Bisarylindenols: Conformation Control Makes Basic Photochromic Properties based on 6π-Electrocyclization Exceptional

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Supplementary Information

SI-1. Experimental details

1. General

Chemical reactions were carried out under a dry nitrogen atmosphere. All solvents including dry tetrahydrofuran (THF) were purchased and used as received. All flash column chromatography were carried out on 230-400 mesh silica gel using ethyl acetate and hexane as eluent. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick silica gel TLC plates.

^{1}H NMR Spectra were recorded in deuteriochloroform ($CDCl_3$) with a 300MHz NMR spectrometer. *J* values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. ^{13}C NMR spectra were recorded in $CDCl_3$ with a 75 MHz NMR spectrometer with the proton-decoupling method. Infrared spectra (IR) were recorded on a FT-IR spectrometer. Low- and high-resolution mass spectra were measured by the electron impact mass spectrometry using a Mass spectrometer. Ultraviolet and visible spectra were recorded on a UV/Vis spectrophotometer. Melting points were measured using hot stage microscope, and those were uncorrected.

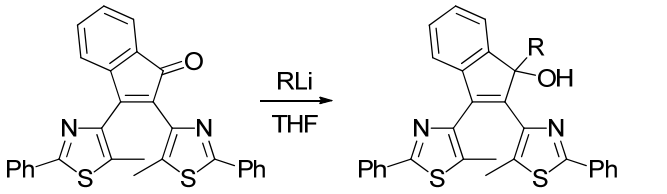
Photochromic reactions were carried out in 10 mm path length quartz cells upon 313 nm light irradiation with a 250 W high-pressure mercury lamp with filters (a HQBP313-UV glass filter and a BPF313 nm glass filter) and 514 nm light irradiation with a 500 W xenon lamp with filters (5 cm water filter, Y-47 glass filter, and KL-50 interference glass filter). During the photoreaction, the solutions in the cell were stirred continuously.

High-performance liquid chromatography equipped with a UV/Vis detector and a column (Agilent ZORBAK RxOSil RRHT, 4.6 mm diameter x 250 mm) was used to determine the conversion ratios and the diastereomer excess values of the

bisarylindenols.

Light intensity was measured with a photometer (Newport 1830-C) calibrated with Parker's $K_3Fe(C_2O_4)_3$ chemical actinometer,[1] and the quantum yields of the photoreactions were determined by a method described in a previous report.[2]

2. Synthesis



2

3a R = CH_3 (82%)
3b R = Ph (45%)
3c R = *t*-Bu (29%)
3d R = CH_2OCH_3 (58%)

Synthesis of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (2)

Synthesis of **2** has been reported elsewhere.[3]

Synthesis of 1-methyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-indenol (3a).

To a solution of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (**2**, 78.1 mg, 0.164 mmol, 1.0 eq) in anhydrous THF (5.0 mL) was added dropwise a diethylether solution of methyllithium (0.98 mol dm^{-3}, 0.25 mL, 0.245 mmol, 1.5 eq) at –78 ^{o}C under a N_2 atmosphere. The mixture was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding H_2O, and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (1% to 5%) as the eluent, to give 66.1 mg (0.134 mmol) of

1-methyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-lindenol (**3a**) as a white solid in 82% yield.

Mp 179 – 181 ^{o}C

^{1}H NMR（300 MHz, $CDCl_3$, TMS）δ/ppm 1.26 (3H, s), 1.89 (3H, s), 1.99 (3H, s), 7.33 (2H, m), 7.45 (6H, m), 7.53 (1H, m), 7.61(1H,m), 7.92 (2H, m), 8.00 (2H, m)

^{13}C NMR（75 MHz, $CDCl_3$, TMS）δ/ppm 12.2, 25.5, 29.7, 82.9, 121.9, 122.4, 126.3, 126.4, 127.2, 128.4, 129.0, 129.1, 129.9, 130.3, 132.0, 132.5, 132.9, 133.5, 133.7, 142.0, 142.0, 147.0, 147.2, 148.5, 165.2, 165.3

IR (neat) ν/cm^{-1} 3406, 2961, 2917, 2849, 1540, 1460, 1259, 1027, 798, 760, 687

LRMS (EI, 70eV) m/z (rel intensity), 492 (M^+, 11.7), 475 ($(M – OH)^+$, 100)

Found: m/z 492.13540. Calcd for $C_{30}H_{24}ON_2S_2$: M, 492.13302

Synthesis of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-phenyl-1-indenol (3b).

To a solution of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (**2**, 119.5 mg, 0.251 mmol, 1.0 eq) in anhydrous THF (5.0 mL) was added dropwise a dibutylether solution of phenyllithium (1.9 mol dm^{-3}, 0.20 mL, 0.38 mmol, 1.5 eq) at –78 ^{o}C under a N_2 atmosphere. The mixture was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding H_2O, and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (1% to 5%) as the eluent, to give 50.7 mg (0.112 mmol) of 1-phenyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-lindenol (**3b**) as a white solid in 45% yield.

Mp 138 – 140 ^{o}C

^{1}H NMR（300 MHz, $CDCl_3$, TMS）δ/ppm 1.86 (3H, s), 2.03 (3H, s), 6.81 (1H, s), 7.20 (6H, m), 7.46 (9H, m), 7.82 (2H, m), 8.02 (2H, m)

^{13}C NMR（75 MHz, $CDCl_3$, TMS）δ/ppm 12.0, 12.3, 14.2, 21.0, 60.4, 87.0, 122.7, 123.3, 125.1, 126.2, 126.4, 126.8, 127.5, 128.1, 128.3, 129.0, 129.9, 130.2, 131.9, 132.8, 132.9, 133.8, 135.6, 142.2, 142.5, 142.8, 146.8, 147.1, 149.8, 165.0, 165.2, 171.1

IR (neat) ν/cm^{-1} 3325, 3054, 3014, 2961, 2919, 2856, 2163, 1969, 1465, 1439, 1260, 1238, 1072, 1024, 971, 801, 759, 688, 674

LRMS (EI, 70eV) m/z (rel intensity %), 554 (M^+, 29.2), 538 ((M – OH + H)$^+$, 44.4), 537 ((M – OH)$^+$, 53.5), 536 ((M – H_2O)$^+$, 100)

Found: m/z 554.15030. Calcd for $C_{35}H_{26}ON_2S_2$: M, 554.14867

Synthesis of 1-*tert*-butyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-indenol (3c).

To a solution of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (**2**, 109.9 mg, 0.231 mmol, 1.0 eq) in anhydrous THF (5.0 mL) was added dropwise a *n*-hexane solution of *tert*-butylllithium (1.77 mol dm^{-3}, 0.18 mL, 0.29 mmol, 1.3 eq) at –78 ^{o}C under a N_2 atmosphere. The mixture was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding H_2O, and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (1% to 5%) as the eluent, to give 35.6 mg (0.0666 mmol) of 1-*tert*-butyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-lindenol (**3c**) as a white solid in 29% yield.

Mp 210 – 212 ^{o}C

^{1}H NMR（300 MHz, $CDCl_3$, TMS）δ/ppm 0.93 (9H, s), 1.83 (3H, s), 1.95 (3H, s), 6.54 (1H, s), 7.26 (2H, m), 7.34 (1H, m), 7.45 (6H, m), 7.62 (1H, m), 7.90 (2H, m), 7.99 (1H, m)

^{13}C NMR（75 MHz, $CDCl_3$, TMS）δ/ppm 12.0, 12.1, 26.3, 38.7, 91.0, 121.9, 124.3, 126.0, 126.2, 126.4, 127.8, 128.9, 129.1, 129.8, 130.3, 132.2, 132.9, 133.9, 137.4, 140.4, 143.4, 146.9, 148.1, 149.1, 165.1, 165.2

IR (neat) ν/cm^{-1} 3375, 3204, 2949, 2359, 2158, 2009, 1517, 1456, 1434, 1229, 970, 760, 684, 599, 492, 459, 418, 403

LRMS (EI, 70eV) m/z (rel intensity %), 534 (M^+, 43.7), 521 (42.2), 516 ($(M - H_2O)^+$, 55.5), 476 ($(M - t\text{-}Bu - H)^+$, 100)

Found: m/z 534.18185. Calcd for $C_{33}H_{30}ON_2S_2$: M, 534.17995

Synthesis of 1-methoxymethyl-2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-indenol (3d).

(Methoxymethyl)tributyltin (109.5 mg, 0.33 mmol, 3.2 eq) in anhydrous THF (0.1 mL) was added dropwise a diethylether solution of *n*-butyllithium (2.63 mol dm$^{-3,}$ 0.07 mL, 0.19 mmol, 1.8 eq) at –78 ^{o}C under a N_2 atmosphere. The resulting solution was stirred at this temperature for 20 min, then a solution of 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (**2**, 48.6 mg, 0.10 mmol, 1.0 eq) in anhydrous THF (0.65 mL) was added quickly through a cannula, and the mixture was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding saturated ammonium chloride, and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous

Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (8% to 15%) as the eluent, to give 30.8 mg (0.0589 mmol) of 1-methoxymethyl-2,3-bis(2-phenyl-5-methyl-4-thiazolyl)-1-lindenol (**3d**) as a white solid in 58% yield.

Mp 215 – 220 ^{o}C

^{1}H NMR（300 MHz, $CDCl_3$, TMS）δ/ppm 1.90 (3H, s), 1.98 (3H, s), 3.25 (3H, s), 3.50 (1H, d), 3.76 (1H, d), 6.21 (1H, s), 7.33 (2H, m), 7.47 (7H, m), 7.71 (1H, m), 7.92 (2H, m), 8.00 (2H, m)

^{13}C NMR（75 MHz, $CDCl_3$, TMS）δ/ppm 12.1, 12.2, 59.8, 77.7, 84.7, 122.4, 123.4, 126.2, 126.4, 127.0, 128.7, 129.0, 129.1, 129.9, 130.3, 131.6, 132.6, 132.9, 133.7, 136.0, 142.8, 145.8, 146.8, 147.3, 165.1, 165.3

IR (neat) ν/cm^{-1} 3398, 2915, 2882, 2816, 2032, 1604, 1526, 1463, 1436, 1411, 1338, 1245, 1200, 1132, 1091, 969, 770, 756, 695

LRMS (EI, 70eV) m/z (rel intensity %) 522 (M^+, 5.2), 477 ($(M - CH_2OCH_3)^+$, 100)

Found: m/z 522.14218 Calcd for $C_{31}H_{26}O_2N_2S_2$: M, 522.14358

References

[1] C. G. Hatchard, C. A. Parker *Proc. R. Soc.* **1956**, *A235*, 518–536.

[2] Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3297 – 3303.

[3] K. Morinaka, T. Ubukata, Y. Yokoyama *Org. Lett.* **2009**, *11*, 3890 – 3893.

SI-2. Change in absorption spectra of bisarylindenols during photoirradiation

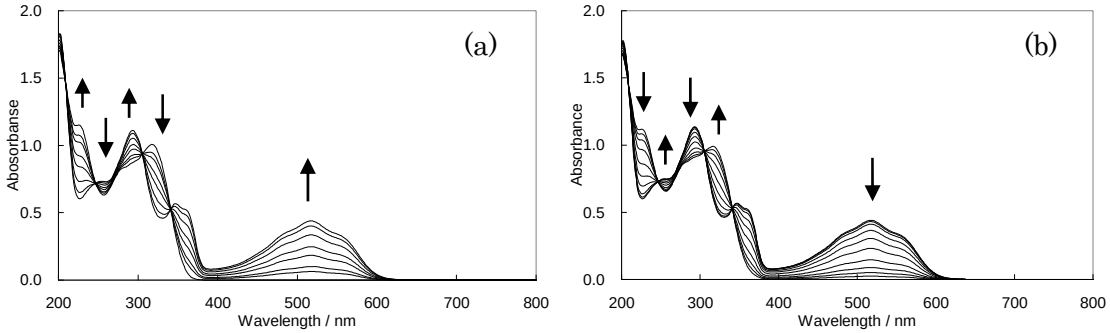


Figure SI-2-1 (a) . The change in absorption spectra from **3a** to pss

Concentration / mol dm^{-3}: 0.396 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 0.148 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 1.5, 2.5, 4.6, 9, 12

Figure SI-2-1 (b) . The change in absorption spectra from pss to **3a**

Concentration / mol dm^{-3}: 0.396 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 2.3 (514 nm)

Irradiation time / min: 0, 0.25, 0.5, 1.5, 3, 6, 10, 15, 25, 40, 60, 90

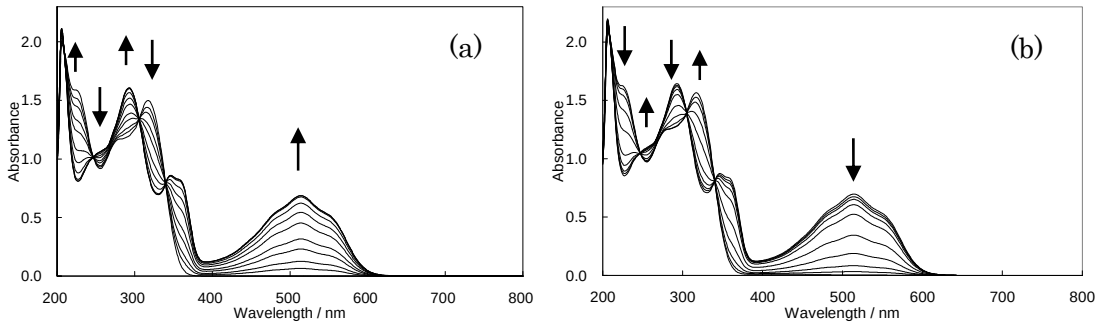


Figure SI-2-2 (a) . The change in absorption spectra from **3a** to pss

Concentration / mol dm^{-3}: 0.510 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 0.146 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 1.5, 2.5, 3.5, 5, 8, 13, 18

