

Supporting Information for

Trimethylsilyl-Induced N–O Bond Cleavage in Nitrous Oxide-Derived Aminodiazotates

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Contents

1. Experimental details.....	2
2. IR spectrum of KN_3	5
3. Copies of NMR spectra	6
Reaction between KHMDS and N_2O	6
$[\text{K}(18\text{-crown-6})]\text{N}_3$	6
$[\text{K}(2.2.2\text{-cryptand})]\text{N}_3$	7
3a	8
Reaction between $\text{KN}(\text{TMS})\text{Dipp}$ and N_2O	9
$\text{KN}(\text{TMS})\text{Mes}^*$	10
Reaction between $\text{KN}(\text{TMS})\text{Mes}^*$ and N_2O	11
Reaction between $\text{LiN}(\text{TMS})\text{Ph}$ and N_2O	12
$\text{LiN}(\text{TMS})\text{Ph}^{\text{OMe}}$	13
Reaction between $\text{LiN}(\text{TMS})\text{Ph}^{\text{OMe}}$ and N_2O	14
5a	15
5b	17
5c	19
4. X-ray structure of $[\text{K}(18\text{-crown-6})]\text{N}_3$	22
5. Crystallographic data.....	23

1. Experimental details

General

Solvents (pentane, hexane, Et₂O, THF) were dried with the Innovative Technology SPS-400-5 solvent purification system. 18-Crown-6 (Sigma Aldrich) was recrystallized from acetonitrile and vacuum-dried before use. Methyl iodide (MeI, Sigma Aldrich) was distilled over CaH₂ and stored over 4 Å molecular sieves. N₂O (Messer Schweiz AG, purity 99.999%), *n*-butyl lithium (*n*BuLi), KHMDS (Sigma Aldrich), 2.2.2-cryptand (TCI), DMF (Acros, extra dry over molecular sieves) were commercially available and used as received. HN(TMS)Dipp,¹ HN(TMS)Mes*,² HN(TMS)Ph,³ and HN(TMS)Ph^{OMe}⁴ were prepared according to the methods described in literature (slight modifications may be applied). LiN(TMS)Ph,^{5,6} LN(TMS)Ph^{OMe}, lithium diisopropylamide (LDA), lithium dicyclohexylamide, and lithium 2,2,6,6-tetramethylpiperidide were prepared by lithiating the corresponding amines with *n*BuLi. KN(TMS)Dipp and KN(TMS)Mes* were prepared by deprotonating the corresponding amines with KH according to the literature procedure.⁷

Preparation of KN₃. A solution of KHMDS (237 mg, 1.19 mmol) in THF (20 mL) was stirred under one atmosphere of N₂O at room temperature (RT) overnight. The obtained solid was collected by filtration and washed with THF to give a white solid (87 mg, yield 90%). IR: $\nu = 642, 649, 1998, 2018, 3286, 3357 \text{ cm}^{-1}$. Elemental analysis for KN₃·(C₄H₈O)_{0.037}, calc. C: 2.12, H: 0.36, N: 50.15; found C: 2.53, H: 0.46, N: 50.51.

Preparation of [K(18-crown-6)]N₃. KHMDS (224 mg, 1.12 mmol) and 18-crown-6 (365 mg, 1.38 mmol) were dissolved in THF (20 mL) and the solution was stirred under one atmosphere of N₂O at RT overnight. The obtained solid was collected by filtration and washed with THF to give an off-white solid (311 mg, yield 80% based on KHMDS). Colorless crystals suitable for X-ray crystallography were grown by slow diffusion of Et₂O into a DMF solution at RT. ¹H NMR (DMSO-d₆, δ ppm) 3.55 (s, 24H, 18-crown-6); ¹³C NMR (DMSO-d₆, δ ppm) 69.47 (18-crown-6). Elemental analysis for KN₃·(C₁₂H₂₄O₆), calc. C: 41.72, H: 7.00, N: 12.16; found C: 41.55, H: 6.98, N: 12.09.

Preparation of [K(2.2.2-cryptand)]N₃. KHMDS (166 mg, 831 μ mol) and 2.2.2-cryptand (377 mg, 1 mmol) were dissolved in a mixed solvent of THF (5 mL) and Et₂O (10 mL) and stirred under one atmosphere of N₂O at room temperature (RT) overnight. The obtained solid was collected by filtration and washed with Et₂O to give an off-white solid (349 mg, yield 92% based on KHMDS). ¹H NMR (DMSO-d₆, δ ppm) 3.55 (s, 12H, OCH₂CH₂O), 3.51 (t, *J* = 4.6 Hz, 12H, OCH₂CH₂N), 2.50 (t, *J* = 4.6 Hz, 12H, OCH₂CH₂N, overlapping with solvent peak). ¹³C NMR (DMSO-d₆, δ ppm) 69.81, 66.99, 53.21. Elemental analysis for KN₃·(C₁₈H₂₆N₂O₆), calc. C: 47.24, H: 7.93, N: 15.30; found C: 47.27, H: 8.08, N: 15.13.

¹ Y.-W. Chao, P. A. Wexler, D. E. Wigley. *Inorg. Chem.* **1989**, *28*, 3860–3868.

² V. D. Romanenko, A. V. Ruban, S. V. Iksanova, L. K. Polyachenko, L. N. Markovski. *Phosphorus Sulfur Silicon Relat Elem* **1985**, *22*, 365–368.

³ A. Schulz, A. Villinger, A. Westenkirchner. *Inorg. Chem.* **2013**, *52*, 11457–11468.

⁴ M. J. Fuchter, C. J. Smith, M. W. S. Tsang, A. Boyer, S. Saubern, J. H. Ryan, A. B. Holmes. *Chem. Commun.* **2008**, 2152–2154.

⁵ J. R. Galsworthy, M. L. H. Green, N. Maxted, M. Müller. *J. Chem. Soc., Dalton Trans.* **1998**, 387–392.

⁶ J. P. Bezombes, P. B. Hitchcock, M. F. Lappert, P. G. Merle. *J. Chem. Soc., Dalton Trans.* **2001**, 816–821.

⁷ C.-C. Tsou, F.-T. Tsai, H.-Y. Chen, I.-J. Hsu, W.-F. Liaw. *Inorg. Chem.* **2013**, *52*, 1631–1639.

Preparation of [K(18-crown-6)]N₃ from TMSN₃ and TMSOK. TMSN₃ (340 μL, 2.57 mmol) was added to a suspension of TMSOK (329 mg, 2.57 mmol) in THF (20 mL) and a large amount of precipitate was immediately developed. The mixture was stirred at RT for 5 h and the volatiles were evaporated. The solid residue was washed with THF and dried. It was then treated with 18-crown-6 (706 mg, 2.67 mmol) in 3 mL of DMF for 15 min, and the mixture was filtered and washed with another 2 mL of THF. Et₂O was added to the filtrate to precipitate out [K(18-crown-6)]N₃, which was filtered off, washed with Et₂O and dried (604 mg, yield 68%). The same spectroscopic and crystallographic characterization was obtained as [K(18-crown-6)]N₃ prepared from KHMDs and N₂O.

Preparation of DippN₃ (3a) from KN(TMS)Dipp. A solution of KN(TMS)Dipp (308 mg, 1.07 mmol) in THF (15 mL) was stirred under 1 atmosphere of N₂O for 1.5 h. The volatiles were evaporated and the residue was extracted with hexane. After passing through a short plug of silica gel, **3a** was obtained by evaporating off the solvent (211 mg, yield 97%). The ¹H NMR spectrum (Figure S7) matched those reported in literature.⁸

Preparation of KN(TMS)Mes*. To a solution of HN(TMS)Mes* (665 mg, 2 mmol) in THF (15 mL) was added KH (96 mg, 2.4 mmol) at RT. The mixture was stirred for 72 h and filtered. The filtrate was concentrated and hexane was added. The crude product that precipitated out was collected by filtration, washed with pentane, extracted with THF, and reprecipitated out with hexane to give a white solid (460 mg, yield 62%). ¹H NMR (THF-d₈, δ ppm) 7.01 (s, 2H, Ar), 1.44 (s, 18H, 2,6-di-*tert*-Bu), 1.20 (s, 9H, 4-*tert*-Bu), 0.07 (s, 9H, TMS).

Preparation of LiN(TMS)Ph^{OMe}. HN(TMS)Ph^{OMe} (963 mg, 4.93 mmol) was dissolved in pentane (20 mL) and cooled down in a liquid nitrogen-cooled cold well. *n*BuLi (1.6M, 3.1 mL, 5 mmol) was added dropwise and the mixture was warmed to RT. After stirred overnight, the precipitates were filtered off, washed with pentane, and dried to give an off-white solid in quantitative yield (990 mg). ¹H NMR (THF-d₈, δ ppm) 6.39 (d, *J* = 8.4 Hz, 2H, 3-Ar), 6.32 (d, *J* = 5.6 Hz, 2H, 2-Ar), 3.55 (s, 3H, OMe), -0.05 (s, 9H, TMS).

The ¹H NMR monitoring of the reactions between MTMSAr and N₂O to generate 3. A J-Young NMR tube containing a THF-d₈ solution of MTMSAr was degassed by performing three freeze-pump-thaw cycles. N₂O was let in and the valve was re-closed. ¹H NMR spectra evolution was monitored.

Preparation of 5a. LDA (281 mg, 2.62 mmol) was dissolved in THF (15 mL) and the solution was stirred under one atmosphere of N₂O overnight. The atmosphere was then switched to N₂ and LiN(TMS)Ph (1.35 g, 7.88 mmol) in THF (10 mL) was added dropwise. The resulting mixture was stirred for another 48 h to achieve gradual dissolution, which was then filtered and concentrated to ca. 2 mL. Pentane was added to precipitate out the crude product, which was collected after filtration and washing with pentane as a light gray solid (230 mg, yield 39%). ¹H NMR (THF-d₈, δ ppm) 7.07 (d, *J* = 8.0 Hz, 2H, 2,6-Ph), 6.94 (t, *J* = 7.6 Hz, 2H, 3,5-Ph), 6.45 (d, *J* = 6.8 Hz, 1H, 4-Ph), 3.21 (sept, *J* = 6.4 Hz, 2H, CH^{*i*Pr}), 1.04 (d, *J* = 5.2 Hz, 12H, Me^{*i*Pr}). ¹³C NMR (THF-d₈, δ ppm) 157.15

⁸ T. S. Pilyugina, R. R. Schrock, A. S. Hock, P. Müller. *Organometallics* **2005**, *24*, 1929–1937.

(1-Ph), 128.17 (3,5-Ph), 117.46 (4-Ph), 116.96 (2,6-Ph), 50.94 (CH^{iPr}), 21.13 (Me^{iPr}), 18.04 (Me^{iPr}). Single crystals suitable for X-ray crystallography were grown by slow diffusion of pentane to a THF solution of **5a** at -40 °C. Due to the instability of the compound, a satisfactory elemental analysis result was not obtained. To the NMR sample of **5a** was added an excess of MeI. After standing overnight, the sample was diluted with MeOH and subjected to mass spectroscopy. [C₁₃H₂₂N₄ + H]⁺ m/z calc. 235.1917, found 235.1926.

Preparation of 5b. Lithium dicyclohexylamide (prepared from 146 mg, 0.8 mmol of dicyclohexylamine and 0.8 mmol of *n*BuLi) was dissolved in THF (10 mL) and the solution was stirred under one atmosphere of N₂O overnight. The atmosphere was then switched to N₂ and LiN(TMS)Ph (417 mg, 2.4 mmol) in THF (10 mL) was added dropwise. The precipitates gradually dissolved within 1 h and the resulting solution was stirred for another 4 days. It was then filtered and concentrated to ca. 2 mL. Pentane was added to precipitate out the crude product, which was collected after filtration and washing with pentane as an off-white solid (120 mg, yield 49%). ¹H NMR (THF-d₈, 0 °C, δ ppm) 7.06 (d, *J* = 5.2 Hz, 2H, 2,6-Ph), 6.94 (t, *J* = 5.0 Hz, 2H, 3,5-Ph), 6.43 (t, *J* = 4.4 Hz, 1H, 4-Ph), 2.88 (t, *J* = 6.8 Hz, 2H, 1-Cy), 1.93 (d, *J* = 7.6 Hz, 2H, 2-Cy), 1.89 (d, *J* = 7.6 Hz, 2H, 3-Cy), 1.72-1.69 (m, 4H, 4,5-Cy, overlapping with solvent peak), 1.58 (d, *J* = 7.2 Hz, 2H, 6-Cy), 1.33 (d, *J* = 7.6 Hz, 2H, 6-Cy), 1.25-1.16 (m, 4H, 4,5-Cy), 1.13 (d, *J* = 8.0 Hz, 2H, 2-Cy), 1.07 (t, *J* = 8.8 Hz, 2H, 3-Cy). ¹³C NMR (THF-d₈, 0 °C, δ ppm) 157.12 (1-Ph), 128.78 (3,5-Ph), 117.24 (4-Ph), 116.77 (2,6-Ph), 58.91 (1-Cy), 31.53 (2-Cy), 27.97 (6-Cy), 27.46 (3-Cy), 27.09 (5-Cy), 26.75 (4-Cy). Elemental analysis for C₁₈H₂₇LiN₄, calc. C: 70.57, H: 8.88, N: 18.29; found C: 70.72, H: 8.19, N: 17.56. To the NMR sample of **5b** was added an excess of MeI. After standing overnight, the sample was diluted with MeOH and subjected to mass spectroscopy. [C₁₉H₃₀N₄ + H]⁺ m/z calc. 315.2549, found 315.2535. [C₁₉H₃₀N₄ + Li]⁺ m/z calc. 321.2631, found 321.2621.

