Supplementary Information for

Impact of Chirality on the Photoinduced Charge Transfer in Linked Systems Containing Naproxen Enantiomers.

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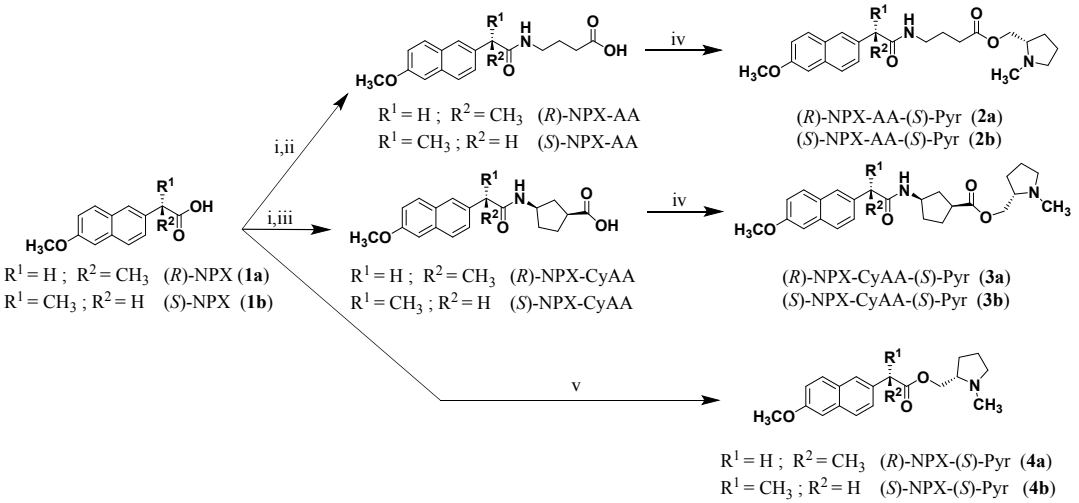
Synthesis and Characterization of Dyads

Materials and solvents. (R)- and (S)-naproxen (NPX), (S)-N-methyl-2-pyrrolidinemethanol, N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDCi), N-hydroxysuccinimide, 2,4,6-trichlorobenzoyl chloride, 4-aminobutyric acid, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), pyridine and triethylamine were purchased from Sigma-Aldrich; (1S,3R)-3-aminocyclopentanecarboxylic acid was provided by Acros Organics. Tetrahydrofuran (THF), ethyl acetate, n-hexane, dichloromethane, methanol, benzene and sodium hydrogen carbonate were from Scharlab. Acetonitrile and benzene for optic measurements were from Cryochrom and Soyuzchemprom, respectively. Deuteroacetonitrile (D 99.9%) and deuterobenzene (D 99.8%) for CIDNP measurements were provided by Aldrich.

Synthesis of dyads. The synthetic strategy employed to prepare the dyads used in this study is outlined in Scheme 1.

Scheme 1. Synthesis of NPX-pyrrolidine dyads: (i) N-hydroxysuccinimide, DCC, THF, rt.; (ii) 4-aminobutyric acid, $NaHCO_3$, H_2O, THF, rt.; (iii) (1S,3R)-3-aminocyclopentanecarboxilic acid, $NaHCO_3$, H_2O, THF, rt.; (iv) 2,4,6-trichlorobenzoyl chloride, Et_3N, (S)-N-methyl-2-pyrrolidinemethanol, DMAP, THF, rt.; (v) EDCi, pyridine, DMAP, (S)-N-methyl-2-pyrrolidinemethanol, N_2, rt.



Synthesis of (R/S)-NPX-amino acids 5(a,b) and 6(a,b). To a cold solution of (R)- or (S)-NPX (2.0 g, 8.7 mmol) in THF (60 mL), DCC (2.0 g, 9.6 mmol) was added portionwise, and the mixture was stirred at 0 ^{0}C for 20 min. Then, N-hydroxysuccinimide (1.0 g, 8.7 mmol) was added and the mixture was stirred overnight at room temperature. The resulting reaction mixture was filtered, and the filtrate was distilled under reduced pressure. The product (3.0 g, 9.0 mmol) was dissolved in THF (35 mL) and was added dropwise, under stirring, to a solution of 4-aminobutyric acid or (1S,3R)-3-aminocyclopentanecarboxylic acid (9.0 mmol) and $NaHCO_3$ (1.5 g, 18 mmol) in distilled water (25 mL) and then stirred at room temperature for 2 days. Afterwards, the reaction was filtered, and the filtrate was concentrated to approximately 25 mL. Then, concentrated hydrochloric acid was added dropwise until pH 5, and the filtrate was extracted with AcOEt (3 x 25 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and concentrated. The crude was purified by column chromatography (CH_2Cl_2/ CH_3OH, 97 : 3) to give **(R)-NPX-AA** (1.8 g, 62 %), **(S)-NPX-AA** (1.6 g, 54%), **(R)-NPX-CyAA** (2.3 g, 69 %) or **(S)-NPX-CyAA** (2.4 g, 77 %), respectively, as white solids.

Synthesis of (R,S)- and (S,S)-NPX-amino acid–pyrrolidine ester dyads 2(a,b) and 3(a,b). 2,4,6-trichlorobenzoyl chloride (381 µL, 2.4 mmol) and Et_3N (621 µL, 4.4 mmol) were added dropwise to a solution of the corresponding NPX-amino acid (2.2 mmol) in anhydrous THF (10 mL) at room temperature under nitrogen. The resulting solution was stirred for 1 h and reacted with a solution of (S)-

N-methyl-2-pyrrolidinemethanol (343 μL, 2.9 mmol) in anhydrous THF (3 mL), in the presence of DMAP (353 mg, 2.9 mmol), overnight at room temperature. Then, the reaction was quenched with saturated aq. $NaHCO_3$ solution, and extracted with AcOEt. The combined organic layers were washed with aqueous acetic acid and brine, dried over anhydrous magnesium sulfate and evaporated under reduced pressure, to get a white solid, which was recrystallized from a mixture of n-hexane : AcOEt (2 : 3). Dyads **2a** (0.7 g, 74 %), **2b** (0.6 g, 62 %), **3a** (0.7 g, 79 %) and **3b** (0.8 g, 83 %) were obtained as white solids.

Synthesis of (R,S)- and (S,S)-NPX-pyrrolidine ester dyads 4(a,b). To a solution of (R)- or (S)-NPX (2 g, 8.7 mmol) in anhydrous pyridine (20 mL), EDCi (1.6 g, 8.7 mmol) and DMAP (10 mg, 0.1 mmol) were added dropwise, at room temperature under nitrogen, and the resulting solution was stirred for 20 min. Then, (S)-N-methyl-2-pyrrolidinemethanol (1.1 mL, 8.9 mmol) was added, and the mixture was stirred 48 h at room temperature. Afterwards, the reaction mixture was distilled under reduced pressure, to get a residue, which was re-dissolved in AcOEt and washed with aqueous hydrochloric acid 1M and brine, dried over anhydrous magnesium sulfate and concentrated. The crude was purified by column chromatography (CH_2Cl_2 : CH_3OH, 97 : 3) to give **4a** (1.4 g, 47 %) or **4b** (1.5 g, 50 %) as orange oils. ^1H NMR and ^{13}C NMR data were found to be coincident with those previously described. [1,2]

Characterization.

(R)-NPX-AA-(S)-Pyr (2a). ^1H NMR (300 MHz, $CDCl_3$): δ 1.45-1.53 (m, 1H), 1.55 (d, J = 7.2 Hz, 3H), 1.62-1.93 (m, 5H), 2.14-2.29 (m, 3H), 2.33 (s, 3H), 2.35-2.43 (m, 1H), 2.98-3.06 (m, 1H), 3.12-3.24 (m, 2H), 3.65 (q, J = 7.2 Hz, 1H), 3.88 (s, 3H), 3.97 (m, 2H), 5.83 (t, J = 5.4 Hz, 1H), 7.08-7.15 (m, 2H), 7.35 (dd, J = 8.4 and 1.8 Hz, 1H), 7.62-7.71 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4 (CH_3), 22.7 (CH_2), 24.4 (CH_2), 28.1 (CH_2), 31.4 (CH_2), 38.9 (CH_2), 41.3 (CH_3), 46.9 (CH), 55.2 (CH_3), 57.4 (CH_2), 63.7 (CH), 66.2 (CH_2), 105.5 (CH), 119.0 (CH), 125.9 (Ar-CH), 126.1 (CH), 127.4 (CH), 128.8 (C), 129.1 (CH), 133.6 (C), 136.4 (C), 157.6 (C), 173.1 (C), 174.4 (C). Exact mass: m/z found 413.2449, calculated for $C_{24}H_{33}N_2O_4$ (MH^+) 413.2440.

(S)-NPX-AA-(S)-Pyr (2b). ^1H NMR (300 MHz, CDCl3): δ 1.44-1.53 (m, 1H), 1.55 (d, J = 7.2 Hz, 3H), 1.62-1.91 (m, 5H), 2.14-2.27 (m, 3H), 2.33 (s, 3H), 2.34-2.40 (m, 1H), 2.97-3.05 (m, 1H), 3.19 (m, 2H), 3.64 (q, J = 7.2 Hz, 1H), 3.88 (s, 3H), 3.92 (dd, J = 11.1 and 5.1 Hz, 1H), 3.99 (dd, J = 10.8 and 5.1 Hz, 1H), 5.80 (br t, J = 5.4 Hz, 1H), 7.07-7.15 (m, 2H), 7.34 (dd, J = 8.4 and 1.8 Hz, 1H), 7.62-7.71 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4 (CH_3), 22.7 (CH_2), 24.4 (CH_2), 28.2 (CH_2), 31.4 (CH_2), 38.9 (CH_2), 41.3 (CH_3), 46.9 (CH), 55.2 (CH_3), 57.5 (CH_2), 63.6 (CH), 66.4 (CH_2), 105.5 (CH), 119.0 (CH), 125.9 (CH), 126.1 (CH), 127.3 (CH), 128.8 (C), 129.1 (CH), 133.6 (C), 136.4 (C), 157.6 (C), 173.1 (C), 174.3 (C). Exact mass: m/z found 413.2440, calculated for $C_{24}H_{33}N_2O_4$ (MH^+) 413.2440.

(R)-NPX-CyAA-(S)-Pyr (3a). ^1H NMR (300 MHz, $CDCl_3$): δ 1.42-1.97 (m, 8H), 1.58 (d, J = 7.2 Hz, 3H), 2.01-2.27 (m, 3H), 2.29-2.40 (m, 1H), 2.34 (s, 3H), 2.74-2.92 (m, 1H), 2.99-3.09 (m, 1H), 3.64 (q, J = 7.2 Hz, 1H), 3.91 (br s, 5H), 4.26-4.38 (m, 1H), 6.10 (br d, J = 6.9 Hz, 1H), 7.09-7.17 (m, 2H), 7.39 (dd, J = 9.0 and 1.8 Hz, 1H), 7.66-7.74 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5 (CH_3), 22.8 (CH_2), 28.2 (CH_2), 28.3 (CH_2), 33.0 (CH_2), 36.1 (CH_2), 41.4 (CH), 41.8 (CH), 47.1 (CH), 51.0 (CH), 55.3 (CH_3), 57.6 (CH_2), 63.8 (CH), 66.8 (CH_2), 105.6 (CH), 118.9 (CH), 126.0 (CH), 126.3 (CH), 127.3 (CH), 129.0 (C), 129.3 (CH), 133.6 (C), 136.6 (C), 157.6 (C), 173.7 (C), 177.3 (C). Exact mass: m/z found 439.2618, calculated for $C_{26}H_{35}N_2O_4$ (MH^+) 439.2597.

(S)-NPX-CyAA-(S)-Pyr (3b). ^1H NMR (300 MHz, CDCl3): δ 1.44-1.94 (m, 8H), 1.55 (d, J = 7.2 Hz, 3H), 2.03-2.28 (m, 3H), 2.29-2.45 (m, 1H), 2.34 (s, 3H), 2.77-2.89 (m, 1H), 3.00-3.09 (m, 1H), 3.64 (q, J = 7.2 Hz, 1H), 3.85-4.00 (m, 2H), 3.90 (s, 3H), 4.25-4.37 (m, 1H), 6.20 (br d, J = 7.5 Hz, 1H), 7.08-7.16 (m, 2H), 7.37 (dd, J = 8.7 and 1.8 Hz, 1H), 7.65-7.72 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4 (CH_3), 22.8 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 32.9 (CH_2), 35.8 (CH_2), 41.4 (CH), 41.7 (CH), 47.0 (CH), 51.0 (CH), 55.2 (CH3), 57.5 (CH2), 63.8 (CH), 66.7 (CH2), 105.5 (CH), 118.9 (CH), 126.0 (CH), 126.2

(CH), 127.3 (CH), 129.0 (C), 129.2 (CH), 133.6 (C), 136.8 (C), 157.5 (C), 173.6 (C), 177.3 (C). Exact mass: m/z found 439.2607, calculated for $C_{26}H_{35}N_2O_4$ (MH^+) 439.2597.

(R)-NPX-AA. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, J = 7.2 Hz, 3H), 1.64-1.76 (m, 2H), 2.26 (t, J = 7.2 Hz, 2H), 3.14-3.29 (m, 2H), 3.69 (q, J = 7.2 Hz, 1H), 3.89 (s, 3H), 5.88 (t, J = 5.7 Hz, 1H), 7.09-7.16 (m, 2H), 7.35 (dd, J = 8.7 and 1.8 Hz, 1H), 7.62-7.73 (m, 3H), 11.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3 (CH_3), 24.5 (CH_2), 31.2 (CH_2), 38.9 (CH_2), 46.8 (CH), 55.3 (CH_3), 105.6 (CH), 119.1 (CH), 126.1 (CH), 126.2 (CH), 127.5 (CH), 128.9 (C), 129.2 (CH), 133.7 (C), 136.1 (C), 157.7 (C), 175.2 (C), 177.5 (C). Exact mass: m/z found 316.1552, calculated for $C_{18}H_{22}NO_4$ (MH^+) 316.1549.

(S)-NPX-AA. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, J = 7.2 Hz, 3H), 1.64-1.76 (m, 2H), 2.25 (m, 2H), 3.14-3.28 (m, 2H), 3.69 (q, J = 7.2 Hz, 1H), 3.88 (s, 3H), 6.00 (t, J = 5.7 Hz, 1H), 7.06-7.15 (m, 2H), 7.35 (dd, J = 8.4 and 1.8 Hz, 1H), 7.62-7.73 (m, 3H), 11.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3 (CH_3), 24.4 (CH_2), 31.2 (CH_2), 38.9 (CH_2), 46.8 (CH), 55.2 (CH_3), 105.6 (CH), 119.1 (CH), 126.0 (CH), 126.1 (CH), 127.5 (CH), 128.9 (C), 129.1 (CH), 133.7 (C), 136.1 (C), 157.6 (C), 175.2 (C), 177.4 (C). Exact mass: m/z found 316.1561, calculated for $C_{18}H_{22}NO_4$ (MH^+) 316.1549.

(R)-NPX-CyAA. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (d, J = 7.2 Hz, 3H), 1.58-1.65 (m, 2H), 1.79-2.15 (m, 4H), 2.76-2.88 (m, 1H), 3.66 (q, J = 7.2 Hz, 1H), 3.88 (s, 3H), 4.25-4.38 (m, 1H), 6.25 (d, J = 7.8 Hz, 1H), 7.06-7.14 (m, 2H), 7.36 (dd, J = 8.4 and 1.8 Hz, 1H), 7.62-7.71 (m, 3H), 10.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3 (CH_3), 28.2 (CH_2), 32.9 (CH_2), 35.7 (CH_2), 41.6 (CH), 46.9 (CH), 51.1 (CH), 55.2 (CH3), 105.6 (CH), 118.9 (CH), 125.9 (CH), 126.1 (CH), 127.3 (CH), 128.9 (C), 129.2 (CH), 133.6 (C), 136.2 (C), 157.5 (C), 174.3 (C), 181.6 (C). Exact mass: m/z found 342.1706, calculated for $C_{20}H_{24}NO_4$ (MH^+) 342.1705.

(S)-NPX-CyAA. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44-2.00 (m, 5H), 1.56 (d, J = 7.2 Hz, 3H), 2.07-2.22 (m, 1H), 2.78-2.89 (m, 1H), 3.65 (q, J = 7.2 Hz, 1H), 3.90 (s, 3H), 4.27-4.38 (m, 1H), 5.99 (d, J = 7.5 Hz, 1H), 7.09-7.16 (m, 2H), 7.35 (dd, J = 8.4 and 1.8 Hz, 1H), 7.62-7.72 (m, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 18.4 (CH_3), 28.2 (CH_2), 32.9 (CH_2), 35.8 (CH_2), 41.5 (CH), 47.0 (CH), 51.1 (CH), 55.3 (CH3), 105.6 (CH), 119.0 (CH), 126.0 (CH), 126.1 (CH), 127.4 (CH), 129.0 (C), 129.2 (CH), 133.7 (C), 136.5 (C), 157.6 (C), 174.0 (C), 181.5 (C). Exact mass: m/z found 342.1714, calculated for $C_{20}H_{24}NO_4$ (MH^+) 342.1705.

Photochemical Properties of Studied Compounds.

Table 1. Emission Quantum Yields and Lifetimes of the Local Excited State of **2 (a,b)** and **3 (a,b)** Dyads (LE) (λ_{max} = 351 nm) and Exciplex in the Process of photoirradiation of Dyad Isomers in Solvents with different Dielectric Constants.

(R)-NPX-AA-(S)-Pyr, **2a**								
	LE					Exciplex		
ε	φ_f	τ_1/ns	A_1/%	τ_2/ns	A_2/%	φ_{exc} (λ_{em}/nm)	τ_{rise}/ns	τ_{fall}/ns
36.8	0.26±0.01	5.09	78	9.45	22	0.005±0.001 (502)	3.82	5.88
29.6	0.30±0.02	4.88	51	8.64	39	0.007±0.001 (496)	4.74	6.68
21.6	0.31±0.02	4.77	51	9.06	49	0.010±0.001 (488)	4.81	8.46
14.5	0.33±0.02	4.15	40	9.55	60	0.013±0.001 (479)	4.10	9.39
8.1	0.43±0.04	3.75	16	12.7	84	0.012±0.002 (455)	3.52	12.9
(S)-NPX-AA-(S)-Pyr, **2b**								
	LE					Exciplex		
ε	φ_f	τ_1/ns	A_1/%	τ_2/ns	A_2/%	φ_{exc} (λ_{em}/nm)	τ_{rise}/ns	τ_{fall}/ns
36.8	0.28±0.01	5.34	73	10.9	27	0.004±0.001 (500)	3.37	6.38
29.6	0.32±0.02	5.11	58	9.74	42	0.007±0.001 (493)	4.31	7.25
21.6	0.36±0.02	4.83	44	9.99	56	0.009±0.001 (486)	4.66	8.82
14.5	0.43±0.02	4.66	33	12.3	67	0.013±0.001 (475)	4.90	10.9
8.1	0.54±0.08	3.73	12	(12.1)	88	0.012±0.002 (453)	3.33	(11.8)
(R)-NPX-CyAA-(S)-Pyr, **3a**								
	LE					Exciplex		
ε	φ_f	τ_1/ns	A_1/%	τ_2/ns	A_2/%	φ_{exc} (λ_{em}/nm)	τ_{rise}/ns	τ_{fall}/ns
36.8	0.17±0.01	2.74	75	10.3	25	0.013±0.001 (506)	2.63	8.89
29.6	0.19±0.01	2.78	66	11.1	34	0.019±0.002 (496)	2.78	11.1
21.6	0.24±0.01	2.81	53	12.9	47	0.025±0.003 (489)	2.88	13.2
14.5	0.33±0.02	2.75	36	14.1	64	0.031±0.003 (476)	2.76	14.4
8.1	0.50±0.05	2.13	11	13.4	89	0.025±0.002 (455)	2.06	13.6
(S)-NPX-CyAA-(S)-Pyr, **3b**								
	LE					Exciplex		
ε	φ_f	τ_1/ns	A_1/%	τ_2/ns	A_2/%	φ_{exc} (λ_{em}/nm)	τ_{rise}/ns	τ_{fall}/ns
36.8	0.23±0.01	4.1	70	10.5	30	0.011±0.001 (500)	3.57	6.59
29.6	0.26±0.01	3.9	60	11.3	40	0.015±0.001 (494)	3.95	11.2
21.6	0.31±0.02	3.7	45	13.2	55	0.022±0.002 (485)	3.87	13.8
14.5	0.43±0.02	3.32	26	14.1	74	0.025±0.003 (472)	3.36	14.5
8.1	0.55±0.08	2.28	6	13.4	94	0.018±0.002 (442)	2.26	12.9

Experimental Details

Preparation of solutions. Stock solutions were prepared in two solvents: acetonitrile (ε = 36.8) [3] or benzene (ε = 2.28) [4] for optic measurements and deuteroacetonitrile (D 99.9%) and deuterobenzene (D 99.8%) for CIDNP measurements. Solvent permittivity values are shown for 293 K. The solvent permittivities for the mixtures were taken from the literature. [5] There is no room for doubt that the linear correlation between solvent polarity and its dielectric coefficient, and so we use both term hereafter. Concentrations of dyads in stock solutions for optic measurements were kept about 1.0×10^{-4} M or 5.0×10^{-3} M for CIDNP experiments to exclude all potential bimolecular reactions.

Fluorescence Measurements. All spectroscopic measurements were performed using a quartz cuvette of 1 cm optical length. Spectra and kinetic curves of luminescence were recorded with an Edinburgh Instruments FLSP-920 spectrofluorometer with either a Xenon lamp or a laser diode EPLED-320 (λ_{ex} = 320 nm, pulse duration 0.6 ns) as excitation sources. The kinetic traces were fitted by biexponential decay (or formation and decay) functions using a reconvolution procedure. For the correct selection of the weak band of exciplex luminescence the spectrum was recorded twice: without a filter and with the step 395 nm filter. The using of step filter allows removing the luminescence of NPX baseband (350 nm) which appears in the second order in the long-wavelength part of the spectrum (700 nm) and distorts the exciplex band. The absorbance at the excitation wavelength was kept ca. 0.1. UV/Visible absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies).

Luminescence quantum yields were measured relative to that of NPX, using the value for the fluorescence quantum yield of naproxen in acetonitrile (0.47, [6]), as it has been previously shown that quantum yield of naproxen fluorescence is basically solvent-independent. All samples were bubbled with argon for 15 min to remove dissolved oxygen just before the experiments. After every experimental series a control fluorescence spectrum was recorded for checking the absence of oxygen in samples. All experiments were performed at room temperature 296 K.

CIDNP Measurements. ^{1}H pseudo steady state (PSS) CIDNP experiments [7] were performed on DPX-200 NMR spectrometer (Bruker, 200 MHz ^{1}H operating frequency, τ(90) = 3.0 μs). The samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of the NMR spectrometer. EMG 101 MSC excimer laser was used as a light source (Lambda Physik, 308 nm, 100 mJ at output window, 20 mJ per pulse in sample volume, with pulse duration 15 ns).

Calculation Details

Computational Methods. In numeric kinetic simulations the differential equations were solved using proprietary software (SPARK) based on the fourth-order Runge-Kutta method. The program allows calculations and fitting to experimental kinetic curves simultaneously at many wavelengths.

