Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 291–294

Synthesis and photophysical properties of carbazolyl-substituted flavones

Konstantin V. Shcherbakov, Mariya A. Panova, Ekaterina F. Zhilina,
Evgeny V. Shchegolkov, Yanina V. Burgart and Victor I. Saloutin

Data on synthetic procedures, NMR, IR spectroscopy and elemental analysis.

Commercially available reagents were used in the work without additional purification, except for 2-(pentafluorophenyl)-4*H*-chromen-4-one **1**. The starting flavone **1** was obtained according to procedure.[S1] ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX-400 (working frequencies 400.13 (^{1}H), 125.76 (^{13}C) and 376.44 MHz (^{19}F)) and Bruker AVANCE III 500 (Bruker BioSpin, Germany) (working frequencies 500.13 (^{1}H) and 470.52 MHz (^{19}F)) spectrometers. $SiMe_4$ (^{1}H, ^{13}C) and C_6F_6 (^{19}F) were used as internal standards. The spectra of all compounds were recorded in $CDCl_3$. ^{1}H, ^{13}C NMR chemical shifts were referenced to the residual $CHCl_3$ signal. Fluorescence spectra of solid powders were recorded using SC-10 module of a FS5 Edinburgh Instruments spectrofluorometer (Edinburgh Instruments Ltd., GB) at room temperature. Absolute quantum yields have been measured using integrating sphere SC-30. The emission lifetimes have been measured using TCSPC option of FS5 Edinburgh Instruments spectrofluorometer. The sample has been excited by EPL-450 picosecond pulsed diode centered at 450 nm. The instrument response function (IRF) has been recorded under described conditions by replacing the sample with a silica diffuser. The time decay data have been analyzed by nonlinear least-squares fitting with deconvolution of the IRF using the Fluoracle software package. IR spectra were recorded in the frequency range from 4000 to 400 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrometer (Perkin Elmer Instruments, USA). Elemental analysis was performed on a Perkin Elmer PE 2400 Series II CHNS-O EA 1108 elemental analyzer (Perkin Elmer Instruments, USA). Melting points were determined on a Stuart SMP3 device (Barloworld Scientific Ltd., GB) in open capillaries. The reaction progress was monitored by TLC on ALUGRAM® XTRA SIL G/UV$_{254}$ plates.

Procedure *A* for the synthesis *i* of carbazolyl-substituted flavones 2–4. Flavone **1** (1 mmol, 312 mg) was dissolved in dry MeCN (5 mL), placed in sealed vial and cooled to 0 °C. Carbazole (2 mmol, 334 mg) and NaOBu^t (2 mmol, 192 mg) was suspended in dry MeCN (10 mL) and stirred at room temperature for 5 min. The mixture was cooled to 0 °C and added to a flavone solution in MeCN while stirring. After 10 min a cooling bath (0 °C) was removed and the reaction continued at room temperature for 24 hrs. At the end of the reaction mixture was diluted with water (20 mL), stirred and cooled. Formed precipitate was filtered off and washed with water. Water solution was neutralized with 0.1 M HCl and extracted with CH_2Cl_2. Organic layer was separated; solvent was removed. Organic residues were combined and purified by column chromatography on silica gel using CH_2Cl_2 and CH_2Cl_2–EtOH mixture (5:1 v/v). If necessary, the precipitate was crystallized from EtOH or EtOH–Me_2CO mixture.

Procedure *B* for the selective synthesis *ii* of *mono*-carbazolyl-substituted flavone 2. Flavone **1** (0.5 mmol, 156 mg) was dissolved in dry MeCN (5 mL), placed in sealed vial and cooled to 0 °C. Carbazole (0.75 mmol, 125 mg) and NaOBu^t (0.75 mmol, 72 mg) was suspended in dry MeCN (10 mL) and stirred at room temperature for 5 min. The mixture was cooled to 0 °C and added to a flavone solution in MeCN while stirring. After 10 min a cooling bath (0 °C) was removed and the reaction was continued at room temperature for 1 h. At the end of the reaction mixture was diluted with water (20 mL), stirred and cooled. Formed precipitate was filtered off and washed with water. Water solution was neutralized with 0.1 M HCl and extracted with

CH_2Cl_2. Organic layer was separated; solvent was removed. Organic residues were combined and purified by column chromatography on silica gel using CH_2Cl_2.

Procedure *C* for the selective synthesis *iii* of *penta*-carbazolyl-substituted flavone 5. Flavone **1** (0.5 mmol, 156 mg) was dissolved in dry MeCN (5 mL), placed in sealed vial and cooled to 0 °C. Carbazole (3 mmol, 502 mg) and $NaOBu^t$ (3 mmol, 288 mg) was suspended in dry MeCN (10 mL) and stirred at room temperature for 5 min. The mixture was cooled to 0 °C and added to a flavone solution in MeCN while stirring. After 10 min a cooling bath (0 °C) was removed and the reaction was continued at room temperature for 1 h, then heated at 80 °C till the end. The reaction progress was monitored by TLC and NMR ^{19}F. At the end of the reaction precipitate was filtered off and washed with water. Residue was crystallized from acetone, filtered off and dried at 150 °C.

2-[4-(9H-Carbazol-9-yl)-2,3,5,6-tetrafluorophenyl]-4H-chromen-4-one **2**: yield 88 mg (19%, procedure *A*), 158 mg (69%, procedure *B*), pale yellow solid, mp 224–225 °C. ^1H NMR (400 MHz) δ: 6.76 (br.s, 1H, C^3H_{Chr}), 7.23 (d.m, 2H, CH_{Cz}, J 8.2 Hz), 7.36–7.40 (m, 2H, CH_{Cz}), 7.47–7.52 (m, 3H, CH_{Cz}, CH_{Chr}), 7.56 (d.d, 1H, CH_{Chr}, J_1 8.4, J_2 0.5 Hz), 7.77 (d.d.d, 1H, CH_{Chr}, J_1 8.7, J_2 7.2, J_3 1.7 Hz), 8.16 (d.m, 2H, CH_{Cz}, J 7.4 Hz), 8.30 (d.d, 1H, CH_{Chr}, J_1 8.0, J_2 1.4 Hz). ^{13}C NMR (126 MHz) δ: 109.9 (s, CH_{Chr}), 112.5 (t, C^1_{ArF}, J 15 Hz), 115.9 (t, CH_{Chr}, J 3 Hz), 118.2 (s, CH_{Chr}), 119.3 (t, C^4_{ArF}, J 14 Hz), 120.6, 121.6, 124.0, 124.3 (all s, CH_{Cz}), 125.9 (s, CH_{Chr}), 126.0, 126.6 (both s, CH_{Cz}), 134.4, 139.6 (both s, $C^{8a}H_{Cz}$, $C^{9a}H_{Cz}$), 144.2 (d.m, $C^{2,6}_{ArF}$, J 256 Hz), 145.1 (d.m, $C^{3,5}_{ArF}$, J 257 Hz), 152.6 (s, C^{8a}_{Chr}), 156.7 (s, C^2_{Chr}), 177.2 (s, C^4_{Chr}). ^{19}F NMR (376 MHz) δ: 21.05–21.17 (m, 2F, $C^{3,5}F$), 23.72–23.83 (m, 2F, $C^{2,6}F$). IR (ν/cm^{-1}): 3051 (CH_{Ar}), 1652 (C=O), 1610, 1514, 1493, 1450 (C=C, C–N), 991 (C–F). Found (%): C, 70.13; H, 3.00; N, 3.04. Calc. for $C_{27}H_{13}F_4NO_2$ (%): C, 70.59; H, 2.85; N, 3.05.

2-[2,4-Di(9H-carbazol-9-yl)-3,5,6-trifluorophenyl]-4H-chromen-4-one **3**: yield 30 mg (5%, procedure *A*), pale yellow solid, mp 279–280 °C. ^1H NMR (400 MHz) δ: 6.28 (d.d, 1H, CH_{Chr}, J_1 8.4, J_2 0.5 Hz), 6.51 (d, 1H, C^3H_{Chr}, $^5J_{HF}$ 1.8 Hz), 7.20–7.54 (m, 14H, CH_{Cz}, CH_{Chr}), 7.93 (d.d, 1H, CH_{Chr}, J_1 8.0, J_2 1.7 Hz), 7.98 (d.m, 2H, CH_{Cz}, J 7.6 Hz), 8.16 (d.m, 2H, CH_{Cz}, J 7.7 Hz). ^{19}F NMR (376 MHz) δ: 25.28 (d.d.d, 1F, C^6F, ^3J 22.4, ^5J 13.1, $^5J_{FH}$ 1.8 Hz), 29.19 (d, 1F, C^5F, ^3J 22.4 Hz), 40.43 (d, 1F, C^3F, ^5J 13.1 Hz). IR (ν/cm^{-1}): 3049, 3022 (CH_{Ar}), 1652 (C=O), 1615, 1603, 1508, 1496, 1474, 1445 (C=C, C–N), 970 (C–F). Found (%): C, 77.06; H, 3.40; N, 4.73. Calc. for $C_{39}H_{21}F_3N_2O_2$ (%): C, 77.22; H, 3.49; N, 4.62.

