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Supporting Information

The Organocatalytic Approach to Enantiopure 2*H*- and 3*H*-Pyrroles: Inhibitors of the Hedgehog Signaling Pathway

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General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography (TLC) on silica gel or aluminium oxide pre-coated plastic sheets (0.2 mm, Macherey-Nagel) or by ASAP-MS (Advion Expression Compact Mass Spectrometer L, APCI/ASAP). Visualization was accomplished by irradiation with UV light at 254 nm and/or phosphomolybdic acid (PMA) or Hanessian's Stain. Column chromatography was performed on Merck silica gel (60, particle size 0.040-0.063 mm) or aluminum oxide (neutral, activated Brockmann I, Sigma-Aldrich; Activity II: 3% H_2O, Activity III: 6% H_2O). Optical rotations were measured on an Autopol IV automatic polarimter (Rudolph Research Analytical). CD spectra were recorded at 20 °C in MeOH using a JASCO J-810 spectropolarimeter and precision cells (quartz suprasil, 2mm, Hellma). Proton, carbon, nitrogen and fluorine NMR spectra were recorded on Bruker Avance III 600 MHz-, Bruker Avance III 500 MHz-, Bruker Avance III 400 MHz- and Bruker Avance III HD 300 MHz-spectrometer in deuterated solvents at ambient temperature unless otherwise stated. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CD_2Cl_2, δ = 5.32 ppm; $CDCl_3$ δ = 7.26 ppm, CD_3CN δ = 1.94 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, triplet = t, q = quartet, m = multiplet, b = broad), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CD_2Cl_2, δ = 53.8 ppm; $CDCl_3$, δ = 77.16 ppm, CD_3CN δ = 118.26 ppm). The ^{15}N- and ^{19}F-chemical shifts were referenced indirectly to the referenced proton frequency with the Ξ-scale with the factors 0.10136767 for ^{15}N (δ(Me*N*O_2)=0ppm) and 0.94094011 for ^{19}F (δ(C*F*Cl_3)=0ppm).[1,2] The ^{15}N chemical shifts were determined from the indirect dimension of a ^{1}H-^{15}N-HMBC. High resolution mass spectra were determined on a Bruker APEX III FTMS (7 T magnet). The enantiomeric ratios were determined by HPLC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures.

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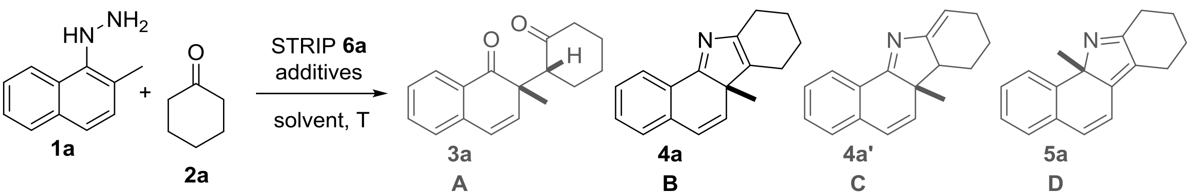
[1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure Appl. Chem.* **2008**, *80*, 59–84.

[2] M. Findeisen, S. Berger, *50 and More Essential NMR Experiments: A Detailed Guide*, Wiley-VCH, **2013**.

Screening of Reaction Conditions

Additive, Solvent and Temperature Screening:



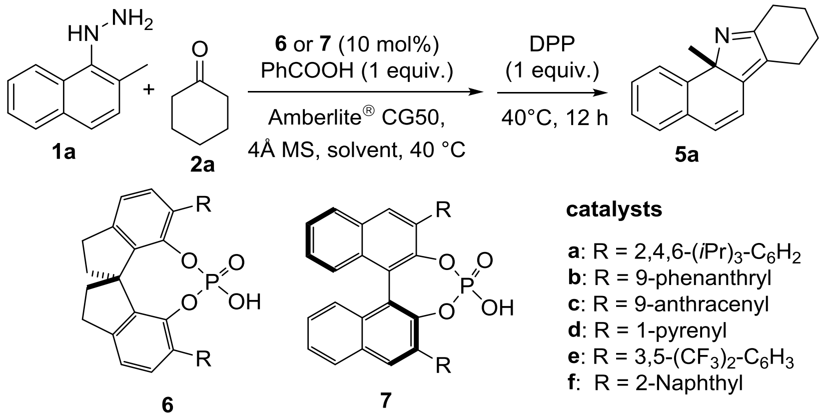
*Optimization towards compound **4a***

Entry	STRIP [mol%]	Addit.1 [mg/mmol]	Addit.2	Addit.3 [mg/mmol]	Solvent	t [d]	T [°C]	Conv. [%]	NMR yield/ee[a)]
1	5	CG50 (500)	/	/	toluene 0.1 M	3d	45	60	**A** 27% - 95:5 **B** 3% - 5:95 **C** 3% - ND[b)] **D** 6% - 18:82
2	5	CG50 (500)	PHCOOH (1 eq.)	/	toluene 0.1 M	3d	30	full	**A** 30% - 96:4 **B** 25% - 6:94 **C** 4% - ND[b)] **D** 5% - ND
3	5	CG50 (500)	PHCOOH (1 eq.)	H_2O (6 eq.)	toluene 0.1 M	3d	30	98	**A** 54% - 92:8 **B** 9% - ND **C** 4% - ND[b)] **D** <5% - ND
4	5	CG50 dried (500)	PHCOOH (1 eq.)	4Å MS (500)	toluene 0.1 M	3d	30	74	**A** 0% - / **B** 51% - 96.5:3.5 **C** 5% - ND[c)] **D** 10%- 77.5:22.5
5	5	CG50 dried (500)	PHCOOH (0.5 eq.)	4Å MS (500)	toluene 0.1 M	4d	30	82	**A** 0% - / **B** 41% - 97.8:2.2 **C** 6% - ND[c)] **D** 12%- 81.5:18.5
6	5	CG50 dried (500)	PHCOOH (1 eq.)	4Å MS (500)	toluene 0.1 M	5d	20	78	**A** 0% - / **B** 53% - 95.5:4.5 **C** 8% - ND[d)] **D** <5% - 67:33
7	10	CG50 dried (500)	PHCOOH (1 eq.)	4Å MS (500)	toluene 0.1 M	4d	20	82	**A** 0% - / **B** 50% - 3:97 **C** 8% - ND[d)] **D** <5% -73.5:26.5
8	10	CG50 dried (500)	PHCOOH (1 eq.)	4Å MS (500)	*p*-xylene 0.1 M	7d	20	full	**A** 0% - / **B** 56%[e)] - 2:98 **C** ND - ND **D** <5% - ND

a) Conversion/NMR yield determined by NMR after basic extraction with KOH (3M), using 1,3,5-trimethoxybenzene as internal standard; ee determined by HPLC analysis on a chiral stationary phase. b) Single diastereoisomer. c) Diastereomeric ratio 1:1. d) Diastereomeric ratio: 1:3. e) Isolated yield.

Catalyst and Solvent Screening:

Reactions were carried out using catalyst (10 mol%), Amberlite® CG50 (500 mg/mmol), 4Å MS (500 mg/mmol) and PhCOOH (1 equiv.) at a concentration of 0.1 M at 40 °C. After full conversion of the hydrazone, diphenyl phosphate (1 equiv.) was added and the reaction was stirred at 40 °C for 12 h.

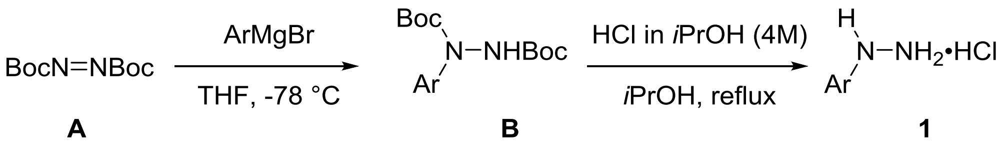


Entry	Catalyst	Solvent	er[a)]	NMR yield[b)]
1	**7a**	CH_2Cl_2	80:20	62%
2	**7a**	chlorobenzene	83:17	57%
3	**7a**	toluene	86:14	69%
4	**7a**	p-xylene	88:12	51%
5[c)]	**7b**	p-xylene	69:31	n.d.
6[c)]	**7c**	p-xylene	58.5:41.5	n.d.
7	**7f**	p-xylene	65:35	61%
8	**6d**	p-xylene	81:19	44%
9	**6e**	p-xylene	69.5:30.5	57%
10	**6a**	p-xylene	90:10	60%[d]

a) Determined by HPLC analysis on a chiral stationary phase. b) NMR yield after basic extraction with KOH (3M), using 1,3,5-trimethoxybenzene as internal standard. c) Reaction was very slow, full conversion after 19 d. d) Isolated yield.

Substrate Synthesis

Hydrazines



All hydrazines were synthesized following a literature procedure.[3]

Procedure Extraction of Hydrazine Salts:

(*Caution*: Some hydrazines were found to be light- and oxygen sensitive. Thus, all solvents were degassed by bubbling argon for 60 min prior to use).

An oven-dried Schlenk tube was set under argon and charged with naphthalen-1-ylhydrazine hydrochloride. Anhydrous CH_2Cl_2 and sat. aq. $NaHCO_3$ were added and the mixture was stirred until all solids were dissolved. The organic layer was transferred to a flame dried Schlenk tube containing anhydrous Na_2SO_4 under argon. This extraction step was repeated four times. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The corresponding naphthalen-1-ylhydrazine was used immediately without further purification.

[3] S. Huang, L. Kötzner, C.-K. De, B. List *J. Am. Chem. Soc.* **2015**, *137*, 3446.

Catalytic Asymmetric Synthesis of 3*H*-Pyrroles

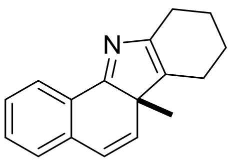
General Procedure for the Synthesis of 3*H*-Pyrroles

Amberlite® CG50 was dried under high vacuum at 100 °C over night and stored in a Schlenk tube under argon. 4Å Molecular sieves was flame dried under high vacuum and stored in Schlenk tube under argon.

A flame-dried Schlenk tube was charged with (*R*)-STRIP or (*S*)-STRIP (10 mol %), $PhCO_2H$ (1.0 equiv.), Amberlite® CG50 (500 mg/mmol), 4Å molecular sieves (500 mg/mmol) and the corresponding ketone (1.0 equiv.) under argon atmosphere. A solution of freshly prepared hydrazine (1.0 equiv.) in degassed *p*-xylene (0.1 M) was added and the reaction was stirred for 3-7 days at 20 °C. The crude reaction mixture was directly purified by column chromatography. In some cases, side prodcut **4a'** could not be completely separated from the desired product via column chromatography. These products were additionally purified by preparative TLC on aluminium oxide.

The racemates were prepared applying the above procedure, using diphenyl phosphate (0.5 equiv.), Amberlite® CG50 (500 mg/mmol), 4Å molecular sieves (500 mg/mmol), the corresponding ketone (1.0 equiv.) and hydrazine stock solution (1.0 equiv., 0.1 M in toluene). The reaction was performed at 20 °C for 3-5 d. The crude reaction mixture was directly submitted to column chromatography on Alox III.

(*S*)-6a-methyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4a



The reaction was performed at 20 °C for 7 d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 13.1 mg, 56% yield.

98:2 er, $[\alpha]_D^{25}$ = −40 (*c* = 0.47, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ =7.76 (d, *J* = 7.6 Hz, 1H), 7.36 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.30 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 9.4 Hz, 1H), 6.31 (d, *J* = 9.3 Hz, 1H), 2.54-2.44 (m, 2H), 2.32-2.17 (m, 2H), 1.83-1.73 (m, 4H), 1.27 (s, 3H) ppm.

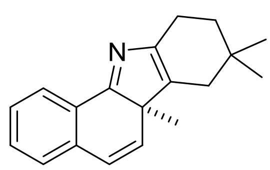
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 184.4, 149.1, 136.9, 134.8, 133.6, 130.7, 130.1, 128.5, 127.7, 126.9, 124.4, 60.4, 26.4, 25.8, 23.6, 23.1, 21.4 ppm.

MS (EI) *m/z* (%): 235 (100), 220 (55), 207 (23), 194 (20), 180 (10), 165 (16), 152 (9).

HRMS (ESI) *m/z* calculated for $C_{17}H_{18}N$ (M+H$^+$) 236.143374, found 236.143250.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 4.08 min, t_{maj} = 5.67 min.

(*R*)-6a,8,8-trimethyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4b



The reaction was performed on a 0.05 mmol scale at 20 °C for 5 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 10.9 mg, 83% yield.

99:1 er, $[\alpha]_D^{25}$ = +104 (*c* = 0.37, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.77-7.75 (m, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.30 (td, *J* = 7.5, 1.3 Hz, 1H), 7.18 (dd, *J* = 7.6, 0.7 Hz, 1H), 6.36 (d, *J* = 9.3 Hz, 1H), 6.28 (d, *J* = 9.3 Hz, 1H), 2.58-2.43 (m, 2H), 2.12-2.07 (m, 1H), 1.99-1.94 (m, 1H), 1.60-1.51 (m, 2H), 1.25 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H) ppm.

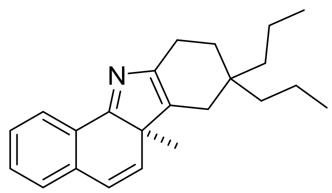
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 184.6, 147.8, 136.9, 134.2, 133.5, 130.8, 130.0, 128.5, 127.7, 126.9, 124.3, 60.3, 36.6, 35.5, 30.2, 29.0, 27.5, 26.4, 23.4 ppm.

MS (EI) *m/z* (%): 263 (100), 248 (46), 235 (11), 207 (44), 194 (95), 165 (16), 152 (8).

HRMS (ESI) *m/z* calculated for $C_{19}H_{22}N$ (M+H$^+$) 264.174674, found 264.174390.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 3.55 min, t_{min} = 5.82 min.

(*R*)-6a-methyl-8,8-dipropyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4c



The reaction was performed on a 0.125 M scale at 20 °C for 3 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 30.2 mg, 76% yield.

97:3 er, $[\alpha]_D^{25}$ = +67 (c = 1.3, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.76 (d, J = 7.5 Hz, 1H), 7.36 (td, J = 7.5, 1.3 Hz, 1H), 7.30 (td, J = 7.5, 1.2 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 6.36 (d, J = 9.3 Hz, 1H), 6.29 (d, J = 9.3 Hz, 1H), 2.53-2.39 (m, 2H), 2.11-2.07 (m, 1H), 2.00-1.96 (m, 1H), 1.66-1.55 (m, 2H), 1.37-1.27 (m, 7H), 1.25 (s, 3H), 1.24-1.20 (m, 1H), 0.92-0.88 (m, 6H) ppm.

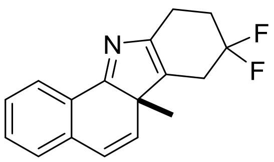
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 184.6, 148.1, 136.9, 134.1, 133.6, 130.8, 130.1, 128.5, 127.7, 126.9, 124.3, 60.5, 40.5, 38.7, 35.4, 33.0, 32.9, 26.5, 22.9, 15.2 ppm.

MS (EI) *m/z* (%): 319 (29), 304 (16), 276 (17), 207 (27), 194 (100), 165 (8), 152 (3).

HRMS (ESI) *m/z* calculated for $C_{23}H_{30}N$ ($M+H^+$) 320. 237274, found 320. 237220.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 2.92 min, t_{min} = 4.80 min.

(*S*)-8,8-difluoro-6a-methyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4d



The reaction was conducted at 30 °C for 5 d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 11.4 mg, 42% yield.

99.5:0.5 er, $[\alpha]_D^{25}$ = −80 (c = 0.22, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.79-7.77 (m, 1H), 7.40 (td, J = 7.5, 1.4 Hz, 1H), 7.33 (td, J = 7.5, 1.2 Hz, 1H), 7.21 (dd, J = 7.6, 0.9 Hz, 1H), 6.40 (d, J = 9.3 Hz, 1H), 6.28 (d, J = 9.3 Hz, 1H), 2.89-2.69 (m, 4H), 2.28-2.19 (m, 2H), 1.30 (s, 3H) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2) δ = 186.7, 147.8, 136.8, 132.4, 131.4, 129.7 (dd, J = 6.7, 5.1 Hz), 129.6, 128.8, 127.9, 127.3, 124.6, 124.0 (t, J = 241 Hz), 60.8, 32.0 (t, J = 28 Hz), 31.4 (t, J = 25 Hz), 26.2, 23.2 (dd, J = 6.4, 5.2 Hz) ppm.

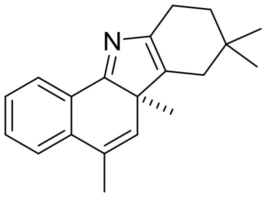
^{19}F NMR (282 MHz, CD_2Cl_2) δ = -95.5 (d, J = 235 Hz, 1F), -97.2 (d, J = 237Hz, 1F) ppm.

MS (EI) *m/z* (%): 271 (100), 256 (23), 236 (26), 207 (18), 192 (6), 165 (12), 152 (5).

HRMS (ESI) *m/z* calculated for $C_{17}H_{16}NF_2$ ($M+H^+$) 272.124531, found 272.124340.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 6.67 min, t_{maj} = 10.6 min.

(*R*)-5,6a,8,8-tetramethyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4e



The reaction was performed at 20 °C for 3 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 15.8 mg, 57% yield.

99:1 er, $[\alpha]_D^{25}$ = +97 (*c* = 0.45, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) *δ* = 7.77-7.75 (m, 1H), 7.44-7.40 (m, 1H), 7.34-7.31 (m, 2H), 6.07 (q, *J* = 1.5 Hz, 1H), 2.57-2.42 (m, 2H), 2.09 (dt, *J* = 17.0, 2.9 Hz, 1H), 2.03 (d, *J* = 1.5 Hz, 3H), 1.96 (dt, *J* = 17.5, 2.4 Hz, 1H), 1.60 (m, 2H), 1.20 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H) ppm.

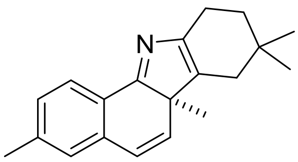
^{13}C NMR (125 MHz, CD_2Cl_2) *δ* = 185.1, 147.9, 138.0, 134.6, 131.8, 130.7, 130.1, 129.7, 128.2, 124.9, 124.3, 59.8, 36.6, 35.5, 30.2, 28.9, 27.6, 25.8, 23.4, 20.0 ppm.

MS (EI) *m/z* (%): 277 (74), 262 (44), 221 (66), 208 (100), 191 (29), 178 (39), 165 (58), 152 (25).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ (M+H$^+$) 278.190324, found 278.190400.

HPLC: Daicel Chiralpak AD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 3.27 min, t_{min} = 4.42 min.

(*R*)-3,6a,8,8-tetramethyl-6a,8,9,10-tetrahydro-7H-benzo[a]carbazole 4f



The reaction was performed at 20 °C for 3 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 16.8 mg, 61% yield.

>99.5:0.5 er, $[\alpha]_D^{25}$ = +146 (*c* = 0.25, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) *δ* = 7.66 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.32 (d, *J* = 9.3 Hz, 1H), 6.27 (d, *J* = 9.3 Hz, 1H), 2.56-2.41 (m, 2H), 2.36 (s, 3H), 2.09 (dt, *J* = 17.0, 2.8 Hz, 1H), 1.96 (dt, *J* = 17.5, 2.2 Hz, 1H), 1.59 (m, 2H), 1.23 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2) *δ* = 184.8, 147.7, 141.1, 136.8, 133.8, 133.6, 129.3, 128.4, 127.4, 127.0, 124.3, 60.4, 36.6, 35.5, 30.2, 29.0, 27.5, 26.7, 23.4, 21.6 ppm.

MS (EI) *m/z* (%): 277 (100), 262 (40), 249 (11), 221 (36), 208 (72), 191 (9), 165 (5).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ (M+H$^+$) 278.190324, found 278.190110.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 4.55 min, t_{min} = 6.81 min.

Catalytic Asymmetric Synthesis of 2*H*-Pyrroles

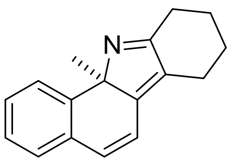
General Procedure for the Synthesis of 2*H*-Pyrroles

A flame-dried Schlenk tube was charged with (*R*)-STRIP or (*S*)-STRIP (10 mol %), $PhCO_2H$ (1.0 equiv.), Amberlite® CG50 (500 mg/mmol), 4Å molecular sieves (500 mg/mmol), and the corresponding ketone (1.0 equiv.) under argon atmosphere. A solution of freshly prepared hydrazine (1.0 equiv.) in degassed *p*-xylene (0.1 M) was added and the reaction was stirred at 40 °C. After full conversion of the hydrazone, diphenyl phosphate (0.5-1.0 equiv.) was added and the reaction was stirred at 40 °C overnight. The crude reaction mixture was directly purified by column chromatography.

Given reaction times are based on full conversion of the hydrazone and before addition of diphenyl phosphate.

The racemates were prepared applying the above procedure, using diphenyl phosphate (1.0 equiv.), Amberlite® CG50 (500 mg/mmol), 4Å molecular sieves (500 mg/mmol), the corresponding ketone (1.0 equiv.) and hydrazine stock solution (1 equiv., 0.1 M in toluene). The reaction was performed at 40 °C for 3-5d. The crude reaction mixture was directly submitted to column chromatography on Alox III.

(*R*)-11a-methyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5a



The reaction was performed at 40 °C for 8 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 14.1 mg, 60 % yield.

90:10 er, $[\alpha]_D^{25}$ = +621 (c = 0.6, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.67-7.65 (m, 1H), 7.20-7.13 (m, 3H), 6.60 (d, J = 9.5 Hz, 1H), 6.57 (d, J = 9.5 Hz, 1H), 2.69-2.66 (m, 2H), 2.60-2.54 (m, 1H), 2.46-2.40 (m, 1H), 1.88-.1.81 (m, 1H), 1.79-1.64 (m, 3H), 1.37 (s, 3H) ppm.

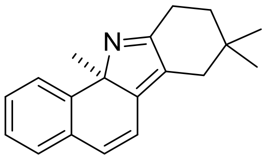
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 174.3, 160.9, 144.9, 133.2, 131.9, 131.3, 129.5, 128.3, 126.8, 125.5, 119.9, 81.6, 32.5, 29.6, 23.5, 23.2 ppm.

MS (ESI) *m/z* (%): 236 (100).

HRMS (ESI) *m/z* calculated for $C_{17}H_{18}N$ (M+H$^+$) 236.143374, found 236.143220.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 4.18 min, t_{maj} = 11.9 min.

(*R*)-8,8,11a-trimethyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5b



The reaction was performed on a 0.05 mmol scale at 30 °C for 5 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 11.9 mg, 90% yield.

95:5 er, $[\alpha]_D^{25}$ = +705 (*c* = 0.5, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.68-7.66 (m, 1H), 7.20-7.13 (m, 3H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.57 (d, *J* = 9.8 Hz, 1H), 2.76-2.65 (m, 2H), 2.34 (d, *J* = 17.0 Hz, 1H), 2.22 (d, *J* = 17.0 Hz, 1H), 1.68-1.60 (m, 2H), 1.37 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2) δ = 173.6, 161.7, 145.0, 133.3, 131.8, 131.2, 129.5, 128.3, 126.8, 125.5, 119.9, 82.3, 37.0, 36.1, 32.9, 30.4, 28.7, 27.5, 25.5 ppm.

^{15}N NMR (51 MHz, CD_2Cl_2) δ = -56.9 ppm.

MS (EI) *m/z* (%): 263 (100), 248 (51), 235 (13), 217 (12), 207 (55), 194 (75), 165 (27), 152 (12).

HRMS (ESI) *m/z* calculated for $C_{19}H_{22}N$ (M+H$^+$) 264.174674, found 264.174600.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 3.98 min, t_{maj} = 8.94 min.

Two step procedure:

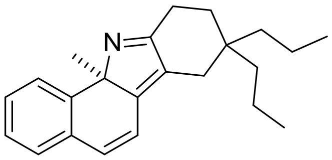
Compound (*R*)-**4b** (10.4 mg, 0.04 mmol) was dissolved in toluene (0.1 M) and diphenyl phosphate (4.9 mg, 0.02 mmol) was added. The reaction mixture was stirred at 40 °C over night and directly purified by coloumn chromatography.

Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 7.1 mg, 68% yield (56% yield over 2 steps).

99:1 er.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 3.97 min, t_{maj} = 9.09 min.

(*R*)-11a-methyl-8,8-dipropyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5c



The reaction was performed at 40 °C for 2 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (10:1) (Alox III), yellow oil, mg, 69% yield.

92.5:7.5 er, $[\alpha]_D^{25}$ = +600 (*c* = 0.9, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) *δ* = 7.68-7.66 (m, 1H), 7.20-7.13 (m, 3H), 6.59 (d, *J* = 9.5 Hz, 1H), 6.57 (d, *J* = 9.5 Hz, 1H), 2.71-2.60 (m, 2H), 2.36 (dd, *J* = 17.0, 1.0 Hz, 1H), 2.22 (d, *J* = 17.0 Hz, 1H), 1.71-1.59 (m, 2H), 1.37 (s, 3H), 1.30-1.16 (m, 8H), 0.92-0-85 (m, 6H) ppm.

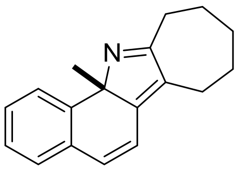
^{13}C NMR (125 MHz, CD_2Cl_2) *δ* = 174.1, 161.7, 144.9, 133.3, 131.7, 131.1, 129.5, 128.3, 126.8, 125.5, 119.9, 82.3, 40.0, 39.0, 35.4, 34.4, 32.9, 32.3, 24.9, 16.8, 15.12, 15.05 ppm.

MS (EI) *m/z* (%): 319(57), 304 (25), 276 (29), 218 (9), 194 (100), 165 (10), 152 (4).

HRMS (ESI) *m/z* calculated for $C_{23}H_{30}N$ (M+H$^+$) 320.237274, found 320.237220.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254, t_{min} = 3.62 min, t_{maj} = 7.41 min.

(*S*)-12a-methyl-7,8,9,10,11,12a-hexahydrobenzo[g]cyclohepta[b]indole 5d



The reaction was performed on a 0.09 M scale at 40 °C for 23 d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (8:1) (Alox III), yellow oil, 12 mg, 53% yield.

90:10 er, $[\alpha]_D^{25}$ = −435 (*c* = 0.4, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) *δ* = 7.67 (d, *J* = 7.35 Hz, 1H), 7.21-7.13 (m, 3H), 6.61 (d, *J* = 9.4 Hz, 1H), 6.57 (d, *J* = 9.5 Hz, 1H), 2.77-2.67 (m, 2H), 2.52-2.47 (m, 1H), 2.43-2.37 (m, 1H), 1.84-1.75 (m, 2H), 1.74-1.61 (m, 3H), 1.59-1.52 (m, 1H), 1.36 (s, 3H) ppm.

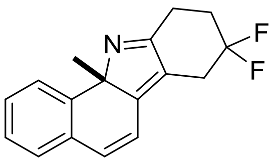
^{13}C NMR (125 MHz, CD_2Cl_2) *δ* = 178.7, 160.3, 144.6, 137.0, 133.3, 131.1, 129.3, 128.3, 126.8, 125.5, 119.9, 81.0, 34.8, 32.7, 32.6, 29.7, 27.7, 26.2 ppm.

MS (EI) *m/z* (%): 249 (100), 234 (44), 220 (26), 206 (24), 194 (95), 178 (14), 165 (25), 152 (13).

HRMS (ESI) *m/z* calculated for $C_{18}H_{20}N$ (M+H$^+$) 250.159024, found 250.158900.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 3.65 min, t_{min} = 11.9 min.

(*S*)-8,8-difluoro-11a-methyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5e



The reaction was performed on a 0.09 M scale at 40 °C for 8 d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (10:1) (Alox III), yellow oil, 12.9 mg, 53% yield.

94:6 er, $[\alpha]_D^{25}$ = −643 (c = 0.625, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.69-7.67 (m, 1H), 7.23-7.16 (m, 3H), 6.66 (d, J = 9.5 Hz,m 1H), 6.57 (d, J = 9.5 Hz, 1H), 3.14-3.05 (m, 1H), 3.00-2.86 (m, 3H), 2.38-2.20 (m, 2H), 1.41 (s, 3H) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2) δ = 170.7, 164.9, 144.5, 133.0, 132.7, 129.9, 128.7, 127.1, 126.0 (dd, J = 5.3, 7.4 Hz), 125.5, 123.7 (t, J = 240 Hz), 119.0, 83.9, 33.0 (t, J = 27 Hz), 32.7, 31.3 (t, J = 25 Hz), 25.1 (dd, J = 5.3, 5.9 Hz) ppm.

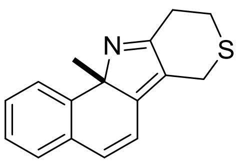
^{19}F NMR (282 MHz, CD_2Cl_2) δ = -96.0 (d, J = 239 Hz, 1F), -97.3 (d, J = 239 Hz, 1F) ppm.

MS (EI) *m/z* (%): 271 (100), 256 (13), 236 (28), 207 (19), 192 (6), 178 (3), 165 (19), 152 (6).

HRMS (ESI) *m/z* calculated for $C_{17}H_{16}NF_2$ (M+H$^+$) 272.124531, found 272.124300.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 6.01 min, t_{min} = 15.6 min.

(*S*)-11a-methyl-7,9,10,11a-tetrahydrobenzo[g]thiopyrano[4,3-b]indole 5f



The reaction was performed on a 0.09 M scale at 40 °C for 9 d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (6:1) (Alox III), yellow oil,12.3 mg, 54% yield.

91:9 er, $[\alpha]_D^{25}$ = −662 (c = 0.35, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.69-7.67 (m, 1H), 7.23-7.16 (m, 3H), 6.65 (d, J = 9.5 Hz, 1H), 6.60 (d, J = 9.5 Hz, 1H), 3.64 (d, J = 16.5 Hz, 1H), 3.56 (d, J = 16.5 Hz, 1H), 3.05-3.02 (m, 2H), 2.95-2.85 (m, 2H), 1.40 (s, 3H) ppm.

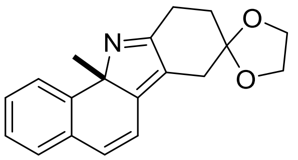
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 171.5, 161.7, 144.4, 132.9, 132.6, 129.8, 128.6, 127.1, 125.6, 119.1, 80.7, 32.5, 32.0, 27.4, 25.5 ppm.

MS (EI) *m/z* (%): 253 (99), 238 (30), 220 (12), 207 (100), 194 (22), 178 (10), 165 (28), 152 (14).

HRMS (ESI) *m/z* calculated for $C_{16}H_{16}NS$ (M+H$^+$) 254.099796, found 254.099800.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 7.93 min, t_{min} = 19.2 min.

(S)-11a-methyl-7,9,10,11a-tetrahydrospiro[benzo[a]carbazole-8,2'-[1,3]dioxolane] 5g



The reaction was performed on a 0.09 M scale at 40°C for 9d, using (*R*)-STRIP as catalyst.

Purification: hexane:EtOAc (8:1 → 1:1) (Alox III), yellow oil, 11.3 mg, 43% yield.

89:11 er, $[\alpha]_D^{25}$ = -514 (*c* = 0.45, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.67-7.66 (m, 1H), 7.20-7.14 (m, 3H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.56 (d, *J* = 9.4 Hz, 1H), 4.01-3.95 (m, 4H), 2.90-2.78 (m, 2H), 2.75 (d, *J* = 18 Hz, 1H), 2.65 (d, *J* = 18 Hz, 1H), 2.04-1.93 (m, 2H), 1.39 (s, 3H) ppm.

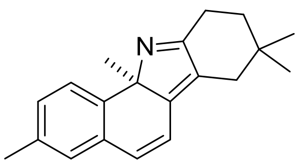
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 172.7, 162.8, 144.8, 133.1, 132.0, 129.9, 129.6, 128.5, 126.9, 125.6, 119.5, 108.6, 83.2, 65.1, 65.0, 33.7, 32.6, 31.9, 26.3 ppm.

MS (EI) *m/z* (%): 293 (100), 278 (8), 249 (19), 234 (7), 220 (11), 207 (57), 194 (21), 178 (12), 165 (20), 152 (10), 99 (44).

HRMS (ESI) *m/z* calculated for $C_{19}H_{20}NO_2$ (M+H$^+$) 294.148854, found 294.148570.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 90:10, 1.0 mL/min, λ = 254 nm, t_{maj} = 5.02 min, t_{min} = 14.1 min.

(*R*)-3,8,8,11a-tetramethyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5h



The reaction was performed at 40 °C for 2 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (12:1) (Alox III), yellow oil, 23.2 mg, 84% yield.

95:5 er, $[\alpha]_D^{25}$ = +603 (*c* = 1.15, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.57-7.55 (m, 1H), 7.02-7.00 (m, 2H), 6.56 (d, *J* = 9.5 Hz, 1H), 6.53 (d, *J* = 9.5 Hz, 1H), 2.76-2.65 (m, 2H), 2.33 (d, *J* = 17.0 Hz, 1H), 2.29 (s, 3H), 2.21 (d, *J* = 17.0 Hz, 1H), 1.68-1.61 (m, 2H), 1.35 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H) ppm.

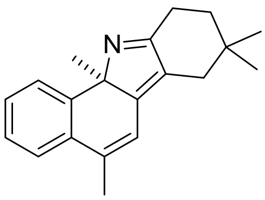
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 173.7, 162.2, 141.9, 136.5, 133.1, 131.6, 131.5, 130.2, 128.9, 125.5, 119.8, 82.2, 37.0, 36.1, 32.9, 30.3, 28.7, 27.5, 25.4, 21.1 ppm.

MS (EI) *m/z* (%): 277 (100), 262 (47), 249 (15), 232 (6), 221 (38), 208 (54), 191 (8), 156 (7).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ (M+H$^+$) 278.190324, found 278.190170.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 3.67 min, t_{maj} = 4.92 min.

(*R*)-5,8,8,11a-tetramethyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5i



The reaction was performed on a 0.05 mmol scale at 30 °C for 3 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 11.5 mg, 83% yield.

95:5 er, $[\alpha]_D^{25}$ = +796 (c = 0.45, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.71-7.69 (m, 1H), 7.41-7.37 (m, 1H), 7.23-7.19 (m, 2H), 6.46 (s, 1H), 2.75-2.64 (m, 2H), 2.31 (d, J = 17.0 Hz, 1H), 2.26 (d, J = 0.5 Hz, 3H), 2.20 (d, J = 17.0 Hz, 1H), 1.67-1.60 (m, 2H), 1.37 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H) ppm.

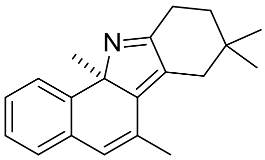
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 174.1, 162.0, 144.5, 137.4, 134.4, 129.8, 128.2, 126.7, 126.1, 125.6, 118.4, 82.0, 36.9, 36.1, 33.0, 30.3, 28.7, 27.6, 25.4, 20.1 ppm.

MS (EI) *m/z* (%): 277 (67), 262 (44), 249 (15), 232 (11), 221 (64), 208 (100), 191 (28), 178 (29), 165 (56), 152 (23).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ (M+H$^+$) 278.190324, found 278.190390.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 98:2, 1.0 mL/min, λ = 254 nm, t_{maj} = 3.99 min, t_{min} = 4.75 min.

(*R*)-6,8,8,11a-tetramethyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5j



The reaction was performed on a 0.075 M scale at 40 °C for 4 d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (15:1) (Alox III), yellow oil, 11.3 mg, 54% yield.

90.5:9.5 er, $[\alpha]_D^{25}$ = +614 (c = 0.325, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.62-7.59 (m, 1H), 7.13-7.07 (m, 3H), 6.29 (s, 1H), 2.76-2.65 (m, 2H), 2.53 (d, J = 17.0 Hz, 1H), 2.37 (d, J = 17.0 Hz, 1H), 2.17 (d, J = 1.4 Hz, 3H), 1.67-1.58 (m, 2H), 1.36 (s, 3H), 1.01 (s, 3H), 0.99 (s, 3H) ppm.

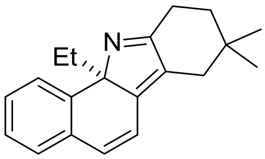
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 173.5, 163.6, 143.6, 134.0, 131.5, 131.3, 128.6, 128.2, 127.3, 126.8, 125.2, 82.9, 39.1, 35.7, 32.2, 30.4, 28.7, 27.9, 25.5, 19.8 ppm.

MS (EI) *m/z* (%): 277 (75), 262 (50), 249 (19), 232 (13), 221 (60), 208 (100), 191 (28), 178 (29), 165 (64), 152 (26).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ (M+H$^+$) 278.190324, found 278.190340.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{min} = 3.34 min, t_{maj} = 4.68 min.

(R)-11a-ethyl-8,8-dimethyl-8,9,10,11a-tetrahydro-7H-benzo[a]carbazole 5k



The reaction was performed at 40°C for 3d, using (*S*)-STRIP as catalyst.

Purification: hexane:EtOAc (12:1) (Alox III), yellow oil, 23 mg, 83% yield.

80:20 er, $[\alpha]_D^{25}$ = +512 (*c* = 0.25, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.65-7.62 (m, 1H), 7.20-7.13 (m, 3H), 6.55 (d, *J* = 9.6 Hz, 1H), 6.53 (d, *J* = 9.6 Hz, 1H), 2.80-2.67 (m, 2H), 2.37 (dd, *J* = 17, 0.9 Hz, 1H), 2.20 (d, *J* = 17 Hz, 1H), 2.11-2.04 (m, 1H), 1.70-1.63 (m, 2H), 1.62-1.55 (m, 1H), 1.01 (s, 6H), 0.52 (t, *J* = 7.3 Hz, 3H) ppm.

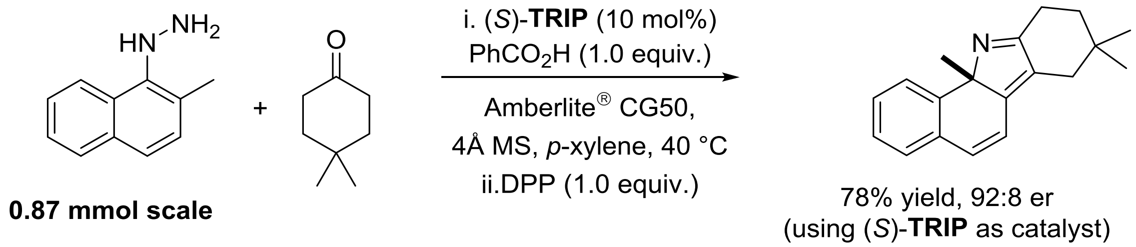
^{13}C NMR (125 MHz, CD_2Cl_2) δ = 174.5, 159.8, 144.7, 133.5, 132.9, 131.4, 129.4, 127.9, 126.8, 126.2, 119.9, 85.4, 38.1, 37.0, 36.1, 30.3, 29.2, 27.0, 25.2, 8.75 ppm.

MS (EI) *m/z* (%): 277 (100), 262 (37), 248 (66), 221 (30), 208 (30), 193 (45), 180 (12), 165 (14).

HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N$ ($M+H^+$) 278.190324, found 278.190110.

HPLC: Daicel Chiralpak OD-3, n-heptane/i-PrOH = 97:3, 1.0 mL/min, λ = 254 nm, t_{maj} = 3.04 min, t_{min} = 3.87 min.

Scale-Up Experiment

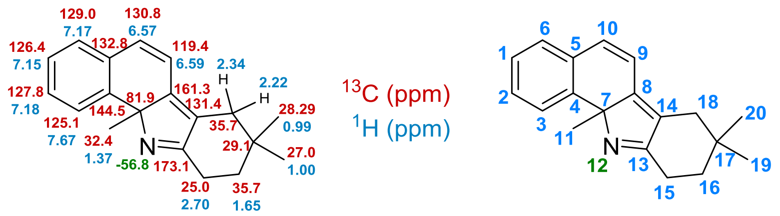


A flame-dried Schlenk tube was charged with (*S*)-TRIP (65.6 mg, 0.087 mmol) $PhCO_2H$ (106 mg, 0.87 mmol), Amberlite® CG50 (435 mg), 4Å molecular sieves (435 mg), and the appropriate ketone (110 mg, 0.87 mmol) under argon atmosphere. A solution of the corresponding freshly prepared hydrazine (150 mg, 0.87 mmol) in degassed *p*-xylene (0.1 M) was added and the reaction was stirred at 40 °C for 4d. After full conversion of the hydrazone, diphenyl phosphate (218 mg, 0.87 mmol) was added and the reaction was stirred at 40 °C overnight. The crude reaction mixture was directly purified by column chromatography.

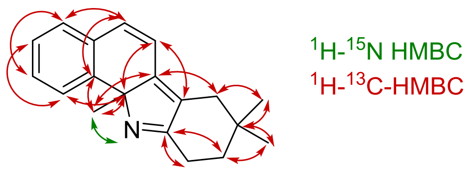
Purification: hexane:EtOAc (20:1) (Alox III), yellow oil, 179 mg
78% yield; 92:8 er

Structure Determination of 2*H*-Pyrroles

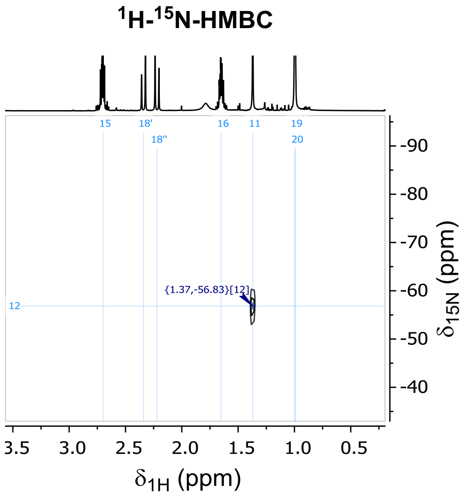
For the structure assignment of 2*H*-pyrroles, compound **5b** was fully characterized by NMR-spectroscopy. The [1,5]-methyl shift could be confirmed by ^{1}H-^{15}N-HMBC measurements which showed the coupling of protons *H*11 of the methyl group to *N*12, indicating that the methyl group is positioned next to the *N*-atom. Additionally, the cross peaks of *H*3, *H*11 and *H*9 to *C*7 in the ^{1}H-^{13}C-HMBC suggest a [1,5]-shift of the methyl group. Also the shift of *C*13 was in agreement with similar literature reported 2*H*-pyrroles.[4]



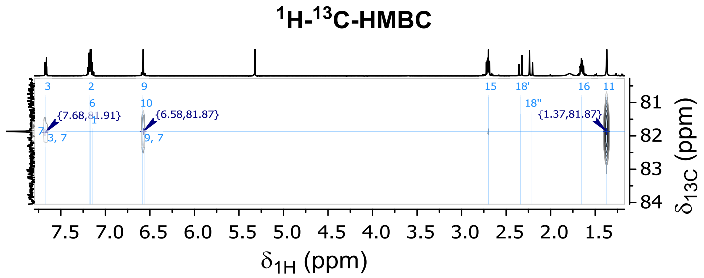
chemical shift assignments



selected correlations from the 2D spectra



Crosspeak between H11 and N12 in the ^{1}H-^{15}N-HMBC.



Slice of ^{1}H-^{13}C-HMBC showing all protons, that couple to C7.

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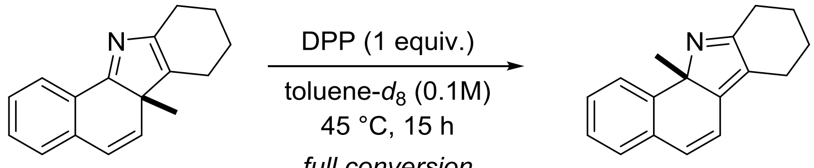
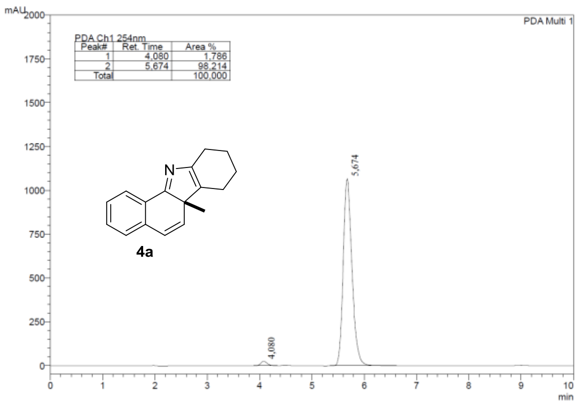
[4] K.-H. Lui, M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1* **1990**, 457-468.

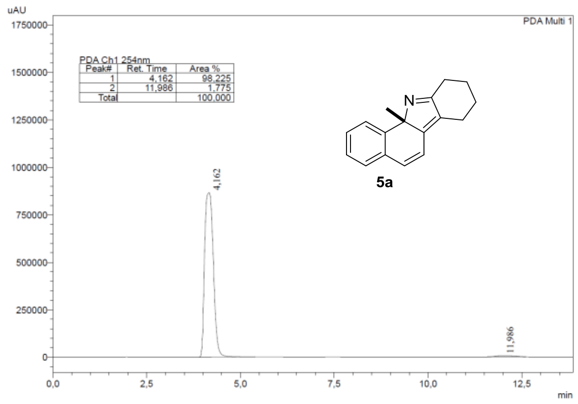
Investigations of [1,5]-Alkyl Shift



4a er = 98:2 **5a** er = 98:2

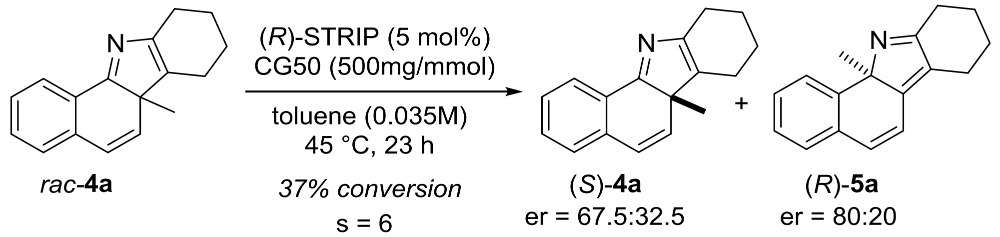
A solution of enantiopure 3*H*-pyrrole **4a** in toluene-d_8 (0.1 M) was treated with diphenyl phosphate (1 equiv.) and stirred at 45 °C. After 15 h **4a** was fully converted into the corresponding 2*H*-pyrrole **5a** without loss of enantioselectivity.





