SUPPORTING INFORMATION

Topological control in photo-induced reactions of benzophenone-aminocholestene dyads

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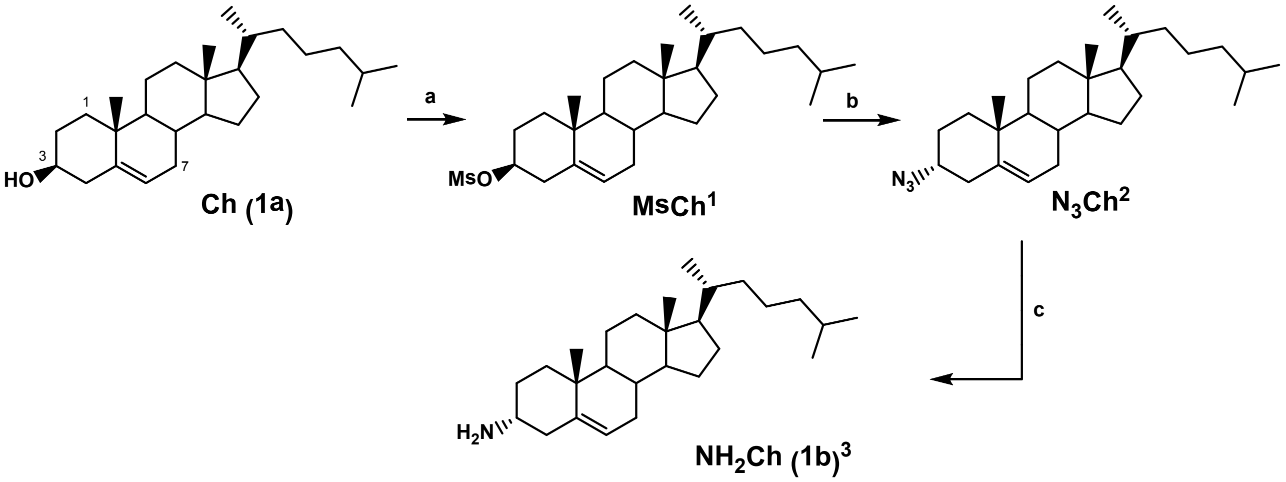
General

All chemicals and solvents were commercially available and used without additional purification. The preparation of 3α-amino-5-cholestene (NH_2Ch) is detailed in the Supporting Information. Irradiations at 254 nm were performed using the Xe lamp of a Photon Technology spectrofluorometer, equipped with a monochromator. All reactions were monitored by analytical TLC with silica gel 60 F_{254} revealed with 2,2-dihydroxyindane-1,3-dione (ninhydrin) and ammonium molybdate reagent. The residues were purified through silica gel 60 (0.063- 0.2 mm). Ultraviolet absorption spectra were recorded on a Varian Cary 300 scan UV/Vis spectrophotometer. ^1H NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ or in CD_3OD as solvents on a Bruker AC-300 at 300 and 75 MHz respectively. NMR chemical shifts are reported in ppm downfield from an internal solvent peak. Exact mass was obtained on a Waters ACQUITY™ XevoQToF Spectrometer.



Scheme 1. Synthesis of **1b**: a) MsCl, pyridine b) NaN_3, DMF c) Ph_3P, THF, H_2O

Synthesis of 3α-amino-5-cholestene (NH_2Ch, 1b)

To a cooled (0 °C) solution of **1a** (500 mg, 1.30 mmol) in anhydrous pyridine (5 mL), methanesulfonyl chloride (MsCl, 0.21 mL, 2.60 mmol) was added dropwise under nitrogen, and the reaction mixture was stirred at room temperature for 7 h. After this time, aqueous HCl 6M (100 mL) was added to the solution, and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were combined, washed with 1M HCl (10 mL), brine (2 x 5 mL), dried over

Na_2SO_4, filtered and concentrated. The resulting crude cholest-5-en-3β-ol methanesulfonate (MsCh) was used directly in the following reaction without further purification. Its ^{1}H NMR data coincide with those previously described[1]. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.70 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 1.04 (s, 3H), 0.95-2.10 (complex signal, 26H), 2.53 (m, 2H), 3.02 (s, 3H), 4.54 (m, 1H), 5.44 (m, 1H).

A solution of MsCh (560 mg, 1.20 mmol) and sodium azide (NaN_3, 130 mg, 2 mmol) in dimethylformamide (DMF, 10 mL) was refluxed for 5 h in absence of light. Afterwards, the solvent was removed under reduced pressure, and the residue was redissolved in CH_2Cl_2 (10 mL) , washed with water, brine, dried over $MgSO_4$ and evaporated. Then, the crude was purified by column chromatography (eluent: hexane-ethyl acetate 99:1 v/v) to afford 3α-azido-5-cholestene[2] (N_3Ch) as a white solid (296 mg, 60 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.70 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 1.03 (s, 3H), 0.99-2.08 (complex signal, 26H), 2.21 (dt, *J* = 14.7 Hz, 2.4 Hz, 1H), 2.54 (brd, *J* = 14.7 Hz, 1H) 3.90 (quint, *J* = 5.7 Hz, 1H), 5.42 (m, 1H).

Triphenylphosphine (Ph_3P, 80 mg, 0.36 mmol) and N_3Ch (100 mg, 0.24 mmol) were dissolved in a mixture of tetrahydrofuran (THF, 2 mL) and water (0.03 mL). The resulting mixture was stirred at 50 ^{0}C for 8 h. Then, 5% methanolic HCl solution (15 mL) was added, and a white precipitate was obtained, which was washed with diethyl ether (20 mL) and filtered through a pad of Celite® to yield pure 3α-amino-5-cholestene chlorhydrate[3] (NH_2Ch, **1b**) (87 mg, 86 %). ^{1}H-NMR (300 MHz, CD_3OD) δ = 0.75 (s , 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.3 Hz, 3H), 1.10 (s, 3H), 1.01-2.19 (complex signal, 27H), 2.80 (brd, *J* = 15.6 Hz, 1H), 3.54 (m, 1H), 5.54 (m, 1H); ^{13}C-NMR (300 MHz, CD_3OD) δ = 12.3, 19.2, 19.3, 21.9, 23.0, 23.2, 25.0, 25.3, 25.6, 29.2, 29.3, 33.0, 33.4, 36.2, 37.1, 37.4, 38.3, 40.7, 41.1, 43.5, 51.1, 57.6, 58.1, 126.9, 136.9.

Laser flash photolysis measurements

Laser flash photolysis studies were done using Nd:YAG laser (λ_{exc} = 355 nm, *ca.* 10 ns pulse width, 10 mJ/pulse) as the excitation source. The LFP system consisted of the pulsed laser, the Xe lamp, a monochromator and a photomultiplier made up of a tube, housing and power supply. The output signal from the oscilloscope was transferred to a personal computer. All experiments were performed at room temperature. The samples were dissolved in dichloromethane to have an absorbance *ca.* 0.30 at 355 nm, and solutions were degased by bubbling nitrogen. As NP does not absorb at 355 nm, under these conditions more than 99 % of the light was always absorbed by the dyads. An energy transfer reaction from dyads **2** and **3** to NP was used to determine the triplet state lifetimes of these dyads in dichloromethane. Thus, solutions of **2** and **3** (0.5 mM) and increasing amounts of the quencher (0.2 mM – 20 mM) were prepared. The rate constants of triplet excited state quenching by NP where determined by the Stern-Volmer equation ($1/\tau = 1/\tau_0 + k$ [Quencher]).[4]

Steady-state photolysis of dyads 2 and 3

Deaerated dichloromethane (40 mL) solutions of **2** or **3** (100 mg, 0.16 mmol) were irradiated for 8 h through Pyrex with a 400 W medium pressure mercury lamp. After this time, the reaction mixtures were concentrated under reduced pressure, and the photomixtures were submitted to silica gel column chromatography, using hexane/ethyl acetate/dichloromethane (70:20:10 v/v/v) as eluent, affording the pure photoproducts **4-7**.

Synthesis of dyads 2 and 3

To a solution of (*S*) or (*R*)-Kp (200 mg, 0,78 mmol) in CH_2Cl_2 (5 mL), dicyclohexylcarbodiimide (DCC, 295 mg, 1.42 mmol) was added portionwise, and the mixture was stirred at 0 ^{0}C for 30 min. Then, a solution of **1b** (295 mg, 0.71 mmol) in CH_2Cl_2 (7 mL) and 4-dimethylaminopyridine (DMAP, 102 mg, 0.85 mmol) were added, and the mixture stirred for further 8 h at the same temperature. Afterwards, the reaction mixture was filtered through a pad of Celite®. The resulting filtrate was washed with brine, water, dried over Na_2SO_4 and evaporated to dryness. The residue obtained was purified by column chromatography (eluent: hexane–dichloromethane-ethyl acetate 90:5:5 v/v/v) to give **2** (342 mg, 77%) and **3** (348 mg, 79%).

