Supporting Information for

Regulation of Saccharide Binding with Basic Poly(ethynylpyridine)s by H^+-Induced Helix Formation

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Experimental Section

General. NMR spectra were recorded on a Varian Gemini 300 spectrometer using tetramethylsilane (TMS) as an internal reference. UV-vis, fluorecence, CD, and IR spectra were measured on JASCO V-560, FP-6500, J-720WI, and FTIR-460plus spectrometers, respectively. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer. THF was freshly distilled from sodium benzophenone ketyl before use, and other solvents were purified with standard methods.

2,6-Dibromo-4-(*N*-methyl-*N*-octylamino)pyridine (5). A NaH (0.97 g, 24 mmol; commercial 60% dispersion was washed thoroughly with hexane before use) suspension in DMF (15 mL) was cooled with an ice bath, and then to the suspension was added slowly *N*-methyloctylamine (3.2 g, 22 mmol). After that, to the mixture was added 2,6-dibromo-4-nitropyridine[1] (6.2 g, 22 mmol) in one portion at 0 °C. The reaction mixture was then stirred for 2 h, being allowed to reach the room temperature. The resulting mixture was cautiously quenched by the addition of water and extracted with AcOEt. The AcOEt extract was washed with brine, dried over Na_2SO_4, and evaporated. The evaporated residue was purified by silica gel column chromatography (AcOEt/hexane, 1:1) to afford **5** (4.3 g, 52%) as orange oil. IR (neat) 2922, 2850, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87−0.93 (m, 3 H), 1.25−1.35 (m, 12 H), 2.94 (s, 3 H), 3.27 (t, J = 7.5 Hz, 2 H), 6.58 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 22.7, 26.7, 26.9, 29.3, 29.4, 31.8, 38.1, 52.1, 108.7, 140.8, 155.8; ESI-HRMS m/z calcd for $C_{14}H_{23}Br_2N_2$ ($M + H^+$): 377.0228; found: 377.0239.

4-(*N*-Methyl-*N*-octylamino)-2,6-bis(trimethylsilylethynyl)pyridine (6). To an *i*-Pr_2NH (40 mL) suspension of $PdCl_2(PPh_3)_2$ (480 mg, 0.69 mmol) and CuI (130 mg, 0.69 mmol) were added **5** (5.2 g, 14 mmol) and (trimethylsilyl)acetylene (4.2 g, 29 mmol) subsequently. The mixture was stirred for 3.5 h at room temperature and concentrated, and the resulting residue was extracted with AcOEt. The AcOEt extract was filtered to remove the insoluble material and washed with 5% aqueous ethylenediamine and brine subsequently. The AcOEt layer was dried over Na_2SO_4 and evaporated. The resulting crude oil including **6** was brought to the next deprotection step without further purification.

2,6-Diethynyl-4-(*N*-methyl-*N*-octylamino)pyridine (7). To a THF (40 mL) solution of **6** (14 mmol) prepared above were added *n*-Bu_4NF (1.0 M THF solution, 25 mL, 25 mmol) and a few drops of H_2O subsequently. The mixture was stirred for 0.5 h at room temperature, concentrated, and diluted with CH_2Cl_2/H_2O. The separated CH_2Cl_2 layer was washed with brine, dried over Na_2SO_4, and evaporated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/hexane, 1:1) to afford **7** (3.0 g, 81% yield from **5**) as orange oil. IR (KBr) 3292, 2925, 2854, 2097, 1593 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86−0.92 (m, 3 H), 1.23−1.35 (m, 12 H), 2.96 (s, 3 H), 3.01 (s, 2 H), 3.30 (t, J = 7.5 Hz, 2 H), 6.66 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 22.7, 26.8, 27.0, 29.3, 29.4, 31.8, 37.8, 51.7, 75.5, 83.3, 109.9, 142.3, 153.3; ESI-HRMS m/z calcd for $C_{18}H_{25}N_2$ ($M + H^+$): 269.2018; found: 269.2006.

2,6-Diiodo-4-(*N*-methyl-*N*-octylamino)pyridine (8). This compound was prepared by the Cu-mediated halogen-exchange procedure reported by us.[2] A mixture of **5** (4.6 g, 12 mmol), CuI (53 g, 280 mmol), and KI (110 g, 660 mg) in DMF (450 mL) was stirred for 14 h at 140 °C. The resulting brown mixture was diluted with AcOEt/aqueous $Na_2S_2O_3$ and filtered to remove insoluble material. The AcOEt layer was washed with 5% aqueous ethylenediamine and brine subsequently, dried over Na_2SO_4, and evaporated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2) to afford **8** (5.0 g, 87%) as orange oil. IR (KBr) 2925, 2853, 1570 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86−0.94 (m, 3 H), 1.22−1.35 (m, 12 H), 2.94 (s, 3 H), 3.23 (t, J = 7.5 Hz, 2 H), 6.84 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 22.7, 26.7, 26.9, 29.3, 29.4, 31.8, 37.9, 51.8, 116.0, 116.3, 154.1; ESI-HRMS *m*/*z* calcd for $C_{14}H_{23}I_2N_2$ ($M + H^+$): 472.9951; found: 472.9964.

2,6-Bis{[6-iodo-4-(*N*-methyl-*N*-octylamino)-2-pyridyl]ethynyl}-4-(*N*-methyl-*N*-octylamino)pyridine (9). To an *i*-Pr_2NH (30 mL)/THF (50 mL) suspension of $Pd(PPh_3)_4$ (310 mg, 260 μmol) and CuI (50 mg, 260 μmol) were added **7** (1.4 g, 5.3 mmol) and an excess of **8** (16 g, 34 mmol). The mixture was stirred for 12 h at room temperature, concentrated, and the resulting residue was diluted with AcOEt. The AcOEt suspension was filtered to remove insoluble material and diluted with further AcOEt. The AcOEt layer was washed with 5% aqueous ethylenediamine and brine subsequently, dried over Na_2SO_4, and evaporated. The evaporated residue was purified by silica gel column chromatography (CH_2Cl_2/hexane, 1:1) to afford **9** (4.0 g, 79% yield based on **7**) as yellow oil. IR (KBr) 2924, 2853, 1582 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz) δ 0.86−0.93 (m, 9 H), 1.22−1.37 (m, 36 H), 2.93 (s, 6 H), 2.97 (s, 3 H), 3.23−3.35 (m, 6 H), 6.82−6.86 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 14.2, 22.7, 26.8, 26.9, 27.0, 27.1, 29.3, 29.4, 29.5, 31.8, 37.9, 51.9, 86.3, 88.1, 110.5, 110.9, 116.0, 118.4, 142.4, 142.6, 153.2, 153.5; ESI-HRMS *m*/*z* calcd for $C_{46}H_{67}I_2N_6$ ($M + H^+$): 957.3517; found: 957.3480.

2-{[6-Iodo-4-(*N*-methyl-*N*-octylamino)-2-pyridyl]ethynyl}-4-(*N*-methyl-*N*-octylamino)-6-{[4-(*N*-methyl-*N*-octylamino)-6-(trimethylsilylethynyl)-2-pyridyl]ethynyl}pyridine (10). To an *i*-Pr_2NH (20 mL)/THF (20 mL) suspension of $Pd_2(dba)_2{\cdot}CHCl_3$ (150 mg, 0.12 mmol), CuI (23 mg, 0.12 mmol), and trimesitylphosphine (140 mg 0.35 mmol) were added **9** (2.4 g, 2.5 mmol) and (trimethylsilyl)acetylene (79 mg, 0.80 mmol) subsequently. The mixture was stirred for 13 h at room temperature and concentrated, and to the residue was added AcOEt. The AcOEt suspension was filtered to remove insoluble material, washed with aqueous 5% ethylenediamine and brine subsequently, dried over Na_2SO_4, and evaporated. The resulting crude oil including **10** was brought to the next deprotection step without further purification.

2-{[6-Ethynyl-4-(*N*-methyl-*N*-octylamino)-2-pyridyl]ethynyl}-6-{[6-iodo-4-(*N*-methyl-*N*-octylamino)-2-pyridyl]ethynyl}-4-(*N*-methyl-*N*-octylamino)pyridine (11). To a THF (30 mL) solution of **10** prepared as above were added *n*-Bu_4NF (1.0 M THF solution, 0.80 mL, 0.80 mmol) and a few drops of H_2O subsequently. The reaction mixture was stirred for 1 h at room temperature, concentrated, and diluted with CH_2Cl_2/H_2O. The separated CH_2Cl_2 layer was washed with brine, dried over Na_2SO_4, and evaporated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/AcOEt/hexane, 1:1:3) to afford **11** (450 mg, 66% based on (trimethylsilyl)acetylene used in the

previous step) as orange oil. IR (KBr) 3305, 2925, 2853, 2102 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.84−0.93 (m, 9 H), 1.22−1.37 (m, 36 H), 2.93 (s, 3 H), 2.96 (s, 6 H), 3.02 (s, 1 H), 3.24−3.35 (m, 6 H), 6.63−6.66 (m, 1 H), 6.81−6.88 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 22.7, 26.7, 26.9, 29.3, 29.5, 31.8, 37.8, 37.9, 51.8, 75.4, 83.3, 86.1, 87.0, 87.1, 88.1, 109.6, 110.4, 110.8, 115.9, 118.4, 142.2, 142.3, 142.5, 142.69, 142.74, 153.2, 153.4; ESI-HRMS *m*/*z* calcd for $C_{18}H_{25}N_2$ ($M + H^+$): 855.4550; found: 855.4590.

Basic Ethynylpyridine Polymer 2. To an *i*-Pr_2NH (80 mL)/DMF (80 mL) suspension of $PdCl_2(PPh_3)_2$ (6.6 mg, 9.4 μmol) and CuI (1.8 mg, 9.4 μmol) was added **11** (800 mg, 940 μmol). The mixture was stirred for 15 h at room temperature. To the reaction mixture was added 3-aminopropyl-functionalized silica gel (1.0 mmol/g, 500 mg) to scavenge the copper salt, and the reslting suspension was filtered. The filtrate was stirred for an additional 1 h at room temperature and concentrated. The concentrated residue was diluted with AcOEt/hexane (1:1, 300 mL), and the solution was centrifuged (2300 rpm; 4 °C; 5 min). The supernatant liquid phase was decanted off. This centrifugal washing manipulation was repeated four times. The obtained precipitate was dried under reduced pressure to yield **2** (380 mg, 48% w/w yield) as brown powder. IR (KBr) 2924, 2852, 1587 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.82−0.94 (m, 3n H), 1.20−1.38 (m, 12n H), 2.90−3.04 (m, 3n H), 3.22−3.38 (m, 2n H), 7.82−7.92 (m, 2n H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 22.7, 26.8, 26.9, 27.1, 29.4, 29.4, 29.5, 31.9, 37.9, 52.0, 87.2, 110.4, 142.8, 153.2.

