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The Huisgen's cycloaddition of BODIPY acetylene and ferrocene azides in supercritical CO_2

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1. General consideration

All reagents and solvents were purchased from commercial suppliers and used without further purification. Reactions were carried out under argon atmosphere in dry solvents and monitored *in situ* by thin-layer chromatography (TLC) carried out on silica gel plates (Merck KGaA; 60 F_{154}), using UV light at 254 nm as the visualizing agent to assure consumption of starting materials prior to work up. NMR spectra were recorded on Bruker Avance II spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{19}F: 376 MHz) at room temperature. Chemical shifts are reported in parts per million (ppm) calibrated using residual non deuterated solvent as internal reference ($CDCl_3$ at δ 7.26 ppm (^{1} H NMR) & δ 77.16 ppm (^{13}C NMR)). Integration is determined as the relative number of atoms. High resolution mass spectrometry was performed on TripleTOF 5600+ (AB Sciex, Canada). The absorption and emission spectra were recorded using Agilent Cary 60 UV-Vis, Hitachi U-2900 and Hitachi F-2700 spectrometer respectively. All spectra were measured at 22 °C in THF without degassing (concentration: $10^{-4} – 10^{-6}$ M). Cyclic voltamm

Copper wire sample preparation

A sample weighed (about 100 mg), taken with an accuracy of 0.1 mg, was dissolved in 69% HNO_3 (for Cu wire) or a mixture of 36% HCl: 98% H_2SO_4 (approximately 1:1) when heated, the resulting solution was transferred to a volumetric flask and made up to 50 ml with deionized water. All acid Panreac, ACS-ISO grade.

ICP-AES analysis of copper wire

Element analysis was performed with an ICP-AES 720 spectrometer (Agilent Technologies, USA) with an axial quartz torch with an inner 1.8-mm diameter injector tube (Agilent Technologies, USA), a double-pass glass cyclonic spray chamber (Agilent Technologies), a OneNeb nebulizer (Agilent Technologies), and a Trident Internal Standard Kit (Glass Expansion USA). For sample introduction, an SPS3 autosampler was used. A peristaltic pump used the white/white polyvinyl chloride pump tube for feeding and the blue/blue pump tube for the drain. A Sc (20 mg L^{-1}) internal standard solution was added online (an orange/blue polyvinyl chloride pump tube) to increase the accuracy of measurements. Conditions of ICP–AES measurements are summed up in Table 1. Results were collected and processed with ICP Expert II software 2.0.5 (Agilent Technologies). Emission lines from Table 2 were used for measurements. All lines were measured simultaneously (a MultiCal mode). Linear or quadratic functions were used for calibration.

For each sample, three replicates were taken for each decomposition method. For each sample, two replicates were performed. Then, 4 ml of solution was needed for each replicate. Then the obtained data were averaged. The quality control of the analysis was carried out using a control sample with a known concentration of each element (20 mg L^{-1} P and S; 40 mg L^{-1} Fe; 200 mg L^{-1} Ca, K, Mg, and Na; 400 mg L^{-1} Si; and 1 mg L^{-1} of the rest). The control sample was prepared from standard solutions other than calibration solutions.

Table S1. Measurement parameters by ICP–AES. **The copper content of the wire sample used as catalyst was proven to be >99%.**

Parameters	Values
Conditions	
Power (kW)	1.50
Plasma-forming flow (L min^{-1})	18.0
Axial flow (L min^{-1})	1.50
Nebulizer flow (L min^{-1})	1.00
Replicate time (s)	10
Stabilization time (s)	30
Sample-injection parameters	
Sample time delay (s)	25
Pump rate (rpm)	12
Washing time (s)	10
Number of replicates	4

Table S2. Wavelengths (nm) for ICP-AES measurements

Elements	Emission lines, nm
Ag	328.07, 338.29
Al	308.22, 394.40, 396.15
As	188.98, 193.70, 197.20, 234.98
B	182.58, 208.89, 208.96, 249.68
Ba	230.42, 233.53, 455.40, 493.41, 614.17
Be	234.86, 249.47, 313.04, 313.11
Ca	315.89, 317.93, 393.37, 396.85, 422.67
Cd	228.80
Co	230.79, 231.160, 237.863, 238.892, 258.03
Cr	267.716, 276.259, 276.653, 313.205
Cu	324.754, 327.400
Fe	238.204, 239.563, 258.590, 259.940, 263.105
K	404.72, 766.49, 769.90
Li	610.37, 670.78
Mg	277.98, 279.55, 279.80, 280.27, 285.21, 383.23, 383.83
Mn	257.61, 259.37, 260.57, 293.305, 293.931, 294.92
Mo	202.03, 281.62, 284.82, 289.10, 313.26, 379.83
Na	568.82, 589.00, 589.59
Ni	216.56, 221.65, 227.02, 230.299, 231.604, 231.10
P	185.88, 213.62, 214.91
Pb	220.35
S	180.67, 181.97, 182.56
Sb	206.83, 217.58, 231.15
Sc	357.63, 424.68, 361.38, 357.25, 335.37
Se	196.03
Si	250.69, 251.43, 251.61, 252.41, 252.85, 288.16
Sn	189.925, 283.998, 317.503, 326.233
Sr	346.445, 407.771, 416.179, 421.552
Ti	334.188, 334.941, 336.122, 337.280, 368.520
V	289.265, 292.401, 311.837
W	207.91, 216.63, 222.59, 222.96, 224.88
Zn	202.55, 206.200, 213.86, 334.56

Table S3 Literature survey of the CuAAC reactions in $scCO_2$

Catalyst	CO_2 pressure, bar	T/°C	t/h	Yield, %	Reference*
CuI with PFL	300 bar	40	3	100	7
CuBr with PFL	300 bar	75	24	90	7
CuBr with 10% Cu^{II}	300 bar	75	24	92	8
CuBr	300 bar	60	36	95	8
CuBr with 10% Cu^{II}	300 bar	60	36	92	8
$CuCl_2$ 20 mol%	300 bar	36	3	0	9
$CuBr_2$ 20 mol%	300 bar	36	3	0	9
$CuSO_4 \cdot 5H_2O$ 20 mol%	300 bar	36	3	5	9
$Cu(OAc)_2 \cdot H_2O$ 20 mol%	300 bar	36	3	99	9
$Cu(NO_3)_2 \cdot 3H_2O$ 20 mol%	300 bar	36	3	5	9
Cu-wire with $Cu(OAc)_2$	85 bar	100	Flow reactor	48	10
Cu-wire	130 bar	35	24–48		11
Cu-wire	130 bar	50	24	93	12
$Cu(OAc)_2 \cdot H_2O$	110 bar	47	48	97	13
$Cu(OAc)_2 \cdot H_2O$	100 bar	47	48	93	13
$Cu(OAc)_2 \cdot H_2O$	80 bar	47	24	90	13
Cu-wire	81 bar	80	8	97	This work

* Reference number from the main text

2. Synthesis and characterization.

Synthesis scheme

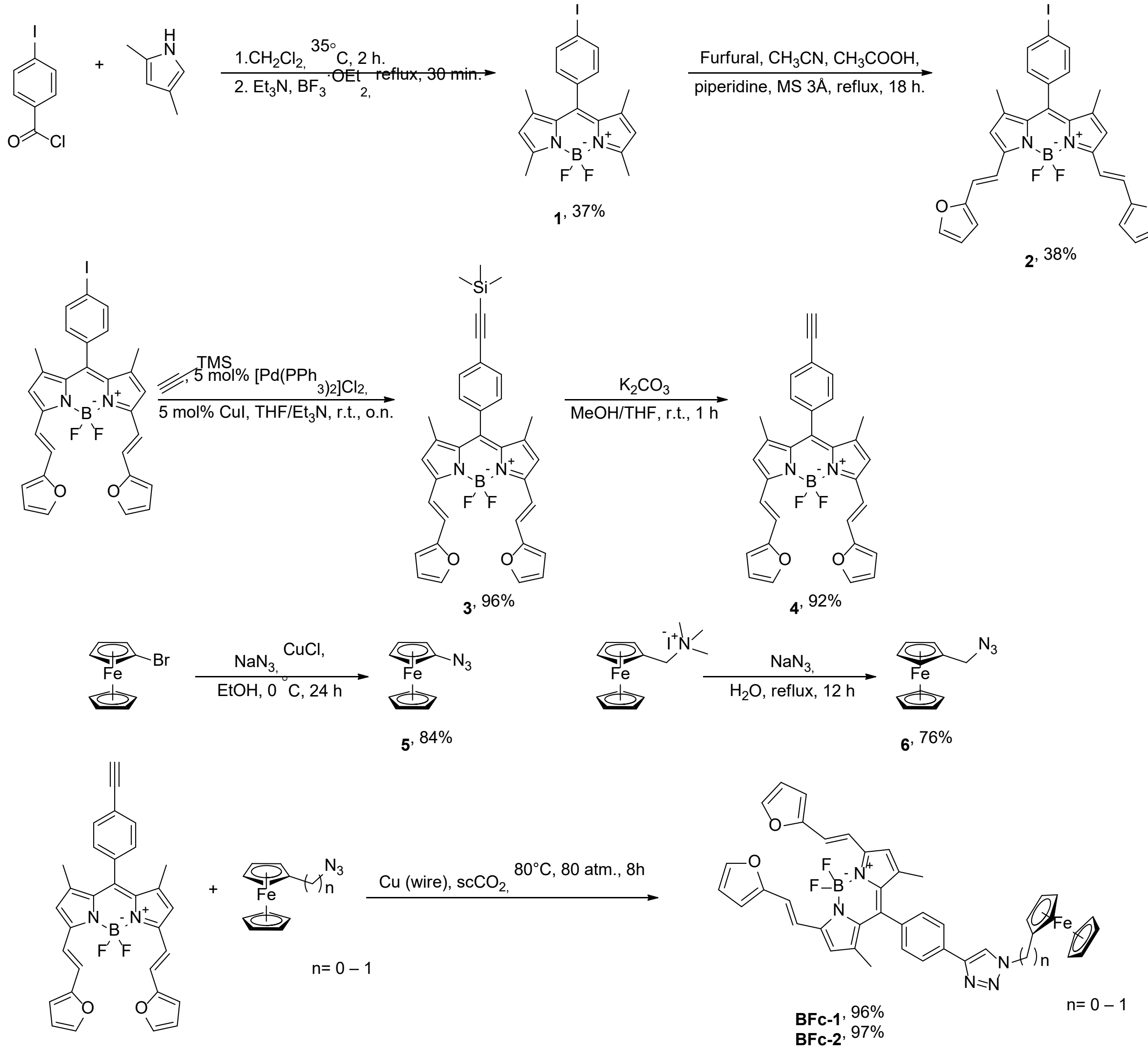

Figure S1. General synthetic scheme.

Synthesis of 4,4-difluoro-1,3,5,7-tetramethyl-8-(4-iodophenyl)-4-bora-3a,4a-diaza-*s*-indacene (1).

Synthesis was performed according to the literature procedure [*Bioorg. Med. Chem.*, 2013, **21**, 5770] with slight modifications. Into 100 ml round bottom flask 4-iodobenzoyl chloride (7.7 mmol, 1.00 equiv.) and 2,4-dimethyl pyrrole (15.7 mmol, 2.04 equiv.) were dissolved in dry DCM. The color of the mixture was immediately changed into bright red. After stiring for 3 h at 35 °C under inert atmosphere, the mixture was cooled down to 0°C with salt-ice bath. Triethylamine (6.4 mL) and $BF_3.Et_2O$ (5 mL) were added dropwise, and the mixture was further refluxed for 30 min. On completion of the reaction (indicated by the bright greenish yellow fluorescence of the reaction mixture), the solvents was evaporated under reduced pressure and the residue was dissolved in DCM. The organic layer was washed with $NaHCO_3$ (1M) (2×100 ml), then HCl (1M) (2×25 ml) and water (2×50 ml), dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The obtained dark red crude product was then purified by column chromatography over silica gel, using DCM/petroleum ether (1:1) as eluent to yield compound **1** as an orange solid. Yield 1.28 g (37%).^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.42 (6 H, s, Me), 2.55 (6 H, s, Me), 5.99 (2H, s, CH-pyrrole), 7.08 – 7.02 (2H, m, Ph), 7.88 – 7.82 (2H, m, Ph). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 14.7, 14.8, 94.9, 121.6, 130.1, 131.2, 134.7, 138.5, 140.2, 143.0, 156.0. ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -146.07 – -146.50 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na]^+$, calculated for $C_{19}H_{18}BF_2IN_2Na$ 473.0468; found 473.0479.

Synthesis of 4,4-difluoro-1,7-dimethyl-3,5-bis[2-(furan-2-yl)vinyl]-8-(4-iodophenyl)-4-bora-3a,4a-diaza-*s*-indacene (2).

Synthesis was performed according to the modified literature procedure [*J. Org. Chem.*, 2021, **86**, 8755]. Into 100 ml round bottom flask BOIDPY (**1**) 300 mg (0.67 mmol, 1 equiv.), furfural 552 µl (6.7 mmol, 10 equiv.), acetic acid (30 µl), piperidine (60 µl), freshly dried molecular sieves (3Å) 2 g and 30 ml of dry CH_3CN were added. Then flask was wrapped with aluminum and mixture refluxed for 18 h with TLC monitoring (EtOAc:Petroleum ether, 1:5). After completion the reaction mixture was cooled down to room temperature and passed through a plug of silica gel. The plug was washed with DCM until liquid became slightly colored. The organic phases were combined and evaporated under reduced pressure. The obtained crude dark blue crystal product was purified by column chromatography over silica gel, using EtOAc/petroleum ether (1:1) as eluent to yield compound **2** as dark blue-copper crystals. Yield 154 mg (38%).^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.46 (6 H, s, Me), 6.49 - 6.46 (2 H, m, Fur), 6.59 – 6.53 (4H, m, Fur), 7.02 (2H, d, J = 16.14 Hz, CH-stilb), 7.11 – 7.06 (2H, m, Ph), 7.52 (2H, d, J = 1.69 Hz, CH-pyrrole), 7.59 (2H, d, J = 16.17 Hz, CH-stilb), 7.87 – 7.83 (2H, m, Ph). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 15.1, 94.9, 112.2, 112.5, 117.5, 118.0, 123.2, 130.6, 134.9, 138.4, 141.7, 144.2, 152.5, 153.1. ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -138.52 – -139.00 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na]^+$, calculated for $C_{29}H_{22}BF_2IN_2Na$ 629.0679; found 629.0693.

Synthesis of [(4-{4,4-difluoro-1,7-dimethyl-3,5-bis[2-(furan-2-yl)vinyl]-4-bora-3a,4a-diaza-*s*-indacene-8-yl}phenyl)ethynyl]trimethylsilane (3).

Synthesis was performed according to the literature procedure [*Angew. Chem. Int. Ed.*, 2021, **60**, 7851]. Into 50 ml round bottom flask BODIPY (**2**) 120 mg (0.198 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (5 mol%) and CuI (5 mol%) were dissolved in a degassed mixture of dry THF and triethylamine (6 mL) (1:1). Ethynyltrimethylsilane (0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at room temperature (20°C) overnigth. On completion of the reaction, as determined by TLC control (EtOAc/petroleum ether (1:5)), the mixture of solvents was evaporated under reduced pressure and the residue was washed with HCl solution (1M) to neutralize the remaining amount of triethylamine present within the medium. The residue was then dissolved in DCM, and the organic layer was washed thrice with brine, dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The obtained crude product was then purified by column chromatography over silica gel using DCM:Petroleum ether as eluent to yield compound **3** as dark blue solid. Yield 110 mg (96%).^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.29 (9 H, s, $Si(Me)_3$), 1.44 (6 H, s, Me), 6.49 – 6.44 (4H, m, Fur), 6.57 – 6.53 (2H, m, Fur), 7.02 (2H, d, J = 16.12 Hz, CH-stilb), 7.25 – 7.29 (2H, m, Ph), 7.52 (2H, d, J = 1.58 Hz, CH-pyrrole), 7.64 – 7.56 (4H, m, CH-stilb, Ph). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 0.045, 15.0, 96.0, 104.4, 112.2, 112.5, 117.6, 118.0, 123.1, 124.0, 128.7, 132.8, 133.5, 135.6, 137.3, 141.8, 144.1, 152.4, 153.1. ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -138.4 – -138.9 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na]^+$, calculated for $C_{34}H_{31}BF_2N_2NaO_2Si$ 599.2108; found 599.2123.

Synthesis of 4,4-difluoro-1,7-dimethyl-3,5-bis[2-(furan-2-yl)vinyl]-8-(4-ethynylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (4).

