Photoactivatable Sensors for Detecting Mobile Zinc

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General Materials and Methods.

Reagents were purchased from commercial sources and used as received. Zinpyr-1 (ZP1) and the diacetylated derivative DA-ZP1 were synthesized as previously described.[1-2] NMR spectra were acquired on a 400 MHz Bruker AVANCE-400 spectrometer. ^{1}H NMR chemical shifts are reported in ppm relative to that of SiMe$_4$ (δ = 0.00) and were referenced internally to residual solvent peaks.[3] Low-resolution electrospray mass spectra were acquired on an Agilent 1100 Series LC/MSD Trap spectrometer. High-resolution mass spectra were acquired on a Bruker Daltonics APEXIV 4.7 tesla Fourier transform ion cyclotron resonance mass spectrometer at the MIT Department of Chemistry Instrumentation Facility. Compounds were purified using Agilent 1200 Series HPLC systems fitted with multi-wavelength detectors and automated fraction collectors using a C18 reverse stationary phase (Zorbax-SB C18 columns: preparative, 7 µm, 21.2 × 250 mm; semi-preparative, 5 µm 9.4 × 250 mm; and analytical, 5 µm, 4.6 × 250 mm) and a mobile phase composed of two solvents (A: H$_2$O + 0.1% (v/v) CF$_3$CO$_2$H; B: CH$_3$CN + 0.1% (v/v) CF$_3$CO$_2$H). UV-visible spectra were recorded on a Varian Cary 50 Bio UV-visible spectrophotometer. Fluorescence measurements were made with a Photon Technologies International 4L-format scanning spectrofluorometer equipped with a temperature-controlled, 4-position sample turret. Quartz cuvettes with 1.00 cm path lengths were used for all spectroscopic measurements. Milli-Q purified water with resistivity of at least 18 MΩ·cm^{-1} was used to prepare all buffers. Aqueous buffers were treated with Chelex® resin according to the manufacturer's instructions prior to use.

Chemical Synthesis.

Scheme S1. Synthesis of 2-(bromomethyl)-1-nitro-3-(trifluoromethyl)benzene (**S1**).
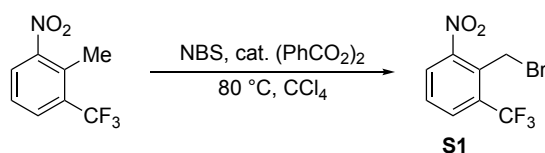
2-(Bromomethyl)-1-nitro-3-(trifluoromethyl)benzene (S1)

In a 50 mL round-bottom pressure vessel, 2-methyl-1-nitro-3-(trifluoromethyl)benzene (1026 mg, 5.00 mmol), *N*-bromosuccinimide (NBS, 797 mg, 5.50 mmol), and benzoyl peroxide (61 mg, 0.25 mmol) were mixed with CCl$_4$ (30 mL). The reaction was heated at 80 °C (oil bath temperature) in ambient light. Additional NBS (445 mg, 0.5 equiv) was added at 24 h. Another portion of NBS (223 mg, 0.25 equiv) was added at 48 h. After 72 h, the solvent was evaporated under vacuum and the crude product was purified by column chromatography (EtOAc:hexanes = 1:8 to 1:6). A colorless oil was obtained (951 mg, 67% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.63 (tq, *J* = 8.1, 0.8 Hz, 1H), 4.93 (s, 2H). ^{19}F NMR (376 MHz, CDCl$_3$) δ −59.4 (s, 3F). EI-MS(+) *m/z* calcd for [M]$^+$ 283, found 283. Spectroscopic data are consistent with reported values.[4]

Scheme S2. Synthesis of 1-(bromomethyl)-3,4,5-trimethoxy-2-nitro-6-(trifluoromethyl)benzene (**S4**).
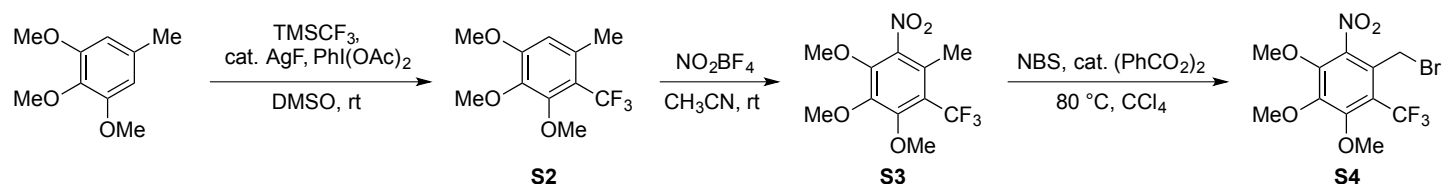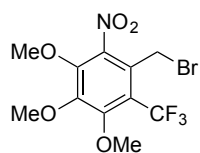

1,2,3-Trimethoxy-5-methyl-4-(trifluoromethyl)benzene (S2)

Anhydrous DMSO (36 mL) was added through a syringe to a Schlenk flask containing 3,4,5-trimethoxytoluene (3.28 g, 18.0 mmol), PhI(OAc)$_2$ (11.6 g, 36.0 mmol), and AgF (571 mg, 4.50 mmol). TMSCF$_3$ (5.31 mL, 36.0 mmol) was added to the flask dropwise. The slightly exothermic reaction was stirred under an inert atmosphere for 12 h. The reaction was mixed with brine (100 mL) and EtOAc (30 mL). The mixture was then filtered and the solid was washed with EtOAc (15 mL). The organic phase was isolated and the aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic phase was washed with brine (30 mL × 3) and dried over MgSO$_4$. The solvent was evaporated under vacuum. The crude product was purified by column chromatography (EtOAc:hexanes = 1:8). A slightly yellow oil was obtained (2.65 g, 59% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.49 (s, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 2.43 (qd, $J_{\text{H-F,through space}}$ = 3.5 Hz, $J_{\text{H-H,through space}}$ = 0.5 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$) δ −54.8 (q, $J_{\text{H-F,through space}}$ = 3.5 Hz, 3F). EI-MS(+) m/z calcd for [M]$^+$ 250, found 250. Spectroscopic data are consistent with reported values.[5]

1,2,3-Trimethoxy-5-methyl-4-nitro-6-(trifluoromethyl)benzene (S3)

In a glovebox, NO$_2$BF$_4$ (1.11 g, 8.40 mmol) was added in one portion to 1,2,3-trimethoxy-5-methyl-4-(trifluoromethyl)benzene (**S2**, 1.75 g, 7.00 mmol) in anhydrous CH$_3$CN (70 mL). The reaction was stirred at room temperature for 30 min. The reaction mixture was removed from the glovebox and quenched with H$_2$O (100 mL). The mixture was extracted with CH$_2$Cl$_2$ (50 mL × 3). The organic phase was dried over MgSO$_4$. The crude product was purified by column chromatography (EtOAc:hexanes = 1:8). A white solid was obtained (378 mg, 18% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.02 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 2.28 (q, $J_{\text{F-H,through space}}$ = 3.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.4 (q, $^3J_{\text{C-F}}$ = 1.7 Hz), 148.0, 145.4, 143.9, 124.8 (q, $^3J_{\text{C-F}}$ = 1.6 Hz), 123.8 (q, $^1J_{\text{C-F}}$ = 275.5 Hz), 119.0 (q, $^2J_{\text{C-F}}$ = 29.6 Hz), 62.4, 62.2 (q, $J_{\text{C-F,through space}}$ = 0.9 Hz), 61.3, 14.6 (q, $J_{\text{C-F,through space}}$ = 4.6 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ −55.0 (q, $J_{\text{F-H,through space}}$ = 2.9 Hz, 3F). EI-MS(+) m/z calcd for [M]$^+$ 295, found 295.

1-(Bromomethyl)-3,4,5-trimethoxy-2-nitro-6-(trifluoromethyl)benzene (S4)

In a 150 mL round bottom pressure vessel, 1,2,3-trimethoxy-5-methyl-4-nitro-6-(trifluoromethyl)benzene (S3, 354 mg, 1.20 mmol), NBS (214 mg, 1.20 mmol), and benzoyl peroxide (9.7 mg, 0.04 mmol) were mixed with CCl$_4$ (60 mL). The reaction was heated at 80 °C (oil bath temperature) in ambient light. Additional NBS (642 mg, 3.0 equiv) was added in three equal portions at 24 h, 48 h, and 72 h. After 96 h, the solvent was evaporated under vacuum and the crude product was purified by column chromatography (EtOAc:hexanes = 1:8). A white solid was obtained (181 mg, 40% yield). The starting material was recovered as a white solid (195 mg, 55% recovered). ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.47 (q, $J_{F-H,\text{through space}}$ = 1.0 Hz, 2H), 4.04 (s, 3H), 3.98 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.9 (q, $^3J_{C-F}$ = 1.6 Hz), 148.6, 147.8, 143.4, 123.8 (q, $^3J_{C-F}$ = 1.2 Hz), 123.4 (q, $^1J_{C-F}$ = 275.9 Hz), 118.7 (q, $^2J_{C-F}$ = 30.1 Hz), 62.6, 62.3 (q, $J_{C-F,\text{through space}}$ = 0.8 Hz), 61.3, 21.5 (q, $J_{C-F,\text{through space}}$ = 5.3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ −55.2 (s, 3F). EI-MS(+) m/z calculated for [M]$^+$ 373, found 373.

Scheme S3. Synthesis of Protected Sensors (**1-4**).
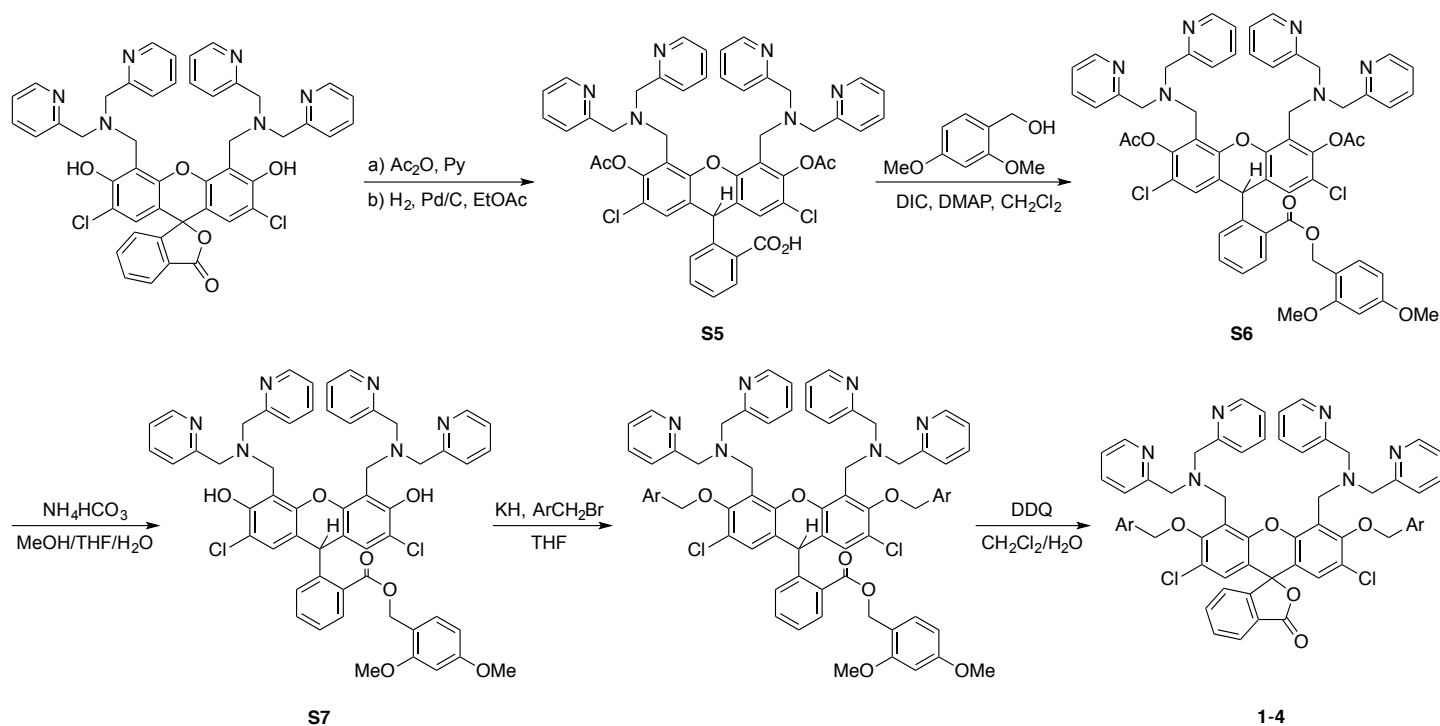
2-(3,6-Diacetoxy-4,5-bis((bis(pyridin-2-ylmethyl)amino)methyl)-2,7-dichloro-9H-xanthen-9-yl)benzoic acid (S5)
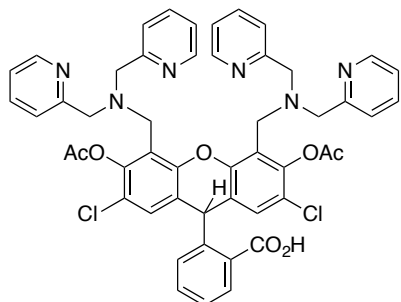
DA-ZP1 (1.09 g, 1.20 mmol) was dissolved in EtOAc (250 mL). The mixture was degassed with N_2 for 15 min. A portion of Pd/C (250 mg, 10 wt %) was added and the reaction was stirred under an H_2 atmosphere for 24 h. Additional Pd/C (500 mg) was added in two equal portions at 24 h and 48 h. After 72 h, the reaction was monitored by ESI-MS to confirm completion of the reduction. The reaction mixture was flushed with N_2 and filtered through Celite. The filtrate was then filtered through a 0.2 μm PTFE syringe filter. The solvent was removed under vacuum to give a slightly pink foam (1.09 g, 100%). The solid was used directly in the next step without further purification. MS (ESI+): m/z calcd for $[M+H]^+$ 909.3, found 909.3.

4,5-Bis((bis(pyridin-2-ylmethyl)amino)methyl)-2,7-dichloro-9-(2-(((2,4-dimethoxybenzyl)oxy)carbonyl)-phenyl)-9H-xanthene-3,6-diyl diacetate (S6)
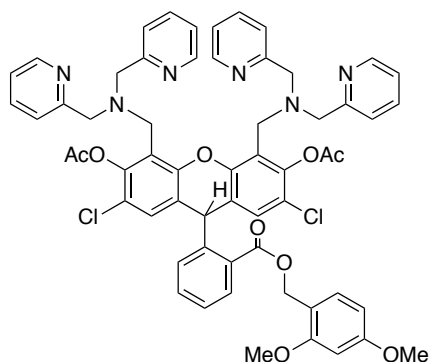
Compound **S5** (1.09 g, 1.20 mmol), *N,N'*-diisopropylcarbodiimide (DIC, 681 mg, 836 μL, 5.40 mmol), and 4-dimethylaminopyridine (DMAP, 7.3 mg, 0.06 mmol) were dissolved in CH_2Cl_2 (60 mL). A portion of 2,4-dimethoxybenzyl alcohol (0.90 g, 5.4 mmol) was then added. The reaction was stirred in the dark for 18 h at room temperature. The solvent was removed under vacuum. The crude product was analyzed by ESI-MS to confirm completion of the reaction and used directly without further purification. MS (ESI+): m/z calcd for $[M+H]^+$ 1059.3, found 1059.4.

2,4-Dimethoxybenzyl 2-(4,5-bis((bis(pyridin-2-ylmethyl)amino)methyl)-2,7-dichloro-3,6-dihydroxy-9H-xanthen-9-yl)benzoate (S7)
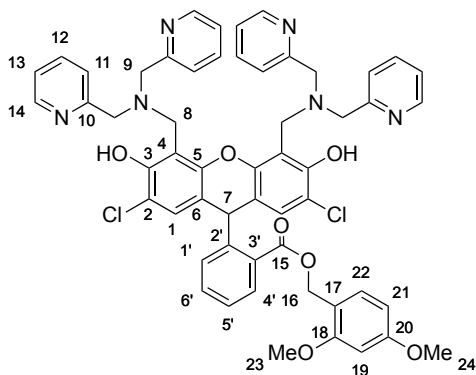
Compound **S6** (ca. 1.20 mmol, crude) was dissolved in a mixture of THF (120 mL) and MeOH (60 mL). An aqueous solution of NH_4HCO_3 (1.93 g, 24.4 mmol, in 60 mL of H_2O) was then added. The reaction was stirred in the dark at room temperature and monitored by ESI-MS. Deacetylation was complete after 3 days. The organic solvents were removed with a rotavap. The crude product in water was dissolved in CH_3CN (ca. 350 mL) and purified by preparative HPLC using solvent gradeint 1 (Table S1). Fractions containing the desired product (t_R = 11.2 min) were combined and lyophilized to give a light orange solid (61 mg, 51%). ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.67 (d, J = 5.6 Hz, 4H), 8.10 (t, J = 7.8 Hz, 4H), 7.71 (dd, J = 7.9, 1.4 Hz, 1H), 7.68 (d, J = 8.2 Hz, 4H), 7.63 (t, J = 6.7 Hz, 4H), 7.41 (td, J = 7.7,

1.4 Hz, 1H), 7.32 – 7.24 (m, 2H), 6.99 (d, J = 8.5 Hz, 1H), 6.70 (s, 2H), 6.50 (s, 1H), 6.49 (dd, J = 8.0, 3.6 Hz, 1H), 5.72 (s, 1H), 5.23 (s, 2H), 4.37 (s, 8H), 4.17 (pseudo q, AB system, J = 13.6 Hz, 4H), 3.76 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, CD$_3$CN) δ 168.9, 162.7, 160.1, 155.2, 152.7, 148.7, 146.5, 144.6, 144.3, 133.3, 132.6, 132.0, 131.2, 130.5, 130.2, 128.0, 126.7, 126.1, 117.6, 116.9, 116.8, 112.8, 105.4, 99.3, 63.7, 58.0, 56.3, 56.0, 49.7, 38.8. ESI-MS(+) m/z calcd for [M+H]$^+$ 975.3, found 975.2.

General procedure for preparation of 1 and other derivatives.

In an anaerobic glovebox, potassium hydride (7.6 mg, 0.192 mmol) was added to a Schlenk flask containing a solution of **S7** (31.2 mg, 0.032 mmol) in THF (4 mL). The reaction was stirred at room temperature for 30 min before the addition of o-nitrobenzyl bromide (34.6 mg, 0.320 mmol). The reaction flask was wrapped with aluminum foil and the reaction was stirred overnight. The reaction was monitored by ESI-MS(+) to confirm the formation of the desired product (m/z calcd for [M+H]$^+$ = 1245.4, found 1245.5). The Schlenk flask was removed from the glovebox and attached to a manifold. The reaction was quenched with water (0.1 mL) and the solvent was evaporated. The crude product was stirred with CH$_2$Cl$_2$/H$_2$O (3.0 mL/0.6 mL). A portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 72.6 mg, 0.320 mmol) was added and the reaction was stirred at room temperature in the dark for 24 h. The organic solvent was evaporated and the residue was dissolved in CH$_3$CN/H$_2$O (27 mL/27 mL). Insoluble material was removed by filtration through a 0.2 μm PTFE syringe filter. The crude product was purified by preparative and semi-preparative HPLC using the solvent gradients indicated below. Fractions containing the desired compound were combined and lyophilized.

4',5'-Bis((bis(pyridin-2-ylmethyl)amino)methyl)-2',7'-dichloro-3',6'-bis((2-nitrobenzyl)oxy)-3H-spiro[isobenzofuran-1,9'-xanthen]-3-one (1)
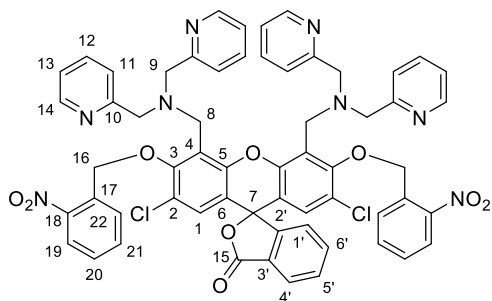
This compound was prepared by using **S7** (0.032 mmol) and o-nitrobenzyl bromide (0.32 mmol) according to the general procedure. The crude material was purified by preparative HPLC using solvent gradient 2 (Table S1). Further purification by semi-preparative HPLC using solvent gradient 3 (Table S1) afforded a slightly yellow solid (19.7 mg, 56% yield). UV (CH$_3$CN) ε_{254} = 45,500 M^{-1}·cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.49 (dd, J = 5.2, 0.7 Hz, 4H), 8.14 (dd, J = 8.2, 1.2 Hz, 2H), 8.05 (d, J = 7.9 Hz, 2H), 8.02 (dt, J = 7.7, 0.9 Hz, 1H), 7.90 – 7.72 (m, 8H), 7.61 (pseudo dt, J = 8.2, 1.4 Hz, 2H), 7.42 (d, J = 7.9 Hz, 4H), 7.38 (dd, J = 7.0, 6.0 Hz, 4H), 7.22 (d, J = 7.7 Hz, 1H), 6.73 (s, 2H), 5.40 (s, 4H), 4.32 (pseudo dd, J = 20.7, 12.7 Hz, 4H), 4.26 (s, 8H). ^{13}C NMR (101 MHz, CD$_3$CN) δ 169.1, 157.3, 156.3, 151.5, 150.0, 147.9, 146.2, 141.9, 136.9, 135.3, 133.7, 131.9, 130.0, 129.8(0), 129.7(8), 127.5, 126.6, 125.9, 125.4, 125.0, 124.9, 124.6, 122.3, 117.7, 81.6, 73.1, 59.3, 50.2. ESI-HRMS(+) m/z calcd for C$_{60}$H$_{47}$Cl$_2$N$_8$O$_9^+$ [M+H]$^+$ 1093.2838, found 1093.2819.

4',5'-Bis((bis(pyridin-2-ylmethyl)amino)methyl)-2',7'-dichloro-3',6'-bis((4,5-dimethoxy-2-nitrobenzyl)oxy)-3H-spiro[isobenzofuran-1,9'-xanthen]-3-one (2)
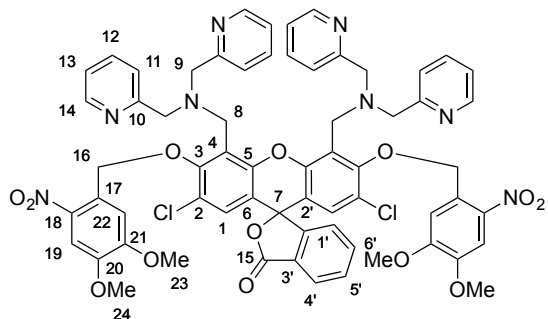
This compound was prepared by using **S7** (0.040 mmol) and 4,5-dimethoxy-2-nitrobenzyl bromide (0.40 mmol) according to the general procedure. The crude material was purified by preparative HPLC using solvent gradient 4 (Table S1). Further purification by semi-preparative HPLC using solvent gradient 5 (Table S1) afforded a slightly yellow solid (21.8 mg, 45% yield). UV (CH$_3$CN) ε_{254} = 55,300 M^{-1}·cm^{-1} and ε_{300} = 14,700 M^{-1}·cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.48 (br dd, J = 5.3, 0.7 Hz, 4H), 8.02 (d, J = 7.7 Hz, 1H), 7.89 (td, J = 7.8, 1.5 Hz, 4H), 7.87 (td, J = 7.9, 1.1 Hz, 1H, overlap with H12), 7.77 (td, J = 7.6, 0.8 Hz, 1H), 7.71 (s, 2H), 7.45 (s, 2H), 7.44 (d, J = 8.5 Hz, 4H), 7.41 (ddd, J = 6.4, 1.9, 0.8 Hz, 4H), 7.23 (d, J = 7.7 Hz, 1H), 6.74 (s, 2H), 5.35 (s, 4H), 4.36 (d, J = 12.6 Hz, 1H), 4.33 (pseudo dd, AB system, J = 12.6, 7.3 Hz, 4H) 4.28 (d, J = 2.0 Hz, 8H), 3.96 (s, 6H), 3.94 (s, 6H). ^{13}C NMR (101 MHz, CD$_3$CN) δ 169.1, 157.0, 156.4, 155.0, 151.5, 150.0, 149.5, 145.8, 142.4, 140.3, 136.9, 131.9, 129.9, 128.4, 127.5, 126.6, 125.7, 125.2, 124.9, 124.6, 122.2, 117.7, 111.4, 109.1, 81.6, 73.3, 59.1, 57.2, 57.1, 50.2. ESI-HRMS(+) m/z calcd for C$_{64}$H$_{55}$Cl$_2$N$_8$O$_{13}$$^+$ [M+H]$^+$ 1213.3260, found 1213.3290.

4',5'-Bis((bis(pyridin-2-ylmethyl)amino)methyl)-2',7'-dichloro-3',6'-bis((2-nitro-6-(trifluoromethyl)benzyl)oxy)-3H-spiro[isobenzofuran-1,9'-xanthen]-3-one (3)

This compound was prepared by using **S7** (0.040 mmol) and 2-(bromomethyl)-1-nitro-3-(trifluoromethyl)benzene (0.40 mmol) according to the general procedure. The crude material was purified by preparative HPLC using solvent gradient 6 (Table S1) to afford a slightly yellow solid (27.7 mg, 56% yield). UV (CH$_3$CN) ε_{254} = 39,900 M^{-1}·cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.53 (d, J = 4.7 Hz, 4H), 8.05 – 8.04 (m, 4H), 8.00 (d, J = 7.7 Hz, 1H), 7.90 (td, J = 7.8, 1.5 Hz, 4H), 7.87 (dd, J = 7.7, 1.0 Hz, 1H), 7.80 (t, J = 8.1 Hz, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.45 (dd, J = 6.7, 6.0 Hz, 4H), 7.32 (d, J = 7.9 Hz, 4H), 7.16 (d, J = 7.7 Hz, 1H), 6.59 (s, 2H), 5.45 (pseudo dd, AB system, J = 12.8 Hz, 4H), 4.14 (s, 8H), 4.08 (pseudo dd, AB system, J = 14.0, 12.3 Hz, 4H). ^{13}C NMR (101 MHz, CD$_3$CN) δ 168.9, 157.3, 156.1, 152.5, 151.1, 149.8, 145.8, 142.4, 136.9, 132.0, 131.9, 131.3 (q, $^3J_{C\text{-}F}$ = 5.7 Hz), 130.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.9, 129.4 (C17 and C19), 127.6, 126.6, 125.3, 125.2, 124.8, 124.3 (q, $^1J_{C\text{-}F}$ = 274.0 Hz), 123.9, 121.9, 117.7, 81.3, 69.1 (q, $J_{C\text{-}F, \text{ through space}}$ = 2.5 Hz), 58.7, 50.20. ^{19}F NMR (376 MHz, CD$_3$CN) δ −58.9 (s, 6F). ESI-HRMS(+) m/z calcd for C$_{62}$H$_{45}$Cl$_2$F$_6$N$_8$O$_9$$^+$ [M+H]$^+$ 1229.2585, found 1229.2595.
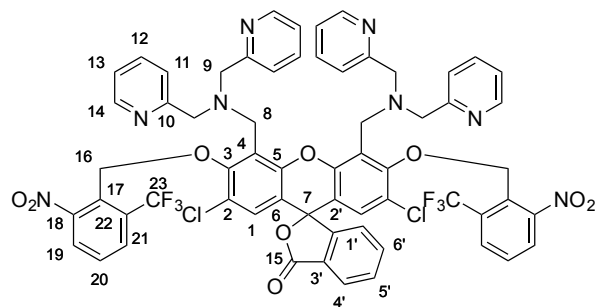
4',5'-Bis((bis(pyridin-2-ylmethyl)amino)methyl)-2',7'-dichloro-3',6'-bis((3,4,5-trimethoxy-2-nitro-6-(trifluoromethyl)benzyl)oxy)-3H-spiro[isobenzofuran-1,9'-xanthen]-3-one (4)
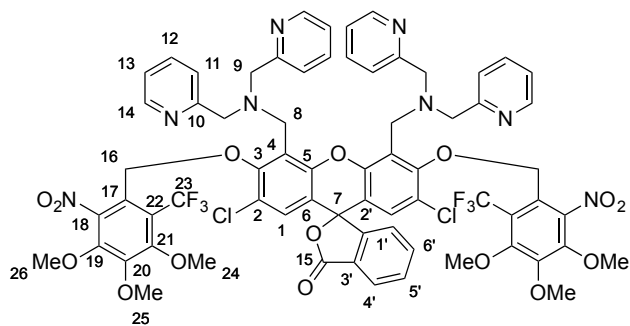
This compound was prepared by using **S7** (0.040 mmol) and 1-(bromomethyl)-3,4,5-trimethoxy-2-nitro-6-(trifluoromethyl)benzene (0.40 mmol) according to the general procedure. The reaction mixture was purified by preparative HPLC using solvent gradient 7 (Table S1) to obtain a slightly yellow solid (16.7 mg, 30% yield). UV (CH$_3$CN) ε_{254} = 22,200 M^{-1}·cm^{-1} and ε_{300} = 3,570 M^{-1}·cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.53 (d, J = 4.9 Hz, 4H), 8.00 (d, J = 7.7 Hz, 1H), 7.91 (td, J = 7.7, 1.1 Hz, 4H), 7.88 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.44 (pseudo t, J = 6.4 Hz, 4H), 7.32 (d, J = 7.9 Hz, 4H), 7.11 (d, J = 7.6 Hz, 1H), 6.58 (s, 2H), 5.15 (pseudo dd, AB system, J = 13.1, 8.7 Hz, 4H), 4.15 (s, 8H), 4.11 (pseudo dd, J = 12.1, 9.0 Hz, 4H), 4.02 (s, 6H), 3.98 (s, 6H), 3.96 (s, 6H). ^{13}C NMR (101 MHz, CD$_3$CN) δ 168.9, 157.5, 156.8 (q, $^3J_{C-F}$ = 1.7 Hz), 156.1, 151.2, 149.7, 149.4, 148.9, 145.8, 144.0, 142.3, 136.9, 131.9, 129.9, 127.5, 126.6, 125.1(5), 125.1(4), 124.7, 124.5 (q, $^1J_{C-F}$ = 275.1 Hz), 123.9, 123.5 (q, $^3J_{C-F}$ = 1.3 Hz), 121.8, 119.3 (q, $^2J_{C-F}$ = 30.0 Hz), 117.6, 81.3, 69.4 (q, $J_{C-F,\text{through space}}$ = 5.7 Hz), 63.4, 63.0 (q, $J_{C-F,\text{through space}}$ = 0.7 Hz), 62.1, 58.9, 50.4. ^{19}F NMR (376 MHz, CD$_3$CN) δ −55.3 (s, 6F). ESI-HRMS(+) m/z calcd for C$_{68}$H$_{57}$Cl$_2$F$_6$N$_8$O$_{15}^+$ [M+H]$^+$ 1409.3219, found 1409.3254

Table S1. HPLC Solvent Gradients.

Gradient	Time (min)	% Solvent B	Gradient	Time (min)	% Solvent B
1	0	25	5	0	10
	2.5	45		5	55
	12.5	55		13	64
	15	100		14	100
	17	100		15	100
	19	0		17	10
	20	0			
2	0	20	6	0	10
	3	50		3	55
	16	63		15	67
	19	100		16	100
	20	100		17	100
	22	20		19	10
	23	20		20	10
3	0	10	7	0	10
	3	60		3	65
	8	65		14	76
	10	100		15	100
	10.5	100		17	10
	12	10		18	10
	13	10			
4	0	25	8	0	10
	3	55		5	10
	16	68		30	100
	16.5	100		33	100
	17.5	100		36	10
	19.5	25		40	10
	20.5	25			

Spectroscopy.

Concentrated stock solutions of each sensor were prepared in DMSO and stored as frozen aliquots at −80 °C. Extinction coefficients were determined in CH_3CN by dissolving lyophilized samples of each sensor in known volumes of CD_3CN (~700 µL) and diluting a small aliquot of each solution (2.000 µL) to 2.000 mL with CH_3CN. Absorption spectra of the dilute solutions were recorded at 25 °C. For compounds **1-3**, a known amount of DMF (~4 µL) was added to each of the CD_3CN stock solutions. For compound **4**, an aliquot (25 µL) of a stock solution of known concentration of CH_2Cl_2 in CD_3CN (~180 mM) was added to the sample. ^1H NMR spectra were collected with 30 s relaxation delay times.[6] The concentration of each sensor stock solution was determined by integrating ^1H NMR peaks of the sensor and comparing them to those arising from the DMF or CH_2Cl_2 standard. These data were used to calculate the following extinction coefficients: for compound **1**, ε_{254} = 45,500 $M^{-1} \cdot cm^{-1}$; for compound **2**, ε_{254} = 55,300 $M^{-1} \cdot cm^{-1}$ and ε_{300} = 14,700 $M^{-1} \cdot cm^{-1}$; for compound **3**, ε_{254} = 39,900 $M^{-1} \cdot cm^{-1}$; for compound **4**, ε_{254} = 22,200 $M^{-1} \cdot cm^{-1}$ and ε_{300} = 3,570 $M^{-1} \cdot cm^{-1}$. For cuvette studies, sensors were irradiated with a 4 W 254 nm compact light source (UVP; UVGL-25 p/n 95-0021-12) or a custom-made 380 nm light source consisting of nine 5 mm 20 mW LED bulbs (Super Bright LEDs, Inc.; p/n RL5-UV0230-380). Both light sources were mounted above a stir plate at a distance of ~5 cm away from the cuvette.

Photocleavage of each of the protected sensors was evaluated by comparing absorption and fluorescence spectra of each molecule before and after irradiation with 254 or 380 nm light in the presence and absence of $ZnCl_2$, as well as by collecting analytical HPLC traces at each time point. For all experiments, the buffer was 50 mM PIPES, 100 mM KCl, pH 7.0. A typical sample consisted of buffer (200 µL), water (1200 µL), acetonitrile (600 µL), and sensor (1.0 µL, final conc. 3 µM). Samples were stirred for ~1 min. The fluorescence emission spectrum of each sample was recorded from 500 − 650 nm, with an excitation wavelength of 490 nm. Background-corrected absorption spectra were also collected at a scan rate of 600 nm/min. An aliquot (50 µL) of each sample was removed for analytical HPLC analysis using solvent gradient 8 (Table S1). Samples were irradiated at either 254 nm or 360 nm for an interval of 15 s. Fluorescence and absorption spectra were collected and another aliquot (50 µL) was removed for HPLC analysis. This procedure was repeated until 90 s of total irradiation time was reached, at which point the irradiation interval was increased to 30 s and then 60 s. The experiment was stopped after 180 or 240 s of total irradiation time. Samples were irradiated in either the absence or presence of $ZnCl_2$ (10 µM final conc.). For the samples irradiated in the absence of $ZnCl_2$, a small amount of $ZnCl_2$ (~1 µL) was added to give a final concentration of 10 µM after the final irradiation period. Fluorescence and absorption spectra were then obtained. After all of the spectroscopic data had been collected, tris(2-pyridylmethyl)amine (TPA; 20 µM final conc.) was added to every sample. Each sample was stirred for 10 min, after which time fluorescence and absorption spectra were recorded. For all measurements, the step size was 1 nm. The integration time was 0.5 s. The slit width was 2 nm. The temperature was 298 K. In the course of

the irradiation experiment, mono-protected intermediates were observed during HPLC analysis of the irradiated samples. Although we were unable to collect a sufficient amount of material for NMR spectroscopic characterization, the mono-protected compounds do not absorb at 520 nm, which suggests that they exist in non-fluorescent lactone forms.
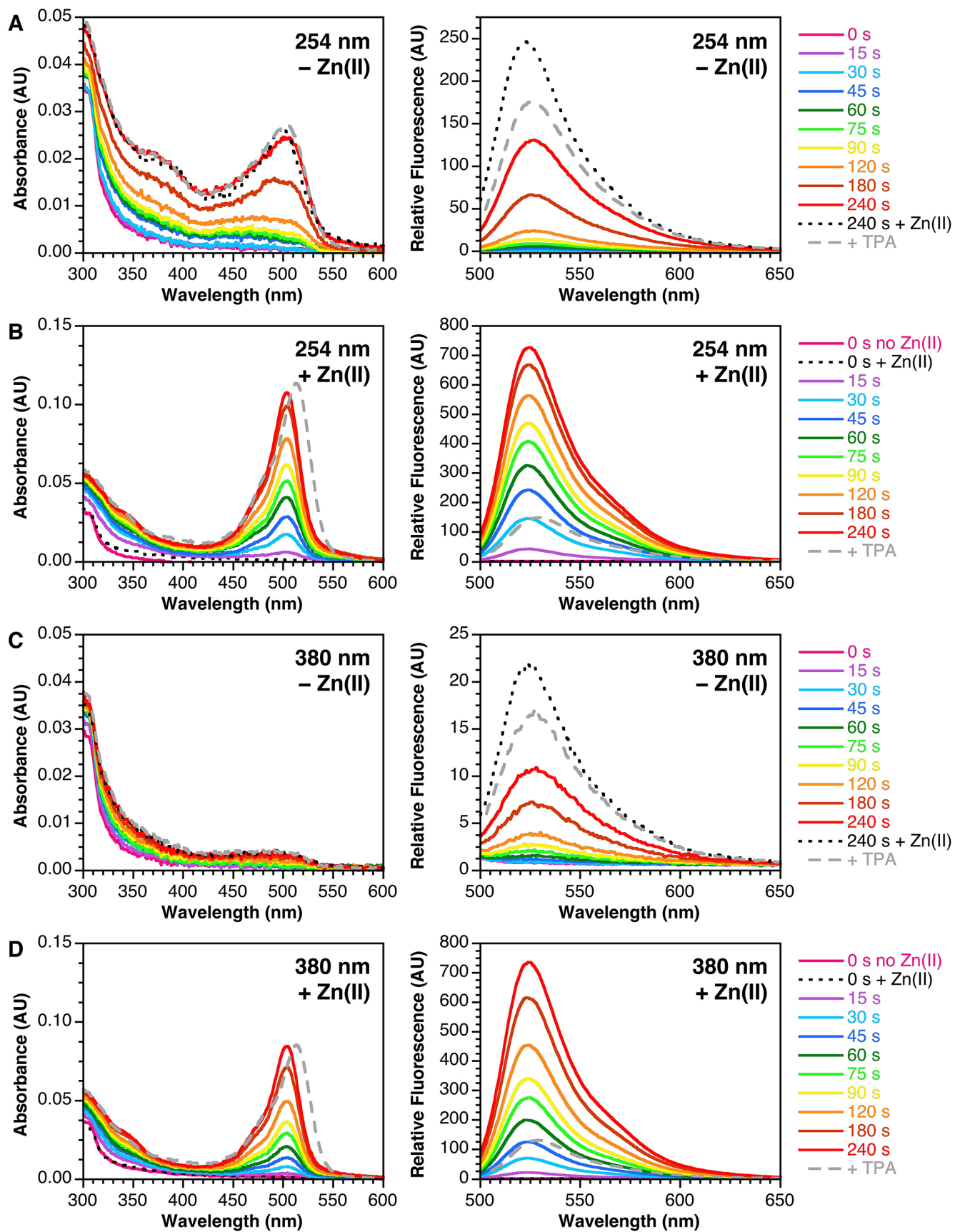
Figure S1. Absorption (left) and fluorescence (right) spectra of **1** after irradiation with 254 nm (A,B) or 380 nm (C,D) light for varying intervals of time in the absence (A,C) and presence (B,D) of ZnCl$_2$, as indicated.
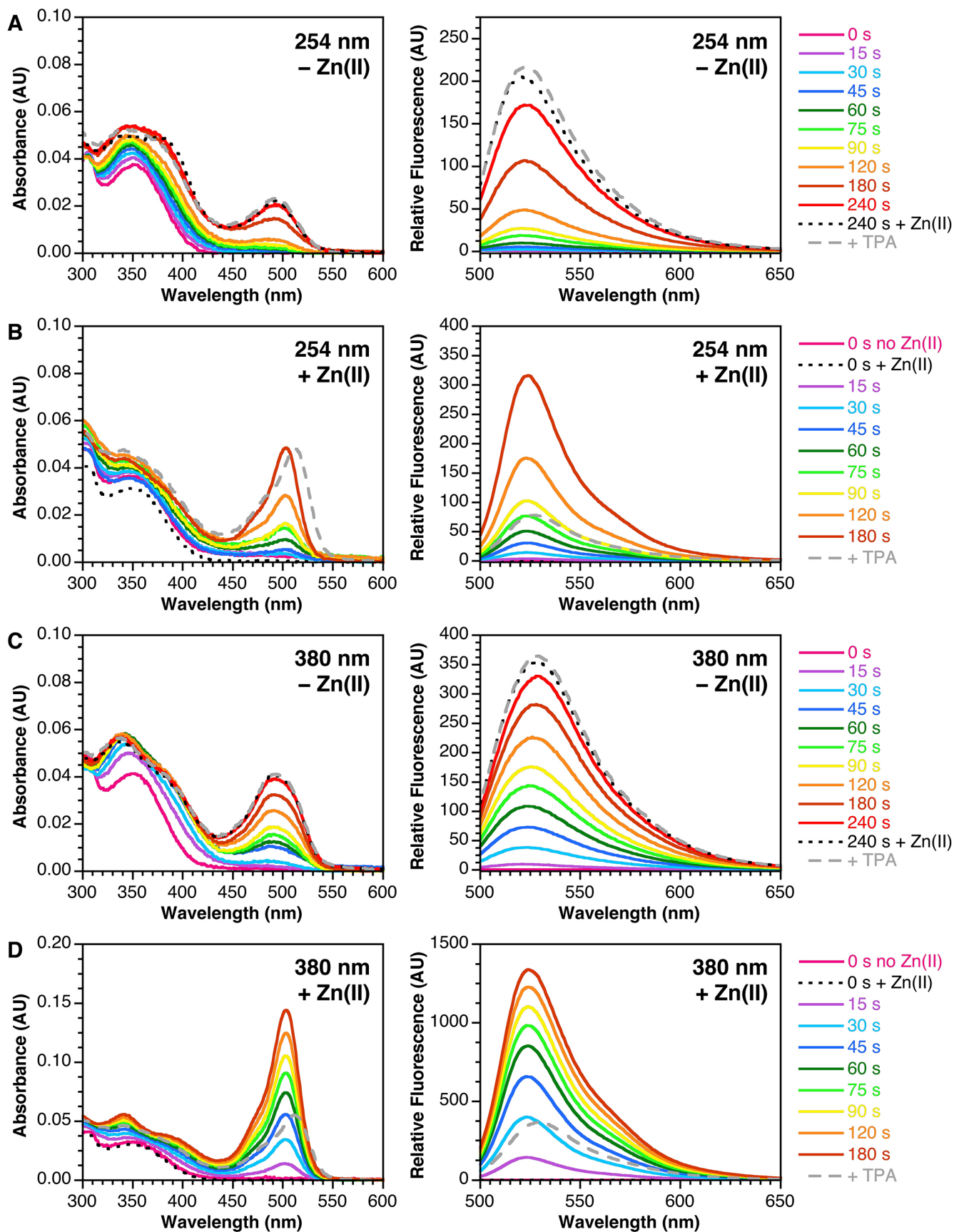
Figure S2. Absorption (left) and fluorescence (right) spectra of **2** after irradiation with 254 nm (A,B) or 380 nm (C,D) light for varying intervals of time in the absence (A,C) and presence (B,D) of ZnCl$_2$, as indicated.
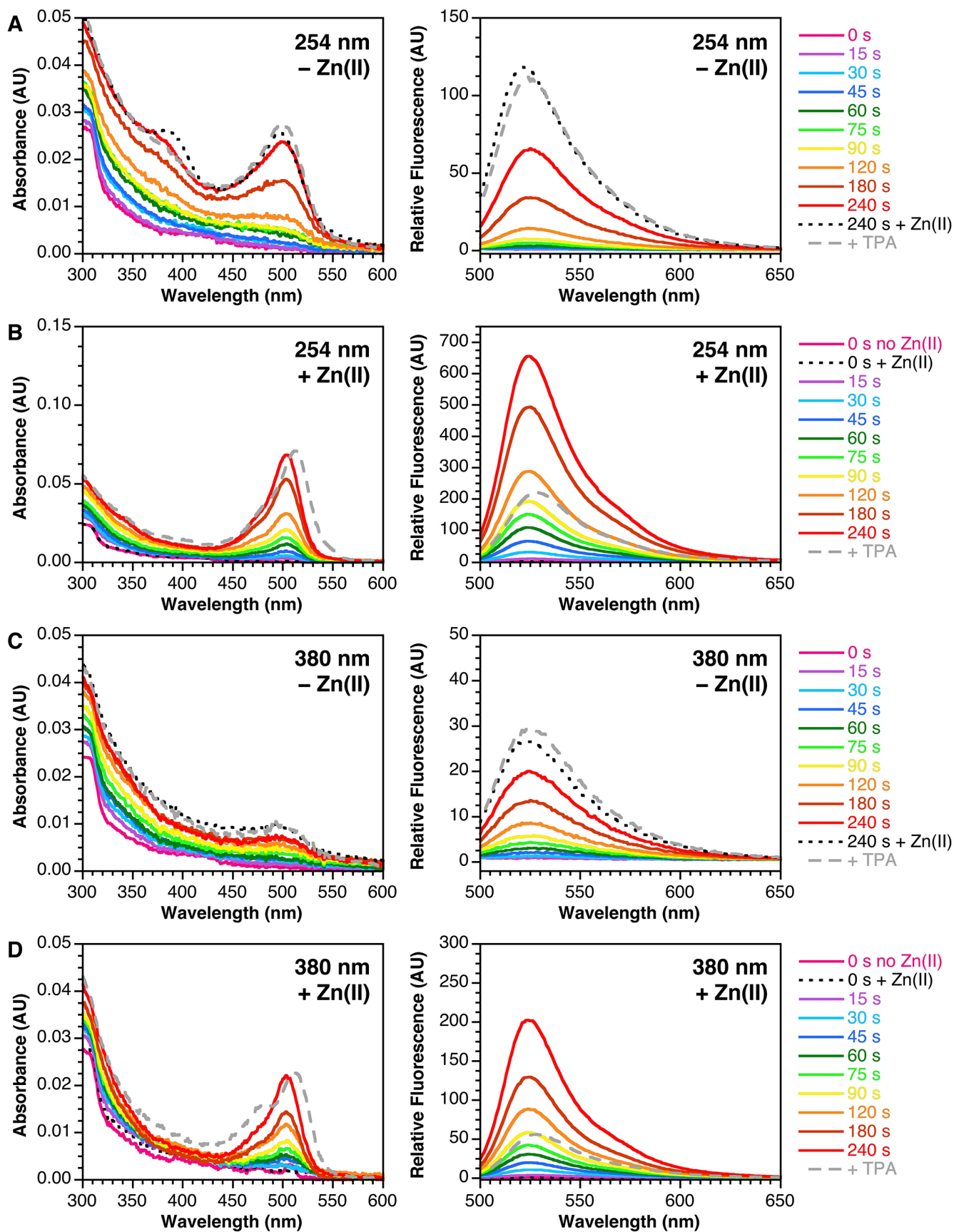
Figure S3. Absorption (left) and fluorescence (right) spectra of **3** after irradiation with 254 nm (A,B) or 380 nm (C,D) light for varying intervals of time in the absence (A,C) and presence (B,D) of ZnCl$_2$, as indicated.

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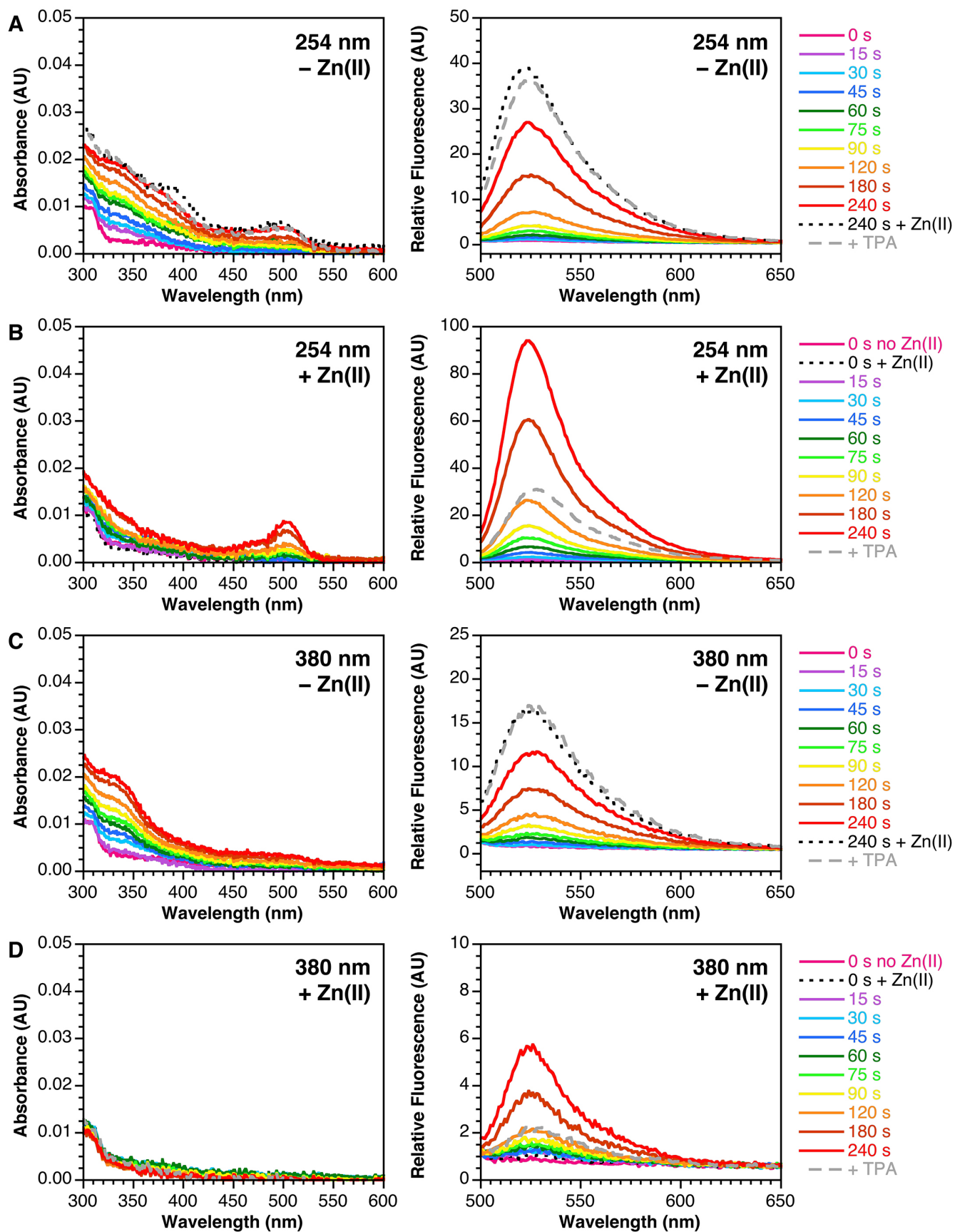
Figure S4. Absorption (left) and fluorescence (right) spectra of **4** after irradiation with 254 nm (A,B) or 380 nm (C,D) light for varying intervals of time in the absence (A,C) and presence (B,D) of ZnCl$_2$, as indicated.

Table S2. Integrated relative fluorescence turn-on after intervals of irradiation of sensors **1**-**4** in the absence of ZnCl$_2$. The corresponding emission spectra are shown in panels A and C (right) in Figures S1-S4.

	254 nm				380 nm			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
0 s	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
15 s	1.1	1.1	1.1	1.1	1.0	5.1	1.1	1.0
30 s	1.4	1.7	1.2	1.2	1.0	18	1.2	1.1
45 s	2.1	3.0	1.5	1.4	1.2	34	1.7	1.2
60 s	3.2	4.9	2.1	1.7	1.3	51	2.2	1.5
75 s	4.6	8.8	3.1	2.1	1.6	68	2.8	1.7
90 s	6.7	12	4.3	2.8	1.9	84	3.6	2.1
120 s	11	22	7.3	4.4	2.4	109	4.9	2.8
180 s	29	48	17	8.7	3.9	137	7.5	4.3
240 s	58	79	31	15	5.6	160	11	6.3
+ Zn(II)	103	92	54	21	9.8	173	14	8.5
+ TPA	79	99	52	20	8.2	177	16	8.9

Table S3. Integrated relative fluorescence turn-on after intervals of irradiation of sensors **1**-**4** in the presence of ZnCl$_2$. The corresponding emission spectra are shown in panels B and D (right) in Figures S1-S4.

	254 nm				380 nm			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
initial	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
0 s + Zn(II)	1.0	1.0	1.2	1.1	0.8	1.1	1.1	1.1
15 s	16	3.1	4.9	1.2	7.8	54	2.3	1.2
30 s	55	9.5	14	1.6	24	152	5.2	1.2
45 s	92	19	28	2.3	44	256	8.6	1.2
60 s	124	31	45	3.3	70	337	13	1.3
75 s	157	46	63	4.7	96	394	17	1.3
90 s	182	62	80	6.6	120	446	23	1.4
120 s	223	106	120	11	162	505	35	1.5
180 s	269	193	208	24	224	560	50	2.1
240 s	295	-	280	36	271	-	78	2.9
+ TPA	65	53	101	14	52	165	24	1.6
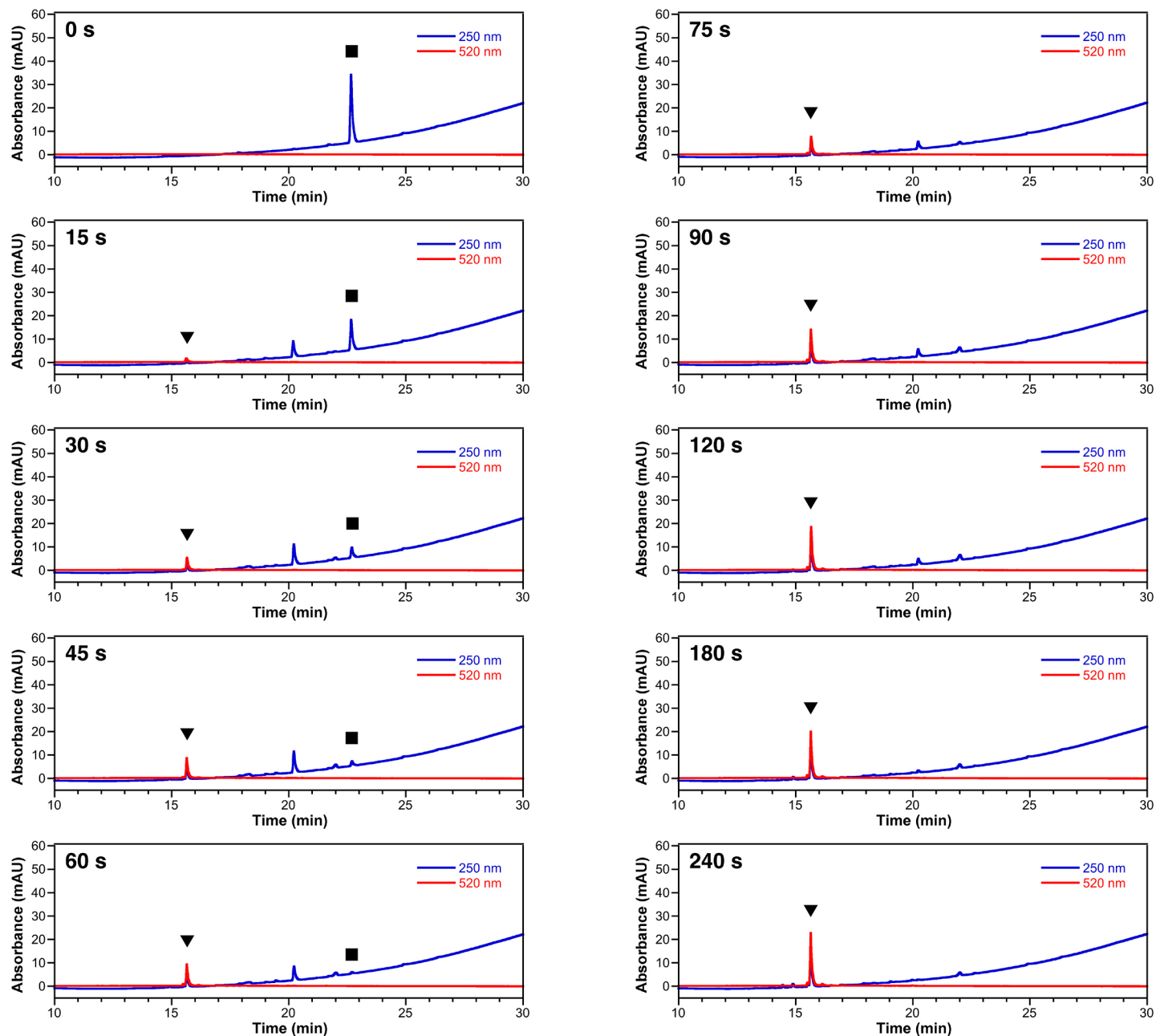
Figure S5. HPLC chromatograms of **1** after irradiation with 254 nm light for varying intervals of time, as indicated, in the presence of 10 μM $ZnCl_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **1** and ZP1 are identified with squares and triangles, respectively. Solvent gradients are given in text.
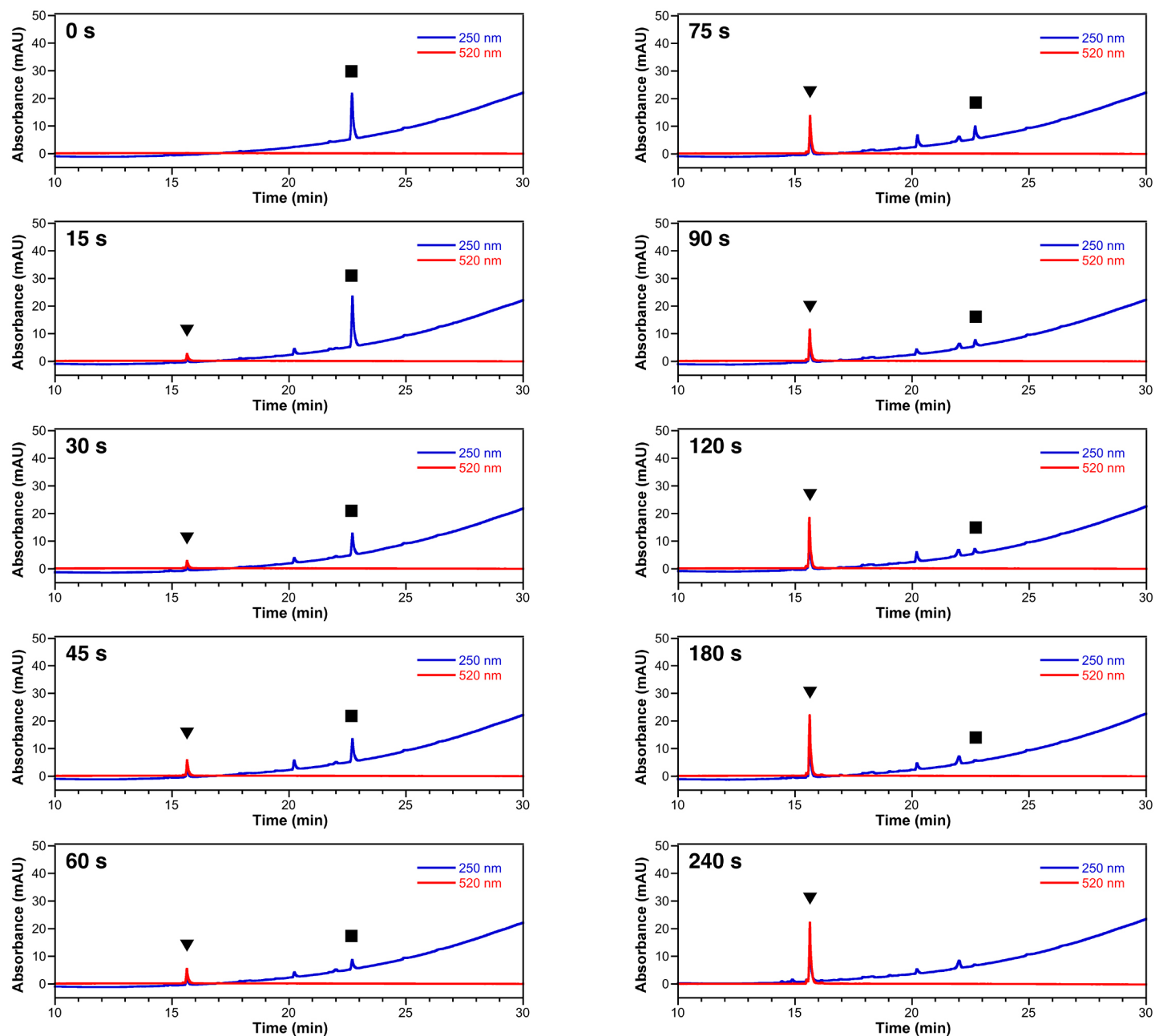
Figure S6. HPLC chromatograms of **1** after irradiation with 380 nm light for varying intervals of time, as indicated, in the presence of 10 µM $ZnCl_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **1** and ZP1 are identified with squares and triangles, respectively. Solvent gradients are given in text.
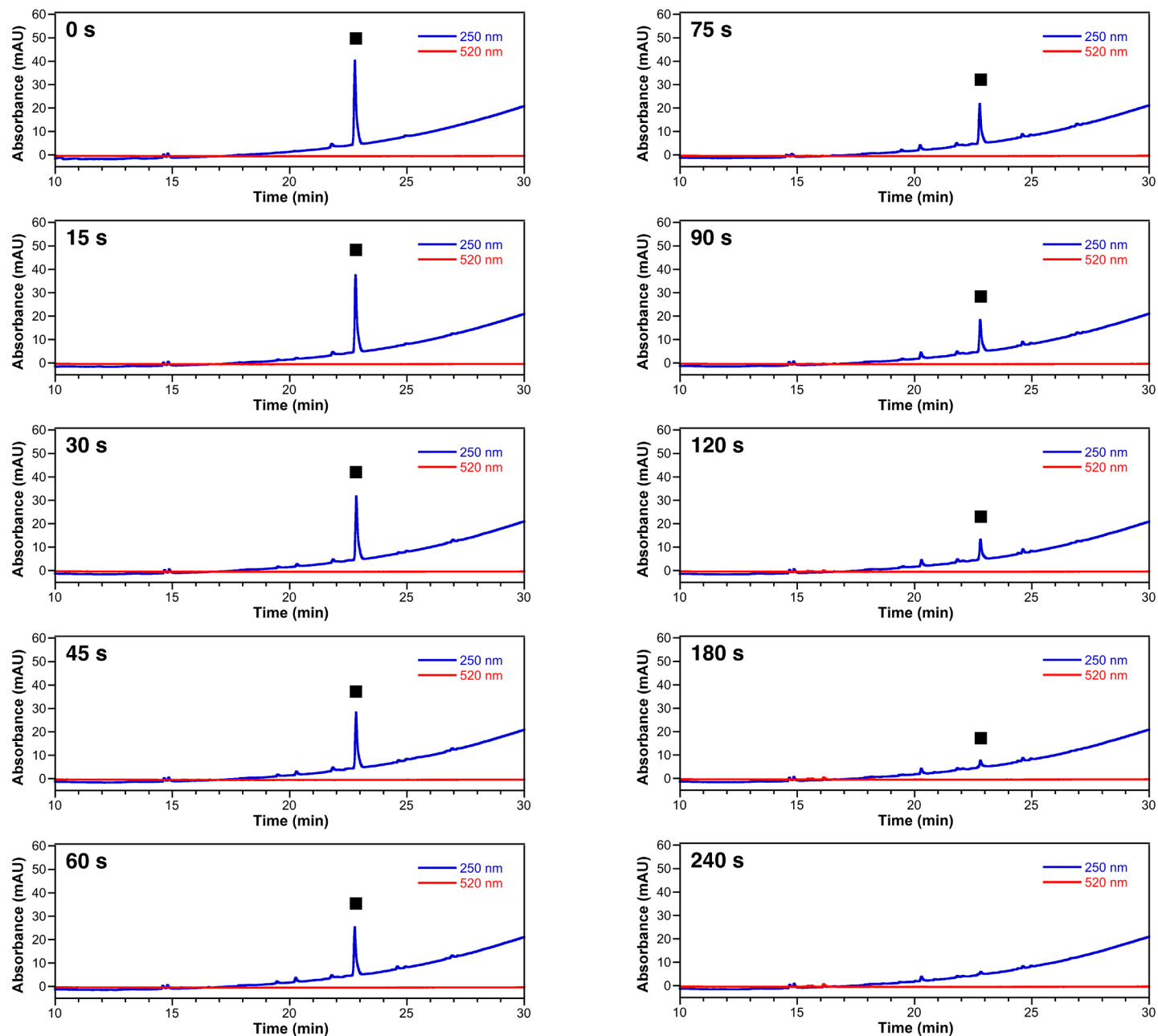
Figure S7. HPLC chromatograms of **1** after irradiation with 254 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **1** are identified with squares. Solvent gradients are given in text.
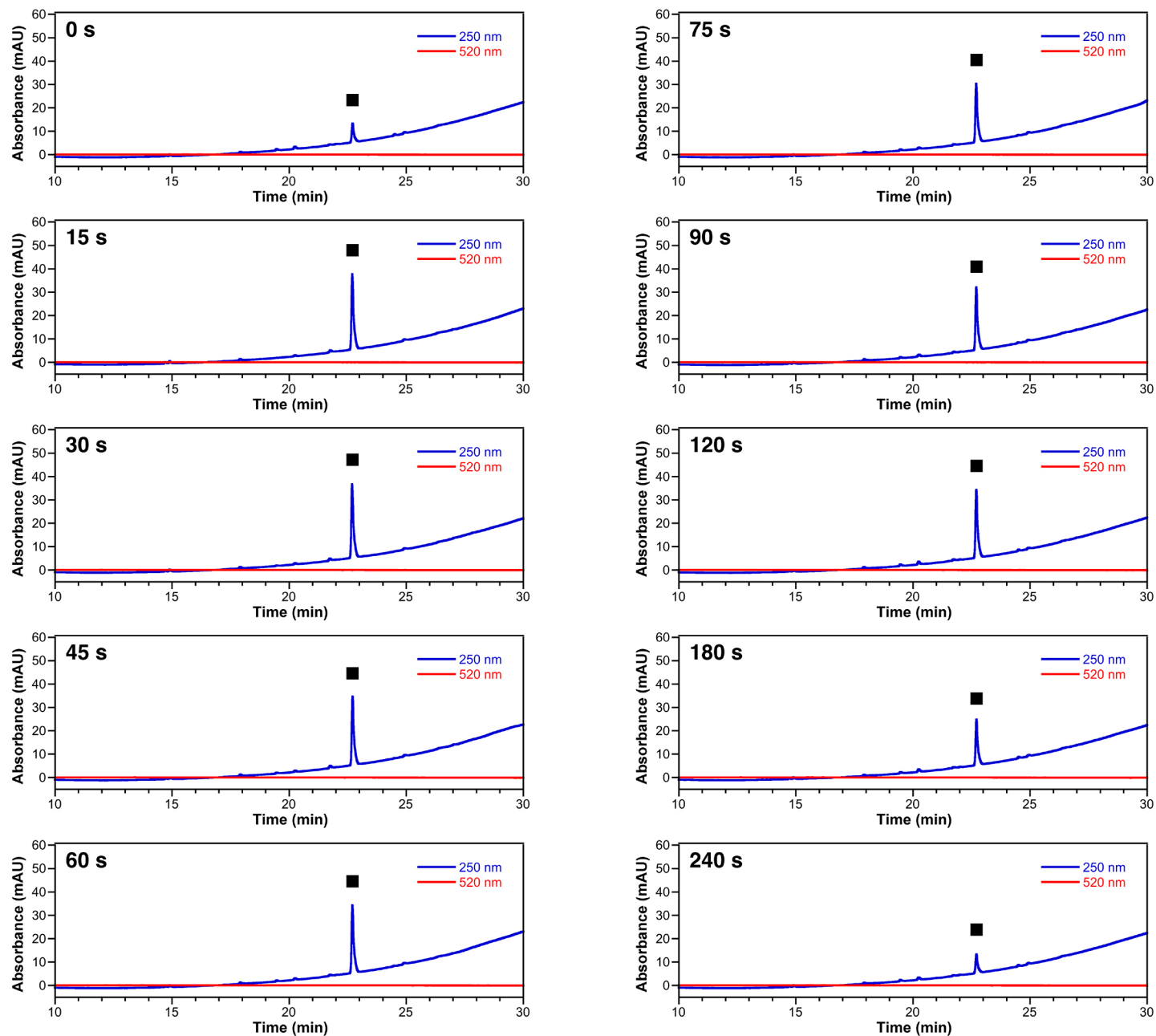
Figure S8. HPLC chromatograms of **1** after irradiation with 380 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **1** are identified with squares. Solvent gradients are given in text.
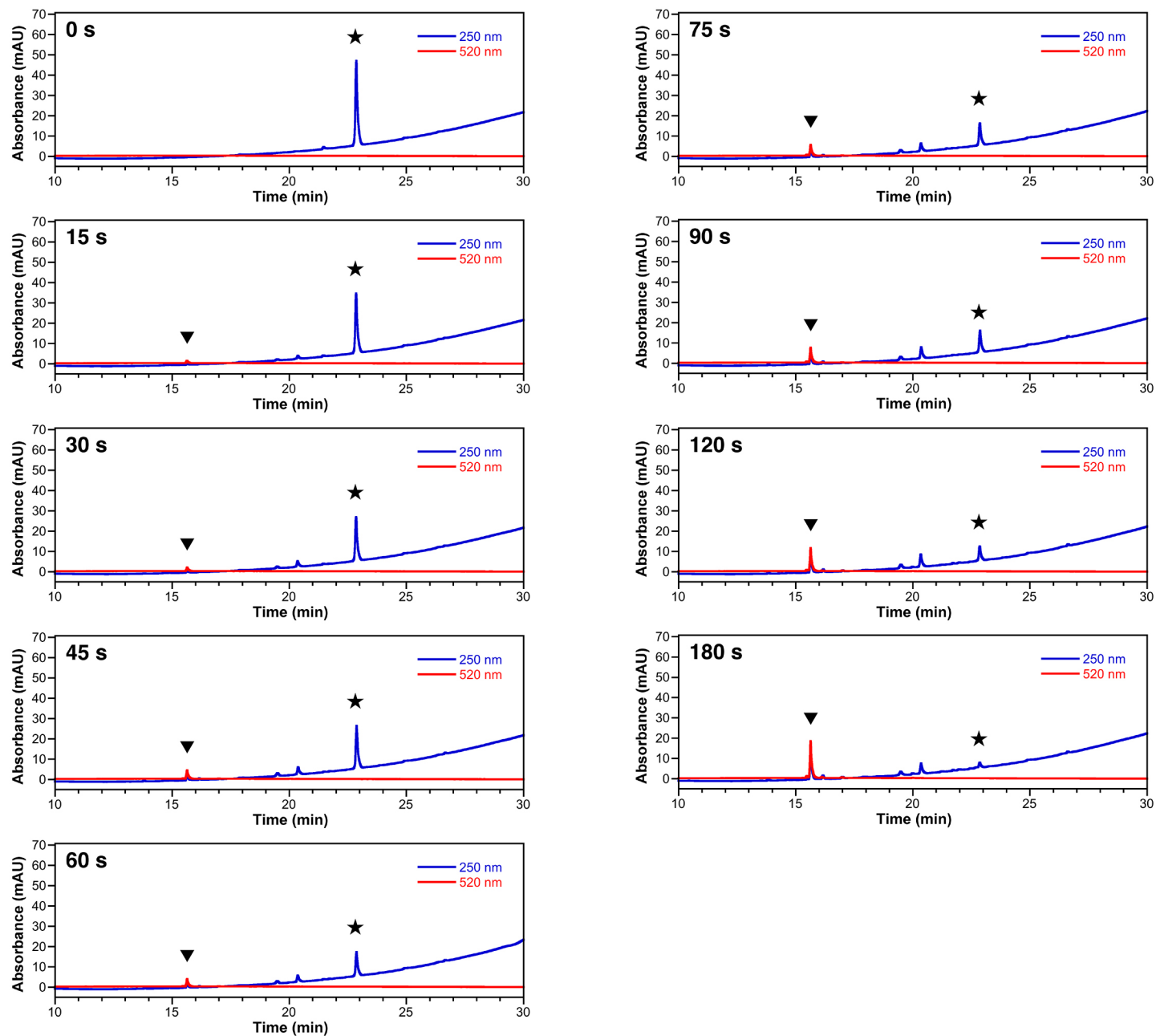
Figure S9. HPLC chromatograms of **2** after irradiation with 254 nm light for varying intervals of time, as indicated, in the presence of 10 μM $ZnCl_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **2** and ZP1 are identified with stars and triangles, respectively. Solvent gradients are given in text.
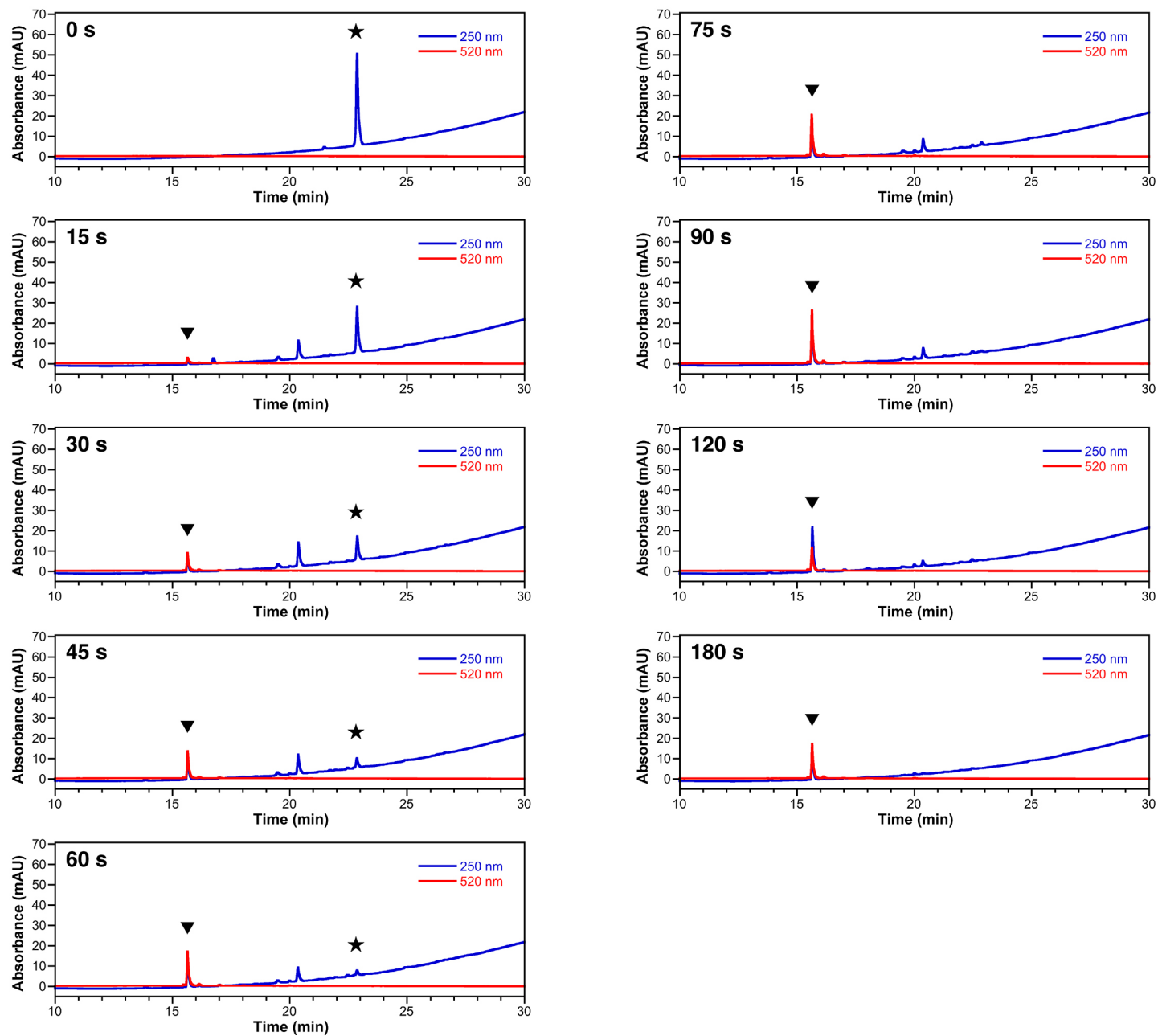
Figure S10. HPLC chromatograms of **2** after irradiation with 380 nm light for varying intervals of time, as indicated, in the presence of 10 μM ZnCl$_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **2** and ZP1 are identified with stars and triangles, respectively. Solvent gradients are given in text.
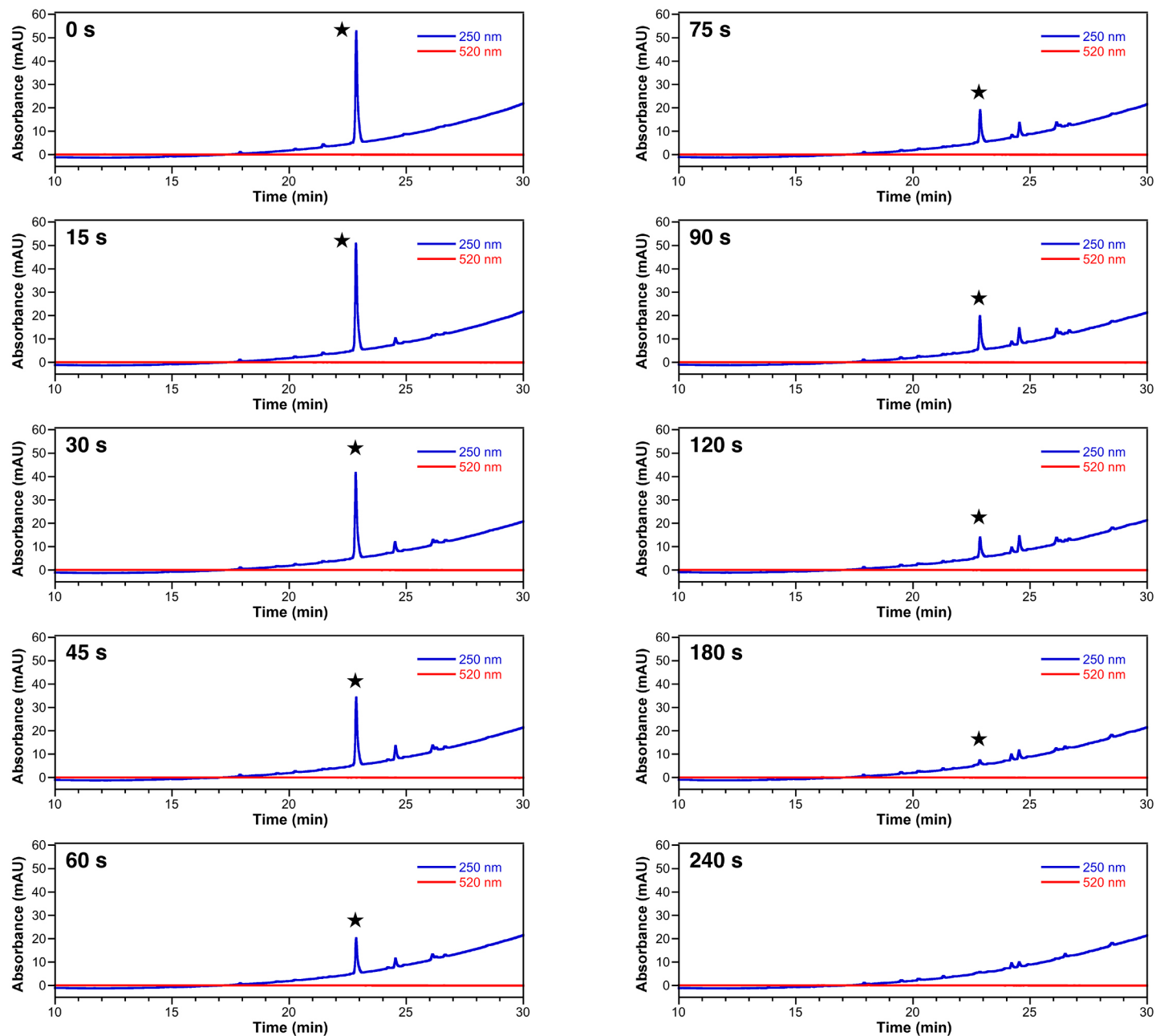
Figure S11. HPLC chromatograms of **2** after irradiation with 254 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **2** are identified with stars. Solvent gradients are given in text.
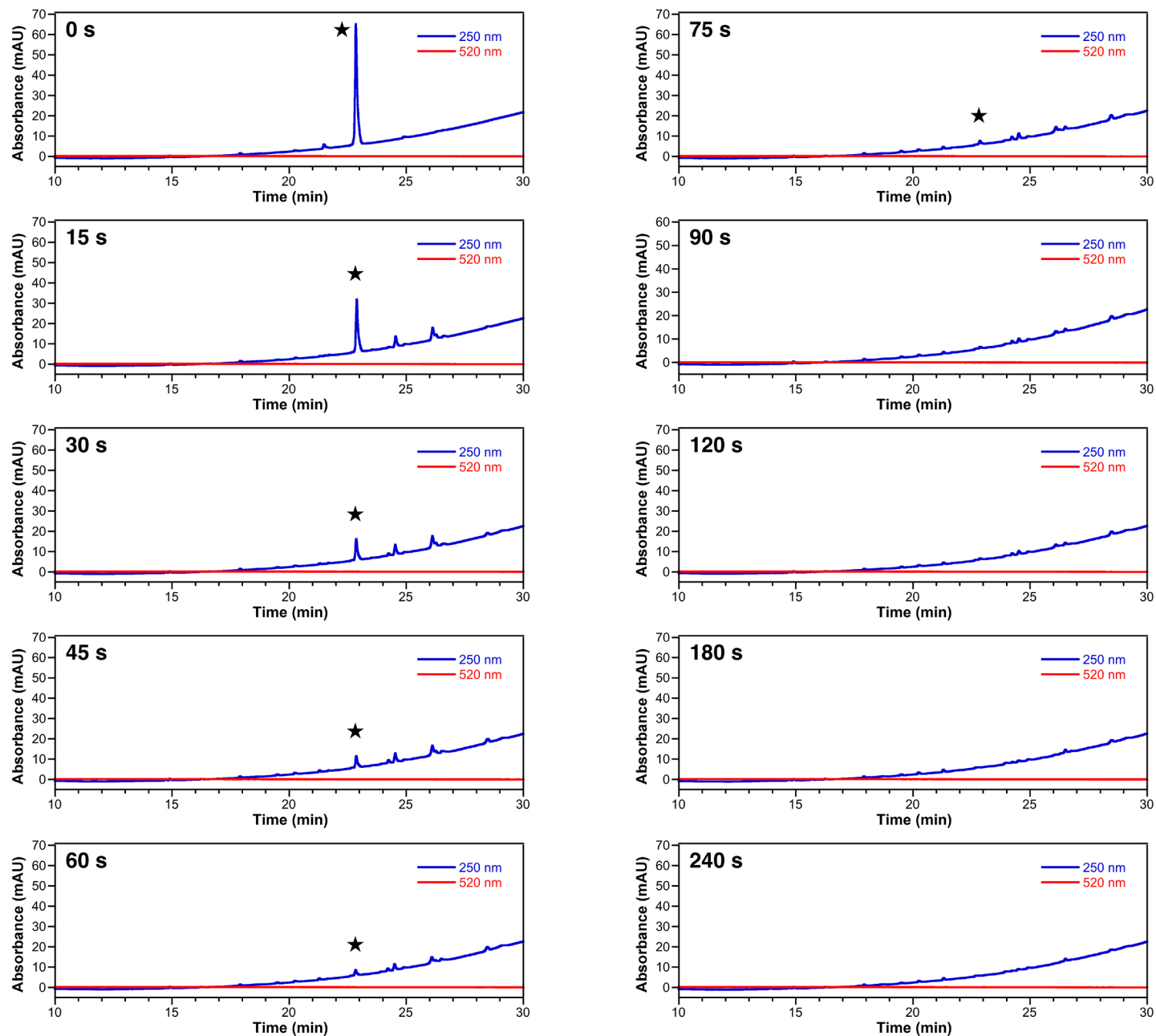
Figure S12. HPLC chromatograms of **2** after irradiation with 380 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **2** are identified with stars. Solvent gradients are given in text.

