Modelling of an Aza-Michael Reaction in the Crystalline State Controlled by *Peri-Peri* Interactions in Naphthalene Systems: Very Long N-C Bonds?

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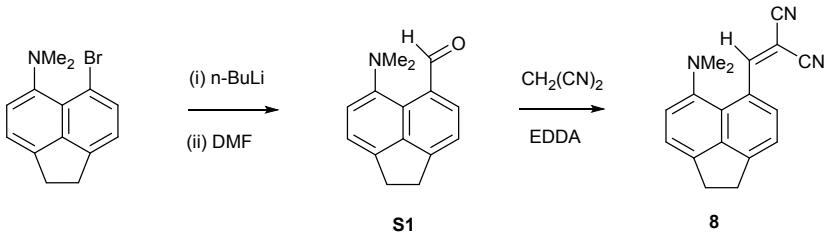
Supplementary Information.

I. Synthesis of Compounds.

General. Solution NMR spectra were measured on a Jeol ECX or EXZ 400 spectrometer at 399.6 MHz for ^{1}H and at 100.5 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling on solids or oils and are reported in cm^{-1}. Mass spectra were recorded using an ESI source on a Waters Xevo QTOF G2 XS with a Waters Acquity UPLC system. Flash chromatography was performed on silica. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University.

1. Preparation of 8.



EDDA = ethylenediammonium diacetate.

6-Dimethylamino-1,2-dihydroacenaphthylene-5-carbaldehyde, S1.

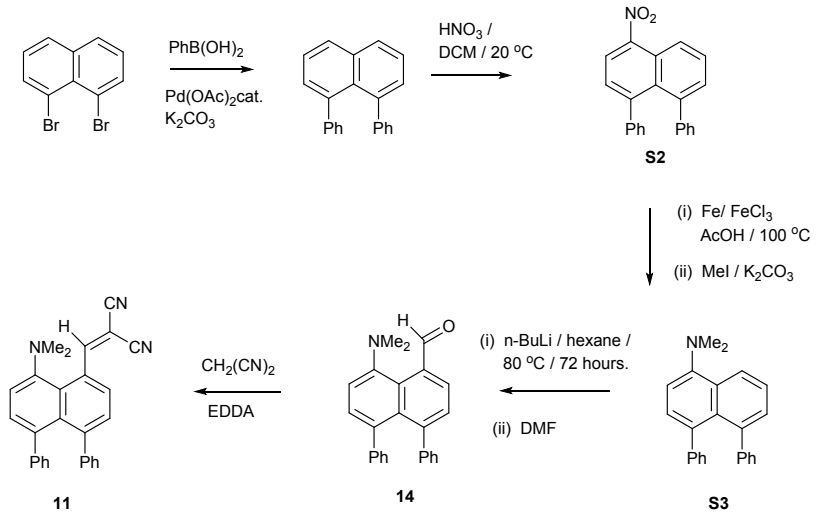
5-Bromo-6-dimethylamino-1,2-dihydroacenaphthylene[S1] (0.50 g, 1.81 mmol) was dissolved in anhydrous THF (15 mL) under nitrogen and cooled to -78℃. *n*-BuLi (1.6M in hexanes, 1.7 mL, 2.72 mmol) was steadily added, and the deep red solution was stirred at -78℃ for 3 h. Anhydrous DMF (0.28 mL, 3.62 mmol) was added and the reaction was allowed to warm to room temperature. After 16 h. the resulting orange solution was quenched with H_2O (10 mL) and stirred for 10 min. The aqueous solution was washed with ethyl acetate (3 x 30 mL) and the combined organic layers washed with H_2O (40 mL) and brine (40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude deep orange oil which was purified by flash column chromatography (1:19 ethyl acetate/petrol 40-60), to give product **S1** as an orange solid (226 mg, 55%), m.p. 96-99 ℃. δ_H (400 MHz, $CDCl_3$, 24 °C): 11.38 (1H, s, C*H*O), 8.06 (1H, d, J = 7.3 Hz, 4-*H*), 7.32 (1H, d, J = 7.3 Hz, 3-*H*), 7.24 - 7.28 (2H, m, 7-, 8-*H*), 3.36 (4H, m, 1-, 2-H_2), 2.76 (6H, s, N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 195.7 (C=O), 153.6, 148.1, 141.9, 141.4, 131.3 (Ar-C_5), 129.2 (4-*C*), 126.5 (Ar-C_1), 120.2, 119.7, 119.4 (4-,7-,8-*C*), 45.1 (N(CH_3)$_2$), 31.1 & 29.8 (1-, 2-*C*); ν_{max}/cm^{-1}: 2819, 2773, 1660 (C=O), 1578, 1500, 1444,

1392, 1332, 1308, 1205, 1185, 1144, 1114, 1049, 961, 840, 821, 773, 657. Found: C, 79.85; H, 6.79; N, 6.18%. Calc. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22%.

2-Cyano-3-(6'-(dimethylamino)-1',2'-dihydroacenaphthylen-5'-yl)propenenitrile, 8.

Malononitrile (44 mg, 0.67 mmol) and ethylenediamine diacetate (8 mg, 0.04 mmol) were added to a solution of dimethylamino aldehyde **S1** (100 mg, 0.44 mmol) in anhydrous methanol (15 mL), and the deep orange solution heated to reflux for 2 h. The solvent was removed *in vacuo* to yield a crude dark orange solid which was purified by flash column chromatography (1:4 ethyl acetate:petrol 40-60) to give product **8** as an orange solid (110 mg, 91%), m.p. 123-126℃. δ_H (400 MHz, $CDCl_3$, 24 °C): 9.43 (1H, s, 3-*H*), 7.85 (1H, d, J = 7.3 Hz, 4'-*H*), 7.28 - 7.37 (3H, m, 3'-, 7'-, 8'-*H*), 3.40 (4H, m, 1'-, 2'-H_2), 2.71 (6H, s, N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 164.6 (3-*C*), 153.4, 147.6, 142.7, 140.9 (Ar-C_4), 130.0 (4'-*C*), 126.1, 124.3 (Ar-C_2), 121.2, 120.8, 119.3 (3'-,6'-,7'-*C*), 114.4 & 113.0 (2 x *C*≡N), 79.5 (2-*C*), 45.4 (N(*C*H_3)$_2$), 31.0 & 29.7 (1'-, 2'-*C*); ν_{max}/cm^{-1}: 2827, 2786, 2221 (C≡N), 1553, 1496, 1474, 1438, 1416, 1362, 1319, 1297, 1274, 1218, 1151, 1088, 1041, 961, 890, 840, 777, 752. Found: C, 78.83; H, 5.79. N: 15.32%. Calc. for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37%.

2. Preparation of 11.



1-Nitro-4,5-diphenylnaphthalene, S2.

4,5-Diphenylnaphthalene[S2] (1.90 g, 6.79 mmol), 1.42 M nitric acid (3.2 ml, 72.1 mmol) and DCM (32 ml) were stirred together at room temperature overnight. The mixture was added to excess aqueous sodium hydrogen carbonate and extracted with DCM (3 x 30 mL). The organic layer was dried with anhydrous sodium sulfate and evaporated, and the residue purified by

chromatography (2:1 hexane/chloroform) to give **S2** as a yellow solid (1.71 g, 80%), m.p. 145-147 °C (lit.[S3] 146-147 °C). δ_H (400 MHz, $CDCl_3$, 24 °C): 8.52 (1H, dd, J = 7.4, 1.2 Hz, 8-*H*), 8.14 (1H, d, J = 7.8 Hz, 2-*H*), 7.75 (1H, dd, J = 8.6, 7.3 Hz, 7-*H*), 7.51-7.55 (2H, m, 3-,6-*H*), 6.95-6.99 (10H, m, 2 x C_6H_5); δ_C (100 MHz, $CDCl_3$, 24 °C): 147.0, 146.8, 142.1, 141.6, 141.4, 132.3, 130.2, 129.8, 129.2 (Ar-C_9), 128.1-126.3 (Ar-C_{12}), 122.3 (Ar-C_1).

1-Dimethylamino-4,5-diphenylnaphthalene, S3.

The following method is adapted from the works of Pla et al.[S1] 1-Nitro-4,5-diphenyl-naphthalene **S2** (1.00 g, 3.08 mmol), was dissolved in ethanol (100 mL), acetic acid (10 mL) added and the reaction heated to 100°C. Iron powder (1.98 g, 35.38 mmol) and iron(III) chloride (0.40 g, 2.46 mmol) were added and the reaction heated at 100°C for a further 3 h. The reaction was cooled, the solvent removed *in vacuo* and the resultant brown oil dissolved in DMF (100 mL). The solution was stirred for 10 min. before being filtered through Celite and concentrated *in vacuo* to give a crude brown oil. Acetonitrile (100 mL) and potassium carbonate (2.55 g, 18.46 mmol) were added to the crude oil and the reaction heated to 50°C for 1 h. Iodomethane (1.15 mL, 18.46 mmol) was added and heating continued for 16 h. The reaction was cooled, diluted with Et_2O (100 mL) and filtered through a small plug of silica gel, eluting with further portions of Et_2O. The solvent was removed *in vacuo* yielding a crude brown oil which was purified by flash column chromatography (40:1 hexane:diethyl ether) to give product **S3** as a pale brown solid (0.89 g, 89%), m.p. 51-54°C. δ_H (400 MHz, $CDCl_3$, 24 °C): 8.44 (1H, dd, J = 8.5, 1.3 Hz, 8-*H*), 7.55 (1H, dd, J = 8.5, 7.0 Hz, 7-*H*), 7.42 (1H, dd, J = 7.0, 1.5 Hz, 6-*H*), 7.34 (1H, d, J = 7.8 Hz, 3-*H*), 7.21 (1H, d, J = 7.8 Hz, 2-*H*), 6.83-7.05 (10H, m, Ar-H_{10}), 2.99 (6H, s, N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 150.7 (1-*C*), 143.5, 143.4, 140.7, 135.3 (Ar-C_4), 130.9 & 130.8 (3-, 6-*C*), 130.6, 130.4 (Ar-C_2), 130.0, 129.8, 127.1, 127.0 (*meta*/*ortho*-C_4), 125.6, 125.3 (*para*-C_2), 124.4 (7-*C*), 124.1 (8-*C*), 113.7 (2-*C*), 45.5 (N(CH_3)$_2$); ν_{max}/cm^{-1}: 3055, 3023, 2937, 1570, 1491, 1441, 1401, 1319, 1193, 1168, 1139, 1072, 952, 908, 826, 773, 695. Found: C, 89.02; H, 6.58; N, 4.39%. Calc. for $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33%.

1-Dimethylamino-4,5-diphenylnaphthalene-8-carbaldehyde, 14.

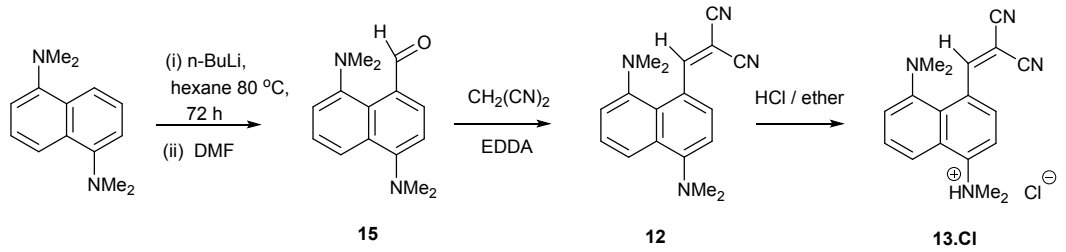
Dimethylaminonaphthalene derivative **S3** (700 mg, 2.17 mmol), dry hexane (20 mL) and *n*-BuLi (2.5M in hexanes, 3.50 mL, 8.68 mmol) were stirred heated to 80°C and the mixture

refluxed for 72 h, resulting in the formation of a grey precipitate. The precipitate was cooled to room temperature, allowed to settle and the supernatant removed. Tetrahydrofuran (20 mL) was added and the reaction mixture was cooled to -78^{o}C before anhydrous DMF (1.34 mL, 17.36 mmol) was added dropwise, with the reaction stirred for a further 18 h at room temperature. The reaction was quenched with a few drops of methanol, diluted with water (100 ml) and extracted with dichloromethane (3 x 50 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (ethyl acetate) to give **14** as an off-white solid (260 mg, 34%), m.p. 177-179^{o}C. δ_H (400 MHz, $CDCl_3$, 24 °C): 10.38 (1H, s, C*H*O), 7.55 (1H, d, J = 6.9 Hz, 2-*H*), 7.39-7.47 (3H, m, 3-, 6-, 7-*H*), 6.89-7.00 (10H, m, Ar-H_{10}), 2.77 (6H, N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 186.7 (*C*HO), 149.0 (8-*C*), 142.6, 142.4, 142.1, 137.7, 137.6, 131.6, 131.4, 131.1, 130.3 (Ar-C_9), 129.8, 129.7, 127.2 (*meta-*,*ortho-C*), 126.1 & 125.9 (*para-C*), 123.9 (2-*C*), 117.6 (Ar-C_1), 44.8 (N(*C*H$_3$)$_2$); ν_{max}/cm^{-1}: 3030, 2986, 2943, 2865, 2831, 1638 (C=O), 1582, 1510, 1491, 1441, 1400, 1364, 1316, 1195, 118, 1154, 1122, 1074, 1042, 1010, 962, 870, 840, 764, 697. Found: C, 85.16; H, 5.79; N, 4.08%. Calc. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99%.

2-Cyano-3-((8'-(dimethylamino)-4',5'-diphenylnaphthalen-1'-yl)propenenitrile, 11.

Dimethylamino-aldehyde **14** (100 mg, 0.28 mmol), malononitrile (60 mg, 0.91 mmol) and ethylenediamine diacetate (10 mg, 0.06 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 24 h. The solvent was removed *in vacuo* and the crude product purified by flash column chromatography (4:1 hexane: ethyl acetate) to give product **11** as a yellow solid (100 mg, 53%), m.p. 138-140 ^{o}C. δ_H (400 MHz, $CDCl_3$, 24 °C): 8.45 (1H, d, J = 1.0 Hz, 3-*H*), 7.44-7.56 (4H, m, 2'-,3'-,6'-,7'-*H*), 6.89-6.96 (10H, m, Ar-H_{10}), 2.82 (6H, s, 8'-N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 161.3 (3-*C*), 147.5 (8'-*C*), 143.9, 141.9, 141.6, 139.4, 132.4, 131.9, 131.5, 130.5, 129.8, 129.7, 128.3, 127.5, 126.6, 126.5, 126.3, 119.2 (Ar-C_{17}), 116.2 & 114.6 (br 2 x C≡N), 65.5 (2-*C*), 45.5 (N(*C*H$_3$)$_2$); ν_{max}/cm^{-1}: 3027, 2980, 2939, 2868, 2834, 2792, 2220 (C≡N), 2207, 1653, 1547, 1508, 1491, 1441, 1388, 1318, 1183, 1154, 1126, 1074, 1034, 1016, 999, 926, 908, 841, 753, 695. Found: C, 83.92; H, 5.26; N, 10.74%. Calc. for $C_{28}H_{21}N_3$: C, 84.18; H, 5.30; N, 10.52%.

3. Preparation of 12 and 13.Cl.



EDDA = ethylenediammonium diacetate.

4,8-*Bis*(dimethylamino)-1-naphthaldehyde, 15.

1,5-*Bis*(dimethylamino)naphthalene (1.00 g, 4.67 mmol) was dissolved in anhydrous hexane (15 mL) and stirred while *n*-BuLi (1.7M in hexanes, 2.75 mL, 4.67 mmol) was steadily added at room temperature. The solution was refluxed for 3 days, over which time a light brown precipitate formed. The supernatant was removed, and the solid was suspended in anhydrous THF (15 mL), cooled to 0 ºC and anhydrous DMF (0.43 mL, 5.61 mmol) added. The solution was left to stir for 24 h. The yellow/brown solution was quenched with H_2O (30 mL) and the reaction extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a deep orange oil. Purification by flash column chromatography (2:3 ethyl acetate/petrol 40-60) gave the product **15** as a dark orange solid (0.40 g, 35 %), m.p. 45-48℃. δ_H (400 MHz, $CDCl_3$, 24 °C): 10.62 (1H, s, 1-C*H*O), 7.93 (1H, dd, J = 8.7, 1.4 Hz, 7-*H*), 7.52 (1H, d, J = 7.8 Hz, 2-*H*), 7.42 (1H, t, J = 8.0 Hz, 6-*H*), 7.25 (1H, dd, J = 7.3, 1.4 Hz, 5-*H*), 6.98 (1H, d, J = 7.8 Hz, 3-*H*), 2.89 (6H, s, 4-N(CH_3)$_2$), 2.67 (6H, s, 8-N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 191.6 (*C*HO), 154.1 (4-*C*), 150.8 (8-*C*), 131.3 (1-*C*), 130.8 (8a-*C*), 130.0 (4a-*C*), 126.0 (2-*C*), 125.8 (6-*C*), 121.1 (7-*C*), 117.9 (5-*C*), 113.3 (3-*C*), 44.9 (2 x N(*C*H_3)$_2$); ν_{max}/cm^{-1}: 2939, 2864, 2827, 2782, 1666 (C=O), 1599, 1576, 1507, 1451, 1405, 1400, 1358, 1353, 1323, 1202, 1183, 1144, 1080, 1049, 1011, 972, 812, 795, 765, 697. Found: C, 74.14; H, 7.26; H,11.51%. Calc. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56%.

2-Cyano-3-(4'-,8'-*bis*(dimethylamino)naphthalen-1'-yl)propenenitrile, 12.

