Supplementary Information

Triazenolysis of Alkenes: Aza-version of Ozonolysis

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Experimental Part

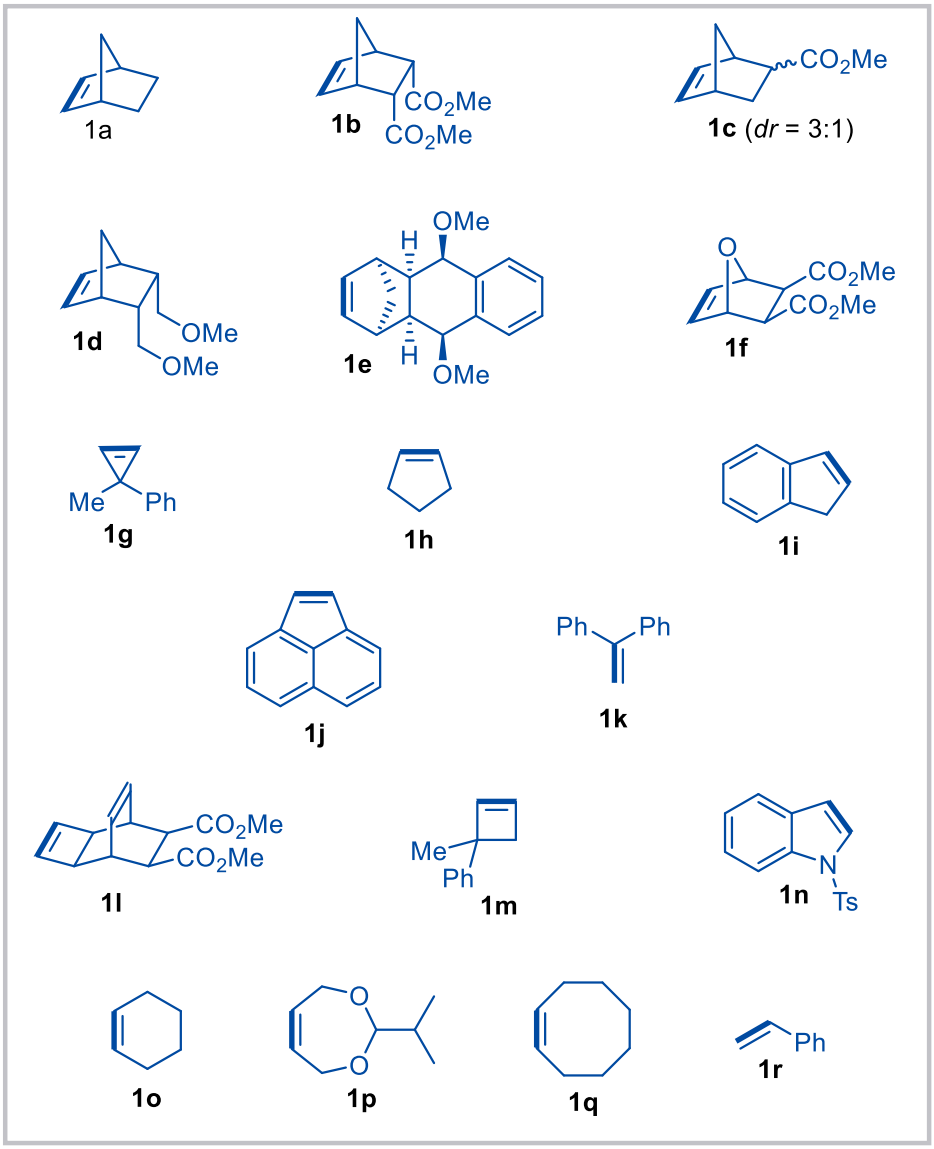
General Information

Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen using Schlenk line technique. Anhydrous THF, MeOH, toluene, DMF, dioxane, Et_2O, heptane packed under inert gas (argon) were used as purchased. All commercially available reagents were used as received. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 plates (particle size 0.040-0.055 mm, 230-400 mesh). NMR spectra were recorded on a Bruker AVII400 spectrometer at 296K. All chemical shifts (δ) are reported in parts per million (ppm) and the residual solvent peak was used as an internal standard for $^{1}H/^{13}C$ NMR: $CDCl_3$ δ=7.28/77.0, DMSO-*d*^{6} 2.50/40.0, C_6D_6 δ=7.16/128.0. ^{19}F signals were referenced to $CFCl_3$. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant(s) (Hz) and integration. In some of the NMR spectra, a signal is present at ~1.55 ppm ($CDCl_3$), ~3.33 (DMSO-*d*^{6}) or ~0.40 ppm (C_6D_6) due to water contamination of the deuterated solvent. High resolution mass spectrometry (HRMS) analyses were conducted on Waters HPLC Acquity - Waters LCT Premier system, using an electrospray ionization (ESI) technique (conditions: MeCN/H_2O (80/20), flow rate: 0.2 ml/min), or on Bruker Maxis Impact system, using an atmospheric-pressure chemical ionization ($APCI^+$) solid probe.

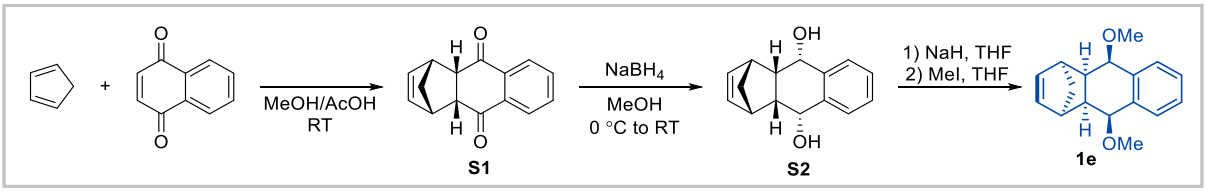
Synthesis of Starting Materials

Synthesis of Alkenes **1**

Alkenes **1a**, **1h-k**, **1o**, **1q** and **1r** were purchased and used as was without further purification. Compounds **1b**,[1,2] **1c**,[3] **1d**,[4] **1f**,[5] **1g**,[6] **1l**,[7] **1m**,[8,9] **1n**[10] and **1p**[11] were synthesized according to the reported procedures. Synthesis of **1e** is described below.



Synthesis of **1e**

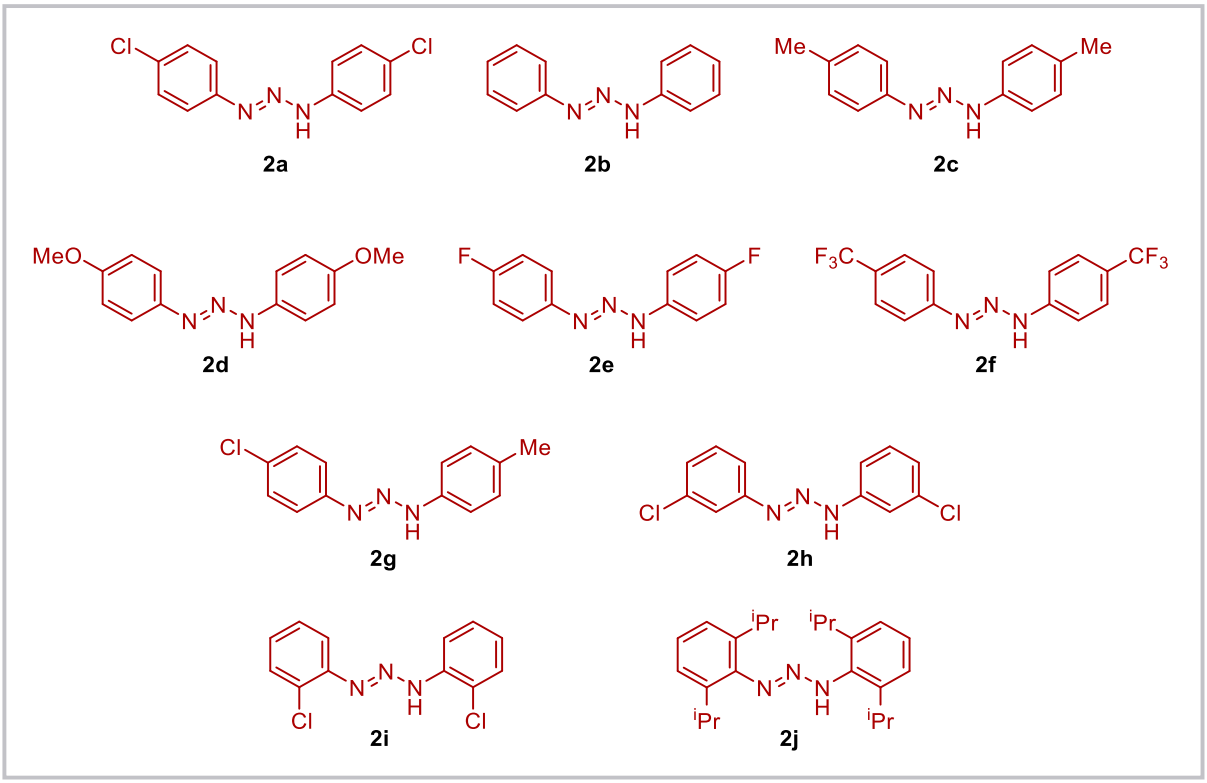


Compounds **S1**[12] and **S2**[13] were obtained by the known literature methods.

Synthesis of **1e***:*
Compound **S2** (10 mmol, 2.28 g, 1 eq) was added in one portion to the sodium hydride (1.2 g, 60% suspension in mineral oil, 3 eq) suspension in THF (20 ml, 0.5 M) at 0 °C. The reaction mixture was stirred 30 minutes at 0 °C and 3 hours at room temperature. The mixture was cooled to 0 °C and methyl iodide (5.48 g, 2.5 ml, 4 eq) was added dropwise. The reaction was allowed to warm to room temperature and was stirred overnight at RT. After the reaction completion (the completion was monitored by TLC analysis), the reaction was quenched at 0 °C with saturated $NaHCO_3$ (20 ml) and the water phase was extracted with EtOAc (2*20 ml). The combined organic phase was washed with brine and dried over Na_2SO_4. The product was purified by flash chromatography using EtOAc:Hex (1:6) as the eluent. White solid (2.15 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.23–7.19 (m, 2H), 5.06 (t, J = 1.6 Hz, 2H), 4.42–4.36 (m, 2H), 3.68 (s, 6H), 3.21–3.14 (m, 2H), 2.94–2.92 (m, 2H), 1.30 (d, J = 8.1 Hz, 1H), 1.24 (d, J = 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 133.2, 126.4, 121.9, 77.5, 58.0, 49.8, 44.7, 40.3. APCI [M + H]$^+$ calcd for $C_{17}H_{21}O_2^+$ 257.1536; found 257.1534.

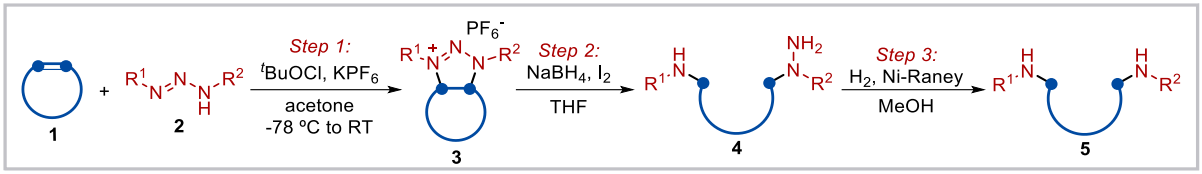
Synthesis of Triazenes **2**

Triazenes **2a-f**,[14] **2g**,[15] **2h**,[14] **2i**[14] and **2j**[16] were synthesized according to the methods reported previously.



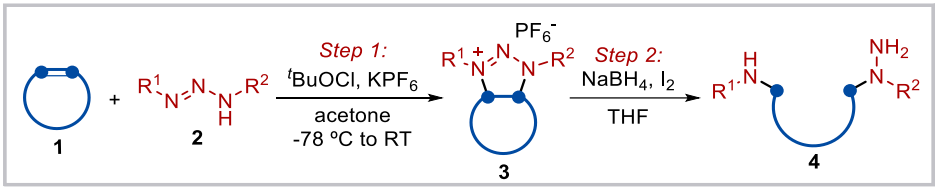
The Reaction Developed

General procedure A for synthesis of diamines 5



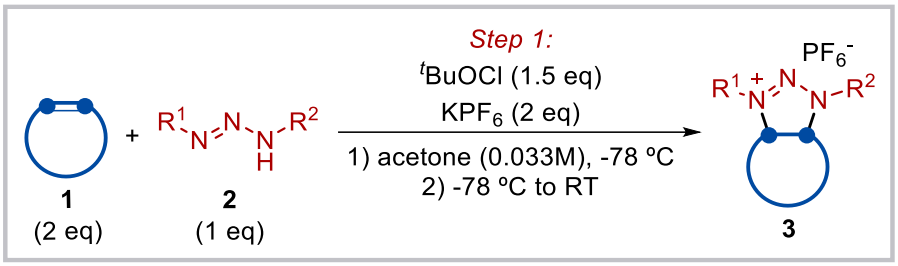
This reaction sequence required three consecutive steps (*Step 1, 2 and 3*) as described below. *Step 1* required small modification of the literature procedure.[17] It was needed to optimize *Step 2* as there was no precedent of such reaction in the literature. *Step 3* was carried out by the literature method.[18]

General procedure B for synthesis of compounds 4



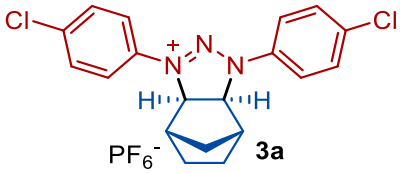
This reaction sequence required three consecutive steps (*Step 1 and 2*) as described below.

Step 1: standard procedure for triazolium salt **3** synthesis



1,3-Diaryl dihydrotriazolium salts **3** were synthesized according to the modified literature procedure.[17] The synthesized salts **3** were purified by wash as stated below and used in the next step without further purification. (3aR,4S,7R,7aS)-1,3-Dibenzyl-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanobenzo[d][1,2,3]triazol-3-ium trifluoromethanesulfonate was synthesized by the different literature method.[19]

Alkene **1** (4 mmol, 2 eq), triazene **2**[1] (2 mmol, 1 eq), KPF_6 (736 mg, 4 mmol, 2 eq) and acetone (60 ml, 0.033M[2]) were added to the Schlenk flask and nitrogen was bubbled for 10 minutes while the reaction mixture was cooled down to -78 °C with stirring (the reaction flask should be protected from light!). ^{t}BuOCl (0.3 ml[3], 234 mg, 1.1 eq) was added dropwise to the cooled solution and the reaction mixture was allowed to warm up to room temperature during the night in the dark. The reaction mixture was filtered through a sinter funnel (to remove KCl) and the precipitate was washed with acetone (until no triazolium was detected by TLC). The solution obtained was evaporated and diethyl ether (50 ml) was added to the solid remaining. The precipitate was triturated with spatula and then was subjected to ultrasound bath for 5 minutes. The precipitate was filtered and washed with Et_2O (3*50 ml) and with toluene (3*50 ml)[4]. The resulting solid was dried in vacuo and used in the next step without further purification. The salts **3** were not characterized except for **3a** as a one representative example shown below.



Example compound **3a** was obtained as a pure solid after it was washed extensively with water (alternatively it may be filtered through small celite pad in DCM). Yellow solid (99% yield). ^{1}H NMR (400 MHz, DMSO-*d*^{6}) δ 8.01 (d, *J* = 8.5 Hz, 4H), 7.76 (d, *J* = 8.5 Hz, 4H), 5.61 (s, 2H), 2.90 (s, 2H), 1.65–1.56 (m, 5H), 1.40 (d, *J* = 11.3 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-*d*^{6}) δ 134.8, 134.5, 130.7, 121.7, 72.9, 42.1, 32.8, 23.5; ^{19}F{^{1}H} NMR (377 MHz, DMSO-*d*^{6}) δ –70.13 (d, *J* = 712.2 Hz). APCI [M – PF_6]$^+$ calcd for $C_{19}H_{18}Cl_2N_3^+$ 358.0878; found 358.0872.

[1] The typical loading was 2 mmol relatively to **2**. The reaction may be scaled up to 10 mmol without yield loss (further scaling was not performed).
[2] The concentration of the triazene **2** is stated. The reaction may be concentrated up to 0.05M without yield drop (further concentration options were not checked).
[3] ^{t}BuOCl density is 0.781 g/ml.
[4] In some cases, the nitrenium cation **3** was soluble in toluene which has to be checked in advance.

Step 2: optimization of **4** synthesis

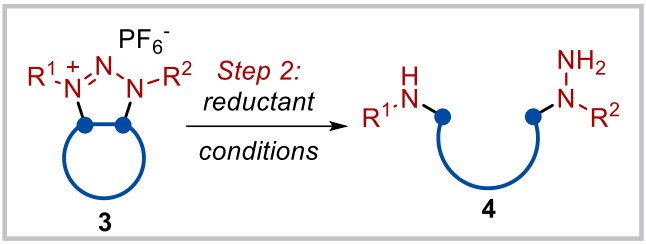


Table S1. Optimization of the *Step 2*.

entry	**Reductant** (5 eq) [b]	**solvent**	**temperature and time** [c]	**additives**	**Isolated yield of 4a (%)** [d]
1	$NaBH_4$	MeOH	1) RT, 1 h 2) 90 °C, 2 h	-	0
2	$NaBH_4$	THF	1) RT, 15 min 2) 90 °C, 15 min	-	81
3	$LiBH_4$	THF	1) RT, 15 min 2) reflux, 10 min	-	82
4	$LiAlH_4$	THF	1) RT, 15 min 2) 90 °C, 15 min	-	32
5	$PhSiH_3$	THF	1) RT, 15 min 2) 90 °C, 2 h	CsF (5 eq)[e]	0
6	$NaBH_4$	toluene	1) RT, 15 min 2) 90 °C, 2h	-	0
7	$NaBH_4$	DMF	1) 0 °C, 1 h 2) 90 °C, 2h	-	0
8	$NaBH_4$	dioxane	1) 0 °C, 1 h 2) 90 °C, 4h	-	12
9	$NaBH_4$	Et_2O	1) 0 °C, 1 h 2) reflux, 15h	-	61
10	$NaBH_4$	THF	1) RT, 15 min 2) reflux, 15 min	-	81
11	$NaBH_4$	THF	1) RT, 15 min 2) 40 °C, 1.5 h	-	77
12	$NaBH_4$	THF	RT, 24 h	-	75
13	$NaBH_4$ (3 eq)	THF	1) RT, 15 min 2) reflux, 15 min	-	64
14	$NaBH_4$ (6 eq)	THF	RT, 10 min	I_2 (1 eq) [f]	85
15	$NaBH_4$ (6 eq)	THF	RT, 1.5 h	I_2 (0.2 eq) [f]	81
16	$NaBH_4$ (6 eq)	THF	RT, 5 min	$BF_3 \times Et_2O$ (1 eq) [f]	72

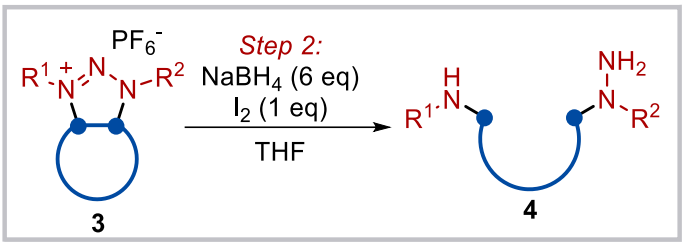
(The table continuation is on the next page)

Table S1 (continuation). Optimization of the *Step 2*.

Experiments which were not depicted in the manuscript (table 1)					
entry	**Reductant** (5 eq) [b]	**solvent**	**temperature and time** [c]	**additives**	**Isolated yield of 4a (%)** [d]
17	$NaBH_4$	MeOH	1) RT, 2 days	-	0
18	$LiAlH_4$	THF	1) RT, 15 min 2) 50 °C, 24 h	-	32
19	$NaBH_3CN$	THF	1) RT, 15 min 2) 90 °C, 2 h	-	0
20	$NaBEt_3H$	THF	1) RT, 15 min 2) 90 °C, 15 min	-	0
21	$BH_3{\times}SMe_2$	THF	1) RT, 15 min 2) 90 °C, 1.5 h	-	0 [g] (**5a**:43%)
22	$NaBH_4$	heptane	1) RT, 15 min 2) 90 °C, 2h	-	0
23	$NaBH_4$ (1.25 eq)	THF	1) RT, 25 min 2) reflux, 15 min	-	73
24	$NaBH_4$ (6 eq)	THF	1) RT, 15 min 2) 90 °C, 15 min	$ZnCl_2$ (2 eq) [f]	82
25	$NaBH_4$ (6 eq)	THF	1) RT, 15 min 2) 90 °C, 15 min	$AlCl_3$ (2 eq) [f]	0
26	$NaBH_4$ (6 eq)	THF	1) -41 °C 2) -41 °C to RT [h]	I_2 (1 eq) [f]	61
27	$NaBH_4$	THF	1) RT, 15 min 2) reflux, 15 min	KPF_6 (1.5 eq)	81

[a] Standard reaction conditions for *Step 2*: **3a** (0.2 mmol), reductant, additive, solvent (2 ml, 0.1 M).
[b] Unless otherwise stated.
[c] The sequence and interval of reaction is indicated: 1) – nitrenium was premixed with reductant for specific period of time; 2) – the reaction mixture was heated up to indicated temperature for specific period of time.
[d] Isolated yields are presented for two-step process.
[e] CsF was premixed with $PhSiH_3$ for 10 minutes.
[f] The additive was premixed with $NaBH_4$ at 0 °C for 5 minutes
[g] Compound **4a** was not detected in the reaction mixture, however, compound **5a** was isolated in 43% yield.
[h] $NaBH_4$ and I_2 were mixed at -41 °C, the reaction mixture was stirred for 15 min and then starting material **3a** was added in one portion. Reaction mixture was allowed to warm up to RT overnight.

Step 2: standard procedure for synthesis of compounds **4**



The Schlenk flask was dried and flushed with nitrogen. Afterwards, it was charged with $NaBH_4$ (46 mg, 1.2 mmol, 6 eq) and THF (2 ml, 0.1M[5]) and the suspension was cooled to 0 °C. Iodine (0.2 mmol, 51 mg, 1 eq) was added to the mixture and the solution was stirred for 5 minutes (until it became colorless). Then triazolium salt **3** (0.2 mmol, 1 eq[6]) was added to the reaction media and the cooling bath was removed. The reaction mixture was stirred for 15-90 minutes (until the solution became colorless and the reaction was finished; monitored by TLC).

Further, there were two methods to work-up the reaction mixture:

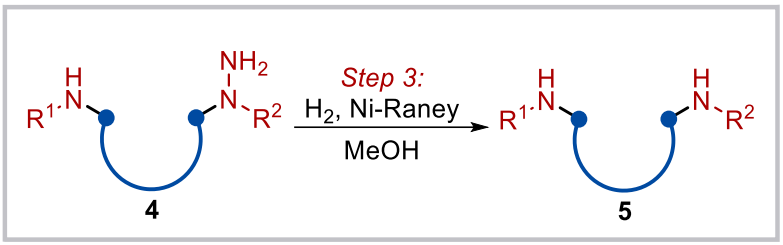
Method A: it was used if the hydrazine **4** was then subjected to further hydrogenation (*Step 3*). The reaction mixture was cautiously quenched with MeOH (1 ml) and then it was evaporated. The residue was dissolved in MeOH (0.05M respectively to **3**) and was used further in *Step 3*.

Method B: it was used if the hydrazine **4** is desired. The reaction mixture was quenched cautiously with $NaHCO_3$(saturated, 10 ml) and then the reaction mixture was extracted with EtOAc (3*15 ml). The combined organic layers were washed with brine (15 ml) and dried over Na_2SO_4. The solution was evaporated and subjected to column chromatography (Si-gel, celite dry loading, eluent as stated below).

NMR of compound **4** was highly dependent on the solvent and concentration. Presumably, compound **4** forms an internal carbamate or hydrocarbonate salt as was demonstrated previously,[21] therefore, NMR sometimes was broad or contained "impurities" of carbamate/hydrocarbonate salt. One example of such phenomena is presented for compound **4p** in NMR pictures.

[5] The concentration of the solvent was calculated respectively to triazolium salt **3**.
[6] Typical loading of the reaction was 0.2 mmol of **3**. The reaction was scaled up to 5 mmol (see the section "Gram Scale"). When the product **4a** was isolated on 5 mmol scale, the yield decreased twice (40% of **4a**), because product **4a** was not stable on silica-gel (**4a** decomposes to **5a** and other unknown compounds). However, the yield of 5 mmol reaction was consistent with 0.2 mmol reaction after hydrogenation (see the section "Gram Scale").

Step 3: standard procedure for hydrogenation of **4** to diamine **5**



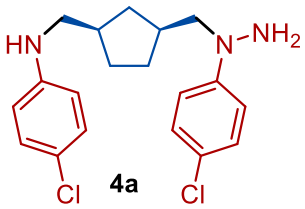
The methanol solution[7] of **4** was obtained from *Step 2*[8] (see above). Nitrogen was bubbled through the solution for 15 minutes and then Ni-Raney[9] was added (40 mg per 0.1 mmol of **4**). The atmosphere in the flask was changed to hydrogen and a balloon with hydrogen gas was attached to the flask. The reaction mixture was stirred overnight at room temperature and was filtered through Celite pad upon completion (monitored by TLC). The solution was evaporated and subjected to column chromatography (Si-gel, celite dry loading, eluent as stated below).

NMR of compound **5** was highly dependent on the solvent and concentration. Presumably, compound **5** forms an internal carbamate or hydrocarbonate salt as was demonstrated previously,[21] therefore, NMR sometimes was broad or contained "impurities" of carbamate/hydrocarbonate salt.

[7] If the THF solution of **4** or THF-MeOH (1:1) solution of **4** was used for hydrogenation *Step 3*, a yield drop and side products were detected.
[8] The typical loading was 0.2 mmol. The reaction may be scaled up to 5 mmol (see the section "Gram Scale").
[9] Ni-Raney was obtained from nickel-aluminum alloy by the literature method.[20] The catalyst was used as a slurry in MeOH and it was proved to be active during approximately three weeks (if the old catalyst was used, the yield drop and side products were detected).

Products **4** Characterization

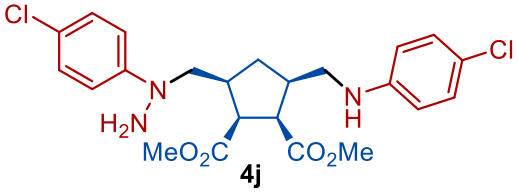
4-Chloro-N-(((1RS,3SR)-3-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentyl)methyl)aniline (**4a**)



4a

Product **4a** was synthesized from alkene **1a** triazene **2a** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:2. Pale yellow oil (62 mg, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2H), 7.15-7.12 (m, 2H), 6.93-6.91 (m, 2H), 6.55-6.53 (m, 2H), 3.78 (brs, 3H), 3.38-3.28 (m, 2H), 3.10-3.01 (m, 2H), 2.48-2.37 (m, 1H), 2.27-2.18 (m, 1H), 2.11-2.04 (m, 1H), 1.91-1.81 (m, 2H), 1.49-1.38 (m, 2H), 1.05-0.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 146.8, 129.0, 128.8, 122.9, 121.8, 114.3, 113.8, 61.3, 49.8, 39.3, 38.0, 36.4, 29.7, 29.4. APCI $[M+H]^+$ calcd for $C_{19}H_{24}Cl_2N_3^+$ 364.1342; found 364.1359.

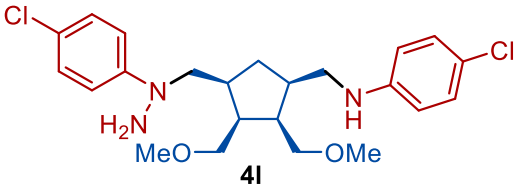
Dimethyl (1SR,2RS,3RS,5SR)-3-(((4-chlorophenyl)amino)methyl)-5-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentane-1,2-dicarboxylate (**4j**)



4j

Product **4j** was synthesized from alkene **1b** triazene **2a** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = 1:3. Pale yellow oil (52 mg, 54% yield).
^{1}H NMR (400 MHz, benzene-d^6-acetone d^6 mixture) δ 7.13–7.06 (m, 4H), 6.80–6.78 (m, 2H), 6.39–6.38 (d, 2H), 3.65–3.57 (m, 2H), 3.44 (s, 3H), 3.31 (s, 3H), 3.14–3.13 (m, 2H), 2.97–2.86 (m, 2H), 2.47–2.41 (m, 1H), 2.34–2.28 (m, 1H), 1.88–1.81 (m, 2H); ^{13}C NMR (101 MHz, benzene-d^6-acetone d^6 mixture) δ 173.7, 172.5, 150.0, 147.6, 129.2 (2C), 125.3, 121.2, 118.7, 113.9, 59.2, 51.2 (2C), 48.9 (2C), 45.3, 40.5, 40.0, 34.5. APCI $[M+H]^+$ calcd for $C_{23}H_{28}{}^{35}Cl_2N_3O_4^+$ 480.1451; found 480.1465.

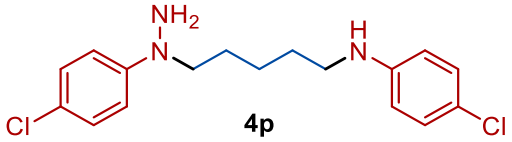
N,N'-(((1RS,3SR,4SR,5RS)-4,5-bis(methoxymethyl)cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**4l**)



4l

Product **4l** was synthesized from alkene **1d** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:2. Pale yellow oil (32 mg, 35% yield).
^{1}H NMR (400 MHz, benzene-*d*^{6}) *δ* 7.36–7.34 (m, 2H), 7.30–7.28 (m, 2H), 6.91–6.89 (m, 2H), 6.45–6.42 (m, 2H), 3.33–3.26 (m, 5H), 3.19–3.12 (m, 7H), 3.04–2.92 (m, 2H), 2.36–2.14 (m, 4H), 1.82–1.74 (m, 1H), 1.34–1.26 (m, 1H); ^{13}C NMR (101 MHz, benzene-*d*^{6}) *δ* 151.3, 147.7, 129.4, 129.1, 122.9, 121.7, 114.5, 113.9, 70.5 (2C), 58.4 (2C), 57.0, 46.0, 43.9, 43.6, 39.6, 37.8, 35.4. APCI [M+H]$^{+}$ calcd for $C_{23}H_{32}{}^{35}Cl_2N_3O_2^{+}$ 452.1866; found 452.1881.

4-chloro-N-(5-(1-(4-chlorophenyl)hydrazinyl)pentyl)aniline (**4p**)



4p

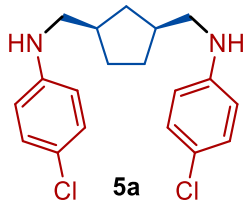
Product **4p** was synthesized from alkene **1h** triazene **2a** (0.2 mmol) by the different method:
Step 1 was performed as described above, *Step 2* was performed as follows.

Procedure of *Step 2*: The Schlenk flask was dried and flushed with nitrogen. Afterwards, it was charged with $NaBH_4$ (38 mg, 1 mmol, 5 eq) and THF (2 ml, 0.1M[10]). Then triazolium salt **3** (0.2 mmol, 1 eq[11]) was added to the reaction media and the reaction mixture was stirred for 15 (until the white suspension was formed). The reaction mixture was heated to reflux for 15 minutes until completion of the reaction (monitored by TLC). The reaction mixture was quenched cautiously with $NaHCO_3$(saturated, 10 ml) and then the reaction mixture was extracted with EtOAc (3*15 ml). The combined organic layers were washed with brine (15 ml) and dried over Na_2SO_4. The solution was evaporated and subjected to column chromatography (eluent for chromatography EtOAc:Hexane = from 1:4 to 1:2, celite dry loading). Pale yellow oil (31 mg, 46% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2H), 7.14-7.12 (m, 2H), 6.92-6.90 (m, 2H), 6.55-6.53 (m, 2H), 3.63 (brs, 3H), 3.40-3.36 (m, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 1.73-1.60 (m, 4H), 1.51-1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 146.7, 129.0, 128.8, 122.9, 121.8, 114.4, 113.8, 55.6, 44.0, 29.2, 25.6, 24.5. APCI [M+H]$^{+}$ calcd for $C_{17}H_{22}Cl_2N_3^{+}$ 338.1185; found 338.1217.

[10] The concentration of the solvent was calculated respectively to triazolium salt **3**.
[11] Typical loading of the reaction was 0.2 mmol of **3**. The reaction was scaled up to 5 mmol (see the section "Gram Scale"). When the product **4a** was isolated on 5 mmol scale, the yield decreased twice (40% of **4a**), because product **4a** was not stable on silica-gel (**4a** decomposes to **5a** and other unknown compounds). However, the yield of 5 mmol reaction was consistent with 0.2 mmol reaction after hydrogenation (see the section "Gram Scale").

Products **5** Characterization

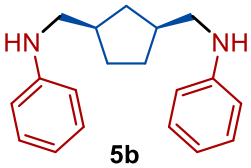
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5a**)



5a

Product **5a** was synthesized from alkene **1a** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:6. Pale yellow oil (56 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (m, 4H), 6.57-6.55 (m, 4H), 3.81 (brs, 2H), 3.10-3.02 (m, 2H), 2.30-2.19 (m, 2H), 2.16-2.10 (m, 1H), 1.95-1.82 (m, 2H), 1.48-1.37 (m, 2H), 0.98 (dt, *J* = 11.9, 9.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 129.0, 121.7, 113.7, 49.6, 39.4, 36.2, 29.5. APCI $[M+H]^+$ calcd for $C_{19}H_{23}Cl_2N_2^+$ 349.1238; found 349.1213.

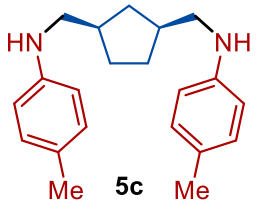
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))dianiline (**5b**)



5b

Product **5b** was synthesized from alkene **1a** triazene **2b** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:10. Pale yellow oil (37 mg, 66% yield).
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.23–7.19 (m, 4H), 6.74 (t, *J* = 7.3 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 4H), 3.14–3.06 (m, 4H), 2.31–2.22 (m, 2H), 2.17–2.13 (m, 1H), 1.92–1.86 (m, 2H), 1.48–1.40 (m, 2H), 1.05–0.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 148.0, 129.2, 117.6, 113.1, 49.8, 39.4, 36.3, 29.6. APCI $[M+H]^+$ calcd for $C_{19}H_{25}N_2^+$ 281.2012; found 281.2016.

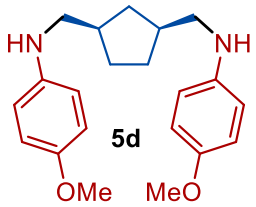
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methylaniline) (**5c**)



5c

Product **5c** was synthesized from alkene **1a** triazene **2c** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:10. Pale yellow oil (48 mg, 77% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.0 Hz, 4H), 6.59 (d, J = 8.4 Hz, 4H), 3.44 (br. s, 2H), 3.12–3.04 (m, 4H), 2.28–2.22 (m, 8H), 2.17–2.11 (m, 1H), 1.91–1.84 (m, 2H), 1.47–1.38 (m, 2H), 1.03–0.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 129.7, 126.7, 113.1, 50.1, 39.5, 36.3, 29.6, 20.3. APCI $[M+H]^+$ calcd for $C_{21}H_{29}N_2^+$ 309.2325; found 309.2302.

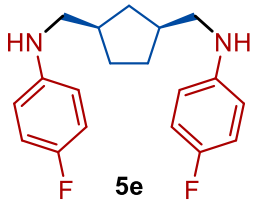
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methoxyaniline) (**5d**)



5d

Product **5d** was synthesized from alkene **1a** triazene **2d** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:3. Pale yellow oil (37 mg, 54% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82–6.79 (m, 4H), 6.64–6.62 (m, 4H), 3.77 (s, 3H), 3.09–3.01 (m, 4H), 2.28–2.11 (m, 3H), 1.91–1.83 (m, 2H), 1.46–1.37 (m, 2H), 1.03–0.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.3, 114.8, 114.3, 55.8, 50.8, 39.5, 36.3, 29.6. APCI $[M+H]^+$ calcd for $C_{21}H_{29}N_2O_2^+$ 341.2224; found 341.2234.

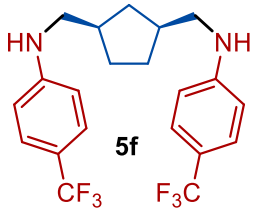
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5e**)



5e

Product **5e** was synthesized from alkene **1a** triazene **2e** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:8. Colorless solid (43 mg, 68% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94–6.90 (m, 3H), 6.59–6.55 (m, 3H), 3.46 (br.s, 1H), 3.10–3.01 (m, 4H), 2.29–2.11 (m, 3H), 1.94–1.86 (m, 2H), 1.47–1.38 M, 2H), 1.04–0.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (d, J = 234.7 Hz), 144.7 (d, J = 2.1 Hz), 115.6 (d, J = 22.1 Hz), 113.5 (d, J = 7.3 Hz), 50.3, 39.5, 36.2, 29.6. ^{19}F{^{1}H} NMR (377 MHz, CDCl3) δ –128.09. APCI $[M+H]^+$ calcd for $C_{19}H_{23}F_2N_2^+$ 1824; found 317.1825.

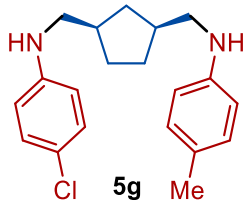
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5f**)



5f

Product **5f** was synthesized from alkene **1a** triazene **2f** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:8. Colorless solid (39 mg, 47% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 4H), 6.64 (d, J = 8.3 Hz, 4H), 4.09 (br. s, 2H), 3.18–3.09 (m, 4H), 2.32–2.25 (m, 2H), 2.19–2.13 (m, 1H), 1.94–1.88 (m, 2H), 1.48–1.39 (m, 2H), 1.05–0.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 126.6 (q, J = 3.8 Hz), 124.9 (q, J = 270.1 Hz), 118.9 (q, J = 33.1 Hz), 112.0, 49.1, 39.3, 36.1, 29.5; ^{19}F{^{1}H} NMR (377 MHz, CDCl3) δ –60.93. APCI $[M+H]^+$ calcd for $C_{21}H_{23}F_6N_2^+$ 417.1760; found 417.1782.

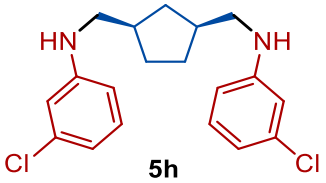
4-chloro-N-(((1RS,3SR)-3-((p-tolylamino)methyl)cyclopentyl)methyl)aniline (**5g**)



5g

Product **5g** was synthesized from alkene **1a** triazene **2g** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:8. Pale yellow oil (39 mg, 59% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (m, 2H), 7.04-7.02 (m, 2H), 6.62-6.60 (m, 2H), 6.55-6.53 (m, 2H), 3.57 (brs, 2H), 3.13-3.01 (m, 4H), 2.28-2.20 (m, 5H), 2.17-2.11 (m, 1H), 1.93-1.84 (m, 2H), 1.47-1.37 (m, 2H), 0.99 (dt, *J* = 12.0, 9.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 145.6, 129.7, 129.0, 126.9, 121.6, 113.7, 113.3, 50.2, 49.6, 39.4 (2C), 36.2, 29.6, 29.6, 20.4. APCI $[M+H]^+$ calcd for $C_{20}H_{26}ClN_2^+$ 329.1779; found 329.1777.

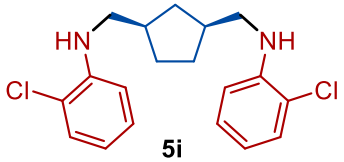
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(3-chloroaniline) (**5h**)



5h

Product **5h** was synthesized from alkene **1a** triazene **2h** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:8. Pale yellow oil (51 mg, 73% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.09 (m, 2H), 6.70-6.68 (m, 2H), 6.62-6.61 (m, 2H), 6.52-6.49 (m, 2H), 3.67 (brs, 2H), 3.11-3.03 (m, 4H), 2.30-2.20 (m, 2H), 2.17-2.10 (m, 1H), 1.93-1.85 (m, 2H), 1.48-1.37 (m, 2H), 0.98 (dt, *J* = 12.1, 9.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 135.0, 130.2, 117.3, 112.4, 111.3, 49.5, 39.3, 36.1, 29.5. APCI $[M+H]^+$ calcd for $C_{19}H_{23}Cl_2N_2^+$ 349.1233; found 349.1231.

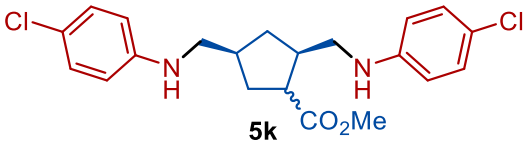
N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(2-chloroaniline) (**5i**)



5i

Product **5i** was synthesized from alkene **1a** triazene **2i** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:30. Pale yellow oil (22 mg, 32% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 2H), 7.20-7.16 (m, 2H), 6.74-6.66 (m, 4H), 4.43 (brs, 2H), 3.17 (d, *J* = 7.0 Hz, 1H), 2.41-2.30 (m, 2H), 2.26-2.19 (m, 1H), 1.98-1.92 (m, 2H), 1.55-1.46 (m, 2H), 1.10-1.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 129.1, 127.8, 119.2, 117.3, 111.5, 49.3, 39.3, 36.1, 29.6. APCI $[M+H]^+$ calcd for $C_{19}H_{23}Cl_2N_2^+$ 349.1233; found 349.1209.

Methyl (2RS,4SR)-2,4-bis(((4-chlorophenyl)amino)methyl)cyclopentane-1-carboxylate (**5k**)

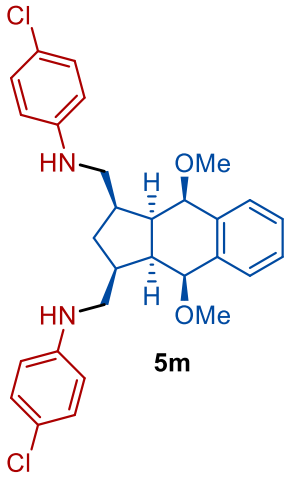


5k

(*dr* = 2.1:1)

Product **5k** was synthesized from alkene **1c** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:2. Pale yellow oil (25 mg, 31% yield, *dr* = 2.1:1).
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.14–7.12 (m, 12.45H), 6.58–6.52 (m, 12.45H), 3.71 (s, 3H), 3.67 (s, 6.34H), 3.19–2.98 (m, 14.56H), 2.68–2.62 (m, 1H), 2.58–2.50 (m, 3.11H), 2.41–2.31 (m, 3.11H), 2.25–2.02 (m, 6.23H), 1.85–1.72 (m, 3.11H), 1.42–1.34 (m, 2.11H), 1.15–1.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 176.2, 175.6, 146.5 (2C), 146.4, 146.3, 129.1 (2C), 129.0 (2C), 122.2 (2C), 122.0, 121.9, 114.0 (2C), 113.9, 113.7, 52.0, 51.7, 49.1, 48.8 (2C), 47.3, 45.7, 45.4, 43.3, 42.6, 38.5, 38.0, 36.3, 34.3, 33.9, 32.8. APCI $[M+H]^+$ calcd for $C_{21}H_{25}{}^{35}Cl_2N_2O_2^+$ 407.1288; found 407.1272.

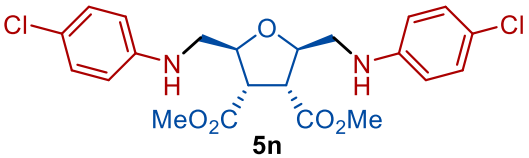
N,N'-(((1R,3S,3aS,4S,9R,9aR)-4,9-dimethoxy-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5m**)



5m

Product **5m** was synthesized from alkene **1e** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:4. Pale yellow oil (24 mg, 24% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.36–7.33 (m, 2H), 7.13–7.10 (m, 4H), 6.52–6.50 (m, 4H), 4.34–4.33 (m, 2H), 4.17 (br. s, 2H), 3.51–3.45 (m, 8H), 3.18 (dd, *J* = 13.1 and 6.9 Hz, 2H), 2.99–2.97 (m, 2H), 2.24–2.21 (m, 2H), 1.55–1.47 (m, 1H), 0.51–0.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 137.4, 129.0, 126.9, 124.1, 121.1, 113.8, 79.1, 57.9, 44.3, 42.9, 42.7, 36.3. APCI $[M+H]^+$ calcd for $C_{29}H_{33}{}^{35}Cl_2N_2O_2^+$ 511.1914; found 511.1918.

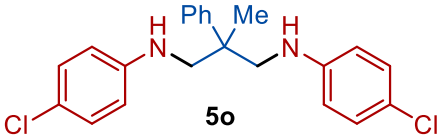
Dimethyl (2R,3R,4S,5S)-2,5-bis(((4-chlorophenyl)amino)methyl)tetrahydrofuran-3,4-dicarboxylate (**5n**)



5n

Product **5n** was synthesized from alkene **1f** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:2. Pale yellow oil (19 mg, 20% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.11 (m, 4H), 6.54–6.51 (m, 4H), 4.46–4.45 (m, 2H), 3.72 (s, 3H), 3.48 (dd, *J* = 13.5 and 3.2 Hz, 2H), 3.32 (dd, *J* = 13.5 and 5.0 Hz, 2H), 3.27–3.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 146.6, 129.1, 122.6, 114.2, 80.3, 52.3, 48.7, 46.7. APCI $[M+H]^+$ calcd for $C_{22}H_{25}{}^{35}Cl_2N_2O_5^+$ 467.1135; found 467.1152.

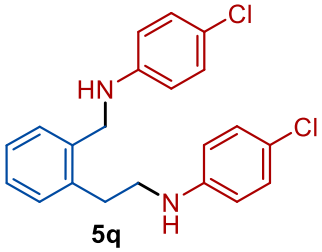
N^1,N^3-bis(4-chlorophenyl)-2-methyl-2-phenylpropane-1,3-diamine (**5o**)



5o

Product **5o** was synthesized from alkene **1g** triazene **2a** (0.2 mmol) by the general procedure B: no hydrogenation was required as extra NH_2-group was removed during the reaction and no compound **4p** was detected in the reaction mixture. Eluent for chromatography EtOAc:Hexane = 1:6. Pale yellow oil (54 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.31 (m, 5H), 7.12-7.10 (m, 4H), 6.55-6.53 (m, 4H), 4.09 (brm, 2H), 3.49 and 3.42 (ABq, *J* = 12.1 Hz, 2H+2H), 1.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 142.5, 129.1, 129.0, 127.2, 126.6, 122.7, 114.5, 53.4, 43.2, 23.4. APCI $[M+H]^+$ calcd for $C_{22}H_{23}Cl_2N_2^+$ 385.1238; found 385.1268.

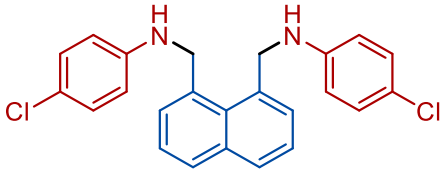
4-chloro-N-(2-(2-((4-chlorophenyl)amino)ethyl)benzyl)aniline (**5q**)



5q

Product **5q** was synthesized from alkene **1i** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:10. Pale yellow oil (51 mg, 68% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.21 (m, 4H), 7.17-7.08 (m, 4H), 6.57-6.52 (m, 4H), 4.24 (s, 2H), 3.81 (brs, 2H), 3.42 (t, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 145.7, 137.7, 136.6, 130.0, 129.5, 129.2, 129.1, 128.2, 127.0, 122.7, 122.6, 114.4, 114.0, 46.5, 45.4, 31.6. APCI $[M+H]^+$ calcd for $C_{21}H_{21}Cl_2N_2^+$ 371.1082; found 371.1079.

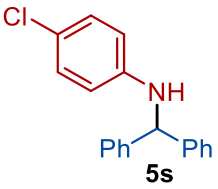
N,N'-(naphthalene-1,8-diylbis(methylene))bis(4-chloroaniline) (**5r**)



5r

Product **5r** was synthesized from alkene **1j** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:10. Pale yellow oil (30 mg, 37% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.59–7.57 (m, 2H), 7.51–7.47 (m, 2H), 7.13–7.11 (m, 4H), 6.49–6.46 (m, 4H), 4.71 (s, 4H), 3.86 (br. s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 134.3, 130.9, 130.5, 129.0, 125.5, 122.5, 114.1, 77.0, 49.5. APCI $[M+H]^+$ calcd for $C_{24}H_{21}{}^{35}Cl_2N_2^+$ 407.1076; found 407.1082.

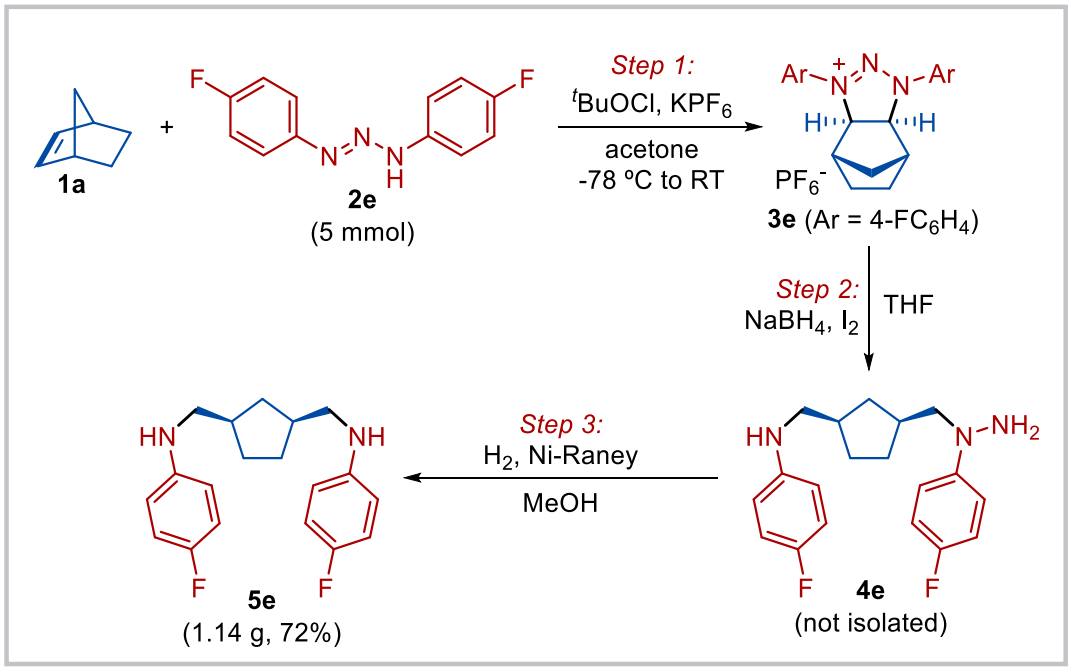
N-benzhydryl-4-chloroaniline (**5s**)



5s

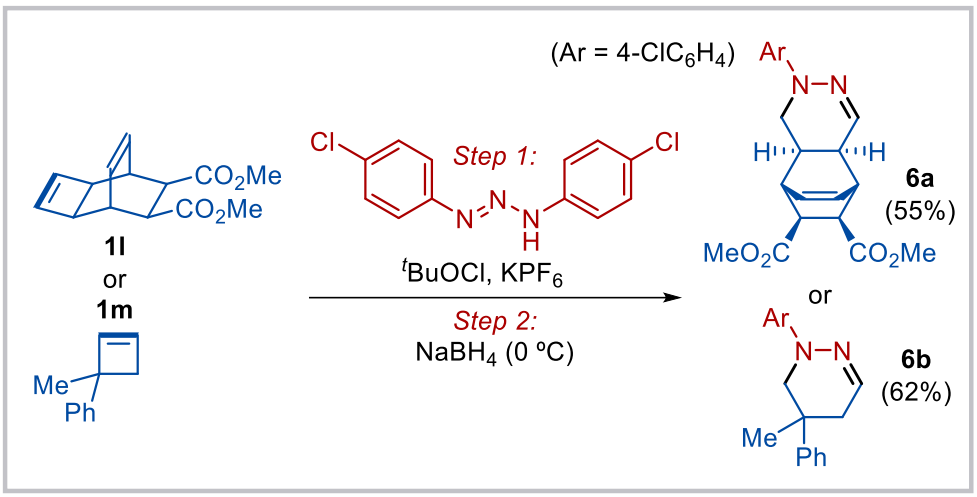
Product **5s** was synthesized from alkene **1k** triazene **2a** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:12. Pale yellow oil (26 mg, 45% yield). The NMR data matches the one previously reported.[22]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 10H), 7.08–7.06 (m, 2H), 6.49–6.47 (m, 2H), 5.47 (s, 1H), 4.36 (br. s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 142.3, 128.9, 128.8, 127.5, 127.4, 122.4, 114.6, 63.1.

Gram Scale Synthesis of **5e**



The reaction was performed according to the procedures described above on the scale of 5 mmol (**2e**, 1.17 g).
The final product was isolated by the flash column chromatography by the following eluent: EtOAc:Hex = 1:10 (until all the by-products are washed away, monitored by TLC) and then the desired product **5e** was washed from the column with EtOAc:Hex = 1:2 mixture. **5e** was obtained as a colorless oil (1.14 g, 72%).

Synthesis of Product 6



General Procedure for Synthesis of **6**:

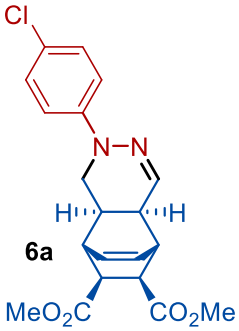
Step 1 was performed according to the standard procedure reported above.

Step 2 procedure:
The Schlenk flask was dried and flushed with nitrogen. Afterwards, it was charged with $NaBH_4$ (38 mg, 1 mmol, 5 eq) and THF (2 ml, 0.1M[12]) and the suspension was cooled to 0 °C. Then triazolium salt **3l** or **3m** (0.2 mmol,[13] 1 eq) was added to the reaction media. The reaction mixture was stirred for 10 minutes at 0 °C (the solution became completely colorless, monitored by TLC). Upon reaction completion, the remaining $NaBH_4$ was quenched with MeOH at 0 °C (1 ml, 15 min). The solvent was evaporated and MeOH was added under nitrogen atmosphere. Ni-Raney (40 mg per 0.1 mmol) was added and the atmosphere in the flask was changed to hydrogen. Reaction mixture was stirred overnight (the hydrogenation step was carried out to get rid of multiple by-products[14]; product **6** may be isolated in similar yield without this step). The reaction mixture was filtered through pad of Celite. The reaction mixture was evaporated, and column chromatography afforded product **6** (Si-gel, celite dry loading, eluent as stated below).

[12] The concentration of the solvent was calculated respectively to triazolium salt **3**.
[13] Typical loading of the reaction was 0.2 mmol of **3**. The reaction was scaled up to 0.5 mmol.
[14] The by-products exhibit similar R_f and isolation of the desired compound **6** becomes difficult without this step.

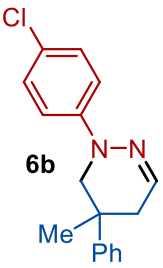
Products **6** Characterization

Dimethyl (4aSR,5RS,8SR,8aRS,9SR,10RS)-2-(4-chlorophenyl)-1,2,4a,5,8,8a-hexahydro-5,8-ethanophthalazine-9,10-dicarboxylate (**6a**)



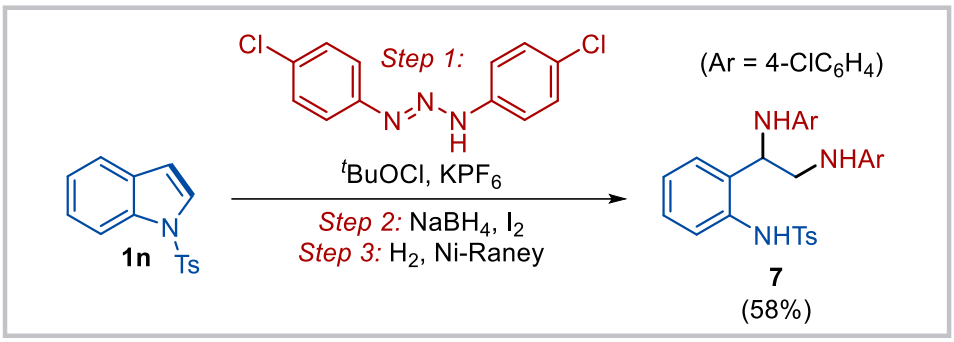
Product **6a** was synthesized from alkene **1l** and triazene **2a** (0.2 mmol) by the general procedure for synthesis of **6**. Eluent for chromatography EtOAc:Hexane = from 1:3 to 1:2. Pale yellow solid (43 mg, 55% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.21 (m, 2H), 7.10-7.08 (m, 2H), 6.85 (d, *J* = 1.6 Hz, 1H), 6.34-6.30 (m, 1H), 6.27-6.23 (m, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.53 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.22-3.15 (m, 3H), 2.97 (d, *J* = 5.7 Hz, 1H), 2.77 (dd, *J* = 11.6, 8.9 Hz, 1H), 2.64-2.58 (m, 1H), 2.39-2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 172.4, 147.6, 144.5, 132.0, 130.4, 128.7, 126.0, 117.0, 51.8, 51.8, 47.1, 46.9, 46.8, 39.1, 37.1, 36.2, 35.3. APCI $[M+H]^+$ calcd for $C_{20}H_{22}ClN_2O_4^+$ 389.1263; found 389.1273.

1-(4-chlorophenyl)-5-methyl-5-phenyl-1,4,5,6-tetrahydropyridazine (**6b**)



Product **6b** was synthesized from alkene **1m** and triazene **2a** (0.2 mmol) by the general procedure for synthesis of **6**. Eluent for chromatography EtOAc:Hexane = from 1:12 to 1:10. Pale yellow oil (35 mg, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.26 (m, 4H), 7.23-7.15 (m, 3H), 7.10-7.06 (m, 2H), 6.82 (dd, *J* = 3.5, 2.5 Hz, 1H), 3.58 (d, *J* = 2.5 Hz) and 3.48 (ABq, *J* = 11.7 Hz, 2H), 2.59 (d, *J* = 18.2 Hz, 1H), 2.26-2.20 (m, 1H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 146.0, 135.6, 128.8, 128.7, 126.8, 125.2, 124.9, 115.0, 53.7, 36.5, 33.3, 26.3. APCI $[M+H]^+$ calcd for $C_{17}H_{18}ClN_2^+$ 285.1159; found 285.1165.

Synthesis of Product 7



Step 1 was performed according to the slightly modified procedure reported above.

Step 1 Reaction Procedure: solutions A and B were prepared as stated below.

Solution A: Triazene **2a**[15] (266 mg, 1 mmol, 1 eq), KPF_6 (368 mg, 2 mmol, 2 eq) and acetone (30 ml, 0.033M)[16] were added to the Schlenk flask and nitrogen was bubbled for 10 minutes while the reaction mixture was cooled down to -78 °C with stirring (the reaction flask should be protected from light!). ^{t}BuOCl (0.2 ml[17], 163 mg, 1.5 eq) was added dropwise to the cooled solution and the reaction mixture was stirred for 1 h at -78 °C.

Solution B: Tosylindole **1n** (542 mg, 2 mmol, 2 eq) was dissolved in acetone (10 ml, 0.2 M) and the resulting solution was cooled to -30 °C.

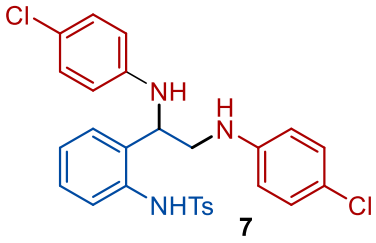
Solution B was added dropwise to solution A and the resulting mixture was allowed to warm up to -10 °C overnight. Then, acetone was evaporated from the reaction mixture under N_2 atmosphere and at 0 °C in the dark.[18] Degassed Et_2O (50 ml) was added and the mixture was triturated for some time under N_2 atmosphere and at 0 °C. Filtration under nitrogen atmosphere allowed the yellow solid which was dried in vacuo at 0 °C for 30 minutes and used without further purification.[19]

Step 2 and *Step 3* were performed according to the standard procedures reported above.

[15] The typical loading was 1 mmol relatively to **2a**. Further upscale was not performed.
[16] The concentration of the triazene **2a** is stated.
[17] ^{t}BuOCl density is 0.781 g/ml.
[18] In this case, product **3** is decomposing at higher temperatures, on the open air or with light.
[19] The next step has to be performed fast as the intermediate salt **3** is not stable in this case.

Product **7** Characterization

N-(2-(1,2-bis((4-chlorophenyl)amino)ethyl)phenyl)-4-methylbenzenesulfonamide (**7**)



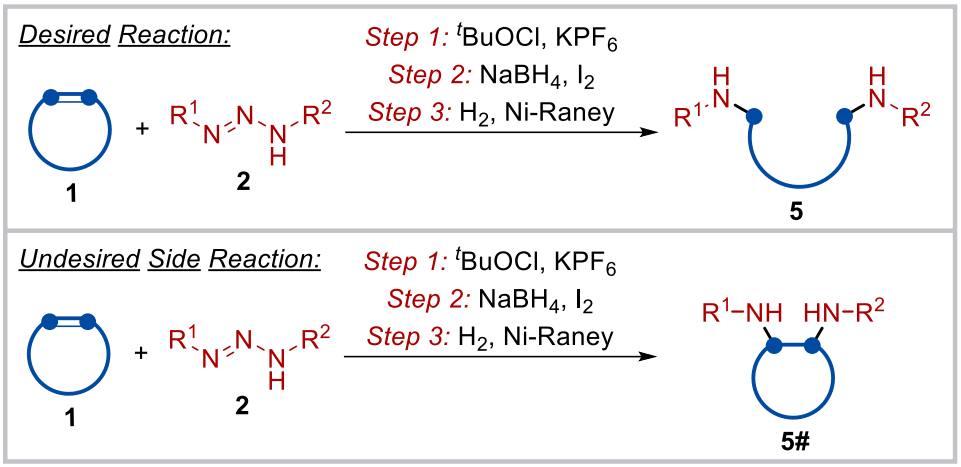
7

Product **7** was synthesized from indole **1n** and triazene **2a** (0.2 mmol) by the general procedure for synthesis of **7**. Eluent for chromatography EtOAc:Hexane =1:4. Colorless solid (61 mg, 58% yield).

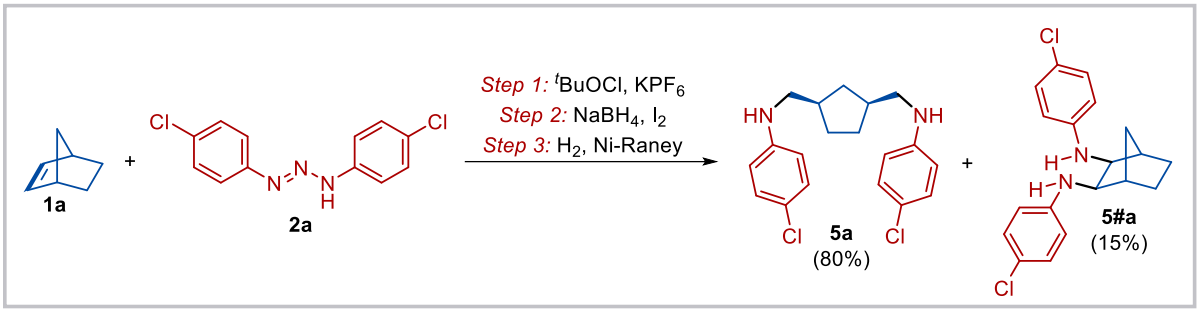
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (br. s, 1H), 7.48–7.46 (m, 2H), 7.43–7.40 (m, 1H), 7.26–7.21 (m, 2H), 7.16–7.11 (m, 3H), 7.09–7.06 (m, 2H), 7.00–6.98 (m, 2H), 6.65–6.62 (m, 2H), 6.52–6.50 (m, 2H), 4.57 (dd, *J* = 9.6 and 4.8 Hz, 1H), 3.52 (dd, *J* = 13.6 and 9.7 Hz, 1H), 3.37 (dd, *J* = 13.6 and 4.8 Hz, 1H), 2.35 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.8, 143.9, 136.5, 135.9, 129.5, 129.3, 129.1, 128.8, 128.2, 127.0, 125.2, 124.8, 123.9, 120.0, 116.9, 115.0 (2C), 58.5, 49.0, 21.5. APCI $[M+H]^+$ calcd for $C_{27}H_{26}{}^{35}Cl_2N_3O_2S^+$ 526.1117; found 526.1162.

Unsuccessful Results and Side Reactions

During the optimization and the scope evaluation, we observed undesired reactivity: compound **5#** was formed instead of or along with the expected product **5**. Below some essential results may be found of this undesired reaction. In some cases, the side product **5#** was the only one observed. Various modification and additional screenings of additives and conditions did not lead to desired reactivity in those cases.



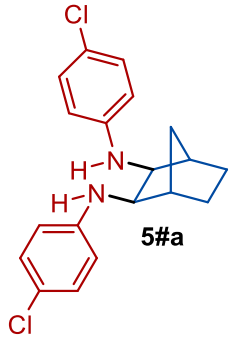
Side Reaction in Case of Alkene **1a** *and Triazene* **2a**



Reaction was performed according to the general conditions A for synthesis of compounds **5** reported above.

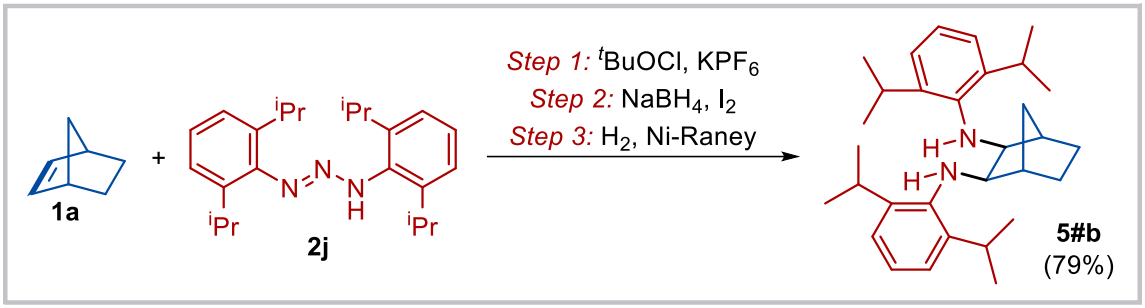
Characterization of the Side Product **5#a**

(1R,2S,3R,4S)-N2,N3-bis(4-chlorophenyl)bicyclo[2.2.1]heptane-2,3-diamine



The product **5#a** was synthesized from alkene **1a** and triazene **2a** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:6. Pale yellow oil (11 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.08 (m, 4H), 6.49-6.47 (m, 4H), 4.51 (brs, 2H), 3.34 (d, *J* = 1.3 Hz, 2H), 2.30 (s, 2H), 1.73-1.61 (m, 3H), 1.37-1.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.9, 129.0, 122.6, 114.7, 61.5, 42.2, 33.6, 26.3. APCI $[M+H]^+$ calcd for $C_{19}H_{21}Cl_2N_2^+$ 347.1076; found 347.1087.

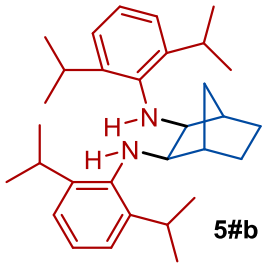
Side Reaction in Case of Alkene **1a** *and Triazene* **2j**



Reaction was performed according to the general conditions A for synthesis of compounds **5** reported above except that the reaction with $NaBH_4$ and I_2 was carried out at reflux in THF overnight and hydrogenation step required 5 days to completely convert corresponding hydrazine **4#b** to **5#b**.

