Supporting Information

for

The synthesis and photophysical properties of tris-coumarins

Łukasz Kielesiński,[a,b] Olaf W. Morawski,[b]* Andrzej L. Sobolewski[b]* and Daniel T. Gryko[a]*

[a]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

[b]Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland.

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1. General information.

Dichloroethane and acetonitrile were dried over phosphorus pentoxide respectively prior to use. All reported NMR spectra (^{1}H NMR and ^{13}C NMR) were recorded using a Varian 500 and 600 spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference, J values are given in Hz. High resolution mass spectra (HRMS) were obtained via electron ionization (EI) and electrospray ionization (ESI). IR spectra were recorded on JASCO FT/IR-6200 Spectrometer. UV-Vis absorption spectra were recorded on PerkinElmer Lambda 35 Spectrometer. Fluorescence spectra were recorded on Fluorolog TCSPC Horiba. Fluorescence lifetimes were measured on Laser Mira Coherent. Chromatography was performed on silica gel 60 (230-400 mesh) and thin layer chromatography was performed on TLC plates (Merck, silica gel 60 F$_{254}$).

2. Synthesis.

General procedure for the synthesis of 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylic acid (2).

To the solution of 4-(ethylamino)-2-hydroxy-5-methylbenzaldehyde (**1**) (3 mmol) in ethanol (5 ml), Meldrum's acid (3,5 mmol), piperidine (0,15 mmol) and acetic acid (0,15 mmol) was added. The reaction mixture was refluxed under argon for 4 h. Then the mixture was cooled to room temperature and the product was filtered and washed with cold solvent. The crude product was crystallized from AcOEt-hexane affording product of analytical purity.

7-(Ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylic acid (2).
Yellow-green precipitate, 0.512g, 69% yield. M.p. 218-221 °C. ^{1}H NMR (DMSO, 500 MHz): δ 12.50 (s, 1H, COOH), 8.52 (s, 1H, CH), 7.43 (s, 1H, Ar), 6.56 (t, J = 5.6 Hz, 1H, NH), 6.48 (s, 1H, Ar), 3.26-3.32 (m, 2H, C*H$_2$*CH$_3$), 2.51 (s, 3H, CH$_3$), 1.20 (t, J = 7.1 Hz, 3H, CH$_2$C*H$_3$*). ^{13}C NMR (DMSO, 125 MHz): δ 14.3, 17.5, 37.9, 94.3, 107.2, 107.8, 121.1, 130.9, 149.8, 153.8, 157.6, 160.4, 165.0. IR (KBr, cm^{-1}): 795, 805, 1425, 1537, 1620, 1738, 2952, 3001, 3343. HRMS (EI): m/z calculated for C$_{13}$H$_{13}$NO$_4$ [M$^{·+}$] = 247.0845; found: 247.0848. Elemental analysis (%): calculated for C$_{13}$H$_{13}$NO$_4$: C, 63.15; H, 5.30; N, 5.67; found: C, 62.93; H, 5.08; N, 5.60.

General procedure for the synthesis of Cy-3Amide-7.

To the ACE tube was added 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylic acid (**2**) (0,6 mmol), dichlorotriphenylphosphorane (1,5 mmol) and dry DCE (20 ml) under argon. The reaction mixture was stirred at 120 °C overnight. Then the mixture was cooled to room temperature and concentrated under reduce pressure. The crud product was purified by column chromatography (silica, AcOEt/hexane/methanol 70:29:1) Crystalized from DCM-hexane afforded product of analytical purity.

Cy-3Amide-7.
White precipitate, 0.090g, 22% yield. M.p. >300 °C. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.95 (s, 1H, CH), 7.62 (s, 1H, CH), 7.43 (s, 1H, Ar), 7.36 (s, 1H, CH), 7.28 (s, 1H, Ar), 7.19 (d, J = 2.4 Hz, 2H, Ar), 6.53 (s, 1H, Ar), 6.51 (s,1H, Ar), 4.38-4.49 (m, 3H, NC*H$_2$*CH$_3$), 3.16-3.26 (m, 3H, NC*H$_2$*CH$_3$), 2.49 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 1.24 (t, J = 7.2 Hz, 3H, NCH$_2$C*H$_3$*), 1.24-1.18 (m, 6H, NCH$_2$C*H$_3$*). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 12.2, 12.3, 12.4,

17.3, 17.6, 17.9, 43.0, 43.1, 116.9, 117.2, 117.3, 117.4, 118.7, 119.1, 126.5, 127.0, 127.3, 130.8, 130.9, 131.8, 132.1, 134.2, 134.6, 136.9, 141.4, 142.2, 142.6, 142.7, 143.7, 150.6, 150.8, 151.4, 156.1, 156.3, 157.4, 163.5, 164.3, 164.5. HRMS (EI): m/z calculated for $C_{39}H_{33}N_3O_9$ [M$^+$] = 687.2217; found: 687.2213.

General procedure for the synthesis of *tert*-butyl 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylate (3).

To the solution of 4-(ethylamino)-2-hydroxy-5-methylbenzaldehyde (**1**) (4,5 mmol) in acetonitrile (10 ml), di-*tert*-butyl malonate ester (6,75 mmol) pyrrolidine (0,75 mmol) and acetic acid (0,75 mmol) was added. The reaction mixture was refluxed under argon for 12 h. Then the mixture was cooled to room temperature, diluted with water and extracted with DCM. The combined organic layers dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, hexane/AcOEt 1:1).

tert-Butyl 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylate (3).
Yellow precipitate, 0.715g, 52% yield. M.p. 176-178 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.29 (s, 1H, CH), 7.17 (s, 1H, Ar), 6.41 (s, 1H, Ar), 4.28 (s, 1H, NH), 3.25-3.31 (m, 2H, NHC*H$_2$*CH$_3$), 2.15 (s, 3H, CH$_3$), 1.58 (s, 9H, *t*-Bu), 1.35 (t, *J* = 7.2 Hz, 3H, NHCH$_2$C*H$_3$*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.3, 16.7, 28.2, 38.2, 81.5, 95.2, 108.1, 111.2, 119.3, 129.8, 148.4, 152.0, 157.4, 158.3, 163.0. IR (KBr, cm^{-1}): 795, 822, 1130, 1160, 1228, 1527, 1626, 1683, 1713, 2976, 3365, 3448. HRMS (EI): m/z calculated for $C_{17}H_{21}NO_4$ [M$^+$] = 303.1471; found: 303.1470. Elemental analysis (%):calculated for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62; found: C, 67.28; H, 6.84; N, 4.47.

General procedure for the synthesis of Bis-coumarin (5).

To a dry Schlenk flask was added 7-(diethylamino)-2-oxo-2*H*-chromene-3-carboxylic acid (**4**) (2,03 mmol), PyClU (2,34 mmol) and dry DCE (10 ml) under argon. DIPEA (7,03 mmol) was subsequently added and the reaction mixture was stirred for 30 minutes at room temperature. Then the *tert*-butyl 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylate (**3**) (1,56 mmol) was added and the mixture was refluxed for 24 hours. The reaction mixture was cooled to room temperature, diluted with water and extracted with DCM. The combined organic layers washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, hexane/AcOEt 2:3). Crystalized from AcOEt-hexane afforded product of analytical purity.

Bis-coumarin (5).
Yellow precipitate, 0.686g, 81% yield. M.p. 156-159 °C. ^{1}H NMR (DMSO, 80°C, 500 MHz): δ 8.41 (s, 1H, CH), 7.95 (s, 1H, CH), 7.69 (s, 1H, Ar), 7.41 (d, *J* = 8.00 Hz, 1H, Ar), 7.26 (s, 1H, Ar), 6.66 (d, *J* = 8.00 Hz, 1H, Ar), 6.39 (s, 1H, Ar), 3.41 (q, *J* = 7.00 Hz, 6H), 2.28 (s, 3H, CH$_3$), 1.51 (s, 9H, *t*-Bu), 1.11 (t, *J* = 7.00 Hz, 9H). ^{13}C NMR (DMSO, 80°C, 125 MHz): δ 11.8, 12.2, 16.6, 25.9, 27.4, 43.7, 81.6, 96.1, 106.4, 109.1, 116.3, 116.6, 116.7, 119.3, 129.6, 130.9, 132.4, 143.0, 144.6, 145.6, 145.7, 151.2, 152.0, 155.4, 156.1, 161.3, 164.5. IR (KBr, cm^{-1}): 814, 990, 1134, 1163, 1250, 1520, 1622, 1711, 1756, 2928, 2970, 3065. HRMS (EI): m/z calculated for $C_{31}H_{34}N_2O_7$ [M$^+$] = 546.2366; found: 546.2377. Elemental analysis (%):calculated for $C_{31}H_{34}N_2O_7$: C, 68.12; H, 6.27; N, 5.12; found: C, 67.98; H, 6.55; N, 4.90.

General procedure for the synthesis of 3Amide-7.

To a dry Schlenk flask was added compound (**6**) (0,4 mmol), PyClU (0,5 mmol) and dry DCE (7 ml) under argon. DIPEA (1,38 mmol) was subsequently added and the reaction mixture was stirred for 30 minutes at room temperature. Then the *tert*-butyl 7-(ethylamino)-6-methyl-2-oxo-2*H*-chromene-3-carboxylate (**3**) (0,31 mmol) was added and the mixture refluxed for 24 hours. The reaction mixture was cooled to room temperature, diluted with water and extracted with DCM. The combined organic layers washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, hexane/AcOEt 4:1 gradually increasing the amount of AcOEt). Crystalized from AcOEt-hexane afforded product of analytical purity.

3Amide-7.
Yellow precipitate, 0.023g, 10% yield. M.p. 224-226 °C. The ^{1}H NMR (mixture of isomers) (CDCl$_3$, 500 MHz): δ 8.36 (s, 0.31H, Ar), 8.26 (s, 1H, Ar), 8.10-7.70 (m, 2H, Ar), 7.60-6.80 (m, 4H, Ar), 6.72-6.48 (m, 1.69H, Ar), 6.40-6.26 (m, 1H, Ar), 4.50-4.00 (m, 2H, NC*H*$_2$CH$_3$), 3.80-3.20 (m, 6H, NC*H*$_2$CH$_3$), 2.50-2.30 (m, 6H, CH$_3$), 1.57 (s, 9H, *t*-Bu), 1.40-1.00 (m, 9H, NCH$_2$C*H*$_3$). Due to the very low solubility we could not register the ^{13}C NMR spectrum. HRMS (ESI-TOF): m/z calculated for $C_{44}H_{45}N_3O_{10}$ [M+H]$^+$ = 776.3183; found: 776.3172.

General procedure for the synthesis of *tert*-butyl 6-amino-2-oxo-2*H*-chromene-3-carboxylate (9).

To the solution of nitrocoumarin (**8**) (0.5 mmol) in ethanol (10 ml), tin dichloride dihydrate (2 mmol) was added. The reaction mixture was heated at 60 °C for 12 hours. Then the mixture was cooled to room temperature and aqueous NaHCO$_3$ was added until the pH was neutral. The aqueous solution was extracted with AcOEt and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, hexane/AcOEt 1:1).

***tert*-Butyl 6-amino-2-oxo-2*H*-chromene-3-carboxylate (9)**.
Yellow precipitate, 0.146g, 56% yield. M.p. 118-119 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.25 (s, 1H, CH), 7.15 (d, *J* = 8.8 Hz, 1H, Ar), 6.96 (dd, *J* = 8.8, 2.7 Hz, 1H, Ar), 6.79 (d, *J* = 2.7 Hz, 1H, Ar), 3.25 (bs, 2H, NH$_2$), 1.60 (s, 9H, *t*-Bu). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 28.1, 82.6, 112.3, 117.4, 118.4, 119.8, 122.0, 143.3, 147.2, 148.4, 157.3, 162.2. HRMS (EI): m/z calculated for $C_{14}H_{15}NO_4$ [M$^{.+}$] = 261.1001; found: 261.1002

General procedure for the synthesis of Bis-coumarin (10).

To a dry Schlenk flask was added 7-(diethylamino)-2-oxo-2*H*-chromene-3-carboxylic acid (**4**) (0,5 mmol), *tert*-butyl 6-amino-2-oxo-2*H*-chromene-3-carboxylate (**9**) (0,5 mmol), EDC·HCl (0,7 mmol), DMAP (cat. amount) and dry DCE (10 ml) under argon. The reaction mixture was stirred at room temperature overnight. Then the mixture was diluted with water and extracted with DCM. The combined organic layers washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was crystalized from AcOEt-cyclohexane afforded product of analytical purity.

Bis-coumarin (10).

Yellow precipitate, 0.221g, 88% yield. M.p. >300 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 11.10 (s, 1H, NH), 8.77 (s, 1H, CH), 8.41 (s, 1H, CH), 8.29 (d, J = 2.5 Hz, 1H, Ar), 7.74 (dd, J = 9.00, 2.5 Hz, 1H, Ar), 7.47 (d, J = 9.00 Hz, 1H, Ar), 7.31 (d, J = 9.00 Hz, 1H, Ar), 6.69 (dd, J = 9.00, 2.00 Hz, 1H, Ar), 6.53 (d, J = 2.00 Hz, 1H, Ar), 3.48 (q, J = 7.5 Hz, 4H, NCH_2CH$_3$), 1.62 (s, 9H, t-Bu), 1.27 (t, J = 7.5 Hz, 6H, NCH$_2$CH_3). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 12.4, 28.1, 45.2, 82.7, 96.2, 108.5, 109.4, 110.4, 117.0, 118.1, 119.6, 119.8, 126.3, 131.5, 135.1, 147.6, 148.7, 151.3, 153.1, 156.9, 157.8, 161.5, 161.8, 163.1. IR (KBr, cm^{-1}): 787, 816, 989, 1207, 1350, 1416, 1508, 1686, 1769, 2968, 3274. HRMS (EI): m/z calculated for C$_{28}$H$_{28}$N$_2$O$_7$ [M^{+}] = 775.3105; found: 504.1906. Elemental analysis (%):calculated for C$_{28}$H$_{28}$N$_2$O$_7$: C, 66.66; H, 5.59; N, 5.55; found: C, 66.43; H, 5.63; N, 5.64.

