

Supporting Information for:

Coumarin-diene photoswitches for rapid and efficient isomerization with visible light.

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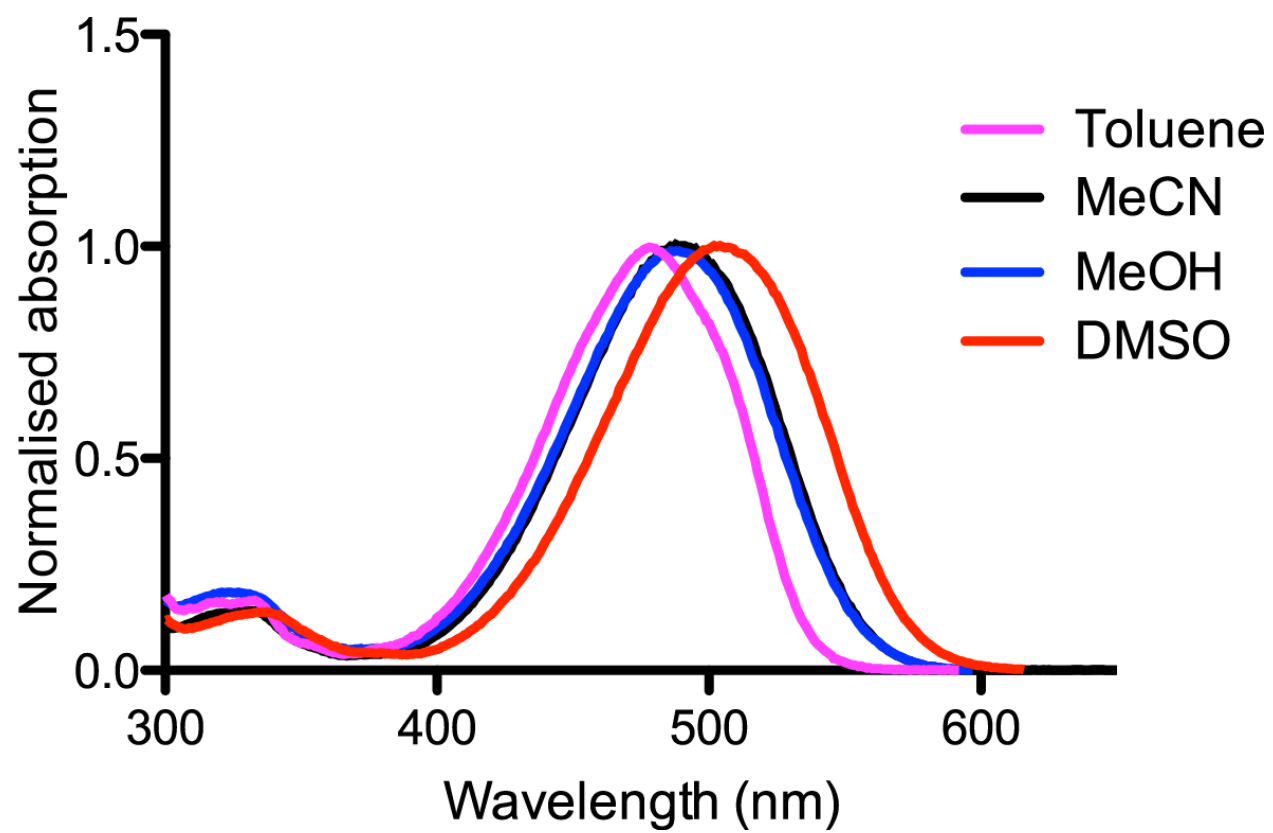


Figure S1. Normalized absorption spectra of pure *trans*-1 in various solvents.

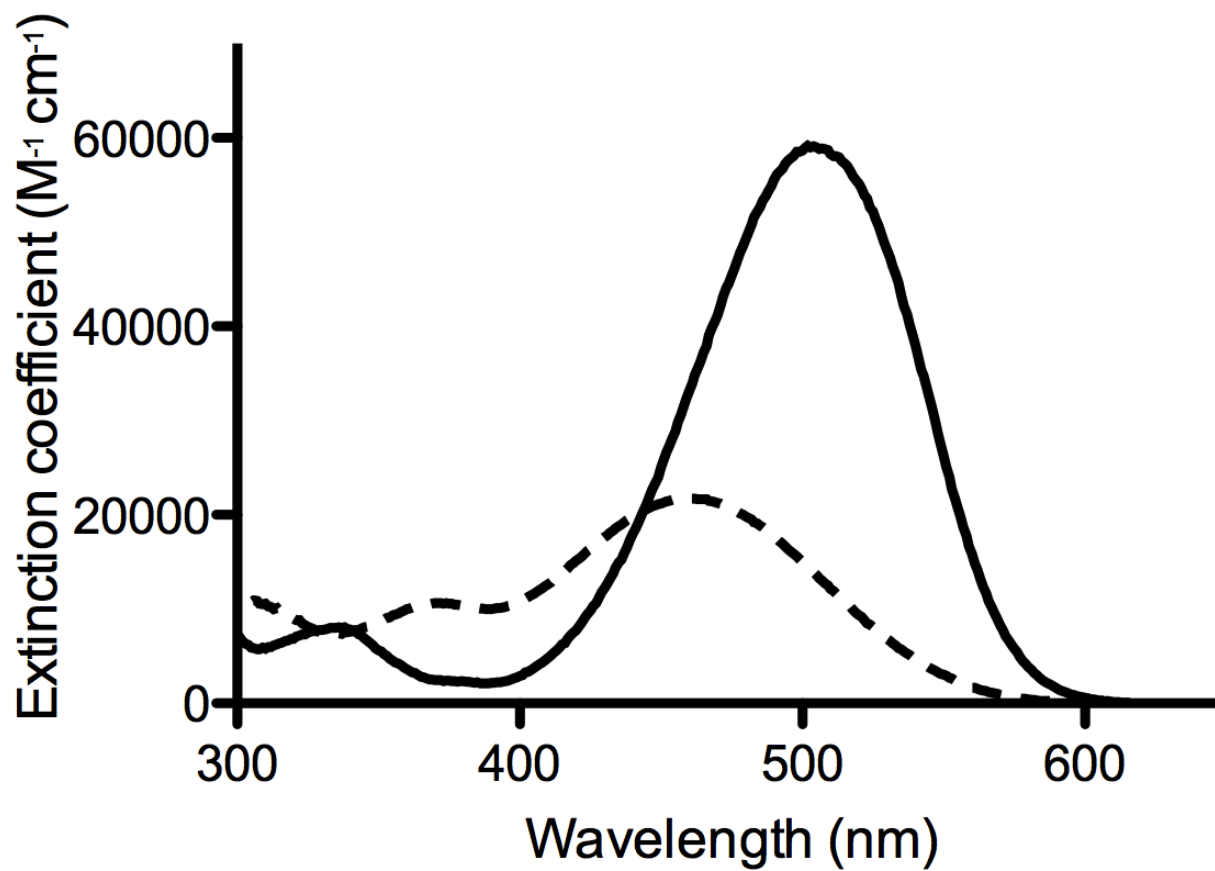


Figure S2. UV-visible absorption spectra of pure *trans*-1 in DMSO (solid line), and the calculated absorption spectrum of *cis*-1 (dashed line).

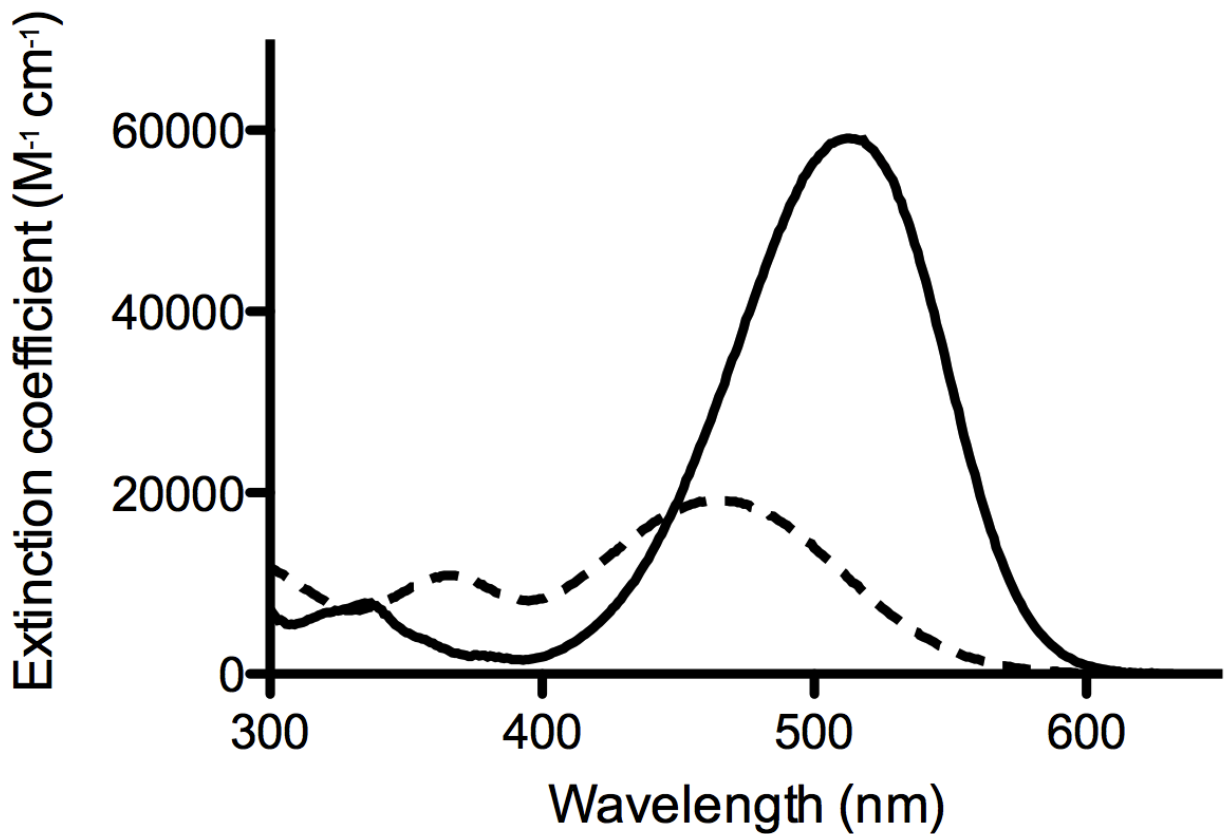


Figure S3. UV-visible absorption spectra of pure *trans*-2 in MeCN (solid line), and the calculated absorption spectrum of *cis*-2 (dashed line).

