Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Highly Stereoselective Intramolecular Buchner Reactions of Diazoacetamides Catalyzed by Ru(II)-Pheox Complex

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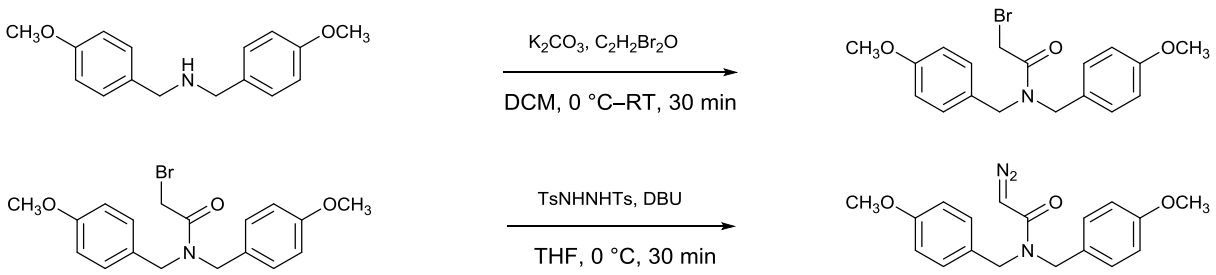
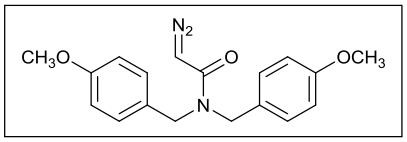
General: All reactions were performed under an atmosphere of argon unless otherwise noted. Dichloromethane (DCM) was purchased from Kanto Chemical Co., Inc.. All reactions were monitored by thin layer chromatography (TLC), glass plates pre-coated with silica gel Merck KGaA 60 F_{254}, layer thickness 0.2 mm. The products were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid or by treatment with a solution of *p*-anisaldehyde. Flash column chromatography was performed using silica gel (Merck, Art. No. 7734). ^{1}H NMR (500 MHz, 400 MHz) and ^{13}C NMR (125 MHz, 100 MHz) spectra were recorded on JEOL JNM-ECX500, JEOL JNM-ECS400 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane (0.00 ppm) in $CDCl_3$. Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Optical rotations were performed with a JASCO P-1030 polarimeter at the sodium D line (1.0 mL sample cell). Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) analyses with a JASCO GULLIVER using Daicel CHIRALPAK or CHIRALCEL columns.

1. Preparation of diazoacetamides



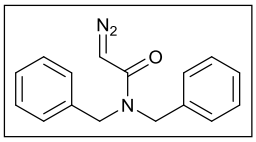
Scheme S1. Synthesis of 2-diazo-N,N-bis(4-methoxybenzyl)acetamide (**1b**).



To a suspension of K_2CO_3 (1.66 g, 12 mmol) and bis(4-methoxybenzyl)amine (2.27 g, 10 mmol) in DCM (20 mL) was added dropwise bromoacetyl bromide (0.95 mL, 11 mmol) at 0°C. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was then extracted three times with DCM (20 mL x 3), dried over Na_2SO_4, and filtered. After evaporation of the solvent, the residue was obtained and used in the next step without purification. The resulting bromoacetamide and *N,N′*-ditosylhydrazine (5.1 g, 15 mmol) were dissolved in THF (20 mL) and cooled down to 0°C, then DBU (3 mL, 20 mmol) was added dropwise and stirred at 0°C for 30 minutes. After quenched with sat. $NaHCO_3$ aq. and extracted with diethyl ether (20 mL x 3) three times, the organic phase was dried over Na_2SO_4 and evaporated to give the crude product. Purification was performed with flash column chromatography on silica gel eluted with *n*–Hexane/EtOAc (1/5 (v/v)) to give 2-diazo-*N*,*N*-bis(4-methoxybenzyl)acetamide (1.66 g, 51% yield) as a yellow oil **1b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (br s, 4H), 6.88 (d, *J* = 8.41 Hz, 4H), 4.98 (s, 1H), 4.35 (br s, 4H), 3.77 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 158.9, 129.38, 128.2, 113.8, 55.1, 48.53, 46.64 ppm. IR (neat) ν 3068, 2928, 2837, 2100, 1606, 1440, 814 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{19}N_3O_3$ $[M+H]^+$: 326.1504 found: 326.1504.

2. Analytical data for diazoacetamides

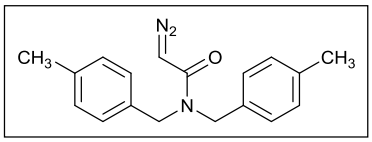
N,N-Dibenzyl-2-diazoacetamide (1a)



Same procedure as described above for **1b**. (48% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.23 (m, 10H), 4.97 (s, 1H), 4.46 (br s, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.61, 136.62, 128.72, 127.52,

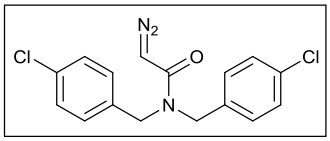
126.56, 49.38, 47.00 ppm. IR (neat) ν 3064, 2921, 2100, 1606, 1427, 727 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{15}N_3O$ $[M+H]^+$: 266.1293 found: 266.1293.

2-Diazo-*N*,*N*-bis(4-methylbenzyl)acetamide (1c)



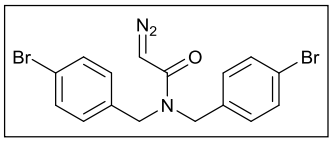
Same procedure as described above for **1b**. (43% yield). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.64 Hz, 4H), 7.11 (br s, 4H), 4.96 (s, 1H), 4.39 (br s, 4H), 2.35 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.59, 137.40, 133.88, 129.56, 127.07, 49.10, 47.12, 21.21 ppm. IR (neat) ν 3052, 2921, 2104, 1603, 1432, 798 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{19}N_3O$ $[M+H]^+$: 294.1606 found: 294.1606.

2-Diazo-*N*,*N*-bis(4-chlorobenzyl)acetamide (1d)



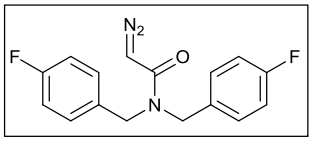
Same procedure as described above for **1b**. (63% yield). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.94 Hz, 4H), 7.14 (d, *J* = 7.94 Hz, 4H), 4.94 (s, 1H), 4.39 (br s, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.64, 135.15, 133.66, 129.11, 128.87, 49.06, 47.24 ppm. IR (neat) ν 3072, 2925, 2109, 1606, 1432, 802 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{13}Cl_2N_3O$ $[M+H]^+$: 334.0513 found: 334.0513.

2-Diazo-*N*,*N*-bis(4-bromobenzyl)acetamide (1e)



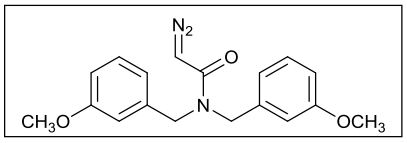
Same procedure as described above for **1b**. (55% yield). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.03 Hz, 4H), 7.08 (d, *J* = 8.03 Hz, 4H), 4.94 (s, 1H), 4.4 (br s, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 135.73, 131.82, 128.70, 121.48, 48.93, 47.08 ppm. IR (neat) ν 3069, 2918, 2103, 1623, 1438, 797 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{13}Br_2N_3O$ $[M+H]^+$: 421.9503 found: 421.9503.

2-Diazo-*N*,*N*-bis(4-fluorobenzyl)acetamide (1f)



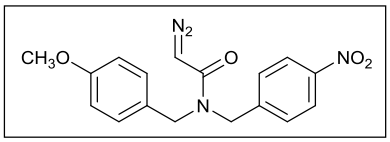
Same procedure as described above for **1b**. (69% yield). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.03 Hz, 4H), 7.03 (t, *J* = 8.03 Hz, 4H), 4.96 (s, 1H), 4.4 (br s, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.52, 163.25, 161.29, 132.41, 128.83, 115.80, 48.82, 47.09 ppm. IR (neat) ν 3072, 2921, 2109, 1599, 1440, 818 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{13}F_2N_3O$ $[M+H]^+$: 302.1108 found: 302.1104.

2-Diazo-*N*,*N*-bis(3-methoxybenzyl)acetamide (1g)



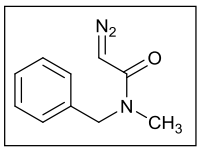
Same procedure as described above for **1b**. (60% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.03 Hz, 2H), 6.84–6.75 (m, 6H), 4.96 (s, 1H), 4.76–4.13 (br s, 4H), 3.79 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.55, 160.02, 138.41, 129.84, 119.63, 113.25, 112.90, 55.20, 49.51, 47.00 ppm. IR (neat) ν 3064, 2937, 2104, 1599, 1427, 782 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{19}N_3O_3$ $[M+H]^+$: 326.1509 found: 326.1504.

2-Diazo-*N*-(4-methoxybenzyl)-*N*-(4-nitrobenzyl)acetamide (1h)



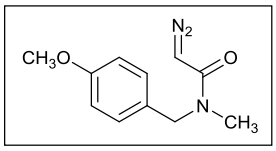
Same procedure as described above for **1b**. (33% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.03 Hz, 2H), 7.38 (d, *J* = 8.03 Hz, 2H), 7.11 (d, *J* = 8.03 Hz, 2H), 6.88 (d, *J* = 8.03 Hz, 2H), 5.04 (br s, 1H), 4.6 (br s, 2H), 4.32 (br s, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.73, 159.46, 147.48, 145.05, 128.49, 127.95, 124.06, 114.47, 55.45, 49.85, 48.95, 47.32 ppm. IR (neat) ν 3076, 2933, 2109, 1606, 1440, 822 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{16}N_4O_4$ $[M+H]^+$: 341.1249 found: 341.1249.

2-Diazo-*N*-benzyl-*N*-methylacetamide (1i)



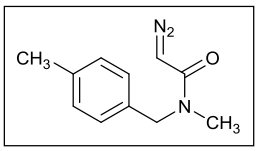
Same procedure as described above for **1b**. (22% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.64 Hz, 2H), 7.29 (d, *J* = 7.64 Hz, 1H), 7.23 (d, *J* = 7.64 Hz, 2H), 4.99 (s, 1H), 4.55 (br s, 2H), 2.85 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.22, 137.05, 128.83, 127.60, 126.64, 51.43, 46.62, 34.59 ppm. IR (neat) ν 3068, 2921, 2104, 1610, 1404, 727 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{11}N_3O$ $[M+H]^+$: 190.0982 found: 190.0980.

2-Diazo-*N*-(4-methoxybenzyl)-*N*-methylacetamide (1j)



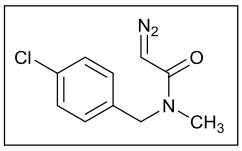
Same procedure as described above for **1b**. (43% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.03 Hz, 2H), 6.87 (d, *J* = 8.03 Hz, 2H), 4.98 (s, 1H), 4.45 (br s, 2H), 3.8 (s, 3H), 2.83 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.11, 159.22, 129.13, 128.82, 114.26, 55.41, 51.24, 46.6, 34.22 ppm. IR (neat) ν 3068, 2933, 2104, 1606, 1455, 814 cm^{-1}. HRMS (DART) calcd for $C_{11}H_{13}N_3O_2$ $[M+H]^+$: 220.1087 found: 220.1086.

2-Diazo-*N*-(4-methylbenzyl)-*N*-methylacetamide (1k)



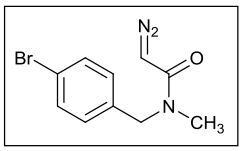
Same procedure as described above for **1b**. (42% yield). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 17.76, 8.02 Hz, 4H), 4.97 (s, 1H), 4.45 (br s, 2H), 2.86 (br s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.29, 136.18, 131.98, 129.38, 121.61, 50.89, 46.7, 34.33, 23.14 ppm. IR (neat) ν 3072, 2921, 2100, 1606, 1399, 798 cm^{-1}. HRMS (DART) calcd for $C_{11}H_{13}N_3O$ $[M+H]^+$: 204.1137 found: 204.1137.

2-Diazo-*N*-(4-chlorobenzyl)-*N*-methylacetamide (1l)



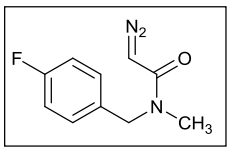
Same procedure as described above for **1b**. (46% yield). Yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.03 Hz, 2H), 7.17 (d, *J* = 8.03 Hz, 2H), 4.97 (s, 1H), 4.49 (br s, 2H), 2.83 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.24, 135.68, 133.40, 128.97, 128.67, 50.77, 46.64, 34.40 ppm. IR (neat) ν 3072, 2916, 2100, 1606, 1404, 791 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{10}ClN_3O$ $[M+H]^+$: 224.0590 found: 224.0590.

2-Diazo-*N*-(4-bromobenzyl)-*N*-methylacetamide (1m)



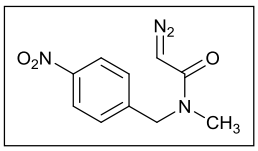
Same procedure as described above for **1b**. (47% yield). Yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.03 Hz, 2H), 7.11 (d, *J* = 8.03 Hz, 2H), 4.97 (s, 1H), 4.47 (br s, 2H), 2.84 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.23, 136.19, 131.89, 129.37, 121.47, 50.98, 46.63, 34.39 ppm. IR (neat) ν 3072, 2925, 2104, 1610, 1399, 746 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{10}BrN_3O$ $[M+H]^+$: 268.0084 found: 268.0085.

2-Diazo-*N*-(4-flourobenzyl)-*N*-methylacetamide (1n)



Same procedure as described above for **1b**. (25% yield). Yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.2 (t, *J* = 8.03 Hz, 2H), 7.01 (t, *J* = 8.03 Hz, 2H), 4.98 (s, 1H), 4.49 (br s, 2H), 2.82 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.29, 163.33, 161.37, 129.35, 115.84, 50.79, 46.69, 34.35 ppm. IR (neat) ν 3072, 2925, 2104, 1606, 1408, 818 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{10}FN_3O$ $[M+H]^+$: 208.0886 found: 208.0886.

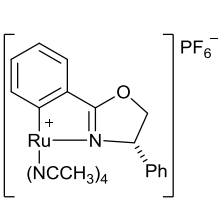
2-Diazo-*N*-(4-nitrobenzyl)-*N*-methylacetamide (1o)



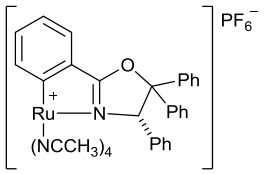
Same procedure as described above for **1b**. (20% yield). Yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.41 Hz, 2H), 7.34 (d, *J* = 8.41 Hz, 2H), 5.04 (s, 1H), 4.59 (br s, 2H), 3.37 (s, 2H), 2.81 (br s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.49, 147.52, 144.94, 128.37, 124.13, 51.04, 46.77, 34.8 ppm. IR (neat) ν 3072, 2928, 2109, 1606, 1479, 727 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{10}N_4O_3$ $[M+H]^+$: 235.0839 found: 235.0831.

3. Asymmetric intramolecular reactions of *N*-diazoacetamides catalyzed by Ru(II)-Pheox complexes.

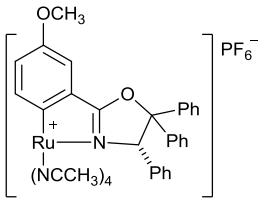
Table S1. Catalyst screening experiments.



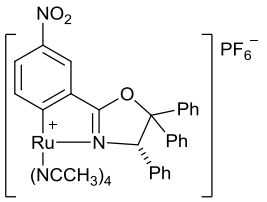
Cat.3: Ru(II)-Pheox



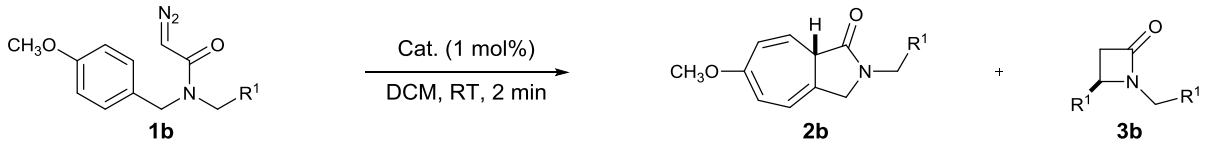
Cat.5



Cat.6



Cat.7



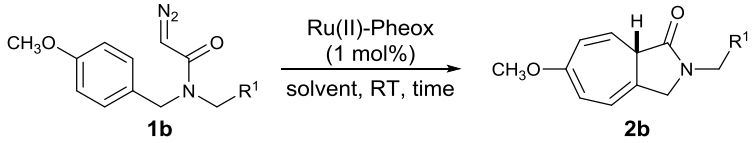
1b **2b** **3b**

R^1 = -C_6H_4(4-OCH_3)

Entry	Cat.	Ratio [**2b** : **3b**][a]	Yield [%][b]	ee [%][c] **2b**
1	Cat. 3	100 : 0	99	99
2	Cat. 5	100 : 0	98	99
3	Cat. 6	100 : 0	98	99
4	Cat. 7	100 : 0	93	99

[a] The ratio was determined ^{1}H NMR from the reaction mixture. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table S2. Optimization of the reaction conditions.



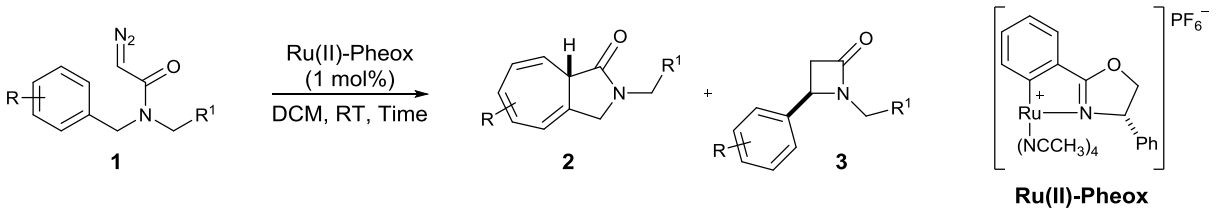
1b **2b**

R^1 = -C_6H_4(4-OCH_3)

Entry	Solvent	Time [min]	Yield [%][a]	**2b** ee [%][b]
1	DCM	2	99	99
2	Toluene	30	98	99
3	Acetone	2	86	99
4	THF	2	99	98
5	Acetonitrile	60	97	98
6	DMF	60	99	96
7	DMSO	5 h	n.r.	_
8	Methanol	2	99	94

[a] Isolated yield. [b] Determined using chiral HPLC analysis

4. General procedure for catalytic asymmetric intramolecular Buchner reaction of diazoacetamides

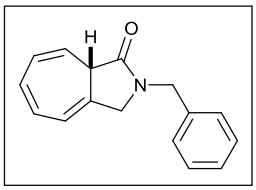


Scheme S2. Catalytic asymmetric intramolecular Buchner reaction of diazoacetamides.

To a stirred mixture of Ru(II)-Pheox catalyst (1.30 mg, 0.002 mmol) in DCM (1.0 mL) was slowly added a solution of diazoacetamides (0.2 mmol) in DCM (2.0 mL) (for 2 minutes with *N*,*N*-bisaryl-2-diazo-acetamides or 4 hours with *N*-aryl-2-diazo-*N*-methylacetamides) under argon atmosphere at room temperature. After the addition completed, the progress of the reaction was monitored by TLC. Upon completion, the solvent was removed and the residue was purified by flash column chromatography on silica gel eluted with *n*–Hexane/ EtOAc or *n*–Hexane/IPA to give the desired product. The regioselective ratios were determined from the crude ^{1}H NMR spectra, and the ee values were determined by chiral HPLC analysis.

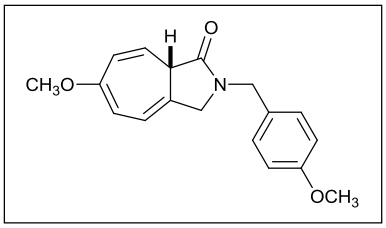
5. Analytical data for asymmetric intramolecular Buchner reaction products

(*S*)-2-Benzyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2a)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1a** (53.1 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/Et_2O as an eluent to give 2-phenyl-3,8a-dihydro cyclohepta[c]pyrrol-1(2H)-one **2a** as colorless oil (92% yield, 43.7 mg, 0.184 mmol), 78% ee. $[\alpha]^{27.6}_D$ = +144.3 (c 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 6.47 (t, *J* = 3.25 Hz, 2H), 6.22–6.17 (m, 1H), 6.08 (ddd, *J* = 4.59, 4.20, 2.29 Hz, 1H), 5.33 (dd, *J* = 9.56, 3.82 Hz, 1H), 4.60 (d, *J* = 14.52 Hz, 1H), 4.54 (d, *J* = 14.52 Hz, 1H), 4.08 (d, *J* = 17.2 Hz, 1H), 4.04 (d, *J* = 17.2 Hz, 1H), 3.15 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.25, 136.10, 130.50, 130.04, 129.30, 128.96, 128.32, 127.93, 127.17, 120.80, 119.70, 50.70, 46.70, 46.47 ppm. IR (neat) ν 3027, 2924, 1683, 1422, 1272, 764 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 14.2 min (major product), tR = 15.9 min (minor product). HRMS (DART) calcd for $C_{16}H_{16}N_1O_1$ $[M+H]^+$: 238.1231 found: 238.1231.

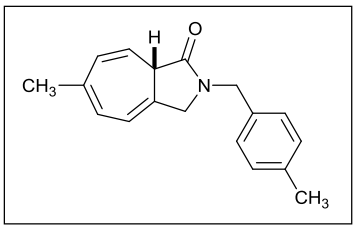
(*S*)-6-Methoxy-2-(4-methoxybenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2b)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of 2-diazo-*N*,*N*-bis(4-methoxybenzyl)acetamide **1b** (65.1 mg, 0.2mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-methoxy-2-(4-methoxybenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **(2b)** as white solid (99% yield, 58.9 mg, 0.198 mmol), 99% ee. $[\alpha]^{26.3}_D$ = –25.34 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.41 Hz, 2H), 6.86 (d, *J* = 8.41 Hz, 2H), 6.05 (dt, *J* = 10.32, 2.29 Hz, 1H), 5.98 (ddd, *J* = 4.97, 4.20, 2.29 Hz, 1H), 5.67 (d, *J* = 8.41 Hz, 1H), 5.51 (dd, *J* = 10.32, 4.2 Hz, 1H), 5.53 (d, *J* = 14.52 Hz, 1H), 4.46 (d, *J* = 14.52 Hz, 1H), 4.03 (d, *J* = 14.91 Hz, 1H), 3.98 (d, *J* = 14.91 Hz, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 3.20 (s, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 173.78, 159.28, 159.24, 129.59, 128.10, 125.15, 123.26, 123.23, 117.71, 114.17, 102.82, 55.34, 54.77, 50.32, 45.98, 45.95 ppm. IR (neat) ν 2992, 2933, 1690, 1511, 1439, 806 cm^{-1}. The ee value was

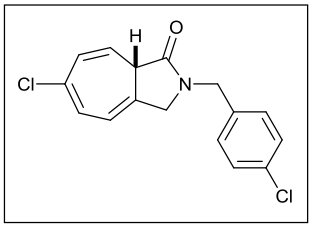
determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 23.1 min (major product), tR = 33.6 min (minor product). HRMS (DART) calcd for $C_{18}H_{19}NO_3$ $[M+H]^+$: 206.0929 found: 206.0929.

(*S*)-6-Methyl-2-(4-methylbenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2c)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of 2-diazo-*N*,*N*-bis(4-methylbenzyl)acetamide **1c** (58.7 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-methyl-2-(4-methylbenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **2c** as colorless oil (93% yield, 49.4 mg, 0.186 mmol), 97% ee. $[\alpha]^{23.9}_D$ = +40.65 (c 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.59 Hz, 2H), 7.13 (d, *J* = 8.59 Hz, 2H), 6.26 (d, *J* = 5.73 Hz, 1H), 6.02 (d, *J* = 9.74 Hz, 1H), 5.95 (d, *J* = 5.73 Hz, 1H), 5.31 (dd, *J* = 9.74, 4.01 Hz, 1H), 4.54 (d, *J* = 14.89 Hz, 1H), 4.49 (d, *J* = 14.89 Hz, 1H), 4.04 (d, *J* = 15.75 Hz, 1H), 3.99 (d, *J* = 15.75 Hz, 1H), 3.12 (s, 1H), 2.33 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.25, 139.37, 137.54, 133.08, 130.34, 129.55, 128.30, 127.11, 126.89, 120.00, 119.31, 50.47, 46.37, 46.15, 24.80, 21.21 ppm. IR (neat) ν 3020, 2917, 1686, 1435, 1268, 806 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 30/1, Flow rate = 1.0 mL/min, tR = 34.1 min (major product), tR = 38.1 min (minor product). HRMS (DART) calcd for $C_{18}H_{20}N_1O_1$ $[M+H]^+$: 266.1544 found: 266.1544.

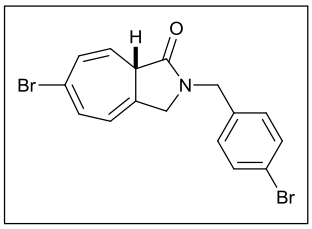
(*S*)-6-Chloro-2-(4-chlorobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2d)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-bis(4-chlorobenzyl)-2-diazoacetamide **1d** (66.8 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-chloro-2-(4-chlorobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **2d** as white solid (96% yield, 58.8 mg, 0.192 mmol), 96% ee. $[\alpha]^{26.3}_D$ = +90.26 (c 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.41 Hz, 2H), 7.20 (d, *J* = 8.41 Hz, 2H), 6.68 (d, *J* = 6.50 Hz, 1H), 6.20 (d, *J* = 9.94 Hz, 1H), 6.02 (ddd, *J* = 4.59, 4.20, 2.29 Hz, 1H), 5.37 (dd, *J* = 9.94, 4.20 Hz, 1H), 4.56 (d, *J* = 14.91 Hz, 1H), 4.49 (d, *J* = 14.91

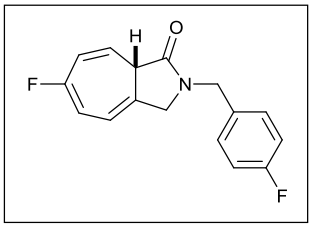
Hz, 1H), 4.06 (d, *J* = 15.29 Hz, 1H), 4.01 (d, *J* = 15.29 Hz, 1H), 3.26 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.23, 135.22, 134.34, 133.95, 129.68, 129.23, 129.18, 129.06, 128.64, 122.35, 118.45, 50.48, 46.04, 45.92 ppm. IR (neat) ν 3029, 2909, 1694, 1491, 1268, 811 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 17.108 min (major product), tR = 15.908 min (minor product). HRMS (DART) calcd for $C_{16}H_{14}Cl_2N_1O_1$ $[M+H]^+$: 306.0452 found: 306.0452.

(*S*)-6-Bromo-2-(4-bromobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2e)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-bis(4-bromobenzyl)-2-diazoacetamide **1e** (84.6 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-bromo-2-(4-bromobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **2e** as white solid (95% yield, 75.1 mg, 0.190 mmol), 95% ee. $[\alpha]^{27.4}_D$ = +107.77 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.60 Hz, 2H), 7.13 (d, *J* = 8.60 Hz, 2H), 6.90 (d, *J* = 6.50 Hz, 1H), 6.32 (d, *J* = 9.94 Hz, 1H), 5.97 (ddd, *J* = 4.59, 4.20, 2.29 Hz, 1H), 5.27 (dd, *J* = 9.94, 4.59 Hz, 1H), 4.54 (d, *J* = 14.71 Hz, 1H), 4.47 (d, *J* = 14.71 Hz, 1H), 4.03 (d, *J* = 15.29 Hz, 1H), 3.98 (d, *J* = 15.29 Hz, 1H), 3.27 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.19, 134.90, 132.38, 132.16, 131.07, 130.03, 129.97, 124.71, 122.33, 122.07, 119.31, 50.50, 46.16, 45.98 ppm. IR (neat) ν 3032, 2909, 1690, 1483, 1264, 798 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 19.9 min (minor product), tR = 27.5 min (major product). HRMS (DART) calcd for $C_{16}H_{14}Br_2N_1O_1$ $[M+H]^+$: 393.9442 found: 393.9442.

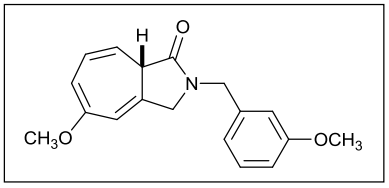
(*S*)-6-Fluoro-2-(4-fluorobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2f)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of 2-diazo-*N*,*N*-bis(4-fluorobenzyl)acetamide **1f** (60.3 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-fluoro-2-(4-fluorobenzyl)-3,8a-

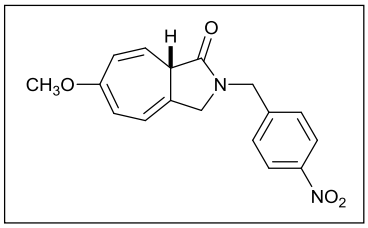
dihydrocyclohepta[c]pyrrol-1(2H)-one **2f** as yellow oil (90% yield, 49.2 mg, 0.180 mmol), 90% ee. $[\alpha]^{24.0}_{D}$ = +63.71 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.59, 5.15 Hz, 2H), 7.03 (d, *J* = 8.59 Hz, 2H), 6.28–6.15 (m, 2H), 6.04–5.99 (m, 1H), 5.49 (m, 1H), 4.57 (d, *J* = 14.60 Hz, 1H), 4.49 (d, *J* = 14.60 Hz, 1H), 4.08 (d, *J* = 15.75 Hz, 1H), 4.00 (d, *J* = 15.75 Hz, 1H), 3.26 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.34, 162.81, 160.93, 130.08, 123.67, 122.34, 116.61, 115.99, 115.82, 110.85, 110.63, 50.57, 46.23, 46.03 ppm. IR (neat) ν 3044, 2919, 1689, 1415, 1224, 754 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 13.9 min (major product), tR = 14.7 min (minor product). HRMS (DART) calcd for $C_{16}H_{14}F_2N_1O_1$ $[M+H]^+$: 274.1043 found: 274.1043.

(*S*)-5-Methoxy-2-(3-methoxybenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2g)



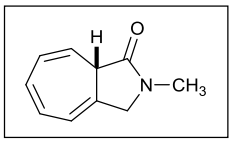
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of 2-diazo-*N*,*N*-bis(3-methoxybenzyl)acetamide **1g** (65.1 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 5-methoxy-2-(3-methoxybenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **2g** as colorless oil (87% yield, 51.8 mg, 0.174 mmol), 74% ee. $[\alpha]^{26.7}_{D}$ = –196.62 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.03 Hz, 1H), 6.87–6.77 (m, 3H), 6.12 (ddd, *J* = 7.07, 4.87, 2.29 Hz, 1H), 5.94 (ddd, *J* = 4.59, 2.29, 1.91, Hz, 1H), 5.65 (dd, *J* = 6.88, 1.91 Hz, 1H), 5.17 (dd, *J* = 9.56, 3.44 Hz, 1H), 4.55 (d, *J* = 14.91 Hz, 1H), 4.52 (d, *J* = 14.91 Hz, 1H), 4.07 (d, *J* = 15.86 Hz, 1H), 4.04 (d, *J* = 15.86 Hz, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.22 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.18, 160.14, 158.96, 137.55, 131.68, 129.94, 125.65, 120.50, 117.97, 115.75, 113.80, 113.37, 102.80, 55.36, 54.76, 50.45, 46.59, 46.02 ppm. IR (neat) ν 3005, 2928, 1690, 1427, 1260, 703 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 20.7 min (major product), tR = 25.8 min (minor product). HRMS (DART) calcd for $C_{16}H_{14}F_2N_1O_1$ $[M+H]^+$: 298.1443 found: 298.1443.

(*S*)-6-Methoxy-2-(4-nitrobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2h)



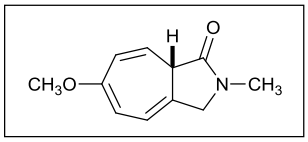
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of 2-diazo-*N*-(4-methoxybenzyl)-*N*-(4-nitrobenzyl)acetamide **1h** (65.1 mg, 0.2mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc as an eluent to give 6-methoxy-2-(4-nitrobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2h**) as yellow oil (84% yield, 52.5 mg, 0.168 mmol), 99% ee. $[\alpha]^{22.7}_{D}$ = –40.09 (c 1.0, $CHCl_3$). ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.87 Hz, 2H), 7.43 (d, *J* = 8.87 Hz, 2H), 6.05 (dt., *J* = 10.31, 2.29 Hz, 1H), 6.04 (ddd., *J* = 4.58, 4.58, 2.29 Hz, 1H), 5.69 (d, *J* = 6.87 Hz, 1H), 5.50 (dd, *J* = 10.31, 4.01 Hz, 1H), 4.70 (d, *J* = 15.46 Hz, 1H), 4.63 (d, *J* = 15.46 Hz, 1H), 4.11 (d, *J* = 14.03 Hz, 1H), 4.04 (d, *J* = 14.03 Hz, 1H), 3.64 (s, 3H) , 3.24 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.43, 159.58, 147.71, 143.67, 128.85, 125.55, 124.18, 122.87, 122.30, 118.34, 102.81, 54.87, 50.70, 46.09, 45.54 ppm. IR (neat) ν 3002, 2921, 1696, 1413, 1217, 702 cm^{-1}.The ee value was determined by chiral HPLC analysis. Column (Chiral IA-3), UV detector 220 nm, eluent: Hex/IPA = 10/1, Flow rate = 1.0 mL/min, tR = 45.2 min (major product), tR = 59.3 min (minor product). HRMS (DART) calcd for $C_{17}H_{17}N_2O_4$ $[M+H]^+$: 313.1188 found: 313.1188.

(*S*)-2-Methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2i)



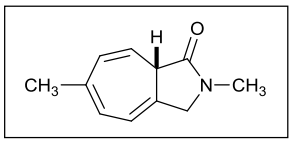
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1i** (37.8 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2i**) as white powder (22 % yield, 7.1 mg, 0.044 mmol), 71% ee. $[\alpha]^{22.8}_{D}$ = +91.67 (c 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (ddd, *J* = 12.23, 10.32, 5.35 Hz, 2H), 6.20–6.15(m, 2H), 5.28 (*J* = 10.32, 4.2 Hz, 1H), 4.23 (d, *J* = 15.29, 1H), 4.19 (d, *J* = 15.29, 1H), 3.08 (s, 1H), 2.97 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.93, 130.53, 130.05, 127.10, 121.22, 120.93, 119.52, 53.42, 46.10, 29.70 ppm. IR (neat) ν 3020, 2920, 1690, 1432, 1276, 703 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min, tR = 19.6 min (major product), tR = 16.2 min (minor product). HRMS (DART) calcd for $C_{10}H_{11}N_1O_1$ $[M+H]^+$: 162.0910 found: 162.0918.

