Supporting Information

Near-Silence of Isothiocyanate-Carbon in ^{13}C-NMR Spectra. A Case Study of Allyl Isothiocyanate

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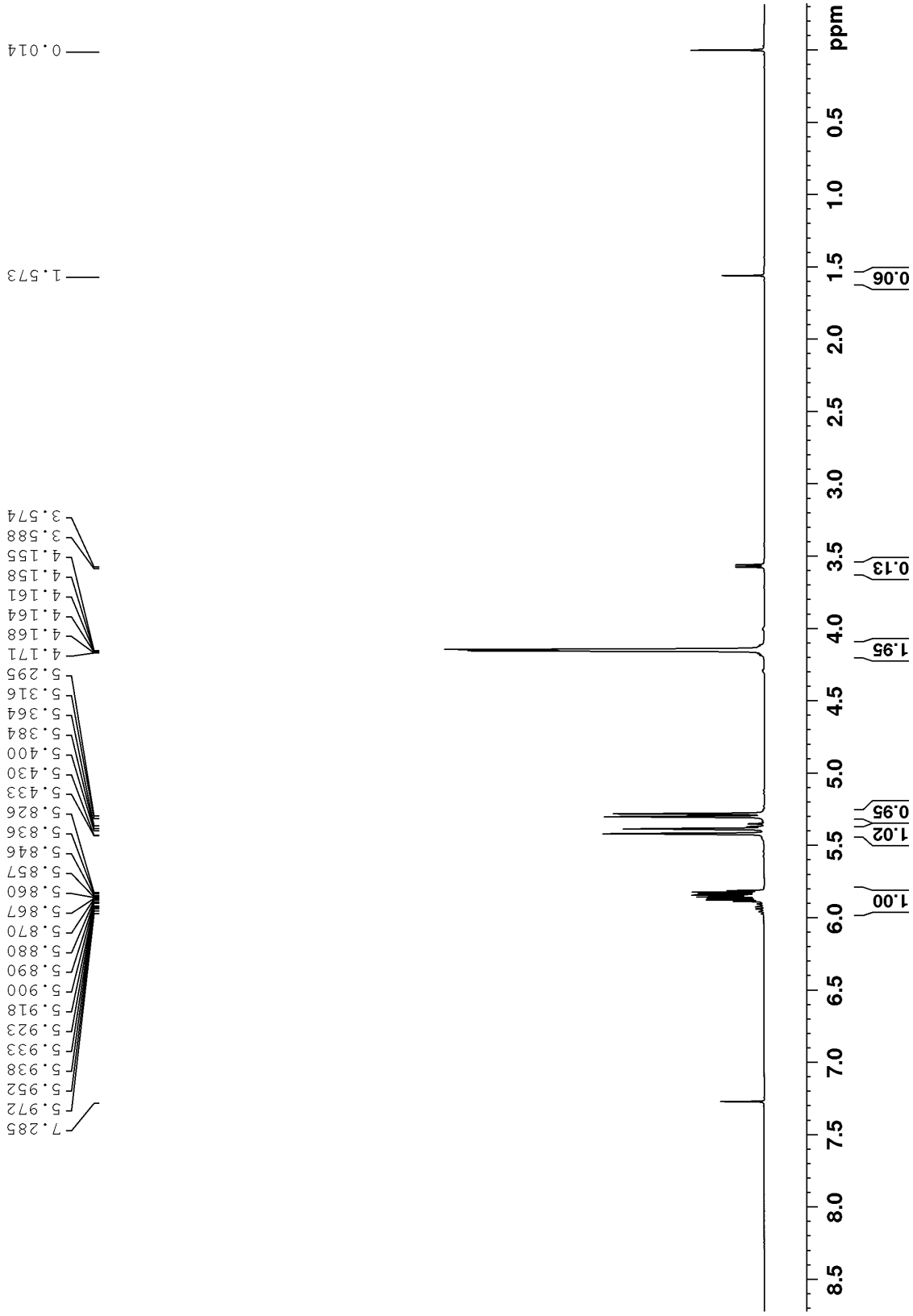
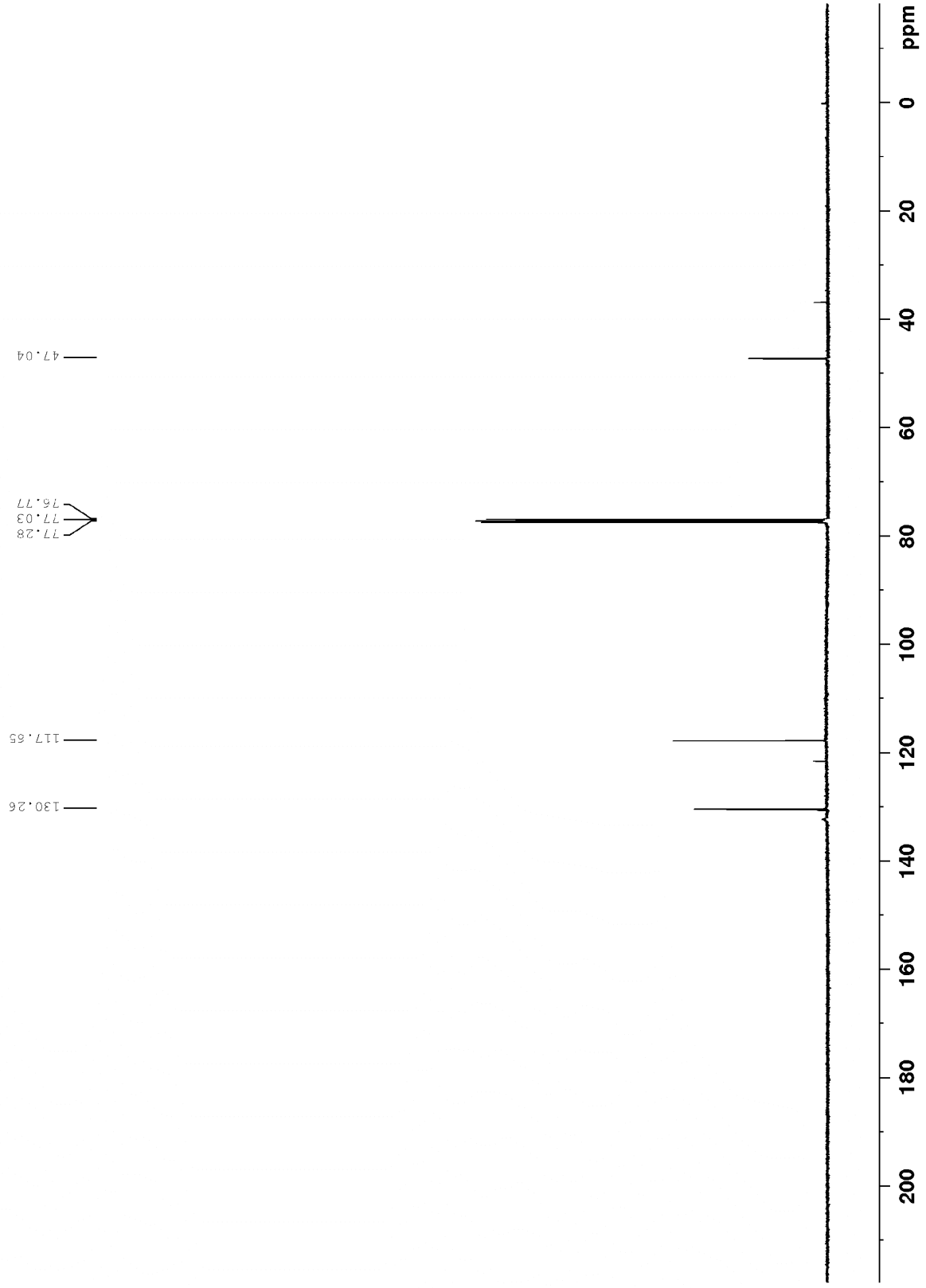
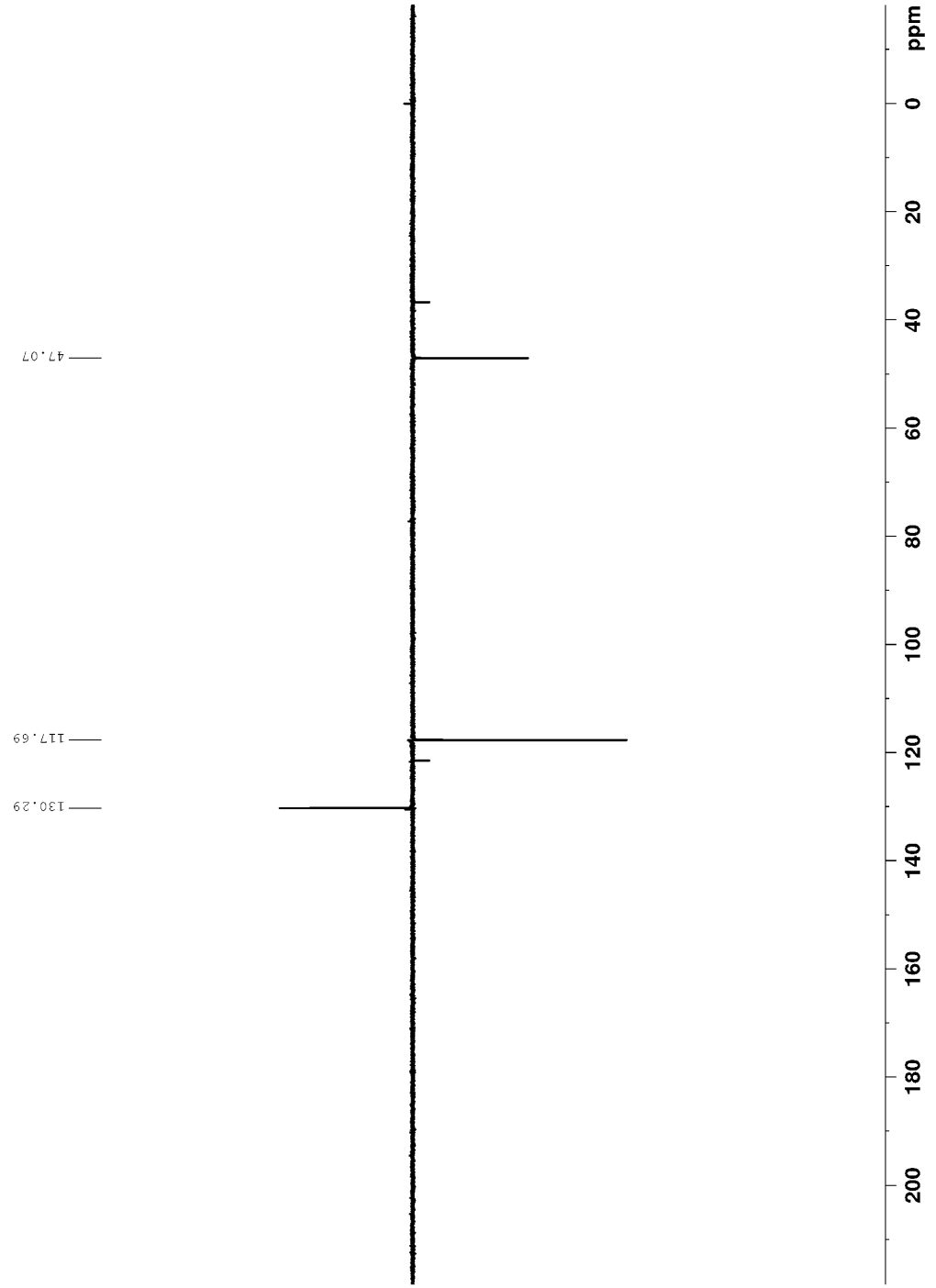
1H NMR of AITC in $CDCl_3$/TMS



