Electronic Supplementary Information

Unexpected intramolecular *N*-arylcyano-β-diketiminate cyclization in new aminoquinoline derivatives complexes of aluminium for CO_2 fixation into cyclic carbonates

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Experimental Section

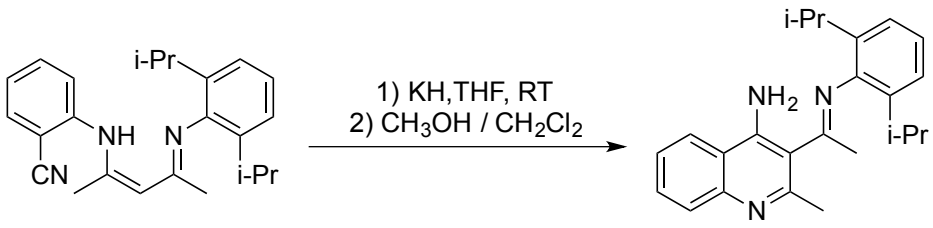
All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from commercial sources, unless otherwise specified. Toluene, dichloromethane and hexane were dried using an Innovative Technology Pure Solv Model PS-MD-5. NMR spectra were recorded on NMR Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [^{1}H and ^{13}C, $\delta(SiMe_4) = 0$] or an external standard [$\delta(BF_3OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR]. Most NMR assignments were supported by additional 2D experiments. HRMS-ESI-MS experiments were carried out using a Thermo Scientific Exactive Plus Orbitrap Spectrometer. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets.

X-Ray diffraction: Data sets for compound **L3** were collected with a Bruker D8 Venture CMOS diffractometer. For compounds **C4** and **L6** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP* (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

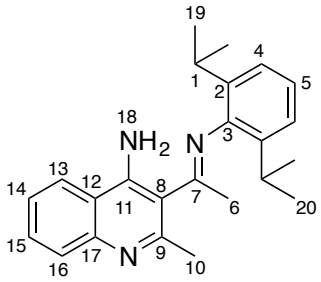
Exceptions and special features: For compound **L3** one *i*Pr group was found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

Synthesis and Characterization of Compounds.

(E)-3-(1-(2,6-diisopropylphenylimino)ethyl)-2-methylquinolin-4-amine (L3).



2-((2Z,4E)-4-(2,6-diisopropylphenylimino)pent-2-en-2-ylamino)benzonitrile (**L_1**)[1] (1,00 g, 2.78 mmol), potassium hydride (0,11 g, 2.78 mmol) and 50 mL of anhydrous THF were added in a dried Schlenk under N_2 atmosphere and the mixture was stirred for 2 hours at room temperature. The reaction evidence hydrogen formation (H_2). When the reaction finished, the mixture was filtered through celite and the solution was transferred to a sealed round flask fitted with Teflon screw cap, heated at 90 °C and stirred for 3 hours. The orange solution was evaporated in vacuum to dryness and the remaining solid was dissolved in 30 mL of methanol / dichloromethane and washed twice with 30 ml of distilled water. The organic phase was dried with anhydrous Na_2SO_4 and concentrated to dryness. Crude product was purified via silica gel chromatography (1:1 Petroleum ether / ethyl acetate). **L3** was obtained as a colorless crystals (0.80 g, 80%).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 7.93 (d, *J* = 8.4 Hz, 1H, H_{16}), 7.80 (d, *J* = 8.3 Hz, 1H, H_{13}), 7.64 (t, *J* = 7.6 Hz, 1H, H_{15}), 7.42 (t, *J* = 7.6 Hz, 1H, H_{14}), 7.23 (d, *J* = 7.6 Hz, 2H, H_4), 7.16 (t, 1H, H_5), 6.24 (s, 2H, H_{18}), 3.02 (hept, 2H, H_1), 2.75 (s, 3H, H_{10}), 2.09 (s, 3H, H_6), 1.29 (d, *J* = 7.0 Hz, 6H, H_{20}), 1.21 (d, *J* = 6.8 Hz, 6H, H_{19}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 170.52 (C_7), 156.28 (C_9), 147.85 (C_{11}), 147.32 (C_{17}), 145.52 (C_2), 135.97 (C_3), 129.96 (C_{15}), 128.99 (C_{16}), 124.75 (C_{14}), 124.34 (C_5), 123.48 (C_4), 120.67 (C_{13}), 117.63 (C_{12}), 115.15 (C_8), 28.41 (C_1), 25.88 (C_{10}), 24.01 (C_{19}), 23.75 (C_6), 23.21 (C_{20}).

[1] Oleksandra S. Trofymchuk, Dmitry V. Gutsulyak, Celso Quintero, Masood Parvez, Constantin G. Daniliuc, Warren E. Piers, Rene S. Rojas, *Organometallics*, **2013**, *32* (24), 7323–7333.

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 7.93/124,75, 117.63 ($H_{16}/C_{14,12}$), 7.80/147.32, 129.96, 117.63 ($H_{13}/C_{17,15,12}$), 7.64/147.32, 124.75, 120.67 ($H_{15}/C_{17,14,13}$), 7.42/128.99, 117.63 (H14/$C_{16,12}$), 7.23/145.52, 135.97, 28.41 ($H_4/_{C2,3,1}$), 7.16/145.52, 135.97 ($H_5/C_{2,3}$), 6.24/117.63, 115.15 ($H_{18}/C_{12,8}$), 3.02/145.52, 135.97, 123.48, 24.01, 23.21 ($H_1/C_{2,3,4,19,20}$), 2.75/156.28, 115.15 ($H_{10}/C_{9,8}$), 2.09/170.52, 135.97, 115.15 ($H_6/C_{7,3,8}$)

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 7.93/128.99 (H_{16}/C_{16}), 7.80/120.67 (H_{13}/C_{13}), 7.64/126.96 (H_{15}/C_{15}), 7.42/124.75 (H_{14}/C_{14}), 7.23/123.48 (H_4/C_4), 7.16/124.34 (H_5/C_5), 3.02/28.41 (H_1/C_1), 2.75/25.88 (H_{10}/C_{10}), 2.09/23.75 (H_6/C_6), 1.29, 1.21/23.21, 24.01 ($H_{20,19}/C_{20,21}$).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.93/7.65 (H_{16}/H_{15}), 7.80/7.42 (H_{13}/H_{14}), 7.64/7.42 (H_{15}/H_{14}), 7.23/7.16 (H_4/H_5), 3.02/1.29, 1.21 ($H_1/H_{20,19}$).

NOESY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 6.24/7.64, 3.02 ($H_{18}/H_{15,1}$), 2.75/2.09 (H_{10}/H_6), 1.29, 1.21/2.09 ($H_{20,19}/H_6$).

FT-IR (KBr): ν / cm^{-1} = 3385, 3288, 3144, 3057, 2959, 2925, 2866, 1624, 1561, 1492, 1458, 1435, 1375, 1363, 1327, 1307, 1236, 1186, 1145, 1123, 1098, 1045, 982, 954, 934, 877, 818, 796, 767, 756, 693, 629, 607.

HRMS (ESI): m/z $[M+H]^+$ for $C_{24}H_{30}N_3$: calc: 360.2440; found: 360.2429.

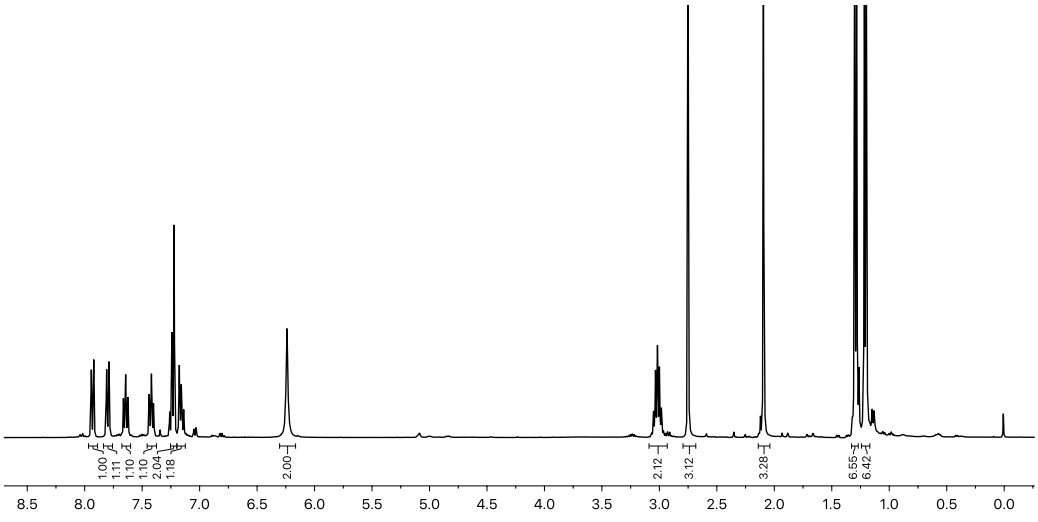


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

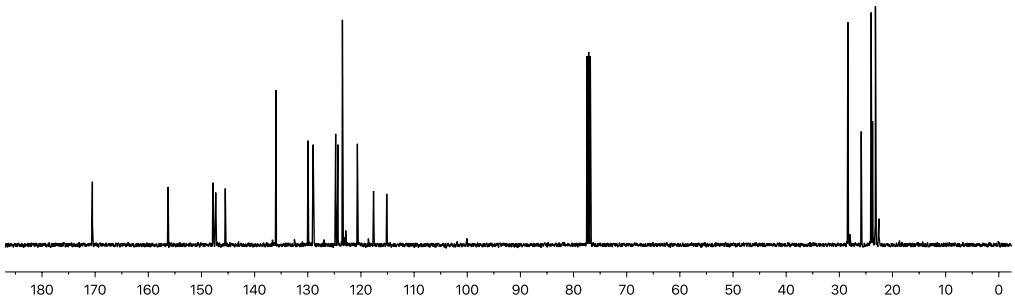


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

X-ray crystal structure analysis of L3: A colorless prism-like specimen of $C_{24}H_{29}N_3$, approximate dimensions 0.084 mm x 0.138 mm x 0.249 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1759 frames were collected. The total exposure time was 23.79 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 41845 reflections to a maximum θ angle of 66.92° (0.84 Å resolution), of which 3670 were independent (average redundancy 11.402, completeness = 99.6%, R_{int} = 4.31%, R_{sig} = 1.85%) and 3268 (89.05%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.0757(4) Å, b = 11.9628(4) Å, c = 13.2380(5) Å, β = 92.8130(10)°, volume = 2068.22(12) Å^3, are based upon the refinement of the XYZ-centroids of 9959 reflections above 20 σ(I) with 6.768° < 2θ < 133.8°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.935. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8810 and 0.9580. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{29}N_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 279 variables converged at R1 = 3.65%, for the observed data and wR2 = 9.13% for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was 0.152 e^-/Å^3 and the largest hole was -0.204 e^-/Å^3 with an RMS deviation of 0.041 e^-/Å^3. On the basis of the final model, the calculated density was 1.155 g/cm^3 and F(000), 776 e^-. The hydrogen atoms at N3 were refined freely. CCDC nr.: 1913072.

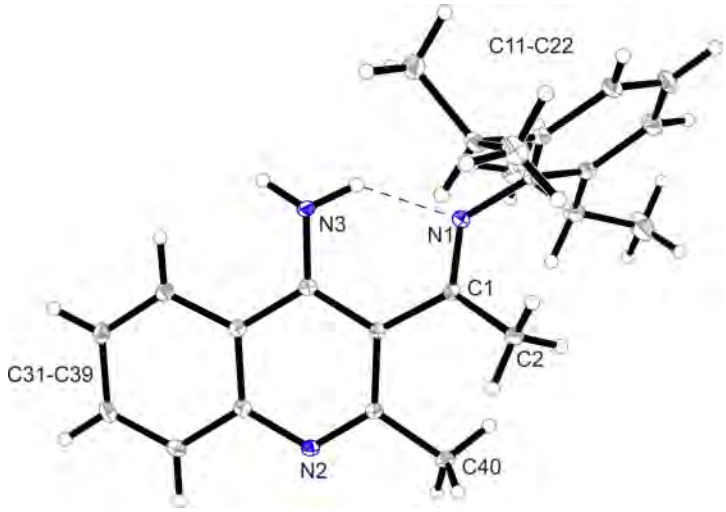


Figure S3. Crystal structure of compound **L3**. (Thermals ellipsoids are shown with 30% probability.)

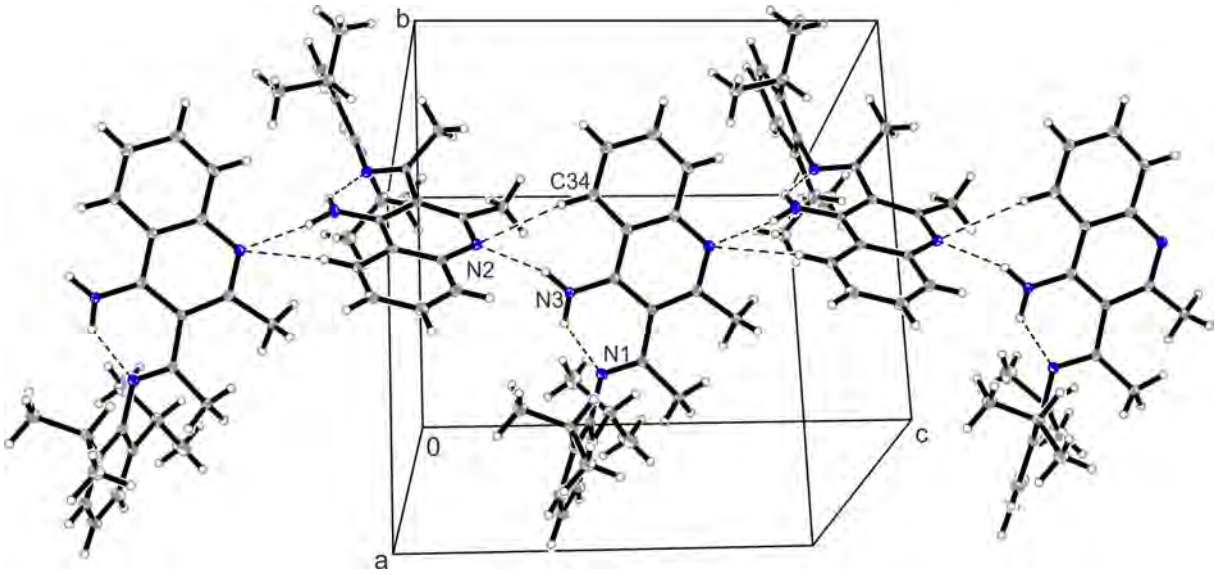


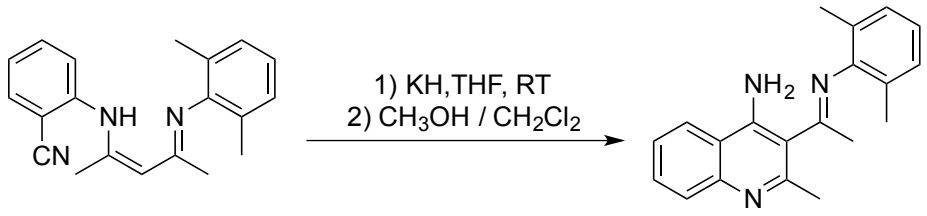
Figure S4. Excerpt of the packing diagram of **L3** presenting chain formation along the *c*-axis involving NH···N and CH···N interactions.

Table S1. Non-covalent intermolecular and intramolecular interactions in compound **L3** (Å and deg)

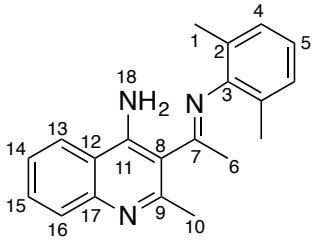
D-H···*A*	*d*(*D*-H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
N3-H3A···N1	0.96(2)	1.89(2)	2.666(1)	136.0(1)
N3-H3B···N2$^{\#1}$	0.91(2)	2.11(2)	2.979(1)	159.5(1)
C34-H34···N2$^{\#1}$	0.95	2.73	3.624(1)	157.1

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, -y+0.5, z-0.5.

(*E*)-3-(1-((2,6-dimethylphenyl)imino)ethyl)-2-methylquinolin-4-amine (L4).



