Supporting Information

Unprecedented Directed Oxidative Cross-Coupling of Sulfahydantoins with Aldehydes *via* a Radical Sulfonate-Sulfinate Conversion.

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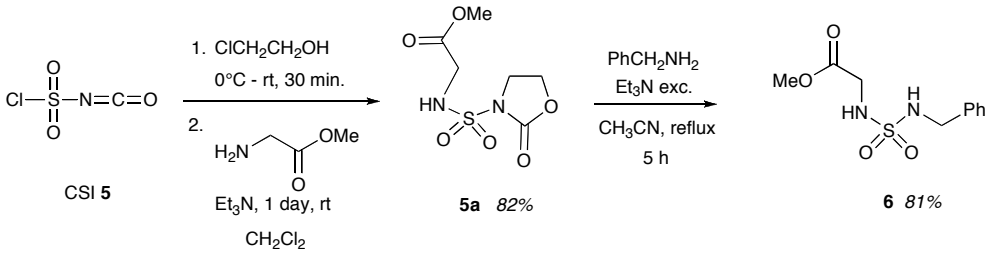
Experimental (Instrumentation, Analysis and Starting Materials).

All reagents were commercially available and used without any further purification. All reactions were carried out under an atmosphere of dry Argon using anhydrous dichloromethane. Anhydrous triethylamine was obtained by distillation from KOH under Argon. Solvents utilized were of spectroscopic grade. ^{1}H and ^{13}C NMR analyses were performed with Bruker Avance DPX 200 MHz, Bruker Avance AM 300 MHz or Bruker AC-400 MHz and are reported in *ppm* and calibrated using residual undeuterated solvents as an internal reference. Data are reported as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qui, quintet, m = multiplet; coupling constant(s) in *Hz*, integration. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved. Carbon (^{13}C) NMR spectra are reported in ppm (δ) relative to residual $CHCl_3$ (δ 77.16) unless noted otherwise. Mass spectra (electrospray ionization mode, ESIMS) were recorded on a Micromass (Manchester, UK) Q-TOF quadrupole mass spectrometer fitted with an electrospray interface. The mass spectrometer was calibrated in the positive- and negative-ion ESI mode. The samples were dissolved in a mixture H_2O/CH_3CN (50/50 v/v). Analytical high performance liquid chromatography (HPLC) was performed on a Waters Millenium 717 equipped with an Autosampler, with a variable wavelength diode detector using a CHROMOLITH RP18 column (50 x 4,6 mm), flow 5 mL/min, linear gradient CH_3CN in water 0-100% (+ 0.1% TFA) in 4.5 min. HRMS analyses were performed by IBMM analytical services.

General experimental procedures.

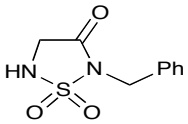
Synthesis of 6 (Two steps). [1,2]



Step 1: To a solution of chlorosulfonyl isocyanate **5** (22 mL, 0.252 mol) in CH_2Cl_2 (100 mL), was added 2-chloroethanol (17 mL, 0.252 mol) at 0 °C. The mixture was stirred for 30 min at r.t. Then the mixture was added to a solution of Gly-OMe (28 g, 0.222 mol) and NEt_3 (30 mL, 0.222 mol) in CH_2Cl_2 (100 mL) at 0 °C. The mixture was stirred for 1 day at r.t. then a solution of NEt_3 (60 mL, 0.444 mol) in CH_2Cl_2 (60 mL) was added. The organic layer was washed with HCl (0.1 M), water and brine then dried over Na_2SO_4. Solvents were removed under *vacuum* and the resulting residue was purified by silica gel chromatography (gradient: AcOEt/CH_2Cl_2 (v/v), 10/90-30/70) to give *N*-sulfonyloxazolidinone **5a** as a white solid (43.5 g, 82%). M.p. 72-73 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 4.50-4.28 (m, 2H); 4.10-3.98 (m, 4 H); 3.76 (s, 3 H); HRMS (*m/z*): $[M+H]^+$ calculated for $C_6H_{11}N_2O_6S$ 239.0338, found 239.0328.

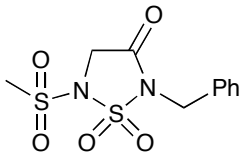
Step 2: To a solution of the *N*-sulfonyloxazolidinone **5a** (30 g, 126 mmol) in CH_3CN (100 mL), NEt_3 (18 mL, 129 mmol) and benzylamine (14 mL, 128 mmol) were added. The mixture was stirred for 5 h at reflux. The mixture was concentrated then residue was purified by silica gel chromatography (gradient: AcOEt/CH_2Cl_2 (v/v), 0/100-5/95) to give compound **6** as a solid (26.4 g, 81%) M.p.: 41-42 °C; ^{1}H NMR ($CDCl_3$, 200 M*Hz*): δ (ppm) 7.33 (m, 5H) 5.02 (*app* t, J = 5.7 *Hz*, 1H); 4.79 (*app* t, J = 6.1 *Hz*, 1H); 4.24 (d, J = 6.1 *Hz*, 2H); 3.80 (d, J = 5.7 *Hz*, 2H); 3.74 (s, 3H); HRMS (*m/z*): $[M+H]^+$ calculated for $C_{10}H_{15}N_2O_4S$ 259.0753, found 259.0761.

Synthesis of 7. To a solution of **6**[1,2] (5.4 g, 20 mmol) in CH_3CN (400 mL) and *tert*-BuOH (200 mL) was added *tert*-BuOK (3.8 g, 34 mol) at r.t. The resulting suspension was stirred for 1 h 30 at 50 °C then NH_4Cl saturated (50 mL) was added. The mixture was concentrated to about 50 mL. The aqueous layer was extracted with AcOEt (5 times). The combined organic layers were dried over Na_2SO_4. Solvent was removed under *vacuum* and the resulting residue was purified by silica gel chromatography (gradient: AcOEt/CH_2Cl_2 (v/v), 0/100-5/95) to give compound **7**[1] as a solid (2.667 g, 53%). M.p.: 147-148 °C; ^{1}H NMR ($CDCl_3$, 200 M*Hz*): δ (ppm) 7.46-7.30 (m, 5H); 4,86 (*br* s, 1H); 4.73 (s, 2H); 4.03 (s, 2H); HRMS (*m/z*): $[M+H]^+$ calculated for $C_9H_{11}N_2O_3S$ 227.0490, found 227.0493.



Synthesis of 8. To a solution of sulfahydantoin **7** (2.26 g, 10 mmol) in CH_2Cl_2 (40 mL) NEt_3 (2.1 mL, 15 mmol) and MsCl (1.2 mL, 15 mmol) were added at 0 °C. The resulting suspension was stirred for 1 h at 0 °C. NH_4Cl (5 mL) was added dropwise to the mixture. The

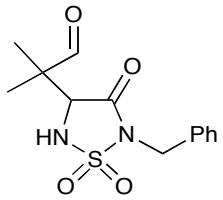
aqueous layer was extracted with CH_2CL_2 (3 times). The combined organic layers were washed with $NaHCO_3$ (1 time) dried over Na_2SO_4. Solvent was removed under *vacuum* and the resulting residue was purified by silica gel chromatography using an AcOEt/CH_2Cl_2 gradient (gradient: AcOEt/CH_2Cl_2 (v/v), 0/100-5/95) to give compound **8** as a white solid (3.038 g, 91%, M.p.: 147-148 °C).



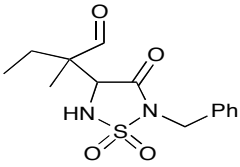
^{1}H NMR (400 M*Hz*, DMSO-d_6): δ (ppm) 7.41-7.36 (m, 4H), 7.35-7.31 (m, 1H), 4.93 (s, 2H), 4.83 (s, 2H), 3.53 (s, 3H); ^{13}C NMR (100 M*Hz*, DMSO-d_6): δ (ppm) 160.6, 134.0, 128.6, 128.1 (2 signals overlapped), 51.8, 43.6, 39.4; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{10}H_{13}N_2O_5S_2$ 305.0266, found 305.0269.

Typical experimental procedure for the radical couplings of 8 with aldehydes (Table 1).

To a solution containing Ms-sulfahydantoin **8** (1.65 mmol, 502 mg) and the suitable aldehyde (1.65 mmol, 502 mg) in CH_2Cl_2 (4 mL), DBU (3.63 mmol, 550 mg) was slowly added (1.82 mmol, 130 mg) at room temperature. The reaction was stirred for 2 hours, then the reaction mixture was quenched with diluted HCl 0,1% (1 time) at 0 °C. The aqueous layer was extracted with CH_2Cl_2 (3 times). The organic layer was dried over anhydrous Na_2SO_4 filtered and concentrated under reduce pressure. The residue was quickly purified by column chromatography on silica gel (3g) (gradient: AcOEt/CH_2Cl_2 (v/v), 5/95-20/80) to afford:



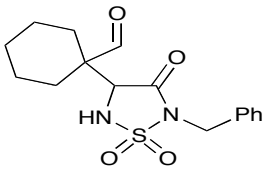
4a as a white solid (Yield: 80%, Mp: 107-108 °C); ^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 9.36 (s, 1H), 7.44-7.39 (m, 2H), 7.38-7.31 (m, 3H), 5.38 (*br* s, 1H), 4.76 (*A*B, *J* = 15.3 *Hz*, 1H), 4.69 (A*B*, *J* = 15.3 *Hz*, 1H), 4.45 (*br* s, 1H), 1.29 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 201.4, 164.6, 132.7, 127.8, 127.7, 127.5, 62.6, 49.0, 43.5, 17.7, 16.5; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{13}H_{17}N_2O_4S$ 297.0908, found 297.0909.



