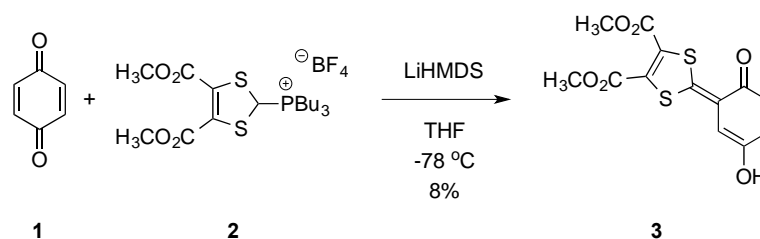


Supporting information

S1. General methods

The chemicals were used as purchased from commercial sources. THF was distilled from a sodium/benzophenone couple. Compound **2** was synthesized by literature procedure (Sato *et al.*, 1979). Flash column chromatography was carried out using silica gel (40-63 μm). Thin-layer chromatography (TLC) was performed using aluminum sheets precoated with silica gel (silica gel 60 F₂₅₄). ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on an instrument with cryoprobe using the residual solvent as the internal standard (DMSO-d₆ $\delta_{\text{H}} = 2.50$ ppm and $\delta_{\text{C}} = 39.52$ ppm). All the chemical shifts are quoted on the δ scale (ppm), and all coupling constants (*J*) are expressed in Hz. In the ¹³C APT spectrum, CH and CH₃ correspond to the negative signals and C and CH₂ to positive signals. The high-resolution mass spectrum (HRMS) was recorded in positive mode on a MALDI FT-ICR instrument equipped with a 7T magnet, using dithranol as the matrix. The melting point is uncorrected. UV-Vis spectroscopic measurements were performed in a 1-cm path length quartz cuvette and all the UV-Vis spectra are solvent corrected. Elemental Analysis was performed at London Metropolitan University.

S2. Experimental



A solution of *p*-benzoquinone **1** (336 mg, 3.11 mmol) in distilled THF (10 mL) was cooled to -78 °C on a dry-ice bath and placed under argon atmosphere. In another flask, the phosphonium salt **2** (2.35 g, 4.63 mmol) was dissolved in distilled THF (40 mL) and also cooled to -78 °C and placed under argon. LiHMDS base was slowly added to the salt solution; an intense red color was observed, and after stirring for 5 min, the solution was cannulated into the flask with the quinone solution under argon. The reaction mixture was stirred for 1 h at -78 °C, before the solvent was evaporated by a flow of nitrogen, while the mixture was kept at 0 °C on an ice bath. Purification by flash column chromatography (40-63 μm SiO₂, 20% EtOAc/CH₂Cl₂) afforded **3** (83 mg, 8%) as a deep purple solid. TLC (20% EtOAc/CH₂Cl₂): R_f = 0.33. M.p. 218-220 °C. ¹H NMR (DMSO-d₆, 500 MHz) δ = 9.70 (s, 1H), 7.15 (dd, *J* = 9.7, 2.9 Hz, 1H), 6.63 (d, *J* = 9.7 Hz, 1H), 6.50 (d, *J* = 2.9 Hz, 1H), 8.35 (s, 6H) ppm. ¹³C NMR (DMSO-d₆, 125 MHz) δ = 174.88, 159.61, 158.03, 147.60, 135.20, 126.11, 120.69,

102.70, 53.95 ppm; two carbon signals are missing. HRMS (MALDI+): $m/z = 326.99912$ $[M+H^+]$.
Calcd. ($C_{13}H_{11}O_6S_2^+$): $m/z = 326.99916$. Elem. Anal. Calcd. ($C_{13}H_{10}O_6S_2$): C 47.85%, H 3.09%;
Found: C 47.53%, H 2.98%. UV-Vis: $\lambda_{\text{acetonitrile}}$ (ϵ) = 350 nm ($6.51 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 522 nm ($10.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$);
 $\lambda_{\text{dichloromethane}}$ (ϵ) = 351 nm ($5.39 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 520 nm ($8.99 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

