Supporting Information for

Multipoint Anchoring of the [2.2.2.2]Metacyclophane Motif to a Gold Surface via Self-Assembly: Coordination Chemistry of a Cyclic Tetraisocyanide Revisited

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Figure S1. FTIR spectrum of **3** (KBr).

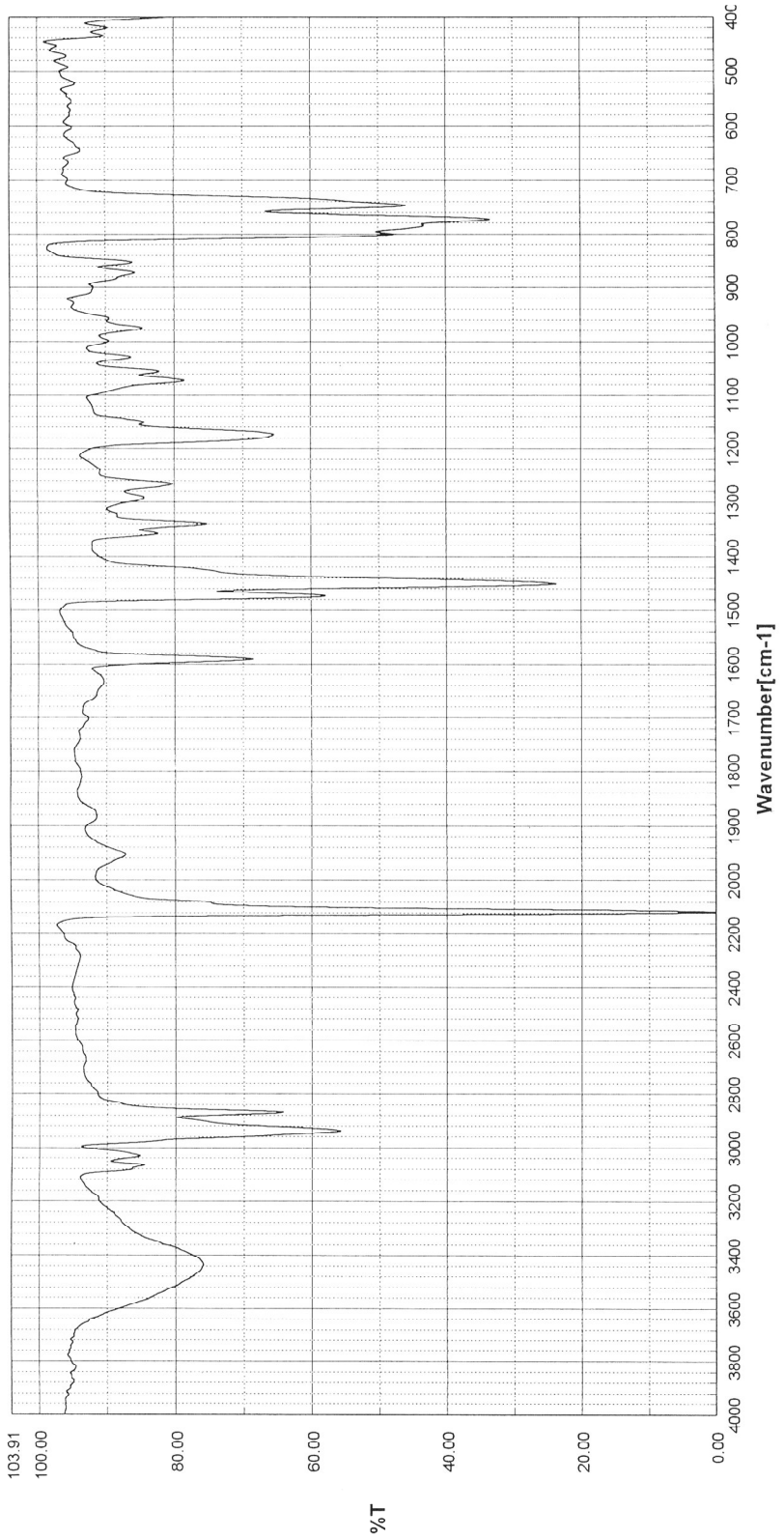


Figure S2. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 25 °C.

