SUPPORTING INFORMATION

Discovering mechanistic insights by application of *tandem* ultrafast multidimensional NMR techniques.

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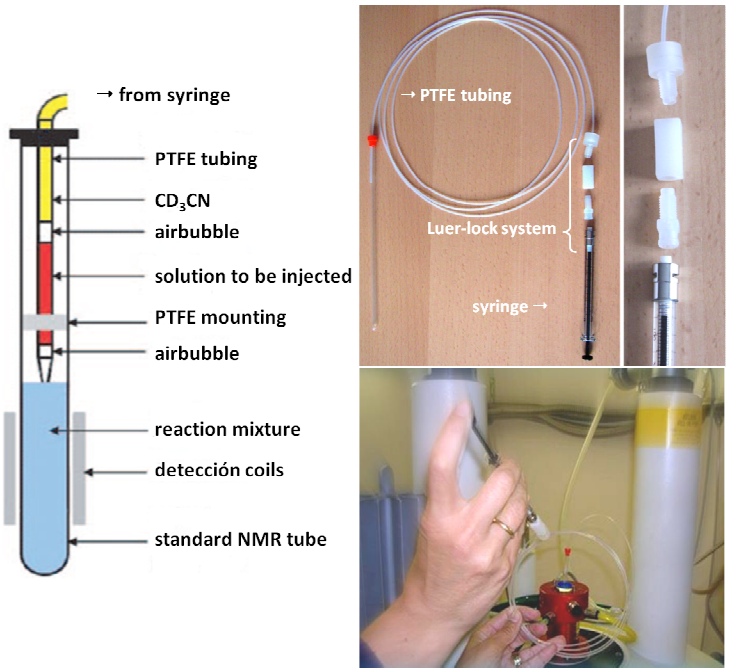
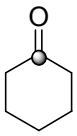
1) Fast mixing device used

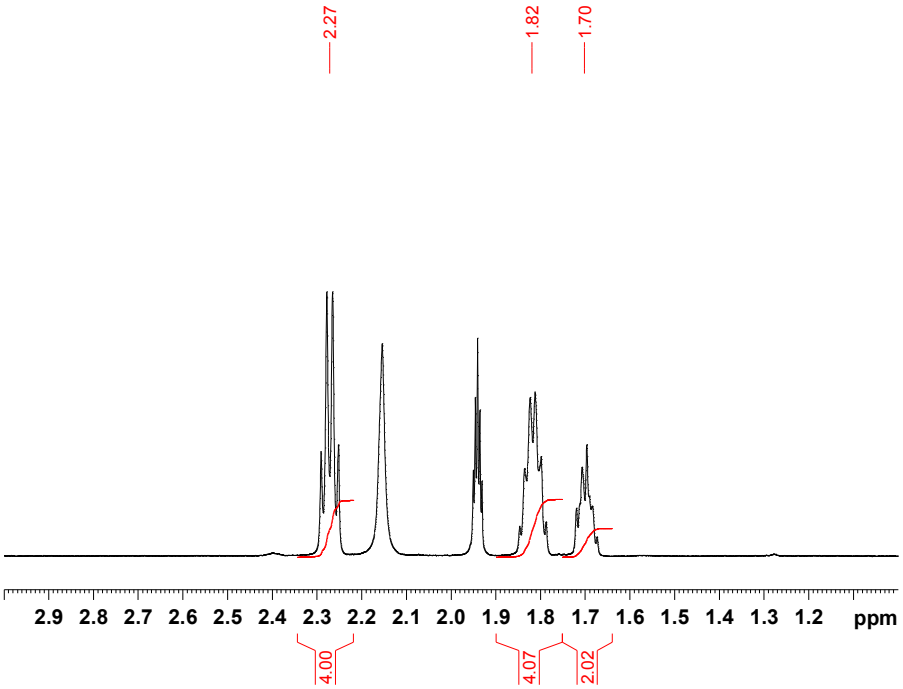


2) H, ^{13}C, TOCSY and HMBC spectra from:

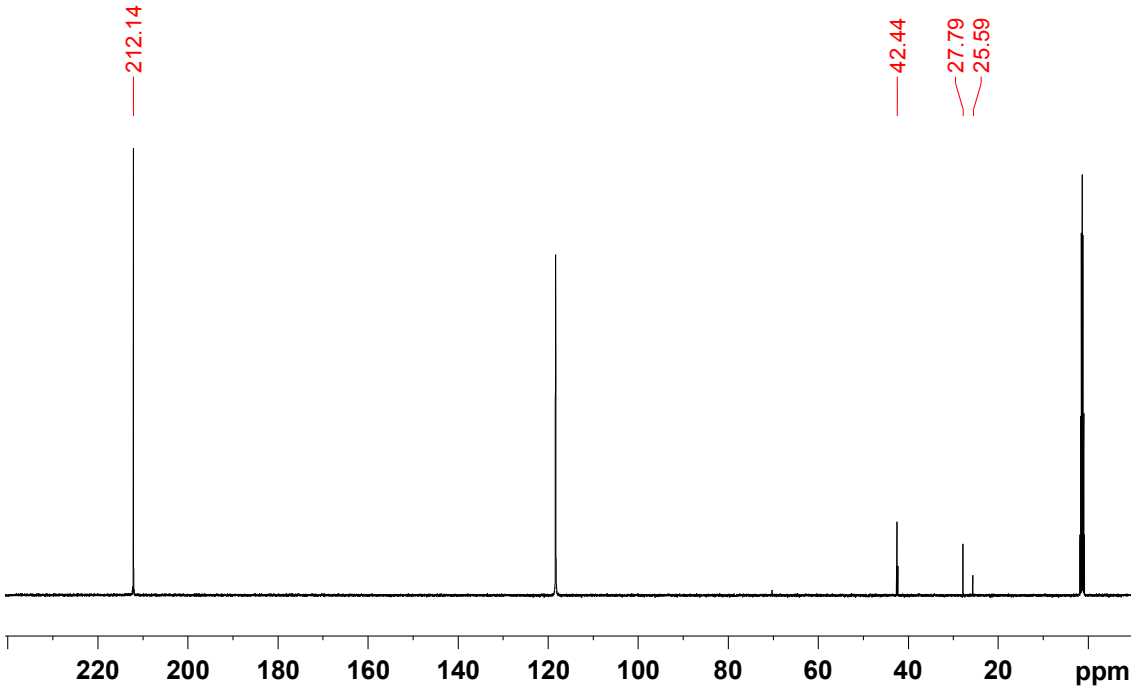
a. ^{13}C-carbonyl-cyclohexanone (**9**)