Naphthaldehyde **15** (750 mg, 3.06 mmol), malononitrile (300 mg, 4.59 mmol) and ethylenediamine diacetate (54 mg, 0.3 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 24 h. The methanol was removed *in vacuo* to give a dep orange oil which was purified by flash column chromatography (1:4 ethyl acetate/petrol 40-60), to

give product **12** as an orange solid (649 mg, 72 %), m.p. 105-108℃. δ_H (400 MHz, CD_2Cl_2, 24 °C): 8.69 (1H, d, J = 0.9 Hz, 3-*H*), 7.99 (1H, dd, J = 8.7, 0.9 Hz, 5'-*H*), 7.48 (1H, t, J = 7.8 Hz, 6'-*H*), 7.44 (1H, dd, J = 7.8, 0.9 Hz, 2'-*H*), 7.37 (1H, dd, J =7.3, 0.9 Hz, 7'-*H*), 7.02 (1H, d, J = 8.2 Hz, 3'-*H*), 2.93 (6H, s, 4'-N(CH_3)$_2$), 2.66 (6H, s, 8'-N(CH_3)$_2$); δ_C (100 MHz, CD_2Cl_2, 24 °C): 165.8 (3-*C*), 154.9 (8'-*C*), 150.2 (4'-*C*), 131.8 (8a'-*C*), 130.1 (4a'-*C*), 128.4 (2'-*C*), 126.2 (6'-*C*), 122.5 (5'-*C*), 122.3 (1'-*C*), 120.0 (7'-*C*), 115.4 & 114.0 (2 x *C*≡N), 113.2 (3'-*C*), 73.0 (2-*C*), 45.3 (4'-N(CH_3)$_2$), 44.8 (8'-N(CH_3)$_2$); δ_H (400 MHz, DMSO-d_6, 24 °C): 8.85 (1H, s, 3-*H*), 8.25 (1H, d, J = 7.6 Hz, 5'-*H*), 7.6-7.73 (2H, m, 6'-,7'-*H*), 7.52 (1H, s, 2'-,3'-*H*), 3.17 (6H, s) & 2.68 (6H, s,) 2 x -N(CH_3)$_2$; δ_C(100 MHz, DMSO-d_6, 24 °C): 161.4 (3-*C*), 149.4 (4'-,8'-*C*), 131.6, 128.0 (Ar-C_2), 127.9 (6'-*C*), 127.1 (2'-*C*), 126.3 (Ar-C_1), 122.3 (5'-*C*), 121.2 (7'-*C*), 116.5 (3'-*C*), 116.4 & 115.2 (2 x *C*≡N), 65.3 (2-*C*), 45.6 & 45.4 (2 x-N(CH_3)$_2$); ν_{max}/cm^{-1}: 2938, 2864, 2837, 2788, 2218 (C≡N),1574, 1555, 1544, 1507, 1462, 1407, 1375, 1325, 1206, 1195, 1144, 1102, 1076, 1045, 977, 919, 837, 812, 798, 774, 749. Found: C, 74.30; H, 6.34; N, 19.34%. Calc. for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.30%.

2-Cyano-3-(8'-dimethylamino-4'-dimethylammonio-naphthalen-1'-yl)propenenitrile chloride, 13.Cl.

Dinitrile **12** (100 mg, 0.34 mmol) was dissolved in anhydrous diethyl ether (10 mL) and ethereal hydrochloric acid (1M, 0.34 mL, 0.34 mmol) was added dropwise with immediate formation of a yellow precipitate. The solution was stirred for a further 3 h. before the solid was collected by careful filtration under a flow of nitrogen. The solid was washed with cold anhydrous diethyl ether and dried under vacuum to give the desired salt **13.Cl** as a yellow solid (80 mg, 71%), m.p. 167-170 ℃. δ_H (400 MHz, CD_2Cl_2, 24 °C): 8.85 (1H, br d, J = 8.2 Hz, 5'-*H*), 8.56 (1H, s, 3-*H*), 7.83 (1H, t, J = 8.0 Hz, 6'-*H*), 7.71 (1H, br d, J = 7.3 Hz, 3'-*H*), 7.60 (1H, d, J = 7.8 Hz, 7'-*H*), 7.54 (1H, d, J = 7.3 Hz, 2'-*H*), 3.33 (6H, s, 4'-N$^+$H(CH_3)$_2$), 2.71 (6H, s, 8'-N(CH_3)$_2$); δ_C (100 MHz, CD_2Cl_2, 24 °C): 163.1 (3-*C*), 150.2 (8'-*C*), 142.9 (br, 4'-*C*), 132.2 (8a'-*C*), 130.6 (br 1'-*C*), 129.6 (6'-*C*), 127.7 (4a'-*C*), 126.8 (2'-*C*), 122.2 (7'-*C*), 121.4 (5'-*C*), 118.0 (br 3'-*C*), 114.7 & 113.3 (2 x *C*≡N), 73.4 (2-*C*), 46.8 (4'-N$^+$H(CH_3)$_2$), 45.4 (8'-N(CH_3)$_2$); ν_{max}/cm^{-1}: 3431, 3022, 2973, 2206 (C≡N), 1516, 1509, 1469, 1453, 1434, 1406, 1362, 1326, 1320, 1187, 1147, 1128, 1043, 990, 967, 887, 749, 782, 749, 692, 659. Found: C, 66.04; H, 5.69; N, 16.98. Calc. for $C_{18}H_{19}N_4Cl$: C, 66.15; H, 5.86; N, 17.14%.

4. Preparation of ^{13}C labelled 13.Cl for solid state NMR measurements.

4,8-*Bis*(dimethylamino)-1-(^{13}C(=O),99%)-naphthaldehyde, **^{13}C(=O)-15.**

1,5-*Bis*(dimethylamino)-1-naphthalene (2.88 g, 13.50 mmol) was dissolved in anhydrous hexane (20 mL) and stirred while *n*-BuLi (1.7M in hexanes, 7.94 mL, 13.50 mmol) was steadily added at room temperature. The solution was refluxed for 3 days, over which time a light brown precipitate formed. The solid was suspended in anhydrous THF (20 mL), cooled to 0 ºC and anhydrous (^{13}C=O)-DMF (1.00 g, 13.50 mmol) added. The solution was left to stir for 24 h. The yellow/brown solution was quenched with H_2O (30 mL) and the reaction extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a deep orange oil. Purification by flash column chromatography (2:3 ethyl acetate/petrol 40-60) gave the product **^{13}C(=O)-15** as a dark orange solid (1.22 g, 35 %). δ_H (400 MHz, $CDCl_3$, 24 °C): 10.41-10.88 (1H, d, J = 186.4 Hz, ^{13}C*H*O), 7.98 (1H, d, J = 8.5 Hz, 7-*H*), 7.55 (1H, dd, J = 7.7, 4.5 Hz, 2-*H*), 7.46 (1H, t, J = 4.4 Hz, 6-*H*), 7.28 (1H, dd, J = 7.4, 1.0 Hz, 5-*H*), 7.00 (1H, d, J = 7.8 Hz, 3-*H*), 2.93 (6H, s, 4-N(CH_3)$_2$), 2.70 (6H, s, 8-N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, *24* °C): 191.5 (^{13}CHO); HRMS (ESI): Found: 244.1534 ($M+H^+$), $C_{14}{}^{13}CH_{19}N_2O$ requires: 244.1536 ($M+H^+$). The doubly^{13}C-labelled 4,8-*bis*(dimethylamino)naphthalene-1,5-*bis*-carbaldehyde was further isolated as a yellow solid (0.38 g, 10%). δ_H (400 MHz, $CDCl_3$, 24 °C): 10.44-10.91 (2H, d, J = 187.1 Hz, ^{13}C*H*O), 7.67 (2H, dd, J = 7.8, 4.5 Hz, 2', 6'-*H*), 7.25 (2H, d, J = 7.8 Hz, 3', 7'-*H*), 2.76 (12H, s, 4', 8'-N(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$, *24* °C): 191.1 (*C*HO); Found: C, 71.05; H, 6.80; N, 10.17%. Calc. for $C_{14}{}^{13}C_2H_{18}N_2O_2$: C, 71.30; H, 6.66; N, 10.29%.

2-Cyano-3-(4'-,8'-*bis*(dimethylamino)naphthalen-1'-yl)-3-(^{13}C,99%)-propenenitrile, 3-^{13}C-12.

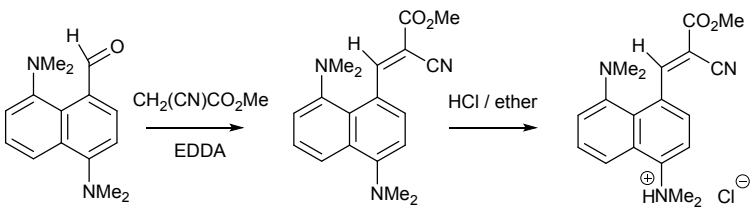
Enriched naphthaldehyde **^{13}C(=O)-15** (500 mg, 1.93 mmol), malononitrile (191 mg, 2.90 mmol) and ethylenediamine diacetate (36 mg, 0.20 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 24 h. The methanol was removed *in vacuo* to give a deep orange oil which was purified by flash column chromatography (1:9 ethyl acetate/petrol 40-60), to give product **3-^{13}C-12** as an orange solid (360 mg, 64 %). δ_H (400 MHz, $CDCl_3$, 24 °C): 8.72 (1H, d, $^1J_{C,H}$ = 172.8 Hz, 3-*H*), 8.01 (1H, d, J = 8.0 Hz, 5'-*H*), 7.44-7.52 (2H, m, 2'-6'-*H*), 7.37 (1H, dd, J =7.3, 1.0 Hz, 7'-*H*), 7.02 (1H, d, J = 7.9 Hz, 3'-*H*), 2.95

(6H, s, 4'-N(C*H*$_3$)$_2$), 2.69 (6H, s, 8'-N(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 165.3 (3-*C*); *HRMS* (ESI) calcd for $C_{17}{}^{13}CH_{19}N_4$ ([M+H]$^+$): 292.1649, found: 292.1649.

Preparation of 2-Cyano-3-(8'-dimethylamino-4'-dimethylammonio-naphthalen-1'-yl)-3-(^{13}C,99%)-propenenitrile chloride, 3-^{13}C-13.Cl.

Enriched dinitrile derivative **3-^{13}C-12** (180 mg, 0.62 mmol) was dissolved in anhydrous diethyl ether (10 mL) and ethereal hydrochloric acid (1M, 0.62 mL, 0.62 mmol) was added dropwise with immediate formation of a yellow precipitate. The solution was stirred for a further 3 h. before the solid was collected by careful filtration under a flow of nitrogen. The solid was washed with cold anhydrous diethyl ether and dried under vacuum to give the desired product **3-^{13}C-13.Cl** as a yellow solid (120 mg, 60%). δ_H (400 MHz, $CDCl_3$, 24 °C): 8.90 (1H, br d, J = 8.2 Hz, 5'-*H*), 8.53 (1H, d, $^1J_{C,H}$ = 174.7 Hz, 3-*H*), 7.83 (1H, t, J = 8.0 Hz, 6'-*H*), 7.75 (1H, br d, J = 7.8 Hz, 3'-*H*), 7.58 (1H, d, J = 7.8 Hz, 7'-*H*), 7.54 (1H, m, 2'-*H*), 3.40 (6H, s, 4'-NH(C*H*$_3$)$_2$), 2.71 (6H, s, 8'-N(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$, 24 °C): 162.5 (3-*C*). δ_H (800 MHz, DMSO-d_6, 24 °C): 8.84 (1H, d, $^1J_{C,H}$ = 176 Hz, 3-*H*), 8.01 (1H, dd, J = 7.9, 1.0 Hz, 7'-*H*), 7.62 (1H, dd, J = 7.4 and 1.4 Hz, 5'-*H*), 7.61 (1H, dd, J = 7.4 and 7.9 Hz, 6'-*H*), 7.46 (1H, ddd, $J_{H,H}$ = 7.8, 1.1 Hz, $J_{C,H}$ = 4.2(to C-3) Hz, 2'-*H*), 7.20 (1H, bd, 7.8 Hz, 3'-*H*), 2.92 (6H, br s, 4'-NMe_2), 2.65 (6H, s, 8'-NMe_2);δ_C (201 MHz, DMSO-d_6, 24 °C): 162.82 (d,$^1J_{CH}$ = 176 Hz, 3-*C*), 152.6 (br, 4'-*C*), 149.14 (8'-*C*), 131.17 (8a'-*C*), 128.48 (4a'-*C*), 127.16 (2'-*C*), 126.41 (6'-*C*), 122.80 (bd, J_{cc}=~56 Hz, 1'-*C*), 121.91 (7'-*C*), 120.19 (5'-*C*), 115.92 (d, $^3J_{CH}$ = 6.9 Hz, *C*N), 114.67 (d, $^3J_{CH}$ = 13 Hz, *C*N), 113.60 (bd, J_{CH} = 159 Hz, 3'-*C*), 66.17 (d, $J_{C,C}$ = 72.6 Hz, 2-*C*), 44.96 (8'- NMe_2), 44.42 (br, 4'-NMe_2).

5. Synthesis of 20 and 21.Cl.



15 **20** **21.Cl**

EDDA = ethylenediammonium diacetate.

Preparation of methyl *E*-2-cyano-3-(4',8'-bis(dimethylamino)naphthalen-1'-yl)-2-propenoate, 20.

4,8-*Bis*(dimethylamino)-1-naphthaldehyde **15** (200 mg, 0.88 mmol), methyl cyanoacetate (0.16 mL, 1.44 mmol) and ethylenediamine diacetate (16 mg, 0.09 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 5h. The methanol was removed *in vacuo* to give a deep orange oil, which was purified by flash column chromatography (15:85 EtOAc/petrol 40-60), to give **20** as an orange solid (120 mg, 42 %), m.p. 80-83℃. δ_H (400 MHz, CD_2Cl_2, 24 °C): 9.16 (1H, s, 3-*H*), 7.99 (1H, d, J = 8.7 Hz, 5'-*H*), 7.50 (1H, d, J = 7.8 Hz, 2'-*H*), 7.46 (1H, t, J = 7.8 Hz, 6'-*H*), 7.31 (1H, d, J =7.3 Hz, 7'-*H*), 7.02 (1H, d, J = 7.8 Hz, 3'-*H*), 3.92 (3H, s, OCH_3), 2.92 (6H, s, 4'-N(CH_3)$_2$), 2.63 (6H, s, 8'-N(CH_3)$_2$); δ_C (100 MHz, CD_2Cl_2, 24 °C): 164.7 (*C*=O), 161.7 (3-*C*), 153.8 (4'-*C*), 150.2 (8'-*C*), 131.7 (8a'-*C*), 130.2 (4a'-*C*), 127.8 (2'-*C*), 125.8 (6'-*C*), 123.7 (1'-*C*), 121.8 (5'-*C*), 119.3 (7'-*C*), 116.5 (*C*≡N), 113.5 (3'-*C*), 94.6 (2-*C*), 52.8 (O*C*H$_3$), 45.3 (8'- N(*C*H$_3$)$_2$), 44.9 (4'-N(*C*H$_3$)$_2$); ν_{max}/cm^{-1}: 2942, 2864, 2830, 2786, 2219 (C≡N), 1718 (C=O), 1576, 1507, 1265, 1231, 1203, 1090, 760. Found: C, 70.48; H, 6.66; N, 13.07%. Calc. for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99%.

Methyl *E*-2-cyano-3-(8'-dimethylamino-4'-dimethylammonio-naphthalen-1'-yl)-2-propenoate chloride, 21.Cl.

Methyl cyanoester **20** (120 mg, 0.37 mmol) was dissolved in anhydrous diethyl ether (10 mL) and ethereal hydrochloric acid (1M, 0.37 mL, 0.37 mmol) was added dropwise with a yellow precipitate forming immediately. The solution was stirred for a further 3 h. before the solid was collected by careful filtration under a nitrogen flow, washed with cold anhydrous diethyl ether and dried under vacuum to give the desired product **21.Cl** as a yellow solid (80 mg, 60%), m.p. 124-127℃. δ_H (400 MHz, CD_2Cl_2, 24 °C): 9.00 (1H, s, 3-*H*), 8.90 (1H, br d, J = 8.1 Hz, 5'-*H*), 7.83 (1H, t, J = 7.6 Hz, 6'-*H*), 7.77 (1H, br d, J = 7.8 Hz, 3'-*H*), 7.54 (2H, m, 2'-, 7'-*H*), 3.95 (3H, s, OCH_3), 3.43 (6H, s, 4'-N$^+$H(CH_3)$_2$), 2.64 (6H, s, 8'-N(CH_3)$_2$); δ_C (100 MHz, CD_2Cl_2, 24 °C): 163.7 (*C*=O), 158.5 (3-*C*), 150.5 (8'-*C*), 140.3 (4'-*C*), 132.7 (1'-*C*), 131.9 (8a'-*C*), 129.8 (6'-*C*), 127.0 (4a'-*C*), 125.7 (2'-*C*), 121.8 (7'-*C*), 120.2 (5'-*C*), 118.0 (3'-*C*), 115.4 (*C*≡N), 95.3 (2-*C*), 53.0 (O*C*H$_3$), 46.9 (4'-N$^+$H(CH_3)$_2$), 45.2 (8'-N(CH_3)$_2$); ν_{max}/cm^{-1}: 2167 (C≡N), 1636 (C=O), 1505, 1459, 1438, 1366, 1269, 1183, 1090, 989, 807, 793, 771. Found: C, 63.10; H, 6.17; N, 11.31%. Calc. for $C_{19}H_{22}N_3O_2Cl$: C, 63.42; H, 6.16; N, 11.68%.

6. Preparation of 24.

Preparation of methyl (E)-2-cyano-3-(8'-(dimethylamino)naphthalen-1'-yl)propenoate, 24.