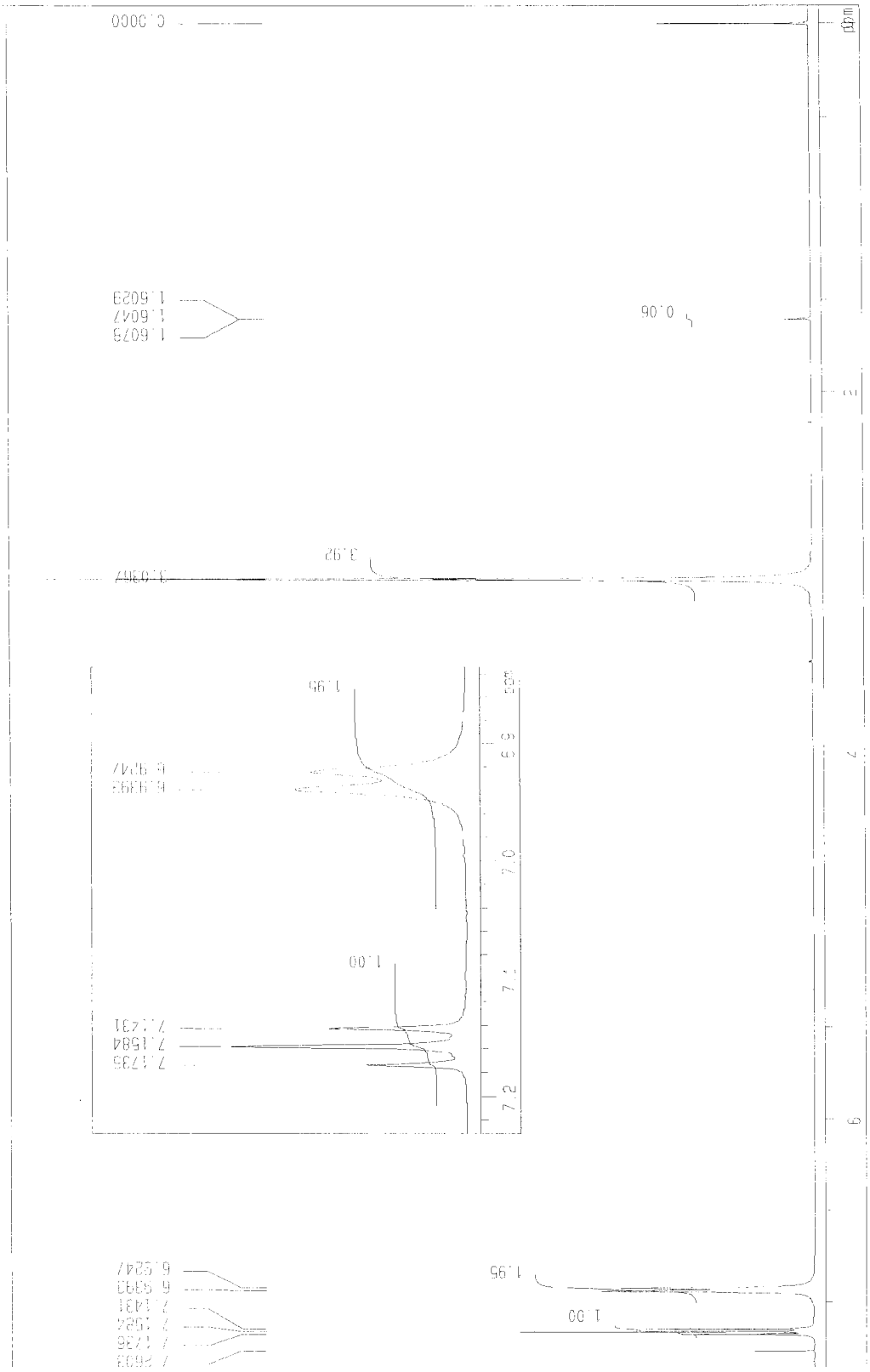


Figure S3. ^{13}C NMR spectrum of **3** in $CDCl_3$ at 25 °C.

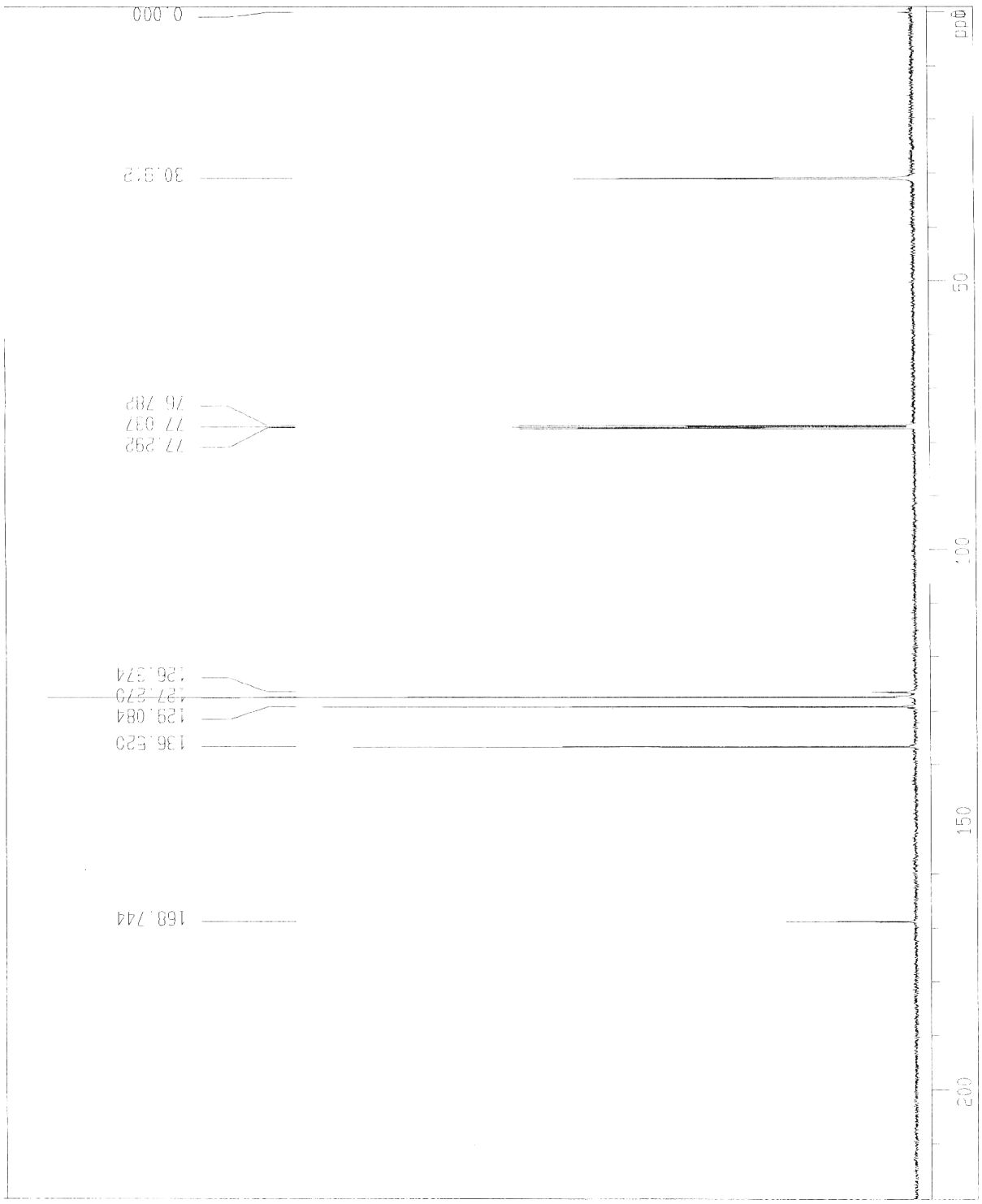


Figure S4. MS (EI+) trace for **3**.

