Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Fixation of nitrous oxide by mesoionic and carbanionic N-heterocyclic carbenes

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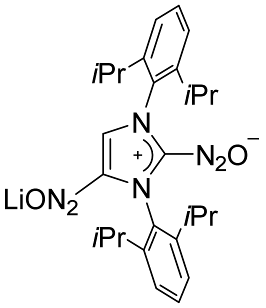
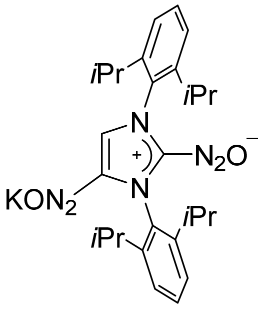
1. General

Unless stated otherwise, the reactions were performed under an atmosphere of dry dinitrogen. Solvents were purified and dried according to standard procedures. The IDipp-N_2O adduct,[1] [IPr(Ph)]I [IPr(C_6H_4-4-Me)]I,[2] and dc-NHC [3] were synthesized according to literature methods. N_2O (99.999%) was purchased from Air-liquide. NMR spectra were measured on a Bruker Avance DPX-400 (^{1}H: 400 MHz). Mass spectra were recorded using a Xevo G2-S QTOF mass spectrometer coupled to the Acquity UPLC Class Binary Solvent manager and BTN sample manager (Waters, Corporation, Milford, MA). The sample manager system temperature was maintained at 30 °C and the injection volume was 5 μL. Mass spectrometer detection was operated in positive ionization using the ZSpray™ dual-orthogonal multimode ESI/APCI/ESCi® source. The TOF mass spectra were acquired in the sensitive mode over the range of m/z 50-1200 at an acquisition rate of 0.036 sec/spectra. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. UV-vis data were recorded on a Cary 60 Spectrometer (Agilent Technologies).

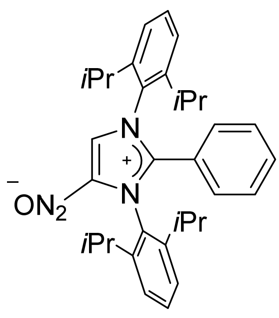
2. Synthesis of the compounds 1−6



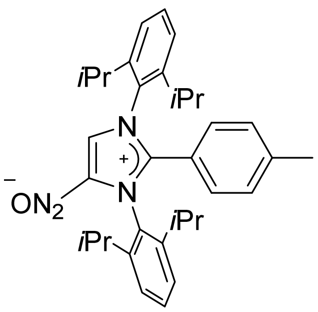
1: N_2O (1 bar) was added to a cooled solution (0 °C) of the ditopic carbaionic NHC (12 mmol, 4.73 g) in THF (100 mL). The reaction mixture was brought to room temperature, and the resulting solution was stirred for 16 h. The solution was then filtered and concentrated under reduced pressure. Few drops of the resulting concentrate were added into a 50 mL Falcon tube half-filled with pentane, which was vigorously shaken, and the procedure was repeated till the compound was fully precipitated as a yellow solid. The latter was isolated by filtration, washed with pentane and dried under vacuum. Crystals, suitable for X-Ray analysis, were obtained by layering hexane onto a solution of **1** in THF. Yield: 3.98 g (68%). Elem. anal. calcd for $C_{27}H_{35}N_6O_2Li \cdot 1.5\ THF \cdot 0.5\ H_2O$: C 65.11; H 8.11; N 13.81. Found: C 65.70; H 7.82; N 14.13. NMR data indicate a mixture of two isomers (**A** and **B**) in a 7:3 ratio. ^{1}H NMR (400 MHz, CD_3OD, δ): 1.11−1.29 (m, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 2.64 (sept, J = 6.9 Hz, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 2.70−2.87 (m, **A** and **B**, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 7.14 (s, isomer **B**, $\mathrm{C}\mathit{H}\mathrm{{=}CN_2O}$), 7.22−7.46 (m, $\mathrm{CH_{arom}}$), 8.15 (s, isomer **A**, $\mathrm{C}\mathit{H}\mathrm{{=}CN_2O}$). ^{13}C{^{1}H} NMR (101 MHz, CD_3OD, δ): 23.35, 23.42, 23.59, 23.62, 23.84, 23.94, 24.46 ($\mathrm{CH(}\mathit{CH}_3\mathrm{)_2}$), 30.37, 30.41, 30.61, 30.68 ($\mathit{C}\mathrm{H(CH_3)_2}$), 105.21 ($\mathit{C}\mathrm{H{=}CN_2O}$, isomer **B**), 114.81 ($\mathit{C}\mathrm{H{=}CN_2O}$, isomer **A**), 124.88, 124.99, 125.23, 131.30, 131.45, 131.52, 131.70, 133.70, 135.33, 144.80, 146.56, 146.60, 147.10, 148.62, 149.70 (C and CH from Ar's). MS (ESI$^-$), found: 475.2820 [M – Li]$^-$; calcd for $C_{27}H_{35}N_6O_2$: 475.2821. UV/Vis (THF): λ_{max} = 318 nm, $\varepsilon = 1.27\times10^4\ M^{-1}cm^{-1}$.



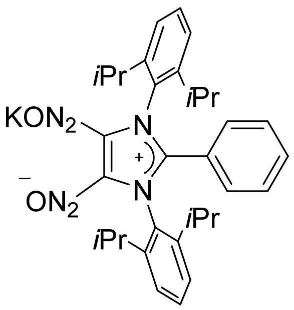
2: A solution of KHMDS (0.91 mmol, 182 mg) in THF (5 mL) was added to a cooled solution (0 °C) of the IDipp-N_2O adduct (0.83 mmol, 360 mg) in THF (50 mL). After addition of N_2O (1 bar), the solution was brought to room temperature and stirred overnight. The resulting orange solution was concentrated under reduced pressure and 100 mL of pentane were added to yield to a yellow precipitate, which was isolated by filtration and dried under vacuum. Yield: 303 mg (71%). Elem. anal. calcd for $C_{27}H_{35}N_6O_2K \cdot 0.5\ THF \cdot 2\ H_2O$: C 59.36; H 7.39; N 14.32. Found C 59.24; H 6.82; N 14.80. NMR data indicate a mixture of two isomers (**A** and **B**) in a 2:1 ratio. ^{1}H NMR (400 MHz, CD_3CN, δ): 1.06−1.28 (m, **A** and **B**, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 1.81 (m, $\mathrm{C}\mathit{H}_2$(3,4), bound THF), 2.67 (sept, J = 6.9 Hz, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 2.74−2.94 (m, **A** and **B**, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.65 (m, $\mathrm{C}\mathit{H}_2$(2,5), bound THF), 6.81 (s, isomer **B**, $\mathrm{C}\mathit{H}\mathrm{{=}CN_2O}$), 7.24−7.48 (m, $\mathrm{CH_{arom}}$), 8.05 (s, isomer **A**, $\mathrm{C}\mathit{H}\mathrm{{=}CN_2O}$). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, δ): 23.06, 23.14, 23.24, 23.47, 23.58, 24.05, 24.08 ($\mathrm{CH(}\mathit{CH}_3\mathrm{)_2}$), 26.14 ($CH_2$(3,4), bound THF), 29.71, 29.74, 29.95 ($CH(CH_3)_2$), 68.17 (CH_2(2,5), bound THF), 100.94 ($CH{=}CN_2O$, isomer **B**), 111.17 ($CH{=}CN_2O$, isomer **A**), 124.32, 124.38, 124.69, 124.76, 130.25, 130.48, 130.58, 130.71, 132.20, 132.99, 134.29, 135.52, 146.28, 146.53, 146.85, 146.92, 149.94, 151.13 (C and CH from Ar's). MS (ESI$^-$), found: 475.2820 [M – K]$^-$; calcd for $C_{27}H_{35}N_6O_2$: 475.2821. UV/Vis (THF): λ_{max} 329 nm, $\varepsilon = 1.43\times10^4$ M^{-1}cm^{-1}.