1-Dimethylamino-8-naphthaldehyde (400 mg, 2.01 mmol), methyl cyanoacetate (0.35 mL, 4.02 mmol) and ethylenediamine diacetate (18 mg, 0.10 mmol) were dissolved in anhydrous methanol (10 mL) under nitrogen and refluxed for 16 h. The solvent was removed *in vacuo* and the residual crude oil triturated with diethyl ether, giving a yellow precipitate. The solid was collected by filtration and washed with diethyl ether (3 x 20 mL) and dried to give **24** as a yellow solid (300 mg, 53%), m.p. 100-103℃. δH (400 MHz, $CDCl_3$, 24 °C): 9.21 (1H, s, 1-*H*), 7.90 (1H, dd, J = 6.9, 2.7 Hz, Ar-H_1), 7.67 (1H, d, J = 7.8 Hz, Ar-H_1), 7.45-7.55 (3H, m, Ar-H_3), 7.35 (1H, d, J = 7.3 Hz, Ar-H_1), 3.94 (3H, s, OCH_3), 2.63 (6H, s, $N(CH_3)_2$); δC (100 MHz, $CDCl_3$, 24 °C): 164.3 (*C*=O), 161.7 (1-*C*), 150.2 (8'-*C*), 135.3, 130.9, 130.3, 129.9 (Ar-C_4), 127.3 (2'-*C*), 126.9, 126.1, 125.5, 119.7 (Ar-C_4), 115.9 (C≡N), 96.1 (2-*C*), 53.0 (OCH_3), 45.4 ($N(CH_3)_2$); ν_{max}/cm^{-1} 3047, 2994, 2950, 2857, 2829, 2788, 2223 (C≡N), 1718 (C=O), 1574, 1438, 1403, 1377, 1340, 1256, 1205, 1185, 1155, 1086, 1045, 1019, 890, 833, 769, 739; *HRMS* (ESI) calcd for $C_{17}H_{17}N_2O_2$ ($[M+H]^+$): 281.1290, found: 281.1284.

II. X-ray Crystallography.

Low temperature (90-150K) X-ray diffraction data (Mo Kα) were measured on an Rigaku Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector and an 700 series Cryostream low temperature system using the CrysAlis-Pro software package.[S4] Multiple measurements at different temperatures were made using automation within the Crysalis software. Structures were solved and refined using the SHELXS and SHELXL suite of programs[S5] using the XSEED interface[S6] or OLEX.[S7] Molecular illustrations were made with Mercury.[S8] Data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC 2016747-2016754 and 2019629.

Table S1. Crystallographic data for **8**, **11** and **12**.

	8	**11**	**12**
Formula	$C_{18}H_{15}N_3$	$C_{28}H_{21}N_3.C_6H_5CH_3$	$C_{18}H_{18}N_4$
Formula weight	277.33	491.61	290.36
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$
a[Å]	9.8149(4)	8.6981(5)	20.7770(7)
b[Å]	9.9853(4)	12.6447(6)	9.3348(2)
c[Å]	15.1587(6)	12.8788(7)	18.1408(6)
α[°]	84.234(3)	81.679(4)	90
β [°]	78.977(4)	77.685(4)	114.584(4)
γ[°]	80.518(3)	78.768(4)	90
V [Å^3]	1434.64(10)	1349.48(12)	3119.46(19)
Z	4	2	8
ρ [g cm^{-3}]	1.265	1.210	1.206
T [*K*]	150.0(1)	150.0(1)	150.0(1)
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.077	0.071	0.074
unique refl.	11282	6693	7948
Refl, I > 2σI	5620	4808	6245
R_1 (I > 2σI)	0.0550	0.0522	0.0637
wR_2	0.1130	0.123	0.1268
Δρ(r) [e Å^{-3}]	0.22/ -0.23	0.30/ -0.26	0.23/ -0.33
Cryst. Solvent.	Methanol	Toluene	DCM

Compound 8.

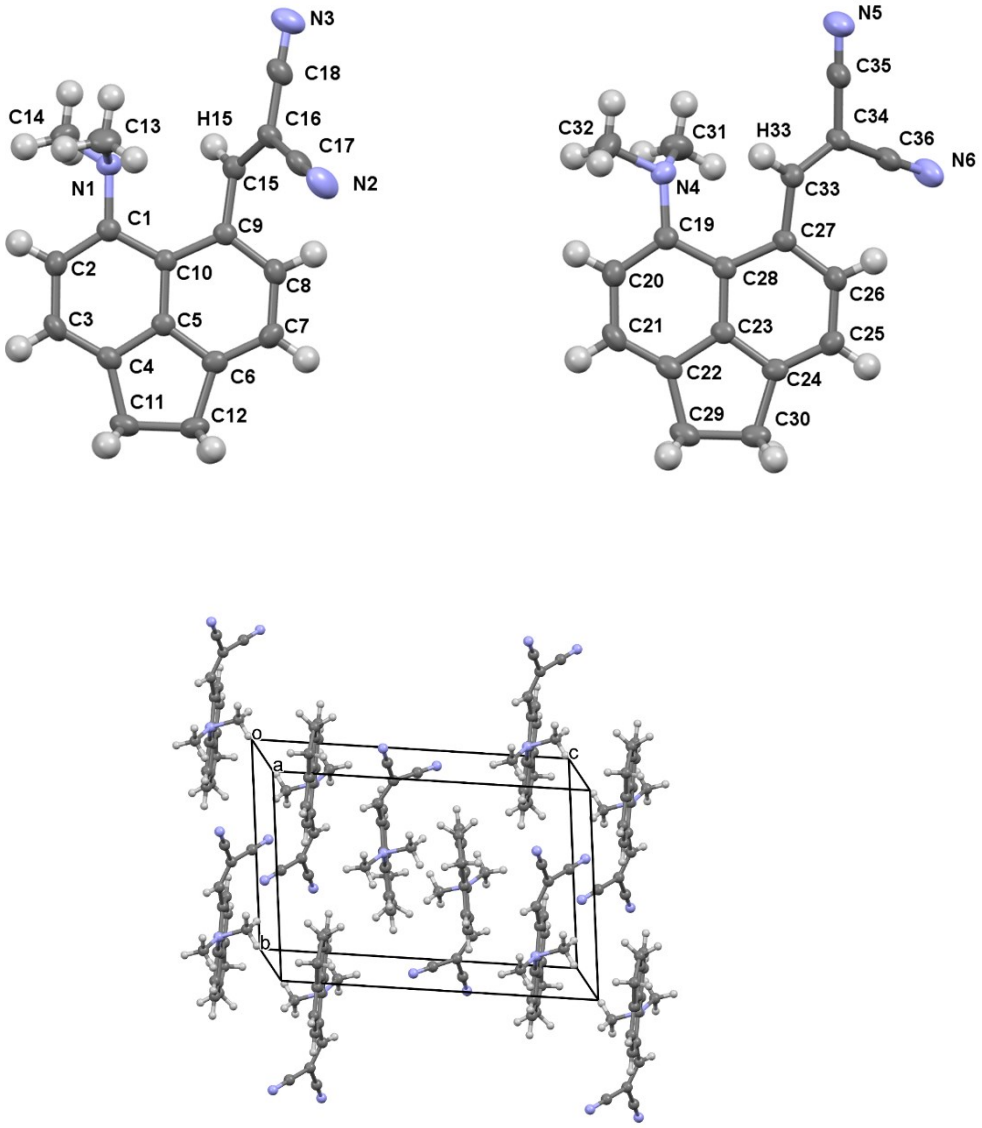


Figure S1. Atomic numbering scheme for the two independent molecules of **8** (top) and the crystal packing arrrangement viewed along the *a* axis (bottom).

Table S2. Bond Lengths for **8** / Å.

N(1)-C(1)	1.435(2)
N(1)-C(13)	1.455(3)
N(1)-C(14)	1.461(2)
N(2)-C(17)	1.143(3)
N(3)-C(18)	1.142(3)

C(1)-C(2)	1.380(3)
C(1)-C(10)	1.422(3)
C(2)-C(3)	1.409(3)
C(3)-C(4)	1.364(3)
C(4)-C(5)	1.408(3)
C(4)-C(11)	1.508(3)
C(5)-C(6)	1.404(3)
C(5)-C(10)	1.404(3)
C(6)-C(7)	1.372(3)
C(6)-C(12)	1.507(3)
C(7)-C(8)	1.408(3)
C(8)-C(9)	1.380(3)
C(9)-C(10)	1.437(3)
C(9)-C(15)	1.465(3)
C(11)-C(12)	1.540(3)
C(15)-C(16)	1.343(3)
C(16)-C(17)	1.439(3)
C(16)-C(18)	1.445(3)
N(4)-C(19)	1.424(2)
N(4)-C(31)	1.460(3)
N(4)-C(32)	1.460(3)
N(5)-C(35)	1.142(3)
N(6)-C(36)	1.142(2)
C(19)-C(20)	1.383(3)
C(19)-C(28)	1.434(3)
C(20)-C(21)	1.402(3)
C(21)-C(22)	1.357(3)
C(22)-C(23)	1.409(3)
C(22)-C(29)	1.503(3)
C(23)-C(24)	1.408(3)
C(23)-C(28)	1.410(3)
C(24)-C(25)	1.370(3)
C(24)-C(30)	1.508(3)
C(25)-C(26)	1.408(3)
C(26)-C(27)	1.389(3)
C(27)-C(28)	1.446(3)
C(27)-C(33)	1.451(3)
C(29)-C(30)	1.543(3)

C(33)-C(34)	1.348(3)
C(34)-C(35)	1.446(3)
C(34)-C(36)	1.440(3)

Table S3. Bond Angles for **8** /°.

C(1)-N(1)-C(13)	112.04(16)
C(1)-N(1)-C(14)	114.03(16)
C(13)-N(1)-C(14)	111.57(17)
C(2)-C(1)-N(1)	122.77(18)
C(2)-C(1)-C(10)	118.98(18)
C(10)-C(1)-N(1)	118.23(16)
C(1)-C(2)-C(3)	123.16(19)
C(4)-C(3)-C(2)	119.09(18)
C(3)-C(4)-C(5)	118.34(18)
C(3)-C(4)-C(11)	132.74(18)
C(5)-C(4)-C(11)	108.91(18)
C(6)-C(5)-C(4)	111.73(17)
C(6)-C(5)-C(10)	124.32(17)
C(10)-C(5)-C(4)	123.93(18)
C(5)-C(6)-C(12)	109.04(17)
C(7)-C(6)-C(5)	118.54(18)
C(7)-C(6)-C(12)	132.39(19)
C(6)-C(7)-C(8)	118.66(19)
C(9)-C(8)-C(7)	123.69(18)
C(8)-C(9)-C(10)	118.63(17)
C(8)-C(9)-C(15)	119.47(17)
C(10)-C(9)-C(15)	121.87(17)
C(1)-C(10)-C(9)	127.30(18)
C(5)-C(10)-C(1)	116.50(17)
C(5)-C(10)-C(9)	116.12(17)
C(4)-C(11)-C(12)	105.12(17)
C(6)-C(12)-C(11)	105.17(17)
C(16)-C(15)-C(9)	124.16(18)
C(15)-C(16)-C(17)	123.05(18)

C(15)-C(16)-C(18)	121.34(18)
C(17)-C(16)-C(18)	115.60(17)
N(2)-C(17)-C(16)	178.4(2)
N(3)-C(18)-C(16)	178.8(2)
C(19)-N(4)-C(31)	112.70(16)
C(19)-N(4)-C(32)	115.08(17)
C(31)-N(4)-C(32)	110.76(18)
N(4)-C(19)-C(28)	119.57(17)
C(20)-C(19)-N(4)	121.81(18)
C(20)-C(19)-C(28)	118.63(18)
C(19)-C(20)-C(21)	123.6(2)
C(22)-C(21)-C(20)	119.28(19)
C(21)-C(22)-C(23)	118.38(19)
C(21)-C(22)-C(29)	132.10(19)
C(23)-C(22)-C(29)	109.51(18)
C(22)-C(23)-C(28)	124.20(19)
C(24)-C(23)-C(22)	111.25(18)
C(24)-C(23)-C(28)	124.55(18)
C(23)-C(24)-C(30)	109.10(18)
C(25)-C(24)-C(23)	118.78(18)
C(25)-C(24)-C(30)	132.12(19)
C(24)-C(25)-C(26)	118.57(19)
C(27)-C(26)-C(25)	123.85(19)
C(26)-C(27)-C(28)	118.60(17)
C(26)-C(27)-C(33)	119.88(18)
C(28)-C(27)-C(33)	121.32(18)
C(19)-C(28)-C(27)	128.54(17)
C(23)-C(28)-C(19)	115.86(17)
C(23)-C(28)-C(27)	115.59(17)
C(22)-C(29)-C(30)	104.82(17)
C(24)-C(30)-C(29)	105.19(17)
C(34)-C(33)-C(27)	128.14(19)
C(33)-C(34)-C(35)	120.15(19)
C(33)-C(34)-C(36)	124.83(18)
C(36)-C(34)-C(35)	115.00(17)
N(5)-C(35)-C(34)	179.3(2)
N(6)-C(36)-C(34)	177.7(2)

Table S4. Torsion Angles for **8** /°.

N(1)-C(1)-C(2)-C(3)	-178.61(18)
N(1)-C(1)-C(10)-C(5)	178.47(15)
N(1)-C(1)-C(10)-C(9)	1.9(3)
C(1)-C(2)-C(3)-C(4)	0.2(3)
C(2)-C(1)-C(10)-C(5)	0.2(3)
C(2)-C(1)-C(10)-C(9)	-176.32(17)
C(2)-C(3)-C(4)-C(5)	0.4(3)
C(2)-C(3)-C(4)-C(11)	179.0(2)
C(3)-C(4)-C(5)-C(6)	177.83(17)
C(3)-C(4)-C(5)-C(10)	-0.6(3)
C(3)-C(4)-C(11)-C(12)	-178.8(2)
C(4)-C(5)-C(6)-C(7)	-176.64(17)
C(4)-C(5)-C(6)-C(12)	1.8(2)
C(4)-C(5)-C(10)-C(1)	0.3(3)
C(4)-C(5)-C(10)-C(9)	177.25(17)
C(4)-C(11)-C(12)-C(6)	1.1(2)
C(5)-C(4)-C(11)-C(12)	-0.1(2)
C(5)-C(6)-C(7)-C(8)	-0.8(3)
C(5)-C(6)-C(12)-C(11)	-1.7(2)
C(6)-C(5)-C(10)-C(1)	-177.95(17)
C(6)-C(5)-C(10)-C(9)	-1.0(3)
C(6)-C(7)-C(8)-C(9)	-0.9(3)
C(7)-C(6)-C(12)-C(11)	176.4(2)
C(7)-C(8)-C(9)-C(10)	1.7(3)
C(7)-C(8)-C(9)-C(15)	-176.33(17)
C(8)-C(9)-C(10)-C(1)	175.85(17)
C(8)-C(9)-C(10)-C(5)	-0.7(2)
C(8)-C(9)-C(15)-C(16)	-51.9(3)
C(9)-C(15)-C(16)-C(17)	-5.7(3)
C(9)-C(15)-C(16)-C(18)	175.85(18)
C(10)-C(1)-C(2)-C(3)	-0.5(3)
C(10)-C(5)-C(6)-C(7)	1.8(3)
C(10)-C(5)-C(6)-C(12)	-179.76(17)
C(10)-C(9)-C(15)-C(16)	130.2(2)
C(11)-C(4)-C(5)-C(6)	-1.1(2)
C(11)-C(4)-C(5)-C(10)	-179.51(17)

C(12)-C(6)-C(7)-C(8)	-178.8(2)
C(13)-N(1)-C(1)-C(2)	82.1(2)
C(13)-N(1)-C(1)-C(10)	-96.1(2)
C(14)-N(1)-C(1)-C(2)	-45.8(3)
C(14)-N(1)-C(1)-C(10)	136.01(18)
C(15)-C(9)-C(10)-C(1)	-6.2(3)
C(15)-C(9)-C(10)-C(5)	177.26(16)
N(4)-C(19)-C(20)-C(21)	178.86(17)
N(4)-C(19)-C(28)-C(23)	-177.15(16)
N(4)-C(19)-C(28)-C(27)	1.9(3)
C(19)-C(20)-C(21)-C(22)	-1.1(3)
C(20)-C(19)-C(28)-C(23)	2.7(2)
C(20)-C(19)-C(28)-C(27)	-178.26(18)
C(20)-C(21)-C(22)-C(23)	1.3(3)
C(20)-C(21)-C(22)-C(29)	-179.9(2)
C(21)-C(22)-C(23)-C(24)	-179.14(17)
C(21)-C(22)-C(23)-C(28)	0.6(3)
C(21)-C(22)-C(29)-C(30)	177.8(2)
C(22)-C(23)-C(24)-C(25)	-179.88(17)
C(22)-C(23)-C(24)-C(30)	0.6(2)
C(22)-C(23)-C(28)-C(19)	-2.6(3)
C(22)-C(23)-C(28)-C(27)	178.20(16)
C(22)-C(29)-C(30)-C(24)	3.4(2)
C(23)-C(22)-C(29)-C(30)	-3.2(2)
C(23)-C(24)-C(25)-C(26)	1.2(3)
C(23)-C(24)-C(30)-C(29)	-2.5(2)
C(24)-C(23)-C(28)-C(19)	177.13(17)
C(24)-C(23)-C(28)-C(27)	-2.1(3)
C(24)-C(25)-C(26)-C(27)	-1.0(3)
C(25)-C(24)-C(30)-C(29)	178.0(2)
C(25)-C(26)-C(27)-C(28)	-0.8(3)
C(25)-C(26)-C(27)-C(33)	174.13(17)
C(26)-C(27)-C(28)-C(19)	-176.86(18)
C(26)-C(27)-C(28)-C(23)	2.2(2)
C(26)-C(27)-C(33)-C(34)	35.9(3)
C(27)-C(33)-C(34)-C(35)	-178.71(19)
C(27)-C(33)-C(34)-C(36)	3.1(3)
C(28)-C(19)-C(20)-C(21)	-1.0(3)

C(28)-C(23)-C(24)-C(25)	0.3(3)
C(28)-C(23)-C(24)-C(30)	-179.23(17)
C(28)-C(27)-C(33)-C(34)	-149.3(2)
C(29)-C(22)-C(23)-C(24)	1.8(2)
C(29)-C(22)-C(23)-C(28)	-178.46(17)
C(30)-C(24)-C(25)-C(26)	-179.3(2)
C(31)-N(4)-C(19)-C(20)	-100.8(2)
C(31)-N(4)-C(19)-C(28)	79.0(2)
C(32)-N(4)-C(19)-C(20)	27.5(3)
C(32)-N(4)-C(19)-C(28)	-152.67(18)
C(33)-C(27)-C(28)-C(19)	8.3(3)
C(33)-C(27)-C(28)-C(23)	-172.67(16)

Compound 11.