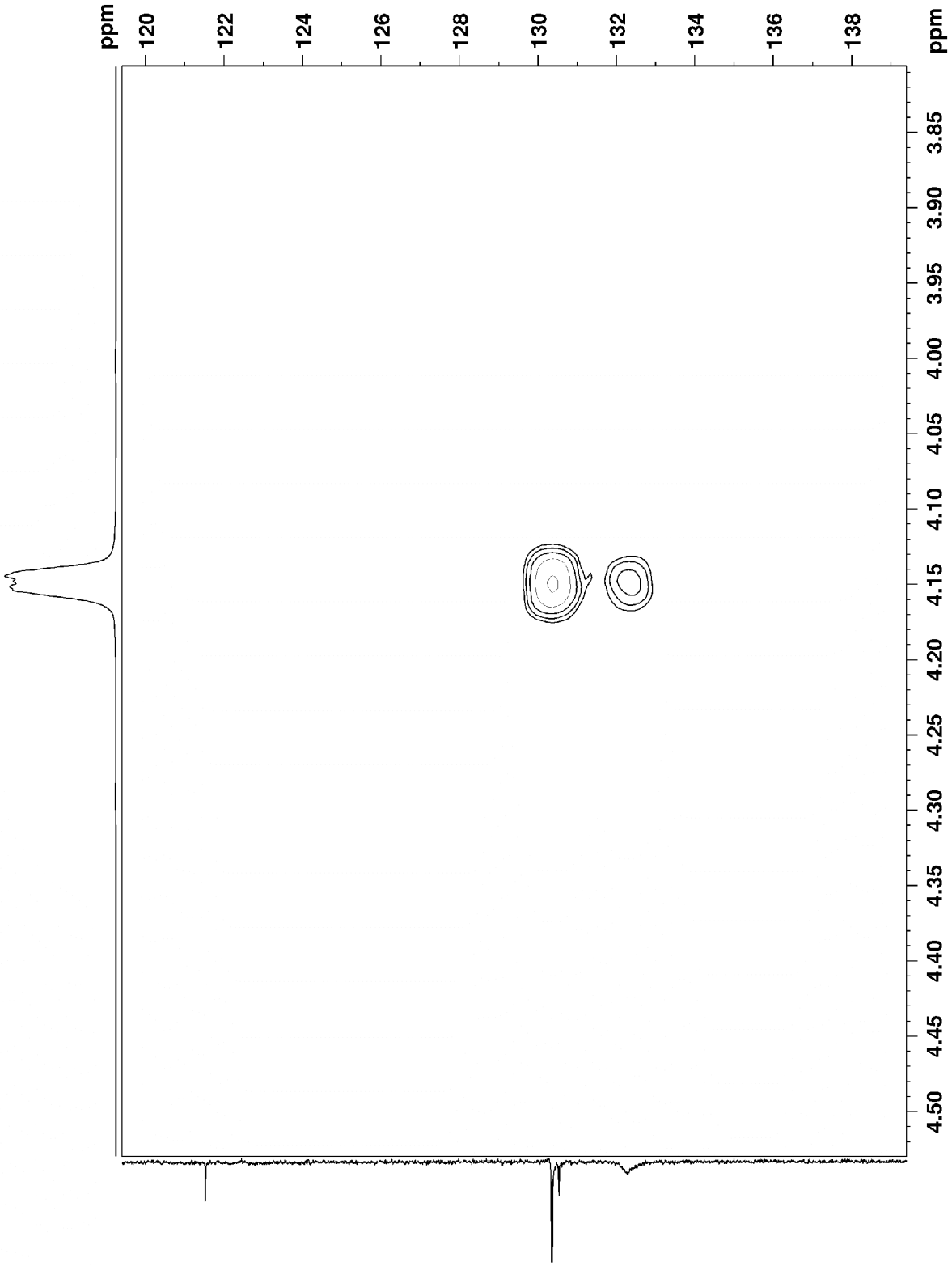
^{13}C NMR of AITC in $CDCl_3$/TMS



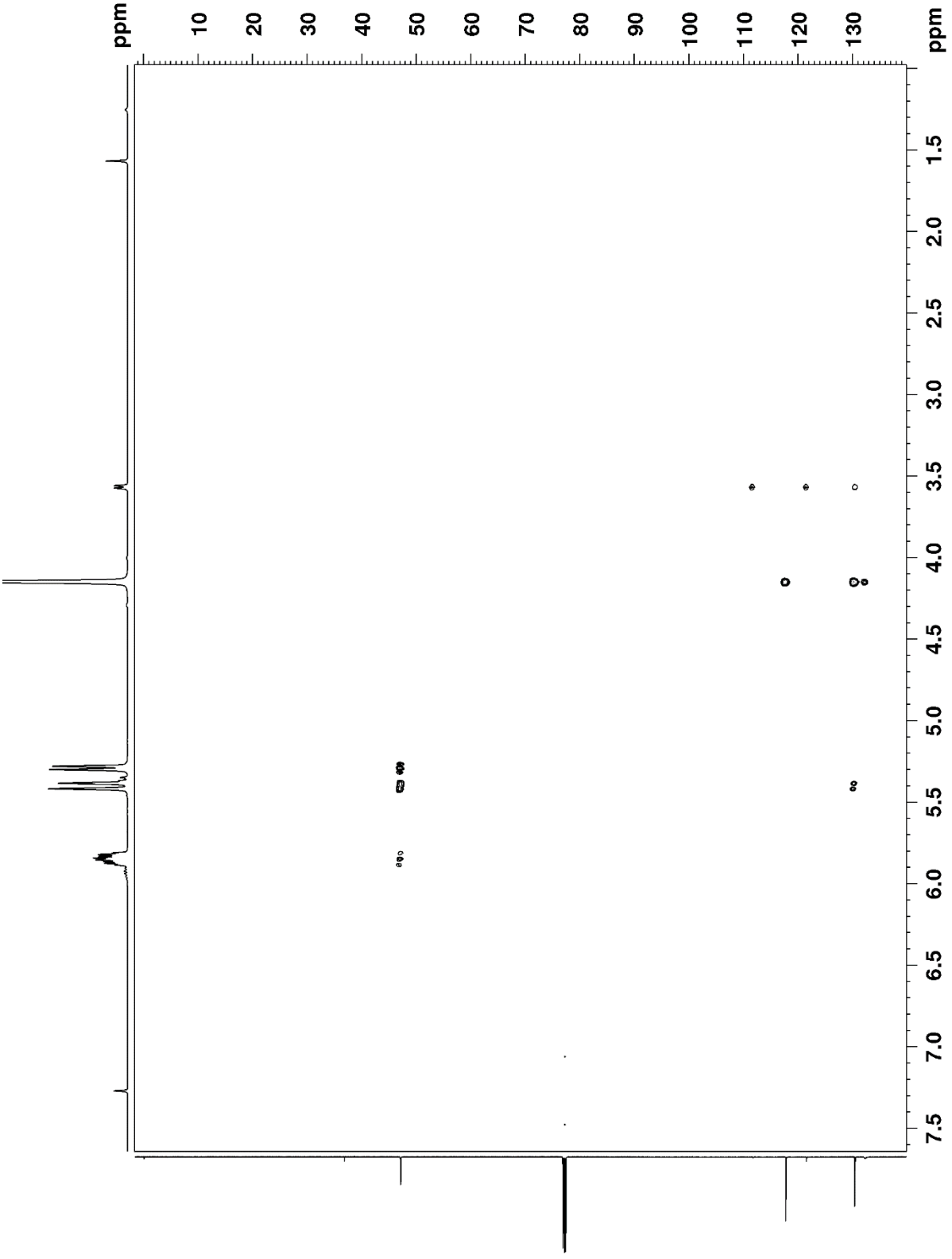
DEPT135 of AITC in $CDCl_3$/TMS