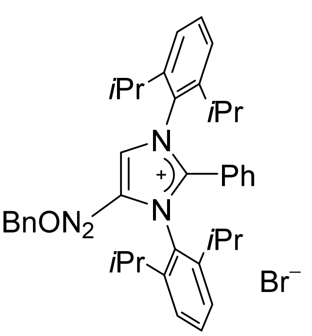
3: KHMDS (6.43 mmol, 1.28 g) was added to a suspension of [IPr(Ph)]I (5.84 mmol, 3.46 g) in THF (150 mL) and the mixture was stirred for 2 h. The solution was then filtered and stirred under an atmosphere of N_2O (1 bar) for 12 h. The resulting orange solution was concentrated under reduced pressure and 400 mL of pentane were added to yield to a yellow precipitate, which was isolated by filtration and dried under vacuum. Yield: 1.9 g (64%). Crystals of the *cis* isomer, suitable for X-Ray analysis, were obtained by slow evaporation of a solution of **3** in a mixture CH_2Cl_2/hexane. Crystals of the *trans* isomer, suitable for X-Ray analysis, were obtained by slow evaporation of a solution of **3** in MeOH. Elem. anal. calcd for $C_{33}H_{40}N_4O \cdot 0.5\ CH_2Cl_2$: C 73.00; H 7.50; N 10.17. Found C 72.15 H 7.76; N 10.15. NMR data indicate a mixture of two isomers (**A** and **B**) in a 1:1 ratio. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 0.91−1.21 (m, **A** and **B**, $CH(CH_3)_2$), 2.39 (sept, $J = 6.9$ Hz, $CH(CH_3)_2$), 2.46−2.68 (m, **A** and **B**, $CH(CH_3)_2$) 6.88 (d, $J = 7.9$ Hz, **A** and **B**, CH_{arom}), 7.08 (t, $J = 7.8$ Hz, **A** and **B**, CH_{arom}), 7.18−7.48 (m, **A** and **B**, CH_{arom}), 8.61 (s, isomer **A**, $CH{=}CN_2O$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, δ): 22.86, 23.02, 23.05, 24.91, 25.04, 25.93, 26.03 ($CH(CH_3)_2$), 29.66, 29.68, 29.98, 30.01 ($CH(CH_3)_2$), 105.50 ($CH{=}CN_2O$, isomer **B)**, 115.46 ($CH{=}CN_2O$, isomer **A**), 122.63, 129.18, 129.22, 129.69, 129.77, 129.93, 130.57, 131.47, 131.52, 131.59, 131.65, 131.83, 131.90, 132.03, 138.38, 138.55, 139.55, 145.59, 145.63, 146.03, 146.07, 152.72 (C and CH from Ar's). MS (ESI$^+$), found: 509.3280 [M + H]$^+$; calcd for $C_{33}H_{41}N_4O$: 509.3285. UV/Vis (THF): λ_{max} 348 nm, $\varepsilon = 1.10\times10^4$ M^{-1}cm^{-1}.



4: KHMDS (2.7 mmol, 538 mg) was added to a suspension of [IPr(C$_6$H$_3$-4-Me)]I (2.45 mmol, 1.6 g) in THF (150 mL) and the mixture was stirred for 2 h. The solution was then filtered and stirred under an atmosphere of N$_2$O (1 bar) for 12 h. The resulting purple solution was concentrated under reduced pressure and 400 mL of pentane were added to yield a light purple precipitate, which was isolated by filtration and dried under vacuum. Yield: 665 mg (60%). Crystals, suitable for X-Ray analysis, were obtained by slow evaporation of a solution of **4** in MeOH. Elem. anal. calcd for $C_{34}H_{42}N_4O$: C 78.12; H 8.10; N 10.72. Found C 78.06; H 8.17; N 10.13. NMR data indicate a mixture of two isomers (**A** and **B**) in a 1:1 ratio. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, δ): 0.91−1.20 (m, **A** and **B**, CH(C*H*$_3$)$_2$), 2.12 (s, **A** and **B,** *p*-C*H*$_3$), 2.38 (sept, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 2.46−2.67 (m, **A** and **B**, C*H*(CH$_3$)$_2$) 6.76 (d, *J* = 8.3 Hz, **A** and **B**, *o/m*- C$_6$*H*$_4$Me), 6.88 (d, *J* = 8.0 Hz, **A** and **B**, *o/m*- C$_6$*H*$_4$Me), 7.17−7.48 (m, **A** and **B**, CH$_{arom}$), 8.57 (s, isomer **A**, C*H*=CN$_2$O). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, δ): 21.02 (*p*-*C*H$_3$), 22.32, 22.48, 22.51, 24.31, 24.44, 25.32, 25.43 (CH(*C*H$_3$)$_2$), 29.09, 29.10, 29.40, 29.43 (*C*H(CH$_3$)$_2$), 105.03 (*C*H=CN$_2$O, isomer **B)**, 114.95 (*C*H=CN$_2$O, isomer **A**), 118.98, 119.06, 124.55, 124.59, 124.82, 124.91, 128.96, 129.20, 129.31, 129.35, 130.08, 130.93, 131.02, 131.06, 131.12, 131.27, 131.39, 137.61, 138.51, 139.54, 142.34, 142.55, 145.06, 145.10, 145.52, 145.56, 151.46. (C and CH from Ar's). MS (ESI$^+$), found: 523.3433 [M + H]$^+$; calcd for $C_{34}H_{43}N_4O$: 523.3437. UV/Vis (THF): λ_{max} 347 nm, ε = 1.38×10^4 M^{-1}cm^{-1}.



5: A solution of KHMDS (0.72 mmol, 144 mg) in THF (5 mL) was added to a cooled solution (0 °C) of **3** (0.65 mmol, 331 mg) in THF (50 mL). After addition of N$_2$O (1 bar), the solution was brought to room temperature and stirred overnight. The resulting orange solution was concentrated under reduced pressure and 100 mL of pentane were added to yield to an orange precipitate, which was isolated by filtration and dried under vacuum. Yield: 321 mg (84%). Elem. anal. calcd for $C_{33}H_{39}N_6O_2K$ • 1 THF: C 67.06; H 6.91; N 13.22. Found C 67.01; H 6.97; N 13.15. ^{1}H NMR (400 MHz, CD$_3$CN, δ): 1.00 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.84 (m, C*H*$_2$(3,4), bound THF), 2.72 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 3.70 (m, C*H*$_2$(2,5), bound THF), 6.98 (d, *J* = 8.1 Hz, 2H, *o*-C$_6$H$_5$), 7.14 (t, *J* = 8.0 Hz, 2H, *p*-Dipp), 7.27 (d, *J* = 7.8 Hz 4H, *m*-Dipp), 7.30 (t, *J* = 7.5 Hz, 1H, *p*-C$_6$H$_5$), 7.45 (t, *J* = 7.8 Hz, 2H, *m*-C$_6$H$_5$), ^{13}C{^{1}H} NMR (101 MHz, CD$_3$CN, δ): 23.28 (CH(*C*H$_3$)$_2$), 24.68 (CH(*C*H$_3$)$_2$), 26.50 (*C*H$_2$(3,4), bound THF), 30.69 (*C*H(CH$_3$)$_2$), 68.86 (*C*H$_2$(2,5), bound THF), 123.47, 125.88, 129.52, 131.09, 131.12, 132.33, 132.50, 133.40, 138.02, 146.61 (C and CH from Ar's). MS (ESI$^-$), found: 551.3135 [M – K]$^-$; calcd for $C_{33}H_{39}N_6O_2$: 551.3132. UV/Vis (THF): λ_{max} 393 nm, $\varepsilon = 1.28\times10^4$ M^{-1}cm^{-1}.



6: Benzyl bromide (1.3 mmol, 0.15 mL) was added to a suspension of **3** (1.1 mmol, 505 mg) in toluene (20 mL) and the mixture was stirred for 12 h at room temperature. The solution was then stirred for 6 h at 40 °C and sonicated for 30 min. The resulting white precipitate was isolated by filtration, washed with hexane, and dried under vacuum. Yield: 530 mg (72%). Crystals, suitable for X-Ray analysis, were obtained by layering hexane onto a solution of **6** in THF. Elem. anal. calcd for $C_{40}H_{47}N_4OBr \cdot 1.5\ H_2O$: C 67.42; H 7.25; N 8.06. Found C 67.93; H 6.75; N 7.52. The NMR data indicate the presence of three isomers (**A**, **B** and **C**). According to the crystallographic analysis, the O-alkylation product can adopt a *cis* or a *trans* configuration with respect to the N=N bond. The third isomer is proposed to be an N-alkylation product. The assumption that the three sets of NMR signals belong to isomers is substantiated by the mass spectrum of **6**, which shows a single peak at *m*/*z* = 599 (see Figure S11 on page S16). ^{1}H NMR (400 MHz, CD_3OD, δ): 0.95−1.23 (m, **A**, **B** and **C**, $CH(C\mathit{H}_3)_2$), 2.22−2.51 (m, **A**, **B** and **C**, $CH(C\mathit{H}_3)_2$), 5.44, 5.53, 5.79 (s, **A**, **B** and **C**, $C\mathit{H}_2\text{-}C_6H_5$), 6.97−7.58 (m, **A**, **B** and **C**, $C\mathit{H}_{arom}$), 8.79, 9.03, 9.15 (s, **A**, **B** and **C**, $C\mathit{H}{=}CN_2O$. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, δ): 21.37, 21.61, 23.43, 23.54, 23.74, 23.99, 24.09 ($CH(C\mathit{H}_3)_2$), 29.42, 29.46, 29.55 ($\mathit{C}H(CH_3)_2$), 75.01, 76.43, 77.19 ($\mathit{C}H_2\text{-}C_6H_5$), 115.26, 119.62, 119.92, 120.11, 124.25, 125.08, 125.13, 125.34, 127.46, 128.52, 129.09, 129.38, 129.78, 129.98, 131.12, 132.29, 132.45, 133.27, 133.52, 135.92, 136.70, 144.44, 144.73, 145.33 (C and CH from Ar's). MS (ESI$^+$), found: 599.3750 [M−Br]$^+$; calcd for $C_{40}H_{47}N_4O$: 599.3759.