Vapor Pressure Osmometry (VPO) Analyses for 2. VPO analyses for **2** were performed on a Gonote OSMOMAT 070 osmometer and benzil was used as a standard. A $CHCl_3$ solutions of six different concentrations of **2** (2.0×10^{-3}, 4.0×10^{-3}, 6.0×10^{-3}, 8.0×10^{-3}, 1.0×10^{-2}, 1.2×10^{-2} mmol/kg, unit concentration) were measured at 40 °C. M_n value of 1.1×10^4 g/mol was given by these analyses.

Evaluation of Binding Strengths of 2 with Glycosides Using Curve-Fitting Method on CD analyses. Polymer **2** (1.0 mM, unit concentration) and TFA (0 or 0.5 mM) were dissolved in CH_2Cl_2 (commercial anhydrous reagent was treated with dry K_2CO_3 before use). This solution was titrated with a solution or solid of guest glycoside, and the observed ellipticity on CD was plotted versus the concentration of the glycoside. The formal binding constants were obtained by iterative curve-fitting measurements based on the following assumptions and equation.[3]

Assumption 1:

The concentration [**2**] was assumed as 2.2×10^{-5} M based on the M_n value (1.1×10^4 g mol^{-1}) measured by VPO.

Assumption 2:

Glycosides and **2** form complexes predominantly in 1:1 manner as the case of oligomeric **1** (n = 24).[4]

Equation:

$$\theta_{obs} = \frac{\theta_{11}}{2K_{11}[\mathbf{2}]_0}\left[1 + K_{11}[\mathbf{2}]_0 + K_{11}[\mathrm{G}]_0 - \left\{(1 + K_{11}[\mathbf{2}]_0 + K_{11}[\mathrm{G}]_0)^2 - 4K_{11}{}^2[\mathbf{2}]_0[\mathrm{G}]_0\right\}^{1/2}\right]$$

K_{11}: the 1:1 binding constant of **2** with glycosides

θ_{obs}: the observed ellipticity

θ_{11}: ellipticity of the 1:1 host-guest complex (at the saturation point)

$[\mathbf{2}]_0$: the total concentration of **2**

$[\mathrm{G}]_0$: the total concentration of guest glycoside

Computational Method. Quantum chemical calculations were carried out with a Gaussian 03 program. The geometry optimization and the evaluation of zero point energy (ZPE) were performed by the use of DFT(B3LYP) method and 6−31G(d) basis sets, and the total energy was calculated by the use of DFT(B3LYP) method and 6−311+G(2d,p) basis sets.

References

(1) Neumann, U.; Vögtle, F. *Chem. Ber.* **1989**, *122*, 589−591.

(2) Suzuki, H.; Kondo, A.; Inouye, M.; Ogawa, T. *Synthesis* **1986**, 121−122.

(3) Connors, K. A. *Binding Constants*, John Wiley & Sons, New York, 1987.

(4) Inouye, M.; Waki, M.; Abe, H. *J. Am. Chem. Soc.* **2004**, *126*, 2022−2027.

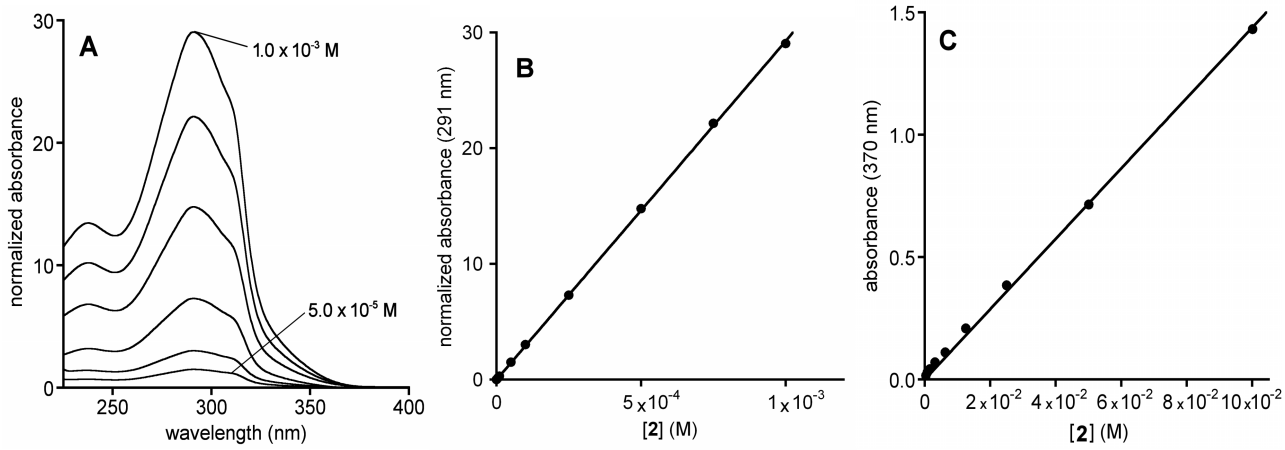


Figure S1. (A) UV-vis spectra of **2** at the concentrations varying from 1.0×10^{-3} to 5.0×10^{-5} M in CH_2Cl_2 at 26 °C. Light path length was 1 or 10 mm, and the measured absorbance was normalized to that for 10 mm. (B) Beer's plot of the normalized absorbance at 291 nm versus the concentration of **2** for analyses shown in (A). (C) Beer's plot of the absorbance at 363 nm versus the concentration of **2** (1.0×10^{-1} to 3.9×10^{-4} M) in $CHCl_3$ at 40 °C (VPO conditions). Light path length = 1 mm.

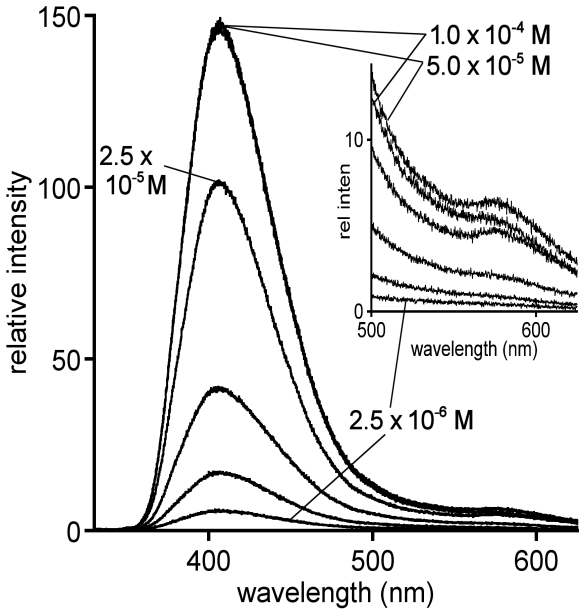


Figure S2. Fluorescence spectra of **2** at the concentration varying from 1.0×10^{-4} to 2.5×10^{-6} M (unit concentration) in CH_2Cl_2 at 26 °C. λ_{ex} = 315 nm, light path length = 10 mm.

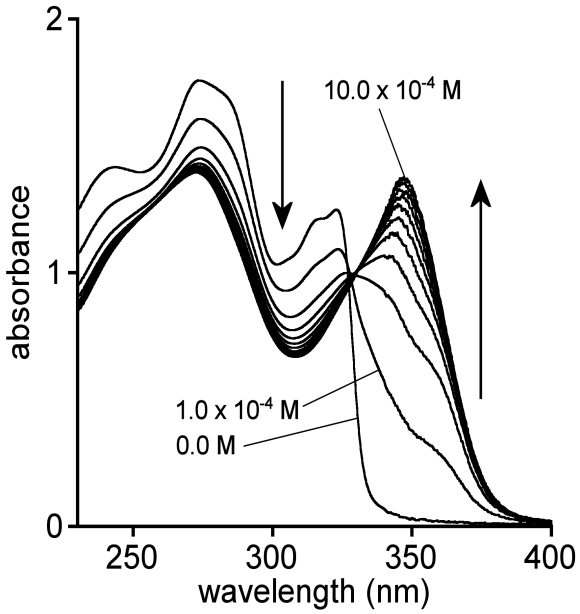


Figure S3. The change of the absorption spectrum of **1** on titration with TFA. Conditions: **1** (1.0×10^{-4} M, unit concentration), TFA (0.0 to 10.0×10^{-4} M), CH_2Cl_2, 26 °C. Light path length = 10 mm.