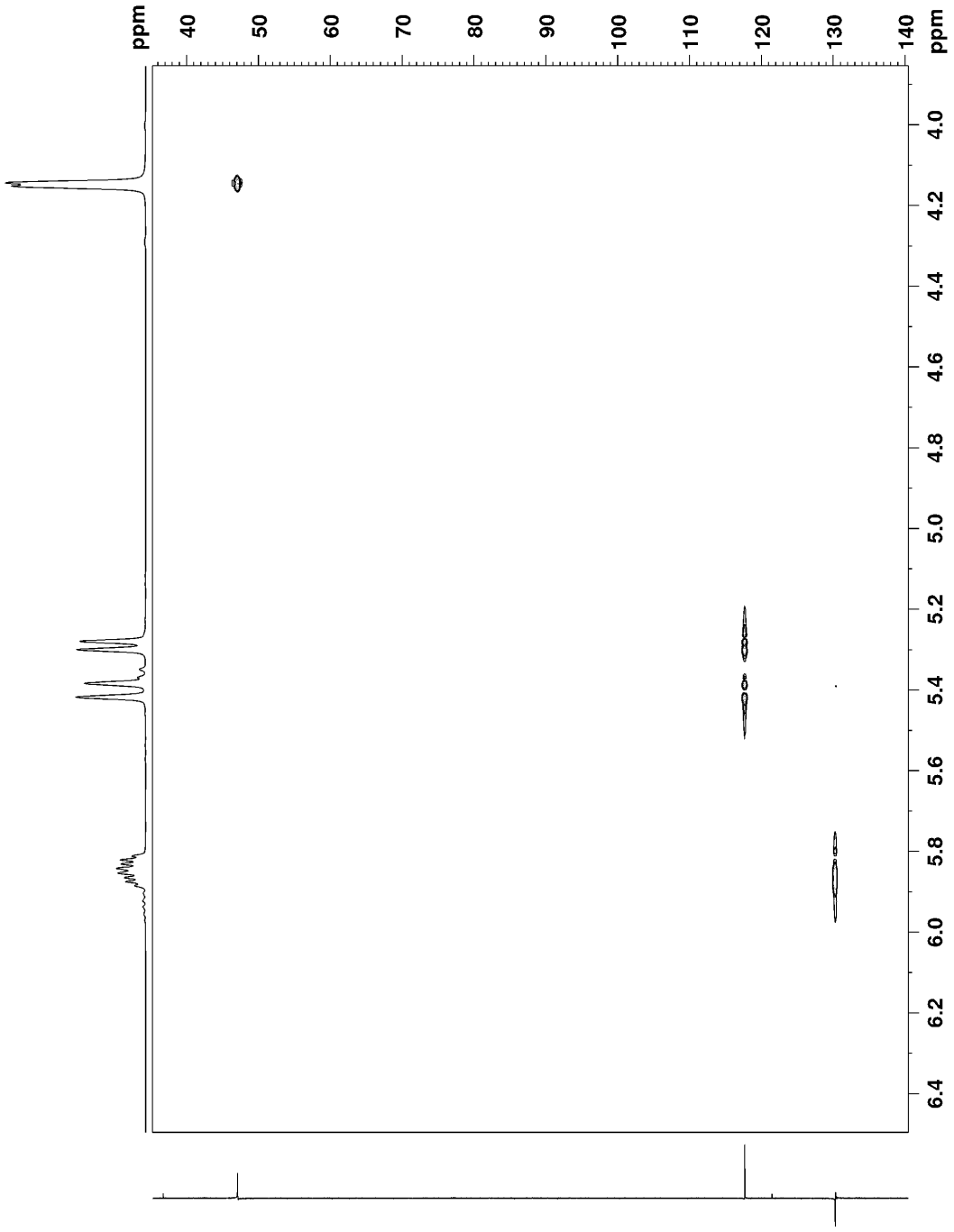
HMBC of AITC in $CDCl_3$/TMS (1/2)



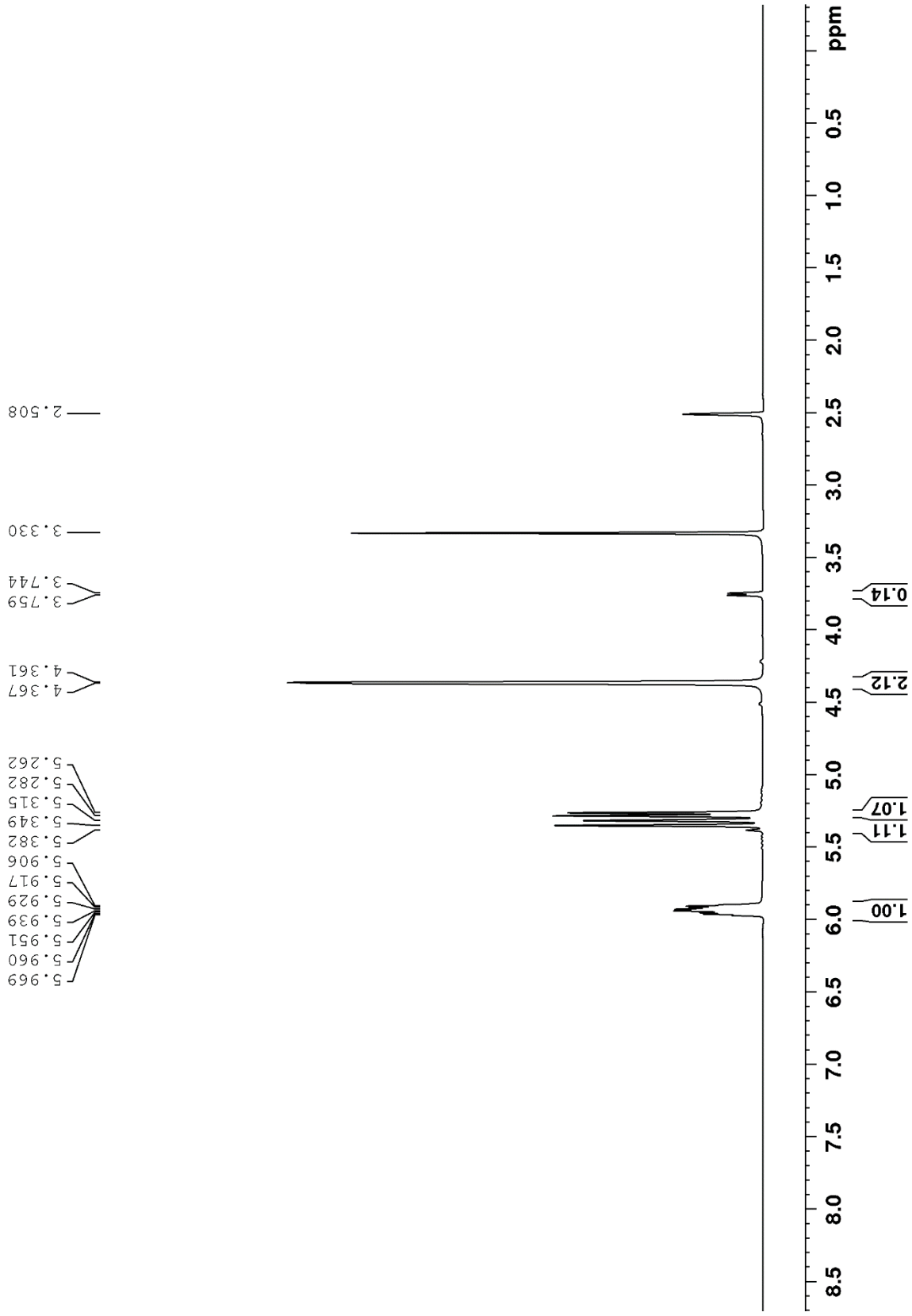
HMBC of AITC in $CDCl_3$/TMS (2/2)