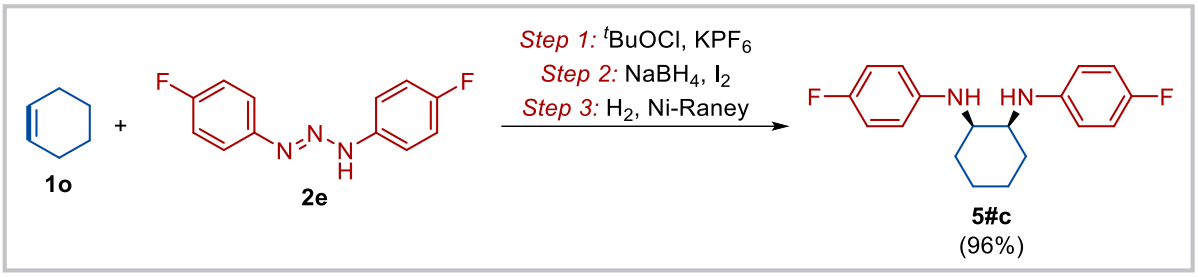
Characterization of the Side Product **5#b**

(1R,2S,3R,4S)-N2,N3-bis(2,6-diisopropylphenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#b**)



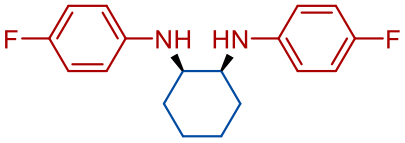
The product **5#b** was synthesized from alkene **1a** and triazene **2j** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:20. White solid (50 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 6H), 3.80 (s, 2H), 3.67 (hept, J = 6.8 Hz, 2H), 3.50 (hept, J = 6.7 Hz, 2H), 2.38 (d, J = 9.9 Hz, 1H), 2.16 (s, 2H), 1.51–1.32 (m, 15H), 1.22 (d, J =7.0 Hz, 6H), 1.19 (d, J = 7.0 Hz, 6H), 1.02 (d, J = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 147.1, 139.6, 126.2, 123.8, 123.3, 73.6, 39.8, 32.6, 28.4, 28.0, 25.9, 25.8, 25.3, 23.9, 23.0. APCI $[M+H]^+$ calcd for $C_{31}H_{47}N_2^+$ 447.3734; found 447.3776.

Side Reaction in Case of Alkene **1o** *and Triazene* **2e**



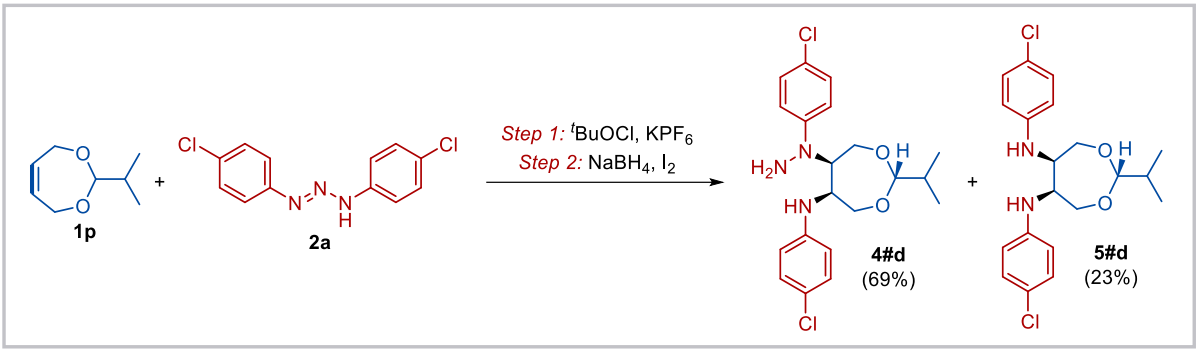
Reaction was performed according to the general conditions A for synthesis of compounds **5** reported above.

Characterization of the Side Product **5#c**
(1R,2S)-N1,N2-bis(4-fluorophenyl)cyclohexane-1,2-diamine(**5#c**)



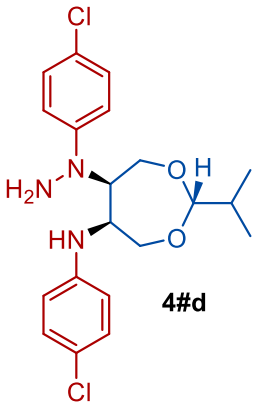
The product **5#e** was synthesized from alkene **1o** and triazene **2e** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:9. Pale yellow oil (58 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90–6.86 (m, 2H), 6.62–6.59 (m, 2H), 3.84 (br. s, 2H), 3.62–3.60 (m, 2H), 1.76–1.47 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0 (d, J = 235.6 Hz), 143.5, 115.7 (d, J = 22.1 Hz), 115.1 (d, J = 7.4 Hz), 53.6, 28.1, 22.1; ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –127.30. APCI $[M+H]^+$ calcd for $C_{18}H_{21}F_2N_2^+$ 303.1667; found 303.1667.

Undesired Reaction in Case of Alkene **1p** *and Triazene* **2a**



Reaction was performed according to the general conditions B for synthesis of compounds **4** reported above.

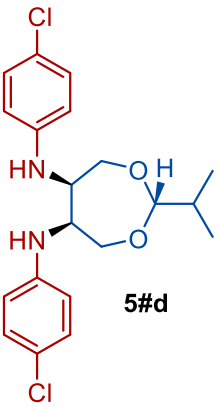
Characterization of the Side Product **4#d**
(2RS,5SR,6RS)-N-(4-chlorophenyl)-6-(1-(4-chlorophenyl)hydrazinyl)-2-isopropyl-1,3-dioxepan-5-amine



4#d

The product **4#d** was synthesized from alkene **1p** and triazene **2a** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:8. Pale yellow oil (57 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.22 (m, 2H), 7.01-6.99 (m, 2H), 6.84-6.82 (m, 2H), 6.36-6.34 (m, 2H), 4.44-4.39 (m, 1H), 4.33 (d, *J* = 7.2 Hz, 1H), 4.10-4.06 (m, 1H), 3.98-3.88 (m, 3H), 3.71 (d, *J* = 12.0 Hz, 1H), 2.00-1.91 (m, 1H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 145.1, 129.2, 129.1, 123.4, 122.8, 115.6, 114.1, 108.2, 66.8, 63.4, 62.2, 53.9, 31.8, 17.9, 17.8. APCI $[M+H]^+$ calcd for $C_{20}H_{26}Cl_2N_3O_2^+$ 410.1397; found 410.1427.

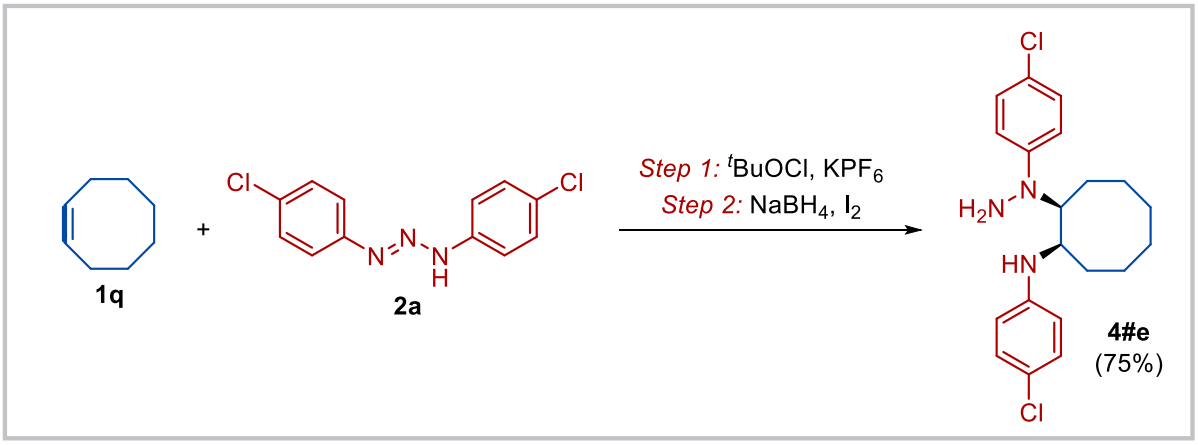
Characterization of the Side Product **5#d**
(2r,5R,6S)-N5,N6-bis(4-chlorophenyl)-2-isopropyl-1,3-dioxepane-5,6-diamine



5#d

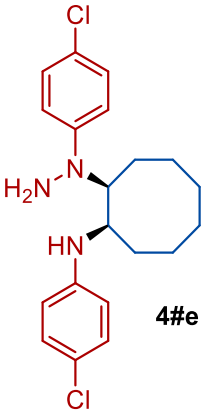
The product **5#d** was synthesized from alkene **1p** and triazene **2a** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:8. Pale yellow oil (18 mg, 23% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (m, 4H), 6.65-6.63 (m, 4H), 4.76 (brs, 2H), 4.35 (d, *J* = 7.3 Hz, 1H), 3.86-3.74 (m, 6H), 1.93-1.81 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.0, 129.3, 125.0, 115.7, 107.9, 64.2, 56.5, 31.8, 17.8. APCI $[M+H]^+$ calcd for $C_{20}H_{25}Cl_2N_2O_2^+$ 395.1288; found 395.1316.

Undesired Reaction in Case of Alkene **1q** *and Triazene* **2a**



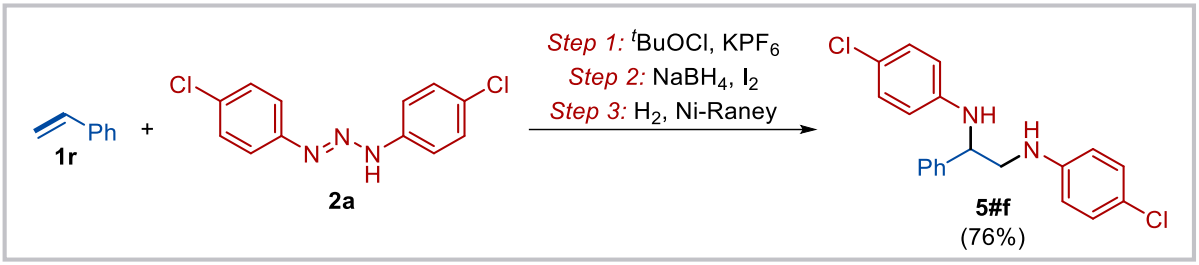
Reaction was performed according to the general conditions B for synthesis of compounds **4** reported above.

Characterization of the Side Product **4#e**
(1RS,2SR)-N-(4-chlorophenyl)-2-(1-(4-chlorophenyl)hydrazinyl)cyclooctan-1-amine



The product **4#e** was synthesized from alkene **1q** and triazene **2a** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:6. Pale yellow oil (57 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2H), 7.11-7.09 (m, 2H), 6.92-6.90 (m, 2H), 6.53-6.51 (m, 2H), 4.05-4.01 (m, 1H), 3.96 (brs, 3H), 3.85-3.83 (m, 2H), 2.22-2.00 (m, 2H), 1.90-1.60 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 145.2, 129.1, 128.9, 123.2, 122.3, 115.2, 114.6, 61.2, 54.4, 31.2, 27.3, 27.2, 25.2, 25.1, 24.2. APCI $[M+H]^+$ calcd for $C_{20}H_{26}Cl_2N_3^+$ 378.1498; found 378.1534.

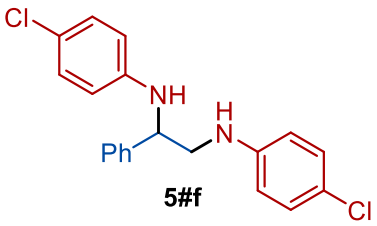
Side Reaction in Case of Alkene **1r** *and Triazene* **2a**



Reaction was performed according to the general conditions A for synthesis of compounds **5** reported above.

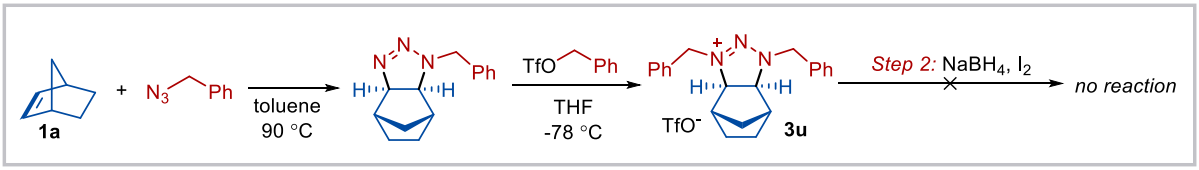
Characterization of the Side Product **5#f**

N1,N2-bis(4-chlorophenyl)-1-phenylethane-1,2-diamine (**5#f**)



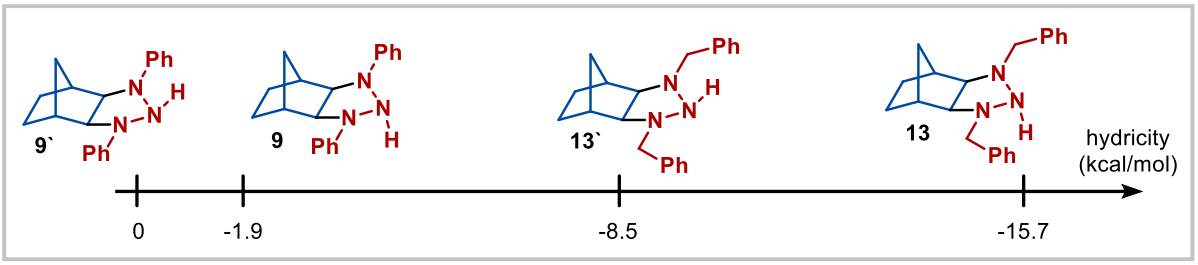
The product **5#f** was synthesized from alkene **1r** and triazene **2a** (0.2 mmol). Eluent for chromatography EtOAc:Hexane = 1:10. Colorless solid (54 mg, 76% yield). NMR data matches the one reported in the literature.[19] ^{1}H NMR (400 MHz, DMSO-d^6/$CDCl_3$ mixture) δ 7.32–7.17 (m, 5H), 7.02–7.00 (m, 2H), 6.88–6.86 (m, 2H), 6.57–6.55 (m, 2H), 6.42–6.40 (m, 2H), 4.49–4.45 (m, 1H), 4.35 (br. s, 2H), 3.33–3.26 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d^6/$CDCl_3$ mixture) δ 145.4, 145.1, 140.5, 128.1, 127.8, 127.7, 126.6, 125.6, 121.1, 120.3, 113.8, 113.7, 56.0, 50.0.

Unsuccessful Reaction in Case of Dibenzyl Nitrenium



Intermediate compound **3u** was synthesized by the literature procedure.[19]

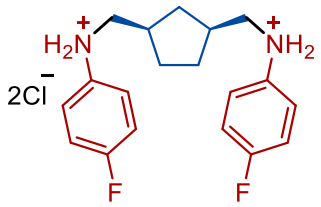
All the attempts to convert compound **3u** to the desired product failed. Presumably, Lewis acidity of **3u** is not substantial enough as we could not detect the formation of **13**/**13`** in the reaction mixture. In particular, from the scheme below obtained by calculations,[20] acidity of diphenyl substituted nitrenium should be higher comparatively to dibenzyl one (because the hydricities of **9** and **9`** are inferior to those of **13** and **13`**).



[20] For more information see the section "Calculations: Comparison of Relative Hydricity".

Crystallography

4-Fluoro-N-(((1S,3R)-3-(((4-fluorophenyl)-l4-azanyl)methyl)cyclo-pentyl)methyl)benzenaminium chloride (5e×2HCl)



5e×2HCl

Sample name: Gandelman80R (CCDC number 2290229)

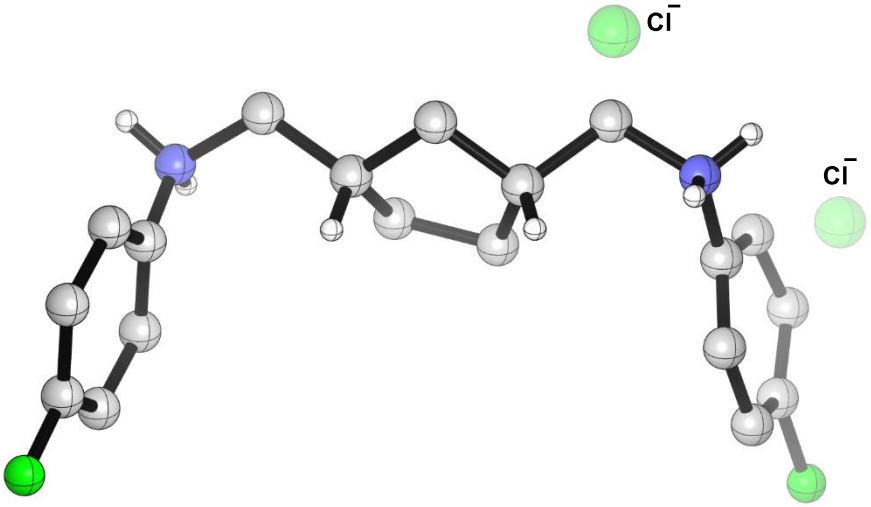


Table Cryst-1 Crystal data and structure refinement for Gandelman80R.

Identification code	Gandelman80R
Empirical formula	$C_{19}H_{24}Cl_2F_2N_2$
Formula weight	389.30
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	30.0058(15)
b/Å	16.2260(5)
c/Å	9.7741(2)
α/°	90
β/°	92.873(3)
γ/°	90
Volume/Å^3	4752.8(3)
Z	8
ρ_{calc}g/cm^3	1.088
μ/mm^{-1}	2.617
F(000)	1632.0
Crystal size/mm^3	0.33 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.194 to 160.488
Index ranges	-38 ≤ h ≤ 37, -20 ≤ k ≤ 20, -7 ≤ l ≤ 12
Reflections collected	22642
Independent reflections	4999 [R_{int} = 0.0905, R_{sigma} = 0.0986]
Data/restraints/parameters	4999/706/361
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0822, wR_2 = 0.2243
Final R indexes [all data]	R_1 = 0.1058, wR_2 = 0.2499
Largest diff. peak/hole / e Å^{-3}	0.89/-0.38

Table Cryst-2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman80R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl1	3419.7(4)	2515.0(5)	2589.0(8)	73.0(4)
Cl2	2512.4(3)	5019.9(5)	3097.7(8)	62.5(3)
F1	4648(5)	4291(11)	1469(19)	145(5)
F1A	4654(10)	4100(20)	850(50)	160(11)

Table Cryst-2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman80R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F2	4601(4)	10775(10)	4030(20)	143(5)
F2A	4592(7)	10975(12)	4930(40)	152(9)
N1	3197.1(10)	6094.3(15)	-429(2)	51.5(6)
N2	3173.7(10)	8894.9(15)	5585(2)	50.8(6)
C1	3251(3)	7148(5)	1395(9)	49(2)
C1A	3222(3)	6917(5)	1832(9)	45.8(18)
C2	2965(2)	7798(4)	2021(6)	53.6(16)
C2A	2943(2)	7220(4)	3027(6)	51.4(15)
C3	3218(4)	8084(7)	3306(10)	49(2)
C3A	3237(4)	7883(6)	3731(10)	47(2)
C4	3416(3)	7268(4)	3895(6)	53.5(16)
C4A	3504(3)	8269(4)	2596(7)	59.7(18)
C5	3532(3)	6765(4)	2617(6)	59.7(18)
C5A	3414(3)	7726(4)	1320(6)	55.8(17)
C6	2949.3(12)	6483(2)	699(3)	56.3(8)
C7	3583.0(12)	5597.9(18)	5(3)	53.0(7)
C8	4007.3(16)	5932(5)	-80(8)	66(2)
C9	4378.7(12)	5493(9)	420(13)	82(3)
C10	4326(3)	4721(9)	1005(15)	89(4)
C11	3901(3)	4387(5)	1091(13)	66(3)
C12	3530(2)	4826(3)	591(8)	55.3(16)
C8A	3993(7)	5819(14)	-380(30)	78(5)
C9A	4355(7)	5330(15)	-90(40)	92(6)
C10A	4244(9)	4601(13)	580(30)	81(5)
C11A	3821(10)	4313(12)	800(30)	67(5)
C12A	3473(8)	4864(9)	577(19)	53.0(7)
C13	2931.9(12)	8515(2)	4369(3)	54.3(7)
C14	3563(5)	9439(10)	5230(20)	53(3)
C14A	3531(6)	9375(16)	5350(30)	49(4)
C19A	3464(7)	10119(18)	4660(30)	53(4)
C18A	3817(8)	10661(13)	4540(30)	79(6)
C17A	4239(7)	10460(11)	5090(30)	99(6)
C16A	4307(6)	9717(12)	5780(30)	104(6)
C15A	3953(7)	9174(11)	5900(30)	73(5)
C15	3989(5)	9128(8)	5439(17)	73(3)
C16	4346(4)	9572(9)	5050(20)	95(4)
C17	4260(5)	10332(9)	4454(19)	94(4)

Table Cryst-2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman80R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C18	3842(6)	10649(9)	4260(20)	75(3)
C19	3483(6)	10202(12)	4650(20)	59(3)

Table Cryst-3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman80R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	140.8(10)	33.6(4)	45.3(4)	-9.5(3)	12.5(4)	-1.4(4)
Cl2	95.2(7)	45.9(5)	46.8(4)	-1.0(3)	8.3(4)	15.2(4)
F1	97(4)	141(8)	203(11)	79(7)	57(6)	77(5)
F1A	93(8)	112(14)	280(30)	92(16)	96(15)	64(9)
F2	84(4)	102(7)	240(13)	72(8)	-25(7)	-45(4)
F2A	98(7)	85(8)	270(20)	50(12)	-28(13)	-47(6)
N1	79.3(18)	32.2(12)	43.3(12)	3.4(9)	7.9(11)	1.2(11)
N2	78.2(18)	29.9(11)	45.3(12)	3.6(9)	11.6(11)	0.0(11)
C1	65(4)	33(4)	49(4)	3(3)	3(3)	7(3)
C1A	58(4)	31(4)	49(4)	-8(3)	10(4)	4(3)
C2	74(4)	38(3)	48(3)	-4(2)	-1(3)	13(3)
C2A	76(4)	33(3)	47(3)	-3(2)	18(3)	-8(3)
C3	60(4)	39(5)	48(5)	-3(3)	5(4)	4(4)
C3A	58(4)	32(4)	52(5)	-5(3)	9(4)	-1(3)
C4	75(4)	46(3)	40(3)	2(2)	12(2)	7(3)
C4A	75(4)	48(4)	57(4)	-7(3)	16(3)	-21(3)
C5	76(4)	54(4)	49(3)	-9(3)	-2(3)	23(3)
C5A	78(5)	42(3)	48(3)	-2(2)	15(3)	-7(3)
C6	67(2)	41.4(16)	61.1(17)	-12.7(13)	3.0(14)	8.6(14)
C7	79(2)	35.3(14)	45.6(15)	1.0(11)	14.9(13)	9.2(13)
C8	78(4)	47(4)	74(5)	6(3)	27(3)	9(3)
C9	66(4)	78(6)	105(7)	10(5)	34(4)	18(3)
C10	72(5)	89(6)	107(8)	25(6)	17(5)	34(5)
C11	86(6)	53(4)	61(6)	19(4)	20(4)	27(4)
C12	74(4)	37(2)	56(3)	8(2)	12(3)	7(3)
C8A	74(6)	59(8)	104(11)	20(8)	34(7)	18(6)
C9A	84(7)	74(9)	123(15)	29(10)	44(8)	29(6)
C10A	68(6)	61(7)	112(13)	20(7)	-9(9)	21(6)
C11A	77(6)	56(7)	66(10)	11(6)	-9(7)	13(5)
C12A	79(2)	35.3(14)	45.6(15)	1.0(11)	14.9(13)	9.2(13)

Table Cryst-3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman80R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	66(2)	36.8(15)	61.3(17)	-11.8(13)	12.4(14)	-3.7(13)
C14	76(4)	28(4)	55(6)	2(4)	5(4)	-15(3)
C14A	77(6)	31(7)	41(6)	7(5)	13(5)	-4(5)
C19A	69(7)	28(7)	62(10)	0(6)	2(7)	-5(6)
C18A	90(7)	50(8)	98(14)	13(7)	5(8)	-18(6)
C17A	84(7)	61(8)	152(15)	20(9)	2(10)	-27(6)
C16A	85(8)	70(9)	156(15)	28(10)	-5(10)	-15(6)
C15A	69(6)	60(7)	91(12)	31(7)	7(7)	-2(5)
C15	75(4)	53(4)	89(8)	23(4)	-11(5)	-13(3)
C16	65(4)	72(6)	147(10)	31(6)	-17(6)	-17(4)
C17	79(5)	67(5)	132(9)	27(6)	-16(6)	-26(4)
C18	95(5)	45(5)	83(6)	25(4)	-1(5)	-16(4)
C19	90(6)	31(5)	55(6)	5(4)	3(5)	-10(4)

Table Cryst-4 Bond Lengths for Gandelman80R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C10	1.259(14)	C7	C12	1.3900
F1A	C10A	1.49(4)	C7	C8A	1.353(19)
F2	C17	1.335(16)	C7	C12A	1.363(14)
F2A	C17A	1.37(2)	C8	C9	1.3900
N1	C6	1.499(4)	C9	C10	1.3900
N1	C7	1.456(4)	C10	C11	1.3900
N2	C13	1.494(4)	C11	C12	1.3900
N2	C14	1.518(14)	C8A	C9A	1.36(2)
N2	C14A	1.355(16)	C9A	C10A	1.40(2)
C1	C2	1.509(11)	C10A	C11A	1.38(2)
C1	C5	1.557(10)	C11A	C12A	1.38(2)
C1	C6	1.543(10)	C14	C15	1.382(13)
C1A	C2A	1.549(10)	C14	C19	1.376(9)
C1A	C5A	1.528(11)	C14A	C19A	1.3900
C1A	C6	1.517(9)	C14A	C15A	1.3900
C2	C3	1.509(12)	C19A	C18A	1.3900
C2A	C3A	1.532(13)	C18A	C17A	1.3900
C3	C4	1.549(11)	C17A	C16A	1.3900
C3	C13	1.548(12)	C16A	C15A	1.3900
C3A	C4A	1.534(11)	C15	C16	1.360(13)

Table Cryst-4 Bond Lengths for Gandelman80R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C3A	C13	1.528(11)	C16	C17	1.383(13)
C4	C5	1.547(8)	C17	C18	1.358(15)
C4A	C5A	1.540(9)	C18	C19	1.367(12)
C7	C8	1.3900			

Table Cryst-5 Bond Angles for Gandelman80R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C6	115.8(2)	C11	C10	C9	120.0
C13	N2	C14	113.8(8)	C10	C11	C12	120.0
C14A	N2	C13	117.3(13)	C11	C12	C7	120.0
C2	C1	C5	105.4(6)	C7	C8A	C9A	121.0(14)
C2	C1	C6	109.5(7)	C8A	C9A	C10A	112.4(17)
C6	C1	C5	110.1(6)	C9A	C10A	F1A	109(2)
C5A	C1A	C2A	101.6(6)	C11A	C10A	F1A	123(2)
C6	C1A	C2A	114.0(7)	C11A	C10A	C9A	127.1(16)
C6	C1A	C5A	111.0(6)	C10A	C11A	C12A	116.7(14)
C1	C2	C3	106.2(7)	C7	C12A	C11A	115.7(14)
C3A	C2A	C1A	104.0(7)	N2	C13	C3	117.1(5)
C2	C3	C4	102.4(7)	N2	C13	C3A	108.9(5)
C2	C3	C13	115.0(8)	C15	C14	N2	118.0(11)
C13	C3	C4	110.6(6)	C19	C14	N2	119.9(11)
C2A	C3A	C4A	105.7(7)	C19	C14	C15	122.0(8)
C13	C3A	C2A	108.2(8)	N2	C14A	C19A	118.9(16)
C13	C3A	C4A	111.5(7)	N2	C14A	C15A	120.8(16)
C5	C4	C3	104.4(6)	C19A	C14A	C15A	120.0
C3A	C4A	C5A	106.1(6)	C18A	C19A	C14A	120.0
C4	C5	C1	105.9(6)	C17A	C18A	C19A	120.0
C1A	C5A	C4A	106.2(6)	F2A	C17A	C18A	120.5(16)
N1	C6	C1	108.5(5)	F2A	C17A	C16A	119.4(16)
N1	C6	C1A	117.6(4)	C18A	C17A	C16A	120.0
C8	C7	N1	119.0(4)	C17A	C16A	C15A	120.0
C8	C7	C12	120.0	C16A	C15A	C14A	120.0
C12	C7	N1	120.9(3)	C16	C15	C14	120.0(8)
C8A	C7	N1	119.5(9)	C15	C16	C17	117.2(9)
C8A	C7	C12A	126.0(13)	F2	C17	C16	118.8(12)
C12A	C7	N1	113.5(10)	F2	C17	C18	118.1(11)

Table Cryst-5 Bond Angles for Gandelman80R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C8	C9	120.0	C18	C17	C16	123.2(9)
C8	C9	C10	120.0	C17	C18	C19	119.7(8)
F1	C10	C9	123.1(12)	C18	C19	C14	117.9(8)
F1	C10	C11	116.9(12)				

Table Cryst-6 Torsion Angles for Gandelman80R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C10	C11	C12	-179.6(10)	C6	C1A	C5A	C4A	156.7(6)
F1A	C10A	C11A	C12A	176(2)	C7	N1	C6	C1	68.0(5)
F2	C17	C18	C19	178.0(12)	C7	N1	C6	C1A	46.5(5)
F2A	C17A	C16A	C15A	-177.6(19)	C7	C8	C9	C10	0.0
N1	C7	C8	C9	175.3(5)	C7	C8A	C9A	C10A	2(4)
N1	C7	C12	C11	-175.2(5)	C8	C7	C12	C11	0.0
N1	C7	C8A	C9A	-174.4(19)	C8	C9	C10	F1	179.6(11)
N1	C7	C12A	C11A	169.7(14)	C8	C9	C10	C11	0.0
N2	C14	C15	C16	175.7(13)	C9	C10	C11	C12	0.0
N2	C14	C19	C18	-176.0(16)	C10	C11	C12	C7	0.0
N2	C14A	C19A	C18A	173(2)	C12	C7	C8	C9	0.0
N2	C14A	C15A	C16A	-173(2)	C8A	C7	C12A	C11A	1(2)
C1	C2	C3	C4	-39.7(9)	C8A	C9A	C10A	F1A	180(2)
C1	C2	C3	C13	-159.8(7)	C8A	C9A	C10A	C11A	8(4)
C1A	C2A	C3A	C4A	30.8(9)	C9A	C10A	C11A	C12A	-13(4)
C1A	C2A	C3A	C13	150.4(6)	C10A	C11A	C12A	C7	8(2)
C2	C1	C5	C4	-4.1(9)	C12A	C7	C8A	C9A	-7(3)
C2	C1	C6	N1	153.5(5)	C13	N2	C14	C15	-103.5(13)
C2	C3	C4	C5	36.2(9)	C13	N2	C14	C19	73.6(10)
C2	C3	C13	N2	-173.2(5)	C13	N2	C14A	C19A	67.3(14)
C2A	C1A	C5A	C4A	35.1(8)	C13	N2	C14A	C15A	-119.4(17)
C2A	C1A	C6	N1	-173.9(5)	C13	C3	C4	C5	159.3(7)
C2A	C3A	C4A	C5A	-9.0(9)	C13	C3A	C4A	C5A	-126.3(8)
C2A	C3A	C13	N2	151.7(5)	C14	N2	C13	C3	48.9(9)
C3	C4	C5	C1	-19.8(9)	C14	C15	C16	C17	0.5(19)
C3A	C4A	C5A	C1A	-16.7(9)	C14A	N2	C13	C3A	67.0(14)
C4	C3	C13	N2	71.4(9)	C14A	C19A	C18A	C17A	0.0
C4A	C3A	C13	N2	-92.4(7)	C19A	C14A	C15A	C16A	0.0
C5	C1	C2	C3	27.5(9)	C19A	C18A	C17A	F2A	177.5(19)
C5	C1	C6	N1	-91.1(7)	C19A	C18A	C17A	C16A	0.0

Table Cryst-6 Torsion Angles for Gandelman80R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5A	C1A	C2A	C3A	-40.5(8)	C18A	C17A	C16A	C15A	0.0
C5A	C1A	C6	N1	72.1(7)	C17A	C16A	C15A	C14A	0.0
C6	N1	C7	C8	-101.6(5)	C15A	C14A	C19A	C18A	0.0
C6	N1	C7	C12	73.7(5)	C15	C14	C19	C18	1.0(13)
C6	N1	C7	C8A	-118.2(18)	C15	C16	C17	F2	-178.3(12)
C6	N1	C7	C12A	72.7(10)	C15	C16	C17	C18	1(2)
C6	C1	C2	C3	145.8(7)	C16	C17	C18	C19	-1(2)
C6	C1	C5	C4	-122.1(7)	C17	C18	C19	C14	0.1(15)
C6	C1A	C2A	C3A	-159.9(7)	C19	C14	C15	C16	-1.4(16)

Table Cryst-7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman80R.

Atom	*x*	*y*	*z*	U(eq)
H1A	3004	5770	-933	62
H1B	3290	6501	-989	62
H2AA	3277	8486	6153	61
H2AB	2977	9201	6050	61
H2BC	2975	9205	6035	61
H2BD	3267	8481	6160	61
H1	3450	7401	719	59
H1AA	3468	6550	2191	55
H2A	2672	7564	2244	64
H2B	2913	8263	1378	64
H2AC	2655	7454	2679	62
H2AD	2885	6764	3667	62
H3	3466	8458	3057	59
H3A	3443	7631	4450	56
H4A	3687	7375	4491	64
H4B	3195	6973	4432	64
H4AA	3826	8275	2866	72
H4AB	3404	8841	2412	72
H5A	3454	6177	2734	72
H5B	3855	6806	2460	72
H5AA	3199	7998	665	67
H5AB	3694	7624	855	67
H6A	2871	6060	1376	68
H6B	2670	6737	319	68

Table Cryst-7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman80R.

Atom	*x*	*y*	*z*	U(eq)
H8	4044	6459	-481	79
H9	4669	5721	361	99
H11	3865	3860	1492	79
H12	3240	4598	650	66
H8A	4029	6322	-862	94
H9A	4650	5469	-316	111
H11A	3771	3763	1089	80
H12A	3177	4739	808	64
H13A	2755	8952	3889	65
H13B	2719	8105	4705	65
H19A	3176	10256	4285	63
H18A	3771	11170	4068	95
H16A	4595	9579	6155	125
H15A	3999	8665	6372	88
H15	4033	8604	5858	87
H16	4642	9368	5180	115
H18	3800	11178	3862	89
H19	3188	10412	4521	71

Table Cryst-8 Atomic Occupancy for Gandelman80R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F1	0.67(3)	F1A	0.33(3)	F2	0.62(3)
F2A	0.38(3)	H2AA	0.62(3)	H2AB	0.62(3)
H2BC	0.38(3)	H2BD	0.38(3)	C1	0.504(5)
H1	0.504(5)	C1A	0.496(5)	H1AA	0.496(5)
C2	0.504(5)	H2A	0.504(5)	H2B	0.504(5)
C2A	0.496(5)	H2AC	0.496(5)	H2AD	0.496(5)
C3	0.504(5)	H3	0.504(5)	C3A	0.496(5)
H3A	0.496(5)	C4	0.504(5)	H4A	0.504(5)
H4B	0.504(5)	C4A	0.496(5)	H4AA	0.496(5)
H4AB	0.496(5)	C5	0.504(5)	H5A	0.504(5)
H5B	0.504(5)	C5A	0.496(5)	H5AA	0.496(5)
H5AB	0.496(5)	C8	0.67(3)	H8	0.67(3)
C9	0.67(3)	H9	0.67(3)	C10	0.67(3)
C11	0.67(3)	H11	0.67(3)	C12	0.67(3)
H12	0.67(3)	C8A	0.33(3)	H8A	0.33(3)

Table Cryst-8 Atomic Occupancy for Gandelman80R.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C9A	0.33(3)	H9A	0.33(3)	C10A	0.33(3)
C11A	0.33(3)	H11A	0.33(3)	C12A	0.33(3)
H12A	0.33(3)	C14	0.62(3)	C14A	0.38(3)
C19A	0.38(3)	H19A	0.38(3)	C18A	0.38(3)
H18A	0.38(3)	C17A	0.38(3)	C16A	0.38(3)
H16A	0.38(3)	C15A	0.38(3)	H15A	0.38(3)
C15	0.62(3)	H15	0.62(3)	C16	0.62(3)
H16	0.62(3)	C17	0.62(3)	C18	0.62(3)
H18	0.62(3)	C19	0.62(3)	H19	0.62(3)

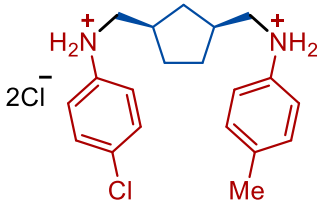
Table Cryst-9 Solvent masks information for Gandelman80R.

Number	**X**	**Y**	**Z**	**Volume**	**Electron count**	**Content**
1	0.000	0.255	-0.867	197.0	62.0	0.25 Dichloroethane
2	0.000	0.745	-0.382	197.0	62.0	0.25 Dichloroethane
3	0.500	0.245	-0.403	197.0	62.0	0.25 Dichloroethane
4	0.500	0.755	-0.971	197.0	62.0	0.25 Dichloroethane

Experimental

Single crystals of **5e**×2HCl [Gandelman80R] were obtained from slow diffusion between DCE/MeOH solution of **5e**×2HCl and EtOAc/Et_2O at RT. A suitable crystal was selected and measured on Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[23] the structure was solved with the olex2.solve[24] structure solution program using Charge Flipping and refined with the SHELXL[25] refinement package using Least Squares minimisation. The graphic representation was obtained with CYLview20 software.[26]

4-Chloro-N-(((1RS,3SR)-3-((p-tolylammonio)methyl)cyclo-pentyl)methyl)benzenaminium (5g×2HCl)



5g×2HCl

Sample name: Gandelman78R (CCDC number 2290228)

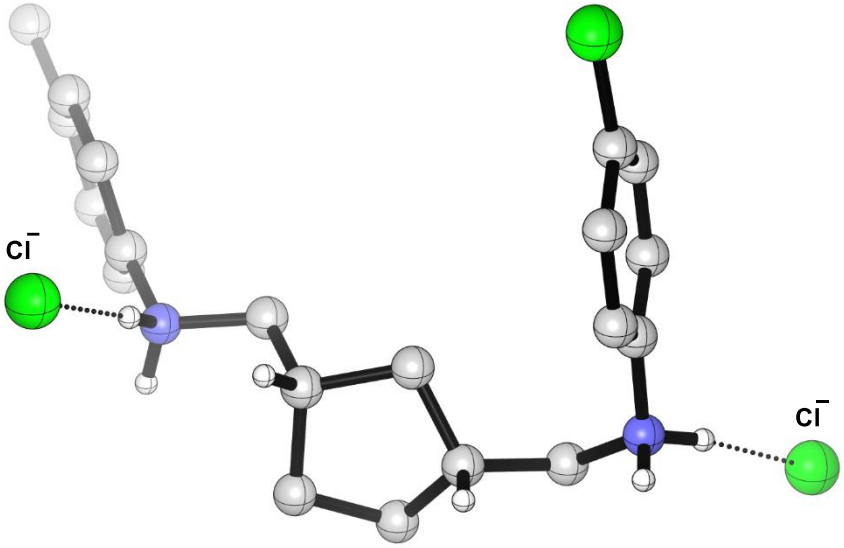


Table Cryst-10 Crystal data and structure refinement for Gandelman78R.

Identification code	Gandelman78R
Empirical formula	$C_{22}H_{29}Cl_9N_2$
Formula weight	640.52
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3275(7)
b/Å	11.3548(8)
c/Å	18.4123(8)
α/°	90
β/°	90.105(4)
γ/°	90
Volume/Å^3	2995.4(3)
Z	4
ρ_{calc}g/cm^3	1.420
μ/mm^{-1}	7.812
F(000)	1312.0
Crystal size/mm^3	0.24 × 0.15 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.168 to 161.442
Index ranges	-15 ≤ h ≤ 18, -13 ≤ k ≤ 14, -23 ≤ l ≤ 21
Reflections collected	23552
Independent reflections	6297 [R_{int} = 0.0910, R_{sigma} = 0.0523]
Data/restraints/parameters	6297/442/393
Goodness-of-fit on F^2	1.243
Final R indexes [I>=2σ (I)]	R_1 = 0.1127, wR_2 = 0.2948
Final R indexes [all data]	R_1 = 0.1299, wR_2 = 0.3179
Largest diff. peak/hole / e Å^{-3}	1.20/-0.67

Table Cryst-11 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman78R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl1	6304(3)	7373(5)	3442(2)	93.9(16)
Cl1A	5420(3)	-1837(6)	5469(3)	101.1(19)
N1	8530(2)	1584(3)	5482.0(16)	50.9(8)
N2	9940(3)	5340(3)	2616.2(15)	52.8(8)

Table Cryst-11 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman78R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	9281(4)	3250(4)	4795(2)	59.4(10)
C2	9163(4)	4001(5)	4090(2)	62.8(11)
C3	10116(3)	4030(4)	3730.8(18)	50.0(9)
C4	10575(4)	2887(4)	3976(2)	59.3(10)
C5	10279(3)	2783(5)	4775(2)	62.6(11)
C6	8538(3)	2270(4)	4788.9(19)	53.7(9)
C7	7750(3)	755(4)	5525(2)	55.7(10)
C8	7875(3)	-380(5)	5266(2)	61.1(11)
C9	7140(4)	-1161(5)	5279(3)	69.1(12)
C10	6278(4)	-820(6)	5545(3)	77.6(14)
C11	6175(4)	306(7)	5813(4)	87.8(17)
C12	6902(4)	1100(6)	5808(3)	73.6(13)
C13	5295(19)	-1360(30)	5700(20)	155(12)
C13A	6210(20)	7160(40)	3190(30)	175(15)
C14	10130(4)	4126(4)	2902.5(19)	55.1(10)
C15	9031(3)	5845(4)	2791.1(18)	51.4(9)
C16	8995(3)	6817(4)	3242.8(18)	48.8(8)
C17	8138(3)	7301(5)	3431(2)	59.2(10)
C18	7323(4)	6803(5)	3158(3)	69.8(12)
C19	7376(4)	5838(6)	2694(3)	73.1(13)
C20	8227(4)	5362(5)	2506(2)	64.3(11)
Cl2	8400.1(7)	3106.5(11)	6877.4(5)	58.9(3)
Cl3	10263.7(6)	4756.7(9)	1043.1(4)	49.0(3)
Cl4	5614(10)	4724(19)	5995(18)	139(5)
Cl5	7426(9)	5313(12)	5285(5)	84(2)
Cl6	6919(6)	6256(10)	6683(5)	83(3)
C21	6800(30)	5110(30)	6090(20)	73(4)
Cl7	3211(4)	5801(7)	1403(3)	125.2(19)
Cl8	3523.7(18)	8343(3)	1222.8(19)	90.0(10)
Cl9	4247(3)	7131(7)	2485.0(15)	172(3)
C32	3331(7)	7140(20)	1862(5)	106(3)
Cl9A	3033(18)	5660(20)	1415(9)	161(8)
C32A	3510(20)	6390(50)	2030(20)	119(7)
Cl7A	3495(9)	7847(17)	1665(13)	142(6)
Cl8A	4596(8)	5940(30)	2272(10)	222(10)
Cl4A	5693(9)	4458(18)	5780(5)	132(4)
C21A	6780(30)	4920(40)	6010(20)	96(6)

Table Cryst-11 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman78R. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl5A	7296(11)	5430(14)	5175(9)	119(3)
Cl6A	6791(12)	6161(13)	6601(8)	145(5)

Table Cryst-12 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman78R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Cl1	61.0(17)	139(4)	82(2)	-4(2)	-9.4(13)	-12.4(17)
Cl1A	63.2(19)	129(4)	111(3)	20(3)	7.9(17)	-17(2)
N1	60.5(18)	63(2)	29.2(14)	7.4(13)	2.1(12)	-1.7(14)
N2	79(2)	60(2)	19.9(13)	-0.2(12)	4.0(12)	-3.9(16)
C1	85(3)	68(3)	25.6(15)	4.0(16)	6.3(15)	-4(2)
C2	83(3)	69(3)	36.6(18)	15.6(18)	12.0(18)	5(2)
C3	75(2)	52(2)	22.6(14)	0.3(13)	3.6(14)	-4.6(17)
C4	78(3)	62(3)	37.6(18)	7.6(17)	3.9(17)	-2(2)
C5	73(3)	78(3)	36.7(18)	15.6(19)	-2.1(16)	-14(2)
C6	68(2)	69(3)	24.2(15)	6.1(15)	2.3(14)	-4.7(18)
C7	52(2)	78(3)	36.9(17)	15.7(18)	-0.4(14)	-2.5(18)
C8	58(2)	81(3)	44(2)	4.3(19)	7.4(16)	-9.6(19)
C9	72(3)	75(3)	60(3)	13(2)	-2(2)	-13(2)
C10	65(3)	98(4)	70(3)	25(3)	-7(2)	-15(2)
C11	50(2)	111(4)	102(4)	17(3)	11(3)	2(2)
C12	55(2)	93(4)	72(3)	2(3)	5(2)	6(2)
C13	89(10)	149(18)	230(30)	-60(20)	31(14)	-26(12)
C13A	81(7)	230(30)	220(30)	-120(20)	-20(16)	-1(13)
C14	88(3)	50(2)	27.6(16)	-2.0(14)	5.7(16)	-1.1(18)
C15	69(2)	63(2)	21.8(13)	3.9(14)	1.0(13)	-10.2(17)
C16	63(2)	55(2)	28.3(15)	4.5(14)	-0.8(13)	-10.8(16)
C17	65(2)	74(3)	38.6(19)	2.4(18)	6.5(16)	-2.6(19)
C18	71(3)	84(3)	54(2)	14(2)	-1(2)	-13(2)
C19	72(3)	95(4)	52(2)	7(2)	-15(2)	-20(2)
C20	81(3)	70(3)	42(2)	-1.4(19)	-11.5(18)	-14(2)
Cl2	59.9(6)	77.2(8)	39.5(5)	-3.1(4)	6.8(4)	-1.5(4)
Cl3	61.5(5)	64.0(6)	21.5(4)	-2.3(3)	2.6(3)	3.3(4)
Cl4	76(3)	149(7)	193(14)	39(9)	-20(7)	-18(4)
Cl5	96(4)	92(4)	63(3)	-18(2)	-8(3)	14(3)
Cl6	98(5)	90(4)	60(3)	-4(2)	21(2)	18(2)

Table Cryst-12 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman78R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	69(8)	67(10)	83(10)	10(7)	-6(8)	12(8)
Cl7	107(2)	154(4)	115(3)	59(3)	-13(2)	-27(2)
Cl8	73.1(12)	112.6(19)	84.3(17)	-13.2(14)	-0.9(10)	5.5(11)
Cl9	91(2)	364(8)	60.9(13)	19(2)	-27.7(12)	-26(3)
C32	62(5)	210(10)	45(4)	23(5)	1(3)	-22(7)
Cl9A	224(17)	142(9)	117(11)	-7(9)	-111(12)	17(11)
C32A	66(11)	207(17)	82(16)	-5(13)	-15(11)	-25(13)
Cl7A	105(6)	163(10)	158(14)	-51(10)	49(7)	-18(6)
Cl8A	77(5)	440(30)	145(10)	94(15)	-26(6)	6(10)
Cl4A	87(4)	225(12)	83(4)	32(4)	-16(2)	-38(5)
C21A	82(8)	101(14)	104(11)	-8(9)	-9(8)	5(10)
Cl5A	103(5)	135(6)	119(6)	-42(5)	44(4)	-11(4)
Cl6A	225(11)	119(6)	92(5)	-15(4)	25(5)	-3(5)

Table Cryst-13 Bond Lengths for Gandelman78R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C18	1.680(8)	C13A	C18	1.65(3)
Cl1A	C10	1.692(7)	C15	C16	1.383(6)
N1	C6	1.496(5)	C15	C20	1.379(6)
N1	C7	1.463(6)	C16	C17	1.390(7)
N2	C14	1.501(6)	C17	C18	1.391(7)
N2	C15	1.460(6)	C18	C19	1.392(9)
C1	C2	1.561(6)	C19	C20	1.378(9)
C1	C5	1.525(8)	Cl4	C21	1.77(5)
C1	C6	1.540(7)	Cl5	C21	1.74(5)
C2	C3	1.519(6)	Cl6	C21	1.71(3)
C3	C4	1.523(6)	Cl7	C32	1.75(2)
C3	C14	1.529(5)	Cl8	C32	1.824(17)
C4	C5	1.536(6)	Cl9	C32	1.742(10)
C7	C8	1.386(8)	Cl9A	C32A	1.56(4)
C7	C12	1.380(7)	C32A	Cl7A	1.79(6)
C8	C9	1.377(7)	C32A	Cl8A	1.70(4)
C9	C10	1.385(9)	Cl4A	C21A	1.70(4)
C10	C11	1.379(11)	C21A	Cl5A	1.80(5)
C10	C13	1.56(2)	C21A	Cl6A	1.78(3)
C11	C12	1.378(9)			

Table Cryst-14 Bond Angles for Gandelman78R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C6	112.9(3)	C16	C15	N2	118.7(4)
C15	N2	C14	116.4(3)	C20	C15	N2	120.3(4)
C5	C1	C2	105.7(3)	C20	C15	C16	121.0(5)
C5	C1	C6	113.4(4)	C15	C16	C17	119.9(4)
C6	C1	C2	108.4(4)	C16	C17	C18	119.4(5)
C3	C2	C1	106.1(4)	C17	C18	Cl1	117.5(5)
C2	C3	C4	103.9(3)	C17	C18	C13A	134.3(12)
C2	C3	C14	116.7(4)	C17	C18	C19	119.6(5)
C4	C3	C14	110.5(3)	C19	C18	Cl1	122.9(5)
C3	C4	C5	103.3(4)	C19	C18	C13A	105.9(12)
C1	C5	C4	104.9(4)	C20	C19	C18	120.9(5)
N1	C6	C1	112.2(3)	C19	C20	C15	119.1(5)
C8	C7	N1	118.7(4)	Cl5	C21	Cl4	116(2)
C12	C7	N1	120.7(5)	Cl6	C21	Cl4	110(2)
C12	C7	C8	120.6(5)	Cl6	C21	Cl5	113(2)
C9	C8	C7	119.6(5)	Cl7	C32	Cl8	110.7(5)
C8	C9	C10	120.6(6)	Cl9	C32	Cl7	112.7(11)
C9	C10	Cl1A	115.4(6)	Cl9	C32	Cl8	108.3(8)
C9	C10	C13	139.6(13)	Cl9A	C32A	Cl7A	103(3)
C11	C10	Cl1A	125.7(5)	Cl9A	C32A	Cl8A	116(3)
C11	C10	C9	118.9(5)	Cl8A	C32A	Cl7A	112(2)
C11	C10	C13	101.3(13)	Cl4A	C21A	Cl5A	106(2)
C12	C11	C10	121.5(6)	Cl4A	C21A	Cl6A	114(3)
C11	C12	C7	118.9(6)	Cl6A	C21A	Cl5A	106(2)
N2	C14	C3	114.4(3)				

Table Cryst-15 Torsion Angles for Gandelman78R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C18	C19	C20	-176.6(4)	C8	C7	C12	C11	-1.5(8)
Cl1A	C10	C11	C12	-175.5(5)	C8	C9	C10	Cl1A	175.6(4)
N1	C7	C8	C9	-177.8(4)	C8	C9	C10	C11	-1.6(8)
N1	C7	C12	C11	177.6(5)	C8	C9	C10	C13	-176(2)
N2	C15	C16	C17	-178.6(3)	C9	C10	C11	C12	1.4(10)
N2	C15	C20	C19	178.4(4)	C10	C11	C12	C7	0.1(10)
C1	C2	C3	C4	27.8(5)	C12	C7	C8	C9	1.3(7)
C1	C2	C3	C14	149.7(4)	C13	C10	C11	C12	177.7(16)

Table Cryst-15 Torsion Angles for Gandelman78R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	C5	C4	-19.5(5)	C13A	C18	C19	C20	176(2)
C2	C1	C6	N1	-173.8(4)	C14	N2	C15	C16	113.6(4)
C2	C3	C4	C5	-40.0(5)	C14	N2	C15	C20	-66.8(5)
C2	C3	C14	N2	77.5(5)	C14	C3	C4	C5	-165.9(4)
C3	C4	C5	C1	36.9(5)	C15	N2	C14	C3	-61.5(5)
C4	C3	C14	N2	-164.1(4)	C15	C16	C17	C18	-0.3(6)
C5	C1	C2	C3	-5.0(5)	C16	C15	C20	C19	-2.0(7)
C5	C1	C6	N1	69.2(4)	C16	C17	C18	Cl1	176.5(4)
C6	N1	C7	C8	90.3(5)	C16	C17	C18	C13A	-174(3)
C6	N1	C7	C12	-88.8(5)	C16	C17	C18	C19	-0.8(7)
C6	C1	C2	C3	-126.9(4)	C17	C18	C19	C20	0.5(8)
C6	C1	C5	C4	99.0(4)	C18	C19	C20	C15	0.9(8)
C7	N1	C6	C1	172.4(4)	C20	C15	C16	C17	1.8(6)
C7	C8	C9	C10	0.3(7)					

Table Cryst-16 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman78R.

Atom	*x*	*y*	*z*	U(eq)
H1A	9076	1178	5522	61
H1B	8497	2093	5862	61
H2A	10389	5832	2790	63
H2B	9998	5322	2124	63
H1	9195	3761	5232	71
H2C	8696	3638	3763	75
H2D	8955	4809	4212	75
H3	10478	4705	3937	60
H4A	11262	2932	3932	71
H4B	10344	2210	3689	71
H5A	10302	1953	4938	75
H5B	10691	3260	5091	75
H6A	7915	2627	4711	64
H6B	8662	1729	4379	64
H8	8464	-618	5081	73
H9	7225	-1941	5104	83
H11	5589	540	6007	105
H12	6821	1872	5996	88
H13A	4984	-1550	5246	232

Table Cryst-16 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman78R.

Atom	*x*	*y*	*z*	U(eq)
H13B	4918	-784	5973	232
H13C	5367	-2074	5996	232
H13D	6013	7214	3701	262
H13E	5840	6562	2942	262
H13F	6118	7927	2956	262
H14A	10749	3867	2726	66
H14B	9658	3580	2700	66
H16	9556	7153	3424	59
H17	8110	7966	3744	71
H19	6819	5503	2505	88
H20	8259	4710	2183	77
H21	7104	4420	6333	88
H32	2738	7299	2131	127
H32A	3097	6369	2467	142
H21A	7152	4261	6218	115

Table Cryst-17 Atomic Occupancy for Gandelman78R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl1	0.509(10)	Cl1A	0.491(10)	C13	0.509(10)
H13A	0.509(10)	H13B	0.509(10)	H13C	0.509(10)
C13A	0.491(10)	H13D	0.491(10)	H13E	0.491(10)
H13F	0.491(10)	Cl4	0.44(4)	Cl5	0.44(4)
Cl6	0.44(4)	C21	0.44(4)	H21	0.44(4)
Cl7	0.745(9)	Cl8	0.745(9)	Cl9	0.745(9)
C32	0.745(9)	H32	0.745(9)	Cl9A	0.255(9)
C32A	0.255(9)	H32A	0.255(9)	Cl7A	0.255(9)
Cl8A	0.255(9)	Cl4A	0.56(4)	C21A	0.56(4)
H21A	0.56(4)	Cl5A	0.56(4)	Cl6A	0.56(4)

Experimental

Single crystals of **5g**×2HCl [Gandelman78R] were obtained from slow diffusion between $CHCl_3$/MeOH solution of **5g**×2HCl and EtOAc/Et_2O at RT. A suitable crystal was selected and measured on Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[23] the structure was solved with the SHELXT[27] structure solution program using Charge Flipping and refined with the SHELXL[25] refinement package using Least Squares minimisation. The graphic representation was obtained with CYLview20 software.[26]

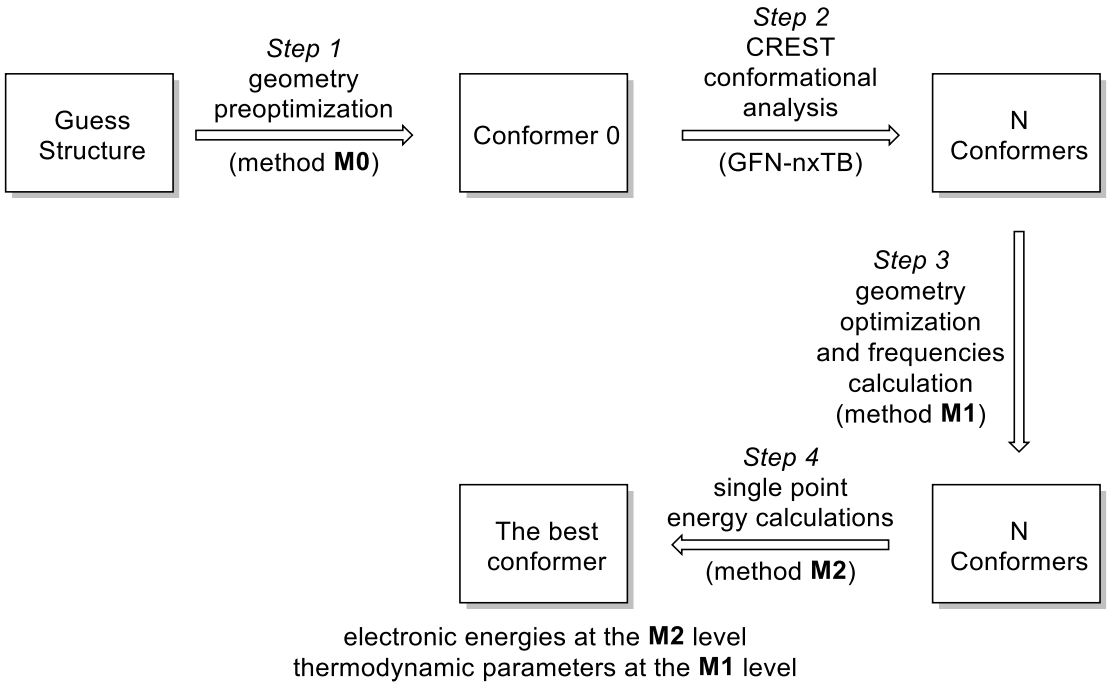
Calculations

General Information

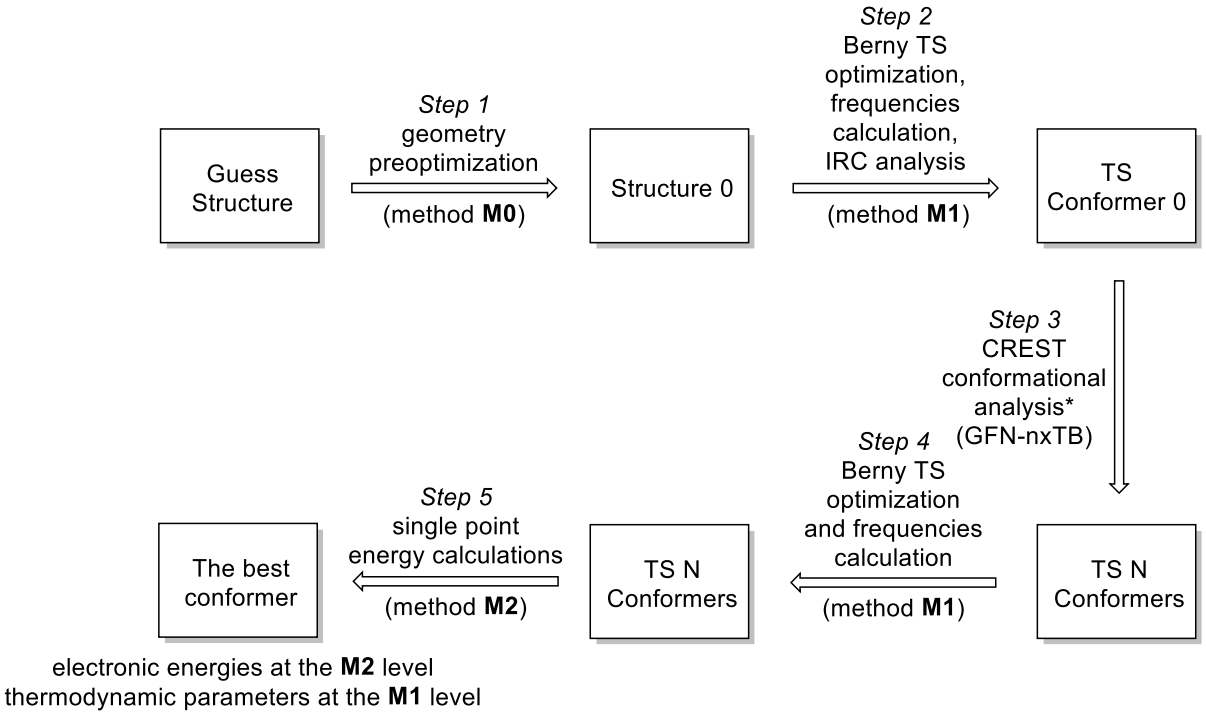
Gaussian 09 was used for the computations.[28] The geometries were optimized and the frequencies calculations were performed by BP86 functional[29,30] with Becke-Johnson damped dispersion correction D3(BJ)[31,32] using def2svp[33] basis set (method **M0**, **M1**). The frequency calculations were performed to validate each structure as a minimum and to evaluate its zero-point energy and the thermal corrections at 298 K. The single point energy calculations were performed by M062x functional[34] with D3 dispersion correction[31]using def2tzvp[35] basis set (method **M2**). Solvation effects were dealt with C-PCM model in THF for single point energy calculations.[36,37]

The lowest energy conformers of intermediates and transition states were found by the conformational search and analysis using CREST program[38] followed by a set of DFT calculations (see the general workflow for the calculations at scheme sC1). The transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations (see the general workflow for the calculations at scheme sC2). The quoted energies include zero-point, enthalpy, and entropic corrections determined from vibrational frequencies. The pictures of TS and intermediates presented were made with CYLview20 software.[26]

Scheme sC1. Calculations workflow for the reaction intermediates.



Scheme sC2. Calculations workflow for the transition states.

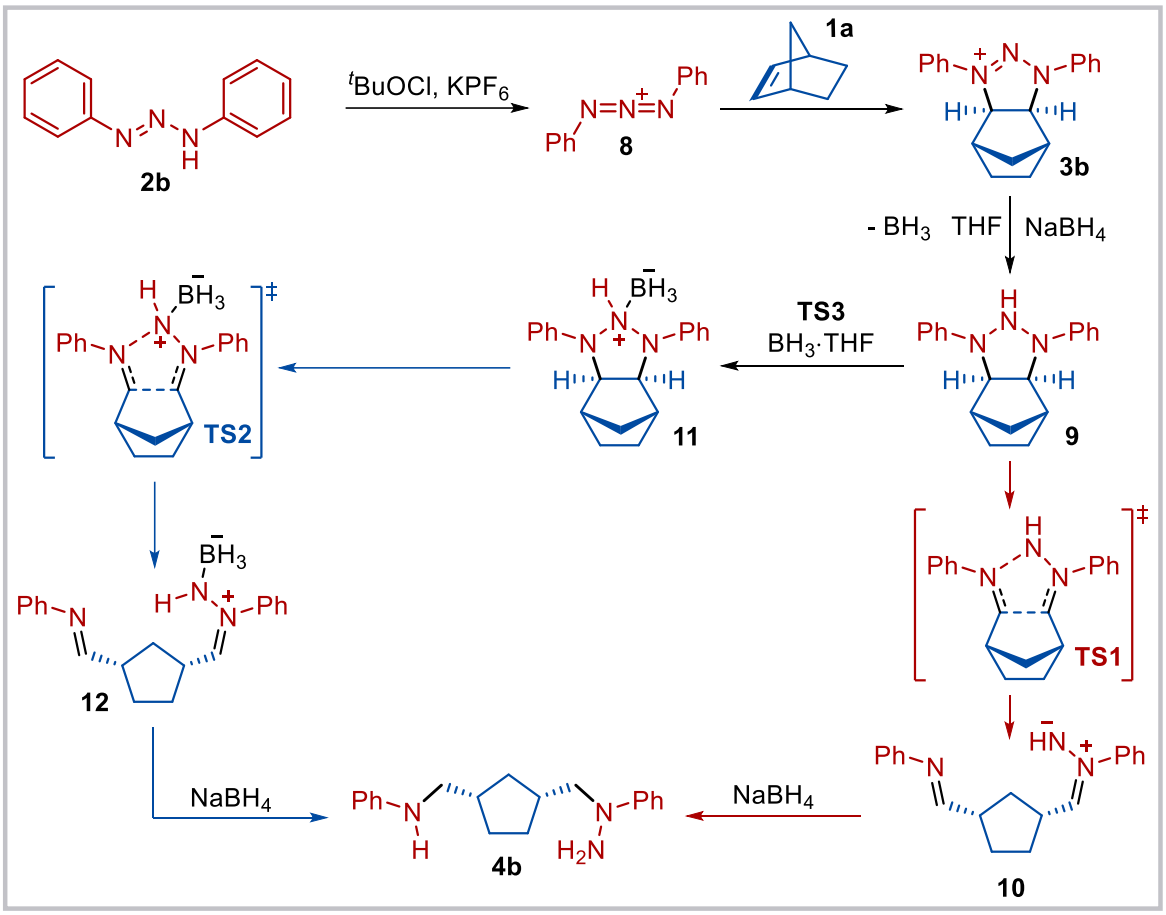


* The coordinates which underwent the most changes in the transformation were frozen.

Discussion of the Reaction Mechanism

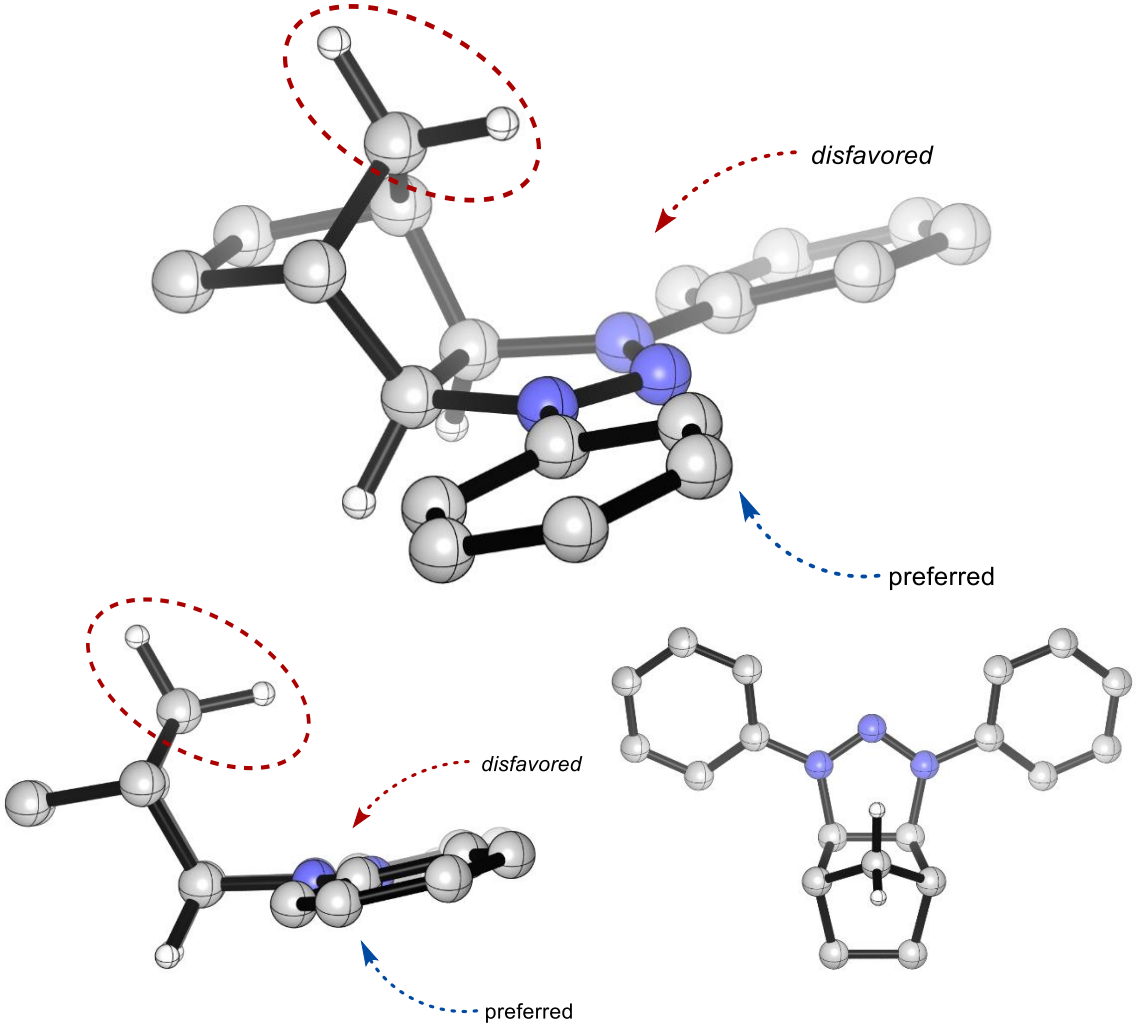
The proposed reaction mechanism is presented in scheme sC3 for norbornene **1a** and triazene **2b**. The transformation discussed starts from generation of triazadienium **8** from triazene **2**. The former cation reacts with alkene via [3+2] cycloaddition to produce nitrenium **3b** which can abstract hydride from $NaBH_4$. Cyclic N-H triazane may exist as two isomers **9** and **9`** depending on the relative position of NH-bond and nitrogen lone pair comparatively to CH_2-bridge of **3b** backbone (see below).