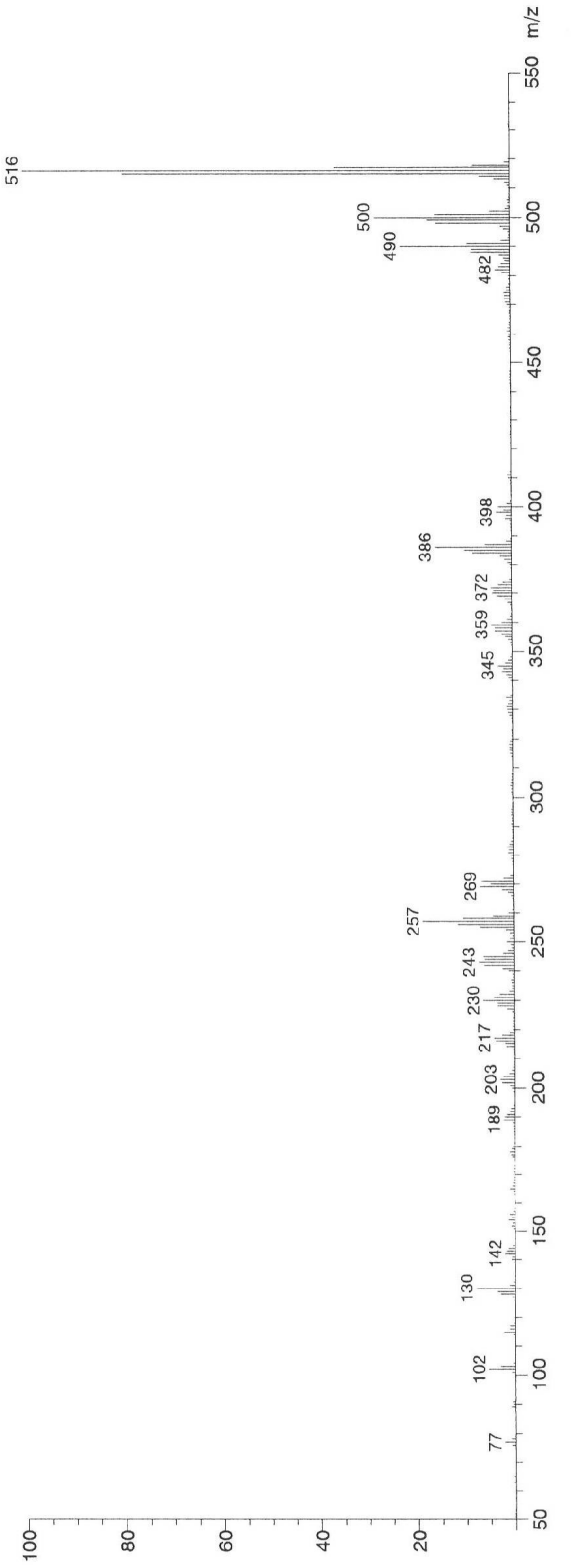


Table S1. HR-MS (EI+) data for **3**.

Base: m/z 516; 52.3% FS TIC: 2546383 (Max Inten : 548007) **#Ions: 137**

Selected Isotopes : $H_{0-40}C_{0-40}{}^{13}C_{0-2}N_{0-4}$ **Error Limit : 10 mmu** **Unsaturation Limits : -1 - 30**

Measured Mass	*% Base*	*Formula*	*Calculated Mass*	*Error*	*Unsaturation*
516.23146	100.0%	$C_{36}H_{29}{}^{13}C\,N_3$	516.23948	8.0	25.0
		$C_{35}H_{28}{}^{13}C_2N_3$	516.23501	3.5	25.5
		$C_{36}H_{28}N_4$	516.23138	-0.1	25.0
		$C_{35}H_{27}{}^{13}C\,N_4$	516.22690	-4.6	25.5
		$C_{34}H_{26}{}^{13}C_2N_4$	516.22243	-9.0	26.0
517.23435	33.0%	$C_{35}H_{29}{}^{13}C_2N_3$	517.24284	8.5	25.0
		$C_{36}H_{29}N_4$	517.23920	4.9	24.5
		$C_{35}H_{28}{}^{13}C\,N_4$	517.23473	0.4	25.0
		$C_{34}H_{27}{}^{13}C_2N_4$	517.23025	-4.1	25.5
518.23647	6.8%	$C_{35}H_{29}{}^{13}C\,N_4$	518.24256	6.1	24.5
		$C_{34}H_{28}{}^{13}C_2N_4$	518.23808	1.6	25.0

Figure S5. FTIR spectrum of **5** (KBr).

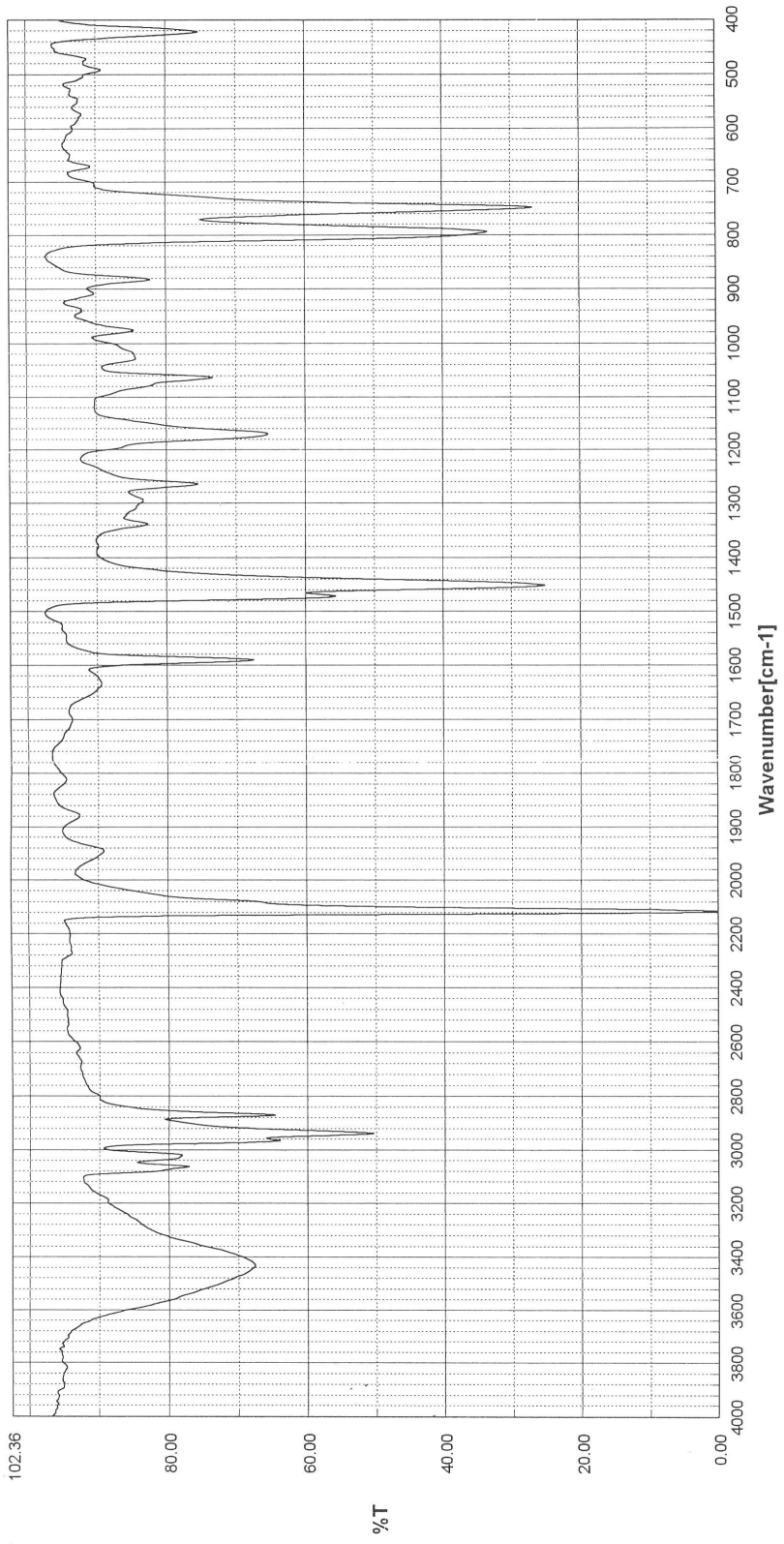


Figure S6. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 25 °C.

