Supplementary Material (ESI) for Chemical Communications

Supporting information

Advanced supramolecular initiator for nitroxide-mediated polymerization containing both metal-ion coordination and hydrogen-bonding sites

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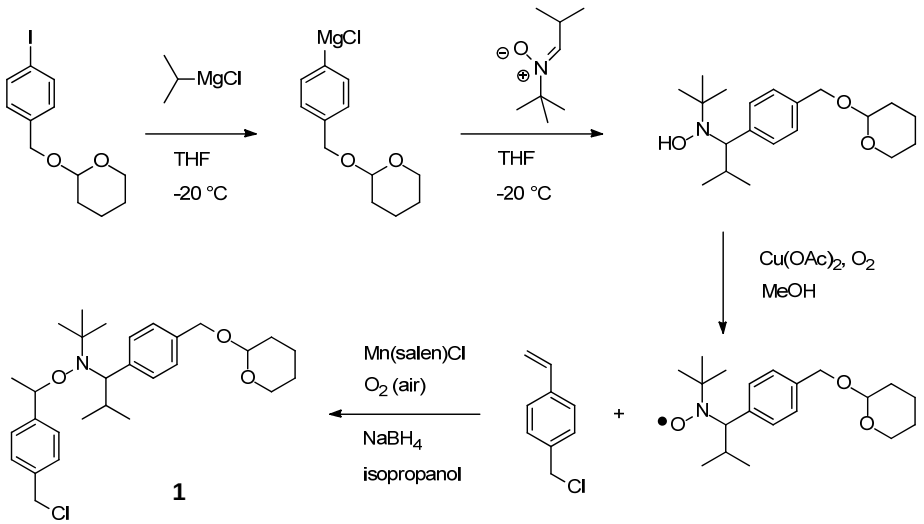
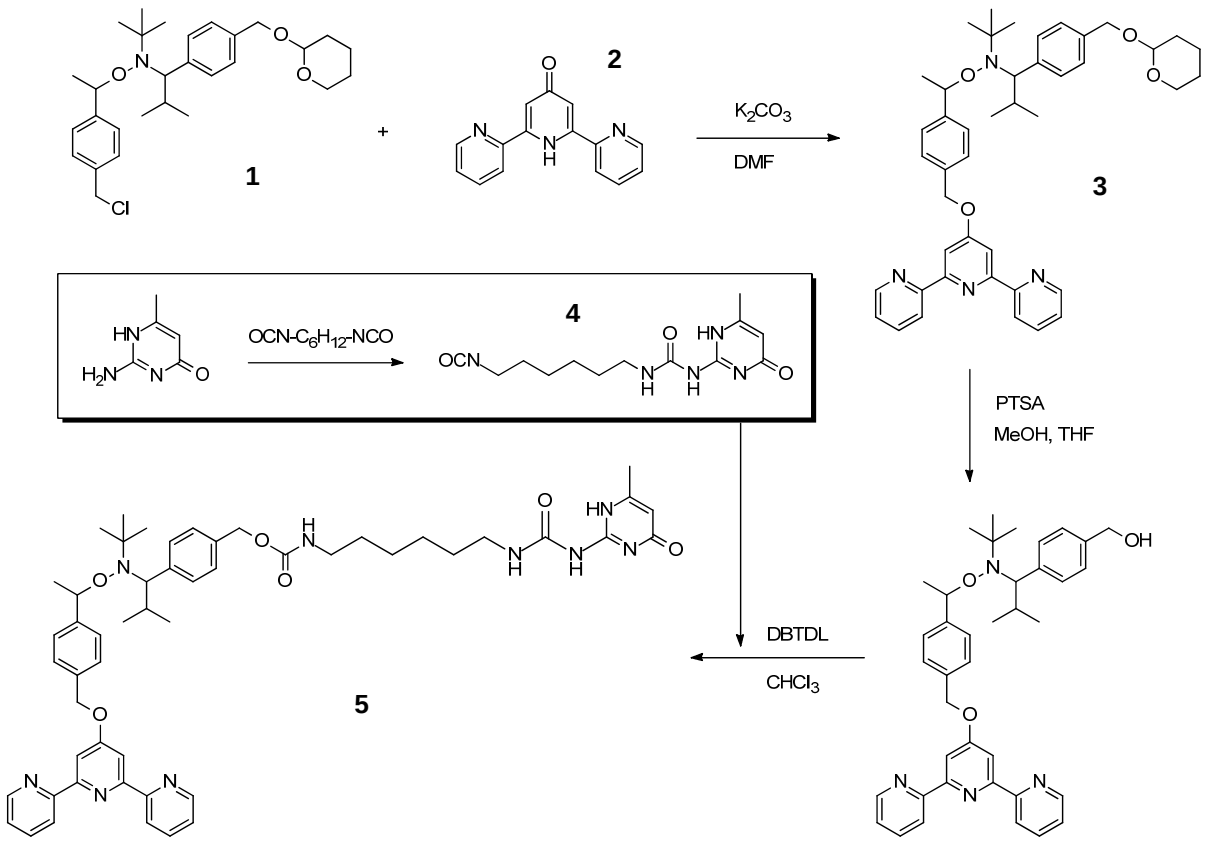
Synthetic strategy

a) Synthesis of the basic framework:



b) Functionalization with supramolecular moieties



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Experimental part

General

Materials

Basic chemicals were received from Aldrich, Fluka and Acros. Solvents were purchased from Biosolve. Unless otherwise stated, the chemicals and solvents were used without further purifications. DMF was dried over molsieves 4A. THF and toluene were dried using a PureSolv-EN^{TM} Solvent Purification System.

Column chromatography was carried out on silica gel 60 and standardized aluminium oxide 90 (Merck). Styrene was freshly purified prior to use by filtration over neutral aluminium oxide 90 (Merck). Deuterated solvents ($CDCl_3$, CD_2Cl_2, THF-d_8) for NMR-spectroscopy were obtained from Cambridge Isotope Laboratories.

Instrumentation

1-D (^1H,^{13}C) and 2-D (^1H-^1H-COSY) nuclear magnetic resonance spectra were recorded on a Varian Mercury 400 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and were calibrated to the residual solvent peaks. 2D (^1H-^1H) DOSY experiments were conducted on a Bruker 400 MHz spectrometer at 298 K.

Two different set-ups for gel permeations chromatography (SEC) have been used: 1) Size exclusion chromatography was performed on a Shimadzu system with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector, an UV-vis detector with 290 nm and 250 nm) and a PSS SDV column utilizing DMA with 2.1 g/L LiCl. Polystyrene was used as the calibration standard. 2) Further size exclusion chromatograms were measured on a Waters SEC system consisting of an isocratic pump, solvent degasser, column oven, photodiode array (PDA) detector, refractive index detector and a Styragel HT 4 SEC column with a precolumn installed. The eluent was *N*,*N*-dimethyl formamide (DMF) containing 0.005 M NH_4PF_6 at a flow speed of 0.5 mL/min. The column temperature was 323 K. GC measurements were performed on an Interscience Trace GC with a Trace Column RTX-5 connected to a PAL autosampler. UV-vis spectra were recorded on a Perkin-Elmer Lamda-45 UV-vis spectro-photometer at room temperature (1 cm cuvettes, chloroform). Elemental analyses were carried out on an EuroVector EuroEA300 elemental analyzer.

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GC-MS measurements were conducted on a Shimadzu GC17A connected to a mass spectrometer. FT-IR spectra were recorded on a Bruker IFS55 FT-IR spectrometer. Matrix-assisted-laser-desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Voyager-DE^{TM} PRO Biospectrometry^{TM} Workstation (Applied Biosystems) time-of-flight mass spectrometer using linear and reflector mode for operation. Dithranol or DCTB were used as matrices and NaI as additive. The spectra were recorded in the positive ion mode and ionization was performed with a 337 nm pulsed nitrogen laser.

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Synthesis of the difunctional initiator

Following compounds were synthesized according to the literature:

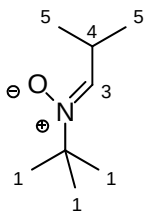
N-tert-Butyl-α-iso-propylnitrone,[1]

4-(tetrahydropyran-2´-yloxymethyl)-iodobenzene,[2]

2,2,5-trimethyl-4-[4´-(tetrahydropyran-2´´-yloxy)methyl]phenyl-3-azahexane-3-nitroxide, "TIPNO-MeO-THP".[2]

Due to more clarity, the structures that are pictured here are related to the ^{1}H-NMR spectra. Hence, only those atoms are labeled bearing hydrogen atoms. The assignment of the ^{13}C-NMR signals relates to the corresponding structures depicted in the spectra part.

***N-tert*-Butyl-α-*iso*-propylnitrone**



A mixture of 2-methyl-2-nitropropane (20.6 g, 0.20 mol), isobutyraldehyde (14.4 g, 0.20 mol) and ammonium chloride (11.8 g, 0.22 mol) are dissolved in water (400 mL) and were cooled in an ice-bath to 5 °C. Subsequently, diethyl ether (200 mL) was added to dissolve the crystallized 2-methyl-2-nitropropane. Zinc powder (52.0 g, 0.80 mol) was added in small portions over 1 h while the reaction mixture was stirred vigorously. The mixture was stirred overnight and allowed to warm to room temperature. Then the solid residues were filtered off and washed three times with methanol (300 mL). Subsequently, the filtrate was extracted with dichloromethane (4 × 50 mL). The combined organic layers were washed with brine (200 mL), dried over magnesium sulfate, and concentrated in vacuum to yield the crude nitrone as a colorless slightly blue, low-melting solid, which crystallized in the fridge.

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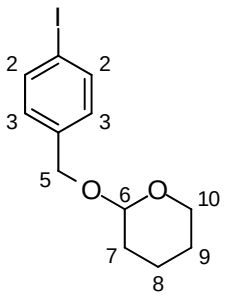
Yield: 12.45 g, 44%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, ^3J = 6.8 Hz, 6H, H^5), 1.45 (s, 9H, H^1), 3.14 (qd, ^3J = 13.8 Hz, ^3J = 6.9 Hz, 1H, H^4), 6.59 (d, ^3J = 7.0 Hz, 1H, H^3) ppm.
^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 18.6 (C^5), 25.9 (C^4), 27.7 (C^1), 68.4 (C^2), 138.5 (C^3) ppm.
GC-MS: *m/z* = 143 ($[M]^+$), 87 ($[MH\text{-}C_4H_9]^+$), 57 ($C_4H_9^+$), 41 ($C_3H_5^+$).

4-(Tetrahydropyran-2´-yloxymethyl)-iodobenzene



4-Iodobenzylalcohol (5.0 g, 21 mmol) and 3,4-dihydro-2*H*-pyran (1.85 g, 22 mmol) were mixed in dichloromethane (30 mL) and 12 drops of concentrated HCl were added. The reaction was monitored by GC-MS and stirred for 12 h. Subsequently, the reaction mixture was washed with water, dried over $MgSO_4$, and concentrated in vacuum to yield the desired protected alcohol as a colorless oil that was purified by column chromatography (AlOx, CH_2Cl_2/small amount of Et_3N).

Yield: 6.6 g, 97%.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.5-1.9 (m, 6H, $H^{7\text{-}9}$), 3.40-3.66 (m, 1H, H^{10}), 3.89 (ddd, ^2J = 11.4 Hz, ^3J = 8.4 Hz, ^3J = 3.1 Hz, 1H, $H^{10'}$), 4.58 (AB, J_{AB} = 12.3 Hz, 2H, H^5), 4.68 (t, ^3J = 3.5 Hz, 1H, H^6), 7.47 (AB_q, $J_{(ortho)}$ = 8.2 Hz, 4H, $H^{2,3}$) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.3 (C^9), 25.4 (C^8), 30.5 (C^7), 62.1 (C^{10}), 68.0 (C^5), 92.9 (C^1), 97.7 (C^6), 129.6 (C^3), 137.3 (C^2), 138.0 (C^4) ppm.
GC-MS: *m/z* = 318 ($[M]^+$), 217 ($[M\text{-}C_5H_9O_2]^+$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$).
Elemental analysis:

$C_{12}H_{15}IO_2$	calcd.:	C	45.30	H	4.75
(M 318.01)	found:	C	45.15	H	4.75

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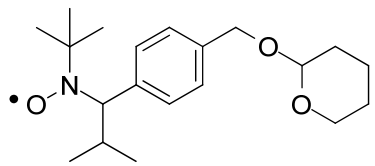
2,2,5-Trimethyl-4-[4´-(tetrahydropyran-2´´-yloxy)methyl]phenyl-3-azahexane-3-nitroxide,

"TIPNO-MeO-THP"



Under an atmosphere of argon, 4-(tetrahydropyran-2´-yloxymethyl)-iodobenzene (5.6 g, 17.6 mmol) was dissolved in dry THF (20 mL) and cooled to –15 °C with an ice/NaCl-bath. Subsequently, isopropyl magnesium chloride in THF (2 M, 9 mL, 18.0 mmol) was added dropwise over 30 min, then the solution was stirred for 2 h at –15 °C. After the addition was complete (monitored by GC-MS), a solution of *N*-*tert*-butyl-α-iso-propylnitrone (2.2 g, 15.4 mmol) in dry THF (20 mL) was added dropwise to the Grignard solution and the stirred mixture was allowed to warm to 10 °C within 12 h. Saturated ammonium chloride solution (4 mL) and water (20 mL) were added to decompose the excess of the Grignard reagent. The reaction mixture was then extracted with diethyl ether (100 mL). The combined organic phases were dried over magnesium sulfate and concentrated in vacuum to yield the crude hydroxylamine as an orange oil (5.8 g).