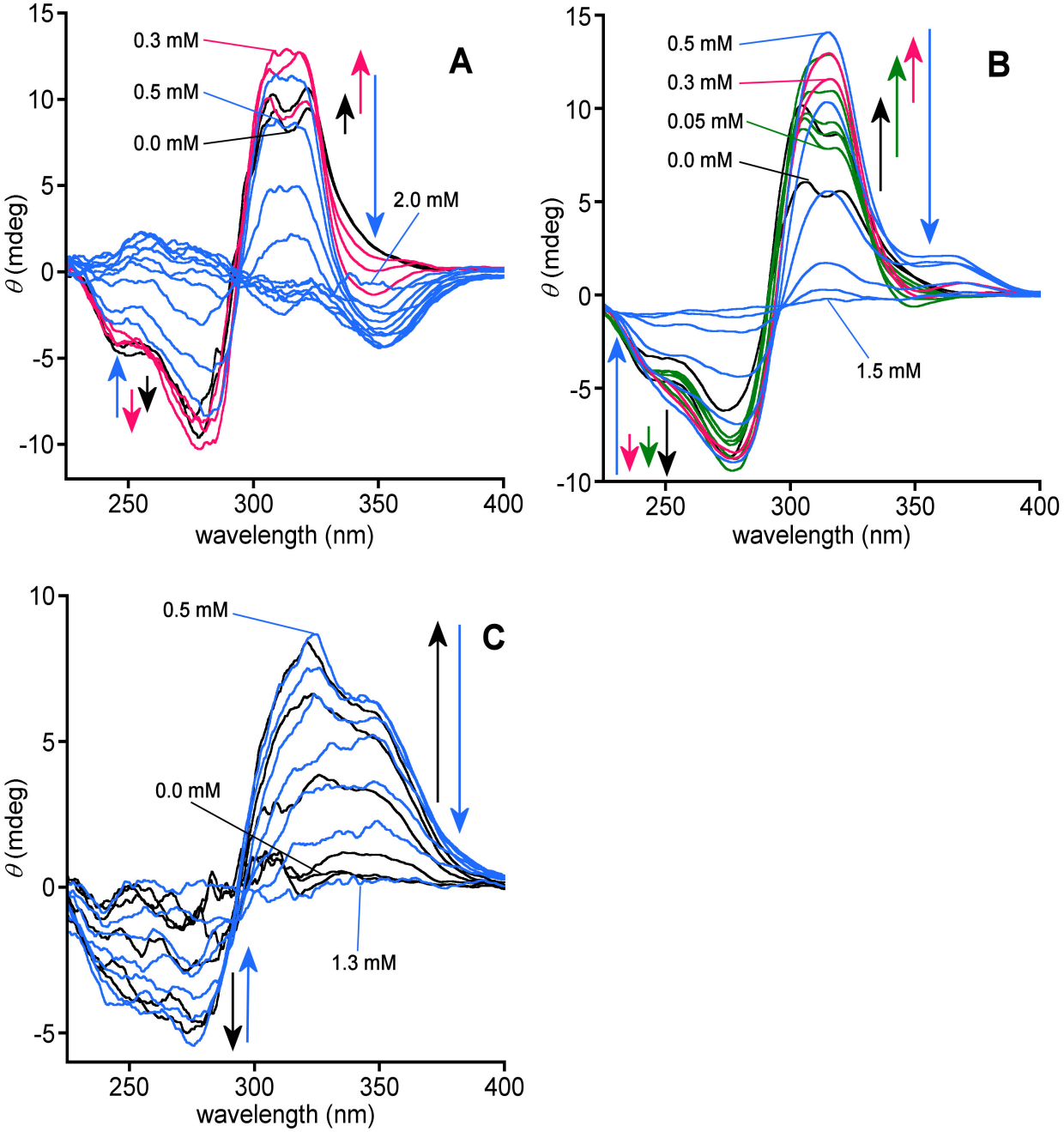


Figure S4. The change of CD spectrum of the complex between **2** and (A) **β-D-Fru**, (B) **β-D-Man**, or (C) **β-D-Gal**, on titration with TFA. Conditions: **2** (1.0 mM, unit concentration), hexose (2.5 mM), TFA ((A) 0 to 0.05 mM/black, 0.1 to 0.3 mM/red, 0.4 to 2.0 mM/blue. (B) 0 to 0.025 mM/black, 0.05 to 0.25 mM/green, 0.3 to 0.4 mM/red, 0.5 to 1.5 mM/blue. (C) 0 to 0.4 mM/black, 0.5 to 1.3 mM/blue), CH_2Cl_2, 26 °C. Light path length = 1 mm.

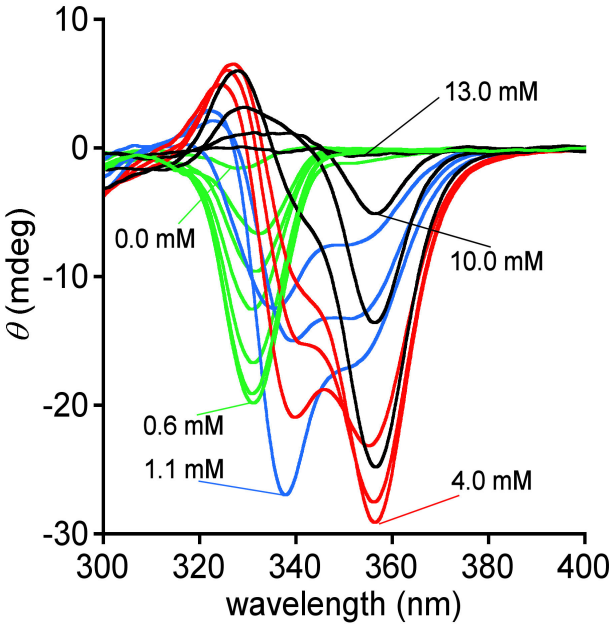


Figure S5. The change of CD spectrum of the complex between **1** and **β-D-Glc** on titration with TFA. Conditions: **1** (1.0 mM, unit concentration), **β-D-Glc** (2.5 mM), TFA (0.0−0.6 mM/green, 0.8−1.1 mM/blue, 2.0−4.0 mM/red, 6.0−13.0 mM/black), CH_2Cl_2, 26 °C. Light path length = 1 mm.

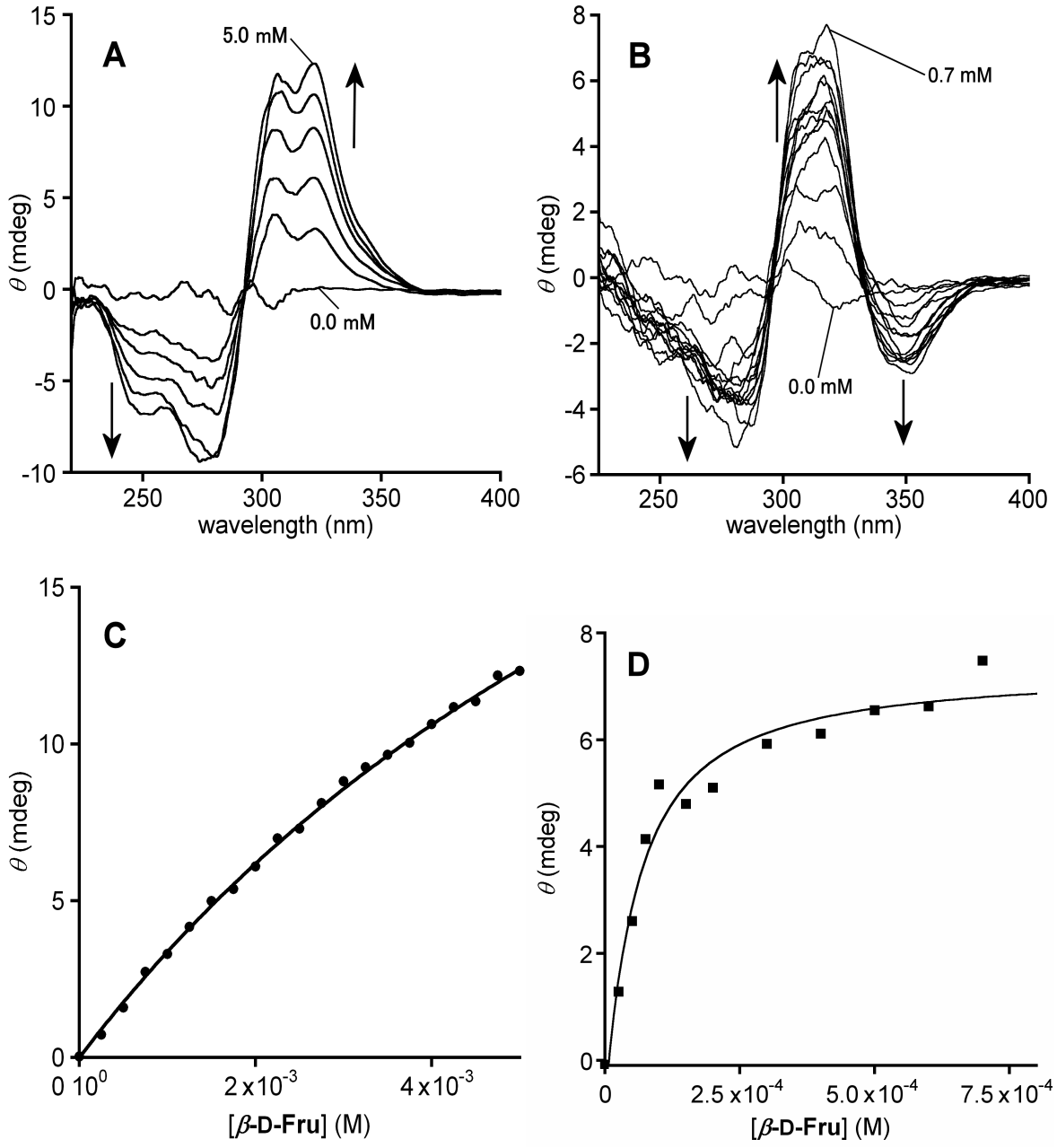


Figure S6. The change of the CD spectrum on the titration of **2** (1.0×10^{-3} M, unit concentration) with ***β*-D-Fru** in CH_2Cl_2 at 26 °C in the (A) absence or (B) presence of TFA (5.0×10^{-4} M). Light path length = 1 mm. The titration curves in the absence (C, 322 nm was observed) or presence (D, 316 nm was observed) of TFA. The lines are theoretical curves obtained by the iterative curve-fitting analyses assuming 1:1 complexation between **2** and ***β*-D-Fru** and the molecular weight of **2** as 1.1×10^4 g mol^{-1}.

