# Cyclization of substitued 2-(2-fluorophenylazo)azines to azino[1,2-*c*]benzo[*d*][1,2,4]triazinium derivatives

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## General methods and synthetic procedures

**Table of Content**:

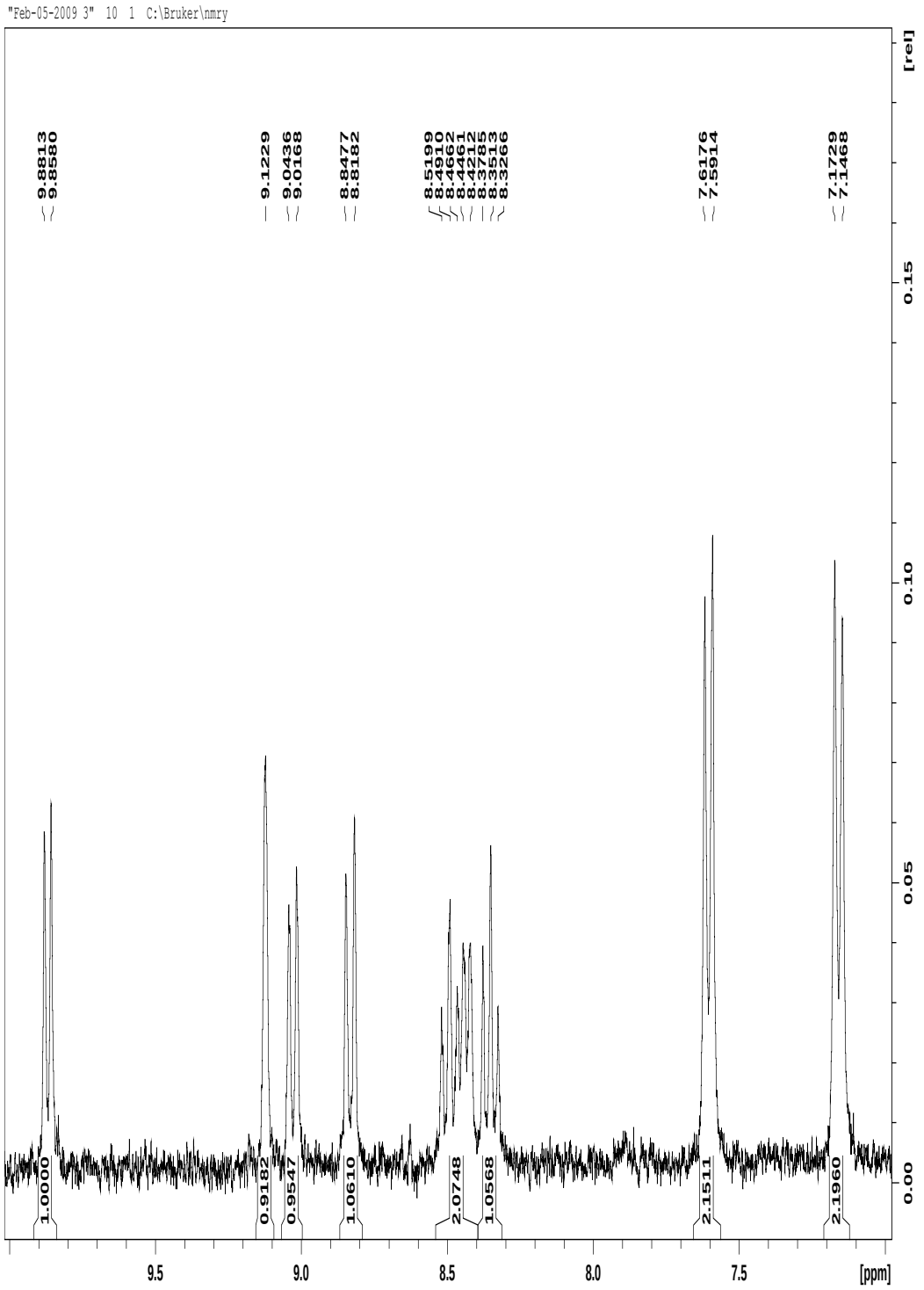
## 1. Additional synthetic procedures

**3-Amino-4-fluorobenzoic acid** [1]. Following a literature procedure [2], 4-fluoro-3-nitrobenzoic acid (1.0 g, 5.4 mmol) was reduced with hydrogen in the presence of Pd/C (60 mg, 10% on charcoal) in EtOH (10 ml) over 24 h. The reaction mixture was passed through Celite, the filtrate was evaporated, and the residue was purified on a silica gel plug (EtOAc) to give 0.75 g (90% yield) of 3-amino-4-fluorobenzoic acid as a white solid: $^1$H NMR (300 MHz, $CD_3CN$) δ 4.40 (bs, 1H), 7.05 (dd, $J_1$ = 10.8 Hz, $J_2$ = 8.6 Hz, 1H), 7.26–7.35 (m, 1H), 7.46 (dd, $J_1$ = 8.8 Hz, $J_2$ = 1.7 Hz, 1H).