After the crude hydroxylamine (5.8 g) was dissolved in methanol (25 mL), a solution of $Cu(OAc)_2$ (330 mg, 1.8 mmol) in methanol (30 mL) and aqueous ammonia (25%, 5 mL) was added. The initially clear orange solution changed to deep green after aeration for 1 h. This solution was subsequently concentrated and dissolved in a mixture of chloroform (50 mL) and water (50 mL). The aqueous layer was extracted with chloroform (3 × 20 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (4 × 20 mL), dried over magnesium sulfate, and concentrated in vacuum. A red oil (5.5 g) was obtained that was purified by column chromatography (silica60, CH_2Cl_2/Et_2O, 20/1) to yield the functional nitroxide as an orange oil.

Yield: 3.5 g, 68% (based on the nitrone).

MALDI-TOF MS (dithranol): *m/z* = 334.50 ($[M]^+$), 318 ($[M\text{-}O]^+$).

Elemental analysis:

$C_{20}H_{32}NO_3$•	calcd.:	C	71.82	H	9.64	N	4.19
(M 334.47)	found:	C	71.61	H	9.86	N	4.33

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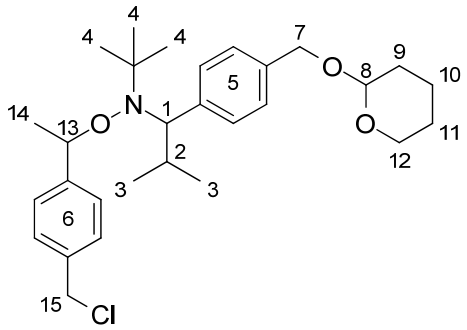
2,2,5-Trimethyl-*N*-((4´-chloromethyl)phenyl)ethoxy-4-(4´´-(tetrahydropyran-2´´´-yloxy)methyl)phenyl-3-azahexane, *"Cl~-TIPNO~THP"* **(1)**



According to general procedures:[2,3]

"TIPNO-MeO-THP" (2.5 g, 7.5 mmol) and 4-vinylbenzyl chloride (1.8 g, 12 mmol) were dissolved in a mixture of isopropyl alcohol (70 mL) and toluene (5 mL) and stirred vigorously. After air was bubbled through the solution for 1 h, (*N,N'-bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato)manganese (III) chloride (Jacobsen's reagent, 1.1 g, 1.8 mmol) and sodium borohydride (0.9 g, 24 mmol) were added in small portions and stirring under aeration was continued for 20 h. The reaction mixture was then filtered with dichloromethane through a layer of silica to remove the solids. The filtrate was concentrated in vacuum and purified by column chromatography (silica 60, dichloromethane) to yield the alkoxyamine **1** as a colorless viscous oil.

Yield: 3.1 g, 80% (mixture of diastereomers).

^{1}H-NMR (400 MHz, CD_2Cl_2, diastereomer a+b): δ = 0.24 (d, ^{3}J = 6.6 Hz, 3H, H^{3}, dst a), 0.55 (d, ^{3}J = 6.6 Hz, 3H, H^{3}, dst b), 0.82 (s, 9H, H^{4}, dst b), 0.96 (d, ^{3}J = 6.3 Hz, 3H, H^{3}, dst a), 1.08 (s, 9H, H^{4}, dst a), 1.30–1.43 (m, 1H, H^{2}, dst a), 1.32 (d, ^{3}J = 6.4 Hz, 3H, H^{3}, dst b), 1.51–1.92 (m, 12H, $H^{9\text{-}11}$, dst a+b), 1.56 (d, ^{3}J = 6.6 Hz, 3H, H^{14}, dst a), 1.64 (d, ^{3}J = 6.6 Hz, 3H, H^{14}, dst b), 2.26–2.43 (m, 1H, H^{2}, dst b), 3.37 (d, ^{3}J = 10.8 Hz, 1H, H^{1}, dst a), 3.47 (d, ^{3}J = 10.6 Hz, 1H, H^{1}, dst b), 3.49–3.58 (m+m, 2H, H^{12}, dst a+b), 3.87–3.96 (m+m, 2H, H^{12}, dst a+b), 4.57 (AB, J_{AB} = 11.6 Hz, 2H, H^{7}, dst a), 4.63 (AB, J_{AB} = 11.8 Hz, 2H, H^{7}, dst b), 4.61 (s, 2H, H^{15}, dst b), 4.65 (s, 2H, H^{15}, dst a), 4.70 (t, ^{3}J = 3.7 Hz, 1H, H^{8}, dst b), 4.74 (t, 1H, H^{8}, dst a), 4.95 (q, ^{3}J = 6.6 Hz, 1H, H^{13}, dst a/b), 4.96 (q, ^{3}J = 6.6 Hz, 1H, H^{13}, dst a/b), 7.17–7.49 (m+m, 16H, $H^{5,6}$, dst a+b) ppm.

^{13}C-NMR (100 MHz, CD_2Cl_2, diastereomer a+b): δ = 19.4, 20.7, 20.8, 21.6, 21.8, 22.7, 24.4, 25.6, 28.0, 28.2, 29.1, 30.6, 30.6, 30.9, 31.7, 32.0, 46.3, 60.4, 60.5, 61.9, 62.0, 68.8, 71.6, 71.7, 82.2, 83.2,

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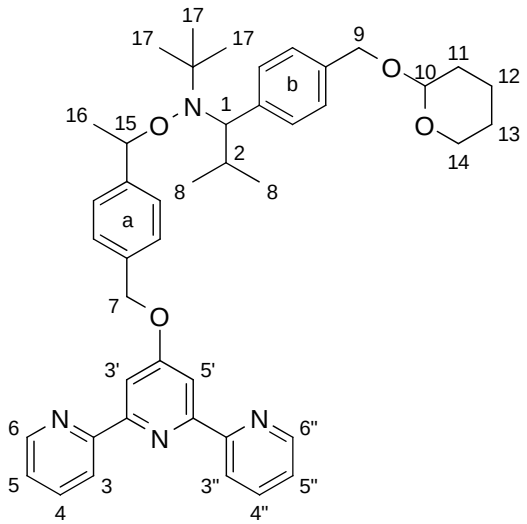
98.0, 98.1, 126.5, 126.6, 126.8, 127.4, 128.4, 128.4, 130.9, 135.9, 136.4, 136.6, 136.7, 141.4, 141.6, 145.2, 146.1 ppm.

Elemental analysis:

$C_{29}H_{42}ClNO_3$ calcd.:	C	71.36	H	8.67	N	2.87
(M 488.10) found:	C	71.53	H	8.56	N	3.13

2,2,5-Trimethyl-*N*-((4´-({*2,2':6',2"*}-terpyridin-*{4'}*-yloxy)methyl)phenyl)ethoxy-4-(4´´-(tetrahydropyran-2´´´-yloxy)methyl)phenyl-3-azahexane, *"tpy~TIPNO~THP"* **(3)**



According to the procedure by Lohmeijer *et al*.:[4]

Anhydrous K_2CO_3 (3.52 g, 25.47 mmol) was added to a solution of 2,6-*bis*-(2'-pyridyl)-4-pyridon[5] (**2**) (1.64 g, 6.58 mmol) in dry DMF (30 mL). After the suspension was heated up to 50 °C, a solution of *"Cl~TIPNO~THP"* **1** (2.30 g, 4.71 mmol) in dry DMF (20 mL) was added dropwise and stirring was continued overnight at 60 °C under an argon atmosphere. The reaction mixture was cooled down, poured into cold water (300 mL) and extracted three times with CH_2Cl_2 (250 mL). The combined organic layers were subsequently washed twice with water to remove residual DMF, dried over Na_2SO_4, filtered and concentrated in vacuum. The crude product (slightly brown viscous oil) was subjected to a filtration column (AlOx, CH_2Cl_2: hexane, 2:1, small amount of Et_3N) to yield **3** as a colorless amorphous solid.

Yield: 2.04 g, 62% (mixture of diastereomers).

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^{1}H-NMR (400 MHz, CD_2Cl_2, diastereomers a+b): δ = 0.18 (d, ^{3}J = 6.6 Hz, 3H, H^{8}, dst a), 0.56 (d, ^{3}J = 6.6 Hz, 3H, H^{8}, dst b), 0.82 (s, 9H, H^{17}, dst b), 0.94 (d, ^{3}J = 6.3 Hz, 3H, H^{8}, dst a), 1.08 (s, 9H, H^{17}, dst a), 1.33 (d, ^{3}J = 6.4 Hz, 3H, H^{8}, dst b), 1.35-1.46 (m, 1H, H^{2}, dst a), 1.49-1.93 (m, 12H, $H^{11,12,13}$, dst a+b), 1.58 (d, ^{3}J = 6.6 Hz, 3H, H^{16}, dst a), 1.66 (d, ^{3}J = 6.6 Hz, 3H, H^{16}, dst b), 2.26-2.46 (m, 1H, H^{2}, dst b), 3.35 (d, ^{3}J = 10.8 Hz, 1H, H^{1}, dst a), 3.48 (d, ^{3}J = 10.8 Hz, 1H, H^{1}, dst b), 3.48-3.57 (m, 2H, H^{14}, dst a+b), 3.85-3.97 (m, 2H, H^{14}, dst a+b), 4.56 (AB_q, J_{AB} = 11.8 Hz, 2H, H^{9}, dst a), 4.63 (AB_q, J_{AB} = 11.8 Hz, 2H, H^{9}, dst b), 4.71 (m, 2H, H^{10}, dst a+b), 4.98 (q, ^{3}J = 6.6 Hz, 2H, H^{15}, dst a+b), 5.32 (s, 2H, H^{7}, dst b), 5.37 (s, 2H, H^{7}, dst a), 7.11-7.58 (m, 16H, $H^{a,b}$, dst a+b), 7.36 (m, 4H, $H^{5,5''}$, dst a+b), 7.88 (dt+dt, ^{3}J = 7.8 Hz, ^{4}J = 1.85 Hz, 4H, $H^{4,4''}$, dst a+b), 8.14 (s, 2H, $H^{3',5'}$, dst b), 8.16 (s, 2H, $H^{3',5'}$, dst a), 8.64 (d, ^{3}J = 8.0 Hz, 4H, $H^{3,3''}$, dst(a+b)), 8.69 (m, 4H, $H^{6,6''}$, dst(a+b)) ppm.

^{13}C-NMR (100 MHz, CD_2Cl_2, diastereomers a+b): δ = 19.4, 20.6, 20.8, 21.6, 21.8, 22.7, 24.4, 25.6 (C^{8}), 28.0 (C^{17}), 28.2 (C^{17}), 30.6 (C^{8}), 31.7, 32.0, 60.4, 60.5, 61.9, 68.8, 69.9 (C^{7}), 71.6, 82.4, 83.2, 98.0 (C^{14}), 98.1 (C^{14}), 107.4 ($C^{3',5'}$), 121.0 ($C^{3,3''}$), 123.8 ($C^{5,5''}$), 126.5, 126.6, 126.8, 127.4, 127.5, 130.9, 134.5, 135.3, 136.4, 136.6, 136.7 ($C^{4,4''}$), 141.4, 141.6, 144.9, 145.8, 149.0 ($C^{6,6''}$), 155.9 ($C^{2,2''}$), 157.2 ($C^{2',6'}$), 166.9 ($C^{4'}$) ppm.

MALDI-TOF-MS (dithranol): *m/z* = 701.43 ($[M+H]^+$), 616.34 ($[MH-C_5H_{10}O]^+$), 599.35 ($[MH-C_5H_{10}O_2]^+$), 367.22 ($[C_{24}H_{20}N_3O+H]^+$), 732.37 ($[C_{48}H_{40}N_6O_2]^+$).

Elemental analysis:

$C_{44}H_{52}N_4O_4$	calcd.:	C	75.40	H	7.48	N	7.99
(M 700.91)	found:	C	75.39	H	7.56	N	8.39

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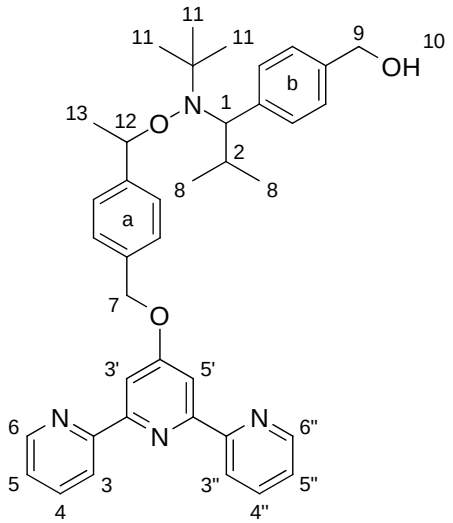
2,2,5-Trimethyl-*N*-((4´-({*2,2':6',2"*}-terpyridin-{*4'*}-yloxy)methyl)phenyl)ethoxy-4-(4´´-hydroxymethyl)phenyl-3-azahexane, *"tpy~TIPNO~OH"*



In accordance to the procedure of Rodlert *et al.*:[2]

"tpy~TIPNO~THP" **3** (2.03 g, 2.90 mmol) was dissolved in a mixture of THF (100 mL) and methanol (100 mL). *Para* toluene sulfonic acid monohydrate (2.00 g, 10.50 mmol) was diluted in THF (20 mL), added dropwise to the clear solution and stirring was continued for 18 h at room temperature. Triethylamine (1.2 g) was added to neutralize the acid and the solution was concentrated. After dissolving in water (20 mL) and dichloromethane (50 mL) the organic phase was washed three times with water, dried over Na_2SO_4 and concentrated in vacuum. The obtained viscous oil was purified by a filtration column (AlOx, CH_2Cl_2), later a gradient of CH_2Cl_2 to diethyl ether and finally acetone was used. Subsequently, the combined fractions were dried over Na_2SO_4 and concentrated in vacuum to yield "tpy~TIPNO~OH" as a white amorphous solid.