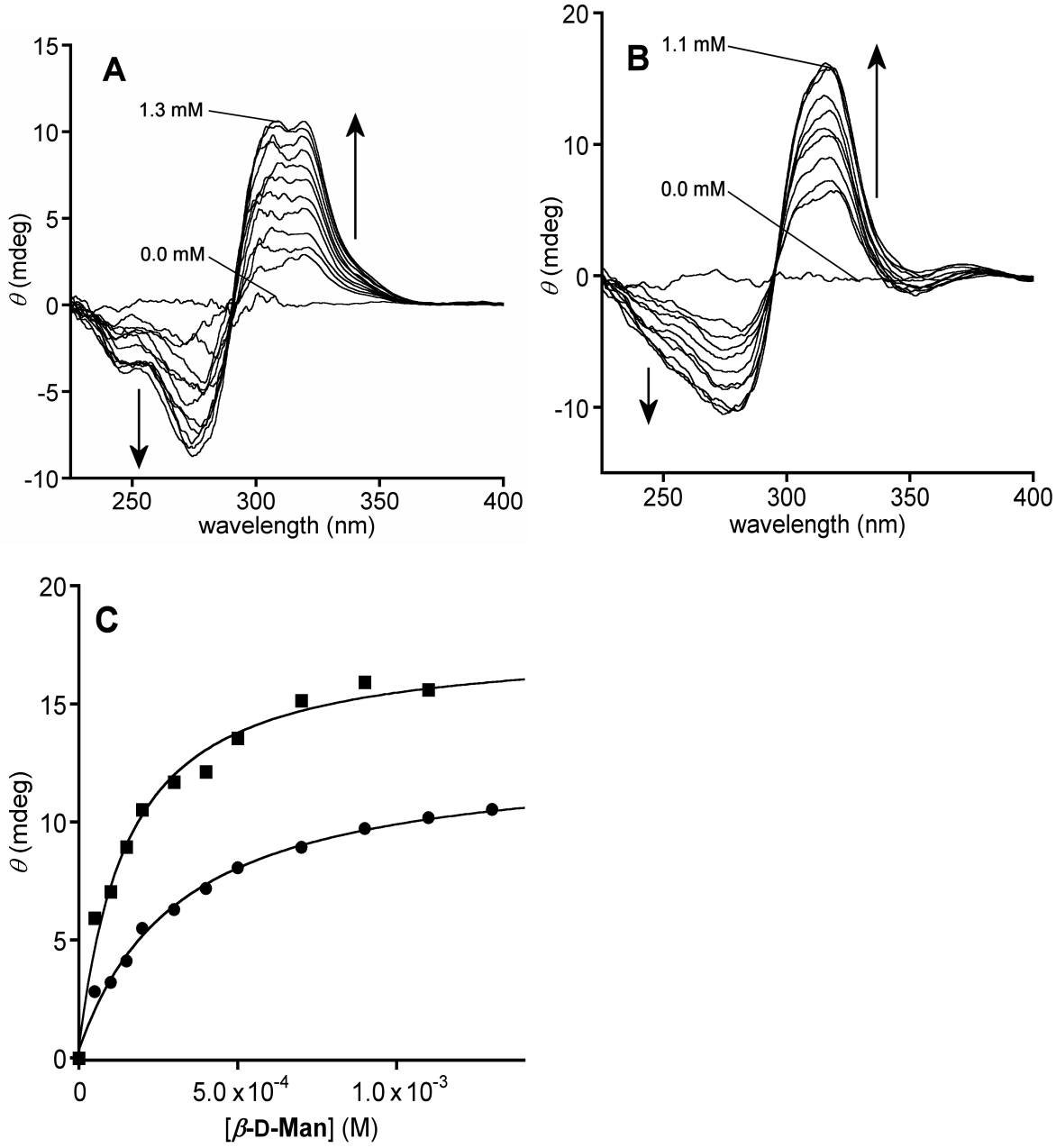


Figure S7. The change of the CD spectrum on the titration of **2** (1.0 mM, unit concentration) with ***β*-D-Man** in CH_2Cl_2 at 26 °C in the (A) absence or (B) presence of TFA (0.5 mM). Light path length = 1 mm. (C) The titration curves in the absence (circles, 318 nm was observed) or presence (squares, 314 nm was observed) of TFA. The lines are theoretical curves obtained by the iterative curve-fitting analyses assuming 1:1 complexation between **2** and ***β*-D-Man** and the molecular weight of **2** as 1.1×10^4 g mol^{-1}.

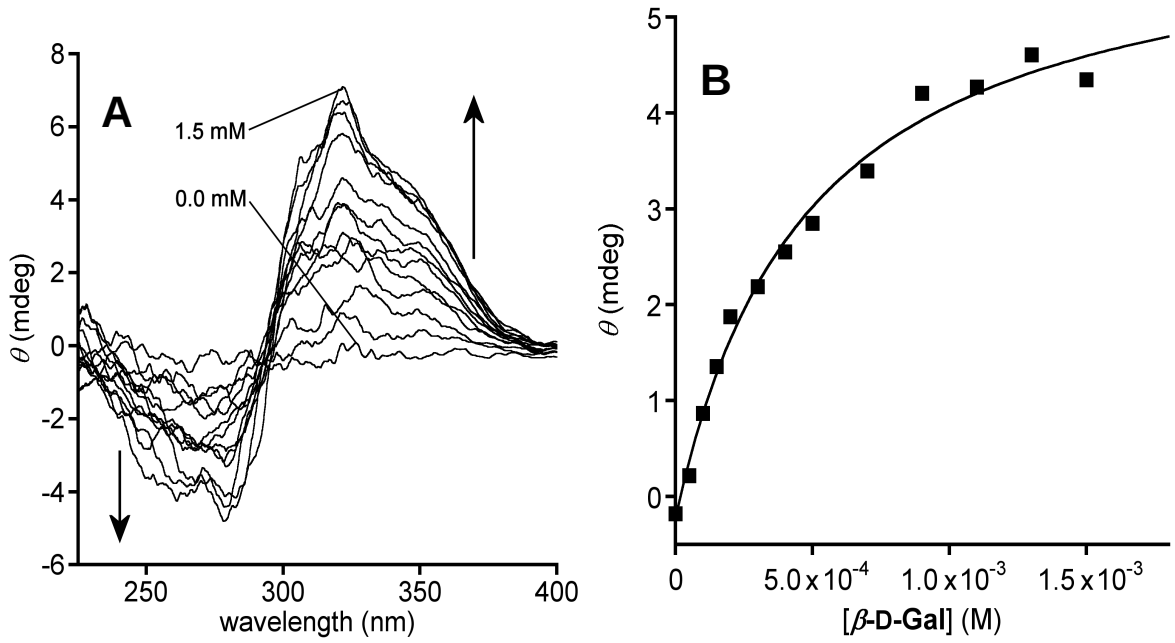
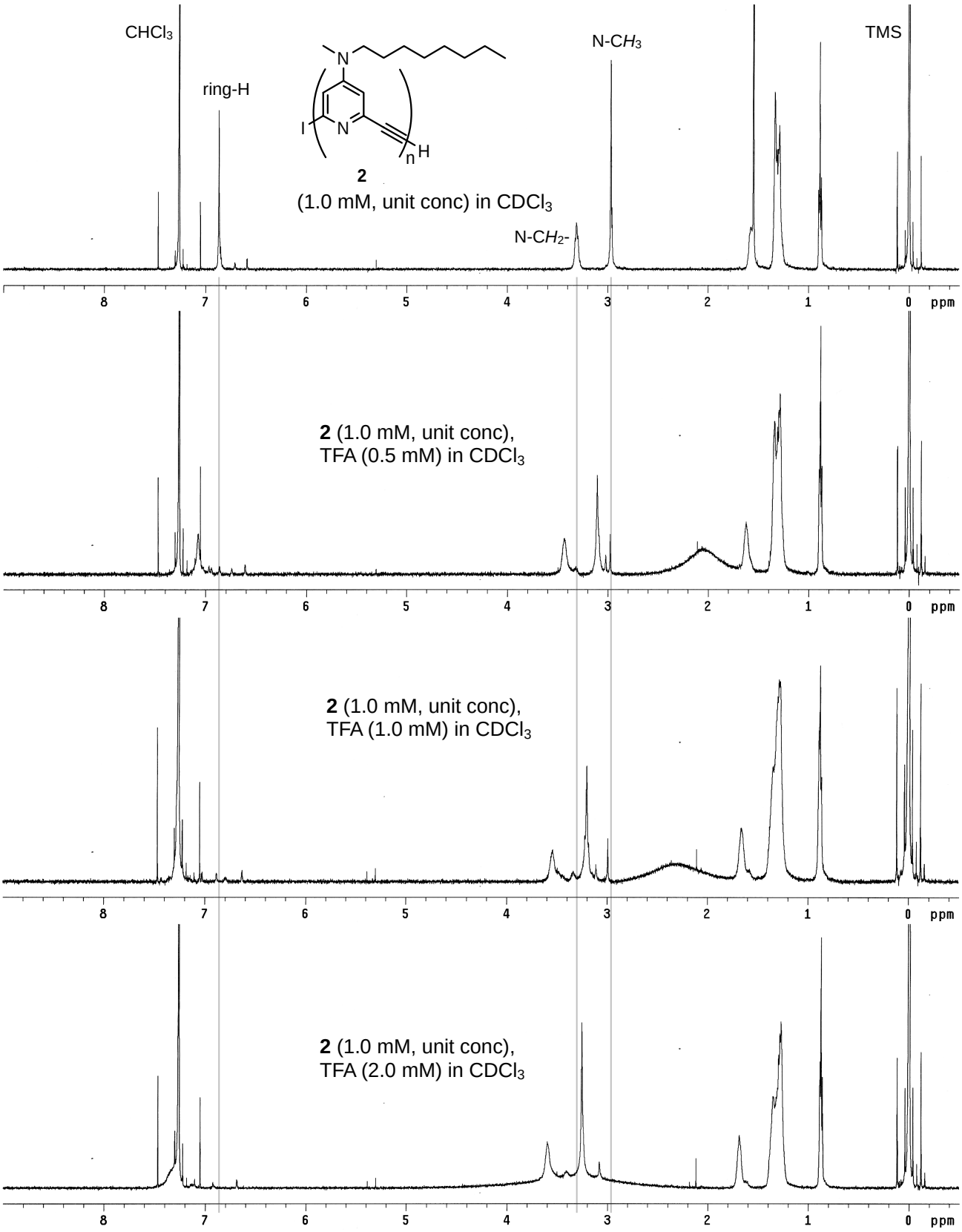


