

Supplementary Information

Reactive Disperse Dyes Bearing Various Blocked Isocyanate Groups for Digital Textile Printing Ink

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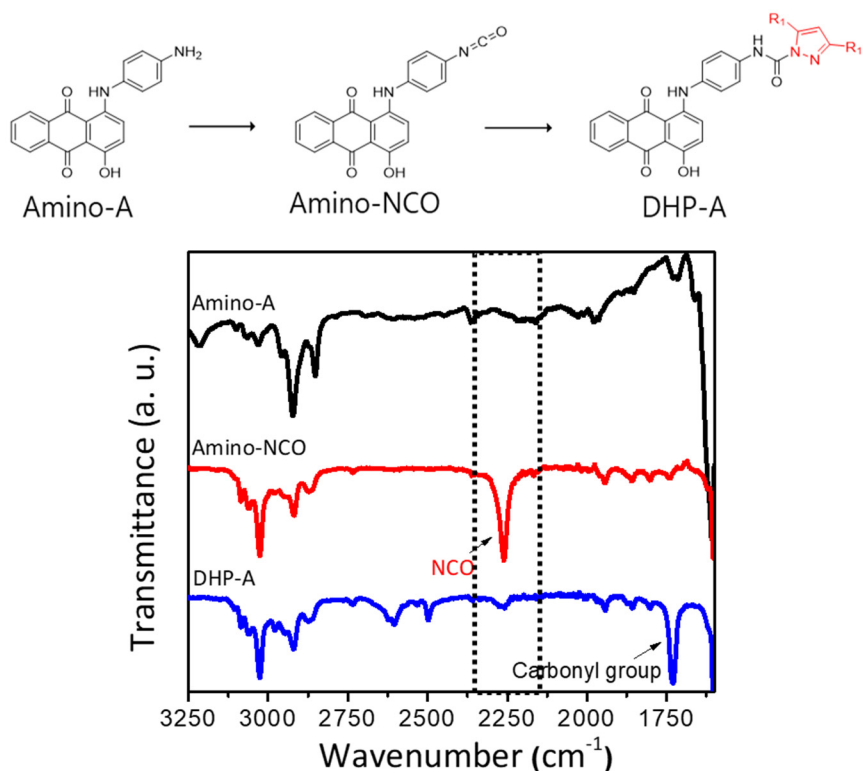


Figure S1. Scheme and FT-IR spectra of isocyanate reaction and confirmed the disappearance of the free isocyanate peak ($2250\text{--}2280\text{ cm}^{-1}$) of NCO group.

