# Electronic Supplementary Information

# A Polycyclic Aromatic Hydrocarbon Diradical with pH-Responsive Magnetic Properties

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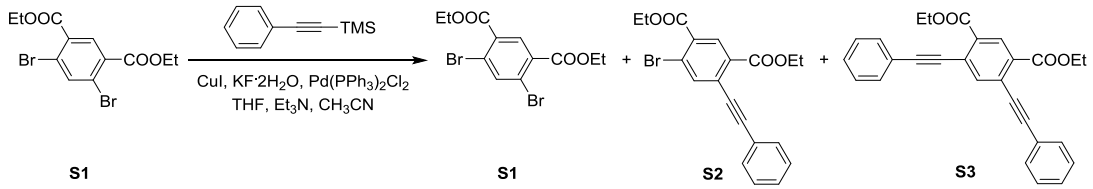
## I. Materials and general methods

**Materials.** Chemicals were used as received unless otherwise indicated. THF and toluene were distilled over appropriate drying reagents under $N_2$. Superdry dichloromethane (DCM) were purchased from J & K. Compounds **3**, **S1** and trimethyl(phenylethynyl)silane were synthesized according to previously described procedures.[1-3]

**General Methods.** Chemicals were used as received unless otherwise indicated. $^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance 400 (400 MHz) in $CDCl_3$ or benzene-$d_6$. Chemical shifts (δ) are reported in parts per million (ppm) with TMS (0 ppm) as the reference for the $^1$H NMR spectra and $CDCl_3$ (77.0 ppm) as the reference for the $^{13}$C NMR spectra. MALDI-TOF mass spectra were recorded on an Ab Sciex 5800 time-of-flight (TOF) mass spectrometer, and ESI mass spectra were recorded on a Bruker Apex IV Fourier transformation mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. THF and toluene were distilled over appropriate drying reagents under $N_2$. Continuous wave (cw) EPR measurements were performed on a Bruker E580 spectrometer using ER 4122 SHQE high sensitive EPR cavity. Oxford ESR900 cryostat was used for temperature control. The fitting of *IT* (*I* is the double integral of the observed ESR spectra) versus *T* of **BCHF1** using modified Bleaney-Bowers equation (1).[4]

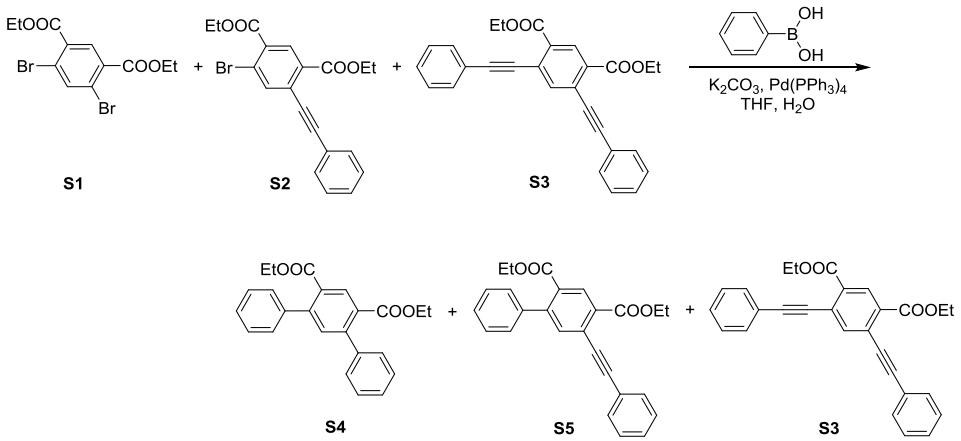
$$IT = \frac{C}{3+\exp(-\frac{2J}{k_B T})} \qquad (1)$$

## II. Synthesis details



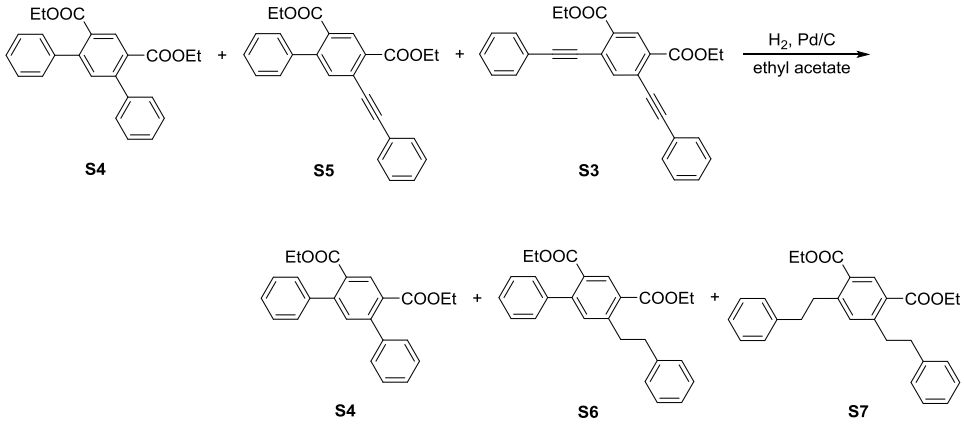

**Synthesis of S2:** A mixture of diethyl 4,6-dibromoisophthalate (**S1**, 5.0 g, 13 mmol), trimethyl(phenylethynyl)silane (2.3 g, 13 mmol), $Pd(PPh_3)_2Cl_2$ (0.19 g, 0.27 mmol), CuI (0.13 g, 0.68 mmol), and $KF{\cdot}2H_2O$ (2.7 g, 29 mmol) in a mixed solvent of THF (20 mL), $Et_3N$ (20 mL) and $CH_3CN$ (15 mL) was heated at 80 °C for 24 h under nitrogen atmosphere. The mixture was then diluted with dichloromethane and washed with saturated aqueous solution ammonium chloride. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography of silica gel (dichloromethane/petroleum ether = 1/1) to afford a mixture of **S1**, **S2** and **S3** as light yellow oil (5.1 g), which was used in the next step without further separation.

Characterization data of **S2**. $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.95 (s, 1H), 7.67 – 7.47 (m, 2H), 7.38 (m, 3H), 4.44 (m, 4H), 1.42 (m, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8, 139.3, 133.2, 131.8, 131.22, 130.7, 129.2, 128.4, 127.6, 125.2, 122.4, 97.9, 86.5, 62.0, 61.6, 14.3, 14.2. HRMS: Calcd. for $C_{20}H_{18}O_4Br^+$ [$M^+$]: 401.038; Found: 401.038.



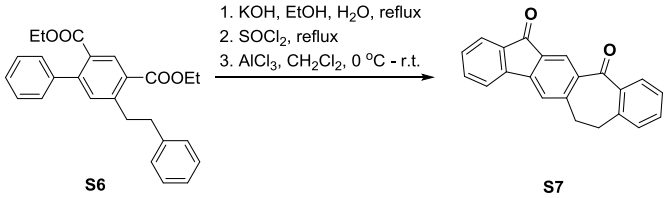

**Synthesis of S5:** A mixture of **S1**, **S2** and **S3** (5.0 g), phenylboronic acid (3.1 g, 25 mmol), $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol), and $K_2CO_3$ (8.6 g, 62 mmol) in THF (25 mL) and $H_2O$ (25 mL) was heated at 80 °C for 24 h under nitrogen atmosphere. The reaction mixture was then diluted with dichloromethane and washed with saturated aqueous solution ammonium chloride. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography of silica gel (dichloromethane/petroleum ether = 1/1) to afford a mixture of **S3**, **S4** and **S5** as light yellow oil (4.9 g), which was used in the next step without further separation.

Characterization data of **S5**. $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.66 (s, 1H), 7.60–7.53 (m, 2H), 7.46–7.30 (m, 8H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 145.5, 139.8, 136.3, 132.3, 131.8, 130.6, 130.3, 128.9, 128.4, 128.2, 128.1, 127.9, 126.3, 122.9, 96.6, 87.8, 61.5, 61.3, 14.4, 13.6. HRMS: Calcd. for $C_{26}H_{23}O_4^+$ ($[M+H]^+$): 399.159; Found: 399.159.




**Synthesis of S6:** A mixture of **S3**, **S4**, **S5** (4.9 g) and 5% Pd/C (0.50 g) in ethyl acetate (100 mL) and methanol (50 mL) was heated to reflux overnight under hydrogen atmosphere. Then the mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was purified with column chromatography of silica gel (dichloromethane/petroleum ether = 1/1) to afford **S6** as light yellow oil (2.80 g, 60% three steps). $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.41 – 7.35 (m, 3H), 7.28 (m, 2H), 7.25–7.18 (m, 5H), 7.15 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.33 (m, 2H), 2.94 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 167.8, 166.5, 146.7, 145.5, 141.5, 140.6, 133.8, 132.6, 129.0, 128.6, 128.4,

128.2, 128.0, 127.6, 126.0, 61.2, 61.0, 37.8, 36.6, 14.3, 13.6. HRMS: Calcd. for $C_{26}H_{26}O_4^+$ [$M^+$]: 402.182; Found: 402.182.



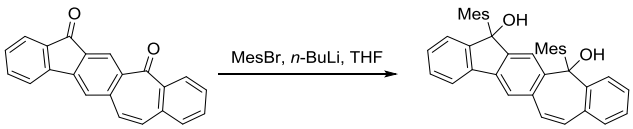

S6 S7

**Synthesis of S7:** To a solution of **S6** (1.51 g, 3.76 mmol) in ethanol (50 mL), a saturated aqueous solution of KOH (4.22 g, 75.2 mmol) was added slowly. The resultant mixture was heated at reflux overnight, cooled to room temperature and then evaporated under reduced pressure. HCl (1 M) was added until pH = 1, and the formed precipitate was filtered and washed with water. The solid was dried at 110 °C, and this crude diacid was dissolved in $SOCl_2$ (50 mL) and heated to reflux for 5 h. Upon removal of the excess $SOCl_2$, the resultant mixture was dissolved in $CH_2Cl_2$ (50 mL), to which $AlCl_3$ (5.01 g, 37.6 mmol) was added slowly at 0 °C. The resultant solution was then stirred at room temperature overnight and then 1 M HCl was added at 0 °C to quench the reaction. The reaction mixture was extracted with dichloromethane 3 times, and the organic layers were combined and washed with saturated brine. The solution was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography of silica gel (dichloromethane) to afford **S7** as a yellow solid (782 mg, 67%). $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.06 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.54 (td, *J* = 7.4, 1.0 Hz, 1H), 7.46 (m, 1H), 7.40 (s, 1H), 7.37 (td, *J* = 7.6, 1.0 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 1H), 3.33 – 3.21 (m, 4H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 193.8, 192.3, 149.4, 147.2, 143.0, 141.6, 139.3, 137.8, 135.1, 134.7, 132.6, 132.6, 130.8, 130.0, 129.3, 126.9, 126.8, 124.4, 121.2, 121.0, 35.6, 34.4. MALDI-TOF-MS: Calcd. for $C_{22}H_{15}O^+$ ([M+H]$^+$): 311.1; Found: 311.1. Elem. Anal.: Calcd. for $C_{22}H_{14}O$: C, 85.14; H, 4.55. Found: C, 84.80; H, 4.59.


S7 1

**Synthesis of 1:** A mixture of **S7** (300 mg, 0.97 mmol) and BPO (12 mg, 0.050 mmol) in $CCl_4$ (40 mL) was heated to reflux, to which NBS (147 mg, 1.07 mmol) was added slowly. The mixture was heated at reflux for 5 h. Upon removal of $CCl_4$, the resultant mixture was dissolved in DMF (20 mL), and DBN (144 mg, 1.16 mmol) was added slowly to it before the mixture was heated at 80 °C for 6 h. Then the mixture was cooled to room temperature, quenched with diluted HCl and extracted in dichloromethane. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography of silica gel (dichloromethane) to afford **1** as a yellow solid (242 mg, 81%). $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.66–7.54 (m, 4H), 7.41 (td, *J* = 7.4, 0.9 Hz, 1H), 7.19 (d, *J* = 12.1 Hz, 1H), 7.10 (d, *J* = 12.1 Hz, 1H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 192.0, 191.8, 146.3, 143.0, 140.5, 139.4, 138.6, 135.5, 134.9, 134.5, 134.4, 134.0, 132.2, 131.2, 130.9, 130.3, 130.3, 129.8, 127.1,

124.7, 122.1, 121.3. HRMS: Calcd. for $C_{22}H_{13}O_2^+$ ([M+H]$^+$): 309.091; Found: 309.091. Elem. Anal.: Calcd. for $C_{22}H_{12}O_2$: C, 85.70; H, 3.92. Found: C, 85.76; H, 3.85.

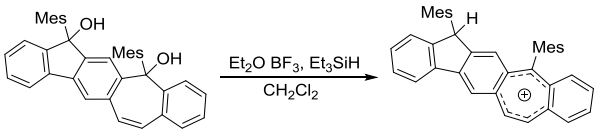



1 2

**Synthesis of 2:** To a solution of 2-bromo-1,3,5-trimethylbenzene (MesBr, 399 mg, 2.00 mmol) in THF (10 mL) under nitrogen atmosphere at -78 °C was added dropwise n-BuLi (2.4 M in hexanes, 0.70 mL, 1.7 mmol), and the mixture was kept at -78 °C for another 1 hour. The lithiate was transferred via syringe to a solution of **1** (103 mg, 0.334 mmol) in THF (15 mL) cooled at -78 °C under nitrogen atmosphere. The reaction mixture was allowed to react at room temperature for 3 h, before quenched with diluted HCl and extracted in $Et_2O$. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography over silica gel (dichloromethane/petroleum ether = 2/1) to afford **2** (two diastereomers) as a white solid.

Characterization data of diastereomer I (17 mg, 9.3%). $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.51 (s, 1H), 7.42 (m, 1H), 7.31 (m, 1H), 7.24 – 7.16 (m, 4H), 7.01 (s, 1H), 6.78 (q, *J* = 11.4 Hz, 2H), 6.65 (s, 1H), 6.49 (d, *J* = 6.9 Hz, 2H), 2.96 (s, 3H), 2.37 (s, 1H), 2.28 (s, 3H), 2.12 (s, 3H), 1.96 (s, 1H), 1.42 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 152.0, 150.9, 145.8, 144.5, 139.0, 138.9, 137.7, 137.5, 137.4, 137.3, 136.4, 136.2, 135.9, 135.3, 133.0, 132.3, 132.0, 131.5, 131.2, 130.6, 130.1, 128.7, 128.5, 128.3, 127.6, 125.7, 124.0, 123.6, 120.2, 119.5, 119.1, 86.6, 79.2, 29.7, 25.9, 23.1, 22.2, 20.9, 20.6, 20.4. HRMS: Calcd. for $C_{40}H_{36}NaO_2^+$ ([M+Na]$^+$): 571.261; Found: 571.261.

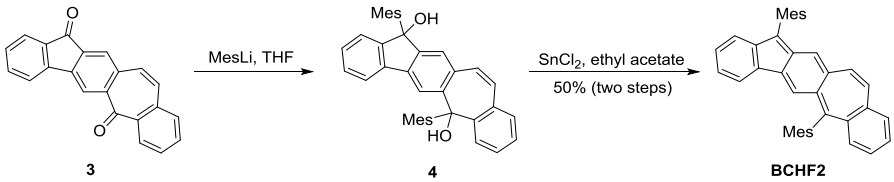
Characterization data of diastereomer II (128 mg, 70%).$^1$H-NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.51 (s, 1H), 7.37 (m, 1H), 7.32 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.16 (m, 3H), 6.99 (s, 1H), 6.83 – 6.68 (m, 2H), 6.51 (s, 3H), 3.02 (s, 3H), 2.47 (s, 1H), 2.23 (s, 3H), 2.18 (s, 1H), 2.13 (s, 3H), 1.49 (s, 3H), 1.32 (s, 3H), 0.98 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 151.6, 151.1, 146.2, 144.4, 139.2, 138.8, 137.7, 137.6, 137.5, 136.9, 136.4, 136.3, 135.9, 135.1, 132.7, 132.2, 132.1, 131.4, 131.4, 130.7, 130.7, 130.0, 128.8, 128.4, 128.2, 127.5, 125.6, 124.4, 123.7, 120.1, 119.5, 119.5, 86.4, 79.1, 25.8, 22.7, 22.1, 21.8, 20.5, 20.4. HRMS: Calcd. for $C_{40}H_{36}NaO_2^+$ ([M+Na]$^+$): 571.261; Found: 571.261.