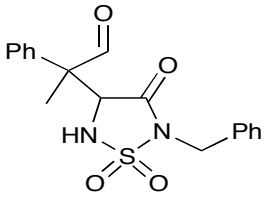
Major diasteroisomer 4b as a bright white solid (Yield: 45%, Mp: 97-98 °C); ^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 9.28 (s, 1H), 7.45-7.40 (m, 2H), 7.37-7.30 (m, 3H), 5.57 (br d, *J* = 6.7 *Hz,* 1H), 4.75 (*A*B, *J* = 15.3 *Hz*, 1H), 4.69 (A*B*, *J* = 15.3 *Hz*, 1H), 4.55 (d, *J* = 6.8 *Hz*, 1H), 1.97 (*app* *A*BX_3, *J* = 15.0, 7.5 *Hz*, 1H), 1.78 (*app* AB*X*$_3$, *J* = 15.0, 7.5 *Hz*, 1H), 1.21 (s, 3H), 0.90 (*app* AB*X*$_3$, *J* = 7.5 *Hz*, 3H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 203.7, 165.8, 134.0, 128.9, 128.8, 128.6, 61.2, 53.8, 44.5, 26.1, 15.6, 8.3; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{14}H_{19}N_2O_4S$, 311.1066, found 311.1076.

Minor diasteroisomer 4b as a bright white solid (Yield: 24%, Mp: 94-95°C); ^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 9.49 (s, 1H), 7.42-7.37 (m, 2H), 7.36-7.30 (m, 3H), 5.54 (*br* d, *J* = 4.9 *Hz*, 1H), 4.74 (*A*B, *J* = 15.3 *Hz*, 1H), 4.66 (A*B*, *J* = 15.3 *Hz*, 1H), 4.52 (br d, *J* = 4.9 *Hz*), 1.73 (*app* *A*BX_3, *J* = 15.0, 7.4 *Hz*, 1H), 1.64 (*app*

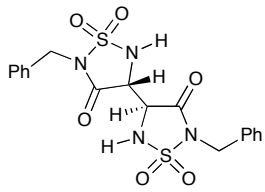
A*B*X$_3$, *J* = 15.1, 7.6 *Hz*, 1H), 1,16 (s, 3H), 0.86 (*app* AB*X*$_3$, *J* = 15.1, 7.5 *Hz*, 3H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 202.7, 166.4, 133.8, 129.0, 128.9, 128.7, 63.6, 52.8, 44.8, 26.3, 14.6, 7.9; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{14}H_{19}N_2O_4S$, 311.1066, found 311.1068.



4d as a bright white solid (Yield: 58%, Mp: 137-138 °C); ^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 9.64 (s, 1H), 7.43-7.38 (m, 2H), 7.37-7.30 (m, 3H), 5.27 (d, *J* = 8.1 *Hz*, 1H), 4.75 (*A*B, *J* = 15.3 *Hz*, 1H), 4.68 (A*B*, *J* = 15.3 *Hz*, 1H), 4.30 (d, *J* = 8.1 *Hz*, 1H), 1.29 (s, 3H), 1.80-1.30 (m, 10H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 205.1, 166.6, 133.9, 128.9 (2 signals overlapped), 128.6, 64.1, 52.1, 44.9, 28.9, 27.3, 24.9, 21.7, 21.6; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{16}H_{21}N_2O_4S$, 337.1220, found 337.1222.

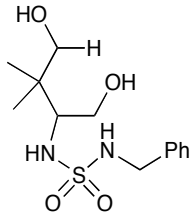


Mixture of diastereoisomers 1:1 4e as a foam (Yield: 85%); ^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 9.47 (s, 1H), 7.46-7.22 (m, 9H), 7.14-7.10 (m, 1H), 5.66 (*br* d, *J* = 6.0 *Hz*, 1H), 4.89 (d, *J* = 6.1 *Hz*, 1H), 4.70 (*A*B, *J* = 15.3 *Hz*, 1H), 4.63 (A*B*, *J* = 15.3 *Hz*, 1H), 1,75 (s, 3H); δ (ppm) 9.26 (s, 1H), 7.46-7.22 (m, 9H), 7.14-7.10 (m, 1H), 5.79 (*br* d, *J* = 6.5 Hz, 1H), 4.93 (d, *J* = 6.6 *Hz*, 1H), 4.59 (*A*B, *J* = 15.5 *Hz*, 1H), 4.54 (A*B*, *J* = 15.5 *Hz*, 1H), 1,67 (s, 3H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 199.2, 198.5, 164.9, 164.7, 133.7, 133.4, 133.3, 129.1, 129.0, 128.7 (3 signals overlapped), 128.6, 128.5, 128.4, 128.3 (2 signals overlapped), 128.1, 127.9, 64.0, 63.8, 57.4, 57.2, 44.2, 43.8, 15.7, 13.6; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{18}H_{19}N_2O_4S$, 359.1066, found 359.1060.



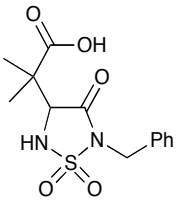
15: white solid (Mp. 222-224°C) ^{1}H NMR (300 M*Hz*, DMSO-d_6): δ (ppm) 9.25 (*br* s, 2H), 7.40-7.28 (m, 10H), 5.01 (s, 2H), 4.74 (*A*B, *J* = 16.1 *Hz*, 2H), 4.67 (A*B*, *J* = 16.1 *Hz*, 2H), ^{13}C NMR (75 M*Hz*, DMSO-d_6): δ (ppm) 165.21, 134.67, 128.42, 127.87, 127.77, 60.47, 43.47; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{18}H_{19}N_4O_6S_2$, 451.0746, found 451.0754.

Synthesis of 16. To a solution of aldehyde **4a** (36 mg, 0.12 mmol) in THF (4 mL) and H_2O (0.5 mL) $NaBH_4$ (46 mg, 1.21 mmol) was added. at 0 °C. The resulting suspension was stirred overnight at r.t., saturated NH_4Cl (0.5 mL) was added dropwise to the mixture, then evaporated. The residue was diluted with water and extracted with CH_2Cl_2 (3 times). The combined organic layers were dried over Na_2SO_4. Solvent was removed under vacuum and the resulting residue was purified by silica gel chromatography to give compound **16** (21 mg, 63%).



^{1}H NMR (400 M*Hz*, $CDCl_3$): δ (ppm) 7.33 (m, 4H), 7.40-30 (m, 1H), 4.24 (d, J = 7.2 *Hz*, 2H), 3.79 (dd, J = 11.7, 4.8 *Hz*, 1H), 3.67 (dd, J = 11.7, 4.8 *Hz*, 1H), 3.59 (br s, 1H), 3.45 (d, J = 10.9 *Hz*, 1H), 3.28 (*app* d, J = 10.9 *Hz*, 1H), 3.26 (t, J = 4.8 *Hz*, 1H), 3.24 (*br* s, 1H), 0.98 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 M*Hz*, $CDCl_3$): δ (ppm) 136.97, 128.92, 128.21, 128.07, 68.67, 61.64, 61.30, 47;67, 38,73, 23.97, 21.55; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{13}H_{23}N_2O_4S$, 303.1379, found 303.1374.

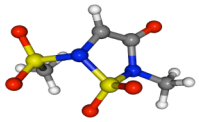
Synthesis of 17. The aldehyde **4a** (75 mg, 0,25 mmol) was placed in a flask with 5 mL of *tert*-butyl alcohol to which was added a solution of 2-methyl-2-butene (400 µL, 3.75 mmol) in THF (2 mL) followed by a solution of sodium hypochlorite (0.203 mg, 2.25 mmol) and monobasic sodium phosphate (234 mg, 1.5 mmol) in 2.5 mL of water.[2,3] As the oxidant was added the solution became bright yellow. The reaction was stirred overnight at r.t., changing from yellow to colorless. It was then concentrated under *vacuum*, diluted with saturated $NaHCO_3$, and extracted once with hexane. The aqueous phase was then acidified with 2 M HCl and extracted with AcOEt (3 times). The combined organic layers then dried over Na_2SO_4. The product was concentrated and the residue was purified by column chromatography on silica gel to afford affording the acid **17** as a solid (44 mg, 56%).



^{1}H NMR (400 M*Hz*, DMSO-d_6): δ (ppm) 7.41 (d, J = 7.1 *Hz*, 2H), 7.32 (m, 2H), 7.28 (t, J = 7.2 *Hz*, 1H), 4.72 (*A*B, J = 15.6 *Hz*, 1H), 4.66 (A*B*, J = 15.6 *Hz*, 1H), 4;59 (s, 1H), 1.27 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 M*Hz*, MeOD): δ (ppm) 168.55, 158.67, 126.68, 120.12, 120.01, 119.57, 57.37, 37.83, 35.49, 13.22, 11.62; HRMS (*m/z*): $[M+H]^+$ calculated for $C_{13}H_{17}N_2O_5S$, 313.0858, found 313.0868.