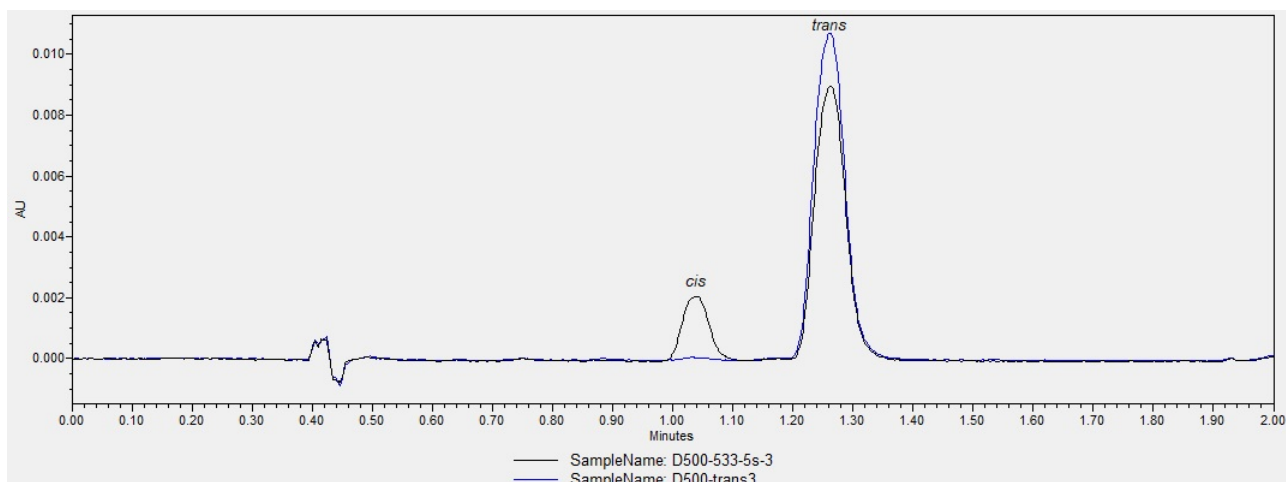


Figure S4. Representative HPLC traces from the experimental determination of the reaction quantum yield for the *trans-cis* isomerization at 533 nm. Samples of *trans*-ceCAM (blue) were irradiated with 533 nm laser light for 5 s and the percent conversion to *cis*-ceCAM was monitored at the isosbestic wavelength of 436 nm (black). Using a power meter and the UV-visible spectrum to calculate the number of photons absorbed, the *trans* to *cis* isomerization quantum yield was determined to be 0.5 (see below).

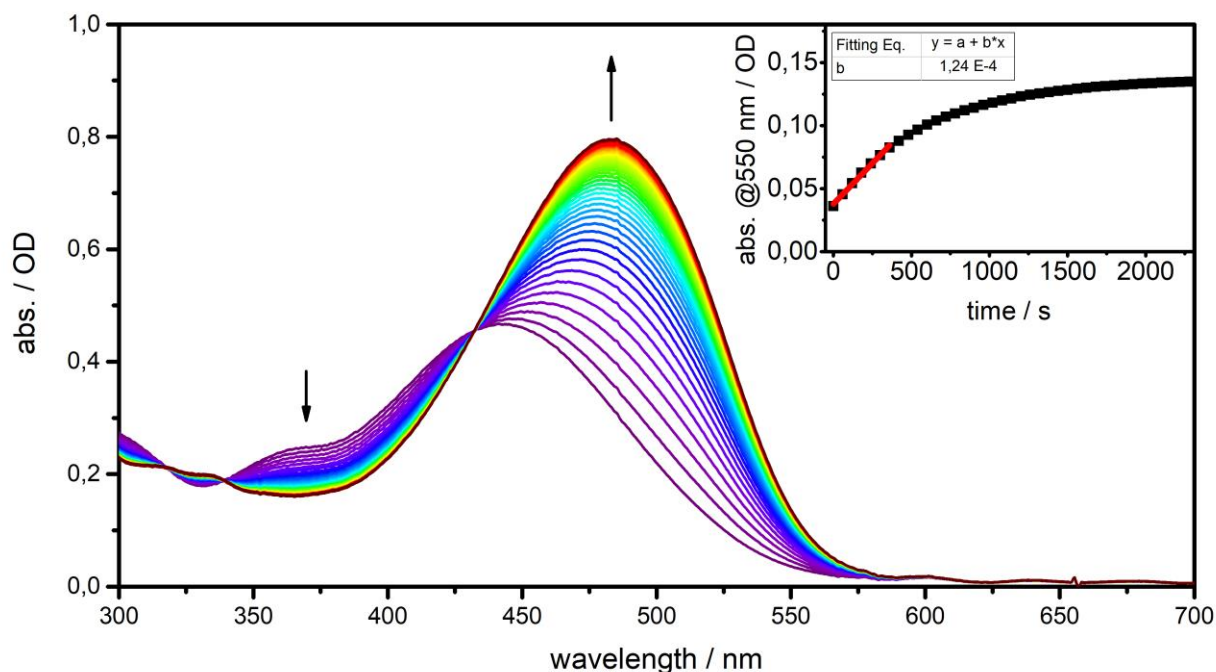


Figure S5. Experimental determination of the reaction quantum yield for the *cis-trans* isomerization reaction at 405 nm. Starting from a photostationary state (93% *cis*), the sample was irradiated with a LED with a central wavelength of 405 nm in combination with a longpass filter (OG400, Schott AG, Mainz, Germany). The time-dependent change of the absorbance was monitored. At 550 nm solely the *trans*-isomer absorbs light, therefore the absorbance at this wavelength for every spectrum the is plotted in an inset (top, right). A linear behavior was observed in the beginning, leading to an asymptotic value in the end, corresponding to the photostationary state. A linear fit of the initial absorbance change was applied, whereas the slope b represents A_{prod}/τ .

This resulted in a reaction quantum yield for the *cis-trans*-isomerization of $\phi_{\text{rqy}}(c-t) = 0.45 \pm 0.04$.

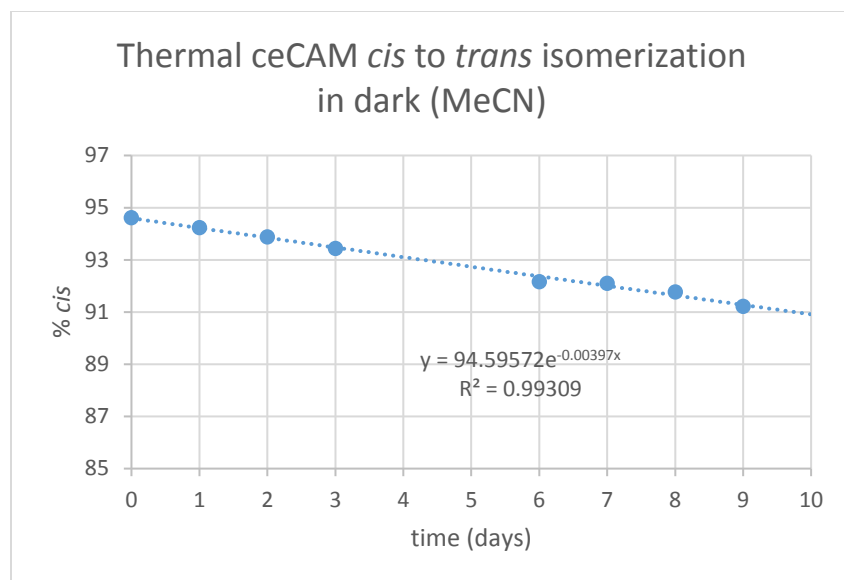


Figure S6. Thermal *cis* to *trans* isomerization of ceCAM. A solution of ceCAM in MeCN was irradiated to the photostationary state with a 530 nm LED and was stored in the dark at room temperature. The conversion of *cis*-ceCAM to *trans*-ceCAM was monitored by HPLC using isocratic elution (70% MeCN/water with 0.1% TFA) with integration of the peaks at the isosbestic point (436 nm) over the course of nine days. The percentage of *cis*-ceCAM in the *cis/trans* mixture was plotted over time and a was fitted to an exponential curve. From the curve, a half-life of 175 days can be calculated for the thermal *cis* to *trans* isomerization of ceCAM.

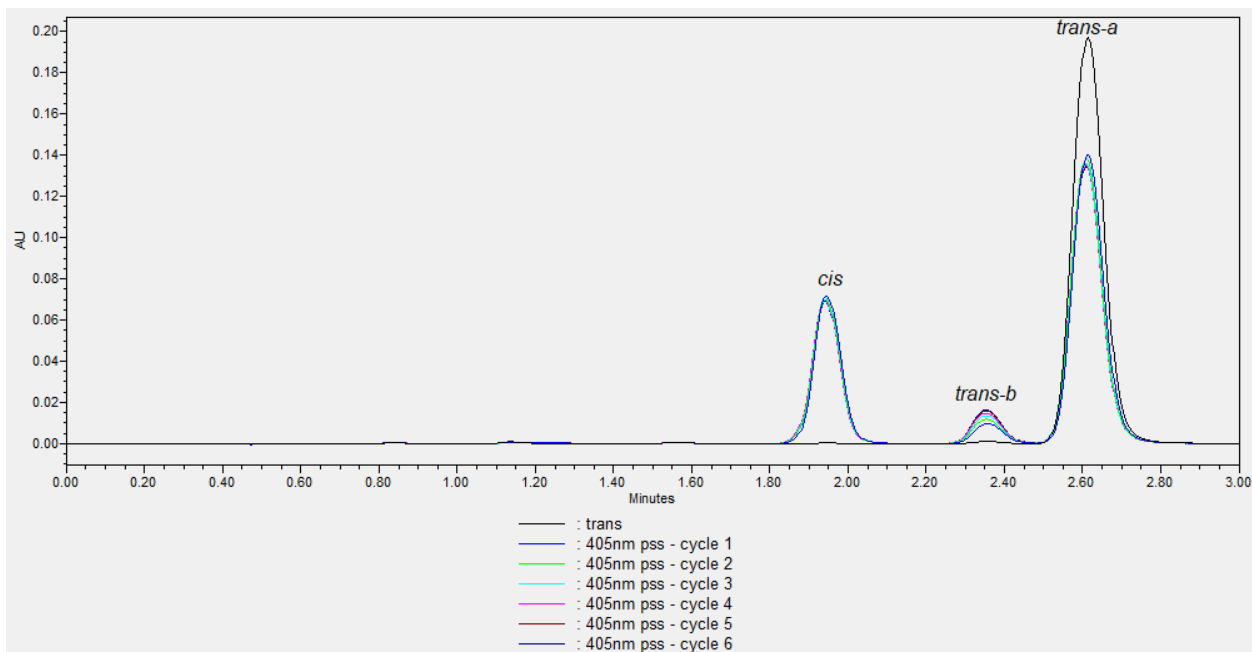


Figure S7. HPLC chromatograms of ceCAM after six cycles of photoswitching with 560 nm LED and 405 nm laser in MeCN. HPLC run with 70% MeCN/H₂O (+0.1% TFA) isocratic conditions and absorbances recorded at 436 nm, the isosbestic point for ceCAM photoswitching in this solvent system. Shown are starting *trans*-ceCAM and the six photostationary states produced from 405 nm illumination. A second *trans* isomer (*trans-b*) appears after first cycle and ratio of the original *trans* isomer (*trans-a*) to *trans-b* becomes constant after several cycles. UV-vis spectra of *trans-a* and *trans-b* are virtually identical (not shown). At sixth cycle, ratio of *trans-a* to *trans-b* is 90:10. The ratio of *cis*-ceCAM to both *trans*-ceCAM isomers is consistent at 29:71 throughout all cycles.