2-(((2*E*,3*Z*)-4-((2,6-dimethylphenyl)amino)pent-3-en-2-ylidene)amino)benzonitrile (1,00 g, 3.3 mmol), potassium hydride (0,13 g, 3.3 mmol) and 50 mL of anhydrous THF were added in a dried Schlenk under N_2 atmosphere and the mixture was stirred for 2 hours at room temperature. The reaction evidence hydrogen formation (H_2). When the reaction finished, the mixture was filtered through celite and the solution was transferred to a sealed round flask fitted with Teflon screw cap, heated at 90 °C and stirred for 3 hours. The orange solution was evaporated in vacuum to dryness and the remaining solid was dissolved in 30 mL of methanol / dichloromethane and washed twice with 30 ml of distilled water. The organic phase was dried with anhydrous Na_2SO_4 and concentrated to dryness. Crude product was purified via silica gel chromatography (1:1 Petroleum ether / ethyl acetate). **L4** was obtained as a colorless crystals (0.82 g, 82%).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 7.91 (d, *J* = 8.4 Hz, 1H, H_{16}), 7.76 (d, *J* = 8.3 Hz, 1H, H_{13}), 7.63 (t, *J* = 7.6 Hz, 1H, H_{15}), 7.39 (t, *J* = 7.6 Hz, 1H, H_{14}), 7.11 (d, *J* = 7.5 Hz, 2H, H_4), 6.98 (t, *J* = 7.5 Hz, 1H, H_5), 6.05 (s, 2H, H_{18}), 2.72 (s, 3H, H_{10}), 2.21 (s, 3H, H_1), 2.03 (s, 3H, H_6).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 170.40 (C_7), 156.06 (C_9), 148.34 (C_3), 147.47 (C_{17}), 147.28 (C_{11}), 129.94 (C_{15}), 128.92 (C_4), 128.64 (C_{16}), 125.25 (C_2), 124.77 (C_{14}), 123.69 (C_5), 120.65 (C_{13}), 117.51 (C_{12}), 115.46 (C_8), 25.60 (C_{10}), 23.22 (C_6), 18.97 (C_1).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 7.91/124.77, 120.65, 117.51 (H_{16}/$C_{14,13,12}$), 7.76/147.28, 129.94, 128.64, 124.77,117.51 (H_{13}/$C_{11,15,16,14,12}$), 7.63/124.77, 120.65 (H_{15}/$C_{14,13}$), 7.39/147.47, 129.94, 128.64, 120.65, 117.51 (H_{14}/$C_{17,15,16,13,12}$), 7.11/148.34, 125.25,123.69, 18.97 (H_4/$C_{3,2,5,1}$), 6.98/128.92, 125.95 (H_5/$C_{4,2}$), 6.05/117.51, 115.46 (H_{18}/$C_{12,8}$), 2.72/156.06, 115.46 (H_{10}/$C_{9,8}$), 2.21/148.34, 128.92, 125.25 (H_1/$C_{3,4,2}$), 2.03/170.40, 115.46 (H_6/$C_{7,8}$).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 7.91/128.64 (H_{16}/C_{16}), 7.76/120.65 (H_{13}/C_{13}), 7.63/129.94 (H_{15}/C_{15}), 7.39/124.77 (H_{14}/C_{14}), 7.11/128.92 (H_4/C_4), 6.98/123.69 (H_5/C_5), 2.72/25.60 (H_{10}/C_{10}), 2.21/18.97 (H_1/C_1), 2.03/23.22 (H_6/C_6).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.91/7.63 (H_{16}/H_{15}), 7.76/7.39 (H_{13}/H_{14}), 7.63/7.39 (H_{15}/H_{14}), 7.11/6.98 (H_4/H_5)

NOESY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.76/6.05 (H_{13}/H_{18}), 7.11, 6.05/2.21 ($H_{4,18}/H_1$), 2.72, 2.21/2.03 ($H_{10,1}/H_6$)

FT-IR (KBr): ν / cm^{-1} = 3456, 3325, 3201, 1643, 1566, 1435, 1365, 1249, 1195, 1126, 1095, 1041, 987, 918, 879, 810, 763, 686, 648, 547, 370.

HRMS (ESI): m/z $[M+H]^+$ for $C_{20}H_{22}N_3$: calc: 304.1814; found: 304.1770.

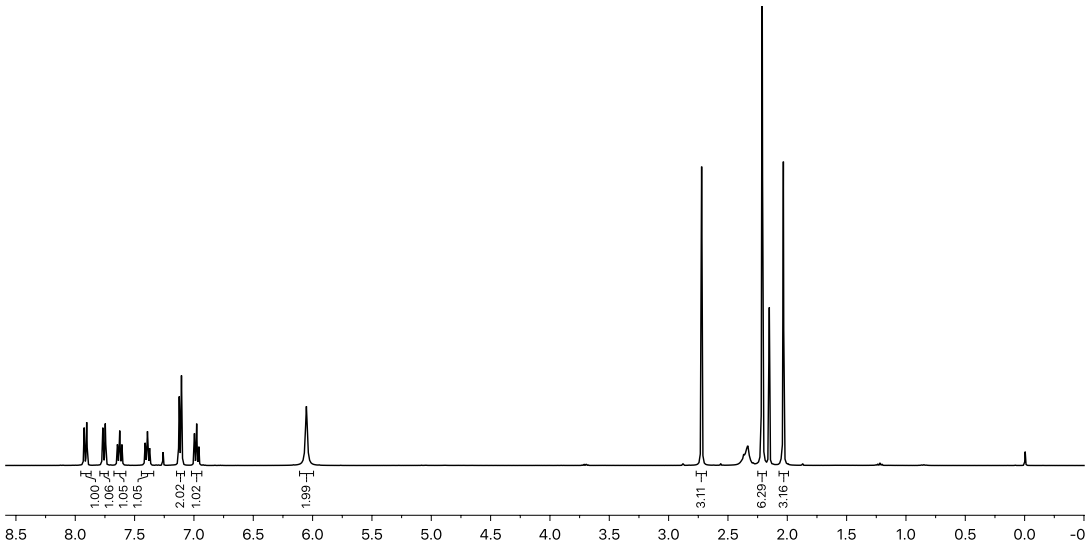


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

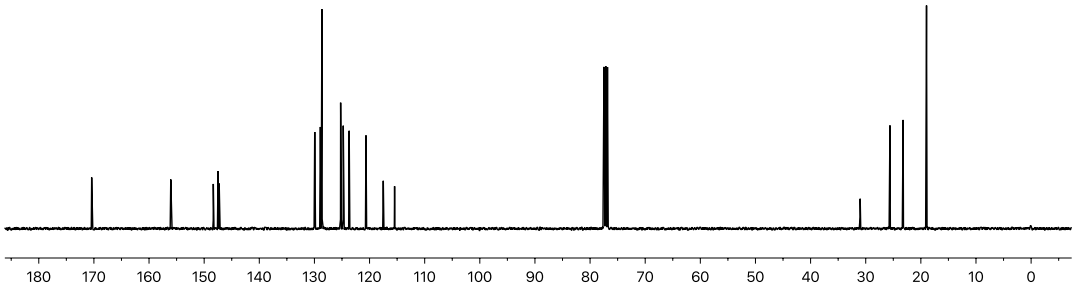
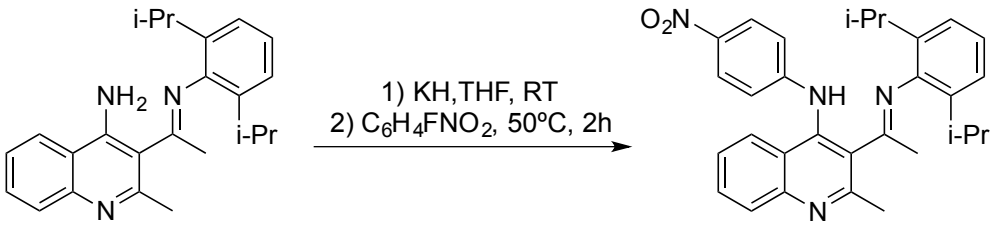
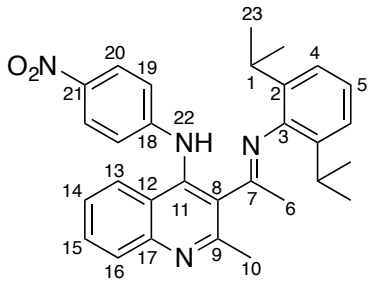


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

(*E*)-3-(1-((2,6-diisopropylphenyl)imino)ethyl)-2-methyl-*N*-(4-nitrophenyl)quinolin-4-amine (L5).



L3 (309 mg, 0.894 mmol), potassium hydride (39.5 mg, 0.984 mmol) and 50 mL of anhydrous THF were added in a dried Schlenk under N_2 atmosphere. The mixture was stirred for 2 hours at room temperature. The reaction evidence hydrogen formation (H_2). When the reaction finished, 104.4 μL of 1-Fluoro-4-nitrobenzene (0.984 mmol) was added, and the mixture was stirred for 1 hour at 50 °C. Finally, the solution was evaporated in vacuum to dryness and the product was purified via silica gel chromatography (3:2 Petroleum ether / ethyl acetate). **L5** was obtained as a light-yellow powder (328 mg, 76%).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.11 (t, *J* = 8.2 Hz, 3H, $_{H20,16}$), 7.72 (t, *J* = 7.6 Hz, 1H, H_{15}), 7.67 (d, *J* = 8.4 Hz, 1H, H_{13}), 7.62 (s, 1H, H_{22}), 7.40 (t, *J* = 7.6 Hz, 1H, H_{14}), 7.22 – 7.12 (m, 3H, $H_{4,5}$), 6.71 (d, *J* = 8.9 Hz, 2H, H_{19}), 2.89 (s, 4H, $H_{10,1}$), 2.05 (s, 3H, H_6), 1.17 (dd, *J* = 6.0 Hz, 12H, H_{23}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 169.30 (C_7), 156.49 (C_9), 150.83 (C_{18}), 148.62 (C_{17}), 144.62 (C_3), 141.01 (C_{21}), 140.63 (C_{11}), 136.31 (C_2), 130.53 (C_{15}), 129.66 (C_{16}), 126.61 (C_{14}), 126.11 (C_{20}), 124.95 (C_5), 124.44 (C_{13}), 123.76 (C_4), 122.36 (C_{12}), 115.36 (C_{19}), 28.40 (C_1), 25.17 (C_{10}), 24.09 (C_{23a}), 23.53 (C_{23b}), 23.31 (C_6).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.11/150,83, 141.01 ($H_{20}/C_{18,21}$), 8.11/126.61, 122.36 ($H_{16}/C_{14,12}$), 7.72/148.62, 124.44 ($H_{15}/C_{17,13}$), 7.67/148.62, 140.63, 130.53 ($H_{13}/C_{17,11,15}$), 7.62/122.36, 115.36 ($H_{22}/C_{12,19}$), 7.40/129.66 (H_{14}/C_{16}), 7.22 – 7.12/144.62, 136.31 ($H_4/C_{3,2}$), 6.71/141.01 ($H_{19/21}$), 2.89/136.31, 123.76 ($H_1/C_{2,4}$), 2.89/156.49 (H_{10}/C_9), 2.05/169.30 (H_6/C_7), 1.17/136.31 (H_{23}/C_2).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.11/129.66, 126.11 ($H_{16,20}/C_{16,20}$), 7.72/130.53 (H_{15}/C_{15}), 7.67/124.44 (H_{13}/C_{13}), 7.40/126.61 (H_{14}/C_{14}), 7.22 – 7.12/123.76, 124.95 ($H_{4,5}/C_{4,5}$), 6.71/115.36 (H_{19}/C_{19}), 2.89/25.17 28.40, ($H_{10,1}/C_{10,1}$), 2.05/23.31 (H_6/C_6), 1.17/24.09, 23.53, ($H_{23}/C_{23a,23b}$).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 8.11/6.71 (H_{20}/C_{19}), (8.11/7.72) (H_{16}/H_{15}), 7.72/7.40 (H_{15}/H_{14}), 7.67/7.40 (H_{13}/H_{14}), 2.89/1.17 (H_1/H_{23}).

NOESY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.67/6.71 (H_{13}/H_{19}), 7.22 – 7.12/2.89, 1.17 ($H_{4,5}/H_{1,23}$), 7.62/2.88 (H_{22}/H_1), 2.89/2.05 ($H_{1,10}/H_6$).

FT-IR (KBr): ν / cm^{-1} = 3335, 2961, 2926, 2868, 1735, 1631, 1598, 1580, 1558, 1518, 1501, 1491, 1458, 1441, 1401, 1381, 1364, 1335, 1264, 1216, 1176, 1159, 1114, 1046, 960, 933, 885, 871, 853, 845, 813, 798, 775, 766, 753, 726, 690, 660, 631, 619

HRMS (ESI): m/z $[M-H]^-$ for $C_{30}H_{31}N_4O_2$: calc: 479.2447; found: 479.2463.

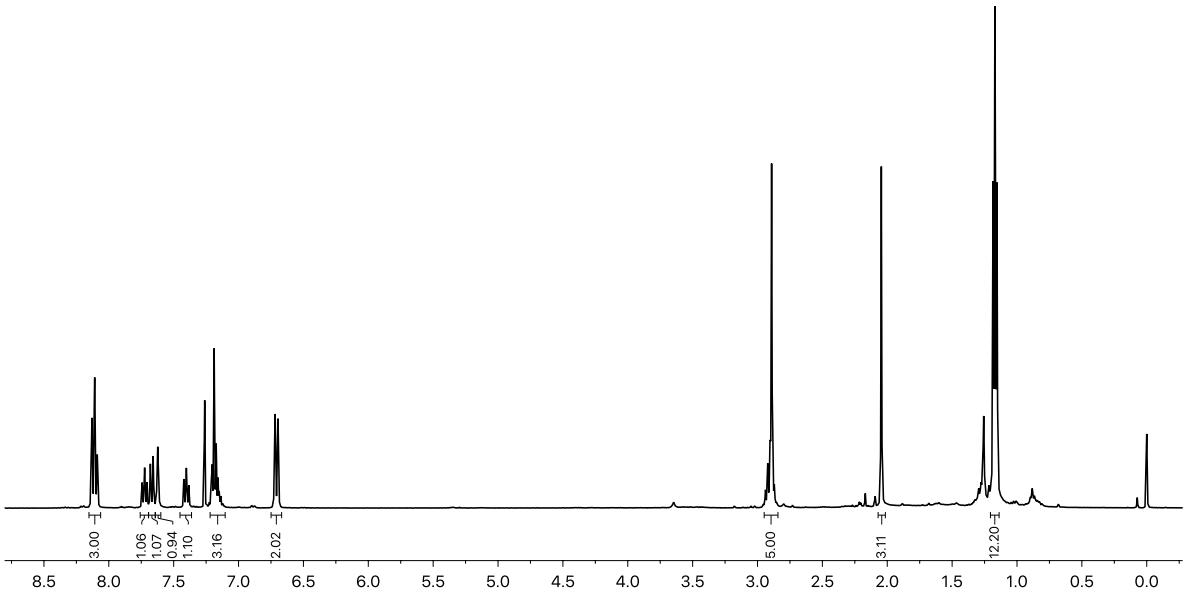


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

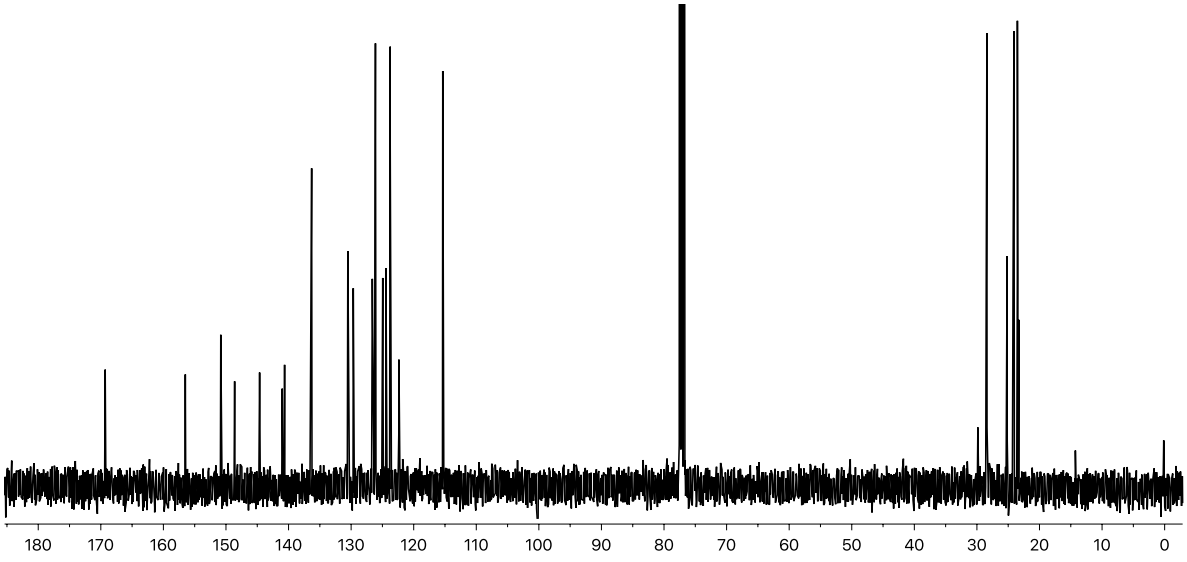
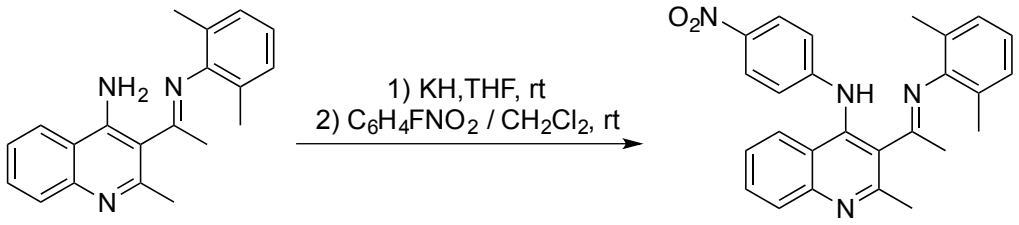
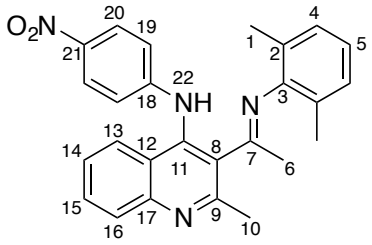


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

(*E*)-3-(1-((2,6-dimethylphenyl)imino)ethyl)-2-methyl-*N*-(4-nitrophenyl)quinolin-4-amine (L6).