Preparation of 5c. Lithium 2,2,6,6-tetramethylpiperidide (127 mg, 0.86 mmol) was dissolved in THF (10 mL) and stirred under one atmosphere of N₂O overnight. The atmosphere was then switched to N₂ and LiN(TMS)Ph (296 mg, 1.33 mmol) in THF (10 mL) was added dropwise. The precipitates gradually dissolved within 1 h and the resulting solution was stirred for 4 days. It was then filtered and most of the solvent was evaporated off. The residue was triturated with pentane, filtered, and dried to give a light pink gray solid (58 mg, yield 25%). The ¹H NMR (THF-d₈, δ ppm) 7.09 (d, *J* = 8.0 Hz, 2H, 2,6-Ph), 6.94 (t, *J* = 7.8 Hz, 2H, 3,5-Ph), 6.46 (t, *J* = 7.2 Hz, 1H, 4-Ph), 1.27 (s, 6H, Me), 1.01 (s, 6H, Me). ¹³C NMR (THF-d₈, δ ppm) 157.06 (1-Ph), 128.70 (3,5-Ph), 117.65 (4-Ph), 117.20 (2,6-Ph). Due to the instability of the compound, satisfactory elemental analysis result was not obtained. To the NMR sample of **5c** was added an excess of MeI. After standing overnight, the sample was diluted with MeOH and subjected to mass spectroscopy. [C₁₆H₂₆N₄ + H]⁺ m/z calc. 275.2236, found 275.2235.

2. IR spectrum of KN₃

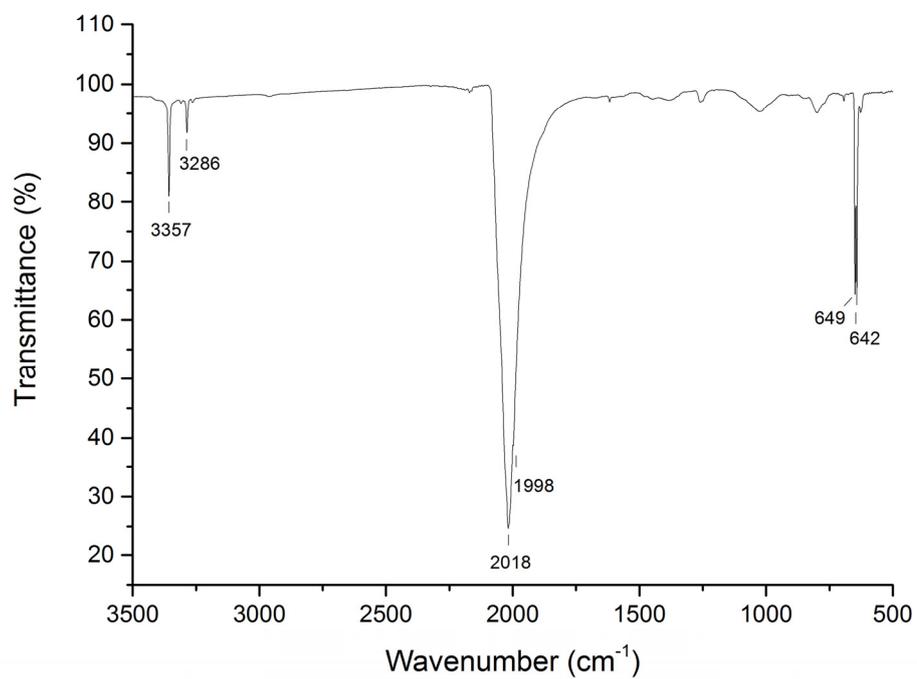
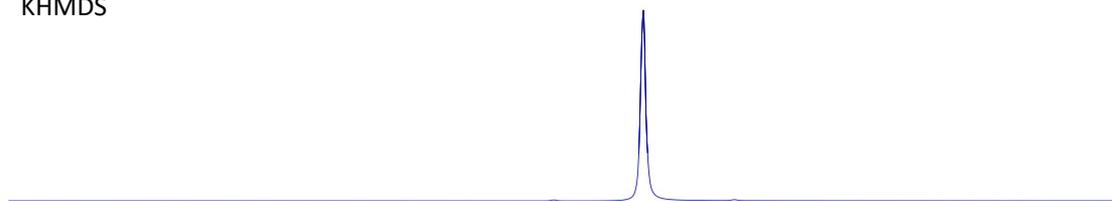


Figure S 1 The IR spectrum of KN₃.

3. Copies of NMR spectra

KHMDS



KHMDS + N₂O



TMSOTMS

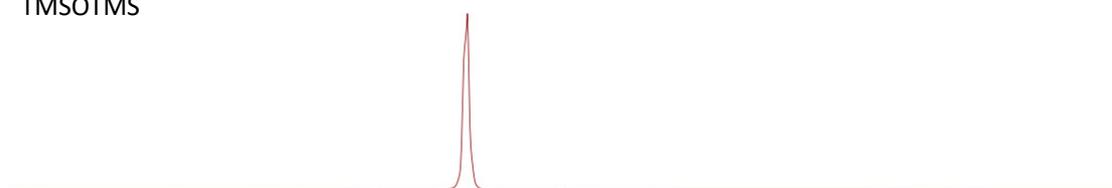


Figure S 2 The ¹H NMR monitoring of KHMDS in THF-d₈ under 1 atmosphere of N₂O.

YZL690
crude

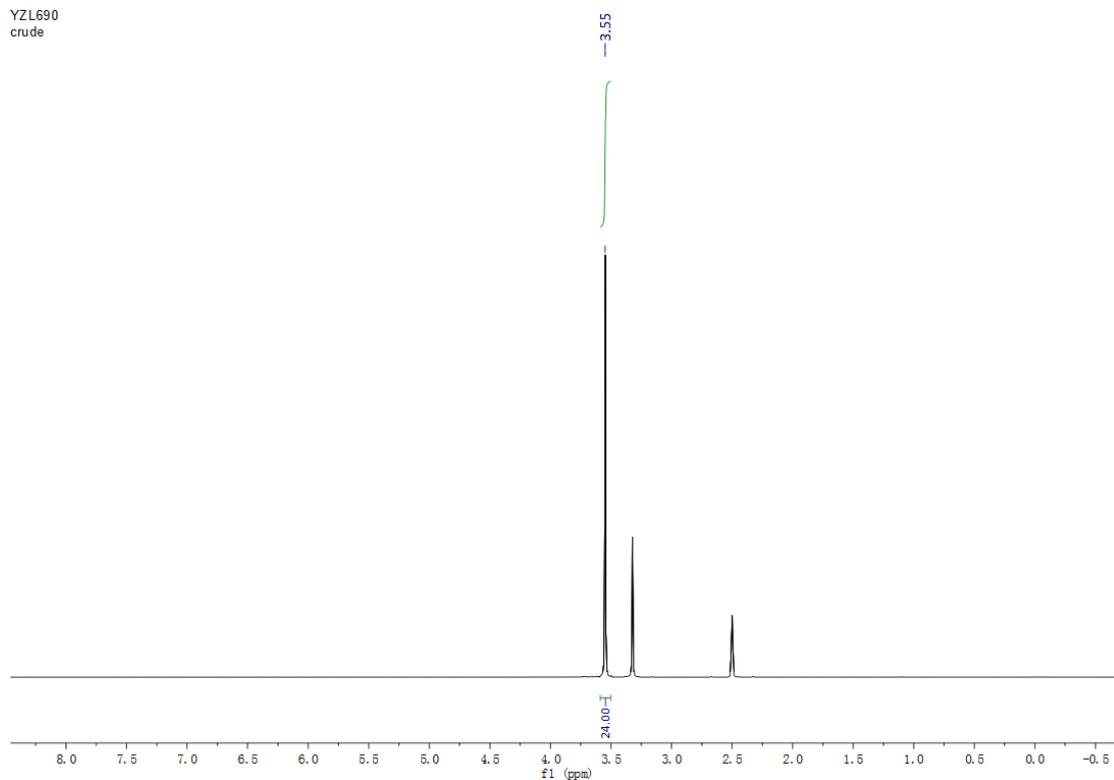


Figure S 3 ¹H NMR spectrum of [K(18-crown-6)]N₃.

YZL690
crude

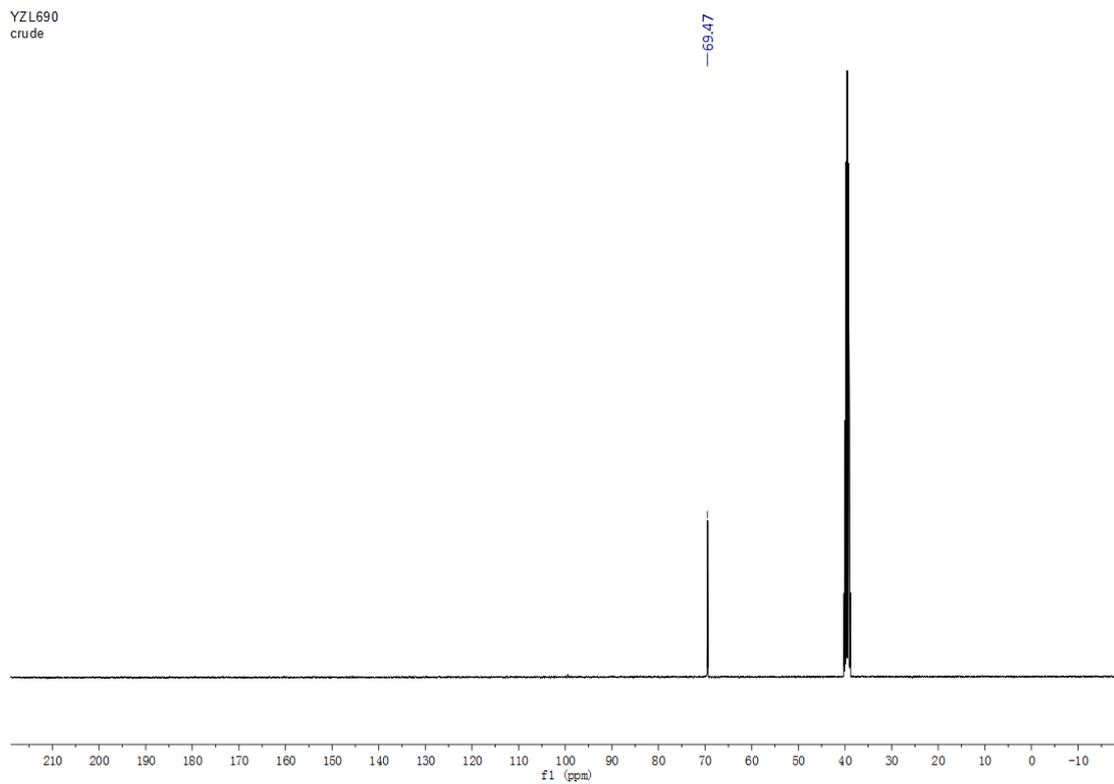


Figure S 4 ¹³C NMR spectrum of [K(18-crown-6)]N₃.