DFT calculations.

Enolate **A**



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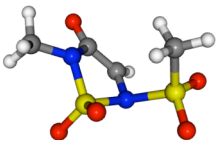
E° = -1438.531807 a.u.
H = -1438.517017 a.u.
G = -1438.572307 a.u.

1	6	0	1.944181	0.656037	1.409232
2	7	0	1.003603	0.718485	0.265217
3	16	0	0.192461	- 0.752131	0.196252
4	7	0	0.336173	- 1.025916	1.895794
5	6	0	1.516299	- 0.320952	2.300942
6	6	0	1.457484	1.308952	- 0.996967
7	8	0	0.955187	- 1.788367	- 0.514955
8	8	0	- 1.205273	- 0.555236	- 0.210045
9	16	0	- 1.152173	- 0.712743	2.882722
10	8	0	- 2.206642	- 1.628346	2.415729
11	8	0	2.944280	1.406600	1.404895
12	8	0	- 0.656003	- 0.851948	4.263733
13	6	0	- 1.659188	1.006304	2.644326
14	1	0	2.197591	0.686035	- 1.512434

15	1	0	0.597321	1.478608	- 1.648315
16	1	0	1.915532	2.266934	- 0.750294
17	1	0	- 2.405256	1.219841	3.411990
18	1	0	- 0.773581	1.629035	2.779918
19	1	0	- 2.072251	1.101897	1.641549
20	1	0	2.084238	- 0.698775	3.136465

Transformation **A** to **B** :

TS1



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E° = -1438.532260 a.u.
H = -1438.518048 a.u.
G = -1438.572125 a.u.

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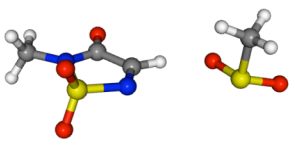
2	6	- 0.000000030	0.000005037	- 0.000008790
3	7	- 0.000002880	0.000004994	0.000001855
4	16	0.000002459	0.000002738	- 0.000008096
5	7	0.000000996	- 0.000001132	- 0.000000762
6	8	- 0.000000489	0.000005541	- 0.000000627
7	6	0.000000865	0.000006952	- 0.000000877
8	8	- 0.000001261	- 0.000005802	- 0.000009356
9	8	0.000000163	- 0.000001644	- 0.000001502
10	16	- 0.000001089	- 0.000006173	0.000002253
11	6	- 0.000000836	- 0.000003534	0.000004598
12	8	- 0.000002511	- 0.000011166	0.000001839
13	8	0.000001845	- 0.000009231	0.000003485
14	1	0.000000255	0.000008399	- 0.000006336
15	1	0.000000868	0.000007928	- 0.000000697
16	1	0.000000786	0.000009796	0.000000420
17	1	- 0.000000070	- 0.000002290	- 0.000003504
18	1	- 0.000000793	- 0.000003521	0.000006430
19	1	0.000000058	- 0.000005486	0.000008883
20	1	- 0.000001082	- 0.000001394	0.000007061

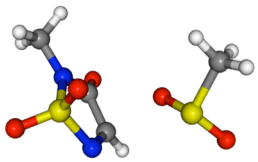
Intermediate



E_e = -1438.701743 a.u. (-24.90 kcal.mol-1)

1	7	- 0.404344	- 0.786492	- 0.204678
2	6	- 0.440022	0.4772710	0.0236580
3	6	- 1.802873	1.1092320	0.2328250
4	7	0.1225390	- 2.745718	0.1302370
5	16	- 2.016798	- 1.389224	- 0.247304
6	8	- 2.007316	2.2890540	0.4661750
7	6	- 4.189532	0.3007120	0.2654860
8	6	- 4.189532	0.3007120	0.2654860
9	8	- 2.359106	- 1.789977	- 1.608587
10	8	- 2.235126	- 2.328529	0.8572500
11	16	3.4139320	0.6407630	- 0.103747
12	8	2.3632100	1.7792480	0.0368180
13	6	3.5774730	0.0978270	1.6461150
14	8	4.8181340	1.2010570	- 0.386739
15	1	- 4.692348	0.0734490	- 0.678618
16	1	- 4.569156	- 0.344226	1.0618430
17	1	- 4.354617	1.3459080	0.5291380
18	1	3.9926270	0.9386260	2.2119750
19	1	2.5917030	- 0.175639	2.0335250
20	1	4.2510990	- 0.764843	1.6718500
21	1	0.4928280	1.0623580	0.0834080

TS2

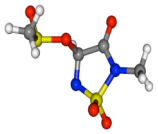


Ee = - 1438.704913 a.u. (freq = -112.4924) (-26.89 kcal.mol-1)
E° = - 1438.575584 a.u.
H = - 1438.560516 a.u.
G = - 1438.618619 a.u.

1	6	- 0.000000877	0.000001004	0.000000387
2	6	0.000001034	- 0.000001745	- 0.000000562
3	7	- 0.000003227	0.000004802	0.000003047
4	16	- 0.000000303	- 0.000001196	0.000001587
5	7	- 0.000002709	0.000000209	0.000002597
6	8	- 0.000000929	- 0.000002319	- 0.000000697
7	6	- 0.000002290	- 0.000002289	- 0.000001373
8	8	- 0.000003005	0.000000593	0.000001013
9	8	0.000000115	0.000000586	0.000001269
10	16	0.000000407	- 0.000004338	0.000000402
11	6	0.000002227	0.000000909	0.000000286
12	8	0.000003373	0.000000448	- 0.000001962

13	8	0.000004325	0.000001269	- 0.000004499
14	1	- 0.000002230	0.000001038	0.000001498
15	1	- 0.000001297	0.000000220	0.000000788
16	1	- 0.000002918	- 0.000000134	- 0.000001001
17	1	- 0.000002737	- 0.000001431	- 0.000003422
18	1	0.000003908	0.000001238	0.000000202
19	1	0.000004280	0.000000469	0.000000502
20	1	0.000002851	0.000000667	- 0.000000061

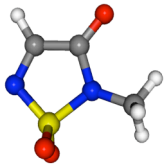
Sulfinate **B**



E_e = - 1438.714253 a.u.
E° = - 1438.583216 a.u.
H = - 1438.568152 a.u.
G = - 1438.627017 a.u.

1	7	0	0.565121	0.813285	- 0.418716
2	6	0	0.221436	- 0.097871	0.610891
3	6	0	1.234187	- 0.009908	1.782495
4	7	0	2.319340	0.682458	1.354674
5	16	0	2.111923	1.168437	- 0.324988
6	8	0	1.072317	- 0.502649	2.896817
7	6	0	3.561194	0.852932	2.090474
8	8	0	3.066025	0.347423	- 1.114308
9	8	0	2.376207	2.621143	- 0.419662
10	16	0	- 0.876657	- 2.047048	- 0.852864
11	8	0	- 2.038836	- 2.614597	- 0.071989
12	6	0	0.112846	- 3.479698	- 1.375406
13	8	0	0.308125	- 1.537930	0.235805
14	1	0	4.381763	0.342678	1.577002
15	1	0	3.800848	1.914518	2.193272
16	1	0	3.422224	0.412788	3.079800
17	1	0	- 0.795919	0.079010	0.971529
18	1	0	0.371492	- 4.057422	- 0.485326
19	1	0	- 0.511471	- 4.066528	- 2.05214
20	1	0	1.007633	- 3.121630	- 1.887479

Radical **C**

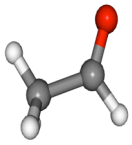


E_e = - 850.169024 a.u.
E° = - 850.086782 a.u.
H = - 850.077334 a.u.
G = - 850.121230 a.u.

1	7	0	2.415985	- 0.464554	0.469736
2	16	0	1.293498	- 0.427744	1.753788

3	7	0	0.109428	0.372187	0.947376
4	6	0	0.613029	0.769361	- 0.258933
5	6	0	1.942797	0.357265	- 0.587846
6	8	0	1.853887	0.347885	2.888660
7	8	0	0.891264	- 1.806176	2.114816
8	8	0	2.629085	0.609992	- 1.601475
9	6	0	3.825975	- 0.755344	0.687234
10	1	0	4.311338	0.007075	1.307940
11	1	0	3.937628	- 1.734282	1.159382
12	1	0	4.302846	- 0.775372	- 0.294273
13	1	0	- 0.004452	1.353679	- 0.929798

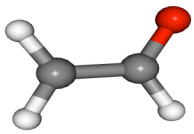
Aldehyde **D**



E_e = - 153.851001 a.u.
E° = - 153.795581 a.u.
H = - 153.790731 a.u.
G = - 153.820563 a.u.

1	6	0	0.017317	- 0.006586	- 0.032058
2	6	0	0.056786	- 0.133145	1.460878
3	8	0	0.816261	0.481837	2.191195
4	1	0	- 0.670648	- 0.845411	1.901067
5	1	0	- 0.988324	0.305080	- 0.341090
6	1	0	0.760222	0.707948	- 0.391756
7	1	0	0.190242	- 0.992022	- 0.482377

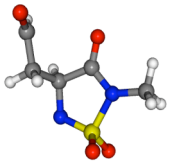
Radical **E**



E_e = - 153.192383 a.u.
E° = - 153.149650 a.u.
H = - 153.145188 a.u.
G = - 153.174575 a.u.