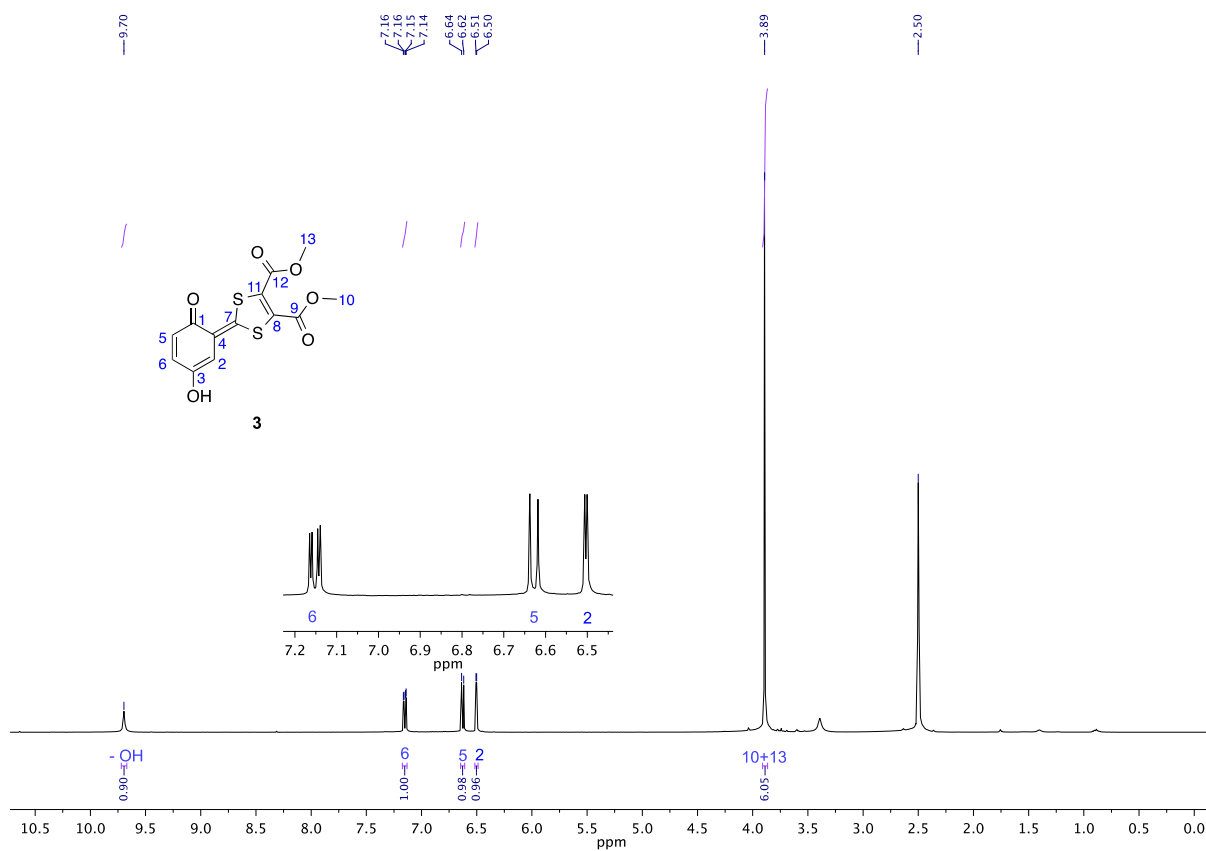
S2.1. ^1H NMR spectrum, **3**.

Figure S1 ^1H NMR spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

^1H NMR (DMSO-d_6 , 500 MHz) δ = 9.70 (s, 1H), 7.15 (dd, J = 9.7, 2.9 Hz, 1H), 6.63 (d, J = 9.7 Hz, 1H), 6.50 (d, J = 2.9 Hz, 1H), 8.35 (s, 6H) ppm.