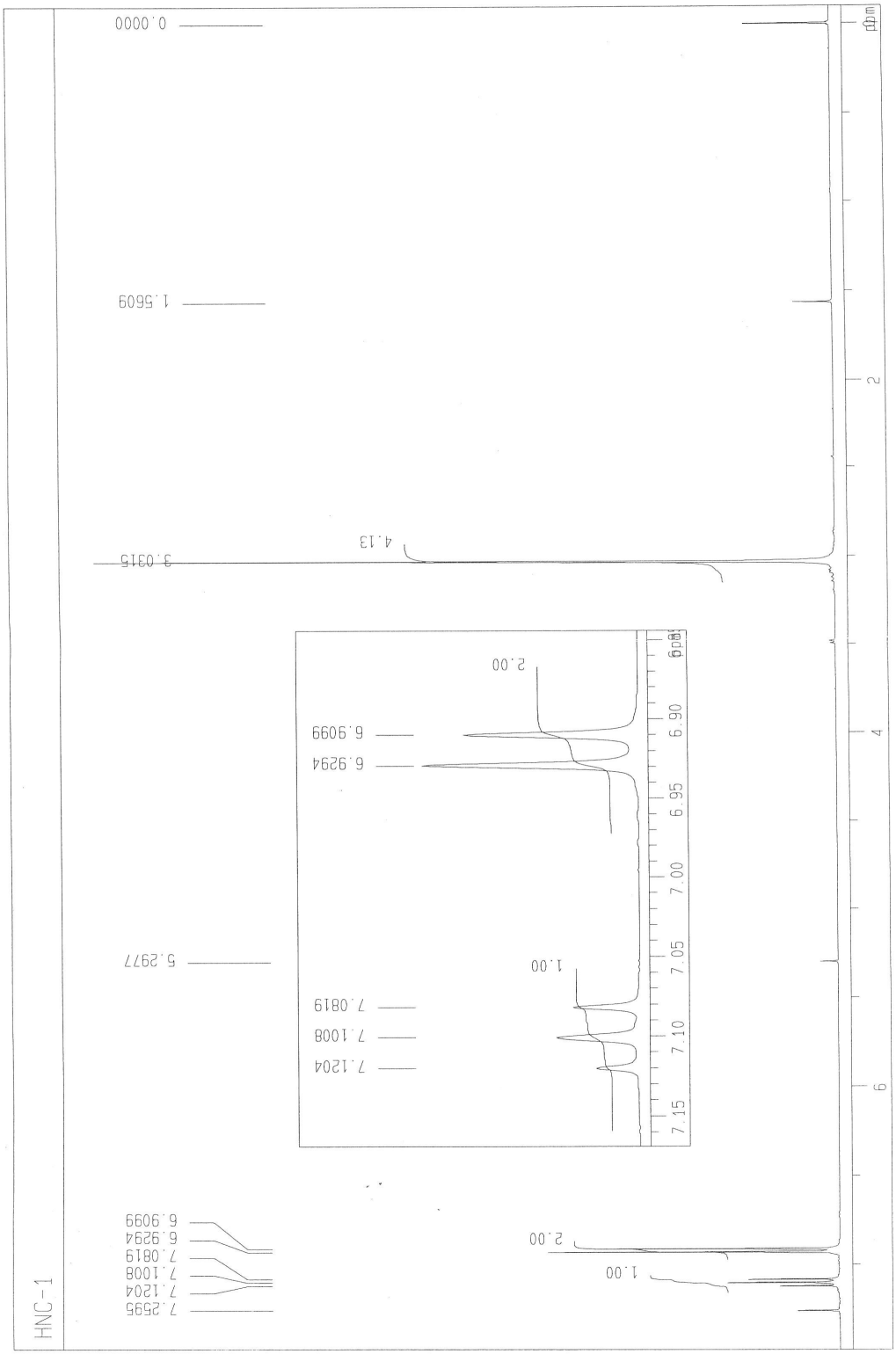


Figure S7. ^{13}C NMR spectrum of **4** in $CDCl_3$ at 25 °C.