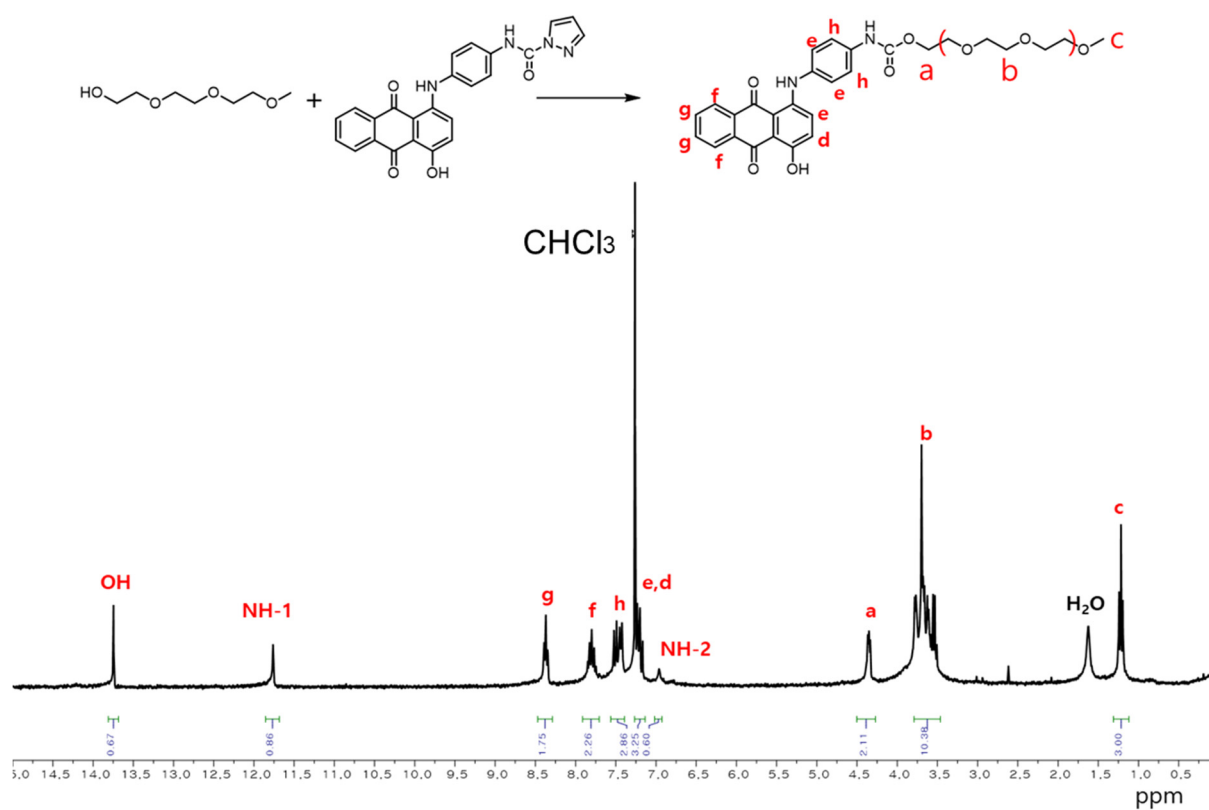
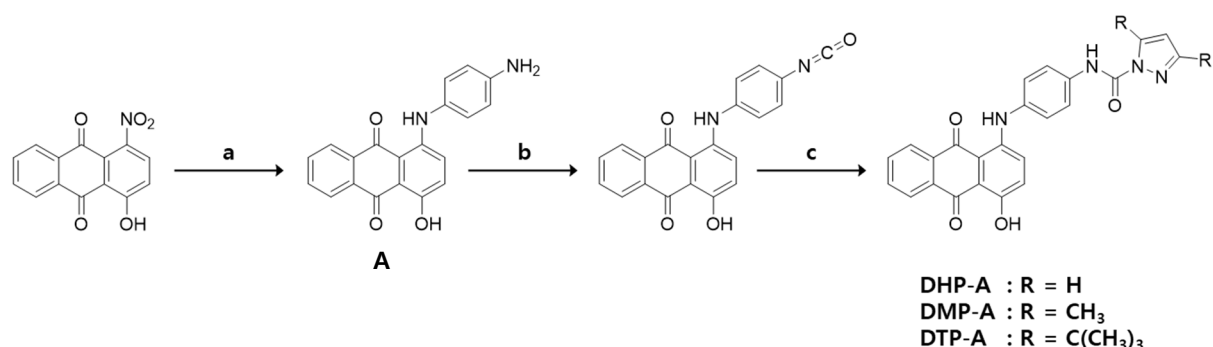


Figure S2. ¹H NMR spectrum of the mixture (after wasing with ethanol and dry) of the reaction of DHP-A with 2-(2-(2-methoxyethoxy)ethoxy)ethan-1-ol at 210 °C for 10 min.

Synthetic scheme of blocked isocyanate dyes



a) 1,4-Diaminobenzene, Nitrobenzene, 150 °C; b) Triethylamine, Triphosgene, 130 °C; c) Pyrazole derivated compounds (pyrazole, dimethyl pyrazole, di-*tert*-butyl pyrazole), toluene 40 °C.

1-((4-Aminophenyl)amino)-4-hydroxyanthracene-9,10-dione (Amino-A, Compound A): 1-Hydroxyl-4-nitro anthraquinone (2.00 g, 7.40 mmol) was dissolved in 60 mL of 4-nitrobenzene at 50 °C in a two-neck round-bottom flask. 1,4-Phenylenediamine (4.00 g, 36.9 mmol) was added to this solution at 150 °C. After 20 min, the reaction mixture was stirred at 210 °C for 12 h. When the mixture cooled to room temperature, ethanol was added to form a precipitate. The precipitate was filtered and washed with ethanol. The blue powder was purified using silica gel column chromatography with a mixed solvent (EtOAc/hexane, 38/62 (v/v)) as the eluent to afford a blue solid (yield 81%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 13.75 (s, 1H), 11.68 (s, 1H), 8.35-8.29 (m, 2H), 8.01-7.89 (m, 2H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.25 (s, 2H).