Data for (*S*)-Kp-NHCh (2) and (*R*)-Kp-NHCh (3)

Compound 2. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.55 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H), 0.85 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.88-1.60 (complex signal, 22H), 1.61-1.81 (m, 4H), 1.88 (dt, J_1 = 12.3 Hz, J_2 = 3.0 Hz, 1H), 2.41 (broad d, *J* = 12.3 Hz, 1H), 3.55 (q, *J* = 7.2 Hz, 1H), 3.96 (m, 1H), 5.10 (broad d, *J* = 5.1 Hz, 1H), 5.28 (d, *J* = 7.8 Hz, 1H), 7.38 - 7.72 (m, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 11.8, 17.9, 18.7, 18.8, 20.7, 22.6, 22.9, 23.8, 24.2, 25.8, 28.1, 28.2, 31.7, 31.8, 34.3, 35.8, 36.2, 37.1, 37.2, 39.5, 39.6, 42.2, 45.7, 47.0, 50.5, 56.1, 56.6, 123.7, 128.4, 128.7, 129.2, 130.0, 131.8, 132.6, 137.4, 138.0, 138.7, 142.2, 172.4, 196.0. Exact mass: *m*/*z* found 622.4606, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

Compound 3. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.56 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.88-1.60 (complex signal, 22H), 1.61-1.83 (m, 4H), 1.90 (dt, J_1 = 12.3 Hz, J_2 = 3.0 Hz, 1H), 2.38 (broad d, *J* = 12.3 Hz, 1H), 3.56 (q, *J* = 7.2 Hz, 1H), 3.97 (m, 1H), 5.01 (broad d, *J* = 5.0 Hz, 1H), 5.33 (d, *J* = 7.8 Hz, ,1H), 7.40 - 7.72 (m, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 11.8, 18.0, 18.7, 18.8, 20.7, 22.6, 22.9, 23.8, 24.2, 25.6, 28.0, 28.2, 31.7, 31.8, 34.4, 35.7, 36.2, 37.1, 37.2, 39.5, 39.6, 42.2, 45.6, 47.2, 50.6, 53.5, 56.1, 56.6, 123.6, 128.3, 128.7, 129.2, 130.0, 131.7, 132.5, 137.4, 137.9, 138.6, 141.8, 172.6, 196.1. Exact mass: *m/z* found 622.4603, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

Photoproduct 4 (21%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.52 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.87 (s, 3H), 0.88 (d, *J* = 6.3 Hz, 3H), 1.48 (d, *J* = 7.5 Hz, 3H), 0.52-2.00 (complex signal, 24H), 2.19 (m, 1H), 2.29 (brd, *J* = 13.8 Hz 1H), 3.44 (m, 2H), 3.82 (m,1H), 5.27 (m, 2H), 6.60 (m, 1H), 7.14-7.41 (m, 7H), 7.79 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 10.8, 18.3, 19.0, 20.1, 22.6, 22.9, 24.0, 25.4, 27.4, 28.1, 28.2, 34.0, 36.0, 36.3, 38.1, 38.5, 38.6, 39.0, 39.6, 42.8, 45.7, 46.9, 47.0, 50.5, 55.6, 83.5, 123.6, 127.1, 127.5, 127.6, 127.7, 128.6, 133.0, 138.3, 141.8, 141.9, 145.7, 149.0, 174.4. Exact mass: m/z found 622.4631, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

Photoproduct 5 (43%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.01 (m, 1 H), 0.50 (s, 3H), 0.87 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 1.64 (d, *J* = 7.2 Hz, 3H), 0.60-2.00 (complex signal, 27 H), 2.10 (dt, *J* = 13.2 Hz, 2.7 Hz, 1H), 2.50 (brd, *J* = 13.2 Hz, 1H), 3.31 (m, 1H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.89 (m, 1H), 5.81 (d, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 4.2 Hz, 1H), 7.32-7.50 (m, 5H), 7.85 (br s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 8.12 (brd, *J* = 8.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 11.6, 13.2, 17.6, 19.0, 19.5, 22.6, 22.8, 23.9, 25.4, 26.7, 27.9, 28.2, 34.1, 35.8, 36.1, 37.6, 37.7, 37.9, 39.0, 39.1, 39.4, 43.2, 45.7, 46.2, 49.8, 51.0, 54.6, 81.9, 123.7, 126.7, 127.1, 127.9, 128.0, 128.3, 130.9, 132.1, 141.5, 141.6, 142.1, 145.3, 172.3. Exact mass: *m/z* found 622.4621, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

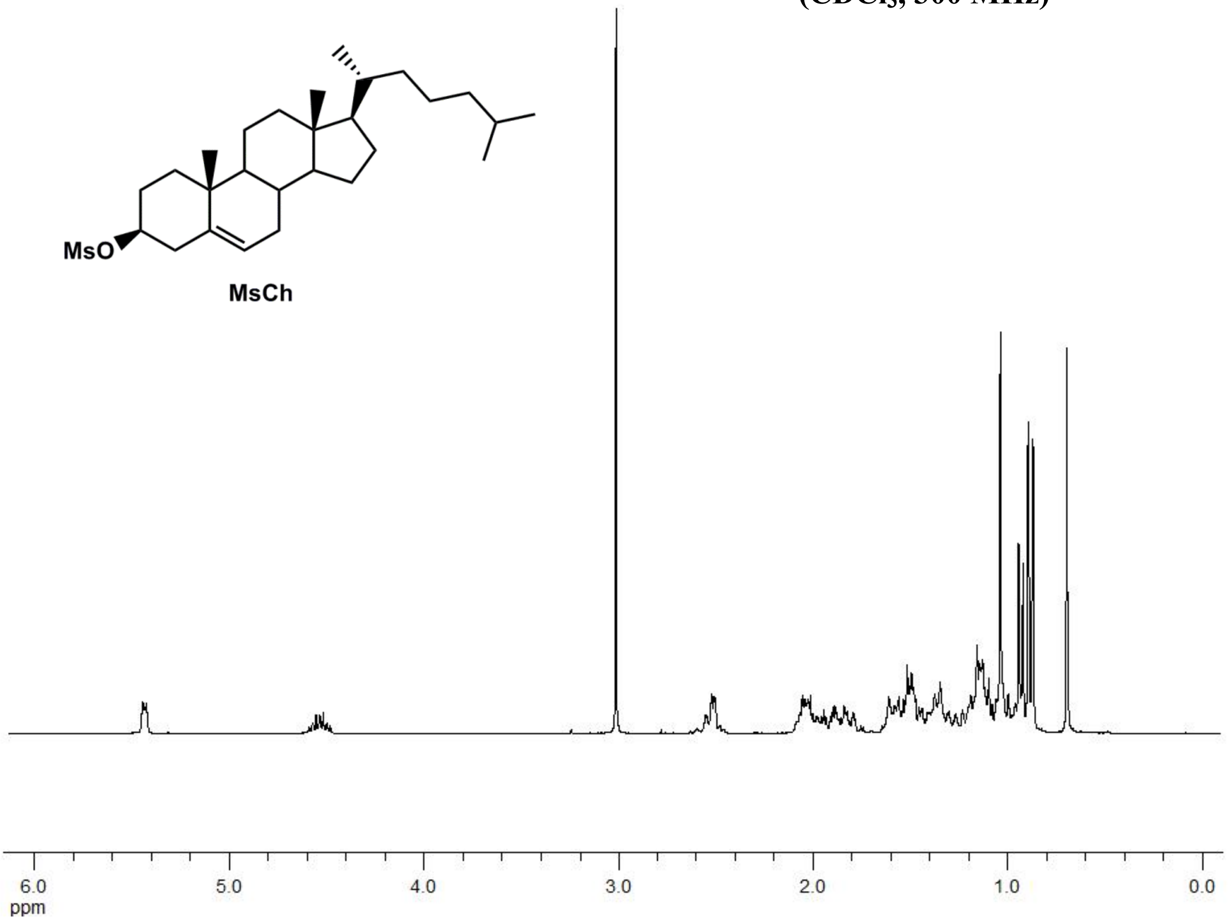
Photoproduct 6 (15%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.52 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.87 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.90-2.00 (complex signal, 27H), 2.13 (m, 1H), 2.23 (brd *J* = 14.1 Hz, 1H), 3.41 (m, 2H), 3.83 (m, 1H), 5.22 (m, 2H), 6.56 (m, 1H), 7.07 (brd, *J* = 7.5 Hz, 1H), 7.20-7.40 (m, 6H), 7.76 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 10.9, 18.5, 19.0, 20.1, 22.6, 22.9, 24.0, 25.8, 27.4, 28.1, 28.2, 31.0, 33.8, 36.0, 36.3, 37.5, 37.8, 38.5, 38.8, 39.6, 42.8, 45.8, 47.1, 50.5, 55.6, 83.5, 126.7, 127.0, 127.5, 127.7, 128.6, 131.0, 140.3, 145.7, 148.8, 148.9, 174.2. Exact mass: *m/z* found 622.4648, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

Photoproduct 7 (54%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.01 (m, 1H), 0.40 (s, 3H), 0.78 (s, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H), 1.58 (d, *J* = 7.5 Hz, 3H), 0.50-2.10 (complex signal, 27 H), 2.06 (dt, *J* = 13.5 Hz, 2.7 Hz, 1H), 2.37 (brd, *J* = 13.5 Hz, 1H), 3.22 (m, 1H), 3.55 (q, *J* = 7.5 Hz, 1H), 3.86 (m, 1H), 5.74 (d, *J* = 7.8 Hz, 1H), 6.02 (d, *J* = 4.2 Hz, 1H), 7.14 (brd, *J* = 7.8 Hz, 1H), 7.23-7.36 (m, 4H), 7.84 (br s, 1H), 7.85 (m,1H), 8.03 (br, *J* = 8.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 11.7, 17.7, 17.9, 19.0, 19.4, 22.6, 22.8, 24.0, 26.1, 26.8, 27.9, 28.2, 34.2, 35.8, 36.1, 37.5, 37.6, 37.8, 38.6, 39.3, 39.5, 43.3, 45.3, 49.0, 49.8, 50.9, 54.6, 82.1, 126.5, 127.4, 127.9, 128.0, 128.2, 128.3, 128.4, 130.9, 141.5, 142.1, 142.8, 145.3, 173.3. Exact mass: *m/z* found 622.4629, calculated for $C_{43}H_{60}NO_2$ (MH^+) 622.4624.

