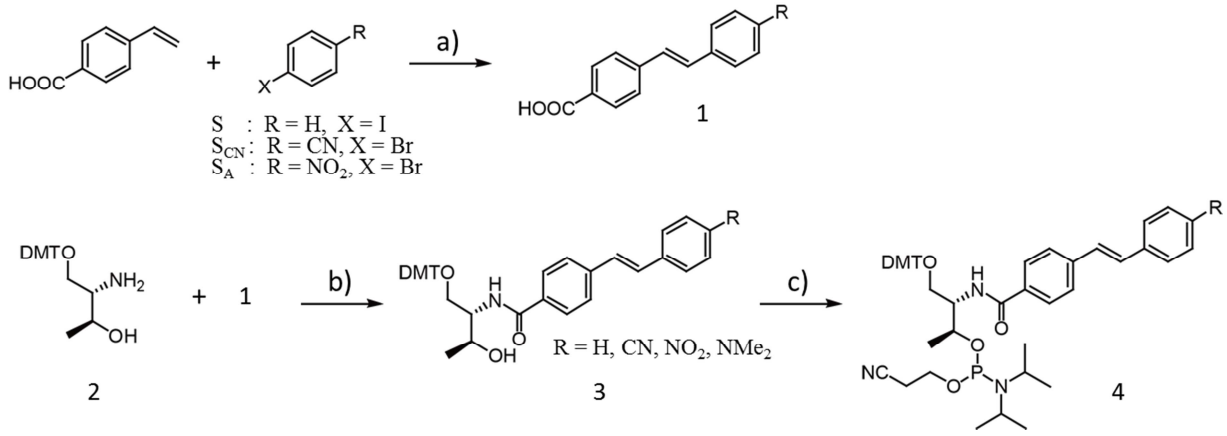
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Efficiency of [2+2] photodimerization of various stilbene derivatives within the DNA duplex scaffold

Tetsuya Doi, Hiromu Kashida,* and Hiroyuki Asanuma*



Scheme S1. Synthesis of phosphoramidite monomers tethering stilbene, *p*-cyanostilbene, *p*-nitrostilbene, and *p*-dimethylaminostilbene. Reagents and conditions: a) $Pd(OAc)_2$, PPh_3, NMe_3, DMF, 100 ^oC, overnight, **S**: 52.2%, $\mathbf{S_{CN}}$: 52.2%, $\mathbf{S_A}$: 72.6%. b) EDC, HOBt, NEt_3, DMF, r.t., overnight, **S**: 69.2%, $\mathbf{S_{CN}}$: 92.5%, $\mathbf{S_A}$: 53.6%, $\mathbf{S_D}$: 57.5%. c) $(iPr)_2NP(Cl)(OCH_2CH_2CN)$, NEt_3, THF, 0 ^oC, 20 min, **S**: 92.3%, $\mathbf{S_{CN}}$: 68.5%, $\mathbf{S_A}$: 77.8%, $\mathbf{S_D}$: 65.2 %.

Compound **1** (R = NMe_2) and compound **2** were synthesized according to the previous reports.[1, 2] The phosphoramidite monomers tethering stilbene (**S**), *p*-cyanostilbene ($\mathbf{S_{CN}}$), *p*-nitrostilbene ($\mathbf{S_A}$), and *p*-dimethylaminostilbene ($\mathbf{S_D}$) were synthesized as follows:

General Procedure for Synthesis of Compound 1 (except for R = NMe_2)

To a stirred solution of iodobenzene (2.04 g, 10 mmol), 4-bromobenzonitrile (1.82 g, 10 mmol), or 4-bromonitrobenzene (2.02 g, 10 mmol) in DMF (30 mL) was added 4-vinylbenzoic acid (1.48 g, 10 mmol), palladium(II) acetate (22.4 mg, 1 mol%), triphenylphosphine (52.5 mg, 2 mol%) and triethylamine (15 mL). After the reaction mixture was heated at 100 ^oC overnight, the solvent was removed by evaporation and filtered with ethyl acetate. The obtained residue was used in the next reaction without further purification. **S**: (Yield: 52.2%) ^{1}H-NMR [DMSO-d_6, 500 MHz] δ=7.97 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.76 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.68 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.40 (m, 5H, aromatic protons and vinyl protons). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 168.6, 142.9, 138.1, 132.4, 131.2, 131.0, 130.3, 129.7, 128.9, 128.3, 127.9. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{15}H_{12}O_2$ 224.0832; found 224.0838. $\mathbf{S_{CN}}$: (Yield: 52.2%) ^{1}H-NMR [DMSO-d_6, 500 MHz] δ=8.00 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.90 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.87 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.80 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.61 (d, *J* = 17 Hz, 1H, vinyl proton), 7.53 (d, *J* = 17 Hz, 1H, vinyl proton). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 168.5, 142.9, 142.1, 135.6, 134.2, 132.6, 131.7, 131.3, 131.1, 130.7, 128.9, 128.5, 127.7, 120.4, 111.5. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{16}H_{11}NO_2$ 249.0784; found 249.0760. $\mathbf{S_A}$: (Yield: 72.6%) ^{1}H NMR [DMSO-d_6, 500MHz] δ=8.30 (d, *J* = 8.5 Hz, 2H, aromatic protons), 8.01 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.95 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.82 (d, *J* = 8.5 Hz, 2H, aromatic protons), 7.66 (d, *J* = 17 Hz, 1H, vinyl proton), 7.61 (d, *J* = 17 Hz, 1H, vinyl proton). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 168.5, 148.0, 145.0, 142.0, 133.6, 132.1, 131.3, 131.1, 130.2, 129.5, 129.2, 128.6, 127.7, 125.5. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{15}H_{11}NO_4$ 269.0683; found 269.0585.

General Procedure for Synthesis of Compound 3

To a stirred solution of 1 (1.0 equiv) and triethylamine (2.8 equiv) in DMF was added HOBt (1.6 equiv), EDC (1.6 equiv) and **2** (1.2 equiv), and the mixture was stirred overnight. Ethyl acetate was added, and

the organic layer was washed with saturated aqueous solution of $NaHCO_3$ and NaCl. After drying over $MgSO_4$, the solvent was removed by evaporation, followed by silica gel column chromatography using hexane and ethyl acetate as eluent (3% triethylamine was added). **S**: (Yield: 69.2%) ^{1}H-NMR [DMSO-d_6, 500 MHz] δ=8.06 (d, *J* = 9.0 Hz, 1H, -N*H*CO-), 7.96 (d, *J* = 8.5 Hz, 2H, aromatic protons of stilbene), 7.76 (d, *J* = 8.5 Hz, 2H, aromatic protons of stilbene), 7.68 (d, *J* = 8.5 Hz, 2H, aromatic protons of stilbene), 7.46-7.23 (m, 14H, aromatic protons of DMT and stilbene and vinyl protons), 6.88 (m, 4H, aromatic protons of DMT), 4.63 (d, *J* = 6.0 Hz, 1H, -O*H*), 4.18 (m, 1H, -CH_2-C*H*(NH-)-$CH(CH_3)$), 4.08 (m, 1H, -C*H*(CH_3)-OH), 3.76 (s, 6H, -C_6H_4-OC*H*$_3$), 3.26, 3.01 (m, each 1H, -C*H*$_2$-ODMT), 1.06 (d, *J* = 6.5 Hz, 3H, -CH(C*H*$_3$)-OH). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 167.6, 159.4, 146.6, 141.2, 138.2, 137.4, 137.3, 134.9, 131.6, 131.2, 130.2, 129.5, 129.3, 129.2, 129.0, 128.1, 128.0, 127.6, 114.5, 86.6, 66.7, 64.5, 56.7, 56.4, 21.8. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{40}H_{39}NO_5$ 613.2823; found 613.2801. **S_{CN}**: (Yield: 92.5%) ^{1}H-NMR [DMSO-d_6, 500 MHz] δ=8.10 (d, *J* = 9.0 Hz, 1H, -N*H*CO-), 7.99 (d, *J* = 8.0 Hz, 2H, aromatic protons of *p*-cyanostilbene), 7.90 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-cyanostilbene), 7.87 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-cyanostilbene), 7.81 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-cyanostilbene), 7.59 (d, *J* = 16.5 Hz, 1H, vinyl proton), 7.47 (d, *J* = 16.5 Hz, 1H, vinyl proton), 7.44-7.26 (m, 9H, aromatic protons of DMT), 6.88 (m, 4H, aromatic protons of DMT), 4.64 (d, *J* = 6.0 Hz, 1H, -O*H*), 4.18 (m, 1H, -CH_2-C*H*(NH-)-$CH(CH_3)$), 4.07 (m, 1H, -C*H*(CH_3)-OH), 3.76 (s, 6H, -C_6H_4-OC*H*$_3$), 3.27, 3.01 (m, each 1H, -C*H*$_2$-ODMT), 1.06 (d, *J* = 6.5 Hz, 3H, -CH(C*H*$_3$)-OH). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 167.5, 159.4, 146.6, 143.0, 140.5, 137.3, 137.2, 135.7, 134.1, 132.8, 131.2, 129.9, 129.4, 129.2, 129.1, 128.8, 128.7, 128.2, 128.0, 114.5, 111.3, 86.6, 66.7, 64.5, 56.7, 56.4, 21.8. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{41}H_{38}N_2O_5$ 638.2775; found 638.2799. **S_A**: (Yield: 53.6%) ^{1}H NMR [DMSO-d_6, 500 MHz] δ=8.30 (d, *J* = 9.0 Hz, 2H, aromatic protons of *p*-nitrostilbene), 8.11 (d, *J* = 8.5 Hz, 1H, -N*H*CO-), 8.00 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-nitrostilbene), 7.95 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-nitrostilbene), 7.83 (d, *J* = 8.5 Hz, 2H, aromatic protons of *p*-nitrostilbene), 7.65 (d, *J*=17 Hz, 1H, vinyl protones), 7.60 (d, *J*=17 Hz, 1H, vinyl protones), 7.45-7.22 (m, 9 H, aromatic protons of DMT), 6.87 (m, 4 H, aromatic protons of DMT), 4.64 (d, *J*=6.0 Hz, 1H, -O*H*), 4.18 (m, 1H, -CH_2-C*H*(NH-)-$CH(CH_3)$), 4.08 (m, 1H, -C*H*(CH_3)-OH), 3.76 (s, 6H, -C_6H_4-OC*H*$_3$), 3.27, 3.02 (m, each 1H, -C*H*$_2$-ODMT), 1.07 (d, *J*=6.0 Hz, 3H, -CH(C*H*$_3$)-OH). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 167.5, 159.4, 147.9, 146.6, 145.2, 140.4, 137.4, 137.2, 135.8, 133.8, 131.2, 129.5, 129.4, 129.2, 129.0, 128.3, 128.0, 125.5, 114.5, 86.6, 66.7, 64.5, 56.7, 56.4, 21.8. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{40}H_{38}N_2O_7$ 658.2674; found 658.2675. **S_D**: (Yield: 57.5%) ^{1}H NMR [DMSO-d_6, 500 MHz] δ=7.99 (d, 1H, *J*=8.5 Hz, -N*H*CO-), 7.92 (d, 2H, *J*=8.5 Hz, aromatic protons of *p*-dimethylaminostilbene), 7.67 (d, 2H, *J*=8.5 Hz, aromatic protons of *p*-dimethylaminostilbene), 7.51 (d, 2H, *J*=9.0 Hz, aromatic protons of *p*-dimethylaminostilbene), 7.44-7.22 (m, 10 H, aromatic protons of DMT and vinyl proton), 7.01 (d, 1H, *J*=16.5 Hz, vinyl proton), 6.88 (m, 4 H, aromatic protons of DMT), 6.77 (d, 2H, *J*=9.0 Hz, aromatic protons of *p*-dimethylaminostilbene), 4.62 (d, 1H, *J*=6.5 Hz, -O*H*), 4.17 (m, 1H, -CH_2-C*H*(NH-)-$CH(CH_3)$), 4.08 (m, 1H, -C*H*(CH_3)-OH), 3.76 (s, 6H, -C_6H_4-OC*H*$_3$), 3.26, 3.02 (m, 1H, -C*H*$_2$-ODMT), 2.99 (s, 6H, -C_6H_4-N(C*H*$_3$)$_2$), 1.06 (d, 3H, *J*=6.0 Hz, -CH(C*H*$_3$)-OH). ^{13}C-NMR [DMSO-d_6, 125 MHz] δ = 167.6, 159.6, 159.5, 159.4, 151.7, 146.6, 142.1, 137.3, 133.8, 132.0, 131.1, 129.3, 129.2, 129.1, 128.0, 126.9, 126.0, 124.0, 114.7, 114.5, 113.6, 87.0, 86.6, 76.4, 66.7, 64.5, 59.4, 56.6, 56.5, 56.4, 21.8. HRMS(FAB) (*m*/*z*): $[M]^+$ Calcd for $C_{42}H_{44}N_2O_5$ 656.3245; found 656.3246.

General Procedure for Synthesis of Compound 4

Triethylamine (5.0 equiv) and 2-cyanoethyl N,N-diisopropylchlorophosphoramidite (2.0 equiv) were added to a solution of compound **3** (1.0 equiv) in THF at 0 ^{o}C. After 20 min of vigorous stirring on ice, an excess of ethyl acetate was added to the reaction mixture, and the mixture was washed with saturated aqueous solution of $NaHCO_3$ and with NaCl. After drying over $MgSO_4$, the solvent was removed by evaporation, followed by silica gel column chromatography using hexane and ethyl acetate as eluent (3% triethylamine was added). **S**: (Yield: 92.3%) ^{31}P NMR [DMSO-d_6, 121 MHz] δ=147.9, 147.7 ppm. **S_{CN}**: (Yield: 68.5%) ^{31}P NMR [DMSO-d_6, 121 MHz] δ=147.9, 147.7 ppm. **S_A**: (Yield: 77.8%) ^{31}P NMR [DMSO-d_6, 121 MHz] δ=147.9, 147.7. **S_D**: (Yield: 65.2%) ^{31}P NMR [DMSO-d_6, 121 MHz] δ=147.9, 147.7.

References

1. Clement, B.; Weide, M.; Ziegler, D. M. *Chem. Res. Toxicol.* **1996**, *9*, 599-604.
2. Hara, Y.; Fujii, T.; Kashida, H.; Sekiguchi, K.; Liang, X.G.; Yoshida, Y.; Asanuma, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 5502 –5506.

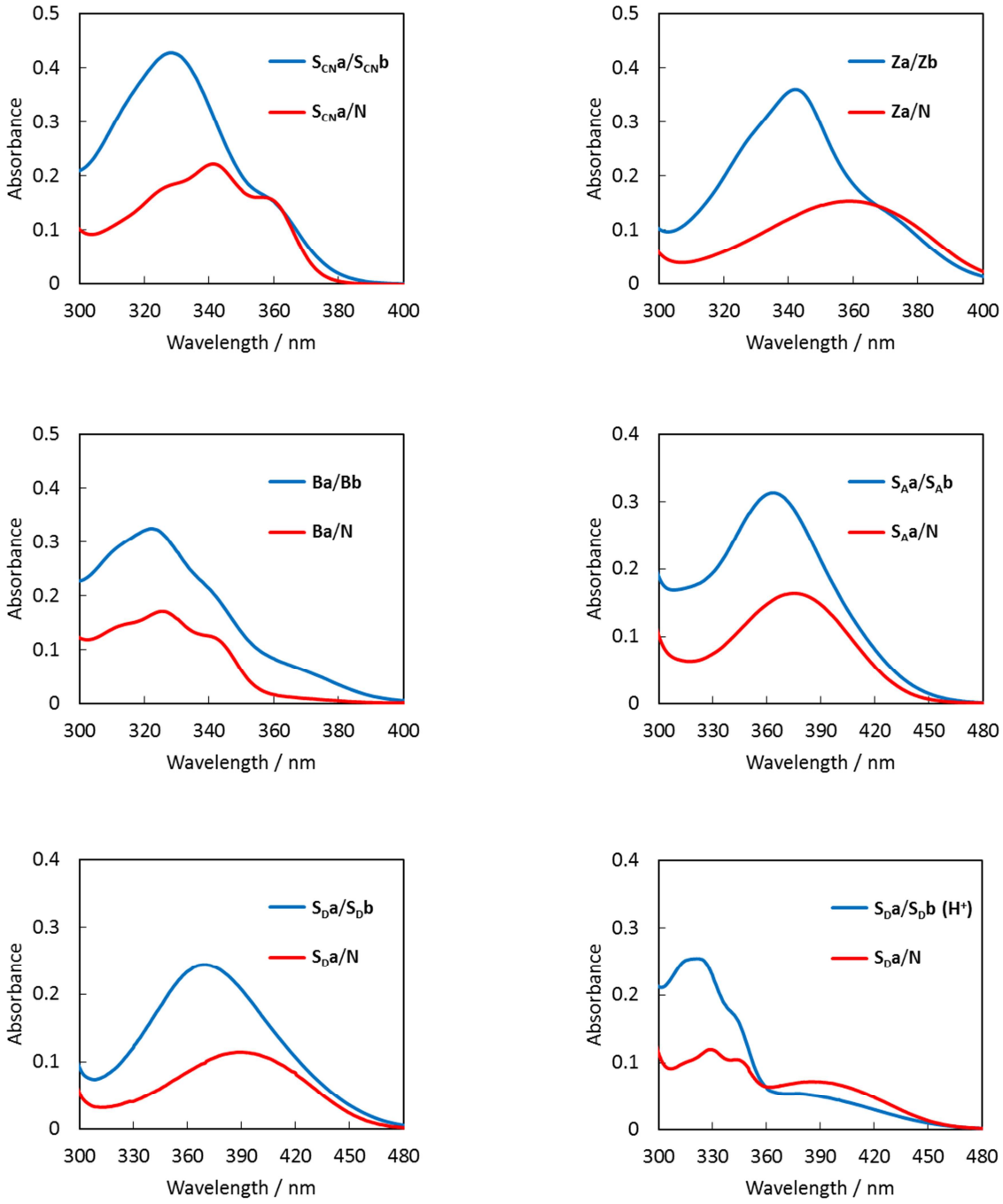


Fig. S1. UV-vis spectra of **Xa**/**Yb** and **Xa**/**N** duplexes (**X, Y** = $\mathbf{S_{CN}}$, **Z**, **B**, $\mathbf{S_A}$ or $\mathbf{S_D}$). Conditions are as follows: [ODN] = 5.0 μM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for $\mathbf{S_D}$, pH 5.0 (10 mM MES buffer) for $\mathbf{S_D(H^+)}$, 20 °C.

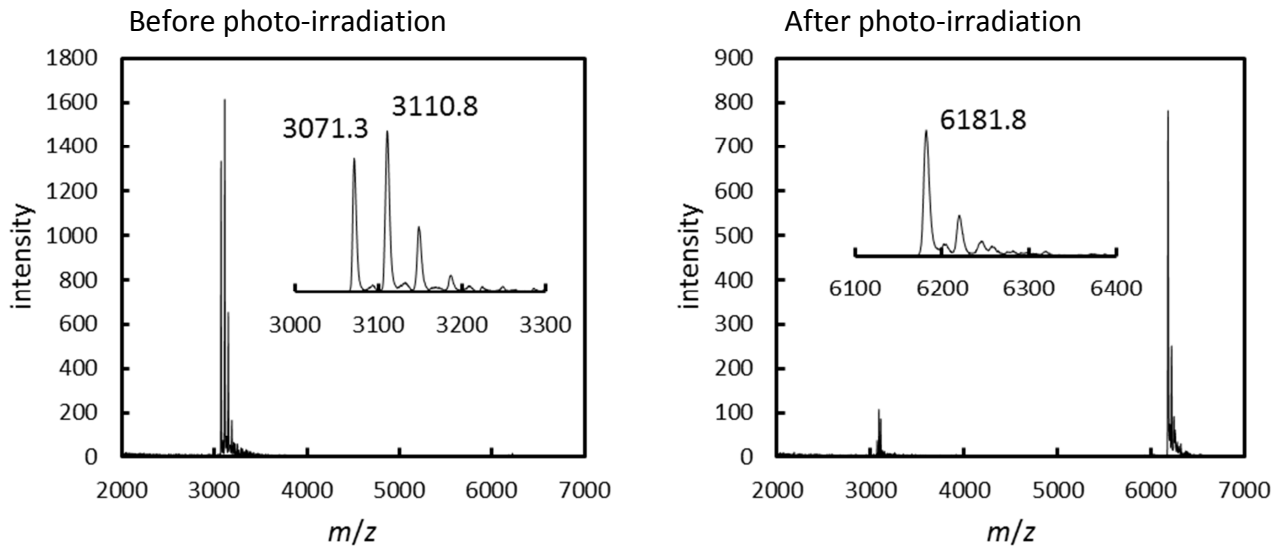


Fig. S2. MALDI-TOF MS charts of **Sa**/**Sb** before and after 180 sec UV irradiation (340 nm). Calculated mass for [**Sa**+H^+]:3072, [**Sb**+H^+]:3112, [**Sa**/**Sb**+H^+]:6182.