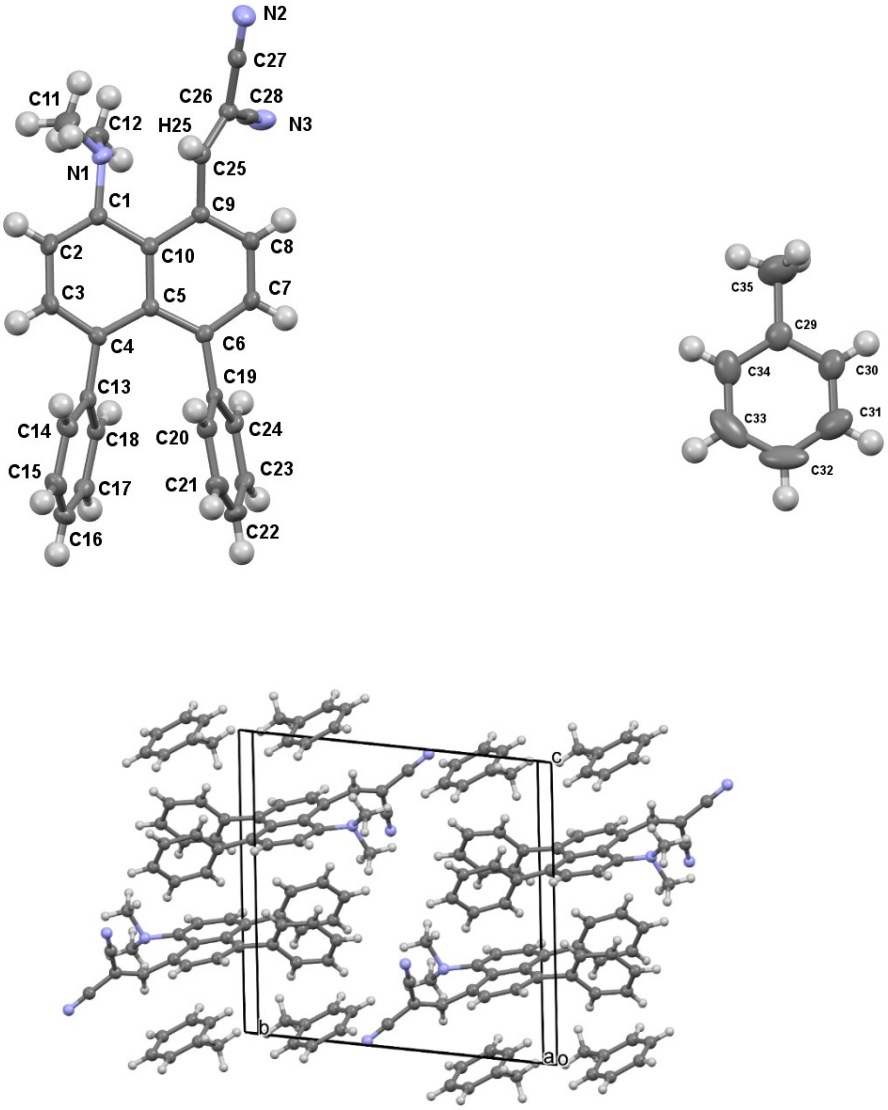


Figure S2. Atomic numbering scheme for **11** and the toluene molecule (top), and the crystal packing diagram of dinitrile **11** as its toluene solvate viewed along the *a* axis.

Table S5. Bond lengths for **11** / Å.

N(1)-C(1)	1.4308(19)
N(1)-C(11)	1.465(2)
N(1)-C(12)	1.460(2)
N(2)-C(27)	1.1439(19)
N(3)-C(28)	1.145(2)

C(1)-C(2)	1.364(2)
C(1)-C(10)	1.4202(19)
C(2)-C(3)	1.399(2)
C(3)-C(4)	1.380(2)
C(4)-C(5)	1.4430(18)
C(4)-C(13)	1.4944(19)
C(5)-C(6)	1.4402(18)
C(5)-C(10)	1.4338(19)
C(6)-C(7)	1.3776(19)
C(6)-C(19)	1.4946(19)
C(7)-C(8)	1.3987(19)
C(8)-C(9)	1.3706(19)
C(9)-C(10)	1.4242(19)
C(9)-C(25)	1.4784(19)
C(13)-C(14)	1.390(2)
C(13)-C(18)	1.3961(19)
C(14)-C(15)	1.389(2)
C(15)-C(16)	1.383(2)
C(16)-C(17)	1.383(2)
C(17)-C(18)	1.386(2)
C(19)-C(20)	1.391(2)
C(19)-C(24)	1.3940(19)
C(20)-C(21)	1.385(2)
C(21)-C(22)	1.388(2)
C(22)-C(23)	1.377(2)
C(23)-C(24)	1.384(2)
C(25)-C(26)	1.356(2)
C(26)-C(27)	1.4358(19)
C(26)-C(28)	1.436(2)
C(29)-C(30)	1.378(2)
C(29)-C(34)	1.371(3)
C(29)-C(35)	1.511(3)
C(30)-C(31)	1.349(3)
C(31)-C(32)	1.373(3)
C(32)-C(33)	1.410(3)
C(33)-C(34)	1.381(3)

Table S6. Bond angles for **11** / º.

C(1)-N(1)-C(11)	115.70(14)
C(1)-N(1)-C(12)	113.55(12)
C(12)-N(1)-C(11)	112.18(14)
C(2)-C(1)-N(1)	124.56(13)
C(2)-C(1)-C(10)	120.11(13)
C(10)-C(1)-N(1)	115.34(12)
C(1)-C(2)-C(3)	118.95(14)
C(4)-C(3)-C(2)	123.67(14)
C(3)-C(4)-C(5)	118.67(13)
C(3)-C(4)-C(13)	115.44(12)
C(5)-C(4)-C(13)	125.88(12)
C(6)-C(5)-C(4)	126.24(13)
C(10)-C(5)-C(4)	116.90(12)
C(10)-C(5)-C(6)	116.83(12)
C(5)-C(6)-C(19)	124.50(12)
C(7)-C(6)-C(5)	119.45(13)
C(7)-C(6)-C(19)	116.02(12)
C(6)-C(7)-C(8)	122.87(13)
C(9)-C(8)-C(7)	119.40(13)
C(8)-C(9)-C(10)	119.79(13)
C(8)-C(9)-C(25)	119.83(12)
C(10)-C(9)-C(25)	119.56(12)
C(1)-C(10)-C(5)	121.21(12)
C(1)-C(10)-C(9)	117.74(12)
C(9)-C(10)-C(5)	121.02(12)
C(14)-C(13)-C(4)	119.31(12)
C(14)-C(13)-C(18)	118.34(13)
C(18)-C(13)-C(4)	122.23(13)
C(15)-C(14)-C(13)	121.16(14)
C(16)-C(15)-C(14)	119.75(15)
C(17)-C(16)-C(15)	119.83(15)
C(16)-C(17)-C(18)	120.38(14)
C(17)-C(18)-C(13)	120.54(14)
C(20)-C(19)-C(6)	121.63(12)
C(20)-C(19)-C(24)	118.69(13)

C(24)-C(19)-C(6)	119.60(13)
C(21)-C(20)-C(19)	120.37(14)
C(20)-C(21)-C(22)	120.23(16)
C(23)-C(22)-C(21)	119.84(15)
C(22)-C(23)-C(24)	120.02(15)
C(23)-C(24)-C(19)	120.79(15)
C(26)-C(25)-C(9)	124.75(13)
C(25)-C(26)-C(27)	119.91(13)
C(25)-C(26)-C(28)	122.72(13)
C(28)-C(26)-C(27)	117.36(13)
N(2)-C(27)-C(26)	178.82(19)
N(3)-C(28)-C(26)	178.48(17)
C(30)-C(29)-C(35)	119.72(18)
C(34)-C(29)-C(30)	119.43(18)
C(34)-C(29)-C(35)	120.85(19)
C(31)-C(30)-C(29)	121.3(2)
C(30)-C(31)-C(32)	120.7(2)
C(31)-C(32)-C(33)	118.7(2)
C(34)-C(33)-C(32)	119.7(2)
C(29)-C(34)-C(33)	120.1(2)

Table S7. Torsion angles for **11** / °.

N(1)-C(1)-C(2)-C(3)	176.07(14)
N(1)-C(1)-C(10)-C(5)	-172.52(12)
N(1)-C(1)-C(10)-C(9)	9.30(19)
C(1)-C(2)-C(3)-C(4)	-2.6(2)
C(2)-C(1)-C(10)-C(5)	7.6(2)
C(2)-C(1)-C(10)-C(9)	-170.61(14)
C(2)-C(3)-C(4)-C(5)	5.7(2)
C(2)-C(3)-C(4)-C(13)	-173.52(14)
C(3)-C(4)-C(5)-C(6)	176.04(13)
C(3)-C(4)-C(5)-C(10)	-2.01(19)
C(3)-C(4)-C(13)-C(14)	-58.17(18)
C(3)-C(4)-C(13)-C(18)	117.80(15)
C(4)-C(5)-C(6)-C(7)	179.19(13)
C(4)-C(5)-C(6)-C(19)	-2.6(2)
C(4)-C(5)-C(10)-C(1)	-4.39(19)
C(4)-C(5)-C(10)-C(9)	173.73(12)
C(4)-C(13)-C(14)-C(15)	177.30(13)
C(4)-C(13)-C(18)-C(17)	-176.90(13)
C(5)-C(4)-C(13)-C(14)	122.69(15)
C(5)-C(4)-C(13)-C(18)	-61.34(19)
C(5)-C(6)-C(7)-C(8)	6.6(2)
C(5)-C(6)-C(19)-C(20)	-62.74(19)
C(5)-C(6)-C(19)-C(24)	120.33(15)
C(6)-C(5)-C(10)-C(1)	177.37(12)
C(6)-C(5)-C(10)-C(9)	-4.51(19)
C(6)-C(7)-C(8)-C(9)	-3.0(2)
C(6)-C(19)-C(20)-C(21)	-179.32(13)
C(6)-C(19)-C(24)-C(23)	179.46(13)
C(7)-C(6)-C(19)-C(20)	115.50(15)
C(7)-C(6)-C(19)-C(24)	-61.43(17)
C(7)-C(8)-C(9)-C(10)	-4.5(2)
C(7)-C(8)-C(9)-C(25)	165.05(13)
C(8)-C(9)-C(10)-C(1)	-173.54(13)
C(8)-C(9)-C(10)-C(5)	8.3(2)
C(8)-C(9)-C(25)-C(26)	51.0(2)
C(9)-C(25)-C(26)-C(27)	-166.23(13)

C(9)-C(25)-C(26)-C(28)	15.3(2)
C(10)-C(1)-C(2)-C(3)	-4.0(2)
C(10)-C(5)-C(6)-C(7)	-2.75(19)
C(10)-C(5)-C(6)-C(19)	175.43(12)
C(10)-C(9)-C(25)-C(26)	-139.40(15)
C(11)-N(1)-C(1)-C(2)	36.9(2)
C(11)-N(1)-C(1)-C(10)	-143.03(15)
C(12)-N(1)-C(1)-C(2)	-94.95(18)
C(12)-N(1)-C(1)-C(10)	85.15(16)
C(13)-C(4)-C(5)-C(6)	-4.8(2)
C(13)-C(4)-C(5)-C(10)	177.10(13)
C(13)-C(14)-C(15)-C(16)	-0.6(2)
C(14)-C(13)-C(18)-C(17)	-0.9(2)
C(14)-C(15)-C(16)-C(17)	-0.3(2)
C(15)-C(16)-C(17)-C(18)	0.6(2)
C(16)-C(17)-C(18)-C(13)	0.0(2)
C(18)-C(13)-C(14)-C(15)	1.2(2)
C(19)-C(6)-C(7)-C(8)	-171.68(13)
C(19)-C(20)-C(21)-C(22)	0.6(2)
C(20)-C(19)-C(24)-C(23)	2.4(2)
C(20)-C(21)-C(22)-C(23)	1.2(2)
C(21)-C(22)-C(23)-C(24)	-1.2(2)
C(22)-C(23)-C(24)-C(19)	-0.7(2)
C(24)-C(19)-C(20)-C(21)	-2.4(2)
C(25)-C(9)-C(10)-C(1)	16.85(19)
C(25)-C(9)-C(10)-C(5)	-161.33(13)
C(29)-C(30)-C(31)-C(32)	0.2(3)
C(30)-C(29)-C(34)-C(33)	-1.8(3)
C(30)-C(31)-C(32)-C(33)	-0.7(3)
C(31)-C(32)-C(33)-C(34)	0.0(3)
C(32)-C(33)-C(34)-C(29)	1.2(3)
C(34)-C(29)-C(30)-C(31)	1.1(3)
C(35)-C(29)-C(30)-C(31)	-179.15(18)
C(35)-C(29)-C(34)-C(33)	178.48(18)

Compound 12.

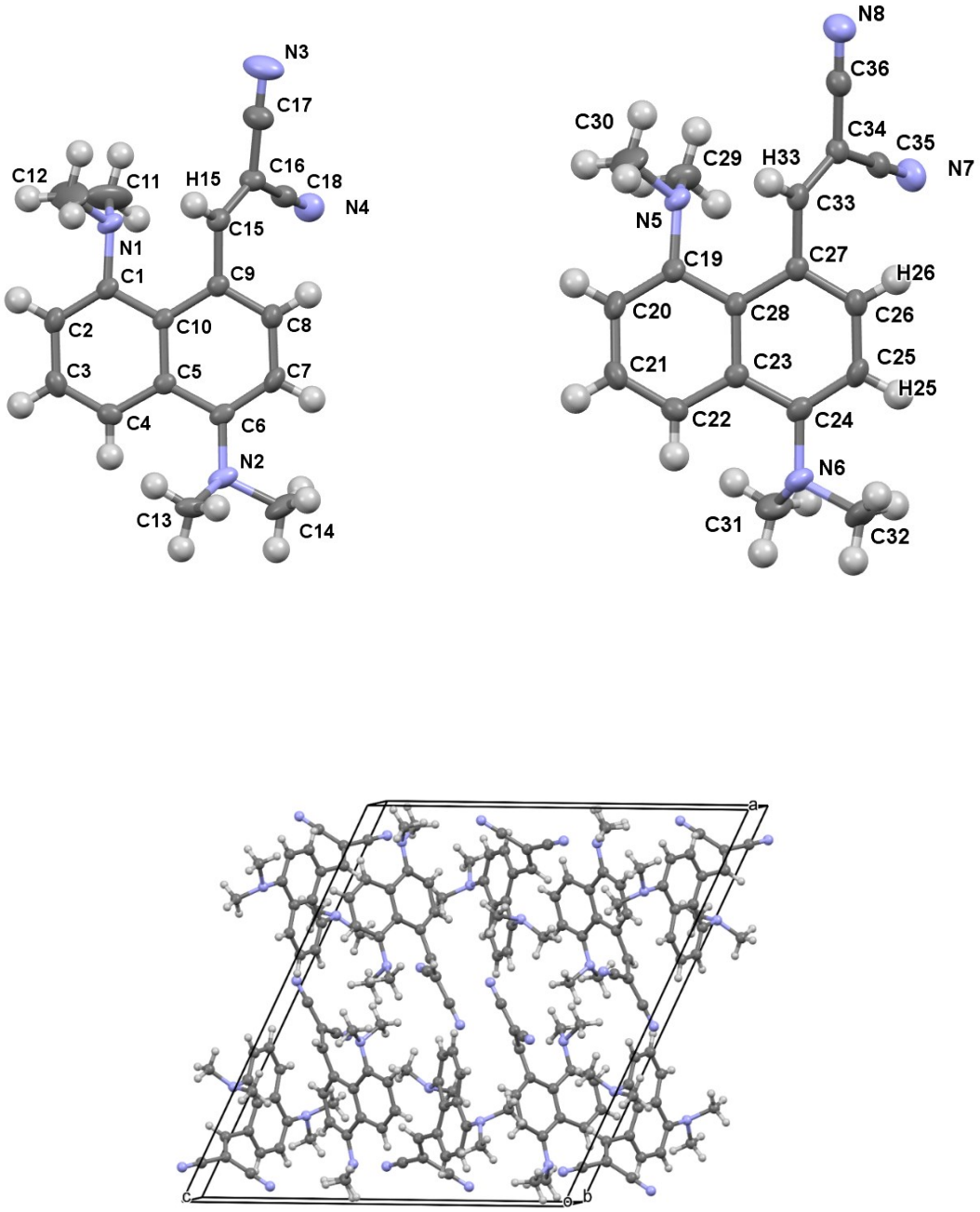


Figure S3. Atomic numbering scheme for the two independent molecules of **12** (top), and the crystal packing viewed along the *b* axis.