CIDNP simulations. To describe the dependence of CIDNP on solvent permittivity theoretically we used method of the calculation based on the Radical pair (RP) theory. This method includes the solution of the master-equation of spin chemistry using Liouvill representation. [8,9]

$$\frac{\partial\rho(\vec{r},t)}{\partial t} = i\hat{L}\rho(\vec{r},t) + \hat{L}(\vec{r})\rho(\vec{r},t) - (\hat{K}(\vec{r}) + i\hat{J}(\vec{r}))\rho(\vec{r},t) \quad \text{(S1)}$$

$$\rho(\vec{r},t) = \begin{pmatrix} \rho_{SS} \\ \rho_{ST} \\ \rho_{TS} \\ \rho_{TT} \\ \rho_{exc} \\ \rho_{*} \end{pmatrix}$$

Here, $\rho(\vec{r},t)$ is the density matrix for the system of reactants; , where ρ_{SS}, ρ_{ST}, ρ_{TS}, ρ_{TT} are matrix elements for the dyad's RP (in the $S-T_0$ approximation), and ρ_{exc} and ρ_{*} are populations of exciplex and excited states, respectively; $\hat{L}$ – the Liouvillian describing the RP spin evolution; $\hat{L}(\vec{r})$ - the operator of RP motion; $\hat{K}(\vec{r})$ – reaction's operator corresponding to the suggested scheme of reaction, $\hat{J}(\vec{r})$ – the operator of exchange interaction.

The CIDNP effect is determined by the following equation

$$P = \langle I_z \rangle = \langle I_z \rangle_S + \langle I_z \rangle_T. \quad \text{(2S)}$$

Here, $\langle I_z \rangle_S = Tr\left(I_z \cdot k_S \int_0^t \hat{P}_S \rho(t)dt\right); \langle I_z \rangle_T = Tr\left(I_z \cdot k_T \int_0^t \hat{P}_T \rho(t)dt\right)$, $\hat{P}_s$ and $\hat{P}_T$ are the projection operators of singlet and triplet states, correspondingly; $\rho(t)$ is the average value of $\rho(\vec{r},t)$ in the reaction zone.

To simplify the theoretical analysis we have used the Laplace transformation and the Green functions technique. [10] We have obtained the integral equation:

$$\tilde{\rho}(\vec{r},s) = \int \hat{G}(\vec{r},\vec{x};s)\rho_0(\vec{x})d\vec{x} - \int \hat{G}(\vec{r},\vec{x};s)(\hat{K}(\vec{x}) + i\hat{J}(\vec{x}))\tilde{\rho}(\vec{x},s)d\vec{x} \quad \text{(3S)}$$

Here, $\hat{G}(\vec{r},\vec{x};s) = \int_0^\infty exp(i\hat{L}t)\varphi(\vec{r},\vec{x};t)exp(-st)dt$

In the continuous–medium approximation we suppose the diffusional motion with the Coulomb interaction of RP centers. In this case, the distribution function $\varphi(\vec{r},\vec{x};t)$ obeys the following equation:

$$\frac{\partial\varphi(\vec{r},\vec{x};t)}{\partial t} + \nabla\left(\nabla\varphi(\vec{r},\vec{x};t) + \varphi(\vec{r},\vec{x};t)\frac{\nabla U(\vec{r})}{k_B T}\right) = -\frac{\delta(\vec{r}-\vec{x})}{D} \quad \text{(4S)}$$

Here, $\vec{x}$ indicates at the initial distance between RP: $\vec{x} = \vec{r}(t=0)$, D – diffusivity of the RP relative motion. The method of solution of the equation (4S) is known. [10]

The solution can be derived analytically under the following approximations:

1. Reaction occurs in a thin spherical layer of thickness ($\Delta \ll r$) where r is the distance between radical centers of biradical-zwitterion.

2. In the coordinate system of one of the radicals the initial location of the other radical is in the reaction zone. The moving radical mostly remains located in the reaction zone.
3. Spin evolution and motion occurs at sufficiently strong Coulomb interaction: $\frac{4sr^4}{D\alpha^2} \ll 1$, where s is the parameter of Laplace transformation and $\alpha = \frac{e^2}{k_B T}$ Onsager radius.
4. CIDNP was calculated for long times, where s is small enough; therefore we use Taylor series for the Green function.

After averaging $\rho(\vec{r},t)$ in the reaction zone we obtain

$$s\tilde{\rho}(s) = (1 + \hat{g}(s)(\hat{U}_0,\hat{J}_0))^{-1}\hat{g}(s)\rho_0 \quad (5S)$$

Here, $\hat{g}(s),\hat{U}_0,\hat{J}_0$, are the average value of $\hat{G}(\vec{r},\vec{x};s),\hat{K}(\vec{x}),\hat{J}(\vec{x})$ in the reaction zone, $\vec{\rho_0} = (k_s\rho_*,0,0,0,k_*\rho_*)^T$.

All calculations were done with using original Mathematica code and a standard desktop computer (Intel core i5 at 3.5 GHz).

To simplify all analytical and numerical calculations we have used the next approximations:

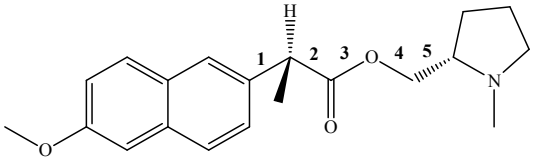
1. Electron-electron exchange interaction in the reaction zone equals infinity: $J \to \infty$.
2. Rates of the singlet recombination and triplet recombination were constant during the calculation; they were given by $k_S = 2k_T$. The rates of all chemical reactions are independent of permittivity (the mean values of rates are used in the calculation).
3. Only one magnetic nucleus of spin $\frac{1}{2}$ on the pyrrolidine fragment interacts with the unpaired electron.
4. There is no spin-spin interaction between electrons and nuclei on the naproxen fragment.

The following parameters were used in the calculations: $a = 20\ G$ for the isotropic HFI constant for both optical isomers on the pyrrolidine fragment; $\omega = 10^{10}\ s^{-1}$ – rate of singlet-triplet interconversion; $k_S = 2k_T = 2 \cdot 10^9\ s^{-1}$ – rate of recombination; $k_e = 0.1k_S$, $k_{exc}^- = k_{exc}^+ = k_S$, $\tau = 10^{-7}\ s$ RP lifetime; the rates k_{esc} and k_*, and the boundary distances R_1 and R_2 were taken from the photochemical experiments; the Onsager radius α, the diffusivity D and the thickness of the reaction zone Δ were free variable parameters. The Onsager radius changes from dyad to dyad because the distribution of electron density and the electric interaction change. Diffusivity in our model is an abstract parameter that occurs on going from microscopic to macroscopic motion.

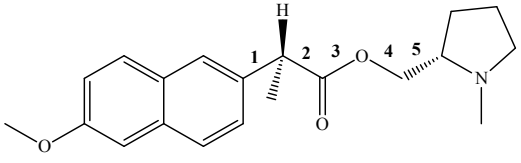
Quantum-Chemical Calculations.

Conformational Analysis.

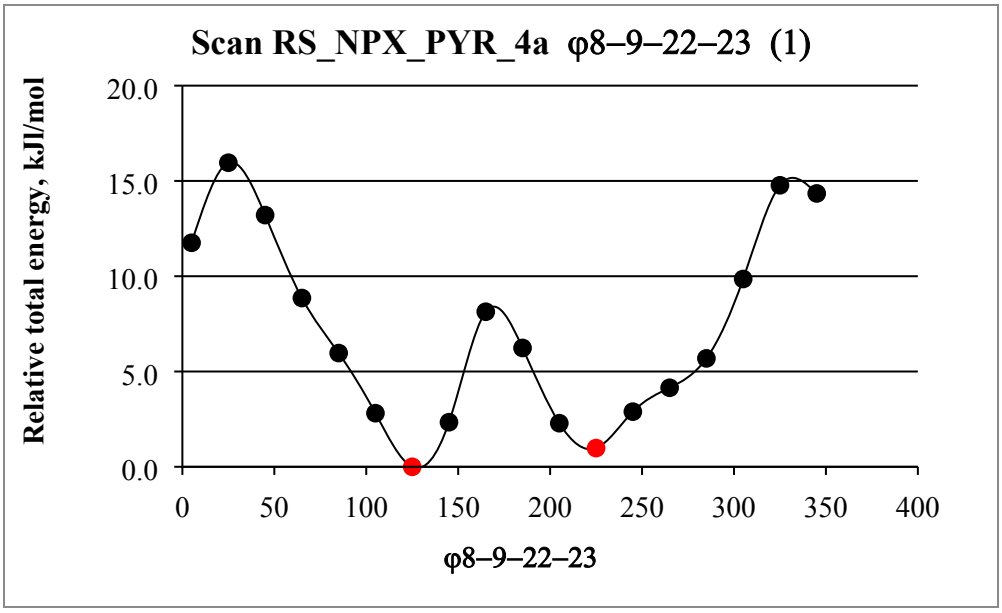
B3LYP/6-31G(d)



4a



4b



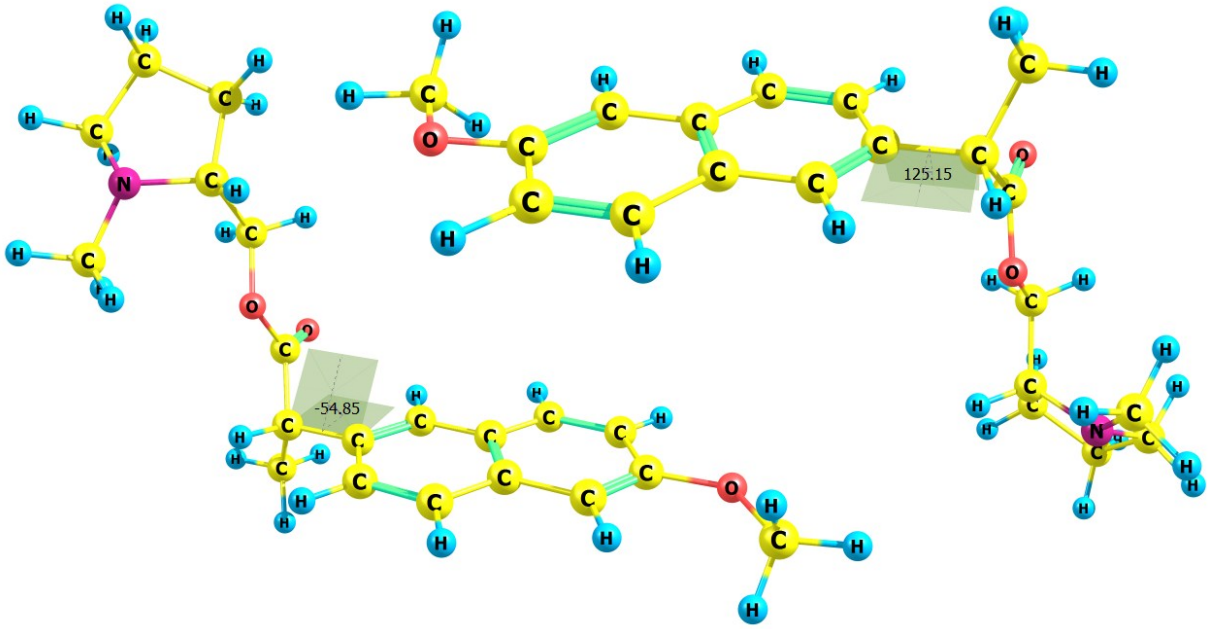
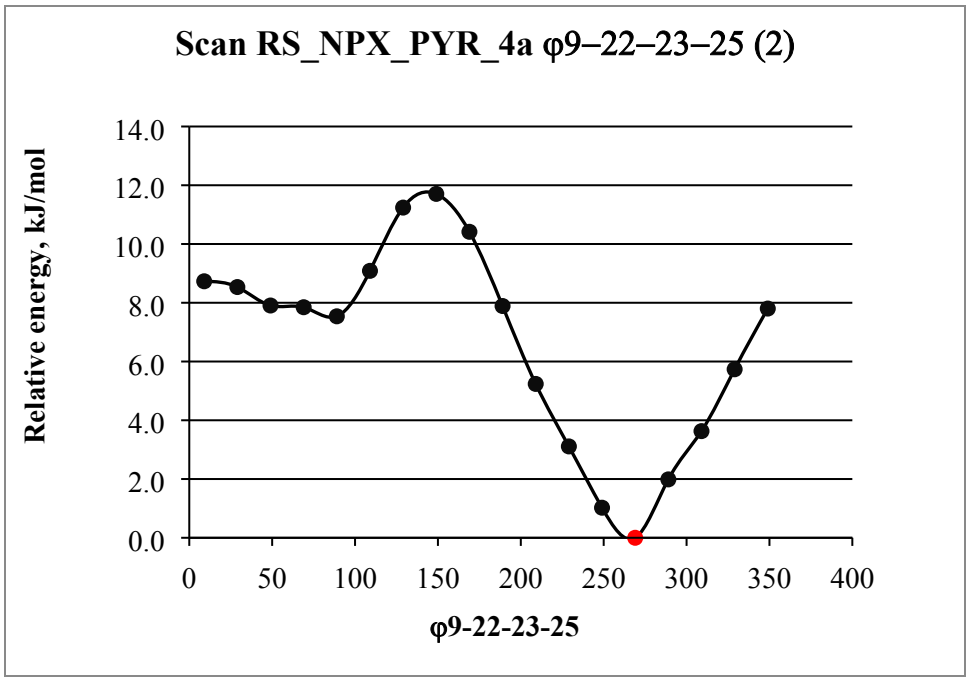


Fig.1. the structures (4a) correspond to a minimum on the potential energy surface (red points in the graph of scan1).



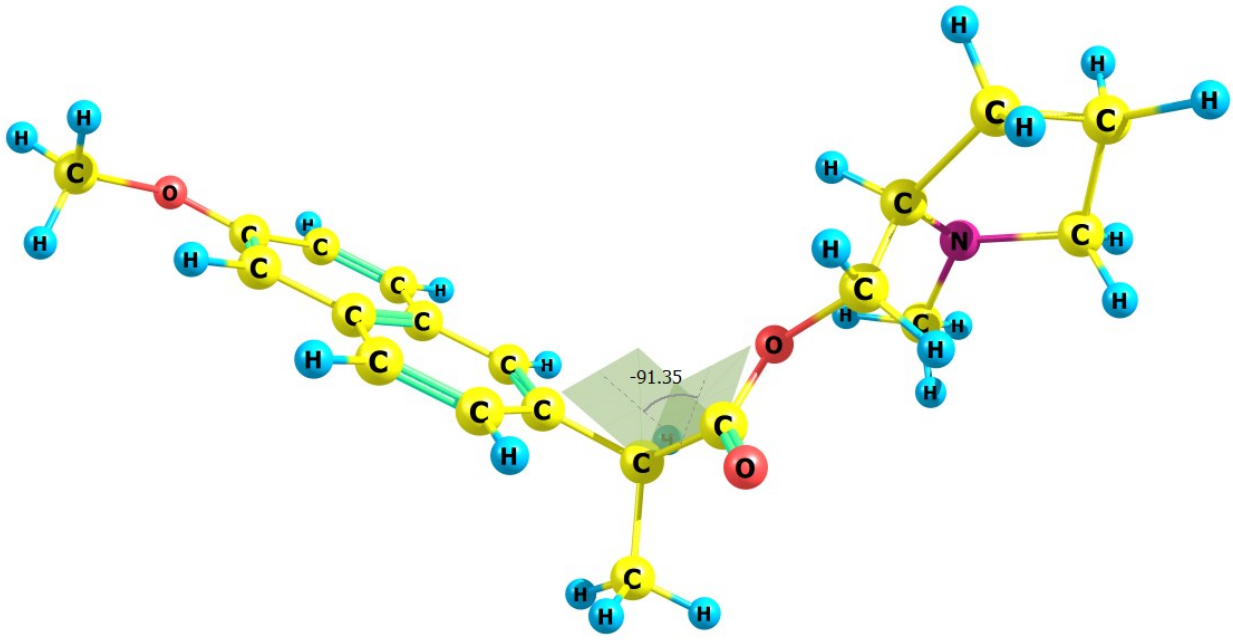


Fig.2. the structure (4a) corresponds to a minimum on the potential energy surface (red points in the graph of scan2).

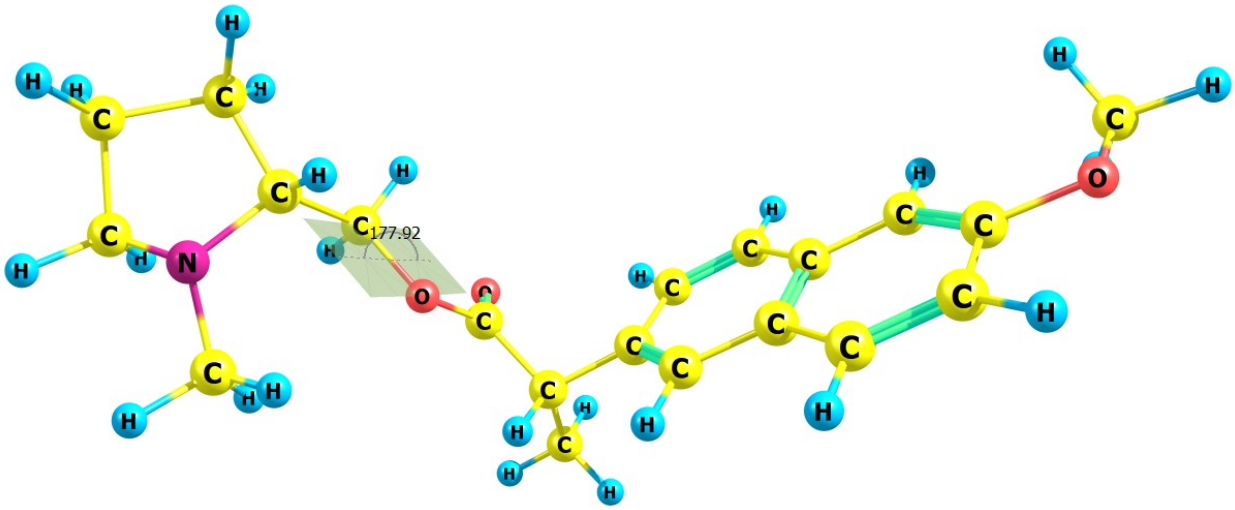
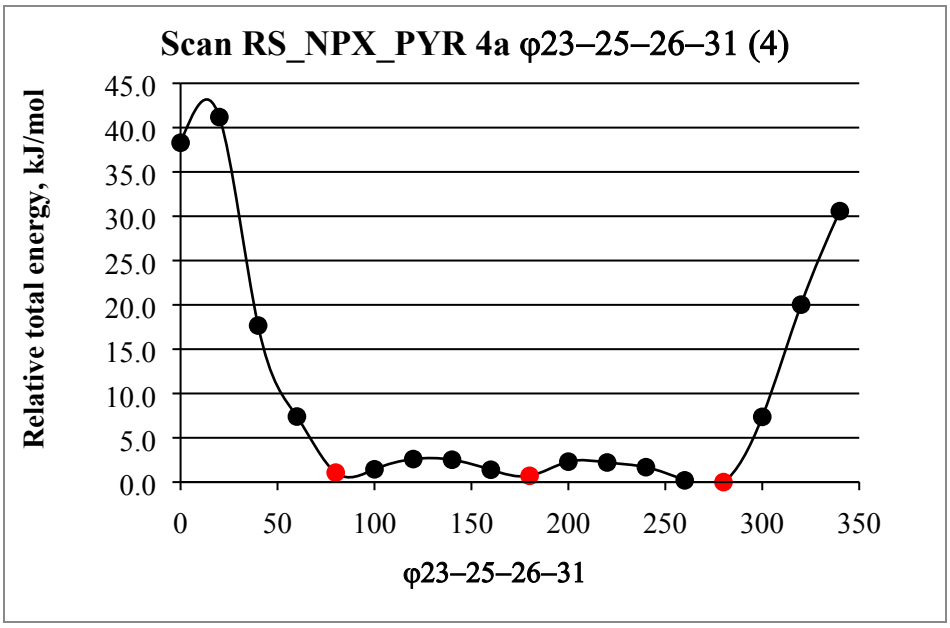


Fig.3. the structure (4a) corresponds to a minimum on the potential energy surface (red point in the graph of scan3).



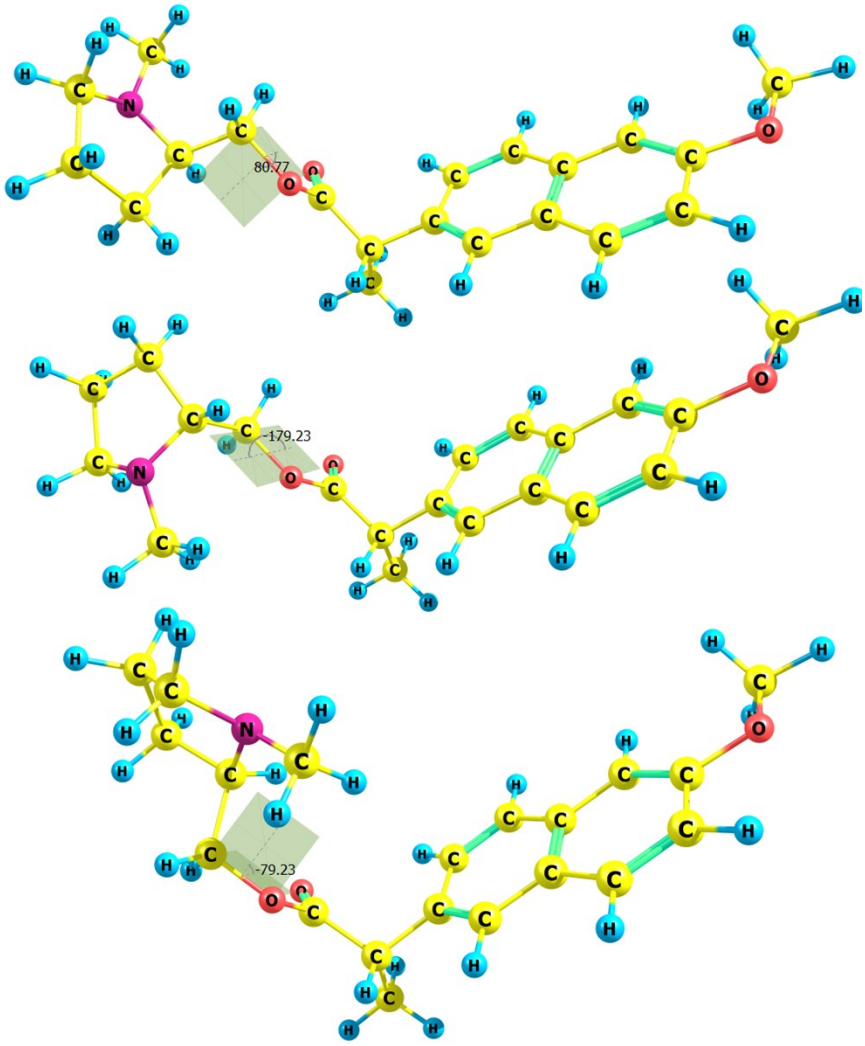


Fig.4. the structures (4a) correspond to a minimum on the potential energy surface (red points in the graph of scan4).