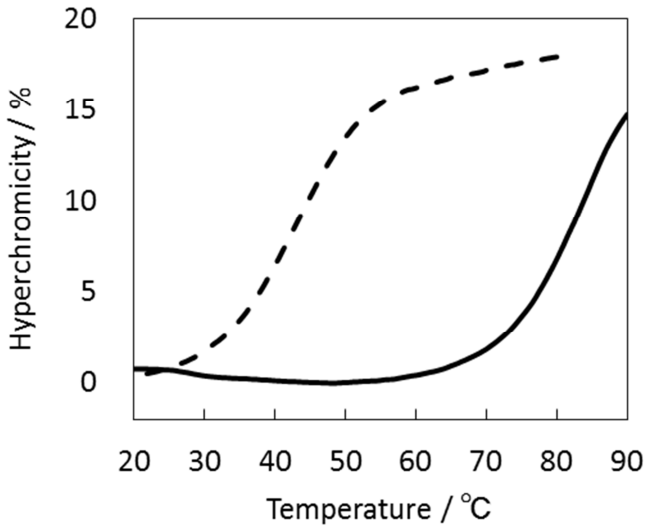


Fig. S3. Melting curves of **Sa**/**Sb** before (broken line) and after 340 nm UV irradiation for 180 sec (solid line). Conditions are as follows: [ODN] = 5.0 μM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer).

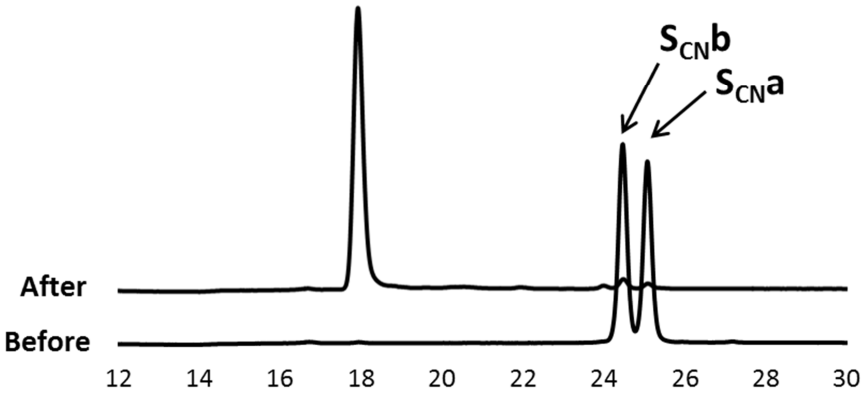


Fig. S4. HPLC chromatograms of **$S_{CN}a$**/**$S_{CN}b$** before and after 300 sec UV irradiation (340 nm).

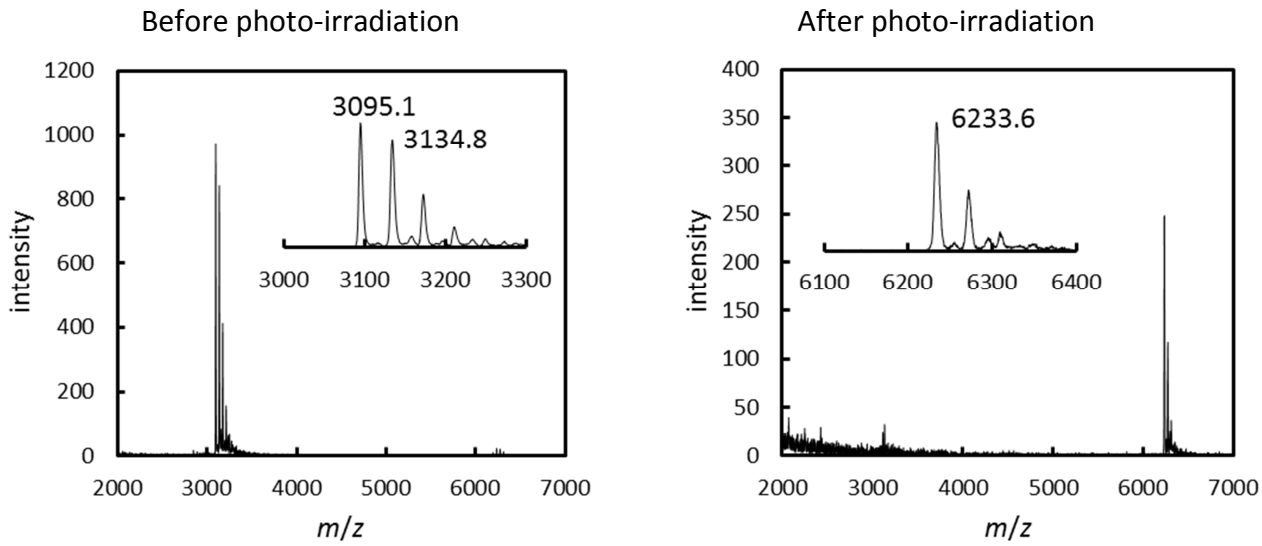


Fig. S5. MALDI-TOFMS charts of $\mathbf{S_{CN}a}$/$\mathbf{S_{CN}b}$ before and after 300 sec UV irradiation (340 nm). Calculated mass for [$\mathbf{S_{CN}a}$+H^+]:3097, [$\mathbf{S_{CN}b}$+H^+]:3137, [$\mathbf{S_{CN}a}$/$\mathbf{S_{CN}b}$+H^+]:6232.

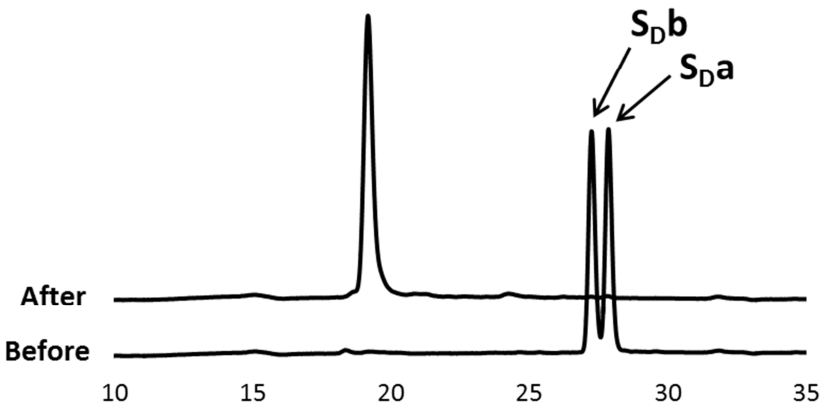


Fig. S6. HPLC chromatograms of **S_Da/S_Db (H^+)** before and after 300 sec UV irradiation (340 nm) at pH5.

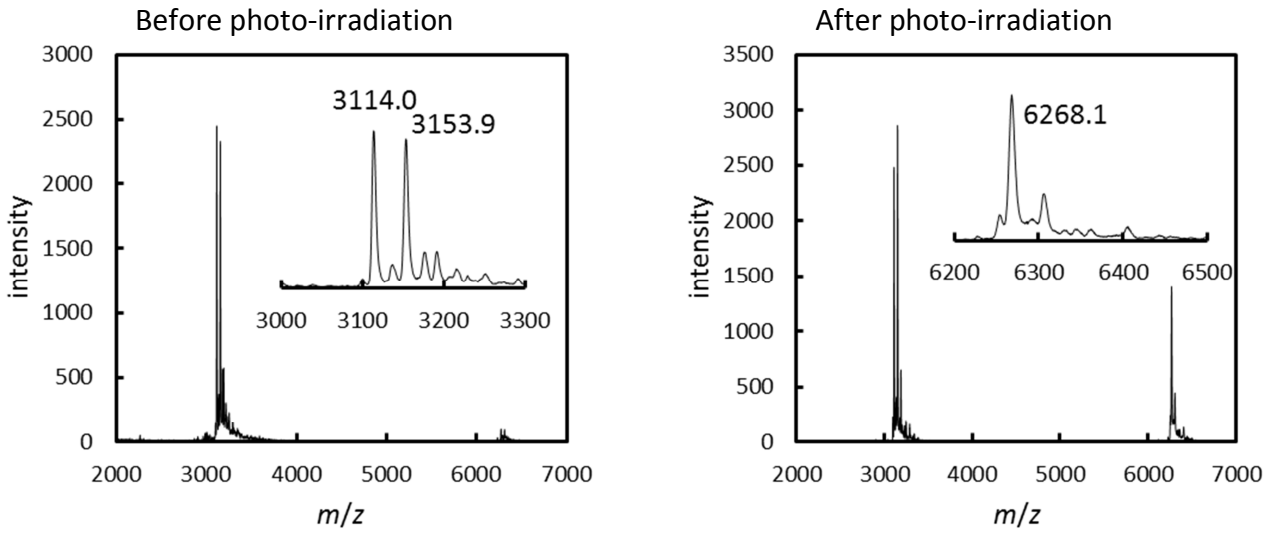


Fig. S7. MALDI-TOFMS charts of **S_Da**/**S_Db (H^+)** before and after 300 sec UV irradiation (340 nm). Calculated mass for [**S_Da**+H^+]:3115, [**S_Db**+H^+]:3155, [**S_Da**/**S_Db**+H^+]:6268.

Table S1. Neighboring base pair dependence of quantum yields of **S**, **Z** and **B**.

	Φ (×10^2)		
	S	**Z**	**B**
Xa/Yb	15	1.7	2.4
Xc/Yd	23	6.9	10
Xe/Yf	12	0.56	0.77

Xa: 5'-GCATC **X** AGTC-3'
Yb: 3'-CGTAG **Y** TCAG-5'

Xc: 5'-GCACT **X** AGTC-3'
Yd: 3'-CGTGA **Y** TCAG-5'

Xe: 5'-GCATC **X** GATC-3'
Yf: 3'-CGTAG **Y** CTAG-5'

(**X, Y** = **S**, **Z**, **B**)

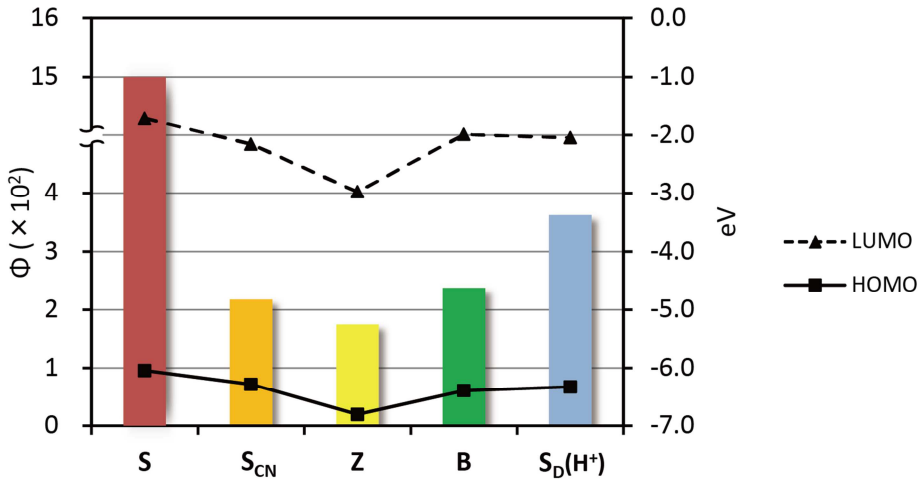


Fig. S8. Quantum yields of homo-photodimerizations (bar graph) and calculated energy level of LUMO and HOMO.

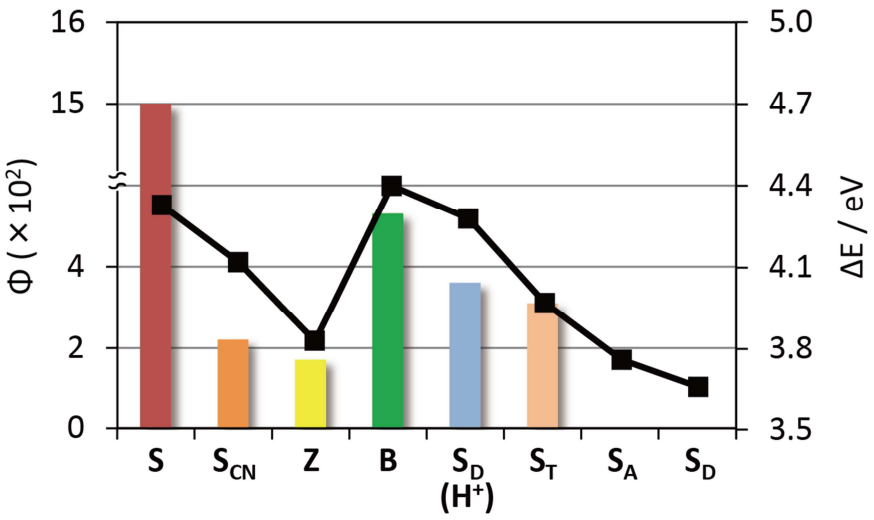


Fig. S9. Quantum yields of homo-photodimerizations (bar graph) and calculated excitation energies (line graph). $\Delta E=E_{LUMO}-E_{HOMO}$. **B** was measured at pH 9. The quantum yield of **B** at pH9 was 5.3.

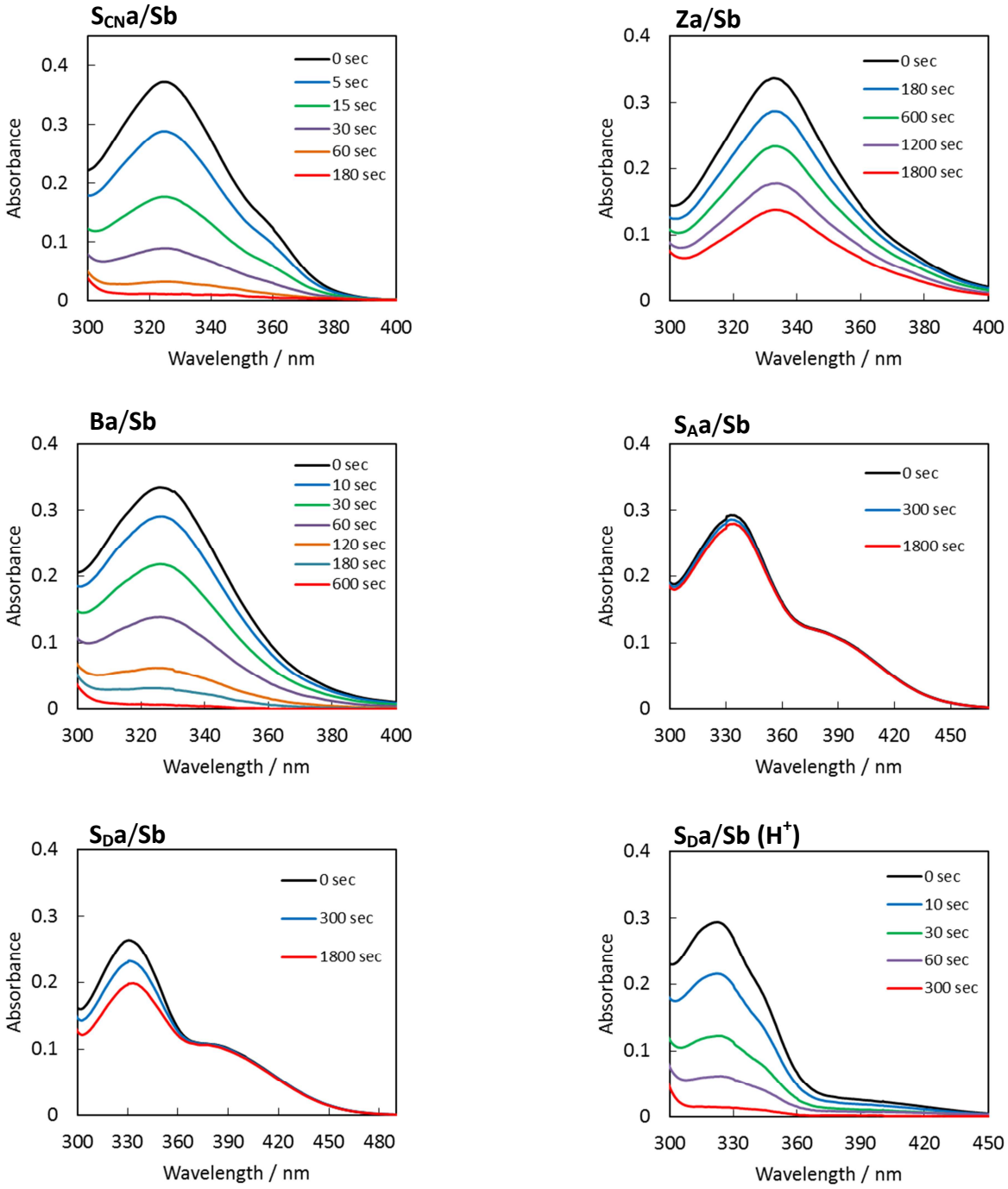


Fig. S10. UV- vis spectra of **Xa**/**Sb** duplexes (**X** = $\mathbf{S_{CN}}$, **Z**, **B**, $\mathbf{S_A}$ or $\mathbf{S_D}$) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for $\mathbf{S_D}$, pH 5.0 (10 mM MES buffer) for $\mathbf{S_D(H^+)}$, 20 ^{o}C.

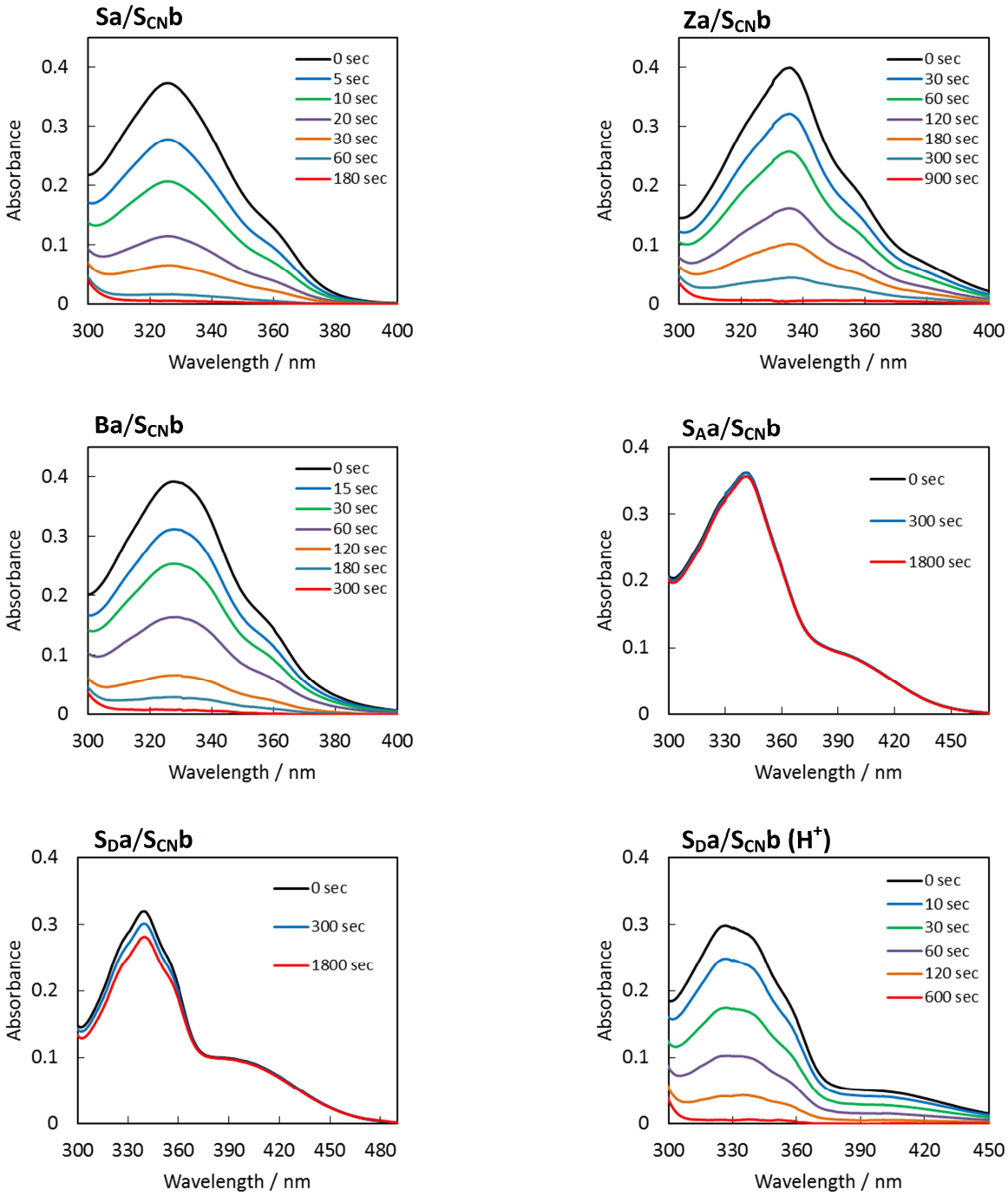


Fig. S11. UV- vis spectra of **Xa**/**S$_{CN}$b** duplexes (**X** = **S**, **Z**, **B**, **S$_A$** or **S$_D$**) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for **S$_D$**, pH 5.0 (10 mM MES buffer) for **S$_D$(H$^+$)**, 20 ^{o}C.