Synthesis was performed according to the literature procedure [*Angew. Chem. Int. Ed.*, 2021, 60, 7851]. BODIPY **3** 50 mg (0.087 mmol, 1 equiv.) was dissolved in a mixture of MeOH (5 mL) and THF (5 mL) in a 25 mL round bottom flask. Solid K_2CO_3 17.4 mg (0.126 mmol, 1.45 equiv.) was added, and the reaction mixture was stirred at room temperature for 1 h. The progress of the reaction was monitored using TLC. On completion, the reaction was immediately quenched with saturated aqueous NH_4Cl (15 mL) and the residue extracted with DCM. The organic layer was washed with brine (3×15 ml), dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure The obtained crude product was then purified by column chromatography over silica gel using DCM/petroleum ether as eluent to yield compound **4** as dark green-gold solid. Yield 40 mg (92%).^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.44 (6 H, s, Me), 3.19 (1 H, s, Acetylene-CH), 6.50 – 6.44 (2H, m, Fur), 6.58 – 6.53 (4H, m, Fur), 7.02 (2H, d, J = 16.25 Hz, CH-stilb), 7.33 – 7.28 (2H, m, Ph), 7.52 (2H, d, J = 1.58 Hz, CH-pyrrole), 7.66 – 7.56 (4H, m, CH-stilb, Ph). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 15.0, 78.7, 83.1, 112.2, 112.5, 117.5, 118.0, 123.0, 123.1, 128.9, 132.9, 133.5, 135.9, 137.1, 141.8, 144.2, 152.5, 153.1. ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -138.5 – -138.9 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na]^+$, calculated for $C_{31}H_{23}BF_2N_2NaO_2$ 527.1713 found 527.1717.

Synthesis of azidoferrocene (5):

Synthesis was performed according to the literature procedure [*Organometallics*, 2019, **38**, 1361] with slight modifications. In 25 ml round bottom flask 500 mg of bromoferrocene (1.89 mmol, 1.00 equiv.) were dissolved in 12 ml of dry ethanol. The reaction mixture was then cooled in an ice bath, 240 mg of cuprous chloride (2.43 mmol, 1.29 equiv) and 280 mg of sodium azide (4.23 mmol, 2.24 equiv) with 0.8 ml of water were added. After stiring in the dark for 24 h at 0°C, reaction mixture was filtered through plug Celite

General method for $scCO_2$ click reaction

Into 50 ml vessel, 25 mg of BODIPY acetylene **4** (0.040 mmol, 1.00 equiv), 0.04 mmol of the corresponding ferrocene azide (1.00 equiv) were added. Copper wire (2 cm×2 mm) freshly purified with 1M nitric acid, washed with deionized water, acetone and finally wiped with a paper towel, was also introduced into the reactor. Then CO_2 from cylinder was fed to adjust the pressure of 65.3 atm. The reactor vessel was heated to 80 °C with thermocouple control and stirring with a magnetic stirrer for 8 h. Under these conditions, a pressure of 80 atm was reached. The reaction mixture was then allowed to cool to room temperature, and the vessel was carefully decompressed to atmospheric pressure. The product was washed out of the reactor with chloroform (3×10 ml), then the organic phase was combined and washed with $NH_4Cl_{(saturated)}$ (1×25 ml). The organic phase was dried over anhydrous Na_2SO_4 and organic solvent was evaporated under reduced pressure. The obtained dark blue solid was pure (TLC, petroleum ether/ethyl acetate (20:1)) and does not require further purification.

BFc-1, Yield 35 mg (96%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.52 (6 H, s, Me), 4.27 (5 H, s, C_5H_5), 4.35 – 4.30 (m, 2 H, C_5H_4), 4.95 – 4.87 (m, 2 H, C_5H_4), 6.50 – 6.45 (2 H, m, Fur), 6.60 – 6.53 (4 H, m, Fur), 7.03 (2 H, d, J = 16.14 Hz, CH-stilb), 7.45 – 7.39 (2 H, m, Ph), 7.52 (2 H, d, J = 1.25 Hz, CH-pyrrole), 7.66 – 7.58 (4 H, d, J = 16.01 Hz, CH-stilb), 8.07 – 8.02 (2 H, m, Ph), 8.08 (1 H, s, CH-triazole). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 15.1, 29.85, 62.31, 67.00, 70.43, 77.36, 93.81, 112.1, 112.5, 117.6, 117.9, 119.6, 123.0, 126.4, 129.4, 131.3, 133.8, 135.2, 137.8, 142.0, 144.1, 147.0, 152.4, 153.1. ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -138.5 – -138.9 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na]^+$, calculated for $C_{41}H_{32}BF_2FeN_5NaO_2$ 754.1859 found 754.1876.

BFc-2, Yield 36 mg (97%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.46 (6 H, s, Me), 4.23 (5 H, s, C_5H_5), 4.27 – 4.25 (m, 2 H, C_5H_4), 4.37 – 4.33 (m, 2 H, C_5H_4), 5.38 (2 H, s, CH_2) 6.49 – 6.45 (2 H, m, Fur), 6.57 – 6.52 (4 H, m, Fur), 7.01 (2 H, d, J = 16.15 Hz, CH-stilb), 7.37 – 7.32 (2 H, m, Ph), 7.51 (2 H, d, J = 1.56 Hz, CH-pyrrole), 7.64 – 7.56 (4 H, d, J = 16.09 Hz, CH-stilb), 7.72 (1 H, s, CH-triazole), 7.97 – 7.90 (2 H, m, Ph). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm) 15.0, 50.5, 53.6, 69.1, 69.2, 69.4, 69.8, 73.3, 77.4, 80.6, 112.0, 112.4, 117.6, 117.9, 119.4, 123.0, 126.4, 129.2, 131.6, 133.7, 135.0, 137.9, 142.0, 144.1, 147.1, 152.3, 153.1 ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): -138.5 – -138.9 (m, BF_2). HRMS (FTMS + cESI) m/z: $[M + Na + DMSO]^+$, calculated for $C_{44}H_{40}BF_2FeN_5NaO_3S$ 846.2155 found 846.2173.

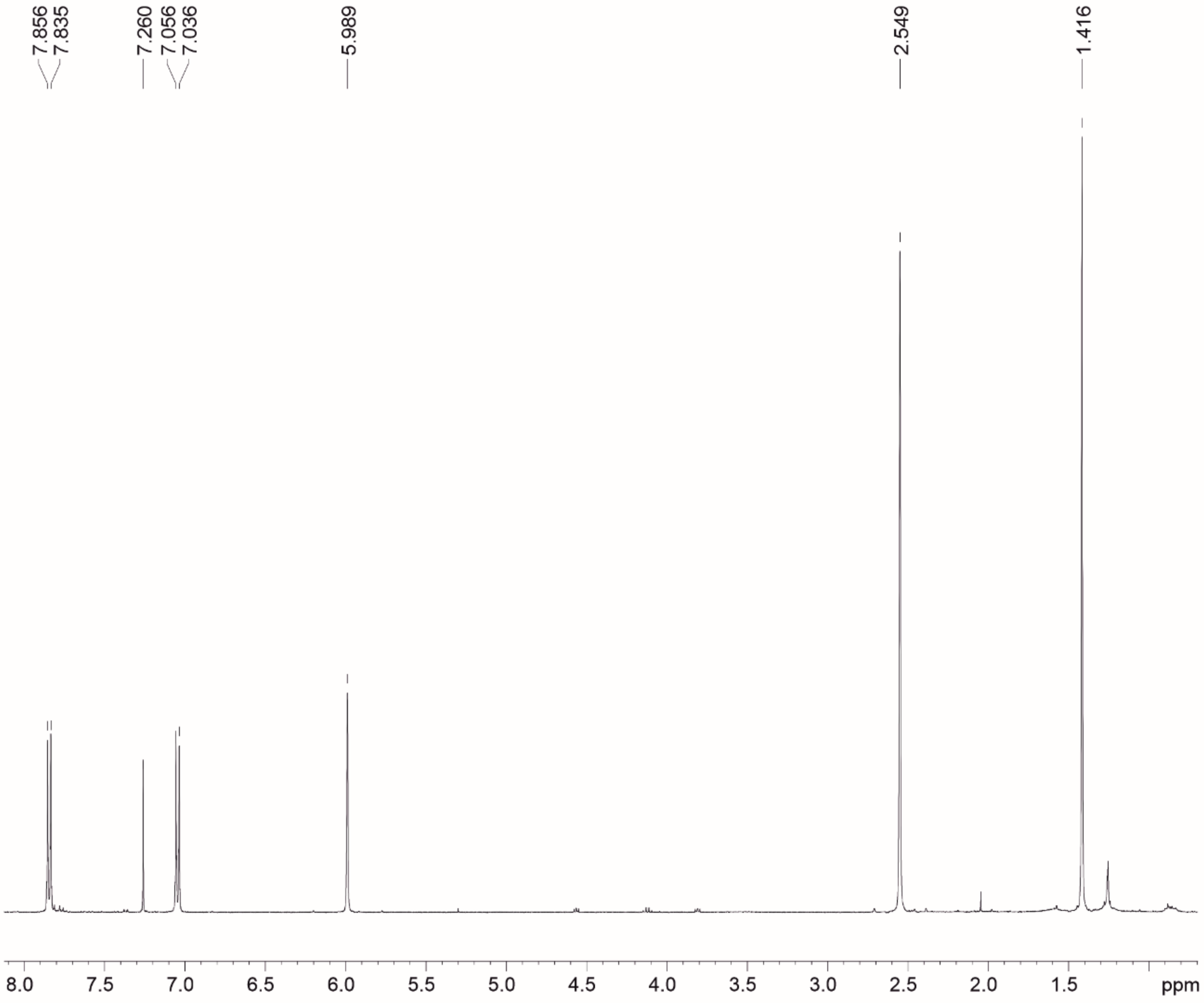

Figure S2. ^{1}H NMR spectra of **1.**

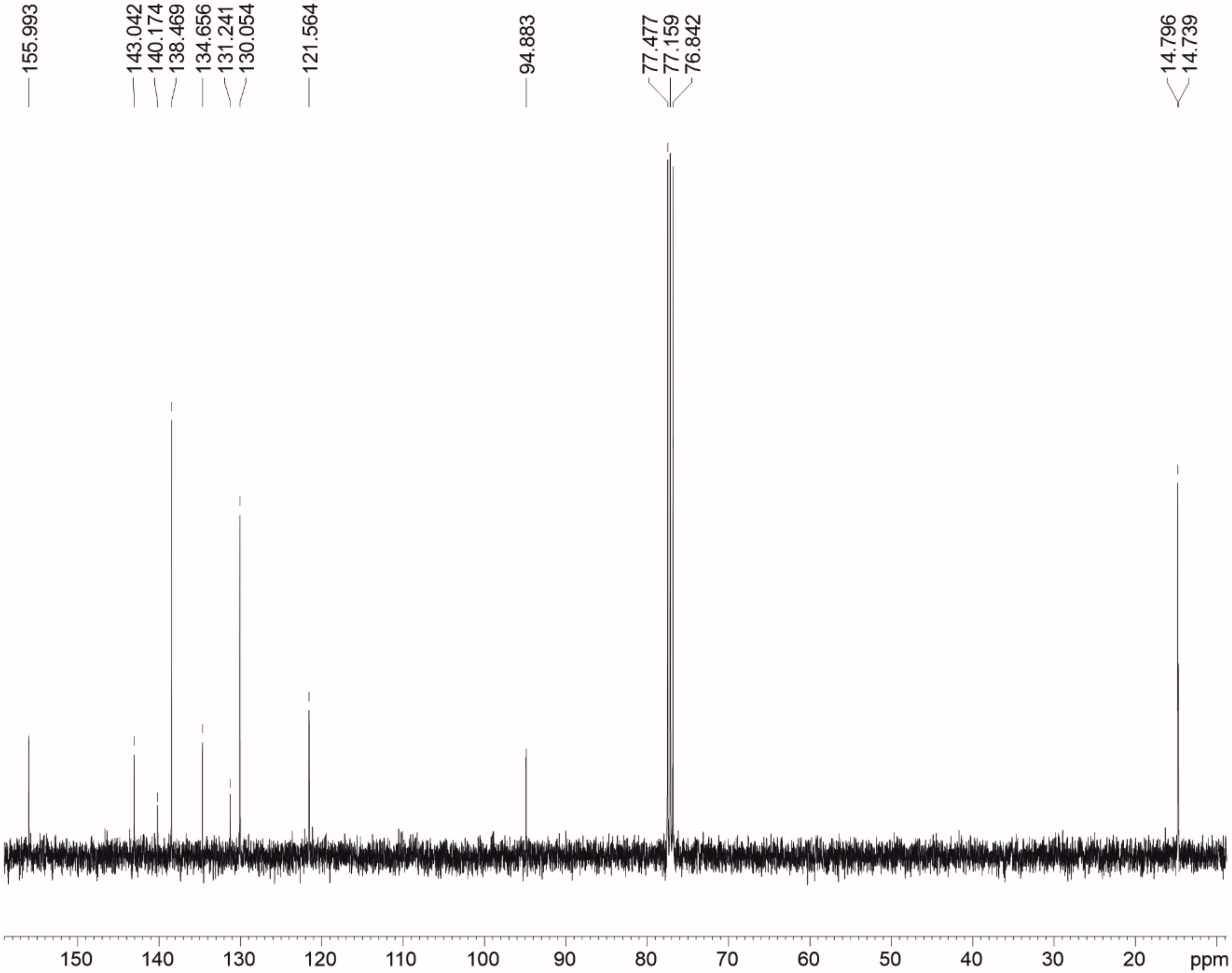

Figure S3. $^{13}C\{^1H\}$ NMR of **1**.

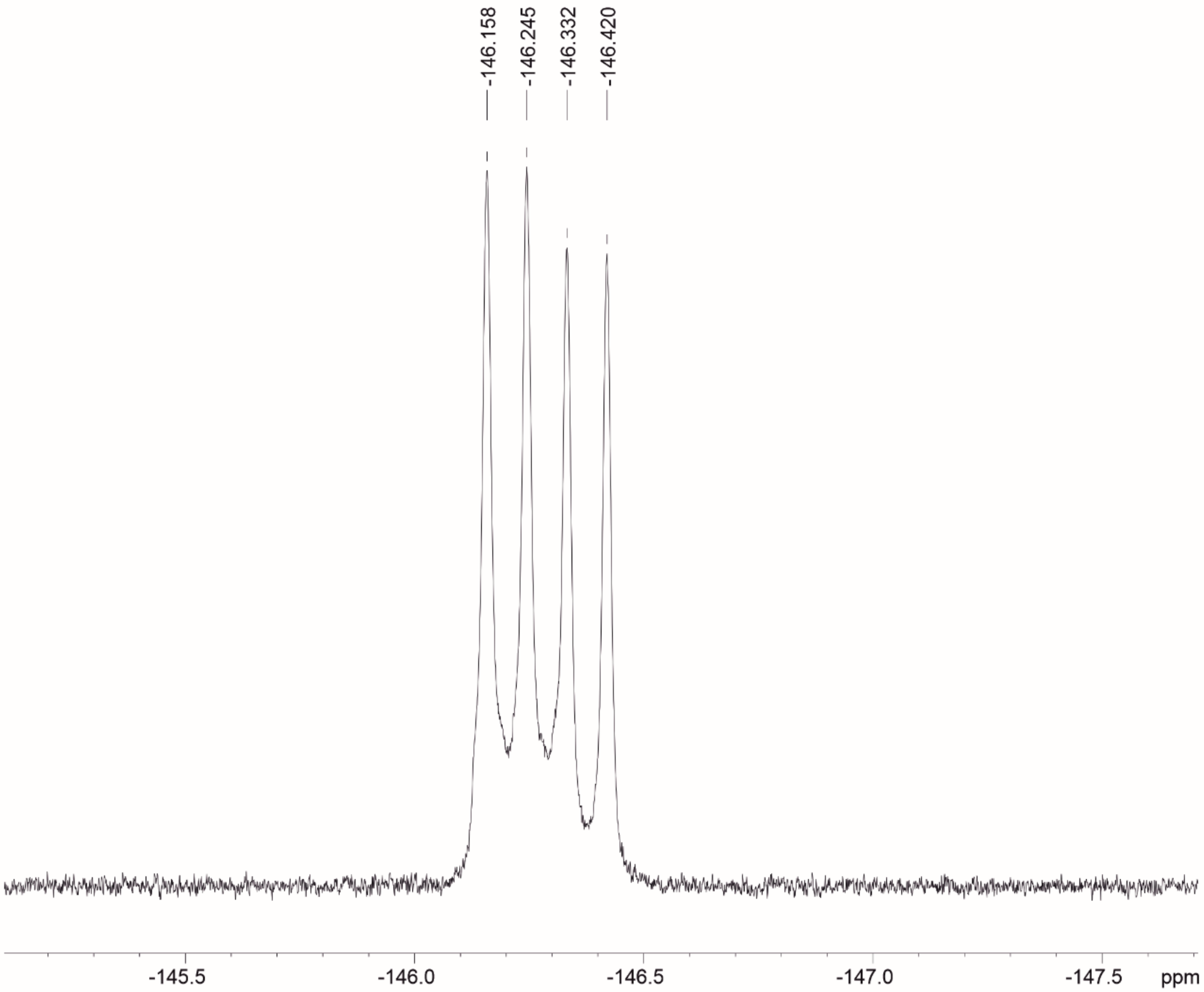

Figure S4. ^{19}F NMR of **1**.