(*S*)-6-Methoxy-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2j)



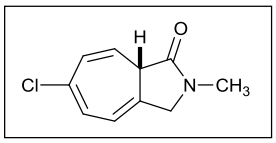
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1j** (44.0 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 6-methoxy-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **(2j)** as white powder (76% yield, 29.0 mg, 0.152 mmol), 99% ee. $[\alpha]^{23.2}_{D}$ = –9.5 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06–6.04 (m, 2H), 5.70 (d, *J* = 7.02 Hz, 1H), 5.47 (dd, *J* = 10.38, 4.27 Hz, 1H), 4.19 (d, *J* = 14.65 Hz, 1H), 4.13 (d, *J* = 14.65 Hz, 1H), 3.64 (s, 3H), 3.15 (s, 1H), 2.96 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.08, 159.45, 125.18, 123.51, 123.40, 117.67, 102.84, 54.89, 53.28, 45.75, 29.72 ppm. IR (neat) ν 3011, 2956, 1697, 1433, 1218, 717 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min, tR = 31.8 min (major product), tR = 29.9 min (minor product). HRMS (DART) calcd for $C_{11}H_{13}N_1O_2$ $[M+H]^+$: 192.1029 found: 192.1024.

(*S*)-2,6-Dimethyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2k)



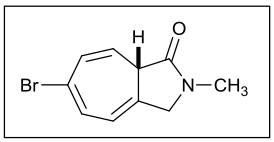
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1k** (40.6 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 2,6-dimethyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one **(2k)** as white powder (67% yield, 23.4 mg, 0.134 mmol), 99% ee. $[\alpha]^{23.3}_{D}$ = +32.6 (c 0.55, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (d, *J* = 6.12 Hz, 1H), 6.05–6.01 (m, 2H), 5.28 (dd, *J* = 9.94, 4.20 Hz, 1H), 4.20 (d, *J* = 15.67 Hz, 1H), 4.15 (d, *J* = 15.67 Hz, 1H), 3.07 (s, 1H), 2.96 (s, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.35, 139.41, 130.25, 127.08, 126.82, 120.07, 119.13, 53.23, 45.78, 29.62, 24.82 ppm. IR (neat) ν 2921, 2857, 1681, 1400, 1255, 735 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min, tR = 17.7 min (major product), tR = 15.9 min (minor product). HRMS (DART) calcd for $C_{11}H_{13}N_1O_1$ $[M+H]^+$: 176.1070 found: 176.1075.

(*S*)-6-Chloro-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2l)



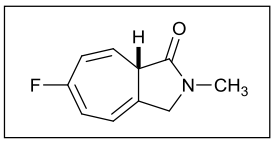
This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1l** (44.7 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 6-chloro-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2l**) as white powder (61% yield, 23.9 mg, 0.122 mmol), 92% ee. $[\alpha]^{24.1}_{D}$ = +42.9 (c 0.1, $CHCl_3$). ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.70 (d, *J* = 6.88 Hz, 1H), 6.19 (dt, *J* = 9.94, 1.91 Hz, 1H), 6.08 (ddd, *J* = 4.59, 4.20, 1.91 Hz, 1H), 5.34 (dd, *J* = 9.94, 4.2 Hz, 1H), 4.22 (d, *J* = 15.67 Hz, 1H), 4.16 (d, *J* = 15.67 Hz, 1H), 3.20 (s, 1H), 2.97 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.23, 135.24, 129.69, 128.92, 128.62, 122.69, 118.17, 53.26, 45.77, 29.73 ppm. IR (neat) ν 3036, 2920, 1694, 1486, 1268, 774 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min, tR = 32.6 min (major product), tR = 20.8 min (minor product). HRMS (DART) calcd for $C_{10}H_{10}Cl_1N_1O_1$ $[M+H]^+$: 196.0527 found: 196.0529.

(*S*)-6-Bromo-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2m)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1m** (53.6 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 6-bromo-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2m**) as white powder (43% yield, 20.8 mg, 0.086 mmol), 96% ee. $[\alpha]^{24.0}_{D}$ = +34.5 (c 0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 6.5 Hz, 1H), 6.31 (d, *J* = 9.94 Hz, 1H), 6.03 (ddd, *J* = 4.59, 4.20, 2.29, 1H), 5.25 (dd, *J* = 9.94, 4.20 Hz, 1H), 4.18 (d, *J* = 15.67 Hz, 1H), 4.13 (d, *J* = 15.67 Hz, 1H), 3.22 (s, 1H), 2.96 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.16, 132.36, 130.86, 130.40, 124.66, 122.63, 118.99, 53.24, 45.82, 29.65 ppm. IR (neat) ν 3032, 2924, 1686, 1399, 1275, 774 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min,tR = 33.0 min (major product), tR = 23.4 min (minor product). HRMS (DART) calcd for $C_{10}H_{10}Br_1N_1O_1$ $[M+H]^+$: 240.0023 found: 240.0024.

(*S*)-6-Fluoro-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2n)



This compound was prepared according to the typical procedure for asymmetric Buchner ring expansion reaction of *N*,*N*-dibenzyl-2-diazoacetamide **1n** (41.4 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/IPA as an eluent to give 6-fluoro-2-methyl-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2n**) as colorless oil (44% yield, 15.6 mg, 0.088 mmol), 92% ee. $[\alpha]^{20.3}_{D}$ = –172.16 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (dd, *J* = 17.97, 8.03 Hz, 1H), 6.18 (tdd, *J* = 8.98, 2.29, 2.29 Hz, 1H), 6.09–6.05 (m, 1H), 5.46 (ddt, *J* = 9.94, 4.97, 4.97 Hz, 1H), 4.23 (d, *J* = 15.29 Hz, 1H), 4.14 (d, *J* = 15.29 Hz, 1H), 3.17 (s, 1H), 2.97 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.34, 128.10, 125.86, 123.86, 122.17, 116.23, 110.58, 53.35, 45.99, 29.74 ppm. IR (neat) ν 3040, 2921, 1690, 1435, 1276, 715 cm^{-1}. The ee value was determined by chiral HPLC analysis. Column (Chiral ID-3), UV detector 220 nm, eluent: Hex/IPA = 5/1, Flow rate = 1.0 mL/min, tR = 23.7 min (major product), tR = 17.6 min (minor product). HRMS (DART) calcd for $C_{10}H_{10}F_1N_1O_1$ $[M+H]^+$: 180.0825 found: 180.0829.

6. X-ray crystal structure of (*S*)-6-Chloro-2-(4-chlorobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (2d)

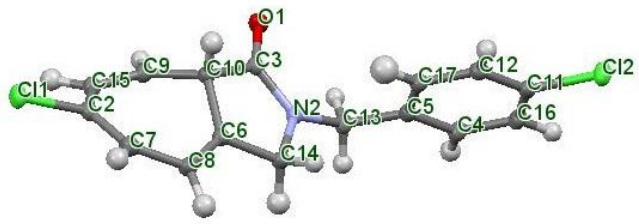


Figure S1. X-ray analysis of (*S*)-6-chloro-2-(4-chlorobenzyl)-3,8a-dihydrocyclohepta[c]pyrrol-1(2H)-one (**2d**).

Crystal data and structure refinement for iw1202

Identification code: iw1202

Formula: C16H13Cl2NO

Temperature (K): 120

Density (CCDC): 1.478

Space group: *P* $2_12_12_1$

Unit cell dimensions:

a = 5.7469(12) Å $\alpha = 90^o$

b = 10.807(2) Å $\beta = 90^o$

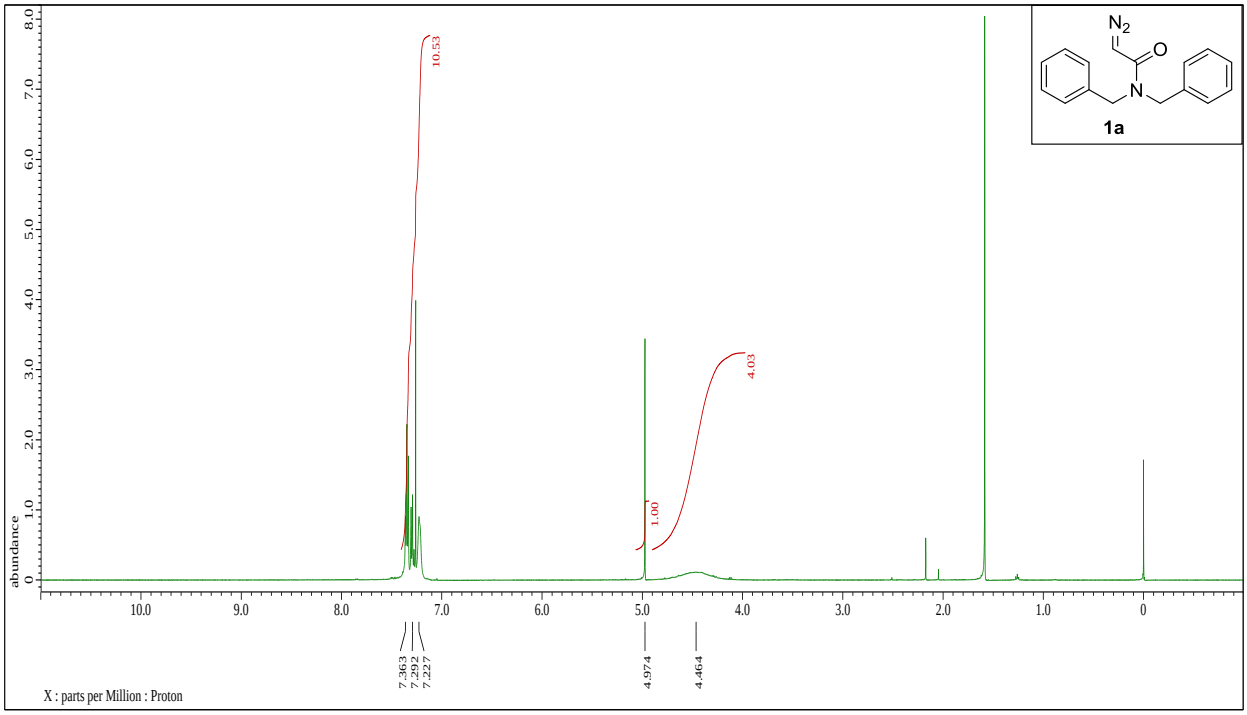
c = 22.158(5) Å $\gamma = 90^o$

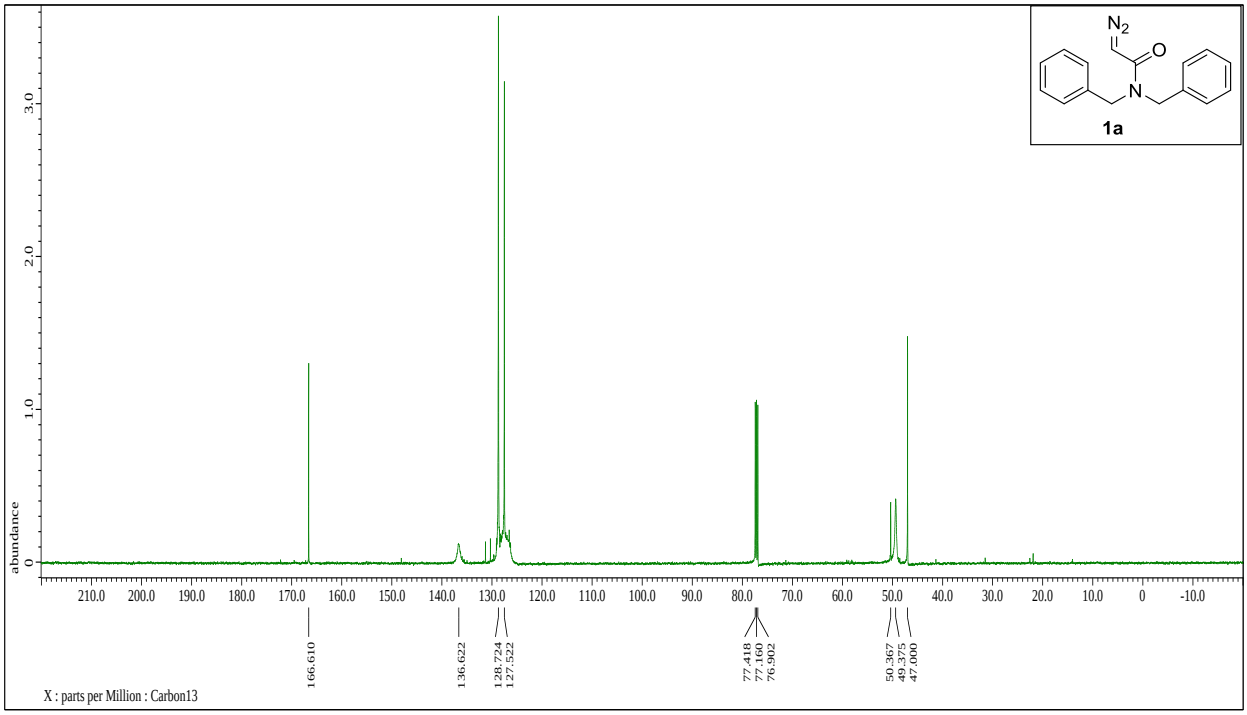
Volume: 1376.16 $Å^3$

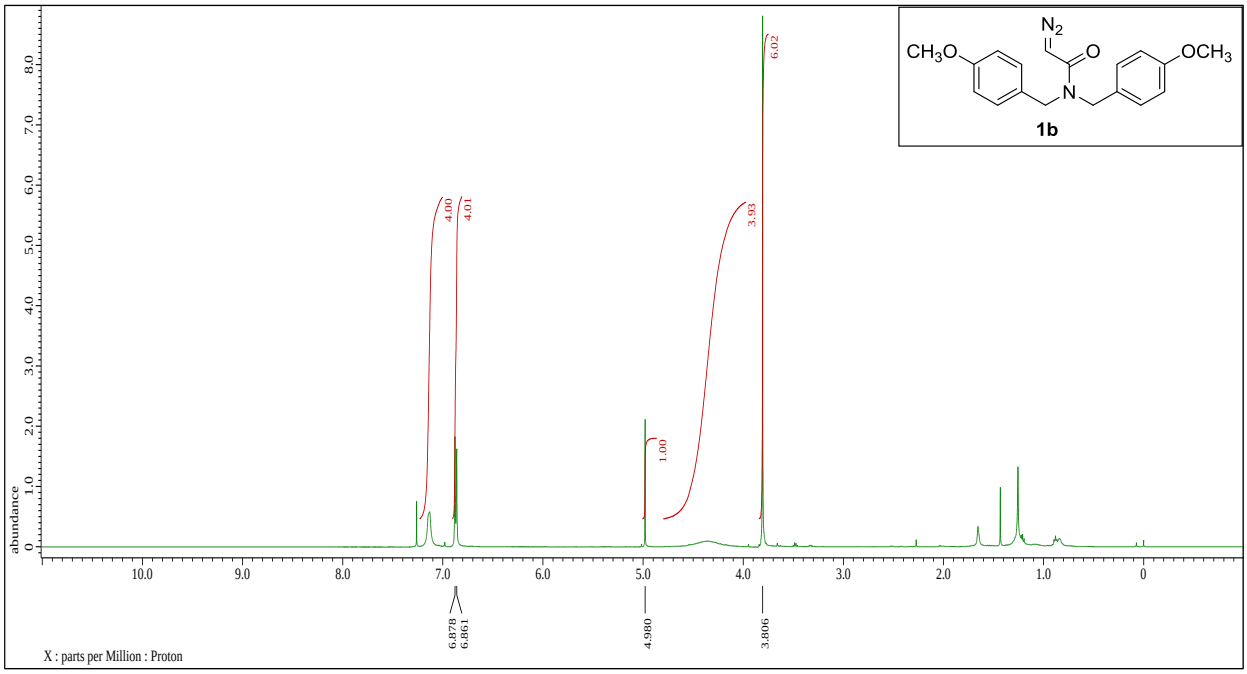
Z: 4

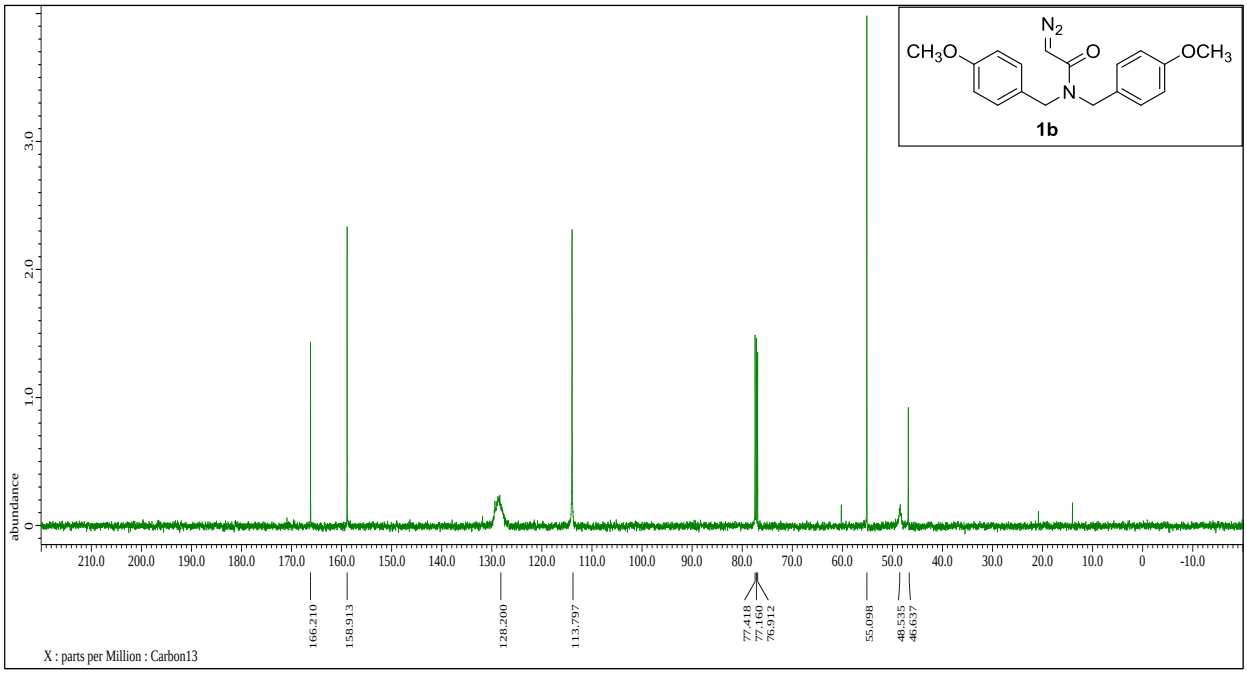
R-Factor: 2.62

7. NMR Spectral Data






N2
CH3O
O
OCH3
N
1b
6.02
4.00
4.01
3.93
1.00
abundance
6.878
6.861
4.980
3.806
X : parts per Million : Proton


N2
CH3O
O
OCH3
N
1b
abundance
166.210
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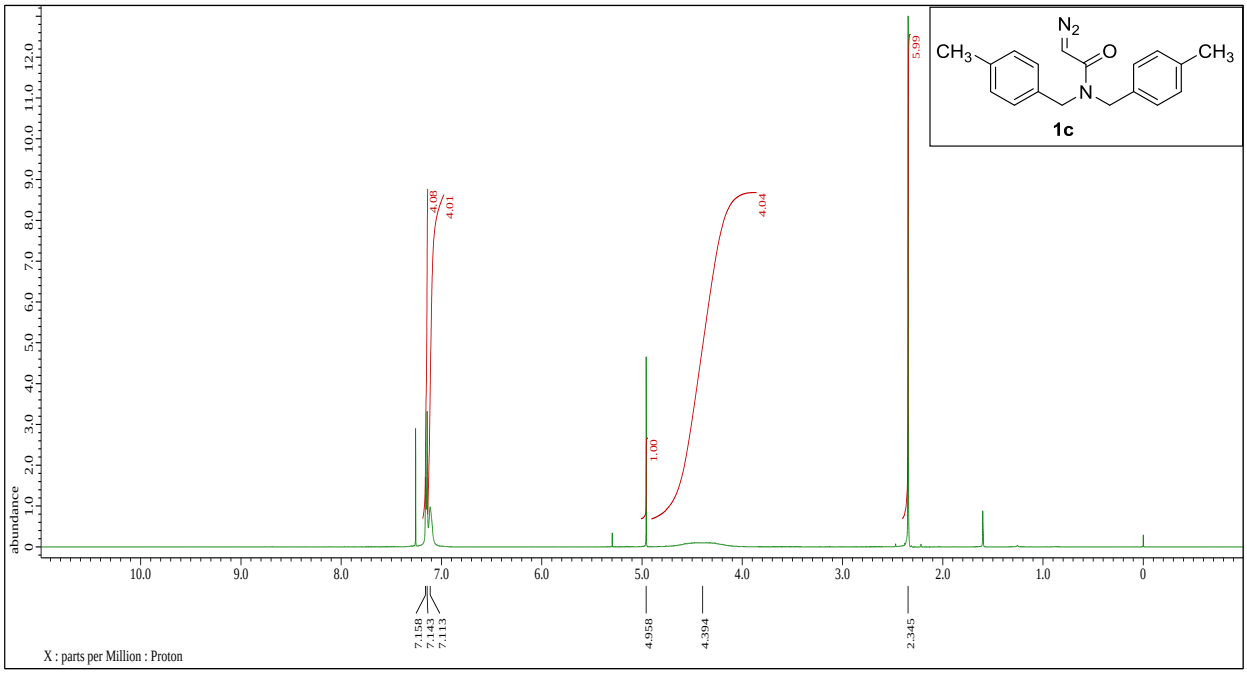
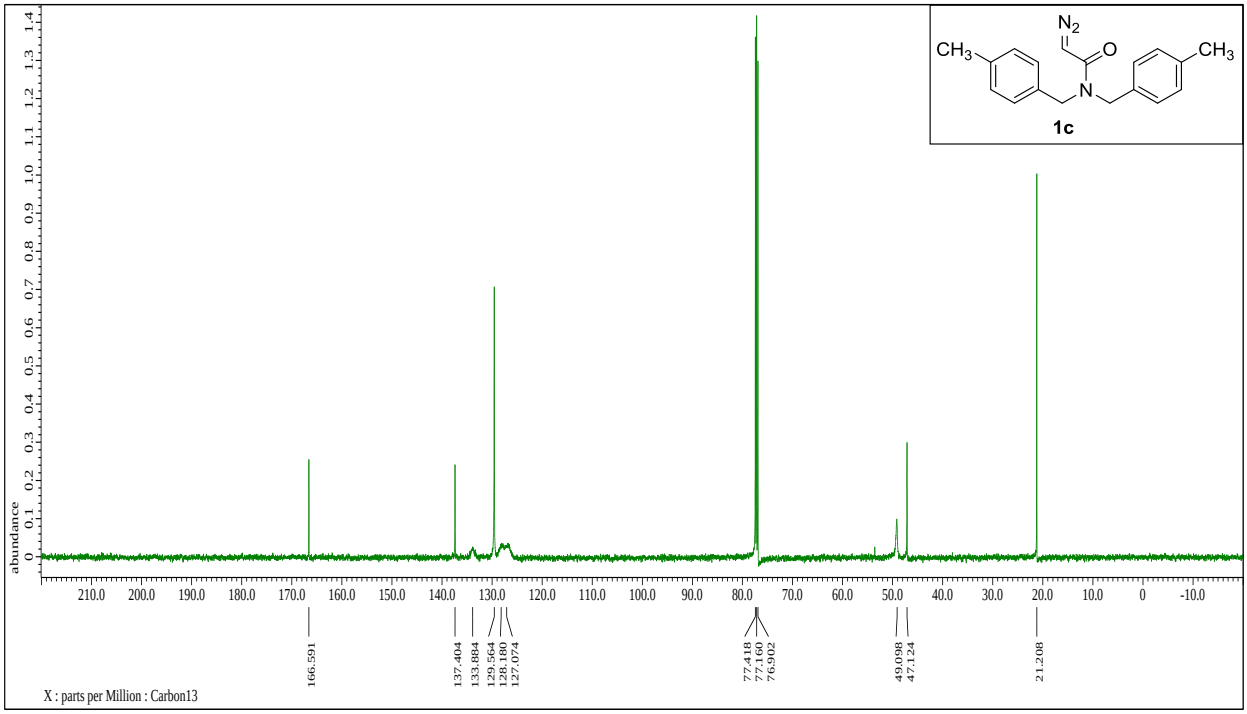
128.200
113.797
77.418
77.160
76.912
55.098
48.535
46.637
X : parts per Million : Carbon13


N2
CH3
O
N
CH3
1c
5.99
4.08
4.01
4.04
1.00
abundance
7.158
7.143
7.113
4.958
4.394
2.345
X : parts per Million : Proton


N2
CH3
O
N
CH3
1c
abundance
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137.404
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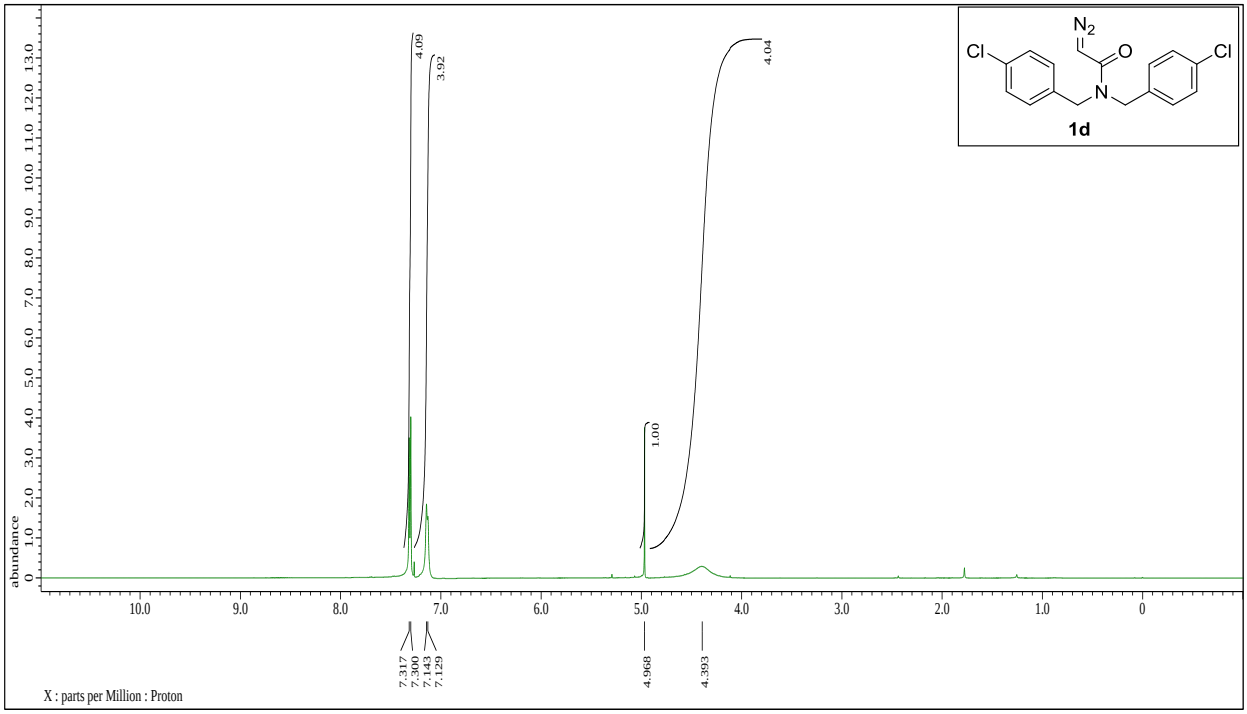
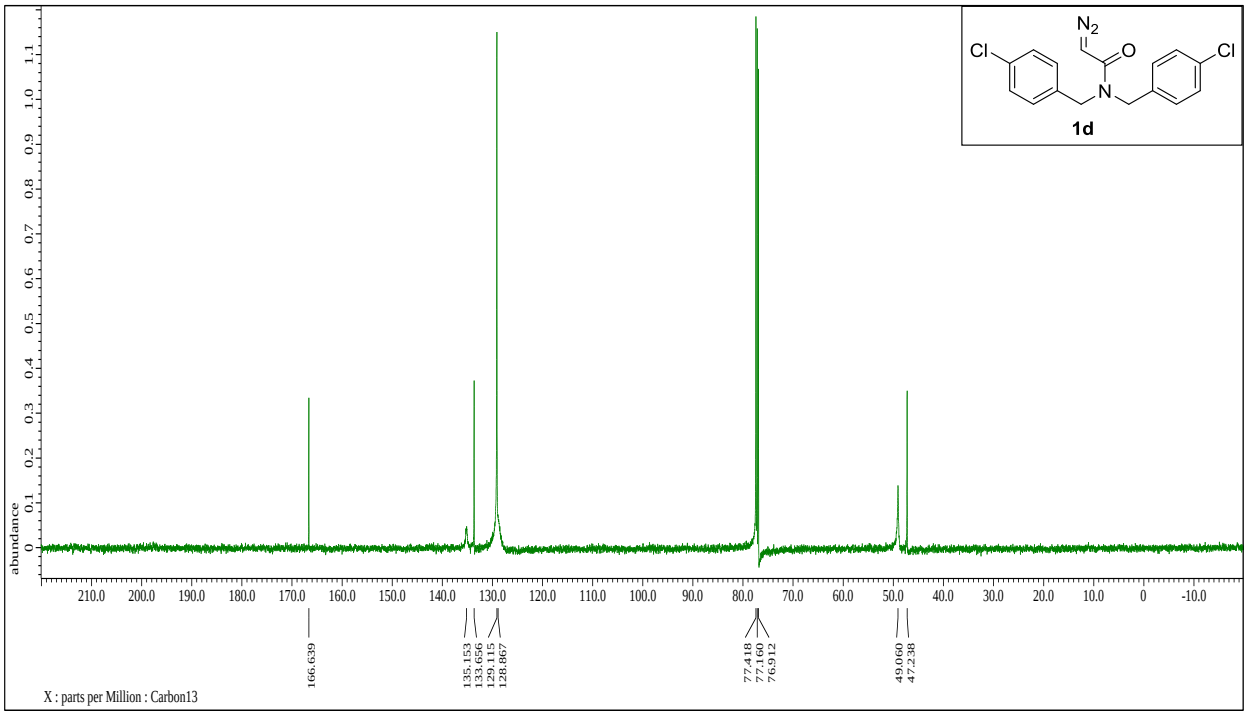
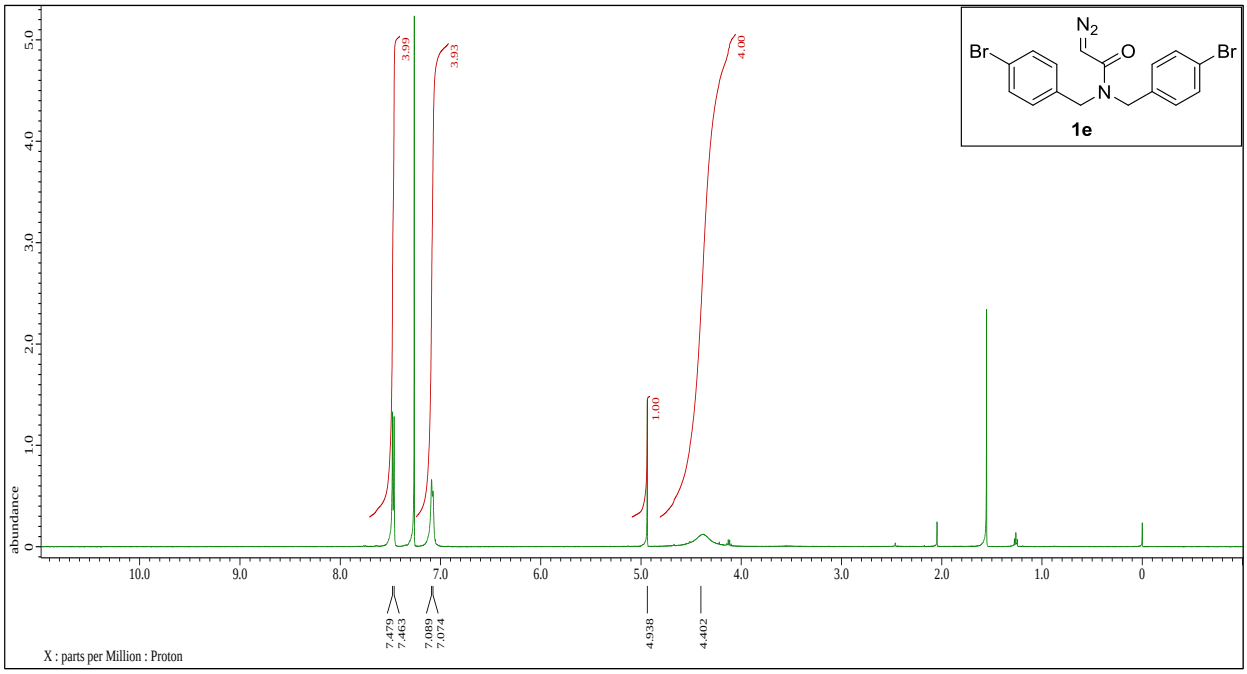
128.180
127.074
77.418
77.160
76.902
49.098
47.124
21.208
X : parts per Million : Carbon13