1	6	0	0.066787	- 0.019576	- 0.059231
2	6	0	- 0.140743	- 0.276090	1.326458
3	8	0	1.172845	- 0.158989	- 0.618163
4	1	0	- 0.803648	0.317203	- 0.647245
5	1	0	- 1.119801	- 0.142509	1.774482
6	1	0	0.688033	- 0.609204	1.943537

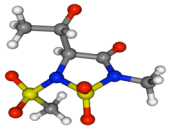
Anion **F**



E_e = - 1003.439493 a.u.
E° = - 1003.307457 a.u.
H = - 1003.294376 a.u.
G = - 1003.347325 a.u.

1	6	0	2.079268	1.513532	- 0.291606
2	7	0	0.896845	0.886036	- 0.496565
3	16	0	0.667186	- 0.385813	0.706051
4	7	0	1.829879	0.050456	1.667133
5	6	0	2.731941	0.982792	0.995767
6	6	0	0.071351	1.012741	- 1.686317
7	8	0	0.810973	- 1.665684	- 0.047478
8	8	0	- 0.691856	- 0.236732	1.287064
9	6	0	4.117819	0.371181	0.667799
10	6	0	5.129609	1.369178	0.173564
11	8	0	5.934224	1.151585	- 0.718800
12	8	0	2.587637	2.373135	- 1.020198
13	1	0	0.117627	0.097549	- 2.284745
14	1	0	- 0.966357	1.210292	- 1.405806
15	1	0	0.456911	1.849478	- 2.272214
16	1	0	2.895193	1.852925	1.647677
17	1	0	4.510486	- 0.032807	1.612137
18	1	0	4.035077	- 0.459324	- 0.039730
19	1	0	5.147768	2.342148	0.704695

Anion **G**

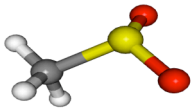


E_e = - 1592.504607 a.u.
E° = - 1592.313435 a.u.
H = - 1592.294986 a.u.
G = - 1592.358713 a.u.

1	7	0	1.153105	0.018487	- 0.102230
2	16	0	1.932188	0.832177	1.153384
3	7	0	0.733891	0.393330	2.292063
4	6	0	- 0.534286	- 0.006033	1.587543
5	6	0	- 0.098973	- 0.514200	0.232715
6	8	0	1.936001	2.273984	0.919389
7	8	0	3.216117	0.189437	1.450484
8	16	0	1.201861	- 0.368005	3.779732
9	8	0	- 0.063218	- 0.586663	4.486672
10	6	0	- 1.578935	1.230726	1.440000
11	6	0	- 1.900142	1.740585	2.866313
12	8	0	- 0.721220	- 1.237763	- 0.524886
13	6	0	1.794575	- 0.123059	- 1.410873
14	8	0	2.237901	0.488511	4.362481
15	8	0	- 2.656808	0.861423	0.734370
16	1	0	1.941041	0.856473	- 1.872247
17	1	0	2.750820	- 0.642797	- 1.317160
18	1	0	1.113111	- 0.715952	- 2.021750
19	1	0	- 1.029753	- 0.790552	2.160082
20	1	0	- 0.961399	2.027378	0.951305

21	1	0	- 2.561041	2.608652	2.767148
22	1	0	- 2.435499	0.967610	3.430682
23	1	0	- 1.013817	2.045351	3.433864
24	6	0	1.911085	- 1.973083	3.376387
25	1	0	2.152921	- 2.438310	4.334003
26	1	0	1.159957	- 2.558374	2.844908
27	1	0	2.805408	- 1.812696	2.776275

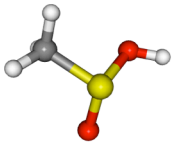
Radical **12**



E_e = - 588.487521 a.u.
E° = - 588.442724 a.u.
H = - 588.436965 a.u.
G = - 588.471007 a.u.

1	16	0	0.116327	- 0.334595	- 0.016767
2	8	0	- 0.127166	- 0.145012	1.446644
3	8	0	1.151543	0.494883	- 0.707476
4	6	0	- 1.480407	- 0.044624	- 0.879177
5	1	0	- 1.323398	- 0.270340	- 1.933253
6	1	0	- 2.216846	- 0.706862	- 0.425713
7	1	0	- 1.731031	1.006548	- 0.723762

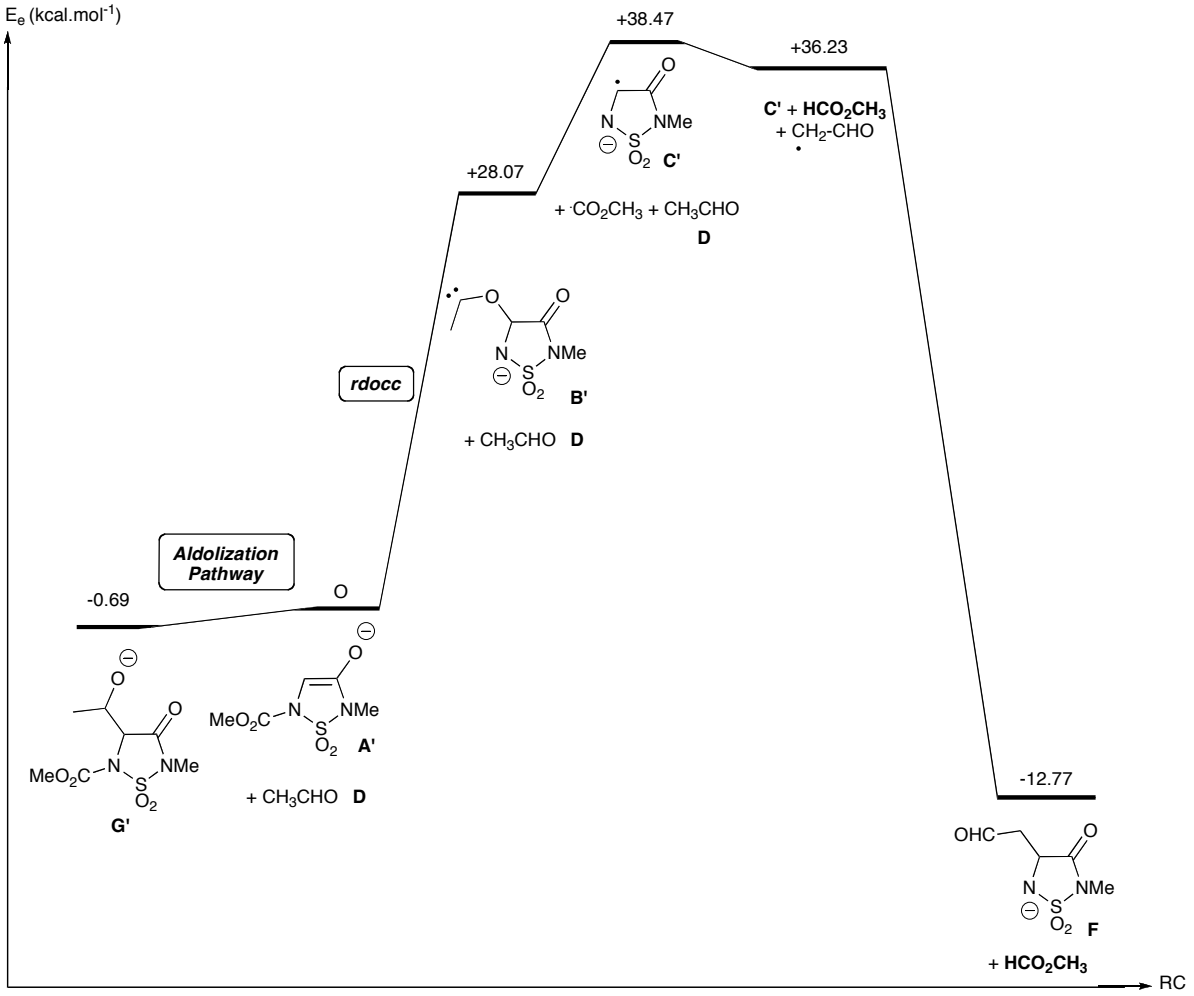
Sulfinic acid **13**



E_e = - 589.129362 a.u.
E° = - 589.073540 a.u.
H = - 589.067287 a.u.
G = - 589.101510 a.u.

1	16	0	- 0.122750	0.106880	- 0.137201
2	8	0	0.065865	0.089175	1.355531
3	8	0	1.338048	- 0.342830	- 0.876601
4	6	0	- 0.900069	- 1.477909	- 0.560888
5	1	0	- 0.993404	- 1.548515	- 1.646001
6	1	0	- 0.273334	- 2.279083	- 0.162793
7	1	0	- 1.884417	- 1.485866	- 0.089147
8	1	0	1.860728	0.464147	- 1.022889

Energetic diagram for the carbamate (Scheme 2)



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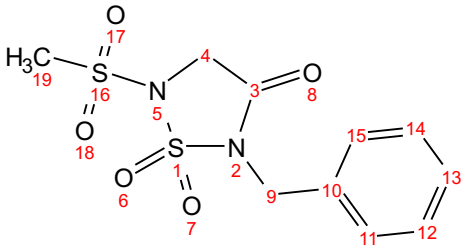
(1) G. Dewynter, M. Abdaoui, Z. Regainia, J.L. Montero, *Tetrahedron*, 1996, **52**, 14217-14224.