Scheme sC3. The proposed reaction mechanism.



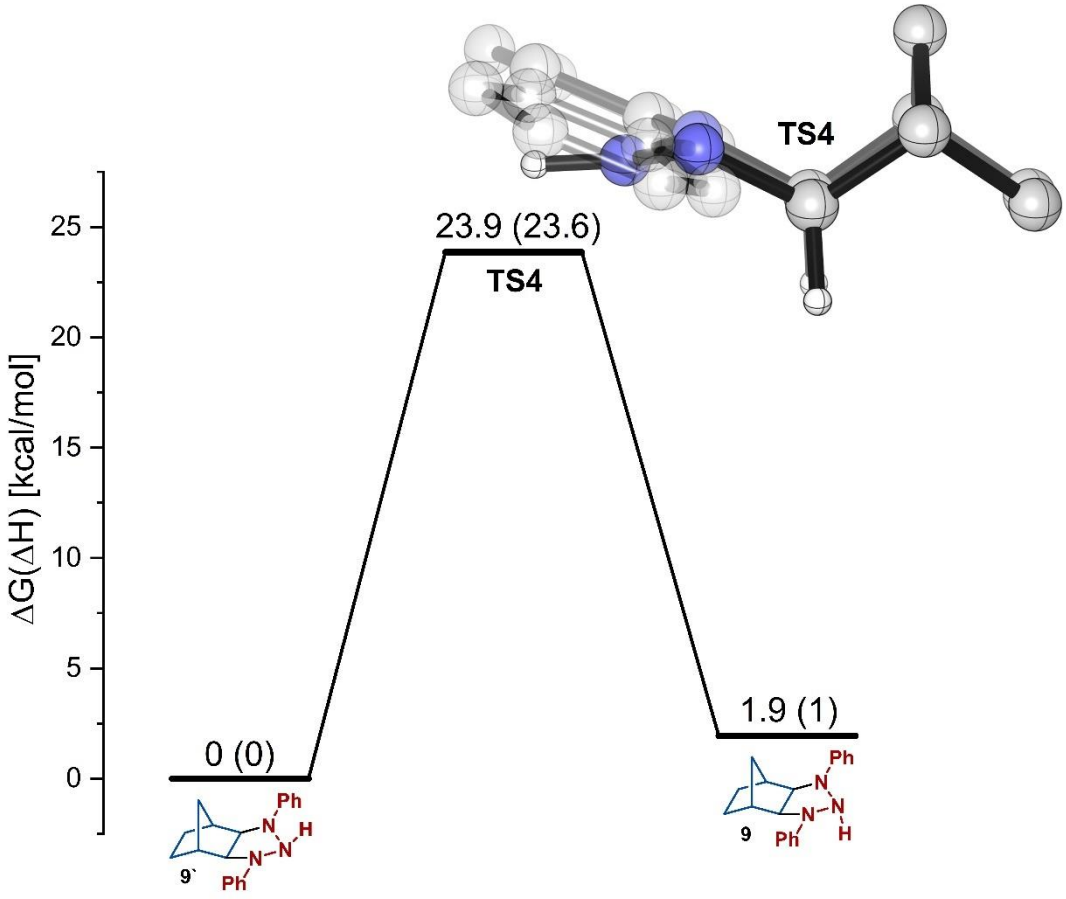
To begin with, we calculated the geometry of cation **3b** (intermediate in the synthesis; scheme sC4). From this geometry, we rationalize that the attack of BH_4^- (step from **3b** to **9**) is preferential from the below (blue arrow, scheme sC4) as there should be more steric clash between borohydride anion and CH_2-bridge (highlighted in red) when the attack happens from above (red arrow, scheme sC4) compared to the other side of the attack which has only two CH bonds.

Scheme sC4. 3D structure of cation **3b**.

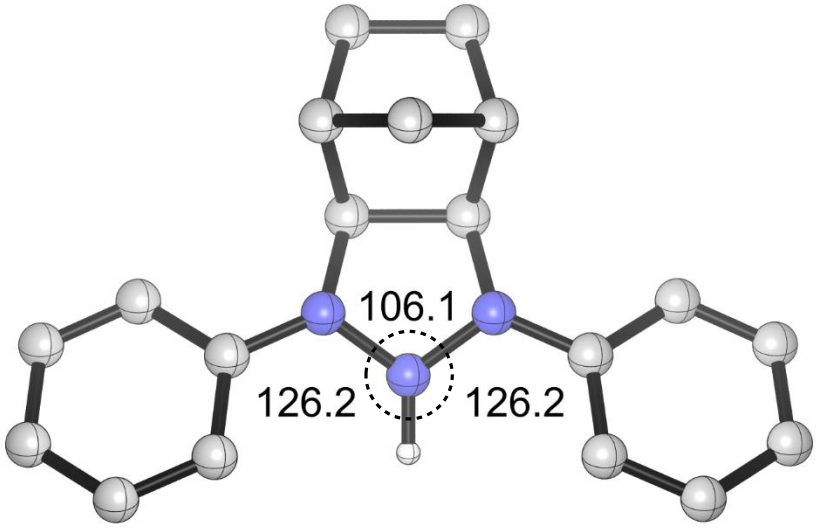


Consequently, we compared two isomers **9** and **9`** and their energies (see the scheme sC5). Accordingly, structure **9`** was slightly more stable than **9**. However, the isomerization barriers from **9`** to **9** and backwards were 23.9 and 22.0 kcal/mol respectively, thus, **9** and **9`** my interconvert during the reaction. **TS4** for this transformation exhibited planar geometry of N-NH-N fragment with 358.5 sum of angles around middle nitrogen (scheme sC6).

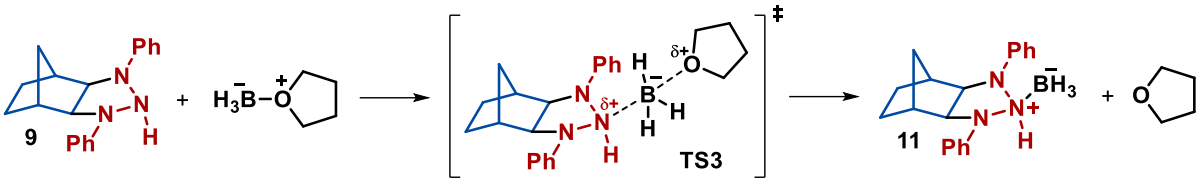
Scheme sC5. Comparison between two diastereomers of NH-triazane.



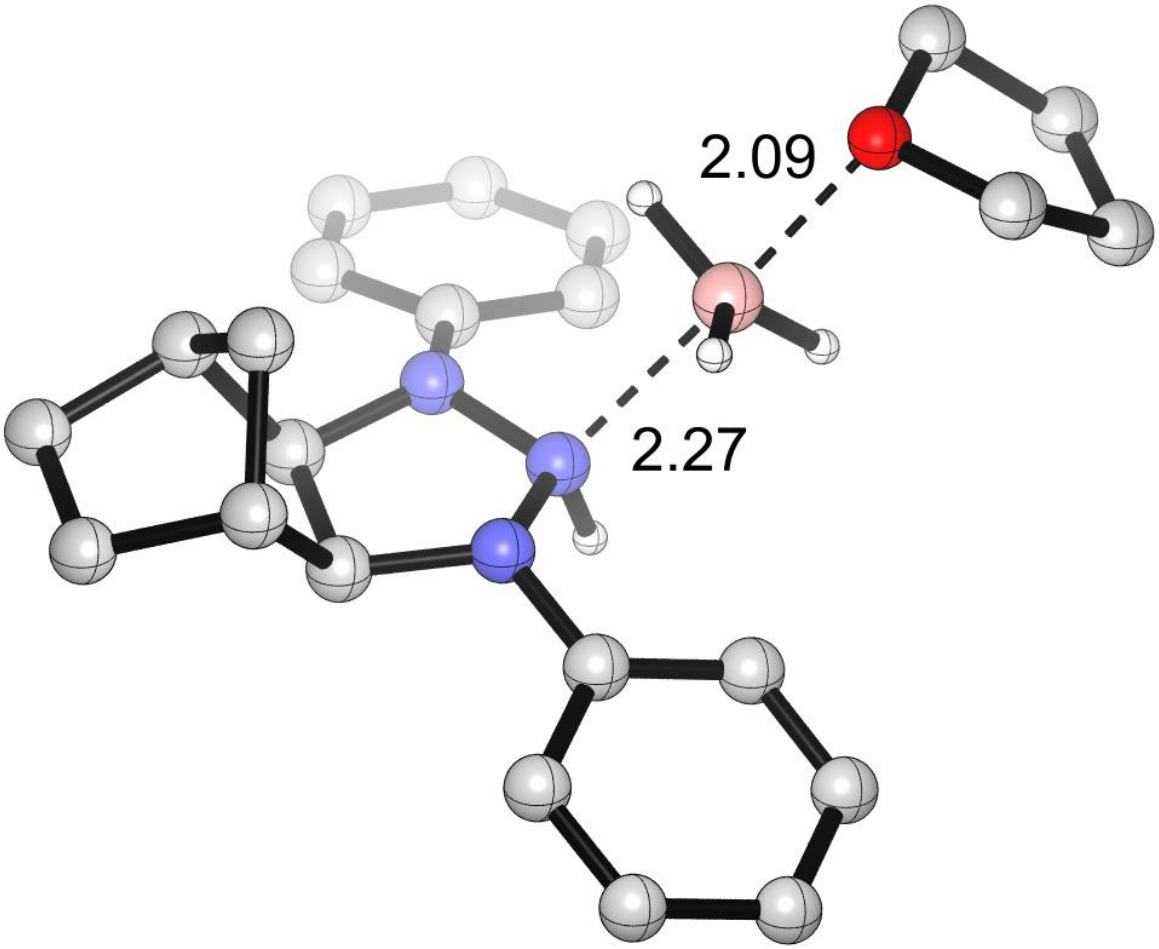
Scheme sC6. **TS4** structure for NH-triazane isomerization.



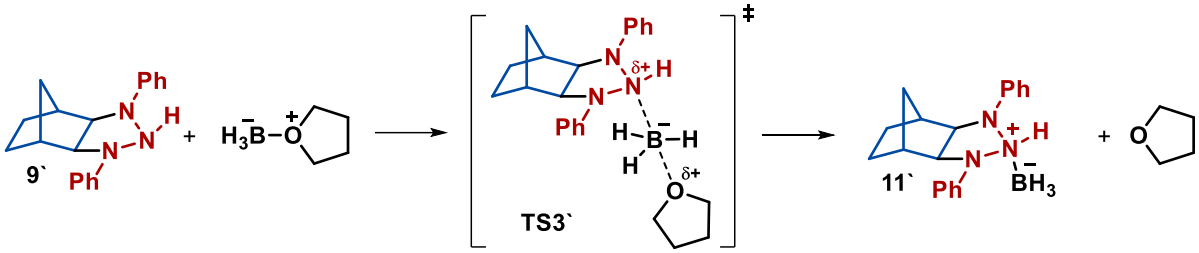
To compare the energies of **9** and **11**, we calculated the following reaction (the energy profile is presented later).



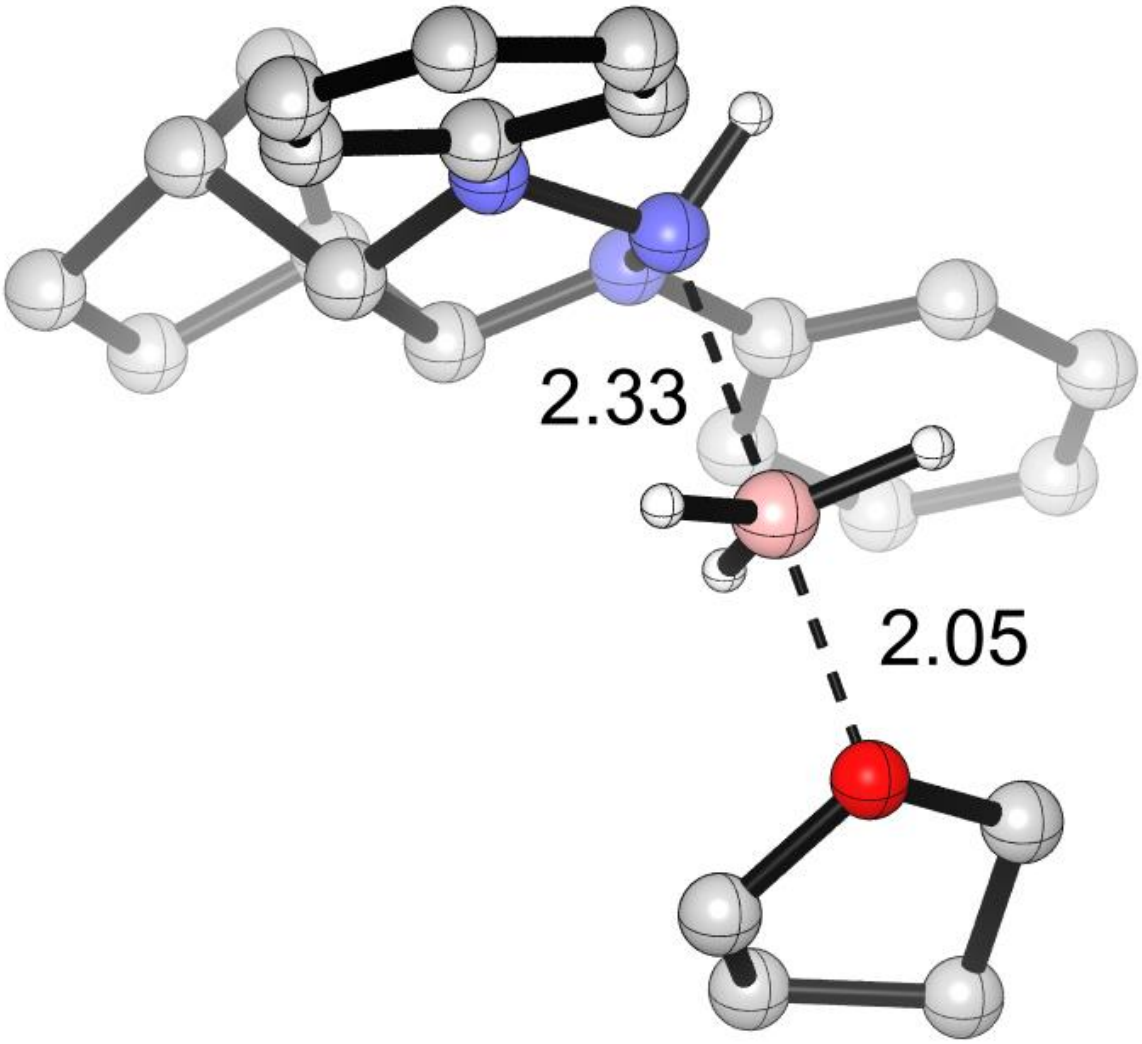
Scheme sC7. Geometry of **TS3**.



To compare the energies of **9`** and **11`**, we calculated the following reaction (the energy profile is presented later).



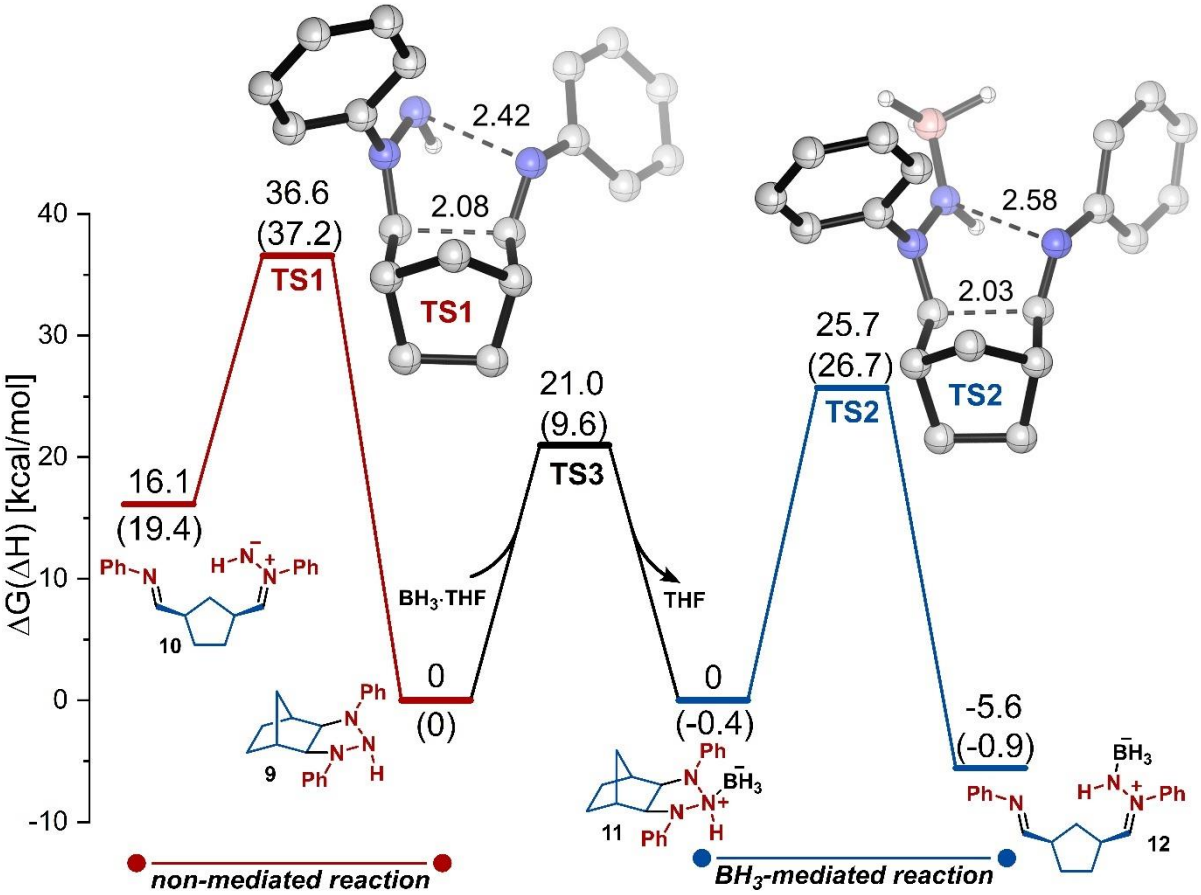
Scheme sC8. Geometry of **TS3`**.



Next, we calculated two possible pathways for the reaction: conversion of **9** to the **10** or transformation **9** to **11** and then to **12**. The result for diastereomer **9** is presented below in scheme sC9.

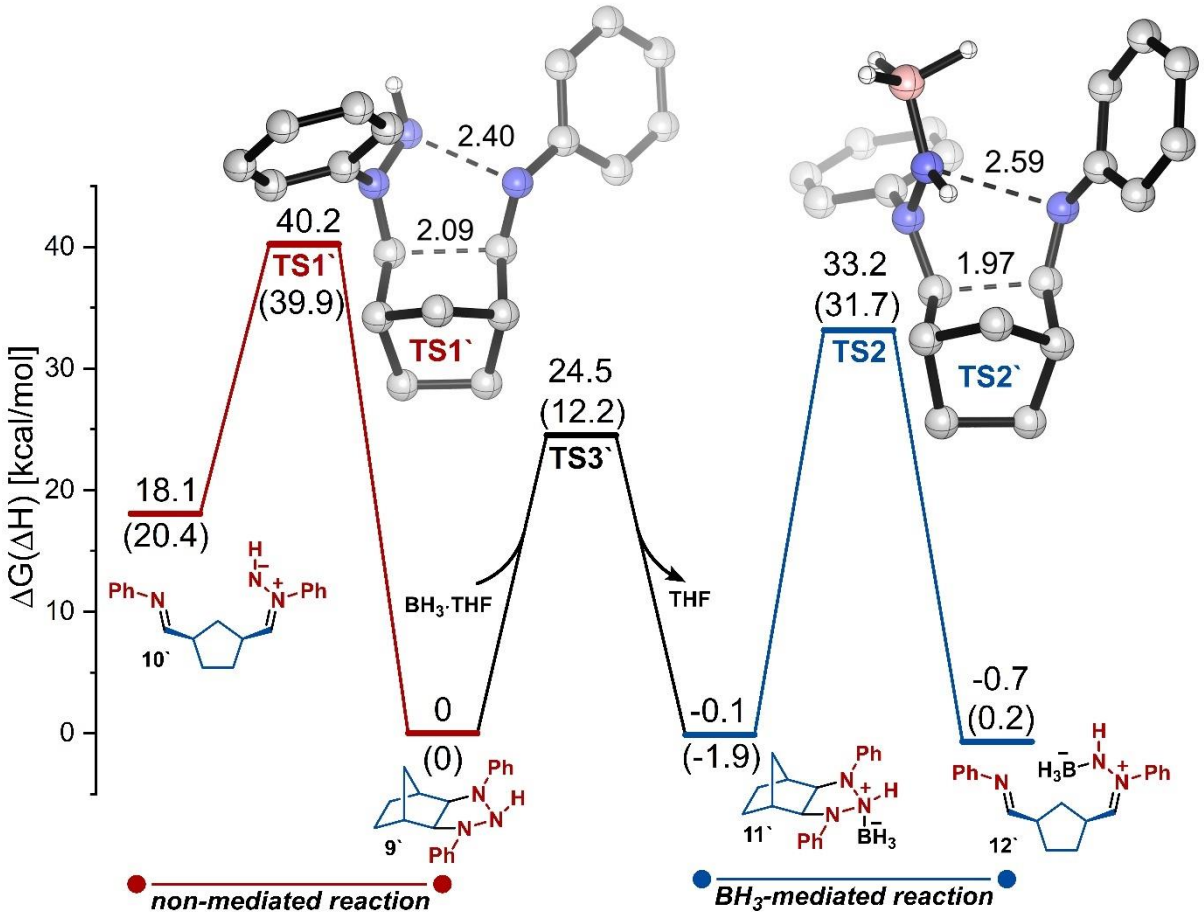
Not surprisingly, BH_3-mediated version is favored in energy as both intermediates **10** and **12** possess some negative charge, but this charge is stabilized in **12** by BH_3, while in **10** it is not. Probably, the activation barrier for BH_3-mediated step is lower than this of non-catalytic reaction for the same reason.

Scheme sC9. Free energy profile for the ring opening step of the reaction from **9**.



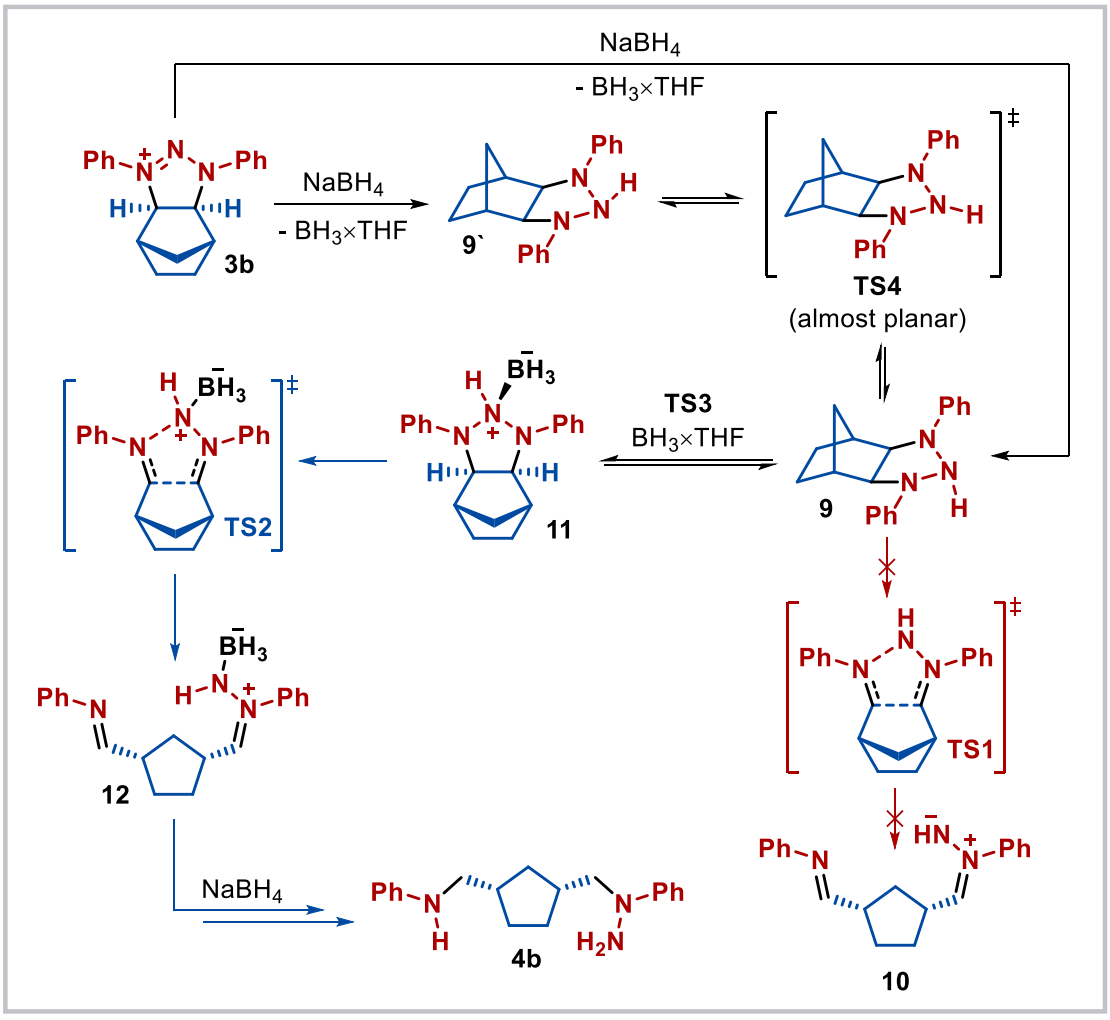
Similarly, reaction from **9`** has lower energy barrier with $BH_3$ impact, and it is more favored to progress via **TS2`** in terms of thermodynamics as well: it is slightly exergonic compared to the non-mediated reaction via **TS1`** with high energy barrier (scheme sC10). Thus, in both cases (**9** and **9`**) rearrangement step is more favorable in BH_3-mediated fashion.

Scheme sC10. Free energy profile for the ring opening step of the reaction from **9`**.



In the scheme sC11 the most probable mechanism of the reaction is presented after evaluation of all obtained calculation results. As was discussed previously, the attack of **3b** with borohydride anion may proceed from two sides of dihydrotriazolium cation: **9** and **9`** are formed. Reaction from **9`** to **12`** is not as feasible as from **9**, thus, we assume that, even though both **9** and **9`** are formed, only reaction from **9** proceeds to **12** is achievable. Indeed **9** and **9`** are interconvertible (see above), therefore, it is more probable that the reaction goes via the pathway with lower energy barriers. In addition, non-mediated reaction by **TS1** to **10** is less potent as the ring opening step is highly endergonic. Further reduction of **12** by the $NaBH_4$ excess and consequent workup should lead to the final product **4b**.

Scheme sC11. Most probable reaction mechanism.



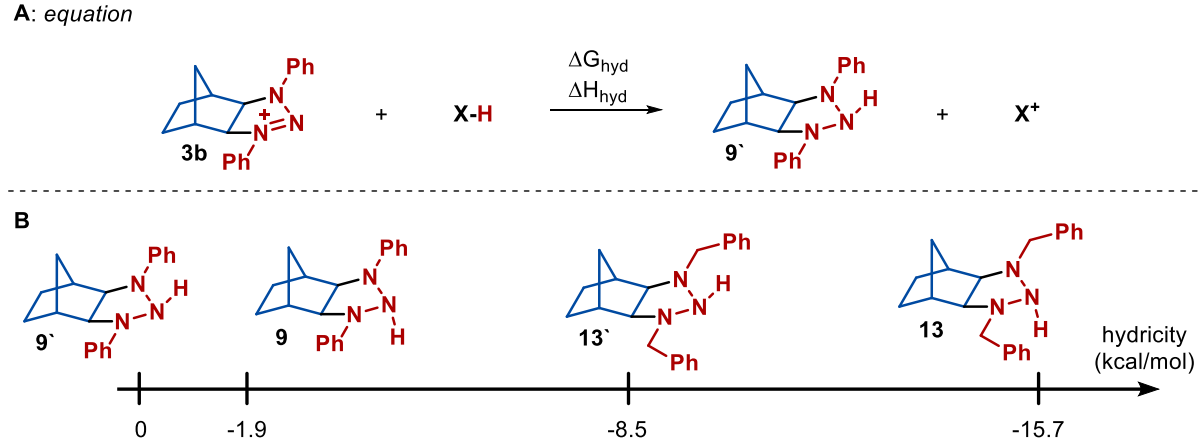
Comparison of the Relative Hydricity

The molecule **9`** was chosen as the reference for the relative hydricity calculations.

Computation of hydricity values (ΔG_{hyd}) relative to **9`** was performed according to the *equation* at scheme sC12A similarly to the previously reported method.[39] Additionally, ΔH_{hyd} of this reaction was calculated and presented in the table sC1.

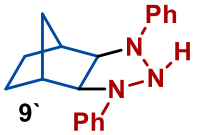
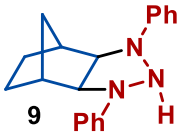
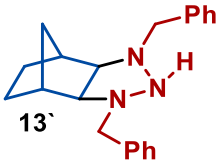
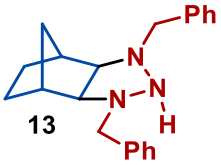
$$\Delta G_{hyd} = [G(\mathbf{9`}) + G(\mathbf{X^+})] - [G(\mathbf{3b}) + G(\mathbf{XH})]$$
$$\Delta H_{hyd} = [H(\mathbf{9`}) + H(\mathbf{X^+})] - [H(\mathbf{3b}) + H(\mathbf{XH})]$$

Scheme sC12.



As constituted above, the relative hydricity of **13** and **13`** is superior to that of **9** and **9`**, thus, relative acidity of the nitrenium counterpart (**X⁺**) should be lower for **13** and **13`** than that for cation **3b**.

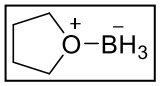
Table sC1. Computed parameters for *equation* (scheme sC12).

E	ΔG_{hyd}^{298} (kcal/mol)	ΔH_{hyd}^{298} (kcal/mol)
 **9`**	0	0
 **9**	-1.9	-1
 **13`**	-8.5	-7.1
 **13**	-15.7	-13.5

Geometry Coordinates

Geometry coordinates are presented for the conformer lowest in energy in every case.

Name: bh3-thf_c4
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran



Electronic energy = -259.070619023 Hartree
Zero-point Energy correction = 0.144439 Hartree
Thermal correction to Energy = 0.151527 Hartree
Thermal correction to Enthalpy = 0.152471 Hartree
Thermal correction to Gibbs Free Energy = 0.113529 Hartree

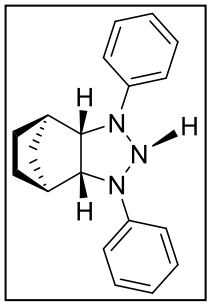
C	-0.13447325	-1.1995098865	-0.1008849245
O	0.6657163382	0.0142473479	-0.3157803302
C	-0.0819105	1.1960600126	0.1037223808
C	-1.5362888425	0.7575376288	-0.012470433
C	-1.4632549034	-0.7020671168	0.4770357491
H	-0.236603848	-1.6890962084	-1.0904633794
H	0.4371311044	-1.8591547809	0.5798286112
H	0.2115757751	1.4393944526	1.1485938767
H	0.2245530213	2.0228786082	-0.563932299
H	-2.21508608	1.3874622256	0.5954427749
H	-1.8750358781	0.8064804005	-1.0689095903
H	-1.4336263652	-0.7290421068	1.5860769201
H	-2.321882265	-1.3185757014	0.1458589825
H	2.6719553774	-1.0234452682	-0.4965182777
H	2.688276264	1.0291289266	-0.2541983739
H	2.2116597716	-0.1963082709	1.3471246566
B	2.2396391336	-0.0521757604	0.1186115685

Name: thf_c1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

Electronic energy = -232.431019210 Hartree
Zero-point Energy correction = 0.113048 Hartree
Thermal correction to Energy = 0.118025 Hartree
Thermal correction to Enthalpy = 0.118969 Hartree
Thermal correction to Gibbs Free Energy = 0.084595 Hartree

C	0.4321027223	-1.1285475762	0.1700949554
O	1.165963282	0.0003621203	-0.2881460569
C	0.4315984468	1.128265207	0.1716187884
C	-1.0593307464	0.7782638268	-0.0595343242
C	-1.0596098553	-0.7783075627	-0.0574551375
H	0.7802583196	-2.0194880928	-0.3908956648
H	0.6259091851	-1.3075359902	1.2593926011
H	0.6234368023	1.3046337082	1.2617275758
H	0.7807018152	2.020537284	-0.3866530015
H	-1.7124336927	1.2106226732	0.7254930318
H	-1.4090011401	1.1714455493	-1.0353972622
H	-1.7100294678	-1.2080612881	0.7312245114
H	-1.4131954137	-1.1741549889	-1.0308092057

Name: tr-noncat-sm_c1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

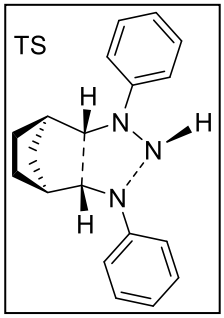


Electronic energy = -900.802717178 Hartree
Zero-point Energy correction = 0.356378 Hartree
Thermal correction to Energy = 0.373713 Hartree
Thermal correction to Enthalpy = 0.374657 Hartree
Thermal correction to Gibbs Free Energy = 0.310545 Hartree

N	1.1030706452	-0.1648137571	0.0744248154
C	0.7849047655	1.1529524709	-0.4826104584
C	1.135267017	2.3349868505	0.4566577126
C	0.7835281119	3.6345099957	-0.3081423849
C	-0.7829657911	3.6346343215	-0.3080565059
C	-1.1348274533	2.3351681956	0.4567842091
H	-1.2126930434	3.6438716422	-1.3313866571
H	-1.1873707666	4.5192460843	0.2236042792

C	0.0002714025	2.2470072912	1.4994378677
C	-0.7847641987	1.15307554	-0.4825144733
H	-2.1679925028	2.2943063214	0.8498937434
H	2.1684700025	2.2939573805	0.8496492143
H	1.2131428593	3.6436791928	-1.3315203197
H	1.1881317698	4.5190567319	0.223475172
H	0.0002239068	1.2883543875	2.0540893851
H	0.0003782123	3.0920006744	2.2179117674
H	-1.2119937261	1.2840660679	-1.5067549924
N	-1.1030824908	-0.1646384612	0.0745901251
H	1.2120230408	1.2839005183	-1.5069043808
C	-2.3713801871	-0.7410076865	-0.0025103515
N	-0.0000775151	-1.041813855	-0.1024913457
C	2.3712834031	-0.7413561597	-0.0026325419
H	-0.0001852307	-1.3550585537	-1.108040579
C	-3.5036178426	0.0285565109	-0.3743774722
C	-2.5490375254	-2.1167266248	0.2996223876
C	-4.7762291593	-0.5620693445	-0.4099350679
H	-3.3937369876	1.090771963	-0.6324289213
C	-3.8266328594	-2.6880751682	0.2525989806
H	-1.6707667986	-2.7145164455	0.5794292793
C	-4.9526978425	-1.9202449677	-0.0978739115
H	-5.6425949034	0.05542954	-0.6961426121
H	-3.9428642007	-3.7564787529	0.4954007198
H	-5.9534603467	-2.3766768632	-0.1319877266
C	3.5036110299	0.0280170656	-0.3746252594
C	2.5487699631	-2.1170652581	0.2996503342
C	4.7761444451	-0.5627787088	-0.4101511559
H	3.3938573077	1.0902143638	-0.6328063353
C	3.8262888883	-2.6885840238	0.2526541992
H	1.6704256455	-2.7147080837	0.5795400996
C	4.9524455439	-1.9209408941	-0.0979381125
H	5.6425817738	0.054573566	-0.6964586447
H	3.9423881381	-3.7569752832	0.4955740238
H	5.953146905	-2.3775083419	-0.1320297199

Name: cis_bp86-gd3bj-noncat_TS_freq
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

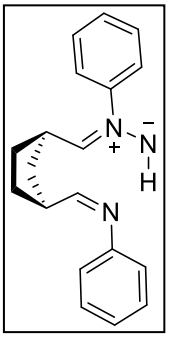


Electronic energy = -900.739670515 Hartree
Zero-point Energy correction = 0.352204 Hartree
Thermal correction to Energy = 0.369983 Hartree
Thermal correction to Enthalpy = 0.370927 Hartree
Thermal correction to Gibbs Free Energy = 0.305792 Hartree

N	-0.93729900	-0.32947700	1.14922900
C	-0.82255200	1.05333900	1.14647600
C	-1.78835800	1.92996200	0.37200200
C	-1.33733200	3.40561200	0.54533800
C	-0.15339100	3.56631000	-0.46144300
C	-0.00531100	2.16092200	-1.09293200
H	0.78432600	3.90044200	0.02897900
H	-0.39502000	4.31444500	-1.24327500
C	-1.46121400	1.66596300	-1.12326600
C	0.80710300	1.26857700	-0.13177900
H	0.48640600	2.17420400	-2.08739900
H	-2.85313500	1.77764600	0.63809600
H	-1.04790300	3.62878300	1.59295100
H	-2.17605400	4.08483800	0.29261400
H	-1.54980700	0.60501400	-1.42123800
H	-2.10103600	2.27444800	-1.79725100
H	1.50172100	1.86178200	0.51884100
N	1.18664700	0.02420500	-0.45964200
H	-0.33861100	1.45125200	2.05453400
C	2.49877800	-0.38918700	-0.22990000
N	0.09261500	-1.10379500	1.38688200
C	-2.02315700	-1.00682500	0.47435500
H	0.83424300	-0.50251700	1.79066500
C	2.77678300	-1.75698300	0.04666700
C	3.60382500	0.50178800	-0.34119100
C	4.09146100	-2.20388000	0.21180900
H	1.92349300	-2.44226000	0.15913200
C	4.92040500	0.04175600	-0.17568900
H	3.42115900	1.55491900	-0.60526800
C	5.17699600	-1.31022100	0.10390000
H	4.27616500	-3.26716500	0.43552900
H	5.75714500	0.75195500	-0.27862300
H	6.21030000	-1.66824800	0.23162000
C	-3.34141100	-0.84012500	0.92556100
C	-1.71796200	-1.85238800	-0.60599000
C	-4.37898800	-1.52036700	0.26689500
H	-3.54538300	-0.19999600	1.79676800

C	-2.76249000	-2.52619900	-1.25535200
H	-0.66810500	-1.92486900	-0.92511100
C	-4.09175700	-2.36031200	-0.82332500
H	-5.41618400	-1.40245300	0.61676700
H	-2.53801700	-3.18302100	-2.11004800
H	-4.90801100	-2.89216600	-1.33638600

Name: cis-noncat-prod-crest_c3
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

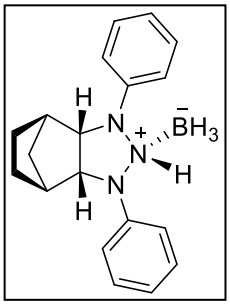


Electronic energy = -900.769203888 Hartree
Zero-point Energy correction = 0.351730 Hartree
Thermal correction to Energy = 0.371072 Hartree
Thermal correction to Enthalpy = 0.372016 Hartree
Thermal correction to Gibbs Free Energy = 0.302727 Hartree

N	-1.2104860232	-0.3330156399	1.3837885359
C	-1.2681101258	0.9997386981	1.3608039598
C	-1.9369050557	1.8204564374	0.2877449195
C	-1.7539103891	3.3241790946	0.6035573124
C	-0.3150733332	3.6515640223	0.1393417831
C	-0.0072305775	2.6200880382	-1.009193291
H	0.4046941561	3.5177505298	0.9749287626
H	-0.2121649408	4.7020120355	-0.1992118758
C	-1.2687344249	1.734374857	-1.1150508073
C	1.2523758067	1.8484769654	-0.7008317388
H	0.1769793205	3.1658663918	-1.9616517413
H	-3.015702446	1.5613011698	0.2051848563
H	-1.929557912	3.5682509672	1.6715260748
H	-2.4879438135	3.9059686321	0.0076159892
H	-1.0237671521	0.7023072789	-1.4233935091
H	-1.9692110929	2.1606837357	-1.8637925478
H	2.1800726995	2.4634035107	-0.5739736872
N	1.2771600989	0.577396283	-0.5426900109
H	-0.6735563258	1.4727706669	2.1576197349
C	2.4833320821	-0.0912868801	-0.2605679219
N	-0.4683142941	-1.0238391505	2.2446894023
C	-1.9649635739	-1.0925483983	0.3973690417
H	-0.7227113656	-2.0134795174	2.0845517796
C	3.6256137127	0.0511848446	-1.08301907
C	2.5245615831	-0.9641547316	0.8529509724
C	4.7955540779	-0.669442987	-0.7918676168
H	3.5748532576	0.7078176087	-1.9660143604
C	3.7058292659	-1.6616939908	1.1419263111

H	1.6202261387	-1.0501143907	1.4865411849
C	4.8428446708	-1.5245250933	0.3224149045
H	5.6769055083	-0.562107426	-1.4443437385
H	3.7384859751	-2.3263157747	2.0202036709
H	5.761832227	-2.0874533741	0.5490092378
C	-3.3593349519	-1.1997496229	0.5094828696
C	-1.2534104576	-1.7572088685	-0.6158894738
C	-4.0578876898	-1.9893689637	-0.4199438379
H	-3.8814289629	-0.6739214191	1.3229131411
C	-1.9635633968	-2.5394225595	-1.5396378683
H	-0.1641453677	-1.6191212928	-0.6768646679
C	-3.3627865426	-2.657290534	-1.4432534316
H	-5.1517623594	-2.086306237	-0.3396681679
H	-1.4195090066	-3.0563540416	-2.345300921
H	-3.9142720378	-3.2742917834	-2.16954043

Name: cis-bp86-gd3bj-BH3_sm
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

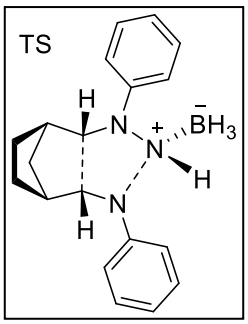


Electronic energy = -927.437308467 Hartree
Zero-point Energy correction = 0.388433 Hartree
Thermal correction to Energy = 0.407464 Hartree
Thermal correction to Enthalpy = 0.408408 Hartree
Thermal correction to Gibbs Free Energy = 0.341090 Hartree

N	0.96318000	-0.05717900	0.24153000
C	0.63097400	1.34461300	0.47177300
C	0.50787100	2.17365000	-0.82427400
C	0.17601300	3.62602400	-0.39934700
C	-1.31351600	3.52375000	0.07418400
H	0.85615600	3.99232200	0.39794300
H	0.28315600	4.31674300	-1.25941500
C	-0.84512300	1.67601600	-1.37717700
H	1.38703100	2.07403200	-1.48967500
C	-1.64115500	2.01688500	-0.09485300
C	-0.84871000	1.28442500	1.01216800
H	-2.72181600	1.78279200	-0.10004800
H	-1.46076900	3.87056000	1.11775000
H	-1.98260200	4.12993800	-0.56869100
H	-0.84224700	0.60025300	-1.62814200
H	-1.19250700	2.25163100	-2.25936600
H	1.30849800	1.82544500	1.21923100
H	-0.94274600	1.81258500	1.98546500
N	-1.11190100	-0.15909300	1.22631300

C	2.31961300	-0.43473400	0.04123600
N	0.17586200	-0.76716100	1.32241400
C	-2.09035500	-0.82589800	0.42162800
B	0.27119100	-2.38420700	1.58436100
H	0.55746300	-0.41208600	2.22252800
C	2.61354800	-1.74139900	-0.41649600
C	3.37710600	0.48995400	0.20069900
C	3.93695400	-2.11598600	-0.67298100
H	1.79014900	-2.45488000	-0.54997000
C	4.70011900	0.11008000	-0.08500000
H	3.17679000	1.51797200	0.53268000
C	4.98905900	-1.19392300	-0.51305700
H	4.14831800	-3.14020700	-1.01776200
H	5.51017400	0.84678600	0.03445600
H	6.02647000	-1.49003400	-0.73242100
C	-3.43075900	-0.70594000	0.83852700
C	-1.78636800	-1.54549700	-0.75235200
C	-4.46280100	-1.27876500	0.07894000
H	-3.64578400	-0.16452300	1.77219500
C	-2.82024700	-2.14331700	-1.48917000
H	-0.74301100	-1.63320500	-1.07997400
C	-4.15957200	-2.00581200	-1.08492800
H	-5.50738500	-1.17447700	0.41157000
H	-2.57431600	-2.71417200	-2.39824200
H	-4.96569300	-2.47039900	-1.67367800
H	0.02510900	-3.01232600	0.56502500
H	-0.57010200	-2.53554200	2.46917700
H	1.41781800	-2.53890700	1.99865400

Name: cis-bp86-gd3bj-BH3_TS-2_freq
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

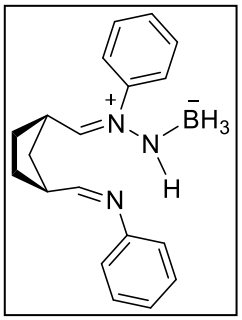


Electronic energy = -927.389196885 Hartree
Zero-point Energy correction = 0.382618 Hartree
Thermal correction to Energy = 0.402650 Hartree
Thermal correction to Enthalpy = 0.403594 Hartree
Thermal correction to Gibbs Free Energy = 0.333919 Hartree

N	1.15632000	0.37422300	-0.67499200
C	0.69134900	1.54666500	-0.20566700
C	-0.19915800	2.42276000	-1.11391200
C	-0.47812900	3.76694900	-0.40030200
C	-1.63966400	3.43177400	0.58848700
H	0.42435500	4.15749000	0.11397800

H	-0.78821000	4.53596200	-1.13603800
C	-1.59440200	1.77752600	-1.16441300
H	0.28748600	2.53857800	-2.10353500
C	-1.91723800	1.92513600	0.34549400
C	-0.83817500	1.13283800	1.06260400
H	-2.94479100	1.62336200	0.62868400
H	-1.38240000	3.64030400	1.64736700
H	-2.54959700	4.02040300	0.35657700
H	-1.57111500	0.73101000	-1.51789600
H	-2.30724800	2.34911300	-1.79538000
H	1.34590600	2.16010500	0.46373700
H	-0.40391400	1.56103900	1.98442200
N	-0.88934400	-0.25166900	1.09943900
C	2.45198000	-0.06206500	-0.43047600
N	0.24202200	-0.89543000	1.38215400
C	-1.90595200	-1.01047600	0.41369200
B	0.49660700	-2.37883500	1.66440100
H	0.97013800	-0.23073100	1.67199100
C	2.78389300	-1.38049000	-0.85825700
C	3.47847900	0.71051900	0.19028900
C	4.06946800	-1.90207100	-0.66850200
H	2.00218800	-1.96932500	-1.35861300
C	4.75829200	0.17620700	0.38206100
H	3.27995900	1.74830900	0.49856100
C	5.06448000	-1.13201800	-0.04154400
H	4.29522000	-2.92475400	-1.00922000
H	5.53735500	0.79501900	0.85625900
H	6.07553300	-1.54131200	0.10768700
C	-3.20083800	-1.06455900	0.94833700
C	-1.57196600	-1.67379800	-0.77964300
C	-4.19064300	-1.78777300	0.26216000
H	-3.41990000	-0.56000700	1.90108700
C	-2.56705100	-2.39353000	-1.45384700
H	-0.54376100	-1.57955000	-1.15930200
C	-3.87504200	-2.45040900	-0.93638400
H	-5.20988500	-1.84309200	0.67420300
H	-2.32053600	-2.91473400	-2.39155900
H	-4.65226100	-3.02023000	-1.46883200
H	-0.48999000	-3.06381300	1.43269000
H	0.91662700	-2.43487600	2.83481900
H	1.48471600	-2.67306800	0.95902100

Name: cis-bp86-gd3bj-BH3_prod
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

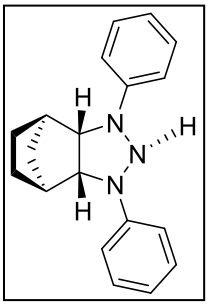


Electronic energy = -927.435066494 Hartree
Zero-point Energy correction = 0.382790 Hartree
Thermal correction to Energy = 0.404470 Hartree
Thermal correction to Enthalpy = 0.405414 Hartree
Thermal correction to Gibbs Free Energy = 0.329961 Hartree

N	1.36568100	0.68724200	-0.54463000
C	1.34648300	1.96951900	-0.49852200
C	0.11636000	2.79554800	-0.78838100
C	-0.24569800	3.72798400	0.42565400
C	-1.71835000	3.39839600	0.76676400
H	0.41686700	3.50505900	1.28977700
H	-0.10184800	4.80167100	0.19261600
C	-1.15210800	1.95653000	-1.06113000
H	0.36859400	3.42189600	-1.67382200
C	-1.90936000	1.93781100	0.29622700
C	-1.30873400	1.00341600	1.31296200
H	-2.98202200	1.69520400	0.13646300
H	-1.96138000	3.54758400	1.83922400
H	-2.40224800	4.04913900	0.18368000
H	-0.90670700	0.94986600	-1.44404100
H	-1.79486500	2.46464200	-1.80917100
H	2.26323500	2.55314500	-0.22765500
H	-0.77733300	1.41049500	2.18952300
N	-1.22045300	-0.31680700	1.18814300
C	2.56972400	-0.02143700	-0.35634700
N	-0.42981700	-1.09870400	1.93688100
C	-1.96303600	-1.00298700	0.14373900
B	-0.77234100	-2.55540400	2.42809900
H	0.14018500	-0.50931200	2.55766100
C	2.54318400	-1.21479100	0.40382400
C	3.78643300	0.39329900	-0.95146200
C	3.72086100	-1.95019400	0.59770300
H	1.59261900	-1.53901000	0.85640900
C	4.95585200	-0.35978700	-0.76501900
H	3.79889200	1.28969600	-1.59138300
C	4.93091200	-1.52875400	0.01579600
H	3.68616600	-2.86803400	1.20506400
H	5.89382900	-0.03431600	-1.24250400
H	5.85005100	-2.11789900	0.15881900
C	-3.35818800	-1.07584700	0.23437600
C	-1.25321400	-1.56865300	-0.92514900
C	-4.06710000	-1.72882700	-0.78721900

H	-3.87138500	-0.64866200	1.10831700
C	-1.97345800	-2.21431900	-1.93976300
H	-0.15875200	-1.47864300	-0.94995000
C	-3.37674100	-2.29500400	-1.87257000
H	-5.16339900	-1.80610600	-0.72616900
H	-1.43327100	-2.66250800	-2.78758200
H	-3.93574000	-2.80942000	-2.66950300
H	-1.19506800	-3.22633600	1.48529900
H	-1.63211200	-2.45862600	3.32884000
H	0.29657300	-2.98604200	2.87793600

Name: cis-noncat-sm_c1_1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

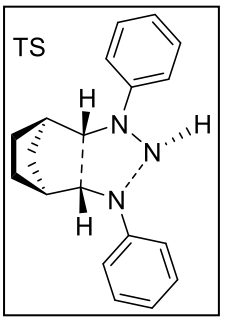


Electronic energy = -900.804717105 Hartree
Zero-point Energy correction = 0.356857 Hartree
Thermal correction to Energy = 0.374134 Hartree
Thermal correction to Enthalpy = 0.375078 Hartree
Thermal correction to Gibbs Free Energy = 0.309453 Hartree

N	1.1779572188	0.2604770508	0.6855938446
C	0.8320174495	1.3882044717	-0.1873334071
C	1.1137101135	2.8071508501	0.3686597738
C	0.814785872	3.8021650409	-0.780892455
C	-0.7471376631	3.7555310382	-0.8974858643
C	-1.1560278806	2.7578691573	0.2154657714
H	-1.0929952075	3.4231491303	-1.8982837622
H	-1.1970707481	4.7519111345	-0.7135155517
C	-0.0959122192	3.0544876474	1.3032707012
C	-0.7428139587	1.3452107033	-0.2669226892
H	-2.217348299	2.8131311703	0.5245268452
H	2.1212681466	2.90136951	0.8167294244
H	1.3256023642	3.5142084266	-1.7228878187
H	1.1692232012	4.8185879038	-0.5155586034
H	-0.1442171117	2.3738186876	2.1766997768
H	-0.143321812	4.0965624525	1.6821829531
H	-1.1057065329	1.1327344766	-1.2925851121
N	-1.1078581477	0.2402759886	0.6205949755
H	1.305698184	1.2372203508	-1.1769022179
C	-2.0095134494	-0.7601270271	0.2221622155
N	0.0196045379	-0.1509112596	1.4018911278
C	2.0381474797	-0.7557866791	0.2164527159
H	-0.0048918923	0.4159864736	2.2609102838
C	-1.9756998486	-2.050521579	0.8059393559

C	-3.0222234154	-0.473145614	-0.7283881253
C	-2.9013019873	-3.0277574146	0.4171918144
H	-1.2130986754	-2.2650547238	1.5658589456
C	-3.9413804423	-1.4639612624	-1.1064019143
H	-3.1083013982	0.5344162071	-1.1603714246
C	-3.8889844819	-2.7505226744	-0.5451638691
H	-2.8470600966	-4.0268319746	0.878712592
H	-4.7160332545	-1.2169696944	-1.8499669216
H	-4.613703322	-3.5227135102	-0.844440207
C	3.150392647	-0.4129478415	-0.5925636803
C	1.8558254342	-2.1099101046	0.5812820537
C	4.0317515637	-1.4064409274	-1.0452237491
H	3.3424736602	0.6396657629	-0.848430594
C	2.7471538577	-3.090496349	0.1240379523
H	1.0017446044	-2.3738626923	1.2169691352
C	3.8388066965	-2.753536199	-0.6957157933
H	4.8883895638	-1.1156778184	-1.6740725509
H	2.5781257738	-4.1404315214	0.41218091
H	4.5339724762	-3.5291977683	-1.051188857

Name: tr_bp86-gd3bj-noncat_TS_freq
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

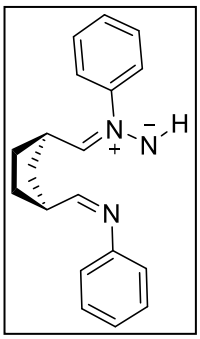


Electronic energy = -900.736792398 Hartree
Zero-point Energy correction = 0.352009 Hartree
Thermal correction to Energy = 0.369837 Hartree
Thermal correction to Enthalpy = 0.370782 Hartree
Thermal correction to Gibbs Free Energy = 0.305626 Hartree

N	-0.94436200	-0.26134700	1.18759600
C	-0.86463800	1.11519800	1.14111400
C	-1.83766600	1.93990000	0.32343100
C	-1.43433900	3.43097700	0.47280800
C	-0.21409600	3.59330700	-0.48970500
C	-0.02776200	2.18475400	-1.10691500
H	0.70149400	3.93689800	0.03461900
H	-0.43013500	4.33580100	-1.28438200
C	-1.47362500	1.66243100	-1.16098700
C	0.78393300	1.31399000	-0.12551900
H	0.47924000	2.20325400	-2.09392100
H	-2.90327400	1.75847500	0.57126300
H	-1.19478600	3.69083000	1.52420500
H	-2.27870100	4.07944000	0.16377500
H	-1.53686400	0.59757300	-1.44971700

H	-2.11056400	2.25111100	-1.85538600
H	1.46454300	1.91425500	0.52896000
N	1.16031000	0.06460200	-0.42933200
H	-0.36916700	1.54277900	2.02615200
C	2.46887100	-0.35784200	-0.20612300
N	0.16275100	-0.87971500	1.53543800
C	-1.97779200	-0.99571400	0.48670000
H	-0.02826600	-1.89464100	1.43508900
C	2.74466000	-1.74533500	-0.06068700
C	3.57800000	0.53282600	-0.21428900
C	4.05198500	-2.21324100	0.09531600
H	1.89695400	-2.44776400	-0.06136900
C	4.88970300	0.05615300	-0.05666700
H	3.40574500	1.60674900	-0.38329100
C	5.14012900	-1.31588200	0.10409500
H	4.23035300	-3.29428300	0.21474800
H	5.72876600	0.77091700	-0.07230500
H	6.16965700	-1.68707100	0.22424600
C	-3.30498000	-0.94429200	0.94230000
C	-1.61011900	-1.79507800	-0.61215300
C	-4.28352300	-1.70544500	0.28136800
H	-3.55728800	-0.32577400	1.81665900
C	-2.59708900	-2.54933800	-1.26336400
H	-0.56413100	-1.75458000	-0.95756400
C	-3.93205300	-2.50741300	-0.81867000
H	-5.32553500	-1.67908900	0.63595800
H	-2.32413100	-3.16626000	-2.13362200
H	-4.70239900	-3.10313100	-1.33233500

Name: tr_bp86-gd3bj-noncat_prod
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

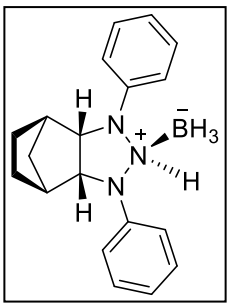


Electronic energy = -900.769205427 Hartree
Zero-point Energy correction = 0.351729 Hartree
Thermal correction to Energy = 0.371071 Hartree
Thermal correction to Enthalpy = 0.372015 Hartree
Thermal correction to Gibbs Free Energy = 0.302729 Hartree

N	-1.18479400	-0.33416300	1.40680500
C	-1.25132400	0.99744600	1.35838000
C	-1.93416500	1.79288200	0.27522800
C	-1.75894200	3.30359900	0.56082100
C	-0.32604500	3.63154200	0.07902400
C	-0.02029900	2.58043500	-1.05228200

H	0.40113800	3.51832100	0.91120800
H	-0.23276700	4.67596200	-0.28033500
C	-1.27642600	1.68435000	-1.13099500
C	1.24708100	1.82341800	-0.73947200
H	0.15246400	3.10943700	-2.01625800
H	-3.01179400	1.52499600	0.20621100
H	-1.92780900	3.56669200	1.62537000
H	-2.50162400	3.86904000	-0.04009400
H	-1.02666400	0.64815800	-1.42113100
H	-1.98571100	2.09118200	-1.88226200
H	2.17156100	2.44684100	-0.63214400
N	1.28160200	0.55587000	-0.55677400
H	-0.65376700	1.48971500	2.14118900
C	2.49433600	-0.09957700	-0.27167400
N	-0.43141800	-1.00337500	2.27513400
C	-1.94174600	-1.11762100	0.44129000
H	-0.68062800	-1.99752700	2.13617000
C	2.54991600	-0.95101800	0.85769300
C	3.62928200	0.03477300	-1.10556800
C	3.73798900	-1.63525500	1.15053500
H	1.65115700	-1.03086500	1.49992500
C	4.80619600	-0.67263100	-0.81007300
H	3.56738000	0.67430100	-2.00033000
C	4.86773000	-1.50618900	0.31971100
H	3.78183200	-2.28294200	2.04089400
H	5.68176100	-0.57194000	-1.47134300
H	5.79216200	-2.05874300	0.54968500
C	-3.33437600	-1.23238000	0.56681800
C	-1.23371100	-1.79660000	-0.56494400
C	-4.03476200	-2.04455900	-0.34156200
H	-3.85369600	-0.69469300	1.37425700
C	-1.94567800	-2.60131500	-1.46770300
H	-0.14598300	-1.65208900	-0.63749900
C	-3.34321000	-2.72713500	-1.35757400
H	-5.12723800	-2.14754800	-0.25047100
H	-1.40446100	-3.12978800	-2.26777000
H	-3.89612500	-3.36182100	-2.06735000

Name: tr_BH3_c7_sm
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

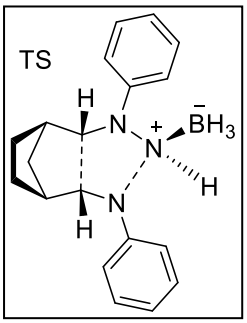


Electronic energy = -927.439497968 Hartree
Zero-point Energy correction = 0.388208 Hartree
Thermal correction to Energy = 0.407481 Hartree
Thermal correction to Enthalpy = 0.408425 Hartree
Thermal correction to Gibbs Free Energy = 0.339519 Hartree

N	-0.64077400	-0.47013700	-0.16670000
C	-0.44584300	0.87651200	-0.74456500
C	-1.95964100	-0.98563300	-0.11692000
C	-1.52316400	1.93466600	-0.39578400
H	-0.29277900	0.78381000	-1.84016700
C	-2.62238100	-1.16918800	-1.35354200
C	-2.65331700	-1.26881400	1.07958200
C	-1.11244600	3.24883800	-1.10725600
C	-1.19062600	2.25592900	1.07907700
H	-2.55344900	1.59425400	-0.61076900
C	-3.94924700	-1.61638900	-1.38995100
H	-2.07774200	-0.96496300	-2.28748900
C	-3.97765600	-1.73444100	1.03080800
H	-2.15966500	-1.16572000	2.05456800
C	0.09910100	3.75489700	-0.25184300
H	-0.84401100	3.07430500	-2.16994600
H	-1.94947300	3.97528900	-1.10080800
C	0.28479000	2.62576200	0.79378900
H	-1.34651200	1.40462700	1.77324100
H	-1.77741500	3.10869200	1.47834500
C	-4.63618100	-1.90601000	-0.19686300
H	-4.44600000	-1.75555300	-2.36300200
H	-4.49809300	-1.96357500	1.97389000
H	1.01550500	3.91984500	-0.85450200
H	-0.13653600	4.71271800	0.25420400
C	0.82616800	1.40388900	0.00670900
H	0.92136300	2.88881100	1.65986100
H	1.63984500	1.70791600	-0.67748400
N	1.32682900	0.27584800	0.80968000
N	0.19450300	-0.58895300	1.04981000
C	2.47096700	-0.39080000	0.22240400
B	0.54773100	-2.10281500	1.57726700
H	-0.30519300	-0.13310000	1.83710500
C	3.70136900	-0.24257200	0.88149500
C	2.39548400	-1.10821200	-0.98840500
H	0.91865000	-2.76070700	0.61579800
H	-0.49200000	-2.51934400	2.07708200

H	1.42009400	-1.90082200	2.42095600
C	4.86564300	-0.80178800	0.32859100
H	3.72262400	0.30850900	1.83309100
C	3.55862900	-1.67473100	-1.53031600
H	1.41968800	-1.24262100	-1.47734800
C	4.79494100	-1.51956400	-0.87685100
H	5.82937500	-0.68553000	0.84848400
H	3.49900600	-2.24818300	-2.46861700
H	-5.67442100	-2.27012400	-0.22592200
H	5.70503300	-1.96586500	-1.30738900

Name: tr_BH3_TS_c7_1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

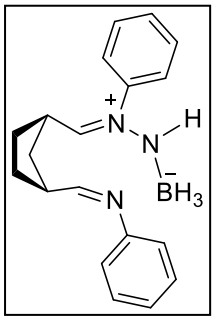


Electronic energy = -927.381409646 Hartree
Zero-point Energy correction = 0.383029 Hartree
Thermal correction to Energy = 0.403011 Hartree
Thermal correction to Enthalpy = 0.403955 Hartree
Thermal correction to Gibbs Free Energy = 0.334454 Hartree

N	-0.84830100	-0.24998700	-0.93155300
C	-0.50182400	1.04537700	-1.10207500
C	-2.03823500	-0.82926000	-0.53901700
C	-1.36043200	2.27937800	-0.74899400
H	0.14825700	1.19057600	-1.99448100
C	-2.00593700	-2.25546300	-0.41640400
C	-3.29751700	-0.19132400	-0.29851900
C	-0.59096900	3.58380000	-1.09515400
C	-1.37958600	2.29599100	0.79395200
H	-2.35181000	2.23742200	-1.24037900
C	-3.14385500	-2.99194700	-0.06959100
H	-1.05520600	-2.75922200	-0.63703600
C	-4.43144200	-0.94110200	0.03957800
H	-3.40555800	0.89453600	-0.39685000
C	0.30600500	3.84750900	0.15568800
H	0.00437800	3.45976900	-2.02437500
H	-1.29335400	4.42162700	-1.27579000
C	0.13793200	2.54661900	0.97549500
H	-1.77141200	1.35711100	1.23601200
H	-1.97977600	3.12808100	1.21777300
C	-4.36730800	-2.34154900	0.16584100
H	-3.07372700	-4.08786400	0.01478500
H	-5.38737400	-0.41892500	0.20768900
H	1.36532700	4.05510700	-0.09809900

H	-0.06590300	4.71052900	0.74395000
C	0.91197700	1.46668200	0.20488000
H	0.48437100	2.62220500	2.02771400
H	1.77481000	1.84896000	-0.36417400
N	1.25142300	0.25668300	0.78312300
N	0.30947700	-0.46845600	1.37671000
C	2.39464700	-0.45100300	0.24497200
B	0.40158400	-1.82713800	2.07224500
H	-0.52157400	0.10403300	1.56436400
C	3.67224600	-0.17931000	0.75320000
C	2.18873600	-1.35640100	-0.80915200
H	1.48058000	-2.36786200	1.87210500
H	-0.57360500	-2.47226800	1.63328800
H	0.12559700	-1.62208700	3.26901900
C	4.77816400	-0.83953100	0.19151300
H	3.79019300	0.52799900	1.58754200
C	3.30207200	-2.00561900	-1.36177900
H	1.15721000	-1.50153000	-1.17082000
C	4.59310200	-1.75160400	-0.86195300
H	5.78770900	-0.64507900	0.58505300
H	3.16102500	-2.71621600	-2.19091700
H	-5.26527200	-2.91783400	0.43711000
H	5.46235100	-2.26852300	-1.29756200

Name: tr_BH3_c7_prod
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

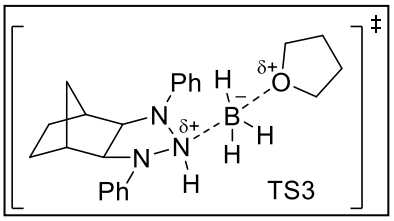


Electronic energy = -927.433359612 Hartree
Zero-point Energy correction = 0.383430 Hartree
Thermal correction to Energy = 0.404747 Hartree
Thermal correction to Enthalpy = 0.405692 Hartree
Thermal correction to Gibbs Free Energy = 0.332464 Hartree

N	-1.17638600	-0.20522500	-1.69663100
C	-1.30183900	1.06281000	-1.54141600
C	-1.87846800	-1.13330000	-0.89838400
C	-2.13064000	1.81711200	-0.50316800
H	-0.72563000	1.69726000	-2.25239400
C	-1.16489300	-1.96727000	-0.00714300
C	-3.27945700	-1.28615800	-1.01984200
C	-1.92130000	3.34889300	-0.61018400
C	-1.67033900	1.49212100	0.93927000
H	-3.19554200	1.53595800	-0.63853400
C	-1.85355000	-2.89008000	0.79219500

H	-0.07422100	-1.87209100	0.09492400
C	-3.95439500	-2.23502600	-0.23522100
H	-3.82830500	-0.66578700	-1.74562500
C	-0.79275500	3.70483700	0.40718700
H	-1.66651000	3.65240800	-1.64694500
H	-2.85873200	3.87914200	-0.34937500
C	-0.39114700	2.36869100	1.09131700
H	-1.50427500	0.41059500	1.10832400
H	-2.44159200	1.82850700	1.66416100
C	-3.24907000	-3.03199500	0.68331100
H	-1.27857600	-3.49629200	1.50909900
H	-5.04513800	-2.34784800	-0.34250300
H	0.08038300	4.19166700	-0.07262900
H	-1.16618300	4.41519800	1.17092700
C	0.78465200	1.74057600	0.40990900
H	-0.15331400	2.53220000	2.17138900
H	1.26979200	2.17778900	-0.47103000
N	1.33775000	0.60875700	0.85443300
N	0.98163000	-0.04096400	1.95955900
C	2.42030800	0.02257200	0.07541000
B	1.43554700	-1.46325800	2.45205500
H	0.28730100	0.48948400	2.49297700
C	3.69499500	-0.08366700	0.65110100
C	2.14784400	-0.41260700	-1.22951500
H	1.64231600	-2.17926400	1.46636300
H	0.48863800	-1.85669100	3.14359400
H	2.46751900	-1.36695100	3.14031100
C	4.73309700	-0.62738400	-0.11789600
H	3.85766800	0.23987400	1.68821100
C	3.19944200	-0.96191700	-1.98324900
H	1.12149100	-0.35869800	-1.62970300
C	4.48739200	-1.06602500	-1.43253400
H	5.74052300	-0.71663100	0.31634500
H	3.00142600	-1.31935300	-3.00534000
H	-3.78330600	-3.76586300	1.30618800
H	5.30630600	-1.49938900	-2.02744200