4.09
3.92
4.04
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.317
7.300
7.143
7.129
4.968
4.393
X : parts per Million : Proton
N2
Cl
O
Cl
N
1d


abundance
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
166.639
135.153
133.656
129.115
128.867
77.418
77.160
76.912
49.060
47.238
X : parts per Million : Carbon13
N2
Cl
O
Cl
N
1d


abundance
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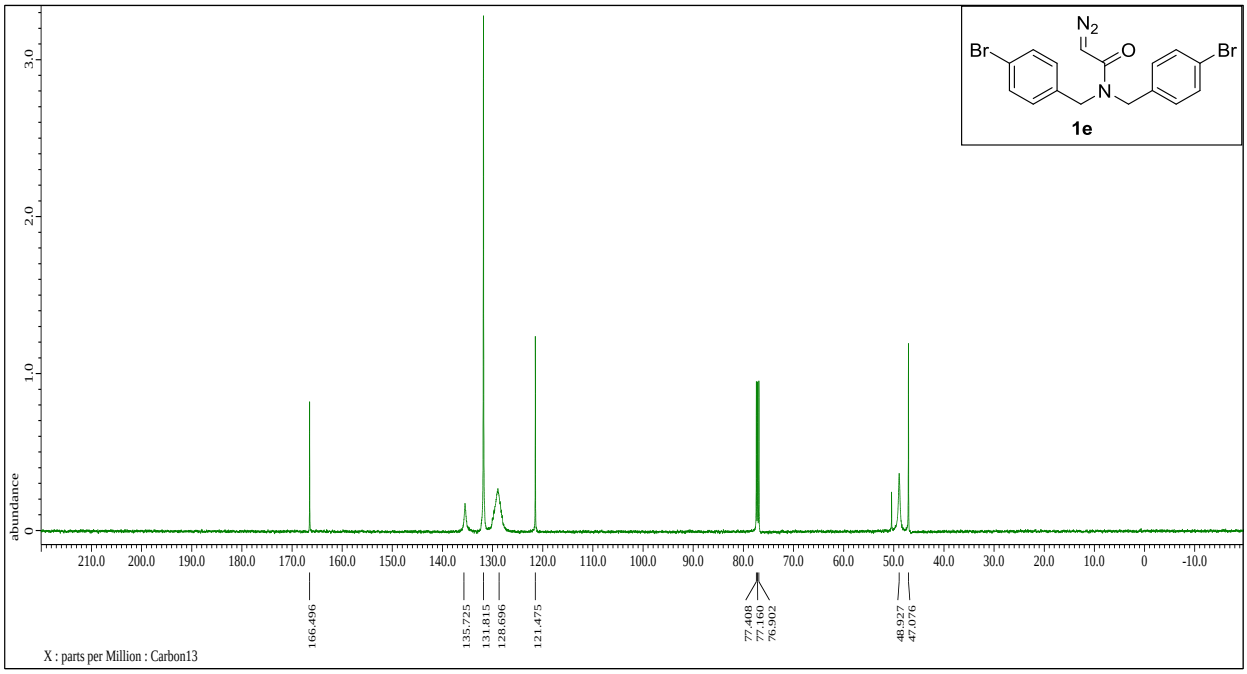
3.93
4.00
1.00
7.479
7.463
7.089
7.074
4.938
4.402
X : parts per Million : Proton
1e


abundance
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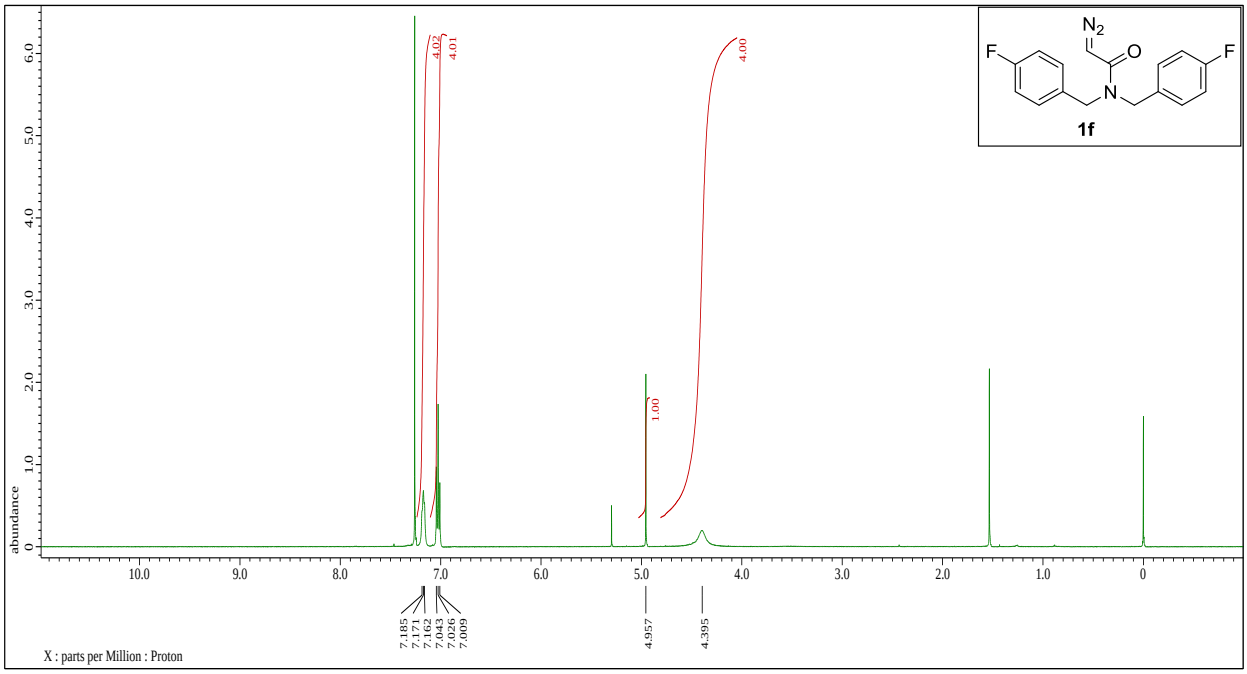
121.475
77.408
77.160
76.902
48.927
47.076
X : parts per Million : Carbon13
1e


1f
abundance
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4.01
4.00
1.00
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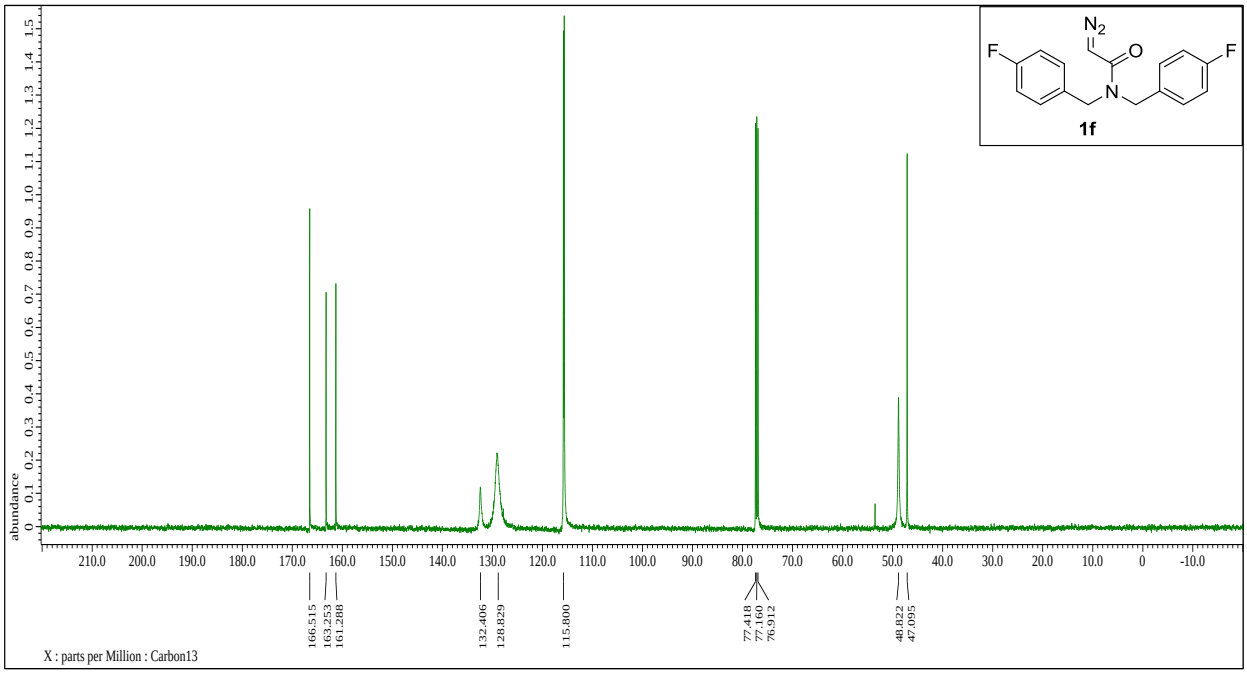
7.171
7.162
7.043
7.026
7.009
4.957
4.395
X : parts per Million : Proton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abundance
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128.829
115.800
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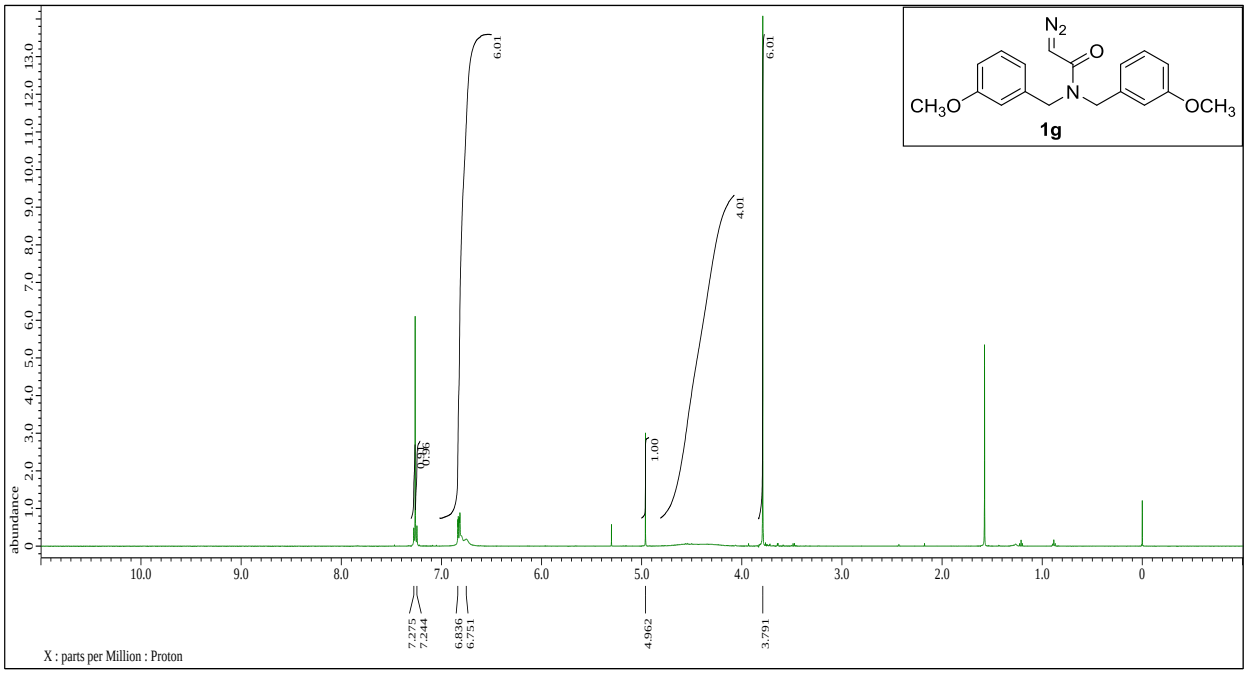
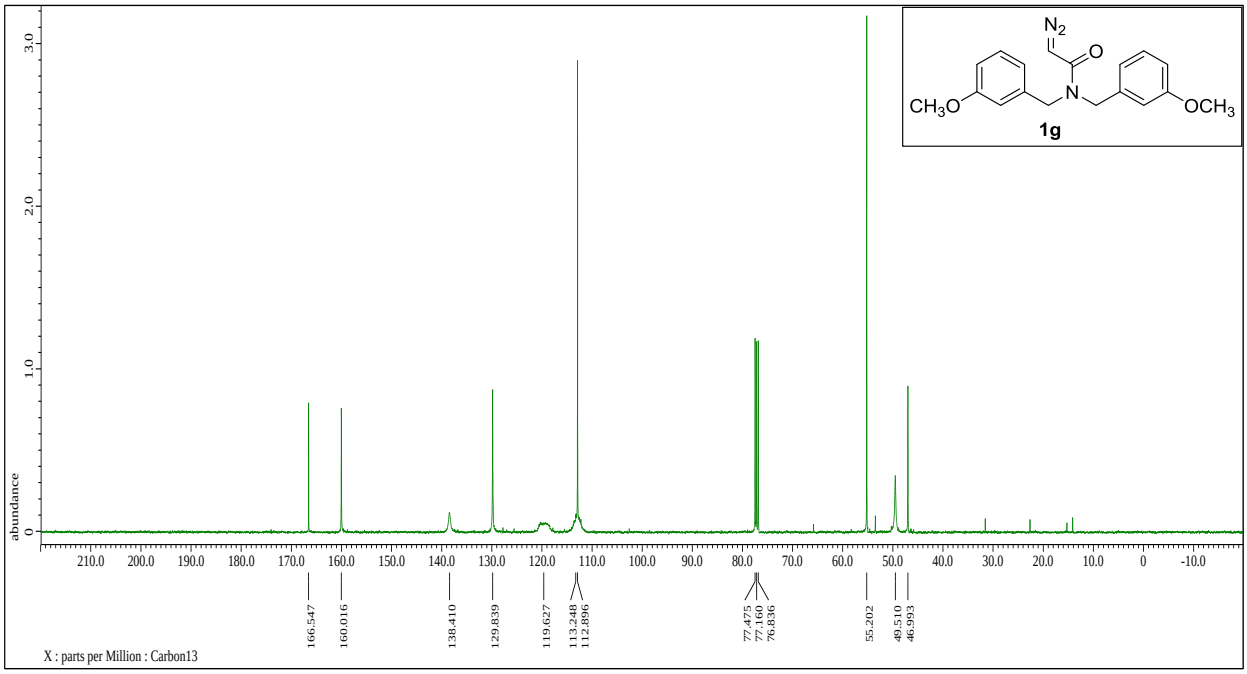
77.160
76.912
48.822
47.095
X : parts per Million : Carbon13


N2
O
N
CH3O
OCH3
1g
abundance
6.01
6.01
4.01
1.00
0.96
0.96
7.275
7.244
6.836
6.751
4.962
3.791
X : parts per Million : Proton


N2
O
N
CH3O
OCH3
1g
abundance
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112.896
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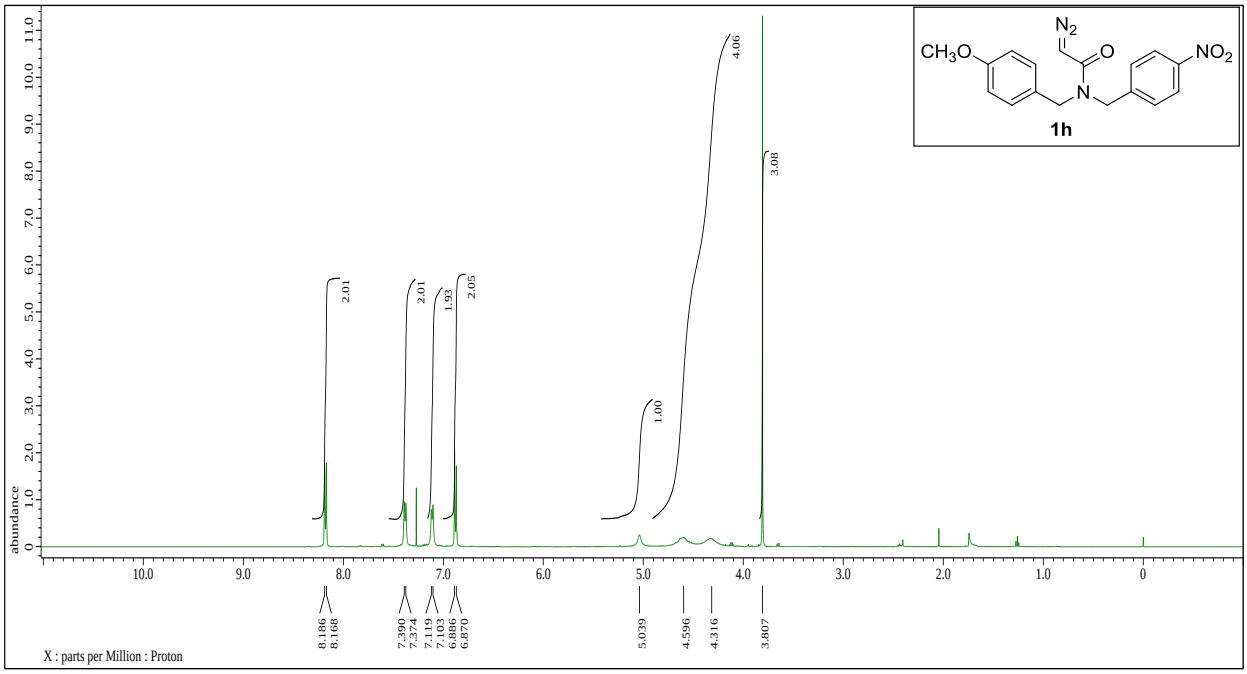
77.160
76.836
55.202
49.510
46.993
X : parts per Million : Carbon13


1h
abundance
X : parts per Million : Proton
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2.01
1.93
2.05
1.00
4.06
3.08
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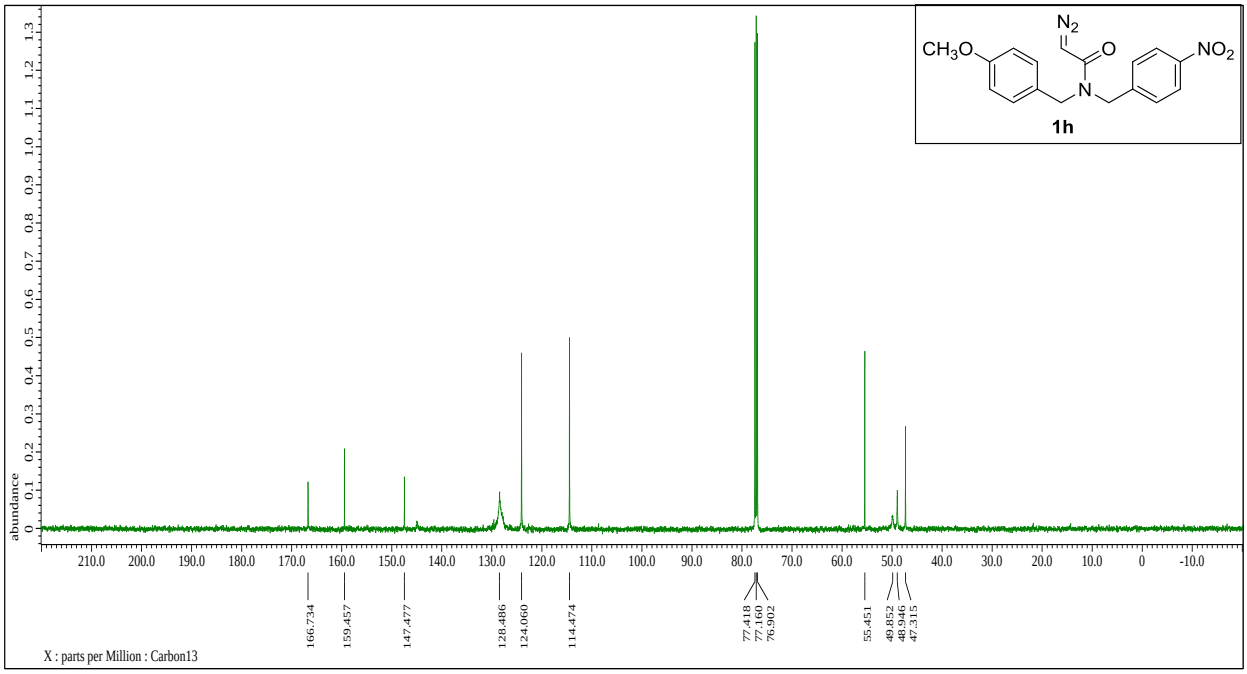
8.168
7.390
7.374
7.119
7.103
6.886
6.870
5.039
4.596
4.316
3.807


1h
abundance
X : parts per Million : Carbon13
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128.486
124.060
114.474
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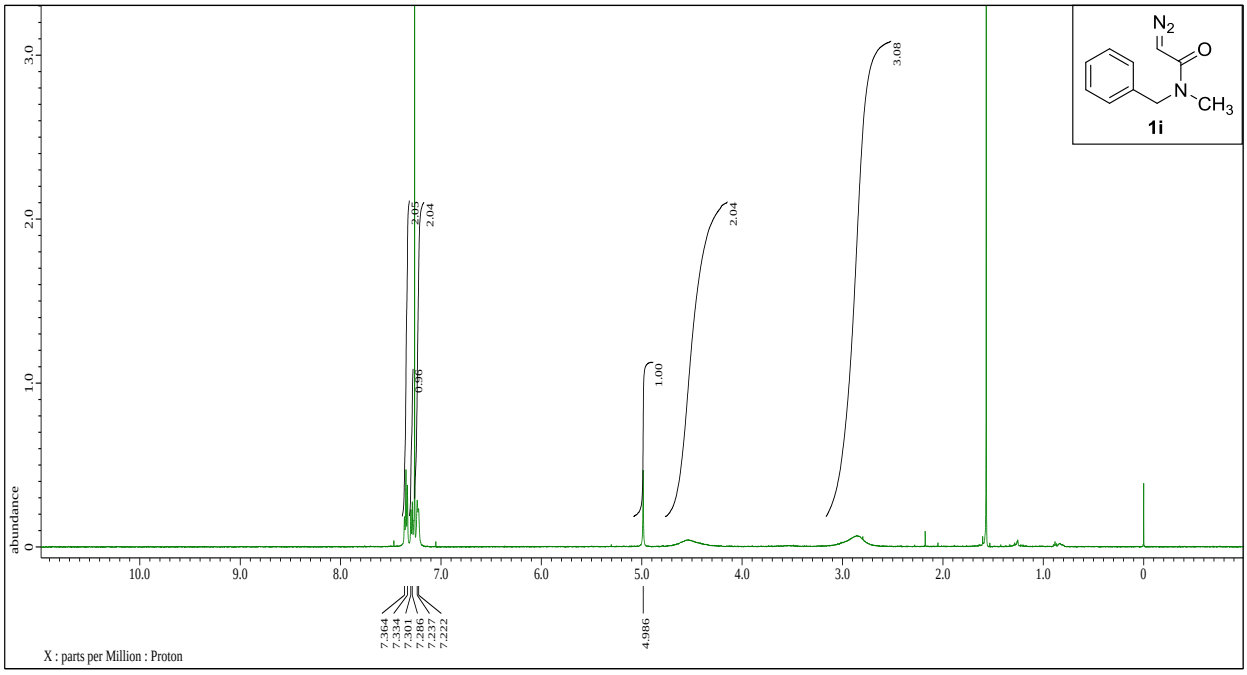
76.902
55.451
49.952
48.946
47.315


1i
abundance
X : parts per Million : Proton
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7.237
7.222
4.986
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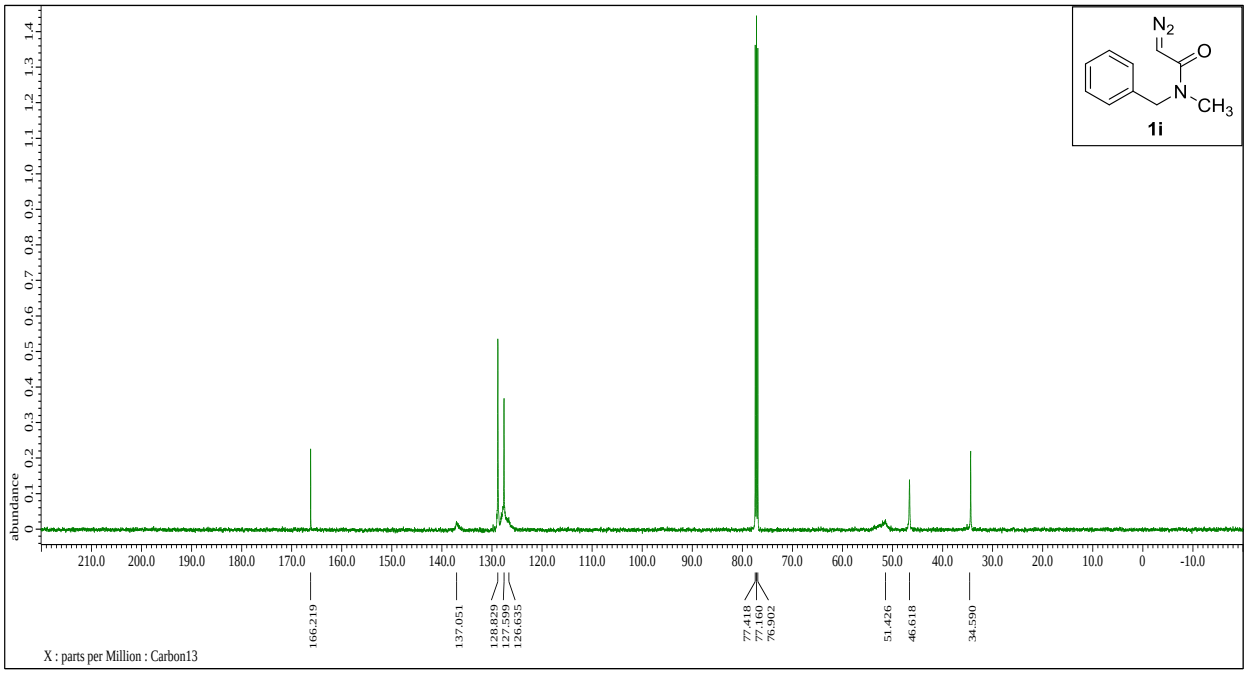
2.04
0.98
1.00
2.04
3.08


1i
abundance
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126.635
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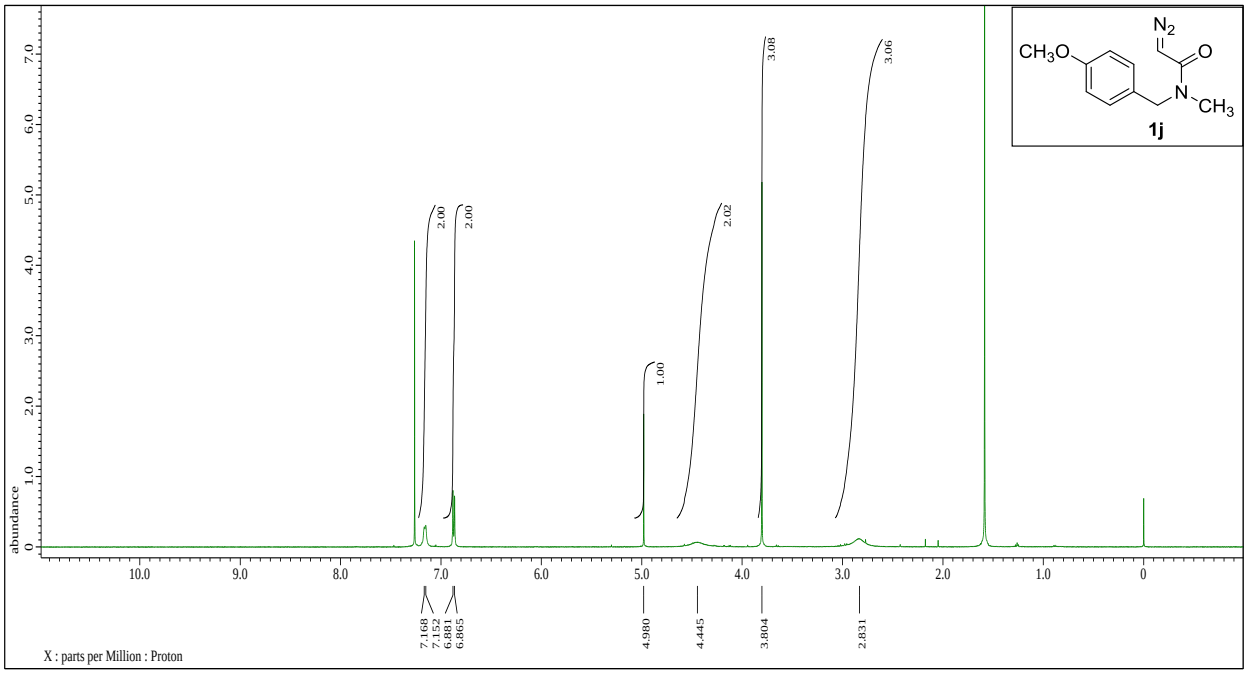
77.160
76.902
51.426
46.618
34.590


abundance
X : parts per Million : Proton
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7.152
6.881
6.865
4.980
4.445
3.804
2.831
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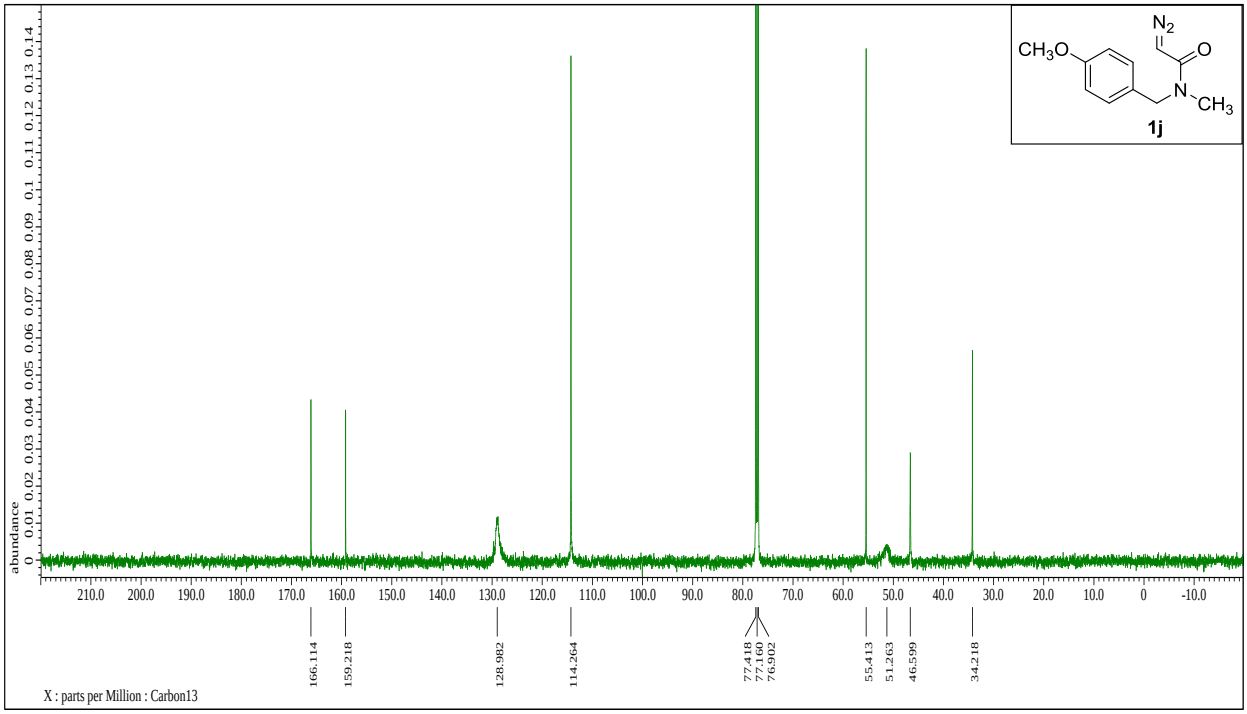
2.00
1.00
2.02
3.08
3.06
1j


abundance
X : parts per Million : Carbon13
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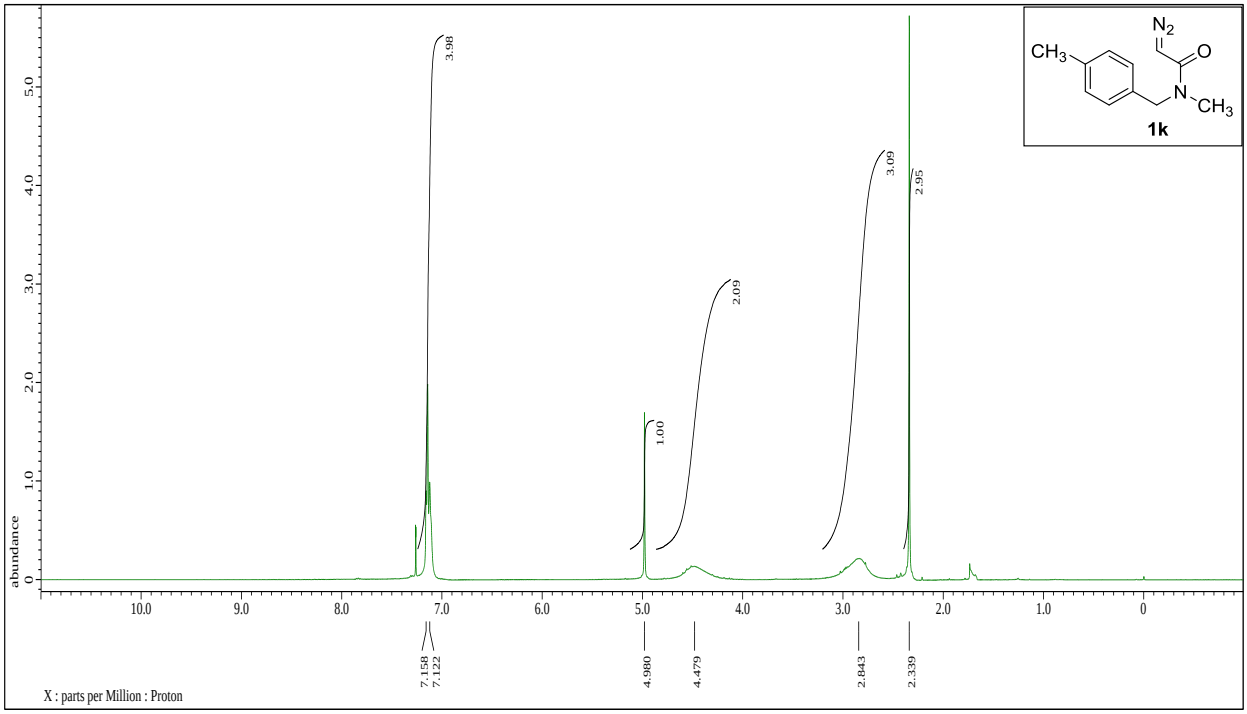
128.982
114.264
77.418
77.160
76.902
55.413
51.263
46.599
34.218
1j


abundance
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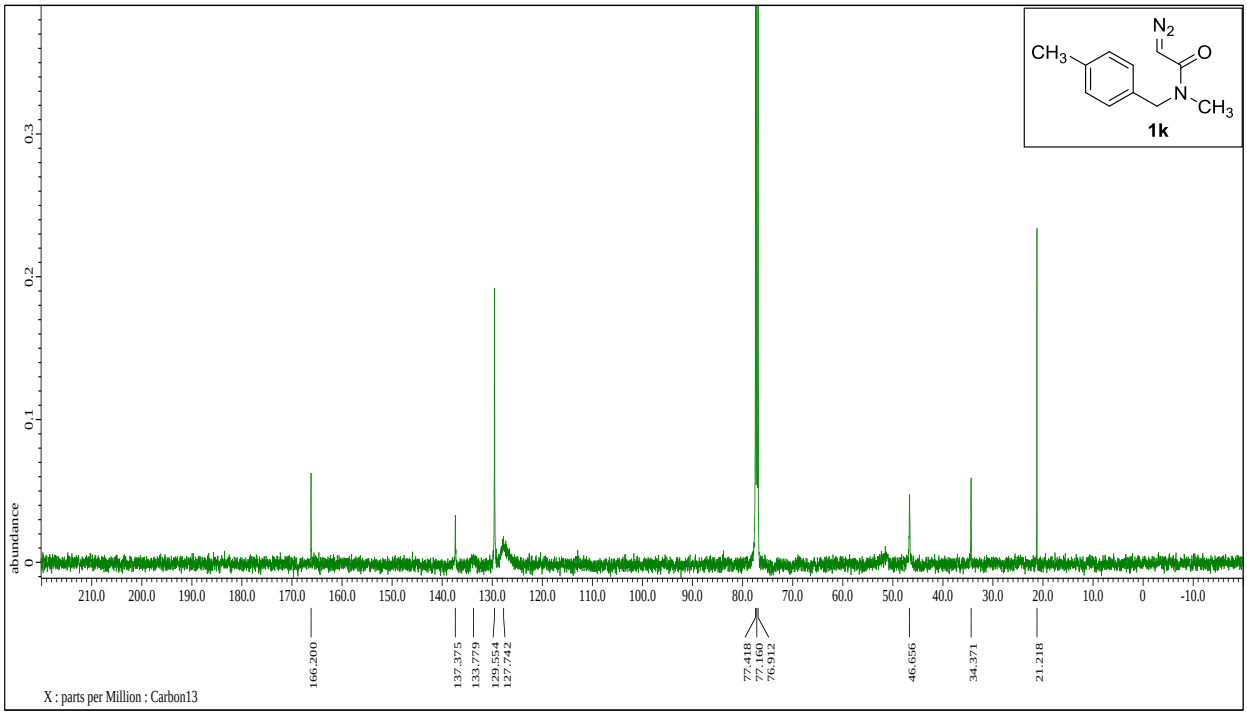
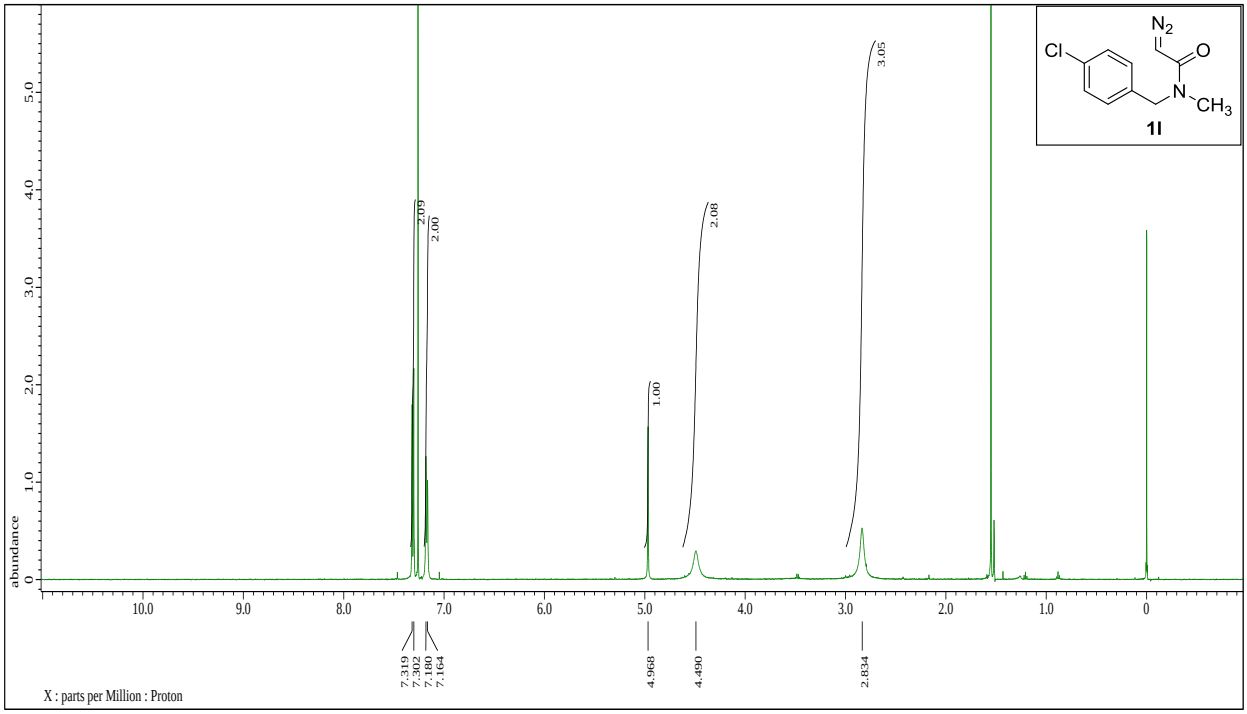
1.00
2.09
3.09
2.95
7.158
7.122
4.980
4.479
2.843
2.339
X : parts per Million : Proton
1k