3. NMR spectra

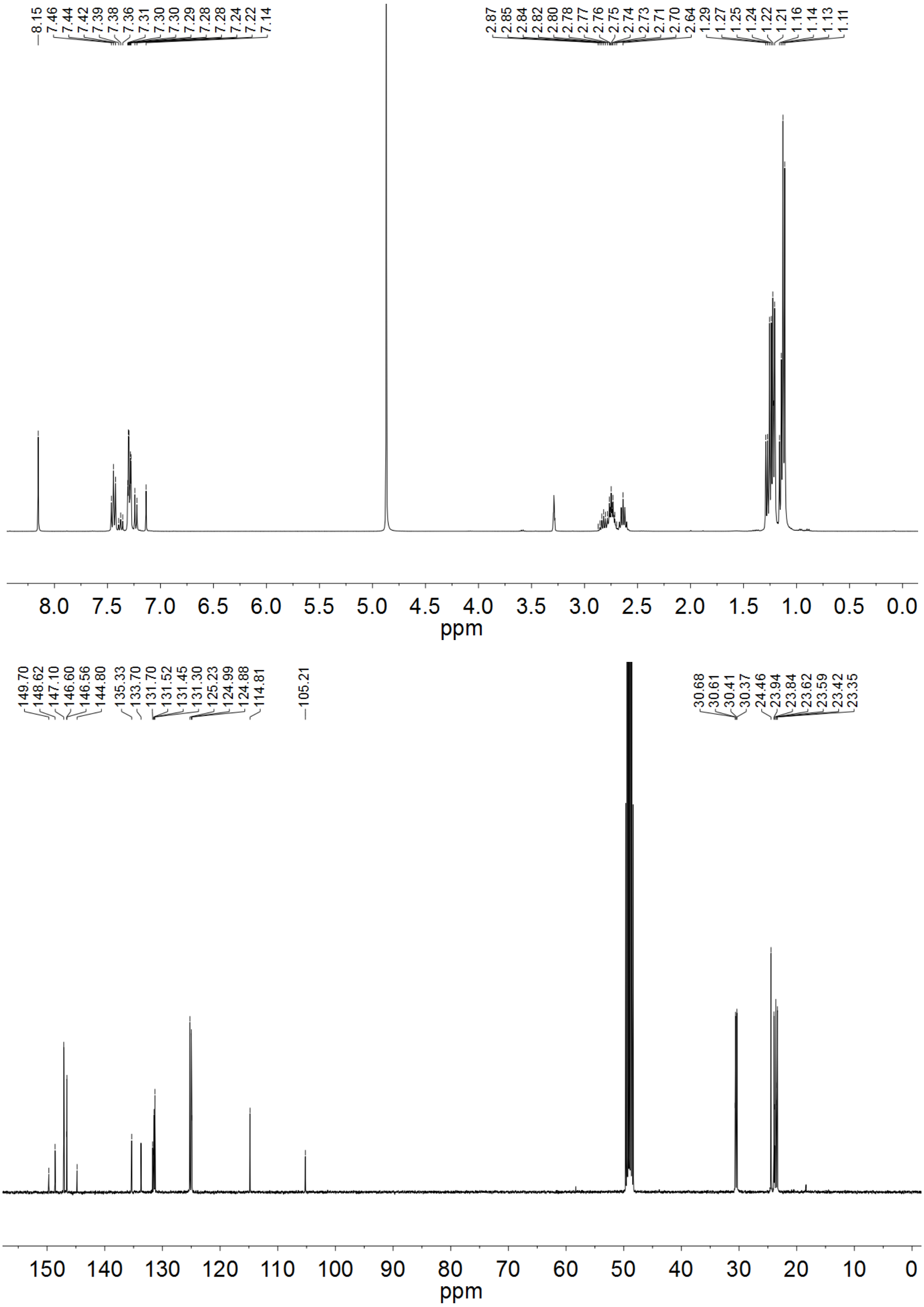


Figure S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1** in CD_3OD.

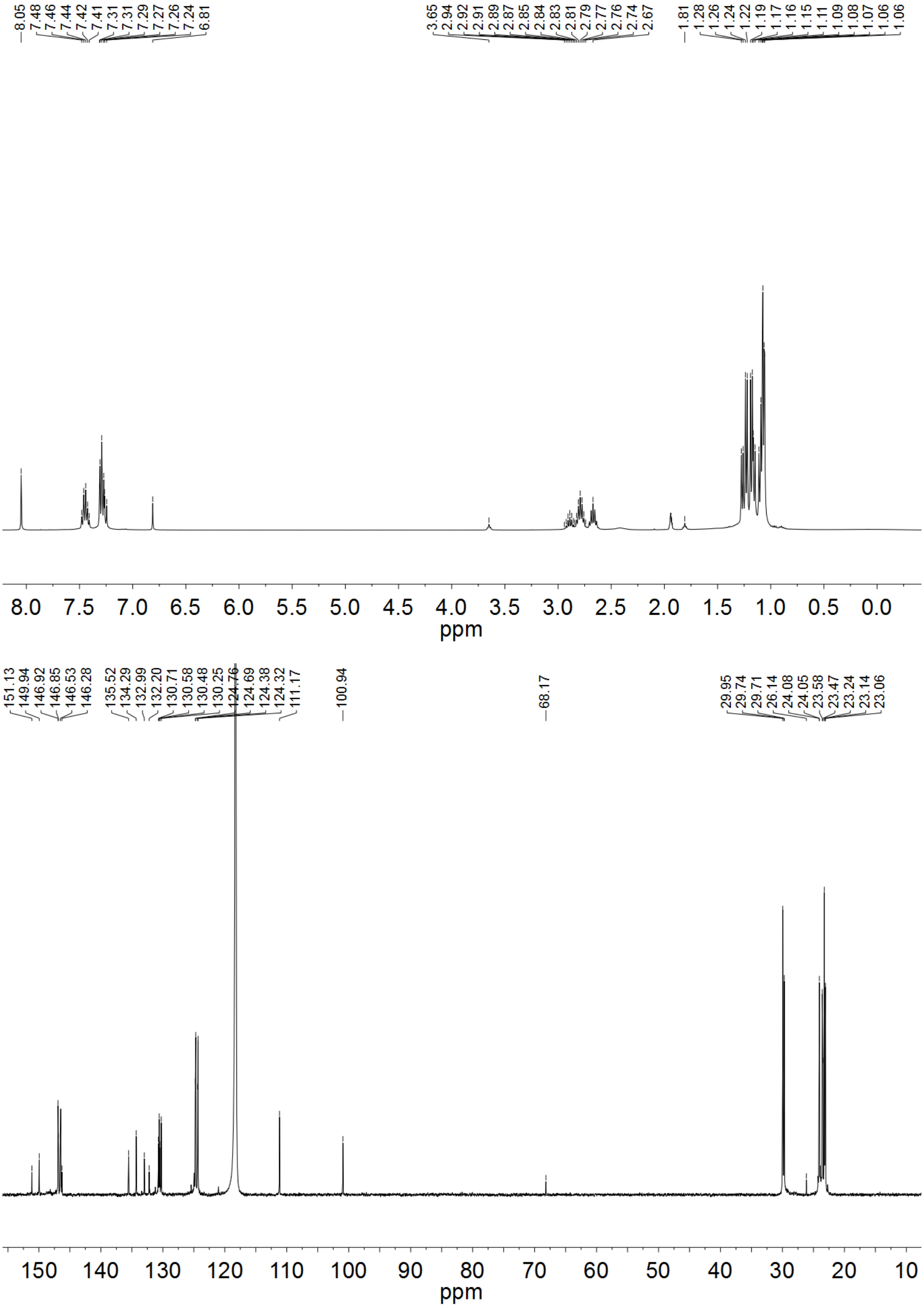


Figure S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2** in CD_3CN.