Name: cis_BH3_sm_attack_TS_c3
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

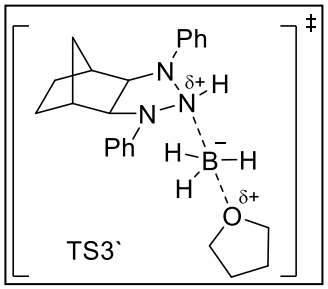


Electronic energy = -1159.85936306 Hartree
Zero-point Energy correction = 0.501798 Hartree
Thermal correction to Energy = 0.527442 Hartree
Thermal correction to Enthalpy = 0.528386 Hartree
Thermal correction to Gibbs Free Energy = 0.443544 Hartree

N	0.95458100	1.12604600	-0.17810300
C	2.36579100	0.77975300	-0.01560800
C	0.56123100	2.35596100	-0.70745800
N	0.17414700	-0.00003600	-0.57505100
C	2.92747400	1.13414500	1.38736900
C	2.36617700	-0.77873000	-0.01559300
H	2.98445700	1.20623700	-0.84004300
C	-0.72371200	2.52660800	-1.28593000
C	1.45360400	3.46013300	-0.68979300
N	0.95513400	-1.12572100	-0.17805900
H	0.10491600	-0.00007400	-1.62780800
C	4.43439500	0.78385300	1.37073000
C	2.32705500	0.00051800	2.24651400
H	2.69266000	2.16865400	1.70157900
C	2.92805500	-1.13281300	1.38738400
H	2.98504200	-1.20492500	-0.84002800
C	-1.09502200	3.76991200	-1.81749300
H	-1.43920300	1.69384800	-1.27739000
C	1.05946400	4.69511800	-1.22333000
H	2.45404500	3.35983800	-0.24763600
C	0.56237900	-2.35584800	-0.70736800
C	4.43479700	-0.78174100	1.37073300
H	4.95252600	1.21369300	0.48794300
H	4.93693200	1.18903100	2.27189100
H	1.21867900	0.00023400	2.24699800
H	2.69693900	0.00062100	3.29212000
H	2.69377800	-2.16743900	1.70161100
H	4.95314400	-1.21131800	0.48794500
H	4.93754700	-1.18665800	2.27189300
C	-0.72249400	-2.52714300	-1.28580100
C	1.45530000	-3.45957700	-0.68970000
C	-1.09320200	-3.77064100	-1.81733000
H	-1.43839600	-1.69473600	-1.27725400

C	1.06175800	-4.69476800	-1.22320200
H	2.45570300	-3.35877600	-0.24757200
C	-0.21410700	4.86448100	-1.79360700
H	-2.09932400	3.87999800	-2.25707700
H	1.76788300	5.53829700	-1.19358500
C	-0.21174300	-4.86477200	-1.79344500
H	-2.09746100	-3.88123500	-2.25688500
H	1.77059500	-5.53759600	-1.19345900
H	-0.51495000	5.83675900	-2.21224900
H	-0.51211400	-5.83720700	-2.21206100
B	-1.73010300	-0.00044800	0.65396400
H	-1.37075000	1.05770600	1.13474000
H	-1.37022600	-1.05837300	1.13485400
H	-2.40991600	-0.00068100	-0.36866800
O	-3.43052500	-0.00079900	1.86839400
C	-4.26592200	-1.14711800	1.64679900
C	-4.26620500	1.14538400	1.64718500
C	-5.17551400	-0.77886700	0.45416700
H	-3.59648800	-2.00927100	1.46493800
H	-4.86467200	-1.34050500	2.56801100
C	-5.17542700	0.77737400	0.45423300
H	-4.86519000	1.33817100	2.56837400
H	-3.59699400	2.00781800	1.46583400
H	-6.19124100	-1.20712900	0.57053500
H	-4.75221300	-1.16924900	-0.49163300
H	-6.19113900	1.20577200	0.57023400
H	-4.75167700	1.16777100	-0.49136000

Name: tr_BH3_sm_attack_TS_1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

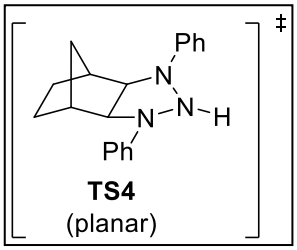


Electronic energy = -1159.85676058 Hartree
Zero-point Energy correction = 0.501787 Hartree
Thermal correction to Energy = 0.527503 Hartree
Thermal correction to Enthalpy = 0.528447 Hartree
Thermal correction to Gibbs Free Energy = 0.443465 Hartree

N	-1.81514000	-0.12392400	-0.53997400
C	-1.69275100	-0.92368800	0.67320300
C	-2.64812400	0.99703300	-0.60004600
N	-0.49690900	0.04843300	-1.11247900
C	-2.72403000	-2.08027200	0.76785900
C	-0.33713600	-1.67541400	0.48503900
H	-1.69234400	-0.27851200	1.58131900
C	-2.50898000	-2.75523400	2.14429000
C	-2.12209300	-3.11460400	-0.20651200
H	-3.76396200	-1.76222700	0.56651800
C	-1.14828600	-3.50723900	1.96216000
H	-2.48329300	-2.01325700	2.96946100
H	-3.33528100	-3.46030900	2.36530500
C	-0.75319300	-3.17001300	0.50384000
H	-0.37506400	-3.17898600	2.68785900
H	-1.26985700	-4.60178700	2.08883800
H	-2.05056600	-2.73427200	-1.24473700
H	-2.65893700	-4.08511400	-0.20581700
H	0.00587000	-3.84284700	0.06206500
H	0.39351600	-1.42210500	1.28687500
N	0.13499700	-1.22568100	-0.81984800
C	1.48830400	-1.31576300	-1.16407500
C	-3.74874100	1.12403600	0.28506300
C	-2.44106400	2.00729300	-1.57411600
H	-0.64671500	0.04982200	-2.13862600
C	2.01038100	-0.57006000	-2.25197400
C	2.36089700	-2.18141100	-0.45720100
C	-4.62499300	2.21304000	0.17355200
H	-3.92525100	0.36951100	1.06324200
C	-3.32550800	3.08976700	-1.66847500
H	-1.56274100	1.97373400	-2.23292000
C	-4.42853600	3.20264400	-0.80440900
H	-5.47334000	2.28784900	0.87244300

H	-3.13636600	3.86663500	-2.42616200
H	-5.11828300	4.05628500	-0.88475700
C	3.35985500	-0.68392600	-2.60677500
H	1.37106200	0.13579300	-2.79845600
C	3.70876500	-2.28934000	-0.83093900
H	1.98991900	-2.76765300	0.39397800
C	4.22424700	-1.54300400	-1.90364700
H	3.74242200	-0.08289300	-3.44695900
H	4.36641800	-2.96682100	-0.26316100
H	5.28351400	-1.62915400	-2.18921500
B	0.75972600	1.70748300	-0.07049700
H	1.31047400	0.73668800	0.42300900
H	1.12224300	2.12123700	-1.15902800
H	-0.23654100	2.17342200	0.45609800
H	3.77981400	3.58798700	-0.12481600
C	3.42072600	2.66498000	0.37634600
O	2.08885900	2.91620100	0.90704400
C	4.28879400	2.23936000	1.57071700
H	3.33047700	1.85794200	-0.38140500
C	2.07375800	2.62735300	2.32308600
C	3.24533600	1.67150100	2.54907600
H	4.80285100	3.11512400	2.02153100
H	5.06368600	1.50190100	1.28118900
H	2.20490300	3.57817000	2.89074600
H	1.07923000	2.20189900	2.56167700
H	3.59117700	1.64755700	3.60203700
H	2.95506300	0.64333900	2.24774300

Name: noncat-sm_NH_flip_flop_TS_planar_1
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

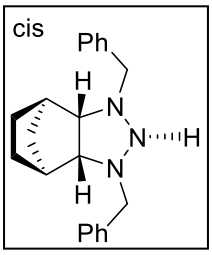


Electronic energy = -900.765093094 Hartree
Zero-point Energy correction = 0.354598 Hartree
Thermal correction to Energy = 0.372092 Hartree
Thermal correction to Enthalpy = 0.373036 Hartree
Thermal correction to Gibbs Free Energy = 0.307855 Hartree

N	1.11735346	-0.15827804	-0.12215343
C	0.79292246	1.20128396	-0.56334443
N	-0.00000154	-0.93327904	-0.44747943
C	2.37533246	-0.72561504	-0.08196143
C	1.13643046	2.29033796	0.48056057
C	-0.79291954	1.20128596	-0.56334243
H	1.20948546	1.41945496	-1.57587543
N	-1.11735454	-0.15827504	-0.12215043
H	-0.00000254	-1.92682304	-0.65405943
C	3.53820046	0.03869496	-0.37785743
C	2.53382046	-2.09972004	0.25602257
C	0.78294246	3.65503196	-0.15951143
C	0.00000446	2.10608996	1.51093257
H	2.16918246	2.21743696	0.87004957
C	-1.13642354	2.29034096	0.48056257
H	-1.20948454	1.41945796	-1.57587343
C	-2.37533454	-0.72560904	-0.08195943
C	4.80659346	-0.55108604	-0.30110043
H	3.44514846	1.09324496	-0.67266043
C	3.81143646	-2.66920804	0.31874157
H	1.64958846	-2.70574804	0.50490857
C	-0.78293254	3.65503396	-0.15950943
H	1.21246946	3.76169096	-1.17739843
H	1.18747446	4.48548596	0.45319157
H	0.00000346	1.10155496	1.97755257
H	0.00000646	2.88230696	2.30316057
H	-2.16917554	2.21744296	0.87005357
H	-1.21246154	3.76169396	-1.17739543
H	-1.18746154	4.48548896	0.45319457
C	-2.53382554	-2.09971304	0.25602357
C	-3.53820054	0.03870396	-0.37785343
C	-3.81144354	-2.66919804	0.31874257
H	-1.64959554	-2.70574404	0.50490957

C	-4.80659554	-0.55107404	-0.30109643
H	-3.44514554	1.09325396	-0.67265543
C	-4.96142854	-1.90605804	0.04533757
H	-3.90793554	-3.73225504	0.59205257
H	-5.69259854	0.06233296	-0.53103543
C	4.96142246	-1.90607104	0.04533457
H	5.69259746	0.06231796	-0.53103943
H	3.90792546	-3.73226504	0.59205157
H	-5.96168054	-2.36134804	0.09573657
H	5.96167446	-2.36136304	0.09573457

Name: Bn2norbornene_NH_cis_sm_c12
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

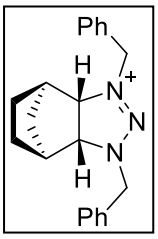


Electronic energy = -979.410757801 Hartree
Zero-point Energy correction = 0.412117 Hartree
Thermal correction to Energy = 0.431868 Hartree
Thermal correction to Enthalpy = 0.432812 Hartree
Thermal correction to Gibbs Free Energy = 0.361851 Hartree

N	-0.7730941426	0.8146729237	0.0621533234
C	-0.0125907857	1.80072218	0.8434473266
C	-0.6351301228	3.218726348	0.8916401265
C	0.2137389421	4.0590275652	1.8775771666
C	1.555081636	4.2754848461	1.096844257
C	1.302200215	3.5494644681	-0.2484457328
H	2.4340902573	3.8590004245	1.6321654728
H	1.7574706405	5.3529854125	0.9298928582
C	-0.2053698857	3.8166955752	-0.4691114238
C	1.3253739798	2.0250566548	0.0377449325
H	1.9850102748	3.8372661666	-1.0708497036
H	-1.7203024182	3.1974382297	1.1084419796
H	0.3596057172	3.5389454798	2.8472163126
H	-0.2850722765	5.0246976242	2.0979201656
H	-0.6292343774	3.2884537241	-1.3461299653
H	-0.4477444747	4.895877798	-0.5661529175
H	2.2274507739	1.7429847469	0.618232521
N	1.1982529829	1.1814495609	-1.1562596301
H	0.1677410624	1.407220798	1.8650095434
N	-0.1455866047	0.6814759493	-1.2279336262

H	-0.6500290669	1.3312613701	-1.8451761372
C	2.2244768732	0.1472153942	-1.3715091556
H	3.2059067779	0.6557940167	-1.2693382288
H	2.1444042185	-0.1770556619	-2.4299096271
C	-0.9776329401	-0.4667480781	0.7397036653
H	-0.0278971358	-1.0256220441	0.9127950384
H	-1.3853267143	-0.2205203908	1.7456602824
C	2.1634210593	-1.0723666652	-0.4731587017
C	2.7558471965	-1.0798552353	0.8090251825
C	1.4566988847	-2.2178973535	-0.8958455789
C	2.6309599963	-2.196313115	1.6524399009
H	3.3327162996	-0.2039643666	1.1486533593
C	1.3505779071	-3.345096792	-0.0658069333
H	0.9734076704	-2.2144669561	-1.8848175663
C	1.9302002465	-3.3348737761	1.2147506247
H	3.0971663856	-2.1854741711	2.6504666381
H	0.8020873911	-4.2322304594	-0.4182056339
H	1.8432633081	-4.2160841674	1.8697742864
C	-1.9739631722	-1.3637885292	0.0343201352
C	-1.9708746237	-2.7495528236	0.2935694251
C	-2.9455251046	-0.8430014166	-0.8431028822
C	-2.9138459039	-3.5972592616	-0.3099179444
H	-1.2133817761	-3.1645828259	0.9769937472
C	-3.8874293993	-1.6885090765	-1.4518733725
H	-2.9504031108	0.2398388819	-1.0383631061
C	-3.8749723612	-3.069688931	-1.1901189989
H	-2.8950851432	-4.6780085663	-0.0959889857
H	-4.6383517347	-1.2650724213	-2.1382589459
H	-4.6108292691	-3.7332460379	-1.6713220993

Name: Bn2norbornene_nitrenium_c3
Charge: 1
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran

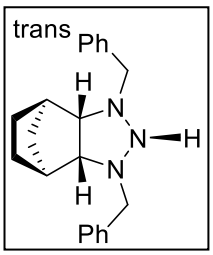


Electronic energy = -978.667055501 Hartree
Zero-point Energy correction = 0.402519 Hartree
Thermal correction to Energy = 0.422242 Hartree
Thermal correction to Enthalpy = 0.423186 Hartree
Thermal correction to Gibbs Free Energy = 0.350898 Hartree

N	-1.0624892296	-0.8589061711	-1.4933672133
C	-0.7846404872	-1.9098244045	-0.4802145769
C	-1.1395657807	-1.539246914	0.9839373569
C	-0.7820216678	-2.7891554331	1.8292149158
C	0.7838168616	-2.7885889758	1.8291258796
C	1.1403682196	-1.538441418	0.9837841699
H	1.2205469741	-3.7190013048	1.4129946096
H	1.1897476622	-2.6743758586	2.852912036
C	0.0000804724	-0.5625574282	1.3453935513
C	0.7855135252	-1.9092776051	-0.4803237548
H	2.1745810889	-1.1719459026	1.1094062206
H	-2.174021214	-1.1734721596	1.1096974018
H	-1.2181243948	-3.7198722189	1.4131063425
H	-1.1879226206	-2.6752630779	2.853048431
H	-0.0002973686	0.3745858284	0.7534724724
H	0.0000558625	-0.2873008423	2.4182007892
H	1.2666998447	-2.8501655205	-0.8167964421
N	1.0624882509	-0.8581957468	-1.4935534695
H	-1.2652314046	-2.8510349888	-0.8166363365
N	-0.0002254782	-0.3139416394	-1.9899283427
C	2.3923096141	-0.355752901	-1.8645865022
H	3.0424327215	-1.2371566862	-2.0358181637
H	2.259876158	0.1711192644	-2.8304454681
C	2.9708450687	0.5496467512	-0.7927994617
C	4.1686074502	0.2096485558	-0.1350785821
C	2.2903124631	1.7313815876	-0.4332964844
C	4.6788541598	1.04044702	0.8772824963
H	4.708355279	-0.7092882192	-0.41670043
C	2.796949122	2.5571807209	0.5812947377
H	1.3608309065	2.0120449481	-0.9554548154
C	3.990179275	2.2099908111	1.2408056445
H	5.6183552735	0.7718509096	1.3838716844
H	2.2644480714	3.4808814157	0.8548332293

H	4.3884625954	2.8587798353	2.0357902791
C	-2.3927003435	-0.357161278	-1.8639299292
H	-2.2609403652	0.1696701811	-2.8299041213
H	-3.0424494514	-1.2389119002	-2.0347853862
C	-2.9712305073	0.5480482954	-0.7919773194
C	-4.1685635234	0.2075250266	-0.133745932
C	-2.2911129055	1.7301283973	-0.4328237444
C	-4.6788031683	1.0381556118	0.8787562991
H	-4.7079864544	-0.7116904124	-0.4150807722
C	-2.7977409634	2.5557622406	0.5819071203
H	-1.3619720691	2.0111994684	-0.955370439
C	-3.990542942	2.2080549525	1.2419184654
H	-5.6179722263	0.7691464102	1.3857419011
H	-2.2655698884	3.4797367669	0.85516346
H	-4.388816881	2.8567124971	2.0370151085

Name: Bn2norbornene_NH_tr_sm_c25
Charge: 0
Multiplicity: 1
Solvatation: cpcm,solvent=TetraHydroFuran



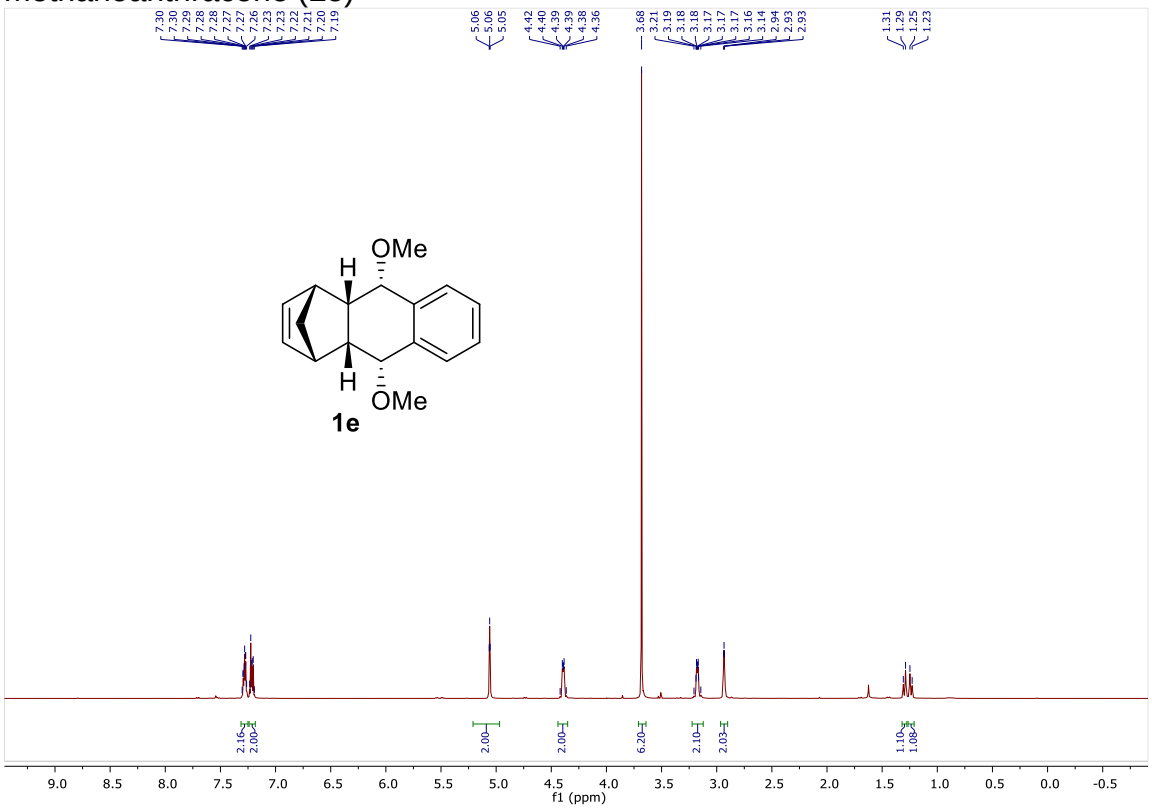
Electronic energy = -979.400173584 Hartree
Zero-point Energy correction = 0.411842 Hartree
Thermal correction to Energy = 0.431465 Hartree
Thermal correction to Enthalpy = 0.432409 Hartree
Thermal correction to Gibbs Free Energy = 0.362694 Hartree

N	-0.4126122194	-0.4418796919	-0.2702593491
C	0.2367590277	-1.7129903137	-0.599861862
C	-0.6568580358	-2.9294692366	-0.9720342068
C	0.3014801957	-4.0909959351	-1.3398616296
C	0.8753536054	-4.5294746205	0.0494314795
C	0.203745459	-3.5388576305	1.0335432757
H	1.983618447	-4.4798104603	0.0929782874
H	0.5868356627	-5.5719202813	0.2944397057
C	-1.199581249	-3.3810471545	0.405003634
C	0.8591655361	-2.1570682793	0.7852292851
H	0.2461426091	-3.836534232	2.098774234
H	-1.4090463425	-2.7093038096	-1.7545569817
H	1.093291261	-3.764272168	-2.0465043012
H	-0.2515159687	-4.9172905549	-1.8310287123
H	-1.8112227485	-2.6129317062	0.9143722677

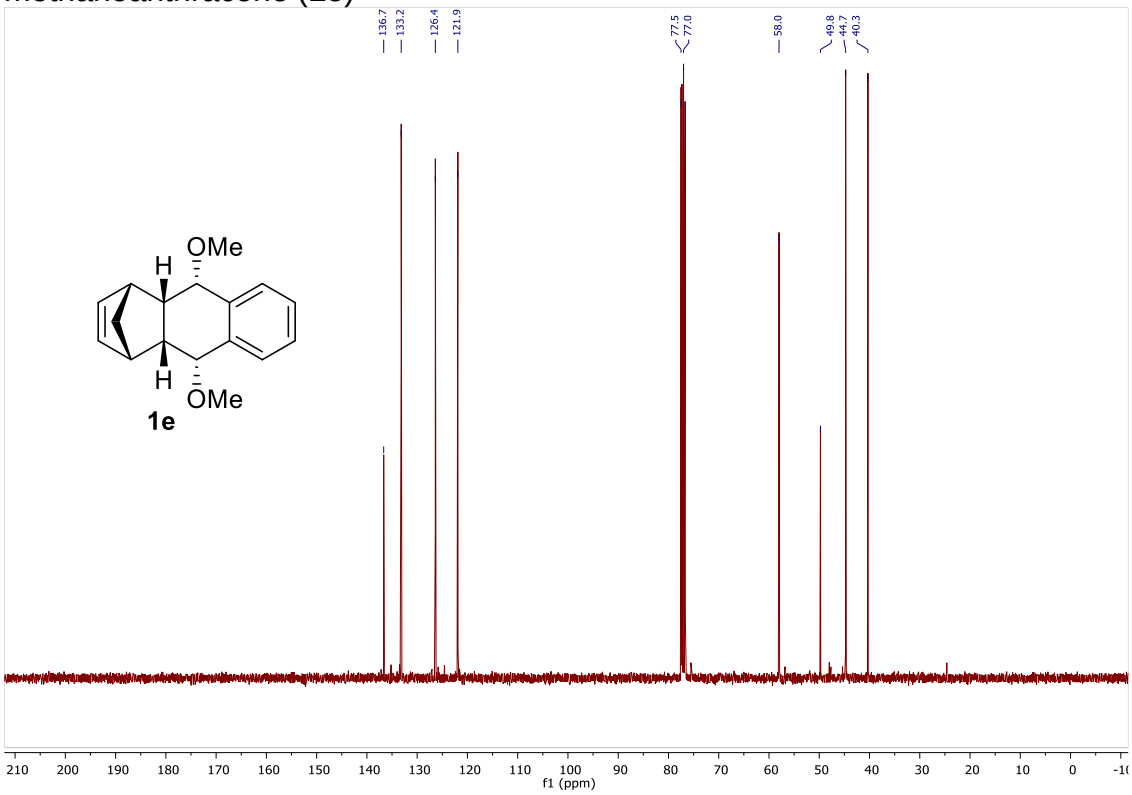
H	-1.7595644554	-4.3393679339	0.3549410572
H	1.961429305	-2.2541766324	0.7609091231
N	0.5026046618	-1.1064628264	1.7463501896
H	1.0080728094	-1.5224114884	-1.3780171691
N	-0.6894964165	-0.5408374689	1.2083893079
H	-0.7403036162	0.440950478	1.5332108532
C	1.5904389664	-0.1264823304	2.0216648642
C	2.0136171037	0.8023309829	0.8991112996
H	2.4529903423	-0.7279116743	2.3766599471
H	1.2550615965	0.4787449494	2.8917268738
C	2.9044637375	0.379309241	-0.1132120912
C	1.510787077	2.1187191826	0.843073699
C	3.248290146	1.2335599527	-1.1703540161
H	3.3395739751	-0.631983496	-0.0677491884
C	1.8626380965	2.9820052508	-0.2064586944
H	0.8311509186	2.4748627897	1.6348913773
C	2.7235271562	2.5388690074	-1.2236653988
H	3.9421939385	0.8866271254	-1.9525525549
H	1.457927449	4.0055236207	-0.2296122337
H	3.0019550798	3.21365217	-2.0484287325
C	-1.6506959965	-0.1184385855	-0.9628089462
C	-2.0451559476	1.3206335325	-0.6881140241
H	-2.4937542704	-0.7967953352	-0.6774660517
H	-1.4602124273	-0.2531355125	-2.0487501028
C	-1.2642021991	2.3726980682	-1.2090909826
C	-3.1481389609	1.6306372612	0.1304511517
C	-1.5937388562	3.7083028142	-0.9346684492
H	-0.3794157911	2.1303231319	-1.8177196985
C	-3.4769574439	2.9685830613	0.4140738332
H	-3.7497143001	0.809516139	0.5536289233
C	-2.7016496365	4.0107021784	-0.1212520558
H	-0.9818009578	4.5218445481	-1.35601446
H	-4.3421332948	3.1969927932	1.0565577318
H	-2.9590584599	5.0595536122	0.0956114753

NMR Spectra

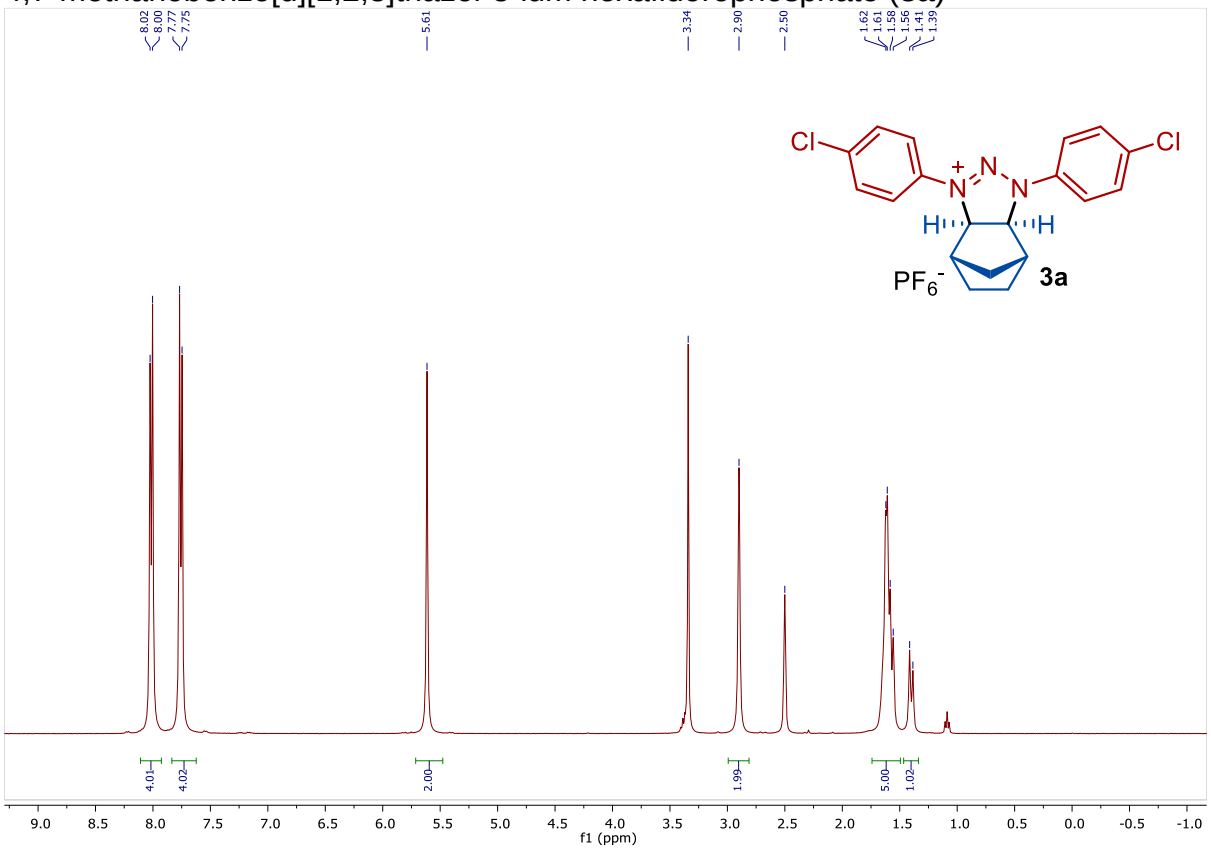
^{1}H NMR of (1*R*,4*S*,4a*R*,9*S*,9a*S*,10*R*)-9,10-dimethoxy-1,4,4a,9,9a,10-hexahydro-1,4-methanoanthracene (**1e**)



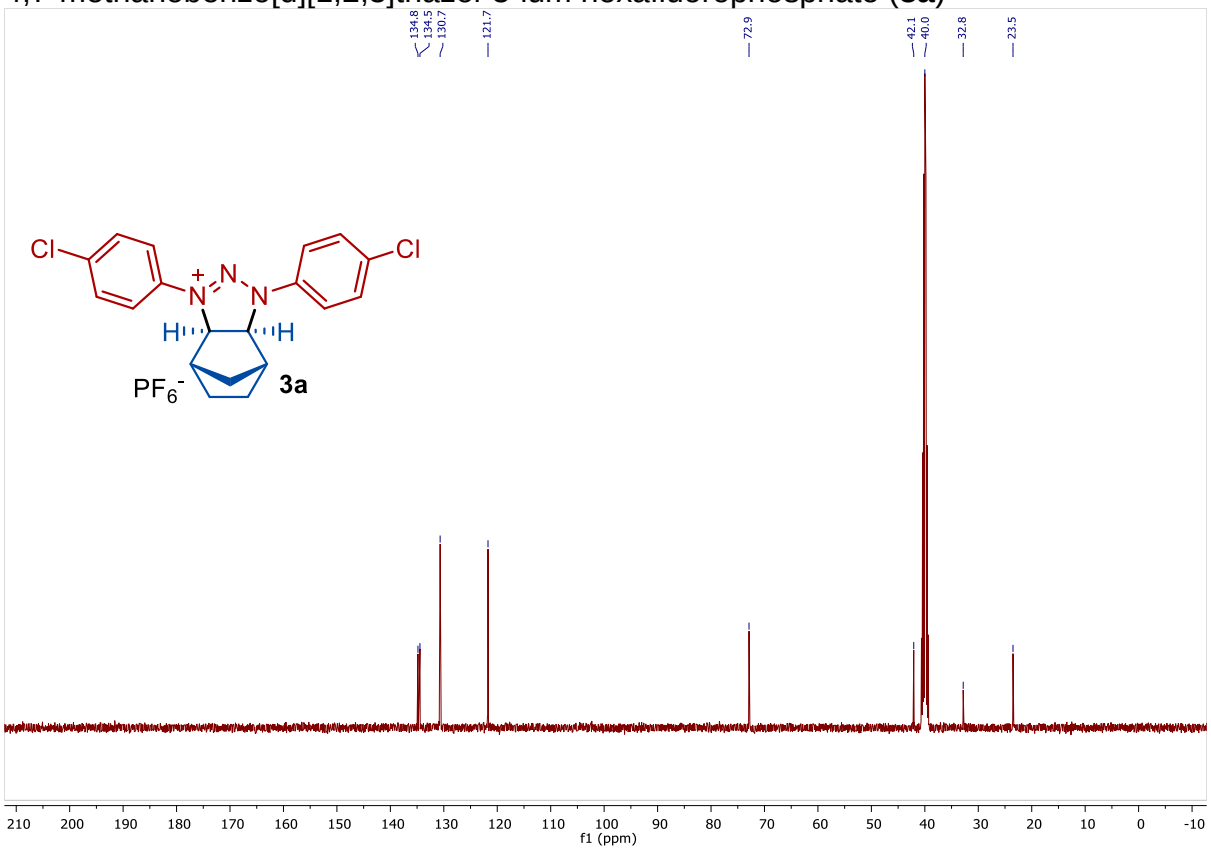
^{13}C NMR of (1*R*,4*S*,4a*R*,9*S*,9a*S*,10*R*)-9,10-dimethoxy-1,4,4a,9,9a,10-hexahydro-1,4-methanoanthracene (**1e**)



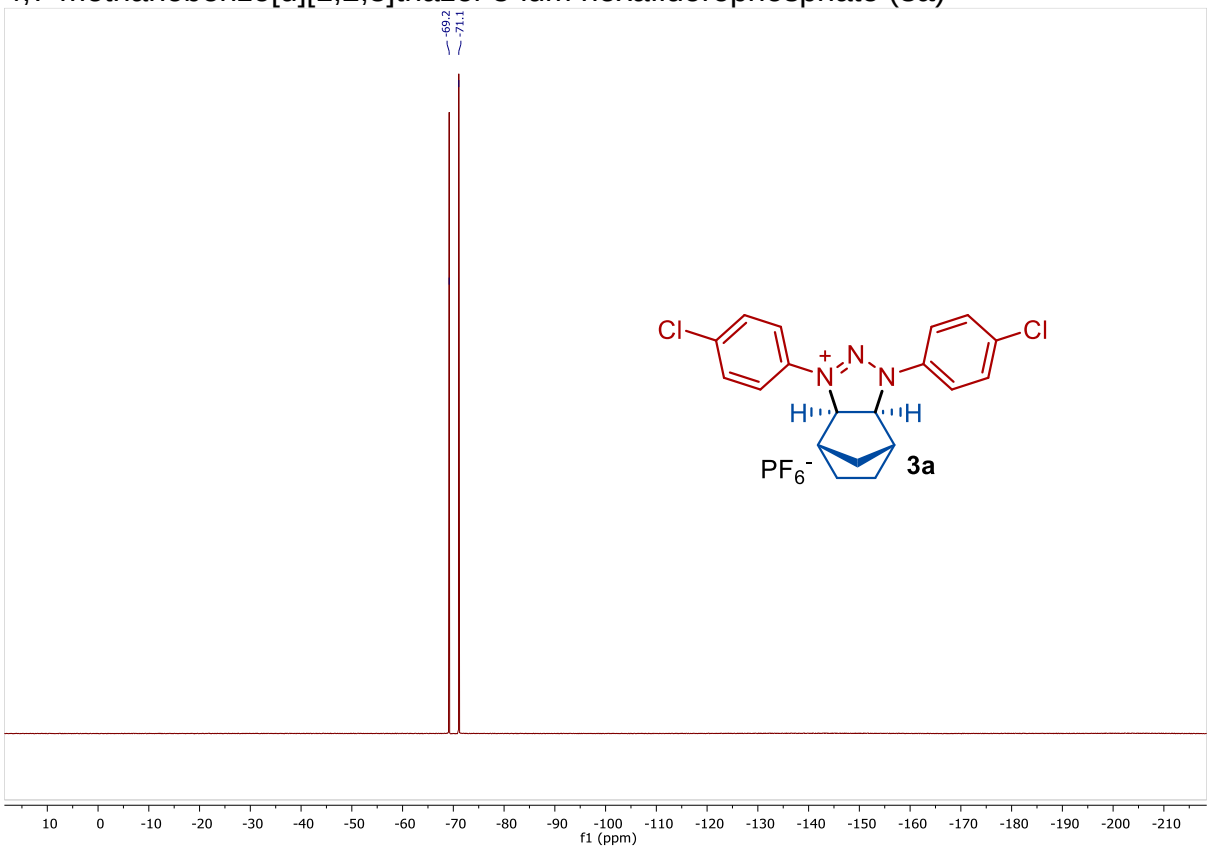
^{1}H NMR of (3aR,4S,7R,7aS)-1,3-bis(4-chlorophenyl)-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanobenzo[d][1,2,3]triazol-3-ium hexafluorophosphate (**3a**)



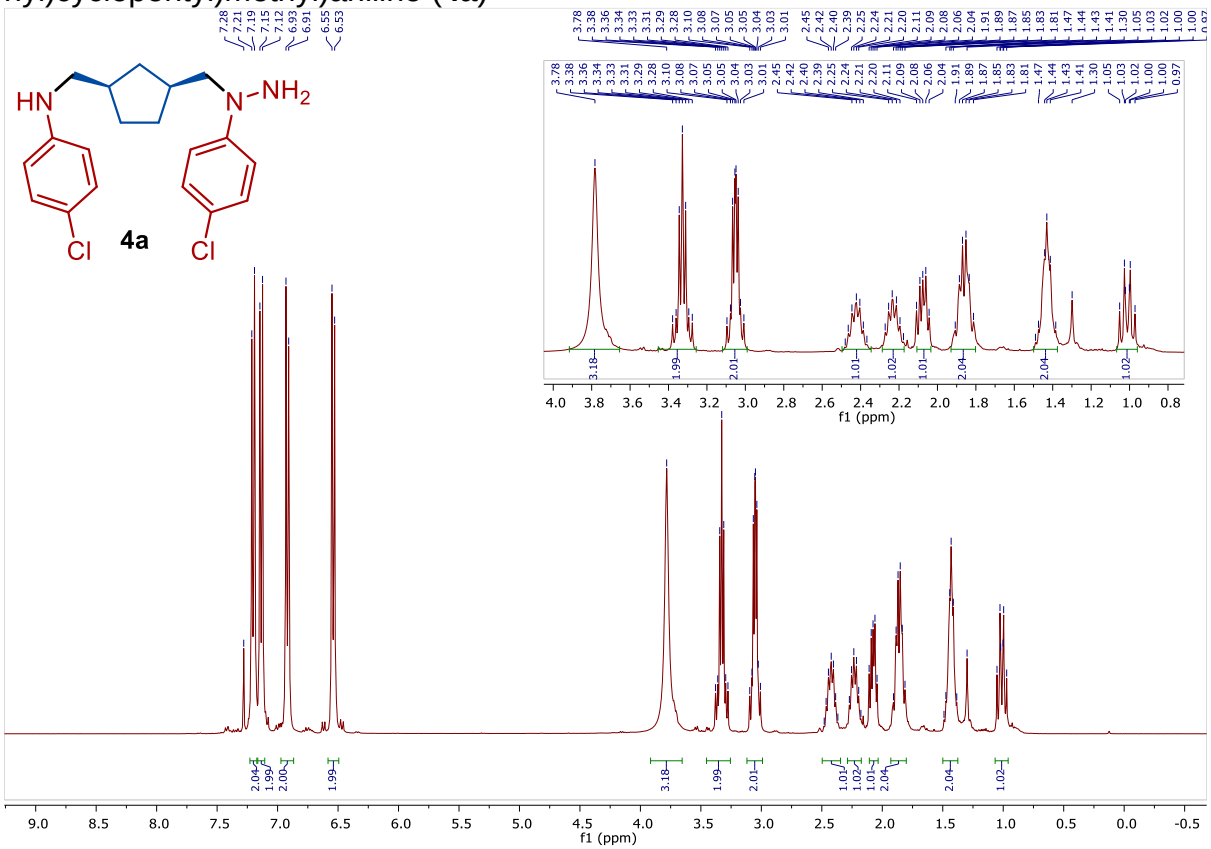
^{13}C NMR of (3aR,4S,7R,7aS)-1,3-bis(4-chlorophenyl)-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanobenzo[d][1,2,3]triazol-3-ium hexafluorophosphate (**3a**)



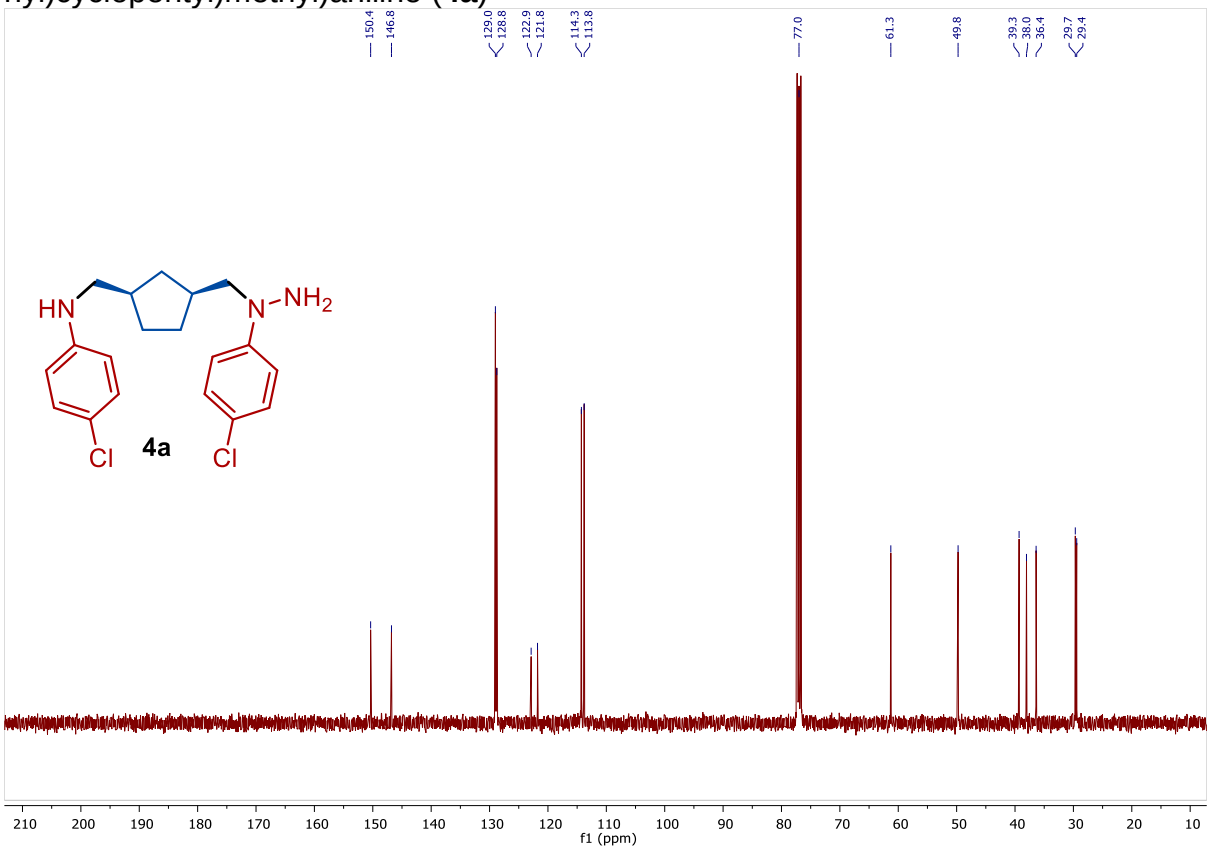
^{19}F NMR of (3aR,4S,7R,7aS)-1,3-bis(4-chlorophenyl)-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanobenzo[d][1,2,3]triazol-3-ium hexafluorophosphate (**3a**)



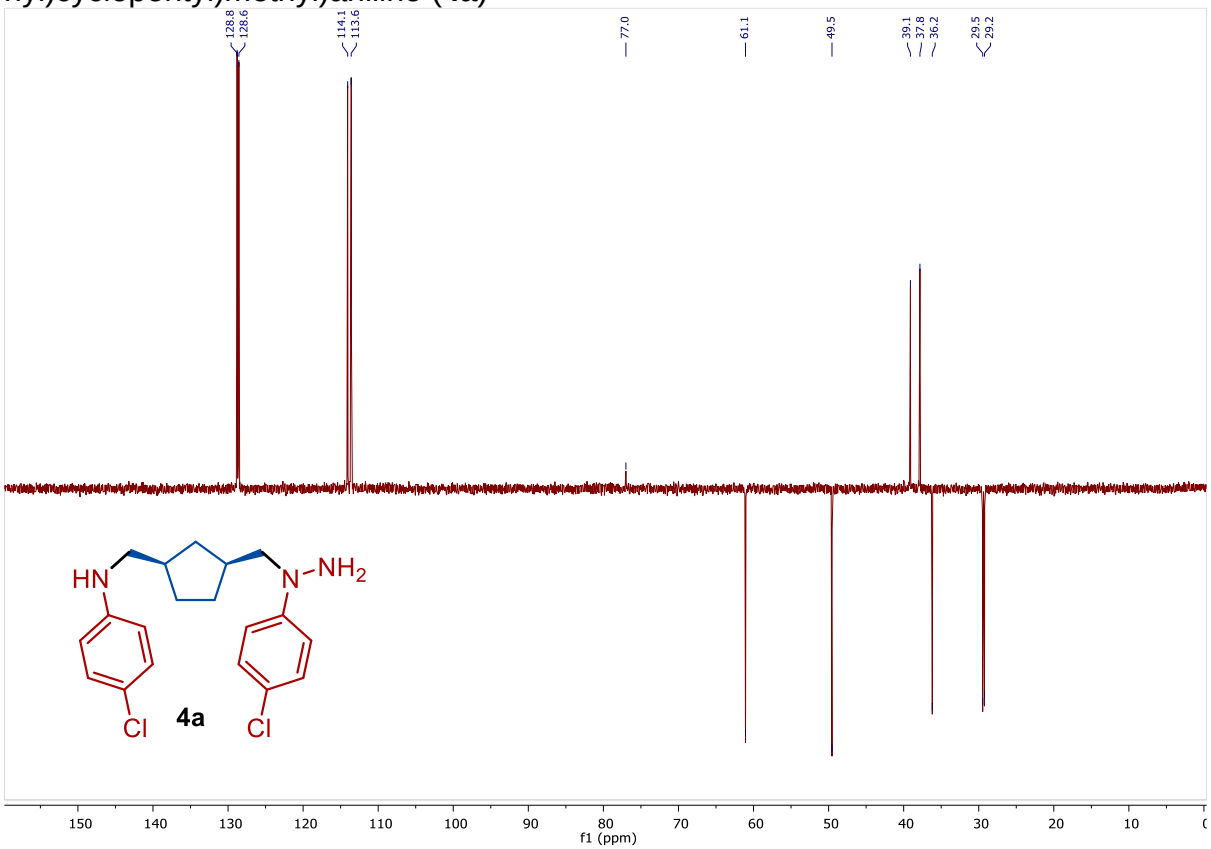
^{1}H NMR of 4-chloro-N-(((1RS,3SR)-3-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentyl)methyl)aniline (**4a**)



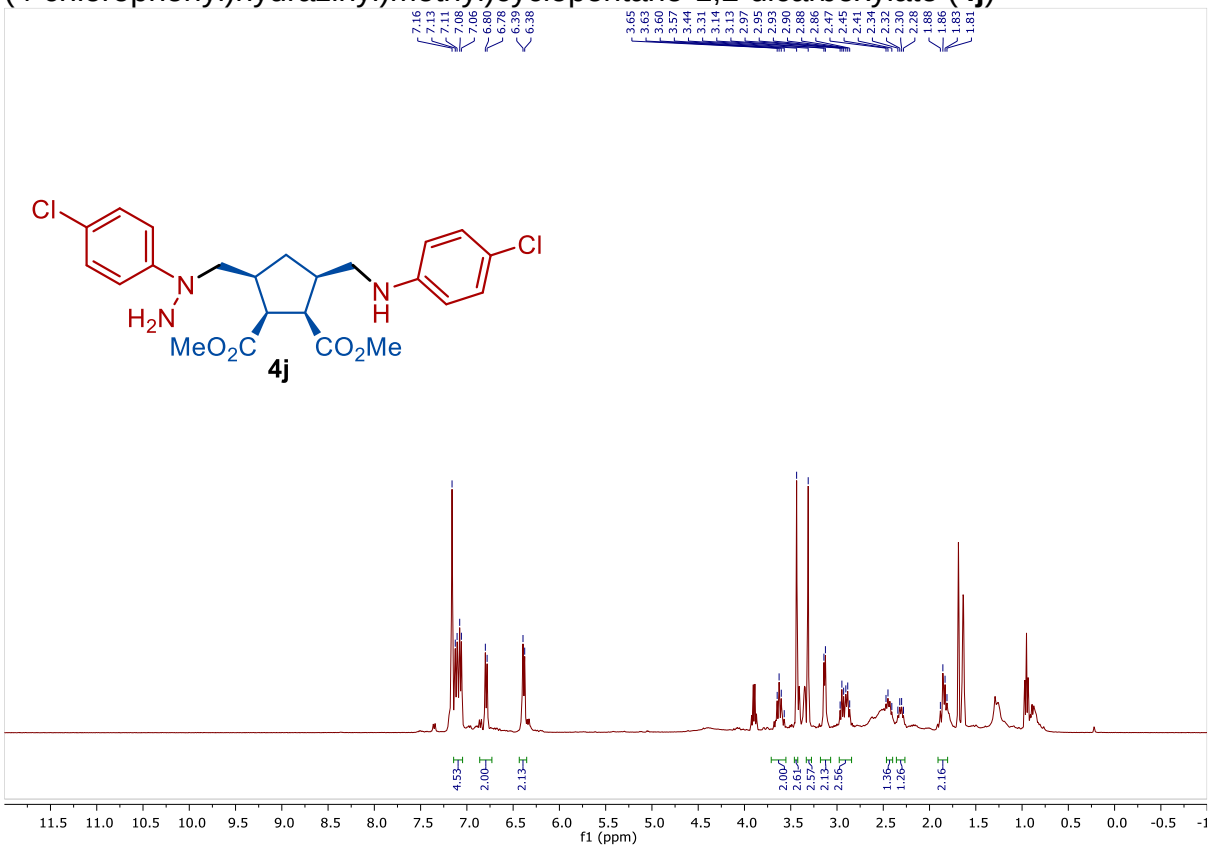
^{13}C NMR of 4-chloro-N-(((1RS,3SR)-3-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentyl)methyl)aniline (**4a**)



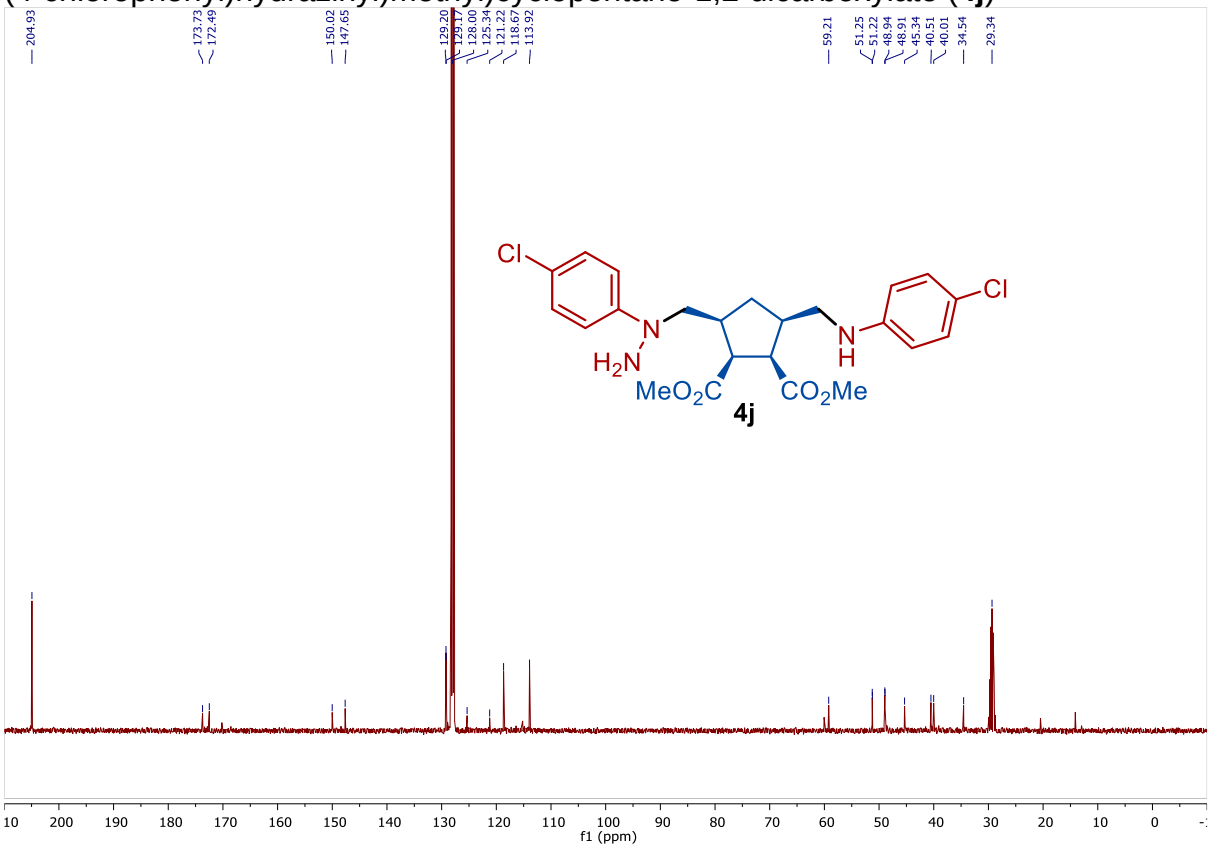
DEPT of 4-chloro-N-(((1RS,3SR)-3-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentyl)methyl)aniline (**4a**)



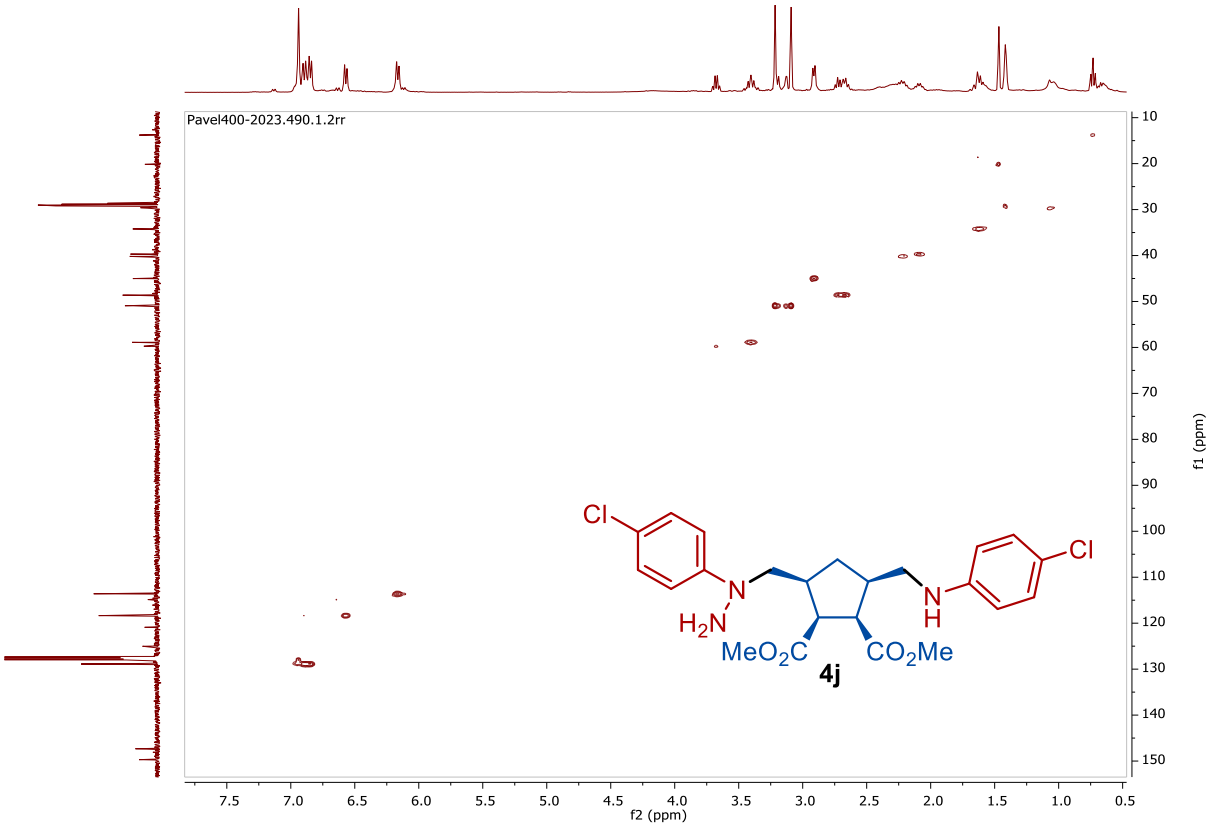
^{1}H NMR of dimethyl (1SR,2RS,3RS,5SR)-3-(((4-chlorophenyl)amino)methyl)-5-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentane-1,2-dicarboxylate (**4j**)



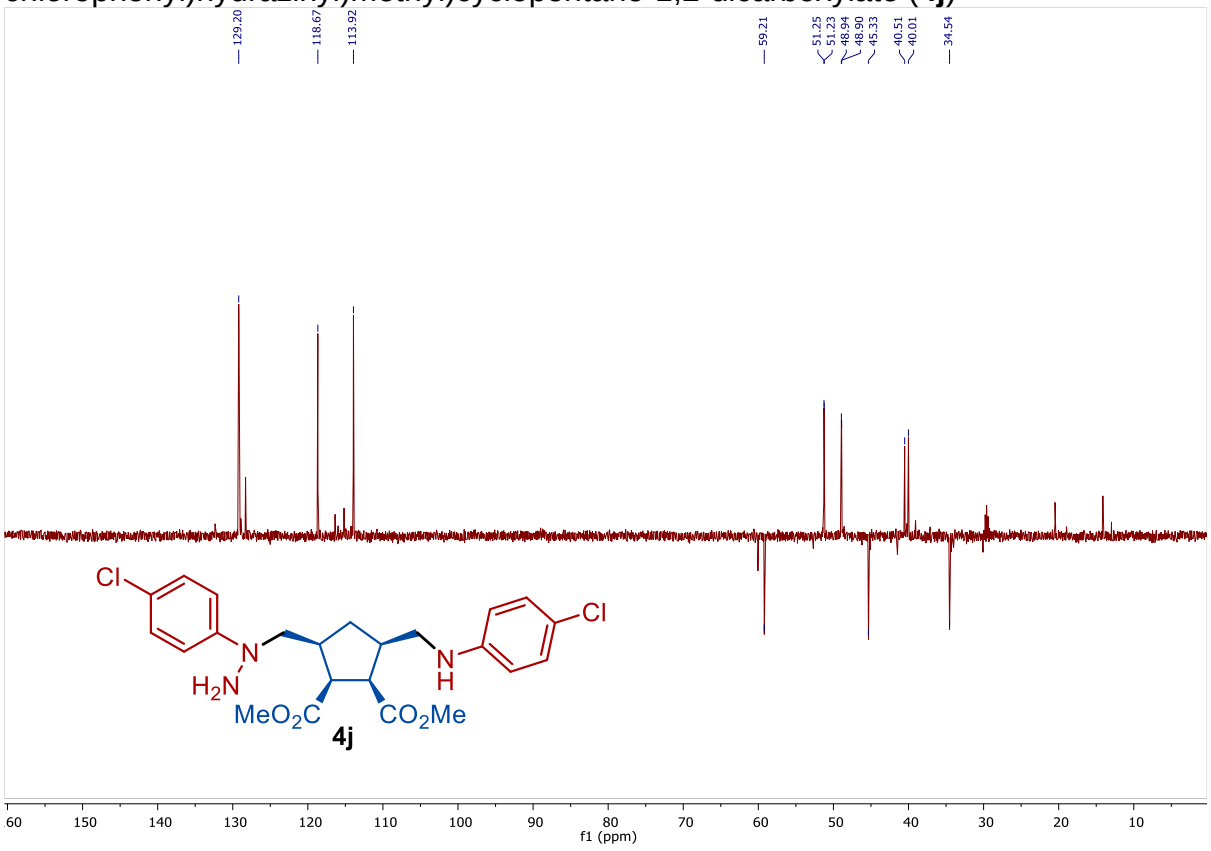
^{13}C NMR of dimethyl (1SR,2RS,3RS,5SR)-3-(((4-chlorophenyl)amino)methyl)-5-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentane-1,2-dicarboxylate (**4j**)



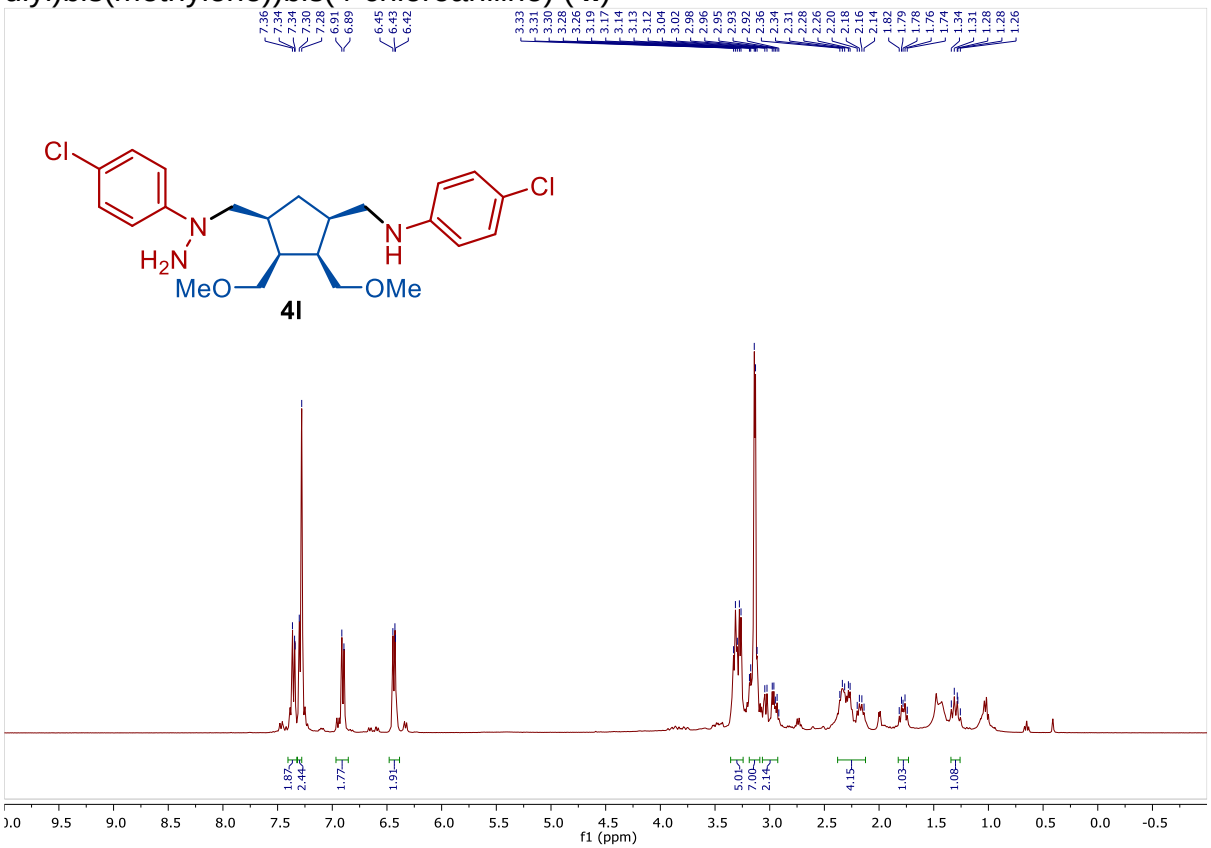
HSQC of dimethyl (1SR,2RS,3RS,5SR)-3-(((4-chlorophenyl)amino)methyl)-5-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentane-1,2-dicarboxylate (**4j**)



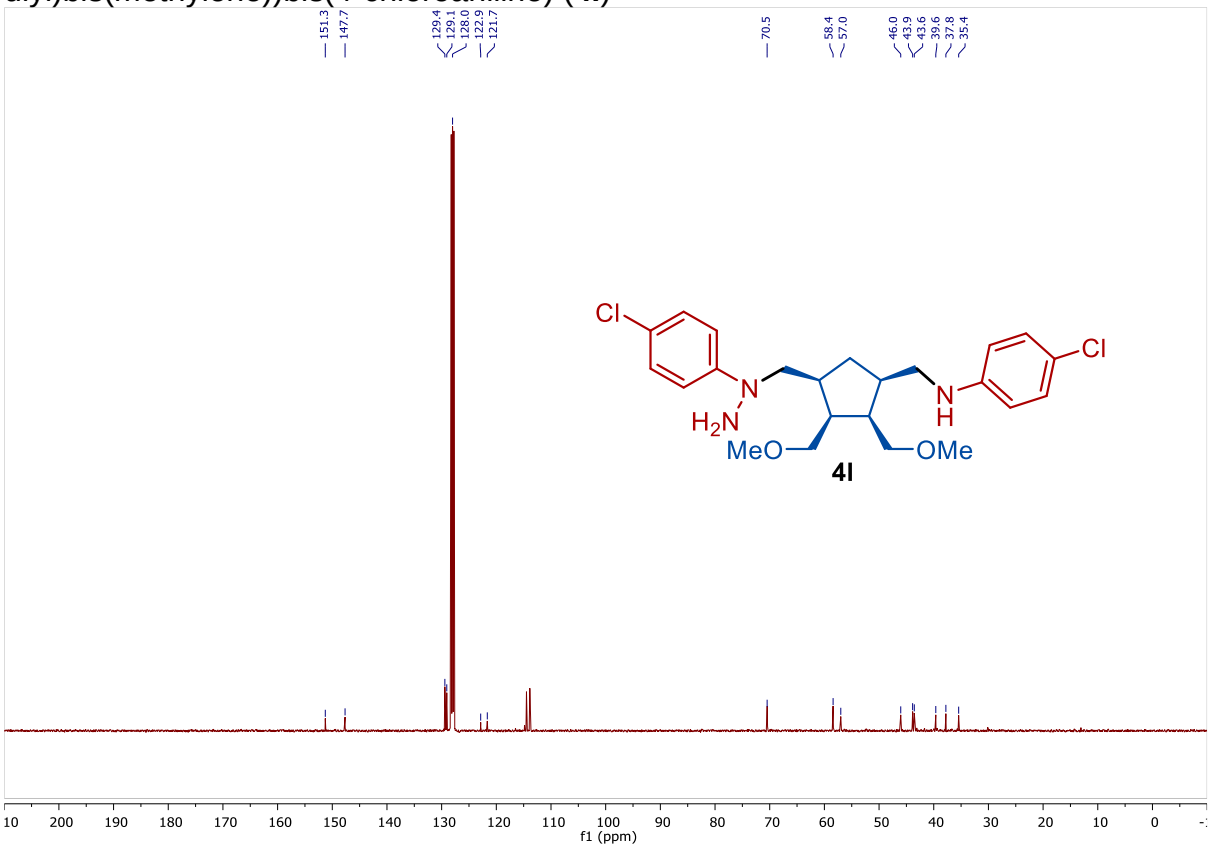
DEPT of dimethyl (1SR,2RS,3RS,5SR)-3-(((4-chlorophenyl)amino)methyl)-5-((1-(4-chlorophenyl)hydrazinyl)methyl)cyclopentane-1,2-dicarboxylate (**4j**)