(2) D. Bouchouk, E. Colacino, L. Toupet, N. Aouf, J. Martinez, G. Dewynter, *Tetrahedron Lett.*, 2009, **50**, 1100-1104.

(3) B. S. Bal, W. E. Childers, H. W. Pinnick, T*etrahedron,* 1981, **37**, 2091-2096.

(4) S. Jiang, P. Li, C.C. Lai, J.A. Kelley, P.P. Roller *J. Org. Chem.*, 2006, **71**, 7307-7314.

YA-sulfa-MS/1
YA-sulfa-MS / DMSO



4.99
4.85
3.53
2.50

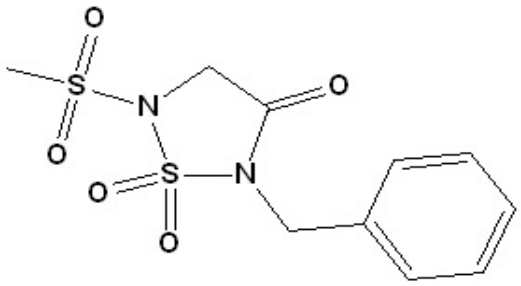
WATER

4.06
1.14
2.00
2.00
3.02

4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

YA-SULFA-MS-CC/2
YA-SULFA-MS-CC / DMSO

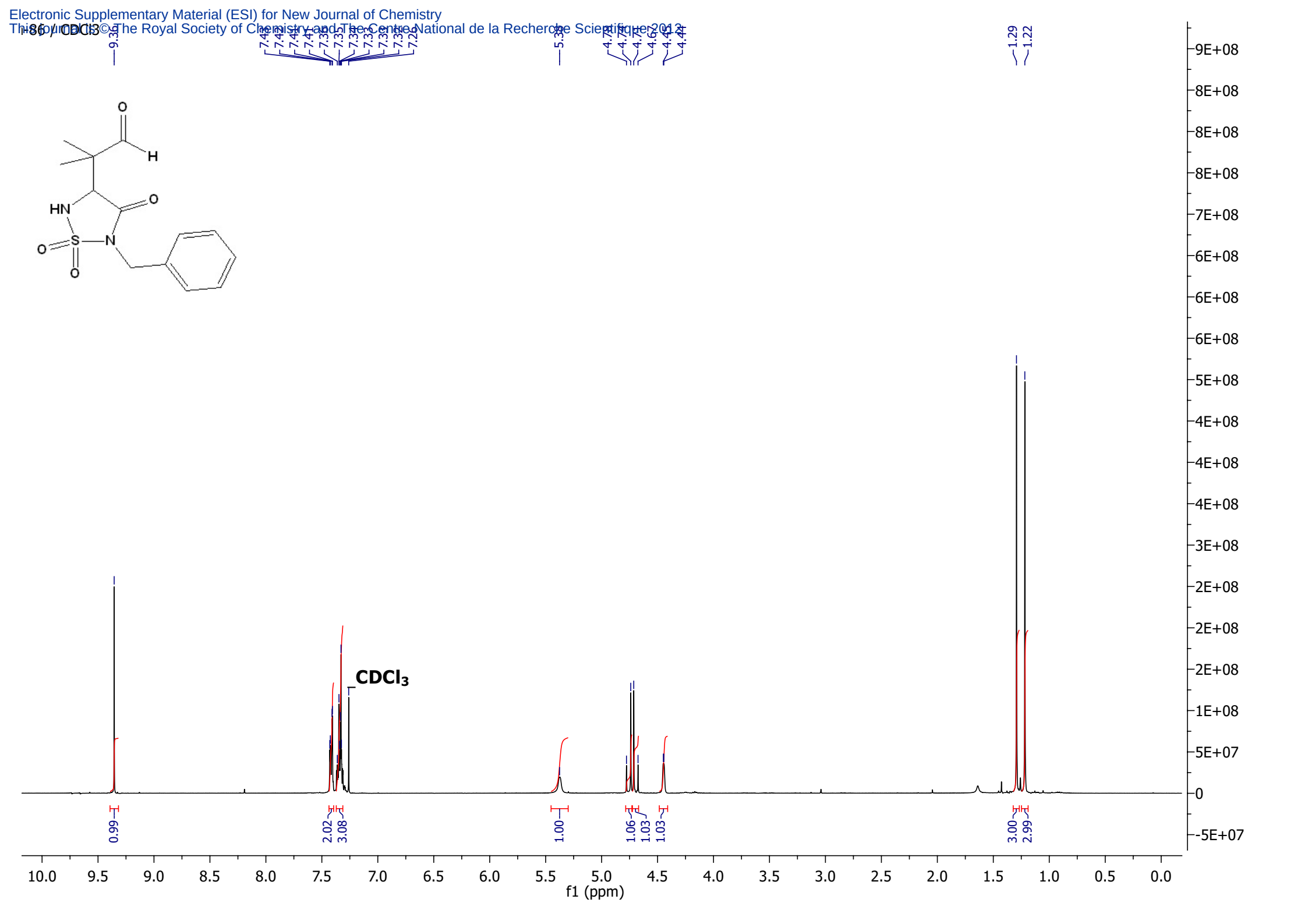


160.57
134.08
128.59
128.18
51.79
43.64
39.52
39.41

DMSO-d_6

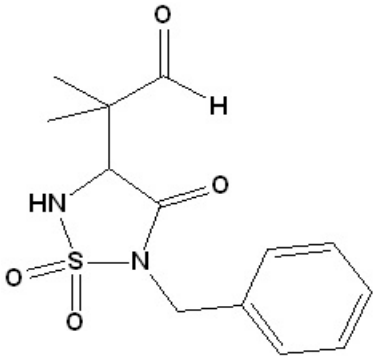
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