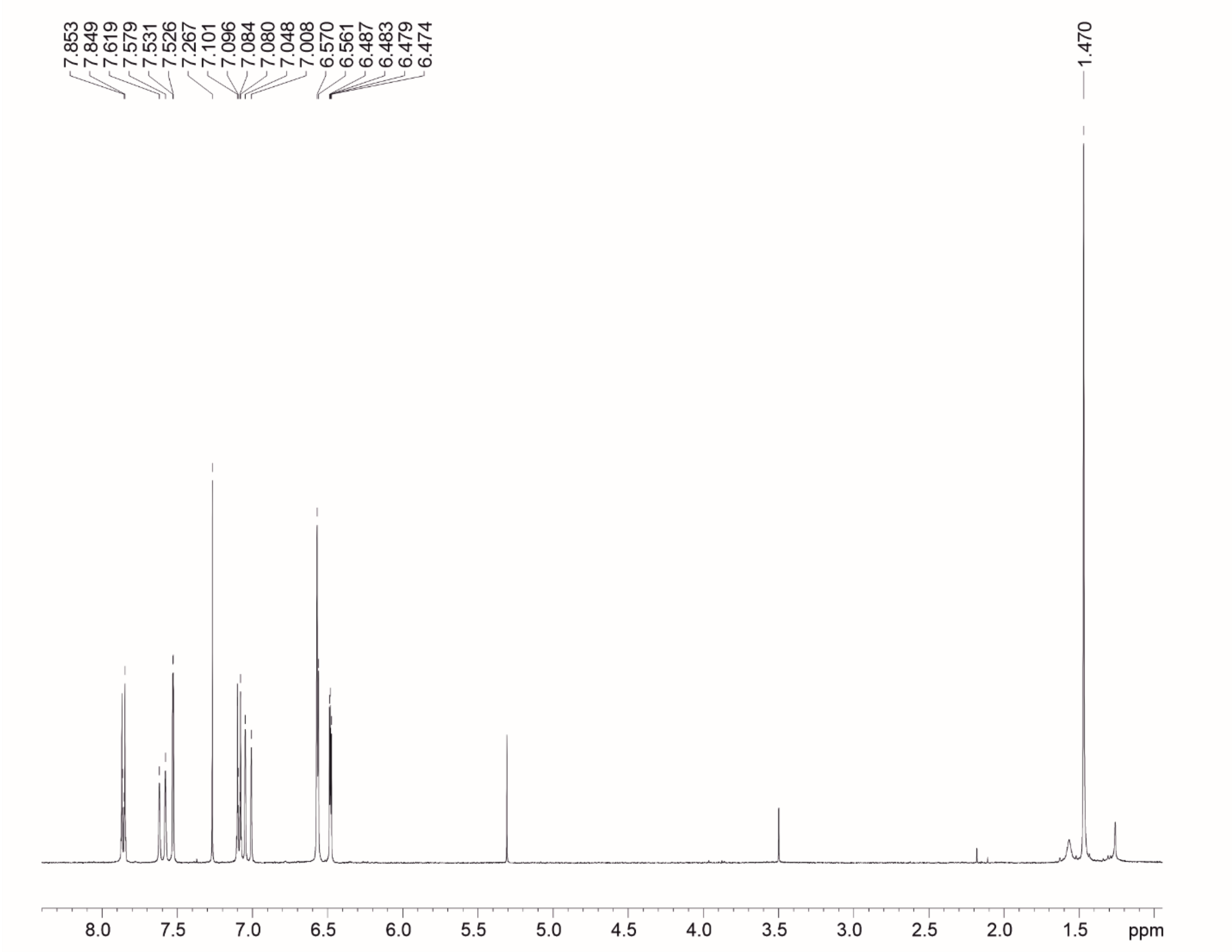

Figure S5. ^{1}H NMR of **2**.

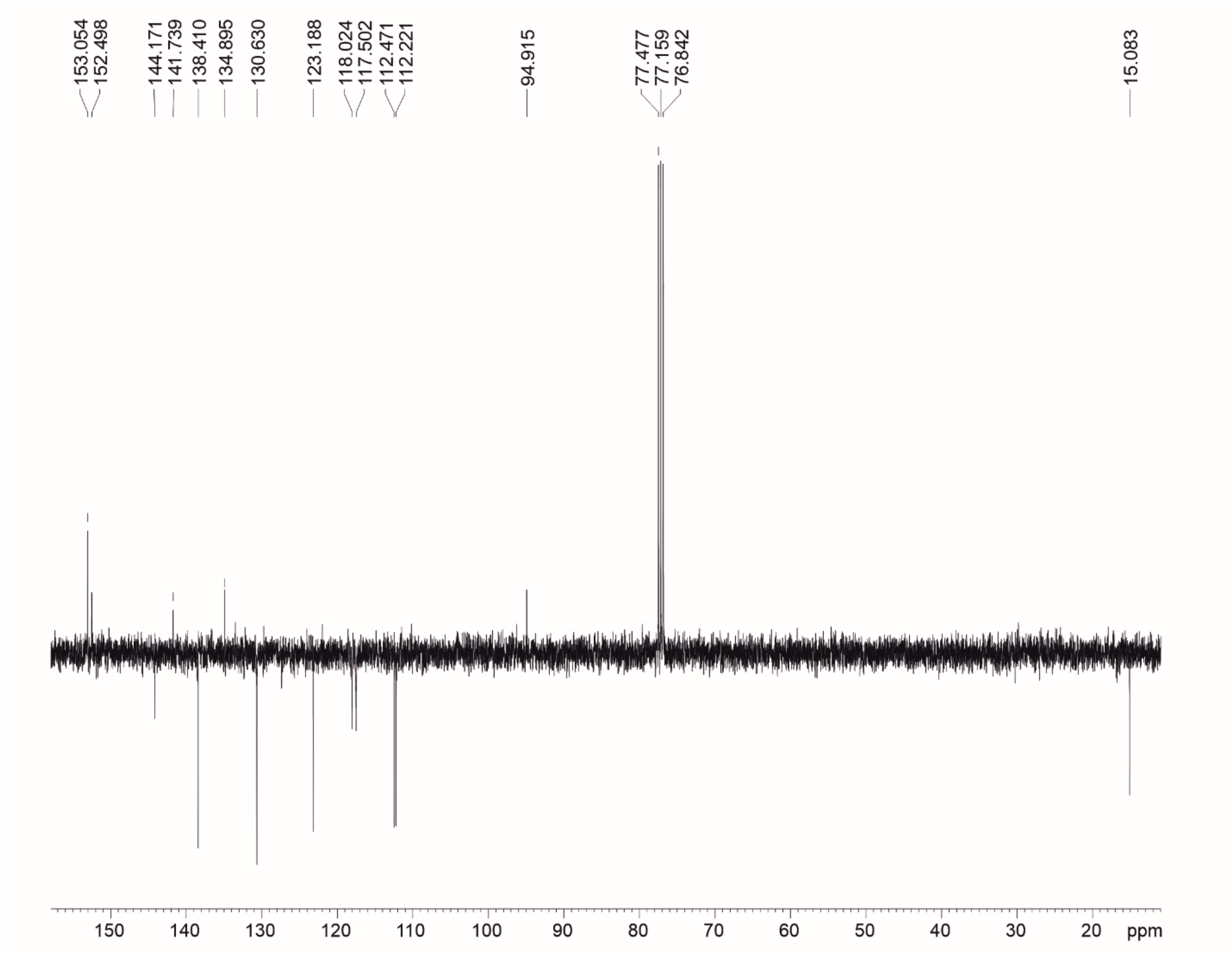

Figure S6. $^{13}C\{^1H\}$ NMR (APT) of **2**.

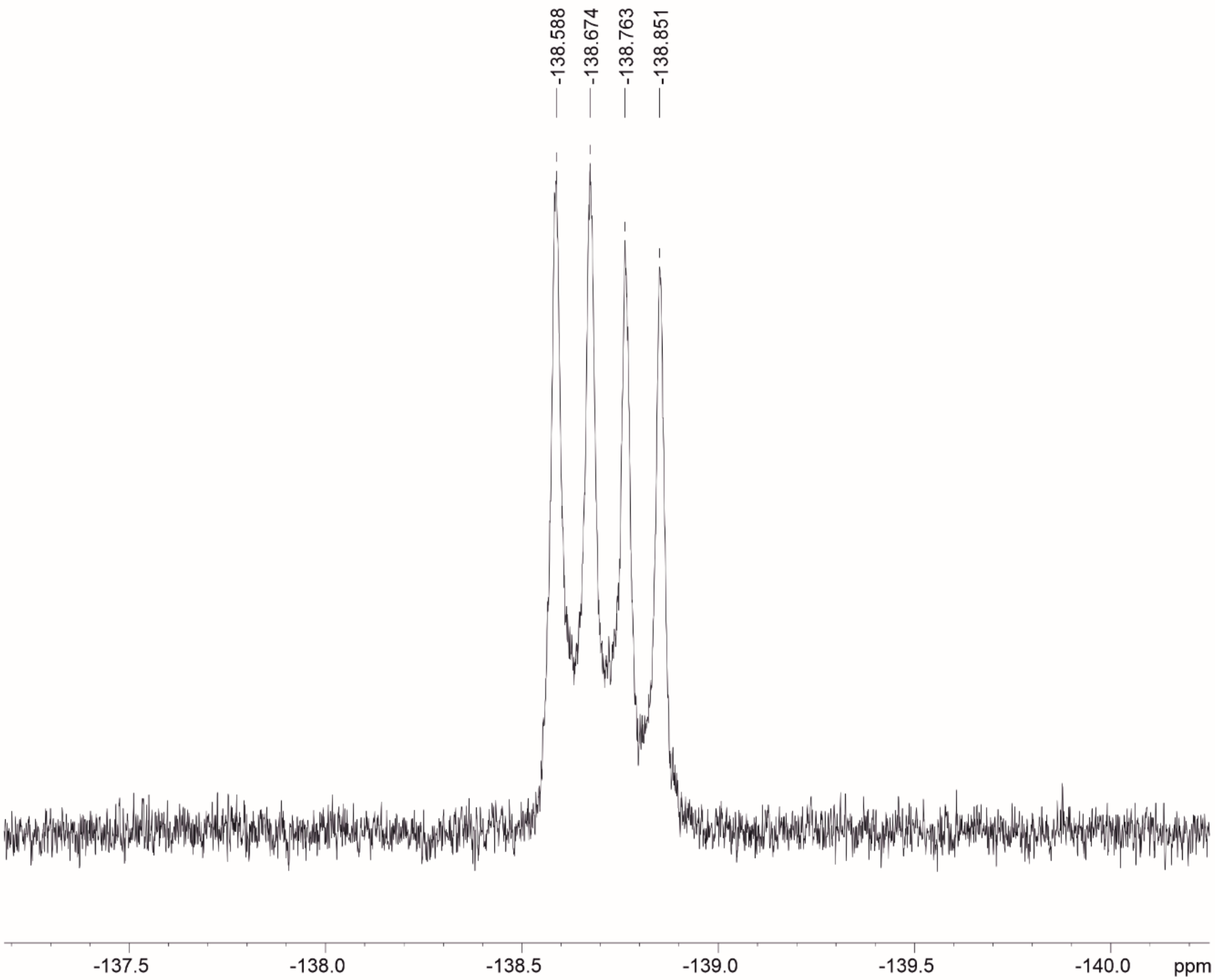

Figure S7. ^{19}F NMR of **2**.

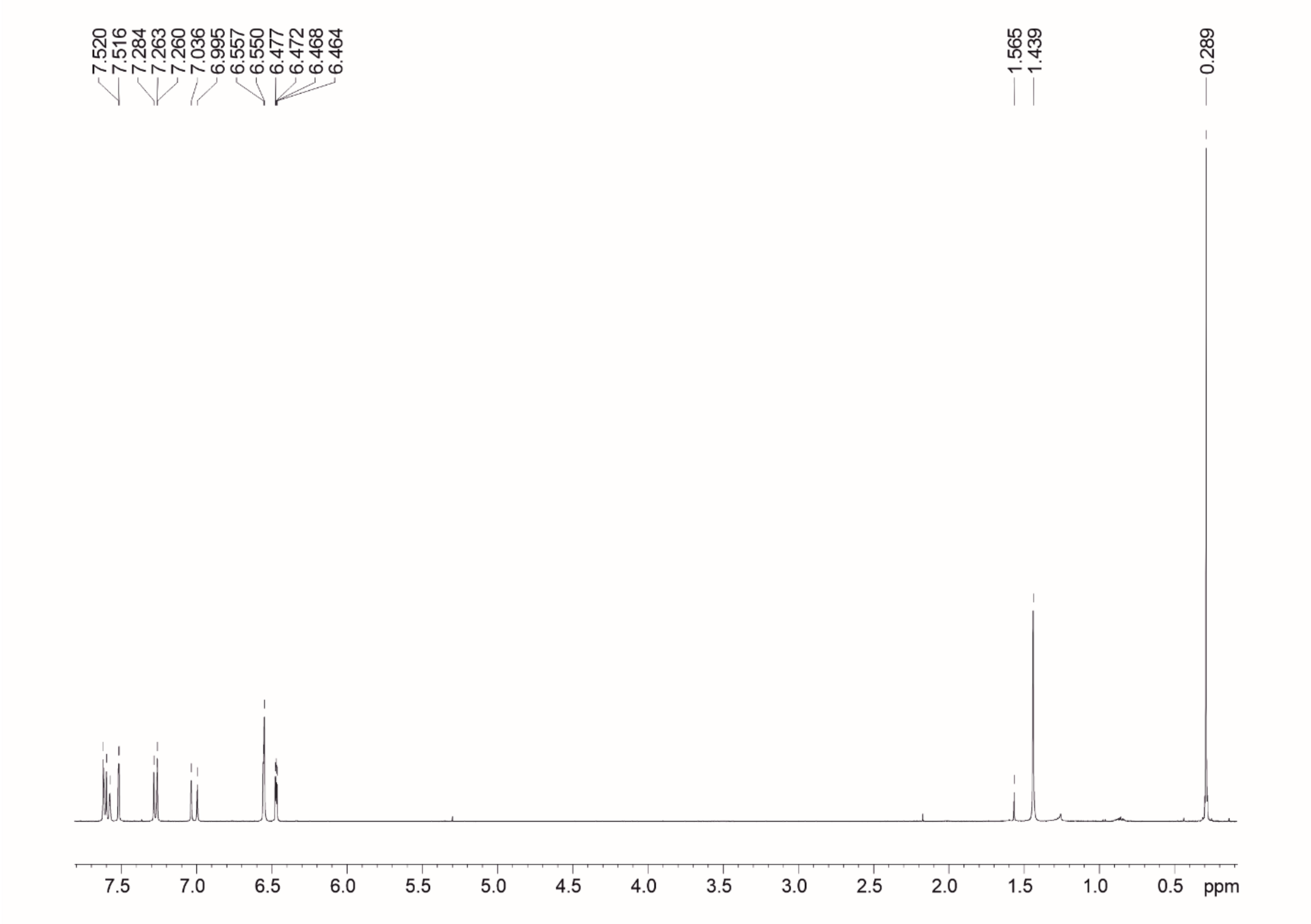

Figure S8. ^{1}H NMR of **3**.