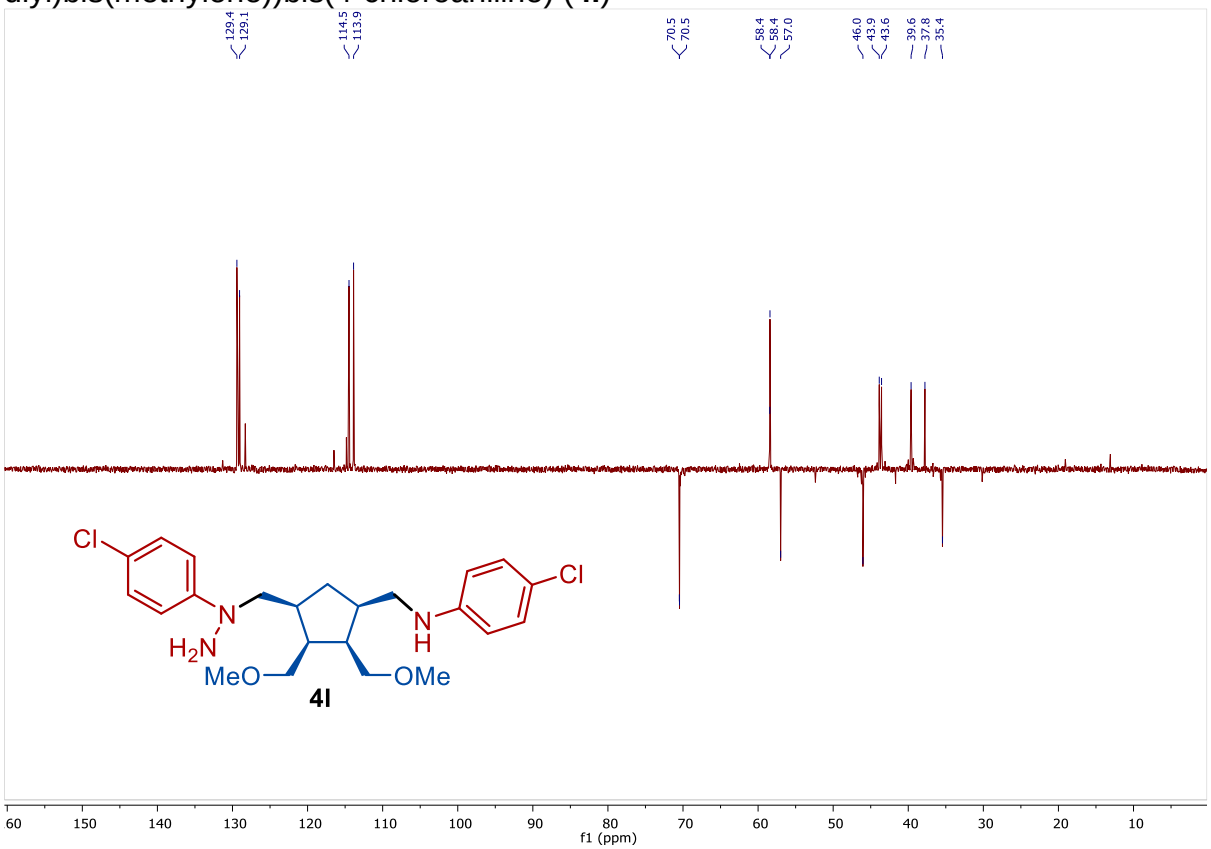
^{1}H NMR of N,N'-(((1RS,3SR,4SR,5RS)-4,5-bis(methoxymethyl)cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**4l**)



^{13}C NMR of N,N'-(((1RS,3SR,4SR,5RS)-4,5-bis(methoxymethyl)cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**4l**)

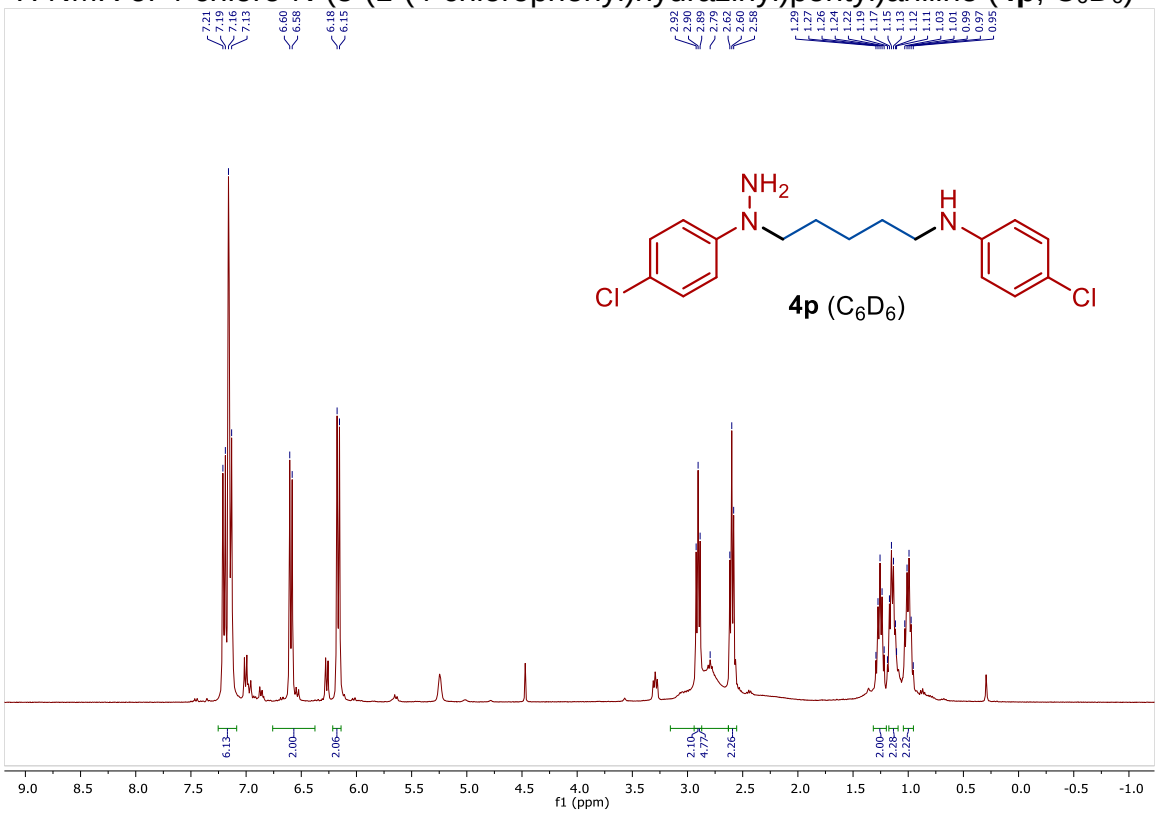


DEPT of N,N'-(((1RS,3SR,4SR,5RS)-4,5-bis(methoxymethyl)cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**4l**)

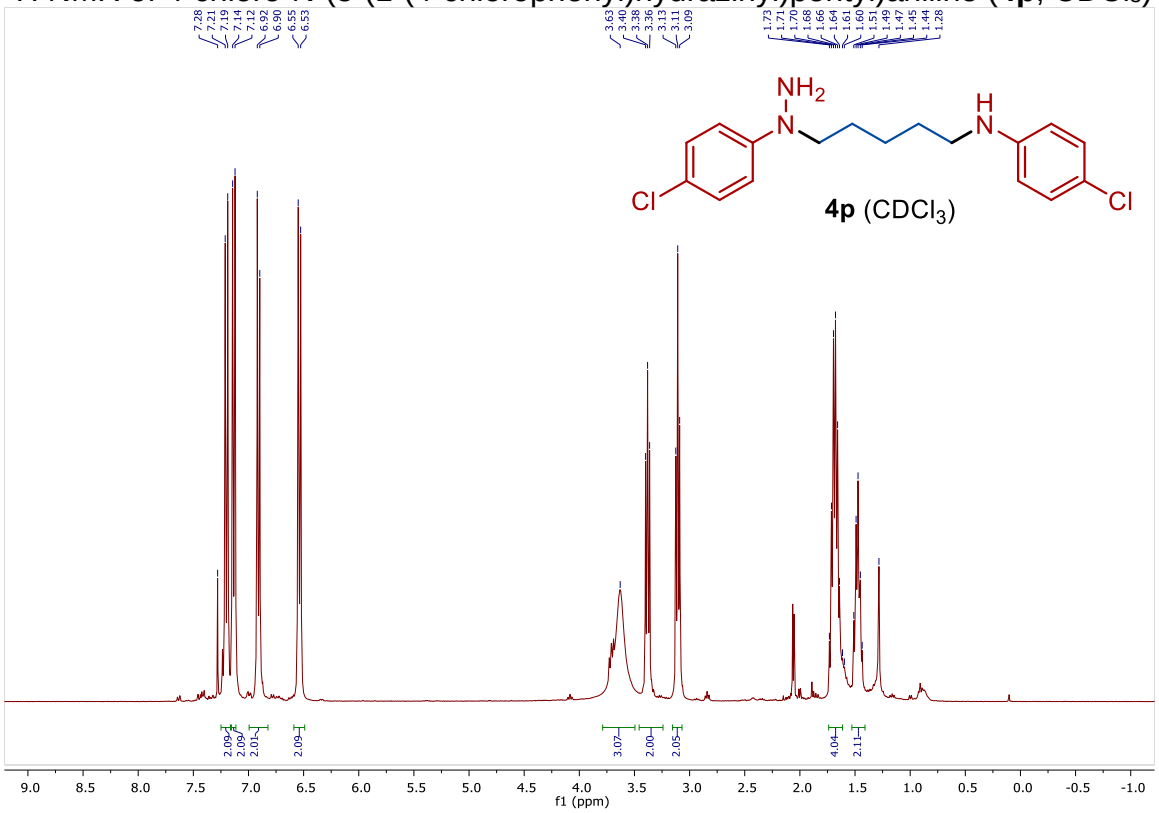


NMR of compound **4p** was highly dependent on the solvent, thus, two ^{1}H NMRs are presented in C_6D_6 and $CDCl_3$. Presumably, this compound forms an internal carbamate or hydrocarbonate salt as was demonstrated previously.[14]

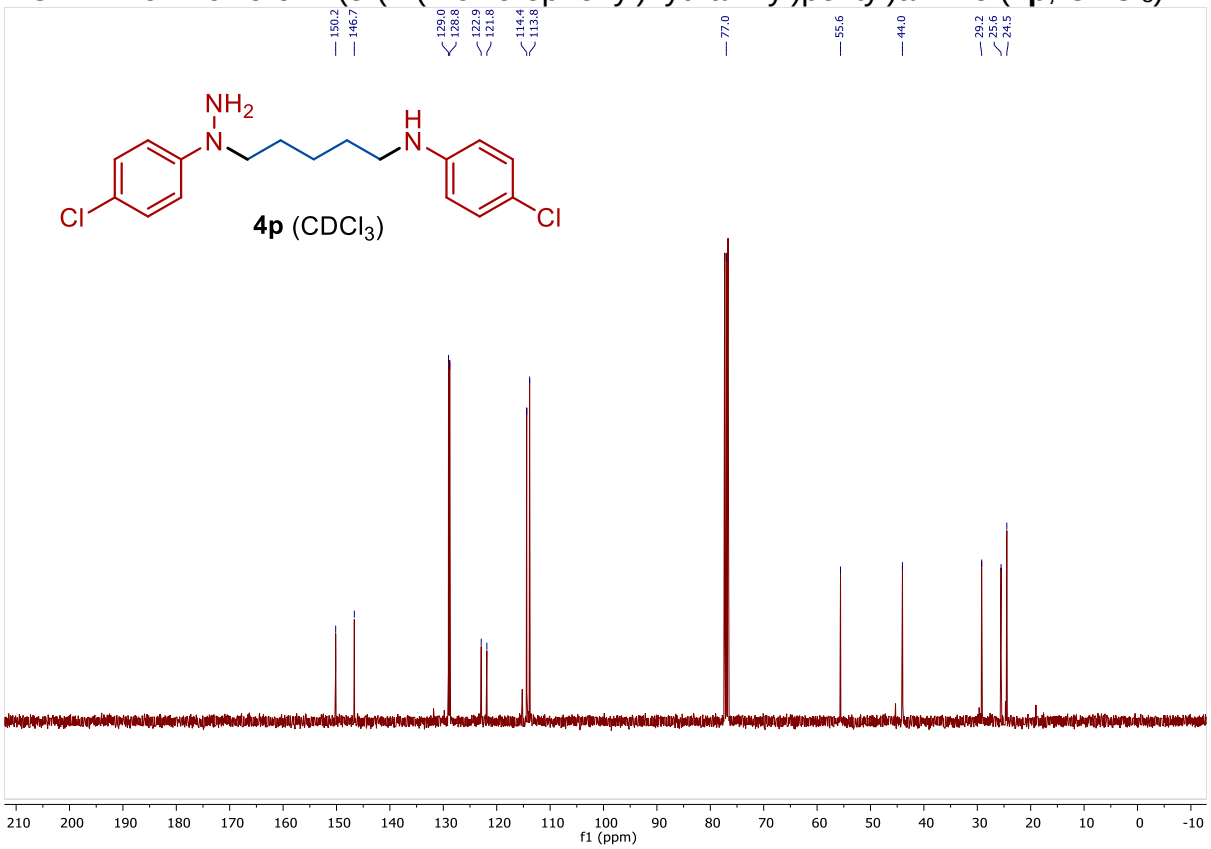
^{1}H NMR of 4-chloro-N-(5-(1-(4-chlorophenyl)hydrazinyl)pentyl)aniline (**4p**, C_6D_6)



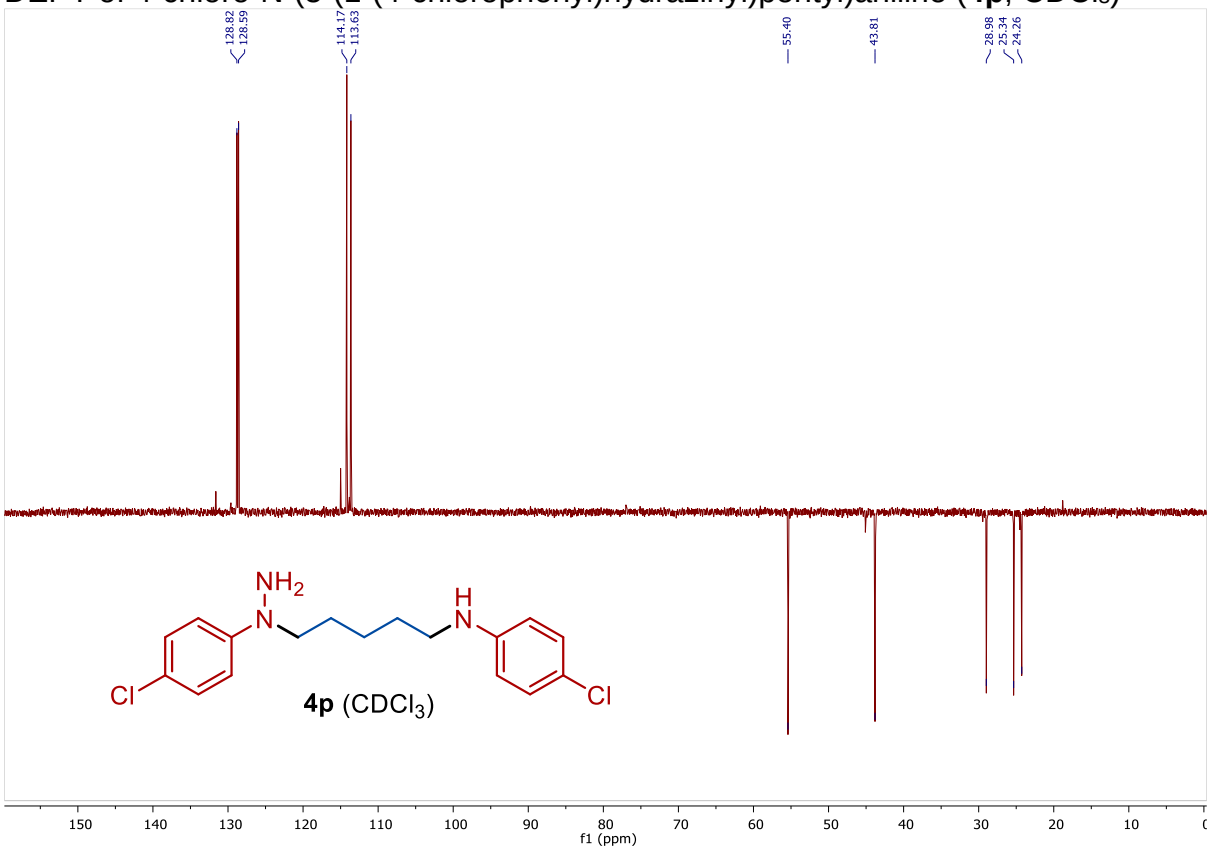
^{1}H NMR of 4-chloro-N-(5-(1-(4-chlorophenyl)hydrazinyl)pentyl)aniline (**4p**, $CDCl_3$)



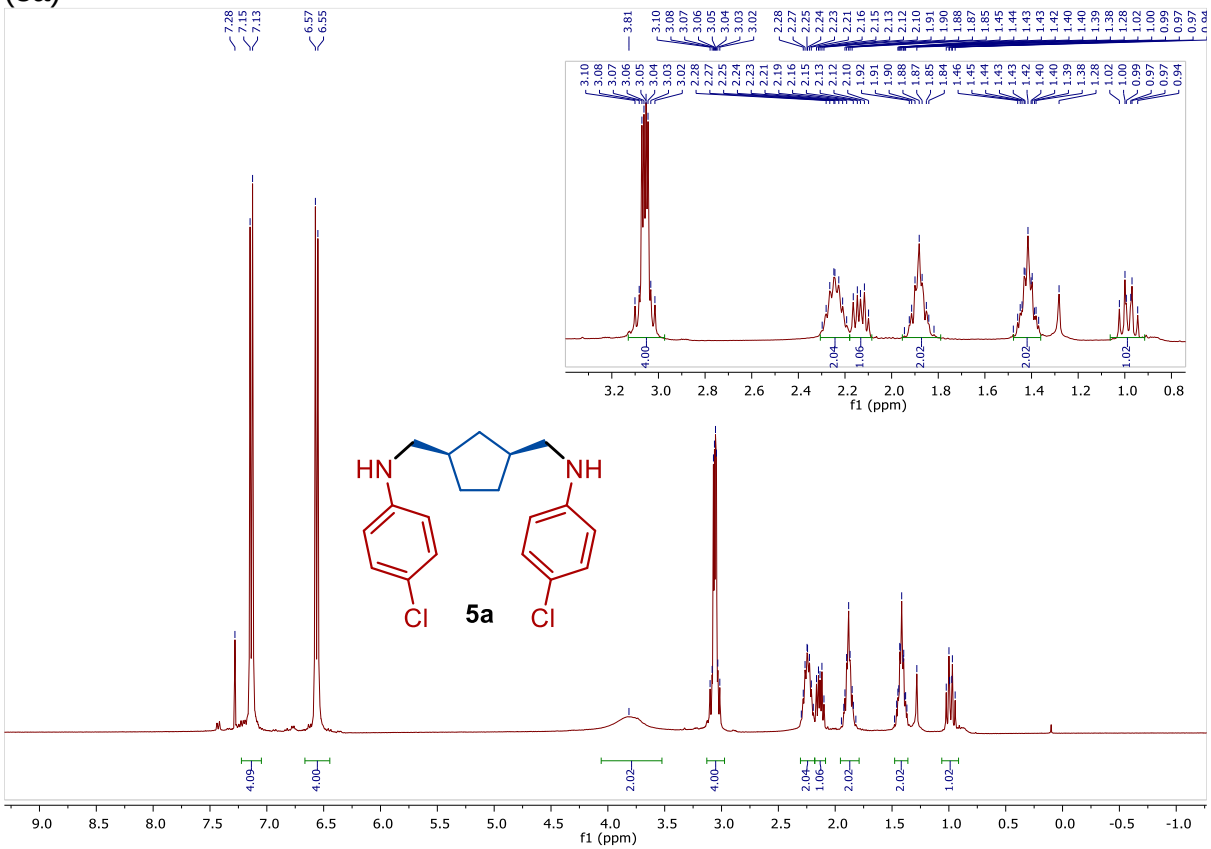
^{13}C NMR of 4-chloro-N-(5-(1-(4-chlorophenyl)hydrazinyl)pentyl)aniline (**4p**, $CDCl_3$)



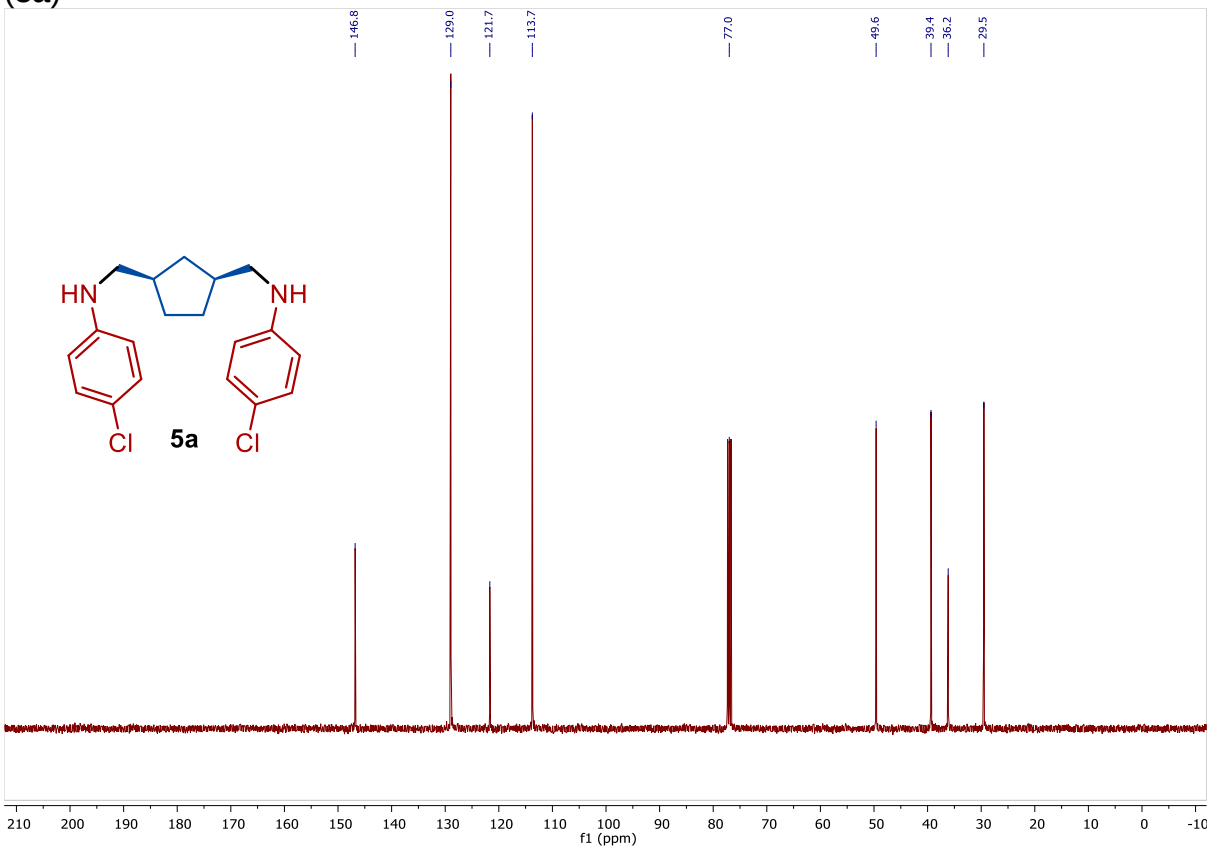
DEPT of 4-chloro-N-(5-(1-(4-chlorophenyl)hydrazinyl)pentyl)aniline (**4p**, $CDCl_3$)



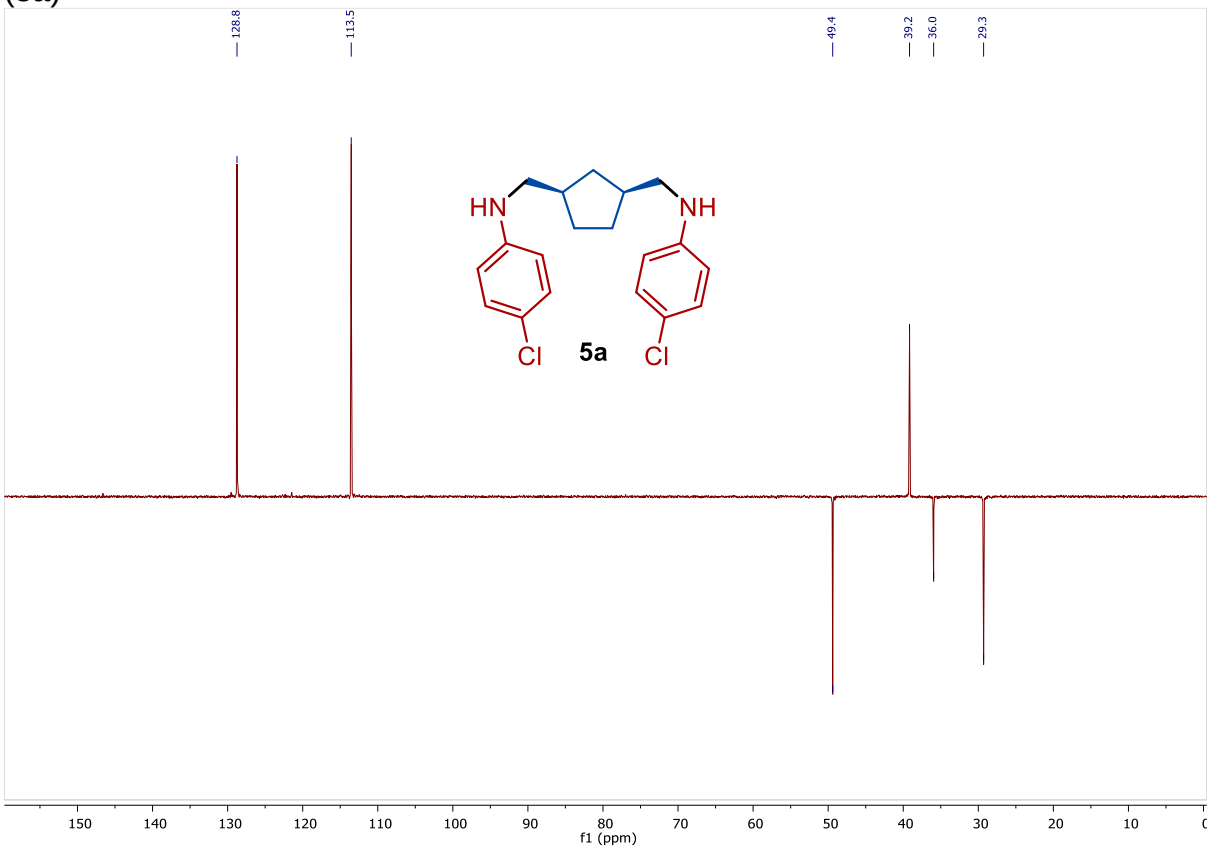
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5a**)



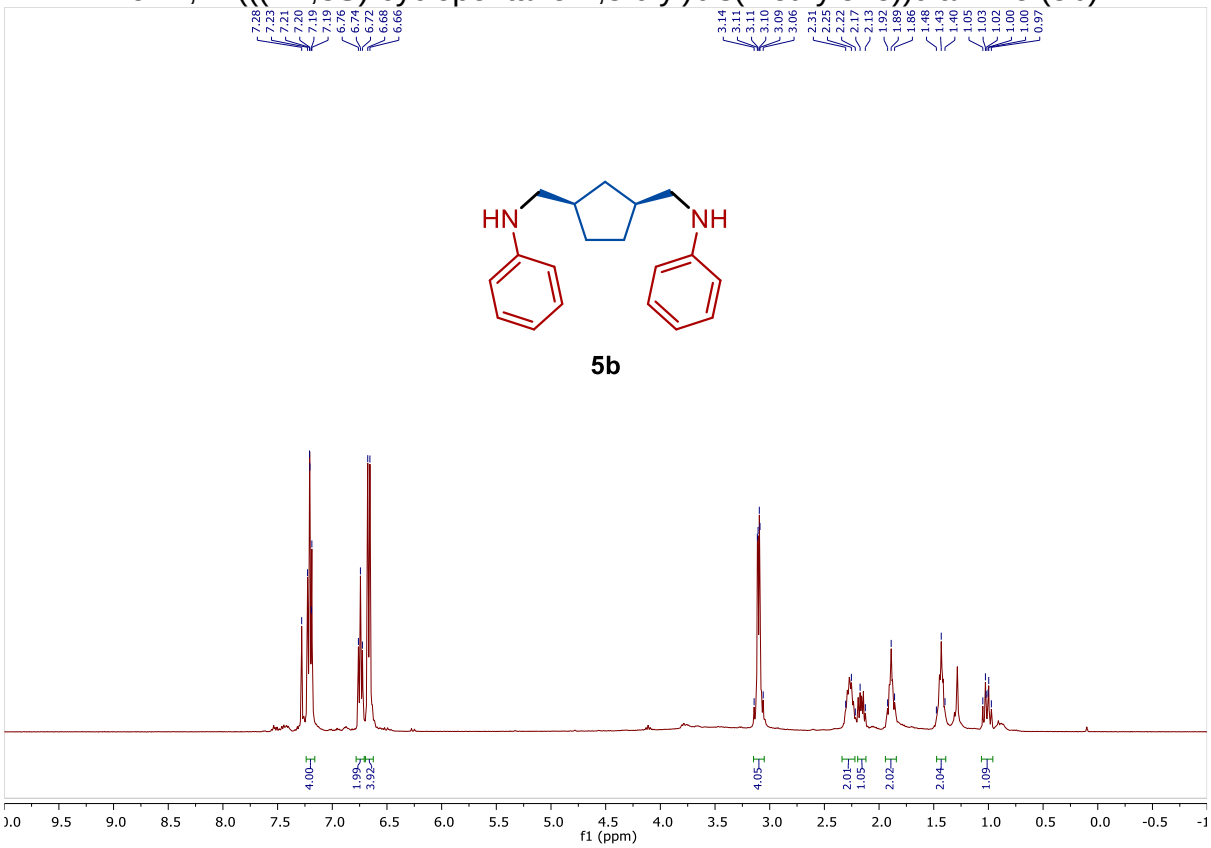
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5a**)



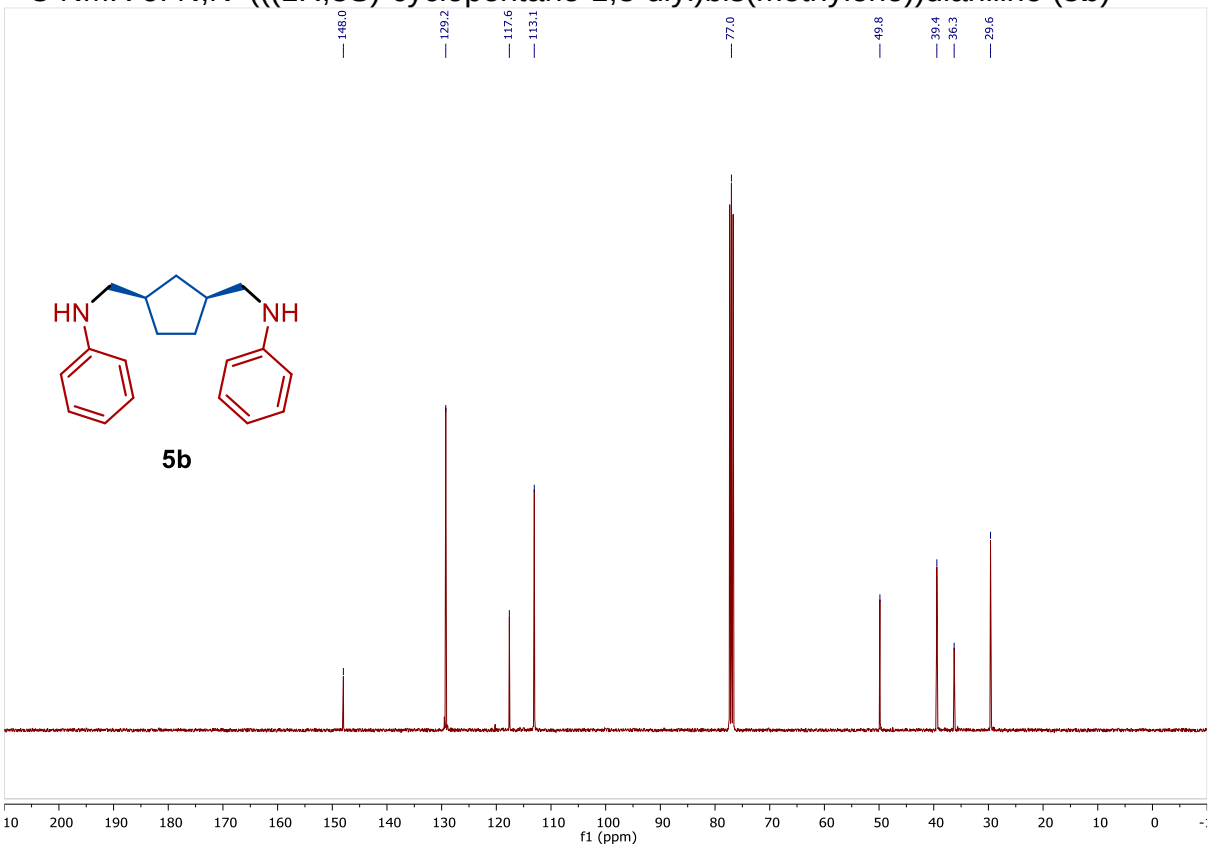
DEPT of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5a**)



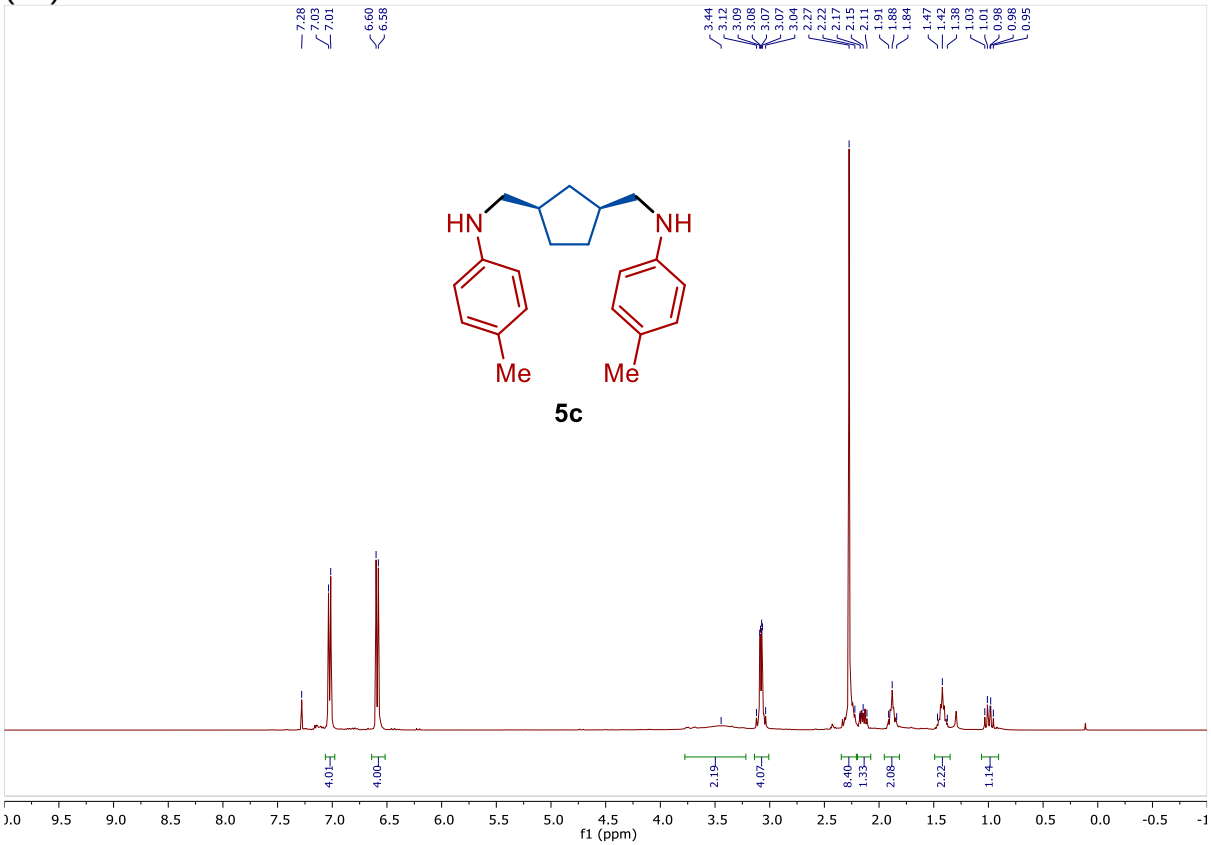
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))dianiline (**5b**)



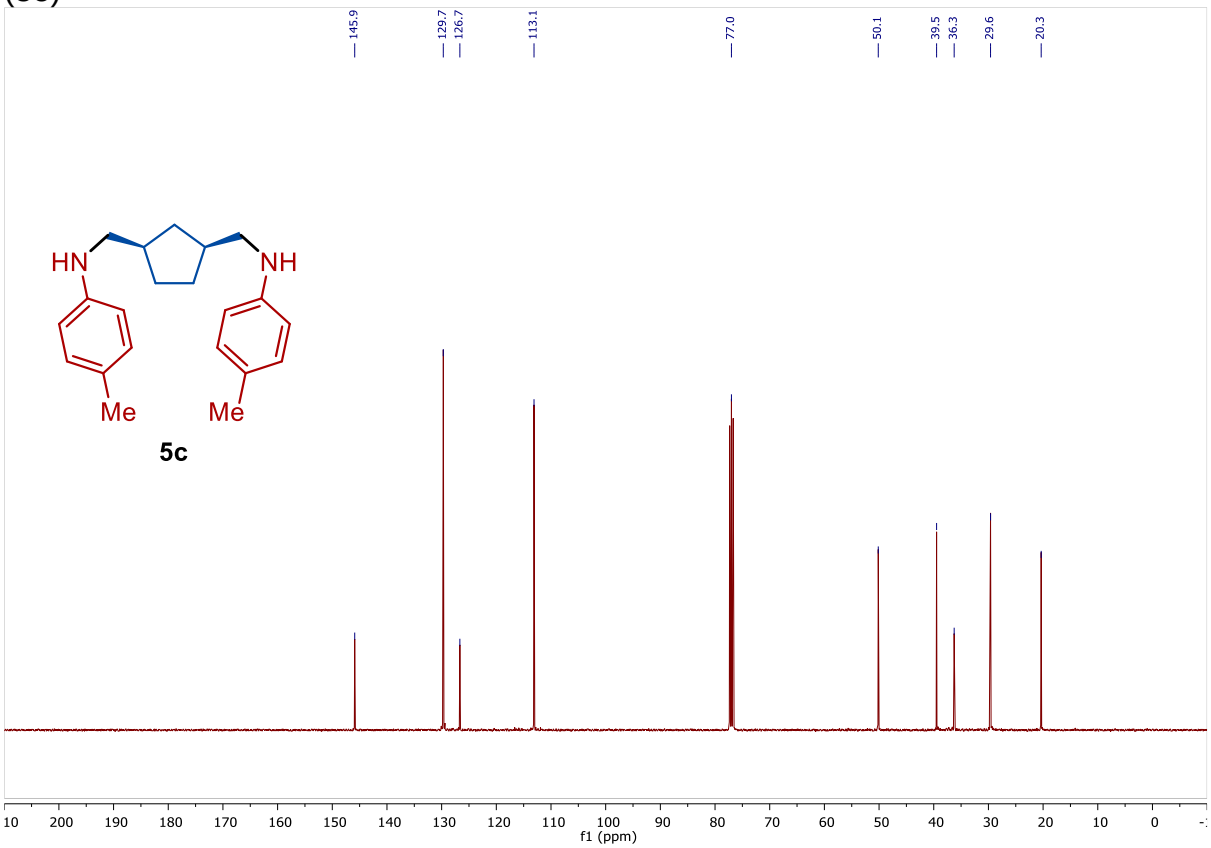
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))dianiline (**5b**)



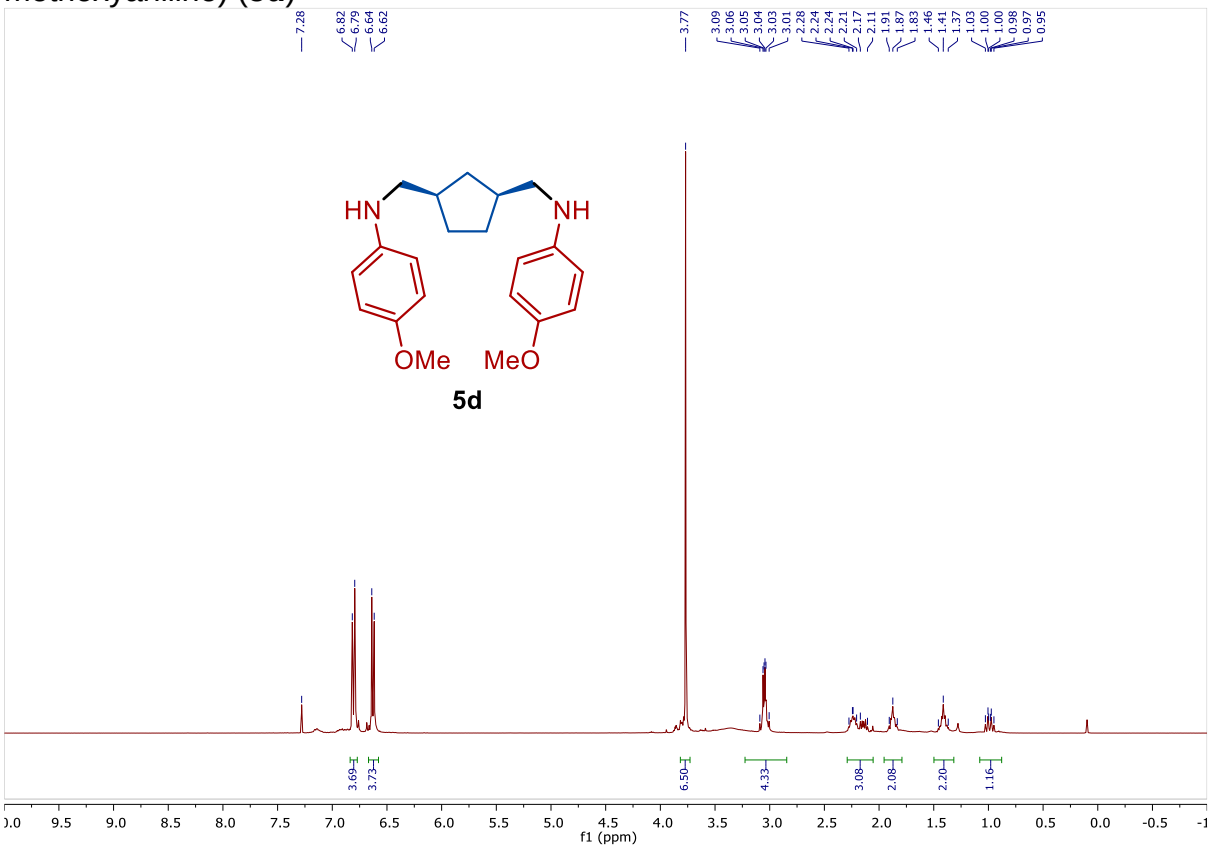
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methylaniline) (**5c**)



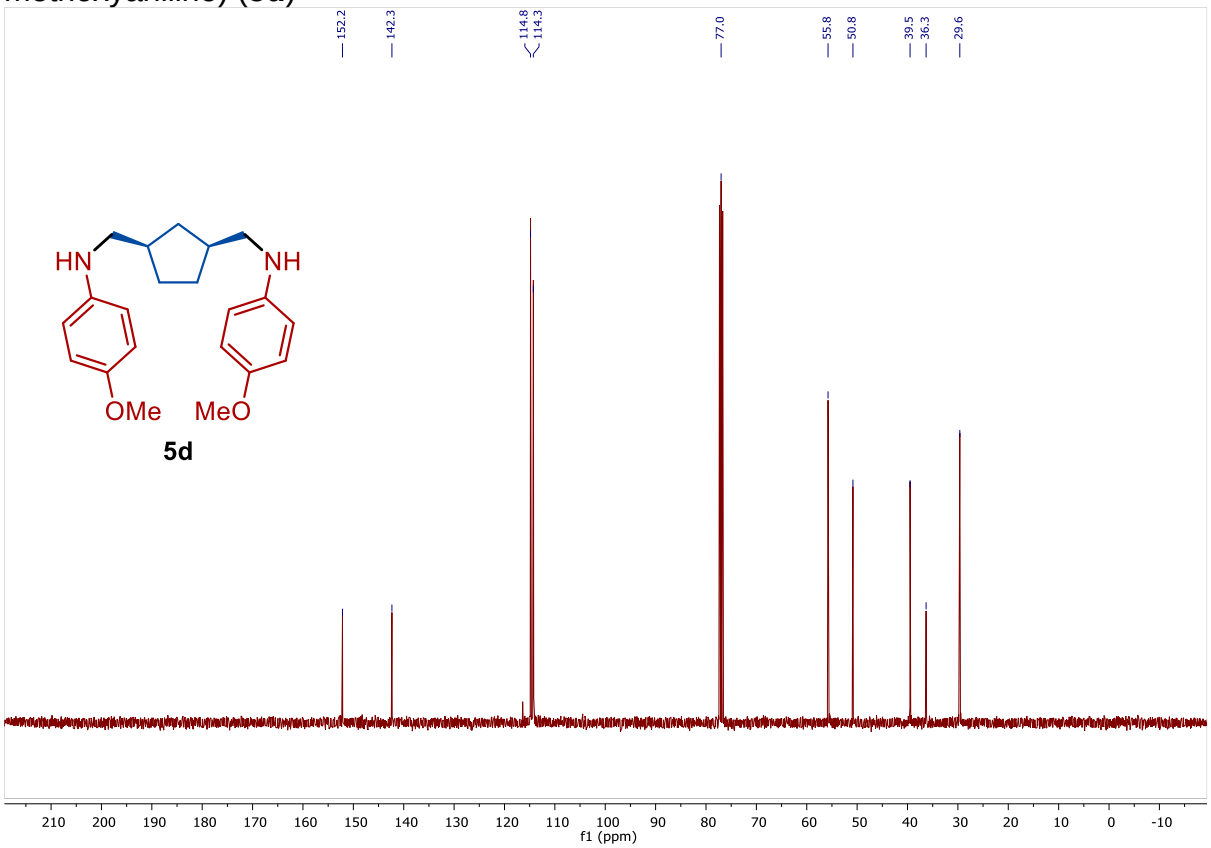
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methylaniline) (**5c**)



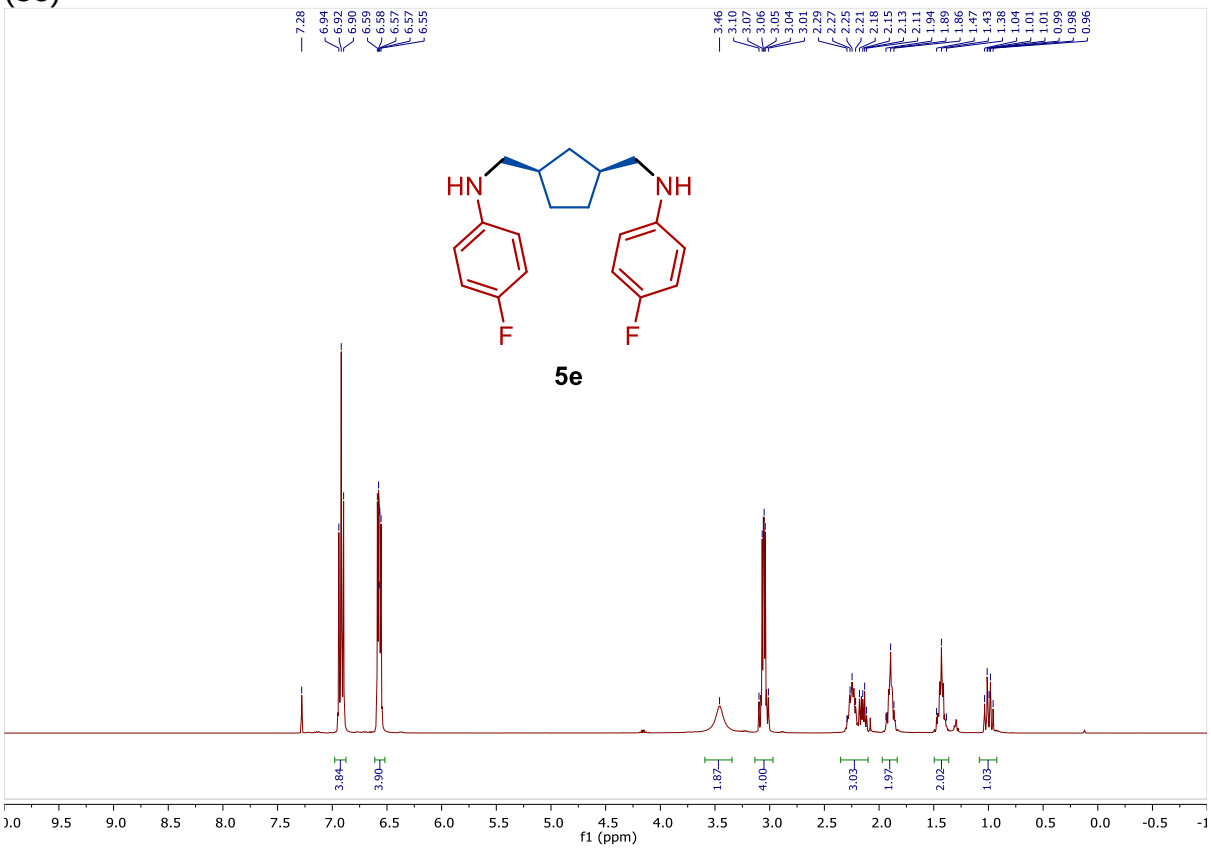
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methoxyaniline) (**5d**)



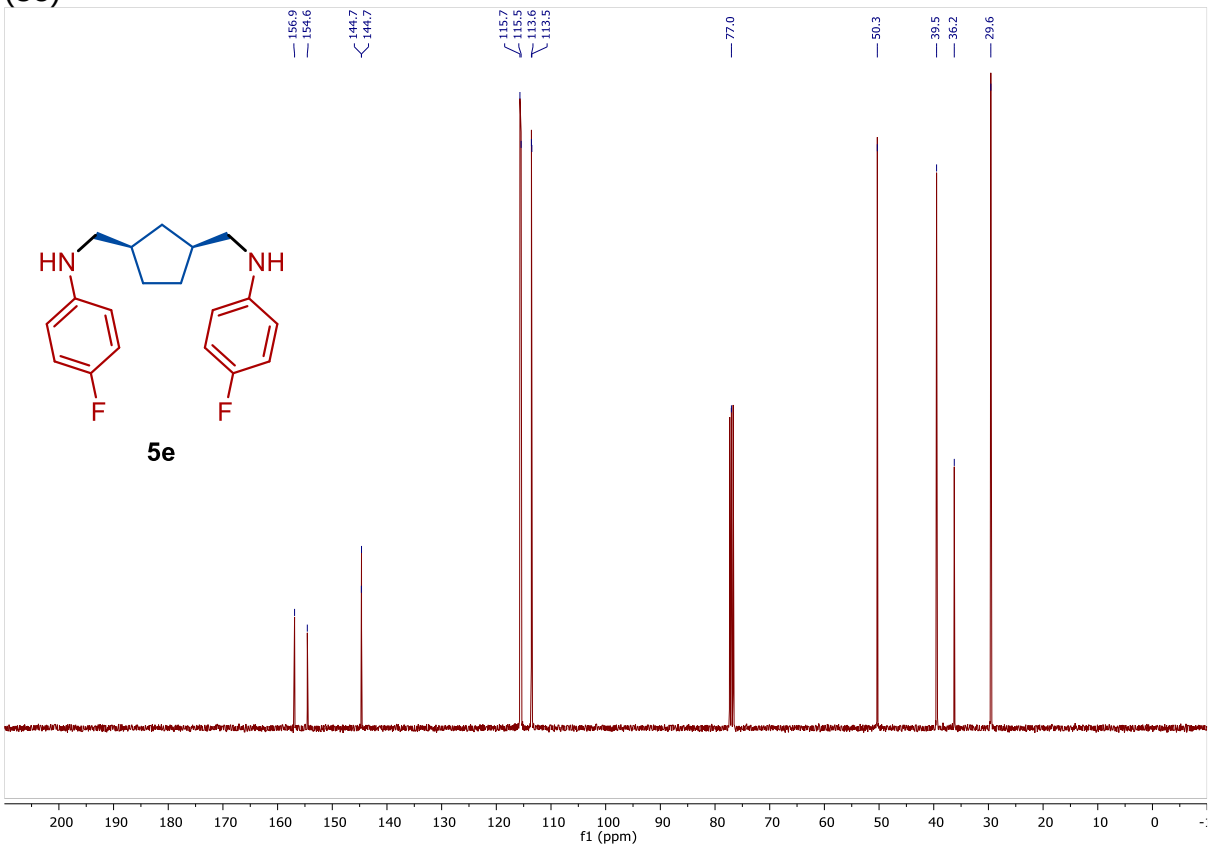
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-methoxyaniline) (**5d**)



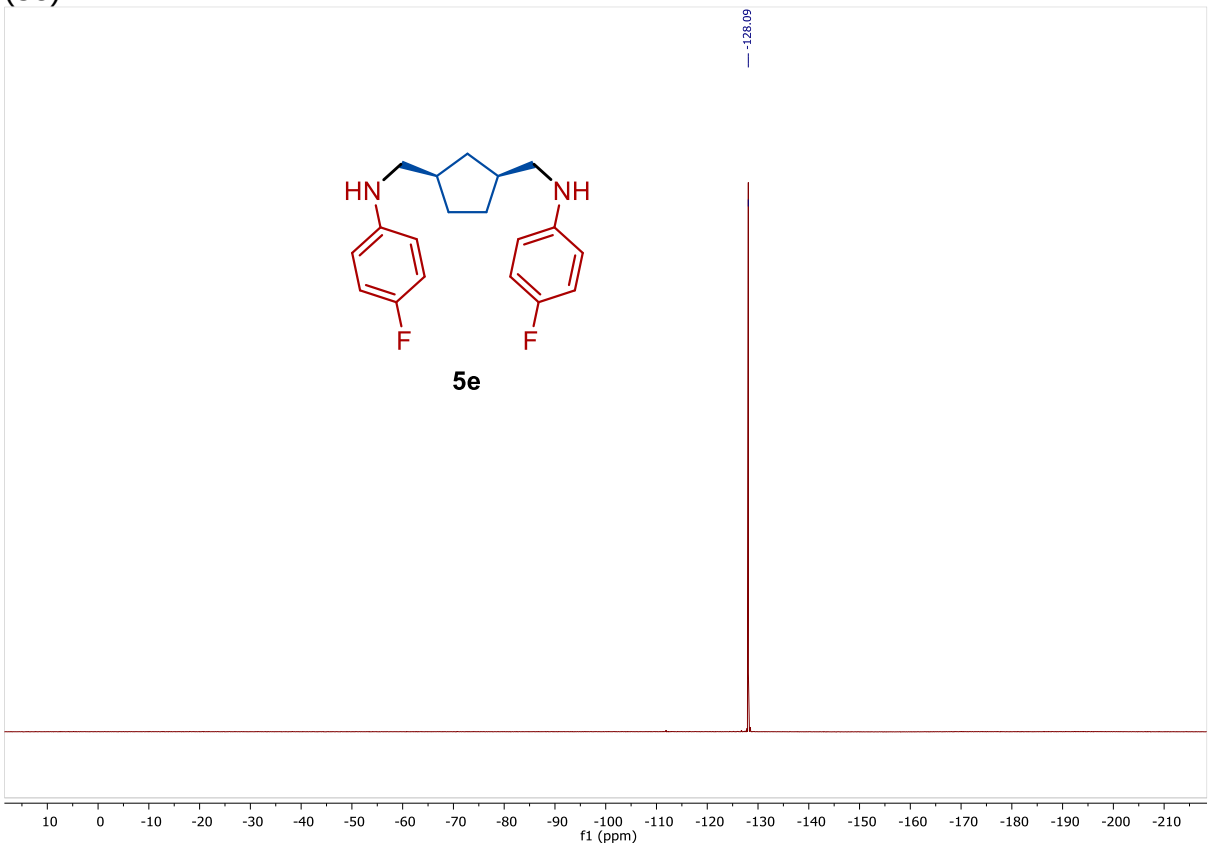
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5e**)



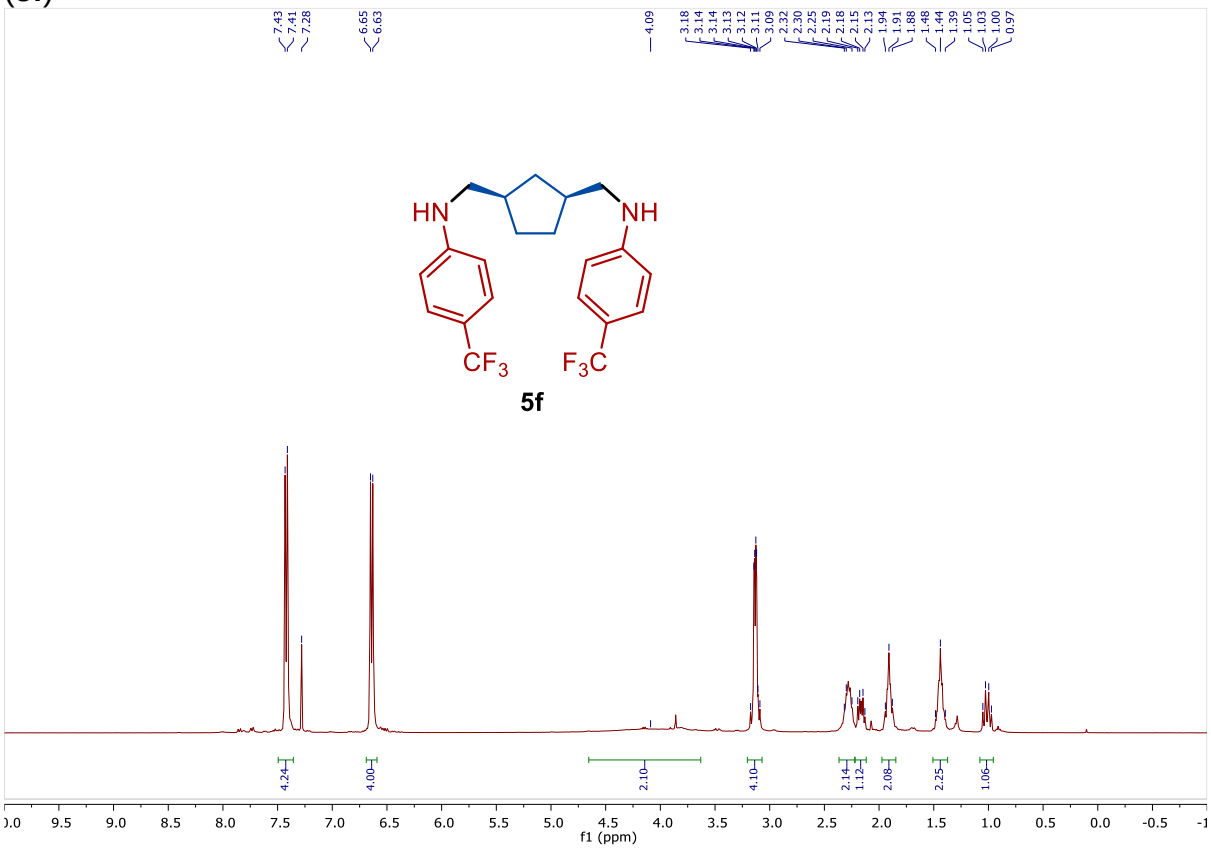
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5e**)



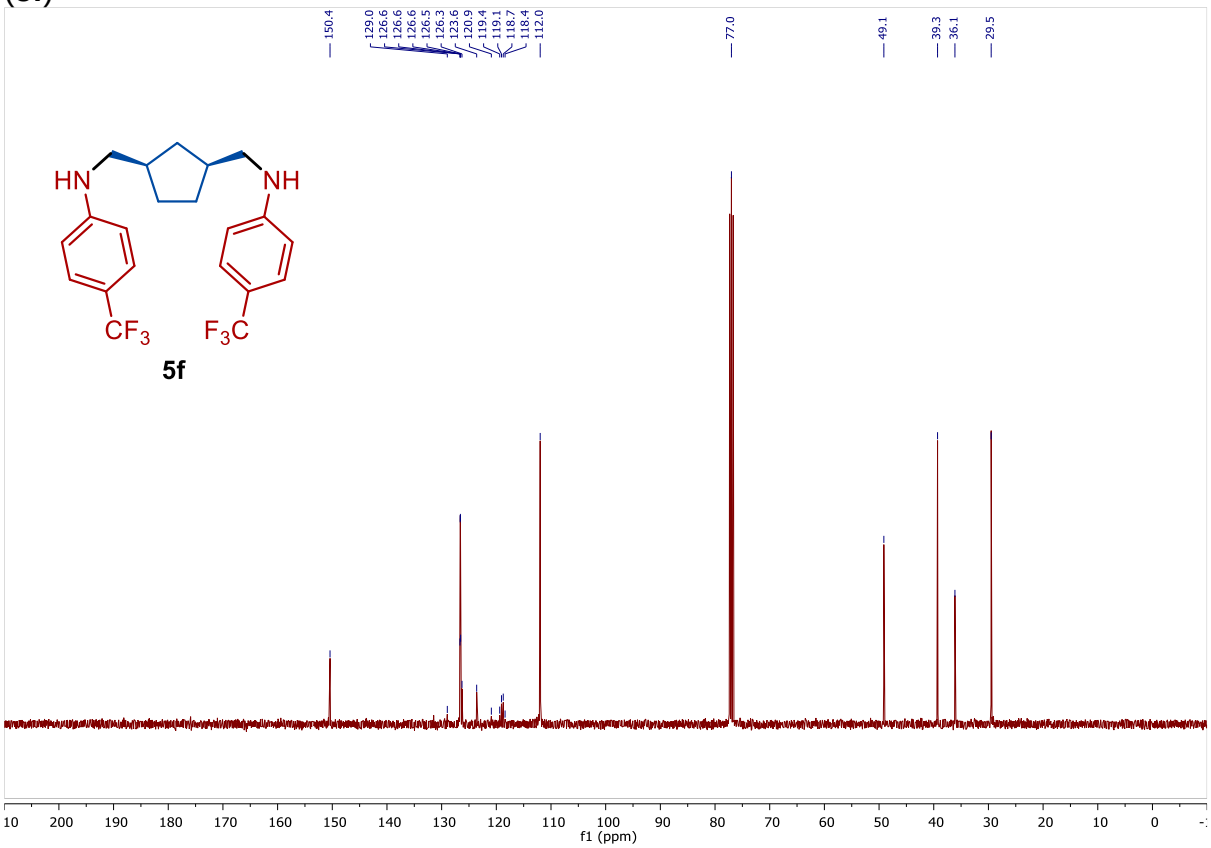
^{19}F NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5e**)



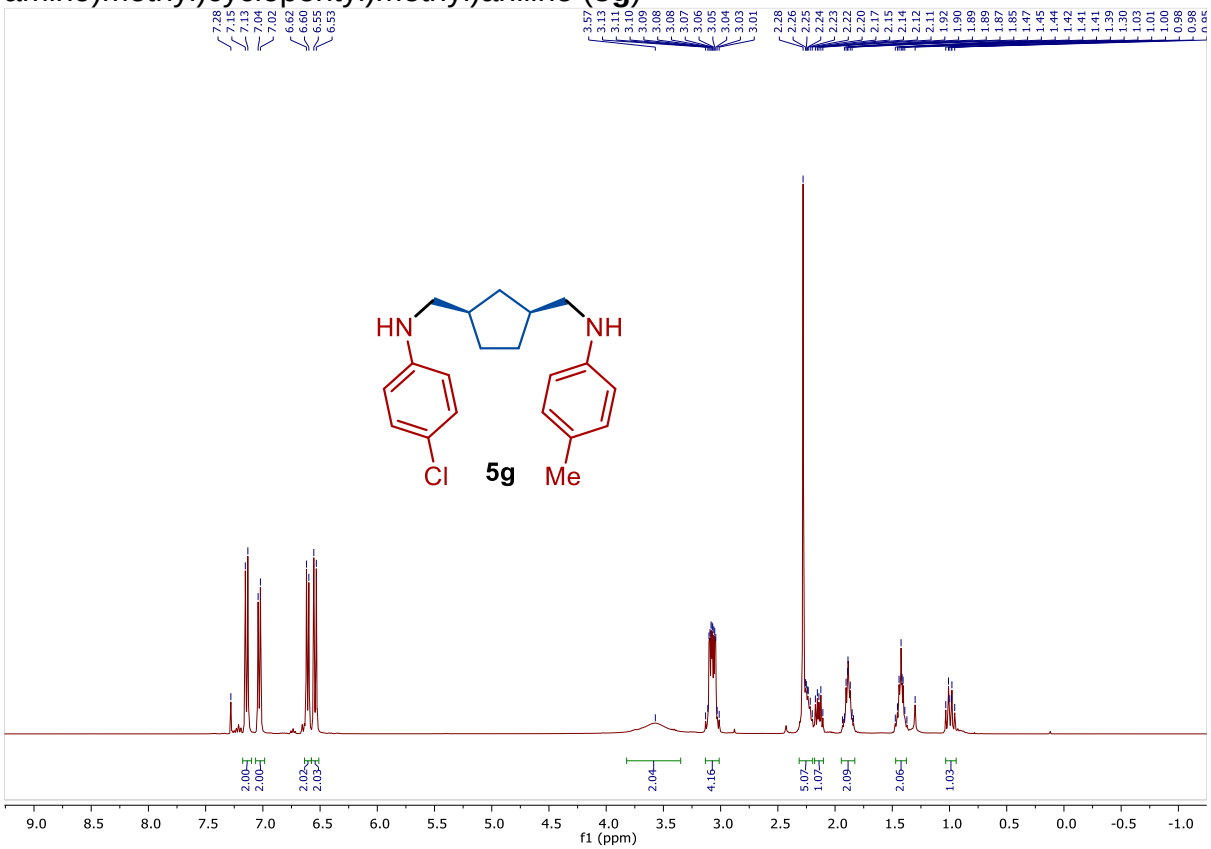
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5f**)



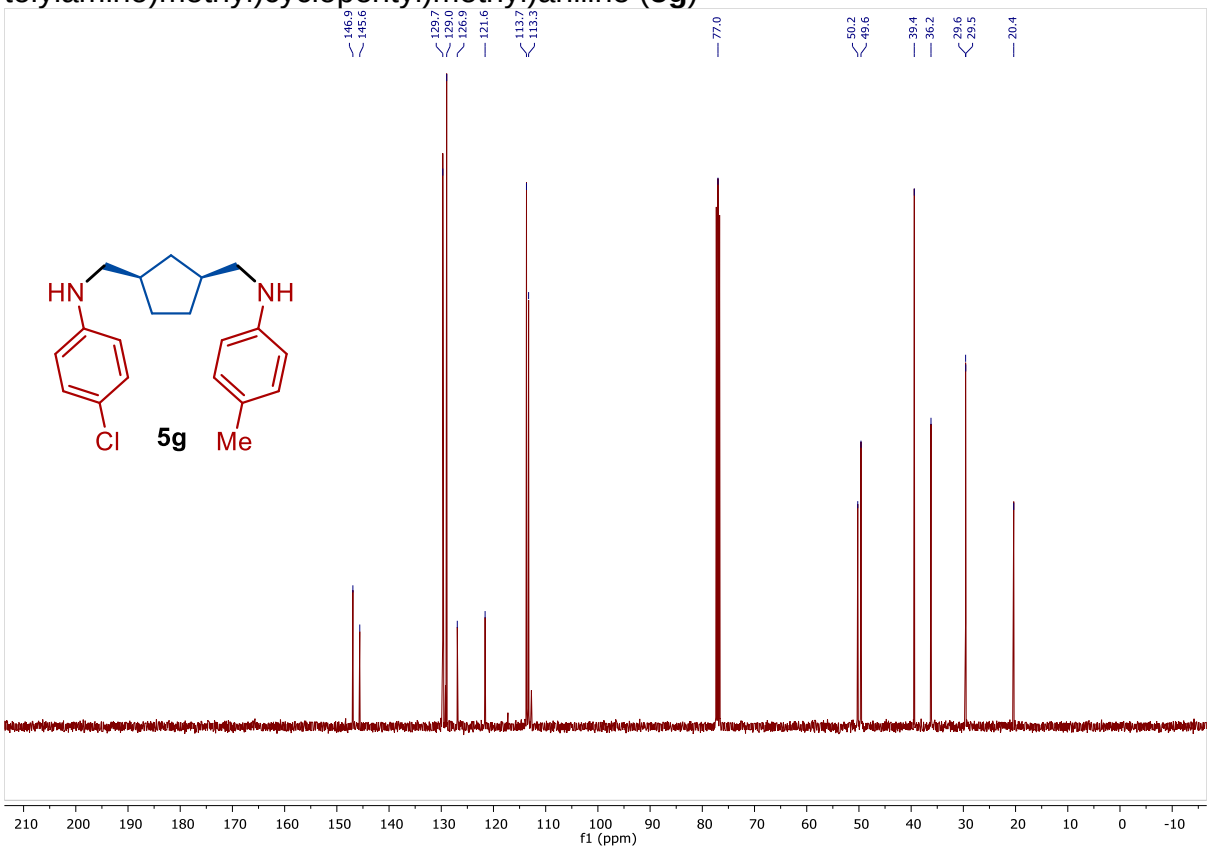
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(4-fluoroaniline) (**5f**)