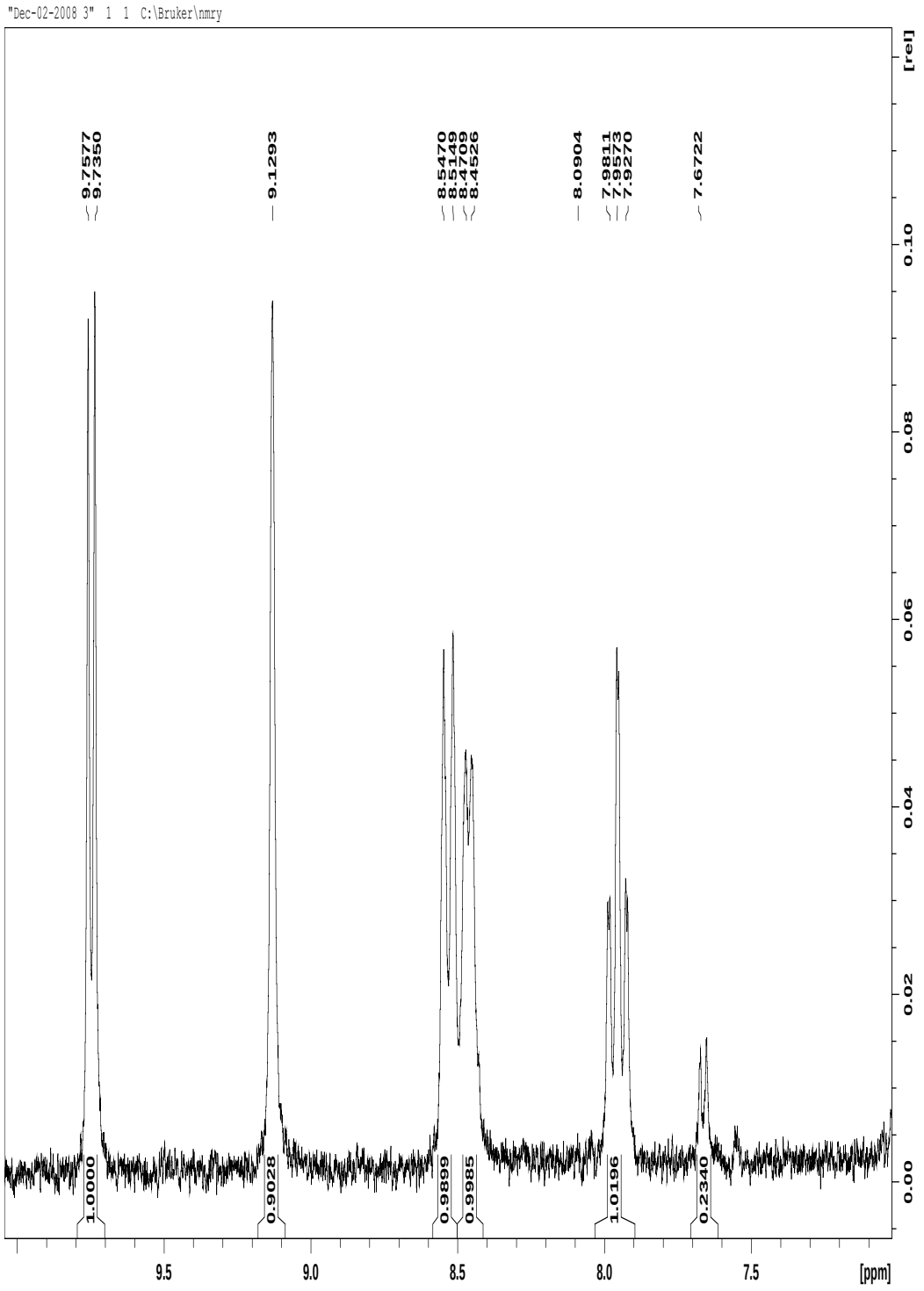
**3-Amino-4-fluorobenzyl alcohol (9e)** [3]. Following literature procedure [3] a solution of 3-amino-4-fluorobenzoic acid (4.0 g, 26.3 mmol) in dry THF (20 ml) was treated with 1 M solution of $BH_3$ in THF (53 mmol, 53 mL) at 0 °C. The reaction mixture was stirred at rt for 24 h, MeOH (10 mL) was slowly added, and stirred for 15 min, the solvents were evaporated, and the residue was purified on a silica gel plug ($CH_2Cl_2$/ EtOAc, 1:1) to give 3.47 g (94% yield) of alcohol **9e** as a white solid: mp 68–70 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 3.74 (bs, 2H), 4.56 (s, 2H), 6.62–6.70 (m, 1H), 6.79 (d, $J$ = 8.6 Hz, 1H), 6.95 (dd, $J_1$ = 10.7 Hz, $J_2$ = 8.4 Hz, 1H).