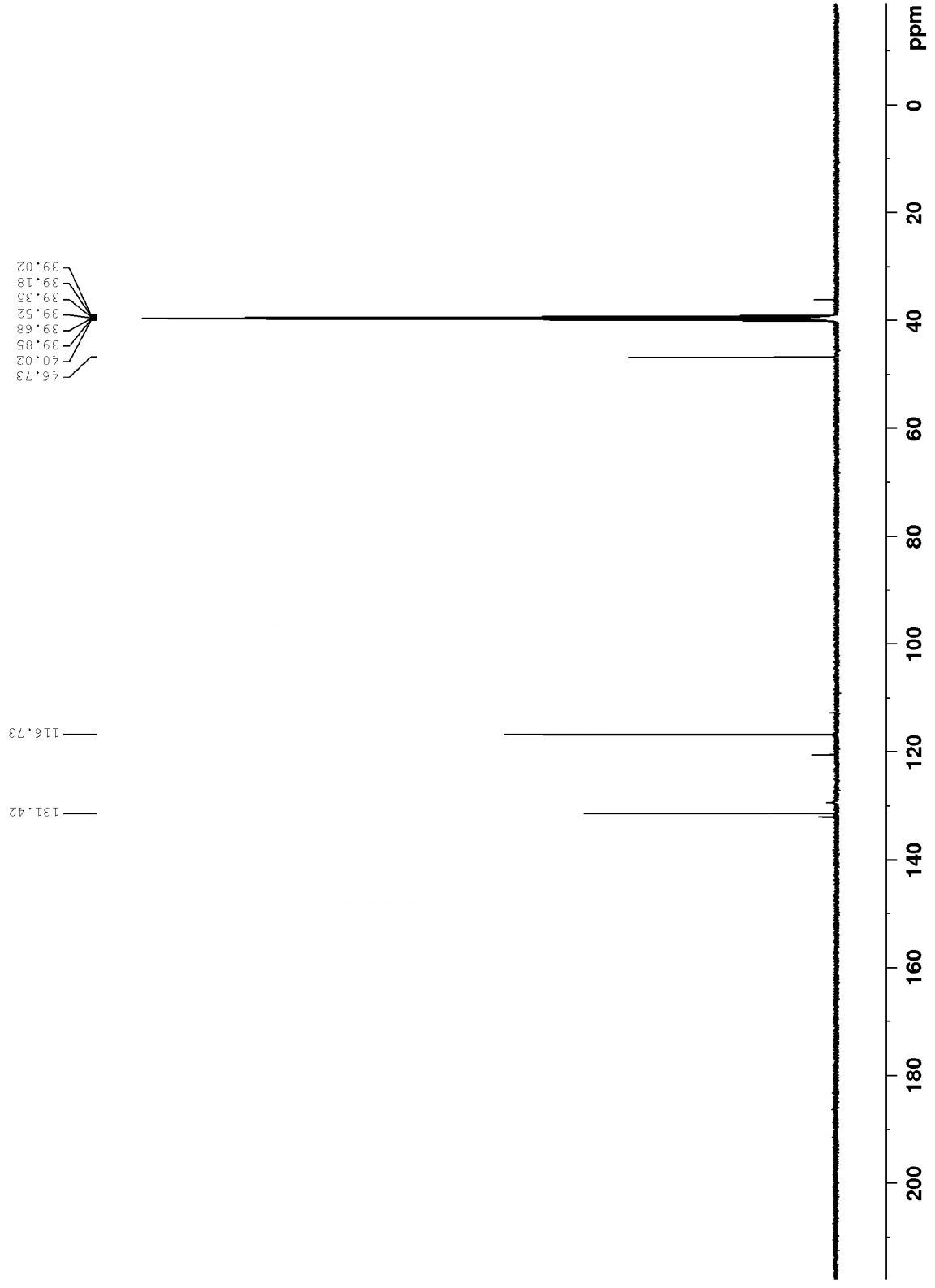
HSQC of AITC in $CDCl_3$/TMS



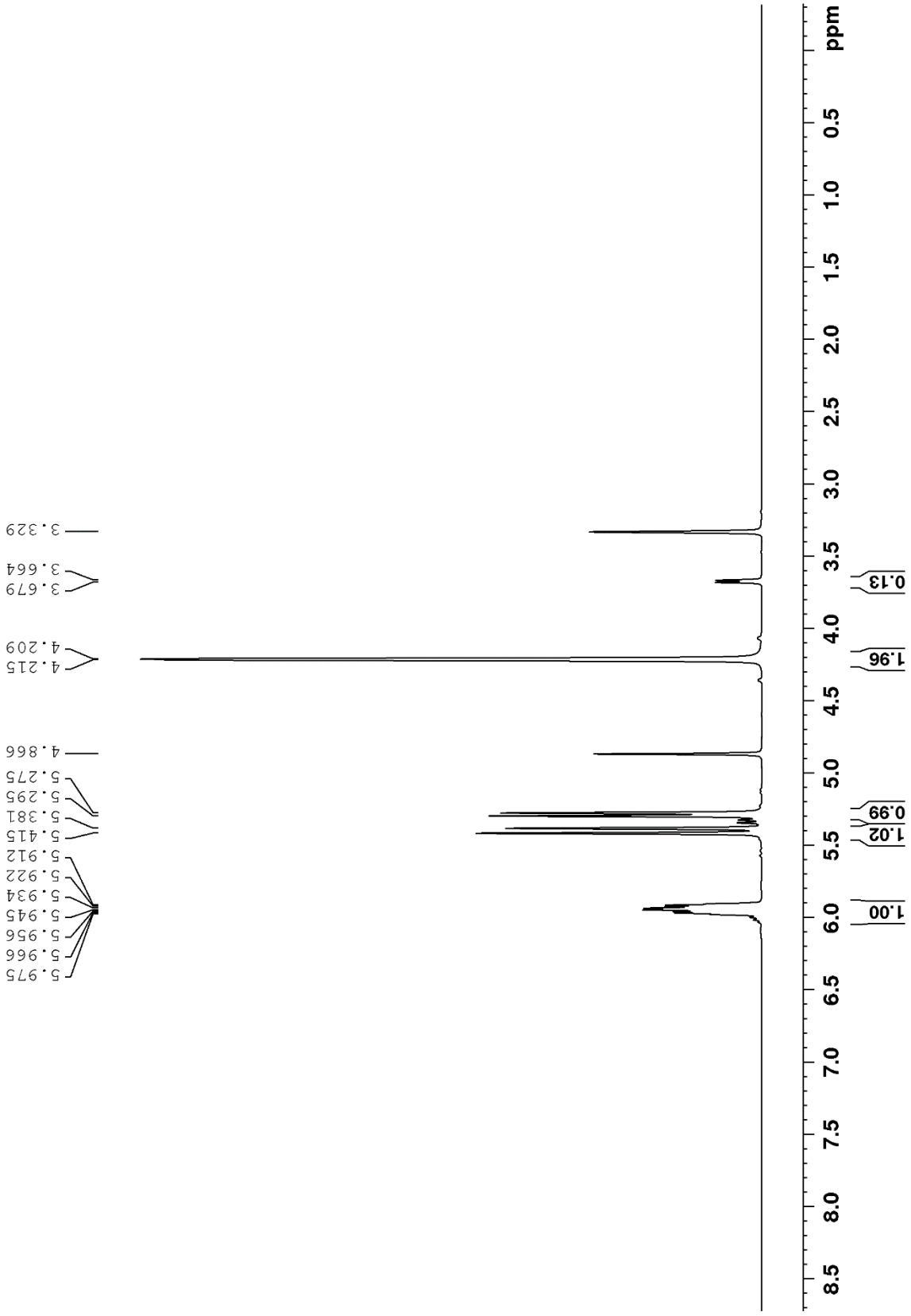
^{1}H NMR of AITC in DMSO-d_6



^{13}C NMR of AITC in DMSO-d_6



^{1}H NMR of AITC in CD_3OD



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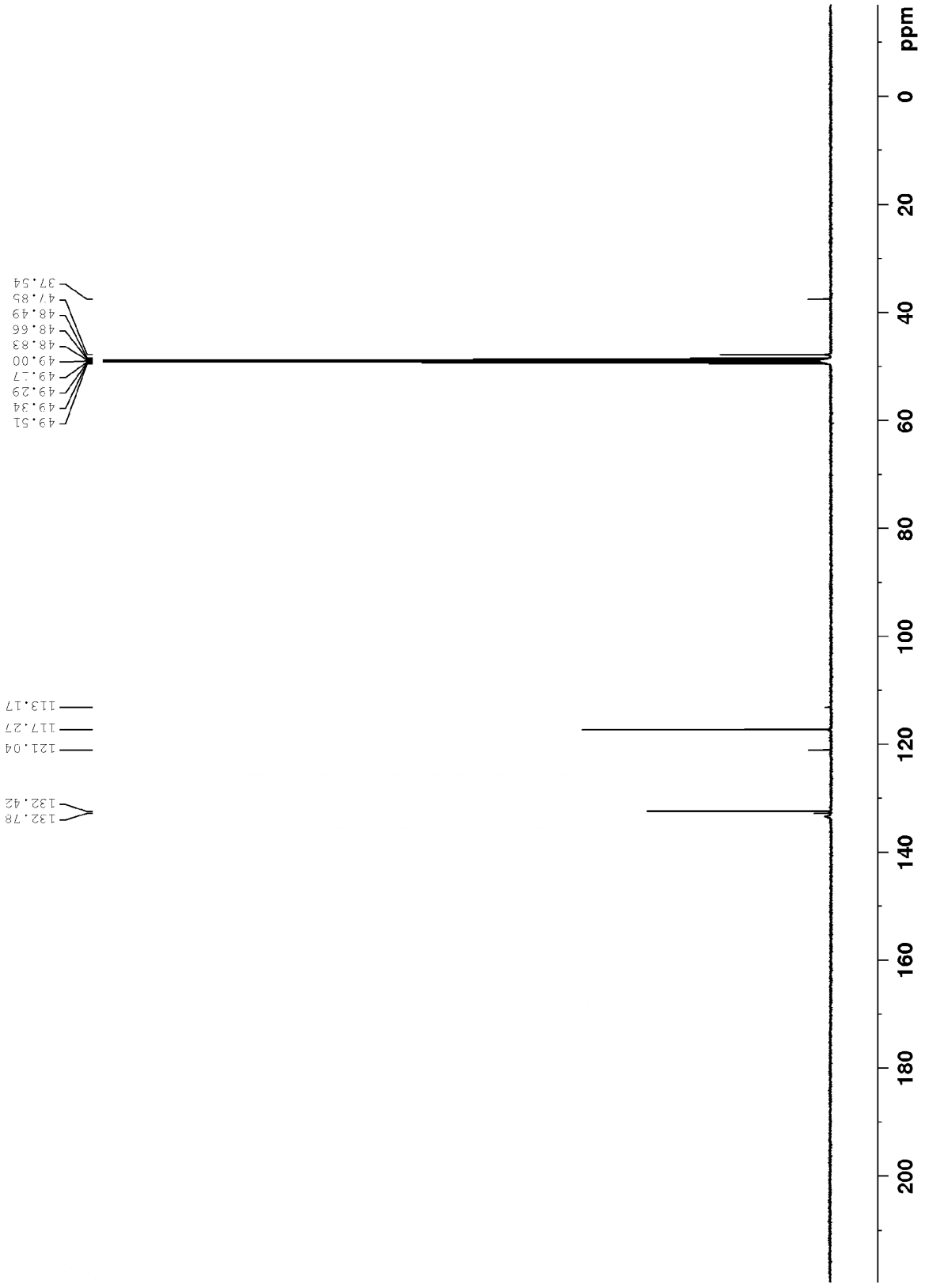

Cartesian Coordinates of Computed Structures of AITC

Unless otherwise noted, the structures were optimized at B3LYP/6-311G(d,p).

M1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.598690	-1.115260	0.000000
2	1	0	1.714170	-1.742050	0.000000
3	1	0	3.562179	-1.610277	0.000000
4	6	0	2.506608	0.207863	0.000000
5	1	0	3.402211	0.823930	0.000000
6	6	0	1.223779	0.995562	0.000000
7	1	0	1.193368	1.651135	-0.880166
8	1	0	1.193368	1.651135	0.880166
9	16	0	-2.704366	-0.160171	0.000000
10	7	0	0.051173	0.172145	0.000000
11	6	0	-1.131981	0.073975	0.000000

M1-120

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.599275	1.522826	0.000000
2	1	0	1.728058	2.167894	0.000000
3	1	0	3.574239	1.995280	0.000000
4	6	0	2.474818	0.202118	0.000000
5	1	0	3.358208	-0.432664	0.000000
6	6	0	1.176901	-0.551661	0.000000
7	1	0	1.123996	-1.200939	0.881794
8	1	0	1.123996	-1.200939	-0.881794
9	16	0	-2.607066	-0.632071	0.000000
10	7	0	0.000000	0.348637	0.000000
11	6	0	-1.116900	-0.115941	0.000000

M1 at 6-31G**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.843115	-0.087863	0.000000
2	1	0	-2.248692	-0.996253	0.000000
3	1	0	-3.922426	-0.197439	0.000000
4	6	0	-2.272572	1.113328	0.000000
5	1	0	-2.880644	2.016281	0.000000

6	6	0	-0.789222	1.377961	0.000000
7	1	0	-0.520036	1.979648	0.880529
8	1	0	-0.520036	1.979648	-0.880529
9	16	0	2.443551	-1.150963	0.000000
10	7	0	0.000000	0.182390	0.000000
11	6	0	1.070747	-0.343962	0.000000