2 BCHF1+H$^+$

**Synthesis of BCHF1+H$^+$:** To a solution of **2** (30 mg, 0.055 mmol) and $Et_3SiH$ (87 µL, 0.55 mmol) in dichloromethane (5 mL) was added $Et_2O{\cdot}BF_3$ (69 µL, 0.55 mmol) at 0 °C, and the mixture was kept at 0 °C for 1 h. The reaction mixture was then diluted with dichloromethane and washed with saturated $NaHCO_3$, water and saturated brine. The organic layer was then dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure to afford **BCHF1+H$^+$** as a red solid (28 mg, counter ion was unknown). $^1$H-NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 11.4 Hz, 1H), 9.36 (s, 1H), 9.21 (d, *J* = 11.4 Hz, 1H), 8.75 (d, *J* = 8.1 Hz, 1H), 8.51 (d, *J* = 6.5 Hz, 1H), 8.46 (t, *J* = 7.4 Hz, 1H), 8.31 (d,

*J* = 8.8 Hz, 1H), 8.04 (t, *J* = 7.7 Hz, 1H), 7.65 (s, 1H), 7.63 – 7.59 (m, 2H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.10 (s, 1H), 6.95 (s, 1H), 6.79 (s, 1H), 6.62 (s, 1H), 5.66 (s, 1H), 2.44 (s, 6H), 2.32 (s, 3H), 1.63 (s, 3H), 1.32 (s, 3H), 0.95 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 179.2, 155.0, 153.5, 152.4, 147.8, 145.1, 144.8, 144.0, 140.0, 139.4, 137.8, 137.6, 137.4, 137.4, 137.3, 136.6, 136.5, 136.3, 134.9, 134.6, 133.8, 133.1, 131.0, 130.9, 130.5, 129.0, 128.6, 126.8, 126.00, 125.0, 49.9, 29.6, 21.3, 21.0, 20.8, 19.9, 19.4, 19.3. HRMS (ESI): Calcd. for $C_{40}H_{35}^+$ ([$M^+$]): 515.273; Found: 515.272.




3 4 BCHF2

**Synthesis of BCHF2:** To a solution of 2-bromo-1,3,5-trimethylbenzene (MesBr, 213 mg, 1.07 mmol) in THF (10 mL) under nitrogen atmosphere at -78 °C was added 2.4 M n-BuLi in hexanes (0.37 mL, 0.89 mmol), and the mixture was kept at -78 °C for another 1 hour. The lithiate was transferred via cannula to a solution of **3** (55 mg, 0.18 mmol) in THF (15 mL) cooled at -78 °C under nitrogen atmosphere. The reaction mixture was allowed to react at room temperature for 3 h, before quenched with diluted HCl and extracted in $Et_2O$. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The residue was transferred into a Schlenk tube along with $SnCl_2$ (135 mg, 0.712 mmol) and ethyl acetate (20 mL) and heated at 80 °C under nitrogen atmosphere for 5 h. The reaction mixture was then diluted with dichloromethane and washed with diluted HCl. The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified with column chromatography over silica gel (dichloromethane/petroleum ether = 1/5) to afford **BCHF2** as a green solid (44 mg, 50%). $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 7.09 – 6.94 (m, 6H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 12.0 Hz, 2H), 6.40 (d, *J* = 12.4 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.06 (s, 6H), 2.04 (s, 6H). $^1$H-NMR (400 MHz, Benzene-$d_6$) δ 7.73 (s, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.14 (m, 2H), 7.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.97 – 6.82 (m, 8H), 6.64 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 6.36 (d, *J* = 12.3 Hz, 1H), 6.18 (d, *J* = 12.3 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 2.14 (s, 6H), 2.01 (s, 6H). EI HR-MS: Calcd. for $C_{40}H_{34}^+$ ($M^+$): 514.2661; Found: 514.2666.

## III. Acid/base response experiments

The absorption and emission spectra of **BCHF1+H$^+$**/ **BCHF1** were recorded using a sealed quartz cell due to the unstability of **BCHF1.** The DBU/TFA vapor-responsive absorption experiments with thin films were performed using a sealed quartz cell connected to a branch tube for storing DBU or TFA droplets. A dilute solution (0.2 mL) of **BCHF1+H$^+$** in $CH_2Cl_2$ ($10^{-4}$ M) was injected to the cell and evaporated under vacuum to obtain a dark red film of **BCHF1+H$^+$**. Degassed DBU (50 μL) was added to the branched tube cooled with liquid nitrogen. The entire apparatus was pumped under vacuum and then warmed to room temperature such as to introduce DBU vapor to the film. The film turned green gradually in 10 minutes and the absorption spectrum was collected. Then degassed TFA vapor was introduced in a similar fashion. The film turned back to dark red in only 1 minute, due to the higher vapor pressure of TFA.

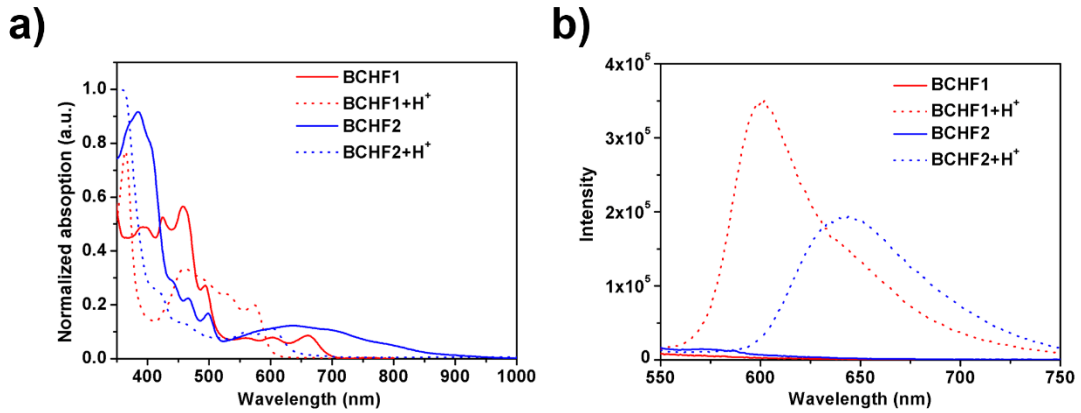



**Fig. S1** (a) The absorption and (b) emission spectra of **BCHF1** (**BCHF1+H$^+$** treated with DBU) and **BCHF2** in comparison to **BCHF1+H$^+$** and **BCHF2+H$^+$** (**BCHF2** treated with TFA) in $CH_2Cl_2$ solution.

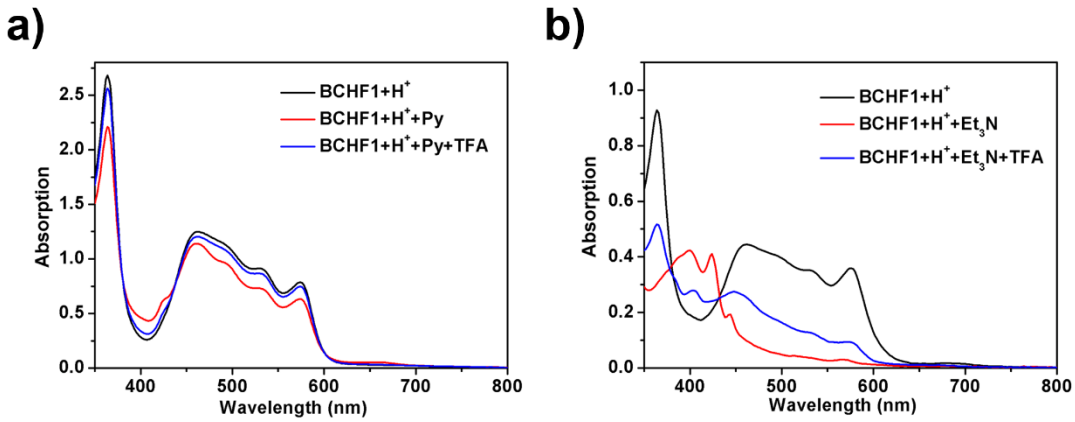



**Fig. S2** (a) Absorption spectra of **BCHF1+H$^+$** in $CH_2Cl_2$ with sequential additions of excess pyridine-$d_5$ (Py, 1000 equiv.) and TFA. (b) Absorption spectra of **BCHF1+H$^+$** in $CH_2Cl_2$ with sequential additions of excess $Et_3N$ (500 equiv.) and TFA.

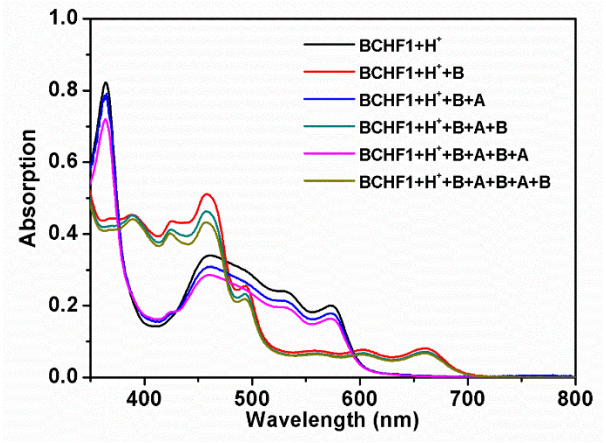



**Fig. S3** Absorption spectra of **BCHF1+H$^+$** in $CH_2Cl_2$ upon sequential additions of DBU (B, 2 equiv. for each addition) and TsOH (A, 2 equiv. for each addition).

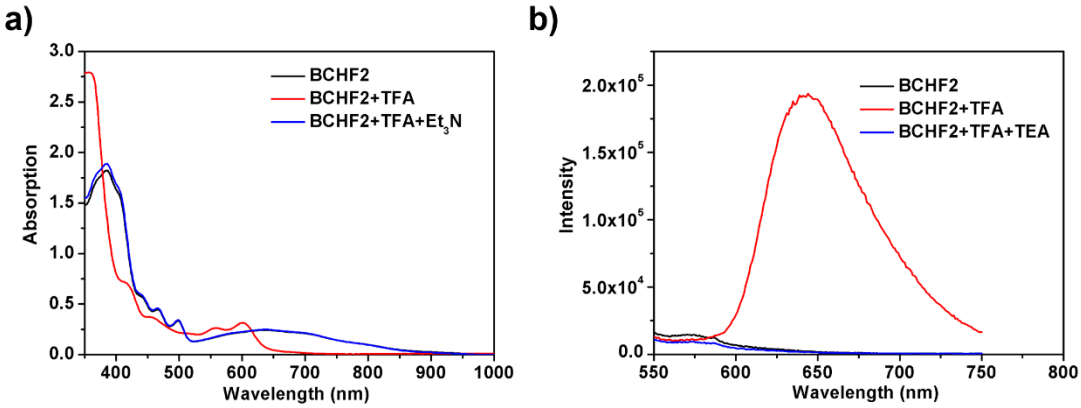



**Fig. S4** Absorption (a) and emission (b) spectra of **BCHF2** in $CH_2Cl_2$ with sequential additions of excess TFA (500 equiv.) and $Et_3N$ (TEA).

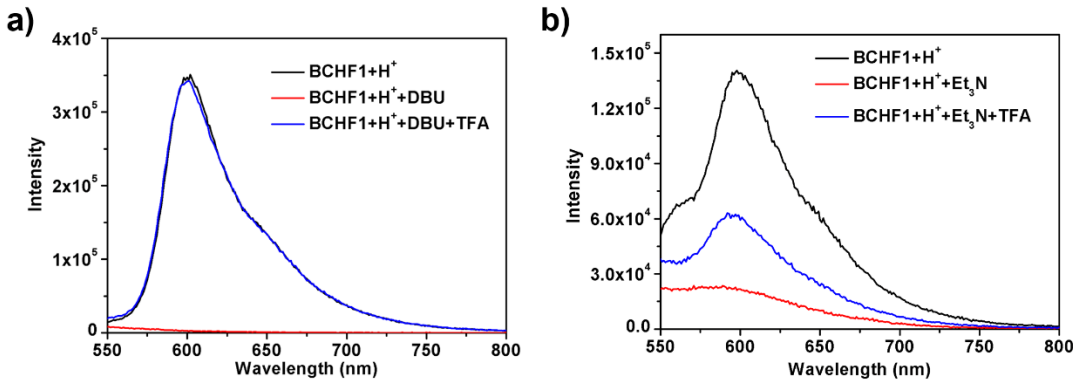



**Fig. S5** Emission spectra of **BCHF1+H$^+$** in $CH_2Cl_2$ with sequential additions of DBU (a, 2 equiv.) or $Et_3N$ (b, 500 equiv.) followed by excessive TFA.

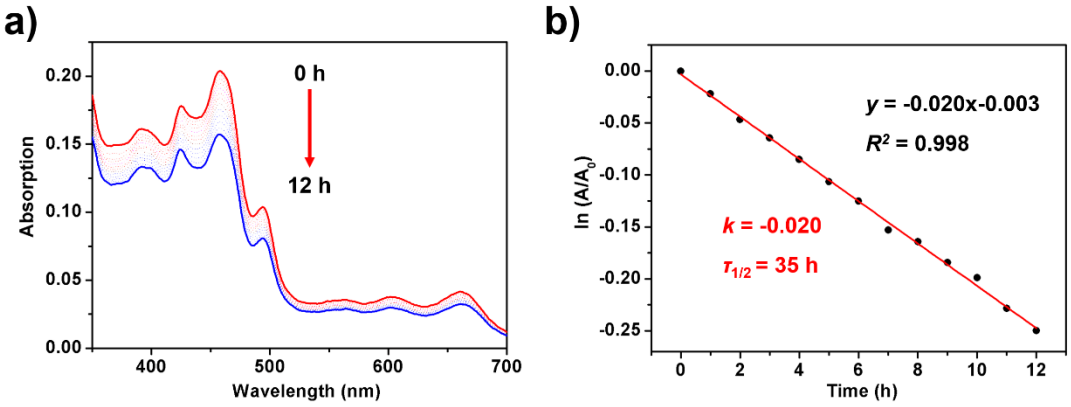



**Fig. S6** (a) The absorption decay of **BCHF1** (**BCHF1+H$^+$** treated with DBU) in $CH_2Cl_2$ under $N_2$ atmosphere; (b) data fitting with the first-order kinetics, offering a decomposition rate constant of $k$ = -0.020 $h^{-1}$ corresponding to a half-life time of $\tau_{1/2}$ = 35 h.

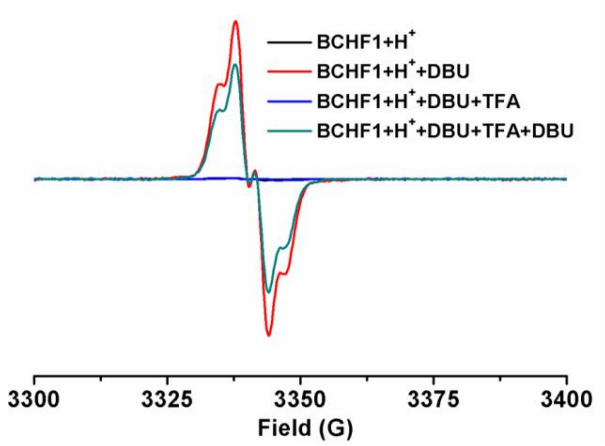



**Fig. S7** EPR spectra of **BCHF1+H$^+$** in $CH_2Cl_2$ upon sequential additions of DBU (2 equiv.), TFA (20 equiv.), and then DBU (20 equiv.) again.

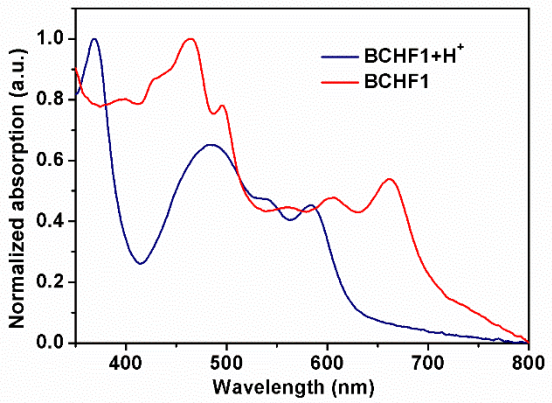



**Fig. S8** Normalized absorptions of **BCHF1+H$^+$** and **BCHF1** in the thin film state (obtained from a DBU-treated solution of **BCHF1+H$^+$** in $CH_2Cl_2$ by evaporation).

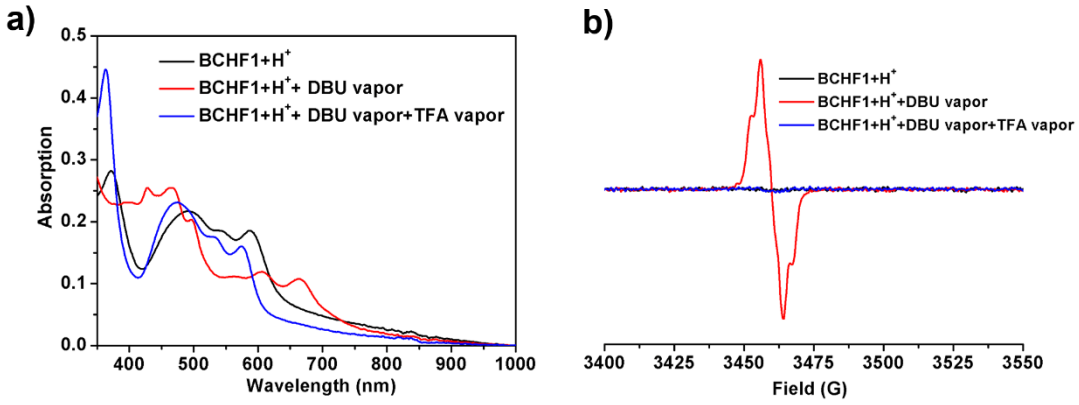



**Fig. S9** (a) Absorption and (b) EPR spectra of **BCHF1+H$^+$** films upon exposure to DBU vapor followed by TFA vapor.