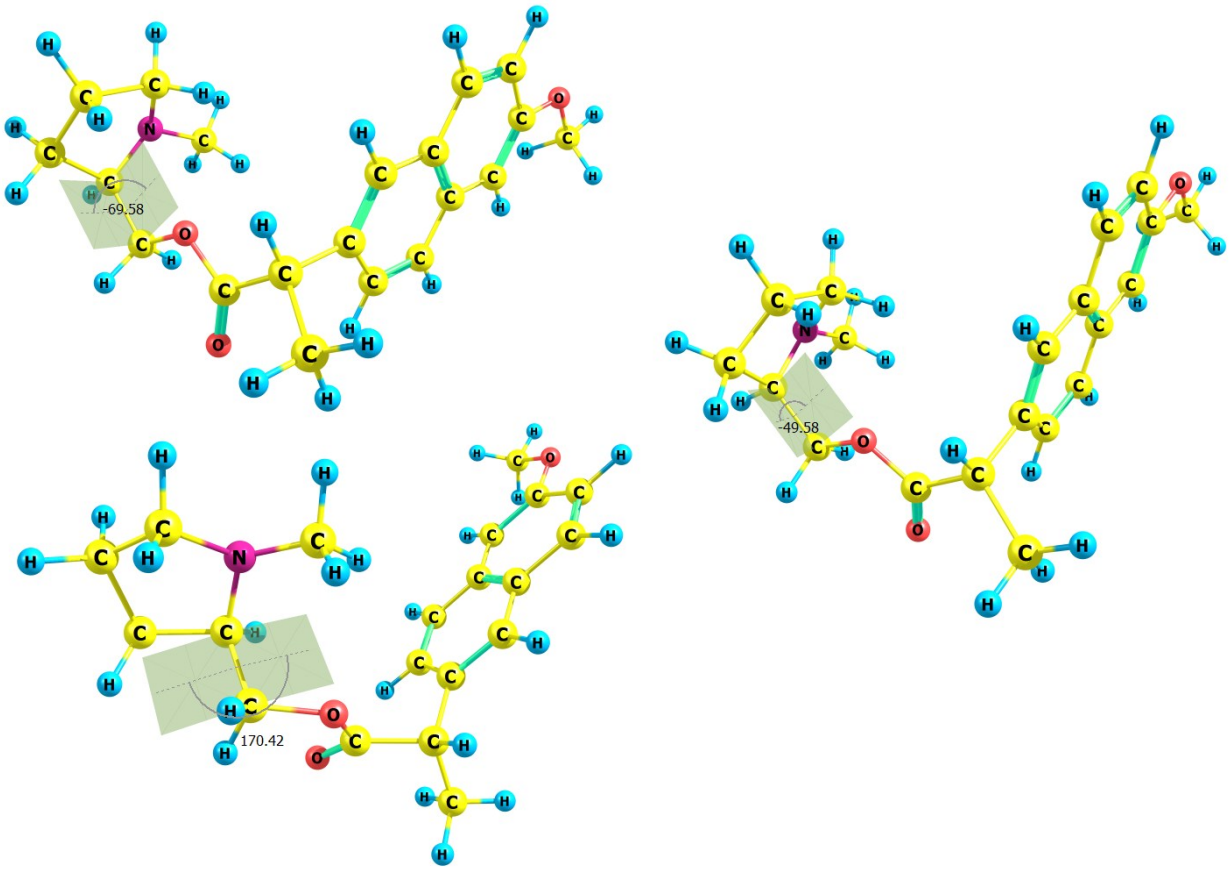
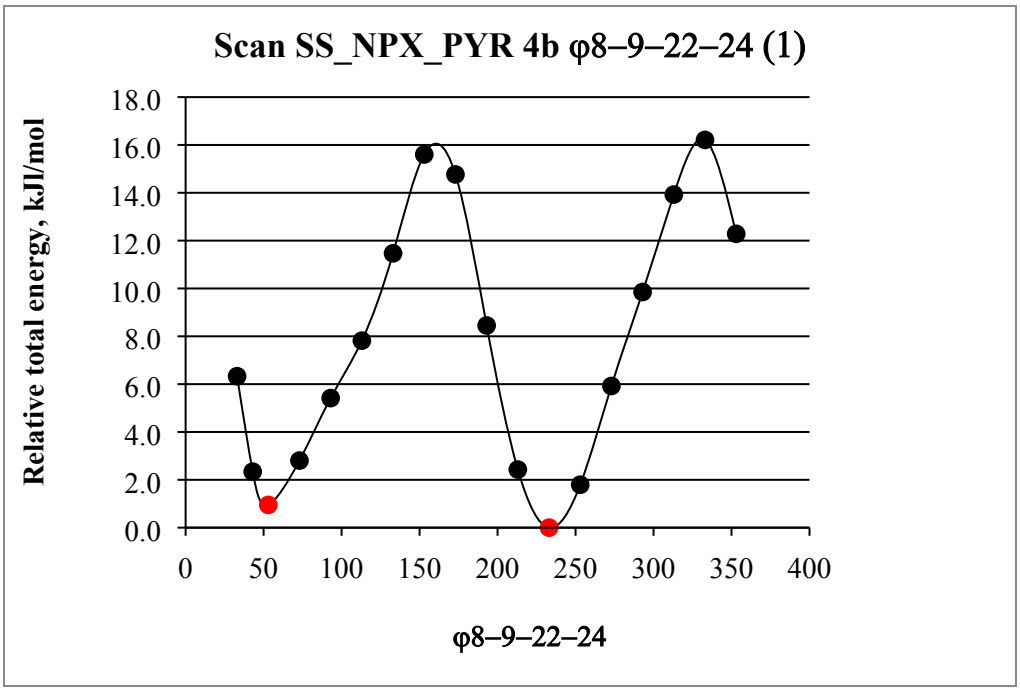


Fig.5. the structures (4a) correspond to a minimum on the potential energy surface (red points in the graph of scan5).



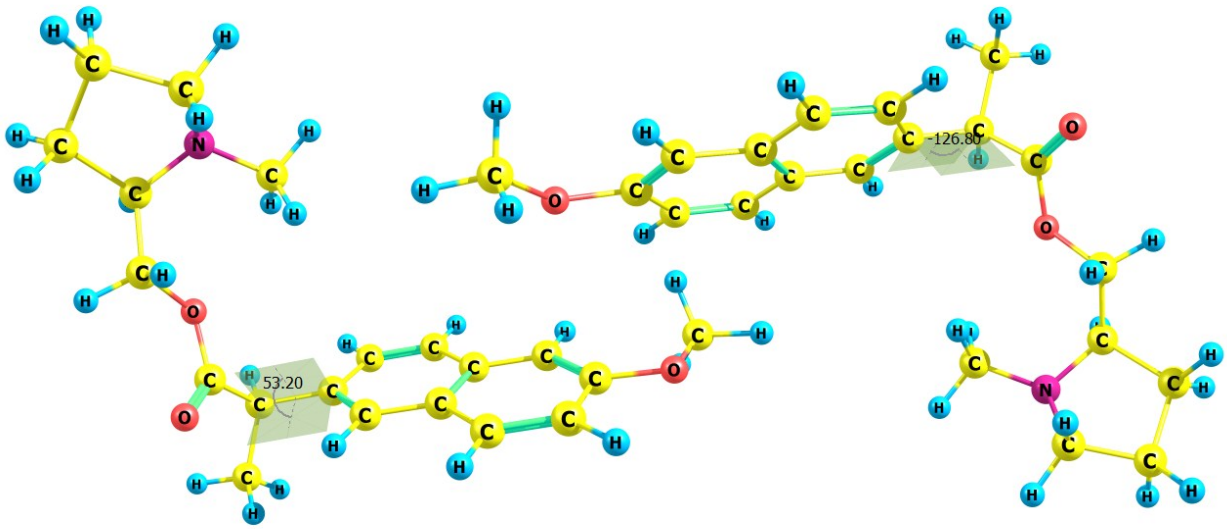
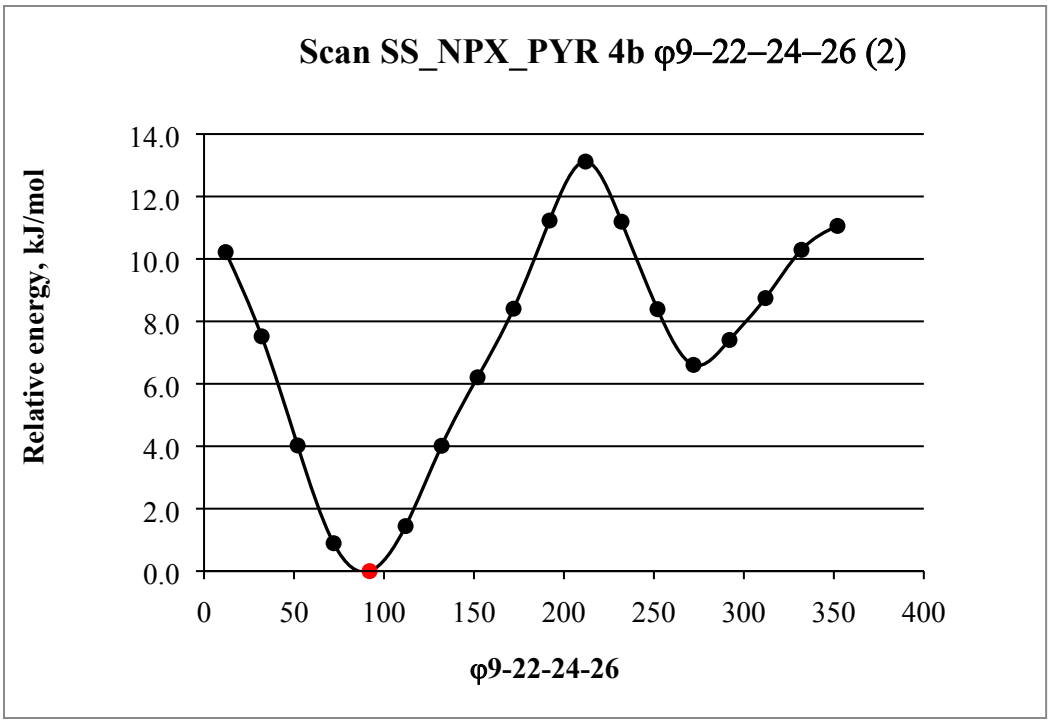


Fig.6. the structures (4b) correspond to a minimum on the potential energy surface (red points in the graph of scan1).



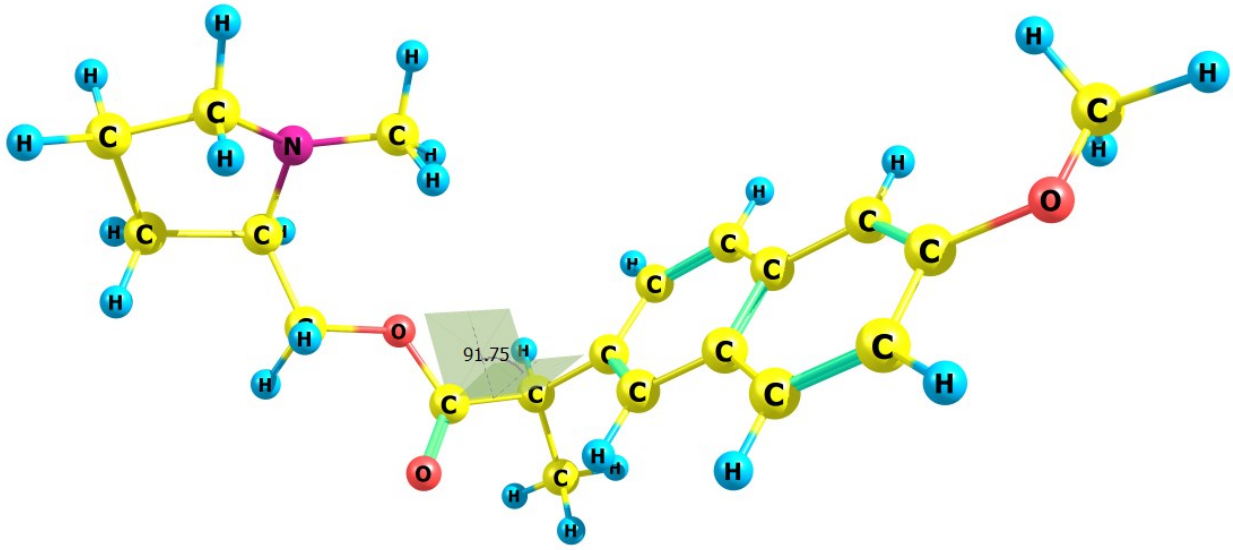
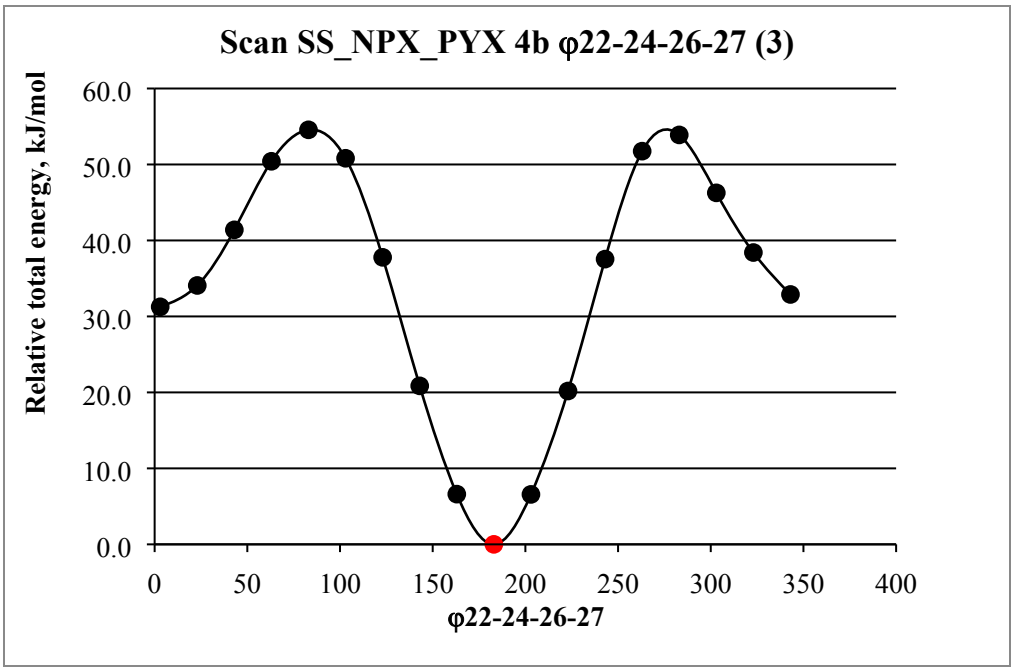


Fig.7. the structure (4b) corresponds to a minimum on the potential energy surface (red point in the graph of scan2).



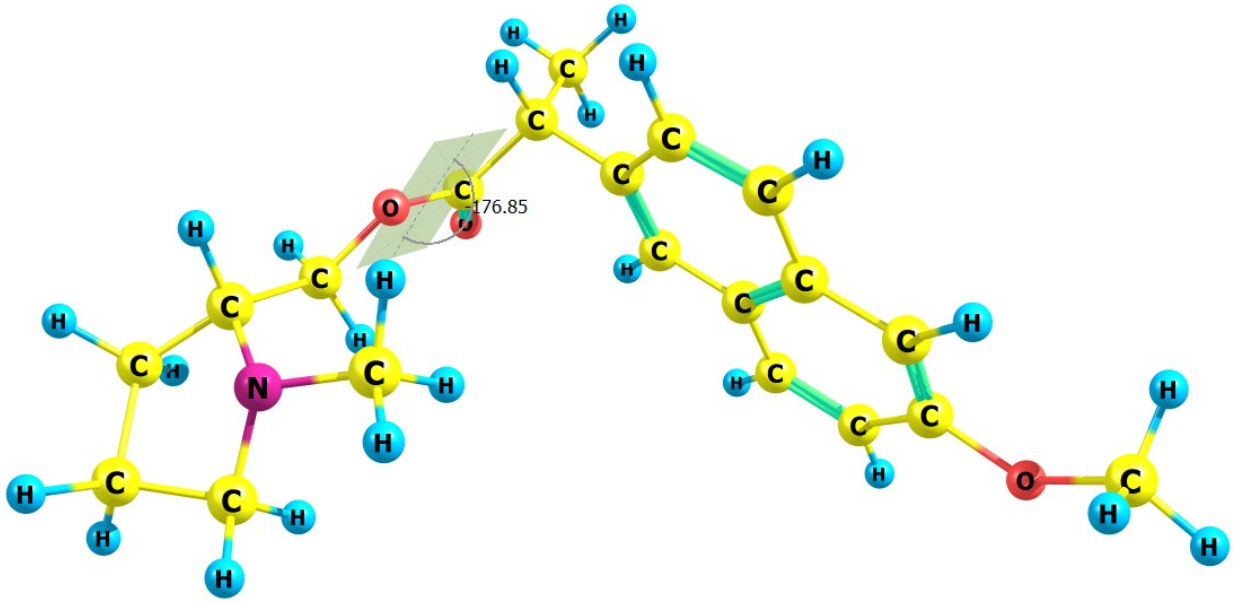
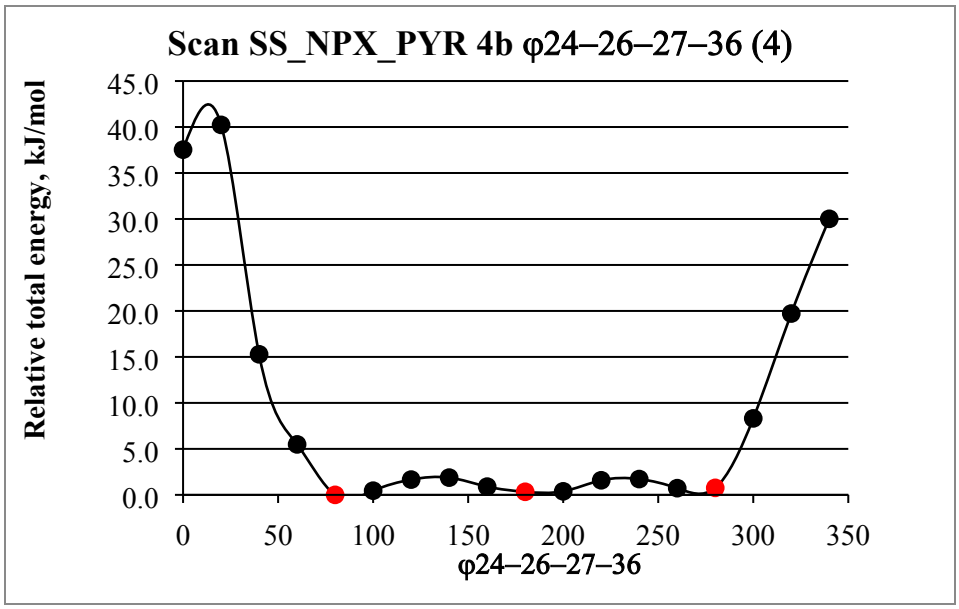


Fig.8. the structure (4b) corresponds to a minimum on the potential energy surface (red point in the graph of scan3).



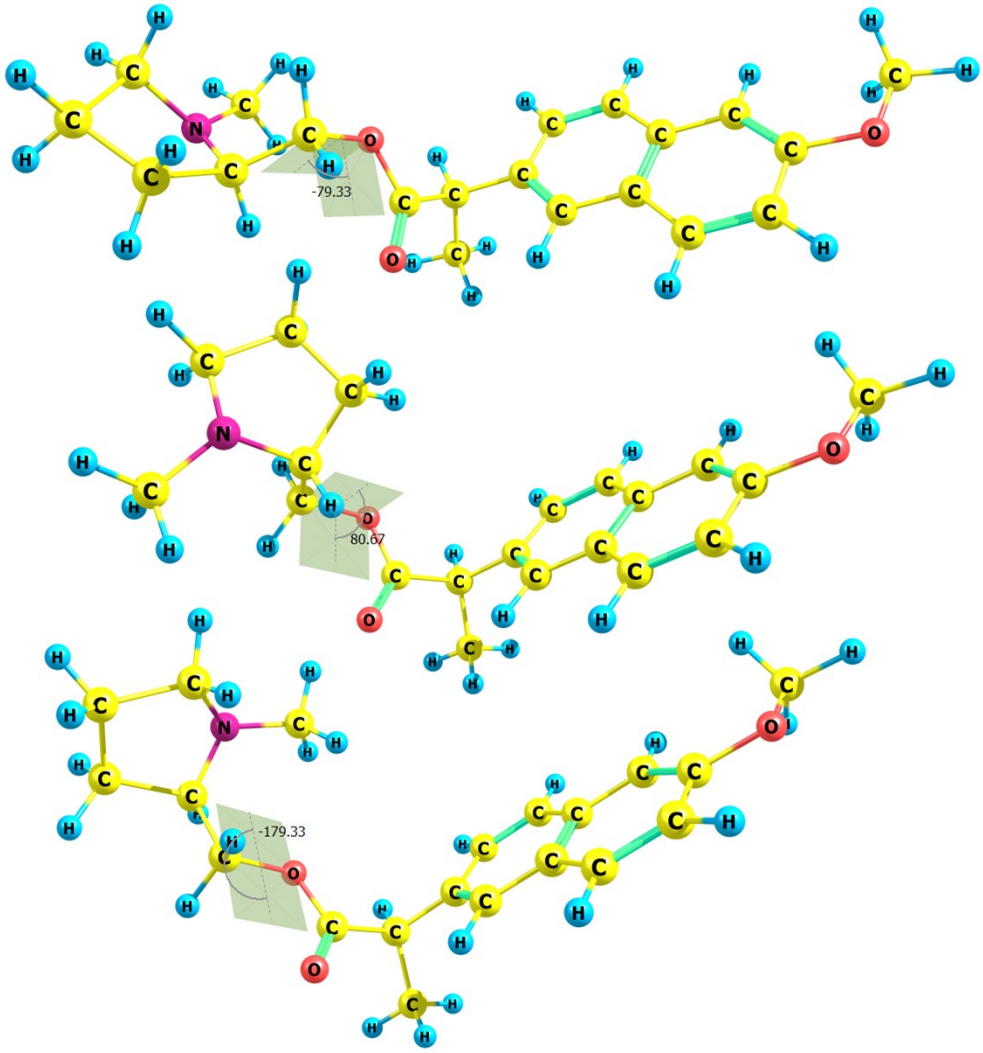
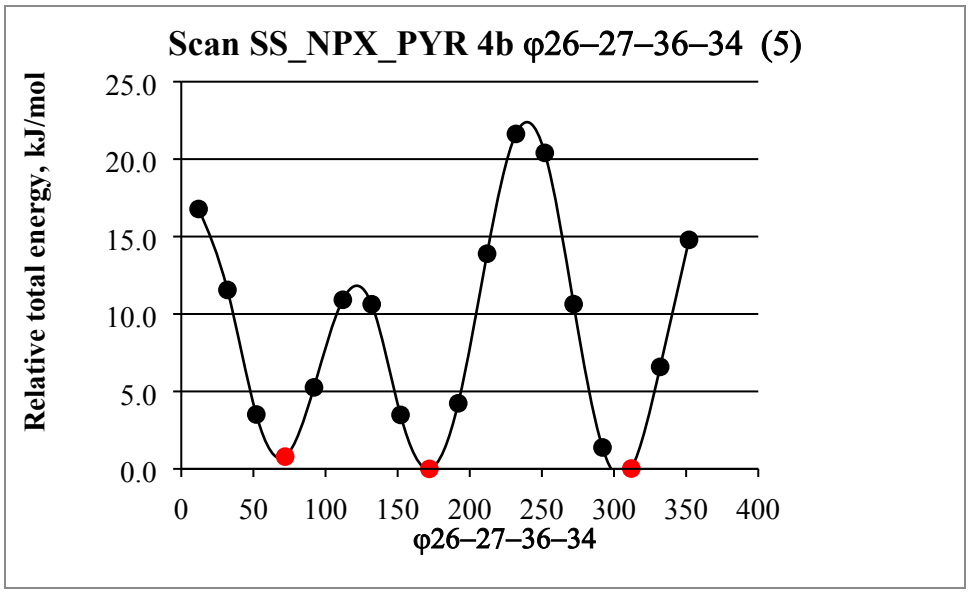


Fig.9. the structures (4b) correspond to a minimum on the potential energy surface (red points in the graph of scan4).