General procedure for the synthesis of 3Amide-6.

To a dry Schlenk flask was added compound (**11**) (0,37 mmol), *tert*-butyl 6-amino-2-oxo-2*H*-chromene-3-carboxylate (**9**) (0,37 mmol), EDC·HCl (0,53 mmol), DMAP (cat. amount) and dry DCE (20 ml) under argon. The reaction mixture was stirred at room temperature for 48 h. Then the mixture was diluted with water and extracted with DCM. The combined organic layers washed with brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was crystalized from methanol afforded product of analytical purity.

3Amide-6.
Yellow precipitate, 0.139g, 54% yield. M.p. >300 °C. ^{1}H NMR (mixture of isomers) (CDCl$_3$, 600 MHz): δ 11.15 (s, 0.60H, NH), 11.07 (s, 0.60H, NH), 11.04 (s, 0.36H, NH), 10.97 (s, 0.19H, NH), 9.03 (s, 0.60H, Ar), 9.01 (s, 0.60H, Ar), 8.94 (s, 0.20H, Ar), 8.78 (s, 0.60H, Ar), 8.42-8.39 (m, 2H, Ar), 8.32-8.29 (m, 1H, Ar), 7.91-7.86 (m, 1H, Ar), 7.76-7.72 (m, 1H, Ar), 7.49-7.46 (m, 1H, Ar), 7.43 (d, J = 8.89 Hz, 1H, Ar), 7.35-7.31 (m, 1H, Ar), 6.71 (dd, J = 8.89, 2.1 Hz, 1H, Ar), 6.54 (d, J = 2.1 Hz, 1H, Ar) 3.60 (s, 1H, NCH_2CH$_3$), 3.48 (q, J = 7.1 Hz, 3H, NCH_2CH$_3$), 1.61 (s, 9H, t-Bu), 1.25 (t, J = 7.1 Hz, 6H, NCH$_2$CH_3). Due to the very low solubility we could not register the ^{13}C NMR spectrum. HRMS (ESI-TOF): m/z calculated for C$_{38}$H$_{33}$N$_3$O$_{10}$ [M+Na]$^{+}$ = 714.2064; found: 714.2065.

3. Computational methods

The ground-state equilibrium geometries of systems studied were determined with the second-order Møller-Plesset (MP2) method [1]. The correlation-consistent split-valence double-ζ basis set with polarization functions on all atoms (cc-pVDZ) [2] was employed in these calculations. Vertical excitation energies and oscillator strengths were calculated with the ADC(2) method [3,4], which is a computationally efficient single-reference propagator method. The MP2 and ADC(2) calculations were carried out with the TURBOMOLE program package [5] making use of the resolution-of-the-identity (RI) approximation [6,7] for the evaluation of the electron-electron repulsion integrals.

It has tuned out, however, that investigated systems are too large for efficient ADC(2) computations. To make such computations feasible it was necessary to truncate some of the methyl groups and to decrease the basis set to def-SV(P) [8]. Thus we decided to compute additionally absorption spectra of the systems with the aid of the TD-DFT method. The TD-DFT method requires a careful selection of the functional for the correct treatment of the CT character of the excited states since standard functionals are known to fail in this respect. The recently introduced M06 suite of density functionals [9] has been shown to provide very good results for noncovalent interactions [9]. The calculations showed that the M06-2X version provides a relatively good reproduction of the RI-ADC(2) results [10]. The equilibrium structures for TD-DFT computations were optimized at the DFT level with the same functional and the dispersion correction of Grimme (D3) [11] as implemented in Turbomole. The cc-pVDZ basis set was used in these computations.

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4. Experimental methods

Spectroscopic grade solvents were purchased from Sigma-Aldrich and used as obtained. **3Amide-6** and **3Amide-7** and **Cy-3Amide-7** are soluble in polar and polarizable solvents. The initial solutions of concentrations about 70 micromoles per liter were diluted to the target $3 \div 6\,\mu M$ used in optical studies. To exclude the presence of dimers the absorption and fluorescence spectra of initial concentrated solutions were compared with those of diluted solutions. All solutions have been bubbled with pure argon gas for 20 minutes before measurement.

All absorption and fluorescence spectra were taken at room temperature (21^0C). Fluorescence spectra were recorded with the aid of a Fluorolog-3 Spectrometer and corrected for the spectral response sensitivity of the photodetector. Perkin Elmer UV/VIS Spectrometer model Lambda 35 was used for absorption spectra measurement.

Fluorescence quantum yields of molecules studied in solvents at 21°C were determined using perylene dissolved in cyclohexane ($\Phi_F = 0.94$) as the standard. Solutions of low absorbance (A < 0.1) were used to avoid reabsorption or concentration quenching. Corrections for refractive index of solvents have been performed in the calculations of quantum yields[1].

Fluorescence kinetics studies of molecules in solvents were performed with the "time correlated" single photon counting (TCSPC) technique. Mode-locked Coherent Mira-HP picosecond laser pumped by a Verdi 18 laser was used for excitation. The fundamental pulses of Mira laser tuned to 790nm were up-converted to 395nm. Fluorescence decays of molecules were excited with pulses of ~30 ps time-width. Original repetition rate of a Mira laser was reduced with the aid of APE Pulse selector to 3.8 MHz. Fluorescence was dispersed with Jarrell-Ash 0.25 m monochromator. Fluorescence photons were detected with a HMP-100-07 hybrid detector and a SPC-150 module inserted into a PC, both from Becker&Hickl GmbH. Fluorescence decays were analyzed with a deconvolution computer program, which uses nonlinear least squares procedure with Marquardt method.[2] Standard χ^2 test was used along with residual and autocorrelation function plots to judge the quality of a fit. Estimated precision of the decay time determination was 10 ps.

Long fluorescence decays of powders were cumulated with TCSPC on Fluorolog 3 and analyzed with deconvolution software provided by the vendor. The 303nm Delta diode of sub-nanosecond pulse width was used for excitation.

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5. Crystallographic data.

Table ST1. Crystallographic data for **Cy-3Amide-7.**

Chemical formula	$C_{40}H_{34}Cl_3N_3O_9$	
Formula weight	807.05 g/mol	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal size	0.102 x 0.124 x 0.286 mm	
Crystal habit	Colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.7636(3) Å	α = 81.027(2)°
	b = 13.1274(3) Å	β = 74.327(2)°
	c = 14.2142(3) Å	γ = 61.2690(10)°
Volume	2009.81(8) Å^3	
Z	2	
Diffractometer	Bruker APEX-II CCD	
Radiation source	fine-focus sealed tube, CuK$_\alpha$	
Reflections collected	48013	
Independent reflections	6109 [R(int) = 0.0972]	
Tmin, Tmax	0.820, 0.930	
Absorption correction	numerical	
Refinement method	Full-matrix least-squares on F^2	
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	
Data / restraints / parameters	6109 / 5 / 503	
Goodness-of-fit on F^2	1.009	
Δ/σ_{max}	0.028	
Final R indices	2175 data; I>2σ(I)	R1 = 0.0938, wR2 = 0.2177
	all data	R1 = 0.2579, wR2 = 0.2875
Largest diff. peak and hole	0.679 and -0.516 eÅ^{-3}	

The crystals of **Cy-3Amide-7** suitable for X-ray crystallography were obtained by diffusion of hexane into a solution of **Cy-3Amide-7** in CHCl$_3$. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a CuK$_\alpha$ fine-focus sealed tube (λ = 1.54178 Å). A total of 4598 frames were collected. The total exposure time was 40.87 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the numerical method (SADABS). The structure was solved and refined using the Bruker SHELXTL Software Package.
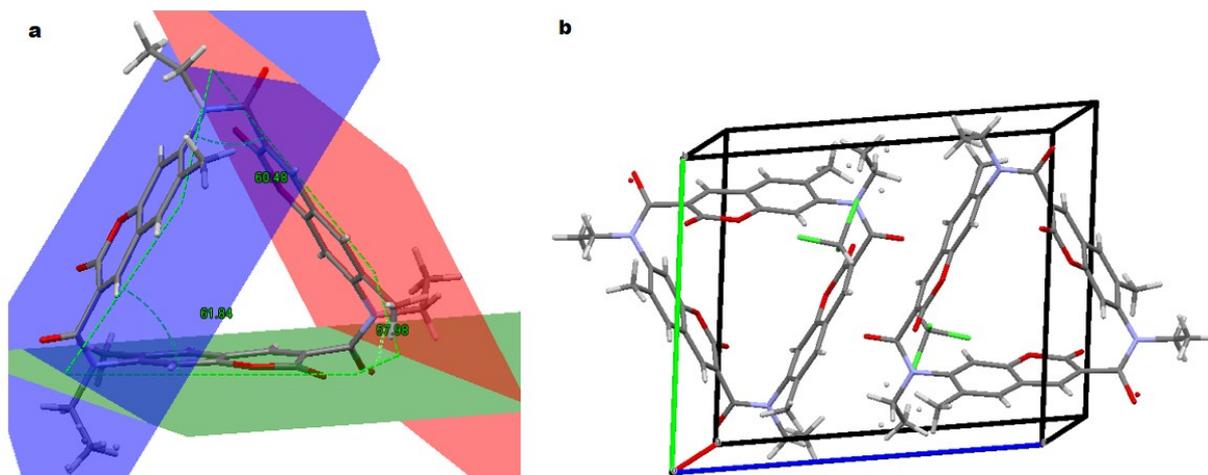
Figure SF1. The planes and the values of dihedral angles between coumarins subunits (a), packing diagram of crystals in elementary cell of **Cy-3Amide-7** (b).

6. Theoretical data.

Table ST2a. Transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the **3Amide-6** conformers computed with ADC(2)/def-SV(P) method at the ground-state MP2/def-SV(P) equilibrium geometry.

State	*trans* ΔE/eV	f	μ/D	State	*ball* ΔE/eV	f	μ/D	State	*cis* ΔE/eV	f	μ/D	State	*clin* ΔE/eV	f	μ/D
S_1	3.39	1.054	28.27	S_1	3.48	0.351	14.35	S_1	2.92	0.092	13.10	S_1	3.45		
S_2	3.53	0.202	26.19	S_2	3.64	0.051	17.18	S_2	3.32	0.243	13.91	S_2	3.70		
S_3	3.55	0.051	23.51	S_3	3.68	0.104	5.96	S_3	3.72	0.222	4.45	S_3	3.74		

Table ST2b. Relative energy (E), transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the **3Amide-6** conformers computed with TDDFT/D3-M06-2X/cc-pVDZ method at the ground-state DFT/D3-M06-2X/cc-pVDZ equilibrium.

State	*trans* E=0.0eV, μ=17.53D ΔE/eV	f	State	*ball* E=0.75eV, μ=5.49D ΔE/eV	f	State	*cis* E=0.96eV, μ=5.87D ΔE/eV	f	State	*clin* E=0.96eV, μ=7.43D ΔE/eV	f
S_1	3.75	1.308	S_1	3.70	0.022	S_1	3.19	0.010	S_1	3.83	0.709
S_2	3.83	0.281	S_2	3.94	0.291	S_2	3.78	0.180	S_2	3.94	0.256
S_3	3.84	0.023	S_3	4.02	0.145	S_3	4.02	0.362	S_3	4.04	0.079
S_4	4.15	0.235	S_4	4.14	0.033	S_4	4.08	0.061	S_4	4.50	0.039
S_5	4.45	0.058	S_5	4.40	0.107	S_5	4.23	0.004	S_5	4.55	0.030
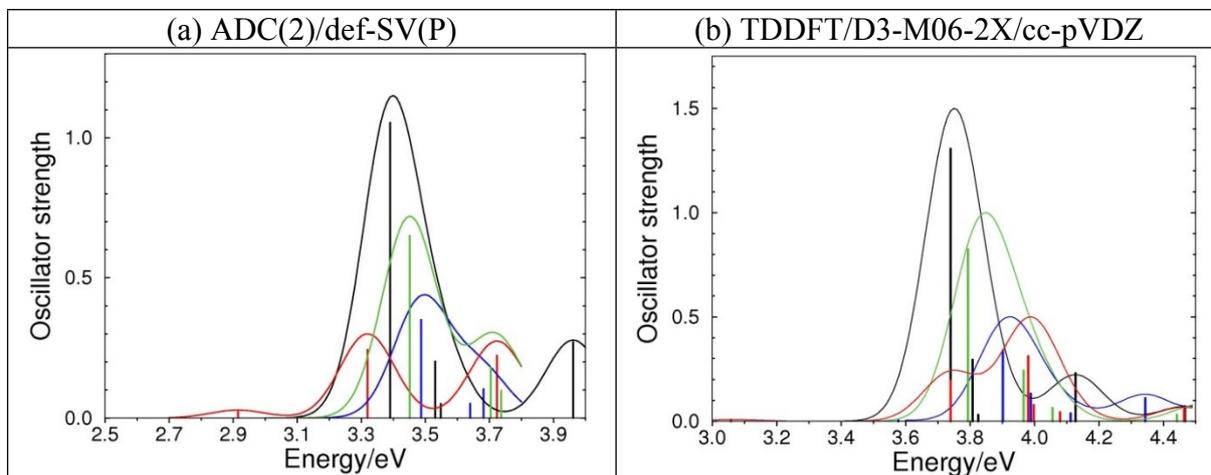
Figure. SF2. Absorption spectra of the lowest-energy **3Amide-6** conformers (*trans*-black, *ball*-blue, *clin*-green, and *cis*-red) computed with the ADC(/def-SV(P)- (a), and with the TDDFT/D3-M06-2X/cc-pVDZ- (b) methods. The computed stick spectra were convoluted with Gaussian function of FWHM=0.2 eV.