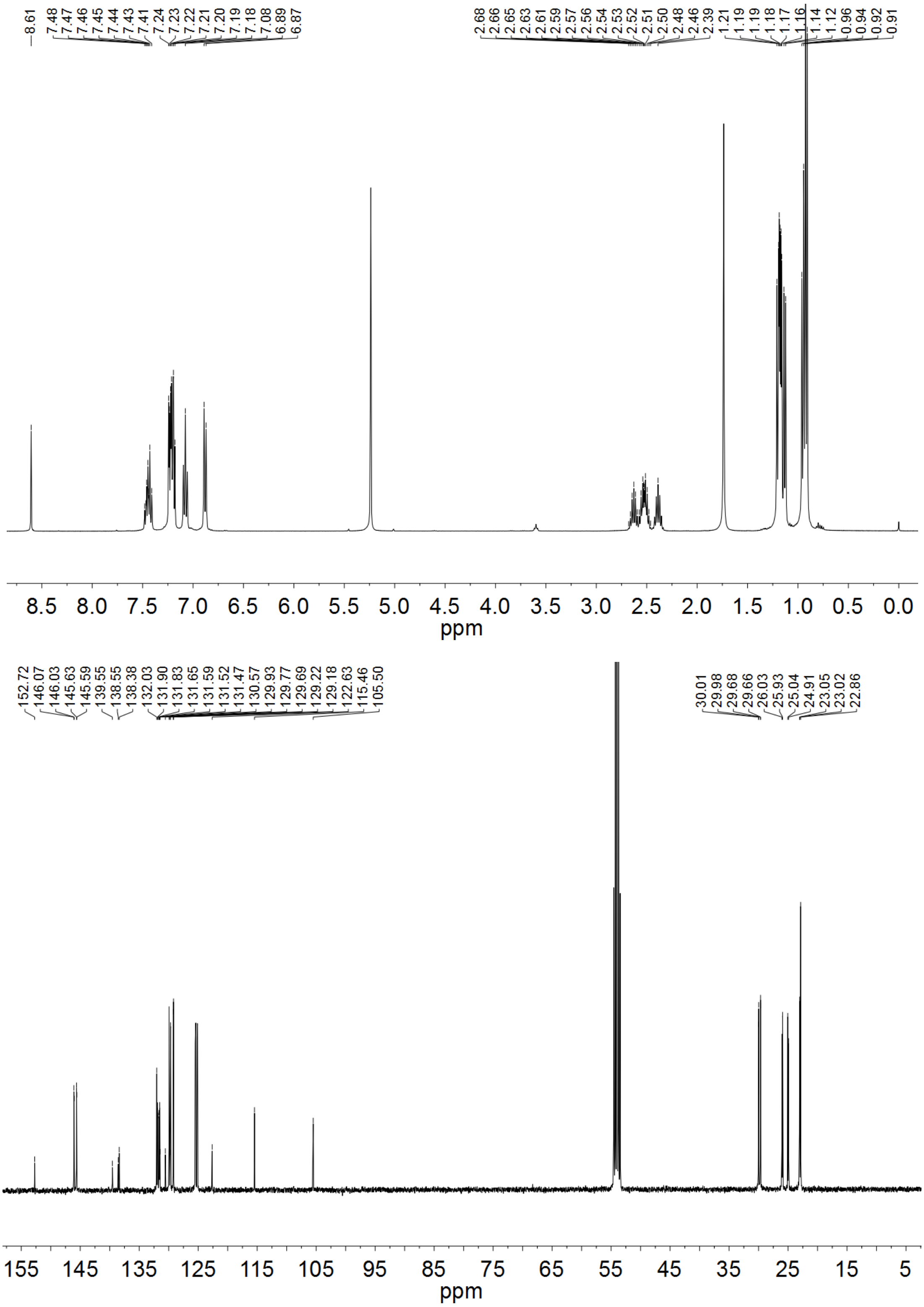


Figure S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3** in CD_2Cl_2.

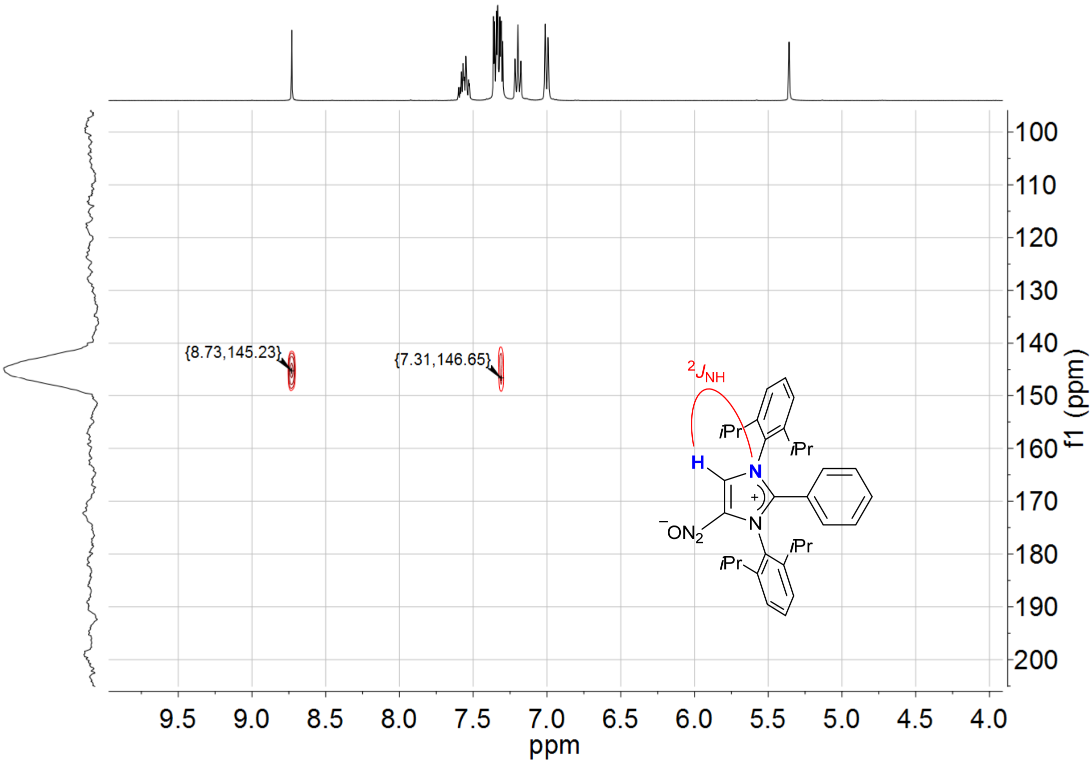


Figure S4 ^{1}H–^{15}N HMBC spectrum of **3** in CD_2Cl_2. The cross peaks at 7.31 ppm and 8.73 ppm are due to $^2J_{NH}$ coupling between the nitrogen of the imidazolium ring and the adjacent CH group. The peak at 7.31 ppm indicates the presence of a second isomer.