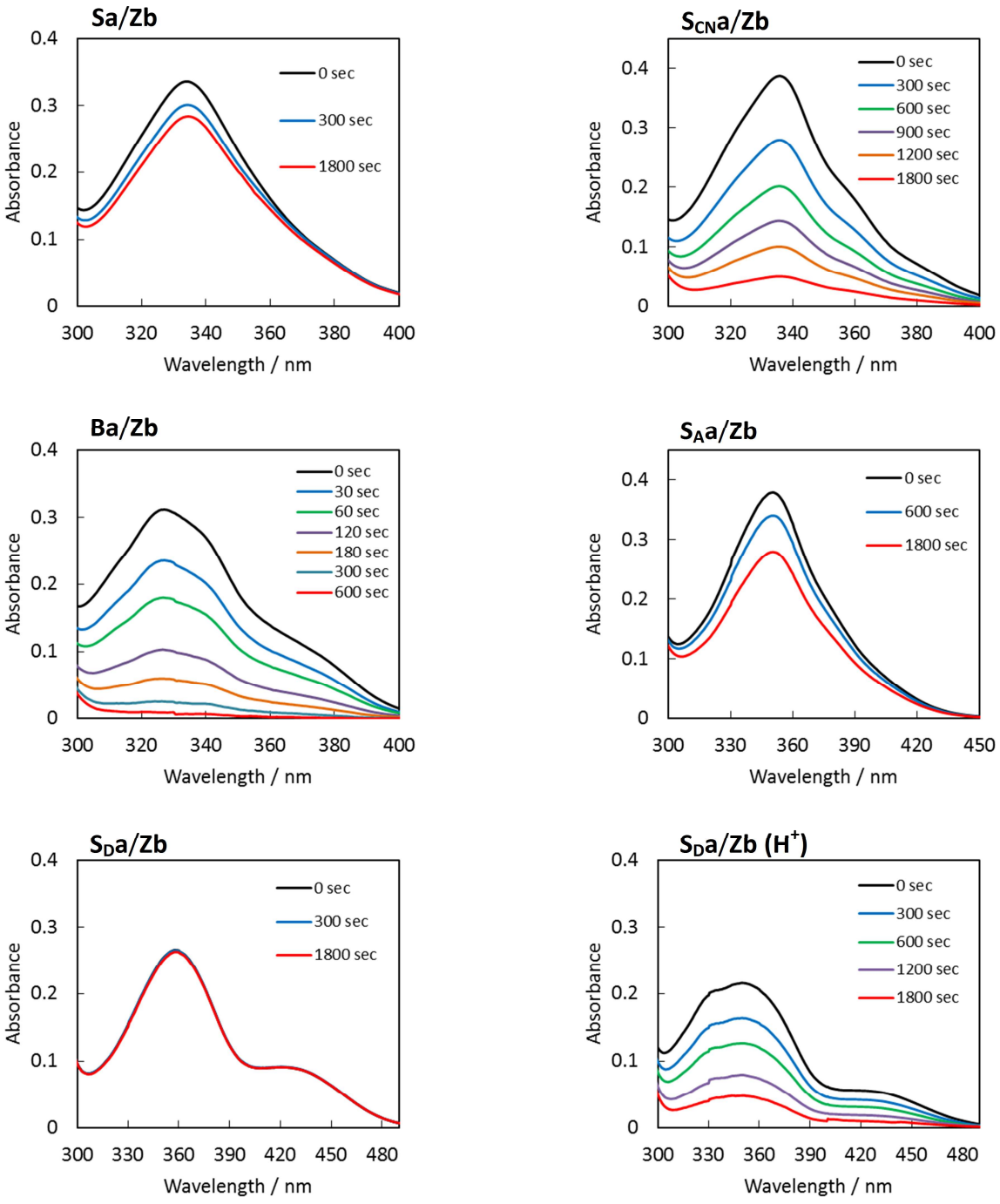


Fig. S12. UV- vis spectra of **Xa**/**Zb** duplexes (**X** = **S**, $\mathbf{S_{CN}}$, **B**, $\mathbf{S_A}$ or $\mathbf{S_D}$) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for $\mathbf{S_D}$, pH 5.0 (10 mM MES buffer) for $\mathbf{S_D(H^+)}$, 20 ^{o}C.

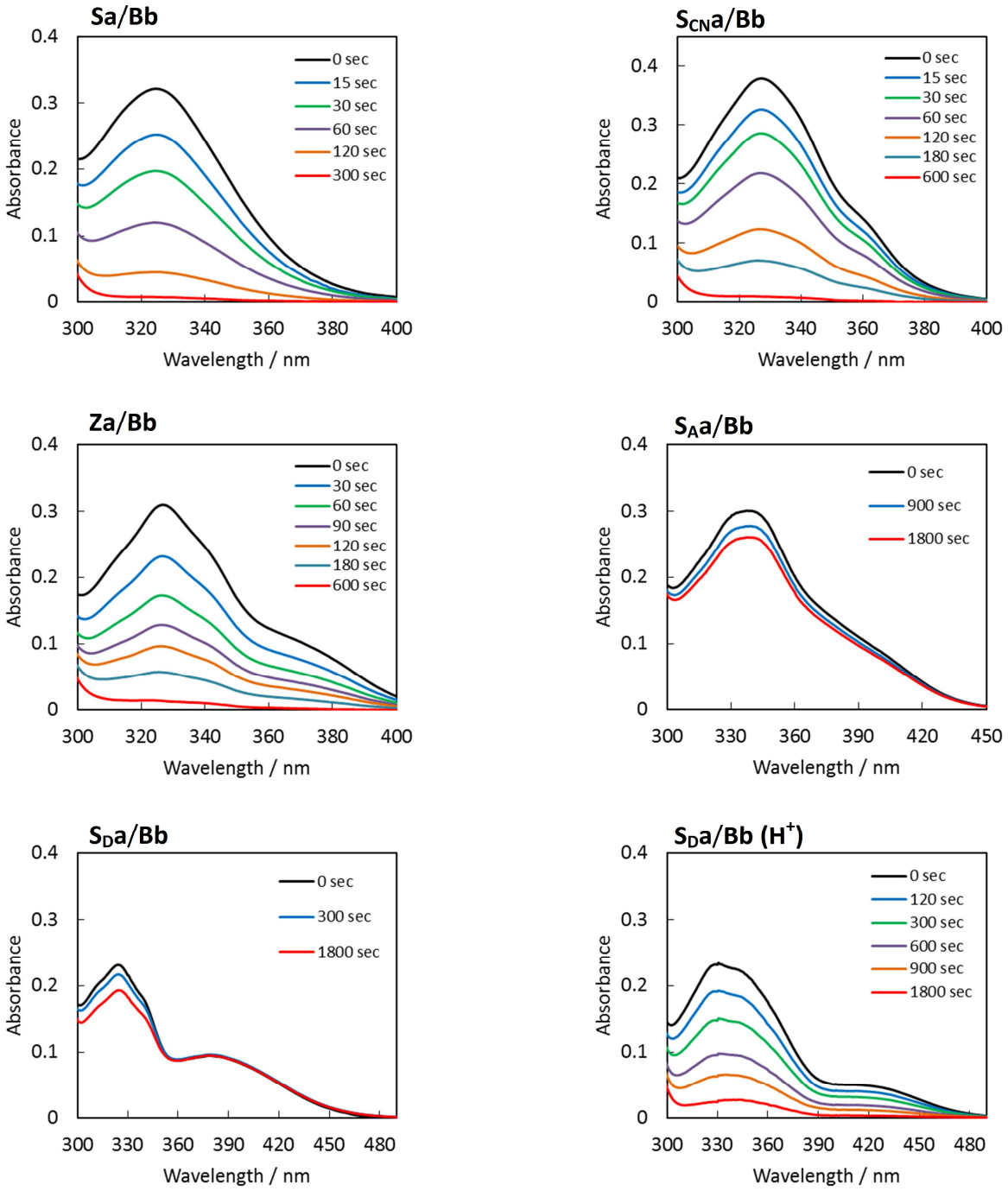


Fig. S13. UV- vis spectra of **Xa**/**Bb** duplexes (**X** = **S**, $\mathbf{S_{CN}}$, **Z**, $\mathbf{S_A}$ or $\mathbf{S_D}$) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for $\mathbf{S_D}$, pH 5.0 (10 mM MES buffer) for $\mathbf{S_D(H^+)}$, 20 ^{o}C.

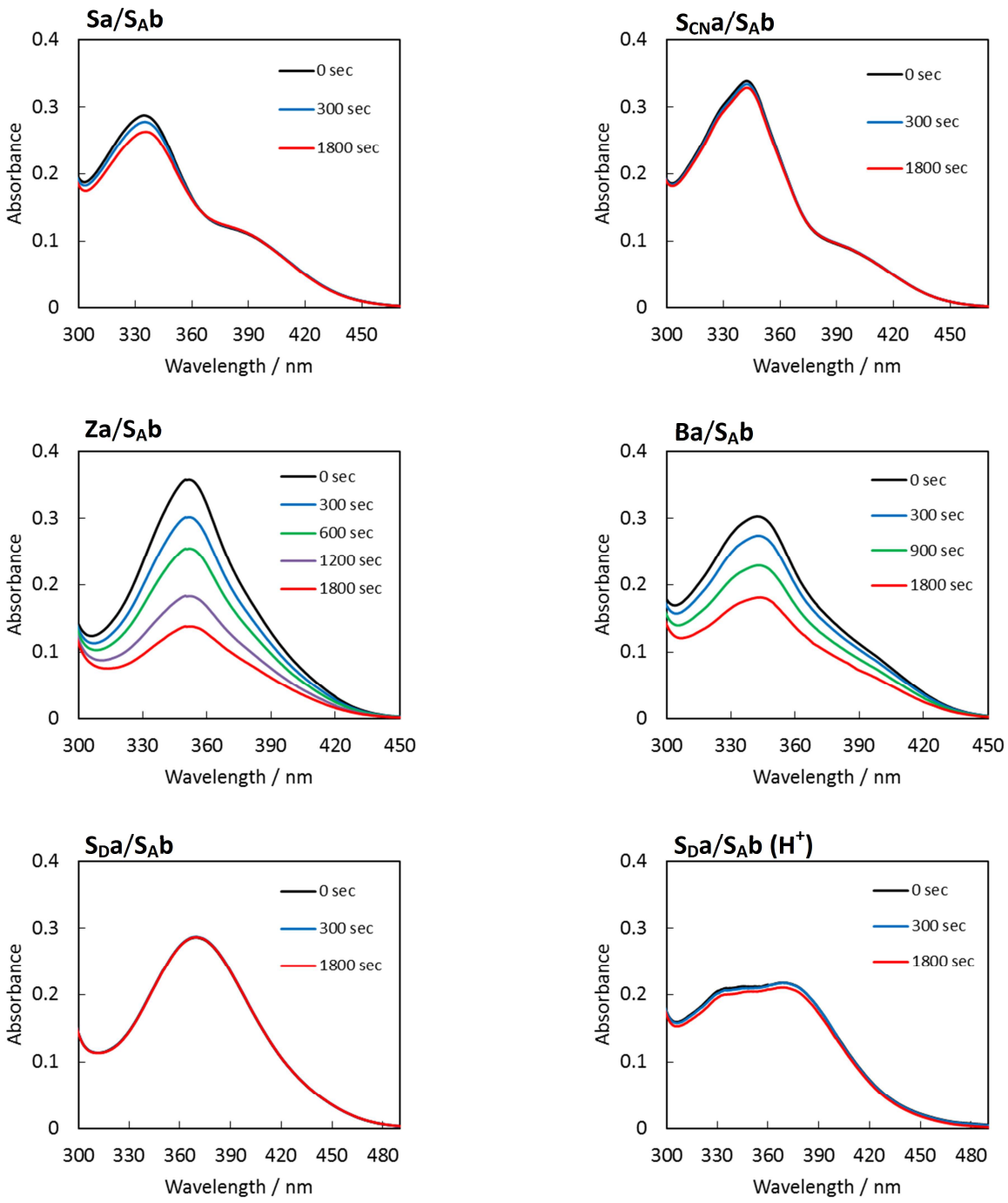


Fig. S14. UV- vis spectra of **Xa**/**S$_A$b** duplexes (**X** = **S**, **S$_{CN}$**, **Z**, **B** or **S$_D$**) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), pH 9.0 (10 mM Tris buffer) for **S$_D$**, pH 5.0 (10 mM MES buffer) for **S$_D$(H$^+$)**, 20 ^{o}C.

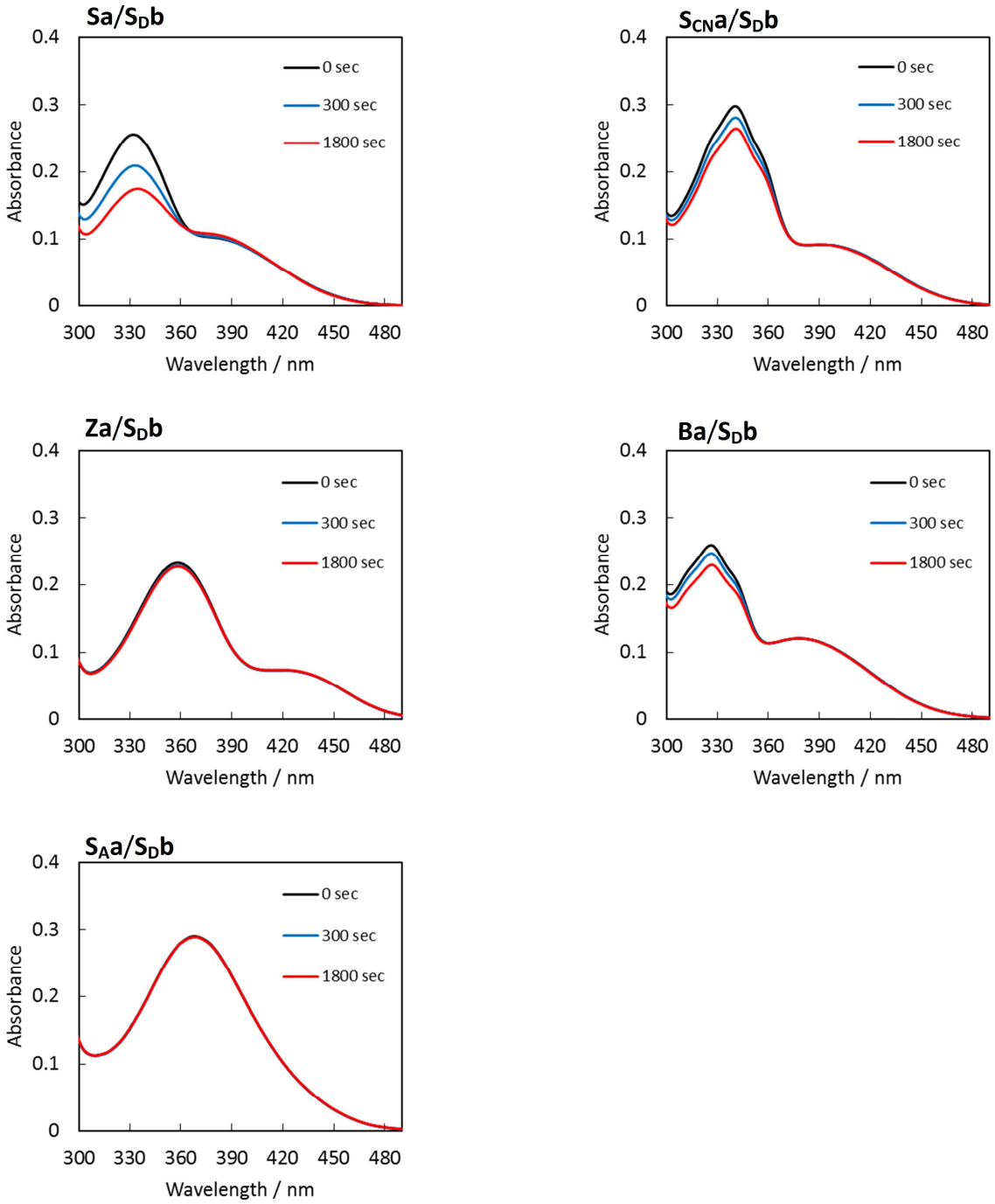


Fig. S15. UV- vis spectra of **Xa**/**S$_D$b** duplexes (**X** = **S**, **S$_{CN}$**, **Z**, **B** or **S$_A$**) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 9.0 (10 mM Tris buffer), 20 ^{o}C.

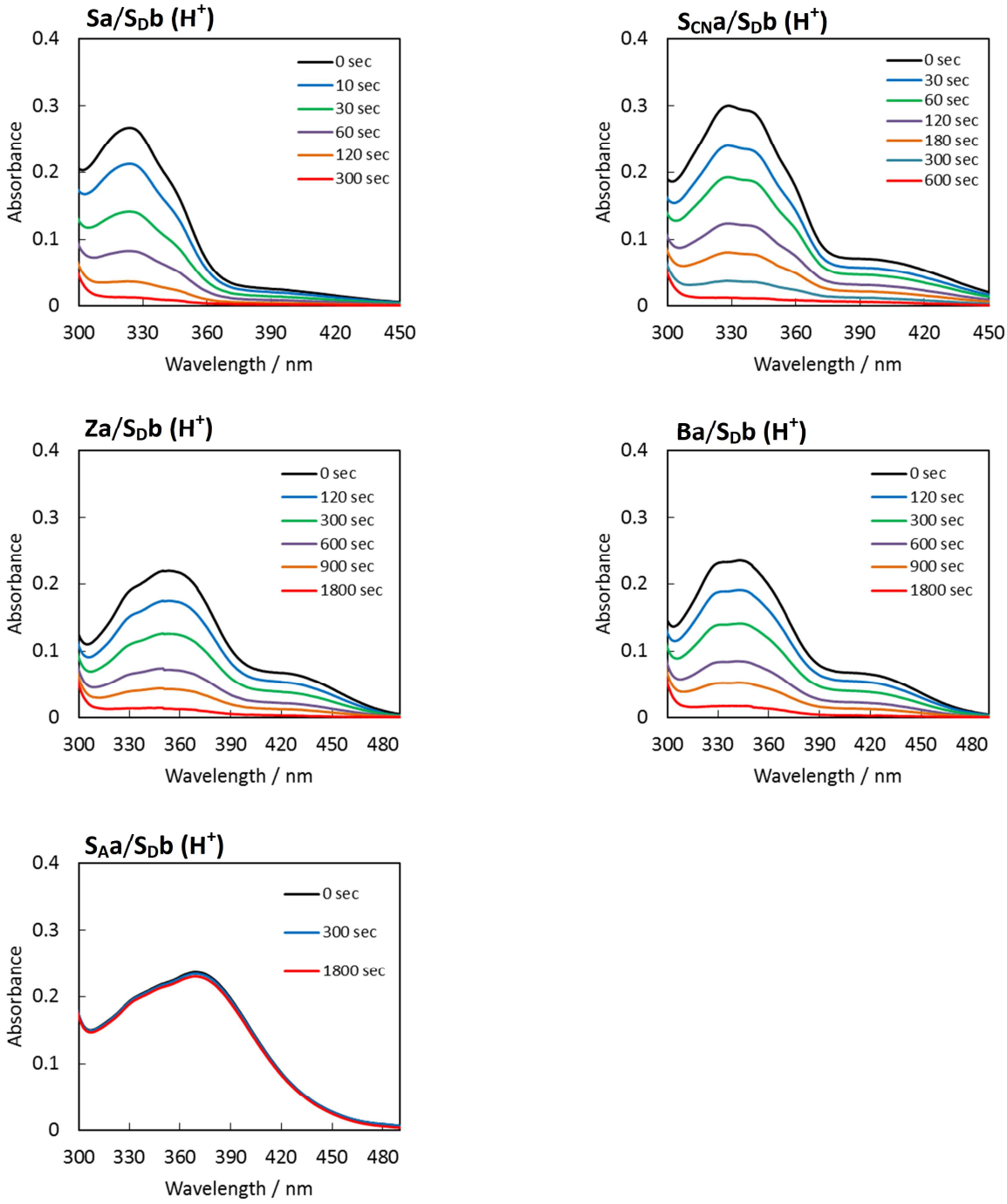


Fig. S16. UV- vis spectra of **Xa/S$_D$b (H$^+$)** duplexes (**X** = **S**, **S$_{CN}$**, **Z**, **B** or **S$_A$**) before and after indicated duration of UV irradiation (340 nm). Conditions are as follows: [ODN] = 5.0 µM, [NaCl] = 100 mM, pH 5.0 (10 mM MES buffer), 20 ^{o}C.