Table ST3a. Transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the truncated **Cy-3Amide-7** *udu* conformer computed with ADC(2)/def-SV(P) method at the ground-state MP2/def-SV(P) equilibrium.

(a) NCH₃ replaced by NH	CCH₃ replaced by CH

State	ΔE/eV	f	μ/D	State	ΔE/eV	f	μ/D
S_0	-	-	5.69	S_0	-	-	5.31
S_1	3.72	0.043	5.94	S_1	3.73	0.045	5.48
S_2	3.89	0.293	5.62	S_2	3.93	0.352	5.31
S_3	3.96	0.324	5.82	S_3	4.01	0.411	5.32

Table ST3b. Relative energy (E), transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the **Cy-3Amide-7** conformers computed with TDDFT/D3-M06-2X/cc-pVDZ method at the ground-state DFT/D3-M06-2X/cc-pVDZ equilibrium.

DFT/D3-M06-2X/cc-pVDZ					
(a) *udu* E=0.0eV, μ=3.59D			(b) *uuu* E=0.36eV, μ=14.42D		
State	ΔE/eV	f	State	ΔE/eV	f
S_1	3.95	0.022	S_1	4.19	0.011
S_2	4.21	0.364	S_2	4.41	0.321
S_3	4.30	0.356	S_3	4.41	0.321
S_4	4.48	0.026	S_4	4.77	0.012
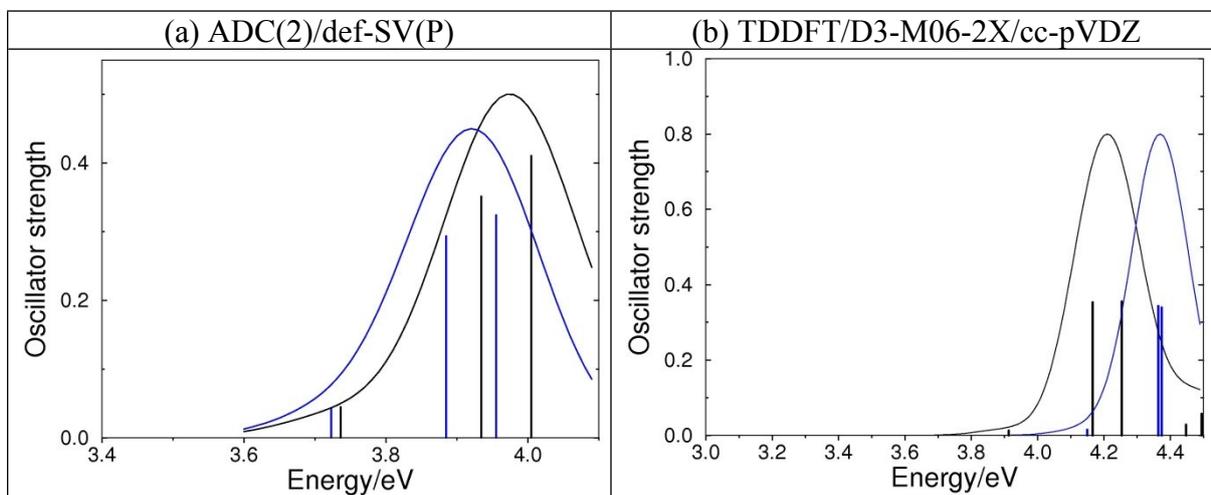
Figure SF3. Absorption spectra of the truncated *udu* conformer of **Cy-3Amide-7** (NCH_3 truncated-black, CCH_3 truncated-blue) computed with the ADC(2)/def-SV(P) method- (a), and (*udu*-black and *uuu*-blue) conformers of **Cy-3Amide-7** computed with the TDDFT/D3-M06-2X/cc-pVDZ method - (b). The computed stick spectra were convoluted with Gaussian function of FWHM=0.2 eV.

Table ST4a. Transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the methyl-truncated **3Amide-7** conformers computed with ADC(2)/def-SV(P) method.

ball	*cis*	*clin*	*trans*

State	ΔE/eV	f	μ/D	State	ΔE/eV	f	μ/D	State	ΔE/eV	f	μ/D	State	ΔE/eV	f	μ/D
S_0	(0.0)	-	6.16	S_0	(0.06)	-	10.93	S_0	(0.16)	-	8.58	S_0	(0.51)	-	18.26
S_1	3.53	0.296	7.21	S_1	3.25	0.041	13.80	S_1	3.69	0.454	12.14	S_1	3.77	1.073	22.74
S_2	3.89	0.037	5.71	S_2	3.73	0.016	11.13	S_2	3.87	0.224	8.08	S_2	3.87	0.306	19.83
S_3	3.98	0.247	3.74	S_3	3.87	0.357	12.48	S_3	4.00	0.241	9.21	S_3	4.07	0.064	20.55

Table ST4b. Relative energy (E), transition energy (ΔE), oscillator strength (f), and dipole moment (μ) of the **3Amide-7** conformers computed with TDDFT/D3-M06-2X/cc-pVDZ method at the ground-state DFT/D3-M06-2X/cc-pVDZ equilibrium.

ball			cis			clin			trans		
E=0.00eV, μ=3.31D			E=0.15eV, μ=9.65D			E=0.20eV, μ=7.57D			E=0.36eV, μ=18.84D		
State	ΔE/eV	f	State	ΔE/eV	f	State	ΔE/eV	f	State	ΔE/eV	f
S_1	3.69	0.392	S_1	3.31	0.042	S_1	3.78	0.693	S_1	3.83	1.588
S_2	3.89	0.003	S_2	3.76	0.044	S_2	4.01	0.266	S_2	4.05	0.376
S_3	4.05	0.298	S_3	4.03	0.392	S_3	4.12	0.338	S_3	4.17	0.008
S_4	4.16	0.043	S_4	4.13	0.033	S_4	4.28	0.078	S_4	4.52	0.119
S_5	4.20	0.440	S_5	4.14	0.370	S_5	4.47	0.59	S_5	4.57	0.048
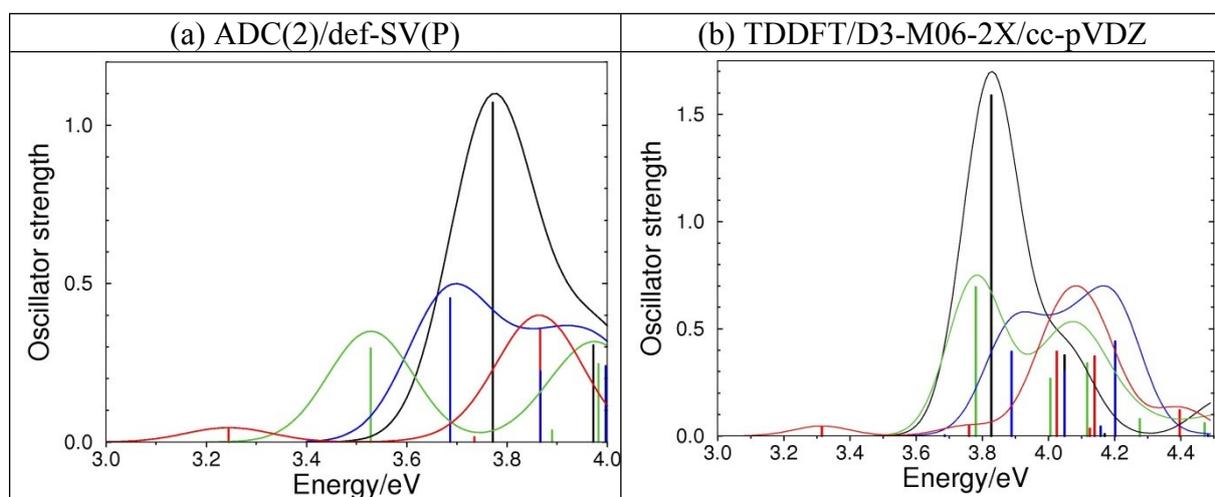
Figure SF4. Absorption spectra of the lowest-energy **3Amide-7** conformers (*trans*-black, *ball*-blue, *clin*-green, and *cis*-red) computed with the ADC(2)/def-SV(P)- (a), and with the

TDDFT/D3-M06-2X/cc-pVDZ- (b) methods. . The computed stick spectra were convoluted with Gaussian function of FWHM=0.2 eV.
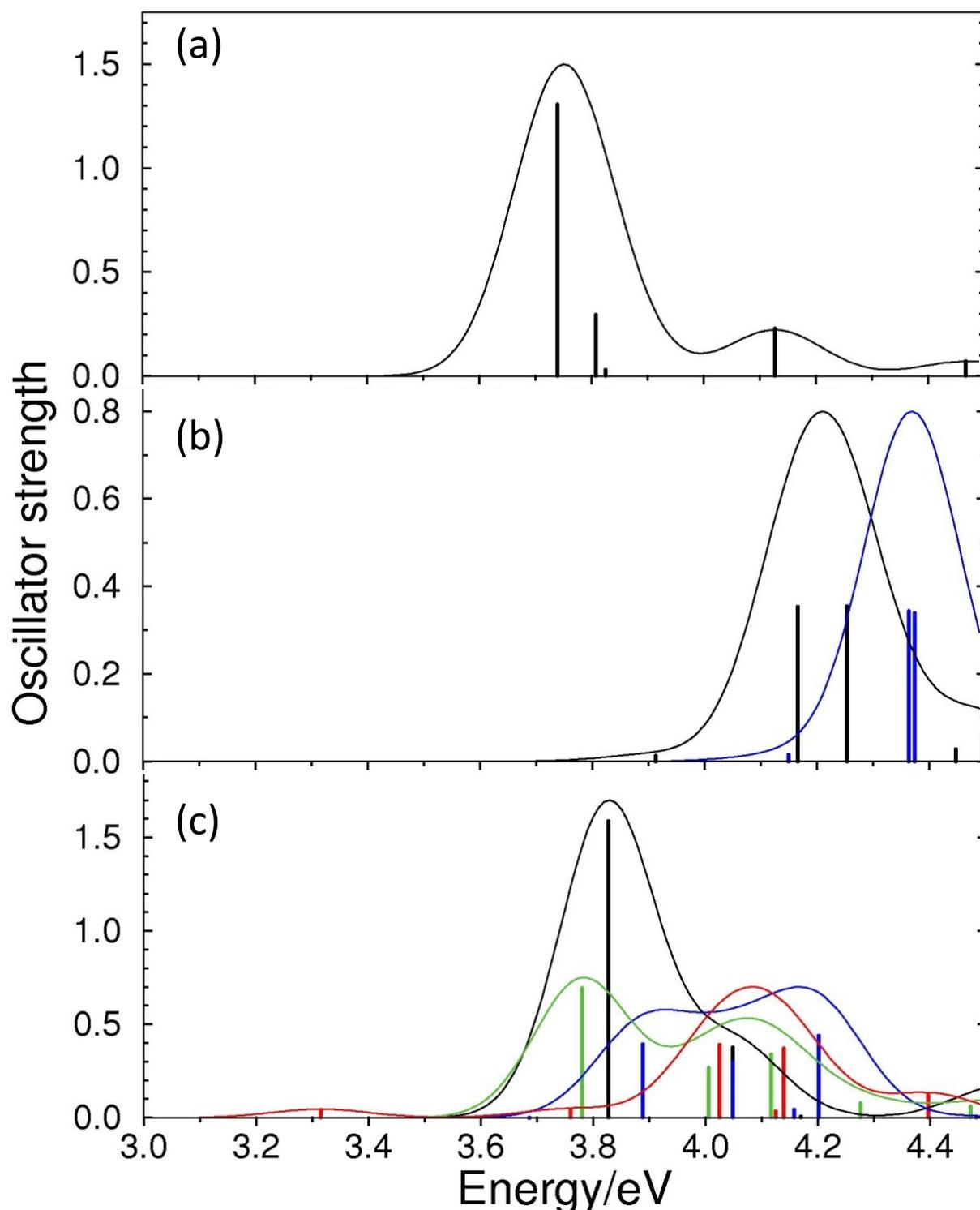
Figure SF5. Absorption spectra of conformers of **3Amide-6** (a), **Cy-3Amide-7** (b), and **3Amide-7** (c) computed with the TD-DFT/D3-M06-2X/cc-pVDZ method at the DFT/D3-M06-2X/cc-pVDZ equilibrium geometry. In (a): *trans* conformer, (b): black – *udu*, blue – *uuu,* (c): black – *trans*, green – *clin*, blue – *ball*, red – *cis*. The computed stick spectra were convoluted with Gaussian function of FWHM=0.2 eV.

7. Spectroscopic data.

7.1 Infrared spectra

The IR spectrum of **3Amide-6** (Figure **SF6**) shows the NH vibration of secondary amide bond that is not present in spectra of **3Amide-7** and **Cy-3Amide-7** which have tertiary amide bond with ethylene group between coumarin subunits. The proximity between amide proton and carbonyl oxygen of the neighboring coumarin subunit may lead in a liquid environment to formation of intramolecular hydrogen bond and rigidifies **3Amide-6** molecule in the planar form.
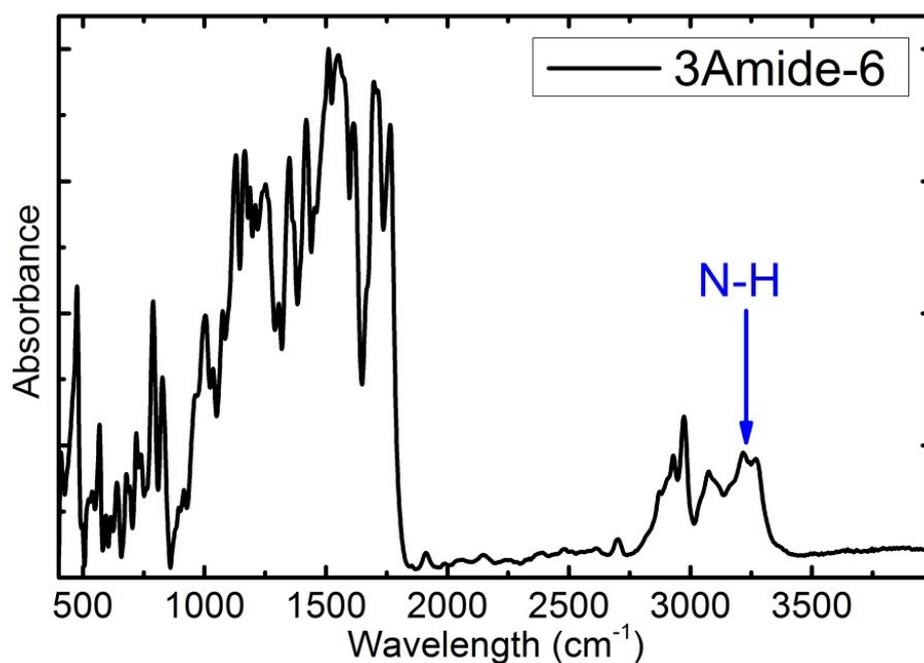
Figure SF6. The IR absorption spectrum of **3Amide-6** in KBr pellet. The arrow points to NH vibration.