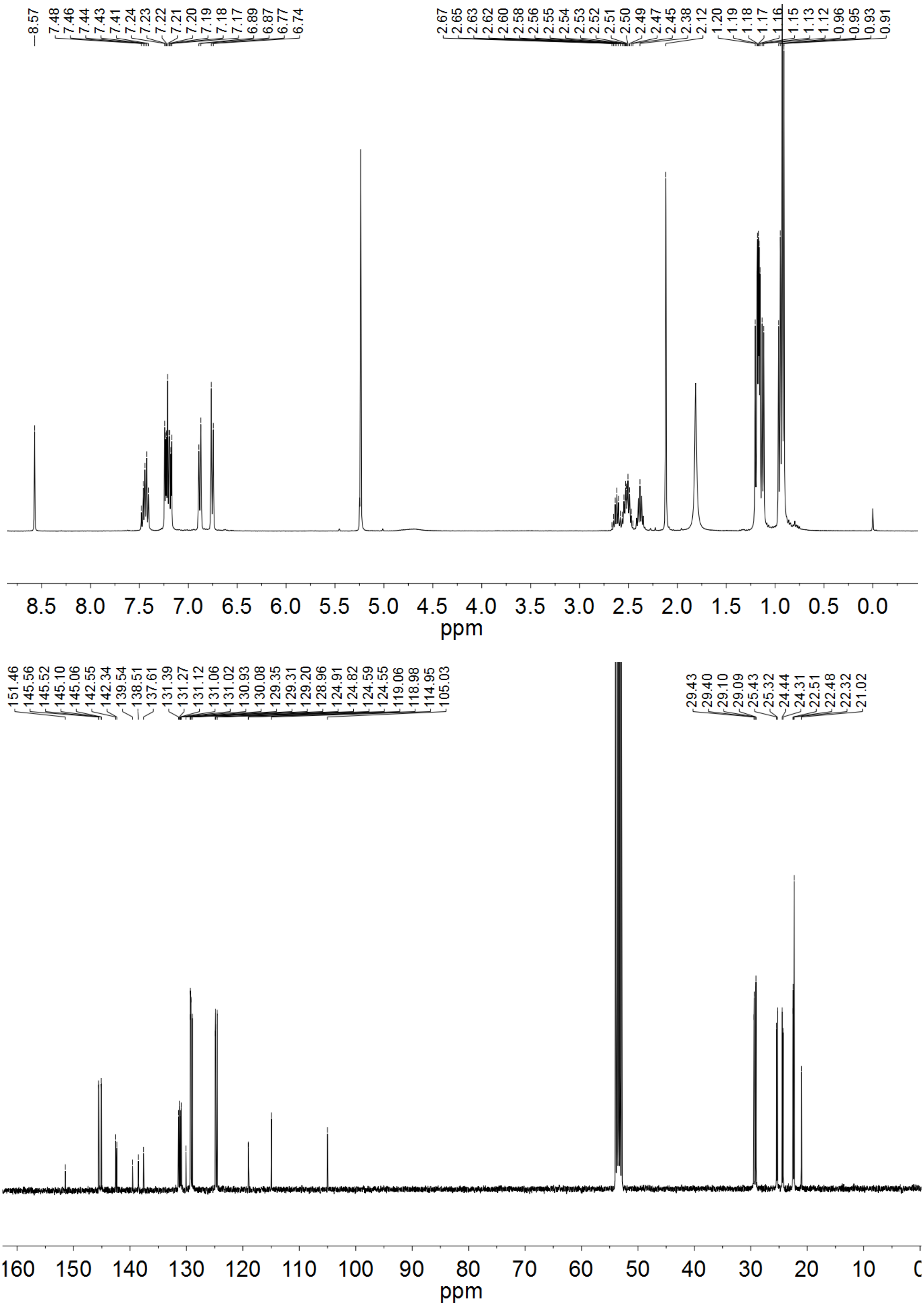
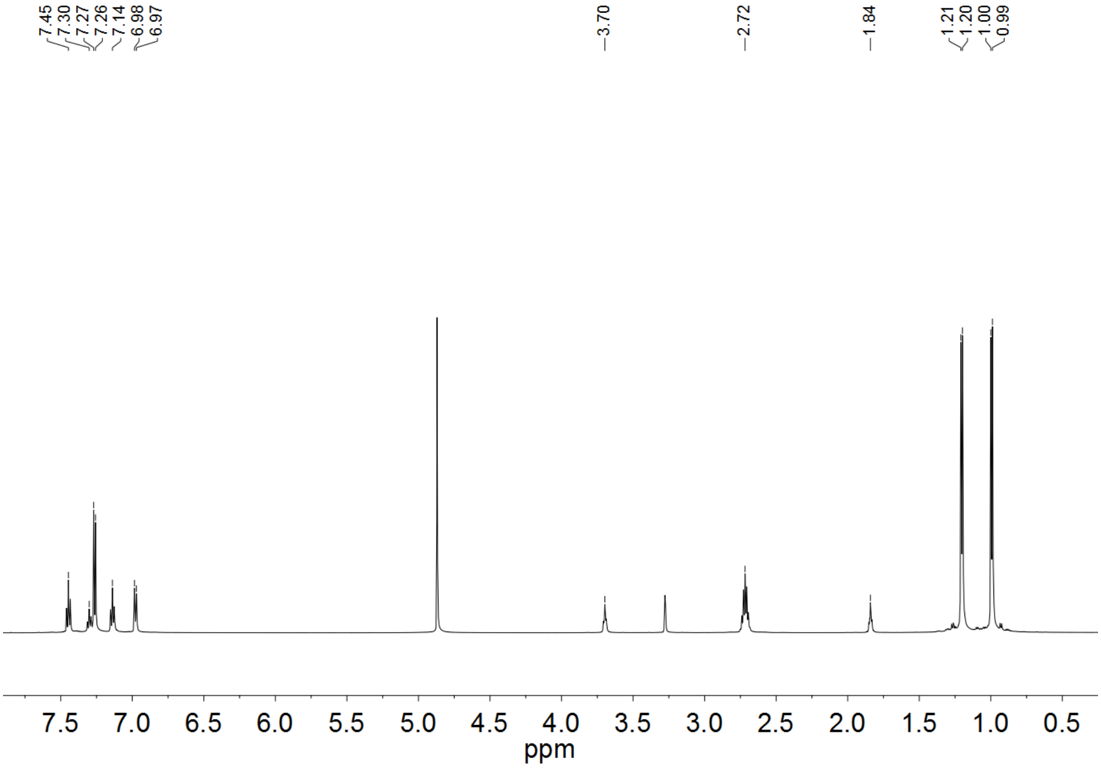


Figure S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4** in CD_2Cl_2.



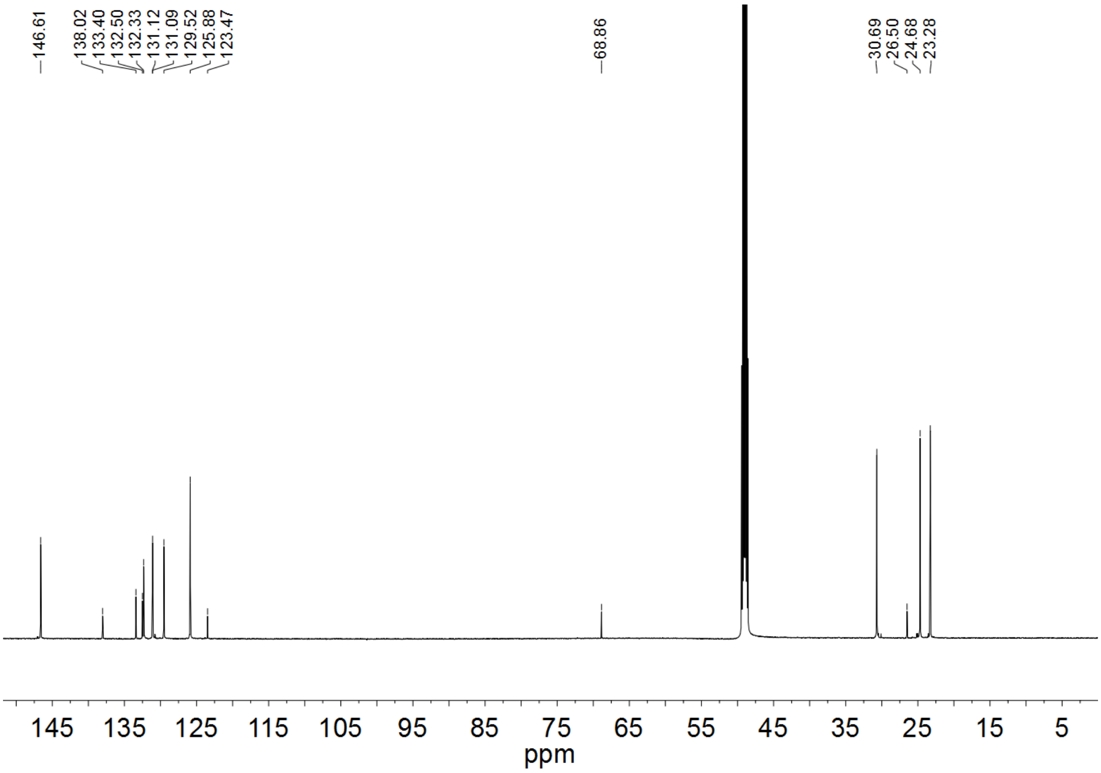


Figure S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **5** in CD_3OD.