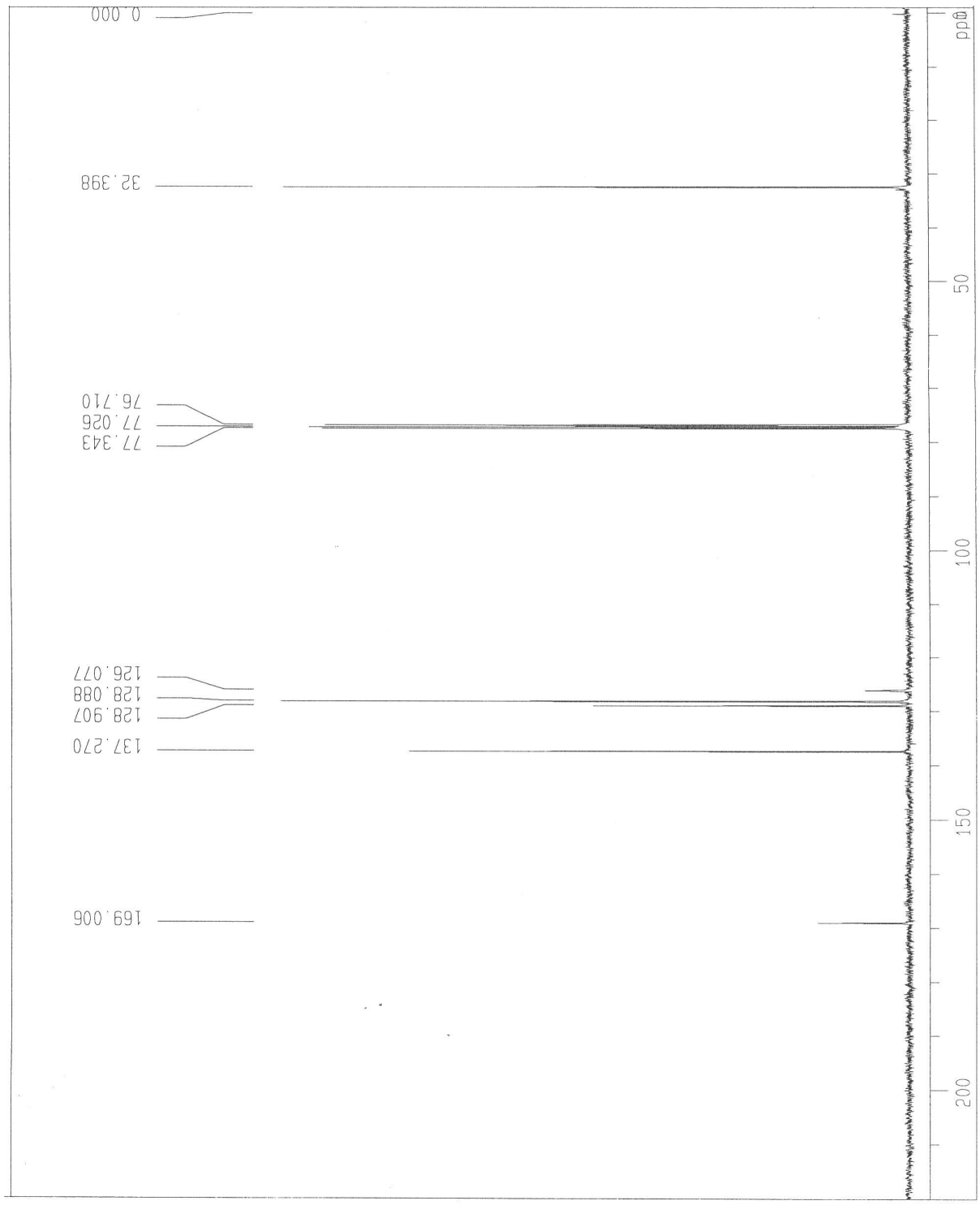


Figure S8. MS (EI+) trace for **4**.

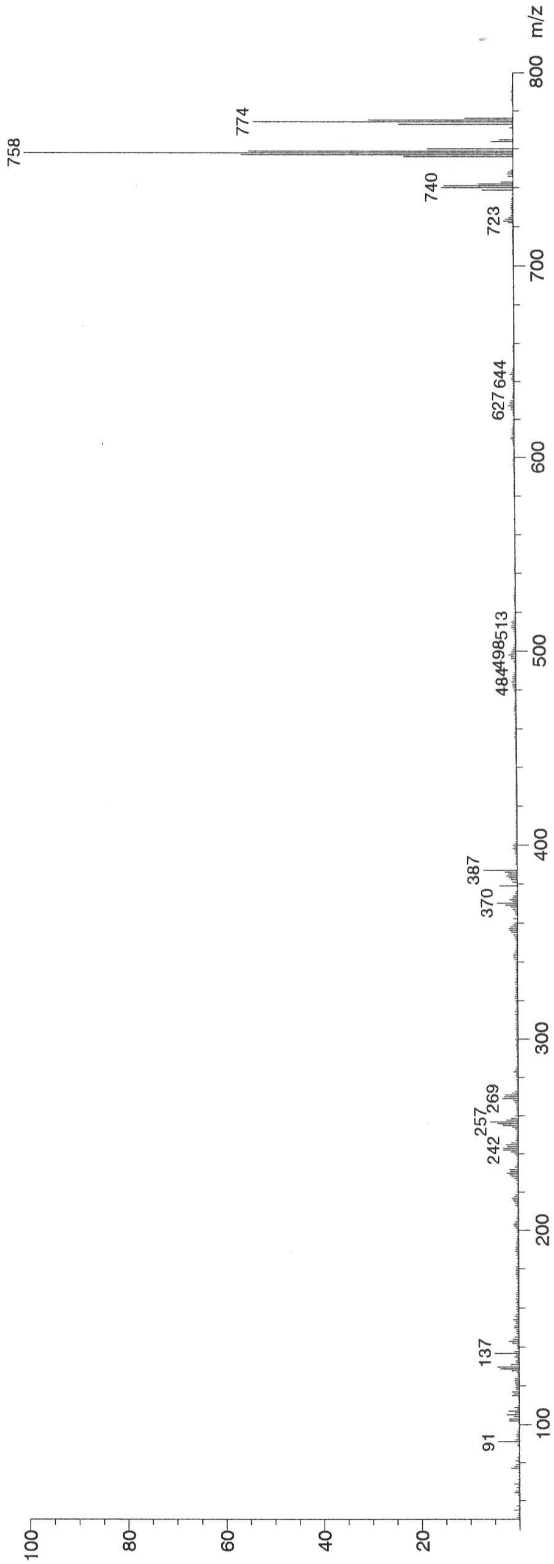


Table S2. HR-MS (EI+) data for **4**.

Base: m/z 774; 1.1%FS TIC: 119474 (Max Inten : 11277) **#Ions: 42**

Selected Isotopes : $H_{0-50}C_{0-60}{}^{13}C_{0-2}N_{0-7}$ **Error Limit : 10 mmu** **Unsaturation Limits : -1 - 50**

Measured Mass	*% Base*	*Formula*	*Calculated Mass*	*Error*	*Unsaturation*
774.34789	100.0%	$C_{54}H_{43}{}^{13}C\,N_5$	774.35517	7.3	37.0
		$C_{53}H_{42}{}^{13}C_2N_5$	774.35070	2.8	37.5
		$C_{54}H_{42}N_6$	774.34707	-0.8	37.0
		$C_{53}H_{41}{}^{13}C\,N_6$	774.34260	-5.3	37.5
		$C_{52}H_{40}{}^{13}C_2N_6$	774.33812	-9.8	38.0
775.34937	60.6%	$C_{53}H_{43}{}^{13}C_2N_5$	775.35852	9.2	37.0
		$C_{54}H_{43}N_6$	775.35489	5.5	36.5
		$C_{53}H_{42}{}^{13}C\,N_6$	775.35042	1.0	37.0
		$C_{52}H_{41}{}^{13}C_2N_6$	775.34595	-3.4	37.5
		$C_{53}H_{41}N_7$	775.34231	-7.1	37.0
776.35513	24.8%	$C_{54}H_{44}N_6$	776.36272	7.6	36.0
		$C_{53}H_{43}{}^{13}C\,N_6$	776.35824	3.1	36.5
		$C_{52}H_{42}{}^{13}C_2N_6$	776.35377	-1.4	37.0
		$C_{53}H_{42}N_7$	776.35014	-5.0	36.5
		$C_{52}H_{41}{}^{13}C\,N_7$	776.34567	-9.5	37.0

Figure S9. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at 25 °C.