M2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.937348	-0.857591	-0.274744
2	1	0	3.369389	-0.344376	-1.128380
3	1	0	3.373274	-1.813080	-0.007297
4	6	0	1.925513	-0.340851	0.411840
5	1	0	1.499717	-0.875559	1.256946
6	6	0	1.299625	0.993644	0.101155
7	1	0	1.772564	1.446960	-0.773580
8	1	0	1.438400	1.687634	0.938604
9	16	0	-2.550484	-0.431903	-0.016074
10	7	0	-0.115597	0.896771	-0.147653
11	6	0	-1.135223	0.293378	-0.070842

M2-120

Center Number	Atomi Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.109934	-0.560331	-0.196559
2	1	0	3.699334	0.338082	-0.351943
3	1	0	3.613233	-1.507703	-0.351071
4	6	0	1.834320	-0.503003	0.168657
5	1	0	1.262638	-1.417442	0.308265
6	6	0	1.093774	0.777894	0.427393
7	1	0	1.742347	1.634501	0.243128
8	1	0	0.750205	0.825862	1.465375
9	16	0	-2.495266	-0.404856	0.051364
10	7	0	-0.094940	0.913281	-0.468004
11	6	0	-1.117847	0.320679	-0.209416

M2 at 6-31G**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.892939	-0.904725	-0.271986
2	1	0	3.285499	-0.466085	-1.186076
3	1	0	3.328653	-1.847722	0.042823
4	6	0	1.928884	-0.314525	0.430772

5	1	0	1.542985	-0.774344	1.338882
6	6	0	1.310697	1.007759	0.053734
7	1	0	1.745030	1.384275	-0.878919
8	1	0	1.511873	1.762173	0.825981
9	16	0	-2.538638	-0.443008	-0.020209
10	7	0	-0.117604	0.930652	-0.108726
11	6	0	-1.127954	0.297367	-0.055566

CTS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.984958	1.381490	0.216015
2	1	0	1.348335	1.520404	1.084484
3	1	0	2.482432	2.264265	-0.167887
4	6	0	2.137806	0.197207	-0.364046
5	1	0	2.773871	0.099039	-1.238761
6	6	0	1.465416	-1.078701	0.113869
7	1	0	1.785621	-1.323428	1.132490
8	1	0	1.759882	-1.921196	-0.515756
9	16	0	-2.375837	0.362681	-0.066225
10	7	0	0.028205	-1.014467	0.113996
11	6	0	-0.977209	-0.390114	0.028672