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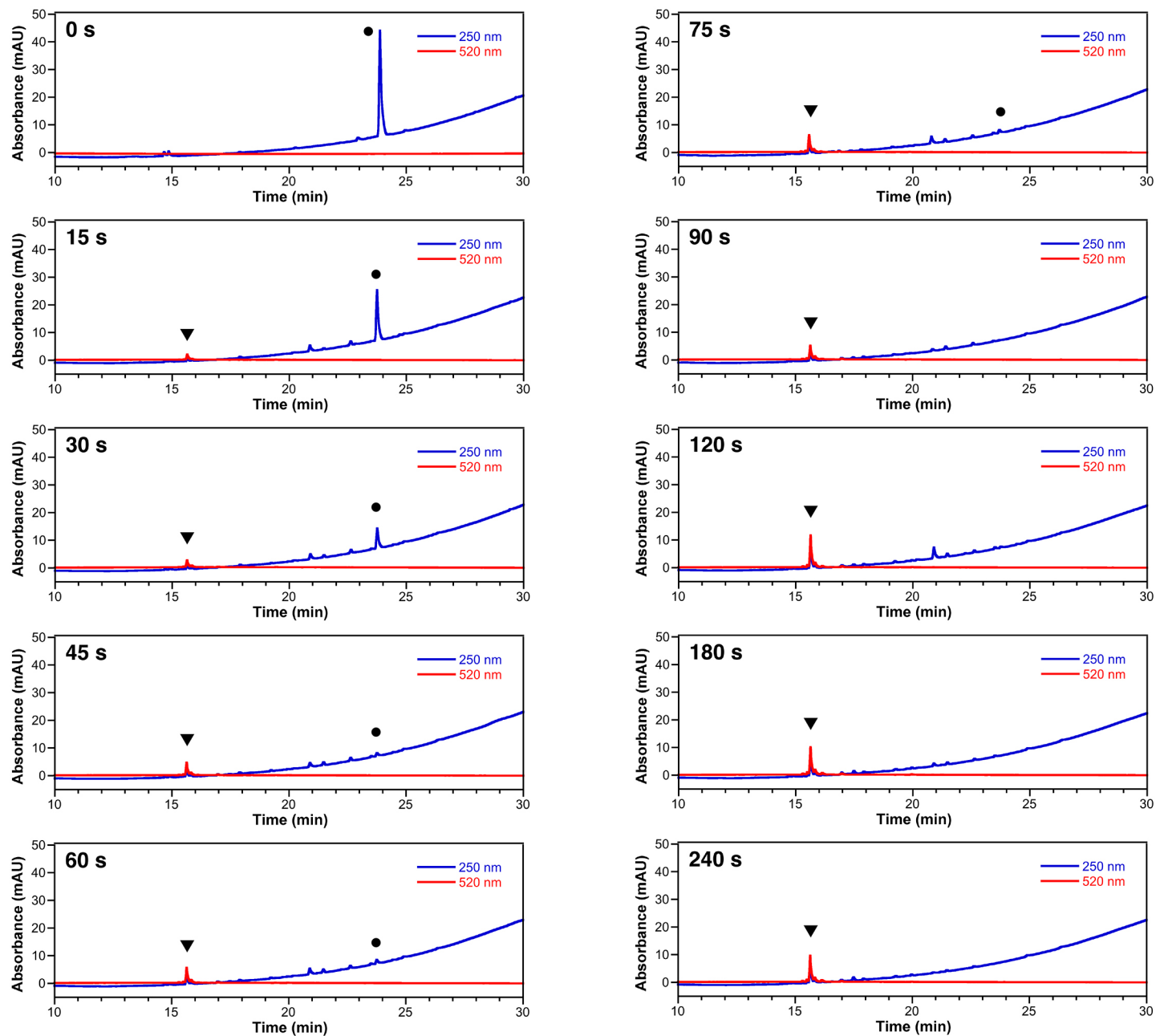
Figure S13. HPLC chromatograms of **3** after irradiation with 254 nm light for varying intervals of time, as indicated, in the presence of 10 μM $ZnCl_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **3** and ZP1 are identified with circles and triangles, respectively. Solvent gradients are given in text.
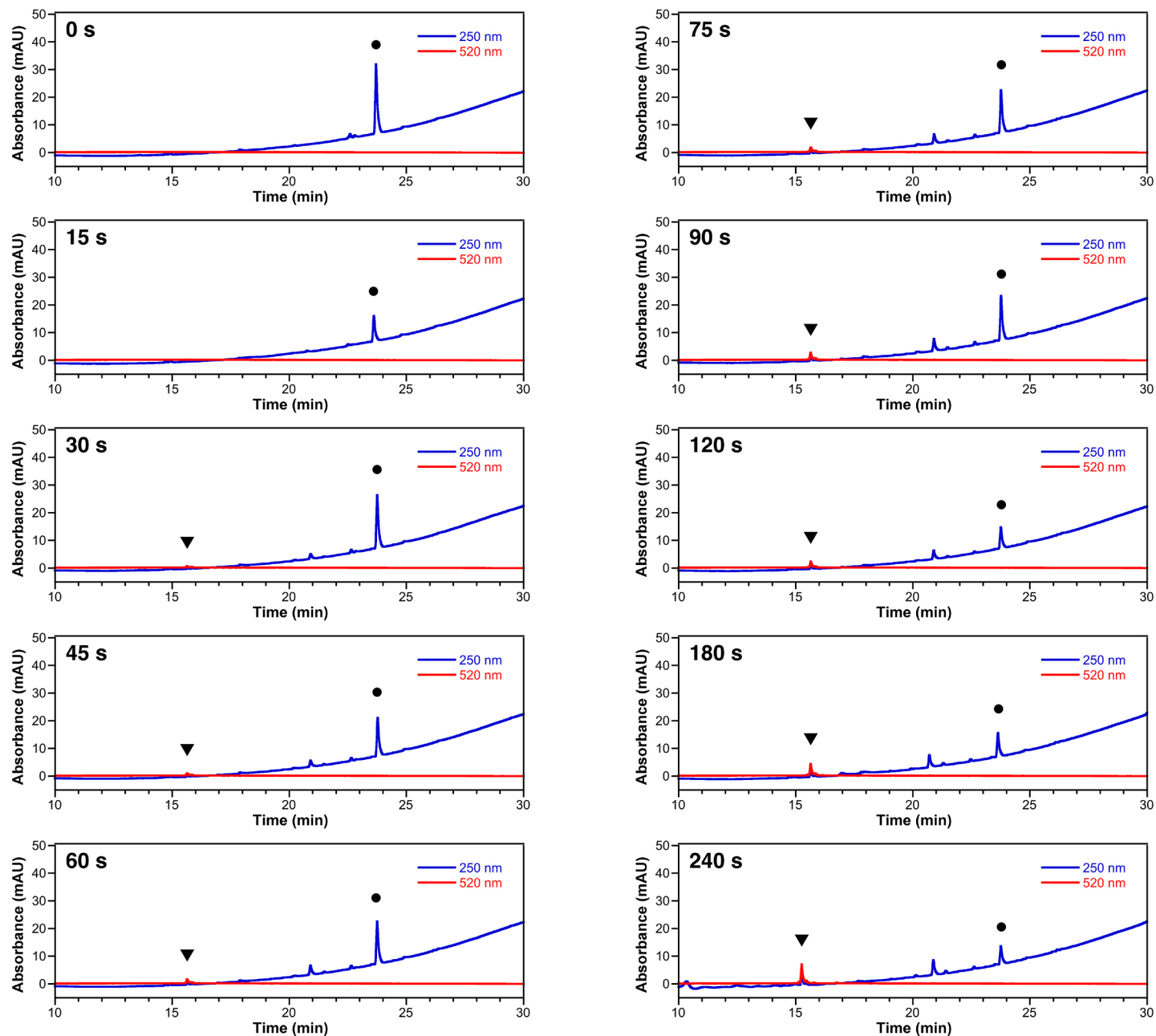
Figure S14. HPLC chromatograms of **3** after irradiation with 380 nm light for varying intervals of time, as indicated, in the presence of 10 μM ZnCl₂. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **3** and ZP1 are identified with circles and triangles, respectively. Solvent gradients are given in text.
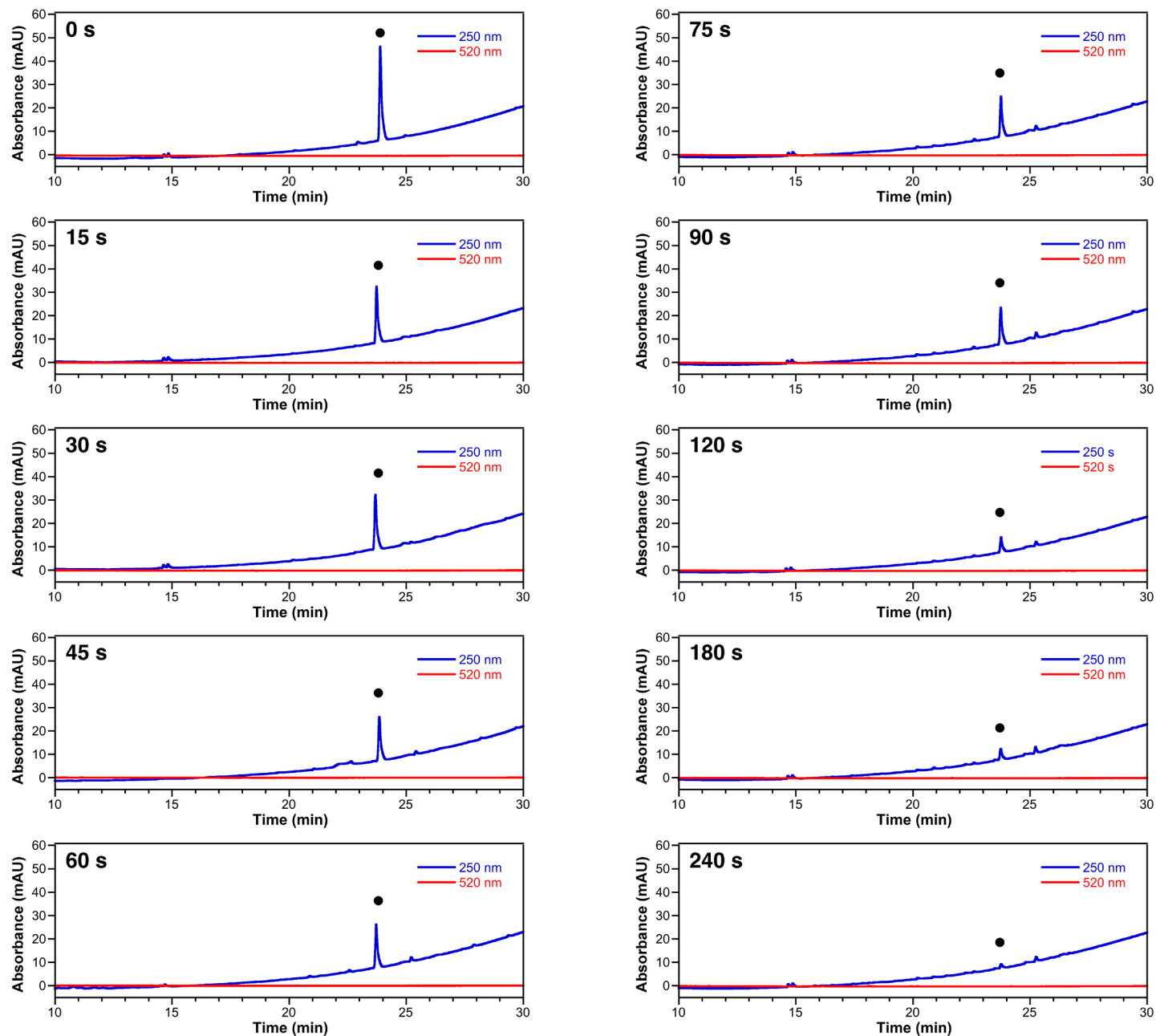
Figure S15. HPLC chromatograms of **3** after irradiation with 254 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **3** are identified with circles. Solvent gradients are given in text.
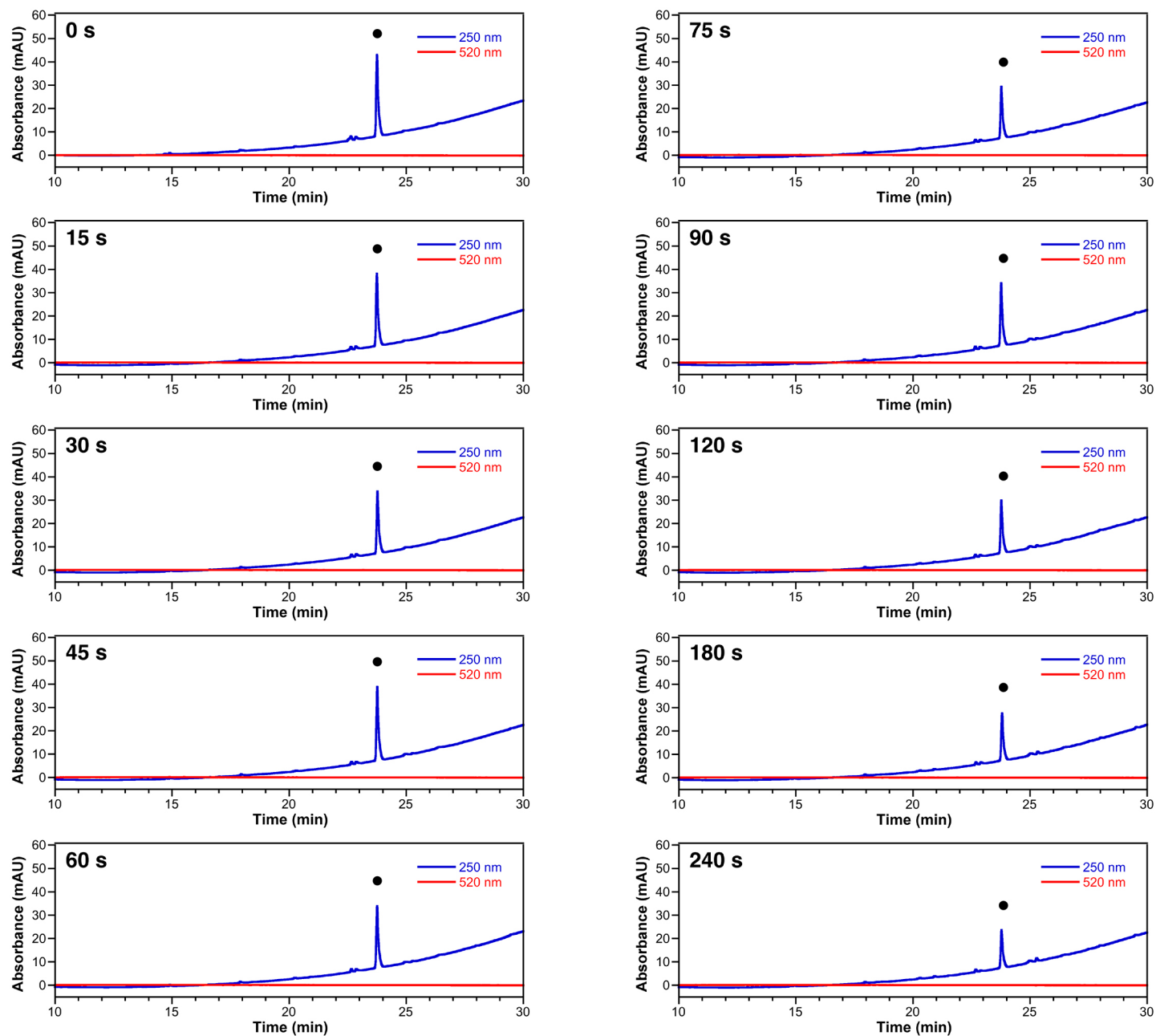
Figure S16. HPLC chromatograms of **3** after irradiation with 380 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **3** are identified with circles. Solvent gradients are given in text.
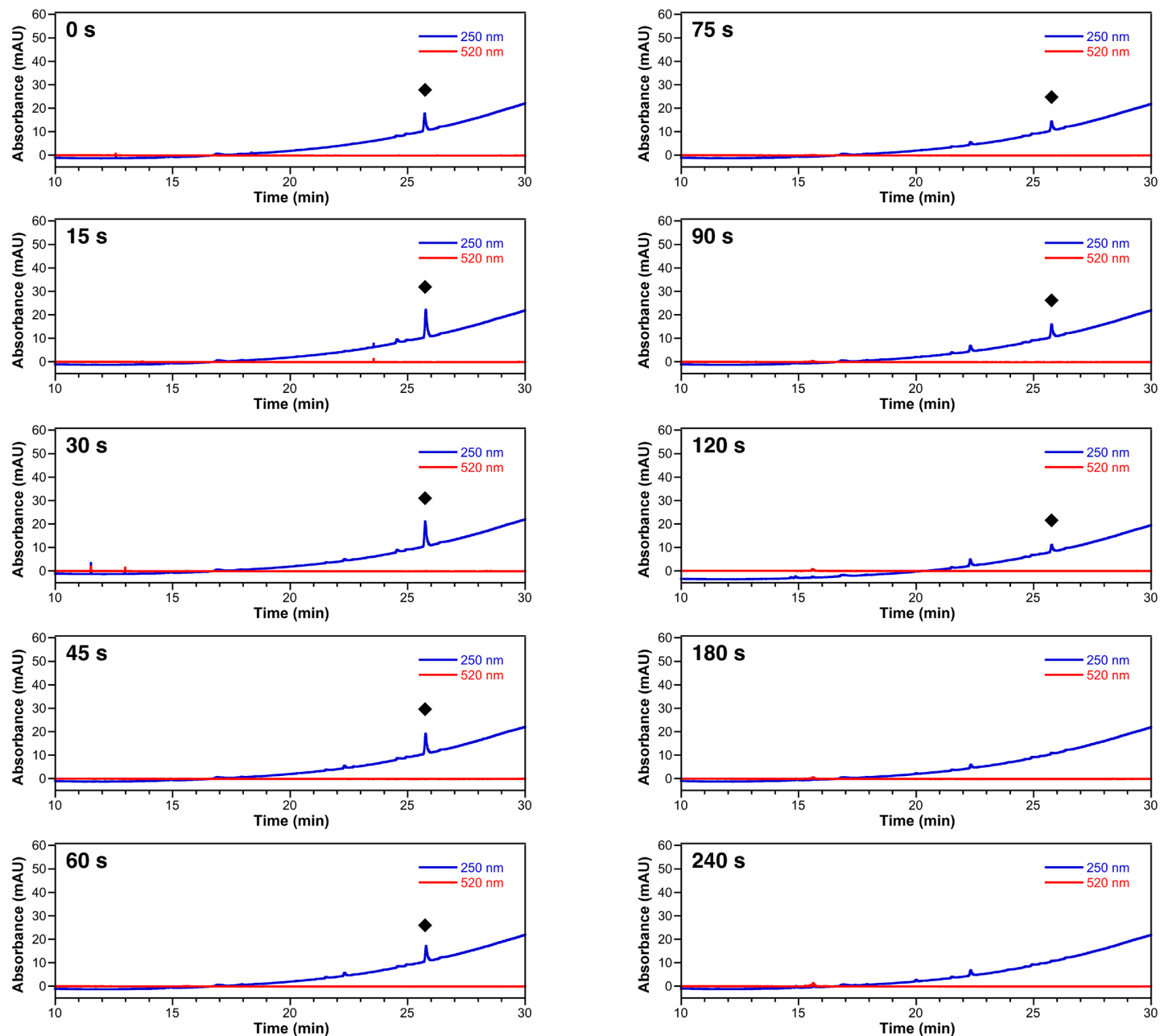
Figure S17. HPLC chromatograms of **4** after irradiation with 254 nm light for varying intervals of time, as indicated, in the presence of 10 μM ZnCl$_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **4** are identified with diamonds. Solvent gradients are given in text.
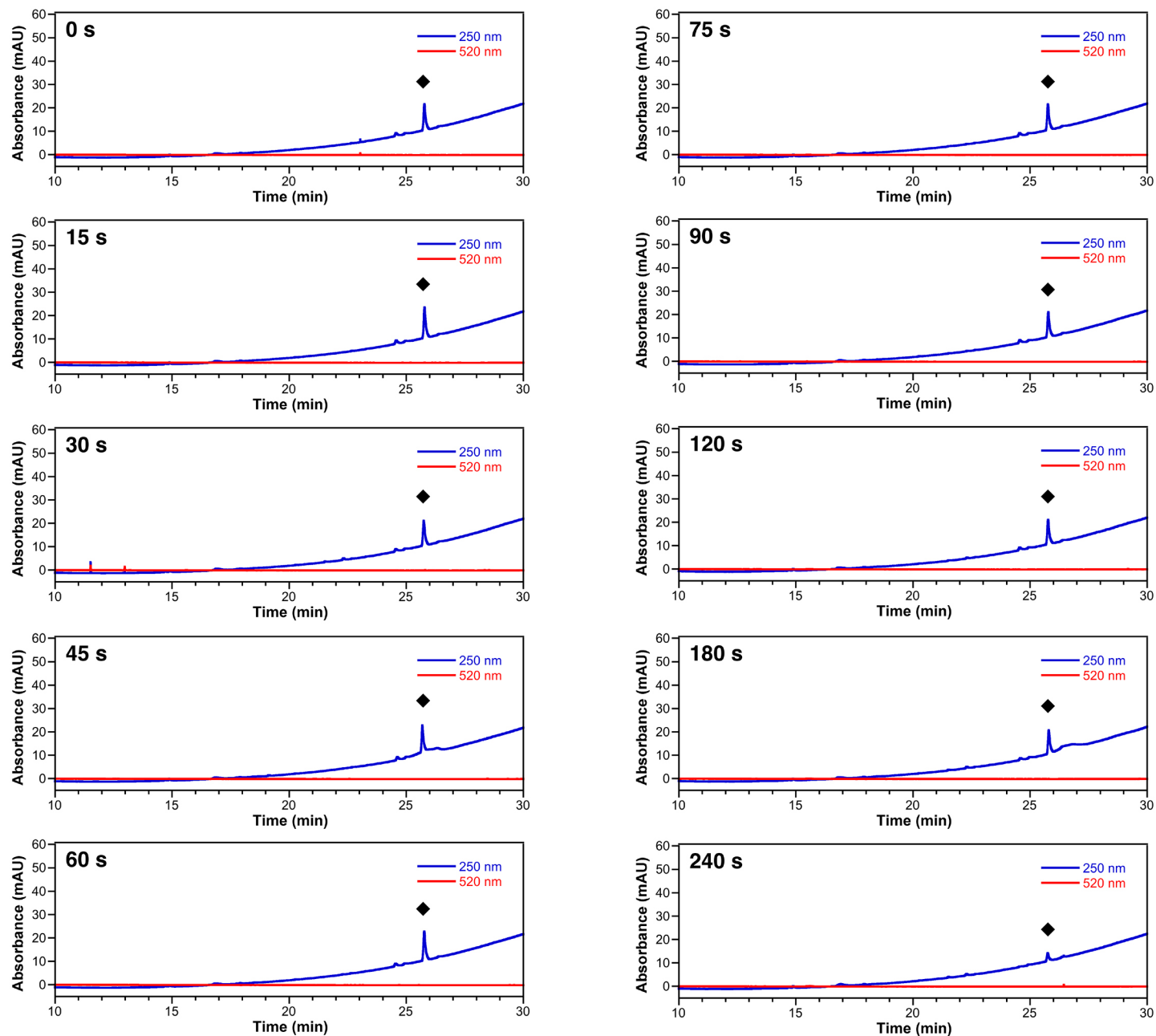
Figure S18. HPLC chromatograms of **4** after irradiation with 380 nm light for varying intervals of time, as indicated, in the presence of 10 μM $ZnCl_2$. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **4** are identified with diamonds. Solvent gradients are given in text.
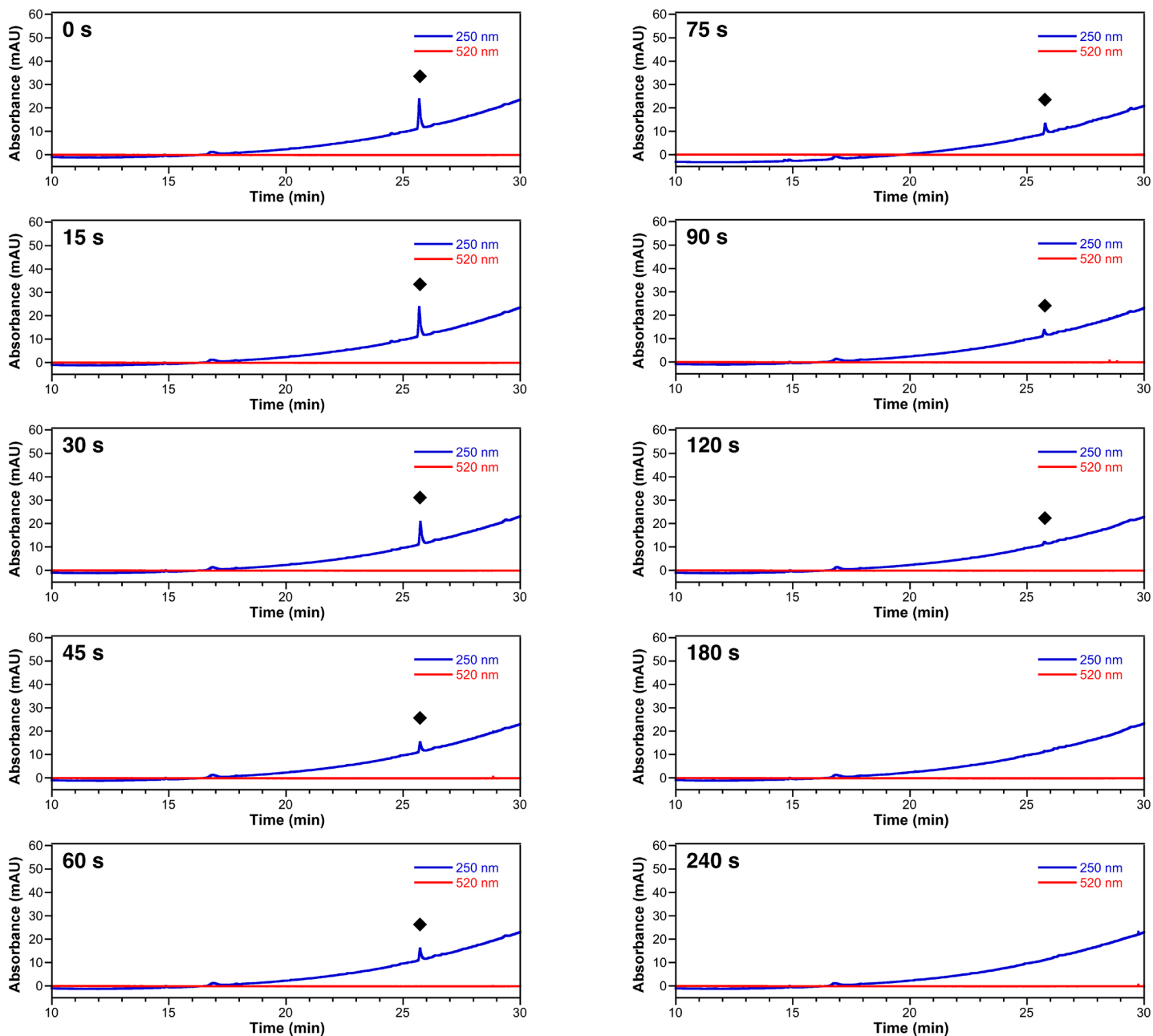
Figure S19. HPLC chromatograms of **4** after irradiation with 254 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **4** are identified with diamonds. Solvent gradients are given in text.
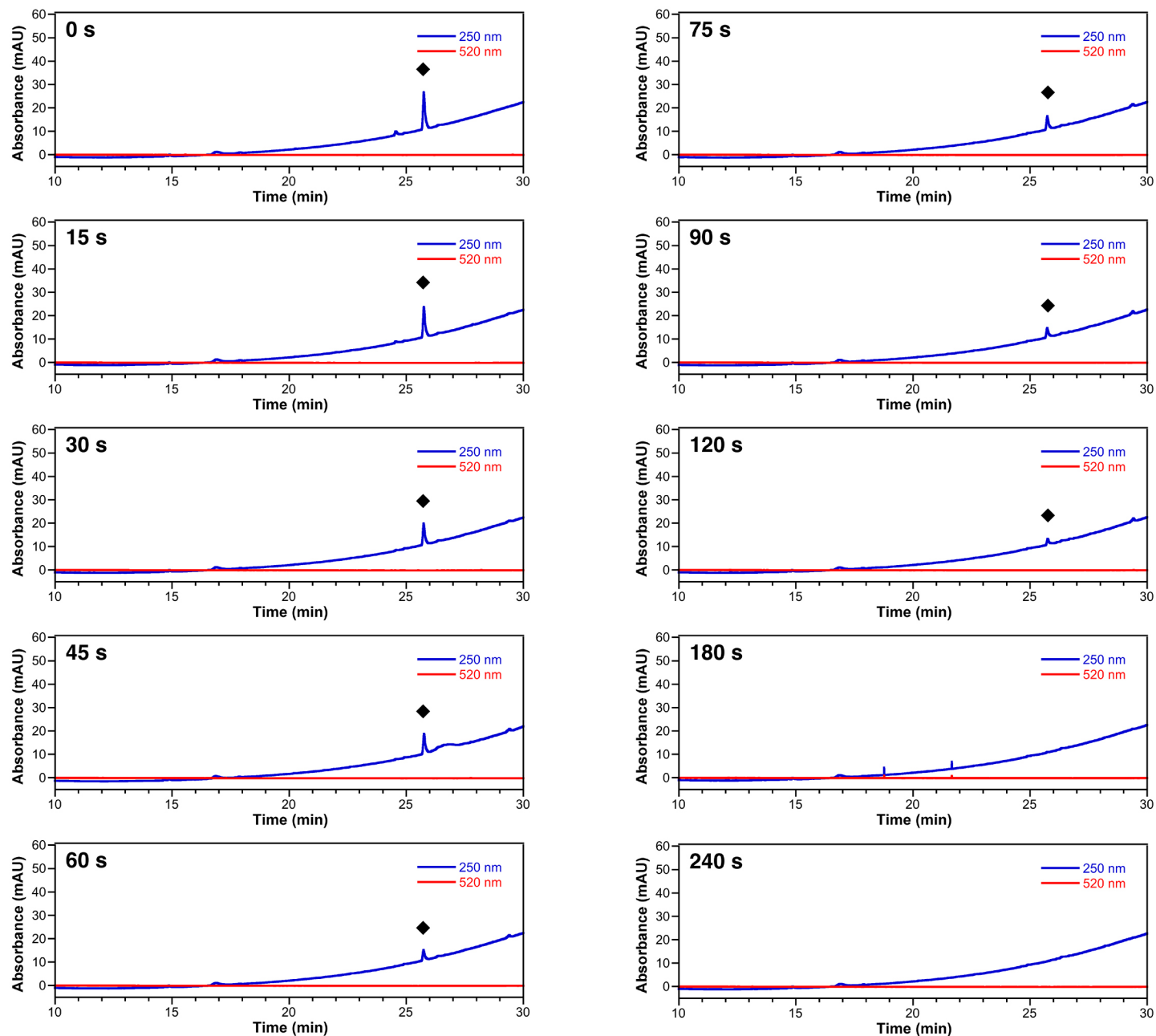
Figure S20. HPLC chromatograms of **4** after irradiation with 380 nm light for varying intervals of time, as indicated. Absorbance monitored at 250 nm (blue) and 520 nm (red). Peaks corresponding to **4** are identified with diamonds. Solvent gradients are given in text.

pH Dependence of the Zinc Response.

The fluorescence of **3** was measured in buffers of various pH values. The following buffers were prepared and treated with Chelex® resin according to the manufacturer's protocols: 50 mM potassium acetate, 100 mM KCl, pH 4.0; 50 mM potassium acetate, 100 mM KCl, pH 5.0; 50 mM PIPES, 100 mM KCl, pH 6.0; 50 mM PIPES, 100 mM KCl, pH 7.0; 50 mM Tris, 100 mM KCl, pH 8.0. A typical sample consisted of 1999 µL buffer and 1 µL sensor (final conc. 0.5 µM). Samples were allowed to stir for ~1 min. The fluorescence emission spectrum from 500 – 650 nm of each sample was recorded with an excitation wavelength of 490 nm. The step size was 1 nm. The integration time was 0.2 s. The slit widths were 3 nm and the temperature was 298 K. Samples were irradiated for 60 s with 254 nm light. The fluorescence of each sample was measured again. Samples were also irradiated in the presence of zinc, in which case a 2.0 µL aliquot of $ZnCl_2$ (final conc. 20 µM) was added to each sample after the initial measurement, but before the 60 s irradiation. All experiments were conducted in triplicate. The integrated emission spectra of the sensor before (F_0) and after (F) irradiation were used to calculate the fluorescence turn-on.
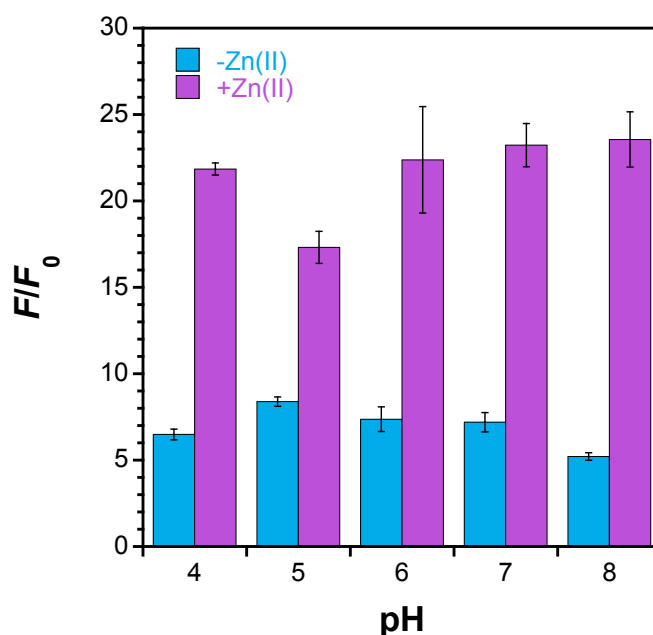
Figure S21. Integrated fluorescence turn-on of **3** in buffers of various pH values after 60 s irradiation with 254 nm light in the presence (purple) and absence (blue) of 20 µM $ZnCl_2$, as described in the text. Error bars are standard error.

Metal Selectivity Studies.

Aqueous stock solutions of metal chloride salts were analytically prepared at the following concentrations: 0.80 M $CaCl_2$ and $MgCl_2$; 0.020 M $CdCl_2$, $CoCl_2$, $CuCl_2$, $MnCl_2$, $NiCl_2$, and $ZnCl_2$. A fresh stock solution of **3** (1.0 mM) in DMSO was also prepared. The buffer was 50 mM PIPES, 100 mM KCl, pH 7.0. Samples were prepared in triplicate and consisted of buffer (1999 µL) and sensor (1.0 µL, final conc. 0.5 µM). Samples were stirred for ~1 min. The fluorescence of each sample was recorded with an excitation wavelength of 490 nm. Emission spectra were collected from 500 – 650 nm. An aliquot (2.0 µL) of the appropriate metal chloride stock solution was added for a final concentration of 20 or 800 µM metal ion. After 1 min of stirring, fluorescence spectra were recorded. Samples were irradiated for 60 s at 254 nm and fluorescence measurements were obtained. For all measurements, the step size was 1 nm. The integration time was 0.2 s. The excitation and emission monochromators were gated with 3 nm slits. The temperature was 298 K. The integrated emission spectra of the sensor before (F_0) and after (F) irradiation were used to calculate the fluorescence turn-on. All experiments were conducted in triplicate.
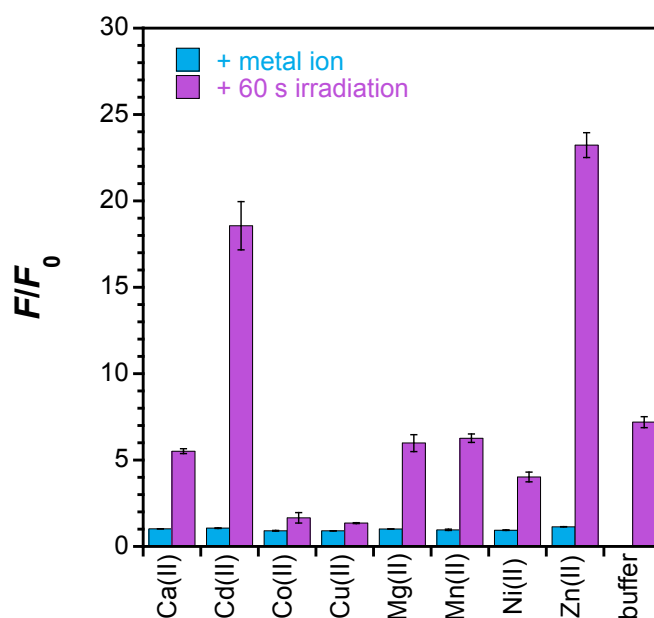
Figure S22. Integrated fluorescence turn-on of **3** upon addition of selected metal chloride salts (blue bars) and after subsequent irradiation with 254 nm light for 60 s (purple bars), as described in the text. Error bars are standard error.

Cell Culture and Imaging Experiments.

HeLa cells (ATTC; CCL-2) were cultured in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% heat-deactivated fetal bovine serum (FBS) and 1% penicillin/streptomycin. The cultures were incubated in a humidified atmosphere with 5% CO_2 at 37 °C. Approximately 48 h before imaging, HeLa cells were plated in glass bottom imaging dishes coated with poly-D-lysine (MatTek; 35 mm dishes, No. 1.5 coverslip, 14 mm glass diameter).

Concentrated (1 mM) stock solutions of the sensor in DMSO were prepared and stored as frozen aliquots at −80 °C. A solution of 20% Pluronic® F-127 (Sigma-Aldrich) in DMSO (w/v) was prepared and stored at room temperature. Immediately before each imaging experiment, a 1 µL aliquot of the sensor stock solution was combined with an equal volume of the Pluronic® F-127 stock solution and mixed gently in a microcentrifuge tube. Dye free DMEM (1 mL) was added to the tube and the resulting solution was mixed thoroughly by pipetting up and down several times. The medium in the imaging dishes was replaced with this solution and the dishes were returned to the incubator. After 15 min, the solution was removed and the cells were washed with phosphate buffered saline (PBS: 0.144 g·L^{-1} KH_2PO_4, 0.795 g·L^{-1} Na_2HPO_4, 9.00 g·L^{-1} NaCl; 2 mL × 3). A fresh portion of dye free DMEM (1 mL) was added to the dish and the cells were imaged.

Imaging was performed using a Zeiss Axiovert 200M inverted epifluorescence microscope fitted with a Hamamatsu EM-CCD digital camera C9100, a MS200 XY Piezo Z stage, and a 63× oil immersion objective. The light source was an X-Cite 120 metal halide lamp (EXFO). Zeiss standard filter sets 49 (excitation G 365 nm; beamsplitter FT 395 nm; emission BP 445/50 nm) and 38 HE (excitation BP 470/40 nm; beamsplitter FT 495 nm; emission BP 525/50 nm) were used to activate the caged sensors and visualize ZP1, respectively. The microscope was operated with Volocity software (version 6.01). Cells were maintained at 37 °C and under a humidified 5% CO_2 atmosphere with an on-stage incubator. Regions of interest (ROI) were identified using differential interference contrast (DIC) microscopy. DIC images were acquired (14 ms exposure time) of each ROI. Fluorescence images were acquired with the Zeiss 38 HE standard green channel filter set and a 300 ms exposure time. The cells were irradiated with UV light using the Zeiss standard filter set 49 for 15 s and the lowest intensity setting for the EXFO lamp. After a 1 min resting period, images of the green channel fluorescence were recorded with a 300 ms exposure time. A solution of warm dye free DMEM (1 mL; ~37 °C) containing 20 μM $ZnCl_2$ and 40 μM sodium pyrithione was gently added to the imaging dish and the cells were allowed to incubate on the microscope stage for 5 min. An additional set of fluorescence images was acquired. A solution of tris(2-pyridylmethyl)amine (TPA; 2 μL of a 20 mM stock solution in DMSO) in warm dye free DMEM (1 mL, 37 °C) was carefully added to the imaging dish and the cells were allowed to incubate on the microscope stage for 10 min. A final series of fluorescence images was acquired. Microscopy data were analyzed in ImageJ (version 1.50b) to quantify the average background corrected fluorescence intensity of each

cell in each ROI. These experiments were repeated multiple times using cells from at least two separate passages.

For some experiments, zinc pyrithione was added before irradiation with UV light using a procedure analogous to that described above. Here, the zinc pyrithione stock solution in DMEM (1 mL) was added before the plate was transferred to the microscope stage. After a 5 min incubation period, the medium was replaced with fresh dye free DMEM and cells were imaged as described above. In some cases, the zinc pyrithione solution was added before the cells were treated with the sensor. In these experiments, the zinc pyrithione solution was removed from the cells after a 5 min incubation period. A fresh solution of the sensor and Pluronic F-127 was added to the imaging dish and the cells were incubated for 15 min before the medium was replaced with fresh dye free DMEM. The cells were imaged as described above.

In separate experiments, the cells were incubated with the sensor and Pluronic F-127 in the presence of 50 μM $ZnCl_2$ for 15 min prior to imaging using the procedure described above. In some cases, a solution of zinc pyrithione was added to the cells before irradiation. Here, after the medium containing the sensor was removed, the cells were incubated with a fresh solution of zinc pyrithione in DMEM for 5 min. After this medium was replaced with dye free DMEM, the cells were imaged in the usual way.
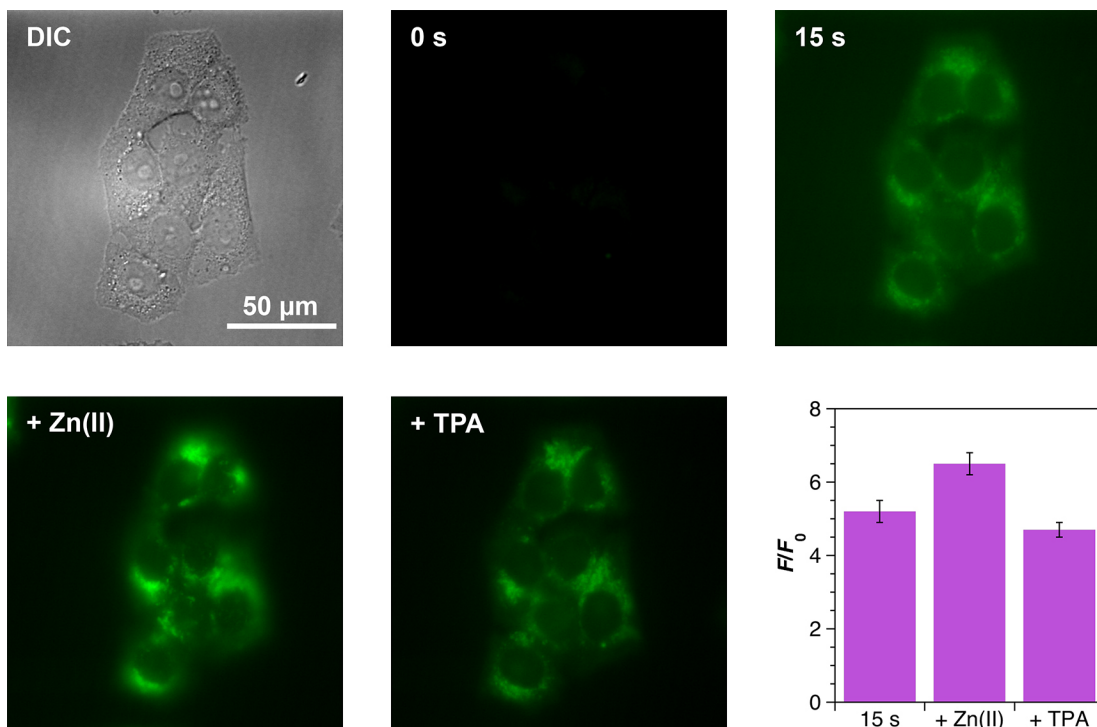
Figure S23. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells treated with 1 µM **3** before and after irradiation with UV light for 15 s and after addition of 10 µM zinc pyrithione and subsequent addition of 13 µM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 51). Error bars are standard error. $p = 1.3 \times 10^{-23}$ (15 s vs. Zn); $p = 2.9 \times 10^{-25}$ (Zn vs. TPA); $p = 4.6 \times 10^{-2}$ (15 s vs. TPA).
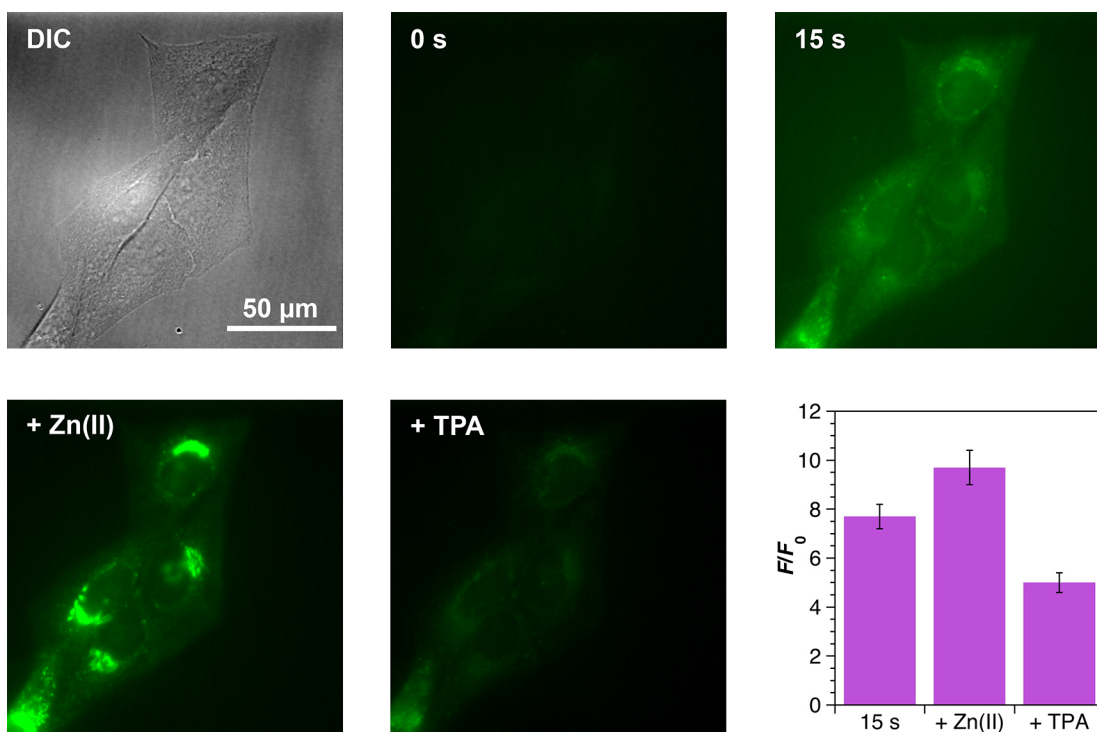
Figure S24. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells treated with 1 µM **1** before and after irradiation with UV light for 15 s and after addition of 10 µM zinc pyrithione and subsequent addition of 13 µM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 52). Error bars are standard error. $p = 4.5 \times 10^{-9}$ (15 s vs. Zn); $p = 8.7 \times 10^{-19}$ (Zn vs. TPA); $p = 1.3 \times 10^{-22}$ (15 s vs. TPA)

S37
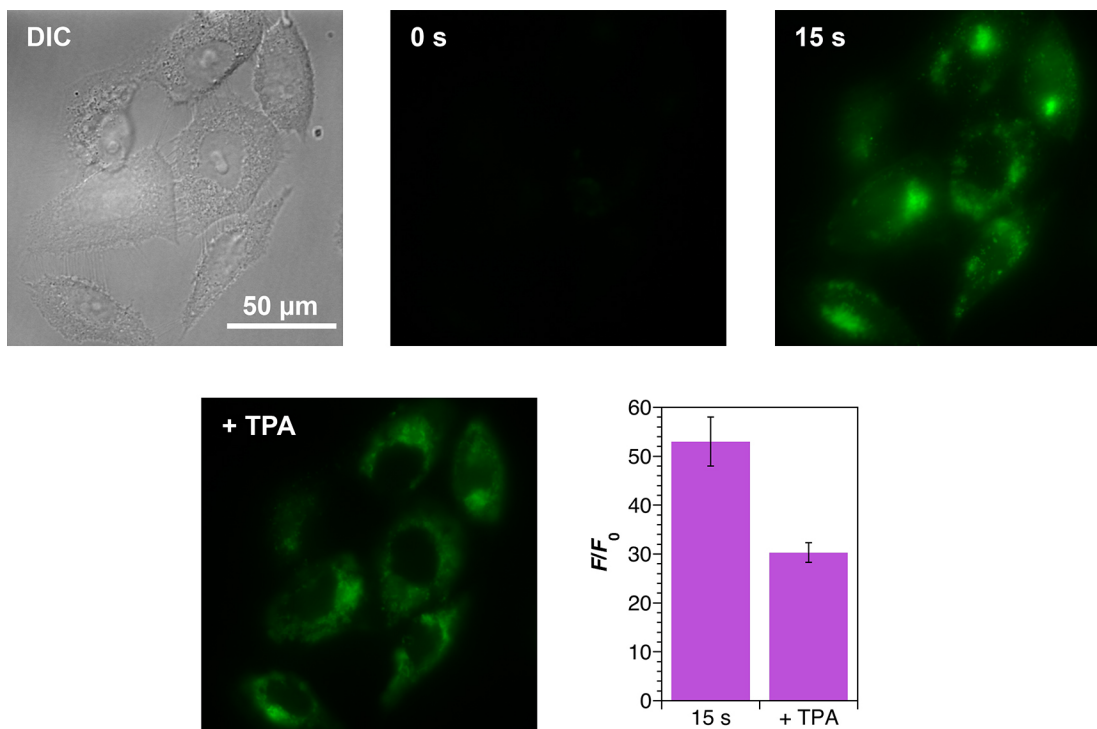
Figure S25. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells treated with 1 μM **1** and then incubated with 10 μM zinc pyrithione before and after irradiation with UV light for 15 s and after subsequent addition of 13 μM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 99). Error bars are standard error. $p = 3.0 \times 10^{-11}$.
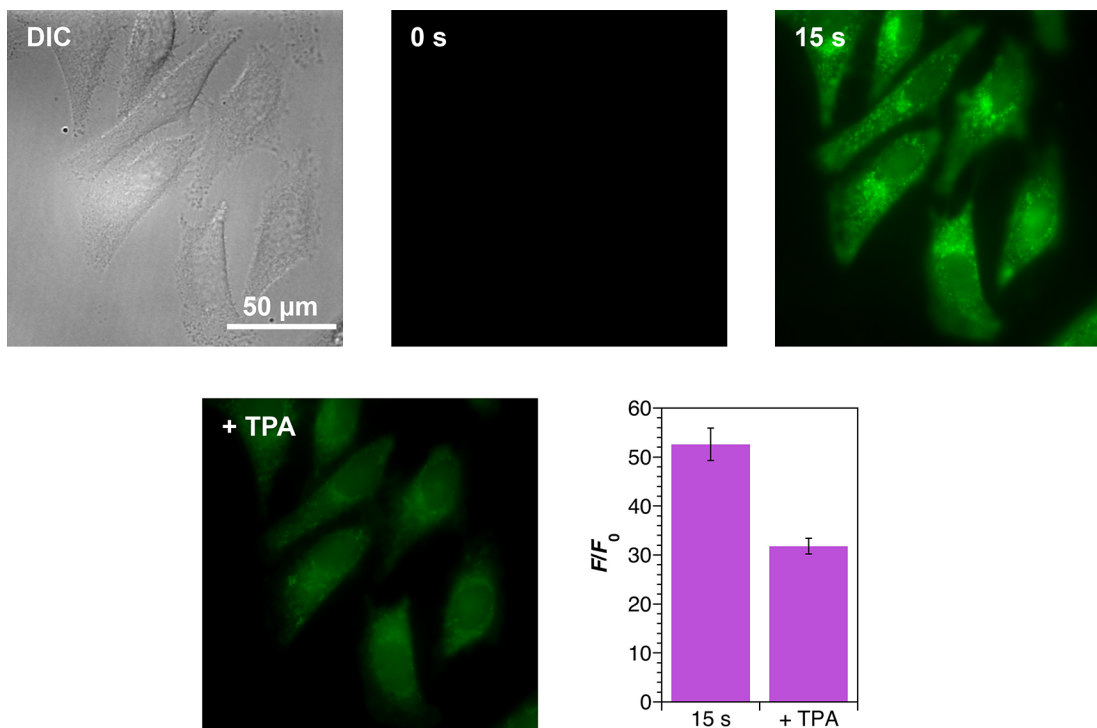
Figure S26. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with a mixture of 1 μM **3** and 50 μM $ZnCl_2$ prior to treatment with 10 μM zinc pyrithione before and after irradiation with UV light for 15 s and after subsequent addition of 13 μM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 88). Error bars are standard error. $p = 3.0 \times 10^{-23}$.
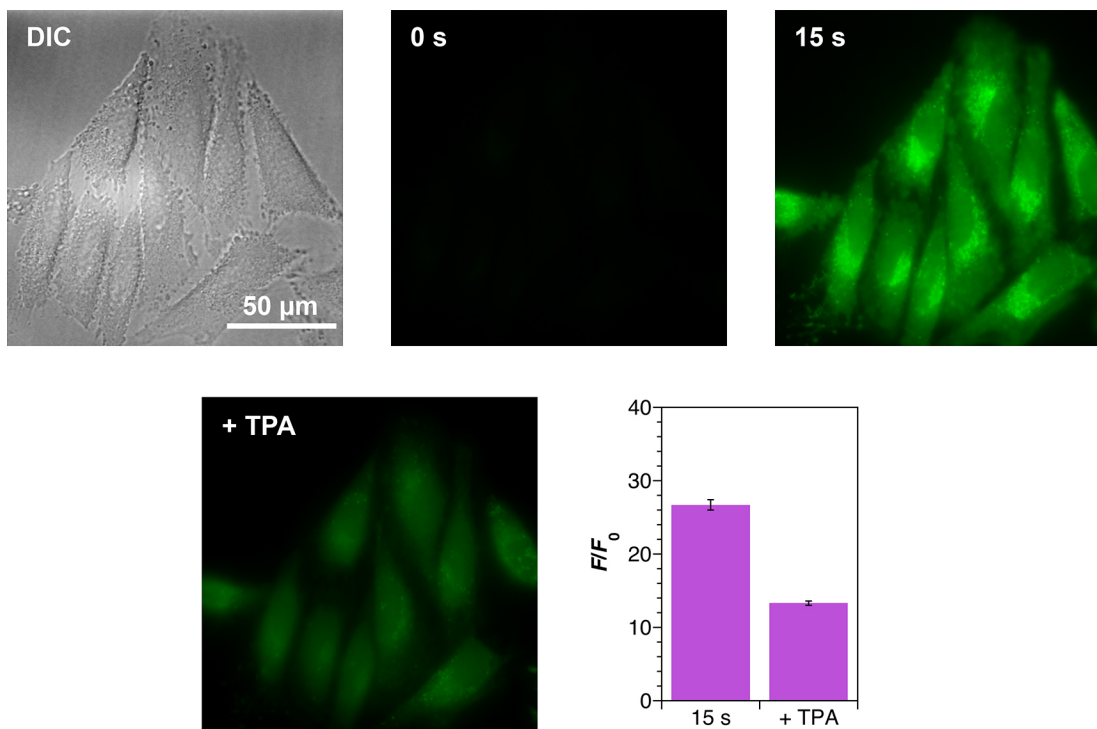
Figure S27. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with 10 μM zinc pyrithione prior to treatment with 1 μM **3** before and after irradiation with UV light for 15 s and after subsequent addition of 13 μM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 98). Error bars are standard error. $p = 1.8 \times 10^{-54}$.
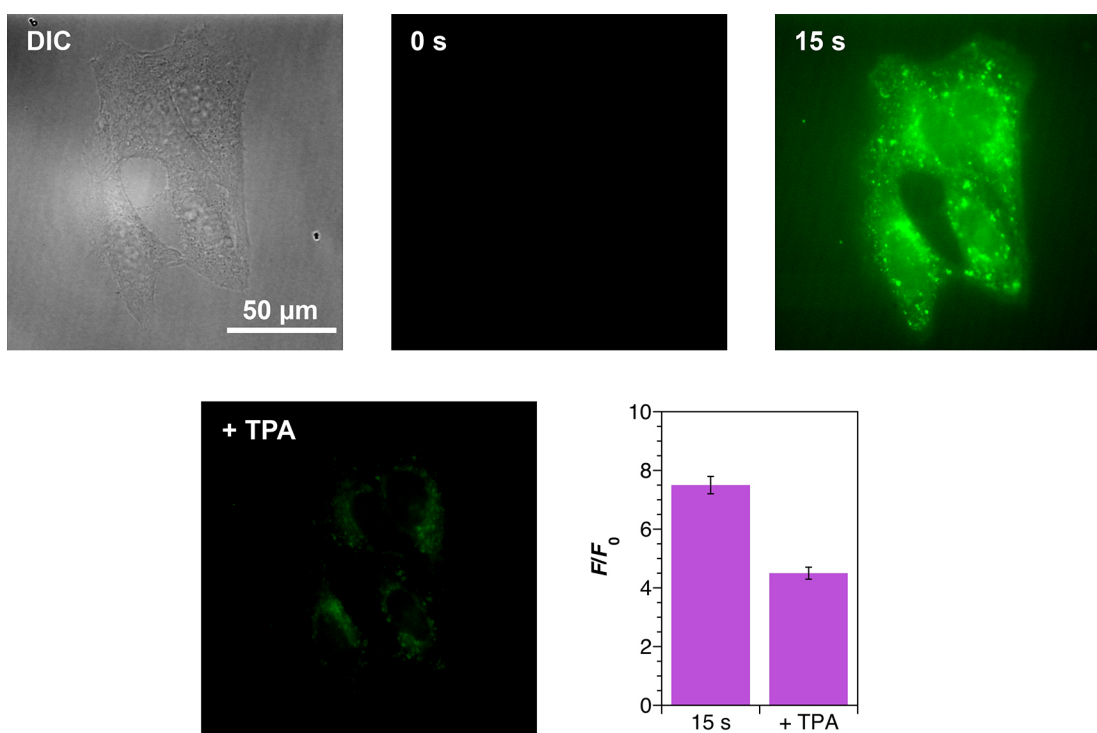
Figure S28. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with a mixture of 1 μM **3** and 50 μM ZnCl$_2$ before and after irradiation with UV light for 15 s and after subsequent addition of 13 μM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 88). Error bars are standard error. $p = 8.4 \times 10^{-29}$.
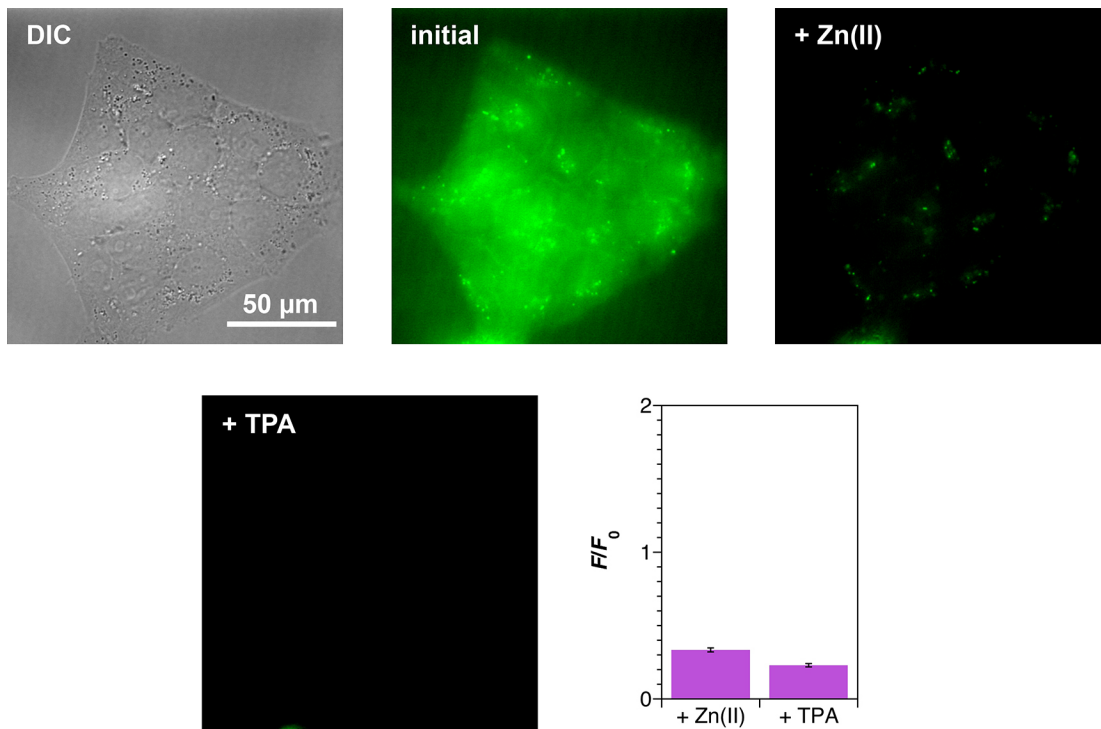
Figure S29. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with a mixture of 1 µM ZP1, 0.02% (w/v) Pluronic F-127, and 50 µM $ZnCl_2$ before and after addition of 10 µM zinc pyrithione, and after subsequent addition of 13 µM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 75). Error bars are standard error. $p = 1.2×10^{-20}$. The decrease in fluorescence upon addition of Zn(II) is due to extracellular sensor being washed away during application of zinc pyrithione.
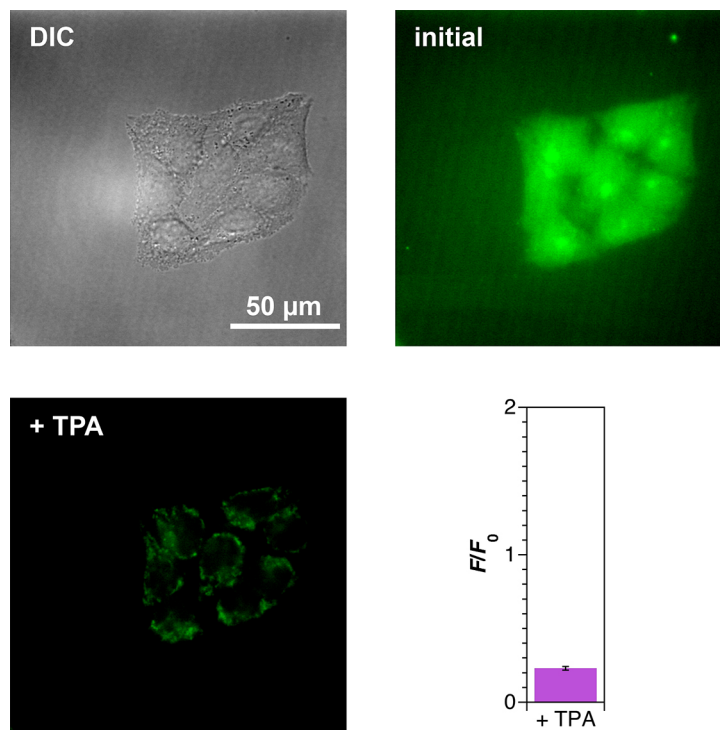
Figure S30. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with 10 µM zinc pyrithione prior to treatment with 1 µM ZP1 and after subsequent addition of 13 µM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 75). Error bars are standard error.