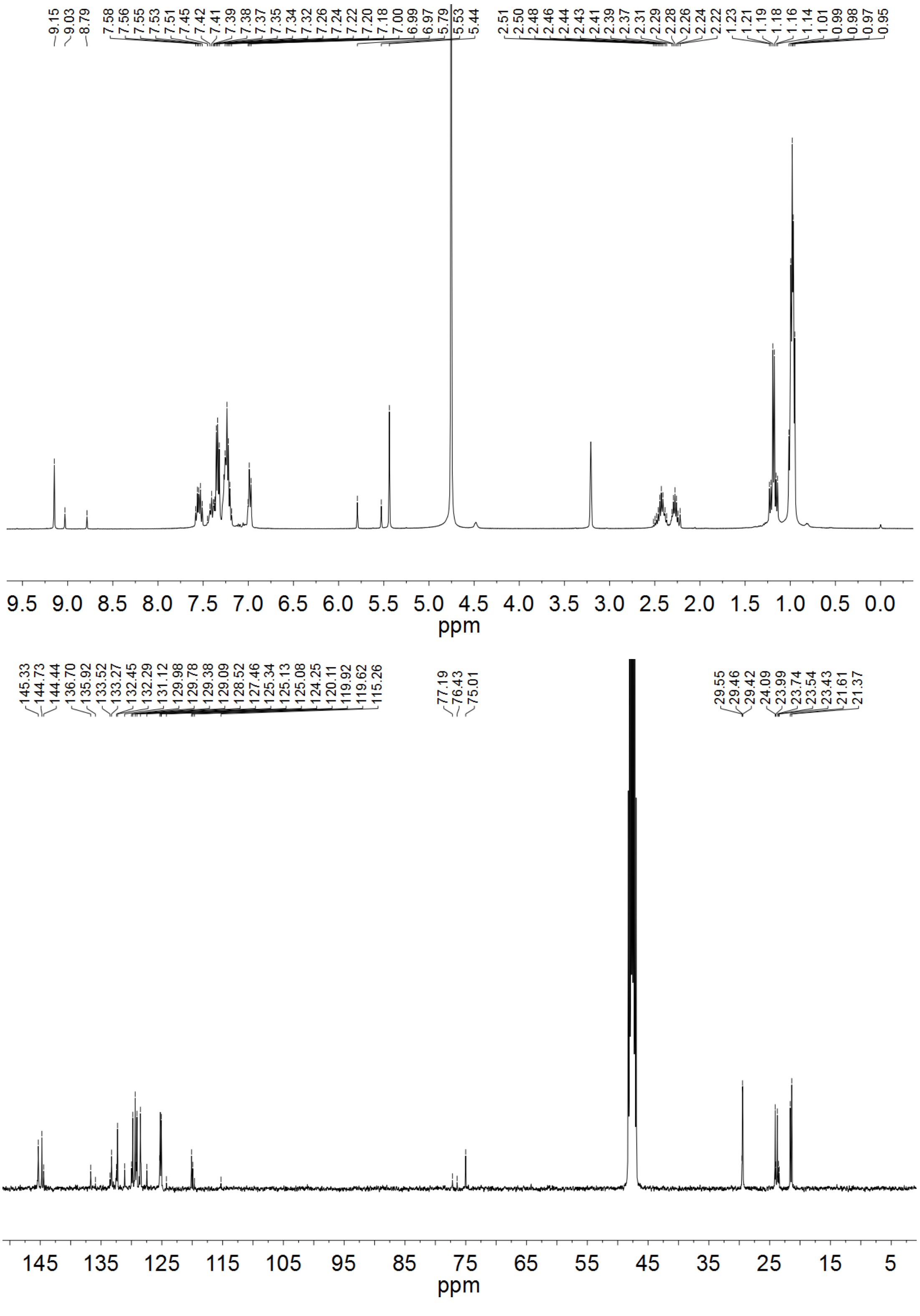


Figure S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **6** in CD_3OD.

4. UV-Vis spectra

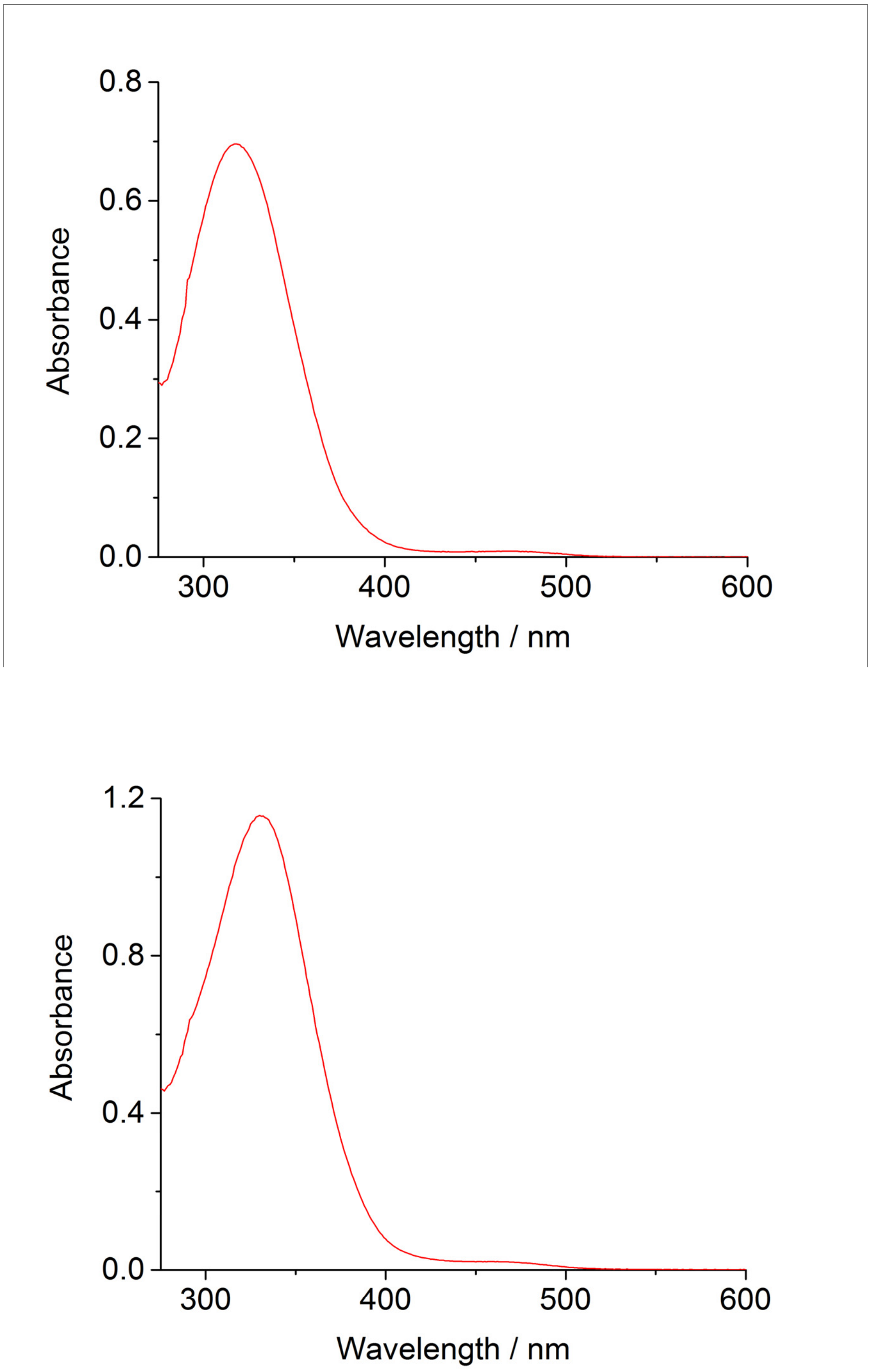
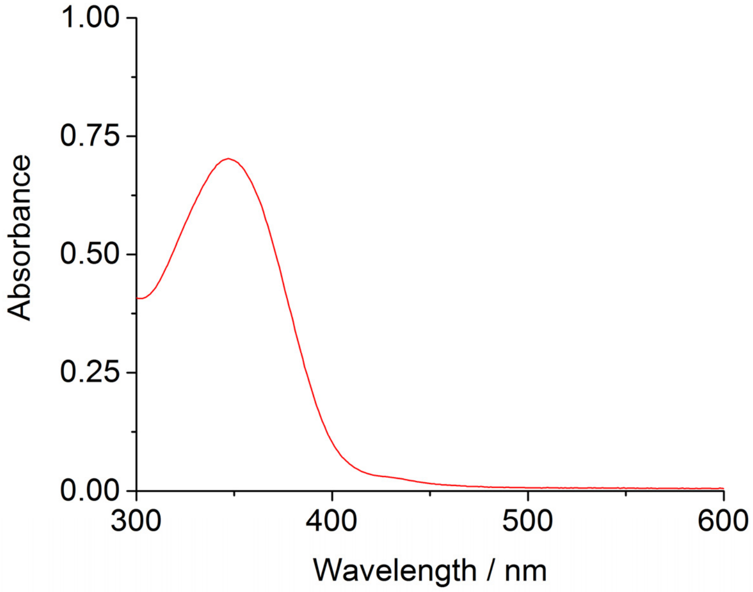


Figure S8 UV-Vis spectra of **1** (top) and **2** (bottom) in THF.