2-[2,4,5-Tri(9H-carbazol-9-yl)-3,6-difluorophenyl]-4H-chromen-4-one **4**: yield 75 mg (10%, procedure *A*), pale yellow solid, mp >350 °C. ^1H NMR (400 MHz) δ: 6.35 (d, 1H, CH_{Chr}, J 8.3 Hz), 6.59 (d, 1H, C^3H_{Chr}, $^5J_{HF}$ 1.8 Hz), 7.06–7.16 (m, 12H, CH_{Cz}), 7.19–7.25 (m, 1H, CH_{Chr}), 7.26–7.31 (m, 2H, CH_{Cz}), 7.38–7.49 (m, 5H, CH_{Cz}, CH_{Chr}), 7.73–7.79 (m, 4H, CH_{Cz}), 7.93 (d.d, 1H, CH_{Chr}, J_1 8.0, J_2 1.6 Hz), 8.03 (d, 2H, CH_{Cz}, J 7.8 Hz). ^{19}F NMR (376 MHz) δ: 41.01 (d, 1F, C^3F, ^5J 13.7 Hz), 45.84 (d.d, 1F, C^6F, ^5J 13.7, $^5J_{FH}$ 1.8 Hz). IR (ν/cm^{-1}): 3049 (CH_{Ar}), 1645 (C=O), 1603, 1496, 1471, 1452, 1443 (C=C, C–N), 972 (C–F). Found (%): C, 81.33; H, 3.85; N, 5.50. Calc. for $C_{51}H_{29}F_2N_3O_2$ (%): C, 81.26; H, 3.88; N, 5.57.

2-[2,3,4,5,6-Penta(9H-carbazol-9-yl)phenyl]-4H-chromen-4-one **5**: yield 430 mg (82%, procedure *C*), pale yellow solid, mp >350 °C. ^1H NMR (500 MHz) δ: 5.62 (s, 1H, C^3H_{Chr}), 5.68 (d, 1H, CH_{Chr}, J 8.2 Hz), 6.62–6.96 (m, 22H, CH_{Cz}), 7.12 (d.d.d, 1H, CH_{Chr}, J_1 8.7, J_2 7.2, J_3 1.6 Hz), 7.20–7.36 (m, 15H, CH_{Cz}, CH_{Chr}), 7.47 (d.d, 1H, CH_{Chr}, J_1 8.0, J_2 1.6 Hz), 7.50–7.59 (m, 4H, CH_{Cz}). IR (ν/cm^{-1}): 3047 (CH_{Ar}), 1662 (C=O), 1626, 1599, 1491, 1479, 1449 (C=C, C–N). Found (%): C, 85.84; H, 4.10; N, 6.67. Calc. for $C_{75}H_{45}N_5O_2$ (%): C, 85.94; H, 4.33; N, 6.68.

XRD Experiments.

The X-ray studies were performed on an Xcalibur 3 CCD (Oxford Diffraction Ltd., Abingdon, UK) diffractometer with a graphite monochromator, λ (MoKα) 0.71073 Å radiation and T 295(2) K. An empirical absorption correction was applied. Using Olex2,[S2] the structure was solved with the Superflip[S3] structure solution program using charge flipping and refined with the SHELXL[S4] refinement package using Least Squares minimization. All non-hydrogen atoms were refined in the anisotropic approximation; H-atoms at the C–H bonds were refined in the "rider" model with dependent displacement parameters. An empirical absorption correction was carried out through spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm by the program “CrysAlisPro” (Rigaku Oxford Diffraction). CCDC numbers 2493000–2493003 contain the supplementary crystallographic data for compounds **1**–**4**.

References

S1. K. V. Shcherbakov, M. A. Panova, Ya. V. Burgart, V. V. Zarubaev, N. A. Gerasimova, N. P. Evstigneeva and V. I. Saloutin, *J. Fluorine Chem*., 2021, **249**, 109857; https://doi.org/10.1016/j.jfluchem.2021.109857.

S2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339; https://doi.org/10.1107/S0021889808042726.

S3. L. Palatinus and G. Chapuis, *J. Appl. Crystallogr*., 2007, **40**, 786; https://doi.org/10.1107/S0021889807029238.

S4. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112; https://doi.org/10.1107/S0108767307043930.

Table S1. ^{19}F NMR data for the reaction mass of flavone **1** with carbazole under condition *i*.

Compound	^{19}F NMR data	
	δ, ppm, J, Hz	Product ratio, %
2	21.06–21.14, m; 23.72–23.83, m	40
3	25.23–25.32, m; 29.19, d, ^{3}J 21.6; 40.43, d, ^{5}J 12.8	16
4	41.01, d, ^{5}J 13.5; 45.85, d, ^{5}J 13.9, $^{5}J_{FH}$ 1.8	44

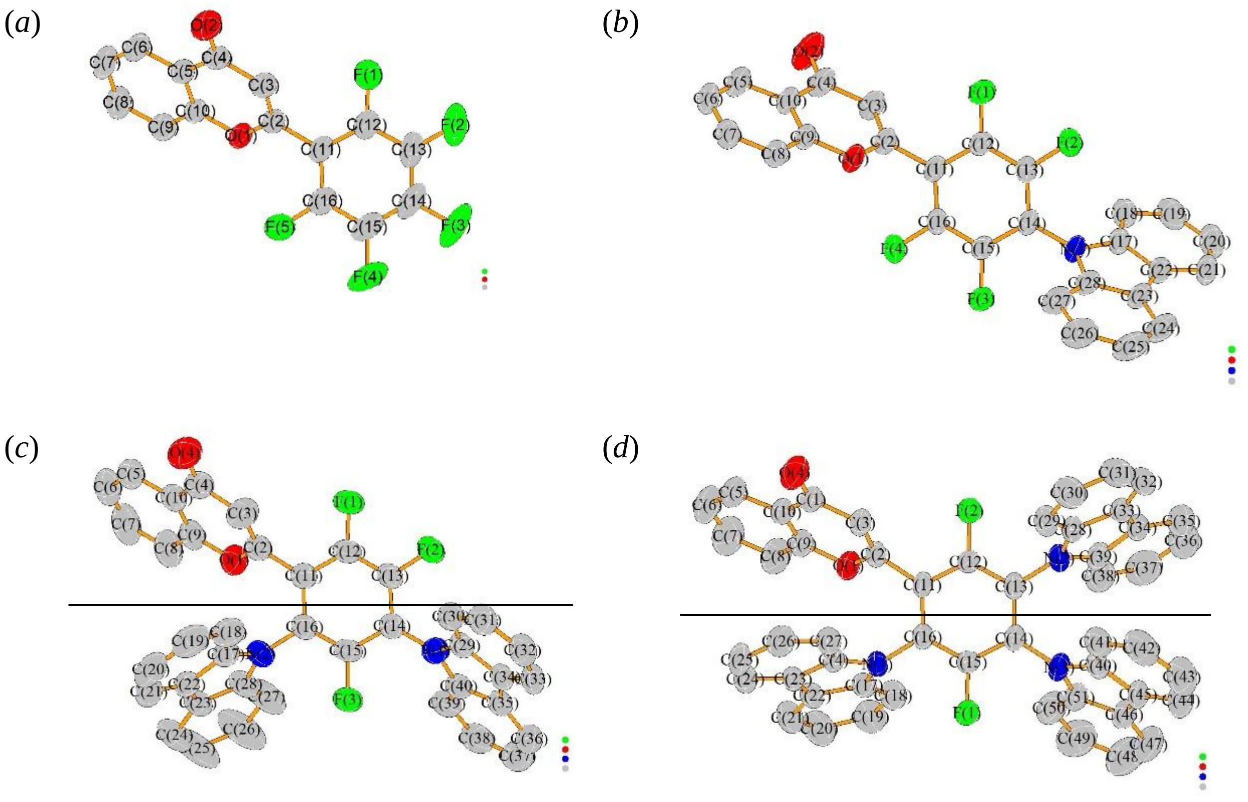

Figure S1. Solid-state structure of flavones **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*). Ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

Table S2. The main crystallographic data for **1**–**4**.