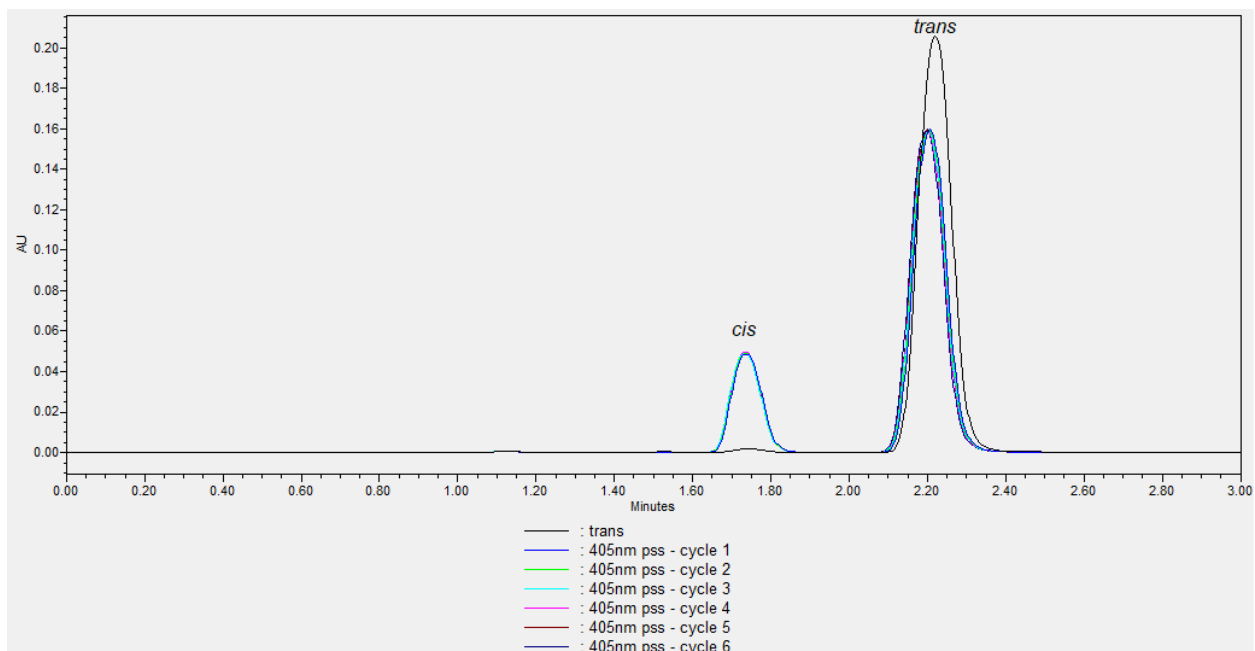


Figure S8. HPLC chromatograms of dcCAM after six cycles of photoswitching with 560 nm LED and 405 nm laser in MeCN. HPLC run with 60% MeCN/H₂O (+0.1% TFA) isocratic conditions and absorbances recorded at 452 nm, the isosbestic point for dcCAM photoswitching in this solvent system. Shown are starting *trans*-dcCAM and the six photostationary states produced from 405 nm illumination. The ratio of *cis*-dcCAM to *trans*-dcCAM is consistent at 21:79 throughout all cycles.

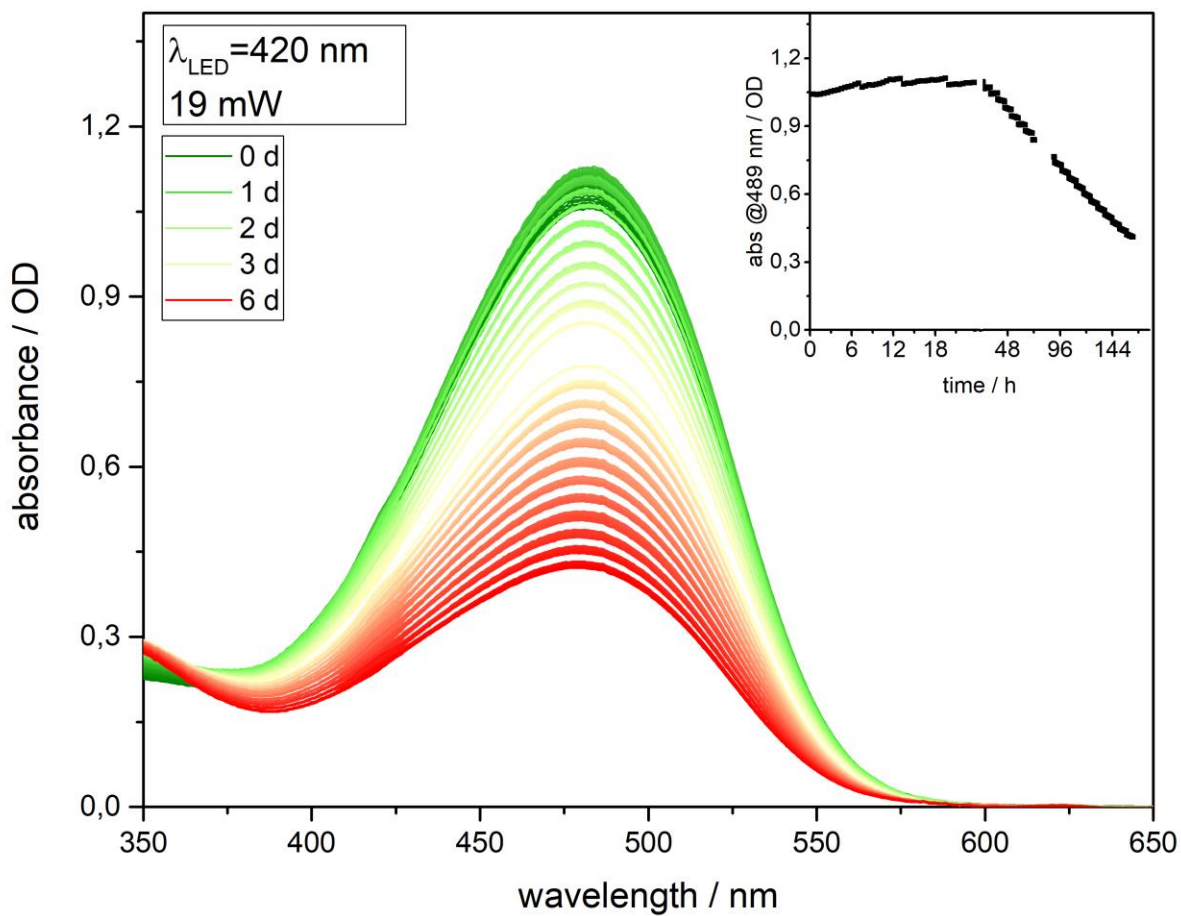


Figure S9. Photodegradation of **1** in MeCN. A solution of **1** was continuously irradiated with a 420 nm LED. After about 18 hours we could detect slow decrease in the absorption intensity.

Table S1. Summary of physical properties of ceCAM (1)

	<i>trans-1</i>	<i>cis-1</i>
ϵ^a (MeCN)	50,300 (489 nm)	18,600 (437 nm)
Abs. edge ^b (MeCN)	582 nm	545 nm
ϵ^a (DMSO)	59,000 (505 nm)	21,800 (460 nm)
Abs. edge ^b (DMSO)	600 nm	589 nm
$\Phi_{\text{isomerization}}$	0.50 (<i>trans</i> to <i>cis</i>)	0.45 (<i>cis</i> to <i>trans</i>)
$t_{1/2}^c$	-	175 d

^aExtinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$) measured at the absorbance maximum. ^bWavelength with 1% of the absorbance of λ_{max} . ^cThermal half-life.

Photolysis apparatus

Figure 1. Lasers: 405 nm and 473 nm (catalog numbers LRD-0405 and LRS-0473, Laserglow, Toronto, Canada), 533 nm (10 W Verdi, Coherent, Palo Alto, CA, USA). LED: 365 nm (catalog number M365LP1, Thorlabs, NJ, USA) with a notch filter (365/20nm, Chroma, Bellows Falls, VT, USA). Figure 2. The 365 nm LED was combined using a long-pass dichroic (387nm, Chroma) with a 530 nm LED (catalog number M530L3, Thorlabs). Figures S4 and S5. A 565 nm LED (catalog number M565L3, Thorlabs) was used. A Cary 50 spectrophotometer (Agilent, Santa Clara, CA, USA) or a Specord S600 (Analytik Jena, Jena, Germany) was used for UV-visible absorption measurements.

Calculation of *cis* spectra

UV-visible spectra were obtained for all-*trans* solutions of the photoswitch in the appropriate solvent. These solutions were then irradiated with a 530 nm-centered LED until the photostationary state (PSS) was reached and UV-visible spectra of the PSS were obtained. The *cis/trans* composition of these solutions were determined by HPLC using the relative integrated areas of the *cis* and *trans* peaks at the isobestic wavelength. The fraction of *trans* at the PSS (F_{trans}) is calculated as $Area_{trans}/(Area_{cis}+Area_{trans})$ and the fraction of *cis* at the PSS (F_{cis}) is calculated as $Area_{cis}/(Area_{cis}+Area_{trans})$. The all-*trans* spectra were transformed as $Y=Y*K$ where $K=F_{trans}$. The resulting transformed all-*trans* spectra were then subtracted from the PSS spectra. The spectra resulting from this subtraction were then transformed as $Y=Y*K$ where $K=1/F_{cis}$, resulting in calculated *cis* spectra of equimolar concentration to the starting all-*trans* solutions.

Quantum yield measurement.

The reaction quantum yield is defined as the (number of reacted molecules)/(number of photons absorbed) as shown in Equation (1):

$$\phi_{rqy} = \frac{N}{N_{\lambda}} \quad (1)$$

For the *trans* to *cis* isomerization a solution of known concentration (OD = 0.09 at 533 nm) was stirred vigorously and photolyzed with 533 nm light in a 1-cm quartz cuvette. The power of the Verdi laser was set at 200 mW and modulated with polarized beam splitter and half-wave plate (Newport, Palo Alto, CA, USA). Power was measured using a calibrated power meter (Thorlabs, catalog number S170C, Thorlabs, Newton, NJ, USA). The extent of photolysis was measured by HPLC (Acuity Arc with 2998 diode array detector, Waters, Milford, MA, USA) by isocratic elution using 20% water/80% MeCN with 0.1% TFA on a C18 4.6 mm x 50 mm column (Waters). The chromatogram was monitored at 436 nm, the isobestic point for the reaction. Starting with pure *trans*-1 ensured that all the initial light was absorbed by this conformation of the switch. We found that 6.77×10^{14} molecules (15%) were isomerized by 1.34×10^{15} absorbed photons, corresponding to a 50% quantum yield. Restricting analysis to 15% photolysis means that even at the end of the photolysis period only 0.3% of 533 nm light is absorbed by *cis*-1, thus most of the absorbed photons cause *trans* to *cis* isomerization.

For the *cis* to *trans* isomerization reaction we used the time-dependent change in the absorption spectrum (Fig. S3) to calculate the quantum yield (Megerle, U. et al., (2010) Photochem. Photobiol. Sci. 9, 1400; Slavov C. et al., (2015) Phys. Chem. Chem. Phys. 17, 14045). An LED with a central wavelength of 405 nm (FWHM = 20 nm) (M405L3, Thorlabs, Newton, NJ, USA) was used in combination with a longpass filter (GG 400, Schott, Mainz, Germany) to initialize *cis* to *trans* isomerization.

For this approach, the number of molecules which undergo a photoreaction (N) was determined using equation (2):

$$N = \frac{A_{\text{prod}} \cdot N_A \cdot V}{\epsilon_{\text{prod}} \cdot d} \quad (2)$$

Where A_{prod} : time-dependent absorbance of the photoproduct, N_A : Avogadro's number, V : sample volume, ϵ_{prod} : molar extinction coefficient of photoproduct (taken at 550 nm), d : path length of the cuvette

The number of photons absorbed by the sample is calculated via Equation (3):

$$N_{\lambda} = \frac{h \cdot c}{P_0 \cdot \lambda_{exc} \cdot \tau \cdot (1 - 10^{A_0(\lambda_{exc})})} \cdot \frac{A_{0,cis}(\lambda_{exc})}{A_{0,trans}(\lambda_{exc}) + A_{0,cis}(\lambda_{exc})} \quad (3)$$

Where h: Planck constant, c: speed of light, P₀: power applied by the LED at sample location, τ: measured time-range; λ_{exc}: excitation wavelength, A₀: initial absorbance at λ_{exc}, A₁/A₀: correction factor to only consider the reacting isomer of interest

The applied power was measured with a calibrated *Gigahertz Optic* optometer sensor (Gigahertz-Optik, Türkenfeld, Germany).