YZL691
crude

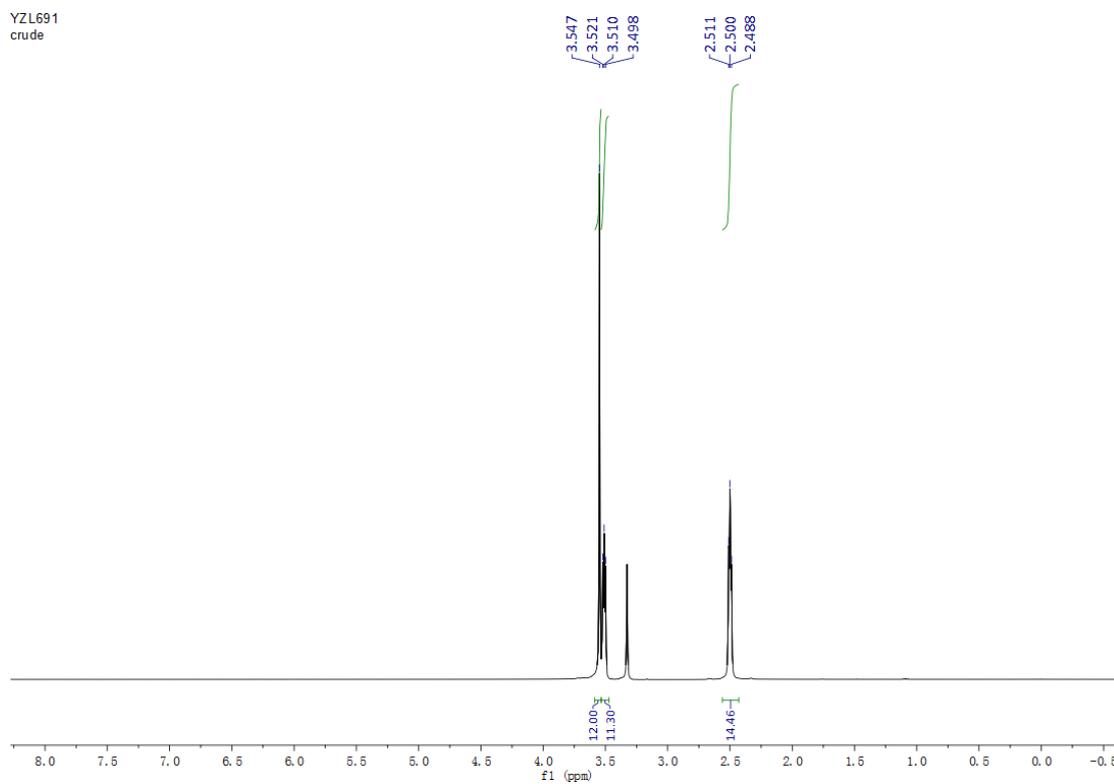


Figure S 5 ¹H NMR spectrum of [K(2.2.2-cryptand)]N₃ in DMSO-d₆.

YZL691
crude

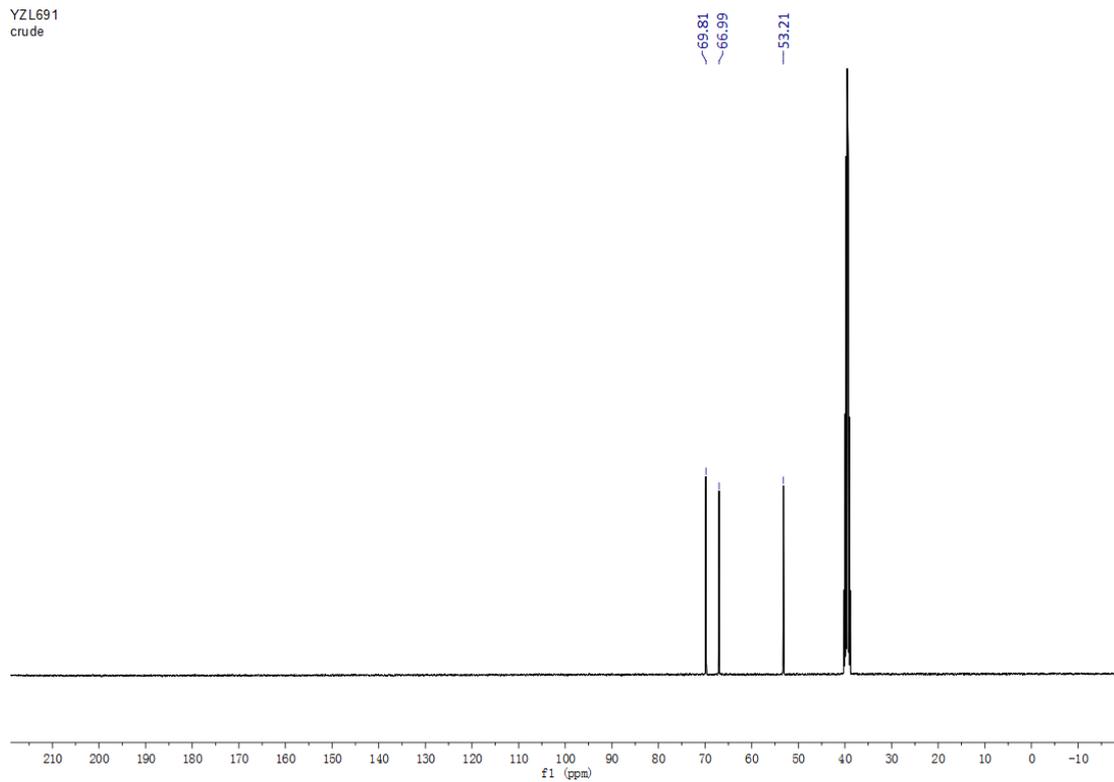


Figure S 6 ^{13}C NMR spectrum of $[\text{K}(2.2.2\text{-cryptand})]\text{N}_3$ in DMSO-d_6 .

YZL613

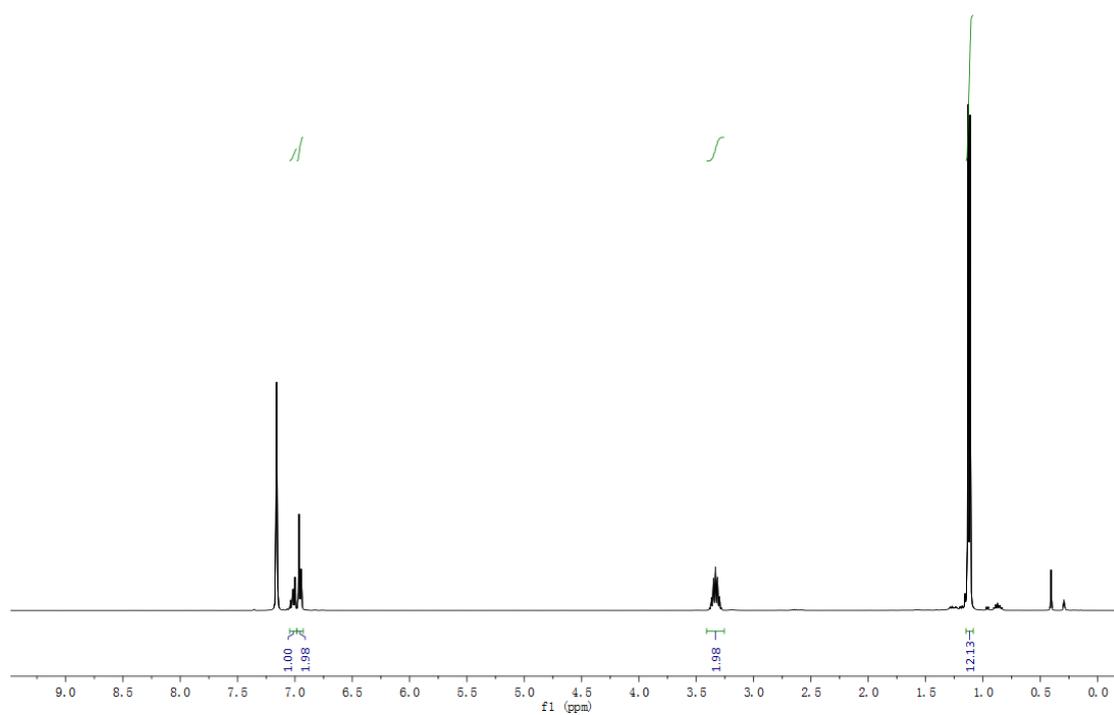


Figure S 7 The ^1H NMR spectrum of **3a** in C_6D_6 .

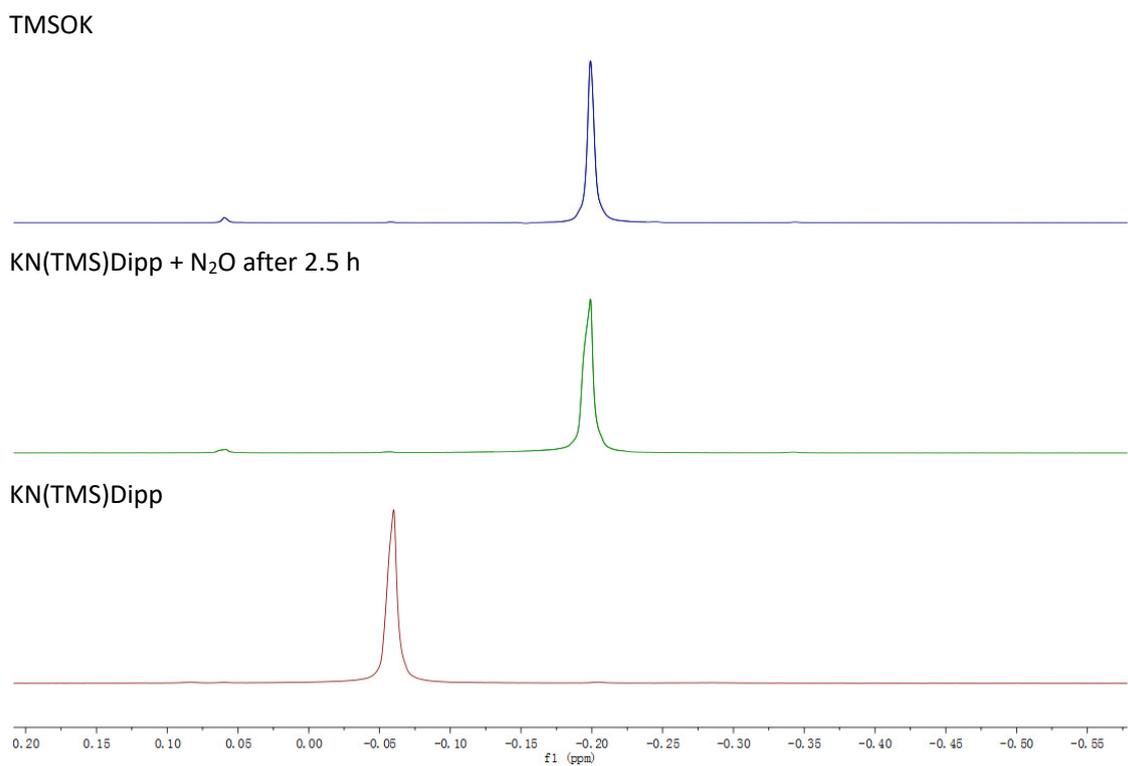
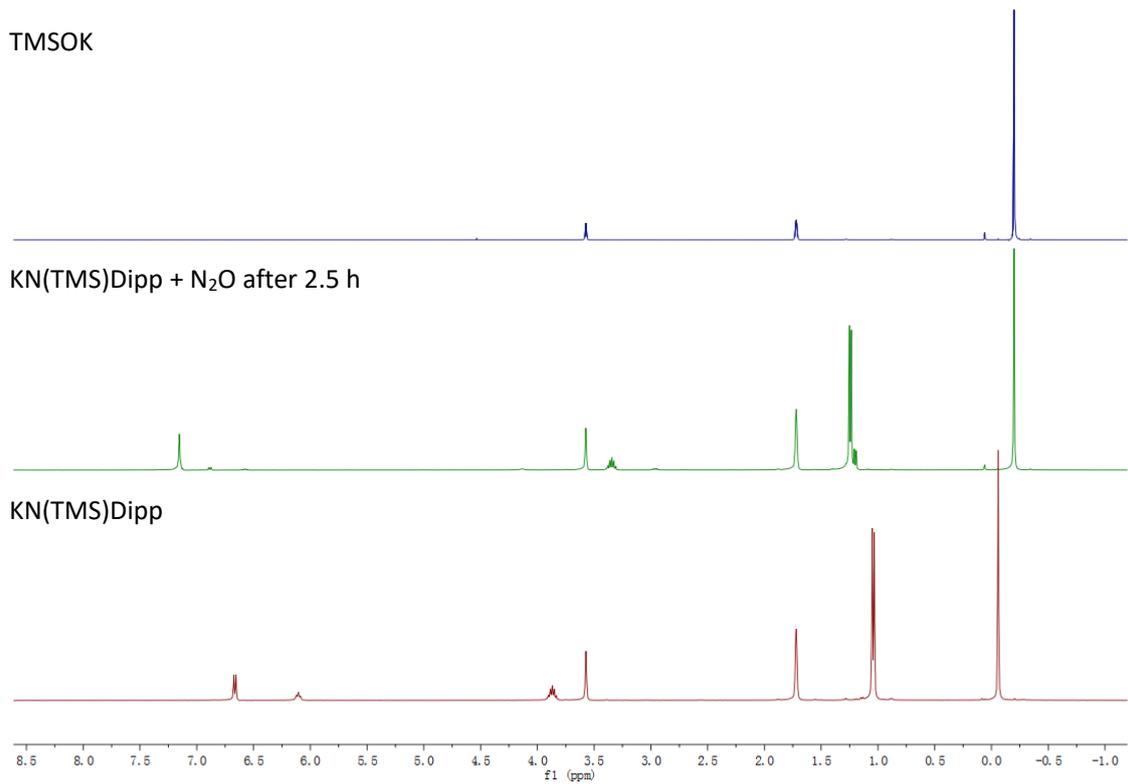


Figure S 8 The ¹H NMR monitoring of KN(TMS)Dipp in THF-d₈ under 1 atmosphere of N₂O.