CTS-120

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.601062	1.117641	0.056016
2	1	0	2.349191	1.551612	1.018790
3	1	0	3.299378	1.671045	-0.561069
4	6	0	2.082967	-0.037354	-0.346774
5	1	0	2.340063	-0.447793	-1.319533
6	6	0	1.134362	-0.860263	0.476131
7	1	0	0.914325	-0.369600	1.427018
8	1	0	1.571558	-1.839459	0.688014
9	16	0	-2.372603	0.514285	0.017922
10	7	0	-0.132576	-1.117100	-0.272498
11	6	0	-1.082531	-0.382469	-0.124120

ETS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.027540	-1.251294	0.000000
2	1	0	-3.882422	-0.581217	0.000000
3	1	0	-3.242769	-2.313001	0.000000

4	6	0	-1.778224	-0.804014	0.000000
5	1	0	-0.944039	-1.498913	0.000000
6	6	0	-1.413452	0.669992	0.000000
7	1	0	-1.835946	1.170414	0.877692
8	1	0	-1.835946	1.170414	-0.877692
9	16	0	2.647154	0.064516	0.000000
10	7	0	0.000000	0.902420	0.000000
11	6	0	1.116992	0.502502	0.000000

ETS1-120

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.262805	-2.948853	0.000000
2	1	0	-1.216197	-3.469653	0.000000
3	1	0	0.627367	-3.566405	0.000000
4	6	0	-0.179539	-1.623633	0.000000
5	1	0	0.796732	-1.148988	0.000000
6	6	0	-1.390585	-0.719579	0.000000
7	1	0	-2.016405	-0.921907	0.874311
8	1	0	-2.016405	-0.921907	-0.874311
9	16	0	1.423963	1.847694	0.000000
10	7	0	-1.137275	0.746745	0.000000
11	6	0	0.000000	1.165154	0.000000

ETS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.330937	-2.722461	0.000000
2	1	0	1.726865	-3.625324	0.000000
3	1	0	3.405494	-2.857760	0.000000
4	6	0	1.790717	-1.510279	0.000000
5	1	0	2.417632	-0.624260	0.000000
6	6	0	0.298545	-1.251144	0.000000
7	1	0	-0.167768	-1.703915	0.882537
8	1	0	-0.167768	-1.703915	-0.882537
9	16	0	-1.806233	2.261736	0.000000
10	7	0	0.000000	0.153702	0.000000
11	6	0	-0.805988	1.025797	0.000000

ETS2-120

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.391273	-0.919982	0.000000
2	1	0	3.267593	-1.999364	0.000000

3	1	0	4.409080	-0.549163	0.000000
4	6	0	2.355891	-0.089091	0.000000
5	1	0	2.510620	0.985561	0.000000
6	6	0	0.911559	-0.529879	0.000000
7	1	0	0.694982	-1.137259	0.884312
8	1	0	0.694982	-1.137259	-0.884312
9	16	0	-2.771074	0.356914	0.000000
10	7	0	0.000000	0.642610	0.000000
11	6	0	-1.198734	0.477050	0.000000

SOSP1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.275087	-1.112436	0.000000
2	1	0	-1.299088	-1.583873	0.000000
3	1	0	-3.138891	-1.765964	0.000000
4	6	0	-2.417295	0.205862	0.000000
5	1	0	-3.407592	0.654577	0.000000
6	6	0	-1.297962	1.219260	0.000000
7	1	0	-1.394839	1.871044	0.877834
8	1	0	-1.394839	1.871044	-0.877834
9	16	0	2.511890	-0.524931	0.000000
10	7	0	0.000000	0.652816	0.000000
11	6	0	1.064512	0.151041	0.000000

SOSP2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.262822	-0.595873	-0.303234
2	1	0	-3.468581	-0.155967	-1.274294
3	1	0	-3.951747	-1.357204	0.043194
4	6	0	-2.220727	-0.221014	0.427853
5	1	0	-2.024644	-0.680164	1.392762
6	6	0	-1.251738	0.858159	0.010706
7	1	0	-1.322164	1.711990	0.696323
8	1	0	-1.496903	1.221780	-0.992182
9	16	0	2.785704	-0.280486	-0.046530
10	7	0	0.095970	0.398498	0.019738
11	6	0	1.238785	0.118371	-0.011906

TOSP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.197325	-1.403146	0.000000

2	1	0	-3.987129	-0.657426	0.000000
3	1	0	-3.508757	-2.440503	0.000000
4	6	0	-1.912501	-1.072048	0.000000
5	1	0	-1.141883	-1.836109	0.000000
6	6	0	-1.416176	0.364495	0.000000
7	1	0	-1.793830	0.896592	0.880466
8	1	0	-1.793830	0.896592	-0.880466
9	16	0	2.770712	0.598588	0.000000
10	7	0	0.000000	0.450675	0.000000
11	6	0	1.175008	0.512152	0.000000

Table S6. NMR Computations for **M1** of **AITC**

Parameter	**M1**	**M1**	**M1**	**M1**
Solvent	none	$CDCl_3$	CD_3OD	DMSO
ε^c		4.7133	32.613	46.826
E(OPT)[d]	-608.423444			
E(SMD)[e]	-608.435643	-608.444550	-608.443153	-608.442155
$\delta(H_a)$	5.83	6.15	6.29	6.30
$\delta(H_b)$	5.36	5.43	6.79	5.44
$\delta(H_c)$	5.76	5.71	5.67	5.67
$\delta(H_{d,e})$	4.49	4.75	4.86	4.86
δ(C1)	119.49	117.34	116.14	116.06
δ(C2)	138.15	140.85	142.36	142.46
δ(C3)	50.16	50.79	51.10	51.12
δ(N4)	106.29	113.37	115.91	116.05
δ(C5)	144.39	143.00	142.54	142.52
δ(S6)	713.05	724.22	727.75	727.95

(a) Chemical shifts computed at GIAO(SMD(B3LYP/6-311+G(2d,p))//B3LYP/6-311G(d,p) and given in ppm.

(b) C-Shifts relative to TMS (shielding: 182.47 ppm) and N-shifts relative to NH_3 (shielding: 258.4 ppm). Isotropic shieldings are given for S.

(c) Dielectric constant of solvent.

(d) Energy computed at B3LYP/6-311G(d,p)) in hartrees.

(e) Energy computed at SMD(B3LYP/6-311+G(2d,p))//B3LYP/6-311G(d,p) in hartrees.

Table S7. NMR Computations for **M2** of **AITC**

Parameter	**M2**	**M2**	**M2**	**M2**
Solvent	none	$CDCl_3$	CD_3OD	DMSO
ε^c		4.7133	32.613	46.826
$E(OPT)^d$	-608.4229679			
$E_{rel}(OPT)^e$	0.30			
$E(SMD)^f$	-608.4352285	-608.444182	-608.443230	-608.441684
$E_{rel}(SMD)^g$	0.26	0.23	-0.05	0.30
$\delta(H_a)$	6.36	6.53	6.60	6.61
$\delta(H_b)$	5.41	5.58	5.63	5.63
$\delta(H_c)$	5.45	5.64	5.71	5.71
$\delta(H_d)$	3.42	3.65	3.75	3.75
$\delta(H_e)$	4.22	4.41	4.49	4.49
δ(C1)	122.75	123.49	123.55	123.55
δ(C2)	142.06	142.82	143.36	143.39
δ(C3)	51.13	50.80	50.74	50.73
δ(N4)	111.52	118.86	121.53	121.68
δ(C5)	144.35	143.16	142.72	142.69
δ(S6)	707.72	718.96	722.65	722.86

(a) Computed at GIAO(SMD(B3LYP/6-311+G(2d,p))//B3LYP/6-311G(d,p) and given in ppm.

(b) C-Shifts relative to TMS (shielding: 182.47 ppm) and N-shifts relative to NH_3 (shielding: 258.4 ppm). Isotropic shieldings are given for S.

(c) Dielectric constant of solvent.

(d) Energy computed at B3LYP/6-311G(d,p)) in hartrees.

(d) Relative energy computed at B3LYP/6-311G(d,p)) in kcal/mol.

(f) Energy computed at SMD(B3LYP/6-311+G(2d,p))//B3LYP/6-311G(d,p) in hartrees.

(g) Relative energy computed at SMD(B3LYP/6-311+G(2d,p))//B3LYP/6-311G(d,p) in kcal/mol.