Equations (2) and (3) yield the final Equation (4):

$$\phi_{rqy} = \frac{A_{prod} \cdot N_A \cdot V}{\epsilon_{prod} \cdot d} \cdot \frac{P_0 \cdot \lambda_{exc} \cdot \tau \cdot (1 - 10^{A_0(\lambda_{exc})})}{h \cdot c} \cdot \frac{A_{0,trans}(\lambda_{exc}) + A_{0,cis}(\lambda_{exc})}{A_{0,cis}(\lambda_{exc})} \quad (4)$$

Where the slope b = A_{prod}/τ from the aforementioned linear fit is applied.

Ultrafast time-resolved spectroscopy.

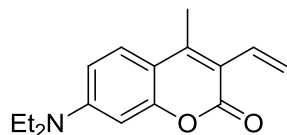
The transient absorption (TA) experiments were performed with a home-built pump-probe setup. An oscillator-amplifier system (Clark, MXR-CPA iSeries, Dexter, MI, USA) operating at a repetition rate of 1 kHz and a central wavelength of 775 nm and a pulse duration of 150 fs provided the laser pulses. For the *cis* to *trans* isomerization, the pump pulse with an excitation wavelength of 362 nm was generated via two nonlinear processes. Firstly, a pump pulse with a wavelength of 680 nm was generated in a home-built two-stage noncollinear optical parametric amplifier (NOPA) and then combined with a part of the fundamental laser pulse of 775 nm in a BBO crystal (Θ=36°), where the sum frequency was generated.

For the *trans* to *cis* isomerization, the pump pulse with an excitation wavelength of 530 nm was generated in a NOPA. For both excitation wavelengths, a prism compressor was used to compress the pump pulses to ~100 fs. The pump pulses were set to an energy of ~30-40 nJ. For the probe pulse, white light (WL) was generated as a supercontinuum in a CaF₂ window covering a range between 390 and 690 nm. The WL pulses were split into two parts: a reference and a signal pulse, whereas only the latter one passed through the sample. Both pulses were

guided to a spectrograph (AMKO Multimode, Tornesch, Germany) equipped with 600 grooves/mm gratings blazed at 300 nm and photodiode arrays (PDA, Hamamatsu Photonics, S8865-64, Hamamatsu, Japan) combined with driver circuits (Hamamatsu Photonics, C9118). The PDA signals were digitized at 12 bits by a data acquisition card (National Instruments, NI-PCI-6110, Austin, TX, USA). The experiments were conducted in fused silica cuvettes with an optical path length of 1 mm, which was moved laterally to enable the exchange of sample between individual laser pulses. The concentration of the sample was set to achieve an optical density of 0.2-0.6 at the excitation wavelength. The angle between the polarization of the pump and probe pulse was set to the magic angle ($\Theta_{\text{ma}} = 54.7^\circ$) to minimize possible effects of anisotropy. The time-resolved data were analyzed by lifetime distribution and global lifetime analysis using OPTIMUS (Slavov, C. et al. (2015) *Anal. Chem.* 87, 2328).

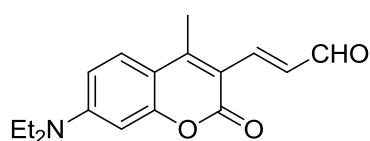
Organic synthesis.

All chemicals were purchased from commercial sources unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on Merck KGaA glass silica gel plates (60 F254) and were visualized with UV light or potassium permanganate staining followed by heating. Flash chromatography was performed using Agela Technologies industrial grade silica (200-300 mesh, 40-60 μm). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on an Oxford 300 MHz NMR spectrometer and the chemical shifts are reported in ppm using the solvent peak as the internal standard (CDCl_3 at 7.26 ppm). Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. Proton-decoupled carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on an Oxford 300 MHz NMR spectrometer and the chemical shifts are reported in ppm using the solvent peak as the internal standard (CDCl_3 at 77.00 ppm, DMF- d_7 carbonyl carbon at 163.15 ppm). High resolution mass spectral data were obtained using an Agilent G1969A ToF LC-MS.



7-(diethylamino)-4-methyl-3-vinyl-2H-chromen-2-one (4): A round-bottomed flask was charged with 3-bromo-7-(diethylamino)-4-methyl-2H-chromen-2-one (Kitamura, K. *et al.*, *Bioorg. Med. Chem. Lett.* **2014**, 24

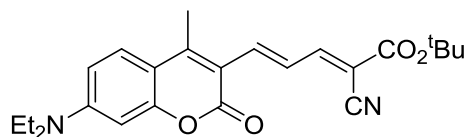
(24), 5660–5662) **3** (1.0 g, 3.22 mmol, 1.0 equiv) which was then dissolved in 1,2-dimethoxyethane (15 mL). To this solution was added tetrakis(triphenylphosphine)palladium(0) (74 mg, 0.0645 mmol, 0.02 equiv), potassium carbonate (445 mg, 3.22 mmol, 1.0 equiv), water (5 mL) and trivinylboroxin-pyridine complex (387 mg, 1.61 mmol, 0.5 equiv) and this solution was sparged with nitrogen gas for 20 min. The solution was heated to reflux temperature under nitrogen atmosphere for 18 h, then removed from heat. Water was added, and the reaction mixture was extracted with DCM (x3), washed with brine, dried over Na₂SO₄, filtered and concentrated. After purification by column chromatography (10% EtOAc/Hex), 742.3 mg of **4** were obtained as a yellow oil (90% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.29 (d, *J* = 8.6 Hz, 1H), 6.59 (dd, *J* = 17.2, 11.0 Hz, 1H), 6.46 (dd, *J* = 10.2, 3.1 Hz, 1H), 6.30 (d, *J* = 2.9 Hz, 1H), 5.95 (dd, *J* = 17.5, 2.3 Hz, 1H), 5.39 (dd, *J* = 11.5, 2.3 Hz, 1H), 3.28 (q, *J* = 7.3 Hz, 4H), 2.27 (s, 3H), 1.09 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 154.1, 149.7, 147.3, 129.1, 125.8, 119.4, 115.5, 109.2, 108.3, 96.6, 44.3, 14.5, 12.1; ESI-MS *m/z* calc'd for C₁₆H₁₉NO₂ [M+H]⁺ 258.1489, found 258.1480.



(E)-3-(7-(diethylamino)-4-methyl-2-oxo-2H-chromen-3-yl)acrylaldehyde (5): A dry, round-bottomed flask was charged with anhydrous DMF (2 mL) and was cooled in an ice bath under

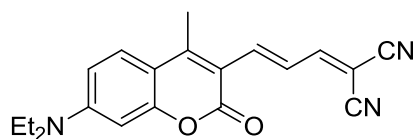
nitrogen atmosphere. To this mixture was slowly added phosphorous oxychloride (109 μL, 1.17 mmol, 3.0 equiv) and the resulting solution was stirred at room temperature for 30 min. After this time, the reaction mixture was once again cooled in an ice bath and a solution of **4** (100 mg, 0.388 mmol, 1.0 equiv), dissolved in anhydrous DMF (3 mL), was slowly added, leading to a dark red solution. After 1 h, 1 M aq. NaOH (15 mL) was added, resulting in a yellow precipitate. The solution was extracted with DCM (x3), washed with brine, dried over Na₂SO₄, filtered and concentrated. After purification by column chromatography (40% EtOAc/Hex – 60% EtOAc/Hex), 77.9 mg of **5** were obtained as a yellow solid (70% yield). ¹H NMR (300 MHz,

CDCl₃) δ 9.61 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 11.4 Hz, 1H), 7.51 (d, *J* = 4.9 Hz, 1H), 7.29 (dd, *J* = 15.5, 7.9 Hz, 1H), 6.61 (dd, *J* = 9.5, 2.9 Hz, 1H), 6.41 (d, *J* = 2.6 Hz, 1H), 3.42 (q, *J* = 7.1 Hz, 4H), 2.52 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 194.9, 159.5, 155.7, 153.7, 151.7, 144.9, 131.2, 127.3, 112.2, 109.4, 109.1, 96.8, 44.8, 14.9, 12.4; ESI-MS *m/z* calc'd for C₁₇H₁₉NO₃ [M+H]⁺ 286.1438, found 286.1439.



***trans*-ceCAM (1):** Note – this procedure was performed under red-filtered light. To a dry, round-bottomed flask was added **5** (100 mg, 0.351 mmol, 1.0 equiv) and absolute

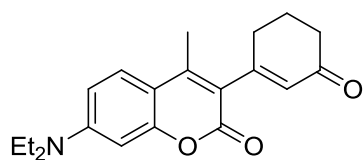
ethanol (15 mL). To this mixture, *t*-butyl cyanoacetate (65.0 μL, 0.456 mmol, 1.3 equiv) and piperidine (3.5 μL, 0.035 mmol, 0.1 equiv) were added, leading to a dark red solution which was heated at reflux temperature for 1 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo and the crude product was purified by column chromatography (20% EtOAc/DCM), resulting in the isolation of 130.2 mg of **1** as red crystals (91% yield). The product was subsequently recrystallized in ethanol to remove trace impurities. ¹H NMR (300 MHz, CDCl₃) δ 7.92–7.83 (m, 2H), 7.53 (d, *J* = 9.5 Hz, 1H), 7.35 (dd, *J* = 10.2, 4.2 Hz, 1H), 6.63 (dd, *J* = 9.3, 2.7 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 3.45 (q, *J* = 7.5 Hz, 4H), 2.52 (s, 3H), 1.55 (s, 9H), 1.24 (t, *J* = 6.0 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 161.8, 159.6, 156.3, 155.6, 152.8, 151.6, 141.0, 127.2, 126.6, 115.0, 113.3, 109.5, 109.4, 104.5, 97.0, 82.9, 44.9, 28.0, 14.9, 12.5; ESI-MS *m/z* calc'd for C₂₄H₂₈N₂O₄ [M+H]⁺ 409.2122, found 409.2123. An NMR solution of the *trans* isomer in CDCl₃ was irradiated with a 565 nm-centered LED to give a photostationary state that was mostly *cis*-**1**: ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, *J* = 12.2 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.09–6.86 (m, 2H), 6.81–6.73 (m, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.45 (q, *J* = 7.0 Hz, 4H), 2.29 (s, 3H), 1.51 (s, 9H), 1.24 (t, *J* = 7.8 Hz, 6H).