CIDNP and quantum mechanical calculations

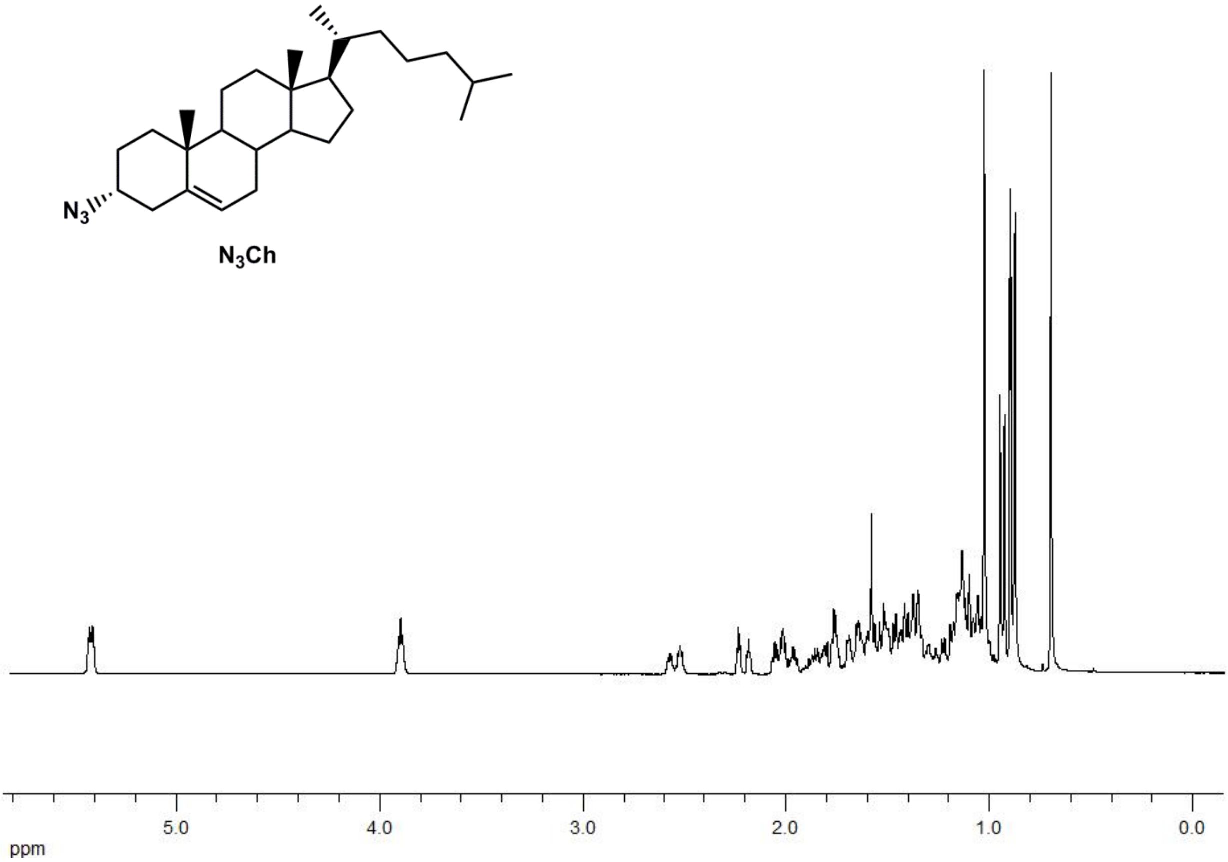
CIDNP spectra were recorded on a 200 MHz Bruker AVANCE DPX spectrometer. Irradiation was carried out by using a frequency-tripled Quantel Nd:YAG Brilliant B laser (10 Hz, 355 nm, ca. 90 mJ per pulse, pulse width ca. 6 ns). The following pulse sequence was used: presaturation – laser flash – RF detection pulse (4 us) – free induction decay. Dark spectra, the same sequence without the laser flash, were always recorded to assure effective suppression of background NMR signals. The concentrations of **2** and **3** were 0.01 M. The hfcs of the free radicals were calculated using the Gaussian 03 package.[5] All calculations (geometry optimizations and single-point calculations) were conducted at the B3LYP[6, 7] level of theory with the TZVP basis set.[8]

(CDCl$_3$, 300 MHz)

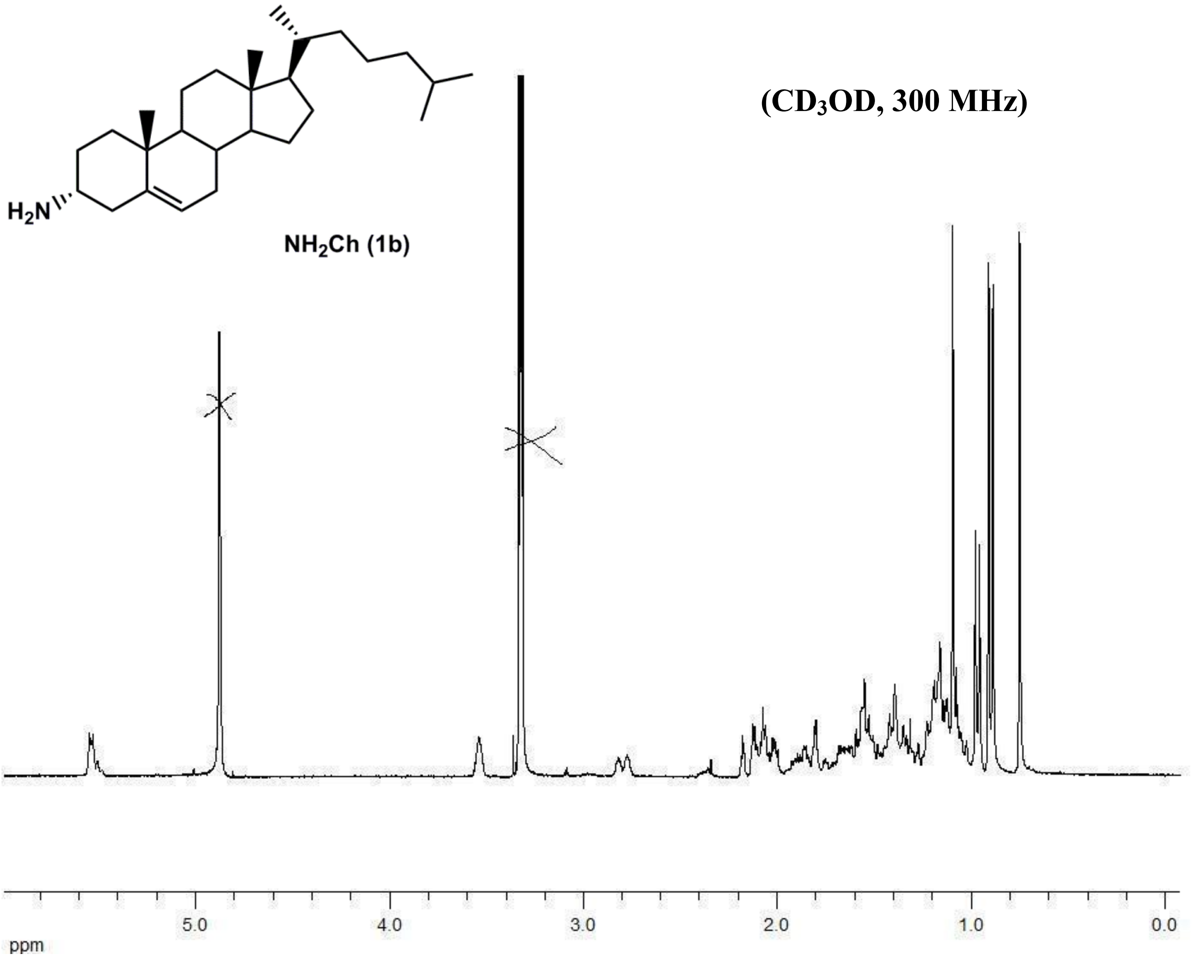


MsCh

(CDCl$_3$, 300 MHz)