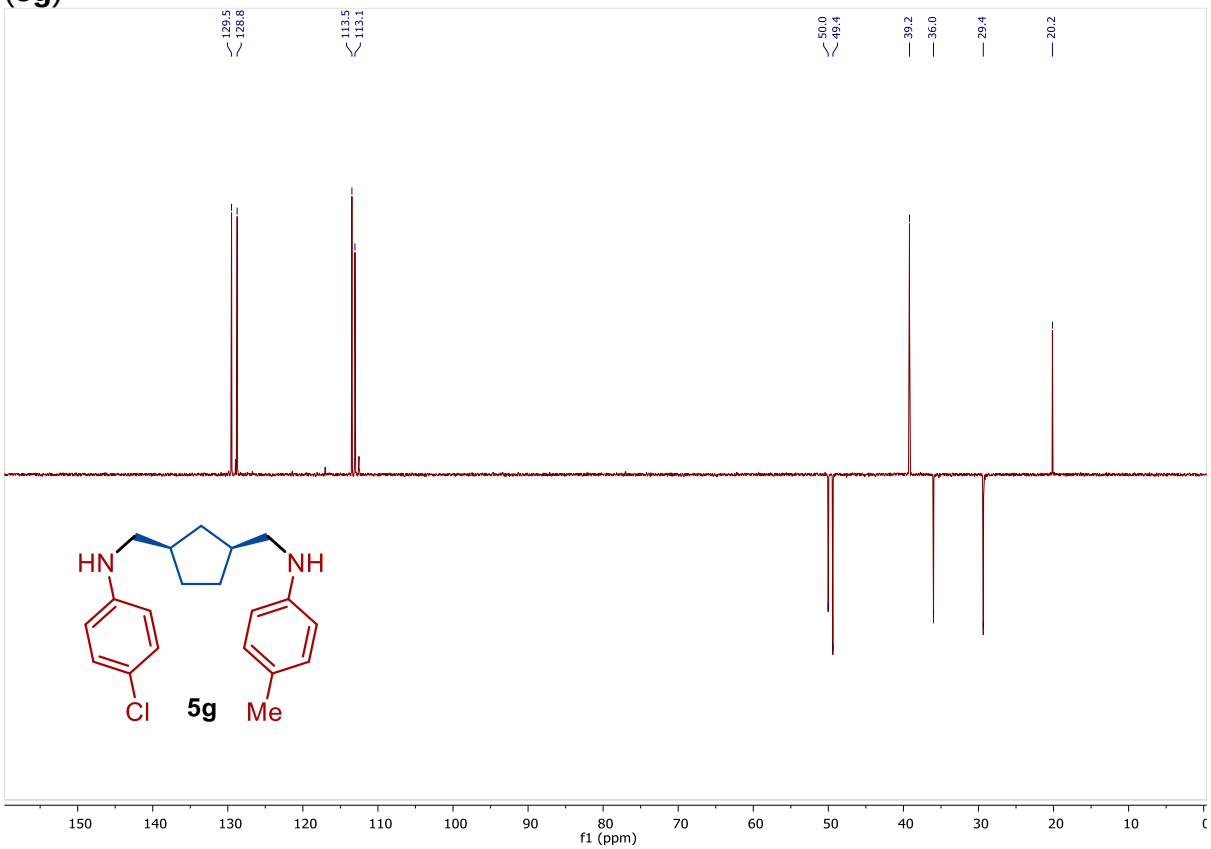
^{1}H NMR of 4-chloro-N-(((1RS,3SR)-3-((p-tolyl-amino)methyl)cyclopentyl)methyl)aniline (**5g**)



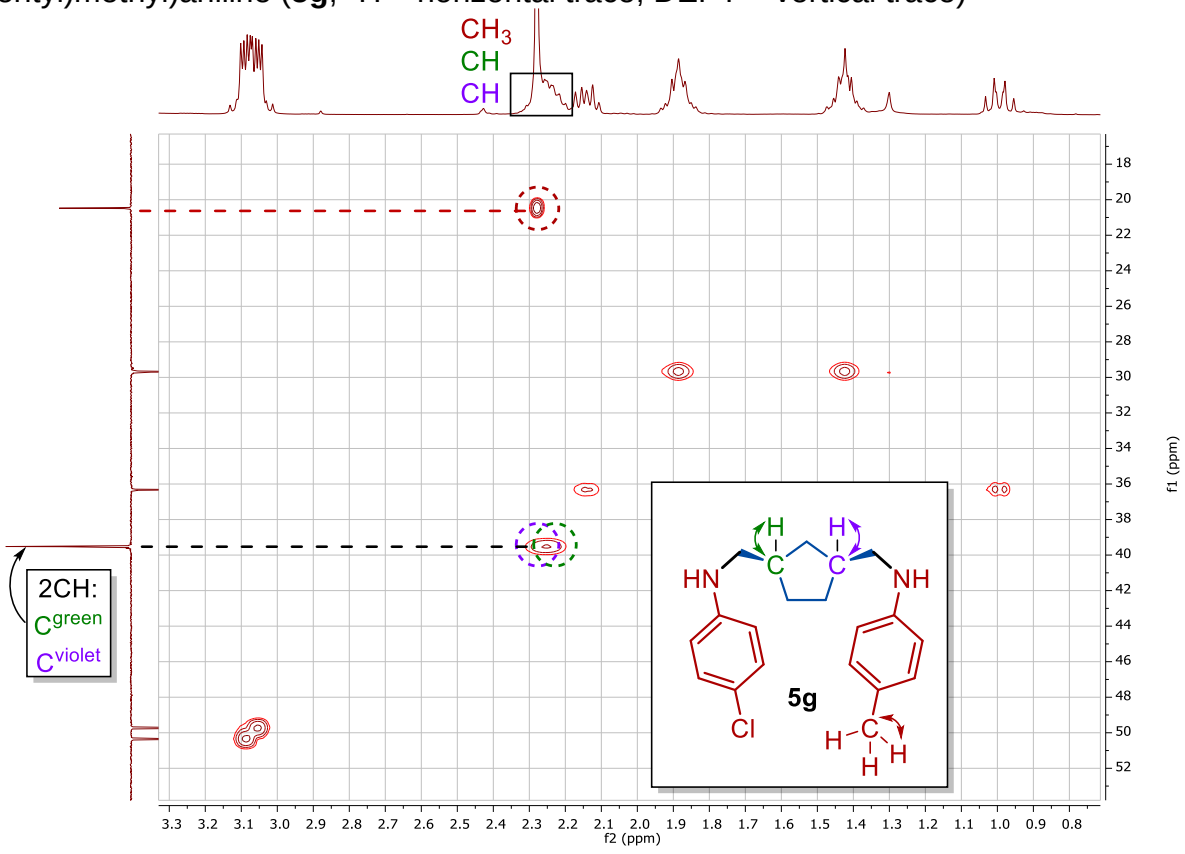
^{13}C NMR of 4-chloro-N-(((1RS,3SR)-3-((p-tolylamino)methyl)cyclopentyl)methyl)aniline (**5g**)



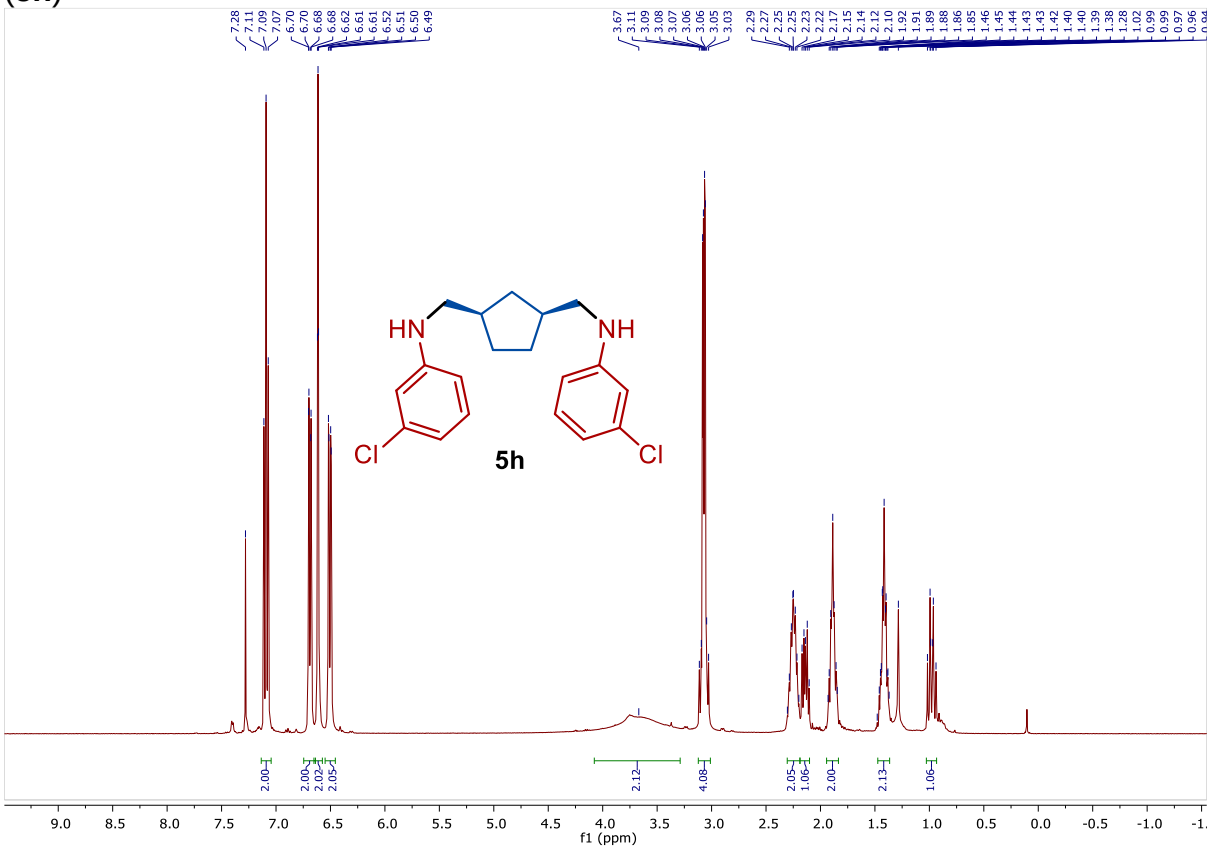
DEPT of 4-chloro-N-(((1RS,3SR)-3-((p-tolylamino)methyl)cyclopentyl)methyl)aniline (**5g**)



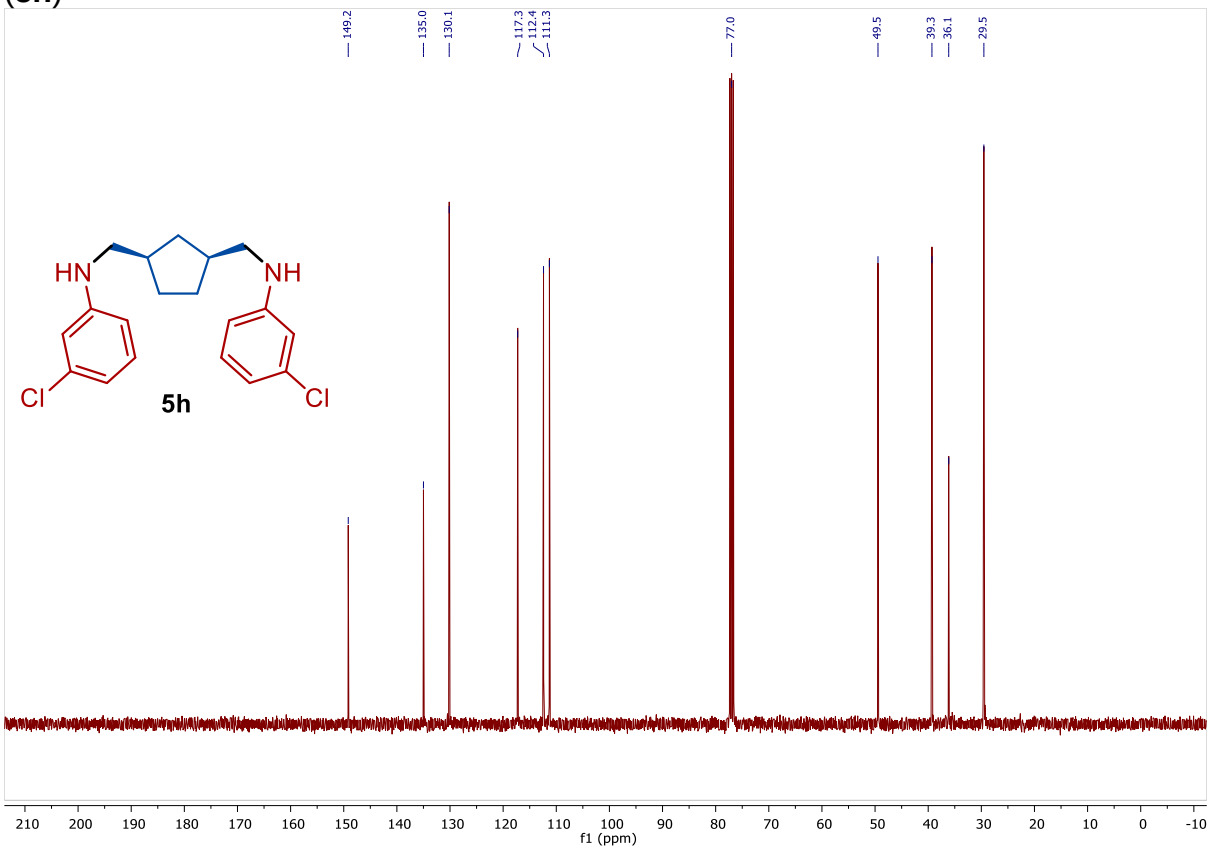
HSQC ^{1}H-^{13}C of 4-chloro-N-(((1RS,3SR)-3-((p-tolylamino)methyl)cyclo-pentyl)methyl)aniline (**5g**; ^{1}H – horizontal trace, DEPT – vertical trace)



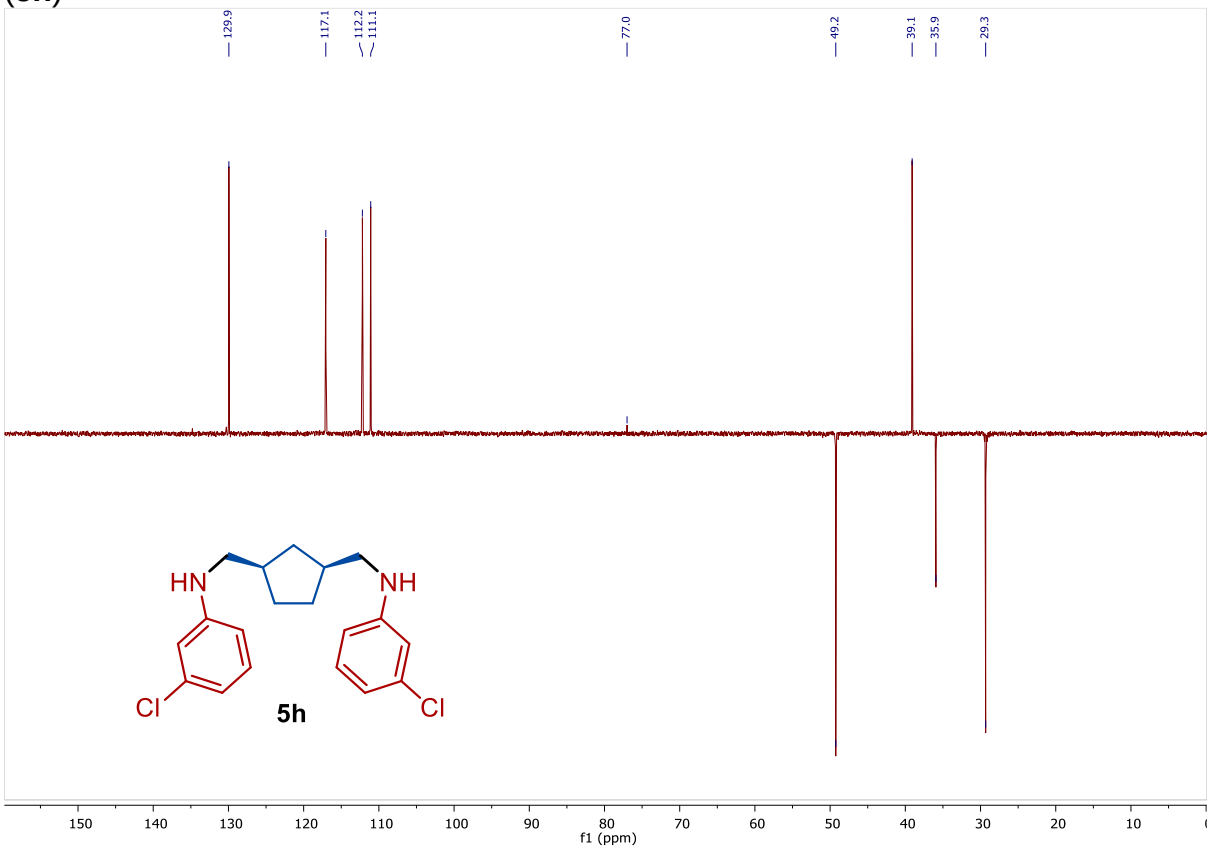
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(3-chloroaniline) (**5h**)



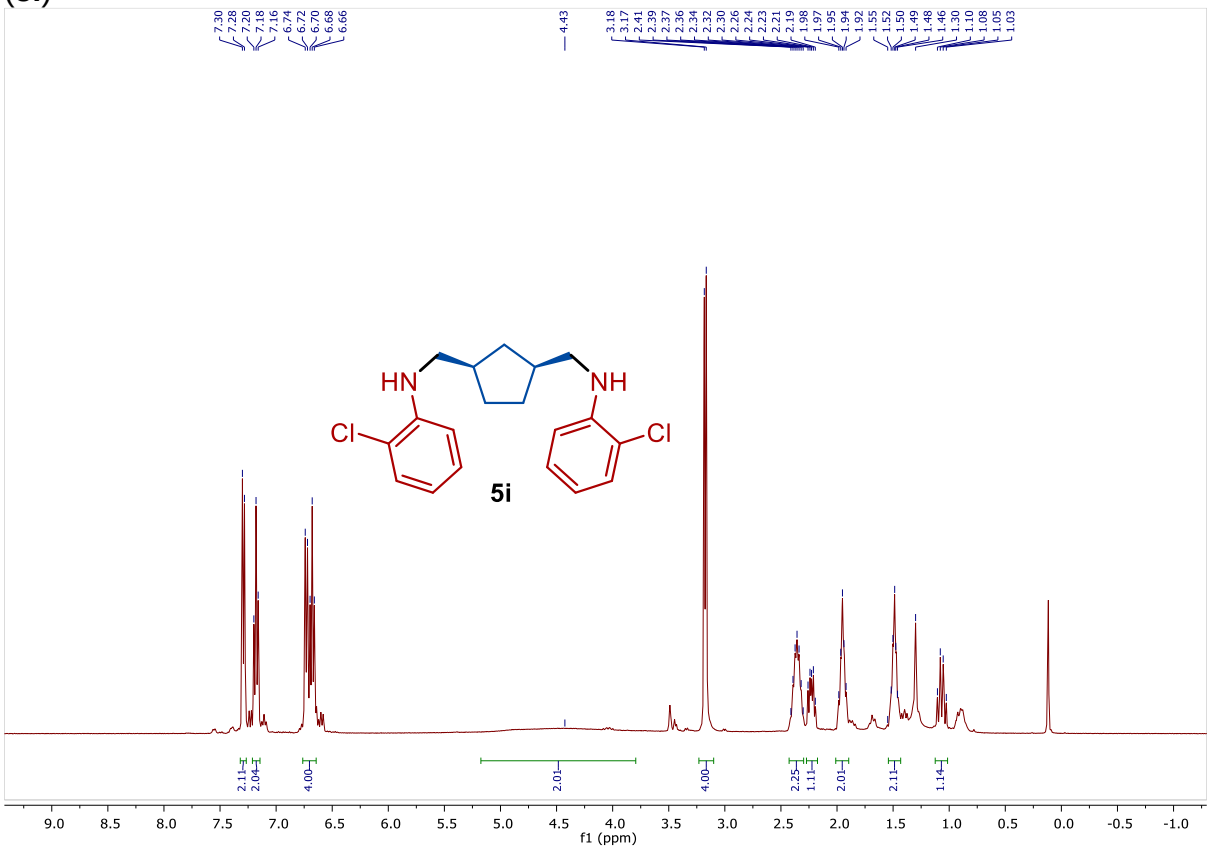
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(3-chloroaniline) (**5h**)



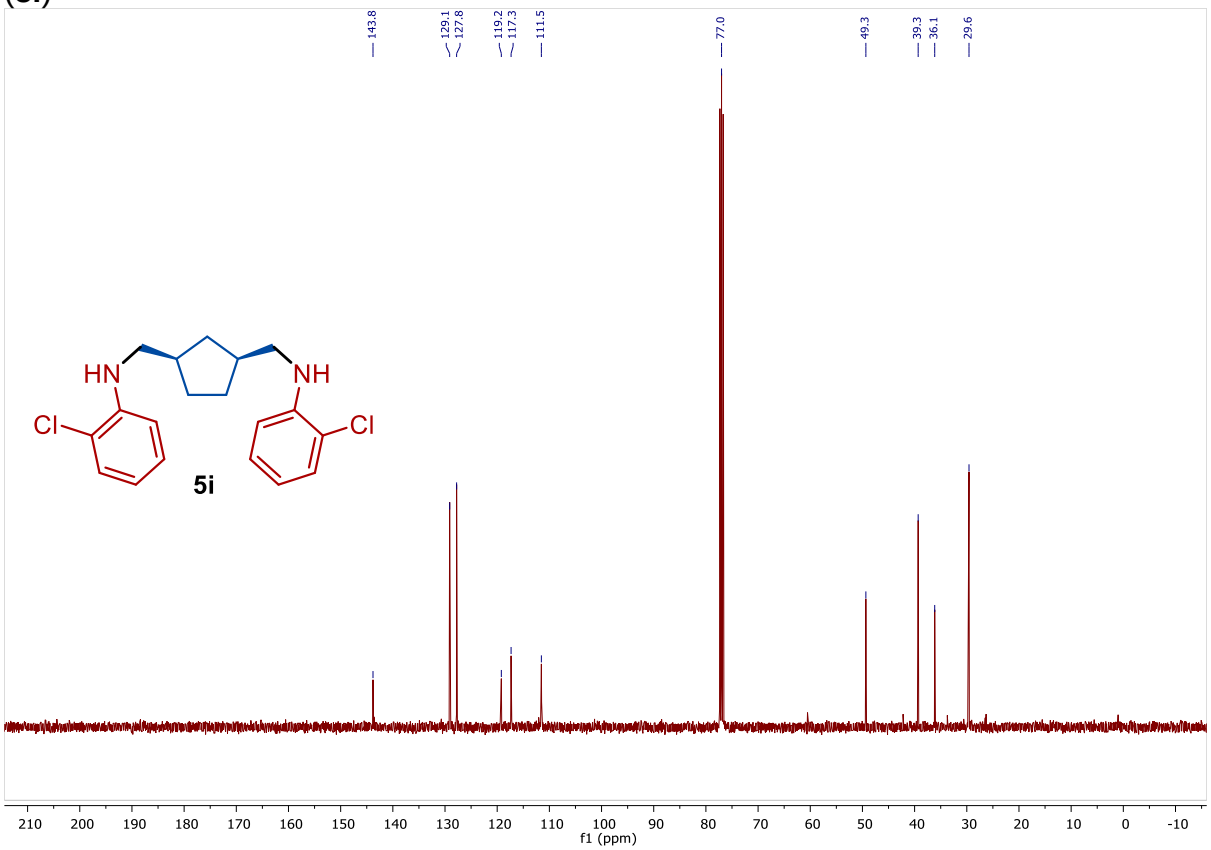
DEPT of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(3-chloroaniline) (**5h**)



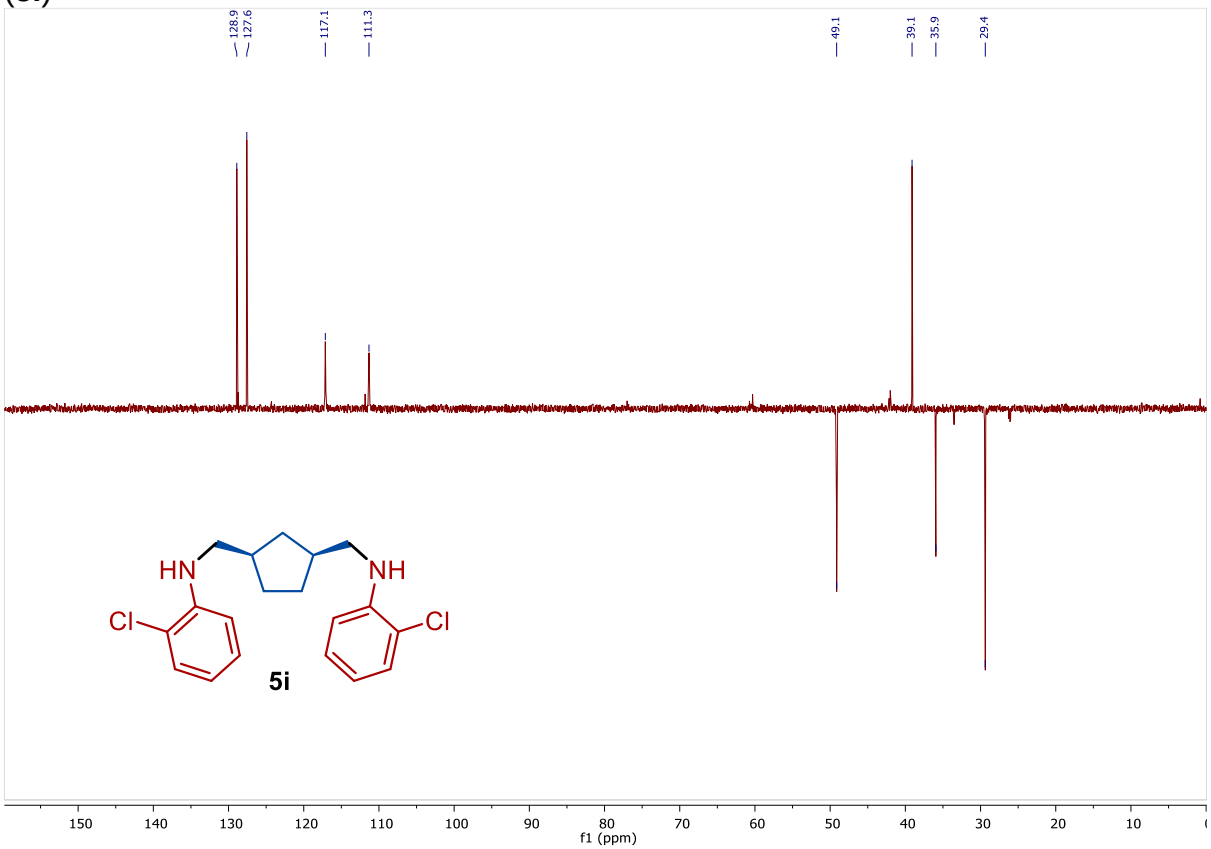
^{1}H NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(2-chloroaniline) (**5i**)



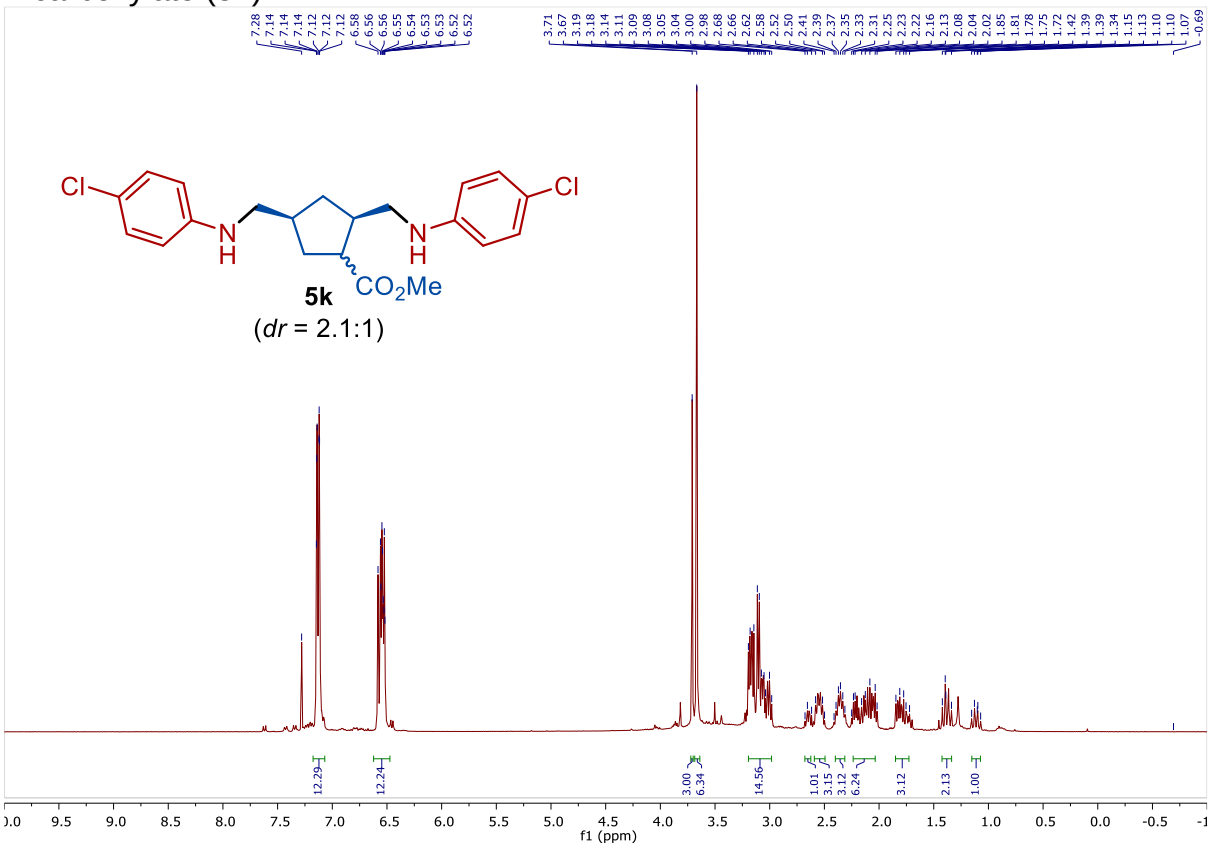
^{13}C NMR of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(2-chloroaniline) (**5i**)



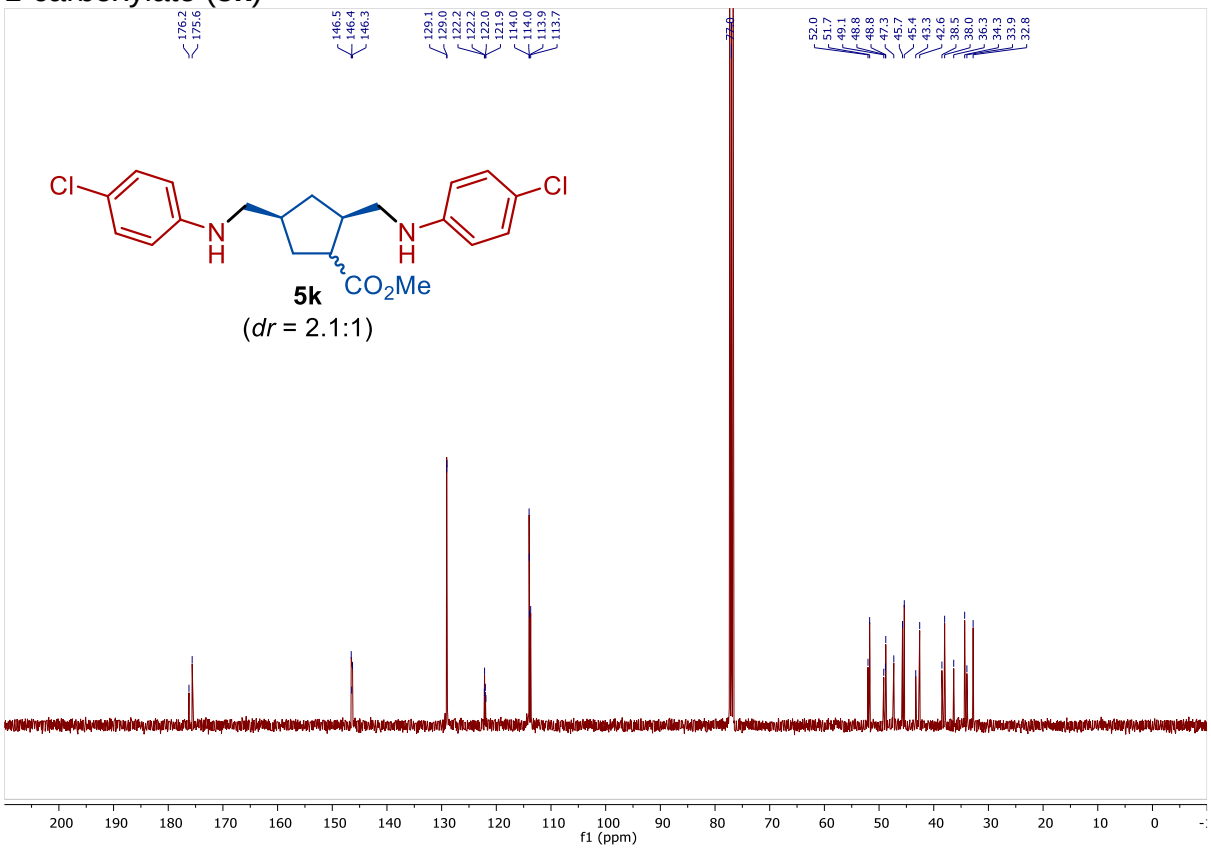
DEPT of N,N'-(((1R,3S)-cyclopentane-1,3-diyl)bis(methylene))bis(2-chloroaniline) (**5i**)



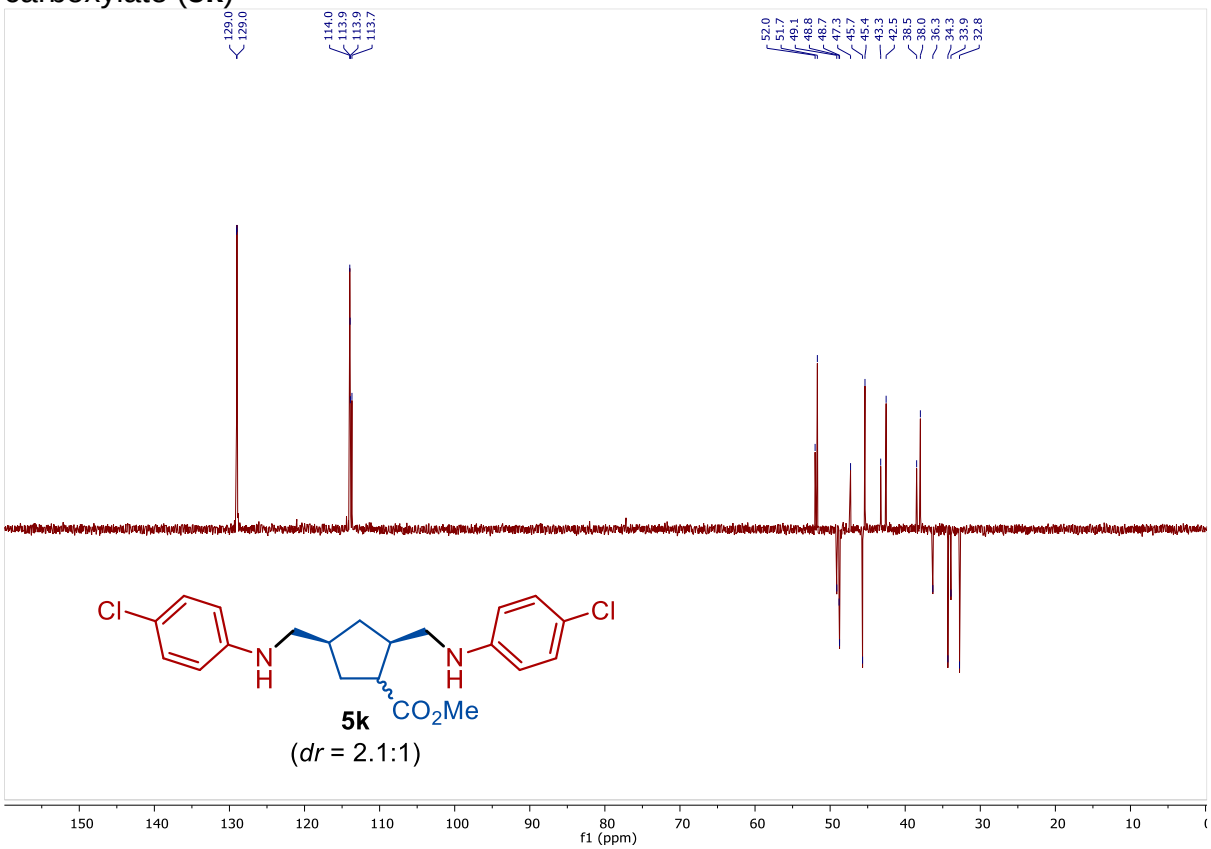
^{1}H NMR of methyl (2RS,4SR)-2,4-bis(((4-chlorophenyl)amino)methyl)cyclopentane-1-carboxylate (**5k**)



^{13}C NMR of methyl (2RS,4SR)-2,4-bis(((4-chlorophenyl)amino)methyl)cyclopentane-1-carboxylate (**5k**)



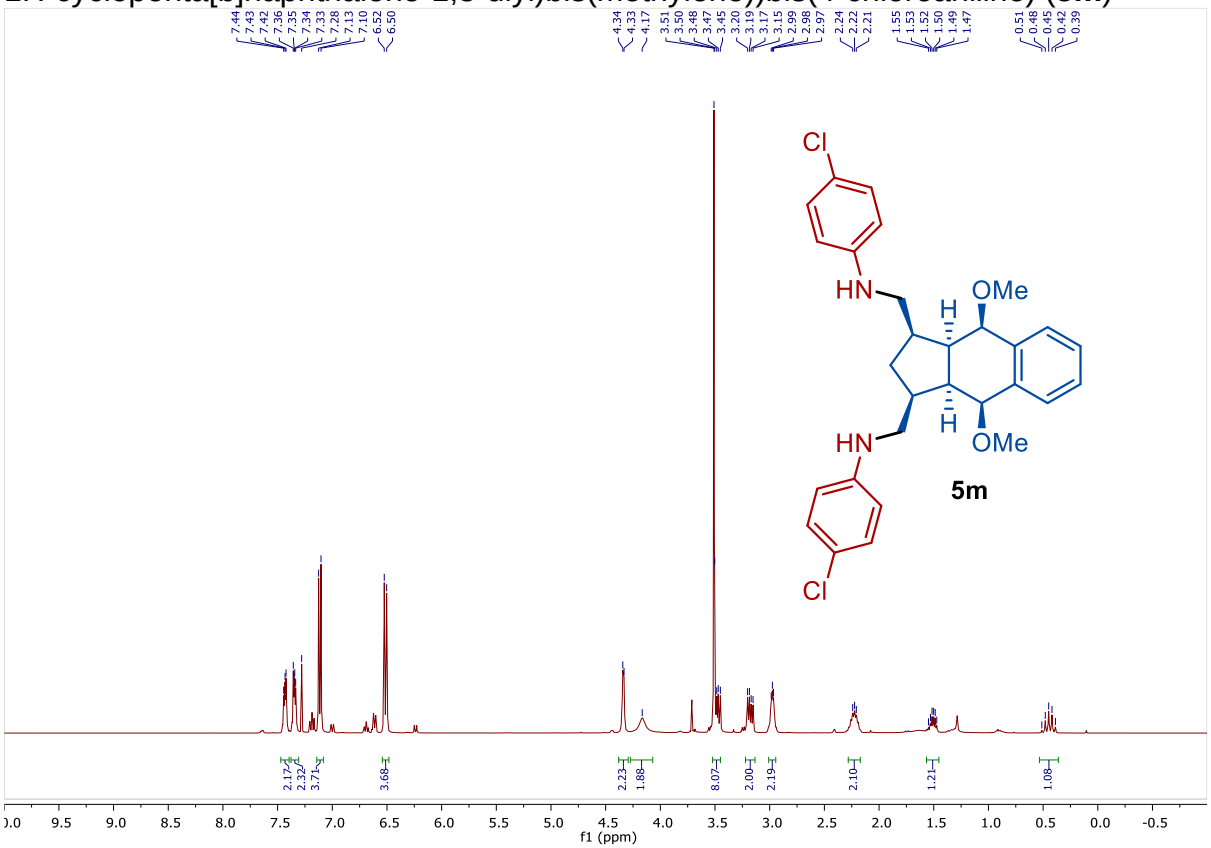
DEPT of methyl (2RS,4SR)-2,4-bis(((4-chlorophenyl)amino)methyl)cyclopentane-1-carboxylate (**5k**)



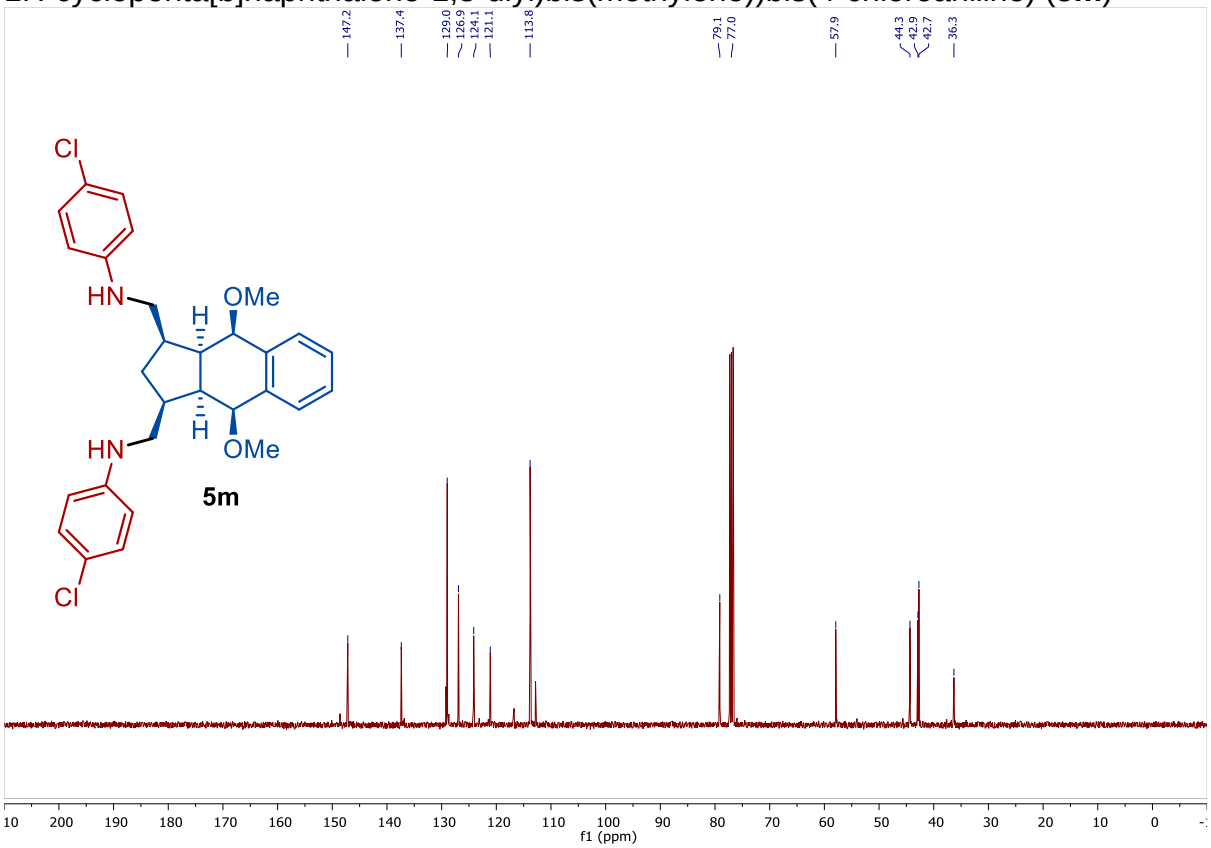
5k

(*dr* = 2.1:1)

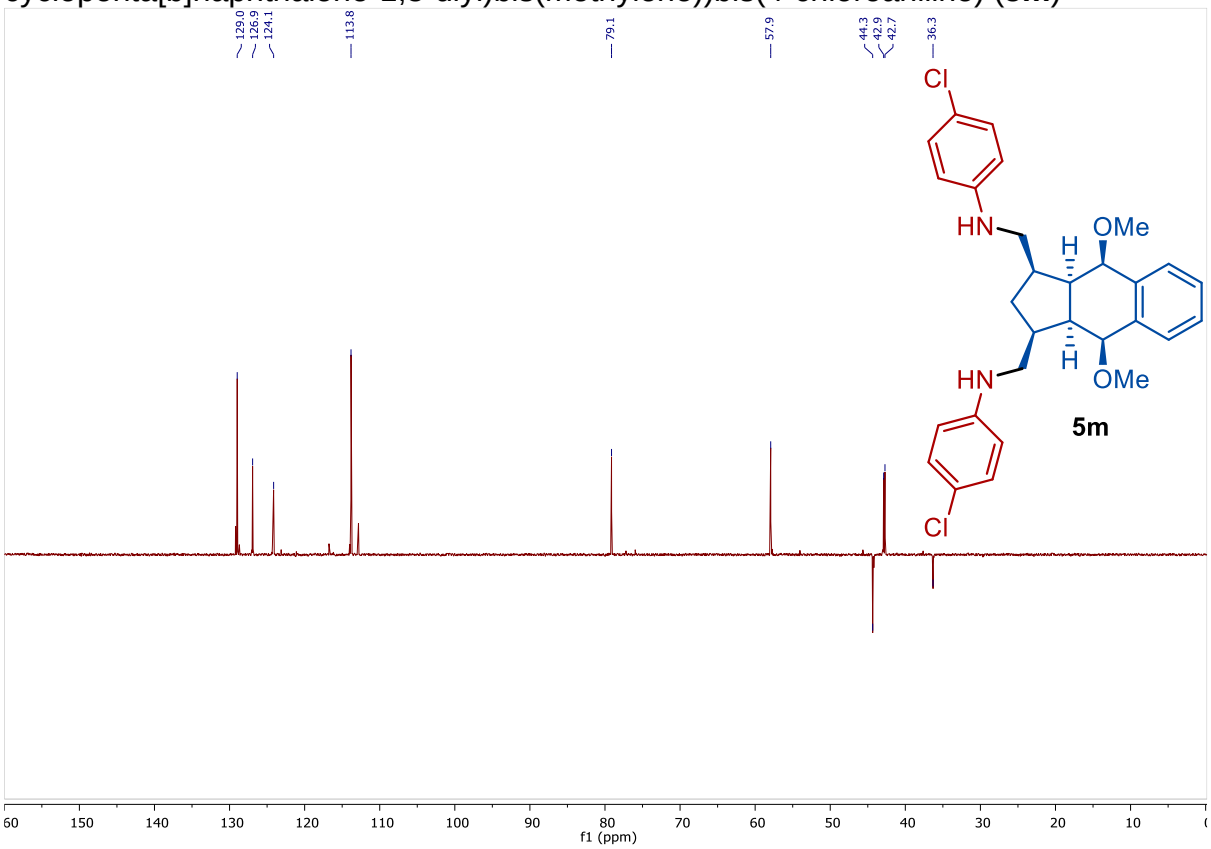
^{1}H NMR of N,N'-(((1R,3S,3aS,4S,9R,9aR)-4,9-dimethoxy-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5m**)



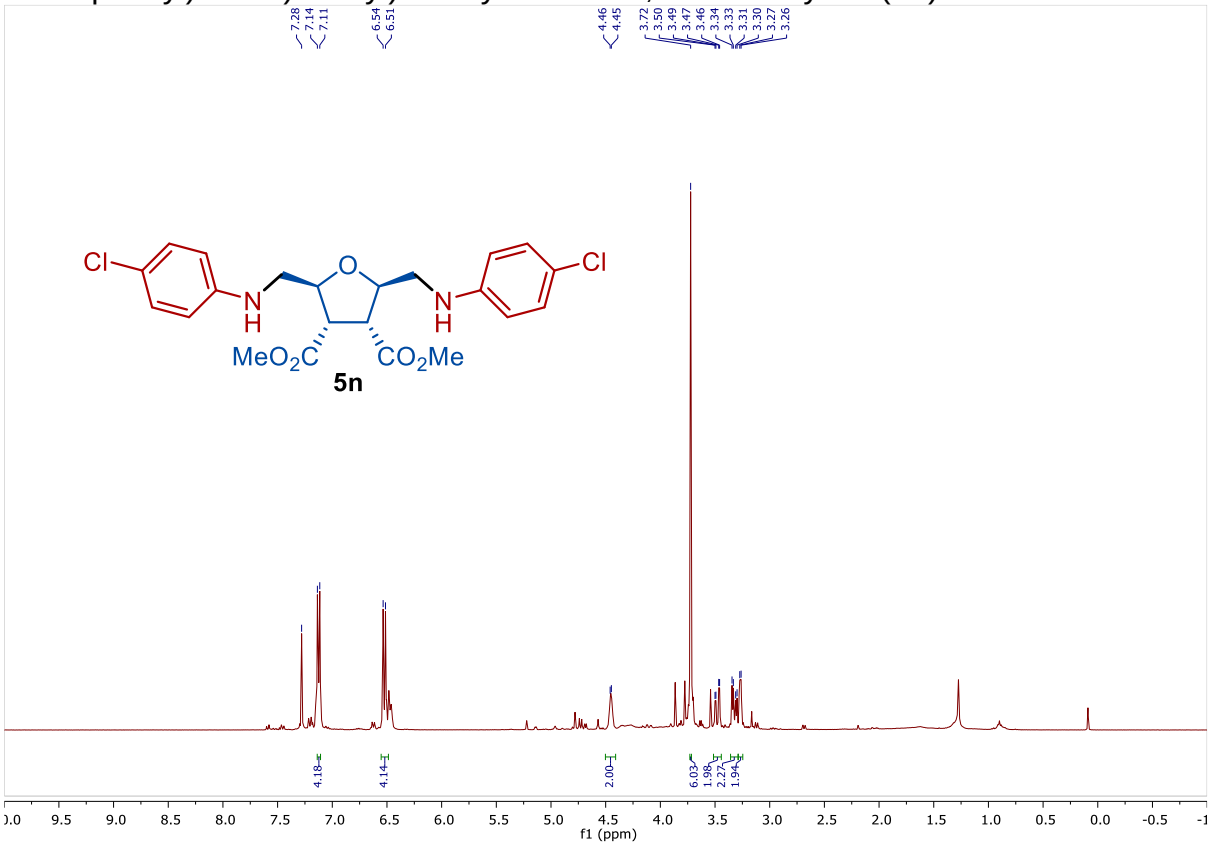
^{13}C NMR of N,N'-(((1R,3S,3aS,4S,9R,9aR)-4,9-dimethoxy-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5m**)



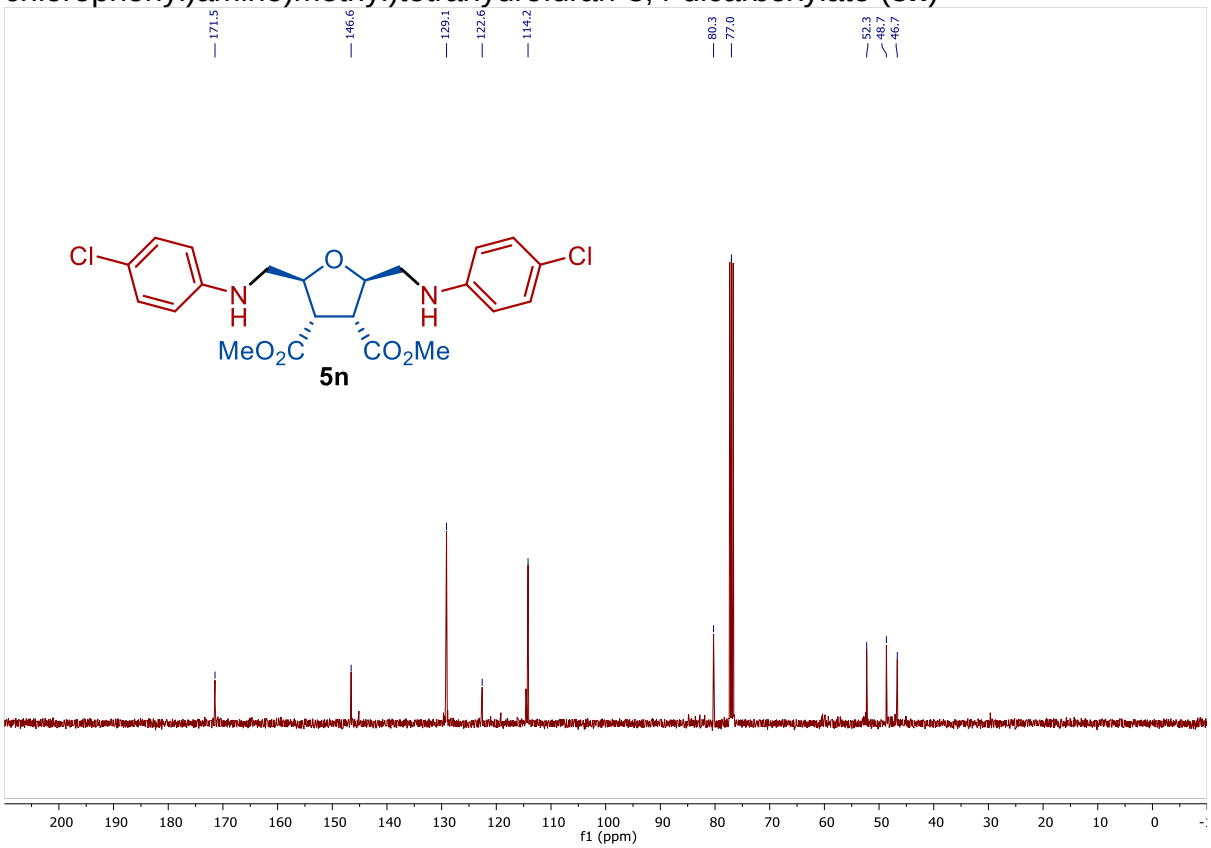
DEPT of N,N'-(((1R,3S,3aS,4S,9R,9aR)-4,9-dimethoxy-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene-1,3-diyl)bis(methylene))bis(4-chloroaniline) (**5m**)



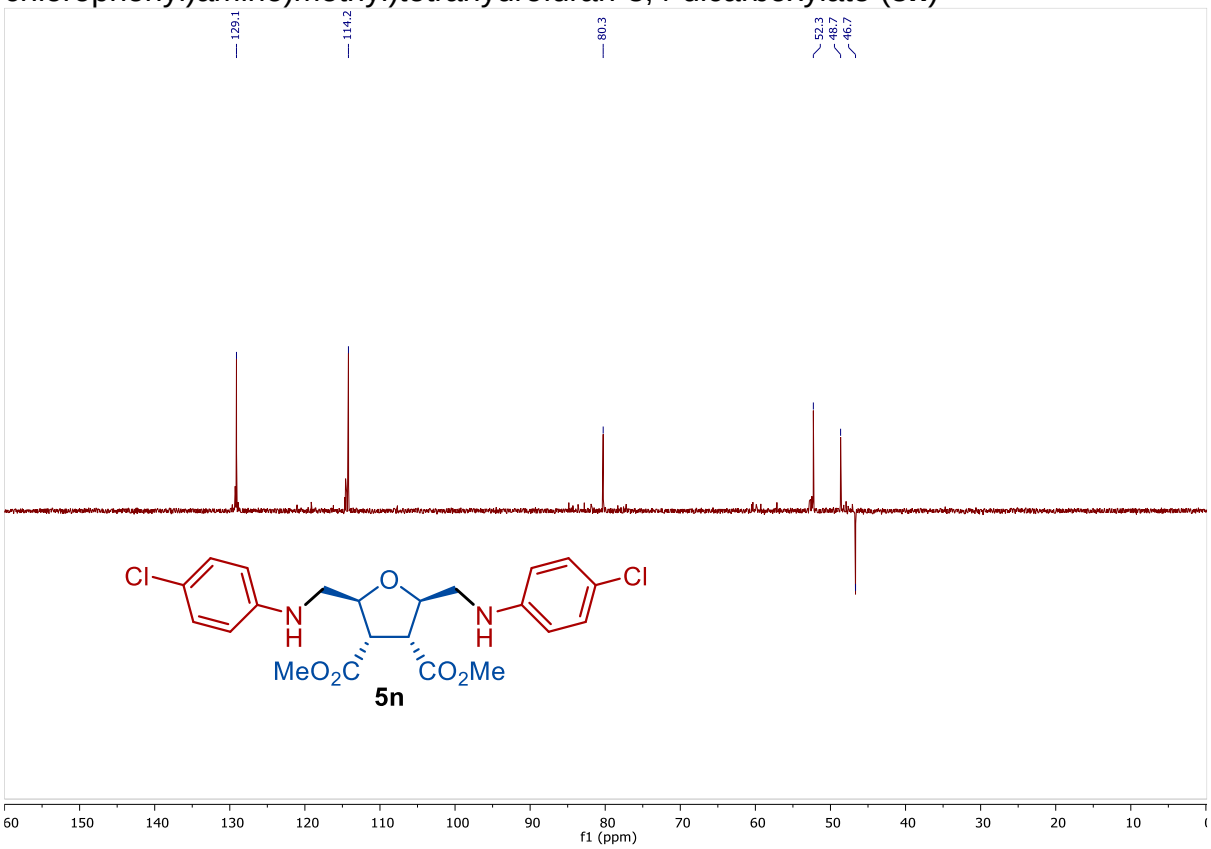
^{1}H NMR of dimethyl (2R,3R,4S,5S)-2,5-bis(((4-chlorophenyl)amino)methyl)tetrahydrofuran-3,4-dicarboxylate (**5n**)



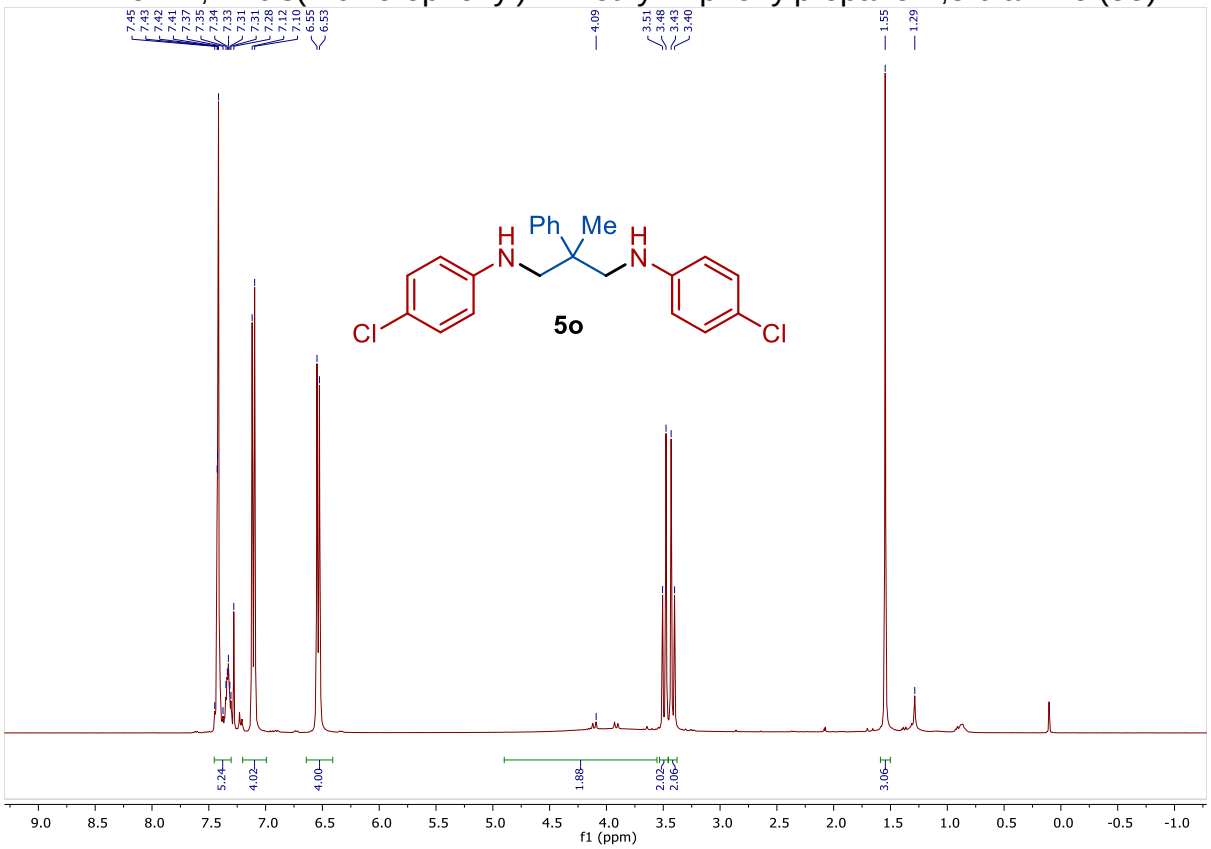
^{13}C NMR of dimethyl (2R,3R,4S,5S)-2,5-bis(((4-chlorophenyl)amino)methyl)tetrahydrofuran-3,4-dicarboxylate (**5n**)



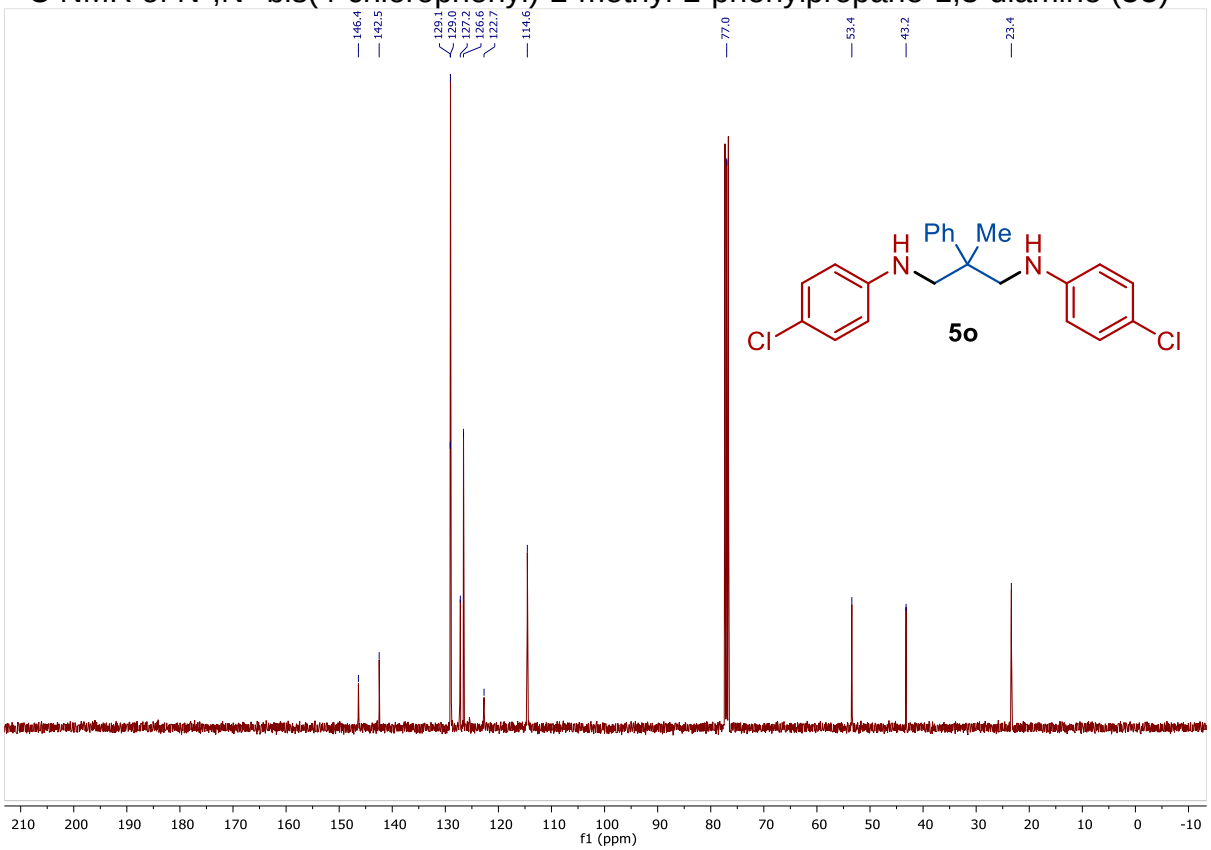
DEPT of dimethyl (2R,3R,4S,5S)-2,5-bis(((4-chlorophenyl)amino)methyl)tetrahydrofuran-3,4-dicarboxylate (**5n**)



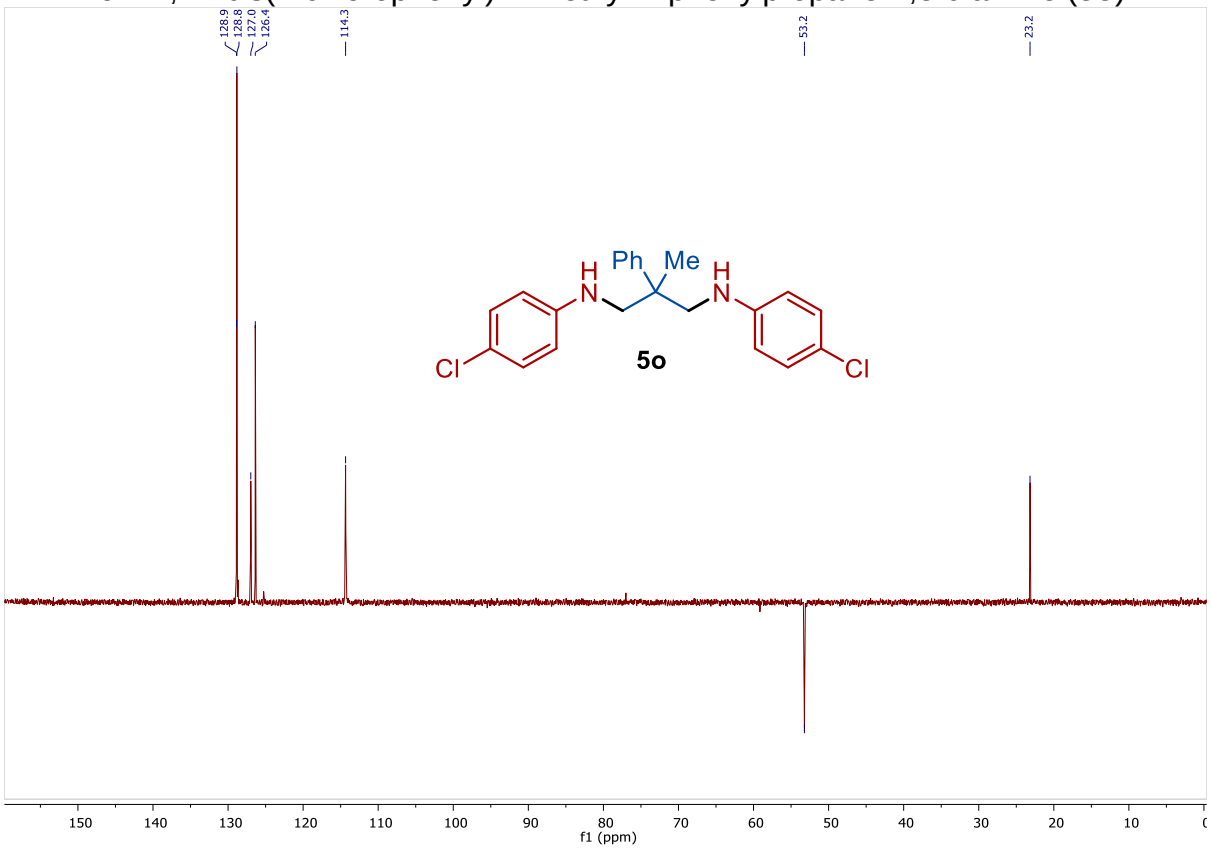
^{1}H NMR of N^{1},N^{3}-bis(4-chlorophenyl)-2-methyl-2-phenylpropane-1,3-diamine (**5o**)



