 145.502
Index ranges	-15 ≤ h ≤ 23, -22 ≤ k ≤ 23, -23 ≤ l ≤ 30
Reflections collected	48729
Independent reflections	8649 [Rint = 0.0865, Rsigma = 0.0420]
Data/restraints/parameters	8649/0/533
Goodness-of-fit on F^2	2.046
Final R indexes [I>=2σ (I)]	R_1 = 0.1907, wR_2 = 0.4861
Final R indexes [all data]	R_1 = 0.2241, wR_2 = 0.5170
Largest diff. peak/hole / e Å^{-3}	3.47/-0.55



CCDC **2027222** (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data request/cif.

Table S4. Crystal Data and Structure Refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{53}H_{34}BF_4NO$
Formula weight	787.62
Temperature/K	296.4(7)
Crystal system	monoclinic
Space group	P21/n
a/Å	16.3530(5)
b/Å	13.2053(3)
c/Å	20.2472(7)
α/°	90
β/°	100.350(3)
γ/°	90
Volume/Å^3	4301.2(2)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.679
F(000)	1632
Crystal size/mm^3	0.3 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.664 to 145.284
Index ranges	$-15 \le h \le 20$, $-10 \le k \le 16$, $-24 \le l \le 21$
Reflections collected	24074
Independent reflections	8346 [Rint = 0.0342, Rsigma = 0.0287]
Data/restraints/parameters	8346/0/583
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0814, wR_2 = 0.2388
Final R indexes [all data]	R_1 = 0.0990, wR_2 = 0.2652
Largest diff. peak/hole / e Å^{-3}	0.83/-0.44



CCDC **2027219** (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data request/cif.

Table S5. Crystal Data and Structure Refinement for **5a**

Identification code	**5a**
Empirical formula	$C_{25}H_{16}O_2$
Formula weight	348.38
Temperature/K	296.75(18)
Crystal system	monoclinic
Space group	P21/c
a/Å	8.30435(19)
b/Å	23.1463(4)
c/Å	9.7550(2)
α/°	90
β/°	108.672(3)
γ/°	90
Volume/Å^3	1776.37(7)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.645
F(000)	728
Crystal size/mm^3	0.8 × 0.5 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.306 to 134.054
Index ranges	$-9 \le h \le 9$, $-27 \le k \le 23$, $-11 \le l \le 11$
Reflections collected	9541
Independent reflections	3168 [Rint = 0.0285, Rsigma = 0.0224]
Data/restraints/parameters	3168/0/244
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1407
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1484
Largest diff. peak/hole / e Å^{-3}	0.16/-0.24

IX. Cell imaging experiments, photostability and cytotoxicity assays

(1) Cell culture

HepG2 cells were incubated in Dublecco's Minimum Eagle's Medium (DMEM)

supplemented with 10% (v/v) fetal bovine serum (FBS), 100.0 units/mL of penicillin, and 100.0 mg/mL of streptomycin at 37 ºC in a humidified atmosphere containing 5% CO_2.

(2) Confocal imaging experiments of 3a or 4a

For subcellular localization experiments, HepG2 cells were incubated with 1.0 μM **3a** or **4a** in PBS (phosphate buffered solution) containing 1% DMSO for 15 min at 37 ºC. After incubation HepG2 cells were washed twice with PBS and 1.0 μM MitoTracker Red FM (**MTR**) was then added to incubate for 15 min. Finally, the cells were washed twice with PBS before imaging. The cells were observed with a Zeiss LSM 780 confocal laser scanning microscope.

(3) Confocal imaging experiments of 5a

For subcellular localization experiments, HepG2 cells were incubated with 1 μM **5a** in PBS (phosphate buffered solution) containing 1% DMSO for 15 min at 37 ºC. After incubation HepG2 cells were washed twice with PBS and 1.0 μM endoplasmic reticulum-tracker red (**ER-Tracker™ Red**) was then added to incubate for 15 min. Finally, the cells were washed twice with PBS before imaging. The cells were observed with a Zeiss LSM 780 confocal laser scanning microscope.

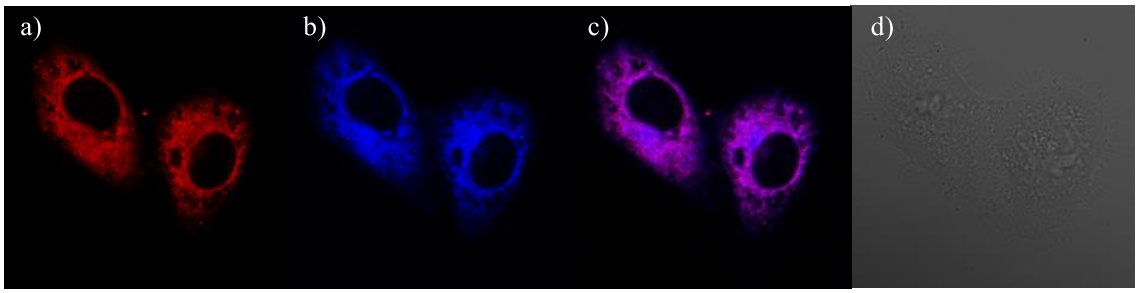


Figure S6. Co-staining of HepG2 cells with **5a** and **ER-Tracker™ Red**: a) fluorescent image of HepG2 cells stained with **ER-Tracker™ Red** (1.0 μM, λ_{ex} = 543 nm, λ_{em} = 600−700 nm); b) fluorescent image of HepG2 cells stained with **5a** (1.0 μM, λ_{ex} = 405 nm, λ_{em} = 450−550 nm); c) merged image of a) and b); d) bright-field image.

(4) Confocal imaging experiment data

Table S6. Manders' coefficients and Pearson's coefficient in confocal imaging experiments

Compd	concentration	λ_{em} (nm)	Manders' coefficients	Pearson's coefficient
3a	1.0 μM	500-600	m_1 = 0.99, m_2 = 0.95	0.89
3b	1.0 μM	550-650	m_1 = 0.96, m_2 = 0.89	0.86
3d	1.0 μM	500-600	m_1 = 0.82, m_2 = 0.88	0.75
3e	1.0 μM	500-600	m_1 = 0.99, m_2 = 1.00	0.94
3h	1.0 μM	500-600	m_1 = 0.96, m_2 = 0.90	0.86
4a	1.0 μM	500-600	m_1 = 0.94, m_2 = 0.99	0.89
5a	1.0 μM	450-550	m_1 = 0.92, m_2 = 1.00	0.92

The Manders' coefficients and Pearson's coefficient were calculated using Image-Pro Plus software.

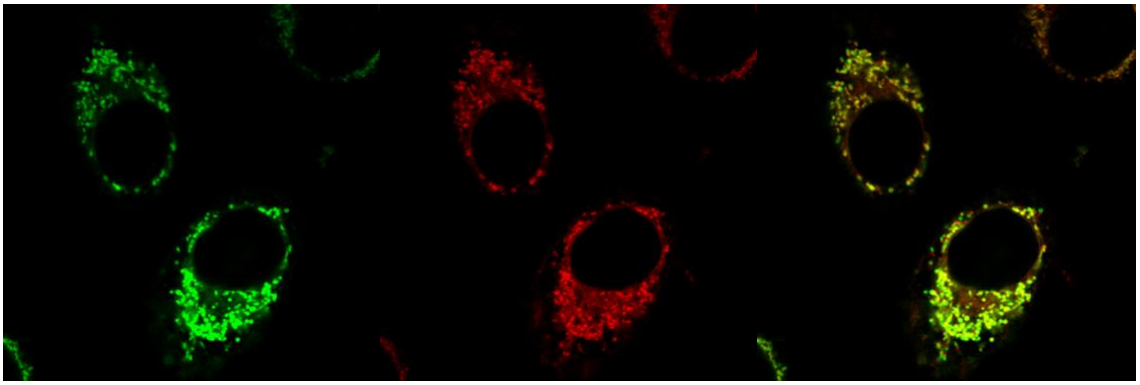


Figure S7. Co-staining of HepG2 cells with **3a** (1.0 μM) and **MTR** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **3a** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−600 nm); (Middle) fluorescent image of HepG2 cells stained with **MTR** for 15 min (λ_{ex} = 543 nm, λ_{em} = 600−700 nm); (Right) merged image.

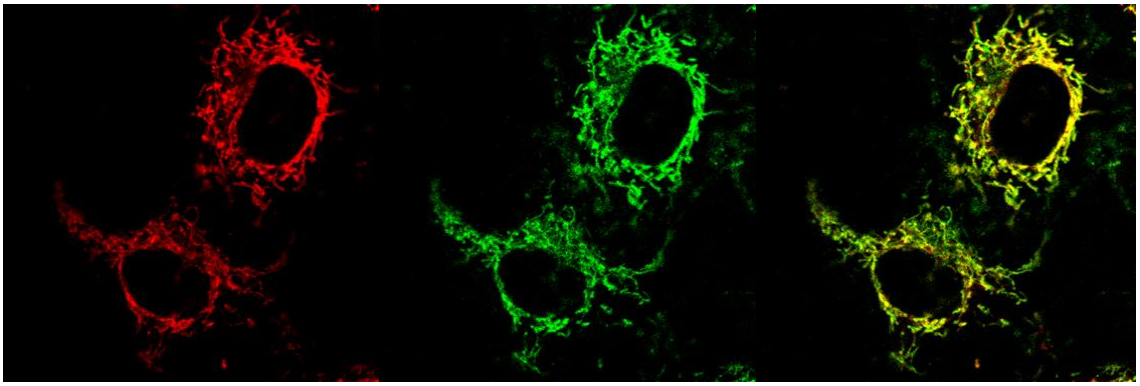


Figure S8. Co-staining of HepG2 cells with **3b** (1.0 μM) and **MTG** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **3b** for 15 min (λ_{ex} = 543 nm, λ_{em} = 550−650 nm); (Middle) fluorescent image of HepG2 cells stained with **MTG** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−540 nm); (Right) merged image.

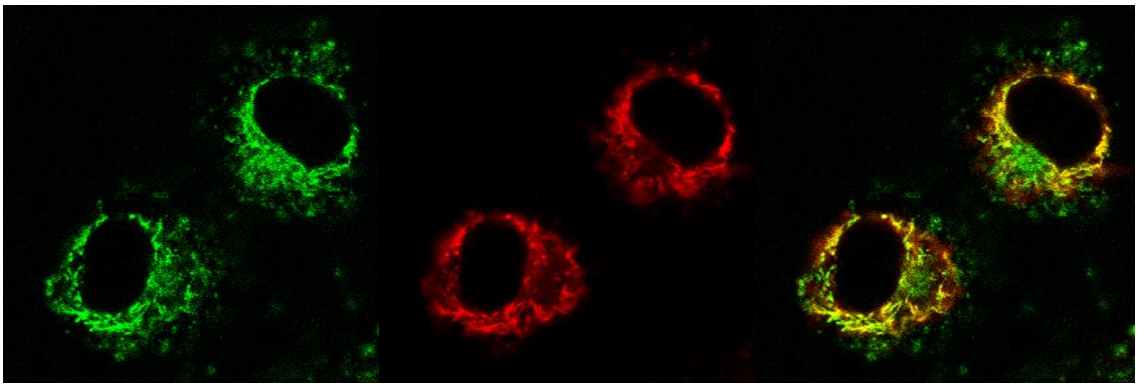


Figure S9. Co-staining of HepG2 cells with **3d** (1.0 μM) and **MTR** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **3d** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−600 nm); (Middle) fluorescent image of HepG2 cells stained with **MTR** for 15 min (λ_{ex} = 543 nm, λ_{em} = 600−700 nm); (Right) merged image.

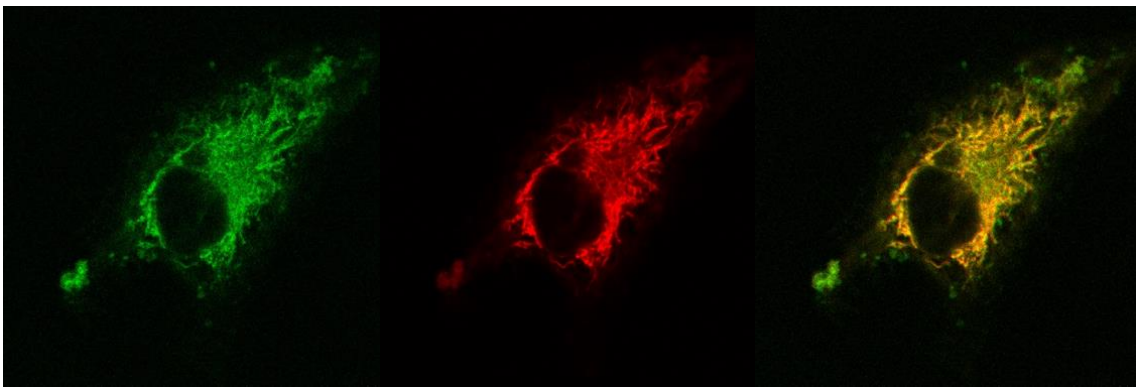


Figure S10. Co-staining of HepG2 cells with **3e** (1.0 μM) and **MTR** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **3e** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−600 nm); (Middle) fluorescent image of HepG2 cells stained with **MTR** for 15 min (λ_{ex} = 543 nm, λ_{em} = 600−700 nm); (Right) merged image.

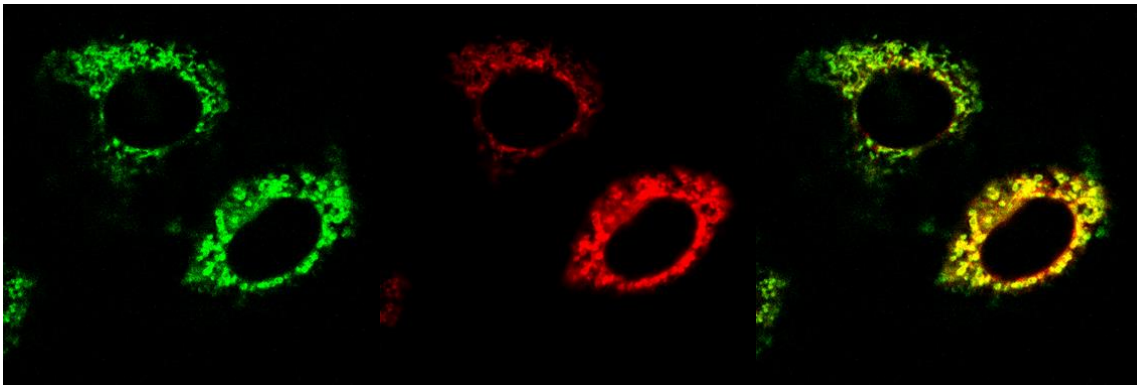


Figure S11. Co-staining of HepG2 cells with **3h** (1.0 μM) and **MTR** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **3h** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−600 nm); (Middle) fluorescent image of HepG2 cells stained with **MTR** for 15 min (λ_{ex} = 543 nm, λ_{em} = 600−700 nm); (Right) merged image.

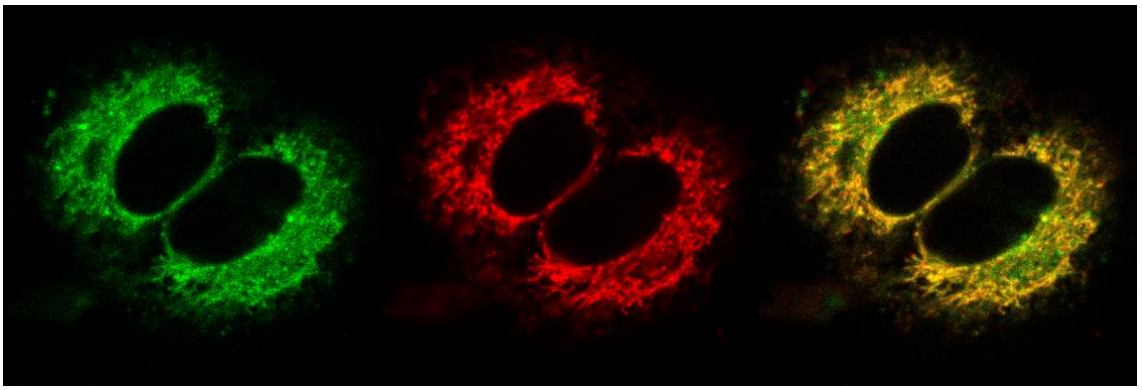


Figure S12. Co-staining of HepG2 cells with **4a** (1.0 μM) and **MTR** (1.0 μM): (Left) fluorescent image of HepG2 cells stained with **4a** for 15 min (λ_{ex} = 488 nm, λ_{em} = 500−600 nm); (Middle) fluorescent image of HepG2 cells stained with **MTR** for 15 min (λ_{ex} = 543 nm, λ_{em} = 600−700 nm); (Right) merged image.