Figure SI-2-2 (b) . The change in absorption spectra from pss to **3a**

Concentration / mol dm^{-3}: 0.510 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 2.2 (514 nm)

Irradiation time / min: 0, 0.5, 1, 2, 4, 9, 15, 22, 30, 60

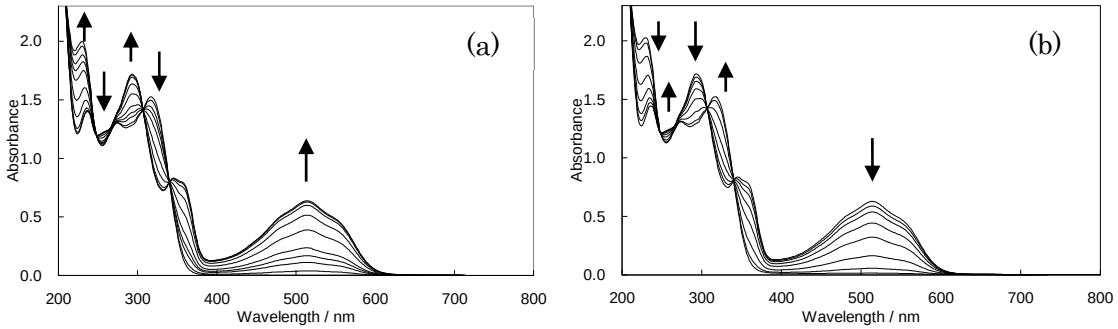


Figure SI-2-3 (a) . The change in absorption spectra from **3a** to pss

Concentration / mol dm^{-3}: 0.510 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 0.147 (313 nm)

Irradiation time / min: 0, 0.167, 0.5, 1, 1.5, 3, 5, 8, 11, 15

Figure SI-2-3 (b) . The change in absorption spectra from pss to **3a**

Concentration / mol dm^{-3}: 0.510 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 2.2 (514 nm)

Irradiation time / min: 0, 0.5, 2, 4, 8, 14, 25, 40, 60

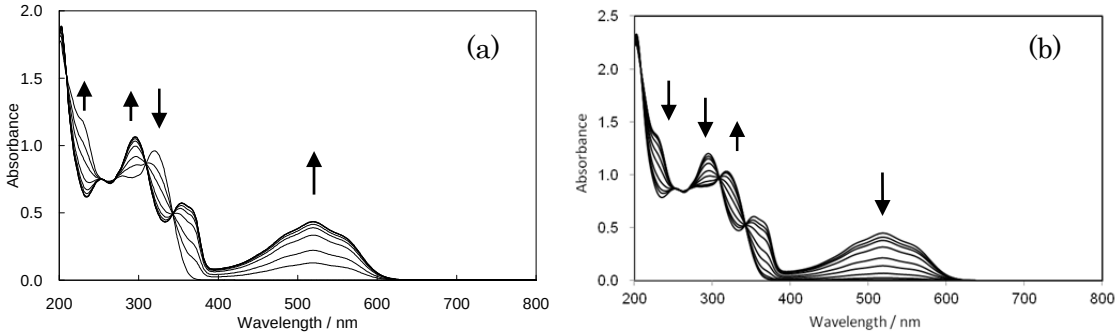


Figure SI-2-4 (a) . The change in absorption spectra from **3b** to pss

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 0.148 (313 nm)

Irradiation time / min: 0, 0.5, 1, 2, 3, 4, 6, 8, 15

Figure SI-2-4 (b) . The change in absorption spectra from pss to **3b**

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 2.3 (514 nm)

Irradiation time / min: 0, 0.5, 1, 2, 4, 6, 9, 13, 18, 28

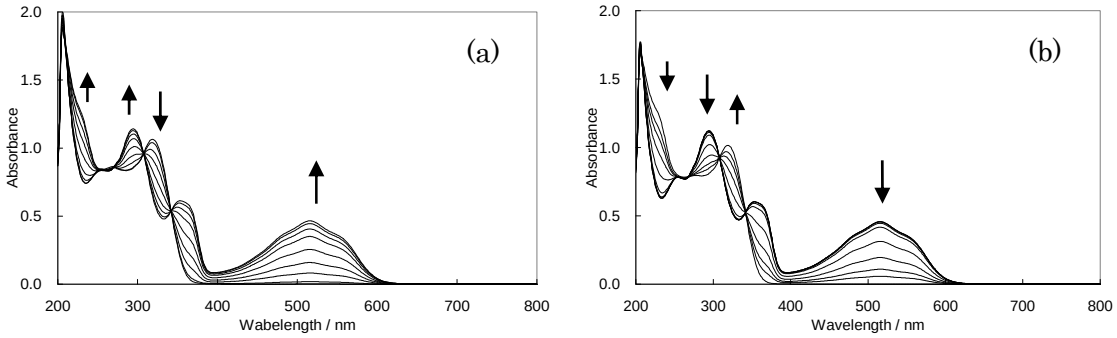


Figure SI-2-5 (a) . The change in absorption spectra from **3b** to pss

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 0.146 (313 nm)

Irradiation time / min: 0, 0.5, 1, 2, 3, 4, 6, 8, 15

Figure SI-2-5 (b) . The change in absorption spectra from pss to **3b**

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 2.2 (514 nm)

Irradiation time / min: 0, 0.5, 1.5, 3, 6, 10, 15, 25, 50

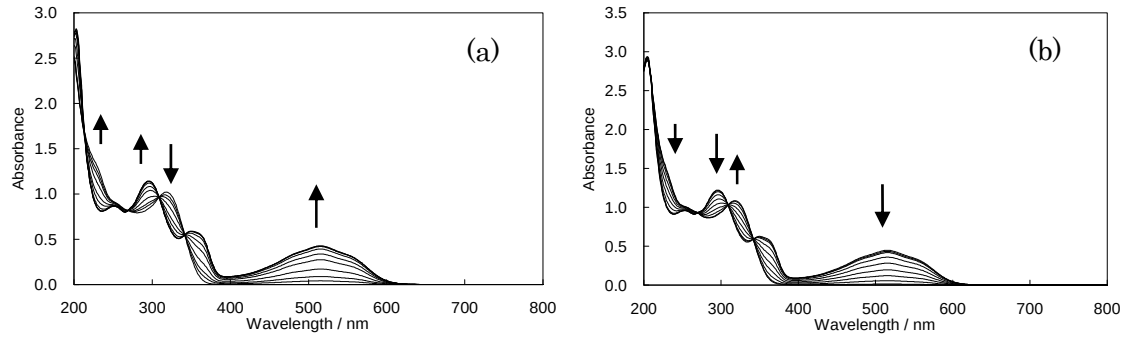


Figure SI-2-6 (a) . The change in absorption spectra from **3b** to pss

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 0.147 (313 nm)

Irradiation time / min: 0, 0.5, 1, 2, 3, 4, 6, 8, 15

Figure SI-2-6 (b) . The change in absorption spectra from pss to **3b**

Concentration / mol dm^{-3}: 0.360 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 2.2 (514 nm)

Irradiation time / min: 0, 0.5, 1, 3, 6, 10, 15, 22, 35, 60

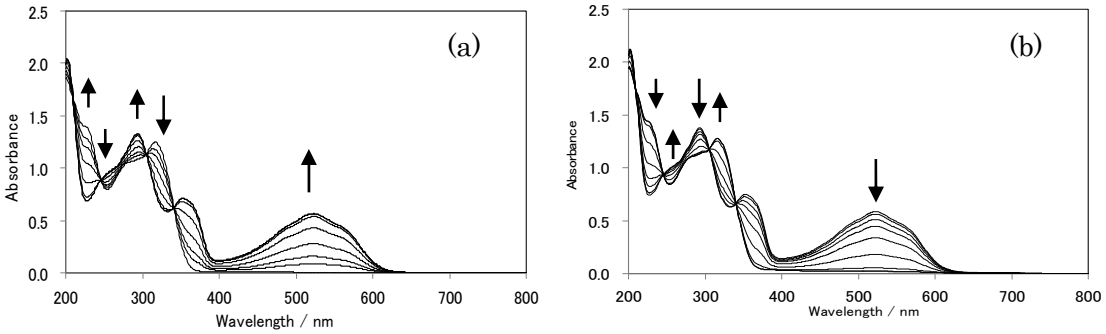


Figure SI-2-7 (a) . The change in absorption spectra from **3c** to pss

Concentration / mol dm^{-3}: 0.450 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 0.153 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 8, 16

Figure SI-2-7 (b) . The change in absorption spectra from pss to **3c**

Concentration / mol dm^{-3}: 0.450 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 2.7 (514 nm)

Irradiation time / min: 0, 0.5, 2, 4, 8, 16, 32, 64, 90

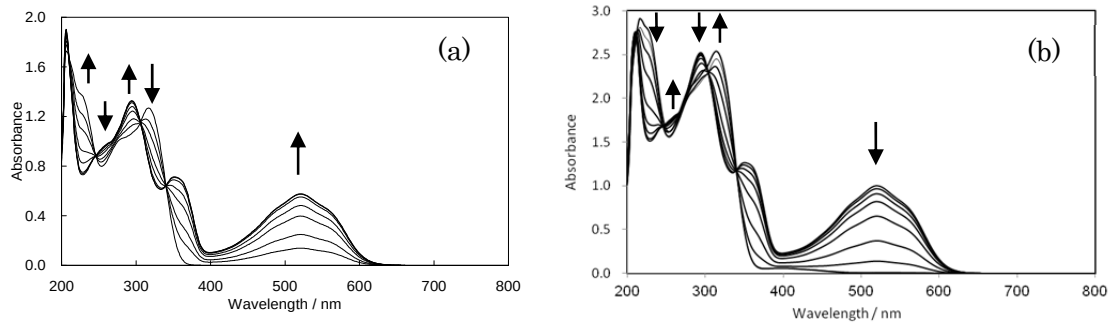


Figure SI-2-8 (a) . The change in absorption spectra from **3c** to pss

Concentration / mol dm^{-3}: 0.450 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 0.130 (313 nm)

Irradiation time / min: 0, 0.5, 1, 2, 3, 5, 8, 15

Figure SI-2-8 (b) . The change in absorption spectra from pss to **3c**

Concentration / mol dm^{-3}: 0.655 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 2.4 (514 nm)

Irradiation time / min: 0, 0.5, 1.5, 3, 6, 12, 20, 40, 90

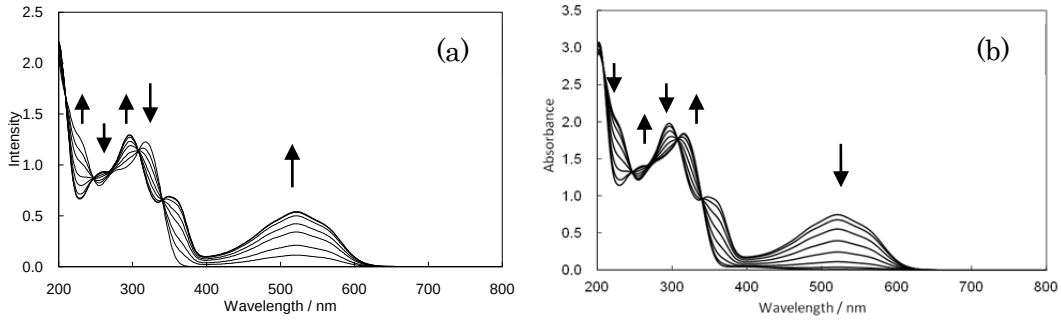


Figure SI-2-9 (a) . The change in absorption spectra from **3c** to pss

Concentration / mol dm^{-3}: 0.450 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 0.140 (313 nm)

Irradiation time / min: 0, 0.5, 1, 2, 3, 5, 8, 15

Figure SI-2-9 (b) . The change in absorption spectra from pss to **3c**

Concentration / mol dm^{-3}: 0.655 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 2.6 (514 nm)

Irradiation time / min: 0, 1, 3, 6, 10, 16, 25, 60

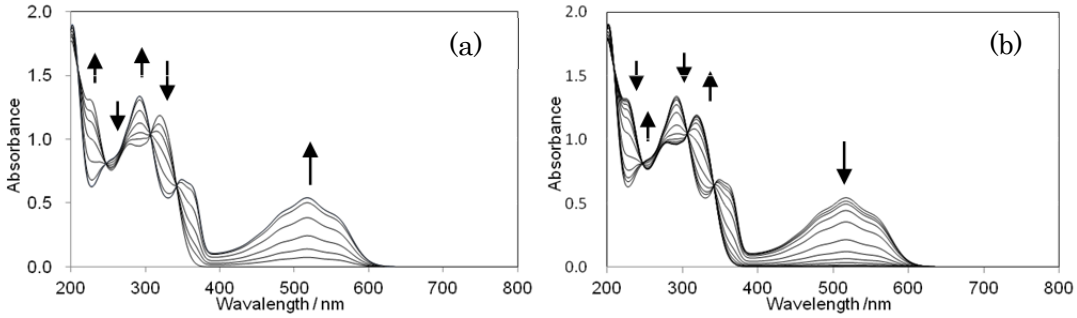


Figure SI-2-10 (a) . The change in absorption spectra from **3d** to pss

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 0.141 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 8, 15

