Supporting Information for

Preparation, Electronic and Liquid Crystalline Properties of Electron-Accepting Azaacene Derivatives

Takashi Takeda,*[1,2] Tomohiro Ikemoto,[2] Shunsuke Yamamoto,[1,2] Wakana Matsuda,[3] Shu Seki,[3] Masaya Mitsuishi[1,2] and Tomoyuki Akutagawa[1,2]

[1] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan*

[2] *Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, Miyagi, 980-8579, Japan*

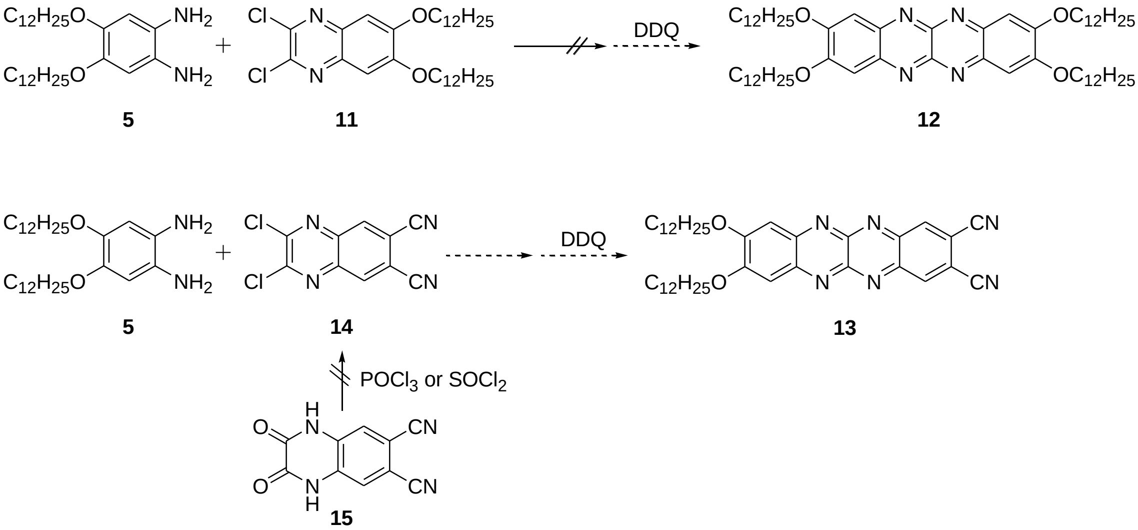
[3] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, Kyoto, 615-8520, Japan*

CONTENTS

Page

1. Attempted synthesis of azaacenes 12 and 13

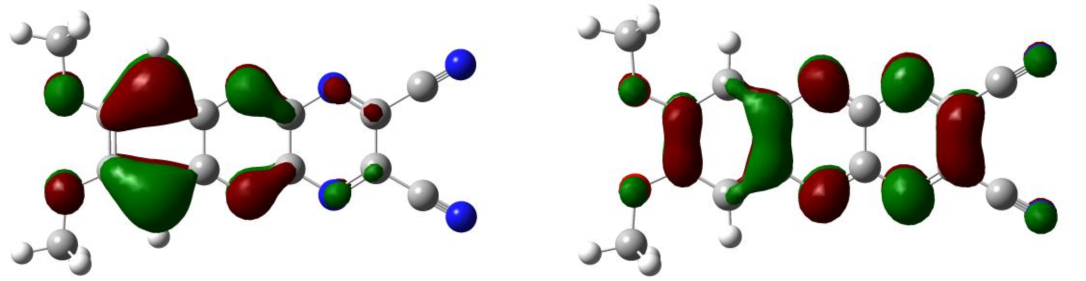
Our attempt to react didodecyloxy-*o*-phenylenediamine **5** and dichlorodidodecylquinoxaline **11** to obtain tetradidecyloxyQQ **12** was unfruitful; only a polymeric tar-like material was obtained. This is probably because dichloroquinoxaline **11** is not sufficiently electron-deficient to induce a substitution reaction. We also sought to obtain dicyanodidodecylQQ **13** from **5** and dichlorodicyanoquinoline **14**. However, we could not obtain **14** from dicyano-1,4-dihydroquinoxalinedione **15** by the reaction with $POCl_3$ or $SOCl_2$, while the corresponding dialkoxy and monocyano derivatives could be obtained by the same reactions.