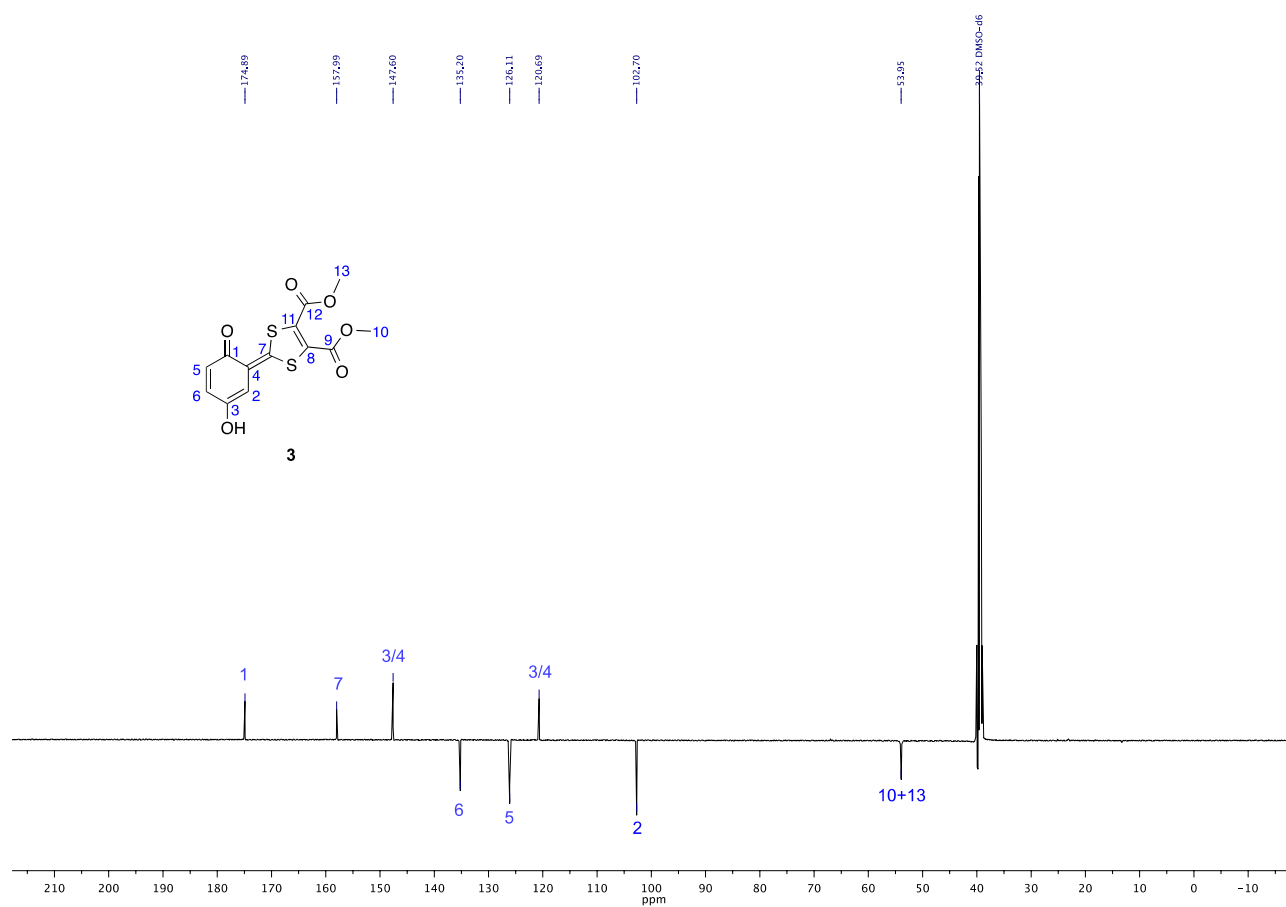
S2.2. ^{13}C APT NMR spectrum, **3.**

Figure S2 ^{13}C APT NMR spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

^{13}C APT NMR (DMSO-d_6 , 125 MHz) $\delta = 174.89, 157.99, 147.60, 135.20, 126.11, 120.69, 102.70, 53.95$ ppm.

Four carbon signals (8, 9, 11 and 12) are missing.