abundance
166.200
137.375
133.779
129.554
127.742
77.418
77.160
76.912
46.656
34.371
21.218
X : parts per Million : Carbon13
1k


abundance
X : parts per Million : Proton
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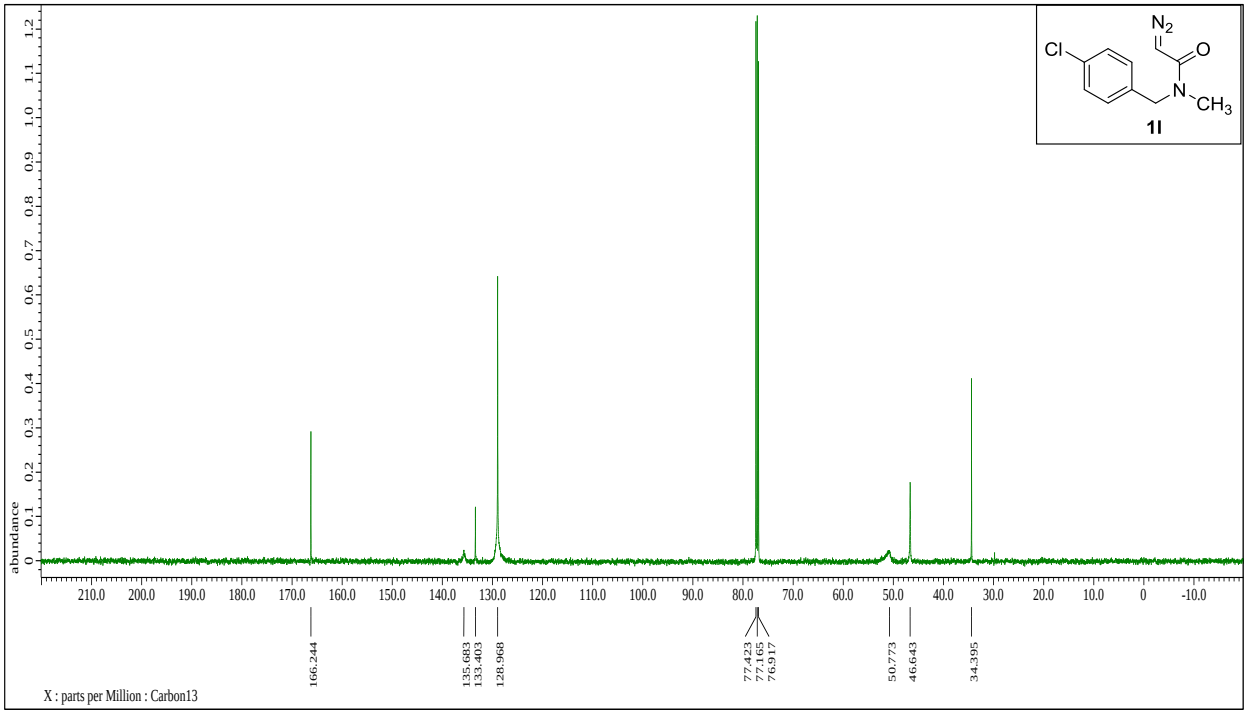
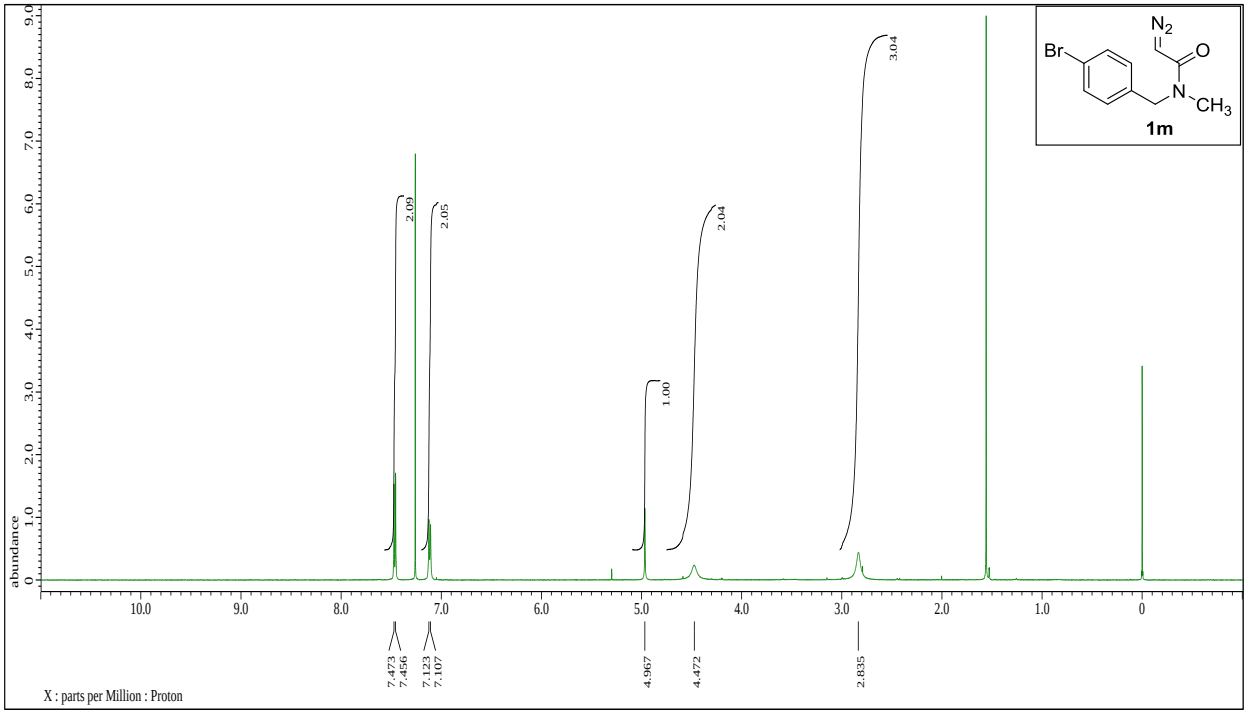
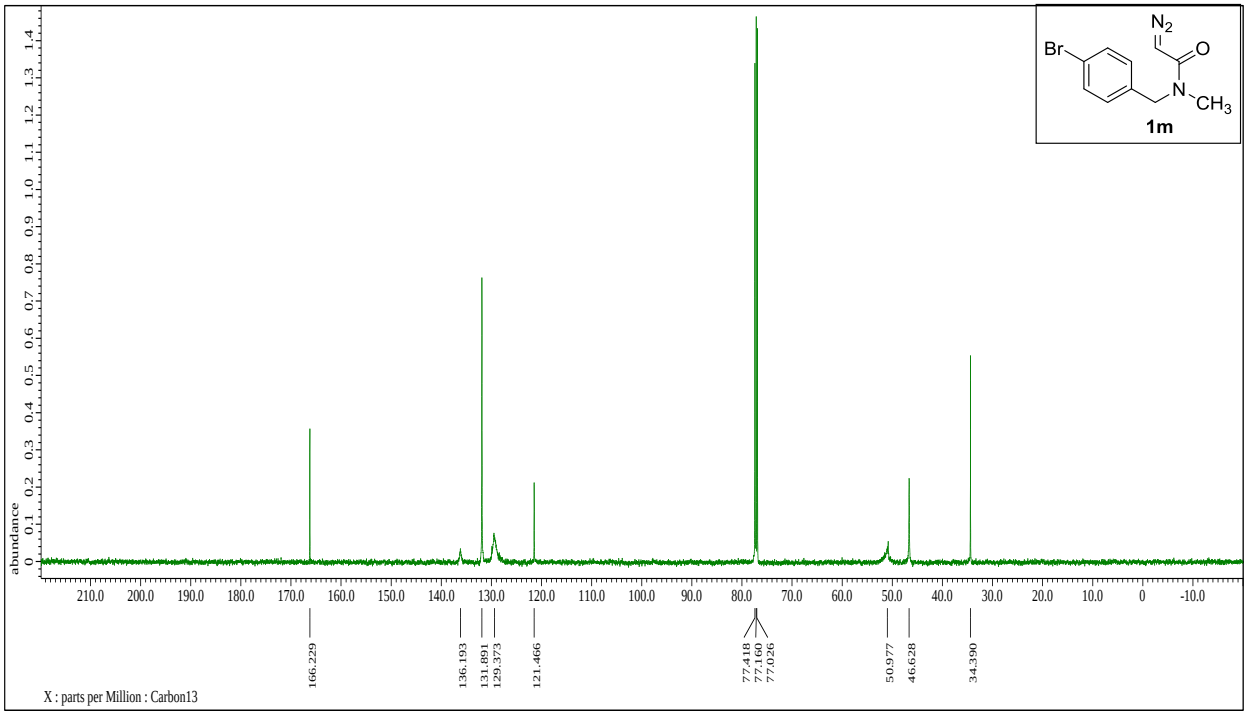
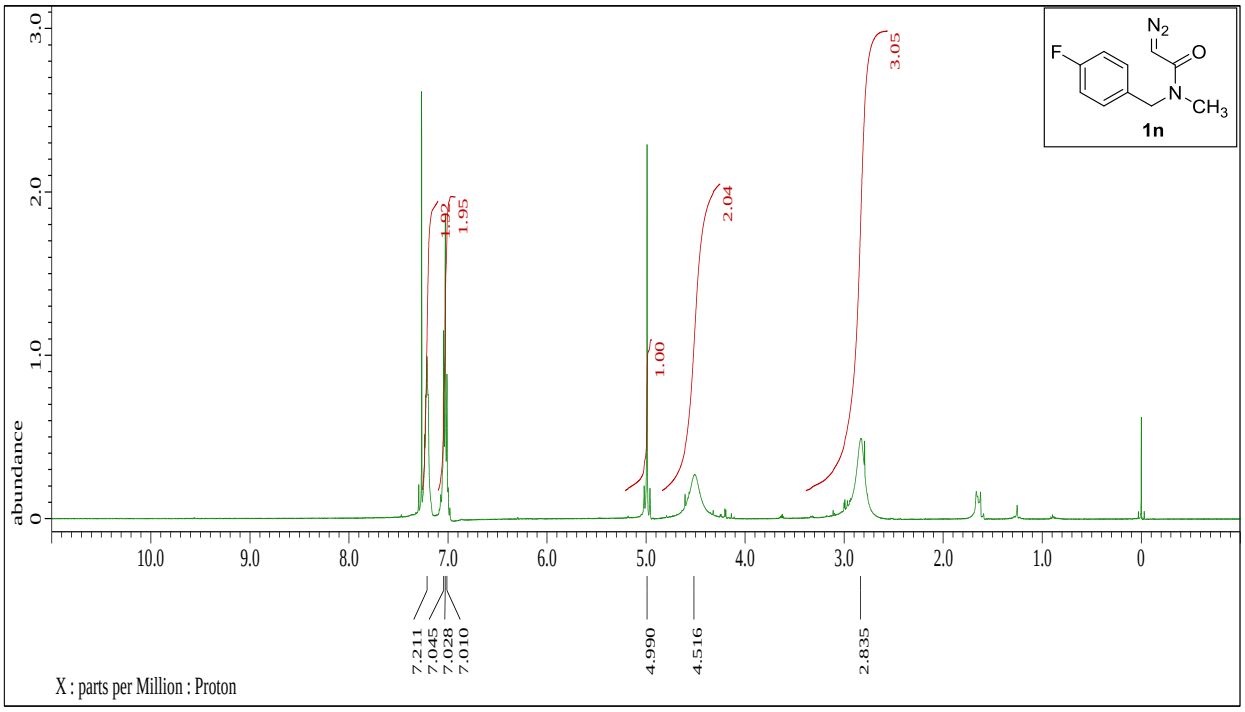
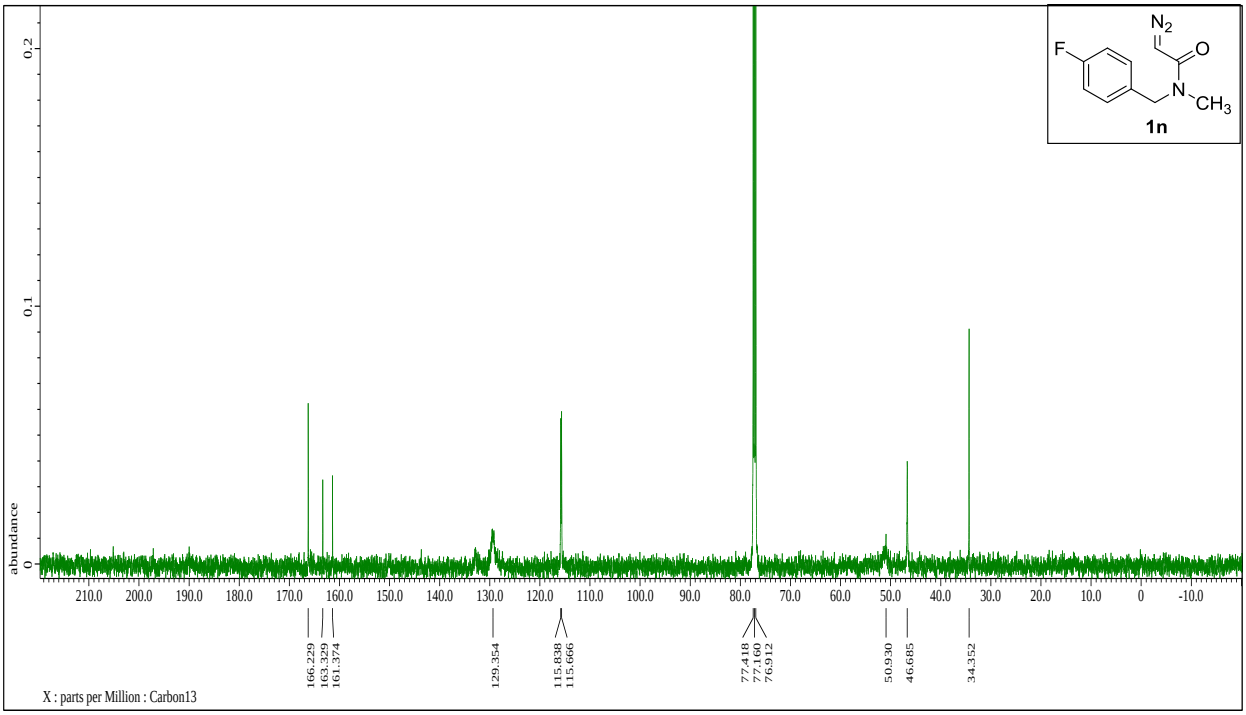
7.302
7.180
7.164
4.968
4.490
2.834
2.09
2.00
1.00
2.08
3.05
1l

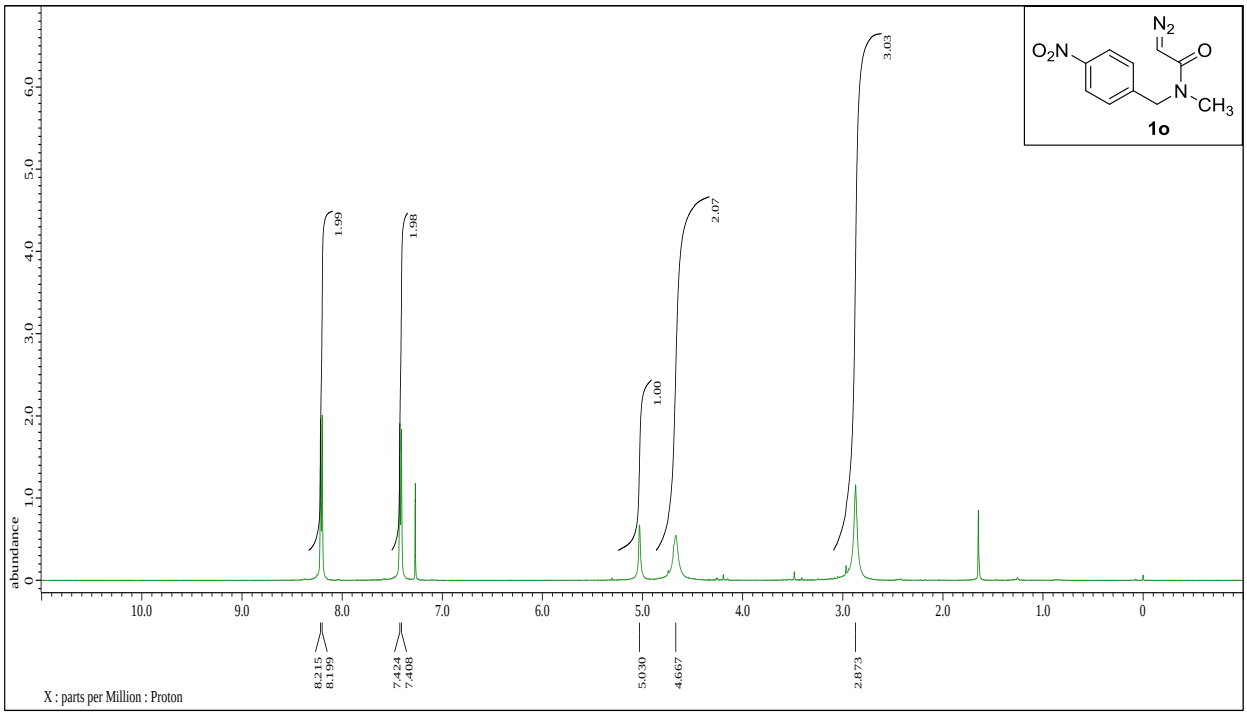

abundance
X : parts per Million : Carbon13
166.244
135.683
133.403
128.968
77.423
77.165
76.917
50.773
46.643
34.395
1l

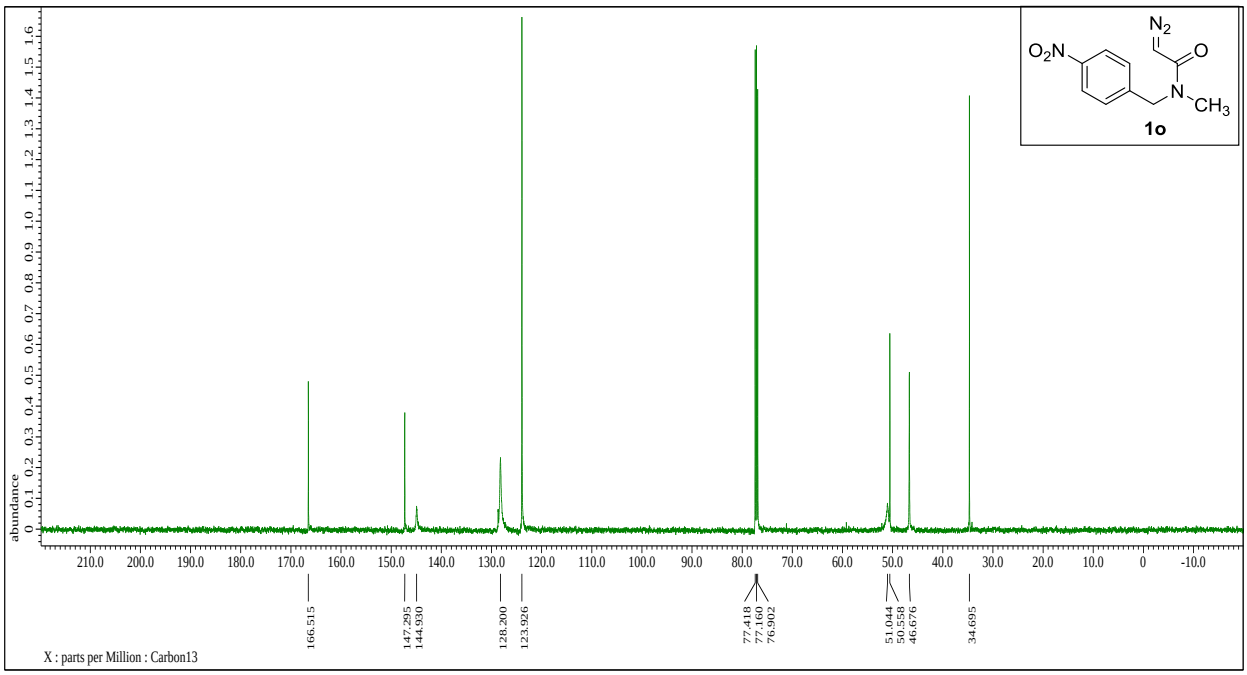

abundance
2.09
2.05
2.04
3.04
1.00
7.473
7.456
7.123
7.107
4.967
4.472
2.835
X : parts per Million : Proton
Br
N2
O
N
CH3
1m

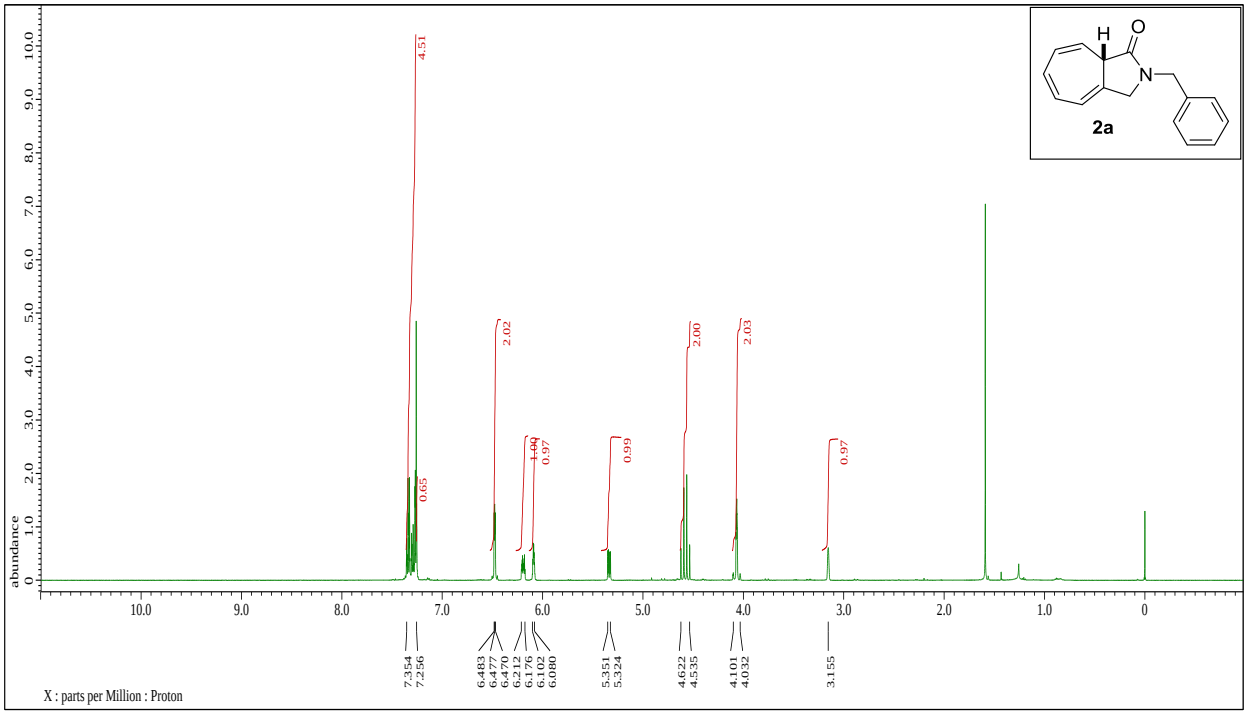

abundance
166.229
136.193
131.891
129.373
121.466
77.418
77.160
77.026
50.977
46.628
34.390
X : parts per Million : Carbon13
Br
N2
O
N
CH3
1m

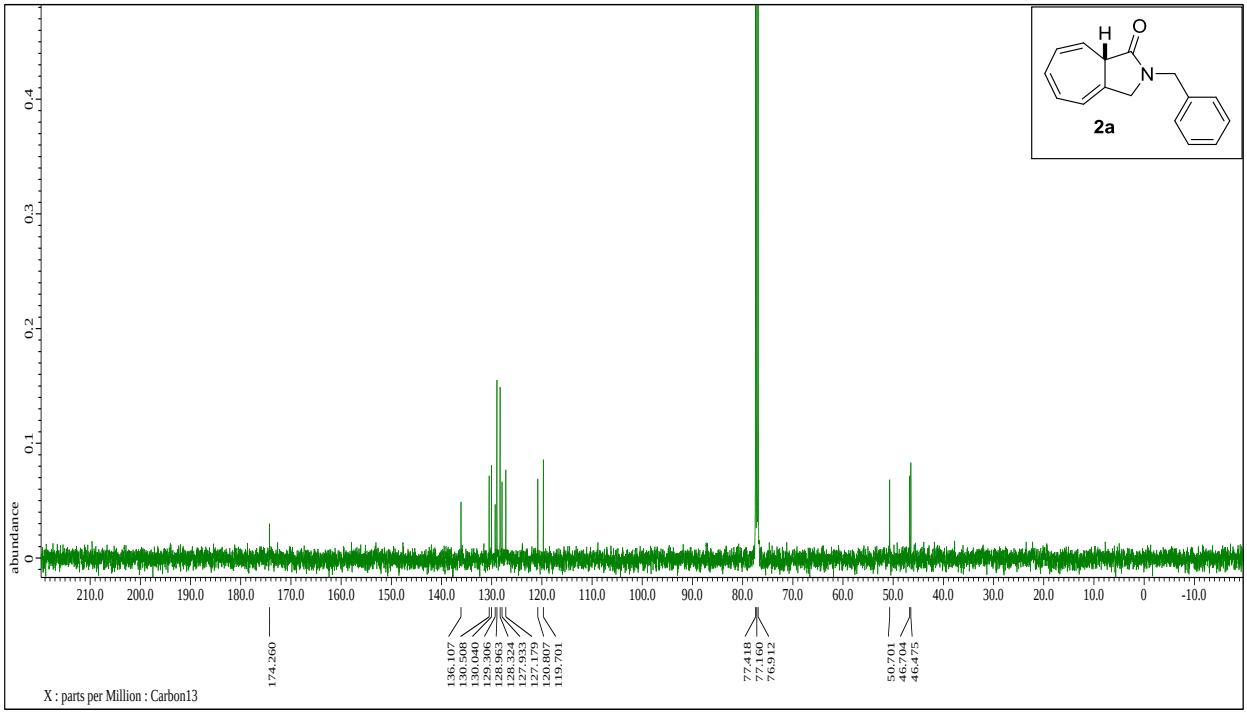

abundance
X : parts per Million : Proton
1n
7.211
7.045
7.028
7.010
4.990
4.516
2.835
1.92
1.95
1.00
2.04
3.05

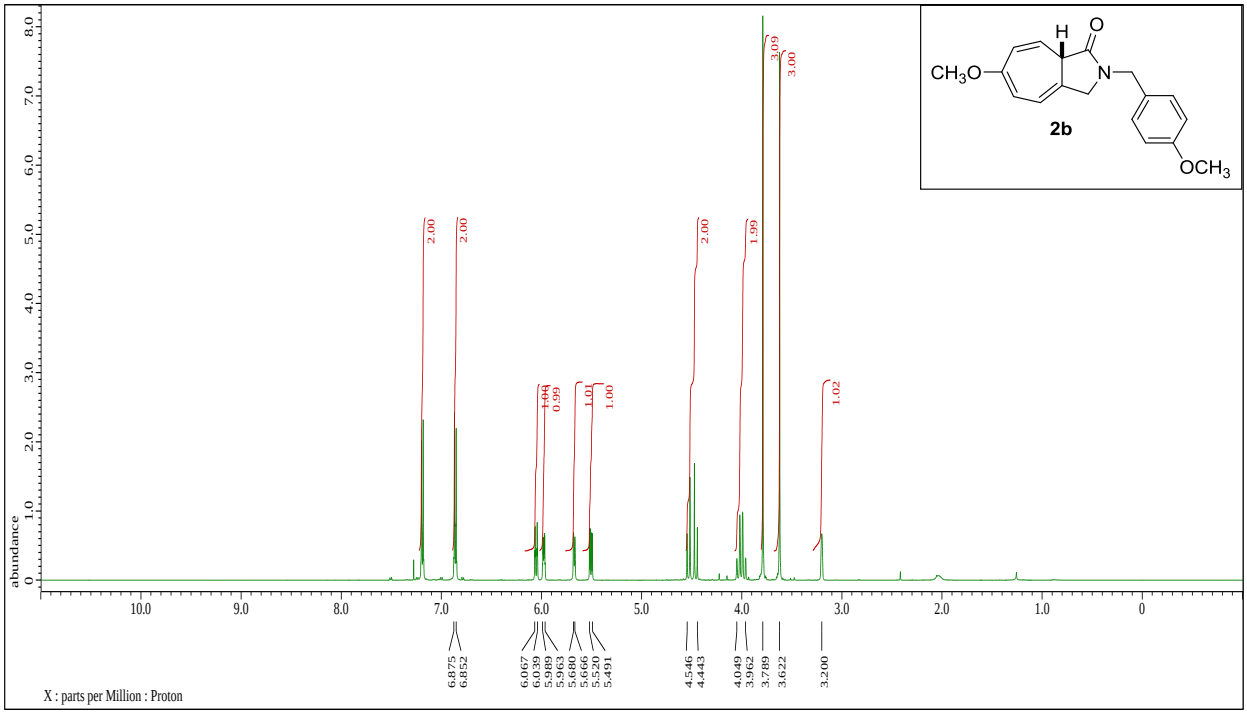

abundance
X : parts per Million : Carbon13
1n
166.229
163.329
161.374
129.354
115.838
115.666
77.418
77.160
76.912
50.930
46.685
34.352

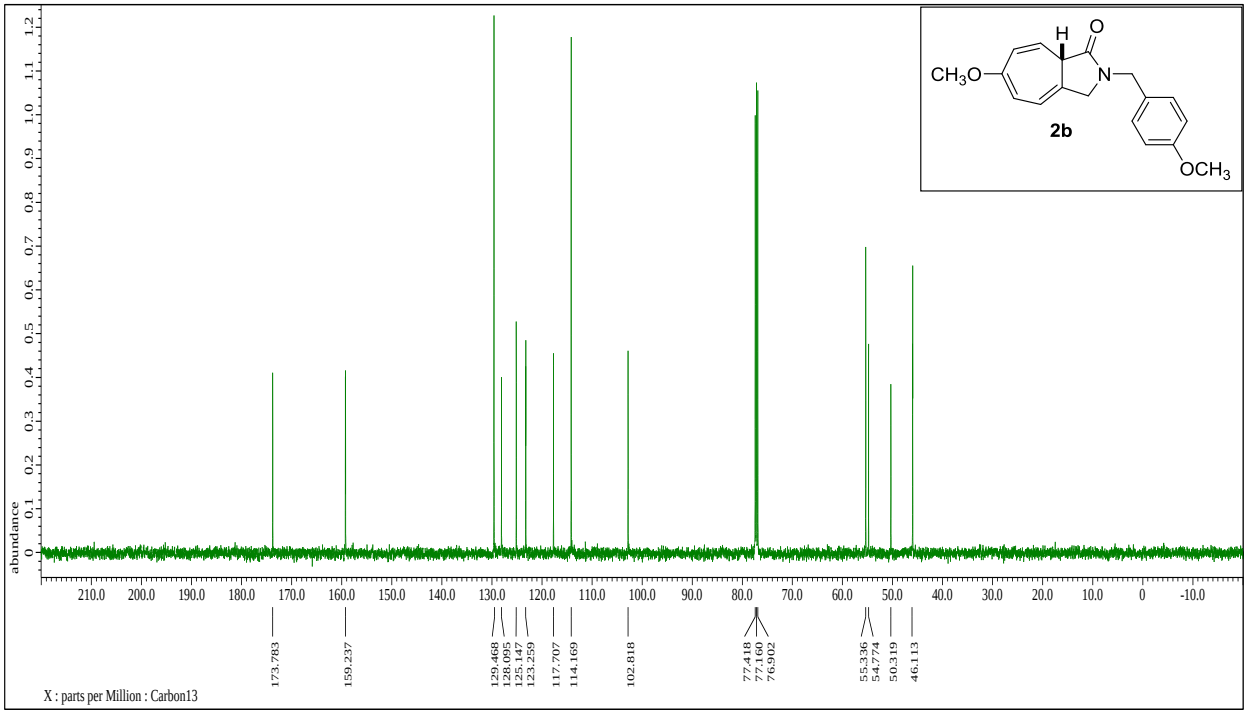

abundance
1.99
1.98
1.00
2.07
3.03
8.215
8.199
7.424
7.408
5.030
4.667
2.873
X : parts per Million : Proton
1o