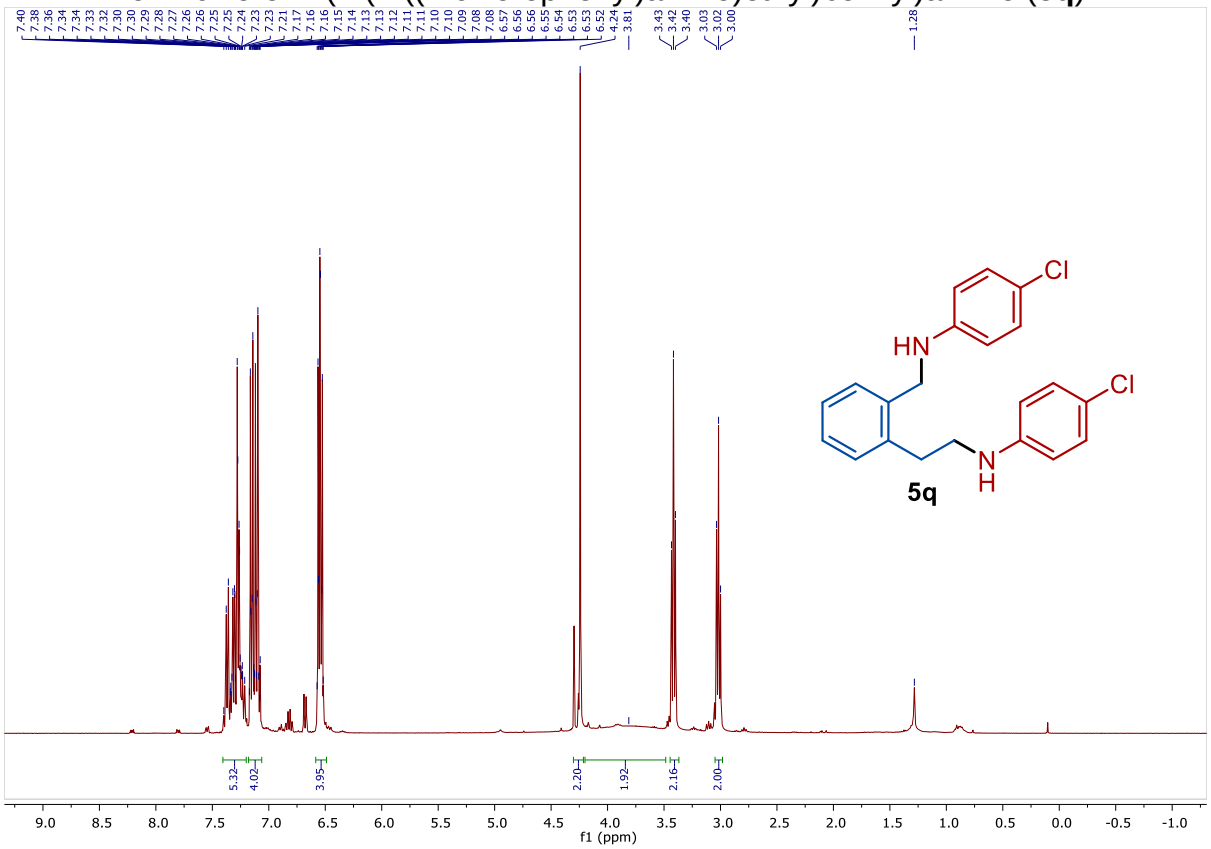
^{13}C NMR of N^{1},N^{3}-bis(4-chlorophenyl)-2-methyl-2-phenylpropane-1,3-diamine (**5o**)



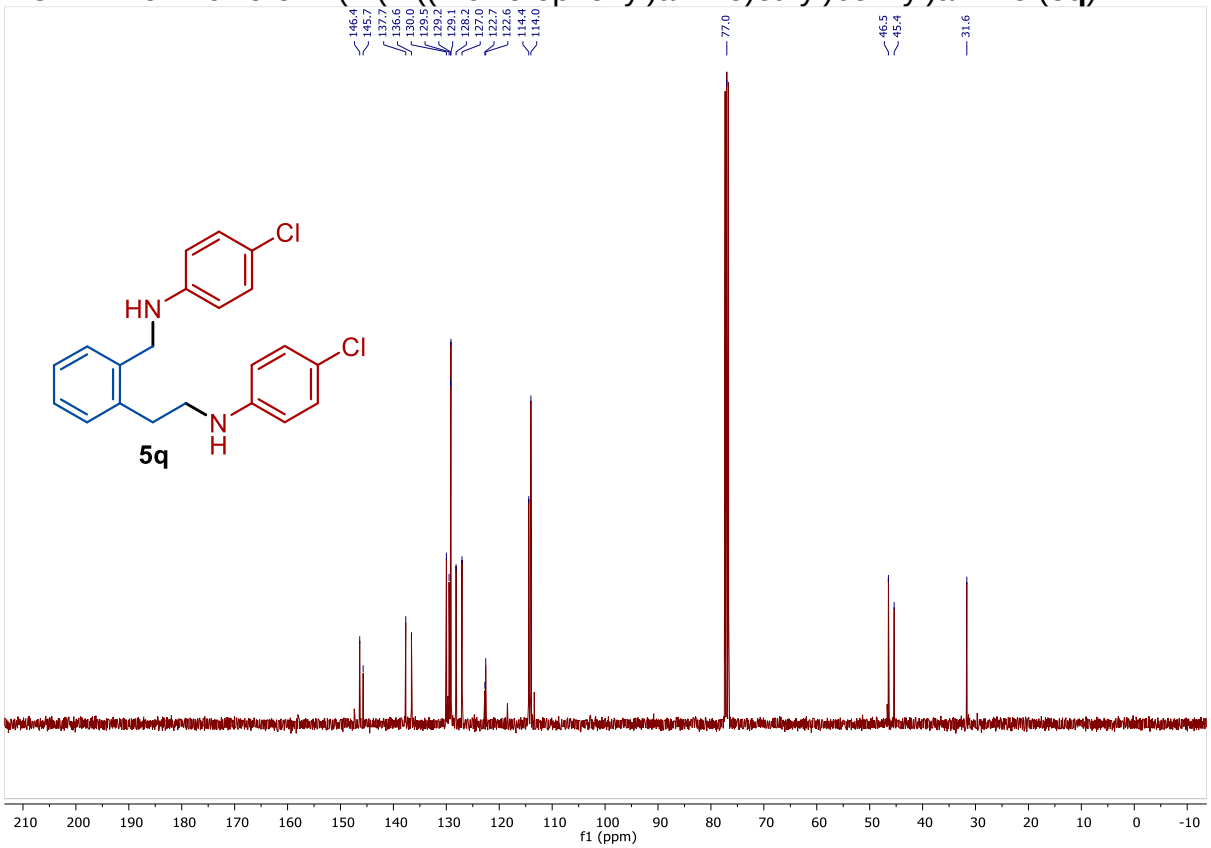
DEPT of N^1,N^3-bis(4-chlorophenyl)-2-methyl-2-phenylpropane-1,3-diamine (**5o**)



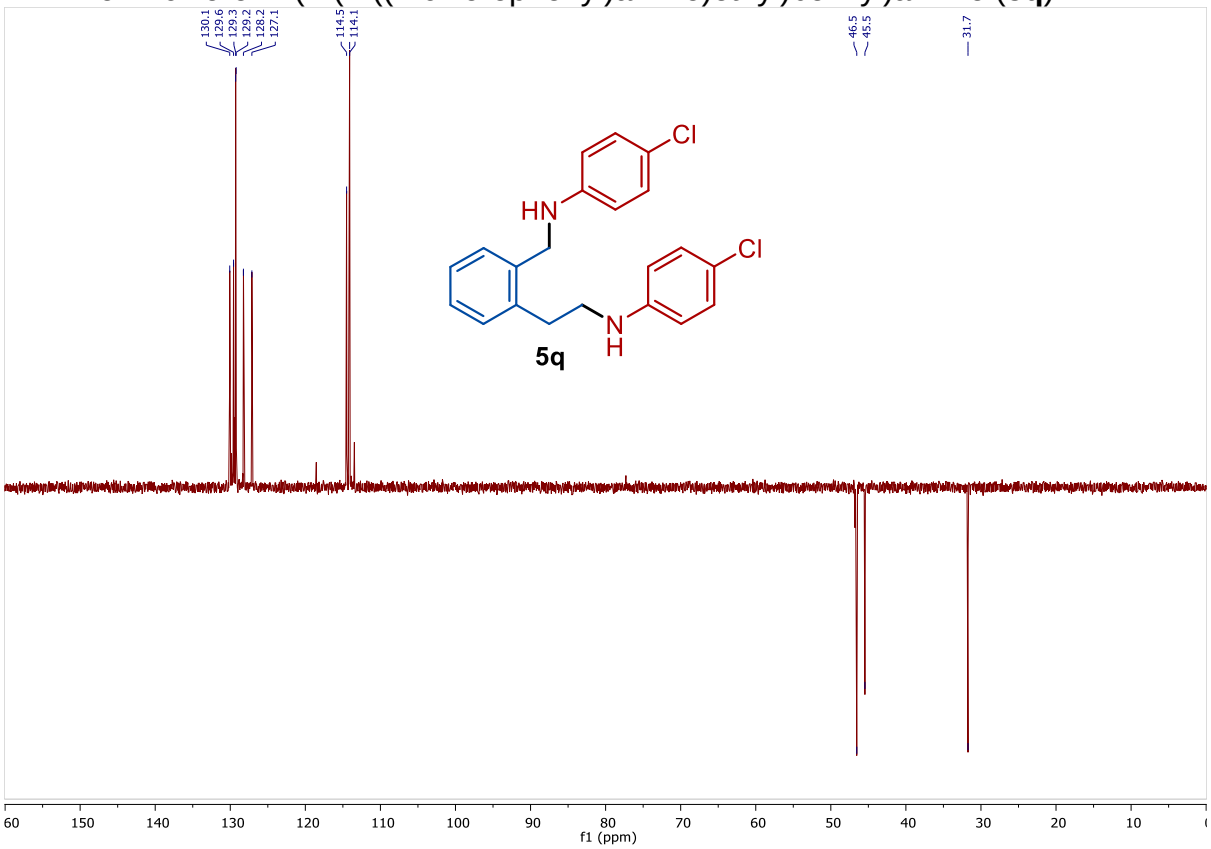
^{1}H NMR of 4-chloro-N-(2-(2-((4-chlorophenyl)amino)ethyl)benzyl)aniline (**5q**)



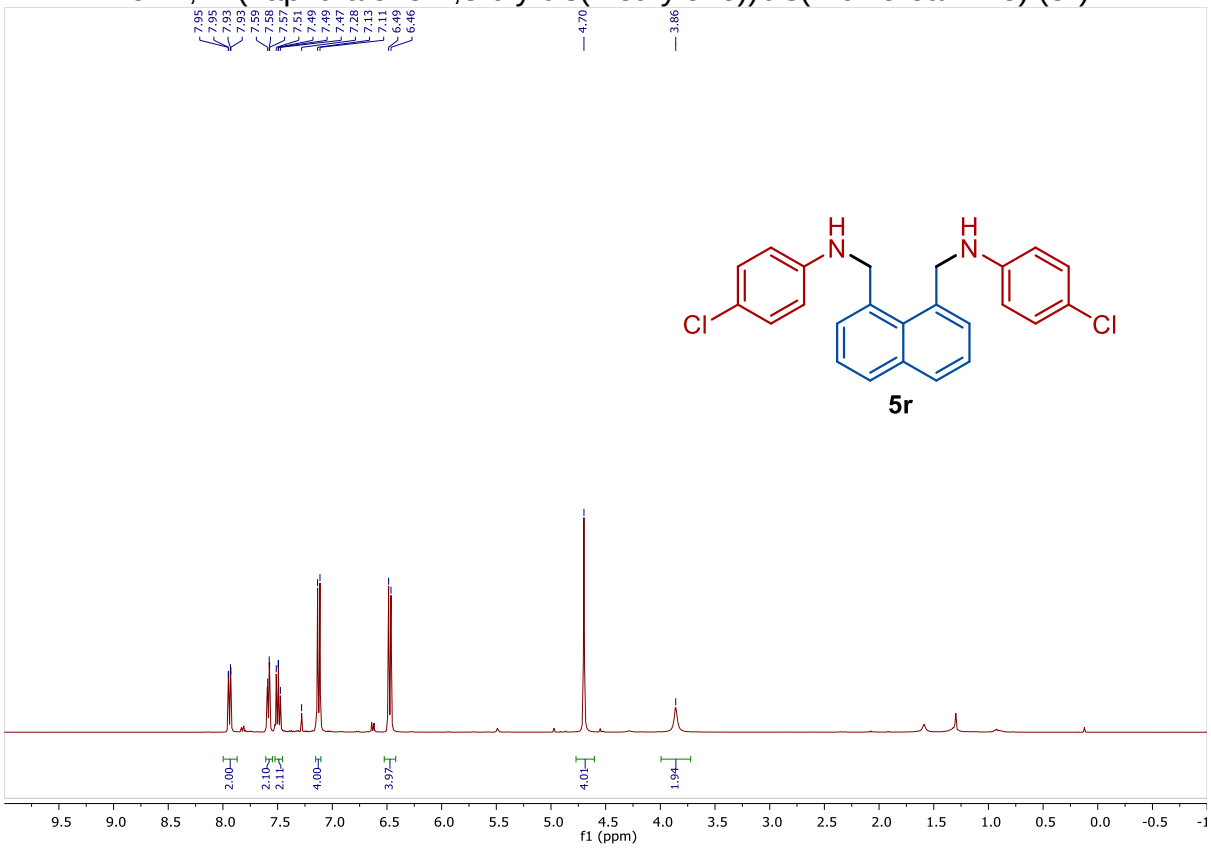
^{13}C NMR of 4-chloro-N-(2-(2-((4-chlorophenyl)amino)ethyl)benzyl)aniline (**5q**)



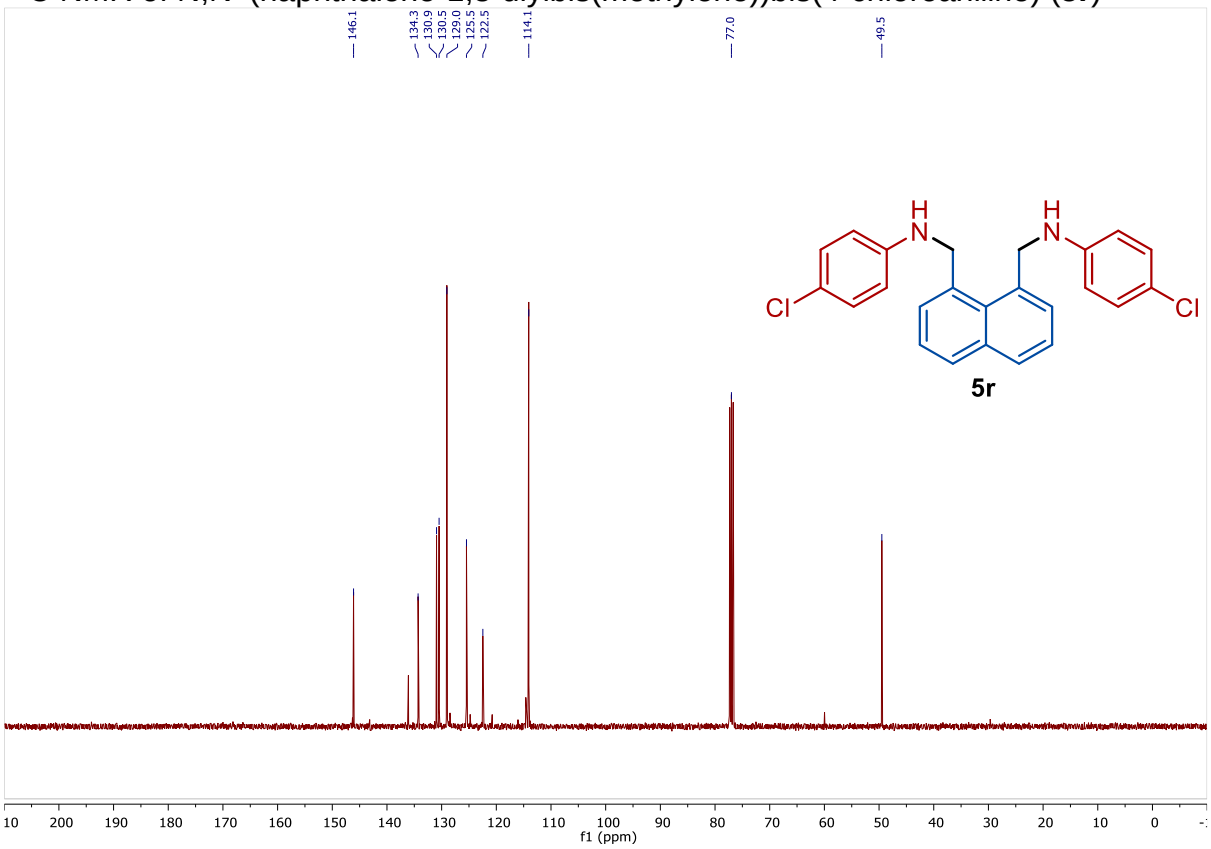
DEPT of 4-chloro-N-(2-(2-((4-chlorophenyl)amino)ethyl)benzyl)aniline (**5q**)



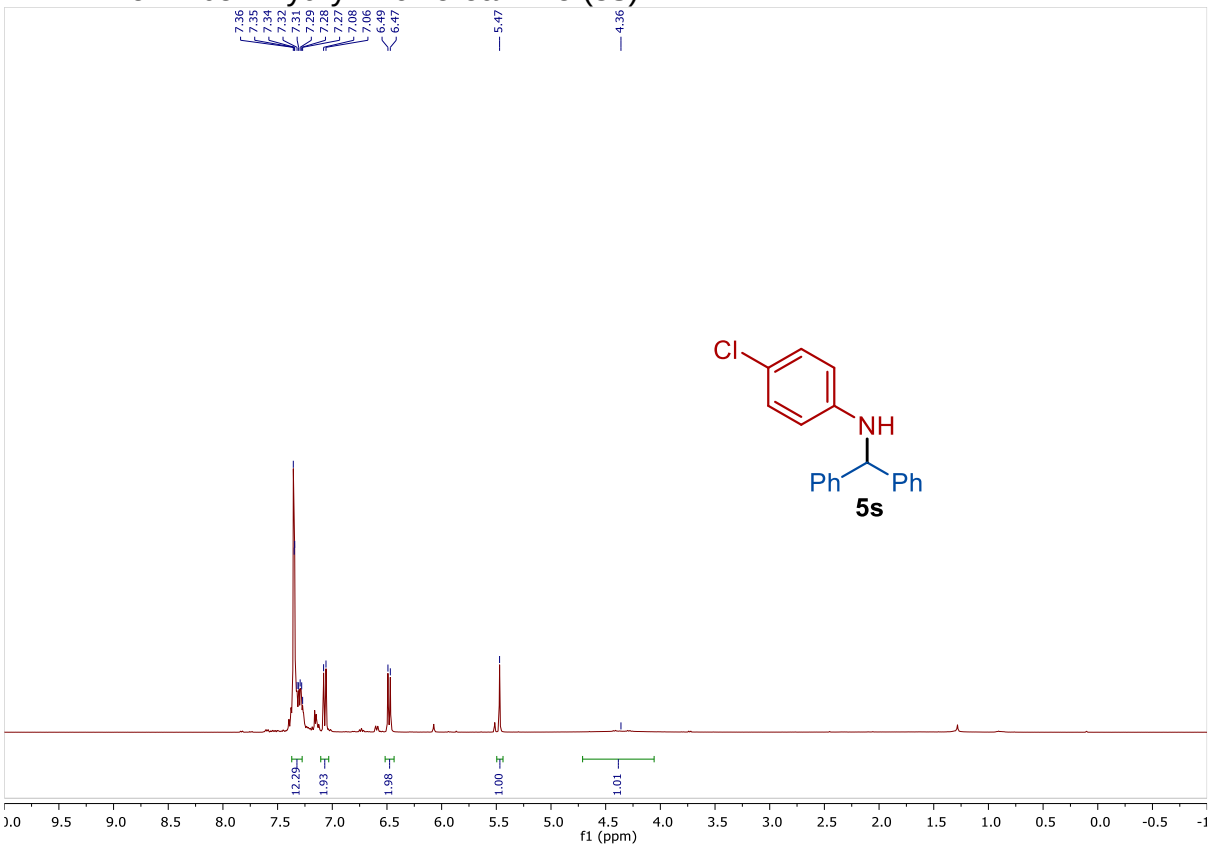
^{1}H NMR of N,N'-(naphthalene-1,8-diylbis(methylene))bis(4-chloroaniline) (**5r**)



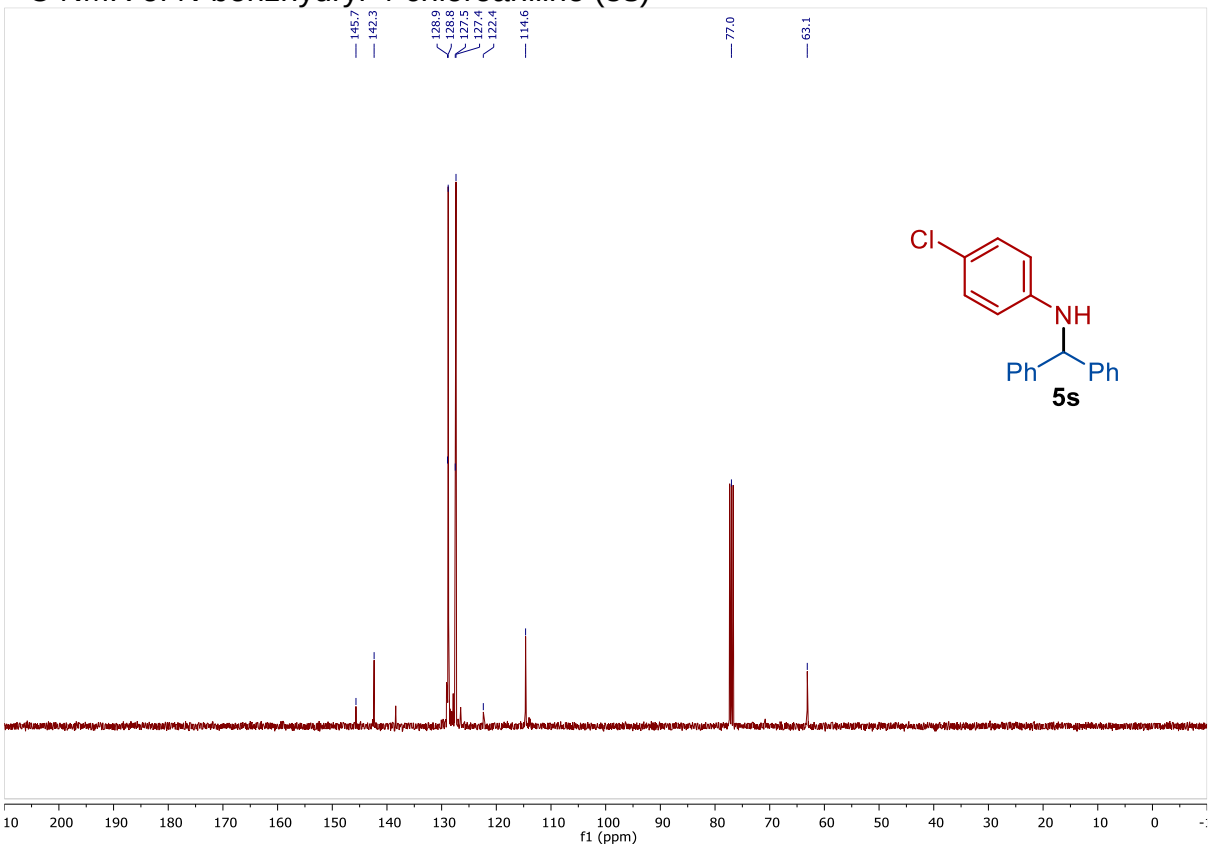
^{13}C NMR of N,N'-(naphthalene-1,8-diylbis(methylene))bis(4-chloroaniline) (**5r**)



^{1}H NMR of N-benzhydryl-4-chloroaniline (**5s**)[21]

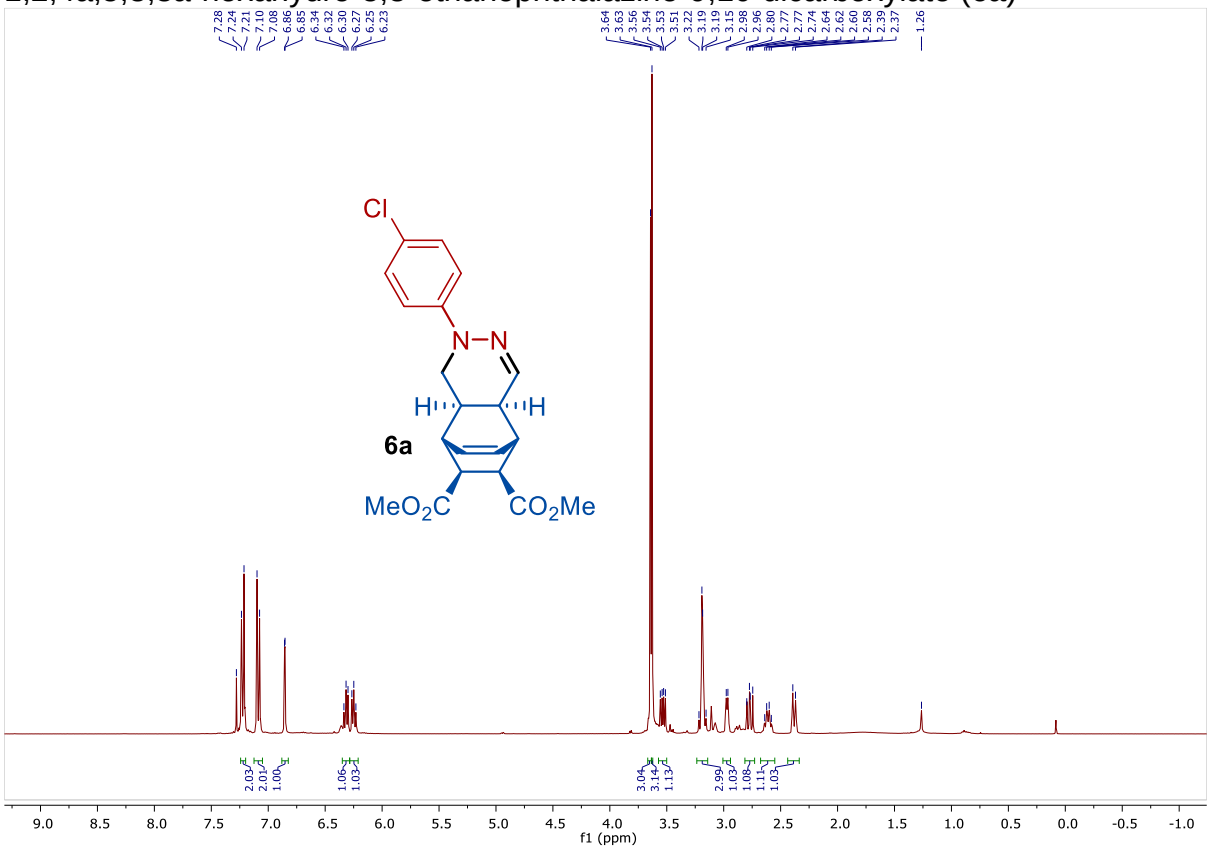


^{13}C NMR of N-benzhydryl-4-chloroaniline (**5s**)

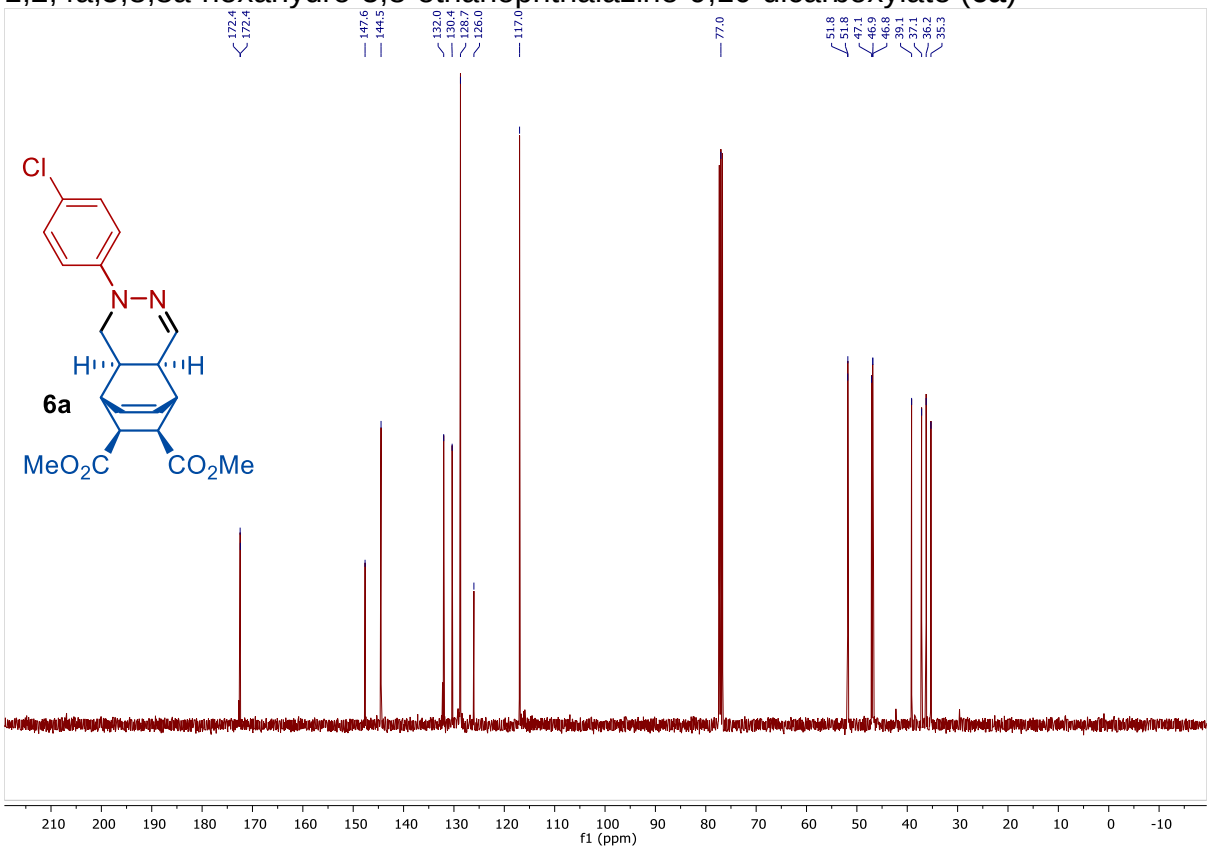


[21] The NMR data matches the one previously reported.[15]

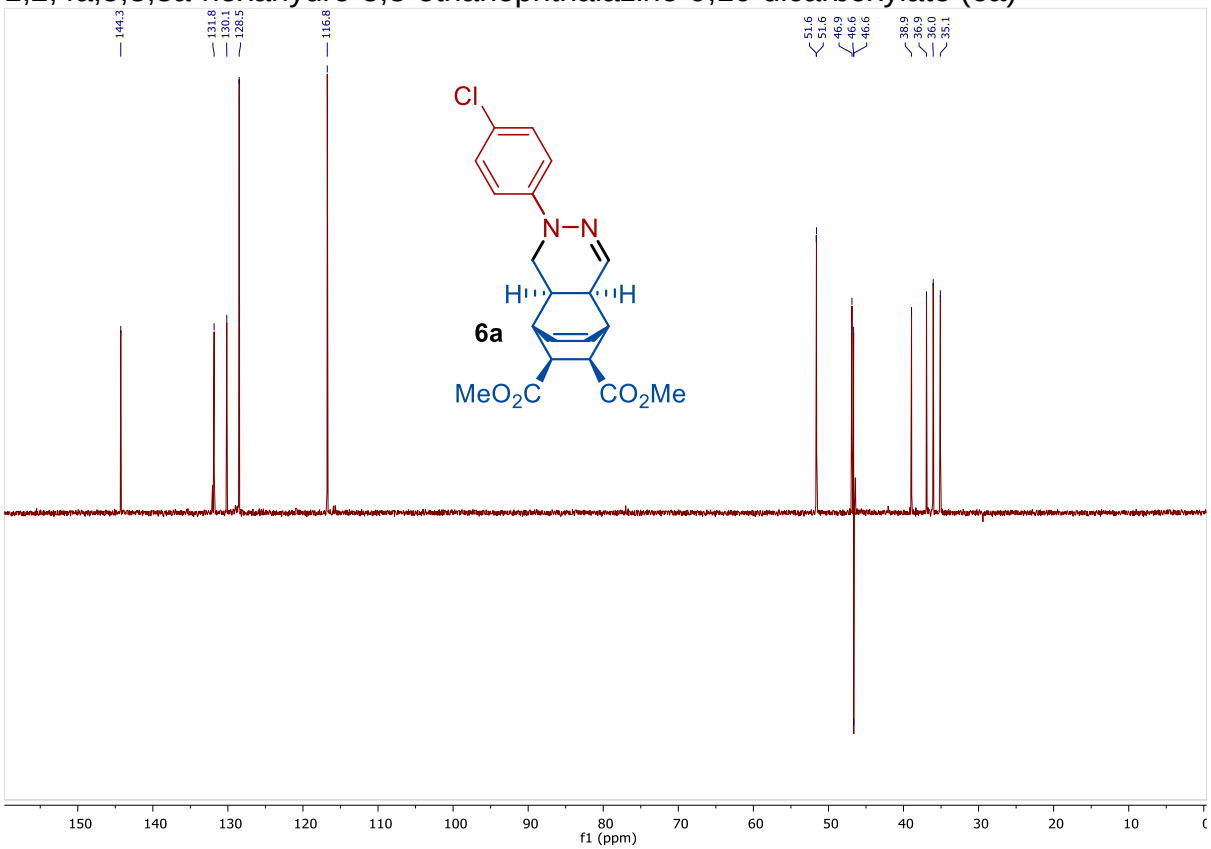
^{1}H NMR of dimethyl (4aSR,5RS,8SR,8aRS,9SR,10RS)-2-(4-chlorophenyl)-1,2,4a,5,8,8a-hexahydro-5,8-ethanophthalazine-9,10-dicarboxylate (**6a**)



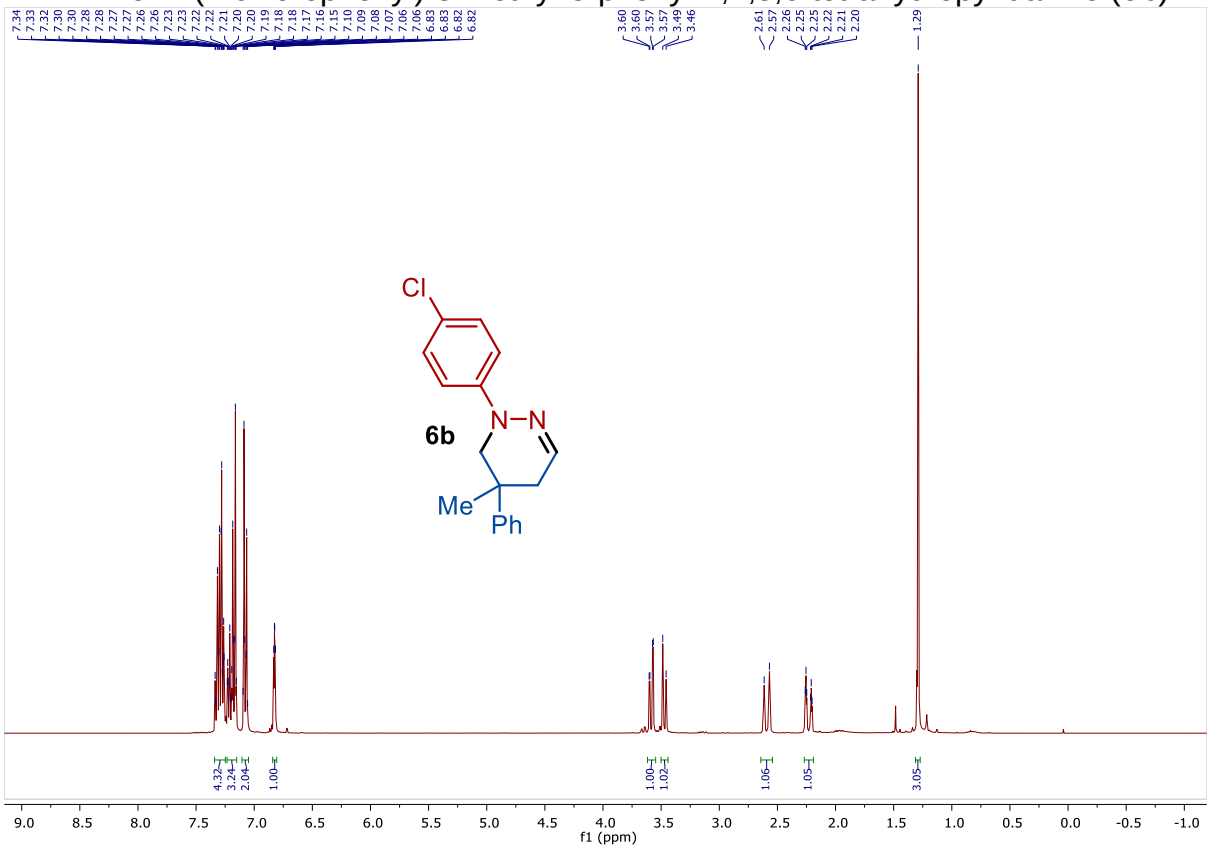
^{13}C NMR of dimethyl (4aSR,5RS,8SR,8aRS,9SR,10RS)-2-(4-chlorophenyl)-1,2,4a,5,8,8a-hexahydro-5,8-ethanophthalazine-9,10-dicarboxylate (**6a**)



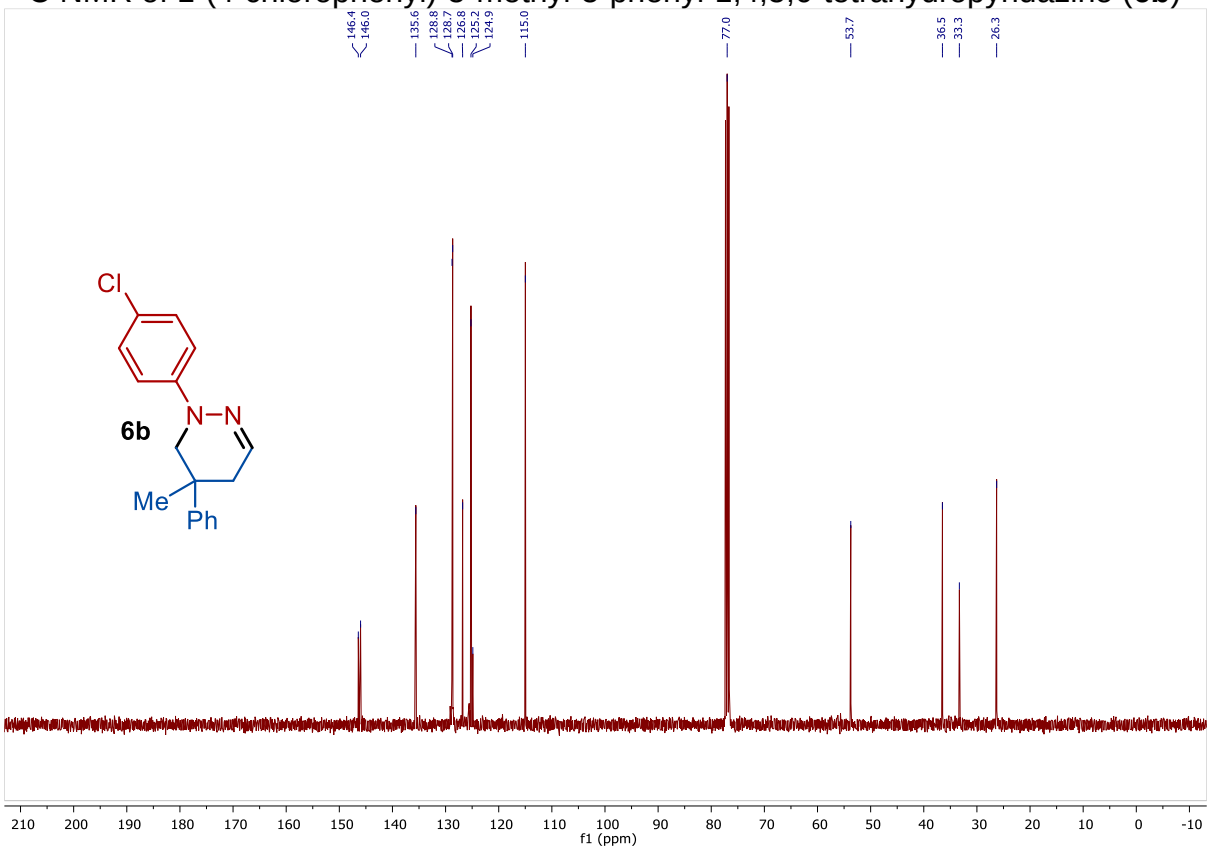
DEPT of dimethyl (4aSR,5RS,8SR,8aRS,9SR,10RS)-2-(4-chlorophenyl)-1,2,4a,5,8,8a-hexahydro-5,8-ethanophthalazine-9,10-dicarboxylate (**6a**)



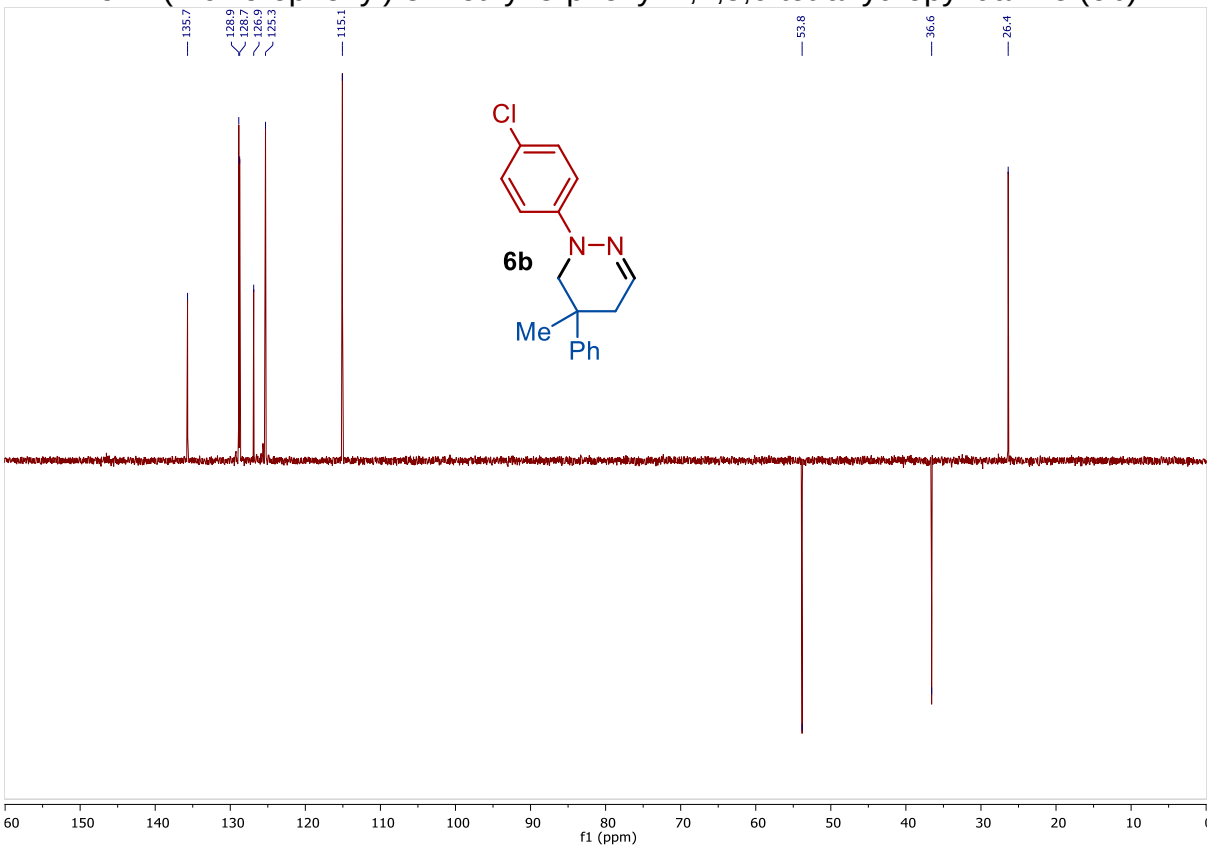
^{1}H NMR of 1-(4-chlorophenyl)-5-methyl-5-phenyl-1,4,5,6-tetrahydropyridazine (**6b**)



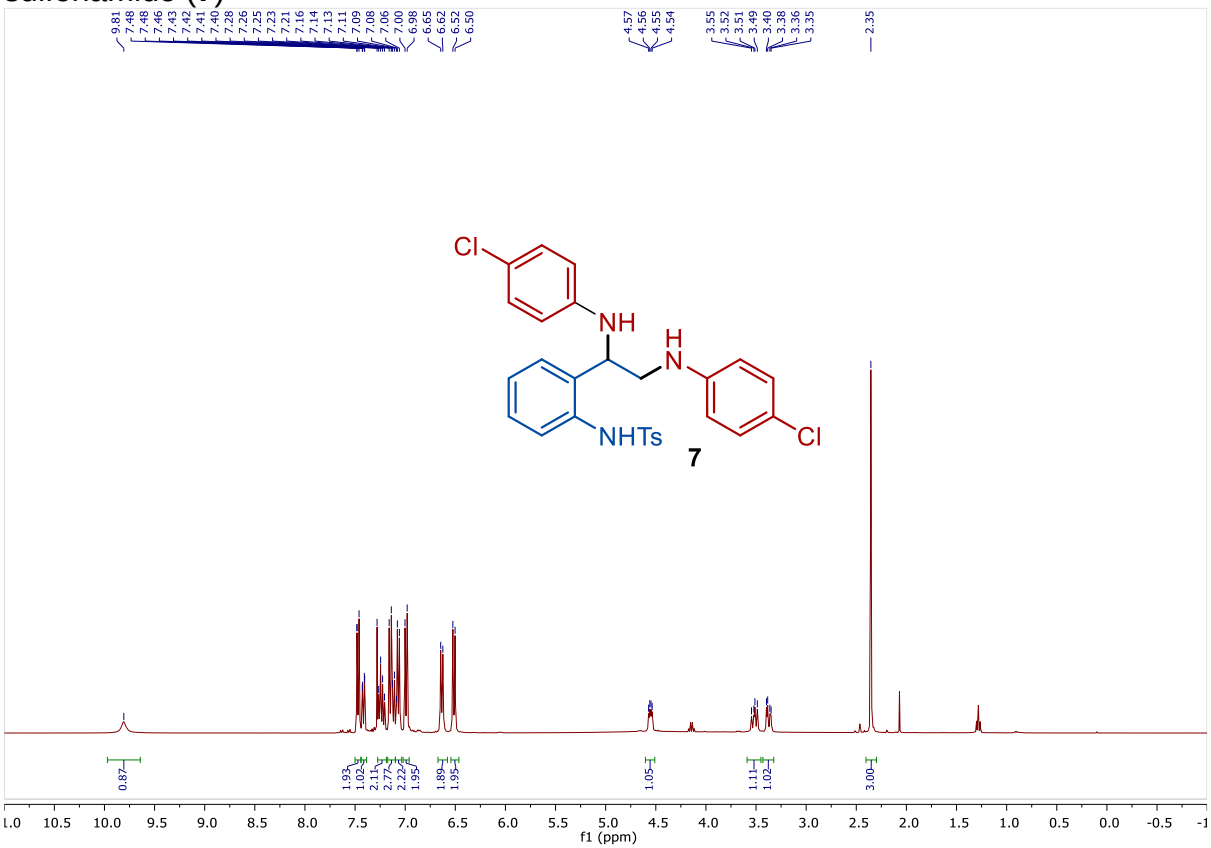
^{13}C NMR of 1-(4-chlorophenyl)-5-methyl-5-phenyl-1,4,5,6-tetrahydropyridazine (**6b**)



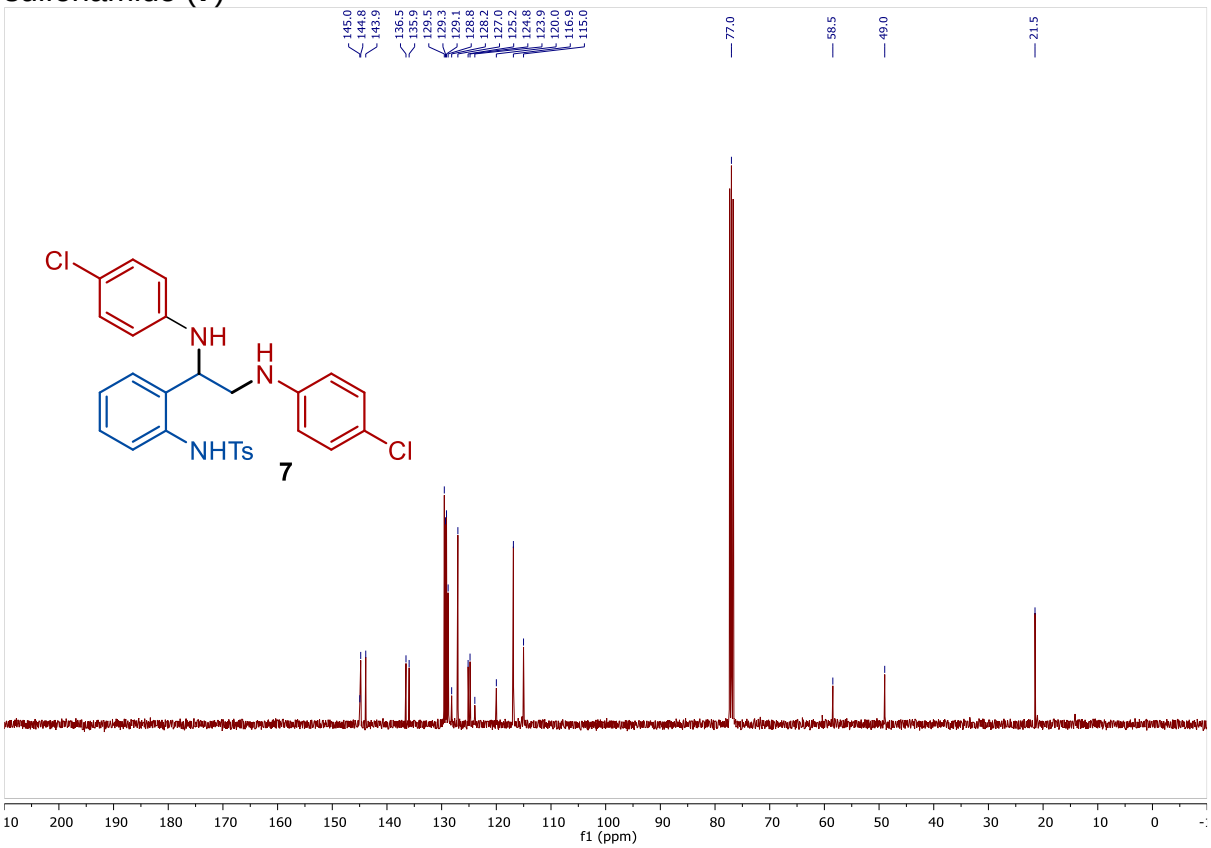
DEPT of 1-(4-chlorophenyl)-5-methyl-5-phenyl-1,4,5,6-tetrahydropyridazine (**6b**)



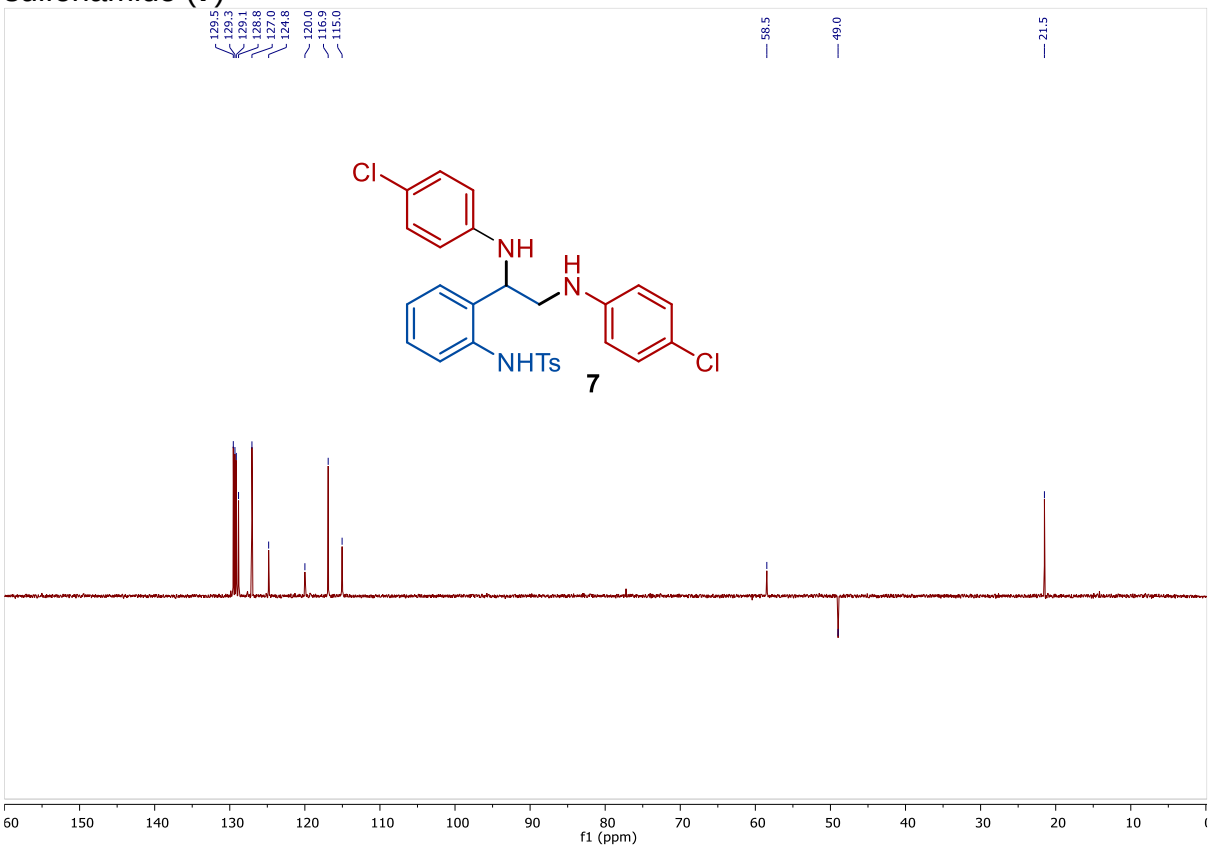
^{1}H NMR of N-(2-(1,2-bis((4-chlorophenyl)amino)ethyl)phenyl)-4-methylbenzene-sulfonamide (**7**)



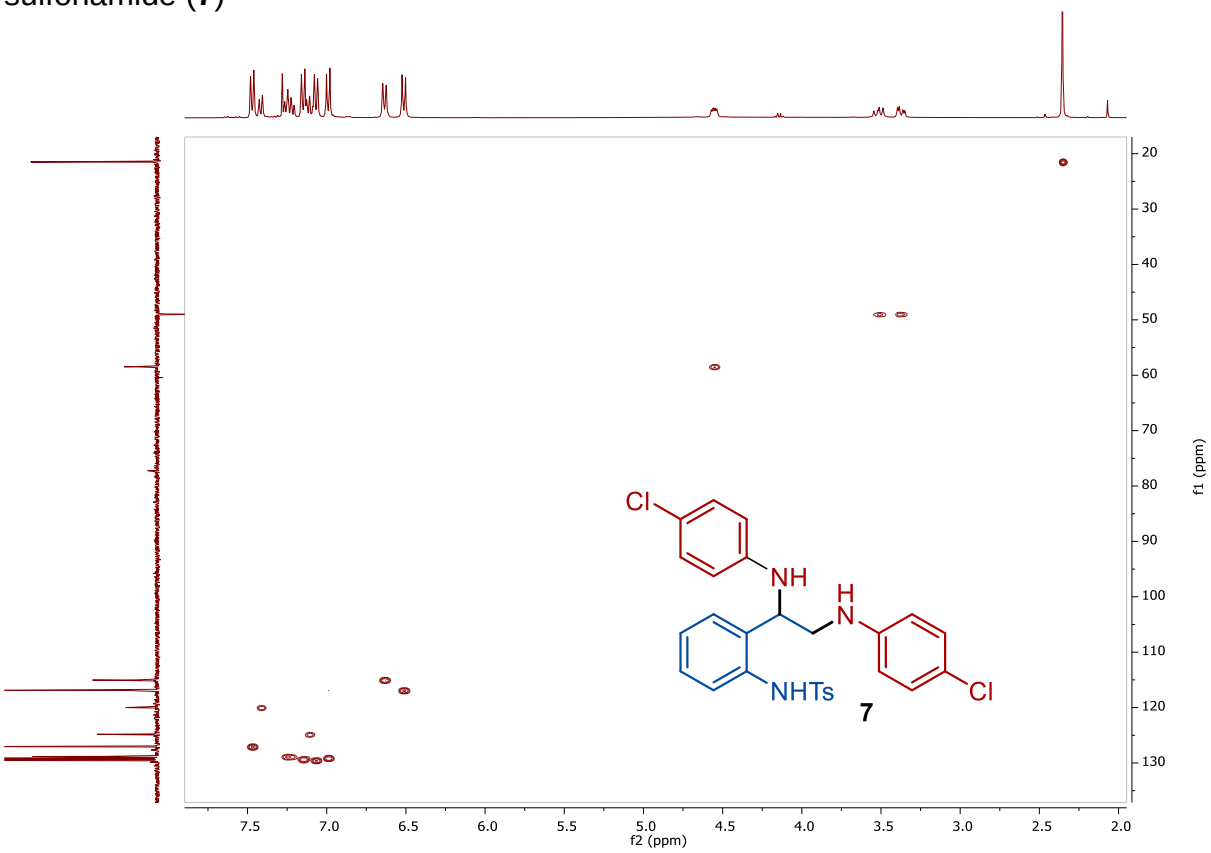
^{13}C NMR of N-(2-(1,2-bis((4-chlorophenyl)amino)ethyl)phenyl)-4-methylbenzene-sulfonamide (**7**)



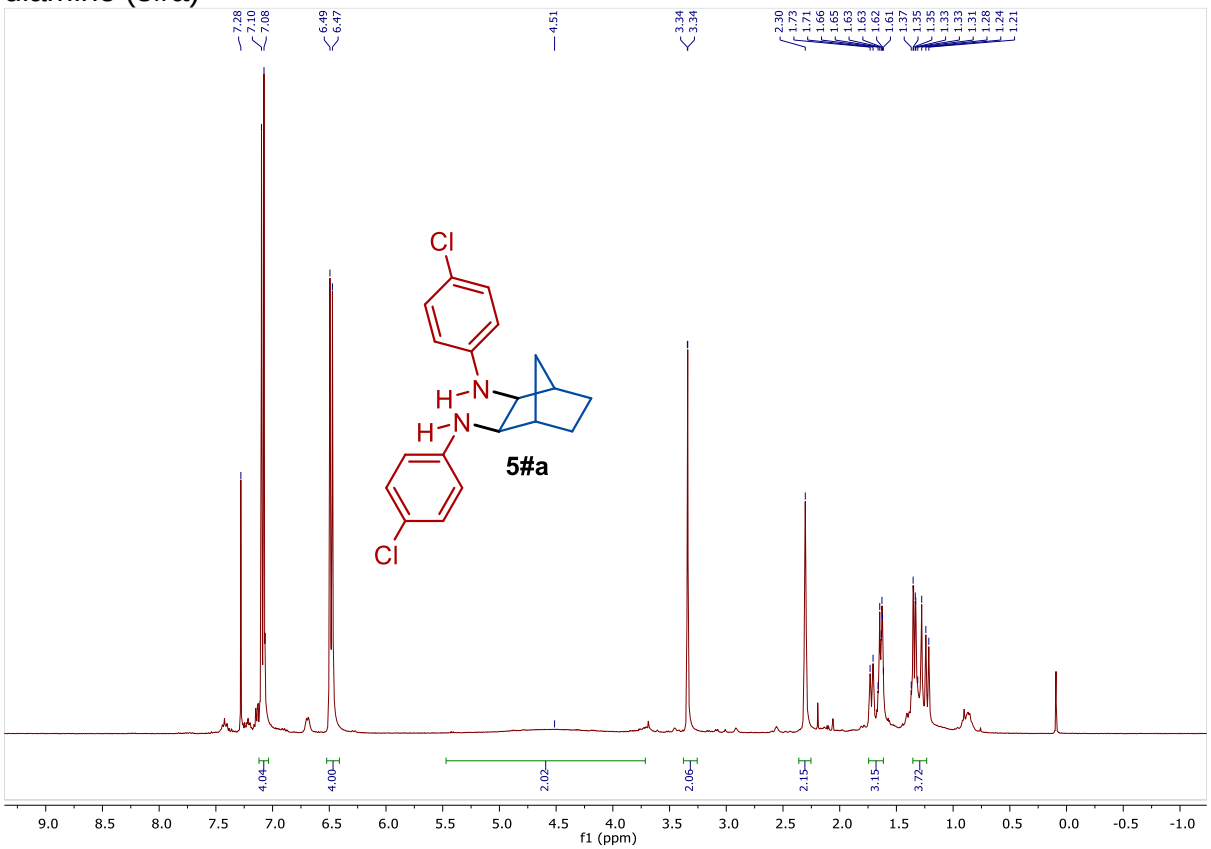
DEPT of N-(2-(1,2-bis((4-chlorophenyl)amino)ethyl)phenyl)-4-methylbenzene-sulfonamide (**7**)



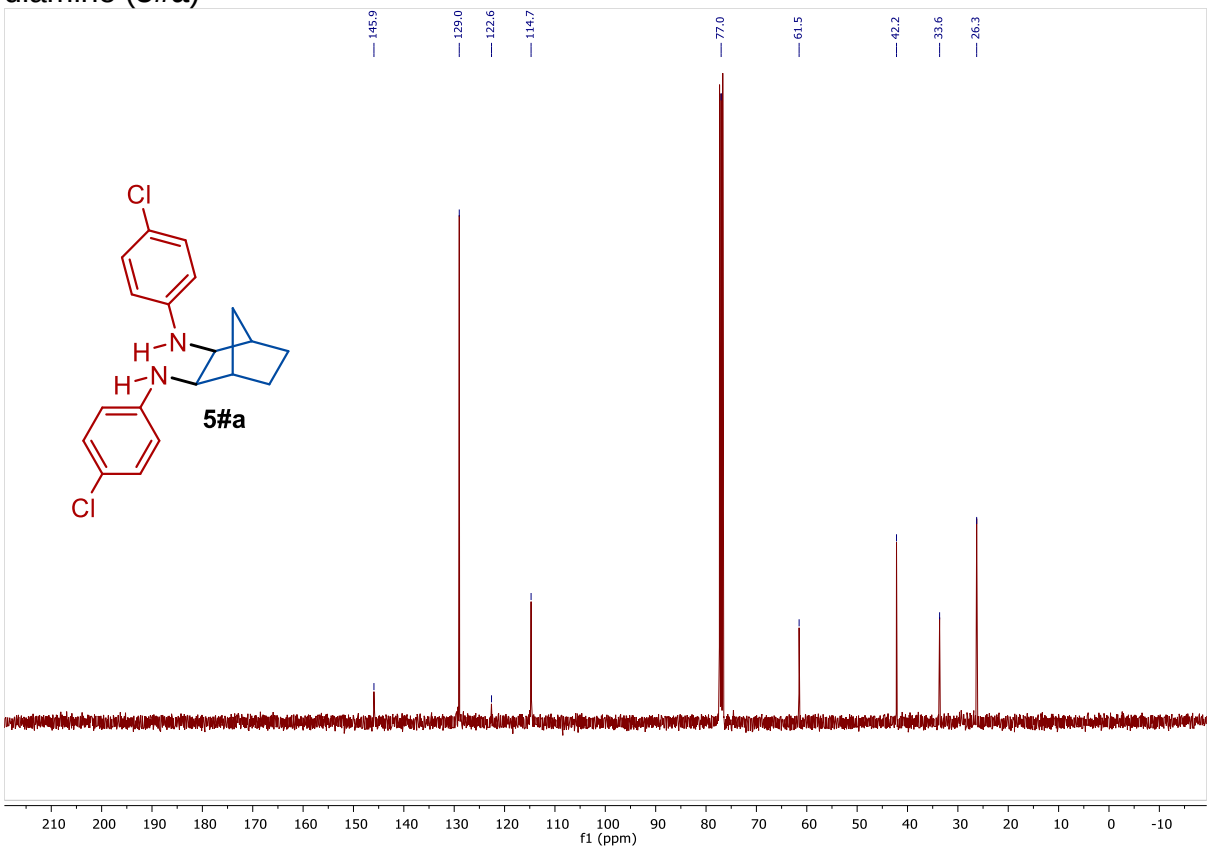
HSQC of N-(2-(1,2-bis((4-chlorophenyl)amino)ethyl)phenyl)-4-methylbenzene-sulfonamide (**7**)



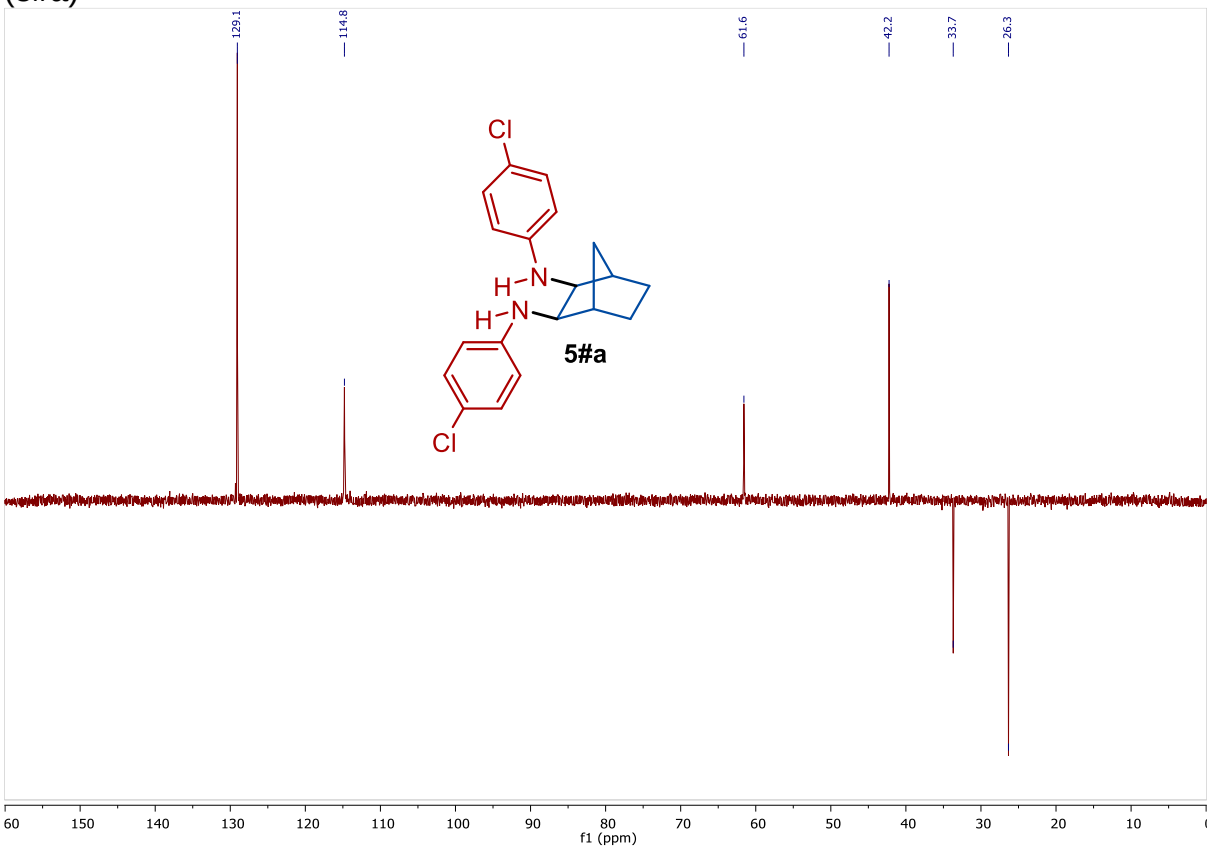
^{1}H NMR of (1R,2S,3R,4S)-N2,N3-bis(4-chlorophenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#a**)