N$_3$Ch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(CD₃OD, 300 MHz)
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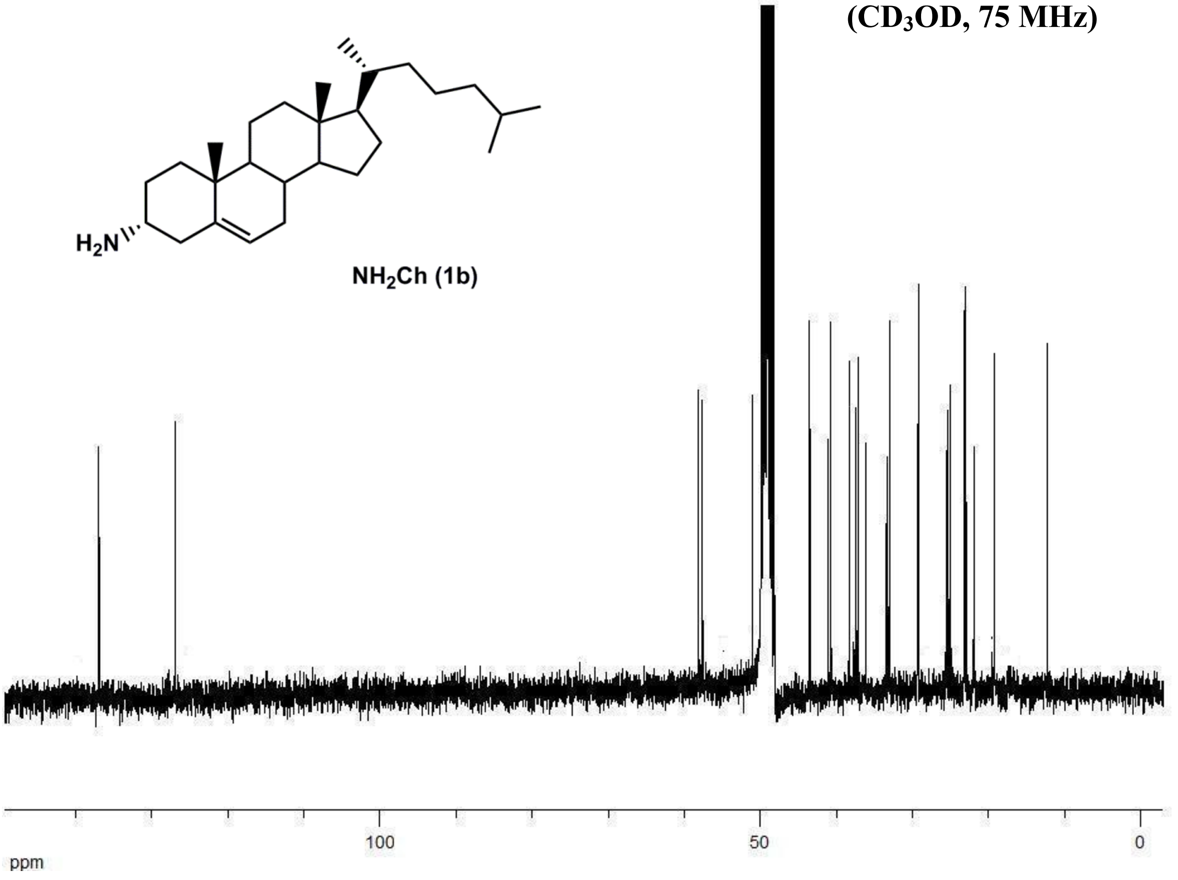
ppm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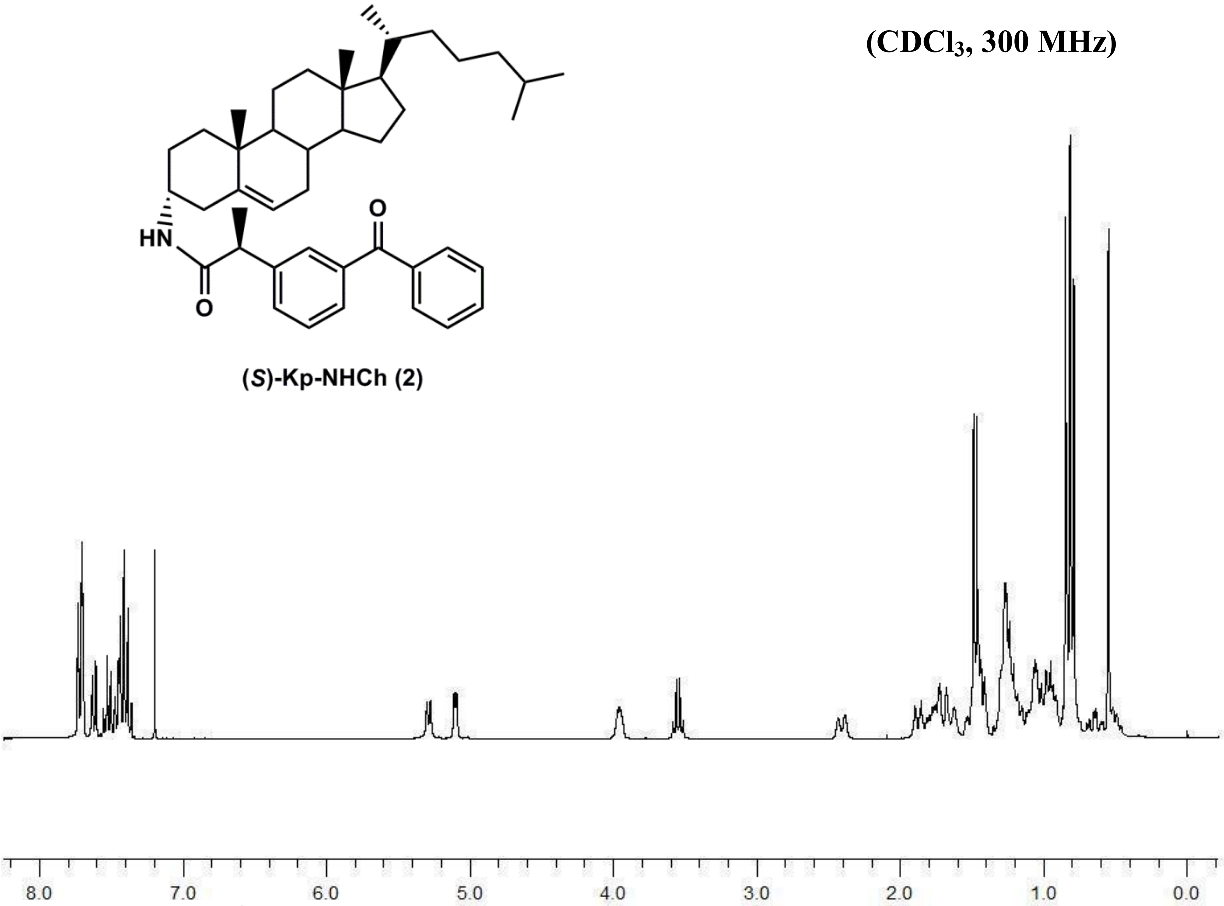
0
ppm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O
O
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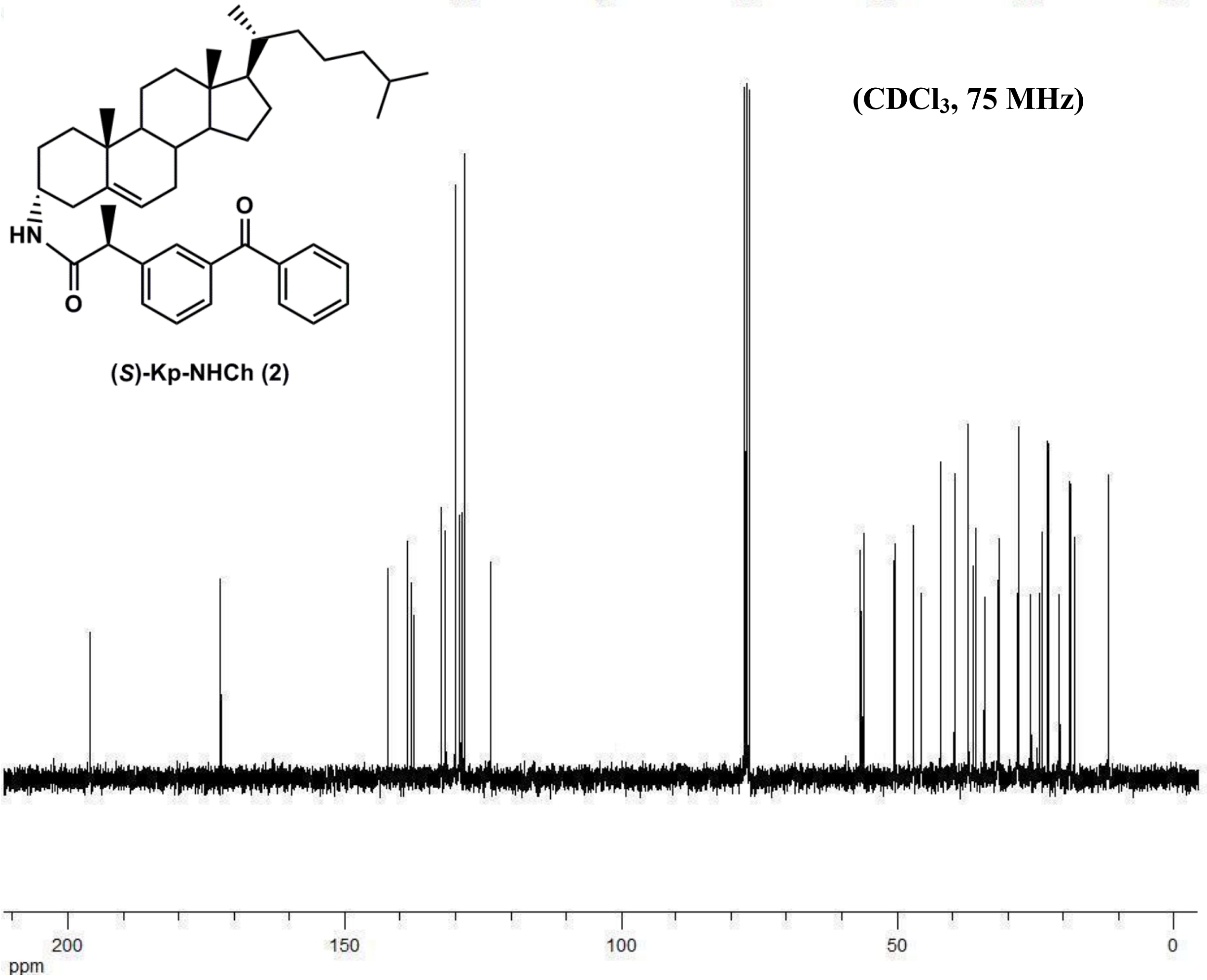
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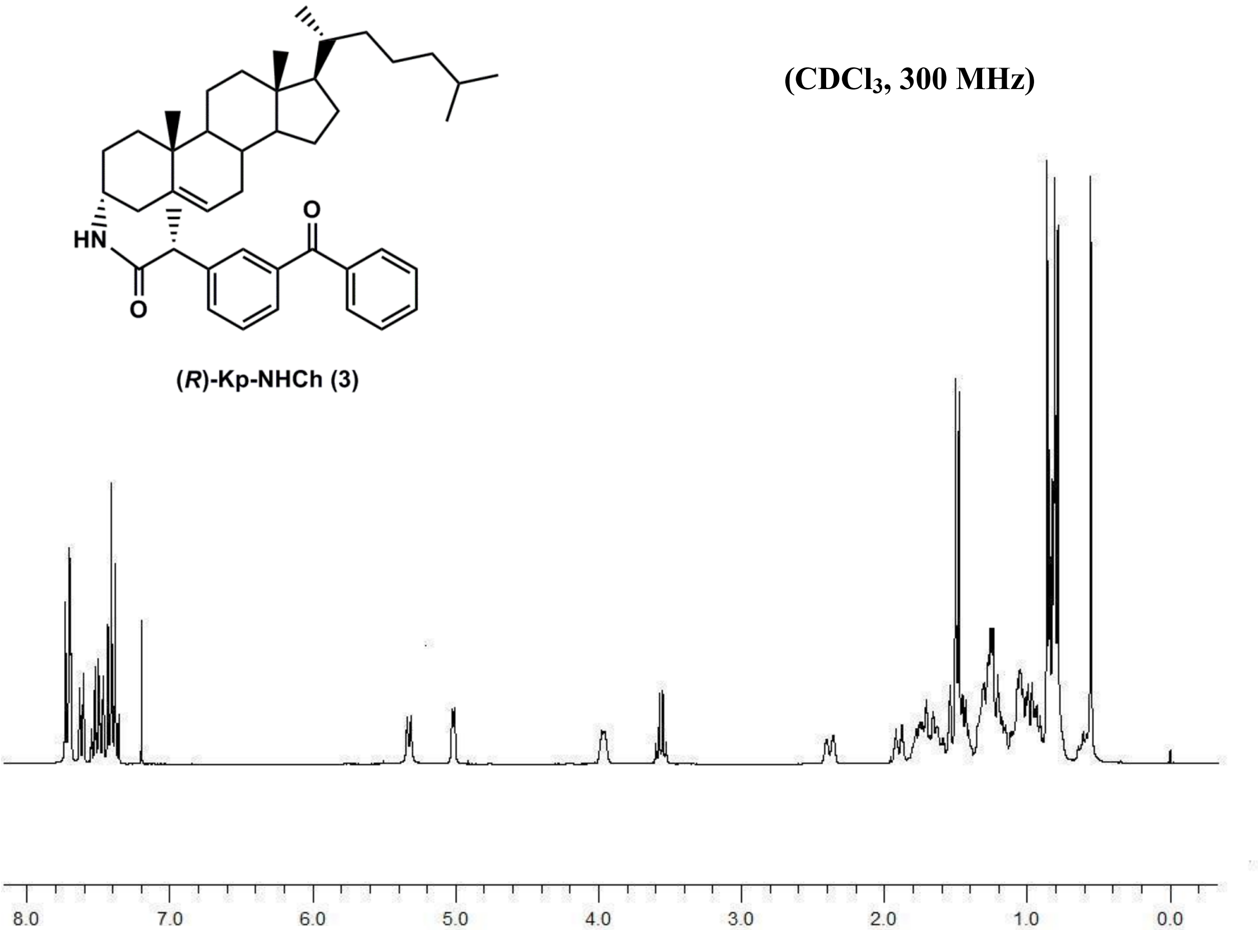
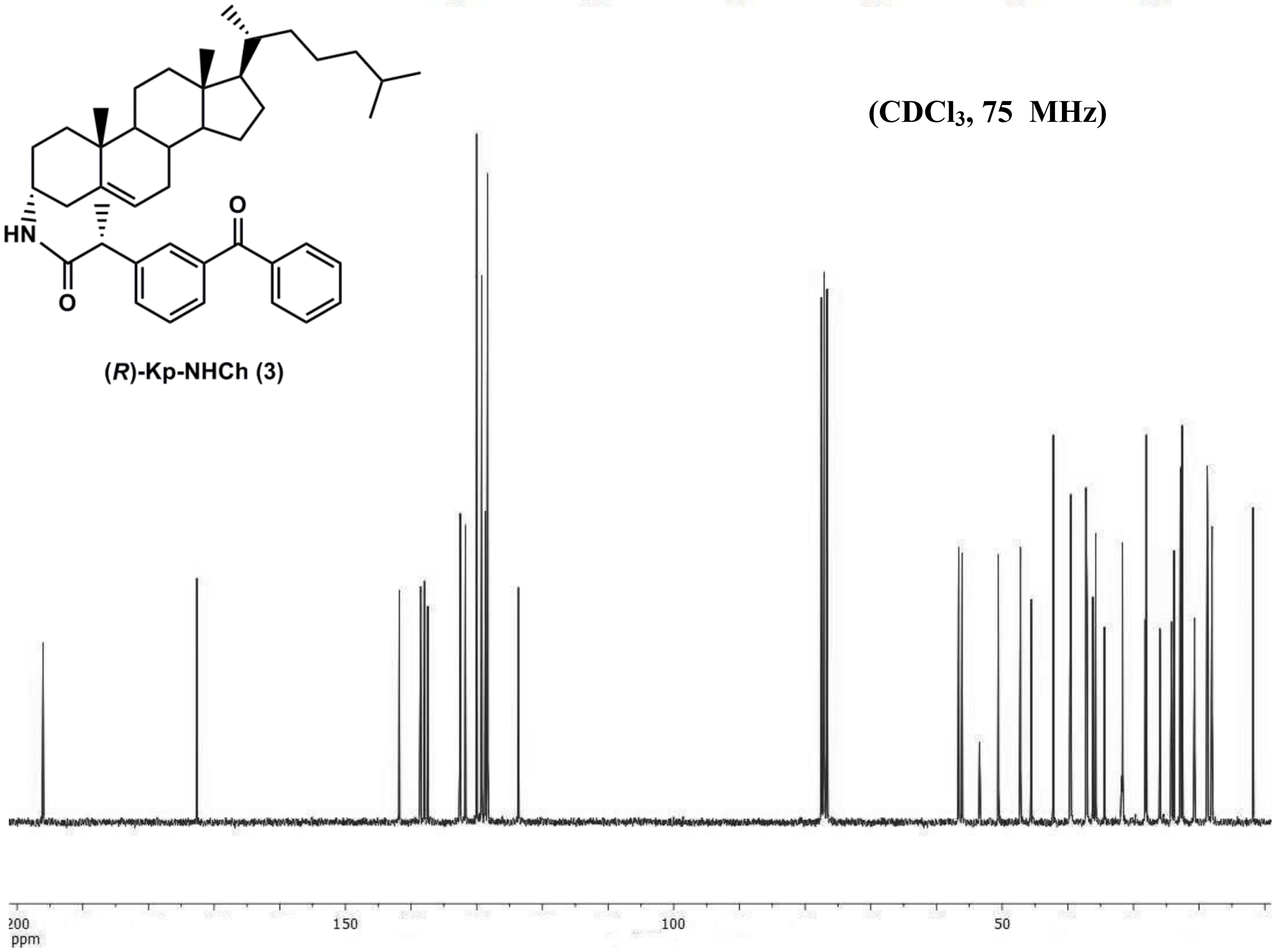
ppm