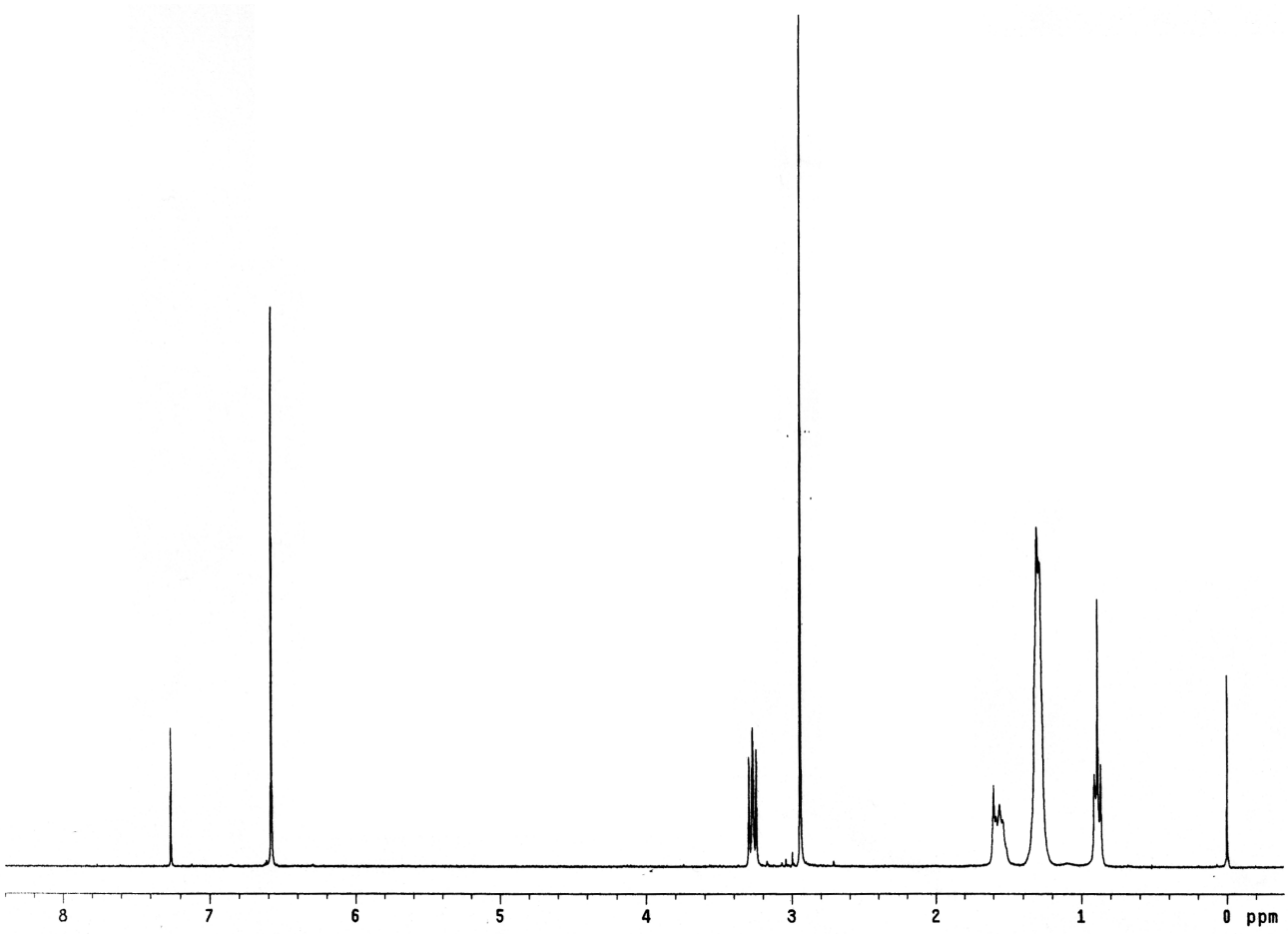
Figure S8. (A) The change of the CD spectrum on the titration of **2** (1.0 mM, unit concentration) with ***β*-D-Gal** in CH_2Cl_2 at 26 °C in the presence of TFA (0.5 mM). Light path length = 1 mm. (B) The titration curves in the presence (343 nm was observed) of TFA. The lines are theoretical curves obtained by the iterative curve-fitting analyses assuming 1:1 complexation between **2** and ***β*-D-Gal** and the molecular weight of **2** as 1.1×10^4 g mol^{-1}.

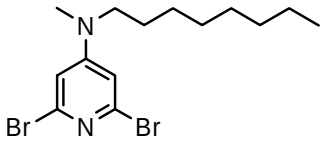
^{1}H NMR spectrum for polymer 2 and the additive effect of TFA



*Gray lines are guides to know downfield movement of peaks.

^{1}H NMR spectra for compounds 5, 7, 8, 9, and 11





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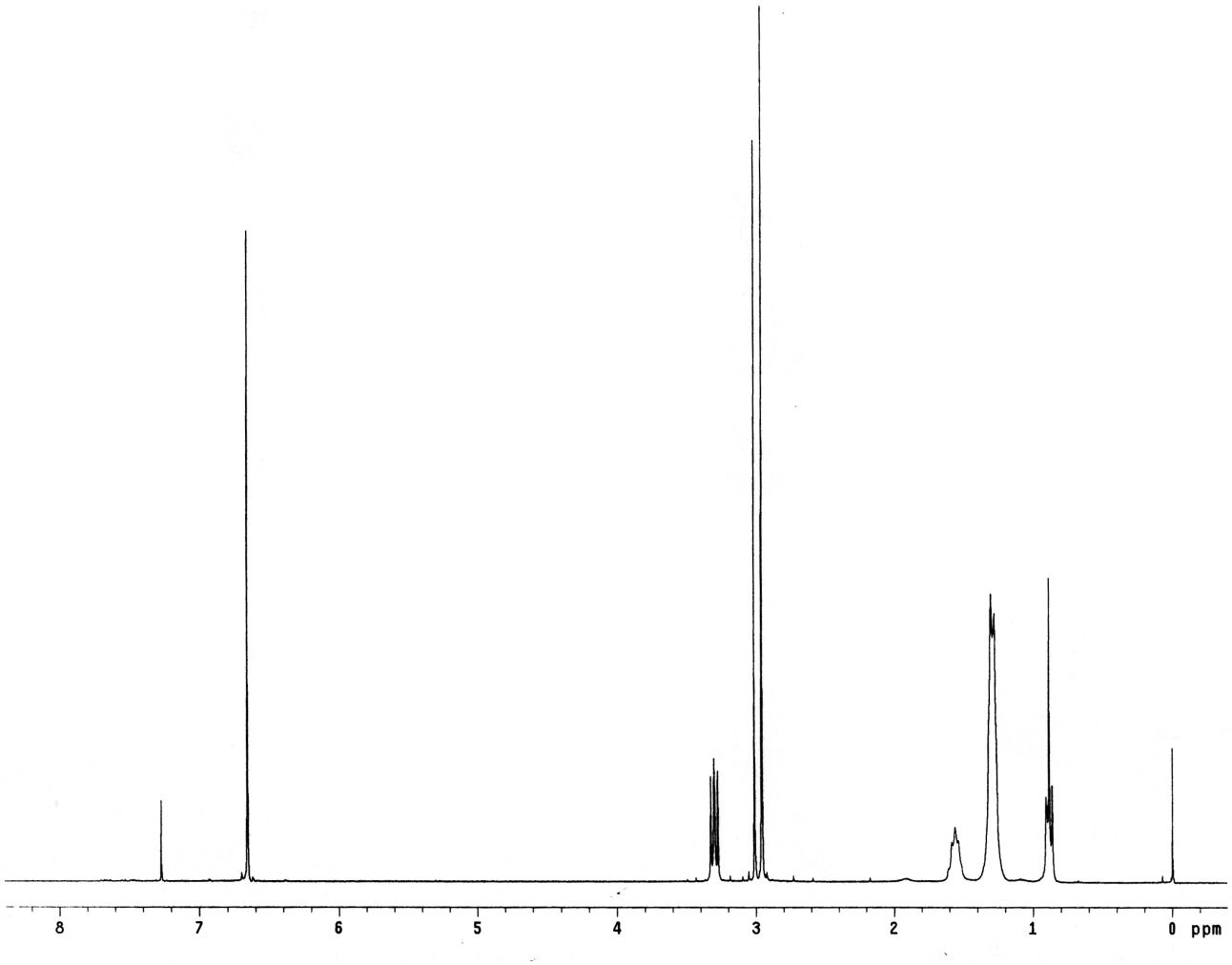