YZ1628
Et2O wash and reprecip, bulk 24 hr

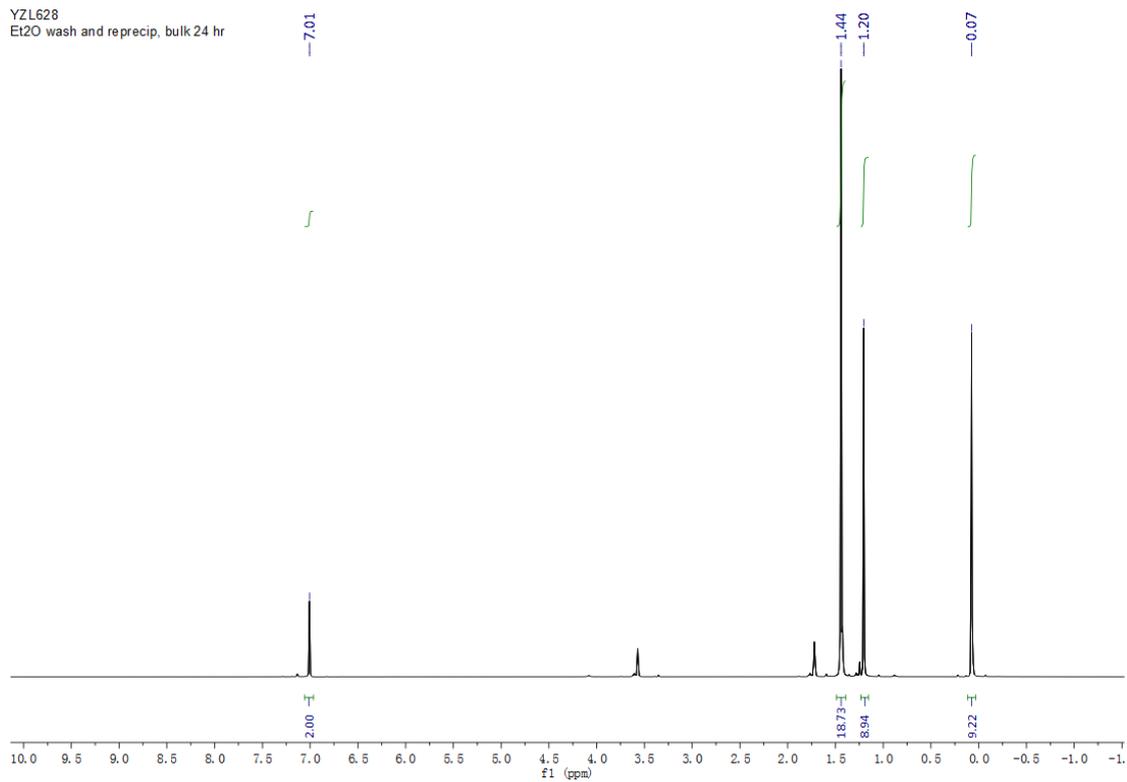


Figure S 9 ^1H NMR spectrum of $\text{KN}(\text{TMS})\text{Mes}^*$ in THF-d_8 .

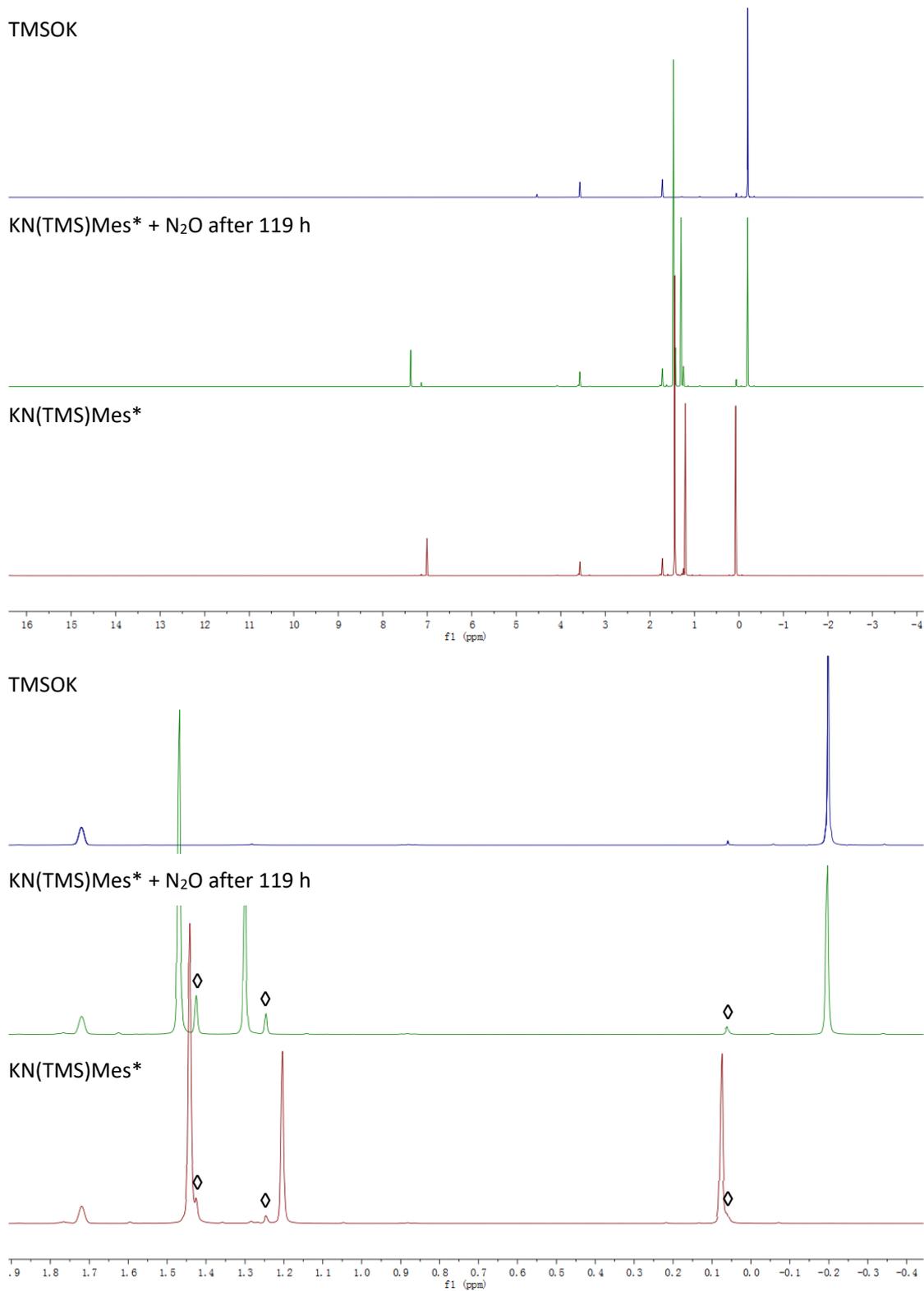


Figure S 10 The ^1H NMR monitoring of KN(TMS)Mes* in THF-d₈ under 1 atmosphere of N₂O. '◊' denotes the impurity peaks pre-existed in the starting KN(TMS)Mes*.

TMSOLi



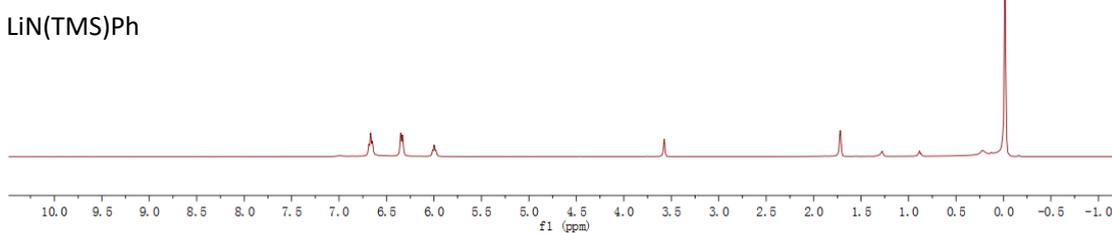
Authentic PhN₃



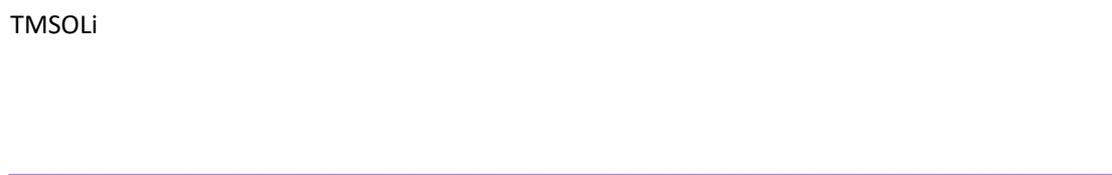
LiN(TMS)Ph + N₂O after 24 h



LiN(TMS)Ph



TMSOLi



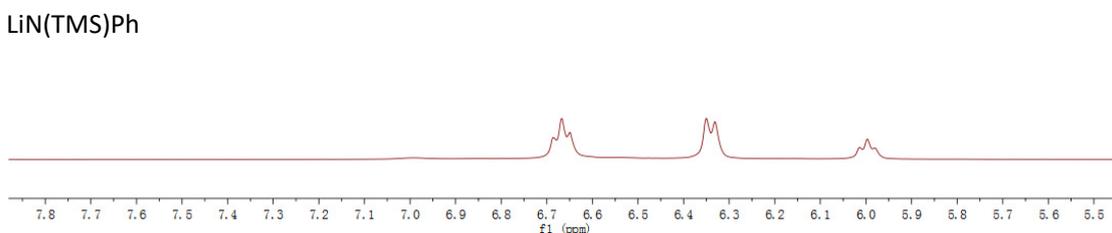
Authentic PhN₃



LiN(TMS)Ph + N₂O after 24 h



LiN(TMS)Ph



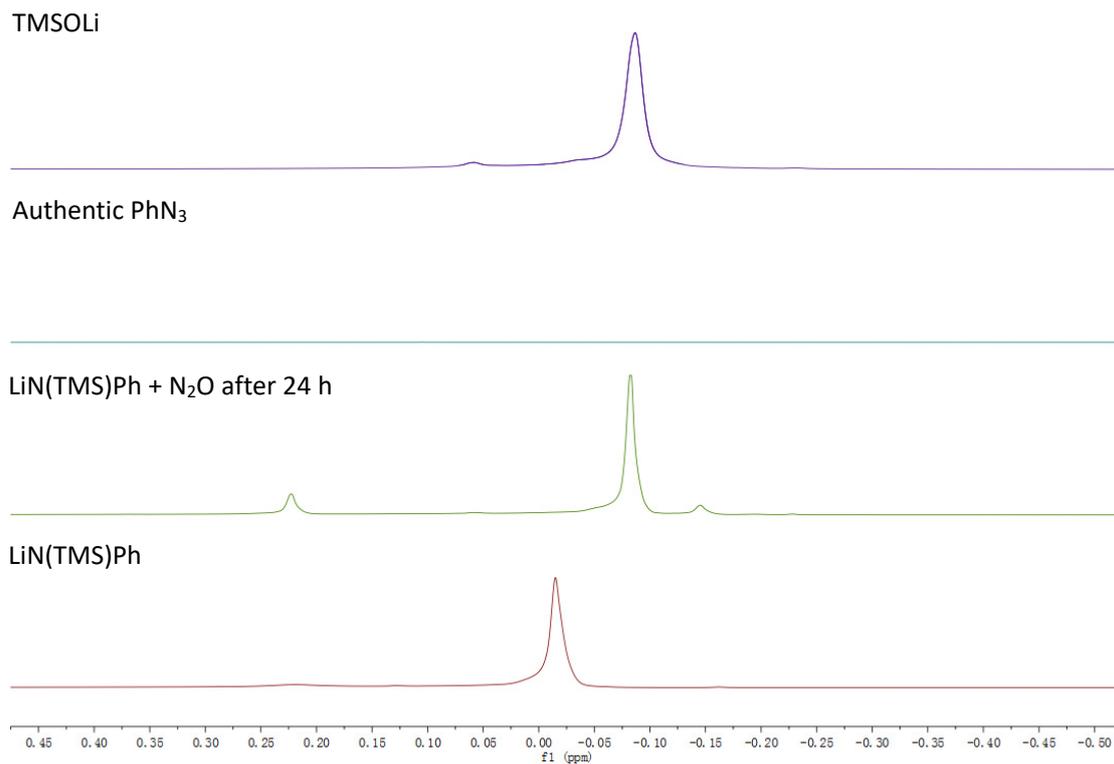


Figure S 11 The ¹H NMR monitoring of LiN(TMS)Ph in THF-d₈ under 1 atmosphere of N₂O.