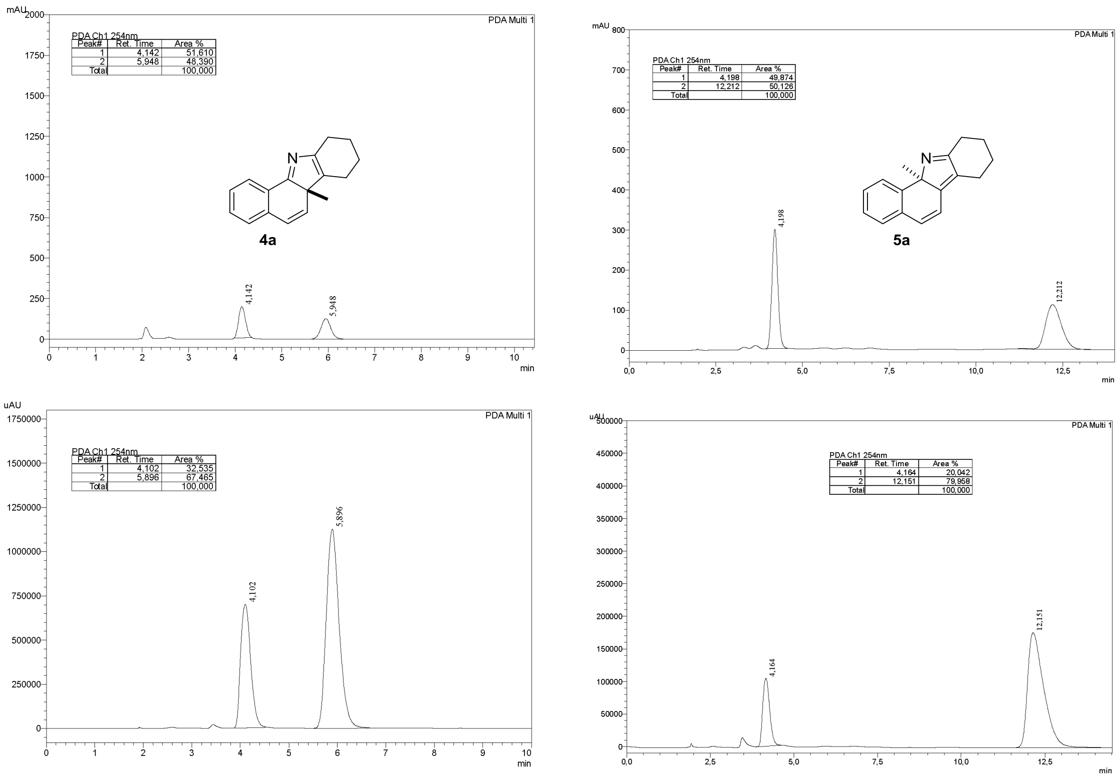
For HPLC traces of racemates: see section HPLC traces.

Kinetic Resolution via [1,5]-Alkyl Shift



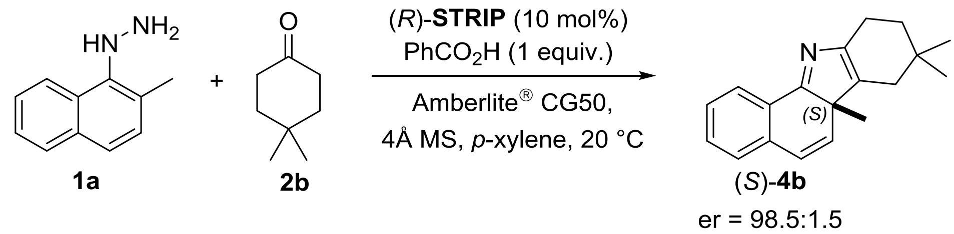
A kinetic resolution of 3*H*-pyrroles **4** via a [1,5]-methyl shift was investigated. Racemic 3*H*-pyrrole **4a** was dissolved in toluene (0.035 M) and treated with (*R*)-STRIP (5 mol%) and CG50 (500 mg/mmol). The mixture was stirred at 45 °C for 23 h, after which 37% of **4a** was converted to **5a**, giving an S-factor of 6 under non-optimized conditions.

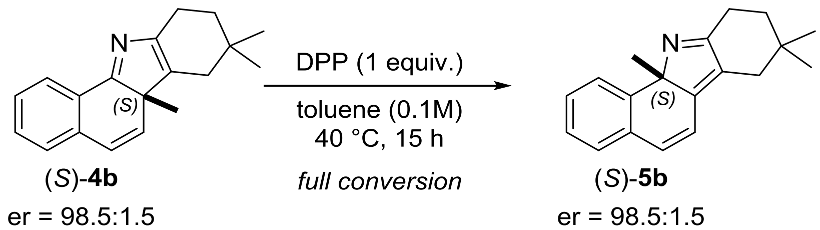
S-factor and Conversion were calculated with the Kagan equation.[5]



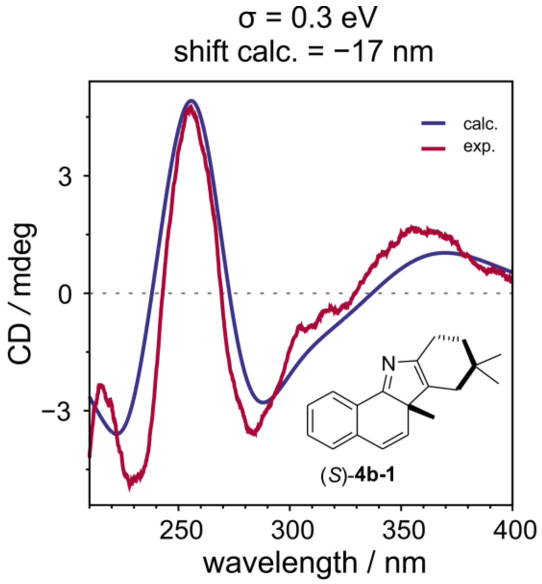
[5] H. B. Kagan, J. C. Fiaud, in *Topics in Stereochemistry*, John Wiley & Sons, Inc., **1988**, 249-330.

Determination of Absolute Configuration





The CD-spectra of (*S*)-**4b** (c = 1.0 x 10^{-4} M) and (*S*)-**5b** (c = 1.0 x 10^{-4} M) were recorded in MeOH (HPLC grade) at 20 °C and compared with the corresponding TD-DFT calculated CD spectra of both possible conformers (*S*)-**4b-1/2** and (*S*)-**5b-1/2** (blue graph, see: chapter *Computational Methods*). After a UV correction of −9 nm to −17 nm and a correction of the σ-value of 0.3 to 0.4 eV, the CD characteristics of the calculated spectra (blue graph) were in good agreement with the experimental spectra (red graph), thus allowing the assignment of the absolute configuration of pyrroles **4b** and **5b**, which were found to be (*S*)-configured, using (*R*)-**STRIP** as catalyst. The retention of stereochemistry during the [1,5]-methyl shift indicates that is stereospecific and occurs in a suprafacial mode.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calc.
exp.
CD / mdeg
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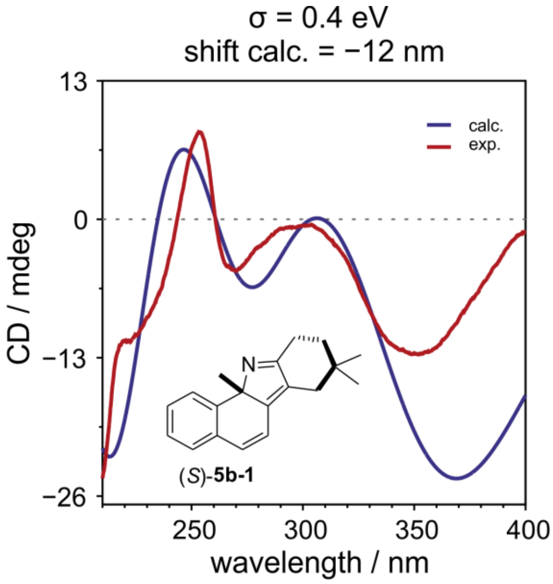
0
−3
250
300
350
400
wavelength / nm
N
(S)-4b-1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calc.
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250
300
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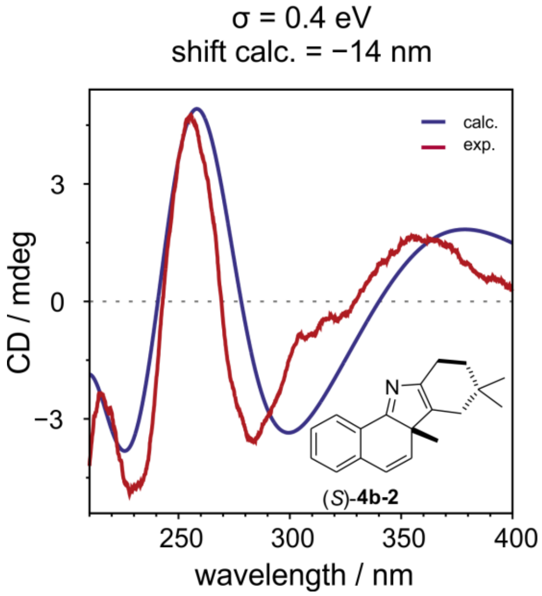
wavelength / nm
N
(S)-5b-1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CD / mdeg
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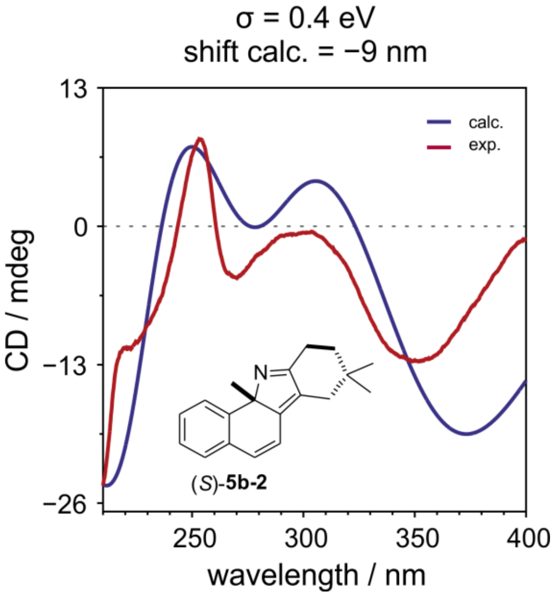
0
−3
250
300
350
400
wavelength / nm
N
(S)-4b-2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calc.
exp.
CD / mdeg
13
0
−13
−26
250
300
350
400
wavelength / nm
N
(S)-5b-2

Biological Part

Biological Assays

Hedgehog pathway inhibition and viability assay

Signal transduction assays through the Hedgehog pathway were conducted, using mouse embryonic mesoderm fibroblast C3H10T1/2 cells. Upon treatment with the SMO agonist Purmorphamine, these multipotent mesenchymal progenitor cells can differentiate into osteoblasts. During differentiation, osteoblast specific genes such as alkaline phosphatase (ALK) are highly expressed. The alkaline phosphatase activity can be monitored via substrate hydrolysis which generates a highly luminescent product. An inhibition of the Hedgehog pathway leads to a reduced luminescence.[6]

Small molecule inhibitor screenings of the Hedgehog pathway were conducted in 384 well format. 800 Cells per well were seeded and grown overnight after which the compounds were added to a final concentration of 10 µM using acoustic nanoliter dispenser ECHO 520. After one hour, Purmorphamine was added to a final concentration of 1.5 µM, whereas the corresponding control cells were not treated with Purmorphamine. After four days, the cell culture medium was aspirated, a commercial luminogenic ALK substrate (CDP-Star, Roche) was added and after one hour, luminescence was read. At the same time, cell viability measurements were conducted to identify and exclude toxic compounds which also lead to a reduced luminescent signal. For the cell viability assay 200 cells per well were seeded, following the same procedure as described for the Hedgehog assay, using cell culture medium alone as control. Cell Titer Glo reagent (Promega), determining the cellular ATP content, was used to measure the cell viability. Hits were defined showing at least a 50% reduction in the luminescent signal in the Hedgehog assay and a minimum of 80% cell viability. A three-fold dilution curve, starting from 10 µM, was used to carry out dose-response analysis for hit compounds. For the calculations of the IC_{50} values, Quattro software suite (Quattro Research GmbH) was used.

Smoothened binding assay using fluorescence microscopy

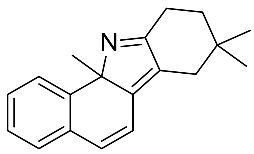
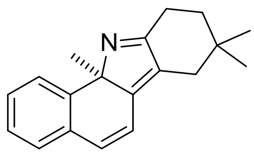
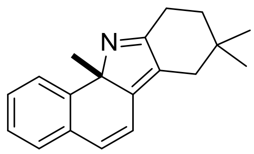
The assay was performed as described in literature.[7] 1.5×10^4 HEK293T cells were seeded on poly-D-lysine-coated coverslips placed in a 24-well plate. After 12 h incubation cells were transfected with the Smoothened expressing plasmid pGEN-mSmo (Addgene no. 37673) using Fugene HD (Promega) according to the manufacturer’s protocol. After 48 h incubation at 37°C cells were washed once with

[6] a) X. Wu, S. Ding, Q. Ding, N. S. Gray, P. G. Schultz *J. Am. Chem. Soc.***2002**, *124*, 14520-14521; b) M. M. Beloti, L. S. Bellesini, A. L. Rosa, *Cell Biol. Int.* **2005**, *29*, 537-541; b) X. Wu,1 J. Walker, J. Zhang, S Ding, P. G. Schultz *Chem. Biol.* 2004, 11, 1229-1238; c) X.-J Li, B.-Y. Hu, S. A. Jones, Y.-S. Zhang, Y. Sha, T. Lavaute, Z.-W. Du, *Stem Cells* **2008**, *26*, 886-893; d) S. Sinha, J. K. Chen, *Nat. Chem. Biol.* **2006**, *2*, 29-30.

[7] S. Sinha, J. K. Chen, *Nat Chem Biol* **2006**, *2*, 29-30.

phosphate-buffered saline (PBS) and fixed with 3% paraformaldehyde for 10 min at room temperature and subsequent permeabilization with 0.2 % sodium azide in 1X PBS for 5 min at room temperature. The cells were washed once with PBS and incubated further in fresh DMEM medium containing 0.5% fetal bovine serum (FBS), 5 nM BODIPY-cyclopamine and various concentrations of the test compounds or DMSO as a control. One hour later cells were washed twice with PBS. Cells were then stained with 1 µg/mL DAPI for 10 min and were mounted on glass slides using Aqua Poly/mount (Polysciences Inc). Images were acquired on an Axiovert Observer Z1 microscope (Carl Zeiss, Germany) using a Plan-Apochromat 63x/1.40 Oil DIC M27 objective.

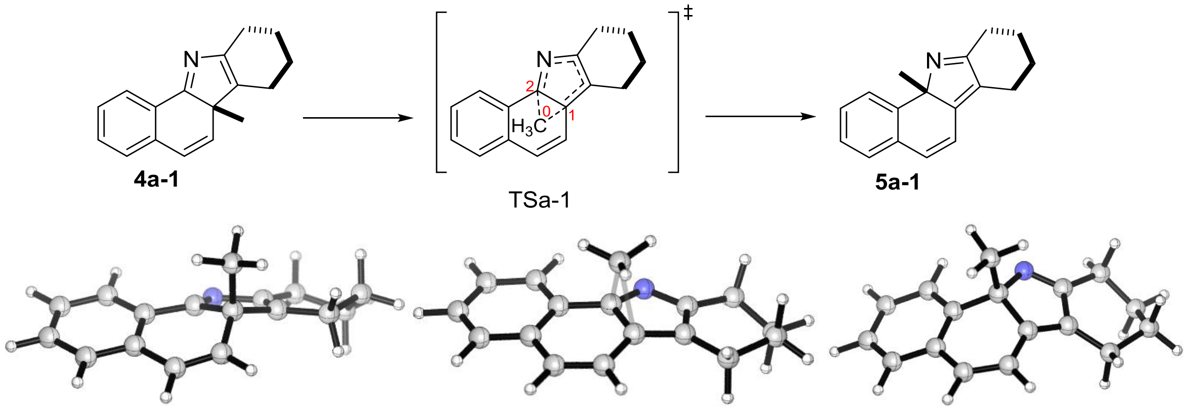
Biological Results

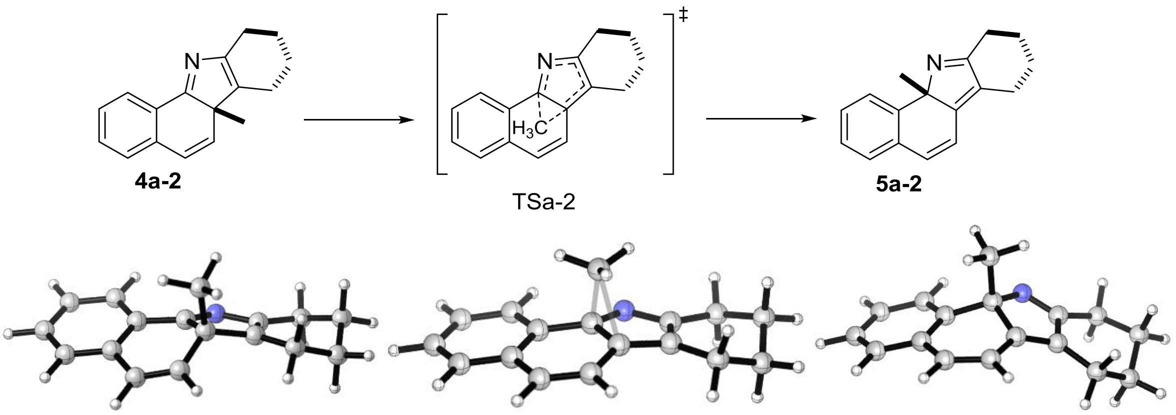
Entry	**Structure**	**Compound**	**mean IC_{50} [µM][a)]**	**IC_{50} [µM][b)] (viability)**
1		*rac*-**5b**	5.06 ± 0.67	inactive
2		(*R*)-**5b**[c)]	6.80 ± 0.82	inactive
3		(*S*)-**5b**	7.58 ± 1.25	inactive

a) Mean IC_{50} values ± standard deviation (n≥3) for inhibition of the Hedgehog signaling pathway as determined in an osteogenesis assay. b) Influence on the viability of C3H10T1/2 cells, using the CellTiter-Glo assay. c) (n≥2).

Computational Part

Calculations of [1,5]-Methyl Shift



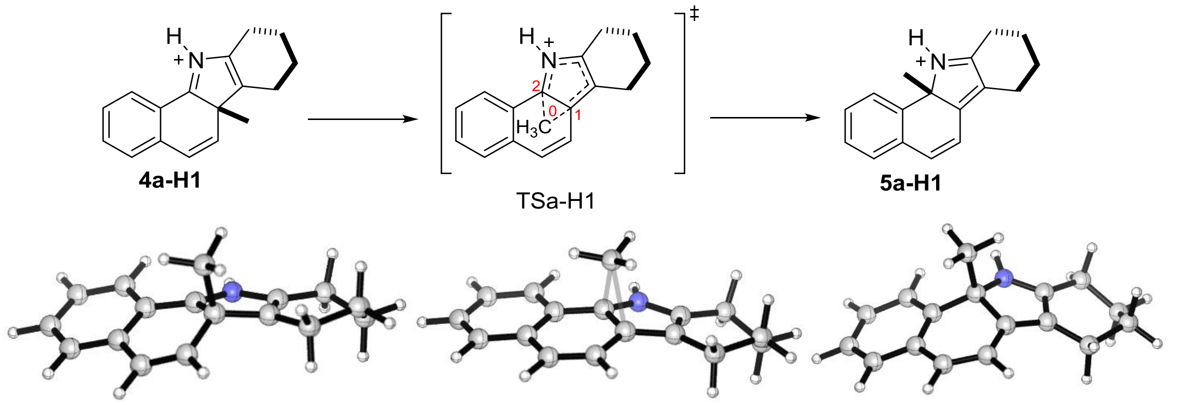


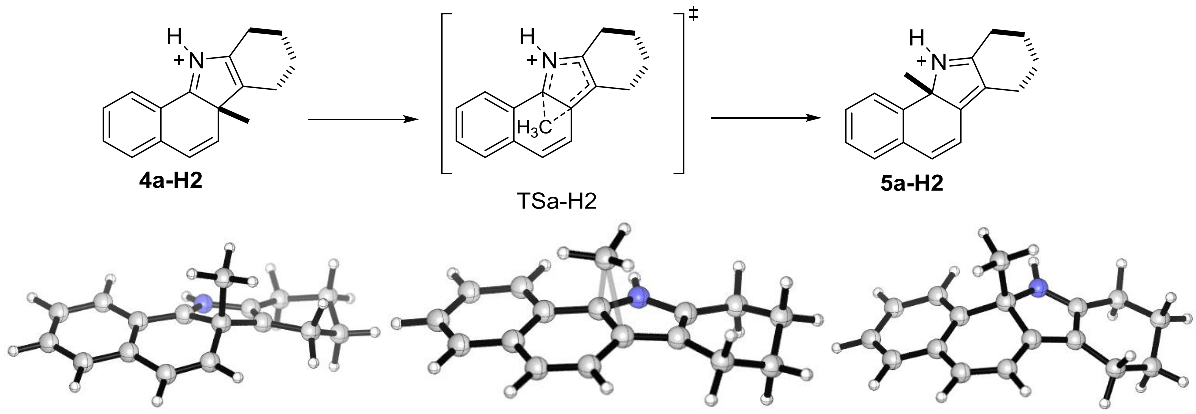
Selected distances for all the computed species at the B3LYP-D3/TZVP level (distance in Å).

	C0-C1	C0-C2
4a-1	1.56	2.50
TSa-1	2.07	2.05
5a-1	2.50	1.55
4a-2	1.56	2.50
TSa-2	2.07	2.05
5a-2	2.50	1.55

Computed relative energy (*E*), enthalpy (*H*), and free energy (*G*) at the B3LYP-D3/TZVP level (energy in kcal/mol).

	E	*H*	*G*
4a-1	0	0	0
TSa-1	29.7	29.7	29.8
5a-1	-5.1	-5.2	-4.9
4a-2	0	0	0
TSa-2	29.7	29.7	29.7
5a-2	-4.9	-5.0	-4.8



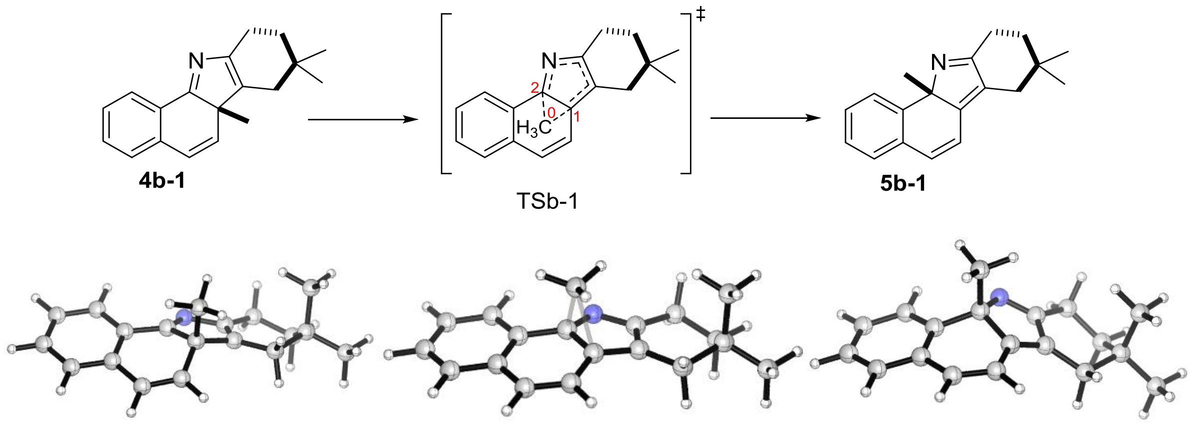


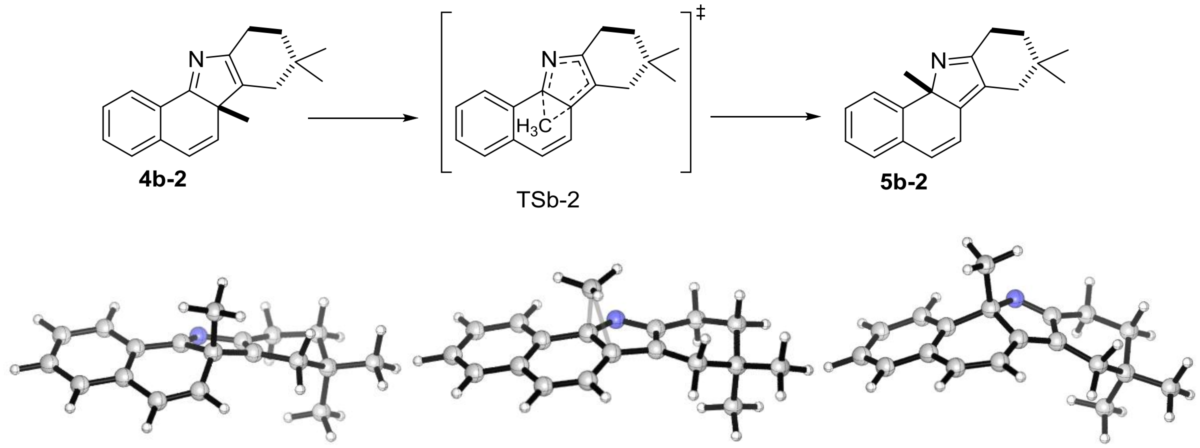
Selected distances for all the computed species at the B3LYP-D3/TZVP level (distance in Å).

	C0-C1	**C0-C2**
4a-H1	1.59	2.45
TSa-H1	2.08	2.05
5a-H1	2.50	1.56
4a-H2	1.59	2.56
TSa-H2	2.07	2.05
5a-H2	2.49	1.56

Computed relative energy (*E*), enthalpy (*H*), and free energy (*G*) at the B3LYP-D3/TZVP level (energy in kcal/mol).

	E	***H***	***G***
4a-H1	0	0	0
TSa-H1	19.2	19.3	19.0
5a-H1	-9.2	-9.2	-9.1
4a-H2	0.1	0.1	0.1
TSa-H2	19.2	19.3	19.0
5a-H2	-9.0	-9.0	-9.0



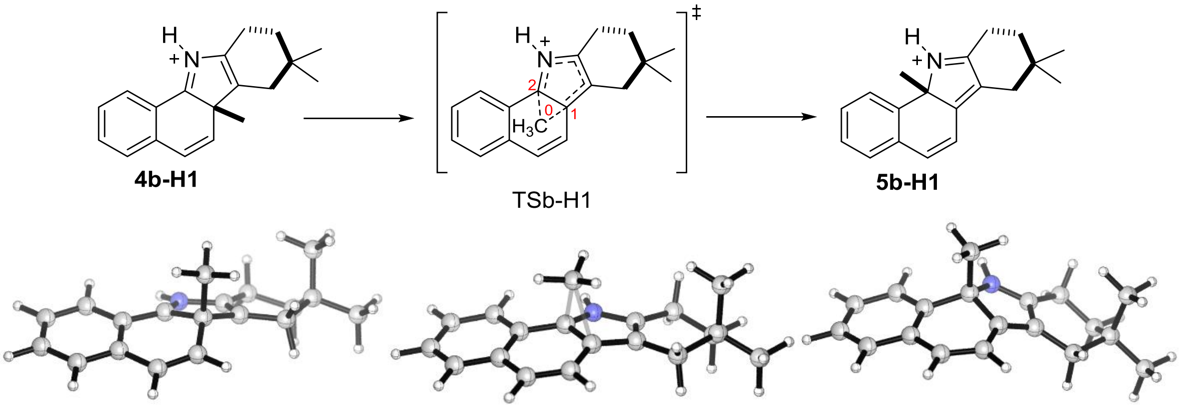


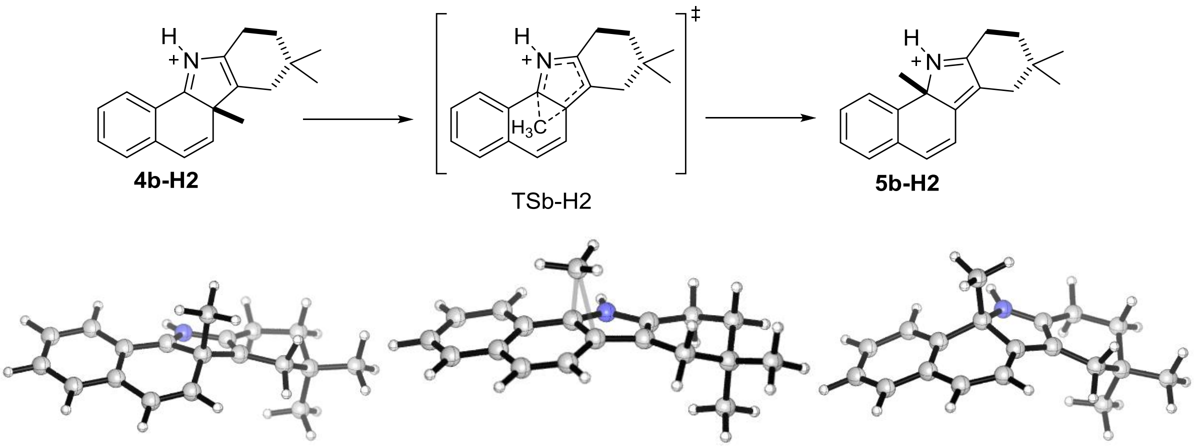
Selected distances for all the computed species at the B3LYP-D3/TZVP level (distance in Å).

	C0-C1	**C0-C2**
4b-1	1.56	2.50
TSb-1	2.07	2.05
5b-1	2.50	1.55
4b-2	1.56	2.50
TSb-2	2.08	2.05
5b-2	2.50	1.55

Computed relative energy (*E*), enthalpy (*H*), and free energy (*G*) at the B3LYP-D3/TZVP level (energy in kcal/mol).

	E	***H***	***G***
4b-1	0	0	0
TSb-1	29.7	29.8	29.7
5b-1	-4.8	-4.9	-4.9
4b-2	0.1	0.2	0
TSb-2	29.8	29.9	29.8
5b-2	-4.8	-4.9	-4.9





Selected distances for all the computed species at the B3LYP-D3/TZVP level (distance in Å).

	C0-C1	C0-C2
4b-H1	1.59	2.45
TSb-H1	2.08	2.05
5b-H1	2.49	1.56
4b-H2	1.59	2.46
TSb-H2	2.08	2.05
5b-H2	2.49	1.56

Computed relative energy (*E*), enthalpy (*H*), and free energy (*G*) at the B3LYP-D3/TZVP level (energy in kcal/mol).

	E	*H*	*G*
4b-H1	0	0	0
TSb-H1	19.2	19.4	19.1
5b-H1	-9.0	-9.0	-9.0
4b-H2	0.2	0.3	0.2
TSb-H2	19.3	19.6	18.8
5b-H2	-9.0	-9.0	-9.1

The [1,5]-methyl shift was calculated for two conformers of pyrroles **4a**/**b** and **5a**/**b** which are very similar in energy (difference ~0.1-0.2 kcal/mol) at room temperature (298.15 K). In the absence of an acid, the energy barrier of the [1,5]-methyl shift is ~30 kcal/mol. Upon full protonation of the nitrogen via a strong acid, the energy barrier is lowered by ~10 kcal/mol to ~20 kcal/mol. For weaker acids, the energy barrier is lowered less.

Computational Methods

All computations were carried out using the Gaussian 09 program package[1]. Geometries were optimized using the B3LYP-D3 functional[2,3] and TZVP basis set[4]. Each stationary point was confirmed to be either a minimum or transition state (TS) structure by using both frequency and intrinsic reaction coordinate (IRC)[5] calculations. The electronic circular dichroism (ECD) spectra were predicted using time-dependent density functional theory (TD-DFT)[6] with the TD-B3LYP-D3/TZVP method with inclusion of continuum solvation[7] (MeOH). The ECD spectra were generated using the program SpecDis.[8] The corresponding settings are given in the individual experiments.

References:

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6. (a) Furche, F.; Ahlrichs. R. *J. Chem. Phys*., **2002,** *117*, 7433. (b) Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. *J. Chem. Phys.*, **2006,** *124*, 094107.
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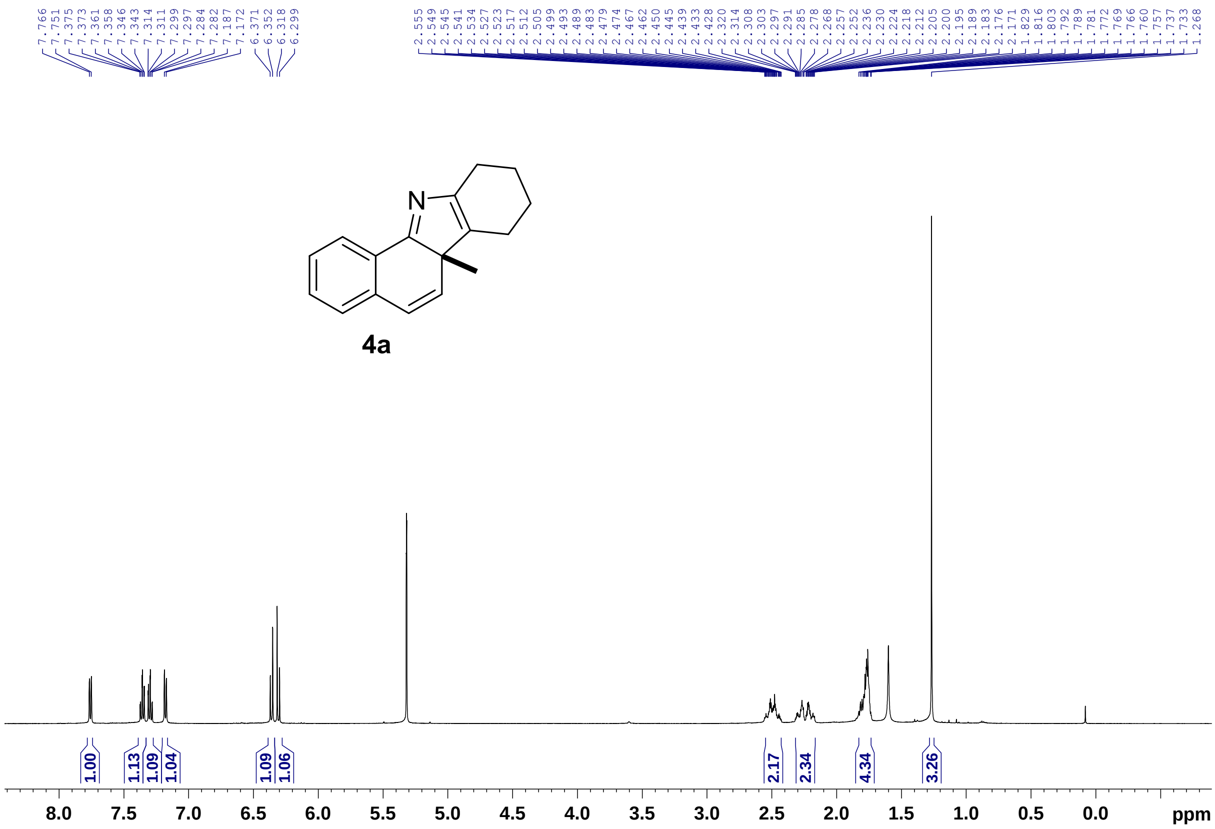
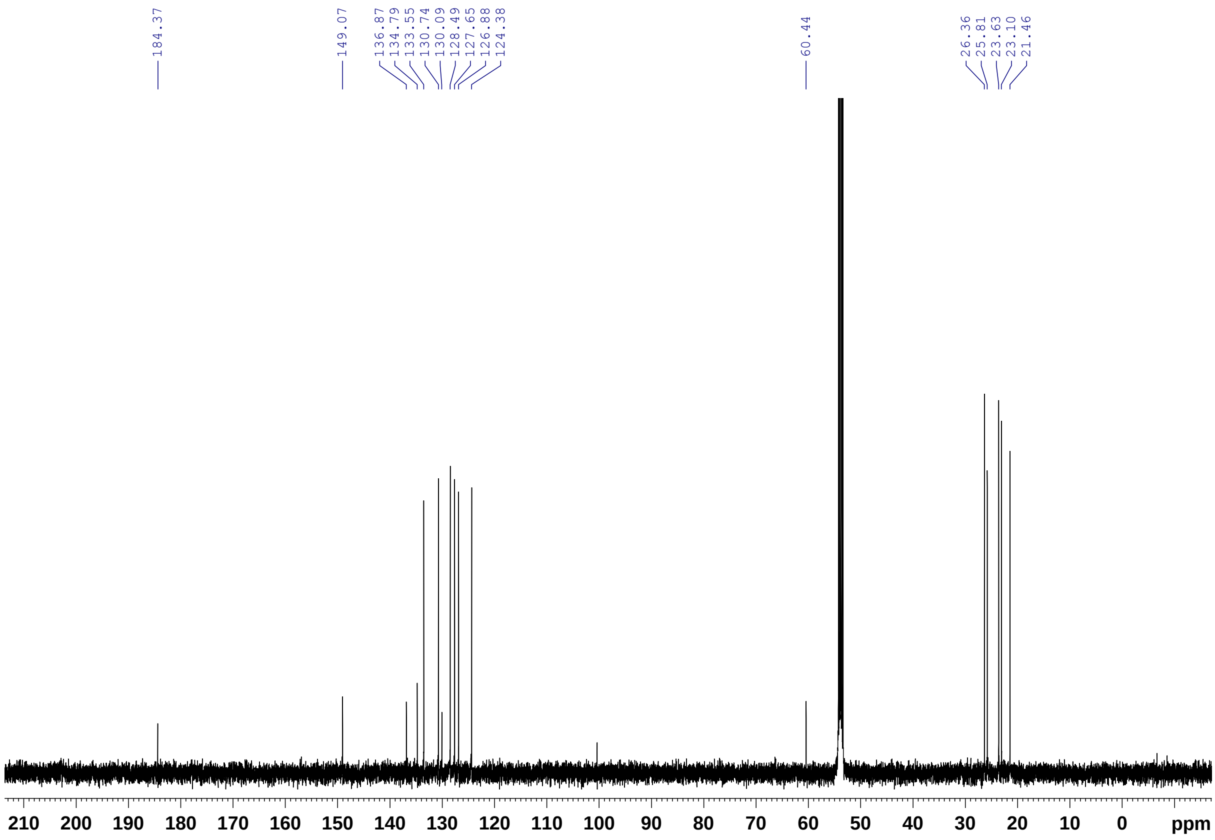
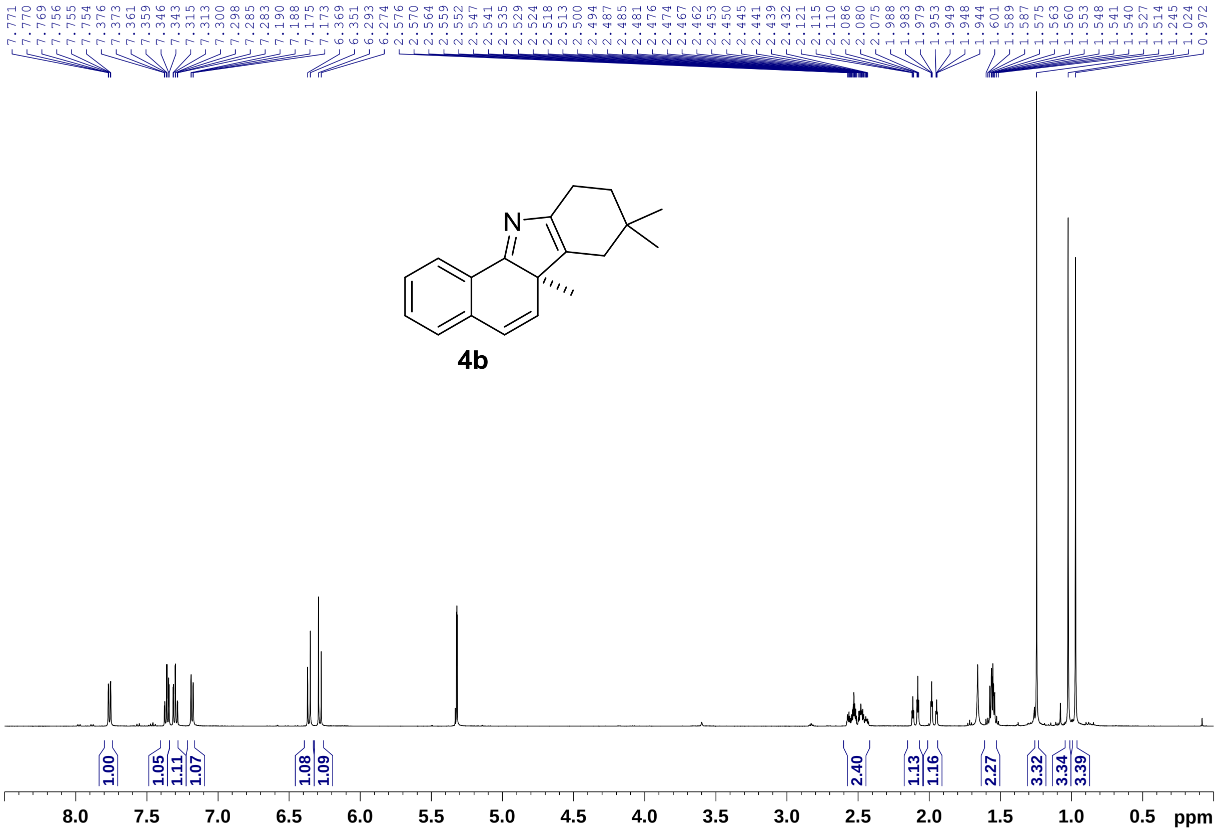
8. a) Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. SpecDis version 1.63, University of Würzburg, Germany, **2015**. b) Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. Chirality **2013**, *25*, 243.