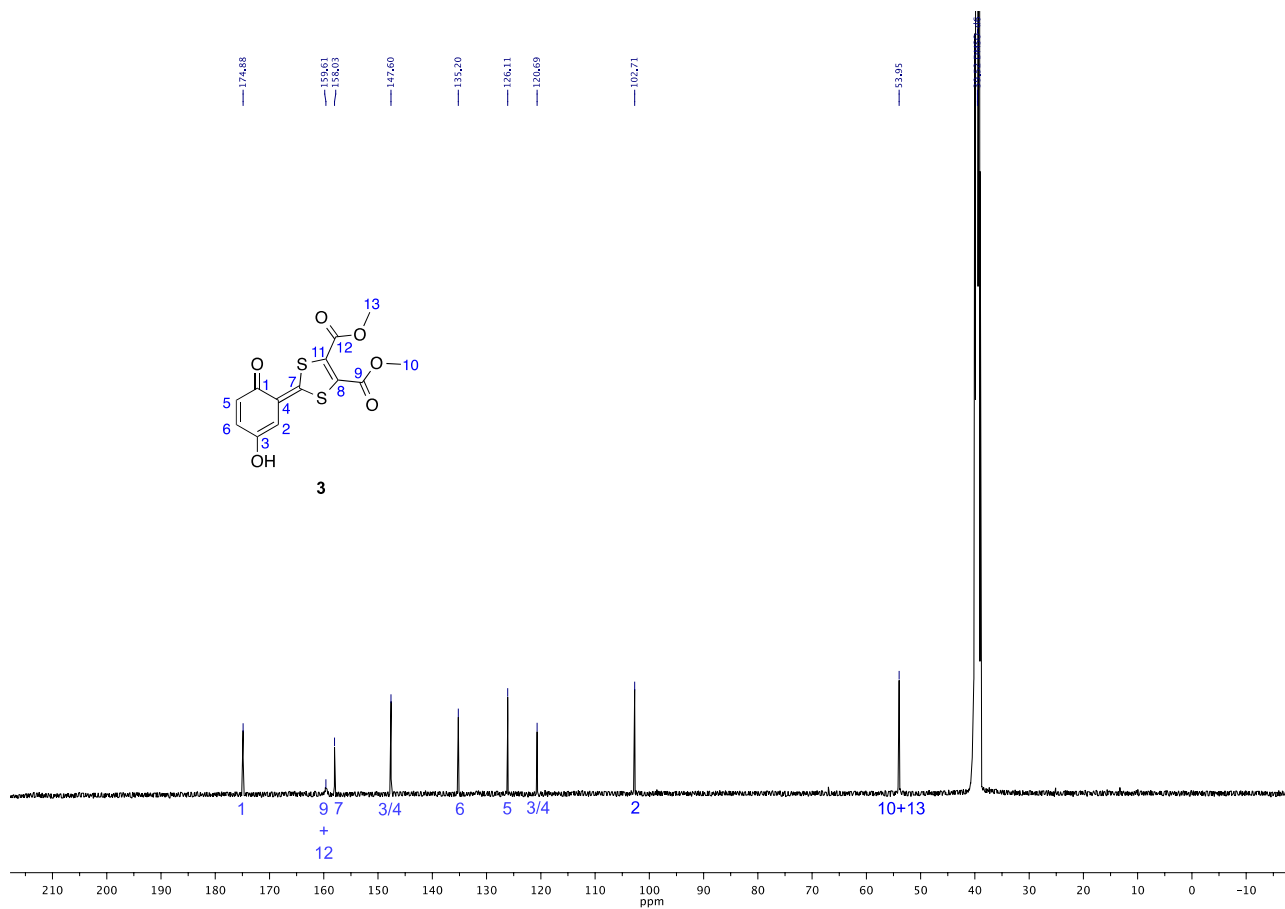
S2.3. ^{13}C NMR spectrum, 3.

Figure S3 ^{13}C NMR spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

^{13}C NMR (DMSO- d_6 , 125 MHz) δ = 174.88, 159.61, 158.03, 147.60, 135.20, 126.11, 120.69, 102.70, 53.95 ppm.

Two carbon signals (8 and 11) are missing.