***trans*-dcCAM (2):** Note – this procedure was performed under red-filtered light. To a dry, round-bottomed flask was added **5** (214.8 mg, 0.753 mmol, 1.0 equiv) and absolute ethanol (15

mL). To this mixture, malononitrile (64.7 mg, 0.979 mmol, 1.3 equiv) and piperidine (7.4 μL,

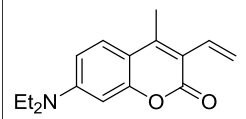
0.0753 mmol, 0.1 equiv) were added, leading to a dark red solution which was heated at reflux temperature for 1 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo and the crude product was purified by column chromatography (DCM – 10% EtOAc/DCM), resulting in the isolation of 222.0 mg of **2** as purple crystals (88% yield). The product was subsequently recrystallized in EtOAc to remove trace impurities. ¹H NMR (300 MHz, CDCl₃) δ 8.11–7.98 (m, 1H), 7.61–7.48 (m, 2H), 7.37 (d, *J* = 14.8 Hz, 1H), 6.72 (dd, *J* = 9.3, 2.5 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.47 (q, *J* = 6.9 Hz, 4H), 2.55 (s, 3H), 1.25 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (75 MHz, DMF-*d*₇) δ 164.9, 160.1, 158.5, 157.3, 153.9, 146.5, 129.8, 125.2, 116.1, 114.2, 112.8, 111.3, 110.6, 97.4, 78.7, 45.7, 15.2, 13.2; ESI-MS *m/z* calc'd for C₂₀H₁₉N₃O₂ [M+H]⁺ 334.1551, found 334.1549. An NMR solution of the *trans* isomer in CDCl₃ was irradiated with a 565 nm-centered LED to give a photostationary state that was mostly *cis*-**2**: ¹H NMR (300 MHz, CDCl₃) δ 7.62–7.46 (m, 2H), 7.10 (d, *J* = 11.2 Hz, 1H), 6.85 (dd, *J* = 11.8, 11.8 Hz, 1H), 6.73 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 4H), 2.34 (s, 1H), 1.24 (t, *J* = 7.1 Hz, 6H).



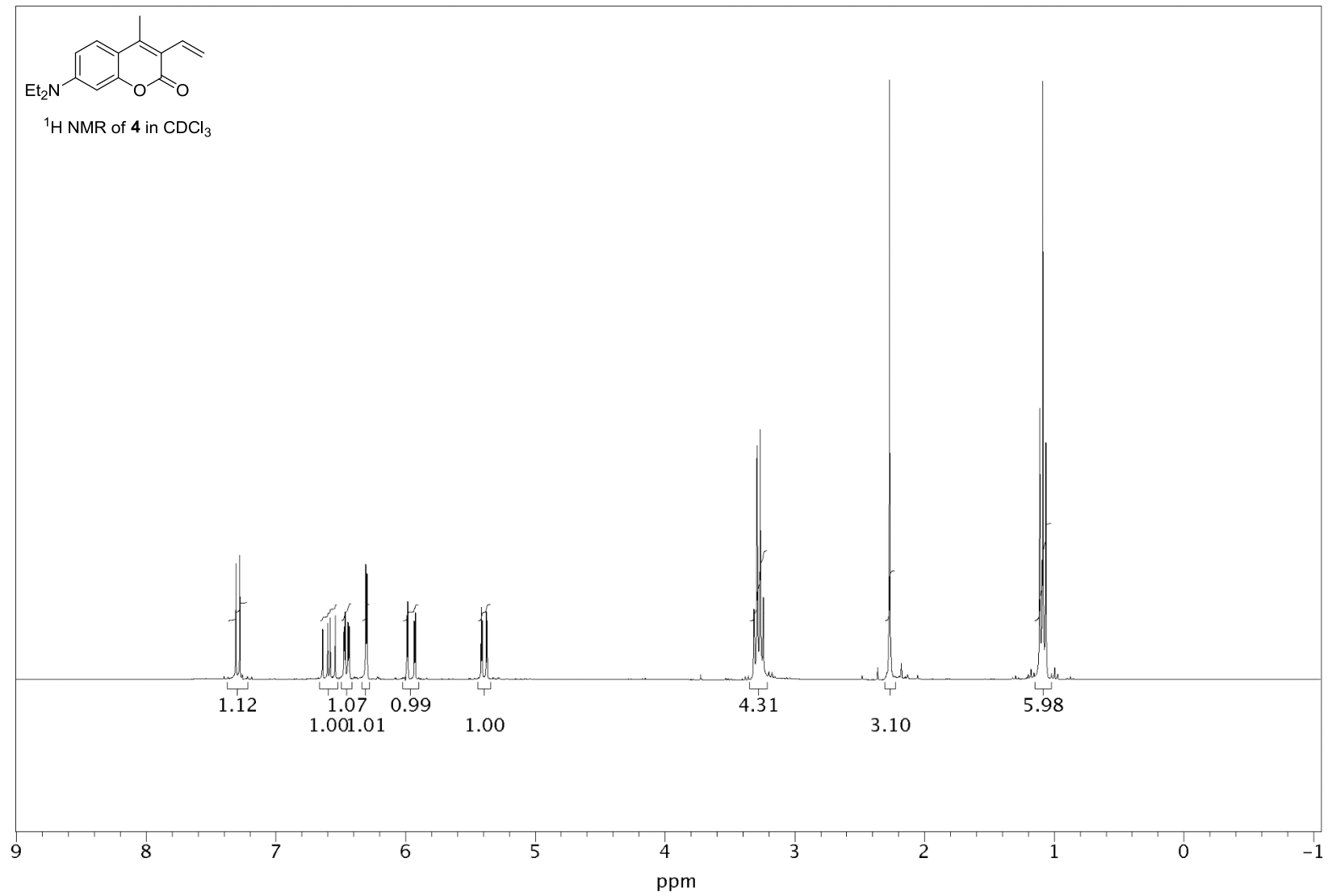
7-(diethylamino)-4-methyl-3-(3-oxocyclohex-1-en-1-yl)-2H-chromen-2-one (6):

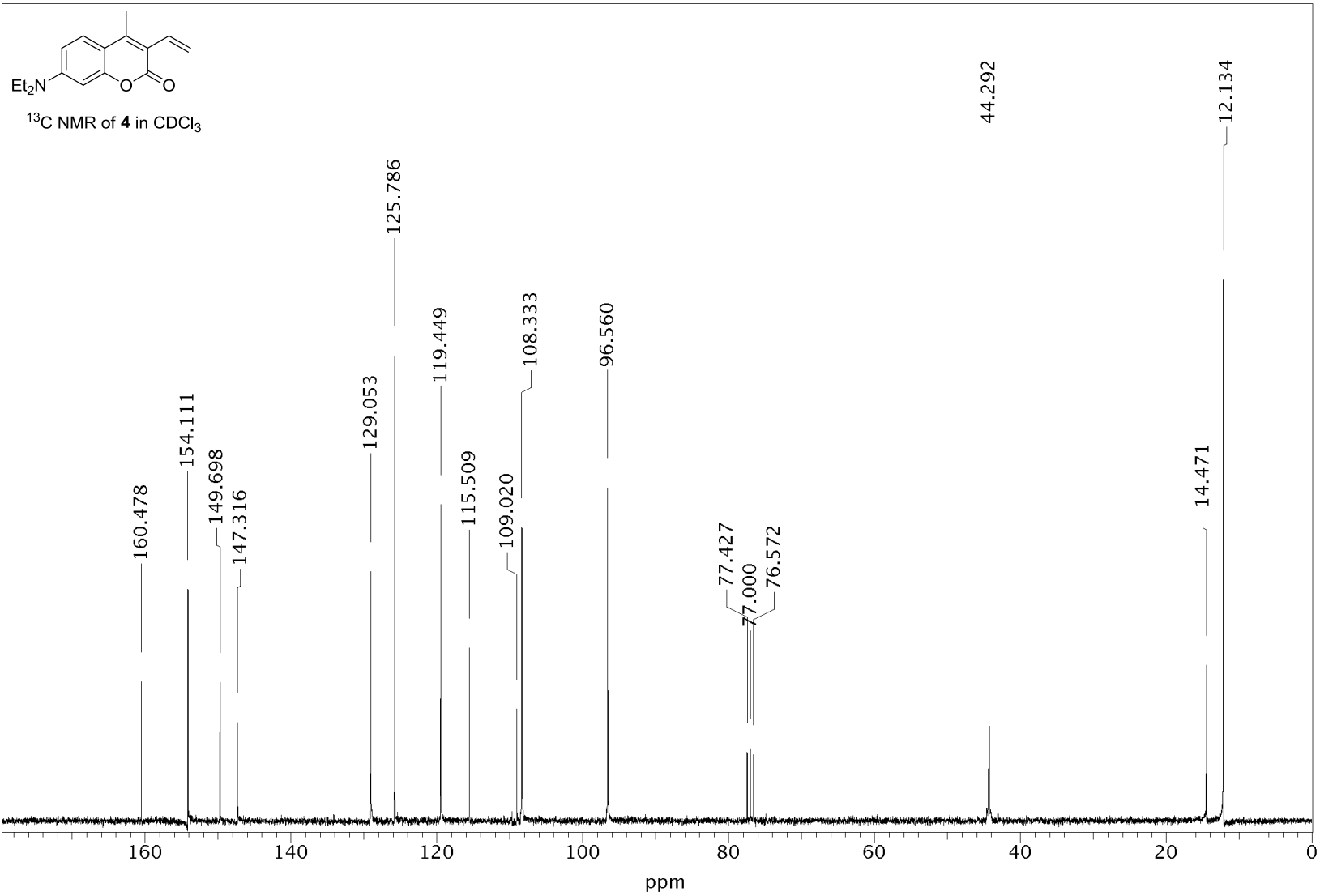
A round-bottomed flask was charged with 3-bromo-7-(diethylamino)-4-methyl-2H-chromen-2-one (Kitamura, K. *et al.*, *Bioorg. Med. Chem. Lett.* **2014**, 24 (24), 5660–5662) **3** (0.3722 g, 1.2 mmol, 1.2 equiv), followed by 1,4-dioxane (4 mL) and 3-(boronic acid pinacol ester)-cyclohex-2-enone (Burger, M. T. *et al.*, US Patent 2010056576 (A1), March 4, 2010) (0.2221 g, 1.0 mmol, 1.0 equiv). To this solution was added a solution of potassium carbonate (0.1382 g, 1.0 mmol, 1.0 equiv) in water (0.5 mL). After sparging with nitrogen gas for 10 min, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (36.6 mg, 0.05 mmol, 0.05 equiv) was added and the reaction mixture was heated at reflux temperature under nitrogen atmosphere. After 2 h, the reaction was cooled to room temperature, EtOAc was added and the solution was filtered through a pad of celite. Water was added to the filtrate and the organics were extracted with EtOAc (x3), washed with brine, dried over Na₂SO₄, filtered and concentrated. After purification by column chromatography (DCM – 30% EtOAc/DCM), 132.4 mg of **6** were obtained as a yellow oil (41% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J* = 9.1 Hz, 1H), 6.58

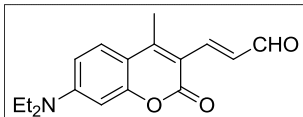
(dd, $J = 9.7, 2.6$ Hz, 1H), 6.45 (d, $J = 2.6$ Hz, 1H), 5.92–5.88 (m, 1H), 3.39 (q, $J = 7.6$ Hz, 4H), 2.61–2.52 (m, 2H), 2.47 (t, $J = 6.3$ Hz, 2H), 2.28 (s, 3H), 2.18–2.07 (m, 2H), 1.17 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.2, 159.8, 158.6, 154.8, 150.3, 147.5, 130.5, 126.2, 119.8, 108.7, 108.5, 44.7, 37.5, 29.9, 22.9, 15.9, 12.4; ^{13}C NMR; ESI-MS m/z calc'd for $\text{C}_{20}\text{H}_{23}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 326.1751, found 326.1753.