Yield: 1.42 g, 70% (mixture of diastereomers).

^{1}H-NMR (400 MHz, CD_2Cl_2, diastereomers a+b): δ = 0.18 (d, ^3J = 6.6 Hz, 3H, H^8, dst a), 0.55 (d, ^3J = 6.6 Hz, 3H, H^8, dst b), 0.81 (s, 9H, H^{11}, dst b), 0.95 (d, ^3J = 6.3 Hz, 3H, H^8, dst a), 1.07 (s, 9H, H^{11}, dst a), 1.33 (d, ^3J = 6.4 Hz, 3H, H^8, dst b), 1.37-1.51 (m, 1H, H^2, dst a), 1.57 (d, ^3J = 6.6 Hz, 3H, H^{13}, dst a), 1.66 (d, ^3J = 6.6 Hz, 3H, H^{13}, dst b), 1.82-1.94 (q+q, 2H, H^{10}, dst a+b), 2.30-2.41 (m, 1H, H^2, dst b),

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3.36 (d, ^{3}J = 10.8 Hz, 1H, H^{1}, dst a), 3.47 (d, ^{3}J = 11.2 Hz, 1H, H^{1}, dst b), 4.61 (d, ^{3}J = 5.6 Hz, 2H, H^{9}, dst a), 4.68 (d, ^{3}J = 5.6 Hz, 2H, H^{9}, dst b), 4.98 (q, ^{3}J = 6.4 Hz, 1H, H^{12}, dst a/b), 4.98 (q, ^{3}J = 6.6 Hz, 1H, H^{12}, dst a/b), 5.32 (s, 2H, H^{7}, dst b), 5.37 (s, 2H, H^{7}, dst a), 7.07-7.59 (m, 16H, $H^{a,b}$, dst a+b), 7.32-7.41 (m, 4H, $H^{5,5''}$, dst a+b), 7.88 (dt+dt, ^{3}J = 7.9 Hz, ^{4}J = 1.8 Hz, 4H, $H^{4,4''}$, dst a+b), 8.14 (s, 2H, $H^{3',5'}$, dst b), 8.16 (s, 2H, $H^{3',5'}$, dst a), 8.62-8.66 (m, 4H, $H^{3,3''}$, dst a+b), 8.68 (dd+dd, ^{3}J = 4.8 Hz, ^{4}J = 1.8 Hz, 4H, $H^{6,6''}$, dst a+b) ppm.

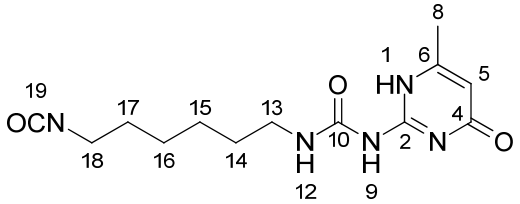
^{13}C-NMR (100 MHz, CD_2Cl_2, diastereomers a+b): δ = 20.6, 20.8, 21.6, 21.8, 22.7, 24.3 (C^{8}), 28.0 (C^{11}), 28.2 (C^{11}), 31.8, 32.0 (C^{8}), 60.4, 60.4, 64.9 (C^{9}), 70.0, 71.7, 82.3, 83.2, 107.4 ($C^{3',5'}$), 107.5 ($C^{3',5'}$), 121.1 ($C^{3,3''}$), 123.9 ($C^{5,5''}$), 125.8, 126.0, 126.5, 127.3, 127.4, 127.5, 131.1, 134.6, 135.3, 136.7 ($C^{4,4''}$), 139.2, 139.4, 141.4, 141.6, 144.9, 145.8, 149.0 ($C^{6,6''}$), 155.9 ($C^{2,2''}$), 157.2 ($C^{2',6'}$), 167.0 ($C^{4'}$) ppm.

MALDI-TOF-MS (dithranol): *m/z* = 617.27 ($[M+H]^+$), 592.19 ($[C_{24}H_{20}N_3O$+dithranol+$H]^+$), 367.22 ($[C_{24}H_{20}N_3O+H]^+$), 732.37 ($[C_{48}H_{40}N_6O_2+H]^+$).

Elemental analysis:

$C_{39}H_{44}N_4O_3$	calcd.:	C	75.94	H	7.19	N	9.08
(M 616.34)	found:	C	76.08	H	7.24	N	8.99

2-(6´-Isocyanato)hexylaminocarbonylamino-6-methyl-4-[1*H*]pyrimidinone, "*OCN-hexyl-UPy"* **(4)**



In accordance to the procedure of Folmer *et al.*:[6]

A suspension of 2-amino-4-hydroxy-6-methylpyrimidine (5.00 g, 40 mmol) in hexamethylene diisocyanate (45.62 g, 0.27 mol) was heated under an argon atmosphere at 95 °C for 18 h. Hexane was subsequently added and the precipitate was filtered, washed with hexane and dried at 50 °C in vacuum to yield **4** as a white powder.

Yield: 11 g, 94%.

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^{1}H-NMR (400 MHz, $CDCl_3$, 50 °C): δ = 1.41 (m, 4H, $H^{15,16}$), 1.61 (m, 4H, $H^{14,17}$), 2.21 (s 3H, H^{8}), 3.27 (m, 4H, H^{8}), 5.79 (s, 1H, H^{5}), 10.10 (s, 1H, H^{12}), 11.82 (s, 1H, H^{9}), 13.07 (s, 1H, H^{1}) ppm.

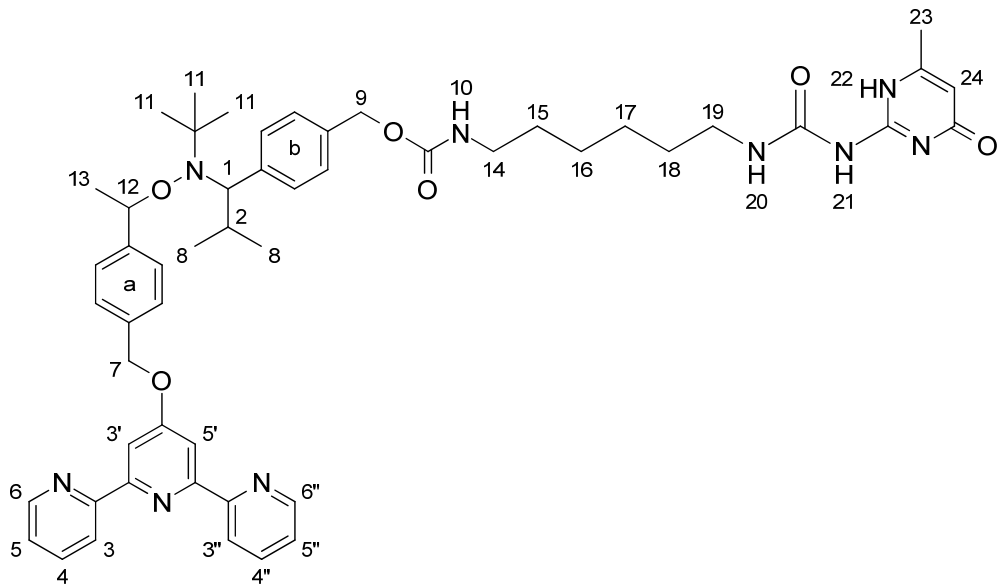
^{13}C-NMR (100 MHz, $CDCl_3$, 50 °C): δ = 18.8, 26.1, 26.2, 29.2, 31.2, 39.7, 42.8, 106.6 (C^{5}), 148.1, 154.7, 156.6, 172.9 ppm.

FT-IR: ν = 3712- 3599 (N-H), 3261 (N-H..N/ N-H..O), 3219 (N-H..N/ N-H..O), 3037 (C-H), 2939 (C-H), 2856 (C-H), 2268 (NCO), 1666 (C=O), 1697 (C=O), 1256 (C-N) cm^{-1}.

Elemental analysis:

$C_{13}H_{19}N_5O_3$	calcd.:	C	53.38	H	6.45	N	24.04
(M 293.15)	found:	C	53.23	H	6.53	N	23.88

2,2,5-Trimethyl-*N*-((4´-({*2,2':6',2"*}-terpyridin-*{4'}*-yloxy)methyl)phenyl)ethoxy-4-{4´´-([(6´´´-(6´´´´-methyl-[1*H*]pyrimidin-4´´´´-on-2´´´´-yl)ureido)hexyl] carbamoyl)oxymethyl}phenyl-3-azahexane, *"tpy~TIPNO~UPy"* **(5)**



According to known procedures:[6,7]

4 (440 mg, 1.48 mmol) was added to a solution of "tpy~TIPNO~OH" (730 mg, 1.18 mmol) in chloroform (30 mL) and the resulting suspension was heated to 65 °C under an argon atmosphere. Then dibutyltin dilaurate (DBTDL, 30 mg) was added in small portions and stirring was continued for 18 h. After filtration (urea derivates) the clear solution was concentrated to 2 mL and diethyl ether (400 mL) was added slowly. After storing the cloudy solution in a freezer overnight, a white

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precipitate was formed that was filtered and dried to yield **5** as a white solid. The solid was dissolved in dichloromethane under moderate heating, the solid residue was removed by filtration and the solvent was evaporated in vacuum. This process was repeated until all solids were soluble in dichloromethane.

Yield: 622 mg, 58% (mixture of diastereomers).

^{1}H-NMR (400 MHz, CD_2Cl_2, diastereomers a+b): δ = 0.17 (d, ^{3}J = 6.6 Hz, 3H, H^{8}, dst a), 0.54 (d, ^{3}J = 6.6 Hz, 3H, H^{8}, dst b), 0.81 (s, 9H, H^{11}, dst b), 0.93 (d, ^{3}J = 6.3 Hz, 3H, H^{8}, dst a), 1.06 (s, 9H, H^{11}, dst a), 1.32 (d, ^{3}J = 6.3 Hz, 3H, H^{8}, dst b), 1.33-1.45 (m, 8H, $H^{16,17}$, dst a+b), 1.46-1.61 (m, 8H, $H^{15,18}$, dst a+b), 1.57 (d, ^{3}J = 6.6 Hz, 3H, H^{13}, dst a), 1.65 (d, ^{3}J = 6.4 Hz, 3H, H^{13}, dst b), 2.13 (s, 6H, H^{23}, dst a+b), 2.27-2.40 (m, 1H, H^{2}, dst b), 3.10-3.27 (m, 8H, $H^{14,19}$, dst a+b), 3.34 (d, ^{3}J = 10.8 Hz, 1H, H^{1}, dst a), 3.47 (d, ^{3}J = 9.7 Hz, 1H, H^{1}, dst b), 4.93-5.00 (m, 2H, H^{12}, dst a+b), 5.02 (s, 2H, H^{9}, dst a), 5.09 (s, 2H, H^{9}, dst b), 5.21-5.29 (m, 2H, H^{10}, dst a+b), 5.30 (s, 2H, H^{7}, dst b), 5.35 (s, 2H, H^{7}, dst a), 5.77 (s, 2H, H^{24}, dst a+b), 7.09-7.60 (m, 16H, $H^{a,b}$, dst a+b), 7.31-7.38 (m, 4H, $H^{5,5''}$, dst a+b), 7.83-7.89 (m, 4H, $H^{4,4''}$, dst a+b), 8.13 (s, 2H, $H^{3',5'}$, dst b), 8.14 (s, 2H, $H^{3',5'}$, dst a), 8.61-8.65 (m, 4H, $H^{3,3''}$, dst a+b), 8.65-8.72 (m, 4H, $H^{6,6''}$, dst a+b), 10.10 (s, 2H, H^{20}, dst a+b), 11.76 (s, 2H, H^{21}, dst a+b), 13.05 (s, 2H, H^{22}, dst a+b) ppm.

^{13}C-NMR (100 MHz, CD_2Cl_2, diastereomers a+b): δ = 18.7, 20.6, 20.8, 21.6, 21.8, 22.7, 24.3, 25.8, 25.9, 26.0, 26.1, 27.0, 28.0, 28.2, 29.2, 29.7, 31.1, 31.7, 32.0, 39.3, 39.4, 40.6, 60.4, 65.6, 66.2, 69.8, 69.9, 71.6, 71.7, 82.4, 83.2, 106.3, 107.3, 107.4, 121.0, 123.8, 126.4, 126.7, 126.9, 127.3, 127.4, 127.5, 131.0, 131.1, 134.6, 134.9, 135.0, 135.3, 136.7, 142.0, 142.2, 144.8, 145.7, 148.4, 149.0, 154.7, 155.9, 156.4, 157.1, 166.9, 172.9 ppm.

MALDI-TOF-MS (dithranol): *m/z* = 910.18 ($[M+H]^{+}$).