Parameter	Compound			
	1	**2**	**3**	**4**
Chemical formula	$C_{15}H_5F_5O_2$	$C_{27}H_{13}F_4NO_2$	$C_{39}H_{21}F_3N_2O_2$	$C_{51}H_{29}F_2N_3O_2$
M	312.19	459.38	606.58	753.77
T, K	295(2)	295(2)	295(2)	295(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$I2/c$	$P2_1/c$
a, Å	13.5265(11)	8.1955(4)	18.1804(7)	17.1059(16)
b, Å	7.6890(9)	10.1025(5)	14.3603(5)	14.2102(7)
c, Å	24.789(2)	12.5294(5)	23.9145(10)	15.3375(7)
α, deg	90.00	89.003(4)	90.00	90.00
β, deg	101.907(9)	86.690(4)	111.014(5)	93.021(5)
γ, deg	90.00	76.431(4)	90.00	90.00
V, Å^3	2522.7(4)	1006.74(9)	5828.3(4)	3723.0(4)
Z	8	2	8	4
d_{calc}, g•cm^{-3}	1.644	1.515	1.383	1.345
μ, mm^{-1}	0.158	0.121	0.099	0.089
θ_{max}, deg	28.3600	31.0530	26.1910	22.0790
T_{min}/T_{max}	0.95265/1.0000	0.92104/1.0000	0.90306/1.0000	0.87399/1.0000
Total reflections	4908	8482	23221	17976
Independent reflections	2870	5446	8233	10177
Unique reflections, I>2σI	1835	3114	4119	3118
R_{int}	0.0217	0.0204	0.0380	0.0713
Refinement parameters	204	307	416	523
GOOF	1.006	1.022	0.999	0.941
R_1 (I>2σI)	0.0442	0.0548	0.0517	0.0703
wR_2 (all reflections)	0.1444	0.1542	0.1525	0.1353
Electron density ($\Delta\rho_{min}/\Delta\rho_{max}$), e•A^{-3}	–0.16/0.18	–0.20/0.18	–0.18/0.17	–0.18/0.16

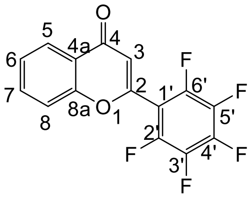

Figure S2. Carbon atom numbering.

Table S3. Selected torsion angles for **1**–**4**.

Compound	Torsion angle (absolute value), deg			
	at Ar-C(1′)[a]	at Ar-C(4′)	at Ar-C(2′)	at Ar-C(5′)
1	51.6(2)	—	—	—
2	57.1(3)	54.1(3)	—	—
3	52.3(3)	59.5(2)	68.9(2)	—
4	54.9(4)	50.7(4)	49.0(4)	58.5(4)

[a] C-atoms numbering is given according to **Figure S2**

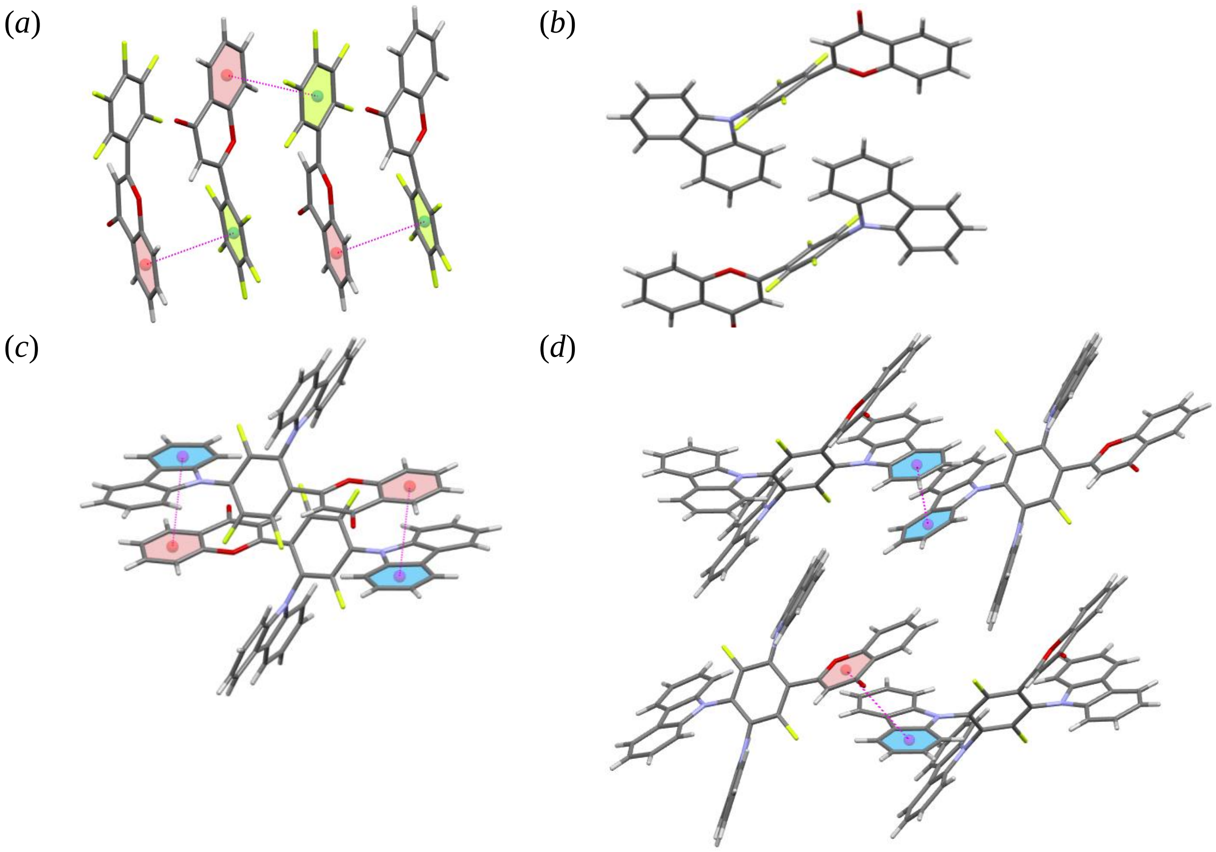

Figure S3. The molecular packing in single crystals of flavones **1** — (*a*), **2** — (*b*), **3** — (*c*), **4** — (*d*).

Table S4. Selected contact distances and NMR data for compounds **1**–**4**.

Compound	$d_{\mathrm{H...F}}$, Å	NMR data for C(3)**H** and C(6′)**F** nuclei[a]			
		^{1}**H**		^{19}**F**	
		δ, ppm	$^{5}J_{\mathrm{HF}}$, Hz	δ, ppm	J, Hz
1	2.74(2)	6.81, s	—	22.94–23.02, m	—
2	2.839	6.76, br.s	—	23.72–23.98, m	—
3	2.715	6.51, d	**1.8**	25.25, d.d.d	^{3}J 22.4, ^{5}J 13.1, $^{5}J_{\mathrm{FH}}$ **1.8**
4	2.657	6.59, d	**1.8**	45.84, d.d	^{5}J 13.7, $^{5}J_{\mathrm{FH}}$ **1.8**

[a] C-atoms numbering is given according to **Figure S2**.

Table S5. Detailed data of the fluorescence lifetime measurements of **1**–**5**: τ – lifetime, f – fractional contribution, τ_{avg} – average lifetime, χ^2 – chi-squared distribution.

Compound	τ_1, ns	f_1, %	τ_2, ns	f_2, %	τ_{avg}, ns	χ^2
1	1.98	44.0	6.26	56.0	**4.37**	1.457
2	3.30	38.3	7.37	61.7	**5.81**	1.027
3	1.33	78.8	4.96	21.2	**2.09**	1.208
4	2.06	67.9	6.00	32.1	**3.32**	1.177
5	3.29	49.7	11.66	50.3	**7.50**	1.089

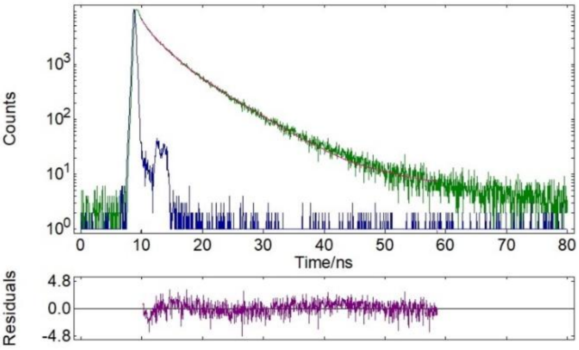

Figure S4. Time-resolved fluorescence lifetime decay profile of solid powder **1** (green), instrumental response function (IRF, blue). λ_{ex} 375 nm, λ_{em} 565 nm.