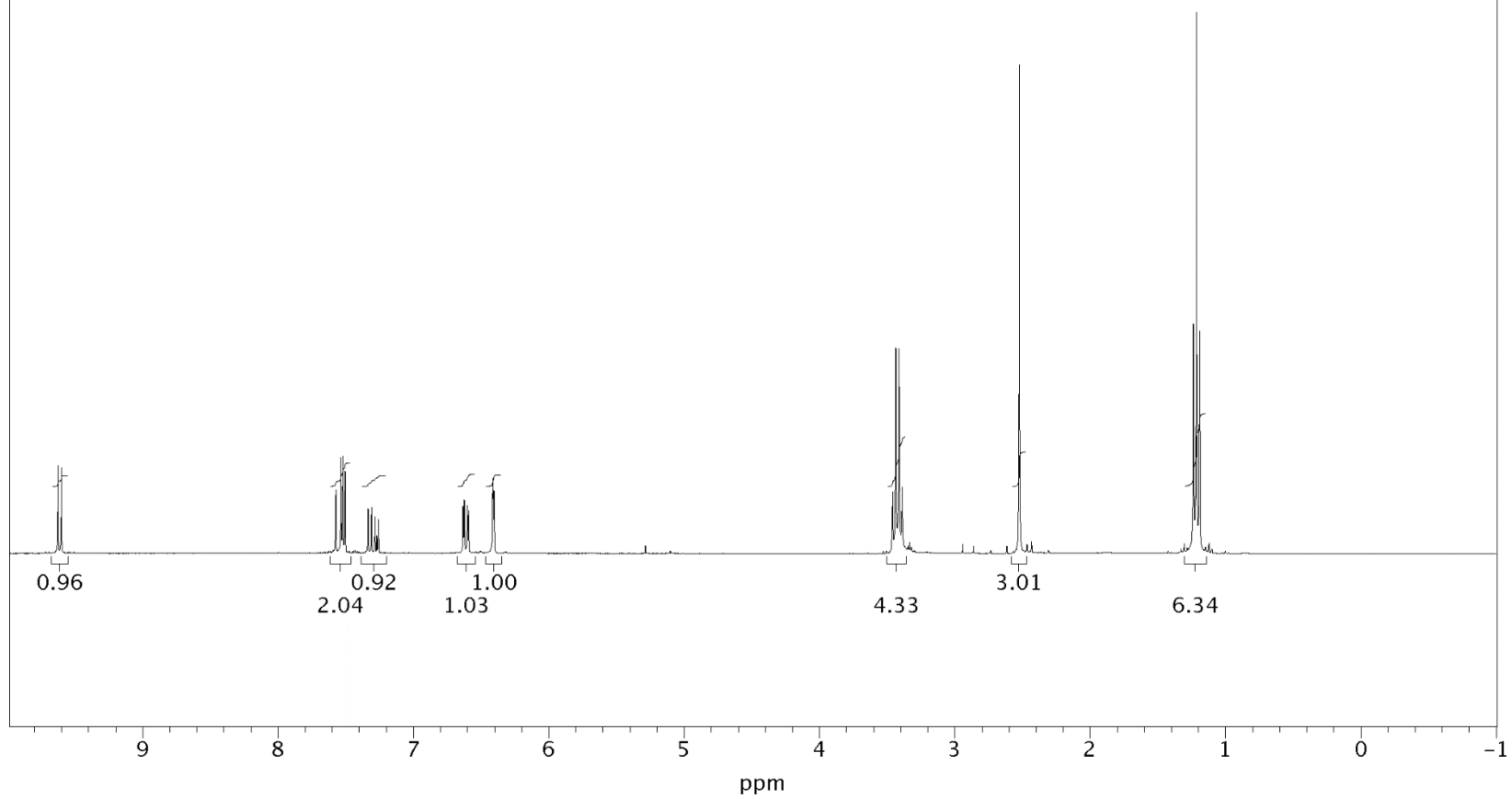
¹H NMR of **4** in CDCl₃

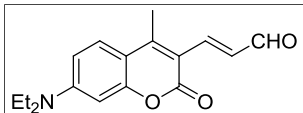




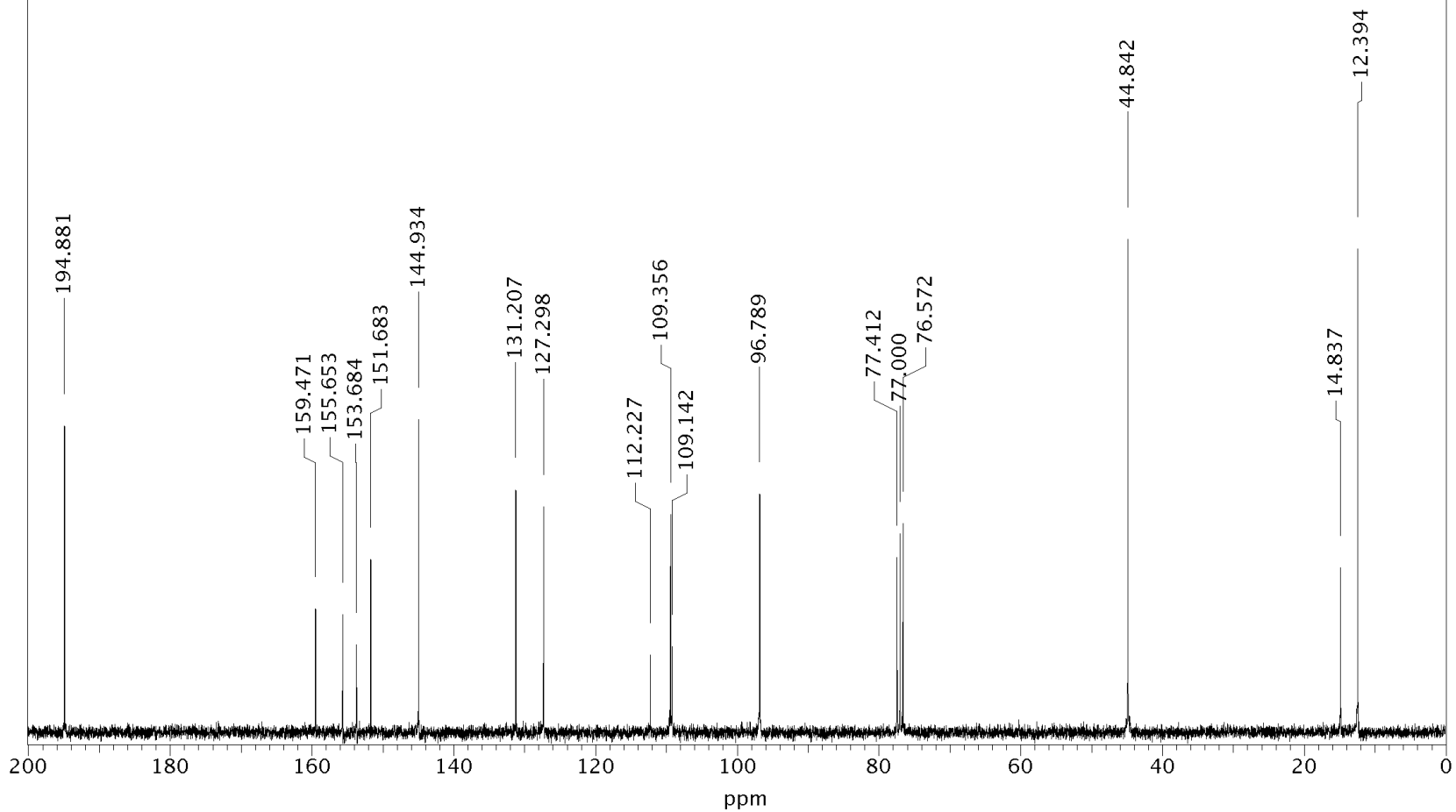


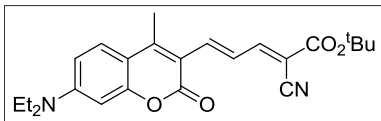
¹H NMR of 5 in CDCl₃



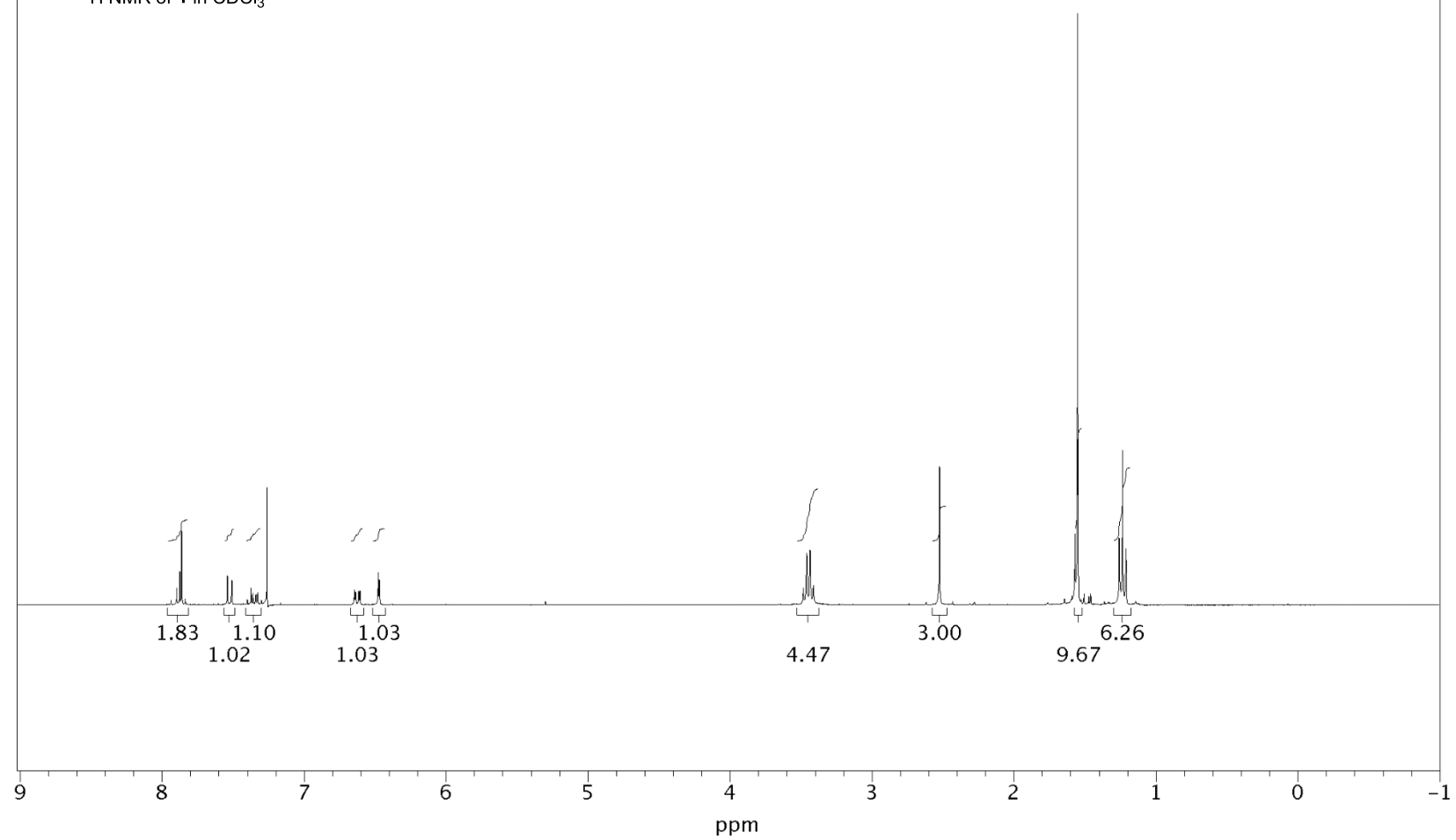


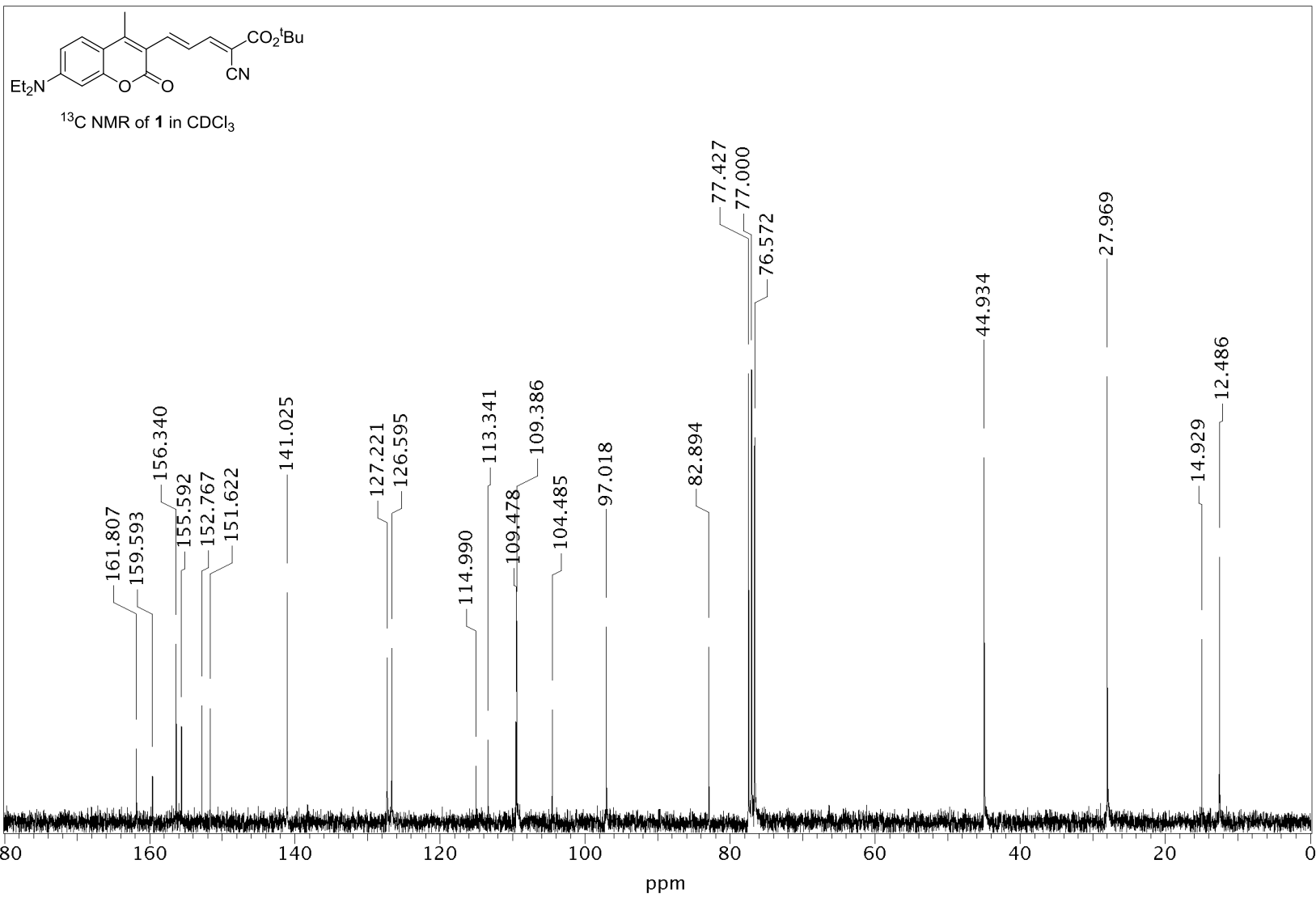