Elemental analysis:

$C_{52}H_{63}N_9O_6$	calcd.:	C	68.62	H	6.98	N	13.85
(M 909.49)	found:	C	68.45	H	7.19	N	13.96

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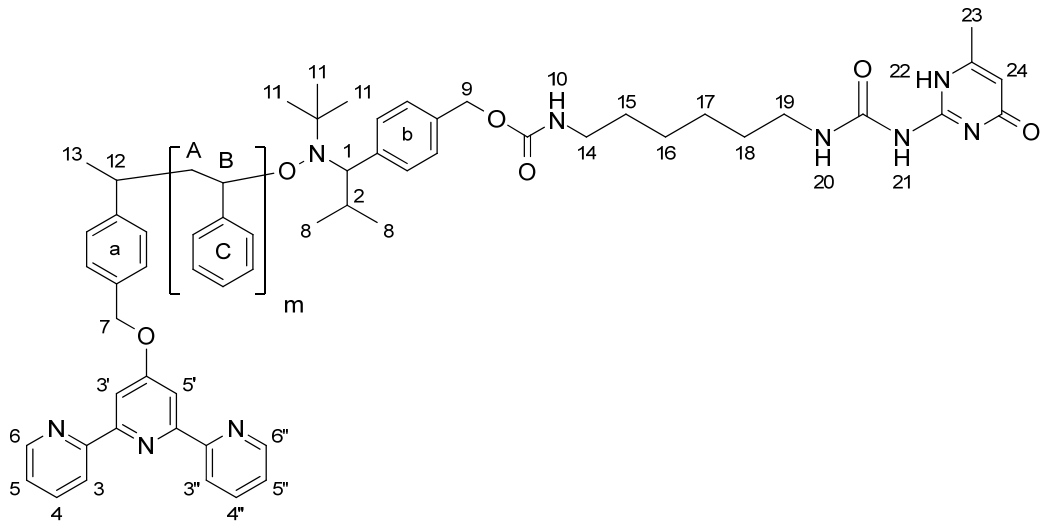
Polymerization with “tpy~TIPNO~UPy”

General procedure for the polymerization of styrene

Styrene was freshly purified by an AlOx filtration prior to use in order to remove the inhibitor. Solvents were used as supplied.

To a clear solution of the initiator in a solvent (toluene or anisole), freshly purified styrene was added to the polymerization vessel. After applying three freeze-pump-thaw-cycles to remove the oxygen, argon was added and the vessel was immersed in an oilbath at 123 °C for a certain period of time. The polymerization was stopped by cooling the reaction mixture to room temperature. To remove of residual monomer the reaction mixture was precipitated from chloroform into cold methanol.



In accordance to the general procedure for the polymerization of styrene following polymerization experiments were conducted:

name	anisole [µL]	M/I	initiator (**5**) [mg]	[mmol]	styrene (M) [mg]	[mmol]
6a	200	35	24	0.026	90	0.870
6b	1800	190	24	0.026	500	4.800
6c	400	200	8	0.009	180	1.750

name	t [min]	conversion [%] (GC)	M_n [g/mol] theoret.	M_n [g/mol] (SEC)	PDI (SEC)	M_n [g/mol] (^{1}H-NMR)
6a	400	50	2,700	6,800	1.07	4,800
6b	210	29	7,400	7,600	1.18	--
6c	360	35	8,000	11,400	1.16	13,700

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The conversion was determined by GC measurements, the molar masses (M_n, M_w) and the polydispersity indices (PDI) were measured by SEC, whereas ^{1}H-NMR spectroscopy was used for the determination of end-group functionality (by integration and comparison of the corresponding end-group signals) and M_n values (by the integration of the polymer backbone to the terpyridine signals).

Analysis of "*tpy~PS$_m$~UPy*" **6a**:

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 0.05-2.71 (set of multiplets, $H^{A,B}$, $H^{2,8,11,13,15-18,23}$), 3.11-3.38 (m, 4H, $H^{14,19}$), 3.85-4.37 (m, 1H, H^{12}), 4.97-5.22 (m, 2H, H^9), 5.26-5.34 (m, 3H, $H^{7,10}$), 5.83 (s, 1H, H^{24}), 6.25-7.54 (m, 200H, $H^{a,b}$, H^C, $H^{5,5''}$), 7.91 (dt, J^3 = 7.8 Hz, J^4 = 1.6 Hz, 2H, $H^{4,4''}$), 8.15-8.24 (m, 2H, $H^{3',5'}$), 8.64-8.76 (m, 4H, $H^{6,6''}$+$H^{3,3''}$), 10.14 (s, 1H, H^{20}), 11.88 (s, 1H, H^{21}), 13.12 (s, 1H, H^{22}) ppm.
SEC (RI): M_n = 6,800 g/mol, PDI = 1.07.

UV-vis titration (7)

According to the literature,[7] **6c (**0.852 mg) was dissolved in chloroform (20 mL) and iron(II) chloride (0.913 mg, 0.0072 mmol) was dissolved in methanol (10 mL). The methanol solution was subsequently added to the polymer solution in steps of 10 µL while the formation of the iron *bis*-complex was monitored by UV-vis spectroscopy after each addition. The equivalence point was reached after adding 70 µL of iron(II) chloride solution. UV-vis: M_n = 9,000 g/mol.

Complexation of *"tpy~PS~UPy"* with nickel(II) acetate tetrahydrate (8)

According to the literature,[8] a solution of macro ligand **6b** (20 mg, 0.003 mmol) in chloroform (200 µL) was mixed with a solution of nickel(II) acetate tetrahydrate (500 µg, 0.002 mmol) in methanol (100 µL). The resultant clear solution was stirred under an argon atmosphere at 40 °C for 24 h. The product was analyzed without further purification by size exclusion chromatography with RI detector to prove the formation of the [*bis*-tpy]nickel(II) complex in DMF.

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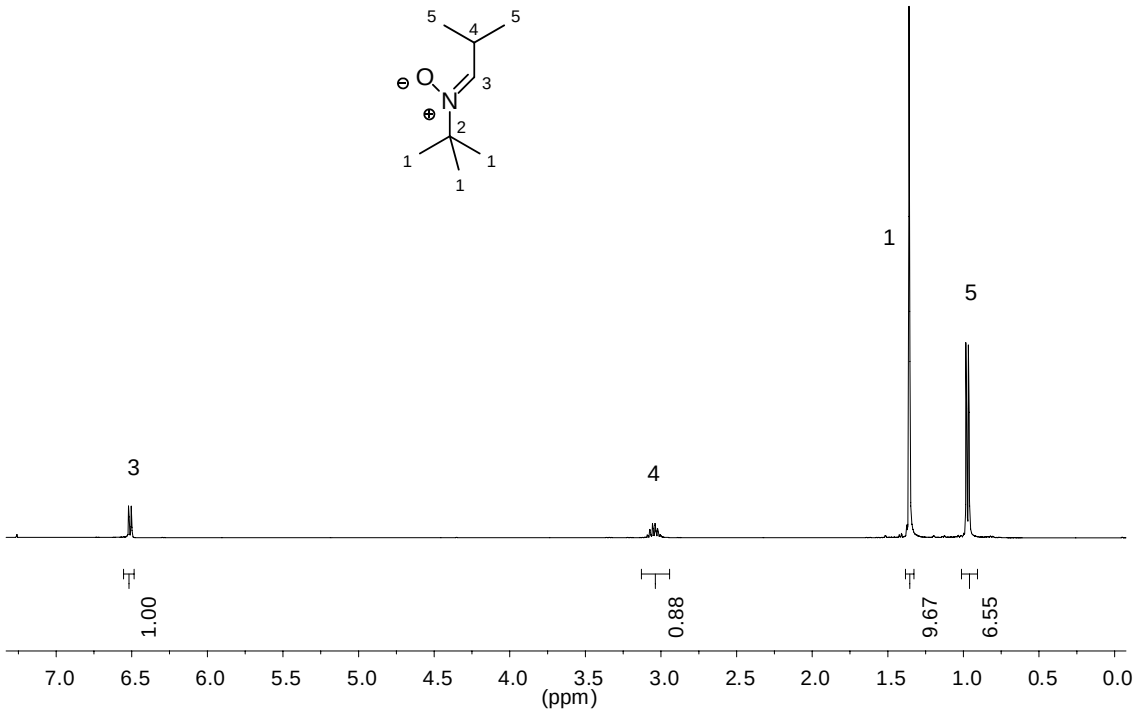
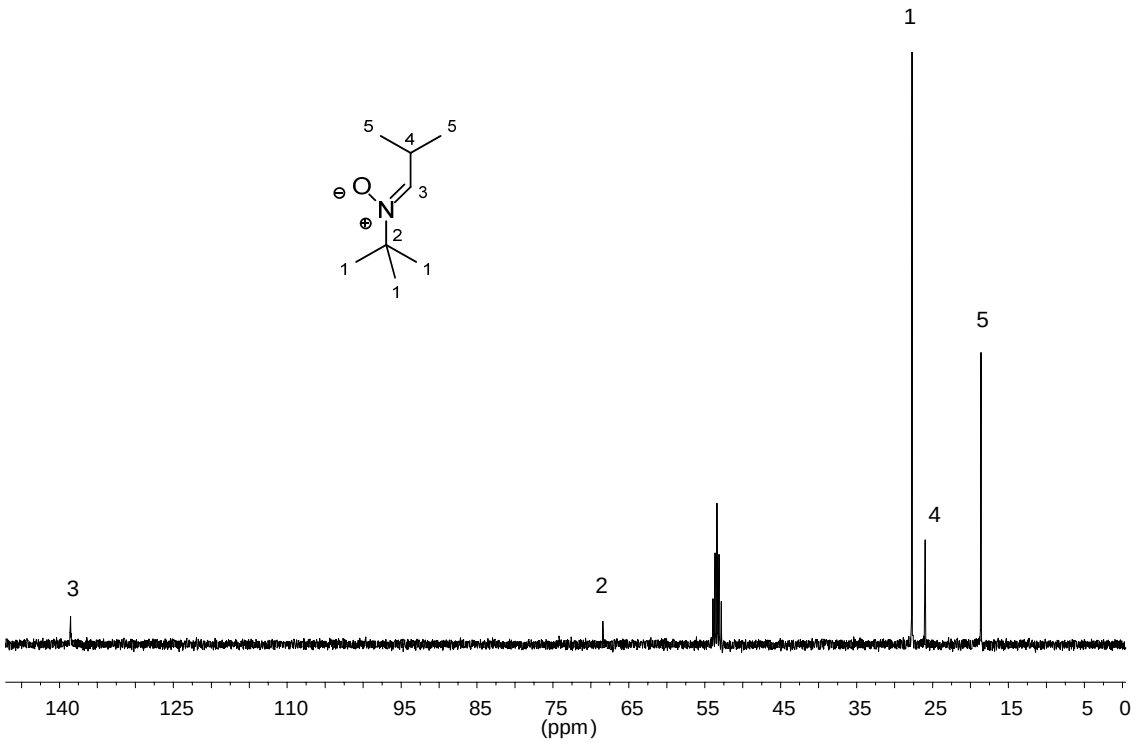
Spectra



[1]H-NMR spectrum of N-tert-butyl-a-iso-propylnitrone (400 MHz, $CDCl_3$).



[13]C-NMR spectrum of N-tert-butyl-a-iso-propylnitrone (100 MHz, CD_2Cl_2).