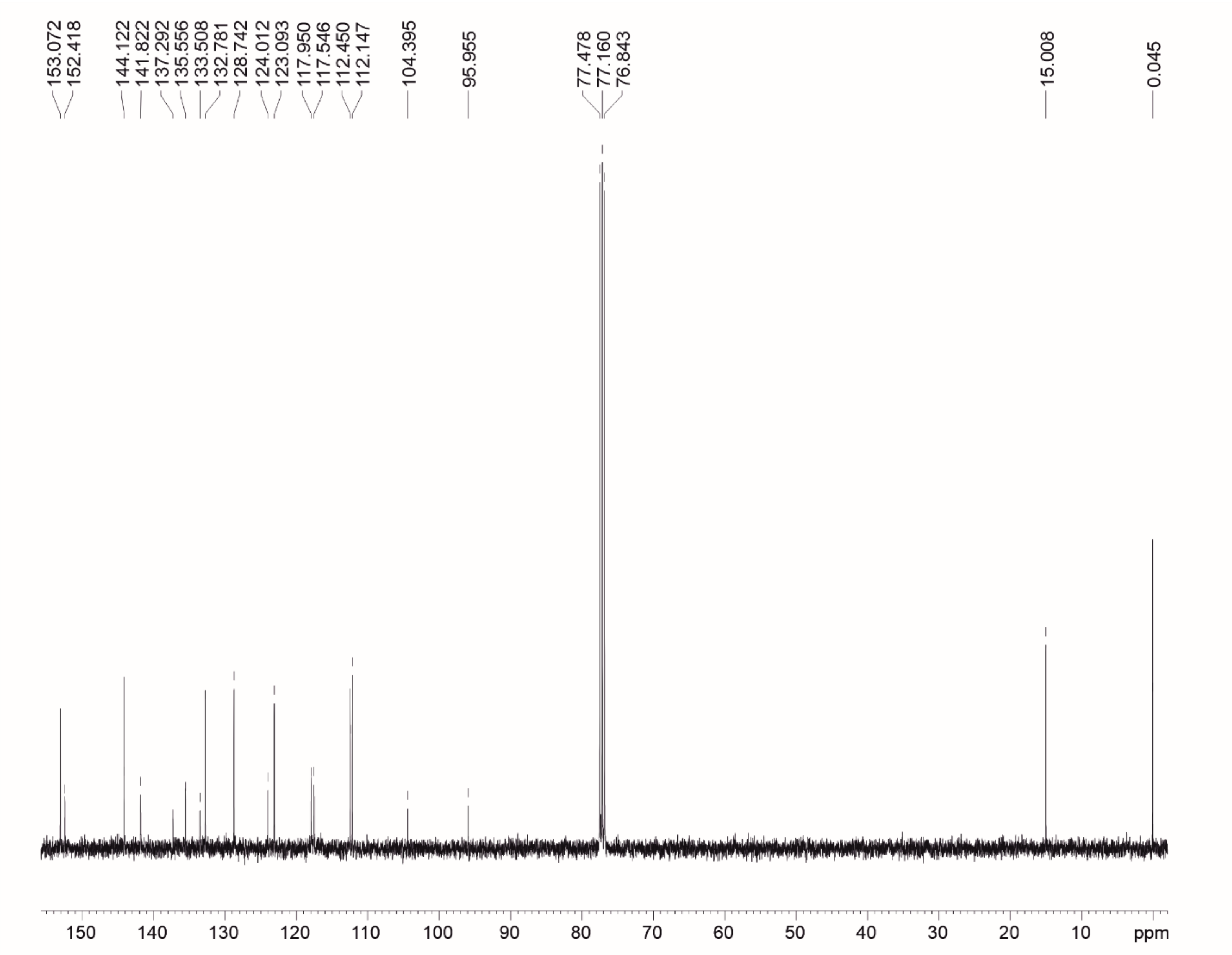

Figure S9. $^{13}C\{^1H\}$ NMR of **3**.

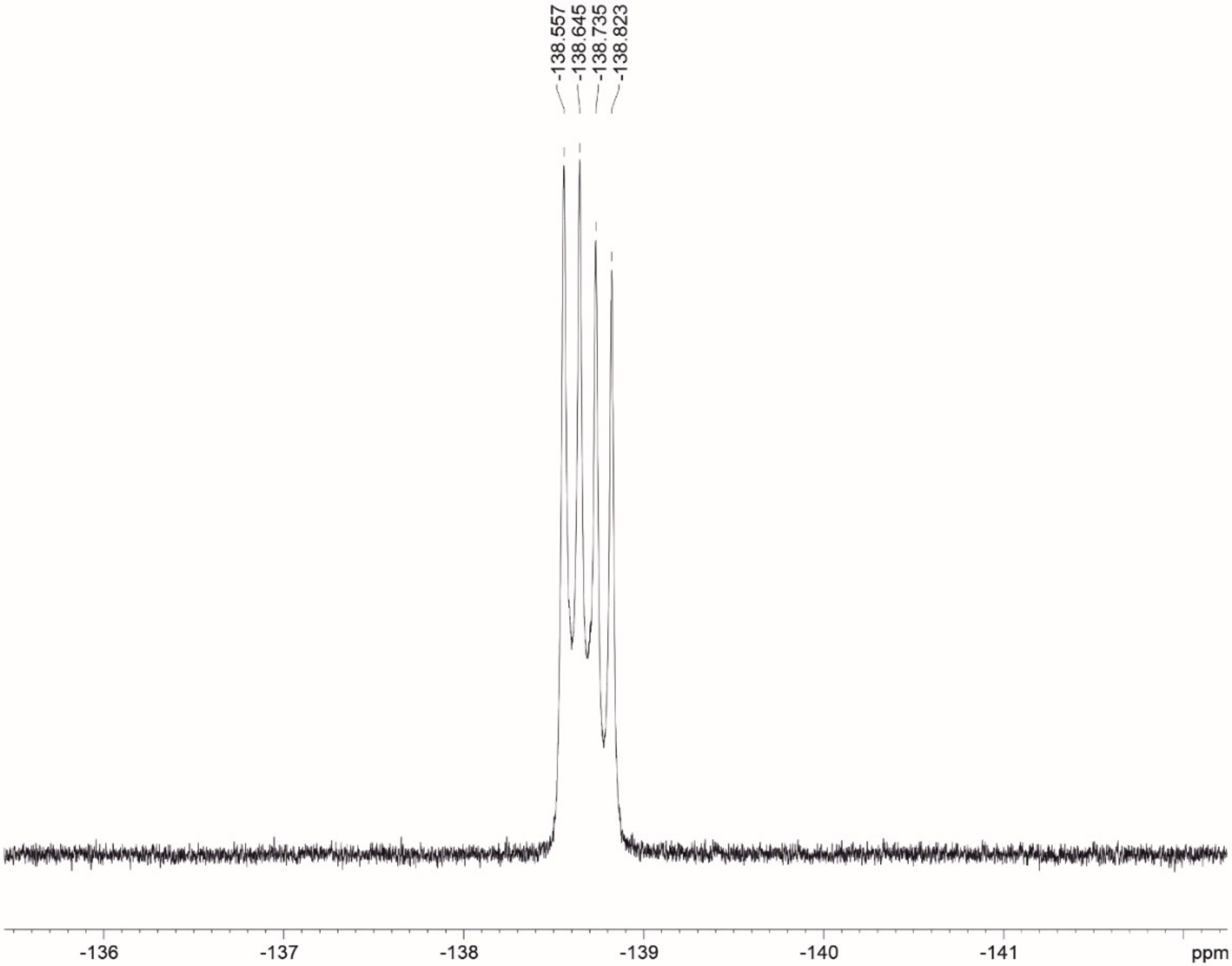

Figure S10. ^{19}F NMR of **3**.

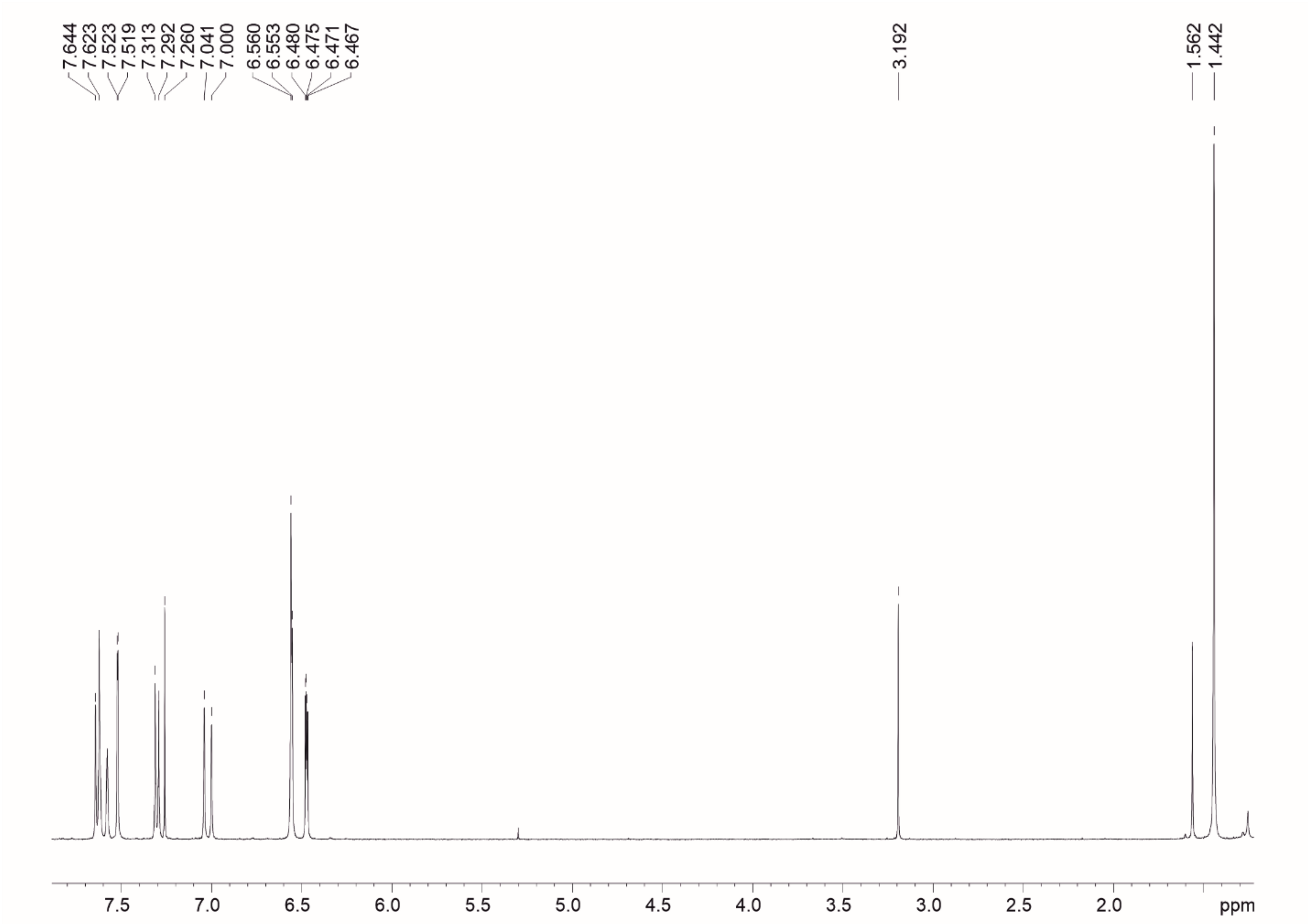

Figure S11. ^{1}H NMR of **4**.

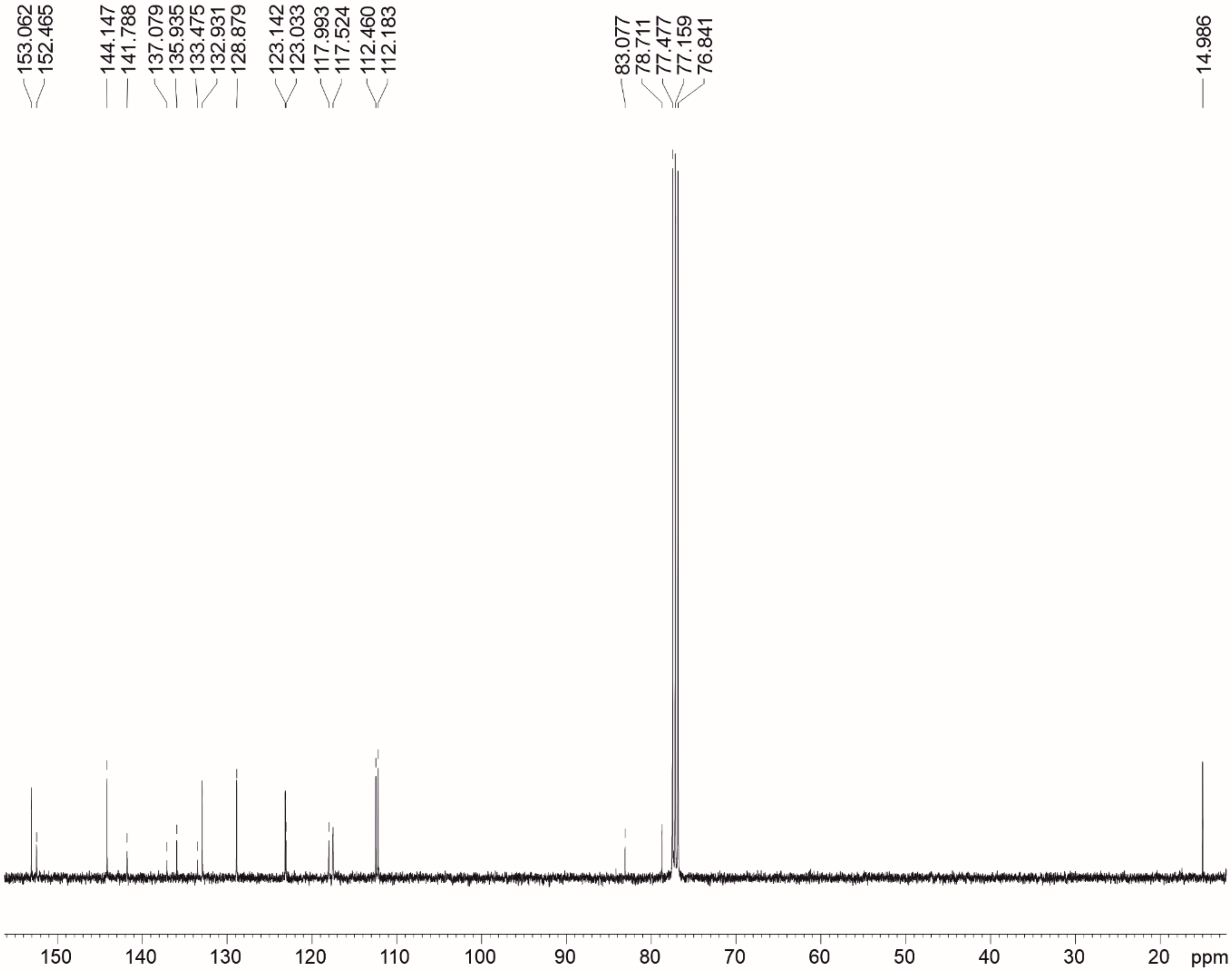

Figure S12. $^{13}C\{^{1}H\}$ NMR of **4**.