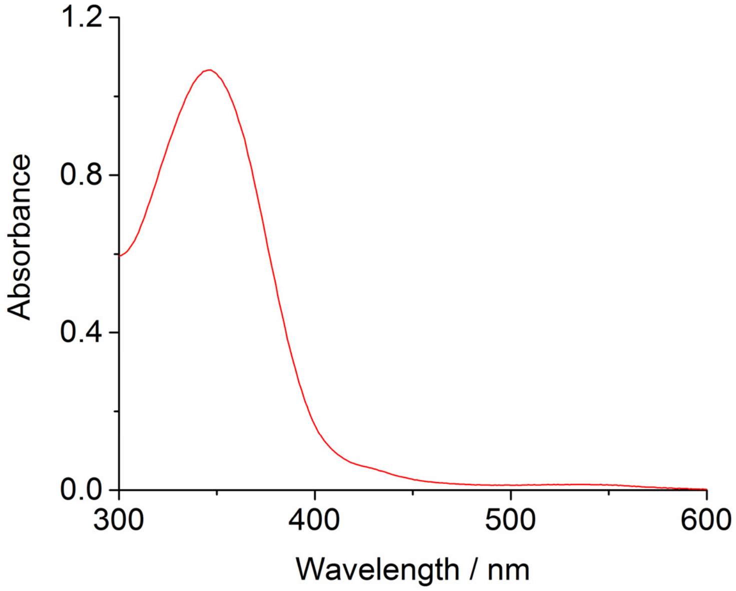


Figure S9 UV-Vis spectra of **3** (top) and **4** (bottom) in THF.

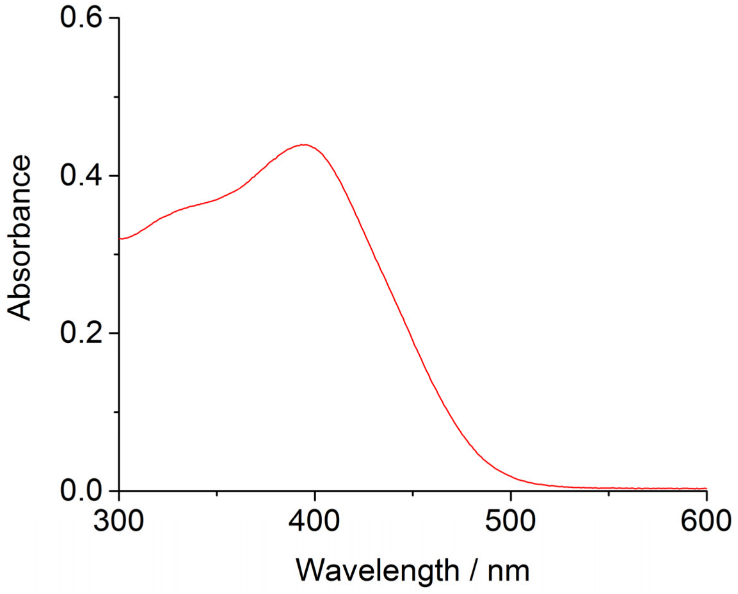


Figure S10 UV-Vis spectrum of **5** in THF.

5. Mass spectrum of 6

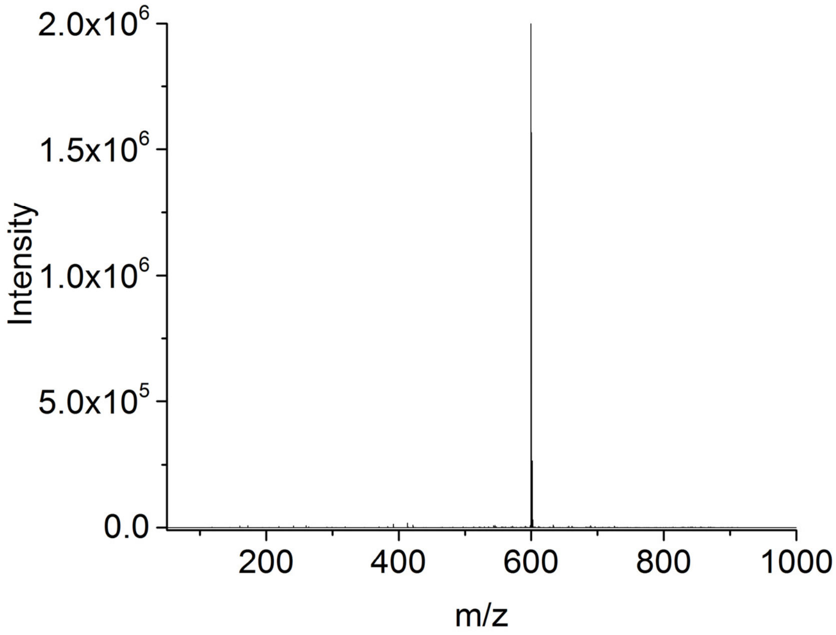


Figure S11 Mass spectrum of **6** in THF.

6. Single crystal X-Ray analyses

Bragg-intensities of **1** were collected at the Swiss-Norwegian Beamline BM01A at the ESRF, Grenoble, France. A wavelength of 0.7129 Å was selected using a Si(111) double crystal monochromator. A combination of curved mirrors and monochromators produced a focused beam at the crystal position. The crystal was maintained at a temperature of 100(2) K using an N_2 Cryostream. The data were collected by means of a Pilatus 2M pixel detector from Dectris Ltd. Cell refinement, data reduction and absorption correction were carried out with the program CrysAlisPro .[4] The solution and refinement for the structure were performed by SHELXT[5] and SHELXL-2016 (release 6),[6] respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions by means of the "riding" model.

Intensity data for **3a**, **3b, 4**, **5** and **6** were measured at low temperature [100.00(10) K, 140.00(10) K, 140.00(10) K, 100.00(10) K and 100.01(10) K], respectively using Cu K_α radiation (1.54184 Å) on a Rigaku SuperNova dual system diffractometer equipped with an Atlas S2 CCD detector. The datasets were reduced and then corrected for absorption with CrysAlisPro.[4] The solutions and refinements for the structures were performed by SHELXT[5] and SHELXL-2016 (release 6),[6] respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions by means of the "riding" model.

In the case of **3b** and **6**, additional electron density found in the difference Fourier map (due to highly disordered solvent), was treated by the SQUEEZE algorithm of PLATON.[7] In the case of **5**, additional electron density found in the difference Fourier map (due to highly disordered solvent), was removed by help of the 'solvent-masking' function in Olex2.[8] The N_2O group is disordered over two positions, partially in the structures of **1**, **4**, **5** and completely in the structure of **6**. The major and minor parts were refined anisotropically, but distance and similarity restraints (DFIX, SADI and SIMU) had to be applied for a convergent least-square refinement.