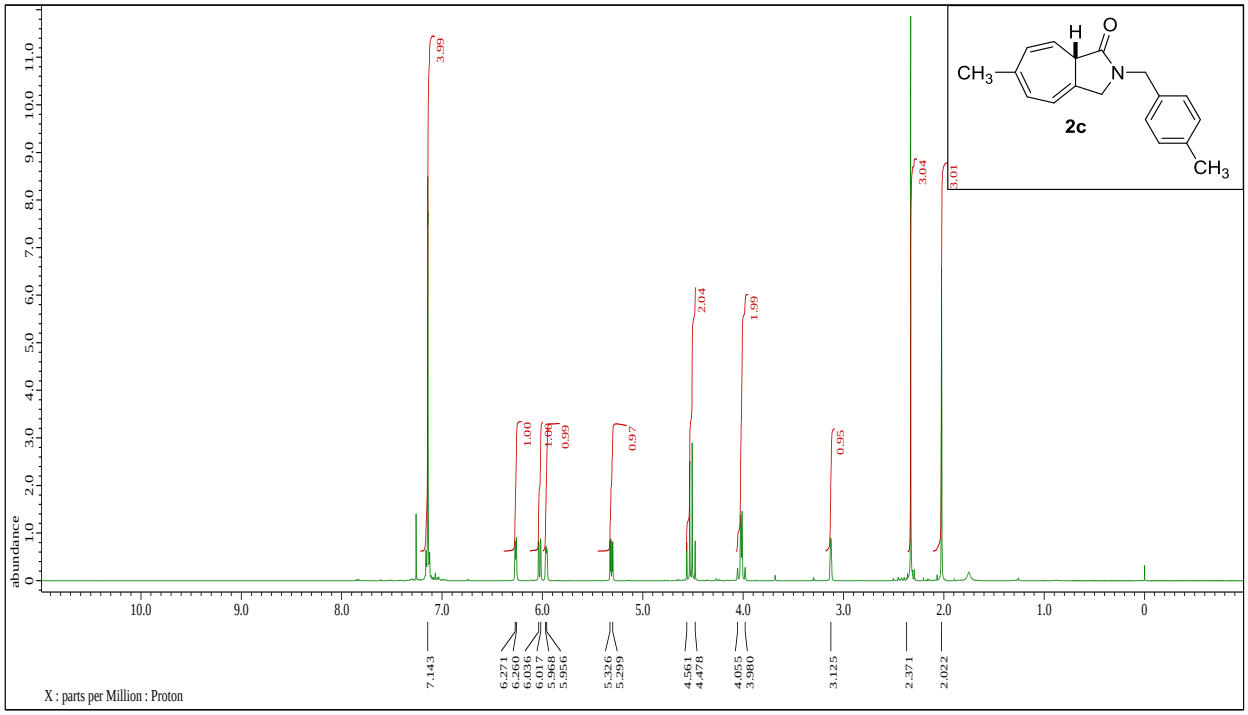

abundance
166.515
147.295
144.930
128.200
123.926
77.418
77.160
76.902
51.044
50.558
46.676
34.695
X : parts per Million : Carbon13
1o

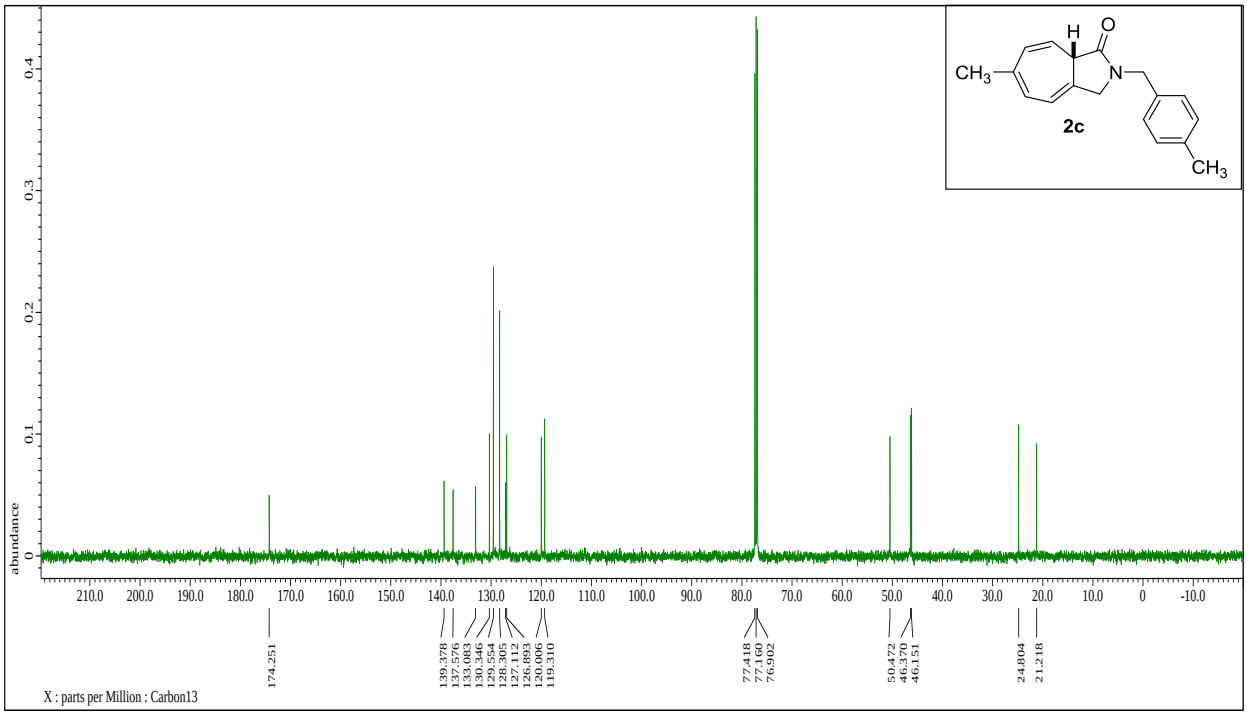

2a
abundance
4.51
2.02
2.00
2.03
0.99
0.97
0.97
0.65
7.354
7.256
6.483
6.477
6.470
6.212
6.176
6.102
6.080
5.351
5.324
4.622
4.535
4.101
4.032
3.155
X : parts per Million : Proton

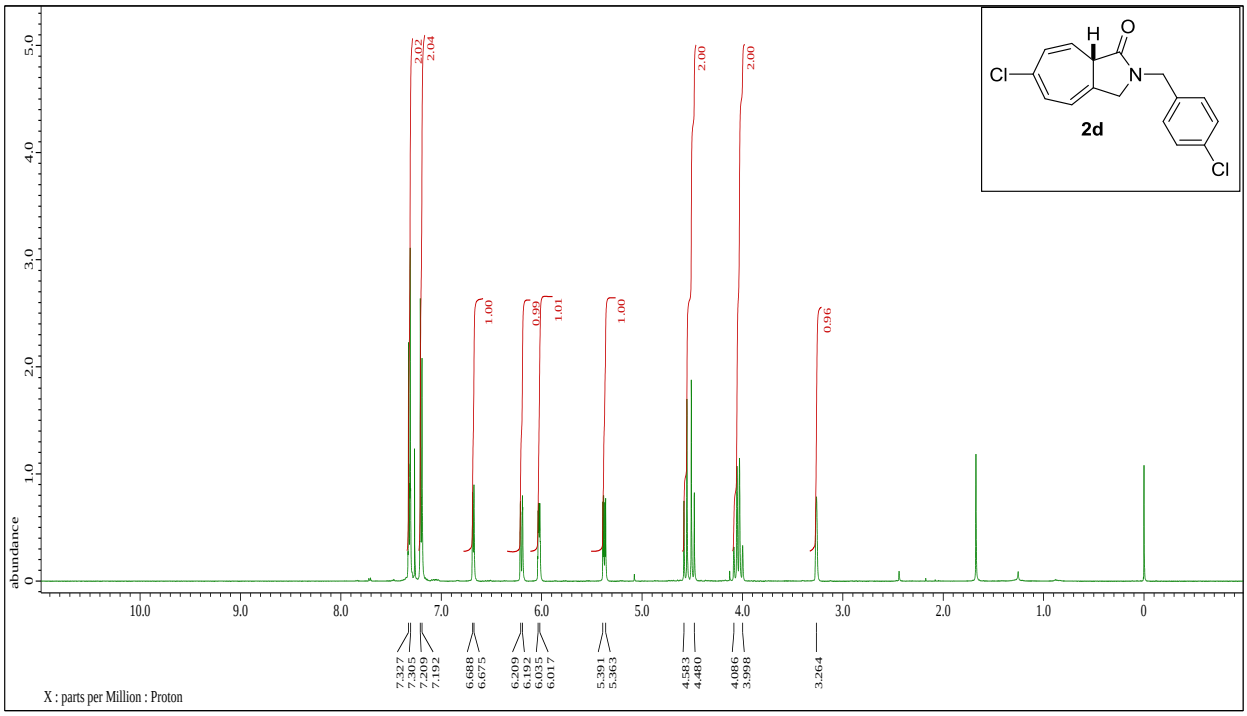

2a
abundance
174.260
136.107
130.508
130.040
129.306
128.963
128.214
127.933
127.179
120.807
119.701
77.418
77.160
76.912
50.701
46.704
46.475
X : parts per Million : Carbon13

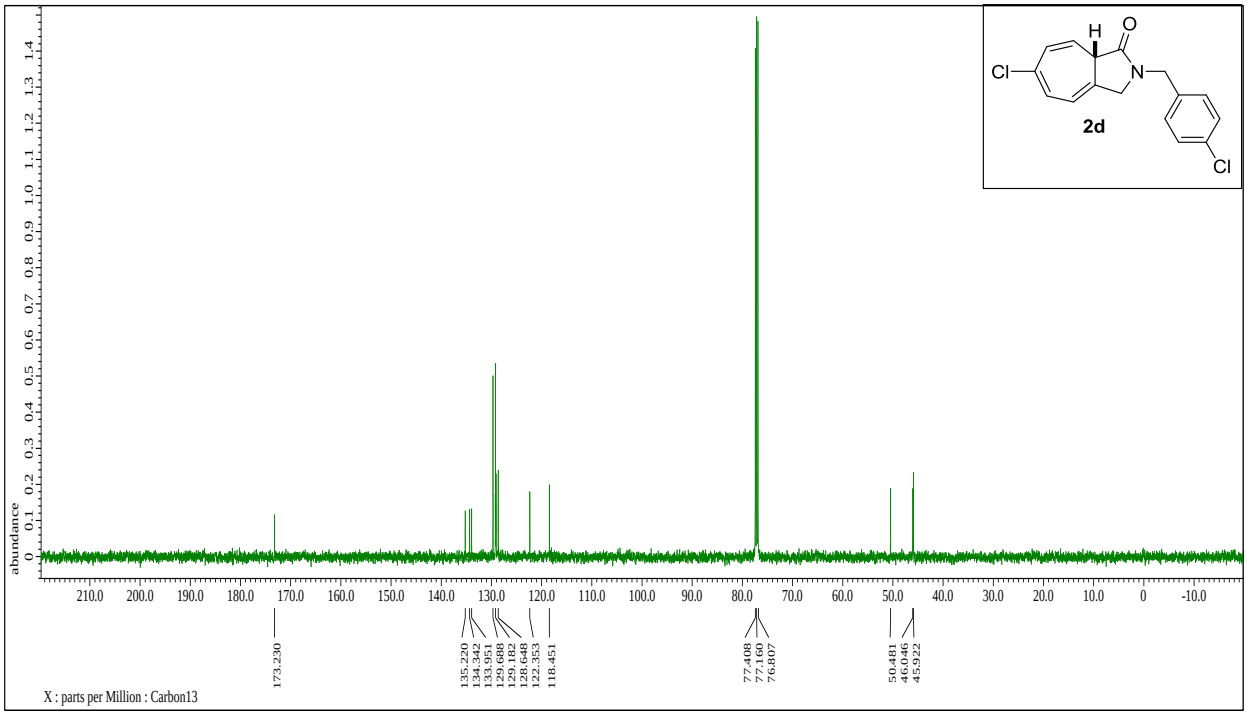

abundance
X : parts per Million : Proton
2b
CH3O
OCH3
6.875
6.852
6.067
6.039
5.989
5.963
5.680
5.666
5.520
5.491
4.546
4.443
4.049
3.962
3.789
3.622
3.200

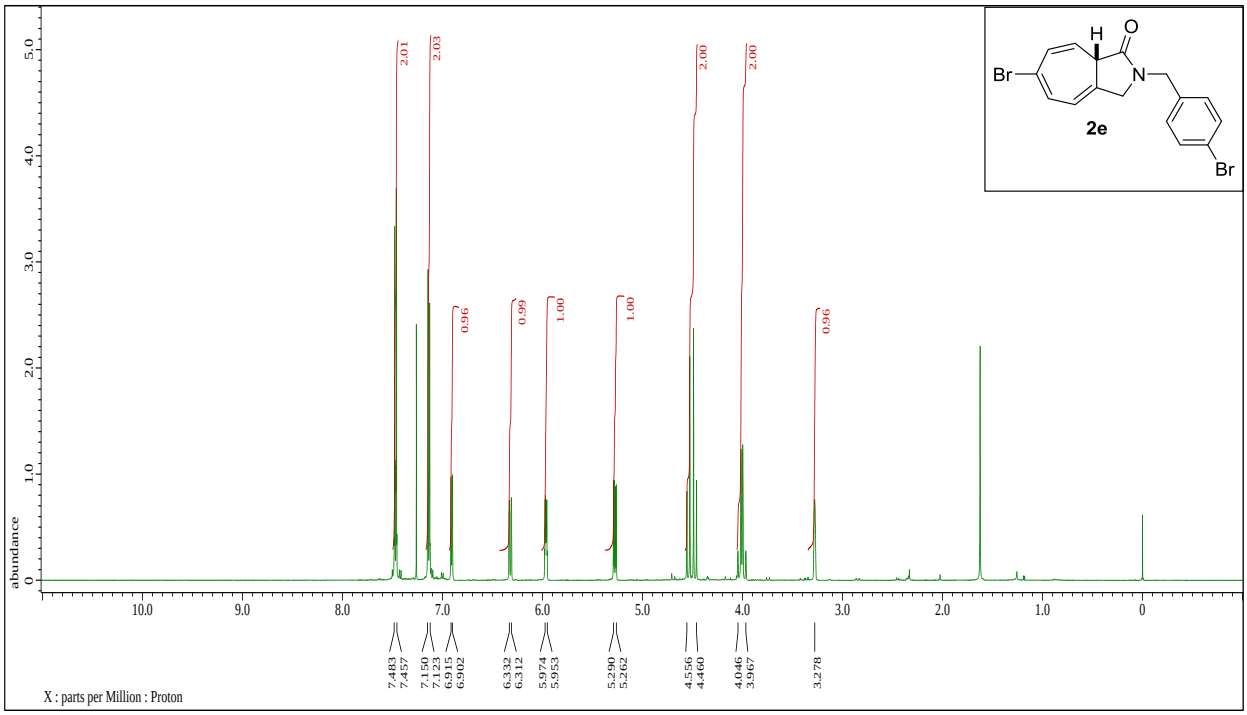

abundance
X : parts per Million : Carbon13
2b
CH3O
OCH3
173.783
159.237
129.468
128.095
125.147
123.259
117.707
114.169
102.818
77.418
77.160
76.902
55.336
54.774
50.319
46.113

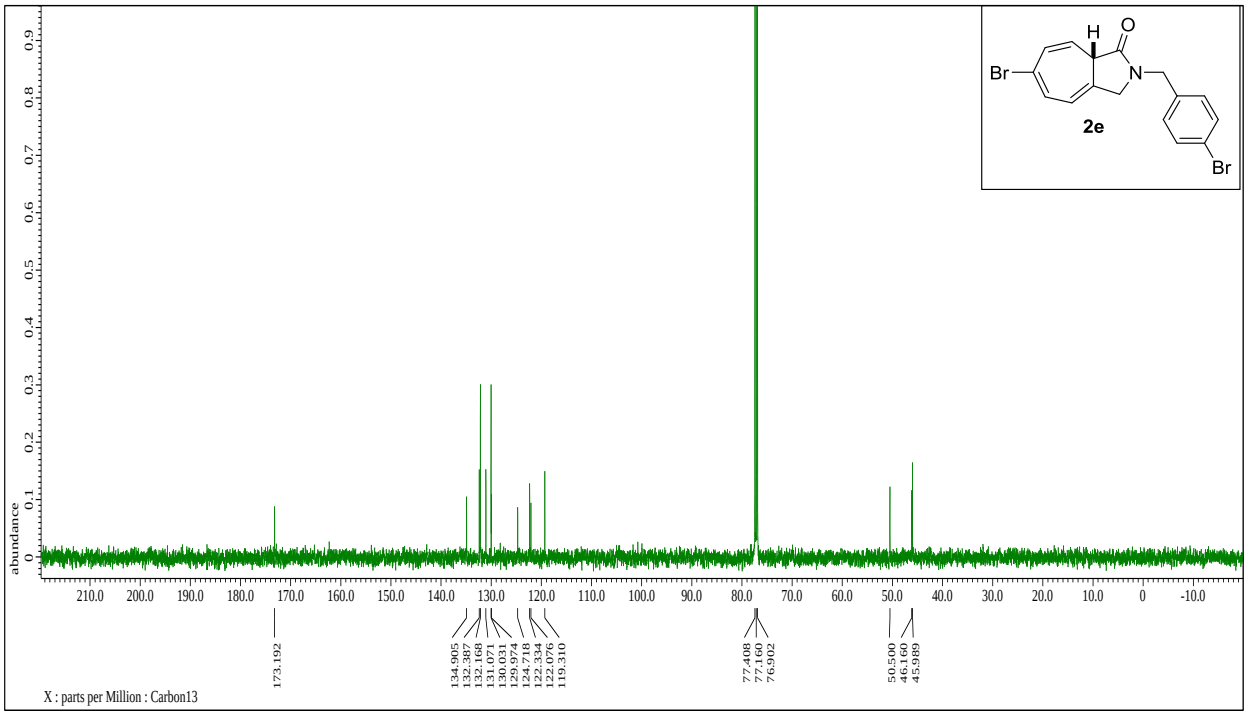

abundance
3.99
1.00
1.06
0.99
0.97
2.04
1.99
0.95
3.04
3.01
7.143
6.271
6.260
6.035
6.017
5.968
5.956
5.326
5.299
4.561
4.478
4.055
3.980
3.125
2.371
2.022
X : parts per Million : Proton
2c

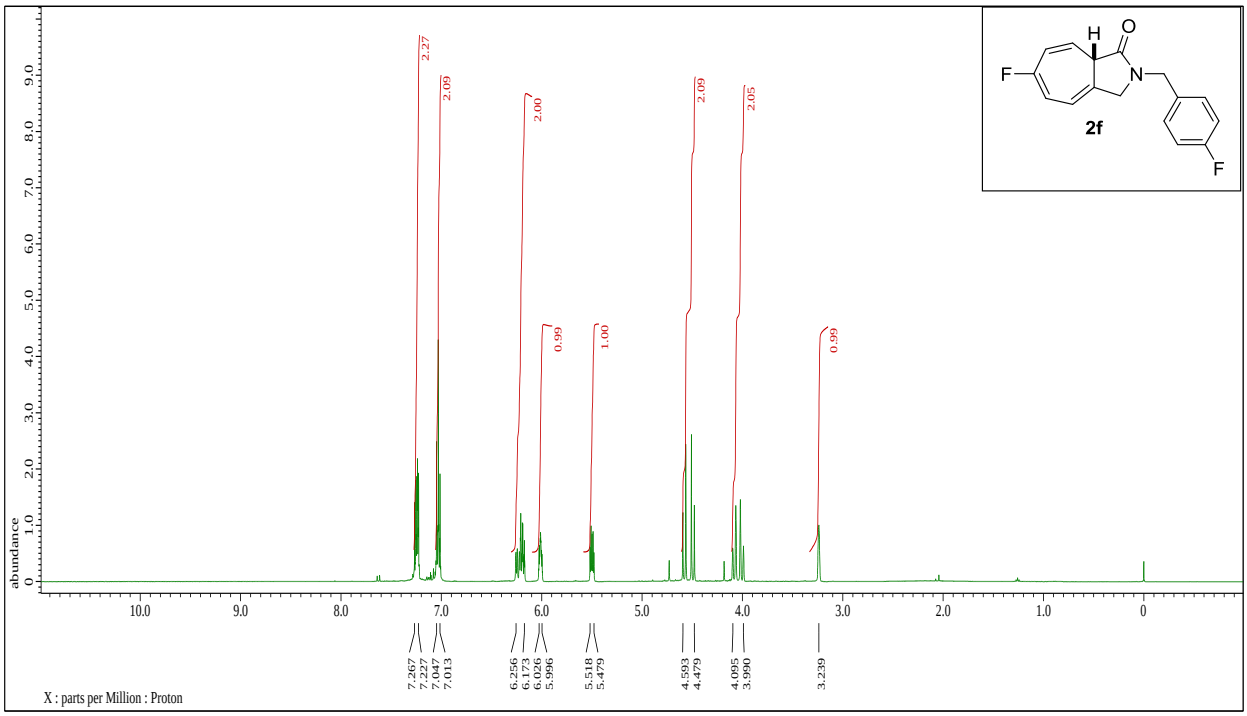

abundance
174.251
139.378
137.756
133.093
130.346
129.554
128.305
127.112
126.893
120.006
119.310
77.418
77.160
76.902
50.472
46.670
46.151
24.804
21.218
X : parts per Million : Carbon13
2c