Total Nuclear Spin-Spin Coupling J (Hz) for AITC

M1, spinspin, mixed

	C1, 1	Hc, 2	Hb, 3	C2, 4	Ha, 5
C1, 1	0.000000D+00				
Hc, 2	0.165069D+03	0.000000D+00			
Hb, 3	0.166415D+03	0.103227D+01	0.000000D+00		
C2, 4	0.779209D+02	-0.318920D+01	0.124988D+01	0.000000D+00	
Ha, 5	-0.202184D+00	0.175455D+02	0.119860D+02	0.162097D+03	0.000000D+00
C3, 6	-0.180544D+01	0.895433D+01	0.124366D+02	0.461893D+02	0.140879D+02
Hd, 7	0.526215D+01	-0.328565D+01	-0.323611D+01	-0.643295D+01	0.346141D+01
He, 8	0.526215D+01	-0.328564D+01	-0.323611D+01	-0.643292D+01	0.346141D+01
S6, 9	-0.307355D-01	-0.562888D-01	0.842503D-03	0.724794D-01	0.823860D-01
N4, 10	0.241523D+01	-0.151628D+00	-0.262971D-01	0.141827D+01	0.540236D+01
C5, 11	-0.866757D-01	0.256728D+00	0.494954D-01	0.407425D+01	0.329359D+01

	C3, 6	Hd, 7	He, 8	S6, 9	N4, 10
C3, 6	0.000000D+00				
Hd, 7	0.145062D+03	0.000000D+00			
He, 8	0.145062D+03	-0.222218D+02	0.000000D+00		
S6, 9	-0.179062D+00	0.212385D+00	0.212354D+00	0.000000D+00	
N4, 10	0.986154D+01	-0.214828D+01	-0.214828D+01	0.121745D+01	0.000000D+00
C5, 11	0.421502D+01	0.174738D+01	0.174750D+01	-0.398731D+02	0.349347D+02

M1, spinspin, mixed, $CDCl_3$

	C1, 1	Hc, 2	Hb, 3	C2, 4	Ha, 5
C1, 1	0.000000D+00				
Hc, 2	0.162803D+03	0.000000D+00			
Hb, 3	0.166686D+03	0.125670D+01	0.000000D+00		
C2, 4	0.756352D+02	-0.313797D+01	0.145273D+01	0.000000D+00	
Ha, 5	0.997919D-01	0.176931D+02	0.121038D+02	0.164534D+03	0.000000D+00
C3, 6	-0.186430D+01	0.899367D+01	0.123538D+02	0.449724D+02	0.141389D+02
Hd, 7	0.517009D+01	-0.322185D+01	-0.319643D+01	-0.657207D+01	0.343011D+01
He, 8	0.517009D+01	-0.322185D+01	-0.319642D+01	-0.657204D+01	0.343012D+01
S6, 9	-0.277405D-01	-0.543060D-01	-0.234936D-02	0.584597D-01	0.884169D-01
N4, 10	0.238863D+01	-0.145536D+00	-0.343445D-01	0.126029D+01	0.547453D+01
C5, 11	-0.123960D+00	0.275802D+00	0.566937D-01	0.409998D+01	0.338105D+01

	C3, 6	Hd, 7	He, 8	S6, 9	N4, 10
C3, 6	0.000000D+00				
Hd, 7	0.148303D+03	0.000000D+00			
He, 8	0.148303D+03	-0.233589D+02	0.000000D+00		
S6, 9	-0.182268D+00	0.182401D+00	0.182351D+00	0.000000D+00	
N4, 10	0.926733D+01	-0.218840D+01	-0.218841D+01	0.106738D+01	0.000000D+00
C5, 11	0.400518D+01	0.209273D+01	0.209298D+01	-0.395853D+02	0.353709D+02

M2, spinspin, mixed

	C1, 1	Hc, 2	Hb, 3	C2, 4	Ha, 5
C1, 1	0.000000D+00				
Hc, 2	0.161716D+03	0.000000D+00			
Hb, 3	0.166719D+03	0.804423D+00	0.000000D+00		
C2, 4	0.751982D+02	-0.234374D+01	0.320158D+00	0.000000D+00	
Ha, 5	0.165774D+01	0.175776D+02	0.113240D+02	0.166451D+03	0.000000D+00
C3, 6	0.333211D+01	0.942461D+01	0.155951D+02	0.418263D+02	0.481581D+01
Hd, 7	0.601493D+01	-0.312087D+00	-0.576441D+00	-0.306454D+01	0.109930D+02
He, 8	0.599649D+01	-0.262141D+01	-0.228841D+01	-0.574388D+01	0.392480D+01
S6, 9	-0.389021D-01	-0.188672D-02	0.127071D-01	0.155233D+00	-0.431469D-01
N4, 10	0.130500D+01	-0.636408D+00	-0.530336D+00	-0.192843D+01	0.804591D+00
C5, 11	-0.582387D-01	0.384136D-01	0.697560D-01	0.149101D+01	-0.103572D+00
	C3, 6	Hd, 7	He, 8	S6, 9	N4, 10
C3, 6	0.000000D+00				
Hd, 7	0.147548D+03	0.000000D+00			
He, 8	0.146039D+03	-0.182073D+02	0.000000D+00		
S6, 9	-0.123367D+00	0.521309D+00	0.362817D+00	0.000000D+00	
N4, 10	0.786380D+01	-0.283470D+00	-0.180214D+01	0.113450D+01	0.000000D+00
C5, 11	0.320566D+01	0.601193D+01	0.333866D+01	-0.401688D+02	0.341655D+02

M2, spinspin, mixed, $CDCl_3$

	C1, 1	Hc, 2	Hb, 3	C2, 4	Ha, 5
C1, 1	0.000000D+00				
Hc, 2	0.161699D+03	0.000000D+00			
Hb, 3	0.166150D+03	0.754637D+00	0.000000D+00		
C2, 4	0.738555D+02	-0.251246D+01	0.797276D+00	0.000000D+00	
Ha, 5	0.180472D+01	0.176626D+02	0.114267D+02	0.166726D+03	0.000000D+00
C3, 6	0.352818D+01	0.947071D+01	0.158478D+02	0.415651D+02	0.470123D+01
Hd, 7	0.592307D+01	-0.307971D+00	-0.598251D+00	-0.331725D+01	0.108596D+02
He, 8	0.580961D+01	-0.262961D+01	-0.236187D+01	-0.589766D+01	0.391542D+01
S6, 9	-0.330398D-01	-0.170489D-02	0.103469D-01	0.145263D+00	-0.346714D-01
N4, 10	0.137340D+01	-0.665001D+00	-0.549539D+00	-0.197819D+01	0.820180D+00
C5, 11	-0.424998D-01	0.349220D-01	0.941979D-01	0.157278D+01	-0.109175D+00
	C3, 6	Hd, 7	He, 8	S6, 9	N4, 10
C3, 6	0.000000D+00				
Hd, 7	0.148957D+03	0.000000D+00			
He, 8	0.148193D+03	-0.192556D+02	0.000000D+00		
S6, 9	-0.126248D+00	0.485224D+00	0.328768D+00	0.000000D+00	
N4, 10	0.707132D+01	-0.361816D+00	-0.191008D+01	0.959957D+00	0.000000D+00
C5, 11	0.268776D+01	0.653428D+01	0.379997D+01	-0.398839D+02	0.343397D+02

Table S8. X-Ray Structures of Alkyl Isothiocyanates

Table S8a. Names and CSD Codes of Alkyl Isothiocyanates

Name	CSD-RefCode
Ethyl 16-isothiocyanatobeyeran-18-oate	BALPUB
t-Butyl(((4S,5R)-5-isothiocyanato-2,2-dimethyl-5-vinyl-1,3-dioxan-4-yl)methoxy)dimethylsilane	CATYON
7-Isothiocyanato-1,2,3,4,5,6,7-heptaphenylcycloheptatriene	CUQSIQ
10S,11R,12R,15S-Hapalindole D	FEHBEZ
1,1'-(Isothiocyanatomethylene)dibenzene	GAQFUB
2,5-Di-isothiocyanato-1,6-methano(10)annulene	JAJVUL
3-(Isothiocyanato)-1,2,3-triphenylcyclopropene	JOCWUU
t-Butyl (2-isothiocyanatoethyl)carbamate	MUMFIK
Triisopropyl((5-(1-isothiocyanatoprop-2-en-1-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)silane	ENEJIR
Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-isothiocyanato-a-D-glucopyranoside	GIVRAF
2,5-Di-isothiocyanato-1,6-methano(10)annulene	JAJVUL
(1R,5R,6R,8S)-Dec(4.4.0)ane-1,5-dimethyl-8-(1'-methylethenyl)-5-isothiocyanate	JOYDEG
t-Butyl (2-isothiocyanatoethyl)carbamate	MUMFIK
(S)-t-Butyl (1-isothiocyanato-3-phenylpropan-2-yl)carbamate	MUMFOQ
4-(5,6-bis(Isothiocyanato)-3,5-di-t-butyl-4-oxo-2-cyclohexadienylidene)-2,6-di-t-butyl-2,5-cyclohexadienone	NUYPOM
2,3,6-Tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetylhexopyranosyl)-N-(thioxomethylene)hexopyranosylamine	PECZON
Dimethyl (Z)-1-isothiocyanato-2-bis(di-isopropylamino)thiophosphoranyl-1,2-dicarboxylate	POHRIN
3-(2-(Isothiocyanato)acetyl)-4,4-dimethyloxazolidin-2-one	ROHDUO
2-Isothiocyanato-trachyopsane	SARCIX
N-(8-(5-(2-Chloropropan-2-yl)-2-methyltetrahydrofuran-2-yl)-1-hydroxy-5-isothiocyanato-2,5-dimethyldecahydronaphthalen-2-yl)formamide	SAWBID
N-(8-(5-Chloro-2,6,6-trimethyltetrahydro-2H-pyran-2-yl)-1-hydroxy-5-isothiocyanato-2,5-dimethyldecahydronaphthalen-2-yl)formamide	SAWBOJ
8-(5-Chloro-2,6,6-trimethyltetrahydro-2H-pyran-2-yl)-5-isothiocyanato-2,5-dimethyl-1-isocyanodecahydronaphthalen-2-ol	SAWBUP
8-(5-Chloro-2,6,6-trimethyltetrahydro-2H-pyran-2-yl)-1-isothiocyanato-5-isocyano-2,5-dimethyldecahydronaphthalen-2-ol	SAWCAW
t-Butyl N-((1R,2R)-2-(isothiocyanato)cyclohexyl)carbamate	TIHHOI
2,3,4- Tri-O-acetyl-b-D-xylopyranosyl isothiocyanate	TIKROV
5-Isothiocyanotopupukeanane	VEDTIH