Copies of NMR Spectra

3*H*-Pyrroles







7.771 7.770 7.769 7.756 7.755 7.754 7.376 7.373 7.361 7.359 7.346 7.343 7.315 7.313 7.300 7.298 7.285 7.283 7.190 7.188 7.175 7.173 6.369 6.351 6.293 6.274 2.576 2.570 2.564 2.559 2.552 2.547 2.541 2.535 2.529 2.524 2.518 2.513 2.500 2.494 2.487 2.485 2.481 2.476 2.474 2.467 2.462 2.453 2.450 2.445 2.441 2.439 2.432 2.121 2.115 2.110 2.086 2.080 2.075 1.988 1.983 1.979 1.953 1.949 1.948 1.944 1.601 1.589 1.587 1.575 1.563 1.560 1.553 1.548 1.541 1.540 1.527 1.514 1.245 1.024 0.972
N
4b
1.00
1.05
1.11
1.07
1.08
1.09
2.40
1.13
1.16
2.27
3.32
3.34
3.39
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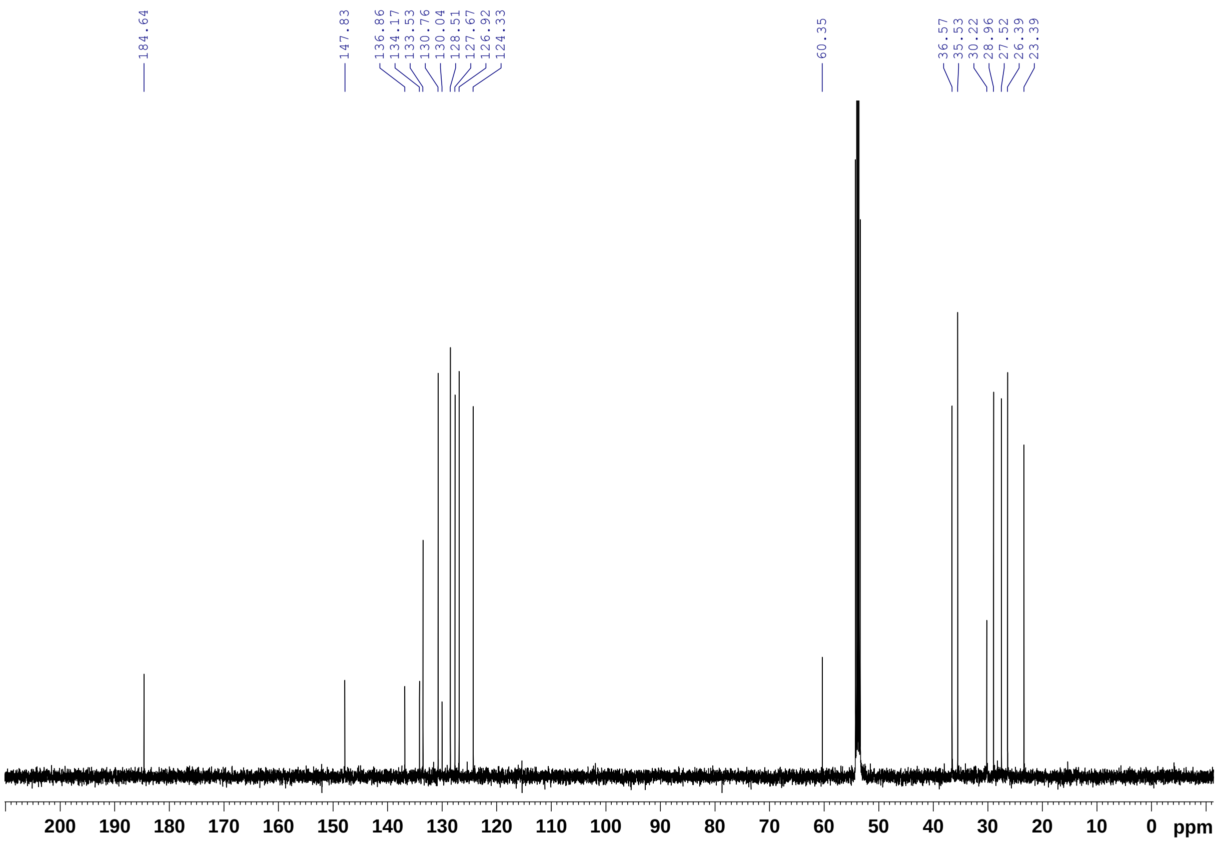

184.64
147.83
136.86 134.17 133.53 130.76 130.04 128.51 127.67 126.92 124.33
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36.57 35.53 30.22 28.96 27.52 26.39 23.39
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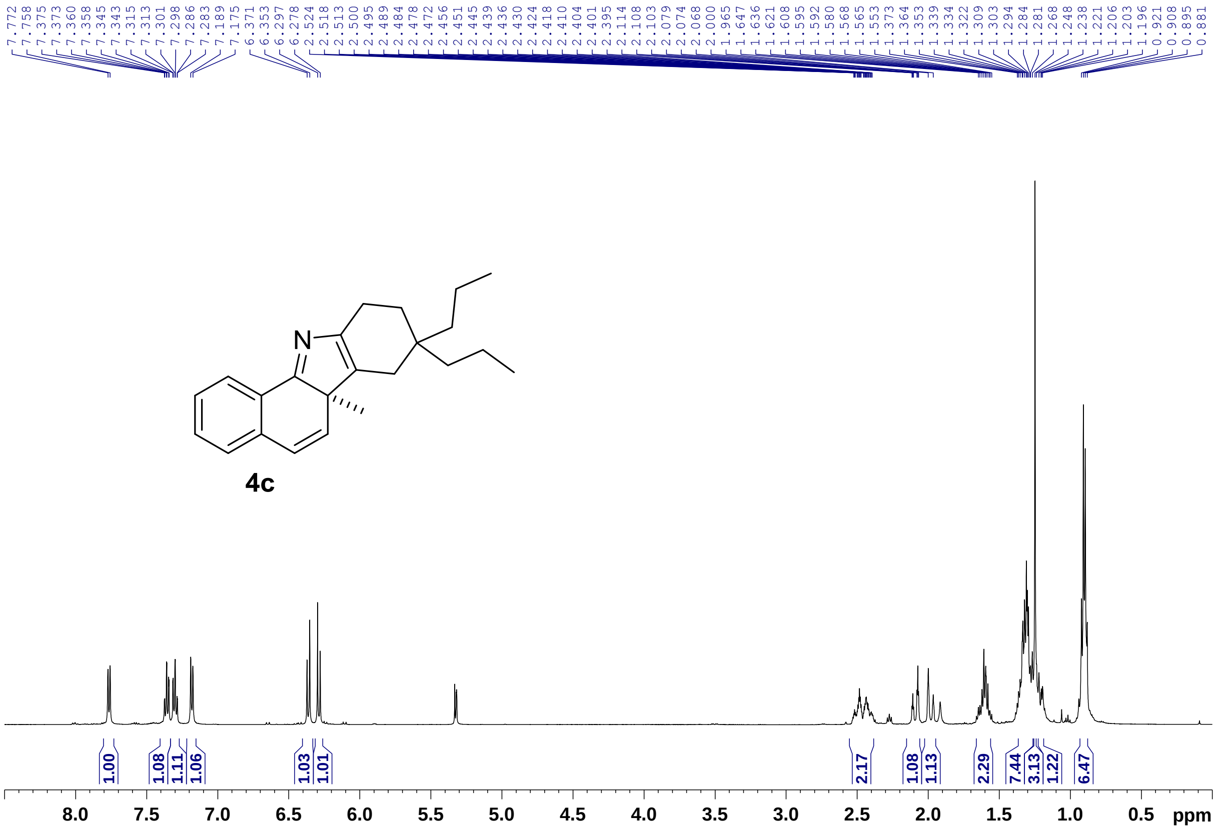
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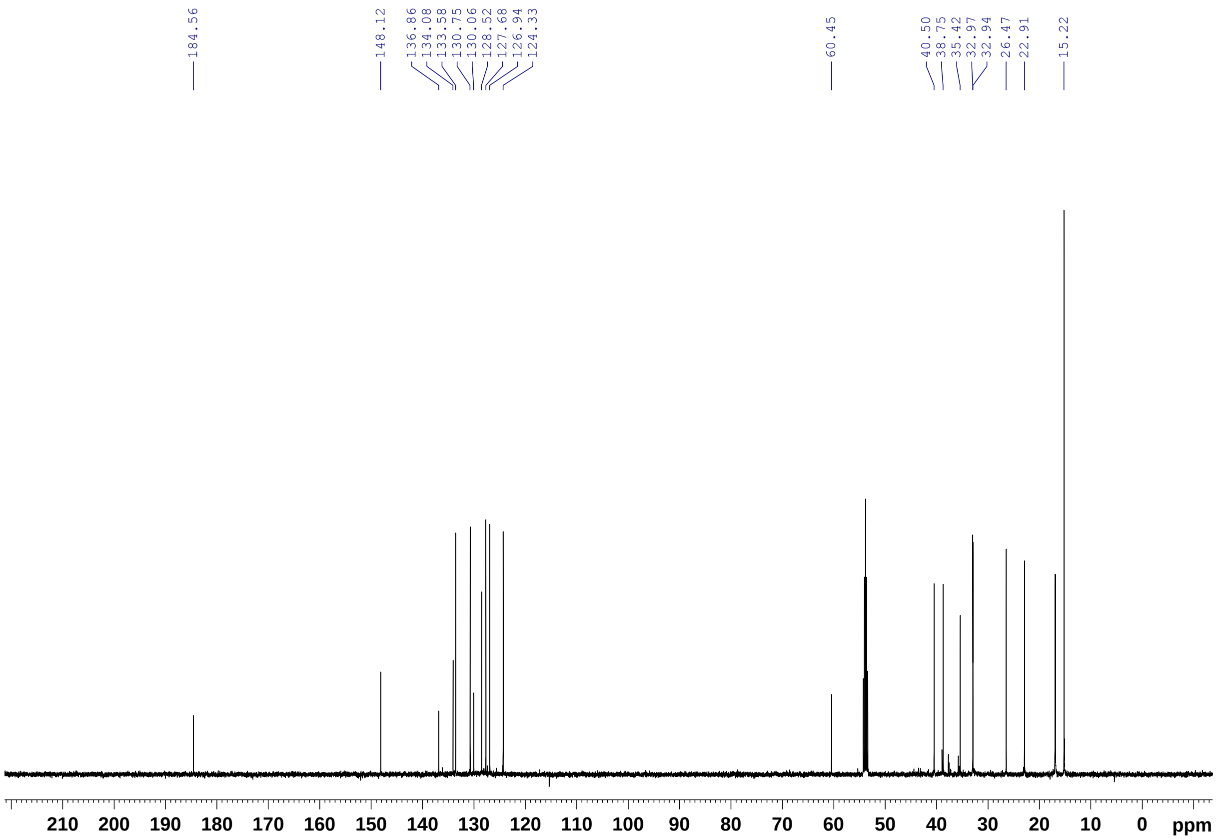
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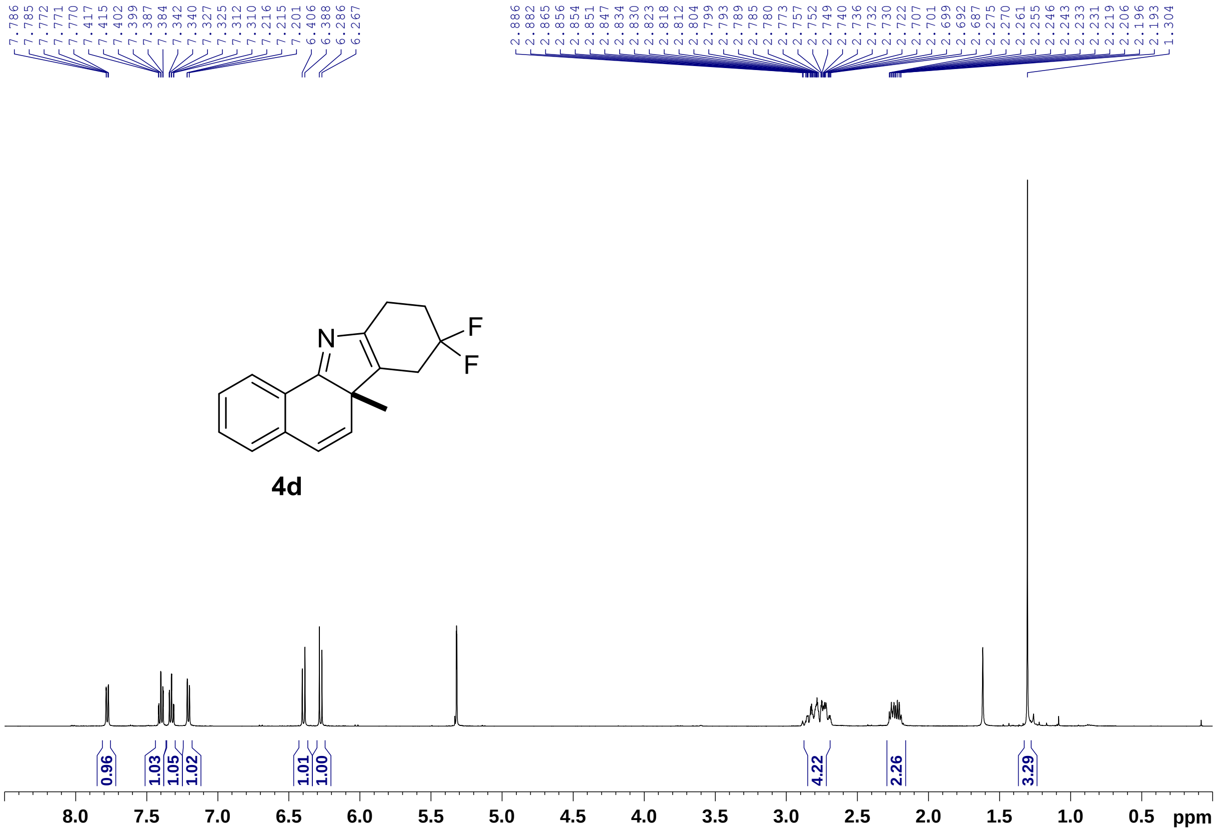
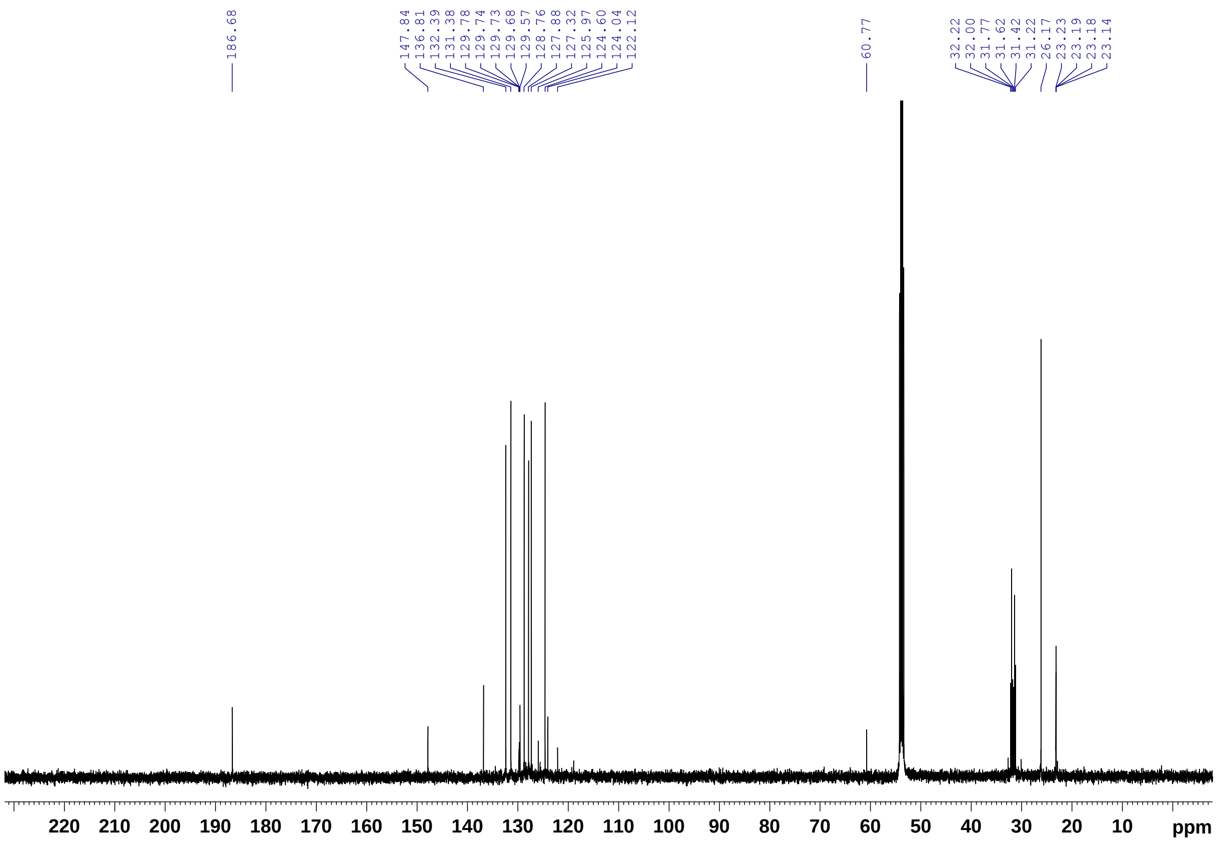
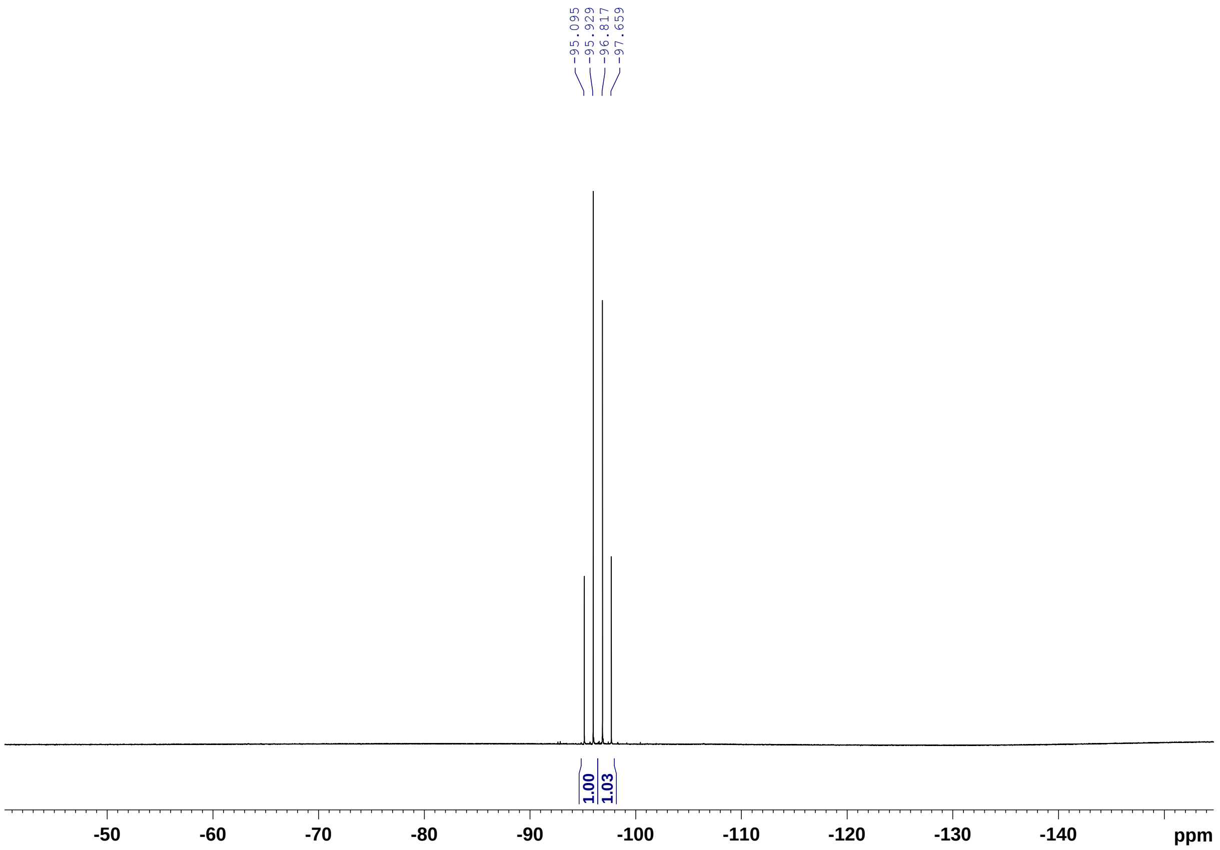

7.786 7.785 7.772 7.771 7.770 7.417 7.415 7.402 7.399 7.387 7.384 7.342 7.340 7.327 7.325 7.312 7.310 7.216 7.215 7.201 6.406 6.388 6.286 6.267
2.886 2.882 2.865 2.856 2.854 2.851 2.847 2.834 2.830 2.823 2.818 2.812 2.804 2.799 2.793 2.789 2.785 2.780 2.773 2.757 2.752 2.749 2.740 2.736 2.732 2.730 2.722 2.707 2.701 2.699 2.692 2.687 2.275 2.270 2.261 2.255 2.246 2.243 2.233 2.231 2.219 2.206 2.193 1.304
N
F
F
4d
0.96 1.03 1.05 1.02 1.01 1.00 4.22 2.26 3.29
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


186.68
147.84 136.81 132.39 131.38 129.78 129.74 129.73 129.68 129.57 128.76 127.88 127.32 125.97 124.60 124.04 122.12
60.77
32.22 32.00 31.77 31.62 31.42 31.22 26.17 23.23 23.19 23.18 23.14
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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-95.929
-96.817
-97.659
1.00
1.03
-50
-60
-70
-80
-90
-100
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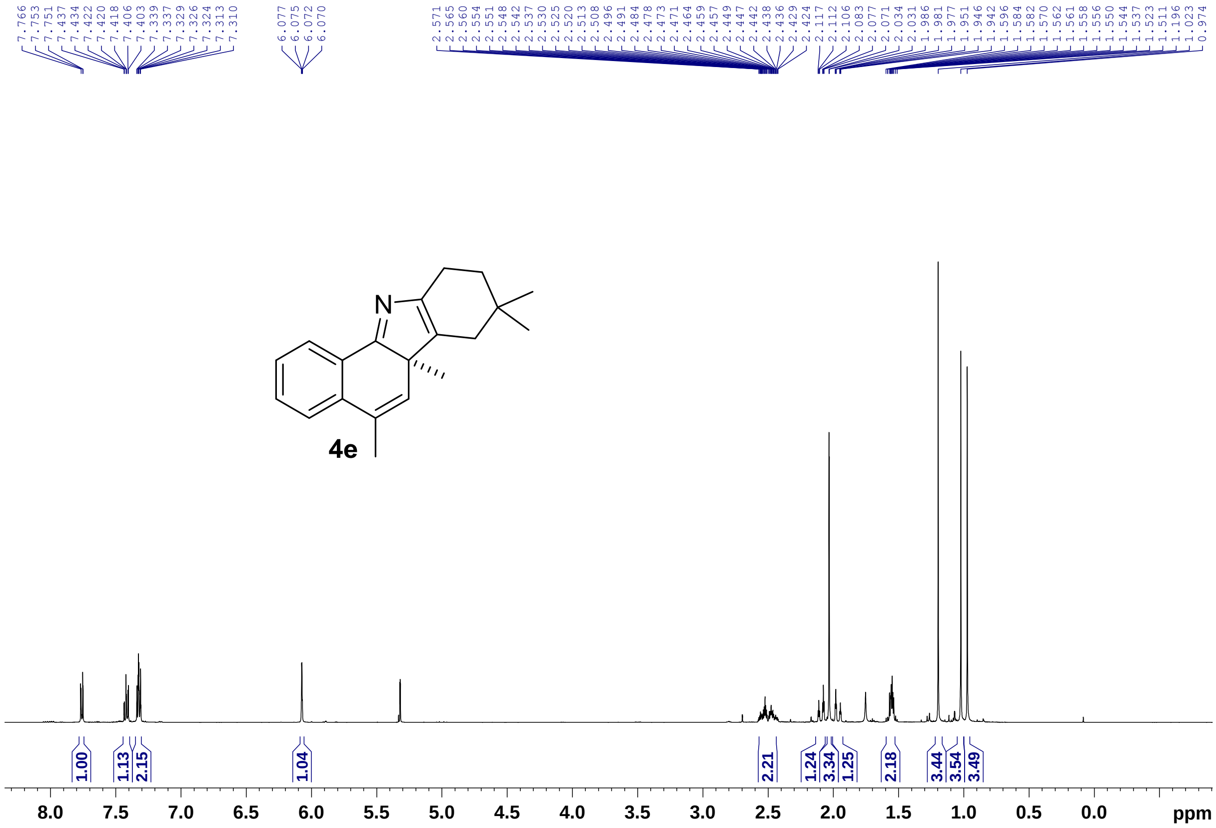
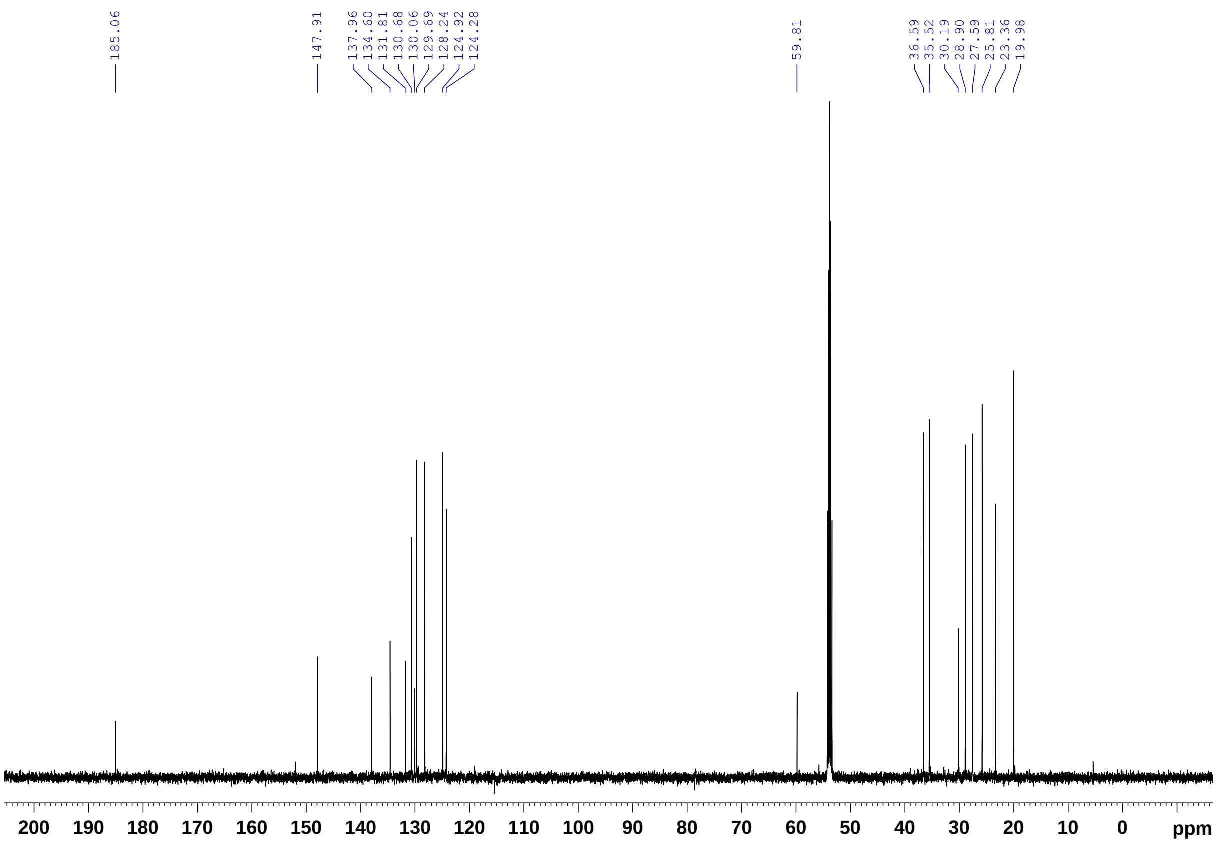
-120
-130
-140
ppm


4e
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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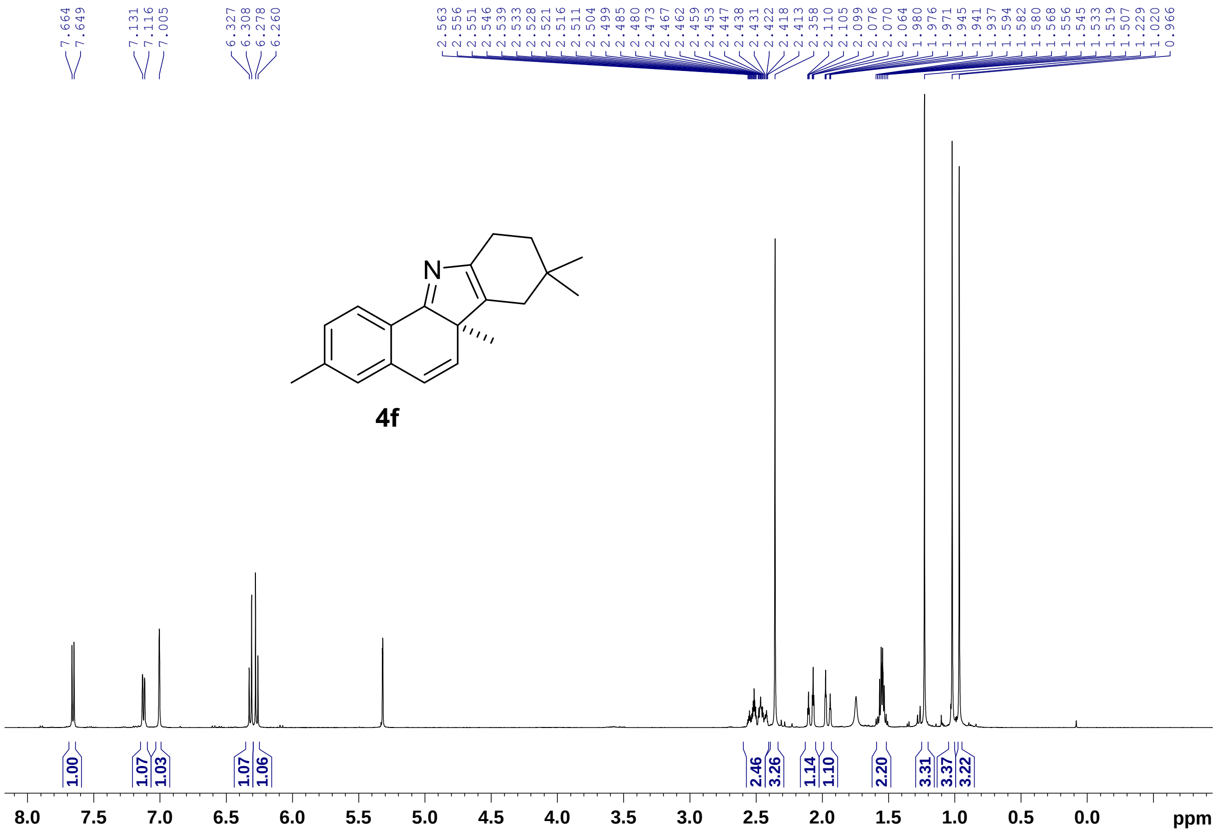
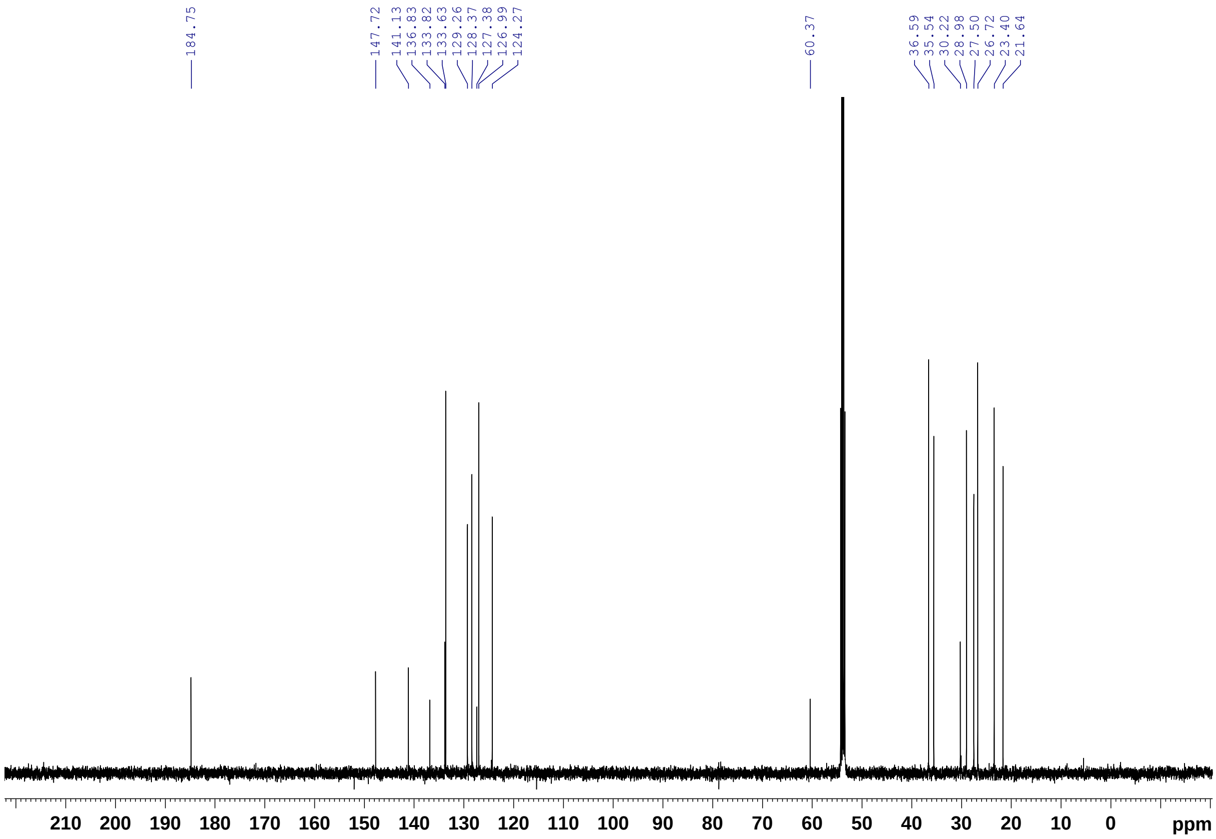
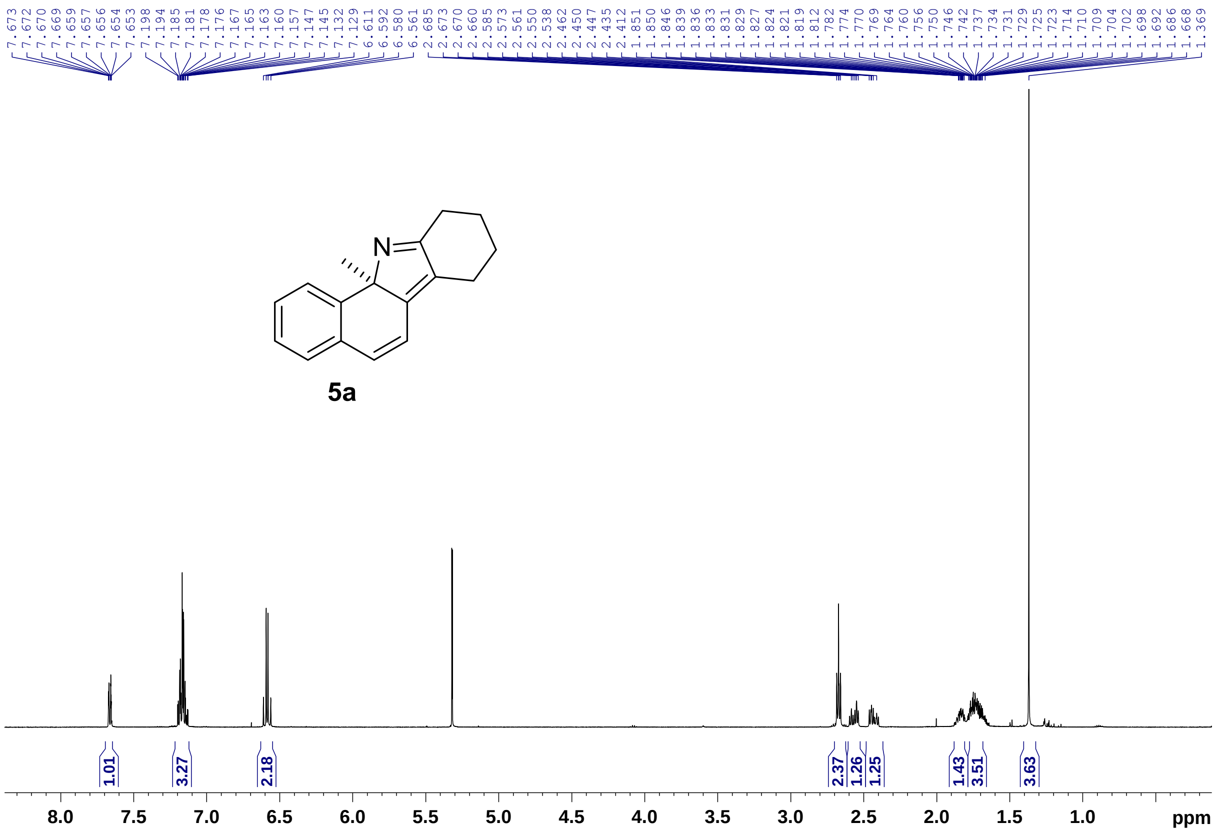
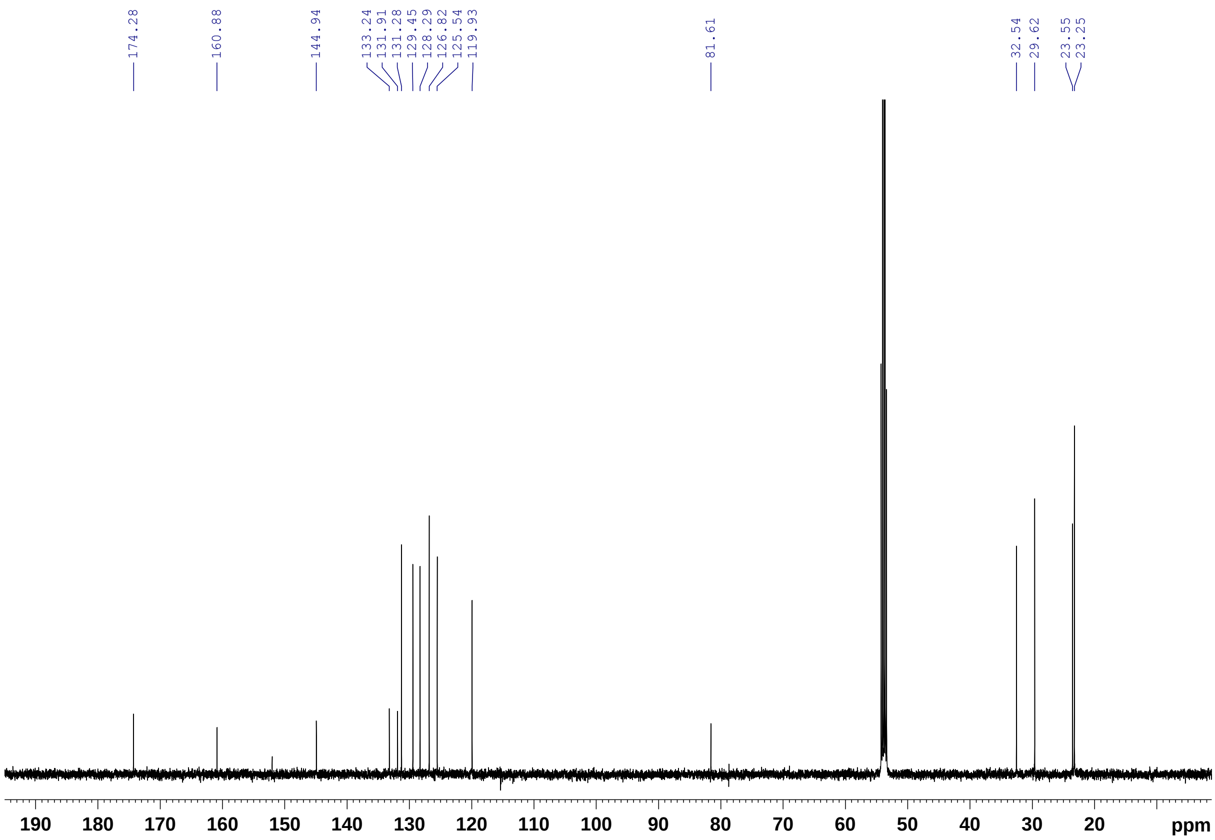
147.91
137.96
134.60
131.81
130.68
130.06
129.69
128.24
124.92
124.28
59.81
36.59
35.52
30.19
28.90
27.59
25.81
23.36
19.98
ppm

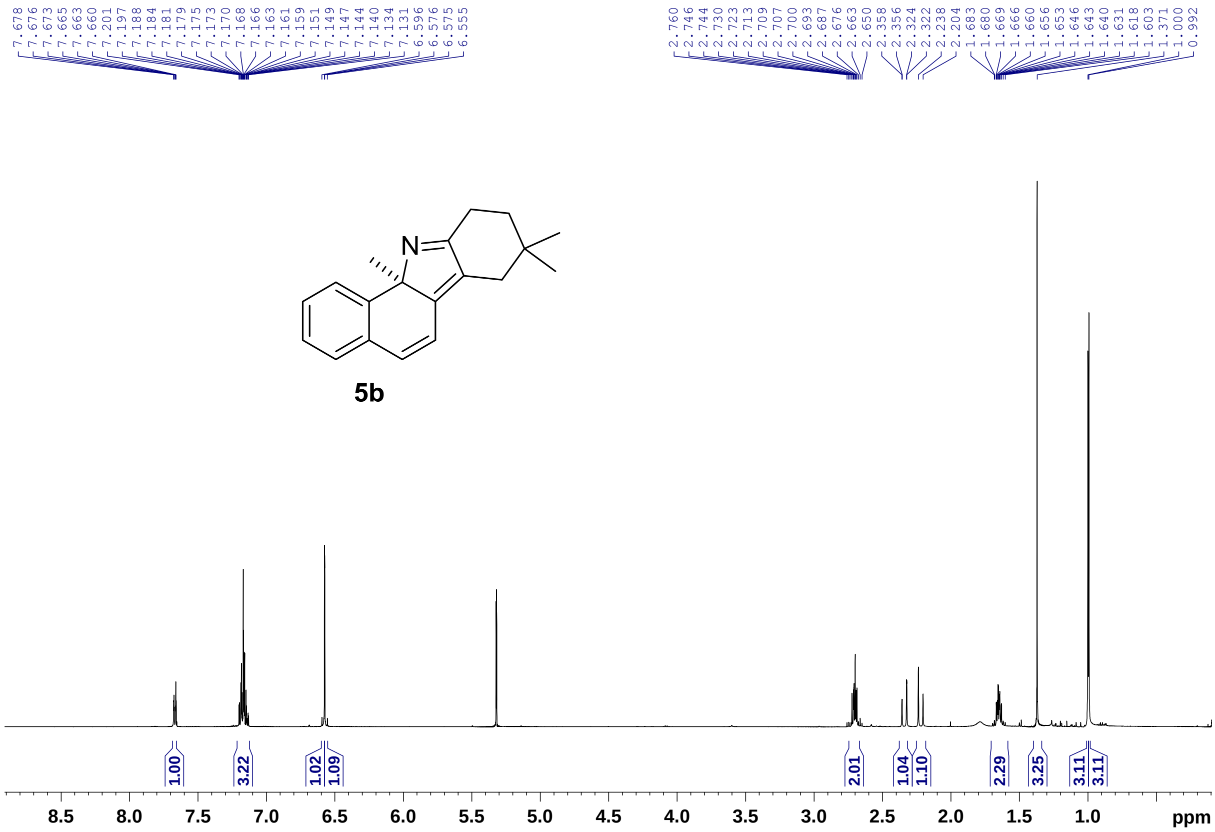

7.664
7.649
7.131
7.116
7.005
6.327
6.308
6.278
6.260
2.563 2.556 2.551 2.546 2.539 2.533 2.528 2.521 2.516 2.511 2.504 2.499 2.485 2.480 2.473 2.467 2.462 2.459 2.453 2.447 2.438 2.431 2.422 2.418 2.413 2.358 2.110 2.105 2.099 2.076 2.070 2.064 1.980 1.976 1.971 1.945 1.941 1.937 1.594 1.582 1.580 1.568 1.556 1.545 1.533 1.519 1.507 1.229 1.020 0.966
N
4f
1.00
1.07
1.03
1.07
1.06
2.46
3.26
1.14
1.10
2.20
3.31
3.37
3.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

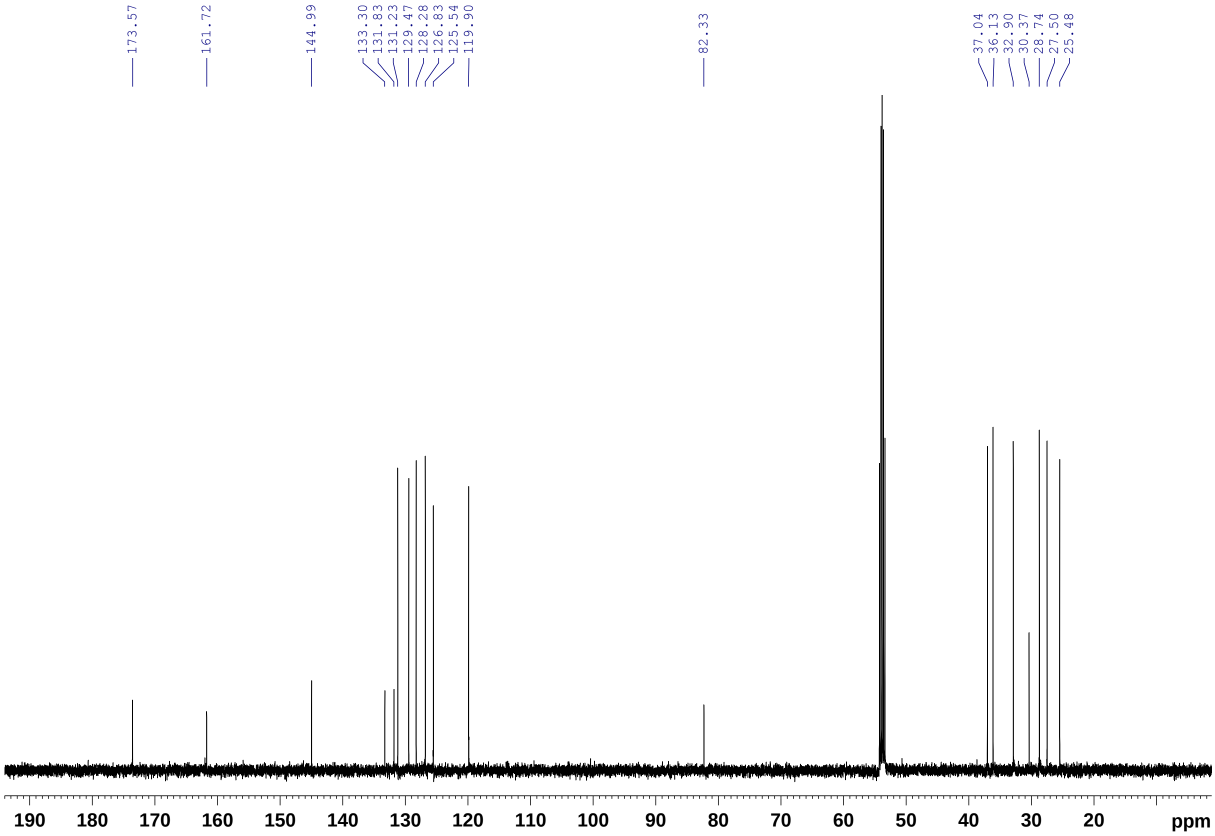

184.75
147.72
141.13
136.83
133.82
133.63
129.26
128.37
127.38
126.99
124.27
60.37
36.59
35.54
30.22
28.98
27.50
26.72
23.40
21.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