7.2 Optical spectra

7.2.1 3Amide-6
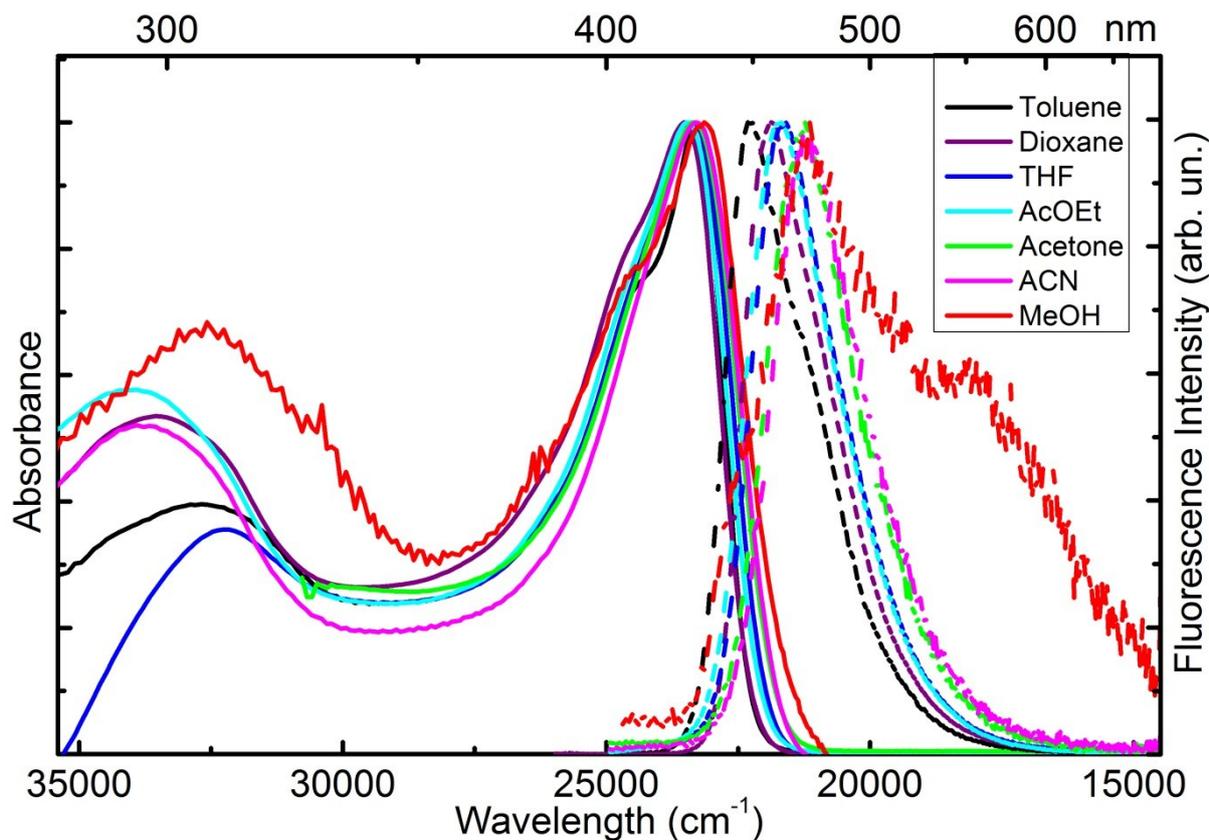
Figure SF7. Normalized absorption (solid lines) and fluorescence (dashed lines) spectra of **3Amide-6** in selected solvents. Excitation at 350 nm.
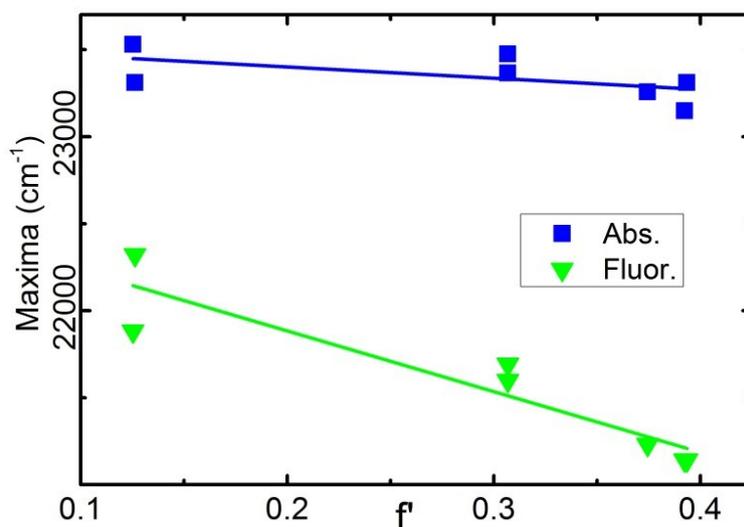
Figure SF8. Solvatochromism of **3Amide-6** absorption (blue squares) and fluorescence (green triangles) spectra versus modified polarity parameter $f' = [(\varepsilon-1)/(2\varepsilon+1)] - \frac{1}{2} \times [(n^2-1)/(2n^2+1)]$. Solid lines represent linear fits to data points: $hc\nu_{abs} = (23528\pm123) - f' \times(645\pm398)$ cm^{-1}, $hc\nu_{flu} = (22581\pm188) - f' \times(3485\pm608)$ cm^{-1}.

16
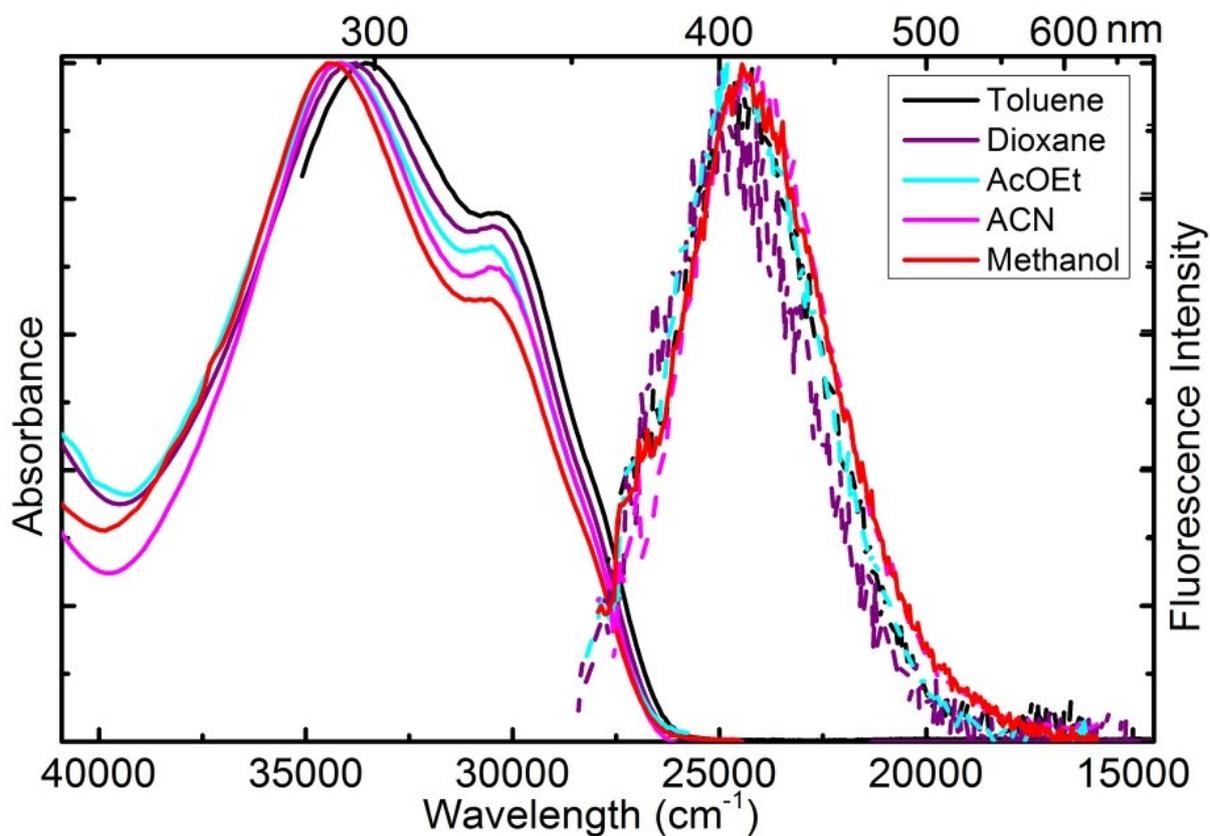
7.2.2 Cy-3Amide-7

Figure SF9. Normalized absorption (solid lines) and fluorescence (dashed lines) spectra of **Cy-3Amide-7** in selected solvents. Excitation at 330 nm.
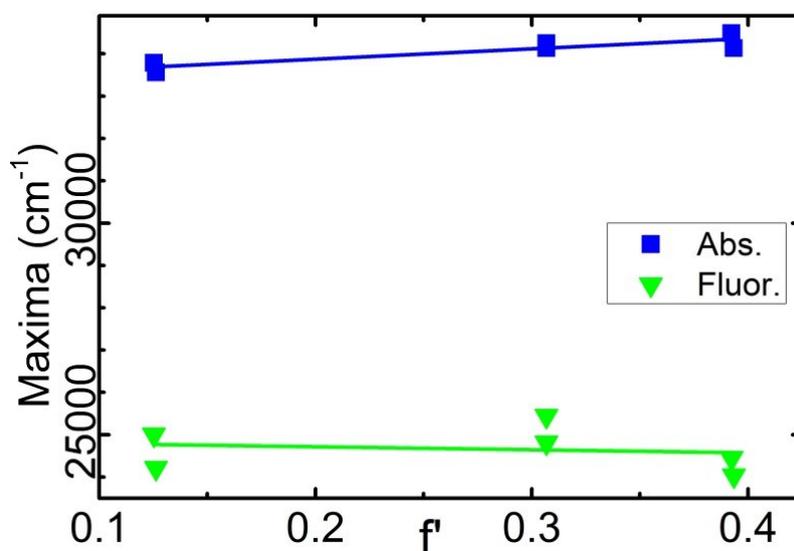
Figure SF10. Solvatochromism of **Cy-3Amide-7** absorption (blue squares) and fluorescence (green triangles) spectra versus modified polarity parameter $f'=[(\varepsilon-1)/(2\varepsilon+1)] - \frac{1}{2} \times[(n^2-1)/(2n^2+1)]$. Solid lines represent linear fits to data points: $hc\nu_{abs} = (33380\pm177) + f' \times(2449\pm597)$ cm^{-1}, $hc\nu_{flu}= (24855\pm632) - f' \times(711\pm219)$ cm^{-1}.