Table S8b. ICT Group Parameters of Alkyl Isothiocyanates

CSD-RefCode	∠(CNC) [°]	∠(NCS) [°]	*d*(CN) [Å]	*d*(NC) [Å]	*d*(CS) [Å]	Comment
BALPUB	154.86	176.86	1.446	1.156	1.569	
CATYON	141.48	173.96	1.456	1.171	1.579	two ether-O contacts with ICT-C
CUQSIQ	165.09	177.07	1.457	1.148	1.575	
FEHBEZ	174.09	177.73	1.430	1.153	1.586	Indole-NH contact with ITC-N
GAQFUB	168.65	177.42	1.447	1.163	1.589	
JAJVUL	175.04	178.99	1.448	1.125	1.573	antiparallel R-NCS pairs
JOCWUU	161.07	176.50	1.466	1.123	1.556	
MUMFIK	156.75	176.06	1.443	1.176	1.590	
ENEJIR	146.06	176.35	1.457	1.161	1.561	neighboring TBDMS protecting group
GIVRAF	159.31	176.70	1.423	1.144	1.598	ether-O contact with ITC-C
JAJVUL	175.04	178.99	1.448	1.125	1.573	neighboring cyclopropane
JOYDEG	174.77	179.16	1.455	1.141	1.572	
MUMFIK	156.75	176.06	1.443	1.176	1.590	
MUMFOQ	176.15	178.42	1.424	1.154	1.591	
NUYPOM	147.54	174.14	1.460	1.152	1.547	
PECZON	173.55	173.50	1.395	1.046	1.473	
POHRIN	145.42	173.27	1.360	1.183	1.561	ester carbonyl-O contact with ITC-C
ROHDUO	144.10	172.62	1.432	1.183	1.585	amide carbonyl-O cont. with ITC-C
SARCIX	156.70	172.58	1.415	1.148	1.566	
SAWBID	153.05	176.85	1.463	1.153	1.584	
SAWBOJ	158.86	177.66	1.458	1.156	1.589	
SAWBUP	147.23	175.89	1.465	1.167	1.576	
SAWCAW	156.68	176.34	1.442	1.156	1.584	
TIHHOI	162.52	176.97	1.444	1.159	1.593	carbamate carbonyl-O contact with ITC-C
TIKROV	151.62	174.33	1.419	1.164	1.558	ester ether-O contact with ITC-C
VEDTIH	159.91	177.75	1.462	1.176	1.551	
Count	26	26	26	26	26	
Average	159.32	176.24	1.441	1.152	1.572	
Std. Dev.	10.60	1.91	0.024	0.027	0.024	

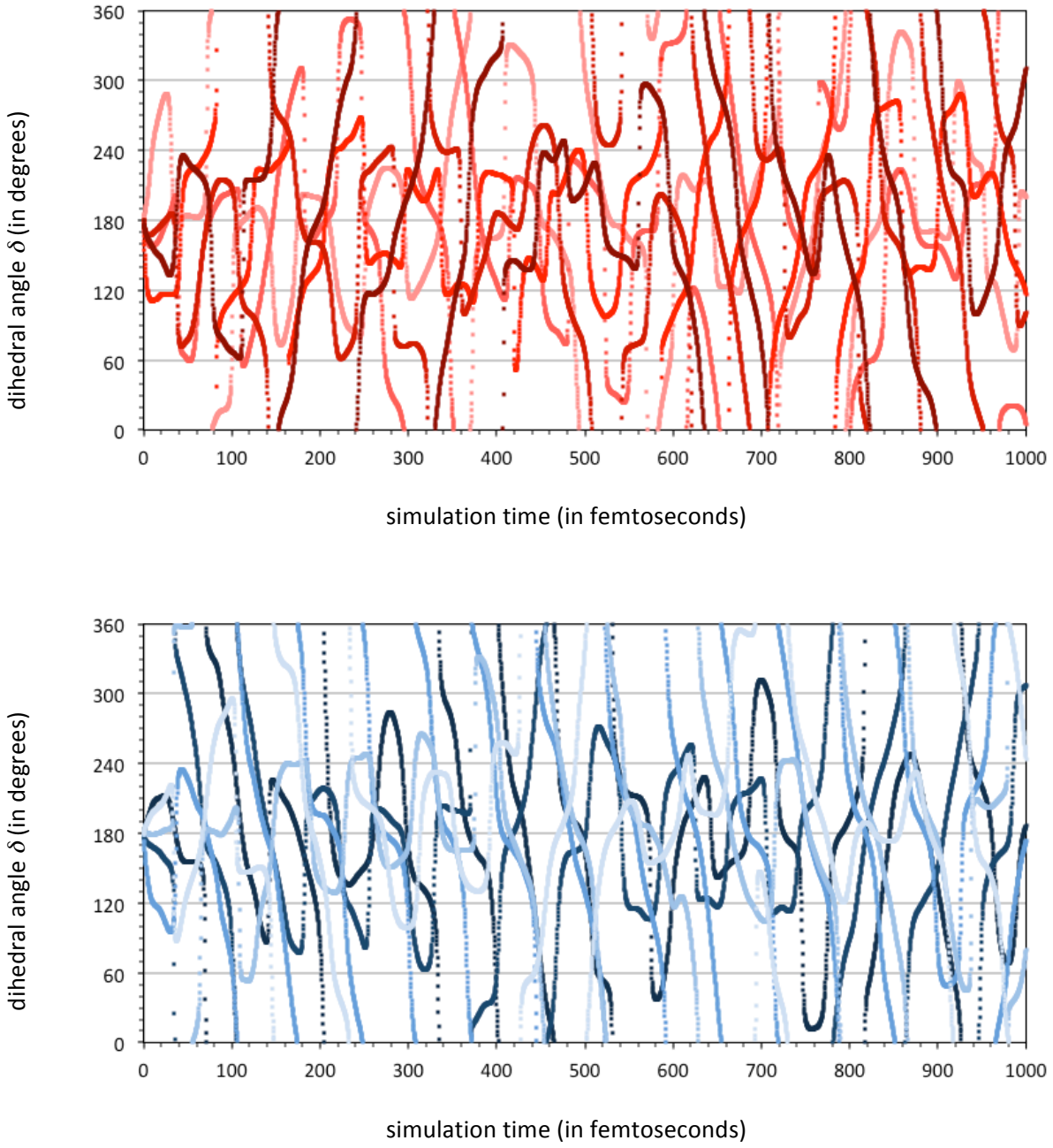

Figure S4b. Variations of dihedral angle δ = ∠(C3–N4–C5–S6) of **AITC** along the ADMP trajectories shown in Figure 4. Trajectories starting at **M1** (ε = 175.7°, δ = 180°) are shown on top (red colors) and those starting at **M2** (ε = 175.4°, δ = 179.1°) are shown on the bottom (blue colors). A dihedral angle δ of about 180° indicates that sulfur is on the side of the N lone pair, and sulfur prefers to be on the side of the N lone pair in **M1** and **M2** (Figure 3). This preference remains noticeable along the trajectories (Figure 4) but the δ-values cover a large transoid region (120° < δ < 240°) and sulfur also spends some time traversing the cisoid regions.