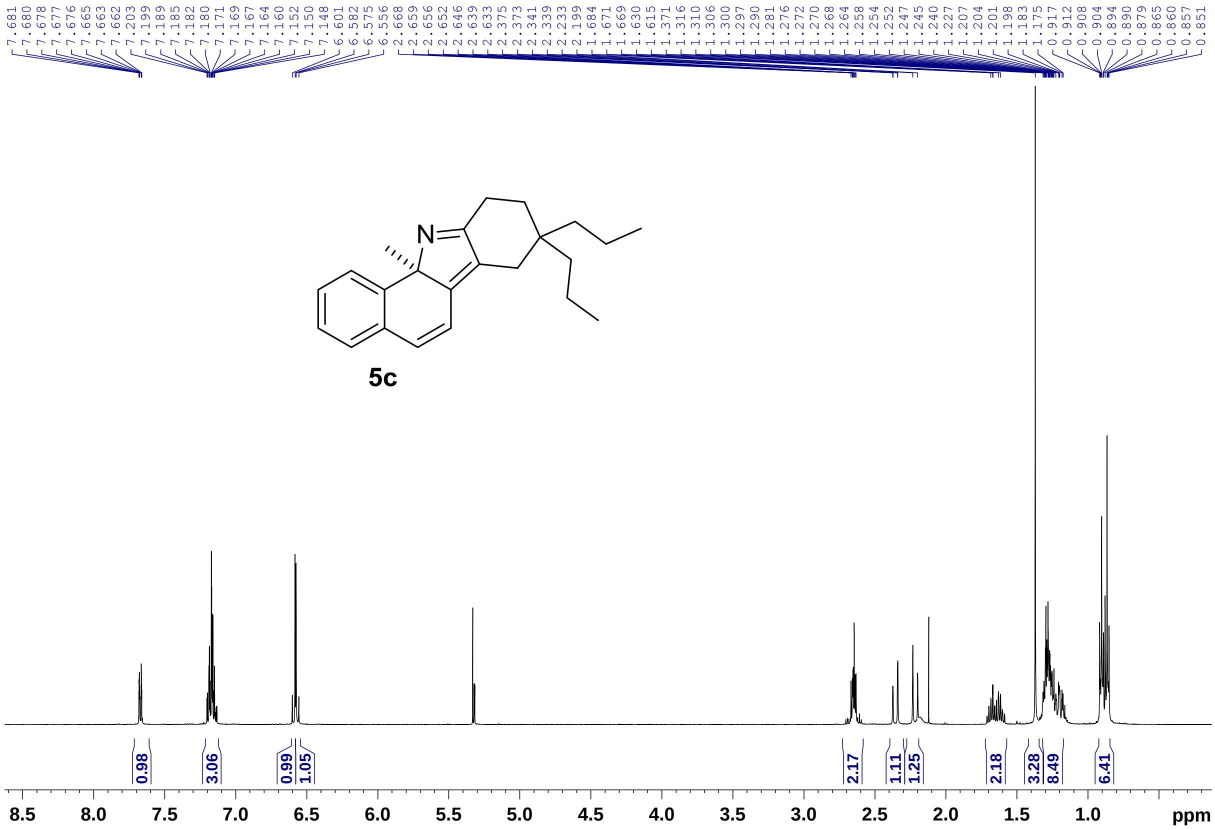
2*H*-Pyrroles

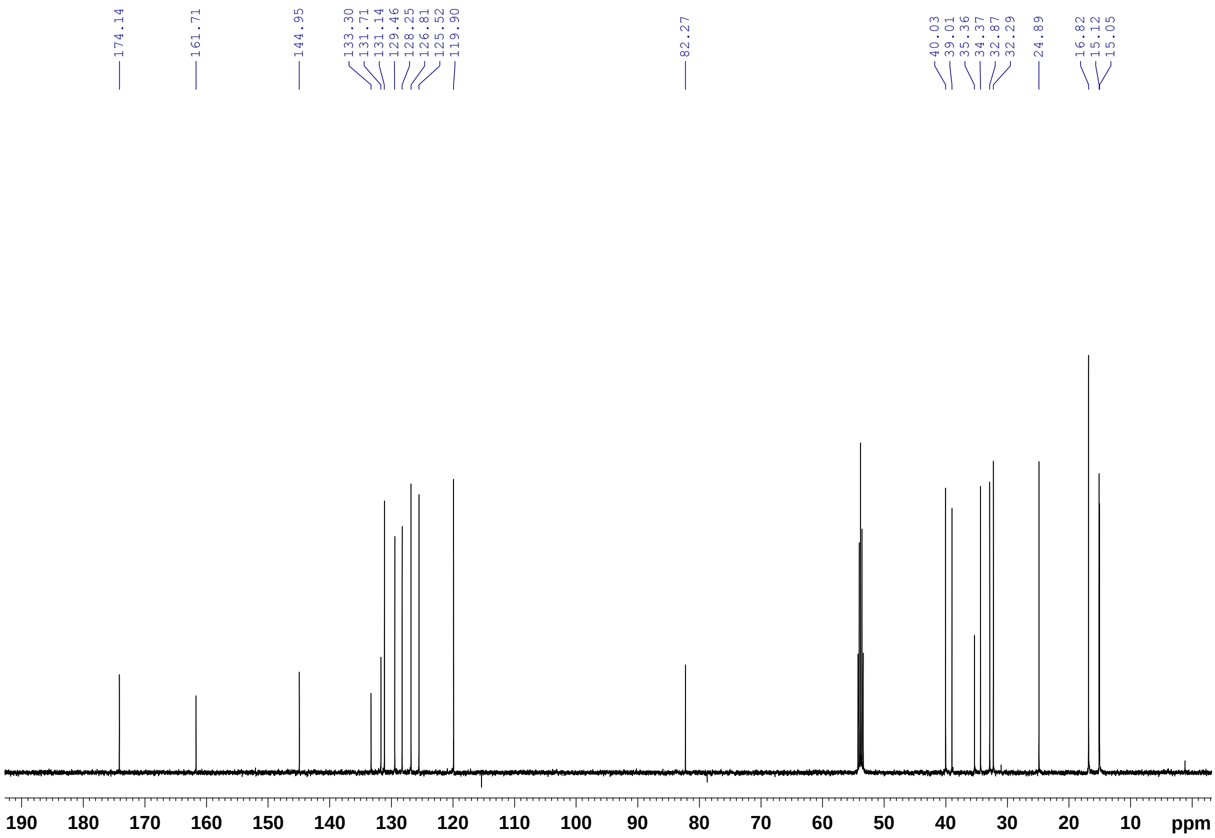


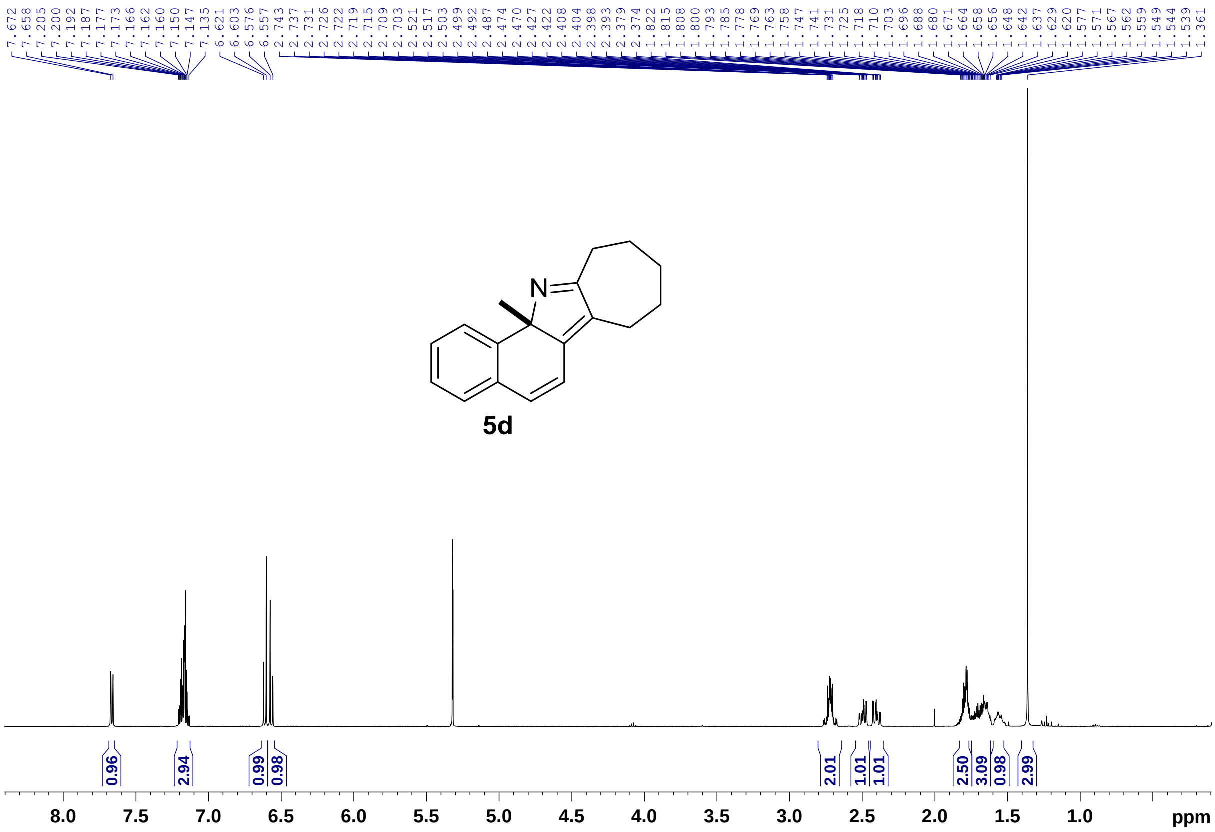


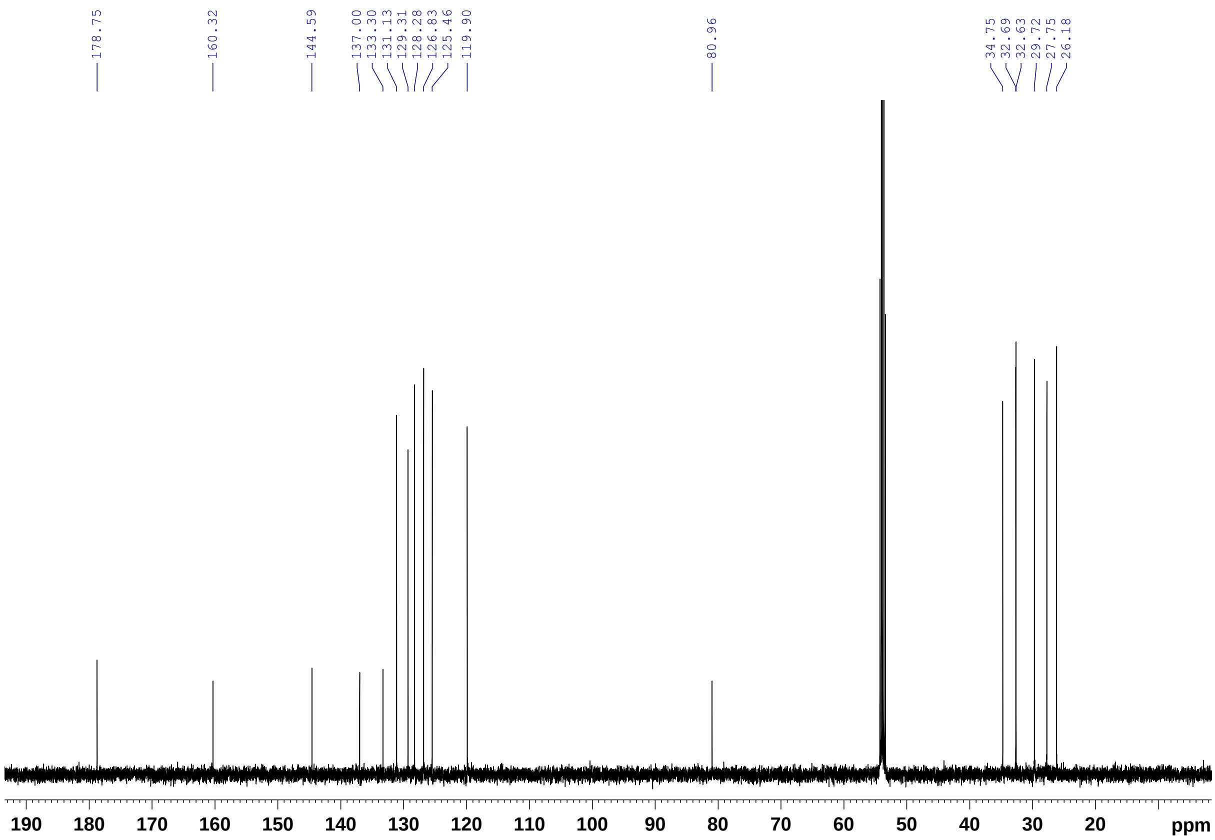

7.678 7.676 7.673 7.665 7.663 7.660 7.201 7.197 7.188 7.184 7.181 7.179 7.175 7.173 7.170 7.168 7.166 7.163 7.161 7.159 7.151 7.149 7.147 7.144 7.140 7.134 7.131 6.596 6.576 6.575 6.555
2.760 2.746 2.744 2.730 2.723 2.713 2.709 2.707 2.700 2.693 2.687 2.676 2.663 2.650 2.358 2.356 2.324 2.322 2.238 2.204 1.683 1.680 1.669 1.666 1.660 1.656 1.653 1.646 1.643 1.640 1.631 1.618 1.603 1.371 1.000 0.992
N
5b
1.00 3.22 1.02 1.09 2.01 1.04 1.10 2.29 3.25 3.11 3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

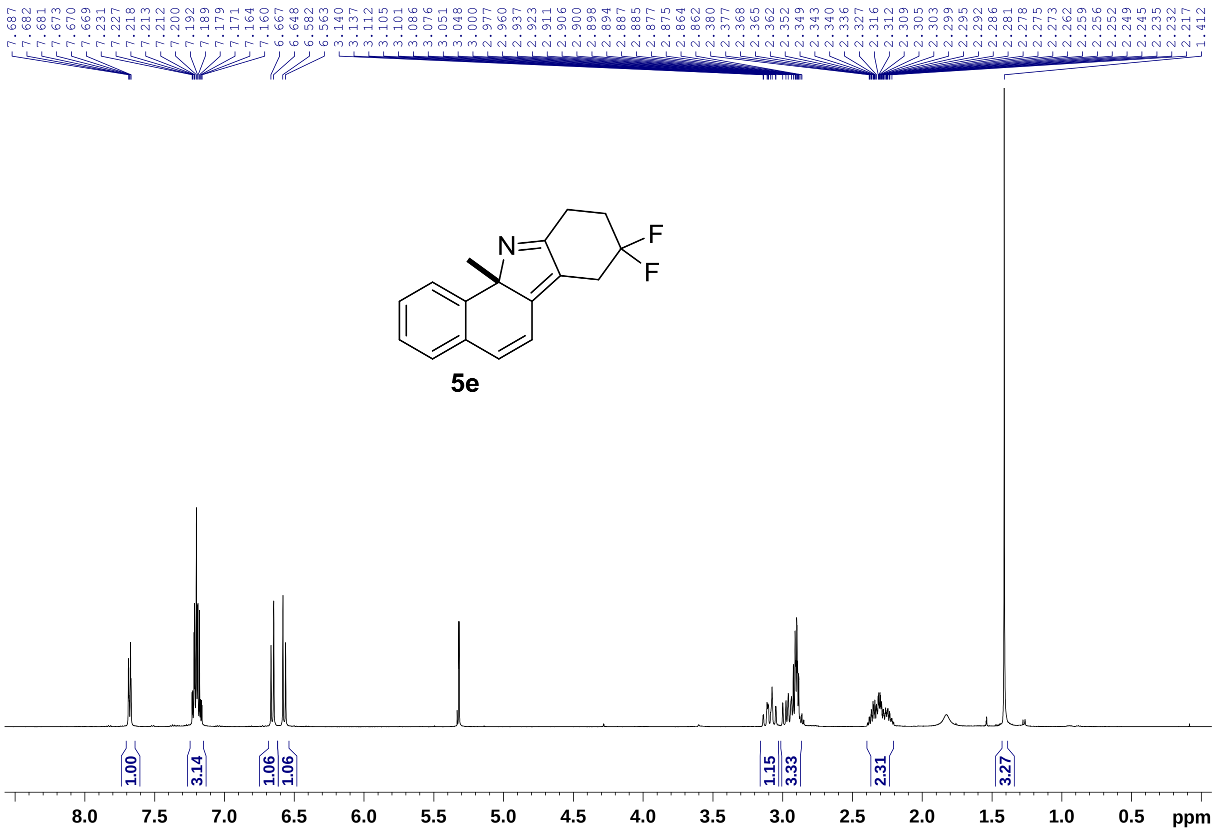

173.57
161.72
144.99
133.30 131.83 131.23 129.47 128.28 126.83 125.54 119.90
82.33
37.04 36.13 32.90 30.37 28.74 27.50 25.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

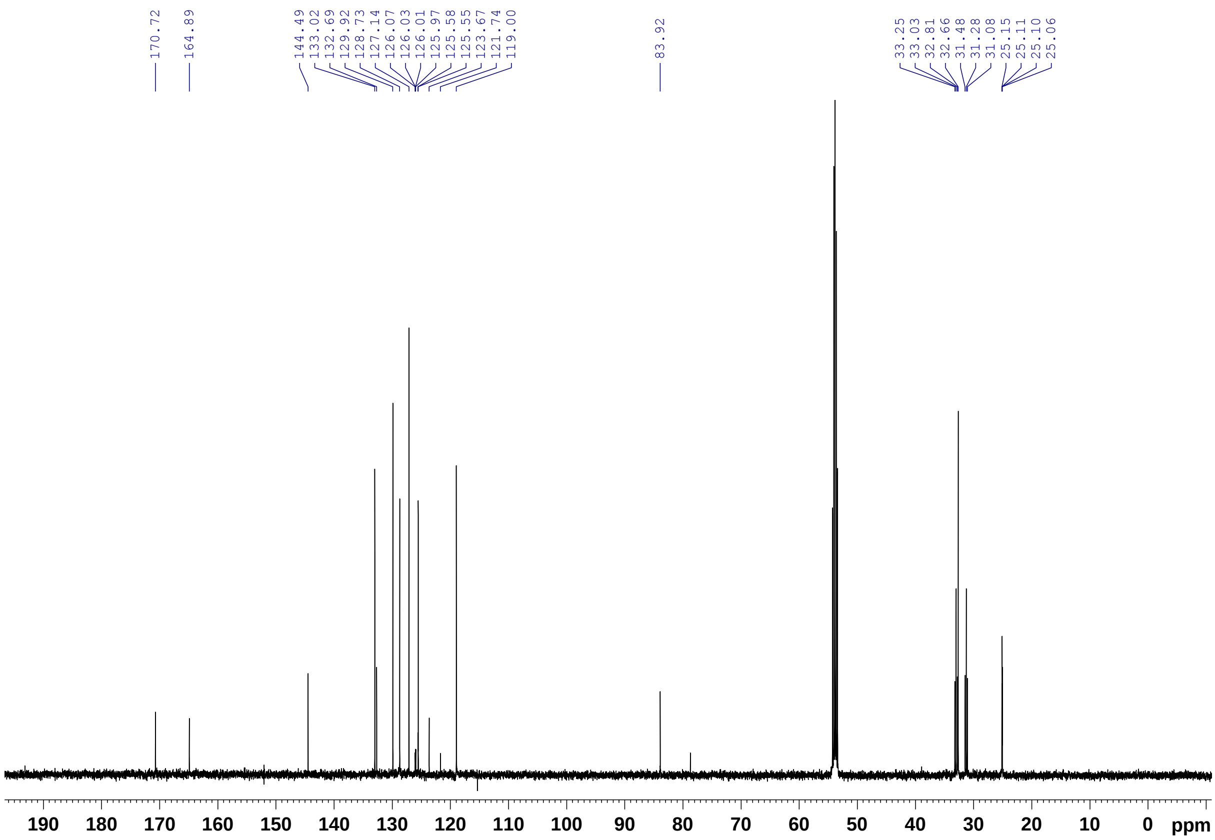

7.681 7.680 7.678 7.677 7.676 7.665 7.663 7.662 7.203 7.199 7.189 7.185 7.182 7.180 7.171 7.169 7.167 7.164 7.160 7.152 7.150 7.148 6.601 6.582 6.575 6.556 2.668 2.659 2.656 2.652 2.646 2.639 2.633 2.375 2.373 2.341 2.339 2.233 2.199 1.684 1.671 1.669 1.630 1.615 1.371 1.316 1.310 1.306 1.300 1.297 1.290 1.281 1.276 1.272 1.270 1.268 1.264 1.258 1.254 1.252 1.247 1.245 1.240 1.227 1.207 1.204 1.201 1.198 1.183 1.175 0.917 0.912 0.908 0.904 0.894 0.890 0.879 0.865 0.860 0.857 0.851
N
5c
0.98 3.06 0.99 1.05 2.17 1.11 1.25 2.18 3.28 8.49 6.41
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

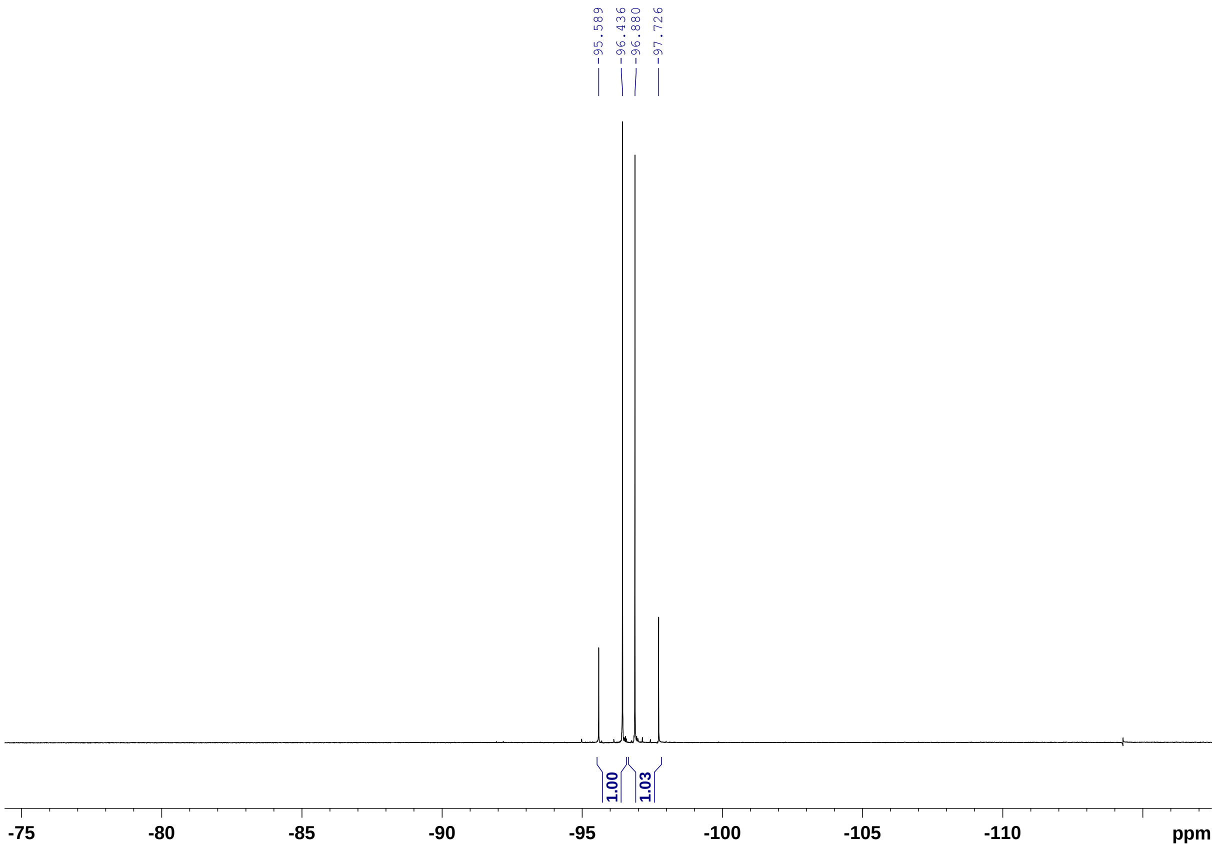

174.14 161.71 144.95 133.30 131.71 131.14 129.46 128.25 126.81 125.52 119.90 82.27 40.03 39.01 35.36 34.37 32.87 32.29 24.89 16.82 15.12 15.05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.672 7.658 7.205 7.200 7.192 7.187 7.177 7.173 7.166 7.162 7.160 7.150 7.147 7.135 6.621 6.603 6.576 6.557 2.743 2.737 2.731 2.726 2.722 2.719 2.715 2.709 2.703 2.521 2.517 2.503 2.499 2.492 2.487 2.474 2.470 2.427 2.422 2.408 2.404 2.398 2.393 2.379 2.374 1.822 1.815 1.808 1.800 1.793 1.785 1.778 1.769 1.763 1.758 1.747 1.741 1.731 1.725 1.718 1.710 1.703 1.696 1.688 1.680 1.671 1.664 1.658 1.656 1.648 1.642 1.637 1.629 1.620 1.577 1.571 1.567 1.562 1.559 1.549 1.544 1.539 1.361
N
5d
0.96
2.94
0.99
0.98
2.01
1.01
1.01
2.50
3.09
0.98
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


178.75
160.32
144.59
137.00 133.30 131.13 129.31 128.28 126.83 125.46 119.90
80.96
34.75 32.69 32.63 29.72 27.75 26.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


N
F
F
5e
1.00
3.14
1.06
1.06
1.15
3.33
2.31
3.27
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


170.72
164.89
144.49
133.02
132.69
129.92
128.73
127.14
126.07
126.03
126.01
125.97
125.58
125.55
123.67
121.74
119.00
83.92
33.25
33.03
32.81
32.66
31.48
31.28
31.08
25.15
25.11
25.10
25.06
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-95.589
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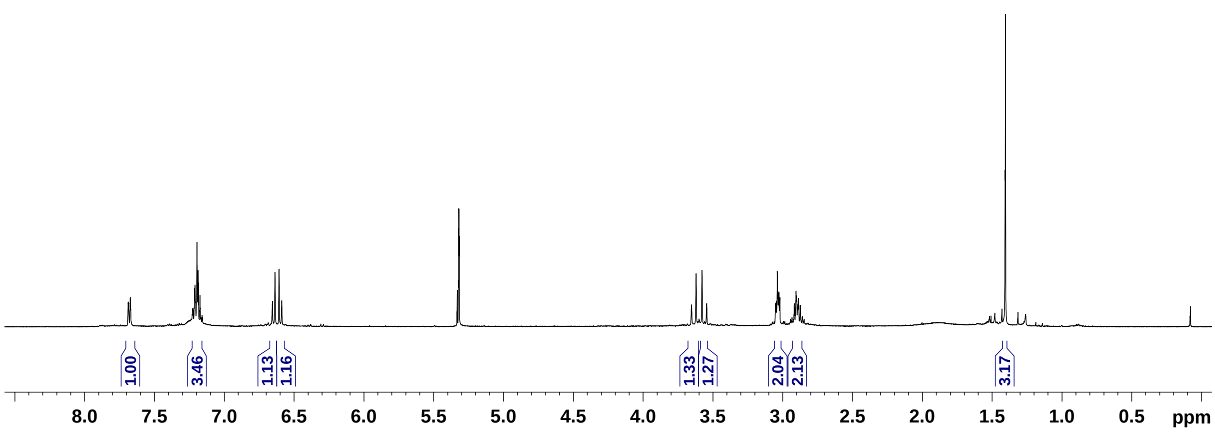
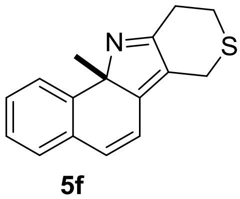
-96.880
-97.726
1.00
1.03
-75
-80
-85
-90
-95
-100
-105
-110
ppm

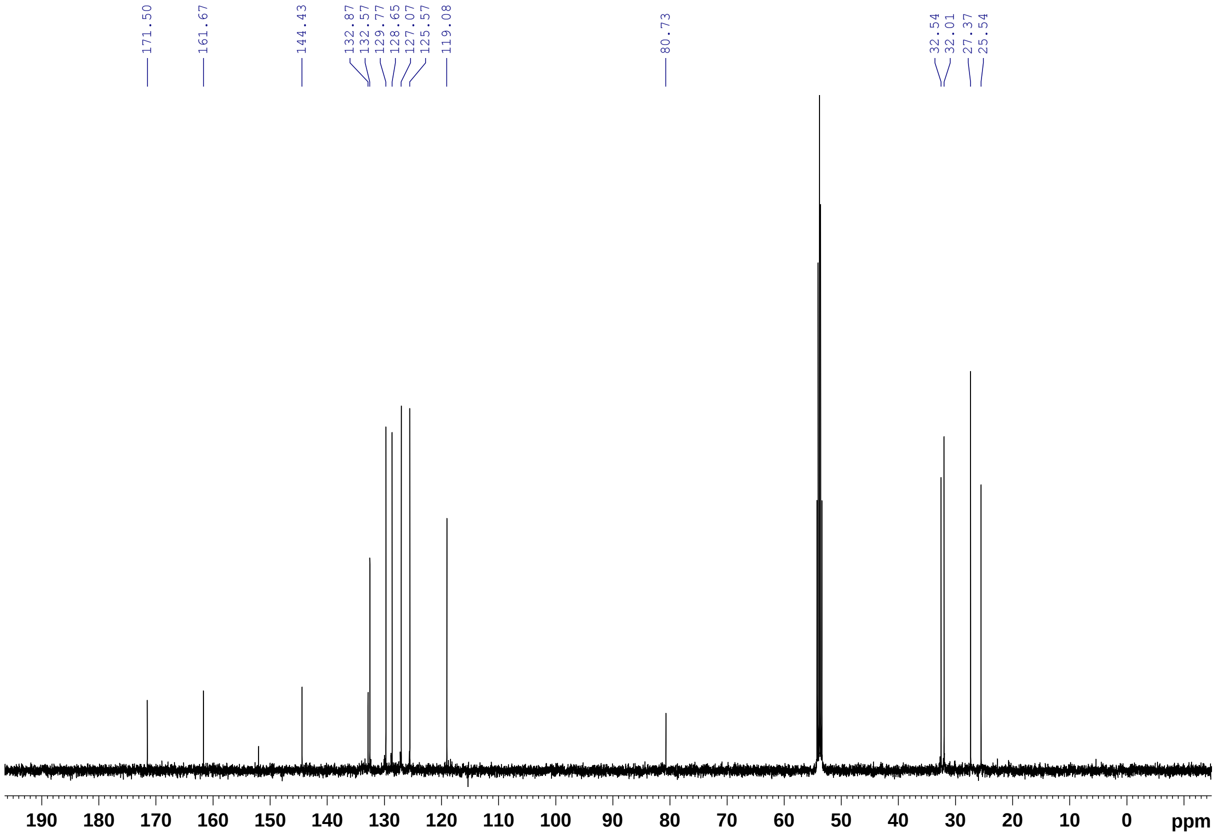


7.688
7.686
7.675
7.673
7.670
7.229
7.226
7.222
7.215
7.213
7.209
7.205
7.196
7.190
7.187
7.184
7.176
7.174
7.172
7.158
6.655
6.636
6.607
6.588
3.654
3.621
3.578
3.545
3.051
3.046
3.039
3.035
3.031
3.027
3.021
2.945
2.943
2.935
2.933
2.920
2.917
2.915
2.907
2.905
2.902
2.901
2.895
2.892
2.889
2.887
2.874
2.859
2.847
1.404
1.00
3.46
1.13
1.16
1.33
1.27
2.04
2.13
3.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

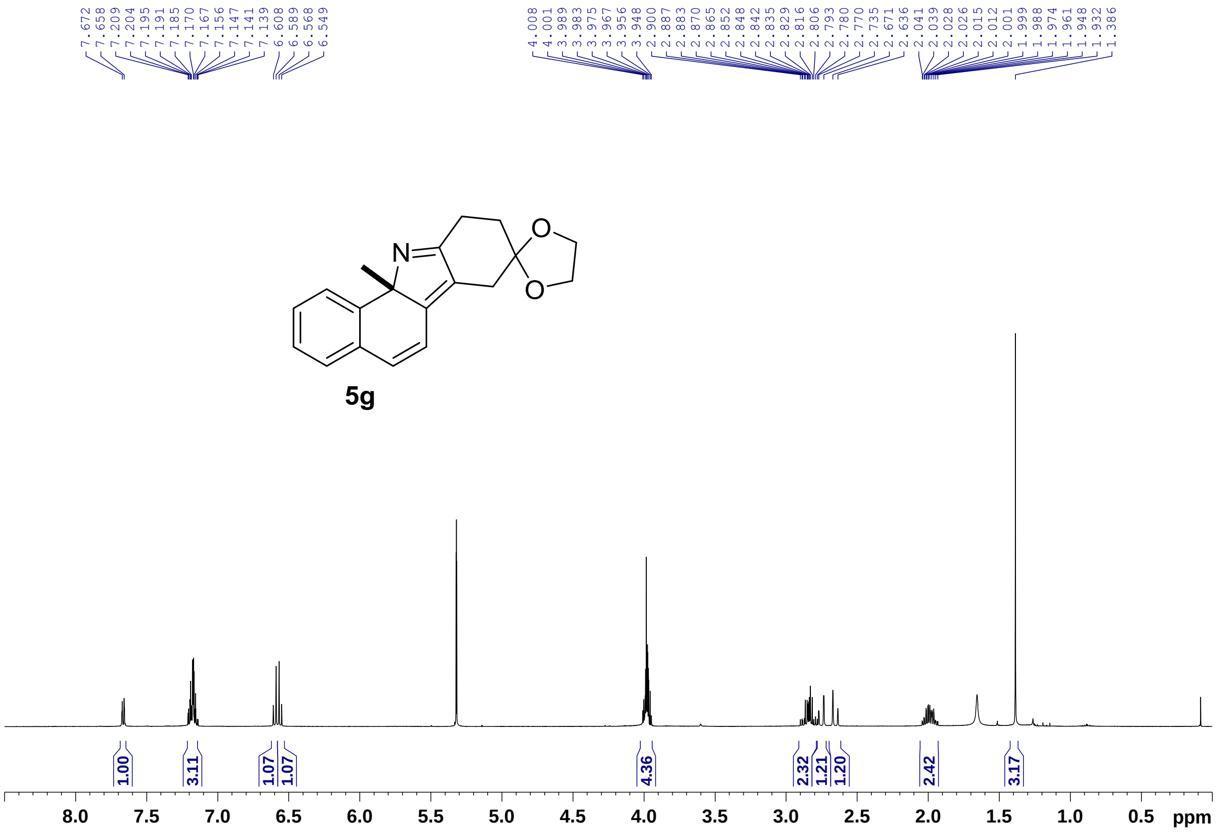


N
S

5f



171.50
161.67
144.43
132.87
132.57
129.77
128.65
127.07
125.57
119.08
80.73
32.54
32.01
27.37
25.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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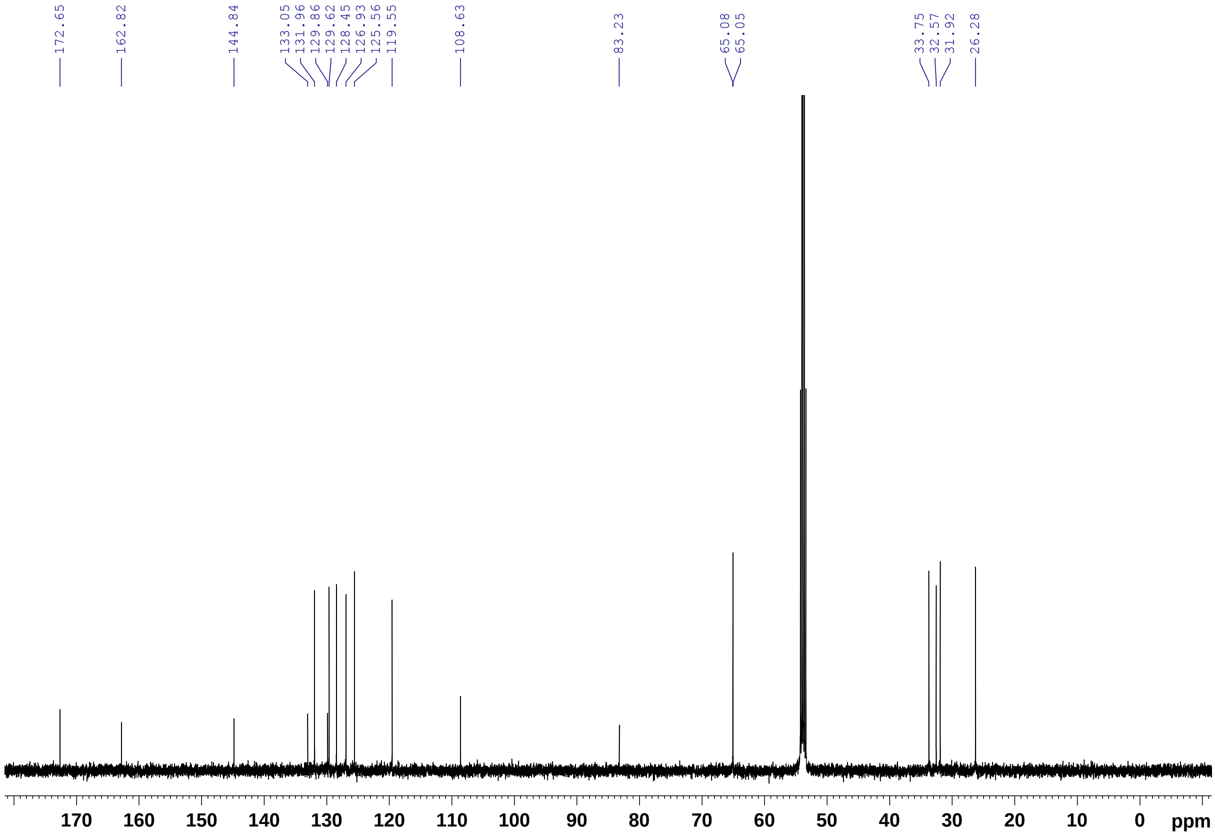
7.191
7.185
7.170
7.167
7.156
7.147
7.141
7.139
6.608
6.589
6.568
6.549
4.008
4.001
3.989
3.983
3.975
3.967
3.956
3.948
2.900
2.887
2.883
2.870
2.865
2.852
2.848
2.842
2.835
2.829
2.816
2.806
2.793
2.780
2.770
2.735
2.671
2.636
2.041
2.039
2.028
2.026
2.015
2.012
2.001
1.999
1.988
1.974
1.961
1.948
1.932
1.386
N
O
O
5g
1.00
3.11
1.07
1.07
4.36
2.32
1.21
1.20
2.42
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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162.82
144.84
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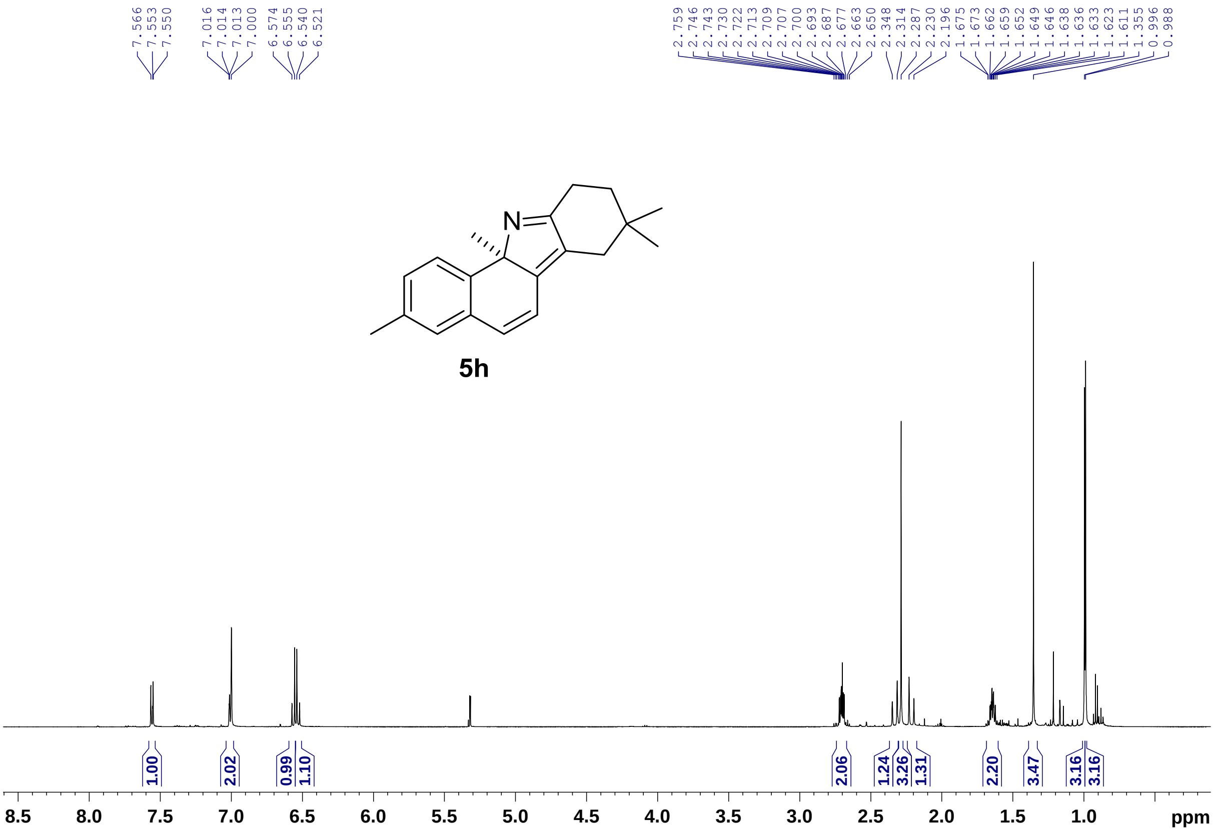
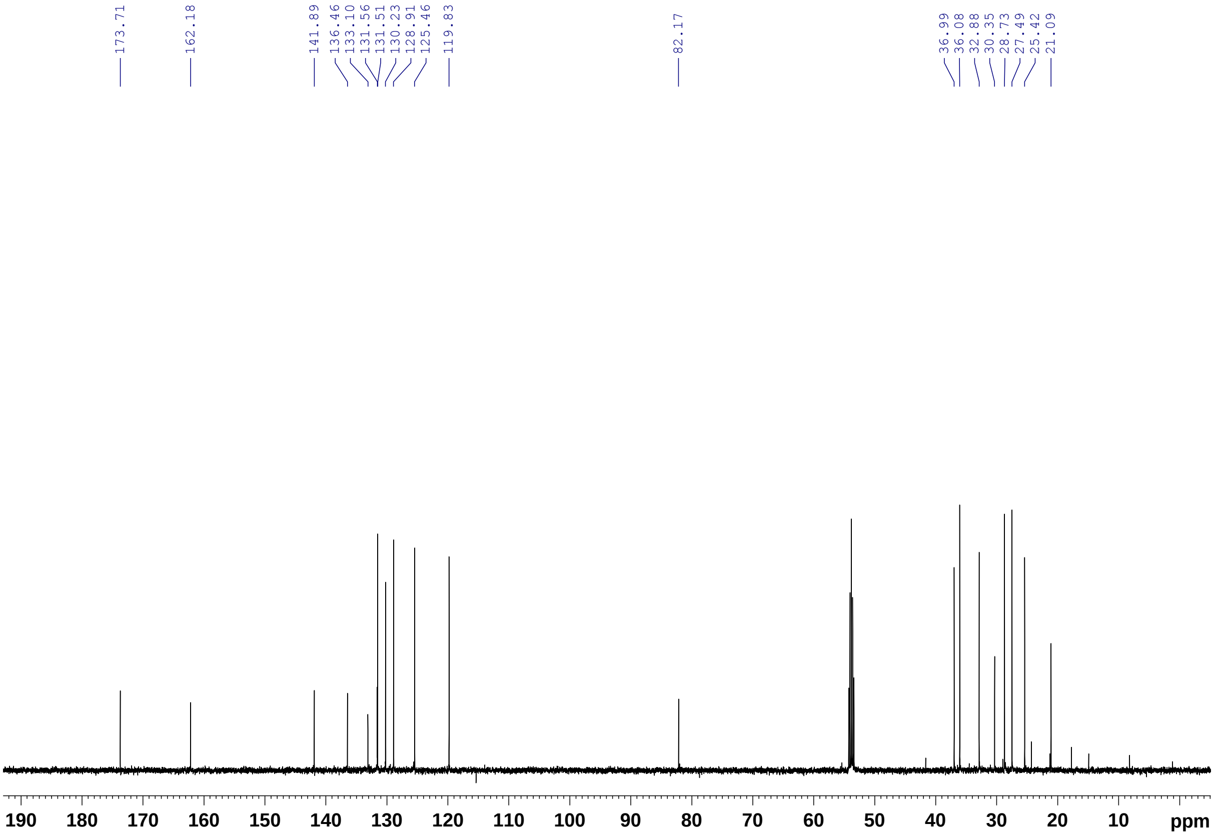
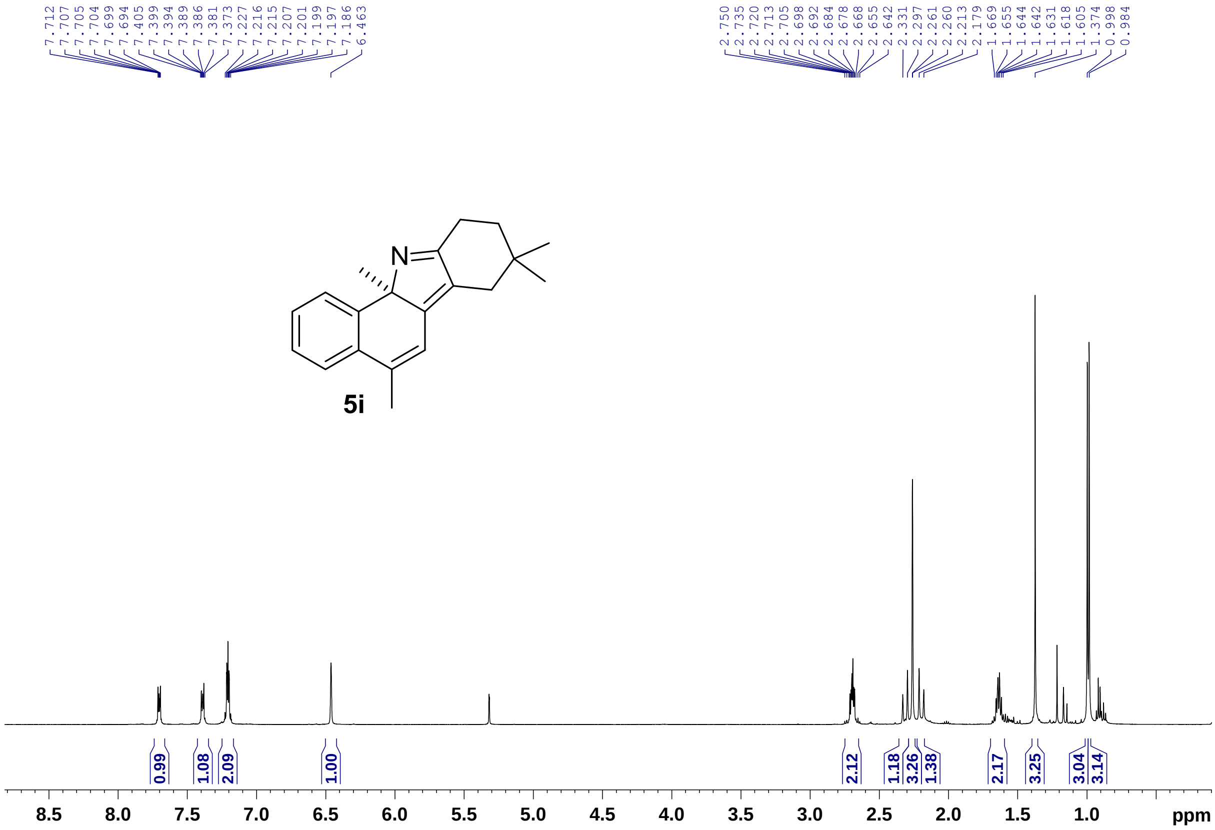
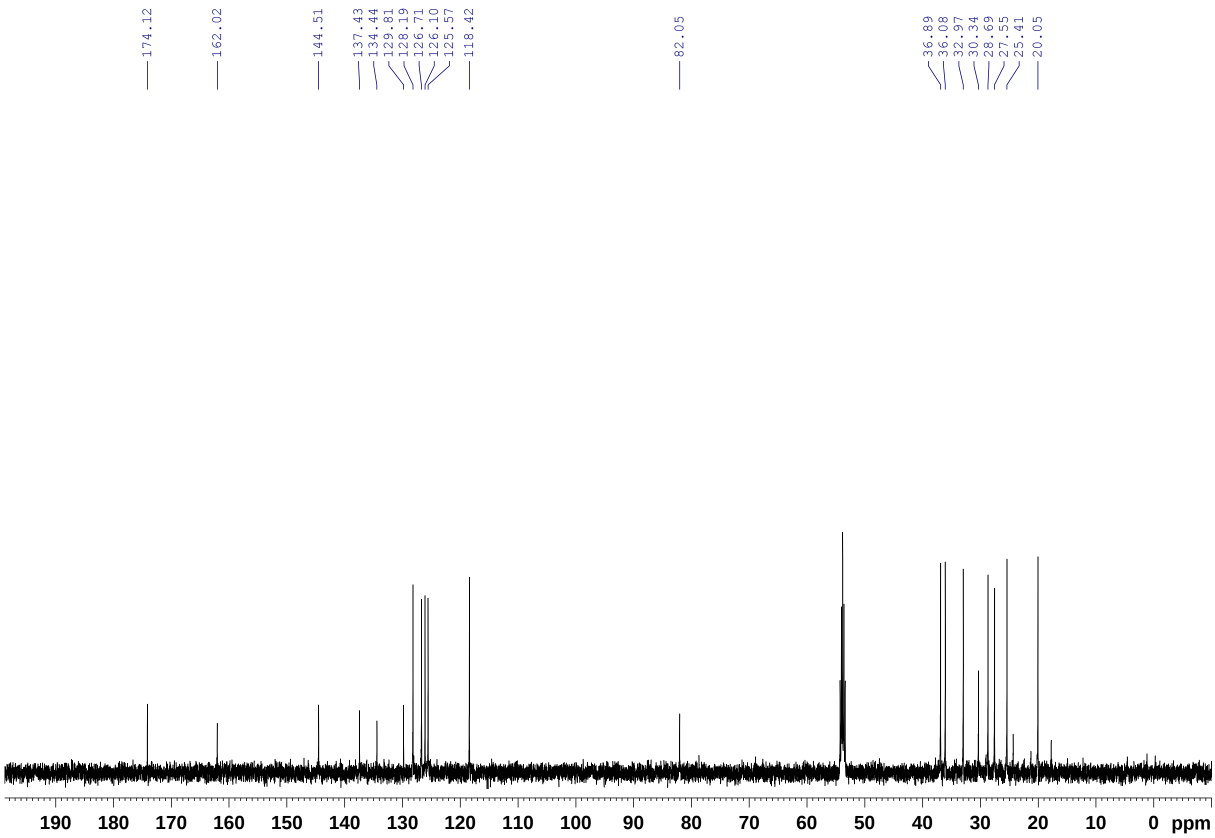
131.96
129.86
129.62
128.45
126.93
125.56
119.55
108.63
83.23
65.08
65.05
33.75
32.57
31.92
26.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

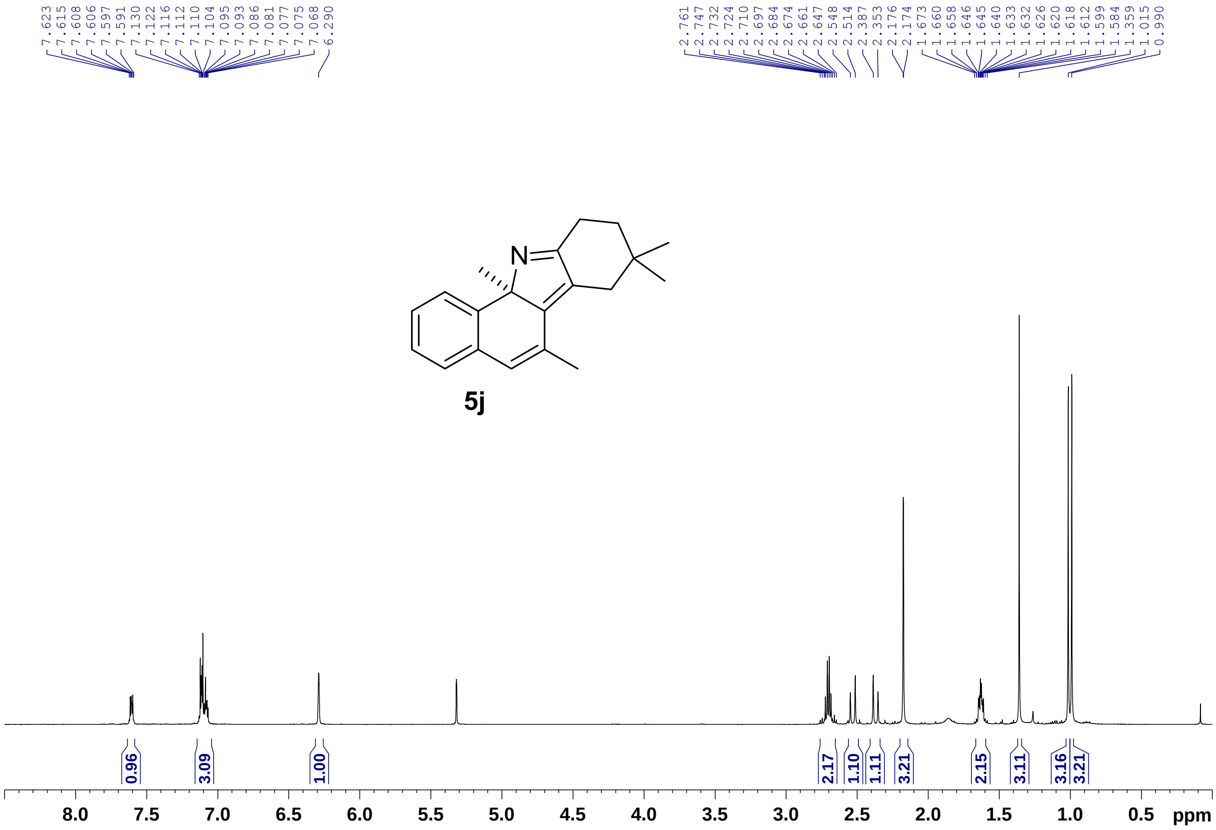

7.566
7.553
7.550
7.016
7.014
7.013
7.000
6.574
6.555
6.540
6.521
2.759
2.746
2.743
2.730
2.722
2.713
2.709
2.707
2.700
2.693
2.687
2.677
2.663
2.650
2.348
2.314
2.287
2.230
2.196
1.675
1.673
1.662
1.659
1.652
1.649
1.646
1.638
1.636
1.633
1.623
1.611
1.355
0.996
0.988
1.00
2.02
0.99
1.10
2.06
1.24
3.26
1.31
2.20
3.47
3.16
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
N