(5) Photostability of representative compounds

HepG2 cells were cultivated with 1.0 μM of **MTG**, **MTR**, **3a**, **4a**, **3b**, **3d** and **3h** in phosphate buffered solution (PBS) containing 1% DMSO at 37 ºC for 15 min. Then, the cells were washed three times with PBS. Finally, the photostability data were tested with

a Zeiss LSM 780 confocal laser scanning microscope.

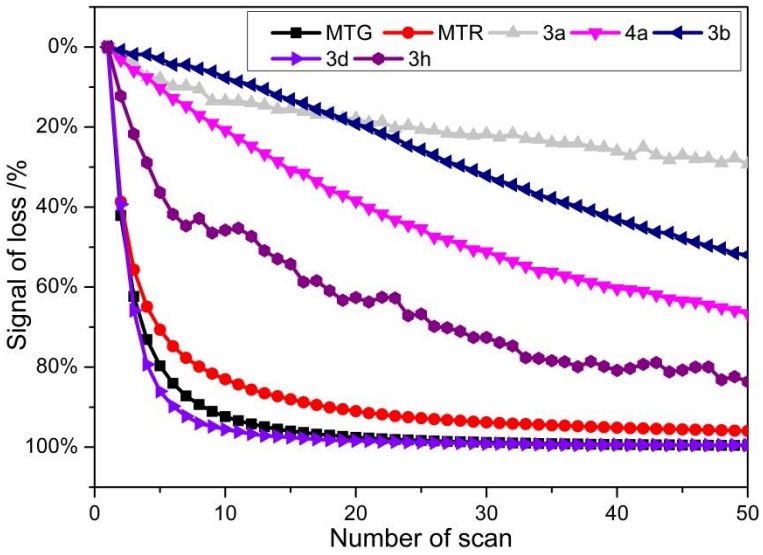


Figure S13. Signal loss (%) of fluorescent emission of **MTG**, **MTR**, **3a**, **4a**, **3b**, **3d** and **3h** in living HepG2 cells with increasing number of scans using confocal microscope (1.0 μM, irradiation time: 5.14 s/scan, respectively). For **MTG**: λ_{ex} = 488 nm, λ_{em} = 500−600 nm; for **MTR**: λ_{ex} = 543 nm, λ_{em} = 600−700 nm; for **3a**, **4a**, **3d** and **3h**: λ_{ex} = 488 nm, λ_{em} = 500−600 nm; for **3b**: λ_{ex} = 543 nm, λ_{em} = 550−650 nm.

(6) Cytotoxicity assays

The cytotoxicity studies of **MTG**, **MTR**, **3a**, **4a**, **5a**, **3b**, **3d**, **3e** and **3h** were examined by CellTiler 96®Aqueous One Solution Cell Proliferation Assay. HepG2 cells were seeded at 1 × 104 cells/well in 96-well culture plates for a stationary culture. After being incubated for 24 h, the medium was replaced with fresh complete medium, and the sample was then added to achieve final concentrations at 0.125, 0.25, 0.5, 1.0, 2.0 and 4.0 μM. After 24 hours of incubation, 20.0 μL of CellTiler 96®Aqueous One Solution in PBS was added to each well and the plates were incubated for an additional 1 hour. Then, the absorbance of each sample was measured on the microplate reader (model 550, BioRad, USA) at a wavelength of 490 nm. The cell viability was calculated by the following formula: (mean optical density (OD) in treated wells/mean OD in control wells) × 100%.

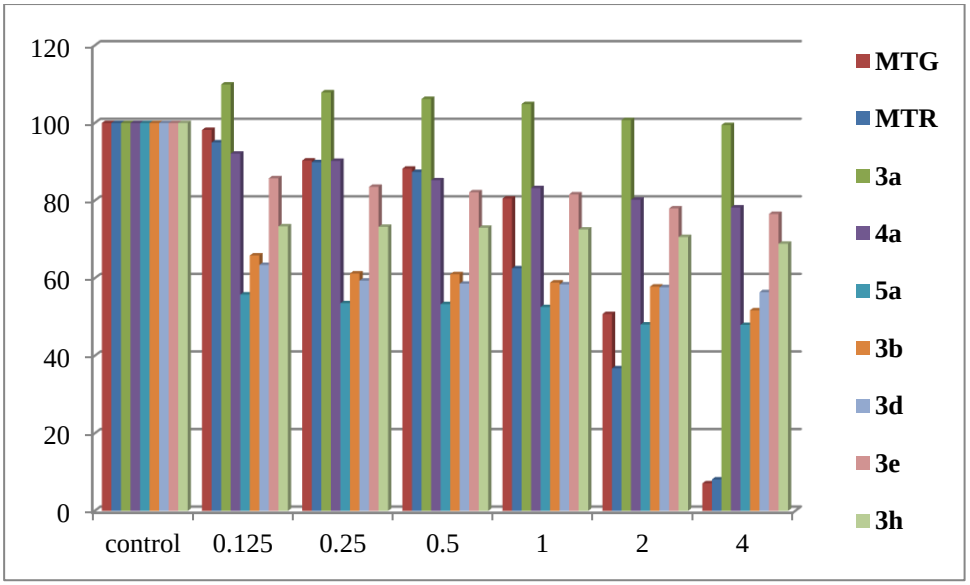


Figure S14. Cell viability values (%) estimated by a CellTiler 96®Aqueous One Solution Cell Proliferation Assay using HepG2 cells, cultured in the presence of 0.125−4.0 μM of **MTG**, **MTR**, **3a**, **4a**, **5a**, **3b**, **3d**, **3e** and **3h** for 24 h at 37 °C, respectively.

X. References

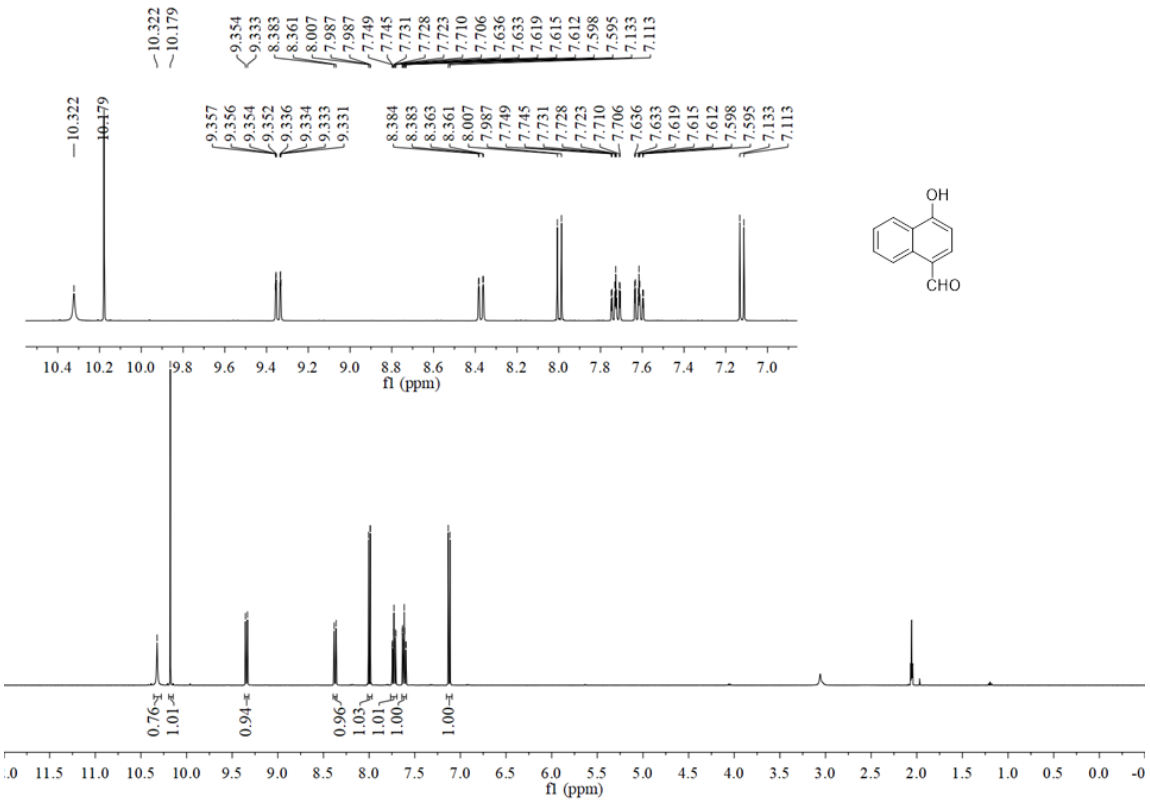
(1) J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

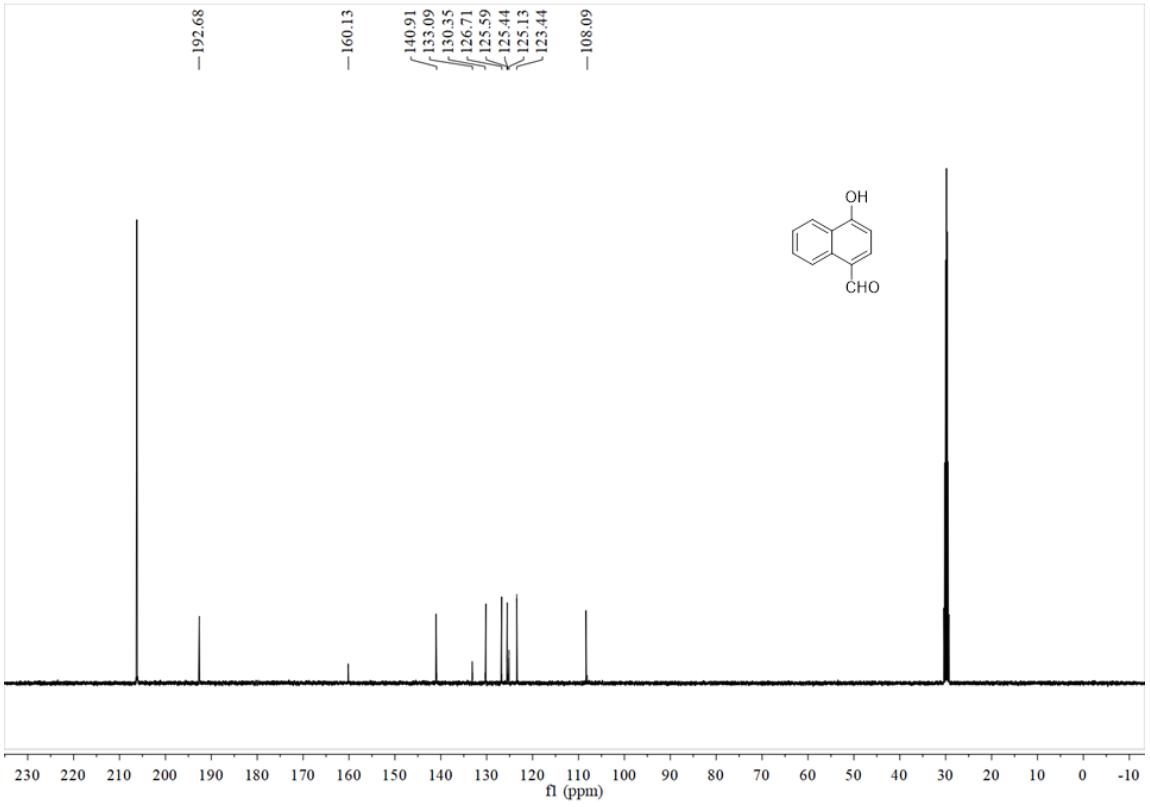
(2) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song and S. Lee, *J. Org. Chem.*, 2010, **75**, 6244.

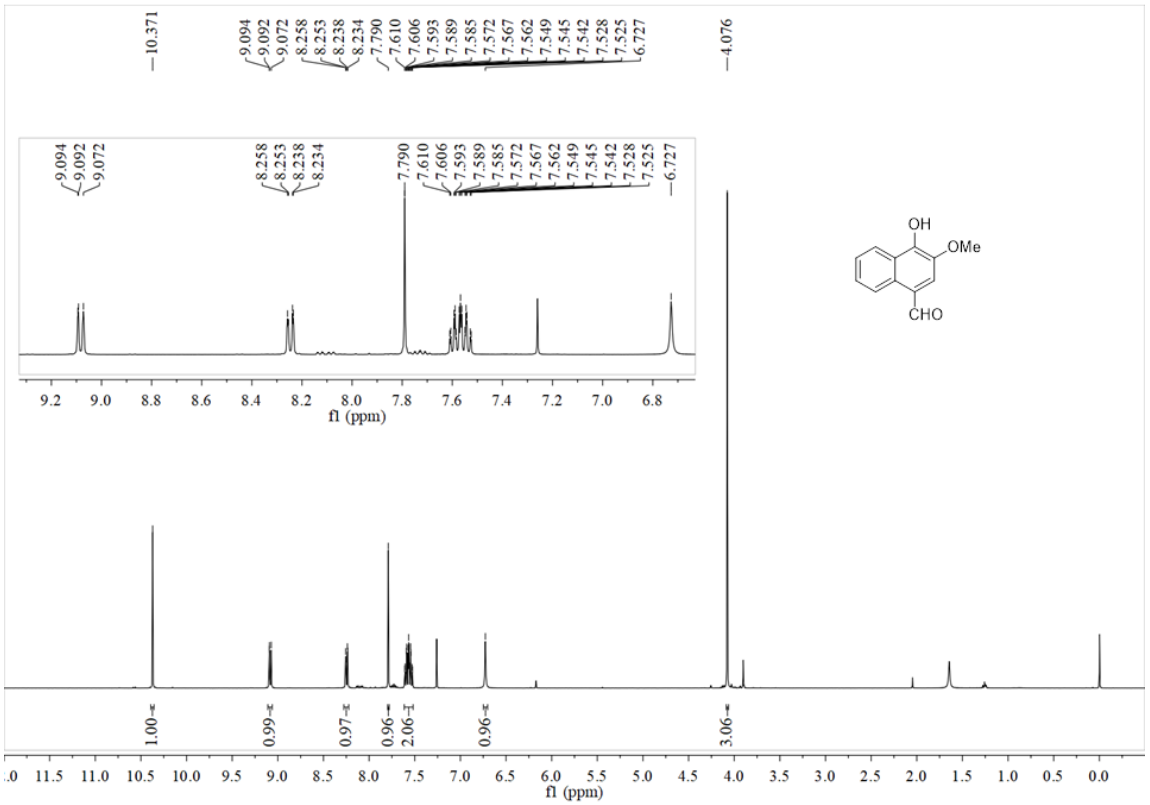
(3) K. Antien, G. Viault, L. Pouysegu, P. A. Peixoto and S. Quideau, *Tetrahedron.*, 2017, **73**, 3684.

(4) T. Si, B. Li, W. Xiong, B. Xu and W. Tang, *Org. Biomol. Chem.*, 2017, **15**, 9903.