S40
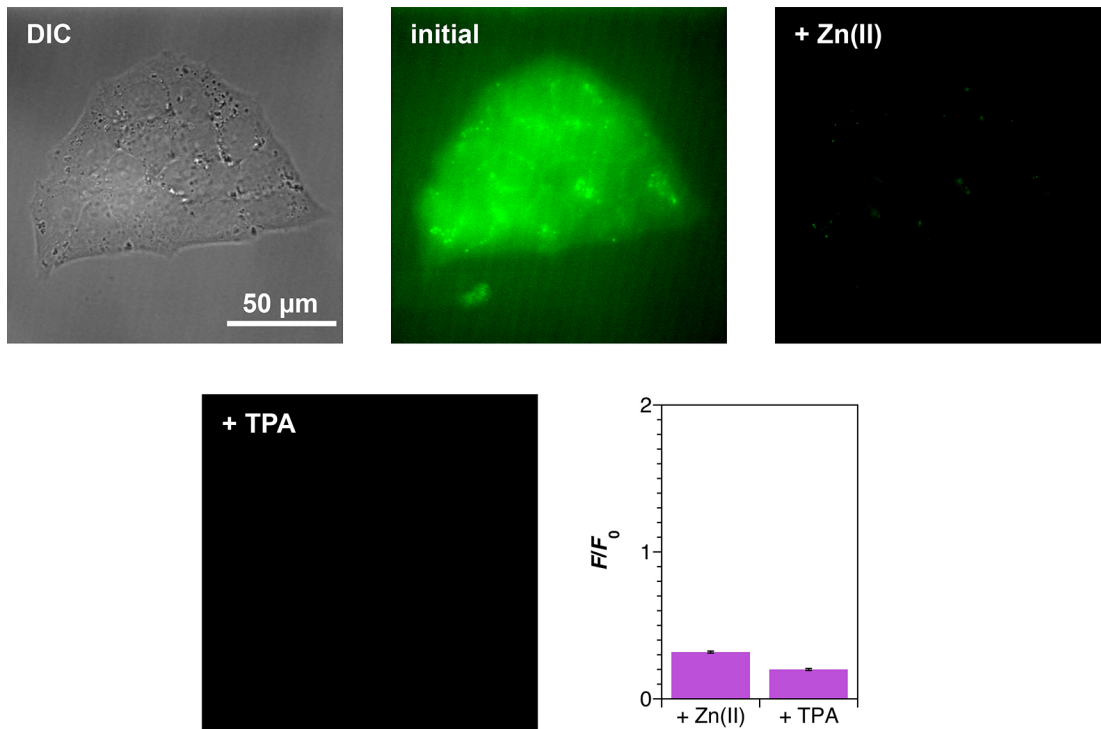
Figure S31. Representative differential interference contrast (DIC, upper left) and fluorescence microscopy images of HeLa cells incubated with a mixture of 1 μM ZP1 and 50 μM $ZnCl_2$ before and after treatment with 10 μM zinc pyrithione before and after subsequent addition of 13 μM TPA, as described in the text. Average integrated fluorescence turn-on for each condition is shown (n = 72). Error bars are standard error. $p = 1.1×10^{-52}$. The decrease in fluorescence upon addition of Zn(II) is due to extracellular sensor being washed away during application of zinc pyrithione.

Experiments in DCN brain slices.

Animals. All procedures were approved by the Institutional Animal Care and Use Committee at the University of Pittsburgh, Pittsburgh, PA

Preparation of DCN brain slices. Male or female ICR mice (Harlan) aged between postnatal day 20 (P20) and P22 were used. Mice were anesthetized with isoflurane then immediately decapitated and brains were rapidly removed. Brain slices were prepared in warm (34 °C) artificial cerebrospinal fluid (ACSF) containing the following (in mM): 130 NaCl, 3 KCl, 1.2 $CaCl_2 \cdot 2H_2O$, 1.3 $MgCl_2 \cdot 6H_2O$, 20 $NaHCO_3$, 3 HEPES, and 10 D-glucose, saturated with 95% O_2/5% CO_2 (v/v), pH = 7.25-7.35, ~300 mOsm. Coronal slices (210 μm thickness) containing cross sections including the molecular and deep layers of the dorsal cochlear nucleus (DCN) were cut using a Vibratome (VT1200S; Leica), then transferred to a holding chamber containing warm ACSF and incubated for ~60 min at 34 °C before initiating imaging experiments. ACSF used for incubating and imaging had the same composition as cutting ACSF, except contaminating zinc was removed by stirring the ACSF with Chelex 100 resin (Bio-Rad) for 1 hour. Chelex resin was filtered using Nalgene rapid flow filters lined with polyethersulfone (0.2 μm pore size), then high purity $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ (99.995%; Sigma-Aldrich) were added to the ACSF. All plastic- and glassware were washed with 5% nitric acid.

Fluorescence imaging and laser photoactivation. Slices were transferred to the imaging chamber and perfused with room temperature recirculating ACSF (1-2 mL/min). Prior to fluorescence imaging, 1 μL **3** (1 mM) was mixed with 1 μL 20% Pluronic F-127 (Invitrogen), then added to the ACSF for a final concentration of 1 μM **3**. Slices were allowed to incubate with **3** in the imaging chamber for 20 min before initiating fluorescence imaging. Images were acquired using an upright microscope (Olympus BX5) with a 20× water immersion objective and epifluorescence optics. The excitation source was a blue LED (470 nm wavelength, M470L3, Thorlabs), and green fluorescent signals were isolated using a GFP filter (U-N41017, Olympus) and acquired using a CCD camera (Retiga 2000R, QImaging). Images of fluorescent signals were captured before and after UV laser photostimulation. Photostimulation with UV laser light (355 nm, ~5.5 mW; DPSS Lasers) was performed under the 20× objective, and the photostimulation grid consisted of 8 × 8 sites (40 μm spacing) positioned to encompass the molecular layer and deep layer of the DCN. Each site was photostimulated with a 1 ms pulse of UV laser light (0.4 s between sites), and photostimulation of the entire grid was repeated 5 times.

Data analysis. All analysis was performed with custom routines in MATLAB (Mathworks) or with Prism 6 (GraphPad). For fluorescent images captured before and after photostimulation, a region of interest was selected containing the top row (molecular layer) or bottom row (deep layer) of the photostimulation grid. Fluorescence intensity was averaged within each region, and the change in intensity (ΔF) was calculated by subtracting the intensity before photostimulation from the intensity after photostimulation. $\Delta F/F$ was calculated by dividing ΔF by the intensity before photostimulation. Statistical comparison of $\Delta F/F$ in the molecular layer versus the deep layer was performed using an unpaired t test with Welch's correction.

Theoretical Calculations.

To examine the influence of the photocleavable protecting groups on the coordination environment of the zinc binding sites, we investigated the structures of **1**, **2**, and **3** with DFT calculations.[7] Geometry optimization was performed at the CPCM(H$_2$O)-B3LYP/6-31G level of theory.[8-9] The starting structural parameters of the ZP1 skeleton, in the lactone form, were adapted from previous calculations.[10] To minimize steric interactions between the photocleavable protecting groups and the ZP1 backbone, the following sets of dihedral angle values were used in the initial structures. For the first set, we used $\varphi_{C1-C2-O6-C7}$ = 90° (*trans* with respect to the di(2-picolyl)amine (DPA) arm), $\varphi_{C2-O6-C7-C8}$ = 180° (*trans* with respect to the fluorescein backbone), and $\varphi_{O6-C7-C8-C9}$ = 90°. For the second set, we used $\varphi_{C1-C2-O6-C7}$ = 90° (*trans* with respect to the di(2-picolyl)amine (DPA) arm), $\varphi_{C2-O6-C7-C8}$ = 180° (*trans* with respect to the fluorescein backbone), and $\varphi_{O6-C7-C8-C9}$ = −90°.

With these initial structures, two local minima, confirmed by frequency analyses at the CPCM(H$_2$O)-B3LYP/6-31G level, were found for each sensor on the potential energy surface. To estimate better the relative energy of each conformer, free energies were calculated by combining single point calculations at the CPCM(H$_2$O)-B3LYP/6-311+G(d,p)//CPCM(H$_2$O)-B3LYP/6-31G level with thermal and entropic corrections obtained at the CPCM(H$_2$O)-B3LYP/6-31G level.
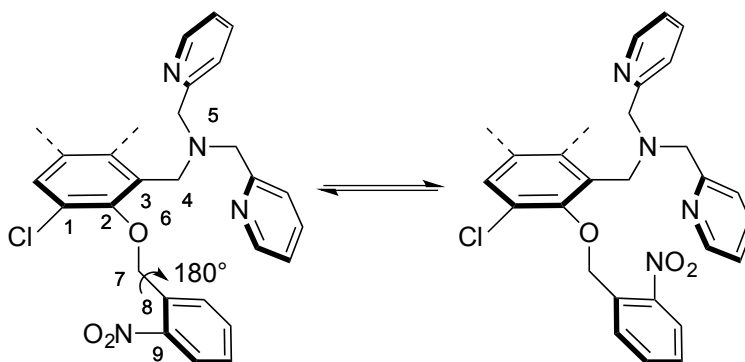
Scheme S4. Initial conformations considered in calculations.

To confirm that the 6-31G basis set is suitable for geometry optimization, we also investigated structures of **1** at the CPCM(H$_2$O)-B3LYP/6-31G(d) and CPCM(H$_2$O)-B3LYP/SVP levels of theory. As shown in Table S4, with the CPCM solvation model, the values of the key dihedral angle $\varphi_{N5-C4-C3-C2}$ are nearly identical at different levels of theory. Compared to the structures predicted at the CPCM(H$_2$O)-B3LYP/6-31G level, slightly smaller $\varphi_{N5-C4-C3-C2}$ values, −73° to −83°, were found at the CPCM(H$_2$O)-B3LYP/SVP level. As discussed below, these values are still significantly larger than the corresponding $\varphi_{N5-C4-C3-C2}$ dihedral angle of ZP1 (−33°). We also performed geometry optimization of **1** in the gas phase to test the influence of the implicit CPCM model on the structure of **1**. The effect of the CPCM model is obvious when comparing the structures of **1-a** at the CPCM(H$_2$O)-B3LYP/6-31G(d) and B3LYP/6-31G(d) levels. Overall, these results suggested that the 6-31G

basis set, although rather small, is likely to provide reasonable geometric predictions. To balance computational efficiency and accuracy, we performed all calculations at the CPCM(H_2O)-B3LYP/6-31G(d) level of theory.

Table S4. Relative energies and $\varphi_{N5-C4-C3-C2}$ of conformers of **1** at different levels of theory.

level		ΔE (kcal/mol)	ΔG (kcal/mol)	$\varphi_{N5-C4-C3-C2}$ (°)
CPCM(H_2O)-B3LYP/6-31G	**1-a**	0.0	0.0	−78.9
	1-b	7.8	10.5	−83.3
CPCM(H_2O)-B3LYP/6-31G(d)	**1-a**	0.0	0.0	−76.4
	1-b	7.3	10.6	−80.3
B3LYP/6-31G(d)	**1-a**	0.0	0.0	−68.2
	1-b	13.8	15.9	−82.6
CPCM(H_2O)-B3LYP/SVP	**1-a**	0.0	0.0	−72.6
	1-b	8.7	12.0	−82.5
B3LYP/SVP	**1-a**	0.0	0.0	−69.5
	1-b	14.5	17.5	−83.4

As depicted in Figures S32-S37, the nitro groups of all three sensors point away from the DPA arms in the preferential conformations. As expected, the zinc binding sites of both the major and minor conformers exhibited a significant geometric deviation from the initial ZP1 coordination environment. The calculated dihedral angle $\varphi_{N5-C4-C3-C2}$ in the lactone form of ZP1 is 33° (Figure S39). In comparison, this angle ranges from 77° to 85° in the protected sensors. This geometry does not allow for the trigonal bipyramidal zinc-binding mode of ZP1 that was previously determined in X-ray crystallography studies.[11] These results are consistent with our initial hypothesis that the introduction of protecting groups on the oxygen atoms diminishes the zinc binding affinities of the sensors compared to ZP1.

Table S5. Energies of conformers of protected ZP1 derivatives at the CPCM(H_2O)-B3LYP/6-31G level of theory.

	E (hartree)	ΔE (kcal/mol)	G (hartree)	ΔG (kcal/mol)	Thermal Correction (hartree)
1-a	-4348.28226382	0.0	-4347.43646600	0.0	0.845797
1-b	-4348.26987344	7.8	-4347.41975200	10.5	0.850122
2-a	-4806.22916340	0.0	-4805.26070100	0.0	0.968462
2-b	-4806.21112366	11.3	-4805.24488000	9.9	0.966244
3-a	-5022.17118093	0.0	-5021.32449300	0.0	0.846688
3-b	-5022.17302438	-1.2	-5021.32269600	1.1	0.850328

Table S6. Energies of conformers of protected ZP1 derivatives at the CPCM(H_2O)-B3LYP/6-311+G(d,p) level of theory.

	E (hartree)	ΔE (kcal/mol)	G (hartree)	ΔG (kcal/mol)
1-a	-4350.23524223	0.0	-4349.38944523	0.0
1-b	-4350.22326838	7.5	-4349.37314638	10.2
2-a	-4808.46242662	0.0	-4807.49396462	0.0
2-b	-4808.45270710	6.1	-4807.48646310	4.7
3-a	-5024.49347851	0.0	-5023.64679051	0.0
3-b	-5024.49314165	0.2	-5023.64281365	2.5

Front View **Top View** **Side View**
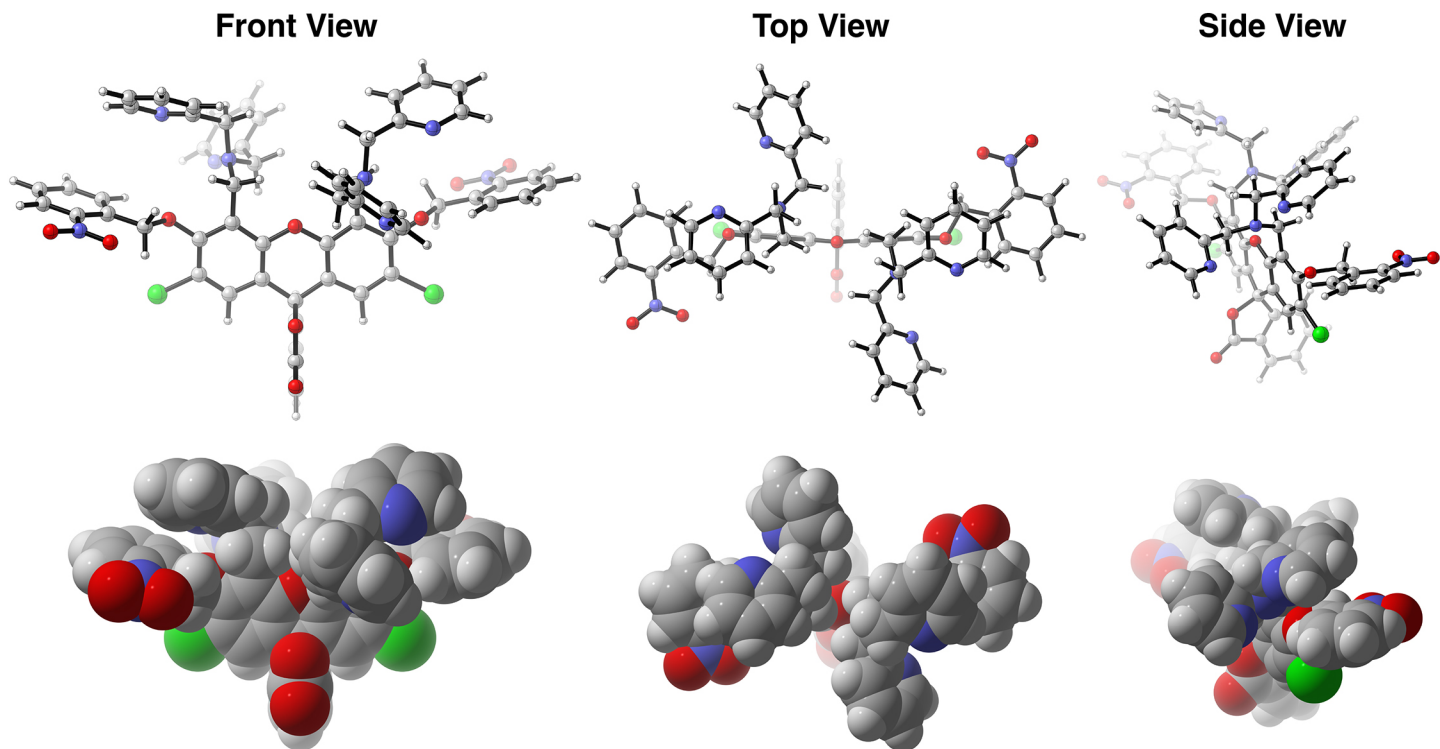
Figure S32. Ball and stick (top) and space filling (bottom) models of conformer **1-a** at the CPCM(H$_2$O)-B3LYP/6-31G level as viewed from the front, top, and side.

Front View **Top View** **Side View**
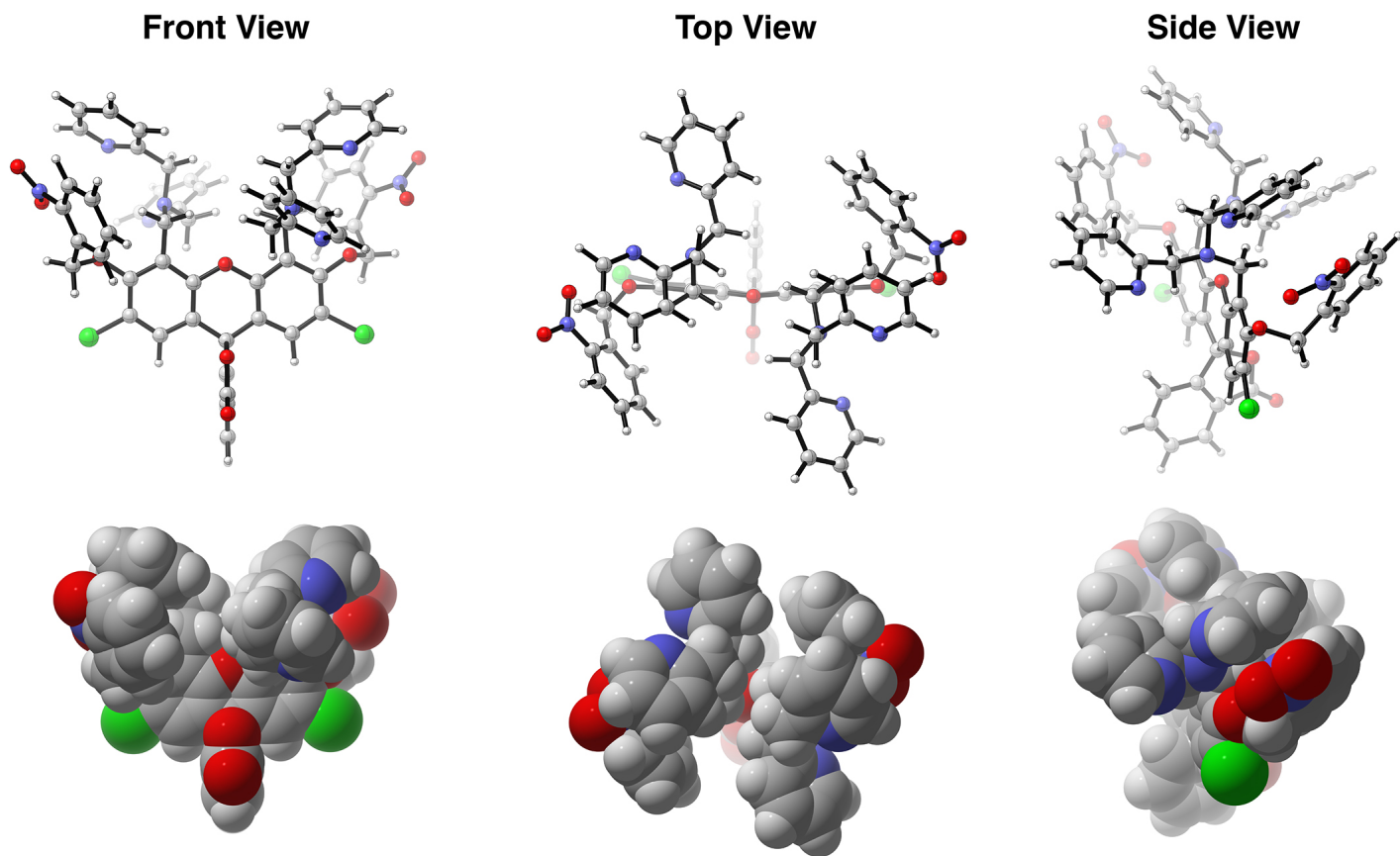
Figure S33. Ball and stick (top) and space filling (bottom) models of conformer **1-b** at the CPCM(H$_2$O)-B3LYP/6-31G level as viewed from the front, top, and side.
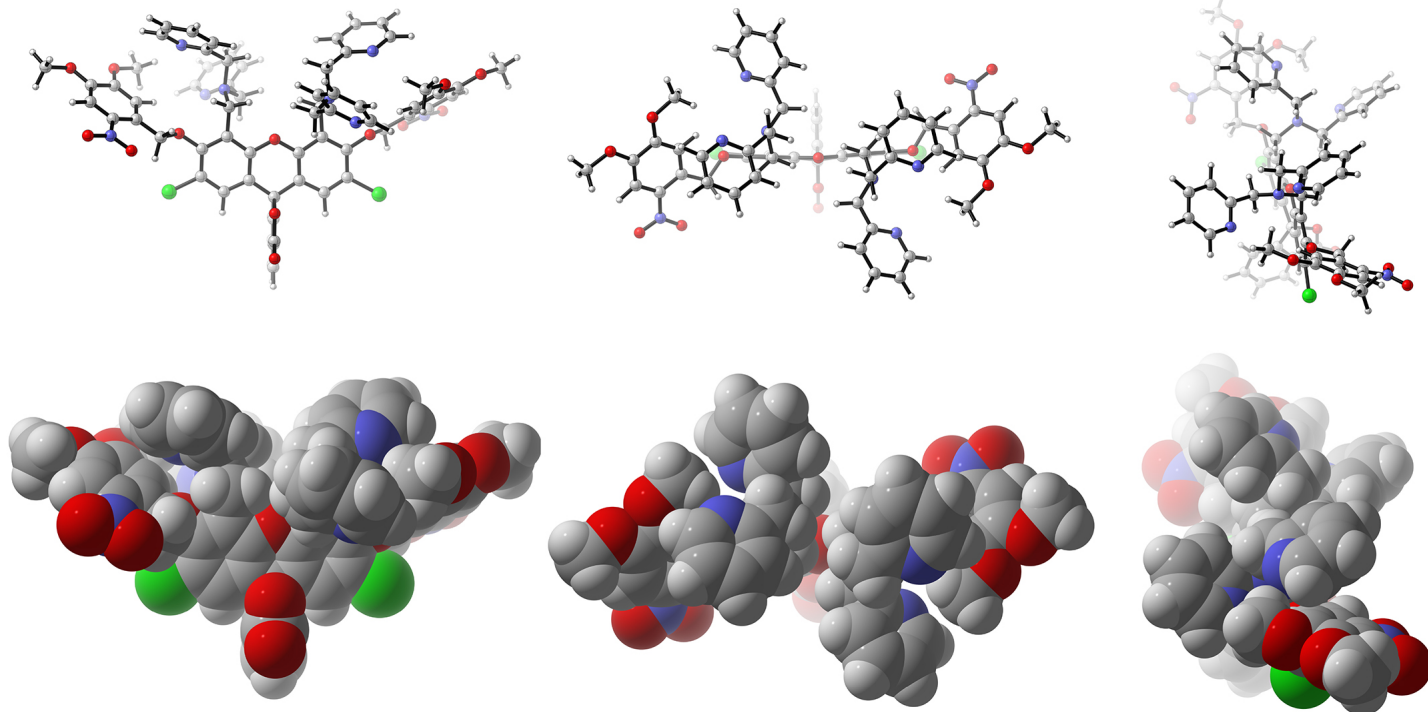
Figure S34. Ball and stick (top) and space filling (bottom) models of conformer **2-a** at the CPCM(H$_2$O)-B3LYP/6-31G level as viewed from the front, top, and side.
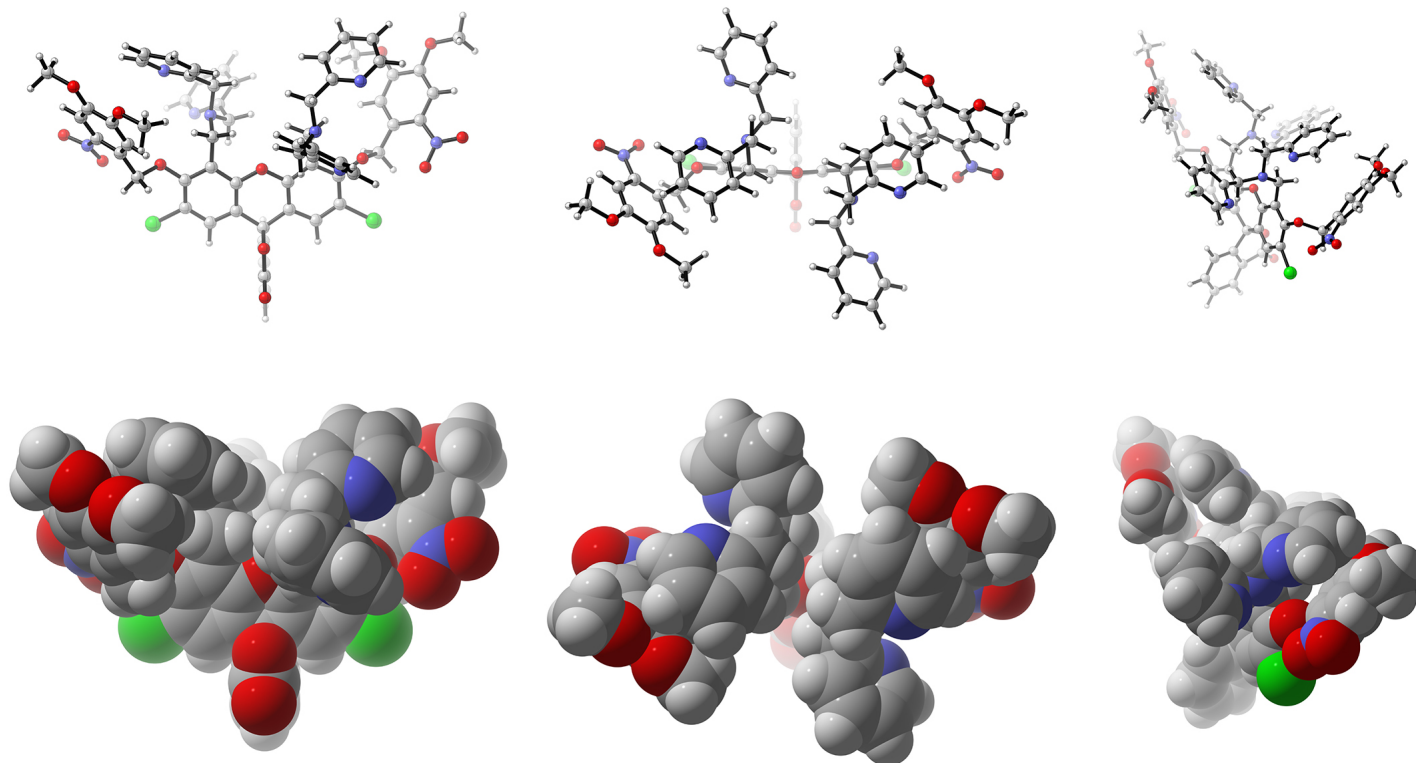
Figure S35. Ball and stick (top) and space filling (bottom) models of conformer **2-b** at the CPCM(H$_2$O)-B3LYP/6-31G level as viewed from the front, top, and side.

Front View **Top View** **Side View**
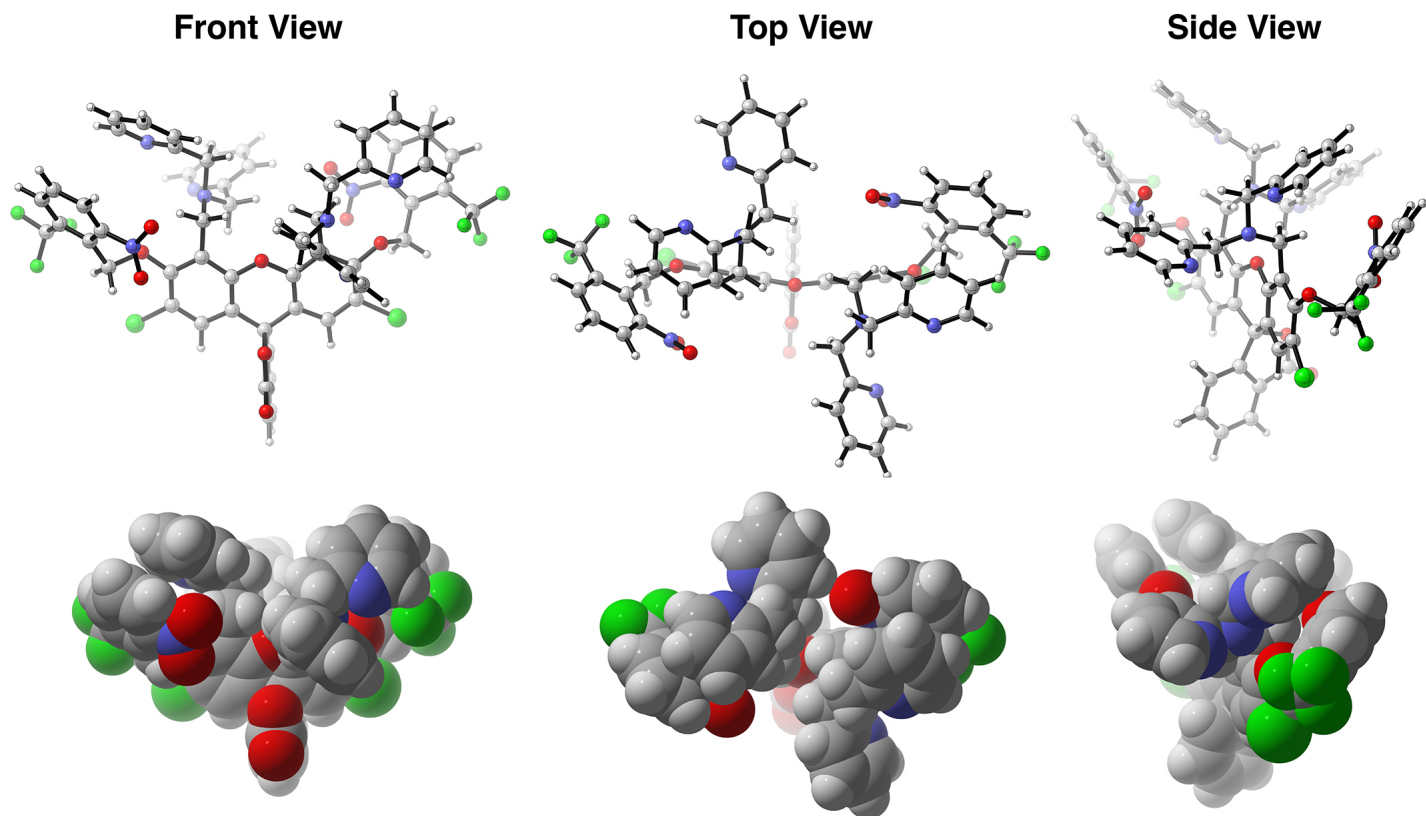
Figure S36. Ball and stick (top) and space filling (bottom) models of conformer **3-a** at the CPCM(H_2O)-B3LYP/6-31G level as viewed from the front, top, and side.

Front View **Top View** **Side View**
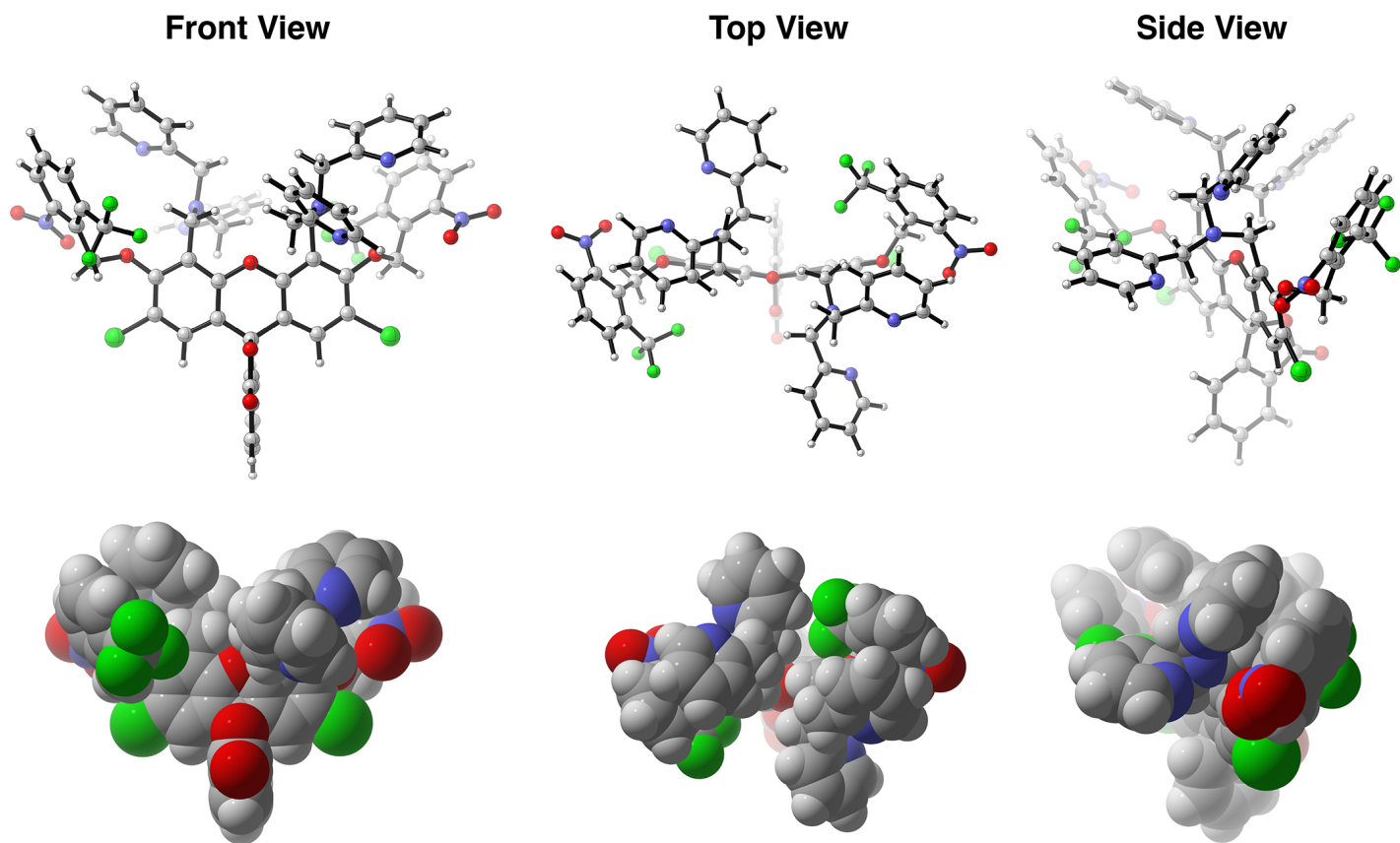
Figure S37. Ball and stick (top) and space filling (bottom) models of conformer **3-b** at the CPCM(H_2O)-B3LYP/6-31G level as viewed from the front, top, and side.

Front View	Top View	Side View
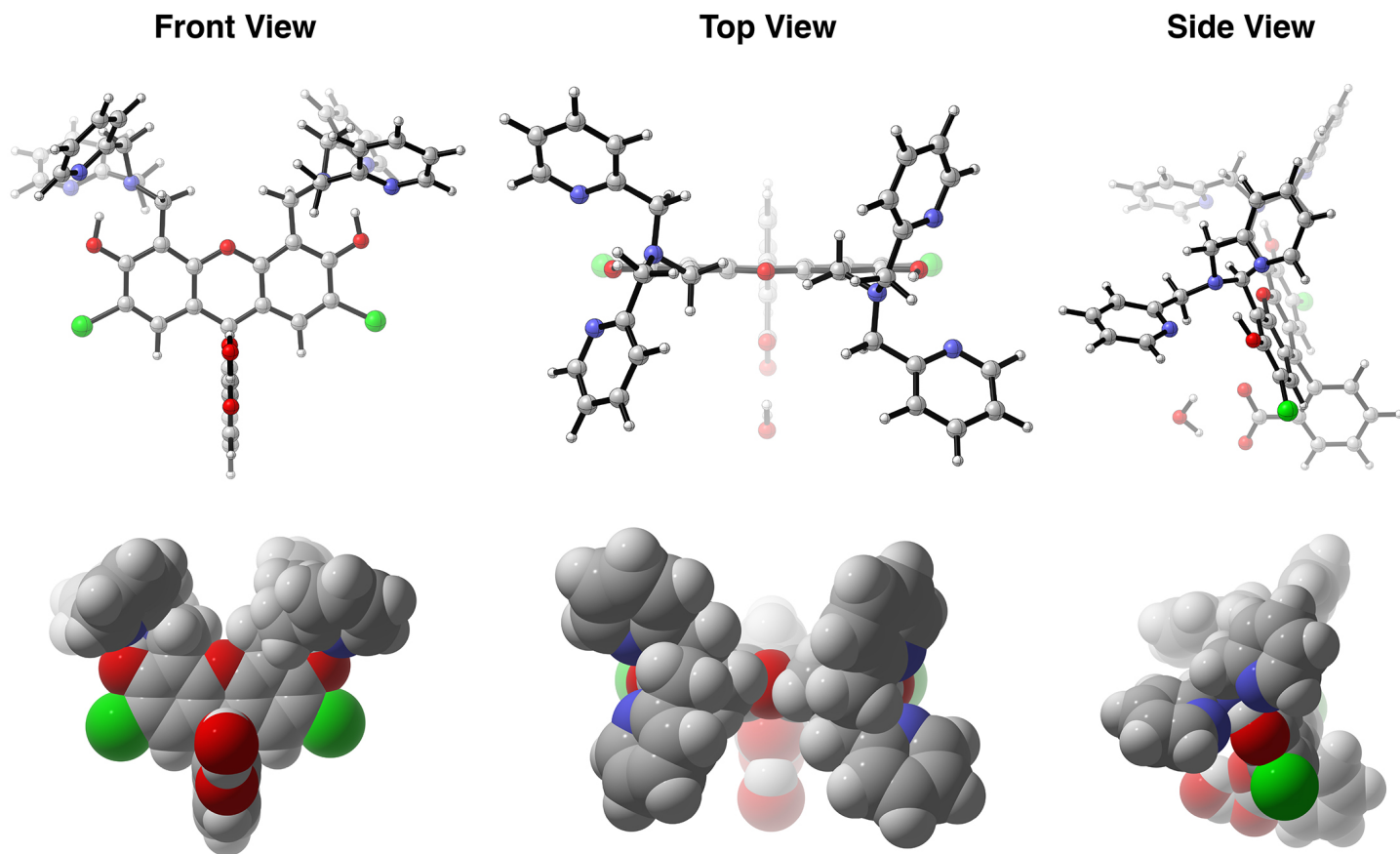
Figure S38. Ball and stick (top) and space filling (bottom) models of ZP1 as viewed from the front, top, and side.
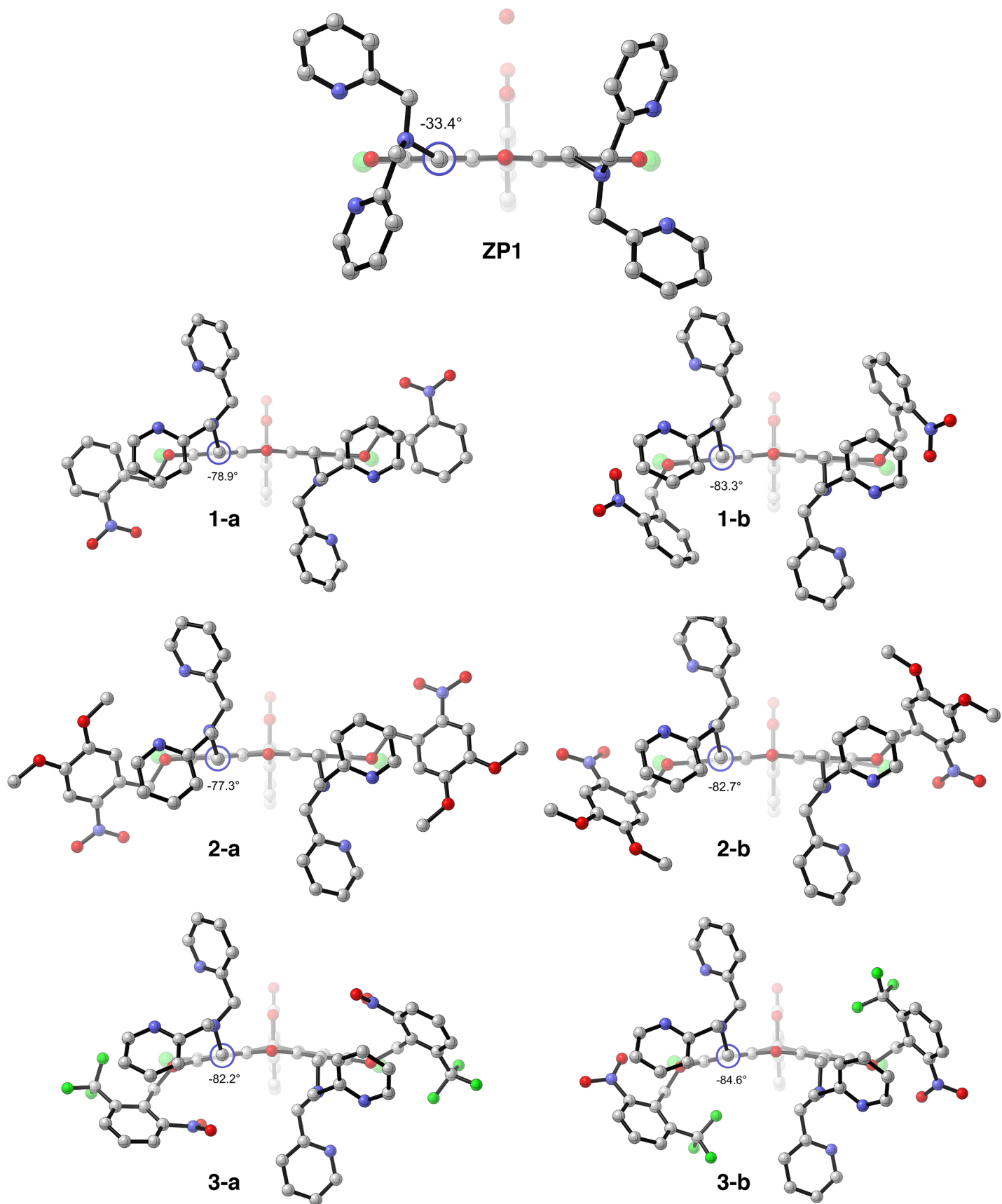
Figure S39. Orientation of the DPA arms in ZP1 and protected sensors. Dihedral angles ($\varphi_{N5\text{-}C4\text{-}C3\text{-}C2}$) of the protected sensors calculated at the CPCM(H_2O)-B3LYP/6-31G level are indicated.

CPCM(H₂O)-B3LYP/6-31G
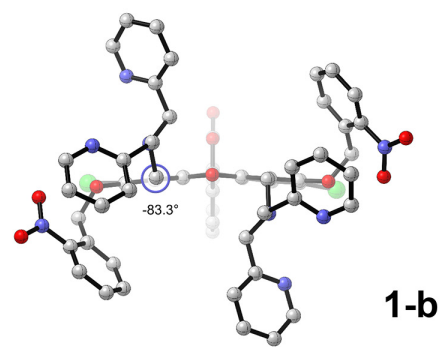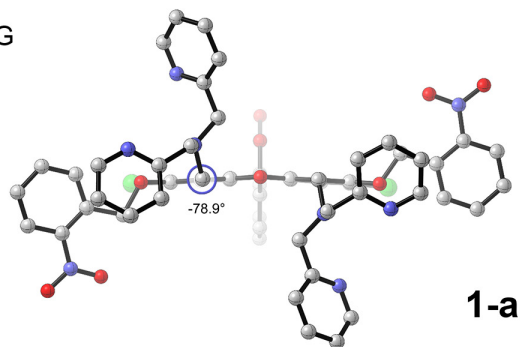
CPCM(H₂O)-B3LYP/6-31G(d)
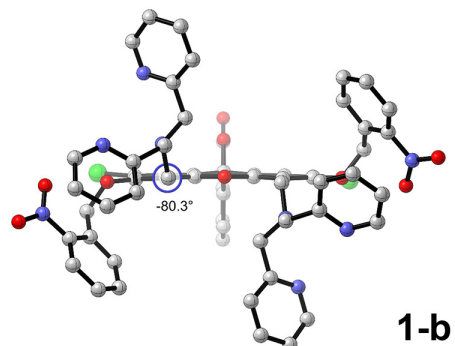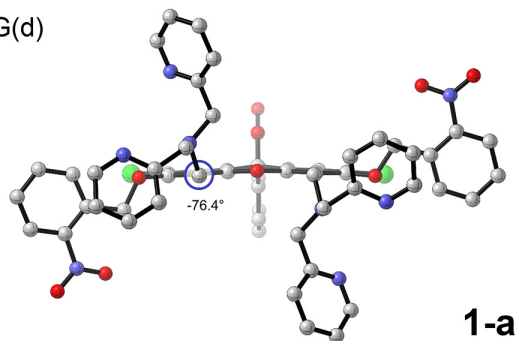
B3LYP/6-31G(d)
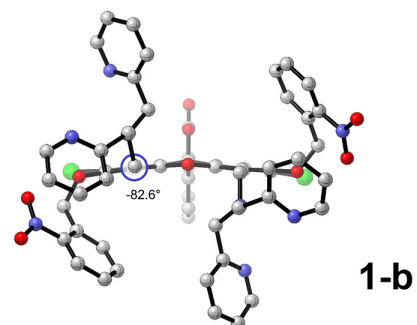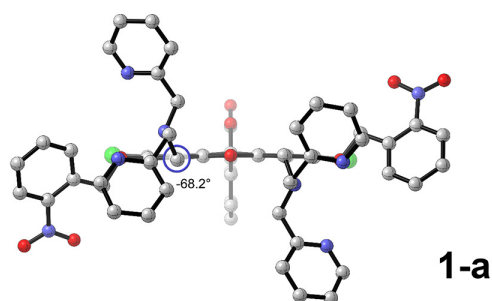
CPCM(H₂O)-B3LYP/SVP
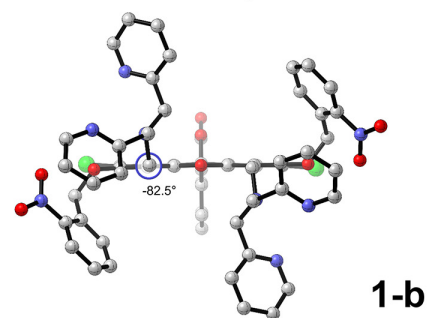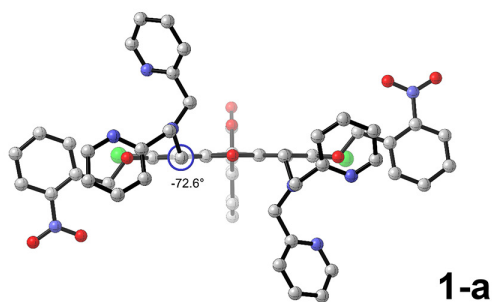
B3LYP/SVP
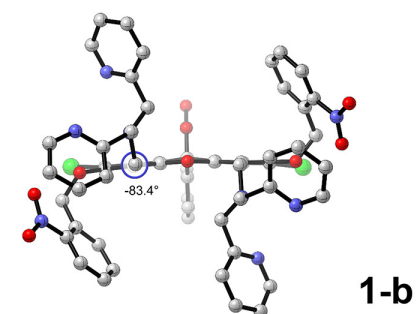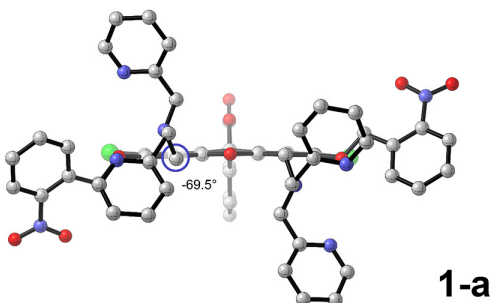
Figure S40. Comparison of **1-a** and **1-b** dihedral angles ($\varphi_{N5\text{-}C4\text{-}C3\text{-}C2}$) calculated at different levels of theory, as indicated.

Optimized Coordinates of 1-a at the CPCM(H₂O)-B3LYP/6-31G level.

Standard orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	17	0	5.285626	3.298677	-0.389743
2	17	0	-5.240608	3.372817	0.254065
3	8	0	4.773524	0.297714	-0.284044
4	8	0	0.020383	0.550539	0.211874
5	8	0	-4.760486	0.362895	0.203945
6	6	0	0.133081	5.346318	1.852696
7	1	0	0.095970	7.998859	0.743421
8	1	0	-0.022542	8.425068	-1.721881
9	1	0	-0.112587	6.529595	-3.309973
10	1	0	-0.087210	4.180094	-2.498703
11	1	0	2.620606	4.320861	-0.059513
12	1	0	-2.541111	4.356965	0.244118
13	8	0	0.119734	3.949740	1.801464
14	8	0	0.190221	5.950739	2.926718
15	6	0	0.069380	5.854073	0.475074
16	6	0	0.056039	7.179590	0.034531
17	6	0	-0.010268	7.409412	-1.343247
18	6	0	-0.061402	6.331099	-2.245084
19	6	0	-0.047302	5.002769	-1.793560
20	6	0	0.018873	4.779934	-0.419381
21	6	0	0.046704	3.458697	0.337176
22	6	0	1.287556	2.629424	0.106703
23	6	0	2.541638	3.241833	-0.039117
24	6	0	3.680625	2.466056	-0.158574
25	6	0	3.622508	1.062347	-0.134700
26	6	0	2.378789	0.418996	-0.023516
27	6	0	1.233576	1.230224	0.101413
28	6	0	-1.188076	1.247432	0.215420
29	6	0	-2.351009	0.452405	0.197864
30	6	0	-3.590379	1.113165	0.182934
31	6	0	-3.631575	2.517552	0.202061
32	6	0	-2.475621	3.277018	0.221091
33	6	0	-1.221760	2.647062	0.223576
34	6	0	2.282813	-1.090949	-0.037226
35	6	0	1.431718	-1.221452	-2.378223
36	6	0	1.856013	-1.480407	-3.808679
37	6	0	1.161433	-2.380005	-4.630247
38	6	0	1.582575	-2.571924	-5.951827
39	6	0	2.689668	-1.857151	-6.418639
40	6	0	3.329501	-0.974599	-5.541019
41	6	0	2.511940	-3.166658	-1.329934
42	6	0	3.765483	-3.686574	-0.660102
43	1	0	6.977097	-3.876259	-1.365430
44	1	0	7.041333	-5.023834	0.854920
45	1	0	-0.562377	-3.040304	4.428315
46	1	0	-1.420931	-3.423277	6.747670
47	1	0	-3.404282	-2.092112	7.535924
48	1	0	-4.429003	-0.437415	5.966445
49	7	0	2.436603	-1.686084	-1.392468
50	7	0	-2.530333	-1.671341	1.529416
51	7	0	2.929488	-0.782281	-4.264569
52	7	0	-5.067408	-3.486728	1.398533
53	6	0	6.068824	-4.014790	-0.788033
54	6	0	6.103403	-4.656320	0.455028
55	6	0	4.903794	-4.811352	1.156361
56	6	0	-2.278730	-1.058867	0.196058
57	6	0	-2.645209	-3.148733	1.430643
58	6	0	-3.896894	-3.615000	0.719880
59	6	0	-3.849537	-4.180985	-0.562743
60	6	0	-5.033981	-4.622292	-1.164958
61	6	0	-6.237800	-4.488052	-0.466592
62	6	0	-6.205859	-3.915937	0.809963
63	6	0	-1.558707	-1.258613	2.572005
64	6	0	-2.049543	-1.543190	3.975488
65	6	0	-1.417157	-2.485403	4.799633
66	6	0	-1.897763	-2.697700	6.097639
67	6	0	-3.000509	-1.960170	6.538787
68	6	0	-3.576160	-1.035177	5.660474
69	1	0	3.092062	-1.496903	0.574384
70	1	0	1.334110	-1.397582	0.429703
71	1	0	1.324515	-0.141324	-2.250559
72	1	0	0.439749	-1.675076	-2.199882
73	1	0	0.305330	-2.918512	-4.238447
74	1	0	1.057357	-3.264960	-6.600078
75	1	0	3.048753	-1.974611	-7.434505
76	1	0	4.188196	-0.395617	-5.866117
77	1	0	2.504734	-3.530524	-2.361446
78	1	0	1.623750	-3.589638	-0.823556
79	1	0	-3.050785	-1.443887	-0.473711
80	1	0	-1.304783	-1.373718	-0.209826
81	1	0	-2.676352	-3.536172	2.452728
82	1	0	-1.756196	-3.584505	0.937210
83	1	0	-2.898832	-4.277022	-1.075875
84	1	0	-7.177023	-4.819430	-0.894035
85	1	0	-7.117380	-3.797029	1.386574
86	1	0	-1.420269	-0.178802	2.479076
87	1	0	-0.571280	-1.731679	2.422301
88	7	0	-3.118245	-0.822795	4.406883
89	6	0	3.721165	-4.320181	0.590615
90	1	0	2.773876	-4.428159	1.107683
91	7	0	4.931628	-3.538614	-1.342118
92	1	0	4.886729	-5.304226	2.122344
93	1	0	-5.014859	-5.062363	-2.156074
94	6	0	-5.524959	0.262792	-1.060672
95	1	0	-5.487928	1.218385	-1.587812
96	1	0	-5.042692	-0.487285	-1.692993
97	6	0	5.665872	0.181658	0.892093
98	1	0	5.681687	1.128690	1.435429
99	1	0	5.253726	-0.579630	1.559565
100	6	0	-6.946652	-0.123581	-0.720894
101	6	0	-7.953728	-0.342833	-1.692067
102	6	0	-7.320643	-0.283559	0.622392
103	6	0	-9.263675	-0.700511	-1.338337
104	6	0	-8.623941	-0.638762	0.983274
105	1	0	-6.568063	-0.128644	1.381944
106	6	0	-9.601706	-0.848868	0.002522
107	1	0	-9.992156	-0.854068	-2.122225
108	1	0	-8.874168	-0.750888	2.032423
109	1	0	-10.612558	-1.123905	0.278477
110	7	0	-7.681022	-0.204517	-3.113495
111	8	0	-8.612325	-0.426730	-3.944926
112	8	0	-6.513679	0.136395	-3.486471
113	6	0	7.045618	-0.195139	0.401444
114	6	0	8.150924	-0.414356	1.259034
115	6	0	7.275615	-0.346313	-0.974935
116	6	0	9.417613	-0.763210	0.766260
117	6	0	8.534879	-0.692927	-1.474074
118	1	0	6.446100	-0.190566	-1.649378
119	6	0	9.612117	-0.903098	-0.603667
120	1	0	10.225809	-0.917052	1.467571
121	1	0	8.672900	-0.798223	-2.544457
122	1	0	10.589174	-1.171747	-0.986794
123	7	0	8.030250	-0.284872	2.702171
124	8	0	9.047755	-0.498635	3.428108
125	8	0	6.905452	0.039641	3.199654

Optimized Coordinates of 1-b at the CPCM(H₂O)-B3LYP/6-31G *level.*

Optimized Coordinates of 1-b at the $CPCM(H_2O)$-B3LYP/6-31G *level.*

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                   Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type        X           Y           Z
---------------------------------------------------------------------
    1        17          0       5.268433    3.552205   -1.085668
    2        17          0      -5.151692    3.788684    0.267125
    3         8          0       4.787492    0.553520   -0.553504
    4         8          0       0.076140    0.911555    0.202668
    5         8          0      -4.705010    0.739661    0.210887
    6         6          0       0.324171    5.737759    1.592626
    7         1          0       0.247724    8.361040    0.417071
    8         1          0      -0.013726    8.724562   -2.047152
    9         1          0      -0.215607    6.789809   -3.576537
   10         1          0      -0.163392    4.461639   -2.705424
   11         1          0       2.666101    4.613743   -0.572718
   12         1          0      -2.458968    4.730044    0.099360
   13         8          0       0.291079    4.341101    1.580079
   14         8          0       0.451032    6.370014    2.644598
   15         6          0       0.185784    6.210411    0.207817
   16         6          0       0.158395    7.524103   -0.266221
   17         6          0       0.012003    7.718941   -1.643262
   18         6          0      -0.102630    6.618415   -2.511731
   19         6          0      -0.073727    5.302190   -2.026571
   20         6          0       0.072208    5.114328   -0.653404
   21         6          0       0.129645    3.813226    0.133948
   22         6          0       1.344522    2.961120   -0.141955
   23         6          0       2.584593    3.542267   -0.446140
   24         6          0       3.706030    2.746074   -0.593116
   25         6          0       3.652344    1.348356   -0.429310
   26         6          0       2.408947    0.731929   -0.196324
   27         6          0       1.283252    1.566493   -0.043346
   28         6          0      -1.128350    1.615854    0.191920
   29         6          0      -2.295536    0.827554    0.251026
   30         6          0      -3.534848    1.491380    0.193102
   31         6          0      -3.560509    2.899190    0.163028
   32         6          0      -2.399855    3.649693    0.118441
   33         6          0      -1.150051    3.012567    0.111888
   34         6          0       2.269999   -0.772744   -0.145773
   35         6          0       1.163557   -0.799090   -2.407554
   36         6          0       1.378597   -1.196882   -3.853350
   37         6          0       0.427086   -1.952120   -4.554741
   38         6          0       0.657188   -2.274139   -5.897903
   39         6          0       1.835431   -1.831584   -6.506532
   40         6          0       2.735606   -1.079338   -5.743562
   41         6          0       1.947110   -2.876623   -1.364972
   42         6          0       3.152339   -3.639029   -0.860428
   43         1          0       6.118125   -4.488179   -2.012958
   44         1          0       6.247207   -5.673062    0.184751
   45         1          0      -0.205426   -1.956134    4.773605
   46         1          0      -0.991351   -2.205001    7.136252
   47         1          0      -3.099455   -1.025846    7.837948
   48         1          0      -4.316361    0.350149    6.141567
   49         7          0       2.156097   -1.413695   -1.491663
   50         7          0      -2.329252   -1.151506    1.808474
   51         7          0       2.521093   -0.762458   -4.447462
   52         7          0      -4.552618   -3.313811    2.005394
   53         6          0       5.291520   -4.443666   -1.311472
   54         6          0       5.362805   -5.106353   -0.080612
   55         6          0       4.269926   -5.014835    0.787270
   56         6          0      -2.210722   -0.674848    0.396692
   57         6          0      -2.207390   -2.628925    1.877376
   58         6          0      -3.387784   -3.385140    1.308815
   59         6          0      -3.269474   -4.169932    0.152680
   60         6          0      -4.373468   -4.904567   -0.296288
   61         6          0      -5.571933   -4.830753    0.420673
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   62         6          0      -5.615761   -4.018915    1.560139
   63         6          0      -1.416710   -0.487881    2.775274
   64         6          0      -1.854605   -0.682346    4.211793
   65         6          0      -1.112775   -1.465145    5.108425
   66         6          0      -1.552493   -1.601769    6.430837
   67         6          0      -2.724143   -0.948399    6.824116
   68         6          0      -3.407369   -0.179844    5.874870
   69         1          0       3.159559   -1.195219    0.325729
   70         1          0       1.404063   -1.028820    0.484019
   71         1          0       1.280878    0.284584   -2.341431
   72         1          0       0.125863   -1.038221   -2.115303
   73         1          0      -0.478421   -2.278589   -4.054696
   74         1          0      -0.067827   -2.858338   -6.454196
   75         1          0       2.053186   -2.057599   -7.543955
   76         1          0       3.658587   -0.710736   -6.180095
   77         1          0       1.711980   -3.254109   -2.364446
   78         1          0       1.077515   -3.096370   -0.716768
   79         1          0      -3.034118   -1.131559   -0.155724
   80         1          0      -1.269516   -1.024038   -0.055091
   81         1          0      -2.125486   -2.894328    2.935319
   82         1          0      -1.280009   -2.970787    1.379789
   83         1          0      -2.325169   -4.208145   -0.379481
   84         1          0      -6.450132   -5.383383    0.108989
   85         1          0      -6.526690   -3.932264    2.143370
   86         1          0      -1.436791    0.583198    2.566360
   87         1          0      -0.373227   -0.829893    2.657813
   88         7          0      -2.990384   -0.042564    4.596771
   89         6          0       3.152689   -4.269174    0.392467
   90         1          0       2.288103   -4.180885    1.041290
   91         7          0       4.213996   -3.728972   -1.703653
   92         1          0       4.284435   -5.513915    1.750109
   93         1          0      -4.297306   -5.521841   -1.184814
   94         6          0      -5.586879    0.813231   -1.003536
   95         1          0      -6.596424    0.778833   -0.609606
   96         1          0      -5.419076    1.768469   -1.500351
   97         6          0       5.866971    0.733714    0.475456
   98         1          0       6.787065    0.546671   -0.066840
   99         1          0       5.849954    1.766107    0.823671
  100         6          0      -5.287328   -0.308279   -1.967982
  101         6          0      -5.921873   -1.571437   -1.980390
  102         6          0      -4.328393   -0.075375   -2.968890
  103         6          0      -5.624308   -2.542520   -2.945436
  104         6          0      -4.000573   -1.046079   -3.920929
  105         1          0      -3.841837    0.893151   -3.005707
  106         6          0      -4.652553   -2.284587   -3.910569
  107         1          0      -6.150123   -3.486816   -2.920748
  108         1          0      -3.248015   -0.831668   -4.671110
  109         1          0      -4.411824   -3.041131   -4.647651
  110         7          0      -6.945721   -1.932039   -1.002826
  111         8          0      -7.754680   -2.863065   -1.297446
  112         8          0      -6.984429   -1.327751    0.110579
  113         6          0       5.672375   -0.192168    1.651151
  114         6          0       6.212599   -1.493368    1.768418
  115         6          0       4.927628    0.281544    2.744774
  116         6          0       6.027094   -2.274012    2.916882
  117         6          0       4.711898   -0.496881    3.886439
  118         1          0       4.522431    1.286448    2.700235
  119         6          0       5.264508   -1.779737    3.973626
  120         1          0       6.474597   -3.257146    2.963065
  121         1          0       4.124712   -0.098581    4.705942
  122         1          0       5.108616   -2.388718    4.855968
  123         7          0       7.020425   -2.092500    0.708623
  124         8          0       7.809802   -3.035717    1.017472
  125         8          0       6.896679   -1.674390   -0.481303
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Optimized Coordinates of 2-a at the CPCM(H₂O)-B3LYP/6-31G level.