Table S2. Melting temperatures of duplexes in homo and hetero combinations.

	T_m / °C[a]						
	Sa	**S_{CN}a**	**Za**	**Ba**	**S_Aa**	**S_Da**[b]	**S_Da(H^+)**[c]
Sb	42.4	46.5	51.1	45.3	48.6	39.4	36.0
S_{CN}b	46.0	53.8	55.4	49.0	56.3	47.7	40.5
Zb	49.7	54.4	53.6	50.4	56.2	47.5	42.2
Bb	44.9	49.5	52.0	46.1	51.3	41.2	42.3
S_Ab	47.9	56.4	57.2	51.3	58.1	47.4	41.4
S_Db[b]	39.6	47.6	48.8	41.4	48.1	37.5	-
S_Db(H^+)[c]	35.0	39.8	44.7	44.2	42.5	-	36.7

[a]Conditions: 5.0 μM DNA, 100 mM NaCl, pH 7.0 (10 mM phosphate buffer). [b]Measured at pH 9 (Tris buffer). [b]Measured at pH 5 (MES buffer).

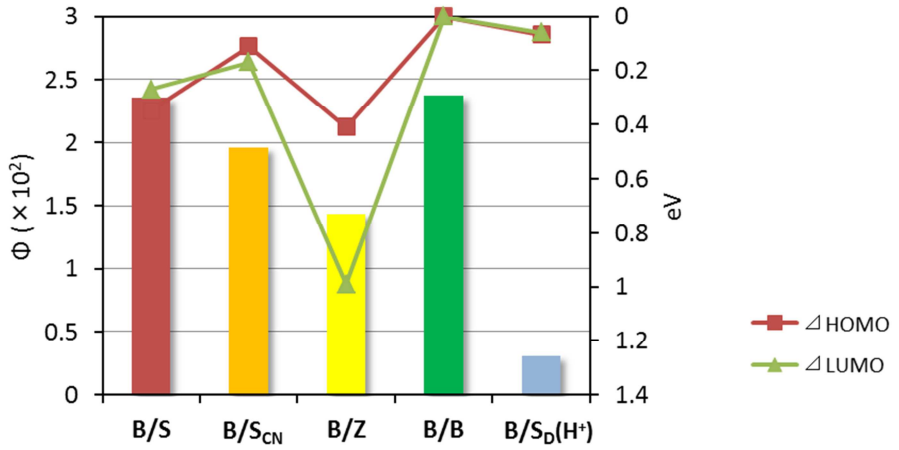


Fig. S17. Quantum yields of photodimerizations of **Ba**/**Yb** duplexes (bar graph) and energy gaps of HOMO or LUMO (line graphs). The energy gaps are displayed in absolute value and the axis is inverted. Note that, **B** should be protonated at pH 5 and hence, **Ba**/**S$_D$b (H$^+$)** showed similar reactivity with **Za**/**S$_D$b (H$^+$)**.

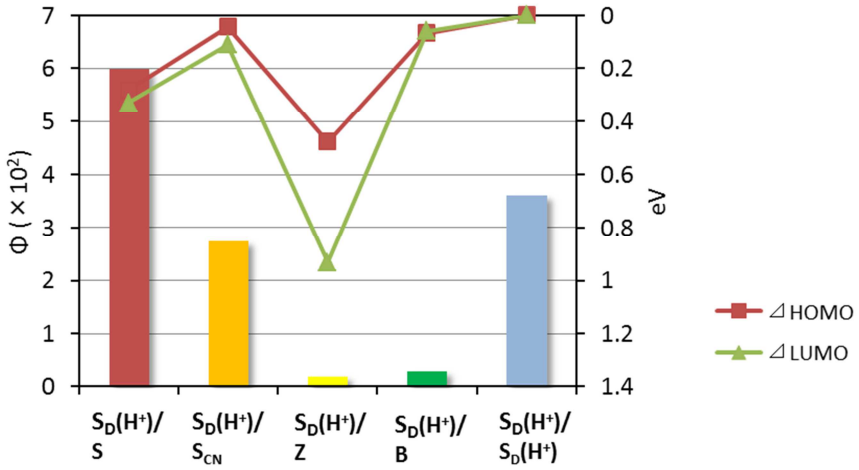


Fig. S18. Quantum yields of photodimerizations of **S_Da/Yb (H^+)** duplexes (bar graph) and energy gaps of HOMO or LUMO (line graphs). The energy gaps are displayed in absolute value and the axis is inverted. Note that, **B** should be protonated at pH 5 and hence, **S_Da/Bb (H^+)** showed similar reactivity with **S_Da/Zb (H^+)**.

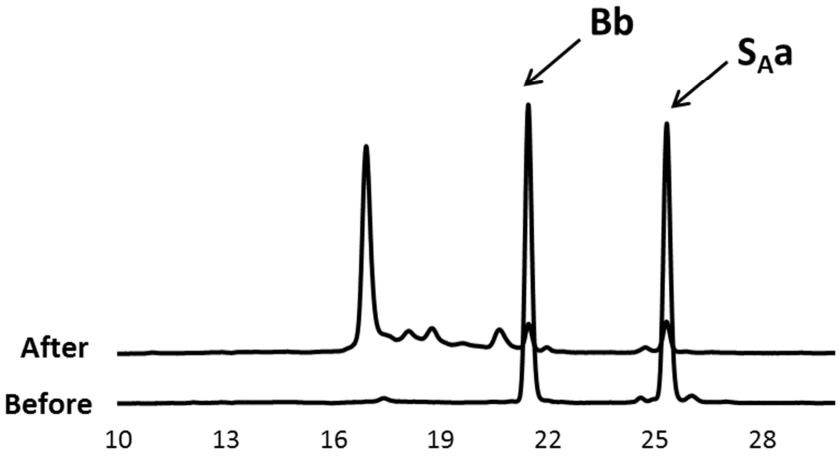


Fig. S19. HPLC chromatograms of **S_Aa**/**Bb** before and after 300 min photo-irradiation (340 nm).

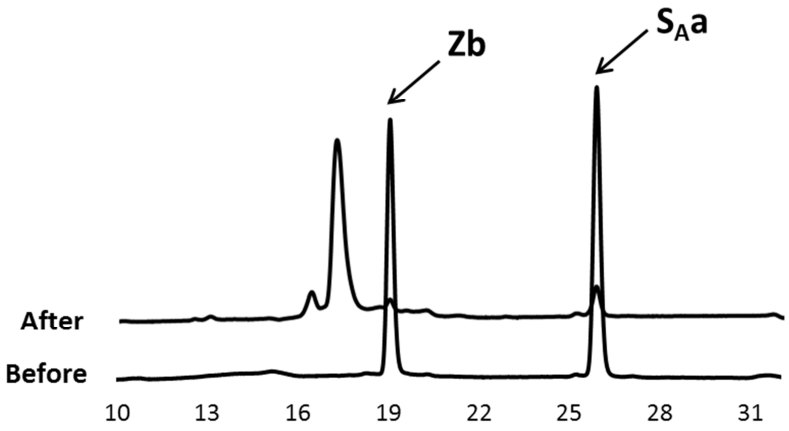


Fig. S20. HPLC chromatograms of **S_Aa**/**Zb** before and after 180 min UV irradiation (340 nm).

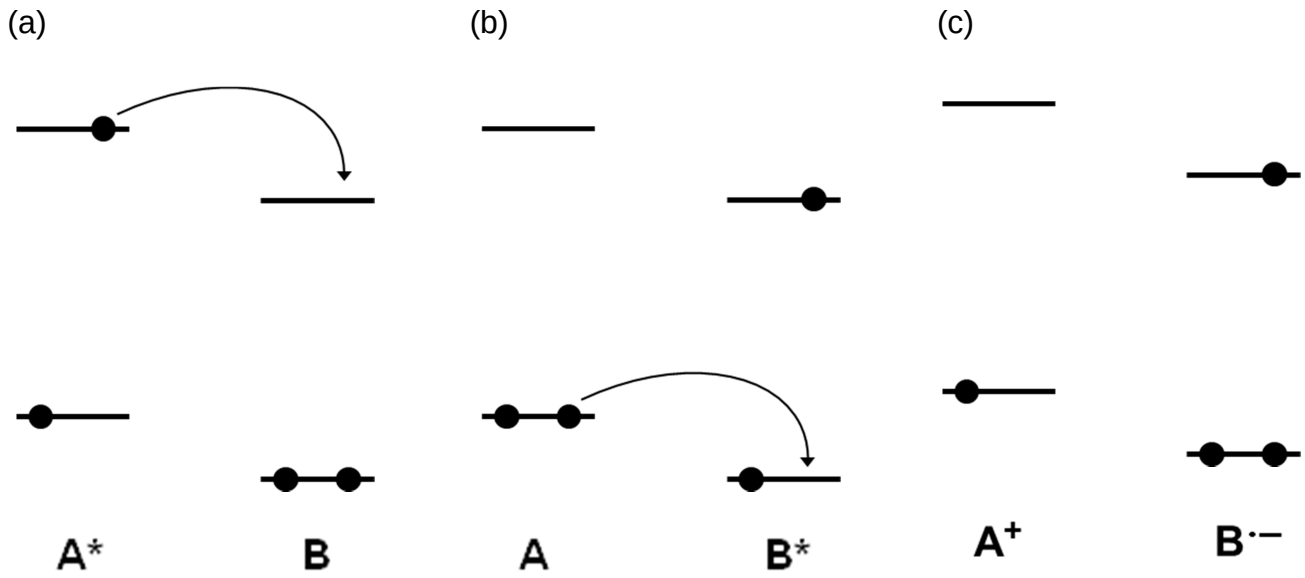
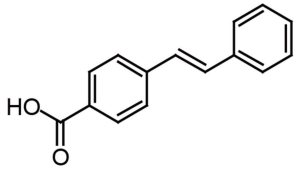
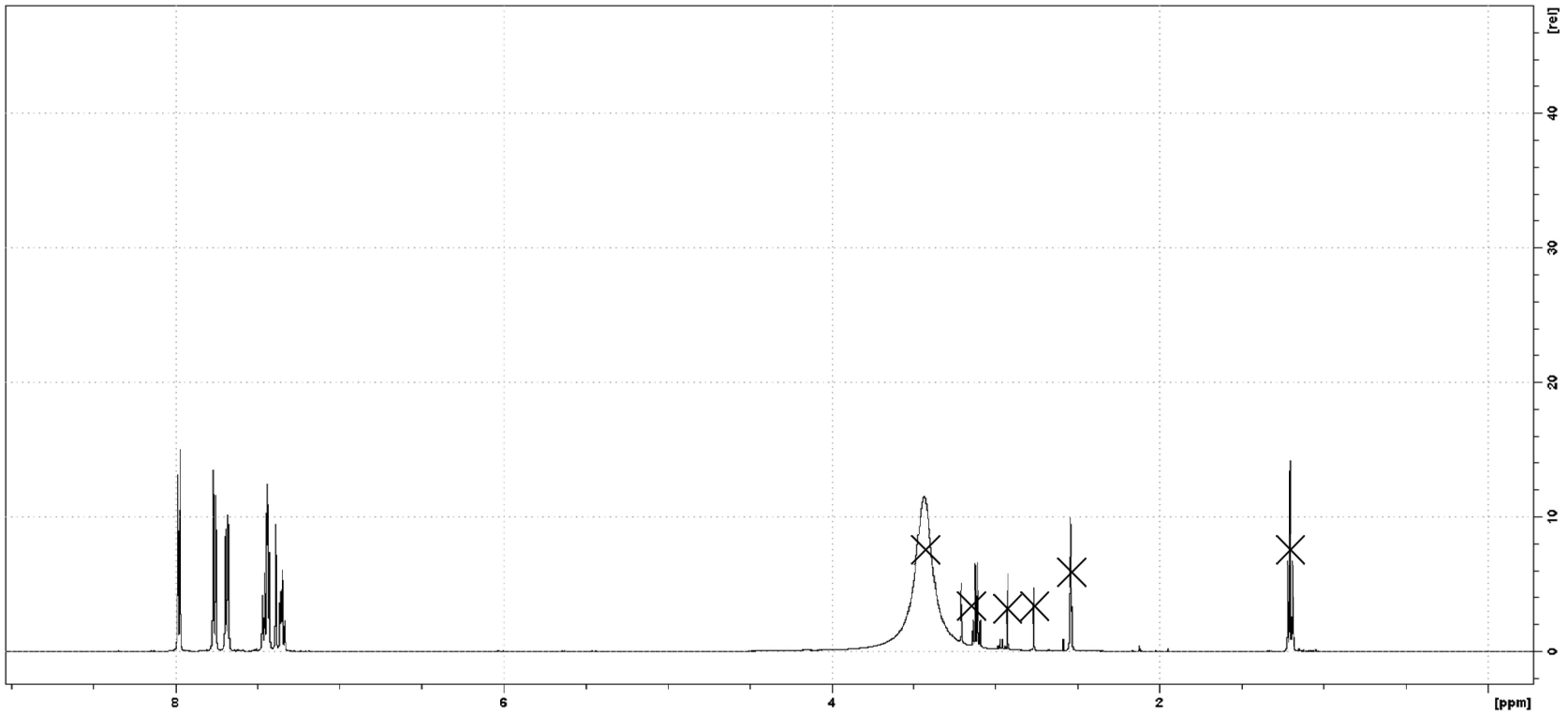


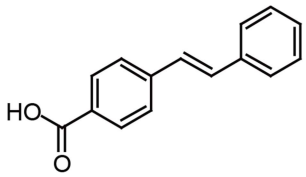
Fig. S21. Schematic energy diagram of the (a) **A** excited state and (b) **B** excited state in **A**/**B** hetero dimer aggregate. (c) Electron transfer from **A** (higher energy level) to **B** (lower energy level) may result the same radical ion pair state.

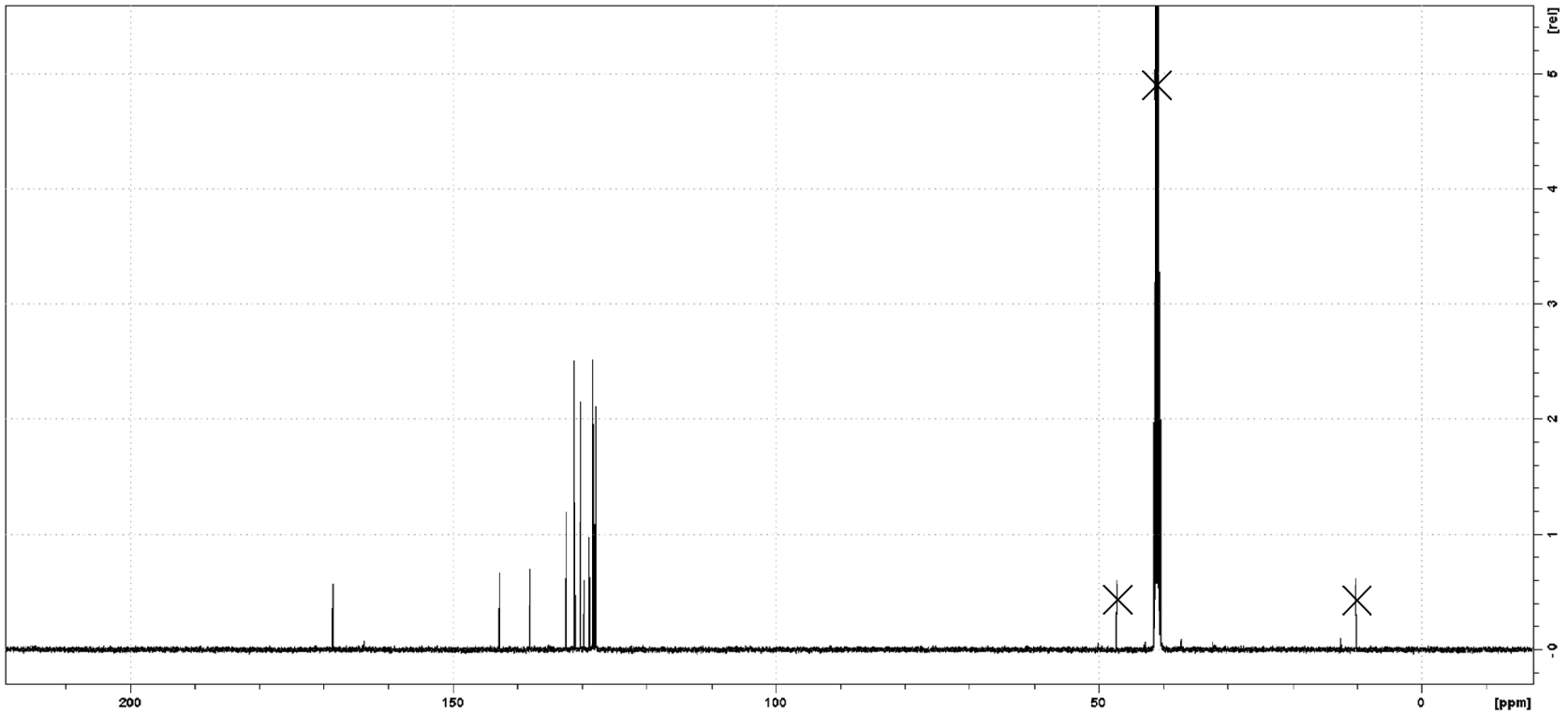
^{1}H-NMR of compound 1 (**S**)



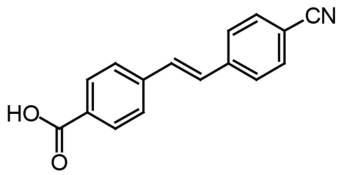


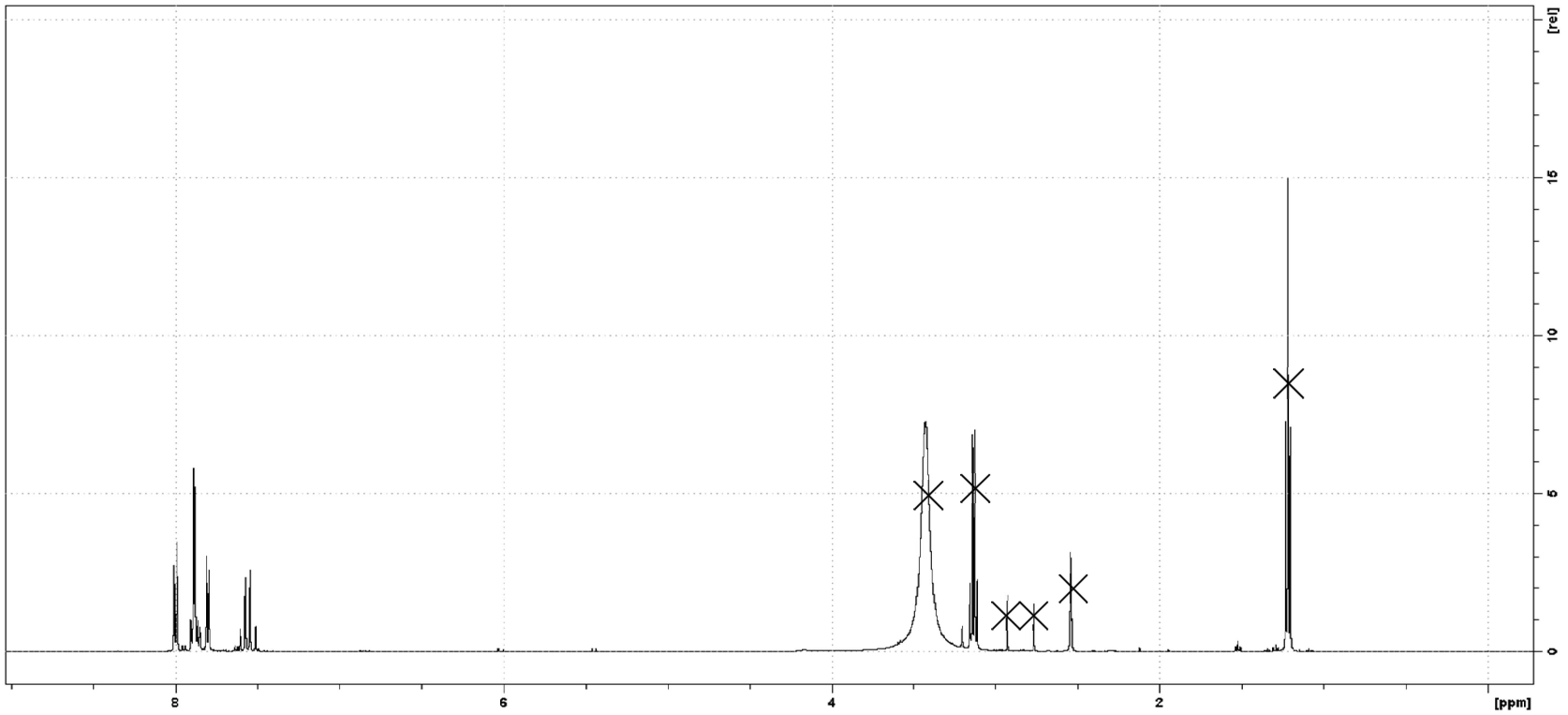
^{13}C-NMR of compound 1 (**S**)