XI. Copies of NMR spectra



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7.585
7.572
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7.562
7.549
7.545
7.542
7.528
7.525
6.727
4.076
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OMe
CHO
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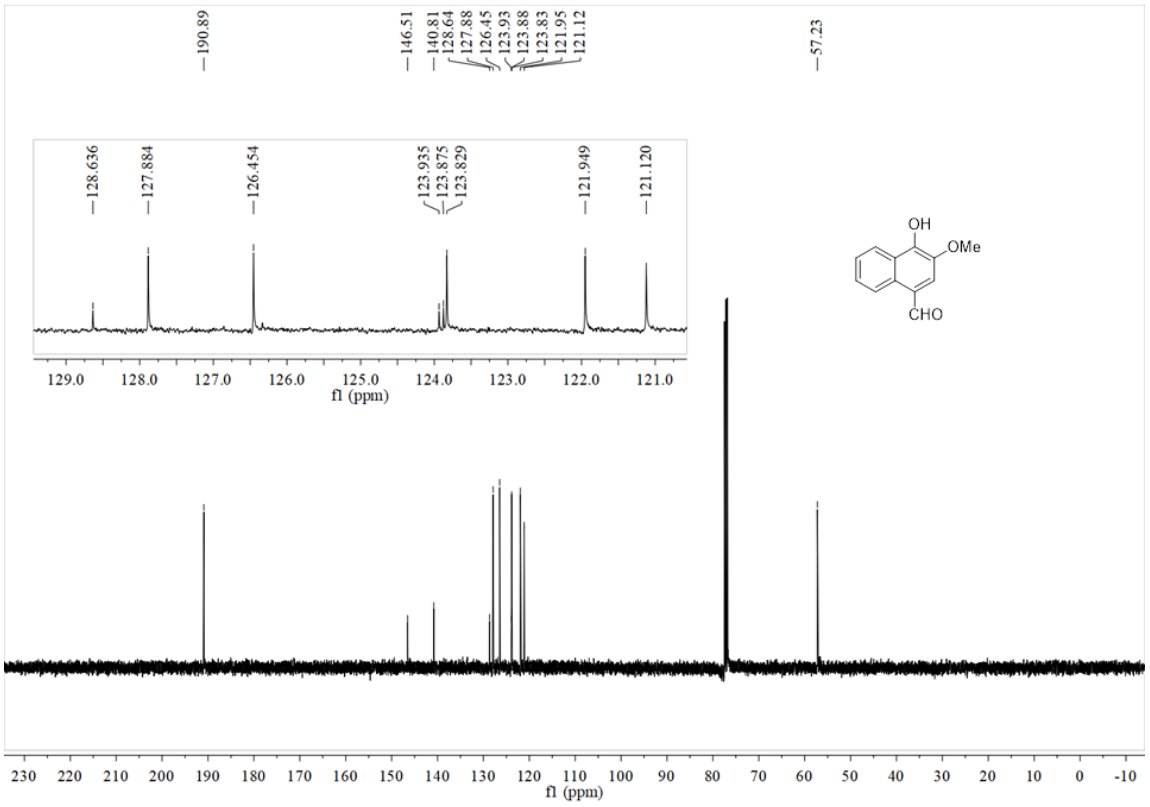
0.97
0.96
2.06
0.96
3.06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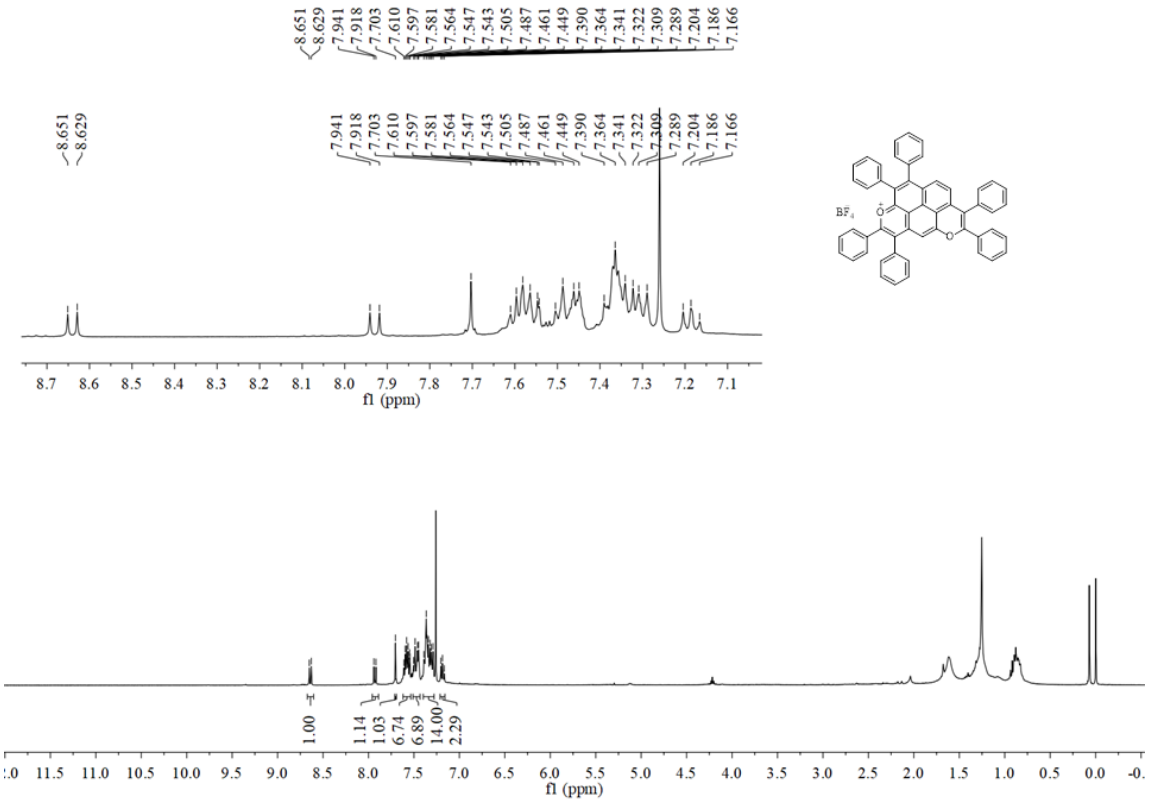
CHO
f1 (ppm)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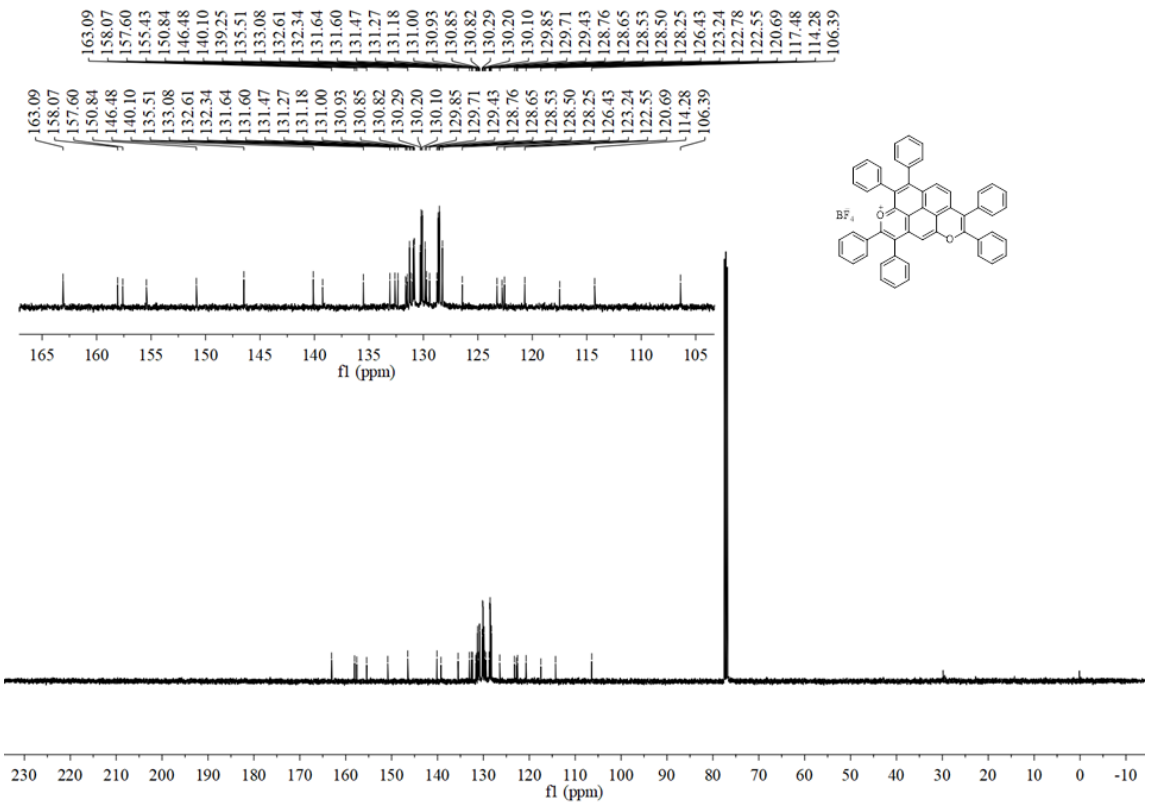
fl (ppm)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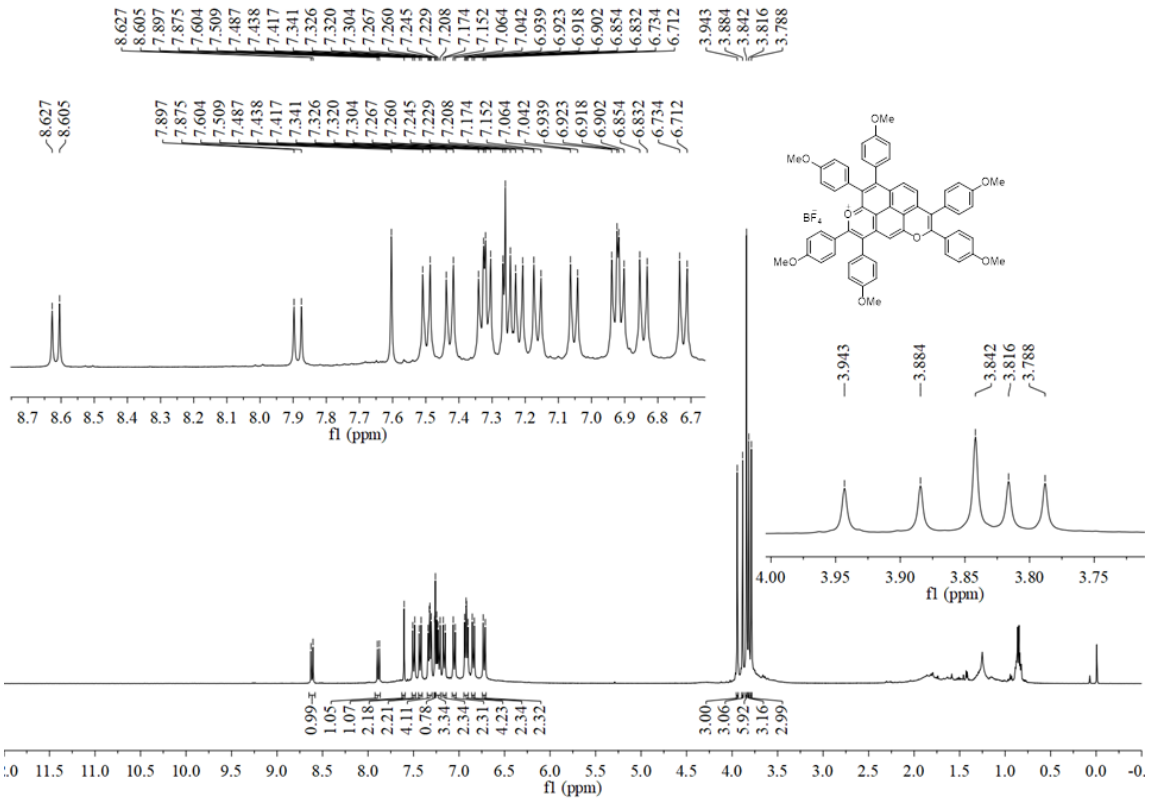
fl (ppm)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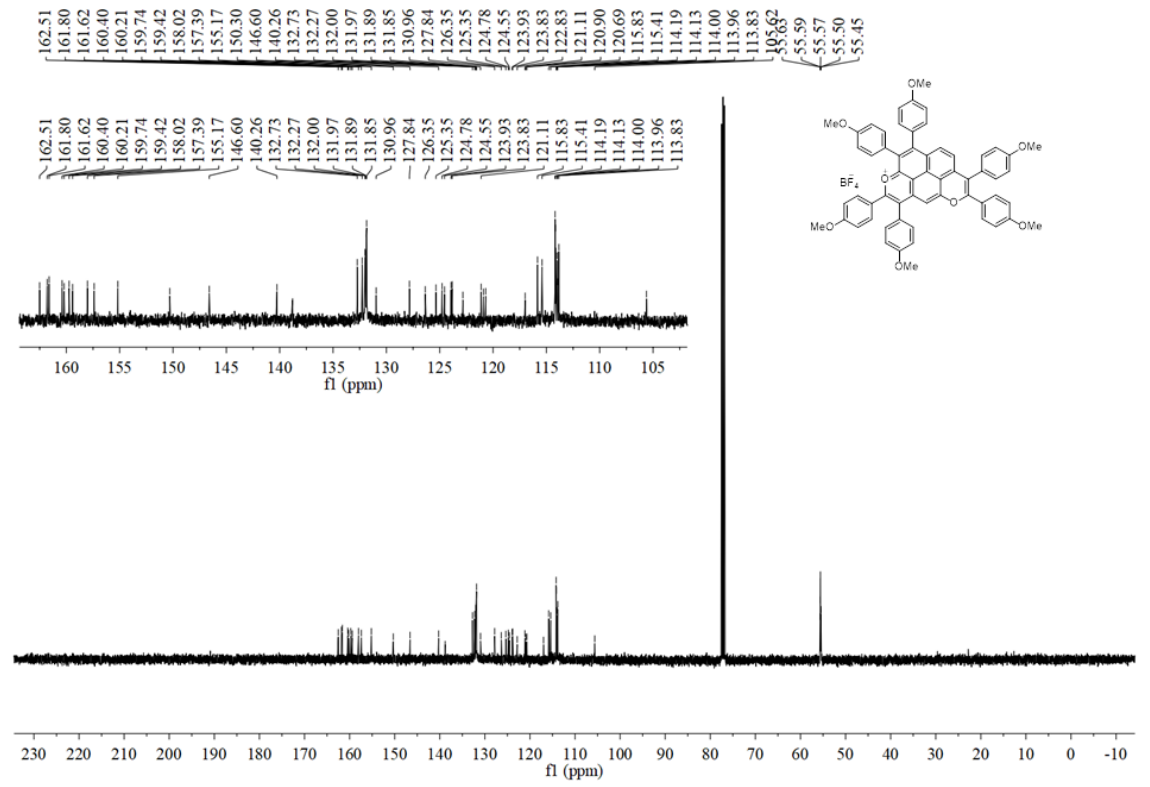