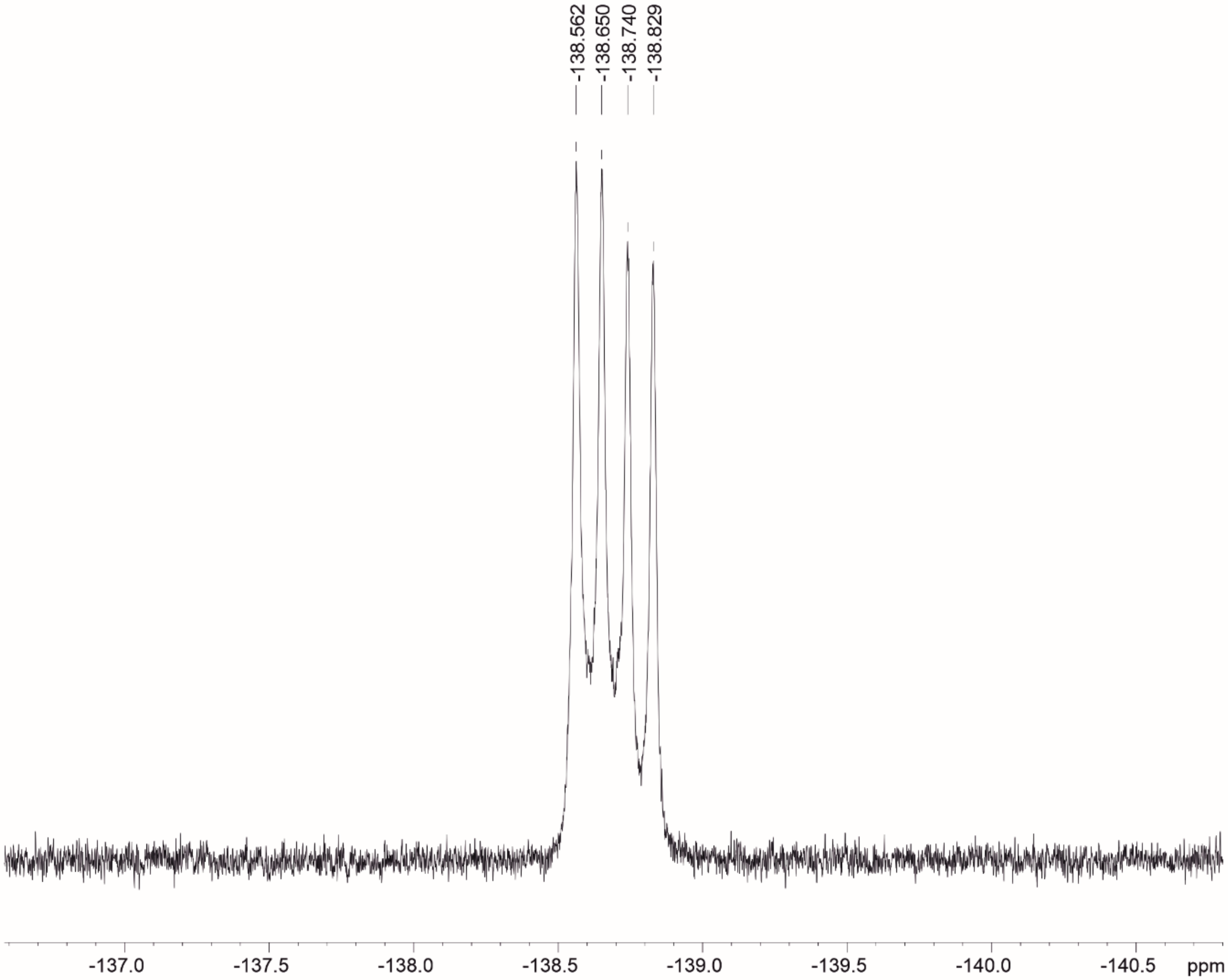

Figure S13. ^{19}F NMR of **4**.

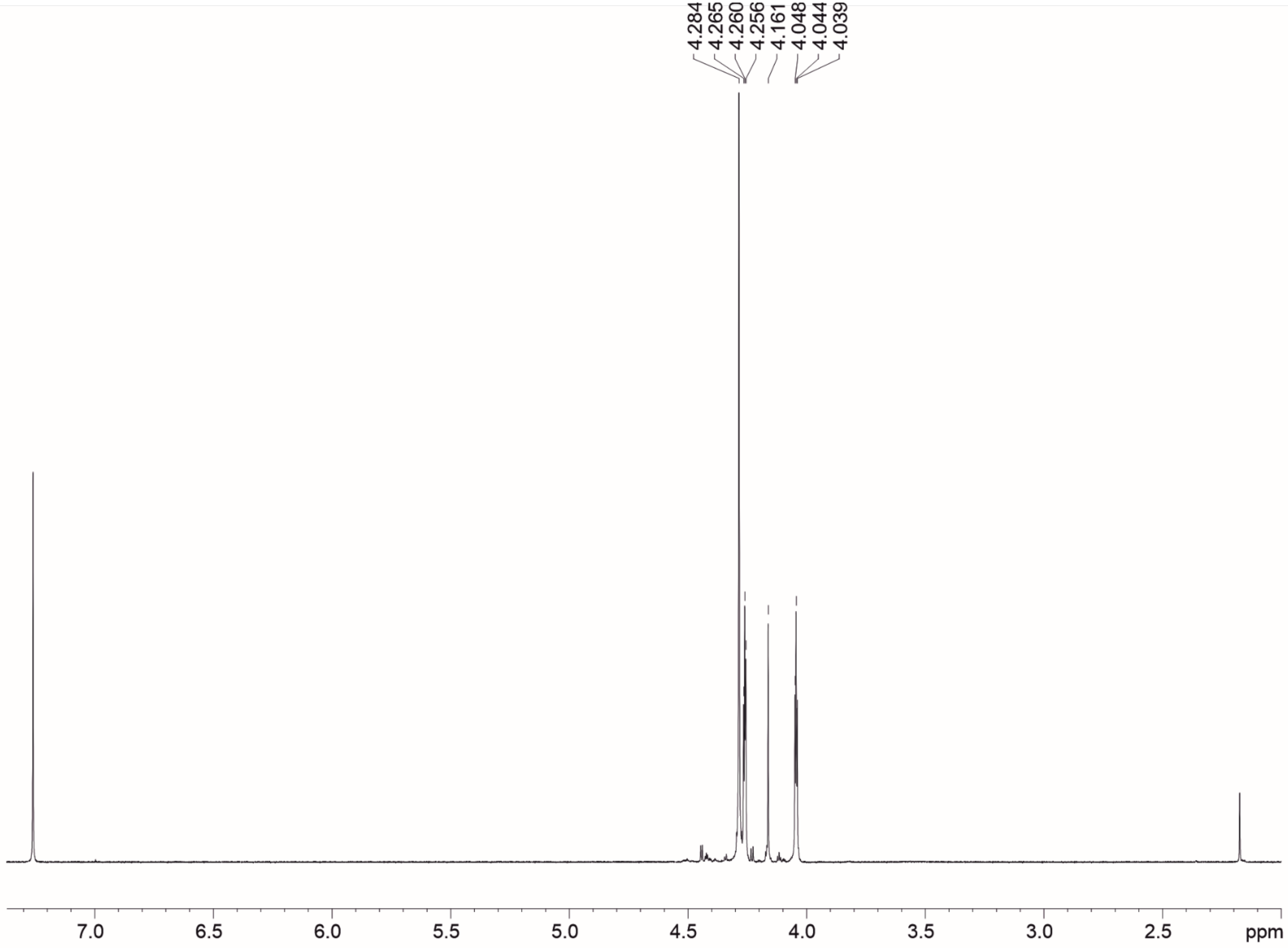

Figure S14. ^{1}H NMR of **5**.

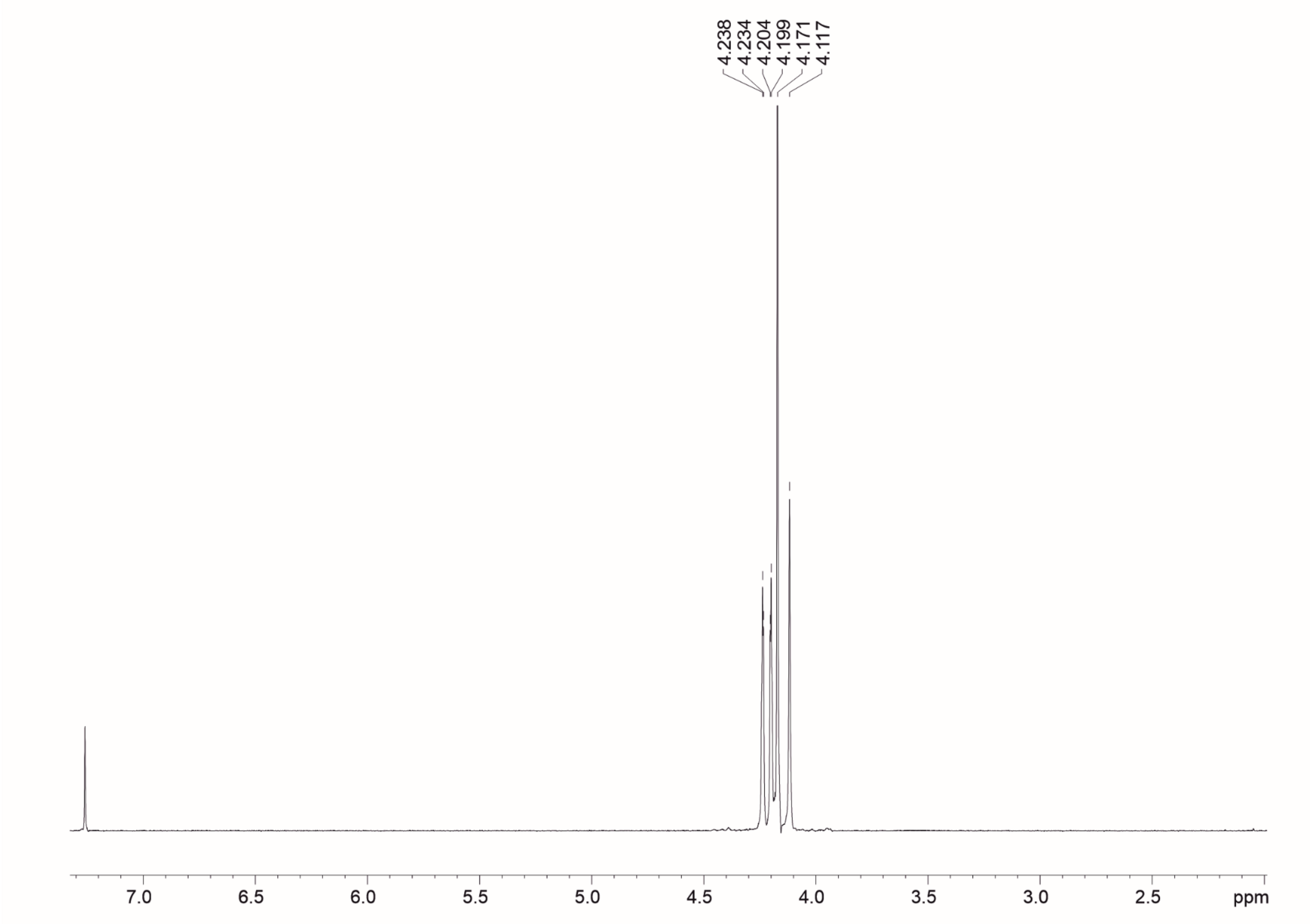

Figure S15. ^{1}H NMR of **6**.

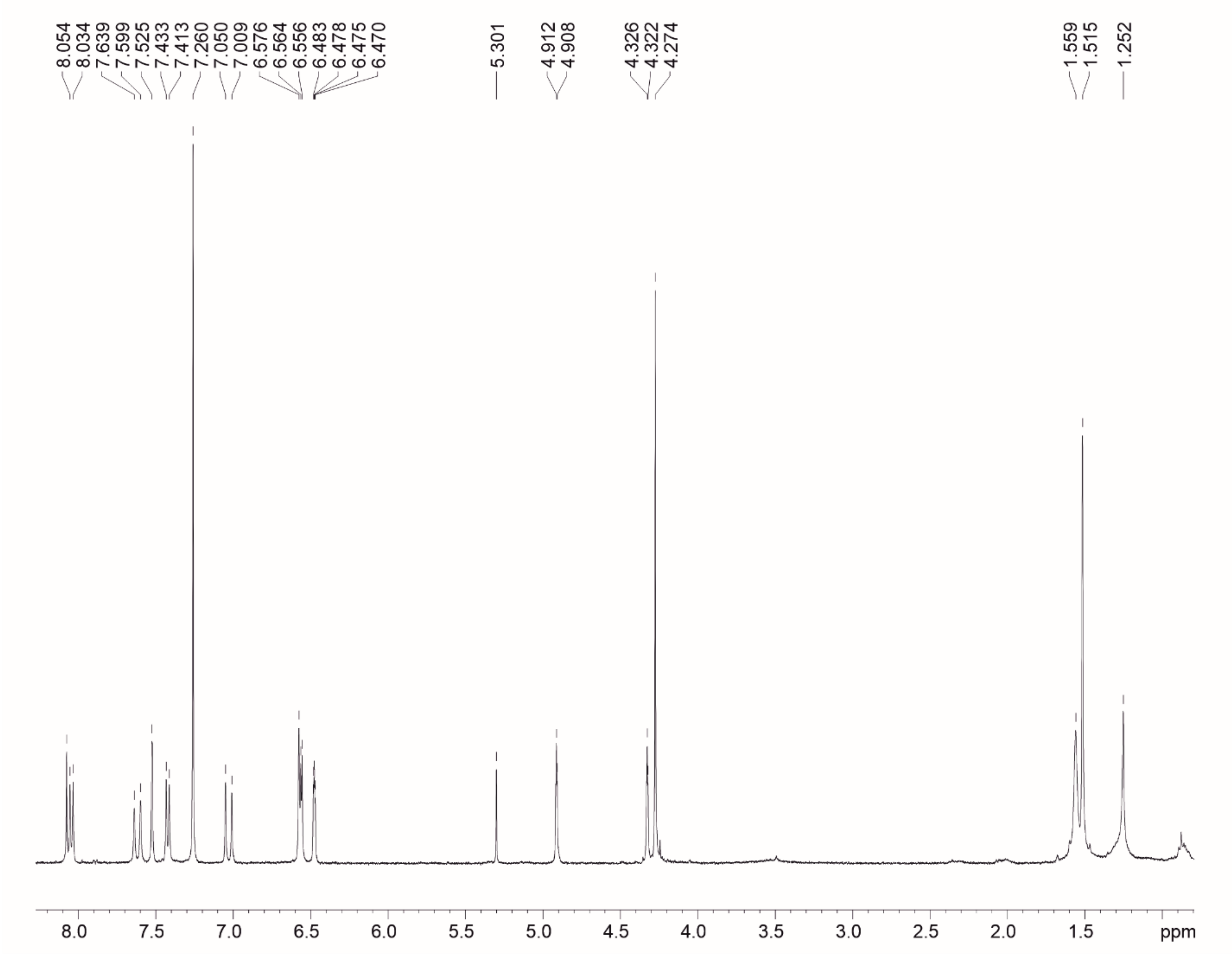

Figure S16. ^{1}H NMR of **BFc-1**.

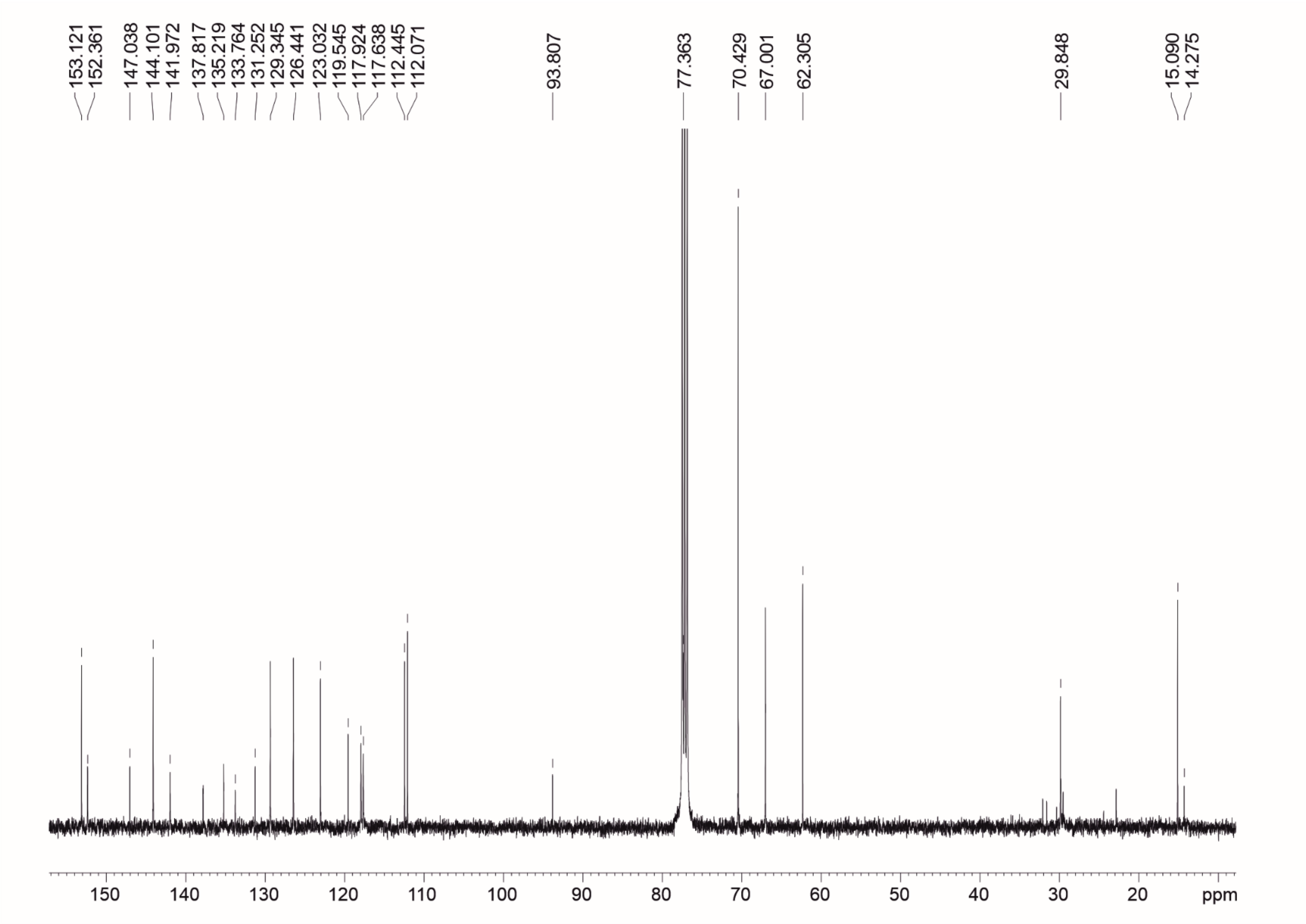

Figure S17. $^{13}C\{^1H\}$ NMR of **BFc-1**.