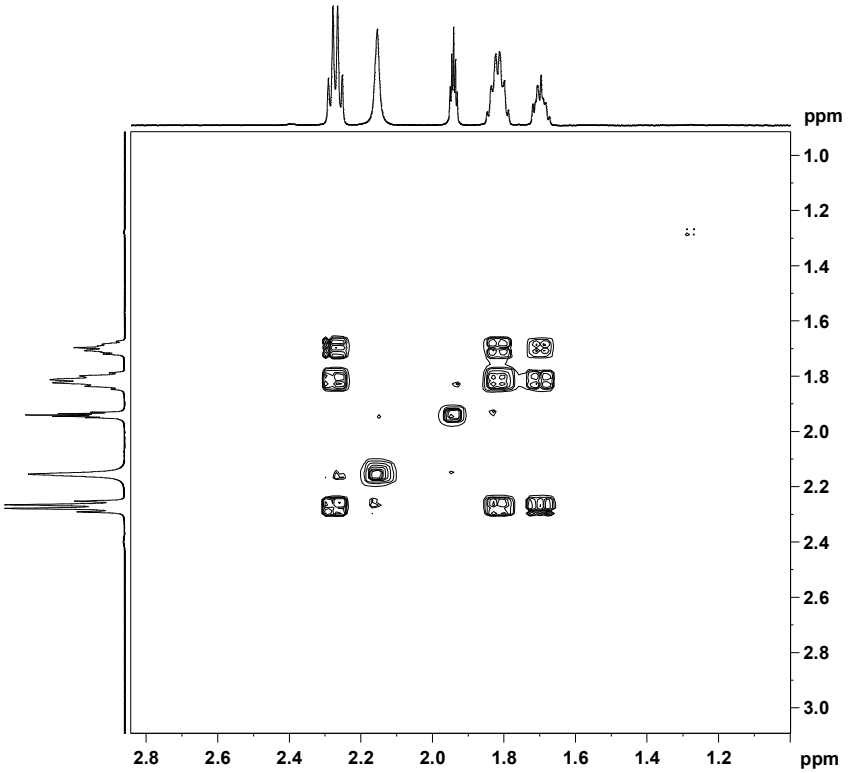
^{1}H-NMR, CD_3CN, 500 MHz



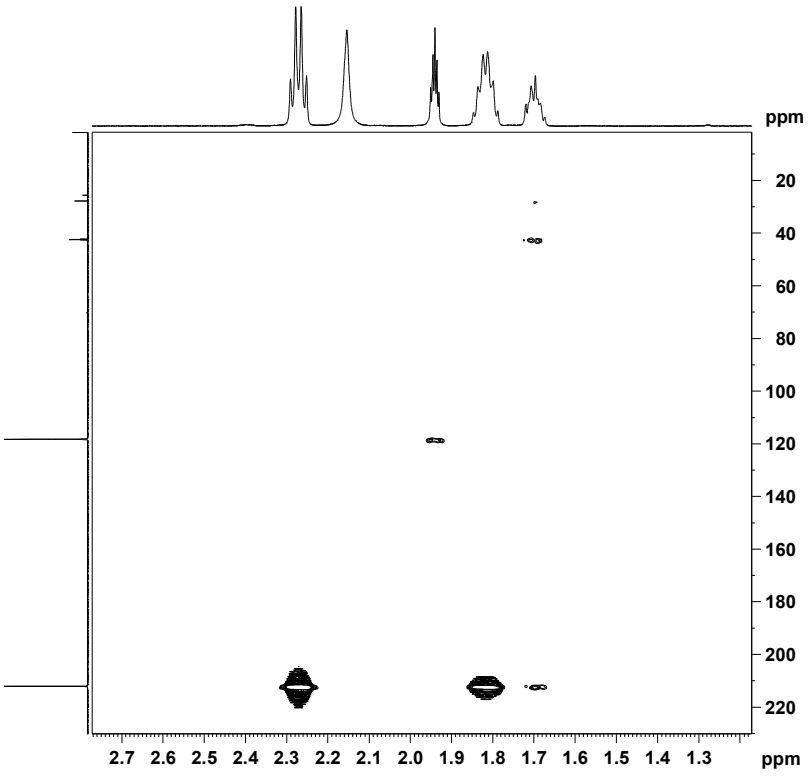
^{13}C-NMR, CD_3CN, 500 MHz



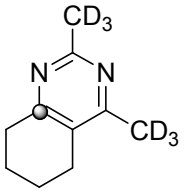