7.2.3 3Amide-7
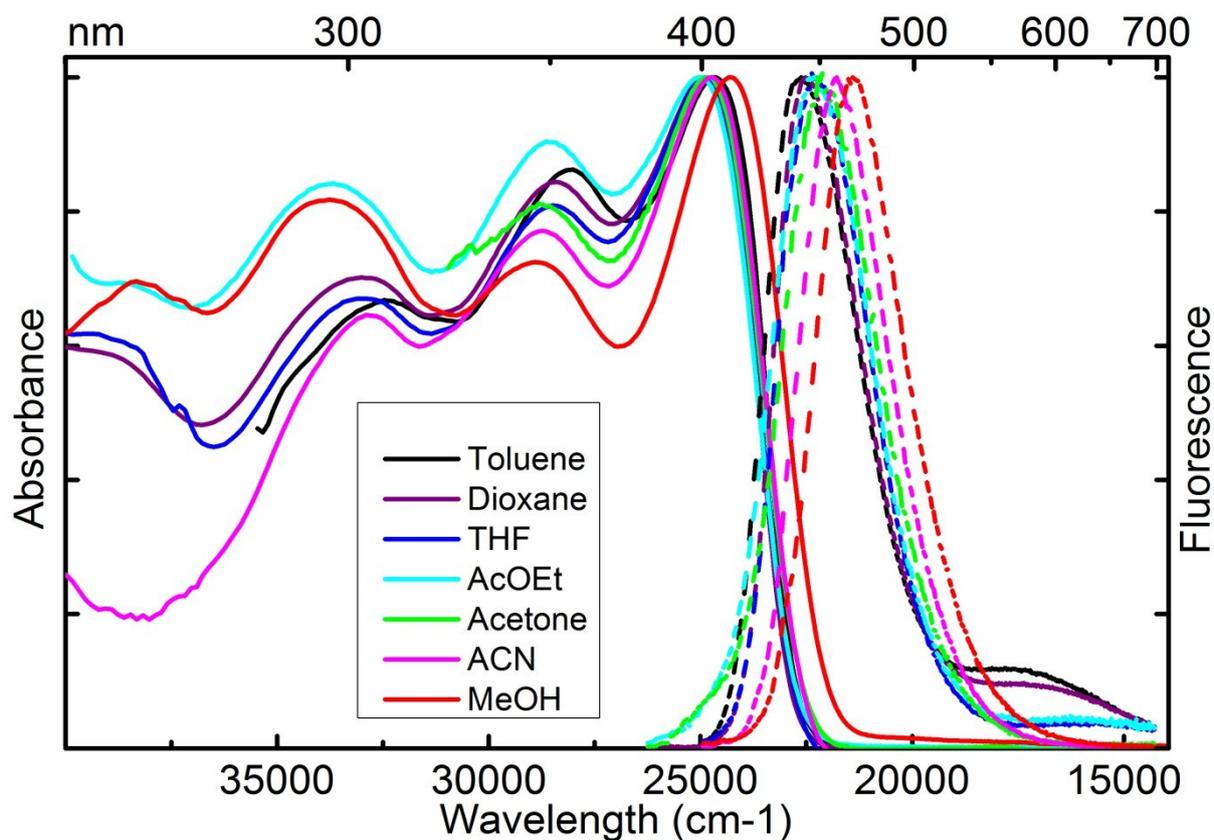
Figure SF11. Normalized absorption (solid lines) and fluorescence (dashed lines) spectra of **3Amide-7** in selected solvents. Excitation at 350 nm.
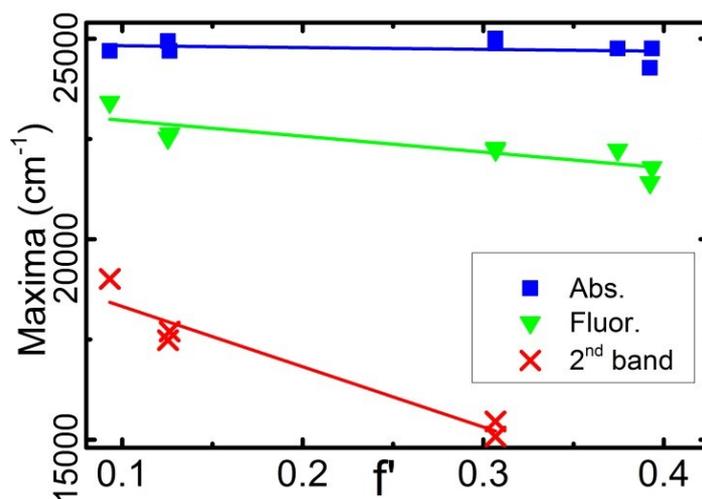
Figure SF12. Solvatochromism of **3Amide-7** absorption (blue squares) and fluorescence spectra - main band (green triangles) and low-energy fluorescence band (red crosses), versus modified polarity parameter $f'=[(\varepsilon-1)/(2\varepsilon+1)] - \frac{1}{2} \times [(n^2-1)/(2n^2+1)]$. Solid lines represent linear fits to data points: $hcv_{abs} = (24865 \pm 198) - f' \times (451 \pm 682)$ cm^{-1}, $hcv_{flu} = (23356 \pm 280) - f' \times (3950 \pm 964)$ cm^{-1} and for the second fluorescence band $hcv_{red\_flu} = (19824 \pm 480) - f' \times (15021 \pm 2245)$ cm^{-1}.
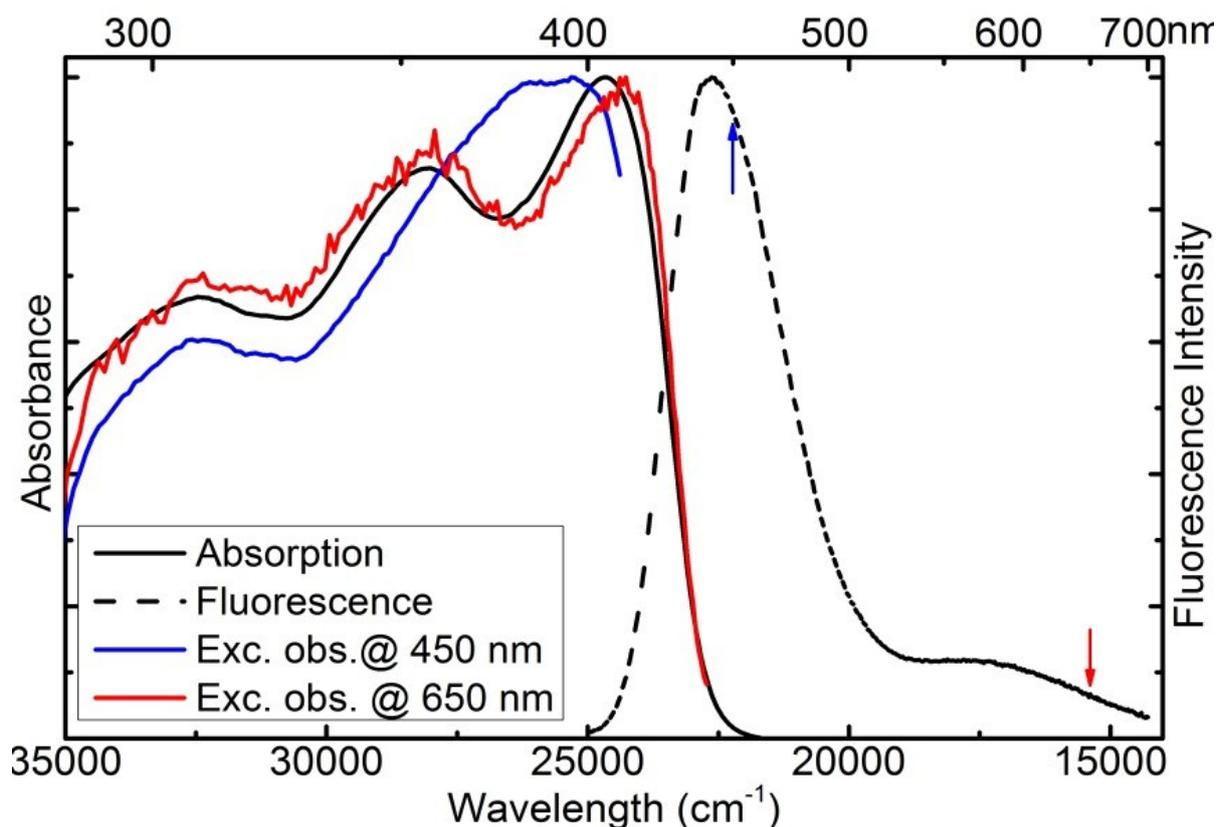
Figure SF13. Normalized absorption (black solid line), fluorescence (black dashed line) and fluorescence excitation (red and blue solid lines) spectra of **3Amide-7** in toluene. Fluorescence spectrum excited at 350 nm. Arrows point at the observation wavelength of fluorescence excitation spectra (450 and 650 nm for the blue and the red arrow/spectrum respectively).

Table ST5. Estimation of **3Amide-7** ground state energy in toluene.*

Conformer	*ball*	*cis*	*clin*	*trans*
a (A)	5.50	6.00	8.00	13.5
μ_g (D)	4.83	10.1	8.20	20.0
ΔE (eV)	0.0419	0.141	0.0392	0.0486
E_{gas} (eV)	0	0.04	0.29	0.56
E_{Solv} (eV)	-0.035	-0.0774	0.257	0.519

*Calculated with $E_{Solv} = E_{gas} - \Delta E$

where E_{Solv} and E_{gas} are the energies of solvated and gas phase ground state, the solvatation energy ΔE is obtained from formula

$$\Delta E = \frac{\mu_g^2}{2\pi\epsilon_0 hca^3} f(\varepsilon)$$

With μ_g being the ground state dipole moment, ε_0 the dielectric constant of vacuum, h the Planck constant, c speed of light and a the Onsager cavity radius. Polarity function

$$f(\varepsilon) = \frac{\epsilon - 1}{2\varepsilon + 1} = 0.2395$$

for toluene. E_{gas}, μ_g and cavity radius a where taken from results for the optimized ground state geometry.

7.2.4 Fluorescence decays
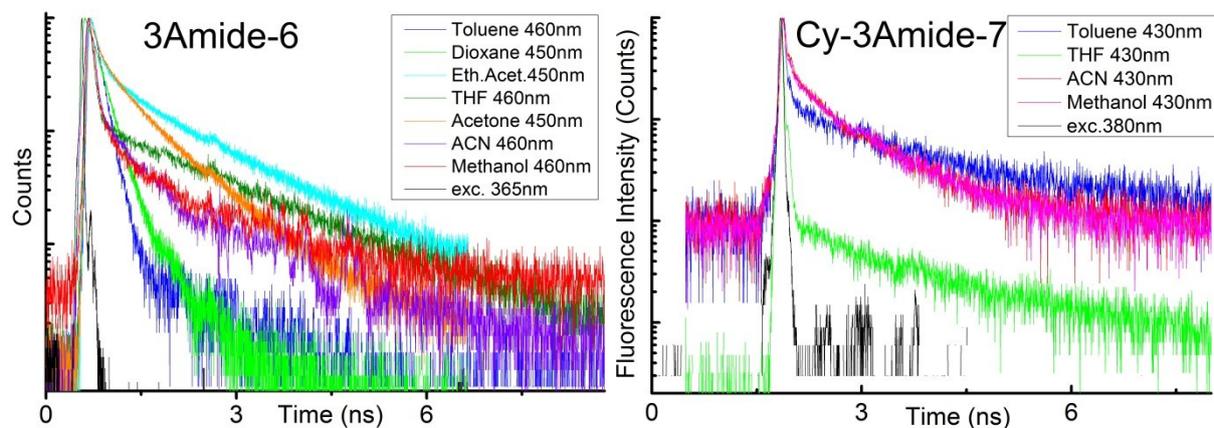
Figure SF14. Normalized fluorescence decays (colored lines) and excitation pulse (black line) **3Amide-6** and **Cy-3Amide-7** in selected solvents. Legends specify colors of decays and observation wavelength. Fluorescence excited at 365 nm. Decays recorded with 3.74 ps per channel resolution.
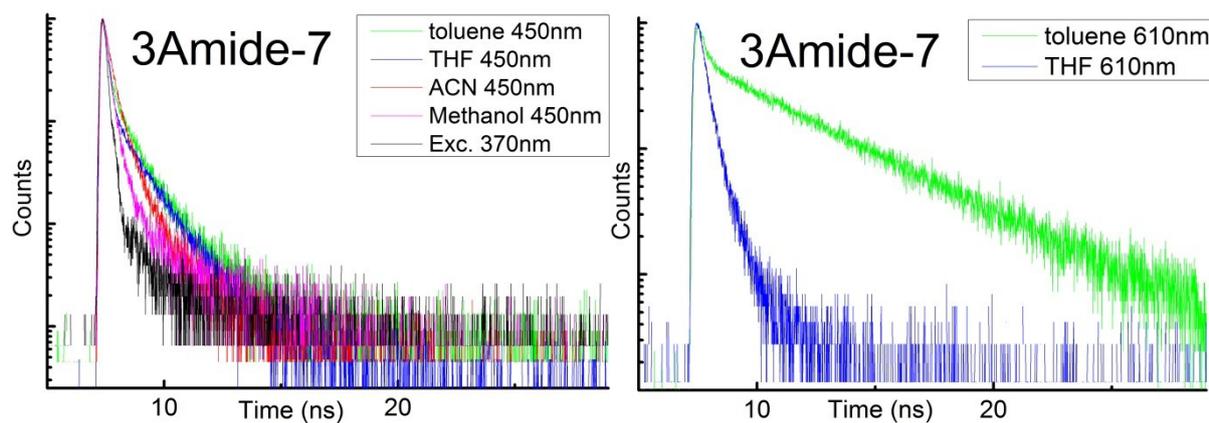
Figure SF15. Normalized fluorescence decays of **3Amide-7** in selected solvents. Legends specify colors of decays and observation wavelength. Fluorescence excited at 365 nm. Decays recorded with 3.74 ps per channel resolution.
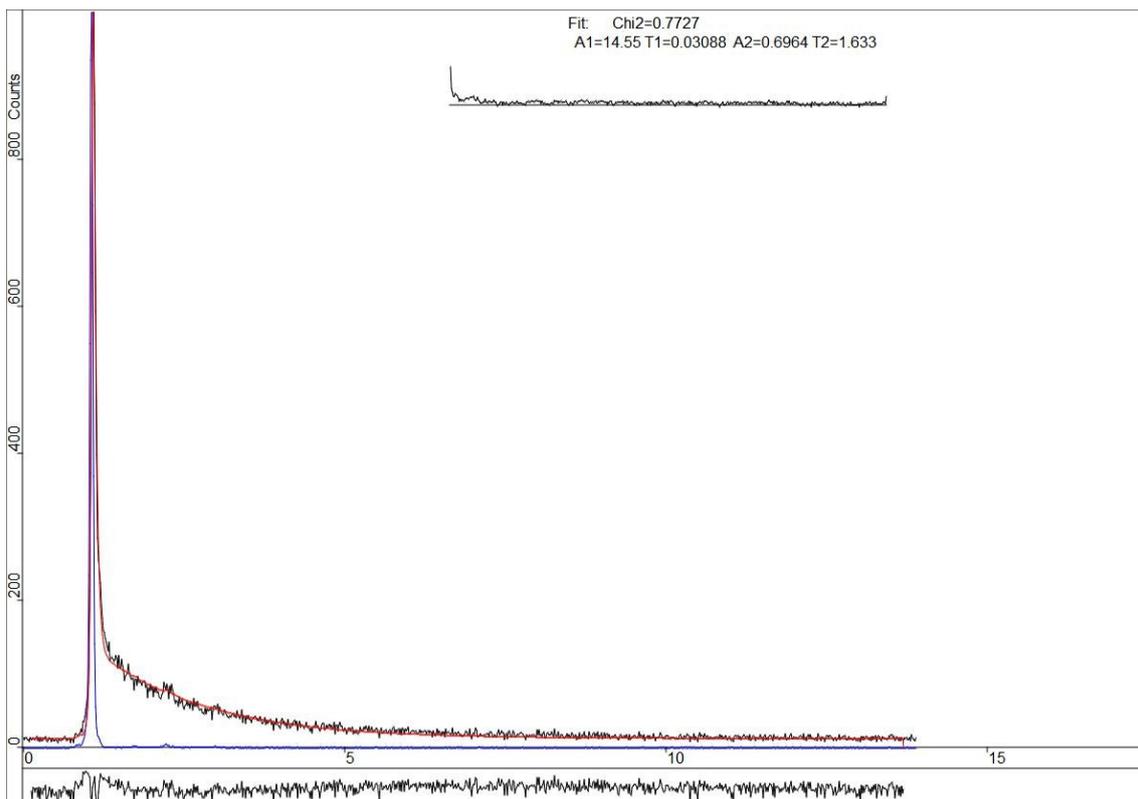
Figure SF16. An example of two-exponential fit (red) to fluorescence decay (black) for **Cy-3Amide-7** in toluene. Decay recorded at 430 nm. Excitation pulse (blue line) at 365nm. Decay recorded with 3.74 ps per channel resolution.