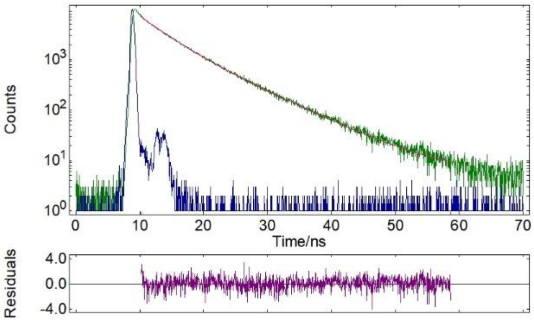

Figure S5. Time-resolved fluorescence lifetime decay profile of solid powder **2** (green), instrumental response function (IRF, blue). λ_{ex} 375 nm, λ_{em} 468 nm.

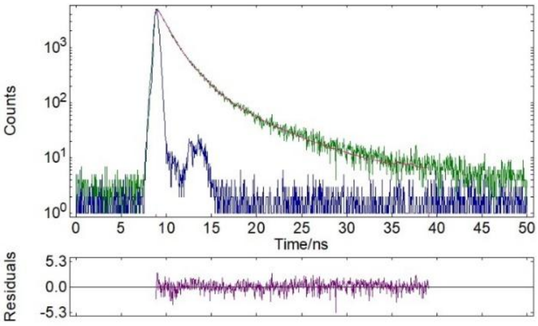

Figure S6. Time-resolved fluorescence lifetime decay profile of solid powder **3** (green), instrumental response function (IRF, blue). λ_{ex} 375 nm, λ_{em} 473 nm.

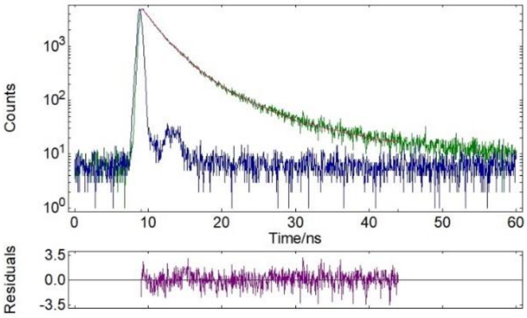

Figure S7. Time-resolved fluorescence lifetime decay profile of solid powder **4** (green), instrumental response function (IRF, blue). λ_{ex} 375 nm, λ_{em} 480 nm.

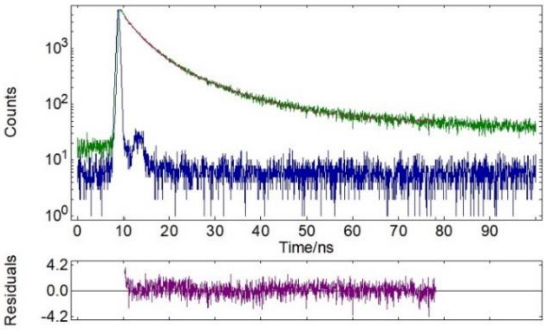

Figure S8. Time-resolved fluorescence lifetime decay profile of solid powder **5** (green), instrumental response function (IRF, blue). λ_{ex} 375 nm, λ_{em} 487 nm.

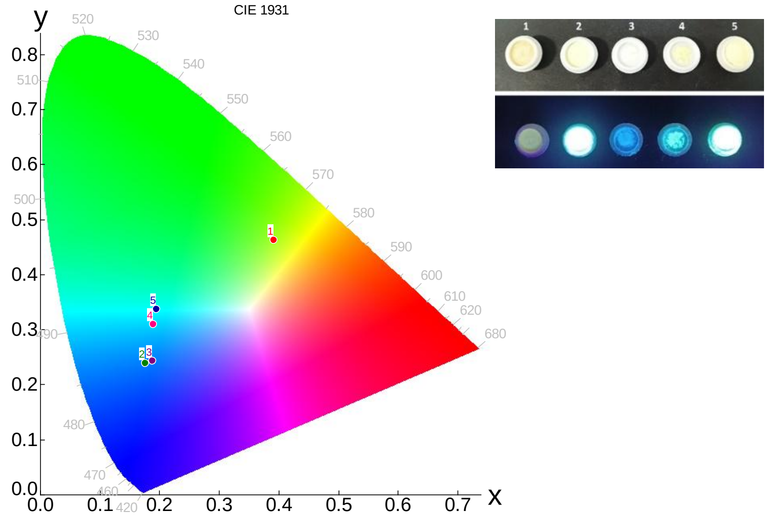

Figure S9. The CIE 1931 chromaticity diagram of chromophores **1** (0.392; 0.462), **2** (0.176; 0.238), **3** (0.189; 0.243), **4** (0.189; 0.309), **5** (0.195; 0.337) in solid state. Inset: photos were taken at daylight and in the upon irradiation with a hand-held UV lamp (λ_{em} 366 nm).

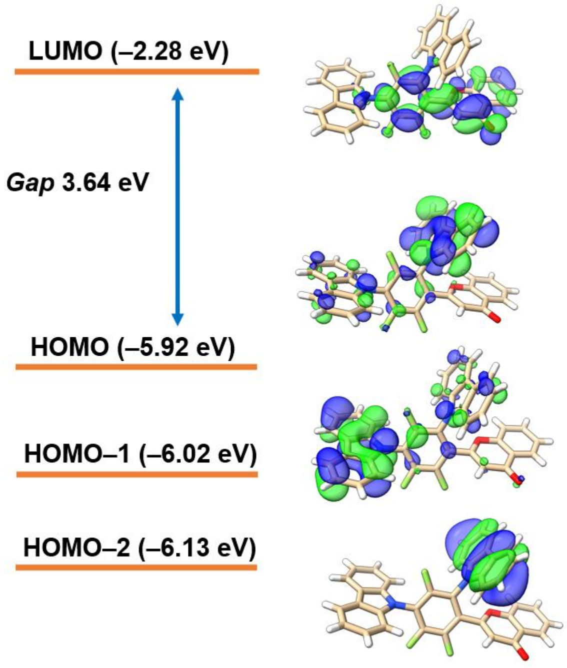

Figure S10. Frontier molecular orbitals (NTO) of compound **3**.

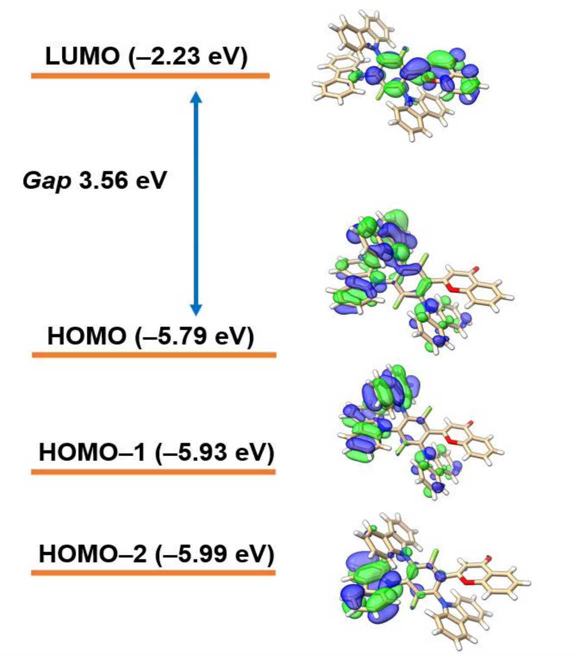

Figure S11. Frontier molecular orbitals (NTO) of compound **4**.