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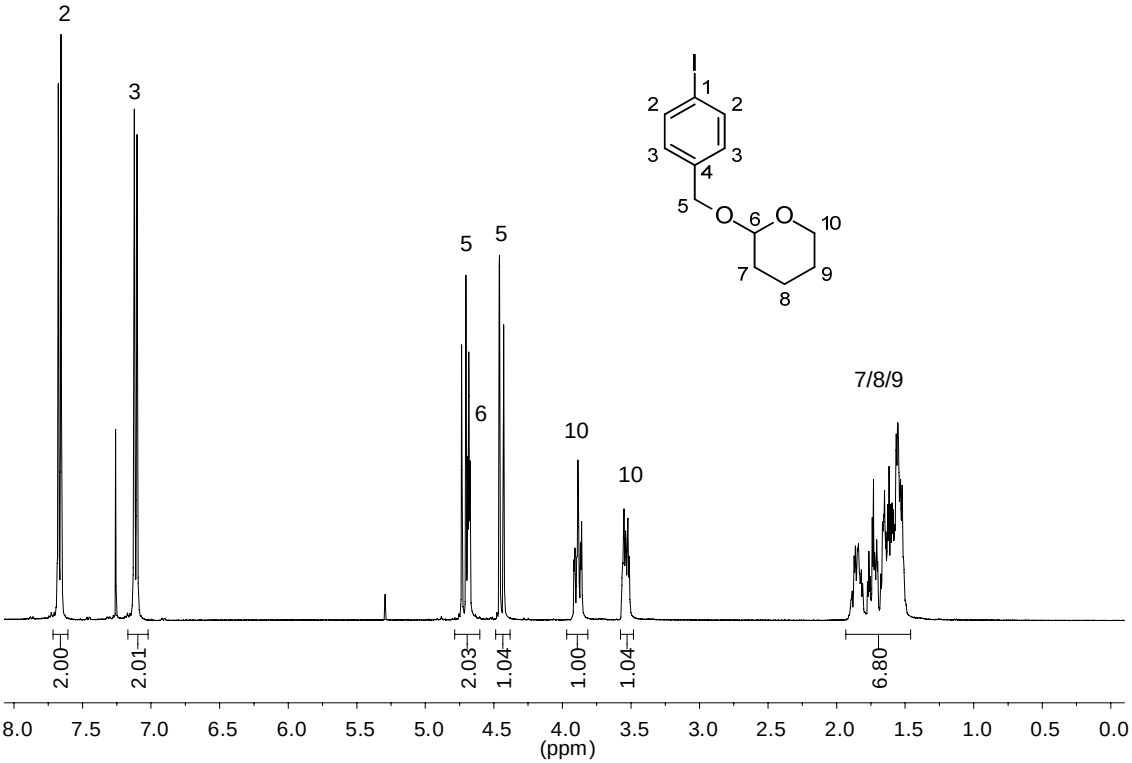
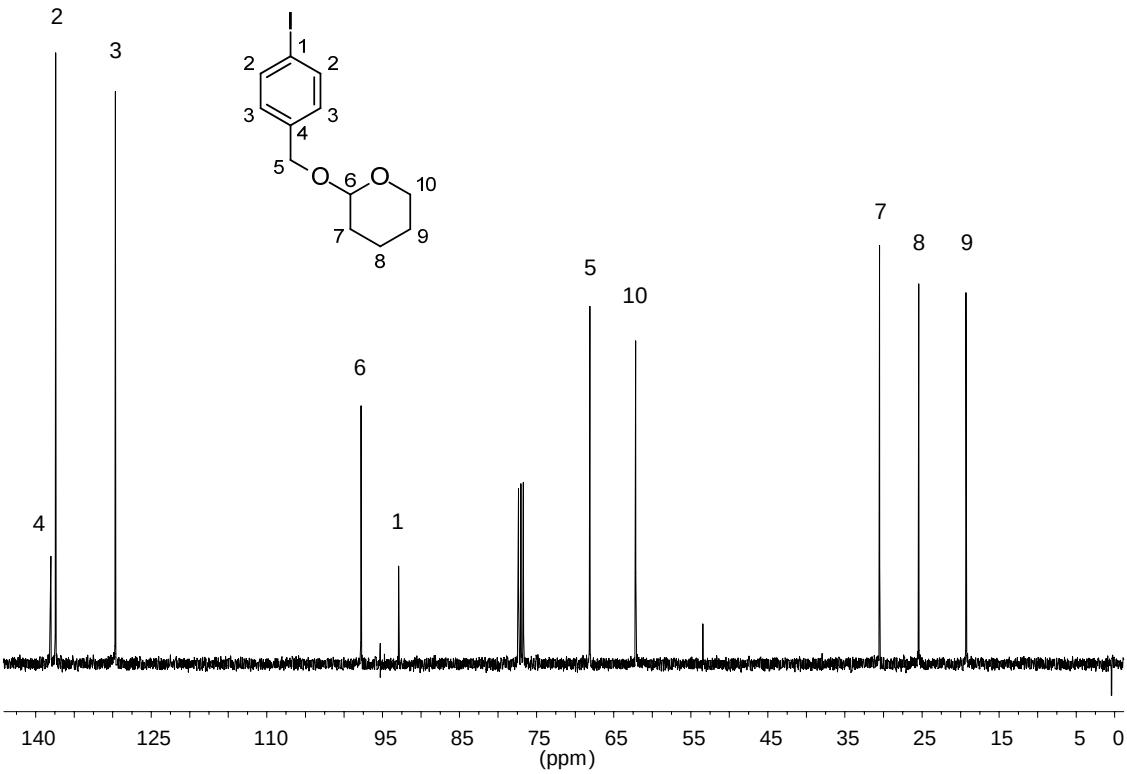
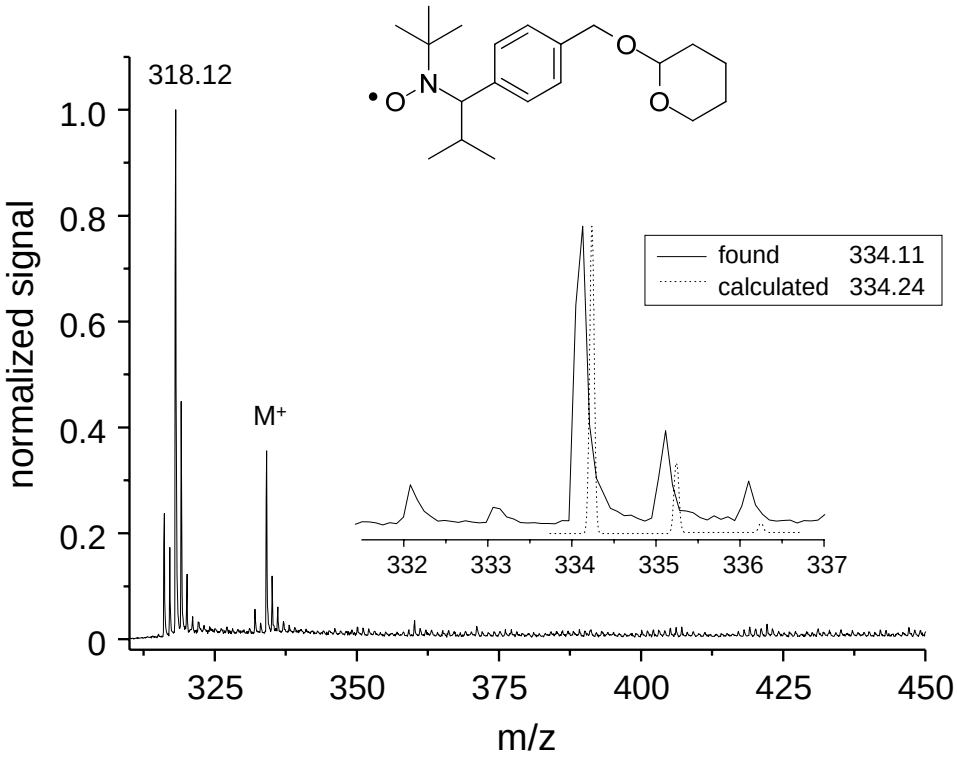


[1]H-NMR spectrum of 4-(tetrahydropyran-2´-yloxymethyl)-iodobenzene (400 MHz, $CDCl_3$).



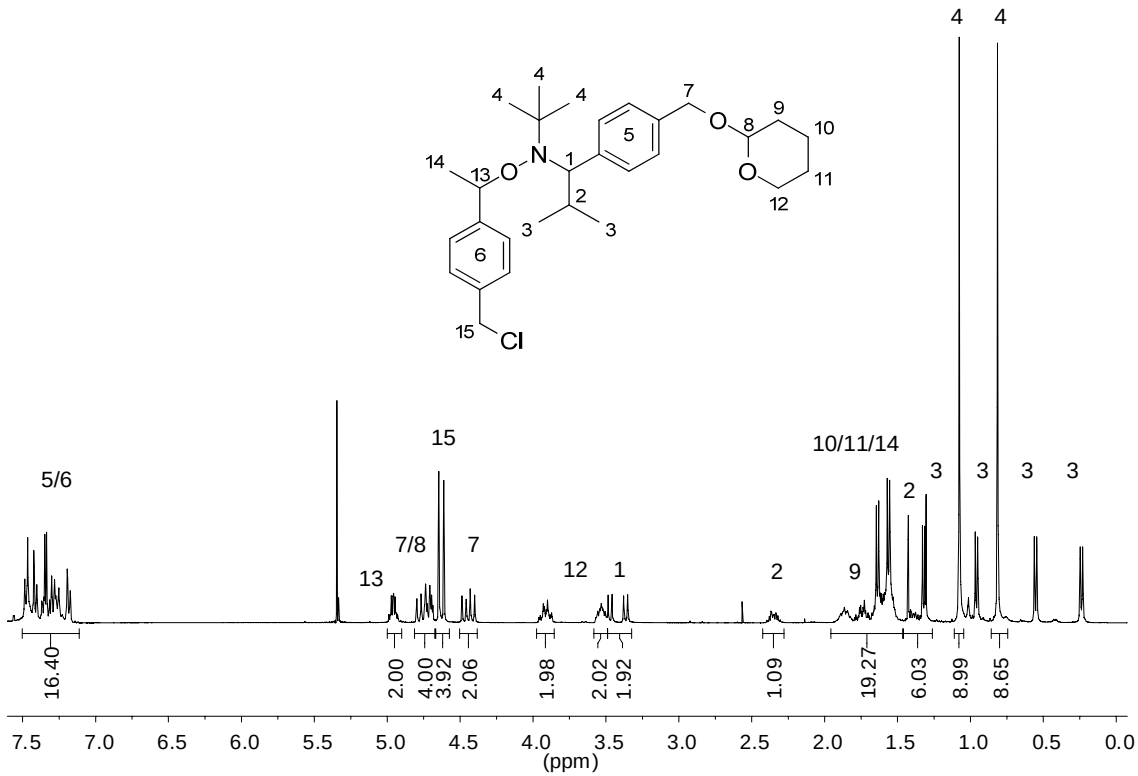
[13]C-NMR spectrum of 4-(tetrahydropyran-2´-yloxymethyl)-iodobenzene (100 MHz, $CDCl_3$).

Supplementary Material (ESI) for Chemical Communications

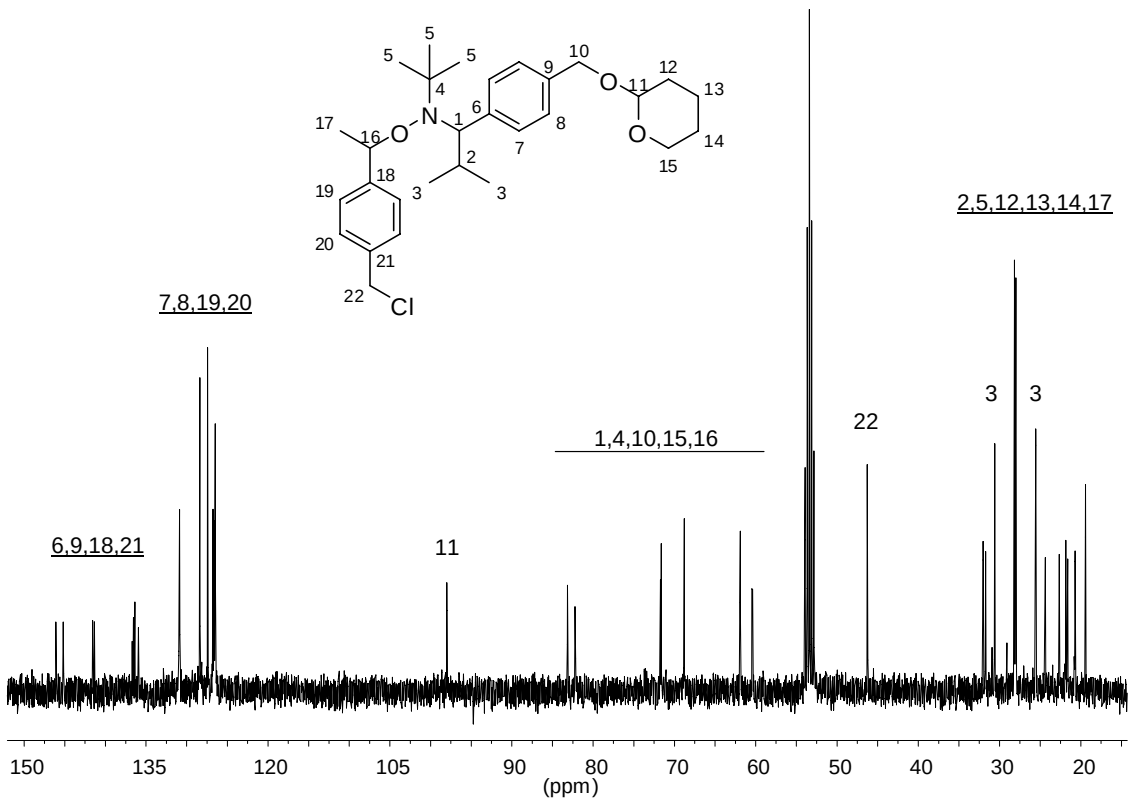


MALDI-TOF MS spectrum of functional TIPNO showing abstraction of oxygen as well as of hydrogen (matrix: dithranol).