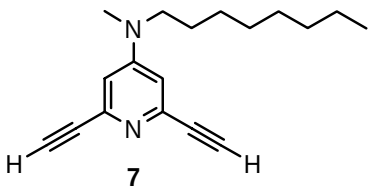

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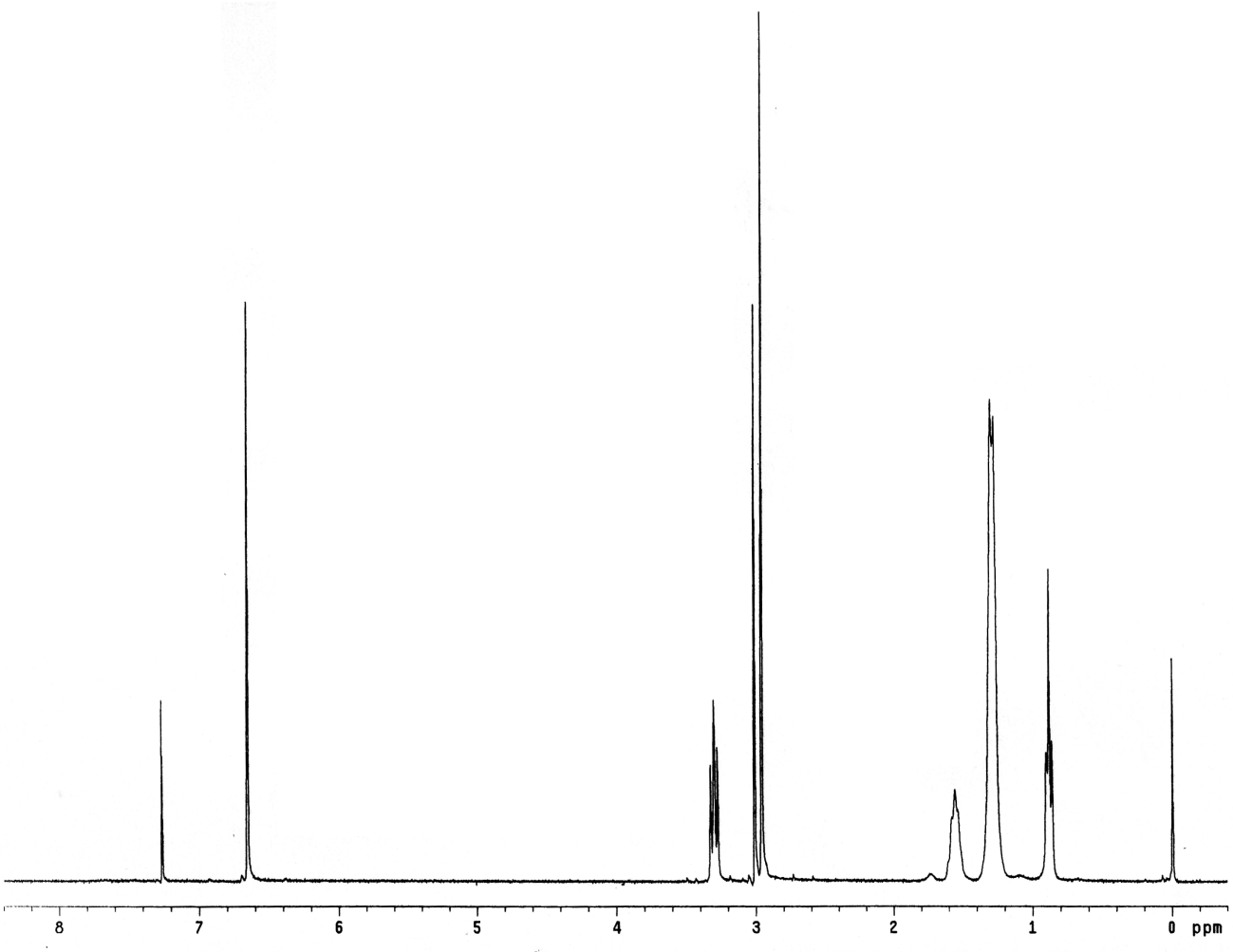

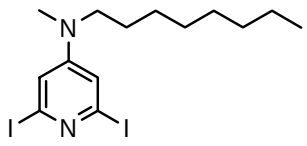

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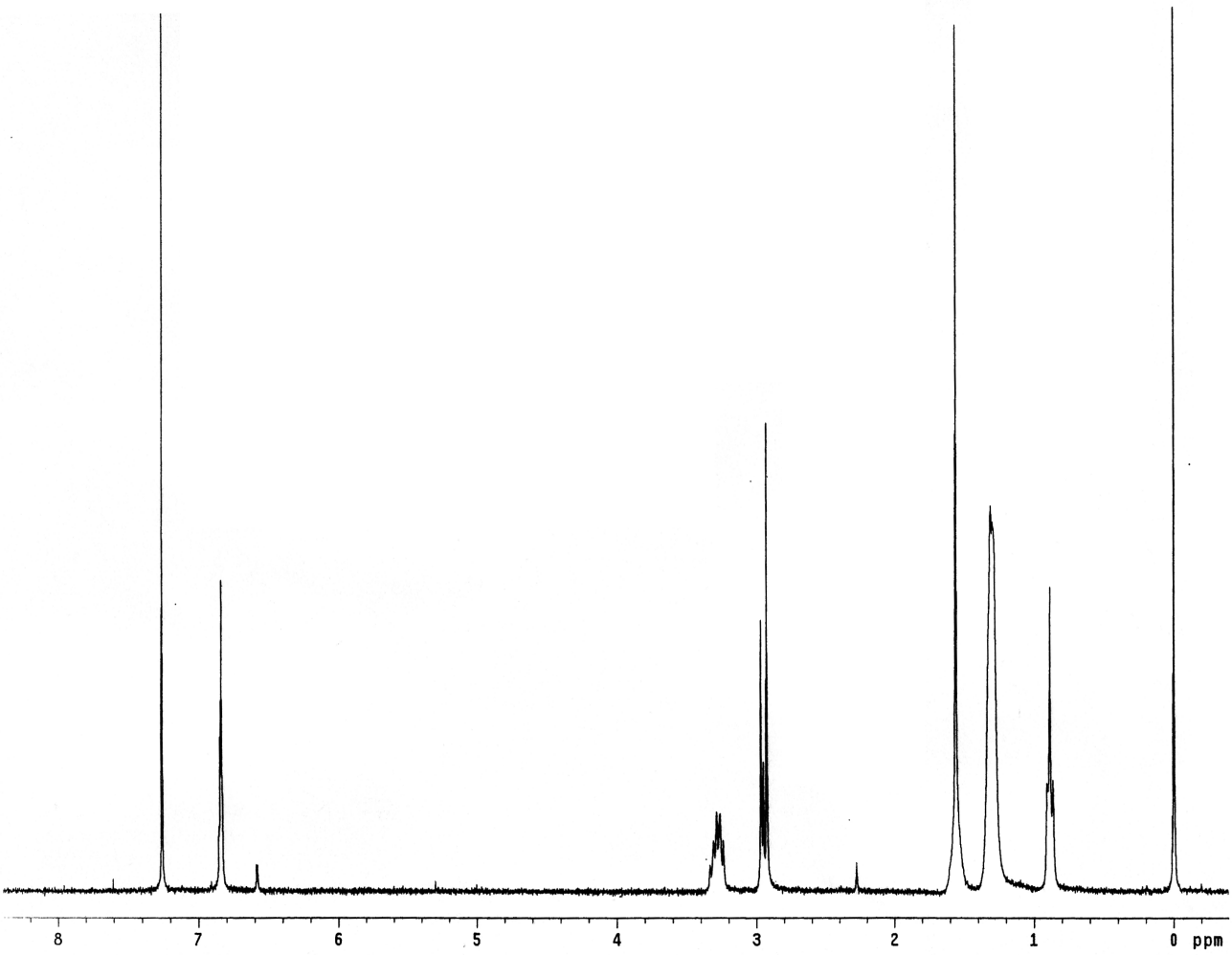

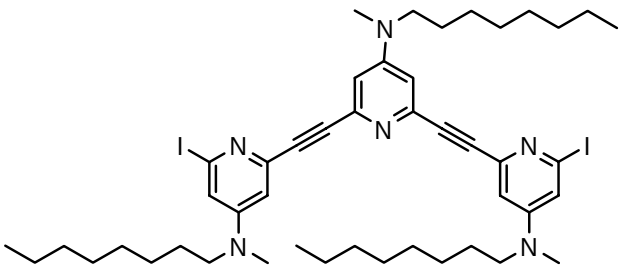

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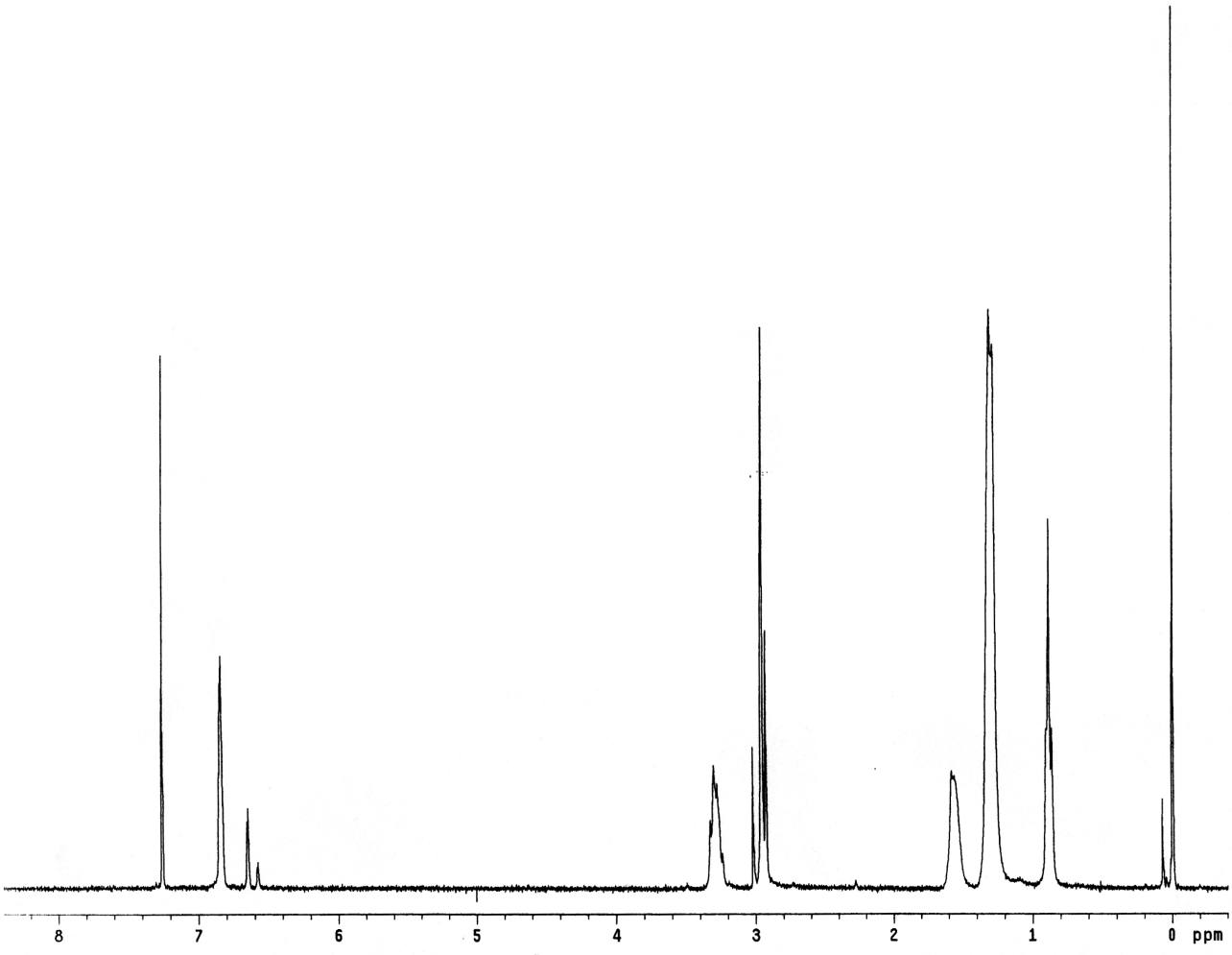

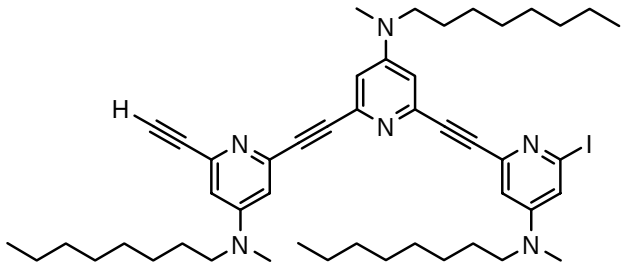

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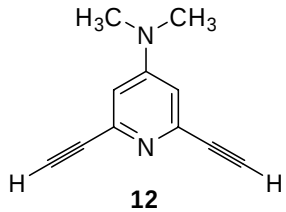
Total energy, zero point energy correction (ZPE), and optimized geometry obtained by DFT method.