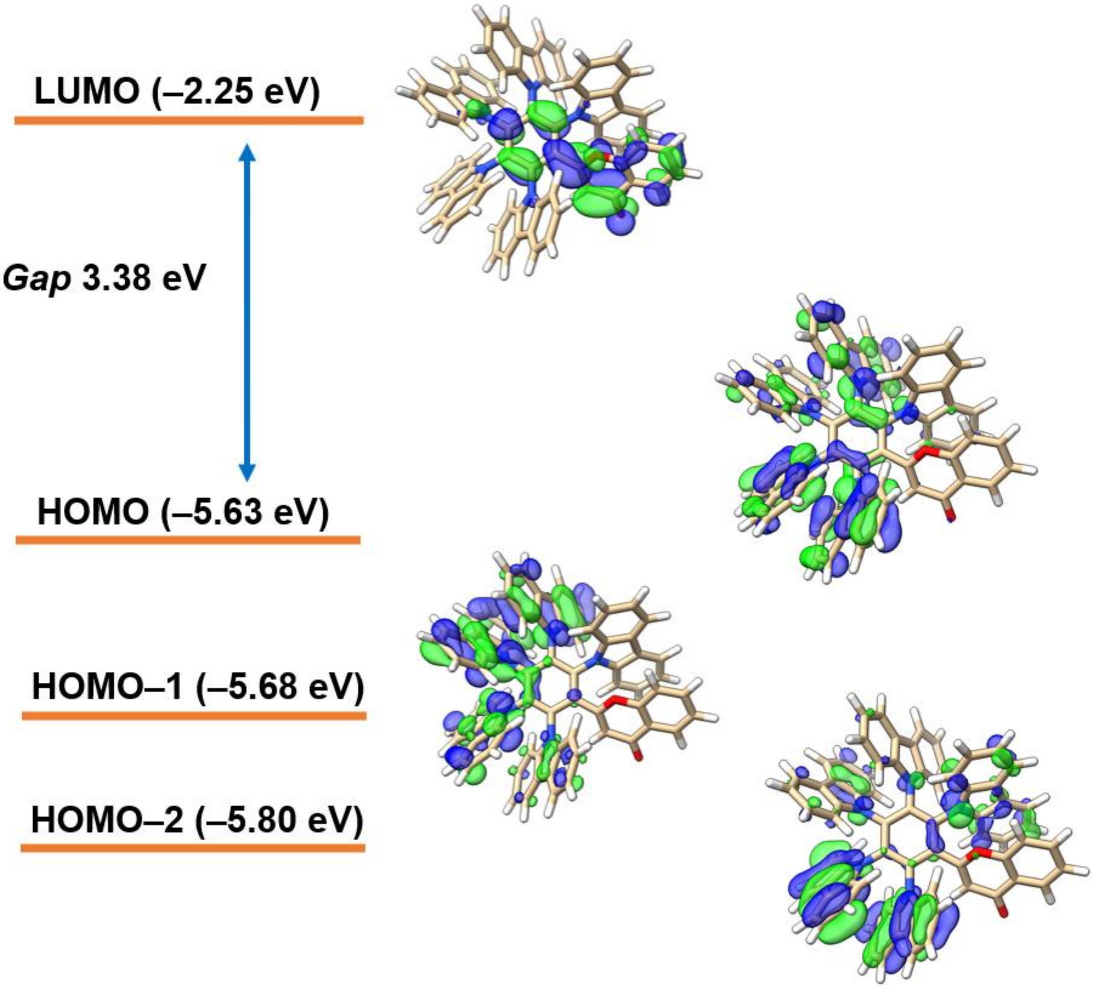

Figure S12. Frontier molecular orbitals (NTO) of compound **5**.

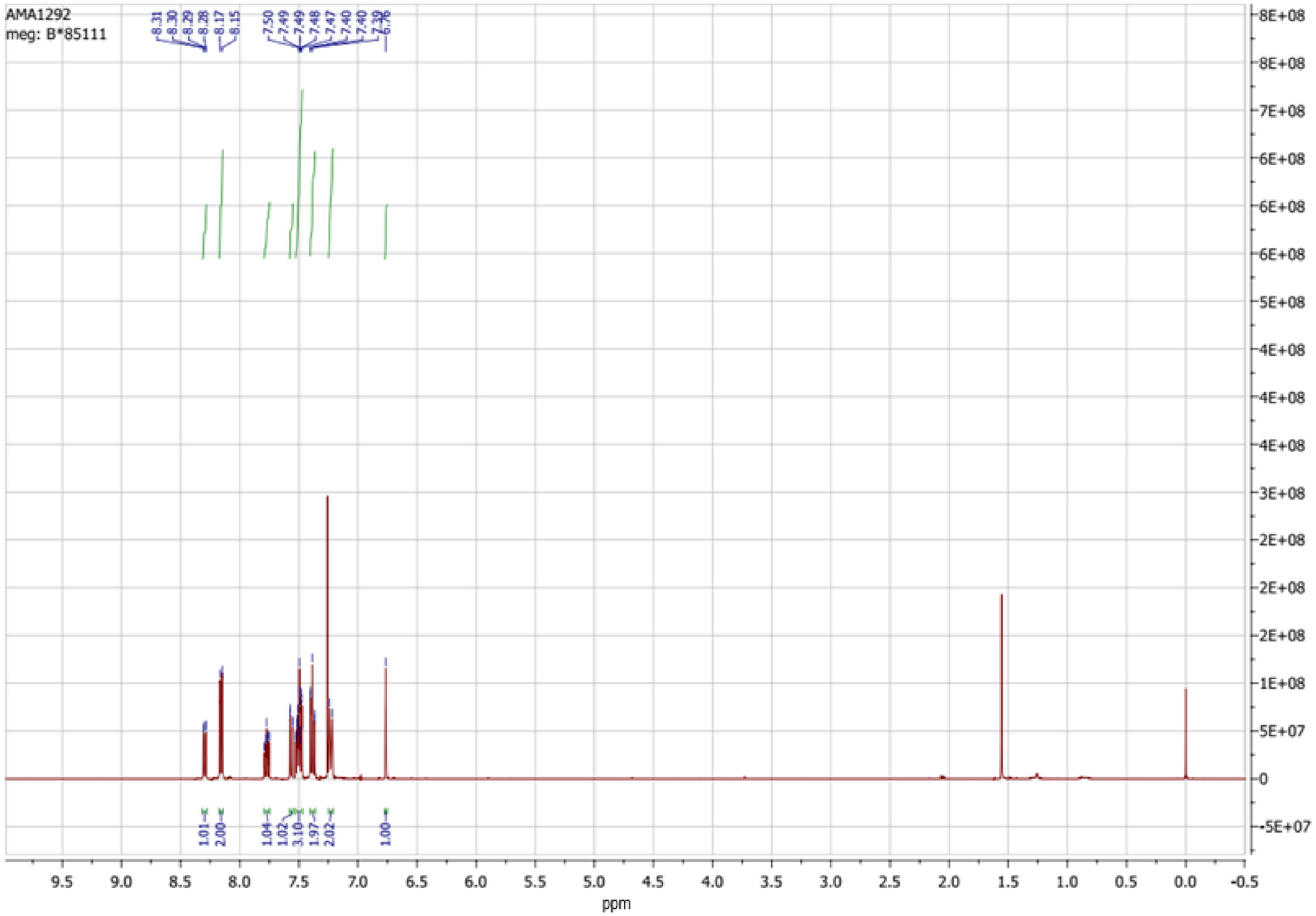

Figure S13. ^{1}H NMR spectrum of **2**.