Figure SI-2-10 (b) . The change in absorption spectra from pss to **3d**

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in hexane

Light intensity / mW cm^{-2}: 2.6 (514 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 8, 16, 32, 40, 50, 65

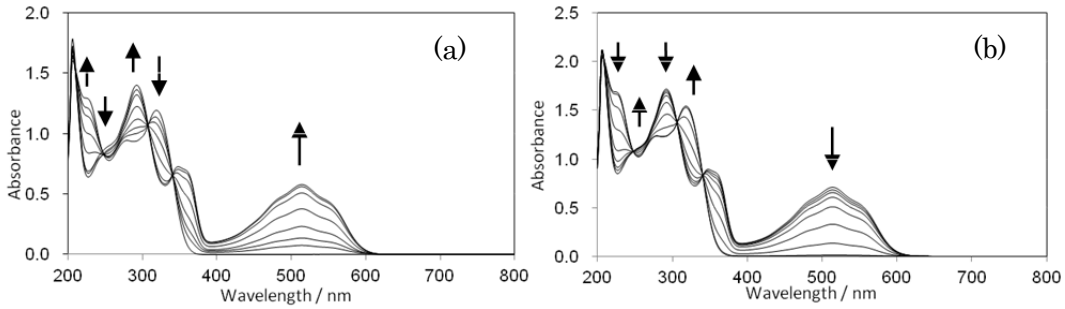


Figure SI-2-11 (a) . The change in absorption spectra from **3d** to pss

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 0.136 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 8, 16

Figure SI-2-11 (b) . The change in absorption spectra from pss to **3d**

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in ethyl ether

Light intensity / mW cm^{-2}: 3.0 (514 nm)

Irradiation time / min: 0, 0.5, 1, 2, 4, 8, 16, 32, 50

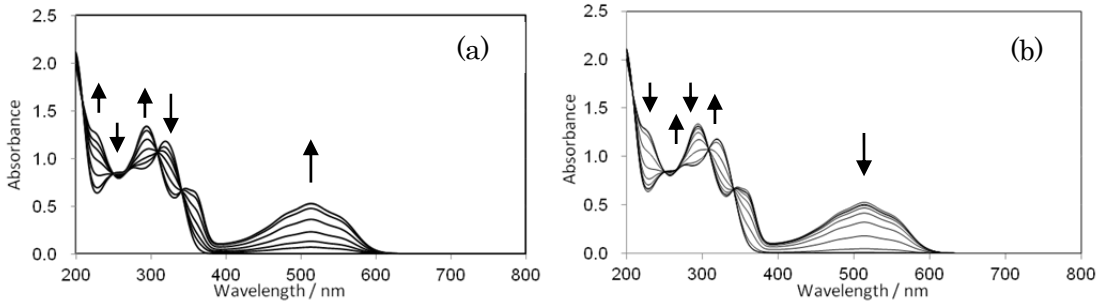


Figure SI-2-12 (a) . The change in absorption spectra from **3d** to pss

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 0.142 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 8, 16

Figure SI-2-12 (b) . The change in absorption spectra from pss to **3d**

Concentration / mol dm^{-3}: 0.375 $x10^{-4}$ in acetonitrile

Light intensity / mW cm^{-2}: 2.3 (514 nm)

Irradiation time / min: 0, 0.67, 1, 2, 4, 8, 16, 32, 50, 70

SI-3. HPLC Chromatograms of 3a – 3d.

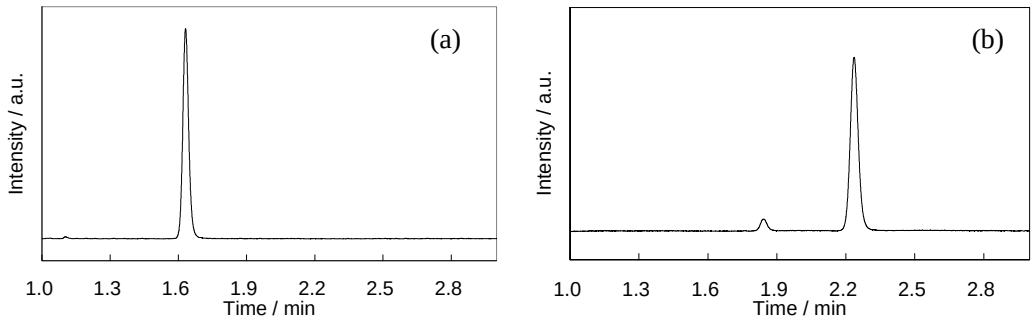


Figure SI-3-1. HPLC chromatograms of **3a** in hexane.

(a) Before irradiation, (b) Pss at 313 nm (**3aC$_{major}$** and **3aC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 516 nm

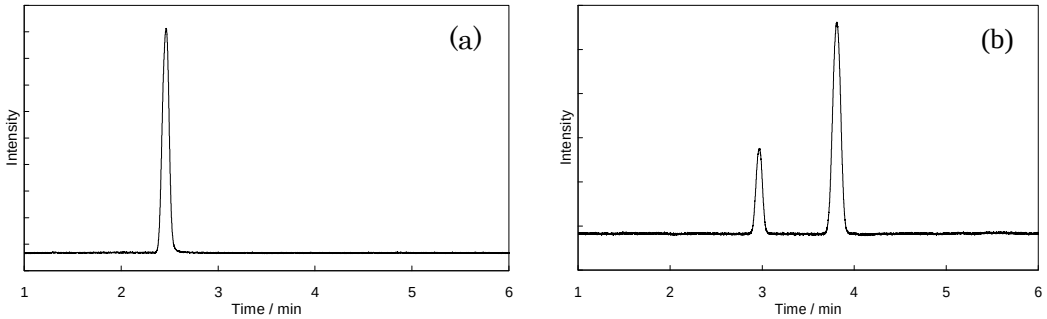


Figure SI-3-2. HPLC chromatograms of **3a** in ethyl ether.

(a) Before irradiation, (b) Pss at 313 nm (**3aC$_{major}$** and **3aC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 516 nm

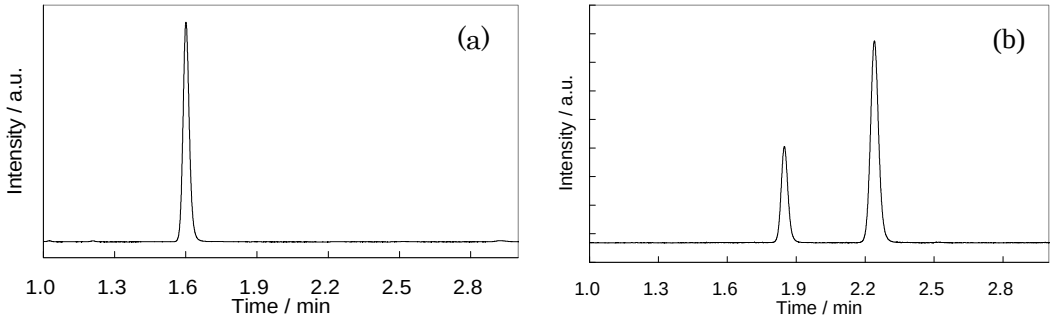


Figure SI-3-3. HPLC chromatograms of **3a** in acetonitrile.

(a) Before irradiation, (b) Pss at 313 nm (**3aC$_{major}$** and **3aC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 516 nm

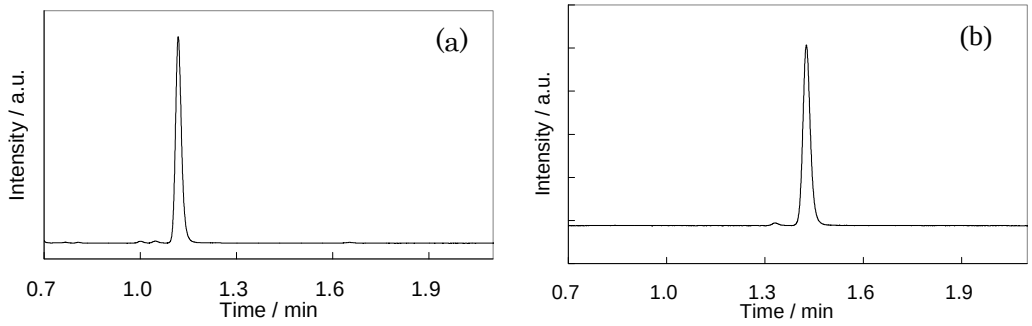


Figure SI-3-4. HPLC chromatograms of **3b** in hexane.

(a) Before irradiation, (b) Pss at 313 nm (**3bC$_{major}$** and **3bC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 308 nm, (b) 518 nm

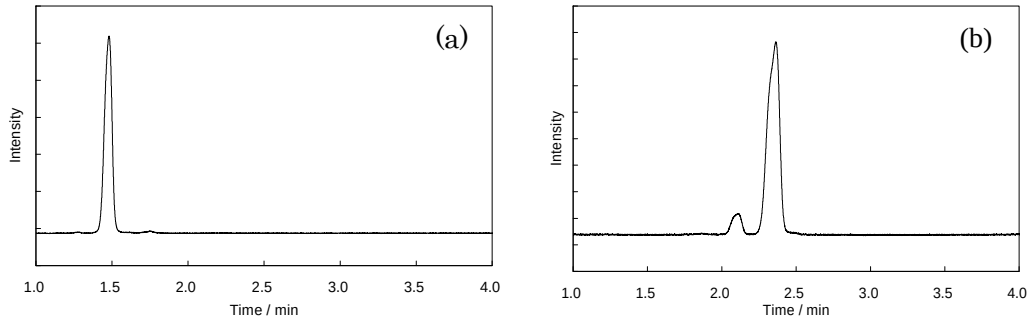


Figure SI-3-5. HPLC chromatograms of **3b** in ethyl ether.

(a) Before irradiation, (b) Pss at 313 nm (**3bC$_{major}$** and **3bC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 308 nm, (b) 518 nm

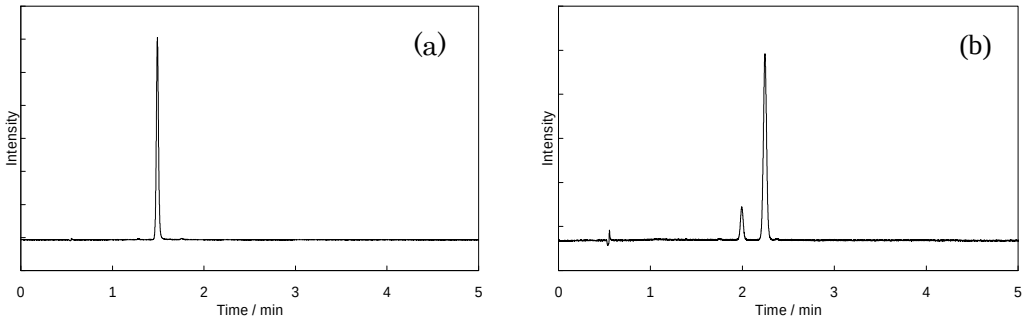


Figure SI-3-6. HPLC chromatograms of **3b** in acetonitrile.

(a) Before irradiation, (b) Pss at 313 nm (**3bC$_{major}$** and **3bC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 308 nm, (b) 518 nm

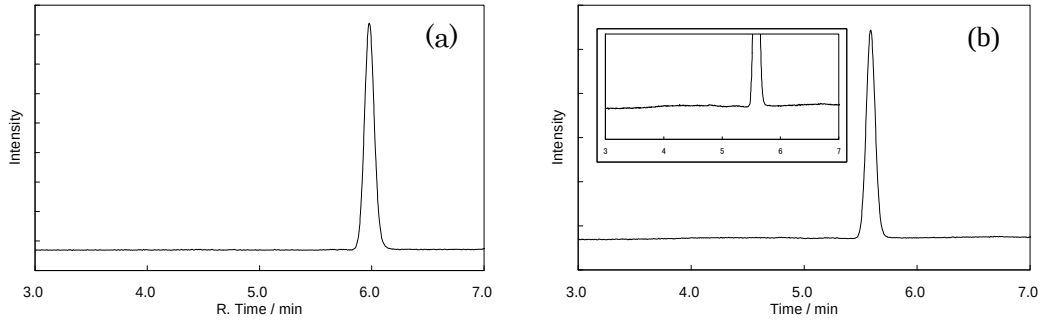


Figure SI-3-7. HPLC chromatograms of **3c** in hexane.