¹³C NMR of **5** in CDCl₃

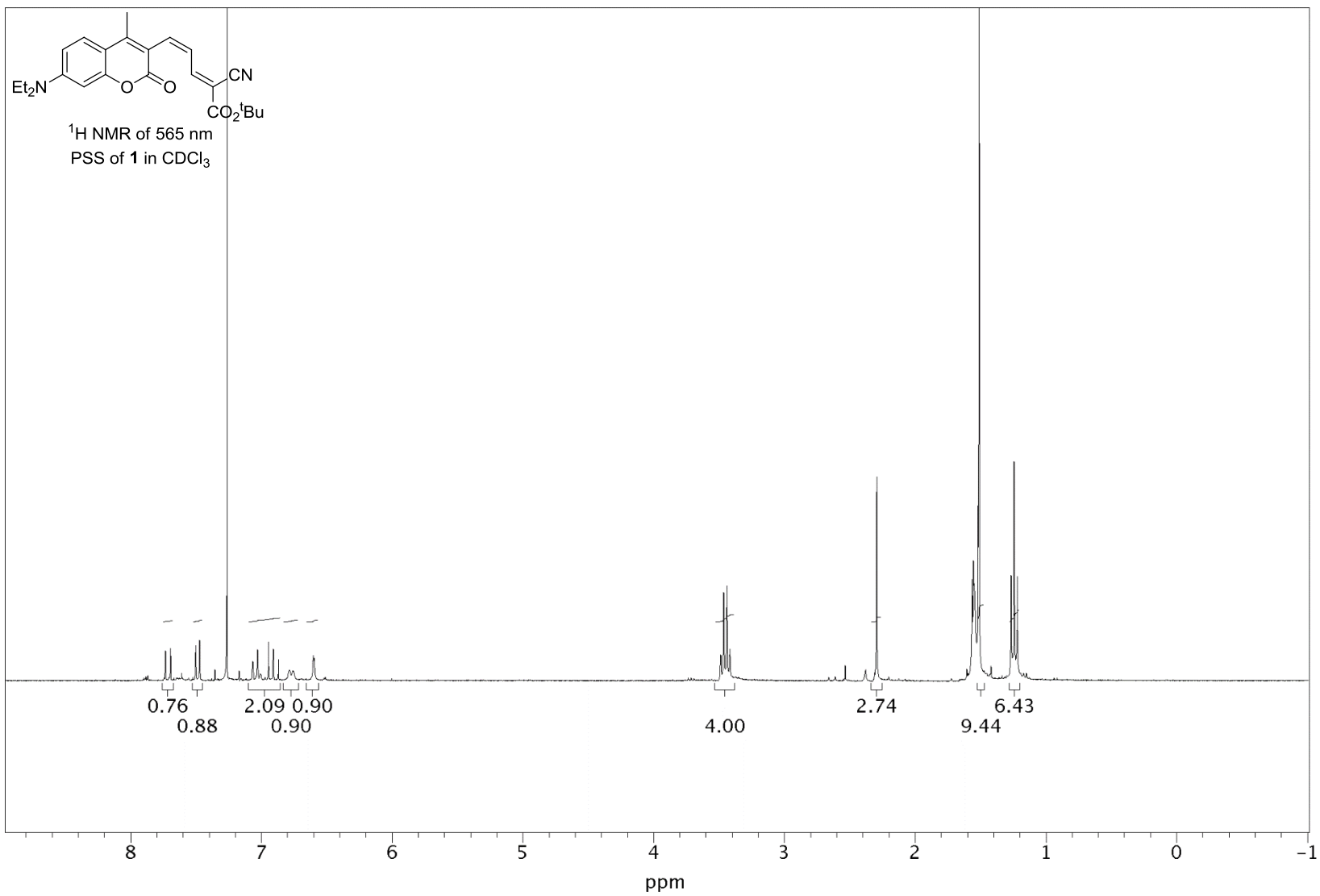


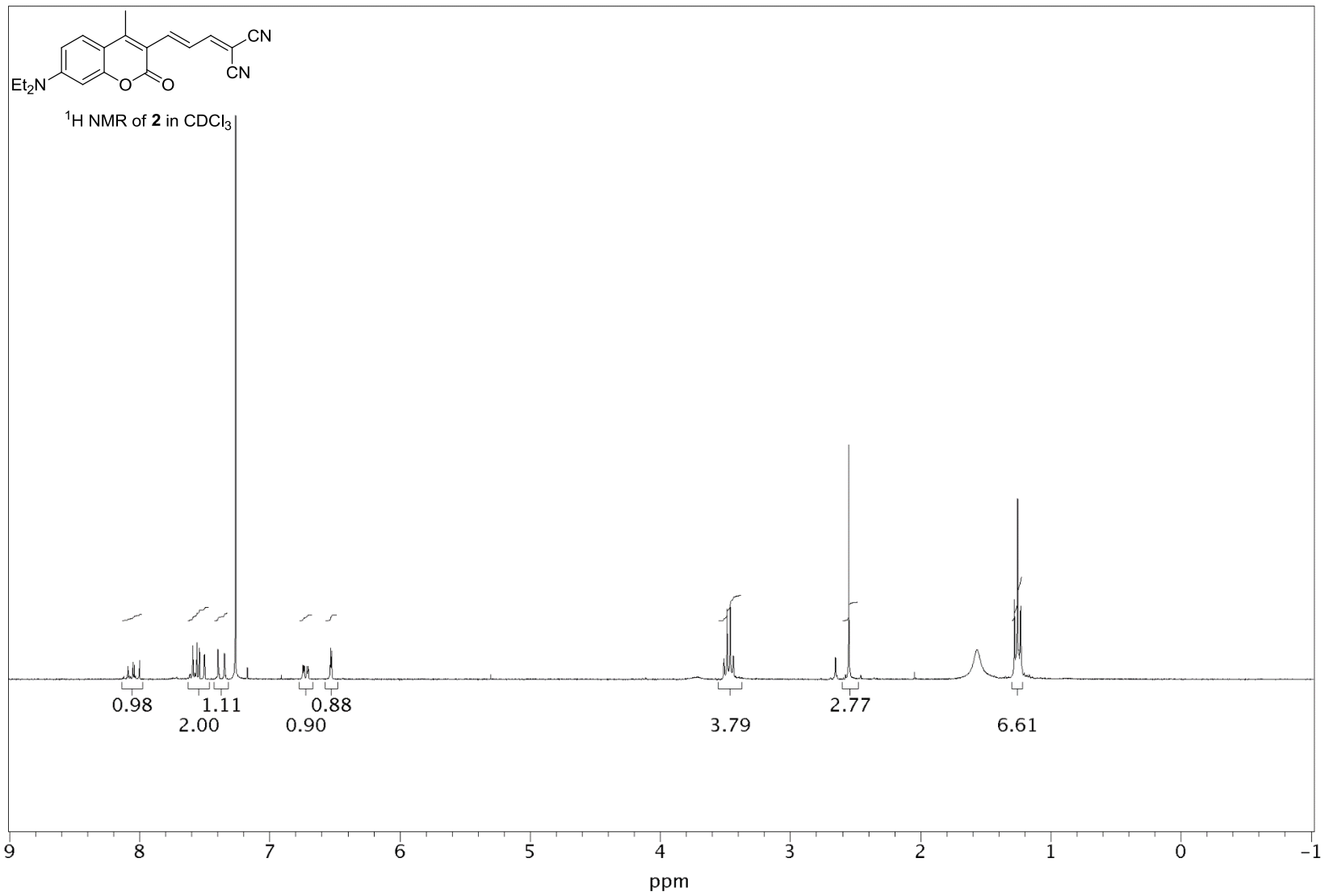


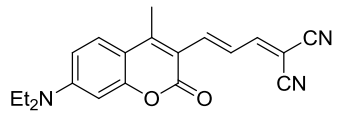
¹H NMR of 1 in CDCl₃



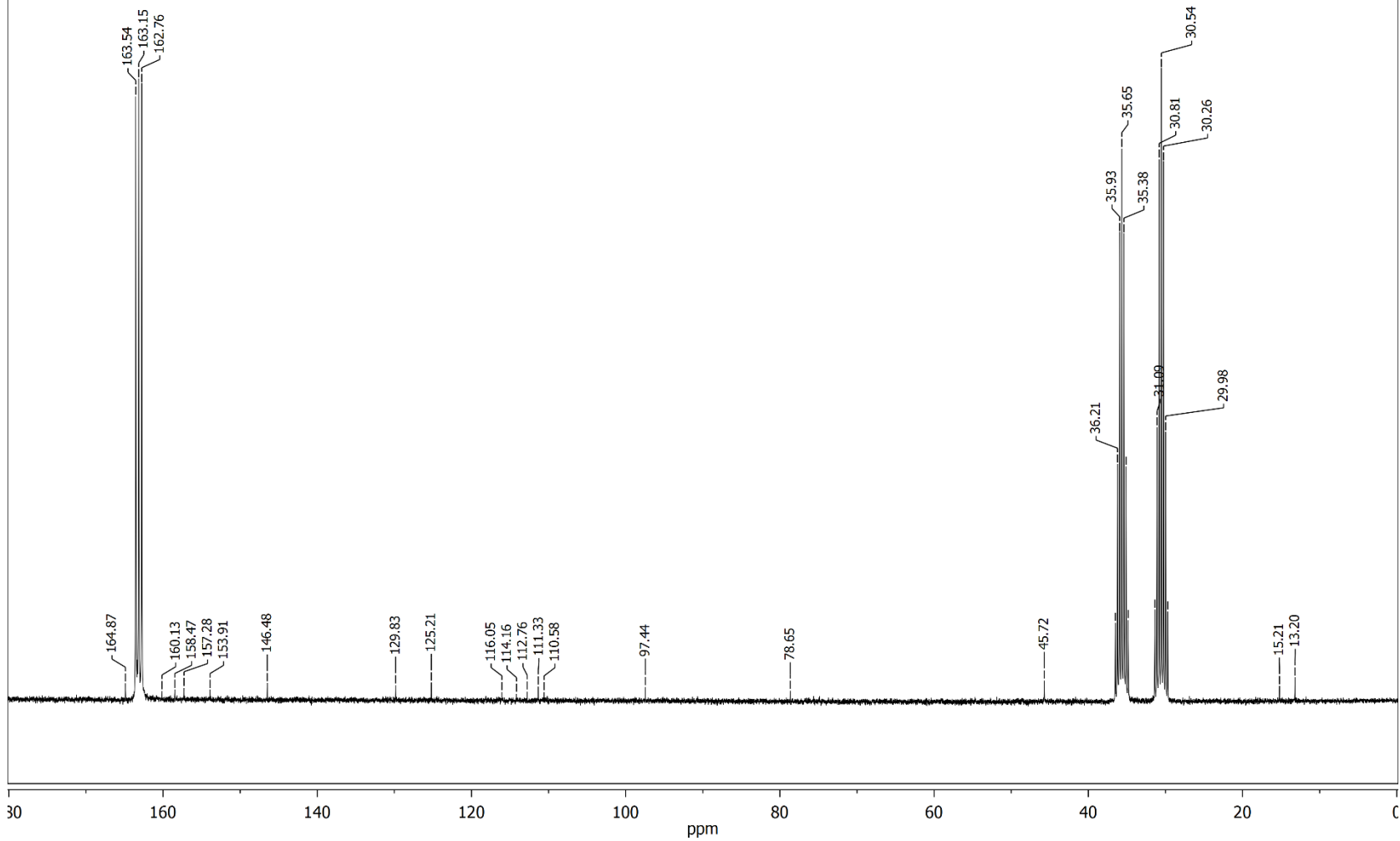


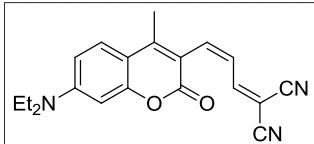