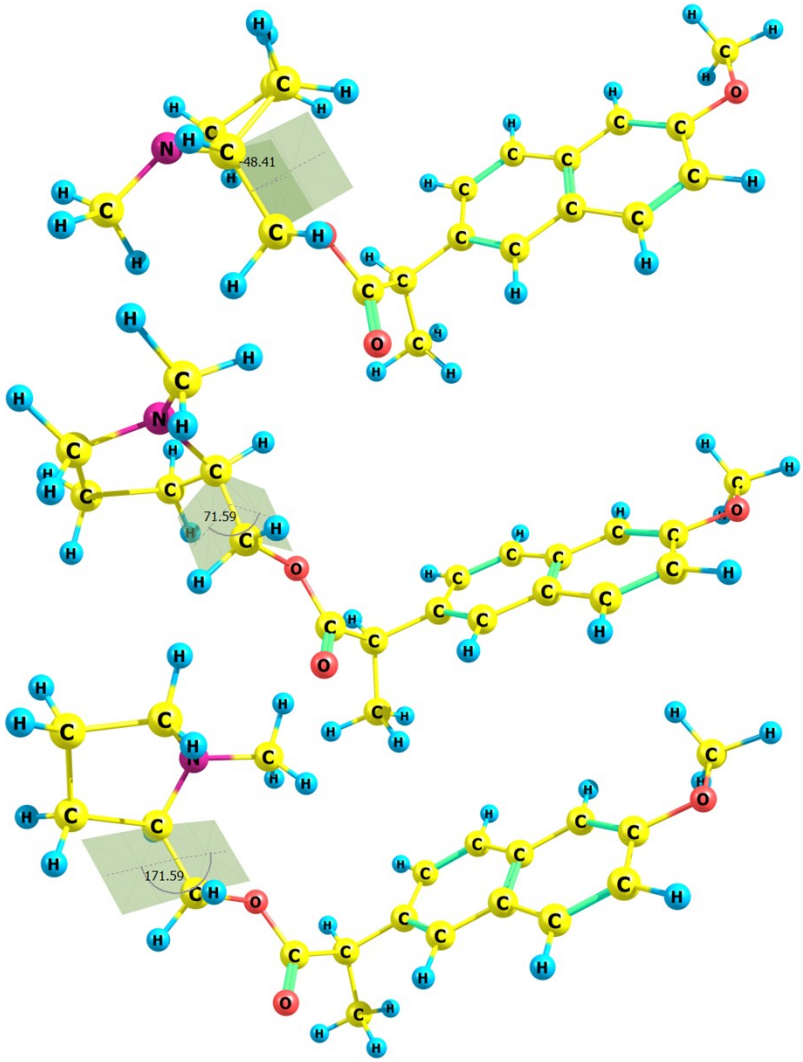
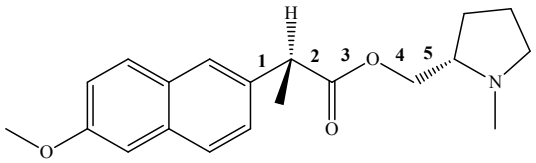


Fig.10. the structures (4b) correspond to a minimum on the potential energy surface (red points in the graph of scan5)

Re-optimization of Stable Conformers B3LYP/6-31G(d,p)

4a scan 4 and scan 5 (fig. 4-5)

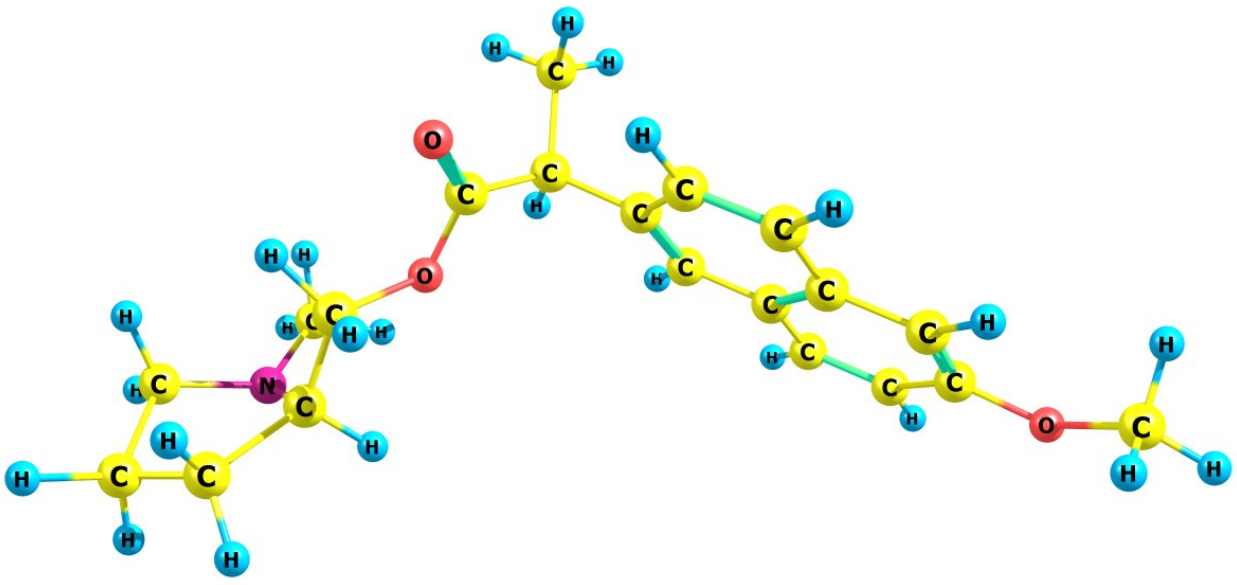


ID structure	φ_1	φ_2	φ_3	φ_4	φ_5	Total energy, a.u.	MB D
4a1	125,668	-91,902	176,986	-178,283	168,378	-1057,614919	12%
4a2	**125,783**	**-84,244**	**175,373**	**-174,728**	**-58,645**	**-1057,615722**	**28%**
4a3	125,674	-87,649	176,384	-173,950	68,430	-1057,614921	12%
4a4	125,688	-92,618	176,441	-87,699	172,049	-1057,615343	1%
4a5	123,320	-93,786	177,483	-110,967	70,440	-1057,6145430	8%
4a6	125,111	-92,728	175,574	137,855	166,248	-1057,6138364	4%
4a7	123,483	-87,499	175,034	112,000	-56,883	-1057,6144351	7%
4a8	125,496	-90,226	177,743	88,744	65,257	-1057,6148334	11%

Structure 4a1

1	-3.055858000	-0.741063000	2.859439000
6	-3.475032000	-0.632064000	1.861955000
6	-4.691756000	-1.190257000	1.566245000
6	-5.247786000	-1.053193000	0.263723000
6	-4.565605000	-0.356374000	-0.713877000
6	-3.302322000	0.229988000	-0.425206000
6	-2.740515000	0.094540000	0.883076000
6	-1.480120000	0.682175000	1.160600000
6	-0.781864000	1.388607000	0.201585000
6	-1.344204000	1.515053000	-1.098095000
6	-2.563937000	0.953374000	-1.399498000
1	-5.259050000	-1.745824000	2.306434000
1	-4.972033000	-0.240712000	-1.712810000
1	-2.977512000	1.057546000	-2.400118000
1	-0.790351000	2.052234000	-1.862653000
1	-1.065065000	0.568920000	2.160484000
8	-6.461957000	-1.654315000	0.101214000
6	-7.085203000	-1.562224000	-1.169585000
1	-7.285284000	-0.518025000	-1.444256000
1	-6.472328000	-2.028315000	-1.952532000
1	-8.030350000	-2.100953000	-1.080816000
6	0.553957000	2.047060000	0.536380000
6	1.620183000	1.576074000	-0.449549000
8	1.844566000	2.086817000	-1.527762000
8	2.274477000	0.489697000	0.012670000
6	3.262847000	-0.082436000	-0.873885000
1	2.766287000	-0.353570000	-1.811735000
1	4.020181000	0.674682000	-1.105793000
6	4.711034000	-2.110610000	-1.262098000
6	6.139401000	-2.190700000	-0.678488000
6	3.871179000	-1.324709000	-0.208818000

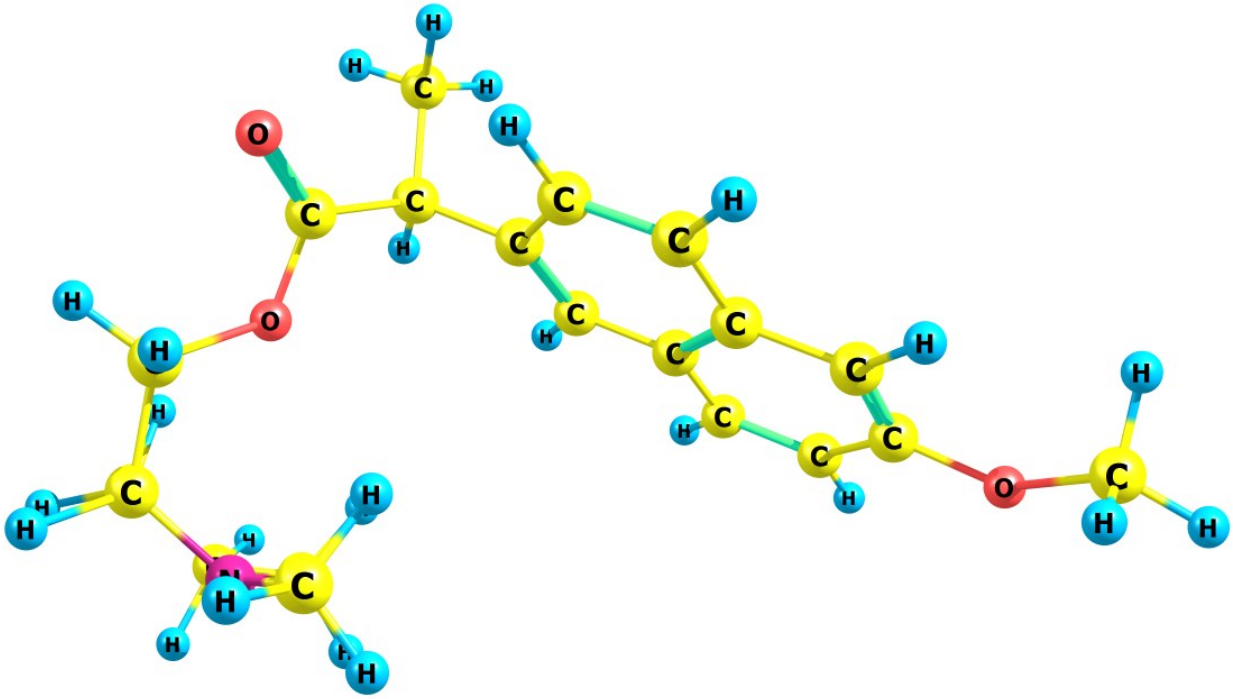
6	6.164058000	-1.033068000	0.322691000
7	4.823139000	-1.088533000	0.886277000
1	4.285429000	-3.098219000	-1.461489000
1	6.915020000	-2.112622000	-1.446750000
1	6.387679000	-0.073146000	-0.188571000
1	6.282798000	-3.135440000	-0.144380000
1	6.912377000	-1.157847000	1.114927000
1	3.034474000	-1.924584000	0.174253000
1	4.719703000	-1.571012000	-2.217005000
6	4.508282000	-0.099620000	1.897390000
1	4.542178000	0.946353000	1.540003000
1	3.506357000	-0.282282000	2.297206000
1	5.227923000	-0.192804000	2.720032000
1	0.856282000	1.704843000	1.531283000
6	0.464733000	3.583693000	0.527566000
1	-0.311811000	3.917480000	1.222702000
1	1.418207000	4.031817000	0.828862000
1	0.222097000	3.952835000	-0.472296000



Structure 4a2

1	-2.388760000	-0.901588000	2.773820000
6	-2.819855000	-0.636170000	1.811373000
6	-4.042653000	-1.137700000	1.447399000
6	-4.614550000	-0.796730000	0.189909000
6	-3.941723000	0.043431000	-0.674964000
6	-2.672142000	0.573604000	-0.314343000
6	-2.094019000	0.232718000	0.948783000
6	-0.826390000	0.764152000	1.297887000
6	-0.136548000	1.609573000	0.451711000
6	-0.715819000	1.941084000	-0.803620000
6	-1.942634000	1.438404000	-1.173322000
1	-4.603299000	-1.801006000	2.098622000
1	-4.360243000	0.315516000	-1.637859000
1	-2.368700000	1.700430000	-2.139208000
1	-0.170499000	2.592262000	-1.481312000
1	-0.398870000	0.493924000	2.261812000
8	-5.832735000	-1.362753000	-0.048313000
6	-6.472485000	-1.073795000	-1.280962000
1	-6.674954000	0.000308000	-1.386562000
1	-5.870520000	-1.411449000	-2.135069000
1	-7.417046000	-1.620511000	-1.264851000
6	1.211458000	2.199258000	0.858493000
6	2.245892000	1.880641000	-0.218664000
8	2.537311000	2.609709000	-1.143745000
8	2.776705000	0.651956000	-0.038818000
6	3.695236000	0.194468000	-1.057587000
1	3.212320000	0.297314000	-2.033489000
1	4.581012000	0.840447000	-1.058726000
6	4.755145000	-1.413453000	0.637691000
6	3.972947000	-2.547307000	1.334577000
6	4.091533000	-1.255978000	-0.761266000

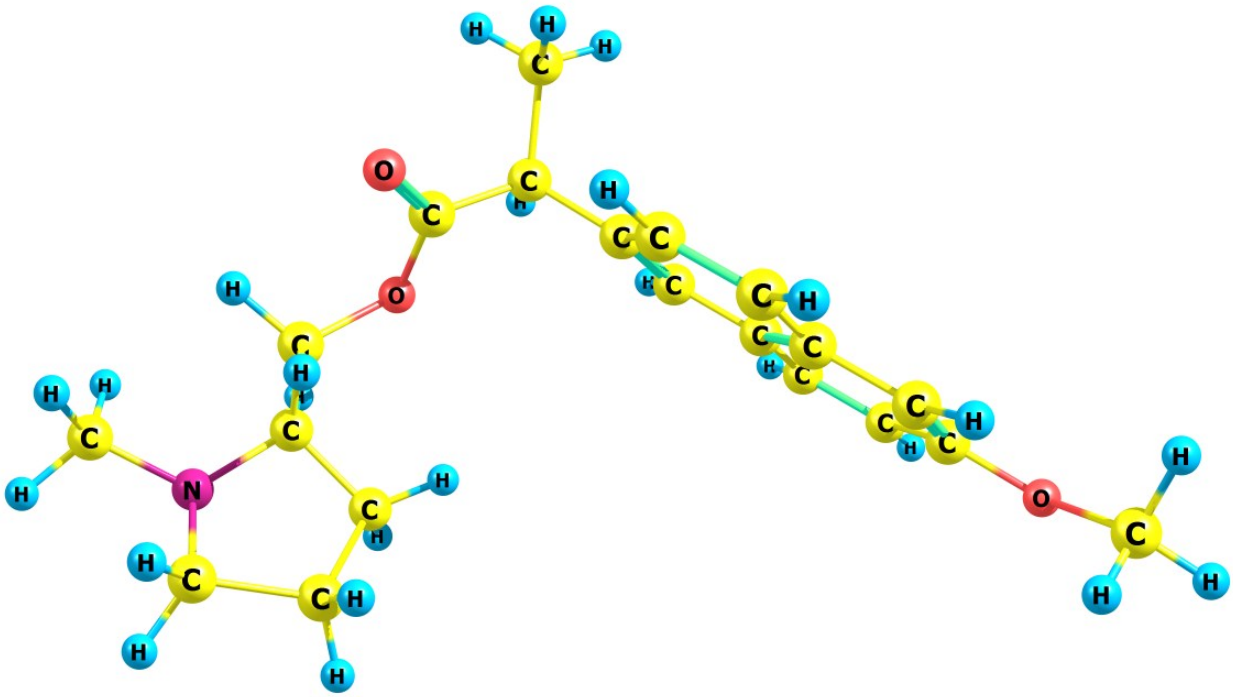
6	2.616755000	-2.517365000	0.623951000
7	2.998511000	-2.240200000	-0.756723000
1	5.824692000	-1.630222000	0.557868000
1	3.892451000	-2.401369000	2.416496000
1	1.959887000	-1.739659000	1.055678000
1	4.457266000	-3.513619000	1.157375000
1	2.081776000	-3.473941000	0.680517000
1	4.798169000	-1.520621000	-1.564688000
1	4.651098000	-0.481547000	1.202052000
6	1.917099000	-2.067135000	-1.703931000
1	1.271280000	-1.193393000	-1.501637000
1	2.320666000	-1.968145000	-2.719135000
1	1.281403000	-2.960216000	-1.689375000
1	1.532551000	1.695537000	1.776324000
6	1.137695000	3.715974000	1.101400000
1	0.391758000	3.935899000	1.871429000
1	2.106529000	4.106154000	1.431826000
1	0.860545000	4.243550000	0.185072000



Structure 4a3

1	-3.090298000	-0.032834000	2.931929000
6	-3.386367000	-0.158531000	1.893137000
6	-4.523372000	-0.860111000	1.585693000
6	-4.918486000	-1.030161000	0.229391000
6	-4.158863000	-0.489486000	-0.789050000
6	-2.976969000	0.242757000	-0.489113000
6	-2.576830000	0.415826000	0.873082000
6	-1.396628000	1.147313000	1.161599000
6	-0.625764000	1.704797000	0.160867000
6	-1.027398000	1.524807000	-1.191044000
6	-2.165125000	0.816366000	-1.503816000
1	-5.147159000	-1.300832000	2.357075000
1	-4.442436000	-0.607938000	-1.829174000
1	-2.455603000	0.686398000	-2.543938000
1	-0.415478000	1.945236000	-1.984262000
1	-1.104005000	1.269306000	2.202933000
8	-6.067288000	-1.746758000	0.060776000
6	-6.530254000	-1.960853000	-1.262740000
1	-6.751087000	-1.012072000	-1.769629000
1	-5.799409000	-2.524290000	-1.857955000
1	-7.448194000	-2.544018000	-1.169606000
6	0.617886000	2.523995000	0.496004000
6	1.819888000	1.951242000	-0.251098000
8	2.186442000	2.299341000	-1.354460000
8	2.414138000	0.970010000	0.459909000
6	3.519345000	0.292086000	-0.179905000
1	3.202623000	-0.050717000	-1.170265000
1	4.334077000	1.009450000	-0.320714000
6	2.858129000	-1.970864000	0.803724000
6	3.194536000	-2.890053000	-0.398150000
6	3.928868000	-0.868422000	0.741214000

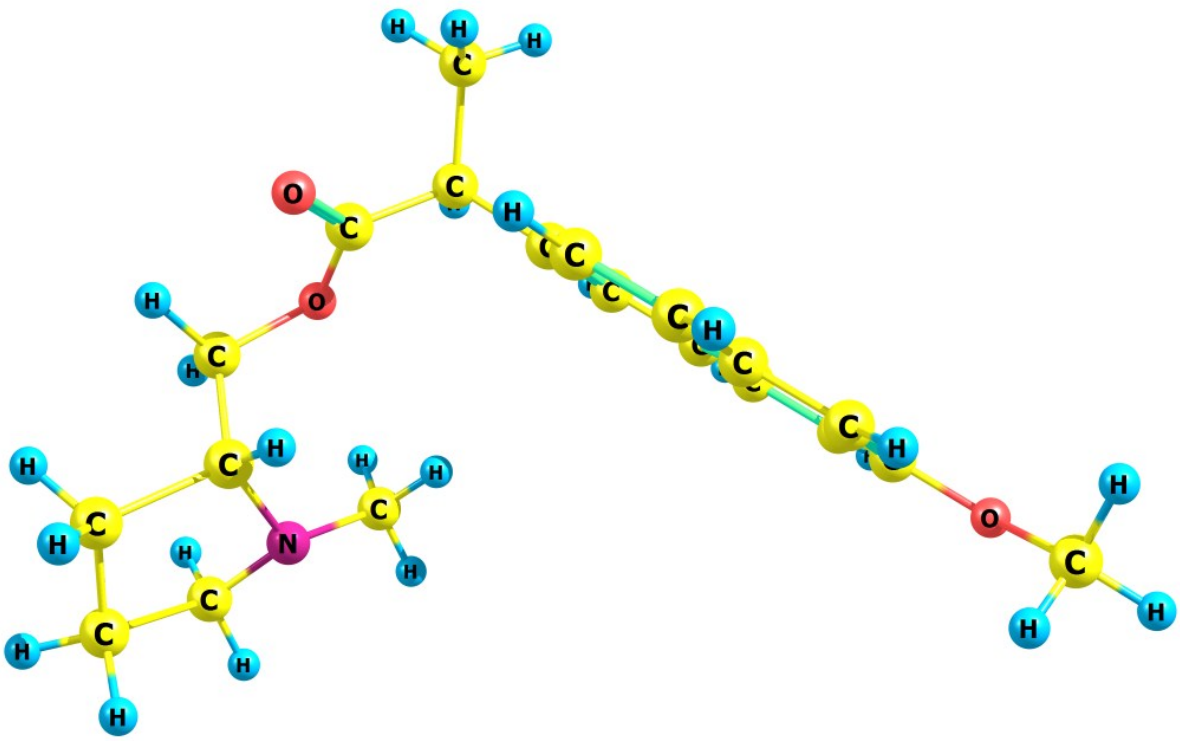
6	4.669727000	-2.566457000	-0.747570000
7	5.098132000	-1.619434000	0.283405000
1	2.967437000	-2.518826000	1.744645000
1	2.543112000	-2.680031000	-1.252499000
1	4.745616000	-2.142501000	-1.766883000
1	3.055427000	-3.945209000	-0.145399000
1	5.318795000	-3.451743000	-0.727366000
1	4.135078000	-0.445012000	1.733470000
1	1.842542000	-1.567333000	0.765557000
6	6.324351000	-0.900461000	0.009257000
1	6.301727000	-0.290429000	-0.914393000
1	6.561359000	-0.237592000	0.849397000
1	7.149785000	-1.615612000	-0.093354000
1	0.816203000	2.407539000	1.566486000
6	0.441918000	4.015829000	0.164163000
1	-0.427949000	4.416976000	0.693404000
1	1.326751000	4.588945000	0.462451000
1	0.296271000	4.160740000	-0.909412000



Structure 4a4

1	-3.006425000	0.174132000	2.883764000
6	-3.247654000	-0.002888000	1.838288000
6	-4.370425000	-0.716100000	1.506297000
6	-4.693912000	-0.953297000	0.141135000
6	-3.878454000	-0.466655000	-0.861302000
6	-2.710213000	0.276343000	-0.535941000
6	-2.381997000	0.516782000	0.835206000
6	-1.214640000	1.258888000	1.148916000
6	-0.388210000	1.762736000	0.163475000
6	-0.718180000	1.514647000	-1.197267000
6	-1.842065000	0.795067000	-1.533449000
1	-5.036501000	-1.115910000	2.264493000
1	-4.106871000	-0.637017000	-1.907805000
1	-2.077186000	0.612541000	-2.579611000
1	-0.061646000	1.891120000	-1.976359000
1	-0.978278000	1.434629000	2.196841000
8	-5.835863000	-1.674362000	-0.052390000
6	-6.229144000	-1.952611000	-1.386543000
1	-6.416655000	-1.029371000	-1.950737000
1	-5.471134000	-2.547587000	-1.913084000
1	-7.154355000	-2.527106000	-1.313791000
6	0.837782000	2.597692000	0.525205000
6	2.078571000	1.988429000	-0.122132000
8	2.458928000	2.228529000	-1.250198000
8	2.691438000	1.123077000	0.715523000
6	3.840061000	0.413651000	0.194224000
1	4.369083000	1.074140000	-0.497323000
1	4.469303000	0.218321000	1.067375000
6	4.716952000	-1.482995000	-1.223851000
6	4.919005000	-2.884441000	-0.602979000
6	3.454144000	-0.893797000	-0.524827000