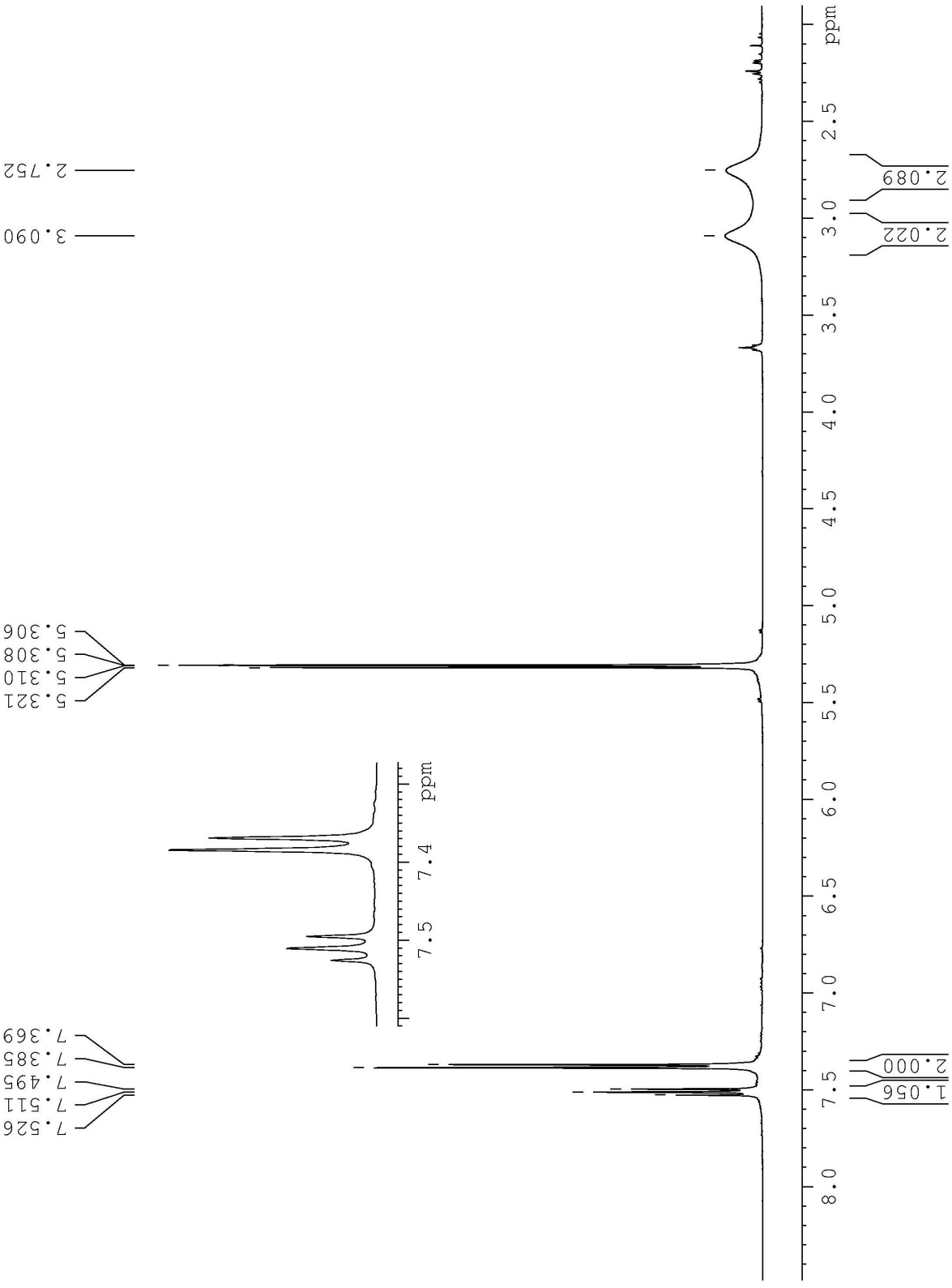


Figure S10. Aliphatic region of the 2D ^{1}H COSY NMR map for **5** in CD_2Cl_2 at 25 °C.

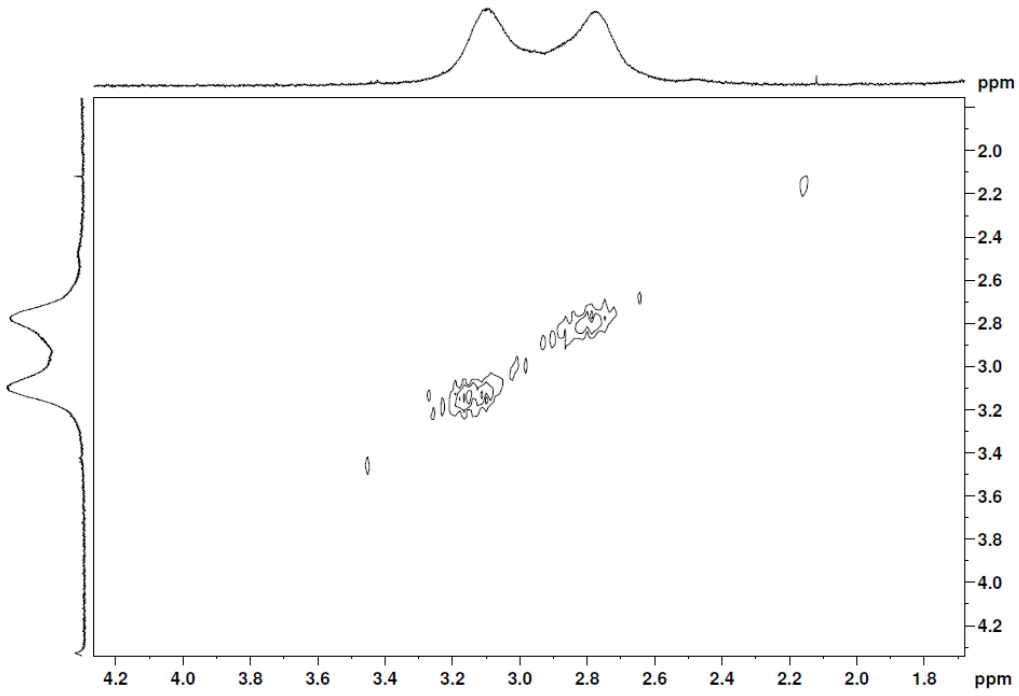
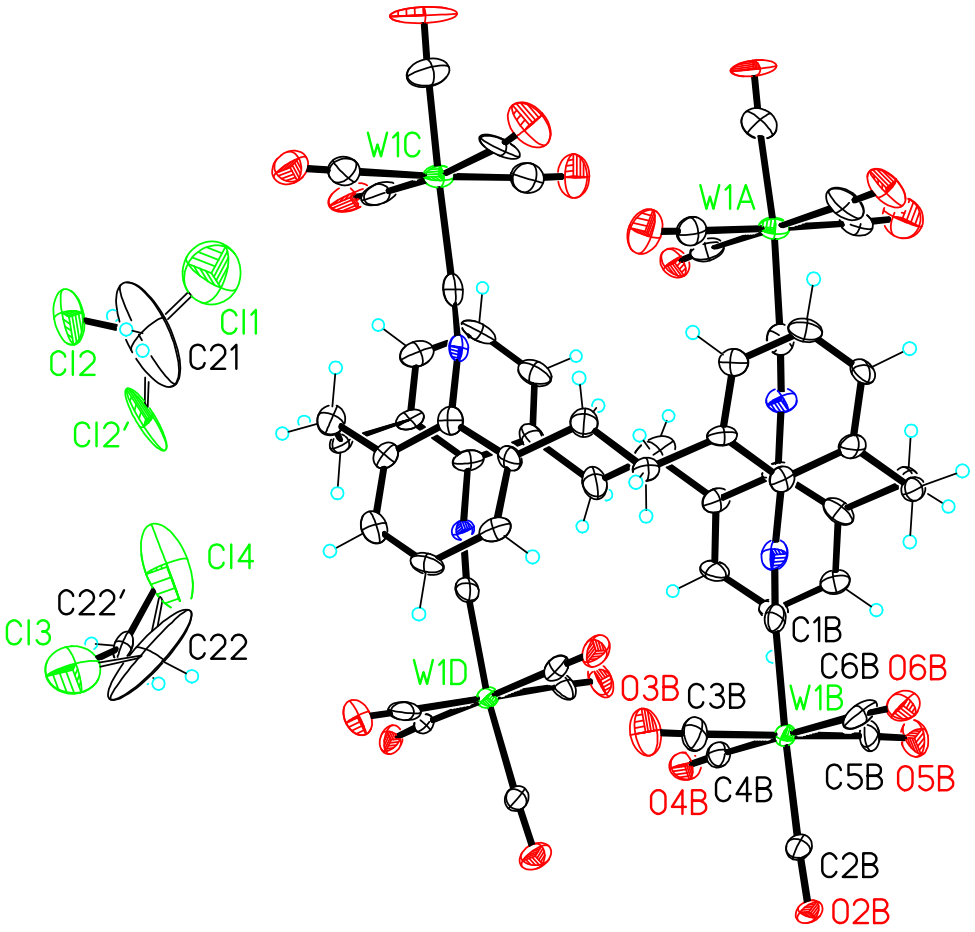