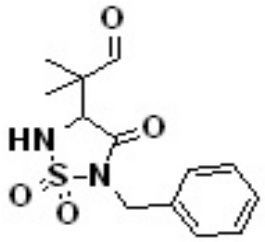


ya-86

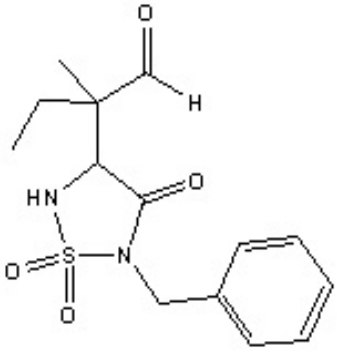
ya-86 / CDCl3

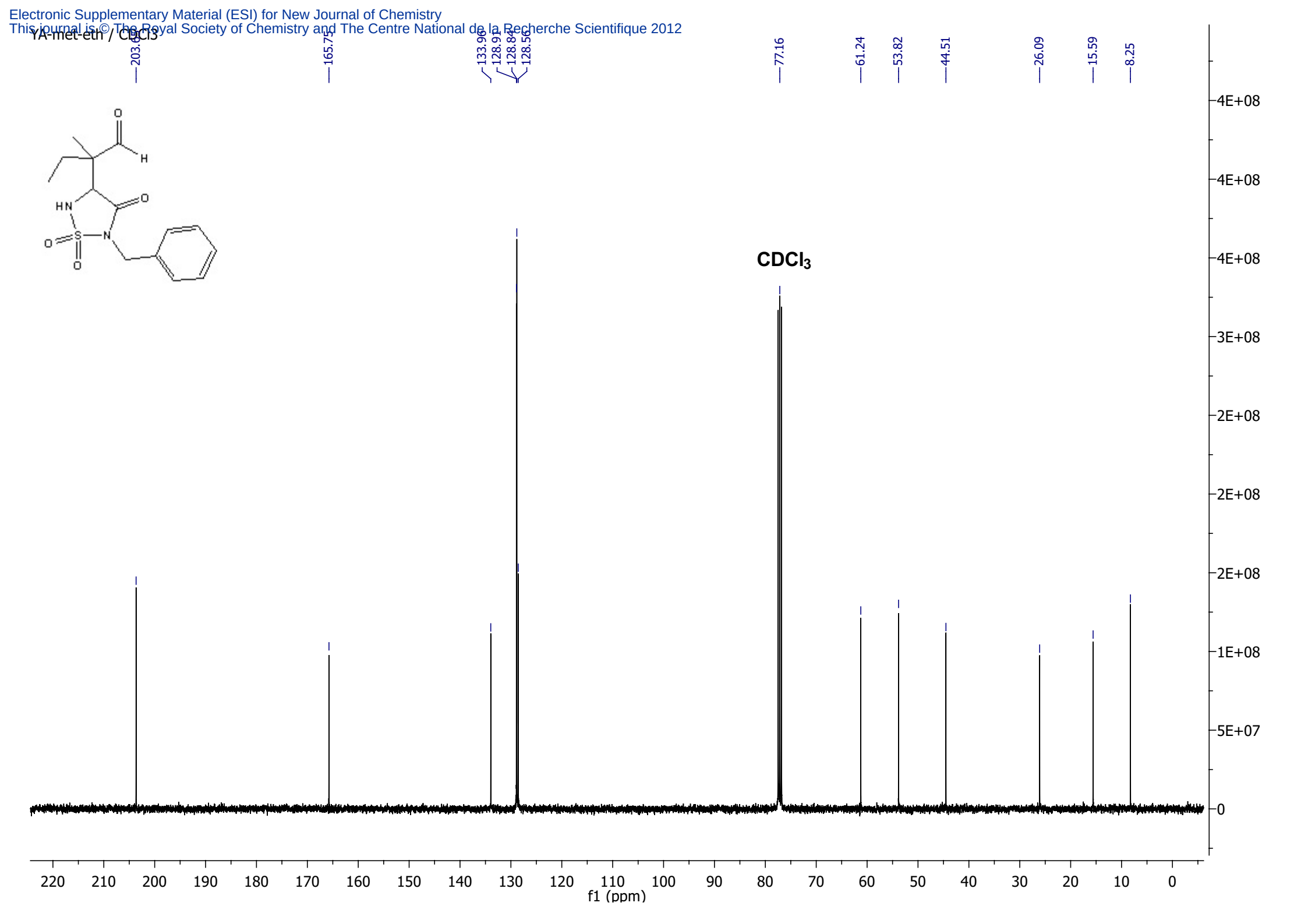


Electronic Supplementary Material (ESI) for New Journal of Chemistry

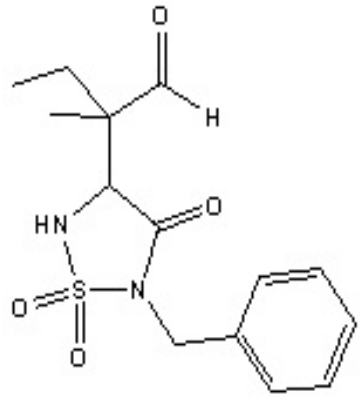


YA-met-eth / CDCl3

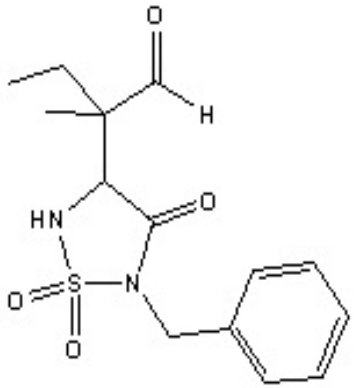


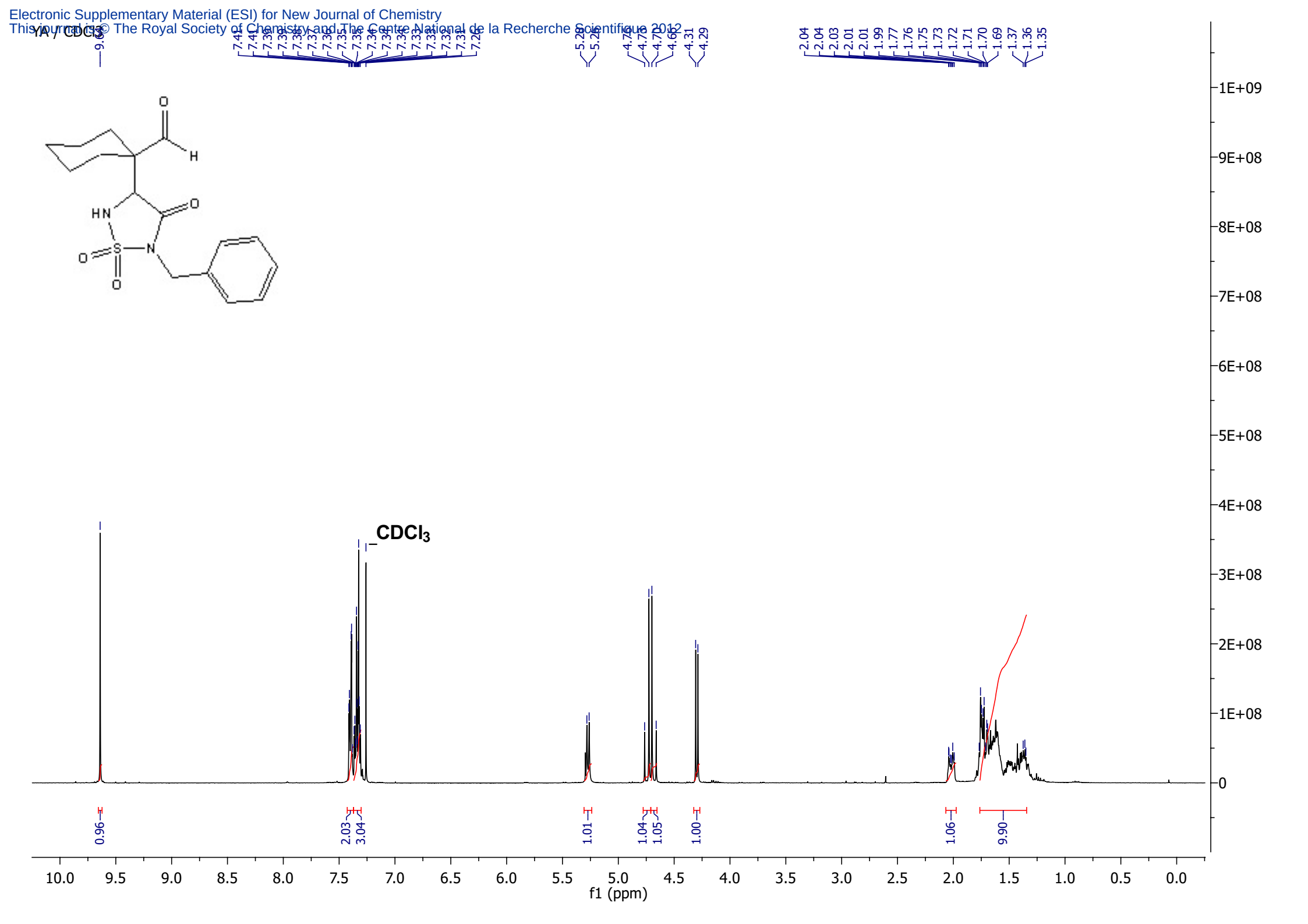


YA-cycloapp 1H
YA-cycloapp / CDCl3

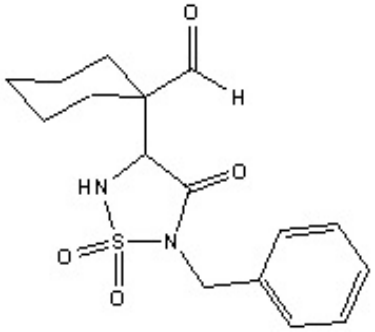


YA-cycloapp/13C

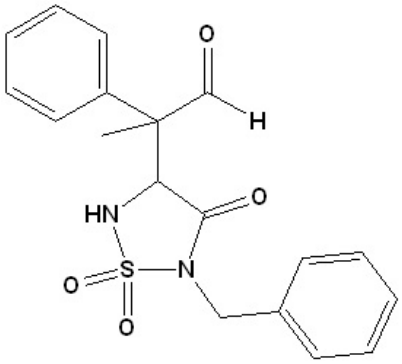




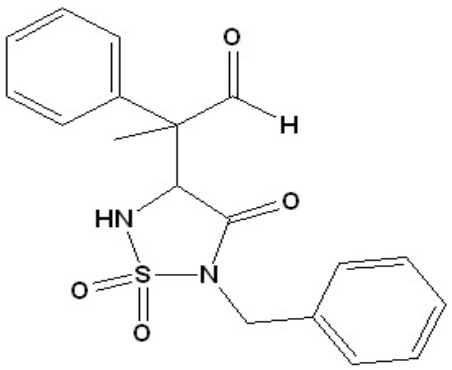
YA / CDCl3



YA arpp / CDCl3



YA arpp / CDCl3



199.34 198.76 165.05 164.85 133.90 133.59 133.16 129.31 129.12 128.98 128.88 128.84 128.79 128.67 128.55 128.47 128.41 128.22 128.03 77.16 64.19 63.97 57.61 57.33 44.38 43.97 15.83 13.73