N-(4-((4-Hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)phenyl)-1H-pyrazole-1-carboxamide (DHP-A): 1-((4-Aminophenyl)amino)-4-hydroxyanthracene-9,10-dione (Amino-A, 0.50 g, 1.51 mmol) and triethylamine (0.23 g, 2.27 mmol) were dissolved in 60 mL of toluene in a two-neck round-bottom flask under a N₂ atmosphere. After a few moments, triphosgene (1.10 g, 3.70 mmol) was slowly added to the reaction solution and the reaction temperature was heated at 130 °C. The isocyanate group of the mixture was confirmed by FT-IR spectroscopy in the range of 2,250–2,280 cm⁻¹. The desired product was obtained after the solvent was removed from the reaction mixture, proceeding to the next step without purification.

The crude reaction mixture was cooled to 40 °C and pyrazole (0.76 g, 2 eq) was added with a small amount of toluene. The disappearance of isocyanate was confirmed of absence of the free isocyanate peak (2,250–2,280 cm⁻¹) in the FT-IR spectra. Upon completion of the reaction, the reaction mixture was extracted with ethylacetate and water. The organic layer was dried with anhydrous MgSO₄, filtered, and reduced, and the crude product was purified using silica gel column chromatography (EtOAc/hexane, 11/89 (v/v)) to afford a blue solid (yield 89%). **¹H NMR** (300 MHz, CDCl₃): δ 13.74 (s, 1H), 11.81 (s, 1H), 9.15 (s, 1H), 8.40–8.34 (m, 2H), 7.84–7.77 (m, 2H), 7.70–7.57 (m, 4H), 7.32–7.20 (m, 4H), 6.49 (s, 1H); **¹³C NMR** (150 MHz, CDCl₃) δ 187.47, 157.99, 142.51, 132.79, 128.36, 126.51, 126.15, 125.86, 125.12, 125.00, 121.32, 120.98, 113.27, 77.45, 77.23, 77.03, 76.60; HRFABMS: calcd. for C₂₄H₁₆N₄O₄ [M+H]⁺ 425.1250, found 425.1246.

N-(4-((4-Hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)phenyl)-3,5-dimethyl-1H-pyrazole-1-carboxamide (DMP-A): Amino-A (0.50 g, 1.51 mmol) and triethylamine (0.23 g, 2.27 mmol) were dissolved in 60 mL toluene under a N₂ atmosphere in a two-neck round-bottom flask. After a few moments, triphosgene (1.10 g, 3.70 mmol) was slowly added to the reaction solution and the reaction temperature was heated at 130 °C. The isocyanate group in the mixture was confirmed by the presence of the peak in the range of 2,250–2,280 cm⁻¹ in the FT-IR spectra. The desired product was obtained after the solvent was removed from the reaction mixture, proceeding to the next step without purification.

The crude reaction mixture (step b) was cooled to 40 °C and 3,5-dimethyl pyrazole (DMPy, 1.07 g, 2 eq) was added with a small amount of toluene. The disappearance of the isocyanate from the reaction mixture was confirmed by the absence of the free isocyanate peak (2,250–2,280 cm⁻¹) in the FT-IR spectra. Upon reaction completion, the reaction mixture was extracted with ethylacetate and water. The organic layer was dried with anhydrous MgSO₄, filtered, and reduced, and the crude product was purified using silica gel column chromatography (EtOAc/hexane, 12/88 (v/v)) to afford a blue solid (yield 88%). **¹H NMR** (300 MHz, CDCl₃): δ 13.76 (s, 1H), 11.82 (s, 1H), 9.32 (s, 1H), 8.40–8.37 (m, 2H), 7.88–7.77 (m, 2H), 7.68–7.57 (m, 4H), 7.31–7.21 (m, 2H), 6.01 (s, 1H), 2.65 (s, 3H), 2.29 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 187.46, 182.87, 158.09, 158.05, 150.55, 134.30, 133.17, 132.97, 128.34, 126.94, 126.90, 126.57, 125.92, 125.14, 125.00, 120.98, 120.96, 113.68, 110.49, 110.18, 106.14, 77.27, 77.24, 77.06, 77.03, 76.85, 76.82, 14.14, 13.99, 13.62, 11.01; HRFABMS: calcd. for C₂₆H₂₀N₄O₄ [M+H]⁺ 453.2944, found 453.2981