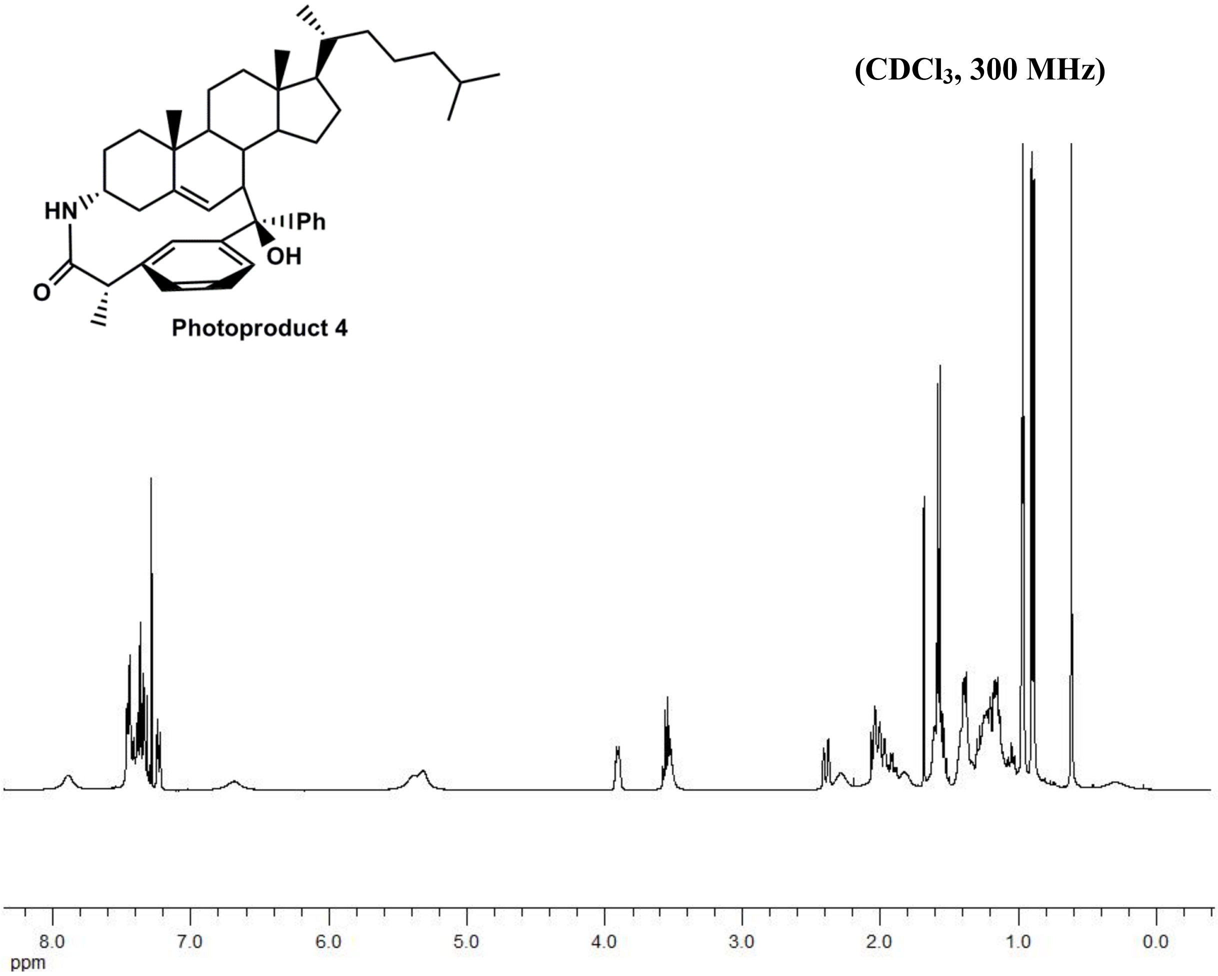
(*R*)-Kp-NHCh (3)

($CDCl_3$, 300 MHz)