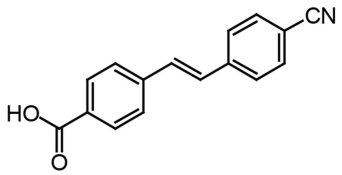


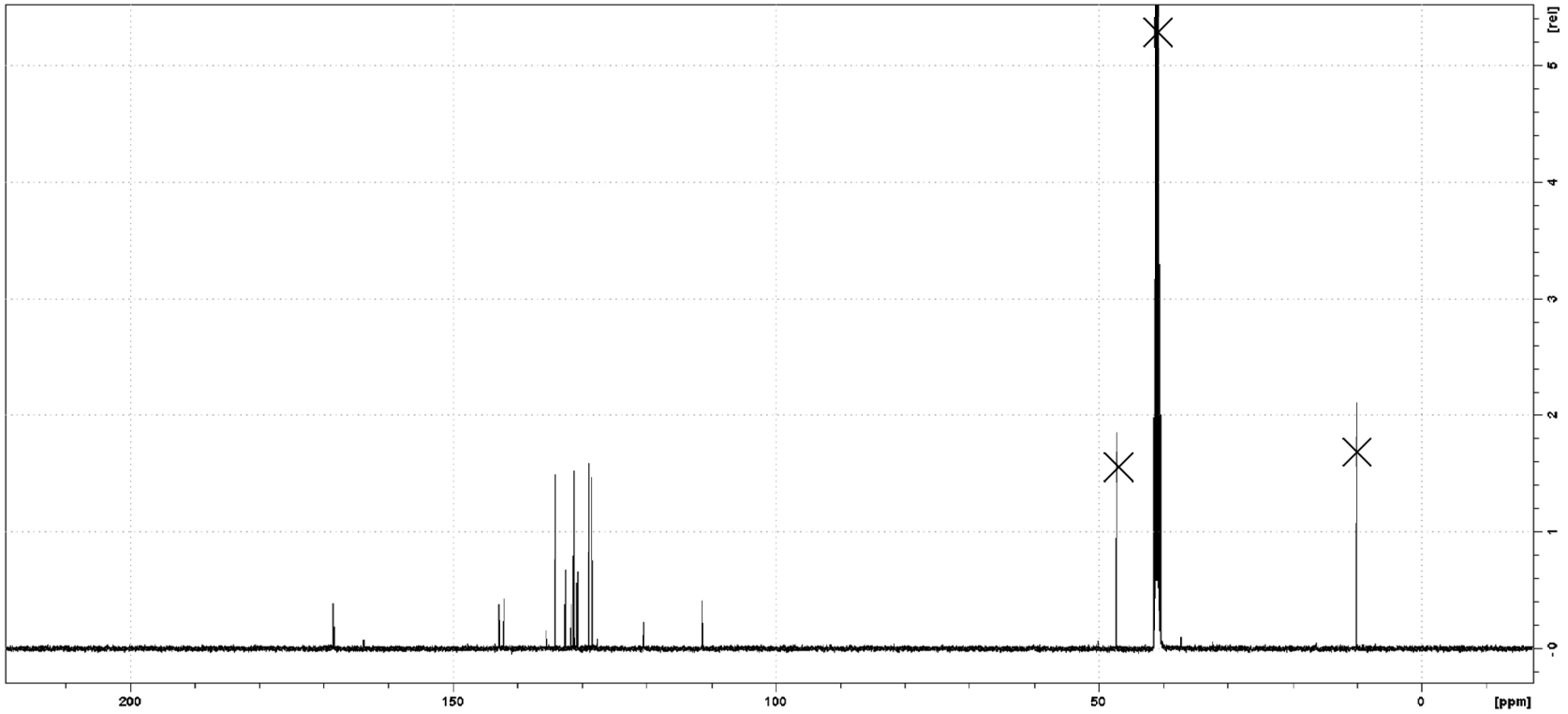
^{1}H-NMR of compound 1 (**S_{CN}**)



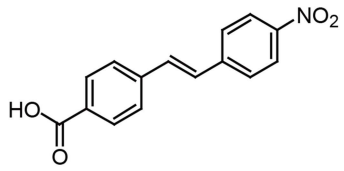


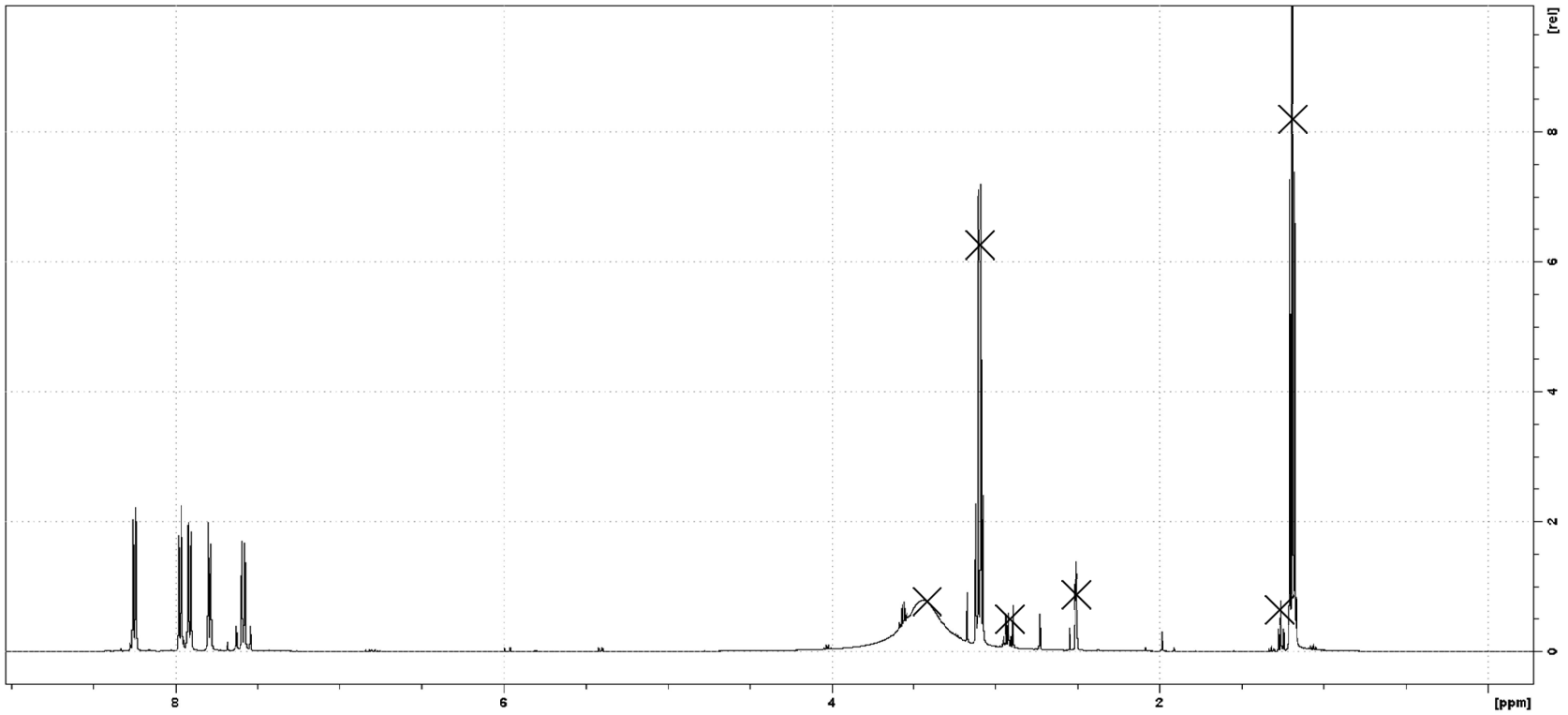
^{13}C-NMR of compound 1 (**S_{CN}**)



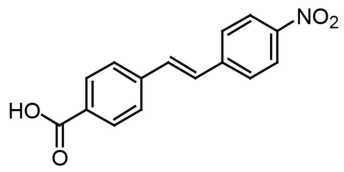


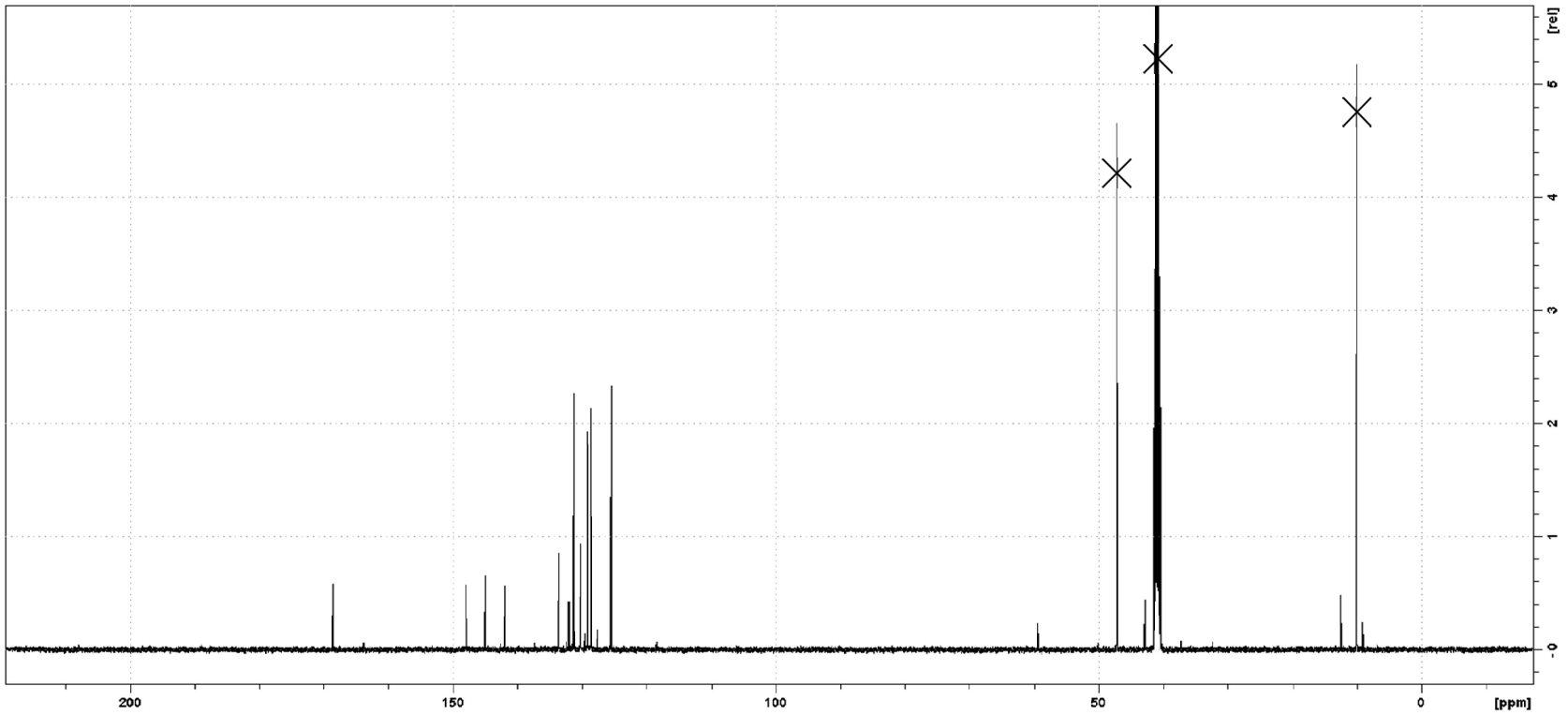
^{1}H-NMR of compound 1 (**S_A**)



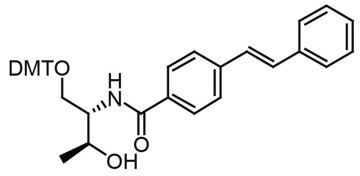


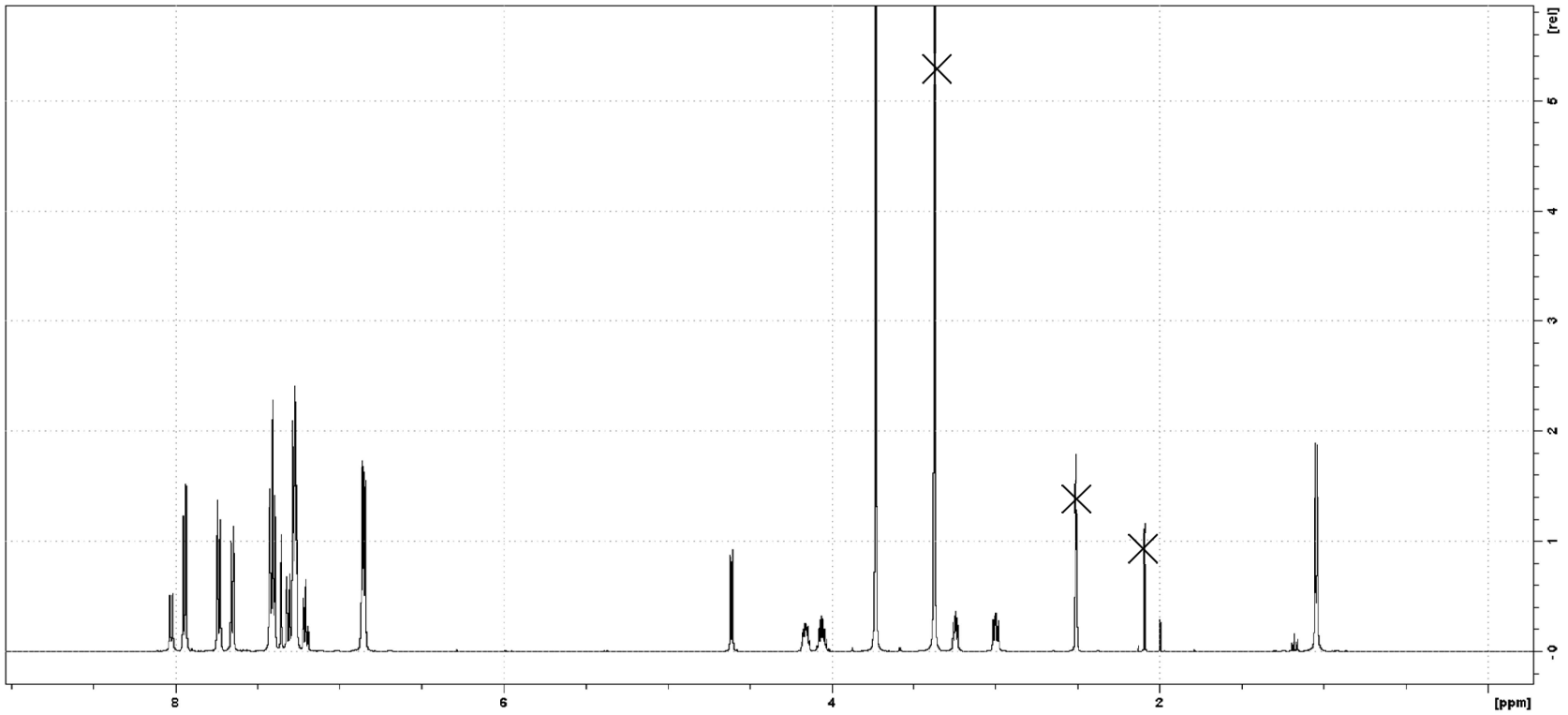
^{13}C-NMR of compound 1 (**S_A**)



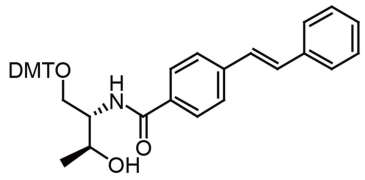


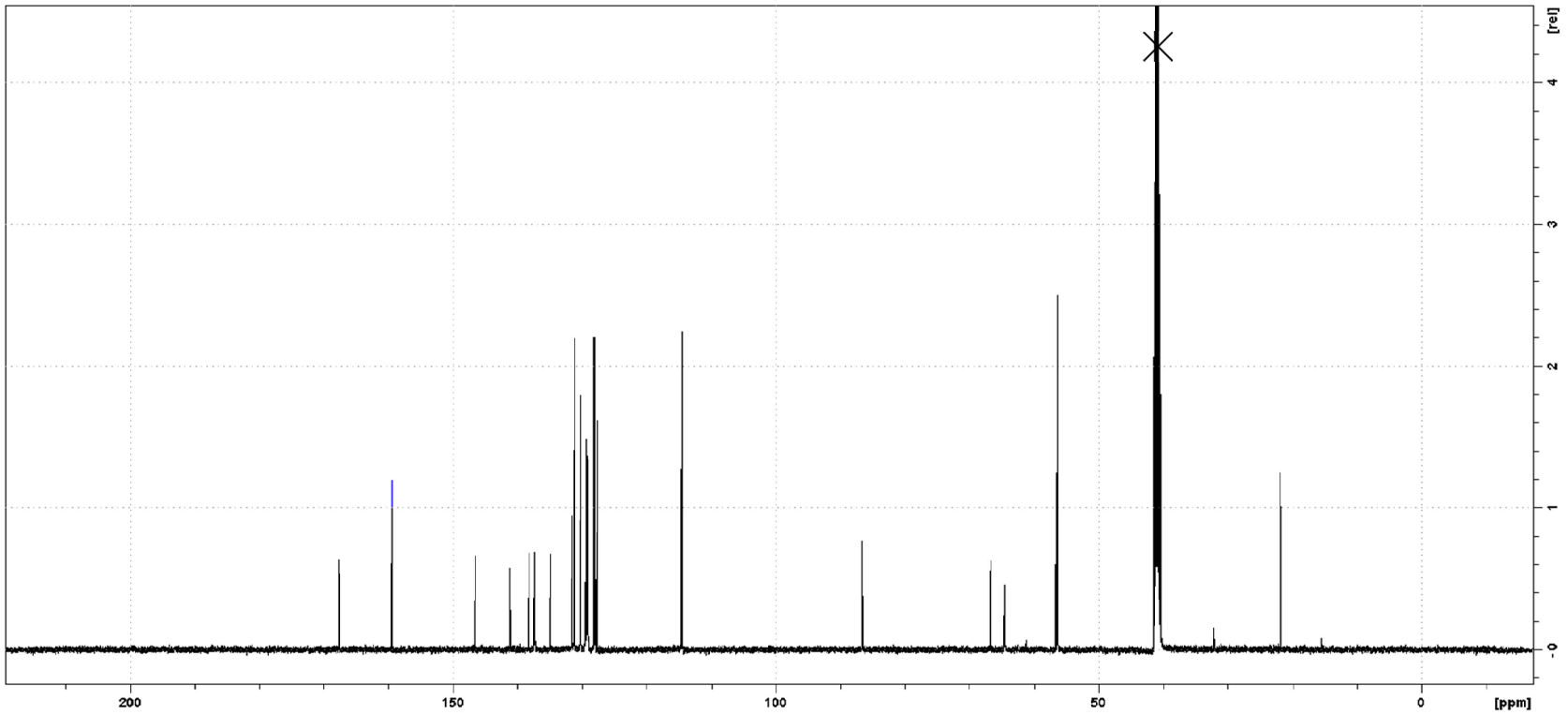
^{1}H-NMR of compound 3 (**S**)