3,5-Di-*tert*-butyl-*N*-(4-((4-hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)phenyl)-1H-pyrazole-1-carboxamide (DTP-A): Amino-A (0.5 g, 1.5 mmol) and triethylamine (0.23 g, 2.27 mmol) were dissolved in a two-neck round-bottom flask containing 60 mL of toluene under a nitrogen atmosphere. After a few moments, triphosgene (1.10 g, 3.70 mmol) was slowly added to the reaction solution and the reaction was heated at 130 °C. The isocyanate group of the mixture was confirmed by the peak in the FT-IR spectra in the range of 2,250–2,280 cm⁻¹. The desired product was obtained after the solvent was removed from the reaction mixture, proceeding to the next step without purification.

The crude reaction mixture (step b) was cooled to 40 °C and 3,5-di-*tert*-butyl pyrazole (DtBPy, 2.09 g, 2 eq) was added with a small amount of toluene. The absence of the free isocyanate peak (2,250–2,280 cm⁻¹) in the FT-IR spectra confirmed that the isocyanate group was no longer present in the reaction mixture. Upon reaction completion, the reaction mixture was extracted with ethylacetate and water. The organic layer was dried with anhydrous MgSO₄, filtered, and reduced, and the crude product was purified using silica gel column chromatography (EtOAc/hexane, 10/90 (v/v)) to afford a blue solid (yield 90%). **¹H NMR** (300 MHz, CDCl₃): δ 13.76 (s, 1H), 11.80 (s, 1H), 9.67 (s, 1H), 8.43-8.37 (m, 2H), 7.88-7.57 (m, 6H), 7.30-7.20 (m, 2H), 6.03 (s, 1H), 1.45-1.35 (m, 18H); **¹³C NMR** (150 MHz, CDCl₃) δ 187.45, 182.81, 157.77, 156.98, 134.29, 132.94, 132.79, 128.34, 126.88, 126.51, 126.18, 126.10, 125.39, 125.22, 123.93, 121.32, 113.66, 99.20, 77.25, 77.04, 76.82, 61.43, 33.24, 32.26, 31.76, 31.60, 30.07, 29.91, 29.44, 22.67, 14.58, 14.14, 8.64; HRFABMS: calcd. for C₃₂H₃₂N₄O₄ [M+H]⁺ 537.2502, found 537.2498