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MeO
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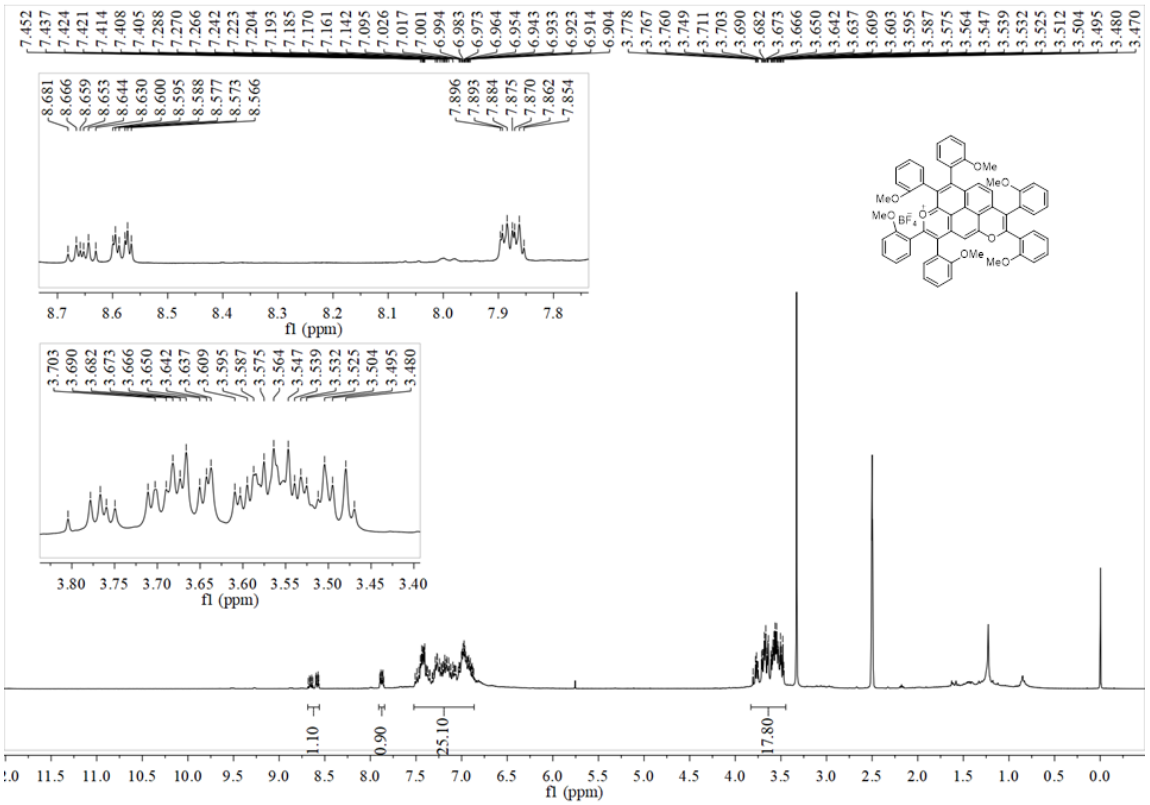
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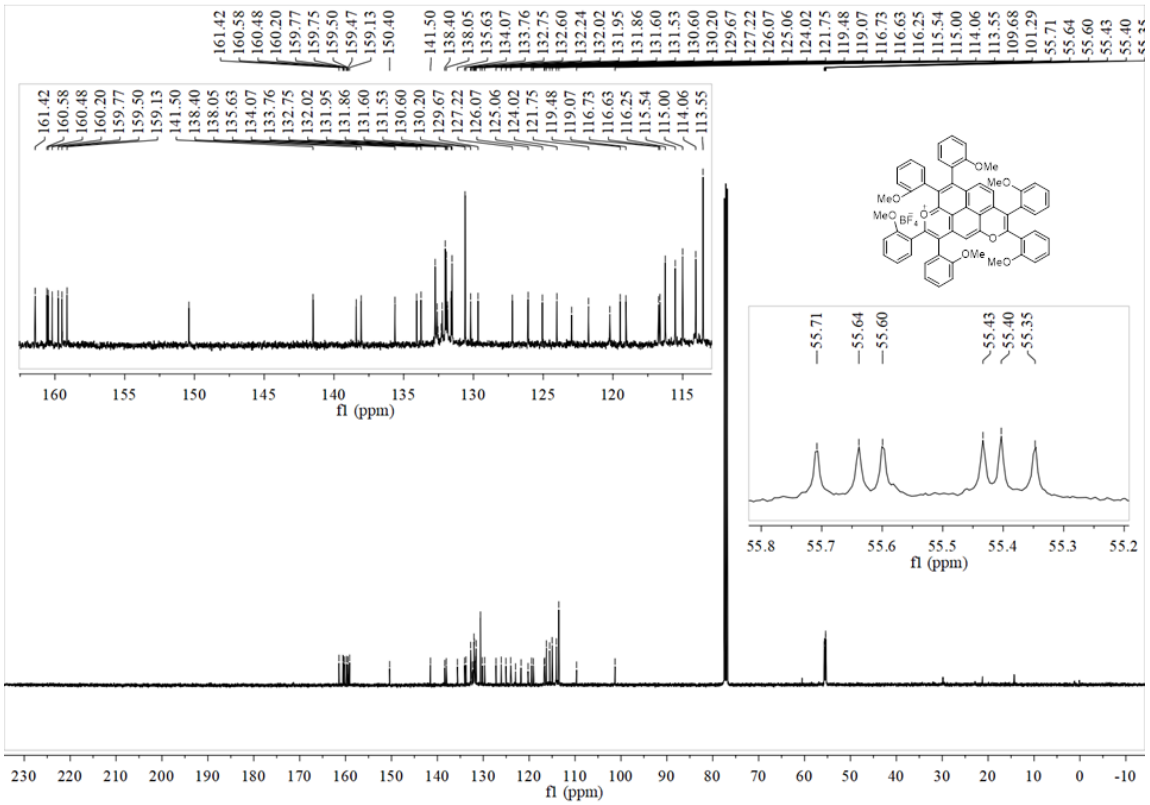
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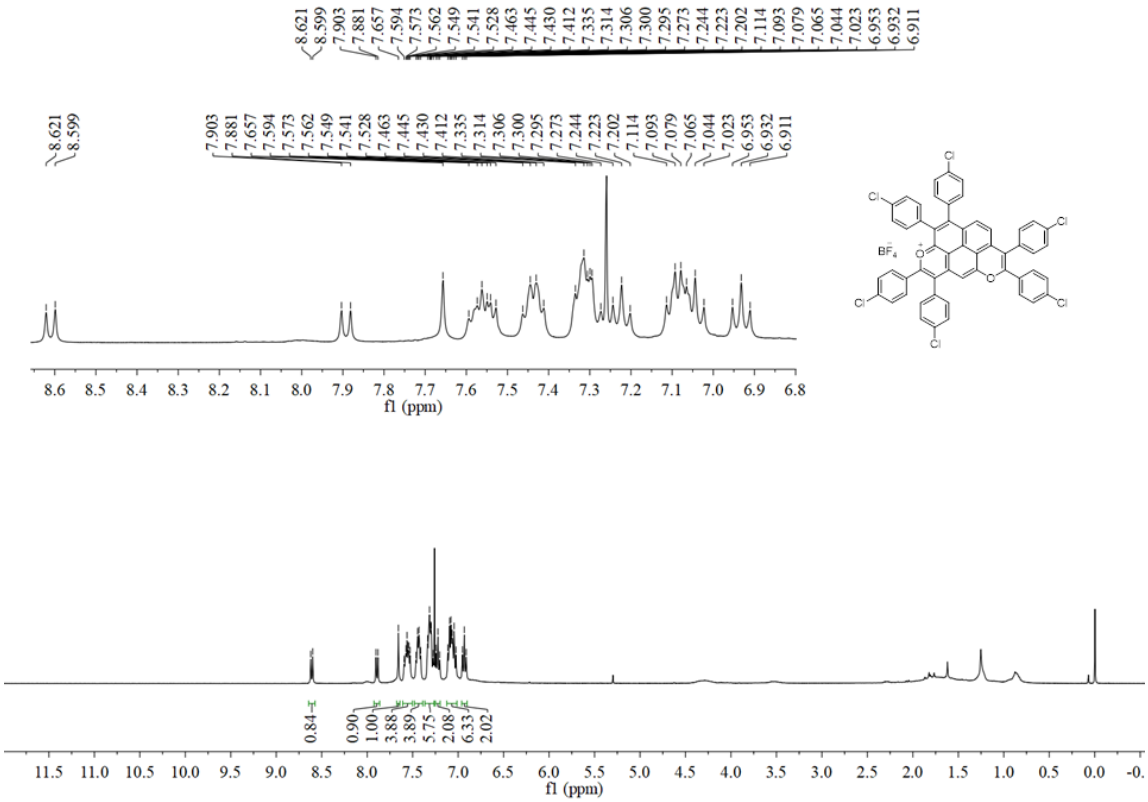
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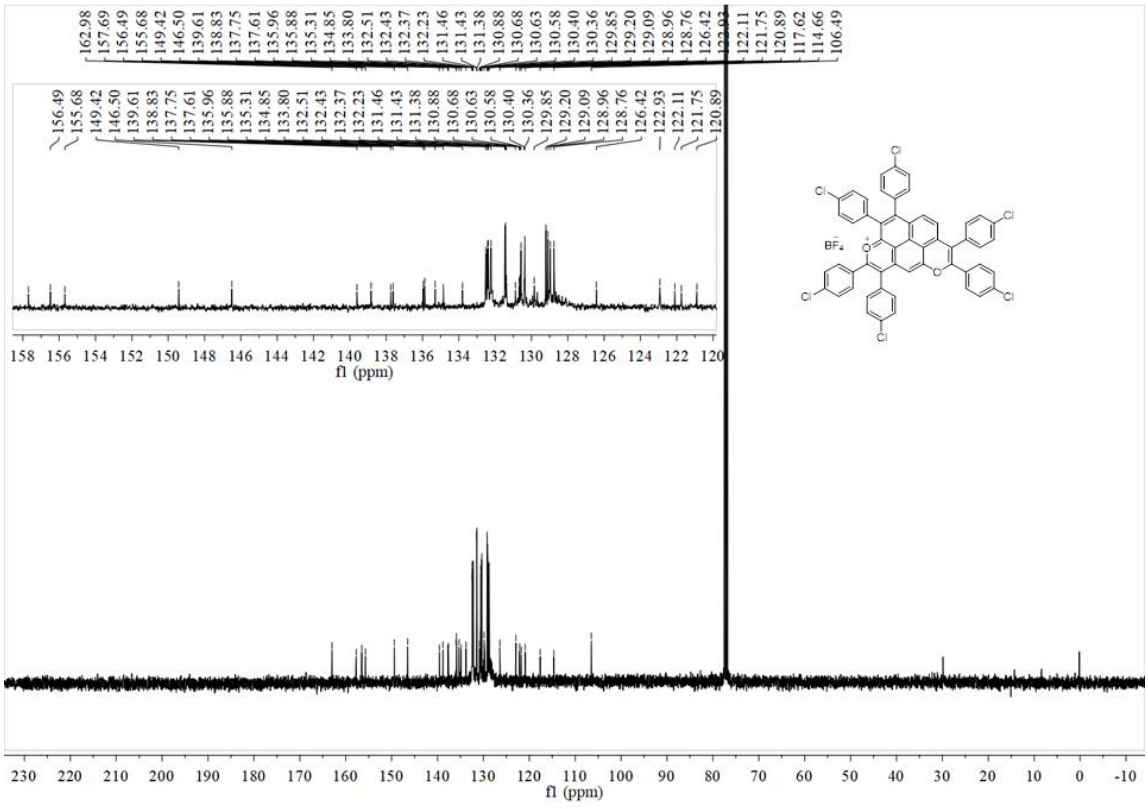
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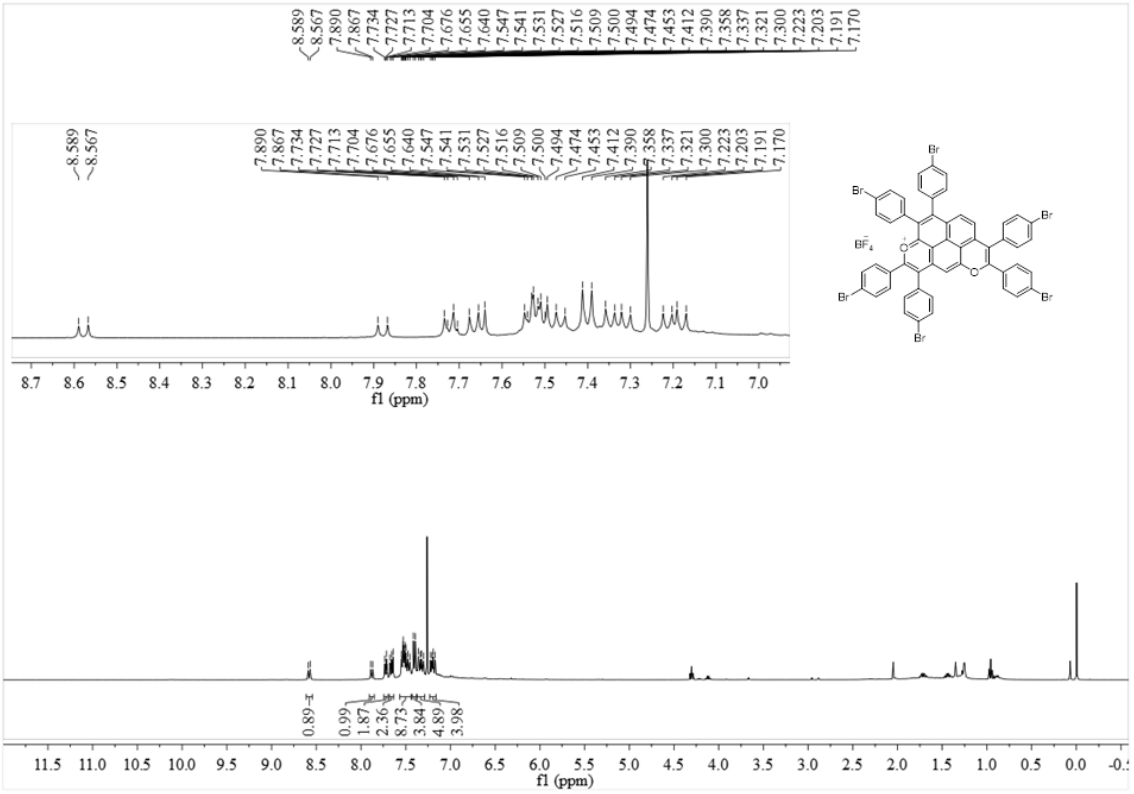
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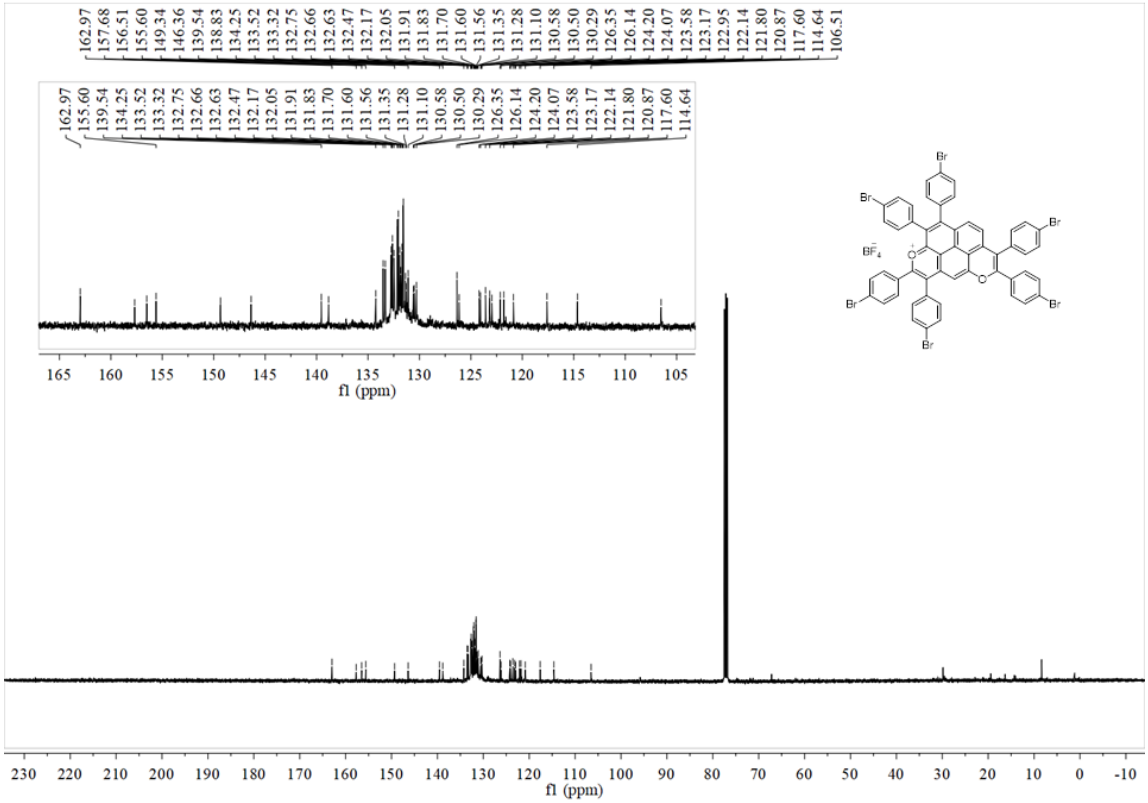
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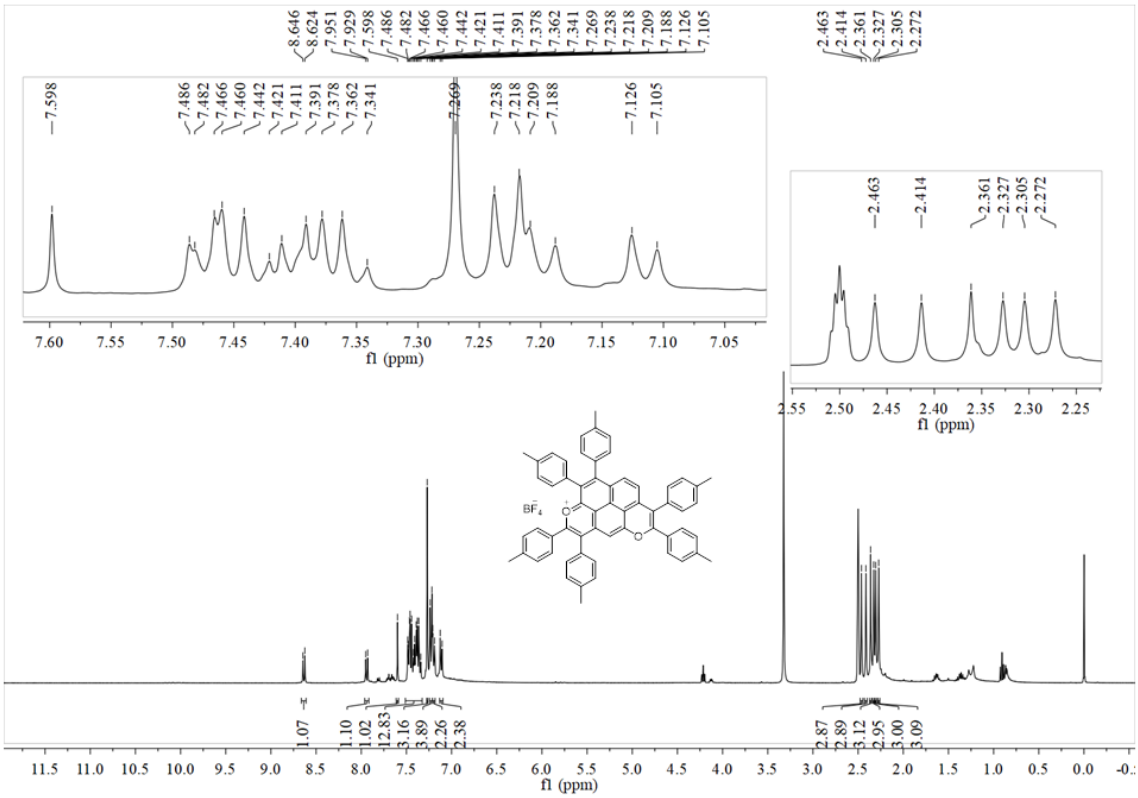