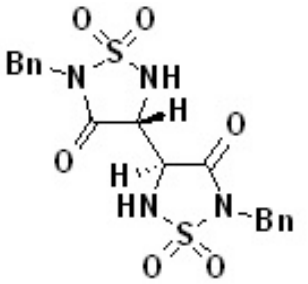
$CDCl_3$

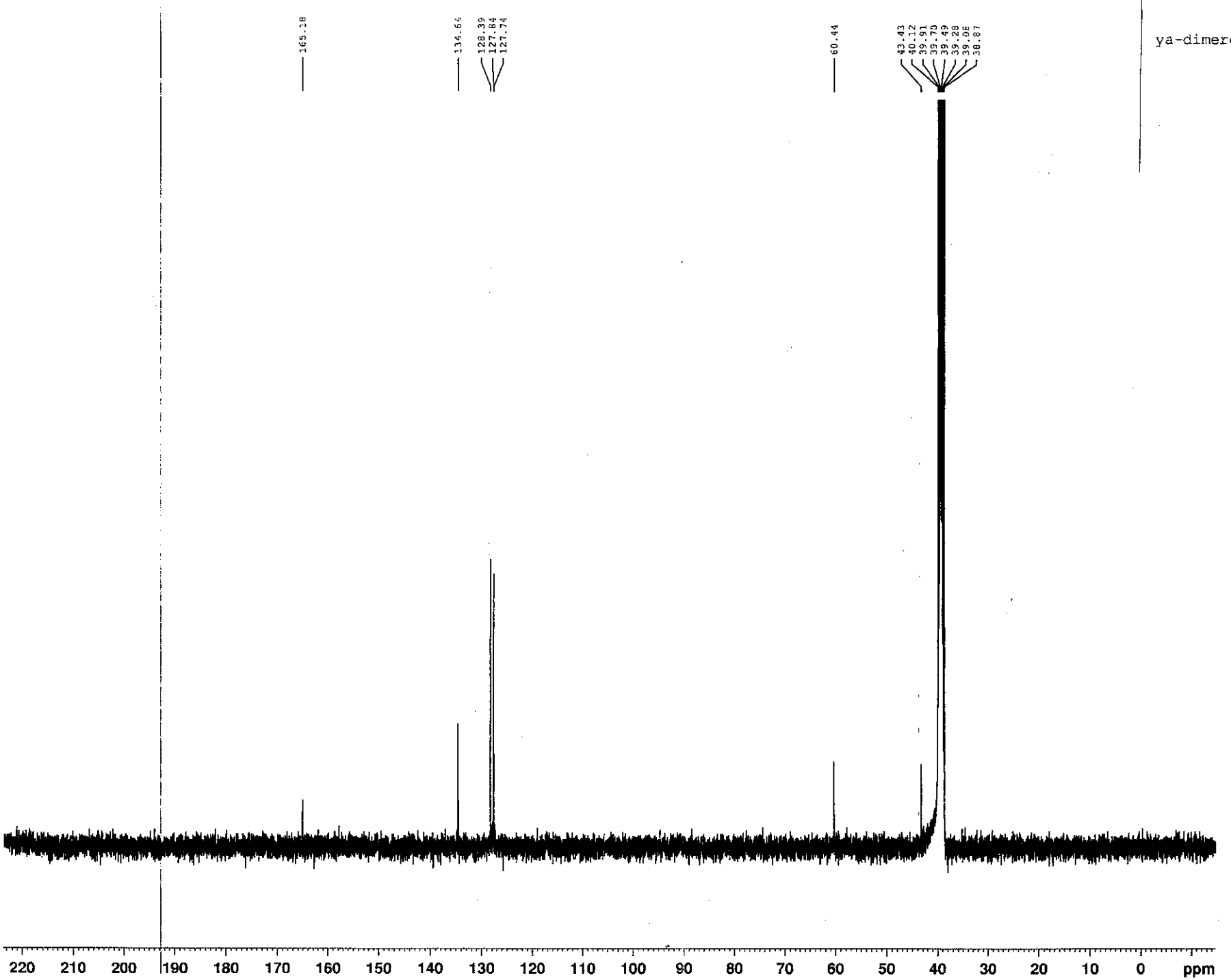
8E+08 8E+08 8E+08 7E+08 6E+08 6E+08 6E+08 5E+08 4E+08 4E+08 4E+08 3E+08 2E+08 2E+08 2E+08 1E+08 5E+07 0 -5E+07

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

ya-dimere
ya-dimere / DMSO





ya-dimere / DMSO

Current Data Parameters
NAME ya-dimere
EXPNO 30
PROCNO 1

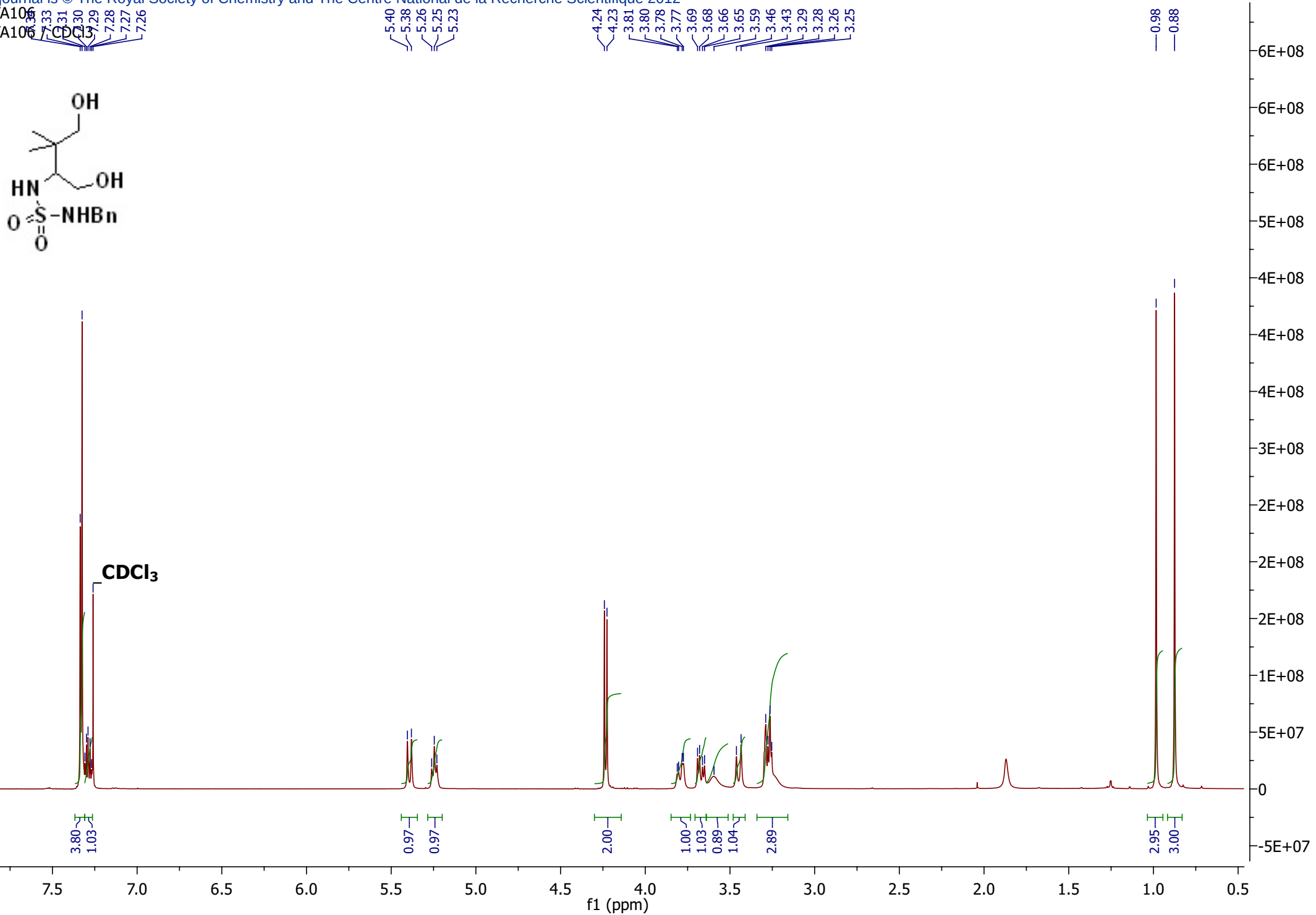
F2 - Acquisition Parameters
Date_ 20110414
Time 0.56
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 4096
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1149.4
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 3.00000000 sec
d11 0.03000000 sec
DELTA 2.90000010 sec
TD0 1

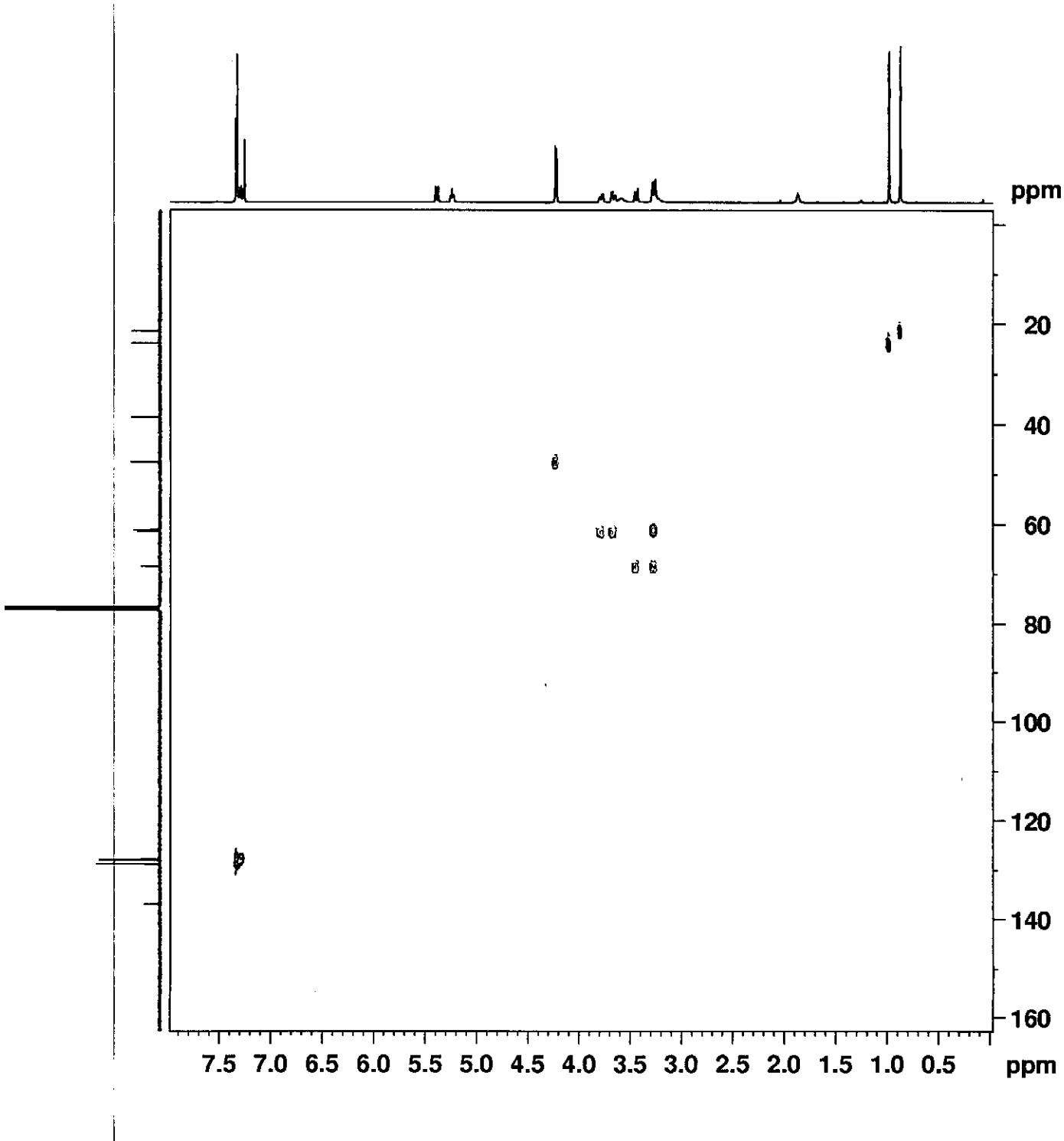
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 -3.00 dB
SFO1 100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.50 dB
PL12 15.22 dB
PL13 120.00 dB
SFO2 400.1316005 MHz