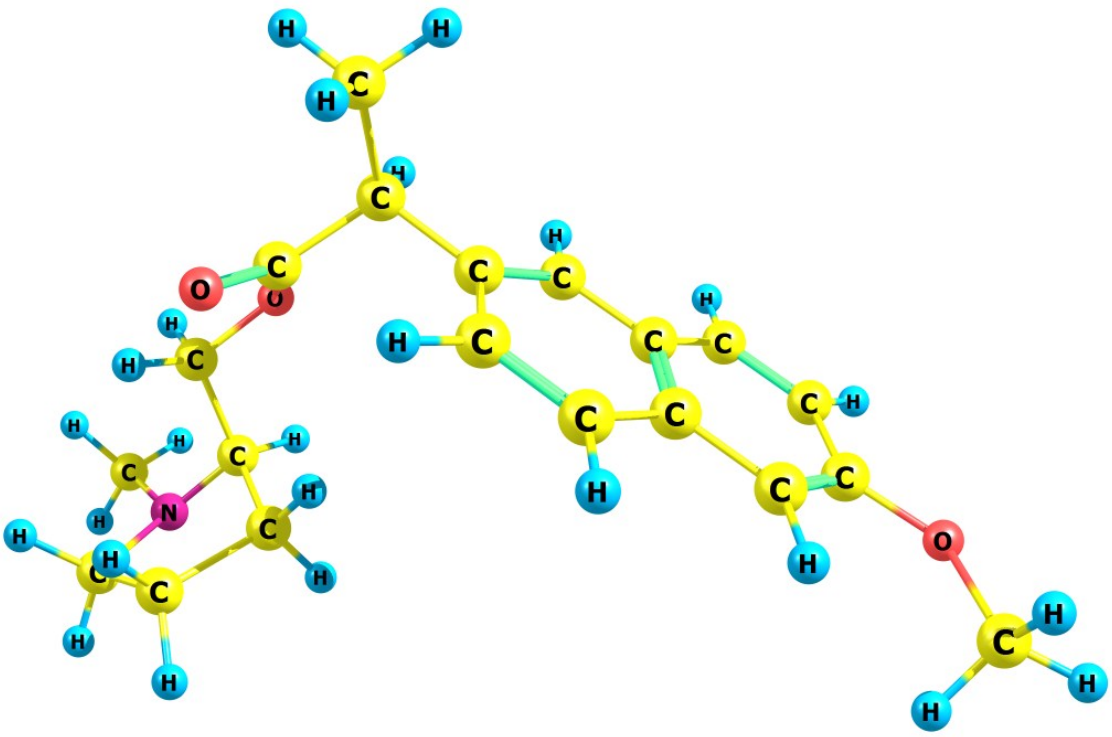
6	4.136707000	-2.794589000	0.710570000
7	2.983430000	-1.995134000	0.325789000
1	4.593846000	-1.521464000	-2.309745000
1	5.974630000	-3.135525000	-0.458745000
1	4.752820000	-2.323999000	1.506061000
1	4.470826000	-3.653405000	-1.240217000
1	3.811280000	-3.770222000	1.091784000
1	2.669196000	-0.641907000	-1.249075000
1	5.589749000	-0.847835000	-1.028126000
6	2.017470000	-1.714550000	1.370012000
1	2.418426000	-1.122762000	2.213317000
1	1.167008000	-1.165192000	0.955344000
1	1.646721000	-2.664687000	1.773732000
1	0.974612000	2.541046000	1.609646000
6	0.684592000	4.069803000	0.102301000
1	-0.214675000	4.497576000	0.556244000
1	1.550600000	4.659920000	0.422373000
1	0.603250000	4.155854000	-0.984378000



Structure 4a5

1	-3.214535000	0.657223000	2.895227000
6	-3.433504000	0.293566000	1.894063000
6	-4.551645000	-0.467779000	1.671810000
6	-4.846383000	-0.948053000	0.365276000
6	-4.007075000	-0.651591000	-0.690347000
6	-2.842210000	0.136419000	-0.478619000
6	-2.543525000	0.622109000	0.832986000
6	-1.379756000	1.407075000	1.033675000
6	-0.527436000	1.720237000	-0.006559000
6	-0.827171000	1.228334000	-1.306742000
6	-1.948075000	0.462249000	-1.533217000
1	-5.236062000	-0.723331000	2.474703000
1	-4.213352000	-1.008837000	-1.693422000
1	-2.160477000	0.093027000	-2.534045000
1	-0.150000000	1.454074000	-2.125389000
1	-1.165625000	1.768465000	2.037812000
8	-5.987103000	-1.691676000	0.280780000
6	-6.353964000	-2.206755000	-0.988925000
1	-6.526900000	-1.400976000	-1.714668000
1	-5.587546000	-2.887045000	-1.383509000
1	-7.282455000	-2.758875000	-0.832568000
6	0.700641000	2.596247000	0.227180000
6	1.953677000	1.846661000	-0.219616000
8	2.372054000	1.822582000	-1.359540000
8	2.520553000	1.192681000	0.817701000
6	3.691572000	0.383508000	0.553824000
1	4.064804000	0.613003000	-0.446259000
1	4.430789000	0.695563000	1.296866000
6	2.435290000	-1.644976000	-0.396001000
6	3.418002000	-1.980193000	-1.542629000
6	3.349852000	-1.111000000	0.717903000

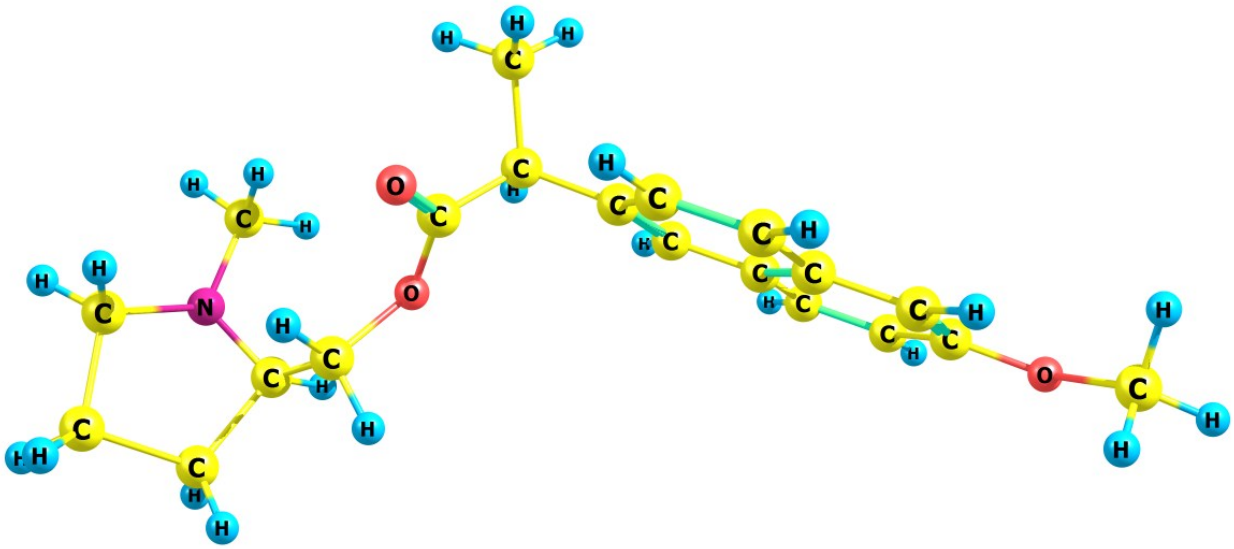
6	4.781652000	-2.203918000	-0.838932000
7	4.506856000	-1.997544000	0.585849000
1	1.941256000	-2.552709000	-0.035202000
1	3.481922000	-1.145501000	-2.247563000
1	5.541664000	-1.500298000	-1.227380000
1	3.096404000	-2.858477000	-2.110104000
1	5.182057000	-3.214908000	-0.993127000
1	2.901096000	-1.242402000	1.711667000
1	1.658219000	-0.937466000	-0.695959000
6	5.660602000	-1.777082000	1.430010000
1	6.271847000	-0.895526000	1.154095000
1	5.340768000	-1.657089000	2.471595000
1	6.318732000	-2.653752000	1.383776000
1	0.790721000	2.767043000	1.304371000
6	0.601681000	3.948567000	-0.501371000
1	-0.303831000	4.477161000	-0.187762000
1	1.468788000	4.578642000	-0.273833000
1	0.566353000	3.805348000	-1.584417000



Structure 4a6

1	-3.404156000	-0.199698000	2.930535000
6	-3.764430000	-0.232967000	1.905029000
6	-5.023676000	-0.704218000	1.637228000
6	-5.503814000	-0.751357000	0.298674000
6	-4.704111000	-0.323248000	-0.742367000
6	-3.395028000	0.168755000	-0.483652000
6	-2.909263000	0.218539000	0.860645000
6	-1.602549000	0.711001000	1.107860000
6	-0.786836000	1.149565000	0.083732000
6	-1.273923000	1.090455000	-1.250651000
6	-2.536435000	0.615686000	-1.523228000
1	-5.682696000	-1.050324000	2.427344000
1	-5.050998000	-0.351775000	-1.769606000
1	-2.891357000	0.574967000	-2.550599000
1	-0.628359000	1.412289000	-2.062625000
1	-1.246643000	0.741897000	2.136083000
8	-6.771252000	-1.240104000	0.169407000
6	-7.325122000	-1.316522000	-1.134175000
1	-7.391316000	-0.324889000	-1.601182000
1	-6.737276000	-1.980047000	-1.782323000
1	-8.329036000	-1.726849000	-1.010924000
6	0.601236000	1.713951000	0.377298000
6	1.642894000	0.945082000	-0.431509000
8	1.959824000	1.208286000	-1.573511000
8	2.149478000	-0.083536000	0.283360000
6	3.081652000	-0.975271000	-0.374086000
1	2.521079000	-1.885752000	-0.614275000
1	3.418292000	-0.515087000	-1.305931000
6	5.065423000	-2.501888000	0.060259000
6	6.218400000	-1.866342000	-0.763961000
6	4.241343000	-1.303341000	0.583376000

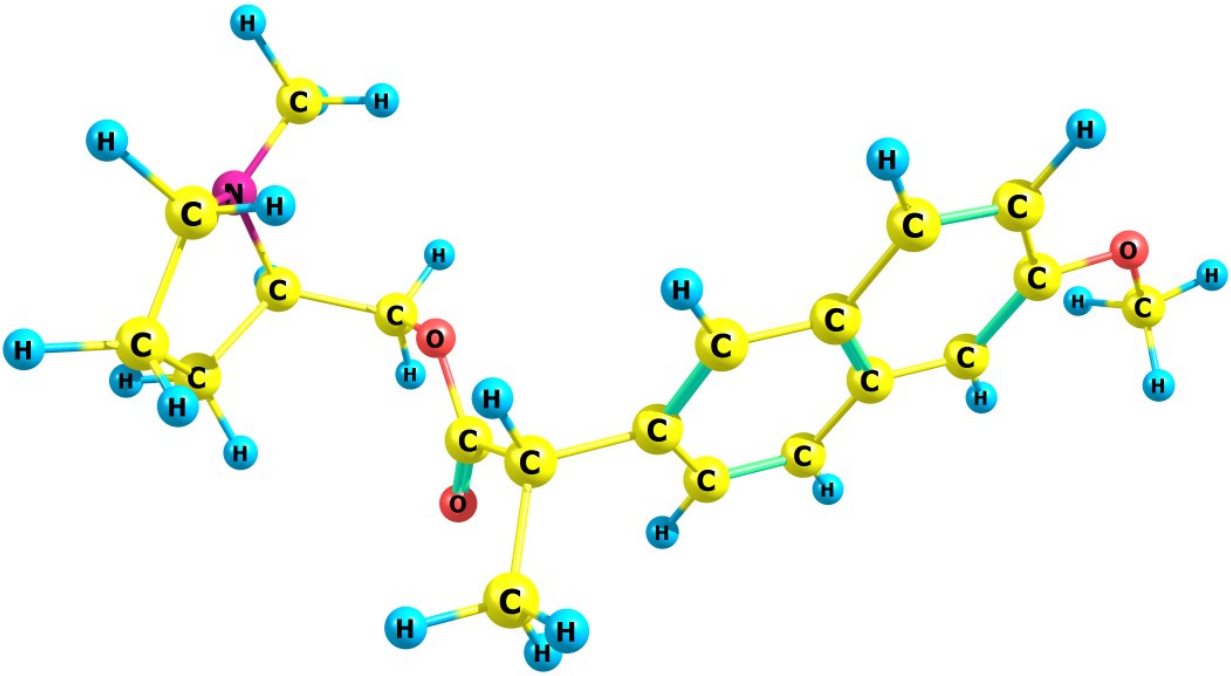
6	6.145623000	-0.356583000	-0.440113000
7	5.278313000	-0.279002000	0.732262000
1	5.468191000	-3.055709000	0.912907000
1	6.098492000	-2.043071000	-1.837346000
1	5.740551000	0.208677000	-1.302253000
1	7.183916000	-2.291191000	-0.474513000
1	7.124084000	0.082143000	-0.208042000
1	3.801068000	-1.513365000	1.566871000
1	4.461803000	-3.201814000	-0.527050000
6	4.889526000	1.063326000	1.119594000
1	4.228394000	1.021797000	1.991050000
1	5.787231000	1.628452000	1.400254000
1	4.377029000	1.631628000	0.321565000
1	0.816985000	1.540565000	1.436223000
6	0.694090000	3.219669000	0.072144000
1	-0.063118000	3.764568000	0.644357000
1	1.681762000	3.612111000	0.339029000
1	0.533479000	3.410580000	-0.991999000



Structure 4a7

1	2.855903000	1.747686000	2.340064000
6	3.325932000	1.212572000	1.518288000
6	4.617729000	1.503211000	1.162954000
6	5.241261000	0.809299000	0.088589000
6	4.549346000	-0.163805000	-0.604938000
6	3.208397000	-0.478496000	-0.250736000
6	2.578289000	0.217030000	0.828430000
6	1.240174000	-0.102464000	1.172092000
6	0.529249000	-1.072890000	0.494585000
6	1.160050000	-1.756125000	-0.580708000
6	2.456897000	-1.467668000	-0.939715000
1	5.195008000	2.261300000	1.682988000
1	5.006125000	-0.704266000	-1.426939000
1	2.922299000	-1.998648000	-1.767098000
1	0.599510000	-2.505757000	-1.132249000
1	0.773297000	0.437475000	1.993826000
8	6.525805000	1.193743000	-0.163616000
6	7.216393000	0.552419000	-1.223791000
1	7.313501000	-0.526758000	-1.045481000
1	6.712942000	0.713420000	-2.186322000
1	8.209006000	1.005404000	-1.253614000
6	-0.899892000	-1.423251000	0.900835000
6	-1.823135000	-1.245483000	-0.302527000
8	-2.094564000	-2.119954000	-1.099735000
8	-2.271363000	0.027754000	-0.381095000
6	-3.073591000	0.400691000	-1.528342000
1	-2.586706000	1.287542000	-1.944897000
1	-3.037066000	-0.407139000	-2.263101000
6	-5.234484000	-0.470933000	-0.427637000
6	-5.166306000	-0.121764000	1.084538000
6	-4.533082000	0.702234000	-1.147231000

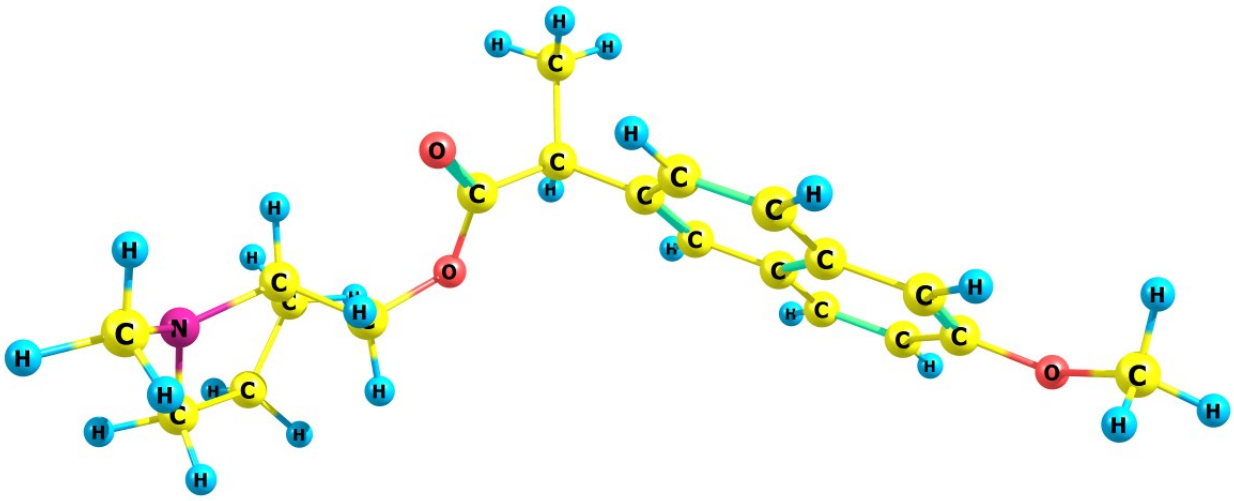
6	-4.642932000	1.331431000	1.142430000
7	-4.765382000	1.819292000	-0.230606000
1	-6.276468000	-0.522604000	-0.756714000
1	-4.498112000	-0.797599000	1.627018000
1	-3.599327000	1.355677000	1.502630000
1	-6.153678000	-0.207722000	1.548006000
1	-5.233116000	1.969144000	1.813825000
1	-5.025944000	0.929527000	-2.105708000
1	-4.767610000	-1.431485000	-0.662820000
6	-4.096096000	3.072521000	-0.506026000
1	-4.278275000	3.373297000	-1.544766000
1	-4.508467000	3.854441000	0.142914000
1	-3.001926000	3.046941000	-0.340890000
1	-1.216481000	-0.701867000	1.661236000
6	-1.017832000	-2.849705000	1.463868000
1	-0.347298000	-2.970226000	2.320339000
1	-2.042636000	-3.056466000	1.791974000
1	-0.754029000	-3.591648000	0.705857000



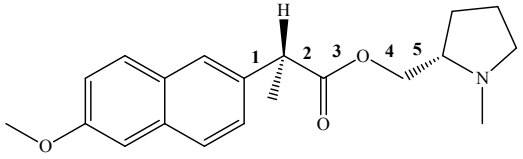
Structure 4a8

1	-3.470619000	-0.645623000	2.875516000
6	-3.803440000	-0.547329000	1.844910000
6	-5.031514000	-1.030154000	1.473373000
6	-5.475361000	-0.906466000	0.127137000
6	-4.671800000	-0.298322000	-0.816775000
6	-3.394851000	0.209205000	-0.449586000
6	-2.945500000	0.086731000	0.902746000
6	-1.670817000	0.595768000	1.258716000
6	-0.852457000	1.213828000	0.334351000
6	-1.303139000	1.327083000	-1.009185000
6	-2.533733000	0.840077000	-1.386766000
1	-5.692575000	-1.514743000	2.185099000
1	-4.991400000	-0.193996000	-1.847940000
1	-2.860944000	0.932802000	-2.419951000
1	-0.655522000	1.794114000	-1.745732000
1	-1.342162000	0.493490000	2.291388000
8	-6.713927000	-1.427702000	-0.109664000
6	-7.228948000	-1.347575000	-1.428841000
1	-7.334170000	-0.304786000	-1.756642000
1	-6.590930000	-1.885643000	-2.142468000
1	-8.213277000	-1.818168000	-1.396549000
6	0.497299000	1.792279000	0.751402000
6	1.599819000	1.206865000	-0.127266000
8	1.958605000	1.671471000	-1.190330000
8	2.106951000	0.077381000	0.414721000
6	3.129873000	-0.609725000	-0.345440000
1	3.018813000	-1.662330000	-0.071196000
1	2.920679000	-0.484317000	-1.409622000
6	4.921042000	-0.368724000	1.468149000
6	5.544087000	-1.786789000	1.407437000
6	4.530474000	-0.071121000	0.011161000

6	5.940138000	-1.983865000	-0.078718000
7	5.624423000	-0.707874000	-0.720995000
1	5.668661000	0.361776000	1.792672000
1	4.821977000	-2.549914000	1.715814000
1	5.381285000	-2.830011000	-0.522704000
1	6.404583000	-1.875972000	2.076934000
1	7.006455000	-2.210126000	-0.210851000
1	4.529796000	1.004703000	-0.204510000
1	4.068963000	-0.304600000	2.151169000
6	5.582277000	-0.717427000	-2.168381000
1	4.850053000	-1.427058000	-2.599769000
1	5.341037000	0.285219000	-2.537752000
1	6.569932000	-0.991489000	-2.559659000
1	0.695889000	1.470150000	1.778558000
6	0.519124000	3.329410000	0.680751000
1	-0.281087000	3.743693000	1.301793000
1	1.477146000	3.723545000	1.037809000
1	0.377992000	3.672702000	-0.347311000



4b scan 4 and scan 5 (fig. 9-10)

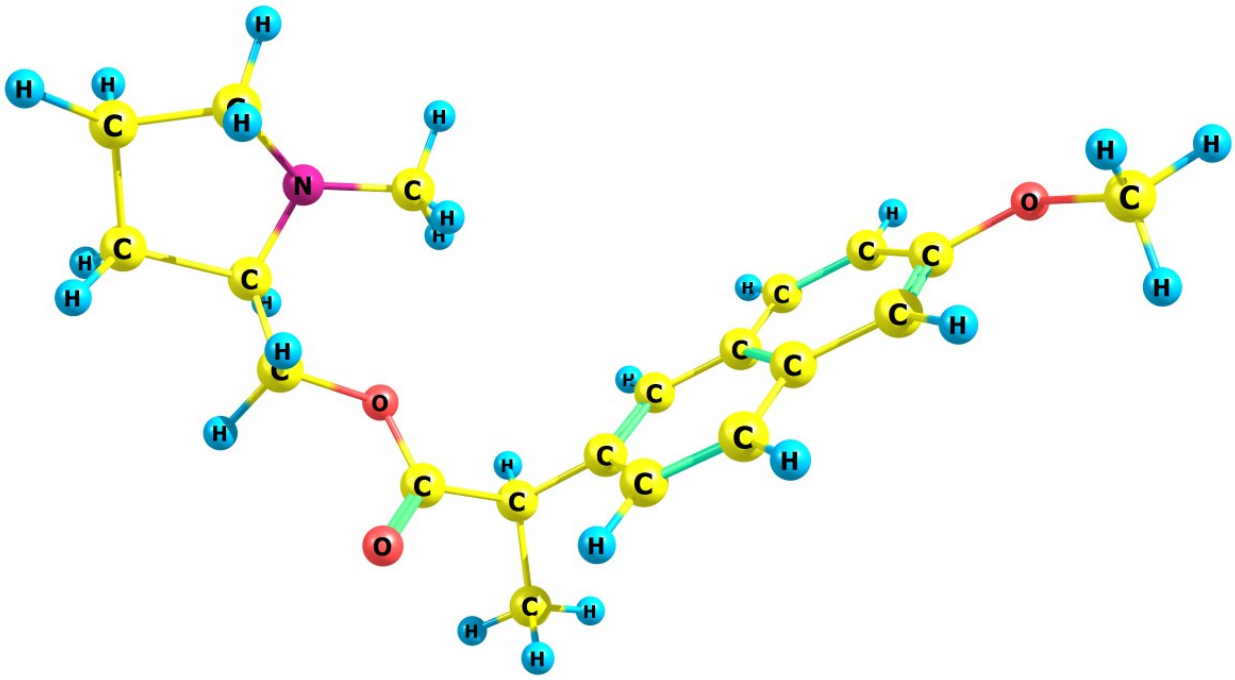


ID structure	$\varphi_{8\text{-}9\text{-}22\text{-}24}$	$\varphi_{9\text{-}22\text{-}24\text{-}26}$	$\varphi_{22\text{-}24\text{-}26\text{-}27}$	$\varphi_{24\text{-}26\text{-}27\text{-}36}$	$\varphi_{26\text{-}27\text{-}36\text{-}34}$	Total energy, a.u.	MBD
4b1	-124,536	91,642	-176,637	-179,812	168,41	-1057,615080	14%
4b2	-123,905	90,288	-176,348	178,722	-58,049	-1057,615651	26%
4b3	-125,381	89,972	-176,414	178,094	68,552	-1057,614758	10%
4b4	-124,818	93,365	-176,794	-86,735	172,545	-1057,614810	11%
4b5	-125,334	90,311	-175,815	-116,193	69,417	-1057,613873	4%
4b6	-125,095	88,693	-177,587	117,548	-62,684	-1057,615439	21%
4b7	-124,362	89,92	-176,531	86,206	62,829	-1057,615044	14%