5h


173.71
162.18
141.89
136.46
133.10
131.56
131.51
130.23
128.91
125.46
119.83
82.17
36.99
36.08
32.88
30.35
28.73
27.49
25.42
21.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.712 7.707 7.705 7.704 7.699 7.694 7.405 7.399 7.394 7.389 7.386 7.381 7.373 7.227 7.216 7.215 7.207 7.201 7.199 7.197 7.186 6.463
2.750 2.735 2.720 2.713 2.705 2.698 2.692 2.684 2.678 2.668 2.655 2.642 2.331 2.297 2.261 2.260 2.213 2.179 1.669 1.655 1.644 1.642 1.631 1.618 1.605 1.374 0.998 0.984
N
5i
0.99 1.08 2.09 1.00 2.12 1.18 3.26 1.38 2.17 3.25 3.04 3.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


174.12 162.02 144.51 137.43 134.44 129.81 128.19 126.71 126.10 125.57 118.42 82.05 36.89 36.08 32.97 30.34 28.69 27.55 25.41 20.05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
5j
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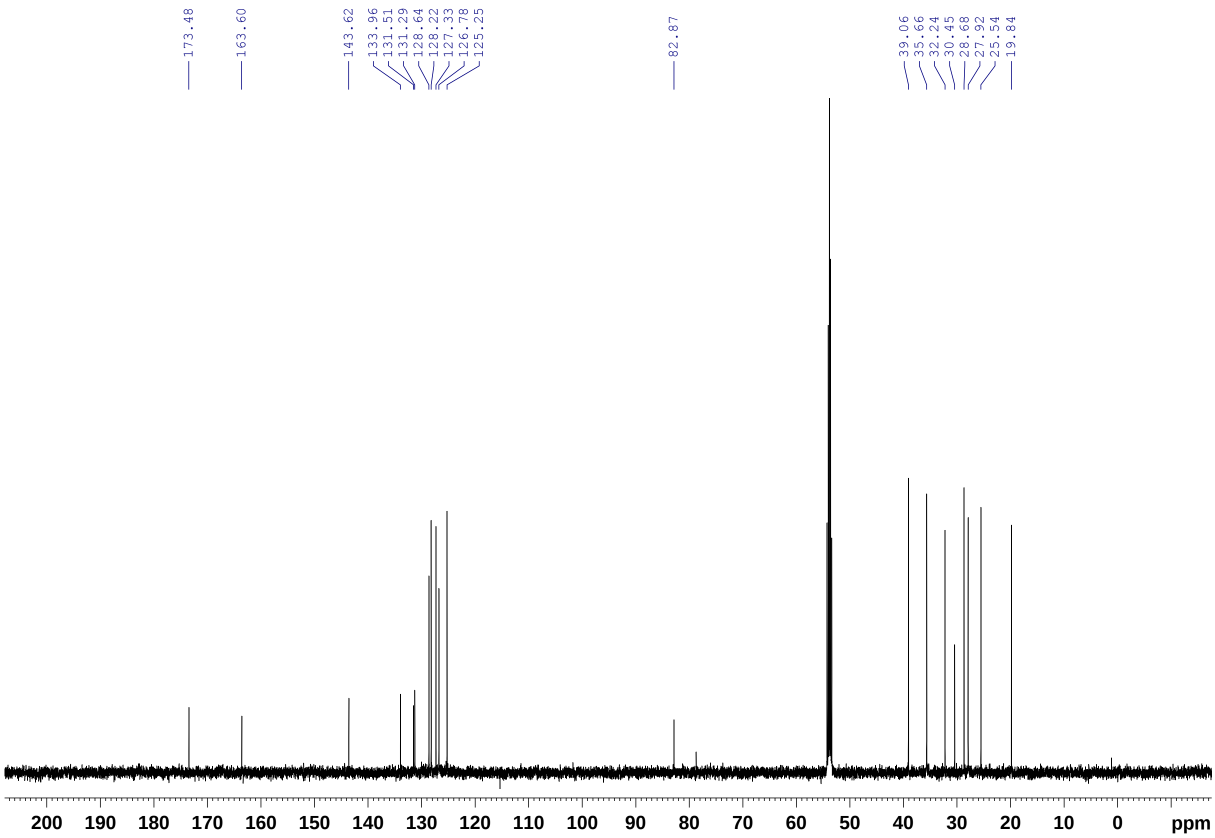
7.608
7.606
7.597
7.591
7.130
7.122
7.116
7.112
7.110
7.104
7.095
7.093
7.086
7.081
7.077
7.075
7.068
6.290
2.761
2.747
2.732
2.724
2.710
2.697
2.684
2.674
2.661
2.647
2.548
2.514
2.387
2.353
2.176
2.174
1.673
1.660
1.658
1.646
1.645
1.640
1.633
1.632
1.626
1.620
1.618
1.612
1.599
1.584
1.359
1.015
0.990
0.96
3.09
1.00
2.17
1.10
1.11
3.21
2.15
3.11
3.16
3.21
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm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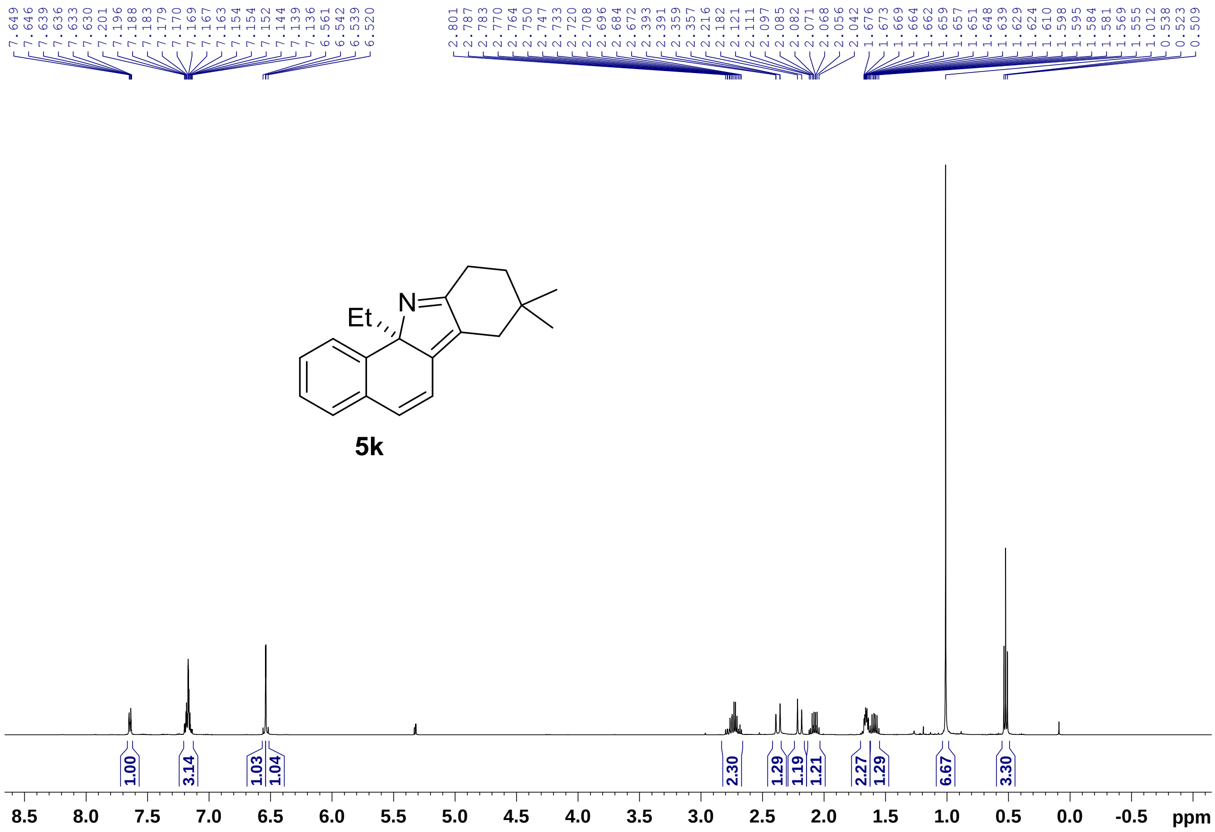
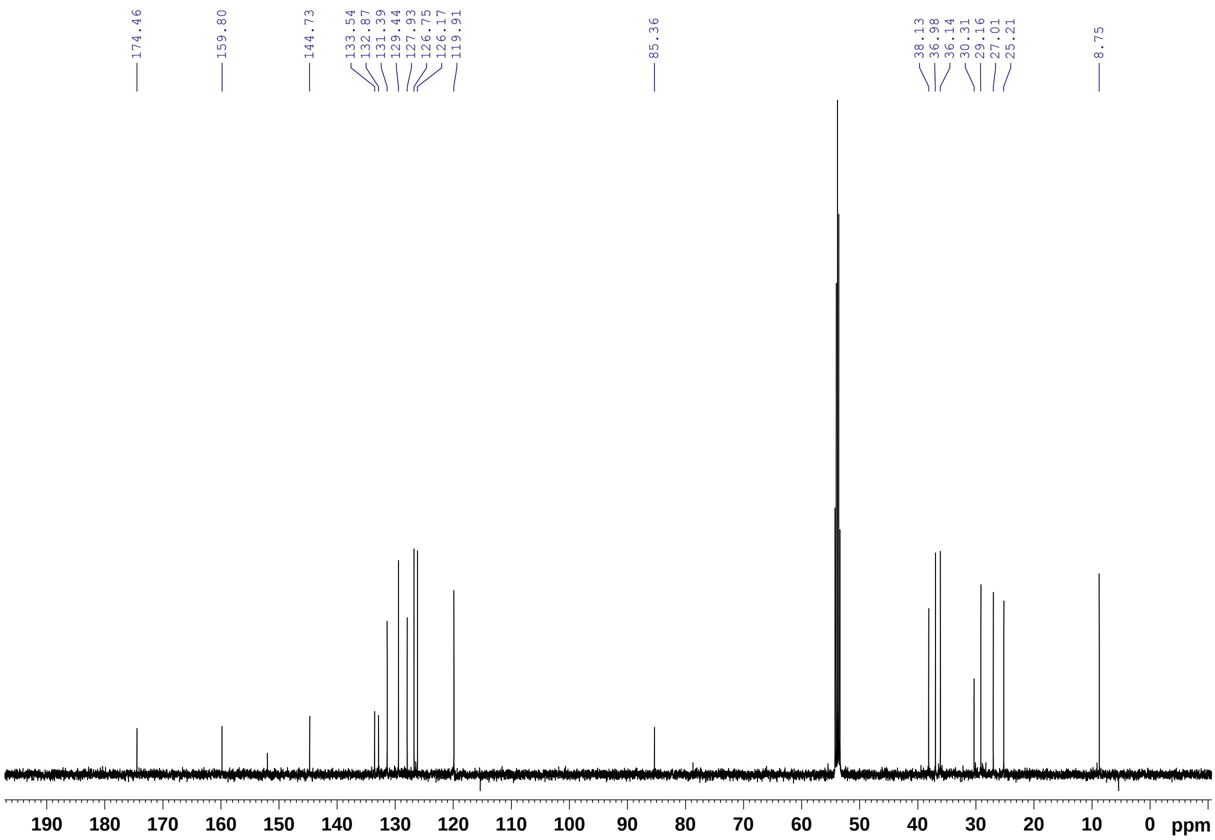
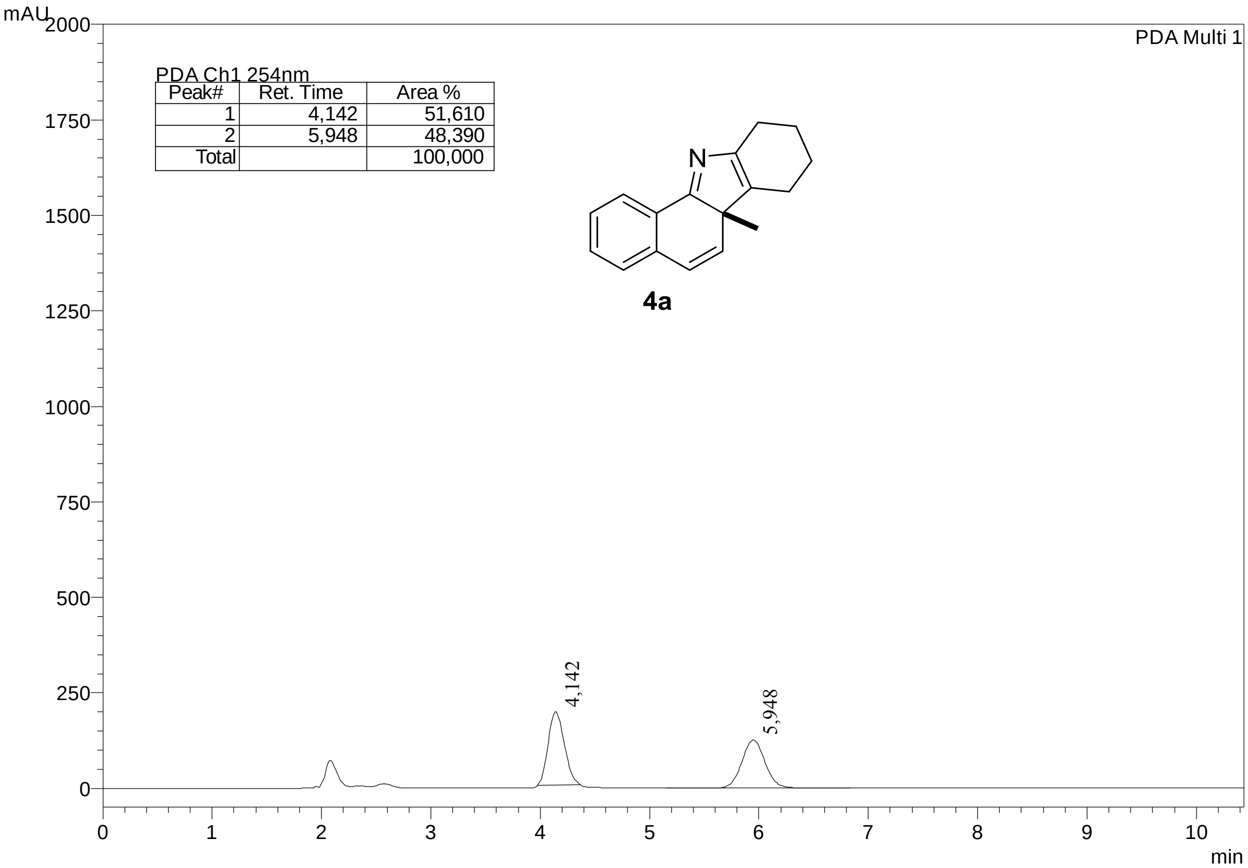
163.60
143.62
133.96
131.51
131.29
128.64
128.22
127.33
126.78
125.25
82.87
39.06
35.66
32.24
30.45
28.68
27.92
25.54
19.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
Et
5k
7.649 7.646 7.639 7.636 7.633 7.630 7.201 7.196 7.188 7.183 7.179 7.170 7.169 7.167 7.163 7.154 7.154 7.152 7.144 7.139 7.139 7.136 6.561 6.542 6.539 6.520
2.801 2.787 2.783 2.770 2.764 2.750 2.747 2.733 2.720 2.708 2.696 2.684 2.672 2.393 2.391 2.359 2.357 2.216 2.182 2.121 2.111 2.097 2.085 2.082 2.071 2.068 2.056 2.042 1.676 1.673 1.669 1.664 1.662 1.659 1.657 1.651 1.648 1.639 1.629 1.624 1.610 1.598 1.595 1.584 1.581 1.569 1.555 1.012 0.538 0.523 0.509
1.00
3.14
1.03
1.04
2.30
1.29
1.19
1.21
2.27
1.29
6.67
3.30
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm

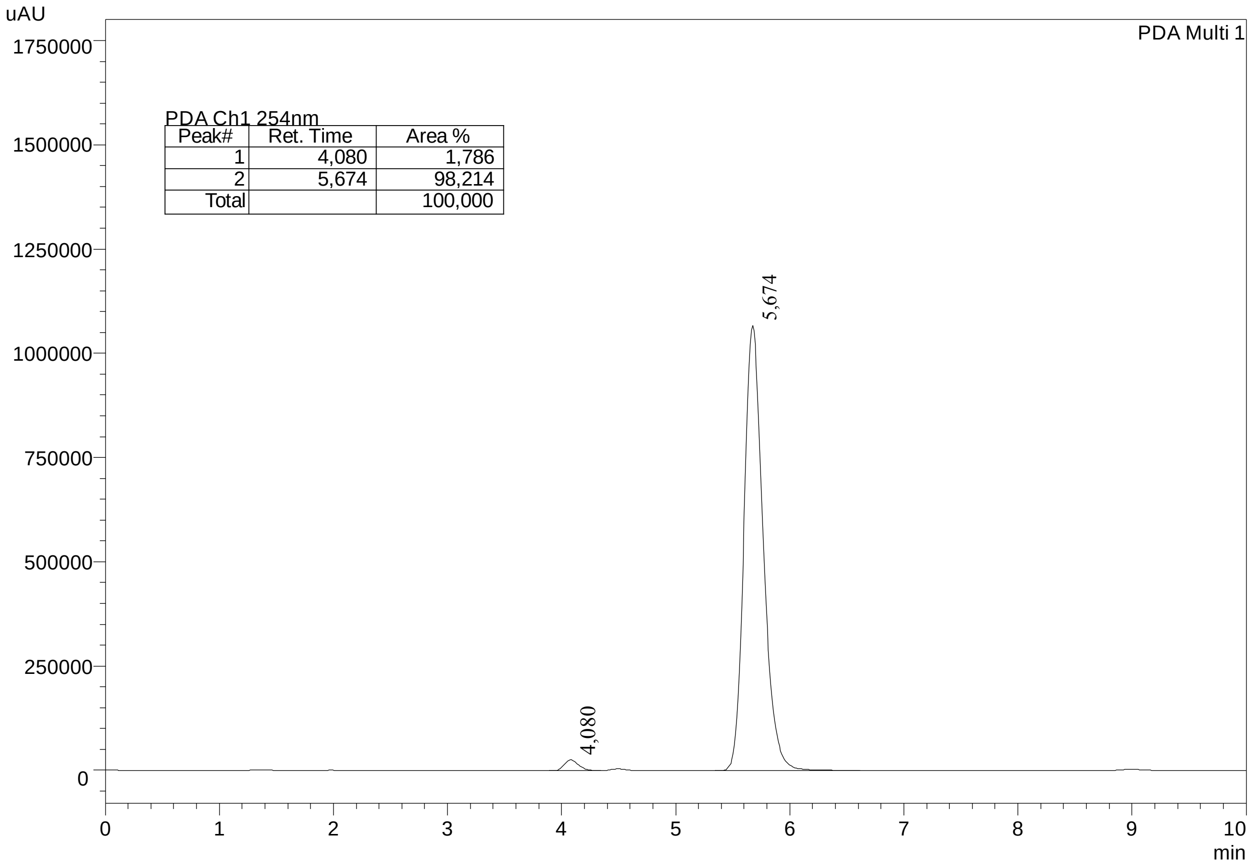

174.46
159.80
144.73
133.54 132.87 131.39 129.44 127.93 126.75 126.17 119.91
85.36
38.13 36.98 36.14 30.31 29.16 27.01 25.21
8.75
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Copies of HPLC Traces



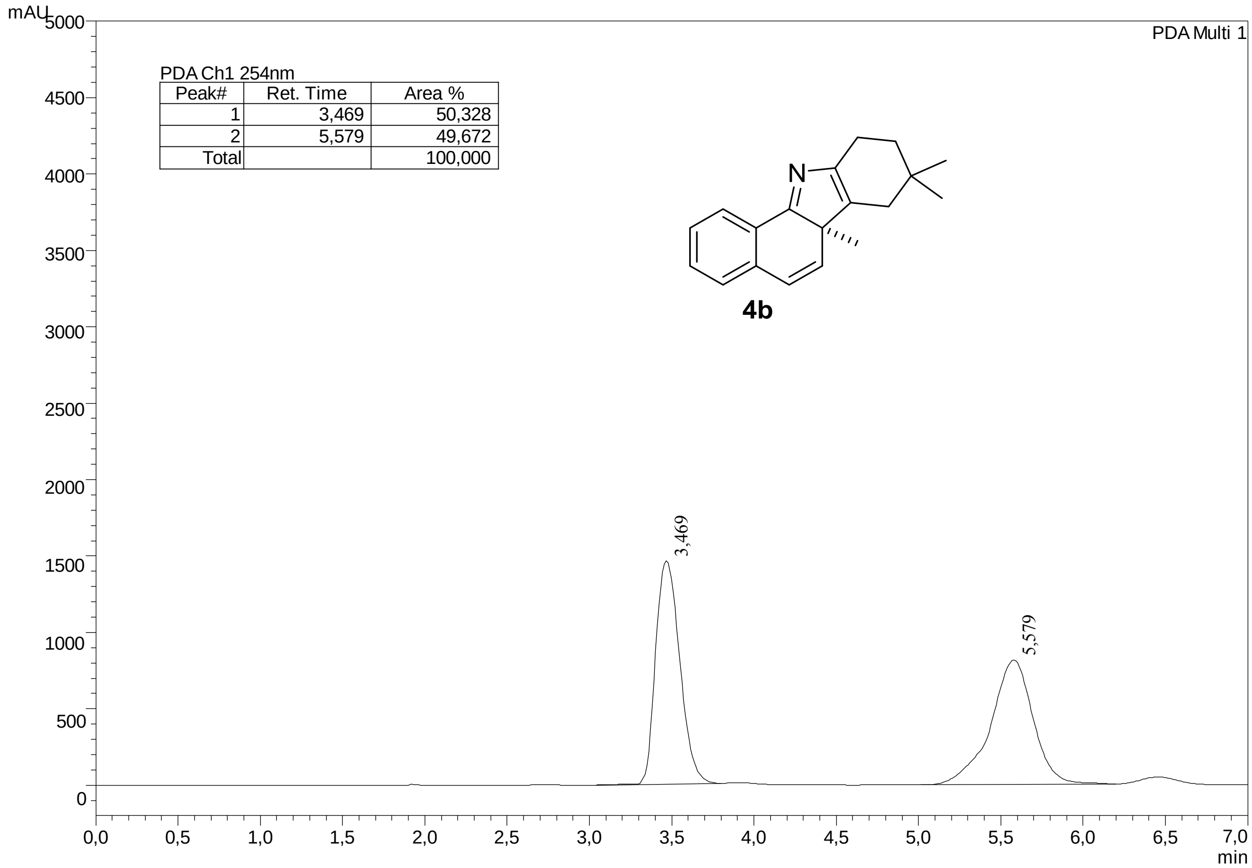
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	4,142	51,610
2	5,948	48,390
Total		100,000

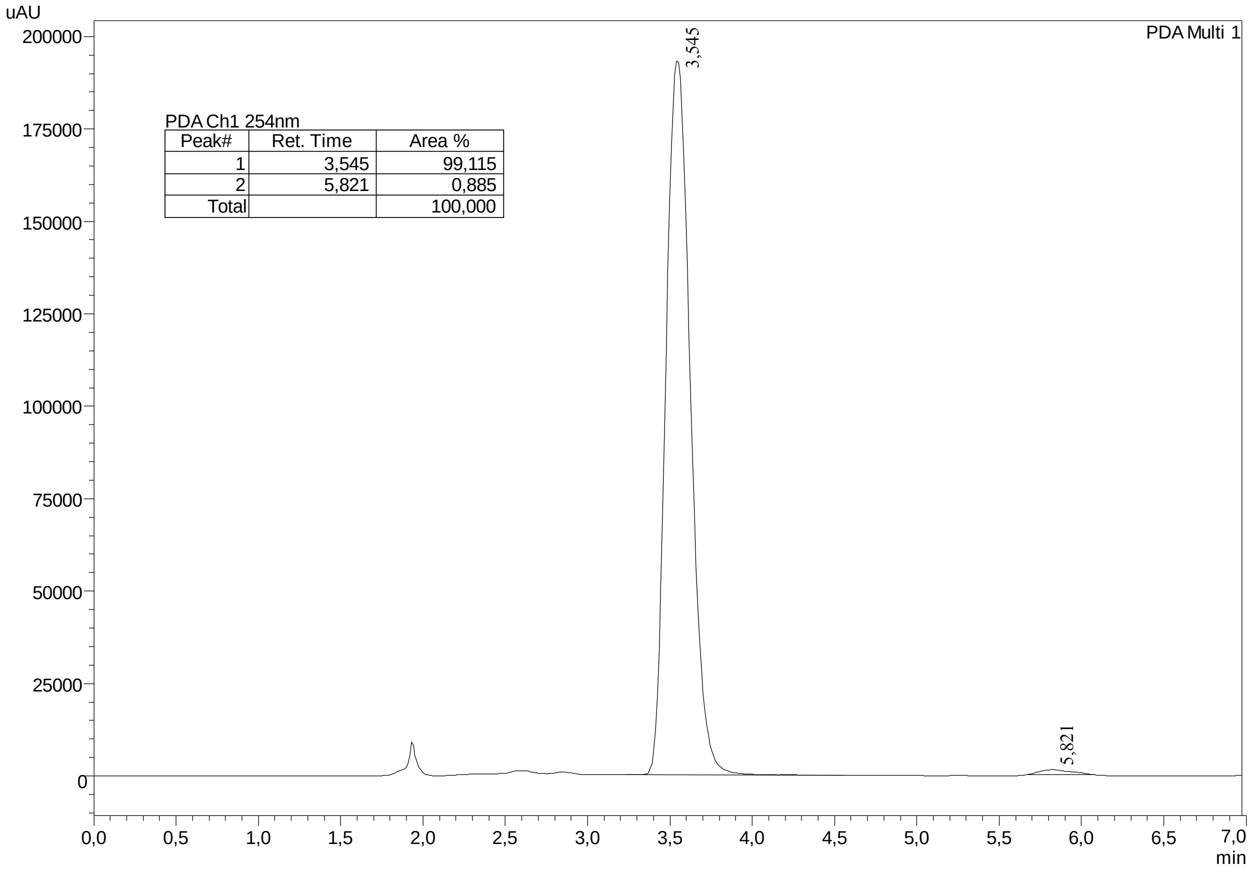


PDA Ch1 254nm

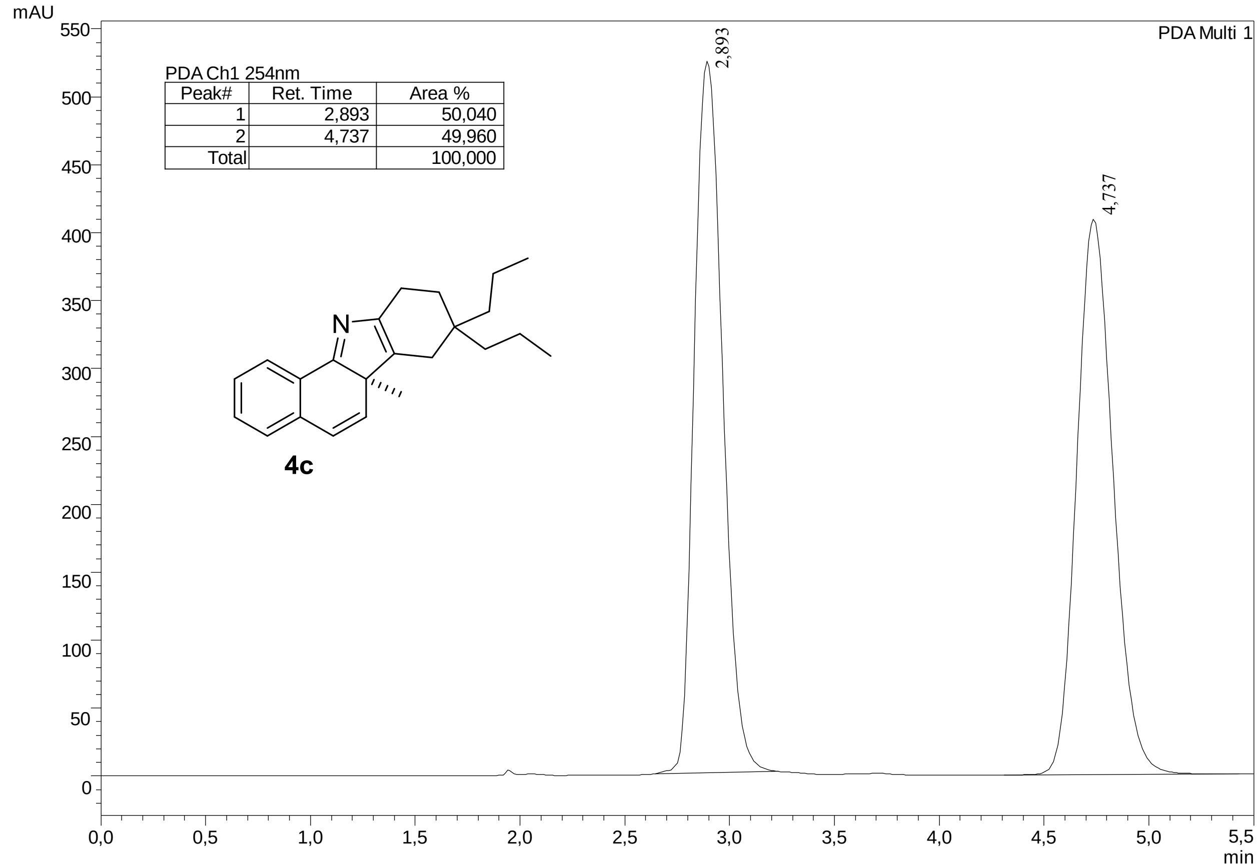
Peak#	Ret. Time	Area %
1	4,080	1,786
2	5,674	98,214
Total		100,000



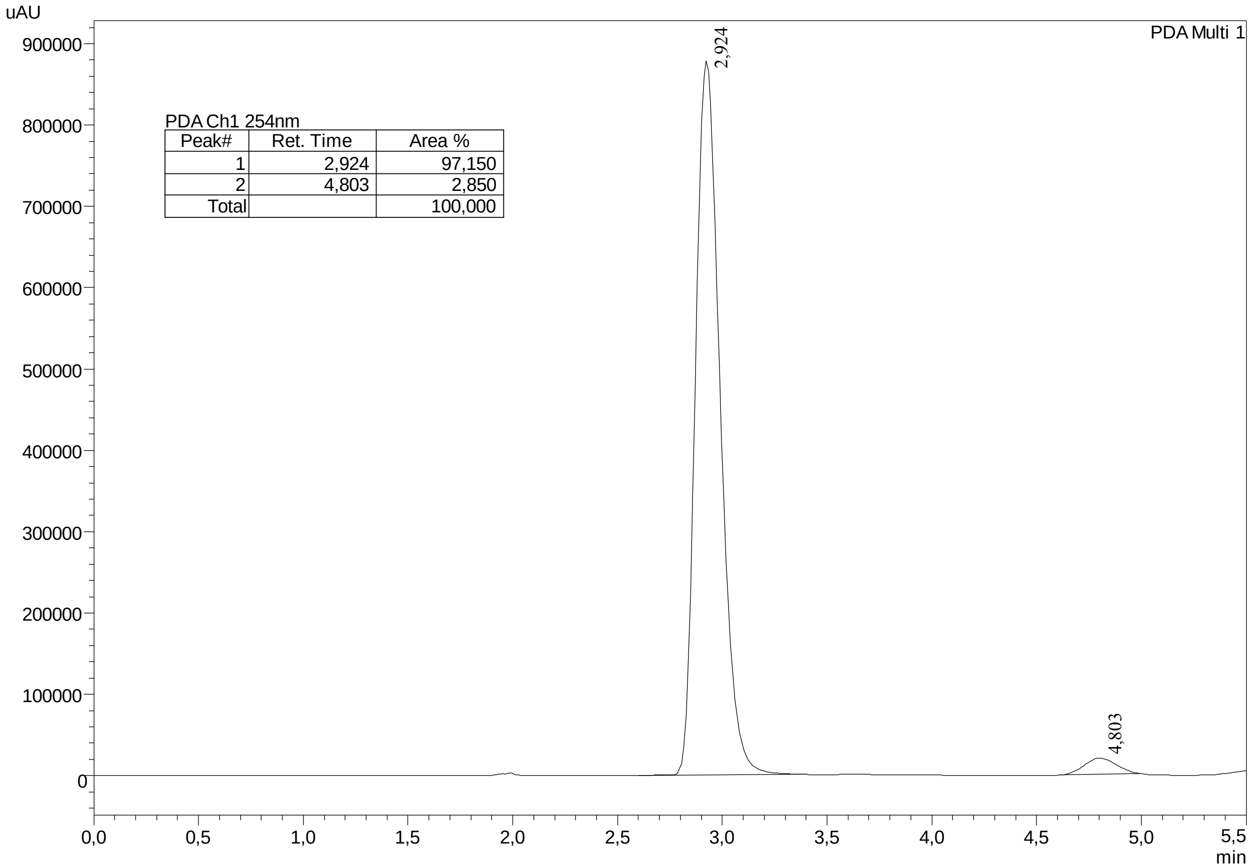
Peak#	Ret. Time	Area %
1	3,469	50,328
2	5,579	49,672
Total		100,000



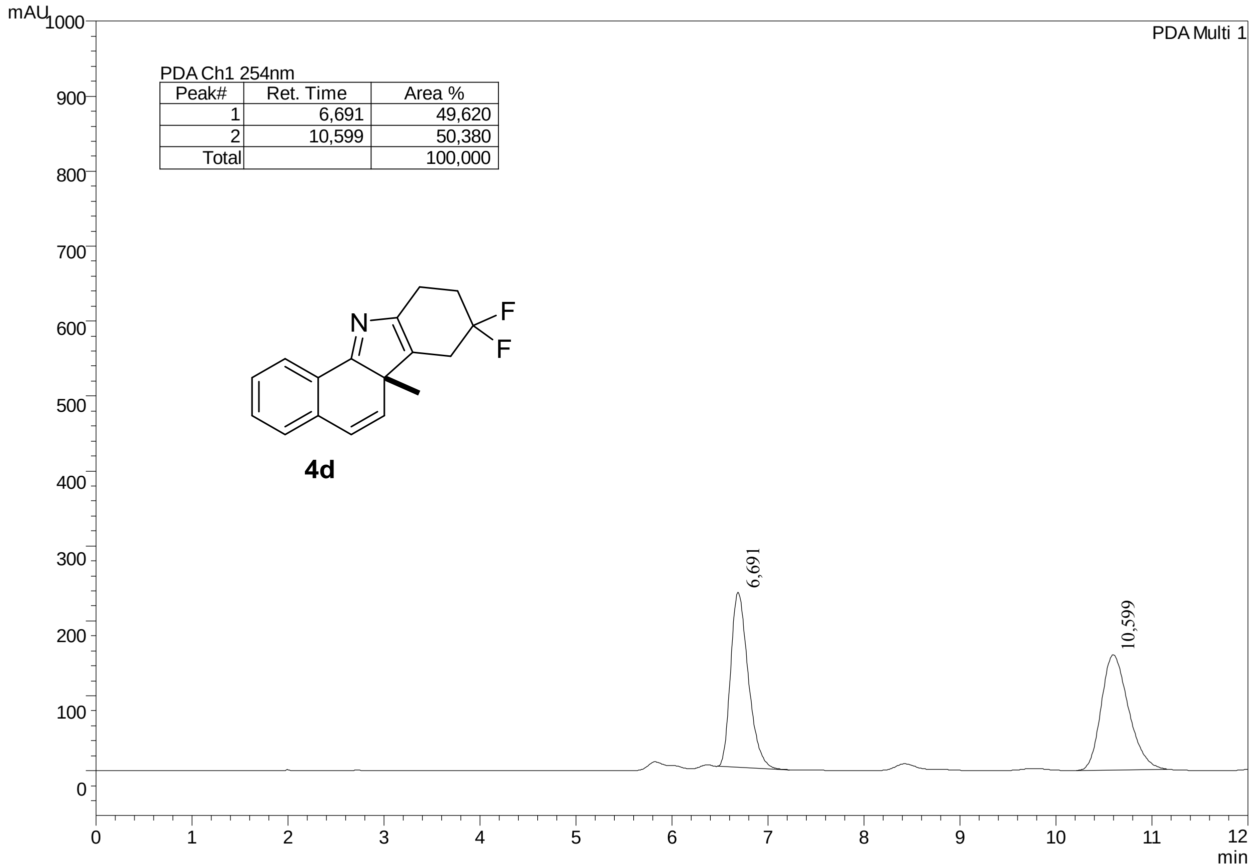
Peak#	Ret. Time	Area %
1	3,545	99,115
2	5,821	0,885
Total		100,000



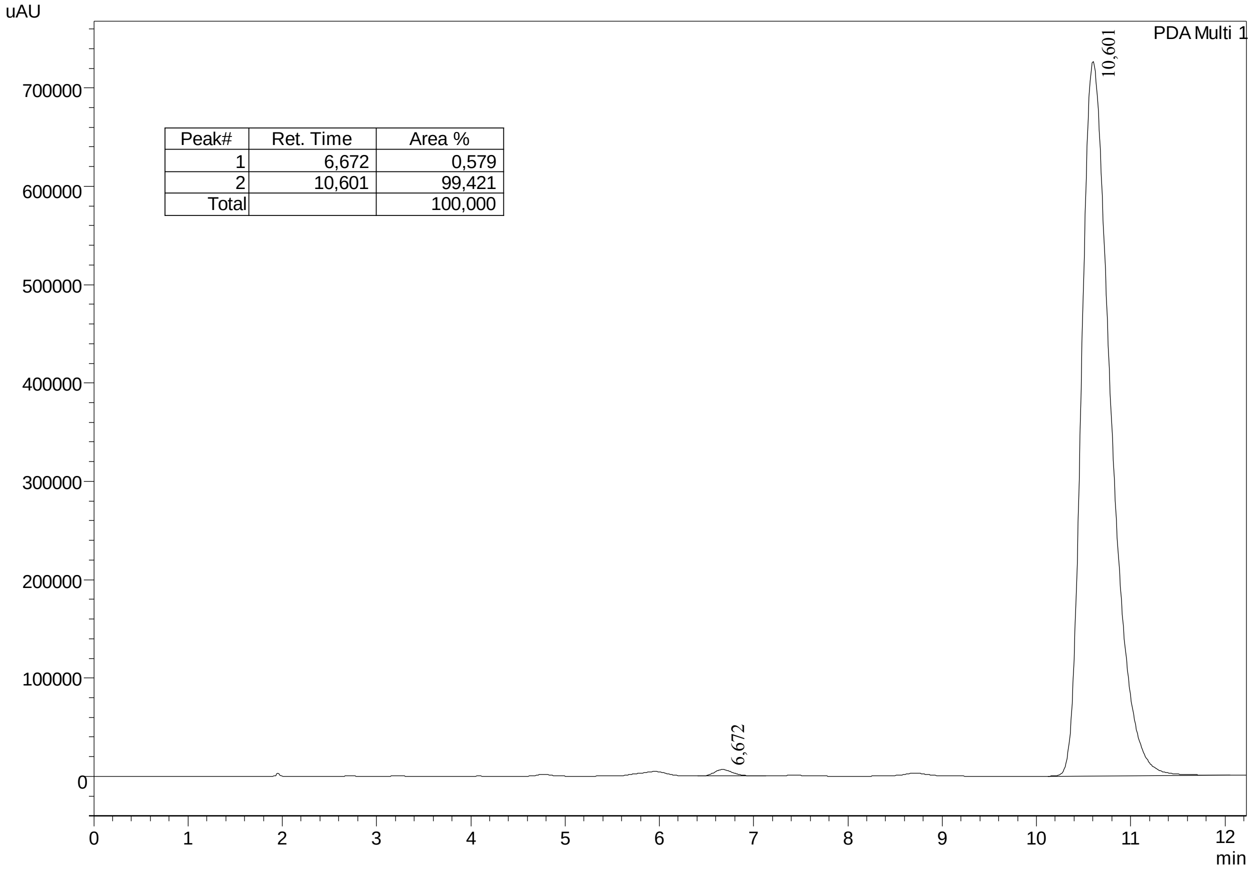
Peak#	Ret. Time	Area %
1	2,893	50,040
2	4,737	49,960
Total		100,000



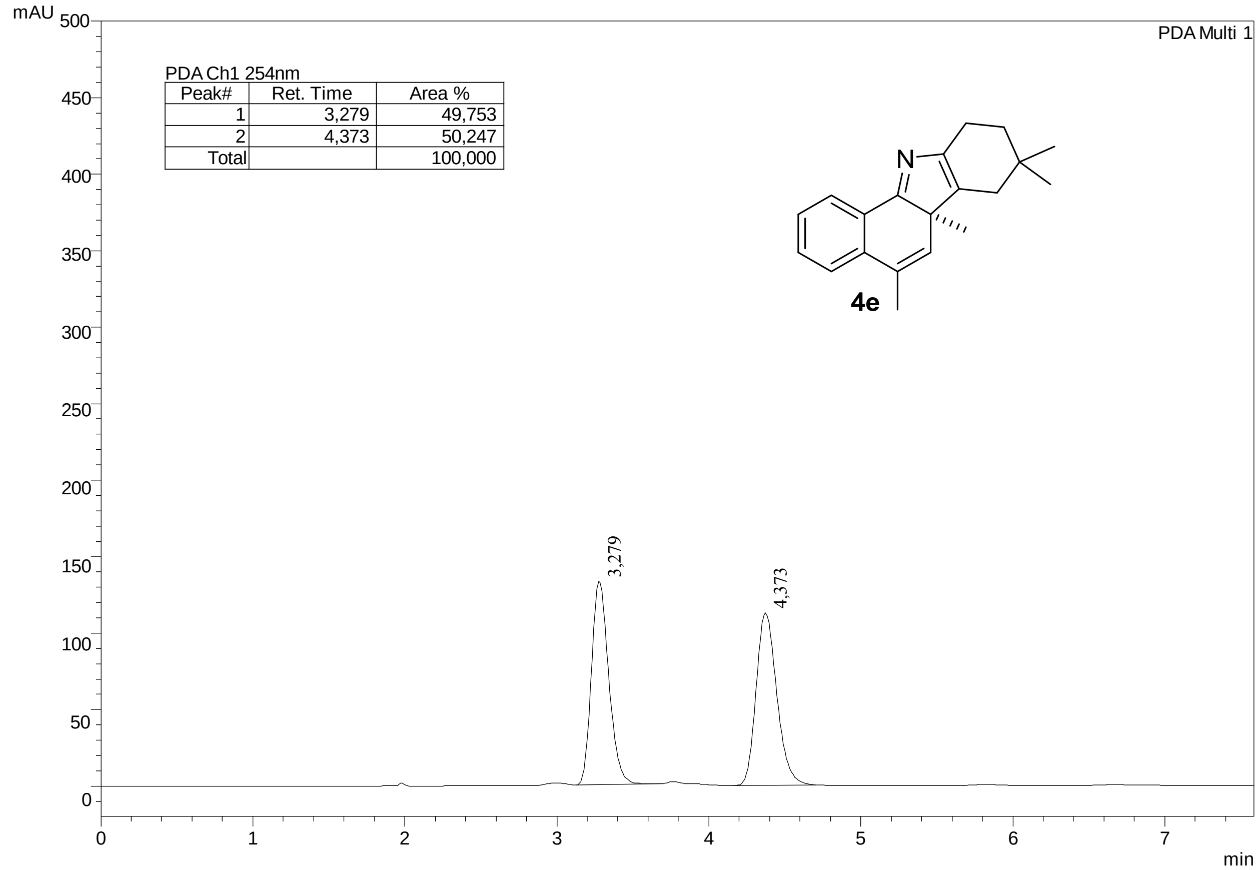
Peak#	Ret. Time	Area %
1	2,924	97,150
2	4,803	2,850
Total		100,000