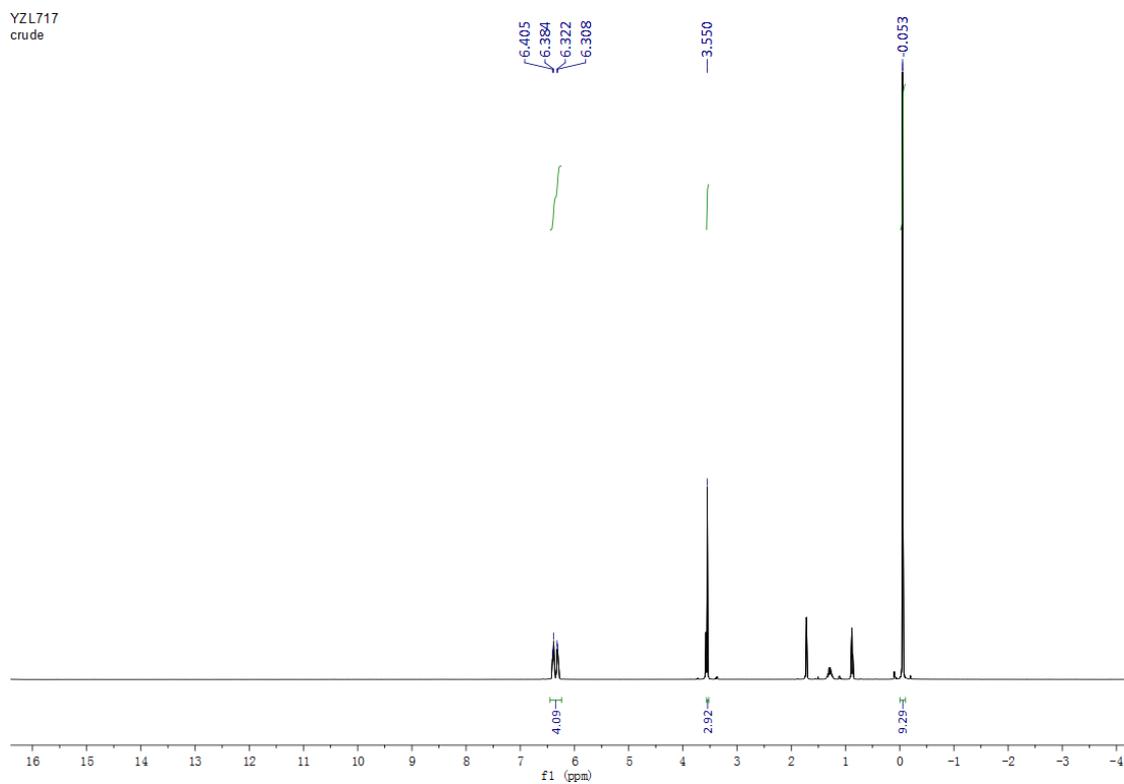
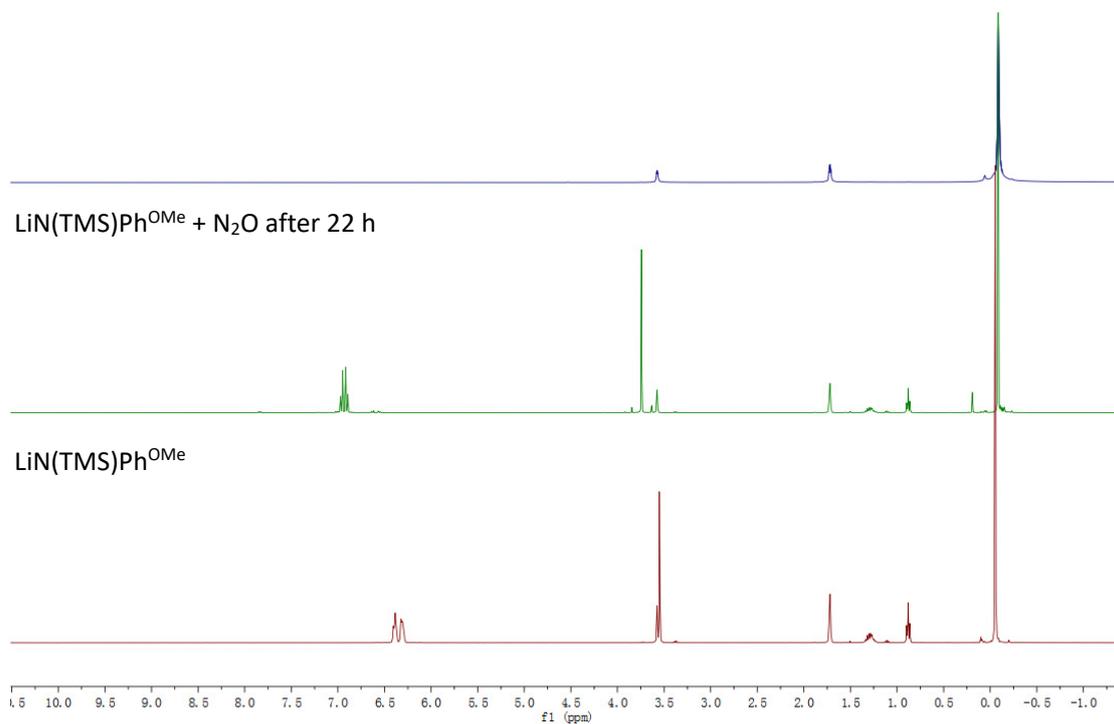


Figure S 12 ¹H NMR spectrum of LiN(TMS)Ph^{OMe} in THF-d₈.

TMSOLi



TMSOLi

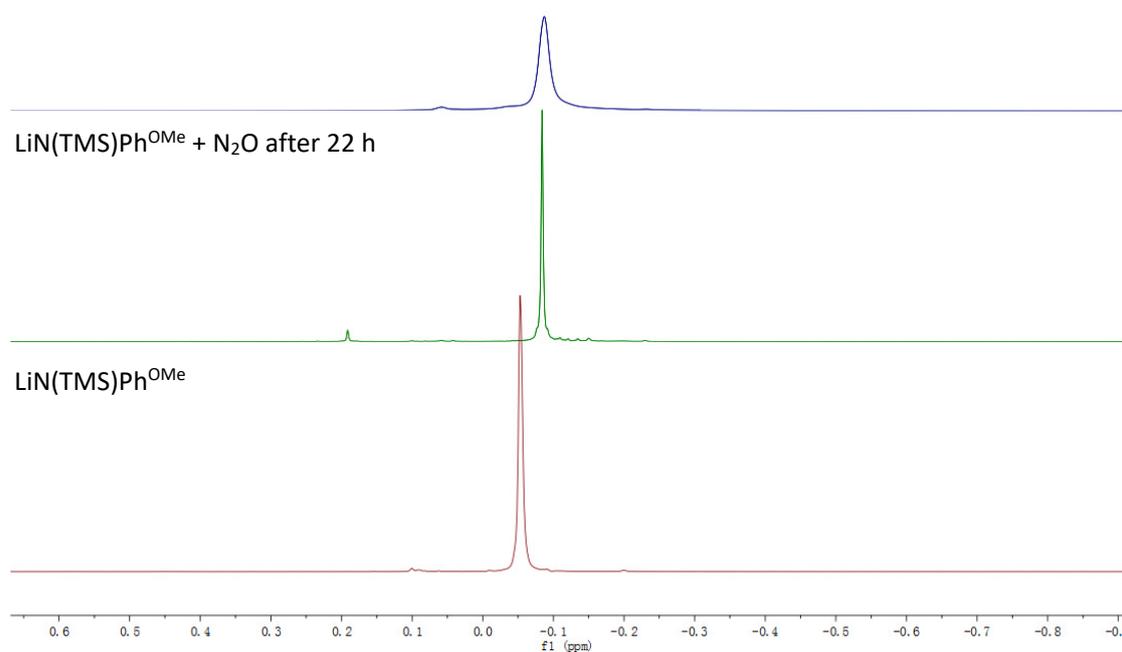


Figure S 13 The ¹H NMR monitoring of LiN(TMS)Ph^{OMe} in THF-d₈ under 1 atmosphere of N₂O.

YZL746
crude

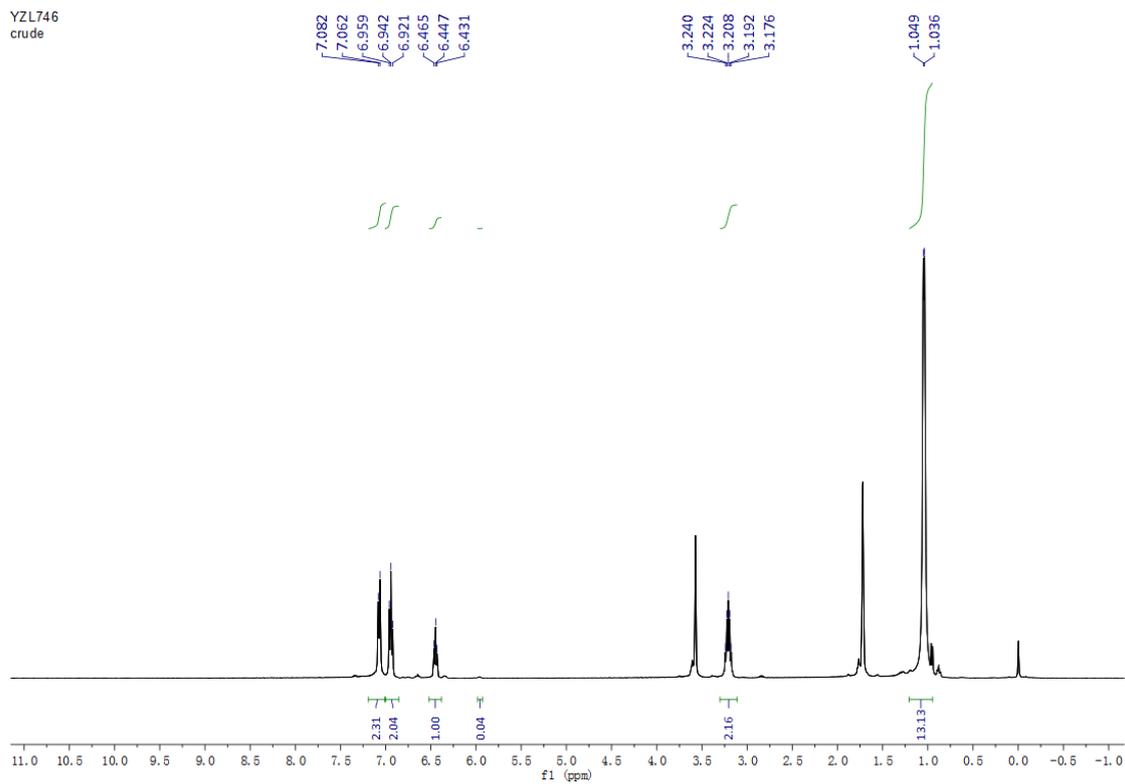


Figure S 14 ¹H NMR spectrum of 5a in THF-d8.