L4 (236 mg, 0.777 mmol), potassium hydride (34.2 mg, 0.854 mmol) and 50 mL of anhydrous THF were added in a dried Schlenk under N_2 atmosphere. The mixture was stirred for 2 hours at room temperature. The reaction evidence hydrogen formation (H_2). When the reaction finished, 90.6 μL of 1-Fluoro-4-nitrobenzene (0.854 mmol) was added, and the mixture was stirred for 1 hour at 50 °C. Finally, the solution was evaporated in vacuum to dryness and the product was purified via silica gel chromatography (3:2 Petroleum ether / ethyl acetate). **L6** was obtained as a light-yellow powder (261 mg, 79%).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.36 (s, 1H, H_{22}), 7.91 (d, *J* = 9.0 Hz, 3H, H_{20}, H_{16}), 7.74 (t, *J* = 7.6 Hz, 1H, H_{15}), 7.56 (d, *J* = 8.3 Hz, 1H, H_{13}), 7.42 (t, *J* = 7.6 Hz, 1H, H_{14}), 7.13 (d, *J* = 7.4 Hz, 2H, H_4), 7.05 (t, 1H, H_5), 6.24 (d, *J* = 8.9 Hz, 2H, H_{19}), 2.65 (s, 3H, H_{10}), 2.11 (s, 3H, H_1), 1.87 (s, 3H, H_6).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 170.12 (C_7), 155.55 (C_9), 151.37 (C_{21}), 148.22 (C_{17}), 146.58 (C_3), 140.02 (C_{11}), 139.68 (C_{18}), 132.04 (C_8), 130.58 (C_{15}), 129.67 (C_{16}), 128.86 (C_4), 126.72 (C_{14}), 126.15 (C_{20}), 124.74 (C_5), 123.57 (C_{13}), 122.99 (C_{12}), 113.39 (C_{19}), 24.70 (C_{10}), 22.68 (C_6), 19.06 (C_1), C2 (N.O)

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.36/113.39, 140.02, 132.04 (H_{22}/$_{C19,12,8}$), 7.91/151.37, 139.68 (H_{20}/$_{C18,21}$), 7.91/126.72, 122.99 (H_{16}/$_{C14,12}$), 7.74/148.22, 123.57 (H_{15}/$C_{17,13}$), 7.56/148.22, 140.02, 130.58 (H_{13}/$_{C17,11,15}$), 7.42/129.67, 122.99 (H_{14}/$_{C16,12}$), 7.13/146.58 (H_4/C_3), 6.24/139.68 (H_{19}/C_{18}).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 7.91/126.15 (H_{20}/C_{20}), 7.91/129.67 (H_{16}/C_{16}), 7.74/130.58 (H_{15}/C_{15}), 7.56/123.57 (H_{13}/C_{13}), 7.42/126.72 (H_{14}/C_{14}),

7.13/128.86 (H_4/C_4), 7.05/124.74 (H_5/C_5), 6.24/113.39 (H_{19}/C_{19}), 2.65/24.70 (H_{10}/C_{10}), 2.21/19.06 (H_1/C_1), 1.87/22.68 (H_6/C_6).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.91/6.24 (H_{20}/H_{19}), 7.91/7.74 (H_{16}/H_{15}), 7.74/7.42 (H_{15}/H_{14}), 7.42/7.56 (H_{14}/H_{13}), 7.13/7.05 (H_4/H_5).

FT-IR (KBr): ν / cm^{-1} = 300, 455, 493, 540, 624, 756, 840, 1103, 1180, 1327, 1381, 1489, 1597, 1658, 3163.

HRMS (ESI): m/z $[M-H]^-$ for $C_{26}H_{23}N_4O_2$: calc: 423.1821; found: 423.1835.

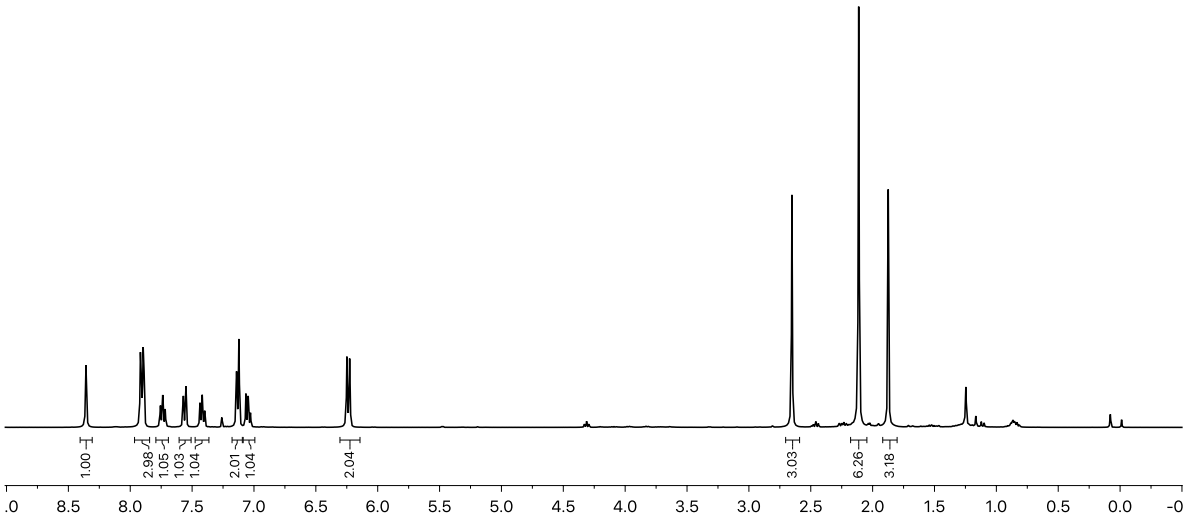


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

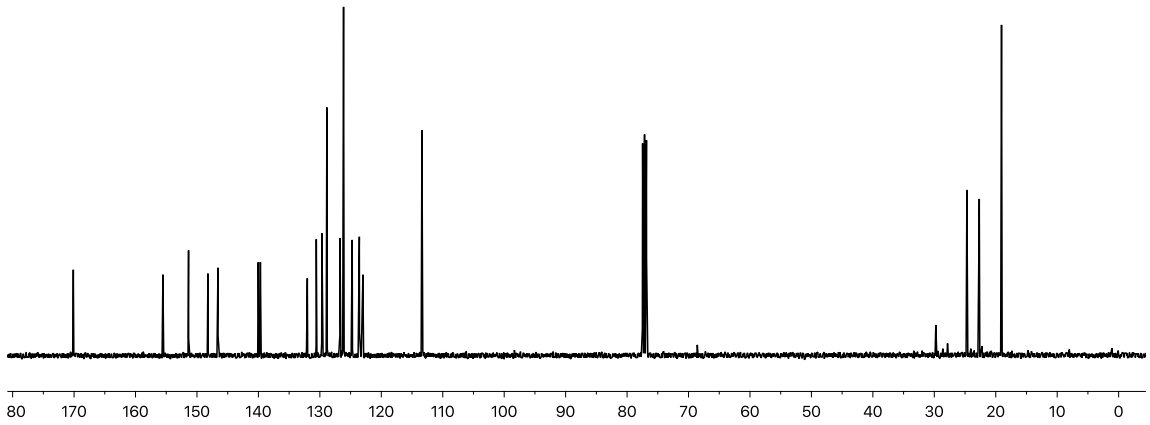


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

X-ray crystal structure analysis of L6: A colorless plate-like specimen of $C_{26}H_{24}N_4O_2$, approximate dimensions 0.050 mm x 0.180 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2084 frames were collected. The total exposure time was 30.62 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 36664 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 3973 were independent (average redundancy 9.228, completeness = 99.7%, R_{int} = 6.78%, R_{sig} = 3.30%) and 3141 (79.06%) were greater than $2\sigma(F^2)$. The final cell constants of a = 25.7345(9) Å, b = 11.2523(4) Å, c = 18.8485(6) Å, β = 124.671(2)°, volume = 4488.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 5485 reflections above 20 σ(I) with 8.355° < 2θ < 132.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.857. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8810 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{26}H_{24}N_4O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 297 variables converged at R1 = 4.27%, for the observed data and wR2 = 11.63% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.156 $e^-/Å^3$ and the largest hole was -0.265 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.256 g/cm^3 and F(000), 1792 e^-. The hydrogen atoms at N3 were refined freely. CCDC nr.: 1913158.

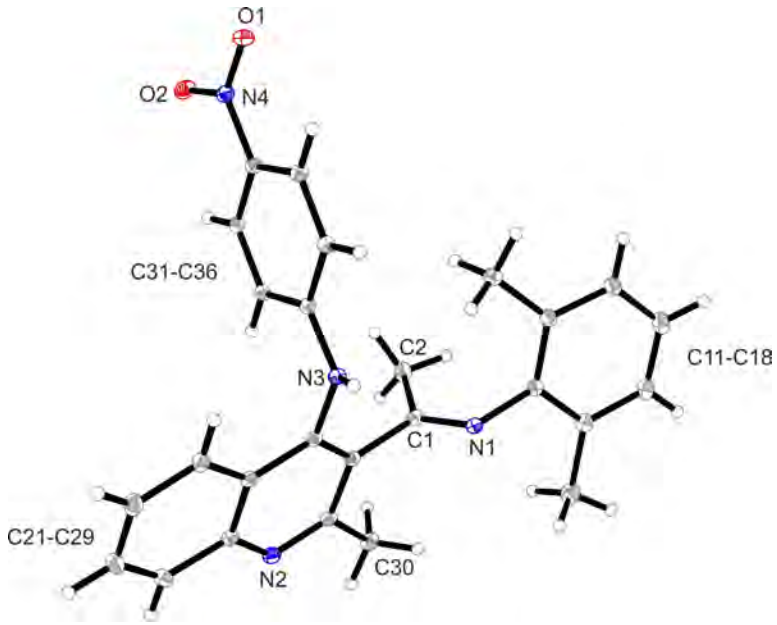


Figure S11. Crystal structure of compound **L6**. (Thermals ellipsoids are shown with 15% probability.)

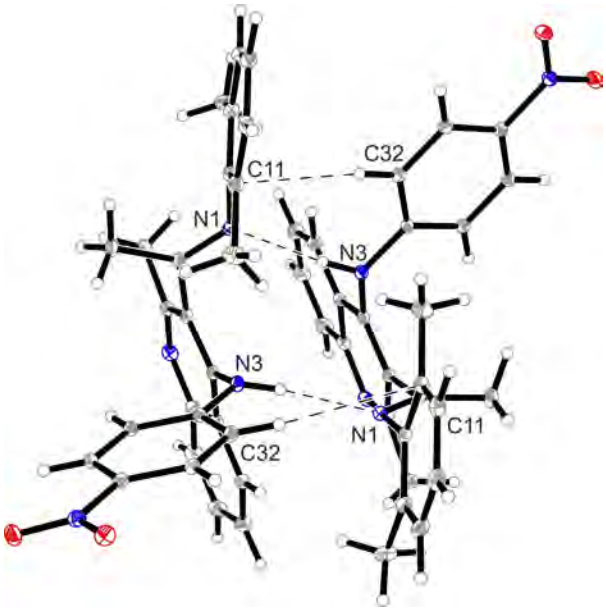


Figure S12. Dimer type formation involving NH···N and additional CH···π interactions.

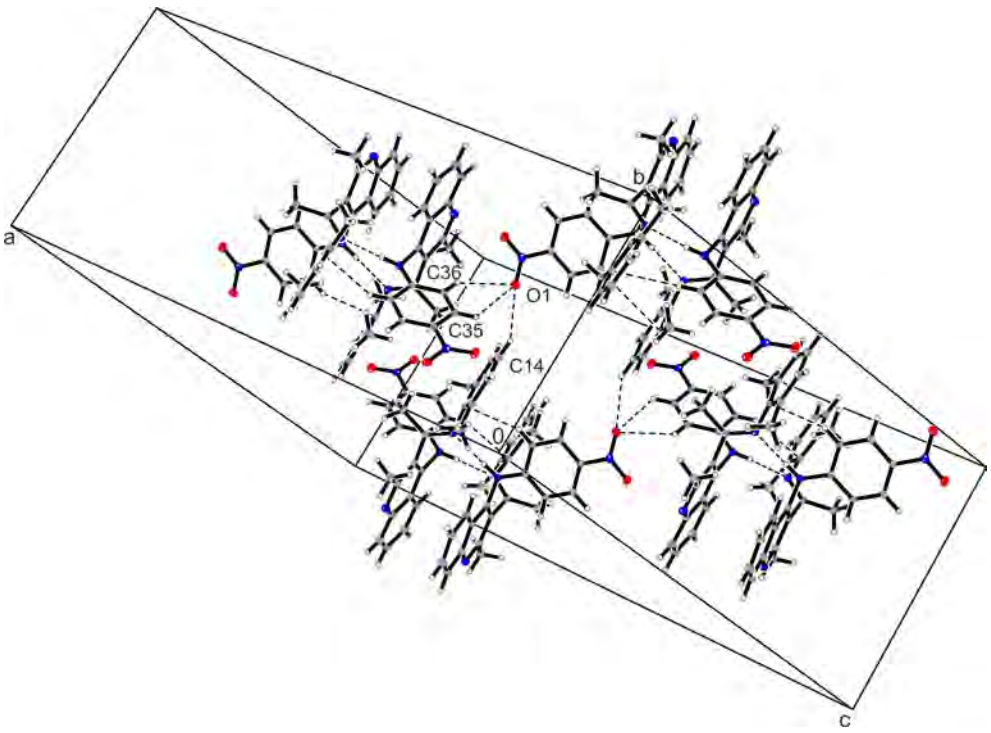


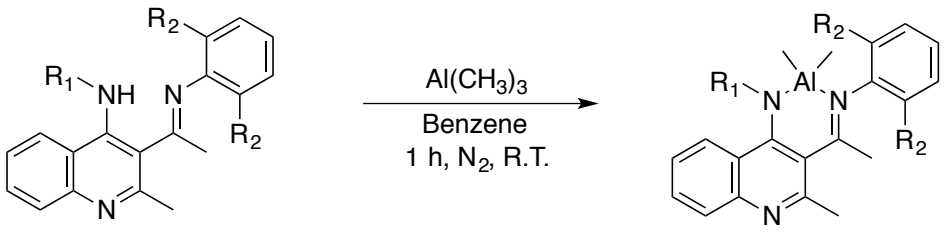
Figure S13. Excerpt of the packing diagram of **L6** presenting the CH···O interactions between the dimeric units.

Table S2. Non-covalent intermolecular and intramolecular interactions in compound **L6** (Å and deg)

D-H···*A*	*d*(*D*-H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
N3-H3···N1$^{\#1}$	0.88(2)	2.09(2)	2.969(2)	174.0(2)
C32-H32···*C*g1$^{\#1}$	0.95	2.64	3.572(5)	165.6
C14-H14···O1$^{\#2}$	0.95	2.55	3.406(2)	150.7
C35-H35···O1$^{\#3}$	0.95	2.69	3.277(2)	120.9
C36-H36···O1$^{\#3}$	0.95	2.59	3.232(2)	125.2

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, y, -z+1.5; $^{\#2}$ x+0.5, -y+0.5, z+0.5; $^{\#3}$ -x+1.5, y-0.5, -z+1.5.

General procedure for synthesis of aluminums complexes derivatives of aminoquinolines (C1-4)

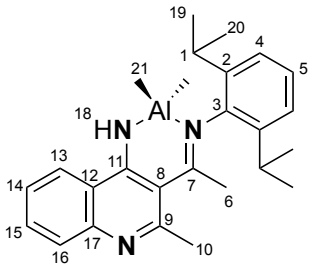


L3: R_1 = H, R_2 = iPr
L4: R_1 = H, R_2 = Me
L5: R_1 = $C_6H_5(NO_2)$, R_2 = iPr
L6: R_1 = $C_6H_5(NO_2)$, R_2 = Me

C1: R_1 = H, R_2 = iPr
C2: R_1 = H, R_2 = Me
C3: R_1 = $C_6H_5(NO_2)$, R_2 = iPr
C4: R_1 = $C_6H_5(NO_2)$, R_2 = Me

Inside of glovebox, trimethylaluminum (48 mg, 0.666 mmol) was added dropwise to a solution of **L3-6** (0.659 mmol), as appropriate, in 5 mL of dry dichloromethane. The mixture was stirred for 2 hours at room temperature. Then, the solvent was evaporated under vacuum and the crude product was washed two times with dry and cold hexane. The resulting solid was filtrated and dry under vacuum. Complexes **C1-4** where obtained as light-yellow powders (95 – 99%).