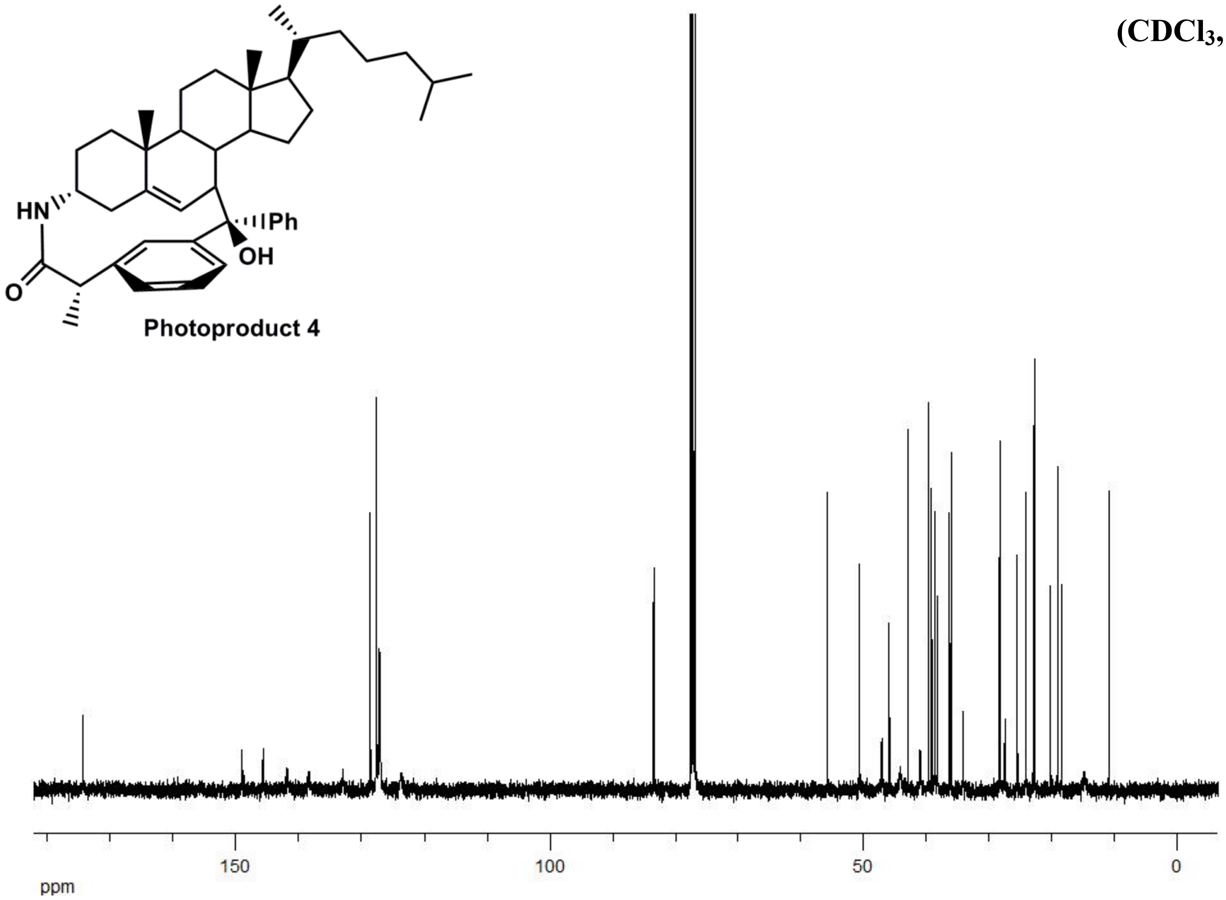
(*R*)-Kp-NHCh (3)

($CDCl_3$, 75 MHz)



Photoproduct 4

(CDCl$_3$, 300 MHz)