7.2.5 Results in powder phase
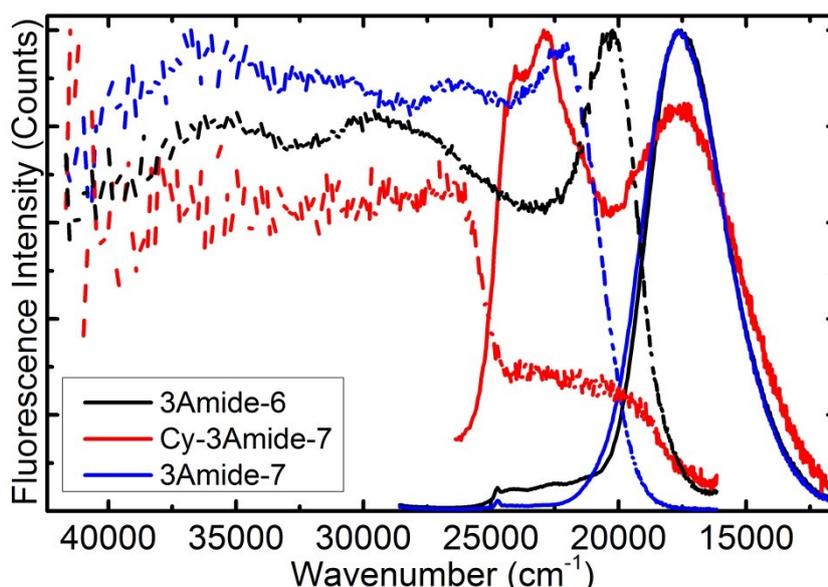
Figure SF17. Normalized fluorescence excitation (dashed) and fluorescence (solid lines) spectra of **3Amide-6** (black), **Cy-3Amide-7** (red) and **3Amide-7** (blue) in powder. Fluorescence spectra excited at 303 nm. Fluorescence excitation spectra recorded with observation at 550 nm (for **3Amide-6** and **3Amide-7**) and 600 nm (for **Cy-3Amide-7**).
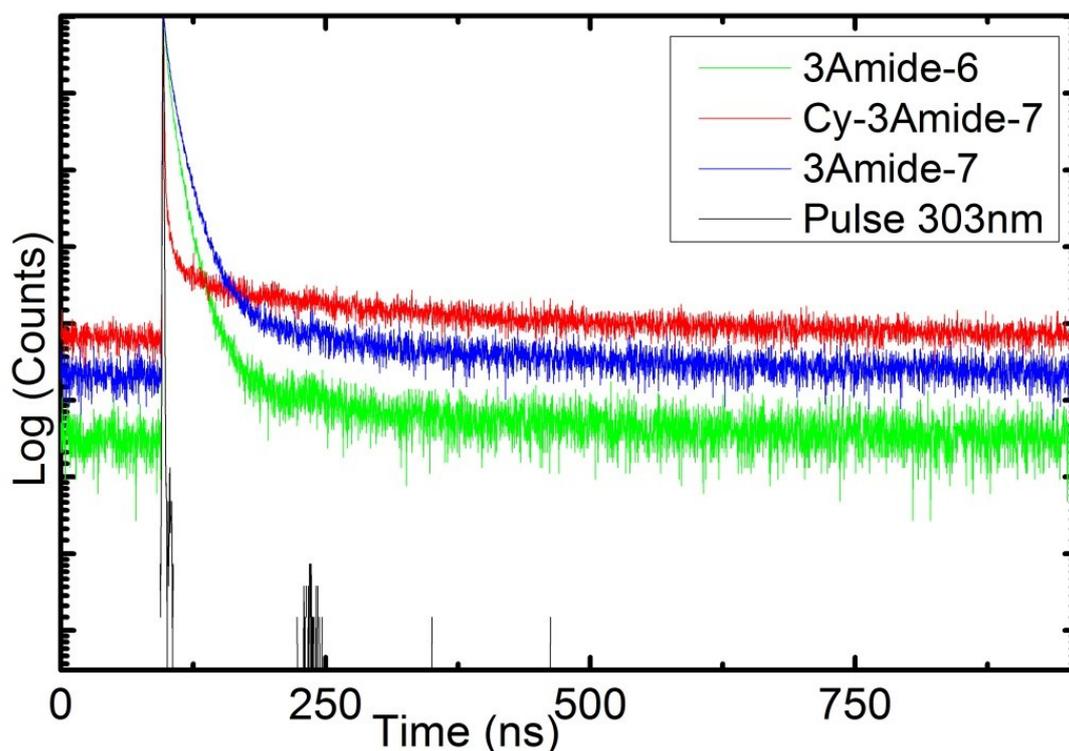
Figure SF18. Semi-logarithmic plot of fluorescence decays of **3Amide-6**, **Cy-3Amide-7** and **3Amide-7** in powder. Legends specify colors of decays. Observation wavelength 550 nm for **3Amide-6** and **3Amide-7** and 600 nm for **Cy-3Amide-7**. Fluorescence excited at 303 nm. Decays recorded with 0.23 ns per channel resolution.

Table ST6. Decay parameters (amplitudes and decay times) for tri-coumarins in powder.

Compound	Observation	A_1	τ_1	A_2	τ_2	A_3	τ_3
	nm		ns		ns		ns
3Amide-6	600	28.2	3.4	62.1	13.2	9.7	154
Cy-3Amide-7	440	62.5	0.4	37.5	10.3		
Cy-3Amide-7	600	32.0	0.5	9.1	7.6	58.9	212.8
3Amide-7	550	19.5	4.2	63.7	16.2	16.7	198

8. Electrochemical studies.

Cyclic voltammetry

Cyclic voltammograms for **Cy-3Amide-7**, **3Amide-7** and **3Amide-6** were measured at room temperature under argon atmosphere, in 0.1 M solution of tetrabutylammonium perchlorate in anhydrous dichloromethane. A glassy carbon working electrode, a Ag/AgCl reference electrode and auxiliary platinum wire were used. All values of E [V] are reported with respect to Fc^+/Fc redox potential.

Table ST7. Redox potentials (vs. Ag/AgCl/NaCl) of the **Cy-3Amide-7**, **3Amide-7** and **3Amide-6**.

Compound	$E^1_{red}{}^{pa}$ [V]	$E^1_{red}{}^{pc}$ [V]	$E^1_{red}{}^{onset}$ [V]	EA [eV]	$E^2_{red}{}^{pa}$ [V]	$E^2_{red}{}^{pc}$ [V]	$E^1_{ox}{}^{pa}$ [V]	$E^1_{ox}{}^{pc}$ [V]	$E^1_{ox}{}^{onset}$ [V]	IP [eV]
Cy-3Amide-7	-0.64	-0.93	-0.70	-3.64		-1.49				
3Amide-7	-0.70	-0.96	-0.73	-3.61			1.22	1.18	1.08	-5.42
3Amide-6	-0.67	-0.98	-0.74	-3.60			1.46	1.27	1.19	-5.53

The ionic potential (IP) (HOMO) and electron affinity (EA) (LUMO) values were estimated from the onset potentials of the first oxidation and reduction events. The ionic potential and electron affinity were calculated according to the following equations:

IP (eV) = -[$E_{ox}{}^{onset}$ – 0.46 + 4.8]
EA (eV) = -[$E_{red}{}^{onset}$ – 0.46 + 4.8]
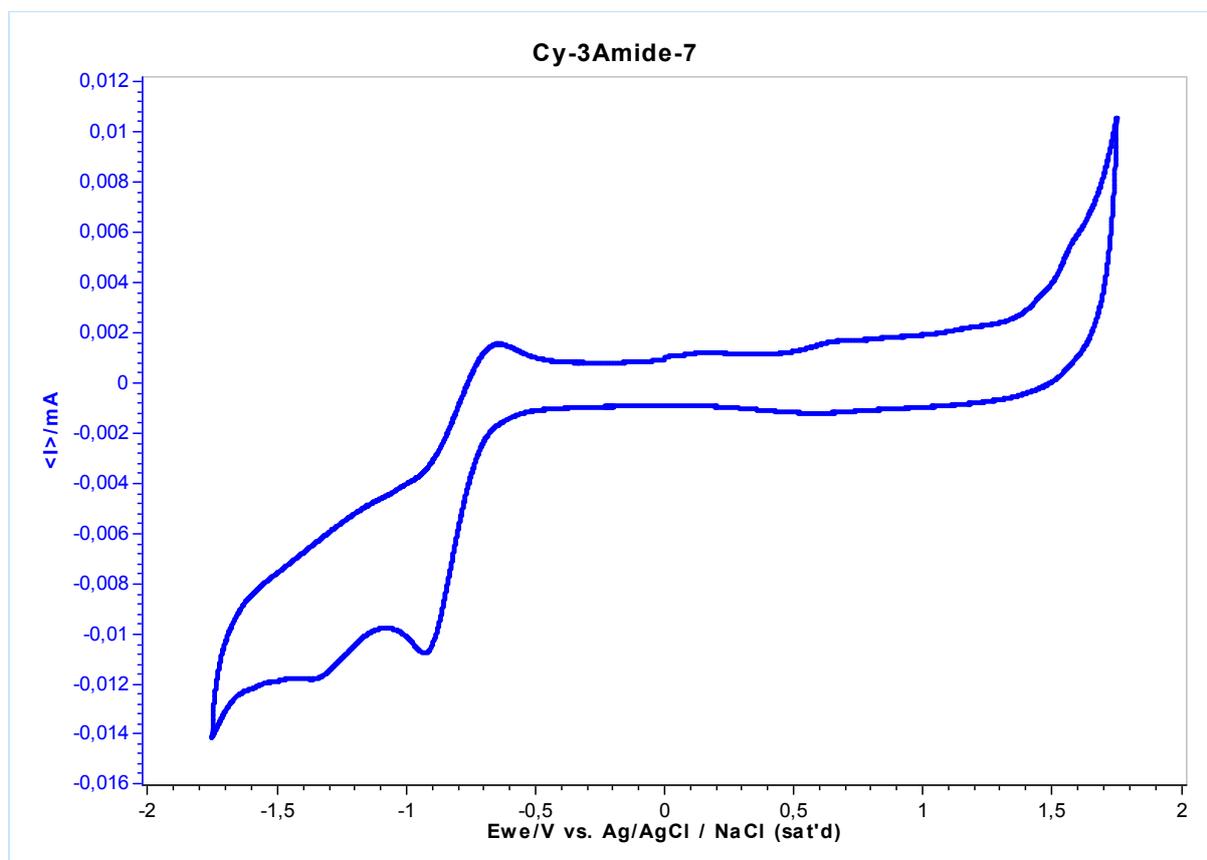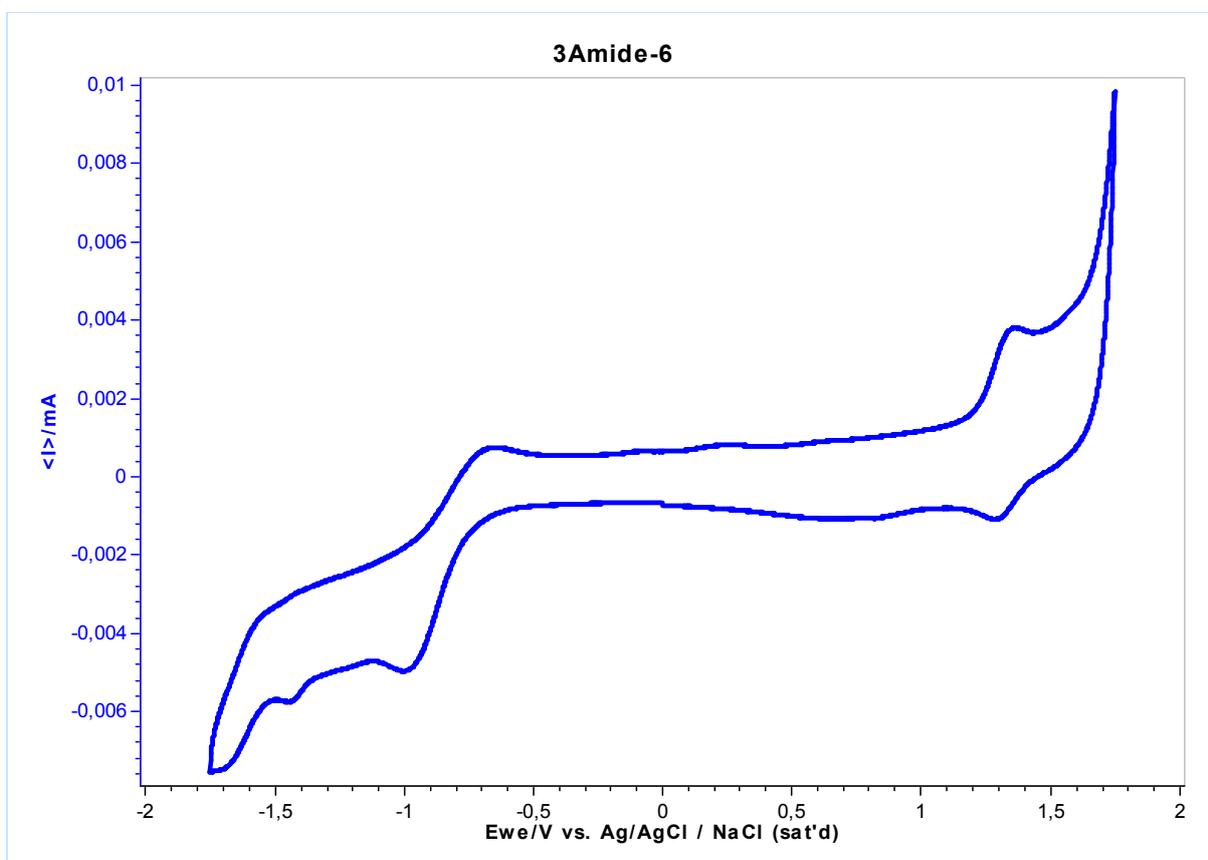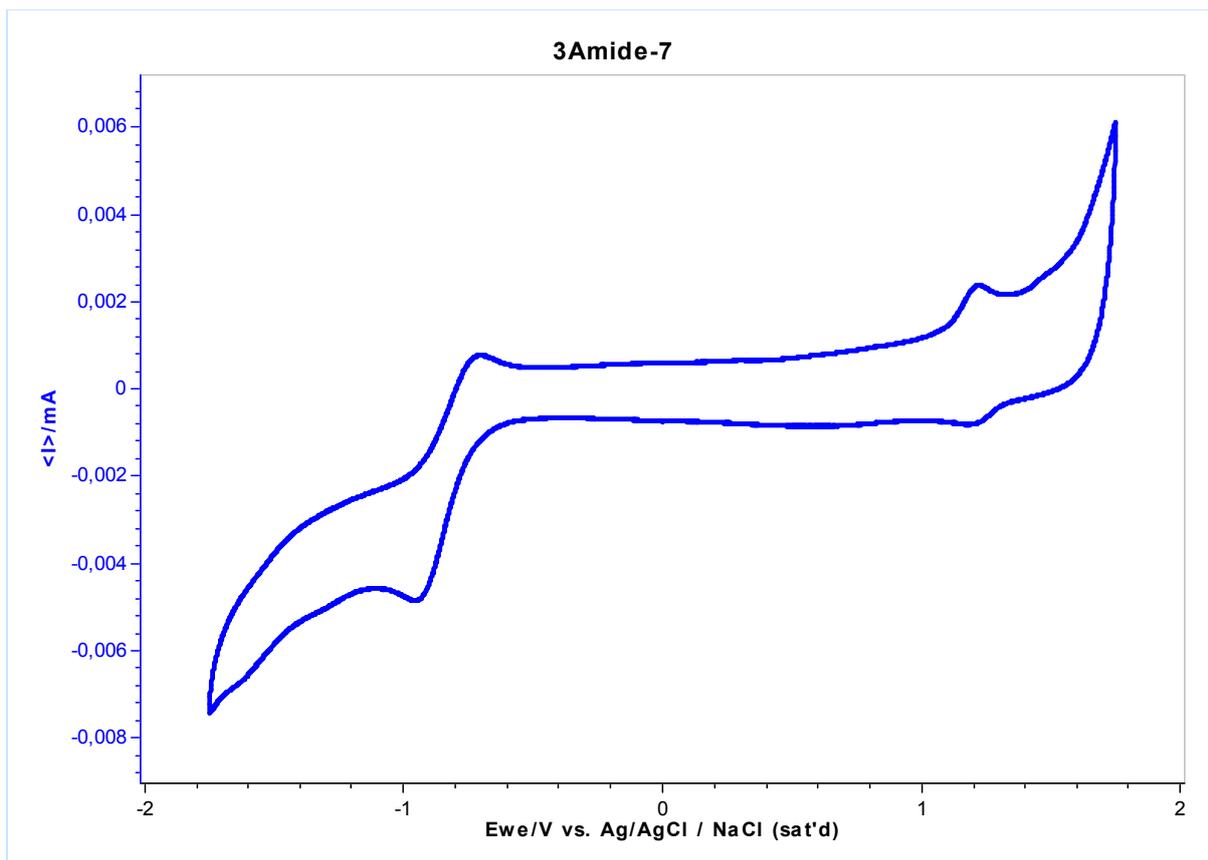
Figure SF19. Cyclic voltammograms for **Cy-3Amide-7**, **3Amide-7** and **3Amide-6** respectively.