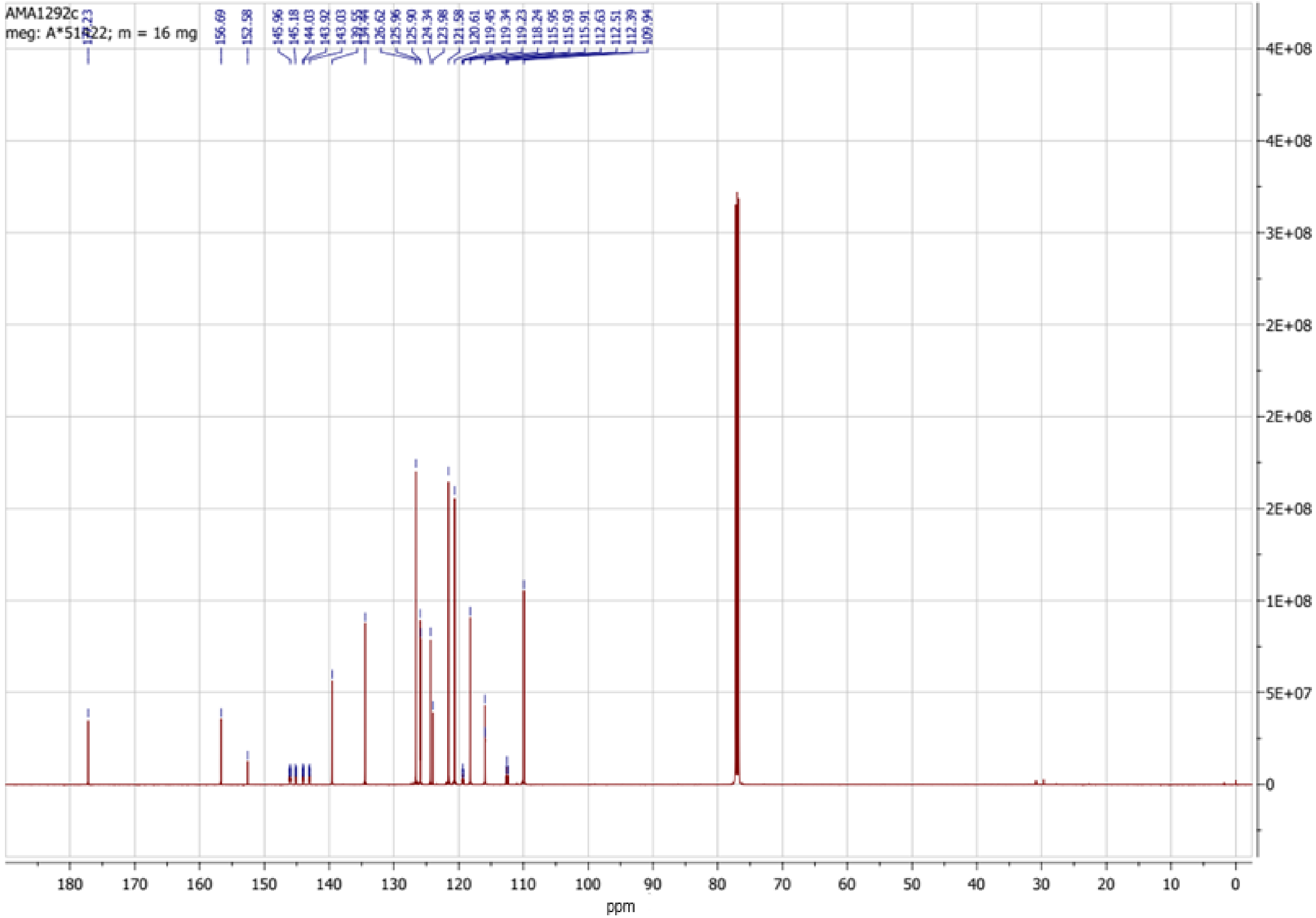

Figure S14. ^{13}C NMR spectrum of **2**.

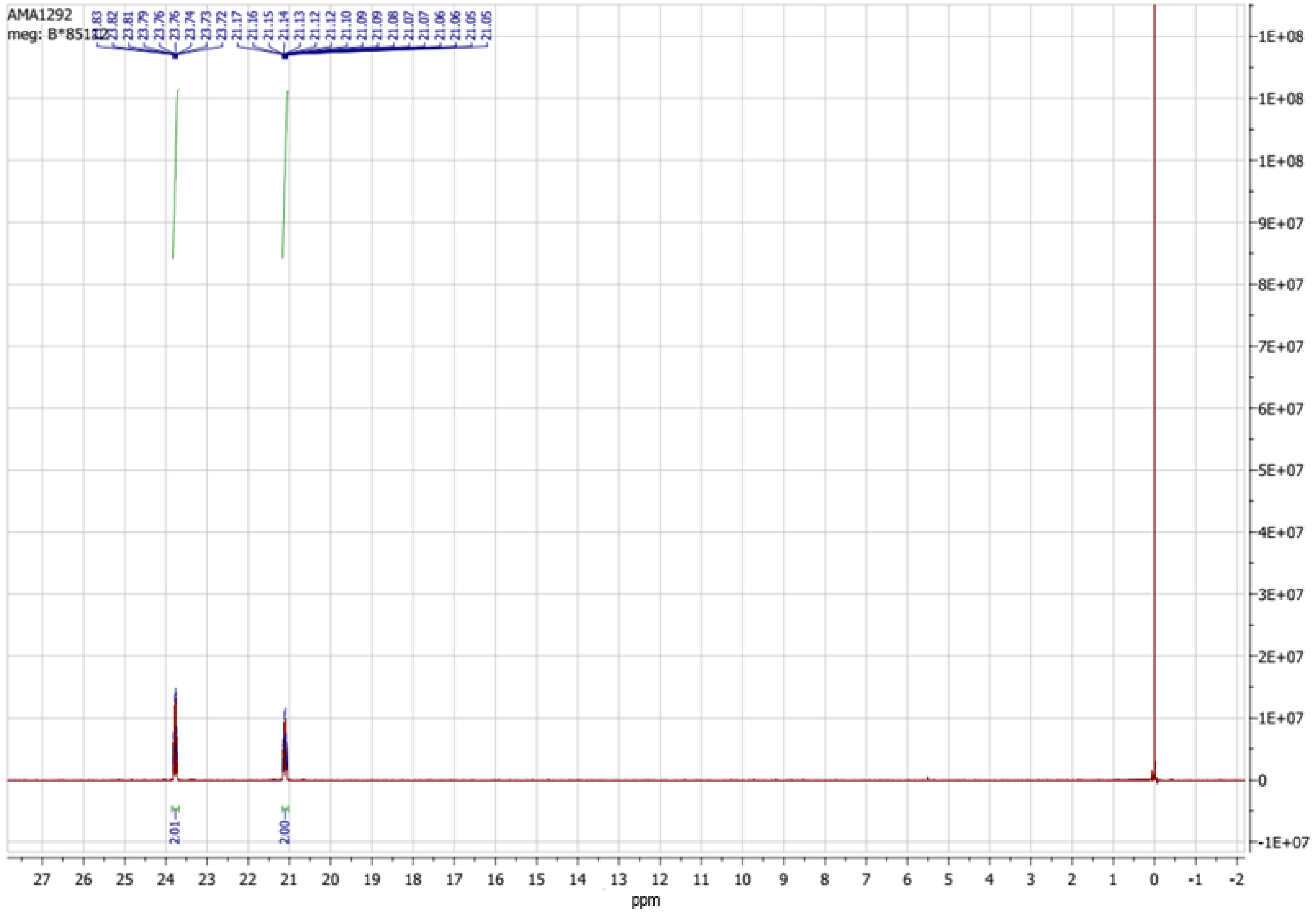

Figure S15. ^{19}F NMR spectrum of **2**.