TOCSY, CD_3CN, 500 MHz



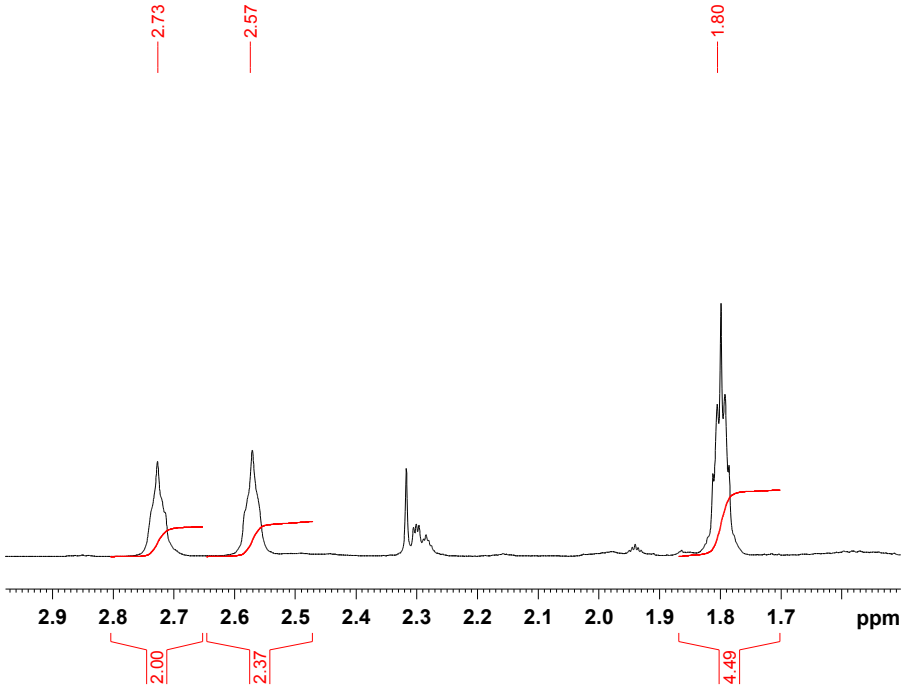
HMBC, CD_3CN, 500 MHz



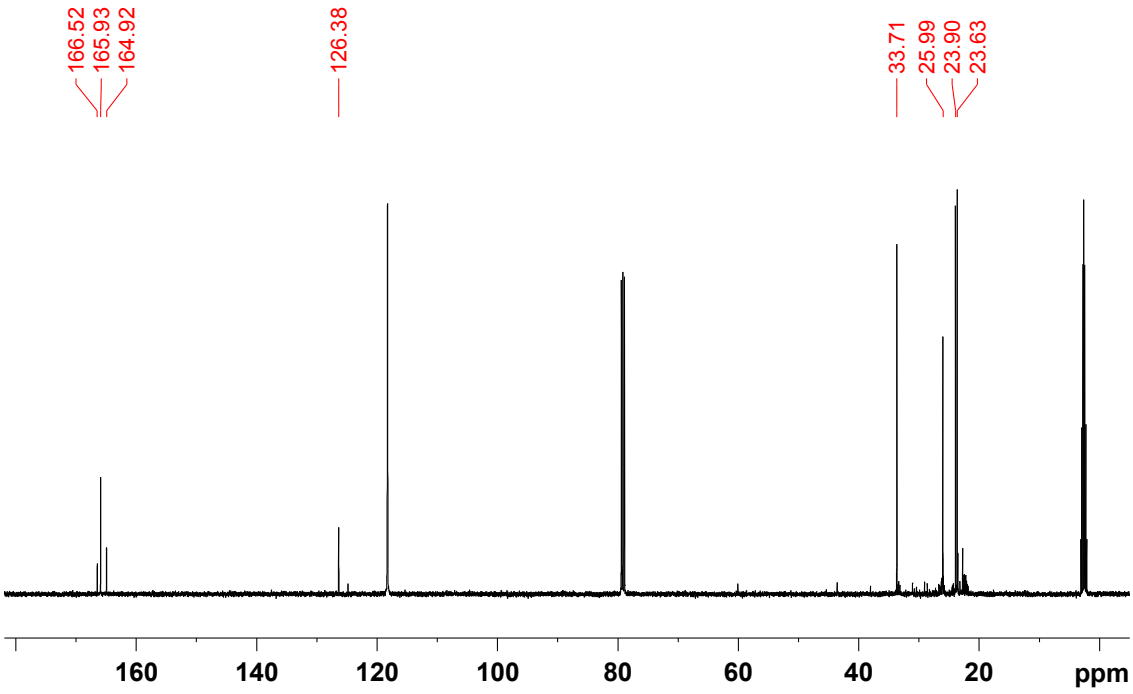
b. 2,4-dimethyl-5,6,7,8-tetrahydroquinazoline-d_6 (**10**)