(a) Before irradiation, (b) Pss at 313 nm (**3cC$_{major}$** only)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 523 nm

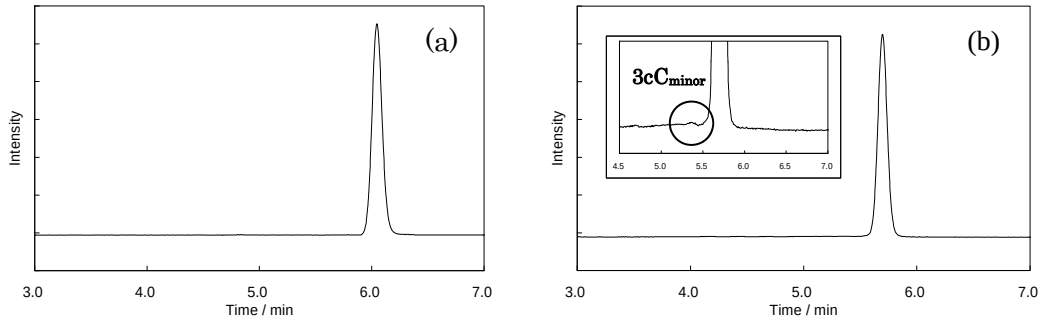


Figure SI-3-8. HPLC chromatograms of **3c** in ethyl ether.

(a) Before irradiation, (b) Pss at 313 nm (**3cC$_{major}$** and **3cC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 523 nm

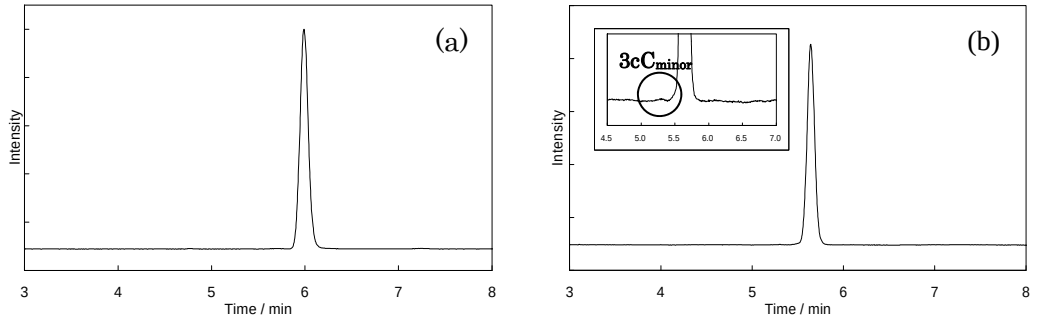


Figure SI-3-9. HPLC chromatograms of **3c** in acetonitrile.

(a) Before irradiation, (b) Pss at 313 nm (**3cC$_{major}$** and **3cC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 305 nm, (b) 523 nm

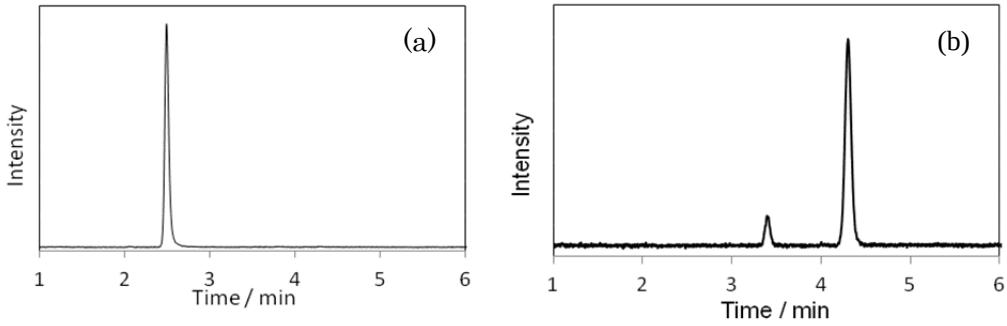


Figure SI-3-10. HPLC chromatograms of **3d** in hexane.

(a) Before irradiation, (b) Pss at 313 nm (**3dC$_{major}$** and **3dC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 311 nm, (b) 480 nm

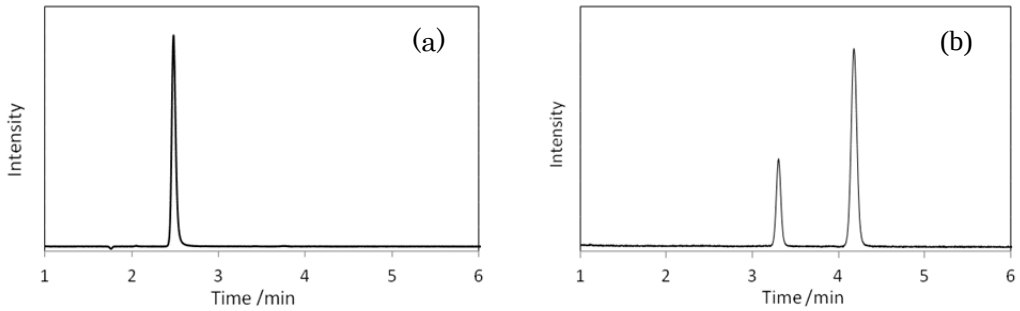


Figure SI-3-11. HPLC chromatograms of **3d** in ethyl ether.

(a) Before irradiation, (b) Pss at 313 nm (**3dC$_{major}$** and **3dC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

Detection wavelength: (a) 308 nm, (b) 516 nm

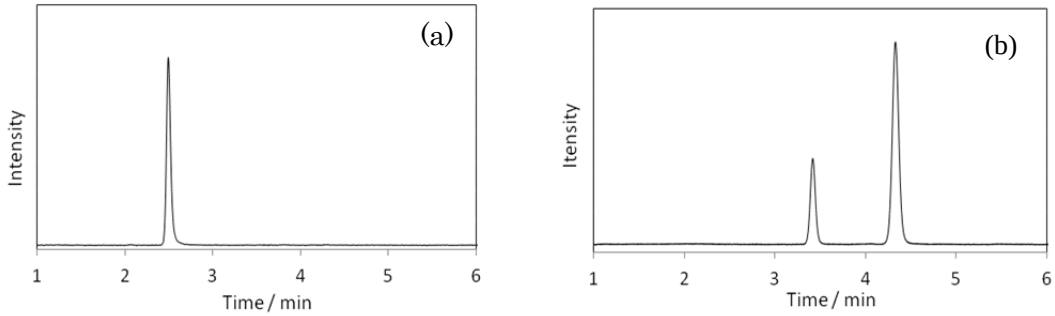
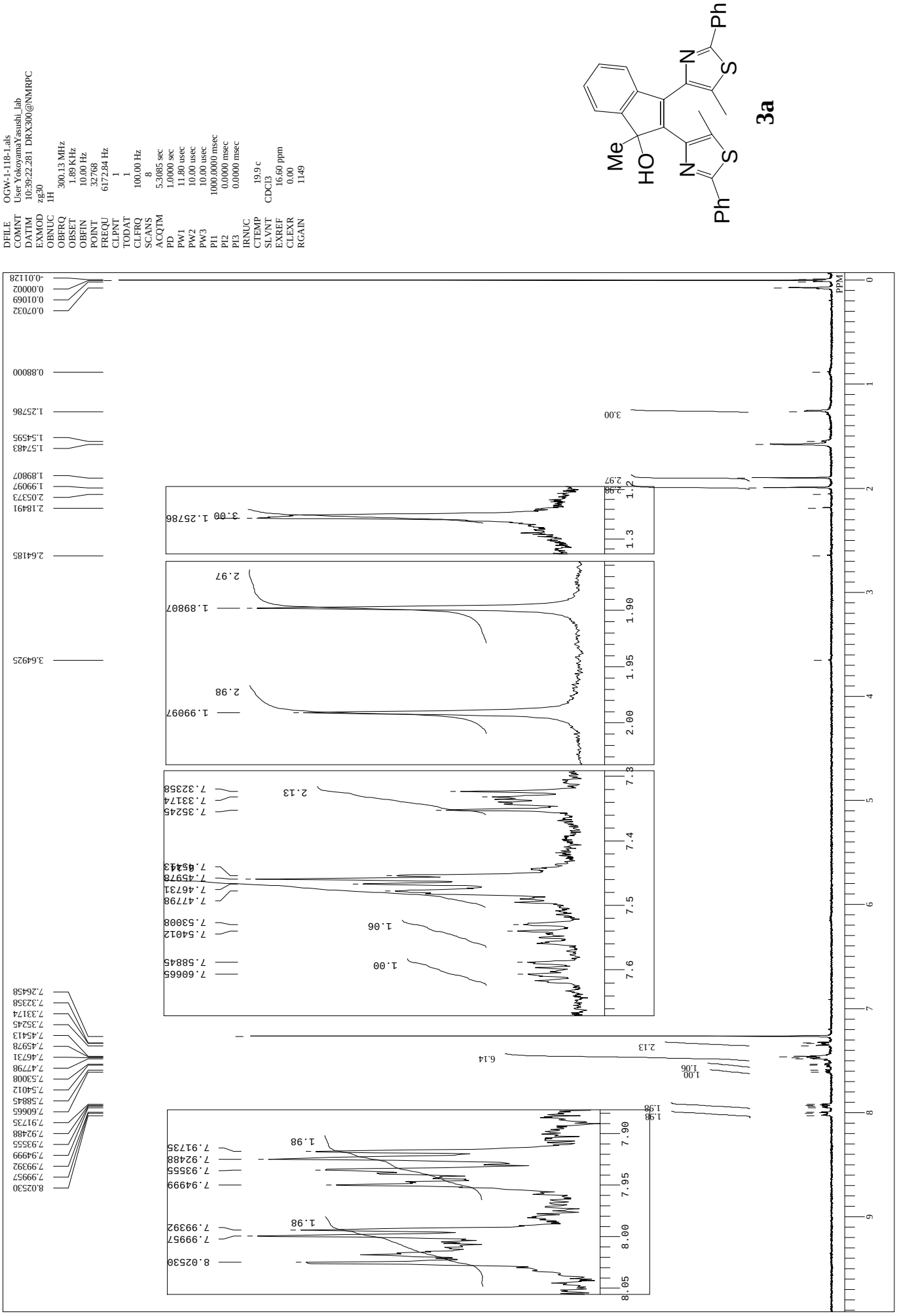


Figure SI-3-12. HPLC chromatograms of **3d** in acetonitrile.

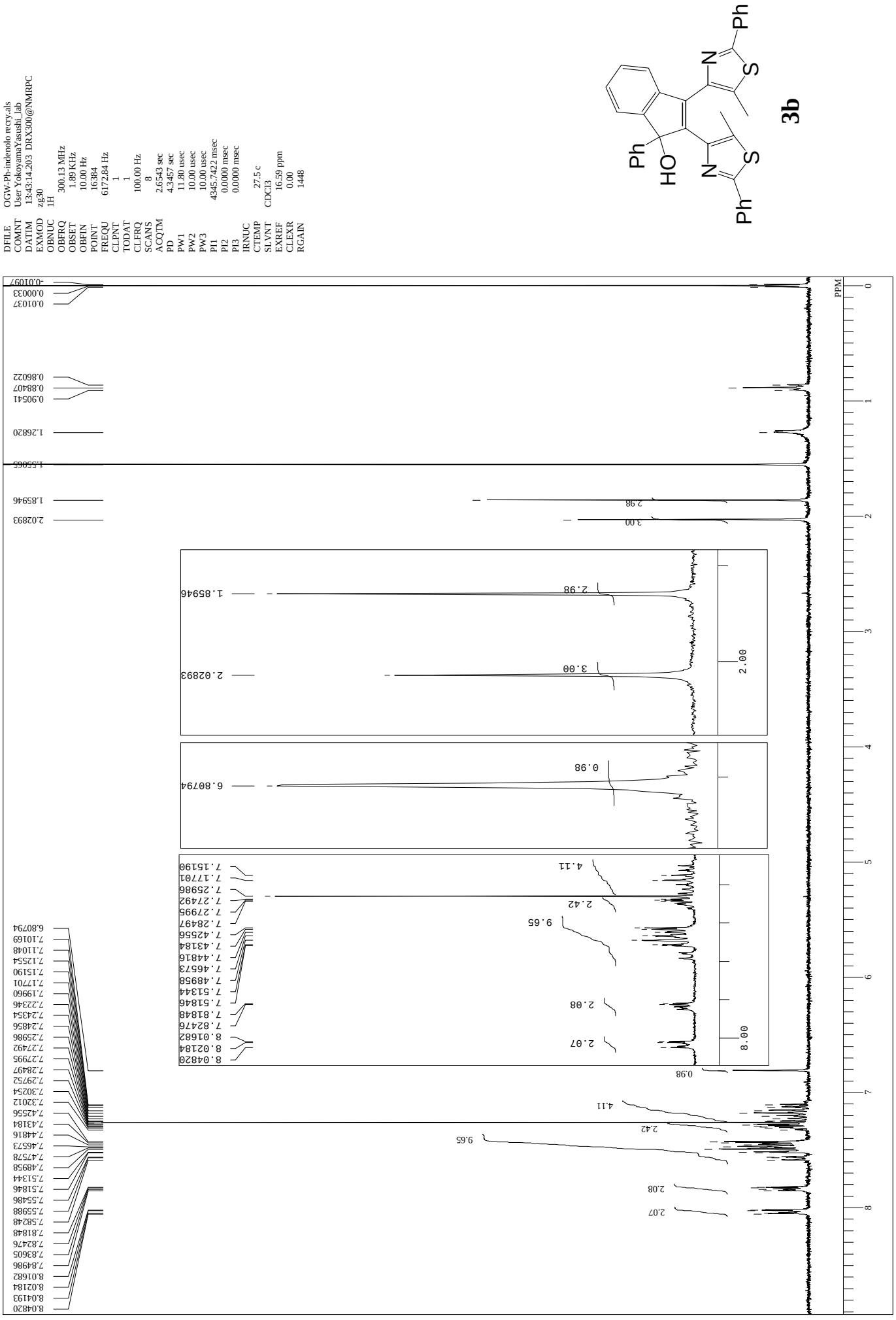
(a) Before irradiation, (b) Pss at 313 nm (**3dC$_{major}$** and **3dC$_{minor}$**)