## IV. DFT calculations

Theoretical calculations were performed with the Gaussian09 program suite.[5] The molecular geometry optimization were carried out using (U)B3LYP method at 6-311G(d) level. Frequency analysis verified that all optimized geometries do not contain any negative frequencies. And the singlet-triplet energy gap ($\Delta E_{S\text{-}T}$) was calculated according to the following equation proposed by Yamaguchi:[6-8]

$$\Delta E_{S-T} = 2J = \frac{2(E_{BS} - E_T)}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}}$$

where $J$ represents the intramolecular exchange interaction in the diradicals, $E_{BS}$ and $E_T$ represent the total energy of the calculated broken-symmetry singlet state and triplet state, $\langle S^2 \rangle_T$ and $\langle S^2 \rangle_{BS}$ represent the total spin angular momentum of the calculated broken-symmetry triplet and singlet states.

The open-shell character of the molecules was characterized with the spin-projected unrestricted Hartree-Fock (PUHF) method, which proves to be an effective way to display the diradical character of molecules.[9] The diradical character ($y_0$) was calculated according to Yamaguchi's scheme:[10]

$$y_0 = 1 - \frac{2T}{1 + T^2}$$

$$T = \frac{n_{HONO} - n_{LUNO}}{2}$$

where $n_{HONO}$ is the occupation number of the highest occupied natural orbital (HONO), and $n_{LUNO}$ is the occupation number of the lowest unoccupied natural orbital (LUNO).

Time-dependent DFT (TD-DFT) calculations are performed at the B3LYP/6-311G(d) level of theory. The UV-Vis spectrum calculation and the transition orbital analysis were performed using a multifunctional wavefunction analyser (Multiwfn).[11]

**Table S1** Summary of calculation results.

| | **BCHF1** | **BCHF2** | **BCHF1+H$^+$** | **BCHF2+H$^+$** |
|---|---|---|---|---|
| $E_{BS}$ (Hartree) | -846.905527 | -846.924823 | – | – |
| $E_T$ (Hartree) | -846.902516 | -846.894816 | – | – |
| $\langle S^2 \rangle_{BS}$ | 0.0000 | 0.0000 | – | – |
| $\langle S^2 \rangle_T$ | 2.0502 | 2.0365 | – | – |
| $\Delta E_{S\text{-}T}$ (kcal/mol) | -1.84 | -18.49 | – | – |
| $y_0$ | 0.44 | 0.28 | – | – |
| Dipole (Debye) | 4.75 | 2.76 | 3.57 | 4.71 |

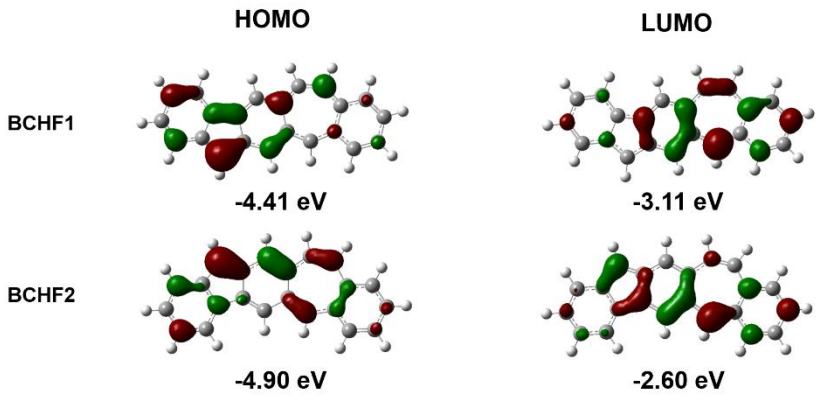



**Fig. S10** Frontier molecular orbitals of **BCHF1** and **BCHF2** optimized at B3LYP/6-311G(d) level.

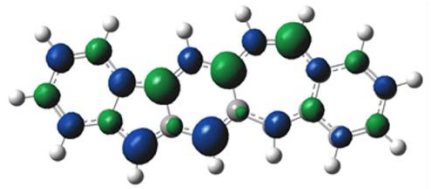


**Fig. S11** Spin density of **BCHF1** optimized at UB3LYP/6-311G(d) level.

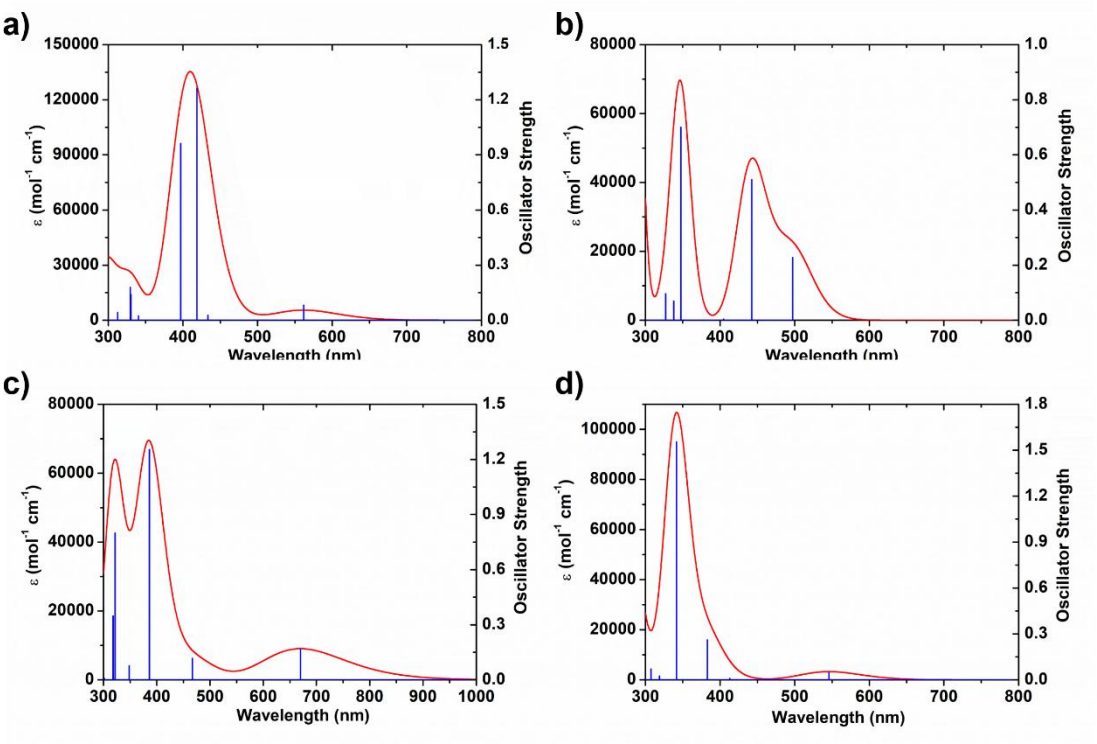



**Fig. S12** Calculated UV-Vis spectra of (a) **BCHF1**, (b) **BCHF1+H$^+$**, (c) **BCHF2** and (d) **BCHF2+H$^+$** at B3LYP/6-311G(d) level.

**Table S2** Selected TD-DFT calculated wavelength, oscillator strength and compositions of major electronic transitions of **BCHF1**.

| Wavelength (nm) | Oscillator strength | Major contributions |
|---|---|---|
| 561.42 | 0.0817 | HOMO → LUMO+1 (67%), HOMO-1 → LUMO (30%) |
| 418.50 | 1.2627 | HOMO-1 → LUMO (41%), HOMO → LUMO+2 (35%) |
| 396.81 | 0.9620 | HOMO → LUMO+2 (61%), HOMO-1 → LUMO (26%) |
| 330.05 | 0.1396 | HOMO-1 → LUMO+1 (41%), HOMO → LUMO+3 (35%) |
| 329.18 | 0.1782 | HOMO → LUMO+3 (48%), HOMO-1 → LUMO+1 (30%) |

**Table S3** Selected TD-DFT calculated wavelength, oscillator strength and compositions of major electronic transitions of **BCHF1+H**$^{+}$.

| Wavelength (nm) | Oscillator strength | Major contributions |
|---|---|---|
| 496.95 | 0.2272 | HOMO → LUMO (88%) |
| 442.14 | 0.5102 | HOMO-1 → LUMO (83%) |
| 347.44 | 0.7006 | HOMO → LUMO+1 (86%) |
| 337.79 | 0.0693 | HOMO-3 → LUMO (70%), HOMO-1 → LUMO+1 (27%) |
| 326.87 | 0.0957 | HOMO-1 → LUMO+1 (44%), HOMO-4 → LUMO (37%) |

**Table S4** Selected TD-DFT calculated wavelength, oscillator strength and compositions of major electronic transitions of **BCHF2**.

| Wavelength (nm) | Oscillator strength | Major contributions |
|---|---|---|
| 669.51 | 0.1679 | HOMO → LUMO (91%), HOMO → LUMO+1 (7%) |
| 466.63 | 0.1174 | HOMO → LUMO+1 (70%), HOMO-1 → LUMO (27%) |
| 386.04 | 1.2537 | HOMO-1 → LUMO (67%), HOMO → LUMO+1 (21%) |
| 321.60 | 0.7994 | HOMO-1 → LUMO+1 (78%) |
| 317.91 | 0.3480 | HOMO-3 → LUMO (59%), HOMO → LUMO+3 (25%) |

**Table S5** Selected TD-DFT calculated wavelength, oscillator strength and compositions of major electronic transitions of **BCHF2+H**$^{+}$.

| Wavelength (nm) | Oscillator strength | Major contributions |
|---|---|---|

| | | |
|---|---|---|
| 545.45 | 0.0488 | HOMO → LUMO (98%) |
| 466.63 | 0.1174 | HOMO → LUMO+1 (70%), HOMO-1 → LUMO (27%) |
| 382.78 | 0.2622 | HOMO-3 → LUMO (41%), HOMO → LUMO+1 (34%) |
| 341.40 | 1.5534 | HOMO-3 → LUMO (44%), HOMO → LUMO+1 (32%) |
| 307.24 | 0.0710 | HOMO-2 → LUMO+1 (50%), HOMO-4 → LUMO (46%) |

## V. X-ray crystallographic analysis

The single crystal of **[BCHF1+H$^+$][BF$_4^-$]** was obtained by slow diffusion of hexane into the DCM solution. The data of single crystal of **[BCHF1+H$^+$][BF$_4^-$]** were collected on a XtaLAB Synergy R, HyPix diffractometer. The crystal was kept at 170.00(10) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

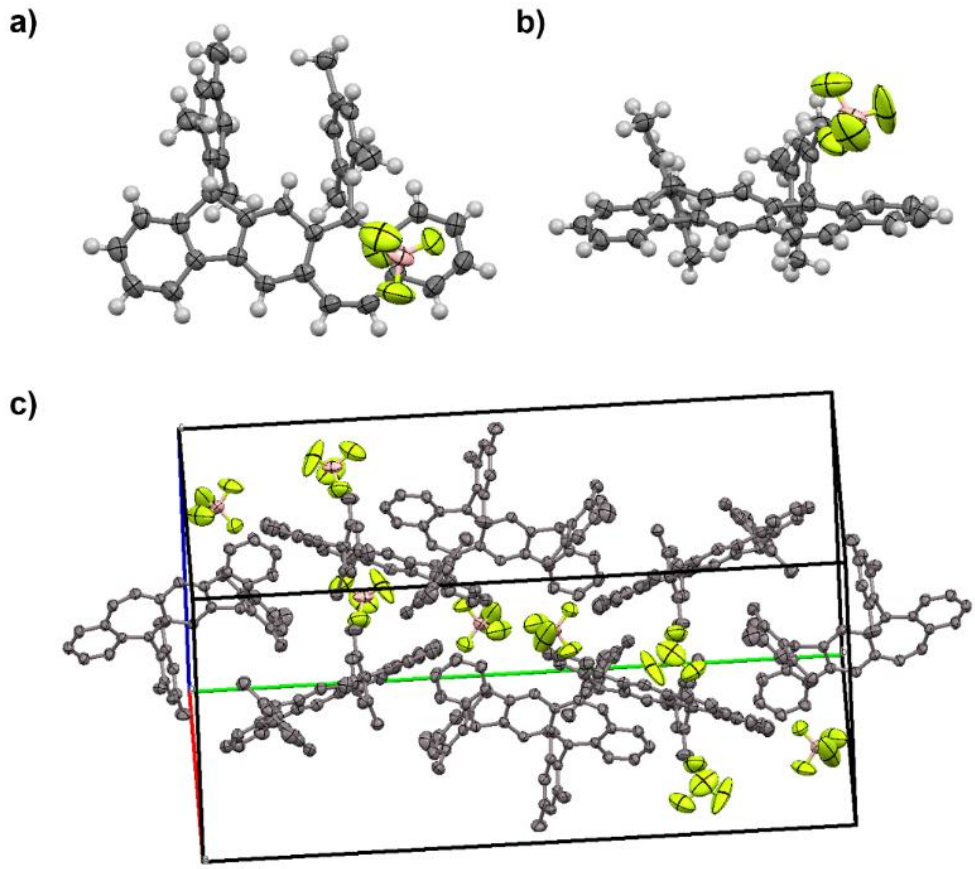



**Fig. S13** Front view (a), side view (b) and unit cell (c) of single crystal of **[BCHF1+H$^+$][BF$_4^-$]**.

**Table S6** Crystal data and structure refinement for **[BCHF1+H$^+$][BF$_4^-$]**.

| | |
|---|---|
| Identification code | **[BCHF1+H$^+$][BF$_4^-$]** |
| Empirical formula | $C_{40}H_{35}BF_4$ |
| Formula weight | 602.49 |
| Temperature/K | 170.00(10) |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 11.99110(10) |
| b/Å | 34.2594(3) |
| c/Å | 15.9758(2) |
| α/° | 90 |
| β/° | 107.6140(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 6255.29(11) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.280 |
| $\mu$/mm$^{-1}$ | 0.723 |
| F(000) | 2528.0 |
| Crystal size/mm$^3$ | 0.3 × 0.15 × 0.05 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.158 to 151.13 |
| Index ranges | -15 ≤ h ≤ 13, -38 ≤ k ≤ 42, -17 ≤ l ≤ 20 |
| Reflections collected | 46687 |
| Independent reflections | 12449 [$R_{int}$ = 0.0322, $R_{sigma}$ = 0.0298] |
| Data/restraints/parameters | 12449/0/823 |
| Goodness-of-fit on F$^2$ | 1.066 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0892, w$R_2$ = 0.2649 |
| Final R indexes [all data] | $R_1$ = 0.1045, w$R_2$ = 0.2848 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.02/-0.81 |