f1 (ppm)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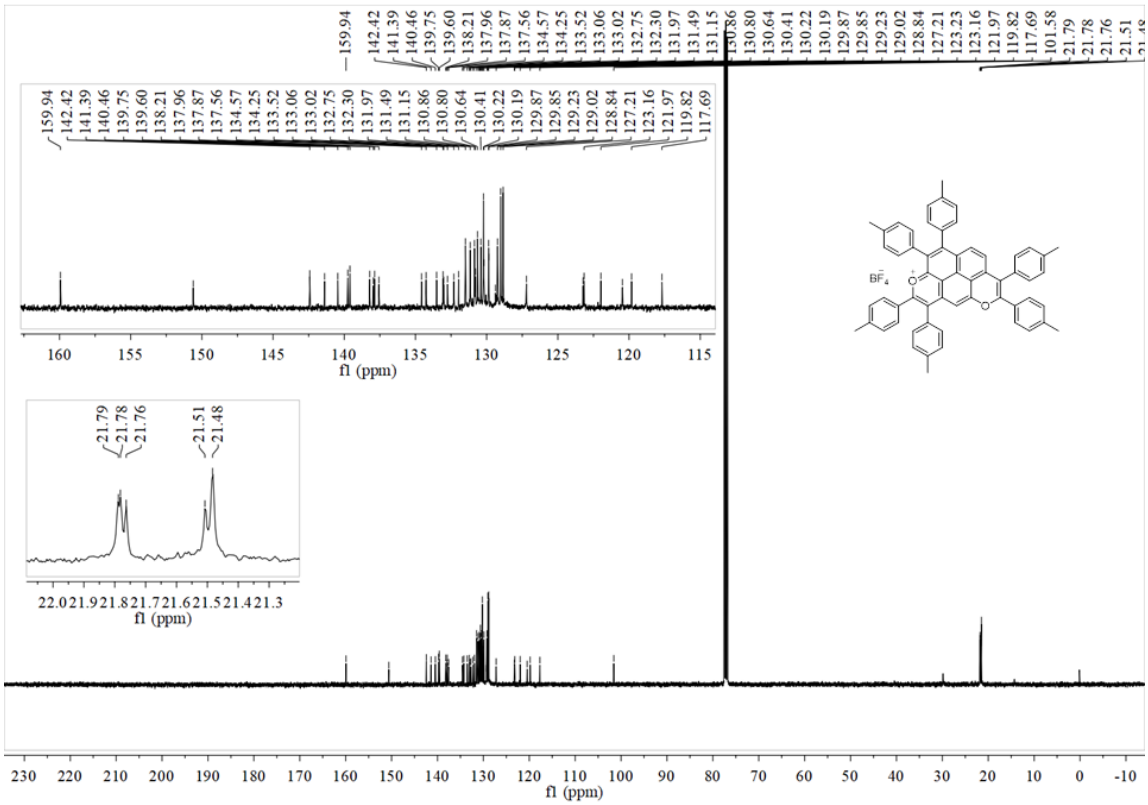
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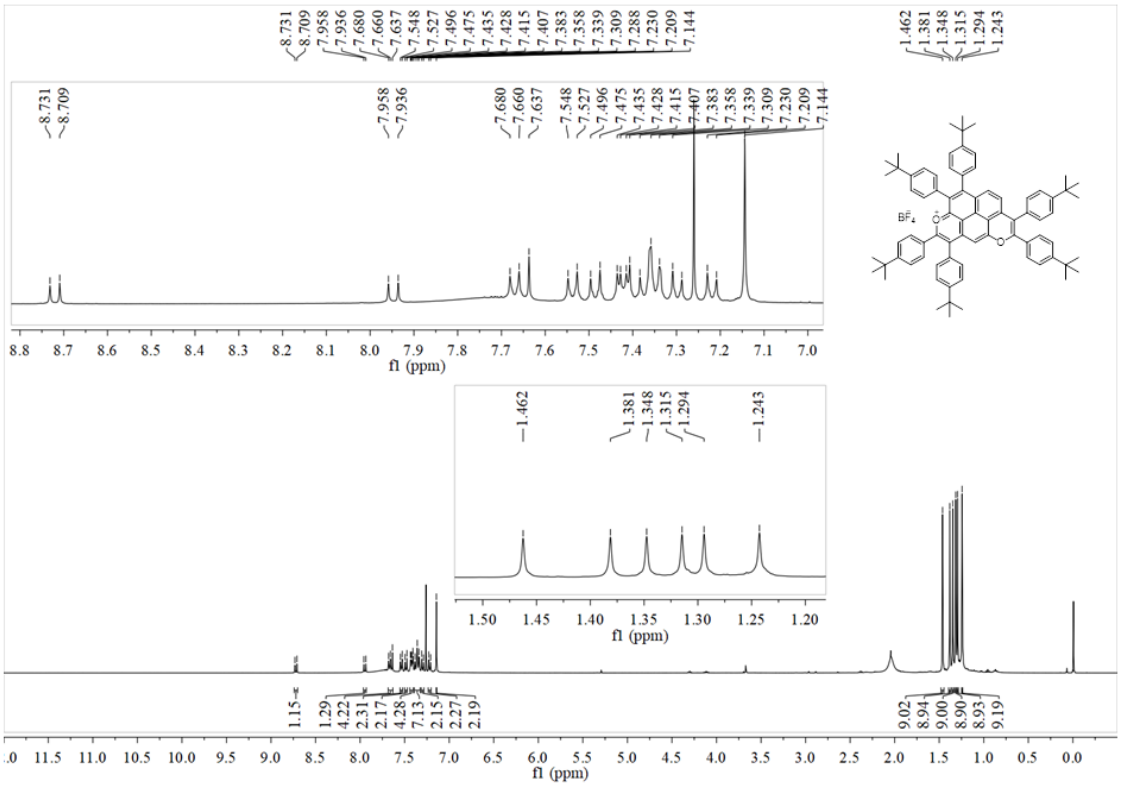
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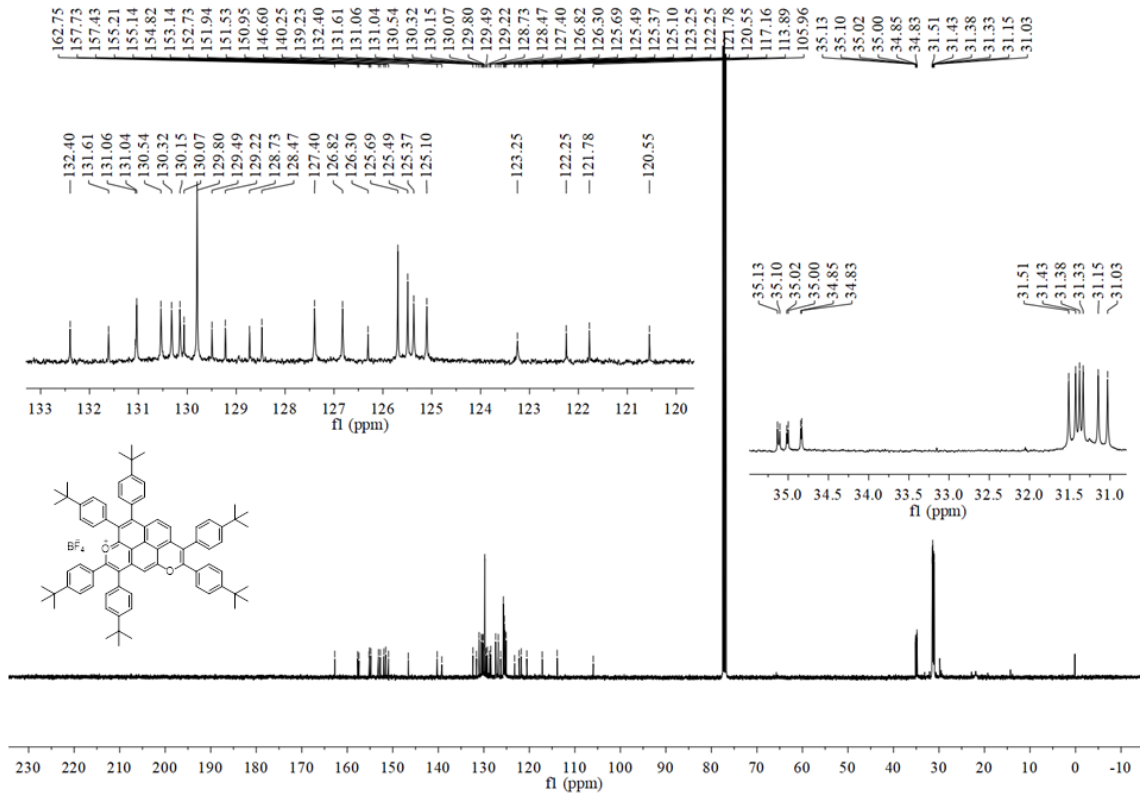
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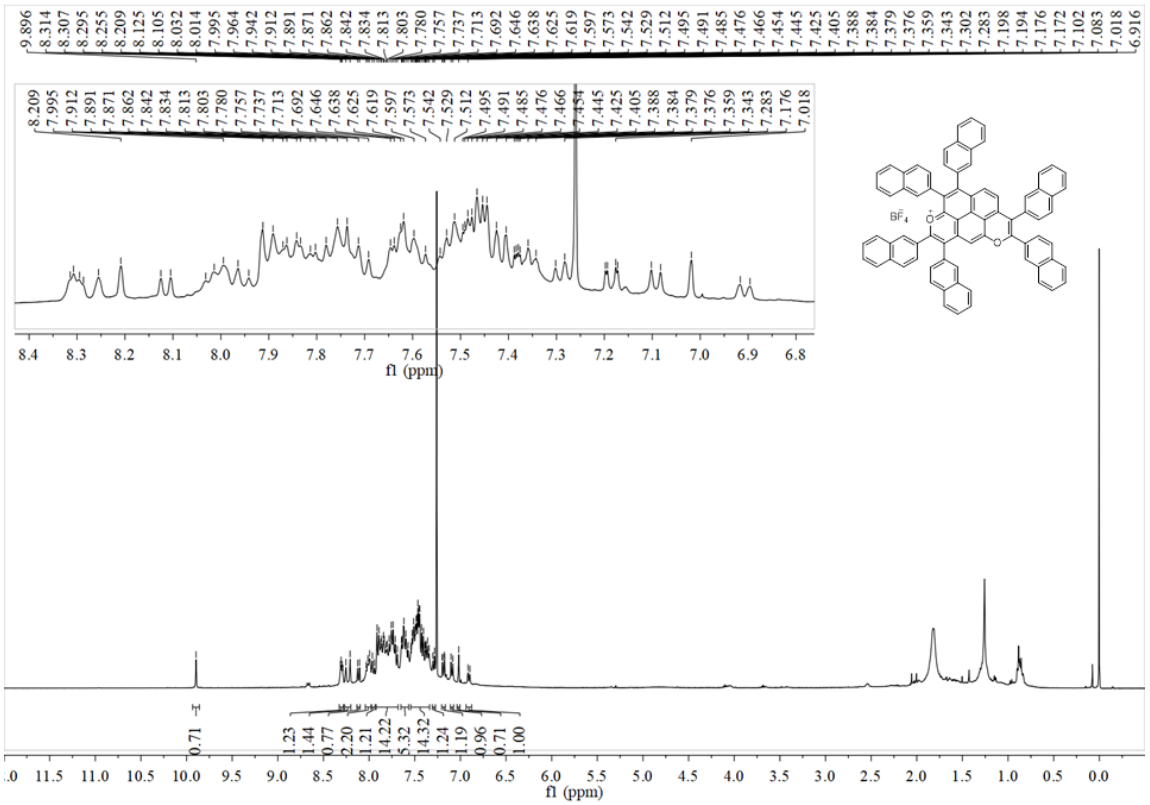
fl (ppm)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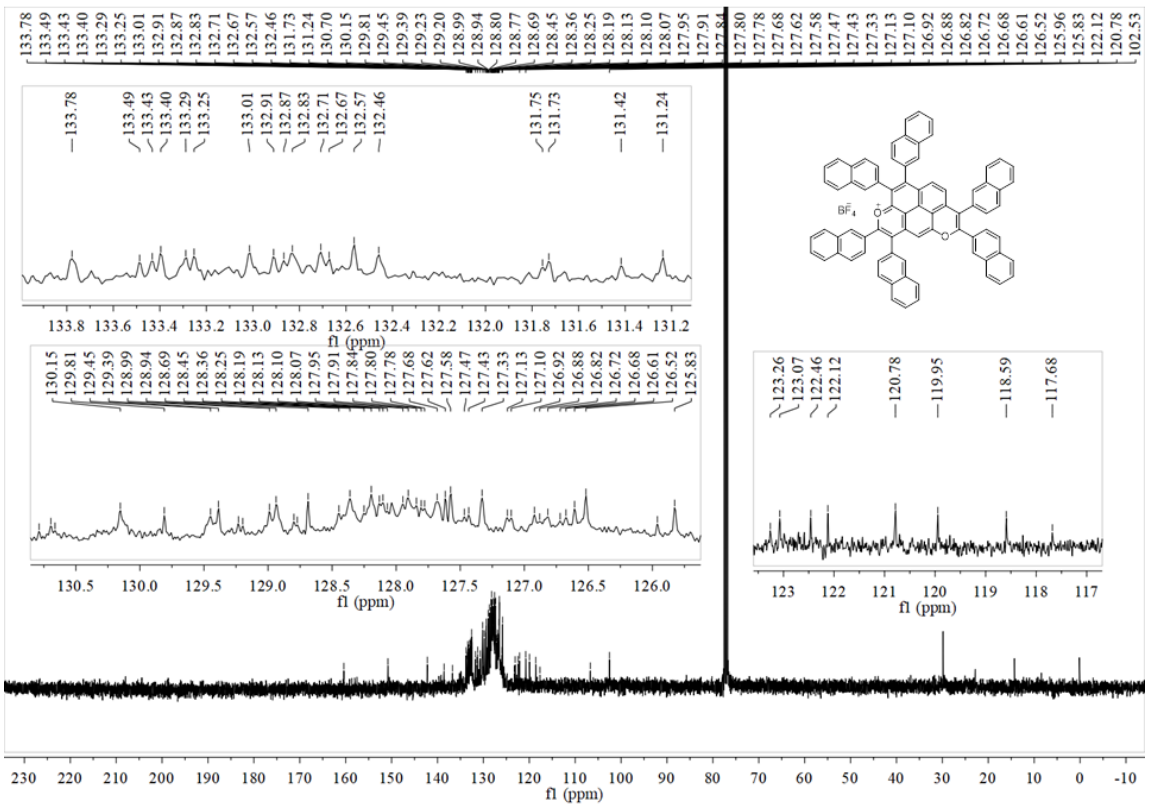
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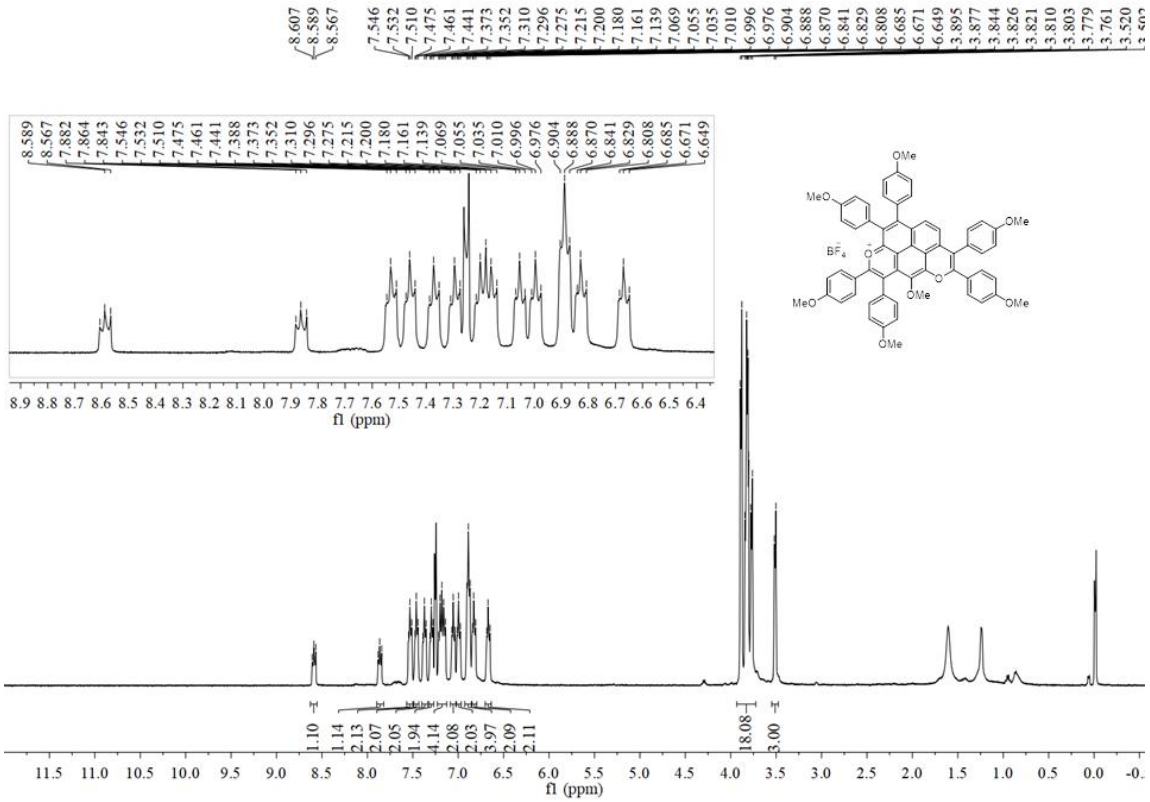
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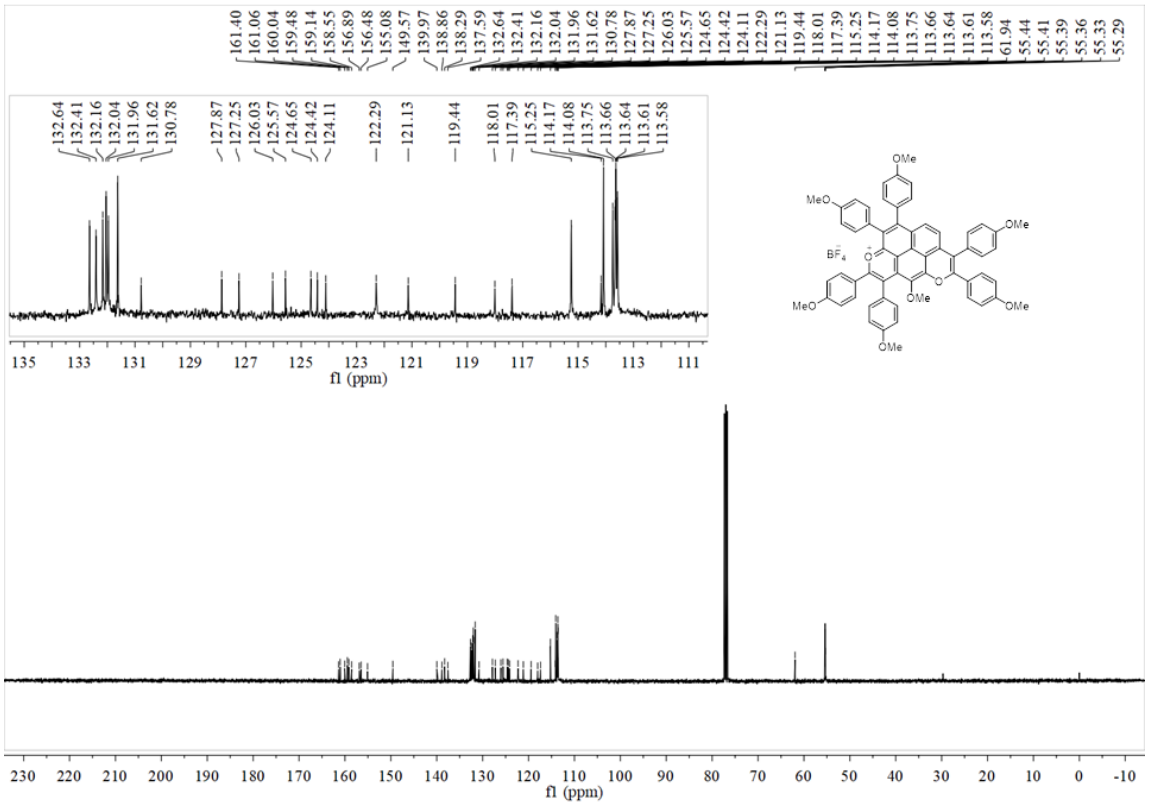
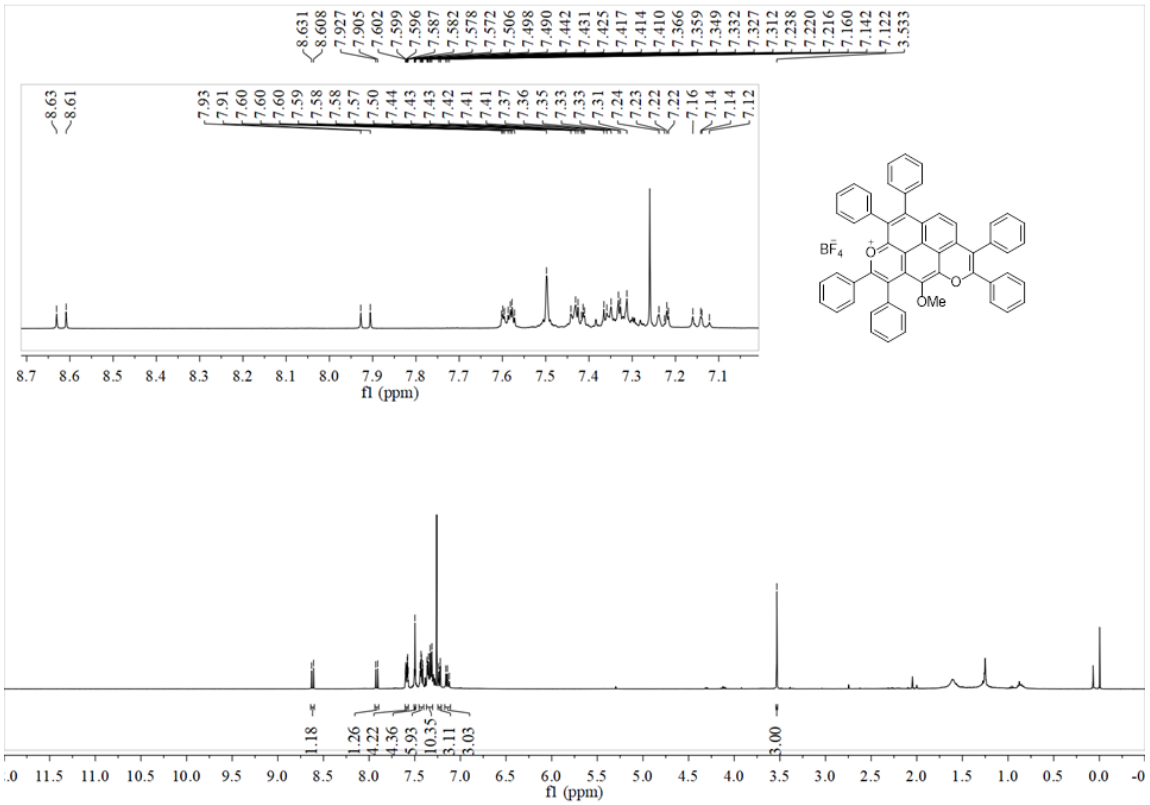