Supplementary Material (ESI) for Chemical Communications

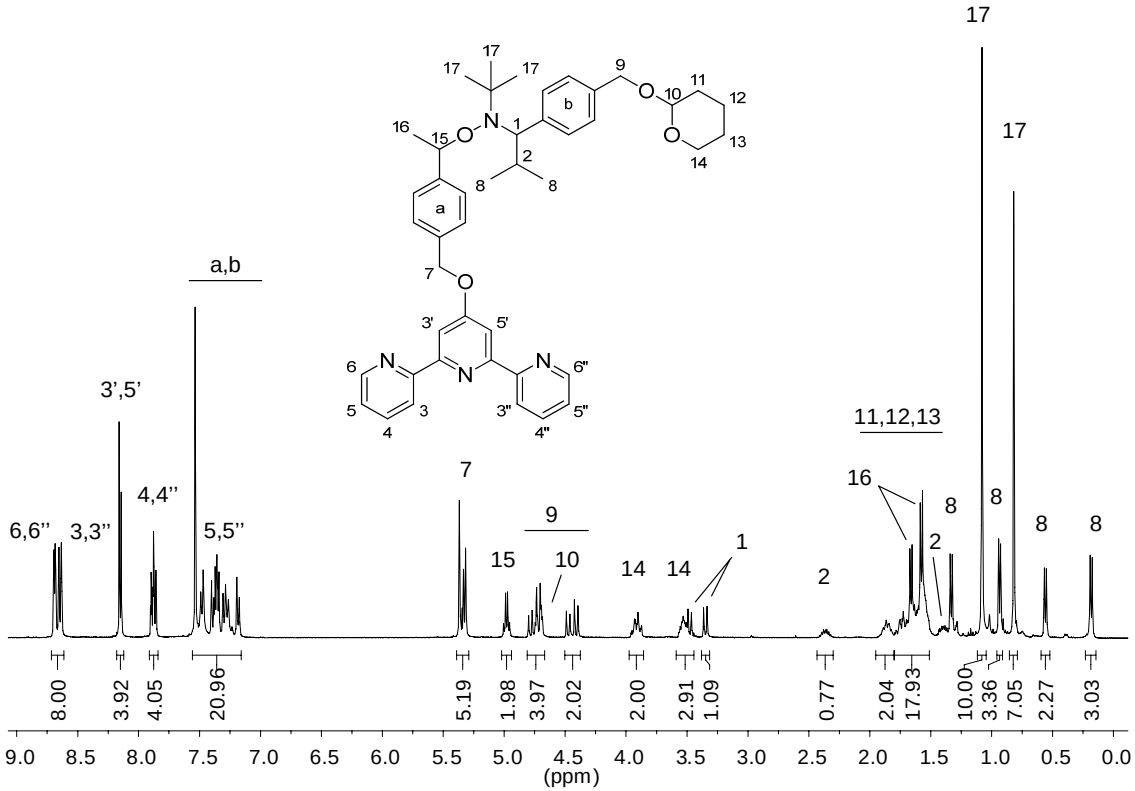


*^{1}H-NMR spectrum of "Cl~TIPNO~THP" **1** (400 MHz, CD_2Cl_2).*

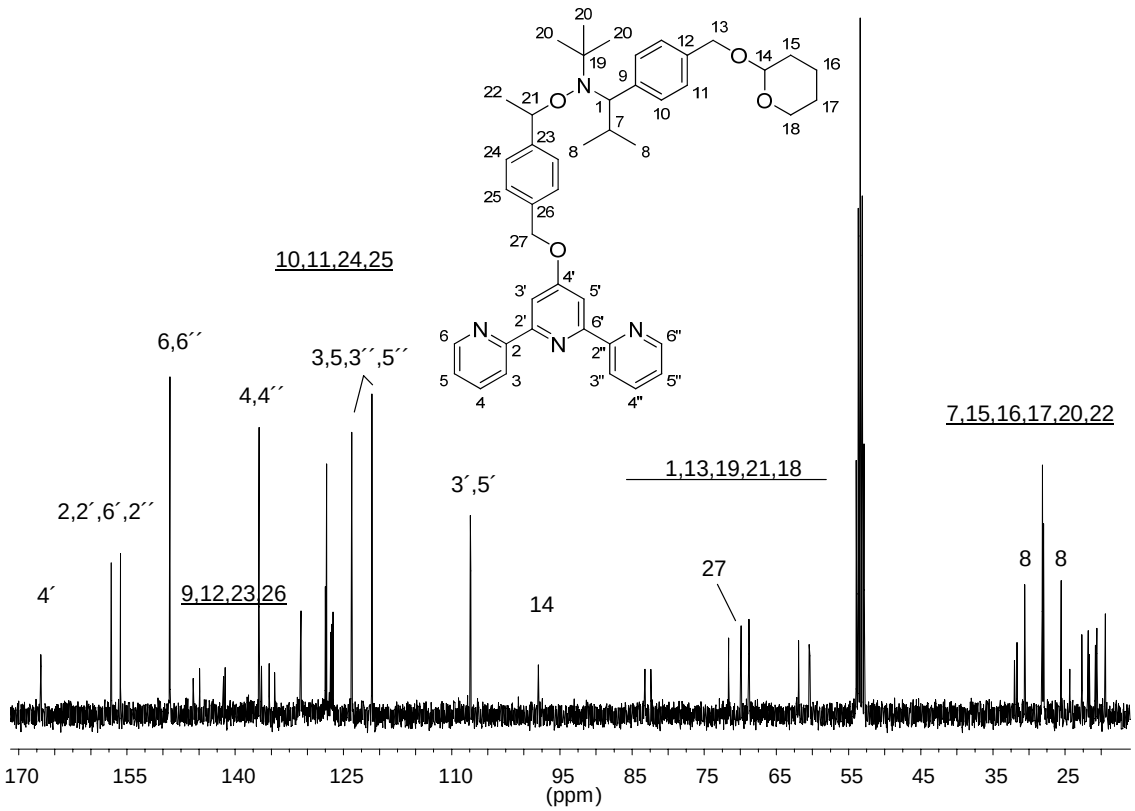


*^{13}C-NMR spectrum of "Cl~TIPNO~THP" **1** (100 MHz, CD_2Cl_2).*

Supplementary Material (ESI) for Chemical Communications

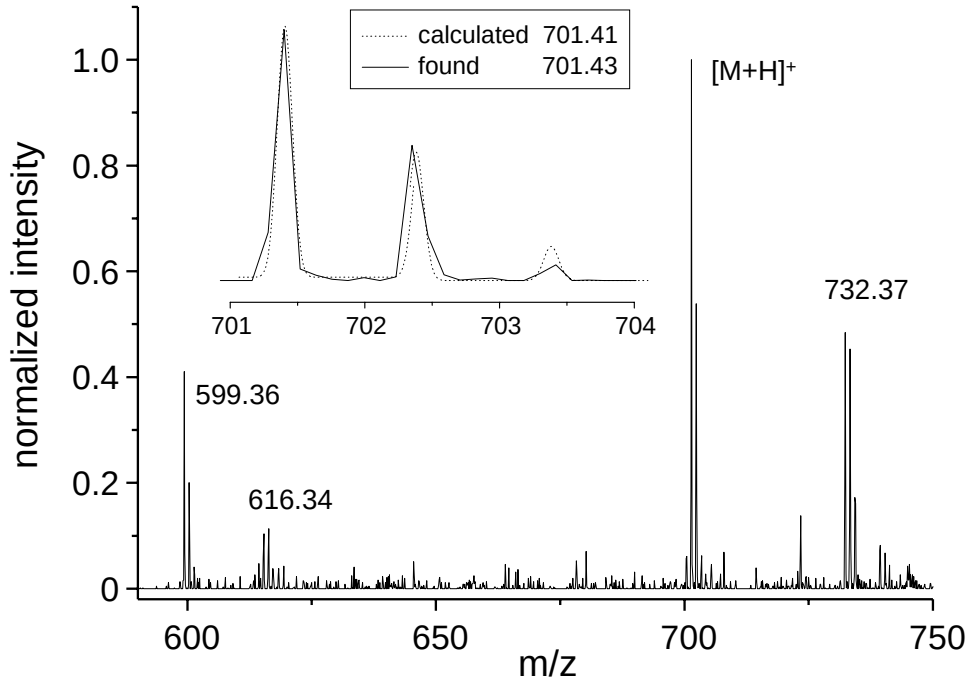


^{1}H-NMR spectrum of "tpy~TIPNO~THP" ***3*** *(400 MHz, CD_2Cl_2).*



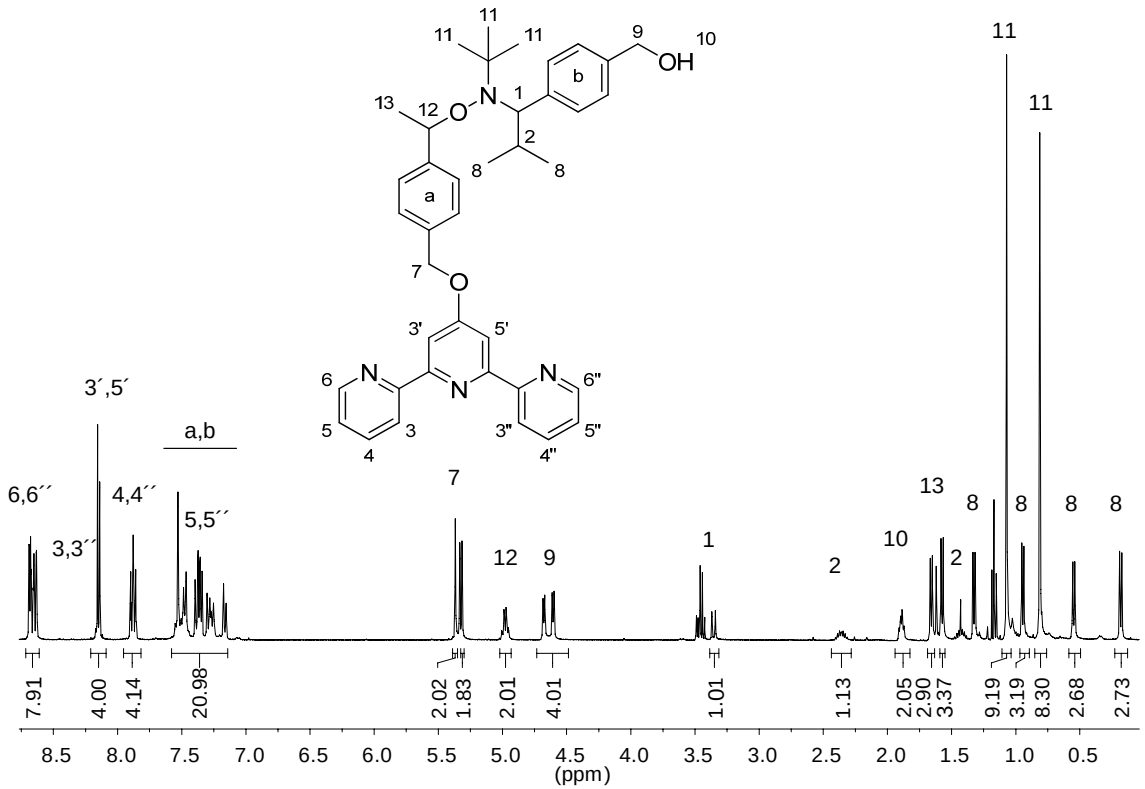
^{13}C-NMR spectrum of "tpy~TIPNO~THP" ***3*** *(100 MHz, CD_2Cl_2).*