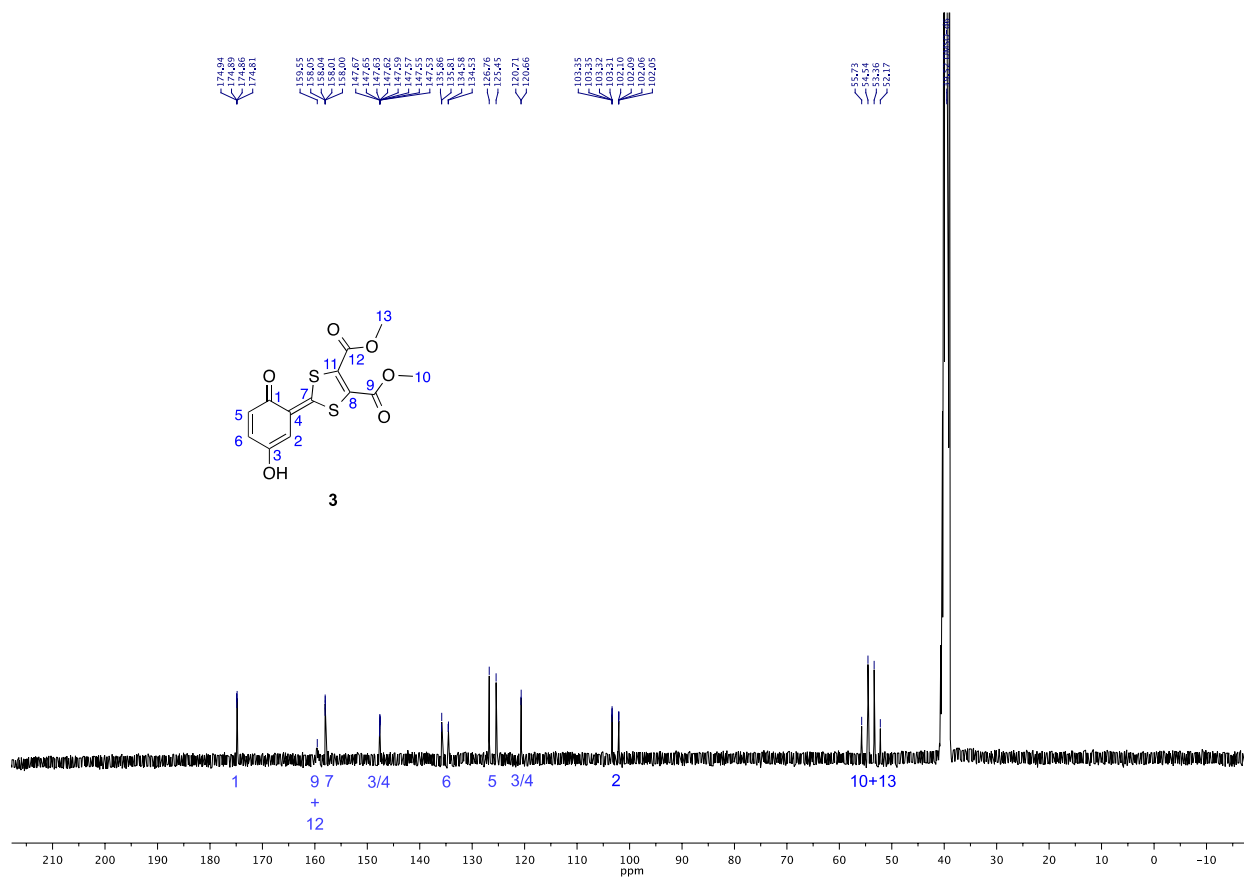
S2.4. ^{13}C GDNR spectrum, **3**.

Figure S4 ^{13}C GDNR spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

^{13}C GDNR (DMSO- d_6 , 125 MHz) δ = 174.88 (dd, J = 6.3, 10.1 Hz), 159.50 (m), 158.03 (dd, J = 1.3, 4.4 Hz), 147.60 (ddd, J = 2.4, 4.6, 10.5 Hz), 135.20 (dd, J = 6.5, 160.6 Hz), 126.11 (d, J = 164.7 Hz), 120.69 (d, J = 5.4 Hz), 102.70 (ddd, J = 1.0, 4.5, 158.4 Hz), 53.95 (d, J = 149.2 Hz) ppm.

Two carbon signals (8 and 11) are missing.