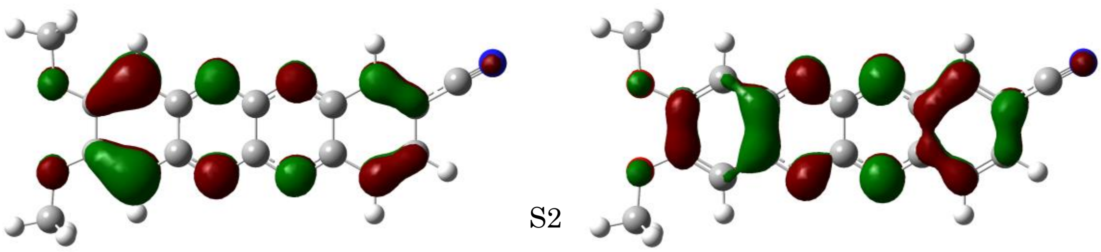
Scheme S1 Attempted syntheses of **12** and **13**.

2. HOMO and LUMO of 1-4

1



2



3

4

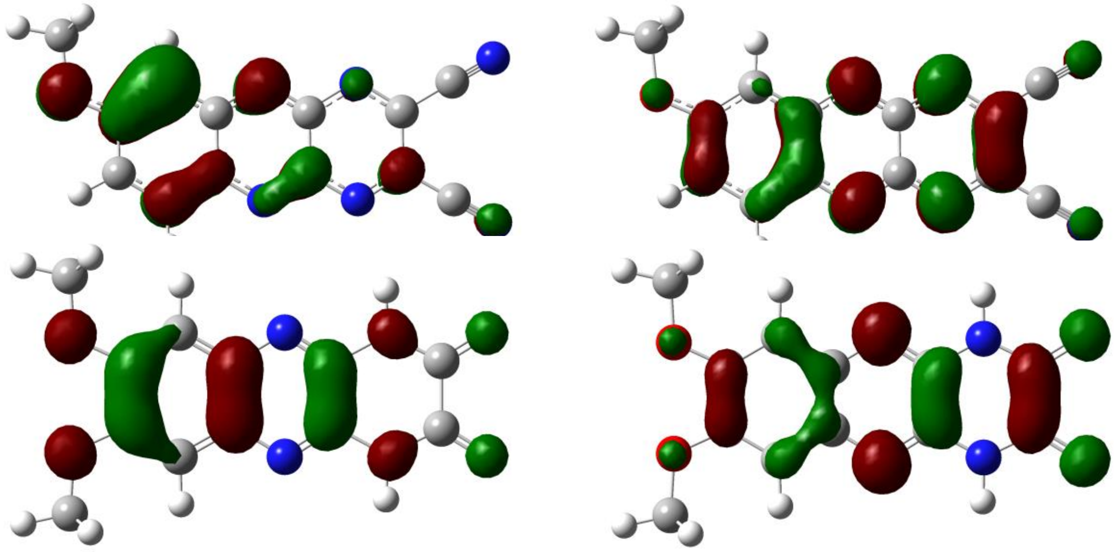


Figure S1 HOMO (left) and LUMO (right) of **1-4**. Alkoxy group(s) was replaced by a methoxy group.