Supplementary Material (ESI) for Chemical Communications

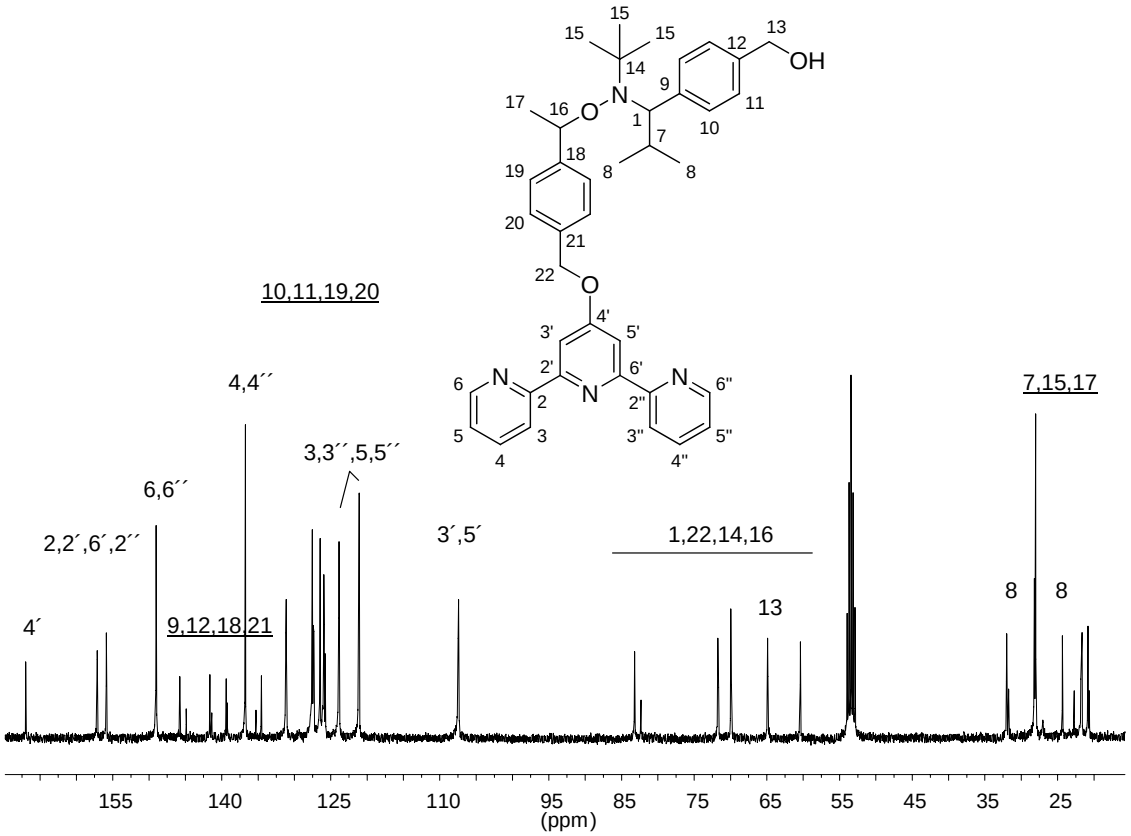


MALDI-TOF mass spectrum of "tpy~TIPNO~THP" ***3*** *(matrix: DCTB).*

Supplementary Material (ESI) for Chemical Communications

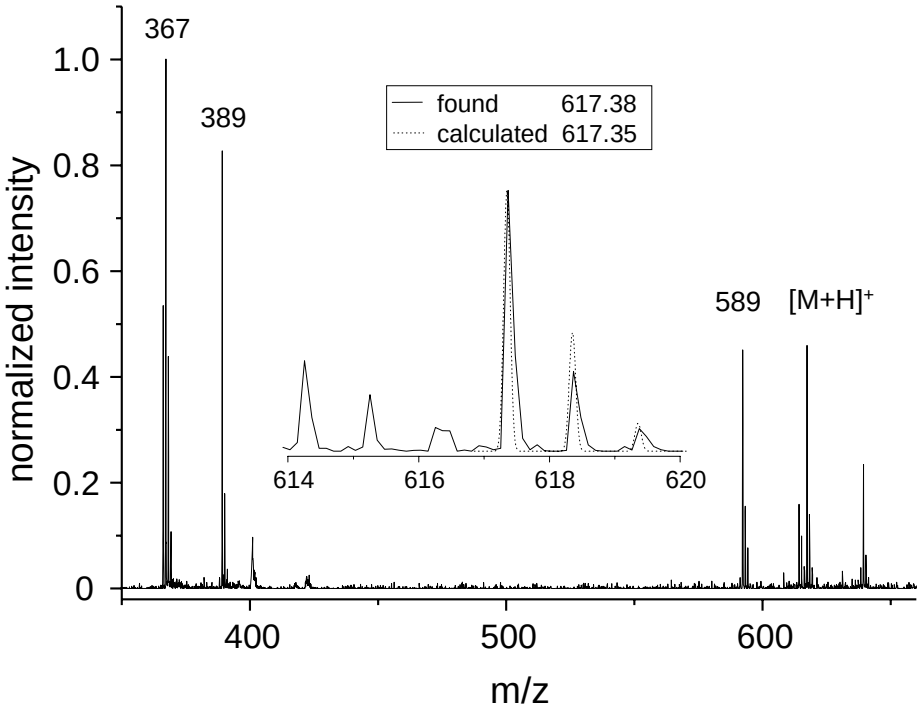


[1]H-NMR spectrum of "tpy~TIPNO~OH" (400 MHz, CD_2Cl_2).



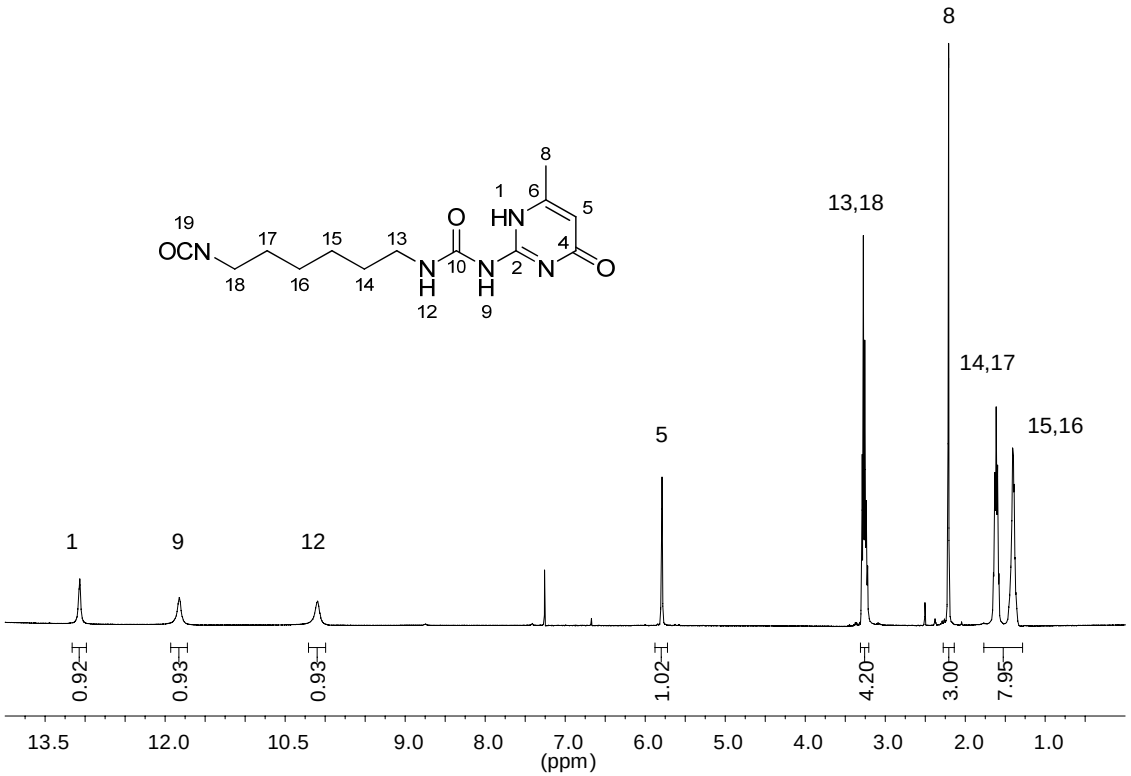
[13]C-NMR spectrum of "tpy~TIPNO~OH" (100 MHz, CD_2Cl_2).

Supplementary Material (ESI) for Chemical Communications

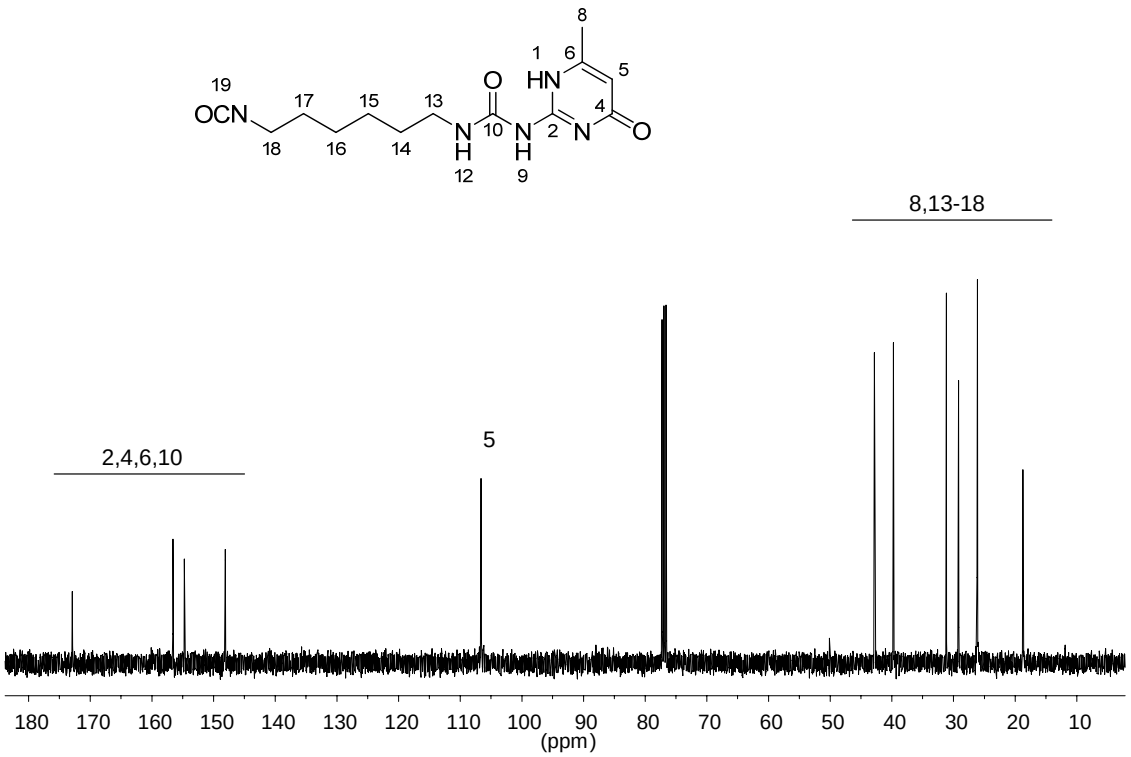


MALDI-TOF MS spectrum of "tpy~TIPNO~OH" (matrix: dithranol).

Supplementary Material (ESI) for Chemical Communications

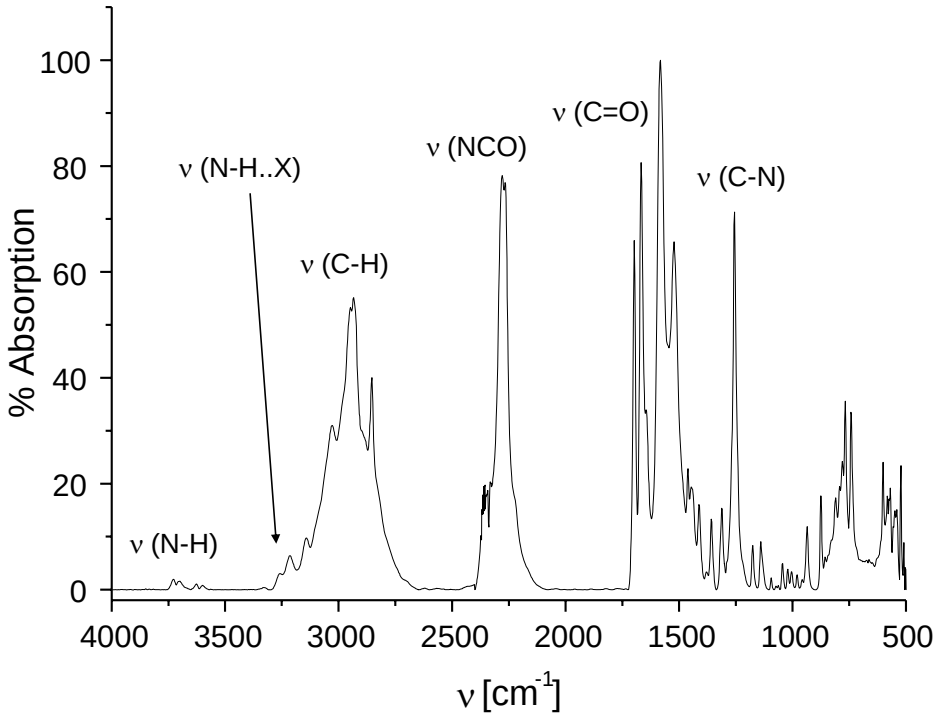


*^{1}H-NMR spectrum of "OCN-hexyl-UPy" **4** (400 MHz, $CDCl_3$).*



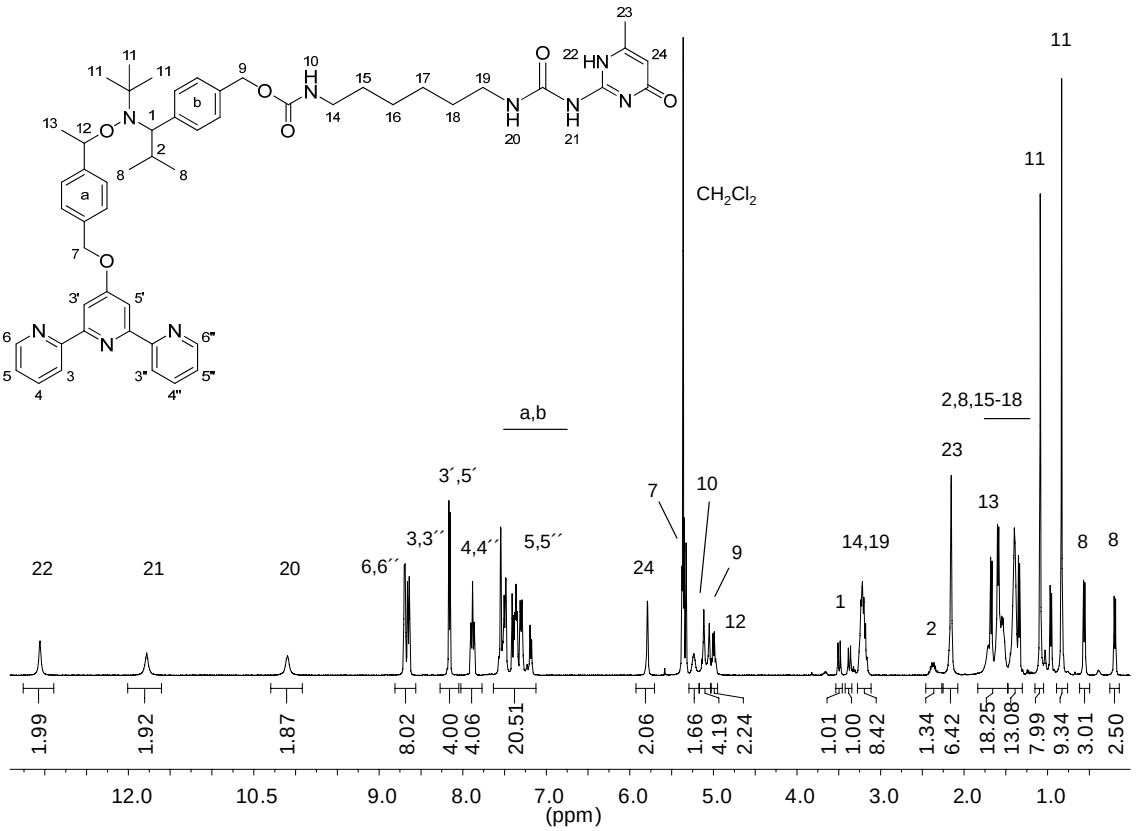
*^{13}C-NMR spectrum of "OCN-hexyl-UPy" **4** (100 MHz, $CDCl_3$).*