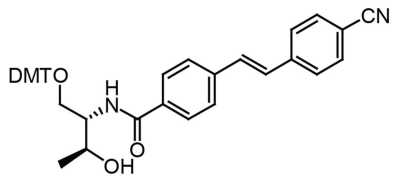


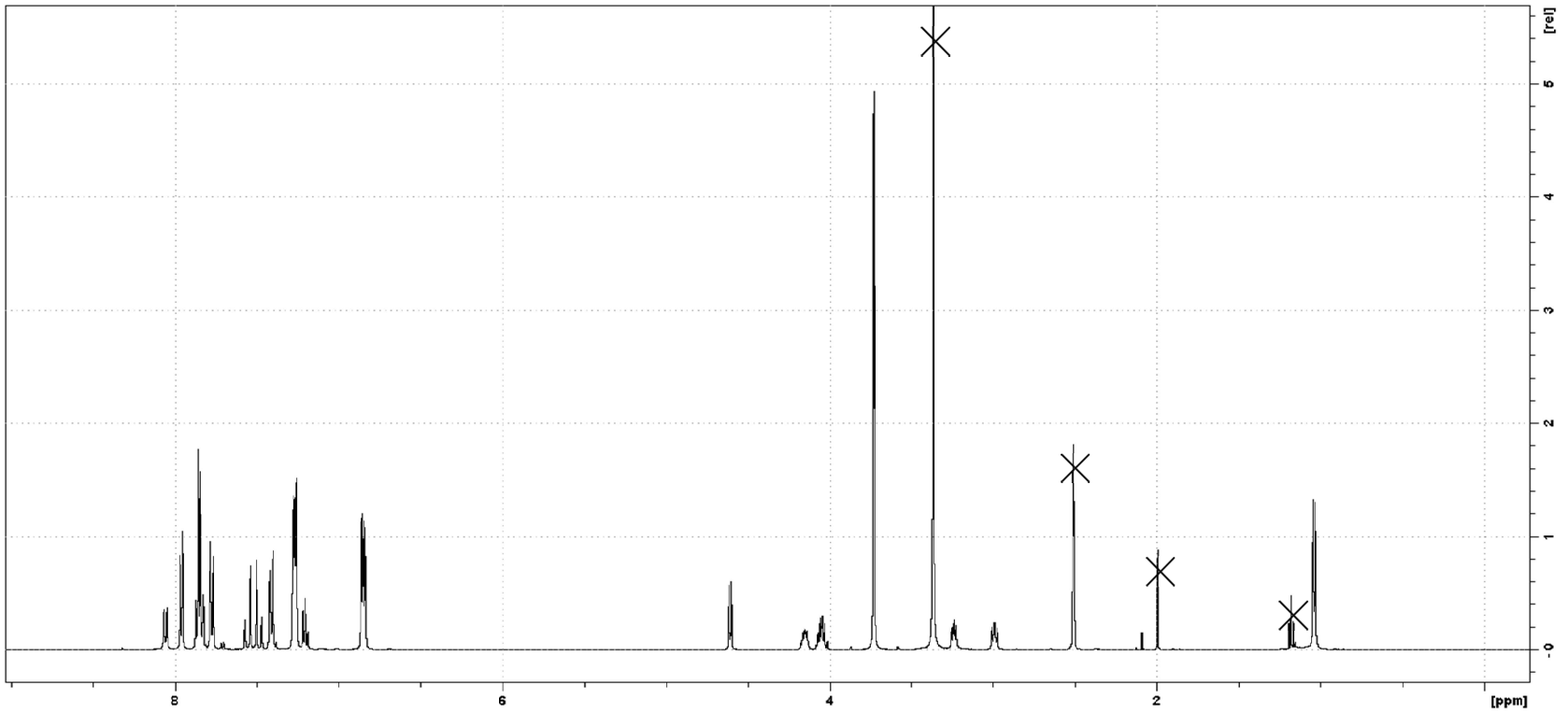
^{13}C-NMR of compound 3 (**S**)



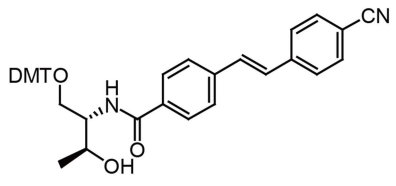


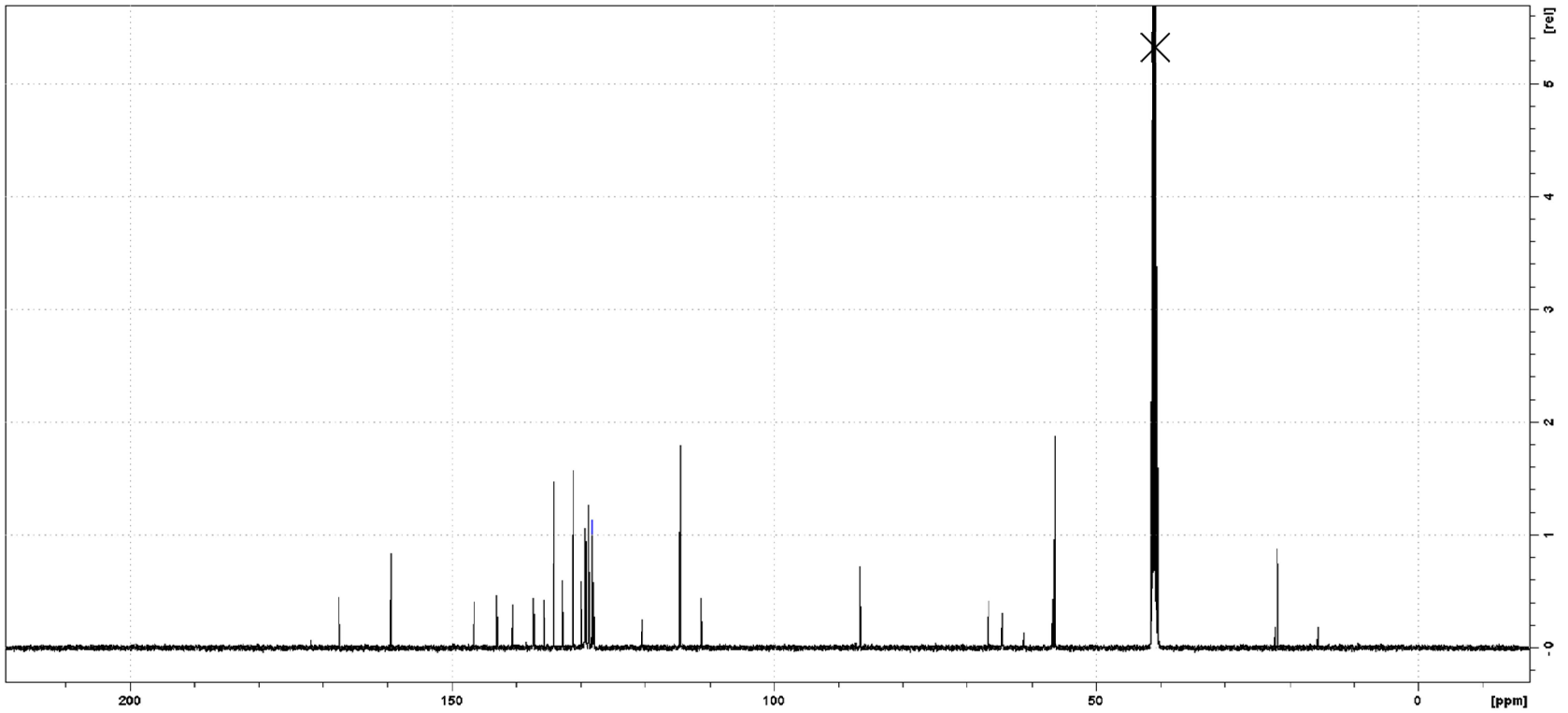
^{1}H-NMR of compound 3 ($\mathbf{S_{CN}}$)



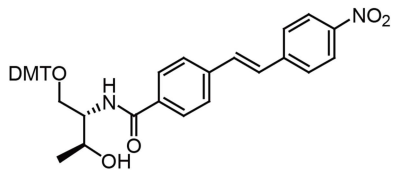


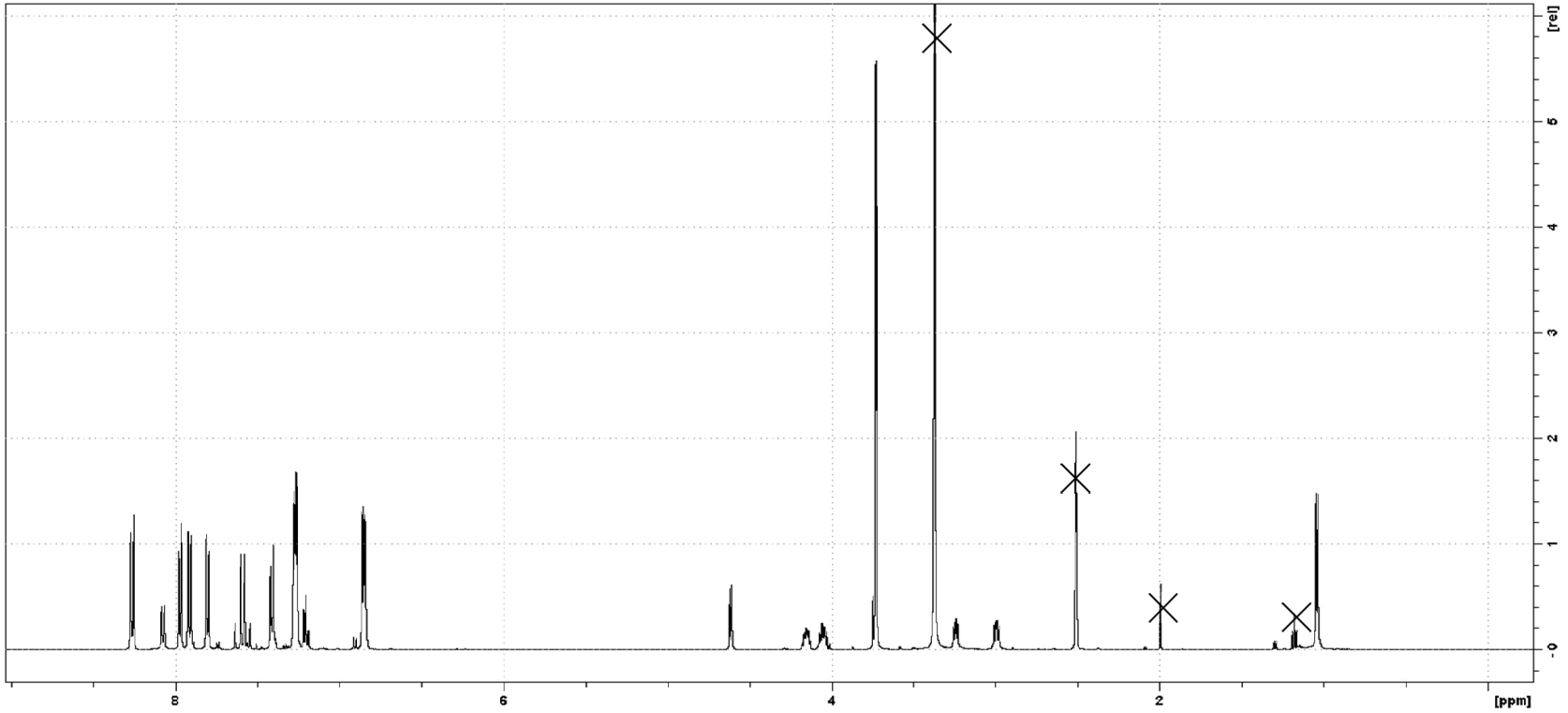
^{13}C-NMR of compound 3 (**S_{CN}**)



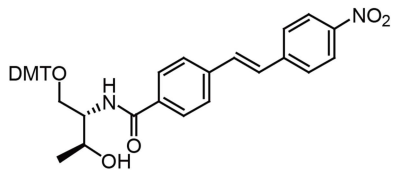


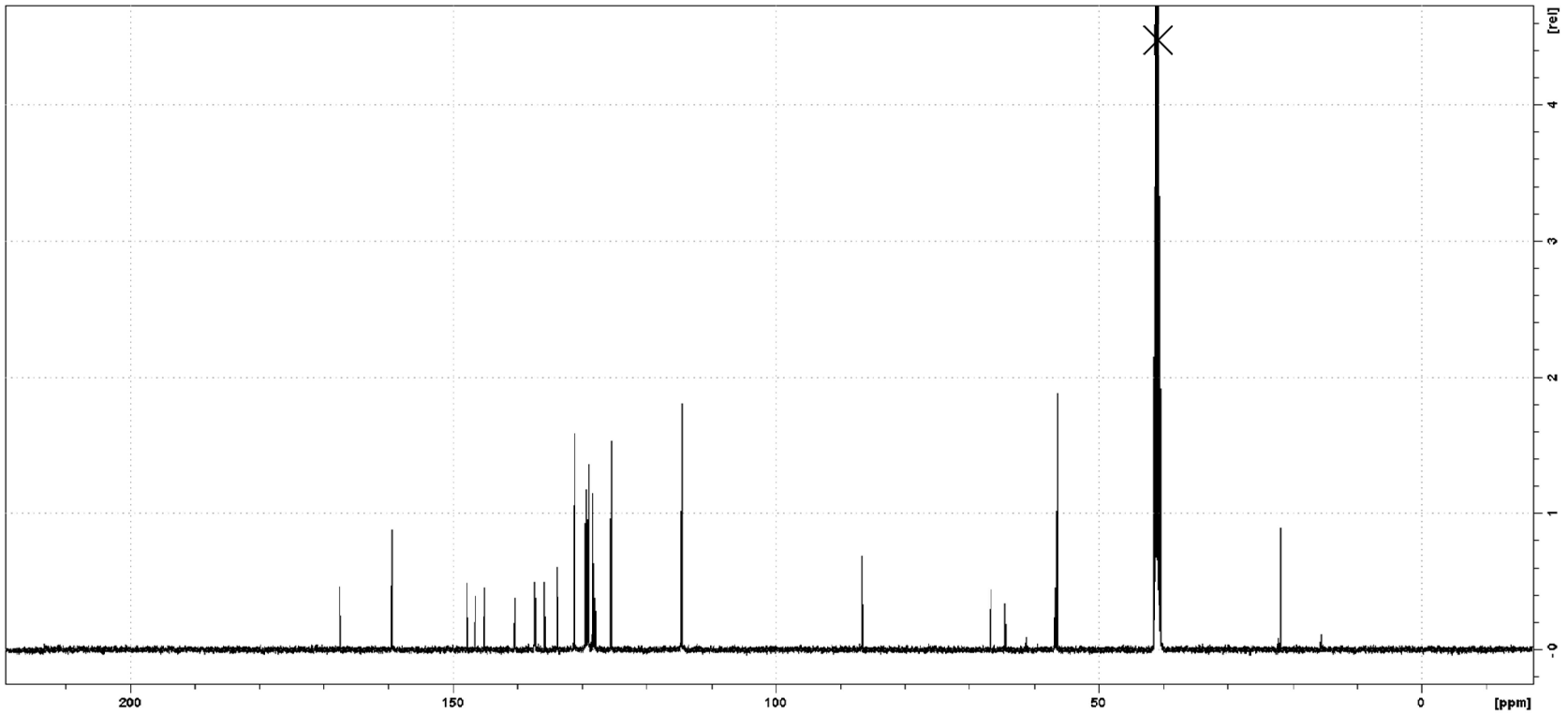
^{1}H-NMR of compound 3 (**S$_A$**)



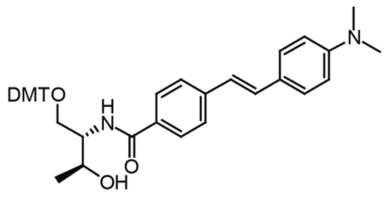


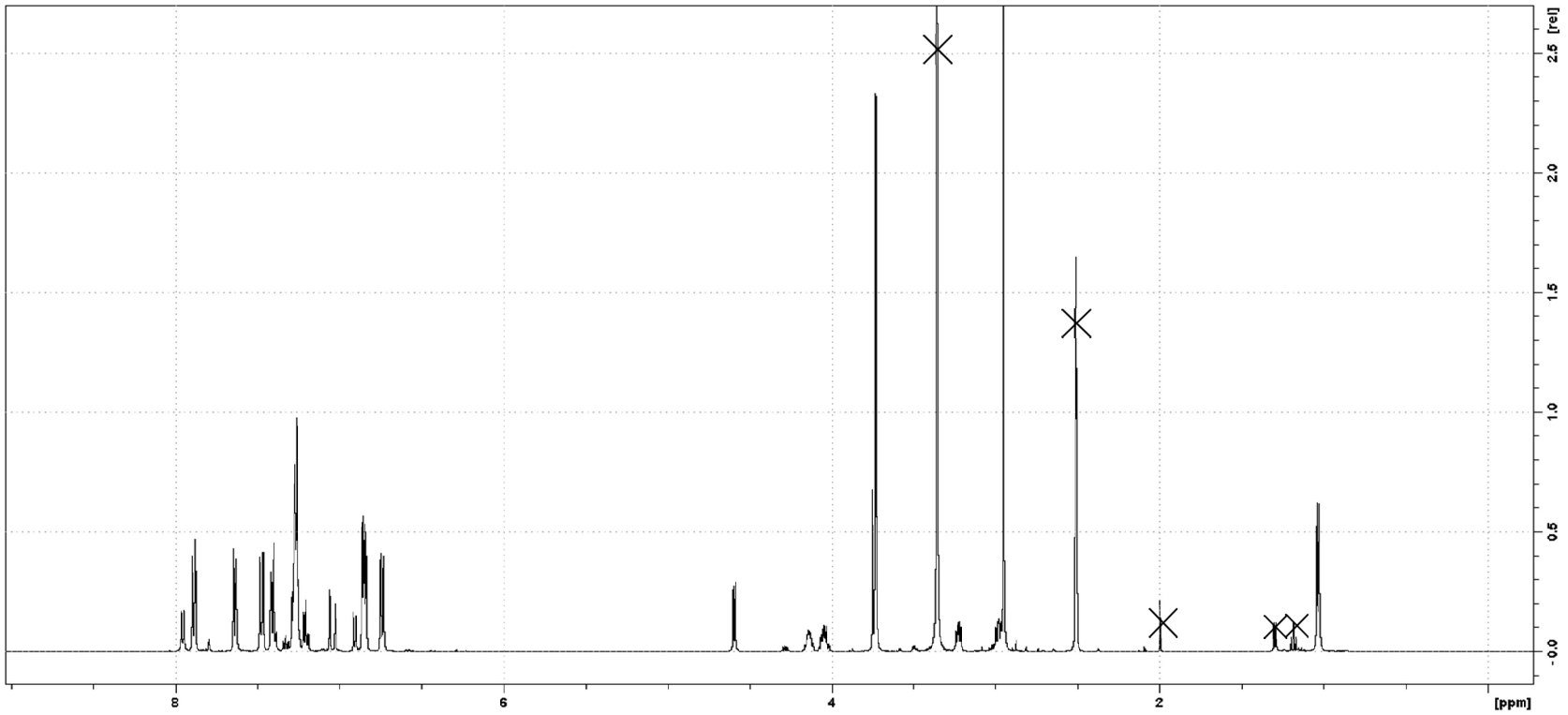
^{13}C-NMR of compound 3 (**S$_A$**)



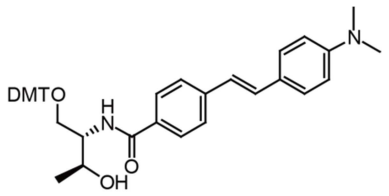


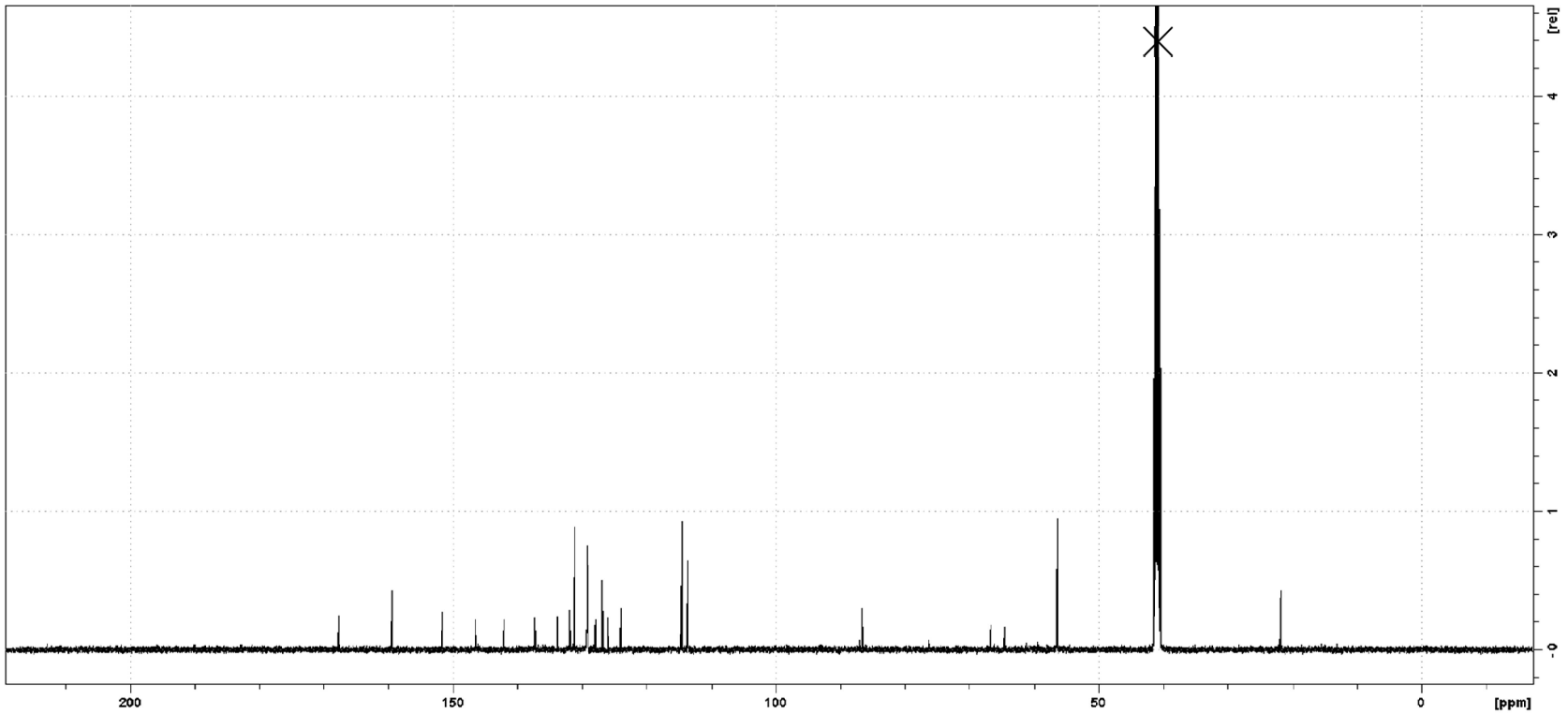
^{1}H-NMR of compound 3 ($\mathbf{S_D}$)