**Table S7** Fractional atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for **[BCHF1+H$^+$][BF$_4^-$]**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| F1 | 8826(4) | 5746.4(13) | 6505(2) | 137.0(15) |
| F2 | 9570(5) | 5364.8(17) | 7552(7) | 285(5) |
| F3 | 7763(5) | 5260.0(16) | 6880(3) | 196(3) |
| F4 | 8239(4) | 5777.0(9) | 7651(2) | 118.1(12) |
| B1 | 8582(5) | 5532.4(13) | 7131(4) | 76.1(14) |
| F1A | 8977(5) | 7291.3(18) | 6253(3) | 182(2) |
| F2A | 7189(4) | 7392.2(13) | 5820(3) | 141.8(15) |
| F3A | 7871(7) | 7011.6(15) | 5013(3) | 246(4) |
| F4A | 8195(4) | 7624.8(16) | 5034(3) | 159.3(18) |
| B1A | 8090(4) | 7303.9(19) | 5524(3) | 77.2(14) |
| C1 | 11704(2) | 5873.9(8) | 5657.9(18) | 42.6(6) |

| | | | | |
|---|---|---|---|---|
| C2 | 11726(3) | 6252.9(9) | 5356(2) | 49.7(7) |
| C3 | 11685(3) | 6310.9(9) | 4486(2) | 54.7(8) |
| C4 | 11645(3) | 5993.5(10) | 3930(2) | 54.5(8) |
| C5 | 11612(3) | 5615.5(9) | 4216.5(19) | 49.9(7) |
| C6 | 11635(3) | 5559.6(8) | 5089.7(18) | 42.3(6) |
| C7 | 11616(2) | 5200.8(8) | 5573.9(17) | 40.2(6) |
| C8 | 11506(3) | 4817.9(8) | 5305.1(17) | 41.6(6) |
| C9 | 11503(2) | 4514.2(8) | 5896.6(17) | 38.7(6) |
| C10 | 11298(3) | 4139.9(8) | 5503.1(18) | 44.6(6) |
| C11 | 11219(3) | 3783.7(8) | 5853.2(18) | 45.5(6) |
| C12 | 11454(2) | 3664.6(8) | 6739.2(18) | 39.8(6) |
| C13 | 11350(3) | 3259.5(8) | 6858(2) | 47.6(7) |
| C14 | 11677(3) | 3089.5(8) | 7672(2) | 49.4(7) |
| C15 | 12137(3) | 3323.2(9) | 8410.3(19) | 48.0(7) |
| C16 | 12193(3) | 3718.3(8) | 8325.5(19) | 45.7(6) |
| C17 | 11828(2) | 3913.5(7) | 7498.7(17) | 37.2(5) |
| C18 | 11825(2) | 4332.3(7) | 7510.7(16) | 35.6(5) |
| C19 | 11666(2) | 4604.9(7) | 6816.9(16) | 36.5(5) |
| C20 | 11719(2) | 5011.5(8) | 7050.3(17) | 37.9(5) |
| C21 | 11704(2) | 5298.5(8) | 6457.0(17) | 38.5(6) |
| C22 | 11730(3) | 5738.2(8) | 6568.3(17) | 41.0(6) |
| C23 | 12716(3) | 5916.4(8) | 7311.9(18) | 42.3(6) |
| C24 | 12437(3) | 6203.3(9) | 7847.3(19) | 49.2(7) |
| C25 | 13336(3) | 6374.7(10) | 8516(2) | 60.0(8) |
| C26 | 14481(3) | 6266.1(11) | 8676(2) | 63.2(9) |
| C27 | 14747(3) | 5990.9(11) | 8134(2) | 59.5(8) |
| C28 | 13889(3) | 5811.6(9) | 7449(2) | 48.9(7) |
| C29 | 11199(3) | 6338.1(10) | 7722(3) | 61.1(9) |
| C30 | 15450(5) | 6439.9(15) | 9436(3) | 93.0(15) |
| C31 | 14274(3) | 5522.0(10) | 6890(2) | 58.1(8) |
| C32 | 12048(2) | 4500.8(7) | 8420.2(16) | 36.6(5) |
| C33 | 11116(2) | 4531.1(7) | 8777.7(17) | 39.2(6) |
| C34 | 11365(3) | 4643.8(8) | 9649.7(19) | 45.4(6) |
| C35 | 12508(3) | 4717.7(9) | 10177.0(19) | 48.4(7) |
| C36 | 13395(3) | 4694.0(9) | 9800.5(19) | 46.9(7) |
| C37 | 13188(2) | 4590.6(8) | 8922.8(17) | 41.5(6) |
| C38 | 9881(3) | 4442.2(10) | 8242(2) | 49.9(7) |
| C39 | 12750(4) | 4812.7(12) | 11133(2) | 67.2(10) |
| C40 | 14191(3) | 4562.7(13) | 8539(2) | 64.4(9) |
| C1A | 4069(3) | 8996.6(9) | 7477(2) | 52.2(7) |
| C2A | 3711(3) | 9358.0(10) | 7688(2) | 56.3(8) |
| C3A | 4322(4) | 9529.5(11) | 8474(3) | 63.0(9) |
| C4A | 5271(4) | 9339.9(12) | 9059(3) | 67.2(9) |
| C5A | 5592(3) | 8968.6(11) | 8862(2) | 61.3(8) |

| | | | | |
|---|---|---|---|---|
| C6A | 4985(3) | 8797.4(10) | 8075(2) | 50.2(7) |
| C7A | 5104(3) | 8412.6(9) | 7706(2) | 48.8(7) |
| C8A | 5808(3) | 8102.5(9) | 8048(2) | 47.9(7) |
| C9A | 5711(3) | 7745.1(10) | 7572(2) | 49.2(7) |
| C10A | 6535(3) | 7455.9(10) | 7985(2) | 56.9(8) |
| C11A | 6734(3) | 7096.9(11) | 7710(2) | 61.0(9) |
| C12A | 6114(3) | 6875.6(10) | 6969(2) | 56.3(8) |
| C13A | 6588(4) | 6504.4(11) | 6890(3) | 70.7(10) |
| C14A | 6022(4) | 6243.4(12) | 6270(3) | 74.0(11) |
| C15A | 4924(4) | 6333.9(11) | 5686(3) | 69.9(10) |
| C16A | 4457(3) | 6694.1(10) | 5717(2) | 56.5(8) |
| C17A | 5029(3) | 6987.5(9) | 6332(2) | 48.7(7) |
| C18A | 4479(3) | 7359.5(9) | 6236.7(19) | 44.9(6) |
| C19A | 4815(2) | 7710.4(9) | 6724(2) | 44.9(6) |
| C20A | 4159(3) | 8053.1(9) | 6386(2) | 47.4(7) |
| C21A | 4298(3) | 8391.0(9) | 6855(2) | 48.8(7) |
| C22A | 3642(3) | 8774.9(9) | 6603(2) | 50.6(7) |
| C23A | 2350(3) | 8747.7(9) | 6119(2) | 49.7(7) |
| C24A | 1893(3) | 8958.4(9) | 5342(2) | 52.3(7) |
| C25A | 735(3) | 8916.8(10) | 4851(2) | 59.9(8) |
| C26A | -7(3) | 8663.5(11) | 5096(2) | 61.3(9) |
| C27A | 446(3) | 8460.4(10) | 5883(3) | 59.0(8) |
| C28A | 1593(3) | 8500.8(9) | 6412(2) | 52.1(7) |
| C29A | 2626(4) | 9247.7(12) | 5008(3) | 68.0(9) |
| C30A | -1255(4) | 8617.9(14) | 4557(3) | 80.3(12) |
| C31A | 1993(3) | 8285.2(11) | 7265(3) | 62.2(9) |
| C32A | 3334(2) | 7395.7(8) | 5505.9(19) | 43.3(6) |
| C33A | 3304(3) | 7494.8(10) | 4653(2) | 51.1(7) |
| C34A | 2220(3) | 7582.6(10) | 4050(2) | 52.5(7) |
| C35A | 1188(3) | 7573.5(9) | 4268(2) | 49.8(7) |
| C36A | 1240(3) | 7448.6(9) | 5100(2) | 46.3(6) |
| C37A | 2293(2) | 7358.3(8) | 5729.3(19) | 42.5(6) |
| C38A | 4404(4) | 7509.5(15) | 4385(3) | 77.4(12) |
| C39A | 52(3) | 7711.6(11) | 3638(3) | 64.1(9) |
| C40A | 2313(3) | 7228.1(10) | 6633(2) | 51.6(7) |

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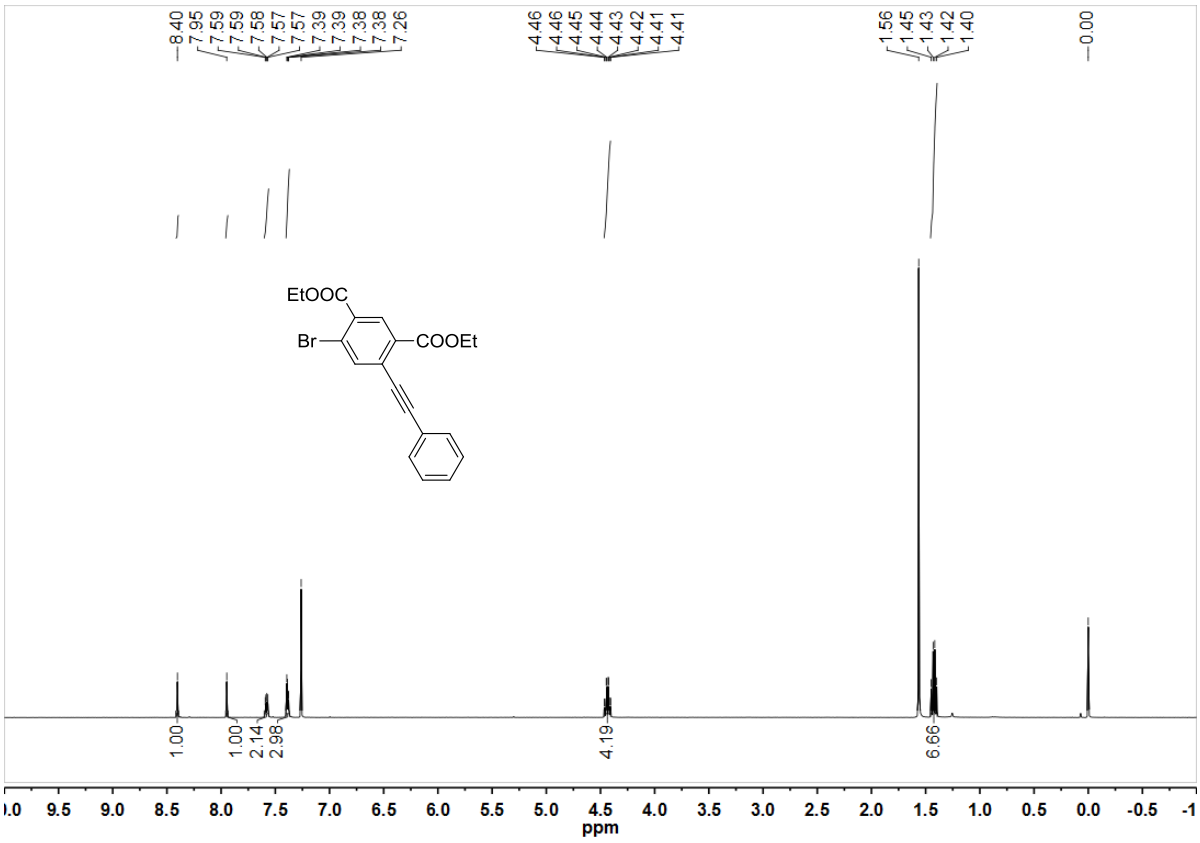
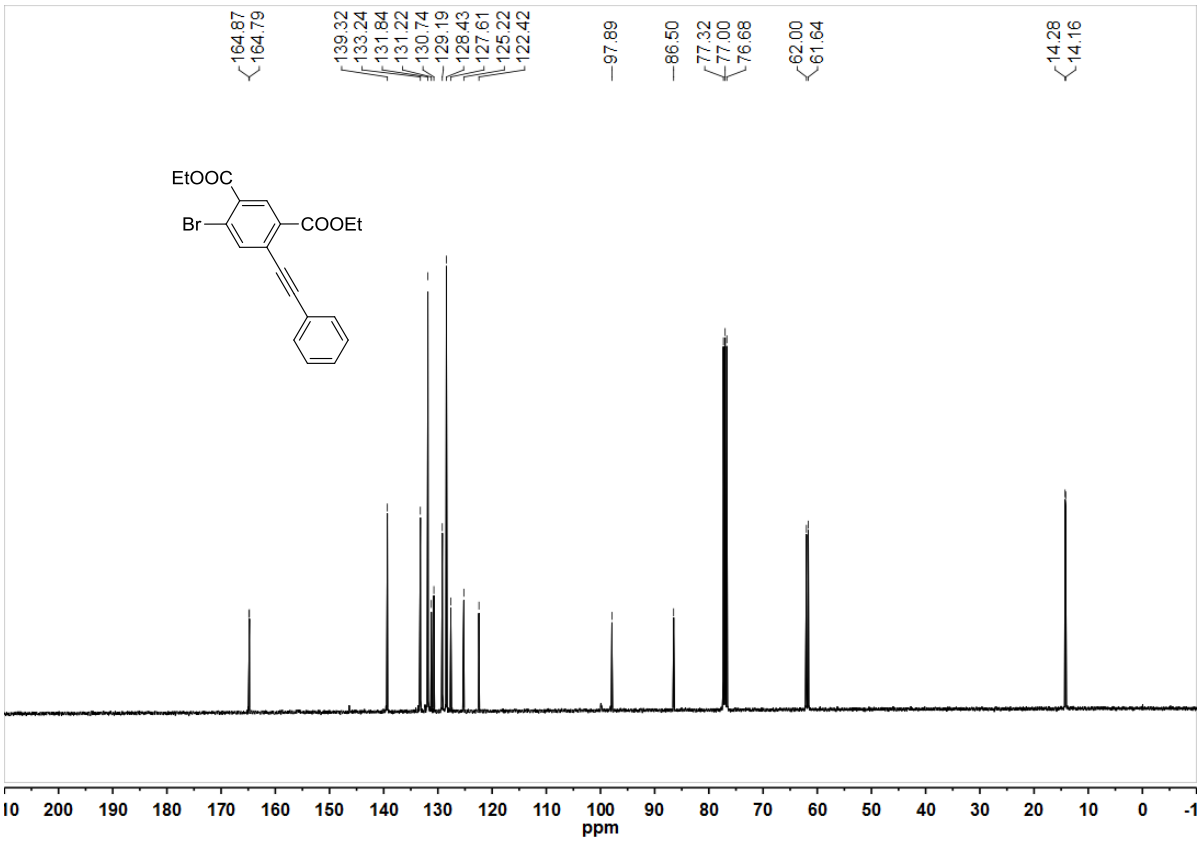
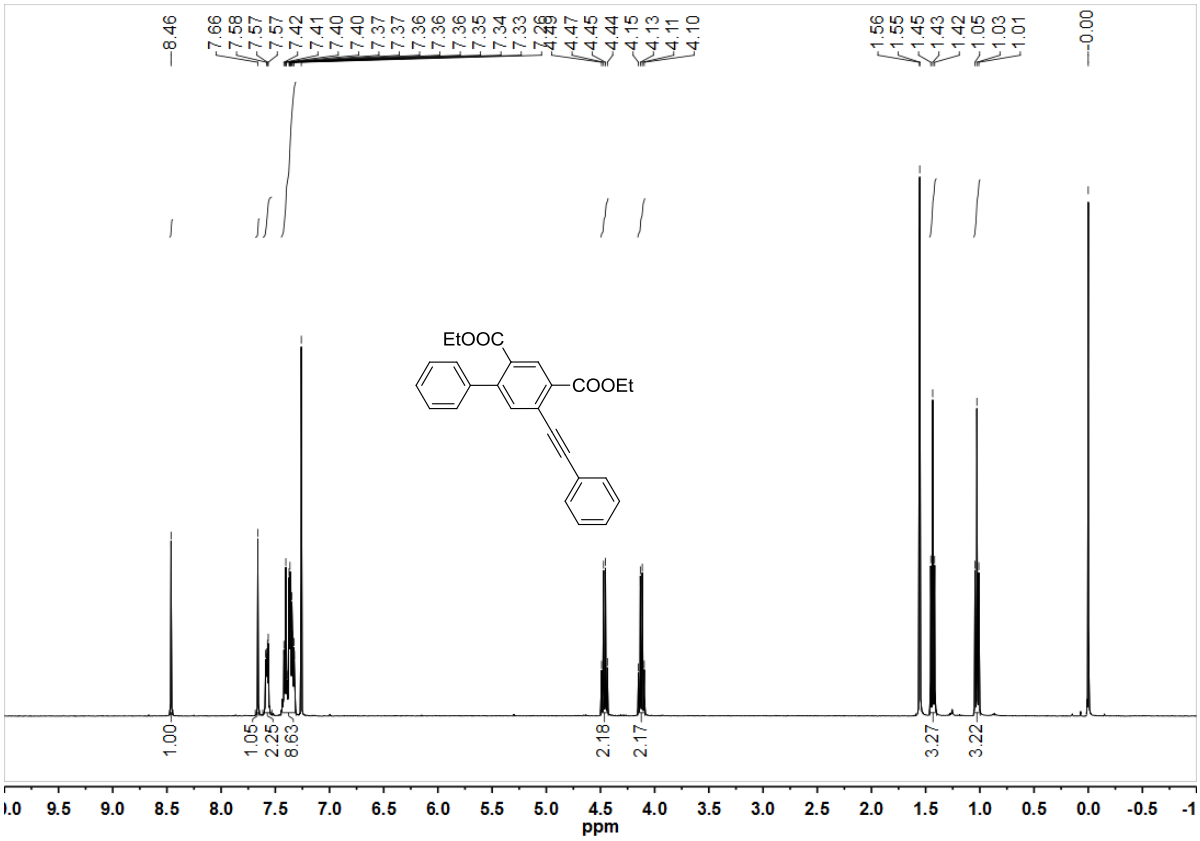
11 T. Lu and F. Chen, *J. Comput. Chem*., 2012, **33**, 580-592.