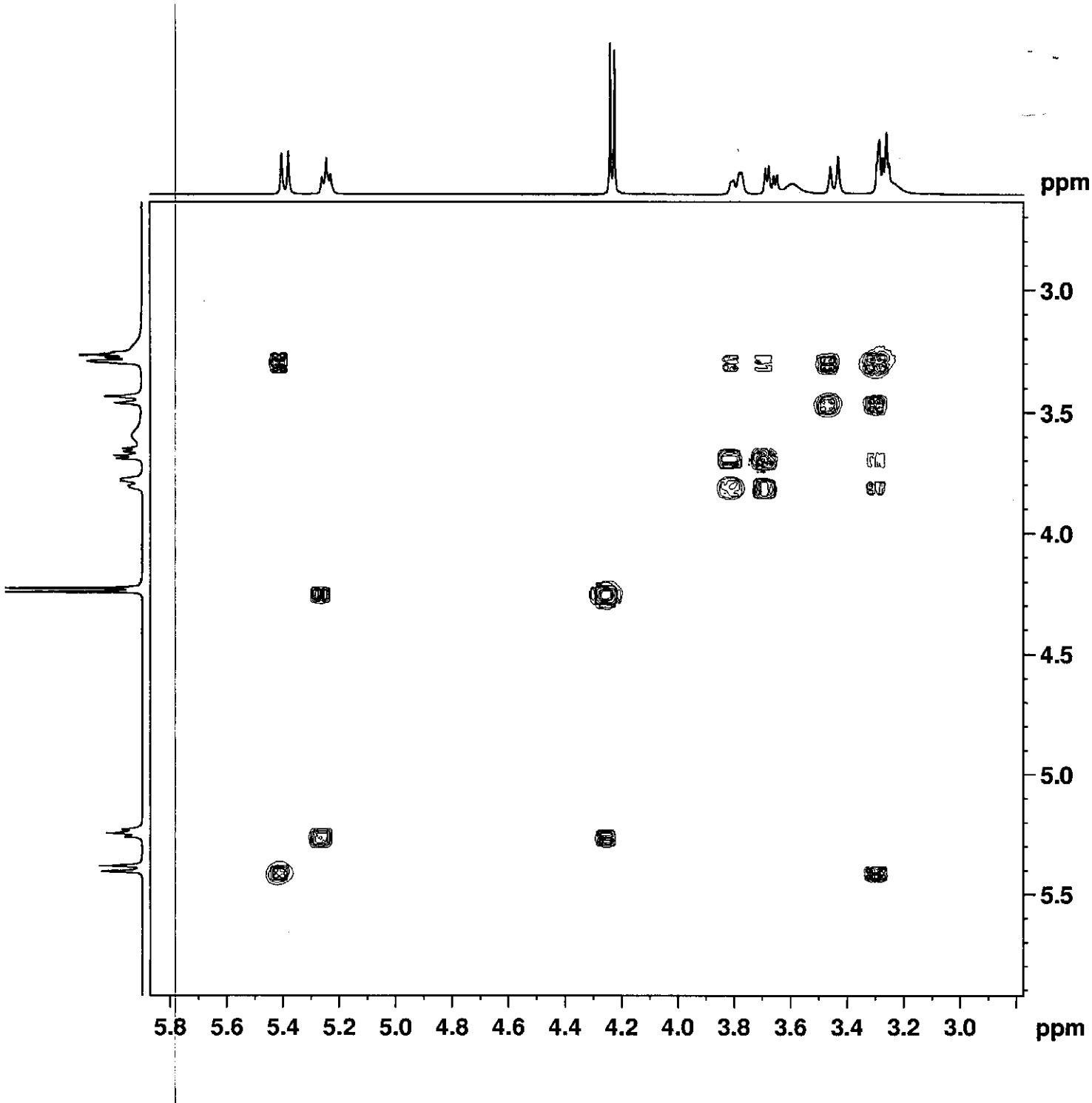
F2 - Processing parameters
SI 32768
SF 100.6128193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

YA106
YA106 / CDCl3





NAME	YA106	
EXPNO	3	
PROCNO	1	
Date_	20110608	
Time	14.04	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	hsqcedetgp	
TD	1024	
SOLVENT	CDCl3	
NS	16	
DS	16	
SWH	3205.128	Hz
FIDRES	3.130008	Hz
AQ	0.1597940	sec
RG	18390.4	
DW	156.000	usec
DE	6.50	usec
TE	296.1	K
CNST2	145.0000000	
D0	0.00000300	sec
D1	1.50000000	sec
D4	0.00172414	sec
D11	0.03000000	sec
D13	0.00000400	sec
D16	0.00020000	sec
D21	0.00345000	sec
IN0	0.00003000	sec
ZGOPTNS		
------- CHANNEL f1 -------		
NUC1	1H	
P1	8.00	usec
P2	16.00	usec
P28	500.00	usec
PL1	-5.00	dB
PL1W	31.45539856	W
SFO1	400.1316005	MHz
------- CHANNEL f2 -------		
CPDPRG2	garp	
NUC2	13C	
P3	9.00	usec
P4	18.00	usec
PCPD2	70.00	usec
PL2	-2.00	dB
PL12	15.82	dB
PL2W	50.55961227	W
PL12W	0.83522552	W
SFO2	100.6208180	MHz
------ GRADIENT CHANNEL -----		
GPNAM1	SINE.100	
GPNAM2	SINE.100	
GPZ1	80.00	%
GPZ2	20.10	%
P16	1000.00	usec
ND0	2	
TD	114	
SFO1	100.6208	MHz
FIDRES	146.199615	Hz
SW	165.639	ppm
FnMODE	Echo-Antiecho	
SI	1024	
SF	400.1300104	MHz
WDW	QSINE	
SSB	2	
LB	0.00	Hz
GB	0	
PC	4.00	
SI	1024	
MC2	echo-antiecho	
SF	100.6127690	MHz
WDW	QSINE	
SSB	2	
LB	0.00	Hz
GB	0	

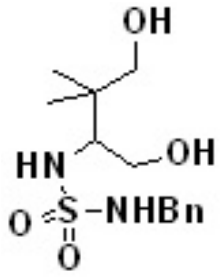


NAME	YA106
EXPNO	4
PROCNO	1
Date_	20110608
Time	14.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	cosygpqf
TD	2048
SOLVENT	CDCl3
NS	8
DS	8
SWH	3205.128 Hz
FIDRES	1.565004 Hz
AQ	0.3195380 sec
RG	64
DW	156.000 usec
DE	6.50 usec
TE	295.9 K
D0	0.00000300 sec
D1	1.48689198 sec
D13	0.00000400 sec
D16	0.00020000 sec
IN0	0.00031200 sec
======== CHANNEL f1 ========	
NUC1	1H
P0	8.00 usec
P1	8.00 usec
PL1	-5.00 dB
PL1W	31.45539856 W
SFO1	400.1316005 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
ND0	1
TD	95
SFO1	400.1316 MHz
FIDRES	33.738171 Hz
SW	8.010 ppm
FnMODE	QF
SI	1024
SF	400.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	4.00
SI	1024
MC2	QF
SF	400.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

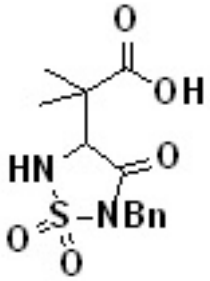
Electronic Supplementary Material (ESI) for New Journal of Chemistry

YA106

YA106 / CDCl3



ya109
YA-109 / MeOD



ya109
YA-109 / MeOD