(3-(1-(2,6-diisopropylphenylimino)ethyl)-2-methylquinolin-4-amine)Al(CH_3)$_2$ (C1).



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ/ppm = 8.08 (d, *J* = 8.2 Hz, 1H, H_{16}), 7.33 (t, J = 8.2 Hz, 1H, H_{15}), 7.20 (d, *J* = 7.4 Hz, 1H, H_{13}), 7.12 – 7.05 (m, 3H, $H_{4\text{-}5}$), 6.97 (t, *J* = 8.2 Hz, 1H, H_{14}), 5.85 (s, 1H, H_{18}), 3.06 (m, 2H, H_1), 2.58 (s, 3H, H_{10}), 1.80 (s, 3H, H_6), 1.28 (d, J = 6.8 Hz, 6H, H_{19}), 0.95 (d, J = 6.9 Hz, 6H, H_{20}), -0.49 (s, 6H, H_{21}).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ/ppm = 176.14 (C_7), 160.09 (C_9), 148.35 (C_{17}), 141.65 (C_2), 140.74 (C_3), 131.21 (C_{15}), 129.50 (C_{16}), 124.85 (C_4), 124.58 (C_{14}), 121.46 (C_{13}), 120.78 (C_{12}), 111.82 (C_8), 28.52 (C_{10}), 28.49 (C_1), 25.28 (C_6), 24.76 (C_{19}), 24.19 (C_{20}), -11.17 (C_{21}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.08/124.58 (H_{16}/C_{14}), 7.33/121.46 (H_{15}/C_{13}), 7.33/148.35 (H_{15}/C_{17}), 7.20/131.21 (H_{13}/C_{15}), 7.20/148.35 (H_{13}/C_{17}), 7.07/124.85 (H_4/C_5), 7.12/141.65 (H_4/C_2), 7.07/140.74 (H_4/C_3), 6.97/129.50 (H_{14}/C_{16}), 6.97/120.78 (H_{15}/C_{12}),

3.06/124.85 (H_1/C_4), 3.06/24.19 (H_1/C_{20}), 3.06/141.65 (H_1/C_2), 2.58/160.09 (H_{10}/C_9), 2.58/111.82 (H_{10}/C_8), 1.80/176.14 (H_6/C_7), 1.80/111.82 (H_6/C_8), 1.28/141.65 (H_{19}/C_2), 1.28/24.19 (H_{19}/C_{20}), 1.28/28.49 (H_{19}/C_1), 0.95/141.65 (H_{20}/C_2), 0.95/24.76 (H_{20}/C_{19}), 0.95/28.49 (H_{20}/C_1).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.08/129.50 (H_{16}/C_{16}), 7.33/131.21 (H_{15}/C_{15}), 7.20/121.46 (H_{13}/C_{13}), 7.08/124.85 (H_4/C_4), 6.97/124.58 (H_{14}/C_{14}), 3.06/28.49 (H_1/C_1), 2.58/28.52 (H_{10}/C_{10}), 1.80/25.28 (H_6/C_6), 1.28/24.76 (H_{19}/C_{19}), 0.95/24.19 (H_{20}/C_{20}), -0.49/-11.17 (H_{21}/C_{21}).

COSY (400 MHz / 400 MHz, C_6D_6, 298 K) δ(1H) / δ(1H): 8.08/7.33 (H_{16}/H_{15}), 7.33/6.97 (H_{15}/H_{14}), 7.20/6.97 (H_{13}/H_{14}), 3.06/1.28 (H_1/H_{19}), 3.06/0.95 (H_1/H_{20}).

FT-IR (ν/cm^{-1}): 3480, 3217 (NH, broad), 3055, 2963, 2924, 2870, 1612 (imine C=N), 1574 (Quinolin), 1527, 1435, 1373, 1319, 1219, 1188, 1126, 1103, 1049, 995, 933, 879, 762, 679, 601, 563, 455.

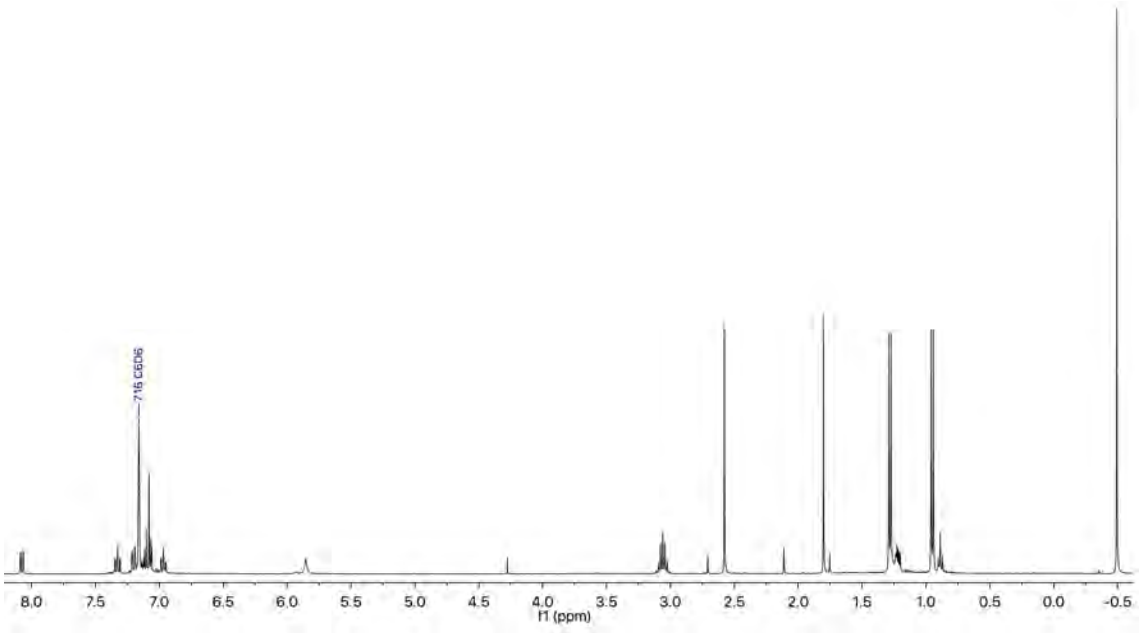


Figure S14. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

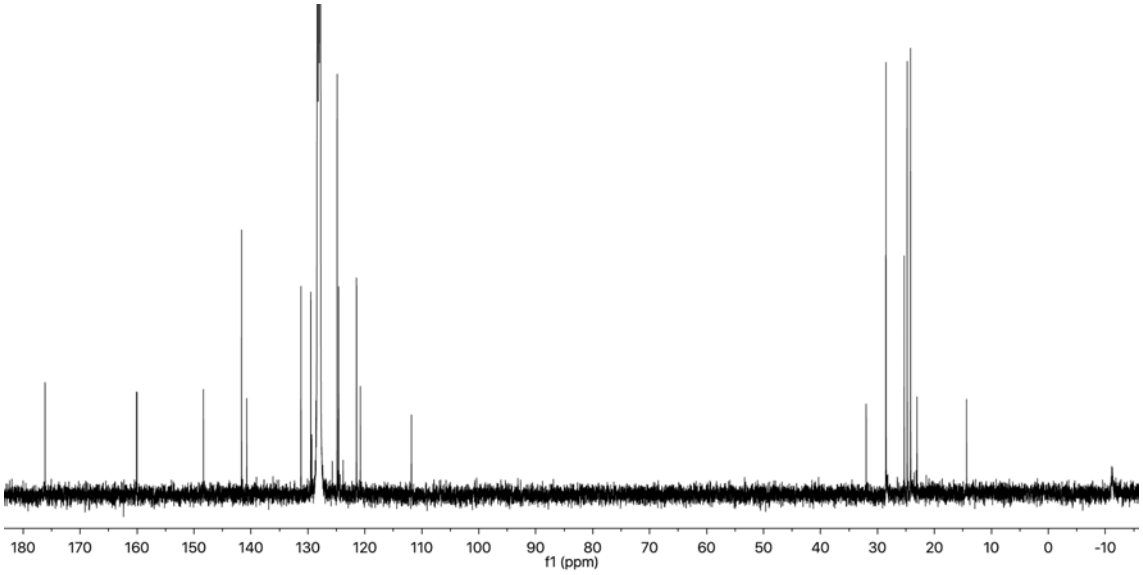
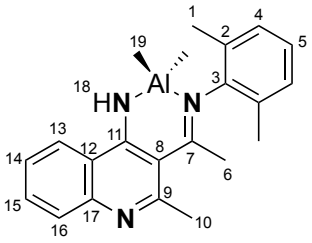


Figure S15. ^{13}C NMR (100 MHz, C_6D_6, 298 K)

(3-(1-((2,6-dimethylphenyl)imino)ethyl)-2-methylquinolin-4-amine)Al(CH_3)$_2$ (C2).



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ/ppm = 8.08 (d, *J* = 8.5 Hz, 1H, H_{16}), 7.36 (t, *J* = 7.6 Hz, 2H, H_{15}), 7.02 (t, *J* = 7.6 Hz, 1H, H_{14}), 6.95 (s, 3H, H_4), 5.96 (s, 1H, H_{18}), 2.51 (s, 3H, H_{10}), 2.03 (s, 6H, H_1), 1.59 (s, 3H, H_6), -0.53 (s, 6H, H_{19}).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ/ppm = 176.07 (C_7), 159.96 (C_9), 148.42 (C_{17}), 143.56 (C_3), 131.20 (C_{16}), 130.84 (C_{15}), 129.37 (C_5), 126.88 (C_4), 124.56 (C_{14}), 121.67 (C_{13}), 120.82 (C_{12}), 111.51 (C_8), 28.33 (C_{10}), 24.41 (C_6), 18.35 (C_1), -10.54 (C_{19}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.08/124.56 (H_{16}/C_{14}), 8.08/120.82 (H_{16}/C_{12}), 7.36/130.84 (H_{15}/C_{15}), 7.36/148.42 (H_{15}/C_{17}), 7.02/131.20 (H_{14}/C_{16}), 7.02/120.82 (H_{14}/C_{12}), 6.95/129.37 (H_4/C_5), 6.95/18.35 (H_4/C_1), 6.95/143.56 (H_4/C_3), 2.51/111.51 (H_{10}/C_8), 2.03/129.37 (H_1/C_5), 2.03/143.56 (H_1/C_3), 1.59/111.51 (H_6/C_8).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.08/131.20 (H_{16}/C_{16}), 7.36/130.84 (H_{15}/C_{15}), 7.02/120.82 (H_{14}/C_{14}), 2.51/28.33 (H_{10}/C_{10}), 2.03/18.35 (H_1/C_6), 1.59/24.41 (H_6/C_6), -0.53/-10.54 (H_{19}/C_{19}).

COSY (400 MHz / 400 MHz, C6D6, 298 K) δ(1H) / δ(1H): 8.08/7.36 (H_{16}/H_{15}), 7.36/7.02 (H_{15}/H_{14}), 6.95/2.03 (H_4/H_1).

FT-IR (ν/cm^{-1}): 3479, 3263 (NH, broad), 2924, 1620 (imine C=N), 1566 (quinoline C=N), 1527, 1496, 1465, 1435, 1365, 1327, 1242, 1195, 1126, 1087, 1033, 995, 871, 763, 686.

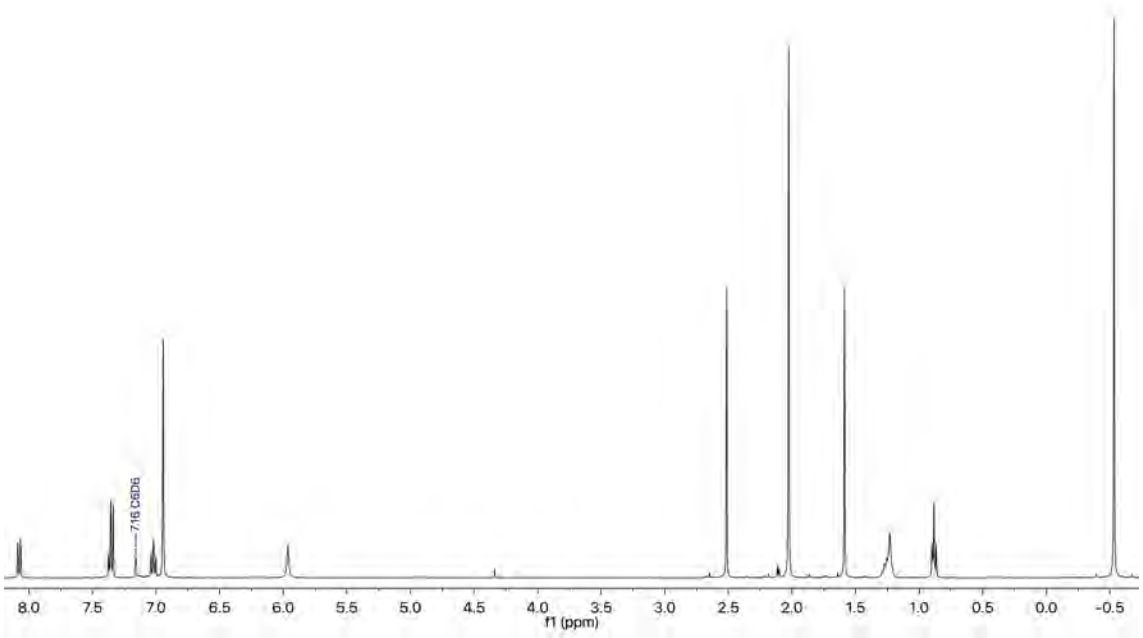


Figure S16. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

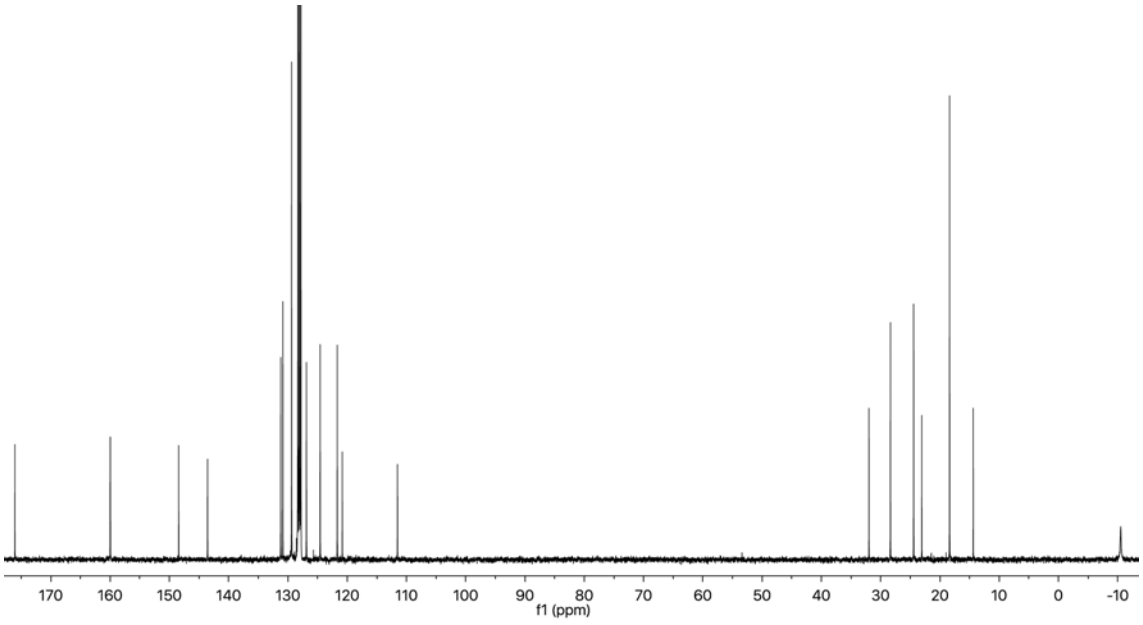
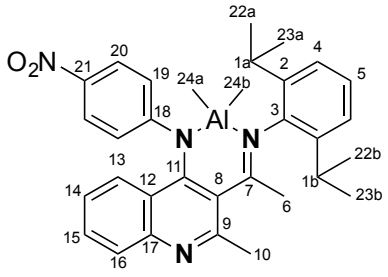


Figure S17. ^{13}C NMR (100 MHz, C_6D_6, 298 K)

(3-(1-((2,6-diisopropylphenyl)imino)ethyl)-2-methyl-*N*-(4-nitrophenyl)quinolin-4-amine)Al(CH_3)$_2$ (C3).