9. Copies of NMR spectra.
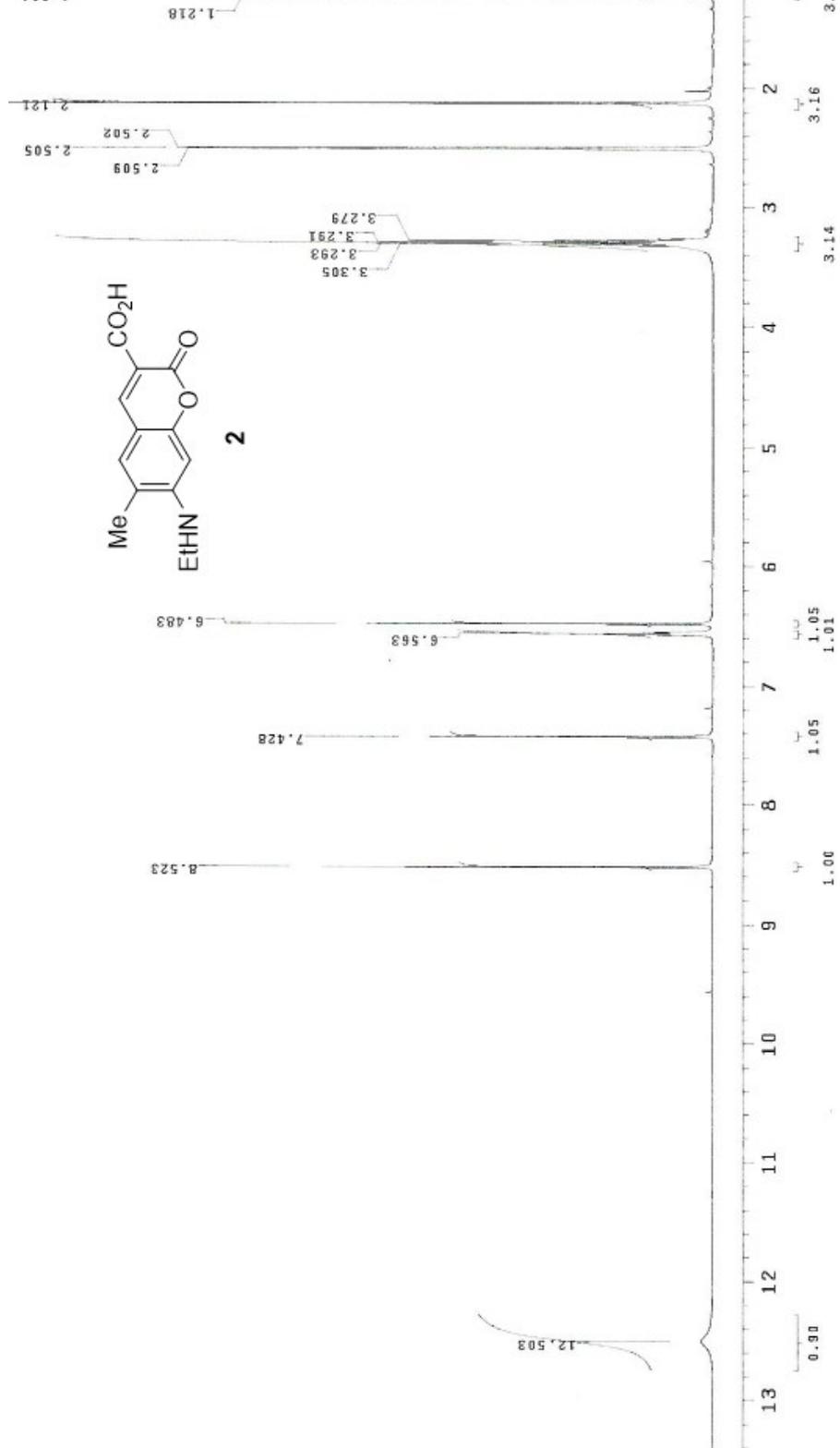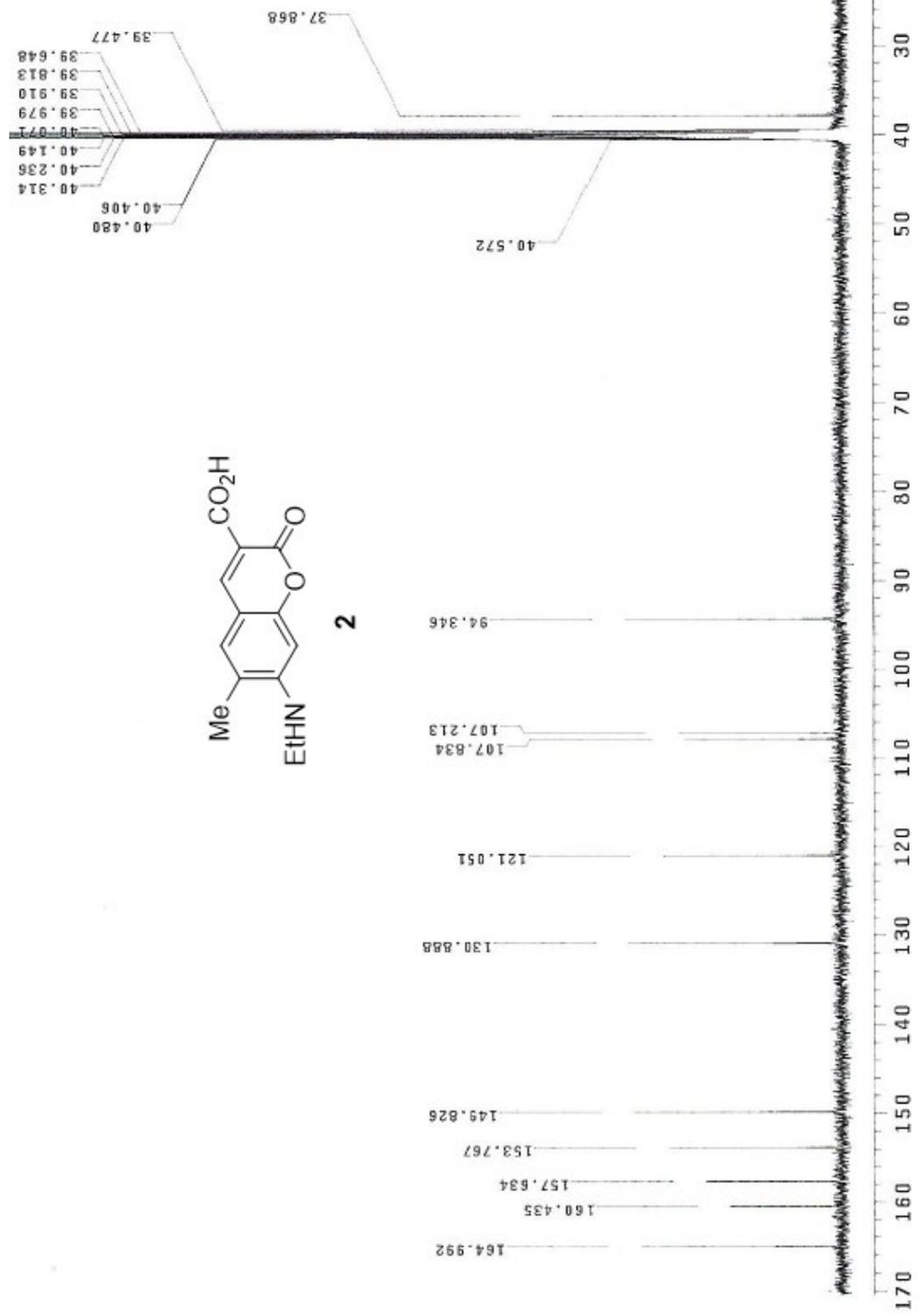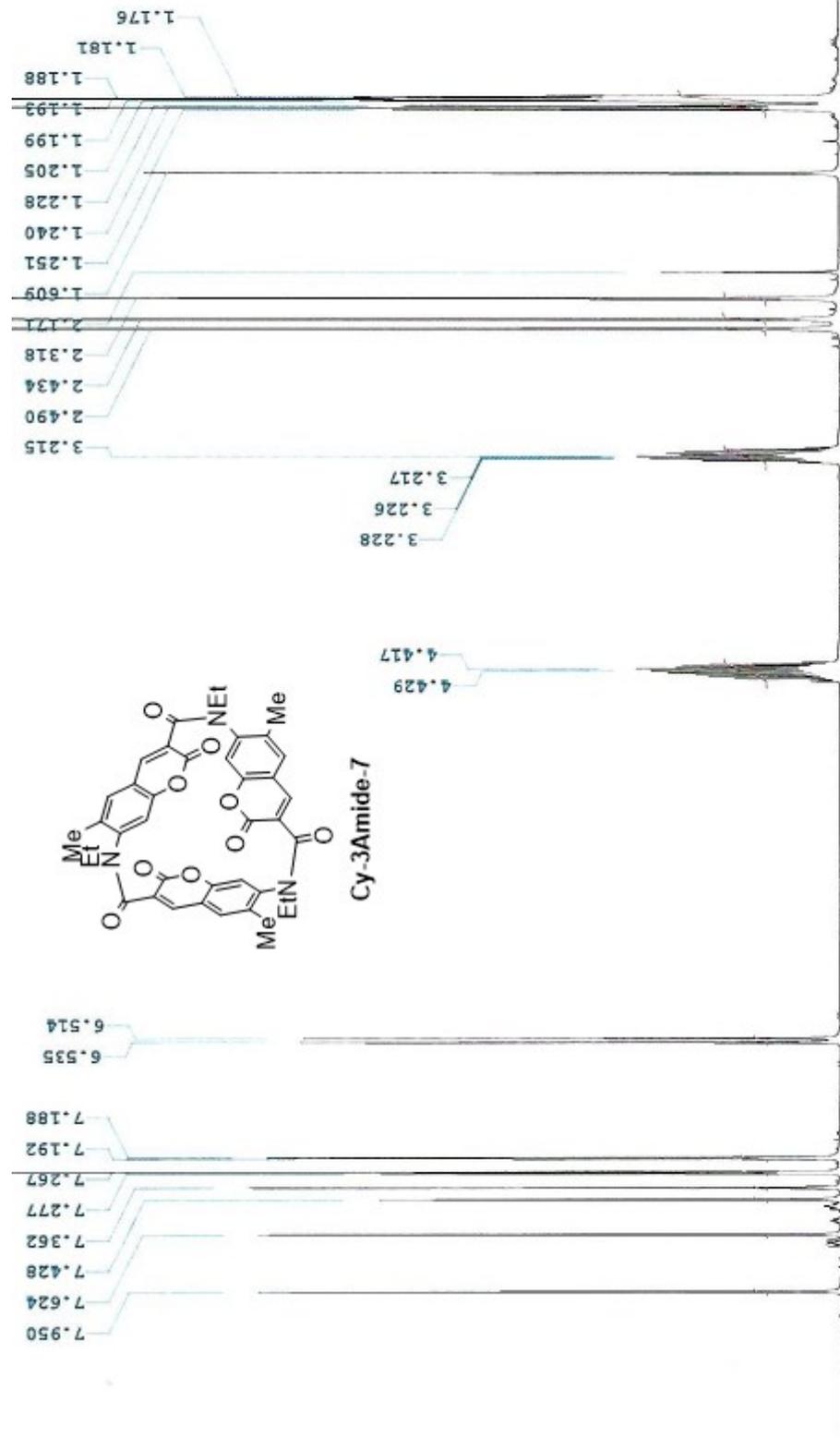
CO$_2$H