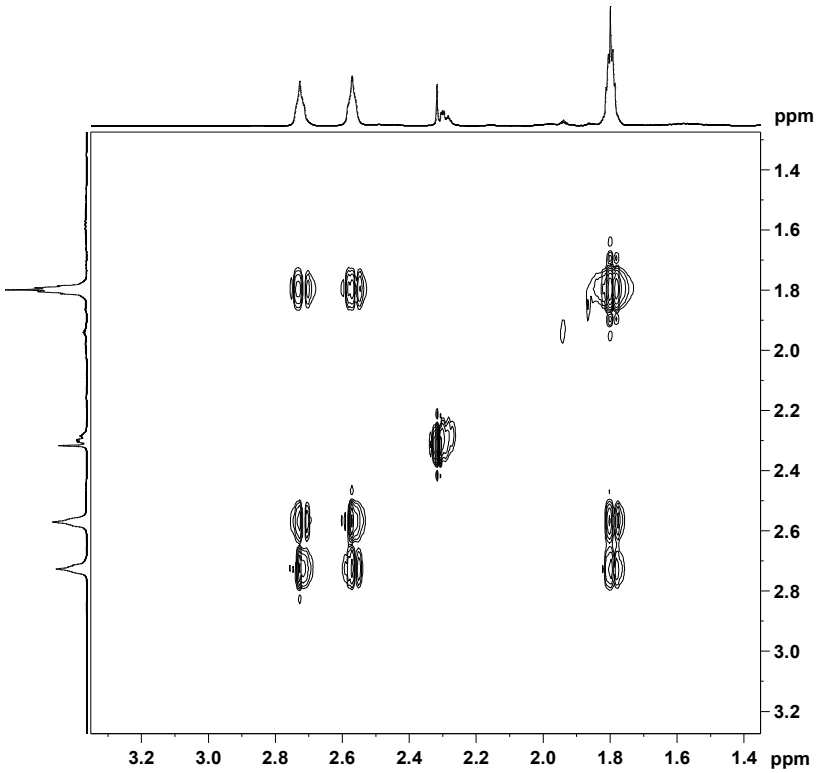
^{1}H-NMR, CD_3CN, 500 MHz



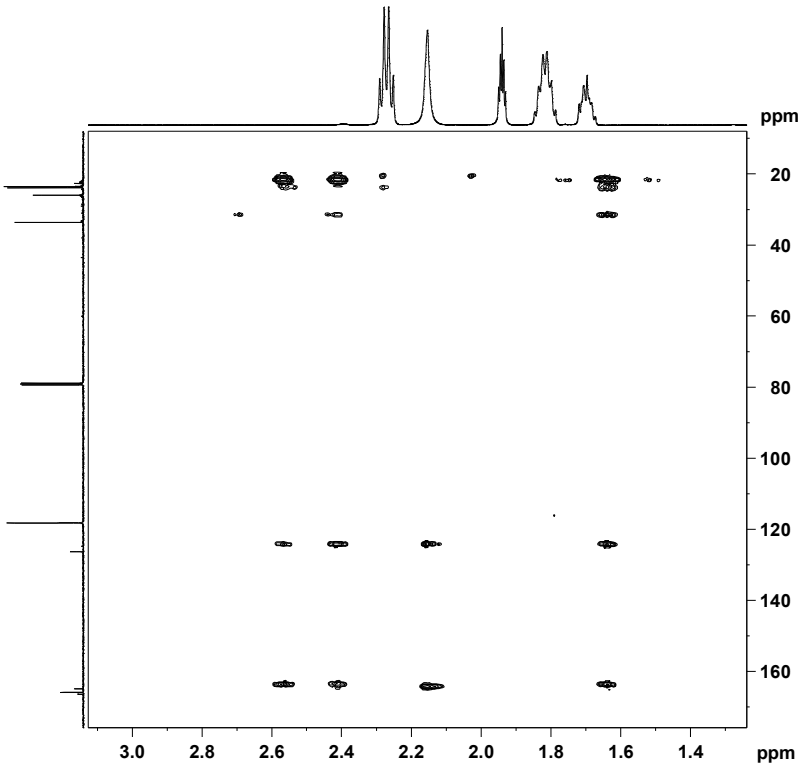
^{13}C-NMR, CD_3CN, 500 MHz



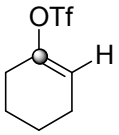
TOCSY, CD_3CN, 500 MHz



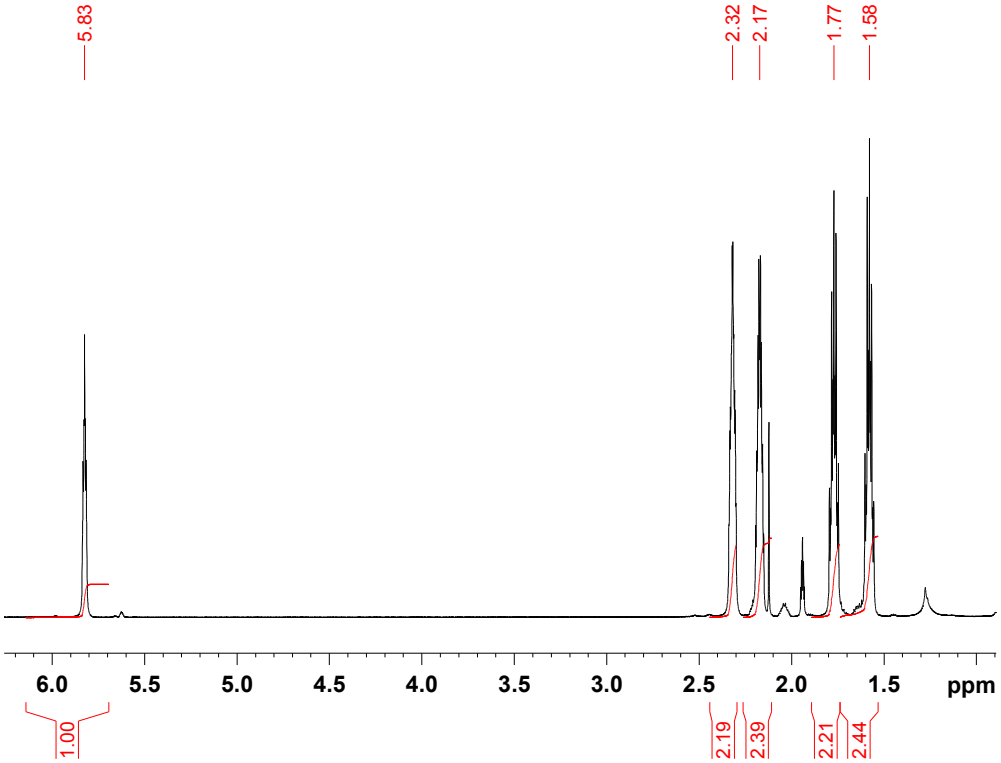
HMBC, CD_3CN, 500 MHz



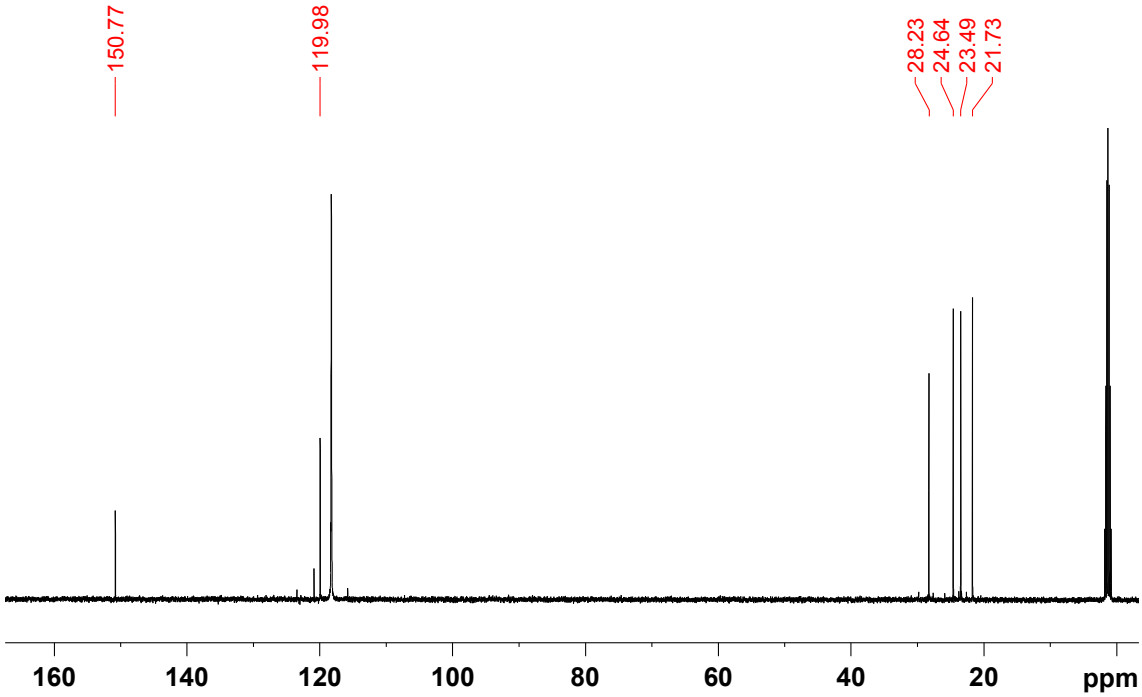
c. 1-Cyclohexenyl-triflate (**15**)



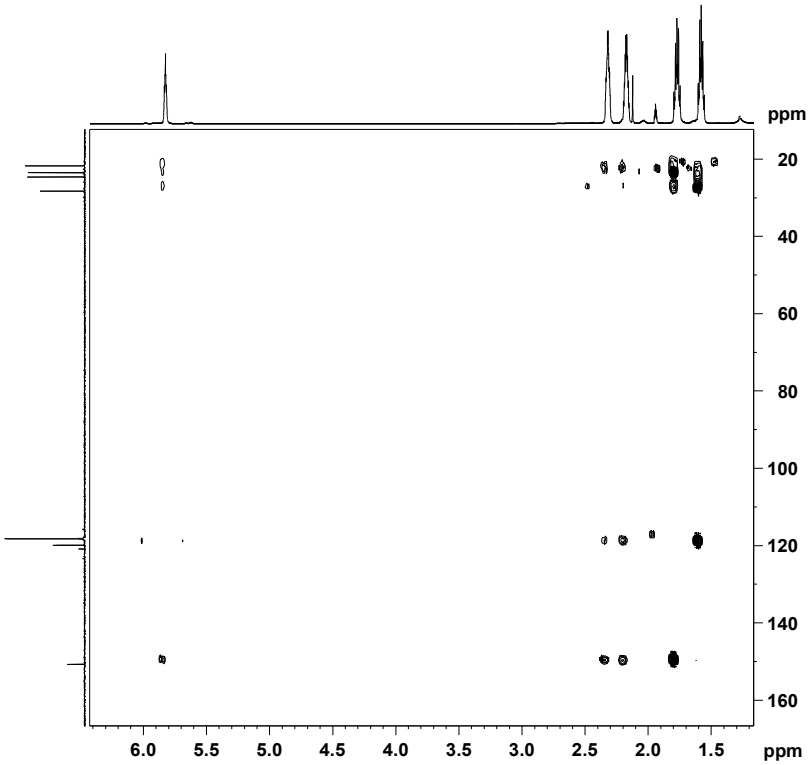
^{1}H-NMR, CD_3CN, 500 MHz



^{13}C-NMR, CD_3CN, 500 MHz



HMBC, CD_3CN, 500 MHz


ppm
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40
60
80
100
120
140
160
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

3) Computational details

Geometry optimizations were carried out with the GAUSSIAN 09[1] suite of programs using the dispersion-corrected metahybrid functional M06-2X[2] in combination with the double-ζ quality plus polarization and diffuse functions 6-31+G(d) basis set. Solvents effects were taken into account using the Polarizable Continuum Model (PCM)[3] in the presence of acetonitrile as solvent. This method is denoted PCM(acetonitrile)/M06-2X/6-31+G(d). All species were characterized by frequency calculations,[4] and have positive definite Hessian matrices, therefore confirming that they are minima on the potential energy surface.

^{13}C-NMR Chemical shifts were estimated with the Gauge-Independent Atomic Orbital (GIAO)[5] method at the GIAO-B3LYP/6-31+G(d) and GIAO-M06-2X/6-31+G(d) levels using the geometries optimized at the PCM(acetonitrile)/M06-2X/6-31+G(d) level. Solvent accounts were also taken into account using the PCM(solvent=acetonitrile) method. The reported chemical shifts were obtained as the difference between the isotropic magnetic shieldings relative to tetramethylsilane (TMS).