^{1}H NMR (400 MHz, $CDCl_3$, 253 K): δ/ppm = 8.23 (d, *J* = 9.1, 2.6 Hz, 1H, H_{16}), 7.94 (d, *J* = 7.7 Hz, 2H, H_{20}), 7.73 (dd, J = 14.2, 7.9 Hz, 2H, H_{19}), 7.33 (m, 4H, $H_{4,5,15}$), 7.18 (d, *J* = 6.0 Hz, 1H, H_{14}), 6.37 (d, *J* = 8.1 Hz, 1H, H_{13}), 2.90 (m, 1H, H_{1a}), 2.84 (s, 3H, H_{10}), 2.38 (s, 3H, H_6), 2.15 (m, 1H, H_{1b}), 1.30 (d, *J* = 6.8 Hz, 3H, H_{22a}), 1.21 (d, *J* = 6.6 Hz, 3H, H_{23a}), 0.80 (d, *J* = 6.7 Hz, 3H, H_{22b}), 0.48 (d, *J* = 6.6 Hz, 3H, H_{23b}), -0.87 (s, 3H, H_{24a}), -1.17 (s, 3H, H_{24b}).

^{13}C NMR (100 MHz, $CDCl_3$, 253 K): δ/ppm = 177.92 (C_7), 157.61 (C_9), 156.56 (C_{21}), 153.80 (C_{18}), 148.89 (C_{11}), 140.41 (C_2), 139.46 (C_3), 138.74 (C_{17}), 131.49 (C_{19}), 128.27 (C_5), 127.31 (C_{12}), 126.27 (C_{16}), 125.83 (C_{15}), 125.36 (C_{20}), 125.13 (C_{14}), 124.66 (C_4), 123.70 (C_8), 120.65 (C_{13}), 28.57 (C_{1a}), 28.41 (C_{1b}), 28.04 (C_{10}), 25.72 (C_6), 24.61 (C_{23a}), 24.28 (C_{22b}), 24.15 (C_{22a}), 23.28 (C_{23b}), -10.26 (C_{24a}), -12.14 (C_{24b}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 253 K) δ(^{1}H) / δ(^{13}C): 8.23/127.31, 125.13 (H_{16}/$C_{12,14}$), 7.94/153.80, 131.49 (H_{20}/$C_{18,19}$), 7.73/156.56, 125.36 (H_{19}/$C_{21,\ 20}$), 7.33/139.46, 128.27 (H_4/$C_{3,\ 5}$), 7.33/140.41 (H_5/C_2), 7.33/120.65 (H_{15}/C_{13}), 7.18/126.27 (H_{14}/C_{16}), 6.37/138.74, 125.83 (H_{13}/$C_{17,15}$), 2.90/140.41, 24.61, 24.15 (H_{1a}/$C_{2,23a,22a}$), 2.84/157.61, 123.70 (H_{10}/$C_{9,8}$), 2.38/177.92, 123.70 (H_6/$C_{7,8}$), 2.15/140.41, 24.28, 23.28 (H_{1b}/$C_{2,22b,23b}$), 1.30/140.41 (H_{22a}/C_2), 1.21/140.41 (H_{23a}/C_2), 0.80/140.41 (H_{22b}/C_2), 0.48/140.41 (H_{23b}/C_2)

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, $CDCl_3$, 253 K) δ(^{1}H) / δ(^{13}C): 8.23/126.27 (H_{16}/C_{16}), 7.94/125.36 (H_{20}/C_{20}), 7.73/131.49 (H_{19}/C_{19}), 7.33/124.66 (H_4/C_4), 7.33/128.27 (H_5/C_5), 7.33/125.83 (H_{15}/C_{15}), 7.18/125.13 (H_{14}/C_{14}), 6.37/120.65 (H_{13}/C_{13}), 2.90/28.57 (H_{1a}/C_{1a}), 2.84/28.04 (H_{10}/C_{10}), 2.38/25.72 (H_6/C_6), 2.15/28.41 (H_{1b}/C_{1b}), 1.30/24.15 (H_{22a}/C_{22a}), 1.21/24.61 (H_{23a}/C_{23a}), 0.80/24.28 (H_{22b}/C_{22b}), 0.48/23.28 (H_{23b}/C_{23b}), -0.87/-10.26 (H_{24a}/C_{24a}), -1.17/-12.14 (H_{24b}/C_{24b}).

COSY (400 MHz / 400 MHz, $CDCl_3$, 253 K) δ(1H) / δ(1H): 8.23/7.33 (H_{16}/H_{15}), 7.94/7.73 (H_{20}/H_{19}), 7.33/7.18 (H_{15}/H_{14}), 7.18/6.43 (H_{14}/H_{13}), 2.90/1.30, 1.21 (H_{1a}/$H_{22a,23a}$), 2.15/0.80, 0.48 (H_{1b}/$H_{22b,\ 23b}$)

FT-IR (ν/cm^{-}1): 3325, 3063, 2963, 2870, 1659 (Imino), 1589 (Quinolin), 1497, 1396, 1327 (NO_2), 1265, 1219, 1180, 1111, 1049, 848, 764, 694, 625, 494, 417.

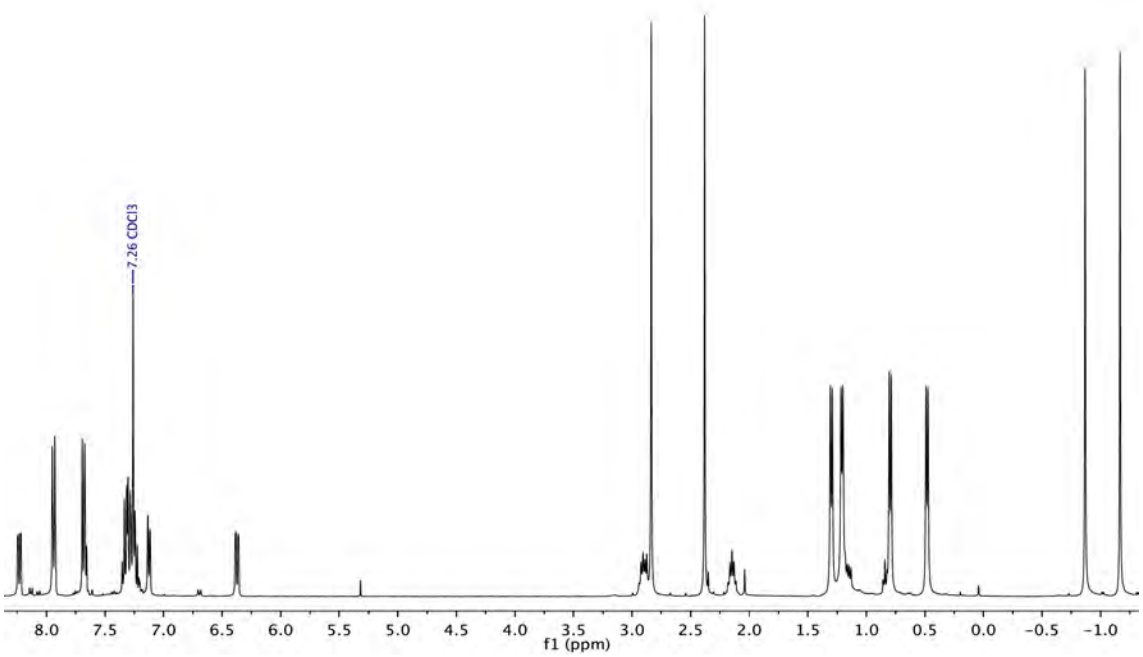


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$, 253 K)

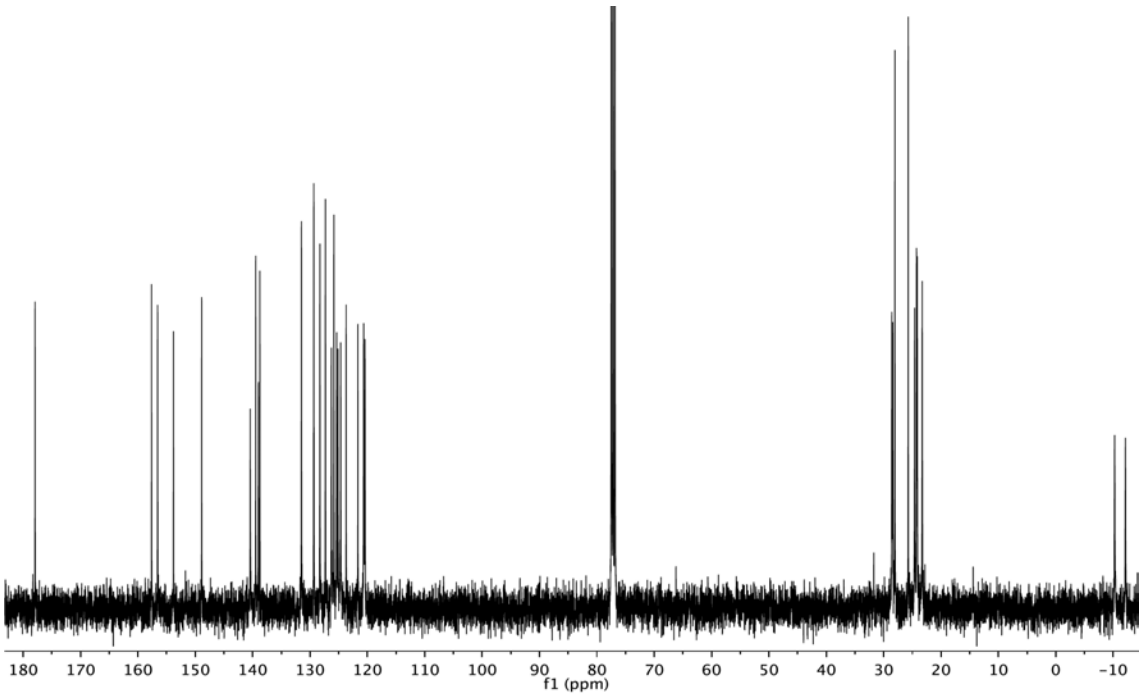
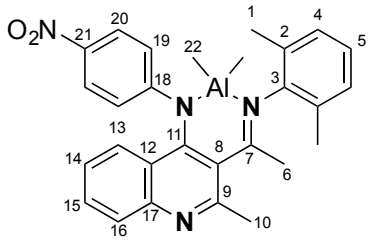


Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$, 253 K)

(*E*)-3-(1-((2,6-dimethylphenyl)imino)ethyl)-2-methyl-*N*-(4-nitrophenyl)quinolin-4-amine)Al(CH_3)$_2$ (C4).



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ/ppm = 8.18 (d, *J* = 8.3 Hz, 1H, H_{16}), 7.94 (d, *J* = 9.1 Hz, 2H, H_{19}), 7.79 (d, *J* = 8.5 Hz, 1H, H_{13}), 7.27 (t, *J* = 7.6 Hz, 1H, H_{15}), 6.92 – 6.86 (m, 2H, H_{14} y H_5), 6.80 (d, 1H, H_4), 6.46 (d, *J* = 7.12 Hz, 2H, H_{20}), 2.52 (s, 3H, H_6), 1.64 (s, 6H, H_1), 1.58 (s, 3H, H_6), -0.72 (s, 6H, H_{22}).

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ/ppm = 178.38 (C_8), 157.55 (C_{21}), 156.26 (C_9), 154.11 (C_{12}), 150.15 (C_{17}), 142.50 (C_3), 140.64 (C_{18}), 131.37 (C_{15}), 130.50 (C_{16}), 129.41 (C_4 y C_5), 127.55 (C_{13}), 125.87 (C_{14}), 123.87 (C_8), 122.39 (C_{19}), 120.67 (C_{20}), 27.45 (C_6), 24.09 (C_{10}), 18.06 (C_1), -10.94 (C_{22}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.18/125.87 (H_{16}/C_{14}), 8.18/154.11 (H_{16}/C_{12}), 7.94/157.55 (H_{19}/C_{21}), 7.79/131.37 (H_{13}/C_{15}), 7.79/150.15 (H_{13}/C_{17}), 7.27/154.11 (H_{15}/C_{12}), 7.27/150.15 (H_{15}/C_{17}), 6.92/130.51 (H_{14}/C_{16}), 6.92/154.11 (H_{14}/C_{12}), 6.80/129.41 (H_4/C_4), 6.80/142.50 (H_4/C_3), 6.46/140.64 (H_{20}/C_{18}), 2.52/123.87 (H_6/C_8), 1.64/129.41 (H_1/C_4), 1.64/142.50 (H_1/C_3), 1.58/123.87 (H_{10}/C_8).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, C_6D_6, 298 K) δ(^{1}H) / δ(^{13}C): 8.18/130.51 (H_{16}/C_{16}), 7.94/122.39 (H_{19}/C_{19}), 7.79/127.55 (H_{13}/C_{13}), 7.27/131.37 (H_{15}/C_{15}), 6.92/125.87 (H_{14}/C_{14}), 6.86/129.41 (H_5/C_5), 6.80/129.41 (H_4/C_4), 6.46/120.67 (H_{20}/C_{20}), 2.52/27.45 (H_6/C_6), 1.64/18.06 (H_1/C_1), 1.58/24.09 (H_{10}/C_{10}) -0.72/-10.94 (H_{22}/C_{22}).

COSY (400 MHz / 400 MHz, C_6D_6, 298 K) δ(1H) / δ(1H): 8.18/7.27 (H_{16}/H_{15}), 7.94/6.46 (H_{19}/H_{20}), 7.79/6.92 (H_{13}/H_{14}), 7.27/6.92 (H_{15}/H_{14}), 6.86/6.80 (H_5/H_4), 6.80/1.64 (H_4/H_1).

FT-IR (ν/cm^{-1}): 3387, 3170, 3062, 2924, 1643 (Imino), 1589 (Quinolin), 1535, 1489, 1365, 1311 (NO_2), 1273, 1219, 1188, 1111, 910, 840, 764, 687, 633.

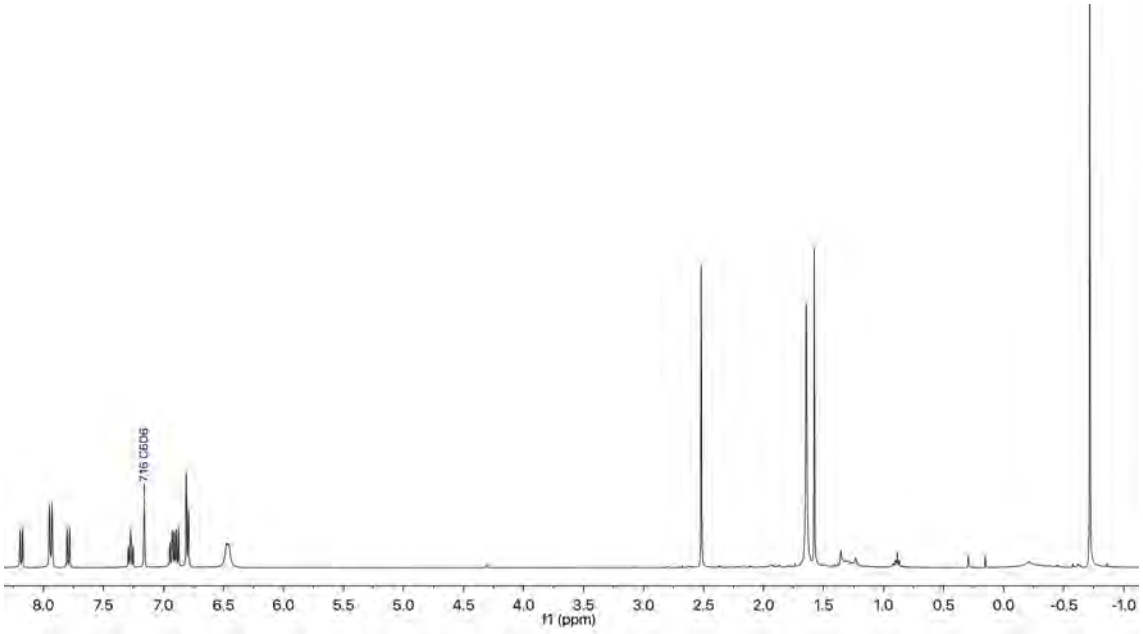


Figure S20. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

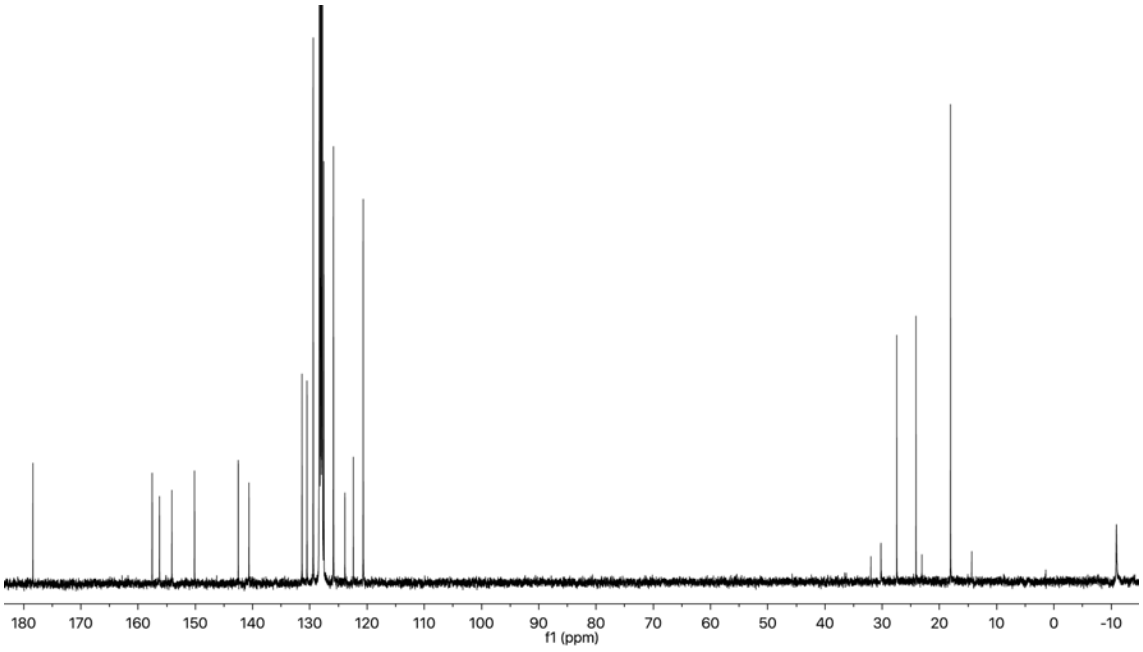


Figure S21. ^{13}C NMR (100 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of C4: A yellow prism-like specimen of $C_{28}H_{29}AlN_4O_2$, approximate dimensions 0.120 mm x 0.180 mm x 0.210 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1717 frames were collected. The total exposure time was 19.81 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33282 reflections to a maximum θ angle of 66.63° (0.84 Å resolution), of which 4337 were independent (average redundancy 7.674, completeness = 98.5%, R_{int} = 4.47%, R_{sig} = 2.47%) and 3766 (86.83%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.1200(2) Å, b = 26.0690(6) Å, c = 10.7107(2) Å, β = 101.9210(10)°, volume = 2491.54(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 9927 reflections above 20 σ(I) with 6.781° < 2θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.866. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8220 and 0.8920. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{28}H_{29}AlN_4O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 322 variables converged at R1 = 3.53%, for the observed data and wR2 = 9.40% for all data. The goodness-of-fit was 1.056. The largest peak in the final difference electron density synthesis was 0.314 $e^-/Å^3$ and the largest hole was -0.327 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.281 g/cm^3 and F(000), 1016 e^-. CCDC nr.: 1913073.