3. TG curves of 1-4

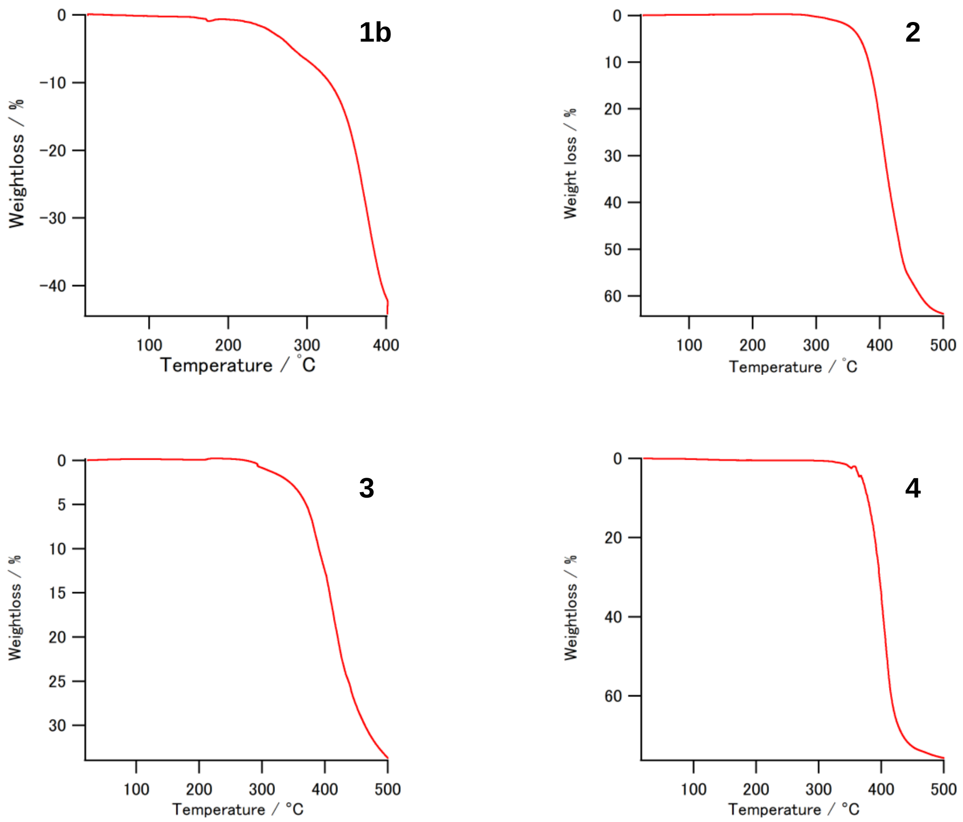


Figure S2 TG curves of **1-4**.

4. Temperature-dependent IR spectrum of 4

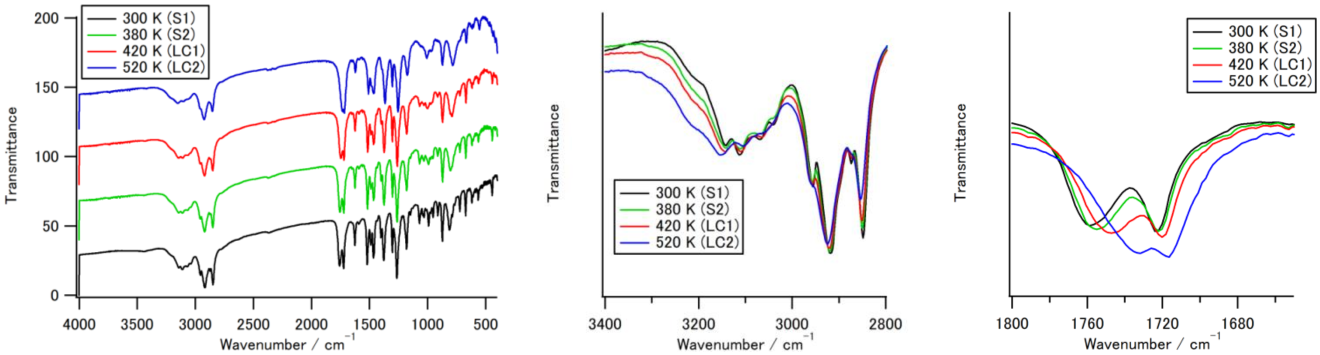


Figure S3 Temperature-dependent IR spectra of **4** (left) and its magnified spectra in the range of 2800-3400 cm^{-1} (center) and 1650-1800 cm^{-1} (right).