Supplementary Material (ESI) for Chemical Communications

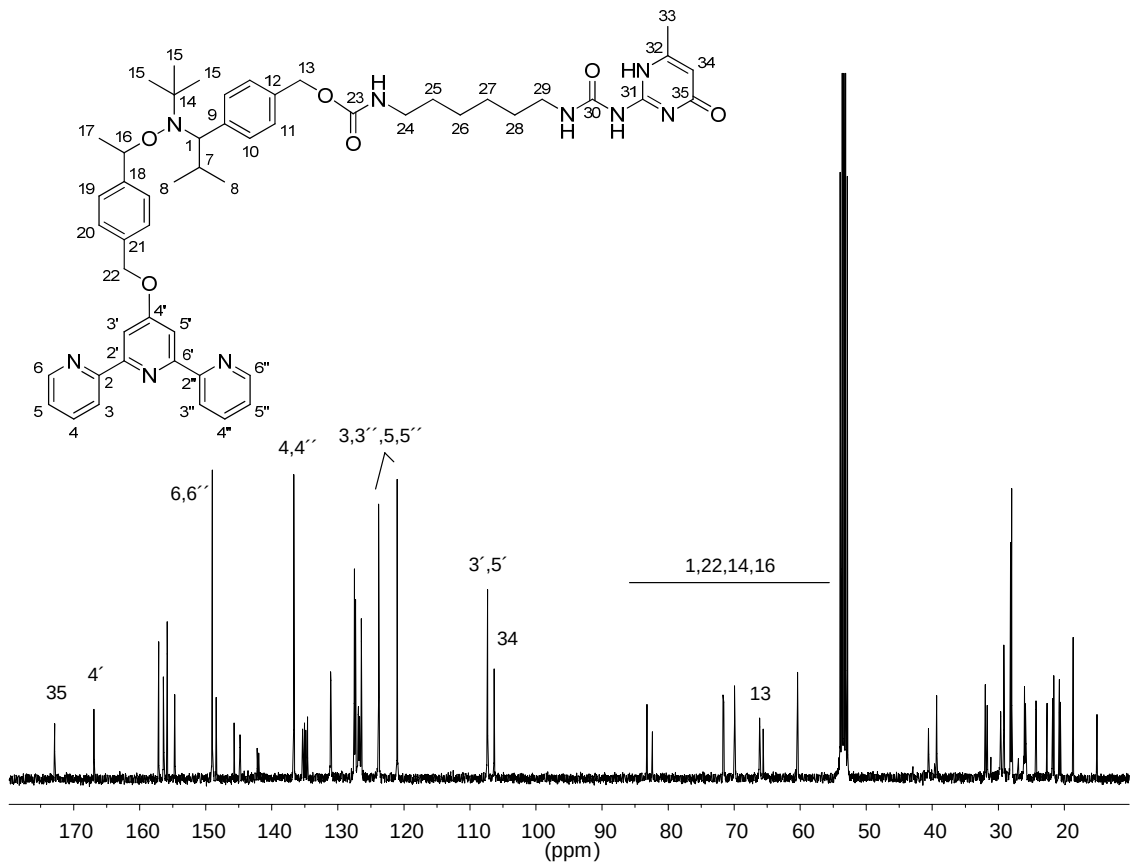


*FT-IR spectrum of building block **4** shows characteristic absorption bands for isocyanate (N=C=O-valence) and for the hydrogen bonding (N-H..X-valence).*

Supplementary Material (ESI) for Chemical Communications

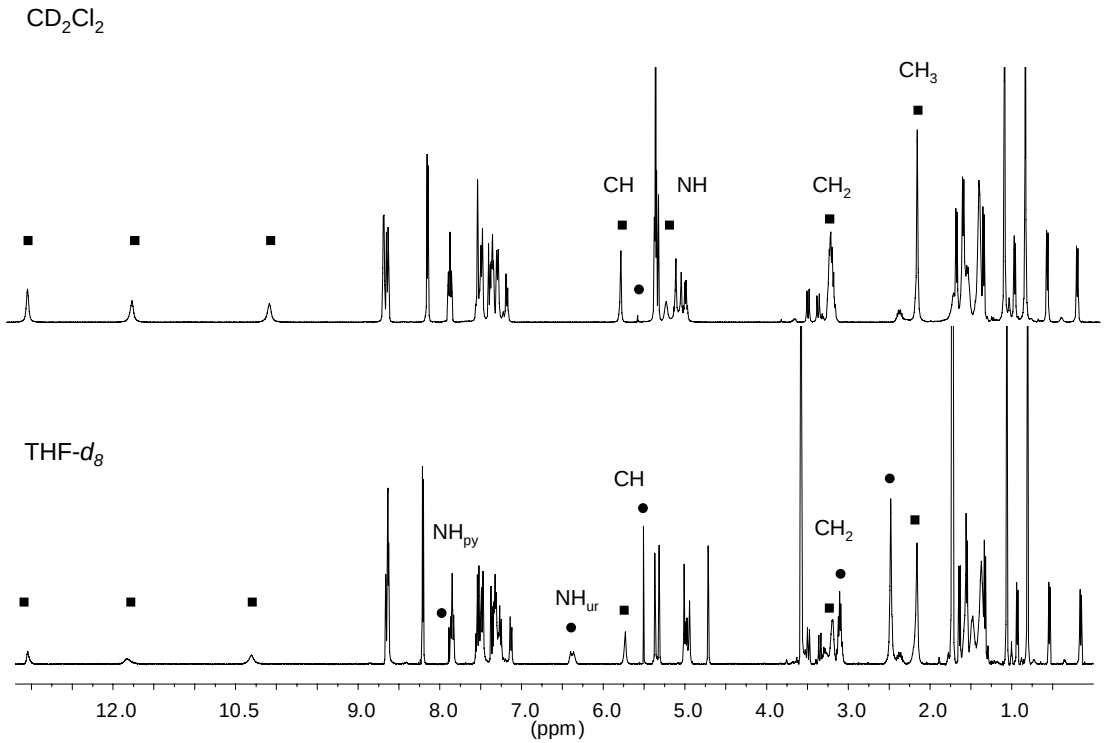


^{1}H-NMR spectrum of "tpy~TIPNO~UPy" ***5*** *(400 MHz, CD_2Cl_2).*

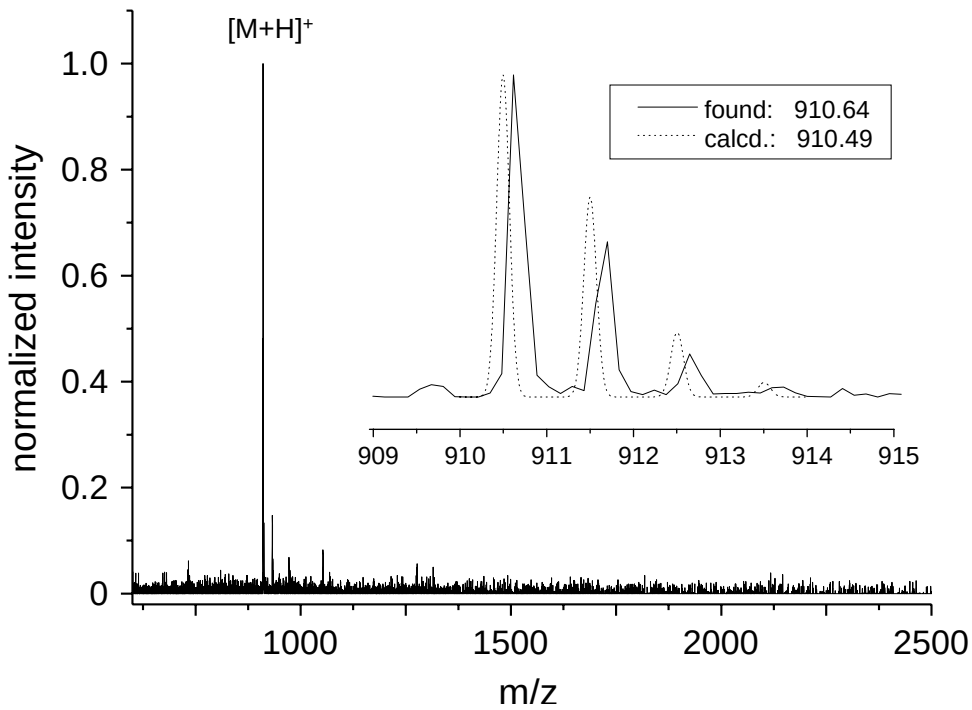


^{13}C-NMR spectrum of "tpy~TIPNO~UPy" ***5*** *(100 MHz, CD_2Cl_2).*

Supplementary Material (ESI) for Chemical Communications

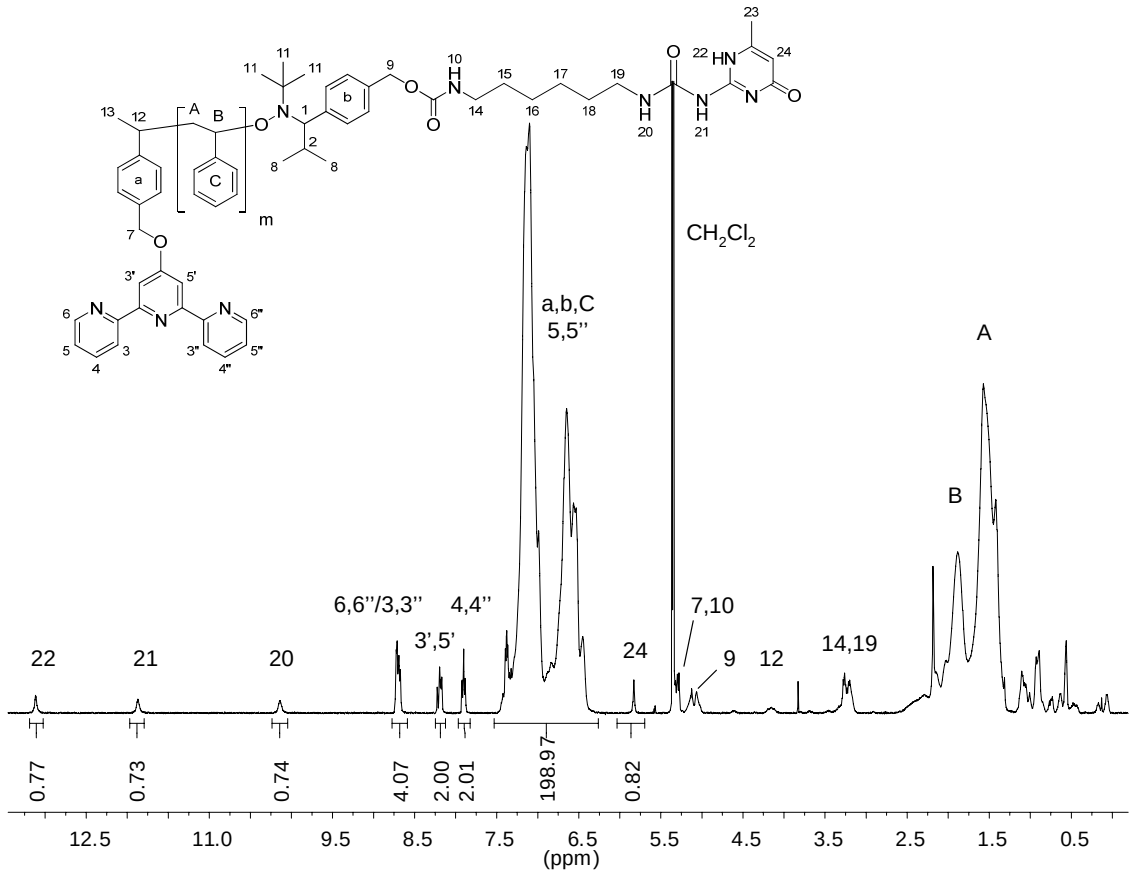


*Comparison of the ^{1}H-NMR spectra of "tpy~TIPNO~UPy"(**5**) in CD_2Cl_2 and THF-d_8 shows the influence of the solvent on the tautomeric equilibrium. Besides the dimeric form of 4[1H]-pyrimidinone (■) also the monomeric form of 4[3H]-pyrimidinone (●) can be observed.*[9]



*MALDI-TOF-MS spectrum of "tpy~TIPNO~Upy" **5** (matrix: DCTB).*

Supplementary Material (ESI) for Chemical Communications



^{1}H-NMR spectrum of "tpy~PS$_{40}$~UPy" ***6*** *(400 MHz, CD_2Cl_2).*

[1] D. Benoit, V. Chaplinski, R. Braslau and C. J. Hawker, *J. Am. Chem. Soc.* **1999**, *121*, 3904– 3920.

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[7] H. Hofmeier, A. El-ghayoury, A. P. H. J. Schenning and U. S. Schubert, *Chem. Commun.* **2004**, 318–319.

[8] M. Chiper, J. M. Kranenburg, M. A. R. Meier and U. S. Schubert, *Macromol. Chem. Phys.* **2007**, *208*, 679–689.

[9] R. P. Sijbesma and E. W. Meijer, *Chem. Commun.* **2003**, 5–16.