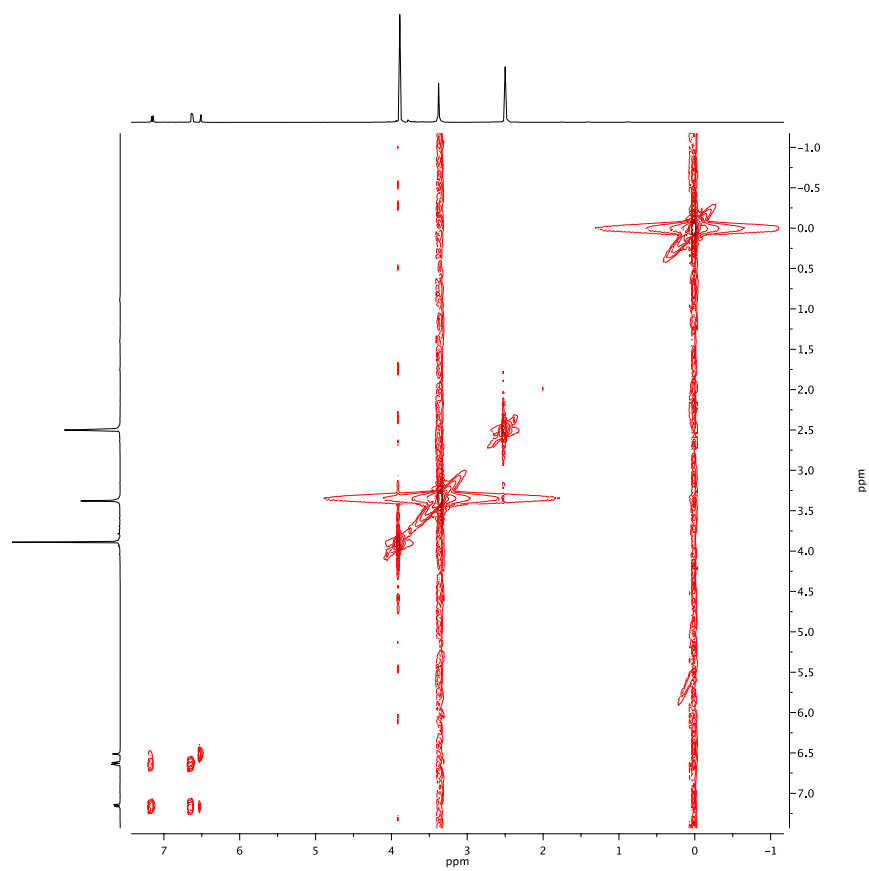
S2.5. ^1H COSY spectrum, **3.**

Figure S5 $^1\text{H}/^{13}\text{C}$ HMBC spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

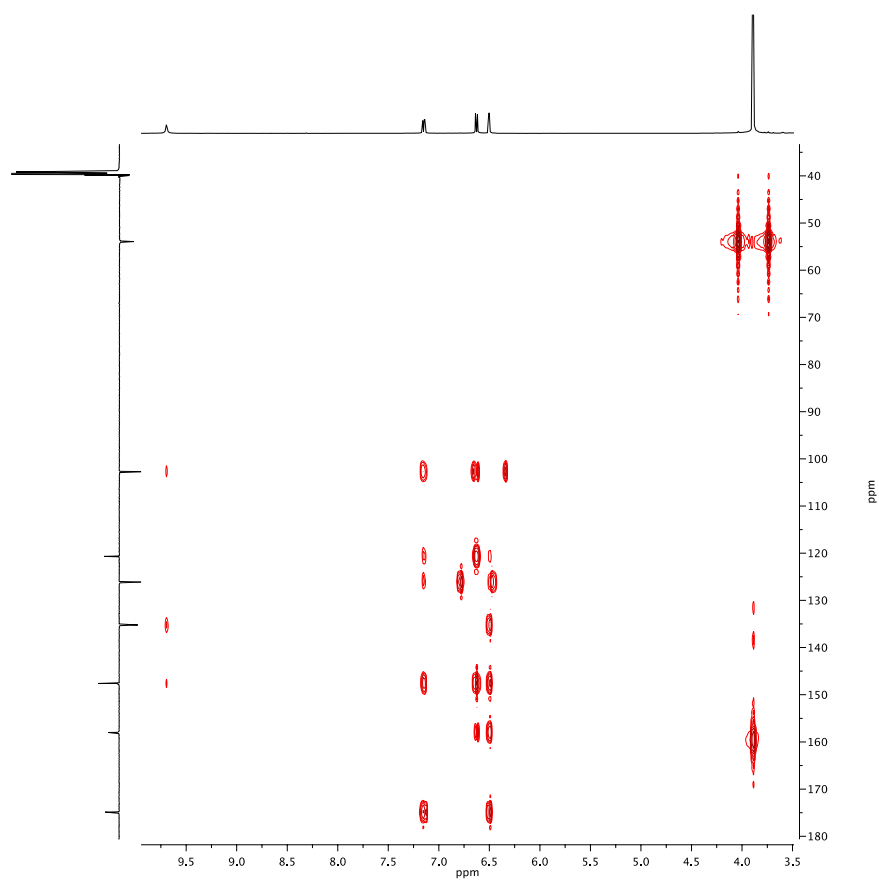
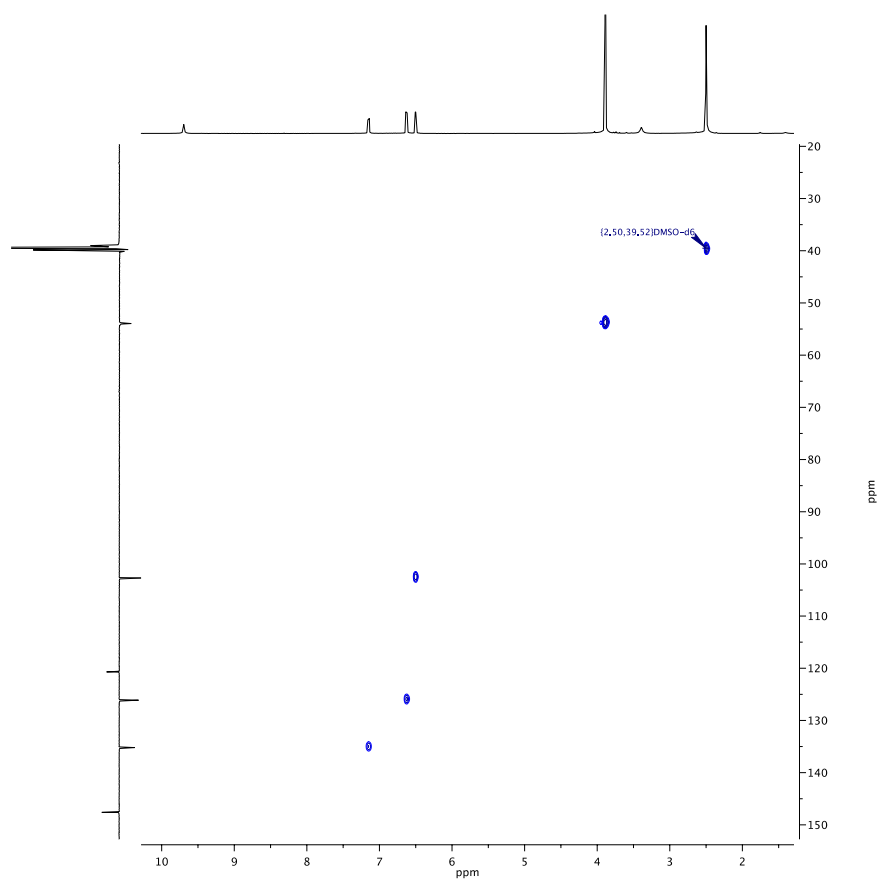
S2.6. $^1\text{H}/^{13}\text{C}$ HMBC spectrum, 3.