Structure 4b1

1	2.850297000	-0.448948000	2.870680000
6	3.201030000	-0.428309000	1.841538000
6	4.349518000	-1.092780000	1.496575000
6	4.816544000	-1.070763000	0.152767000
6	4.115005000	-0.380716000	-0.815926000
6	2.921504000	0.314461000	-0.476641000
6	2.450160000	0.296257000	0.873530000
6	1.260459000	0.994920000	1.201921000
6	0.546138000	1.698127000	0.252078000
6	1.015689000	1.703686000	-1.089895000
6	2.165846000	1.034247000	-1.440429000
1	4.928826000	-1.647206000	2.228266000
1	4.453238000	-0.352934000	-1.846056000
1	2.509248000	1.047888000	-2.472421000
1	0.445222000	2.235016000	-1.846260000
1	0.915689000	0.974007000	2.234215000
8	5.969862000	-1.769183000	-0.056703000
6	6.504081000	-1.792584000	-1.370501000
1	5.804958000	-2.254376000	-2.080330000
1	6.755378000	-0.782325000	-1.719875000
1	7.413566000	-2.393501000	-1.314756000
6	-0.708301000	2.478218000	0.636967000
1	-0.949894000	2.232963000	1.676062000
6	-1.879836000	2.012518000	-0.223993000
8	-2.159133000	2.456949000	-1.318583000
8	-2.560053000	1.010906000	0.371948000
6	-3.648370000	0.438148000	-0.388333000
1	-4.370333000	1.232155000	-0.607256000
1	-3.262179000	0.066133000	-1.343922000
6	-0.516477000	3.998882000	0.498345000
1	-1.408594000	4.537038000	0.837705000

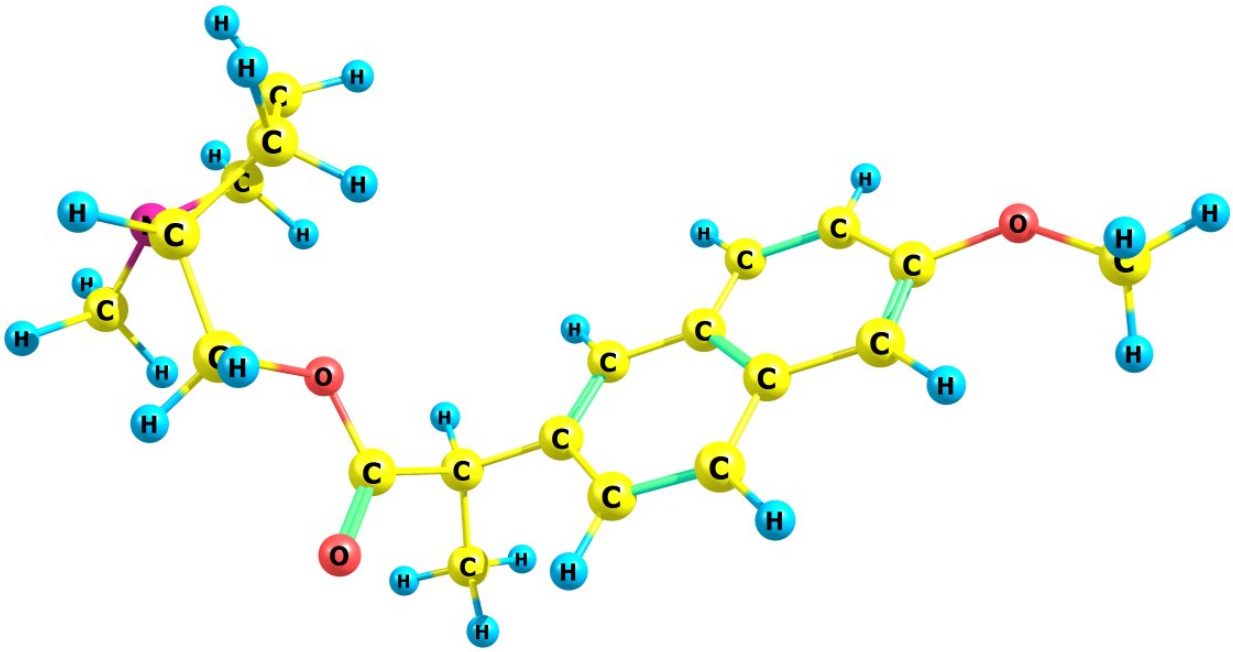
1	0.336883000	4.325444000	1.100685000
1	-0.335675000	4.274231000	-0.543949000
6	-5.646946000	-1.093079000	-0.234807000
6	-5.504786000	-2.601628000	-0.539394000
6	-4.304950000	-0.674121000	0.440883000
6	-3.988078000	-2.809763000	-0.533822000
7	-3.563405000	-1.938156000	0.552318000
1	-6.505879000	-0.876767000	0.406927000
1	-5.974919000	-2.887910000	-1.485421000
1	-3.548772000	-2.534783000	-1.515673000
1	-5.956438000	-3.198457000	0.259445000
1	-3.690727000	-3.844873000	-0.326345000
1	-4.466557000	-0.269254000	1.449404000
1	-5.795977000	-0.528666000	-1.163451000
6	-2.139149000	-1.897957000	0.823624000
1	-1.525422000	-1.512712000	-0.010441000
1	-1.944255000	-1.267111000	1.695797000
1	-1.793736000	-2.913928000	1.050530000



Structure 4b2

1	2.516247000	-1.531252000	2.444321000
6	3.011001000	-1.078926000	1.588043000
6	4.263885000	-1.498099000	1.221737000
6	4.919712000	-0.911996000	0.103277000
6	4.298215000	0.084233000	-0.623238000
6	2.998588000	0.531757000	-0.258209000
6	2.336484000	-0.054519000	0.865920000
6	1.040542000	0.398908000	1.221326000
6	0.401439000	1.396752000	0.512493000
6	1.063097000	1.969909000	-0.607863000
6	2.320061000	1.550494000	-0.979012000
1	4.785565000	-2.278660000	1.766690000
1	4.780432000	0.543204000	-1.479370000
1	2.809922000	1.998588000	-1.840602000
1	0.556894000	2.739785000	-1.183261000
1	0.549337000	-0.056602000	2.079306000
8	6.160346000	-1.417962000	-0.154042000
6	6.882134000	-0.884903000	-1.252801000
1	6.348884000	-1.044515000	-2.199417000
1	7.073253000	0.188836000	-1.124881000
1	7.832232000	-1.421621000	-1.277253000
6	-0.979313000	1.894373000	0.932508000
1	-1.342477000	1.241101000	1.732339000
6	-1.943656000	1.754090000	-0.242813000
8	-2.120990000	2.592023000	-1.102401000
8	-2.559659000	0.552016000	-0.232849000
6	-3.437520000	0.274090000	-1.347960000
1	-4.217476000	1.040716000	-1.378258000
1	-2.866385000	0.348720000	-2.280261000
6	-0.951469000	3.350046000	1.429900000
1	-1.942856000	3.662991000	1.775925000

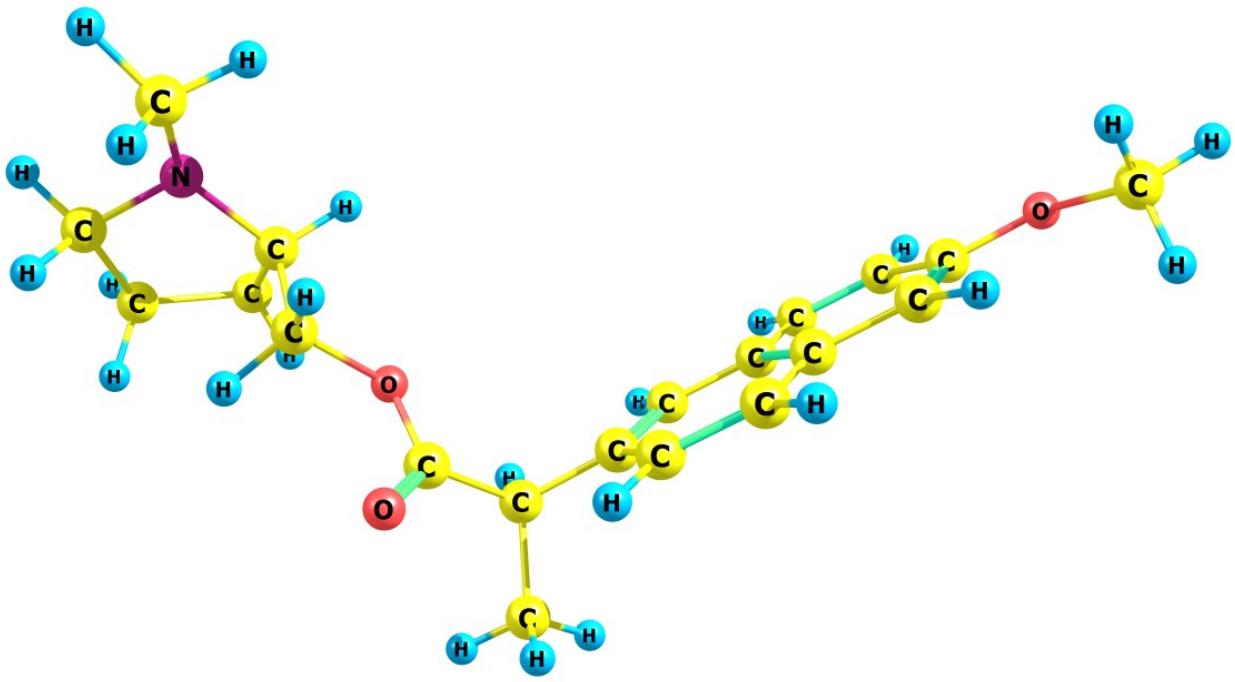
1	-0.245813000	3.448513000	2.260592000
1	-0.646932000	4.028881000	0.629149000
6	-2.915597000	-2.225814000	-1.107128000
6	-3.259740000	-3.058290000	0.146152000
6	-4.020853000	-1.133801000	-1.190353000
6	-4.056624000	-2.071367000	1.003541000
7	-4.849404000	-1.364890000	0.003757000
1	-2.875040000	-2.833451000	-2.016160000
1	-2.369836000	-3.444343000	0.653131000
1	-3.378673000	-1.405271000	1.569890000
1	-3.896856000	-3.908950000	-0.118867000
1	-4.717955000	-2.565794000	1.726641000
1	-4.649298000	-1.276040000	-2.084577000
1	-1.937292000	-1.750943000	-0.984955000
6	-5.682588000	-0.283605000	0.481554000
1	-5.121160000	0.569453000	0.907001000
1	-6.310864000	0.095458000	-0.333732000
1	-6.352384000	-0.663166000	1.262196000



Structure 4b3

1	3.166762000	-0.231025000	2.955501000
6	3.531491000	-0.299435000	1.933327000
6	4.717449000	-0.935167000	1.670970000
6	5.202461000	-1.029765000	0.336682000
6	4.481491000	-0.481971000	-0.705793000
6	3.249256000	0.181796000	-0.452623000
6	2.759042000	0.279439000	0.887392000
6	1.529481000	0.943169000	1.129343000
6	0.793844000	1.503812000	0.104266000
6	1.283977000	1.397187000	-1.225923000
6	2.472701000	0.757252000	-1.493573000
1	5.313309000	-1.379274000	2.462237000
1	4.833466000	-0.544101000	-1.729833000
1	2.831041000	0.682774000	-2.517854000
1	0.699164000	1.817561000	-2.039137000
1	1.168920000	1.008750000	2.154317000
8	6.392478000	-1.685848000	0.213043000
6	6.944420000	-1.824575000	-1.086133000
1	6.278392000	-2.395234000	-1.746918000
1	7.150750000	-0.846916000	-1.541663000
1	7.881474000	-2.369519000	-0.958207000
6	-0.507242000	2.248224000	0.393428000
1	-0.759159000	2.084616000	1.446177000
6	-1.634669000	1.646527000	-0.441922000
8	-1.929353000	1.993293000	-1.567119000
8	-2.253431000	0.644025000	0.217108000
6	-3.288508000	-0.055225000	-0.511273000
1	-4.072373000	0.657184000	-0.790051000
1	-2.856922000	-0.453466000	-1.434368000
6	-0.388881000	3.758101000	0.120724000
1	-1.315171000	4.277573000	0.390407000

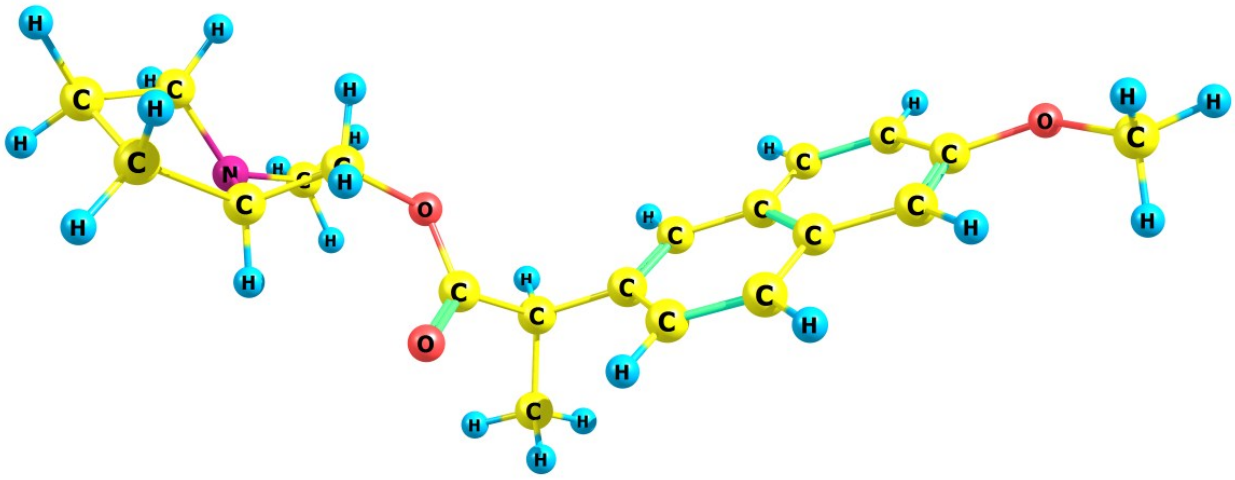
1	0.431564000	4.181582000	0.708247000
1	-0.195506000	3.946966000	-0.938383000
6	-4.584961000	-0.623837000	1.618015000
6	-6.036277000	-0.458123000	1.097840000
6	-3.812711000	-1.171492000	0.405531000
6	-6.111479000	-1.354453000	-0.164641000
7	-4.817646000	-2.036566000	-0.213607000
1	-4.551064000	-1.362981000	2.424203000
1	-6.250252000	0.584417000	0.841037000
1	-6.300391000	-0.742002000	-1.066966000
1	-6.767997000	-0.755063000	1.854786000
1	-6.918384000	-2.097256000	-0.115212000
1	-2.950278000	-1.777799000	0.712869000
1	-4.156151000	0.307447000	1.998759000
6	-4.496960000	-2.693785000	-1.463266000
1	-4.470142000	-2.020777000	-2.341856000
1	-3.521917000	-3.187692000	-1.382649000
1	-5.246714000	-3.467640000	-1.668673000



Structure 4b4

1	3.341010000	-1.096043000	2.734982000
6	3.725705000	-0.831041000	1.752944000
6	4.981500000	-1.233756000	1.378438000
6	5.493172000	-0.891972000	0.095599000
6	4.727974000	-0.151540000	-0.783461000
6	3.423029000	0.275452000	-0.412220000
6	2.905709000	-0.065728000	0.876712000
6	1.603552000	0.364850000	1.237191000
6	0.822081000	1.110984000	0.377478000
6	1.340206000	1.440744000	-0.904598000
6	2.599272000	1.035620000	-1.284846000
1	5.613902000	-1.817256000	2.040239000
1	5.099434000	0.118235000	-1.766121000
1	2.978465000	1.294621000	-2.270897000
1	0.721346000	2.007872000	-1.593810000
1	1.222705000	0.096712000	2.221103000
8	6.753285000	-1.353569000	-0.151299000
6	7.337484000	-1.055346000	-1.408949000
1	6.752625000	-1.481312000	-2.235021000
1	7.435527000	0.027951000	-1.559752000
1	8.329492000	-1.510477000	-1.395238000
6	-0.560521000	1.597124000	0.804601000
1	-0.800826000	1.124186000	1.761900000
6	-1.602979000	1.129258000	-0.207563000
8	-1.882163000	1.714613000	-1.234464000
8	-2.157805000	-0.044201000	0.167860000
6	-3.113152000	-0.633440000	-0.745253000
1	-2.792039000	-0.417169000	-1.767285000
1	-3.047159000	-1.709696000	-0.561241000
6	-0.618561000	3.127860000	0.957711000
1	-1.602043000	3.447360000	1.320469000

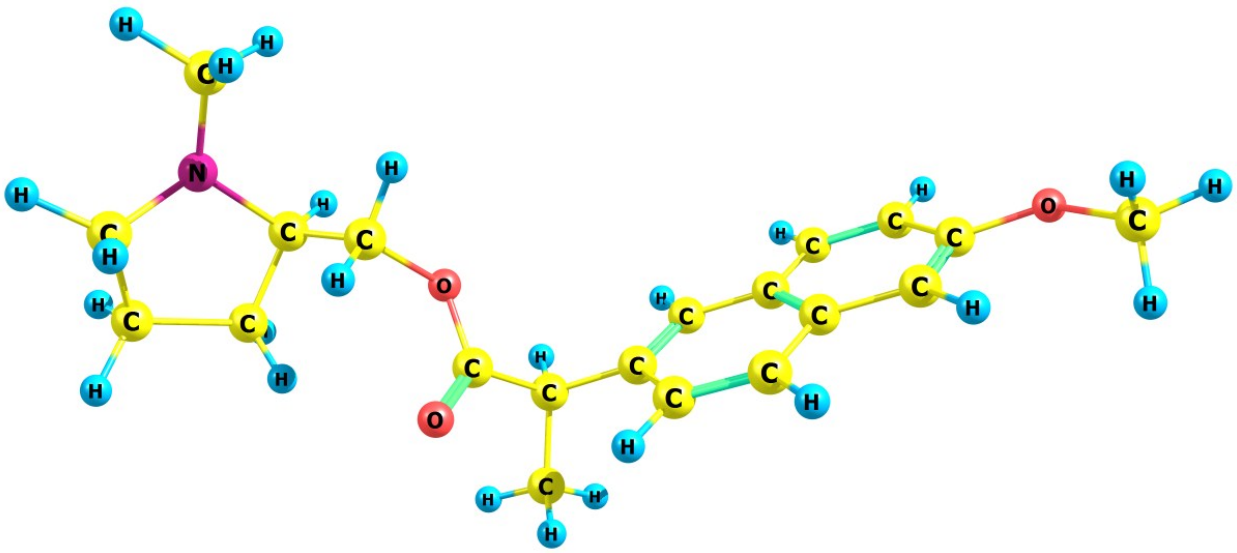
1	0.140602000	3.461642000	1.671797000
1	-0.438353000	3.620785000	-0.001146000
6	-5.460022000	-0.658855000	-1.675219000
6	-6.540474000	-1.515620000	-0.973556000
6	-4.548825000	-0.115388000	-0.532543000
6	-5.918748000	-1.806711000	0.395774000
7	-5.231695000	-0.557828000	0.690502000
1	-5.893091000	0.155458000	-2.262478000
1	-6.790632000	-2.422853000	-1.532480000
1	-5.237737000	-2.682197000	0.342687000
1	-7.459295000	-0.936307000	-0.838637000
1	-6.660614000	-2.023593000	1.173964000
1	-4.500163000	0.980475000	-0.538504000
1	-4.873287000	-1.271253000	-2.370706000
6	-4.526247000	-0.491468000	1.954539000
1	-3.685153000	-1.201740000	2.049073000
1	-4.126169000	0.517012000	2.103692000
1	-5.234139000	-0.698512000	2.766445000



Structure 4b5

1	3.550413000	-0.161741000	2.927669000
6	3.864778000	-0.215570000	1.888042000
6	5.097779000	-0.724467000	1.571468000
6	5.517690000	-0.799205000	0.214017000
6	4.685507000	-0.359769000	-0.796376000
6	3.403033000	0.171568000	-0.486918000
6	2.977692000	0.248677000	0.876426000
6	1.696892000	0.779527000	1.174350000
6	0.849908000	1.230319000	0.181510000
6	1.277095000	1.145135000	-1.171802000
6	2.512975000	0.632293000	-1.493444000
1	5.780800000	-1.080766000	2.336273000
1	4.986176000	-0.408790000	-1.837284000
1	2.821903000	0.571813000	-2.534598000
1	0.606852000	1.478546000	-1.958920000
1	1.386639000	0.830180000	2.216445000
8	6.764202000	-1.324911000	0.036022000
6	7.257724000	-1.433803000	-1.289350000
1	6.623166000	-2.087911000	-1.902009000
1	7.331982000	-0.450517000	-1.772537000
1	8.253872000	-1.871826000	-1.204307000
6	-0.508256000	1.835726000	0.527965000
1	-0.685351000	1.672646000	1.595751000
6	-1.603955000	1.091539000	-0.231197000
8	-1.985621000	1.378855000	-1.347801000
8	-2.069859000	0.051021000	0.493694000
6	-3.051841000	-0.824967000	-0.109902000
1	-3.180491000	-0.550288000	-1.158993000
1	-2.621964000	-1.828440000	-0.045467000
6	-0.570489000	3.341869000	0.218997000
1	-1.534108000	3.764183000	0.525134000