YZL746
crude

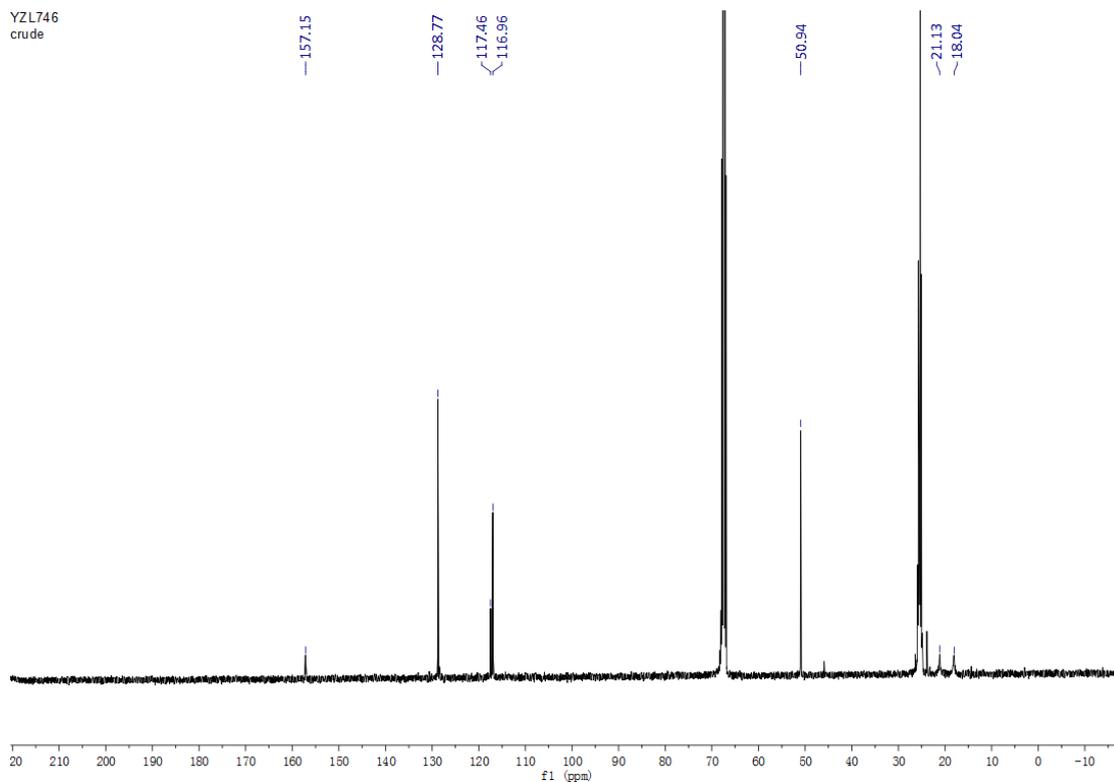


Figure S 15 ¹³C NMR spectrum of 5a in THF-d8.

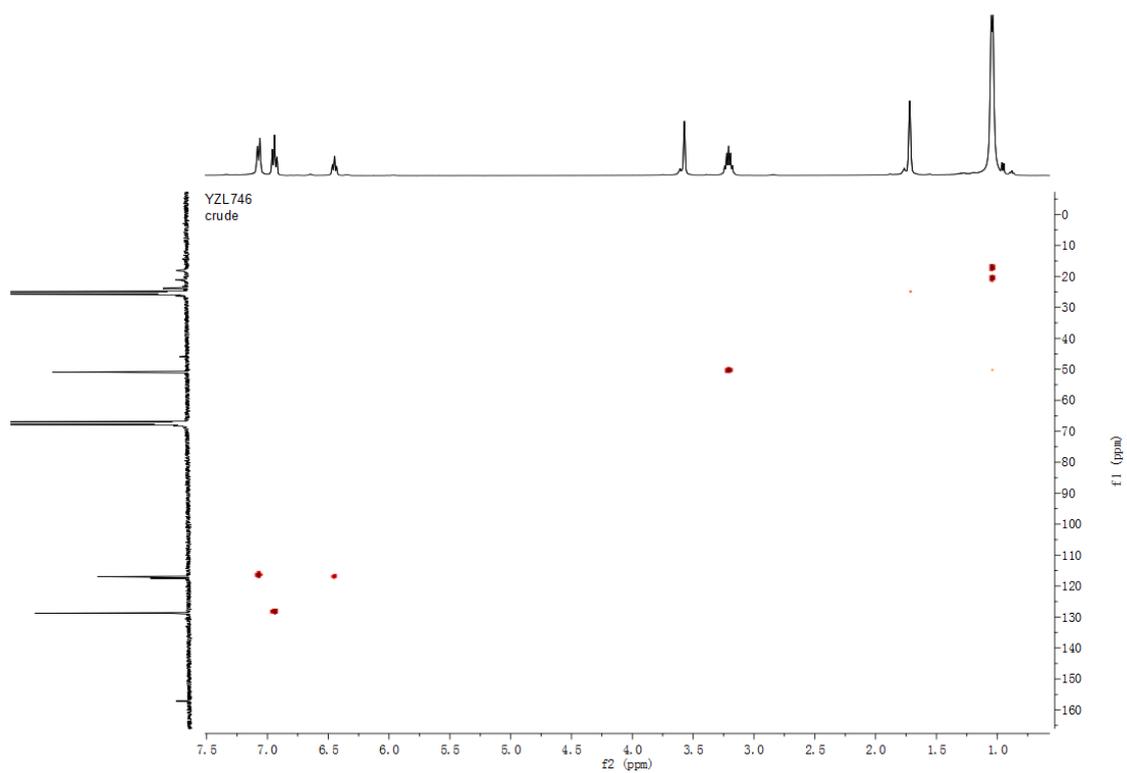


Figure S 16 HSQC spectrum of **5a** in THF-d8.

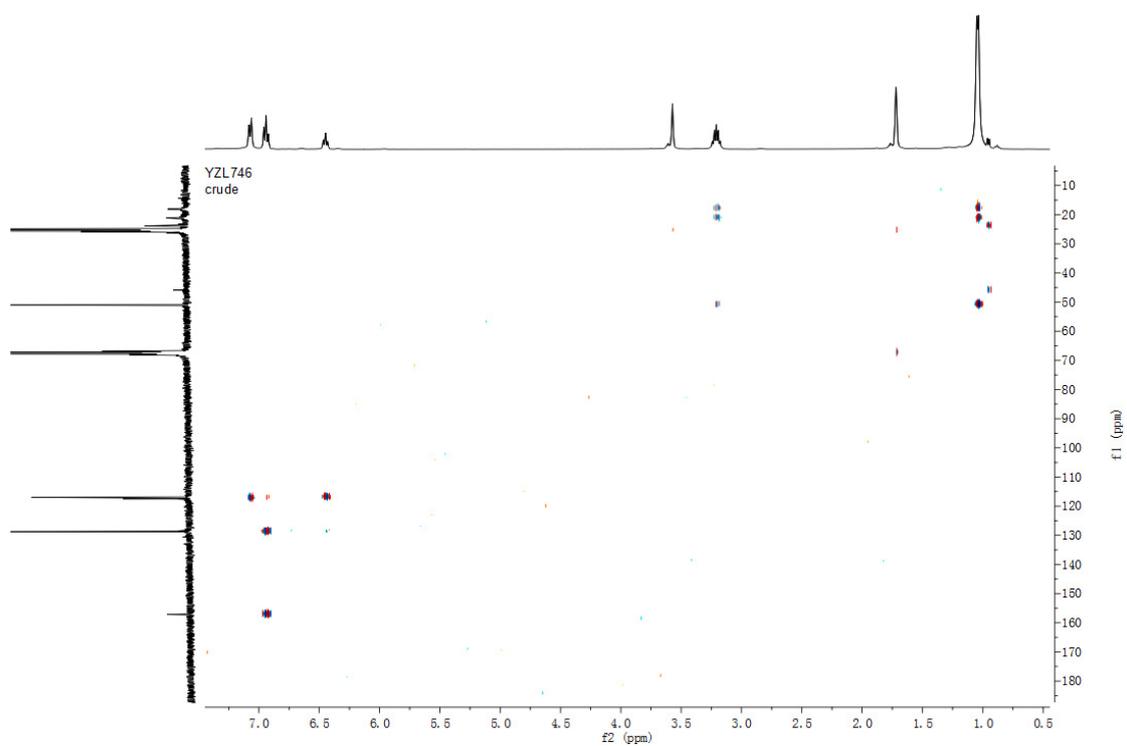


Figure S 17 HMBC spectrum of **5a** in THF-d8.

YZL770

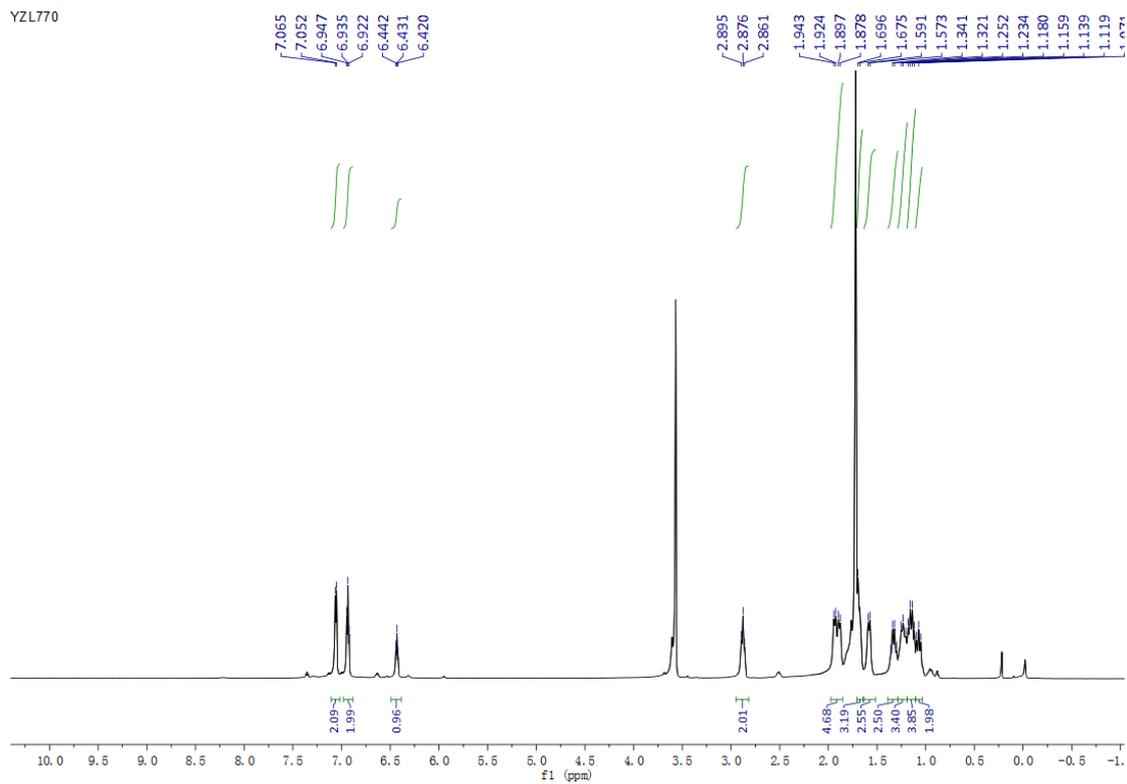


Figure S 18 ^1H NMR spectrum of **5b** in THF- d_8 at 0 °C.

YZL770

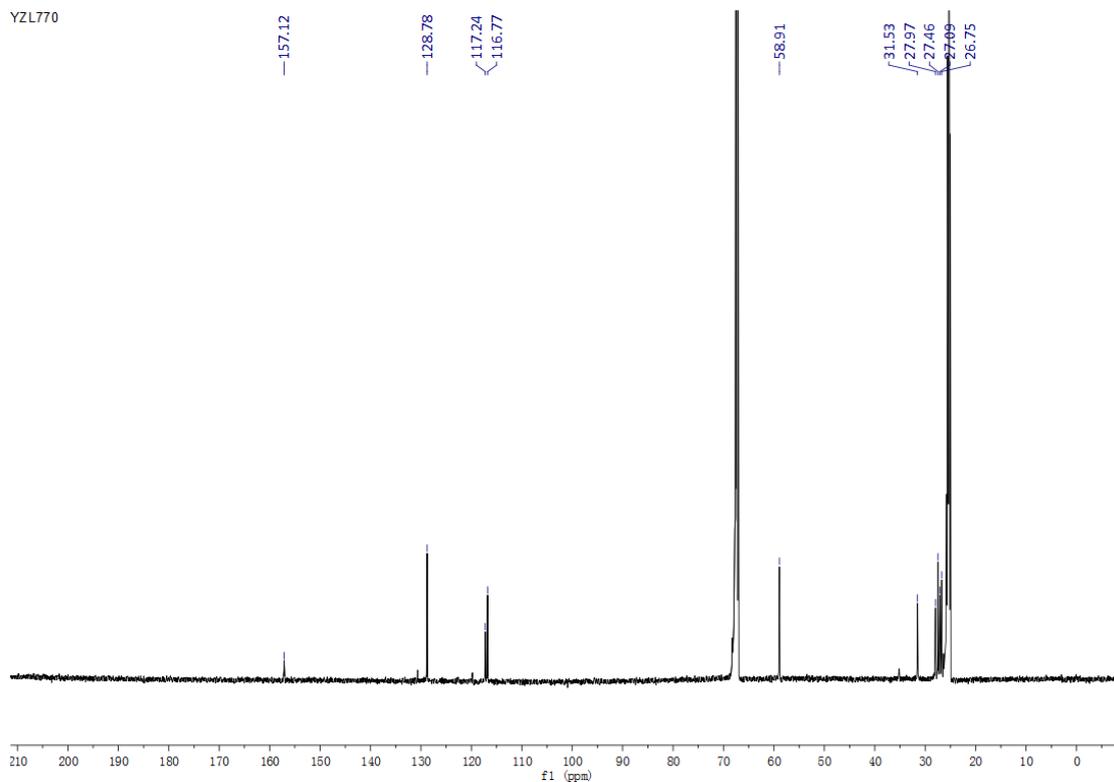


Figure S 19 ^{13}C NMR spectrum of **5b** in THF- d_8 at 0 °C.