Wakosil 5SIL, 10 % ethyl acetate / *n*-hexane, 0.5 ml min^{-1}

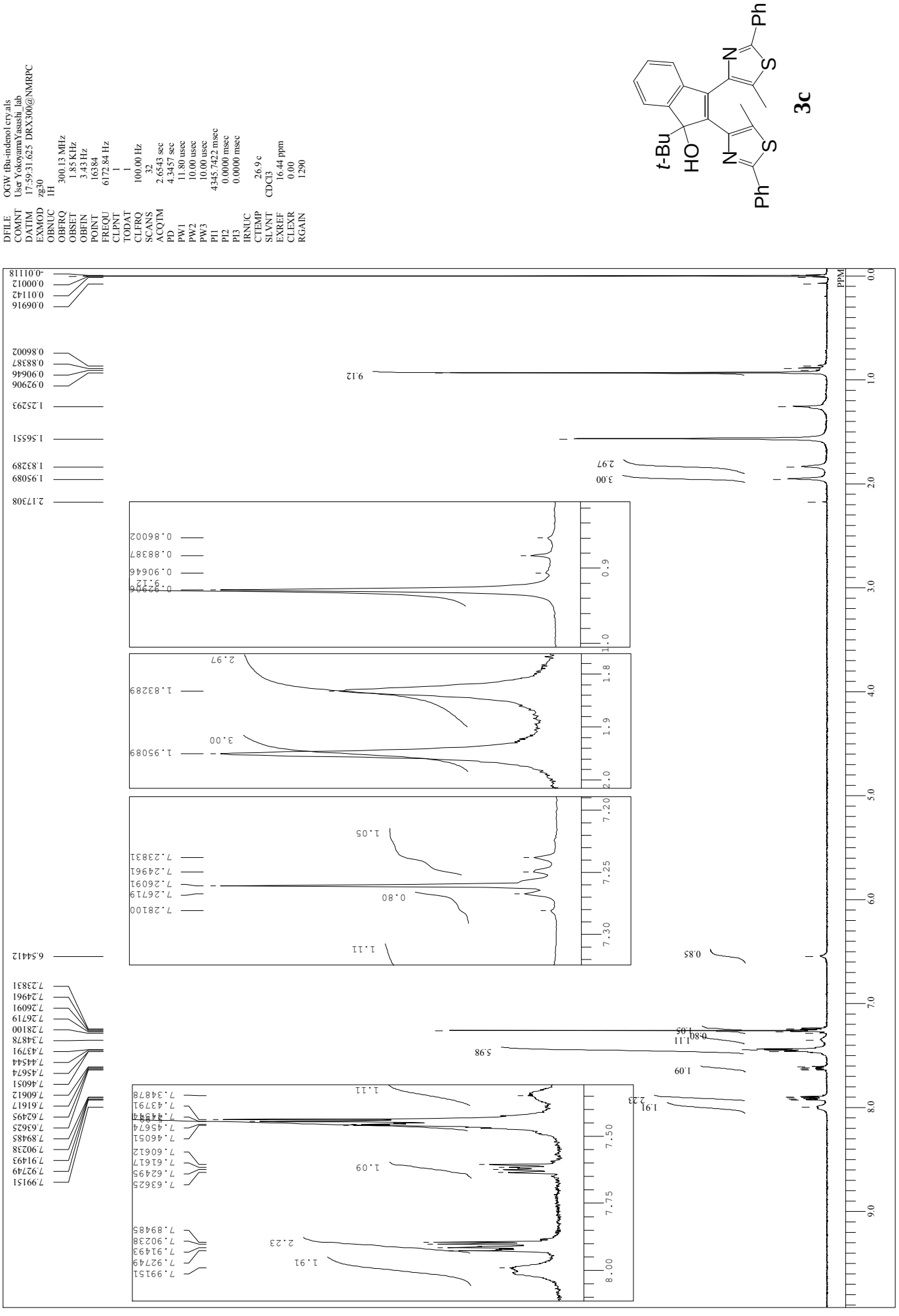
Detection wavelength: (a) 307 nm, (b) 516 nm



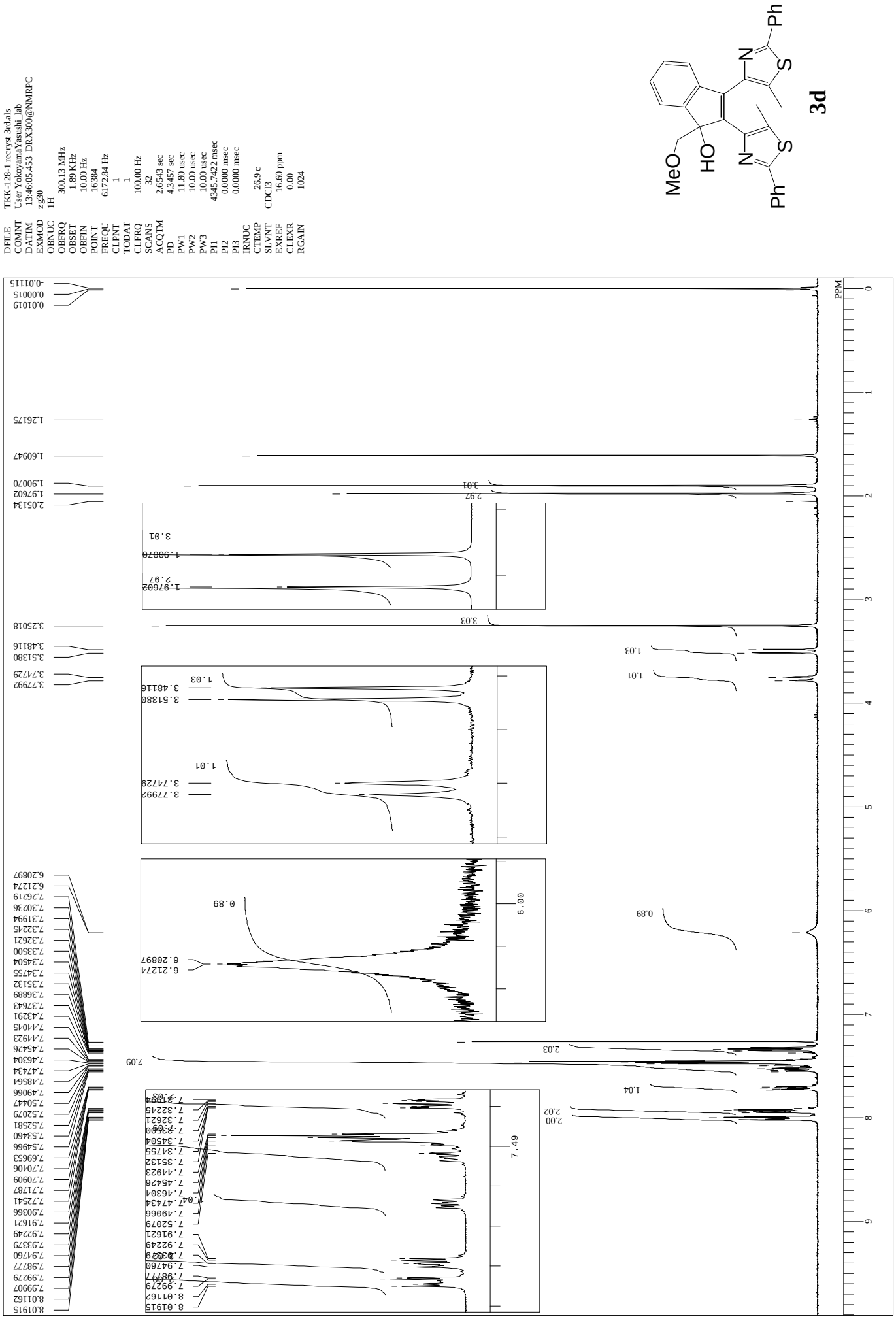
SI-4-1. ^{1}H NMR spectrum of compound 3a (300MHz, $CDCl_3$, TMS)



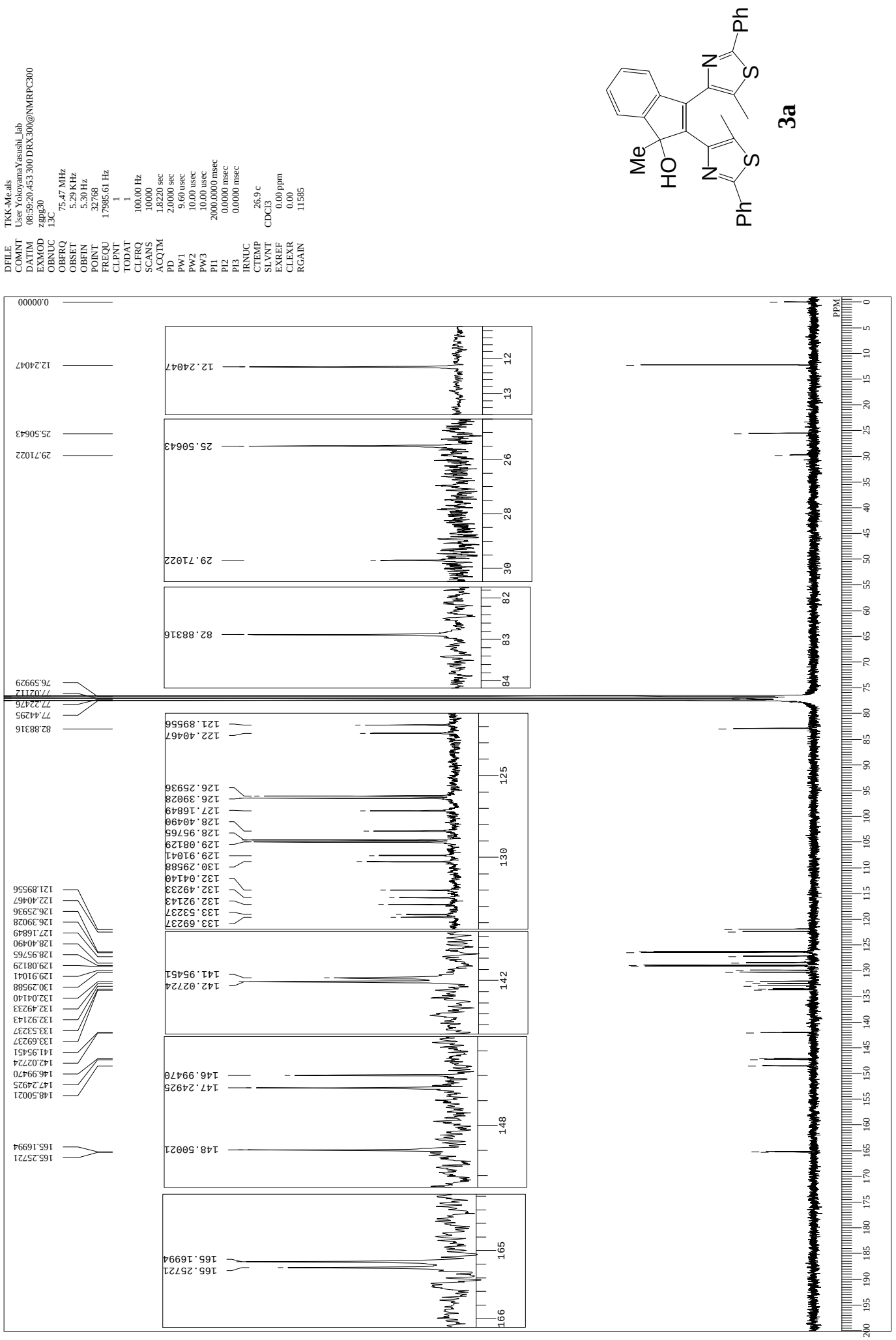
SI-4-2. ^{1}H NMR spectrum of compound 3b (300MHz, $CDCl_3$, TMS)