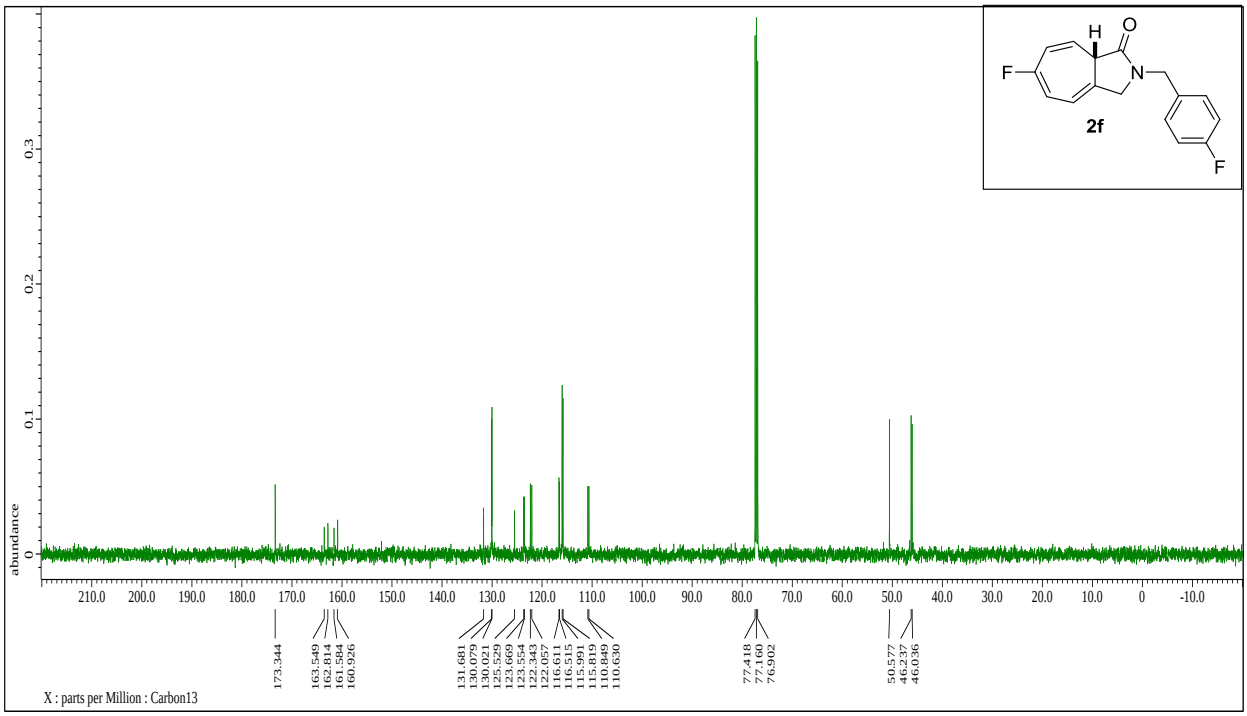

2d
abundance
X : parts per Million : Proton

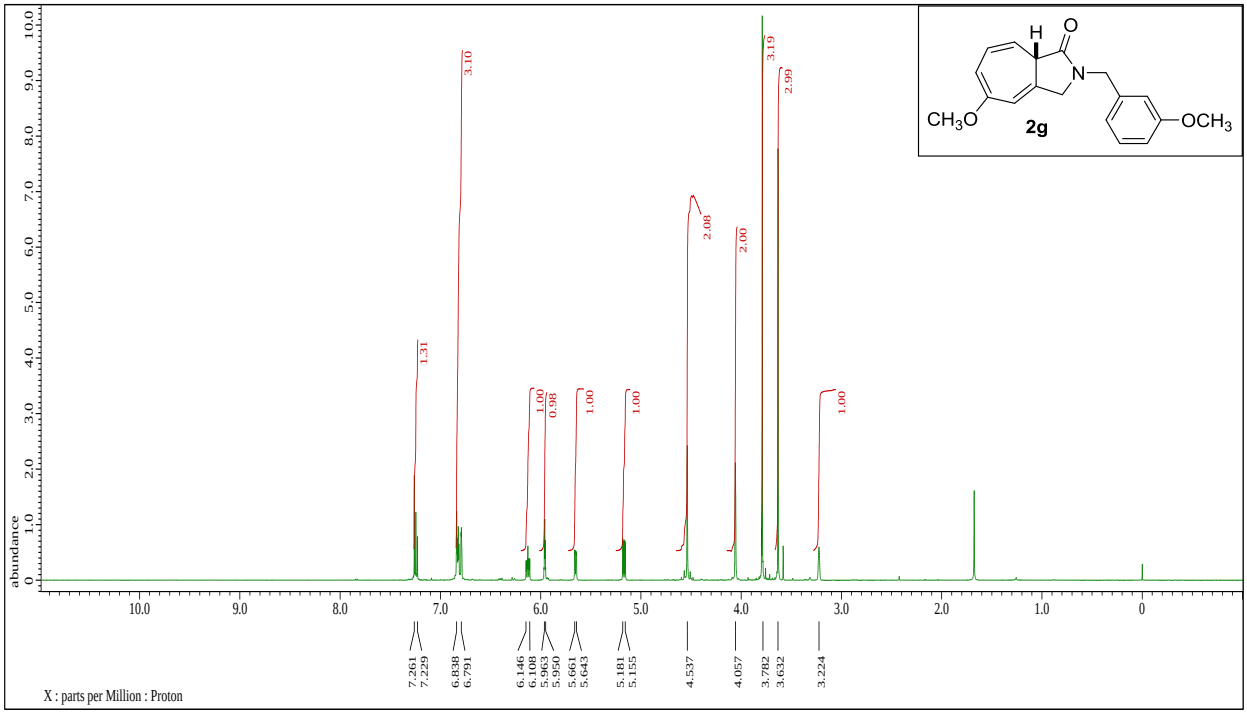

2d
abundance
X : parts per Million : Carbon13

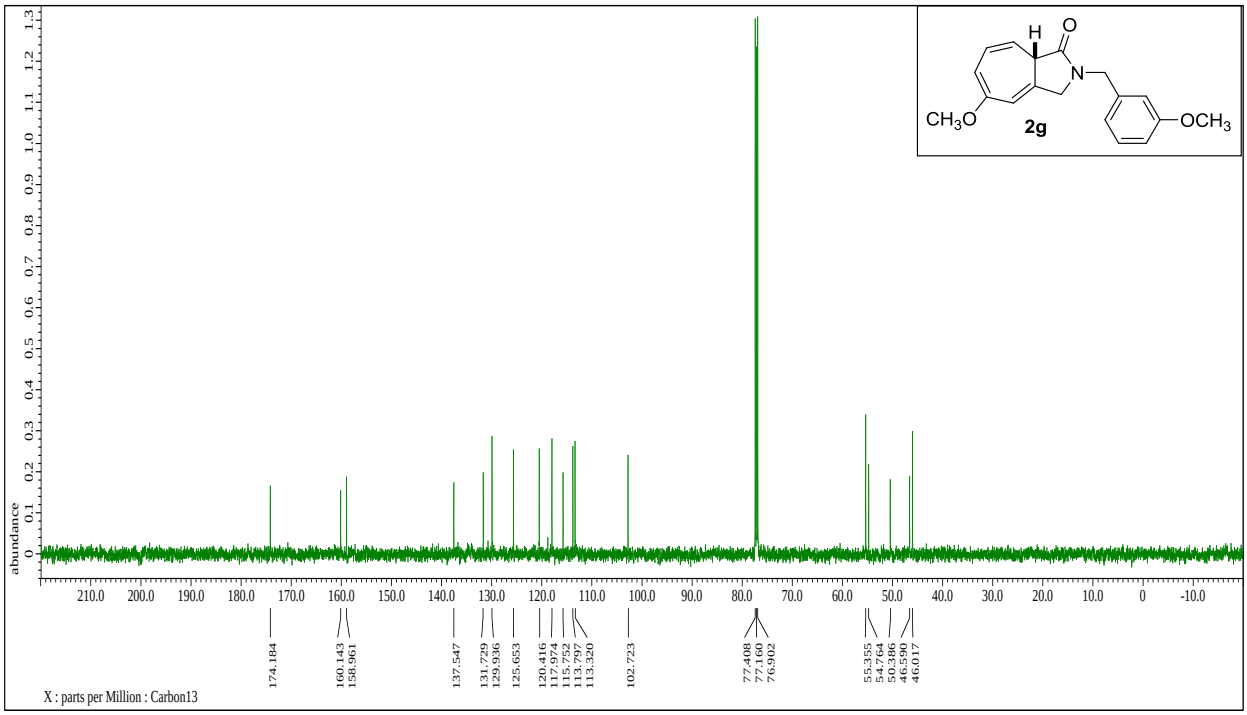

2e
abundance
X : parts per Million : Proton

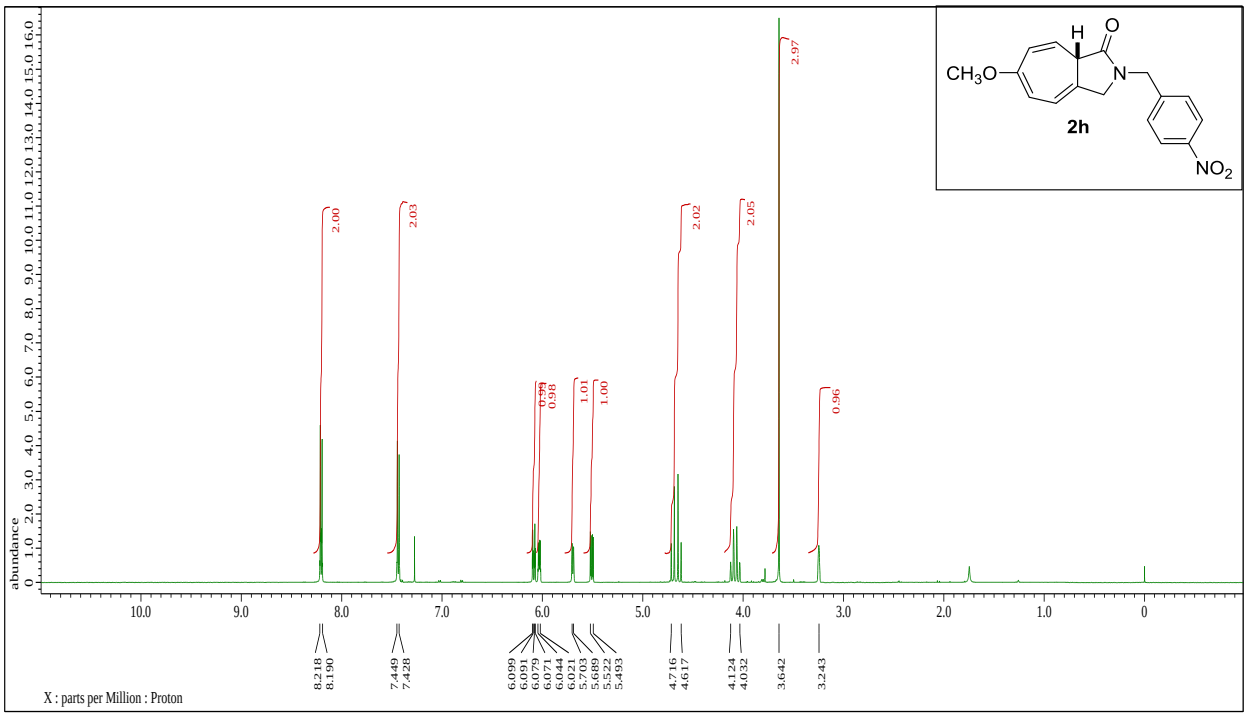

2e
abundance
X : parts per Million : Carbon13

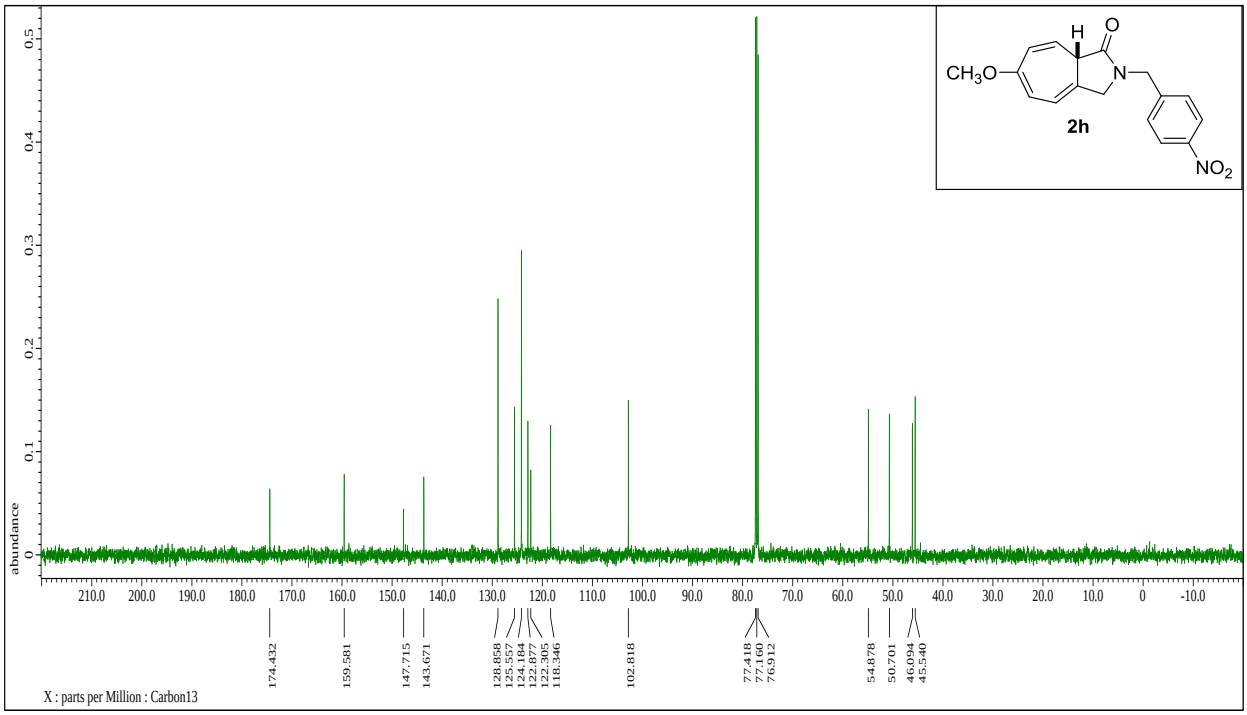

2f
abundance
X : parts per Million : Proton

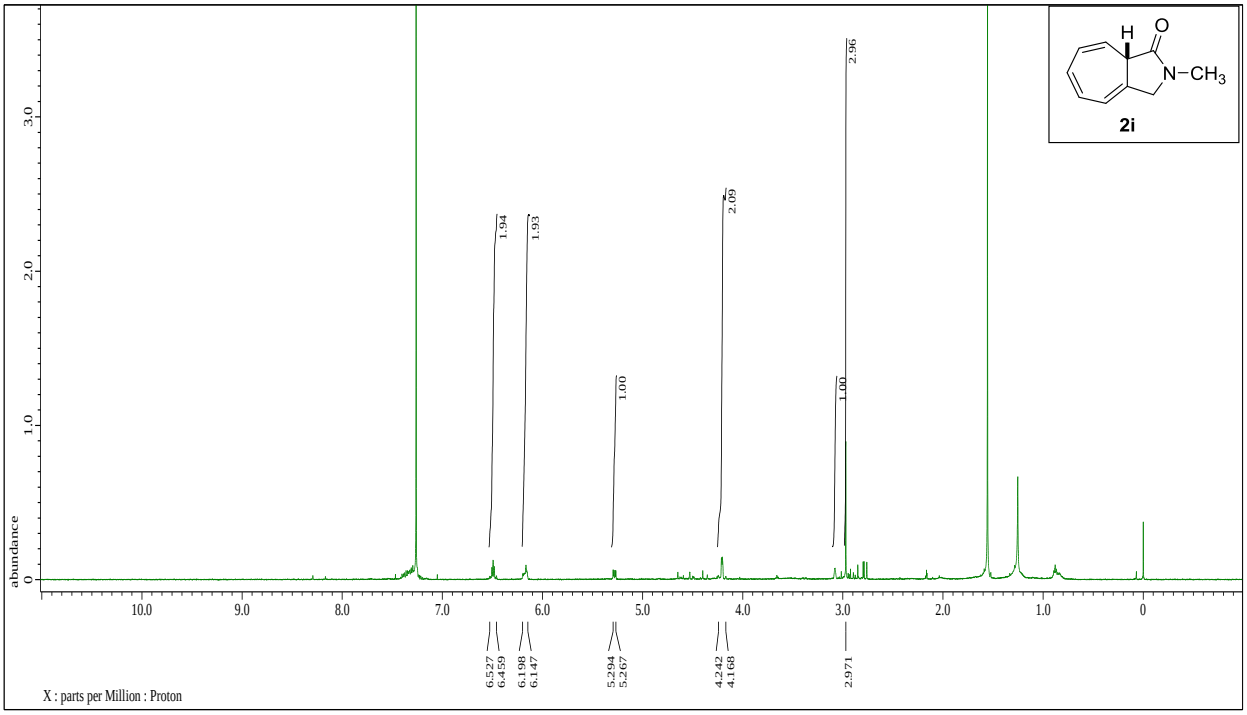

2f
abundance
X : parts per Million : Carbon13

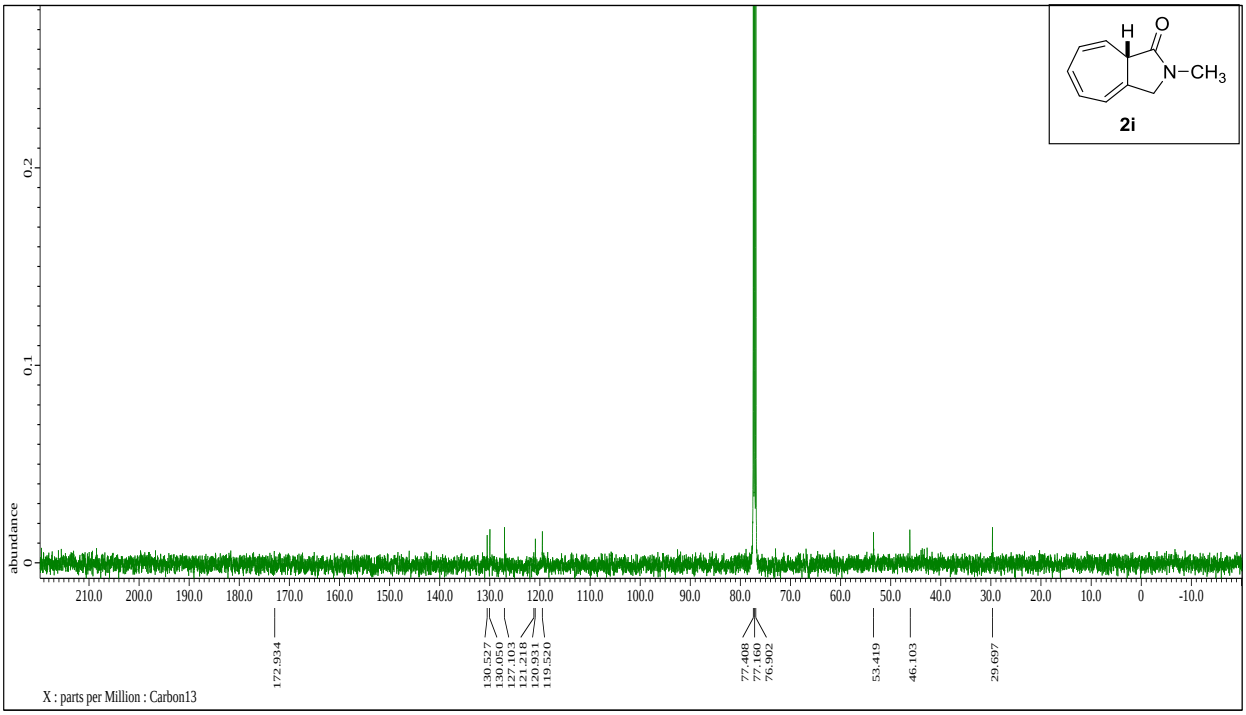

abundance
X : parts per Million : Proton
2g
CH3O
OCH3
3.10
3.19
2.99
2.08
2.00
1.31
1.00
0.98
1.00
1.00
1.00

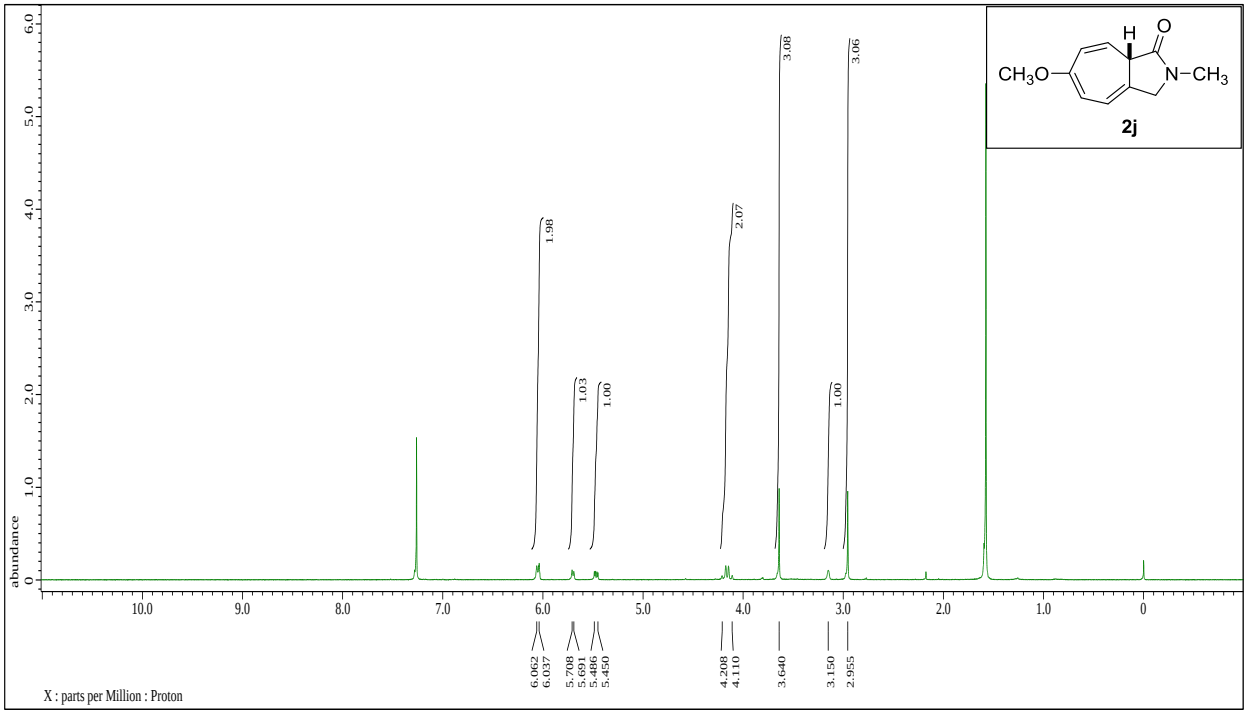

abundance
X : parts per Million : Carbon13
2g
CH3O
OCH3
174.184
160.143
158.961
137.547
131.729
129.936
125.653
120.416
117.974
115.792
113.797
113.320
102.723
77.408
77.160
76.902
55.355
54.764
50.386
46.590
46.017

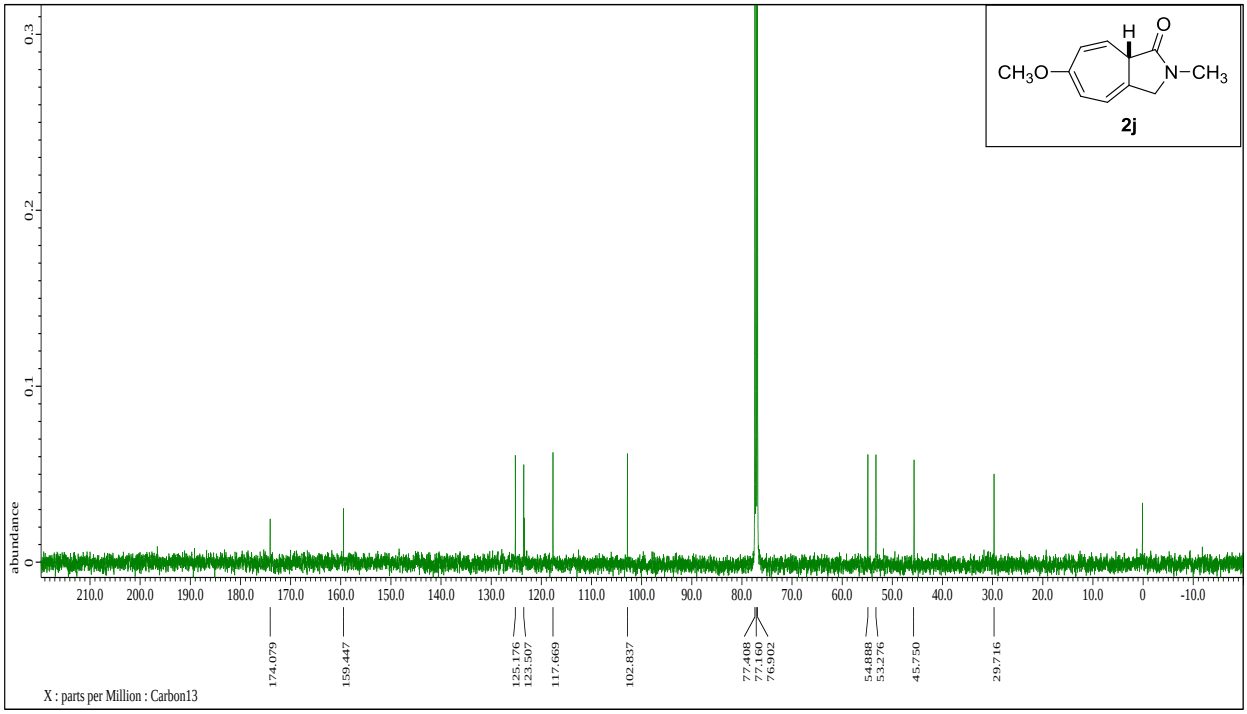

abundance
X : parts per Million : Proton
2h
CH3O
NO2
2.00
2.03
0.99
0.98
1.01
1.00
2.02
2.05
2.97
0.96
8.218
8.190
7.449
7.428
6.099
6.091
6.079
6.071
6.044
6.021
5.703
5.689
5.522
5.493
4.716
4.617
4.124
4.032
3.642
3.243

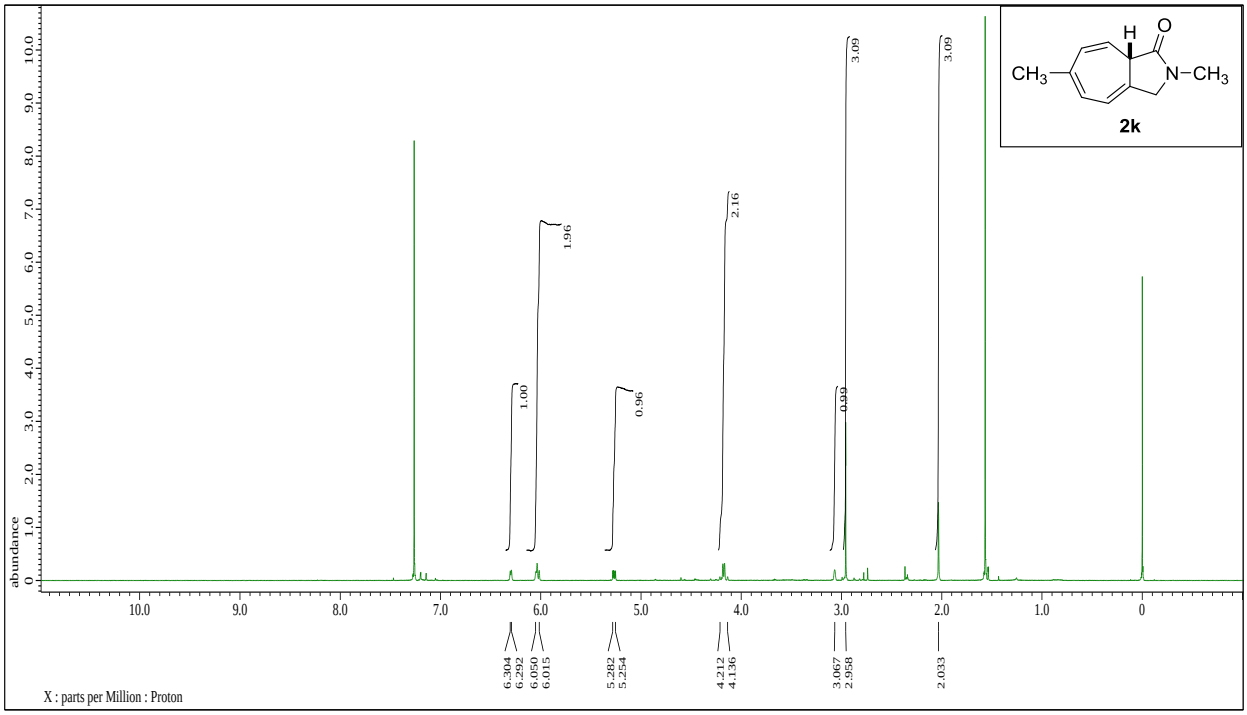

abundance
X : parts per Million : Carbon13
2h
CH3O
NO2
174.432
159.581
147.715
143.671
128.858
125.557
124.184
122.877
122.305
118.346
102.818
77.418
77.160
76.912
54.878
50.701
46.094
45.540

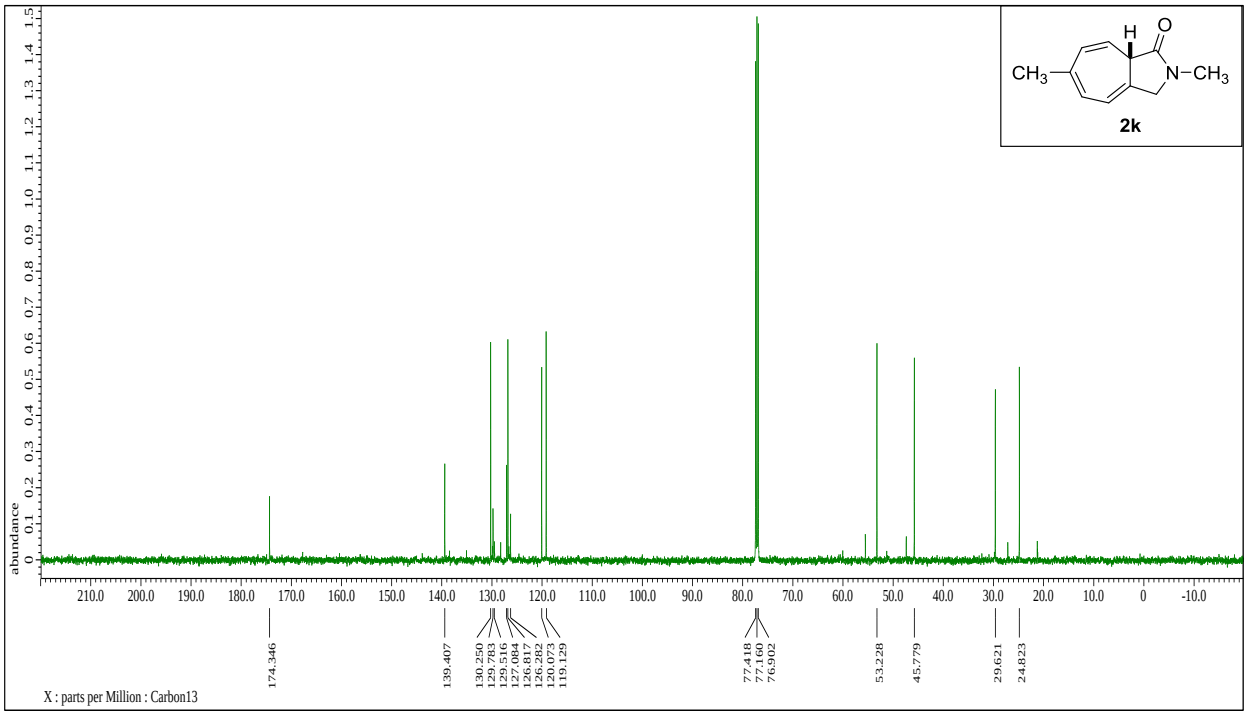

2i
abundance
X : parts per Million : Proton

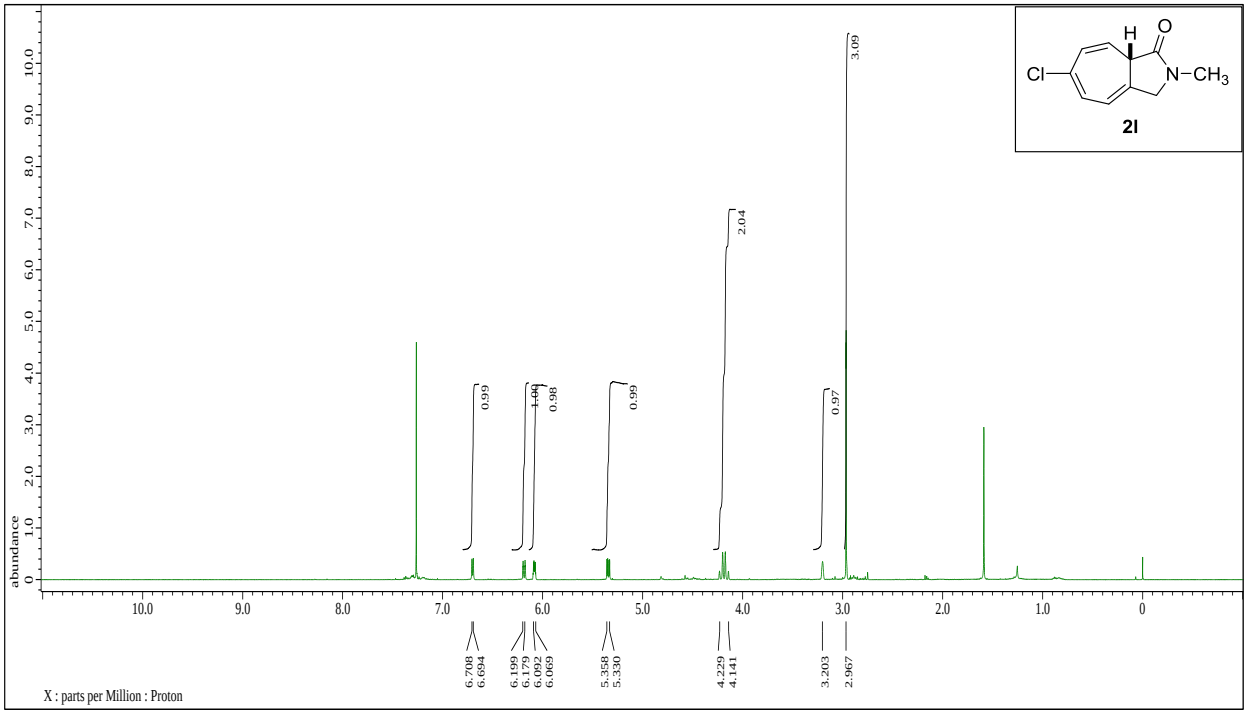

2i
abundance
X : parts per Million : Carbon13

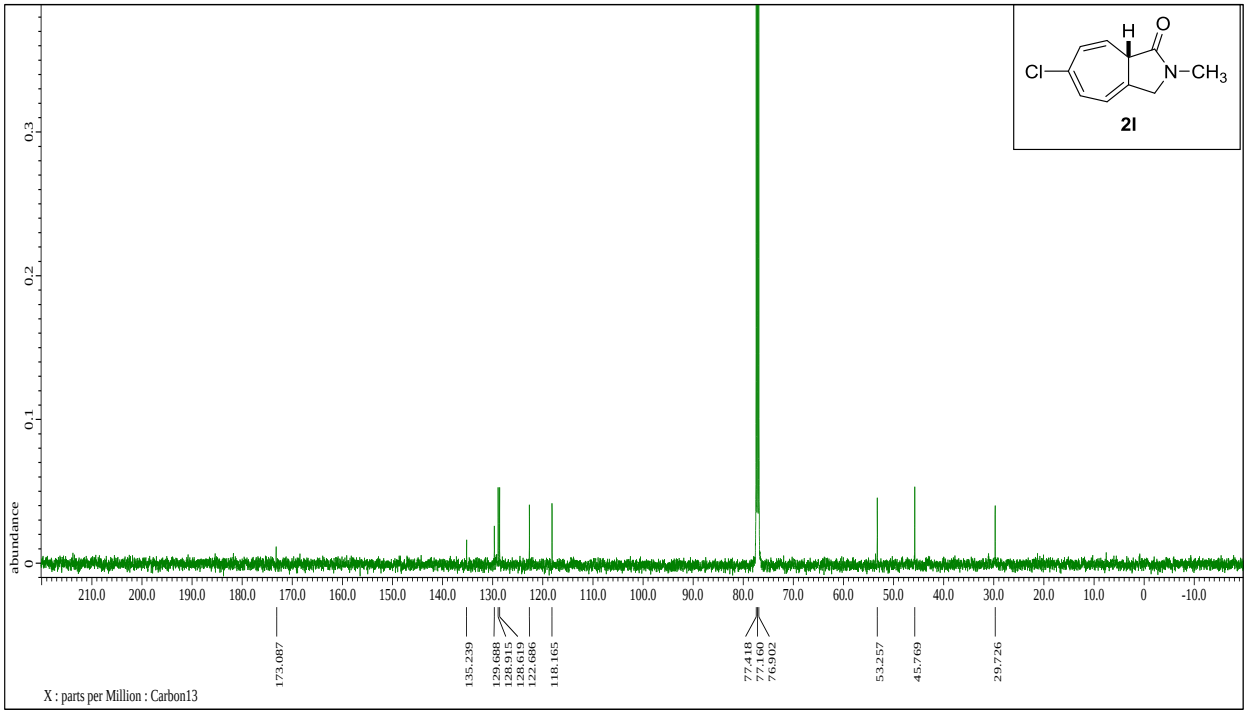

abundance
X : parts per Million : Proton
1.98
1.03
1.00
2.07
3.08
3.06
1.00
6.062
6.037
5.708
5.691
5.466
5.450
4.208
4.110
3.640
3.150
2.955
2j

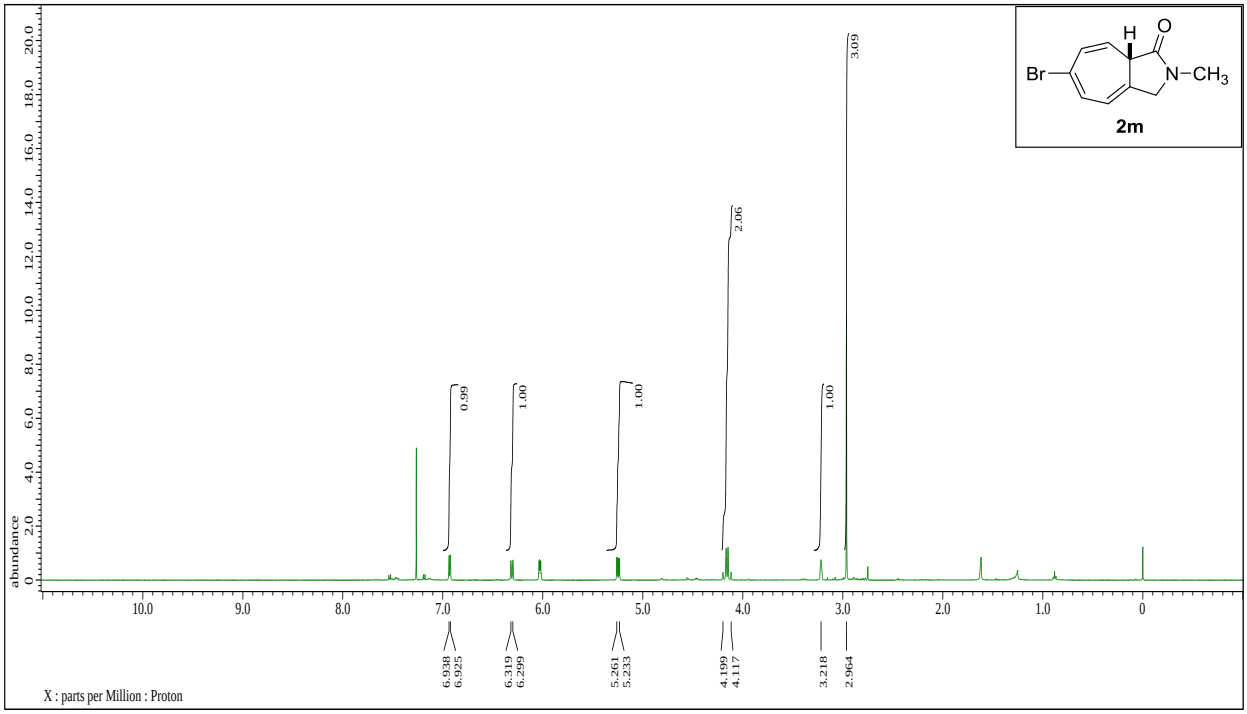

abundance
X : parts per Million : Carbon13
174.079
159.447
125.176
123.507
117.669
102.837
77.408
77.160
76.902
54.888
53.276
45.750
29.716
2j

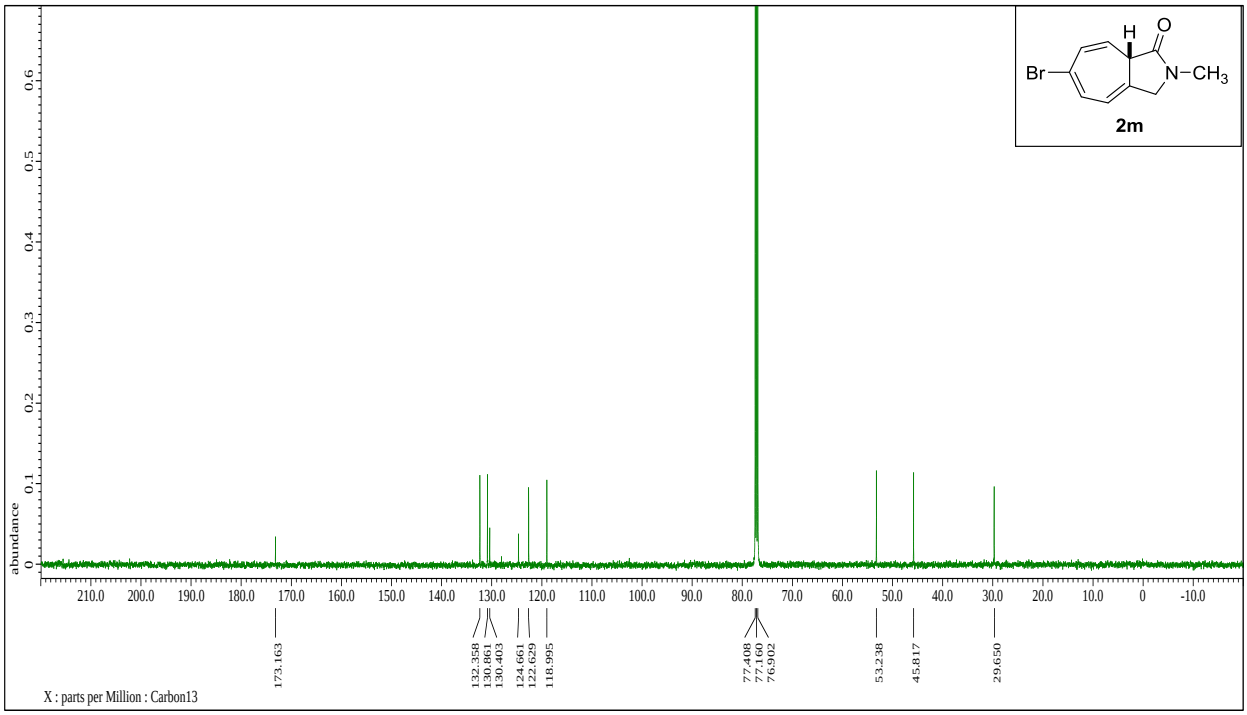

abundance
1.00
1.96
0.96
2.16
0.99
3.09
3.09
6.304
6.292
6.050
6.015
5.282
5.254
4.212
4.136
3.067
2.958
2.033
X : parts per Million : Proton
2k

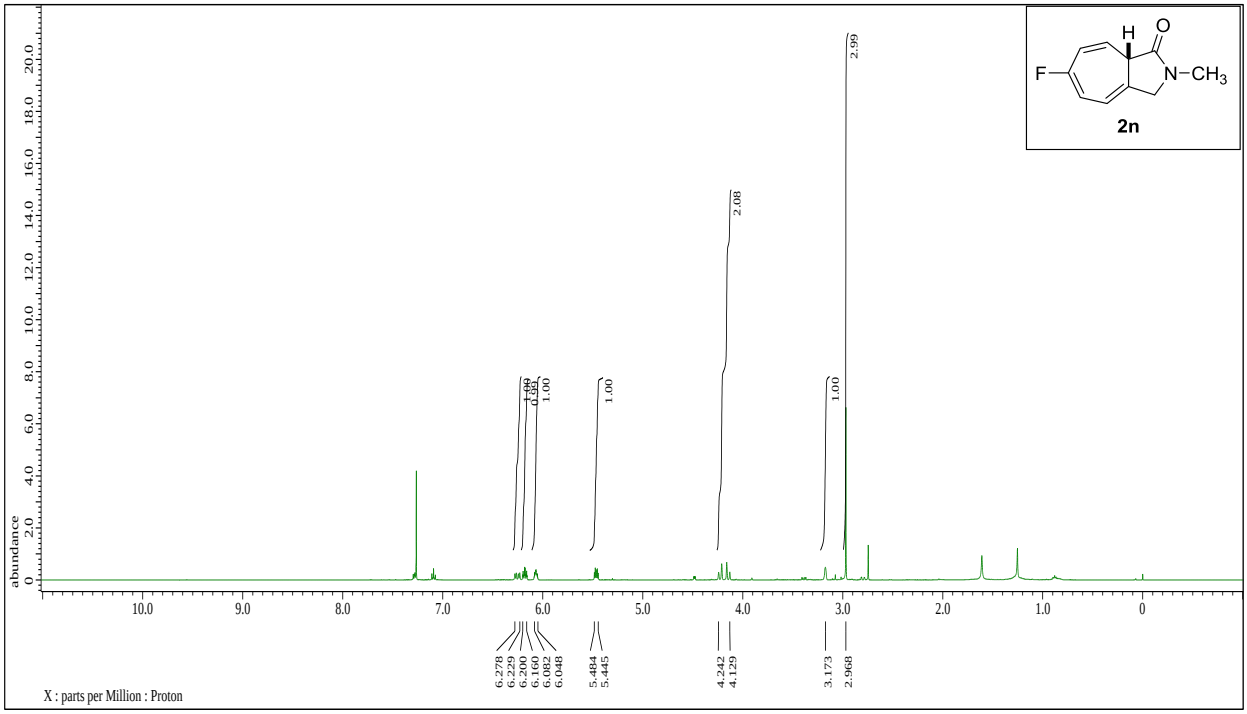

abundance
174.346
139.407
130.250
129.783
129.516
127.084
126.817
126.282
120.073
119.129
77.418
77.160
76.902
53.228
45.779
29.621
24.823
X : parts per Million : Carbon13
2k

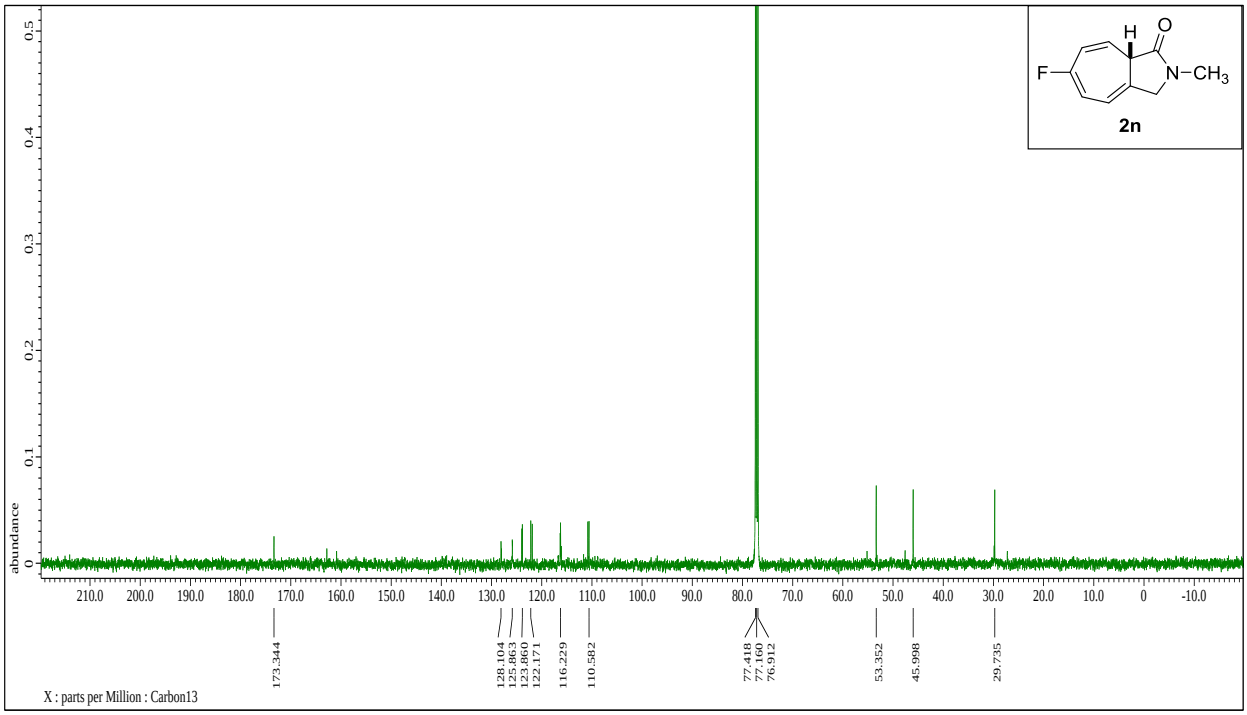

abundance
X : parts per Million : Proton
2I
3.09
2.04
0.99
1.04
0.98
0.99
0.97
6.708
6.694
6.199
6.179
6.092
6.069
5.358
5.330
4.229
4.141
3.203
2.967


abundance
X : parts per Million : Carbon13
2I
173.087
135.239
129.688
128.915
128.619
122.686
118.165
77.418
77.160
76.902
53.257
45.769
29.726