5. Time-of-flight measurement of 4

Charge-carrier properties were also measured using the time-of-flight method. Samples were made from a chlorobenzene solution of **4** in a liquid crystal cell with a 2 μm gap between two ITO electrodes. The solution was introduced at 130 °C and allowed to cool. The samples were connected to a voltage amplifier (NF, HVA4321) driven by a function generator (NF, WF1966) and excited by a Q-switched Nd:YAG laser (5 ns, 10 Hz, 355 nm). The output signal was filtered by a band-pass filter (NF, HVA 4321) and amplified by a signal amplifier (Femto, DHPVA) before acquisition by an oscilloscope (Textronix, TDS3052B). However, this attempt was not successful due to the low break-down voltage of the samples. Thus, further investigations of charge-carrier transport were performed using the TRMC technique, as shown in the main text.

6. ^{1}H and ^{13}C NMR spectra of 2-4

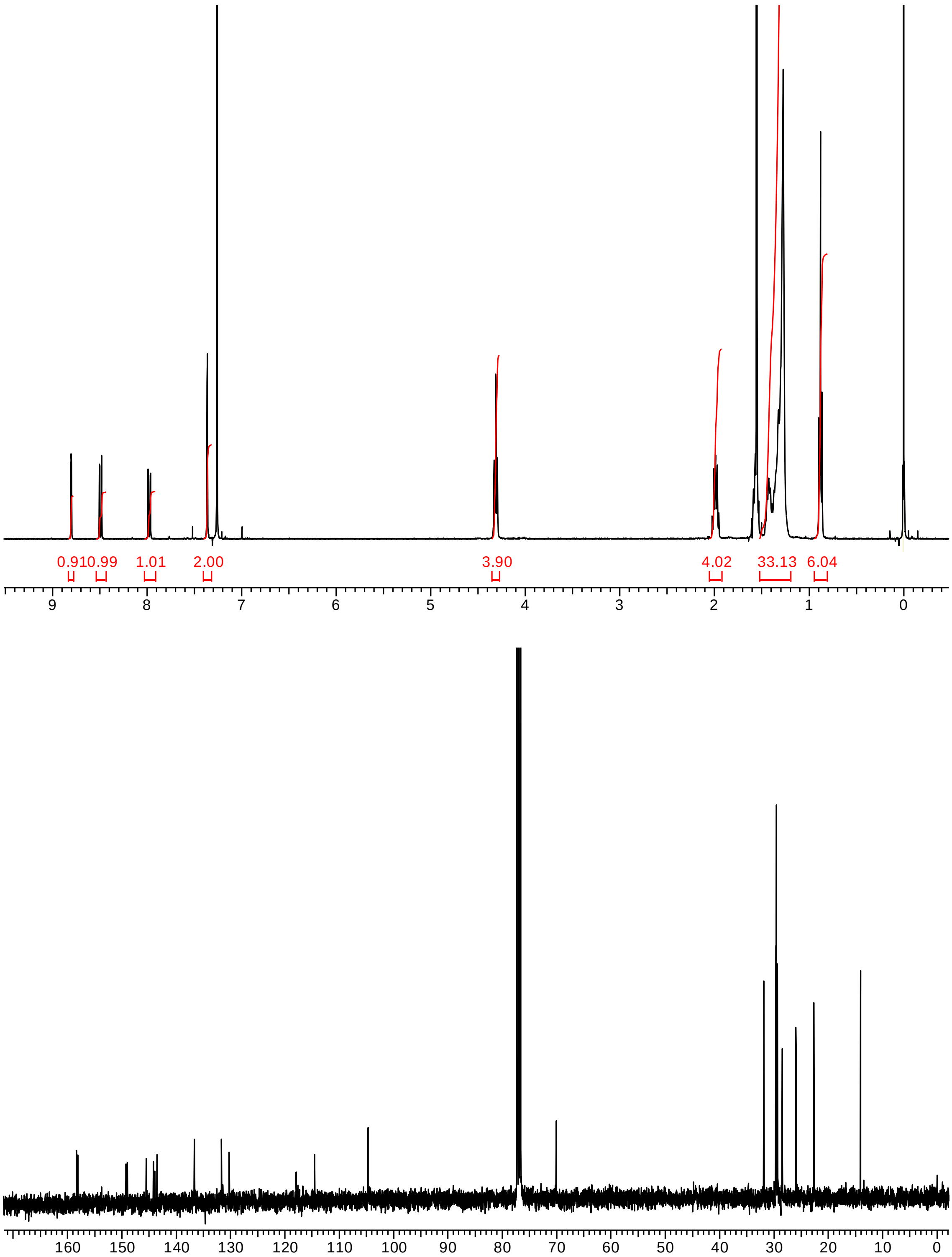
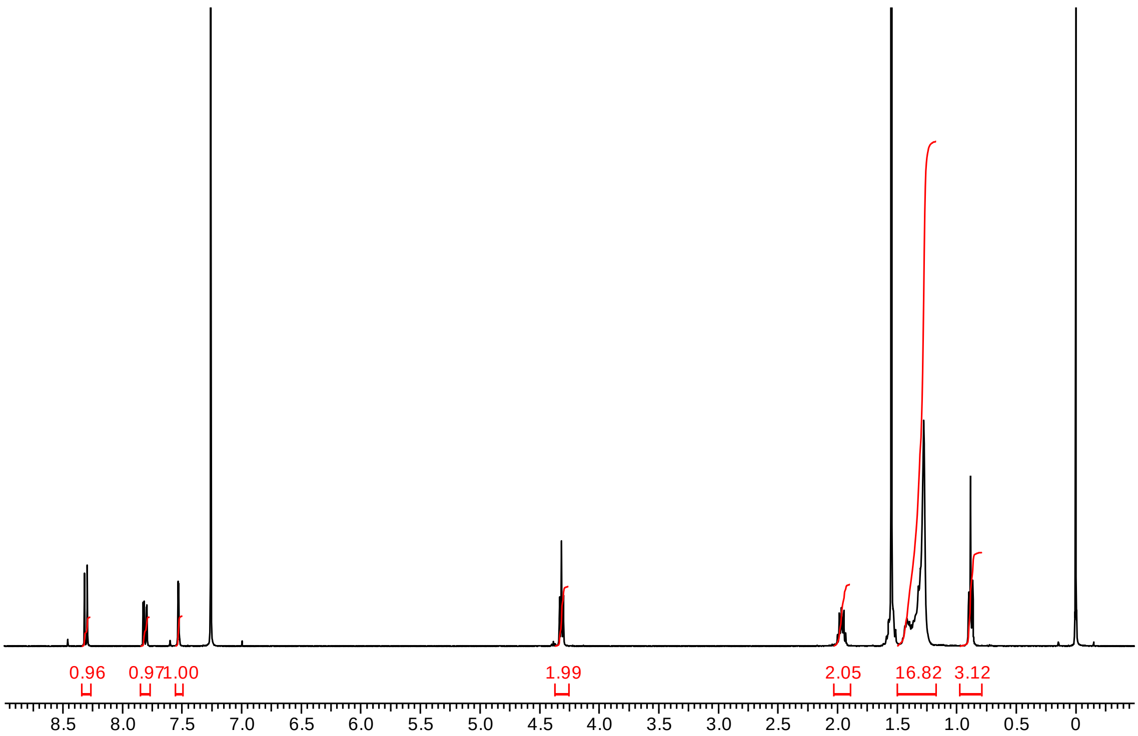


Figure S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2** in $CDCl_3$.