Photoproduct 4

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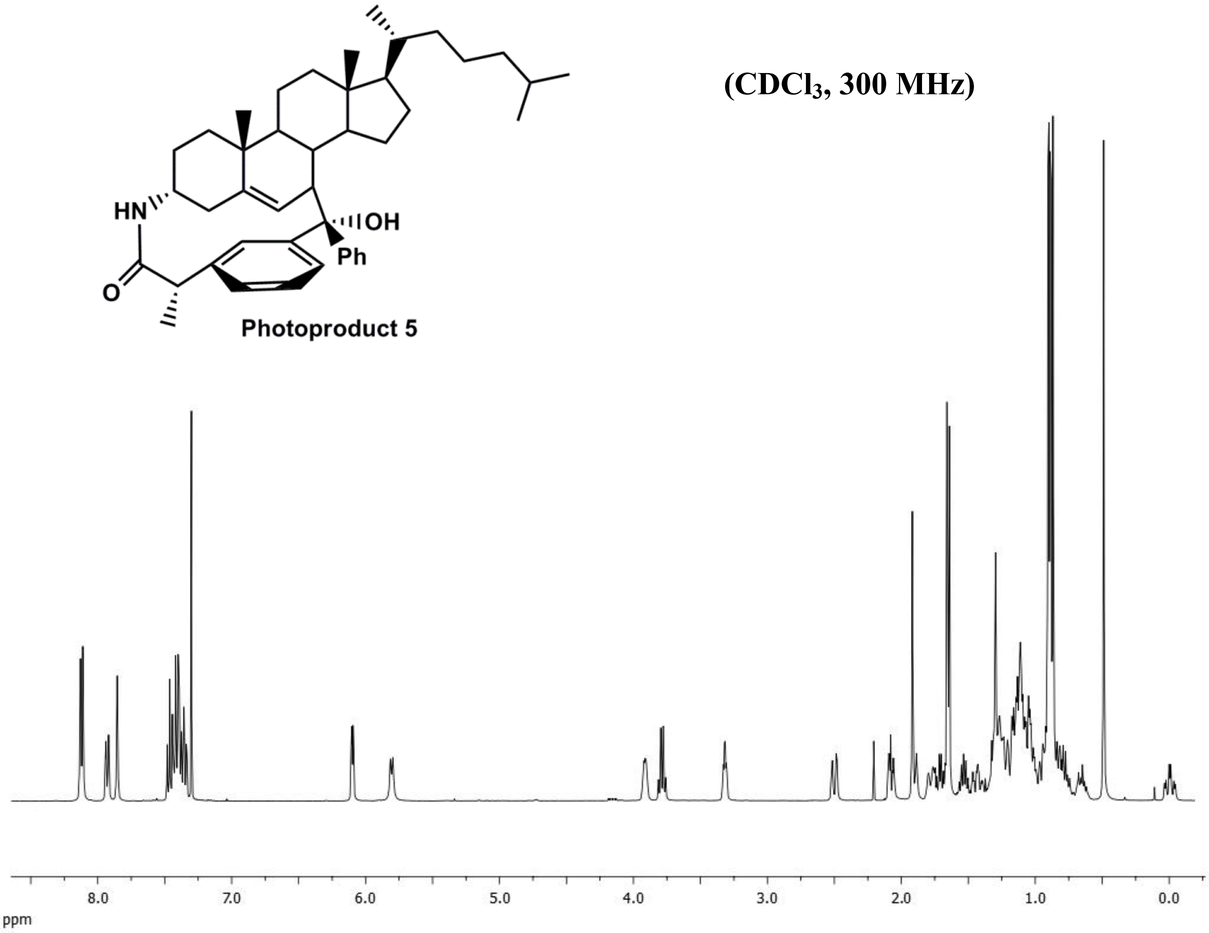
Photoproduct 5
(CDCl$_3$, 300 MHz)
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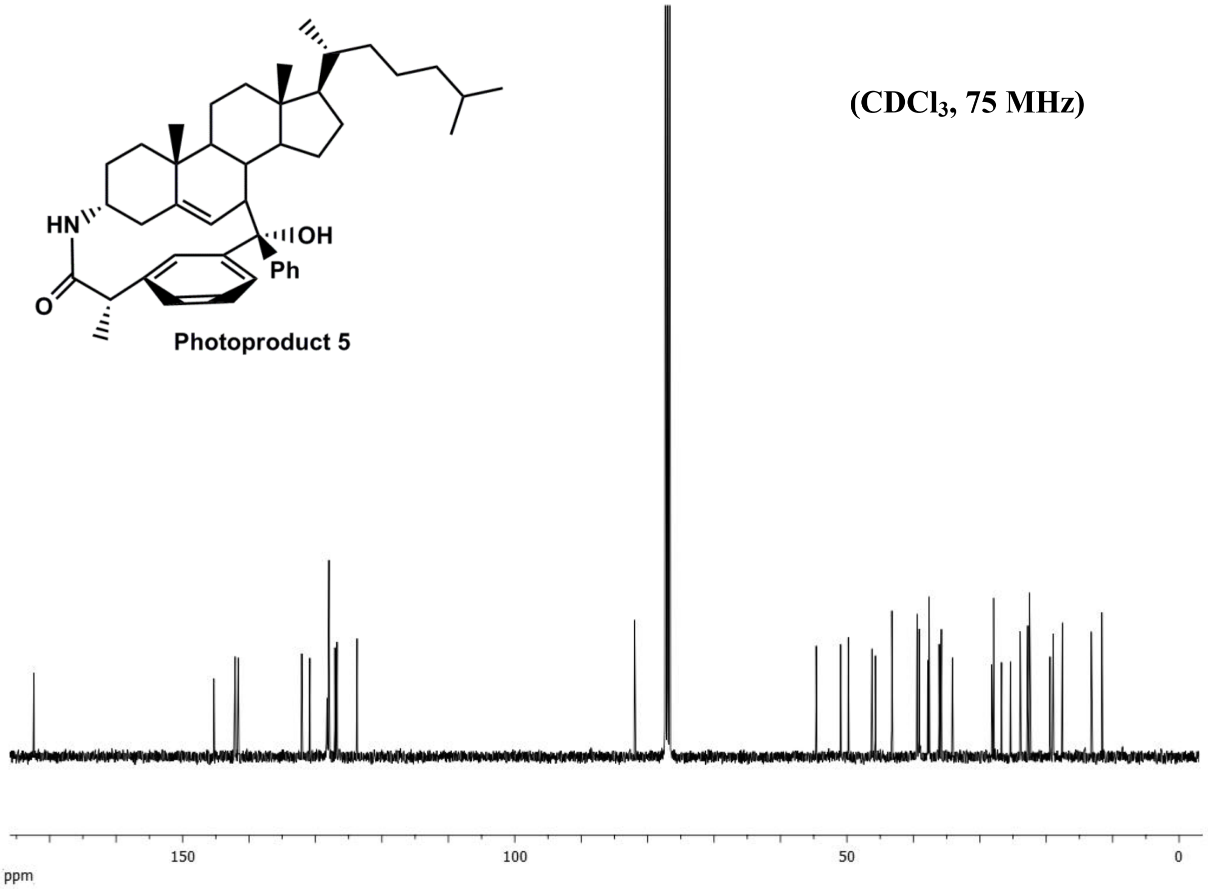
ppm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50
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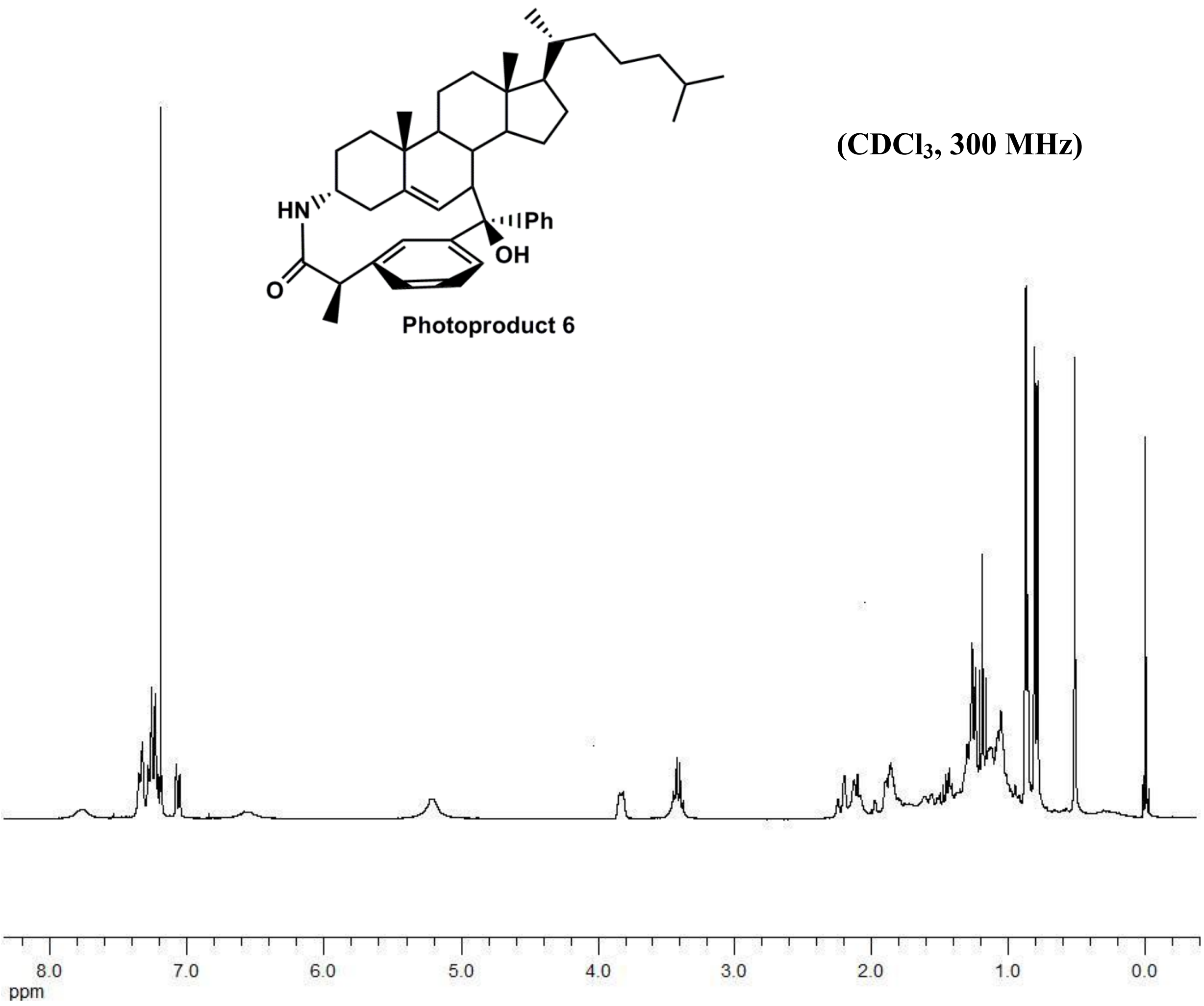
HN
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Ph
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Photoproduct 6
(CDCl₃, 300 MHz)
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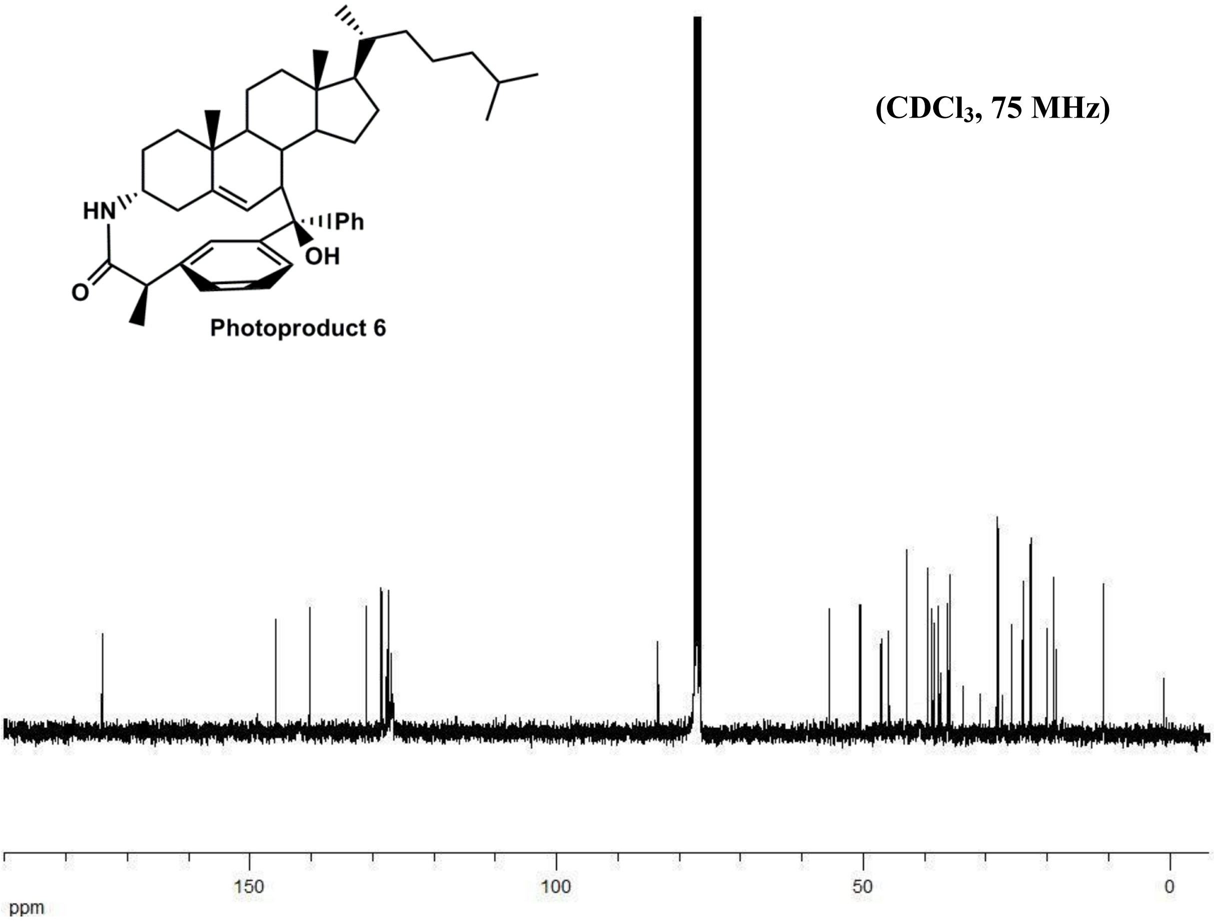
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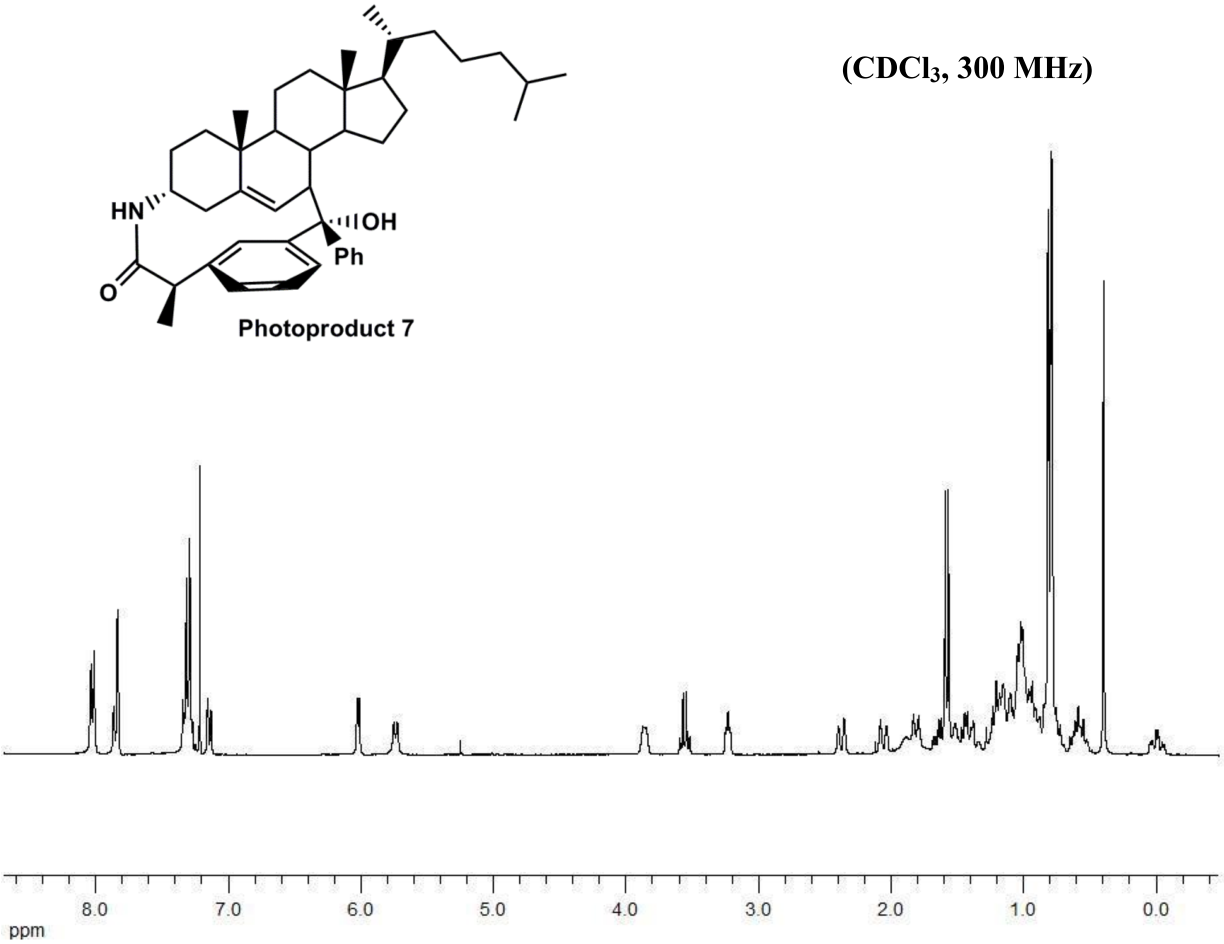
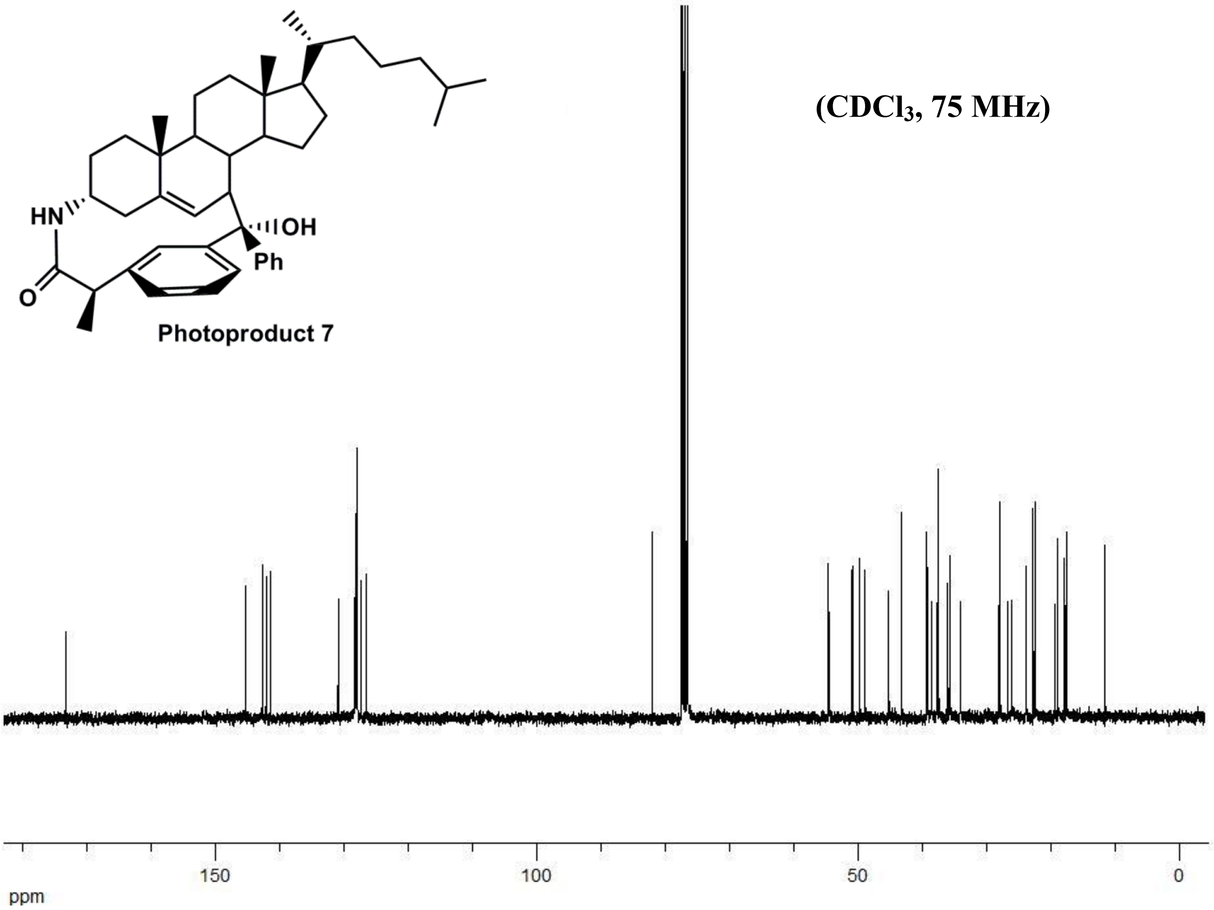