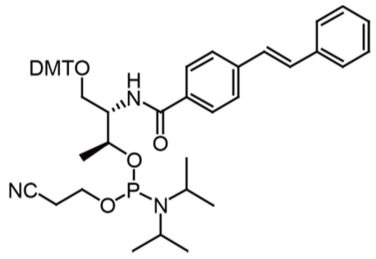


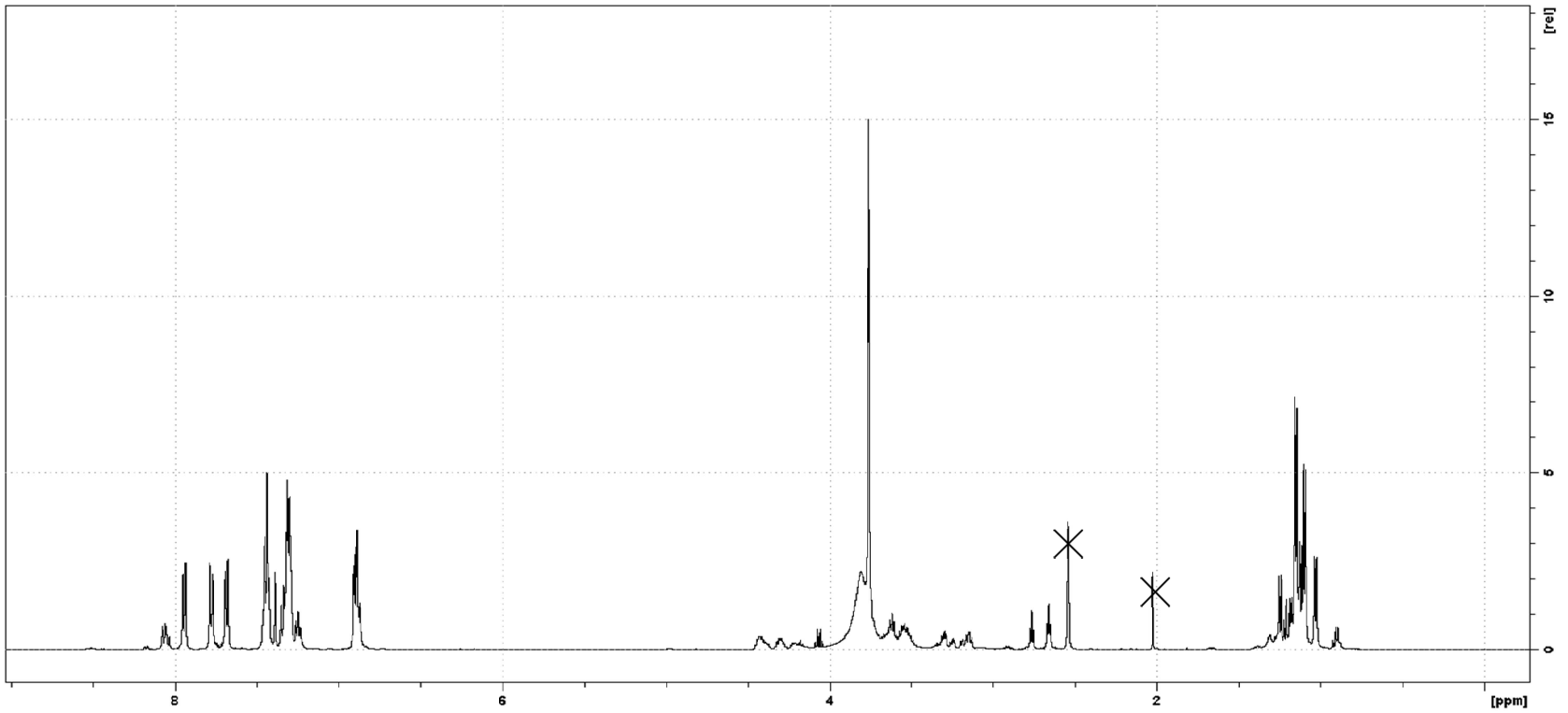
^{13}C-NMR of compound 3 (**S_D**)



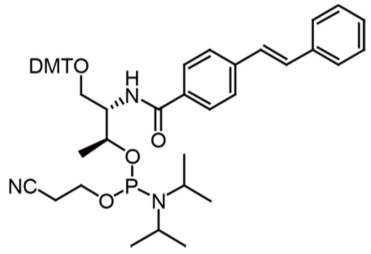


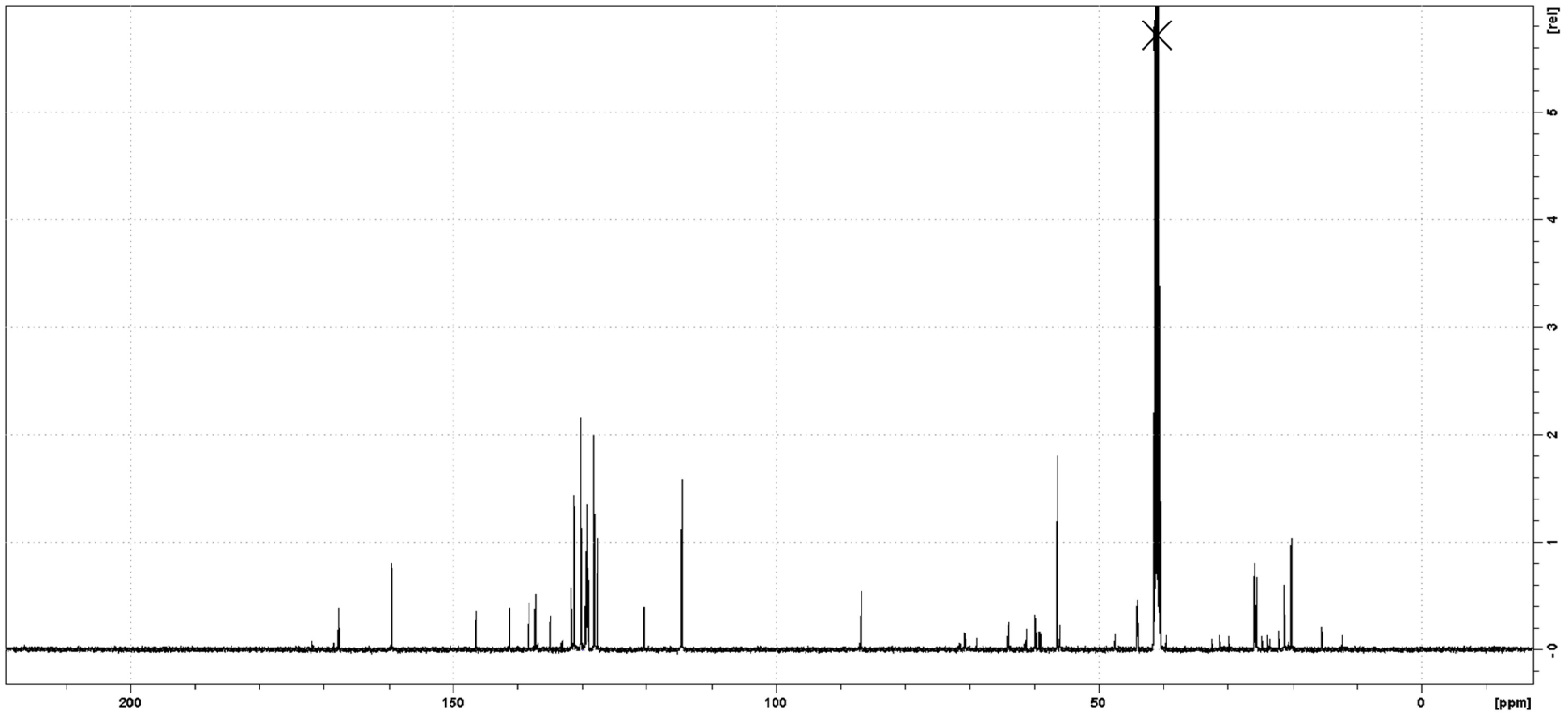
^{1}H-NMR of compound 4 (**S**)



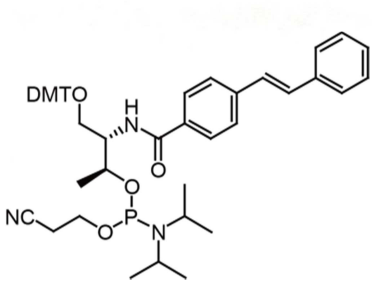


^{13}C-NMR of compound 4 (**S**)

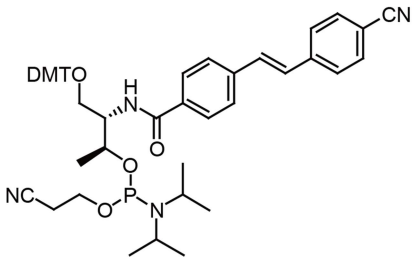


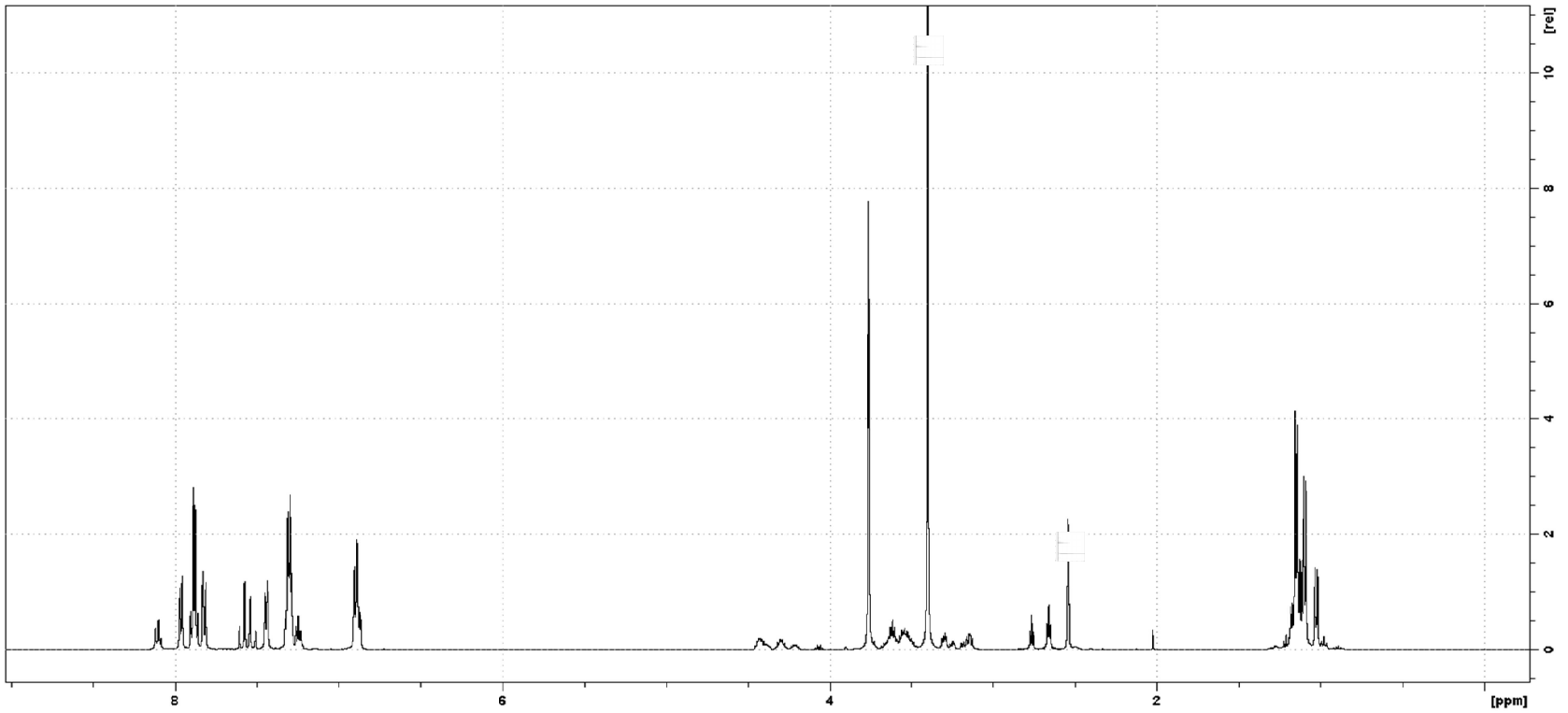


^{31}P-NMR of compound 4 (**S**)

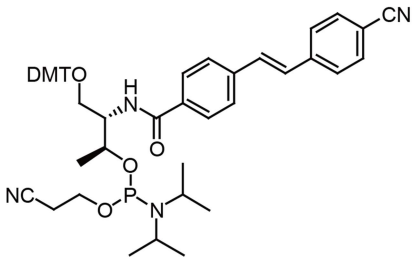


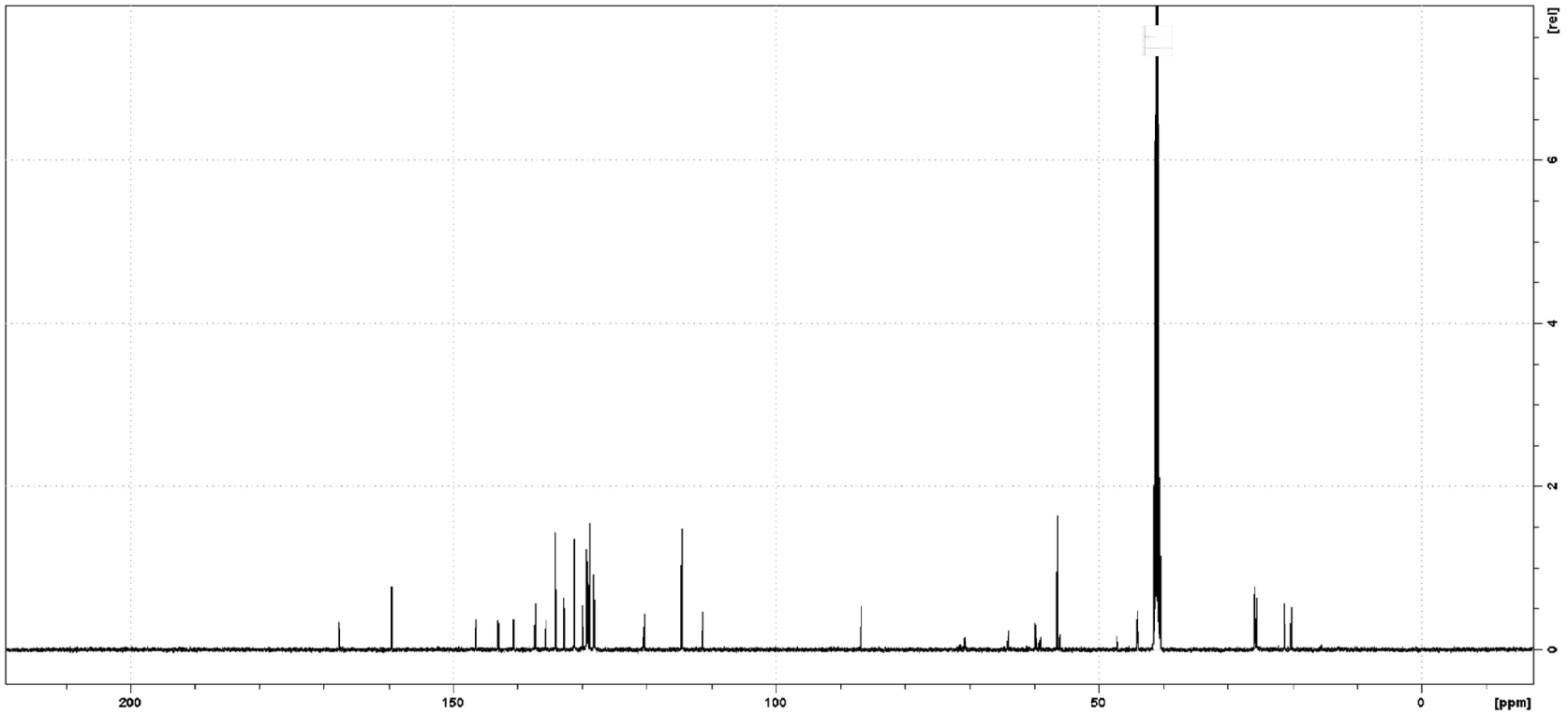
^{1}H-NMR of compound 4 (**S_{CN}**)



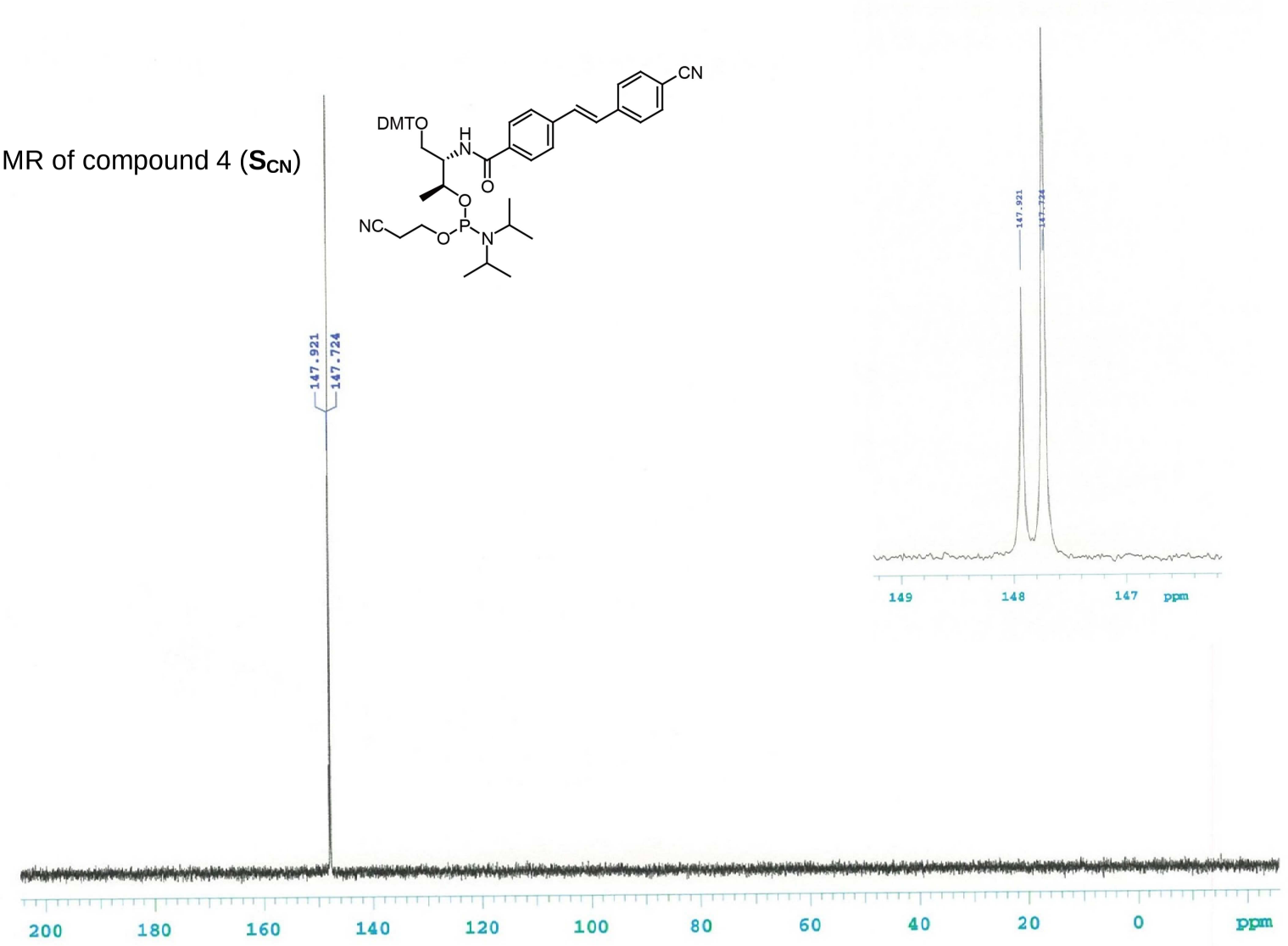


^{13}C-NMR of compound 4 (**S_{CN}**)