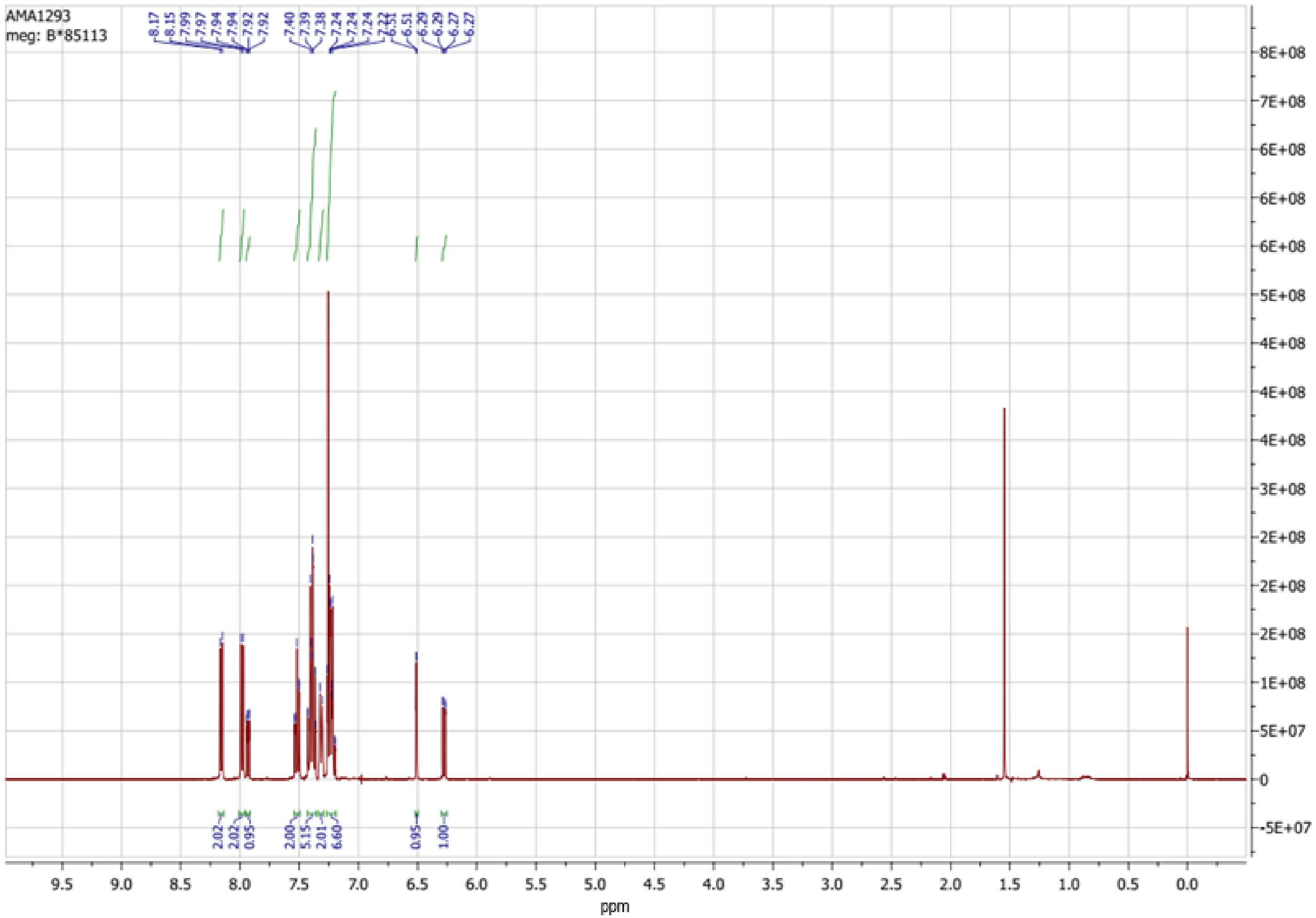

Figure S16. ^{1}H NMR spectrum of **3**.

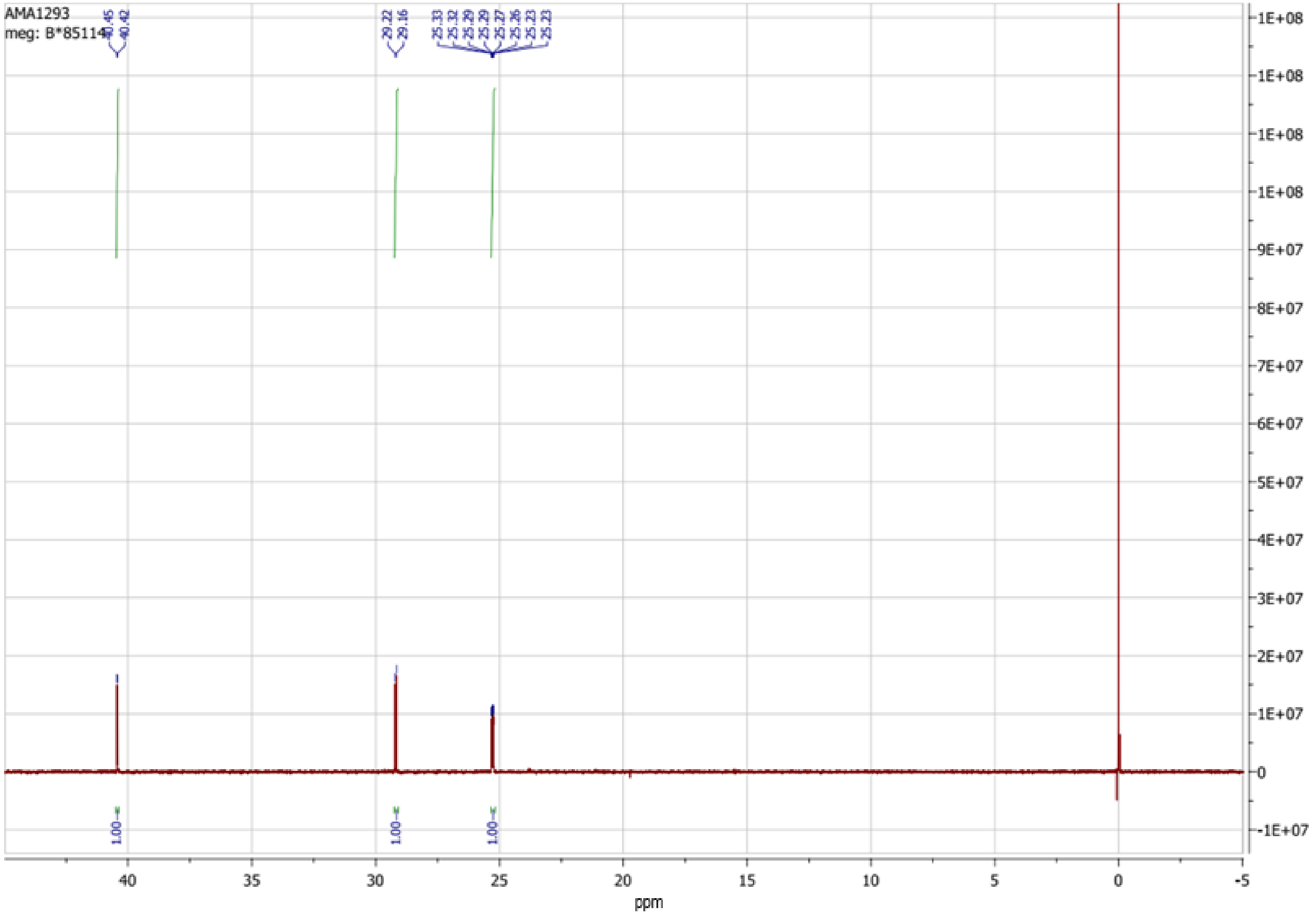

Figure S17. ^{19}F NMR spectrum of **3**.

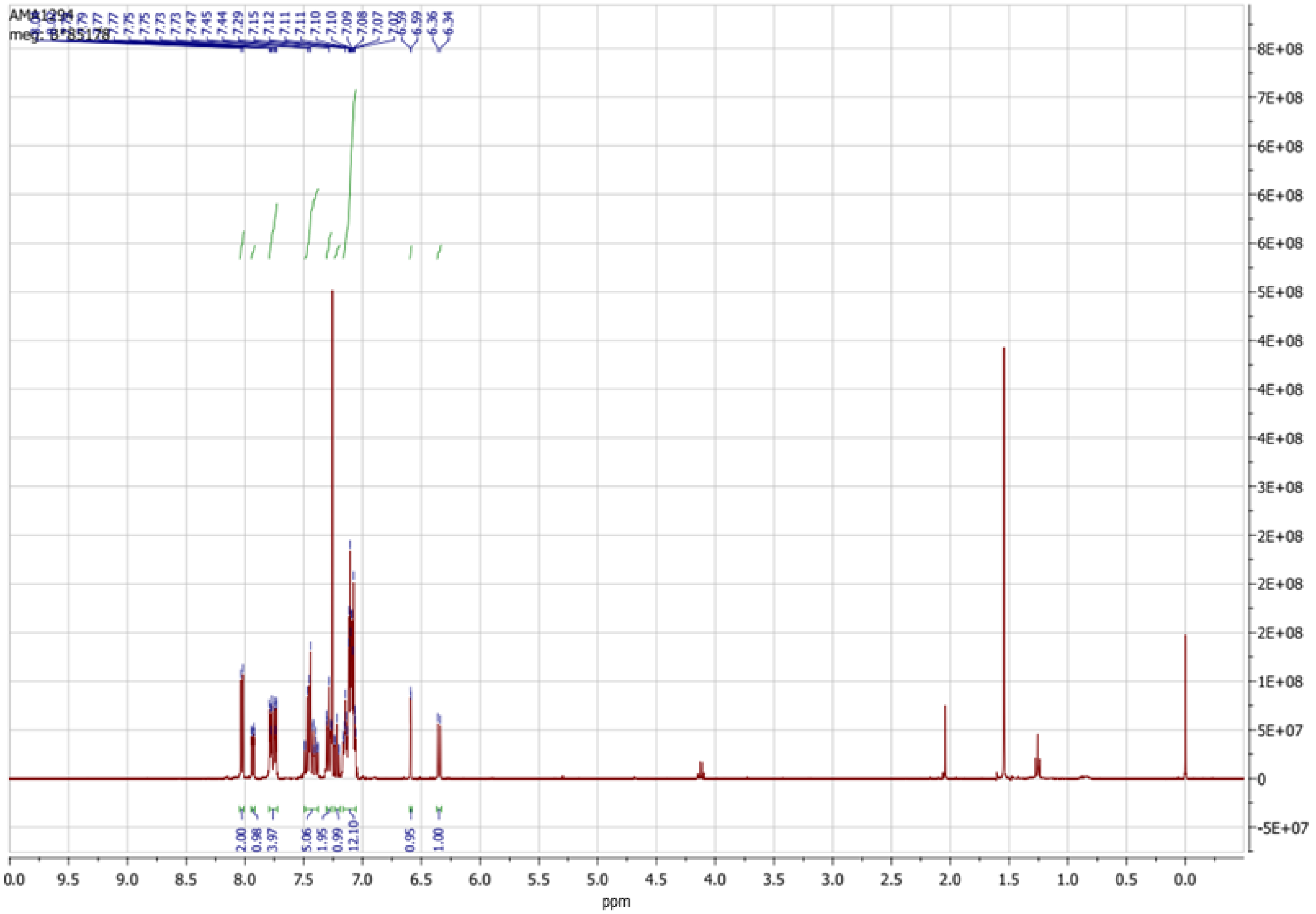

Figure S18. ^{1}H NMR spectrum of **4** (contains residual signals of ethanol and acetone).