Peak#	Ret. Time	Area %
1	6,691	49,620
2	10,599	50,380
Total		100,000

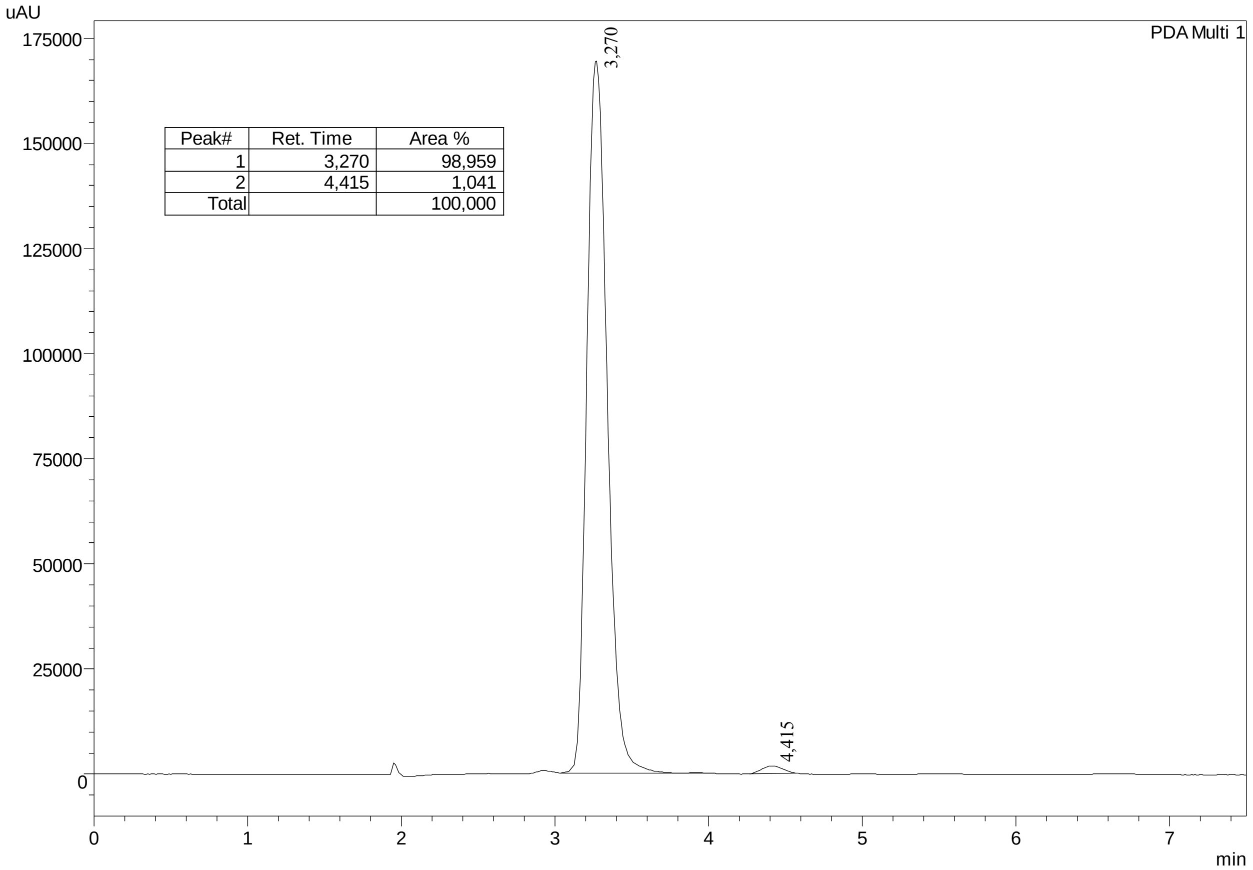


Peak#	Ret. Time	Area %
1	6,672	0,579
2	10,601	99,421
Total		100,000

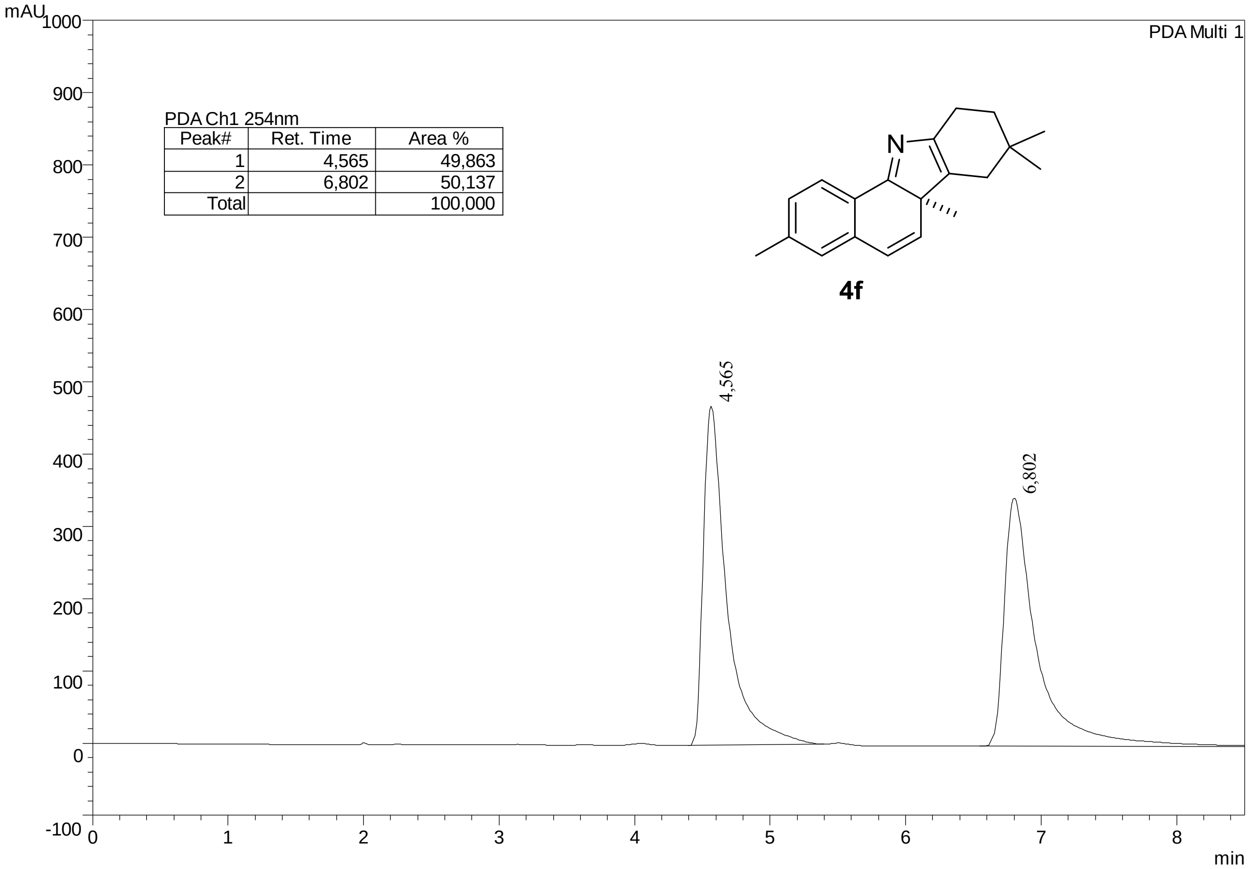


PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,279	49,753
2	4,373	50,247
Total		100,000



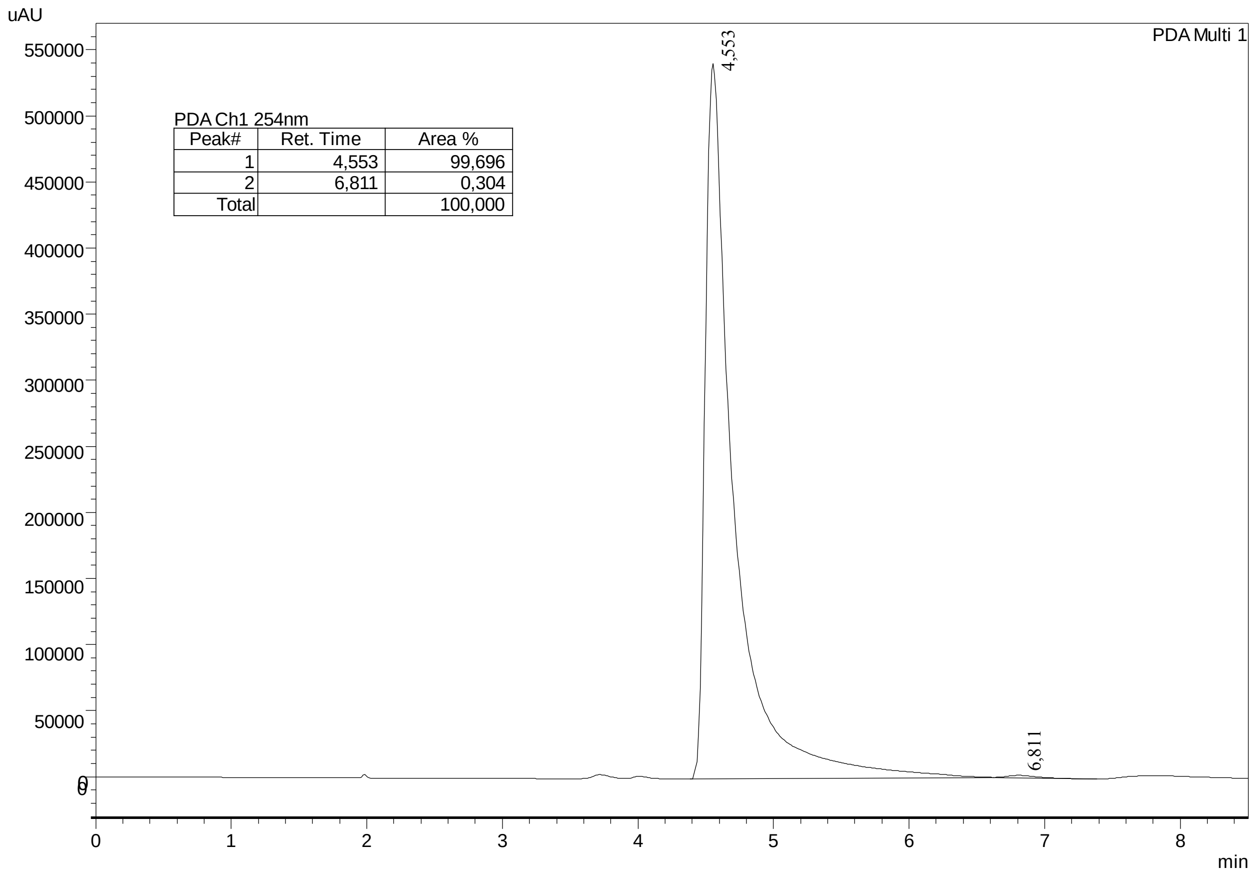
Peak#	Ret. Time	Area %
1	3,270	98,959
2	4,415	1,041
Total		100,000



PDA Ch1 254nm

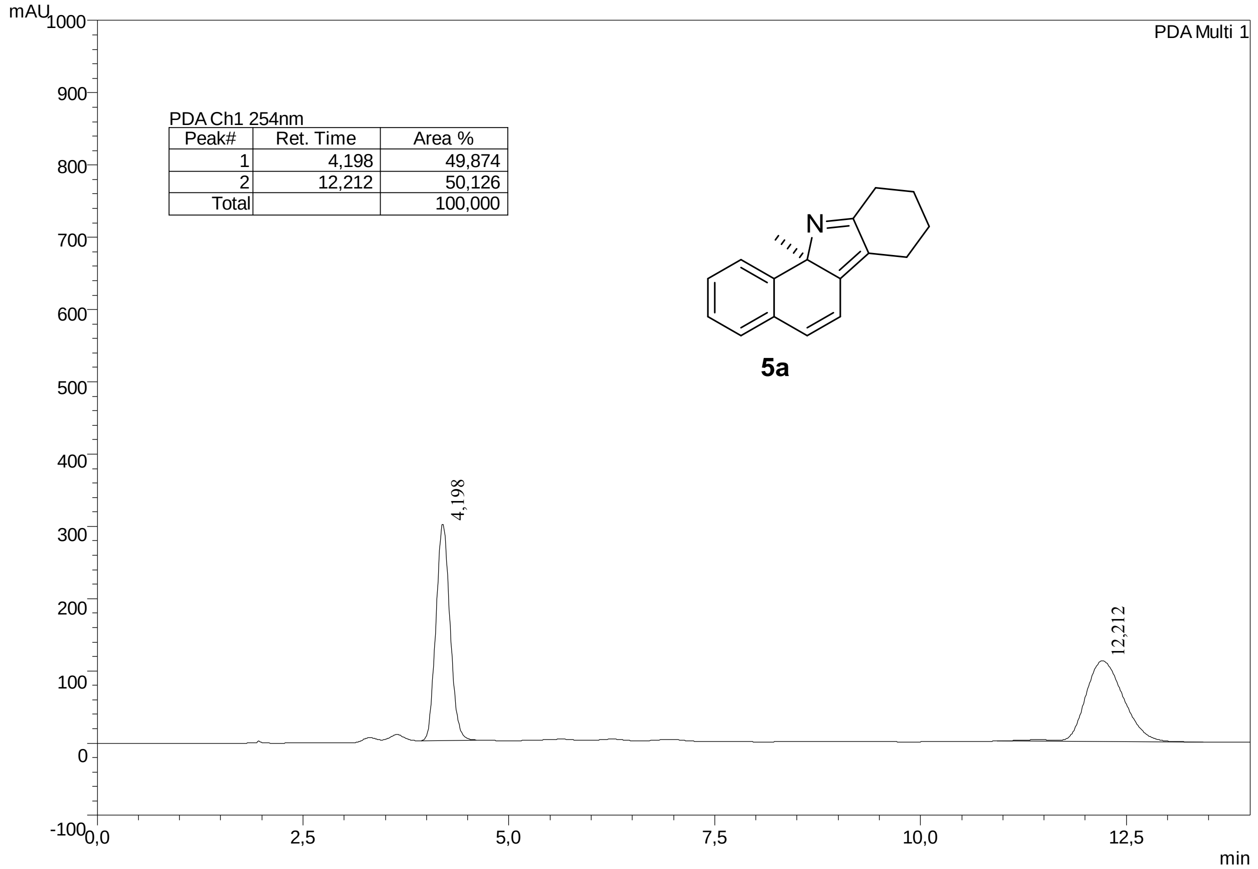
Peak#	Ret. Time	Area %
1	4,565	49,863
2	6,802	50,137
Total		100,000

4f



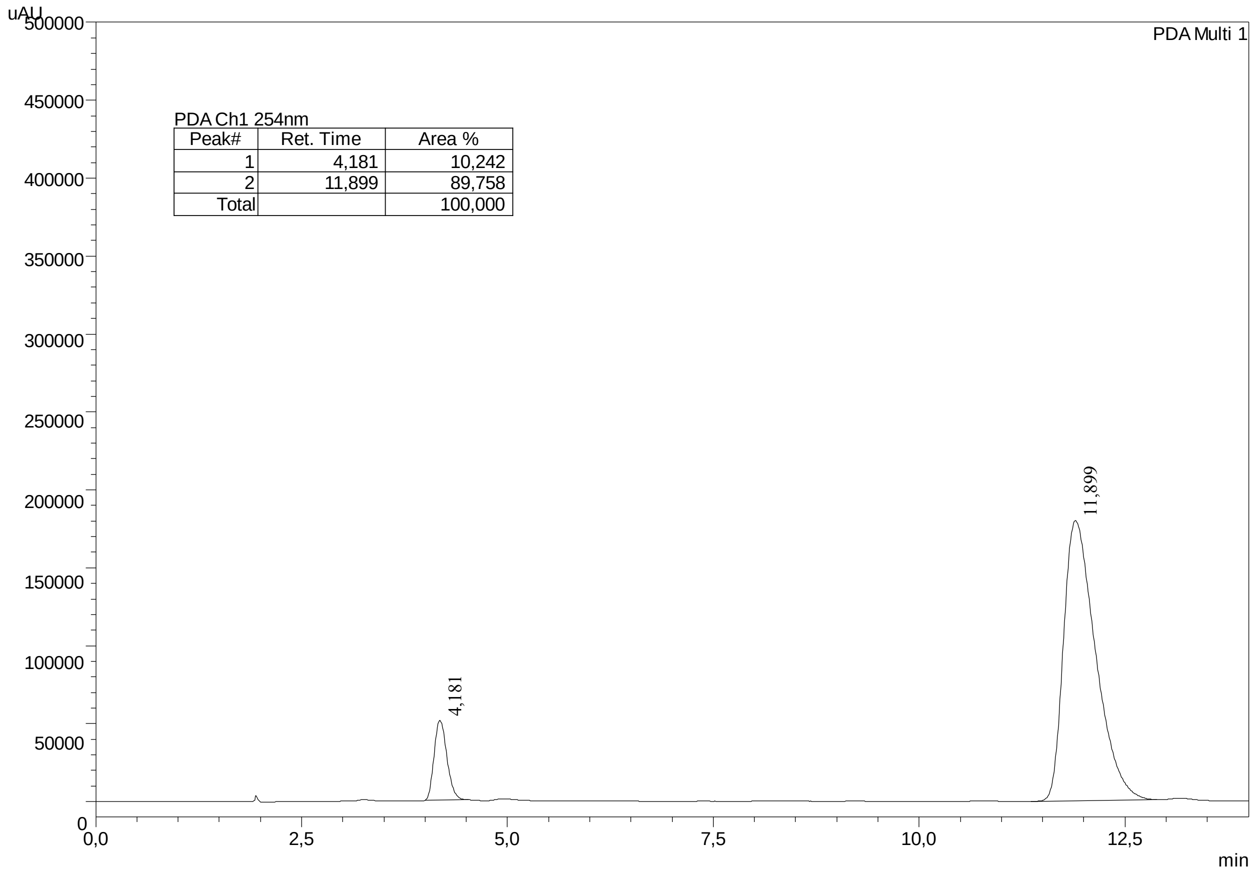
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	4,553	99,696
2	6,811	0,304
Total		100,000



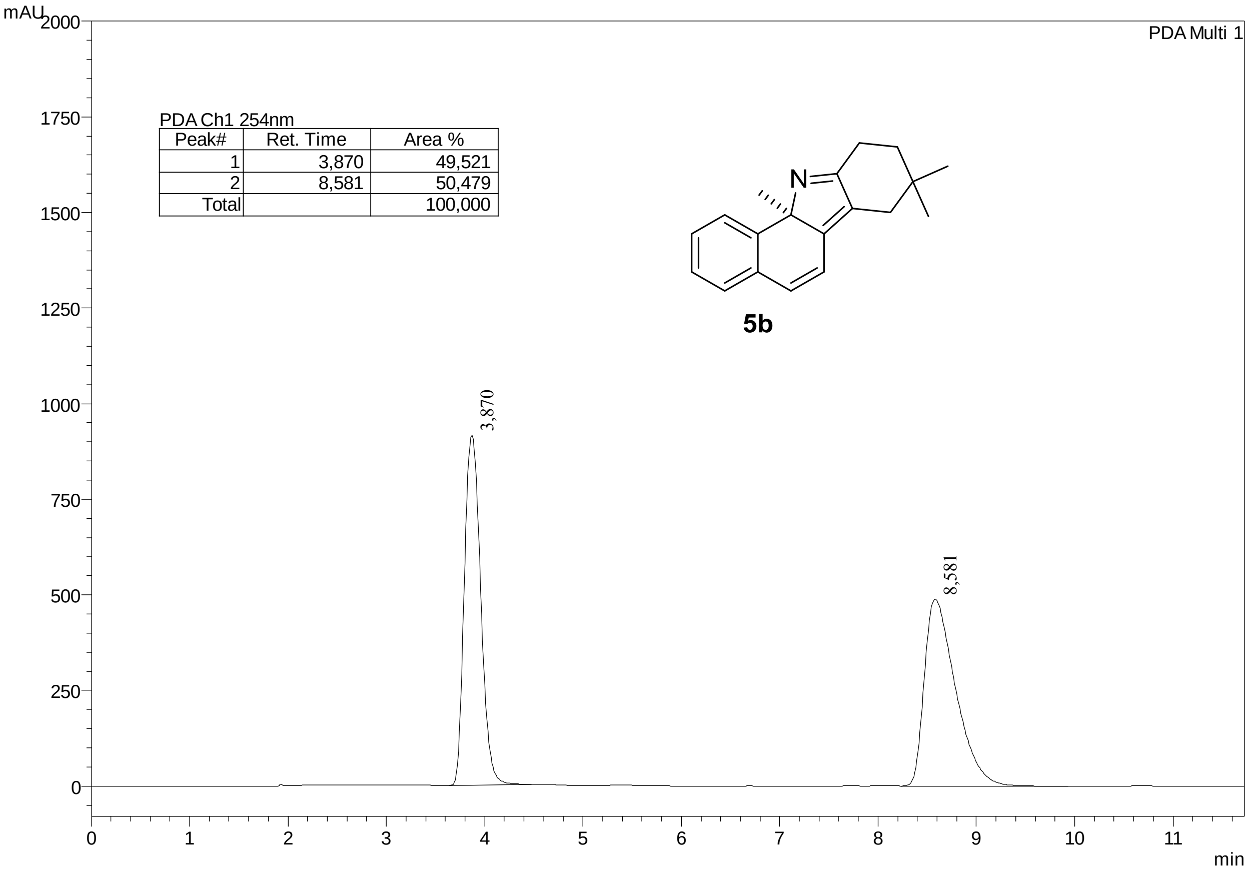
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	4,198	49,874
2	12,212	50,126
Total		100,000



PDA Ch1 254nm

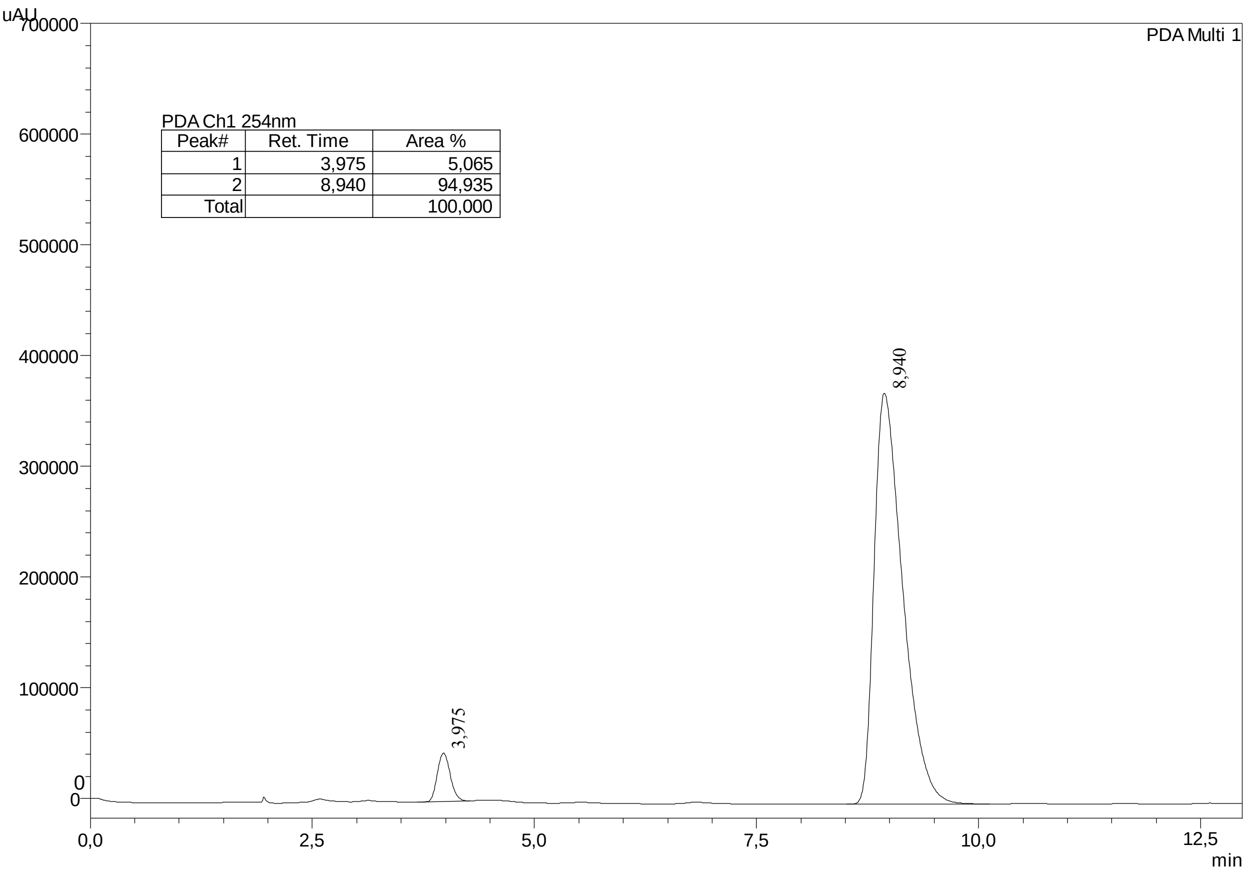
Peak#	Ret. Time	Area %
1	4,181	10,242
2	11,899	89,758
Total		100,000



PDA Ch1 254nm

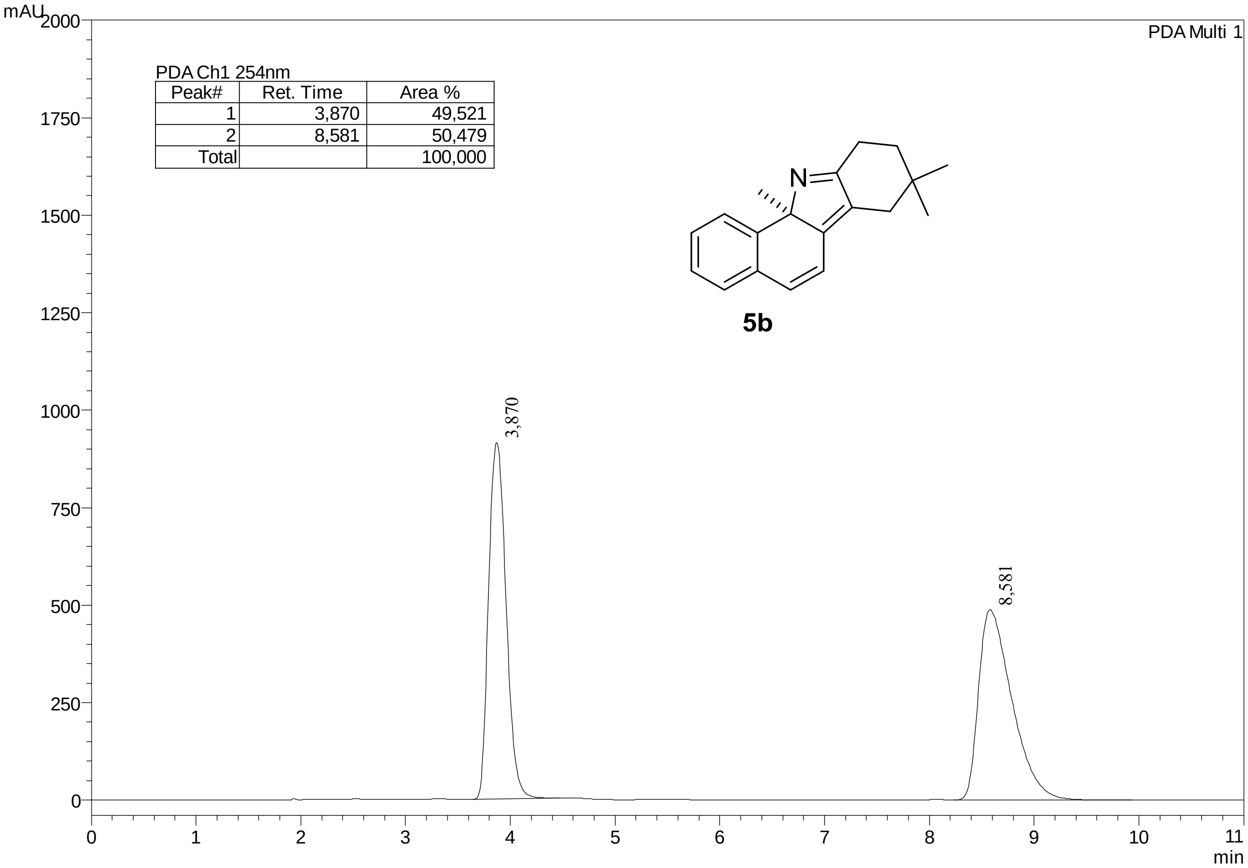
Peak#	Ret. Time	Area %
1	3,870	49,521
2	8,581	50,479
Total		100,000

5b



PDA Ch1 254nm

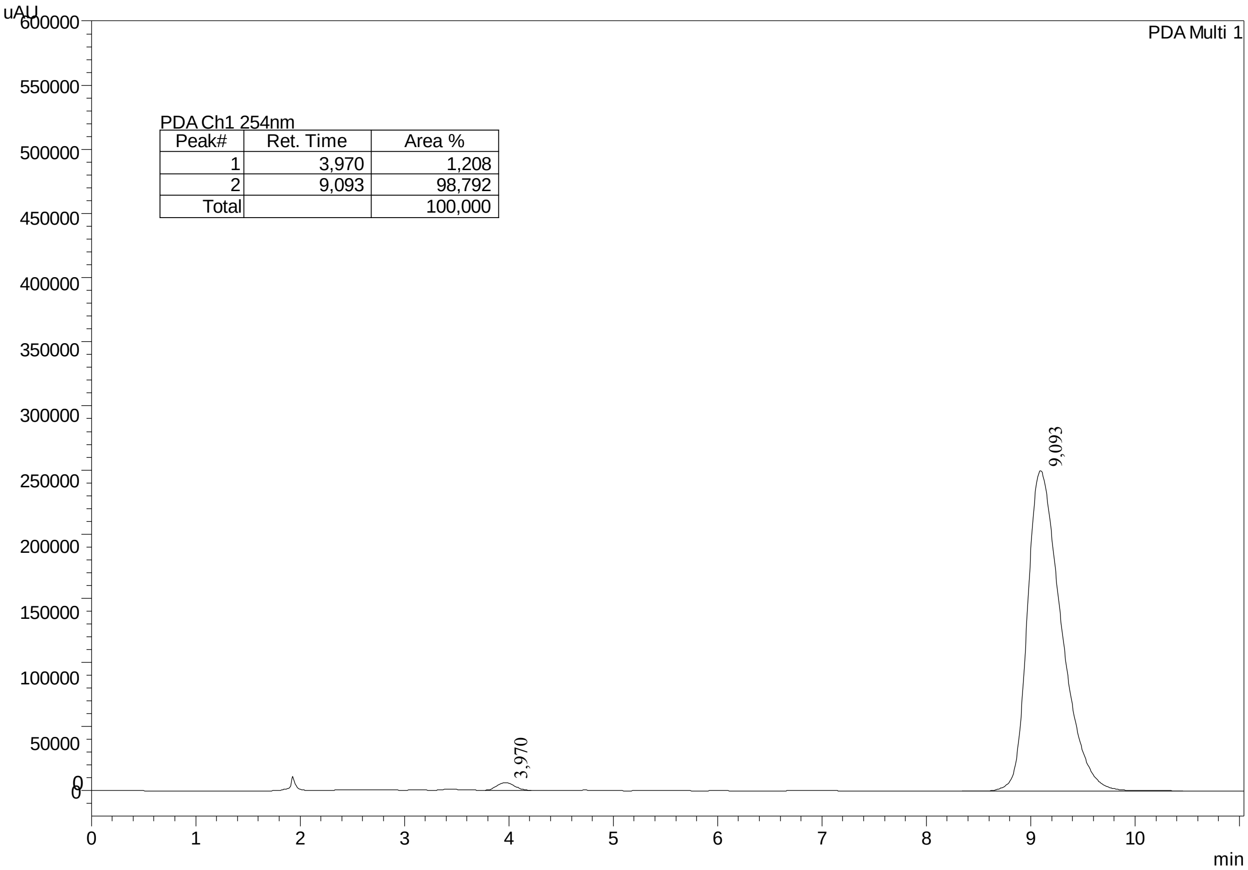
Peak#	Ret. Time	Area %
1	3,975	5,065
2	8,940	94,935
Total		100,000



5b

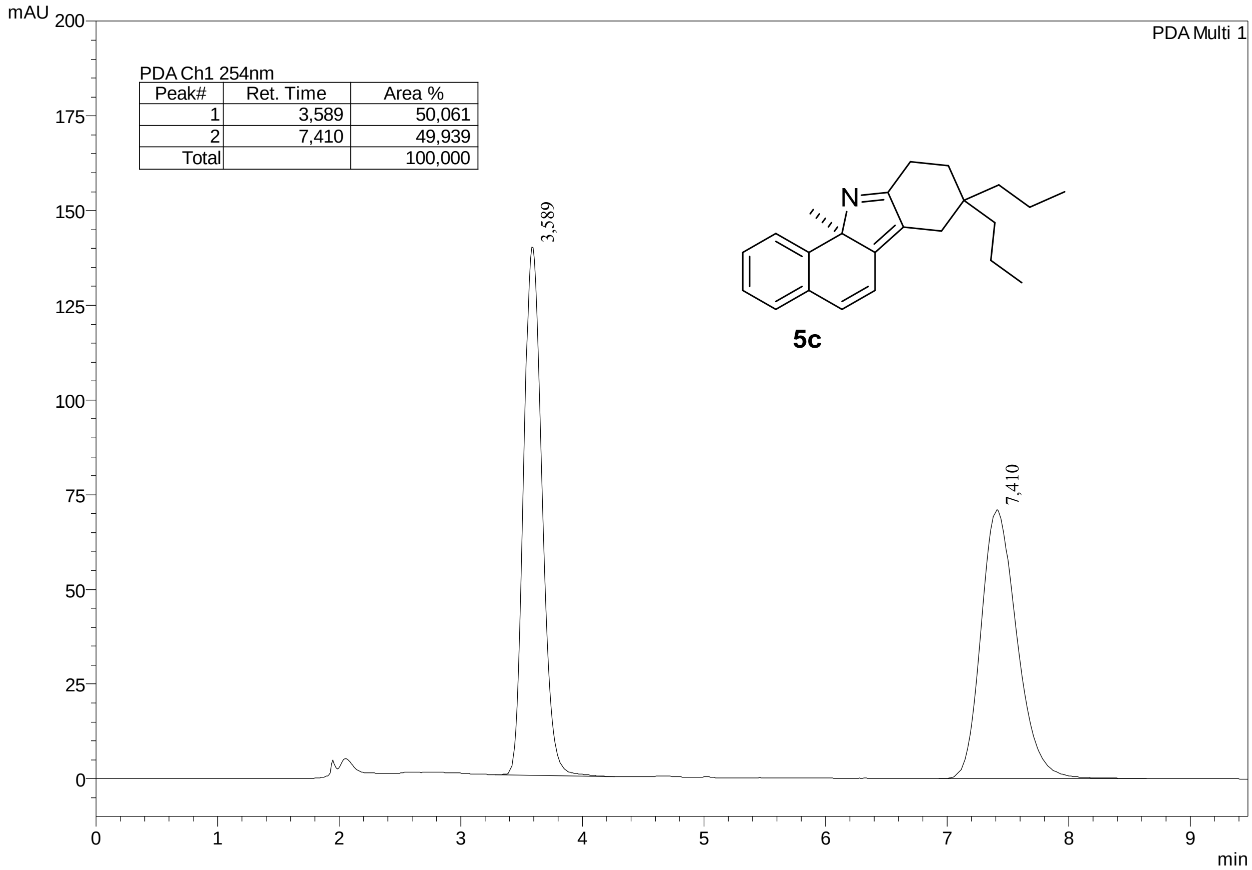
PDA Ch1 254nm

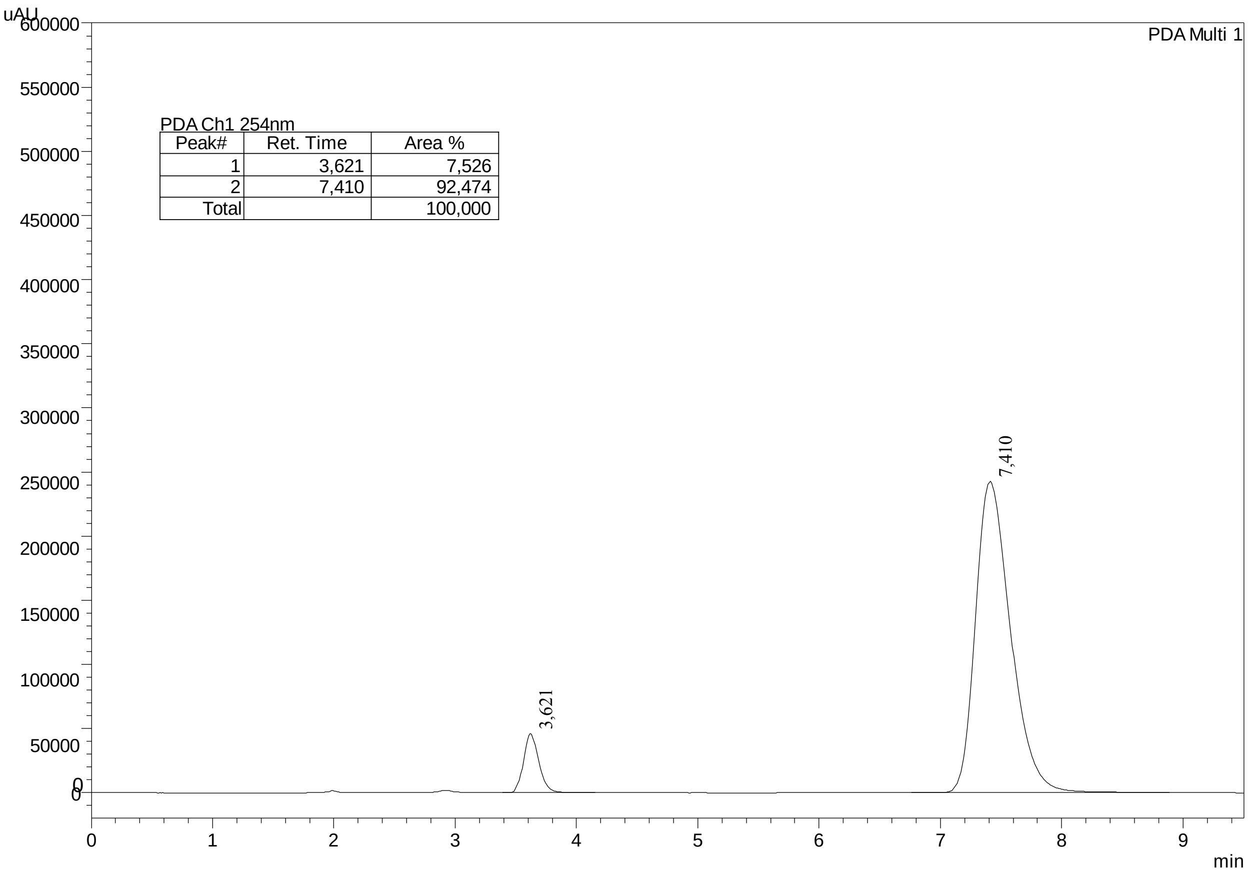
Peak#	Ret. Time	Area %
1	3,870	49,521
2	8,581	50,479
Total		100,000

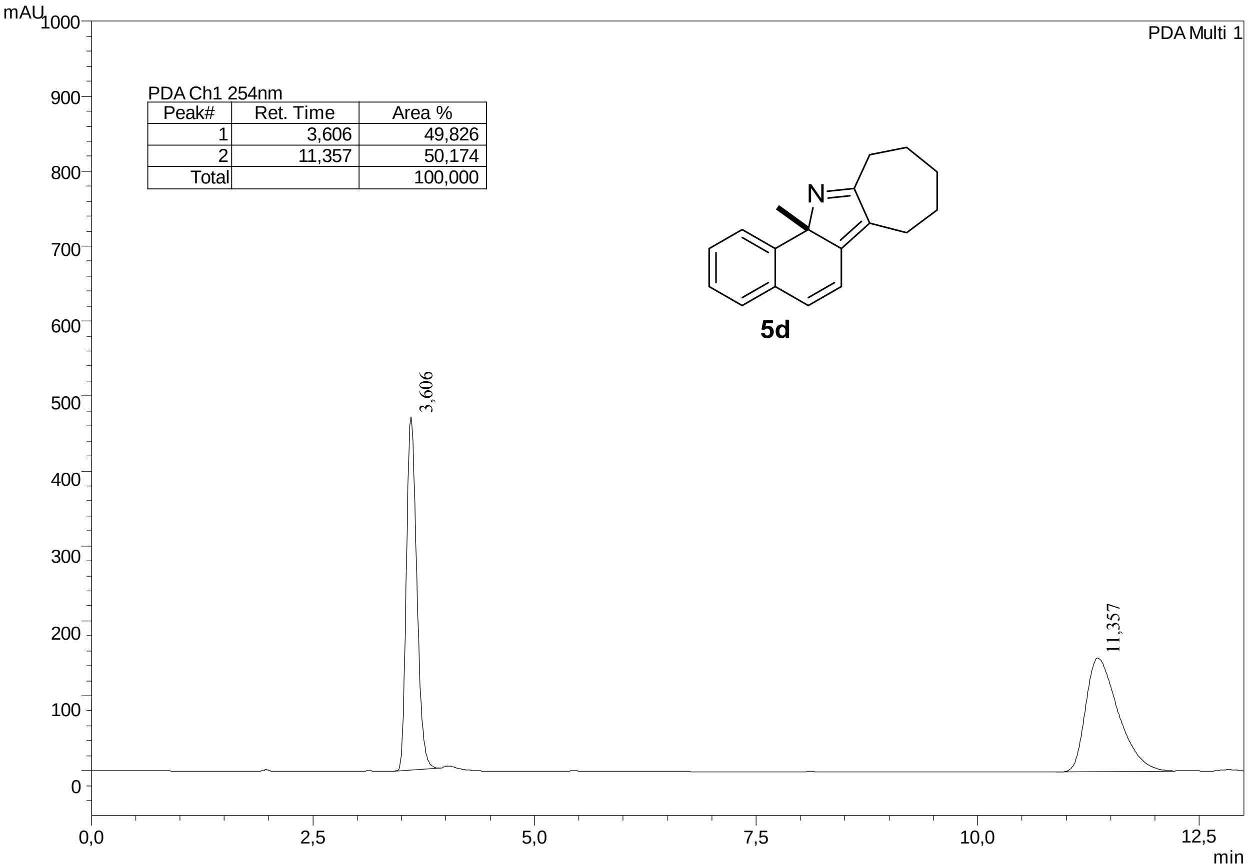


PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,970	1,208
2	9,093	98,792
Total		100,000

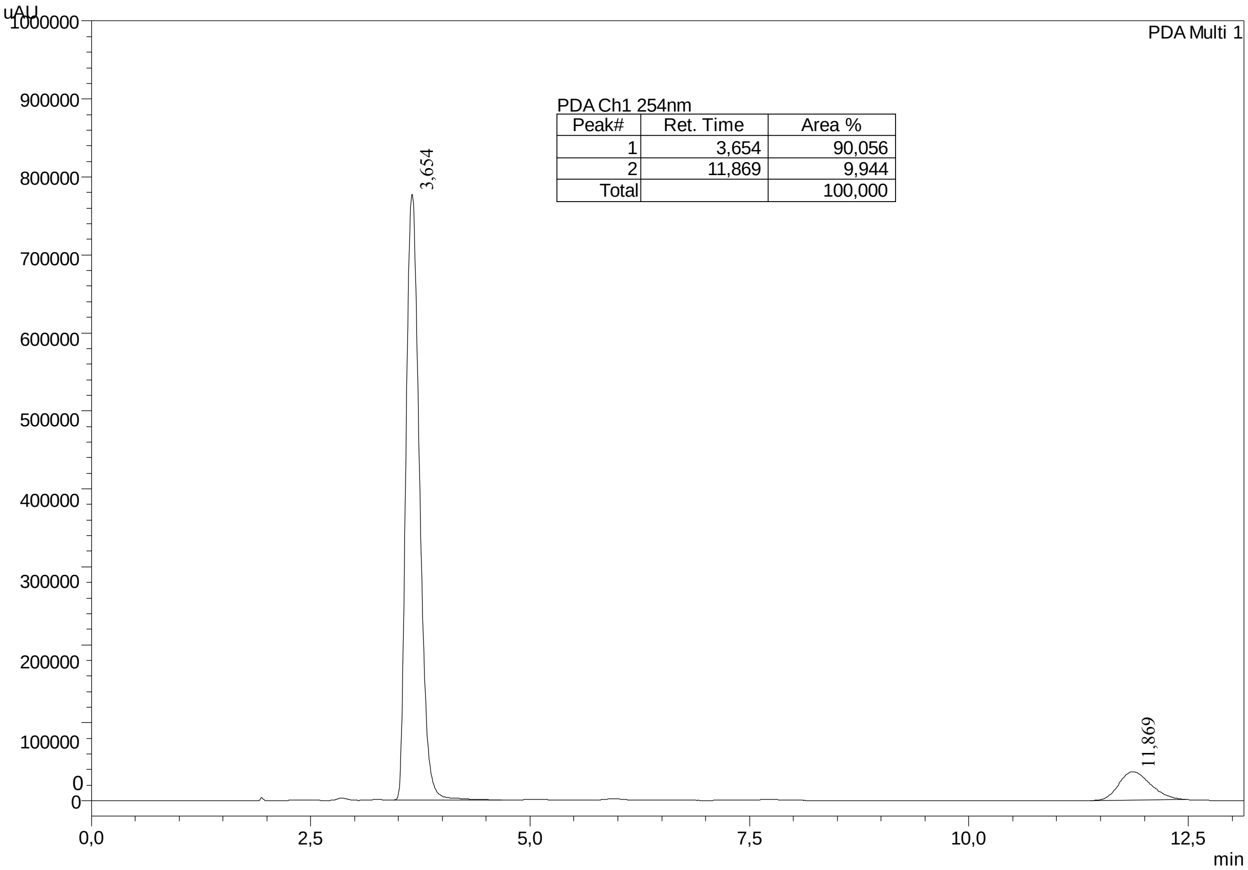

mAU
PDA Multi 1
PDA Ch1 254nm
Peak# Ret. Time Area %
1 3,589 50,061
2 7,410 49,939
Total 100,000
3,589
7,410
N
5c
min


uAU
PDA Multi 1
PDA Ch1 254nm
Peak# Ret. Time Area %
1 3,621 7,526
2 7,410 92,474
Total 100,000
3,621
7,410
min



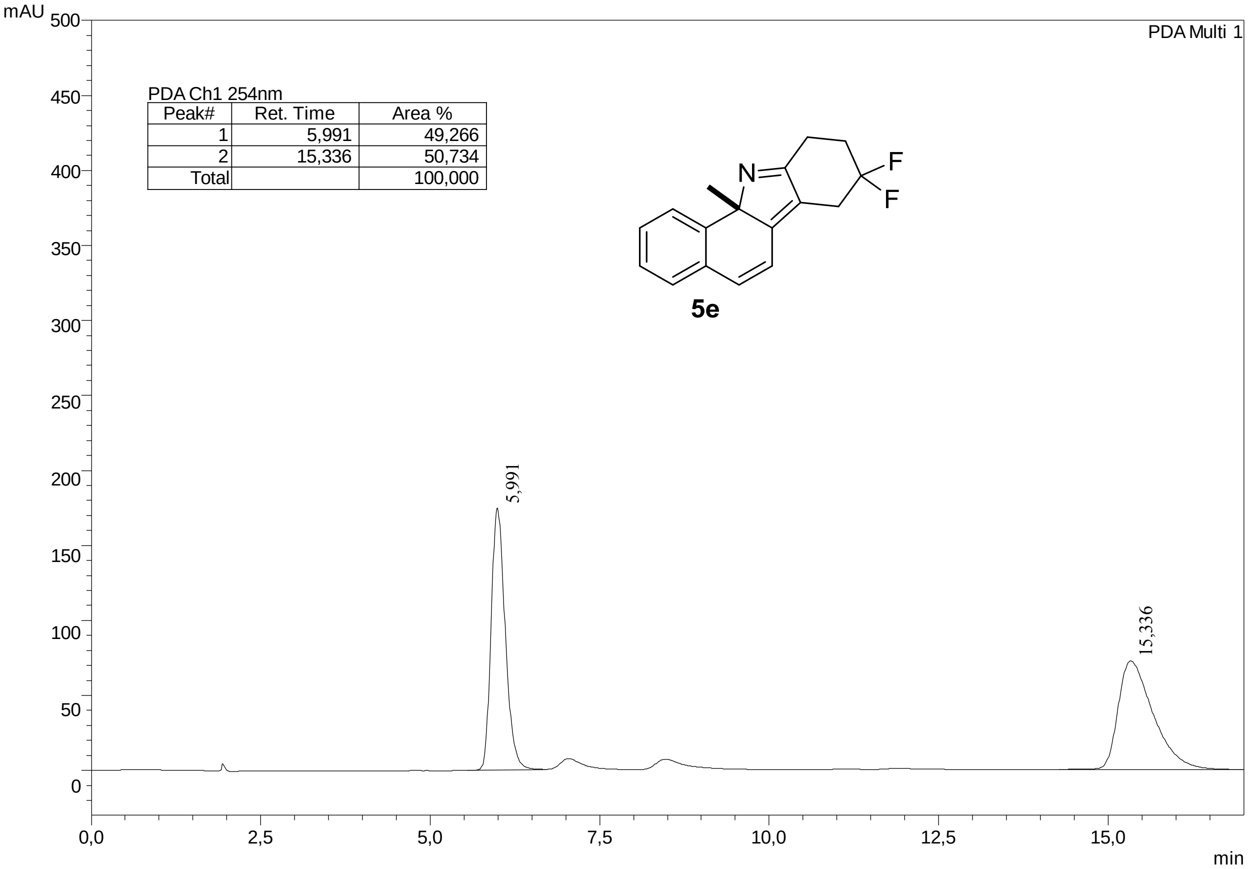
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,606	49,826
2	11,357	50,174
Total		100,000