Crystallographic data have been deposited to the CCDC and correspond to the following codes: **1** (1532912), **3a** (1532913), **3b** (1532914), **4** (1532915), **5** (1532916), **6** (1532917). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk)

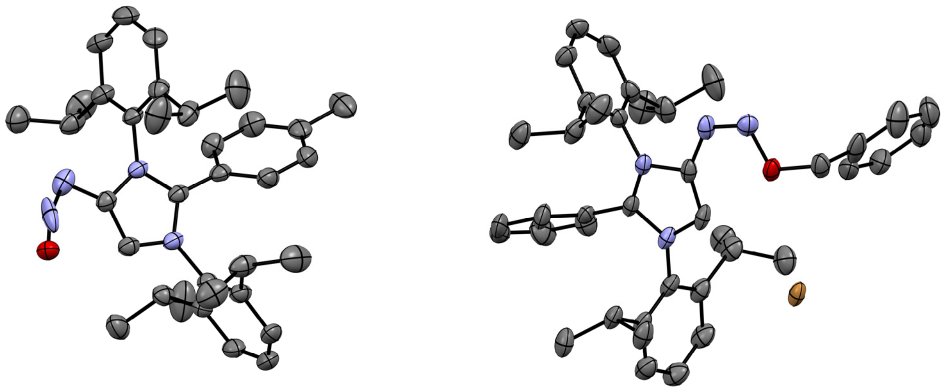


Figure S12 Molecular structures of **4** (left) and **6** (right) in the solid state with ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

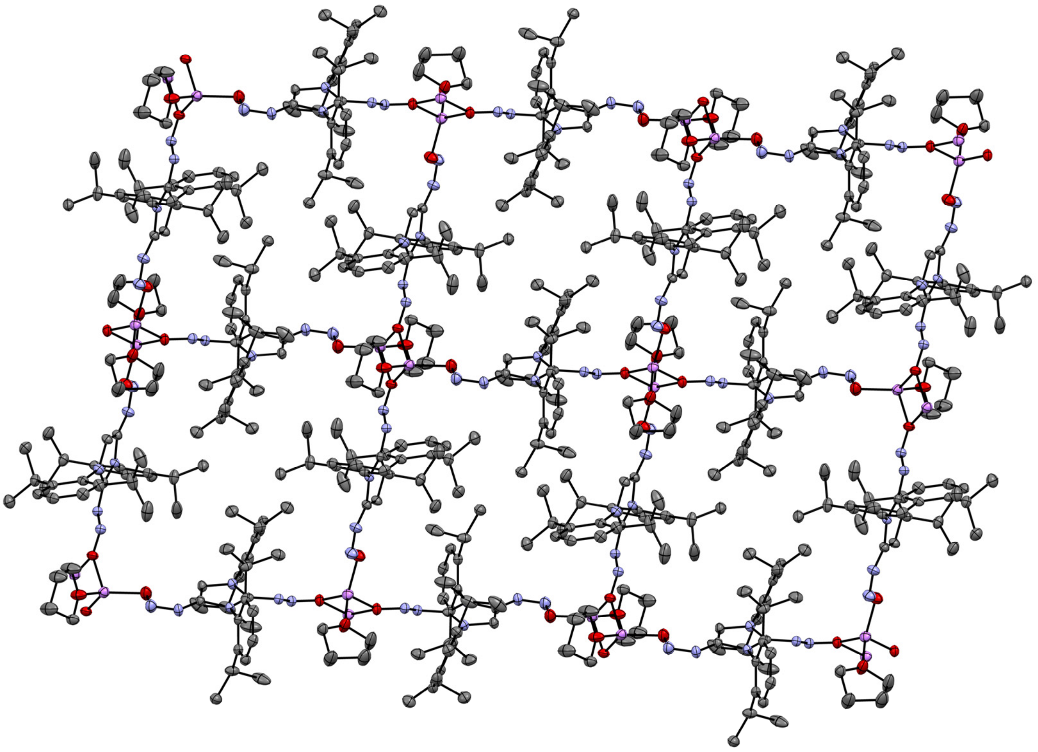


Figure S13 Extended polymeric structure of **1** in the solid state with ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Compound	**1**	**3a**	**3b**
Empirical formula	$C_{35}H_{51}LiN_6O_4$	$C_{35}H_{48}N_4O_3$	$C_{33}H_{40}N_4O$
Mol. Weight / g mol^{-1}	626.75	572.77	508.69
Crystal size / mm^3	0.300 x 0.250 x 0.050	0.496 x 0.298 x 0.059	0.183 x 0.156 x 0.117
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a / Å	15.33916(12)	15.0226(3)	10.63123(15)
b / Å	15.62771(7)	11.73248(17)	15.7365(3)
c / Å	15.99955(12)	19.0842(3)	18.2828(3)
α / °	90	90	90
β / °	112.0396(9)	105.0138(18)	90
γ / °	90	90	90
Volume / Å^3	3555.08(5)	3248.81(10)	3058.68(8)
Z	4	4	4
Density g/cm^{-3}	1.171	1.171	1.105
Temperature / K	100(2) K	100.00(10)	140.00(10)
Absorption Coeff. / mm^{-1}	0.077	0.589	0.522
F(000)	1352	1240	1096
Θ range / °	1.573 to 24.793	4.339 to 76.152	3.706 to 75.954
Index ranges	$-18 \le h \le 18, -18 \le k \le 18, -18 \le l \le 18$	$-13 \le h \le 18, -14 \le k \le 14, -23 \le l \le 23$	$-13 \le h \le 13, -19 \le k \le 15, -21 \le l \le 22$
Reflections collected	131249	22242	6276
Independent reflections	5741 [$R_{(int)}$ = 0.0241]	6696 [$R_{(int)}$ = 0.0347]	6276 [R(int) = 0.0405]
Absorption correction	Semi-empirical from equivalents	Gaussian	Gaussian
Max. & min. transmission	1.00000 and 0.94379	0.973 and 0.841	0.956 and 0.934
Data / restraints / param.	5741 / 19 / 463	6696 / 0 / 391	6276 / 0 / 351
Goodness-of-fit on F^2	1.045	1.045	1.034
Final R indices [I > 2 s (I)]	$R_1 = 0.0445$, $wR_2 = 0.1224$	$R_1 = 0.0508$, $wR_2 = 0.1367$	$R_1 = 0.0404$, $wR_2 = 0.1055$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.1233$	$R_1 = 0.0578$, $wR_2 = 0.1423$	$R_1 = 0.0462$, $wR_2 = 0.1091$
Extinction coefficient	0.0022(5)	n/a	n/a
Larg. diff. peak/hole / eÅ^{-3}	0.577 and -0.278	0.762 and -0.328	0.422 and -0.204

Table S1 Crystallographic data for **1**, **3a** and **3b**.

Compound	**4**	**5**	**6**
Empirical formula	$C_{35}H_{46}N_4O_2$	$C_{78}H_{102}K_2N_{12}O_9$	$C_{40}H_{47}BrN_4O$
Mol. Weight / g mol^{-1}	554.76	1429.91	679.72
Crystal size / mm^3	0.338 x 0.273 x 0.198	0.466 x 0.283 x 0.158	0.654 x 0.498 x 0.347
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/n$	$C2/c$
a / Å	9.56973(17)	16.89427(17)	14.5259(3)
b / Å	16.6800(3)	12.89091(13)	19.9419(3)
c / Å	20.6981(4)	20.8753(2)	29.1694(6)
α / °	90	90	90
β / °	101.3468(19)	109.3465(12)	101.0551(18)
γ / °	90	90	90
Volume / Å^3	3239.32(10)	4289.55(8)	8292.8(3)
Z	4	2	8
Density g/cm^{-3}	1.138	1.110	1.089
Temperature / K	140.00(10) K	100.00(10)	100.01(10)
Absorption Coeff. / mm^{-1}	0.553	1.431	1.584
F(000)	1200	1536	2864
Θ range / °	4.357 to 75.920	2.932 to 76.053	3.087 to 75.948
Index ranges	$-9 \leq h \leq 11, -20 \leq k \leq 14, -24 \leq l \leq 25$	$-21 \leq h \leq 15, -15 \leq k \leq 13, -22 \leq l \leq 26$	$-15 \leq h \leq 18, -23 \leq k \leq 25, -36 \leq l \leq 27$
Reflections collected	12724	30509	29275
Independent reflections	6556 [$R_{(int)}$ = 0.0222]	8828 [$R_{(int)}$ = 0.0271]	8514 [$R_{(int)}$ = 0.0253]
Absorption correction	Gaussian	Gaussian	Gaussian
Max. & min. transmission	0.927 and 0.893	0.833 and 0.659	0.685 and 0.494
Data / restraints / param.	6556 / 69 / 408	8828 / 245 / 537	8514 / 115 / 461
Goodness-of-fit on F^2	1.036	1.029	1.055
Final R indices [I > 2 s (I)]	$R_1 = 0.0579$, $wR_2 = 0.1609$	$R_1 = 0.0886$, $wR_2 = 0.2284$	$R_1 = 0.0405$, $wR_2 = 0.1036$
R indices (all data)	$R_1 = 0.0698$, $wR_2 = 0.1723$	$R_1 = 0.0931$, $wR_2 = 0.2326$	$R_1 = 0.0426$, $wR_2 = 0.1048$
Extinction coefficient	n/a	n/a	n/a
Larg. diff. peak/hole / eÅ^{-3}	0.487 and -0.554	1.522 and -1.725	0.599 and -0.591

Table S2 Crystallographic data for **4**, **5** and **6**.

7. References

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