f1 (ppm)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7.596
7.587
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7.578
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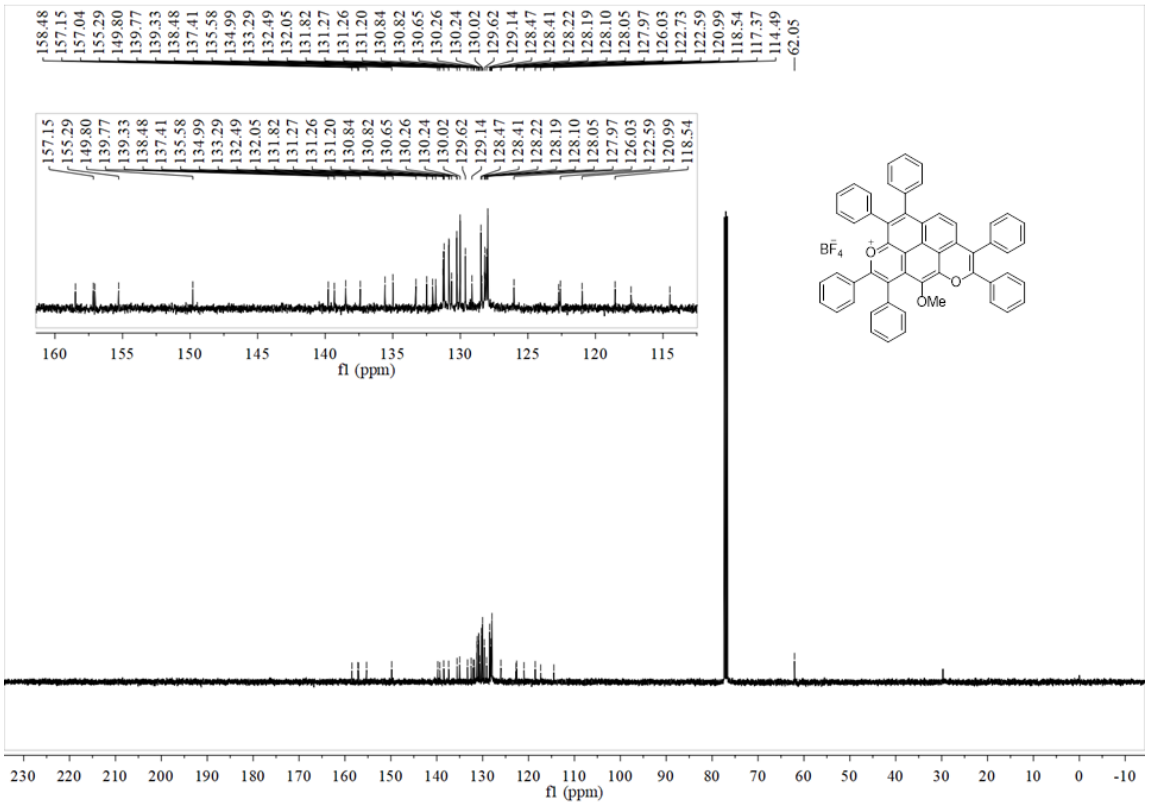
7.506
7.498
7.490
7.442
7.431
7.425
7.417
7.414
7.410
7.366
7.359
7.349
7.332
7.327
7.312
7.238
7.220
7.216
7.160
7.142
7.122
3.533
8.63
8.61
7.93
7.91
7.60
7.60
7.60
7.59
7.58
7.58
7.57
7.50
7.44
7.43
7.43
7.42
7.41
7.41
7.37
7.36
7.35
7.33
7.33
7.31
7.24
7.23
7.22
7.22
7.16
7.14
7.14
7.12
BF4
O
OMe
8.7 8.6 8.5 8.4 8.3 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)
1.18
1.26
4.22
4.36
5.93
10.35
3.11
3.03
3.00
.0 11.5 11.0 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
f1 (ppm)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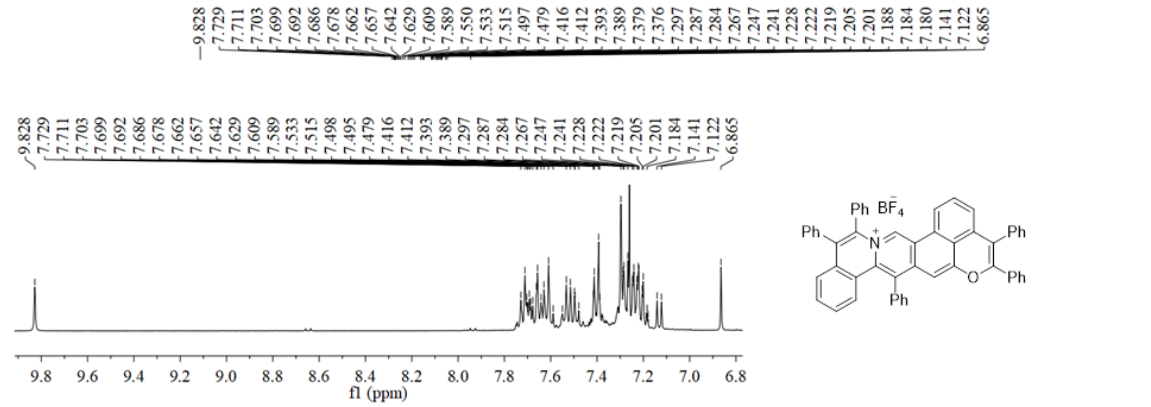
157.15
157.04
155.29
149.80
139.77
139.33
138.48
137.41
135.58
134.99
133.29
132.49
132.05
131.82
131.27
131.26
131.20
130.84
130.82
130.65
130.26
130.24
130.02
129.62
129.14
128.47
128.41
128.22
128.19
128.10
128.05
127.97
126.03
122.73
122.59
120.99
118.54
117.37
114.49
62.05
157.15
155.29
149.80
139.77
139.33
138.48
137.41
135.58
134.99
133.29
132.49
132.05
131.82
131.27
131.26
131.20
130.84
130.82
130.65
130.26
130.24
130.02
129.62
129.14
128.47
128.41
128.22
128.19
128.10
128.05
127.97
126.03
122.59
120.99
118.54
BF4
O
OMe
160 155 150 145 140 135 130 125 120 115
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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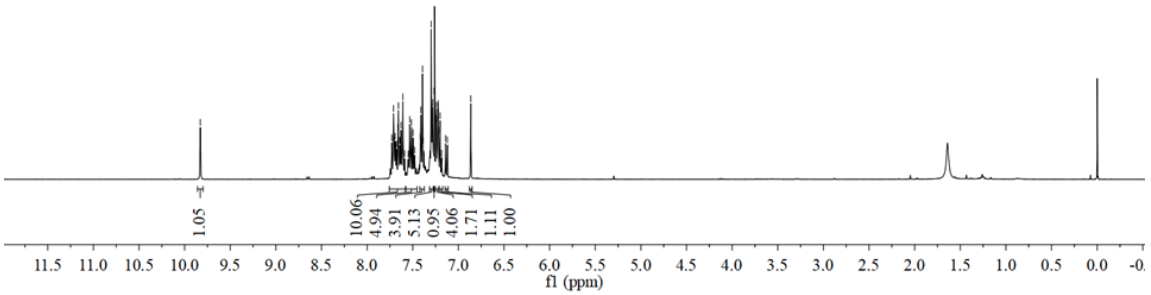
7.729
7.711
7.703
7.699
7.692
7.686
7.678
7.662
7.657
7.642
7.629
7.609
7.589
7.550
7.533
7.515
7.497
7.479
7.416
7.412
7.393
7.389
7.379
7.376
7.297
7.287
7.284
7.267
7.247
7.241
7.228
7.222
7.219
7.205
7.201
7.188
7.184
7.180
7.141
7.122
6.865
Ph
BF4
N
O
f1 (ppm)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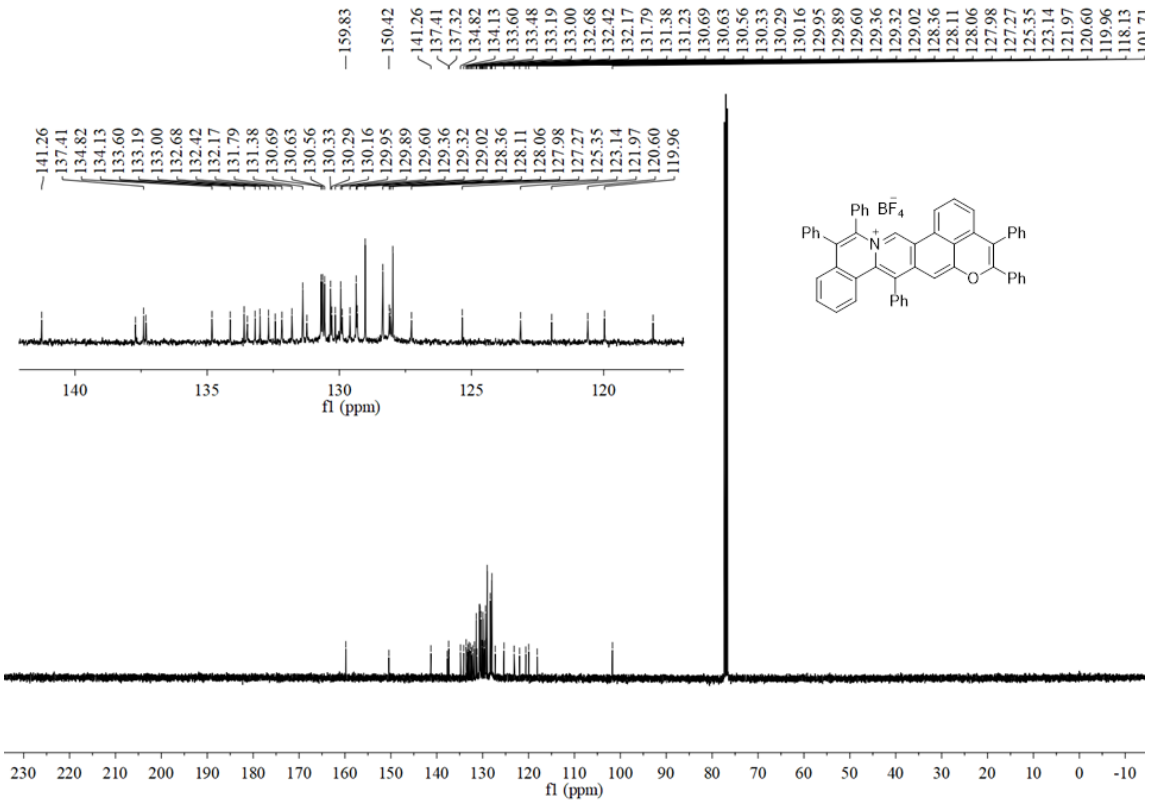
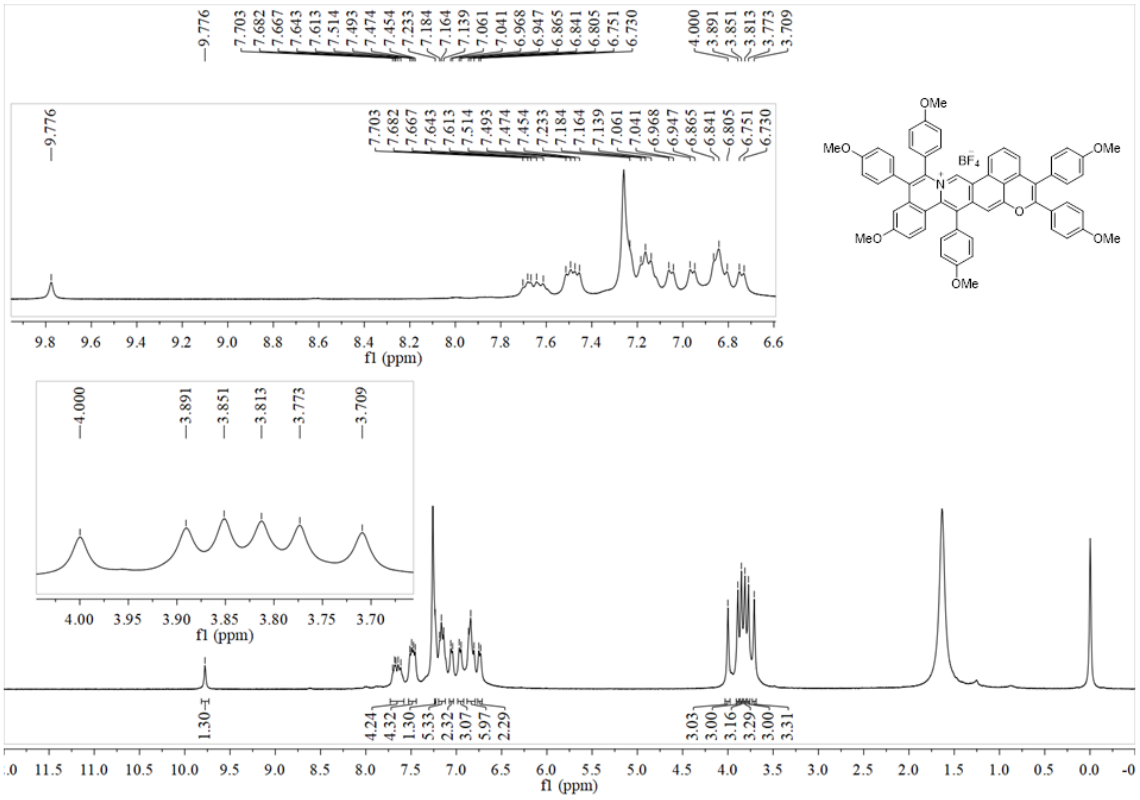
10.06
4.94
3.91
5.13
0.95
4.06
1.71
1.11
1.00
f1 (ppm)