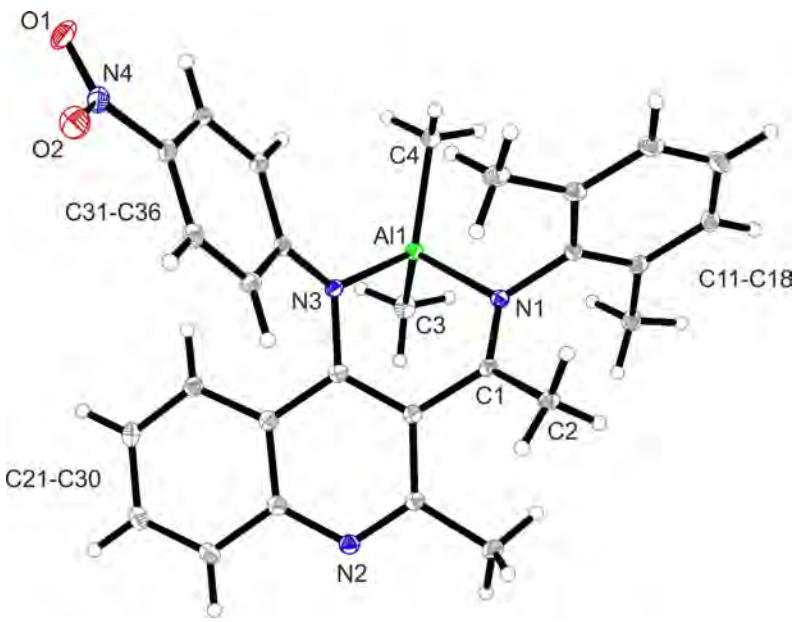


Figure S22. Crystal structure of compound **C4**. (Thermals ellipsoids are shown with 30% probability.)

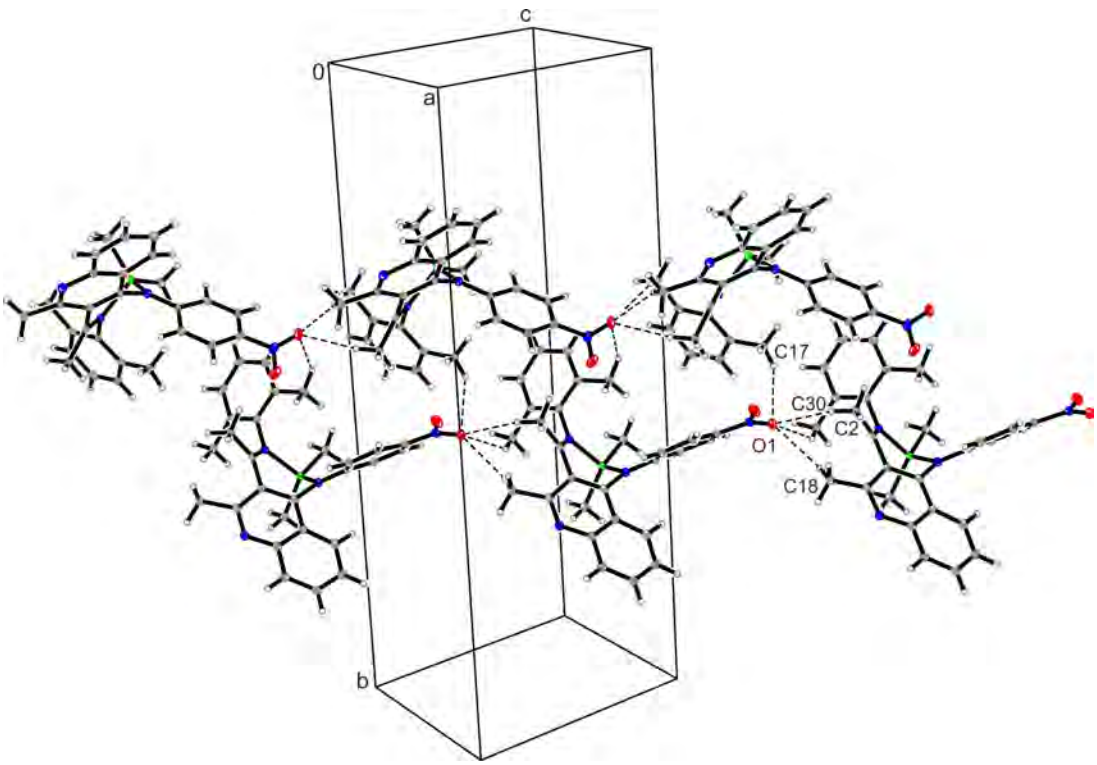


Figure S23. Excerpt of the packing diagram of **C4** presenting chain formation perpendicular to the ac-diagonal involving CH···O interactions.

Table S3. Non-covalent intermolecular and intramolecular interactions in compound **C4** (Å and deg)

D-H···*A*	*d*(*D*-H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
C2-H2A···O1$^{\#1}$	0.98	2.44	3.407(2)	169.8
C18-H18C···O1$^{\#1}$	0.98	2.58	3.328(2)	133.0
C30-H30B···O1$^{\#1}$	0.98	2.67	3.514(2)	143.9
C17-H17B···O1$^{\#2}$	0.98	2.58	3.221(1)	122.7

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x+1, y, z+1; $^{\#2}$ x+0.5, -y+1.5, z+0.5.

Table S4. Bond lengths (Å) for C4.

Al1-N3	1.8974(13)	Al1-C3	1.9468(17)
Al1-C4	1.9591(16)	Al1-N1	1.9959(13)
C1-N1	1.297(2)	C1-C21	1.483(2)
C1-C2	1.504(2)	C2-H2A	0.98
C2-H2B	0.98	C2-H2C	0.98
C3-H3A	0.98	C3-H3B	0.98
C3-H3C	0.98	C4-H4A	0.98
C4-H4B	0.98	C4-H4C	0.98
C11-C16	1.396(2)	C11-C12	1.403(2)
C11-N1	1.4520(19)	C12-C13	1.394(2)
C12-C17	1.504(2)	C13-C14	1.385(3)
C13-H13	0.95	C14-C15	1.381(2)
C14-H14	0.95	C15-C16	1.395(2)
C15-H15	0.95	C16-C18	1.507(2)
C17-H17A	0.98	C17-H17B	0.98
C17-H17C	0.98	C18-H18A	0.98
C18-H18B	0.98	C18-H18C	0.98
C21-C22	1.399(2)	C21-C29	1.441(2)
C22-N3	1.4080(19)	C22-C23	1.432(2)
C23-C28	1.414(2)	C23-C24	1.417(2)
C24-C25	1.368(2)	C24-H24	0.95
C25-C26	1.412(2)	C25-H25	0.95
C26-C27	1.366(2)	C26-H26	0.95
C27-C28	1.416(2)	C27-H27	0.95
C28-N2	1.369(2)	C29-N2	1.314(2)
C29-C30	1.508(2)	C30-H30A	0.98
C30-H30B	0.98	C30-H30C	0.98
C31-N3	1.386(2)	C31-C36	1.410(2)
C31-C32	1.410(2)	C32-C33	1.374(2)
C32-H32	0.95	C33-C34	1.390(2)
C33-H33	0.95	C34-C35	1.390(2)
C34-N4	1.447(2)	C35-C36	1.378(2)
C35-H35	0.95	C36-H36	0.95
N4-O2	1.233(2)	N4-O1	1.2381(19)

Table S5. Bond angles (°) for C4.

N3-Al1-C3	109.68(7)	N3-Al1-C4	118.60(7)
C3-Al1-C4	115.12(8)	N3-Al1-N1	89.36(6)
C3-Al1-N1	111.47(7)	C4-Al1-N1	109.75(6)
N1-C1-C21	118.79(13)	N1-C1-C2	121.54(14)
C21-C1-C2	119.56(13)	C1-C2-H2A	109.5
C1-C2-H2B	109.5	H2A-C2-H2B	109.5
C1-C2-H2C	109.5	H2A-C2-H2C	109.5
H2B-C2-H2C	109.5	Al1-C3-H3A	109.5
Al1-C3-H3B	109.5	H3A-C3-H3B	109.5
Al1-C3-H3C	109.5	H3A-C3-H3C	109.5
H3B-C3-H3C	109.5	Al1-C4-H4A	109.5
Al1-C4-H4B	109.5	H4A-C4-H4B	109.5
Al1-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	C16-C11-C12	122.84(14)
C16-C11-N1	118.22(13)	C12-C11-N1	118.93(14)
C13-C12-C11	117.09(15)	C13-C12-C17	121.65(15)
C11-C12-C17	121.26(14)	C14-C13-C12	121.32(16)
C14-C13-H13	119.3	C12-C13-H13	119.3
C15-C14-C13	120.07(16)	C15-C14-H14	120.0
C13-C14-H14	120.0	C14-C15-C16	121.12(16)
C14-C15-H15	119.4	C16-C15-H15	119.4
C15-C16-C11	117.51(15)	C15-C16-C18	121.19(15)
C11-C16-C18	121.29(14)	C12-C17-H17A	109.5
C12-C17-H17B	109.5	H17A-C17-H17B	109.5
C12-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C22-C21-C29	118.96(14)
C22-C21-C1	120.34(13)	C29-C21-C1	120.67(13)
C21-C22-N3	121.14(14)	C21-C22-C23	118.38(14)
N3-C22-C23	120.29(13)	C28-C23-C24	118.66(14)
C28-C23-C22	117.73(14)	C24-C23-C22	123.53(14)
C25-C24-C23	120.68(15)	C25-C24-H24	119.7
C23-C24-H24	119.7	C24-C25-C26	120.42(15)
C24-C25-H25	119.8	C26-C25-H25	119.8
C27-C26-C25	120.12(15)	C27-C26-H26	119.9
C25-C26-H26	119.9	C26-C27-C28	120.57(15)
C26-C27-H27	119.7	C28-C27-H27	119.7

N2-C28-C23	123.10(14)	N2-C28-C27	117.43(14)
C23-C28-C27	119.41(15)	N2-C29-C21	122.69(14)
N2-C29-C30	114.23(13)	C21-C29-C30	123.01(14)
C29-C30-H30A	109.5	C29-C30-H30B	109.5
H30A-C30-H30B	109.5	C29-C30-H30C	109.5
H30A-C30-H30C	109.5	H30B-C30-H30C	109.5
N3-C31-C36	121.93(14)	N3-C31-C32	120.02(14)
C36-C31-C32	118.02(14)	C33-C32-C31	120.76(15)
C33-C32-H32	119.6	C31-C32-H32	119.6
C32-C33-C34	119.72(15)	C32-C33-H33	120.1
C34-C33-H33	120.1	C33-C34-C35	121.07(14)
C33-C34-N4	119.52(15)	C35-C34-N4	119.40(15)
C36-C35-C34	119.05(15)	C36-C35-H35	120.5
C34-C35-H35	120.5	C35-C36-C31	121.26(15)
C35-C36-H36	119.4	C31-C36-H36	119.4
C1-N1-C11	118.66(13)	C1-N1-Al1	120.42(11)
C11-N1-Al1	120.06(9)	C29-N2-C28	118.94(13)
C31-N3-C22	119.07(12)	C31-N3-Al1	131.09(10)
C22-N3-Al1	108.96(10)	O2-N4-O1	122.84(14)
O2-N4-C34	119.14(15)	O1-N4-C34	118.02(15)

Table S6. Torsion angles (°) for C4.

C16-C11-C12-C13	-2.1(2)	N1-C11-C12-C13	178.99(13)
C16-C11-C12-C17	178.52(14)	N1-C11-C12-C17	-0.3(2)
C11-C12-C13-C14	0.1(2)	C17-C12-C13-C14	179.46(15)
C12-C13-C14-C15	1.1(2)	C13-C14-C15-C16	-0.5(2)
C14-C15-C16-C11	-1.4(2)	C14-C15-C16-C18	178.07(15)
C12-C11-C16-C15	2.8(2)	N1-C11-C16-C15	-178.35(13)
C12-C11-C16-C18	-176.71(14)	N1-C11-C16-C18	2.2(2)
N1-C1-C21-C22	-41.7(2)	C2-C1-C21-C22	134.61(15)
N1-C1-C21-C29	140.25(15)	C2-C1-C21-C29	-43.4(2)
C29-C21-C22-N3	-173.44(13)	C1-C21-C22-N3	8.5(2)
C29-C21-C22-C23	1.5(2)	C1-C21-C22-C23	-176.52(13)
C21-C22-C23-C28	2.2(2)	N3-C22-C23-C28	177.25(13)
C21-C22-C23-C24	-174.41(14)	N3-C22-C23-C24	0.6(2)
C28-C23-C24-C25	3.0(2)	C22-C23-C24-C25	179.65(15)
C23-C24-C25-C26	0.2(2)	C24-C25-C26-C27	-2.4(2)
C25-C26-C27-C28	1.1(2)	C24-C23-C28-N2	172.94(14)
C22-C23-C28-N2	-3.9(2)	C24-C23-C28-C27	-4.2(2)
C22-C23-C28-C27	178.97(14)	C26-C27-C28-N2	-175.13(15)

C26-C27-C28-C23	2.2(2)	C22-C21-C29-N2	-4.3(2)
C1-C21-C29-N2	173.76(14)	C22-C21-C29-C30	172.55(14)
C1-C21-C29-C30	-9.4(2)	N3-C31-C32-C33	178.42(14)
C36-C31-C32-C33	-3.6(2)	C31-C32-C33-C34	2.2(2)
C32-C33-C34-C35	1.2(2)	C32-C33-C34-N4	-177.24(14)
C33-C34-C35-C36	-3.0(2)	N4-C34-C35-C36	175.44(14)
C34-C35-C36-C31	1.4(2)	N3-C31-C36-C35	179.70(14)
C32-C31-C36-C35	1.8(2)	C21-C1-N1-C11	178.79(13)
C2-C1-N1-C11	2.5(2)	C21-C1-N1-Al1	9.43(18)
C2-C1-N1-Al1	-166.84(11)	C16-C11-N1-C1	93.89(17)
C12-C11-N1-C1	-87.20(17)	C16-C11-N1-Al1	-96.70(14)
C12-C11-N1-Al1	82.21(15)	C21-C29-N2-C28	2.8(2)
C30-C29-N2-C28	-174.28(14)	C23-C28-N2-C29	1.3(2)
C27-C28-N2-C29	178.55(14)	C36-C31-N3-C22	20.0(2)
C32-C31-N3-C22	-162.19(14)	C36-C31-N3-Al1	-148.05(13)
C32-C31-N3-Al1	29.8(2)	C21-C22-N3-C31	-121.77(16)
C23-C22-N3-C31	63.35(19)	C21-C22-N3-Al1	48.69(16)
C23-C22-N3-Al1	-126.19(12)	C3-Al1-N3-C31	-139.47(14)
C4-Al1-N3-C31	-4.35(16)	N1-Al1-N3-C31	107.90(14)
C3-Al1-N3-C22	51.61(12)	C4-Al1-N3-C22	-173.28(10)
N1-Al1-N3-C22	-61.02(10)	C33-C34-N4-O2	-166.22(14)
C35-C34-N4-O2	15.3(2)	C33-C34-N4-O1	13.8(2)
C35-C34-N4-O1	-164.66(14)		

Table S7. Hydrogen bond distances (Å) and angles (°) for C4.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C2-H2A···O1	0.98	2.44	3.407(2)	168.8

CO_2 / Epoxide catalyst study.