NMR spectrum of blocked isocyanate dyes

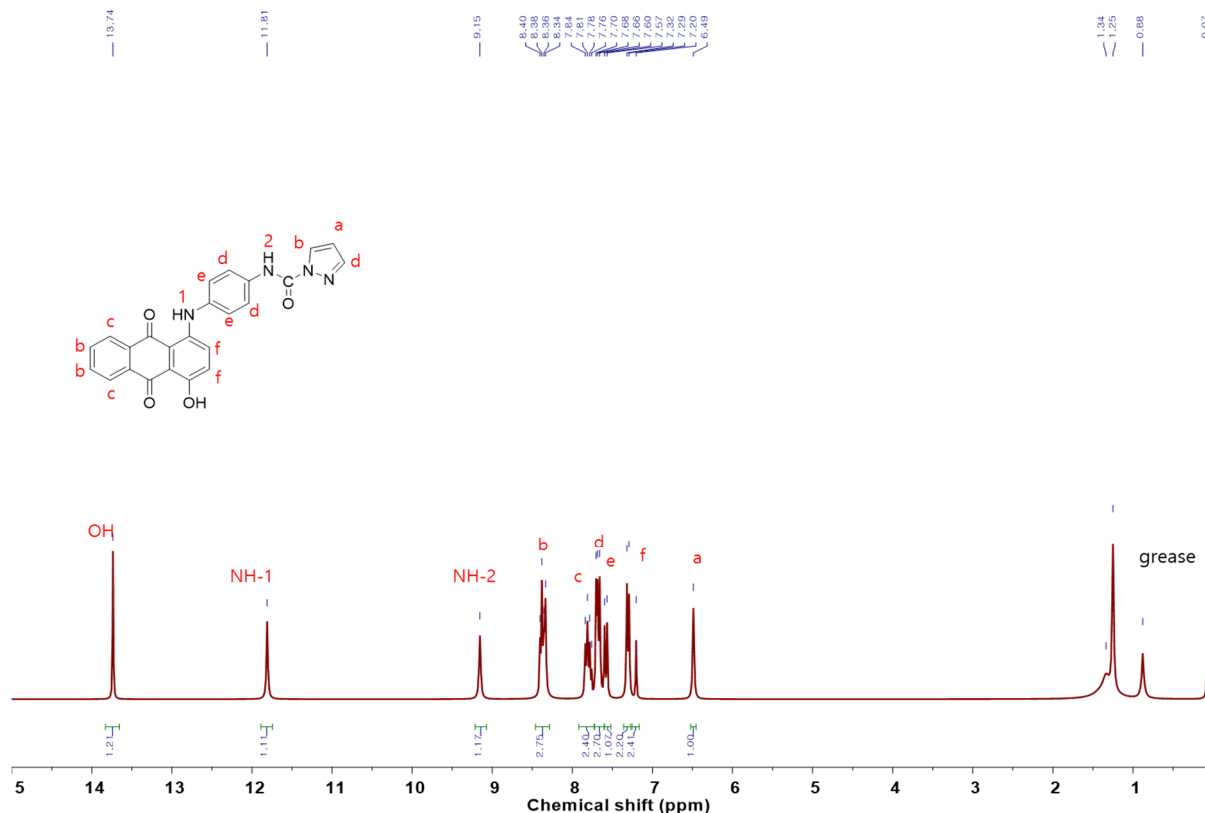


Figure S3. H-NMR spectrum of DHP-A