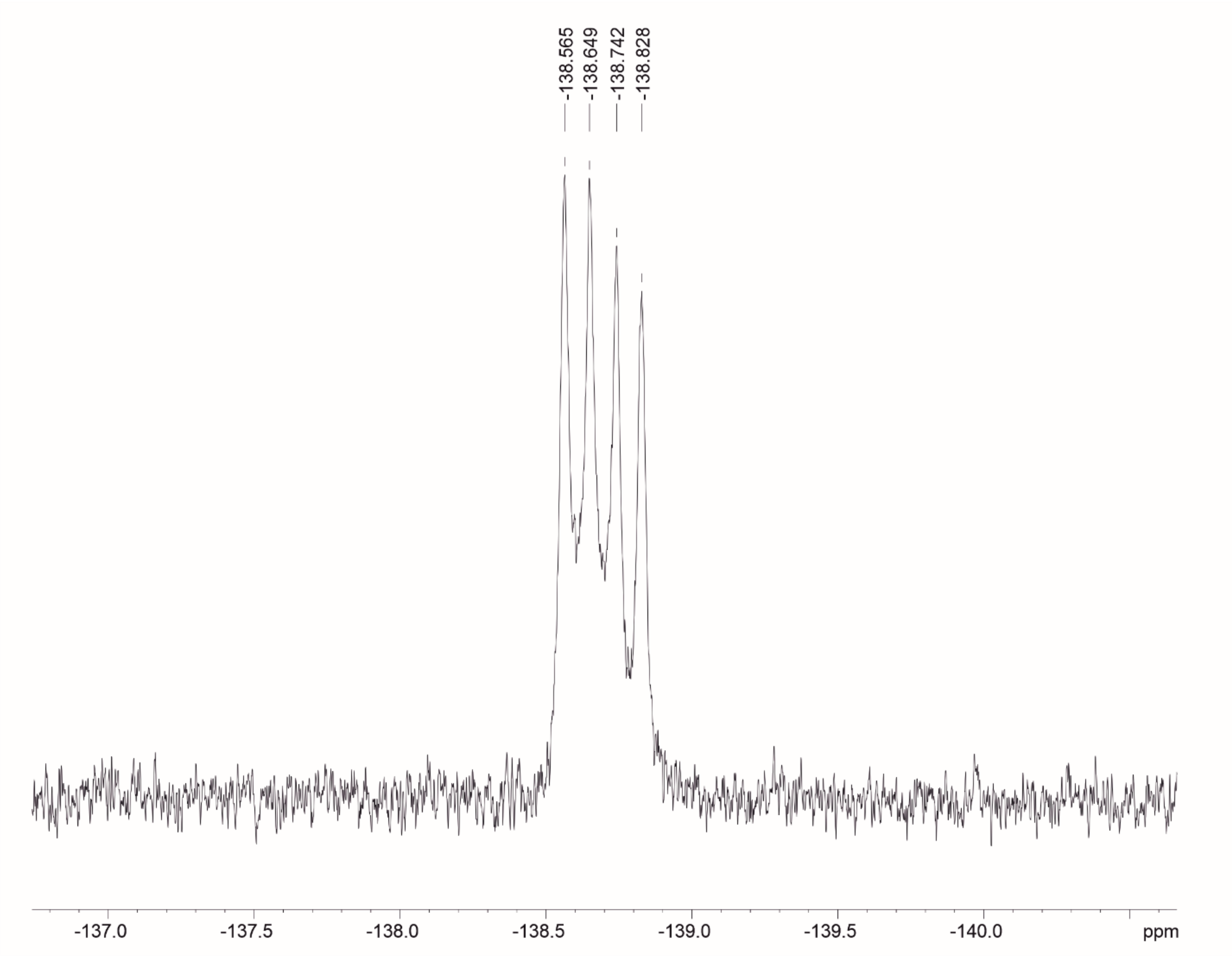

Figure S18. ^{19}F NMR of **BFc-1**.

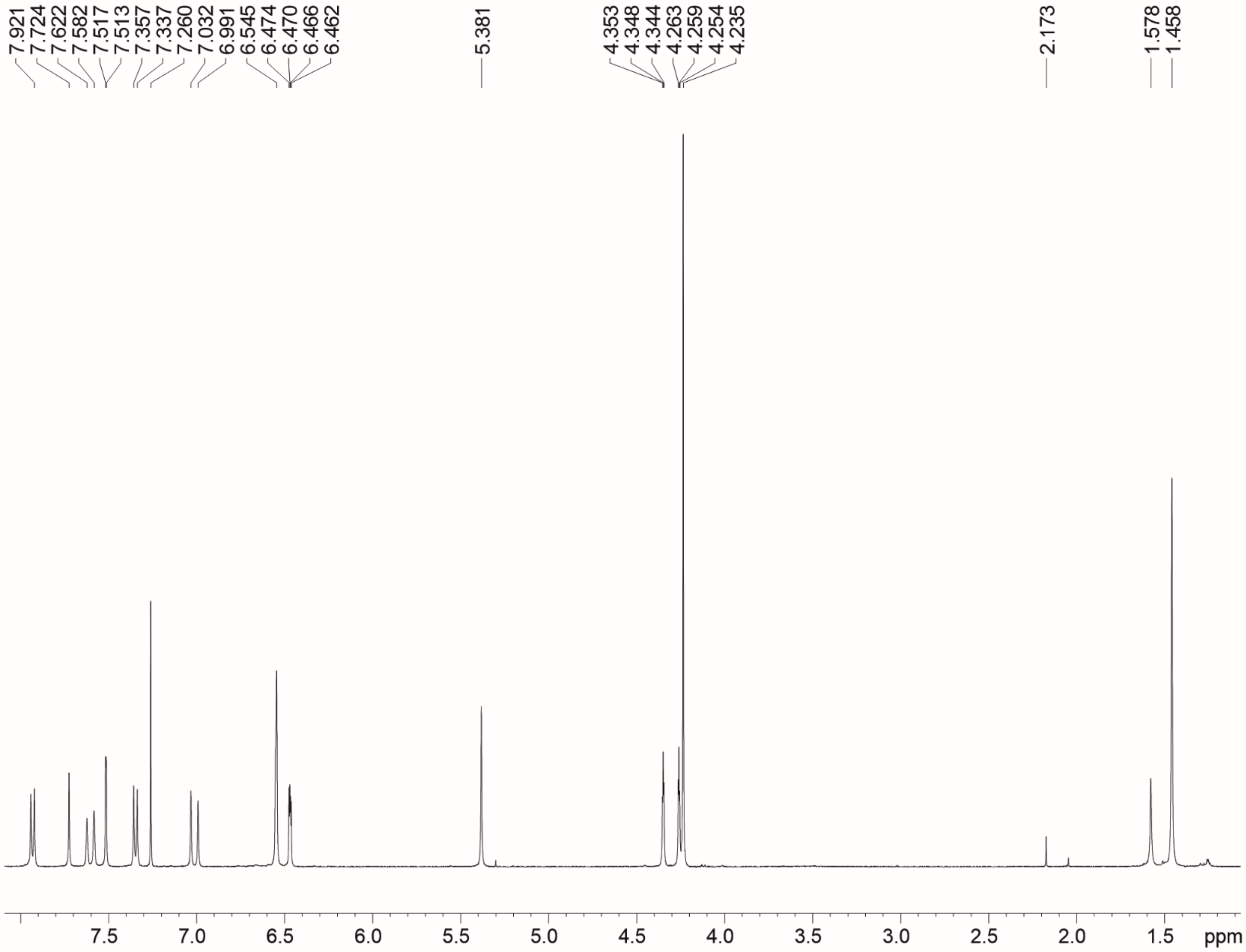

Figure S19. ^{1}H NMR of **BFc-2**.

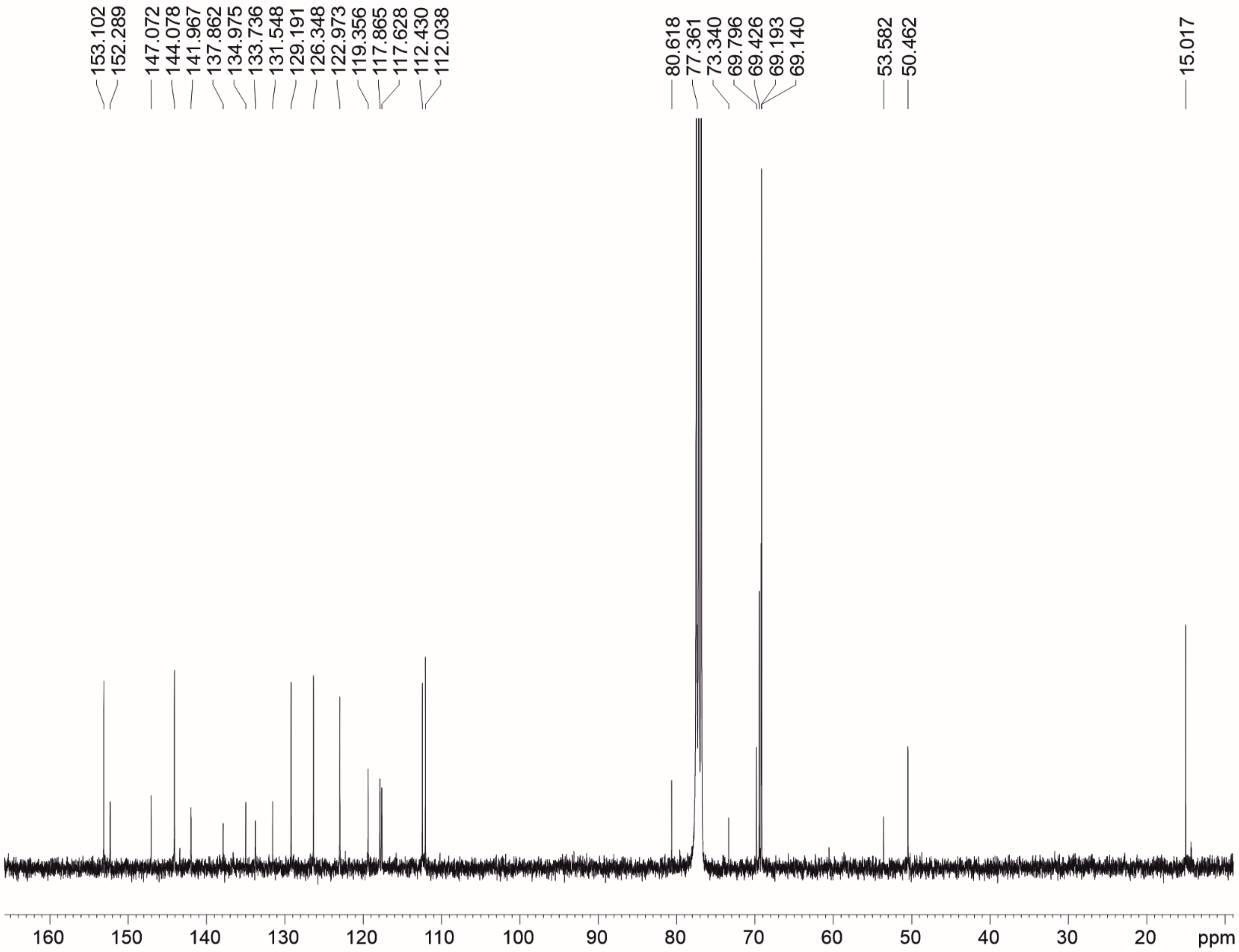

Figure S20. $^{13}C\{^1H\}$ NMR of **BFc-2**.

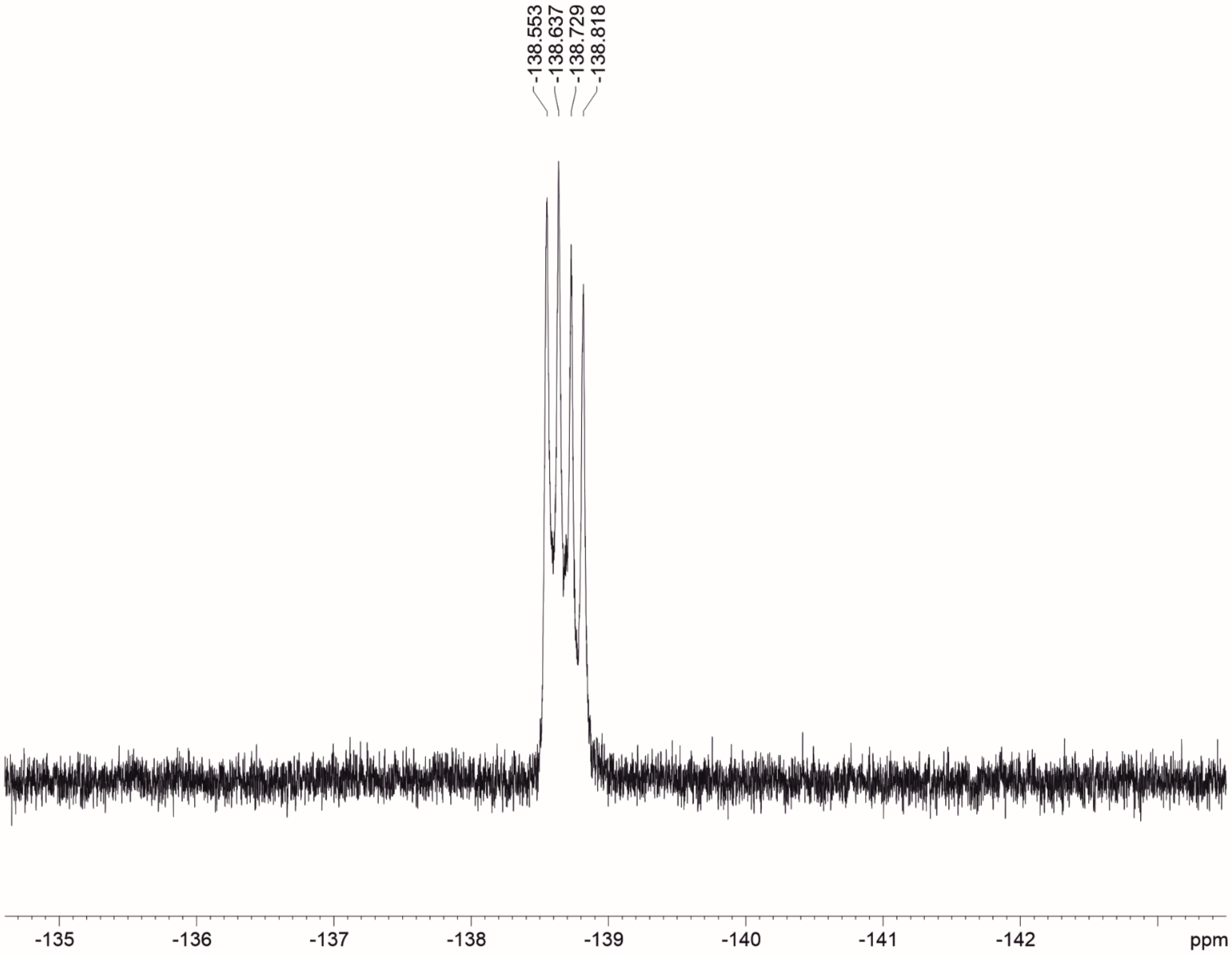

Figure S21. ^{19}F NMR of **BFc-2**.