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[1] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[2] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res*. **2008**, *41*, 157-167.

[3] (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys*. **1981**, *55*, 117-129. (b) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *J. Comp. Chem*. **1994**, *15*, 1127-1138. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A*, **1998**, *102*, 1995-2001.

[4] McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625-2633.

[5] Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260.

4) Atom coordinates and absolute energies of the theoretical calculations

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM-(toluene)B3LYP/6-31+G(d).

9 E= -309.637838

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.006595	1.258822	-0.289527
2	6	0	-1.779158	-0.000001	0.106569
3	6	0	-1.006594	-1.258822	-0.289529
4	6	0	0.390372	-1.280659	0.355249
5	6	0	1.144799	0.000000	0.071884
6	6	0	0.390372	1.280660	0.355247
7	1	0	-1.553664	-2.160090	0.005216
8	1	0	-1.947618	-0.000002	1.192786
9	1	0	-2.765191	-0.000001	-0.370740
10	1	0	-0.900852	1.291807	-1.382010
11	1	0	-1.553665	2.160089	0.005221
12	1	0	0.276091	-1.356870	1.446411
13	1	0	0.988475	-2.130702	0.016221
14	1	0	0.276095	1.356873	1.446410
15	1	0	0.988475	2.130701	0.016215
16	1	0	-0.900847	-1.291804	-1.382012
17	8	0	2.286691	0.000000	-0.356635

10 E= -498.633328

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.040751	-0.608678	0.006507
2	7	0	1.989073	0.728730	-0.031034
3	6	0	0.778827	1.299218	-0.036263
4	6	0	-0.399214	0.538003	0.000703
5	6	0	-0.234864	-0.849225	0.013187
6	7	0	0.981156	-1.417526	0.019935
7	6	0	-1.763140	1.189108	0.002381
8	1	0	-1.963828	1.596551	-0.999436
9	1	0	-1.759697	2.048006	0.683466
10	6	0	-1.416361	-1.787647	0.026417
11	1	0	-1.510494	-2.193366	1.043647
12	1	0	-1.186516	-2.637289	-0.624924
13	6	0	-2.719518	-1.100436	-0.377857
14	1	0	-3.564802	-1.768589	-0.185131
15	1	0	-2.710300	-0.893516	-1.456665
16	6	0	-2.876101	0.212967	0.386573
17	1	0	-2.831024	0.009764	1.465193
18	1	0	-3.850191	0.670306	0.185847
19	6	0	3.400526	-1.247884	0.057163
20	1	0	3.657970	-1.488565	1.095004
21	1	0	3.407662	-2.179579	-0.512649
22	1	0	4.158631	-0.567137	-0.333640

23	6	0	0.727738	2.800234	-0.081732
24	1	0	0.069410	3.147009	-0.885330
25	1	0	0.329822	3.202129	0.857437
26	1	0	1.729890	3.201894	-0.237608

12 E= -1327.699501

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.207343	-0.027232	-0.165475
2	6	0	4.547093	0.756601	0.970993
3	6	0	3.044706	0.742580	0.863286
4	6	0	2.380556	-0.100242	0.062221
5	6	0	3.047612	-1.159816	-0.777971
6	6	0	4.505461	-1.370697	-0.366458
7	1	0	4.847646	0.335629	1.941634
8	1	0	4.898068	1.795627	0.972153
9	1	0	5.142174	0.554805	-1.095088
10	1	0	6.271010	-0.174877	0.049025
11	1	0	2.474522	-2.090056	-0.686488
12	1	0	2.985836	-0.862806	-1.835315
13	1	0	4.537308	-1.937084	0.574038
14	1	0	5.021216	-1.971007	-1.123003
15	1	0	2.480197	1.438475	1.483014
16	7	0	0.963860	-0.128899	0.006475
17	6	0	0.305713	0.873070	-0.364573
18	6	0	0.692112	2.221948	-0.873044
19	1	0	0.099860	2.461559	-1.759191
20	1	0	0.490320	2.979580	-0.109949
21	1	0	1.755434	2.232467	-1.113161
22	16	0	-1.793197	-0.569393	0.230291
23	8	0	-1.628808	-1.681287	-0.675143
24	8	0	-1.102597	0.772055	-0.343243
25	8	0	-1.588491	-0.700957	1.653057
26	6	0	-3.511431	0.083734	-0.022286
27	9	0	-3.695635	0.392911	-1.295539
28	9	0	-3.706849	1.151157	0.734284
29	9	0	-4.354770	-0.876057	0.331791