Table S8. Bond lengths for **12** / Å.

N(1)-C(1)	1.434(2)
N(1)-C(11)	1.451(3)
N(1)-C(12)	1.445(3)
N(5)-C(19)	1.426(2)
N(5)-C(29)	1.456(2)
N(5)-C(30)	1.455(2)
N(2)-C(6)	1.400(2)
N(2)-C(13)	1.470(2)
N(2)-C(14)	1.460(2)
N(6)-C(24)	1.413(2)
N(6)-C(31)	1.465(3)
N(6)-C(32)	1.456(2)
C(5)-C(10)	1.422(2)
C(5)-C(6)	1.444(2)
C(5)-C(4)	1.411(2)
N(4)-C(18)	1.143(2)
N(7)-C(35)	1.144(2)
C(28)-C(27)	1.429(2)
C(28)-C(23)	1.422(2)
C(28)-C(19)	1.425(2)
N(8)-C(36)	1.149(2)
C(10)-C(1)	1.418(2)
C(10)-C(9)	1.425(2)
C(27)-C(33)	1.471(2)
C(27)-C(26)	1.369(2)
C(23)-C(24)	1.438(2)
C(23)-C(22)	1.415(2)
C(1)-C(2)	1.370(2)
C(33)-C(34)	1.350(2)
C(19)-C(20)	1.370(2)
C(34)-C(35)	1.439(2)
C(34)-C(36)	1.437(2)
C(9)-C(15)	1.470(2)
C(9)-C(8)	1.371(2)
C(6)-C(7)	1.377(2)

C(4)-C(3)	1.364(2)
C(18)-C(16)	1.437(3)
C(24)-C(25)	1.373(2)
C(16)-C(15)	1.356(2)
C(16)-C(17)	1.438(3)
C(26)-C(25)	1.403(2)
C(22)-C(21)	1.366(2)
C(7)-C(8)	1.400(2)
C(20)-C(21)	1.403(3)
C(3)-C(2)	1.397(3)
N(3)-C(17)	1.143(2)

Table S9. Bond angles for **12** / °.

C(1)-N(1)-C(11)	112.72(15)
C(1)-N(1)-C(12)	114.05(16)
C(12)-N(1)-C(11)	114.5(2)
C(19)-N(5)-C(29)	113.21(14)
C(19)-N(5)-C(30)	115.92(16)
C(30)-N(5)-C(29)	113.35(17)
C(6)-N(2)-C(13)	116.24(14)
C(6)-N(2)-C(14)	116.46(16)
C(14)-N(2)-C(13)	110.00(14)
C(24)-N(6)-C(31)	115.17(15)
C(24)-N(6)-C(32)	115.76(16)
C(32)-N(6)-C(31)	110.27(16)
C(10)-C(5)-C(6)	119.06(15)
C(4)-C(5)-C(10)	118.13(14)
C(4)-C(5)-C(6)	122.74(15)
C(23)-C(28)-C(27)	120.02(14)
C(23)-C(28)-C(19)	119.16(14)
C(19)-C(28)-C(27)	120.81(15)
C(5)-C(10)-C(9)	120.34(14)
C(1)-C(10)-C(5)	119.22(15)
C(1)-C(10)-C(9)	120.27(15)
C(28)-C(27)-C(33)	121.40(14)

C(26)-C(27)-C(28)	118.62(15)
C(26)-C(27)-C(33)	119.60(15)
C(28)-C(23)-C(24)	118.94(15)
C(22)-C(23)-C(28)	118.30(15)
C(22)-C(23)-C(24)	122.75(15)
C(10)-C(1)-N(1)	115.81(15)
C(2)-C(1)-N(1)	123.52(15)
C(2)-C(1)-C(10)	120.65(15)
C(34)-C(33)-C(27)	124.98(15)
C(28)-C(19)-N(5)	116.07(14)
C(20)-C(19)-N(5)	123.83(15)
C(20)-C(19)-C(28)	120.07(16)
C(33)-C(34)-C(35)	122.69(16)
C(33)-C(34)-C(36)	121.50(16)
C(36)-C(34)-C(35)	115.73(15)
C(10)-C(9)-C(15)	122.17(14)
C(8)-C(9)-C(10)	118.28(15)
C(8)-C(9)-C(15)	119.42(15)
N(2)-C(6)-C(5)	118.83(15)
C(7)-C(6)-N(2)	122.67(15)
C(7)-C(6)-C(5)	118.38(15)
N(7)-C(35)-C(34)	178.8(2)
C(3)-C(4)-C(5)	121.24(16)
N(4)-C(18)-C(16)	178.0(2)
N(6)-C(24)-C(23)	118.09(15)
C(25)-C(24)-N(6)	122.88(15)
C(25)-C(24)-C(23)	118.99(15)
C(18)-C(16)-C(17)	115.01(16)
C(15)-C(16)-C(18)	123.01(16)
C(15)-C(16)-C(17)	121.95(17)
C(27)-C(26)-C(25)	121.75(16)
C(16)-C(15)-C(9)	123.14(16)
C(21)-C(22)-C(23)	120.67(16)
C(24)-C(25)-C(26)	121.31(16)
C(6)-C(7)-C(8)	121.29(15)
N(8)-C(36)-C(34)	179.2(2)
C(9)-C(8)-C(7)	122.09(16)
C(19)-C(20)-C(21)	120.19(16)

C(4)-C(3)-C(2)	120.82(16)
C(22)-C(21)-C(20)	120.91(16)
C(1)-C(2)-C(3)	119.92(16)
N(3)-C(17)-C(16)	178.4(2)

Table S10. Torsion angles for **12** / °.

N(1)-C(1)-C(2)-C(3)	176.98(15)
N(5)-C(19)-C(20)-C(21)	178.09(16)
N(2)-C(6)-C(7)-C(8)	-177.89(15)
N(6)-C(24)-C(25)-C(26)	-177.41(16)
C(5)-C(10)-C(1)-N(1)	-177.03(13)
C(5)-C(10)-C(1)-C(2)	1.4(2)
C(5)-C(10)-C(9)-C(15)	-171.22(14)
C(5)-C(10)-C(9)-C(8)	4.5(2)
C(5)-C(6)-C(7)-C(8)	6.2(2)
C(5)-C(4)-C(3)-C(2)	1.7(3)
C(28)-C(27)-C(33)-C(34)	-137.28(17)
C(28)-C(27)-C(26)-C(25)	-1.3(2)
C(28)-C(23)-C(24)-N(6)	-177.88(14)
C(28)-C(23)-C(24)-C(25)	4.3(2)
C(28)-C(23)-C(22)-C(21)	5.0(2)
C(28)-C(19)-C(20)-C(21)	0.2(3)
C(10)-C(5)-C(6)-N(2)	176.65(14)
C(10)-C(5)-C(6)-C(7)	-7.3(2)
C(10)-C(5)-C(4)-C(3)	-1.5(2)
C(10)-C(1)-C(2)-C(3)	-1.4(2)
C(10)-C(9)-C(15)-C(16)	-131.19(18)
C(10)-C(9)-C(8)-C(7)	-5.9(2)
C(27)-C(28)-C(23)-C(24)	-7.4(2)
C(27)-C(28)-C(23)-C(22)	171.38(14)
C(27)-C(28)-C(19)-N(5)	8.1(2)
C(27)-C(28)-C(19)-C(20)	-173.92(15)
C(27)-C(33)-C(34)-C(35)	8.1(3)
C(27)-C(33)-C(34)-C(36)	-175.19(15)
C(27)-C(26)-C(25)-C(24)	-1.9(3)
C(23)-C(28)-C(27)-C(33)	-166.86(14)
C(23)-C(28)-C(27)-C(26)	6.0(2)
C(23)-C(28)-C(19)-N(5)	-171.06(14)
C(23)-C(28)-C(19)-C(20)	6.9(2)
C(23)-C(24)-C(25)-C(26)	0.3(3)
C(23)-C(22)-C(21)-C(20)	2.2(3)
C(1)-C(10)-C(9)-C(15)	13.7(2)

C(1)-C(10)-C(9)-C(8)	-170.56(15)
C(33)-C(27)-C(26)-C(25)	171.64(15)
C(19)-C(28)-C(27)-C(33)	14.0(2)
C(19)-C(28)-C(27)-C(26)	-173.14(14)
C(19)-C(28)-C(23)-C(24)	171.70(14)
C(19)-C(28)-C(23)-C(22)	-9.5(2)
C(19)-C(20)-C(21)-C(22)	-4.9(3)
C(9)-C(10)-C(1)-N(1)	-1.9(2)
C(9)-C(10)-C(1)-C(2)	176.59(15)
C(6)-C(5)-C(10)-C(1)	177.10(14)
C(6)-C(5)-C(10)-C(9)	2.0(2)
C(6)-C(5)-C(4)-C(3)	-178.53(15)
C(6)-C(7)-C(8)-C(9)	0.5(3)
C(4)-C(5)-C(10)-C(1)	0.0(2)
C(4)-C(5)-C(10)-C(9)	-175.14(14)
C(4)-C(5)-C(6)-N(2)	-6.4(2)
C(4)-C(5)-C(6)-C(7)	169.71(15)
C(4)-C(3)-C(2)-C(1)	-0.2(3)
C(18)-C(16)-C(15)-C(9)	10.6(3)
C(24)-C(23)-C(22)-C(21)	-176.18(16)
C(26)-C(27)-C(33)-C(34)	49.9(2)
C(15)-C(9)-C(8)-C(7)	170.00(16)
C(22)-C(23)-C(24)-N(6)	3.4(2)
C(22)-C(23)-C(24)-C(25)	-174.51(16)
C(8)-C(9)-C(15)-C(16)	53.1(2)
C(13)-N(2)-C(6)-C(5)	-62.4(2)
C(13)-N(2)-C(6)-C(7)	121.72(18)
C(17)-C(16)-C(15)-C(9)	-171.52(16)
C(14)-N(2)-C(6)-C(5)	165.48(15)
C(14)-N(2)-C(6)-C(7)	-10.4(2)
C(29)-N(5)-C(19)-C(28)	87.41(18)
C(29)-N(5)-C(19)-C(20)	-90.5(2)
C(31)-N(6)-C(24)-C(23)	69.2(2)
C(31)-N(6)-C(24)-C(25)	-113.0(2)
C(32)-N(6)-C(24)-C(23)	-160.07(17)
C(32)-N(6)-C(24)-C(25)	17.7(3)
C(30)-N(5)-C(19)-C(28)	-139.13(19)
C(30)-N(5)-C(19)-C(20)	43.0(3)

C(11)-N(1)-C(1)-C(10)	100.6(2)
C(11)-N(1)-C(1)-C(2)	-77.8(2)
C(12)-N(1)-C(1)-C(10)	-126.6(2)
C(12)-N(1)-C(1)-C(2)	54.9(3)

Table S11. Crystallographic data for **13.Cl.0.5H$_2$O** at 200, 150 and 100 K.

	200 K	**150 K**	**100 K**
Formula	$C_{18}H_{19}N_4$.Cl. 0.5H_2O	$C_{18}H_{19}N_4$.Cl. 0.5H_2O	$C_{18}H_{19}N_4$.Cl. 0.5H_2O
Formula Weight	335.83	335.83	335.83
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Fdd2*	*Fdd2*	*Fdd2*
a[Å]	44.405(2)	44.3129(10)	44.6056(9)
b[Å]	22.8205(11)	22.7477(5)	22.6655(5)
c[Å]	7.0822(7)	7.0353(2)	6.8677(2)
V [Å^3]	7176.7(8)	7091.7(3)	6943.3(3)
Z	16	16	16
ρ [g cm^{-3}]	1.243	1.258	1.285
T [*K*]	200(2)	150.0(2)	100.0(2)
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.221	0.224	0.229
unique refl.	4055	5224	5128
Refl, I > 2σI	3663	4914	4972
R_1(I > 2σI)	0.0463	0.0396	0.0333
wR_2	0.0910	0.0919	0.0760
$\Delta\rho$(r) [e Å^{-3}]	0.170/ -0.179	0.243/ -0.209	0.273/ -0.182
Cryst. Solvent.	Methanol	Methanol	Methanol

Table S12. Summary of crystallographic data for **13.Cl.0.5H$_2$O** at temperatures 90-200 K.

T/K	200	180	160	150	142	140
a[Å]	44.405(2)	44.4167(13)	44.4380(17)	44.3129(10)	44.3265(15)	44.3430(14)
b[Å]	22.8205(11)	22.8075(6)	22.8176(8)	22.7477(5)	22.7426(9)	22.7394(8)
c[Å]	7.0822(7)	7.0798(4)	7.0471(5)	7.0353(2)	7.0164(3)	7.0089(2)
V [Å^3]	7176.7(8)	7172.1(5)	7145.6(6)	7091.7(3)	7073.2(4)	7067.3(4)
ρ [g cm^{-3}]	1.243	1.244	1.249	1.258	1.261	1.263
unique refl.	4055	4036	4030	5224	4107	4104
Refl, I > 2σI	3663	3677	3701	4914	3817	3778
R_1(I > 2σI)	0.0463	0.0430	0.0421	0.0396	0.0379	0.0378
wR_2	0.0910	0.0887	0.0851	0.0919	0.0826	0.0837

T/ K	138	136	134	132	130	128
a[Å]	44.3901(15)	44.4350(15)	44.4818(18)	44.5206(13)	44.5571(14)	44.5663(13)
b[Å]	22.7070(8)	22.7202(8)	22.6958(9)	22.6875(7)	22.6797(8)	22.6708(7)
c[Å]	6.9970(3)	6.9824(3)	6.9602(3)	6.9416(2)	6.9279(2)	6.9175(2)
V [Å^3]	7052.7(4)	7049.3(4)	7026.7(5)	7011.4(4)	7000.9(4)	6989.1(4)
ρ [g cm^{-3}]	1.265	1.266	1.270	1.273	1.274	1.277
unique refl.	4104	4104	4089	4079	4078	4070
Refl, I > 2σI	3827	3795	3784	3774	3783	3769
R_1(I > 2σI)	0.0375	0.0382	0.0382	0.0377	0.0378	0.0367
wR_2	0.0798	0.0829	0.0793	0.0787	0.0807	0.0789

T/K	120	110	100	90
a[Å]	44.649(2)	44.6988(14)	44.6586(17)	44.6908(13)
b[Å]	22.6659(9)	22.6997(6)	22.6565(7)	22.6919(6)
c[Å]	6.9115(5)	6.8815(3)	6.8837(4)	6.8619(3)
V [Å^3]	6994.5(7)	6982.4(5)	6964.9(5)	6958.8(4)
ρ [g cm^{-3}]	1.276	1.278	1.281	1.282
unique refl.	3967	3961	3948	3945
Refl, I > 2σI	3731	3737	3763	3730
R_1(I > 2σI)	0.0384	0.0366	0.0357	0.0349
wR_2	0.0793	0.0756	0.0764	0.0745

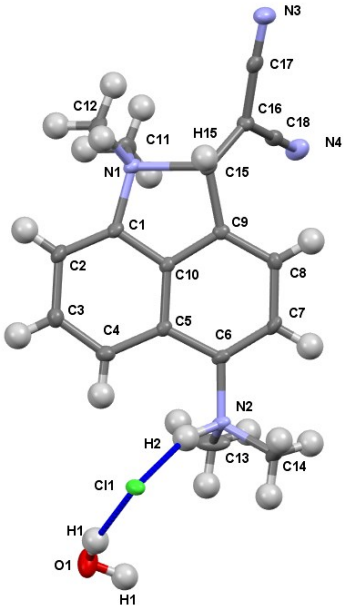


Figure S4. Atomic numbering scheme for **13.Cl.0.5H$_2$O** at 100 K.

13.Cl.0.5H_2O at 200 K.

Table S13. Bond Lengths for **13.Cl.0.5H_2O** / Å at 200 K.

N(1)-C(1)	1.437(4)
N(1)-C(11)	1.462(5)
N(1)---C(15)	2.167(4)
N(1)-C(12)	1.476(4)
N(2)-C(6)	1.477(3)
N(2)-C(13)	1.497(5)
N(2)-C(14)	1.494(4)
N(3)-C(17)	1.142(4)
N(4)-C(18)	1.135(4)
C(1)-C(2)	1.357(4)
C(1)-C(10)	1.408(4)
C(2)-C(3)	1.412(4)
C(3)-C(4)	1.367(4)
C(4)-C(5)	1.410(4)
C(5)-C(6)	1.425(4)
C(5)-C(10)	1.419(4)
C(6)-C(7)	1.353(4)
C(7)-C(8)	1.414(4)
C(8)-C(9)	1.368(4)
C(9)-C(10)	1.419(4)
C(9)-C(15)	1.481(4)
C(15)-C(16)	1.369(4)
C(15)-H(15)	0.96(3)
C(16)-C(17)	1.434(4)
C(16)-C(18)	1.430(5)

Table S14. Bond Angles for **13.Cl.0.5H_2O** / ^{o} at 200 K.