## 2. $^{1}$H NMR Spectra for selected compounds.

a) recrystallized tosylate of **1b** in $CD_3CN$.



b) Crude reaction mixture of **4d** in the presence of $CaCl_2$ in $CD_3CN$.



## 3. Selected interatomic distances

**Table S1**: Selected interatomic distanes (Å) for species involved in the formation of triazinium from azoazines.[a]

| | Azopyridines | | | | *cis*-azoazine | | TS | | cycloadduct | |
|---|---|---|---|---|---|---|---|---|---|---|
| | R | X | Y | Z | C–F | C···N | C–F | C···N | C–F | C–N |
| **a** | H | H | H | H | 1.351 | 3.151 | 1.375 | 1.916 | 1.446 | 1.458 |
| **b** | Me | H | H | H | 1.351 | 3.149 | 1.375 | 1.918 | 1.448 | 1.457 |
| **c** | Me | F | H | H | 1.347 | 3.101 | 1.373 | 1.928 | 1.447 | 1.459 |
| **d** | Me | F | F | H | 1.346 | 3.160 | 1.371 | 1.930 | 1.445 | 1.461 |
| **f** | CN | H | H | H | 1.351 | 3.166 | 1.371 | 1.917 | 1.439 | 1.456 |
| **g** | OMe | H | H | H | 1.351 | 3.146 | 1.376 | 1.922 | 1.449 | 1.457 |
| **h** | Me | H | H | OMe | 1.353 | 3.158 | 1.379 | 1.900 | 1.452 | 1.449 |
| **i** | Me | H | H | CN | 1.345 | 3.116 | 1.370 | 1.927 | 1.441 | 1.462 |
| azopyrazine | | | | | 1.351 | 3.161 | 1.372 | 1.910 | 1.441 | 1.453 |
| azopyrimidine | | | | | 1.349 | 3.218 | 1.373 | 1.914 | 1.438 | 1.456 |

[a] B3LYP/6-311G(2d,p) level calculations.

## 4. Archive for selected DFT calculations.

**1c**


1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-311G(2d,p)\C12H9F1N3(1+)\PIOTR\29-Apr-2
013\0\\#P B3LYP/6-311G(2d,p) FOpt(tight) fcheck Geom(nodistance, noang
le) #P freq(noraman, ReadIso)\\9-F benzotriazinium-4-Me cation, Cs\\1,
1\C,0.0178059915,0.,0.0073685734\C,0.0040713352,0.,1.4073209964\C,1.20
4966345,0.,2.0700132519\C,2.413821106,0.,1.3474791116\C,2.3893500442,0
.,-0.0632379945\C,1.1780623753,0.,-0.7457583291\N,3.5803328104,0.,2.07
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\C,6.0408565658,0.,-0.4825917856\C,6.2075262131,0.,-1.8529218683\C,5.0
299434563,0.,-2.6361893706\C,3.7958427135,0.,-2.0605081187\N,3.6485238
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.,-0.6370054562\H,1.2652785747,0.,3.1504486635\H,-0.9443994001,0.,1.92
77226719\H,1.0835274257,0.,-1.8210387895\H,6.877220449,0.,0.2035758035
\H,5.0895126131,0.,-3.7170028497\H,2.8926399188,0.,-2.6467141489\H,7.6
71482959,0.8784703673,-3.1396793226\H,8.3574864436,0.,-1.7625321239\H,
7.671482959,-0.8784703673,-3.1396793226\\Version=EM64L-G09RevC.01\Stat
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0.,-1.69817\Quadrupole=15.198246,-15.8407133,0.6424672,0.,-17.2322961,