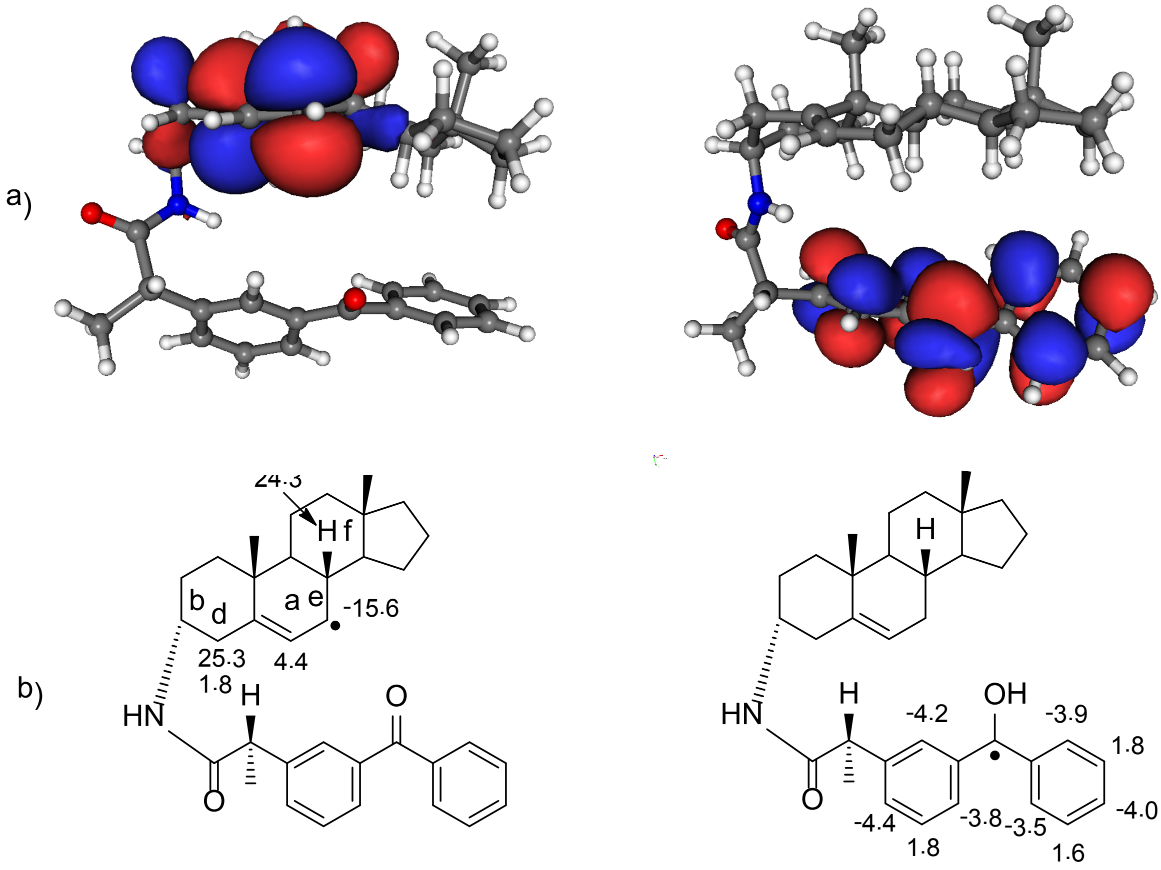
Photoproduct 7

(CDCl$_3$, 300 MHz)

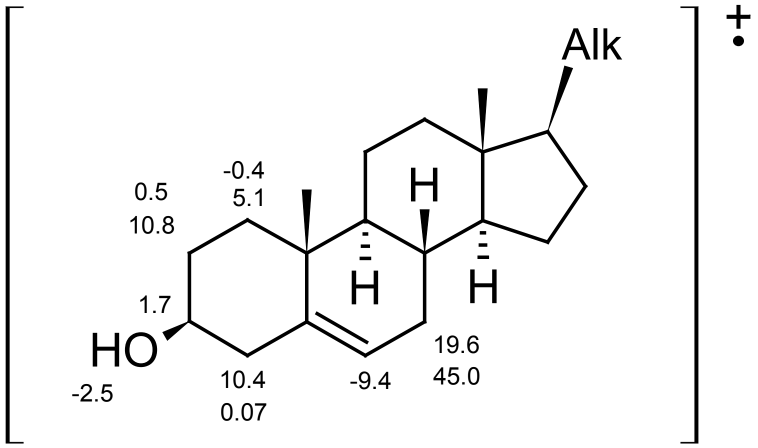


Photoproduct 7

(CDCl$_3$, 75 MHz)



SOMO visualization (a) and calculated (B3LYP/TZVP) hfcs **(> 1 G)** of radicals **A** and **B**, which were used to predict hfcs in biradical 3••.



Calculated (B3LYP/TZVP) hyperfine coupling constants of Ch-radical cation.

1. Q. Sun, S. Cai and B. R. Peterson, *Org. Lett.*, 2009, **11**, 567-570.
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