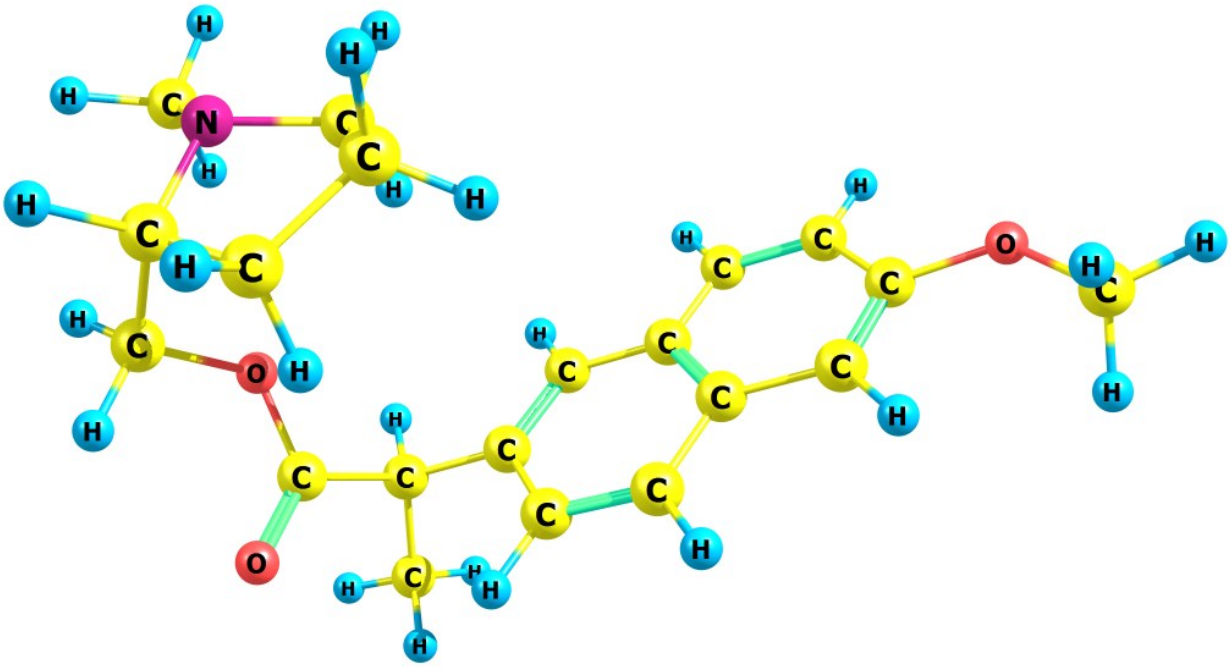
1	0.225787000	3.866565000	0.756005000
1	-0.449432000	3.524107000	-0.851900000
6	-5.055157000	0.656487000	0.493800000
6	-6.396429000	0.358338000	-0.224119000
6	-4.368583000	-0.727110000	0.684076000
6	-6.206269000	-1.059192000	-0.775108000
7	-5.395844000	-1.687711000	0.261021000
1	-5.214330000	1.159605000	1.451822000
1	-6.626851000	1.088725000	-1.005704000
1	-5.709929000	-1.037799000	-1.766467000
1	-7.222785000	0.361027000	0.493804000
1	-7.149711000	-1.605322000	-0.897810000
1	-4.120117000	-0.913134000	1.738244000
1	-4.425301000	1.312056000	-0.114819000
6	-5.009077000	-3.065296000	0.039107000
1	-4.393751000	-3.232725000	-0.865468000
1	-4.447622000	-3.437237000	0.904275000
1	-5.910821000	-3.681296000	-0.060852000



Structure 4b6

1	2.406438000	-0.194673000	2.953103000
6	2.762441000	-0.116875000	1.928567000
6	3.989711000	-0.625319000	1.590044000
6	4.464076000	-0.528590000	0.251956000
6	3.690904000	0.078944000	-0.717521000
6	2.415383000	0.612840000	-0.384650000
6	1.935432000	0.517500000	0.959407000
6	0.661904000	1.052853000	1.280999000
6	-0.126345000	1.671368000	0.330501000
6	0.356178000	1.760190000	-1.004113000
6	1.585691000	1.245981000	-1.348742000
1	4.627376000	-1.110323000	2.322494000
1	4.034120000	0.163487000	-1.742888000
1	1.937494000	1.320920000	-2.375231000
1	-0.265565000	2.231664000	-1.760003000
1	0.310332000	0.972417000	2.307944000
8	5.698162000	-1.073108000	0.049127000
6	6.243407000	-1.018695000	-1.259438000
1	5.612964000	-1.556616000	-1.979808000
1	6.372099000	0.017863000	-1.598218000
1	7.219236000	-1.503872000	-1.198939000
6	-1.478212000	2.272204000	0.707124000
1	-1.704489000	1.968478000	1.734142000
6	-2.563376000	1.679593000	-0.189238000
8	-2.906939000	2.145175000	-1.256176000
8	-3.066459000	0.546251000	0.349581000
6	-4.072965000	-0.182797000	-0.393450000
1	-4.946491000	-0.232348000	0.263522000
1	-4.334351000	0.382081000	-1.291507000
6	-1.482517000	3.807594000	0.610558000
1	-2.445642000	4.216278000	0.935652000

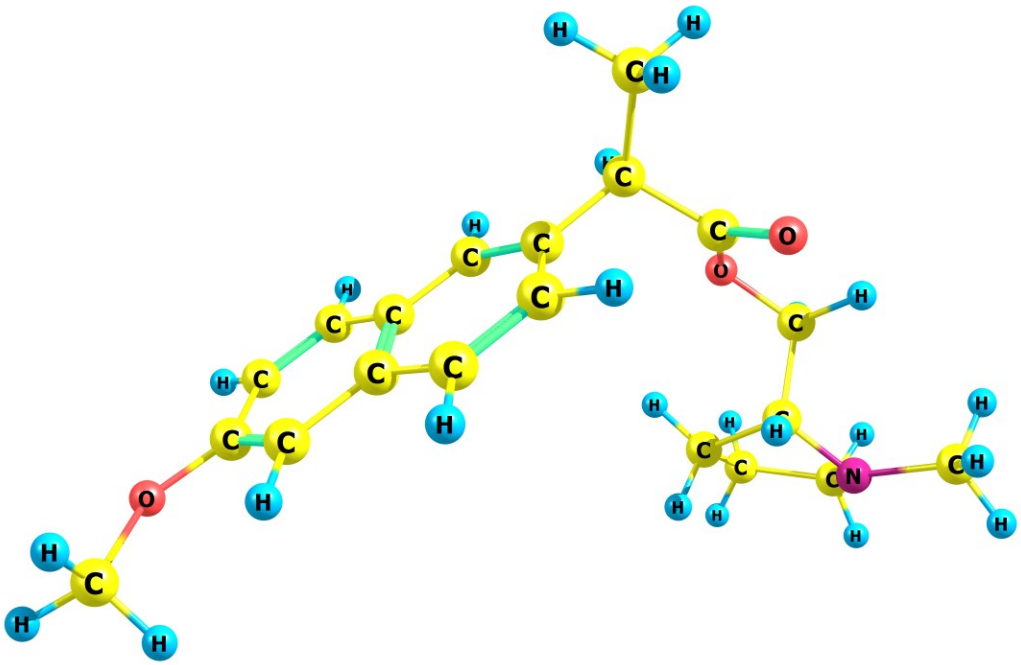
1	-0.694977000	4.224227000	1.246099000
1	-1.311291000	4.133486000	-0.418583000
6	-2.342395000	-1.560438000	-1.705556000
6	-1.269380000	-2.420216000	-1.000070000
6	-3.583476000	-1.590718000	-0.767710000
6	-1.717734000	-2.412429000	0.464594000
7	-3.172341000	-2.456080000	0.346222000
1	-2.586428000	-1.940515000	-2.702168000
1	-0.258719000	-2.023615000	-1.135050000
1	-1.351414000	-1.507867000	0.983364000
1	-1.287868000	-3.446075000	-1.383273000
1	-1.361331000	-3.285831000	1.025726000
1	-4.447528000	-2.055155000	-1.271125000
1	-1.989357000	-0.533153000	-1.836139000
6	-3.923360000	-2.383233000	1.580623000
1	-3.800219000	-1.432659000	2.132515000
1	-4.992454000	-2.523806000	1.377729000
1	-3.605873000	-3.196903000	2.243521000



Structure 4b7

1	-3.209963000	0.258455000	-2.879196000
6	-3.418599000	0.039081000	-1.834728000
6	-4.528897000	-0.690905000	-1.497313000
6	-4.810330000	-0.982310000	-0.133343000
6	-3.965337000	-0.533432000	0.862269000
6	-2.808908000	0.225470000	0.531148000
6	-2.524040000	0.522117000	-0.838689000
6	-1.369614000	1.281191000	-1.158222000
6	-0.514280000	1.747569000	-0.179793000
6	-0.799628000	1.442312000	1.179106000
6	-1.910704000	0.705773000	1.521337000
1	-5.216953000	-1.062774000	-2.250088000
1	-4.161351000	-0.745806000	1.907692000
1	-2.112191000	0.479862000	2.566060000
1	-0.119140000	1.788384000	1.951937000
1	-1.166096000	1.499208000	-2.205081000
8	-5.945000000	-1.713330000	0.066263000
6	-6.299668000	-2.040394000	1.400119000
1	-5.526956000	-2.653523000	1.882650000
1	-6.470496000	-1.138396000	2.002654000
1	-7.226720000	-2.612634000	1.333239000
6	0.701070000	2.596054000	-0.544802000
1	0.792877000	2.596393000	-1.635622000
6	1.962321000	1.943205000	0.015543000
8	2.417310000	2.149641000	1.122321000
8	2.498416000	1.079611000	-0.874577000
6	3.659177000	0.329607000	-0.442594000
1	4.198986000	0.104512000	-1.366355000
1	4.274160000	0.969838000	0.193447000
6	0.578339000	4.043619000	-0.038216000
1	1.435268000	4.644312000	-0.362769000

1	-0.335562000	4.500762000	-0.429998000
1	0.544320000	4.072370000	1.053927000
6	2.458855000	-1.928033000	-0.593467000
6	3.559115000	-2.759126000	-1.301557000
6	3.243793000	-0.956046000	0.302109000
6	4.822930000	-2.578351000	-0.421950000
7	4.369855000	-1.789450000	0.724224000
1	1.842077000	-2.573489000	0.039309000
1	3.743017000	-2.391439000	-2.316424000
1	5.626331000	-2.072573000	-0.991636000
1	3.270441000	-3.810282000	-1.393122000
1	5.241203000	-3.531406000	-0.072132000
1	2.666904000	-0.652386000	1.184224000
1	1.794734000	-1.409810000	-1.290727000
6	5.410989000	-1.195084000	1.536286000
1	6.085047000	-0.509998000	0.986404000
1	4.961075000	-0.636177000	2.364171000
1	6.034711000	-1.988562000	1.966341000

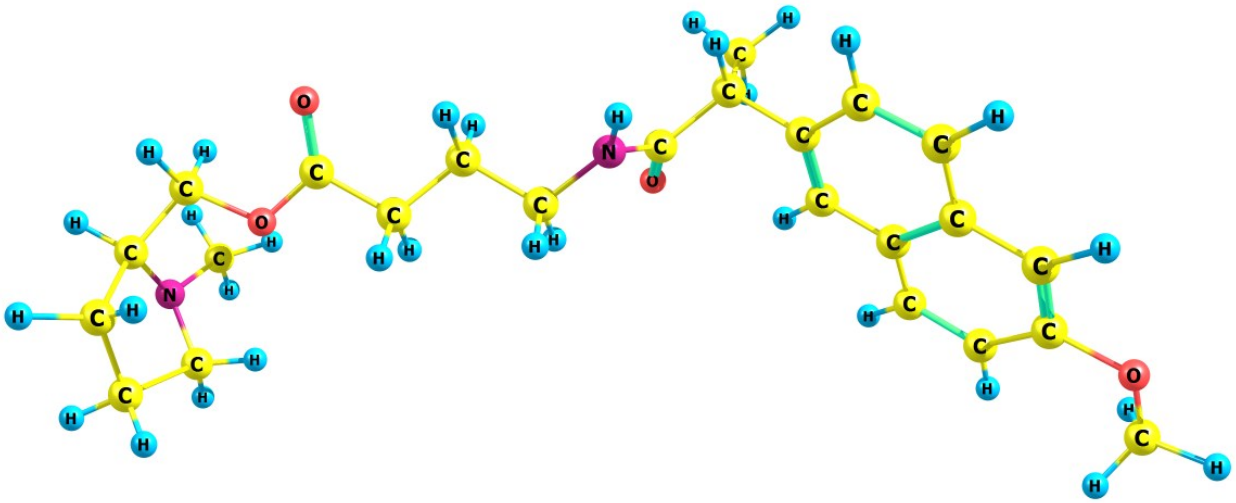


Optimization in the Presence of Solvent

Structure 2a

1	-5.104800000	1.528607000	-2.099975000
6	-5.675708000	1.248827000	-1.220930000
6	-6.811084000	1.953241000	-0.895829000
6	-7.563652000	1.594824000	0.251767000
6	-7.155491000	0.538184000	1.040578000
6	-5.992738000	-0.197105000	0.722311000
6	-5.228617000	0.159934000	-0.434384000
6	-4.060238000	-0.575937000	-0.755772000
6	-3.639137000	-1.631749000	0.023164000
6	-4.402888000	-1.978525000	1.170096000
6	-5.539730000	-1.289007000	1.510096000
1	-7.122062000	2.778696000	-1.521750000
1	-7.745560000	0.281747000	1.912852000
1	-6.107012000	-1.572543000	2.390492000
1	-4.077631000	-2.811344000	1.786327000
1	-3.482794000	-0.287698000	-1.627750000
8	-8.700070000	2.242860000	0.643758000
6	-9.163179000	3.344320000	-0.123926000
1	-9.413960000	3.048016000	-1.148641000
1	-8.429074000	4.157457000	-0.149569000
1	-10.064937000	3.693878000	0.376423000
6	-2.401894000	-2.448277000	-0.337684000
6	-1.209515000	-1.516586000	-0.606183000
8	-1.021989000	-0.997790000	-1.696211000
8	5.646592000	-0.096517000	0.366775000
6	6.973306000	-0.668852000	0.462967000
1	7.089044000	-1.408420000	-0.332341000
1	7.070262000	-1.194417000	1.416995000
6	7.850145000	1.514001000	1.480380000
6	7.814989000	2.871081000	0.747918000

6	8.015951000	0.446195000	0.363446000
6	7.336740000	2.493541000	-0.655221000
7	8.022028000	1.226205000	-0.883179000
1	8.655704000	1.458660000	2.214751000
1	7.164441000	3.597305000	1.239819000
1	6.237061000	2.399939000	-0.683319000
1	8.818459000	3.299240000	0.686271000
1	7.630556000	3.222864000	-1.416879000
1	8.983218000	-0.068393000	0.457214000
1	6.910263000	1.348195000	2.010912000
6	7.735140000	0.543114000	-2.125947000
1	6.688864000	0.204057000	-2.224211000
1	8.387402000	-0.328727000	-2.235407000
1	7.947609000	1.214361000	-2.962789000
1	-2.160242000	-3.079428000	0.524898000
6	-2.643688000	-3.360162000	-1.552436000
1	-3.519946000	-3.990063000	-1.384502000
1	-1.779603000	-4.005053000	-1.734854000
1	-2.808411000	-2.757580000	-2.446006000
7	-0.398471000	-1.296091000	0.468789000
1	-0.621101000	-1.752587000	1.338974000
6	0.756725000	-0.411413000	0.422736000
1	0.696060000	0.299367000	1.255186000
1	0.670294000	0.154867000	-0.505812000
6	2.086872000	-1.171637000	0.467204000
1	2.141600000	-1.783060000	1.373067000
1	2.129643000	-1.866503000	-0.375554000
6	3.287195000	-0.227151000	0.421311000
1	3.298727000	0.359536000	-0.502882000
1	3.244930000	0.506503000	1.235414000
6	4.613098000	-0.951354000	0.535607000
8	4.752028000	-2.127969000	0.756399000



```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-AA-S_Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527888 (Hartree/Particle)
Thermal correction to Energy=                    0.558126
Thermal correction to Enthalpy=                  0.559070
Thermal correction to Gibbs Free Energy=         0.460594
Sum of electronic and zero-point Energies=          -1344.073714
Sum of electronic and thermal Energies=             -1344.043477
Sum of electronic and thermal Enthalpies=           -1344.042532
Sum of electronic and thermal Free Energies=        -1344.141008

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=2 Diff= 2.87D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days  2 hours  3 minutes  9.4 seconds.
File lengths (MBytes):  RWF=   2945 Int=      0 D2E=      0 Chk=     44 Scr=      1
Normal termination of Gaussian 09 at Wed Mar  2 17:38:20 2016.
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```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-AA-S_Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527584 (Hartree/Particle)
Thermal correction to Energy=                    0.557797
Thermal correction to Enthalpy=                  0.558741
Thermal correction to Gibbs Free Energy=         0.460305
Sum of electronic and zero-point Energies=          -1344.092791
Sum of electronic and thermal Energies=             -1344.062578
Sum of electronic and thermal Enthalpies=           -1344.061633
Sum of electronic and thermal Free Energies=        -1344.160070

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 4.56D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 19 hours  6 minutes 36.7 seconds.
File lengths (MBytes):  RWF=   3206 Int=      0 D2E=      0 Chk=     58 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 17:24:10 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-AA-S_Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527916 (Hartree/Particle)
Thermal correction to Energy=                    0.558074
Thermal correction to Enthalpy=                  0.559018
Thermal correction to Gibbs Free Energy=         0.461350
Sum of electronic and zero-point Energies=          -1344.081699
Sum of electronic and thermal Energies=             -1344.051542
Sum of electronic and thermal Enthalpies=           -1344.050597
Sum of electronic and thermal Free Energies=        -1344.148265

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 3.59D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 20 hours 26 minutes 29.6 seconds.
File lengths (MBytes):  RWF=   3206 Int=      0 D2E=      0 Chk=     60 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 20:10:05 2016.
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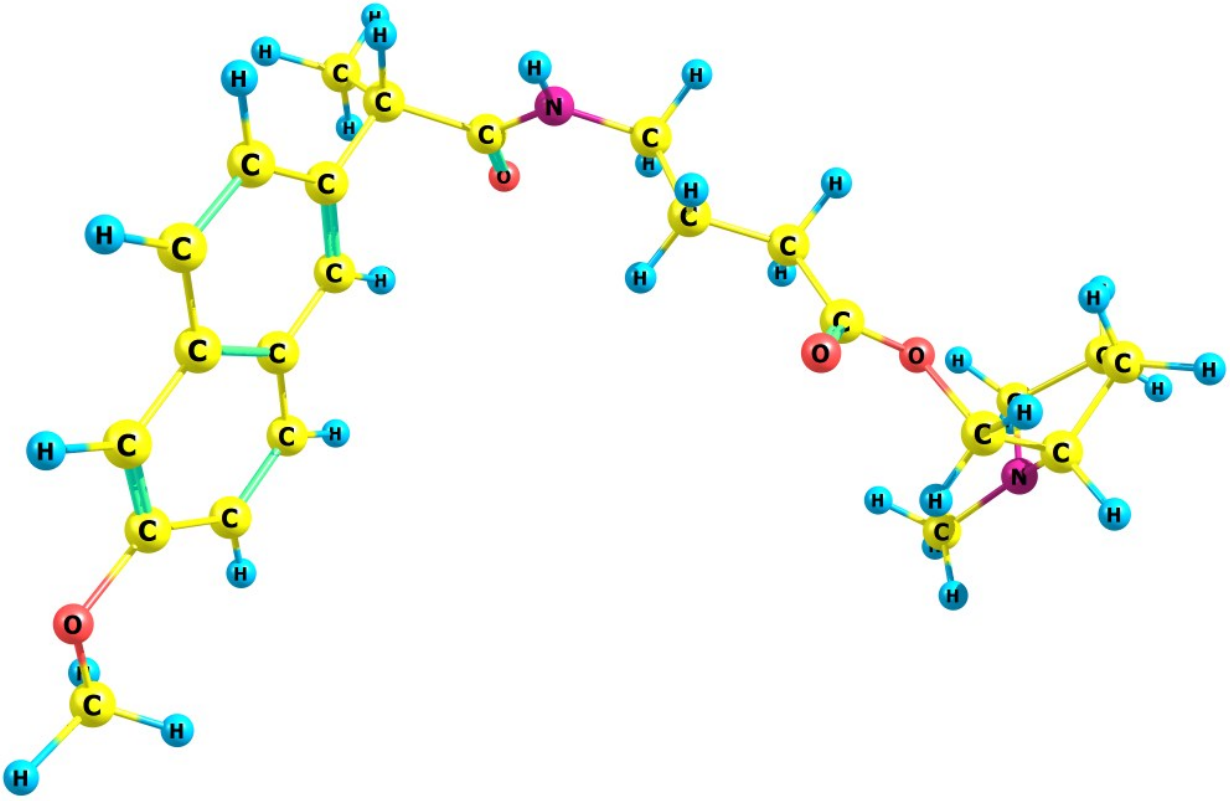
Structure 2b

1	3.723739000	1.241440000	-2.354554000
6	4.244254000	1.362923000	-1.410483000
6	4.891569000	2.545496000	-1.138258000
6	5.573769000	2.712807000	0.093977000
6	5.586319000	1.688412000	1.018934000
6	4.928440000	0.467121000	0.756726000
6	4.239139000	0.290992000	-0.485628000
6	3.580159000	-0.936063000	-0.751971000
6	3.586803000	-1.967820000	0.161523000
6	4.271038000	-1.782738000	1.393205000
6	4.920208000	-0.609297000	1.683556000
1	4.874508000	3.342068000	-1.869912000
1	6.112967000	1.838274000	1.954321000
1	5.436607000	-0.490519000	2.630353000
1	4.281829000	-2.592821000	2.116174000
1	3.052345000	-1.055696000	-1.692125000
8	6.240814000	3.852420000	0.441826000
6	6.267630000	4.939927000	-0.470966000
1	5.261232000	5.320904000	-0.677909000
1	6.753949000	4.665680000	-1.413856000
1	6.850260000	5.719919000	0.016760000
6	2.916799000	-3.306336000	-0.135276000
1	2.868912000	-3.866532000	0.805207000
6	1.483215000	-3.088005000	-0.642586000
8	1.238798000	-2.838817000	-1.813316000
8	-4.575403000	0.277078000	0.571013000
6	-5.215040000	1.414265000	1.198856000
1	-4.586574000	2.294019000	1.044938000
1	-5.281124000	1.241312000	2.276669000
6	3.715196000	-4.137344000	-1.154433000
1	3.270696000	-5.128012000	-1.284729000

1	4.747108000	-4.259627000	-0.818164000
1	3.717073000	-3.638922000	-2.124091000
6	-7.509001000	0.343900000	0.792361000
6	-8.041176000	0.003099000	-0.615474000
6	-6.612254000	1.599519000	0.603109000
6	-7.000148000	0.633787000	-1.541911000
7	-6.673927000	1.870873000	-0.840969000
1	-8.313832000	0.526806000	1.506541000
1	-8.155777000	-1.071588000	-0.772140000
1	-6.129188000	-0.032924000	-1.665444000
1	-9.011391000	0.476797000	-0.783840000
1	-7.395399000	0.858278000	-2.537774000
1	-7.032116000	2.463456000	1.138083000
1	-6.909032000	-0.482579000	1.178666000
6	-5.647007000	2.702777000	-1.430055000
1	-4.648144000	2.233230000	-1.462276000
1	-5.563004000	3.644140000	-0.878402000
1	-5.930558000	2.951796000	-2.456539000
7	0.512618000	-3.187845000	0.312637000
1	0.798984000	-3.321357000	1.269866000
6	-0.890147000	-2.904744000	0.045036000
1	-1.501024000	-3.729789000	0.429852000
1	-0.993389000	-2.892638000	-1.040957000
6	-1.356788000	-1.575722000	0.649524000
1	-1.216358000	-1.583340000	1.734517000
1	-0.730912000	-0.766496000	0.263509000
6	-2.825846000	-1.293382000	0.335857000
1	-2.989839000	-1.162421000	-0.737753000
1	-3.458197000	-2.140392000	0.630988000
6	-3.362440000	-0.072342000	1.054941000
8	-2.809623000	0.512936000	1.951596000



```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-AA-S_Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527932 (Hartree/Particle)
Thermal correction to Energy=                    0.558127
Thermal correction to Enthalpy=                  0.559071
Thermal correction to Gibbs Free Energy=         0.461026
Sum of electronic and zero-point Energies=          -1344.073532
Sum of electronic and thermal Energies=             -1344.043337
Sum of electronic and thermal Enthalpies=           -1344.042392
Sum of electronic and thermal Free Energies=        -1344.140437