C(1)-N(1)-C(11)	112.1(3)
C(1)-N(1)-C(12)	114.5(3)
C(11)-N(1)-C(12)	113.6(3)

C(6)-N(2)-C(13)	111.5(2)
C(6)-N(2)-C(14)	114.9(3)
C(14)-N(2)-C(13)	110.7(3)
C(2)-C(1)-N(1)	125.8(3)
C(2)-C(1)-C(10)	121.2(3)
C(10)-C(1)-N(1)	113.0(3)
C(1)-C(2)-C(3)	118.7(3)
C(4)-C(3)-C(2)	121.5(3)
C(3)-C(4)-C(5)	120.8(3)
C(4)-C(5)-C(6)	126.5(3)
C(4)-C(5)-C(10)	117.5(3)
C(10)-C(5)-C(6)	116.0(3)
C(5)-C(6)-N(2)	117.6(2)
C(7)-C(6)-N(2)	120.7(2)
C(7)-C(6)-C(5)	121.7(2)
C(6)-C(7)-C(8)	121.2(3)
C(9)-C(8)-C(7)	120.0(3)
C(8)-C(9)-C(10)	118.9(2)
C(8)-C(9)-C(15)	123.5(3)
C(10)-C(9)-C(15)	117.5(2)
C(1)-C(10)-C(5)	120.1(3)
C(1)-C(10)-C(9)	117.8(2)
C(5)-C(10)-C(9)	122.1(2)
C(16)-C(15)-C(9)	122.2(3)
N(1)---C(15)-C(9)	90.6(2)
N(1)---C(15)-C(16)	113.2(2)
N(1)---C(15)-H(15)	85.2(17)
C(9)-C(15)-H(15)	117.7(16)
C16-C(15)-H(15)	116.2(16)
C(15)-C(16)-C(17)	122.6(3)
C(15)-C(16)-C(18)	121.5(3)
C(18)-C(16)-C(17)	115.8(3)
N(3)-C(17)-C(16)	177.8(4)
N(4)-C(18)-C(16)	178.3(4)

Table S15. Torsion angles for **13.Cl.0.5H$_2$O** / º at 200 K.

N(1)-C(1)-C(2)-C(3)	-176.2(3)
N(1)-C(1)-C(10)-C(5)	173.4(2)
N(1)-C(1)-C(10)-C(9)	-6.4(4)
N(2)-C(6)-C(7)-C(8)	-178.9(3)
C(1)-C(2)-C(3)-C(4)	1.2(5)
C(2)-C(1)-C(10)-C(5)	-5.7(4)
C(2)-C(1)-C(10)-C(9)	174.5(3)
C(2)-C(3)-C(4)-C(5)	-2.2(5)
C(3)-C(4)-C(5)-C(6)	-179.9(3)
C(3)-C(4)-C(5)-C(10)	-0.7(4)
C(4)-C(5)-C(6)-N(2)	-4.3(4)
C(4)-C(5)-C(6)-C(7)	178.7(3)
C(4)-C(5)-C(10)-C(1)	4.6(4)
C(4)-C(5)-C(10)-C(9)	-175.7(3)
C(5)-C(6)-C(7)-C(8)	-2.0(4)
C(6)-C(5)-C(10)-C(1)	-176.2(2)
C(6)-C(5)-C(10)-C(9)	3.6(4)
C(6)-C(7)-C(8)-C(9)	1.4(4)
C(7)-C(8)-C(9)-C(10)	1.6(4)
C(7)-C(8)-C(9)-C(15)	-173.9(3)
C(8)-C(9)-C(10)-C(1)	175.6(3)
C(8)-C(9)-C(10)-C(5)	-4.2(4)
C(8)-C(9)-C(15)-C(16)	-53.0(4)
C(9)-C(15)-C(16)-C(17)	167.8(3)
C(9)-C(15)-C(16)-C(18)	-16.6(5)
C(10)-C(1)-C(2)-C(3)	2.7(4)
C(10)-C(5)-C(6)-N(2)	176.6(2)
C(10)-C(5)-C(6)-C(7)	-0.4(4)
C(10)-C(9)-C(15)-C(16)	131.5(3)
C(11)-N(1)-C(1)-C(2)	82.3(4)
C(11)-N(1)-C(1)-C(10)	-96.7(3)
C(12)-N(1)-C(1)-C(2)	-48.9(5)
C(12)-N(1)-C(1)-C(10)	132.1(3)
C(13)-N(2)-C(6)-C(5)	-78.8(4)
C(13)-N(2)-C(6)-C(7)	98.2(4)

C(14)-N(2)-C(6)-C(5)	154.2(3)
C(14)-N(2)-C(6)-C(7)	-28.7(4)
C(15)-C(9)-C(10)-C(1)	-8.7(4)
C(15)-C(9)-C(10)-C(5)	171.6(3)

Table S16. Hydrogen bonding for **13.Cl.0.5H$_2$O** / º at 200 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N2-H2	0.98	2.08	160	3.020(2)	Cl1
O1-H1	0.93(5)	2.27(6)	166(5)	3.192(4)	Cl1

13.Cl.0.5H$_2$O at 150 K.

Table S17. Bond Lengths for **13.Cl.0.5H$_2$O** / Å at 150 K.

N(1)-C(1)	1.442(3)
N(1)-C(11)	1.465(4)
N(1)-C(12)	1.475(3)
N(1)---C(15)	2.098(4)
N(2)-C(6)	1.476(3)
N(2)-C(13)	1.497(4)
N(2)-C(14)	1.495(4)
N(3)-C(17)	1.142(4)
N(4)-C(18)	1.138(4)
C(1)-C(2)	1.360(4)
C(1)-C(10)	1.406(3)
C(2)-C(3)	1.413(4)
C(3)-C(4)	1.368(4)
C(4)-C(5)	1.413(4)
C(5)-C(6)	1.425(3)
C(5)-C(10)	1.416(3)
C(6)-C(7)	1.357(4)
C(7)-C(8)	1.413(4)

C(8)-C(9)	1.368(3)
C(9)-C(10)	1.420(4)
C(9)-C(15)	1.482(3)
C(15)-C(16)	1.378(4)
C(15)-H(15)	0.97(3)
C(16)-C(17)	1.435(4)
C(16)-C(18)	1.428(4)

Table S18. Bond Angles for **13.Cl.0.5H_2O** / º at 150 K.

C(1)-N(1)-C(11)	111.8(2)
C(1)-N(1)-C(12)	114.3(2)
C(11)-N(1)-C(12)	113.2(3)
C(6)-N(2)-C(13)	111.4(2)
C(6)-N(2)-C(14)	114.8(2)
C(14)-N(2)-C(13)	110.7(2)
C(2)-C(1)-N(1)	126.2(2)
C(2)-C(1)-C(10)	121.4(2)
C(10)-C(1)-N(1)	112.4(2)
C(1)-C(2)-C(3)	118.2(2)
C(4)-C(3)-C(2)	121.8(3)
C(3)-C(4)-C(5)	120.7(2)
C(4)-C(5)-C(6)	127.1(2)
C(4)-C(5)-C(10)	117.2(2)
C(10)-C(5)-C(6)	115.7(2)
C(5)-C(6)-N(2)	117.3(2)
C(7)-C(6)-N(2)	120.9(2)
C(7)-C(6)-C(5)	121.7(2)
C(6)-C(7)-C(8)	121.4(2)
C(9)-C(8)-C(7)	119.7(2)
C(8)-C(9)-C(10)	118.9(2)
C(8)-C(9)-C(15)	124.5(3)
C(10)-C(9)-C(15)	116.5(2)
C(1)-C(10)-C(5)	120.5(2)
C(1)-C(10)-C(9)	117.1(2)
C(5)-C(10)-C(9)	122.4(2)

C(16)-C(15)-C(9)	121.6(2)
N(1)---C(15)-C(9)	91.8(2)
N(1)---C(15)-C(16)	113.2(2)
N(1)---C(15)-H(15)	87.6(16)
C(9)-C(15)-H(15)	116.5(15)
C16-C(15)-H(15)	116.3(16)
C(15)-C(16)-C(17)	122.5(2)
C(15)-C(16)-C(18)	121.5(2)
C(18)-C(16)-C(17)	116.0(2)
N(3)-C(17)-C(16)	177.5(3)
N(4)-C(18)-C(16)	178.7(3)

Table S19. Torsion Angles for **13.Cl.0.5H_2O**/ ° at 150 K.

N(1)-C(1)-C(2)-C(3)	176.0(2)
N(1)-C(1)-C(10)-C(5)	-173.2(2)
N(1)-C(1)-C(10)-C(9)	6.6(3)
N(2)-C(6)-C(7)-C(8)	178.8(2)
C(1)-C(2)-C(3)-C(4)	-1.8(4)
C(2)-C(1)-C(10)-C(5)	5.3(4)
C(2)-C(1)-C(10)-C(9)	-174.9(2)
C(2)-C(3)-C(4)-C(5)	2.8(4)
C(3)-C(4)-C(5)-C(6)	179.8(3)
C(3)-C(4)-C(5)-C(10)	0.2(4)
C(4)-C(5)-C(6)-N(2)	3.8(4)
C(4)-C(5)-C(6)-C(7)	-179.2(3)
C(4)-C(5)-C(10)-C(1)	-4.1(4)
C(4)-C(5)-C(10)-C(9)	176.1(2)
C(5)-C(6)-C(7)-C(8)	1.9(4)
C(6)-C(5)-C(10)-C(1)	176.2(2)
C(6)-C(5)-C(10)-C(9)	-3.6(3)
C(6)-C(7)-C(8)-C(9)	-1.2(4)
C(7)-C(8)-C(9)-C(10)	-1.9(4)
C(7)-C(8)-C(9)-C(15)	173.9(2)
C(8)-C(9)-C(10)-C(1)	-175.5(2)
C(8)-C(9)-C(10)-C(5)	4.4(4)

C(8)-C(9)-C(15)-C(16)	51.4(4)
C(9)-C(15)-C(16)-C(17)	-165.6(3)
C(9)-C(15)-C(16)-C(18)	17.9(5)
C(10)-C(1)-C(2)-C(3)	-2.3(4)
C(10)-C(5)-C(6)-N(2)	-176.6(2)
C(10)-C(5)-C(6)-C(7)	0.5(4)
C(10)-C(9)-C(15)-C(16)	-132.7(3)
C(11)-N(1)-C(1)-C(2)	-81.0(3)
C(11)-N(1)-C(1)-C(10)	97.3(3)
C(12)-N(1)-C(1)-C(2)	49.1(4)
C(12)-N(1)-C(1)-C(10)	-132.5(3)
C(13)-N(2)-C(6)-C(5)	79.3(3)
C(13)-N(2)-C(6)-C(7)	-97.8(3)
C(14)-N(2)-C(6)-C(5)	-153.8(2)
C(14)-N(2)-C(6)-C(7)	29.1(3)
C(15)-C(9)-C(10)-C(1)	8.4(3)
C(15)-C(9)-C(10)-C(5)	-171.8(2)

Table S20. Hydrogen bonding for **13.Cl.0.5H$_2$O**/ ^{o} at 150 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N2-H2	0.98	2.082	160	3.020(2)	Cl1
O1-H1	0.89(4)	2.30(4)	167(4)	3.187(3)	Cl1

13.Cl.0.5H$_2$O at 100 K.

Table S21. Bond Lengths for **13.Cl.0.5H$_2$O** / Å at 100 K.

N(1)-C(1)	1.471(3)
N(1)-C(11)	1.486(3)
N(1)-C(12)	1.490(3)
N(1)-C(15)	1.749(3)
N(2)-C(6)	1.476(3)
N(2)-C(13)	1.500(4)

N(2)-C(14)	1.495(3)
N(3)-C(17)	1.149(3)
N(4)-C(18)	1.149(3)
C(1)-C(2)	1.357(3)
C(1)-C(10)	1.396(3)
C(2)-C(3)	1.419(3)
C(3)-C(4)	1.372(3)
C(4)-C(5)	1.417(3)
C(5)-C(6)	1.423(3)
C(5)-C(10)	1.411(3)
C(6)-C(7)	1.365(4)
C(7)-C(8)	1.420(3)
C(8)-C(9)	1.366(3)
C(9)-C(10)	1.407(3)
C(9)-C(15)	1.504(3)
C(15)-C(16)	1.431(3)
C(15)-H(15)	0.95(2)
C(16)-C(17)	1.423(3)
C(16)-C(18)	1.416(3)

Table S22. Bond Angles for **13.Cl.0.5H_2O**/ ^{o} at 100 K.

C(1)-N(1)-C(11)	109.50(19)
C(1)-N(1)-C(12)	113.38(18)
C(1)-N(1)-C(15)	103.21(16)
C(11)-N(1)-C(12)	110.9(2)
C(11)-N(1)-C(15)	109.35(17)
C(12)-N(1)-C(15)	110.17(19)
C(6)-N(2)-C(13)	111.28(18)
C(6)-N(2)-C(14)	114.6(2)
C(14)-N(2)-C(13)	111.1(2)
C(2)-C(1)-N(1)	128.3(2)
C(2)-C(1)-C(10)	122.5(2)
C(10)-C(1)-N(1)	109.0(2)
C(1)-C(2)-C(3)	116.6(2)
C(4)-C(3)-C(2)	122.6(2)

C(3)-C(4)-C(5)	120.5(2)
C(4)-C(5)-C(6)	129.3(2)
C(10)-C(5)-C(4)	116.5(2)
C(10)-C(5)-C(6)	114.1(2)
C(5)-C(6)-N(2)	117.2(2)
C(7)-C(6)-N(2)	121.0(2)
C(7)-C(6)-C(5)	121.7(2)
C(6)-C(7)-C(8)	122.2(2)
C(9)-C(8)-C(7)	118.3(2)
C(8)-C(9)-C(10)	118.97(19)
C(8)-C(9)-C(15)	130.0(2)
C(10)-C(9)-C(15)	110.93(19)
C(1)-C(10)-C(5)	121.1(2)
C(1)-C(10)-C(9)	114.3(2)
C(9)-C(10)-C(5)	124.6(2)
C(9)-C(15)-N(1)	98.19(18)
C(16)-C(15)-N(1)	115.90(19)
C(16)-C(15)-C(9)	118.65(19)
N(1)-C(15)-H(15)	99.0(16)
C(9)-C(15)-H(15)	109.6(15)
C(16)-C(15)-H(15)	113.0(15)
C(17)-C(16)-C(15)	122.8(2)
C(18)-C(16)-C(15)	120.6(2)
C(18)-C(16)-C(17)	116.6(2)
N(3)-C(17)-C(16)	176.9(3)
N(4)-C(18)-C(16)	179.5(3)

Table S23. Torsion Angles for **13.Cl.0.5H$_2$O**/ º at 100 K.

N(1)-C(1)-C(2)-C(3)	174.1(2)
N(1)-C(1)-C(10)-C(5)	-171.74(19)
N(1)-C(1)-C(10)-C(9)	7.4(3)
N(1)-C(15)-C(16)-C(17)	89.6(3)
N(1)-C(15)-C(16)-C(18)	-89.0(3)
N(2)-C(6)-C(7)-C(8)	178.3(2)
C(1)-N(1)-C(15)-C(9)	19.92(19)
C(1)-N(1)-C(15)-C(16)	147.38(19)

C(1)-C(2)-C(3)-C(4)	-2.4(4)
C(2)-C(1)-C(10)-C(5)	4.4(3)
C(2)-C(1)-C(10)-C(9)	-176.5(2)
C(2)-C(3)-C(4)-C(5)	3.0(4)
C(3)-C(4)-C(5)-C(6)	-179.9(2)
C(3)-C(4)-C(5)-C(10)	0.1(3)
C(4)-C(5)-C(6)-N(2)	3.5(4)
C(4)-C(5)-C(6)-C(7)	-180.0(2)
C(4)-C(5)-C(10)-C(1)	-3.7(3)
C(4)-C(5)-C(10)-C(9)	177.3(2)
C(5)-C(6)-C(7)-C(8)	2.0(3)
C(6)-C(5)-C(10)-C(1)	176.3(2)
C(6)-C(5)-C(10)-C(9)	-2.7(3)
C(6)-C(7)-C(8)-C(9)	-1.2(3)
C(7)-C(8)-C(9)-C(10)	-1.4(3)
C(7)-C(8)-C(9)-C(15)	174.2(2)
C(8)-C(9)-C(10)-C(1)	-175.6(2)
C(8)-C(9)-C(10)-C(5)	3.5(3)
C(8)-C(9)-C(15)-N(1)	167.5(2)
C(8)-C(9)-C(15)-C(16)	42.0(4)
C(9)-C(15)-C(16)-C(17)	-154.0(2)
C(9)-C(15)-C(16)-C(18)	27.4(4)
C(10)-C(1)-C(2)-C(3)	-1.3(3)
C(10)-C(5)-C(6)-N(2)	-176.53(19)
C(10)-C(5)-C(6)-C(7)	-0.1(3)
C(10)-C(9)-C(15)-N(1)	-16.6(2)
C(10)-C(9)-C(15)-C(16)	-142.2(2)
C(11)-N(1)-C(1)-C(2)	-76.4(3)
C(11)-N(1)-C(1)-C(10)	99.5(2)
C(11)-N(1)-C(15)-C(9)	-96.57(19)
C(11)-N(1)-C(15)-C(16)	30.9(3)
C(12)-N(1)-C(1)-C(2)	48.0(3)
C(12)-N(1)-C(1)-C(10)	-136.1(2)
C(12)-N(1)-C(15)-C(9)	141.28(18)
C(12)-N(1)-C(15)-C(16)	-91.3(2)
C(13)-N(2)-C(6)-C(5)	81.2(3)
C(13)-N(2)-C(6)-C(7)	-95.2(3)
C(14)-N(2)-C(6)-C(5)	-151.6(2)

C(14)-N(2)-C(6)-C(7)	31.9(3)
C(15)-N(1)-C(1)-C(2)	167.2(2)
C(15)-N(1)-C(1)-C(10)	-16.9(2)
C(15)-C(9)-C(10)-C(1)	8.1(3)
C(15)-C(9)-C(10)-C(5)	-172.9(2)

Table S24. Hydrogen bonding for **13.Cl.0.5H$_2$O** / º at 100 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N2-H2	0.98	2.10	159	3.033(2)	Cl1
O1-H1	0.90(3)	2.28(3)	168(3)	3.162(2)	Cl1

Table S25. Crystallographic data for **21.Cl.0.5H$_2$O** and **24.**

T/K	**21.Cl.0.5H$_2$O** **260 K**	**21.Cl.0.5H$_2$O** **150 K**	**24** **150 K**
Formula	$C_{18}H_{19}N_4$.Cl. 0.5H_2O	$C_{19}H_{22}N_3O_2$.Cl. 0.5H_2O	$C_{17}H_{16}N_2O_2$
Formula weight	368.85	368.85	280.32
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Fdd2*	*Fdd2*	*P-1*
a[Å]	48.4820(18)	48.2476(11)	8.6964(8)
b[Å]	22.8029(9)	22.8006(6)	9.2214(7)
c[Å]	6.7460(3)	6.6691(2)	10.4886(8)
α [º]	90	90	102.971(7)
β [º]	90	90	101.832(7)
γ [º]	90	90	113.041(8)
V [Å^3]	7457.9(5)	7336.5(3)	712.90(11)
Z	16	16	2
ρ [g cm^{-3}]	1.314	1.336	1.306
T [*K*]	260(2)	150.0(2)	150.0(2)
λ (Å)	0.71073	0.71073	0.71073

μ (mm^{-1})	0.225	0.229	0.087
unique refl.	4286	4465	3523
Refl, I > 2σI	2977	4051	2719
R_1(I > 2σI)	0.0600	0.0351	0.0472
wR_2	0.1070	0.0780	0.1135
$\Delta\rho$(r) [e Å^{-3}]	0.208/ -0.197	0.199/ -0.231	0.266/ -0.222
Cryst. Solvent.	Acetonitrile	Acetonitrile	Ether

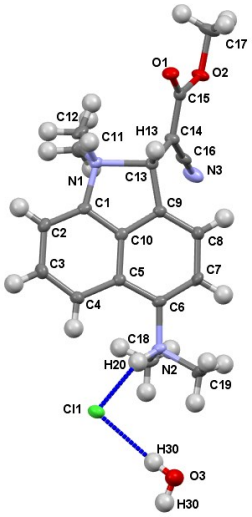


Figure S5. Atomic numbering scheme for **21.Cl.0.5H$_2$O**

21.Cl.0.5H$_2$O at 260 K.