Standard orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	17	0	5.283023	3.767934	-0.260097
2	17	0	-5.250273	3.772903	0.067905
3	8	0	4.794505	0.753770	-0.032251
4	8	0	0.024970	0.980967	0.199276
5	8	0	-4.742772	0.750224	-0.015068
6	6	0	0.039453	5.815890	1.753377
7	1	0	0.025470	8.441236	0.578613
8	1	0	-0.000268	8.806187	-1.899110
9	1	0	-0.014078	6.872135	-3.442467
10	1	0	-0.002896	4.542751	-2.572582
11	1	0	2.603200	4.766529	-0.043649
12	1	0	-2.562541	4.767765	0.115114
13	8	0	0.037461	4.418248	1.735128
14	8	0	0.050958	6.445826	2.814017
15	6	0	0.025330	6.290291	0.362450
16	6	0	0.019261	7.604594	-0.110822
17	6	0	0.004877	7.800187	-1.495415
18	6	0	-0.002983	6.699928	-2.371868
19	6	0	0.003193	5.383135	-1.887532
20	6	0	0.017451	5.194593	-0.506884
21	6	0	0.025398	3.892062	0.281776
22	6	0	1.279868	3.067876	0.119967
23	6	0	2.533476	3.687960	0.008707
24	6	0	3.683309	2.921152	-0.040272
25	6	0	3.637730	1.518478	0.035772
26	6	0	2.395336	0.865748	0.107870
27	6	0	1.237481	1.668804	0.146084
28	6	0	-1.186915	1.669031	0.134759
29	6	0	-2.342789	0.865569	0.060581
30	6	0	-3.586458	1.517305	0.001488
31	6	0	-3.638047	2.921723	0.033831
32	6	0	-2.488615	3.688353	0.090613
33	6	0	-1.231037	3.067916	0.135645
34	6	0	2.304977	-0.644000	0.149521
35	6	0	1.734196	-0.769793	-2.285863
36	6	0	2.299795	-1.139699	-3.641145
37	6	0	1.603238	-1.979170	-4.522436
38	6	0	2.154300	-2.272127	-5.775906
39	6	0	3.390012	-1.714862	-6.117395
40	6	0	4.024392	-0.883825	-5.187106
41	6	0	2.389104	-2.783287	-1.049396
42	6	0	3.437430	-3.455160	-0.189697
43	1	0	6.607159	-4.306161	-0.468723
44	1	0	6.194300	-5.249336	1.811768
45	1	0	-0.912438	-2.410537	4.516255
46	1	0	-2.055159	-2.923176	6.682662
47	1	0	-4.297537	-1.880018	7.141339
48	1	0	-5.286927	-0.372647	5.409898
49	7	0	2.539894	-1.310614	-1.164269
50	7	0	-2.582850	-1.303908	1.332138
51	7	0	3.500895	-0.597086	-3.974149
52	7	0	-4.723494	-3.562189	0.786548
53	6	0	5.632021	-4.221720	-0.001068
54	6	0	5.398977	-4.746801	1.273795
55	6	0	4.121646	-4.608880	1.826012
56	6	0	-2.248470	-0.644384	0.037120
57	6	0	-2.445101	-2.778990	1.229724
58	6	0	-3.454329	-3.439319	0.316097
59	6	0	-3.087731	-3.942025	-0.941288
60	6	0	-4.046128	-4.584176	-1.733763
61	6	0	-5.350825	-4.711474	-1.246850
62	6	0	-5.643305	-4.185558	0.015389
63	6	0	-1.845445	-0.770472	2.503905
64	6	0	-2.504227	-1.131170	3.818753
65	6	0	-1.882254	-1.981724	4.744166
66	6	0	-2.521833	-2.266166	5.957014
67	6	0	-3.768761	-1.689192	6.214701
68	6	0	-4.325012	-0.847536	5.244857
69	1	0	3.069255	-1.023359	0.832658
70	1	0	1.325184	-0.927333	0.563481
71	1	0	1.747397	0.319611	-2.204096
72	1	0	0.679305	-1.093650	-2.227666
73	1	0	0.644355	-2.392691	-4.229393
74	1	0	1.628918	-2.920783	-6.468393
75	1	0	3.851540	-1.912725	-7.077859
76	1	0	4.980713	-0.424661	-5.416590
77	1	0	2.470295	-3.194131	-2.059597
78	1	0	1.384459	-3.044042	-0.664811
79	1	0	-2.957143	-1.029053	-0.700619
80	1	0	-1.239188	-0.928500	-0.298633
81	1	0	-2.587953	-3.185046	2.234917
82	1	0	-1.424460	-3.054316	0.901886
83	1	0	-2.065530	-3.835031	-1.287611
84	1	0	-6.122392	-5.206274	-1.825085
85	1	0	-6.641732	-4.261312	0.432696
86	1	0	-1.840997	0.318827	2.420417
87	1	0	-0.792871	-1.106112	2.514781
88	7	0	-3.715963	-0.569170	4.070534
89	6	0	3.130245	-3.956887	1.083889
90	1	0	2.127961	-3.841078	1.481635
91	7	0	4.679791	-3.589304	-0.724045
92	1	0	3.899465	-5.002270	2.811933
93	1	0	-3.777926	-4.978251	-2.707893
94	6	0	-5.526527	0.693078	-1.270023
95	1	0	-5.758944	1.704659	-1.604574
96	1	0	-4.918095	0.213295	-2.042488
97	6	0	5.669163	0.729023	1.162682
98	1	0	5.941120	1.749040	1.437425
99	1	0	5.111946	0.292620	1.996960
100	6	0	-6.780953	-0.095920	-0.976617
101	6	0	-7.838407	-0.264312	-1.897159
102	6	0	-6.922086	-0.706354	0.275713
103	6	0	-8.993579	-1.002646	-1.568521
104	6	0	-8.051455	-1.456040	0.610751
105	6	0	-9.112281	-1.600660	-0.327302
106	1	0	-9.768876	-1.088115	-2.314643
107	7	0	-7.791533	0.303256	-3.216038
108	8	0	-8.805730	0.190908	-3.979099
109	8	0	-6.730277	0.904310	-3.598100
110	6	0	6.886454	-0.093877	0.812962
111	6	0	7.995030	-0.260335	1.671784
112	6	0	6.937333	-0.740638	-0.427989
113	6	0	9.111436	-1.033987	1.294803
114	6	0	8.028654	-1.524129	-0.809877
115	6	0	9.141632	-1.667200	0.066074
116	1	0	9.928915	-1.117256	1.994451
117	7	0	8.042960	0.345276	2.973552
118	8	0	9.095990	0.220187	3.680183
119	8	0	7.025882	0.992565	3.397557
120	1	0	6.089467	-0.631160	-1.085376
121	1	0	-6.114469	-0.595336	0.981572
122	8	0	-8.215819	-2.092587	1.809619
123	8	0	-10.194135	-2.349396	0.086285
124	8	0	10.181212	-2.450351	-0.390056
125	8	0	8.106566	-2.196161	-1.998205
126	6	0	11.349697	-2.626869	0.472173
127	1	0	11.070786	-3.116262	1.410548
128	1	0	12.023400	-3.265927	-0.095299
129	1	0	11.830005	-1.665226	0.678022
130	6	0	6.989533	-2.099190	-2.953728
131	1	0	6.855554	-1.062529	-3.274868
132	1	0	7.299153	-2.714726	-3.796042
133	1	0	6.072106	-2.489653	-2.503824
134	6	0	-7.159259	-1.987474	2.830769
135	1	0	-7.026102	-0.944397	3.130918
136	1	0	-7.532660	-2.573114	3.668511
137	1	0	-6.222436	-2.406085	2.451739
138	6	0	-11.312279	-2.527316	-0.839902
139	1	0	-10.987994	-3.048549	-1.745984
140	1	0	-12.032354	-3.136570	-0.297136
141	1	0	-11.758608	-1.562630	-1.100633

S54

Optimized Coordinates of 2-b at the CPCM(H₂O)-B3LYP/6-31G *level.*

Standard orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	17	0	5.190870	4.025532	-0.824673
2	17	0	-5.234706	4.034917	0.371992
3	8	0	4.748014	0.948282	-0.417468
4	8	0	0.027459	1.220209	0.219518
5	8	0	-4.736465	0.944832	0.246249
6	6	0	0.158491	6.053412	1.705085
7	1	0	0.048353	8.678495	0.534983
8	1	0	-0.177583	9.043489	-1.932554
9	1	0	-0.312559	7.109296	-3.469993
10	1	0	-0.227430	4.780127	-2.603718
11	1	0	2.568598	4.992428	-0.346861
12	1	0	-2.570669	4.996433	0.217143
13	8	0	0.154373	4.656770	1.688322
14	8	0	0.254126	6.685277	2.760759
15	6	0	0.034349	6.527545	0.319374
16	6	0	-0.011832	7.841824	-0.151831
17	6	0	-0.138160	8.037483	-1.530700
18	6	0	-0.214813	6.937204	-2.403773
19	6	0	-0.167246	5.620563	-1.921437
20	6	0	-0.041654	5.431858	-0.546391
21	6	0	0.028873	4.129070	0.238060
22	6	0	1.265196	3.304251	-0.020850
23	6	0	2.502652	3.915586	-0.262969
24	6	0	3.645174	3.147981	-0.407345
25	6	0	3.616090	1.744292	-0.299968
26	6	0	2.376206	1.100574	-0.108635
27	6	0	1.228757	1.905948	0.031750
28	6	0	-1.188502	1.905537	0.227687
29	6	0	-2.343753	1.099702	0.259022
30	6	0	-3.598189	1.742062	0.239424
31	6	0	-3.644156	3.149316	0.241002
32	6	0	-2.493252	3.917017	0.210916
33	6	0	-1.233349	3.303599	0.190359
34	6	0	2.272303	-0.406235	-0.066654
35	6	0	1.316863	-0.453253	-2.396245
36	6	0	1.673853	-0.810689	-3.823947
37	6	0	0.852719	-1.637334	-4.604379
38	6	0	1.221334	-1.926458	-5.923926
39	6	0	2.403510	-1.378540	-6.430654
40	6	0	3.168176	-0.558100	-5.593499
41	6	0	2.054086	-2.516357	-1.302537
42	6	0	3.196072	-3.257464	-0.643657
43	1	0	6.293083	-4.084733	-1.397080
44	1	0	6.165134	-5.211752	0.830582
45	1	0	-0.270393	-1.852375	4.666572
46	1	0	-1.094348	-2.256787	6.994384
47	1	0	-3.258249	-1.193603	7.711118
48	1	0	-4.491086	0.227163	6.063643
49	7	0	2.254469	-1.051773	-1.414252
50	7	0	-2.355608	-0.968608	1.700979
51	7	0	2.820008	-0.273630	-4.319037
52	7	0	-4.474614	-3.241050	1.626702
53	6	0	5.384417	-4.038829	-0.805392
54	6	0	5.308863	-4.676382	0.437985
55	6	0	4.113266	-4.588887	1.157714
56	6	0	-2.234797	-0.406195	0.321046
57	6	0	-2.162646	-2.439070	1.690750
58	6	0	-3.265487	-3.215939	1.006608
59	6	0	-3.032813	-3.926233	-0.180426
60	6	0	-4.065942	-4.685654	-0.742191
61	6	0	-5.309444	-4.711882	-0.103325
62	6	0	-5.467746	-3.972237	1.073779
63	6	0	-1.493869	-0.320625	2.723193
64	6	0	-1.953942	-0.610228	4.136703
65	6	0	-1.202061	-1.413324	5.006606
66	6	0	-1.663120	-1.636899	6.309745
67	6	0	-2.865822	-1.048177	6.711328
68	6	0	-3.557811	-0.254603	5.789419
69	1	0	3.144015	-0.803213	0.458617
70	1	0	1.377599	-0.682944	0.511889
71	1	0	1.385136	0.631960	-2.299546
72	1	0	0.269353	-0.740639	-2.196201
73	1	0	-0.059926	-2.044570	-4.182683
74	1	0	0.598488	-2.565595	-6.540359
75	1	0	2.725793	-1.575538	-7.446567
76	1	0	4.088409	-0.106554	-5.950777
77	1	0	1.947804	-2.903598	-2.320338
78	1	0	1.114349	-2.745126	-0.763623
79	1	0	-3.046514	-0.841811	-0.265903
80	1	0	-1.283297	-0.711556	-0.140934
81	1	0	-2.126881	-2.764654	2.734564
82	1	0	-1.191678	-2.704549	1.230084
83	1	0	-2.055398	-3.888194	-0.649047
84	1	0	-6.138863	-5.278619	-0.509323
85	1	0	-6.416982	-3.965339	1.599878
86	1	0	-1.555819	0.758429	2.570909
87	1	0	-0.434346	-0.612150	2.612524
88	7	0	-3.120473	-0.033796	4.529949
89	6	0	3.044775	-3.869876	0.609134
90	1	0	2.102635	-3.786532	1.139968
91	7	0	4.357571	-3.344560	-1.344097
92	1	0	4.012907	-5.069747	2.124702
93	1	0	-3.902016	-5.244879	-1.656872
94	6	0	-5.682997	1.083944	-0.911662
95	1	0	-6.349710	1.916627	-0.715125
96	1	0	-5.085695	1.284093	-1.804167
97	6	0	5.870905	1.181620	0.551260
98	1	0	6.512997	1.960736	0.154740
99	1	0	5.431386	1.505058	1.497568
100	6	0	-6.433797	-0.208748	-1.085672
101	6	0	-7.593212	-0.594115	-0.379624
102	6	0	-5.971309	-1.091359	-2.075249
103	6	0	-8.260794	-1.799608	-0.665369
104	6	0	-6.616024	-2.295252	-2.369017
105	6	0	-7.786912	-2.653338	-1.647564
106	1	0	-9.147385	-2.035703	-0.097316
107	7	0	-8.191945	0.224517	0.655813
108	8	0	-9.323870	-0.122946	1.126371
109	8	0	-7.585755	1.258860	1.075676
110	6	0	6.615785	-0.110489	0.754969
111	6	0	7.657742	-0.599381	-0.061143
112	6	0	6.288785	-0.871062	1.889346
113	6	0	8.348726	-1.783015	0.257941
114	6	0	6.952994	-2.055894	2.215505
115	6	0	8.008414	-2.516647	1.382476
116	1	0	9.143725	-2.099836	-0.399630
117	7	0	8.106302	0.087022	-1.255947
118	8	0	9.181659	-0.305992	-1.814668
119	8	0	7.425247	1.051446	-1.724850
120	1	0	5.500622	-0.506701	2.534871
121	1	0	-5.086292	-0.811382	-2.631079
122	8	0	-6.200881	-3.182690	-3.323623
123	8	0	-8.366760	-3.855307	-1.985701
124	8	0	8.616022	-3.691583	1.763968
125	8	0	6.664785	-2.830001	3.305839
126	6	0	9.739896	-4.190464	0.968138
127	1	0	10.556149	-3.462080	0.953005
128	1	0	10.058796	-5.099301	1.474265
129	1	0	9.420860	-4.421955	-0.052390
130	6	0	5.574509	-2.433563	4.203961
131	1	0	4.624253	-2.405910	3.663892
132	1	0	5.549830	-3.208223	4.967247
133	1	0	5.784370	-1.462476	4.660373
134	6	0	-5.004447	-2.879752	-4.117105
135	1	0	-4.125383	-2.802752	-3.471696
136	1	0	-4.900151	-3.725036	-4.793779
137	1	0	-5.143636	-1.956511	-4.686112
138	6	0	-9.591158	-4.262672	-1.292898
139	1	0	-10.390168	-3.533633	-1.457819
140	1	0	-9.859389	-5.218344	-1.738572
141	1	0	-9.407528	-4.386728	-0.221527

Optimized Coordinates of 3-a at the **CPCM(H₂O)-B3LYP/6-31G** *level.*

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                Standard orientation:
-----------------------------------------------------------
Center    Atomic    Atomic          Coordinates (Angstroms)
Number    Number    Type         X          Y          Z
-----------------------------------------------------------
    1       17        0       5.231460   3.471361  -1.055814
    2       17        0      -5.179010   3.553999  -0.454769
    3        8        0       4.757677   0.420453  -0.239470
    4        8        0       0.072465   0.844334   0.393496
    5        8        0      -4.631198   0.448022  -0.146412
    6        6        0       0.108263   5.705742   1.402447
    7        1        0       0.079269   8.269319   0.098268
    8        1        0       0.020970   8.511317  -2.393516
    9        1        0      -0.013179   6.503032  -3.839347
   10        1        0       0.009180   4.219520  -2.853633
   11        1        0       2.634987   4.493044  -0.652165
   12        1        0      -2.520075   4.531102  -0.427917
   13        8        0       0.105066   4.310444   1.455210
   14        8        0       0.133822   6.390505   2.428865
   15        6        0       0.076615   6.110332  -0.010475
   16        6        0       0.064229   7.399364  -0.548488
   17        6        0       0.031557   7.526371  -1.940875
   18        6        0       0.012120   6.384320  -2.761744
   19        6        0       0.024616   5.093341  -2.212259
   20        6        0       0.057336   4.973144  -0.824202
   21        6        0       0.073878   3.712546   0.025989
   22        6        0       1.319380   2.871972  -0.112812
   23        6        0       2.560135   3.436446  -0.431858
   24        6        0       3.698823   2.648040  -0.491199
   25        6        0       3.658811   1.267769  -0.215950
   26        6        0       2.410239   0.662604   0.043008
   27        6        0       1.276465   1.490319   0.109523
   28        6        0      -1.142590   1.501459   0.189403
   29        6        0      -2.288841   0.689762   0.225081
   30        6        0      -3.527505   1.290627  -0.082090
   31        6        0      -3.581459   2.682035  -0.281851
   32        6        0      -2.436619   3.463218  -0.275099
   33        6        0      -1.182477   2.879422  -0.060329
   34        6        0       2.271900  -0.835480   0.187226
   35        6        0       1.255840  -1.008049  -2.103958
   36        6        0       1.488849  -1.515388  -3.513346
   37        6        0       0.458506  -2.137031  -4.235208
   38        6        0       0.699427  -2.560687  -5.547551
   39        6        0       1.965113  -2.353932  -6.105046
   40        6        0       2.938505  -1.720580  -5.324710
   41        6        0       2.038631  -3.011422  -0.918035
   42        6        0       3.241756  -3.707220  -0.319363
   43        1        0       6.293670  -4.497319  -1.272805
   44        1        0       6.340437  -5.584106   0.978222
   45        1        0      -0.695271  -1.601100   5.289479
   46        1        0      -1.627482  -1.322243   7.595235
   47        1        0      -3.566801   0.244052   7.931874
   48        1        0      -4.474612   1.460818   5.945282
   49        7        0       2.219974  -1.554838  -1.121088
   50        7        0      -2.521323  -0.983618   2.063165
   51        7        0       2.715401  -1.304246  -4.058117
   52        7        0      -5.172693  -2.454049   2.370001
   53        6        0       5.428937  -4.451568  -0.618346
   54        6        0       5.454279  -5.058546   0.642179
   55        6        0       4.314017  -4.968388   1.446439
   56        6        0      -2.208272  -0.768726   0.620801
   57        6        0      -2.723366  -2.419047   2.371173
   58        6        0      -4.030734  -2.985610   1.860212
   59        6        0      -4.059054  -4.049780   0.947376
   60        6        0      -5.290873  -4.587879   0.556057
   61        6        0      -6.465158  -4.039812   1.080717
   62        6        0      -6.357576  -2.970473   1.976855
   63        6        0      -1.560812  -0.341408   2.994028
   64        6        0      -2.100252  -0.223041   4.403936

   65        6        0      -1.532654  -0.935857   5.470162
   66        6        0      -2.054371  -0.777794   6.759940
   67        6        0      -3.132636   0.091395   6.950577
   68        6        0      -3.642920   0.771400   5.838973
   69        1        0       3.134584  -1.231027   0.725410
   70        1        0       1.377454  -1.052963   0.790527
   71        1        0       1.382590   0.077770  -2.116878
   72        1        0       0.207800  -1.210817  -1.820201
   73        1        0      -0.515403  -2.272578  -3.776811
   74        1        0      -0.085024  -3.043579  -6.120480
   75        1        0       2.194101  -2.668659  -7.116699
   76        1        0       3.930922  -1.532225  -5.722481
   77        1        0       1.853617  -3.451614  -1.902337
   78        1        0       1.149563  -3.218199  -0.292574
   79        1        0      -2.951258  -1.334761   0.058398
   80        1        0      -1.215976  -1.168795   0.363137
   81        1        0      -2.725351  -2.514028   3.461564
   82        1        0      -1.884570  -3.033233   1.994797
   83        1        0      -3.130303  -4.451628   0.557128
   84        1        0      -7.439296  -4.426817   0.805498
   85        1        0      -7.244849  -2.510634   2.399811
   86        1        0      -1.371444   0.668580   2.625159
   87        1        0      -0.591333  -0.871466   3.012769
   88        7        0      -3.144578   0.626411   4.591219
   89        6        0       3.195583  -4.281759   0.959267
   90        1        0       2.294467  -4.196648   1.556676
   91        7        0       4.351728  -3.791963  -1.099051
   92        1        0       4.293264  -5.423188   2.430874
   93        1        0      -5.330623  -5.415290  -0.143914
   94        6        0      -5.598282   0.586092  -1.267725
   95        1        0      -6.458938   1.129604  -0.899808
   96        1        0      -5.139484   1.153704  -2.074141
   97        6        0       6.059678   0.840282   0.341422
   98        1        0       6.681323   1.216027  -0.460759
   99        1        0       5.897814   1.631986   1.068459
  100        6        0      -5.980450  -0.794365  -1.765080
  101        6        0      -5.079664  -1.638823  -2.446127
  102        6        0      -7.283822  -1.308154  -1.579066
  103        6        0      -5.438144  -2.896212  -2.941653
  104        6        0      -7.664318  -2.555140  -2.096180
  105        6        0      -6.745647  -3.345725  -2.784986
  106        1        0      -4.696932  -3.496173  -3.451932
  107        1        0      -8.675869  -2.907356  -1.948105
  108        1        0      -7.042451  -4.306525  -3.185173
  109        7        0      -3.683833  -1.252850  -2.684193
  110        8        0      -2.818085  -2.177973  -2.669977
  111        8        0      -3.395724  -0.044730  -2.912584
  112        6        0       6.675162  -0.370474   1.012353
  113        6        0       6.118940  -0.965315   2.163352
  114        6        0       7.840188  -0.983907   0.500603
  115        6        0       6.674063  -2.088824   2.782918
  116        6        0       8.420609  -2.096496   1.127369
  117        6        0       7.840399  -2.647594   2.268626
  118        1        0       6.194264  -2.501724   3.659701
  119        1        0       9.320282  -2.532070   0.715030
  120        1        0       8.290190  -3.506418   2.749773
  121        7        0       4.906294  -0.436213   2.799865
  122        8        0       4.144185  -1.262474   3.380816
  123        8        0       4.675016   0.806531   2.772569
  124        6        0      -8.306584  -0.538540  -0.797453
  125        6        0       8.502520  -0.459777  -0.738652
  126        9        0       9.619263  -1.199171  -1.101265
  127        9        0       8.940592   0.863884  -0.599866
  128        9        0       7.651522  -0.462892  -1.847678
  129        9        0      -7.875940  -0.250383   0.501765
  130        9        0      -9.507246  -1.221281  -0.668892
  131        9        0      -8.623767   0.697150  -1.376506
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Optimized Coordinates of 3-b at the CPCM(H₂O)-B3LYP/6-31G *level.*

Standard orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	17	0	5.210773	3.320454	-1.562511
2	17	0	-5.188490	3.534493	-0.839681
3	8	0	4.718350	0.382917	-0.552153
4	8	0	0.062558	0.926353	0.273557
5	8	0	-4.670254	0.543451	-0.086979
6	6	0	0.148736	5.821412	0.858165
7	1	0	0.110262	8.287522	-0.618788
8	1	0	0.009980	8.358118	-3.120120
9	1	0	-0.059957	6.255400	-4.423142
10	1	0	-0.034147	4.045724	-3.284225
11	1	0	2.624969	4.428324	-1.195926
12	1	0	-2.518390	4.518130	-0.925664
13	8	0	0.141200	4.433448	1.008147
14	8	0	0.196484	6.575662	1.833917
15	6	0	0.092720	6.126495	-0.578624
16	6	0	0.078600	7.375353	-1.203838
17	6	0	0.022534	7.406594	-2.600892
18	6	0	-0.017371	6.211006	-3.340458
19	6	0	-0.003276	4.960740	-2.703710
20	6	0	0.052361	4.935635	-1.311149
21	6	0	0.076058	3.737551	-0.375615
22	6	0	1.310490	2.875470	-0.477228
23	6	0	2.545909	3.395210	-0.884681
24	6	0	3.670145	2.585737	-0.910436
25	6	0	3.620904	1.232605	-0.526171
26	6	0	2.380254	0.672009	-0.160957
27	6	0	1.260629	1.521474	-0.124533
28	6	0	-1.152999	1.570569	0.033422
29	6	0	-2.304455	0.781196	0.194268
30	6	0	-3.542001	1.353750	-0.158777
31	6	0	-3.587732	2.705662	-0.543722
32	6	0	-2.440567	3.476664	-0.643177
33	6	0	-1.188319	2.911618	-0.370270
34	6	0	2.235574	-0.802007	0.136947
35	6	0	1.102801	-1.163526	-2.086452
36	6	0	1.270640	-1.820170	-3.443160
37	6	0	0.207282	-2.501437	-4.054426
38	6	0	0.389575	-3.065155	-5.322932
39	6	0	1.632810	-2.935103	-5.949092
40	6	0	2.642810	-2.235598	-5.279473
41	6	0	1.855397	-3.066424	-0.723821
42	6	0	3.079288	-3.766725	-0.174164
43	1	0	5.960241	-4.852106	-1.345455
44	1	0	6.200457	-5.688514	0.998588
45	1	0	-0.435770	-0.800681	5.401067
46	1	0	-1.278523	-0.316403	7.706646
47	1	0	-3.305825	1.149801	7.968004
48	1	0	-4.387168	2.065809	5.908195
49	7	0	2.080129	-1.647746	-1.084391
50	7	0	-2.455389	-0.670464	2.224821
51	7	0	2.475333	-1.684601	-4.056784
52	7	0	-4.984870	-2.204048	3.021614
53	6	0	5.178008	-4.678501	-0.613181
54	6	0	5.311593	-5.145612	0.699149
55	6	0	4.273970	-4.895718	1.602233
56	6	0	-2.224385	-0.621790	0.751906
57	6	0	-2.562476	-2.068836	2.704789
58	6	0	-3.891807	-2.727773	2.406593
59	6	0	-3.981675	-3.864325	1.590087
60	6	0	-5.223316	-4.485086	1.408940
61	6	0	-6.346895	-3.947431	2.044329
62	6	0	-6.180794	-2.804216	2.834209
63	6	0	-1.492046	0.123512	3.027326
64	6	0	-1.973886	0.370598	4.441477
65	6	0	-1.308950	-0.174502	5.549588
66	6	0	-1.780663	0.098528	6.839420
67	6	0	-2.907474	0.912388	6.988366
68	6	0	-3.514795	1.423863	5.835914
69	1	0	3.132924	-1.148031	0.652283
70	1	0	1.383524	-0.942184	0.820137
71	1	0	1.269611	-0.090921	-2.214896
72	1	0	0.057149	-1.292990	-1.754925
73	1	0	-0.749269	-2.577632	-3.550000
74	1	0	-0.422607	-3.594886	-5.809033
75	1	0	1.817334	-3.357740	-6.929984
76	1	0	3.619655	-2.103266	-5.734211
77	1	0	1.558808	-3.588327	-1.638296
78	1	0	1.021930	-3.166688	-0.003155
79	1	0	-3.005041	-1.227159	0.291005
80	1	0	-1.252112	-1.066484	0.488547
81	1	0	-2.446252	-2.045534	3.792498
82	1	0	-1.742684	-2.693517	2.305069
83	1	0	-3.090667	-4.259308	1.114209
84	1	0	-7.325879	-4.399691	1.935903
85	1	0	-7.027384	-2.355077	3.343965
86	1	0	-1.380679	1.094826	2.541332
87	1	0	-0.492650	-0.346416	3.055418
88	7	0	-3.066049	1.166358	4.587510
89	6	0	3.144975	-4.196559	1.159005
90	1	0	2.320204	-3.992645	1.833246
91	7	0	4.090587	-4.005753	-1.050507
92	1	0	4.339026	-5.238904	2.629074
93	1	0	-5.309581	-5.368561	0.785902
94	6	0	-5.531969	0.431241	-1.299589
95	1	0	-6.405542	1.056660	-1.146231
96	1	0	-4.981112	0.805822	-2.160142
97	6	0	5.978641	0.791064	0.129164
98	1	0	6.660869	1.177192	-0.620774
99	1	0	5.759187	1.581152	0.843733
100	6	0	-5.938572	-1.013242	-1.513255
101	6	0	-7.105392	-1.564461	-0.943217
102	6	0	-5.213071	-1.868503	-2.377917
103	6	0	-7.547623	-2.863333	-1.217520
104	6	0	-5.635203	-3.178790	-2.641636
105	6	0	-6.801695	-3.677608	-2.061514
106	1	0	-8.462058	-3.215925	-0.761098
107	1	0	-5.055694	-3.802785	-3.308021
108	1	0	-7.125917	-4.688902	-2.270428
109	7	0	-7.961189	-0.792084	-0.035501
110	8	0	-9.191557	-1.087222	0.004743
111	8	0	-7.446161	0.111124	0.683547
112	6	0	6.567276	-0.419472	0.823313
113	6	0	7.443524	-1.319506	0.180443
114	6	0	6.309251	-0.679143	2.190318
115	6	0	8.040221	-2.399612	0.840250
116	6	0	6.888869	-1.767536	2.855564
117	6	0	7.752891	-2.630099	2.180558
118	1	0	8.714035	-3.044089	0.292779
119	1	0	6.666810	-1.934467	3.900596
120	1	0	8.198986	-3.470323	2.696669
121	7	0	7.820206	-1.163710	-1.230125
122	8	0	8.930978	-1.648137	-1.597466
123	8	0	7.031430	-0.577883	-2.025236
124	6	0	-3.993395	-1.381695	-3.100852
125	6	0	5.442170	0.240042	2.996889
126	9	0	-3.023306	-0.843359	-2.248421
127	9	0	-4.281040	-0.372746	-4.028272
128	9	0	-3.355683	-2.391138	-3.813166
129	9	0	4.183329	0.451076	2.424558
130	9	0	5.209279	-0.232534	4.279877
131	9	0	6.004108	1.515293	3.147277

Optimized Coordinates of 1-a at the CPCM(H₂O)-B3LYP/6-31G(d) level.

$E = -4349.306463$

Sum of electronic and thermal free energies = −4348.465679

```
                 Standard orientation:
---------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number      Type        X           Y           Z
---------------------------------------------------------------
    1        17          0      -5.215230    3.324357    0.233376
    2        17          0       5.198892    3.344395   -0.531161
    3         8          0      -4.716664    0.362821    0.284066
    4         8          0      -0.010509    0.607107   -0.249687
    5         8          0       4.729379    0.389708   -0.314680
    6         6          0      -0.121268    5.413647   -1.884558
    7         1          0      -0.051473    8.043536   -0.679991
    8         1          0       0.100830    8.367571    1.800216
    9         1          0       0.194225    6.411168    3.306651
   10         1          0       0.140039    4.095919    2.403789
   11         1          0      -2.606385    4.364994   -0.151839
   12         1          0       2.556763    4.376737   -0.515241
   13         8          0      -0.115086    4.044457   -1.866468
   14         8          0      -0.186089    6.039945   -2.919527
   15         6          0      -0.038072    5.890010   -0.490425
   16         6          0      -0.009251    7.196688   -0.002172
   17         6          0       0.075517    7.367457    1.378763
   18         6          0       0.128582    6.254547    2.234046
   19         6          0       0.098586    4.949190    1.733743
   20         6          0       0.014484    4.786608    0.354139
   21         6          0      -0.032046    3.513682   -0.477370
   22         6          0      -1.268956    2.675046   -0.236537
   23         6          0      -2.523417    3.284547   -0.121848
   24         6          0      -3.665980    2.519927    0.038581
   25         6          0      -3.592147    1.114658    0.083605
   26         6          0      -2.347406    0.476914   -0.002940
   27         6          0      -1.201498    1.281153   -0.168144
   28         6          0       1.177876    1.287956   -0.307781
   29         6          0       2.339622    0.489951   -0.279552
   30         6          0       3.582103    1.136306   -0.318572
   31         6          0       3.642275    2.539653   -0.411664
   32         6          0       2.484644    3.297736   -0.439936
   33         6          0       1.229297    2.682248   -0.380715
   34         6          0      -2.254933   -1.033986    0.075943
   35         6          0      -1.453528   -1.104999    2.392858
   36         6          0      -1.871719   -1.326705    3.835072
   37         6          0      -1.147126   -2.174883    4.679616
   38         6          0      -1.554369   -2.327293    6.005887
   39         6          0      -2.675111   -1.626528    6.445190
   40         6          0      -3.334942   -0.802009    5.530671
   41         6          0      -2.513365   -3.040662    1.400540
   42         6          0      -3.743044   -3.597511    0.708466
   43         1          0      -6.957439   -3.741412    1.286134
   44         1          0      -6.939664   -5.024097   -0.850114
   45         1          0       0.475876   -3.186406   -4.286650
   46         1          0       1.285335   -3.697715   -6.598062
   47         1          0       3.309034   -2.470749   -7.457974
   48         1          0       4.404781   -0.802148   -5.966413
   49         7          0      -2.465525   -1.570432    1.433567
   50         7          0       2.547540   -1.688810   -1.494179
   51         7          0      -2.953689   -0.645107    4.257463
   52         7          0       5.055715   -3.432185   -1.183455
   53         6          0      -6.020908   -3.914798    0.758717
   54         6          0      -6.014191   -4.632983   -0.439342
   55         6          0      -4.792466   -4.829958   -1.079088
   56         6          0       2.266581   -1.022254   -0.208311
   57         6          0       2.639581   -3.145375   -1.301847
   58         6          0       3.879633   -3.582166   -0.545280
   59         6          0       3.790568   -4.142842    0.734021
   60         6          0       4.955886   -4.561179    1.378005
   61         6          0       6.174370   -4.405929    0.720907
   62         6          0       6.165882   -3.836664   -0.554632
   63         6          0       1.555464   -1.361721   -2.529035
   64         6          0       2.024793   -1.727862   -3.925091
   65         6          0       1.345004   -2.678648   -4.694261
   66         6          0       1.797582   -2.962706   -5.983649
   67         6          0       2.917468   -2.286840   -6.462442
   68         6          0       3.530361   -1.353299   -5.623126
   69         1          0      -3.036468   -1.461091   -0.557875
   70         1          0      -1.291219   -1.361675   -0.343725
   71         1          0      -1.328674   -0.028211    2.246370
   72         1          0      -0.468359   -1.574730    2.217386
   73         1          0      -0.278852   -2.705974    4.300764
   74         1          0      -1.006937   -2.981203    6.678840
   75         1          0      -3.032267   -1.709642    7.466829
   76         1          0      -4.211736   -0.235134    5.840649
   77         1          0      -2.528358   -3.388204    2.438393
   78         1          0      -1.605441   -3.461831    0.929258
   79         1          0       3.021687   -1.371939    0.499956
   80         1          0       1.286983   -1.321281    0.195952
   81         1          0       2.677762   -3.603147   -2.295214
   82         1          0       1.739860   -3.541591   -0.795151
   83         1          0       2.821971   -4.250064    1.213383
   84         1          0       7.108874   -4.717426    1.176771
   85         1          0       7.099429   -3.702129   -1.098375
   86         1          0       1.397853   -0.279642   -2.507262
   87         1          0       0.577820   -1.837491   -2.330011
   88         7          0       3.105234   -1.069581   -4.386226
   89         6          0      -3.639462   -4.303000   -0.495794
   90         1          0      -2.668922   -4.436678   -0.964400
   91         7          0      -4.921971   -3.407430    1.330318
   92         1          0      -4.734989   -5.382054   -2.012893
   93         1          0       4.910111   -4.999107    2.371098
   94         6          0       5.427443    0.329954    0.945772
   95         1          0       5.401396    1.306049    1.437205
   96         1          0       4.915448   -0.379419    1.603306
   97         6          0      -5.570677    0.175913   -0.861526
   98         1          0      -5.617577    1.093689   -1.452605
   99         1          0      -5.144134   -0.602805   -1.501539
  100         6          0       6.858734   -0.096266    0.692322
  101         6          0       7.784493   -0.397719    1.714349
  102         6          0       7.323582   -0.213078   -0.623300
  103         6          0       9.097118   -0.794462    1.440156
  104         6          0       8.632692   -0.601360   -0.908712
  105         1          0       6.636603    0.002482   -1.431104
  106         6          0       9.526165   -0.894410    0.123069
  107         1          0       9.760346   -1.012685    2.266971
  108         1          0       8.952813   -0.673915   -1.943811
  109         1          0      10.545739   -1.195843   -0.093419
  110         7          0       7.418823   -0.301919    3.128378
  111         8          0       8.211793   -0.724988    3.972628
  112         8          0       6.329999    0.204743    3.422444
  113         6          0      -6.951812   -0.217661   -0.378033
  114         6          0      -8.024918   -0.548386   -1.233663
  115         6          0      -7.211965   -0.272308    0.996924
  116         6          0      -9.284879   -0.909371   -0.745261
  117         6          0      -8.465201   -0.629017    1.494908
  118         1          0      -6.408171   -0.033429    1.680791
  119         6          0      -9.508651   -0.949183    0.624642
  120         1          0     -10.068802   -1.150831   -1.450987
  121         1          0      -8.623554   -0.655369    2.568868
  122         1          0     -10.485812   -1.226347    1.006248
  123         7          0      -7.876944   -0.526853   -2.689893
  124         8          0      -8.827560   -0.892480   -3.385146
  125         8          0      -6.804181   -0.141055   -3.168428
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Optimized Coordinates of 1-b at the CPCM(H₂O)-B3LYP/6-31G(d) *level.*

$E = -4349.294769$

Sum of electronic and thermal free energies = −4348.448758

```
                    Standard orientation:
---------------------------------------------------------------
Center     Atomic      Atomic            Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
---------------------------------------------------------------
    1        17          0       -5.172832    3.661627    0.124462
    2        17          0        5.227974    3.578816   -0.696720
    3         8          0       -4.712874    0.657108    0.061322
    4         8          0        0.010133    0.888975   -0.232604
    5         8          0        4.741607    0.612207   -0.255066
    6         6          0       -0.041288    5.751250   -1.810424
    7         1          0        0.050208    8.333077   -0.504722
    8         1          0        0.187188    8.559066    1.986982
    9         1          0        0.245643    6.544981    3.417369
   10         1          0        0.171363    4.266938    2.424849
   11         1          0       -2.559509    4.662978   -0.216150
   12         1          0        2.610501    4.622838   -0.608520
   13         8          0       -0.049923    4.382264   -1.844368
   14         8          0       -0.091751    6.416972   -2.821363
   15         6          0        0.036903    6.173553   -0.398731
   16         6          0        0.077219    7.460111    0.139937
   17         6          0        0.153314    7.576310    1.526994
   18         6          0        0.186579    6.430591    2.339032
   19         6          0        0.145332    5.146090    1.788349
   20         6          0        0.070021    5.038003    0.402998
   21         6          0        0.015654    3.797676   -0.476762
   22         6          0       -1.231377    2.965479   -0.273963
   23         6          0       -2.484376    3.581741   -0.191218
   24         6          0       -3.636881    2.826374   -0.067840
   25         6          0       -3.581249    1.416240   -0.032671
   26         6          0       -2.331456    0.776108   -0.035379
   27         6          0       -1.177307    1.573170   -0.185361
   28         6          0        1.204258    1.557995   -0.311561
   29         6          0        2.357878    0.746034   -0.289068
   30         6          0        3.611503    1.377574   -0.317907
   31         6          0        3.677819    2.779998   -0.466964
   32         6          0        2.527487    3.547710   -0.496297
   33         6          0        1.266618    2.949969   -0.398316
   34         6          0       -2.228958   -0.723980    0.151096
   35         6          0       -1.278366   -0.536040    2.424003
   36         6          0       -1.598806   -0.667485    3.902003
   37         6          0       -0.768579   -1.394034    4.762681
   38         6          0       -1.087178   -1.464817    6.119783
   39         6          0       -2.227514   -0.806017    6.573121
   40         6          0       -2.994712   -0.103108    5.640780
   41         6          0       -2.262850   -2.610769    1.663592
   42         6          0       -3.565038   -3.303324    1.309836
   43         1          0       -6.584881   -3.479268    2.549992
   44         1          0       -6.876063   -5.136032    0.711763
   45         1          0        0.120614   -2.448863   -4.423331
   46         1          0        0.824952   -2.967759   -6.767511
   47         1          0        2.990812   -1.998715   -7.610276
   48         1          0        4.324889   -0.563887   -6.070225
   49         7          0       -2.309699   -1.143624    1.568362
   50         7          0        2.412091   -1.383074   -1.607302
   51         7          0       -2.699483   -0.025578    4.337826
   52         7          0        4.660873   -3.443084   -1.605881
   53         6          0       -5.757245   -3.704477    1.879265
   54         6          0       -5.924196   -4.633077    0.848582
   55         6          0       -4.838883   -4.885523    0.011921
   56         6          0        2.248855   -0.764729   -0.271586
   57         6          0        2.302592   -2.845968   -1.498322
   58         6          0        3.518282   -3.525916   -0.898442
   59         6          0        3.426868   -4.258792    0.289972
   60         6          0        4.551578   -4.938748    0.759174
   61         6          0        5.734909   -4.858478    0.027761
   62         6          0        5.734444   -4.092551   -1.140863
   63         6          0        1.463522   -0.871839   -2.610057
   64         6          0        1.862652   -1.238240   -4.027898
   65         6          0        1.047843   -2.050369   -4.824561
   66         6          0        1.441795   -2.338577   -6.132055
   67         6          0        2.639826   -1.805184   -6.601517
   68         6          0        3.386142   -1.002818   -5.734986
   69         1          0       -3.065468   -1.199567   -0.366258
   70         1          0       -1.303394   -1.087743   -0.321755
   71         1          0       -1.238970    0.531322    2.193926
   72         1          0       -0.273464   -0.950201    2.227206
   73         1          0        0.112713   -1.894699    4.372495
   74         1          0       -0.456943   -2.024104    6.805457
   75         1          0       -2.518961   -0.829123    7.618473
   76         1          0       -3.889632    0.428863    5.960799
   77         1          0       -2.040311   -2.863229    2.705158
   78         1          0       -1.443126   -3.028748    1.050886
   79         1          0        3.041884   -1.167884    0.362521
   80         1          0        1.288576   -1.052225    0.183672
   81         1          0        2.182461   -3.240156   -2.512403
   82         1          0        1.399725   -3.139786   -0.931555
   83         1          0        2.486404   -4.300022    0.831497
   84         1          0        6.636377   -5.371155    0.347631
   85         1          0        6.642487   -4.003269   -1.734897
   86         1          0        1.464362    0.218953   -2.544172
   87         1          0        0.429930   -1.211263   -2.419191
   88         7          0        3.018685   -0.716775   -4.480246
   89         6          0       -3.641824   -4.206740    0.244444
   90         1          0       -2.773631   -4.379386   -0.384691
   91         7          0       -4.612449   -3.054775    2.118858
   92         1          0       -4.919377   -5.596787   -0.805151
   93         1          0        4.502048   -5.519438    1.675900
   94         6          0        5.622499    0.840694    0.883729
   95         1          0        6.630988    0.912878    0.485646
   96         1          0        5.363467    1.787280    1.359828
   97         6          0       -5.658602    0.755540   -1.043799
   98         1          0       -6.630398    0.979579   -0.611134
   99         1          0       -5.366468    1.578268   -1.697975
  100         6          0        5.489134   -0.260799    1.913697
  101         6          0        6.245440   -1.448560    1.946065
  102         6          0        4.579375   -0.070660    2.962761
  103         6          0        6.109830   -2.390561    2.968548
  104         6          0        4.410496   -1.014286    3.976367
  105         1          0        3.999102    0.847082    2.986760
  106         6          0        5.179631   -2.178597    3.980794
  107         1          0        6.725569   -3.280337    2.950953
  108         1          0        3.688253   -0.832563    4.766172
  109         1          0        5.062423   -2.916243    4.767915
  110         7          0        7.232811   -1.763342    0.905859
  111         8          0        8.126620   -2.566425    1.183447
  112         8          0        7.117499   -1.232344   -0.201143
  113         6          0       -5.677831   -0.516146   -1.864599
  114         6          0       -6.494936   -1.636816   -1.618291
  115         6          0       -4.866731   -0.573411   -3.005926
  116         6          0       -6.511193   -2.747775   -2.464563
  117         6          0       -4.849888   -1.686509   -3.846930
  118         1          0       -4.242903    0.283448   -3.243037
  119         6          0       -5.676512   -2.777818   -3.576951
  120         1          0       -7.167617   -3.576704   -2.234197
  121         1          0       -4.200565   -1.693945   -4.716858
  122         1          0       -5.677326   -3.645914   -4.227943
  123         7          0       -7.387232   -1.698207   -0.454005
  124         8          0       -8.337785   -2.482960   -0.495755
  125         8          0       -7.140483   -0.982662    0.519449
---------------------------------------------------------------
```

Optimized Coordinates of 1-a at the **B3LYP/6-31G(d)** *level.*

$E = -4349.260154$

Sum of electronic and thermal free energies = -4348.418465

Standard orientation:
```
---------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type          X            Y            Z
---------------------------------------------------------------------
   1         17          0       -5.213268     3.567349    -0.011759
   2         17          0        5.214317     3.506747    -0.510882
   3          8          0       -4.727070     0.586811     0.106202
   4          8          0       -0.014244     0.804778    -0.232598
   5          8          0        4.710472     0.539780    -0.250915
   6          6          0       -0.027884     5.689238    -1.776752
   7          1          0        0.020202     8.244457    -0.431841
   8          1          0        0.083146     8.440689     2.072032
   9          1          0        0.103810     6.406790     3.475163
  10          1          0        0.063596     4.143447     2.446692
  11          1          0       -2.588896     4.577064    -0.306587
  12          1          0        2.585407     4.549930    -0.512782
  13          8          0       -0.035131     4.314317    -1.822038
  14          8          0       -0.047986     6.374042    -2.767770
  15          6          0        0.008255     6.088714    -0.350659
  16          6          0        0.030074     7.366517     0.206902
  17          6          0        0.064874     7.464097     1.597093
  18          6          0        0.076628     6.307783     2.393534
  19          6          0        0.054332     5.032440     1.822530
  20          6          0        0.019981     4.943024     0.433945
  21          6          0       -0.007341     3.717847    -0.471254
  22          6          0       -1.259345     2.880686    -0.304920
  23          6          0       -2.515034     3.496241    -0.262677
  24          6          0       -3.671801     2.744268    -0.148915
  25          6          0       -3.610876     1.337985    -0.092919
  26          6          0       -2.365773     0.692507    -0.130898
  27          6          0       -1.205122     1.487262    -0.228373
  28          6          0        1.181091     1.478291    -0.265642
  29          6          0        2.338468     0.676276    -0.189074
  30          6          0        3.588785     1.310069    -0.236402
  31          6          0        3.659706     2.711405    -0.361549
  32          6          0        2.505078     3.473336    -0.412396
  33          6          0        1.243700     2.870282    -0.358208
  34          6          0       -2.280262    -0.821149    -0.095978
  35          6          0       -2.015980    -0.866883     2.352882
  36          6          0       -2.719502    -1.224806     3.650117
  37          6          0       -2.073598    -1.963365     4.647807
  38          6          0       -2.749465    -2.240693     5.836485
  39          6          0       -4.050607    -1.769905     5.988962
  40          6          0       -4.611673    -1.039202     4.938237
  41          6          0       -2.478184    -2.894998     1.129824
  42          6          0       -3.337921    -3.604352     0.100443
  43          1          0       -6.488099    -4.385698    -0.241464
  44          1          0       -5.650854    -5.416728    -2.356625
  45          1          0        1.292336    -2.776831    -4.540080
  46          1          0        2.636106    -3.546810    -6.505901
  47          1          0        5.047167    -2.839035    -6.659030
  48          1          0        5.975694    -1.400863    -4.842666
  49          7          0       -2.672142    -1.443709     1.179432
  50          7          0        2.715042    -1.602849    -1.201219
  51          7          0       -3.974244    -0.766214     3.796929
  52          7          0        4.605840    -3.749407    -0.004956
  53          6          0       -5.431329    -4.335601    -0.498939
  54          6          0       -4.965314    -4.910725    -1.683514
  55          6          0       -3.605113    -4.815437    -1.967044
  56          6          0        2.244478    -0.829831    -0.040865
  57          6          0        2.497681    -3.035704    -0.992081
  58          6          0        3.279629    -3.623511     0.168001
  59          6          0        2.637108    -4.041875     1.339700
  60          6          0        3.393145    -4.604696     2.367628
  61          6          0        4.769150    -4.729345     2.192688
  62          6          0        5.320923    -4.284259     0.989068
  63          6          0        2.156452    -1.168057    -2.481729
  64          6          0        2.943439    -1.692264    -3.670244
  65          6          0        2.336953    -2.495749    -4.642270
  66          6          0        3.086799    -2.923235    -5.738282
  67          6          0        4.420814    -2.535110    -5.825659
  68          6          0        4.938583    -1.731924    -4.806234
  69          1          0       -2.954317    -1.221517    -0.860041
  70          1          0       -1.259897    -1.117928    -0.389126
  71          1          0       -2.050243     0.221159     2.249792
  72          1          0       -0.948041    -1.156343     2.423000
  73          1          0       -1.056253    -2.312203     4.492467
  74          1          0       -2.267761    -2.813257     6.624734
  75          1          0       -4.619395    -1.956656     6.894941
  76          1          0       -5.624275    -0.646773     5.022758
  77          1          0       -2.742574    -3.294362     2.113690
  78          1          0       -1.412604    -3.149027     0.943748
  79          1          0        2.864600    -1.133304     0.809151
  80          1          0        1.204967    -1.089552     0.219464
  81          1          0        2.818373    -3.551494    -1.902314
  82          1          0        1.419125    -3.259510    -0.847302
  83          1          0        1.560974    -3.927365     1.439254
  84          1          0        5.402166    -5.160589     2.962397
  85          1          0        6.392789    -4.361276     0.813596
  86          1          0        2.202139    -0.075911    -2.512217
  87          1          0        1.091197    -1.452457    -2.595346
  88          7          0        4.230302    -1.314112    -3.754051
  89          6          0       -2.778802    -4.151209    -1.060988
  90          1          0       -1.712611    -4.054887    -1.247822
  91          7          0       -4.648306    -3.702085     0.379266
  92          1          0       -3.193795    -5.247700    -2.875414
  93          1          0        2.915960    -4.937975     3.285528
  94          6          0        5.506093     0.489046     0.943052
  95          1          0        5.821113     1.493241     1.235746
  96          1          0        4.910781     0.080482     1.767949
  97          6          0       -5.621019     0.379247    -0.998748
  98          1          0       -5.977171     1.335028    -1.389524
  99          1          0       -5.092033    -0.128951    -1.813045
 100          6          0        6.702653    -0.394162     0.651215
 101          6          0        7.810880    -0.526290     1.512104
 102          6          0        6.739169    -1.124245    -0.544958
 103          6          0        8.912170    -1.325339     1.193478
 104          6          0        7.829123    -1.933276    -0.864478
 105          1          0        5.894857    -1.061576    -1.221130
 106          6          0        8.922035    -2.033663    -0.001418
 107          1          0        9.736603    -1.374345     1.893397
 108          1          0        7.816051    -2.490903    -1.796563
 109          1          0        9.773327    -2.659364    -0.252676
 110          7          0        7.861965     0.163034     2.807933
 111          8          0        8.926639     0.167069     3.425246
 112          8          0        6.827555     0.696257     3.223471
 113          6          0       -6.773094    -0.464583    -0.489743
 114          6          0       -7.942538    -0.729742    -1.230709
 115          6          0       -6.701359    -1.017315     0.796706
 116          6          0       -8.997346    -1.487658    -0.715243
 117          6          0       -7.745144    -1.783362     1.314455
 118          1          0       -5.808296    -0.851877     1.387168
 119          6          0       -8.899139    -2.018214     0.564856
 120          1          0       -9.871954    -1.644759    -1.333538
 121          1          0       -7.646764    -2.202303     2.311805
 122          1          0       -9.714418    -2.610728     0.969337
 123          7          0       -8.112397    -0.229763    -2.601782
 124          8          0       -9.217863    -0.342655    -3.130817
 125          8          0       -7.132194     0.270317    -3.163084
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Optimized Coordinates of 1-b at the B3LYP/6-31G(d) *level.*

E = −4349.238096

Sum of electronic and thermal free energies = −4348.393169

```
                  Standard orientation:
---------------------------------------------------------------
Center     Atomic     Atomic         Coordinates (Angstroms)
Number     Number     Type        X          Y          Z
---------------------------------------------------------------
   1         17         0       5.251123   3.349197  -1.139648
   2         17         0      -5.034753   3.720641   0.236458
   3          8         0       4.752618   0.392534  -0.578814
   4          8         0       0.102549   0.840763   0.229849
   5          8         0      -4.637404   0.704280   0.229263
   6          6         0       0.411457   5.678074   1.459753
   7          1         0       0.342437   8.262859   0.177494
   8          1         0       0.070729   8.522805  -2.306838
   9          1         0      -0.146474   6.525499  -3.745765
  10          1         0      -0.104959   4.237616  -2.771626
  11          1         0       2.731013   4.475125  -0.613824
  12          1         0      -2.388875   4.661994   0.081525
  13          8         0       0.364257   4.305972   1.479321
  14          8         0       0.556215   6.341951   2.455415
  15          6         0       0.261327   6.111307   0.050481
  16          6         0       0.241979   7.401923  -0.476383
  17          6         0       0.091015   7.534880  -1.855968
  18          6         0      -0.033289   6.399540  -2.672533
  19          6         0      -0.012347   5.110707  -2.132077
  20          6         0       0.135824   4.985907  -0.753360
  21          6         0       0.191200   3.740605   0.118855
  22          6         0       1.384609   2.853884  -0.162473
  23          6         0       2.629564   3.403794  -0.483730
  24          6         0       3.742838   2.596519  -0.644048
  25          6         0       3.655198   1.197523  -0.470682
  26          6         0       2.398967   0.611906  -0.238214
  27          6         0       1.291347   1.464545  -0.055832
  28          6         0      -1.075081   1.547173   0.219852
  29          6         0      -2.250682   0.774372   0.312000
  30          6         0      -3.485919   1.437930   0.221690
  31          6         0      -3.511589   2.849039   0.164865
  32          6         0      -2.336985   3.579595   0.111329
  33          6         0      -1.093506   2.939432   0.110271
  34          6         0       2.235499  -0.894034  -0.225533
  35          6         0       0.963828  -0.909448  -2.351874
  36          6         0       1.103036  -1.175967  -3.839570
  37          6         0       0.313774  -2.129539  -4.494586
  38          6         0       0.484816  -2.330459  -5.865008
  39          6         0       1.435078  -1.566974  -6.537449
  40          6         0       2.163814  -0.628614  -5.801539
  41          6         0       1.942062  -2.938116  -1.487900
  42          6         0       3.211282  -3.667146  -1.092872
  43          1         0       6.053186  -4.414638  -2.510393
  44          1         0       6.438667  -5.582353  -0.338601
  45          1         0      -0.329053  -2.007526   4.910057
  46          1         0      -1.107793  -2.022524   7.290101
  47          1         0      -3.006283  -0.502223   7.937139
  48          1         0      -4.008115   0.957040   6.176171
  49          7         0       2.069538  -1.479290  -1.571619
  50          7         0      -2.325423  -1.105141   1.957631
  51          7         0       2.007762  -0.426248  -4.491002
  52          7         0      -4.640274  -3.145475   2.236454
  53          6         0       5.290136  -4.397074  -1.734006
  54          6         0       5.506780  -5.057634  -0.521422
  55          6         0       4.501828  -5.005968   0.440299
  56          6         0      -2.187574  -0.722218   0.540052
  57          6         0      -2.284925  -2.562835   2.104763
  58          6         0      -3.493423  -3.293789   1.553181
  59          6         0      -3.392522  -4.125945   0.432210
  60          6         0      -4.519487  -4.829206   0.004237
  61          6         0      -5.712570  -4.668402   0.703585
  62          6         0      -5.715798  -3.809317   1.806924
  63          6         0      -1.351904  -0.469020   2.854601
  64          6         0      -1.781309  -0.527182   4.308966
  65          6         0      -1.148034  -1.368775   5.230638
  66          6         0      -1.581463  -1.374715   6.556869
  67          6         0      -2.631486  -0.535467   6.918426
  68          6         0      -3.192751   0.278115   5.930111
  69          1         0       3.140886  -1.337224   0.193852
  70          1         0       1.395631  -1.161425   0.438679
  71          1         0       0.987030   0.173649  -2.225931
  72          1         0      -0.023166  -1.268544  -2.001045
  73          1         0      -0.418928  -2.704768  -3.934500
  74          1         0      -0.109822  -3.071115  -6.393804
  75          1         0       1.608422  -1.686423  -7.602767
  76          1         0       2.907829  -0.003659  -6.293731
  77          1         0       1.672216  -3.297100  -2.484874
  78          1         0       1.121944  -3.228224  -0.798253
  79          1         0      -3.017865  -1.191902   0.008589
  80          1         0      -1.251809  -1.113488   0.104891
  81          1         0      -2.247074  -2.778696   3.176322
  82          1         0      -1.364012  -2.985778   1.650782
  83          1         0      -2.442848  -4.225940  -0.086918
  84          1         0      -6.620368  -5.181236   0.403084
  85          1         0      -6.629985  -3.654953   2.377237
  86          1         0      -1.286367   0.586888   2.588517
  87          1         0      -0.338980  -0.904527   2.745778
  88          7         0      -2.785286   0.293529   4.659196
  89          6         0       3.336674  -4.293703   0.152376
  90          1         0       2.528550  -4.230902   0.876522
  91          7         0       4.173257  -3.727916  -2.028365
  92          1         0       4.622534  -5.506689   1.397384
  93          1         0      -4.464475  -5.489696  -0.857542
  94          6         0      -5.435908   0.743161  -0.979315
  95          1         0      -6.457030   0.577878  -0.652867
  96          1         0      -5.364286   1.730539  -1.440616
  97          6         0       5.777509   0.556531   0.434422
  98          1         0       6.686285   0.185235  -0.026373
  99          1         0       5.902104   1.615658   0.668461
 100          6         0      -4.976155  -0.291035  -1.991332
 101          6         0      -5.497978  -1.588945  -2.150201
 102          6         0      -3.945092   0.077926  -2.869388
 103          6         0      -5.020537  -2.465445  -3.127099
 104          6         0      -3.435910  -0.794876  -3.829395
 105          1         0      -3.537972   1.081880  -2.791177
 106          6         0      -3.977363  -2.074345  -3.959056
 107          1         0      -5.478595  -3.442057  -3.215764
 108          1         0      -2.624947  -0.475477  -4.477467
 109          1         0      -3.599598  -2.761115  -4.710531
 110          7         0      -6.601298  -2.105292  -1.312134
 111          8         0      -7.225541  -3.077797  -1.739530
 112          8         0      -6.830312  -1.559285  -0.235328
 113          6         0       5.435068  -0.177667   1.718274
 114          6         0       5.821401  -1.488505   2.060329
 115          6         0       4.673280   0.515901   2.671357
 116          6         0       5.464455  -2.071882   3.278268
 117          6         0       4.289436  -0.060217   3.880999
 118          1         0       4.380677   1.538815   2.452865
 119          6         0       4.685043  -1.362757   4.185587
 120          1         0       5.809814  -3.074907   3.492946
 121          1         0       3.692488   0.512068   4.585100
 122          1         0       4.400725  -1.821690   5.127638
 123          7         0       6.657979  -2.323811   1.172596
 124          8         0       7.215441  -3.300532   1.676677
 125          8         0       6.748828  -2.018751  -0.014521
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Optimized Coordinates of 1-a at the **CPCM(H₂O)-B3LYP/SVP** *level.*

$E = -4346.563925$

Sum of electronic and thermal free energies = −4345.725283

```
                Standard orientation:
---------------------------------------------------------------
Center     Atomic     Atomic        Coordinates (Angstroms)
Number     Number     Type        X          Y          Z
---------------------------------------------------------------
   1         17          0      -5.250020   3.154829   -0.228180
   2         17          0       5.200494   3.172469   -0.486159
   3          8          0      -4.735910   0.187338   -0.033727
   4          8          0      -0.015676   0.459436   -0.170352
   5          8          0       4.707487   0.220478   -0.074364
   6          6          0      -0.034945   5.253100   -1.942062
   7          1          0      -0.046997   7.892097   -0.729387
   8          1          0      -0.049482   8.211947    1.765259
   9          1          0      -0.041737   6.245544    3.274897
  10          1          0      -0.031456   3.925151    2.362194
  11          1          0      -2.628895   4.200607   -0.464340
  12          1          0       2.568782   4.212155   -0.559170
  13          8          0      -0.027228   3.890135   -1.915599
  14          8          0      -0.037904   5.874576   -2.974735
  15          6          0      -0.037810   5.731013   -0.541295
  16          6          0      -0.043651   7.038531   -0.048109
  17          6          0      -0.044991   7.206771    1.338003
  18          6          0      -0.040602   6.090243    2.193368
  19          6          0      -0.034746   4.784379    1.687893
  20          6          0      -0.033440   4.623748    0.303264
  21          6          0      -0.027529   3.354198   -0.538191
  22          6          0      -1.276460   2.511688   -0.367844
  23          6          0      -2.540396   3.116609   -0.384887
  24          6          0      -3.694529   2.353902   -0.284973
  25          6          0      -3.620327   0.947458   -0.175173
  26          6          0      -2.366115   0.316927   -0.131665
  27          6          0      -1.208141   1.119658   -0.229156
  28          6          0       1.170910   1.131579   -0.211489
  29          6          0       2.334892   0.341155   -0.089353
  30          6          0       3.584248   0.980962   -0.139191
  31          6          0       3.648246   2.380356   -0.321620
  32          6          0       2.487704   3.133671   -0.419160
  33          6          0       1.227912   2.522860   -0.360251
  34          6          0      -2.280940  -1.186047    0.036296
  35          6          0      -1.846217  -1.083866    2.457130
  36          6          0      -2.547690  -1.139865    3.803006
  37          6          0      -1.993549  -1.838289    4.885615
  38          6          0      -2.660807  -1.835724    6.113751
  39          6          0      -3.862591  -1.135722    6.220930
  40          6          0      -4.338601  -0.468126    5.086493
  41          6          0      -2.694858  -3.114104    1.445795
  42          6          0      -3.840691  -3.734258    0.667914
  43          1          0      -7.107948  -3.880294    0.917220
  44          1          0      -6.858023  -5.297836   -1.126148
  45          1          0       1.157504  -3.384704   -4.307926
  46          1          0       2.418106  -3.846632   -6.429699
  47          1          0       4.571652  -2.592973   -6.845953
  48          1          0       5.342071  -0.948580   -5.129165
  49          7          0      -2.644395  -1.655302    1.377027
  50          7          0       2.652530  -1.903757   -1.137801
  51          7          0      -3.704953  -0.465564    3.911436
  52          7          0       5.146687  -3.638527   -0.647524
  53          6          0      -6.112370  -4.074177    0.500531
  54          6          0      -5.977253  -4.868676   -0.643712
  55          6          0      -4.692290  -5.093344   -1.138727
  56          6          0       2.262779  -1.163529    0.065573
  57          6          0       2.740589  -3.340430   -0.884724
  58          6          0       3.945239  -3.746962   -0.056373
  59          6          0       3.803036  -4.238948    1.249553
  60          6          0       4.942059  -4.625559    1.961177
  61          6          0       6.187777  -4.509985    1.343677
  62          6          0       6.231167  -4.009757    0.037104
  63          6          0       1.865678  -1.595549   -2.327823
  64          6          0       2.601017  -1.925744   -3.615018
  65          6          0       2.092216  -2.862892   -4.525715
  66          6          0       2.794751  -3.118792   -5.706594
  67          6          0       3.984941  -2.429553   -5.939463
  68          6          0       4.413506  -1.511145   -4.973834
  69          1          0      -2.985469  -1.648726   -0.670967
  70          1          0      -1.268799  -1.526574   -0.257236
  71          1          0      -1.675855  -0.021254    2.228985
  72          1          0      -0.845190  -1.558809    2.541515
  73          1          0      -1.050818  -2.376716    4.764205
  74          1          0      -2.247961  -2.374414    6.970407
  75          1          0      -4.422492  -1.102024    7.157960
  76          1          0      -5.278104   0.095277    5.138251
  77          1          0      -2.830818  -3.393404    2.501909
  78          1          0      -1.736814  -3.570624    1.111885
  79          1          0       2.958988  -1.457026    0.865362
  80          1          0       1.248341  -1.445075    0.409614
  81          1          0       2.832902  -3.846891   -1.857257
  82          1          0       1.815253  -3.728236   -0.404930
  83          1          0       2.810596  -4.318568    1.699128
  84          1          0       7.107730  -4.801340    1.855013
  85          1          0       7.194015  -3.909978   -0.478130
  86          1          0       1.672169  -0.512752   -2.336871
  87          1          0       0.875510  -2.099295   -2.326341
  88          7          0       3.746250  -1.261492   -3.844917
  89          6          0      -3.607395  -4.517142   -0.472719
  90          1          0      -2.586899  -4.671247   -0.830680
  91          7          0      -5.079372  -3.522970    1.142397
  92          1          0      -4.534533  -5.706775   -2.029392
  93          1          0       4.855658  -5.010539    2.980387
  94          6          0       5.565633   0.344189    1.063029
  95          1          0       5.491801   1.347240    1.503877
  96          1          0       5.239802  -0.369172    1.836779
  97          6          0      -5.637266   0.060769   -1.136586
  98          1          0      -5.606111   0.954232   -1.773966
  99          1          0      -5.322575  -0.789277   -1.763287
 100          6          0       6.992988   0.056943    0.647110
 101          6          0       8.101382   0.100729    1.523190
 102          6          0       7.264025  -0.277516   -0.688906
 103          6          0       9.405854  -0.166641    1.089472
 104          6          0       8.561057  -0.546540   -1.130839
 105          1          0       6.427789  -0.330963   -1.384362
 106          6          0       9.639671  -0.490690   -0.242821
 107          1          0      10.217259  -0.113559    1.813390
 108          1          0       8.727929  -0.802696   -2.179703
 109          1          0      10.655495  -0.699440   -0.583890
 110          7          0       7.943009   0.431836    2.947677
 111          8          0       8.941781   0.474224    3.650664
 112          8          0       6.813009   0.650236    3.370900
 113          6          0      -7.038385  -0.165866   -0.608793
 114          6          0      -8.191561  -0.244146   -1.421789
 115          6          0      -7.235472  -0.309078    0.773658
 116          6          0      -9.469585  -0.447597   -0.886683
 117          6          0      -8.505046  -0.517327    1.316599
 118          1          0      -6.363713  -0.260908    1.424478
 119          6          0      -9.629367  -0.586902    0.488069
 120          1          0     -10.318937  -0.493598   -1.566274
 121          1          0      -8.614428  -0.626289    2.398140
 122          1          0     -10.623630  -0.749549    0.908546
 123          7          0      -8.109578  -0.113239   -2.884242
 124          8          0      -9.149814  -0.060792   -3.523472
 125          8          0      -6.998611  -0.066157   -3.401175
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Optimized Coordinates of 1-b at the CPCM(H₂O)-B3LYP/SVP *level.*