0.\PG=CS [SG(C12H7F1N3),X(H2)]\\

**4c-Z**

1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-311G(2d,p)\C12H9F2N3\PIOTR\29-Apr-2013\
0\\#P B3LYP/6-311G(2d,p) FOpt(tight) fcheck Geom(nodistance, noangle)
#P freq(noraman, ReadIso)\\2,4-F2 azopyridine-4-Me cis, C1\\0,1\C,-0.0
061411562,-0.0000713278,0.0462928849\C,-0.0151048614,-0.1225055246,1.4
261272362\C,1.1988148844,-0.1346708017,2.0940043743\C,2.4075272993,0.0
351879764,1.4163129272\C,2.3583792644,0.1328791056,0.025945836\C,1.168
9827465,0.1126882611,-0.6769437292\N,3.6041758817,-0.1322454407,2.1829
299587\N,4.6143205451,0.5821480854,2.0855604206\C,4.661321178,1.800472
6574,1.3346174794\C,5.8777883923,2.0992033972,0.723716429\C,6.01533624
15,3.3029440582,0.0444275763\C,4.9213729183,4.1717936506,0.0702746209\
C,3.7687448473,3.7990658064,0.7479965418\N,3.6209323194,2.6274439319,1
.3674885553\C,7.2828059833,3.6590486179,-0.6839390607\F,3.5065620503,0
.225551025,-0.6724427806\F,-1.1738726135,-0.010532899,-0.6229832234\H,
1.2357866506,-0.2646807008,3.1680701448\H,-0.9549047369,-0.2270911053,
1.9510959522\H,1.1629288106,0.1839643557,-1.7558176618\H,6.6887679206,
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2.921390921,4.4761256277,0.8005297263\H,7.5436021739,4.7085525581,-0.5
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237568\PG=C01 [X(C12H9F2N3)]\\

**10c-TS**

1\1\GINC-OCTOPUS\FTS\RB3LYP\6-311G(2d,p)\C12H9F2N3\PIOTR\29-Apr-2013\0
\\#P B3LYP/6-311G(2d,p) FOpt(QST3) fcheck Geom(nodistance, noangle) #P
freq(noraman, ReadIso)\\2,4-F2 azopyridine-4-Me cis, C1\\0,1\C,0.0175
479482,-0.0055450549,0.0162540436\C,-0.0007866297,-0.0284516267,1.4176
455102\C,1.2119732447,-0.029317196,2.0672326776\C,2.423429207,0.044320
9145,1.3596510903\C,2.4071275507,-0.0272087887,-0.0738519271\C,1.16153
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**10c**

1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-311G(2d,p)\C12H9F2N3\PIOTR\29-Apr-2013\
0\\#P B3LYP/6-311G(2d,p) FOpt(tight) fcheck Geom(nodistance, noangle)
#P freq(noraman, ReadIso)\\9-F benzotriazinium-4-Me adduct, C1\\0,1\C,
0.0219240382,0.0036762265,0.016301023\C,0.0062378724,-0.0083300212,1.4
498524641\C,1.1896293728,-0.0085518562,2.1027821268\C,2.4282382739,0.0

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## 13-Z

1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-311G(2d,p)\C14H12F1N1\PIOTR\23-Jun-2013\0\\#P B3LYP/6-311G(2d,p) FOpt(tight) fcheck Geom(nodistance, noangle) #P freq(noraman, ReadIso)\\2-F-phenyl-CHCH-pyridine-4-Me cis\\0,1\C,-3.5098202455,1.7253921278,0.638245091\C,-3.7913660006,0.3640736688,0.6778609175\C,-2.9055232292,-0.539950937,0.109454089\C,-1.7058945326,-0.1272006541,-0.4860752454\C,-1.4747000812,1.2482909699,-0.5245989844\C,-2.3462300774,2.1714207271,0.0240331849\C,-0.827292743,-1.1276844441,-1.1125525095\C,0.5049244345,-1.2770059441,-1.0739346691\C,1.5187231755,-0.5454840488,-0.3056475558\C,2.8695566878,-0.7166935118,-0.6351498772\C,3.860623207,-0.0570366766,0.082937339\C,3.4418935651,0.7506690601,1.138563693\C,2.0826571944,0.8544116906,1.4107953682\N,1.1349422105,0.2310046643,0.7197899629\C,5.3168581426,-0.1938760861,-0.2742752726\F,-0.3811005093,1.7182234135,-1.1543238471\H,-4.1971157905,2.4412438603,1.0725627515\H,-3.1287250461,-1.6007127145,0.1357874943\H,-2.1027201648,3.2238448461,-0.0455912282\H,3.1388068248,-1.3675607013,-1.4599878499\H,4.1603109832,1.2871021415,1.7479566738\H,1.7406954984,1.470893089,2.2379268097\H,5.6429153151,0.6462700358,-0.8948362307\H,5.5056304966,-1.1102505842,-0.8353441093\H,5.9452207696,-0.2016736017,0.6183128806\H,-1.36763389,-1.8742185851,-1.689563598\H,0.9099216451,-2.0869185207,-1.6738974554\H,-4.7011258399,0.0078997152,1.1452391773\\Version=EM64L-G09RevC.01\State=1-A\HF=-695.4860054\RMSD=7.353e-09\RMSF=6.996e-07\Dipole=0.5607088,-0.212017,0.0432391\Quadrupole=7.2460054,-1.5827996,-5.6632058,-0.4110655,-1.4895755,4.4245951\PG=C01 [X(C14H12F1N1)]\\@