Table S26. Bond lengths for **21.Cl.0.5H$_2$O** at 260 K / Å.

O(1)-C(15)	1.217(5)
O(2)-C(15)	1.369(5)
O(2)-C(17)	1.430(5)
O(3)-H(30)	0.87(6)
N(1)-C(1)	1.474(5)
N(1)-C(12)	1.484(4)
N(1)-C(11)	1.487(5)
N(1)-C(13)	1.754(6)

N(2)-C(6)	1.471(5)
N(2)-C(18)	1.501(6)
N(2)-C(19)	1.503(6)
N(2)-H(20)	0.98(4)
N(3)-C(16)	1.140(5)
C(1)-C(2)	1.350(6)
C(1)-C(10)	1.388(5)
C(2)-C(3)	1.418(5)
C(3)-C(4)	1.367(5)
C(4)-C(5)	1.410(6)
C(5)-C(10)	1.402(5)
C(5)-C(6)	1.422(5)
C(6)-C(7)	1.360(6)
C(7)-C(8)	1.417(5)
C(8)-C(9)	1.351(5)
C(9)-C(10)	1.394(6)
C(9)-C(13)	1.495(6)
C(13)-C(14)	1.442(5)
C(13)-H(13)	0.88(4)
C(14)-C(16)	1.406(5)
C(14)-C(15)	1.411(5)

Table S27. Bond angles for **21.Cl.0.5H_2O** at 260 K / º.

C(15)-O(2)-C(17)	115.9(3)
C(1)-N(1)-C(12)	113.3(3)
C(1)-N(1)-C(11)	110.6(3)
C(12)-N(1)-C(11)	109.6(3)
C(1)-N(1)-C(13)	103.2(3)
C(12)-N(1)-C(13)	110.4(3)
C(11)-N(1)-C(13)	109.6(3)
C(6)-N(2)-C(18)	109.3(3)
C(6)-N(2)-C(19)	114.7(4)
C(18)-N(2)-C(19)	111.8(3)
C(6)-N(2)-H(20)	111(2)
C(18)-N(2)-H(20)	106(3)

C(19)-N(2)-H(20)	103(2)
C(2)-C(1)-C(10)	121.9(4)
C(2)-C(1)-N(1)	127.6(4)
C(10)-C(1)-N(1)	110.4(4)
C(1)-C(2)-C(3)	116.9(4)
C(4)-C(3)-C(2)	122.3(4)
C(3)-C(4)-C(5)	120.7(4)
C(10)-C(5)-C(4)	116.1(4)
C(10)-C(5)-C(6)	114.9(4)
C(4)-C(5)-C(6)	128.9(4)
C(7)-C(6)-C(5)	121.5(4)
C(7)-C(6)-N(2)	119.7(4)
C(5)-C(6)-N(2)	118.3(4)
C(6)-C(7)-C(8)	121.4(4)
C(9)-C(8)-C(7)	118.9(4)
C(8)-C(9)-C(10)	119.6(4)
C(8)-C(9)-C(13)	128.1(4)
C(10)-C(9)-C(13)	112.3(4)
C(1)-C(10)-C(9)	114.2(4)
C(1)-C(10)-C(5)	122.0(4)
C(9)-C(10)-C(5)	123.7(4)
C(14)-C(13)-C(9)	117.6(3)
C(14)-C(13)-N(1)	115.4(3)
C(9)-C(13)-N(1)	99.0(3)
C(14)-C(13)-H(13)	110(3)
C(9)-C(13)-H(13)	116(3)
N(1)-C(13)-H(13)	96(3)
C(16)-C(14)-C(15)	120.5(3)
C(16)-C(14)-C(13)	121.2(4)
C(15)-C(14)-C(13)	118.3(3)
O(1)-C(15)-O(2)	121.1(4)
O(1)-C(15)-C(14)	126.4(4)
O(2)-C(15)-C(14)	112.5(4)
N(3)-C(16)-C(14)	179.3(5)

Table S28. Torsion angles for **21.Cl.0.5H_2O** at 260 K / º.

C(12)-N(1)-C(1)-C(2)	-56.6(5)
C(11)-N(1)-C(1)-C(2)	66.9(5)
C(13)-N(1)-C(1)-C(2)	-176.0(4)
C(12)-N(1)-C(1)-C(10)	127.1(4)
C(11)-N(1)-C(1)-C(10)	-109.4(4)
C(13)-N(1)-C(1)-C(10)	7.7(4)
C(10)-C(1)-C(2)-C(3)	-0.1(6)
N(1)-C(1)-C(2)-C(3)	-176.0(4)
C(1)-C(2)-C(3)-C(4)	1.8(6)
C(2)-C(3)-C(4)-C(5)	-1.3(6)
C(3)-C(4)-C(5)-C(10)	-0.9(6)
C(3)-C(4)-C(5)-C(6)	175.8(4)
C(10)-C(5)-C(6)-C(7)	-1.5(6)
C(4)-C(5)-C(6)-C(7)	-178.2(4)
C(10)-C(5)-C(6)-N(2)	170.7(3)
C(4)-C(5)-C(6)-N(2)	-6.0(6)
C(18)-N(2)-C(6)-C(7)	89.7(5)
C(19)-N(2)-C(6)-C(7)	-36.8(5)
C(18)-N(2)-C(6)-C(5)	-82.7(4)
C(19)-N(2)-C(6)-C(5)	150.8(4)
C(5)-C(6)-C(7)-C(8)	0.1(6)
N(2)-C(6)-C(7)-C(8)	-172.0(4)
C(6)-C(7)-C(8)-C(9)	0.6(6)
C(7)-C(8)-C(9)-C(10)	0.2(6)
C(7)-C(8)-C(9)-C(13)	-179.7(4)
C(2)-C(1)-C(10)-C(9)	-179.3(4)
N(1)-C(1)-C(10)-C(9)	-2.7(4)
C(2)-C(1)-C(10)-C(5)	-2.2(6)
N(1)-C(1)-C(10)-C(5)	174.4(3)
C(8)-C(9)-C(10)-C(1)	175.3(4)
C(13)-C(9)-C(10)-C(1)	-4.8(5)
C(8)-C(9)-C(10)-C(5)	-1.7(6)
C(13)-C(9)-C(10)-C(5)	178.1(3)
C(4)-C(5)-C(10)-C(1)	2.6(5)
C(6)-C(5)-C(10)-C(1)	-174.5(3)
C(4)-C(5)-C(10)-C(9)	179.5(4)

C(6)-C(5)-C(10)-C(9)	2.3(5)
C(8)-C(9)-C(13)-C(14)	-46.6(6)
C(10)-C(9)-C(13)-C(14)	133.5(4)
C(8)-C(9)-C(13)-N(1)	-171.6(4)
C(10)-C(9)-C(13)-N(1)	8.6(4)
C(1)-N(1)-C(13)-C(14)	-136.0(3)
C(12)-N(1)-C(13)-C(14)	102.6(4)
C(11)-N(1)-C(13)-C(14)	-18.2(4)
C(1)-N(1)-C(13)-C(9)	-9.5(3)
C(12)-N(1)-C(13)-C(9)	-130.9(3)
C(11)-N(1)-C(13)-C(9)	108.3(3)
C(9)-C(13)-C(14)-C(16)	-24.2(6)
N(1)-C(13)-C(14)-C(16)	92.1(5)
C(9)-C(13)-C(14)-C(15)	156.5(4)
N(1)-C(13)-C(14)-C(15)	-87.2(5)
C(17)-O(2)-C(15)-O(1)	-0.1(6)
C(17)-O(2)-C(15)-C(14)	179.3(4)
C(16)-C(14)-C(15)-O(1)	-178.0(5)
C(13)-C(14)-C(15)-O(1)	1.3(7)
C(16)-C(14)-C(15)-O(2)	2.6(6)
C(13)-C(14)-C(15)-O(2)	-178.1(4)

Table S29. Hydrogen bonding for **21.Cl.0.5H_2O** / º at 260 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O3-H30	0.87(6)	2.40(6)	178(7)	3.265(4)	Cl1
N2-H20	0.98(4)	2.06(4)	155(3)	2.981(4)	Cl1

21.Cl.0.5H_2O at 150 K.

Table S30. Bond lengths for **21.Cl.0.5H_2O** at 150 K / Å.

O(1)-C(15)	1.221(3)
O(2)-C(15)	1.368(3)
O(2)-C(17)	1.432(3)
O(3)-H(30)	0.84(4)
N(1)-C(1)	1.476(3)
N(1)-C(11)	1.490(3)
N(1)-C(12)	1.499(3)
N(1)-C(13)	1.705(3)
N(2)-C(6)	1.471(3)
N(2)-C(19)	1.501(3)
N(2)-C(18)	1.505(3)
N(2)-H(20)	0.92(3)
N(3)-C(16)	1.154(3)
C(1)-C(2)	1.358(3)
C(1)-C(10)	1.392(3)
C(2)-C(3)	1.424(3)
C(3)-C(4)	1.372(3)
C(4)-C(5)	1.421(3)
C(5)-C(10)	1.406(3)
C(5)-C(6)	1.423(3)
C(6)-C(7)	1.366(3)
C(7)-C(8)	1.414(3)
C(8)-C(9)	1.361(3)
C(9)-C(10)	1.396(3)
C(9)-C(13)	1.499(3)
C(13)-C(14)	1.452(3)
C(13)-H(13)	0.92(2)
C(14)-C(16)	1.408(3)
C(14)-C(15)	1.418(3)

Table S31. Bond angles for **21.Cl.0.5H$_2$O** at 150 K / °.

C(15)-O(2)-C(17)	115.04(18)
C(1)-N(1)-C(11)	110.12(18)
C(1)-N(1)-C(12)	112.96(17)
C(11)-N(1)-C(12)	109.19(18)
C(1)-N(1)-C(13)	103.77(16)
C(11)-N(1)-C(13)	110.41(16)
C(12)-N(1)-C(13)	110.30(17)
C(6)-N(2)-C(19)	115.3(2)
C(6)-N(2)-C(18)	109.38(18)
C(19)-N(2)-C(18)	111.32(19)
C(6)-N(2)-H(20)	112.6(17)
C(19)-N(2)-H(20)	103.0(17)
C(18)-N(2)-H(20)	104.7(17)
C(2)-C(1)-C(10)	121.8(2)
C(2)-C(1)-N(1)	128.2(2)
C(10)-C(1)-N(1)	109.9(2)
C(1)-C(2)-C(3)	116.7(2)
C(4)-C(3)-C(2)	122.9(2)
C(3)-C(4)-C(5)	120.0(2)
C(10)-C(5)-C(4)	116.3(2)
C(10)-C(5)-C(6)	114.6(2)
C(4)-C(5)-C(6)	129.0(2)
C(7)-C(6)-C(5)	121.6(2)
C(7)-C(6)-N(2)	119.4(2)
C(5)-C(6)-N(2)	118.5(2)
C(6)-C(7)-C(8)	121.6(2)
C(9)-C(8)-C(7)	118.7(2)
C(8)-C(9)-C(10)	119.4(2)
C(8)-C(9)-C(13)	129.2(2)
C(10)-C(9)-C(13)	111.33(19)
C(1)-C(10)-C(9)	113.7(2)
C(1)-C(10)-C(5)	122.2(2)
C(9)-C(10)-C(5)	124.0(2)
C(14)-C(13)-C(9)	116.81(19)
C(14)-C(13)-N(1)	115.23(18)
C(9)-C(13)-N(1)	100.12(16)

C(14)-C(13)-H(13)	111.9(15)
C(9)-C(13)-H(13)	114.2(15)
N(1)-C(13)-H(13)	96.3(15)
C(16)-C(14)-C(15)	120.1(2)
C(16)-C(14)-C(13)	121.4(2)
C(15)-C(14)-C(13)	118.5(2)
O(1)-C(15)-O(2)	121.5(2)
O(1)-C(15)-C(14)	126.0(2)
O(2)-C(15)-C(14)	112.48(19)
N(3)-C(16)-C(14)	179.6(3)

Table S32. Torsion angles for **21.Cl.0.5H$_2$O** at 150 K / º.

C(11)-N(1)-C(1)-C(2)	66.7(3)
C(12)-N(1)-C(1)-C(2)	-55.6(3)
C(13)-N(1)-C(1)-C(2)	-175.1(2)
C(11)-N(1)-C(1)-C(10)	-109.6(2)
C(12)-N(1)-C(1)-C(10)	128.1(2)
C(13)-N(1)-C(1)-C(10)	8.6(2)
C(10)-C(1)-C(2)-C(3)	0.7(3)
N(1)-C(1)-C(2)-C(3)	-175.3(2)
C(1)-C(2)-C(3)-C(4)	1.1(4)
C(2)-C(3)-C(4)-C(5)	-0.9(4)
C(3)-C(4)-C(5)-C(10)	-1.1(3)
C(3)-C(4)-C(5)-C(6)	175.7(2)
C(10)-C(5)-C(6)-C(7)	-1.6(3)
C(4)-C(5)-C(6)-C(7)	-178.4(2)
C(10)-C(5)-C(6)-N(2)	170.02(18)
C(4)-C(5)-C(6)-N(2)	-6.8(3)
C(19)-N(2)-C(6)-C(7)	-36.5(3)
C(18)-N(2)-C(6)-C(7)	89.8(3)
C(19)-N(2)-C(6)-C(5)	151.6(2)
C(18)-N(2)-C(6)-C(5)	-82.0(3)
C(5)-C(6)-C(7)-C(8)	-0.1(3)
N(2)-C(6)-C(7)-C(8)	-171.7(2)
C(6)-C(7)-C(8)-C(9)	1.0(4)

C(7)-C(8)-C(9)-C(10)	0.0(3)
C(7)-C(8)-C(9)-C(13)	179.6(2)
C(2)-C(1)-C(10)-C(9)	179.9(2)
N(1)-C(1)-C(10)-C(9)	-3.5(3)
C(2)-C(1)-C(10)-C(5)	-2.7(3)
N(1)-C(1)-C(10)-C(5)	173.85(18)
C(8)-C(9)-C(10)-C(1)	175.3(2)
C(13)-C(9)-C(10)-C(1)	-4.3(3)
C(8)-C(9)-C(10)-C(5)	-2.0(3)
C(13)-C(9)-C(10)-C(5)	178.38(19)
C(4)-C(5)-C(10)-C(1)	2.9(3)
C(6)-C(5)-C(10)-C(1)	-174.4(2)
C(4)-C(5)-C(10)-C(9)	179.9(2)
C(6)-C(5)-C(10)-C(9)	2.7(3)
C(8)-C(9)-C(13)-C(14)	-45.7(3)
C(10)-C(9)-C(13)-C(14)	134.0(2)
C(8)-C(9)-C(13)-N(1)	-170.8(2)
C(10)-C(9)-C(13)-N(1)	8.8(2)
C(1)-N(1)-C(13)-C(14)	-136.46(19)
C(11)-N(1)-C(13)-C(14)	-18.5(2)
C(12)-N(1)-C(13)-C(14)	102.3(2)
C(1)-N(1)-C(13)-C(9)	-10.26(19)
C(11)-N(1)-C(13)-C(9)	107.71(19)
C(12)-N(1)-C(13)-C(9)	-131.52(17)
C(9)-C(13)-C(14)-C(16)	-24.4(3)
N(1)-C(13)-C(14)-C(16)	92.8(3)
C(9)-C(13)-C(14)-C(15)	156.1(2)
N(1)-C(13)-C(14)-C(15)	-86.7(3)
C(17)-O(2)-C(15)-O(1)	1.3(3)
C(17)-O(2)-C(15)-C(14)	180.0(2)
C(16)-C(14)-C(15)-O(1)	-178.7(2)
C(13)-C(14)-C(15)-O(1)	0.8(4)
C(16)-C(14)-C(15)-O(2)	2.7(3)
C(13)-C(14)-C(15)-O(2)	-177.8(2)

Table S29. Hydrogen bonding for **21.Cl.0.5H$_2$O** / ^{o} at 150 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O3-H30	0.85(4)	2.42(4)	174(4)	3.266(2)	Cl1
N2-H20	0.92(3)	2.11(3)	158(2)	2.986(2)	Cl1

Crystal Structure of 24.