Figure S6 $^1\text{H}/^{13}\text{C}$ HMBC spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

S2.7. $^1\text{H}/^{13}\text{C}$ HSQC spectrum, **3.**

$^1\text{H}/^{13}\text{C}$ HSQC spectrum of the Michael adduct **3** recorded in deuterated dimethylsulfoxide.

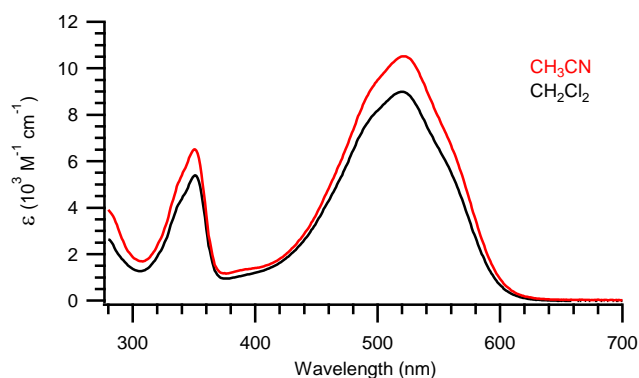
S2.8. UV-Vis spectroscopy, 3.

Figure S7 UV-Vis absorption spectra of compound **3** in CH_3CN (red curve) and CH_2Cl_2 (black curve) at 25 °C.

Table S1 Absorption maxima (λ) and molar absorptivities (ϵ) for compound **3** in CH_3CN and CH_2Cl_2 at 25 °C.

	λ_1 (nm)	ϵ_1 ($\text{M}^{-1} \text{ cm}^{-1}$)	λ_2 (nm)	ϵ_2 ($\text{M}^{-1} \text{ cm}^{-1}$)
CH_3CN	350	6.51×10^3	522	10.5×10^3
CH_2Cl_2	351	5.39×10^3	520	8.99×10^3