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=2 Diff= 3.10D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 19 hours 24 minutes 15.1 seconds.
File lengths (MBytes):  RWF=   2896 Int=      0 D2E=      0 Chk=     44 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 12:37:12 2016.
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#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-AA-S_Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527646 (Hartree/Particle)
Thermal correction to Energy=                    0.557782
Thermal correction to Enthalpy=                  0.558726
Thermal correction to Gibbs Free Energy=         0.461041
Sum of electronic and zero-point Energies=          -1344.092630
Sum of electronic and thermal Energies=             -1344.062495
Sum of electronic and thermal Enthalpies=           -1344.061550
Sum of electronic and thermal Free Energies=        -1344.159235

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 3.55D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days  1 hours 20 minutes 54.2 seconds.
File lengths (MBytes):  RWF=   3204 Int=      0 D2E=      0 Chk=     57 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 17:57:14 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-AA-S_Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.527830 (Hartree/Particle)
Thermal correction to Energy=                    0.557997
Thermal correction to Enthalpy=                  0.558941
Thermal correction to Gibbs Free Energy=         0.461044
Sum of electronic and zero-point Energies=          -1344.081574
Sum of electronic and thermal Energies=             -1344.051407
Sum of electronic and thermal Enthalpies=           -1344.050463
Sum of electronic and thermal Free Energies=        -1344.148360

Charge =  0 Multiplicity = 1

Stoichiometry    C24H32N2O4
Framework group  C1[X(C24H32N2O4)]
Deg. of freedom   180
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 1.48D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 21 hours  8 minutes 45.5 seconds.
File lengths (MBytes):  RWF=   3203 Int=      0 D2E=      0 Chk=     60 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 20:55:53 2016.
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Structure 3a

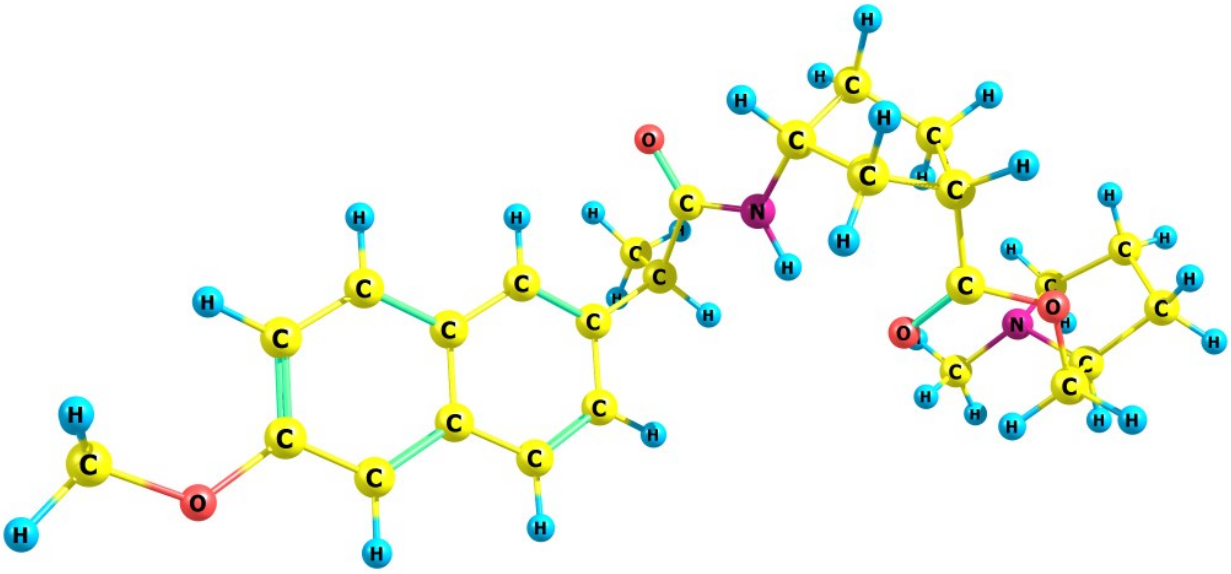
6	6.846683000	0.493840000	-0.320551000
6	6.950757000	-0.894139000	-0.592532000
6	5.876563000	-1.726015000	-0.350525000
6	4.665687000	-1.215051000	0.166204000
6	4.553693000	0.184936000	0.443459000
6	5.675248000	1.009113000	0.183632000
8	8.076267000	-1.485066000	-1.094974000
6	3.536567000	-2.038166000	0.421682000
6	2.374455000	-1.503938000	0.918881000
6	2.254857000	-0.116085000	1.200104000
6	3.338217000	0.701129000	0.960140000
6	9.208351000	-0.676234000	-1.376472000
6	0.953249000	0.427100000	1.781478000
6	0.475179000	1.643687000	0.971801000
7	-0.463725000	1.374086000	0.028666000
8	0.931364000	2.765915000	1.154144000
6	-0.950511000	2.398108000	-0.892994000
6	-2.157739000	3.171109000	-0.329557000
6	-3.353077000	2.218566000	-0.527398000
6	-3.000612000	1.363329000	-1.800737000
6	-1.536675000	1.745118000	-2.156141000
6	-3.153255000	-0.106860000	-1.478670000
8	-2.315887000	-0.777514000	-0.910673000
8	-4.342612000	-0.582096000	-1.886425000
6	-4.708569000	-1.924016000	-1.493273000
6	-5.722392000	-1.893467000	-0.351268000
7	-5.191683000	-1.258286000	0.859744000
6	-6.349108000	-0.783063000	1.615789000
6	-7.241555000	-0.172232000	0.535580000
6	-7.019656000	-1.103080000	-0.678799000
6	-4.271219000	-2.078306000	1.629756000

6	1.096773000	0.805667000	3.265571000
1	7.682411000	1.154958000	-0.506787000
1	5.977588000	-2.783271000	-0.567183000
1	5.601514000	2.071854000	0.389089000
1	3.603688000	-3.100910000	0.213008000
1	1.522473000	-2.151554000	1.101329000
1	3.258483000	1.765608000	1.152217000
1	8.984492000	0.085869000	-2.131544000
1	9.595064000	-0.190180000	-0.473566000
1	9.965634000	-1.353959000	-1.767855000
1	0.199319000	-0.362139000	1.694181000
1	-0.814471000	0.430935000	-0.089826000
1	-0.115430000	3.065488000	-1.109330000
1	-2.295765000	4.086700000	-0.914926000
1	-2.006000000	3.462406000	0.710309000
1	-3.466565000	1.565445000	0.340076000
1	-4.298870000	2.746867000	-0.655945000
1	-3.682412000	1.598165000	-2.617876000
1	-1.548169000	2.485780000	-2.959064000
1	-0.945577000	0.894559000	-2.498487000
1	-3.806882000	-2.472894000	-1.225064000
1	-5.157977000	-2.379646000	-2.377317000
1	-5.982808000	-2.951938000	-0.152426000
1	-6.871748000	-1.614993000	2.127114000
1	-6.039457000	-0.067286000	2.381867000
1	-6.898370000	0.838707000	0.305998000
1	-8.288118000	-0.112469000	0.839826000
1	-6.914510000	-0.534082000	-1.603075000
1	-7.854786000	-1.794231000	-0.810672000
1	-3.384603000	-2.309650000	1.037518000
1	-4.730228000	-3.025111000	1.970861000
1	-3.940561000	-1.523972000	2.511224000

1 0.130432000 1.094619000 3.689154000

1 1.776682000 1.651485000 3.372622000

1 1.488867000 -0.037977000 3.838134000



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#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-RS-CyAA-S_Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.565045 (Hartree/Particle)
Thermal correction to Energy=                    0.595601
Thermal correction to Enthalpy=                  0.596545
Thermal correction to Gibbs Free Energy=         0.498947
Sum of electronic and zero-point Energies=          -1421.481215
Sum of electronic and thermal Energies=             -1421.450659
Sum of electronic and thermal Enthalpies=           -1421.449715
Sum of electronic and thermal Free Energies=        -1421.547314

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 8.35D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days 23 hours 37 minutes 51.7 seconds.
File lengths (MBytes):  RWF=   3517 Int=      0 D2E=      0 Chk=     50 Scr=      1
Normal termination of Gaussian 09 at Wed Mar  2 18:48:11 2016.
```
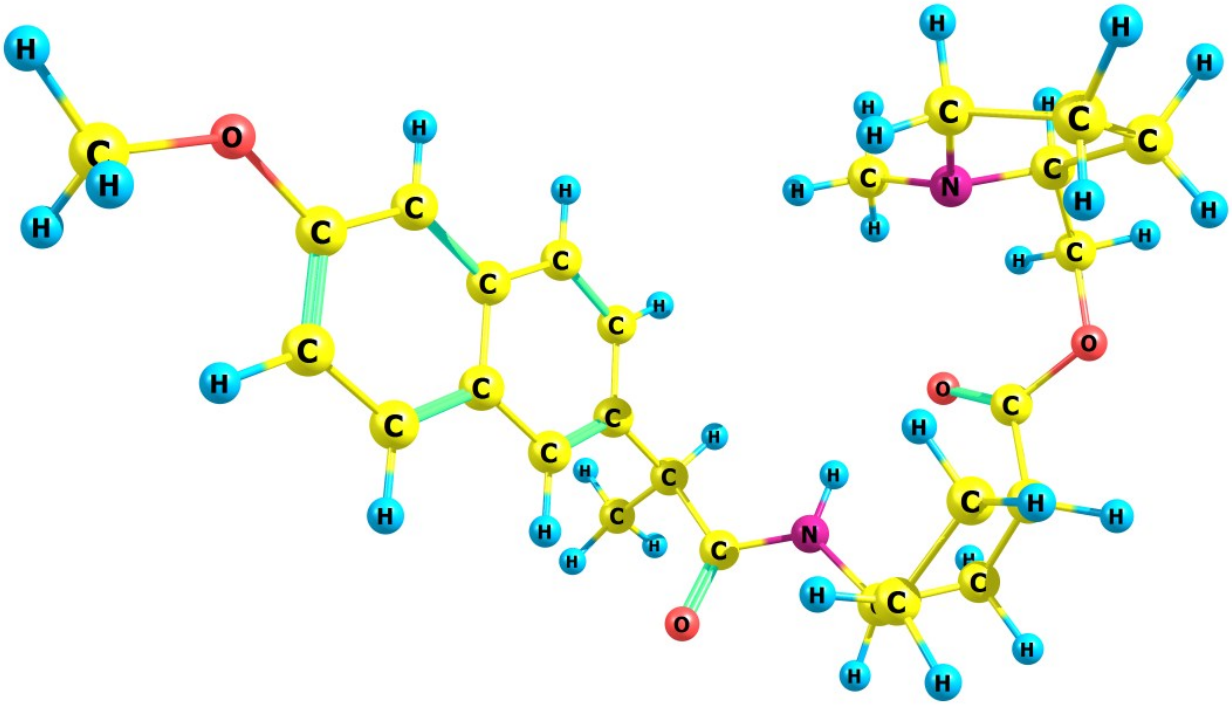

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-RS-cyAA-S_Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.564373 (Hartree/Particle)
Thermal correction to Energy=                    0.594961
Thermal correction to Enthalpy=                  0.595905
Thermal correction to Gibbs Free Energy=         0.498517
Sum of electronic and zero-point Energies=          -1421.497342
Sum of electronic and thermal Energies=             -1421.466755
Sum of electronic and thermal Enthalpies=           -1421.465811
Sum of electronic and thermal Free Energies=        -1421.563199

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 9.59D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days 17 hours 49 minutes 16.0 seconds.
File lengths (MBytes):  RWF=   3791 Int=      0 D2E=      0 Chk=     61 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 19:42:05 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-RS-cyAA-S_Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.564873 (Hartree/Particle)
Thermal correction to Energy=                    0.595391
Thermal correction to Enthalpy=                  0.596335
Thermal correction to Gibbs Free Energy=         0.499360
Sum of electronic and zero-point Energies=          -1421.487984
Sum of electronic and thermal Energies=             -1421.457466
Sum of electronic and thermal Enthalpies=           -1421.456522
Sum of electronic and thermal Free Energies=        -1421.553498

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 6.36D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days  0 hours 53 minutes 28.2 seconds.
File lengths (MBytes):  RWF=   3790 Int=      0 D2E=      0 Chk=     61 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 23:09:48 2016.
```

Structure 3b

6	5.388601000	-0.352729000	1.230683000
6	5.405054000	-1.445984000	0.327565000
6	4.490678000	-1.500438000	-0.704975000
6	3.532156000	-0.478041000	-0.878929000
6	3.510555000	0.628787000	0.028363000
6	4.462032000	0.651986000	1.076460000
8	6.290725000	-2.483382000	0.411144000
6	2.574037000	-0.498024000	-1.928037000
6	1.657982000	0.515388000	-2.064132000
6	1.631814000	1.620413000	-1.170316000
6	2.552319000	1.659902000	-0.145563000
6	7.254089000	-2.481458000	1.454183000
6	0.627667000	2.746140000	-1.398482000
6	-0.061918000	3.141095000	-0.083038000
7	-1.316560000	2.650128000	0.083986000
8	0.490861000	3.847720000	0.751749000
6	-2.094603000	2.914495000	1.293306000
6	-1.774608000	1.923081000	2.428084000
6	-2.535274000	0.638691000	2.045162000
6	-3.792746000	1.125428000	1.232687000
6	-3.587042000	2.651536000	1.033817000
6	-3.863504000	0.371840000	-0.076966000
8	-3.282189000	0.696690000	-1.091845000
8	-4.637018000	-0.722315000	0.027483000
6	-4.653759000	-1.654087000	-1.077653000
6	-3.781307000	-2.870595000	-0.774971000
7	-2.369010000	-2.526191000	-0.588134000
6	-1.784191000	-3.622842000	0.182697000
6	-2.841833000	-3.907728000	1.250608000
6	-4.178117000	-3.624993000	0.522590000
6	-1.645225000	-2.212305000	-1.809584000

1	-0.133443000	2.372686000	-2.091194000
1	6.100935000	-0.299888000	2.042865000
1	4.521446000	-2.345178000	-1.383561000
1	4.455157000	1.486248000	1.769968000
1	2.576512000	-1.329167000	-2.625809000
1	0.936151000	0.479510000	-2.874289000
1	2.540937000	2.490800000	0.551323000
1	7.921750000	-1.614897000	1.388806000
1	6.781722000	-2.502218000	2.442861000
1	7.837241000	-3.391143000	1.318902000
1	-1.729012000	2.048222000	-0.618801000
1	-1.891075000	3.943313000	1.592629000
1	-2.158837000	2.330384000	3.369664000
1	-0.701724000	1.769069000	2.546263000
1	-1.910744000	-0.001827000	1.419133000
1	-2.830995000	0.047148000	2.912663000
1	-4.707185000	0.915236000	1.787565000
1	-4.172532000	3.190604000	1.782175000
1	-3.906430000	2.997115000	0.049631000
1	-4.334258000	-1.138053000	-1.982098000
1	-5.695012000	-1.961798000	-1.187193000
1	-3.903208000	-3.550546000	-1.642166000
1	-1.621095000	-4.518427000	-0.448184000
1	-0.815651000	-3.327933000	0.594132000
1	-2.713489000	-3.221911000	2.090517000
1	-2.777470000	-4.926194000	1.638024000
1	-4.843774000	-3.020349000	1.139387000
1	-4.706345000	-4.547884000	0.274130000
1	-2.073057000	-1.328872000	-2.285521000
1	-1.655873000	-3.049913000	-2.532226000
1	-0.605774000	-1.981100000	-1.567243000
6	1.295712000	3.983361000	-2.026155000

1	0.550304000	4.743253000	-2.277740000
1	2.002317000	4.422416000	-1.321041000
1	1.831053000	3.706519000	-2.937217000



```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-RS-CyAA-S_Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.565039 (Hartree/Particle)
Thermal correction to Energy=                    0.595604
Thermal correction to Enthalpy=                  0.596548
Thermal correction to Gibbs Free Energy=         0.499432
Sum of electronic and zero-point Energies=          -1421.481871
Sum of electronic and thermal Energies=             -1421.451306
Sum of electronic and thermal Enthalpies=           -1421.450361
Sum of electronic and thermal Free Energies=        -1421.547478

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=1 Diff= 1.59D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       2 days  2 hours 50 minutes 31.1 seconds.
File lengths (MBytes):  RWF=   3517 Int=      0 D2E=      0 Chk=     50 Scr=      1
Normal termination of Gaussian 09 at Wed Mar  2 23:50:50 2016.
```

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-RS-cyAA-S_Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.564380 (Hartree/Particle)
Thermal correction to Energy=                    0.594983
Thermal correction to Enthalpy=                  0.595927
Thermal correction to Gibbs Free Energy=         0.498759
Sum of electronic and zero-point Energies=          -1421.497337
Sum of electronic and thermal Energies=             -1421.466734
Sum of electronic and thermal Enthalpies=           -1421.465790
Sum of electronic and thermal Free Energies=        -1421.562957

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=1 Diff= 1.19D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 19 hours 10 minutes 39.8 seconds.
File lengths (MBytes):  RWF=   3789 Int=      0 D2E=      0 Chk=     61 Scr=      1
Normal termination of Gaussian 09 at Fri Mar  4 00:00:36 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-RS-cyAA-S_Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.564696 (Hartree/Particle)
Thermal correction to Energy=                    0.595333
Thermal correction to Enthalpy=                  0.596277
Thermal correction to Gibbs Free Energy=         0.498437
Sum of electronic and zero-point Energies=          -1421.488334
Sum of electronic and thermal Energies=             -1421.457697
Sum of electronic and thermal Enthalpies=           -1421.456753
Sum of electronic and thermal Free Energies=        -1421.554593

Charge =  0 Multiplicity = 1

Stoichiometry    C26H34N2O4
Framework group  C1[X(C26H34N2O4)]
Deg. of freedom   192
Full point group                 C1      NOp   1
RotChk:  IX=1 Diff= 1.12D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 13 hours 49 minutes 46.1 seconds.
File lengths (MBytes):  RWF=   3786 Int=      0 D2E=      0 Chk=     61 Scr=      1
Normal termination of Gaussian 09 at Fri Mar  4 01:57:52 2016.
```

Structure 4a (geometrical parameters see higher)

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-S-Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415612 (Hartree/Particle)
Thermal correction to Energy=                    0.438561
Thermal correction to Enthalpy=                  0.439505
Thermal correction to Gibbs Free Energy=         0.360440
Sum of electronic and zero-point Energies=          -1057.466313
Sum of electronic and thermal Energies=             -1057.443365
Sum of electronic and thermal Enthalpies=           -1057.442420
Sum of electronic and thermal Free Energies=        -1057.521486

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 2.45D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days  1 hours  1 minutes 32.8 seconds.
File lengths (MBytes):  RWF=   1554 Int=      0 D2E=      0 Chk=     29 Scr=      1
Normal termination of Gaussian 09 at Wed Mar  2 16:58:49 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-S-Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415062 (Hartree/Particle)
Thermal correction to Energy=                    0.438065
Thermal correction to Enthalpy=                  0.439010
Thermal correction to Gibbs Free Energy=         0.359734
Sum of electronic and zero-point Energies=          -1057.477478
Sum of electronic and thermal Energies=             -1057.454474
Sum of electronic and thermal Enthalpies=           -1057.453530
Sum of electronic and thermal Free Energies=        -1057.532806

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 6.27D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 23 hours 51 minutes 24.7 seconds.
File lengths (MBytes):  RWF=   1749 Int=      0 D2E=      0 Chk=     39 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 18:32:23 2016.
```

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

R-NPX-S-Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415466 (Hartree/Particle)
Thermal correction to Energy=                    0.438407
Thermal correction to Enthalpy=                  0.439351
Thermal correction to Gibbs Free Energy=         0.360282
Sum of electronic and zero-point Energies=          -1057.470987
Sum of electronic and thermal Energies=             -1057.448046
Sum of electronic and thermal Enthalpies=           -1057.447102
Sum of electronic and thermal Free Energies=        -1057.526171

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 1.29D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 15 hours 14 minutes  7.4 seconds.
File lengths (MBytes):  RWF=   1747 Int=      0 D2E=      0 Chk=     40 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 21:45:07 2016.
```

Structure 4b (geometrical parameters see higher)

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-S-Pyr

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415546 (Hartree/Particle)
Thermal correction to Energy=                    0.438518
Thermal correction to Enthalpy=                  0.439463
Thermal correction to Gibbs Free Energy=         0.360294
Sum of electronic and zero-point Energies=          -1057.466403
Sum of electronic and thermal Energies=             -1057.443430
Sum of electronic and thermal Enthalpies=           -1057.442486
Sum of electronic and thermal Free Energies=        -1057.521655

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 1.32D-15
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       1 days  0 hours 49 minutes  6.3 seconds.
File lengths (MBytes):  RWF=   1554 Int=      0 D2E=      0 Chk=     29 Scr=      1
Normal termination of Gaussian 09 at Wed Mar  2 16:53:51 2016.
```

```
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-S-Pyr Acetonitrile

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415250 (Hartree/Particle)
Thermal correction to Energy=                    0.438195
Thermal correction to Enthalpy=                  0.439139
Thermal correction to Gibbs Free Energy=         0.360187
Sum of electronic and zero-point Energies=          -1057.477280
Sum of electronic and thermal Energies=             -1057.454335
Sum of electronic and thermal Enthalpies=           -1057.453391
Sum of electronic and thermal Free Energies=        -1057.532343

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 5.81D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days 10 hours 48 minutes 44.6 seconds.
File lengths (MBytes):  RWF=   1747 Int=      0 D2E=      0 Chk=     38 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 22:42:14 2016.


#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311G(d,p) Freq

S-NPX-S-Pyr Benzene

- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

Zero-point correction=                           0.415444 (Hartree/Particle)
Thermal correction to Energy=                    0.438400
Thermal correction to Enthalpy=                  0.439345
Thermal correction to Gibbs Free Energy=         0.360296
Sum of electronic and zero-point Energies=          -1057.471048
Sum of electronic and thermal Energies=             -1057.448092
Sum of electronic and thermal Enthalpies=           -1057.447147
Sum of electronic and thermal Free Energies=        -1057.526196

Charge =  0 Multiplicity = 1

Stoichiometry    C20H25NO3
Framework group  C1[X(C20H25NO3)]
Deg. of freedom   141
Full point group                 C1      NOp   1
RotChk:  IX=0 Diff= 7.57D-16
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
Job cpu time:       0 days  7 hours  0 minutes 29.2 seconds.
File lengths (MBytes):  RWF=   1746 Int=      0 D2E=      0 Chk=     38 Scr=      1
Normal termination of Gaussian 09 at Thu Mar  3 23:50:32 2016.
```

References

[1] Pischel, U.; Abad, S.; Miranda, M. A. *Chem. Commun*. **2003**, 1088-1089.

[2] Abad, S.; Pischel, U.; Miranda, M. A. *Photochem. Photobiol. Sci.* **2005**, *4*, 69-74.

[3] Cunningham, G. P.; Vidulich, J. A.; Kay, R. L. *J. Chem. Eng. Data.* **1967**, *12*, 336-337.

[4] Marriot, A. A.; Smith, E. R. *Table of Dielectric Constants of Pure Liquids*, NBS: Washington, DC, **1951**.

[5] Ahadov, Y. J. *Dielectricheskie Svoystva Binarnyh Rastvorov*, Nauka: Russia, **1977**.

[6] Jiménez, M. C.; Pischel, U.; Miranda, M. A. *J. Photochem. Photobiol. C.* **2007**, *8*. 128-142.

[7] Goez M. *Chem. Phys. Lett.* **1992**, *188*, 451-456

[8] Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions,* Akadémiai Kiadó, Budapest, Hungary, **1984.**

[9] Purtov, P. A.; Doktorov, A. B. *Chem. Phys.* **1993**, *178*, 47-65.

[10] Doktorov, A. B.; Purtov, P. A. *Khim. Fiz.* **1985**, *4*, 1587-1594.