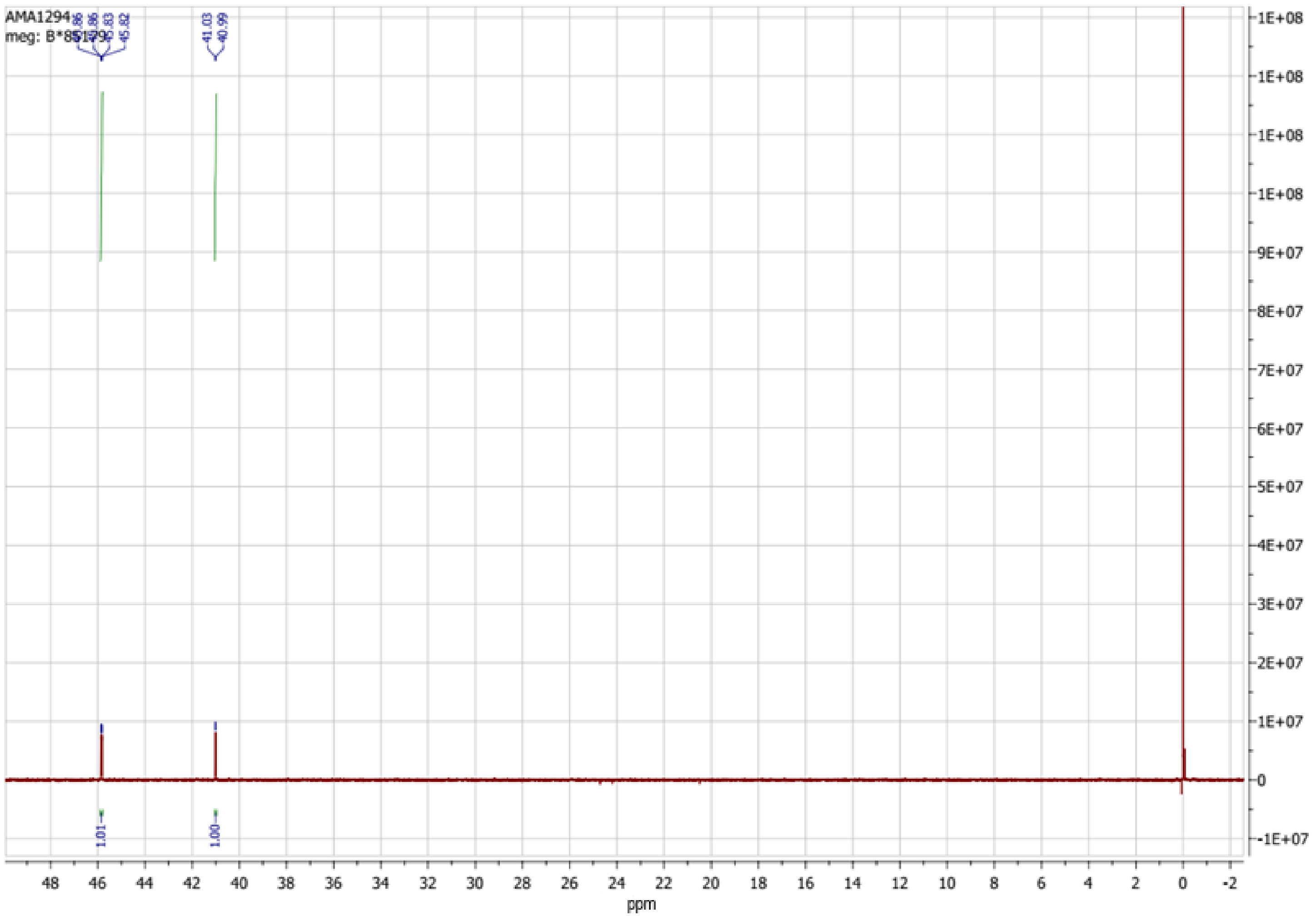

Figure S19. ^{19}F NMR spectrum of **4**.

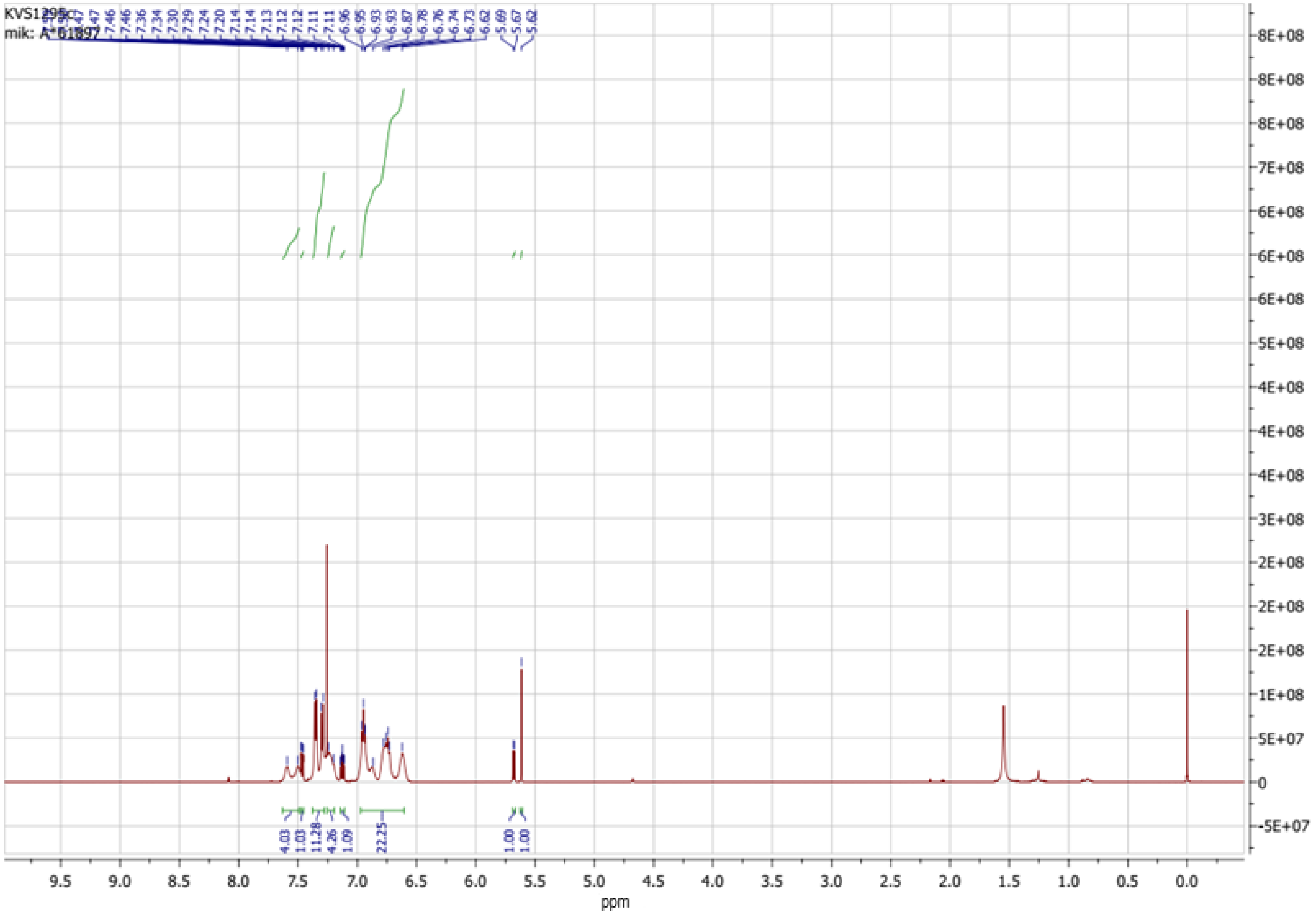

Figure S20. ^{1}H NMR spectrum of **5**.