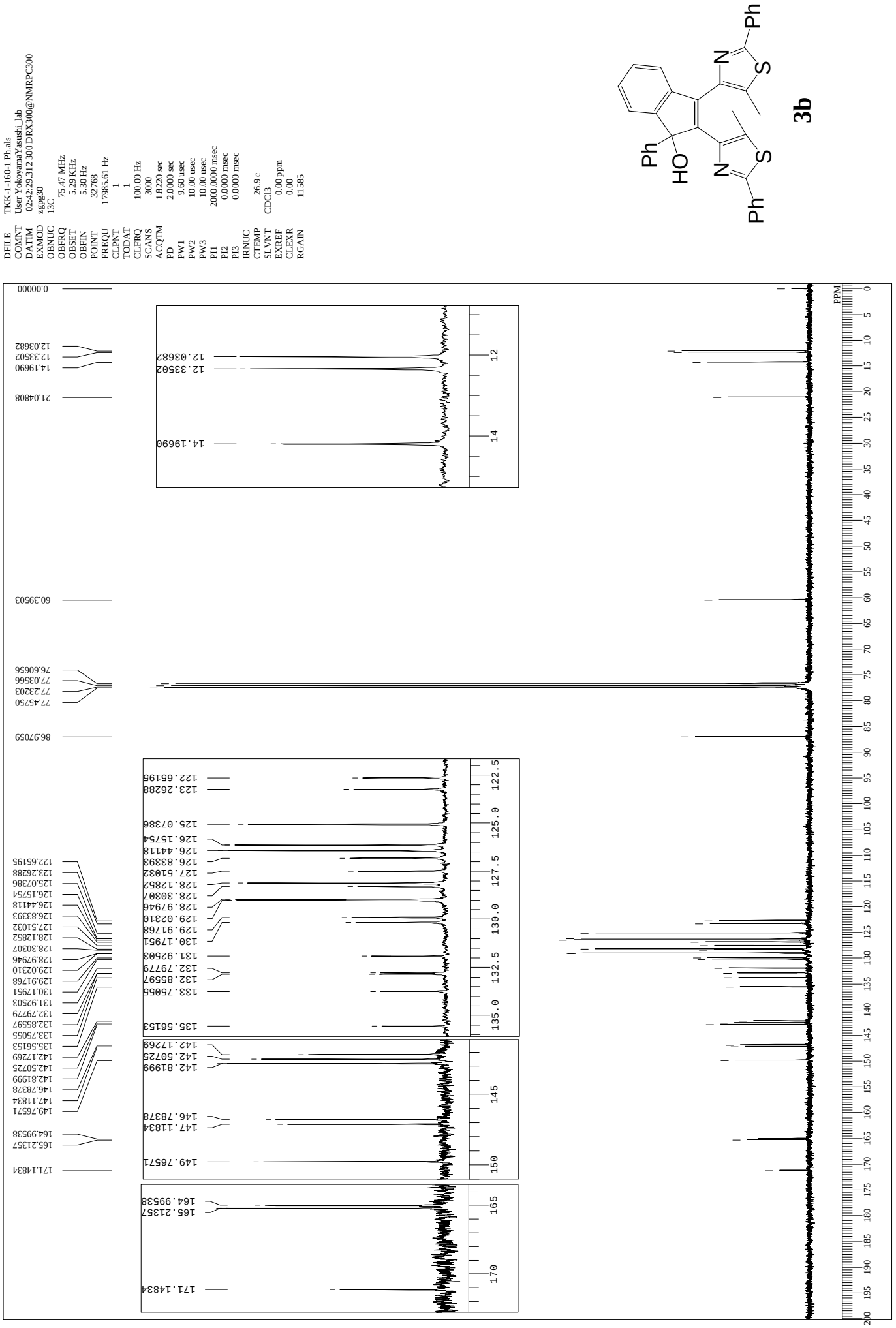
SI-4-3. ^{1}H NMR spectrum of compound 3c (300MHz, $CDCl_3$, TMS)



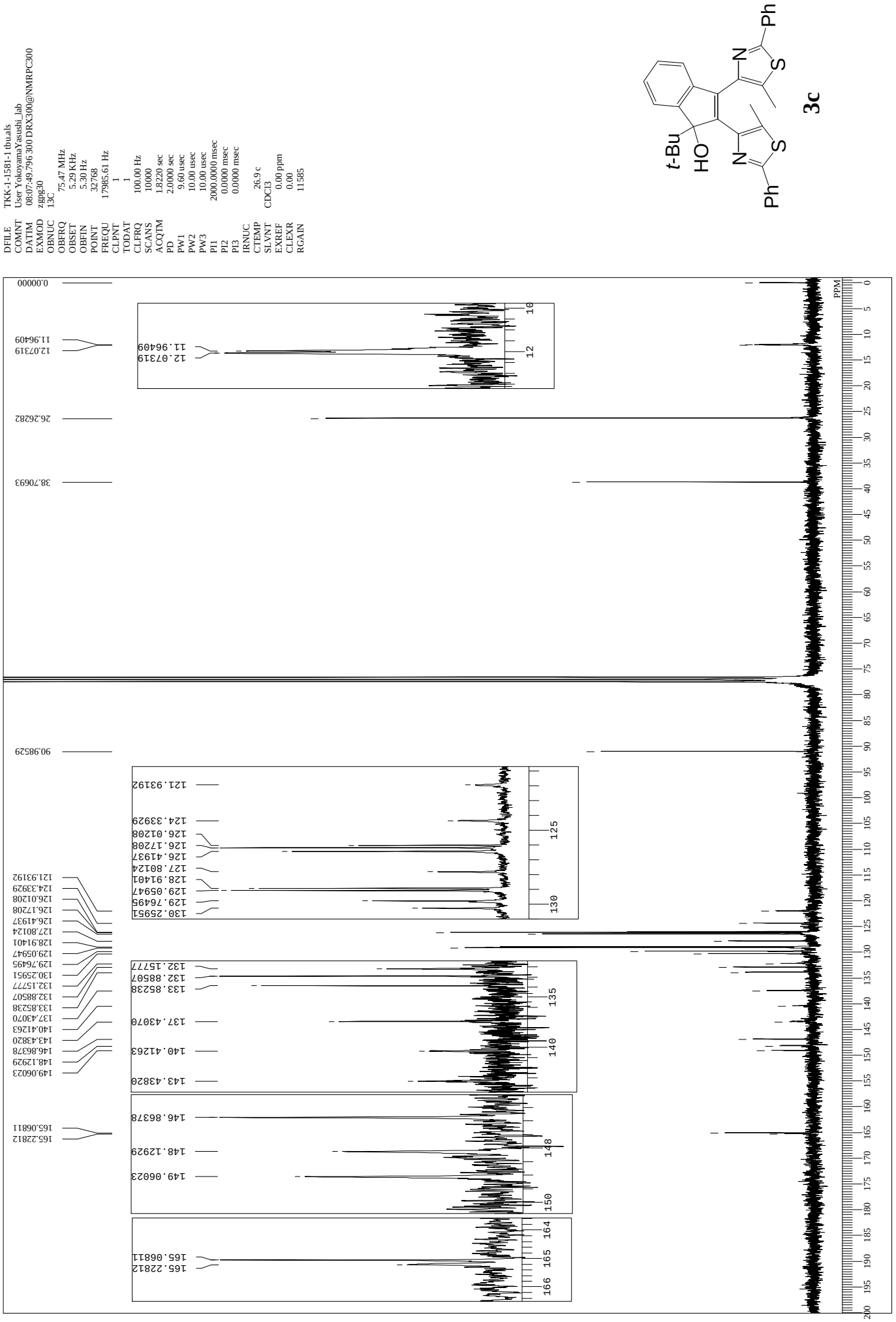
SI-4-4. ^{1}H NMR spectrum of compound 3d (300MHz, $CDCl_3$, TMS)



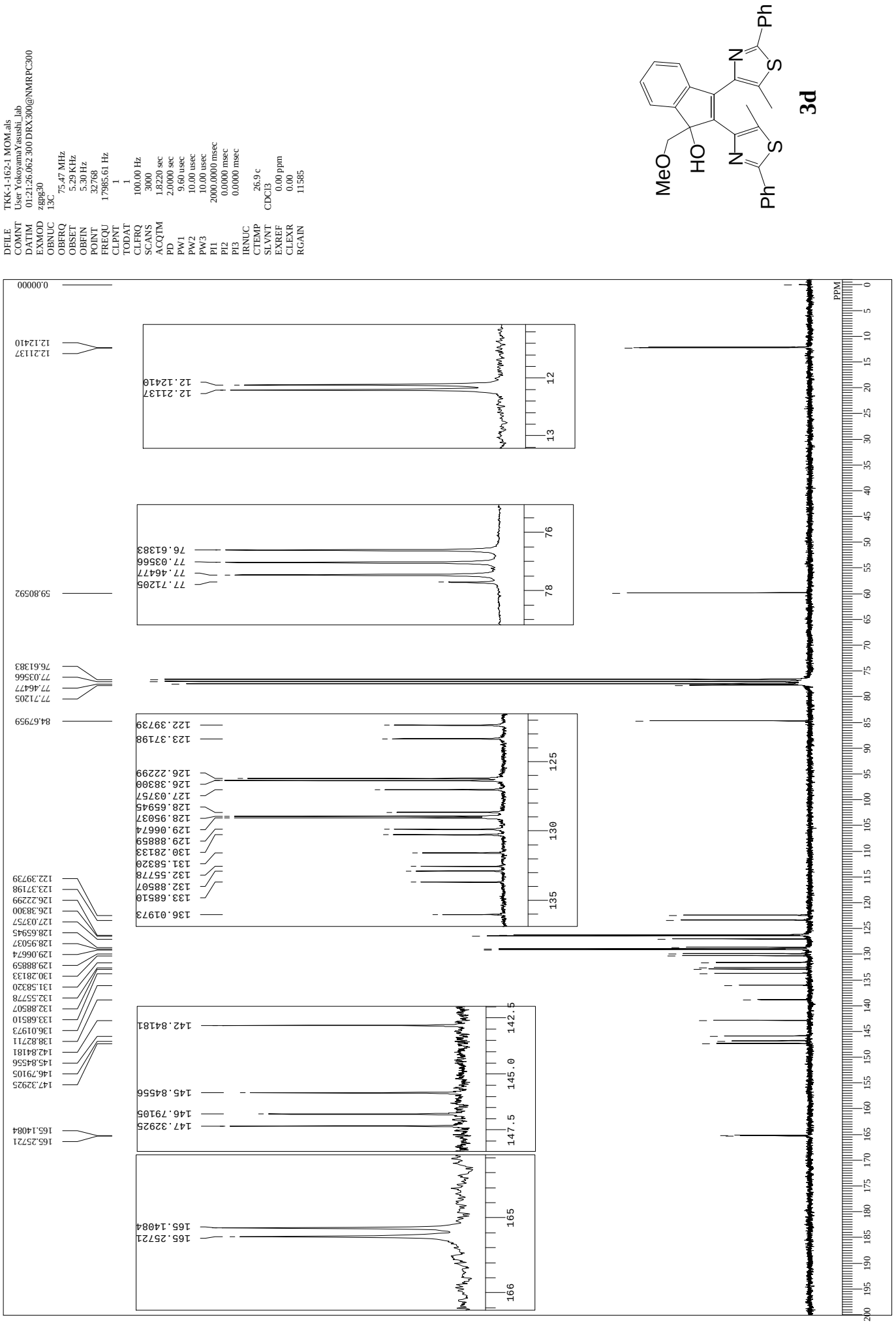
SI-5-1. ^{13}C NMR spectrum of compound 3a (75MHz, $CDCl_3$, TMS)



SI-5-2. ^{13}C NMR spectrum of compound 3b (75MHz, $CDCl_3$, TMS)



SI-5-3. ^{13}C NMR spectrum of compound 3c (75MHz, $CDCl_3$, TMS)



SI-5-4. ^{13}C NMR spectrum of compound 3d (75MHz, $CDCl_3$, TMS)

SI-6. X-ray crystallographic analysis data of 3b

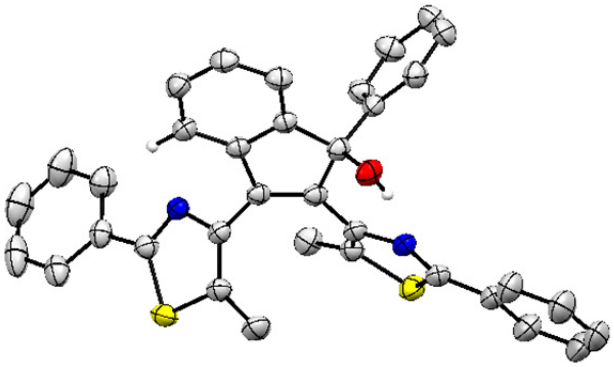


Figure SI-6-1. ORTEP drawing of bisarylindenol **3b** with 50% probability of thermal ellipsoids. Atom colors: White; Hydrogen, Grey; Carbon, Blue; Nitrogen, Red; Oxygen, Yellow; Sulfur. For clarity, most of hydrogen atoms and a chloroform molecule are removed from the figure. The deposition number is CCDC 882504.

Title (type here to add)

Abstract

(type here to add abstract)

Comment

The stucture of the title compound, (I), is shown below. Dimensions are available in the archived CIF.

For related literature, see [type here to add references to related literature].

Experimental

(type here to add preparation details)

Refinement

All the H-atoms could be located in difference Fourier maps. The O—H hydrogen atom was freely refined: O1—H1 = 0.74 (3) Å. The C-bound H-atoms were subsequently refined as riding atoms, with C—H = 0.95 (aromatic) and 0.98 (methyl) Å, and U_{iso}(H) = 1.2U_{eq}(C).