3. Absorbance and luminescence experiments.

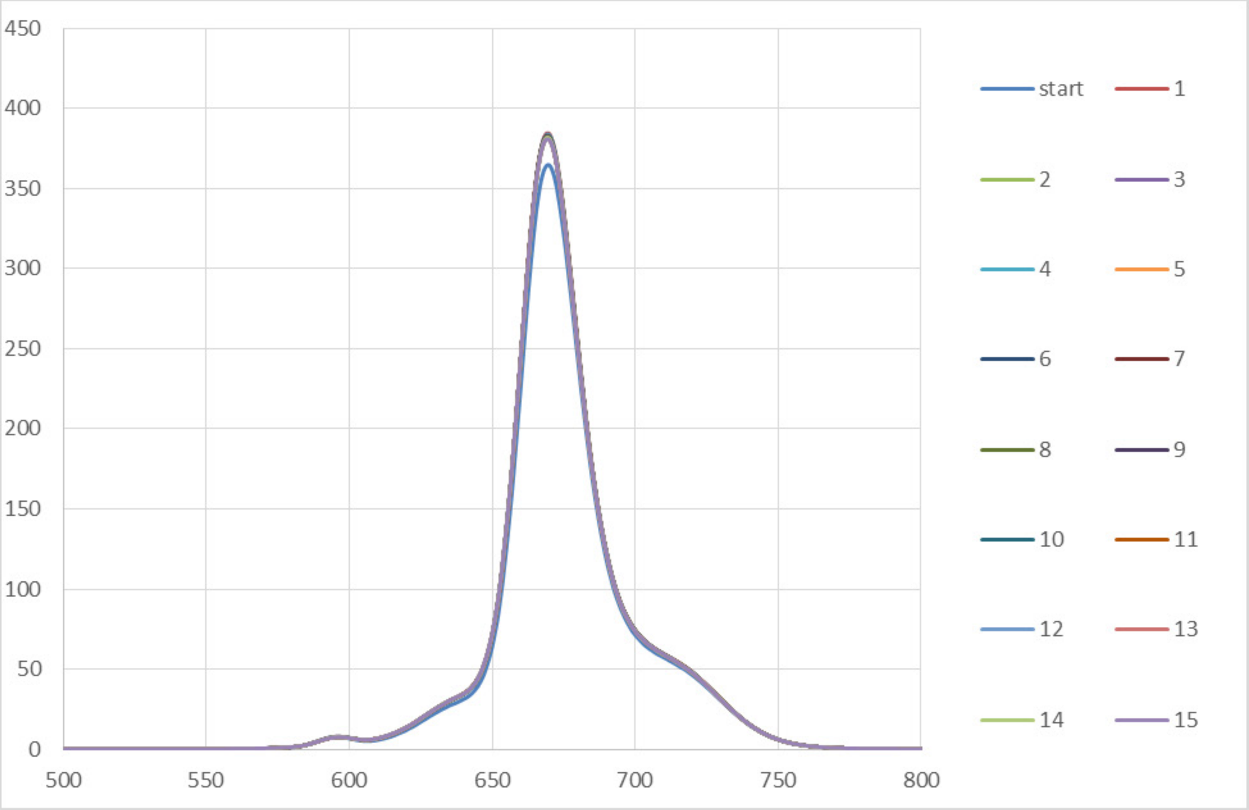

Figure S22. Absolute luminescence spectra of **BFc-1** ($5 \cdot 10^{-6}$ M) in THF solution before and after addition of 1.0 eq. $Fe(ClO_4)_3$. Spectrum recording every minute, $\lambda_{ex} = 595$ nm.

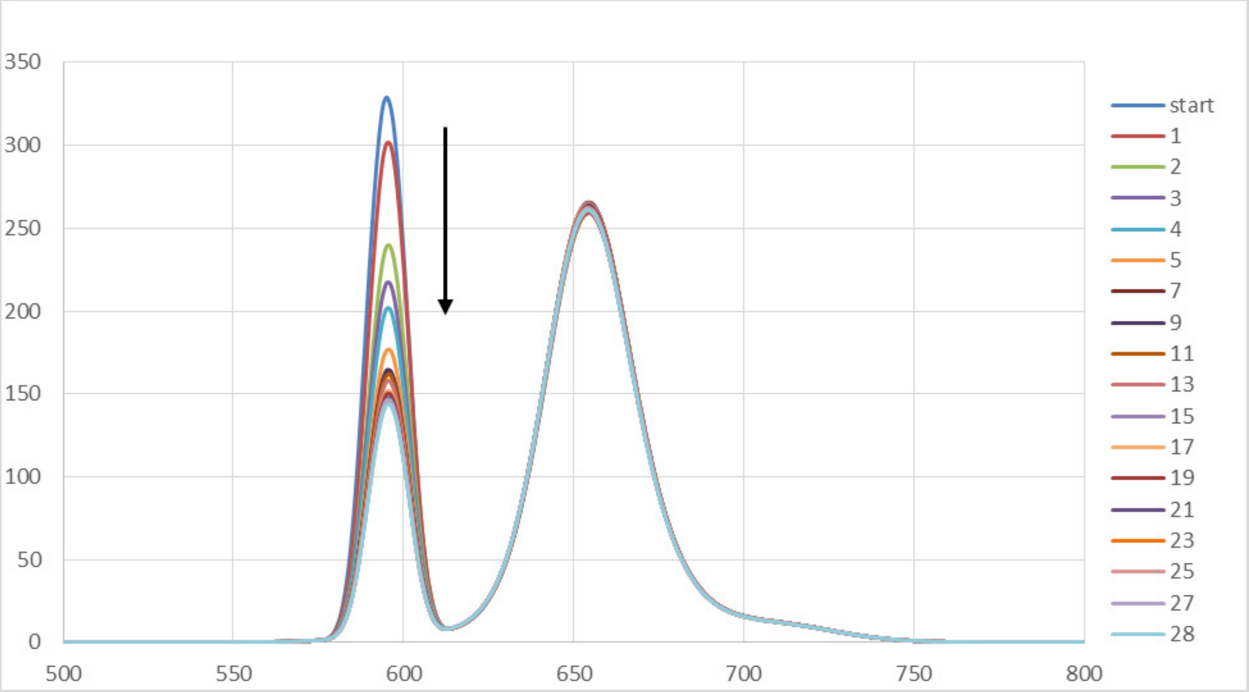

Figure S23. Absolute luminescence spectra of **BFc-1** ($1 \cdot 10^{-6}$ M) in CH_3CN solution before and after addition of 1.0 eq. $Fe(ClO_4)_3$. Spectrum recording every minute, $\lambda_{ex} = 595$ nm.

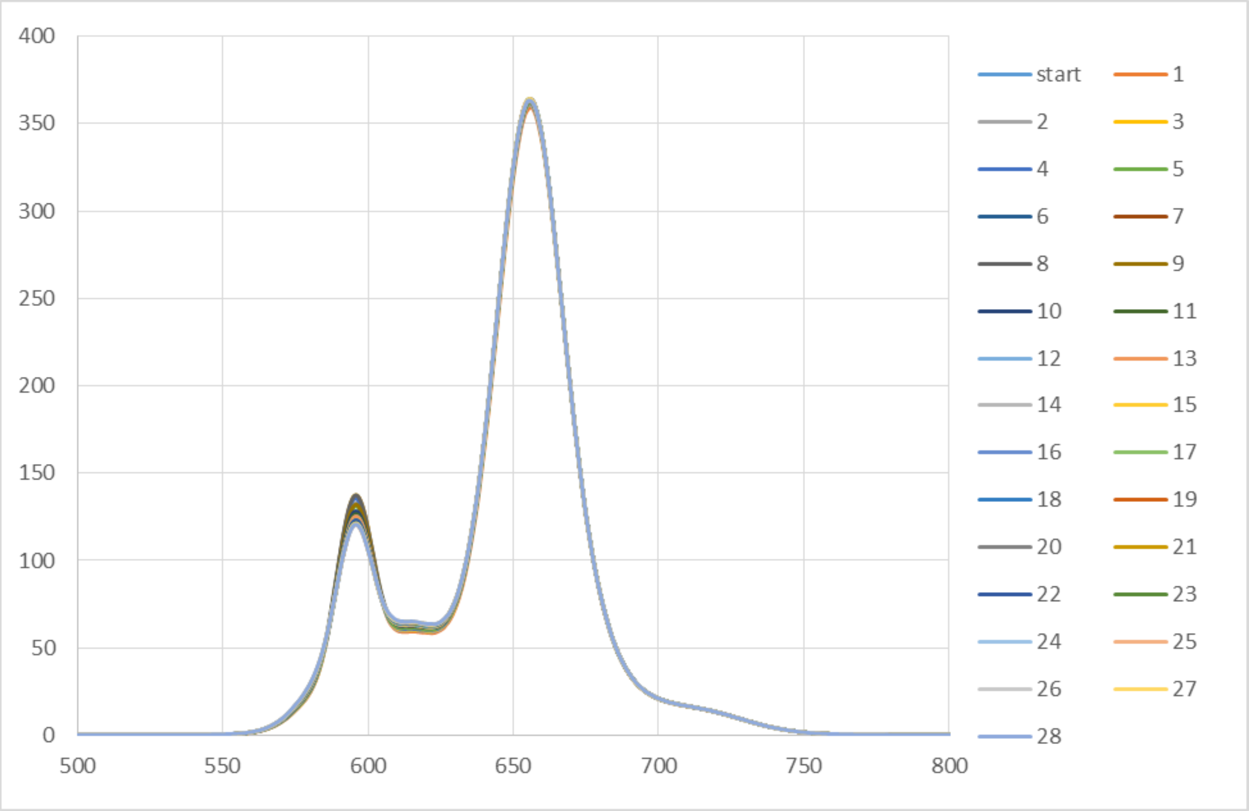

Figure S24. Absolute luminescence spectra of **BFc-2** ($1 \cdot 10^{-6}$ M) in THF solution before and after addition of 1.0 eq. $Fe(ClO_4)_3$. Spectrum recording every minute, λ_{ex} = 595 nm.

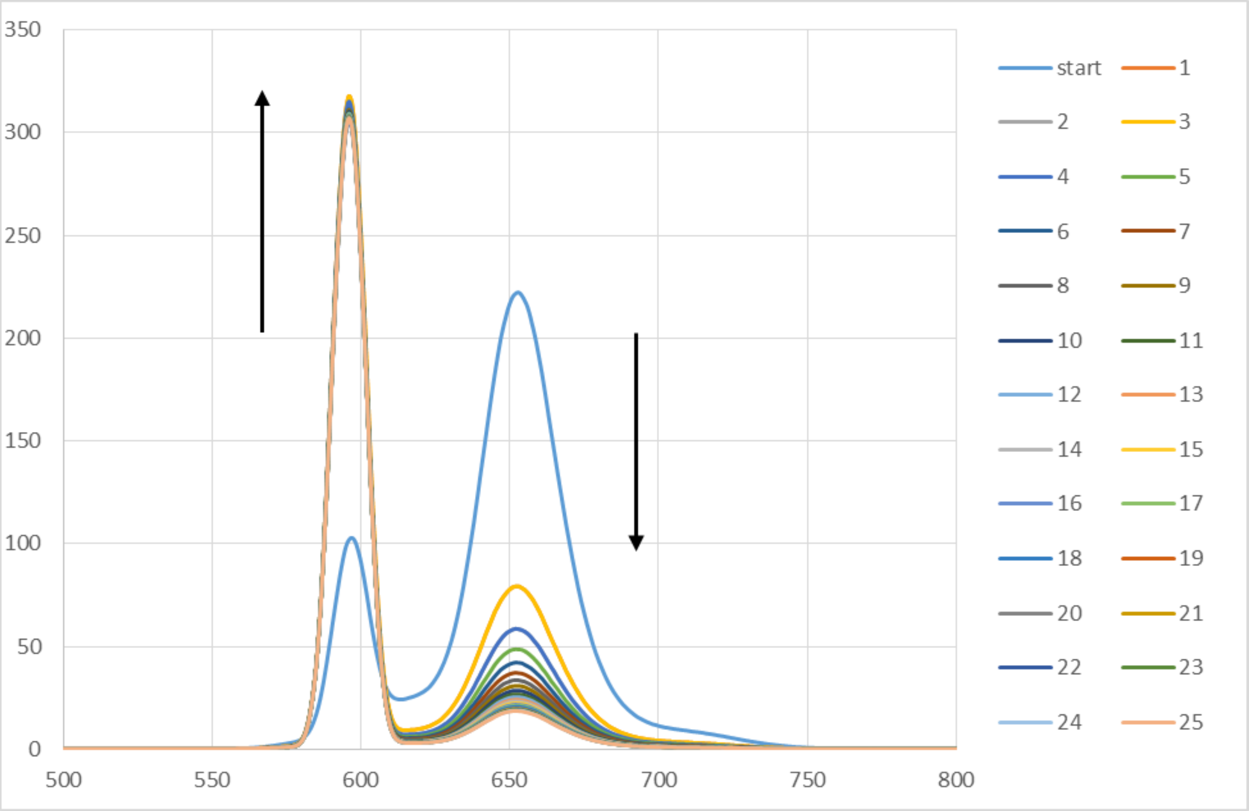

Figure S25. Absolute luminescence spectra of **BFc-2** ($1 \cdot 10^{-6}$ M) in CH_3CN solution before and after addition of 1.0 eq. $Fe(ClO_4)_3$. Increase in luminescence intensity for 565 nm: 3 times. Spectrum recording every minute, λ_{ex} = 595 nm.

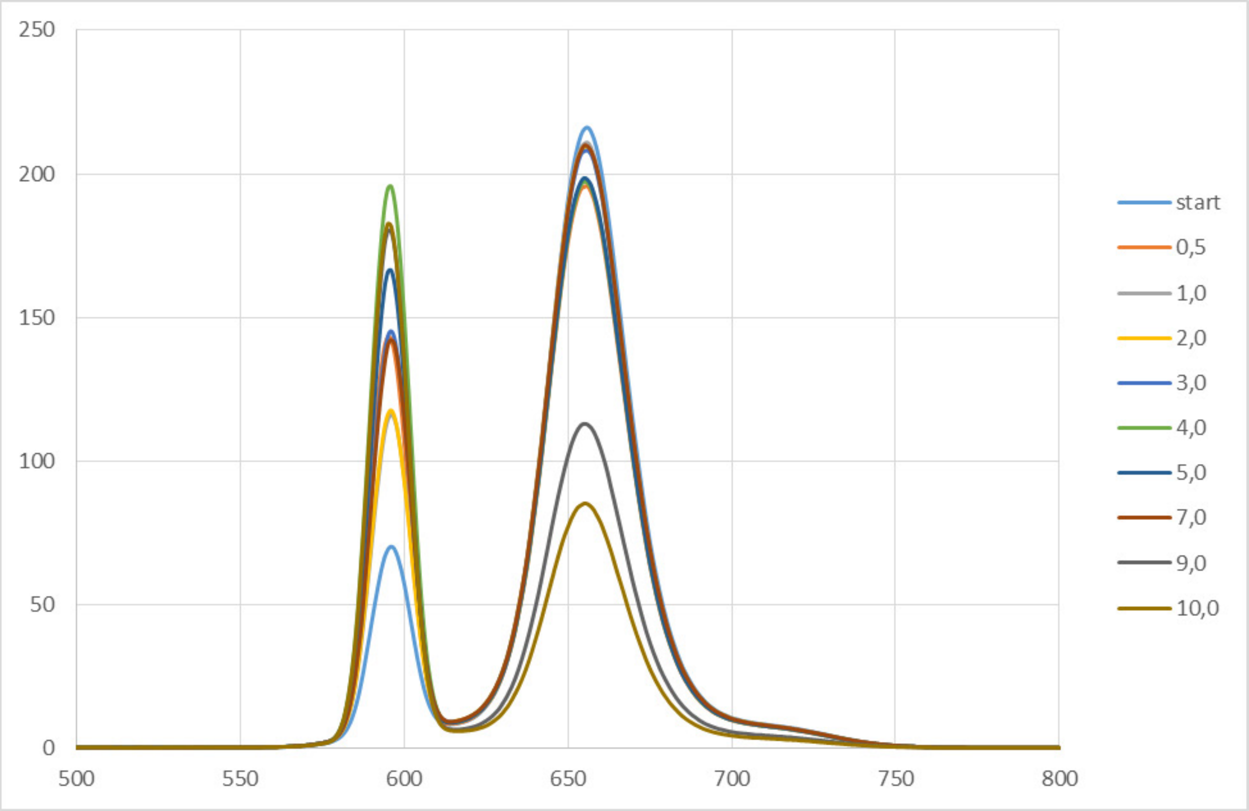

Figure S26. Absolute luminescence spectra of **BFc-1** ($1 \cdot 10^{-6}$ M) in THF solution before and after addition of $Cu(ClO_4)_2$. Spectrum recorded at λ_{ex} = 595 nm.