## VII. Copies of $^{1}$H- and $^{13}$C-NMR spectra

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4.45
4.44
4.15
4.13
4.11
4.10
1.56
1.55
1.45
1.43
1.42
1.05
1.03
1.01
0.00
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COOEt
1.00
1.05
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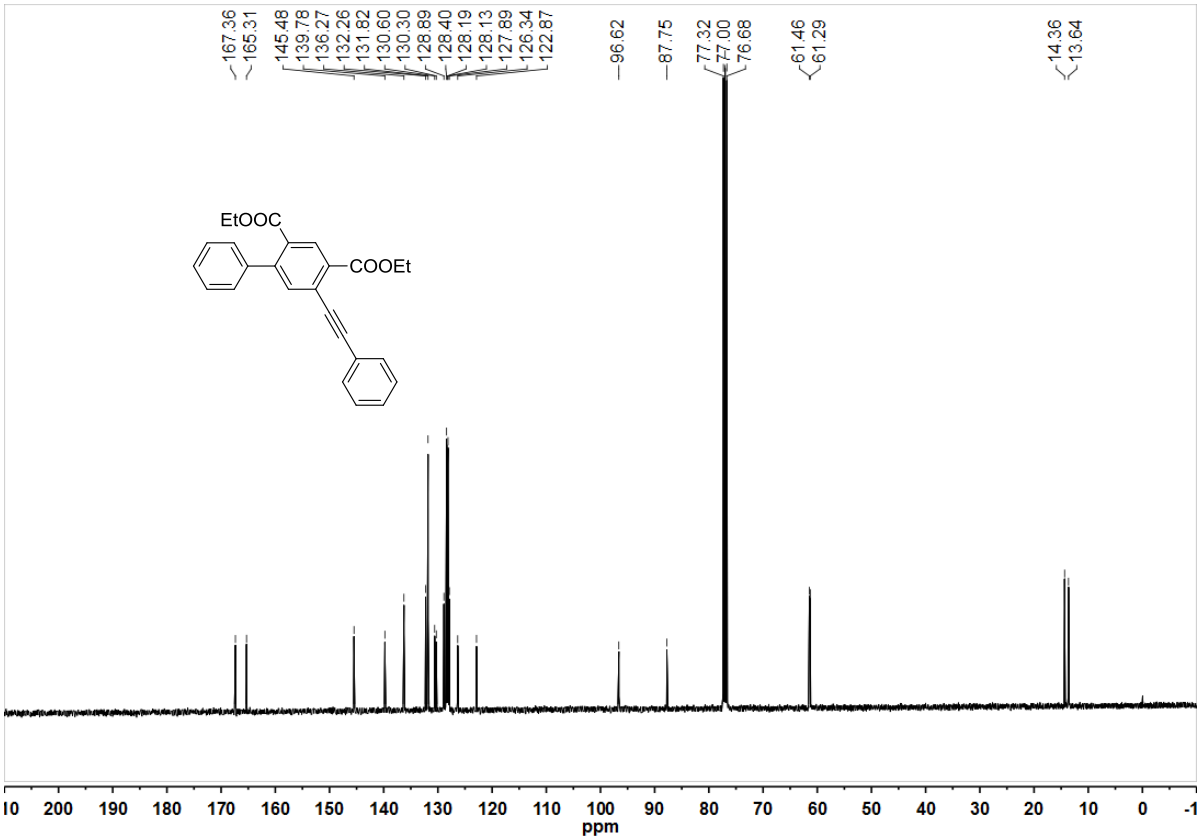
2.18
2.17
3.27
3.22
ppm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132.26
131.82
130.60
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128.89
128.40
128.19
128.13
127.89
126.34
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77.32
77.00
76.68
61.46
61.29
14.36
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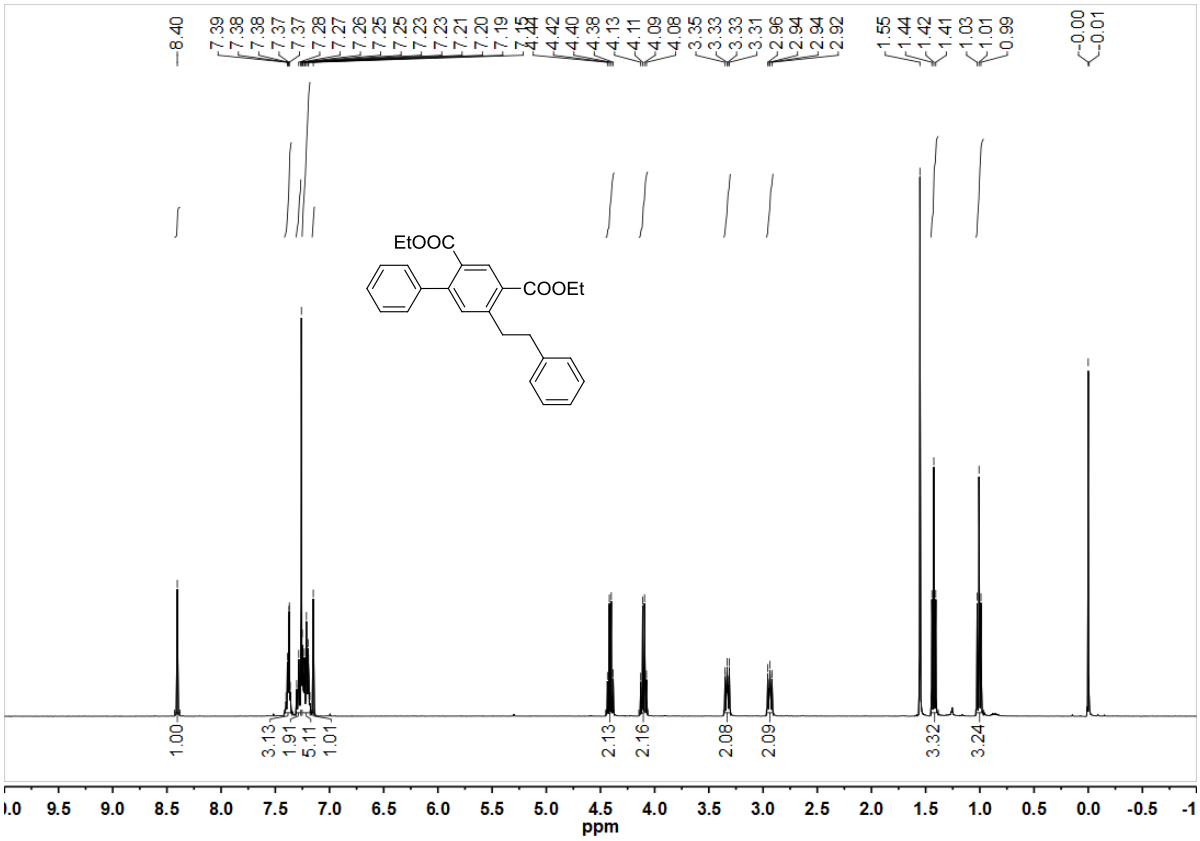
COOEt
ppm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7.20
7.19
4.42
4.40
4.38
4.13
4.11
4.09
4.08
3.35
3.33
3.33
3.31
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2.94
2.94
2.92
1.55
1.44
1.42
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0.00
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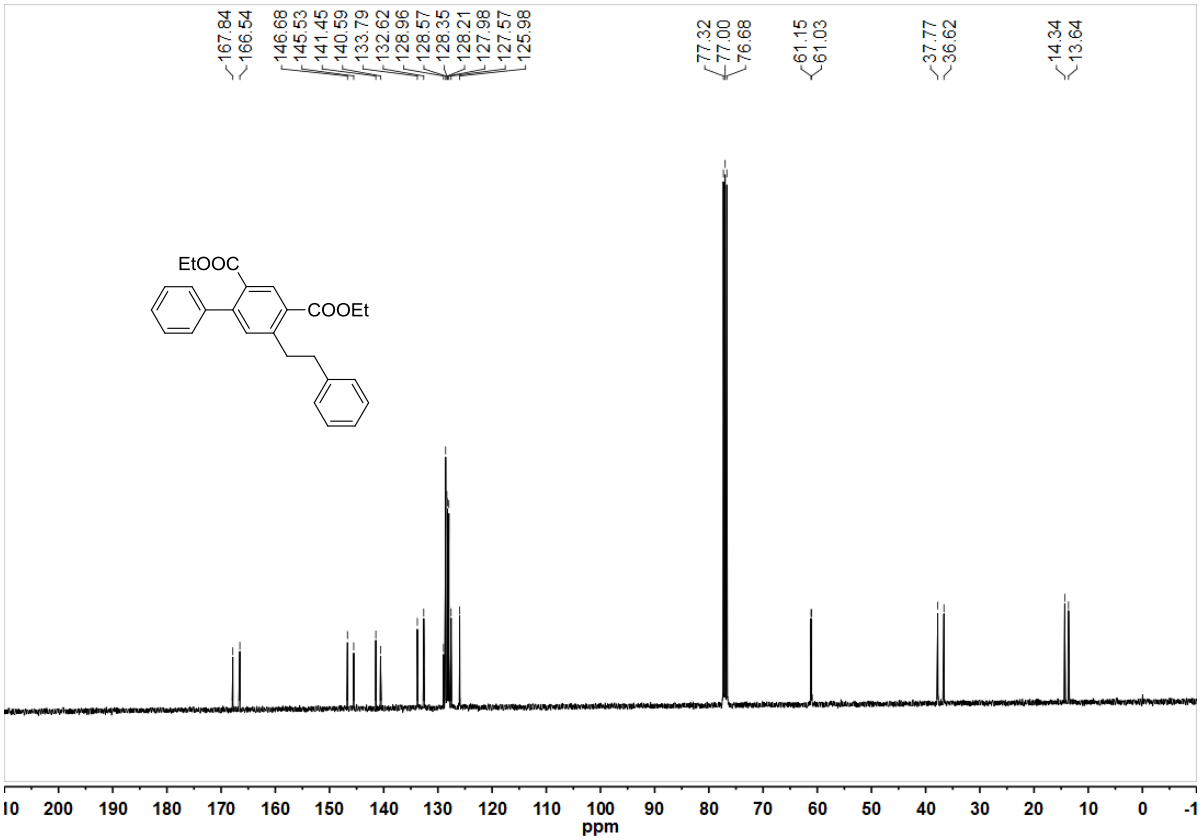
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140.59
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132.62
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127.57
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76.68
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61.03
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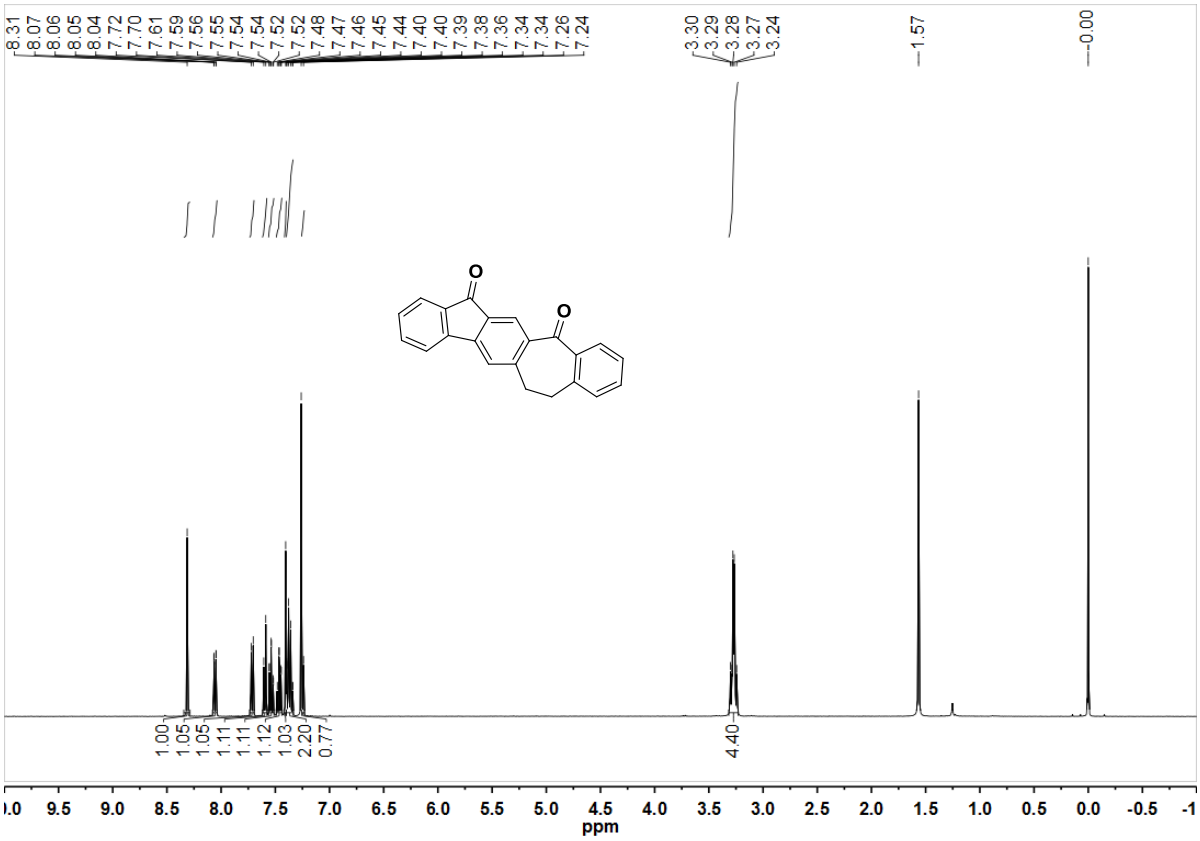
EtOOC
COOEt
ppm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7.38
7.36
7.34
7.34
7.26
7.24
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3.29
3.28
3.27
3.24
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1.05
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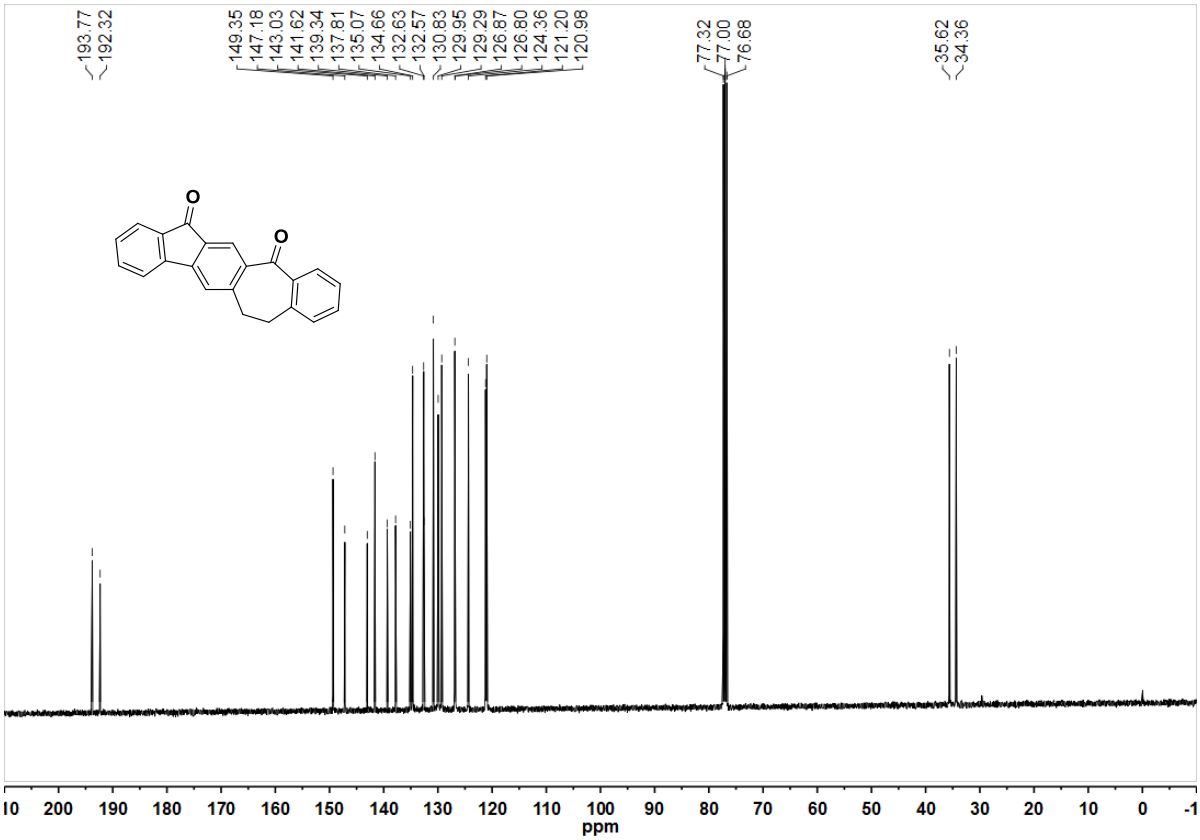
ppm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141.62
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132.57
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129.95
129.29
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121.20
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77.00
76.68
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O
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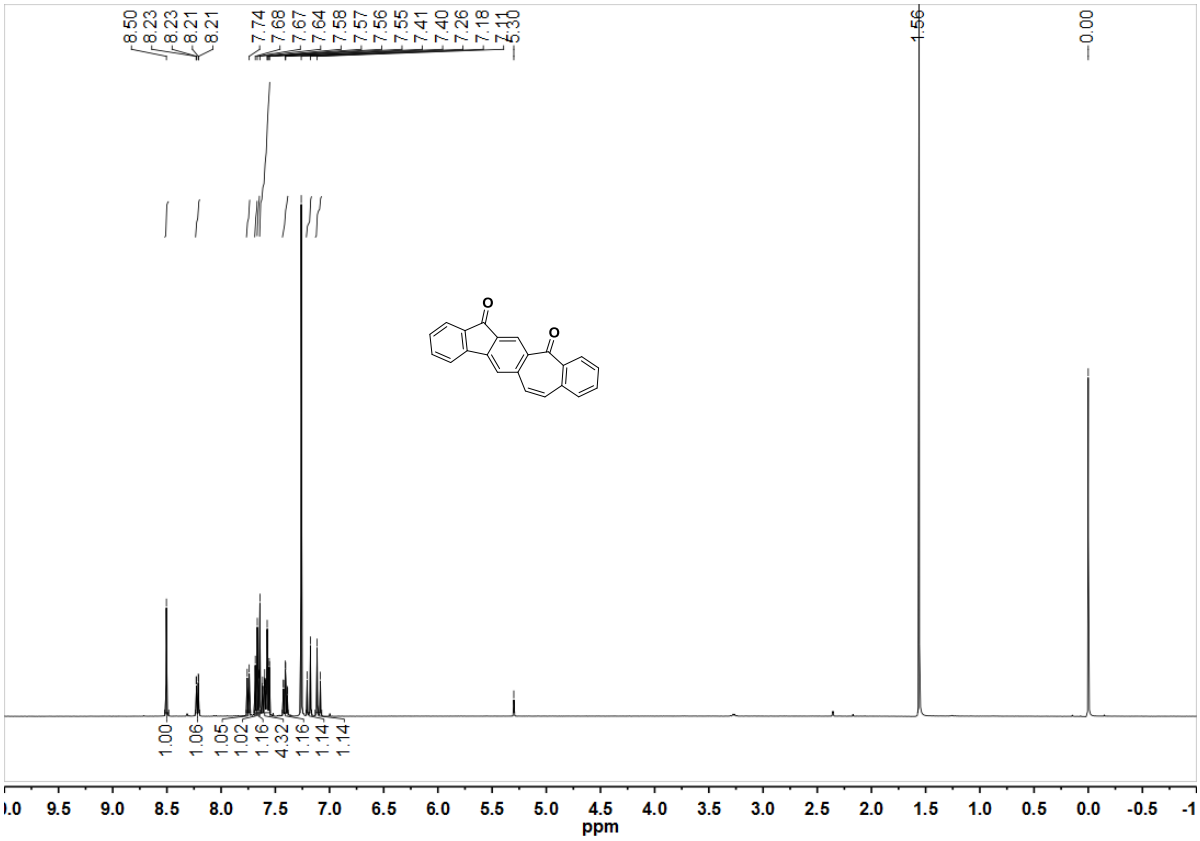
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7.67
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7.57
7.56
7.55
7.41
7.40
7.26
7.18
7.11
5.30
1.56