$E = -4346.550117$

Sum of electronic and thermal free energies $= -4345.706139$

```
              Standard orientation:
---------------------------------------------------------------
Center   Atomic   Atomic        Coordinates (Angstroms)
Number   Number    Type       X          Y          Z
---------------------------------------------------------------
   1       17        0     -5.200795   3.649725   -0.026668
   2       17        0      5.207087   3.549574   -0.875404
   3        8        0     -4.727610   0.656205    0.064308
   4        8        0     -0.002907   0.899825   -0.204169
   5        8        0      4.725695   0.611078   -0.295964
   6        6        0     -0.067556   5.702079   -1.977798
   7        1        0      0.021277   8.330793   -0.745203
   8        1        0      0.164369   8.628611    1.747994
   9        1        0      0.231121   6.649211    3.238986
  10        1        0      0.158962   4.336800    2.308481
  11        1        0     -2.595355   4.658845   -0.387939
  12        1        0      2.597994   4.609455   -0.803593
  13        8        0     -0.073491   4.338632   -1.962493
  14        8        0     -0.121089   6.331980   -3.003881
  15        6        0      0.013099   6.168104   -0.575412
  16        6        0      0.052065   7.471258   -0.072176
  17        6        0      0.131436   7.627240    1.313097
  18        6        0      0.169271   6.503322    2.157912
  19        6        0      0.129129   5.201969    1.642486
  20        6        0      0.050518   5.053629    0.258755
  21        6        0     -0.004524   3.791240   -0.592089
  22        6        0     -1.251050   2.960807   -0.358829
  23        6        0     -2.510191   3.574115   -0.314618
  24        6        0     -3.664130   2.820167   -0.165309
  25        6        0     -3.602555   1.408931   -0.064023
  26        6        0     -2.346605   0.776688   -0.034711
  27        6        0     -1.190036   1.571688   -0.206767
  28        6        0      1.186141   1.556608   -0.328155
  29        6        0      2.343984   0.746574   -0.279335
  30        6        0      3.601008   1.371379   -0.369207
  31        6        0      3.665258   2.769154   -0.588077
  32        6        0      2.510886   3.535435   -0.635640
  33        6        0      1.248971   2.944789   -0.488479
  34        6        0     -2.230186  -0.709700    0.224817
  35        6        0     -1.410674  -0.323227    2.539099
  36        6        0     -1.847970  -0.391420    3.991619
  37        6        0     -1.028037  -0.963190    4.975654
  38        6        0     -1.467956  -0.985158    6.302241
  39        6        0     -2.714400  -0.435620    6.602997
  40        6        0     -3.460260   0.116457    5.554848
  41        6        0     -2.151432  -2.517973    1.831784
  42        6        0     -3.380239  -3.330881    1.470167
  43        1        0     -6.425001  -3.707448    2.629838
  44        1        0     -6.532854  -5.429122    0.822739
  45        1        0      0.070049  -2.524950   -4.343432
  46        1        0      0.849579  -3.152443   -6.646161
  47        1        0      3.091981  -2.294393   -7.431898
  48        1        0      4.422418  -0.851316   -5.885093
  49        7        0     -2.296075  -1.074397    1.650151
  50        7        0      2.303490  -1.453824   -1.479620
  51        7        0     -3.044460   0.143095    4.286929
  52        7        0      4.488107  -3.583994   -1.536686
  53        6        0     -5.553972  -3.884990    1.987931
  54        6        0     -5.619925  -4.850445    0.976257
  55        6        0     -4.491854  -5.041675    0.177740
  56        6        0      2.228680  -0.759185   -0.182989
  57        6        0      2.162297  -2.898669   -1.306216
  58        6        0      3.392203  -3.599717   -0.760406
  59        6        0      3.359056  -4.285304    0.462759
  60        6        0      4.495395  -4.981059    0.884917
  61        6        0      5.631431  -4.962722    0.075099
  62        6        0      5.573487  -4.241038   -1.123105
  63        6        0      1.415724  -0.942648   -2.523797
  64        6        0      1.849223  -1.364163   -3.916661
  65        6        0      1.032985  -2.173187   -4.720956
  66        6        0      1.467913  -2.521474   -6.002684
  67        6        0      2.706048  -2.050362   -6.439805
  68        6        0      3.448544  -1.244633   -5.568497
  69        1        0     -3.063681  -1.219182   -0.279140
  70        1        0     -1.296742  -1.081516   -0.240951
  71        1        0     -1.451385   0.735524    2.247658
  72        1        0     -0.350305  -0.643002    2.459047
  73        1        0     -0.058609  -1.386098    4.701979
  74        1        0     -0.846858  -1.427034    7.085499
  75        1        0     -3.104323  -0.428490    7.623109
  76        1        0     -4.441067   0.563318    5.759053
  77        1        0     -1.957573  -2.703351    2.899049
  78        1        0     -1.273630  -2.911057    1.274163
  79        1        0      3.058487  -1.134092    0.432557
  80        1        0      1.291774  -1.010410    0.352199
  81        1        0      1.967087  -3.337930   -2.296167
  82        1        0      1.285923  -3.146515   -0.668959
  83        1        0      2.451458  -4.277120    1.070665
  84        1        0      6.544483  -5.489190    0.359841
  85        1        0      6.450706  -4.202566   -1.779865
  86        1        0      1.456407   0.155142   -2.499643
  87        1        0      0.356178  -1.234181   -2.365450
  88        7        0      3.037414  -0.906478   -4.344487
  89        6        0     -3.355207  -4.267302    0.426373
  90        1        0     -2.453093  -4.389812   -0.177295
  91        7        0     -4.468363  -3.149772    2.236678
  92        1        0     -4.494138  -5.781365   -0.626810
  93        1        0      4.491395  -5.527369    1.831497
  94        6        0      5.645244   0.857880    0.793775
  95        1        0      6.650025   0.737617    0.380436
  96        1        0      5.536428   1.890810    1.146332
  97        6        0     -5.666849   0.648700   -1.036129
  98        1        0     -6.663264   0.619023   -0.587818
  99        1        0     -5.573120   1.577668   -1.611920
 100        6        0      5.395806  -0.072868    1.962638
 101        6        0      5.991838  -1.338293    2.144786
 102        6        0      4.515047   0.353606    2.969890
 103        6        0      5.728320  -2.133276    3.265167
 104        6        0      4.220358  -0.438671    4.081954
 105        1        0      4.056565   1.341122    2.879753
 106        6        0      4.827124  -1.689047    4.230189
 107        1        0      6.230894  -3.094689    3.360258
 108        1        0      3.522055  -0.072965    4.837970
 109        1        0      4.607559  -2.314777    5.097523
 110        7        0      6.954461  -1.888772    1.172963
 111        8        0      7.755099  -2.720188    1.575693
 112        8        0      6.900400  -1.503963    0.013041
 113        6        0     -5.430089  -0.517506   -1.973760
 114        6        0     -6.024715  -1.791935   -1.863196
 115        6        0     -4.567310  -0.322992   -3.064655
 116        6        0     -5.780076  -2.812873   -2.787575
 117        6        0     -4.289604  -1.340309   -3.980750
 118        1        0     -4.110079   0.659783   -3.201371
 119        6        0     -4.896613  -2.591565   -3.841779
 120        1        0     -6.281713  -3.771231   -2.661767
 121        1        0     -3.605474  -1.150203   -4.810619
 122        1        0     -4.690752  -3.392005   -4.555162
 123        7        0     -6.963830  -2.116600   -0.773687
 124        8        0     -7.768737  -3.016220   -0.966446
 125        8        0     -6.885506  -1.487503    0.272535
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Optimized Coordinates of 1-a at the **B3LYP/SVP** *level.*

$E = -4346.521105$

Sum of electronic and thermal free energies = −4345.682251

```
                 Standard orientation:
---------------------------------------------------------------
Center     Atomic     Atomic        Coordinates (Angstroms)
Number     Number     Type         X          Y          Z
---------------------------------------------------------------
   1         17          0      -5.208320   3.528335   -0.083745
   2         17          0       5.228143   3.470364   -0.370554
   3          8          0      -4.715085   0.532082    0.006342
   4          8          0      -0.005127   0.773513   -0.221531
   5          8          0       4.709184   0.489088   -0.132410
   6          6          0       0.015453   5.644337   -1.763649
   7          1          0       0.026985   8.217975   -0.431031
   8          1          0       0.029440   8.429021    2.081964
   9          1          0       0.020809   6.396050    3.500569
  10          1          0       0.009297   4.119956    2.480354
  11          1          0      -2.587050   4.545235   -0.321633
  12          1          0       2.608483   4.520022   -0.408452
  13          8          0       0.010964   4.275677   -1.791382
  14          8          0       0.018698   6.317465   -2.755573
  15          6          0       0.016621   6.055673   -0.335653
  16          6          0       0.022978   7.338418    0.216705
  17          6          0       0.024257   7.444077    1.609064
  18          6          0       0.019282   6.290366    2.412721
  19          6          0       0.012850   5.010161    1.846860
  20          6          0       0.011542   4.912131    0.456132
  21          6          0       0.006505   3.684379   -0.448038
  22          6          0      -1.248963   2.844266   -0.305326
  23          6          0      -2.508164   3.458102   -0.286649
  24          6          0      -3.671084   2.705865   -0.204505
  25          6          0      -3.610910   1.294724   -0.156505
  26          6          0      -2.359657   0.652487   -0.171388
  27          6          0      -1.193651   1.447031   -0.237388
  28          6          0       1.188128   1.438622   -0.220220
  29          6          0       2.347252   0.636676   -0.125112
  30          6          0       3.603677   1.267907   -0.138711
  31          6          0       3.677121   2.674925   -0.248799
  32          6          0       2.519786   3.436849   -0.317731
  33          6          0       1.254864   2.834584   -0.298975
  34          6          0      -2.279477  -0.859918   -0.134855
  35          6          0      -2.091106  -0.895294    2.326939
  36          6          0      -2.853353  -1.238163    3.595944
  37          6          0      -2.223759  -1.890385    4.666824
  38          6          0      -2.951822  -2.152234    5.829998
  39          6          0      -4.287554  -1.755822    5.885642
  40          6          0      -4.828683  -1.111976    4.766451
  41          6          0      -2.514849  -2.930673    1.097251
  42          6          0      -3.371776  -3.636565    0.062435
  43          1          0      -6.545009  -4.341897   -0.334188
  44          1          0      -5.687546  -5.441209   -2.415005
  45          1          0       1.426775  -2.559675   -4.685646
  46          1          0       2.859007  -3.259733   -6.625040
  47          1          0       5.318393  -2.684775   -6.572209
  48          1          0       6.205576  -1.442394   -4.588007
  49          7          0      -2.671391  -1.483466    1.131477
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Optimized Coordinates of 1-b at the **B3LYP/SVP** *level.*

E = −4346.497978

Sum of electronic and thermal free energies = −4345.654287

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3	8	0	4.740837	0.460786	-0.379712
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6	6	0	0.278957	5.588828	1.779889
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85	1	0	-6.485026	-4.098373	2.291597
86	1	0	-1.347964	0.301659	2.524776
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117	6	0	4.211261	-0.113664	4.057450
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121	1	0	3.629140	0.461376	4.781373
122	1	0	4.220333	-1.930352	5.240063
123	7	0	6.506636	-2.384589	1.278886
124	8	0	7.016106	-3.390768	1.749281
125	8	0	6.614775	-2.041213	0.113647

Figure S41. Analytical HPLC traces of purified **1**. Absorbance monitored at 520 nm (top) and 250 nm (bottom) using solvent gradient 8 (Table S1).

Figure S42. Analytical HPLC traces of purified **2**. Absorbance monitored at 520 nm (top) and 250 nm (bottom) using solvent gradient 8 (Table S1).
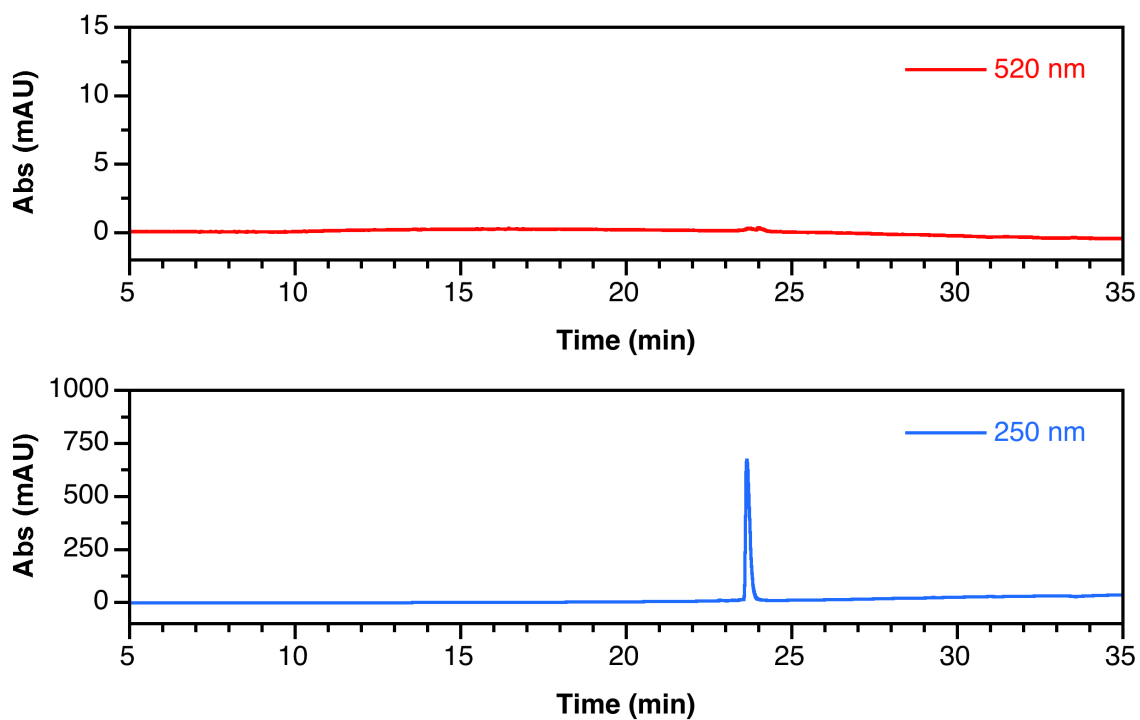
Figure S43. Analytical HPLC traces of purified **3**. Absorbance monitored at 520 nm (top) and 250 nm (bottom) using solvent gradient 8 (Table S1).
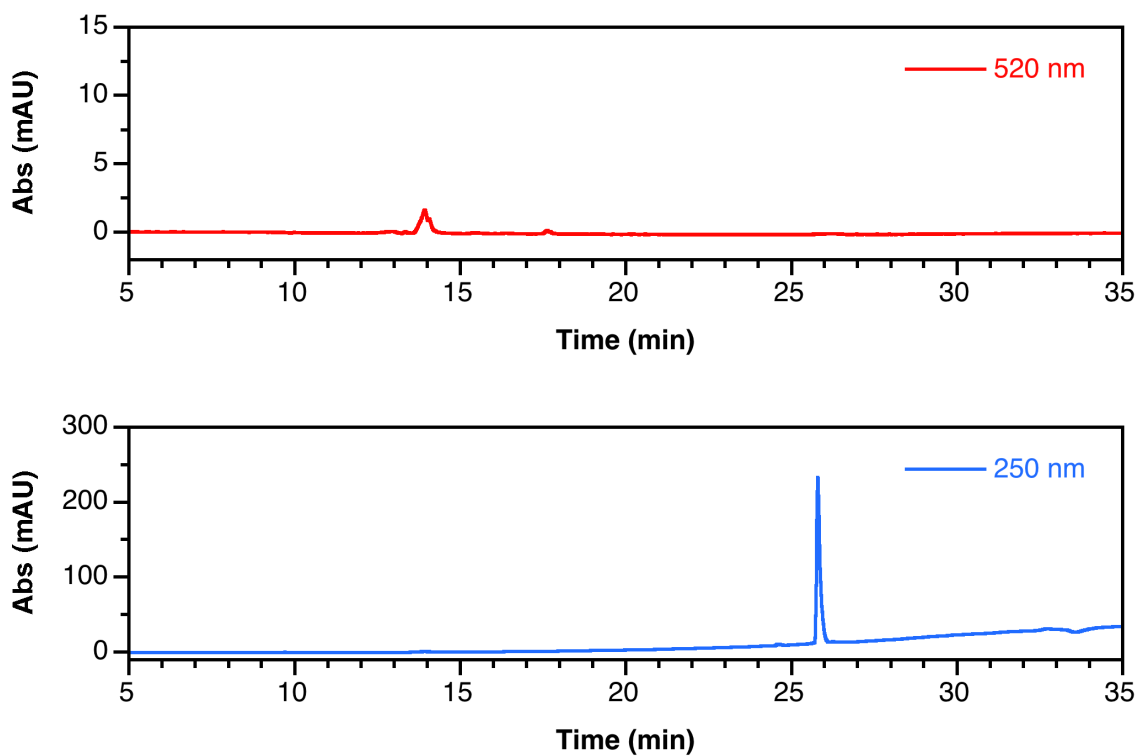
Figure S44. Analytical HPLC traces of purified **4**. Absorbance monitored at 520 nm (top) and 250 nm (bottom) using solvent gradient 8 (Table S1).

NMR Spectra.

Figure S45. ¹H NMR spectrum of **S2**.

Figure S46. ¹⁹F NMR spectrum of **S2**.

Figure S47. ¹H NMR spectrum of **S3**.
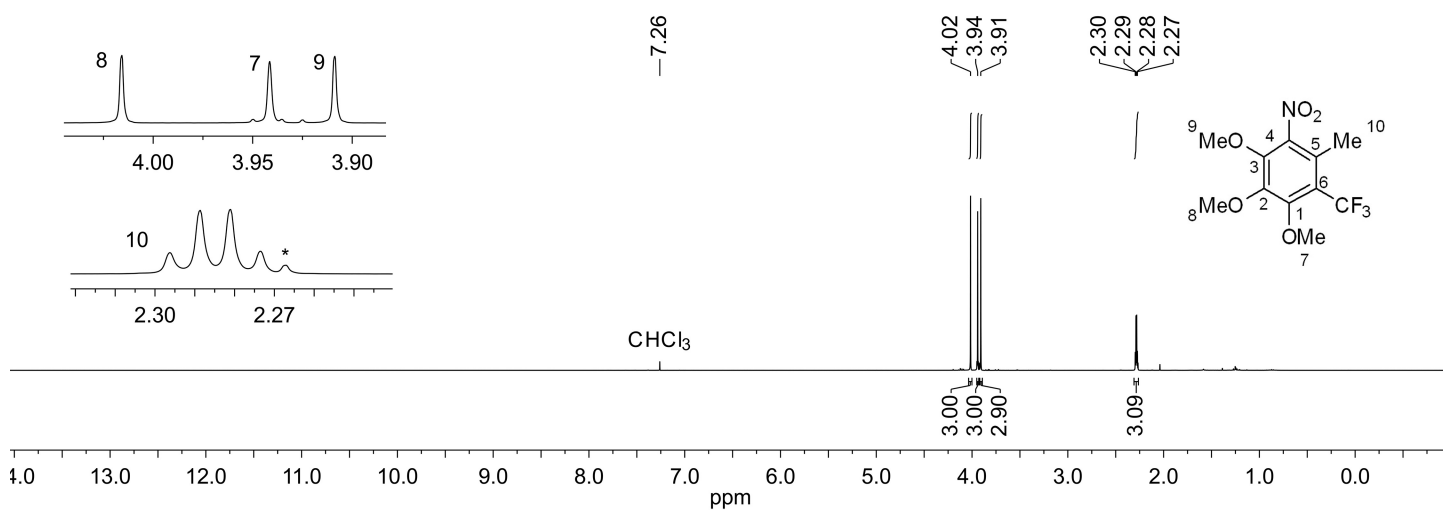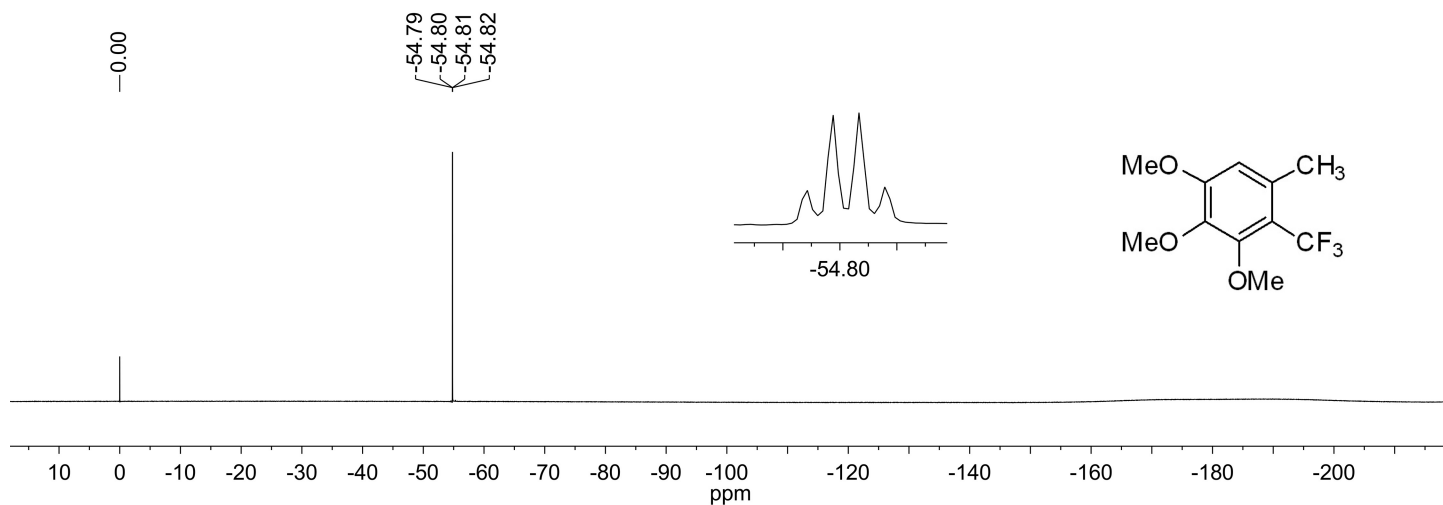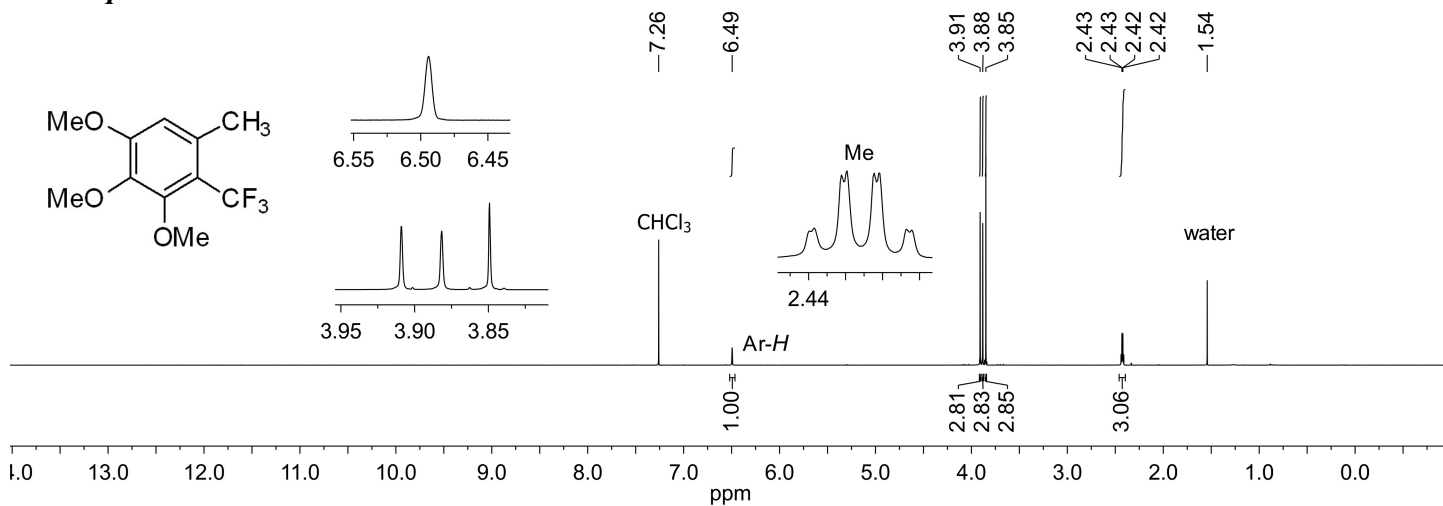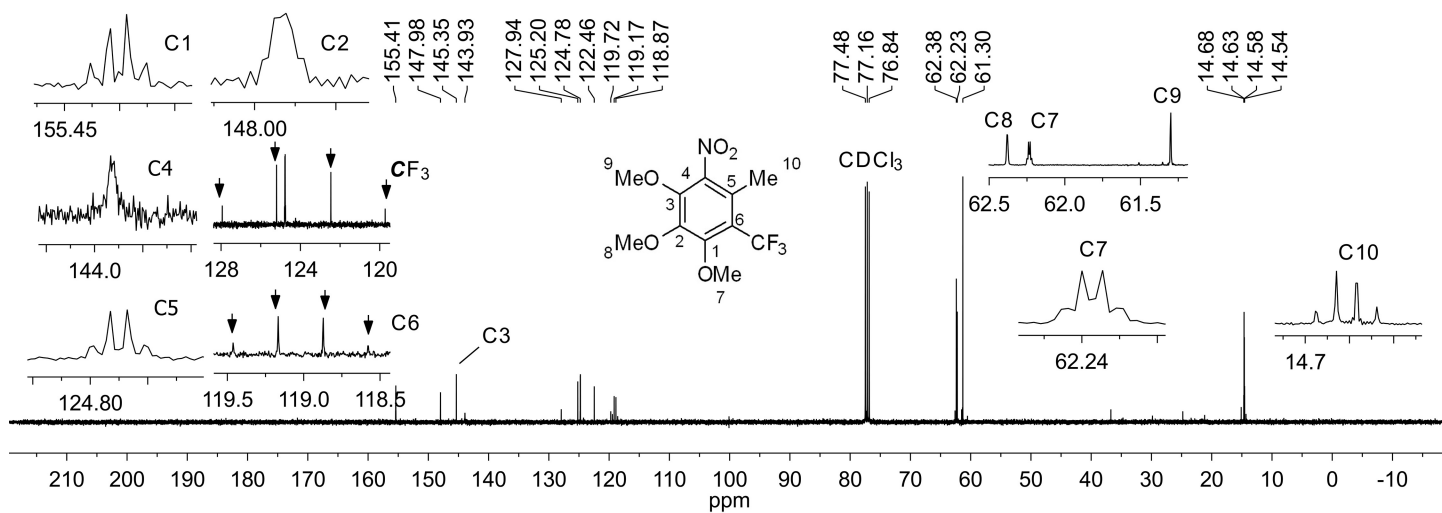
Figure S48. $^{13}C\{^1H\}$ NMR spectrum of **S3**.
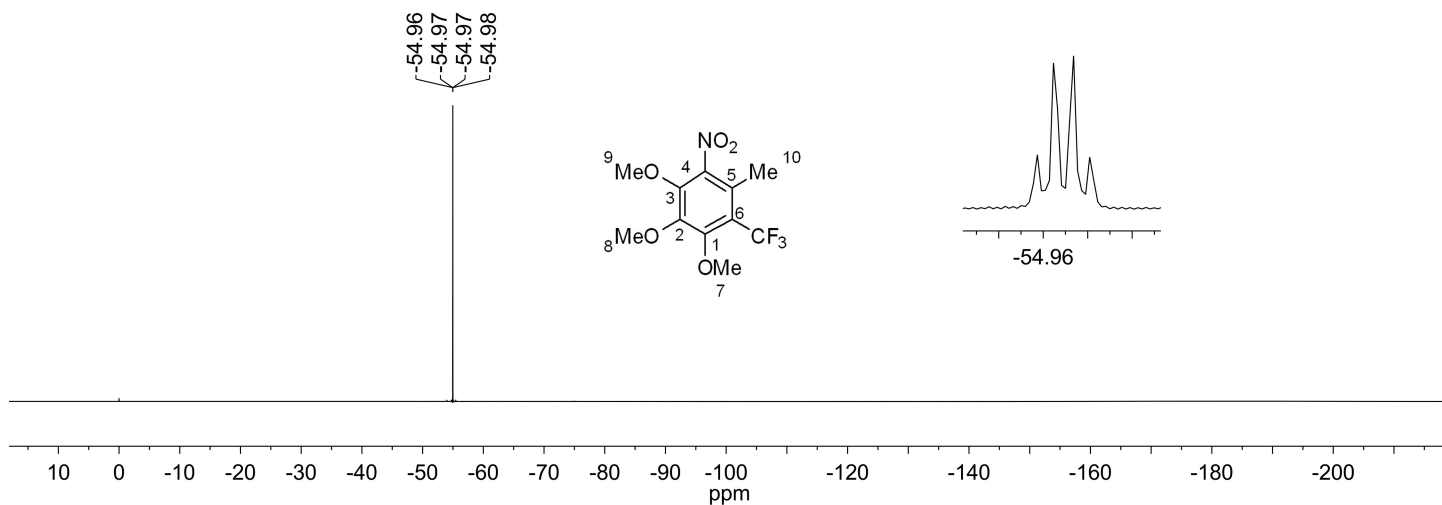
Figure S49. ^{19}F NMR spectrum of **S3**.
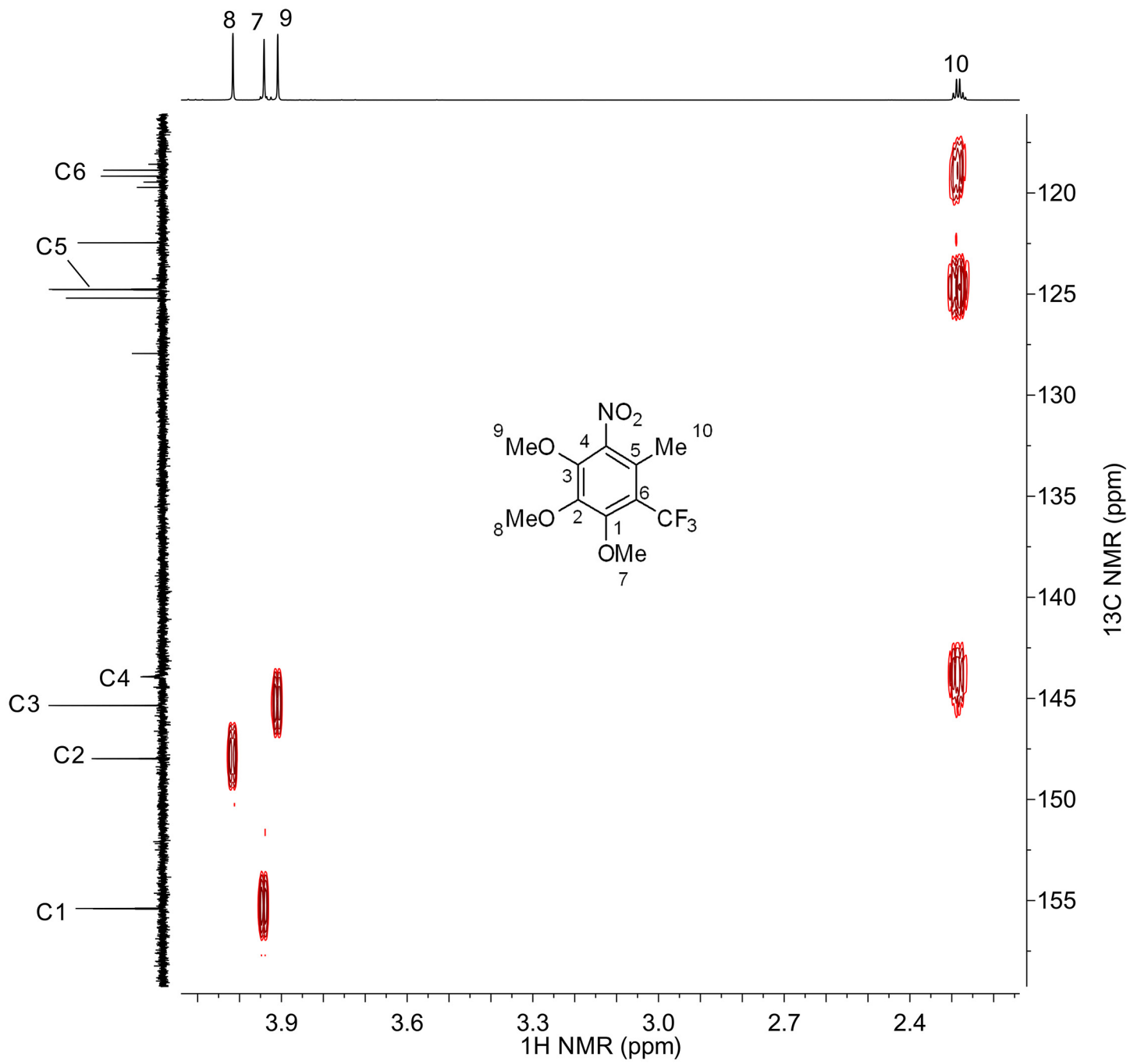
Figure S50. ^{1}H-^{13}C HMBC spectrum of **S3**.
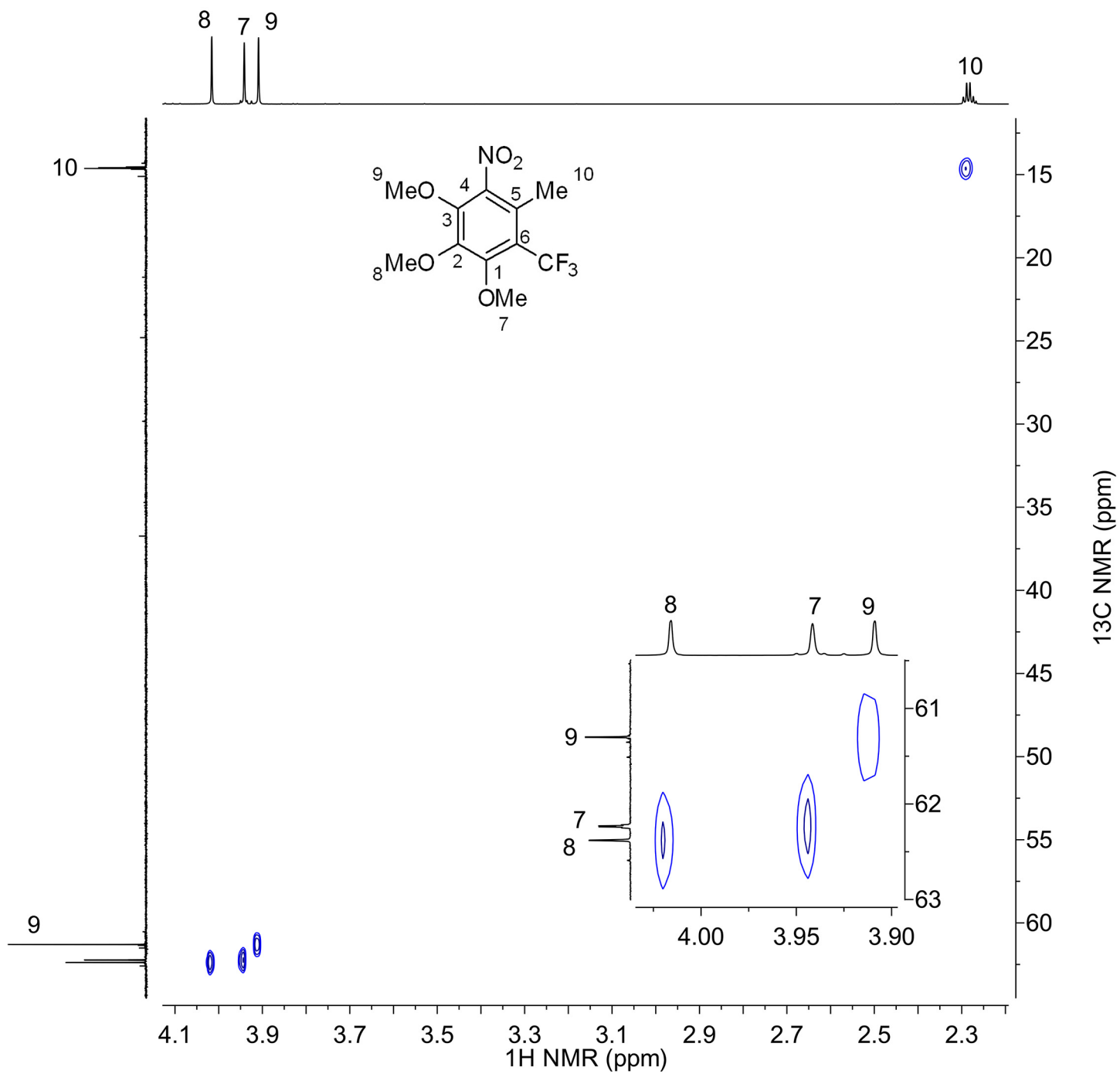
Figure S51. ^{1}H-^{13}C HSQC spectrum of **S3**.

Figure S52. ^{1}H NMR spectrum of **S4**.

Figure S53. ^{13}C{^{1}H} NMR spectrum of **S4**.

Figure S54. ^{19}F NMR spectrum of **S4**.