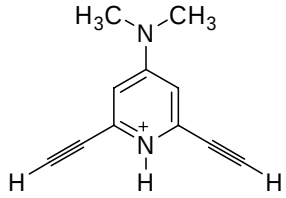


12

Total energy = −534.699903166 hartree
Zero-point energy correction (ZPE) = 0.179477 hartree
Total energy including ZPE = −534.520426 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.399663
C	1.227157	0.000000	2.096954
C	2.393044	-0.015402	1.301594
C	2.278529	-0.014690	-0.093373
H	-0.949349	-0.001190	1.918476
H	3.381570	-0.029126	1.740982
N	1.110001	-0.005830	-0.761002
C	2.568347	-0.088851	4.144412
H	3.238492	0.729124	3.852072
H	2.412355	-0.022552	5.222280
H	3.076110	-1.040481	3.928787
C	0.056829	-0.073106	4.247177
H	0.301180	-0.009638	5.308680
H	-0.624590	0.753485	4.010352
H	-0.478829	-1.018088	4.074008
N	1.283531	0.016801	3.470628
C	3.478660	-0.026563	-0.885732
C	-1.260997	0.004068	-0.691493
C	-2.335845	0.008276	-1.244421
H	-3.272817	0.011596	-1.753497
C	4.504625	-0.035968	-1.524760
H	5.396769	-0.044477	-2.108788

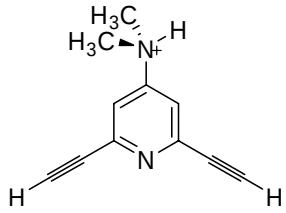


12H$^+$-ring

Total energy = −535.096467900 hartree
Zero-point energy correction (ZPE) = 0.193702 hartree
Total energy including ZPE = −534.902766 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.378889
C	1.226464	0.000000	2.111581
C	2.434100	0.000653	1.348231
C	2.399374	0.000645	-0.030223
H	-0.957260	0.000116	1.879242
H	3.403660	0.001285	1.824291
C	2.518072	-0.001118	4.185530
H	3.106378	0.892488	3.950052
H	2.312575	-0.001634	5.254569
H	3.106124	-0.894613	3.948973
C	-0.012913	-0.001809	4.217050
H	0.219133	-0.002242	5.280642
H	-0.607368	0.891490	3.996305
H	-0.606195	-0.895607	3.995154
N	1.243292	-0.000453	3.455905
C	3.565605	0.001180	-0.839004
C	-1.186233	-0.000096	-0.779150
C	-2.188373	0.000081	-1.454260
H	-3.079639	0.000063	-2.045720
C	4.550423	0.001896	-1.539142
H	5.426509	0.002363	-2.152863
N	1.191335	0.000000	-0.678143
H	1.178561	0.000000	-1.692315



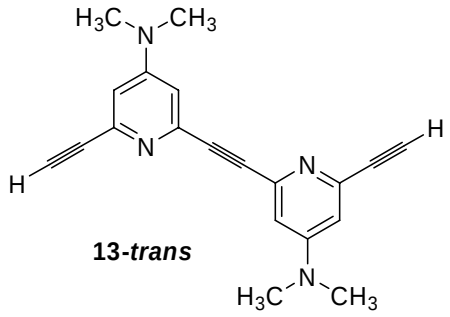
12H$^+$-amino

Total energy = −535.050747905 hartree
Zero-point energy correction (ZPE) = 0.194090 hartree
Total energy including ZPE = −534.856658 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.413053
C	1.232110	0.000000	2.045458
C	2.418371	0.000135	1.327882
C	2.311910	0.000412	-0.079941
H	-0.941279	-0.000051	1.955331
H	3.397937	0.000138	1.792198

N	1.131441	0.000250	-0.722096
C	1.884386	1.254911	4.108658
H	1.367181	2.117759	3.688390
H	1.777727	1.229655	5.194347
H	2.937987	1.276168	3.832320
C	1.884337	-1.255693	4.108092
H	1.777499	-1.231051	5.193775
H	1.367237	-2.118329	3.687259
H	2.937974	-1.276752	3.831861
C	3.499356	0.000278	-0.872709
C	-1.241908	0.000273	-0.703389
C	-2.305520	0.000723	-1.276668
H	-3.235144	0.001014	-1.803862
C	4.518008	0.000596	-1.522464
H	5.405999	0.000654	-2.117068
N	1.260422	-0.000235	3.537327
H	0.279119	-0.000253	3.836531

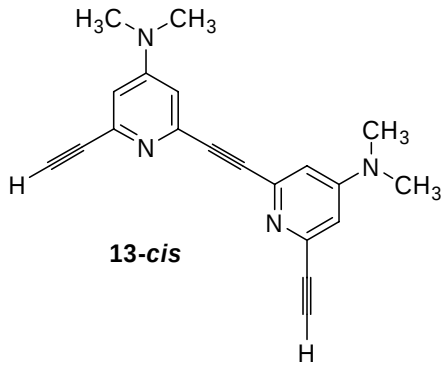


Total energy = −992.044458405 hartree
Zero-point energy correction (ZPE) = 0.331603 hartree
Total energy including ZPE = −991.712855 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.281733
C	1.399824	0.000000	2.337291
C	2.145866	-0.006421	1.139894
C	1.398824	0.000491	-0.058036
H	1.878294	0.006733	3.307495
H	1.878375	0.007642	-1.027769
C	-0.736601	0.005043	3.510753
C	-1.320160	0.010165	4.574991
C	-2.056797	0.017412	5.803981
C	-3.456620	0.022147	5.748326
C	-4.202754	0.027583	6.945656
H	-3.934960	0.023362	4.778038
C	-2.056904	0.035302	8.085623
C	-3.455720	0.041392	8.143536
H	-3.935246	0.058196	9.113159
N	-0.715457	-0.001277	1.139125

N	-1.341400	0.022370	6.946603
C	4.245891	0.075827	-0.116622
H	4.042273	1.019076	-0.644625
H	5.317085	0.022727	0.084203
H	3.989499	-0.753007	-0.788534
C	-6.302507	0.129408	8.201181
H	-6.096828	1.077698	8.719342
H	-7.373835	0.076343	8.001024
H	-6.047781	-0.692928	8.881582
C	-0.742083	0.003897	-1.232574
C	-1.314878	0.046297	9.318191
C	-1.338005	0.006840	-2.284300
H	-1.883020	0.009613	-3.200764
C	-0.719086	0.055423	10.369954
H	-0.174108	0.063477	11.286409
N	3.520687	-0.020244	1.140211
N	-5.577687	0.018275	6.945350
C	4.245436	0.073674	2.398392
H	5.316625	0.020314	2.197770
H	4.041073	1.015936	2.927278
H	3.987931	-0.755853	3.068572
C	-6.301960	0.108032	5.686581
H	-6.095496	1.047307	5.153128
H	-6.046118	-0.725284	5.020573
H	-7.373304	0.057785	5.887240



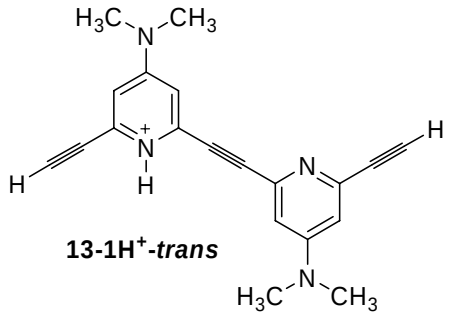
13-*cis*

Total energy = −992.041457988 hartree
Zero-point energy correction (ZPE) = 0.331360 hartree
Total energy including ZPE = −991.710098 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.281984
C	1.400779	0.000000	2.335400
C	2.146304	0.008464	1.137851
C	1.399040	0.000174	-0.059031
H	1.882270	-0.008122	3.304285
H	1.877686	-0.007030	-1.029239
C	-0.737459	-0.004951	3.511321

C	-1.343159	-0.008605	4.563346
C	-2.036071	-0.014228	5.818332
C	-1.286815	-0.045175	7.002678
C	-1.948287	-0.054831	8.248626
H	-0.207223	-0.059535	6.932531
C	-4.009202	0.013916	6.964391
C	-3.358072	-0.015777	8.203717
H	-3.956555	-0.007097	9.104942
N	-0.713944	0.001410	1.139565
N	-3.382236	0.013907	5.774745
C	4.246208	-0.089653	-0.120114
H	3.987413	0.728035	-0.804161
H	5.317517	-0.030690	0.078666
H	4.043466	-1.041406	-0.633160
C	-1.980029	0.011348	10.697398
H	-2.717087	-0.793859	10.806863
H	-1.271389	-0.071587	11.523004
H	-2.507184	0.972206	10.791957
C	-0.742915	-0.004773	-1.231694
C	-5.446966	0.049866	6.940658
C	-1.339467	-0.008575	-2.282920
H	-1.889015	-0.012065	-3.196713
C	-6.655246	0.079450	6.952853
H	-7.721109	0.106024	6.936680
N	-1.259246	-0.102362	9.439039
N	3.522526	0.026659	1.136360
C	0.192858	-0.029419	9.436784
H	0.629600	-0.849665	8.853560
H	0.564288	0.919868	9.022618
H	0.556402	-0.119699	10.461677
C	4.247725	-0.080131	2.392017
H	3.980056	0.736260	3.074280
H	4.055787	-1.033084	2.907510
H	5.318314	-0.009655	2.192997