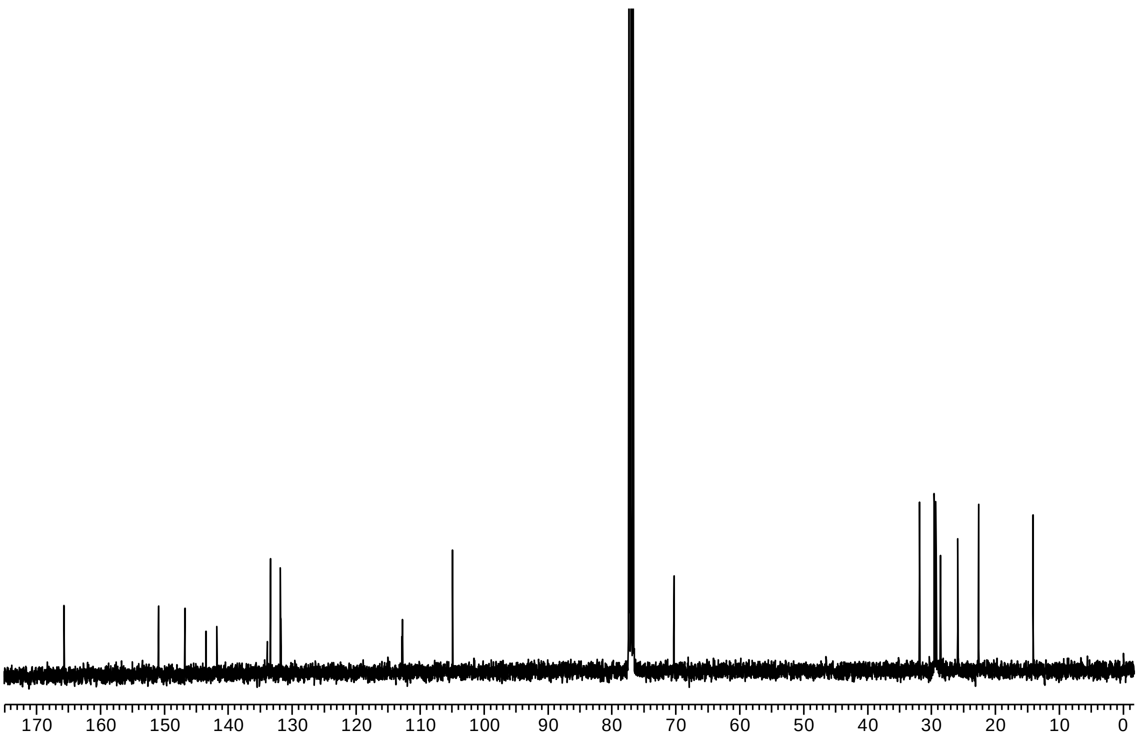


Figure S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3** in $CDCl_3$.