S72
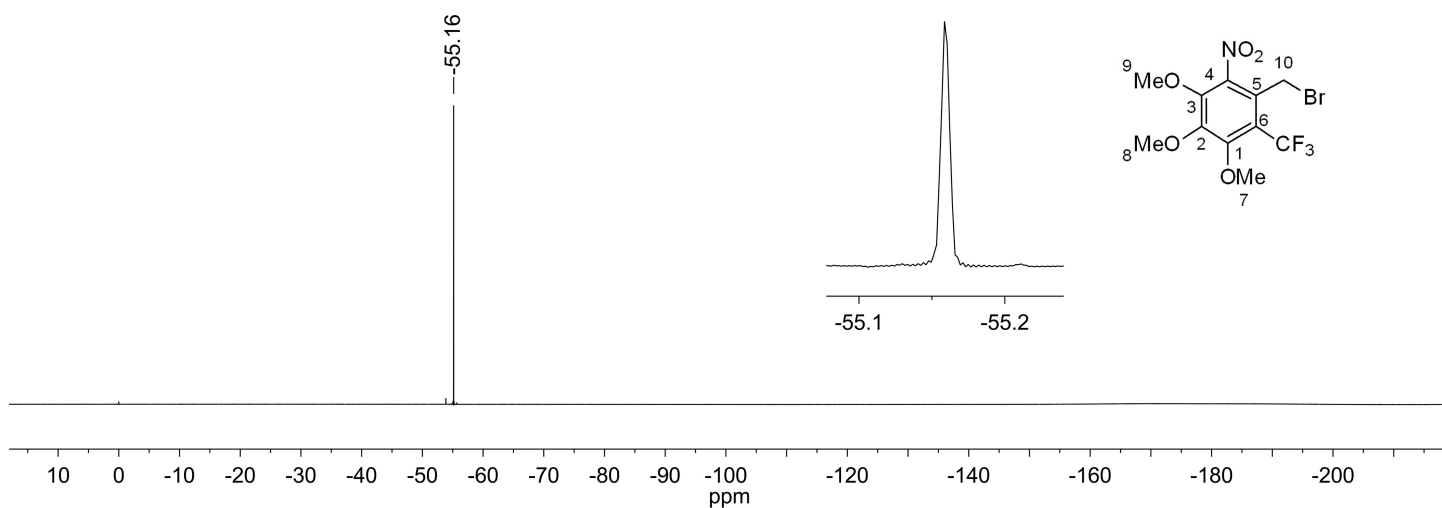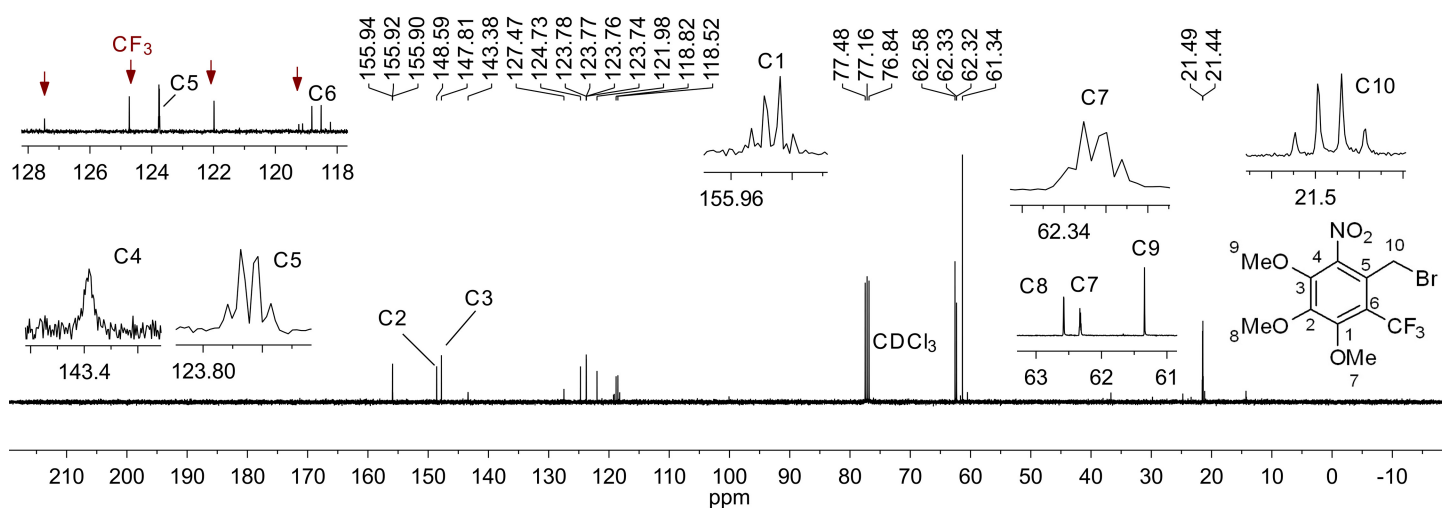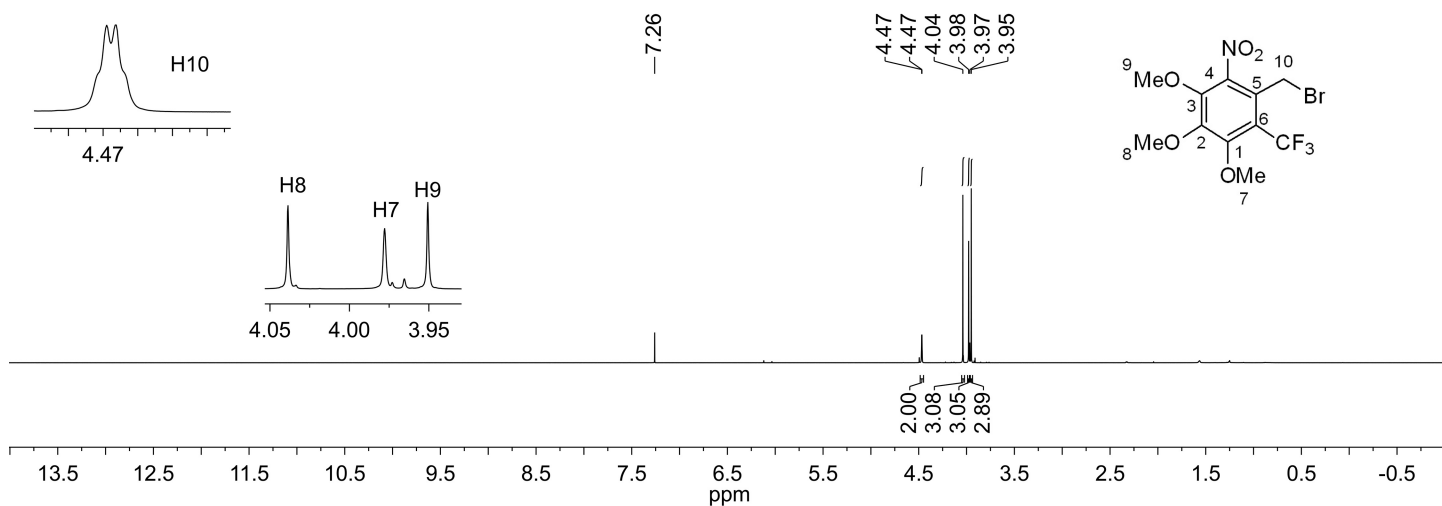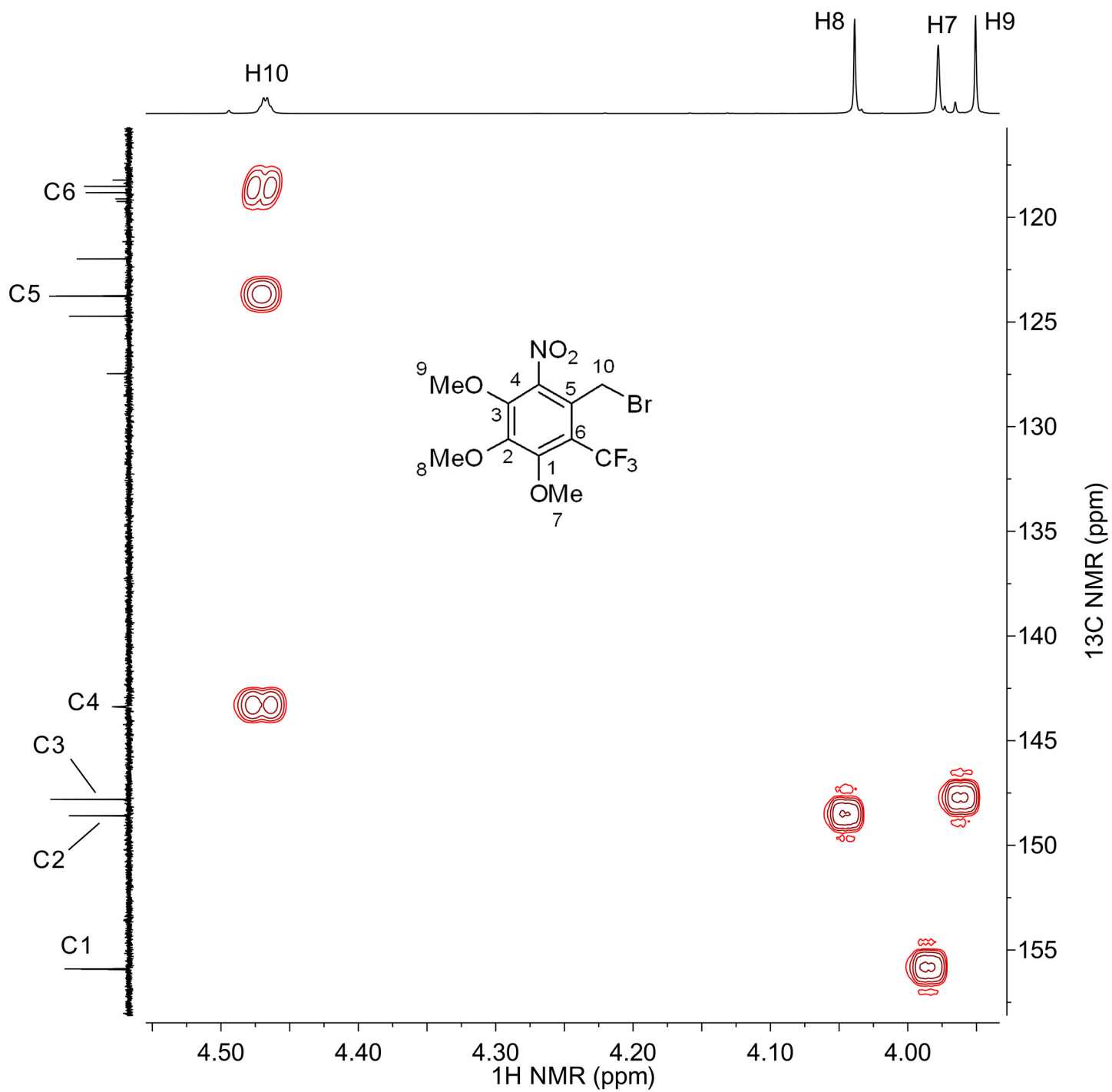
Figure S55. ^{1}H-^{13}C HMBC spectrum of **S4**.
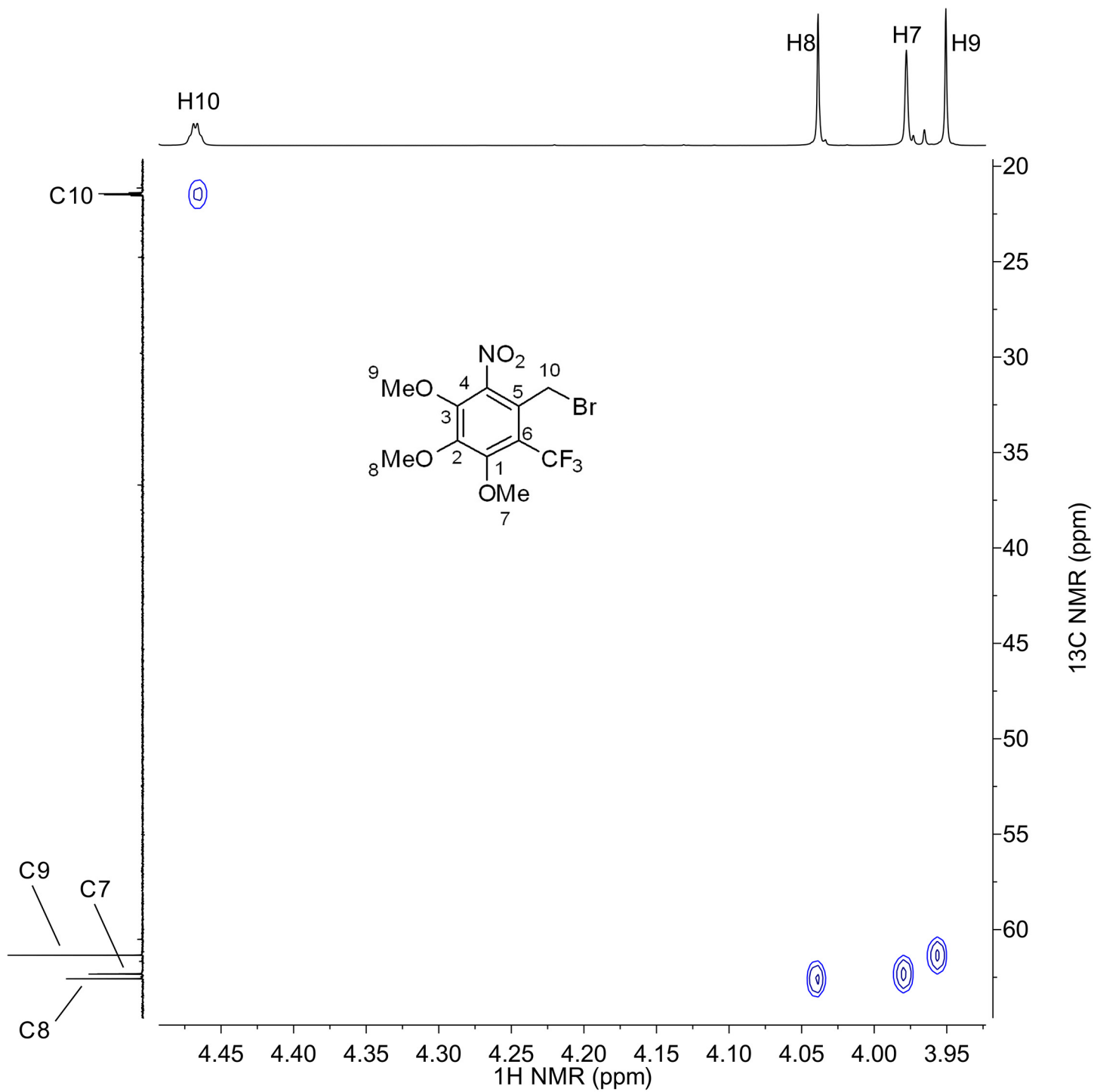
Figure S56. ^{1}H-^{13}C HSQC spectrum of **S4**.
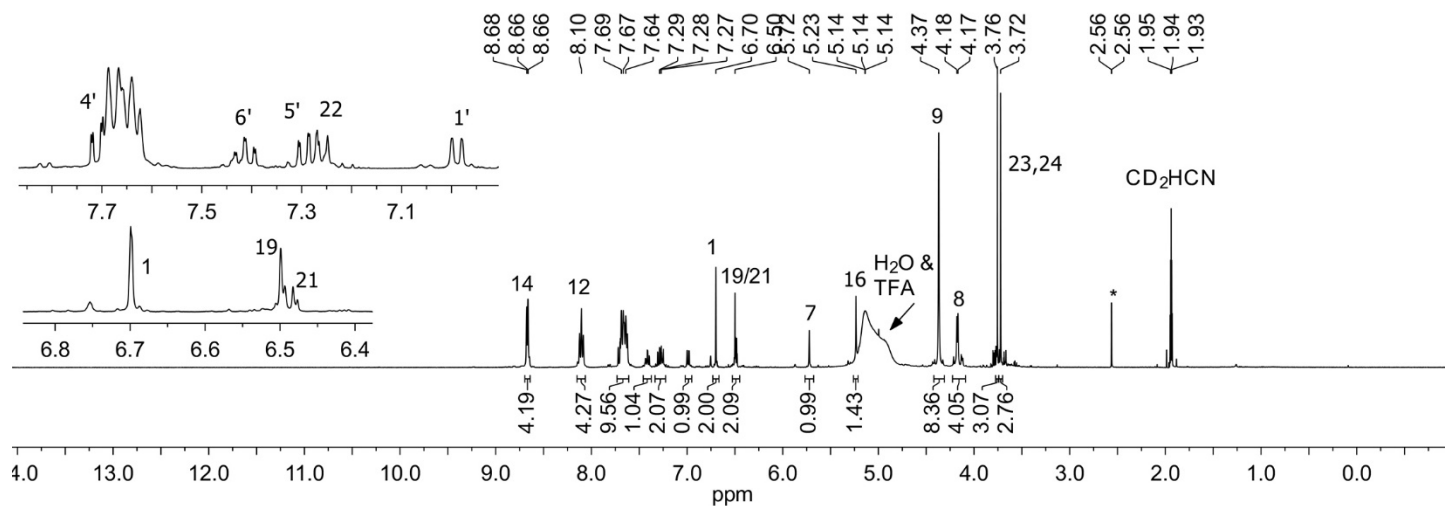
Figure S57. ^{1}H NMR spectrum of **S5**.
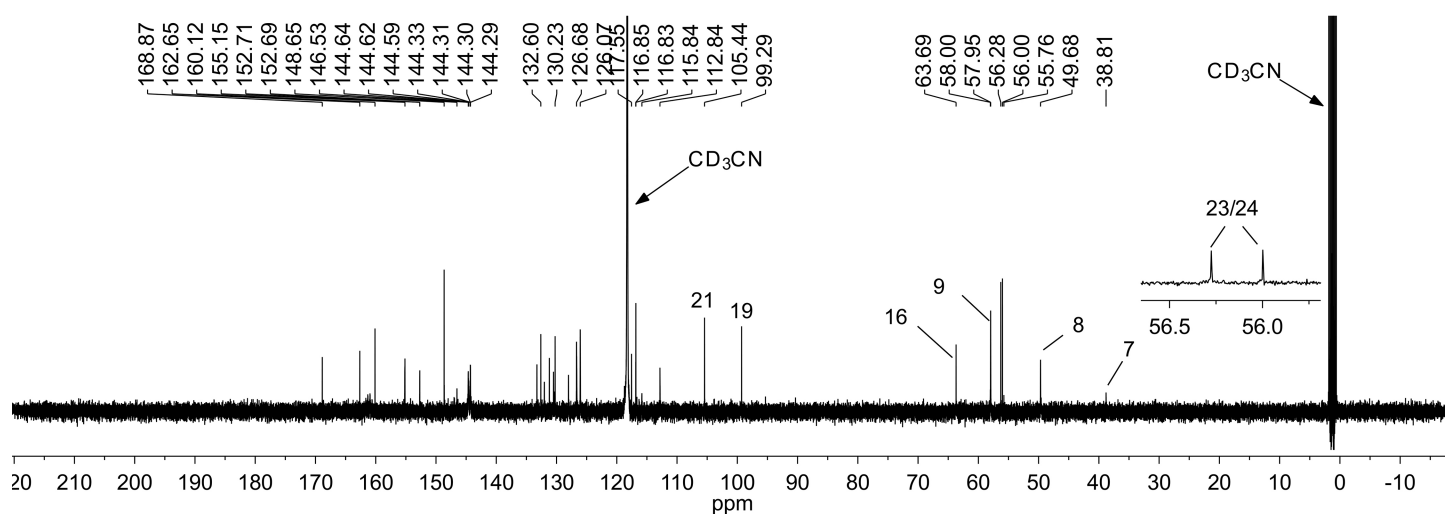
Figure S58. ^{13}C{^{1}H} NMR spectrum of **S5**.
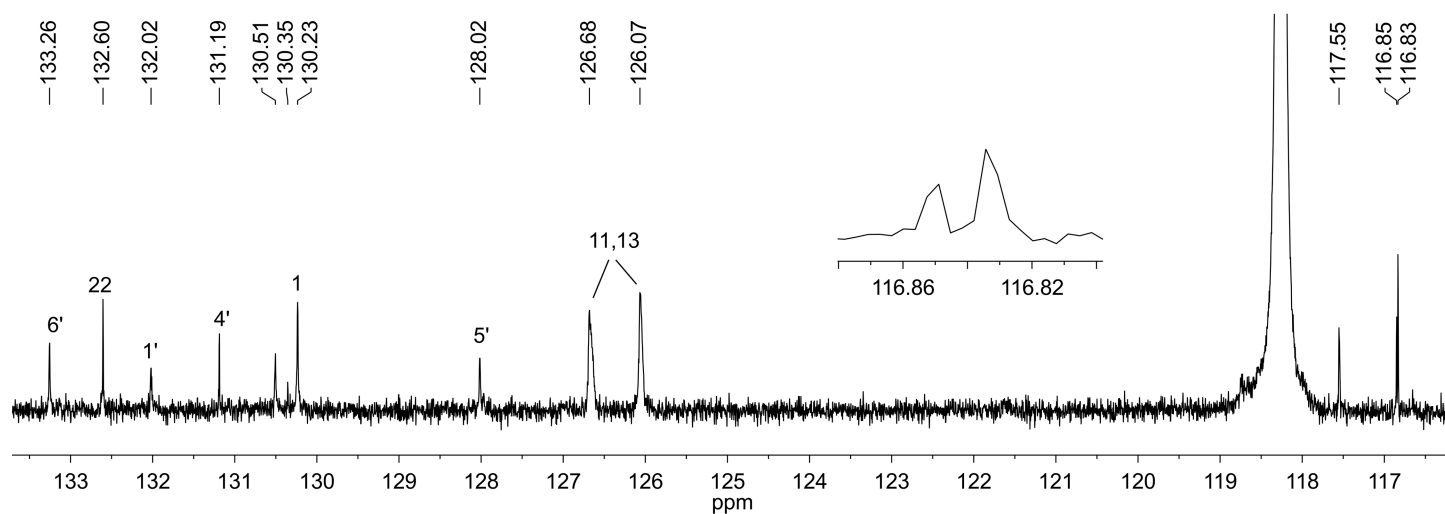
Figure S59. Expansion of ^{13}C{^{1}H} NMR spectrum of **S5** from 116 to 134 ppm.
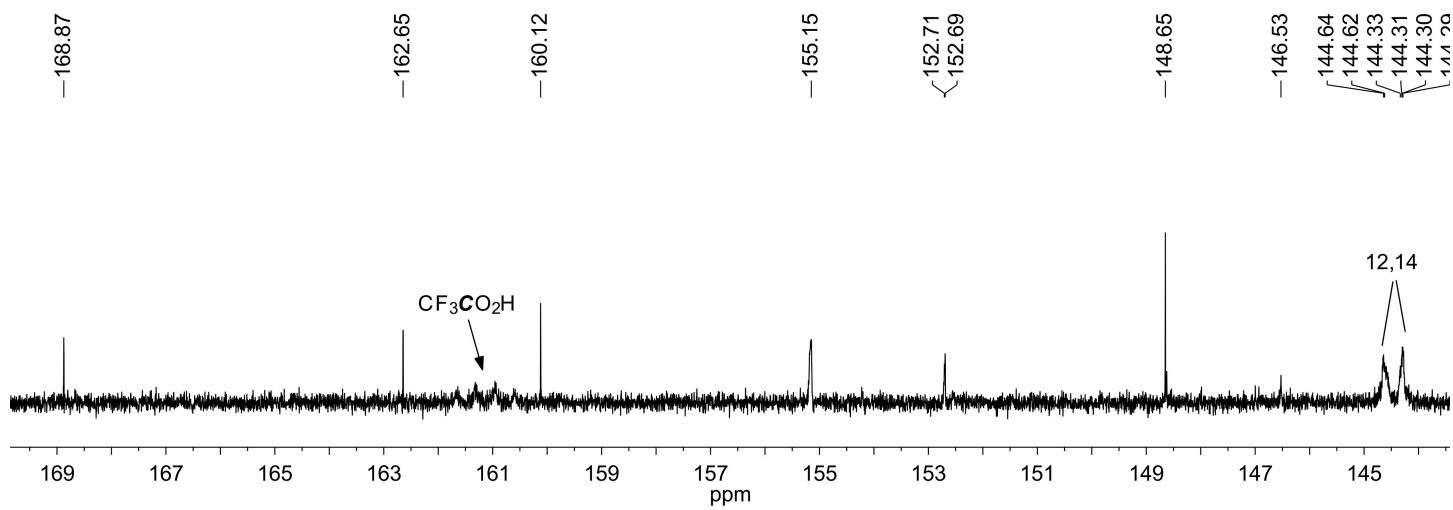
Figure S60. Expansion of $^{13}C\{^1H\}$ NMR spectrum of **S5** from 144 to 170 ppm.
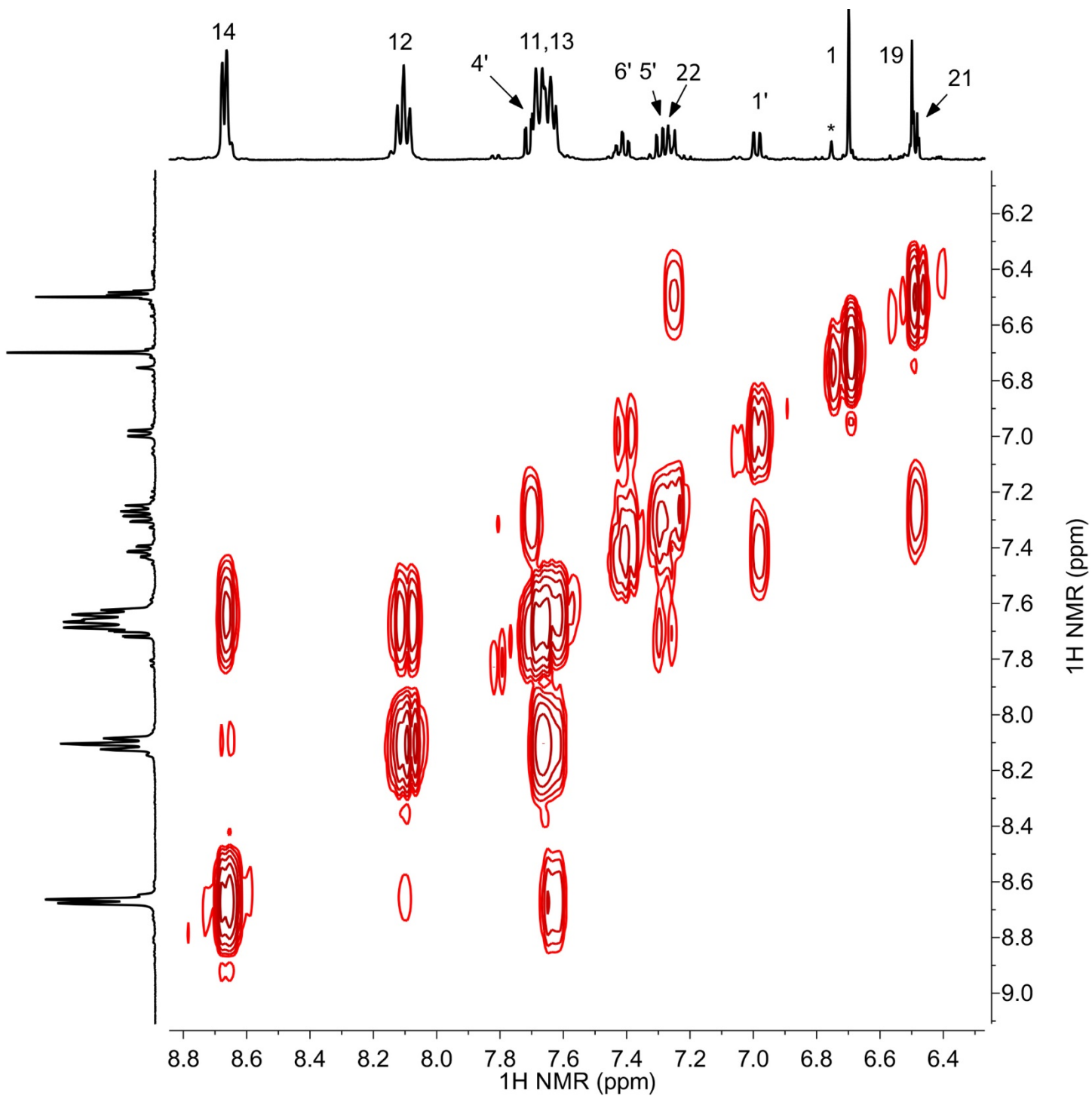
Figure S61. ^{1}H-^{1}H COSY spectrum of **S5** aromatic region.
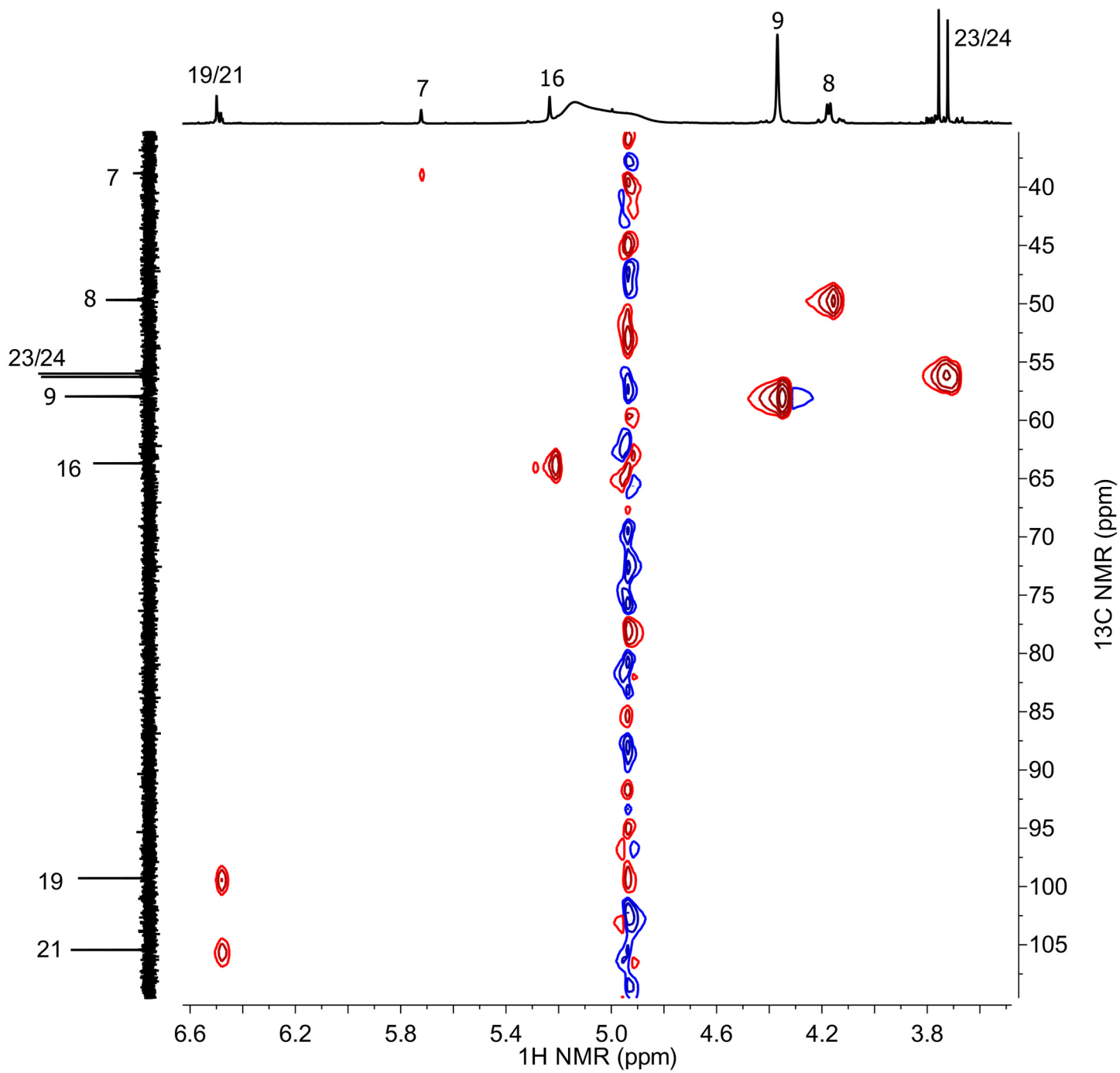
Figure S62. ^{1}H-^{13}C HSQC spectrum of **S5** aliphatic region.
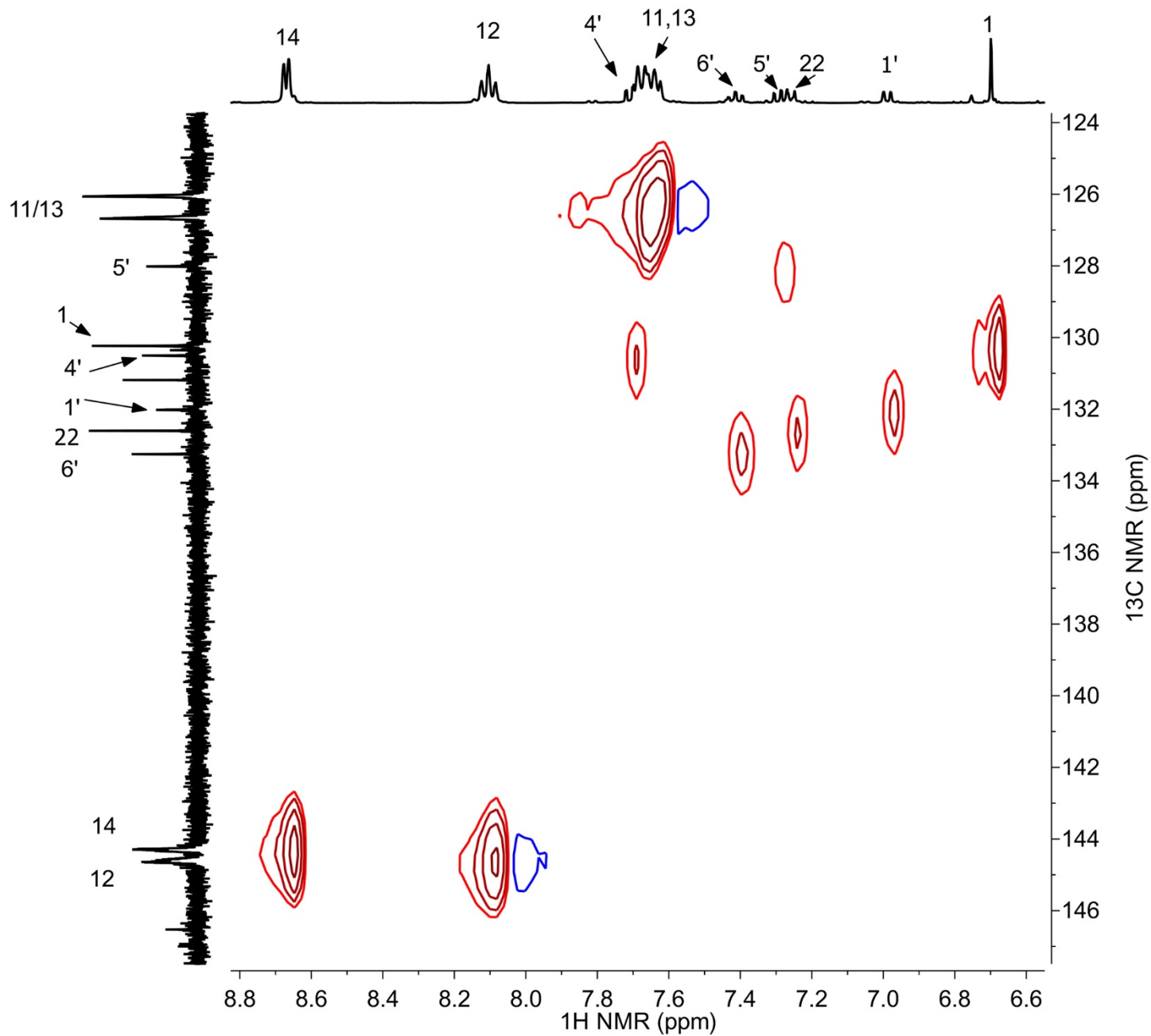
Figure S63. ^{1}H-^{13}C HSQC spectrum of **S5** aromatic region.
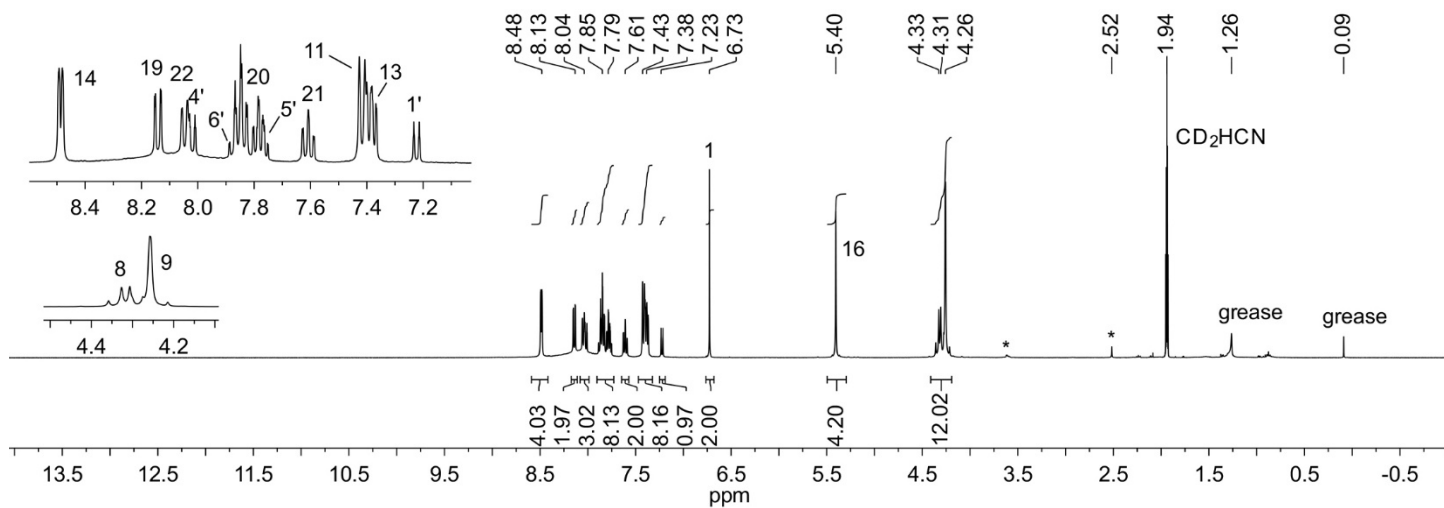
Figure S64. ^{1}H NMR spectrum of **1**.
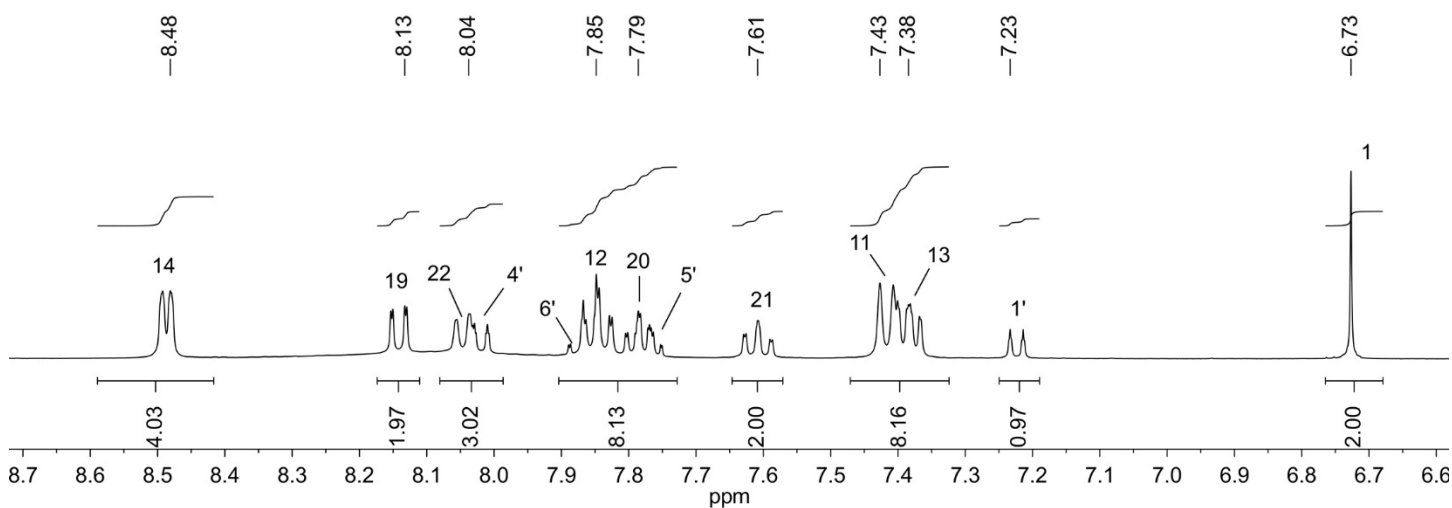
Figure S65. Expansion of ^{1}H NMR spectrum of **1**.
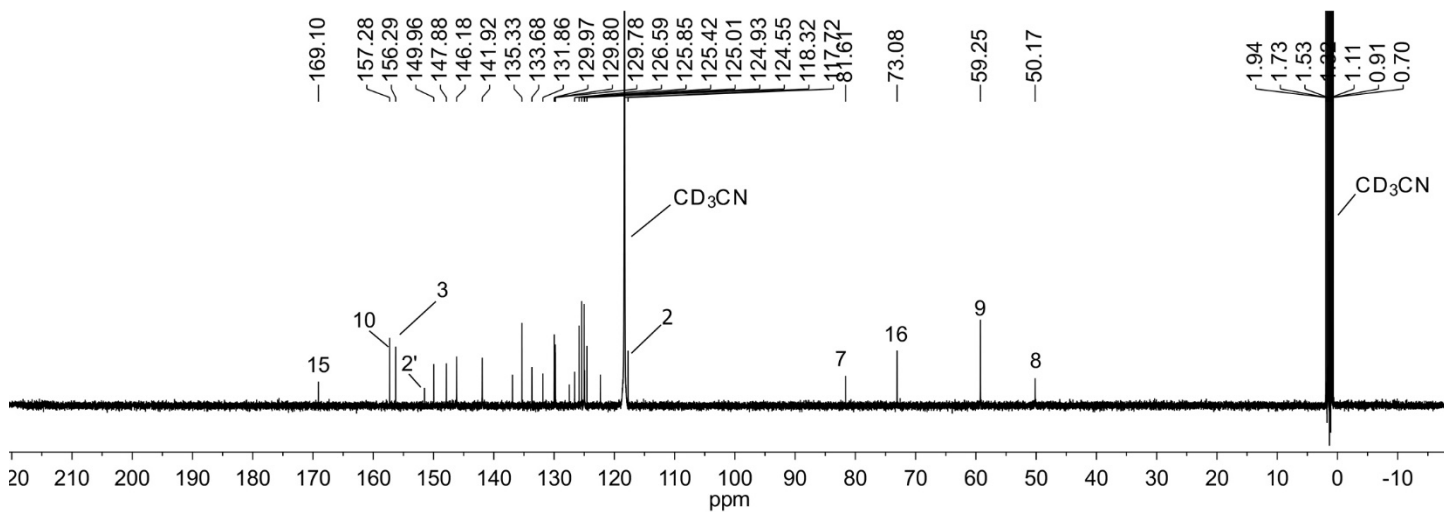
Figure S66. ^{13}C{^{1}H} NMR spectrum of **1**.
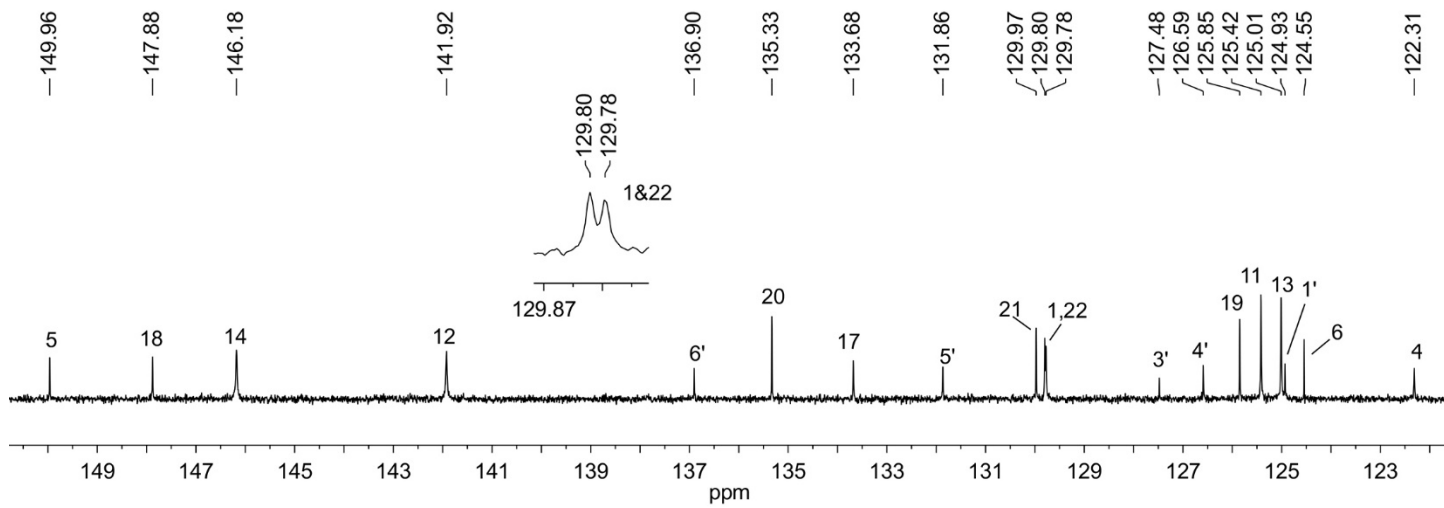
Figure S67. Expansion of $^{13}C\{^1H\}$ NMR spectrum of **1**.
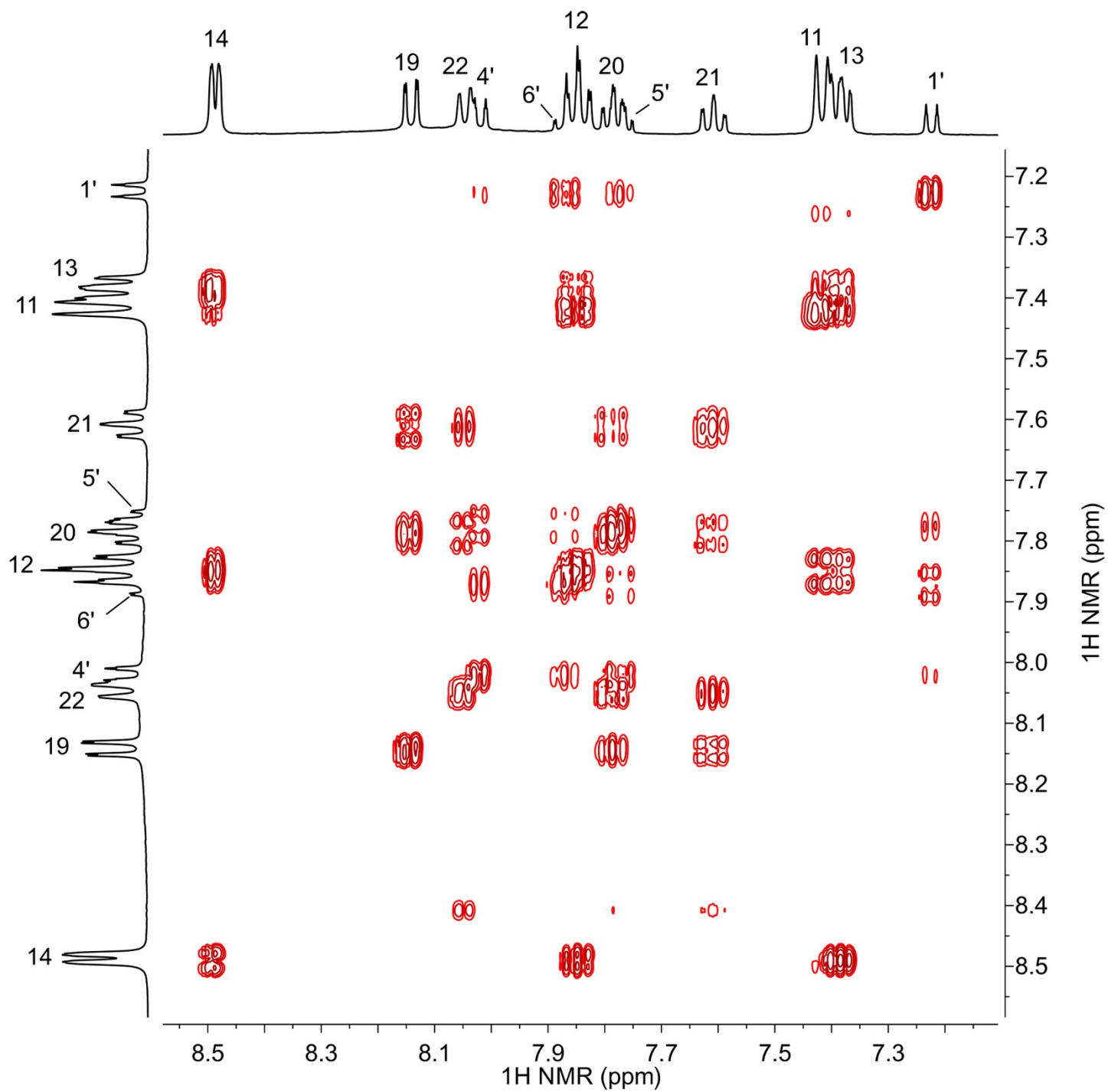
Figure S68. ^{1}H-^{1}H COSY spectrum of **1**.
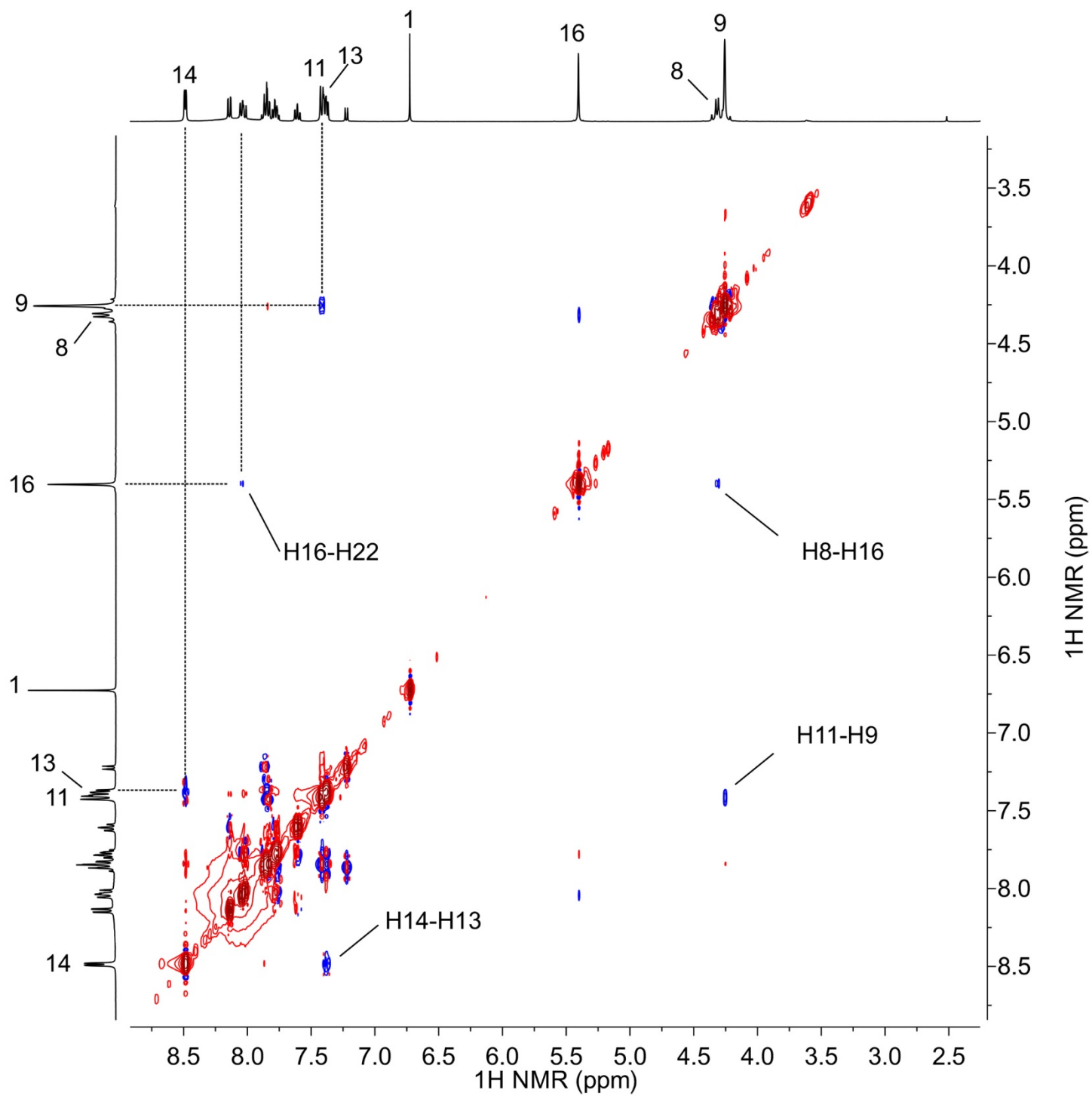
Figure S69. ^{1}H-^{1}H NOESY spectrum of **1**.
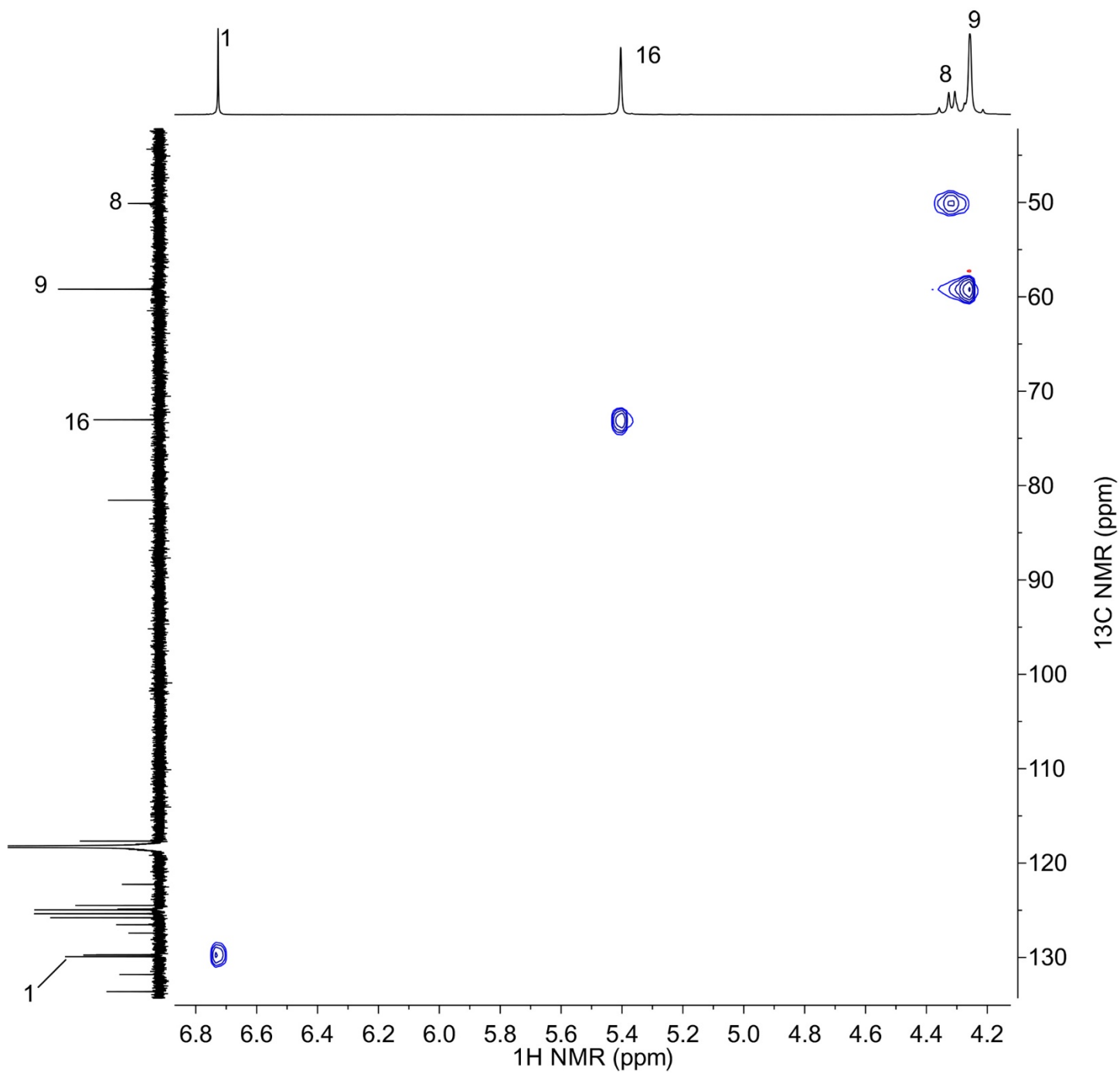
Figure S70. ^{1}H-^{13}C HSQC spectrum of **1** from 4.2 to 6.8 ppm (^{1}H) and 40 to 135 ppm (^{13}C).
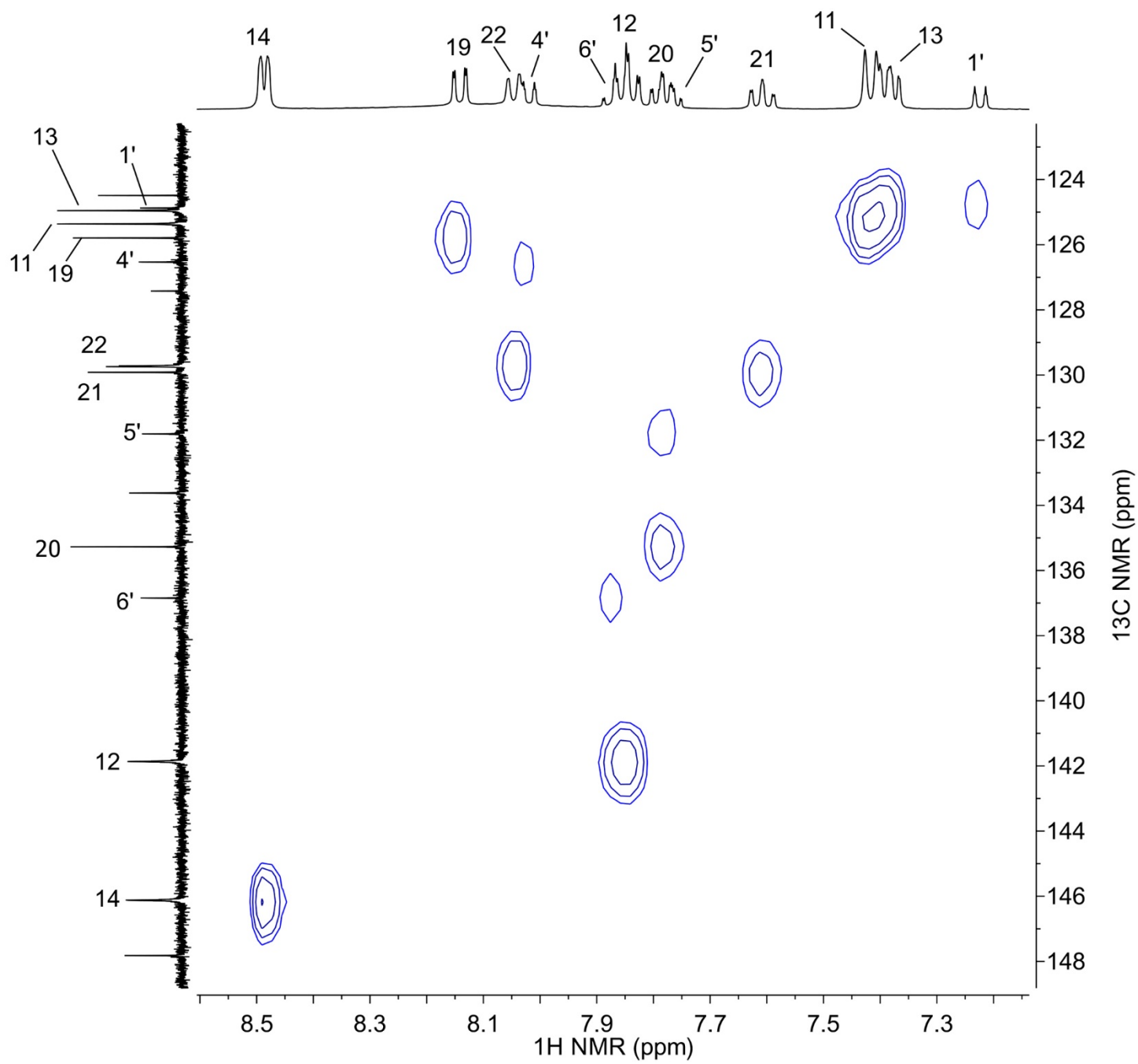
Figure S71. ^{1}H-^{13}C HSQC spectrum of **1** from 7.2 to 8.6 ppm (^{1}H) and 123 to 148 ppm (^{13}C).
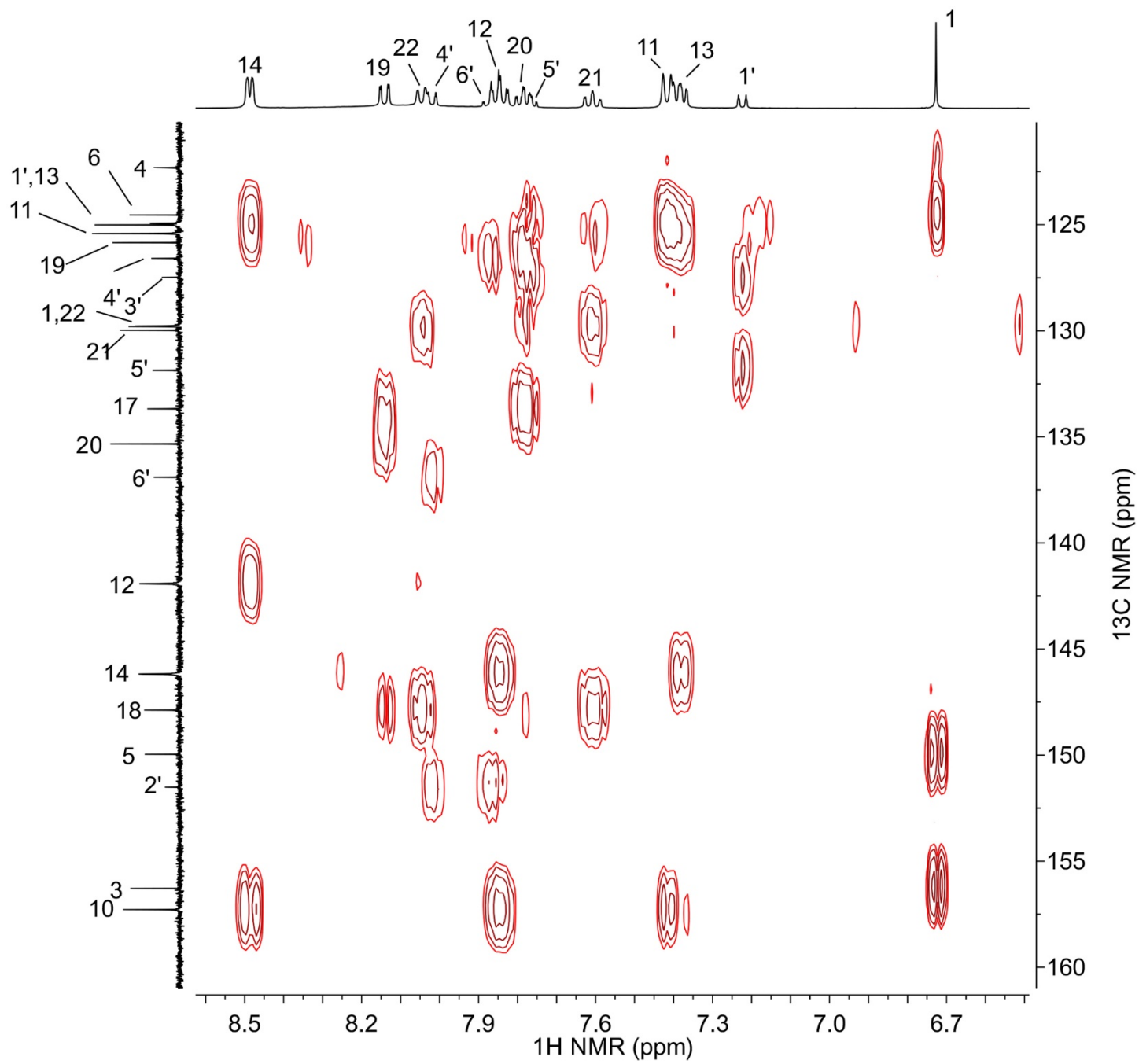
Figure S72. ^{1}H-^{13}C HMBC spectrum of **1** from 6.5 to 8.6 ppm (^{1}H) and 120 to 160 ppm (^{13}C).
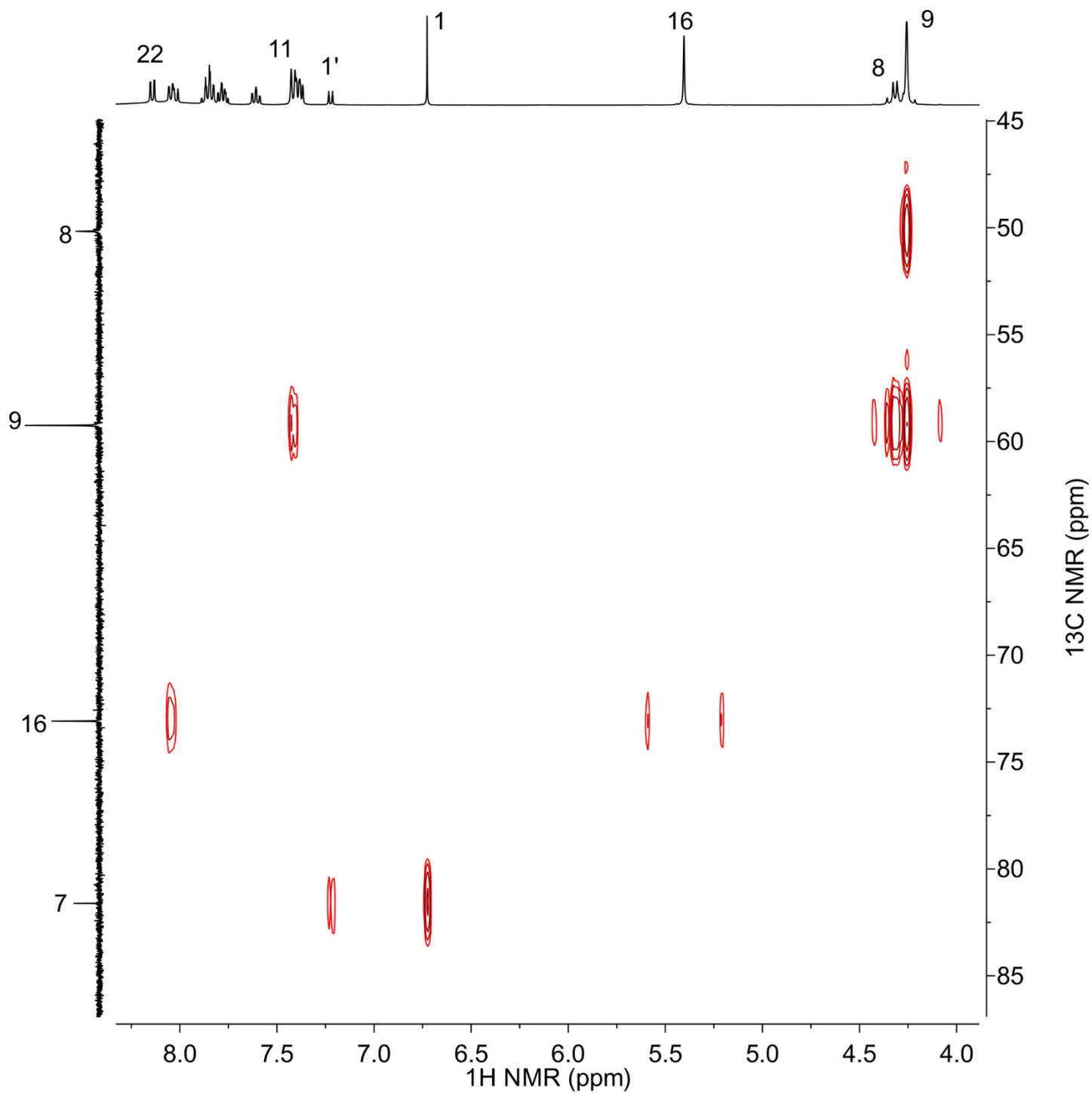
Figure S73. ^{1}H-^{13}C HMBC spectrum of **1** from 4.0 to 8.3 ppm (^{1}H) and 45 to 85 ppm (^{13}C).
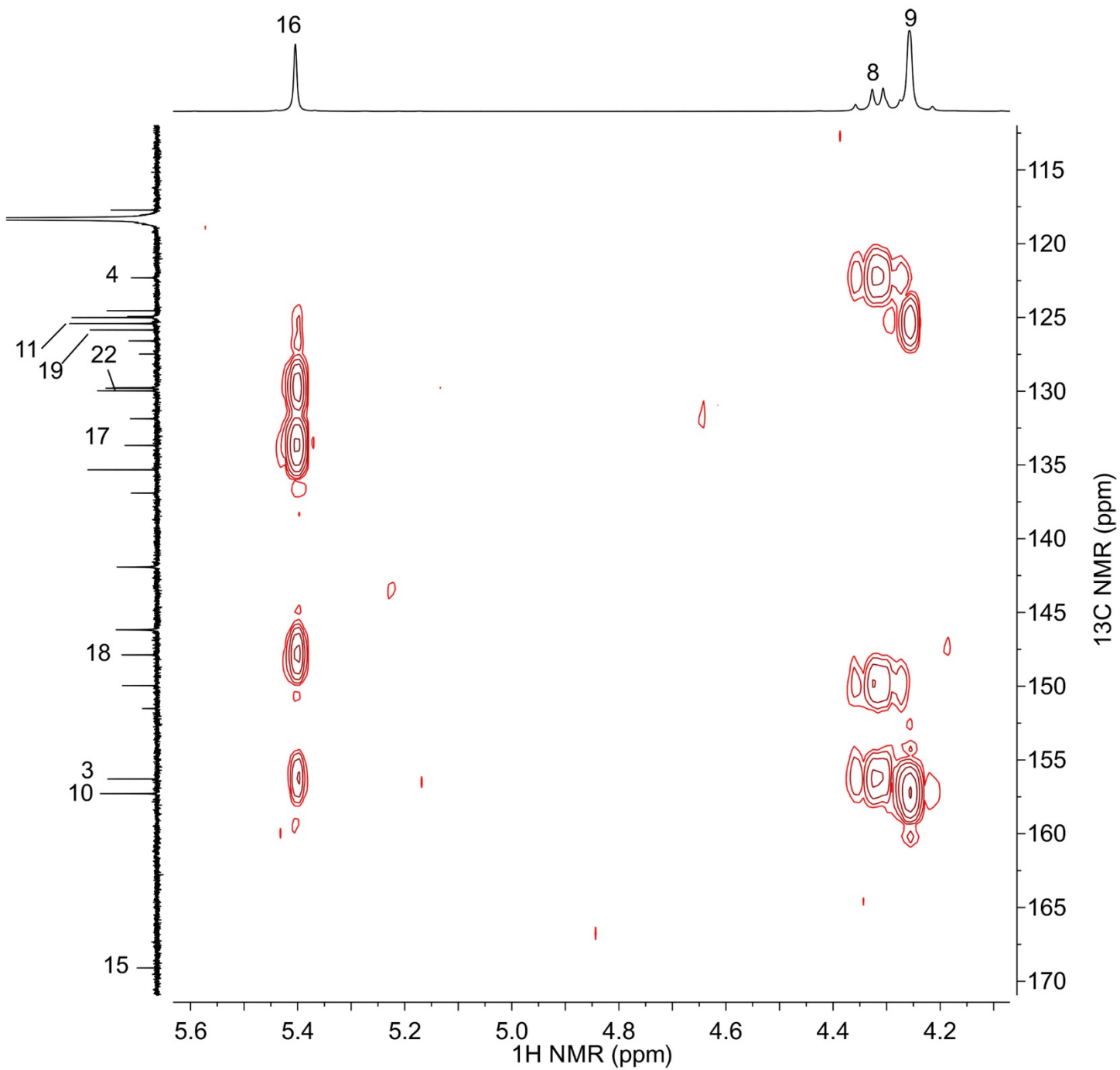
Figure S74. ^{1}H-^{13}C HMBC spectrum of **1** from 4.1 to 5.6 ppm (^{1}H) and 110 to 170 ppm (^{13}C).
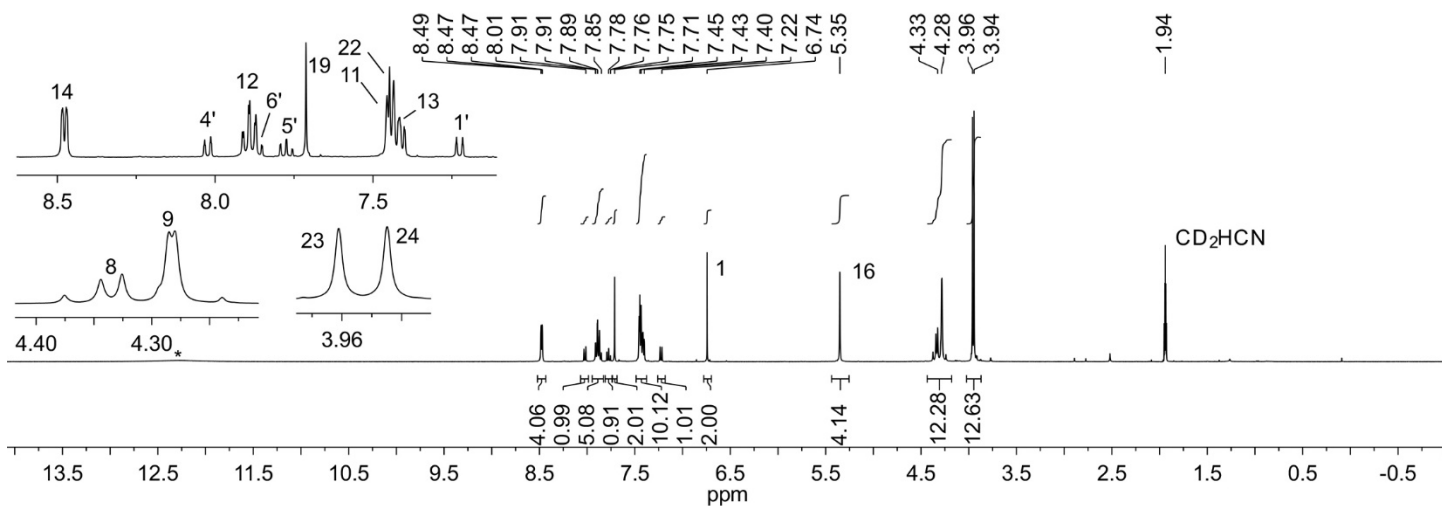
Figure S75. ^{1}H NMR spectrum of **2**.
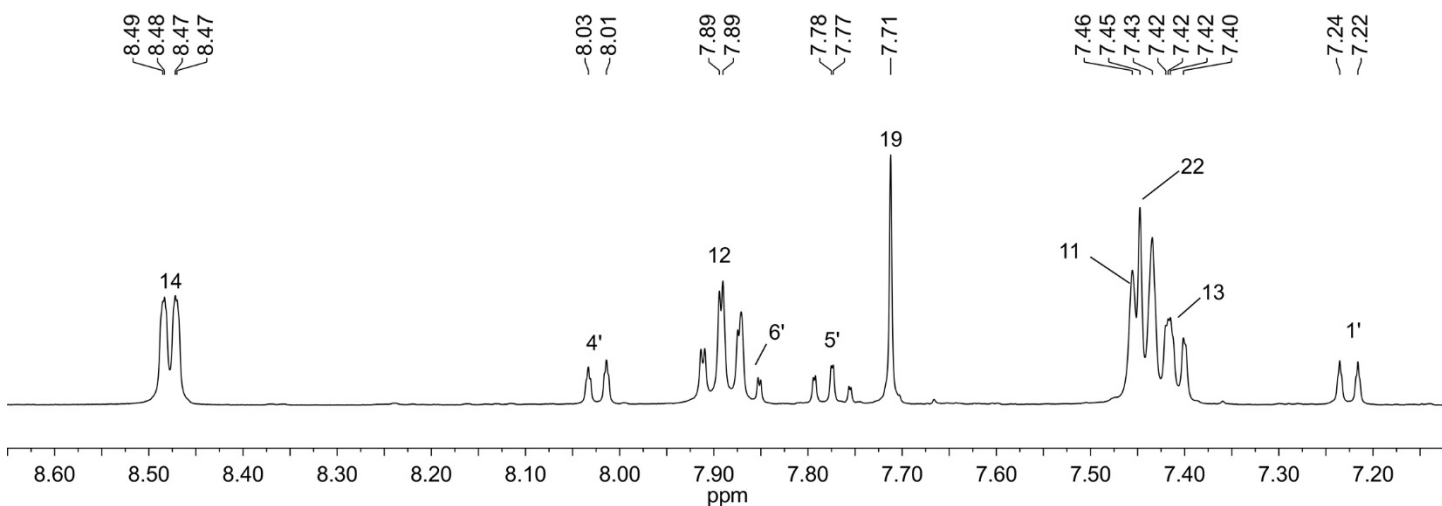
Figure S76. Expansion of ^{1}H NMR spectrum of **2**.
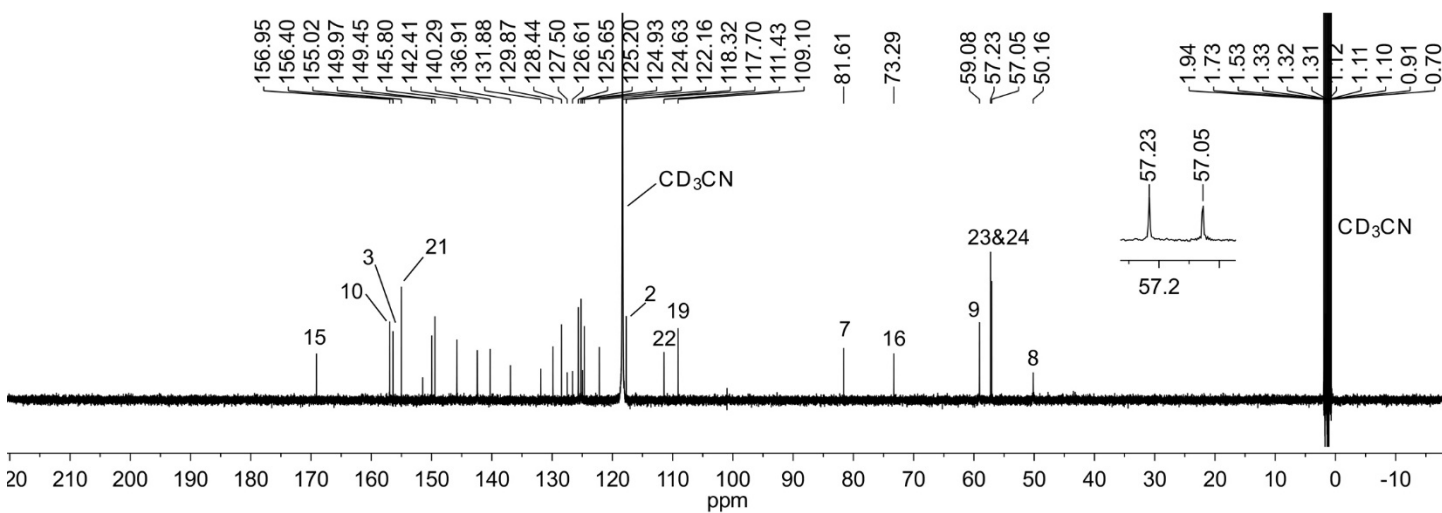
Figure S77. ^{13}C{^{1}H} NMR spectrum of **2**.
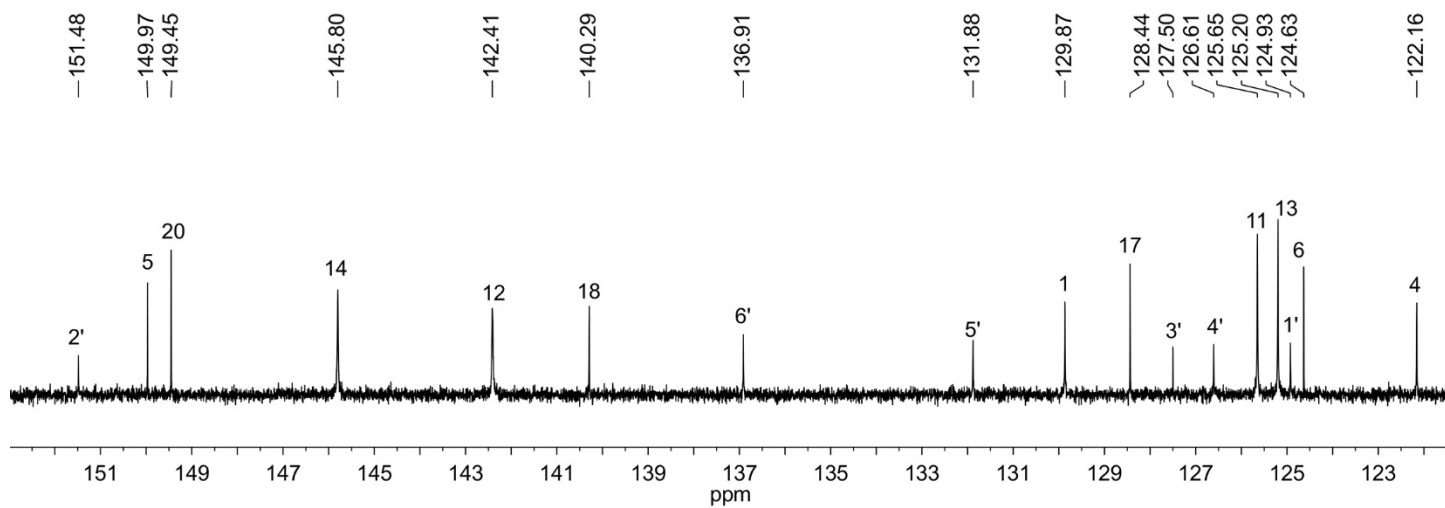
Figure S78. Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **2**.