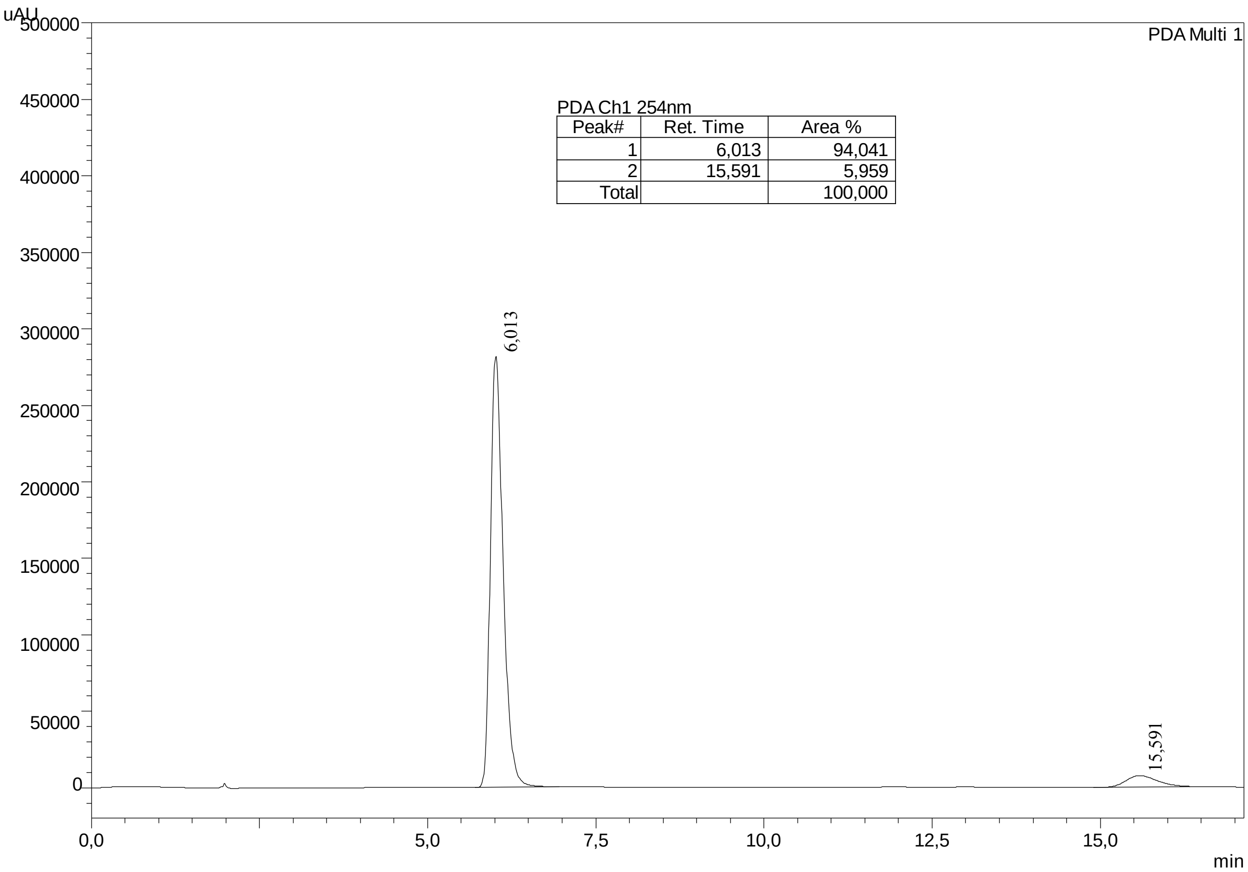
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,654	90,056
2	11,869	9,944
Total		100,000



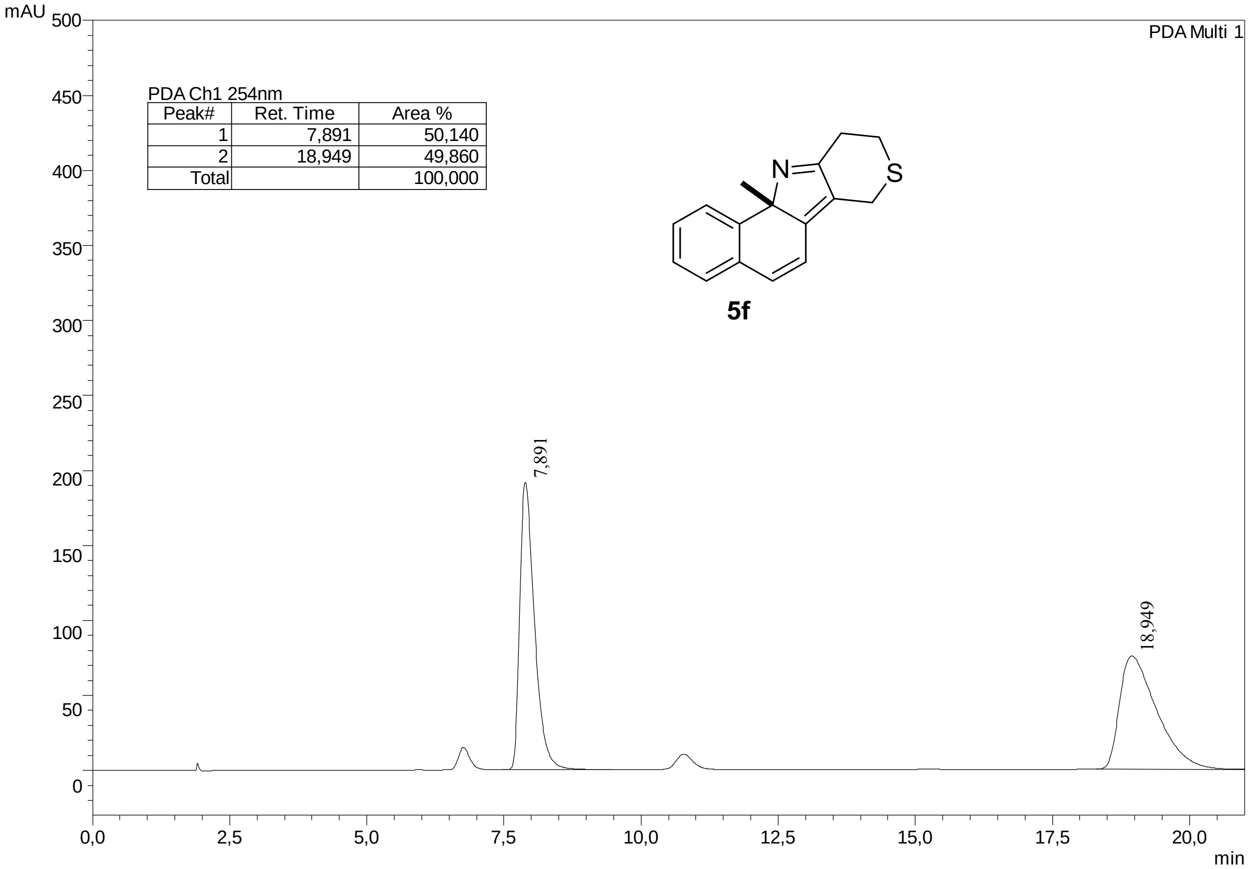
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	5,991	49,266
2	15,336	50,734
Total		100,000



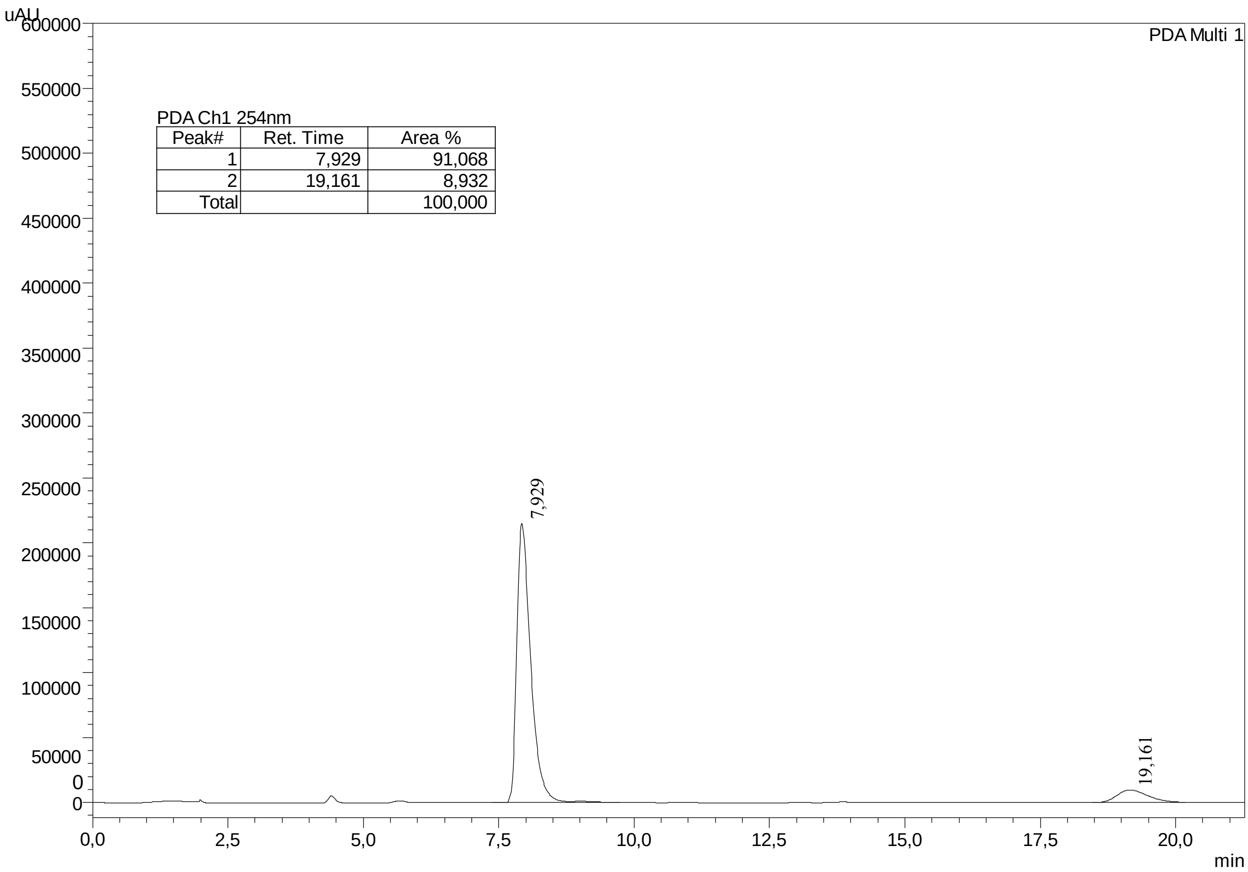
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	6,013	94,041
2	15,591	5,959
Total		100,000



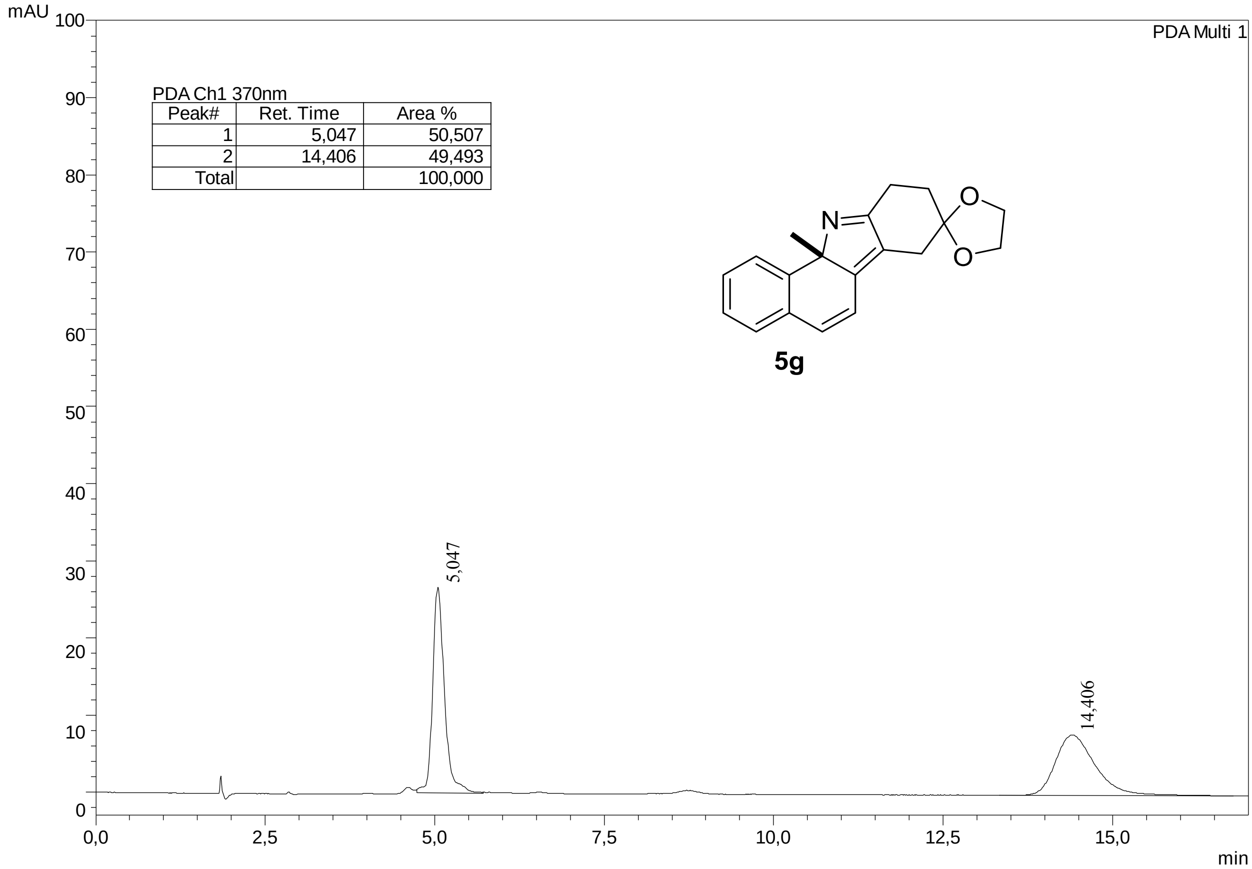
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	7,891	50,140
2	18,949	49,860
Total		100,000



PDA Ch1 254nm

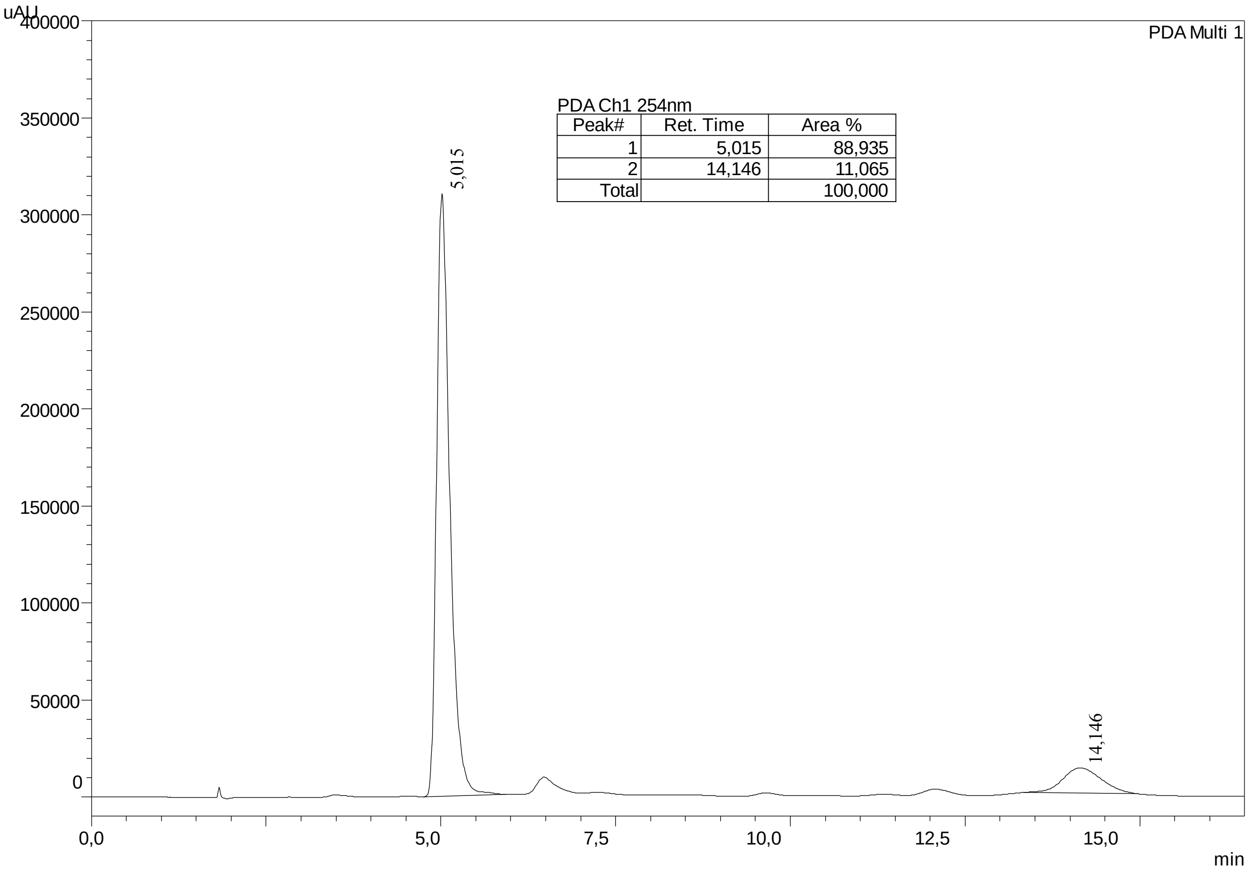
Peak#	Ret. Time	Area %
1	7,929	91,068
2	19,161	8,932
Total		100,000



PDA Ch1 370nm

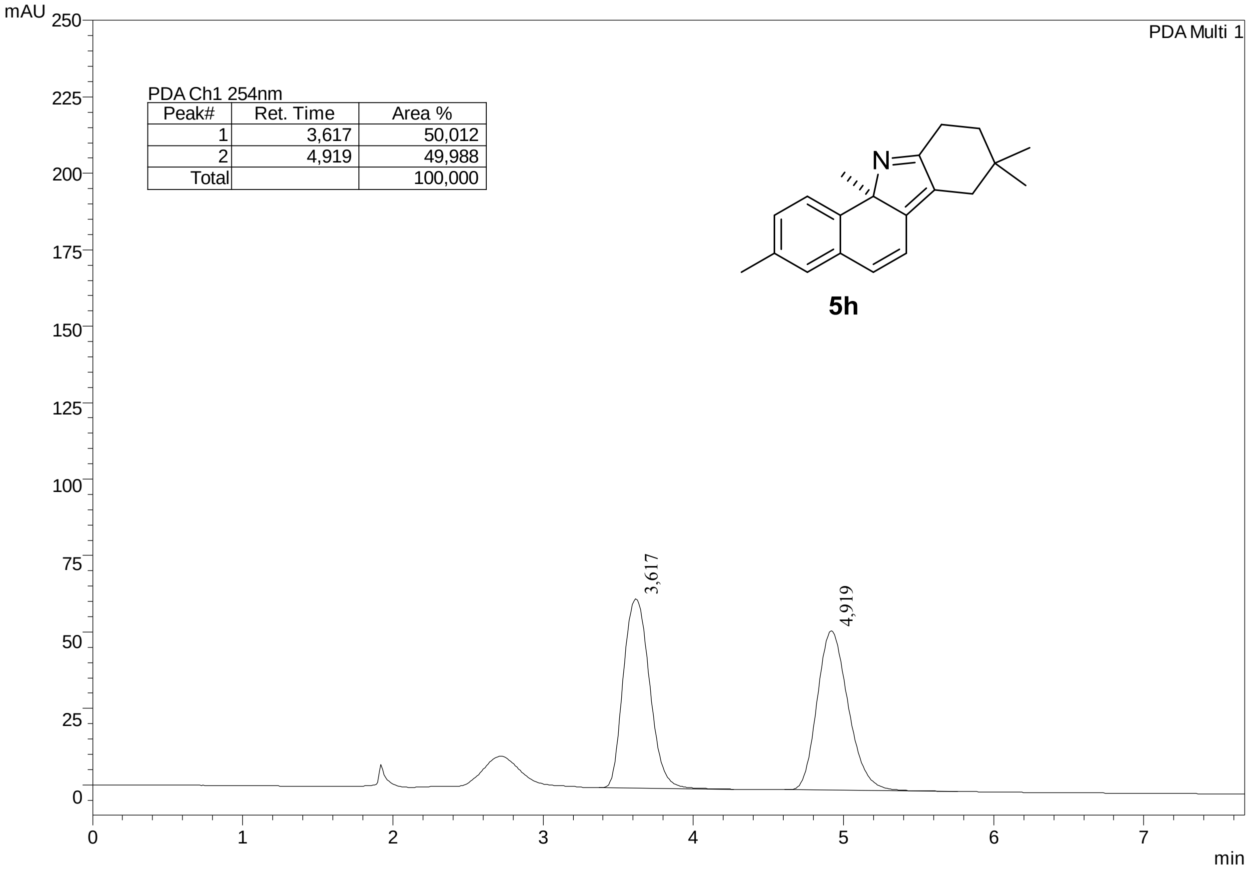
Peak#	Ret. Time	Area %
1	5,047	50,507
2	14,406	49,493
Total		100,000

5g



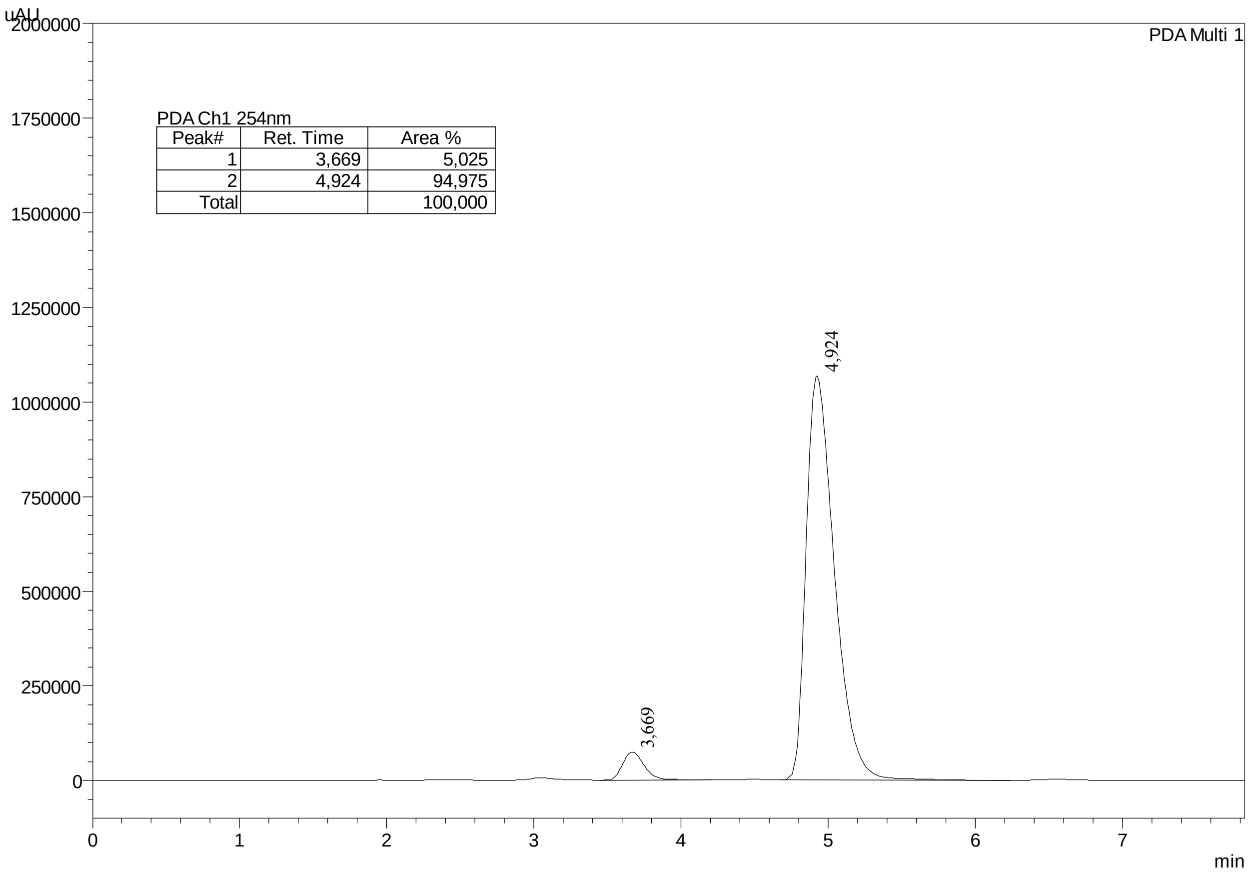
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	5,015	88,935
2	14,146	11,065
Total		100,000



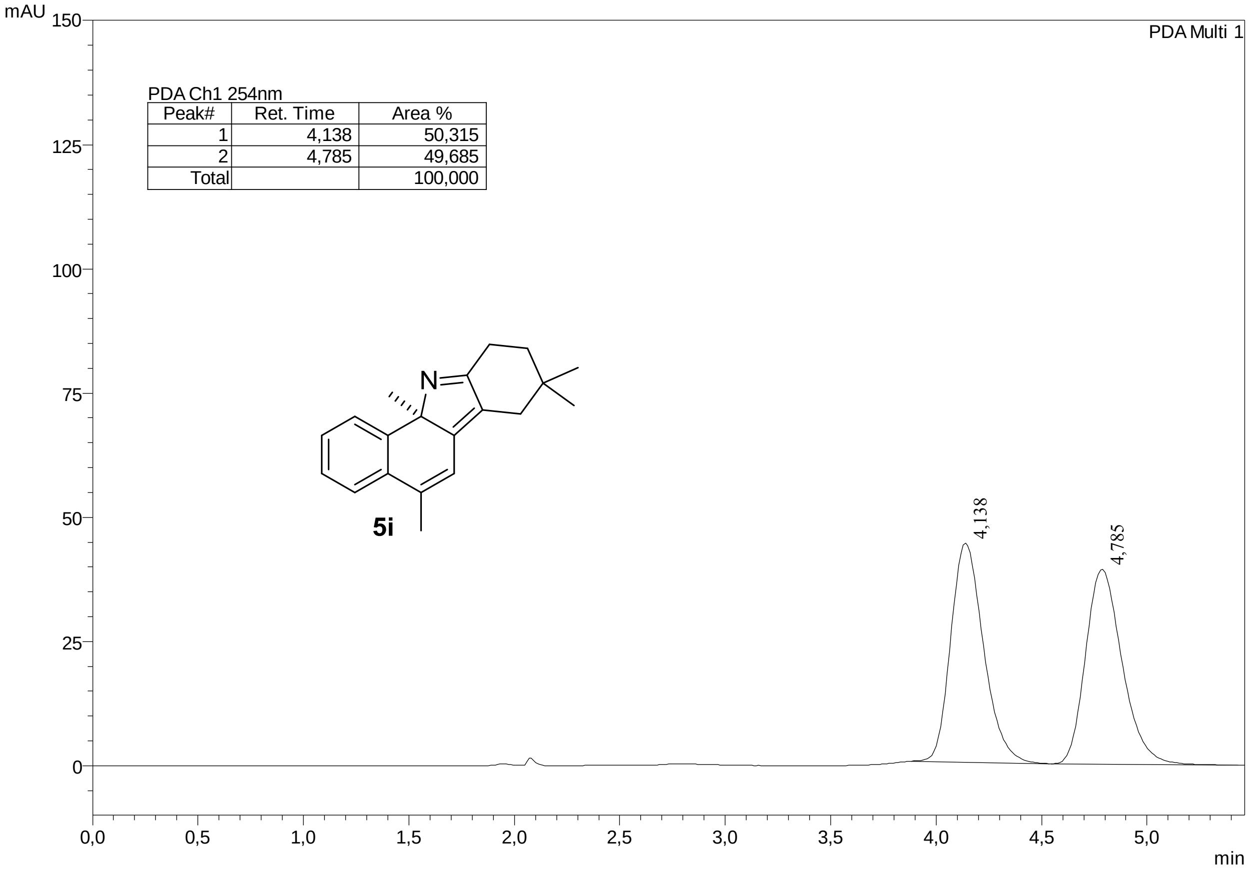
PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,617	50,012
2	4,919	49,988
Total		100,000

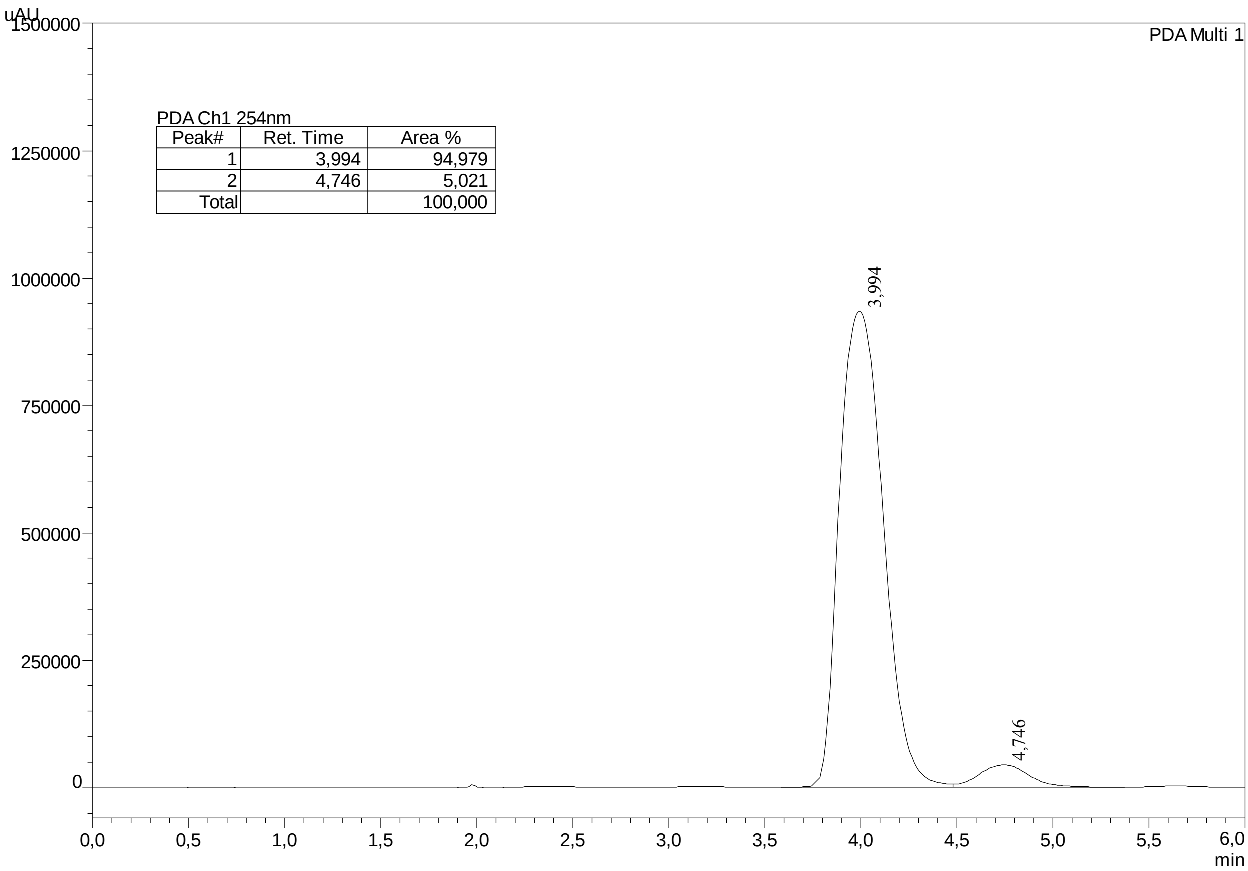


PDA Ch1 254nm

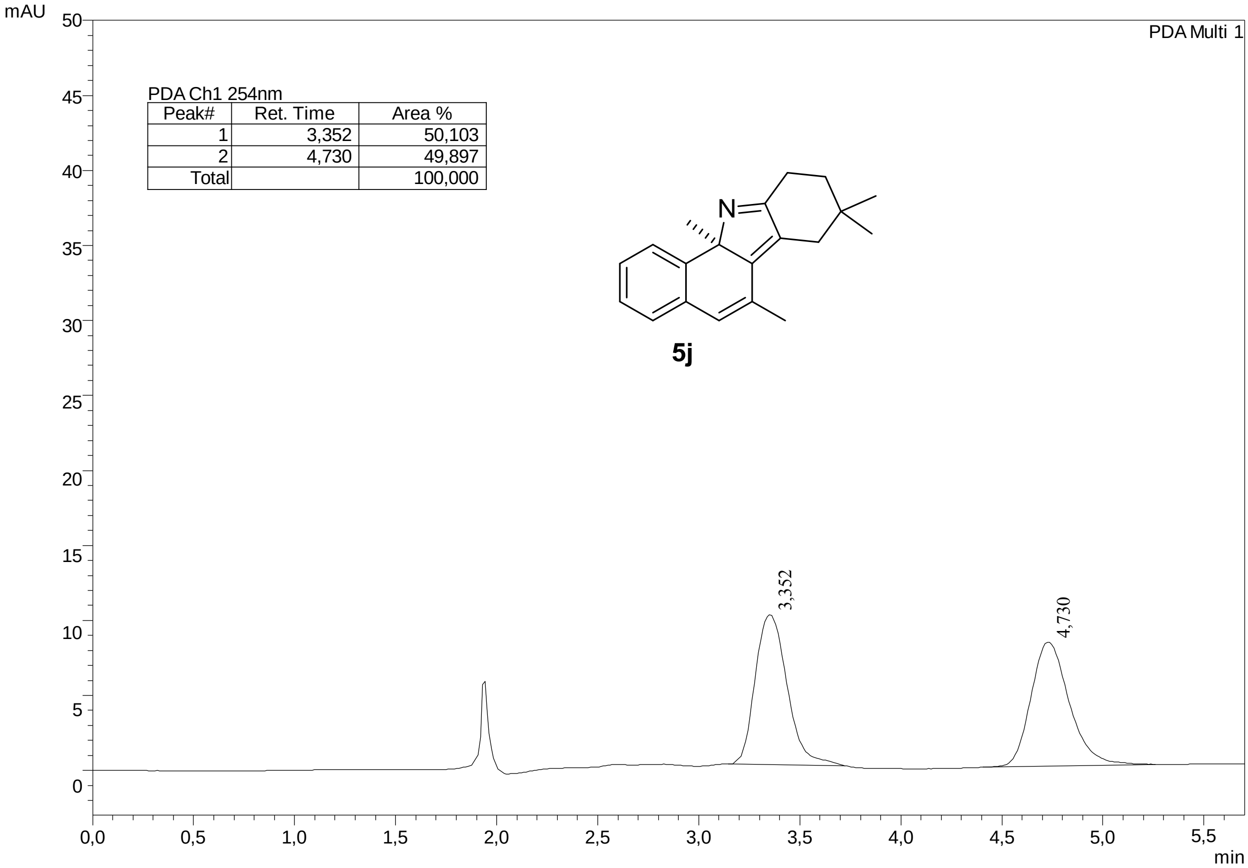
Peak#	Ret. Time	Area %
1	3,669	5,025
2	4,924	94,975
Total		100,000



Peak#	Ret. Time	Area %
1	4,138	50,315
2	4,785	49,685
Total		100,000



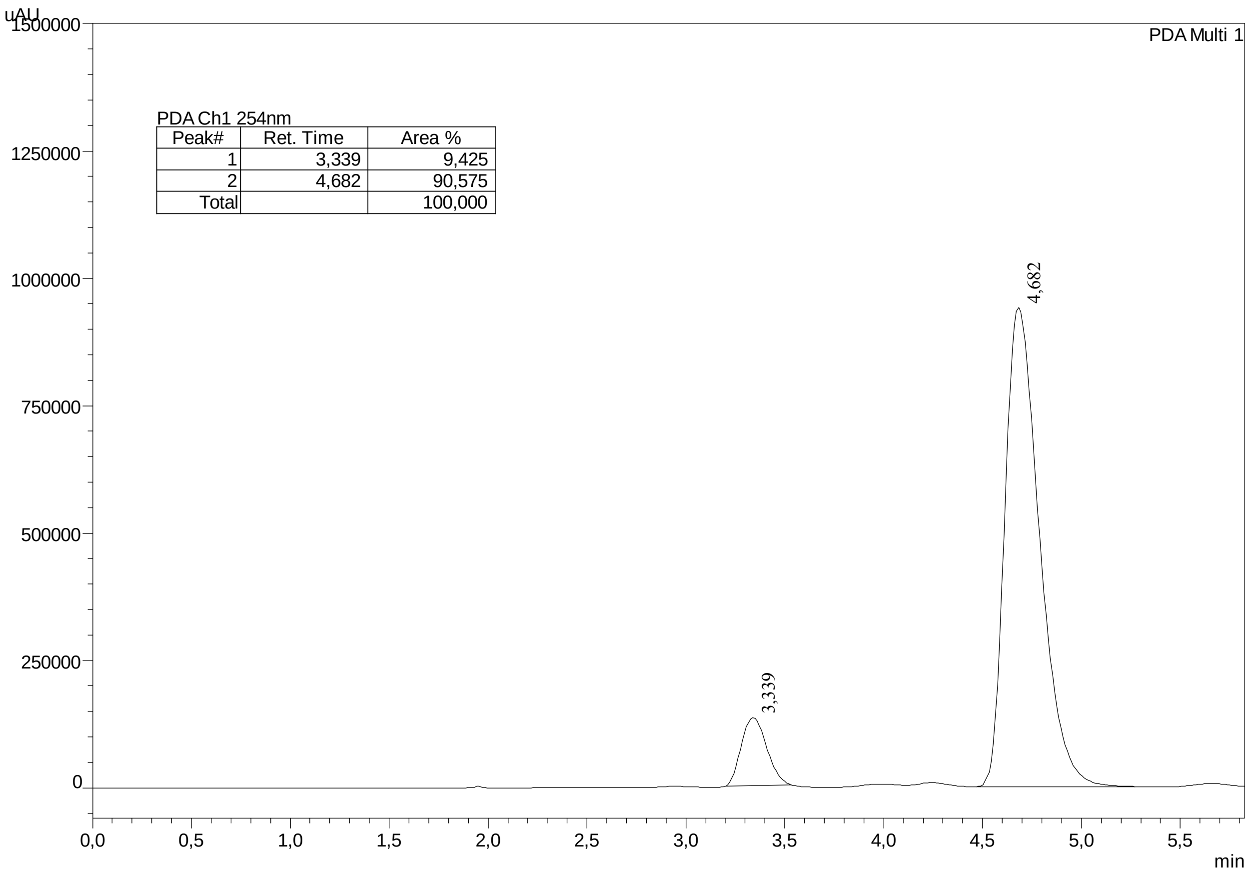
Peak#	Ret. Time	Area %
1	3,994	94,979
2	4,746	5,021
Total		100,000



PDA Ch1 254nm

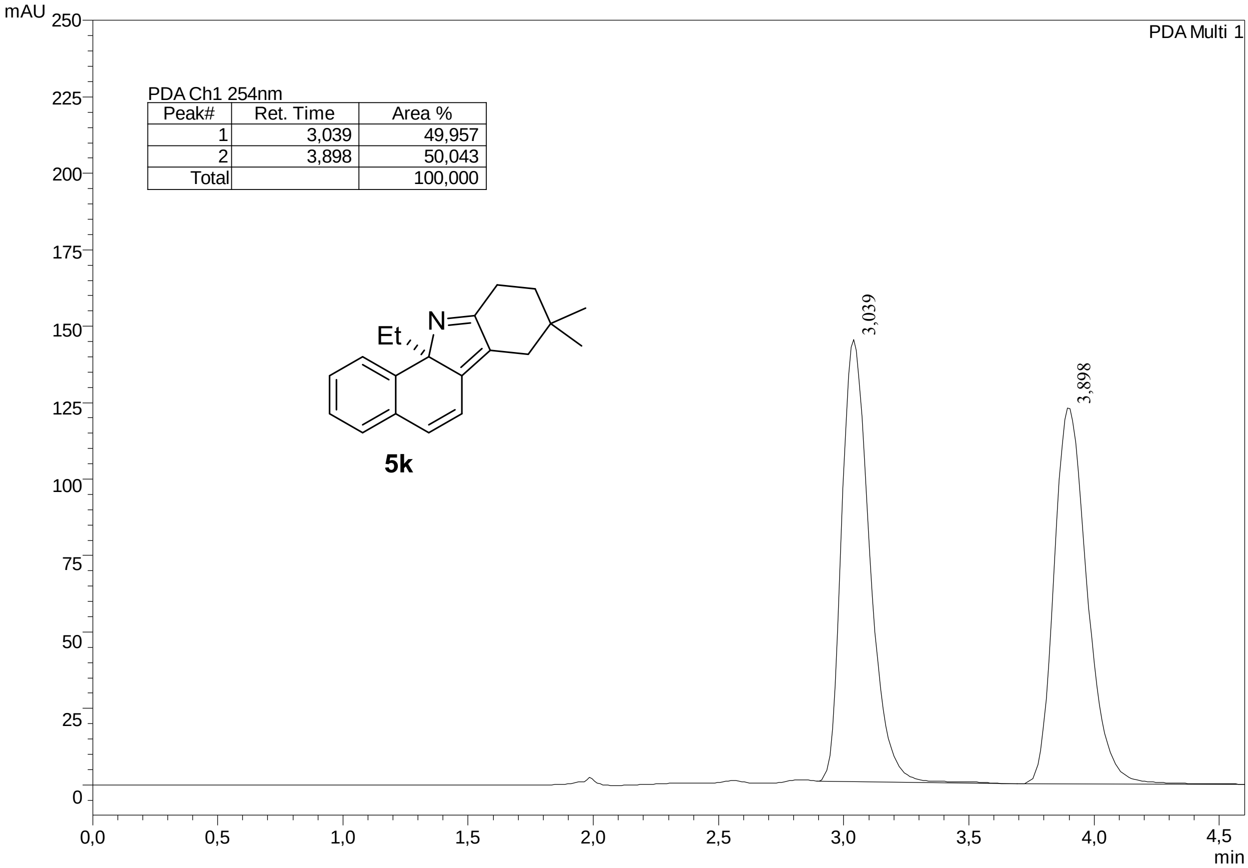
Peak#	Ret. Time	Area %
1	3,352	50,103
2	4,730	49,897
Total		100,000

5j

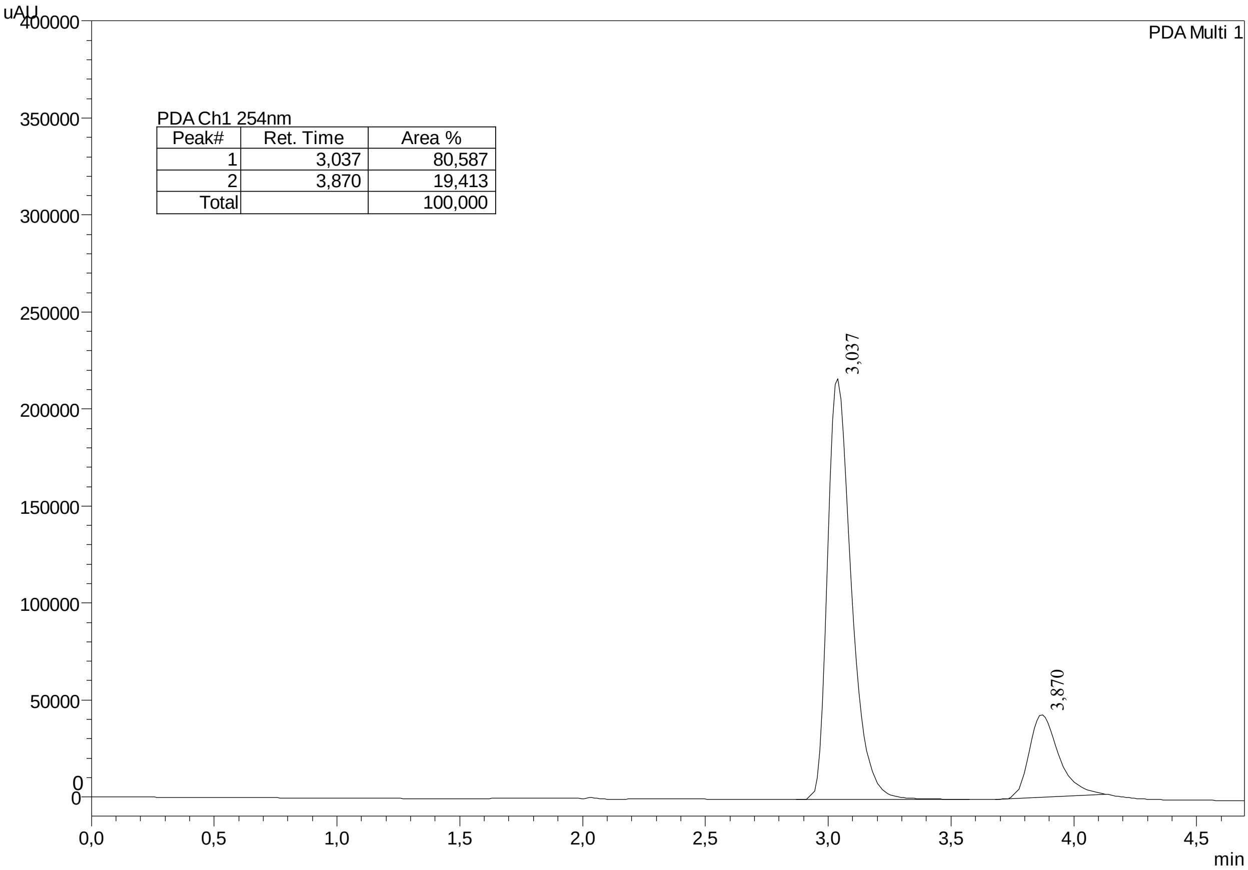


PDA Ch1 254nm

Peak#	Ret. Time	Area %
1	3,339	9,425
2	4,682	90,575
Total		100,000



Peak#	Ret. Time	Area %
1	3,039	49,957
2	3,898	50,043
Total		100,000



Peak#	Ret. Time	Area %
1	3,037	80,587
2	3,870	19,413
Total		100,000

Cartesian coordinates (Å) for all computed species and imaginary frequencies for transition state species

4a-1:

C	4.56931600	-0.39390200	-0.19883700
C	3.80584200	0.71595100	-0.53391400
C	2.41758700	0.69690400	-0.39303900
C	1.80126500	-0.48157400	0.08913900
C	2.57338000	-1.59771900	0.40120600
C	3.95376000	-1.55248600	0.26817800
H	2.09200100	2.64871400	-1.31196700
H	5.64557600	-0.35954900	-0.30849700
H	4.28647400	1.60839600	-0.91607000
C	1.59398500	1.84037200	-0.78916100
C	0.35029600	-0.46811200	0.15800800
H	2.07549600	-2.49278200	0.74927900
H	4.55074300	-2.41803500	0.52422000
C	0.28520100	1.91591800	-0.52687700
H	-0.29566700	2.78333600	-0.81713900
C	-1.78805900	0.40321500	0.01658100
N	-0.44353400	-1.47119100	-0.01167500
C	-0.37613400	0.85158500	0.30178000
C	-0.30145800	1.29884200	1.79680900
H	-0.88178900	2.21142000	1.93637400
H	-0.70834100	0.51982600	2.44167600
H	0.73164100	1.49871500	2.07841400
C	-1.76035500	-0.93697500	-0.08984600
C	-3.02911700	1.22742400	-0.01153500
H	-3.01283200	1.98136200	0.78275900
H	-3.08407800	1.79111700	-0.95233500
C	-2.95601300	-1.80018500	-0.30271800
H	-2.73690300	-2.55243400	-1.06470200
H	-3.17781100	-2.35609000	0.61576500
C	-4.26758500	0.33088300	0.13899200
C	-4.15792500	-0.93809300	-0.71372700
H	-4.04682900	-0.65134700	-1.76429200
H	-5.07862800	-1.52038300	-0.64129000
H	-5.16768400	0.88904900	-0.12712800
H	-4.37055400	0.04472200	1.19042400