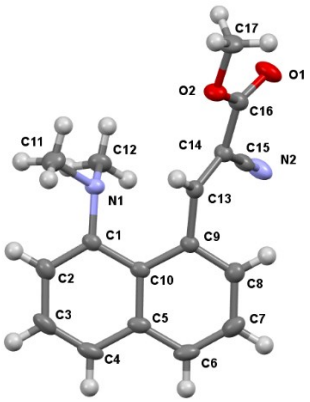


Figure S6. Atomic numbering scheme for **24**.

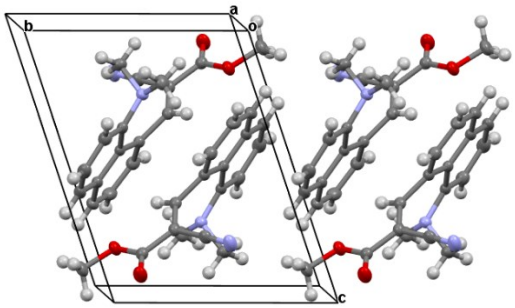


Figure S7. Crystal packing arrangement for **24**.

The $Me_2N\cdots C$ distance is 2.595(2) Å and the alkene C(13)-C(14) distance is 1.3485(18) Å with a N···C=C angle of 116.23(12)^o. This is very similar to that observed for the corresponding ethyl ester.[S7] The $Me_2N\cdots C$ distance is 2.531(2) Å and the alkene bond length is 1.346(2) Å with a N···C=C angle of 114.4(2)^o.

Table S30. Bond lengths for **24**.

O(1)-C(16)	1.2026(16)
O(2)-C(16)	1.3393(16)
O(2)-C(17)	1.4487(17)
N(1)-C(1)	1.4259(17)
N(1)-C(11)	1.4586(18)
N(1)-C(12)	1.4639(17)
N(2)-C(15)	1.1462(18)
C(1)-C(2)	1.3759(18)
C(1)-C(10)	1.4203(19)
C(2)-C(3)	1.411(2)
C(3)-C(4)	1.355(2)
C(4)-C(5)	1.417(2)
C(5)-C(6)	1.413(2)
C(5)-C(10)	1.4271(19)
C(6)-C(7)	1.363(2)
C(7)-C(8)	1.407(2)
C(8)-C(9)	1.377(2)
C(9)-C(10)	1.4334(18)
C(9)-C(13)	1.4772(19)
C(13)-C(14)	1.3485(18)
C(14)-C(15)	1.4420(18)
C(14)-C(16)	1.4851(19)

Table S31. Bond angles for **24**.

C(16)-O(2)-C(17)	114.87(11)
C(1)-N(1)-C(11)	115.60(11)
C(1)-N(1)-C(12)	111.86(11)
C(11)-N(1)-C(12)	110.93(12)
C(2)-C(1)-N(1)	123.15(13)
C(2)-C(1)-C(10)	120.01(13)
C(10)-C(1)-N(1)	116.82(11)
C(1)-C(2)-C(3)	120.44(14)

C(4)-C(3)-C(2)	120.81(14)
C(3)-C(4)-C(5)	120.66(14)
C(4)-C(5)-C(10)	119.00(14)
C(6)-C(5)-C(4)	121.39(13)
C(6)-C(5)-C(10)	119.61(13)
C(7)-C(6)-C(5)	120.69(14)
C(6)-C(7)-C(8)	120.19(14)
C(9)-C(8)-C(7)	121.49(14)
C(8)-C(9)-C(10)	119.31(13)
C(8)-C(9)-C(13)	117.89(12)
C(10)-C(9)-C(13)	122.53(12)
C(1)-C(10)-C(5)	118.90(12)
C(1)-C(10)-C(9)	122.56(12)
C(5)-C(10)-C(9)	118.54(13)
C(14)-C(13)-C(9)	123.96(12)
C(13)-C(14)-C(15)	121.31(13)
C(13)-C(14)-C(16)	124.71(12)
C(15)-C(14)-C(16)	113.98(11)
N(2)-C(15)-C(14)	178.73(16)
O(1)-C(16)-O(2)	124.10(13)
O(1)-C(16)-C(14)	123.68(13)
O(2)-C(16)-C(14)	112.18(11)

Table S32. Torsion angles for **24**.

N(1)-C(1)-C(2)-C(3)	176.98(12)
N(1)-C(1)-C(10)-C(5)	-173.86(11)
N(1)-C(1)-C(10)-C(9)	5.45(18)
C(1)-C(2)-C(3)-C(4)	-2.0(2)
C(2)-C(1)-C(10)-C(5)	4.62(18)
C(2)-C(1)-C(10)-C(9)	-176.07(12)
C(2)-C(3)-C(4)-C(5)	2.0(2)
C(3)-C(4)-C(5)-C(6)	-179.44(13)
C(3)-C(4)-C(5)-C(10)	1.3(2)
C(4)-C(5)-C(6)-C(7)	-179.68(13)
C(4)-C(5)-C(10)-C(1)	-4.57(18)

C(4)-C(5)-C(10)-C(9)	176.09(11)
C(5)-C(6)-C(7)-C(8)	2.6(2)
C(6)-C(5)-C(10)-C(1)	176.19(12)
C(6)-C(5)-C(10)-C(9)	-3.15(18)
C(6)-C(7)-C(8)-C(9)	-1.0(2)
C(7)-C(8)-C(9)-C(10)	-2.72(19)
C(7)-C(8)-C(9)-C(13)	171.48(12)
C(8)-C(9)-C(10)-C(1)	-174.62(12)
C(8)-C(9)-C(10)-C(5)	4.70(18)
C(8)-C(9)-C(13)-C(14)	55.15(18)
C(9)-C(13)-C(14)-C(15)	12.5(2)
C(9)-C(13)-C(14)-C(16)	-166.72(13)
C(10)-C(1)-C(2)-C(3)	-1.4(2)
C(10)-C(5)-C(6)-C(7)	-0.5(2)
C(10)-C(9)-C(13)-C(14)	-130.85(14)
C(11)-N(1)-C(1)-C(2)	34.45(18)
C(11)-N(1)-C(1)-C(10)	-147.12(12)
C(12)-N(1)-C(1)-C(2)	-93.79(15)
C(12)-N(1)-C(1)-C(10)	84.64(14)
C(13)-C(9)-C(10)-C(1)	11.46(19)
C(13)-C(9)-C(10)-C(5)	-169.23(11)
C(13)-C(14)-C(16)-O(1)	171.91(14)
C(13)-C(14)-C(16)-O(2)	-5.9(2)
C(15)-C(14)-C(16)-O(1)	-7.4(2)
C(15)-C(14)-C(16)-O(2)	174.82(12)
C(17)-O(2)-C(16)-O(1)	-1.7(2)
C(17)-O(2)-C(16)-C(14)	176.05(12)

III. Solid State NMR studies on **13.Cl.0.5H_2O.**

Carbon ^{13}C CP MAS NMR spectra were recorded on Bruker AVANCE-II spectrometer at 8.5 T magnetic field, with ^{13}C resonance frequency 90.41 MHz using a cryoMAS NMR probe for 1.8 mm od Si_3N_4 rotors and a He-flow cryostat from Janis Research Inc. The temperature was controlled by a LakeShore '332' temperature controller and Cernox temperature sensors. According to earlier calibrations the temperature of rotating sample was 5% higher than the read-out temperature of the controller and was corrected correspondingly.

Spin-lattice relaxation times of carbons were measured in a 14.1T magnetic field with 4 mm sample. It turned out, that the relaxation of carbons is very slow, T_1^{13C} = 170 s, whereas the relaxation of protons is conveniently fast: T_1^{1H} = 0.94 s at 300K and 13 s at 39 K (at 360 MHz, 8.5T field). It was not possible to record ^{13}C MAS NMR spectrum at 8.5 T with cryoMAS probe with simple one pulse excitation, despite the ^{13}C enriched sample. Therefore, in all cryoMAS experiments a 2 ms cross polarization (CP) was used. The sample spinning speed in cryoMAS experiment was 22.5 kHz. At that high spinning speed the proton decoupling at comparatively low power level was not effective and the resolution in cryoMAS spectra is lower than that in the spectrum recorded at 14.1 T field (Fig S6). In a N_2 atmosphere, the RF amplitudes at CP were approximately 78 and 55 kHz for ^1H and ^{13}C, respectively. Due to the arcing during long CP pulses in a He atmosphere, the RF power was turned down to 32 and 18 kHz, respectively. At CP low power levels the signal was about 1.5 times smaller. The spectra presented in the Figure 11 (main article) have been recorded in N_2 atmosphere down to 85 K, and below that, in a helium atmosphere. The intensities are normalized by the number of scans.

Figure 11 (main article) shows that below T~140 K, the amplitude of the main peak decreases and broadens with decreasing temperature. At the lowest temperature the signal grows again, but it remains broad. There is no sign of a growing line at about 100 ppm. Suppression of some signals at cross polarization may be caused by ineffective cross polarization at certain dynamics. As an example, this happens in alanine with CH_3 resonance over a broad temperature region (see Fig. S8).

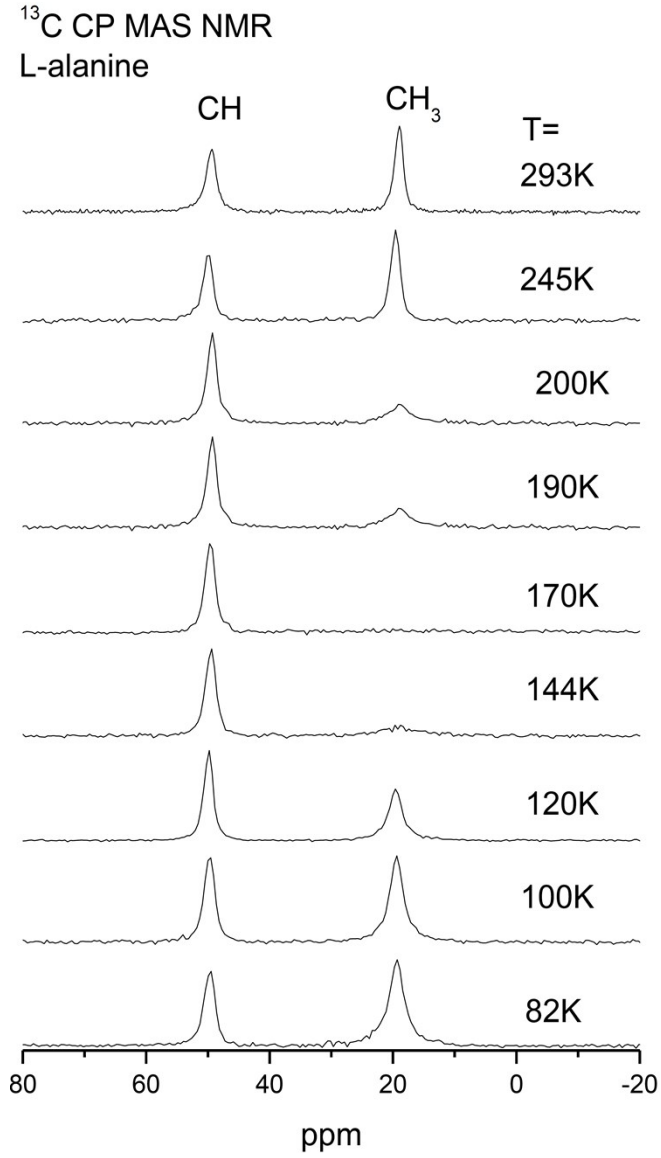


Figure S6. ^{13}C CPMAS NMR spectra of L-alanine, ^{13}C isotope enriched in CH and CH_3 positions. The signal of methyl carbons is severely suppressed in a broad temperature range between 100 K to 200 K due to molecular dynamics hindering ^{1}H to ^{13}C polarization transfer for methyl carbons (I. Heinmaa, *et al* [S10]).

At high field the CP MAS NMR spectrum of **13.Cl.0.5H_2O** consists of the main line at 156 ppm and a number of lines belonging to the un-enriched carbons of the molecule (Fig. S9).

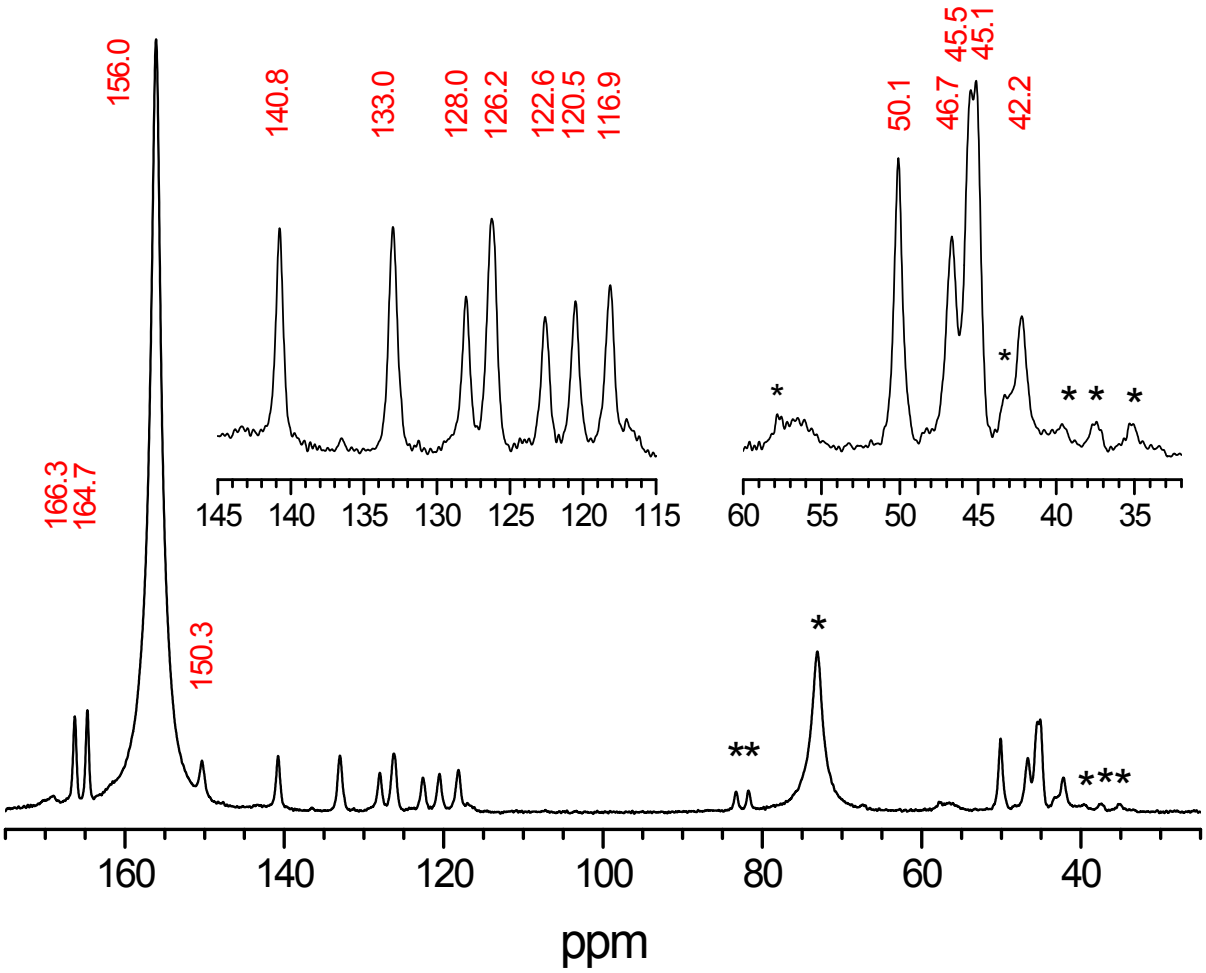
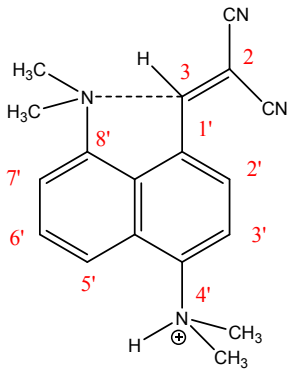


Figure S9. ^{13}C NMR CP MAS spectrum of **13.Cl.0.5H$_2$O** at 300 K. The asterisks denote spinning sidebands which occur at multiple of sample spinning speed from the main line. The spectrum has been recorded on Bruker AVANCE-2-600 NMR spectrometer with home-built MAS probe for 4x25 mm rotors, ^{13}C resonance frequency 150.9 MHz, sample spinning rate 12.5 kHz, contact time 2 ms, 1000 scans, relaxation delay 5s.

Table S33. Assignment of room temperature ^{13}C NMR spectra from solution and solid state for **13.Cl.0.5H$_2$O.**



Site	400 MHz, CD_2Cl_2 δ_C ppm	600 MHz solid δ_C ppm
C-3	163.1	156.1
C-2	73.4	56.5
CN	114.7	116.7
CN	113.3	116.7
C-1′	130.6	133.0
C-2′	126.8	128.0
C-3′	118.0	118.1
C-4′	142.9	140.8
C-4a′	127.7	126.2
C-5′	121.4	120.5
C-6′	129.6	126.2
C-7′	122.2	122.6
C-8′	150.2	150.3
C8a′	132.2	133.0
C-(4′-NH(CH_3)$_2$)	46.8	46.6, 50.1 *
C-(8′-N(CH_3)$_2$)	45.4	45.1, 45.5 *

* the assignment is arbitrary.

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