159.83
150.42
141.26
137.41
137.32
134.82
134.13
133.60
133.48
133.19
133.00
132.68
132.42
132.17
131.79
131.38
131.23
130.69
130.63
130.56
130.33
130.29
130.16
129.95
129.89
129.60
129.36
129.32
129.02
128.36
128.11
128.06
127.98
127.27
125.35
123.14
121.97
120.60
119.96
118.13
Ph
BF4
N
O
f1 (ppm)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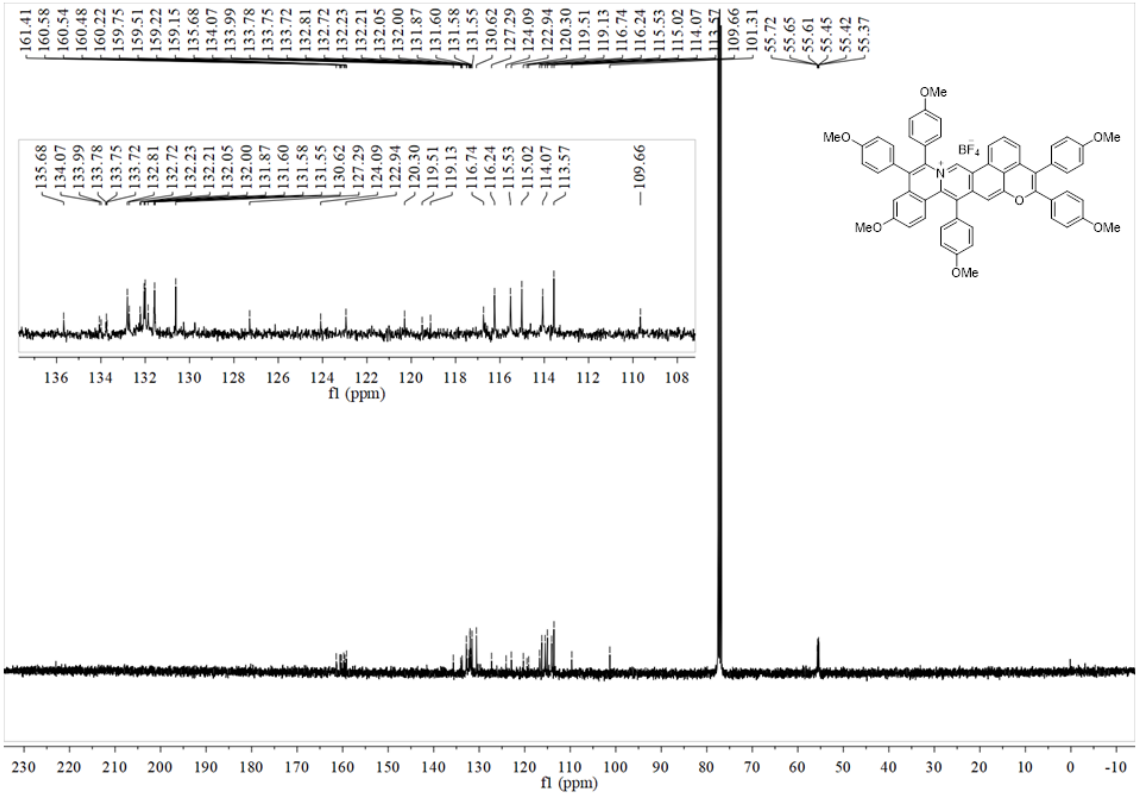
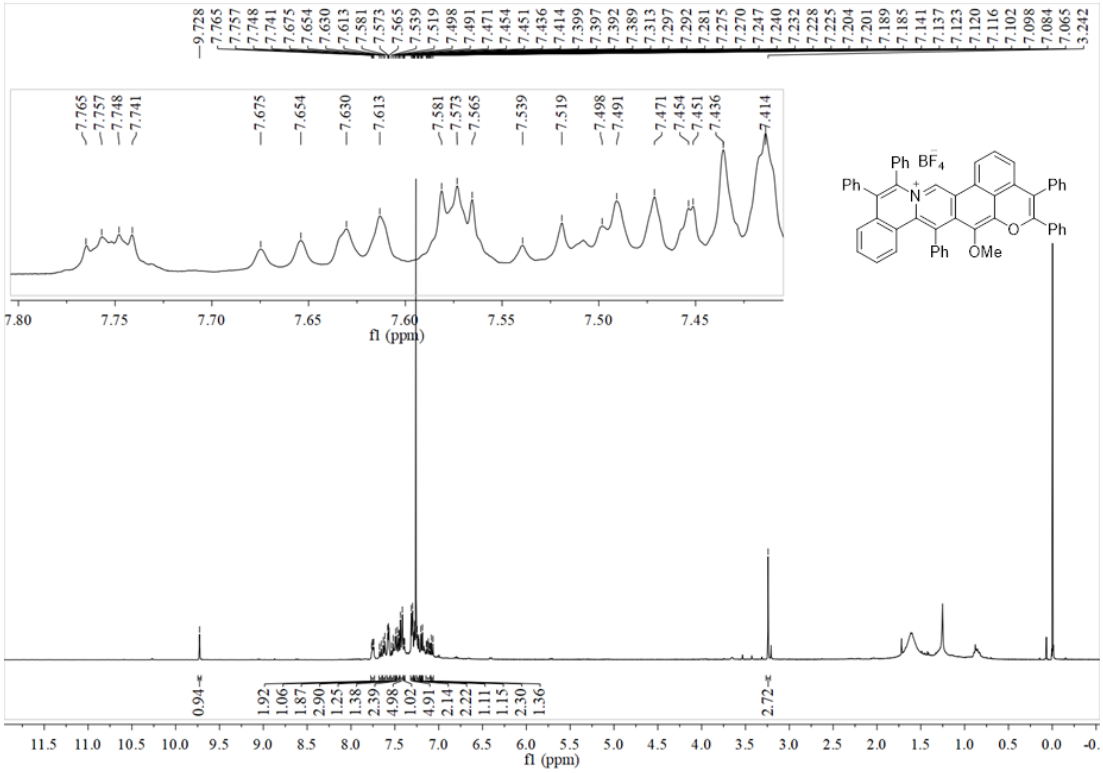
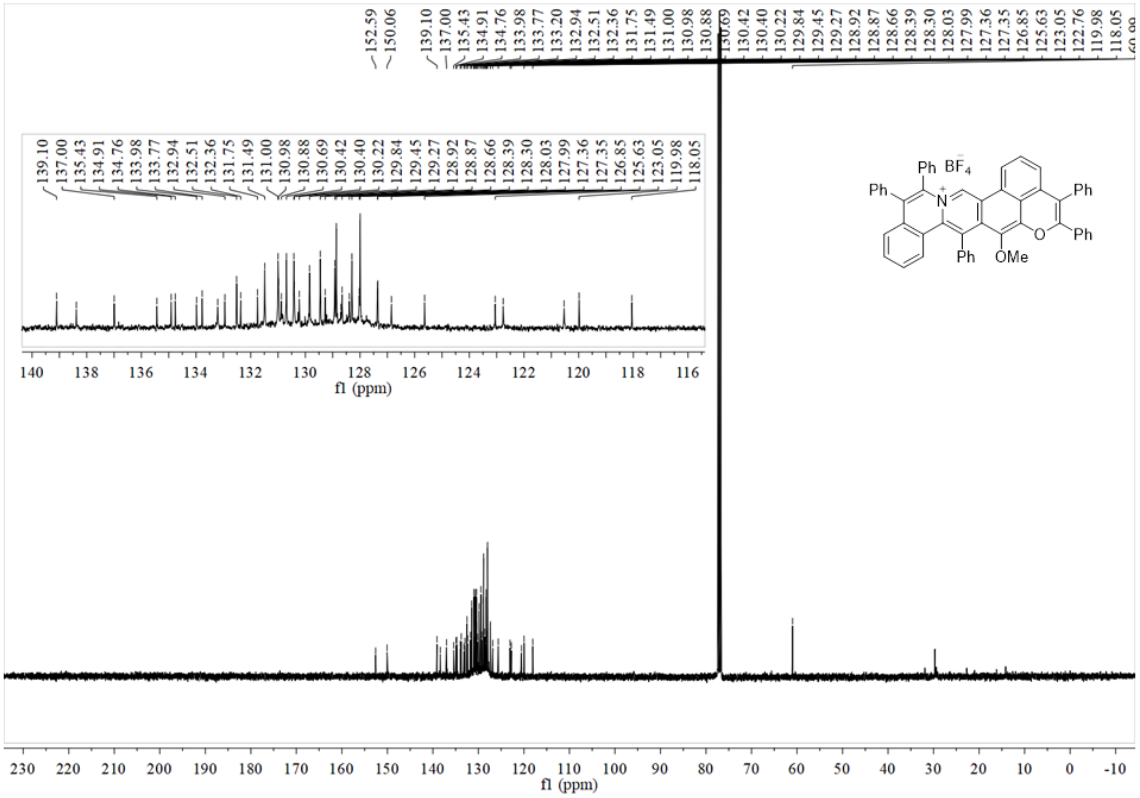
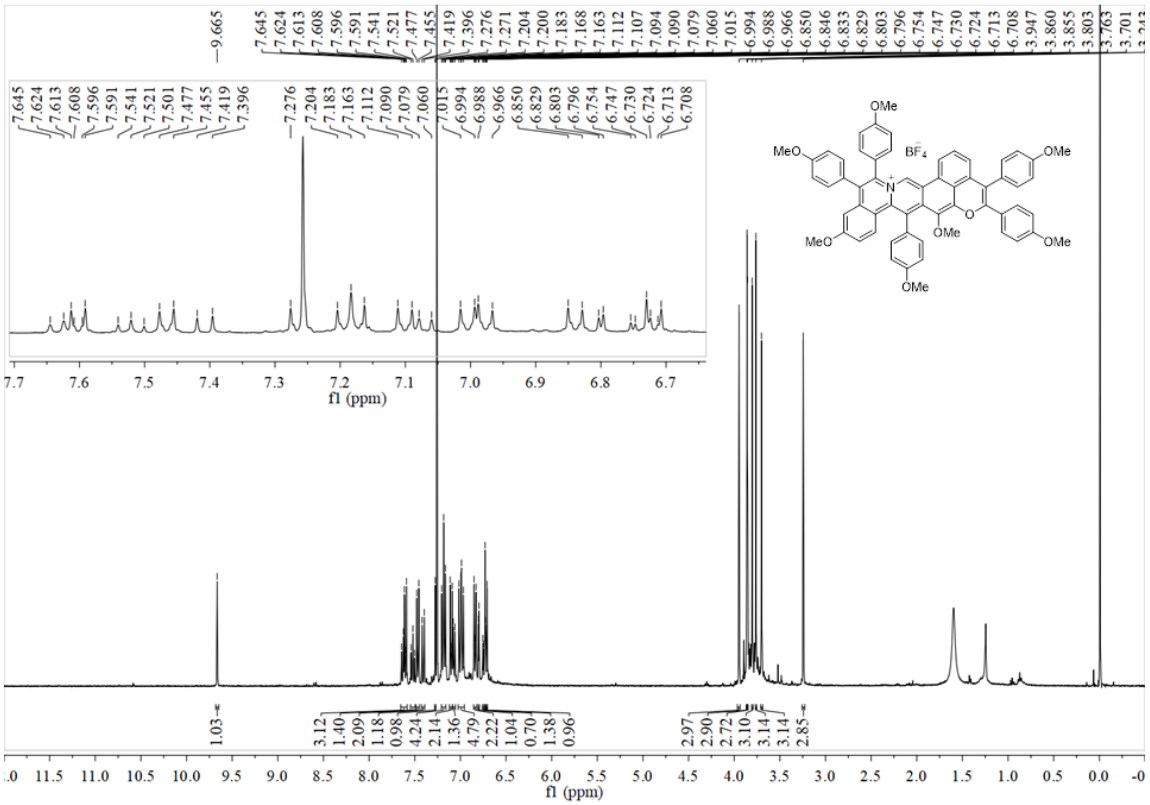
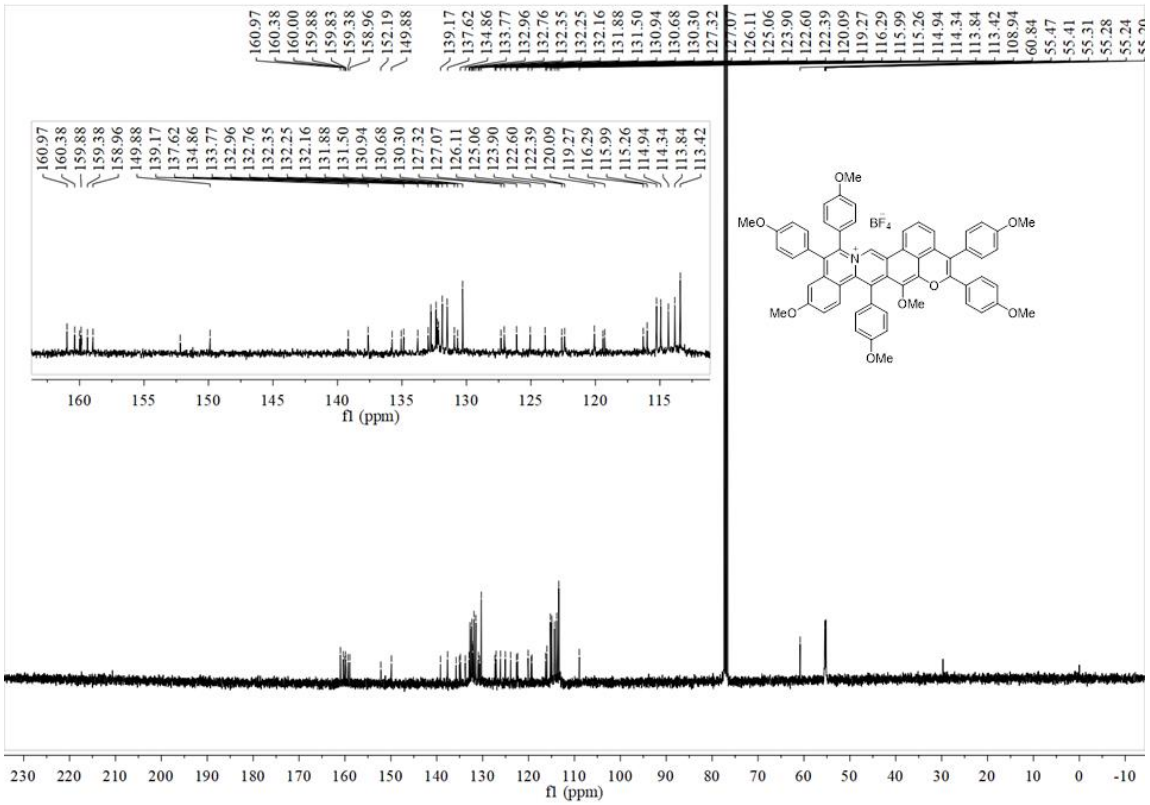
7.682
7.667
7.643
7.613
7.514
7.493
7.474
7.454
7.233
7.184
7.164
7.139
7.061
7.041
6.968
6.947
6.865
6.841
6.805
6.751
6.730
4.000
3.891
3.851
3.813
3.773
3.709
fl (ppm)
OMe
MeO
BF4
N
O