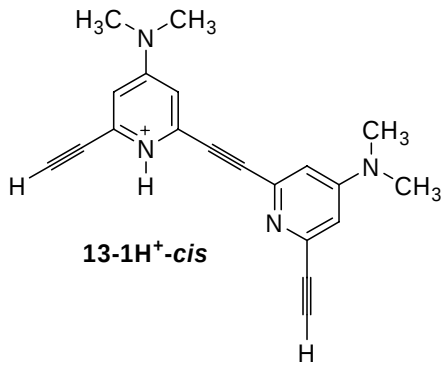
13-1H$^+$-*trans*

Total energy = −992.451090698 hartree
Zero-point energy correction (ZPE) = 0.345926 hartree
Total energy including ZPE = −992.105165 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000

C	0.000000	0.000000	2.275305
C	1.395172	0.000000	2.356717
C	2.150674	-0.000117	1.158291
C	1.400841	0.000000	-0.040111
H	1.871204	0.000131	3.328350
H	1.886302	0.000195	-1.006813
C	-0.779150	0.000121	3.477122
C	-1.472454	-0.000003	4.476828
C	-2.349984	0.000036	5.578272
C	-3.729031	0.000268	5.443864
C	-4.578834	0.000169	6.584966
H	-4.126913	0.000502	4.439766
C	-2.572136	-0.000184	7.972673
C	-3.945215	0.000075	7.867662
H	-4.518783	0.000252	8.782727
N	-0.719834	0.000000	1.137771
C	4.249601	0.000643	-0.099777
H	4.021320	0.892190	-0.697680
H	5.319254	-0.000681	0.110240
H	4.019667	-0.889045	-0.699746
C	-6.774795	0.000018	7.660024
H	-6.601446	0.893437	8.270299
H	-7.817963	-0.000868	7.347922
H	-6.600163	-0.892775	8.270821
C	-0.731193	0.000207	-1.234581
C	-1.887072	-0.000335	9.217235
C	-1.320334	0.000347	-2.289451
H	-1.851087	0.000495	-3.215395
C	-1.292885	-0.000337	10.269322
H	-0.774568	-0.000414	11.204499
N	3.516038	-0.000367	1.161773
N	-5.921207	0.000218	6.466914
C	4.243849	0.000830	2.423958
H	5.314368	-0.000229	2.218700
H	4.014994	0.892969	3.022108
H	4.013776	-0.889542	3.024213
C	-6.547937	0.000772	5.140068
H	-6.265241	0.893560	4.571314
H	-6.265418	-0.891666	4.570682
H	-7.630101	0.000856	5.260146
N	-1.802693	-0.000241	6.837961
H	-0.793540	-0.000545	6.930670

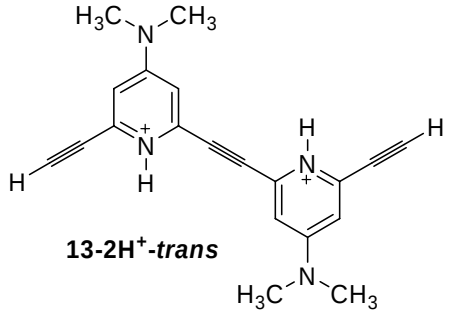


13-1H$^+$-*cis*

Total energy = −992.451701191 hartree
Zero-point energy correction (ZPE) = 0.346110 hartree
Total energy including ZPE = −992.105591 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.404943
C	1.384918	0.000000	2.412735
C	2.125610	0.000000	1.197116
C	1.377794	0.000000	-0.021303
H	1.877007	0.000000	3.373990
H	1.865337	0.000000	-0.984853
C	-0.804449	0.000000	3.560815
C	-1.592430	0.000310	4.487605
C	-2.554334	0.000565	5.548430
C	-2.120329	0.000669	6.876482
C	-3.087682	0.001036	7.911423
H	-1.059402	0.000357	7.088618
C	-4.755319	0.000950	6.126072
C	-4.437599	0.001050	7.490906
H	-5.248671	0.001098	8.206507
N	-3.837733	0.000710	5.140697
C	4.212571	0.000000	-0.077688
H	3.982312	0.893063	-0.669326
H	5.280379	-0.000064	0.135561
H	3.982219	-0.892990	-0.669397
C	-3.773143	0.001483	10.259937
H	-4.410161	-0.889451	10.190326
H	-3.299550	0.002451	11.241779
H	-4.410932	0.891725	10.188979
C	-0.796324	0.000000	-1.176080
C	-6.135128	0.000938	5.732434
C	-1.488005	0.000012	-2.166726
H	-2.095009	0.000045	-3.046981
C	-7.304974	0.000908	5.430231
H	-8.335379	0.000871	5.152061
N	-0.660185	0.000000	1.199905
H	-1.674767	0.000000	1.206283
N	3.473972	0.000000	1.189963
C	4.221502	0.000000	2.451480
H	3.994034	0.892930	3.044652
H	3.993937	-0.892869	3.044705
H	5.287826	-0.000070	2.231199
N	-2.738198	0.001287	9.231168
C	-1.332727	0.000574	9.615770
H	-0.811660	-0.891092	9.242569
H	-0.810658	0.891355	9.241878
H	-1.260366	0.000982	10.703393



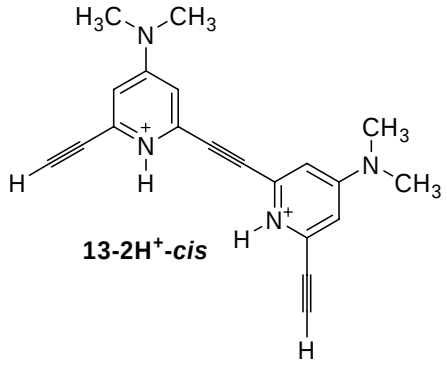
13-2H$^+$-*trans*

Total energy = −992.764084489 hartree
Zero-point energy correction (ZPE) = 0.359965 hartree
Total energy including ZPE = −992.404119 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.399587
C	1.377076	0.000000	2.422388
C	2.130709	-0.000069	1.200971
C	1.379610	0.000000	-0.014200
H	1.870045	0.000062	3.383521
H	1.867965	0.000077	-0.977734
C	-0.790346	0.000039	3.583136
C	-1.481339	-0.000012	4.581927
C	-2.271672	-0.000006	5.765488
C	-3.648743	0.001347	5.742724
C	-4.402342	0.001293	6.964159
H	-4.141743	0.002445	4.781606
C	-2.271607	-0.001568	8.165072
C	-3.651217	-0.000222	8.179313
H	-4.139541	-0.000326	9.142861
C	4.217624	-0.000088	-0.067195
H	3.987170	0.894847	-0.654559
H	5.283861	-0.000896	0.150751
H	3.986036	-0.894213	-0.655327
C	-6.489287	0.002373	8.232311
H	-6.257803	0.896499	8.820497
H	-7.555515	0.003032	8.014324
H	-6.258769	-0.892564	8.819630
C	-0.789241	0.000066	-1.176933
C	-1.482362	-0.003074	9.342010
C	-1.462327	0.000109	-2.180959
H	-2.049864	0.000145	-3.076131
C	-0.809707	-0.004327	10.346323
H	-0.222358	-0.005453	11.241619
N	3.470819	-0.000197	1.202225
N	-5.742453	0.002596	6.962902
C	4.222157	0.000016	2.466403
H	5.287344	-0.000610	2.243455
H	3.997108	0.895786	3.055205
H	3.996275	-0.895034	3.055965
C	-6.493773	0.004367	5.698711
H	-6.267279	0.899950	5.110188

H	-6.269317	-0.890872	5.108882
H	-7.558958	0.005421	5.921661
N	-1.604584	-0.001446	6.964395
H	-0.591047	-0.002452	6.975841
N	-0.667052	-0.000035	1.200666
H	-1.680591	-0.000042	1.189188



13-2H$^+$-*cis*

Total energy = −992.763794096 hartree
Zero-point energy correction (ZPE) = 0.359763 hartree
Total energy including ZPE = −992.404031 hartree

The optimized Cartesian coordinate:

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.399651
C	1.377222	0.000000	2.422277
C	2.130836	0.000000	1.200889
C	1.379494	0.000000	-0.014189
H	1.868903	0.000000	3.384216
H	1.866969	0.000000	-0.978273
C	-0.786000	0.000000	3.586159
C	-1.448972	0.000095	4.603789
C	-2.216022	0.000130	5.802633
C	-1.637958	0.000643	7.052882
C	-2.449874	0.000658	8.236347
H	-0.559334	0.001031	7.113157
C	-4.410388	-0.000365	6.773780
C	-3.865073	0.000122	8.041000
H	-4.549438	0.000097	8.876904
C	4.217836	0.000000	-0.067729
H	3.986864	0.894485	-0.655524
H	5.283946	0.000000	0.150559
H	3.986853	-0.894490	-0.655513
C	-2.765360	0.001264	10.658186
H	-3.395852	-0.893558	10.685279
H	-2.134300	0.002043	11.544757
H	-3.396832	0.895416	10.684435
C	-0.789653	0.000000	-1.176655
C	-5.805939	-0.000888	6.527904
C	-1.462811	0.000001	-2.180648

H	-2.051006	0.000001	-3.075418
C	-6.996307	-0.001337	6.317738
H	-8.052528	-0.001732	6.141705
N	-0.667105	0.000000	1.200684
H	-1.680441	0.000000	1.187518
N	3.470935	0.000000	1.201594
C	4.222657	0.000000	2.465502
H	3.997468	0.895373	3.054791
H	3.997484	-0.895382	3.054785
H	5.287802	0.000000	2.242206
N	-1.906904	0.001152	9.461507
C	-0.446925	0.001552	9.637420
H	0.001056	-0.893788	9.193185
H	0.000609	0.896965	9.192880
H	-0.220049	0.001785	10.701812
N	-3.582373	-0.000355	5.677856
H	-4.004524	-0.000719	4.756525