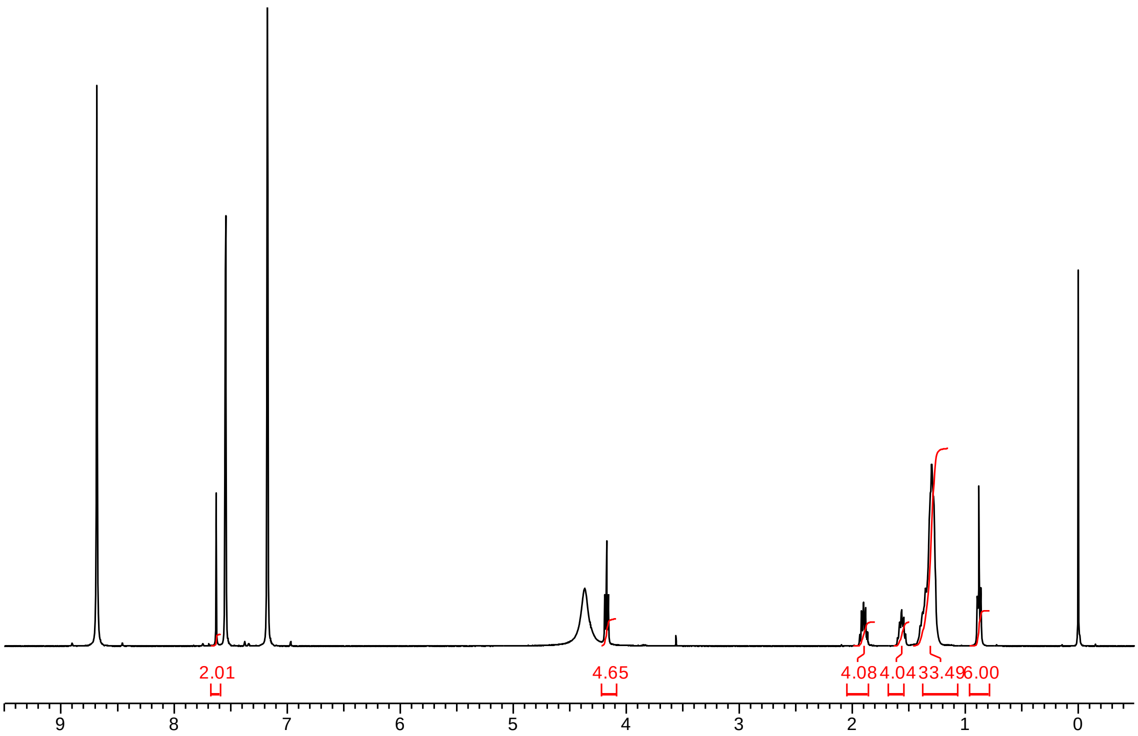


Figure S6 ^{1}H NMR spectrum of **4** in pyridine-d_5 at 60 °C. The ^{13}C NMR spectrum of **4** could not be measured due to its low solubility.

7. Cartesian coordinates of the optimized structures of 1-4

Cartesian coordinates of the optimized structure of **1**.
Alkoxy groups was replaced by a methoxy group.

E = -1017.20202371 a. u.
Number of imaginary frequency: 0

	X	Y	Z		Z	Y	Z
C	3.349261	0.730844	0.000041	N	-2.521247	1.421521	0.000197
C	2.165624	1.423167	0.000079	C	-4.882012	-1.446598	-0.000167
C	0.919972	0.729360	0.000261	C	-4.882012	1.446601	-0.000241
C	0.919972	-0.729360	0.000284	N	-5.893035	-2.019288	-0.000575
C	2.165623	-1.423167	0.000063	N	-5.893034	2.019292	-0.000476
C	3.349258	-0.730845	0.000064	O	4.577210	-1.275043	-0.000184
C	-1.355865	-0.721152	0.000108	O	4.577217	1.275038	-0.000179
C	-1.355865	0.721153	0.000195	C	4.683548	-2.698431	-0.000218
C	-3.636273	0.722206	0.000193	H	4.219518	-3.127696	0.894695
C	-3.636273	-0.722203	0.000548	H	4.219344	-3.127666	-0.895055
H	2.127912	2.504282	0.000059	H	5.751521	-2.913757	-0.000325

H	2.127912	-2.504283	0.000041	C	4.683574	2.698425	-0.000203
N	-0.214525	-1.429989	0.000262	H	4.219364	3.127674	-0.895031
N	-0.214525	1.429990	0.000270	H	4.219561	3.127689	0.894720
N	-2.521248	-1.421519	0.000228	H	5.751549	2.913739	-0.000322

Cartesian coordinates of the optimized structure of **2**.
Alkoxy groups was replaced by a methoxy group.