Computing details

Data collection: RAPID AUTO (Rigaku, 2009); cell refinement: RAPID AUTO; data reduction: RAPID AUTO; program(s) used to solve structure: Il Milione (Burla, *et al.*, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Acknowledgements

(type here to add acknowledgements)

References

?

2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1-phenylinden-1-ol

Crystal data

$C_{35}H_{26}N_2OS_2 \cdot CHCl_3$	$F(000)$ = 1392
M_r = 674.07	D_x = 1.395 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54187 Å
Hall symbol: -P 2ybc	Cell parameters from 50965 reflections
a = 14.4711 (2) Å	θ = 3.1–68.3°
b = 28.8500 (5) Å	μ = 4.06 mm^{-1}
c = 7.6973 (1) Å	T = 193 K
β = 93.099 (1)°	Block, orange
V = 3208.86 (8) Å^3	0.50 × 0.40 × 0.10 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID	
	5867 independent reflections

	5867 independent reflections
diffractometer	
Radiation source: rotating anode	5332 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.039$
Detector resolution: 10.000 pixels mm^{-1}	$\theta_{max} = 68.2°$, $\theta_{min} = 3.1°$
ω scans	$h = -17\rightarrow17$
Absorption correction: numerical *NUMABS* (Rigaku, 1999)	$k = -34\rightarrow34$
$T_{min} = 0.217$, $T_{max} = 0.666$	$l = -9\rightarrow9$
57196 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.146$	$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 2.1419P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
5867 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
404 parameters	$\Delta\rho_{min} = -0.68$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00075 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.19299 (10)	0.11918 (4)	−0.07928 (15)	0.1073 (4)
Cl2	0.28466 (7)	0.03451 (3)	0.01586 (13)	0.0786 (3)
Cl3	0.37921 (8)	0.12100 (4)	0.06891 (14)	0.1026 (4)
S1	0.75203 (4)	0.02839 (2)	0.37588 (8)	0.04280 (18)
S2	0.37319 (4)	0.08206 (2)	0.57301 (8)	0.04114 (18)
O1	0.80568 (12)	0.09819 (6)	1.0065 (2)	0.0416 (4)
N1	0.79021 (12)	0.04710 (6)	0.6954 (3)	0.0352 (4)
N2	0.46694 (12)	0.15612 (6)	0.6313 (2)	0.0323 (4)
C1	0.76689 (15)	0.13279 (7)	0.8912 (3)	0.0332 (5)
C2	0.69287 (15)	0.11226 (7)	0.7633 (3)	0.0314 (4)
C3	0.60922 (15)	0.13130 (7)	0.7879 (3)	0.0312 (4)
C4	0.61864 (15)	0.16631 (7)	0.9282 (3)	0.0314 (4)
C5	0.55413 (16)	0.19530 (7)	0.9994 (3)	0.0364 (5)
H5	0.4916	0.1956	0.9547	0.044*
C6	0.58276 (17)	0.22391 (8)	1.1372 (3)	0.0418 (5)

H6	0.5395	0.2442	1.1862	0.050*
C7	0.67375 (18)	0.22324 (8)	1.2041 (3)	0.0423 (5)
H7	0.6917	0.2425	1.3002	0.051*
C8	0.73901 (17)	0.19462 (8)	1.1320 (3)	0.0394 (5)
H8	0.8015	0.1944	1.1766	0.047*
C9	0.71070 (15)	0.16652 (7)	0.9939 (3)	0.0328 (5)
C10	0.84173 (15)	0.15916 (7)	0.7990 (3)	0.0340 (5)
C11	0.82165 (16)	0.18216 (8)	0.6422 (3)	0.0396 (5)
H11	0.7617	0.1793	0.5865	0.048*
C12	0.88752 (18)	0.20915 (9)	0.5663 (3)	0.0469 (6)
H12	0.8726	0.2247	0.4596	0.056*
C13	0.97501 (18)	0.21343 (10)	0.6459 (4)	0.0491 (6)
H13	1.0205	0.2318	0.5938	0.059*
C14	0.99617 (17)	0.19094 (9)	0.8015 (4)	0.0491 (6)
H14	1.0563	0.1940	0.8564	0.059*
C15	0.93024 (16)	0.16392 (9)	0.8782 (3)	0.0424 (5)
H15	0.9455	0.1486	0.9852	0.051*
C16	0.72089 (15)	0.07769 (7)	0.6374 (3)	0.0326 (5)
C17	0.69195 (15)	0.07326 (7)	0.4658 (3)	0.0355 (5)
C18	0.81220 (16)	0.01861 (8)	0.5732 (3)	0.0380 (5)
C19	0.62387 (18)	0.10079 (9)	0.3548 (3)	0.0442 (6)
H19A	0.5630	0.0858	0.3541	0.053*
H19B	0.6445	0.1023	0.2358	0.053*
H19C	0.6195	0.1322	0.4020	0.053*
C20	0.88222 (17)	−0.01827 (8)	0.5962 (4)	0.0443 (6)
C21	0.9267 (2)	−0.02531 (10)	0.7593 (4)	0.0570 (7)
H21	0.9108	−0.0068	0.8553	0.068*
C22	0.9944 (2)	−0.05936 (11)	0.7816 (5)	0.0688 (9)
H22	1.0244	−0.0640	0.8931	0.083*
C23	1.0182 (2)	−0.08625 (11)	0.6445 (6)	0.0710 (10)
H23	1.0650	−0.1091	0.6606	0.085*
C24	0.9743 (2)	−0.08007 (11)	0.4840 (6)	0.0719 (10)
H24	0.9903	−0.0990	0.3892	0.086*
C25	0.9060 (2)	−0.04608 (9)	0.4590 (4)	0.0570 (7)
H25	0.8757	−0.0421	0.3474	0.068*
C26	0.51912 (15)	0.11994 (7)	0.7001 (3)	0.0326 (5)
C27	0.47982 (16)	0.07685 (8)	0.6836 (3)	0.0365 (5)
C28	0.38935 (15)	0.14156 (8)	0.5579 (3)	0.0349 (5)
C29	0.51581 (19)	0.03120 (8)	0.7494 (4)	0.0493 (6)
H29A	0.4648	0.0130	0.7933	0.059*
H29B	0.5630	0.0363	0.8437	0.059*
H29C	0.5432	0.0143	0.6545	0.059*
C30	0.32265 (16)	0.17217 (9)	0.4640 (3)	0.0386 (5)
C31	0.22987 (17)	0.16044 (11)	0.4334 (4)	0.0499 (6)
H31	0.2063	0.1323	0.4775	0.060*
C32	0.1718 (2)	0.19093 (14)	0.3364 (4)	0.0678 (9)
H32	0.1087	0.1831	0.3121	0.081*
C33	0.2060 (3)	0.23222 (14)	0.2761 (4)	0.0721 (10)
H33	0.1662	0.2525	0.2099	0.087*
C34	0.2961 (2)	0.24421 (12)	0.3105 (4)	0.0651 (8)
H34	0.3185	0.2731	0.2713	0.078*
C35	0.35510 (19)	0.21420 (10)	0.4026 (3)	0.0488 (6)

H35	0.4183	0.2224	0.4242	0.059*
C36	0.2731 (2)	0.09311 (11)	0.0671 (4)	0.0599 (7)
H36	0.2492	0.0954	0.1863	0.072*
H1	0.815 (2)	0.0785 (11)	0.948 (4)	0.042 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1320 (10)	0.1017 (8)	0.0866 (7)	0.0498 (7)	−0.0094 (6)	0.0029 (6)
Cl2	0.0917 (6)	0.0545 (5)	0.0914 (6)	0.0038 (4)	0.0217 (5)	0.0048 (4)
Cl3	0.1058 (8)	0.1235 (9)	0.0816 (7)	−0.0523 (7)	0.0339 (6)	−0.0376 (6)
S1	0.0481 (3)	0.0373 (3)	0.0432 (4)	0.0009 (2)	0.0043 (3)	−0.0072 (2)
S2	0.0380 (3)	0.0347 (3)	0.0501 (4)	−0.0072 (2)	−0.0031 (2)	−0.0001 (2)
O1	0.0470 (10)	0.0351 (9)	0.0416 (10)	0.0081 (7)	−0.0066 (7)	0.0061 (8)
N1	0.0351 (9)	0.0271 (9)	0.0434 (11)	0.0023 (7)	0.0023 (8)	0.0014 (8)
N2	0.0322 (9)	0.0282 (9)	0.0362 (10)	0.0012 (7)	−0.0003 (7)	0.0012 (7)
C1	0.0344 (11)	0.0298 (10)	0.0350 (12)	0.0033 (8)	−0.0024 (9)	0.0026 (9)
C2	0.0357 (11)	0.0253 (10)	0.0331 (11)	0.0001 (8)	−0.0008 (8)	0.0035 (8)
C3	0.0348 (11)	0.0258 (10)	0.0327 (11)	0.0006 (8)	−0.0006 (8)	0.0036 (8)
C4	0.0366 (11)	0.0260 (10)	0.0314 (11)	−0.0004 (8)	0.0012 (8)	0.0045 (8)
C5	0.0366 (11)	0.0310 (11)	0.0418 (13)	0.0012 (9)	0.0030 (9)	0.0004 (9)
C6	0.0462 (13)	0.0355 (12)	0.0446 (14)	0.0028 (10)	0.0098 (10)	−0.0054 (10)
C7	0.0513 (14)	0.0375 (12)	0.0380 (13)	−0.0047 (10)	0.0025 (10)	−0.0064 (10)
C8	0.0428 (12)	0.0373 (12)	0.0375 (12)	−0.0040 (9)	−0.0021 (10)	−0.0010 (9)
C9	0.0368 (11)	0.0295 (10)	0.0322 (11)	−0.0001 (8)	0.0015 (9)	0.0031 (8)
C10	0.0334 (11)	0.0297 (10)	0.0387 (12)	0.0029 (8)	0.0008 (9)	−0.0047 (9)
C11	0.0380 (12)	0.0389 (12)	0.0412 (13)	−0.0026 (9)	−0.0032 (10)	0.0018 (10)
C12	0.0497 (14)	0.0488 (14)	0.0420 (14)	−0.0069 (11)	0.0012 (11)	0.0038 (11)
C13	0.0421 (13)	0.0489 (14)	0.0573 (16)	−0.0068 (11)	0.0101 (11)	0.0008 (12)
C14	0.0323 (12)	0.0498 (15)	0.0645 (17)	−0.0013 (10)	−0.0030 (11)	−0.0025 (12)
C15	0.0376 (12)	0.0405 (13)	0.0483 (14)	0.0048 (10)	−0.0039 (10)	0.0011 (10)
C16	0.0326 (10)	0.0242 (10)	0.0410 (12)	−0.0009 (8)	0.0012 (9)	0.0020 (8)
C17	0.0373 (11)	0.0299 (11)	0.0392 (12)	−0.0034 (9)	0.0019 (9)	0.0005 (9)
C18	0.0375 (12)	0.0282 (11)	0.0485 (14)	−0.0014 (9)	0.0051 (10)	0.0008 (9)
C19	0.0491 (14)	0.0447 (13)	0.0386 (13)	0.0028 (11)	0.0003 (10)	0.0065 (10)
C20	0.0394 (12)	0.0300 (11)	0.0642 (17)	0.0006 (9)	0.0080 (11)	−0.0009 (11)
C21	0.0521 (15)	0.0443 (15)	0.074 (2)	0.0140 (12)	0.0006 (14)	0.0015 (13)
C22	0.0568 (17)	0.0514 (17)	0.097 (3)	0.0173 (14)	−0.0034 (17)	0.0102 (17)
C23	0.0497 (16)	0.0420 (16)	0.122 (3)	0.0141 (13)	0.0126 (18)	0.0054 (17)
C24	0.0641 (19)	0.0421 (16)	0.112 (3)	0.0085 (14)	0.027 (2)	−0.0166 (17)
C25	0.0571 (16)	0.0395 (14)	0.075 (2)	0.0049 (12)	0.0115 (14)	−0.0110 (13)
C26	0.0357 (11)	0.0279 (10)	0.0343 (11)	0.0013 (8)	0.0022 (9)	0.0008 (8)
C27	0.0376 (11)	0.0312 (11)	0.0408 (12)	−0.0027 (9)	0.0022 (9)	0.0022 (9)
C28	0.0359 (11)	0.0328 (11)	0.0359 (12)	−0.0003 (9)	0.0008 (9)	0.0002 (9)
C29	0.0510 (14)	0.0320 (12)	0.0645 (17)	−0.0002 (10)	−0.0010 (12)	0.0078 (11)
C30	0.0361 (11)	0.0455 (13)	0.0340 (12)	0.0074 (10)	0.0000 (9)	−0.0016 (10)
C31	0.0382 (13)	0.0635 (17)	0.0474 (15)	0.0059 (11)	−0.0012 (11)	−0.0091 (12)
C32	0.0405 (14)	0.105 (3)	0.0571 (18)	0.0248 (16)	−0.0089 (13)	−0.0171 (18)
C33	0.074 (2)	0.089 (3)	0.0526 (18)	0.0398 (19)	−0.0064 (15)	0.0088 (17)
C34	0.073 (2)	0.0672 (19)	0.0551 (17)	0.0269 (16)	0.0042 (15)	0.0169 (15)
C35	0.0512 (14)	0.0499 (15)	0.0451 (14)	0.0089 (11)	0.0020 (11)	0.0105 (11)
C36	0.0706 (19)	0.0622 (18)	0.0474 (16)	0.0002 (15)	0.0086 (14)	−0.0051 (13)