General procedure for catalyst screening

Styrene oxide **Xa** (1.7 mmol), **C1-4** (17.0 μmol) and TBAI (17.0 μmol) were placed in an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor Carousel 12 Place Reaction Station. The reaction mixture was stirred at 80 °C and 1 bar of CO_2 pressure for 24 h. Then the conversion of styrene oxide **Xa** into styrene carbonate **Ya** was determined by ^{1}H NMR spectroscopy analyses.

General procedure for cyclic carbonates synthesis

Epoxide **Xa–h** (1.7 mmol), **C3** (25.5 μmol) and TBAI (25.5 μmol) were placed an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor. The reaction mixture was stirred at 80 °C for 24 h. The conversion of epoxide to cyclic carbonate was determined by ^{1}H NMR spectroscopy analyses. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated under vacuum to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent gradient as follow: hexane, hexane:EtOAc (9:1), hexane:EtOAc (6:1), hexane:EtOAc (3:1) and EtOAc to give the pure cyclic carbonate. Cyclic carbonates **Ya–h** are all known compounds and the spectroscopic data for samples prepared using catalyst **C3** were consistent with those reported in the literature.[2,3,4,5,6,7]

Cyclic carbonate Ya-h characterization

Styrene carbonate (Ya): Obtained as a white solid. (251.1 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.33–7.50 (m, 5H, ArH), 5.68 (t, *J*=8.0 Hz, 1H, PhCHO), 4.83 (t, *J*=8.4 Hz, 1H, OCH_2), 4.36 ppm (t, *J*=8.6 Hz, 1H, OCH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.7, 135.7, 129.6, 129.1, 125.7, 77.9, 71.0 ppm.

[2] J. Martínez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North, A. Rodríguez-Diéguez, *Chem. Eur. J.* **2015**, *21*, 9850–9862.
[3] J. A. Castro-Osma, M. North, W. K. Offermans, W. Leitner, T. E. Muller, *ChemSusChem* **2016**, *9*, 791–794.
[4] J. Steinbauer, A. Spannenberg, T. Werner, *Green Chem.* **2017**, *19*, 3769–3779.
[5] J. Rintjema, A. W. Kleij, *ChemSusChem* **2017**, *10*, 1274–1282.
[6] D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North, R. S. Rojas, *ChemCatChem* **2018**, *10*, 2271–2277.
[7] Y. R. Yepes, C. Quintero, D. O. Meléndez, C. G. Daniliuc, J. Martínez, R. S. Rojas, *Organometallics* **2018**, DOI: 10.1021/acs.organomet.8b00795.

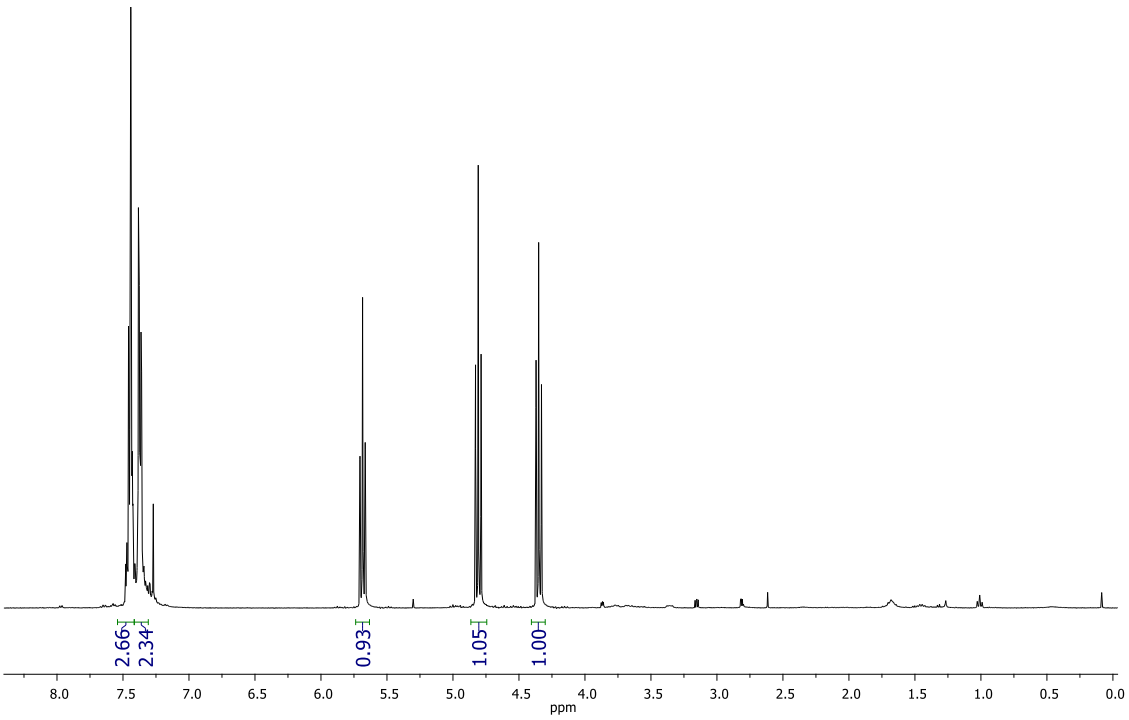


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

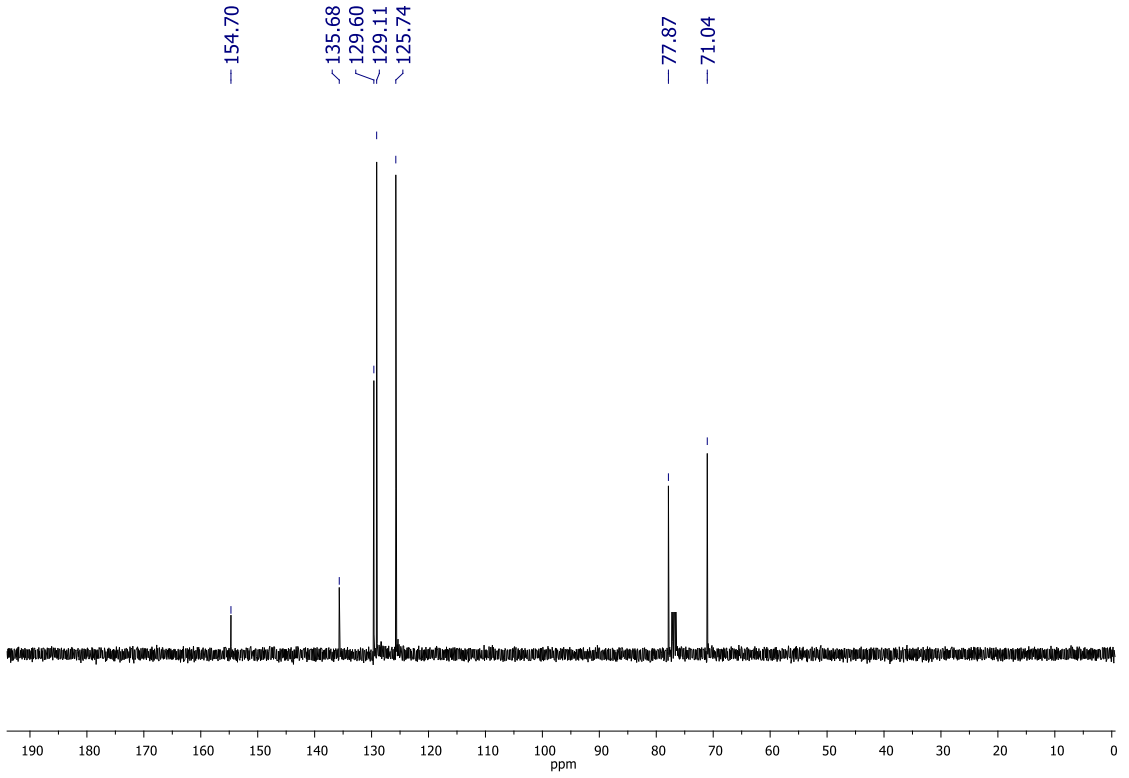


Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

1,2-Hexylene carbonate (Xb): Obtained as a colourless liquid (225.5 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.66–4.76 (m, 1H, OCH), 4.53 (t, *J*=8.3 Hz, 1H, OCH_2), 4.08 (dd, *J*=8.0, 7.0 Hz, 1H, OCH_2), 1.62–1.86 (m, 2H, CH_2), 1.30–1.52 (m, 4H, $2OCH_2$), 0.93 ppm (t, *J*=7.0 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.0, 77.0, 69.3, 33.5, 26.4, 22.2, 13.7 ppm.

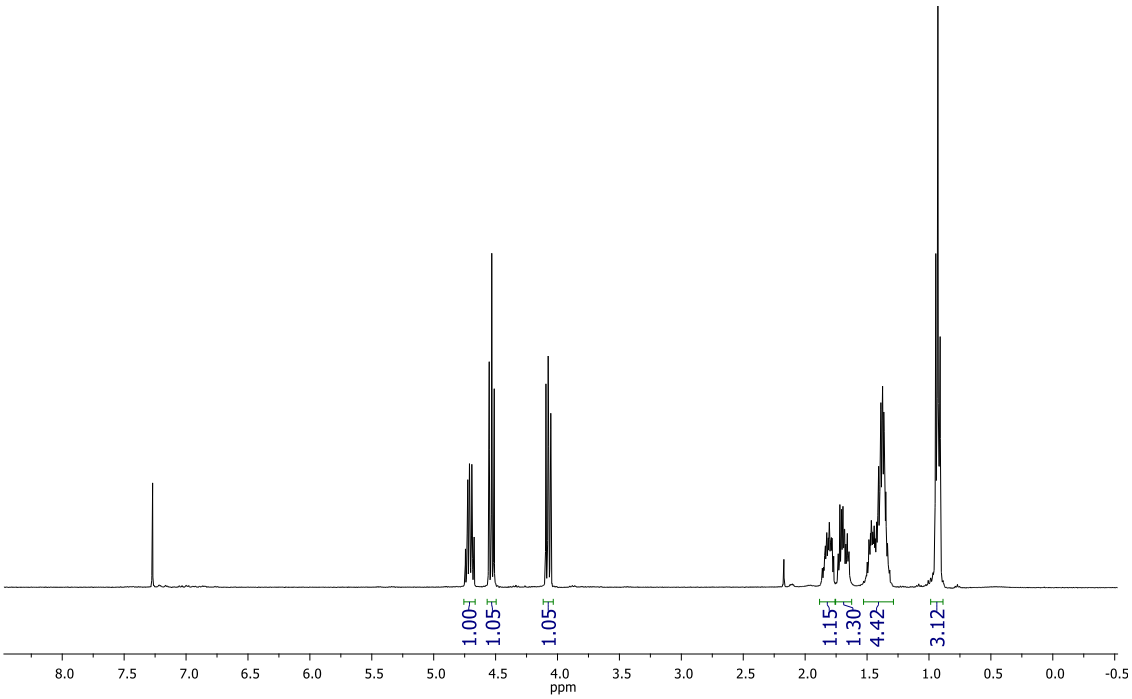


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

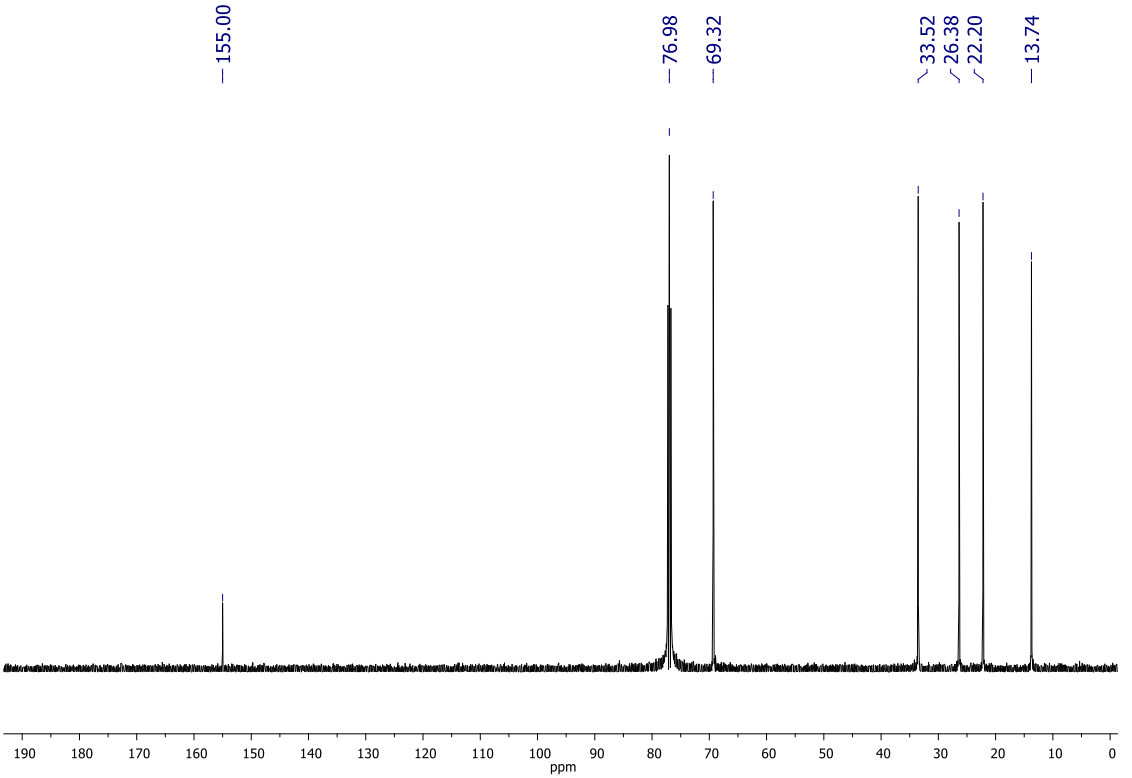


Figure S27. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

3-Phenoxyproplylene carbonate (Xc): Obtained as a white solid. (287.2 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.28–7.34 (m, 2H, 2OArH), 7.02 (t, *J*=7.2 Hz, 1H ArH), 6.88–6.94 (m, 2H, 2OArH), 5.00–5.05 (m, 1H, OCH), 4.50–4.64 (m, 2H, OCH_2), 4.24 (dd, *J*=10.6, 4.2 Hz, 1H, CH_2OPh), 4.15 ppm (dd, J=10.6, 4.2 Hz, 1H, CH_2OPh); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 157.7, 154.6, 129.7, 122.0, 114.6, 74.1, 66.9, 66.2 ppm.