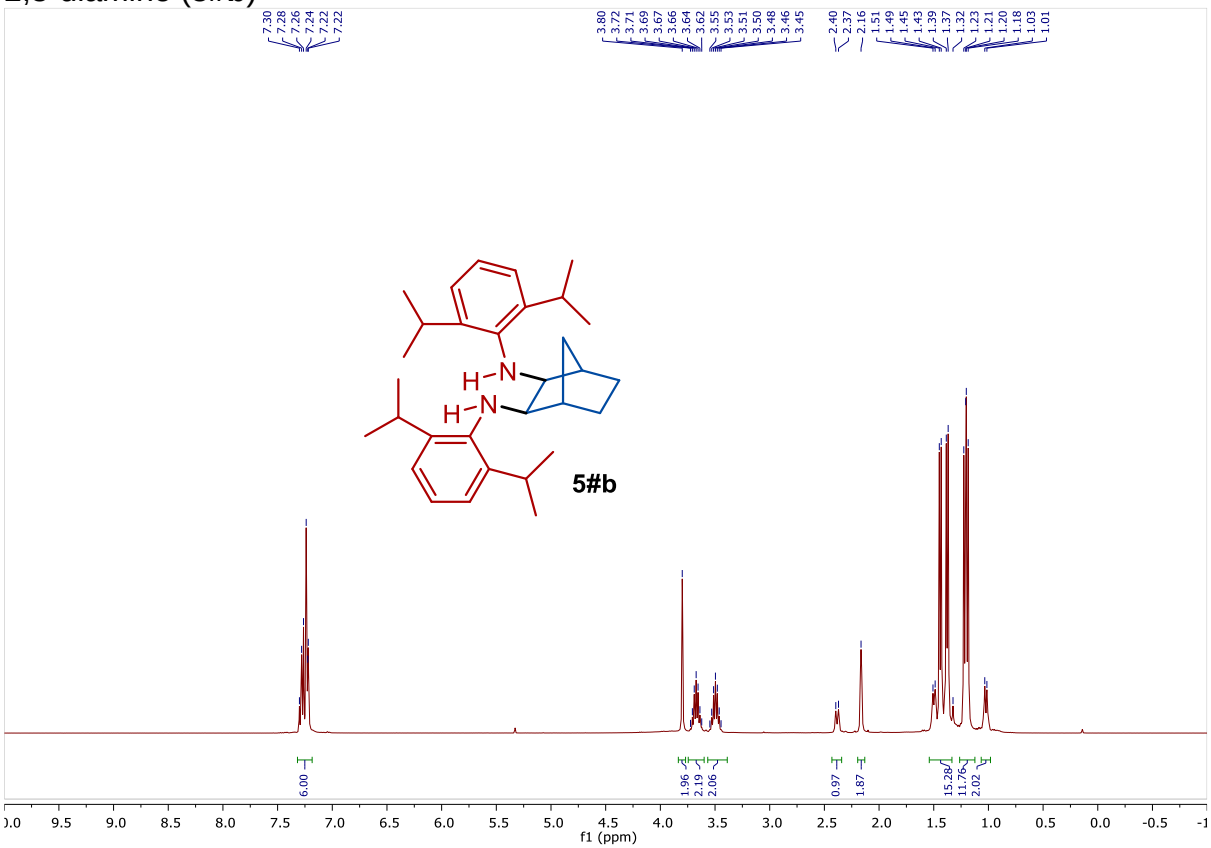
^{13}C NMR of (1R,2S,3R,4S)-N2,N3-bis(4-chlorophenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#a**)



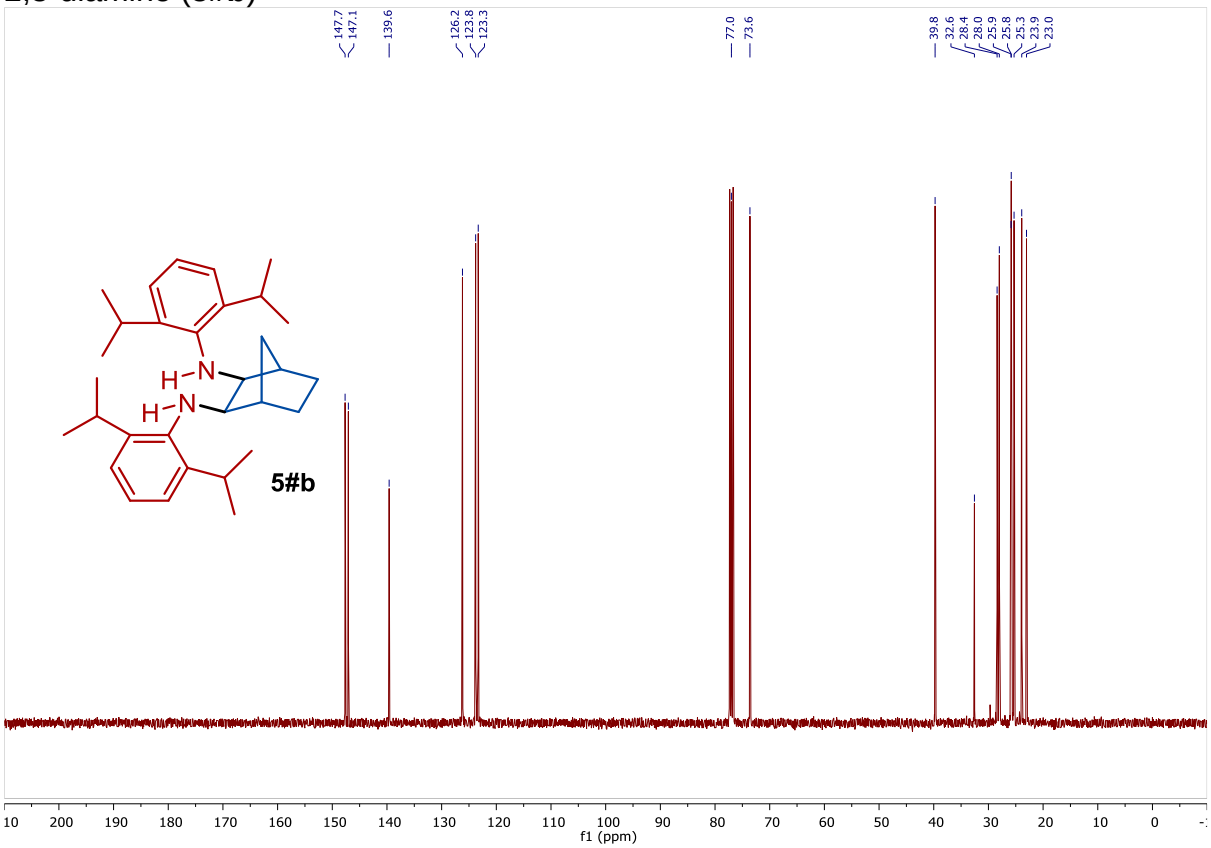
DEPT of (1R,2S,3R,4S)-N2,N3-bis(4-chlorophenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#a**)



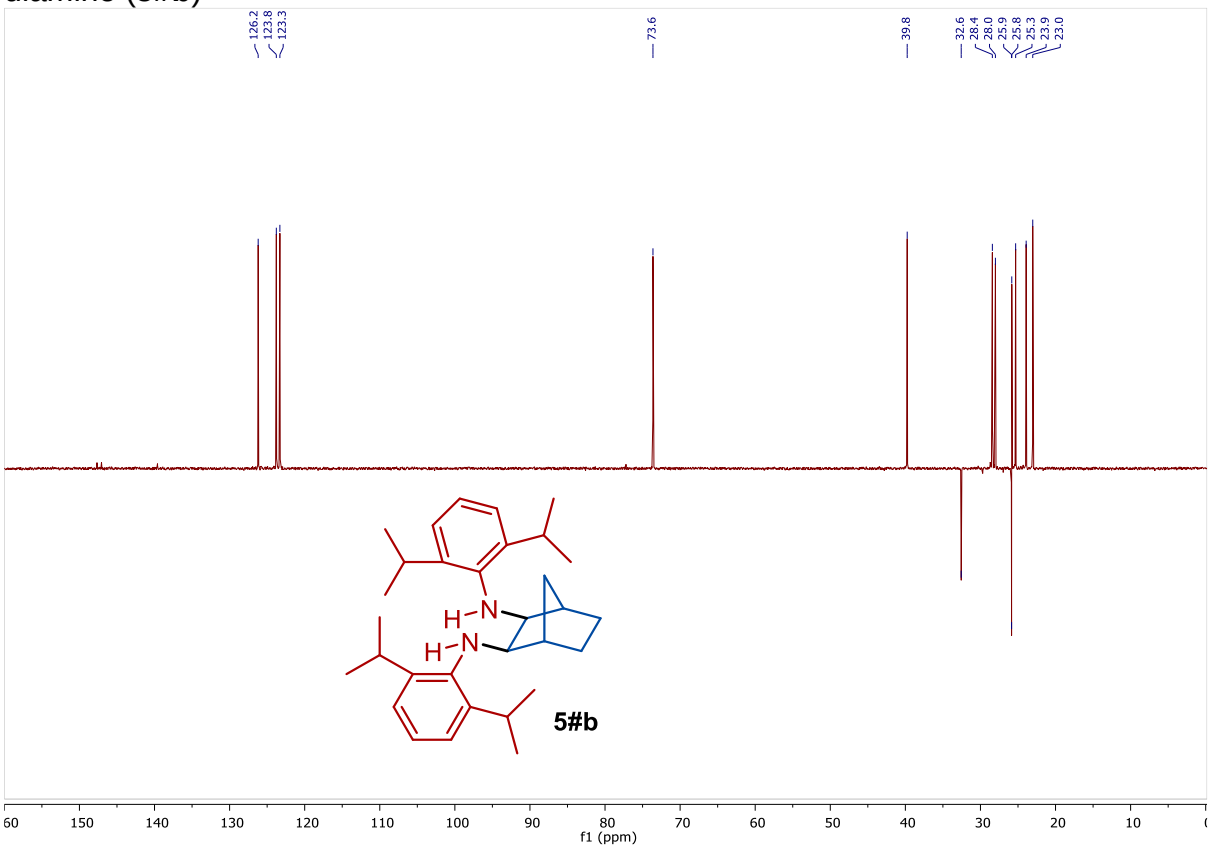
^{1}H NMR of (1R,2S,3R,4S)-N2,N3-bis(2,6-diisopropylphenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#b**)



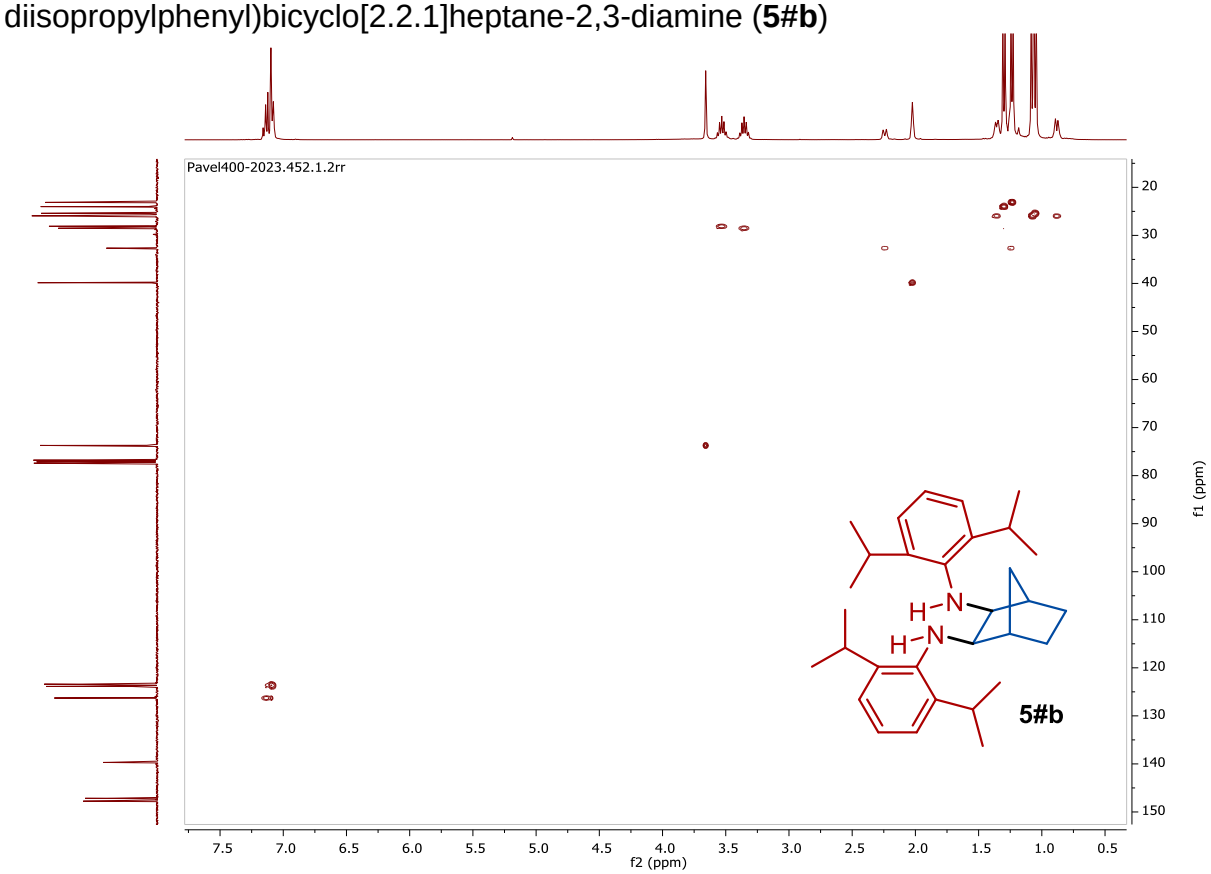
^{13}C NMR of (1R,2S,3R,4S)-N2,N3-bis(2,6-diisopropylphenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#b**)



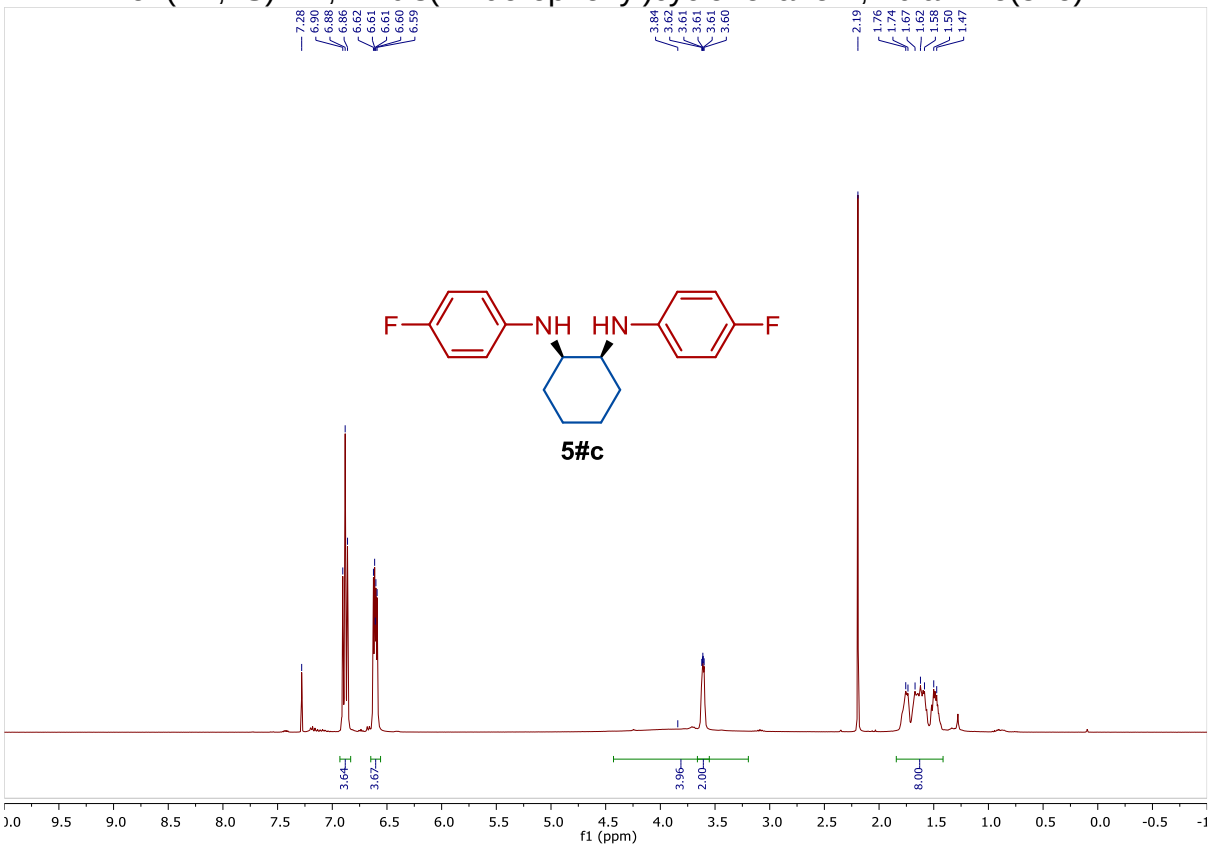
DEPT of (1R,2S,3R,4S)-N2,N3-bis(2,6-diisopropylphenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#b**)



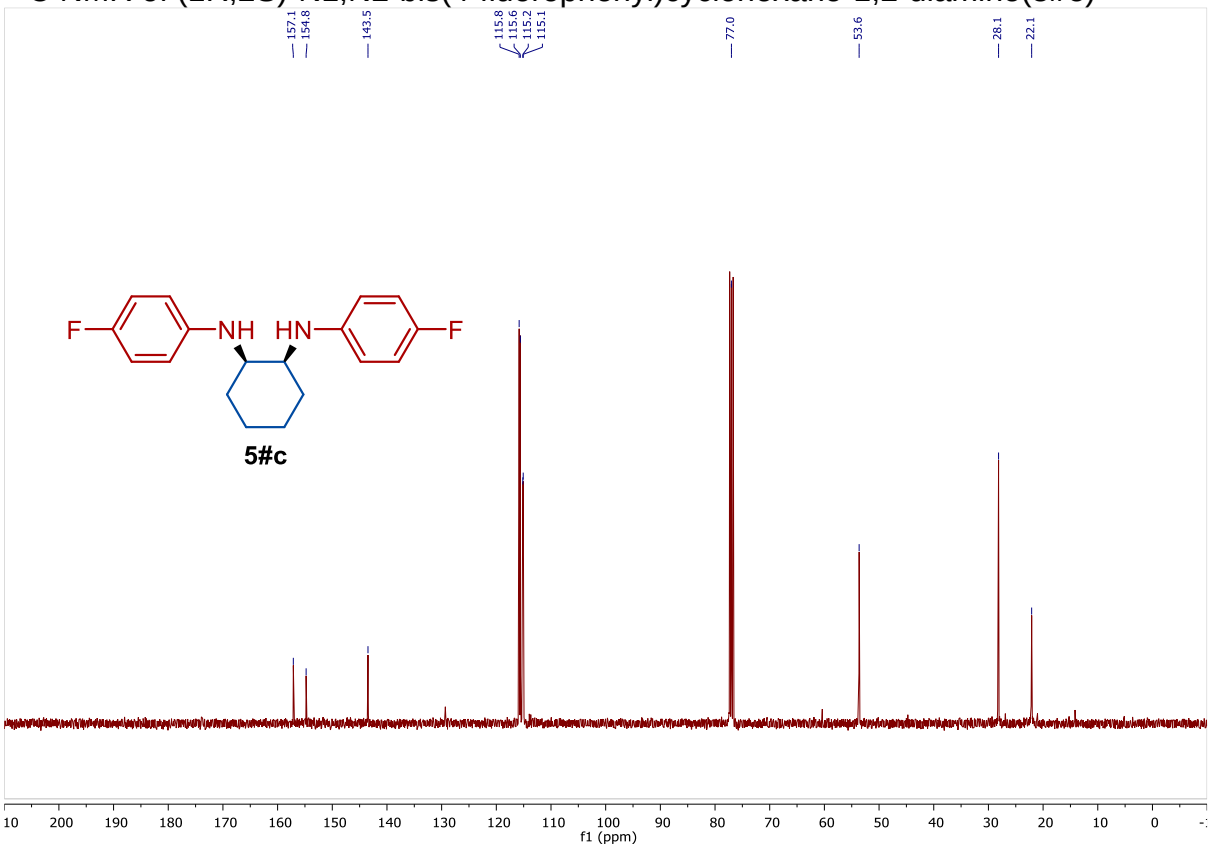
HSQC NMR of (1R,2S,3R,4S)-N2,N3-bis(2,6-diisopropylphenyl)bicyclo[2.2.1]heptane-2,3-diamine (**5#b**)



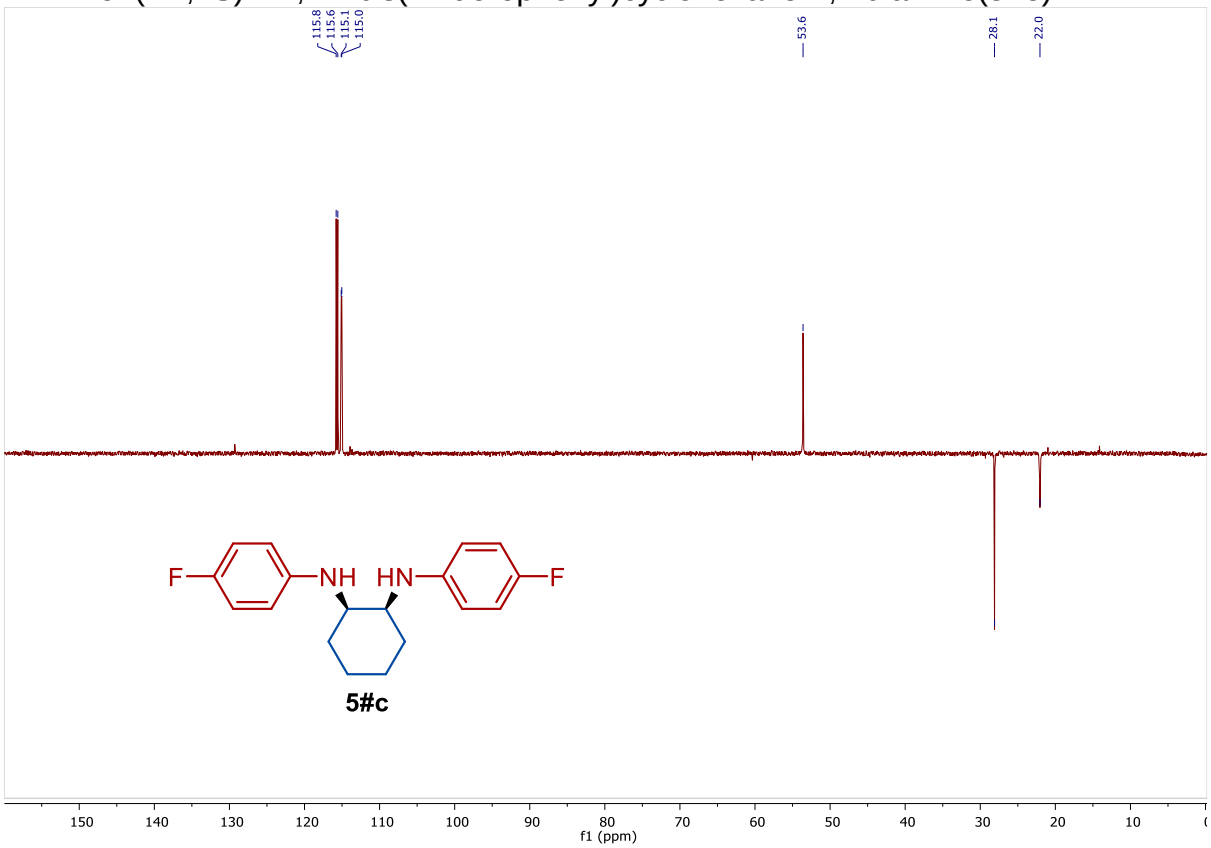
^{1}H NMR of (1R,2S)-N1,N2-bis(4-fluorophenyl)cyclohexane-1,2-diamine(**5#c**)



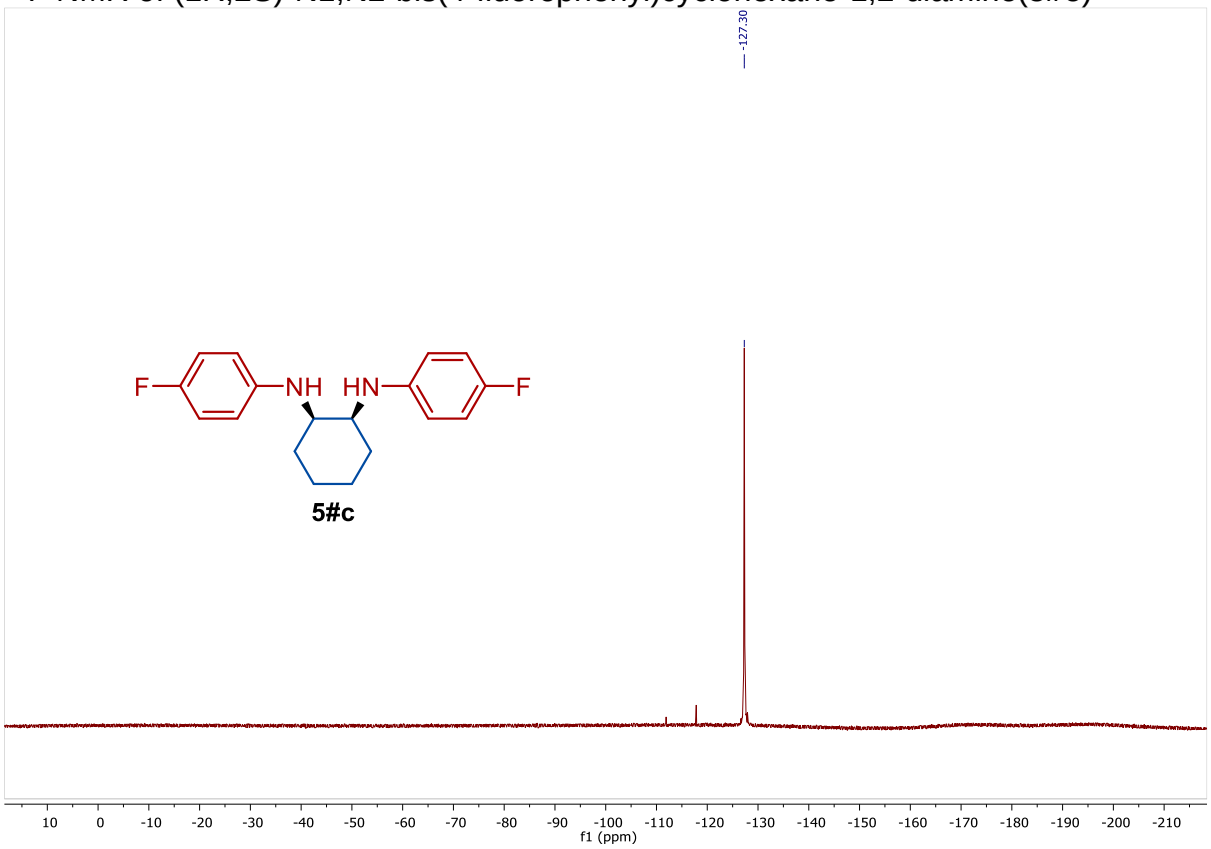
^{13}C NMR of (1R,2S)-N1,N2-bis(4-fluorophenyl)cyclohexane-1,2-diamine(**5#c**)



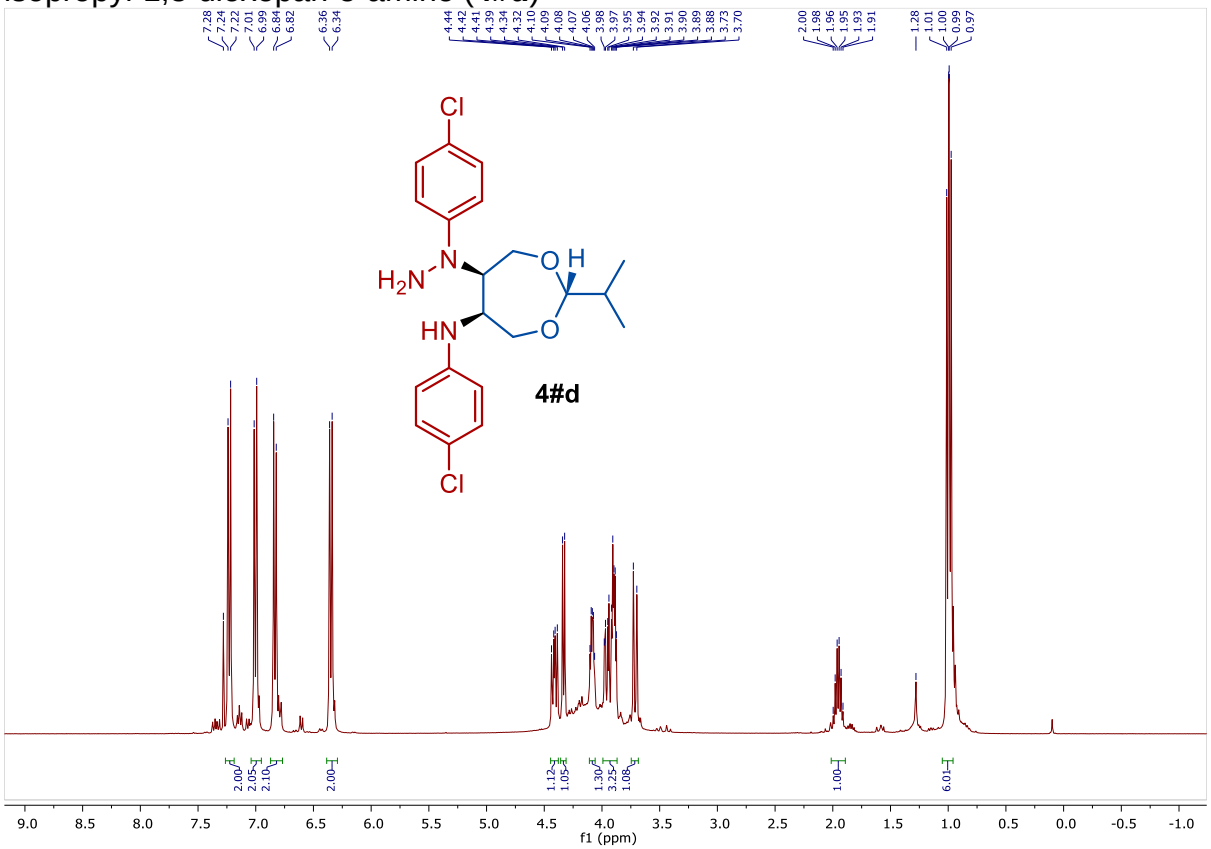
DEPT of (1R,2S)-N1,N2-bis(4-fluorophenyl)cyclohexane-1,2-diamine(**5#c**)



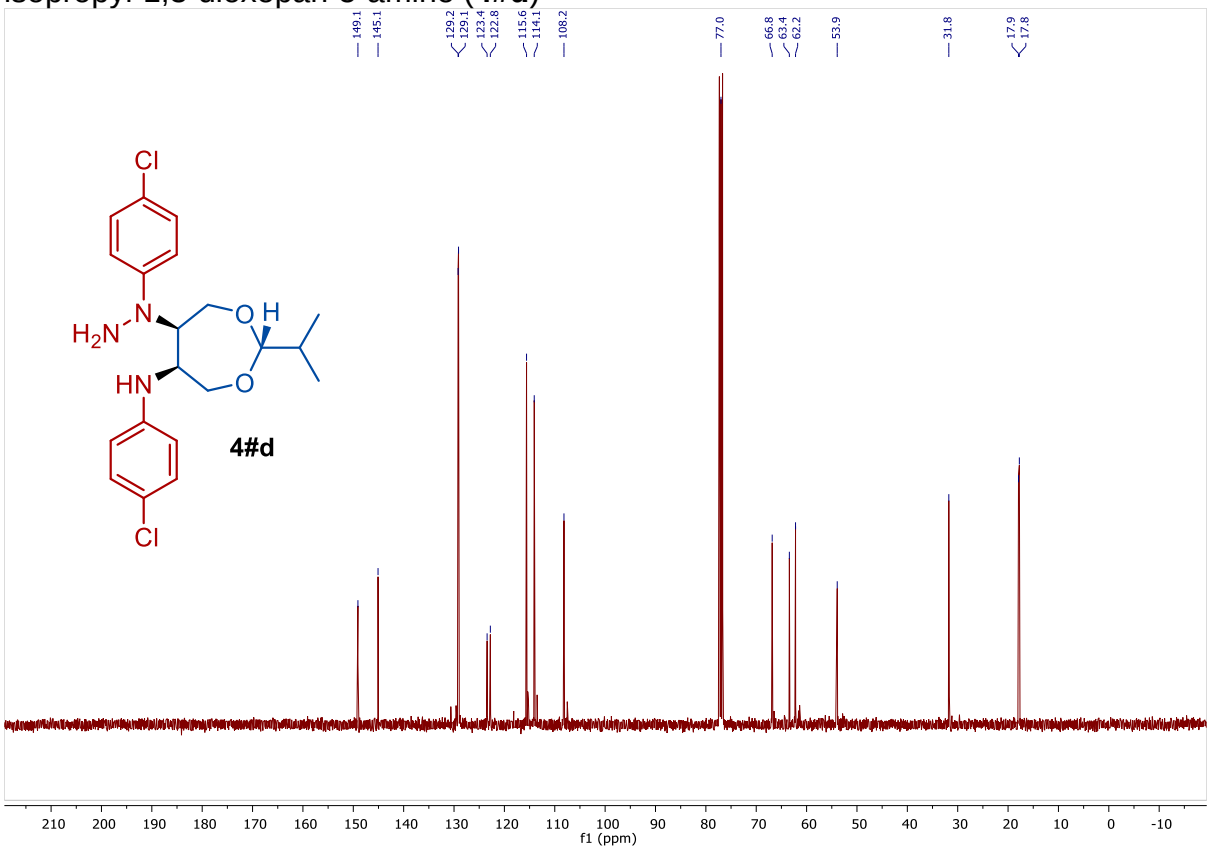
^{19}F NMR of (1R,2S)-N1,N2-bis(4-fluorophenyl)cyclohexane-1,2-diamine(**5#c**)



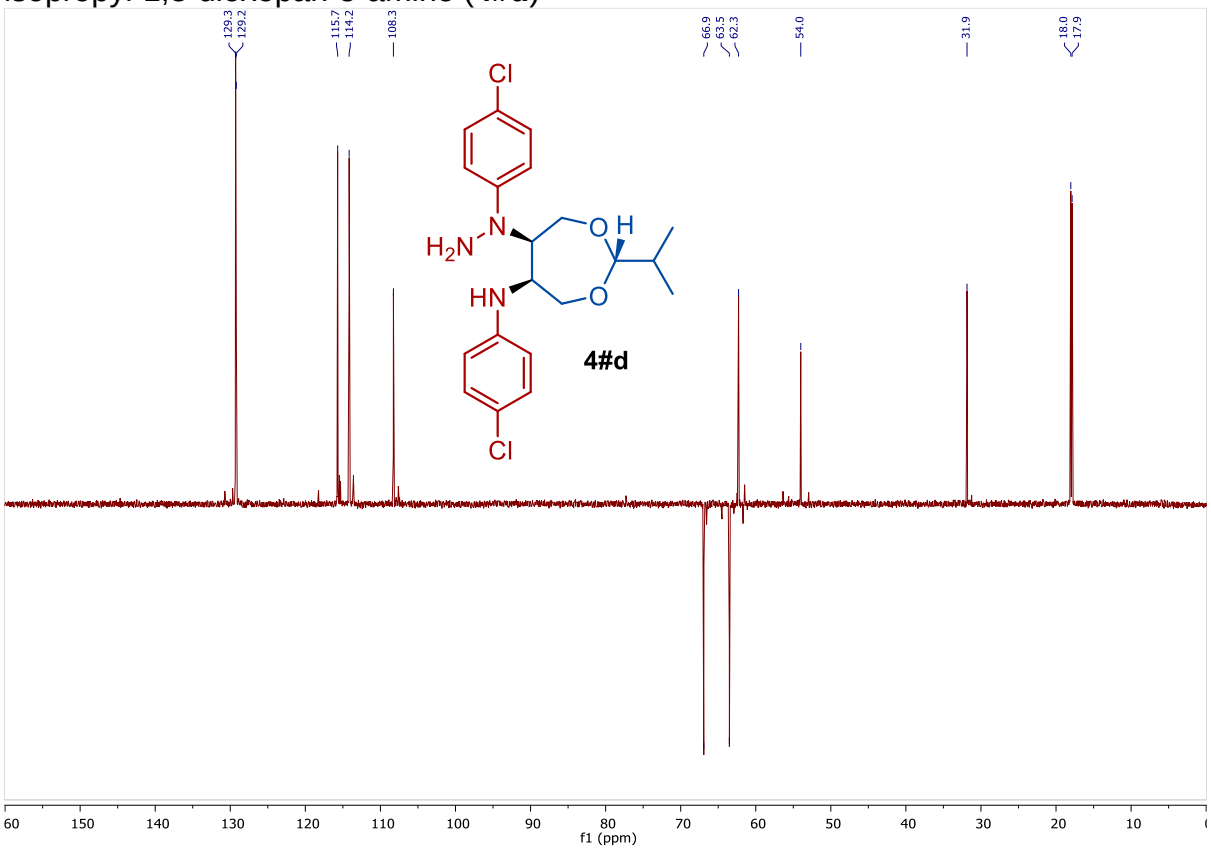
^{1}H NMR of (2RS,5SR,6RS)-N-(4-chlorophenyl)-6-(1-(4-chlorophenyl)hydrazinyl)-2-isopropyl-1,3-dioxepan-5-amine (**4#d**)



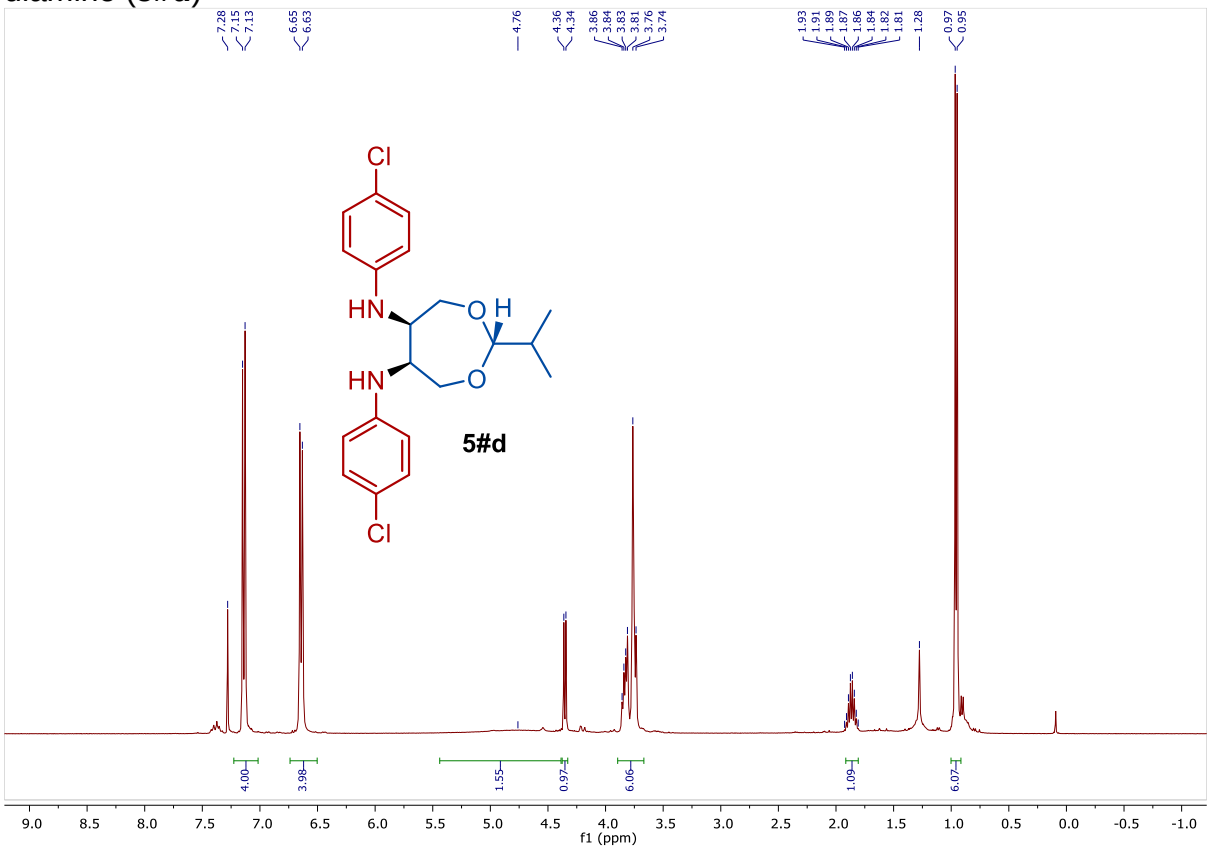
^{13}C NMR of (2RS,5SR,6RS)-N-(4-chlorophenyl)-6-(1-(4-chlorophenyl)hydrazinyl)-2-isopropyl-1,3-dioxepan-5-amine (**4#d**)



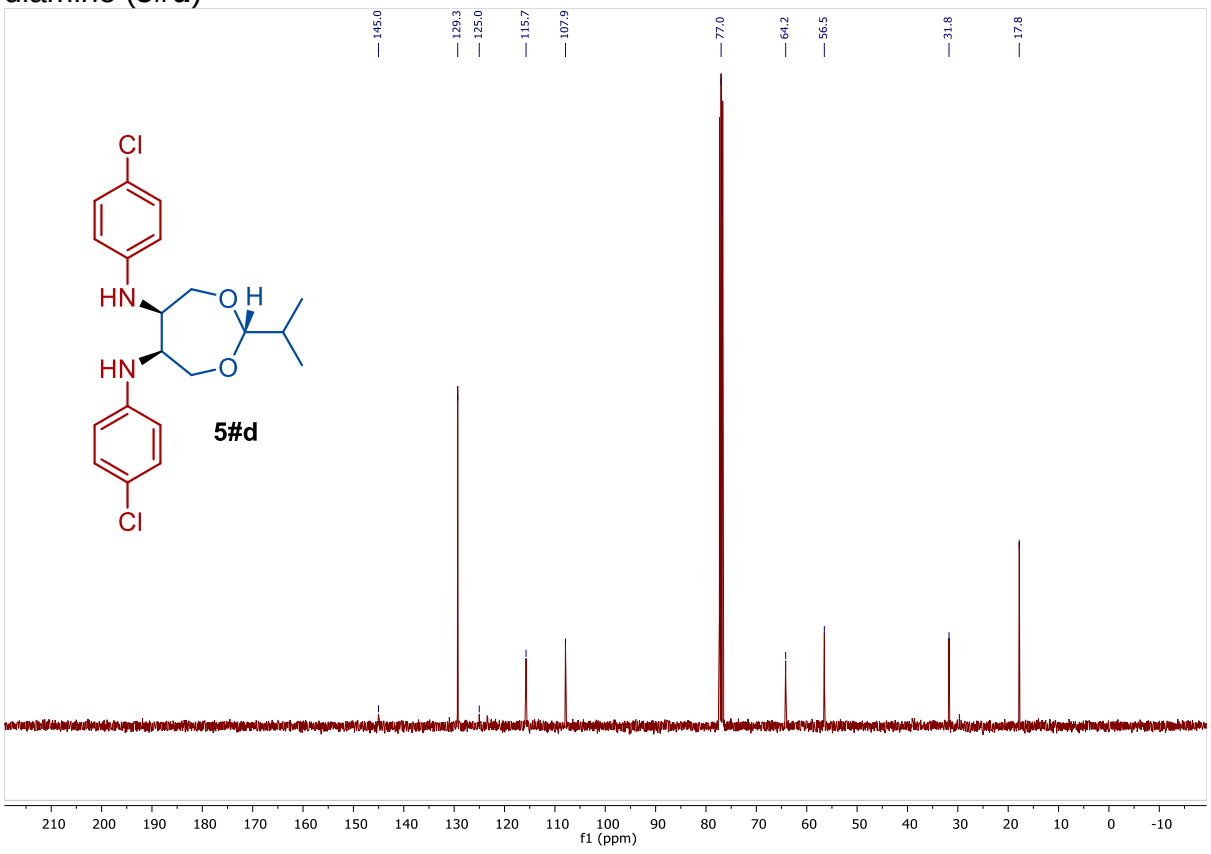
DEPT of (2RS,5SR,6RS)-N-(4-chlorophenyl)-6-(1-(4-chlorophenyl)hydrazinyl)-2-isopropyl-1,3-dioxepan-5-amine (**4#d**)



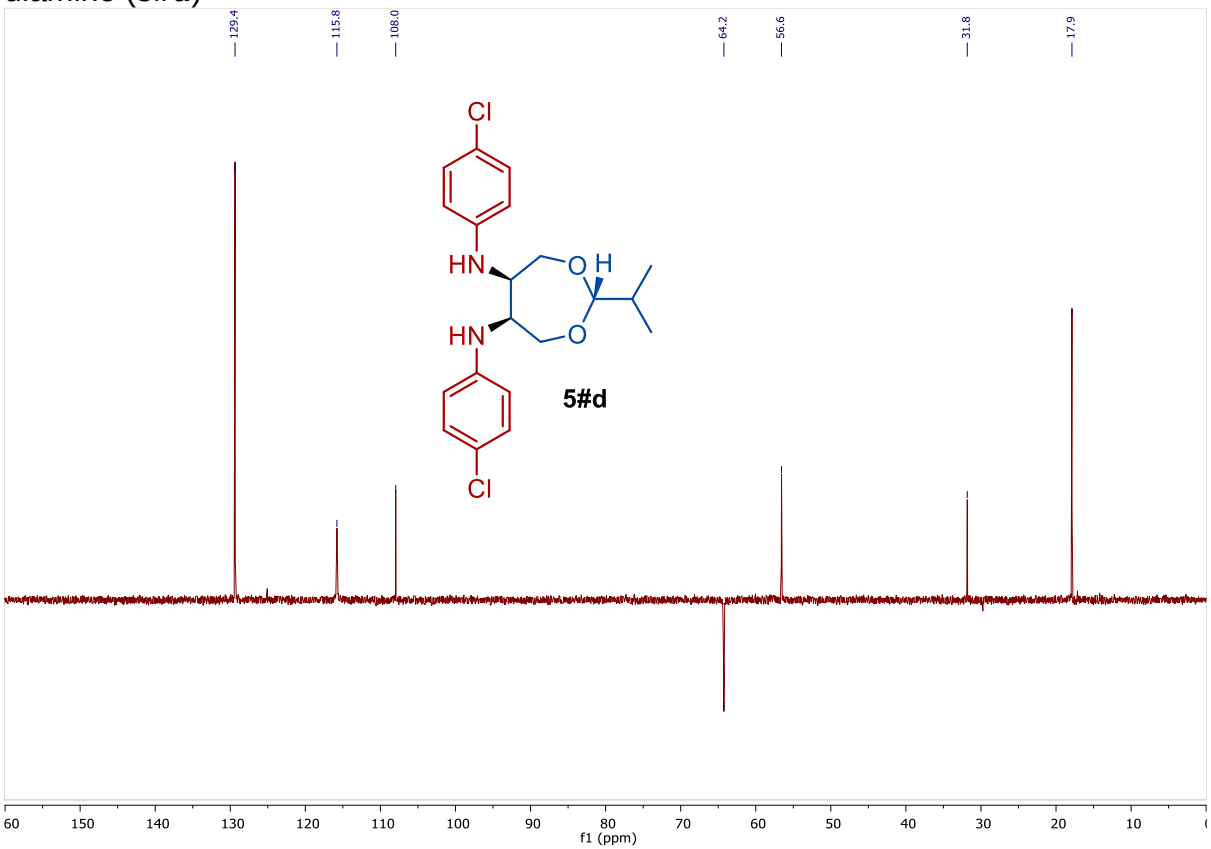
^{1}H NMR of (2r,5R,6S)-N5,N6-bis(4-chlorophenyl)-2-isopropyl-1,3-dioxepane-5,6-diamine (**5#d**)



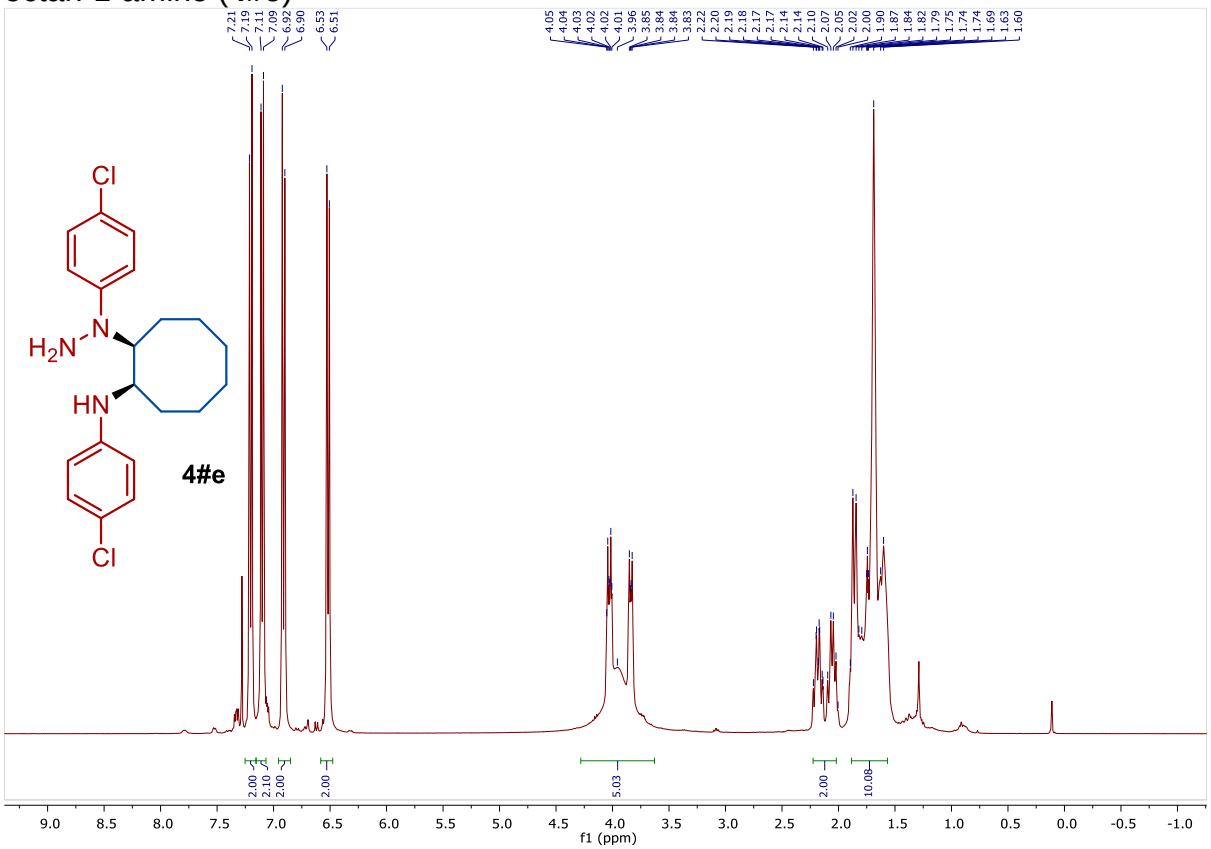
^{13}C NMR of (2r,5R,6S)-N5,N6-bis(4-chlorophenyl)-2-isopropyl-1,3-dioxepane-5,6-diamine (**5#d**)



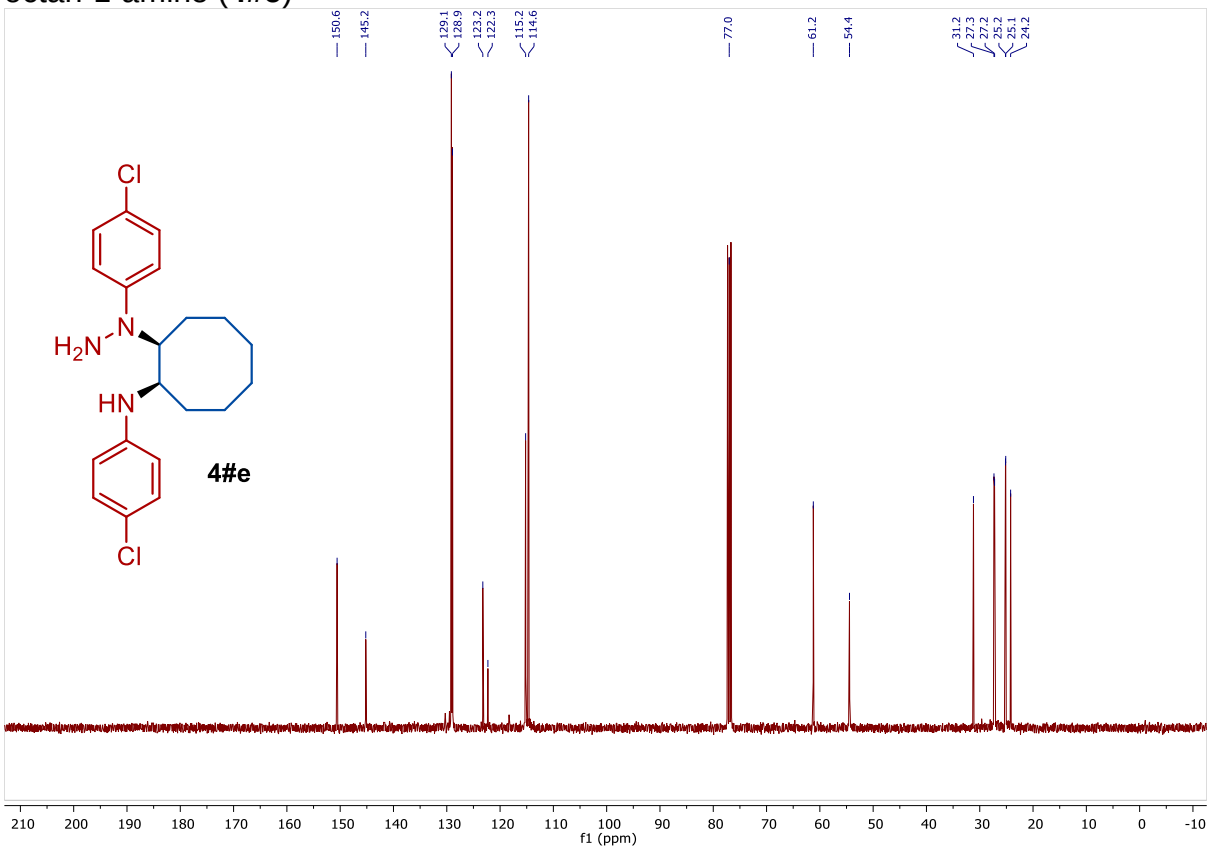
DEPT of (2r,5R,6S)-N5,N6-bis(4-chlorophenyl)-2-isopropyl-1,3-dioxepane-5,6-diamine (**5#d**)



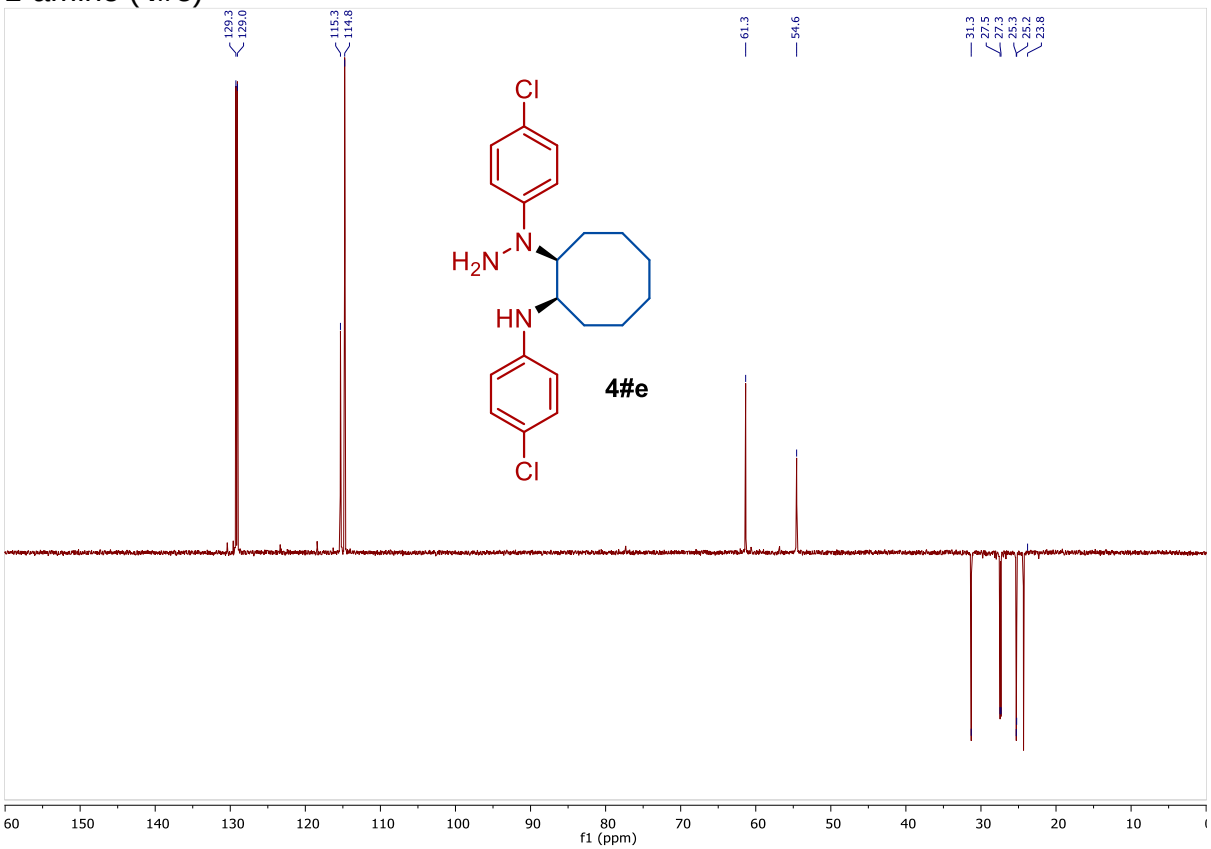
^{1}H NMR of (1RS,2SR)-N-(4-chlorophenyl)-2-(1-(4-chlorophenyl)hydrazinyl)cyclo-octan-1-amine (**4#e**)



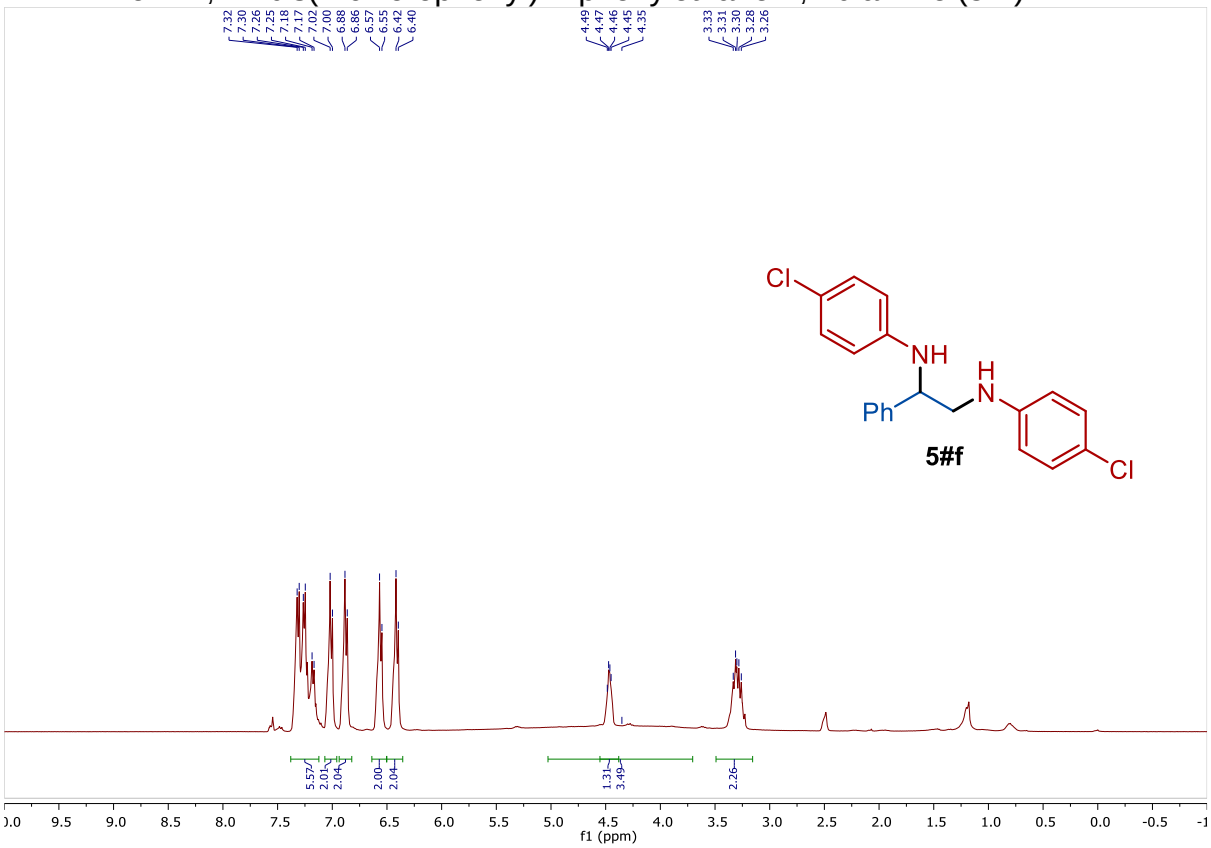
^{13}C NMR of (1RS,2SR)-N-(4-chlorophenyl)-2-(1-(4-chlorophenyl)hydrazinyl)cyclo-octan-1-amine (**4#e**)



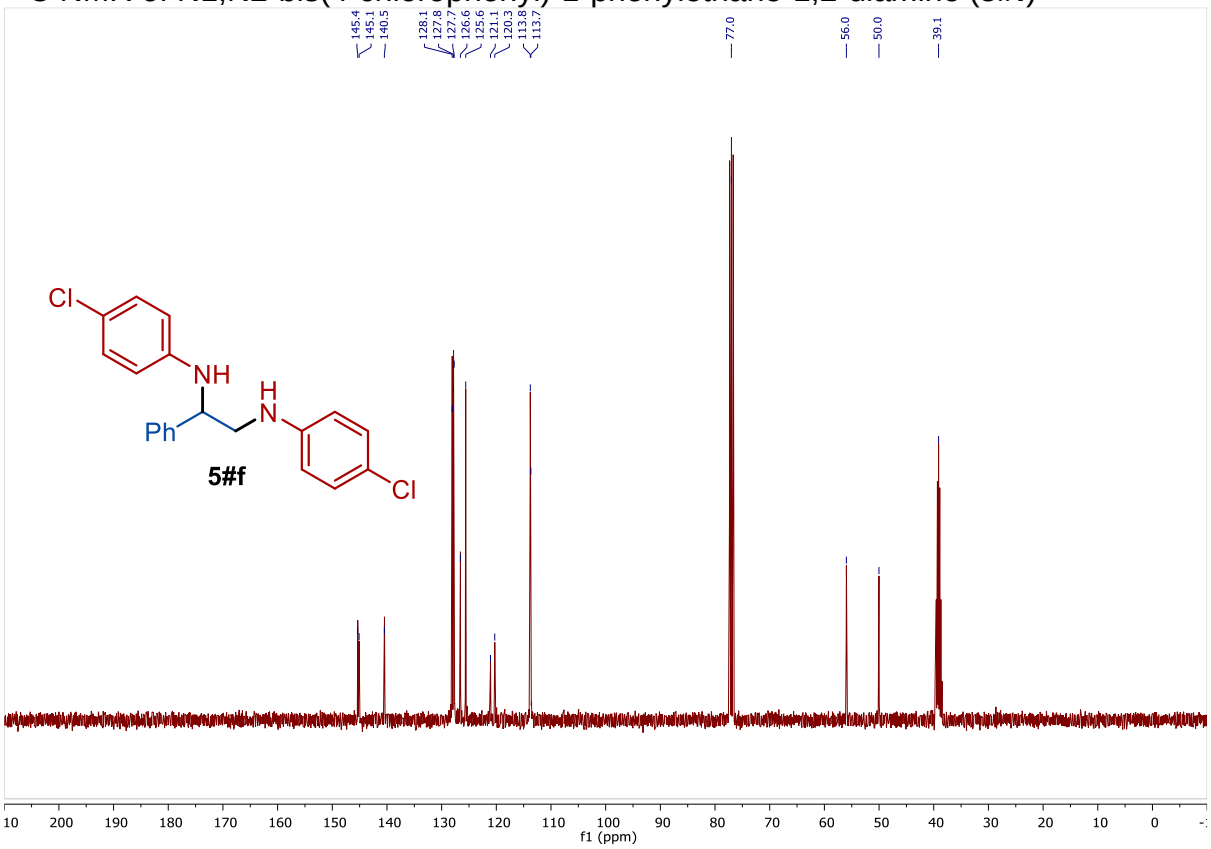
DEPT of (1RS,2SR)-N-(4-chlorophenyl)-2-(1-(4-chlorophenyl)hydrazinyl)cyclo-octan-1-amine (**4#e**)



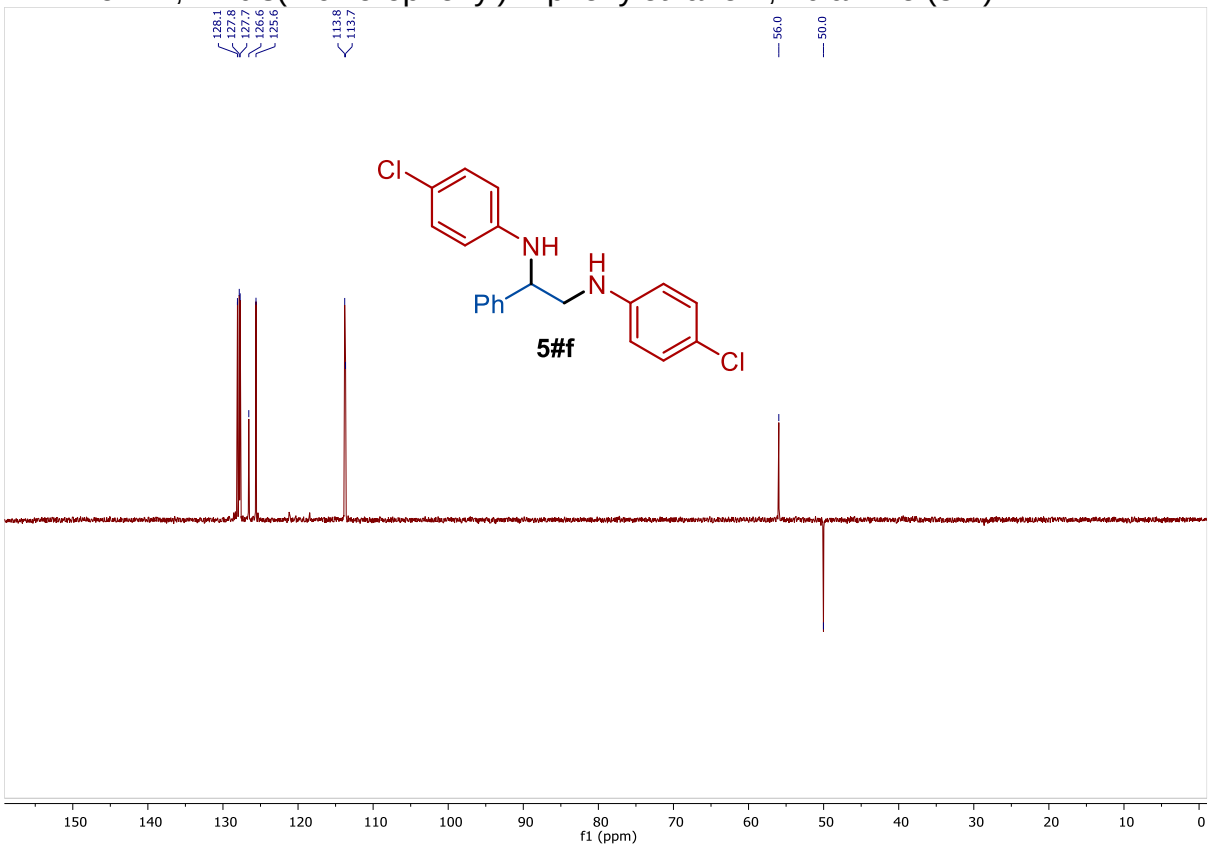
^{1}H NMR of N1,N2-bis(4-chlorophenyl)-1-phenylethane-1,2-diamine (**5#f**)



^{13}C NMR of N1,N2-bis(4-chlorophenyl)-1-phenylethane-1,2-diamine (**5#f**)



DEPT of N1,N2-bis(4-chlorophenyl)-1-phenylethane-1,2-diamine (**5#f**)



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