13 E= -1327.706825

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.003008	-1.164408	0.418480
2	6	0	-5.297921	0.244646	-0.102929
3	6	0	-4.071375	1.106076	-0.133721
4	6	0	-2.848374	0.579974	-0.002782
5	6	0	-2.512883	-0.881593	0.150166
6	6	0	-3.733245	-1.727326	-0.222238
7	1	0	-5.709747	0.200889	-1.121373
8	1	0	-6.060814	0.739082	0.508808
9	1	0	-4.873143	-1.128534	1.507959
10	1	0	-5.857300	-1.817200	0.216251
11	1	0	-1.650574	-1.118817	-0.480962
12	1	0	-2.207395	-1.070355	1.187717
13	1	0	-3.848420	-1.734714	-1.313709
14	1	0	-3.564646	-2.760935	0.093760
15	1	0	-4.183500	2.179136	-0.267593
16	7	0	-1.749334	1.441602	-0.015777
17	6	0	-0.773352	2.043925	-0.020196
18	6	0	0.430333	2.848672	-0.025804
19	1	0	1.011612	2.609001	0.867326
20	1	0	1.008714	2.599933	-0.918217
21	1	0	0.149615	3.904197	-0.026774
22	16	0	1.915448	-0.985420	-0.111241
23	8	0	1.857770	-1.693327	1.174122
24	8	0	0.799216	-0.055128	-0.355629
25	8	0	2.304572	-1.802303	-1.267249
26	6	0	3.352431	0.156357	0.101767
27	9	0	3.156167	0.974135	1.143123
28	9	0	3.523437	0.912501	-0.987834
29	9	0	4.479915	-0.526419	0.317010

14 E= -1460.363501

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.482860	2.866708	0.936760
2	6	0	2.778466	2.167003	1.350585
3	6	0	3.013559	0.914056	0.551117
4	6	0	2.355752	0.649797	-0.586074
5	6	0	1.356310	1.580955	-1.224841
6	6	0	1.394456	2.970614	-0.586656
7	1	0	3.633616	2.847254	1.225923
8	1	0	2.751706	1.909140	2.416239
9	1	0	0.625586	2.289575	1.308921
10	1	0	1.429471	3.859703	1.395318
11	1	0	1.566477	1.635591	-2.299632
12	1	0	0.360810	1.129407	-1.121226
13	1	0	2.269844	3.519561	-0.959185
14	1	0	0.506180	3.536412	-0.886547
15	1	0	3.767360	0.212529	0.906955
16	7	0	2.623367	-0.515338	-1.344933
17	6	0	2.445358	-1.680446	-0.905486
18	6	0	2.729909	-2.958100	-1.618725
19	1	0	3.454775	-3.552277	-1.054636
20	1	0	1.811180	-3.543685	-1.719474
21	1	0	3.130786	-2.723798	-2.604370
22	7	0	1.876764	-1.875974	0.402199
23	6	0	1.237578	-1.925009	1.354109
24	6	0	0.463398	-1.971543	2.569976
25	1	0	0.867130	-1.231578	3.266395
26	1	0	-0.576099	-1.726659	2.312395
27	1	0	0.529902	-2.973711	2.999791
28	16	0	-2.153297	-0.919129	0.003162
29	8	0	-2.487895	-1.133531	1.421084
30	8	0	-2.994105	-1.638632	-0.959311
31	8	0	-0.708012	-0.938676	-0.282135
32	6	0	-2.607971	0.849247	-0.276990
33	9	0	-3.905947	1.048299	-0.031421
34	9	0	-2.363809	1.203426	-1.542244
35	9	0	-1.903004	1.655476	0.522766

15 E= -1195.028778

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.973050	0.056254	0.504287
2	6	0	3.509579	-1.131666	-0.344086
3	6	0	2.033837	-1.064564	-0.637504
4	6	0	1.347669	0.055089	-0.435775
5	6	0	1.876207	1.373214	0.029305
6	6	0	3.407907	1.369641	-0.041100
7	1	0	4.058898	-1.159446	-1.295272
8	1	0	3.729714	-2.077511	0.163233
9	1	0	3.629928	-0.081805	1.538313
10	1	0	5.066709	0.090519	0.528181
11	1	0	1.455555	2.166434	-0.599841
12	1	0	1.529785	1.562210	1.054208
13	1	0	3.721091	1.491738	-1.086052
14	1	0	3.801105	2.224571	0.517072
15	1	0	1.524955	-1.945063	-1.022767
16	16	0	-1.014417	-0.515872	0.403593
17	8	0	-0.676904	0.032863	1.698479
18	8	0	-1.222044	-1.936062	0.235666
19	8	0	-0.055540	0.063739	-0.731696
20	6	0	-2.536882	0.346759	-0.204498
21	9	0	-3.540116	0.000229	0.590351
22	9	0	-2.800533	-0.027326	-1.446123
23	9	0	-2.361503	1.657054	-0.155108