TSa-1: (imaginary frequency: 595.3616*i* cm^{-1})

C	4.51438000	-0.40283900	-0.35108400
C	3.79840300	0.78139500	-0.41344600
C	2.40866000	0.79128400	-0.24547400
C	1.74836400	-0.43676800	-0.00078900
C	2.47442100	-1.62353200	0.04683900
C	3.85070700	-1.60780900	-0.12445400
H	2.20952700	2.93026900	-0.57411500
H	5.58831700	-0.39217200	-0.48428600
H	4.31222700	1.71662300	-0.60055500
C	1.65193600	2.02786000	-0.35351800
C	0.30398600	-0.40265200	0.17494200
H	1.93979500	-2.54880800	0.21348400
H	4.41000200	-2.53357700	-0.08412300
C	0.31125700	2.08253800	-0.21579500
H	-0.22487700	3.01524800	-0.33790600
C	-1.77456900	0.49781800	-0.07210300
N	-0.53931500	-1.45063500	0.08387000
C	-0.41879000	0.86871200	0.06923500
C	0.06057900	0.42383200	2.03647500
H	-0.15338400	1.45562500	2.28195400
H	-0.71359100	-0.26857200	2.33519400
H	1.06140800	0.13944500	2.33744500
C	-1.77145300	-0.90010800	-0.05891600
C	-3.00535800	1.33910400	-0.21404500
H	-2.98885900	2.18148600	0.48489100
H	-3.05324900	1.78159000	-1.21710800
C	-3.01915500	-1.71381100	-0.16763700
H	-2.83529800	-2.58022700	-0.80656400
H	-3.27368200	-2.11345100	0.82086900
C	-4.26144500	0.48744700	0.02419500
C	-4.17702200	-0.86009300	-0.69963800
H	-4.03179100	-0.68167700	-1.77008100
H	-5.11836100	-1.40361400	-0.59572400
H	-4.37319000	0.30574600	1.09844400
H	-5.14919000	1.03623600	-0.29763800

5a-1:

C	4.26166800	-0.40571400	-0.89408400
C	3.63127200	0.80476600	-0.64216200
C	2.31861900	0.84311800	-0.16355600
C	1.65193900	-0.37360800	0.08945000
C	2.28490200	-1.57857900	-0.16715000
C	3.58370200	-1.59806000	-0.66914500
H	2.19854100	3.02057200	-0.12961300
H	5.27555300	-0.41869400	-1.27248900
H	4.15169400	1.73646500	-0.82973900
C	1.62235200	2.11336500	0.00786500
C	0.29592900	-0.29900900	0.75215300
H	1.75054300	-2.49942400	0.02351600
H	4.06509000	-2.54425100	-0.88058300
C	0.28873200	2.17931700	0.21075900
H	-0.22784700	3.13137600	0.20189000
C	-1.70398700	0.58633300	0.01760300
N	-0.62301600	-1.41131800	0.49198600
C	-0.44115500	0.94966000	0.33332100
C	0.52869600	-0.27684300	2.28773000
H	-0.42694300	-0.17505300	2.80231100
H	1.00272600	-1.20866000	2.59118000
H	1.17444000	0.55906700	2.55625400
C	-1.74083700	-0.88165100	0.13546700
C	-2.86963900	1.38557200	-0.47606100
H	-2.96100800	2.32421300	0.07641700
H	-2.69162600	1.66452800	-1.52160800
C	-3.00069300	-1.64891000	-0.12733300
H	-2.75805300	-2.60429100	-0.59422900
H	-3.46076900	-1.88223700	0.83941800
C	-4.17191600	0.57743700	-0.39624900
C	-3.98968600	-0.83118600	-0.96773200

H	-3.62493700	-0.75720000	-1.99774100
H	-4.94921200	-1.34977300	-1.01172300
H	-4.49253300	0.50077500	0.64803000
H	-4.96393400	1.10576300	-0.93045200

4a-2:

C	4.57026800	-0.38755800	-0.21614200
C	3.80883900	0.74119800	-0.48688900
C	2.42031600	0.71539200	-0.35086900
C	1.80139700	-0.48837100	0.05981700
C	2.57132900	-1.62196800	0.30715800
C	3.95218400	-1.57083300	0.17998700
H	2.09777900	2.71773300	-1.15542700
H	5.64682300	-0.34820600	-0.32109600
H	4.29134600	1.65411200	-0.81442700
C	1.59833100	1.88065200	-0.68149100
C	0.35006700	-0.47658400	0.12556900
H	2.07155800	-2.53541600	0.60046000
H	4.54743700	-2.45095400	0.38533800
C	0.28937600	1.94213800	-0.41678300
H	-0.28960500	2.82630200	-0.65605600
C	-1.78644400	0.40459200	0.02977700
N	-0.44429400	-1.46614400	-0.10773200
C	-0.37545800	0.83296200	0.34764200
C	-0.30790600	1.19688200	1.86562800
H	-0.88938100	2.10027900	2.05280700
H	-0.71854300	0.38333800	2.46383600
H	0.72379400	1.38023700	2.16349800
C	-1.76136700	-0.92795100	-0.14824000
C	-3.02298700	1.23515900	0.02475200
H	-3.26847000	1.56072800	1.04425900
H	-2.87101500	2.15465500	-0.55111000
C	-2.96184900	-1.78190800	-0.37376700
H	-2.98899100	-2.10994600	-1.41924700
H	-2.88610900	-2.69269400	0.22547900
C	-4.19299700	0.43252400	-0.56574200
C	-4.23416600	-0.99887200	-0.02016500
H	-5.11390000	-1.52124000	-0.40125800
H	-4.33714200	-0.96023100	1.06910700
H	-5.13576200	0.94343900	-0.35954800
H	-4.08336800	0.39613900	-1.65394700

TSa-2: (imaginary frequency: 600.8037*i* cm^{-1})

C	4.51504700	-0.38854700	-0.36717100
C	3.79977500	0.79774000	-0.36886300
C	2.40975800	0.79973600	-0.20350300
C	1.74803200	-0.43896200	-0.02486900
C	2.47337000	-1.62703000	-0.03862400
C	3.85013800	-1.60324300	-0.20592600
H	2.21331800	2.95298400	-0.42269100
H	5.58926200	-0.37150300	-0.49744600
H	4.31440200	1.74117900	-0.50595100
C	1.65450500	2.04111200	-0.24914200
C	0.30329500	-0.41230300	0.15113600
H	1.93797800	-2.55944900	0.07831100
H	4.40879000	-2.53023700	-0.21318600
C	0.31391100	2.09018000	-0.10990200
H	-0.22051500	3.02895600	-0.18309400
C	-1.77323700	0.50244400	-0.05169800
N	-0.54193000	-1.45311100	0.00864200
C	-0.41759600	0.86406100	0.11207800
C	0.06042600	0.31690700	2.05285200
H	1.05966500	0.01371200	2.34033300
H	-0.15005100	1.33547400	2.35129700
H	-0.71682100	-0.38740200	2.31298500
C	-1.77373600	-0.89471500	-0.10483200
C	-3.00295800	1.35058200	-0.13635000
H	-3.27066500	1.74223600	0.85387100
H	-2.83513100	2.22619100	-0.77115400
C	-3.02266800	-1.70028000	-0.26560600
H	-3.05416100	-2.09579500	-1.28716500
H	-2.98955900	-2.57035700	0.39357800
C	-4.17380100	0.52265200	-0.68418300
C	-4.26679600	-0.84284000	0.00365600
H	-5.16193700	-1.37323800	-0.32766900
H	-4.37383900	-0.68997900	1.08296600
H	-4.03314900	0.37087600	-1.75921400
H	-5.10887500	1.07316900	-0.56058000

5a-2:

C	4.26841100	-0.38733200	-0.89245700
C	3.64081000	0.81547500	-0.59997700
C	2.32514800	0.84094500	-0.12882200
C	1.65283900	-0.38207800	0.07530000
C	2.28267100	-1.57913400	-0.22219400
C	3.58465800	-1.58463200	-0.71630500
H	2.21187700	3.01572600	-0.01712600
H	5.28478600	-0.39030400	-1.26433100
H	4.16589400	1.75148400	-0.74912900
C	1.63135100	2.10636300	0.08306000
C	0.29398900	-0.32284800	0.73227400
H	1.74377000	-2.50430300	-0.06906900
H	4.06425300	-2.52408600	-0.95950900
C	0.29617400	2.17114500	0.27840900
H	-0.21506300	3.12552600	0.30183400
C	-1.70349800	0.58903900	0.02563200
N	-0.62511000	-1.42427300	0.43566300
C	-0.43861900	0.94018300	0.34890600
C	0.51923500	-0.34156800	2.26942900
H	-0.43851600	-0.24732600	2.78148300
H	0.98433100	-1.28521100	2.54941400
H	1.16974800	0.48150100	2.56436300
C	-1.73868800	-0.88279900	0.08345500
C	-2.89796400	1.41153200	-0.34507200
H	-3.32995700	1.84604200	0.56462100
H	-2.60652100	2.25491400	-0.97601100
C	-2.97287900	-1.64561000	-0.29426500
H	-2.82713100	-2.03812300	-1.30660000
H	-3.08439100	-2.51162500	0.35950700
C	-3.96965400	0.55741500	-1.03697100

C	-4.21606500	-0.74869000	-0.27683500
H	-5.06216100	-1.28565900	-0.70969400
H	-4.48872500	-0.51578500	0.75809200
H	-3.64868000	0.32277300	-2.05712000
H	-4.89526600	1.12994600	-1.12177300

4a-H1:

C	4.56881700	-0.38714300	-0.25399200
C	3.81343300	0.74128000	-0.53510300
C	2.42904400	0.73444200	-0.36607400
C	1.81767700	-0.46605700	0.09038000
C	2.59115000	-1.60467000	0.35619200
C	3.96146600	-1.56226600	0.19436000
H	2.12627700	2.74013000	-1.15754400
H	5.64206800	-0.35747800	-0.38646900
H	4.29779500	1.63982800	-0.89391000
C	1.61898900	1.90061900	-0.70016300
C	0.39702400	-0.43193300	0.17251300
H	2.12097600	-2.50839500	0.72368800
H	4.56216900	-2.43296600	0.41678800
C	0.30912100	1.96578900	-0.44507200
H	-0.26991500	2.85578200	-0.65140700
C	-1.78025700	0.41511500	-0.00861900
N	-0.47276100	-1.41178700	0.05766500
C	-0.36475500	0.84581700	0.28795300
C	-0.32535300	1.22728600	1.82824700
H	-0.92515000	2.12389000	1.96819400
H	-0.74144000	0.42138800	2.43065100
H	0.69912700	1.43049300	2.13043400
C	-1.80751200	-0.92302800	-0.06799000
C	-3.00280300	1.26016400	-0.09316300
H	-2.98052100	2.04474900	0.66840800
H	-3.01311900	1.78184100	-1.05732300
C	-2.99933700	-1.79127300	-0.25498300
H	-2.79605000	-2.57834500	-0.98651600
H	-3.24782600	-2.29393500	0.68579600
C	-4.26361700	0.39502600	0.06772900
C	-4.17210900	-0.91317900	-0.72496600
H	-4.04089100	-0.68648500	-1.78628400
H	-5.10178500	-1.47384000	-0.63316500
H	-0.22567400	-2.38760200	-0.03671500
H	-5.13880800	0.96160800	-0.24964300
H	-4.40377300	0.16593100	1.12787000

TSa-H1: (imaginary frequency: 479.5455*i* cm^{-1})

C	4.53168100	-0.36810700	-0.38055600
C	3.80509100	0.80689700	-0.44765700
C	2.41723100	0.80269300	-0.25834600
C	1.77655000	-0.43360900	0.01044400
C	2.51871800	-1.61175600	0.07519300
C	3.88919500	-1.57929800	-0.12135400
H	2.19383700	2.93416400	-0.58009200
H	5.60232600	-0.34888200	-0.53143500
H	4.30586700	1.74437200	-0.65172200
C	1.65008900	2.02535600	-0.35541100
C	0.34549200	-0.37946300	0.20058200
H	2.03324800	-2.55709600	0.28177900
H	4.46161200	-2.49539400	-0.07306000
C	0.30871000	2.07236600	-0.19538700
H	-0.24273600	2.99646700	-0.29445800
C	-1.78036300	0.48748700	-0.06942200
N	-0.55759300	-1.39860400	0.07216100
C	-0.39866500	0.84972600	0.07644100
C	0.07255900	0.44080200	2.05637400
H	-0.54399000	1.29677500	2.29027800
H	-0.33565000	-0.48767800	2.43317000
H	1.12192400	0.60578300	2.25699800
C	-1.83325700	-0.87917100	-0.07187700
C	-2.98956900	1.35814000	-0.20396300
H	-2.94624000	2.18568200	0.50892800
H	-3.00643100	1.81516000	-1.19884900
C	-3.06780900	-1.69755000	-0.19361300
H	-2.89828900	-2.54646200	-0.86100400
H	-3.32163400	-2.11792300	0.78589800
C	-4.26588900	0.53195000	0.02032500
C	-4.21518700	-0.81393900	-0.70867200
H	-4.08130000	-0.64419300	-1.78028900
H	-5.15913200	-1.34462100	-0.58802200
H	-0.33848900	-2.37957400	0.11661600
H	-4.39599500	0.35579200	1.09234300
H	-5.13323600	1.10271000	-0.31081000

5a-H1:

C	4.33756600	-0.31087500	-0.84695300
C	3.66345800	0.87625500	-0.60245200
C	2.33687500	0.86492800	-0.15910800
C	1.70214500	-0.37478300	0.06152400
C	2.38263900	-1.55452100	-0.17173700
C	3.69492700	-1.52500300	-0.64301100
H	2.15409300	3.02814400	-0.11831500
H	5.35945200	-0.29033900	-1.19945700
H	4.15858600	1.82539900	-0.76281000
C	1.60637200	2.10377700	0.01730300
C	0.33301700	-0.32439300	0.69832700
H	1.90663400	-2.51180400	0.00004000
H	4.21100300	-2.45319100	-0.84760400
C	0.26537600	2.14497700	0.22749600
H	-0.27438300	3.08167800	0.21087000
C	-1.72977200	0.57051200	0.01730100
N	-0.62637800	-1.37572200	0.34623200
C	-0.43414800	0.91190900	0.31679400
C	0.51949800	-0.35428300	2.24490000
H	-0.44647000	-0.28366100	2.74386800
H	1.01832200	-1.27914800	2.53145800
H	1.14263400	0.48465500	2.54699100
C	-1.80228800	-0.85158100	0.04573900
C	-2.89858200	1.41683500	-0.38370300
H	-2.95039500	2.30958200	0.24184800
H	-2.74658200	1.76885300	-1.40942700
C	-3.04236800	-1.62378300	-0.21653900

H	-2.81218800	-2.54144000	-0.76211800
H	-3.44544100	-1.93279600	0.75575600
C	-4.20919800	0.62154500	-0.30208400
C	-4.07513600	-0.75639200	-0.95272500
H	-3.77500800	-0.64452100	-1.99803500
H	-5.03353400	-1.27424300	-0.95355300
H	-0.47773900	-2.35580700	0.53052000
H	-4.50084700	0.50185300	0.74557100
H	-5.00578300	1.18610300	-0.78566100

4a-H2:

C	4.57024600	-0.38079000	-0.26508900
C	3.81818900	0.76343400	-0.48451300
C	2.43306300	0.74960300	-0.32245900
C	1.81737700	-0.47338300	0.06256700
C	2.58750100	-1.62705300	0.26574600
C	3.95862500	-1.57837900	0.11231100
H	2.13676800	2.79739600	-1.00050400
H	5.64413800	-0.34583400	-0.39089600
H	4.30567800	1.68014500	-0.78902600
C	1.62629100	1.93411800	-0.59371100
C	0.39641100	-0.44068700	0.14117900
H	2.11399000	-2.54952500	0.57838900
H	4.55664700	-2.46177900	0.28663400
C	0.31566300	1.98725200	-0.34017400
H	-0.26004300	2.88942200	-0.49666500
C	-1.77862600	0.41885100	0.00147200
N	-0.47441400	-1.41085700	-0.03220200
C	-0.36358700	0.82989800	0.32687100
C	-0.33124100	1.12995900	1.88560600
H	-0.93038800	2.01928900	2.06895700
H	-0.75261200	0.29444000	2.44222700
H	0.69192100	1.31468200	2.20381200
C	-1.80930500	-0.91464200	-0.12521700
C	-2.99740100	1.27092500	-0.05476600
H	-3.24035000	1.63705500	0.94960900
H	-2.81137700	2.16075500	-0.66229100
C	-3.00620300	-1.77395900	-0.32674600
H	-3.02855900	-2.14923600	-1.35542500
H	-2.96730700	-2.65073000	0.32538700
C	-4.17599200	0.46713500	-0.62925800
C	-4.26358100	-0.93848300	-0.02722500
H	-5.14173700	-1.45773200	-0.40971600
H	-4.38728100	-0.86193500	1.05639700
H	-0.22850200	-2.38077400	-0.17690900
H	-5.10566300	1.00691900	-0.45052700
H	-4.05901200	0.39065000	-1.71360500

TSa-H2: (imaginary frequency: 483.3233*i* cm^{-1})

C	4.53177900	-0.35169800	-0.39630000
C	3.80616000	0.82575000	-0.40007100
C	2.41784600	0.81223400	-0.21442600
C	1.77554100	-0.43653900	-0.01576400
C	2.51674600	-1.61710900	-0.01543200
C	3.88773000	-1.57489900	-0.20663800
H	2.19708700	2.95840500	-0.41808100
H	5.60281800	-0.32499300	-0.54318600
H	4.30804600	1.77267200	-0.55089500
C	1.65219700	2.03915700	-0.24441500
C	0.34429000	-0.39151700	0.17558900
H	2.02990500	-2.57206000	0.13655700
H	4.45935400	-2.49275800	-0.20807500
C	0.31096200	2.07884500	-0.08131500
H	-0.23835000	3.00830100	-0.12646100
C	-1.78004400	0.49238900	-0.04483700
N	-0.56076800	-1.40069100	-0.00734400
C	-0.39799300	0.84394400	0.12300800
C	0.08031800	0.32720200	2.07442600
H	-0.56884300	1.14282600	2.35933500
H	-0.28658600	-0.63576400	2.40441600
H	1.12442300	0.52255500	2.27451100
C	-1.83687300	-0.87215000	-0.11556000
C	-2.98590900	1.37104700	-0.14083000
H	-3.22929200	1.77803500	0.84718200
H	-2.78242800	2.23111900	-0.78290200
C	-3.07437500	-1.68134700	-0.27275400
H	-3.10515900	-2.08872400	-1.28925200
H	-3.06049300	-2.54061600	0.40304400
C	-4.17778800	0.57064700	-0.68679800
C	-4.30538200	-0.79764000	-0.01151800
H	-5.19824300	-1.31243100	-0.36497700
H	-4.42509700	-0.66147500	1.06691100
H	-0.34472400	-2.38333400	-0.00288400
H	-4.05255200	0.43183700	-1.76442800
H	-5.09571600	1.14134600	-0.54759700

5a-H2:

C	4.33662100	-0.28642900	-0.85795200
C	3.66684500	0.89072100	-0.55931800
C	2.33956400	0.86387900	-0.11862000
C	1.69986100	-0.38237200	0.04364300
C	2.37562200	-1.55259600	-0.24424100
C	3.68877700	-1.50612200	-0.71204500
H	2.16472500	3.02328800	0.02202800
H	5.35917500	-0.25368300	-1.20757600
H	4.16602300	1.84432400	-0.67417400
C	1.61318100	2.09576200	0.11372500
C	0.33139900	-0.35422000	0.68289700
H	1.89556100	-2.51494400	-0.11823800
H	4.20147200	-2.42577000	-0.95930500
C	0.27190200	2.13292900	0.32438100
H	-0.26292100	3.07189500	0.35349600
C	-1.72975900	0.57405000	0.04265700
N	-0.63092600	-1.38700600	0.29107300
C	-0.43251900	0.89962500	0.35562200
C	0.51997300	-0.44599300	2.22711200
H	-0.44502300	-0.38926700	2.72964900
H	1.01230900	-1.38533900	2.47530900
H	1.14934600	0.37567100	2.56165800
C	-1.80394400	-0.84751200	0.00522300

C	-2.90963400	1.44026300	-0.27422200
H	-3.30002500	1.86337300	0.65709800
H	-2.60011700	2.28717500	-0.88923200
C	-3.03220000	-1.60601100	-0.34187000
H	-2.90200700	-1.98721000	-1.36171400
H	-3.13040800	-2.48364800	0.30179800
C	-4.01512500	0.63713900	-0.97468500
C	-4.26970200	-0.70002400	-0.27589000
H	-5.11146800	-1.21733700	-0.73477800
H	-4.53826900	-0.52564600	0.76950900
H	-0.48418500	-2.37424100	0.43262700
H	-3.73205000	0.45480000	-2.01565500
H	-4.93083500	1.22706200	-0.99852300

4b-1:

C	-5.16705600	0.22889200	-0.10869000
C	-4.36799600	-0.86399100	-0.41495400
C	-2.97751400	-0.77778200	-0.33248600
C	-2.39668800	0.45049900	0.06114800
C	-3.20566300	1.54819600	0.34436500
C	-4.58664000	1.43683400	0.27000300
H	-2.60157500	-2.76052600	-1.16105600
H	-6.24411200	0.14255800	-0.17224600
H	-4.82240600	-1.79589100	-0.72890800
C	-2.11988100	-1.90471400	-0.70246600
C	-0.94520800	0.50323200	0.07266800
H	-2.73542400	2.48149600	0.62366500
H	-5.21161900	2.28897600	0.50316100
C	-0.79955400	-1.90983400	-0.49250500
H	-0.19235500	-2.76588700	-0.76178700
C	1.22376000	-0.28118900	-0.11386600
N	-0.20377400	1.53028900	-0.17400800
C	-0.15445800	-0.77522700	0.25097800
C	-0.14730000	-1.14506600	1.76893500
H	0.48056800	-2.02181300	1.93052200
H	0.24831000	-0.31572700	2.35535600
H	-1.15787400	-1.37533200	2.10383800
C	1.13121300	1.04941600	-0.27854200
C	2.49575700	-1.05272300	-0.15590600
H	2.52594800	-1.79811500	0.64708900
H	2.55404700	-1.62523000	-1.09082000
C	2.28503400	1.94722100	-0.55196900
H	2.03211000	2.64492900	-1.35429500
H	2.48711300	2.56685000	0.32882100
C	3.73015600	-0.12753500	-0.03909400
C	3.51716700	1.11539600	-0.93119400
H	3.40835100	0.77730900	-1.96635800
H	4.41362400	1.73985600	-0.89798900
C	3.91758400	0.29351800	1.42392800
H	4.73824500	1.00788300	1.52007100
H	3.01703400	0.75658300	1.82787700
H	4.15361800	-0.57325100	2.04523400
C	4.97543500	-0.87993000	-0.51073500
H	5.12184900	-1.79558000	0.06756000
H	4.89111000	-1.15709600	-1.56400600
H	5.87097900	-0.26530200	-0.39537600

TSb-1: (imaginary frequency: 594.5028*i* cm^{-1})

C	5.11933100	-0.18358400	-0.27245400
C	4.33452600	0.95696100	-0.32041400
C	2.94192100	0.87735500	-0.20306300
C	2.35056400	-0.39640000	-0.02504400
C	3.14586500	-1.53837500	0.00811900
C	4.52369300	-1.43385100	-0.11217000
H	2.62402800	3.01098400	-0.46702600
H	6.19454300	-0.10330700	-0.36561700
H	4.79642500	1.92737600	-0.45702400
C	2.11521500	2.06961400	-0.29721200
C	0.90161500	-0.45512400	0.10120100
H	2.66306500	-2.49924600	0.12379000
H	5.13705300	-2.32515700	-0.08326500
C	0.76970800	2.03874200	-0.20786300
H	0.18181800	2.94119300	-0.31888100
C	-1.21846300	0.32804500	-0.18933500
N	0.12606000	-1.54796500	-0.04983200
C	0.10642000	0.77408700	0.00997200
C	0.54913100	0.29203600	1.97897900
H	0.25525900	1.29755000	2.24905700
H	-0.18260800	-0.46216300	2.23099900
H	1.55783500	0.06759600	2.30313700
C	-1.13175400	-1.06602600	-0.21669700
C	-2.48999800	1.09943300	-0.34759100
H	-2.51779100	1.95632400	0.33460100
H	-2.55787700	1.51901300	-1.35890500
C	-2.33083400	-1.94031100	-0.36693200
H	-2.10880300	-2.75257900	-1.06259200
H	-2.54530500	-2.42118400	0.59315600
C	-3.72925400	0.20947100	-0.09766100
C	-3.54170800	-1.12894900	-0.84390000
H	-3.42668900	-0.90943600	-1.90997900
H	-4.45100200	-1.72731600	-0.74402000
C	-3.90080800	-0.03361400	1.40721200
H	-4.72186900	-0.72863400	1.59787500
H	-2.99794800	-0.44701100	1.85700000
H	-4.12869300	0.90260800	1.92161300
C	-4.97621200	0.91441300	-0.63506500
H	-5.10275800	1.89508600	-0.16963400
H	-4.90933900	1.06163700	-1.71539400
H	-5.87549800	0.32889100	-0.43057500

5b-1:

C	4.87288500	-0.09797200	-0.89448600
C	4.15046600	1.04071900	-0.56662500
C	2.83299700	0.94659100	-0.10883700
C	2.25711500	-0.33170400	0.04448000
C	2.98093900	-1.46428000	-0.28945900
C	4.28347600	-1.35049700	-0.76910100
H	2.54945700	3.10080800	0.07753600
H	5.88937100	-0.00818400	-1.25509800
H	4.60177500	2.01965500	-0.67671600

C	2.04179800	2.14584000	0.14309500
C	0.89538000	-0.40591800	0.69390300
H	2.51519700	-2.43379000	-0.17516800
H	4.83687000	-2.24033800	-1.04059600
C	0.70522200	2.09753400	0.33231000
H	0.11816600	3.00651300	0.38317200
C	-1.16329300	0.37926200	0.01164200
N	0.06132500	-1.56152500	0.35136100
C	0.06907900	0.81175300	0.35876500
C	1.11765700	-0.47383700	2.23050400
H	0.15445600	-0.47468800	2.74105700
H	1.65451800	-1.38896700	2.47401900
H	1.70107500	0.38480100	2.56236700
C	-1.09250800	-1.09095900	0.02641700
C	-2.38460800	1.12089900	-0.42577500
H	-2.50349400	2.04845500	0.14176500
H	-2.26400500	1.41896000	-1.47416200
C	-2.29729500	-1.92618900	-0.28137500
H	-2.00346300	-2.78275000	-0.88983600
H	-2.67218800	-2.33828900	0.65983100
C	-3.66206200	0.26199400	-0.30881800
C	-3.39616900	-1.10710900	-0.96969100
H	-3.11762100	-0.93238500	-2.01395800
H	-4.32303900	-1.68560700	-0.98913000
C	-4.04397500	0.09168900	1.16705300
H	-4.90161200	-0.57664000	1.27208400
H	-3.22454600	-0.31717300	1.75915300
H	-4.31475200	1.05543000	1.60340700
C	-4.80548100	0.96119800	-1.04659700
H	-4.97872000	1.96093400	-0.64135400
H	-4.58118700	1.06372400	-2.11072200
H	-5.73527700	0.39612500	-0.95161200

4b-2:

C	-5.12511600	0.16325100	-0.39296300
C	-4.27943300	-0.92169800	-0.57989100
C	-2.90643800	-0.80293200	-0.36071800
C	-2.39083600	0.44939500	0.04750500
C	-3.24375900	1.53790500	0.21046800
C	-4.60808300	1.39463500	0.00114700
H	-2.41016200	-2.80257400	-1.07883600
H	-6.18840100	0.05190900	-0.56196300
H	-4.68277700	-1.87275200	-0.90594300
C	-1.99439800	-1.92228600	-0.60240000
C	-0.94857200	0.53230500	0.20188900
H	-2.82133100	2.48950600	0.50405700
H	-5.26871500	2.24023100	0.14121000
C	-0.70361700	-1.89250700	-0.25609400
H	-0.05676300	-2.74426300	-0.43017300
C	1.24001800	-0.21440400	0.26657000
N	-0.20320300	1.56256300	-0.01666000
C	-0.15908600	-0.72185900	0.51172600
C	-0.30093500	-1.04601800	2.03344700
H	0.32120200	-1.90576000	2.28464600
H	0.02091600	-0.19195600	2.62955300
H	-1.33657400	-1.28484200	2.27248800
C	1.14409500	1.10665200	0.04056100
C	2.52072400	-0.96543200	0.36674800
H	2.73930000	-1.20386300	1.41571900
H	2.44769400	-1.93140100	-0.14687200
C	2.30535200	2.01373700	-0.16543300
H	2.34668400	2.32538300	-1.21484900
H	2.16956300	2.93200800	0.41137700
C	3.69689500	-0.15783900	-0.23184200
C	3.60226100	1.30570800	0.24957900
H	4.46680000	1.86237200	-0.12089000
H	3.67189800	1.30948400	1.34191700
C	5.01920700	-0.76098800	0.24585800
H	5.86964900	-0.24146200	-0.20136600
H	5.11453700	-0.68914300	1.33183700
H	5.09006200	-1.81615200	-0.02929600
C	3.63866700	-0.22092900	-1.76349500
H	3.78580300	-1.24631000	-2.10993300
H	2.67816000	0.12435200	-2.14618700
H	4.42320000	0.39713500	-2.20583700

TSb-2: (imaginary frequency: 595.8766*i* cm^{-1})

C	5.05576900	-0.14644800	-0.56187600
C	4.26647300	0.98849400	-0.47185300
C	2.89371600	0.89158200	-0.21575900
C	2.32824600	-0.39424100	-0.04110400
C	3.12627300	-1.52990200	-0.14742500
C	4.48396500	-1.40803600	-0.40368200
H	2.54214400	3.03255800	-0.34190400
H	6.11523300	-0.05276300	-0.76176600
H	4.70868900	1.96824900	-0.60677100
C	2.05751000	2.07989600	-0.16455700
C	0.90068400	-0.47108800	0.23219400
H	2.66136700	-2.49942000	-0.03041300
H	5.09988600	-2.29455600	-0.48235600
C	0.72951300	2.03351700	0.06716000
H	0.13089900	2.93569100	0.06539200
C	-1.24076900	0.30746200	0.21228200
N	0.11686700	-1.56084700	0.10748000
C	0.09698400	0.75456200	0.29237100
C	0.74888100	0.17500800	2.17562000
H	1.78309300	-0.07256100	2.38020700
H	0.49720600	1.16739700	2.52571400
H	0.03728400	-0.58652600	2.46110900
C	-1.15340200	-1.08255200	0.10336300
C	-2.52487900	1.07140100	0.25764600
H	-2.75543500	1.37252500	1.28770600
H	-2.45229500	2.00092700	-0.31755400
C	-2.35755200	-1.95600200	-0.01514700
H	-2.41102300	-2.34261600	-1.03812000
H	-2.24648500	-2.83191200	0.62756200
C	-3.70215800	0.22886800	-0.28512200
C	-3.63407200	-1.18243300	0.33641200
H	-4.51163600	-1.75551900	0.02604100
H	-3.69964900	-1.07669100	1.42421600

C	-5.02315400	0.88995300	0.11260500
H	-5.87432800	0.33934200	-0.29430100
H	-5.13411700	0.92588500	1.19888200
H	-5.07651600	1.91421900	-0.26460600
C	-3.62124800	0.14747700	-1.81522400
H	-3.76652600	1.13546200	-2.25762100
H	-2.65381000	-0.22591900	-2.15088100
H	-4.39673700	-0.51295700	-2.21032300

5b-2:

C	4.67011600	-0.01310500	-1.20921800
C	3.99826800	1.09043100	-0.70219400
C	2.74767600	0.95070700	-0.09363400
C	2.19108300	-0.33967800	0.02682900
C	2.86399000	-1.43667700	-0.48489200
C	4.09677100	-1.27557100	-1.11270300
H	2.49541900	3.08118700	0.29656900
H	5.63372700	0.11246700	-1.68567800
H	4.43532600	2.07820600	-0.78818900
C	1.99602400	2.12087100	0.34578100
C	0.91722600	-0.47215200	0.82804300
H	2.41280800	-2.41526700	-0.39206500
H	4.60900800	-2.13692100	-1.52188900
C	0.69131100	2.05010100	0.68851800
H	0.12000500	2.94910400	0.88361400
C	-1.20684900	0.34630400	0.45674600
N	0.04880600	-1.60369700	0.49343100
C	0.05879800	0.76172500	0.68528300
C	1.32069300	-0.65109000	2.31762000
H	0.42505500	-0.69629100	2.93738700
H	1.88007600	-1.57866100	2.42667800
H	1.94214600	0.18370800	2.64093100
C	-1.13328100	-1.11893100	0.33274900
C	-2.48676800	1.10253700	0.31048500
H	-2.89383700	1.31780300	1.30583100
H	-2.31296300	2.07185500	-0.16510900
C	-2.34462500	-1.92947100	-0.01750500
H	-2.22653900	-2.28321300	-1.04530800
H	-2.37984800	-2.82426800	0.60600500
C	-3.54585600	0.30576000	-0.48214100
C	-3.63685200	-1.11413700	0.11454800
H	-4.45846300	-1.65497100	-0.36158800
H	-3.90030500	-1.02039000	1.17319300
C	-4.90302400	0.99737600	-0.34020200
H	-5.66783800	0.48080700	-0.92417700
H	-5.22881800	1.01234200	0.70247900
H	-4.85402200	2.03042700	-0.69217500
C	-3.15831900	0.25425800	-1.96545900
H	-3.18357000	1.25589800	-2.39988800
H	-2.15298900	-0.14084500	-2.11514300
H	-3.85432300	-0.37264500	-2.52740900

4b-H1:

C	-5.16574700	0.19687600	-0.16729100
C	-4.36360600	-0.90436700	-0.42523600
C	-2.97594400	-0.81951400	-0.31261700
C	-2.41134700	0.43079900	0.06272200
C	-3.23270800	1.54073200	0.30519600
C	-4.60405100	1.42169700	0.20022600
H	-2.59951800	-2.84283400	-1.02310000
H	-6.24024100	0.10675300	-0.25474200
H	-4.81356400	-1.84268900	-0.72158400
C	-2.11966500	-1.95834800	-0.62466700
C	-0.98873900	0.47179700	0.09380700
H	-2.79692000	2.48401100	0.61043400
H	-5.24054000	2.27105600	0.40495300
C	-0.79952300	-1.94533700	-0.41924300
H	-0.18271200	-2.81344300	-0.60868800
C	1.22241100	-0.27303600	-0.13142600
N	-0.17436000	1.48776000	-0.09205500
C	-0.15832400	-0.75985500	0.23505600
C	-0.12040900	-1.07057500	1.79151100
H	0.53140700	-1.92727300	1.94758600
H	0.27421200	-0.21764800	2.34105500
H	-1.12094500	-1.31187200	2.14193600
C	1.17820700	1.06057500	-0.24430700
C	2.48089500	-1.05894600	-0.22238800
H	2.49945800	-1.84508500	0.53845400
H	2.50821400	-1.57903800	-1.18703600
C	2.32499900	1.97268900	-0.47706200
H	2.08978600	2.70818500	-1.25139500
H	2.54272200	2.53939500	0.43396700
C	3.73119900	-0.15801200	-0.06950100
C	3.53873900	1.12901200	-0.90218000
H	3.42162500	0.85150100	-1.95290000
H	4.43999400	1.73948300	-0.83620600
C	3.93718300	0.18687900	1.41099500
H	4.77637500	0.87337200	1.53385400
H	3.05583100	0.65414100	1.85400000
H	4.15867900	-0.71262800	1.98767000
C	4.95607500	-0.91083600	-0.59166900
H	5.09248800	-1.85326400	-0.05756900
H	4.85789700	-1.13685500	-1.65532900
H	5.86212400	-0.31834900	-0.45620100
H	-0.47372900	2.44538400	-0.21632300

TSb-H1: (imaginary frequency: 478.2103*i* cm^{-1})

C	5.13214200	-0.13562200	-0.29717900
C	4.33359800	0.99234700	-0.35273700
C	2.94307700	0.89335200	-0.21621200
C	2.37510800	-0.39017200	-0.01327000
C	3.18946200	-1.52038200	0.03954400
C	4.56102900	-1.39391300	-0.10355000
H	2.59381400	3.01641200	-0.47585600
H	6.20400500	-0.04272000	-0.40629700
H	4.77972700	1.96626100	-0.50690700
C	2.10244600	2.06769100	-0.30107300
C	0.93803000	-0.43422300	0.12571700
H	2.75883000	-2.50136800	0.19527600
H	5.18966000	-2.27283900	-0.06428900

C	0.75612100	2.02329000	-0.18874400
H	0.14933100	2.91305500	-0.27813500
C	-1.22942100	0.30724200	-0.18798500
N	0.10592500	-1.50288200	-0.06331800
C	0.12066200	0.74955700	0.01618600
C	0.55682400	0.30658800	1.99929400
H	-0.15631900	1.08148600	2.24108600
H	0.24442000	-0.67231800	2.33796600
H	1.57749900	0.57649500	2.23134300
C	-1.19554700	-1.05834600	-0.23158800
C	-2.48434100	1.10549700	-0.33262200
H	-2.48544000	1.94612000	0.36747400
H	-2.52621700	1.54568200	-1.33420500
C	-2.37868900	-1.93937500	-0.38831700
H	-2.16949900	-2.73996000	-1.10268000
H	-2.59315800	-2.42923900	0.56721100
C	-3.74103800	0.23383500	-0.09623300
C	-3.58029800	-1.10223600	-0.85325400
H	-3.47032100	-0.88877200	-1.91955700
H	-4.49064300	-1.69261800	-0.74322200
C	-3.92277600	-0.01643300	1.40666100
H	-4.75999700	-0.69252900	1.58787400
H	-3.03475200	-0.45466300	1.86631400
H	-4.13443000	0.91908500	1.92690900
C	-4.96837900	0.96848500	-0.63851900
H	-5.07862300	1.94631600	-0.16558600
H	-4.89300400	1.12235500	-1.71674900
H	-5.87895900	0.40011900	-0.44285000
H	0.38454400	-2.46928800	-0.03860400

5b-H1:

C	4.94355400	-0.00927300	-0.81840000
C	4.17756600	1.10584900	-0.51353200
C	2.84755300	0.96754600	-0.10261700
C	2.30438600	-0.32771600	0.02241700
C	3.07528300	-1.43579900	-0.27290700
C	4.39026200	-1.27841800	-0.71017100
H	2.50193500	3.10386900	0.07151100
H	5.96747200	0.11024200	-1.14438300
H	4.60308200	2.09740100	-0.60061800
C	2.02316200	2.13471200	0.13767400
C	0.92724800	-0.42082800	0.63548400
H	2.66917000	-2.43479400	-0.17512300
H	4.97825300	-2.15029900	-0.96280400
C	0.68005700	2.06215400	0.32369000
H	0.07109700	2.95495800	0.35561700
C	-1.19020400	0.36156700	-0.01479300
N	0.05193500	-1.51554900	0.20537500
C	0.07378000	0.77750400	0.32223800
C	1.09637700	-0.53441700	2.18066000
H	0.12168000	-0.56491500	2.66656300
H	1.65821200	-1.43684800	2.41786100
H	1.65235000	0.32698100	2.54431000
C	-1.15794100	-1.06030700	-0.07414000
C	-2.41532700	1.14036600	-0.37345600
H	-2.49933200	2.02540500	0.26069800
H	-2.31543000	1.50643700	-1.40066400
C	-2.34151100	-1.89903800	-0.38023700
H	-2.06104100	-2.72530300	-1.03753100
H	-2.67061000	-2.35615400	0.55952400
C	-3.69952900	0.28822400	-0.26253300
C	-3.46972800	-1.05278700	-0.98894200
H	-3.23754300	-0.85076600	-2.03775900
H	-4.38991000	-1.63764700	-0.97970000
C	-4.05039300	0.05834600	1.21345900
H	-4.91304300	-0.60327800	1.30817100
H	-3.22726500	-0.38243800	1.77982300
H	-4.30328300	1.00365600	1.69544900
C	-4.84899400	1.03092000	-0.94679700
H	-5.00283400	2.01167700	-0.49331200
H	-4.64768100	1.17833900	-2.00962900
H	-5.78148000	0.47205600	-0.85497200
H	0.26905400	-2.49136300	0.33675900

4b-H2:

C	-5.11635600	0.14826600	-0.44582400
C	-4.28017300	-0.94953900	-0.58308200
C	-2.91185800	-0.84027600	-0.33634200
C	-2.40148300	0.43047300	0.04748900
C	-3.25501500	1.53583800	0.16776500
C	-4.60788900	1.39297100	-0.06817800
H	-2.44203400	-2.88173900	-0.93026200
H	-6.17564600	0.03944800	-0.63654200
H	-4.68781300	-1.90417800	-0.88846300
C	-2.01499500	-1.97628500	-0.51893600
C	-0.98890400	0.49280800	0.21492200
H	-2.86238900	2.49511000	0.48160200
H	-5.27106900	2.23938600	0.04244200
C	-0.72297000	-1.93647800	-0.18162000
H	-0.08156500	-2.80252400	-0.27375300
C	1.24154000	-0.22699300	0.24409900
N	-0.17139200	1.51136900	0.06213500
C	-0.16367100	-0.71958500	0.49075400
C	-0.28016800	-0.97766300	2.05302900
H	0.35842600	-1.82254500	2.30184700
H	0.05333800	-0.10238100	2.60810900
H	-1.30895500	-1.21671300	2.31130200
C	1.19479500	1.10002600	0.07162700
C	2.51058900	-0.99858700	0.30409500
H	2.71941700	-1.28042600	1.34274900
H	2.41275800	-1.93831600	-0.24779200
C	2.34861100	2.01663400	-0.10663000
H	2.39443000	2.36333700	-1.14405000
H	2.23754100	2.90933800	0.51465300
C	3.69863200	-0.18198200	-0.26439400
C	3.63258900	1.26214500	0.27810700
H	4.49819900	1.82157500	-0.07829800
H	3.70571100	1.22911400	1.36835600
C	5.00835200	-0.82669300	0.19346800
H	5.86649200	-0.30380800	-0.23134500

H	5.10391000	-0.80204600	1.28097700
H	5.06278000	-1.86895800	-0.12694600
C	3.63967600	-0.18500100	-1.79768200
H	3.77030700	-1.19729700	-2.18338500
H	2.68878000	0.19207000	-2.17757000
H	4.43694300	0.43291400	-2.21382300
H	-0.46762600	2.45858400	-0.13075900

TSb-H2: (imaginary frequency: 482.5328*i* cm^{-1})

C	5.06804300	-0.09348300	-0.58483800
C	4.26475900	1.02874300	-0.49265400
C	2.89618400	0.90972700	-0.21938900
C	2.35592400	-0.38788200	-0.03269700
C	3.17452800	-1.51203800	-0.12891500
C	4.52356300	-1.36557800	-0.40576200
H	2.51515900	3.04083500	-0.32129300
H	6.12244200	0.01478700	-0.79919200
H	4.68960400	2.01376100	-0.63598500
C	2.04753300	2.07944900	-0.15056800
C	0.94080400	-0.45215000	0.25157600
H	2.76561900	-2.50413500	0.01458200
H	5.15530000	-2.23982900	-0.48207800
C	0.72048800	2.01710100	0.09894200
H	0.10620700	2.90571000	0.12629100
C	-1.25023100	0.28568000	0.20795300
N	0.09700100	-1.51553700	0.08344500
C	0.11293800	0.72848000	0.29704000
C	0.75170300	0.17114700	2.19108600
H	0.08957400	0.94740900	2.54728300
H	0.44301100	-0.81857800	2.50049800
H	1.79711800	0.40276300	2.33956800
C	-1.21639600	-1.07497000	0.08310500
C	-2.51608000	1.07781800	0.24290400
H	-2.72028300	1.40047600	1.27013400
H	-2.41251400	1.99206900	-0.34751400
C	-2.40547200	-1.95473800	-0.03722100
H	-2.46527200	-2.33492400	-1.06216200
H	-2.30435900	-2.83127700	0.60824500
C	-3.71574400	0.25522200	-0.28618500
C	-3.66953600	-1.16102700	0.32644600
H	-4.54823100	-1.72285400	0.00764600
H	-3.73077200	-1.07326600	1.41461600
C	-5.01577500	0.93941900	0.14049600
H	-5.88216700	0.40968900	-0.25836300
H	-5.11052500	0.96871400	1.22793600
H	-5.05493400	1.96592000	-0.22915500
C	-3.65974600	0.18269400	-1.81818400
H	-3.79115700	1.17516500	-2.25188000
H	-2.70956500	-0.21064000	-2.18324200
H	-4.45757700	-0.45477400	-2.20305400
H	0.37939700	-2.47994500	0.03419800

5b-H2:

C	4.76458900	0.09736500	-1.12334000
C	4.03788600	1.17013000	-0.62867900
C	2.76777600	0.97723900	-0.07544100
C	2.24721100	-0.33116500	-0.00362200
C	2.98025100	-1.39776600	-0.48762900
C	4.23233300	-1.18383900	-1.06384300
H	2.44043200	3.08418200	0.33290000
H	5.74133900	0.25958400	-1.55762600
H	4.44694600	2.17125100	-0.67582100
C	1.97480000	2.10692300	0.36577000
C	0.95257900	-0.49635000	0.75752300
H	2.59272000	-2.40726900	-0.43109000
H	4.78820100	-2.02174500	-1.46213100
C	0.66381200	2.00086800	0.70300900
H	0.06355900	2.87946600	0.89322400
C	-1.22907100	0.31132700	0.42759800
N	0.03832500	-1.55970400	0.33331800
C	0.06405500	0.71343300	0.65425300
C	1.30448900	-0.74191300	2.25553800
H	0.39460800	-0.82783700	2.84856000
H	1.89197200	-1.65482200	2.34394000
H	1.89813300	0.09116000	2.62547500
C	-1.19580200	-1.09713300	0.22338400
C	-2.49784700	1.09724300	0.33298500
H	-2.85450200	1.31694900	1.34457600
H	-2.30815900	2.06228200	-0.14180100
C	-2.38921900	-1.91011800	-0.11370600
H	-2.29272200	-2.21544800	-1.16098900
H	-2.39318200	-2.83427500	0.47012700
C	-3.60199300	0.33806500	-0.43757300
C	-3.67900600	-1.10577600	0.09959900
H	-4.50437100	-1.63219200	-0.38068500
H	-3.90809100	-1.07347300	1.16796300
C	-4.94398000	1.03088100	-0.19372700
H	-5.73986500	0.54598200	-0.76093800
H	-5.21791000	1.00344000	0.86268100
H	-4.90331400	2.07627600	-0.50466100
C	-3.29105700	0.34742800	-1.94042400
H	-3.33961700	1.36454300	-2.33142700
H	-2.29494800	-0.03724600	-2.16890700
H	-4.01658100	-0.25468200	-2.48990300
H	0.27624100	-2.53923500	0.33325900