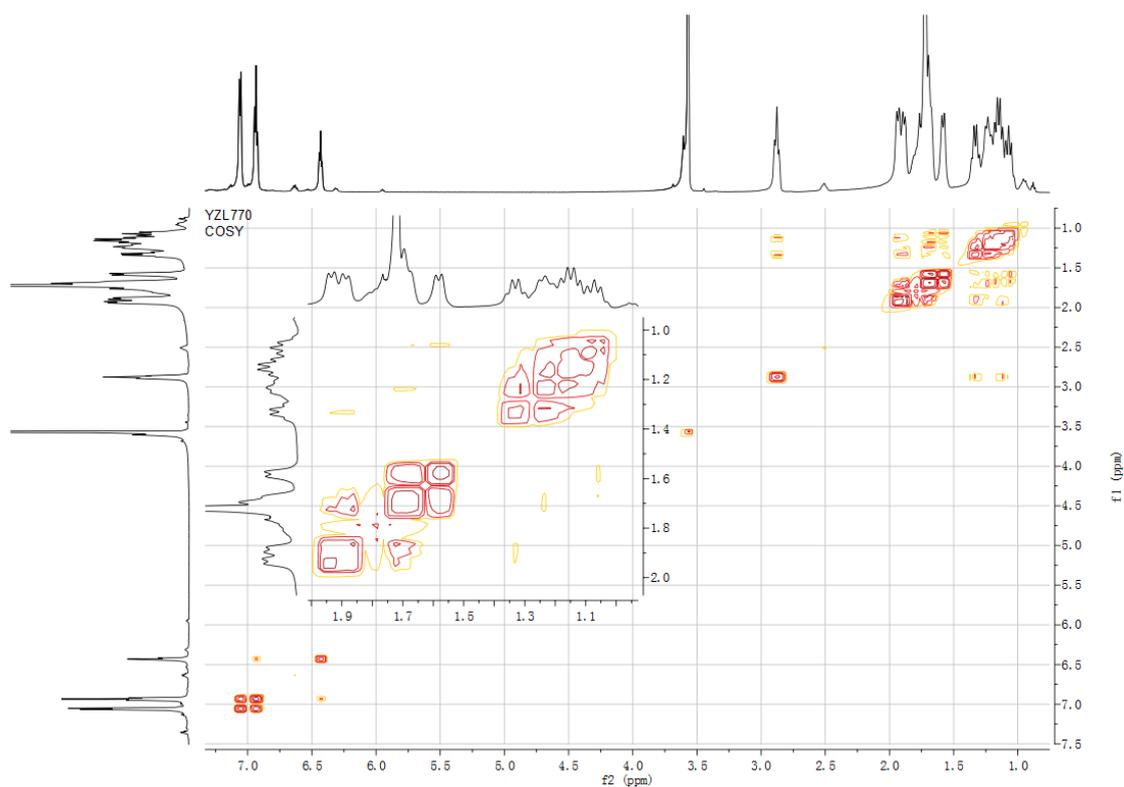


Figure S 20 COSY spectrum of **5b** in THF-d8 at 0 °C. The inset shows the zoomed correlation between 2–6-Cy protons.

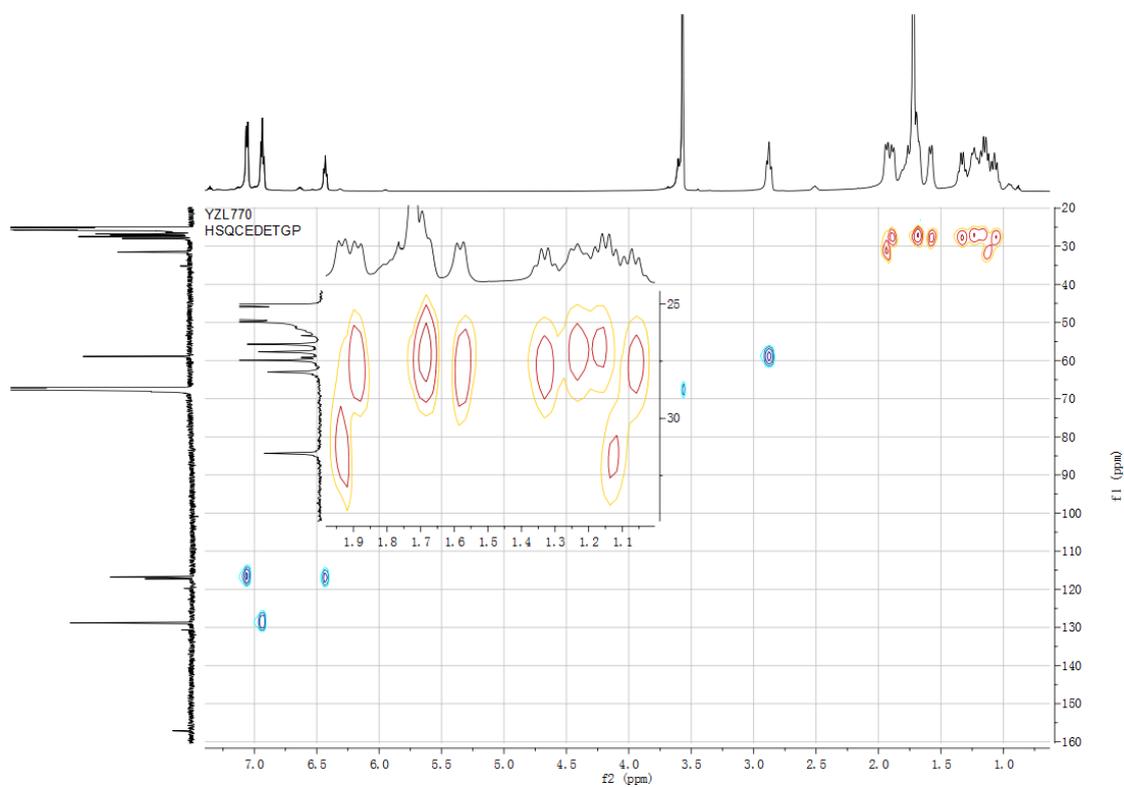


Figure S 21 HSQC spectrum of **5b** in THF-d8 at 0 °C. The inset shows the zoomed correlation between 2–6-Cy carbons and protons.

YZL751
crude

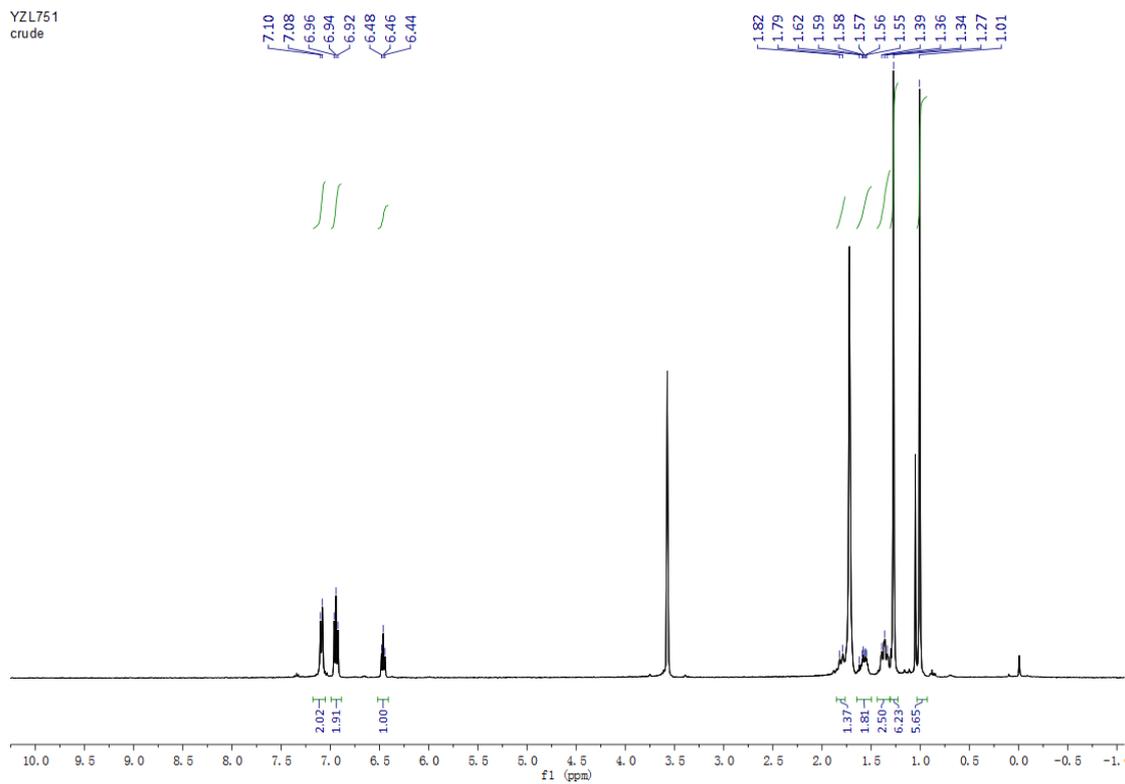


Figure S 22 ^1H NMR spectrum of **5c** in THF-d₈.

YZL751

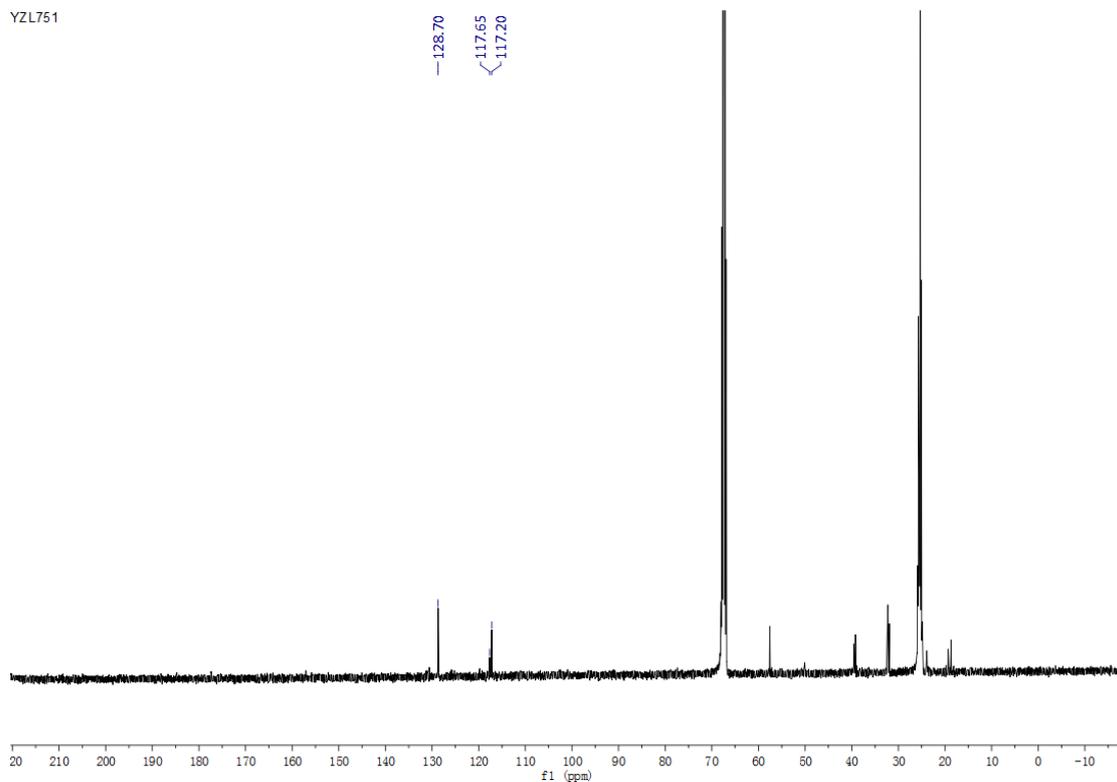


Figure S 23 ^{13}C NMR spectrum of **5c** in THF-d₈.