E = -1078.61990539 a. u.
Number of imaginary frequency: 0

	X	Y	Z		X	Y	Z
C	4.065073	-0.603347	0.000000	H	-4.033146	-2.889518	-0.000002
C	2.930307	-1.368127	-0.000001	C	-6.728000	0.860142	0.000001
C	1.636871	-0.756875	-0.000001	N	-7.786166	1.343650	0.000001
C	1.545096	0.703467	0.000000	N	0.377865	1.331923	0.000001
C	2.751669	1.473189	0.000001	N	0.557398	-1.527697	-0.000001
C	3.973349	0.857752	0.000001	N	-1.919158	1.183338	0.000001
C	-0.733346	0.555108	0.000001	N	-1.740612	-1.670865	-0.000001
C	-0.642119	-0.897608	-0.000001	O	5.168325	1.477381	0.000001
C	-2.919118	-1.039957	-0.000001	O	5.328033	-1.068617	-0.000001
C	-3.009048	0.406331	0.000000	C	5.182456	2.902992	0.000002
H	2.960972	-2.449551	-0.000002	H	4.690906	3.302730	-0.894302
H	2.645196	2.549818	0.000002	H	4.690907	3.302729	0.894306
C	-4.295910	1.022688	0.000001	H	6.234172	3.188435	0.000002
H	-4.344321	2.105568	0.000002	C	5.521040	-2.480925	-0.000001
C	-5.432662	0.244990	0.000000	H	5.083611	-2.938980	0.894413
C	-5.343681	-1.191380	-0.000001	H	5.083612	-2.938979	-0.894416
H	-6.261193	-1.769540	-0.000001	H	6.600285	-2.631955	-0.000001
C	-4.126503	-1.808990	-0.000001				

Cartesian coordinates of the optimized structure of **3**.
Alkoxy groups was replaced by a methoxy group.

E = -902.67570177 a. u.
Number of imaginary frequency: 0

	X	Y	Z		X	Y	Z
C	2.483559	-2.017983	-0.000092	N	-1.797103	1.417675	0.000239
C	1.330714	-1.165695	-0.000017	N	-2.169127	-1.403872	0.000084
C	1.530424	0.278546	0.000062	C	-4.132233	1.749118	-0.000076
C	2.850826	0.807362	0.000043	C	-4.512702	-1.118345	-0.000205
C	3.926704	-0.052213	-0.000020	N	-5.060632	2.447583	-0.000247
C	-0.728330	0.569134	0.000010	N	-5.591452	-1.550140	-0.000414

C	-0.922214	-0.860647	-0.000004	O	5.223111	0.316962	-0.000024
C	-3.182115	-0.566313	0.000284	C	5.531862	1.710948	0.000037
C	-2.990083	0.869231	0.000459	H	5.133384	2.201763	-0.894812
H	2.318630	-3.089603	-0.000149	H	5.133418	2.201678	0.894948
H	2.954294	1.884301	0.000086	H	6.619583	1.773927	0.000020
N	0.489892	1.122762	0.000069	C	3.733304	-1.479585	-0.000082
N	0.116351	-1.712220	-0.000040	H	4.622010	-2.101625	-0.000128

Cartesian coordinates of the optimized structure of **4**.
Alkoxy groups was replaced by a methoxy group.

E = -983.23861658 a. u.
Number of imaginary frequency: 0

	X	Y	Z		X	Y	Z
C	4.207853	0.770347	0.000040	H	2.942934	-2.383776	-0.000069
C	1.736724	0.713997	-0.000188	N	2.960763	1.369544	-0.000078
C	1.736724	-0.713997	-0.000249	H	2.942934	2.383775	-0.000014
C	4.207853	-0.770347	0.000134	O	5.241251	-1.405147	0.000092
C	-0.539406	-0.714127	-0.000112	O	5.241251	1.405147	0.000335
C	-0.539406	0.714127	-0.000089	O	-4.198288	-1.283883	0.000031
C	-1.773870	1.411620	-0.000024	O	-4.198287	1.283883	0.000155
H	-1.738113	2.493112	-0.000024	C	-4.281604	-2.703047	0.000197
C	-2.966549	0.721429	0.000062	H	-3.812501	-3.131497	0.894350
C	-2.966549	-0.721429	0.000006	H	-5.346053	-2.938786	-0.000165
C	-1.773871	-1.411620	-0.000043	H	-3.812057	-3.131655	-0.893635
H	-1.738113	-2.493112	-0.000067	C	-4.281603	2.703047	-0.000007
N	0.628264	-1.415488	-0.000237	H	-3.812574	3.131495	-0.894200
N	0.628264	1.415488	-0.000174	H	-5.346052	2.938787	0.000444
N	2.960763	-1.369545	-0.000035	H	-3.811981	3.131657	0.893785