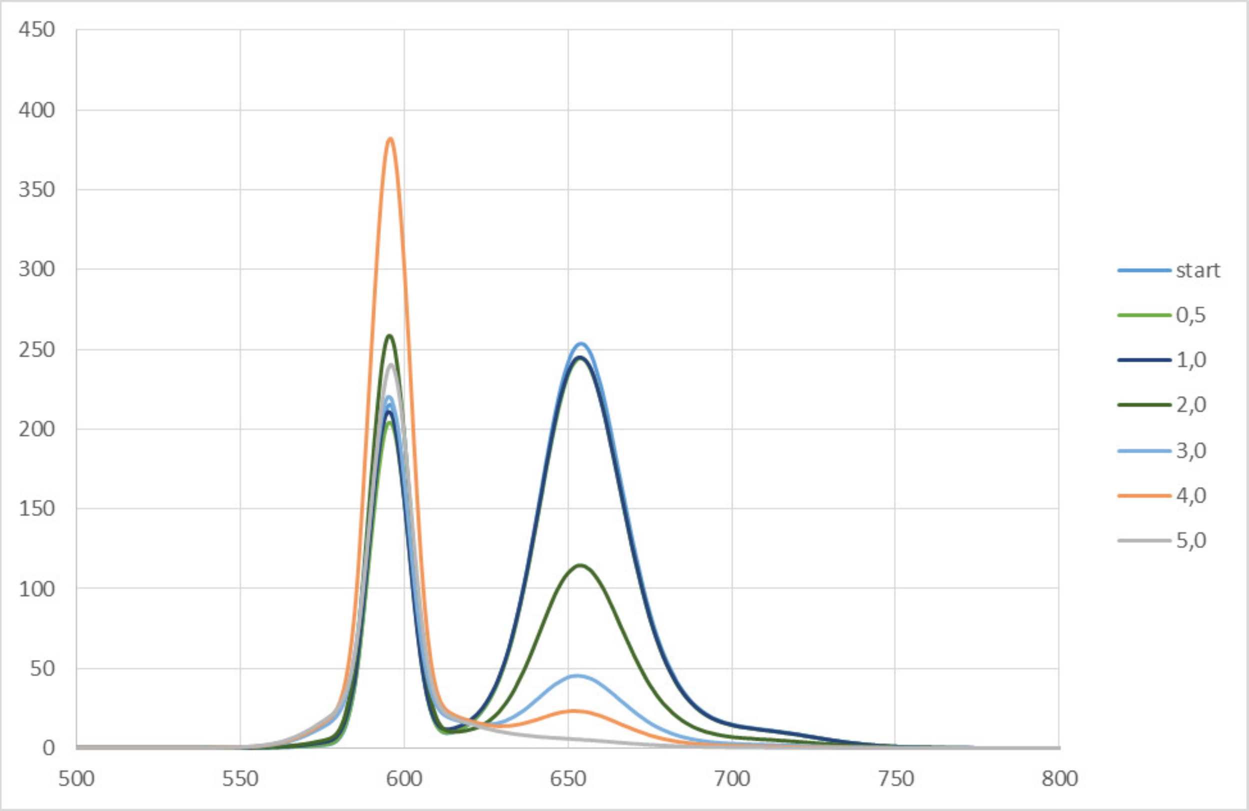

Figure S27. Absolute luminescence spectra of **BFc-1** ($1 \cdot 10^{-6}$ M) in CH_3CN solution before and after addition of $Cu(ClO_4)_2$. Spectrum recorded at λ_{ex} = 595 nm.

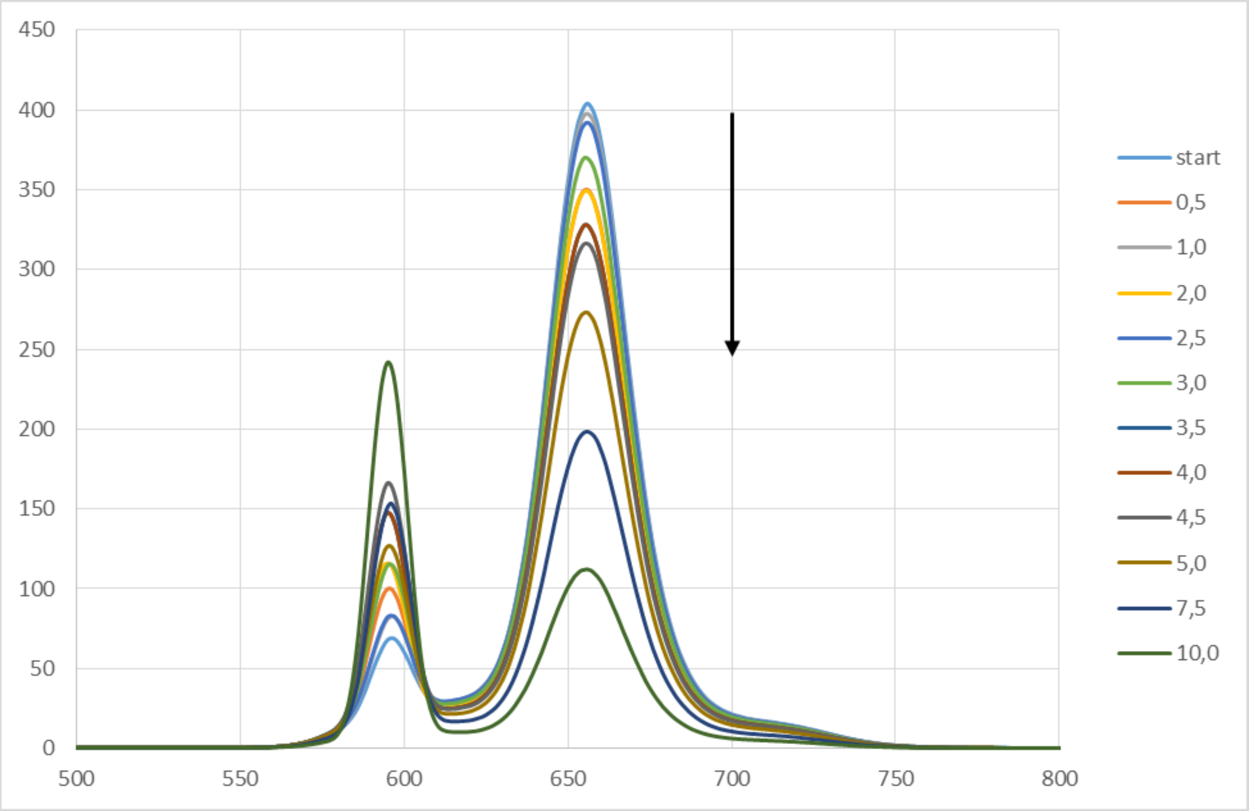

Figure S28. Absolute luminescence spectra of **BFc-2** ($1 \cdot 10^{-6}$ M) in THF solution before and after addition of $Cu(ClO_4)_2$. Spectrum recorded at λ_{ex} = 595 nm.

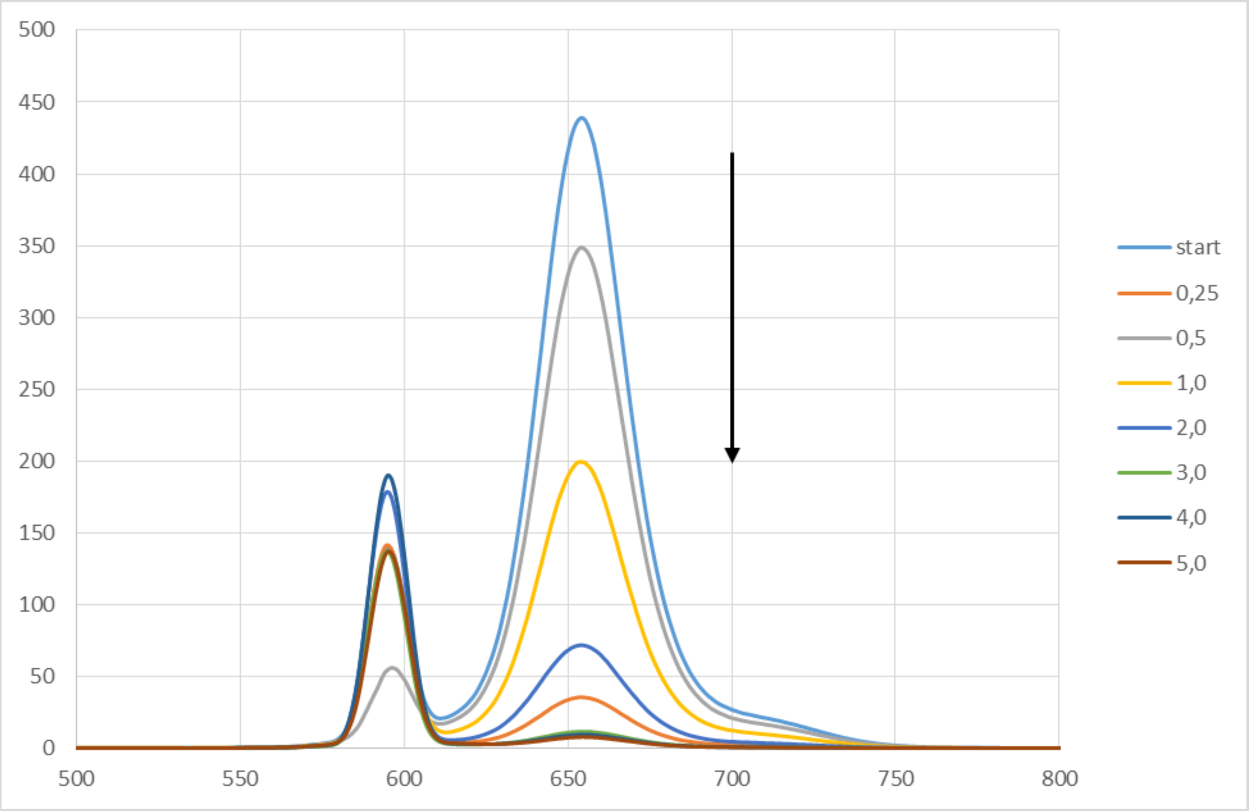

Figure S29. Absolute luminescence spectra of **BFc-2** ($1 \cdot 10^{-6}$ M) in CH_3CN solution before and after addition of $Cu(ClO_4)_2$. Spectrum recorded at λ_{ex} = 595 nm.

4. Electrochemical study

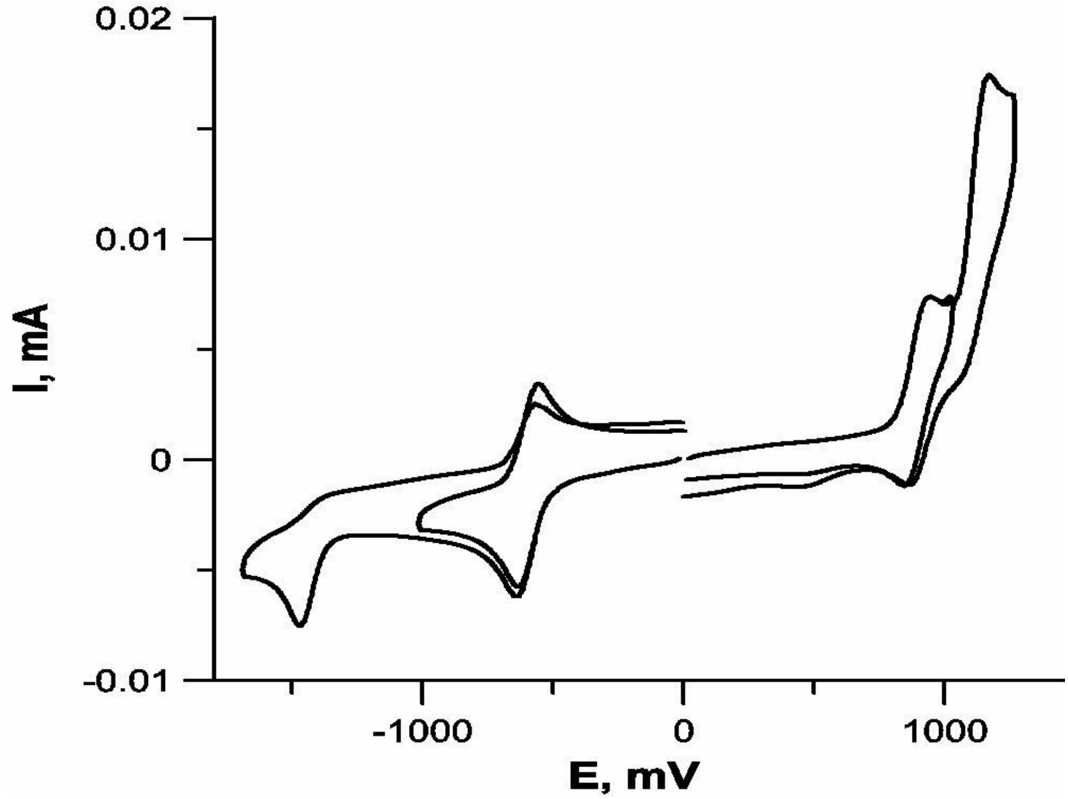

Figure S30. Cyclic voltammogramm of **BFc-1** in DMF solution in presence of $1\cdot10^{-3}$ M $Bu_4N^+ClO_4^-$

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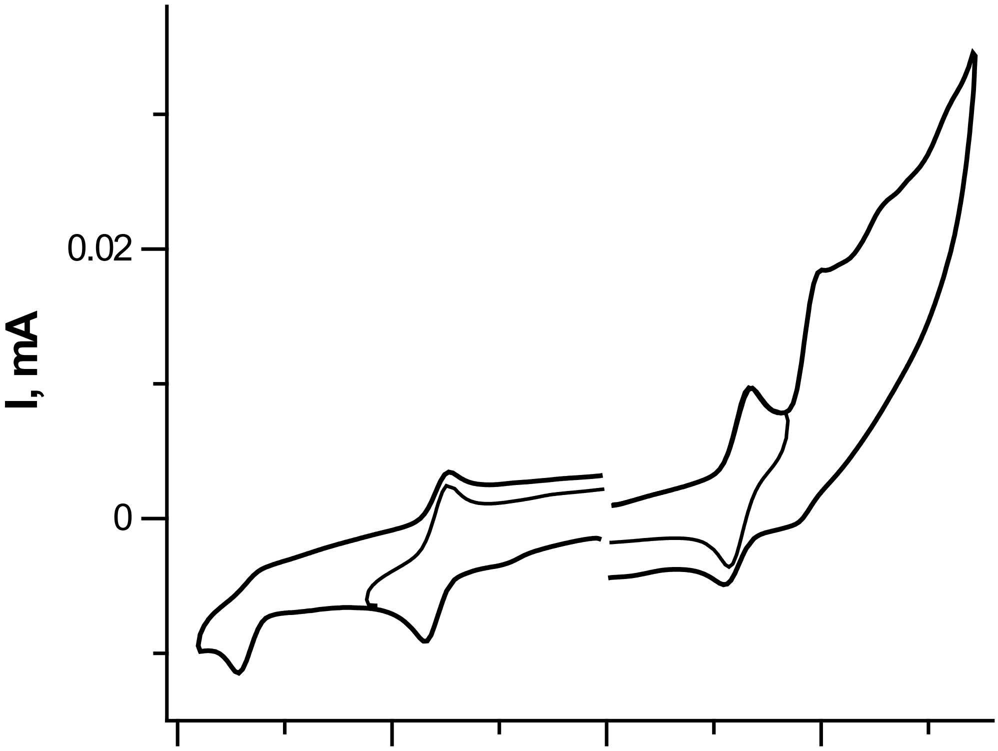

Figure S31. Cyclic voltammogramm of **BFc-2** in DMF solution in presence of $1\cdot10^{-3}$ M $Bu_4N^+ClO_4^-$

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Table S4. Electrochemical potentials of compounds **BFc-1** and **BFc-2** in DMF, measured relative to Ag/AgCl/KCl(sat) by the CV method in the presence of $1 \cdot 10^{-3}$ M $Bu_4N^+ClO_4^-$ on a GC electrode, potential scan rate 100 $mV \cdot s^{-1}$.

Compound	*Epc*, V	$E_{1/2}^{Red}$, V	*Epa*, V	$E_{1/2}^{Ox}$, V
BFc-1	– 0.63/– 0.56; – 1.47	– 0.60; – 1.48	0.92/0.84; 1.15	0.90; 1.13
BFc-2	– 084/– 0.69; – 1.72	– 0.78	0.68/0.59; 1.00; 1.28; 1.58	0.64; 0.98; 1.27