Geometric parameters (Å, º)

Cl1—C36	1.743 (3)	C14—C15	1.388 (4)
Cl2—C36	1.746 (3)	C14—H14	0.9500
Cl3—C36	1.732 (3)	C15—H15	0.9500
S1—C17	1.725 (2)	C16—C17	1.370 (3)
S1—C18	1.732 (3)	C17—C19	1.496 (3)
S2—C27	1.728 (2)	C18—C20	1.473 (3)
S2—C28	1.737 (2)	C19—H19A	0.9800
O1—C1	1.431 (3)	C19—H19B	0.9800
O1—H1	0.74 (3)	C19—H19C	0.9800
N1—C18	1.301 (3)	C20—C25	1.384 (4)
N1—C16	1.392 (3)	C20—C21	1.394 (4)
N2—C28	1.299 (3)	C21—C22	1.392 (4)
N2—C26	1.377 (3)	C21—H21	0.9500
C1—C9	1.518 (3)	C22—C23	1.369 (5)
C1—C10	1.529 (3)	C22—H22	0.9500
C1—C2	1.534 (3)	C23—C24	1.370 (6)
C2—C3	1.352 (3)	C23—H23	0.9500
C2—C16	1.463 (3)	C24—C25	1.398 (4)
C3—C26	1.472 (3)	C24—H24	0.9500
C3—C4	1.480 (3)	C25—H25	0.9500
C4—C5	1.388 (3)	C26—C27	1.370 (3)
C4—C9	1.399 (3)	C27—C29	1.495 (3)
C5—C6	1.390 (3)	C28—C30	1.469 (3)
C5—H5	0.9500	C29—H29A	0.9800
C6—C7	1.388 (4)	C29—H29B	0.9800
C6—H6	0.9500	C29—H29C	0.9800
C7—C8	1.392 (3)	C30—C31	1.392 (3)
C7—H7	0.9500	C30—C35	1.392 (4)
C8—C9	1.381 (3)	C31—C32	1.403 (4)
C8—H8	0.9500	C31—H31	0.9500
C10—C11	1.394 (3)	C32—C33	1.380 (5)
C10—C15	1.395 (3)	C32—H32	0.9500
C11—C12	1.384 (3)	C33—C34	1.362 (5)
C11—H11	0.9500	C33—H33	0.9500
C12—C13	1.382 (4)	C34—C35	1.384 (4)
C12—H12	0.9500	C34—H34	0.9500
C13—C14	1.382 (4)	C35—H35	0.9500
C13—H13	0.9500	C36—H36	1.0000

C17—S1—C18	90.63 (11)	C17—C19—H19B	109.5
C27—S2—C28	89.95 (11)	H19A—C19—H19B	109.5
C1—O1—H1	104 (2)	C17—C19—H19C	109.5
C18—N1—C16	111.6 (2)	H19A—C19—H19C	109.5
C28—N2—C26	111.42 (18)	H19B—C19—H19C	109.5
O1—C1—C9	109.10 (18)	C25—C20—C21	118.7 (3)
O1—C1—C10	111.79 (17)	C25—C20—C18	121.6 (3)
C9—C1—C10	109.61 (17)	C21—C20—C18	119.6 (2)
O1—C1—C2	111.47 (18)	C22—C21—C20	120.1 (3)
C9—C1—C2	101.94 (17)	C22—C21—H21	119.9
C10—C1—C2	112.44 (18)	C20—C21—H21	119.9
C3—C2—C16	130.7 (2)	C23—C22—C21	120.6 (3)
C3—C2—C1	110.65 (19)	C23—C22—H22	119.7

C16—C2—C1	118.65 (18)	C21—C22—H22	119.7
C2—C3—C26	128.5 (2)	C22—C23—C24	119.9 (3)
C2—C3—C4	109.37 (19)	C22—C23—H23	120.1
C26—C3—C4	122.07 (19)	C24—C23—H23	120.1
C5—C4—C9	120.1 (2)	C23—C24—C25	120.3 (3)
C5—C4—C3	131.5 (2)	C23—C24—H24	119.8
C9—C4—C3	108.37 (18)	C25—C24—H24	119.8
C4—C5—C6	118.7 (2)	C20—C25—C24	120.3 (3)
C4—C5—H5	120.7	C20—C25—H25	119.9
C6—C5—H5	120.7	C24—C25—H25	119.9
C7—C6—C5	120.9 (2)	C27—C26—N2	115.8 (2)
C7—C6—H6	119.6	C27—C26—C3	126.7 (2)
C5—C6—H6	119.6	N2—C26—C3	117.47 (18)
C6—C7—C8	120.7 (2)	C26—C27—C29	129.3 (2)
C6—C7—H7	119.7	C26—C27—S2	108.77 (17)
C8—C7—H7	119.7	C29—C27—S2	121.95 (18)
C9—C8—C7	118.4 (2)	N2—C28—C30	123.3 (2)
C9—C8—H8	120.8	N2—C28—S2	113.99 (16)
C7—C8—H8	120.8	C30—C28—S2	122.65 (17)
C8—C9—C4	121.2 (2)	C27—C29—H29A	109.5
C8—C9—C1	129.2 (2)	C27—C29—H29B	109.5
C4—C9—C1	109.58 (19)	H29A—C29—H29B	109.5
C11—C10—C15	118.4 (2)	C27—C29—H29C	109.5
C11—C10—C1	121.25 (19)	H29A—C29—H29C	109.5
C15—C10—C1	120.2 (2)	H29B—C29—H29C	109.5
C12—C11—C10	121.1 (2)	C31—C30—C35	119.6 (2)
C12—C11—H11	119.4	C31—C30—C28	122.6 (2)
C10—C11—H11	119.4	C35—C30—C28	117.8 (2)
C13—C12—C11	119.9 (2)	C30—C31—C32	118.8 (3)
C13—C12—H12	120.1	C30—C31—H31	120.6
C11—C12—H12	120.1	C32—C31—H31	120.6
C12—C13—C14	119.8 (2)	C33—C32—C31	120.3 (3)
C12—C13—H13	120.1	C33—C32—H32	119.8
C14—C13—H13	120.1	C31—C32—H32	119.8
C13—C14—C15	120.5 (2)	C34—C33—C32	120.7 (3)
C13—C14—H14	119.8	C34—C33—H33	119.6
C15—C14—H14	119.8	C32—C33—H33	119.6
C14—C15—C10	120.3 (2)	C33—C34—C35	119.9 (3)
C14—C15—H15	119.8	C33—C34—H34	120.1
C10—C15—H15	119.8	C35—C34—H34	120.1
C17—C16—N1	115.3 (2)	C34—C35—C30	120.6 (3)
C17—C16—C2	128.4 (2)	C34—C35—H35	119.7
N1—C16—C2	116.15 (19)	C30—C35—H35	119.7
C16—C17—C19	131.2 (2)	Cl3—C36—Cl1	111.29 (19)
C16—C17—S1	108.80 (17)	Cl3—C36—Cl2	110.87 (18)
C19—C17—S1	120.00 (18)	Cl1—C36—Cl2	109.88 (18)
N1—C18—C20	124.2 (2)	Cl3—C36—H36	108.2
N1—C18—S1	113.56 (17)	Cl1—C36—H36	108.2
C20—C18—S1	122.21 (19)	Cl2—C36—H36	108.2
C17—C19—H19A	109.5		

O1—C1—C2—C3	116.7 (2)	N1—C16—C17—C19	−176.4 (2)

C9—C1—C2—C3	0.5 (2)	C2—C16—C17—C19	−0.9 (4)
C10—C1—C2—C3	−116.8 (2)	N1—C16—C17—S1	1.3 (2)
O1—C1—C2—C16	−64.4 (2)	C2—C16—C17—S1	176.79 (18)
C9—C1—C2—C16	179.38 (18)	C18—S1—C17—C16	−0.20 (17)
C10—C1—C2—C16	62.1 (2)	C18—S1—C17—C19	177.78 (19)
C16—C2—C3—C26	4.7 (4)	C16—N1—C18—C20	−178.9 (2)
C1—C2—C3—C26	−176.6 (2)	C16—N1—C18—S1	1.9 (2)
C16—C2—C3—C4	−177.5 (2)	C17—S1—C18—N1	−1.02 (18)
C1—C2—C3—C4	1.2 (2)	C17—S1—C18—C20	179.8 (2)
C2—C3—C4—C5	179.2 (2)	N1—C18—C20—C25	−176.8 (2)
C26—C3—C4—C5	−2.9 (4)	S1—C18—C20—C25	2.3 (3)
C2—C3—C4—C9	−2.6 (2)	N1—C18—C20—C21	2.6 (4)
C26—C3—C4—C9	175.36 (19)	S1—C18—C20—C21	−178.3 (2)
C9—C4—C5—C6	−0.6 (3)	C25—C20—C21—C22	0.8 (4)
C3—C4—C5—C6	177.5 (2)	C18—C20—C21—C22	−178.6 (3)
C4—C5—C6—C7	−0.7 (4)	C20—C21—C22—C23	0.0 (5)
C5—C6—C7—C8	1.5 (4)	C21—C22—C23—C24	−0.8 (5)
C6—C7—C8—C9	−0.9 (4)	C22—C23—C24—C25	0.7 (5)
C7—C8—C9—C4	−0.5 (3)	C21—C20—C25—C24	−0.9 (4)
C7—C8—C9—C1	179.4 (2)	C18—C20—C25—C24	178.5 (3)
C5—C4—C9—C8	1.2 (3)	C23—C24—C25—C20	0.1 (5)
C3—C4—C9—C8	−177.2 (2)	C28—N2—C26—C27	−1.8 (3)
C5—C4—C9—C1	−178.64 (19)	C28—N2—C26—C3	−179.97 (19)
C3—C4—C9—C1	2.9 (2)	C2—C3—C26—C27	52.4 (4)
O1—C1—C9—C8	60.1 (3)	C4—C3—C26—C27	−125.2 (2)
C10—C1—C9—C8	−62.6 (3)	C2—C3—C26—N2	−129.7 (2)
C2—C1—C9—C8	178.1 (2)	C4—C3—C26—N2	52.8 (3)
O1—C1—C9—C4	−120.05 (19)	N2—C26—C27—C29	−177.3 (2)
C10—C1—C9—C4	117.24 (19)	C3—C26—C27—C29	0.7 (4)
C2—C1—C9—C4	−2.1 (2)	N2—C26—C27—S2	1.1 (3)
O1—C1—C10—C11	157.5 (2)	C3—C26—C27—S2	179.09 (18)
C9—C1—C10—C11	−81.4 (3)	C28—S2—C27—C26	−0.14 (18)
C2—C1—C10—C11	31.2 (3)	C28—S2—C27—C29	178.3 (2)
O1—C1—C10—C15	−27.9 (3)	C26—N2—C28—C30	−175.9 (2)
C9—C1—C10—C15	93.2 (2)	C26—N2—C28—S2	1.6 (2)
C2—C1—C10—C15	−154.2 (2)	C27—S2—C28—N2	−0.87 (18)
C15—C10—C11—C12	−0.1 (4)	C27—S2—C28—C30	176.7 (2)
C1—C10—C11—C12	174.6 (2)	N2—C28—C30—C31	−159.4 (2)
C10—C11—C12—C13	0.3 (4)	S2—C28—C30—C31	23.2 (3)
C11—C12—C13—C14	−0.4 (4)	N2—C28—C30—C35	21.3 (3)
C12—C13—C14—C15	0.2 (4)	S2—C28—C30—C35	−156.1 (2)
C13—C14—C15—C10	0.0 (4)	C35—C30—C31—C32	1.9 (4)
C11—C10—C15—C14	−0.1 (4)	C28—C30—C31—C32	−177.4 (2)
C1—C10—C15—C14	−174.8 (2)	C30—C31—C32—C33	−1.5 (4)
C18—N1—C16—C17	−2.1 (3)	C31—C32—C33—C34	−0.4 (5)
C18—N1—C16—C2	−178.18 (19)	C32—C33—C34—C35	1.9 (5)
C3—C2—C16—C17	39.1 (4)	C33—C34—C35—C30	−1.4 (5)
C1—C2—C16—C17	−139.6 (2)	C31—C30—C35—C34	−0.5 (4)
C3—C2—C16—N1	−145.5 (2)	C28—C30—C35—C34	178.9 (3)
C1—C2—C16—N1	35.9 (3)		

SI-7. X-ray crystallographic analysis data of positive H – N interactions in 3b and DFT calculations of 3b and $3bC_{major}$.

Table 1. X-ray crystallographic analysis data of positive H – N interactions in **3b**, and the comparison of them with DFT calculation results of **3b** and $\mathbf{3bC_{major}}$.

	OH–N Distance/ pm	(Indene-Ph)CH–N Distance/ pm
3b (X-ray)	215.7	274.3
3b (DFT)[a]	200.4	273.7
$\mathbf{3bC_{major}}$ (DFT)[a]	255.1	268.1

[a] DFT calculations to optimize the structures in vacuum were done with Spartan'08 with B3LYP/6-31G**.