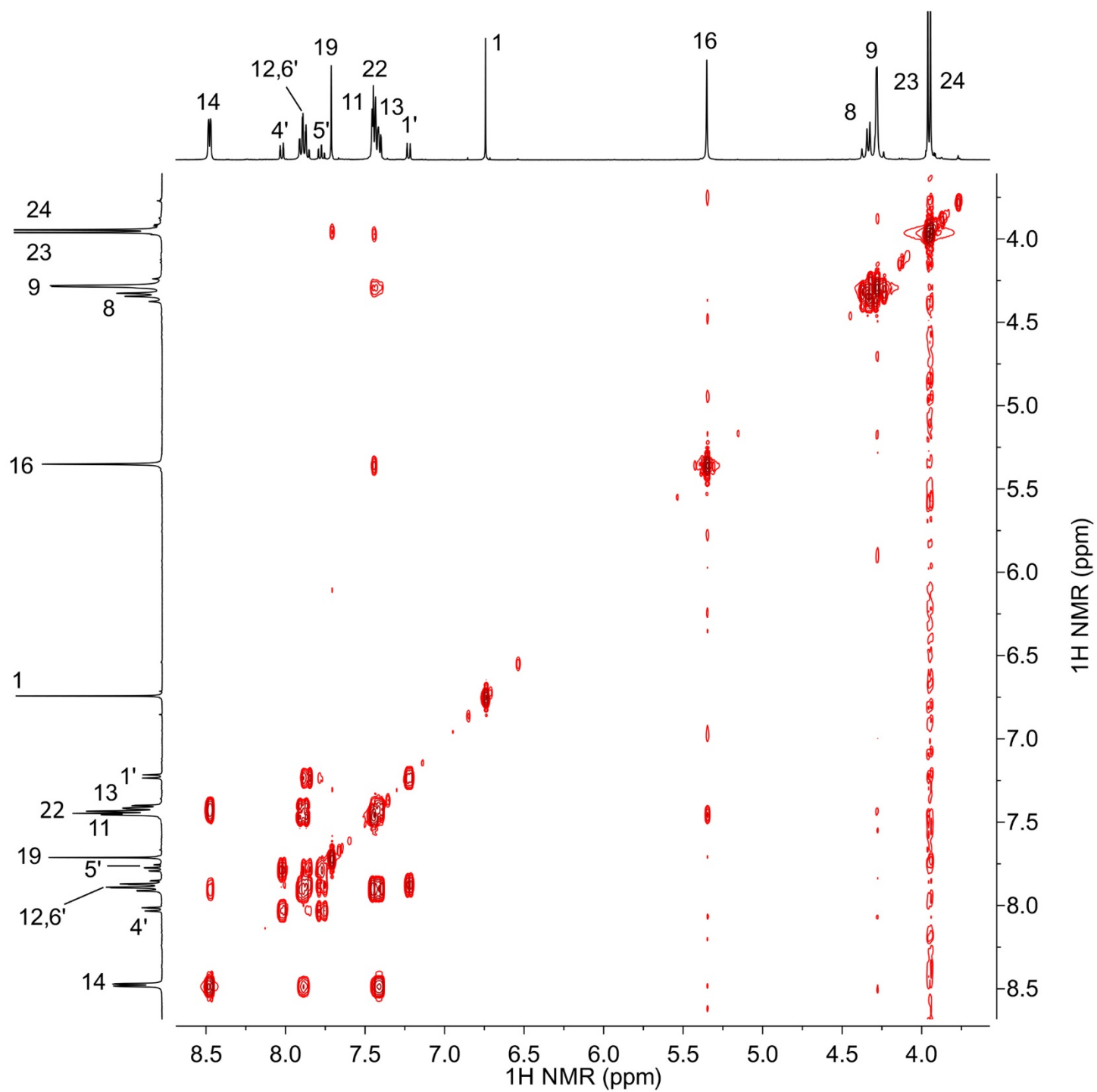
Figure S79. ^{1}H-^{1}H COSY spectrum of **2**.
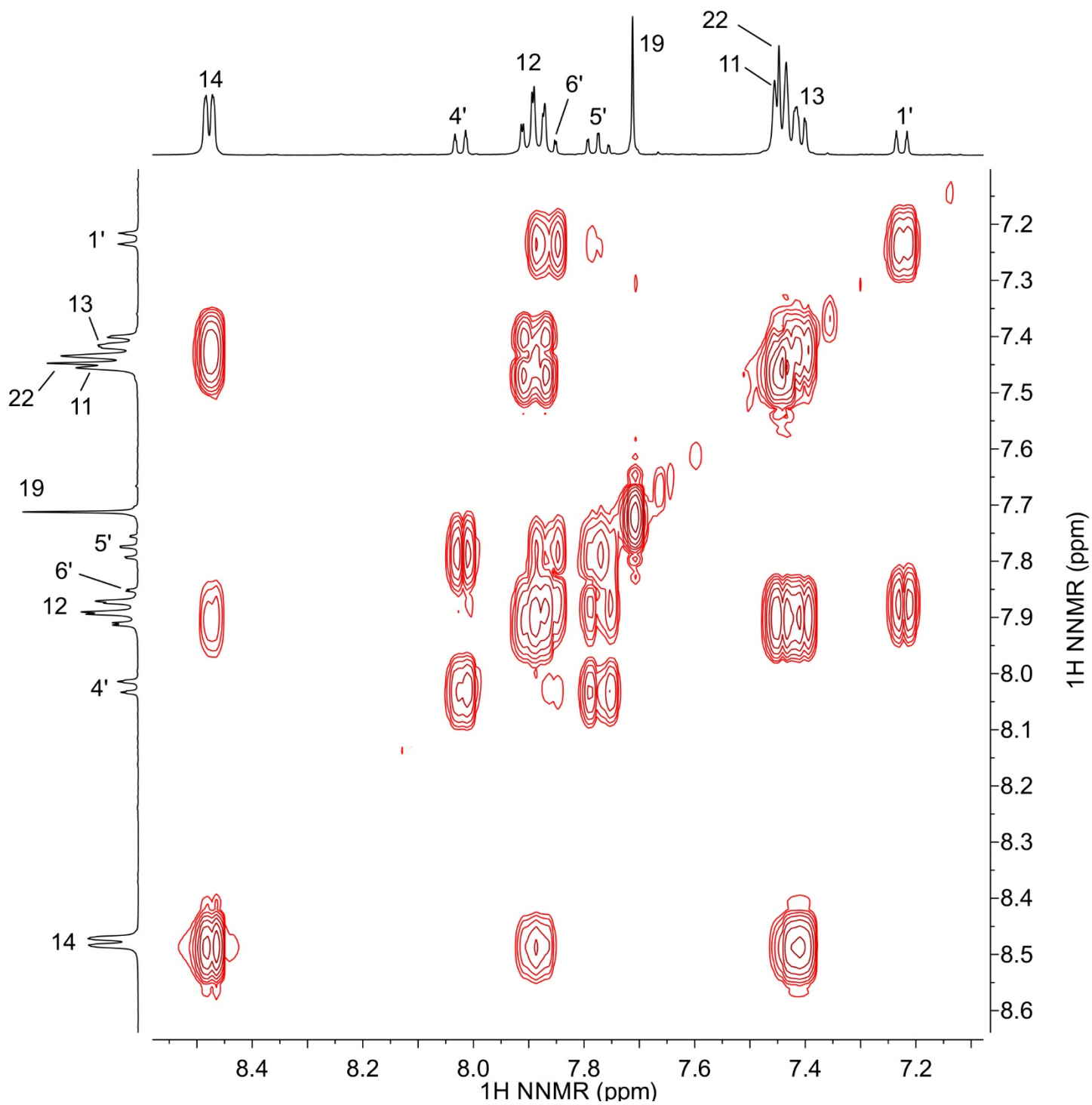
Figure S80. Expansion of ^{1}H-^{1}H COSY spectrum of **2**.
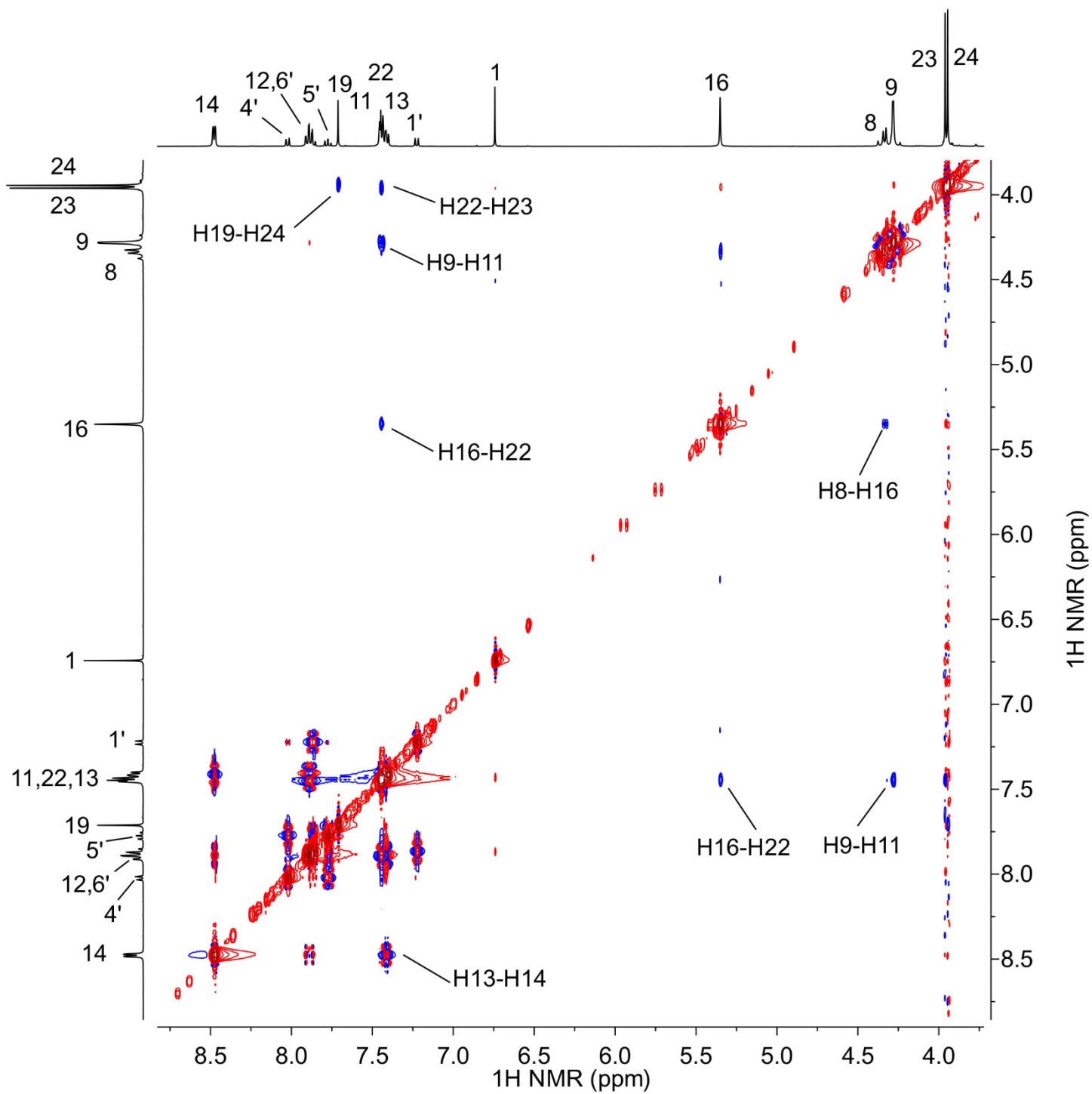
Figure S81. ^{1}H-^{1}H NOESY spectrum of **2**.
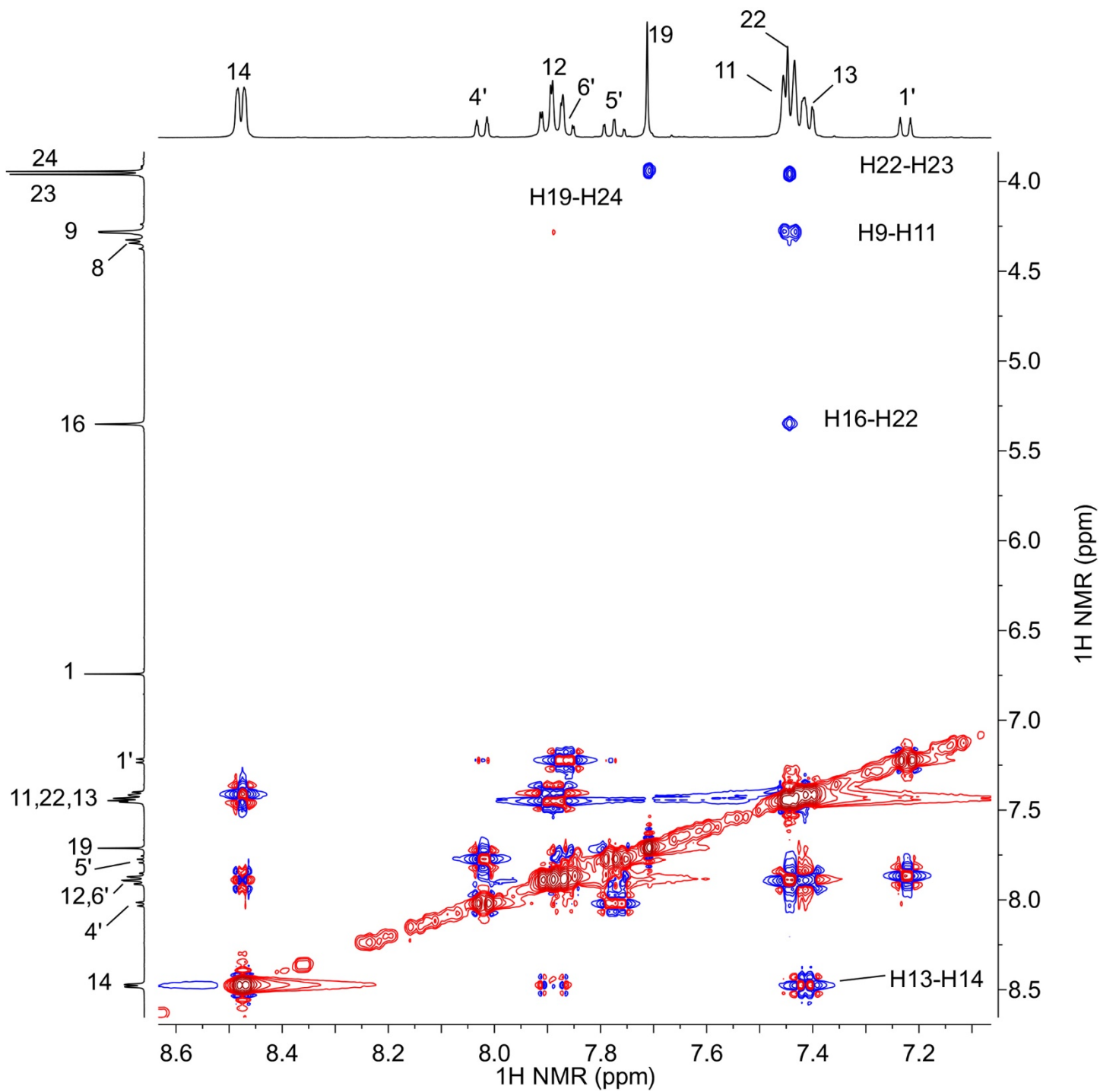
Figure S82. Expansion of ^{1}H-^{1}H NOESY spectrum of **2**.
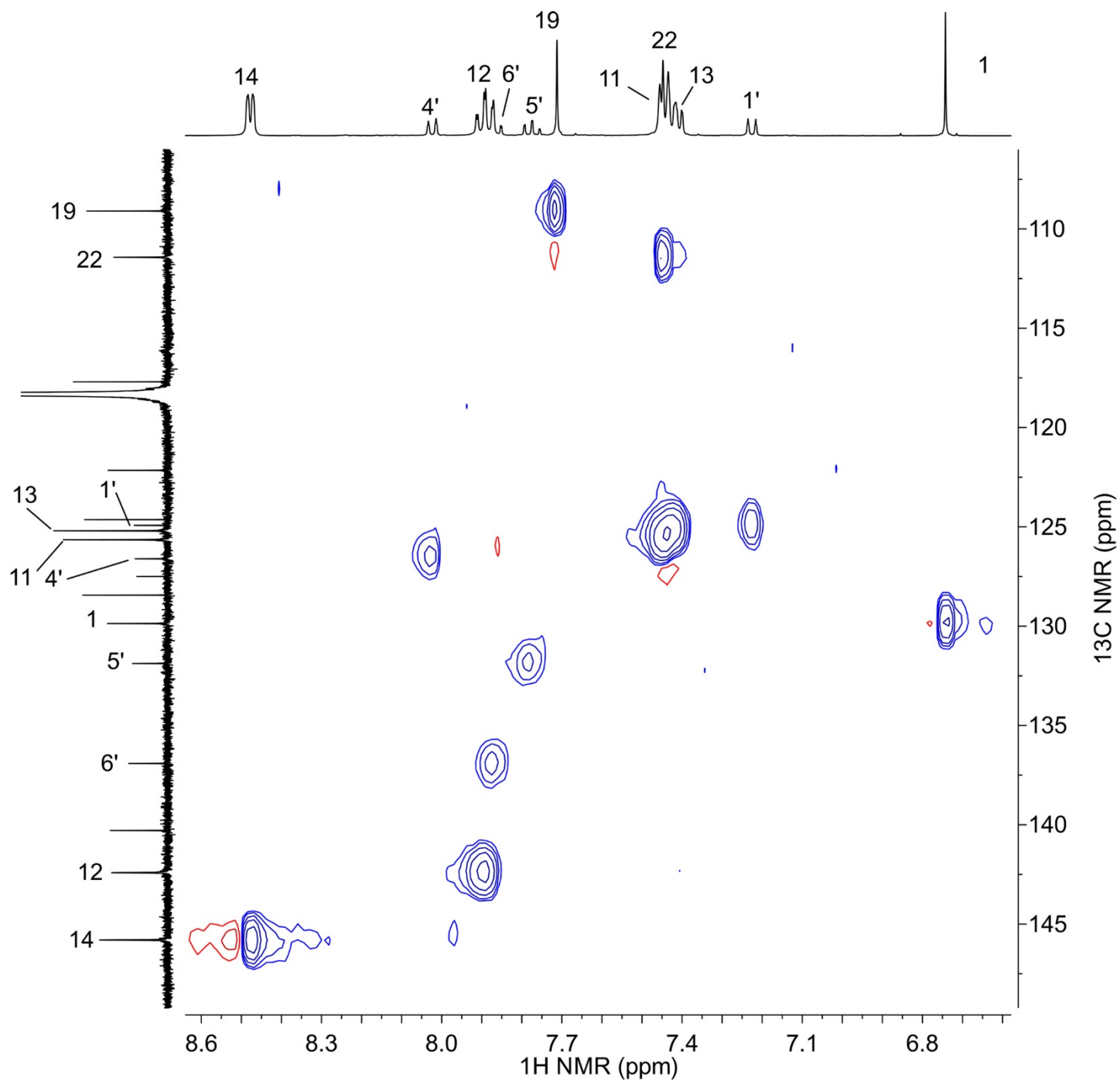
Figure S83. ^{1}H-^{13}C HSQC spectrum of **2** from 6.6 to 8.6 ppm (^{1}H) and 100 to 150 ppm (^{13}C).
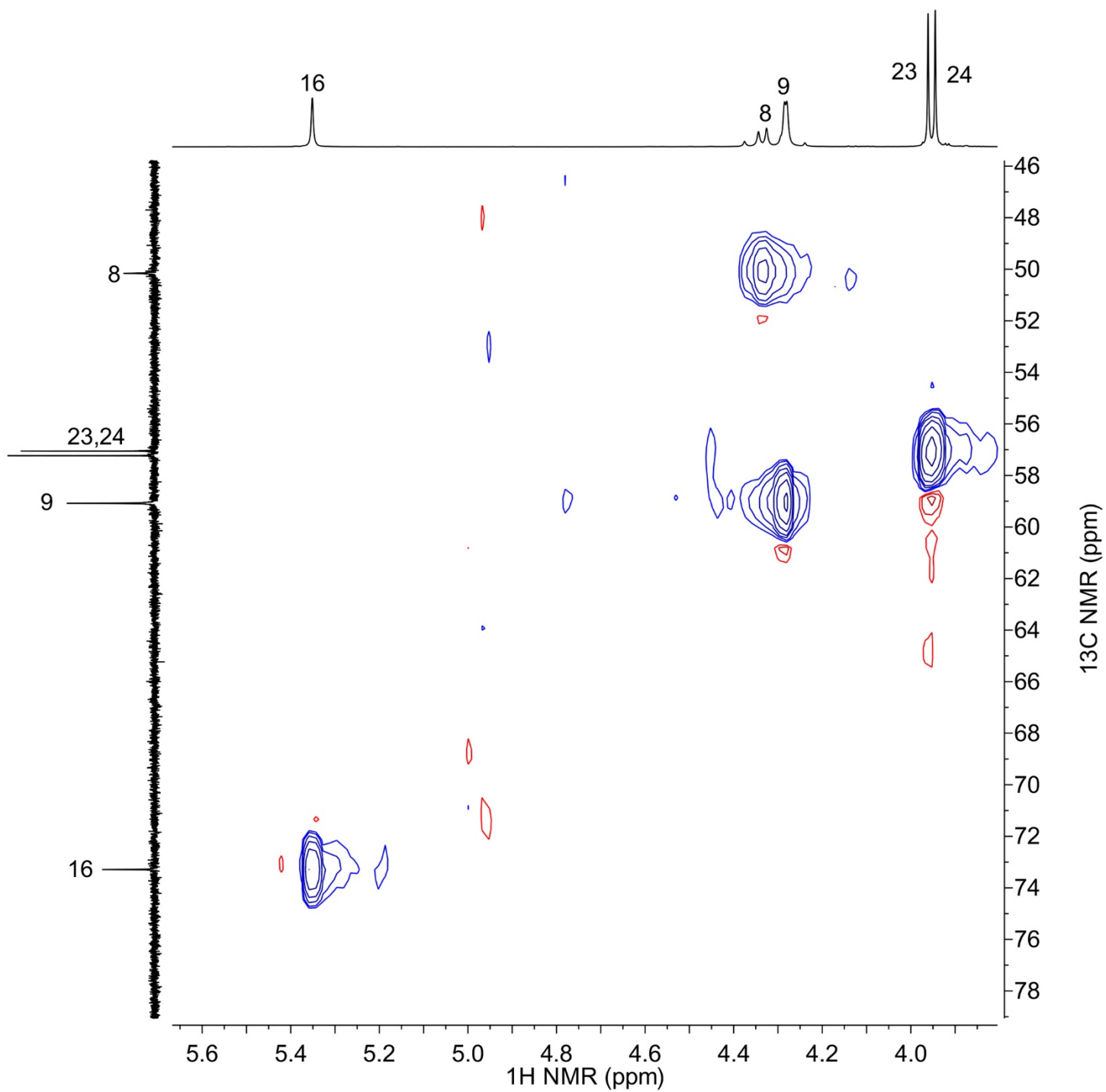
Figure S84. ^{1}H-^{13}C HSQC spectrum of **2** from 3.8 to 5.7 ppm (^{1}H) and 46 to 78 ppm (^{13}C).
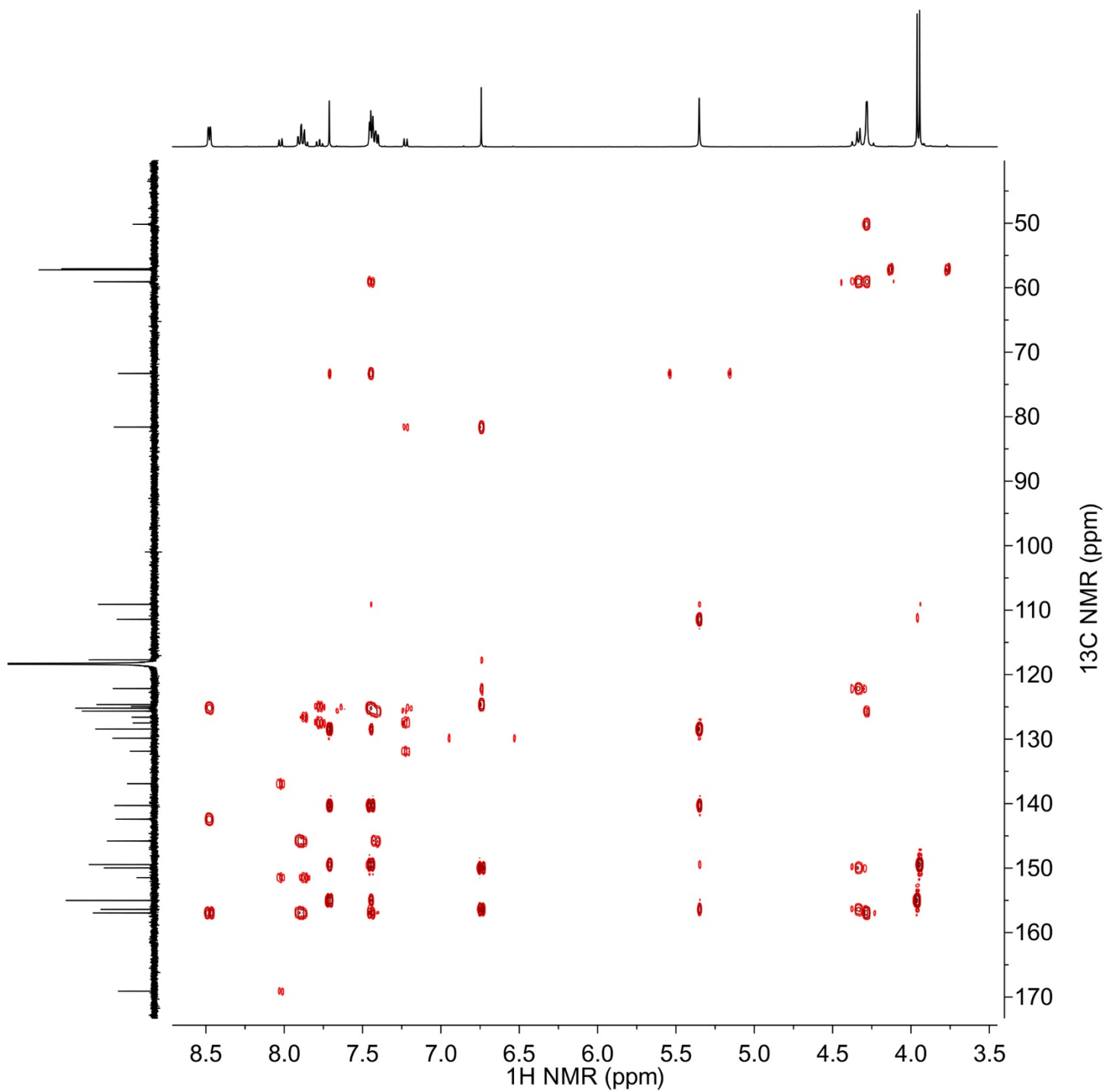
Figure S85. ^{1}H-^{13}C HMBC spectrum of **2**.
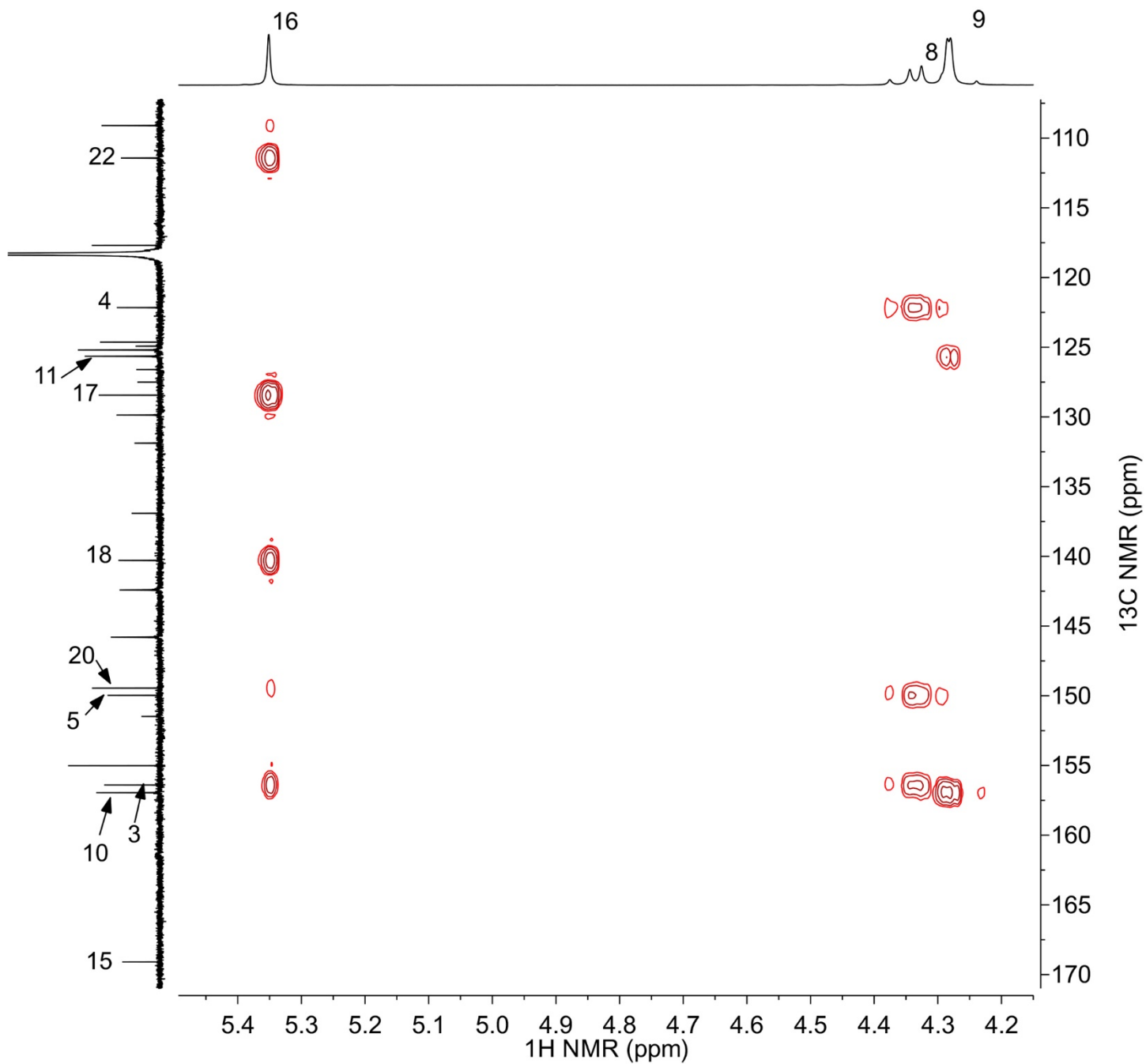
Figure S86. Expansion of ^{1}H-^{13}C HMBC spectrum of **2** from 4.2 to 5.5 ppm (^{1}H) and 105 to 170 ppm (^{13}C).
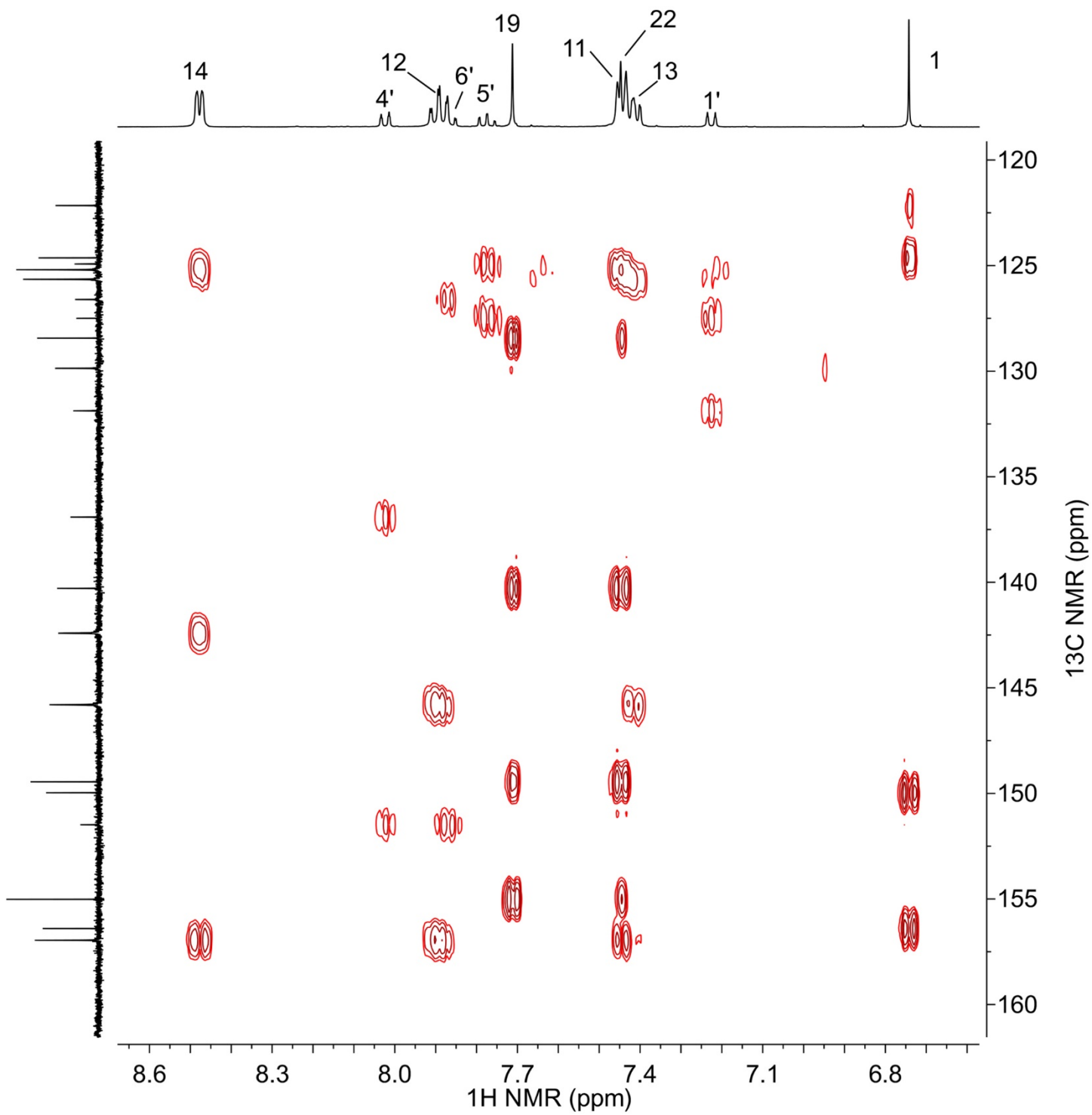
Figure S87. Expansion of ^{1}H-^{13}C HMBC spectrum of **2** from 6.6 to 8.7 ppm (^{1}H) and 120 to 160 ppm (^{13}C).
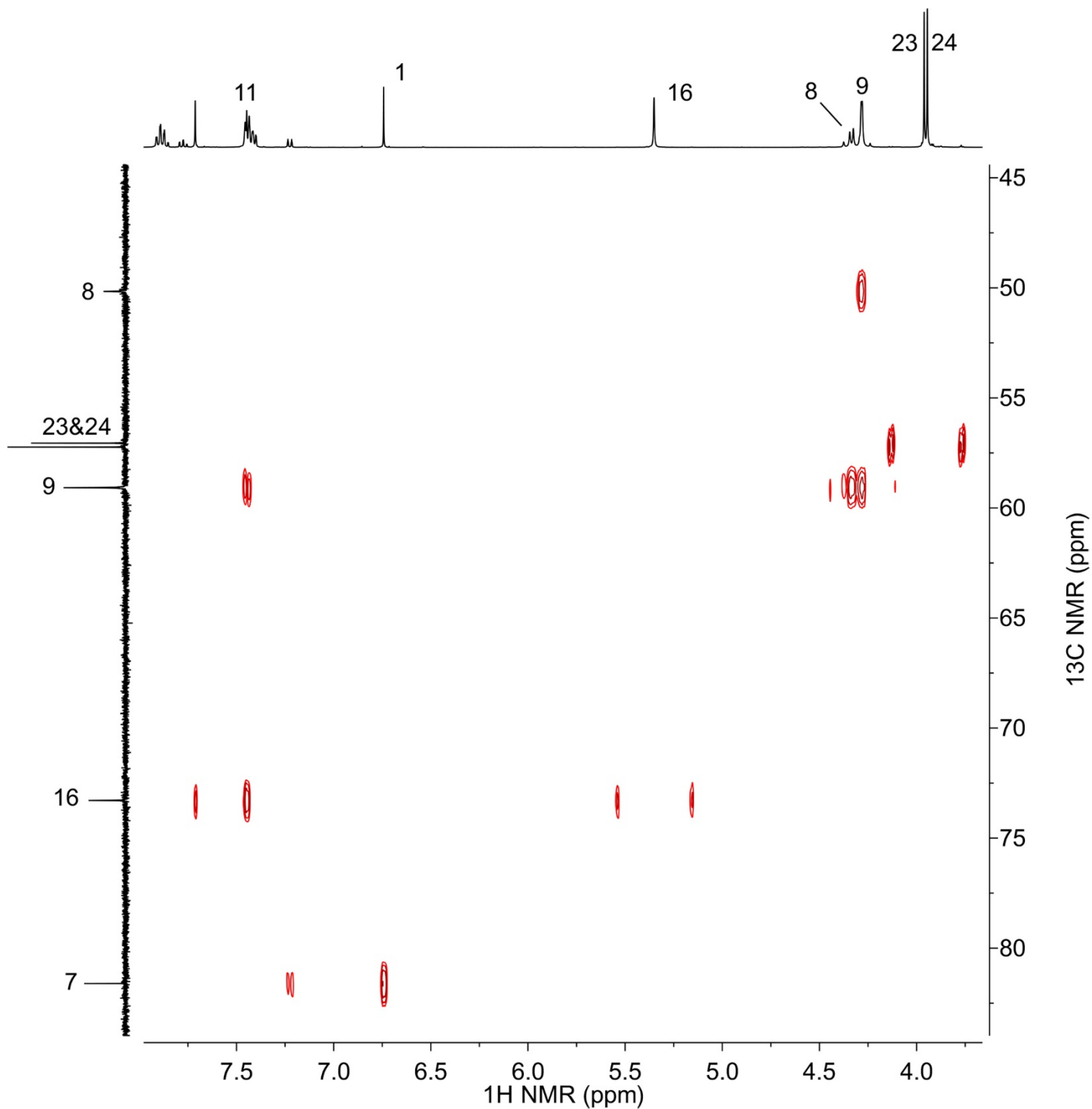
Figure S88. Expansion of ^{1}H-^{13}C HMBC spectrum of **2** from 3.7 to 8.0 ppm (^{1}H) and 45 to 90 ppm (^{13}C).
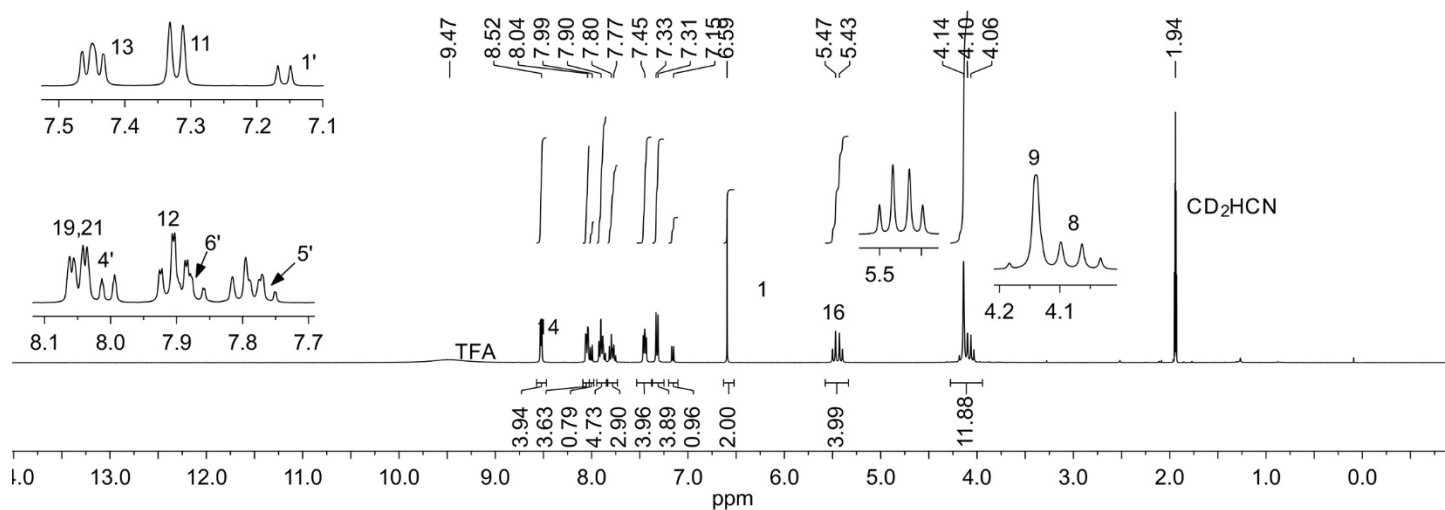
Figure S89. ^{1}H NMR spectrum of **3**.
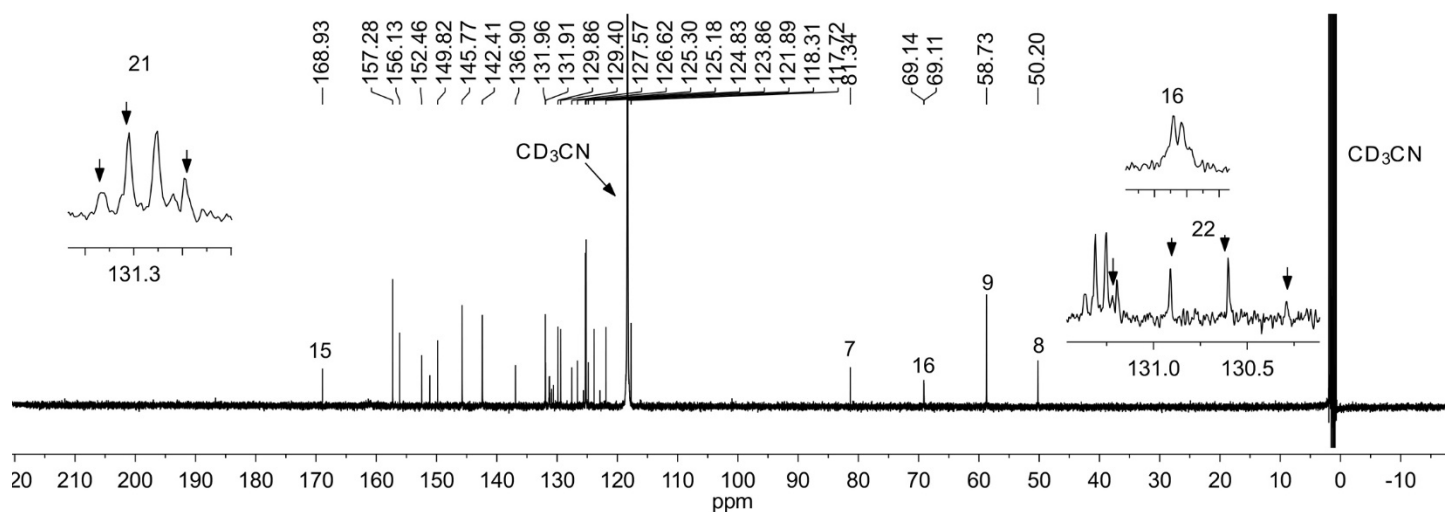
Figure S90. ^{13}C{^{1}H} NMR spectrum of **3**.
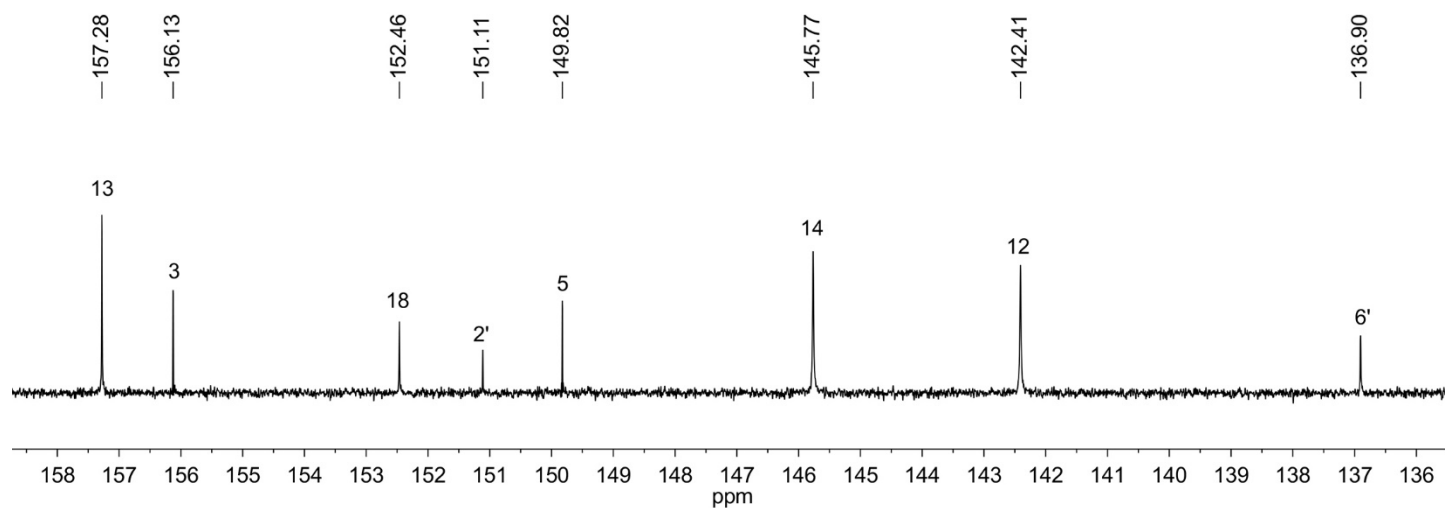
Figure S91. Expansion of ^{13}C{^{1}H} NMR spectrum of **3** from 136 to 159 ppm.
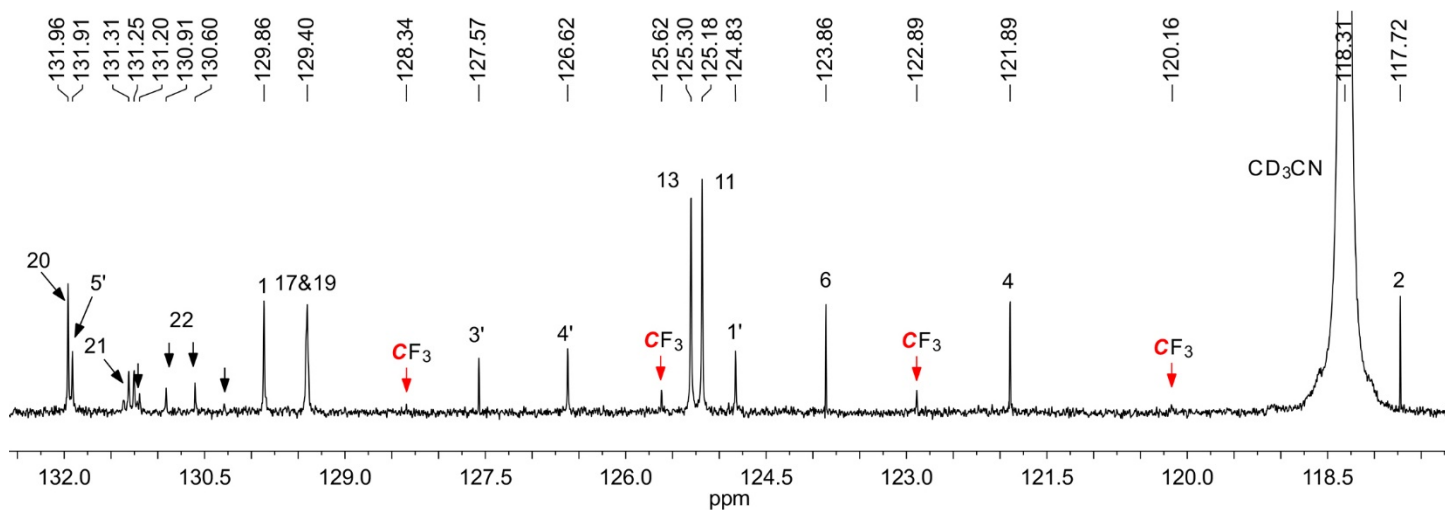
Figure S92. Expansion of $^{13}C\{^1H\}$ NMR spectrum of **3** from 117 to 132 ppm.
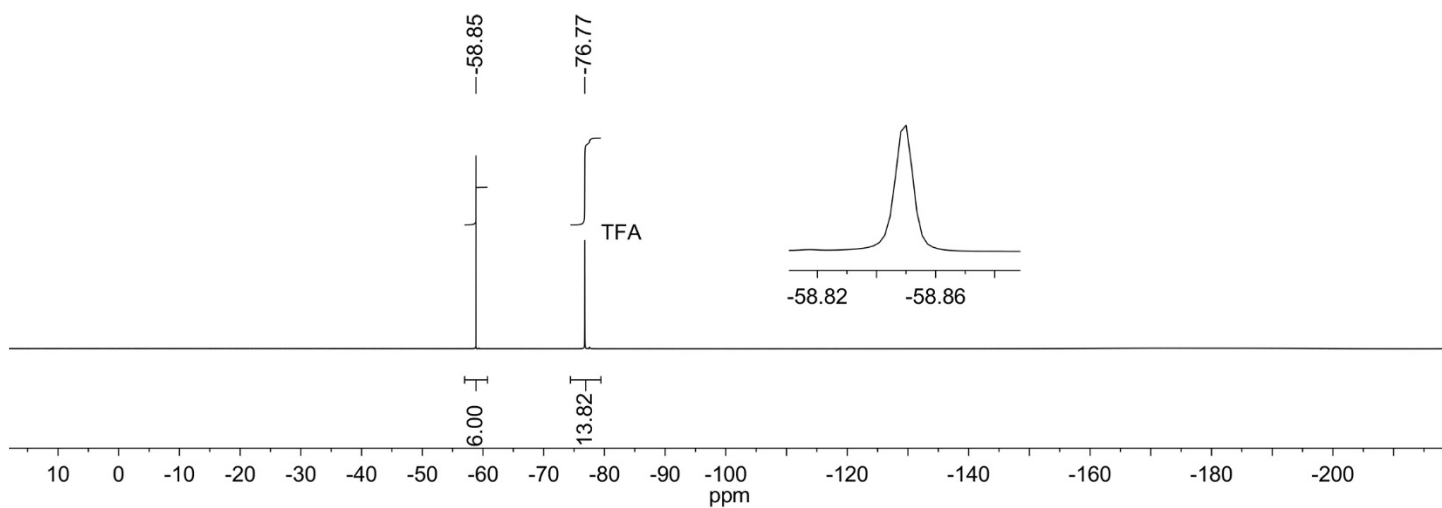
Figure S93. ^{19}F NMR spectrum of **3**.
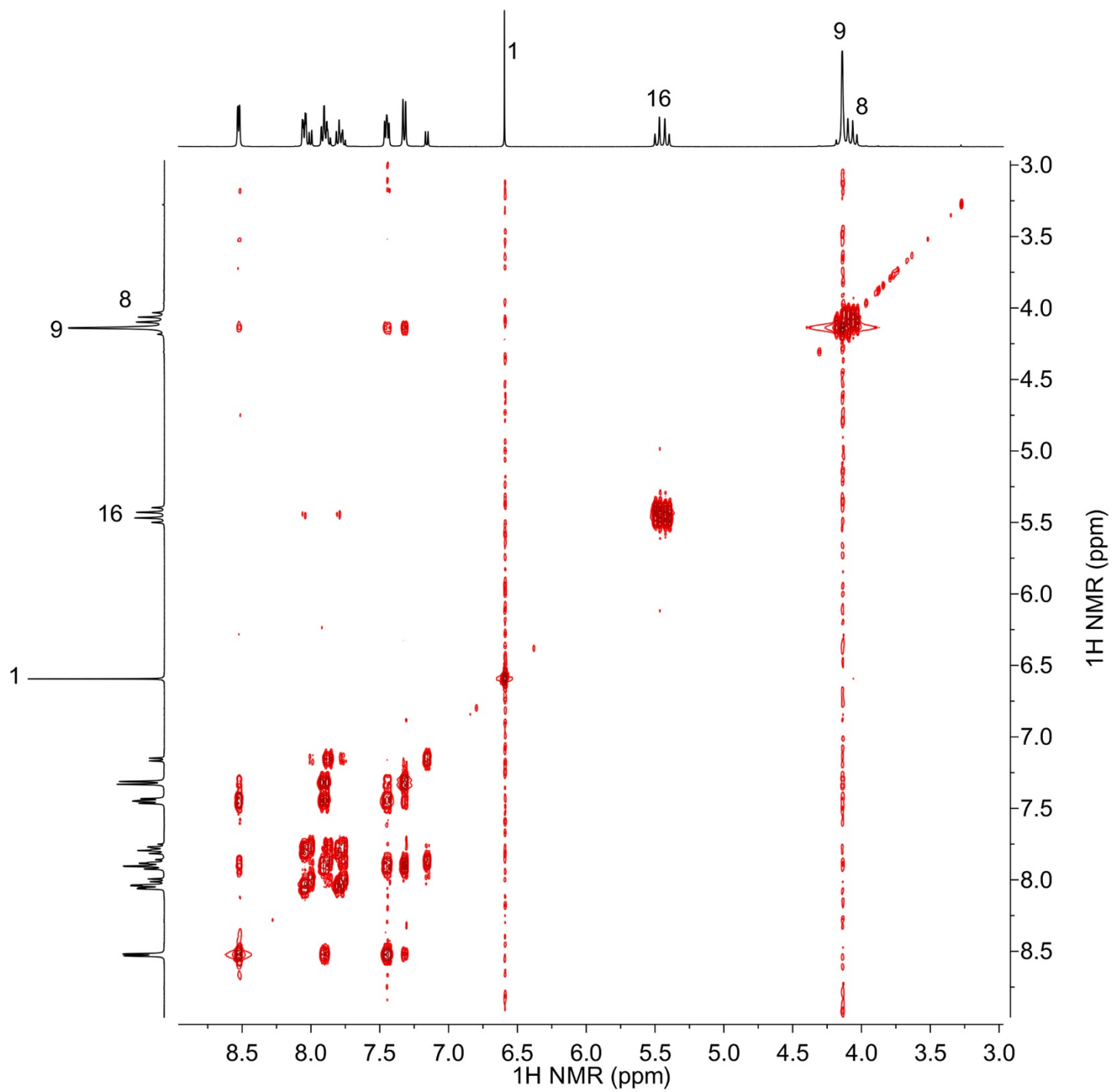
Figure S94. ^{1}H-^{1}H COSY spectrum of **3**.
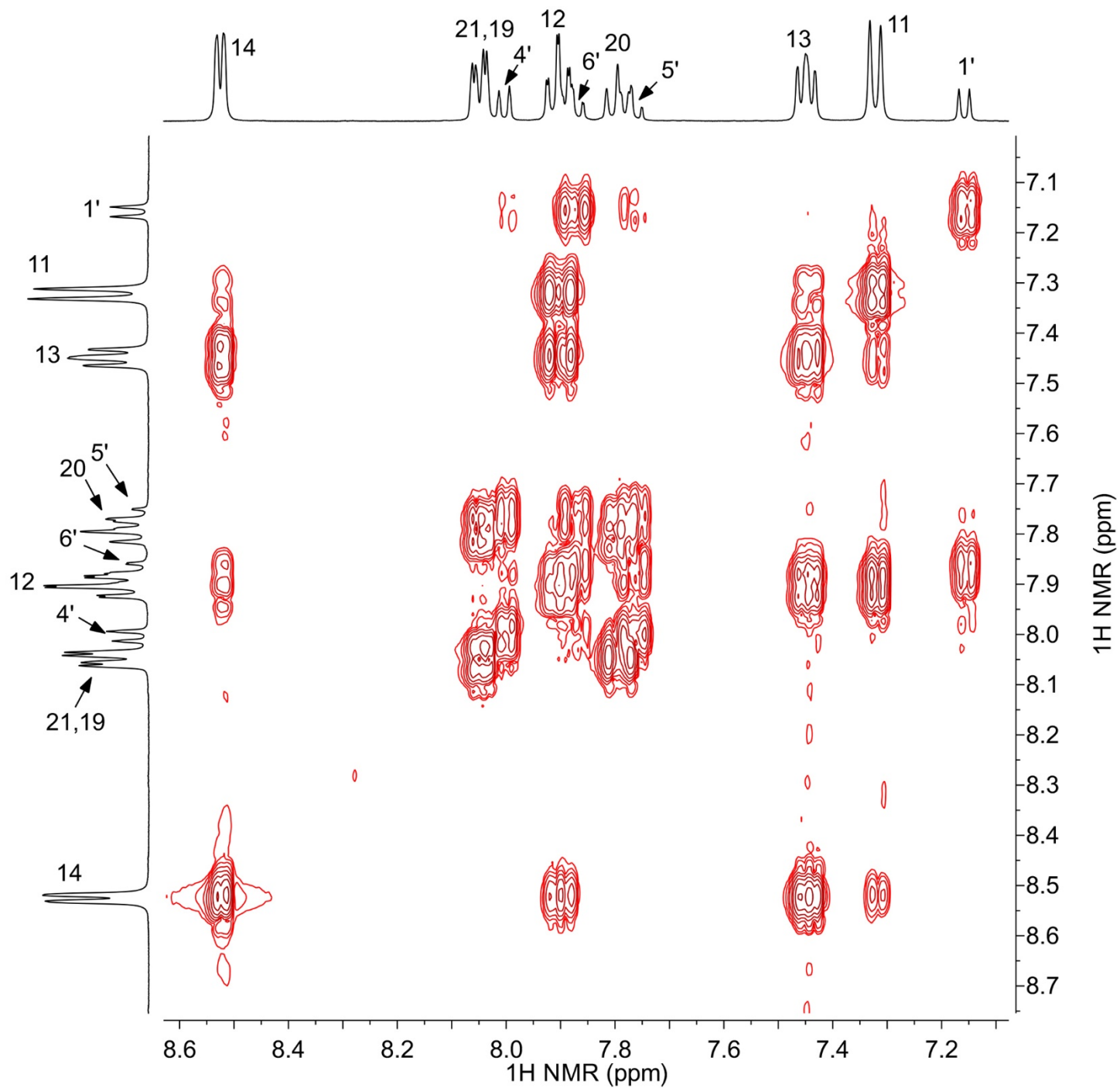
Figure S95. Expansion of ^{1}H-^{1}H COSY spectrum of **3**.
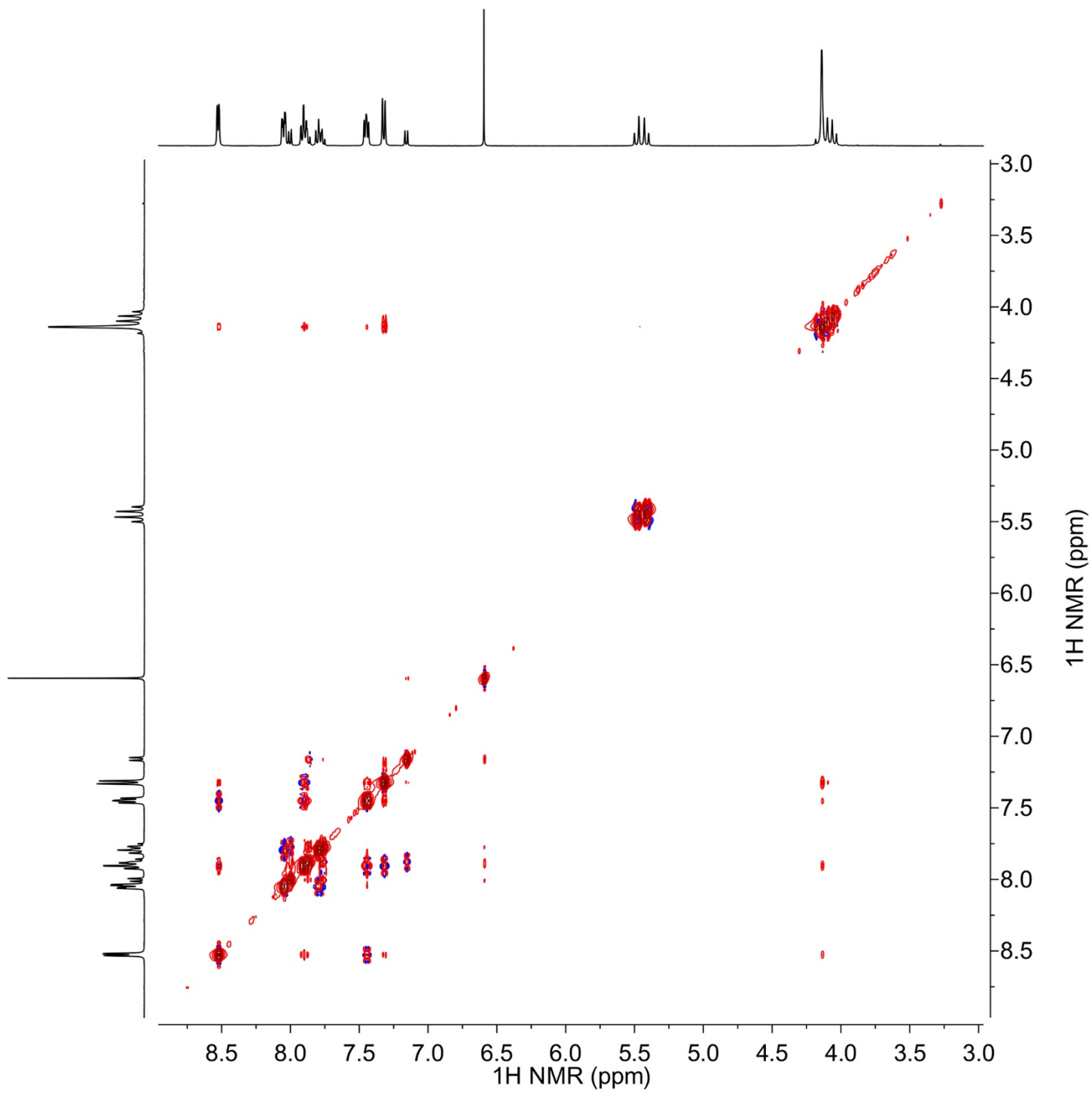
Figure S96. ^{1}H-^{1}H NOESY spectrum of **3**.
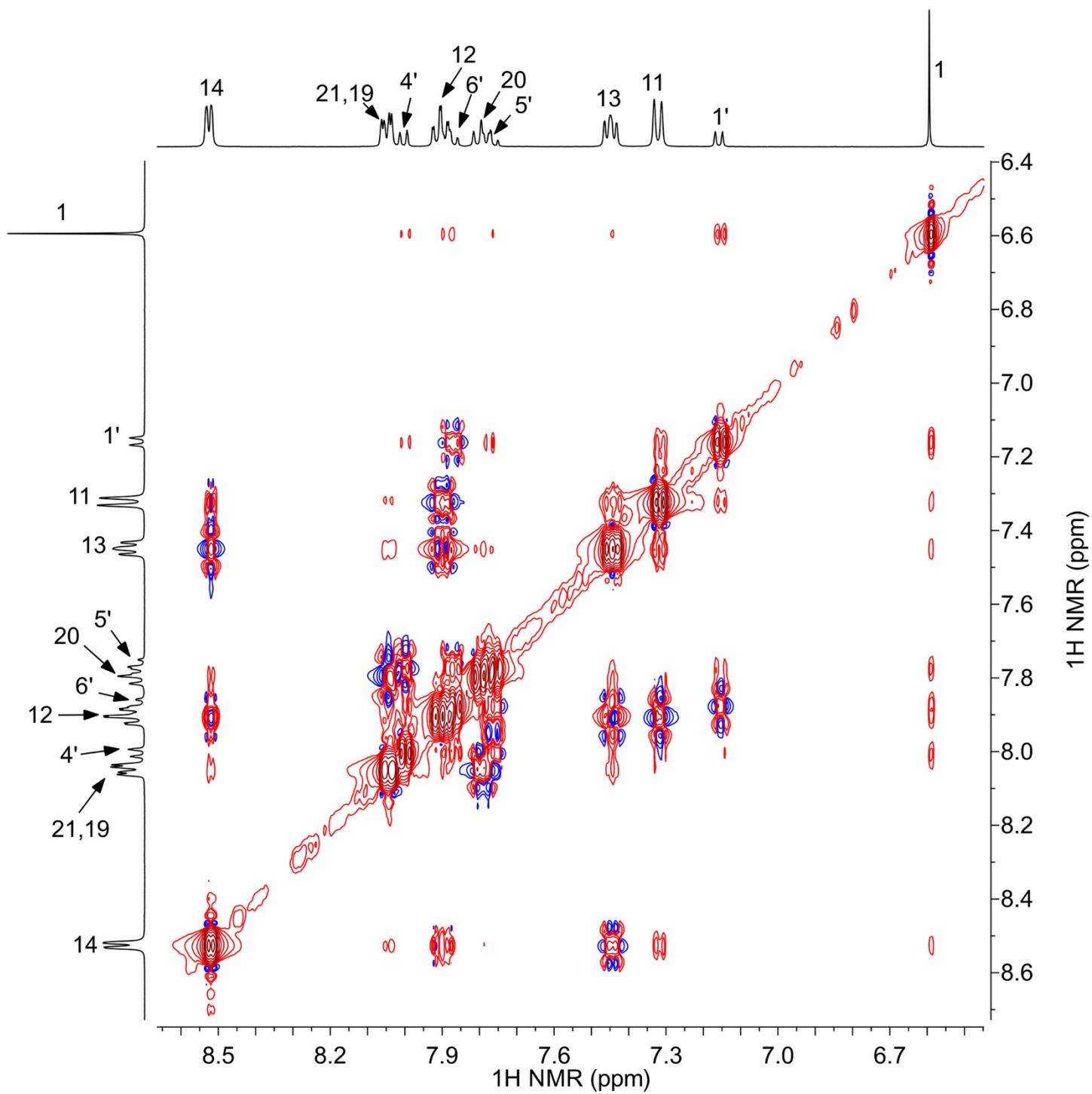
Figure S97. Expansion of ^{1}H-^{1}H NOESY spectrum of **3** from 6.4 to 8.7 ppm.
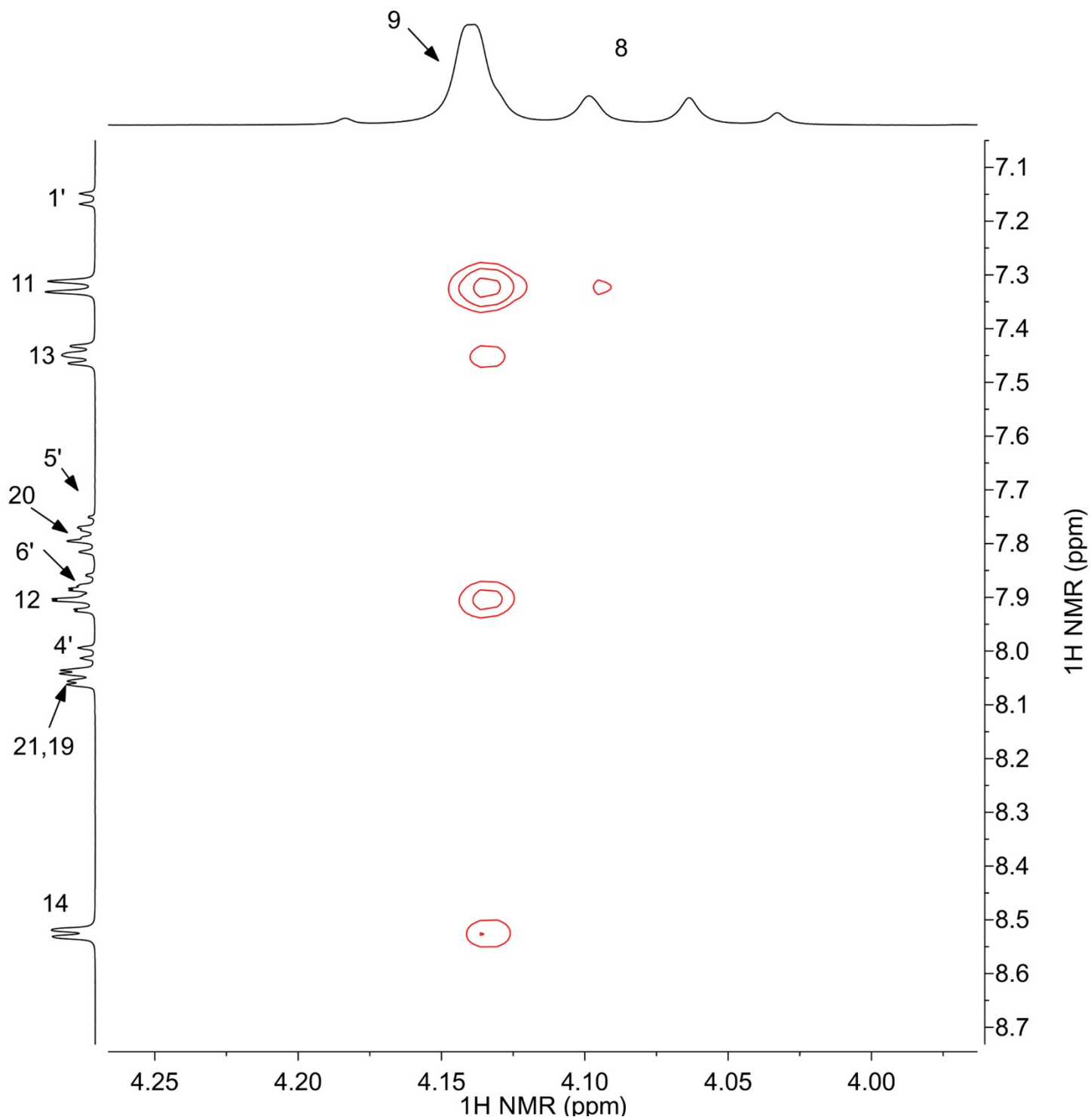
Figure S98. Expansion of ^{1}H-^{1}H NOESY spectrum of **3** from 4.0 to 4.3 ppm.
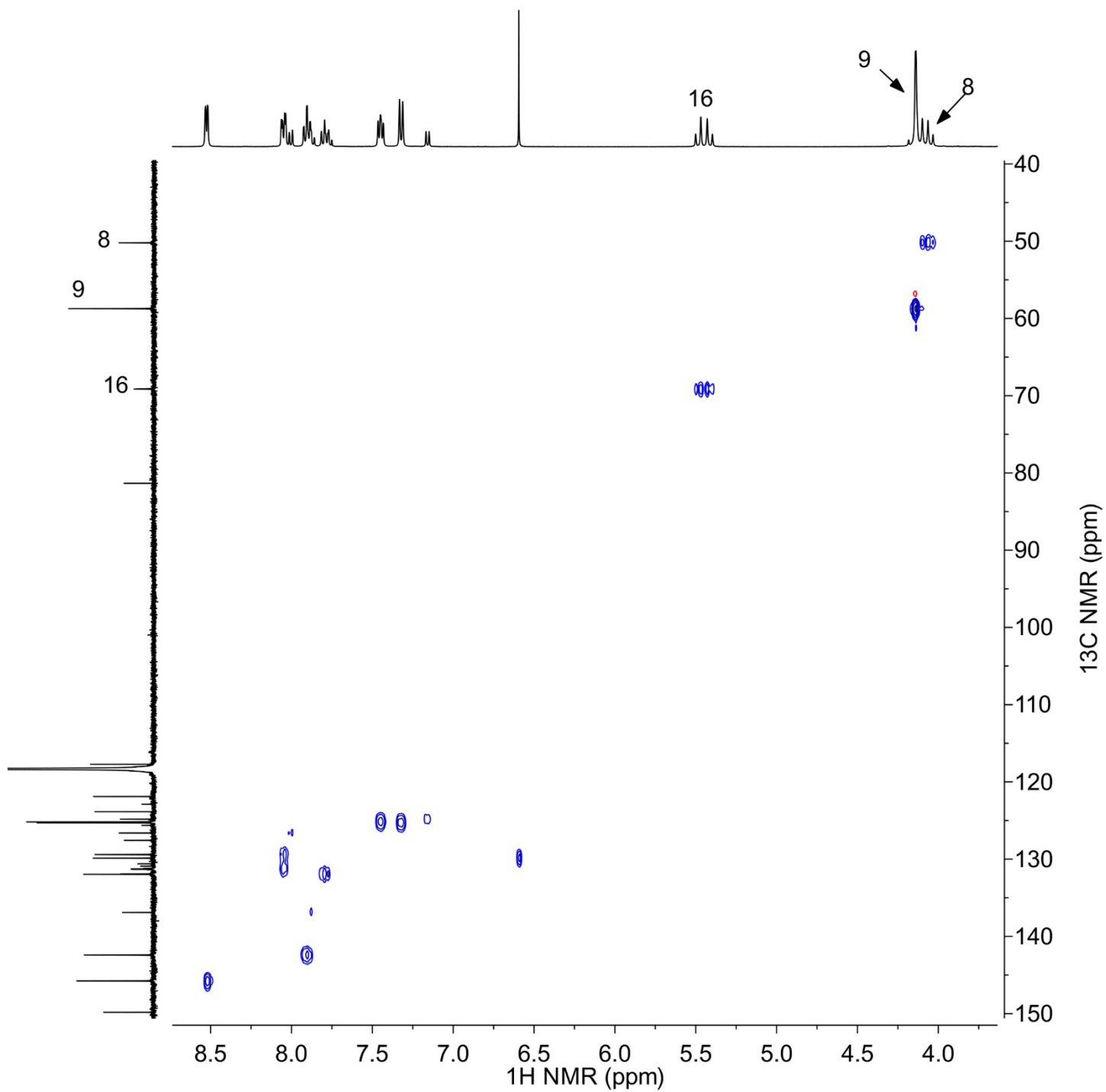
Figure S99. ^{1}H-^{13}C HSQC spectrum of **3**.
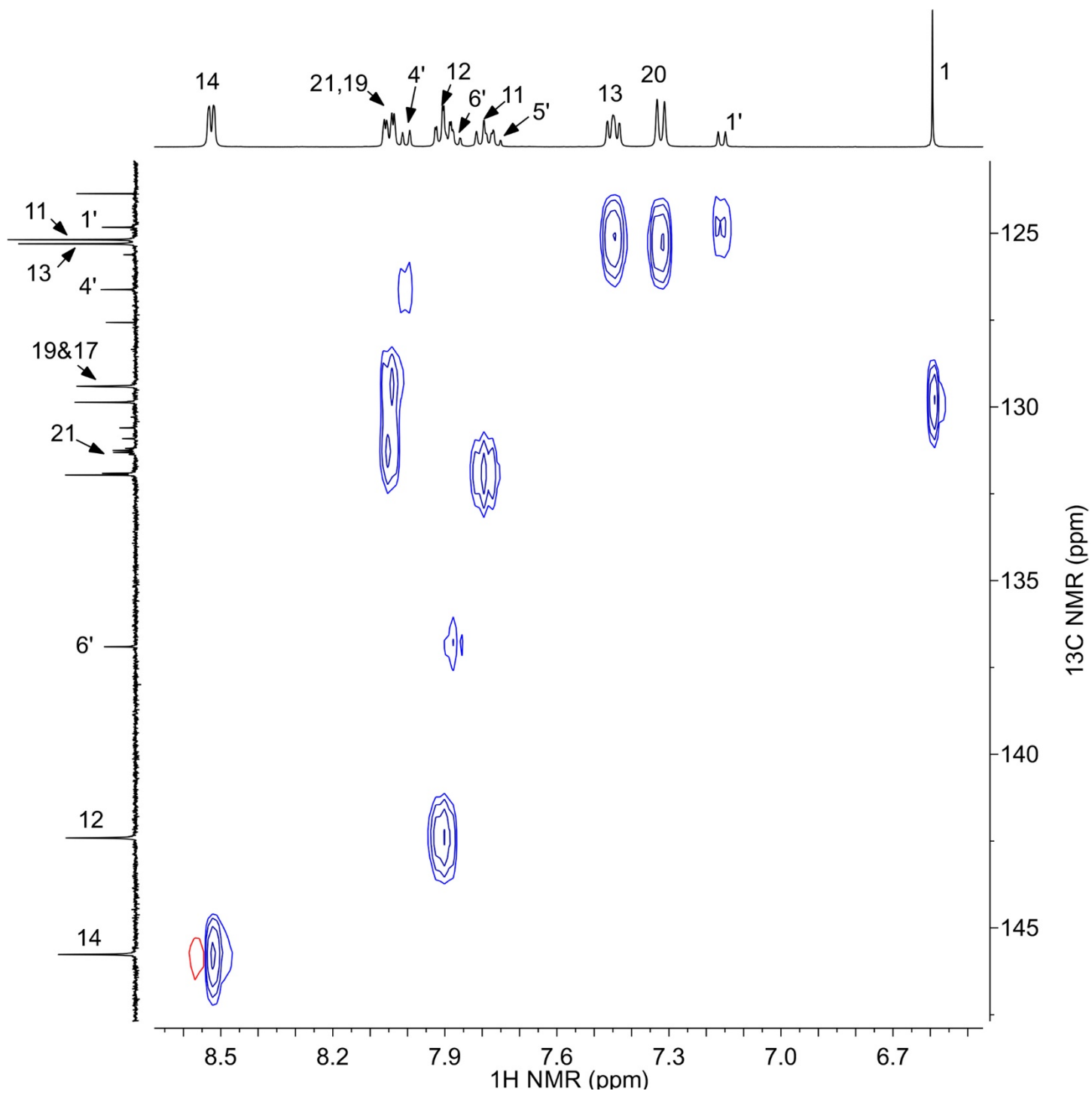
Figure S100. Expansion of ^1H-^{13}C HSQC spectrum of **3**.
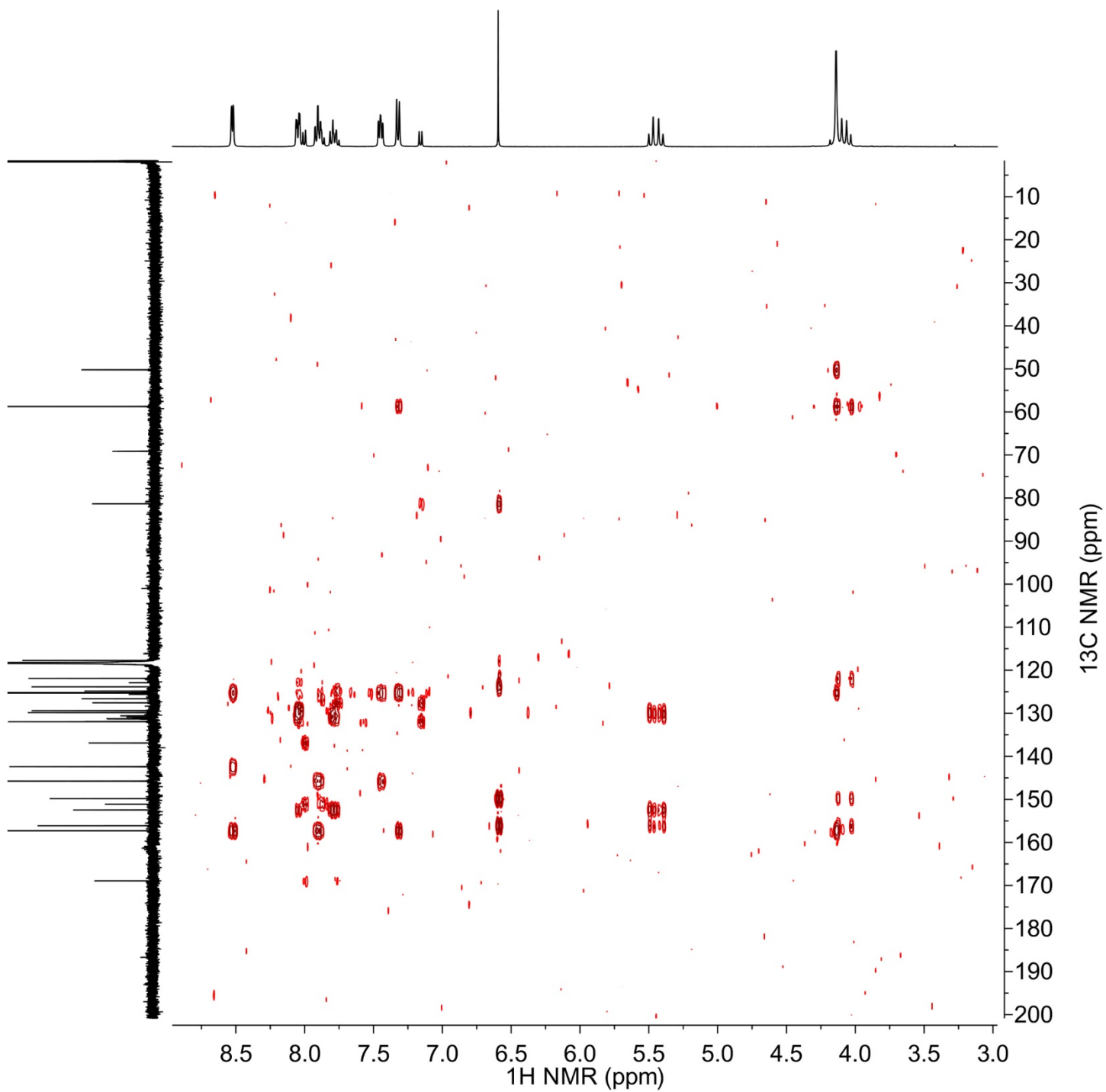
Figure S101. ^{1}H-^{13}C HMBC spectrum of **3**.
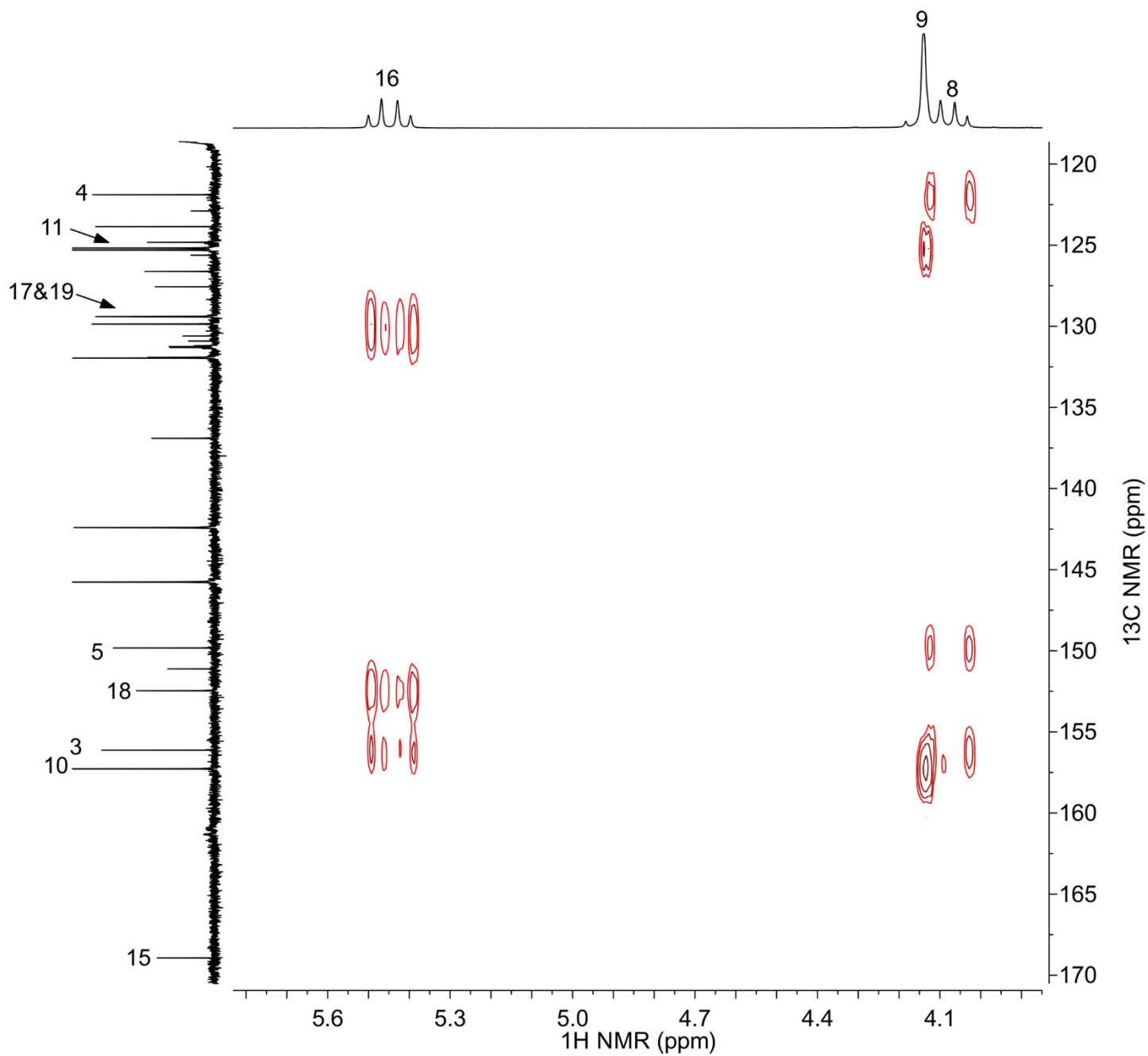
Figure S102. Expansion of ^{1}H-^{13}C HMBC spectrum of **3** from 3.9 to 5.8 ppm (^{1}H) and 120 to 170 ppm (^{13}C).