Figure S11. Thermal ellipsoid plot for **5**·2CH_2Cl_2.



Comment:

Both of the CH_2Cl_2 solvent molecules of crystallization present in the asymmetric unit of **5**·2CH_2Cl_2 are disordered with two slightly different orientations for each in the crystal. The two orientations for the first CH_2Cl_2 molecule have the methylene carbon C(21) and one chlorine atom Cl(1) in common and the two orientations for the second CH_2Cl_2 molecule have both Cl atoms in common. There are therefore two alternate (partial occupancy) positions for Cl(2) and methylene carbon C(22). This disorder was modeled by restraining all seven (with the disorder) C-Cl bonds to have a common value near that of a free variable that was refined in least-squares cycles. The two Cl···Cl separations for the two orientations of the first CH_2Cl_2 molecule were restrained to idealized tetrahedral values by requiring them to be 1.633 times this free variable that refined to a final value of 1.707(6)Å. The major orientation for the first CH_2Cl_2 molecule is occupied 62% of the time and the major orientation for the second CH_2Cl_2 molecule is occupied 84% of the time. Mild restraints had to be imposed on the anisotropic thermal parameters of C(8D) and the two partial-occupancy methylene carbon atoms for the second CH_2Cl_2 molecule.

Table S3. Cartesian coordinates for the DFT-optimized structure of **3** (see Figure 4).

Atom	X	Y	Z
N1	1.9302	1.0716	1.7151
N2	-2.0609	1.0297	-1.5701
N3	-2.8014	-3.2108	-1.1019
N4	3.6857	-2.4945	1.007
C1	1.5425	0.3579	2.5686
C2	-1.3662	0.4947	-2.3571
C3	-3.1769	-3.7371	-2.0873
C4	4.2075	-2.937	1.9667
C5	2.3768	1.975	0.7585
C6	3.7358	1.965	0.3897
C7	4.1653	2.9558	-0.5023
H1	5.2136	2.9879	-0.7912
C8	3.272	3.8873	-1.028
H2	3.6265	4.6518	-1.7145
C9	1.9155	3.8309	-0.6936
H3	1.2283	4.5429	-1.1402
C10	1.4354	2.8711	0.2004
C11	-0.0285	2.7242	0.5666
H4	-0.193	3.0855	1.5921
H5	-0.2612	1.6543	0.6008
C12	-1.0397	3.4143	-0.3777
H6	-1.0141	4.5011	-0.237
H7	-0.7614	3.2166	-1.4186
C13	-2.8967	1.6965	-0.6817
C14	-2.4435	2.9116	-0.1183
C15	-3.3166	3.5988	0.7283
H8	-2.9952	4.5403	1.1676
C16	-4.589	3.0962	1.0112
H9	-5.2591	3.6512	1.6625
C17	-4.9989	1.8828	0.4608
H10	-5.9885	1.4934	0.6895
C18	-4.1623	1.1486	-0.3902
C19	-4.6126	-0.1896	-0.9371
H11	-3.9989	-0.4829	-1.7925
H12	-5.642	-0.0938	-1.3053
C20	-4.6044	-1.3341	0.1192
H13	-5.2691	-1.0536	0.9449
H14	-5.0429	-2.2197	-0.3534
C21	-2.3736	-2.5892	0.0668
C22	-3.2442	-1.6698	0.6926
C23	-2.808	-1.0715	1.8794
H15	-3.4629	-0.3676	2.3864
C24	-1.553	-1.3626	2.4117
H16	-1.2173	-0.8784	3.3238
C25	-0.7127	-2.272	1.7702
H17	0.261	-2.4761	2.2019
C26	-1.0997	-2.9121	0.5884
C27	-0.2245	-3.964	-0.0738
H18	-0.4945	-4.0571	-1.1292
H19	-0.4723	-4.9405	0.3684
C28	1.2997	-3.7795	0.0669
H20	1.5805	-3.7761	1.1241
H21	1.7737	-4.6819	-0.3472
C29	3.0899	-1.9726	-0.1364
C30	1.9022	-2.567	-0.6227
C31	1.3446	-2.0238	-1.7844
H22	0.4258	-2.436	-2.1877
C32	1.9413	-0.9478	-2.4411
H23	1.4766	-0.5421	-3.3343
C33	3.1118	-0.3838	-1.9386
H24	3.5696	0.4591	-2.4495
C34	3.7063	-0.8722	-0.77
C35	4.95	-0.2091	-0.2164
H25	5.4935	0.2503	-1.0505
H26	5.6187	-0.9556	0.2263
C36	4.6838	0.8853	0.8639
H27	4.3024	0.4116	1.7718
H28	5.651	1.3346	1.1215

Table S4. Cartesian coordinates for the DFT-optimized structure of **3A** (see Figure 7).