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1.06
1.05
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1.16
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1.16
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O
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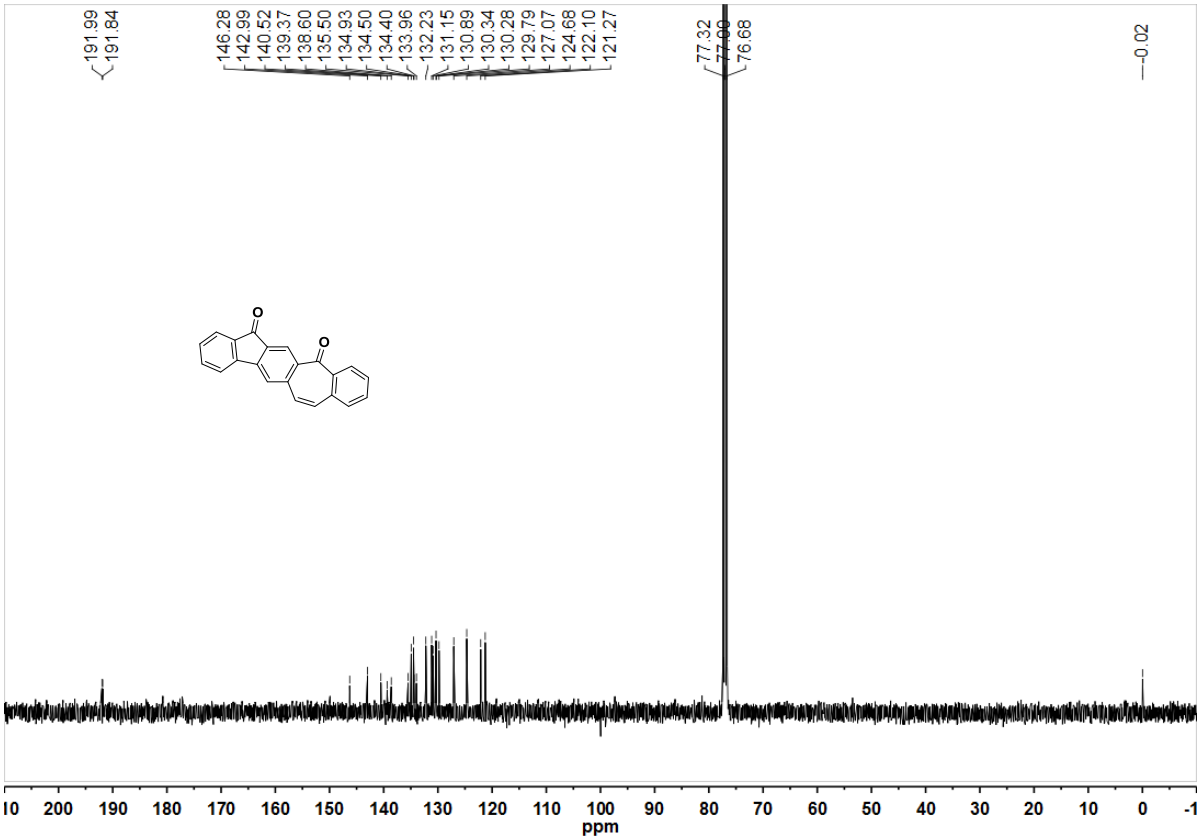
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130.89
130.34
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127.07
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77.00
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0.02
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O
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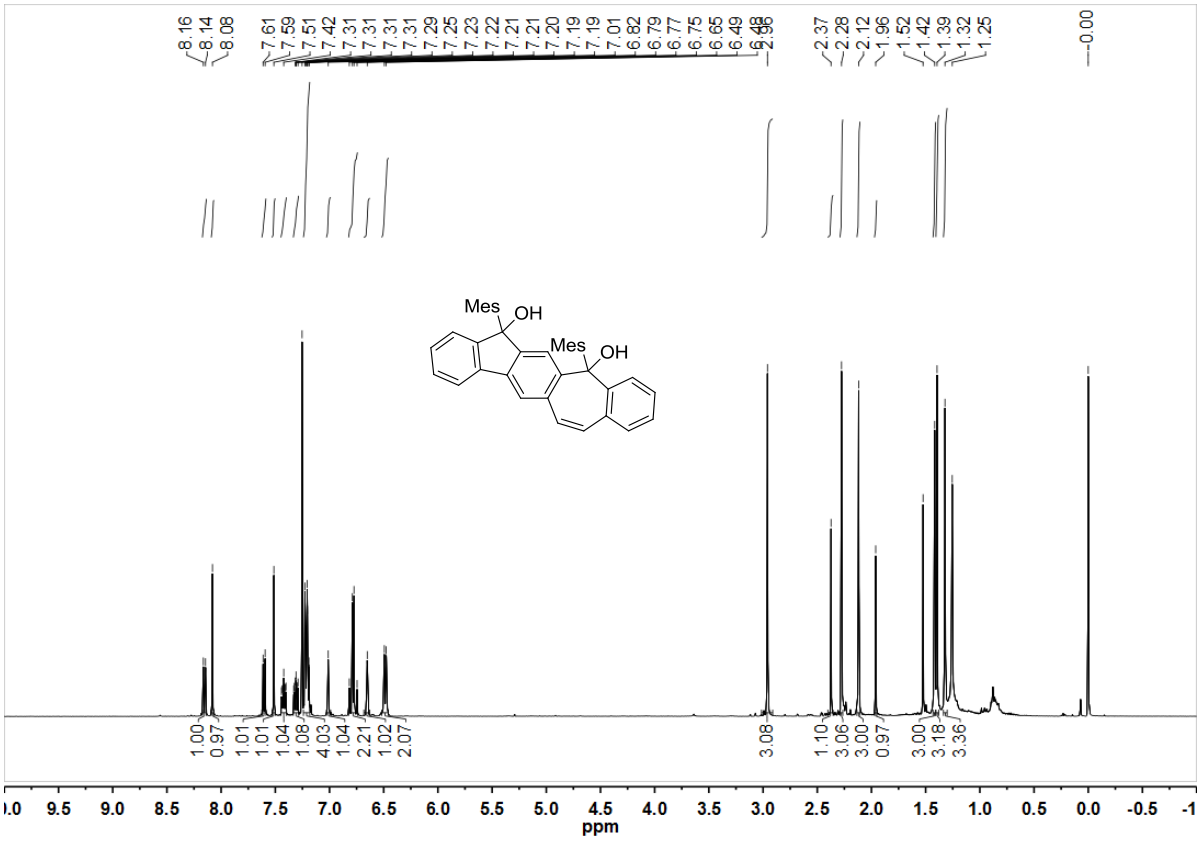
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7.23
7.22
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7.21
7.20
7.19
7.19
7.01
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6.79
6.77
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6.49
6.48
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2.28
2.12
1.96
1.52
1.42
1.39
1.32
1.25
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Mes
OH
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0.97
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1.01
1.04
1.08
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2.07
3.08
1.10
3.06
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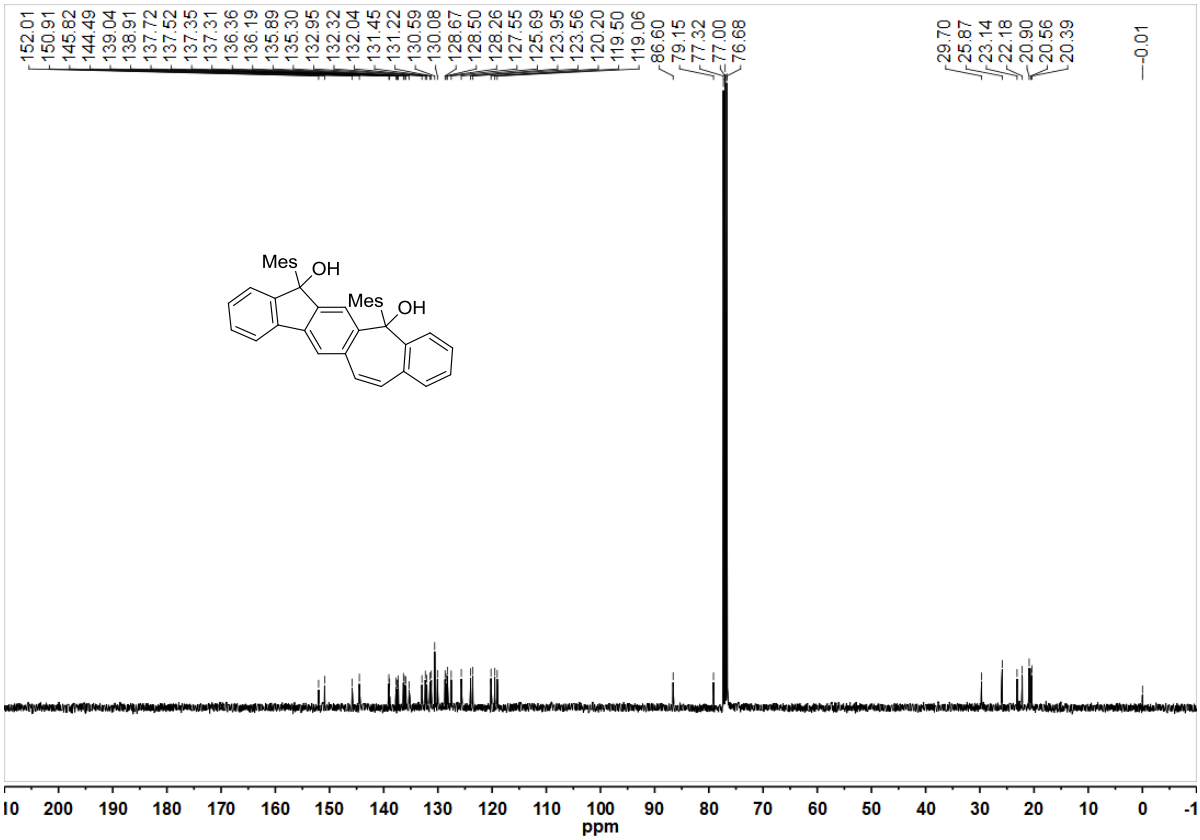
ppm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132.04
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OH
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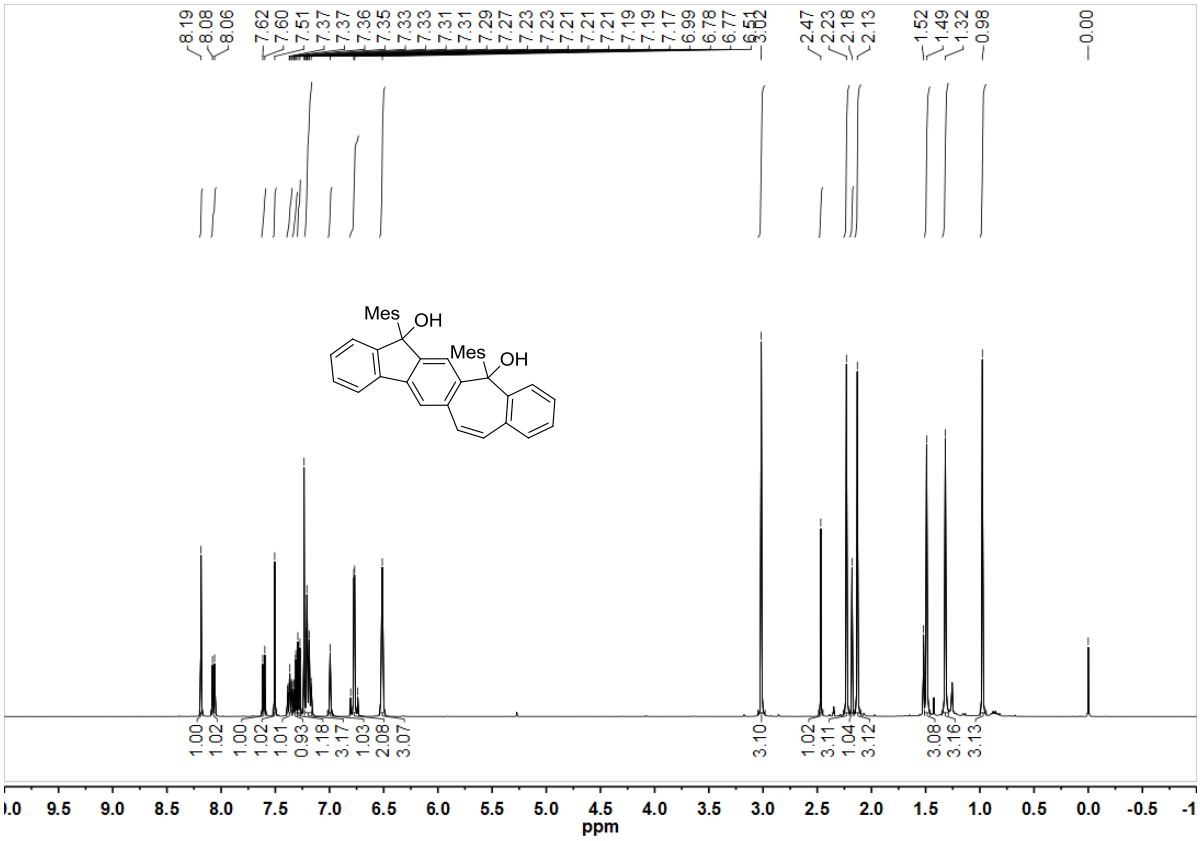
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6.77
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2.23
2.18
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1.02
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3.12
3.08
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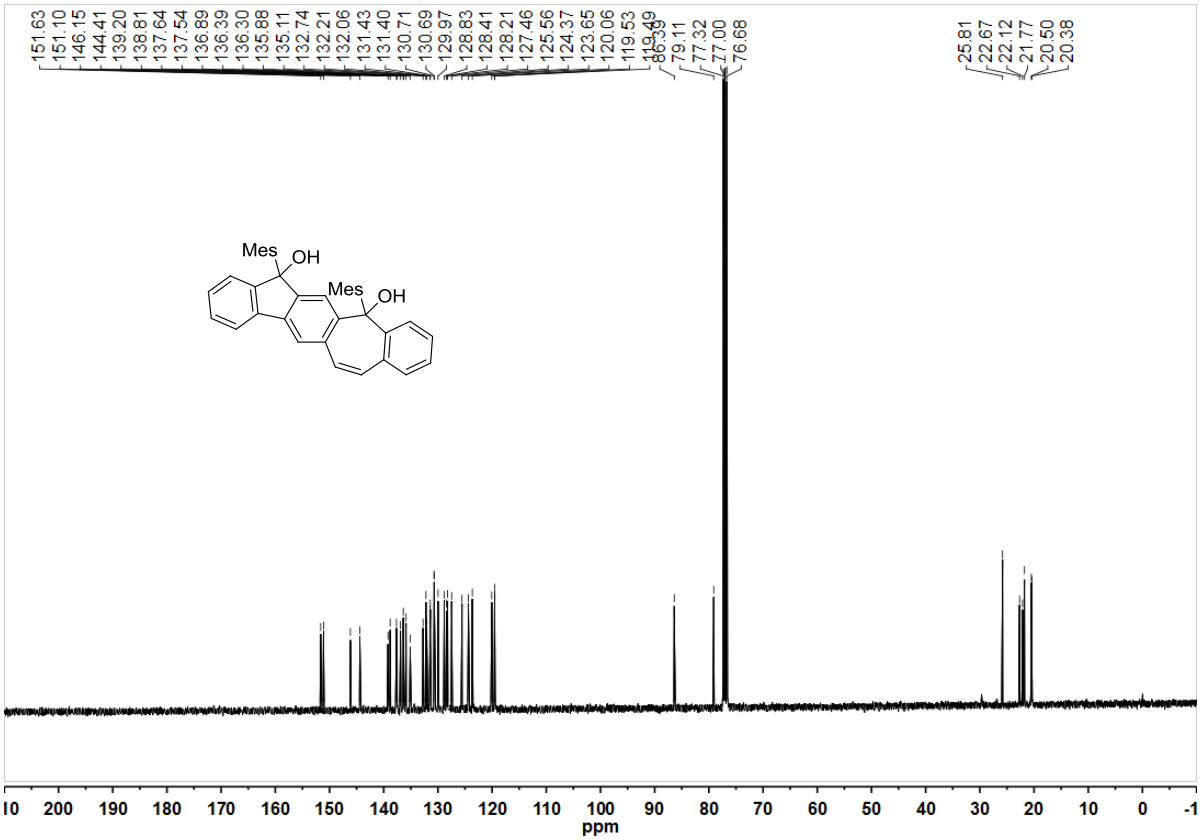
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128.21
127.46
125.56
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123.65
120.06
119.53
86.39
79.11
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77.00
76.68
25.81
22.67
22.12
21.77
20.50
20.38
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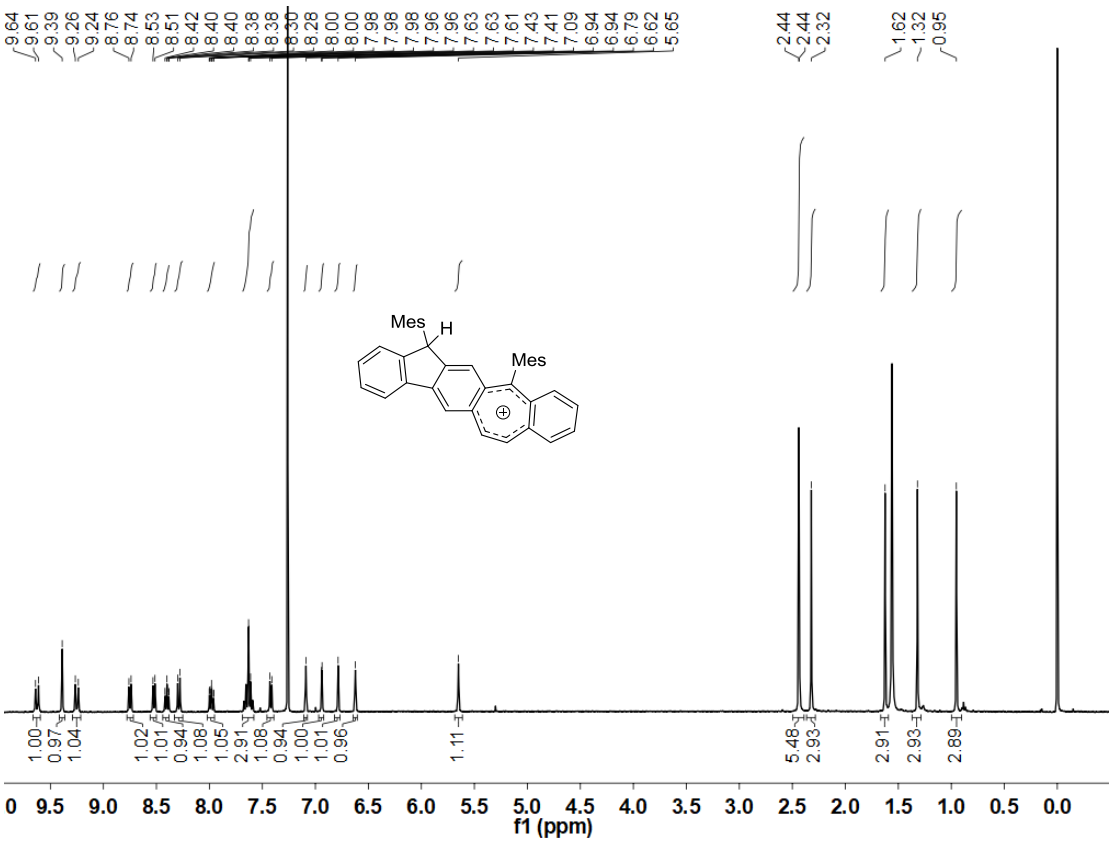
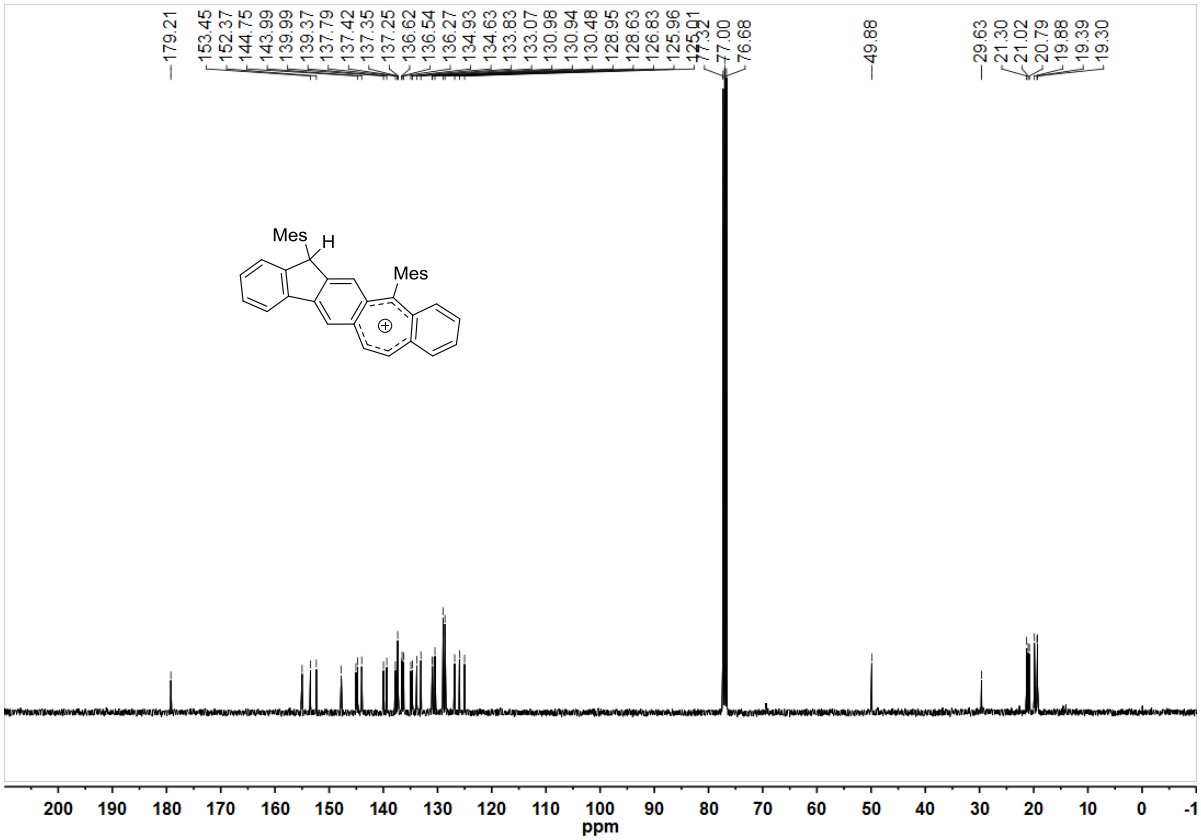
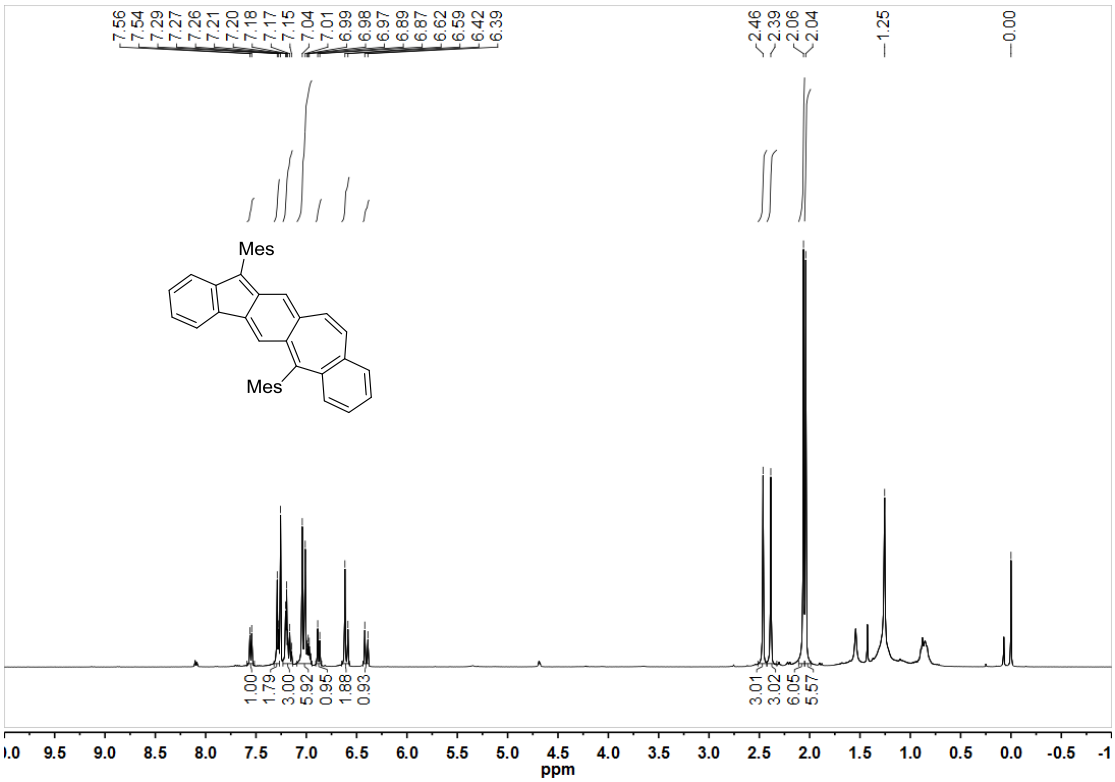
OH
Mes
OH
ppm