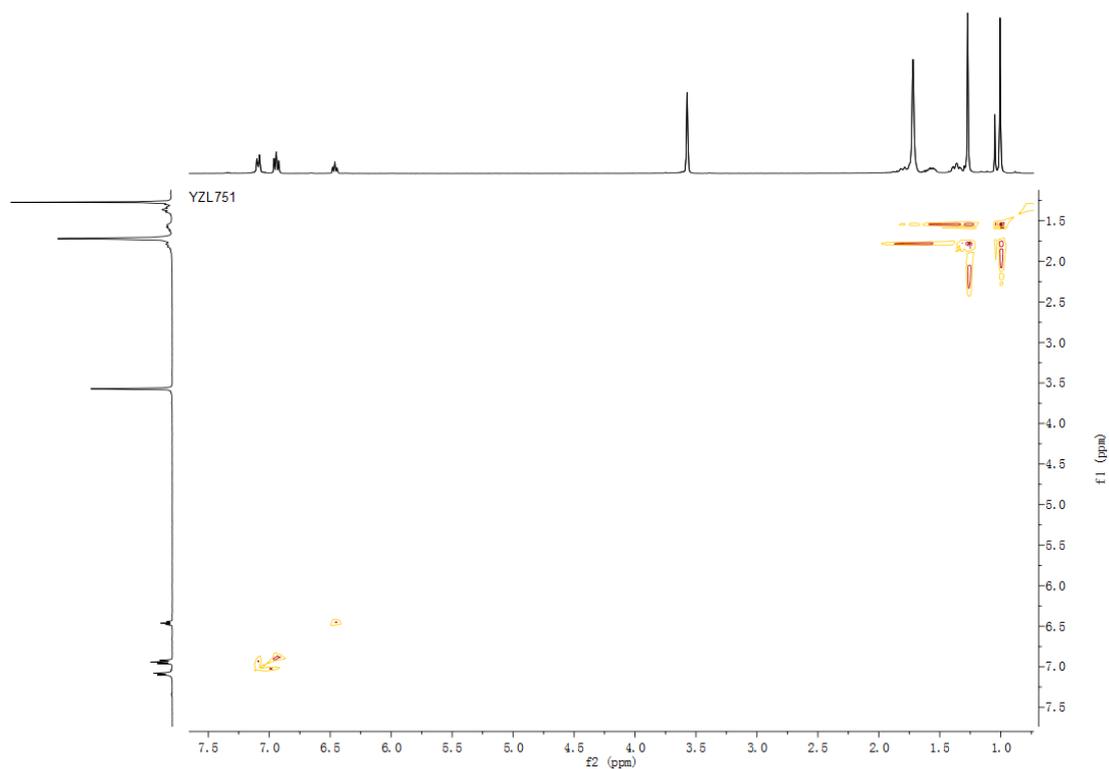


Figure S 24 COSY spectrum of **5c** in THF-d8.

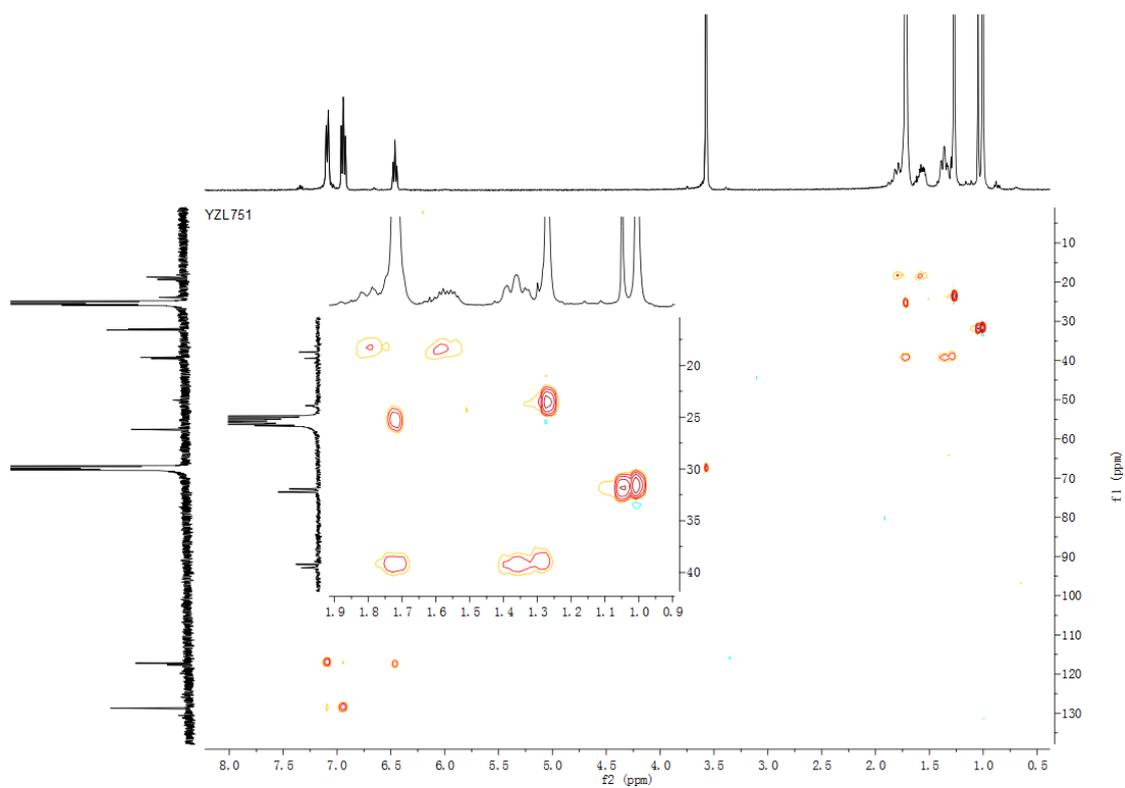


Figure S 25 HSQC spectrum of **5c** in THF-d8. The inset shows the zoomed correlation between aliphatic carbons and protons.

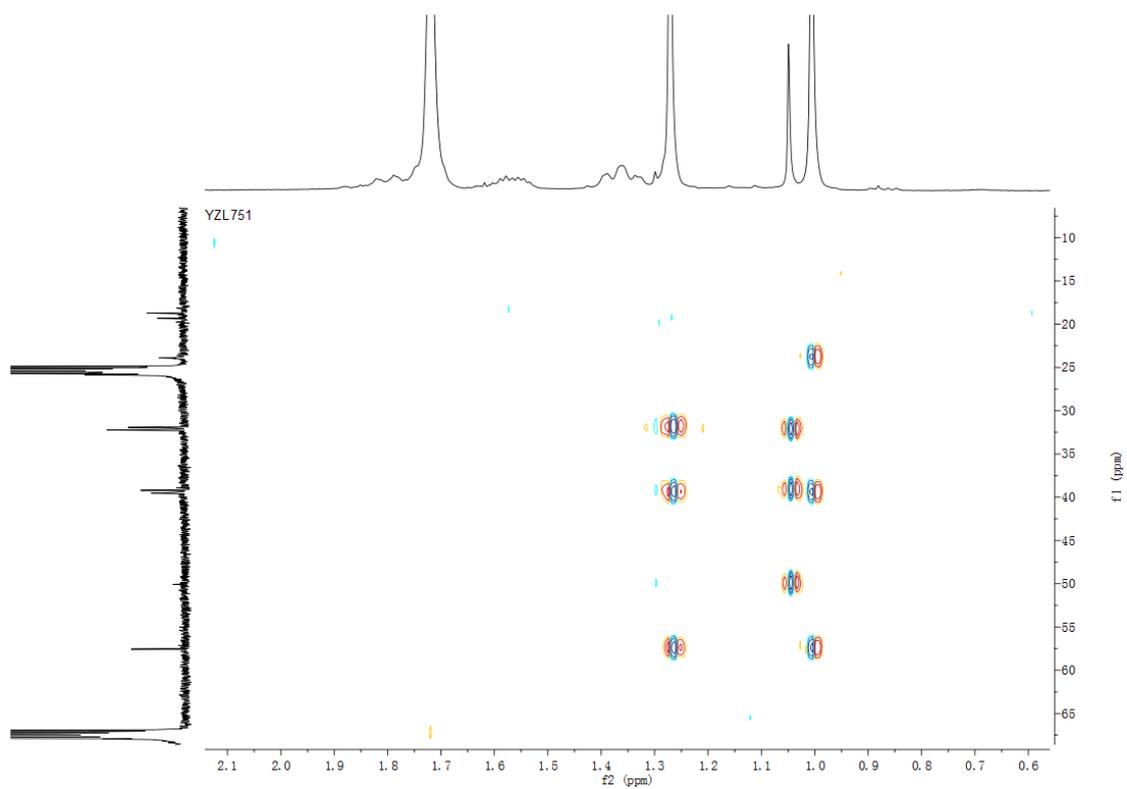


Figure S 26 HMBC spectrum of **5c** in THF-d8 with zoomed aliphatic region.

4. X-ray structure of $[\text{K}(\text{18-crown-6})]\text{N}_3$

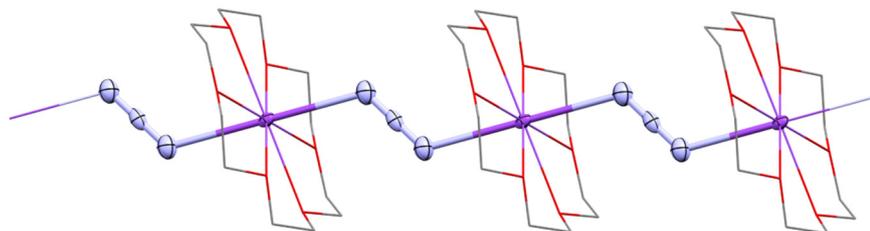


Figure S 27 The crystal structure of $[\text{K}(\text{18-crown-6})]\text{N}_3$.

5. Crystallographic data

Bragg-intensities of **4**, **5a** and **[K(18-crown-6)]N₃** were measured at low temperature using Cu K α radiation on a Rigaku SuperNova dual system diffractometer equipped with an Atlas type CCD detectors. The datasets were reduced and then corrected for absorption by means of CrysAlisPro,⁹ with the help of a set of faces enclosing the crystals as snugly as possible.

The structures were solved and then refined by SHELXT¹⁰ and SHELXL-2018 (release 3),¹¹ respectively. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom.

The structure of **4** was refined as a two-component inversion twin yielding a BASF parameter of 0.5(8).

CCDC numbers 1854213-5 for compounds **[K(18-crown-6)]N₃**, **4** and **5a** contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

⁹ *CrysAlis PRO*. Rigaku Oxford Diffraction 2015.

¹⁰ G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3–8.

¹¹ G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3–8.

Table S1. Crystal data and structure refinement for **4**, **5a** and **[K(18-crown-6)]N₃**.

	4	5a	[K(18-crown-6)]N₃
Empirical formula	C ₁₀ H ₁₃ LiN ₂ O	C ₁₂ H ₁₉ LiN ₄	C ₁₂ H ₂₄ KN ₃ O ₆
Formula weight	184.16	226.25	345.44
Temperature/K	100.00(10)	140.00(10)	140.00(10)
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
Crystal system	tetragonal	orthorhombic	monoclinic
Space group	$P\bar{4}2_1c$	$Pbca$	$P2_1/c$
a/Å	15.1759(11)	9.4084(3)	7.94945(15)
b/Å	15.1759(11)	14.9712(5)	13.91619(19)
c/Å	8.7134(8)	18.6036(7)	7.49899(13)
α /°	90	90	90
β /°	90	90	96.5035(16)
γ /°	90	90	90
Volume/Å ³	2006.8(3)	2620.42(16)	824.24(2)
Z	8	8	2
$\rho_{\text{calc}}/\text{cm}^3$	1.219	1.147	1.392
μ/mm^{-1}	0.623	0.546	3.115
F(000)	784.0	976.0	368.0
Crystal size/mm ³	0.450 × 0.076 × 0.064	0.247 × 0.219 × 0.093	0.762 × 0.468 × 0.134
2 θ range for data collection/°	8.24 to 152.442	9.508 to 150.684	11.202 to 152.58
Index ranges	-18 ≤ h ≤ 18 -18 ≤ k ≤ 18 -8 ≤ l ≤ 10	-11 ≤ h ≤ 11 -12 ≤ k ≤ 18 -23 ≤ l ≤ 22	-9 ≤ h ≤ 9 -17 ≤ k ≤ 12 -9 ≤ l ≤ 9
Reflections collected	11932	18442	6751
Independent reflections	2066 [$R_{\text{int}} = 0.0425$]	2692 [$R_{\text{int}} = 0.0419$]	1710 [$R_{\text{int}} = 0.0198$]
Data/restraints/parameters	2066/0/128	2692/0/230	1710/0/104
Goodness-of-fit on F^2	1.098	1.056	1.042
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0777$ $wR_2 = 0.2109$	$R_1 = 0.0401$ $wR_2 = 0.1041$	$R_1 = 0.0240$ $wR_2 = 0.0646$
Final R indexes [all data]	$R_1 = 0.0828$ $wR_2 = 0.2183$	$R_1 = 0.0537$ $wR_2 = 0.1129$	$R_1 = 0.0246$ $wR_2 = 0.0651$
Largest diff. peak/hole / e Å ⁻³	0.66/-0.35	0.43/-0.22	0.28/-0.18