Atom	X	Y	Z
C1	-4.5148	-1.3251	-2.0181
C2	-3.8	-2.4175	-1.5243
C3	-3.1706	-2.374	-0.2748
C4	-3.2888	-1.171	0.4557
C5	-3.9915	-0.04	-0.0192
C6	-4.609	-0.1524	-1.2699
H1	-5.0069	-1.3929	-2.9849
H2	-3.7442	-3.3318	-2.1109
C7	-2.5139	-3.6358	0.2785
H3	-2.5932	-4.4064	-0.498
H4	-3.1374	-3.9925	1.1109
N1	-2.7254	-1.1118	1.7192
C8	-4.1319	1.2141	0.8287
H5	-5.1564	1.2497	1.2269
H6	-3.4753	1.1472	1.6986
H7	-5.1815	0.6853	-1.6591
C9	-3.8673	2.5662	0.1125
H8	-4.5772	2.6969	-0.7122
H9	-4.0844	3.3595	0.8363
C10	-2.4626	2.7227	-0.4275
C11	-2.1943	2.4337	-1.7712
C12	-0.9054	2.5319	-2.2866
C13	0.1514	2.9092	-1.4576
C14	-0.0563	3.2157	-0.1099
C15	-1.3835	3.1403	0.3816
H10	-3.0127	2.1276	-2.4162
H11	-0.7184	2.3058	-3.3332
H12	1.1522	2.9589	-1.8687
C16	1.064	3.6279	0.8225
H13	0.8667	4.6533	1.1671
H14	1.0044	3.0187	1.728
N2	-1.6344	3.5233	1.6995
C17	2.514	3.6358	0.2785
H15	2.5932	4.4064	-0.4979
H16	3.1374	3.9924	1.1109
C18	3.1706	2.374	-0.2748
C19	3.8	2.4175	-1.5244
C20	4.5148	1.325	-2.0182
C21	4.609	0.1524	-1.2699
C22	3.9914	0.04	-0.0192
C23	3.2888	1.171	0.4557
N3	2.7254	1.1118	1.7192
C24	4.1319	-1.2141	0.8288
H17	3.4752	-1.1472	1.6986
H18	5.1563	-1.2497	1.2269
C25	3.8673	-2.5662	0.1125
H19	4.5773	-2.6969	-0.7122
H20	4.0844	-3.3595	0.8363
H21	5.1815	-0.6854	-1.6591
H22	5.0068	1.3928	-2.985
H23	3.7441	3.3317	-2.111
C26	2.4627	-2.7228	-0.4274
C27	2.1943	-2.4338	-1.7712
C28	0.9054	-2.532	-2.2866
C29	-0.1514	-2.9092	-1.4576
C30	0.0564	-3.2157	-0.1099
C31	1.3835	-3.1403	0.3816
H24	3.0128	-2.1277	-2.4162
H25	0.7185	-2.306	-3.3332
H26	-1.1521	-2.9589	-1.8687
C32	-1.064	-3.6278	0.8225
H27	-0.8667	-4.6532	1.1672
H28	-1.0044	-3.0186	1.728
N4	1.6344	-3.5232	1.6996
C33	-2.2541	-1.0695	2.7969
C34	-1.8525	3.9042	2.7968
C35	2.2541	1.0696	2.7969
C36	1.8525	-3.9041	2.7969

Table S5. Cartesian coordinates for the DFT-optimized structure of **3B** (see Figure 7).

Atom	X	Y	Z
C1	2.6124	-2.6965	-2.2683
C2	3.5733	-1.8279	-1.7574
C3	3.6504	-1.5599	-0.3864
C4	2.7381	-2.2308	0.4579
C5	1.6994	-3.0554	-0.0375
C6	1.6782	-3.2849	-1.4162
H1	2.5803	-2.9068	-3.3341
H2	4.2858	-1.3574	-2.4297
C7	4.6912	-0.5976	0.1542
H3	5.4054	-0.3724	-0.646
H4	5.2699	-1.0904	0.9458
N1	2.9152	-2.1218	1.8339
H5	0.9283	-3.9418	-1.8367
C8	0.6931	-3.6723	0.9214
H6	1.2041	-4.4449	1.5139
H7	0.3908	-2.9127	1.6515
C9	-0.5788	-4.3256	0.3165
H8	-0.2942	-5.0959	-0.4094
H9	-1.0705	-4.8569	1.1402
C10	-1.5847	-3.3895	-0.3323
C11	-1.7601	-3.3548	-1.7204
C12	-2.6867	-2.4983	-2.3122
C13	-3.4451	-1.6313	-1.5256
C14	-3.3252	-1.6255	-0.133
C15	-2.4198	-2.5504	0.4378
H10	-1.1759	-4.0219	-2.3478
H11	-2.8131	-2.4998	-3.3916
H12	-4.1487	-0.9611	-2.0057
C16	-4.1446	-0.7169	0.7674
H13	-3.5515	-0.4717	1.6526
H14	-5.0069	-1.2822	1.1511
C17	-4.6912	0.5975	0.1545
H15	-5.4055	0.3722	-0.6458
H16	-5.2699	1.0903	0.946

Atom	X	Y	Z
C18	-3.6505	1.5598	-0.3863
C19	-3.5735	1.8279	-1.7573
C20	-2.6128	2.6966	-2.2682
C21	-1.6785	3.285	-1.4162
C22	-1.6995	3.0553	-0.0375
C23	-2.7381	2.2307	0.4579
H17	-4.2861	1.3574	-2.4295
H18	-2.5808	2.907	-3.334
H19	-0.9288	3.942	-1.8368
N2	-2.9151	2.1214	1.8339
N3	-2.4089	-2.6882	1.8201
C24	-0.6931	3.6722	0.9213
H20	-0.3907	2.9126	1.6514
H21	-1.204	4.4448	1.5139
C25	0.5788	4.3256	0.3163
H22	0.2941	5.0958	-0.4097
H23	1.0705	4.8568	1.14
C26	1.5846	3.3894	-0.3326
C27	1.7597	3.3544	-1.7207
C28	2.6862	2.4978	-2.3125
C29	3.4448	1.631	-1.5259
C30	3.3252	1.6254	-0.1333
C31	2.4199	2.5505	0.4375
H24	1.1754	4.0214	-2.3481
H25	2.8124	2.4991	-3.392
H26	4.1482	0.9607	-2.006
C32	4.1446	0.7169	0.7671
H27	5.007	1.2822	1.1507
H28	3.5516	0.4718	1.6524
N4	2.4095	2.6887	1.8198
C33	3.1895	-2.0854	2.9815
C34	-2.5185	-2.8587	2.9819
C35	-3.1885	2.0861	2.9818
C36	2.5195	2.8596	2.9815

Complete reference 27:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.