## 13-Z TS

1\1\GINC-OCTOPUS\FTS\RB3LYP\6-311G(2d,p)\C14H12F1N1\PIOTR\24-Jun-2013\0\\#P B3LYP/6-311G(2d,p) FOpt(QST3) fcheck Geom(nodistance, noangle) #P freq(noraman, ReadIso)\\2-F-phenyl-CHCH-pyridine-4-Me cis\\0,1\C,-2.7754206201,1.4607082771,1.0928189764\C,-3.4193723167,0.3351911971,0.5465818116\C,-2.8368517693,-0.3034452605,-0.5263764964\C,-1.6121235657,0.1219140249,-1.0680610692\C,-0.9917846599,1.3147113226,-0.5499216649\C,-1.6052128327,1.953781518,0.5677575795\C,-0.8871578525,-0.6639902786,-2.0125822161\C,0.4735175604,-0.7001968834,-2.0698410565\C,1.2935226678,-0.1053106674,-1.0525963977\C,2.6170416299,-0.5333175945,-0.8206421517\C,3.3534970961,-0.0496586794,0.2413580255\C,2.7272723578,0.8680913513,1.1068588986\C,1.4324439339,1.2506061613,0.8509672317\N,0.7557011276,0.8108705589,-0.2128587565\C,4.7675765601,-0.4957752419,0.493607926\

F,-0.5485131499,2.2125831954,-1.5220872716\H,-3.2349469917,1.985571544
,1.9236305366\H,-3.3015004202,-1.1858301207,-0.9553102702\H,-1.1813309
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33\H,3.25615174,1.2863807729,1.9541050126\H,0.8999412442,1.9462418104,
1.4903942758\H,5.4465971996,0.3607760573,0.5149699569\H,5.1137505084,-
1.1854255769,-0.2763257752\H,4.8521395057,-0.9970258998,1.4616011999\H
,-1.4496595322,-1.3472452563,-2.6427520223\H,0.9688672039,-1.363787787
7,-2.7667538959\H,-4.3525622166,-0.0188054441,0.9640269187\\Version=EM
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\Dipole=1.3886805,-0.6556405,0.6464334\Quadrupole=4.3771447,-2.7606909
,-1.6164538,0.2111741,0.8234512,6.399751\PG=C01 [X(C14H12F1N1)]\\@

**13-Z-cycloadduct**

1\1\GINC-OCTOPUS\FTS\RB3LYP\6-311G(2d,p)\C14H12F1N1\PIOTR\24-Jun-2013\
0\\#P B3LYP/6-311G(2d,p) FOpt(QST3) fcheck Geom(nodistance, noangle) #
P freq(noraman, ReadIso)\\2-F-phenyl-CHCH-pyridine-4-Me cis\\0,1\C,-2.
7754206201,1.4607082771,1.0928189764\C,-3.4193723167,0.3351911971,0.54
65818116\C,-2.8368517693,-0.3034452605,-0.5263764964\C,-1.6121235657,0
.1219140249,-1.0680610692\C,-0.9917846599,1.3147113226,-0.5499216649\C
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,-1.4496595322,-1.3472452563,-2.6427520223\H,0.9688672039,-1.363787787
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\Dipole=1.3886805,-0.6556405,0.6464334\Quadrupole=4.3771447,-2.7606909
,-1.6164538,0.2111741,0.8234512,6.399751\PG=C01 [X(C14H12F1N1)]\\@

## 4. References

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