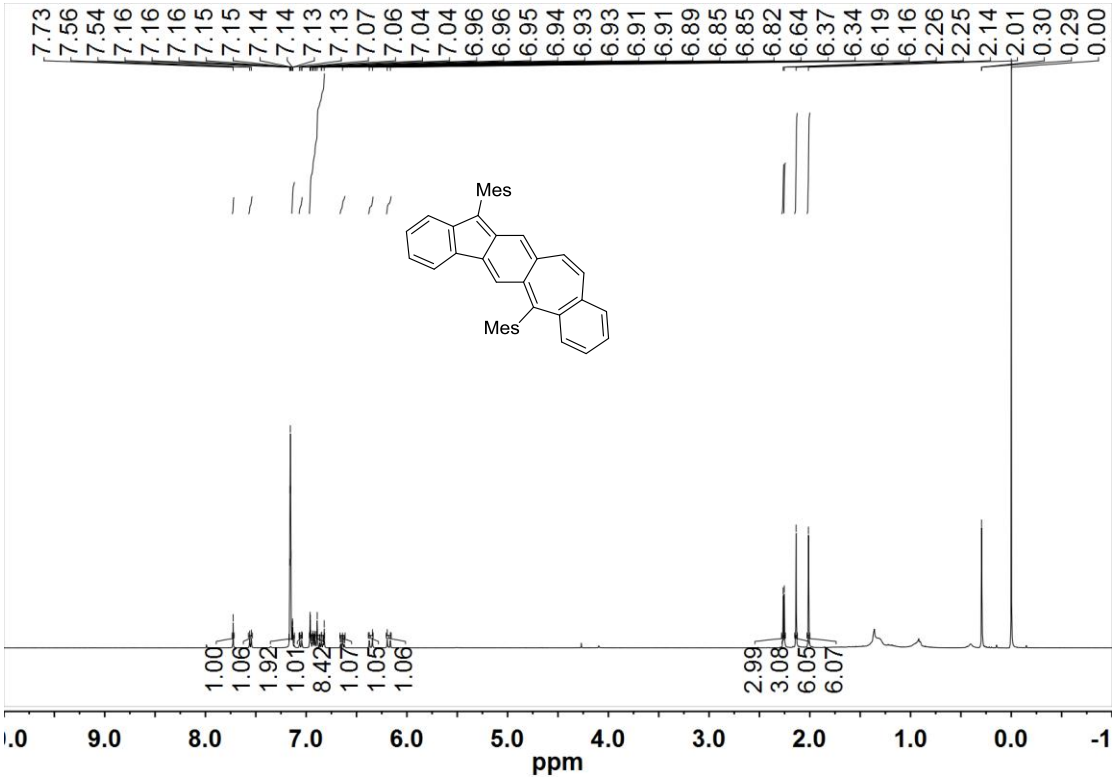



In $CDCl_3$




In Benzene-$d_6$




## VIII. Cartesian coordinates of the optimized geometry

Cartesian Coordinates of **BCHF1** (closed-shell).

| | | | |
|---|---|---|---|
| C | -1.62959200 | -1.16034400 | 0.00097000 |
| C | -1.94322400 | 0.28756600 | 0.00022400 |
| C | -0.92502800 | 1.22097500 | 0.00026000 |
| C | 0.43182300 | 0.85070400 | 0.00073200 |
| C | 0.75828100 | -0.59509000 | 0.00107900 |
| C | -0.29701500 | -1.54174500 | 0.00139500 |
| C | -2.83140800 | -1.88021400 | 0.00091300 |
| C | -3.89561800 | -0.94562800 | 0.00016500 |
| C | -3.35923800 | 0.39928200 | -0.00028500 |
| C | 1.38731900 | 1.88597600 | 0.00138400 |
| C | 2.76651600 | 1.88791700 | 0.00149700 |
| C | 3.69492900 | 0.81605000 | 0.00041000 |
| C | 3.35460200 | -0.58317600 | -0.00004200 |
| C | 2.04561300 | -1.12644600 | 0.00081500 |
| C | -5.29982800 | -1.12004600 | -0.00026300 |
| C | -6.11634300 | -0.00985800 | -0.00111400 |
| C | -5.58589600 | 1.30744800 | -0.00157400 |
| C | -4.22228700 | 1.51192600 | -0.00116600 |
| C | 5.07737500 | 1.15312500 | -0.00026600 |
| C | 6.06831800 | 0.20167900 | -0.00146800 |
| C | 5.73757500 | -1.17014500 | -0.00197200 |
| C | 4.41589300 | -1.53722700 | -0.00119000 |
| H | -1.16387300 | 2.28117900 | -0.00000200 |
| H | -0.03729200 | -2.59675400 | 0.00178800 |
| H | -2.93082100 | -2.95768300 | 0.00151200 |
| H | 0.94529900 | 2.88031900 | 0.00182500 |
| H | 3.22189400 | 2.87440500 | 0.00219400 |
| H | 2.05012600 | -2.21454200 | 0.00110100 |
| H | -5.72757600 | -2.11815600 | 0.00008500 |
| H | -7.19476300 | -0.13943600 | -0.00145500 |
| H | -6.26473000 | 2.15391800 | -0.00226300 |
| H | -3.82041300 | 2.52135200 | -0.00152700 |
| H | 5.34458100 | 2.20499100 | 0.00012900 |
| H | 7.10971500 | 0.50726100 | -0.00202100 |
| H | 6.51810900 | -1.92272300 | -0.00291300 |
| H | 4.15314400 | -2.59050200 | -0.00149400 |

Cartesian Coordinates of **BCHF1** (open-shell singlet).