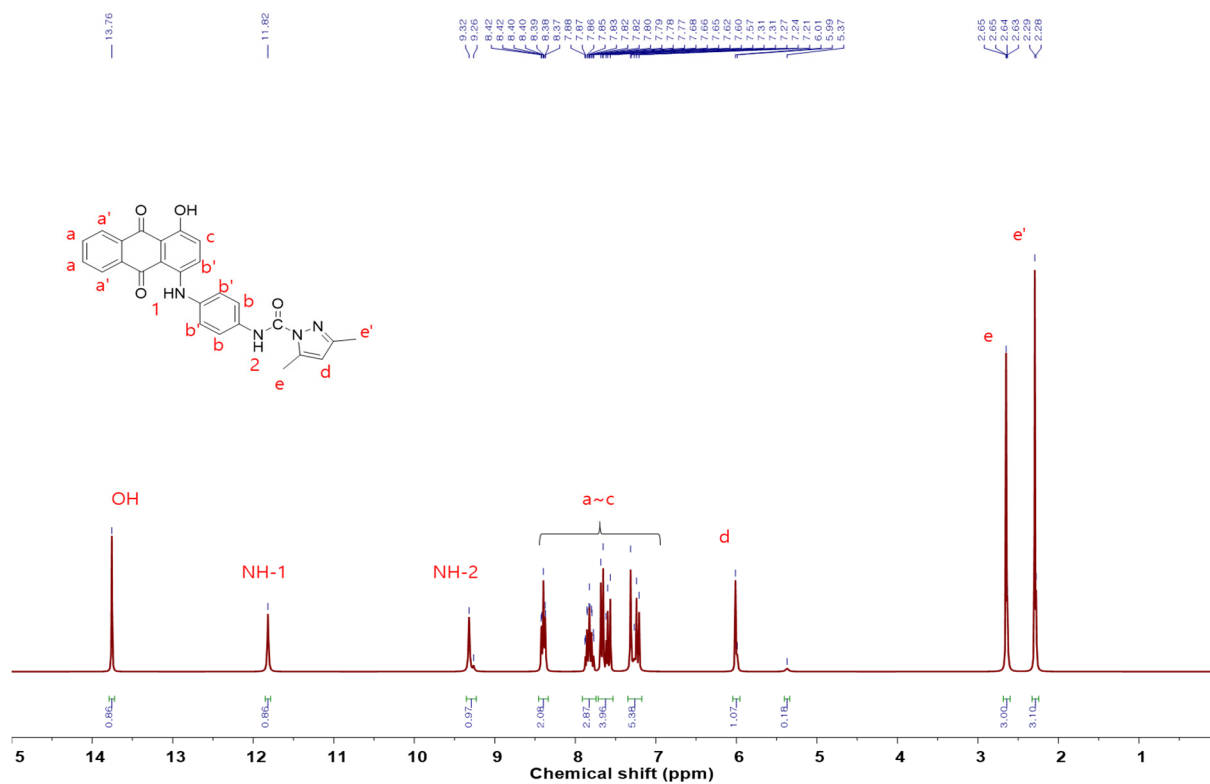


Figure S4. H-NMR spectrum of DMP-A

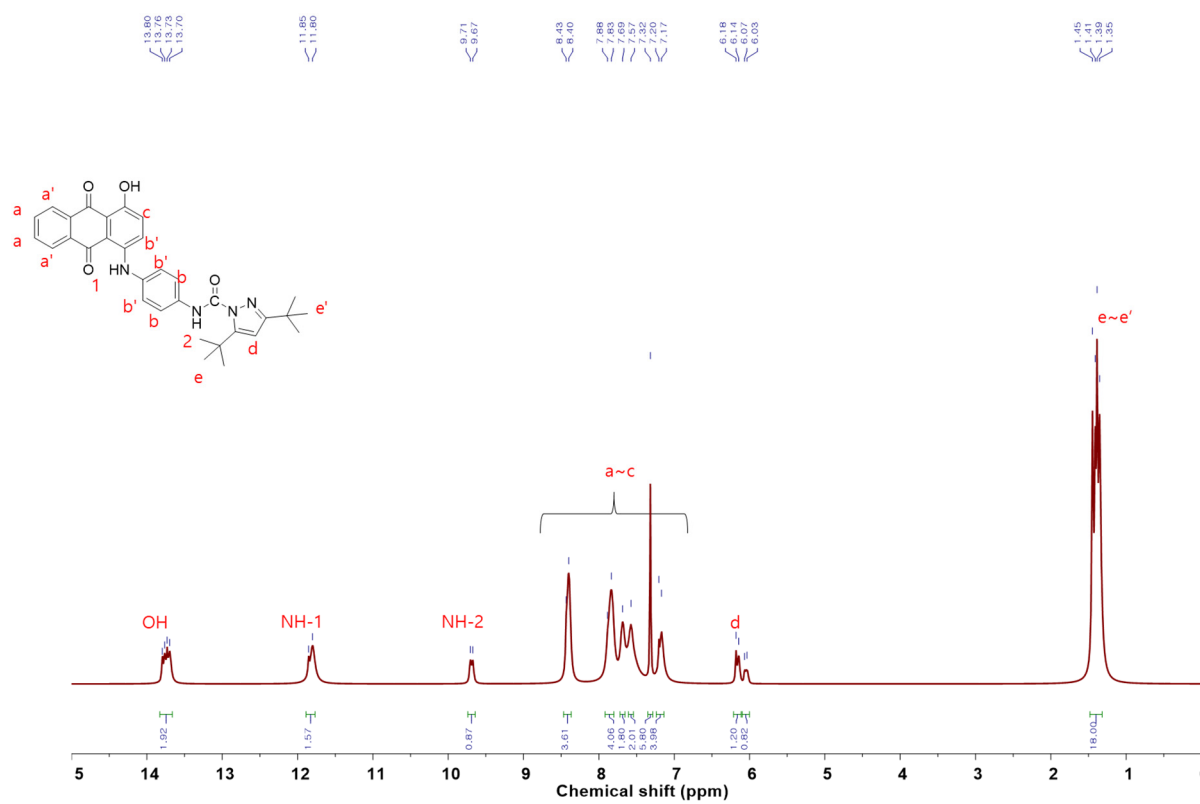


Figure S5. H-NMR spectrum of DTP-A