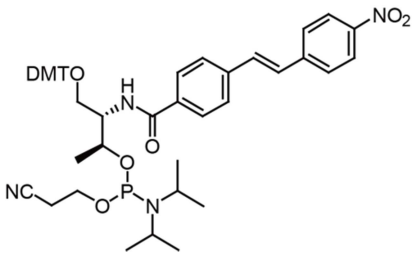


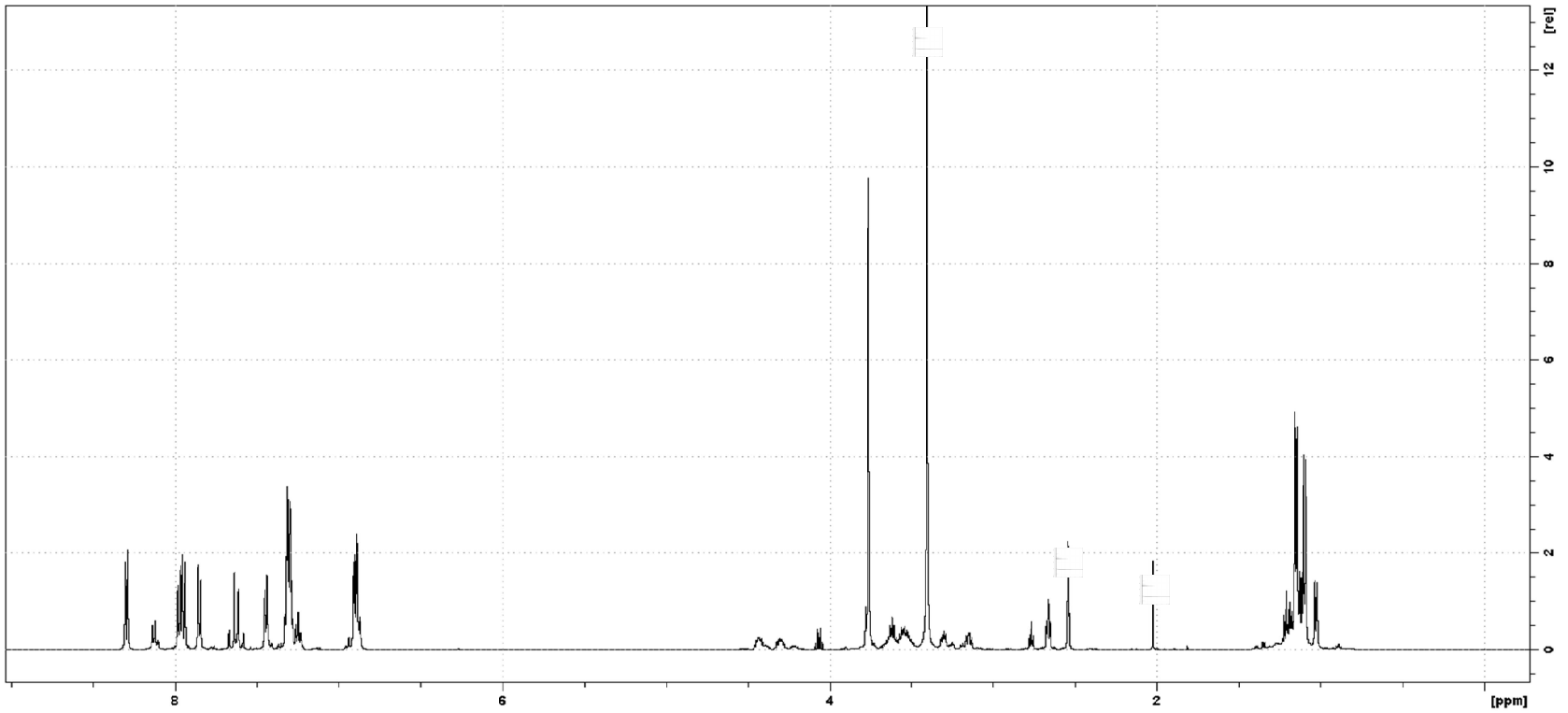


^{31}P-NMR of compound 4 (**S_{CN}**)

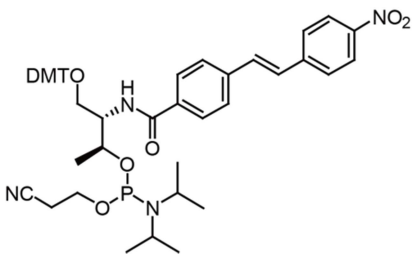


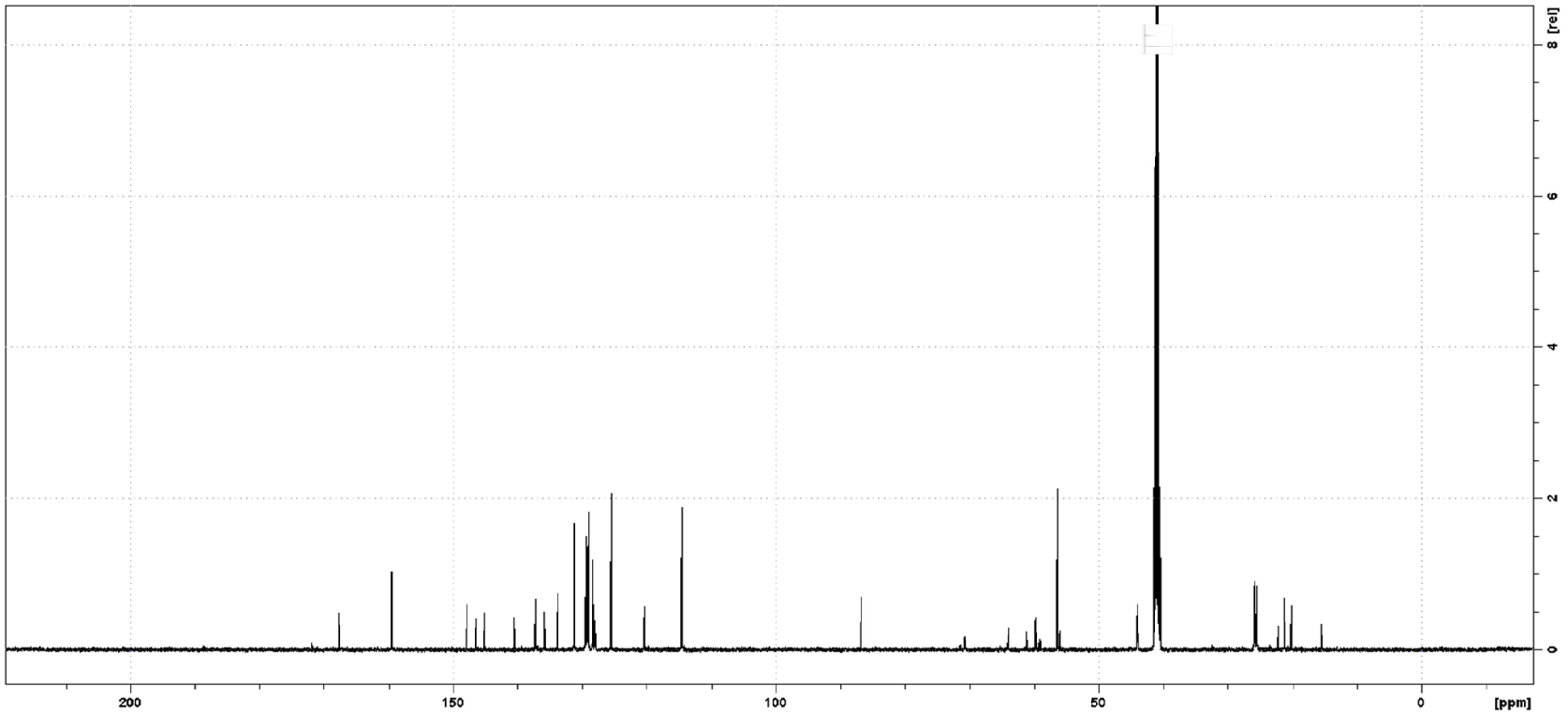
^{1}H-NMR of compound 4 (**S$_A$**)



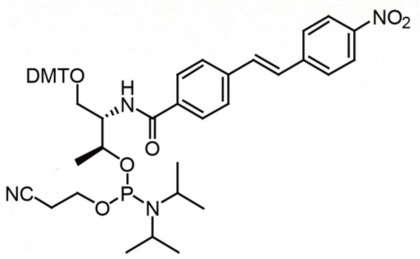


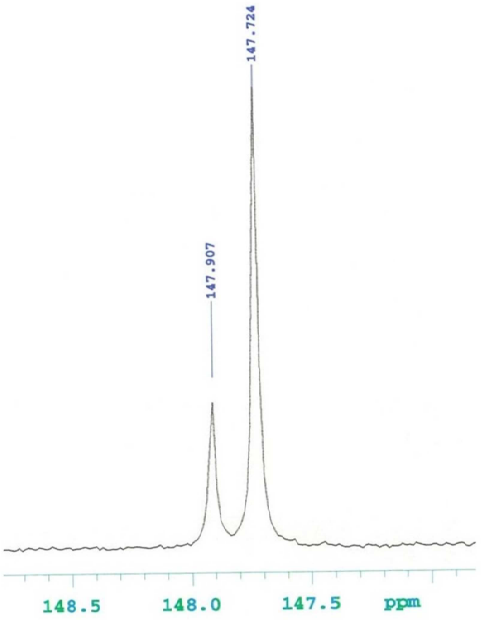
^{13}C-NMR of compound 4 (**S_A**)

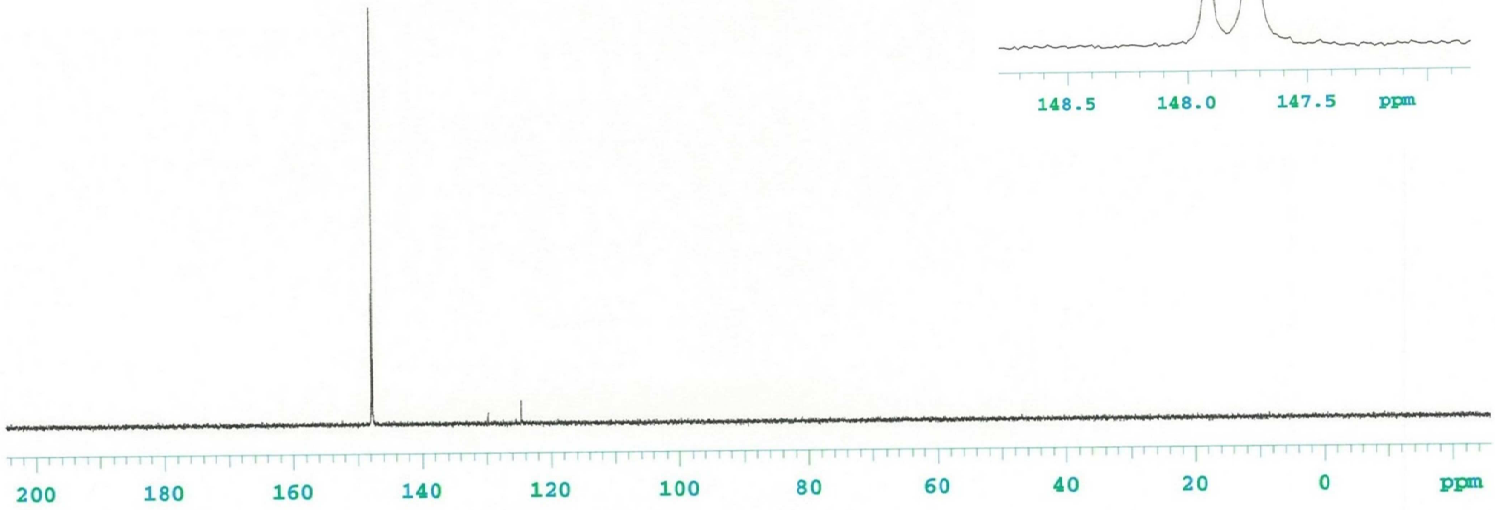




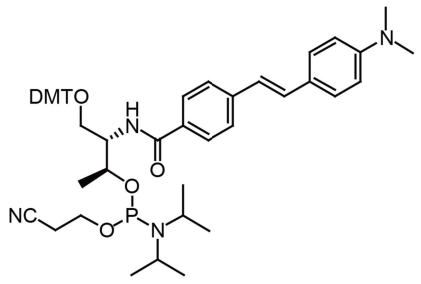
^{31}P-NMR of compound 4 (**S_A**)

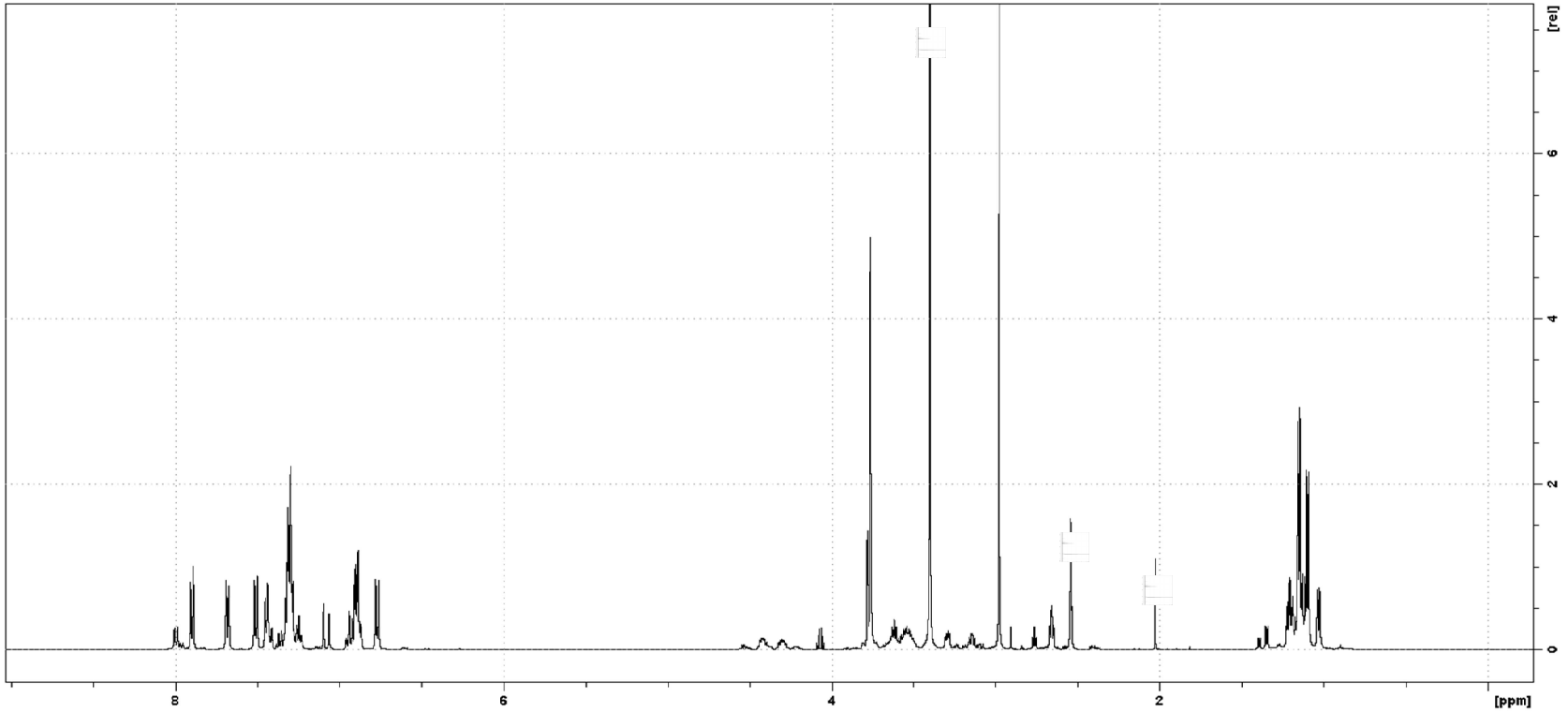




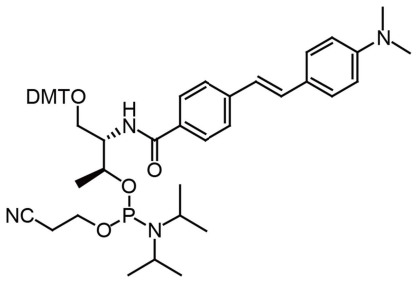


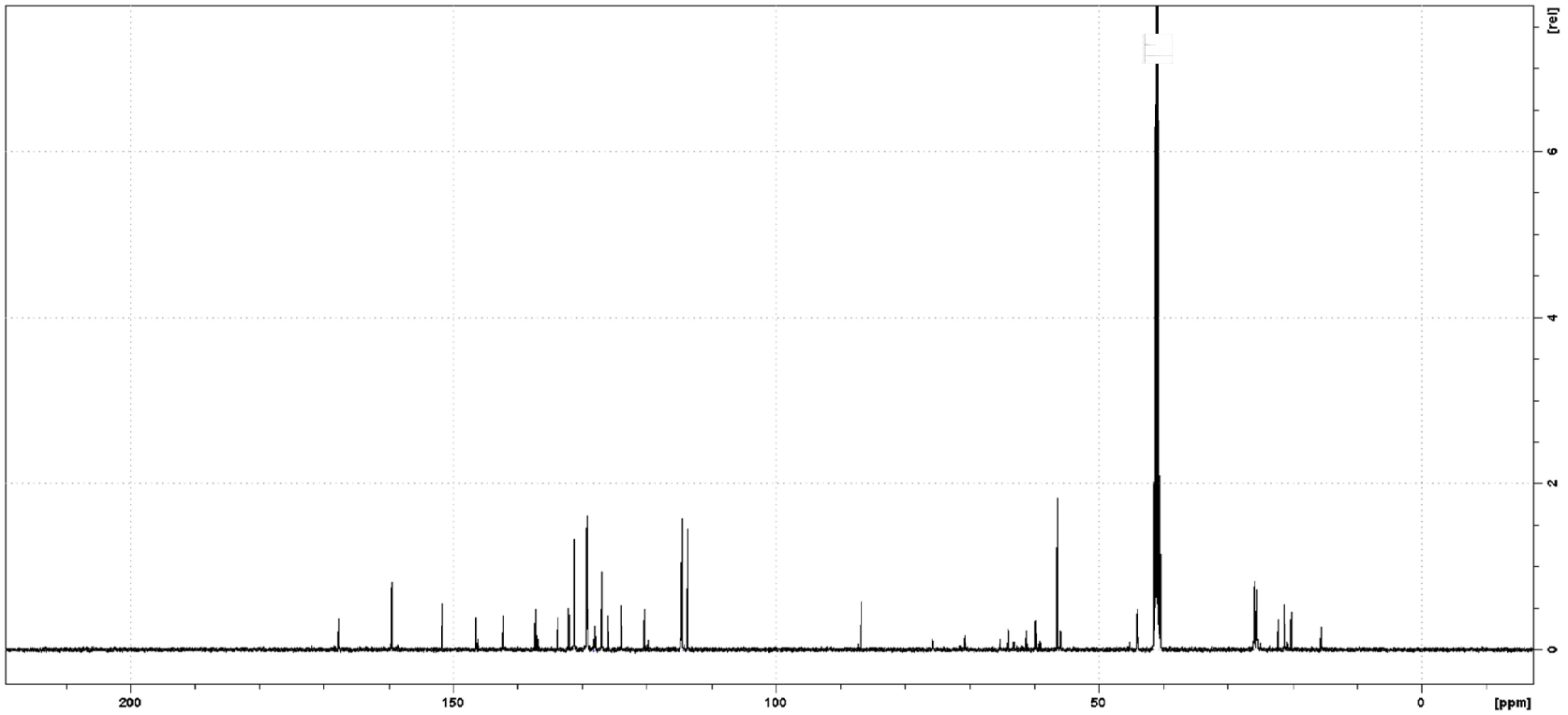
^{1}H-NMR of compound 4 (**S_D**)





^{13}C-NMR of compound 4 (**S_D**)





^{31}P-NMR of compound 4 (**S_D**)