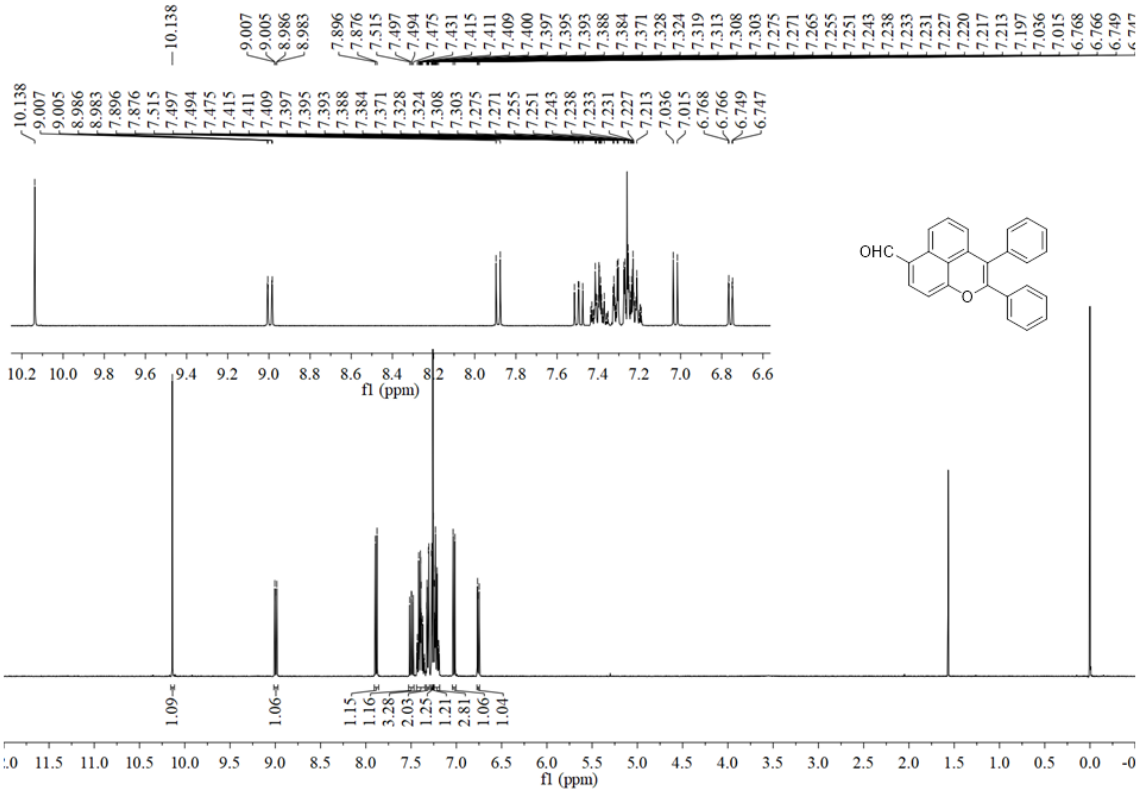

161.41
160.58
160.54
160.48
160.22
159.75
159.51
159.22
159.15
135.68
134.07
133.99
133.78
133.75
133.72
132.81
132.72
132.23
132.21
132.05
132.00
131.87
131.60
131.58
131.55
130.62
127.29
124.09
122.94
120.30
119.51
119.13
116.74
116.24
115.53
115.02
114.07
113.57
109.66
101.31
55.72
55.65
55.61
55.45
55.42
55.37
fl (ppm)
OMe
MeO
BF4
N
O


9.728
7.765
7.757
7.748
7.741
7.675
7.654
7.630
7.613
7.581
7.573
7.565
7.539
7.519
7.498
7.491
7.471
7.454
7.451
7.436
7.414
7.399
7.397
7.392
7.389
7.313
7.297
7.292
7.281
7.275
7.270
7.247
7.240
7.232
7.228
7.225
7.204
7.201
7.189
7.185
7.141
7.137
7.123
7.120
7.116
7.102
7.098
7.084
7.065
3.242
Ph
BF4
Ph
N
Ph
O
Ph
Ph
OMe
f1 (ppm)
0.94
1.92
1.06
1.87
2.90
1.25
1.38
2.39
4.98
1.02
4.91
2.14
2.22
1.11
1.15
2.30
1.36
2.72


152.59
150.06
139.10
137.00
135.43
134.91
134.76
133.98
133.77
133.20
132.94
132.51
132.36
131.75
131.49
131.00
130.98
130.88
130.69
130.42
130.40
130.22
129.84
129.45
129.27
128.92
128.87
128.66
128.39
128.30
128.03
127.99
127.36
127.35
126.85
125.63
123.05
122.76
119.98
118.05
Ph
BF4
Ph
N
Ph
O
Ph
Ph
OMe
f1 (ppm)


f1 (ppm)


f1 (ppm)


10.138
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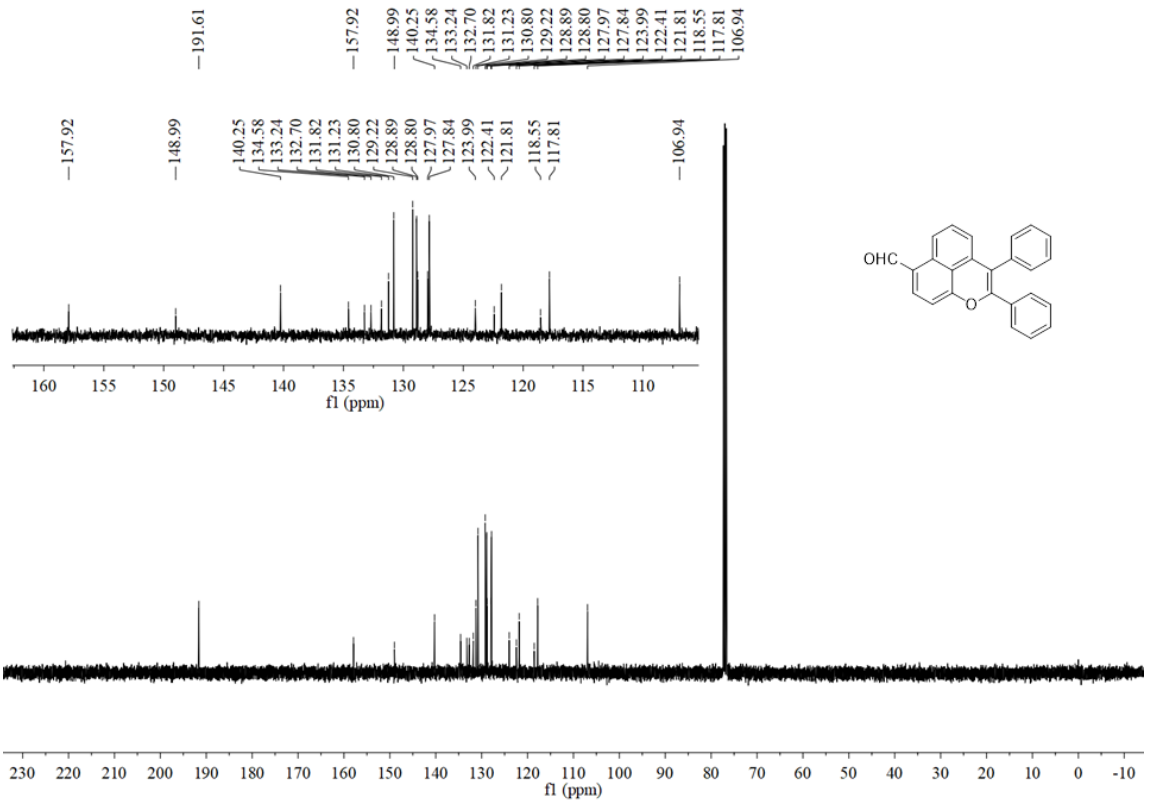
9.005
8.986
8.983
7.896
7.876
7.515
7.497
7.494
7.475
7.431
7.415
7.411
7.409
7.400
7.397
7.395
7.393
7.388
7.384
7.371
7.328
7.324
7.319
7.313
7.308
7.303
7.275
7.271
7.265
7.255
7.251
7.243
7.238
7.233
7.231
7.227
7.220
7.217
7.213
7.197
7.036
7.015
6.768
6.766
6.749
6.747
OHC
O
f1 (ppm)
1.09
1.06
1.15
1.16
3.28
2.03
1.25
1.21
2.81
1.06
1.04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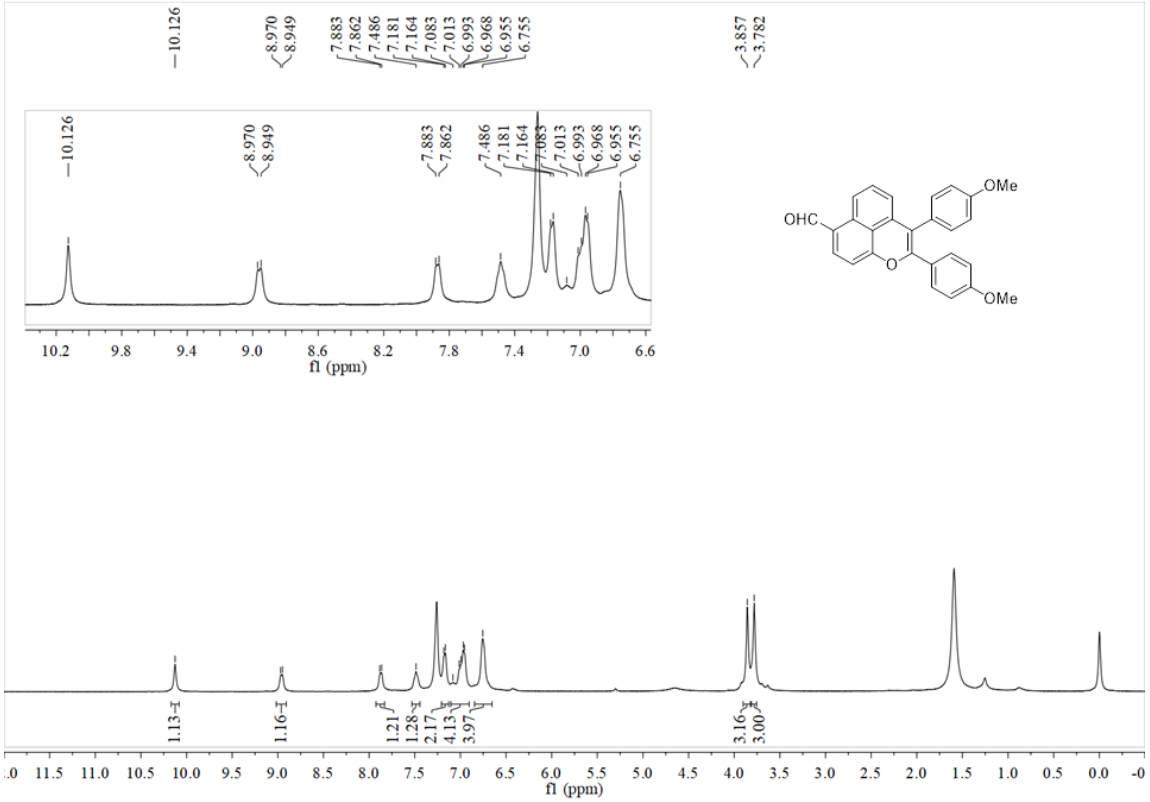
148.99
140.25
134.58
133.24
132.70
131.82
131.23
130.80
129.22
128.89
128.80
127.97
127.84
123.99
122.41
121.81
118.55
117.81
106.94
OHC
O
f1 (ppm)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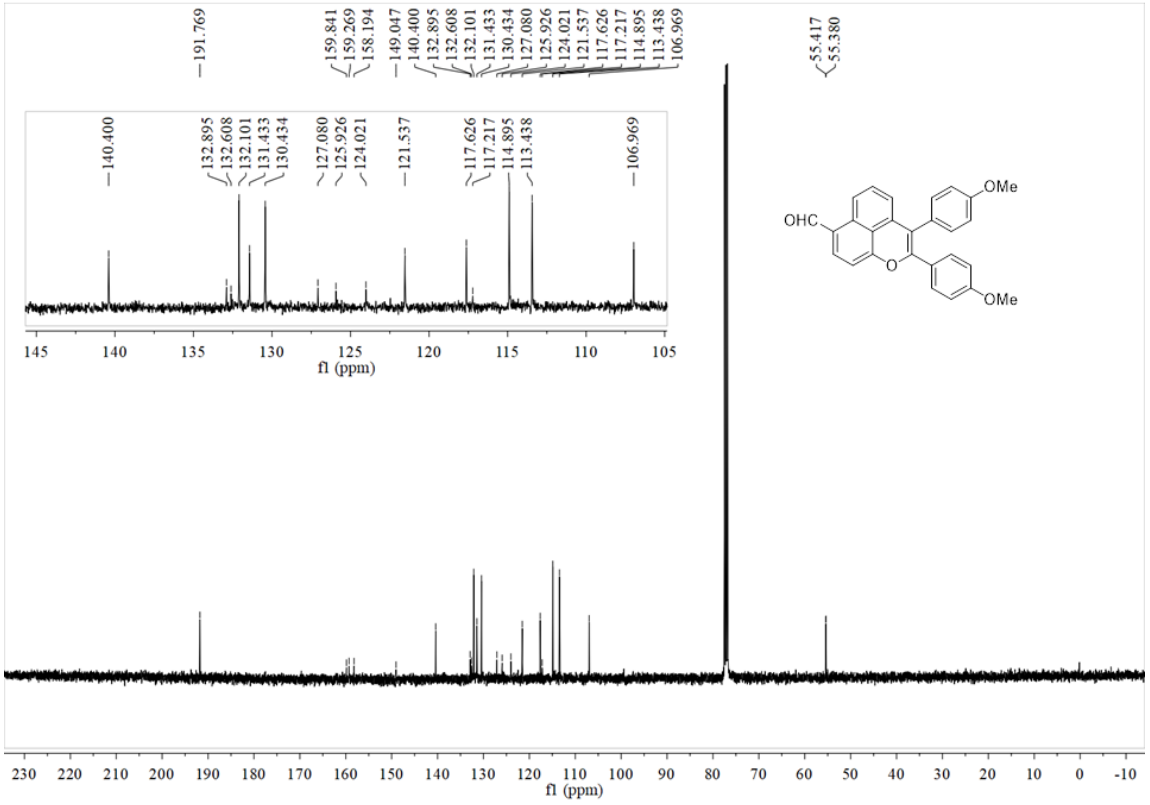
8.949
7.883
7.862
7.486
7.181
7.164
7.083
7.013
6.993
6.968
6.955
6.755
3.857
3.782
OHC
OMe
OMe
O
f1 (ppm)
1.13
1.16
1.21
1.28
2.17
4.13
3.97
3.16
3.00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159.269
158.194
149.047
140.400
132.895
132.608
132.101
131.433
130.434
127.080
125.926
124.021
121.537
117.626
117.217
114.895
113.438
106.969
55.417
55.380
OHC
OMe
OMe
O
f1 (ppm)