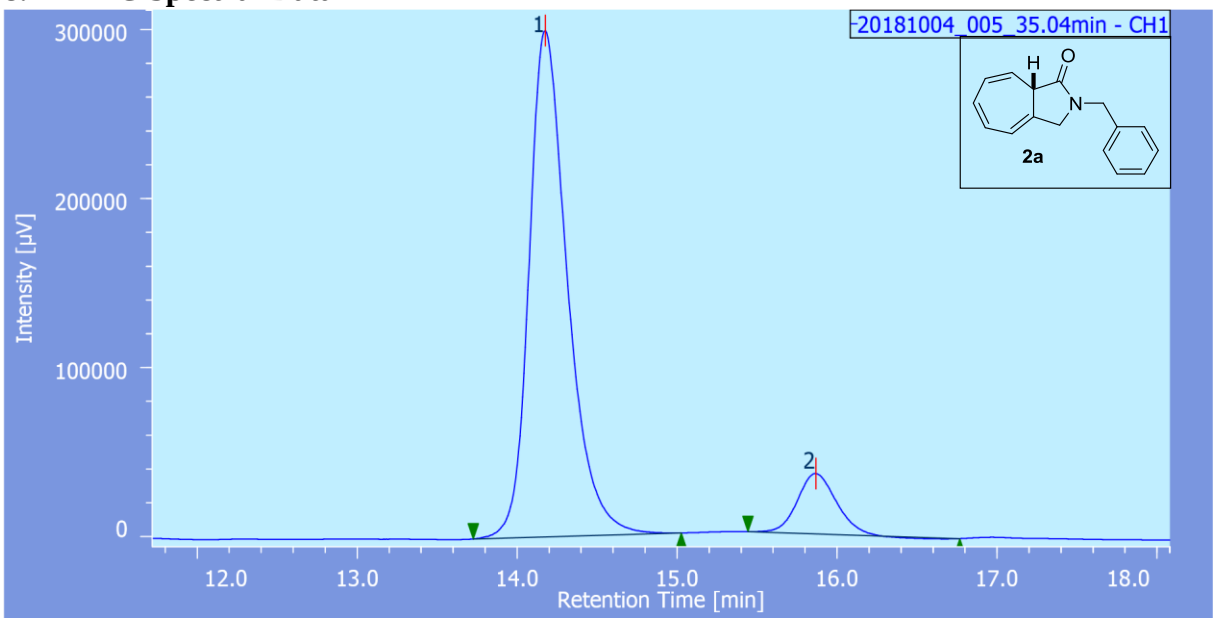

2m
abundance
X : parts per Million : Proton
0.99
1.00
1.00
2.06
1.00
3.09
6.938
6.925
6.319
6.299
5.261
5.233
4.199
4.117
3.218
2.964


2m
abundance
X : parts per Million : Carbon13
173.163
132.358
130.861
130.403
124.661
122.629
118.995
77.408
77.160
76.902
53.238
45.817
29.650

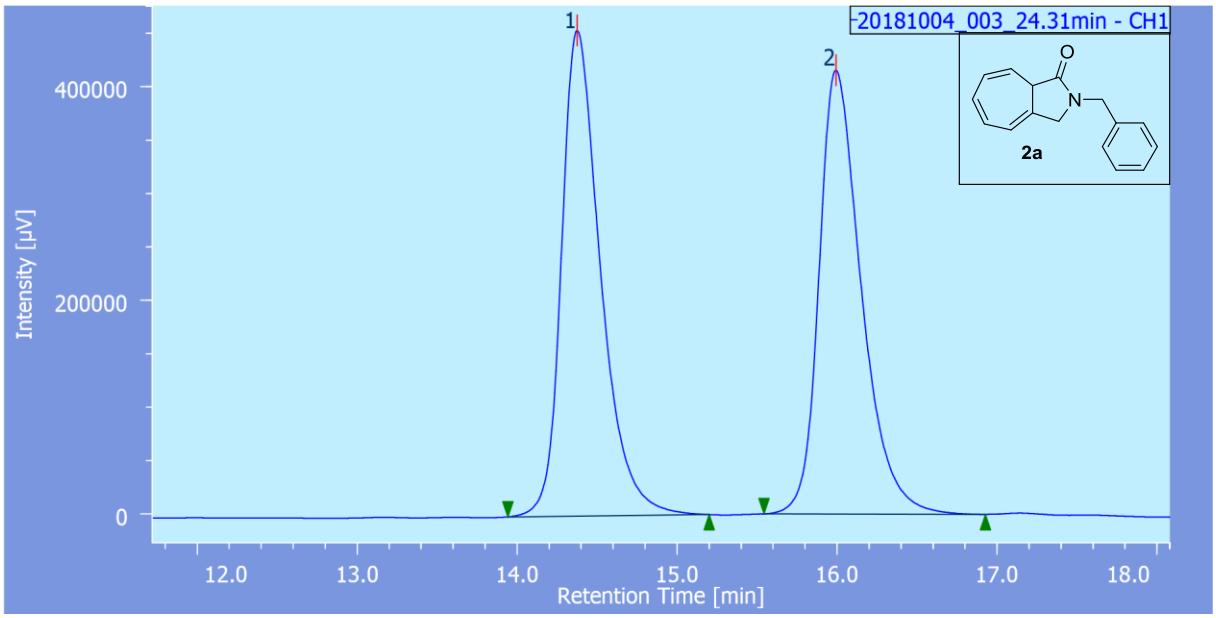

abundance
X : parts per Million : Proton
2n
6.278
6.229
6.200
6.160
6.082
6.048
5.484
5.445
4.242
4.129
3.173
2.968
1.00
2.08
2.99


abundance
X : parts per Million : Carbon13
2n
173.344
128.104
125.863
123.960
122.171
116.229
110.582
77.418
77.160
76.912
53.352
45.998
29.735

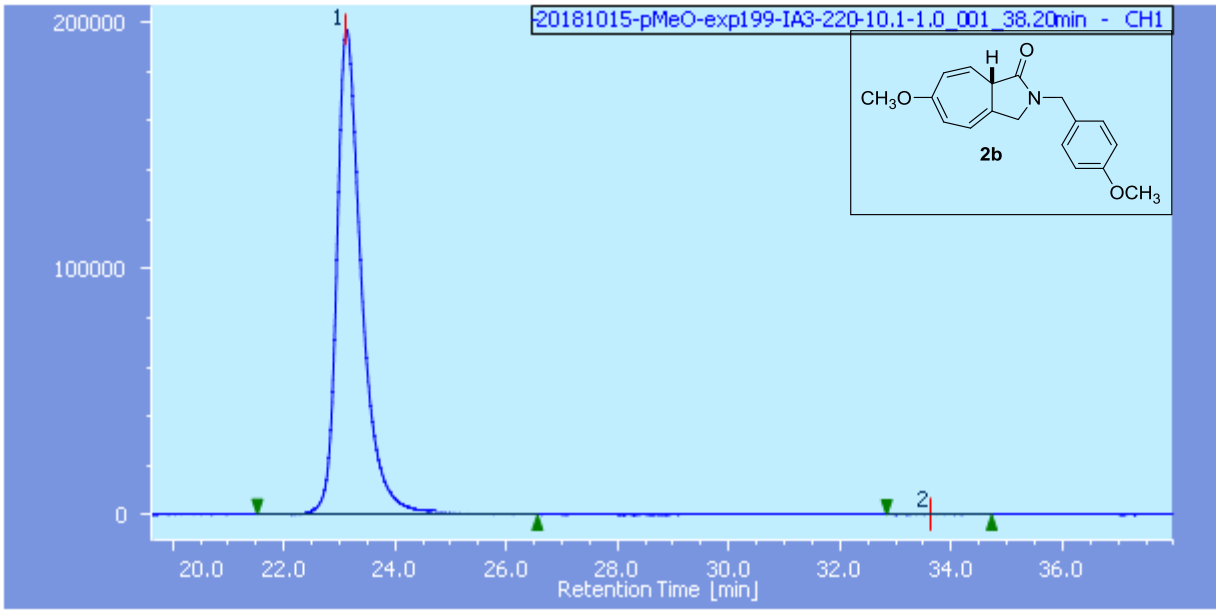
8. HPLC Spectral Data



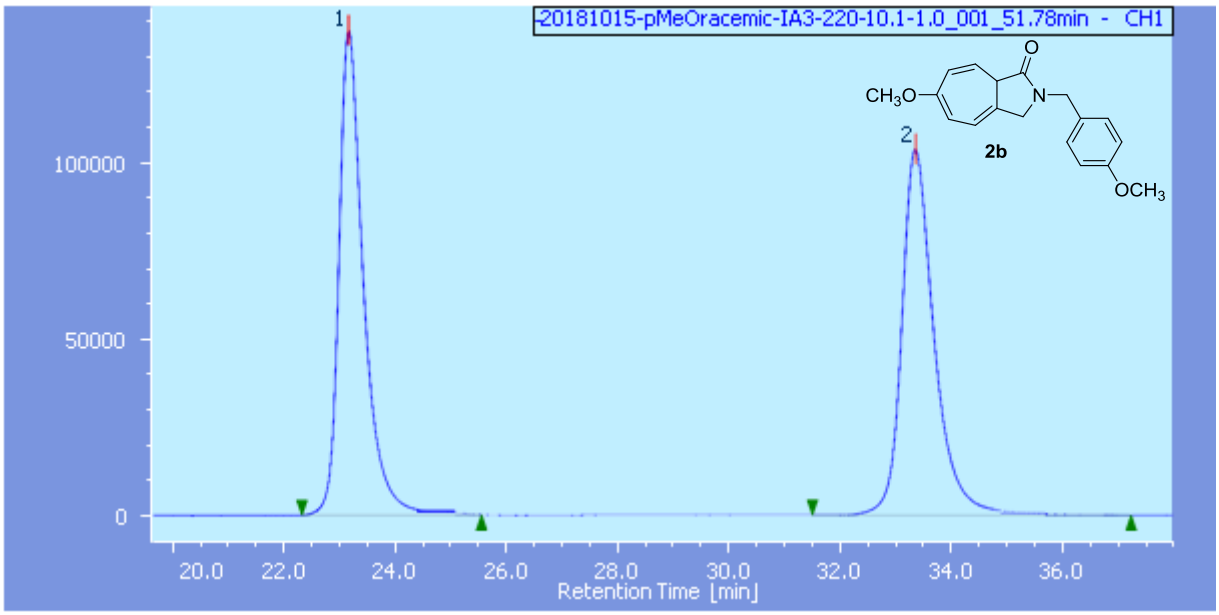
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	14.175	4998378	299334	89.146	89.343
2	15.867	608581	35704	10.854	10.657



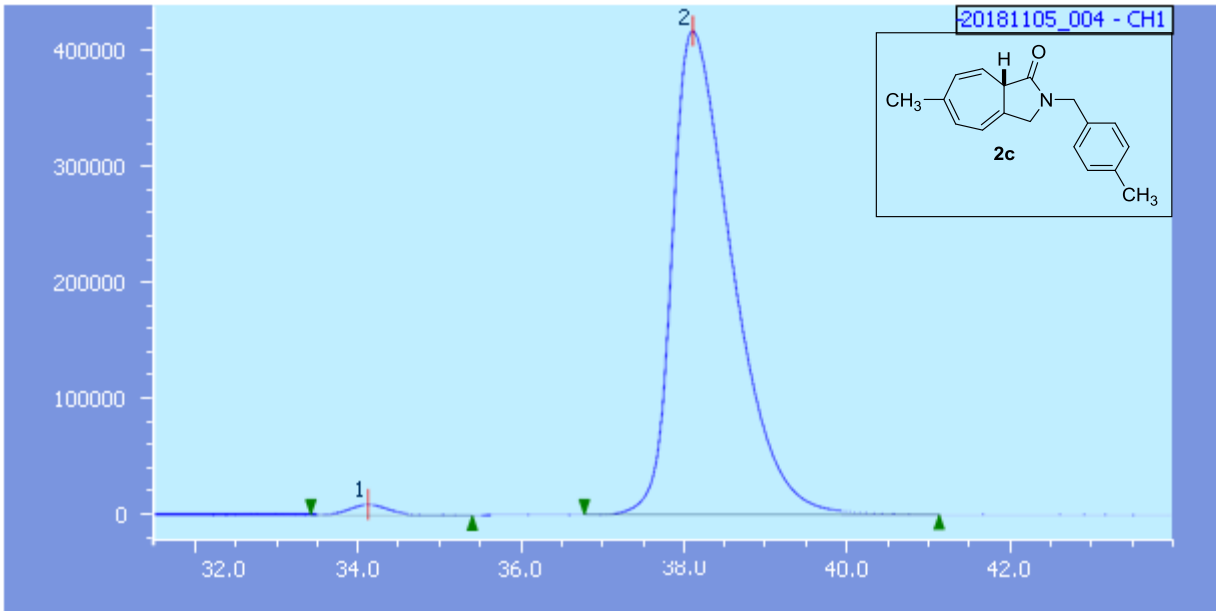
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	14.375	7722581	454495	50.284	52.250
2	15.992	7635293	415356	49.716	47.750



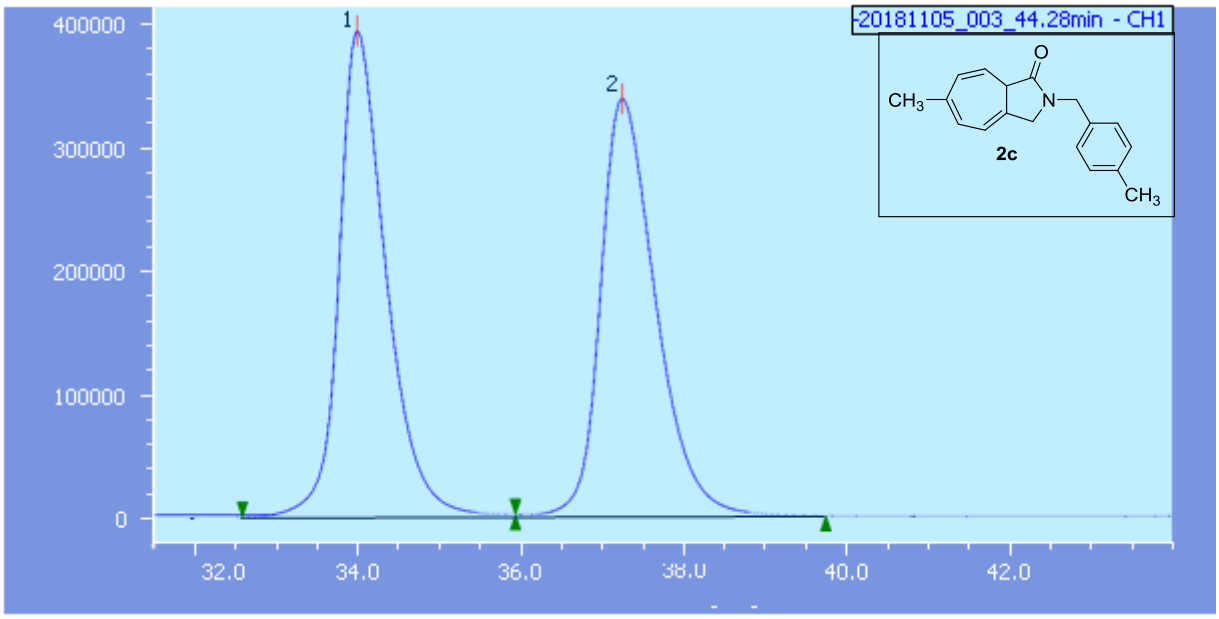
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	23.125	6146103	196853	99.840	99.845
2	33.617	9858	305	0.160	0.155



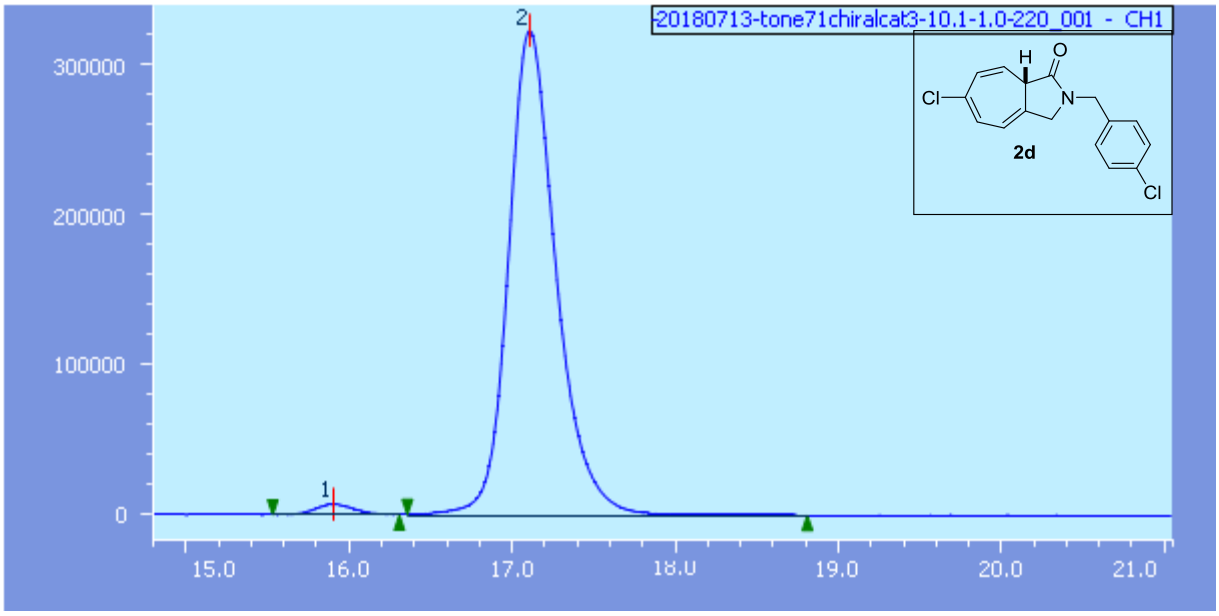
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	23.133	4234078	137212	50.121	56.990
2	33.325	4123603	103552	49.879	43.010



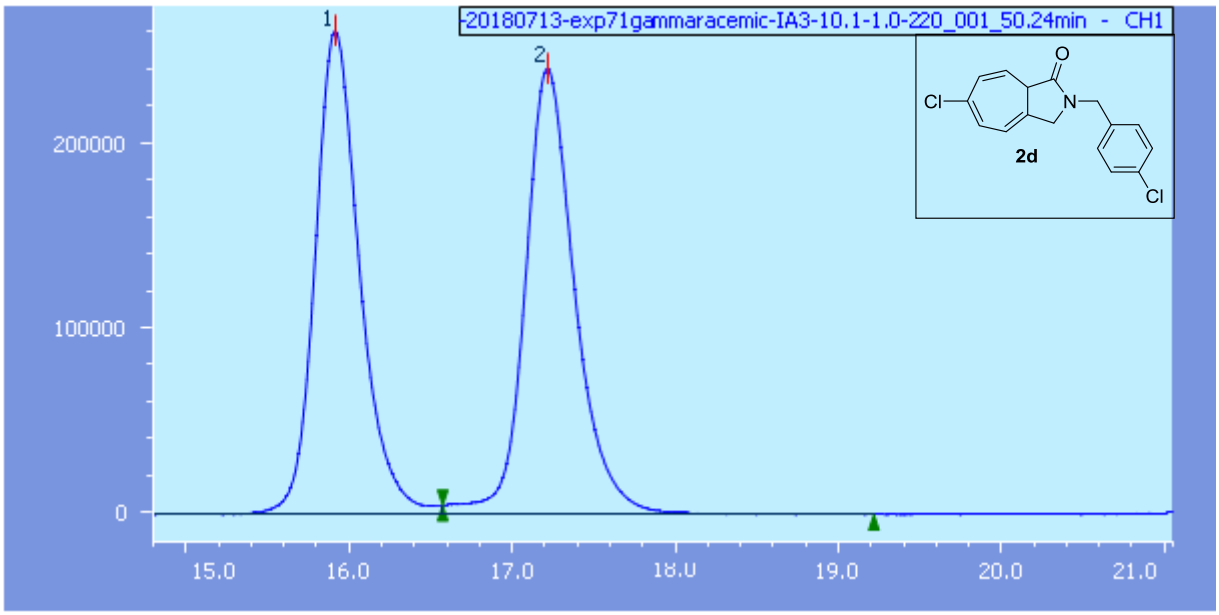
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	34.125	295038	8787	1.361	2.064
2	38.108	21383869	416923	98.639	97.936



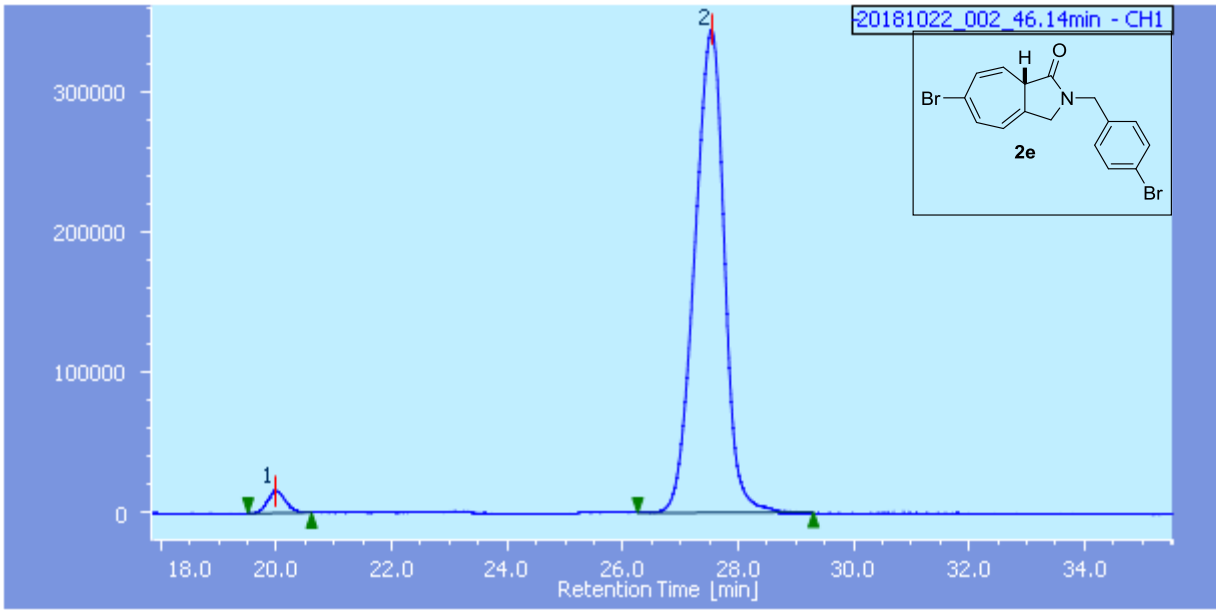
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	33.967	15960801	394027	49.677	53.750
2	37.217	16168539	339041	50.323	46.250



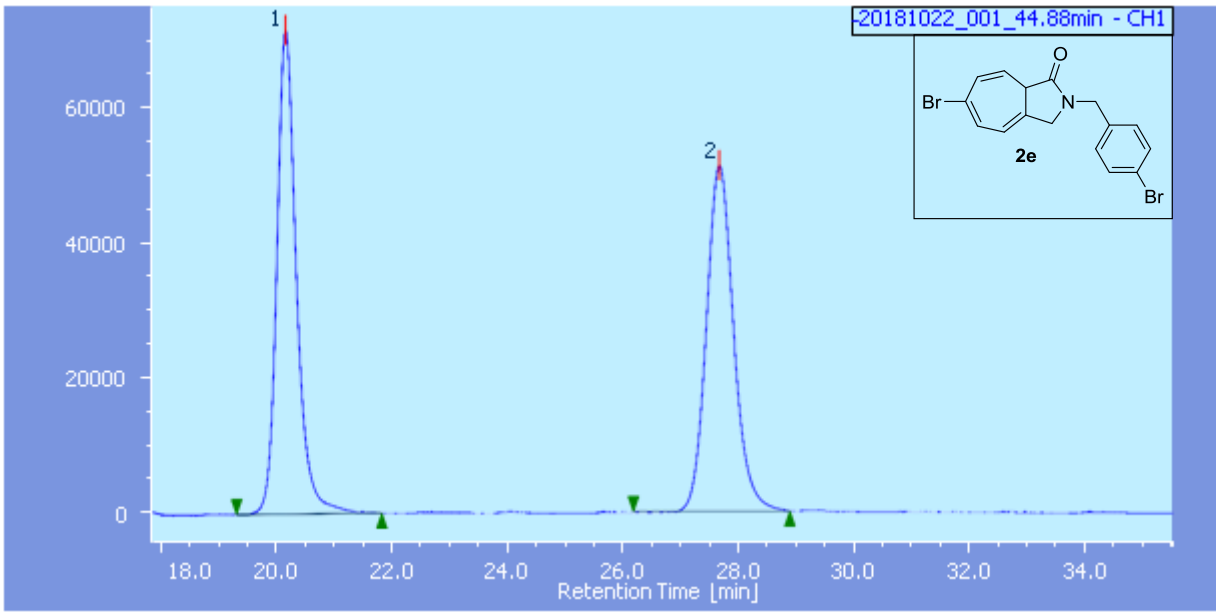
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	15.908	123785	7090	1.851	2.148
2	17.108	6565407	323049	98.149	97.852



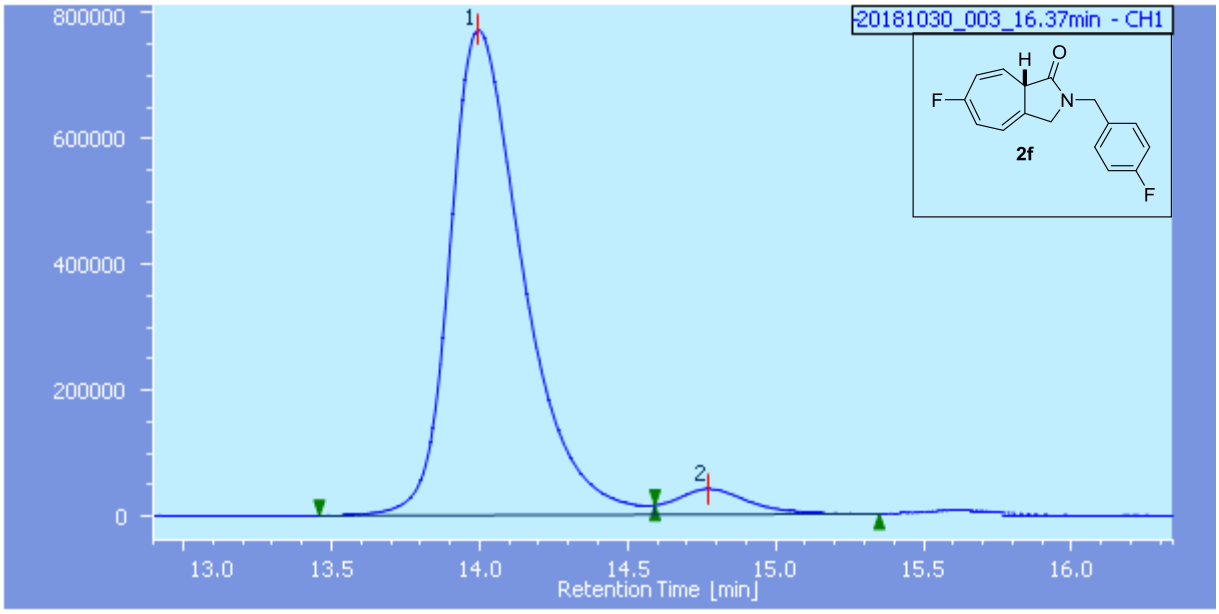
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	15.917	4998114	261500	49.299	52.029
2	17.217	5140338	241108	50.701	47.971



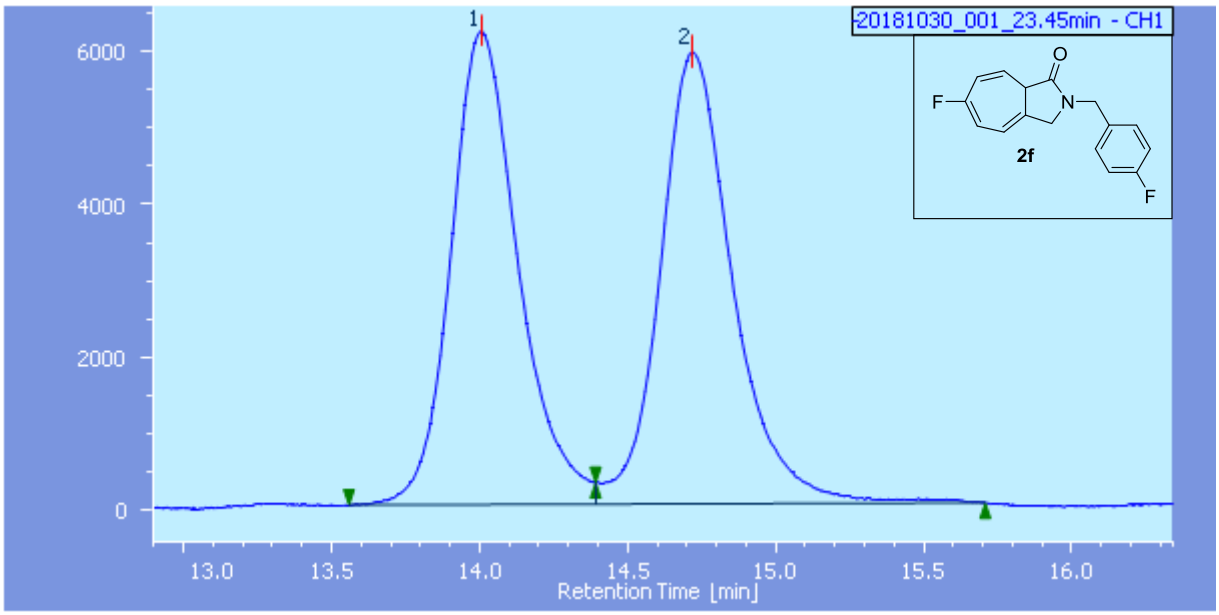
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	19.992	342399	15821	2.722	4.406
2	27.533	12237527	343240	97.278	95.594



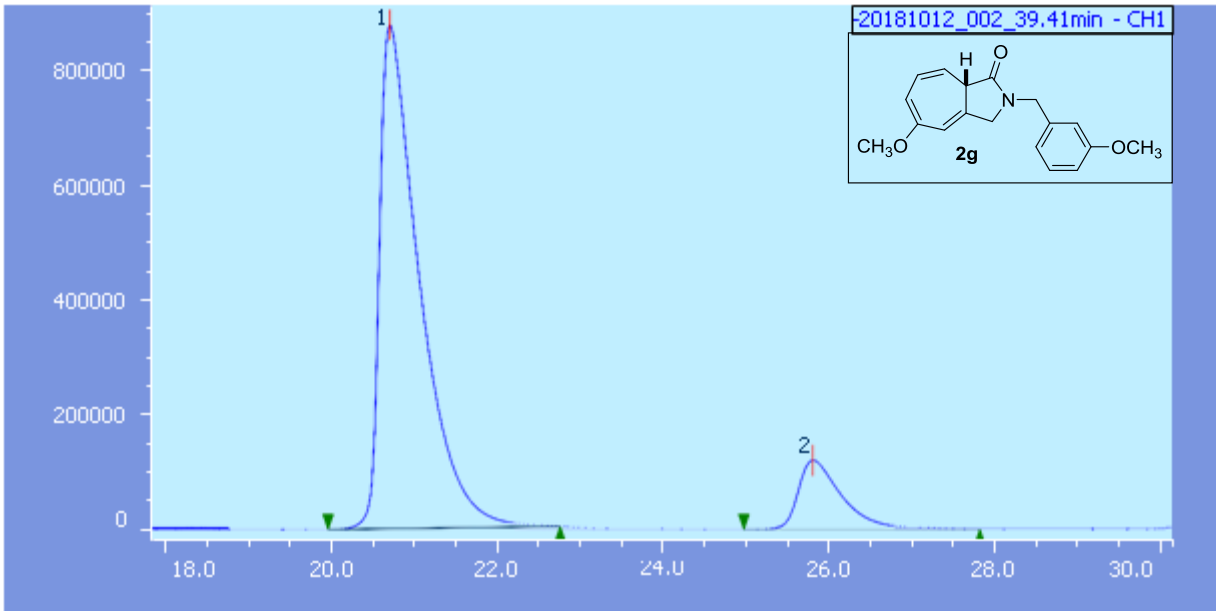
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.133	1689569	71715	50.168	58.329
2	27.642	1678278	51234	49.832	41.671



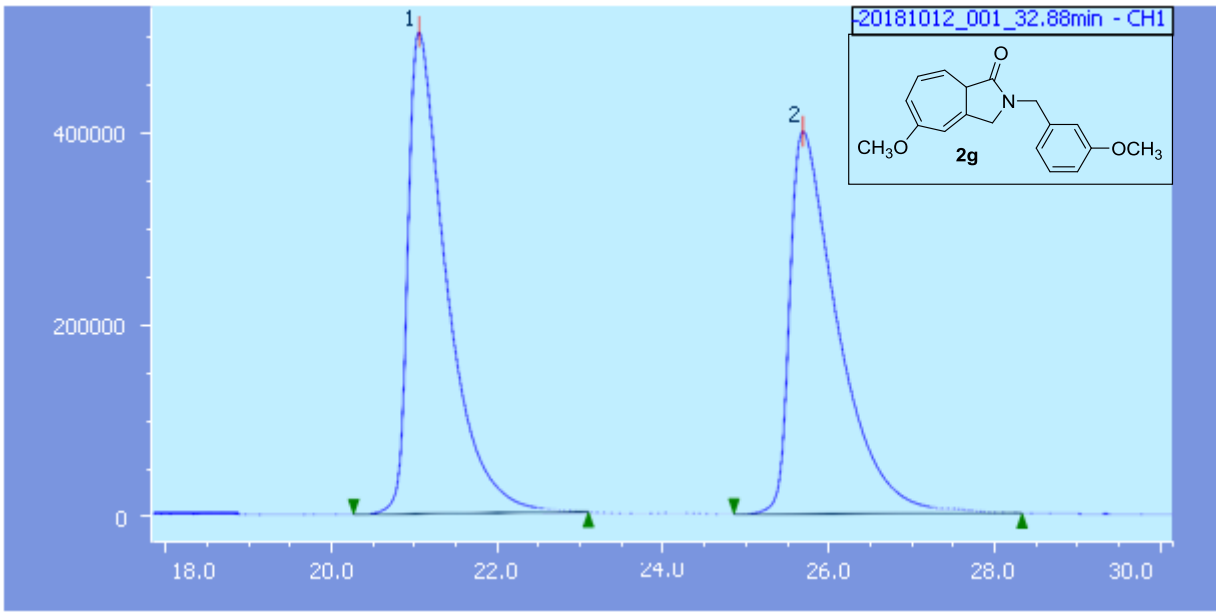
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	13.992	13211783	769810	95.041	95.032
2	14.775	689306	40241	4.959	4.968