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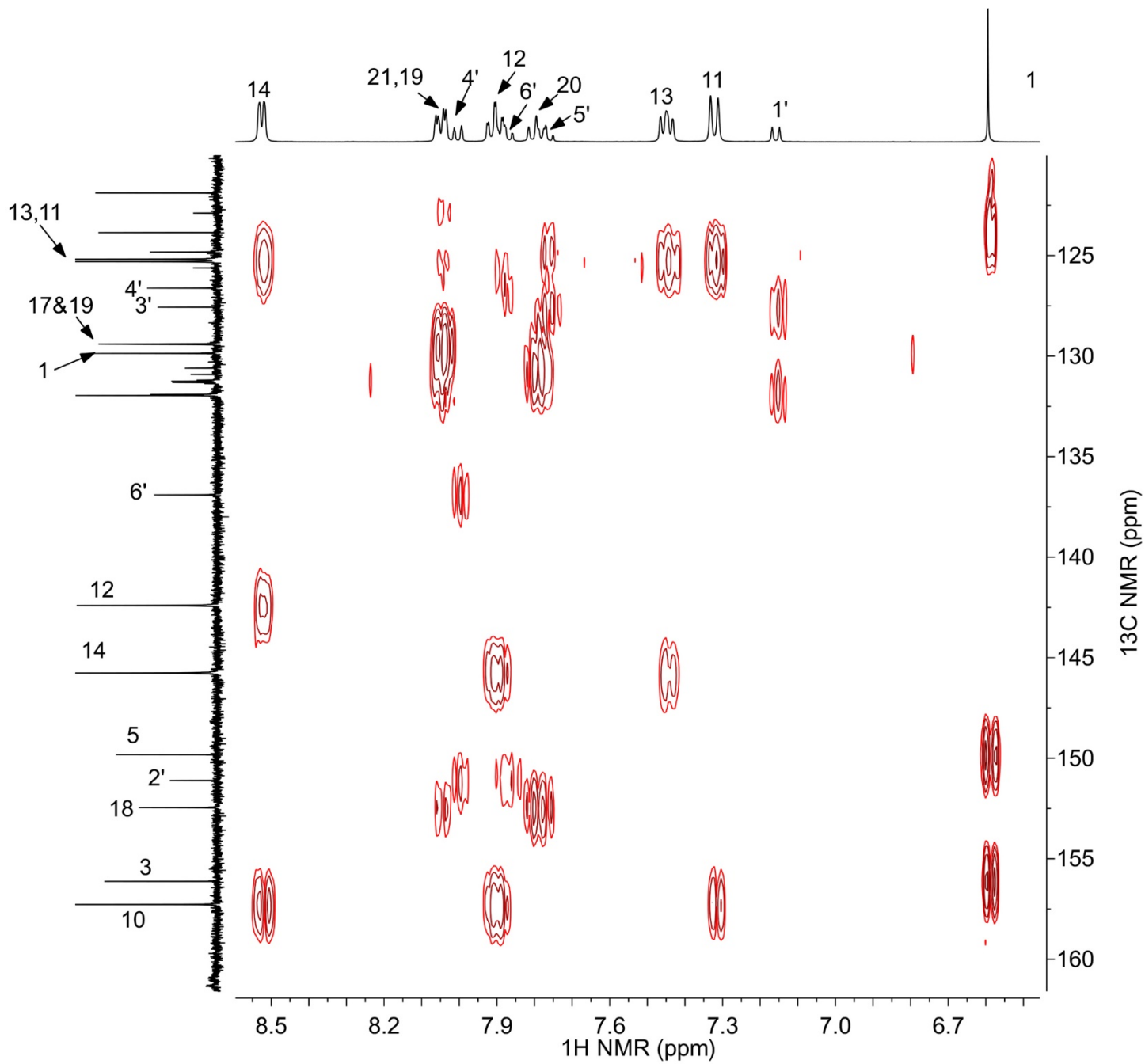
Figure S103. Expansion of ^1H-^{13}C HMBC spectrum of **3** from 6.5 to 8.6 ppm (^1H) and 120 to 160 ppm (^{13}C).
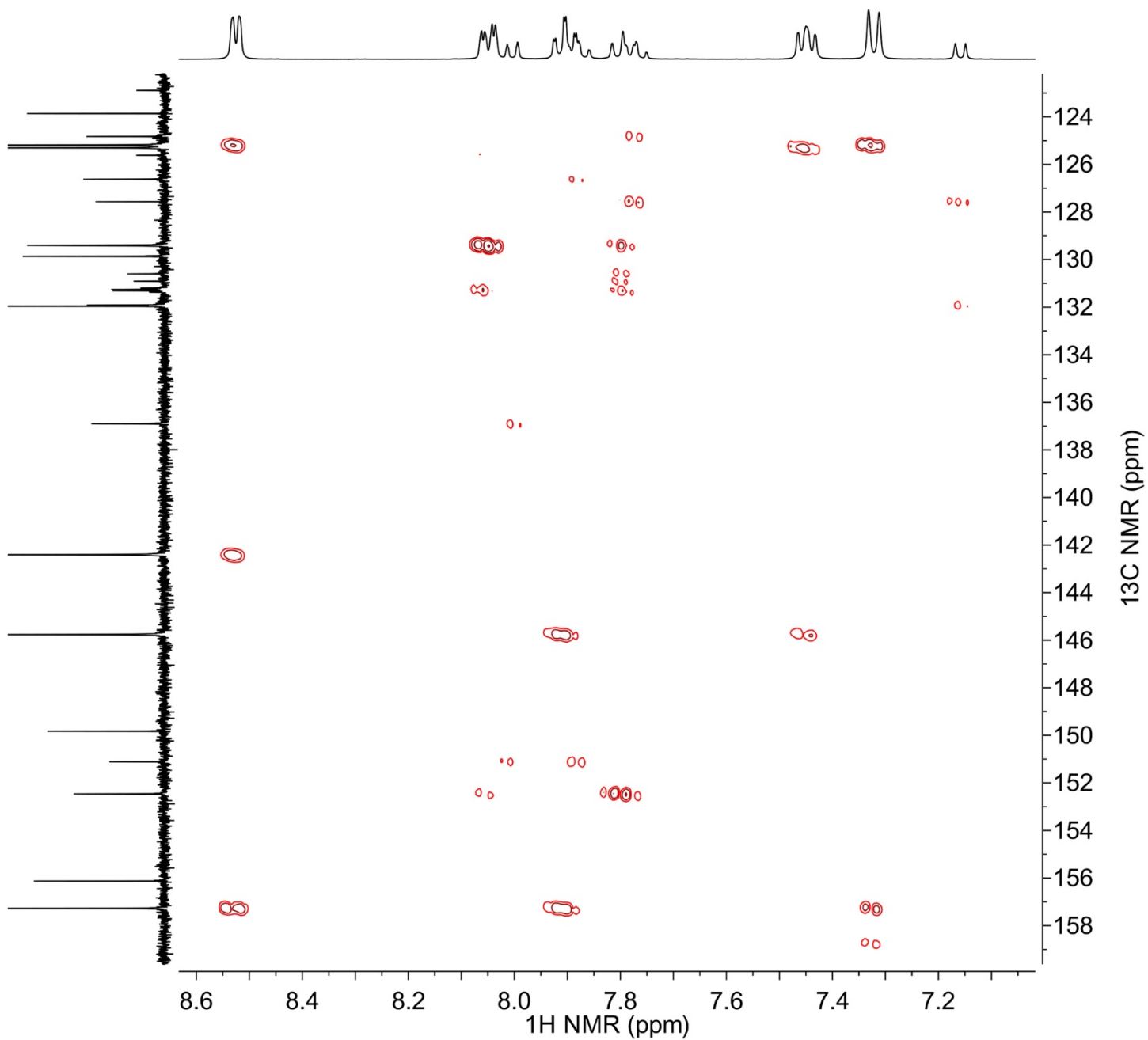
Figure S104. Expansion of high-resolution ^{1}H-^{13}C HMBC spectrum of **3** from 7.1 to 8.6 ppm (^{1}H) and 122 to 160 ppm (^{13}C).
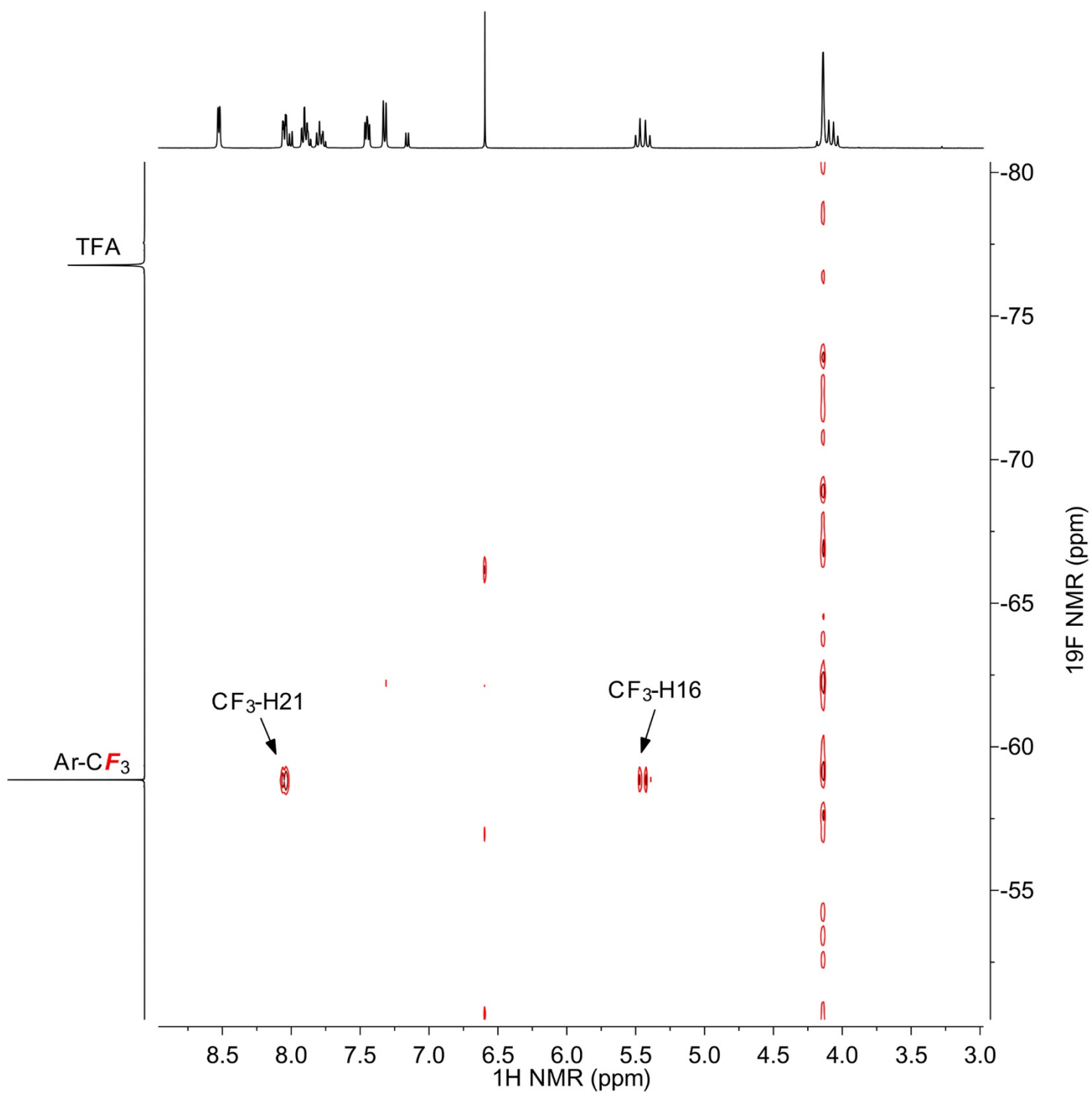
Figure S105. ^{1}H-^{19}F HOESY spectrum of **3**.
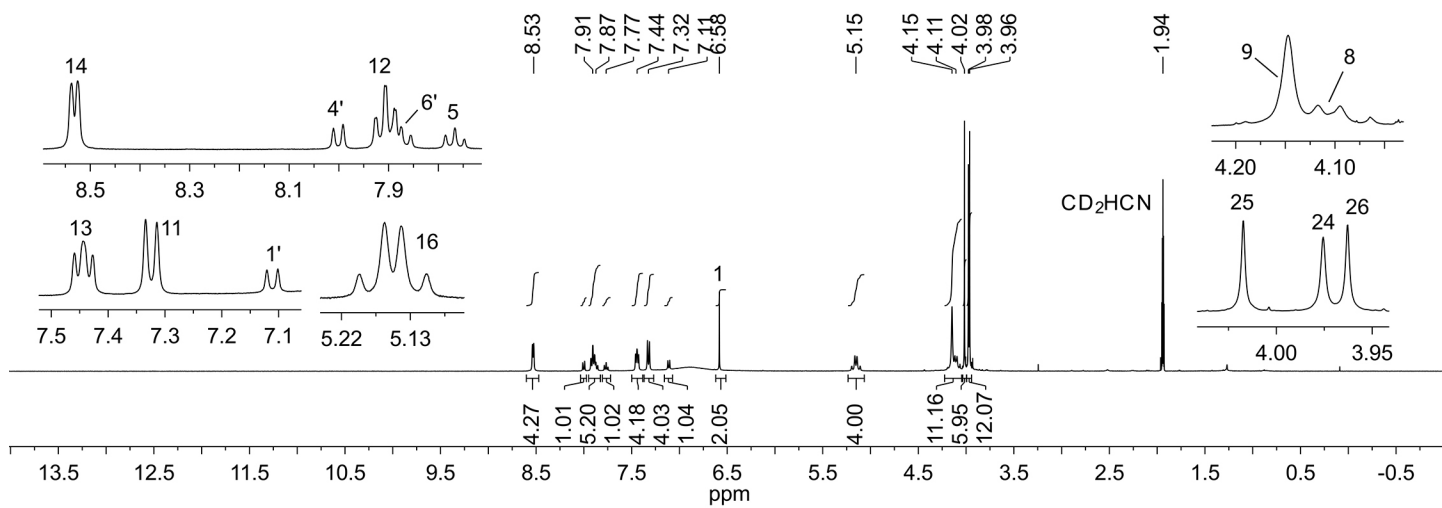
Figure S106. ^{1}H NMR spectrum of **4**.
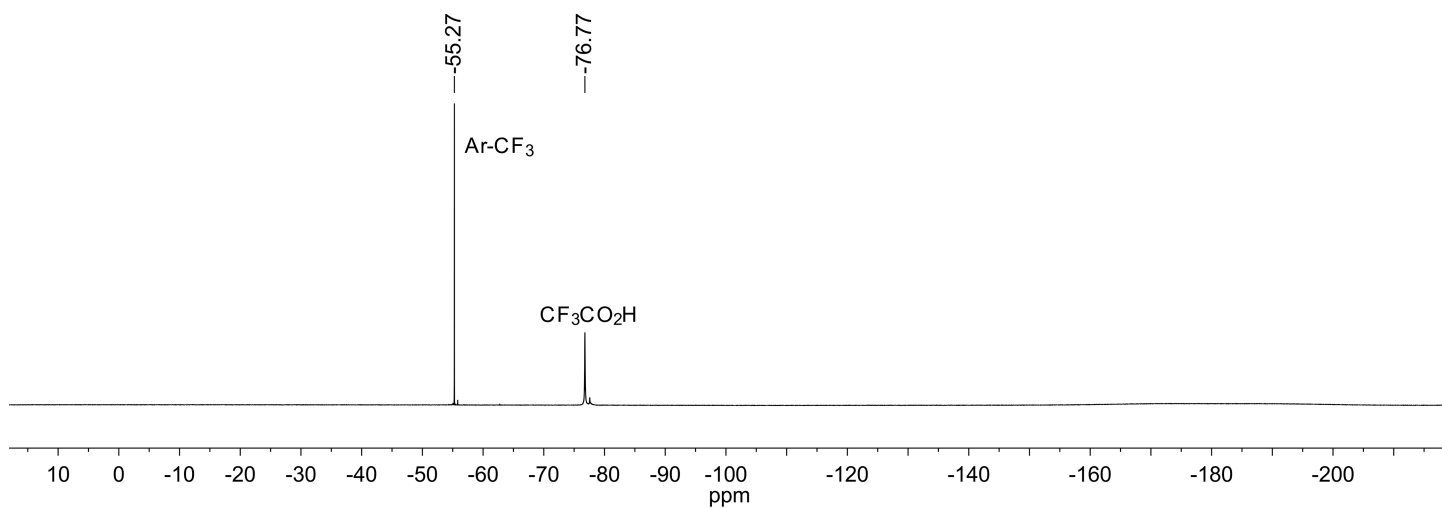
Figure S107. ^{19}F NMR spectrum of **4**.
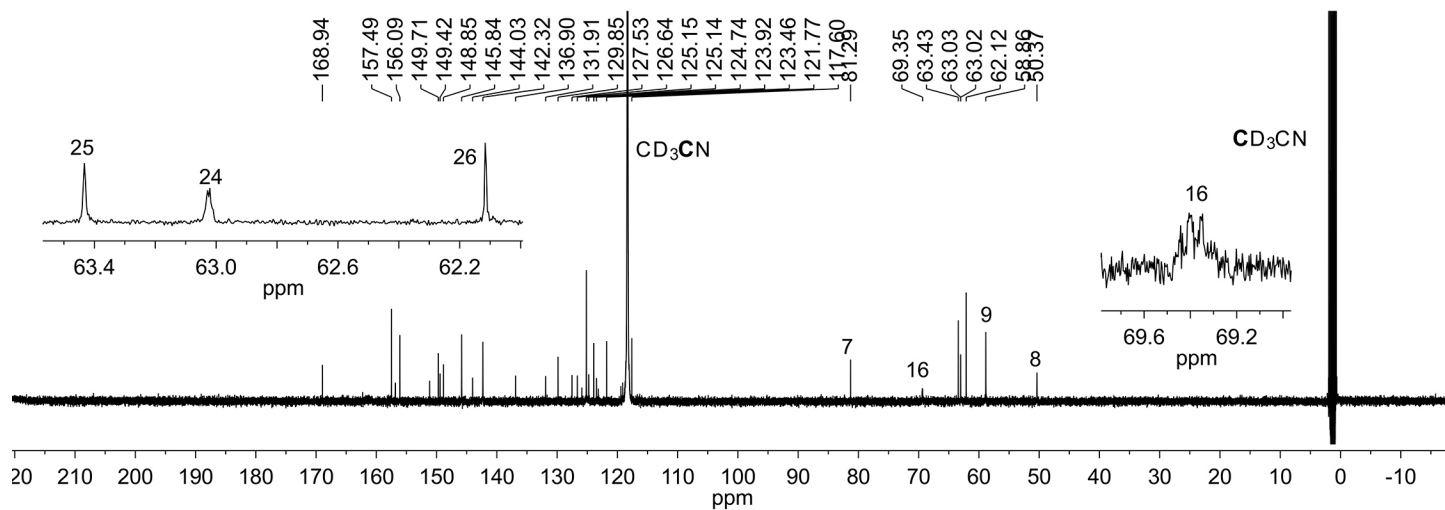
Figure S108. $^{13}C\{^1H\}$ NMR spectrum of **4**.
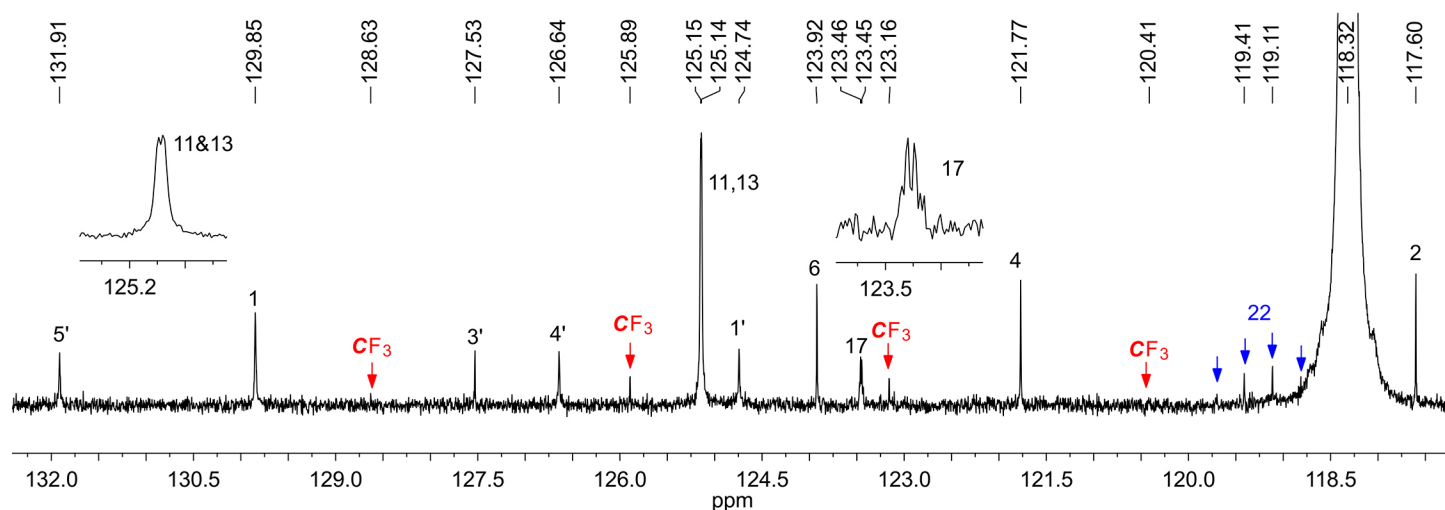
Figure S109. Expansion of $^{13}C\{^1H\}$ NMR spectrum of **4** from 117 to 132 ppm.
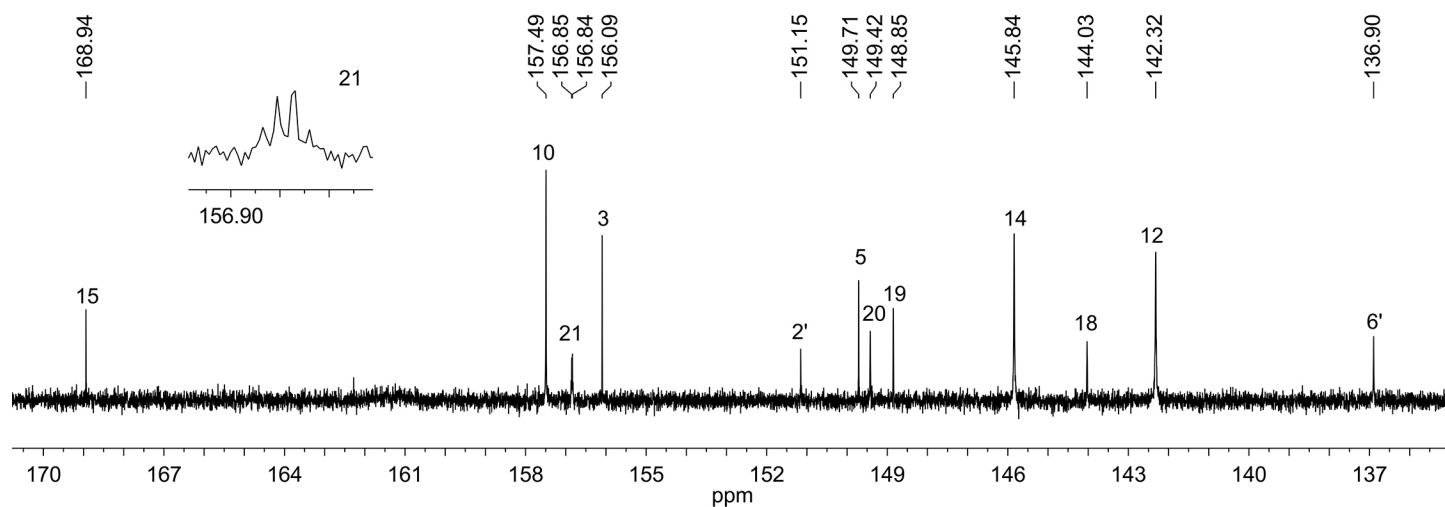
Figure S110. Expansion of $^{13}C\{^1H\}$ NMR spectrum of **4** from 135 to 171 ppm.
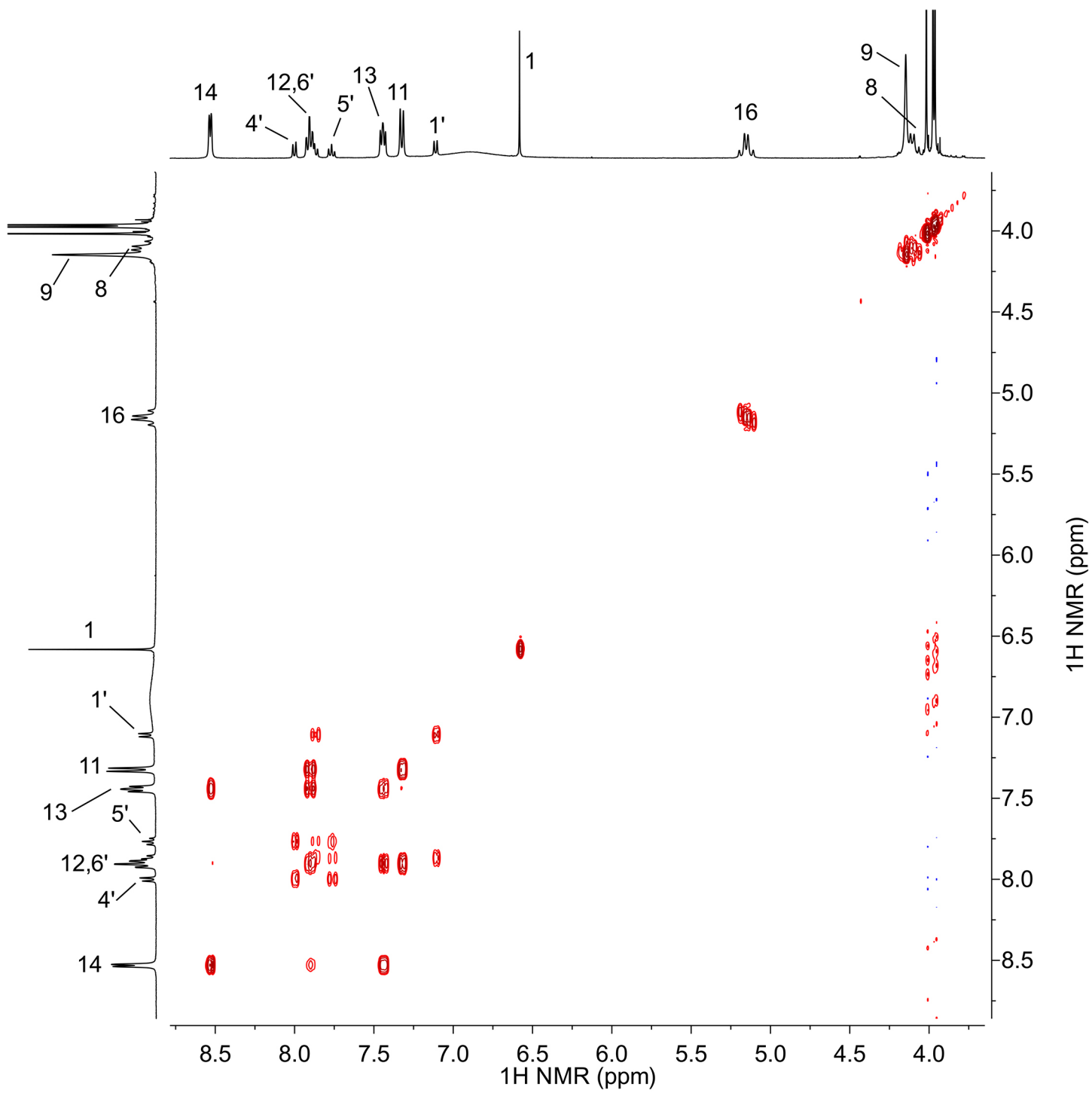
Figure S111. ^{1}H-^{1}H COSY spectrum of **4**.
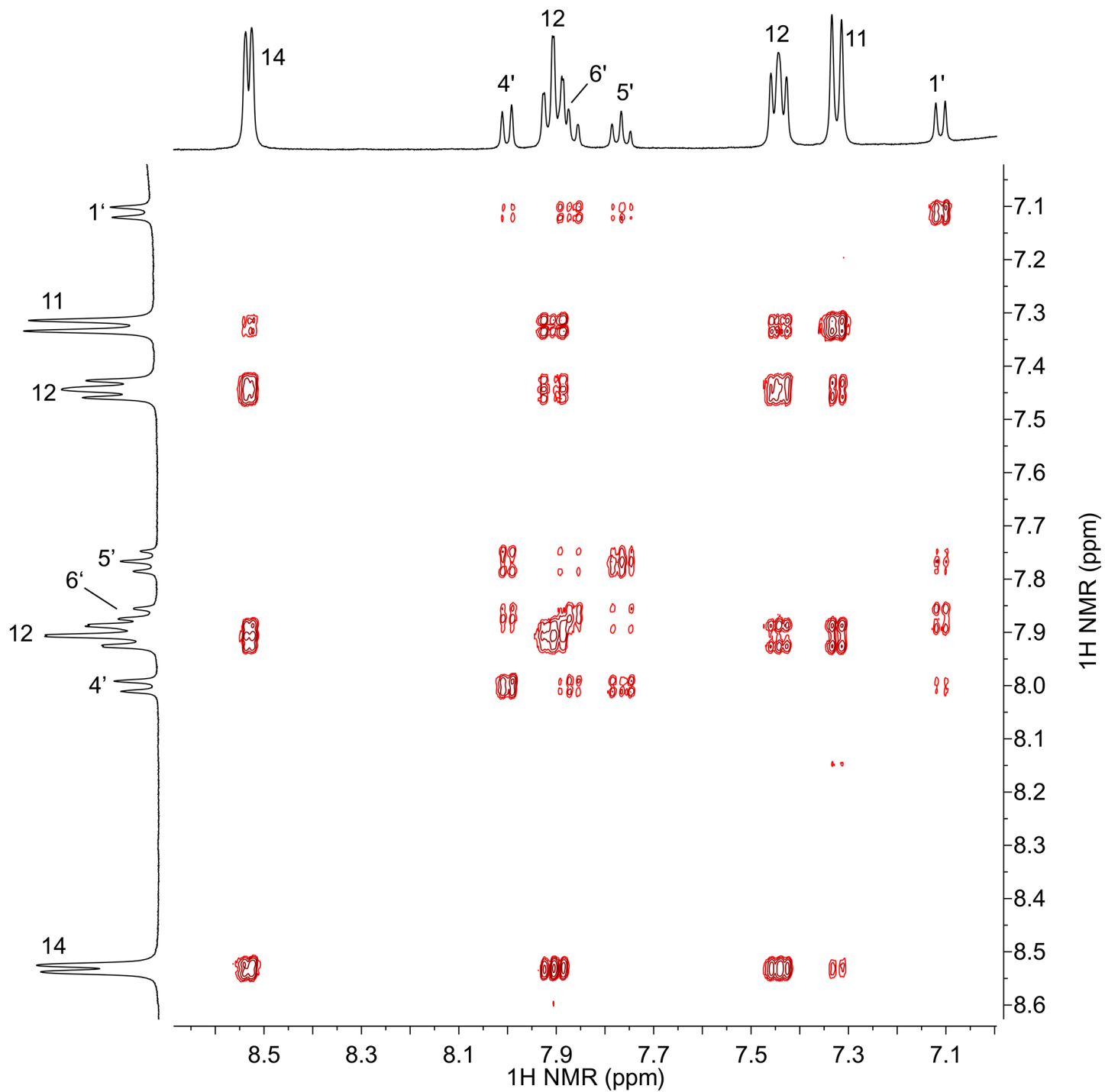
Figure S112. Expansion of ^{1}H-^{1}H COSY spectrum of **4**.
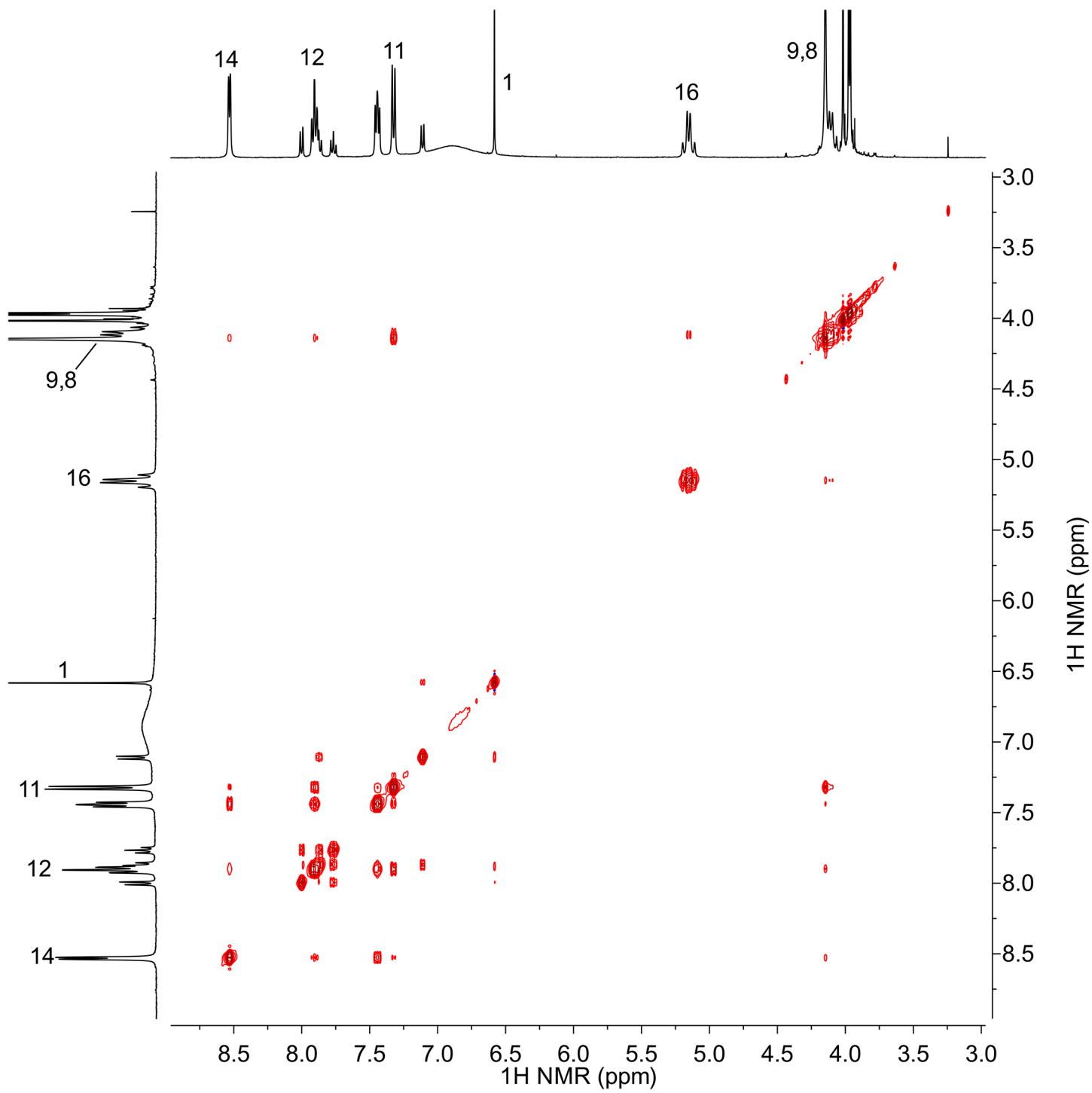
Figure S113. ^{1}H-^{1}H NOESY spectrum of **4**.
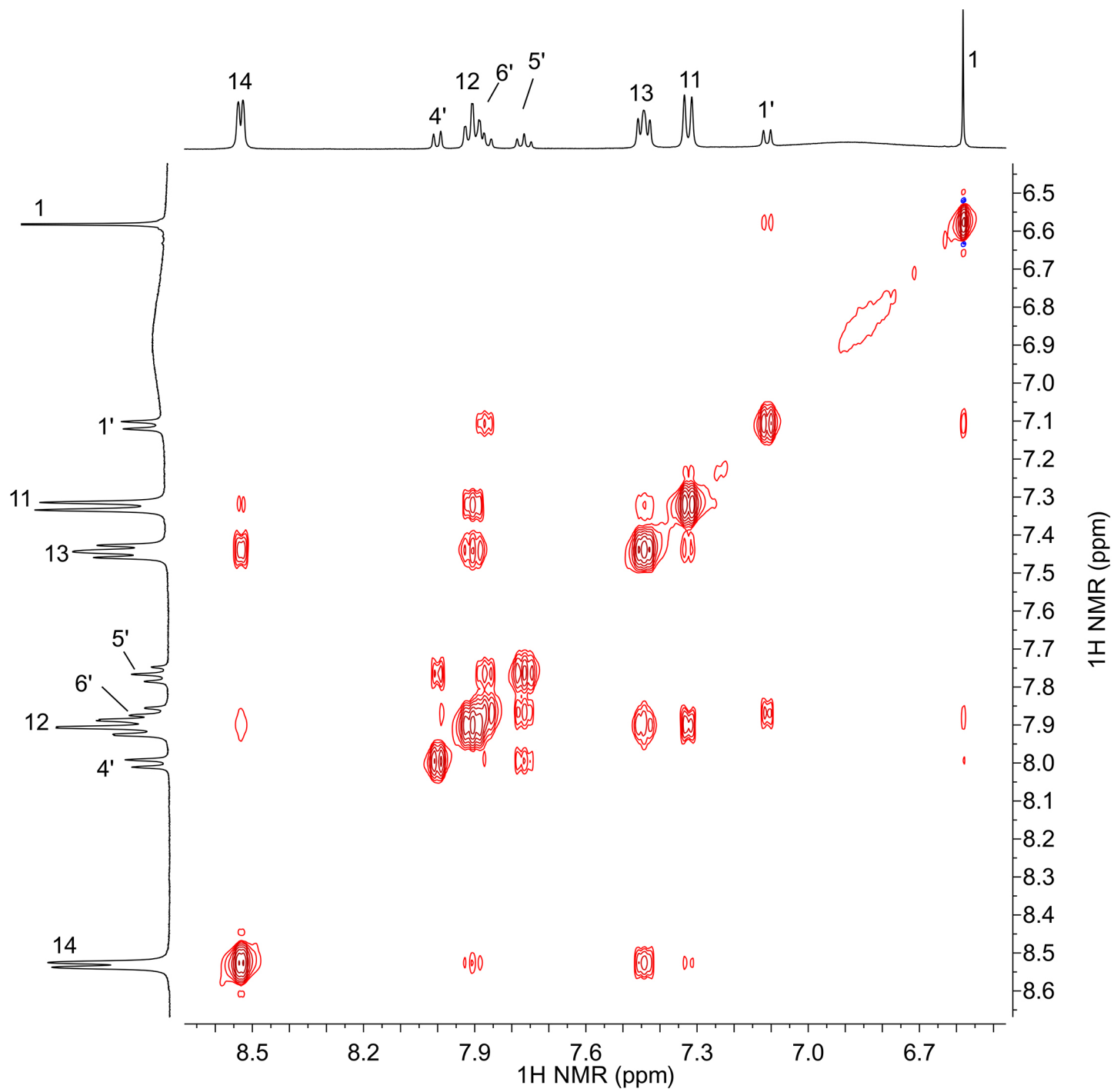
Figure S114. Expansion of ^{1}H-^{1}H NOESY spectrum of **4**.
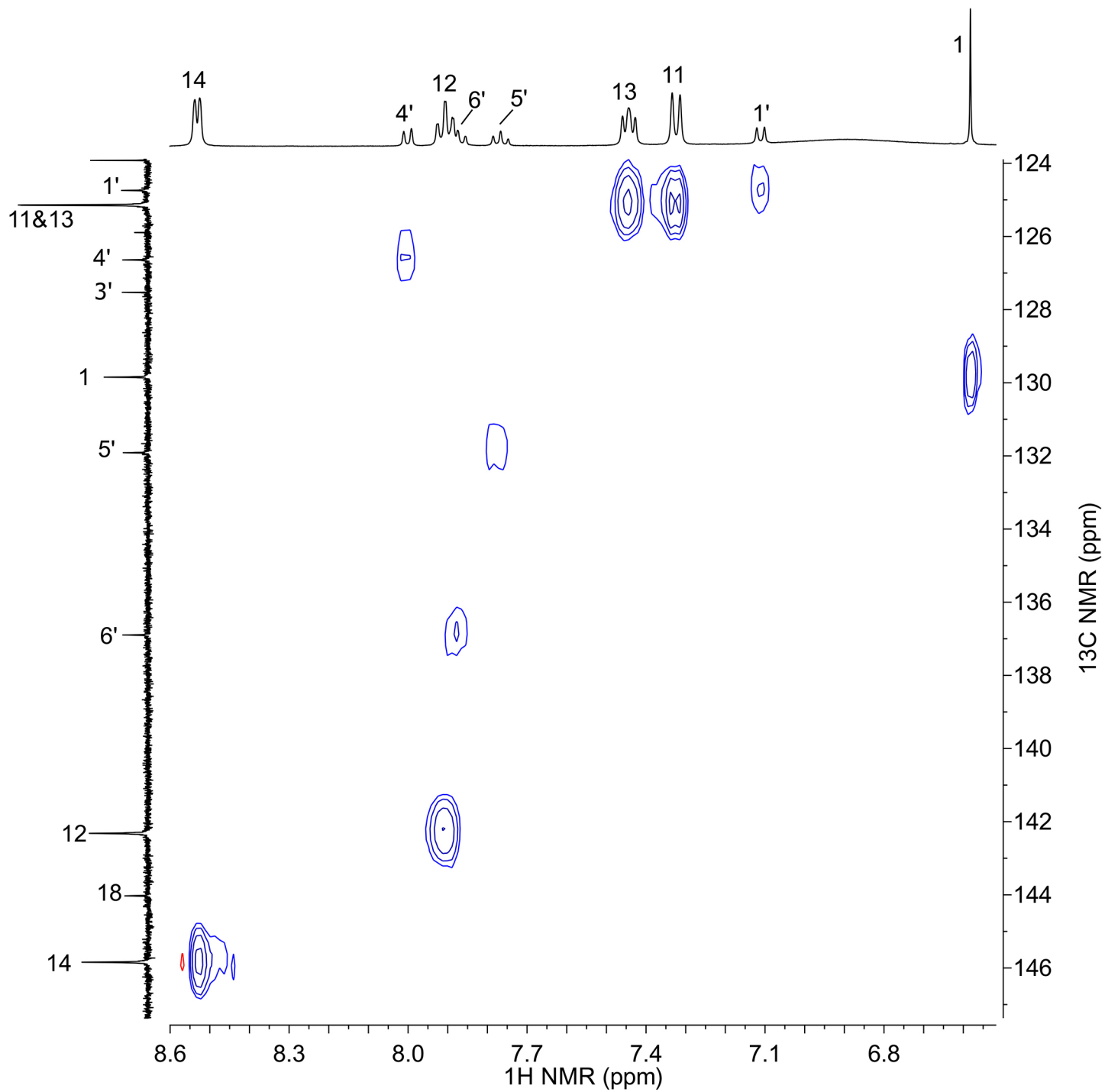
Figure S115. Expansion of ^{1}H-^{13}C HSQC spectrum of **4** from 6.5 to 8.6 ppm (^{1}H) and 124 to 147 ppm (^{13}C).
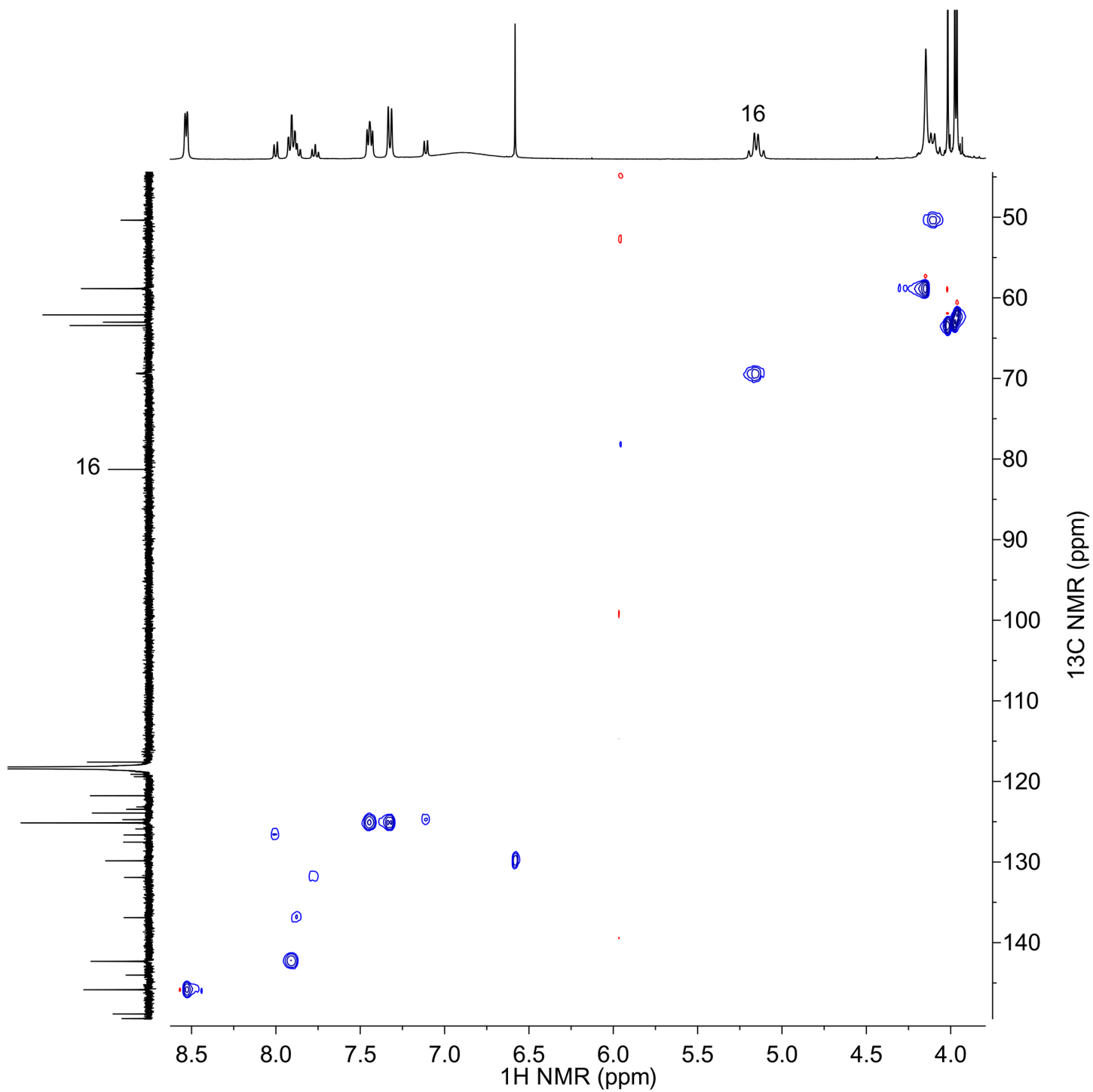
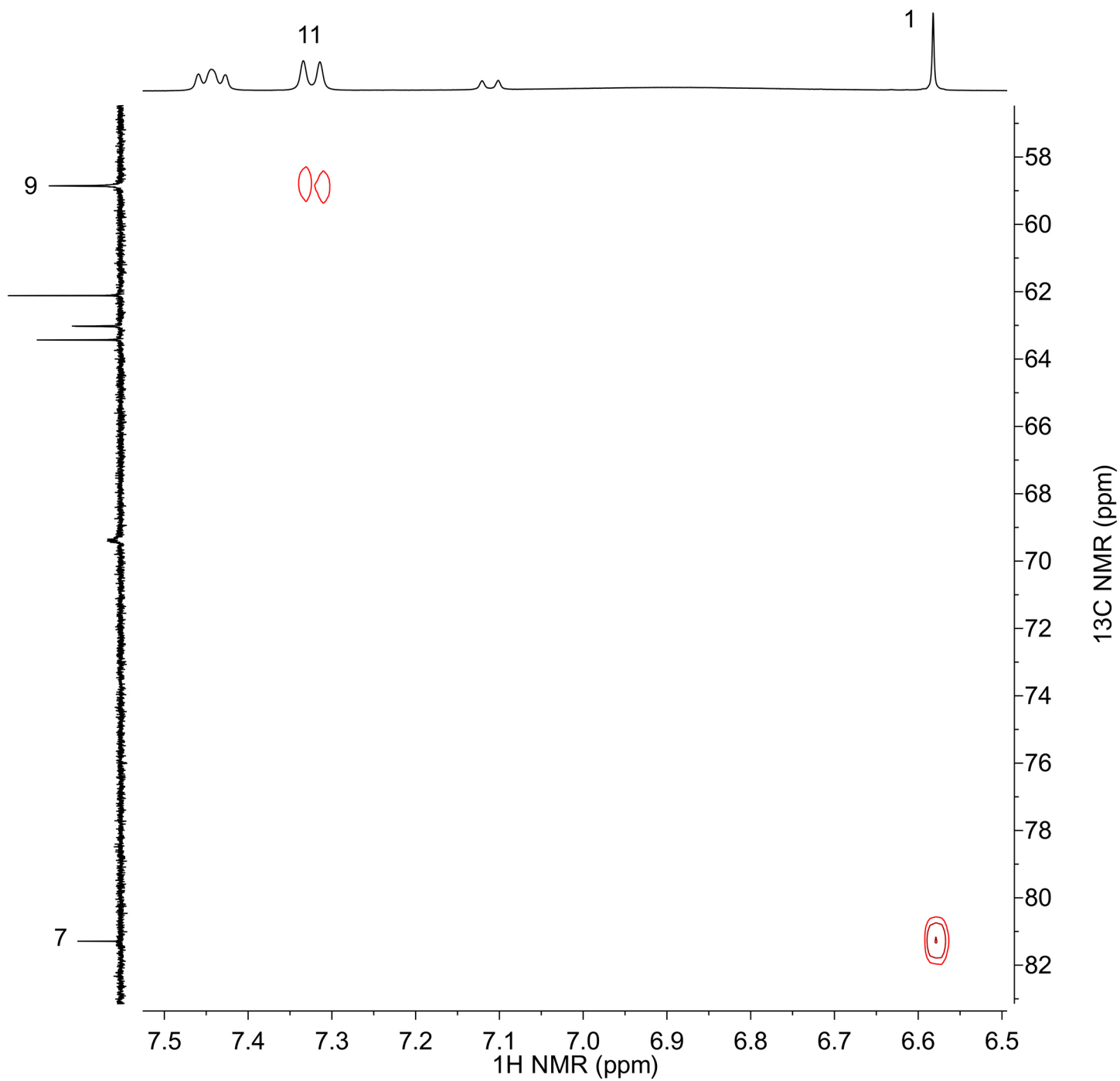**Figure S116.** Expansion of ^{1}H-^{13}C HSQC spectrum of **4** from 3.9 to 8.6 ppm (^{1}H) and 45 to 150 ppm (^{13}C).
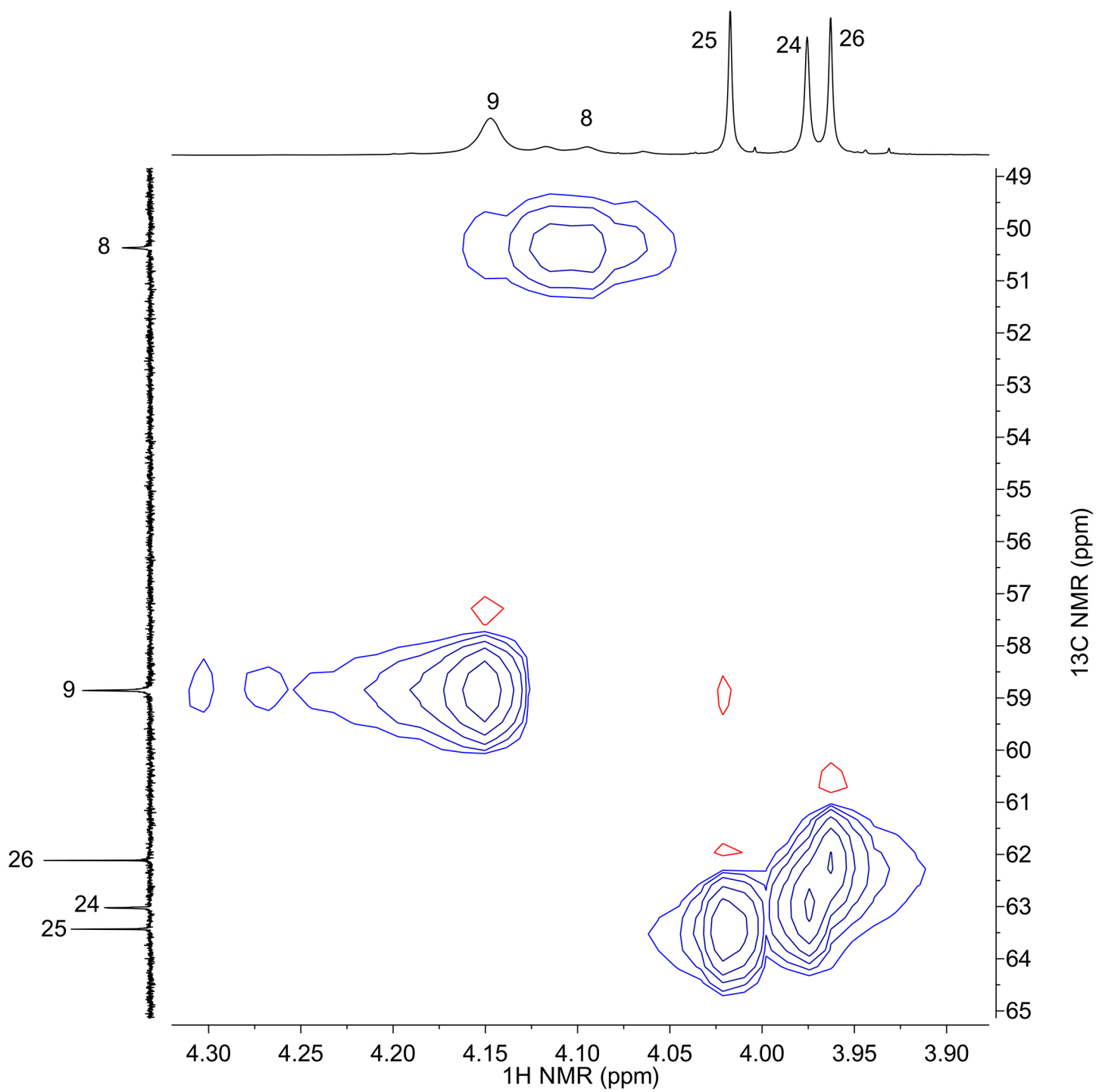
Figure S117. Expansion of ^{1}H-^{13}C HSQC spectrum of **4** from 3.9 to 4.3 ppm (^{1}H) and 49 to 65 ppm (^{13}C).
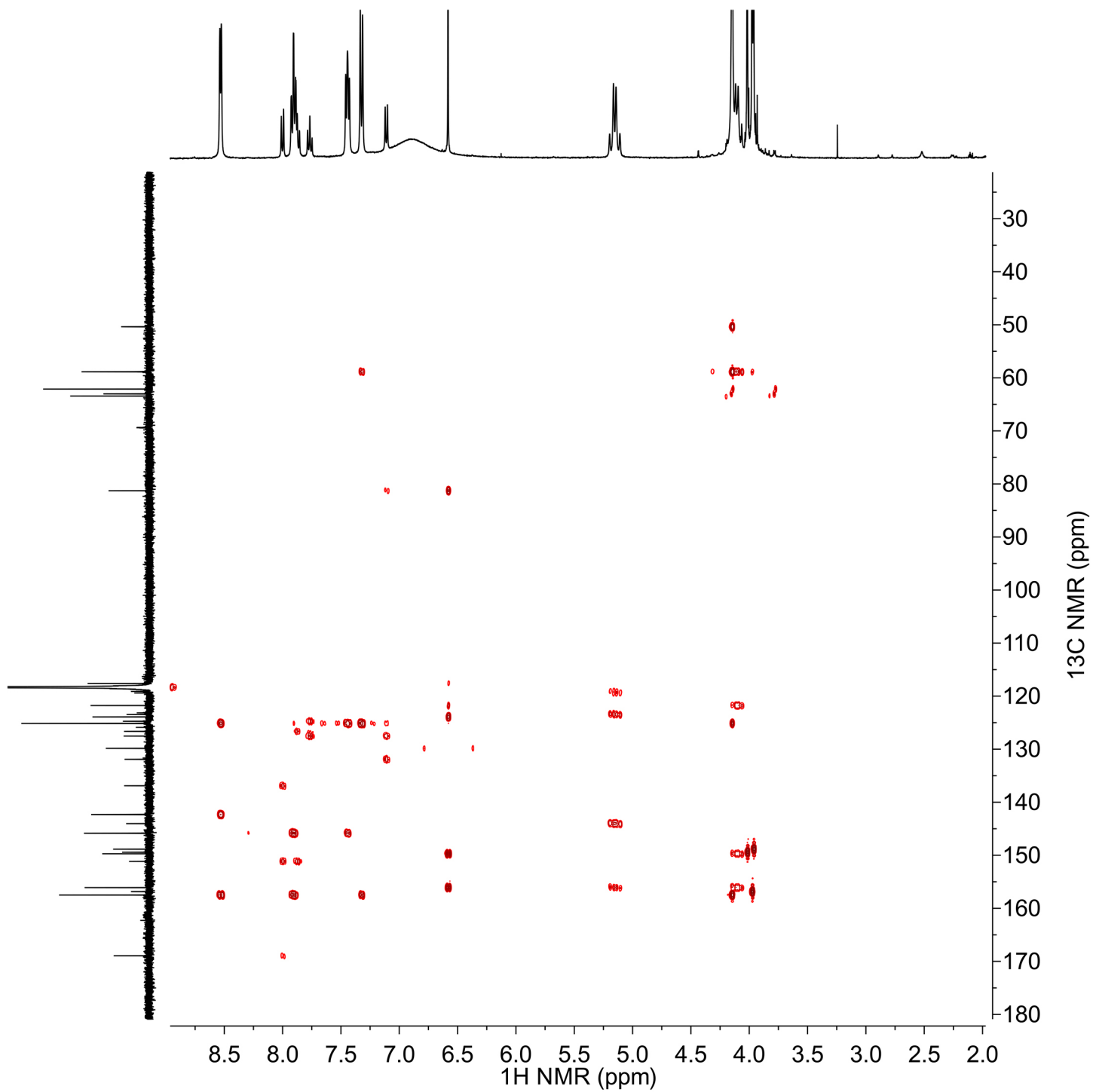
Figure S118. ^{1}H-^{13}C HMBC spectrum of **4.**
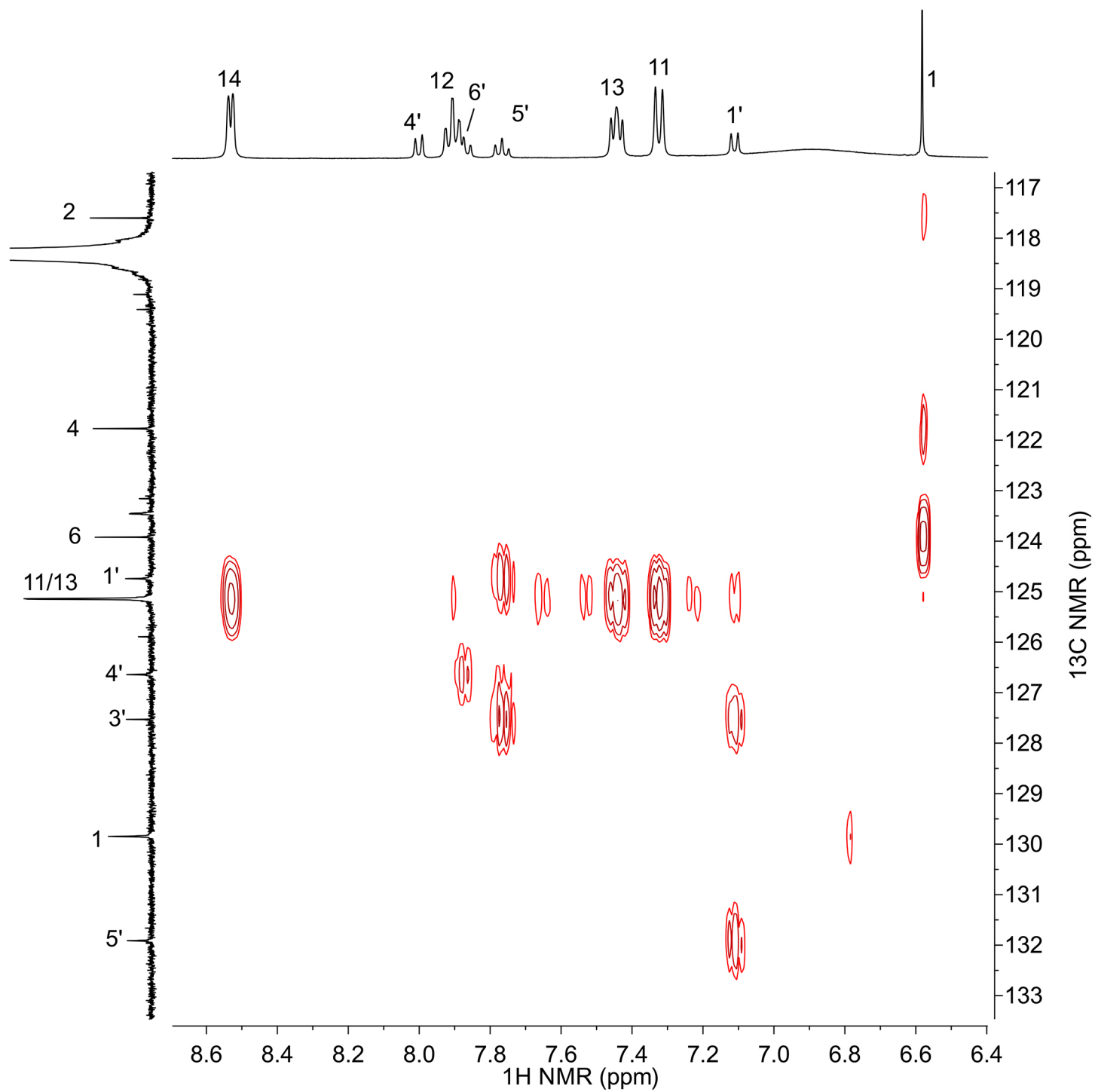
Figure S119. Expansion of ^{1}H-^{13}C HMBC spectrum of **4** from 6.4 to 8.6 ppm (^{1}H) and 117 to 133 ppm (^{13}C).
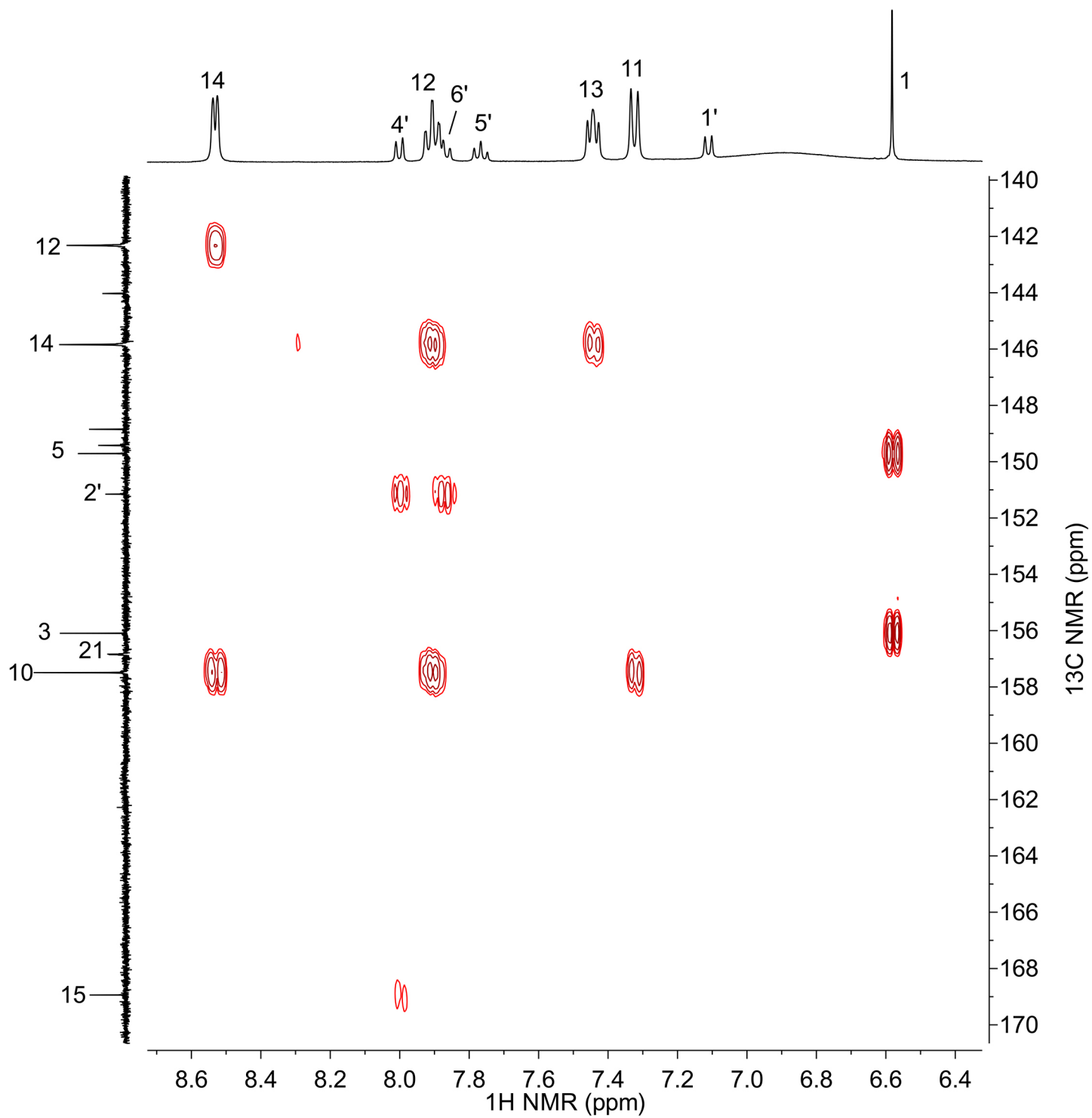
Figure S120. Expansion of ^{1}H-^{13}C HMBC spectrum of **4** from 6.4 to 8.6 ppm (^{1}H) and 140 to 170 ppm (^{13}C).
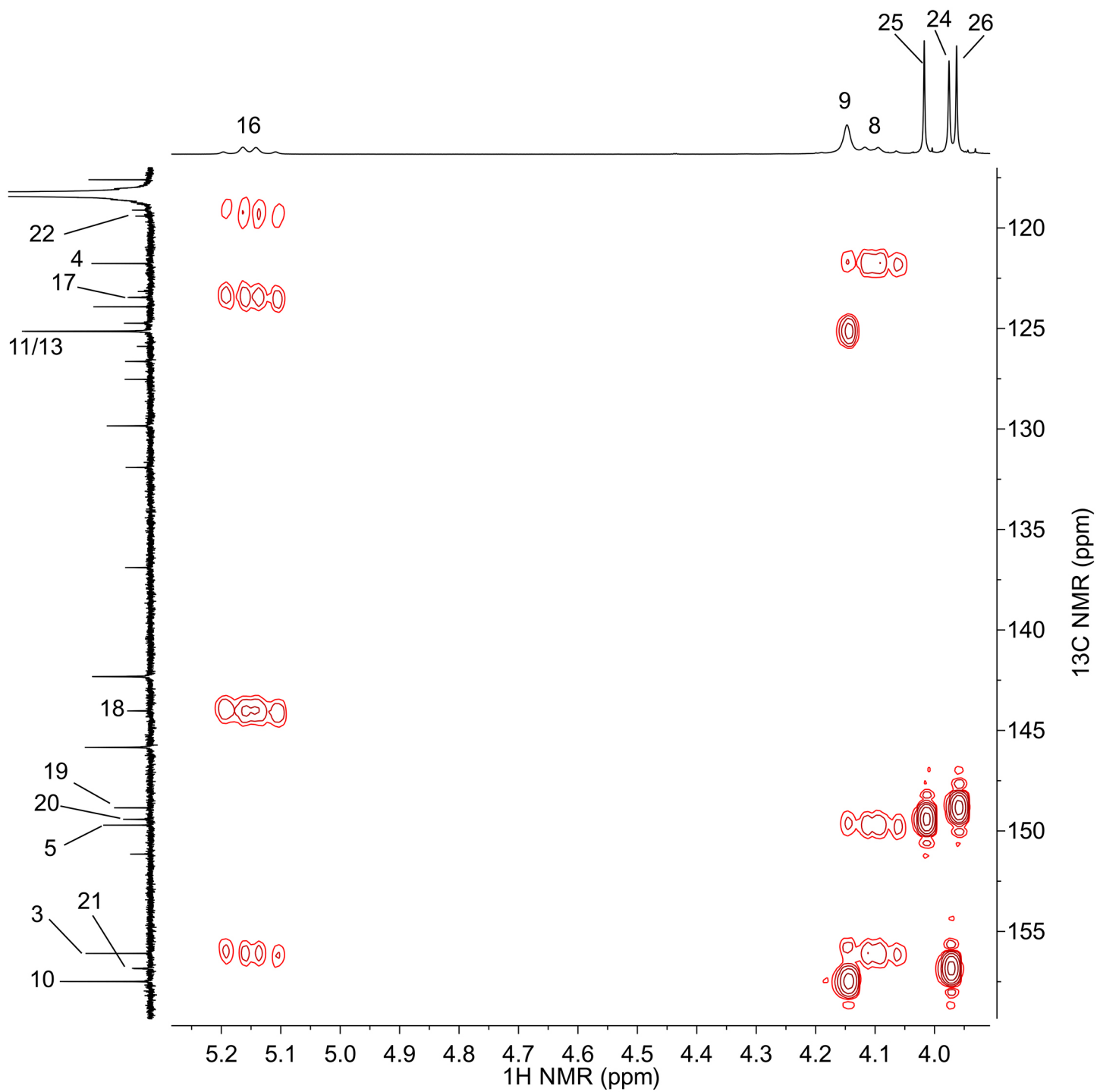
Figure S121. Expansion of ^{1}H-^{13}C HMBC spectrum of **4** from 3.9 to 5.3 ppm (^{1}H) and 115 to 160 ppm (^{13}C).

Figure S122. Expansion of ^{1}H-^{13}C HMBC spectrum of **4** from 6.5 to 7.5 ppm (^{1}H) and 57 to 83 ppm (^{13}C).

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