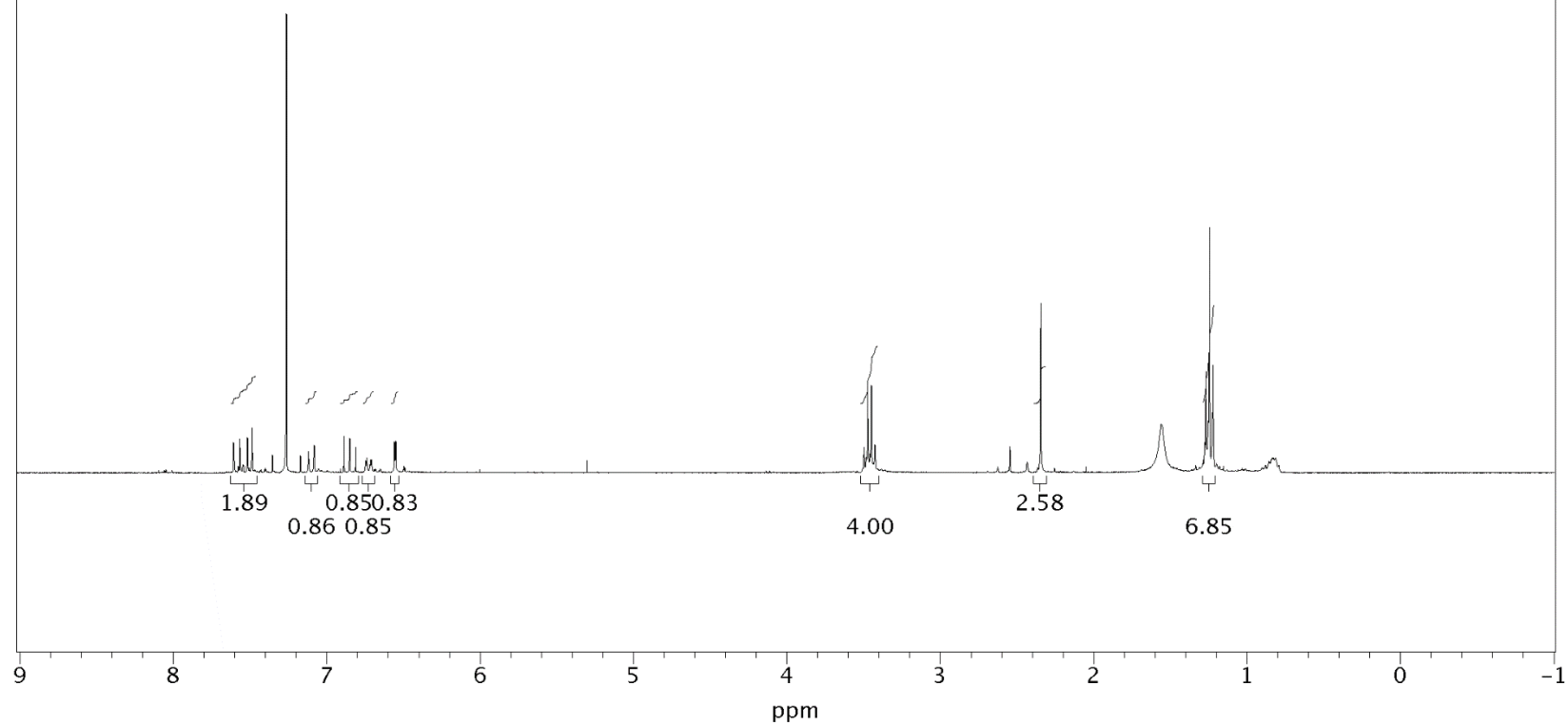


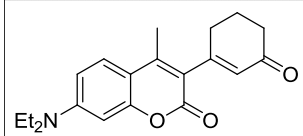
^{13}C NMR of **2** in DMF- d_7



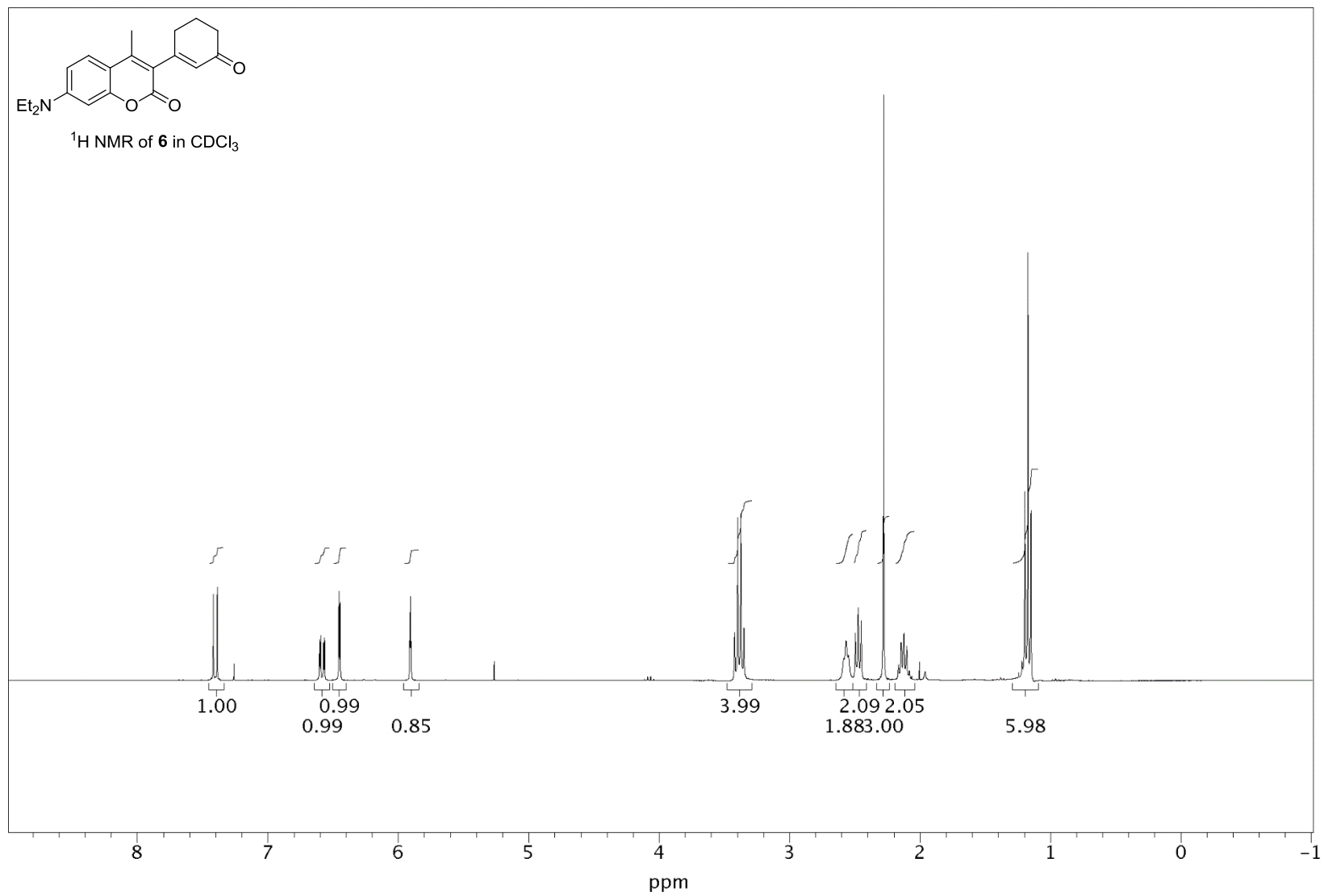


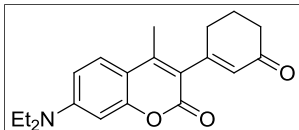
¹H NMR of 565 nm
PSS of **2** in CDCl₃





^1H NMR of **6** in CDCl_3





^{13}C NMR of **6** in CDCl_3