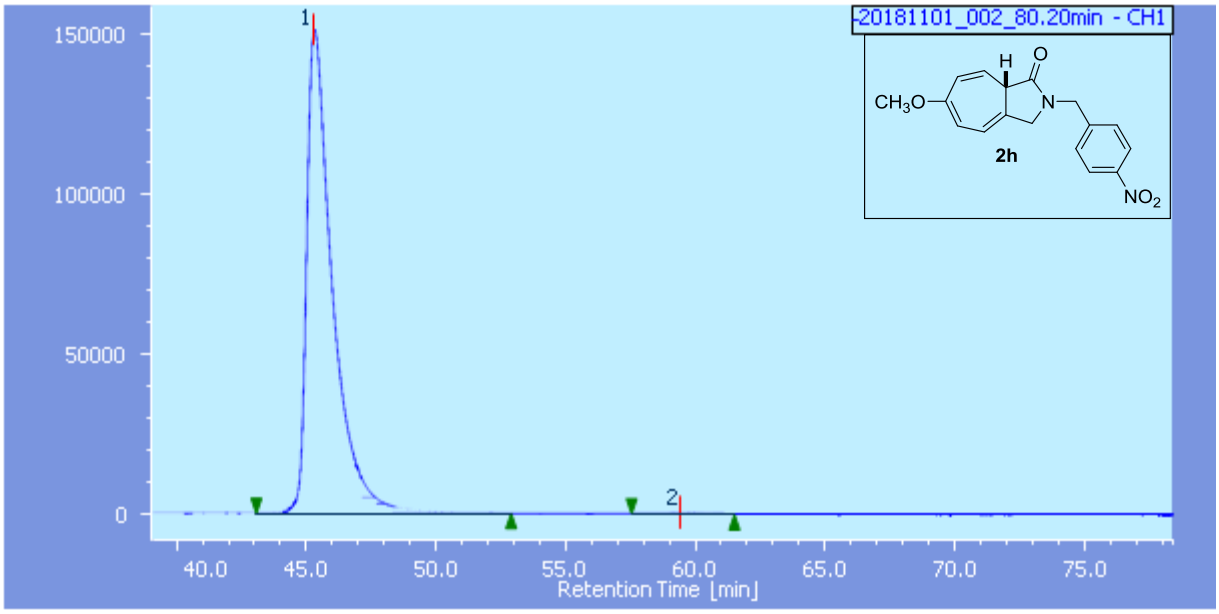
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	14.008	98046	6202	49.186	51.143
2	14.717	101291	5925	50.814	48.857



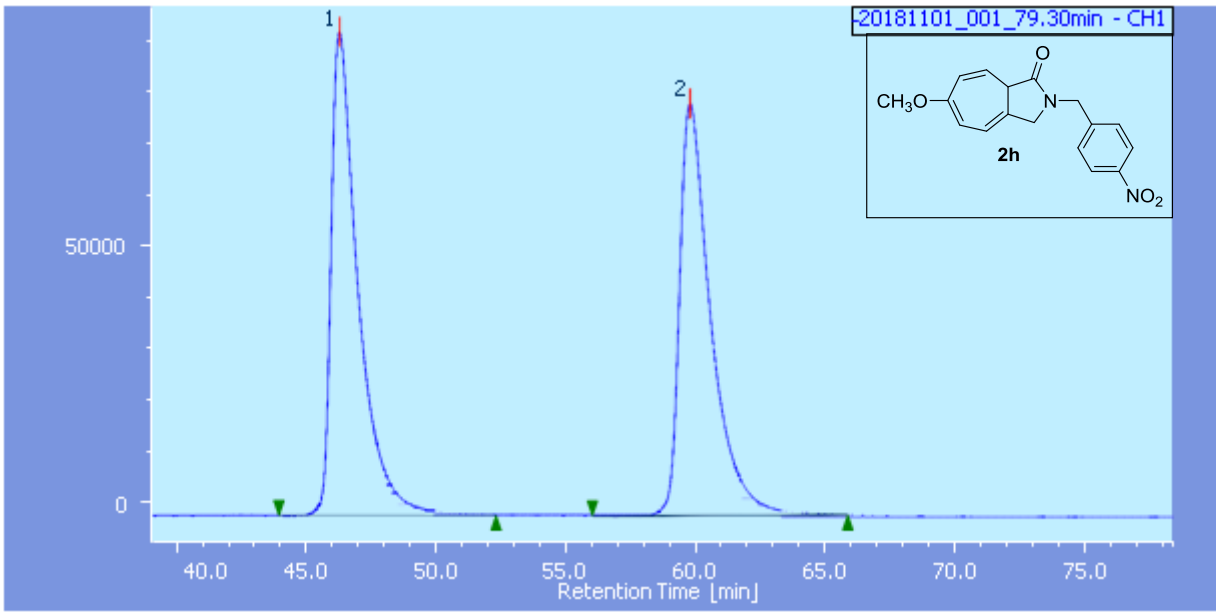
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.700	29448287	876831	86.893	87.930
2	25.808	4441998	120360	13.107	12.070



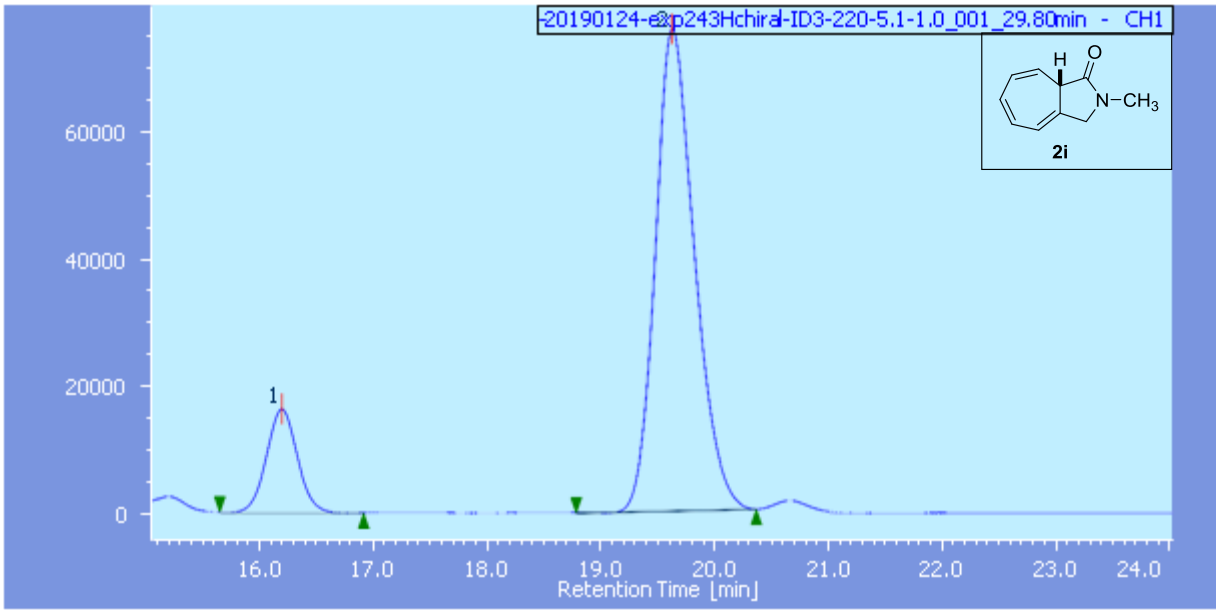
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	21.033	16376122	503364	50.237	55.731
2	25.667	16221879	399841	49.763	44.269



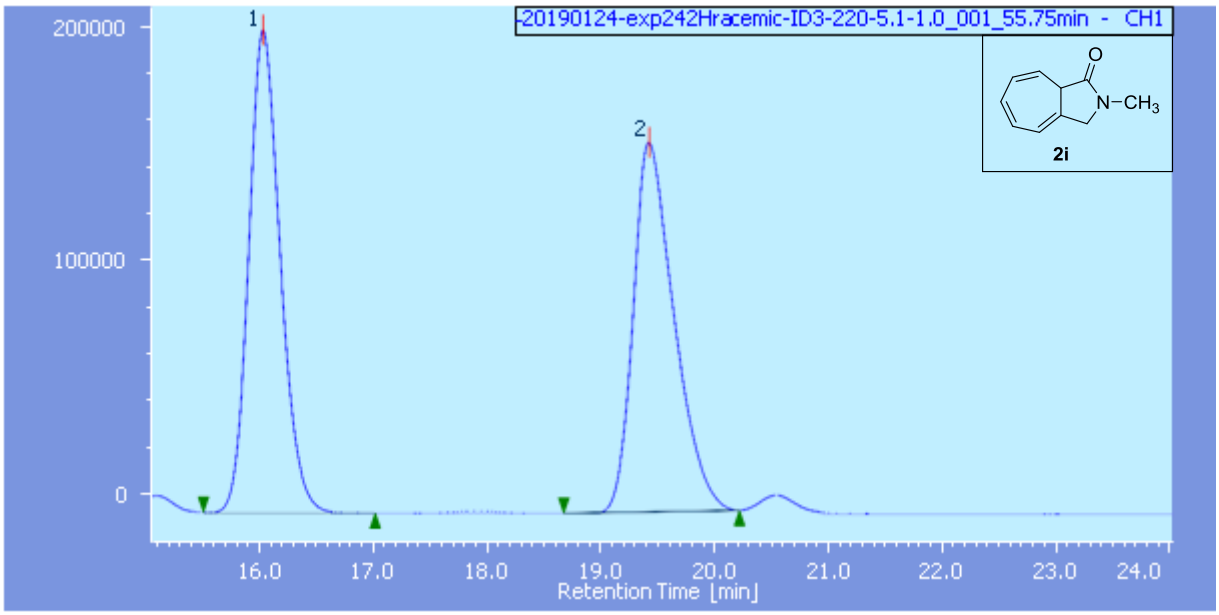
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	45.267	10518585	151022	99.593	99.630
2	59.375	43024	561	0.407	0.370



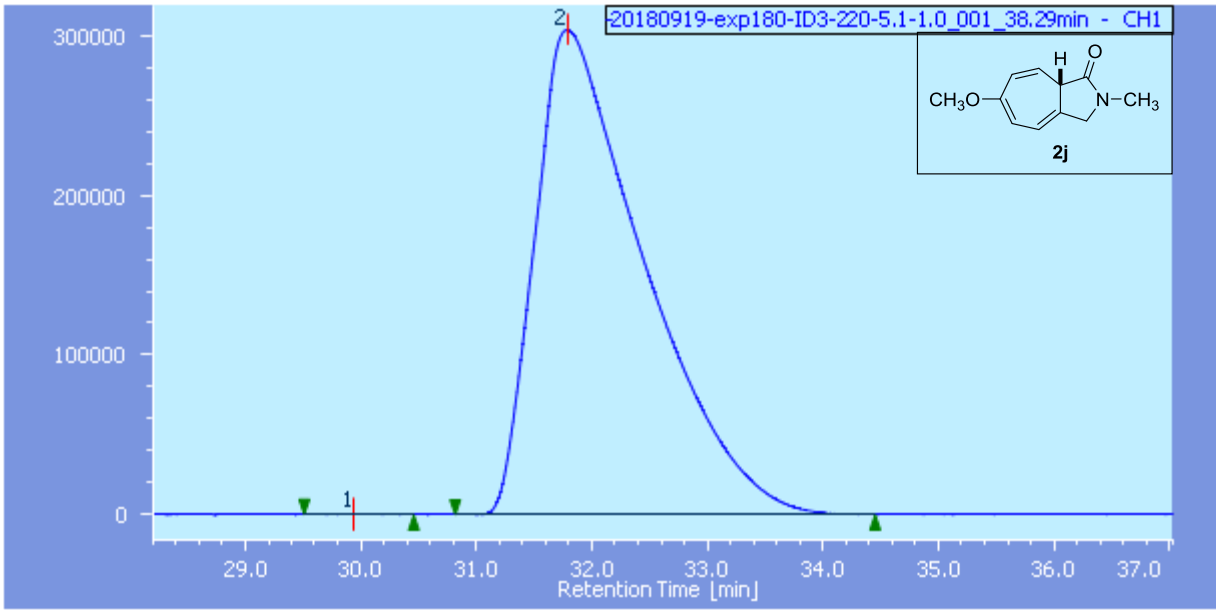
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	46.208	6857632	94333	50.173	53.968
2	59.725	6810218	80461	49.827	46.032



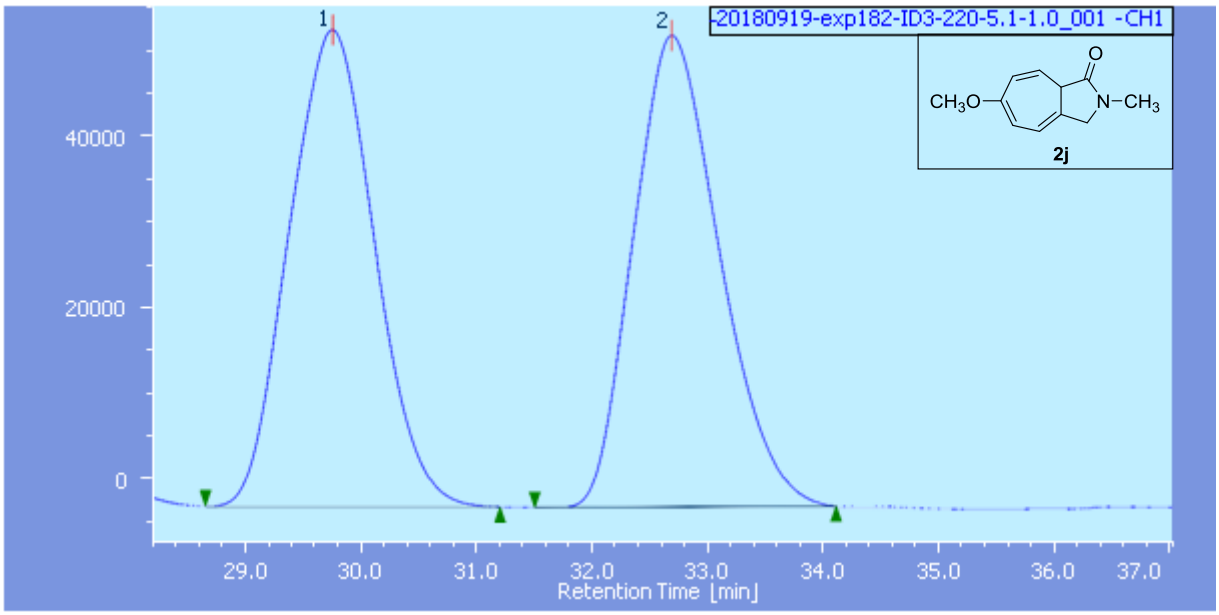
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	16.192	306518	16310	14.422	17.682
2	19.617	1818808	75934	85.578	82.318



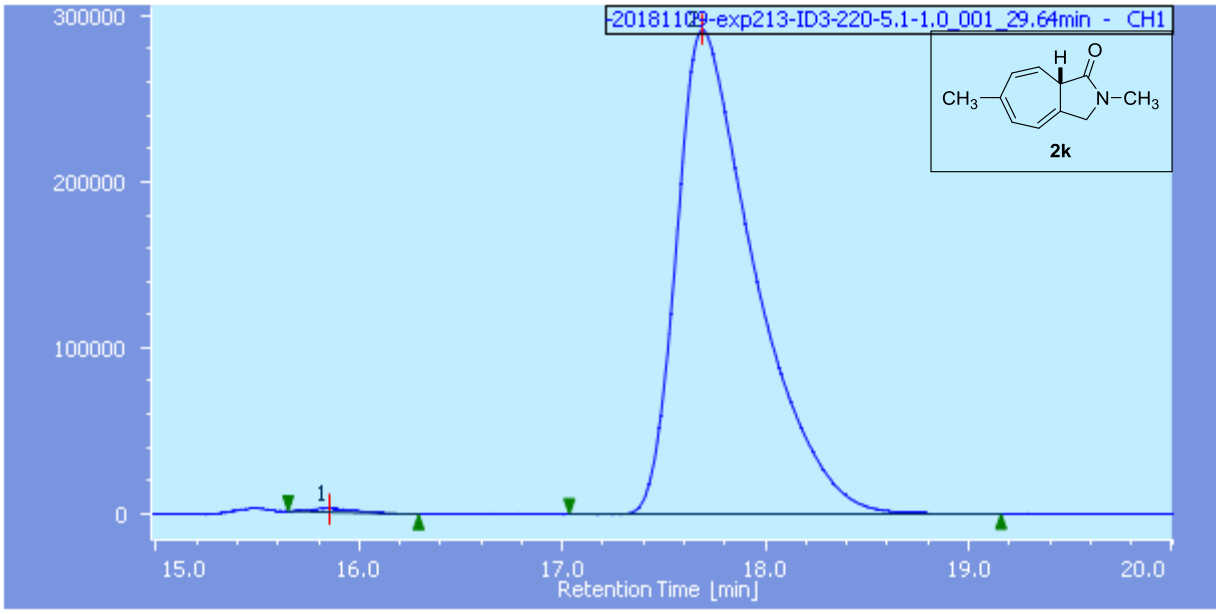
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	16.025	3954021	205833	50.172	56.646
2	19.417	3926904	157533	49.828	43.354



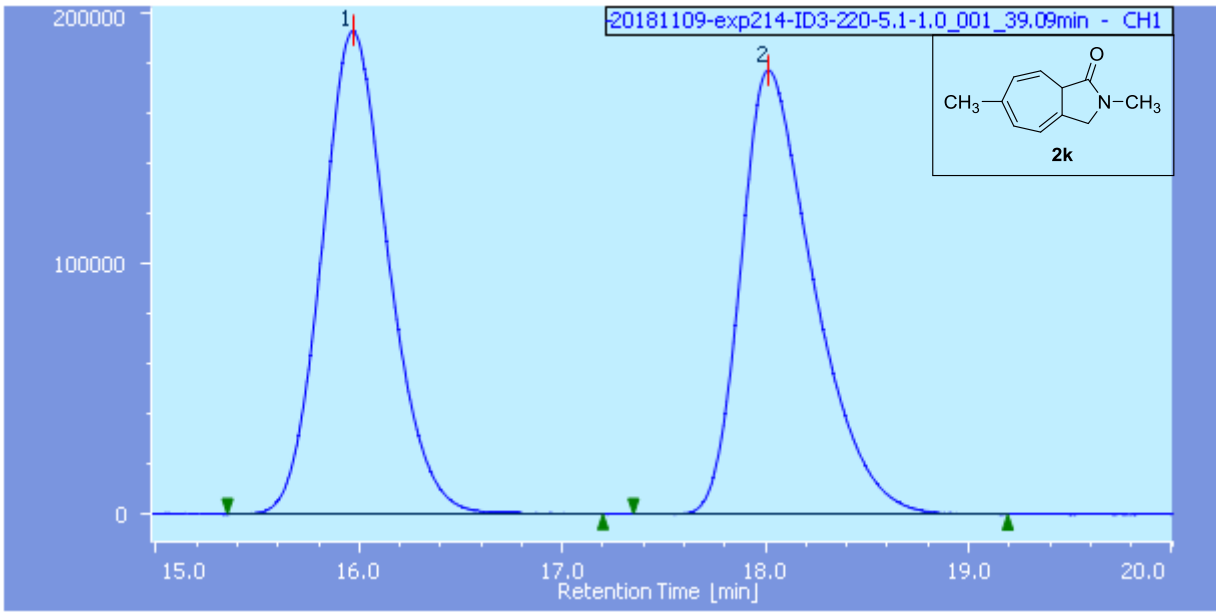
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	29.942	15701	530	0.078	0.174
2	31.783	20074522	304757	99.922	99.826



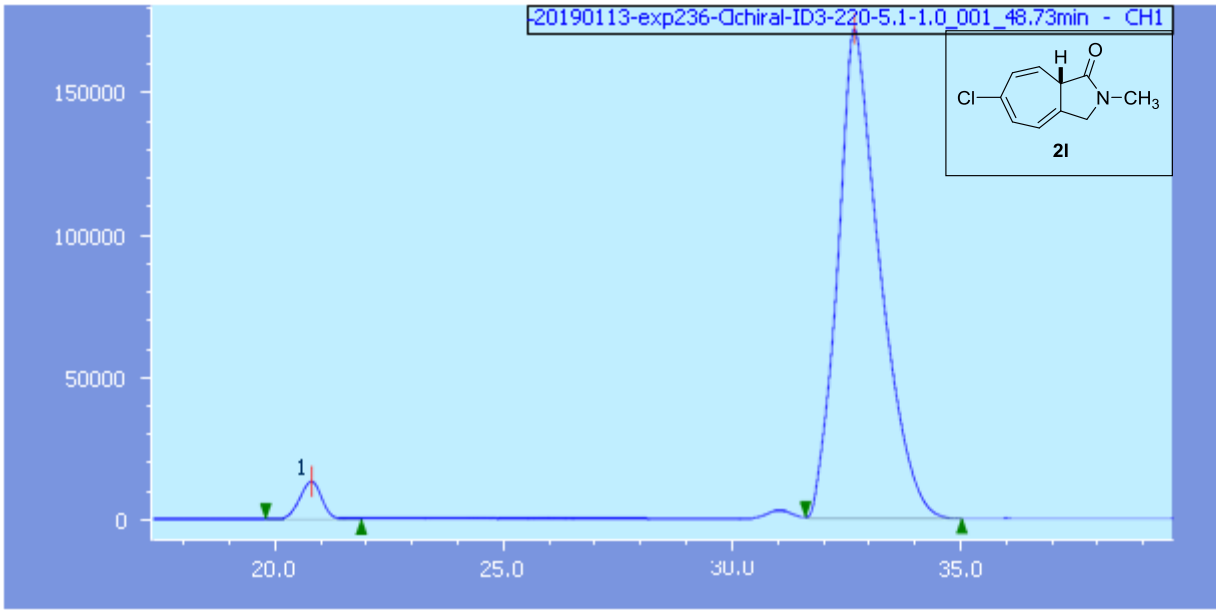
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	29.742	2845125	55576	50.019	50.264
2	32.675	2842914	54992	49.981	49.736



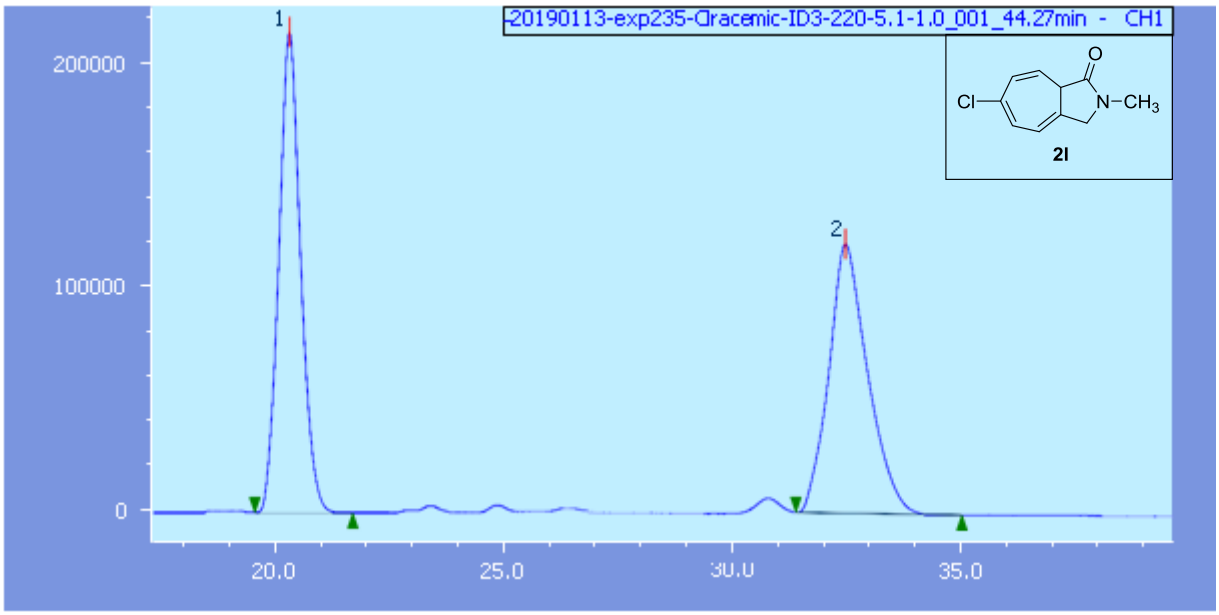
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	15.850	28737	1989	0.368	0.677
2	17.692	7782124	291612	99.632	99.323



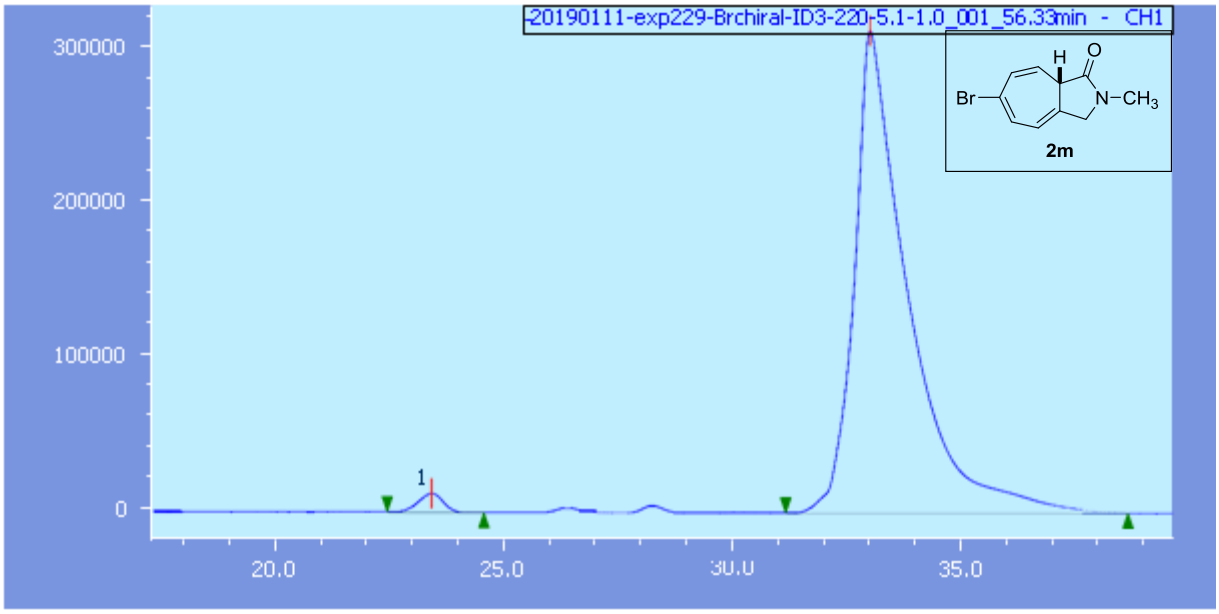
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	15.967	4407082	192794	49.790	52.096
2	18.017	4444247	177287	50.210	47.904



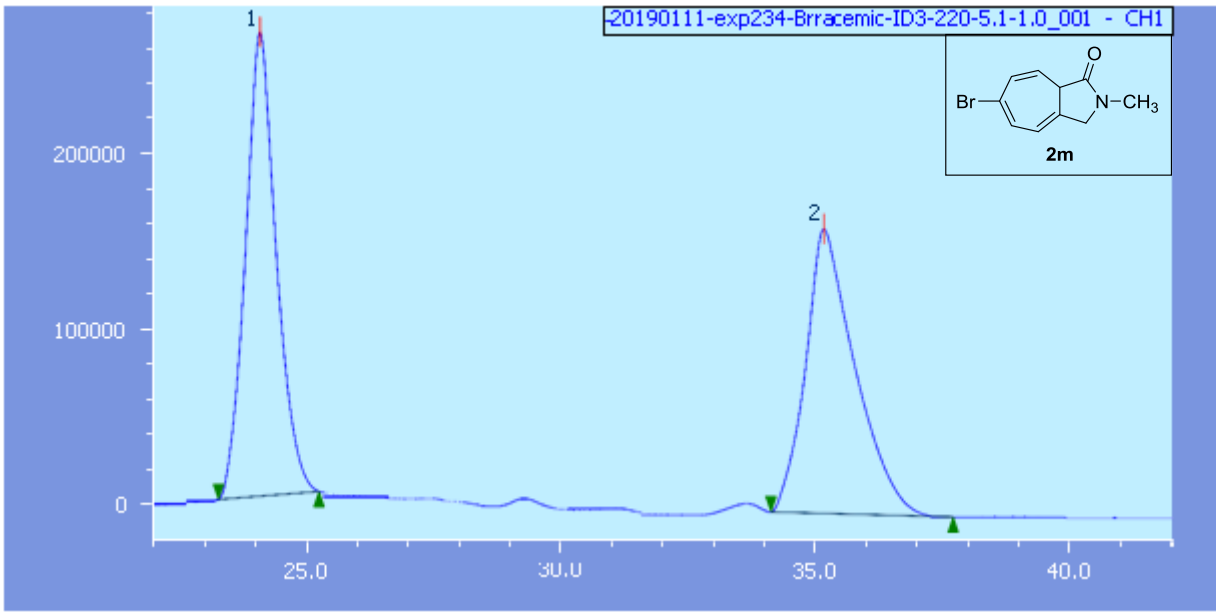
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.758	445946	13306	3.909	7.211
2	32.642	10963663	171225	96.091	92.789



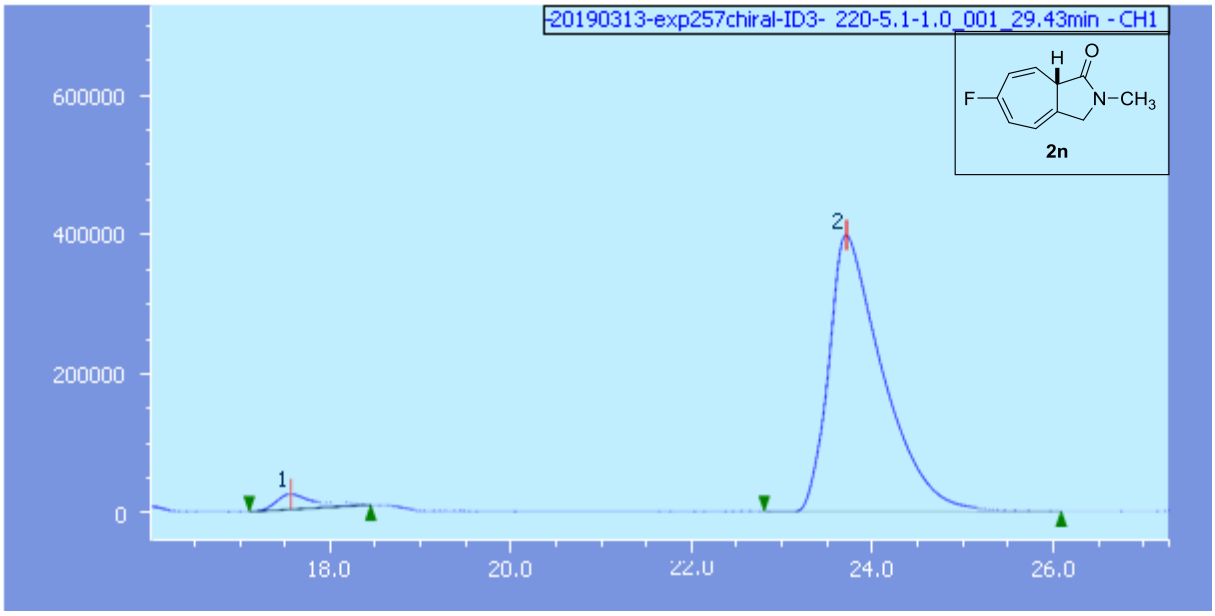
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.275	7136884	215242	50.024	64.095
2	32.442	7129926	120577	49.976	35.905



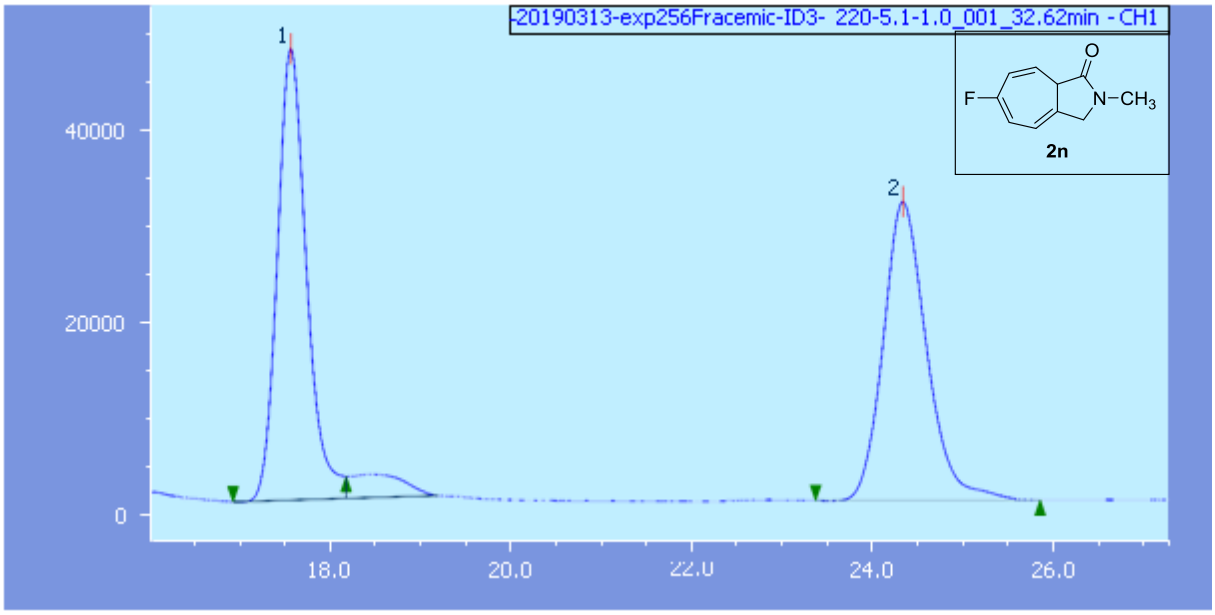
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	23.383	463948	12299	1.772	3.767
2	32.983	25721764	341184	98.228	96.233



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	24.050	11156150	264719	50.414	61.992
2	35.133	10973026	162302	49.586	38.008



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	17.558	677713	21987	3.961	5.259
2	23.700	16432700	396131	96.039	94.741



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	17.550	1055700	47015	50.449	60.178
2	24.317	1036894	31112	49.551	39.822