Me

EtHN

2

37.868
39.477
39.648
39.813
39.910
39.979
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40.149
40.236
40.314
40.406
40.480
40.572
94.346
107.213
107.834
121.051
130.888
149.826
153.767
157.634
160.435
164.992

1.176
1.181
1.188
1.193
1.199
1.205
1.228
1.240
1.251
1.609
2.171
2.318
2.434
2.490
3.215

3.217
3.226
3.228

4.417
4.429

Cy-3Amide-7

6.514
6.535

7.188
7.192
7.267
7.277
7.362
7.428
7.624
7.950

CO₂t-Bu

EtHN

Me

3

1.336
1.350
1.365
1.585

2.154

3.263
3.273
3.277
3.288

6.407

7.165
7.265

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2.18
1.03
1.00

1
2
3
4
5
6
7
8

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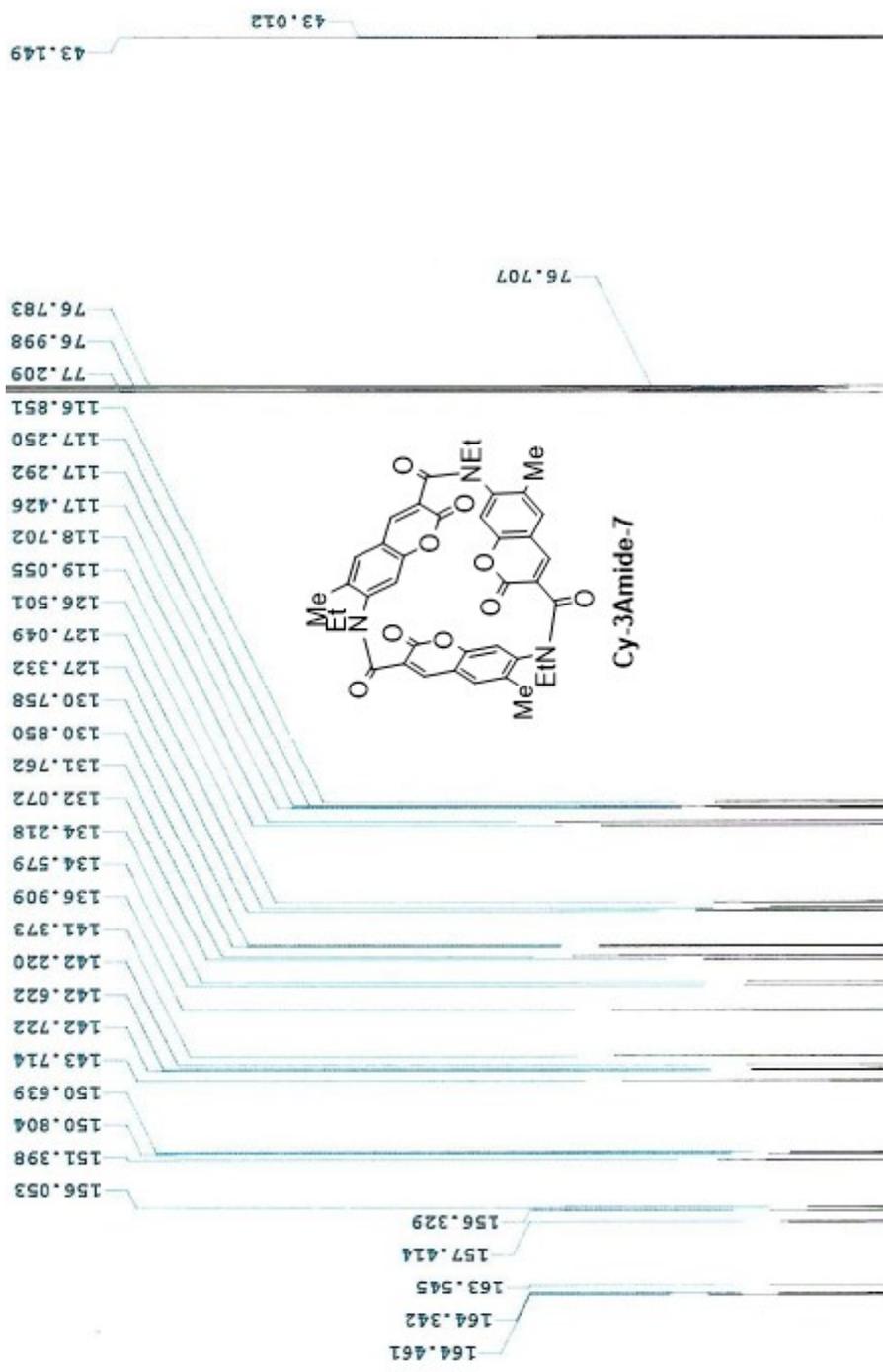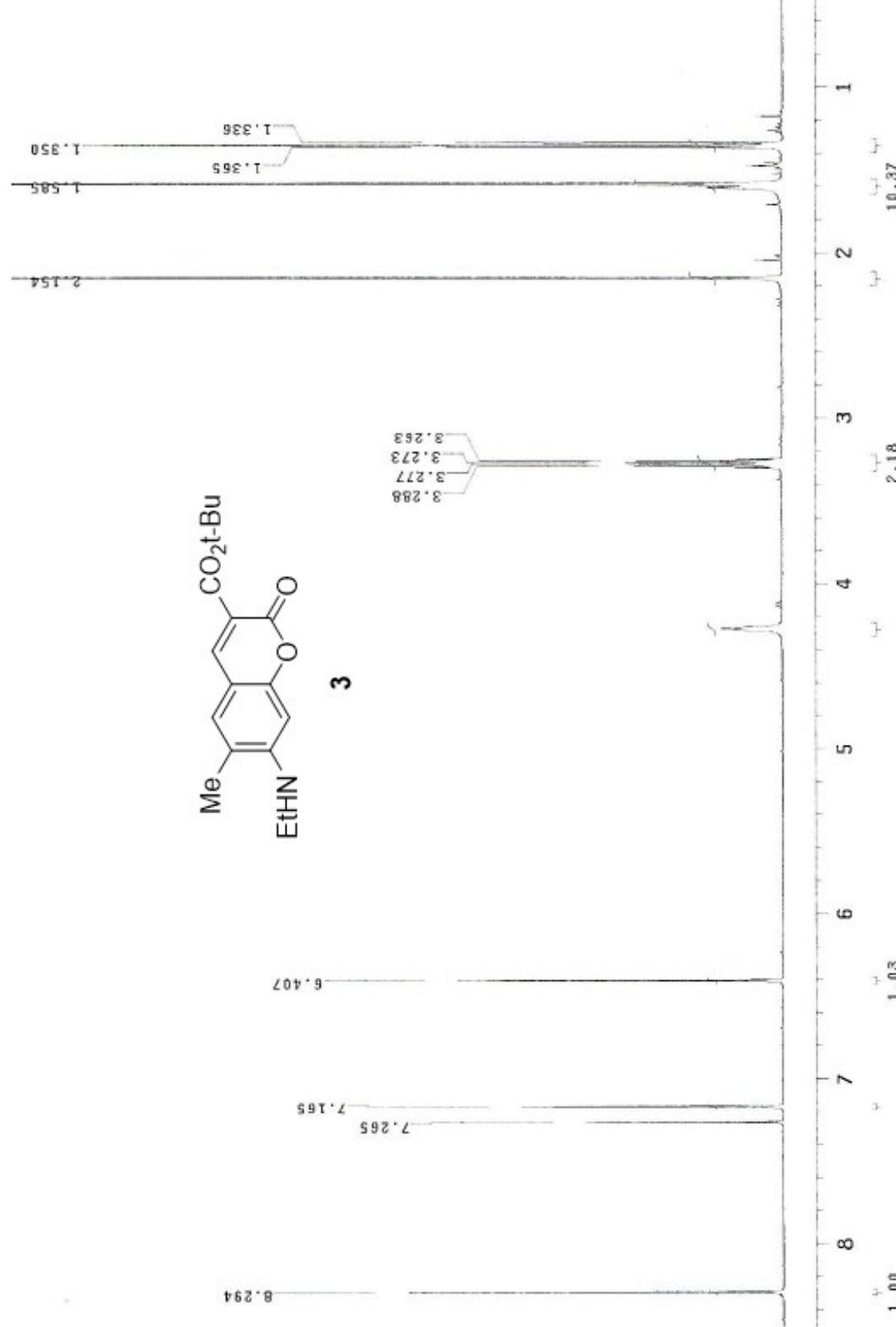
38.185

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158.343
163.002

CO₂t-Bu

Me

EtHN

3

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0.946

1.105
1.119
1.144
1.401
1.511
1.091

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2.474
2.477
2.481
2.485
2.488
2.499

3.026

3.377
3.391
3.405
3.418

6.658
6.656
6.674

7.263
7.398
7.414
7.685
7.953

8.413

CO₂t-Bu

Me

N
Et

Et₂N

5

1 2.04
2 7.38
3 10.46
6 2.36
7 2.28
8 2.34
2.23

25.811

27.350
38.999
39.164
39.330
39.500
39.587
39.666
39.753
39.831
39.918
40.001
40.089
43.676

81.597

96.084

106.389
109.149

116.291
116.718
119.344

125.618
130.938

142.959
144.619
145.737

151.182
155.390
156.056
161.290
164.468

CO_2t-Bu

OMe

Et

N

Et

Et_2N

5

1.160
1.174
1.183
1.207
1.222
1.236
1.259
1.570
1.613
2.316
2.380
2.394
2.407
2.417
2.443
3.364
3.379
3.393
3.416
3.430
3.443
3.454

7.266

8.259

3Amide-7

33

1.60 — 8.56

3.25 —   1.96

CO$_2$t-Bu

9

H$_2$N

6.79
6.80
6.95
6.95
6.97
6.97
7.14
7.16

1.03
1.03
1.00

8.25 —   1.00

0.03

28.11

82.63

112.32
117.36
118.43
119.77
122.01

143.28
147.19
148.37

157.31

162.23

CO₂t-Bu

$CO_2t\text{-}Bu$

O

O

H₂N

H_2N

9

(ppm)

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

1.254
1.269
1.283
1.615

3.466
3.481
3.495
3.509

CO₂t-Bu

NH

10

Et₂N

6.530
6.534
6.683
6.687
6.701
6.706

7.267
7.300
7.318
7.467
7.485
7.728
7.733
7.746
7.751
8.288
8.293
8.408
8.766

11.079

6.00
10.43

3.88

0.99

0.96
0.87
1.00
0.98

0.97

1
2
3
4
5
6
7
8
9
10
11

CO₂t-Bu

$CO_2t\text{-}Bu$

12.418

28.133

45.226

76.751
77.004
77.261
77.385
82.725

96.627

108.547
109.356
110.382
117.023
118.094
119.561
119.796
126.289
131.458
135.124
147.628
148.667
151.339
153.050
156.922
157.846
161.461
161.778
163.149

NH

Et₂N

10

1.241
1.250
1.262
1.274
1.559
1.608

CO2t-Bu

3.476
3.488

3Amide-6

Et2N

7.249

7.472

8.308
8.312
8.399
8.403
8.407
8.779
9.013

11.065
11.154

29.687
36.827
67.039
71.311
73.074
76.806
77.017
77.228
115.027
116.311
122.339
127.271
127.784
128.179
128.401
128.470
128.562
129.030
135.165
137.230
137.315
148.098
148.807
169.584
170.355

CO₂t-Bu

3Amide-6

Et₂N

40
60
80
100
120
140
160
180