| | | | |
|---|---|---|---|
| C | -1.62958400 | -1.16028400 | 0.00039800 |
| C | -1.94320700 | 0.28757700 | 0.00006400 |
| C | -0.92499000 | 1.22101700 | 0.00007900 |
| C | 0.43181600 | 0.85077300 | 0.00029400 |
| C | 0.75829600 | -0.59504900 | 0.00044800 |
| C | -0.29708100 | -1.54171900 | 0.00058400 |
| C | -2.83144200 | -1.88022300 | 0.00039500 |

| | | | |
|---|---|---|---|
| C | -3.89559500 | -0.94569700 | 0.00007700 |
| C | -3.35919100 | 0.39930500 | -0.00014200 |
| C | 1.38737300 | 1.88605600 | 0.00058800 |
| C | 2.76651300 | 1.88796100 | 0.00065800 |
| C | 3.69494600 | 0.81602900 | 0.00018900 |
| C | 3.35459500 | -0.58318900 | -0.00002200 |
| C | 2.04554200 | -1.12644200 | 0.00033500 |
| C | -5.29984700 | -1.12007300 | -0.00007800 |
| C | -6.11631300 | -0.00989700 | -0.00043800 |
| C | -5.58584500 | 1.30744600 | -0.00066300 |
| C | -4.22226600 | 1.51193400 | -0.00051900 |
| C | 5.07736100 | 1.15306500 | -0.00008600 |
| C | 6.06830800 | 0.20159300 | -0.00060600 |
| C | 5.73754800 | -1.17019400 | -0.00084100 |
| C | 4.41583600 | -1.53723900 | -0.00051900 |
| H | -1.16387000 | 2.28121600 | -0.00004000 |
| H | -0.03736700 | -2.59673300 | 0.00075500 |
| H | -2.93078100 | -2.95769800 | 0.00067200 |
| H | 0.94534900 | 2.88040400 | 0.00077600 |
| H | 3.22195100 | 2.87442900 | 0.00097300 |
| H | 2.05005600 | -2.21454200 | 0.00045300 |
| H | -5.72760900 | -2.11818200 | 0.00008800 |
| H | -7.19474300 | -0.13943700 | -0.00056000 |
| H | -6.26470400 | 2.15389800 | -0.00095700 |
| H | -3.82039600 | 2.52136700 | -0.00070000 |
| H | 5.34461000 | 2.20492400 | 0.00009900 |
| H | 7.10971500 | 0.50715700 | -0.00083200 |
| H | 6.51807100 | -1.92279100 | -0.00124800 |
| H | 4.15307700 | -2.59051500 | -0.00066200 |

Cartesian Coordinates of **BCHF1** (triplet).

| | | | |
|---|---|---|---|
| C | -1.63405300 | -1.12363500 | 0.00018900 |
| C | -1.94717400 | 0.27989700 | 0.00015700 |
| C | -0.92268500 | 1.20139800 | 0.00005700 |
| C | 0.43499600 | 0.80696400 | 0.00002400 |
| C | 0.76870000 | -0.60105400 | 0.00003800 |
| C | -0.30307700 | -1.53418600 | 0.00012600 |
| C | -2.84997100 | -1.85448400 | 0.00011300 |
| C | -3.94106500 | -0.92176300 | 0.00003800 |
| C | -3.40344400 | 0.40543000 | 0.00007100 |
| C | 1.40591900 | 1.87469800 | -0.00002300 |
| C | 2.76087200 | 1.87382400 | -0.00002700 |
| C | 3.72858800 | 0.79369300 | -0.00000100 |
| C | 3.39038200 | -0.59789500 | -0.00008400 |
| C | 2.07442800 | -1.15220100 | -0.00008600 |

| | | | |
|---|---|---|---|
| C | -5.32560100 | -1.11813500 | -0.00009600 |
| C | -6.16629500 | -0.00496700 | -0.00017400 |
| C | -5.63740300 | 1.28906600 | -0.00011500 |
| C | -4.25221000 | 1.50181900 | 0.00001200 |
| C | 5.08374900 | 1.16086100 | 0.00006700 |
| C | 6.11161300 | 0.22630700 | 0.00003600 |
| C | 5.79026800 | -1.13285000 | -0.00008500 |
| C | 4.46379000 | -1.52597600 | -0.00014500 |
| H | -1.14413400 | 2.26508100 | 0.00001600 |
| H | -0.06556800 | -2.59379000 | 0.00014400 |
| H | -2.94267100 | -2.93353400 | 0.00019200 |
| H | 0.95558800 | 2.86499600 | -0.00004900 |
| H | 3.21660700 | 2.86143500 | -0.00005500 |
| H | 2.07603500 | -2.23930500 | -0.00014300 |
| H | -5.74179800 | -2.12102300 | -0.00013200 |
| H | -7.24260000 | -0.14332700 | -0.00028100 |
| H | -6.30896200 | 2.14156100 | -0.00017100 |
| H | -3.85975900 | 2.51430900 | 0.00006300 |
| H | 5.32892200 | 2.21889700 | 0.00014000 |
| H | 7.14647600 | 0.55108800 | 0.00010000 |
| H | 6.57529300 | -1.88232000 | -0.00013300 |
| H | 4.22460800 | -2.58493300 | -0.00023400 |

Cartesian Coordinates of **BCHF2** (closed-shell).

| | | | |
|---|---|---|---|
| C | -6.00027500 | -0.74663200 | 0.00017400 |
| C | -5.21895200 | -1.90694000 | -0.00015400 |
| C | -3.82461400 | -1.82170300 | -0.00027500 |
| C | -3.22678500 | -0.56762900 | -0.00006700 |
| C | -4.01962400 | 0.61716000 | 0.00028400 |
| C | -5.41232700 | 0.51846800 | 0.00039600 |
| C | -1.82987000 | -0.14006700 | -0.00012100 |
| C | -1.83398500 | 1.32684500 | 0.00021100 |
| C | -3.13558400 | 1.76847600 | 0.00044500 |
| C | -0.66090800 | -0.82121900 | -0.00042900 |
| C | 0.62329300 | -0.14334800 | -0.00034500 |
| C | 0.61585000 | 1.33070800 | -0.00015700 |
| C | -0.58488100 | 2.00316500 | 0.00012000 |
| C | 1.72538200 | -0.96244500 | -0.00037500 |
| C | 3.15256500 | -0.74419200 | -0.00010000 |
| C | 3.80795800 | 0.52087200 | -0.00012100 |
| C | 3.13459900 | 1.80411300 | -0.00044600 |
| C | 1.82199700 | 2.12935300 | -0.00042500 |
| C | 3.95217700 | -1.90845000 | 0.00019600 |
| C | 5.33597200 | -1.85920800 | 0.00050000 |
| C | 5.97479500 | -0.61841300 | 0.00048400 |

| | | | |
|---|---|---|---|
| C | 5.21490400 | 0.54155600 | 0.00016400 |
| H | -7.08253700 | -0.83322100 | 0.00026000 |
| H | -5.70006200 | -2.87954500 | -0.00031700 |
| H | -3.22438600 | -2.72716500 | -0.00052600 |
| H | -6.03193600 | 1.41026000 | 0.00065600 |
| H | -3.46153200 | 2.80144000 | 0.00072600 |
| H | -0.65255300 | -1.90765500 | -0.00067800 |
| H | -0.57583100 | 3.08963400 | 0.00022300 |
| H | 1.47751400 | -2.02163100 | -0.00054200 |
| H | 3.81721400 | 2.65048500 | -0.00068300 |
| H | 1.62075700 | 3.19861900 | -0.00063800 |
| H | 3.45597800 | -2.87408600 | 0.00019400 |
| H | 5.91362900 | -2.77738000 | 0.00073900 |
| H | 7.05808900 | -0.55744600 | 0.00071100 |
| H | 5.71552900 | 1.50487200 | 0.00013200 |

Cartesian Coordinates of **BCHF2** (open-shell singlet).

| | | | |
|---|---|---|---|
| C | -6.00027500 | -0.74663200 | 0.00017400 |
| C | -5.21895200 | -1.90694000 | -0.00015500 |
| C | -3.82461400 | -1.82170300 | -0.00027600 |
| C | -3.22678400 | -0.56762900 | -0.00006700 |
| C | -4.01962400 | 0.61716000 | 0.00028400 |
| C | -5.41232600 | 0.51846800 | 0.00039600 |
| C | -1.82987000 | -0.14006700 | -0.00012100 |
| C | -1.83398500 | 1.32684500 | 0.00021200 |
| C | -3.13558400 | 1.76847600 | 0.00044500 |
| C | -0.66090800 | -0.82121900 | -0.00043000 |
| C | 0.62329300 | -0.14334800 | -0.00034500 |
| C | 0.61585000 | 1.33070800 | -0.00015800 |
| C | -0.58488100 | 2.00316500 | 0.00012000 |
| C | 1.72538200 | -0.96244500 | -0.00037500 |
| C | 3.15256500 | -0.74419200 | -0.00010000 |
| C | 3.80795700 | 0.52087200 | -0.00012100 |
| C | 3.13459900 | 1.80411300 | -0.00044600 |
| C | 1.82199700 | 2.12935300 | -0.00042500 |
| C | 3.95217700 | -1.90845000 | 0.00019600 |
| C | 5.33597200 | -1.85920800 | 0.00050100 |
| C | 5.97479400 | -0.61841300 | 0.00048500 |
| C | 5.21490400 | 0.54155600 | 0.00016400 |
| H | -7.08253700 | -0.83322100 | 0.00026000 |
| H | -5.70006200 | -2.87954500 | -0.00031700 |
| H | -3.22438500 | -2.72716500 | -0.00052600 |
| H | -6.03193600 | 1.41026000 | 0.00065700 |
| H | -3.46153200 | 2.80144000 | 0.00072600 |

| | | | |
|---|---|---|---|
| H | -0.65255300 | -1.90765500 | -0.00067900 |
| H | -0.57583100 | 3.08963400 | 0.00022300 |
| H | 1.47751400 | -2.02163100 | -0.00054300 |
| H | 3.81721400 | 2.65048400 | -0.00068400 |
| H | 1.62075700 | 3.19861900 | -0.00063900 |
| H | 3.45597800 | -2.87408600 | 0.00019400 |
| H | 5.91362900 | -2.77738000 | 0.00073900 |
| H | 7.05808800 | -0.55744600 | 0.00071100 |
| H | 5.71552900 | 1.50487200 | 0.00013200 |

Cartesian Coordinates of **BCHF2** (triplet).

| | | | |
|---|---|---|---|
| C | -6.02704700 | -0.74000700 | 0.00011900 |
| C | -5.22711700 | -1.89629300 | 0.00023000 |
| C | -3.83220300 | -1.81069500 | 0.00021800 |
| C | -3.23222600 | -0.55806300 | 0.00008300 |
| C | -4.04549900 | 0.63047100 | -0.00001400 |
| C | -5.44975400 | 0.52069500 | 0.00000000 |
| C | -1.83667300 | -0.13375700 | 0.00004600 |
| C | -1.82861400 | 1.29189500 | -0.00005100 |
| C | -3.19535800 | 1.76166600 | -0.00009600 |
| C | -0.64082000 | -0.82651700 | -0.00005200 |
| C | 0.61038100 | -0.15769400 | -0.00017700 |
| C | 0.61227300 | 1.27516300 | -0.00016600 |
| C | -0.61849900 | 1.96814000 | -0.00015000 |
| C | 1.77699900 | -1.00027900 | -0.00042500 |
| C | 3.16609100 | -0.75552600 | -0.00021100 |
| C | 3.81582600 | 0.53035000 | 0.00013800 |
| C | 3.11984200 | 1.79481000 | 0.00009000 |
| C | 1.80025000 | 2.10307200 | -0.00009900 |
| C | 4.01578200 | -1.90492200 | -0.00033300 |
| C | 5.38939000 | -1.81407200 | -0.00003600 |
| C | 6.01216700 | -0.55568600 | 0.00038800 |
| C | 5.22178500 | 0.58218400 | 0.00044800 |
| H | -7.10753600 | -0.83977000 | 0.00013100 |
| H | -5.70243700 | -2.87190500 | 0.00033000 |
| H | -3.23373800 | -2.71669500 | 0.00031800 |
| H | -6.07031400 | 1.41169200 | -0.00007300 |
| H | -3.50906000 | 2.79791300 | -0.00013100 |
| H | -0.64009400 | -1.91260900 | -0.00003400 |
| H | -0.60176300 | 3.05422200 | -0.00019700 |
| H | 1.52837100 | -2.05851100 | -0.00071700 |
| H | 3.78608200 | 2.65497400 | 0.00020600 |
| H | 1.58263800 | 3.16864800 | -0.00012200 |
| H | 3.54638500 | -2.88378000 | -0.00065200 |

| | | | |
|---|---|---|---|
| H | 5.98915500 | -2.71891900 | -0.00013300 |
| H | 7.09350400 | -0.47378000 | 0.00064400 |
| H | 5.69695700 | 1.55891000 | 0.00073200 |

Cartesian Coordinates of **BCHF1+H$^+$** (closed-shell).

| | | | |
|---|---|---|---|
| C | 6.10408900 | 0.10333800 | -0.00044800 |
| C | 5.53289400 | 1.38384000 | -0.00048200 |
| C | 4.15460600 | 1.54000200 | -0.00024400 |
| C | 3.35180100 | 0.39168500 | 0.00005000 |
| C | 3.92972600 | -0.89739800 | 0.00011300 |
| C | 5.30920800 | -1.04372400 | -0.00015500 |
| C | 1.90913300 | 0.25169400 | 0.00017400 |
| C | 1.58466500 | -1.14156100 | 0.00032100 |
| C | 2.85403600 | -1.96028000 | 0.00043400 |
| C | 0.90096000 | 1.20474800 | 0.00015800 |
| C | -0.45347700 | 0.83129500 | 0.00019100 |
| C | -0.78886800 | -0.58188500 | 0.00023200 |
| C | 0.28233700 | -1.53935000 | 0.00038800 |
| C | -1.40889100 | 1.89398900 | 0.00022500 |
| C | -2.77390100 | 1.88963300 | 0.00022000 |
| C | -3.71737700 | 0.81795100 | 0.00009000 |
| C | -3.38119000 | -0.58064700 | -0.00013900 |
| C | -2.07633100 | -1.12351000 | 0.00000600 |
| C | -5.08513400 | 1.17377700 | 0.00014300 |
| C | -6.08497000 | 0.22373300 | -0.00015300 |
| C | -5.76198900 | -1.14598100 | -0.00054700 |
| C | -4.44344600 | -1.53109800 | -0.00049300 |
| H | 7.18410600 | 0.00397700 | -0.00066200 |
| H | 6.17635000 | 2.25627900 | -0.00071300 |
| H | 3.71625600 | 2.53233000 | -0.00028100 |
| H | 5.76875100 | -2.02648500 | -0.00015300 |
| H | 2.91580100 | -2.61238400 | 0.87886800 |
| H | 2.91573400 | -2.61300000 | -0.87753500 |
| H | 1.14842400 | 2.26054000 | 0.00018100 |
| H | 0.02796800 | -2.59446800 | 0.00052200 |
| H | -0.96102100 | 2.88358700 | 0.00026700 |
| H | -3.22895100 | 2.87596100 | 0.00029400 |
| H | -2.07793700 | -2.21059300 | -0.00006000 |
| H | -5.34704600 | 2.22594900 | 0.00044100 |
| H | -7.12383400 | 0.53421200 | -0.00004200 |
| H | -6.54888600 | -1.89112400 | -0.00092900 |
| H | -4.19300400 | -2.58627800 | -0.00069400 |

Cartesian Coordinates of **BCHF2+H$^+$** (closed-shell).

| | | | |
|---|---|---|---|
| C | 5.95015900 | -0.84425200 | 0.00014400 |
| C | 5.12815800 | -1.97750300 | 0.00056700 |
| C | 3.74483400 | -1.84687500 | 0.00056400 |
| C | 3.19521100 | -0.56157600 | 0.00007400 |
| C | 4.02386500 | 0.57792500 | -0.00023800 |
| C | 5.40472300 | 0.44023400 | -0.00023100 |
| C | 1.80428300 | -0.12289900 | 0.00003000 |
| C | 1.77855600 | 1.30649400 | -0.00011200 |
| C | 3.18860300 | 1.84004600 | -0.00051200 |
| C | 0.61953600 | -0.82206800 | -0.00038200 |
| C | -0.63517200 | -0.14554600 | -0.00026800 |
| C | -0.65097500 | 1.30515900 | 0.00005200 |
| C | 0.58966500 | 1.99087300 | -0.00000500 |
| C | -1.77029600 | -0.97545200 | -0.00038600 |
| C | -3.15754100 | -0.75163800 | -0.00021300 |
| C | -3.81437400 | 0.53372500 | 0.00017900 |
| C | -3.15244100 | 1.79025000 | 0.00048800 |
| C | -1.81915300 | 2.11192400 | 0.00042600 |
| C | -3.97274900 | -1.92664100 | -0.00034300 |
| C | -5.34122700 | -1.85861100 | -0.00010000 |
| C | -5.97723200 | -0.59864400 | 0.00009700 |
| C | -5.23093000 | 0.55748700 | 0.00023600 |
| H | 7.02763800 | -0.96756400 | 0.00015600 |
| H | 5.57686800 | -2.96448000 | 0.00093600 |
| H | 3.11340000 | -2.72938000 | 0.00102100 |
| H | 6.05432300 | 1.30935900 | -0.00045900 |
| H | 3.37753700 | 2.47009700 | 0.87648400 |
| H | 3.37706700 | 2.46922800 | -0.87825700 |
| H | 0.62083900 | -1.90663400 | -0.00079700 |
| H | 0.58261600 | 3.07592100 | -0.00010100 |
| H | -1.51628700 | -2.03240200 | -0.00062800 |
| H | -3.82295000 | 2.64469600 | 0.00082100 |
| H | -1.61595200 | 3.17904900 | 0.00071200 |
| H | -3.48239100 | -2.89384300 | -0.00073500 |
| H | -5.93387200 | -2.76592600 | 0.00005700 |
| H | -7.06000700 | -0.54162100 | 0.00002200 |
| H | -5.73185500 | 1.51902100 | 0.00037300 |