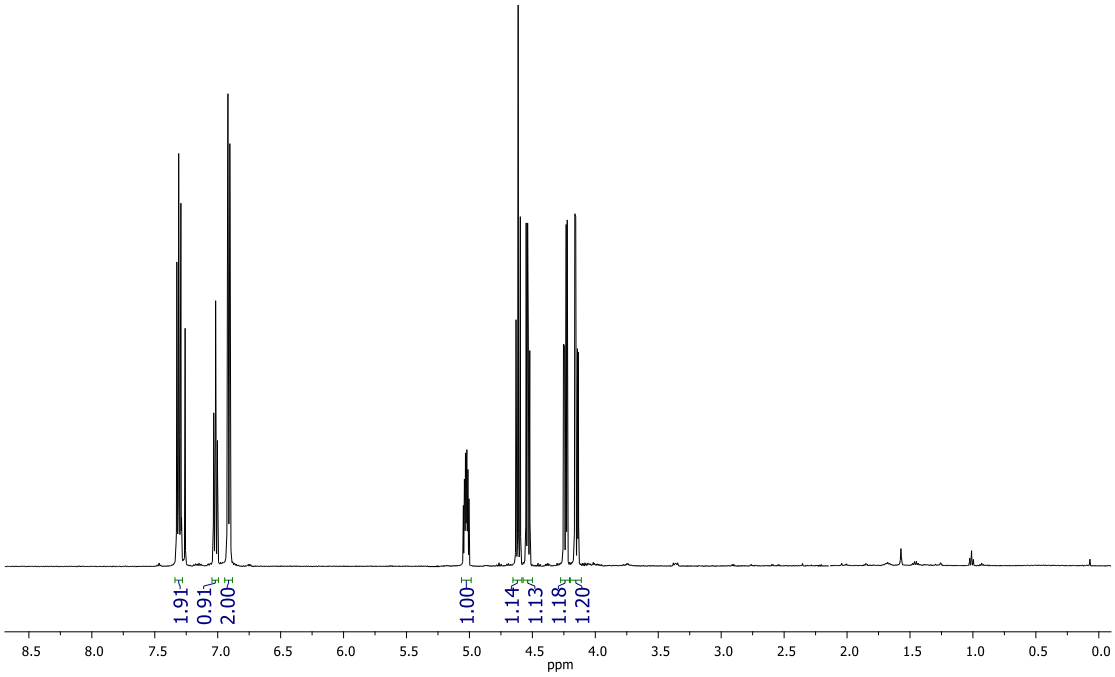


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

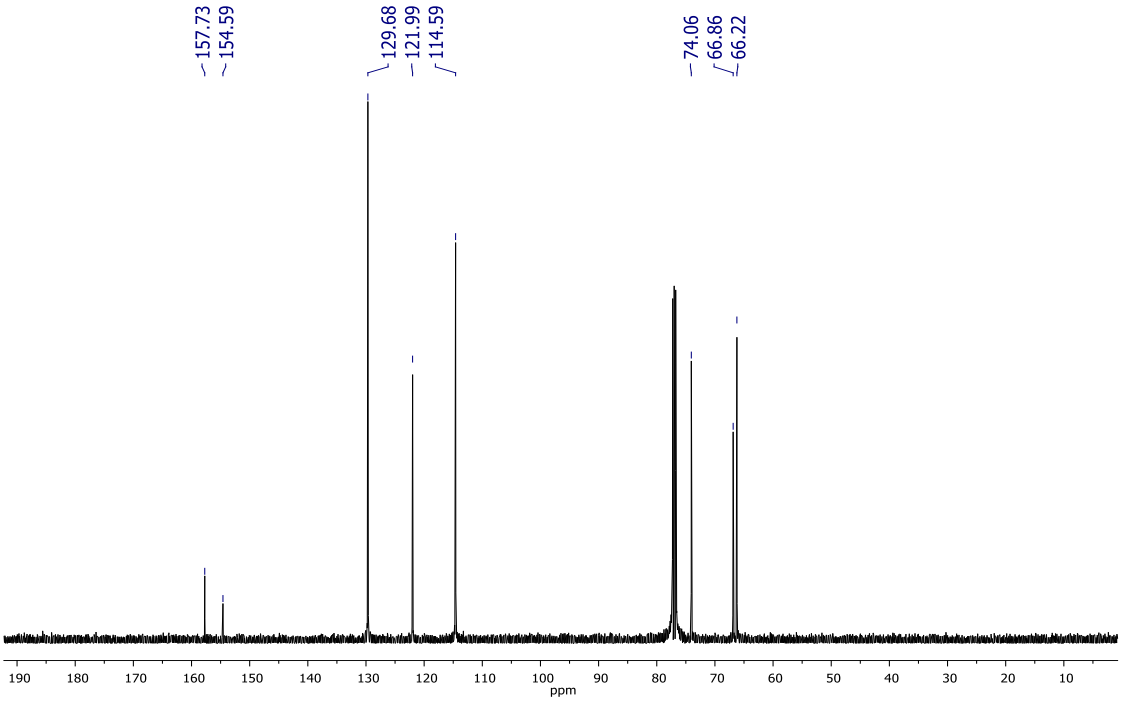


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

4-Chlorostyrene carbonate (Xd): Obtained as a white solid. (263.3 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.42 (d, *J*=8.0 Hz, 2H, ArH), 7.31 (d, *J*=8.0 Hz, 2H, ArH), 5.67 (t, *J*=8.0 Hz, 1H, OCH), 4.81 (t, *J*=8.0 Hz, 1H, OCH), 4.31 ppm (t, *J*=7.5 Hz, 1H, OCH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.3, 136.3, 130.2, 129.8, 126.4, 78.8, 71.7 ppm.

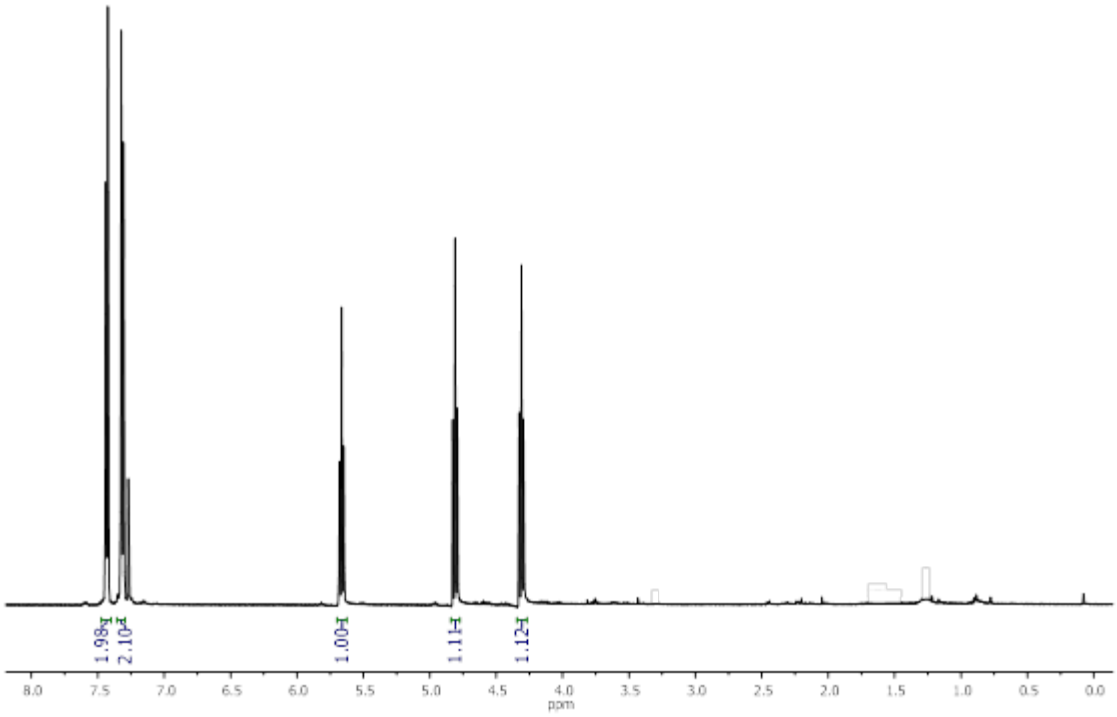


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

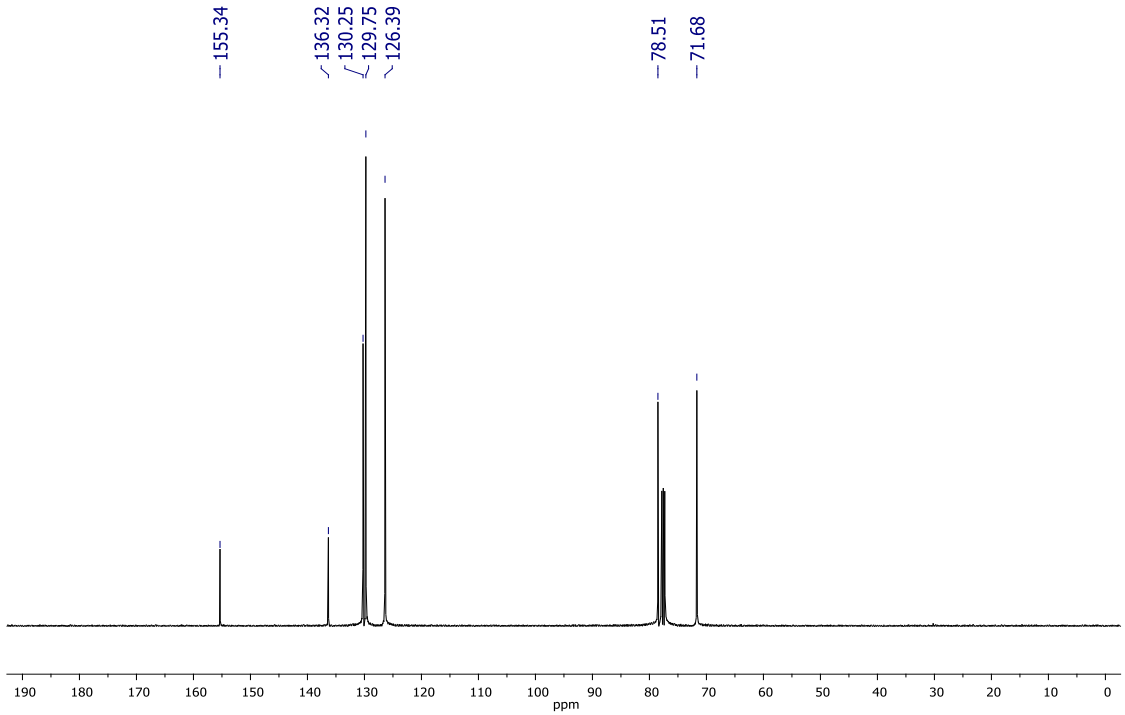


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

4-Bromostyrene carbonate (Xe): Obtained as a white solid. (392.5 mg, 95%) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.41 (m, 2H, ArH), 7.30 (m, 2H, ArH), 5.67 (t, *J*=7.0 Hz, 1H, OCH), 4.81 (t, *J*=8.0 Hz, 1H, OCH_2), 4.30 ppm (dd, *J*=8.8, 7.6 Hz, 1H, OCH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.0, 136.2, 134.8, 130.0, 127.8, 77.7, 71.5 ppm.

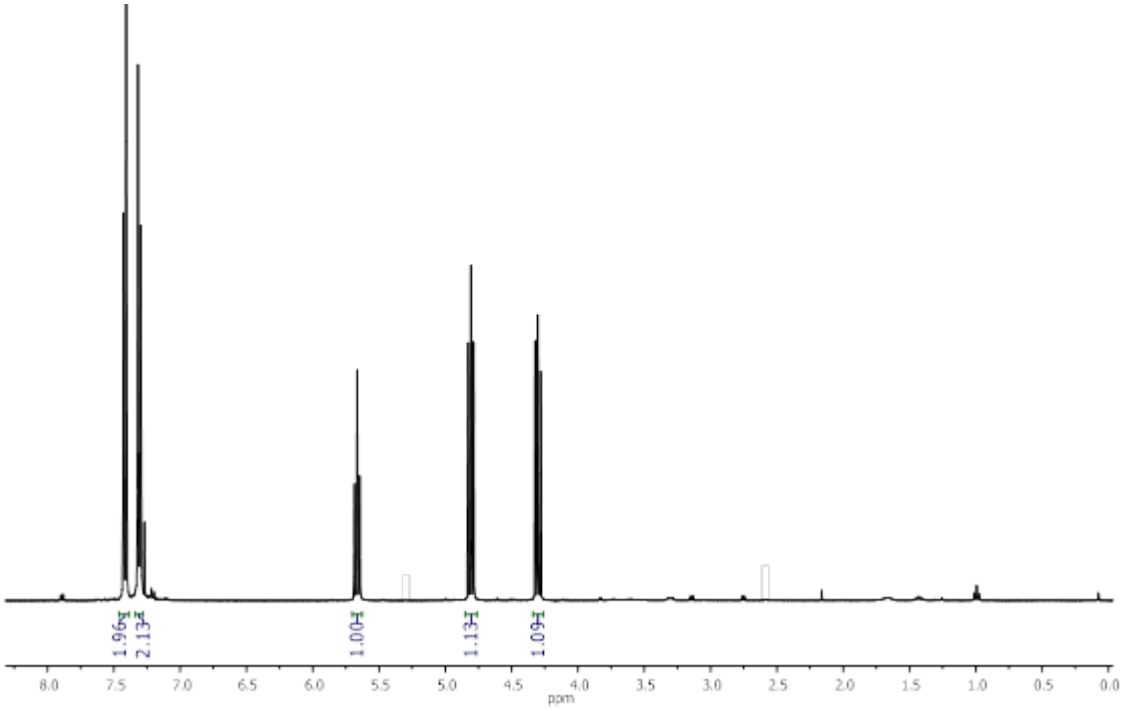


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

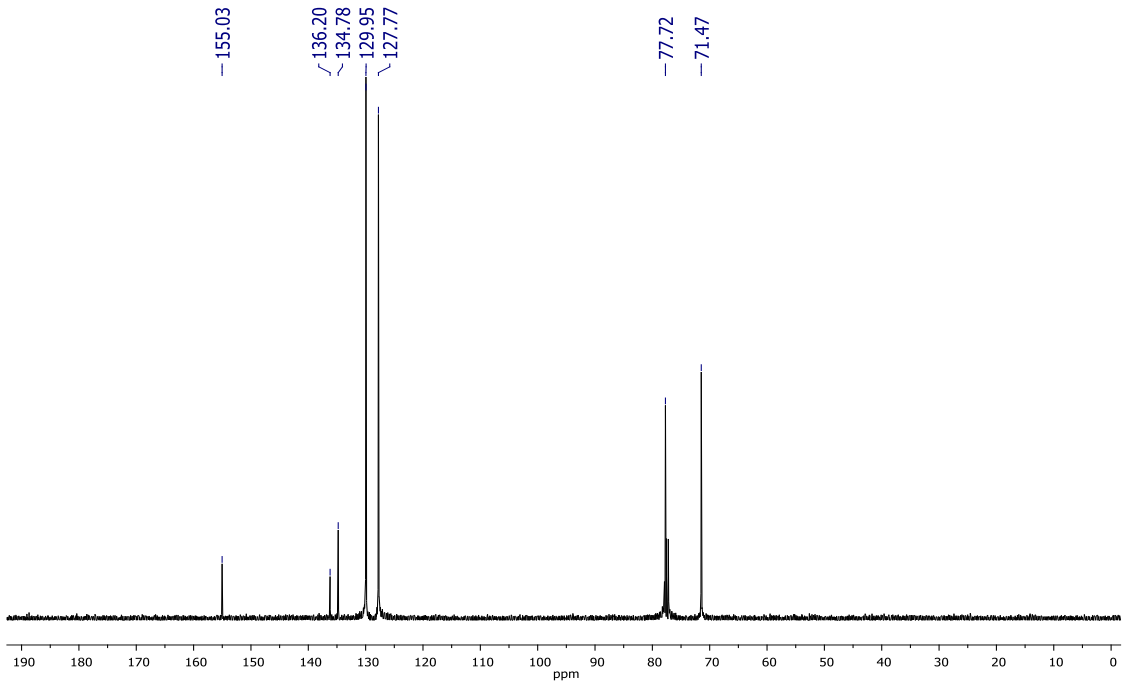


Figure S33. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

3-Chloropropylene carbonate (Xf): Obtained as a colourless liquid. (211.2 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 5.01-4.92 (m, 1H, OCH), 4.58 (t, *J*=8.6 Hz, 1H, CH_2Cl), 4.39 (dd, *J*=9.0, 8.7 Hz, 1H, CH_2Cl), 3.78 (dd, *J*=12.0, 7.0 Hz, 1H, CH_2O), 3.72 ppm (dd, *J*=12.5, 4.0 Hz, CH_2O); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.7, 74.8, 67.5, 44.2 ppm.

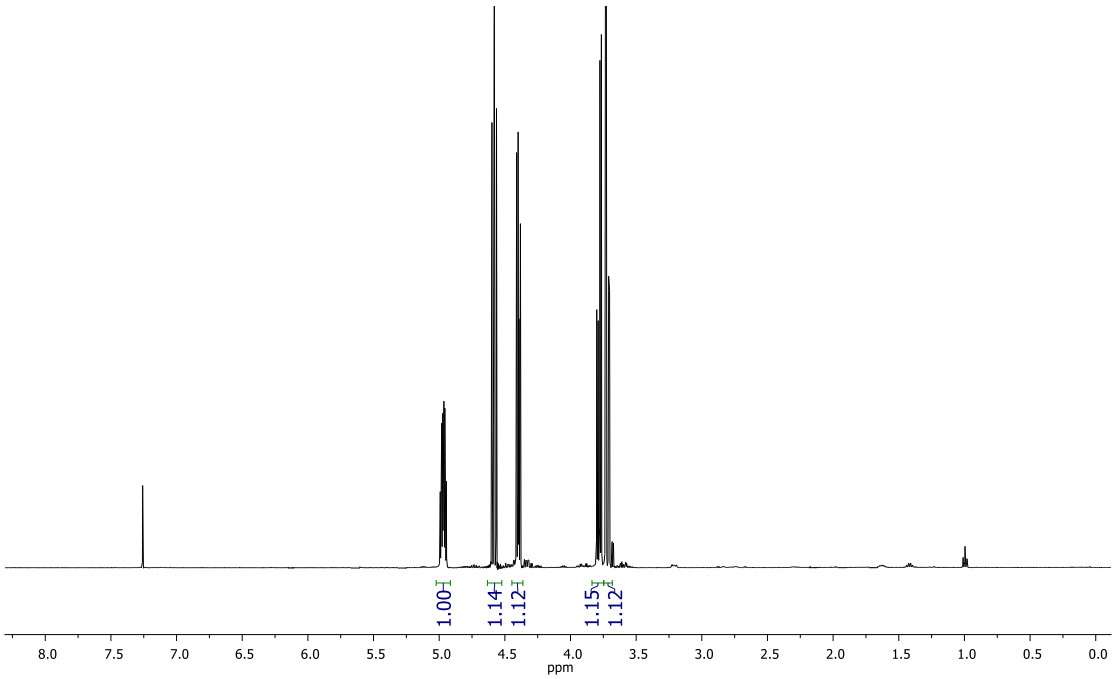


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

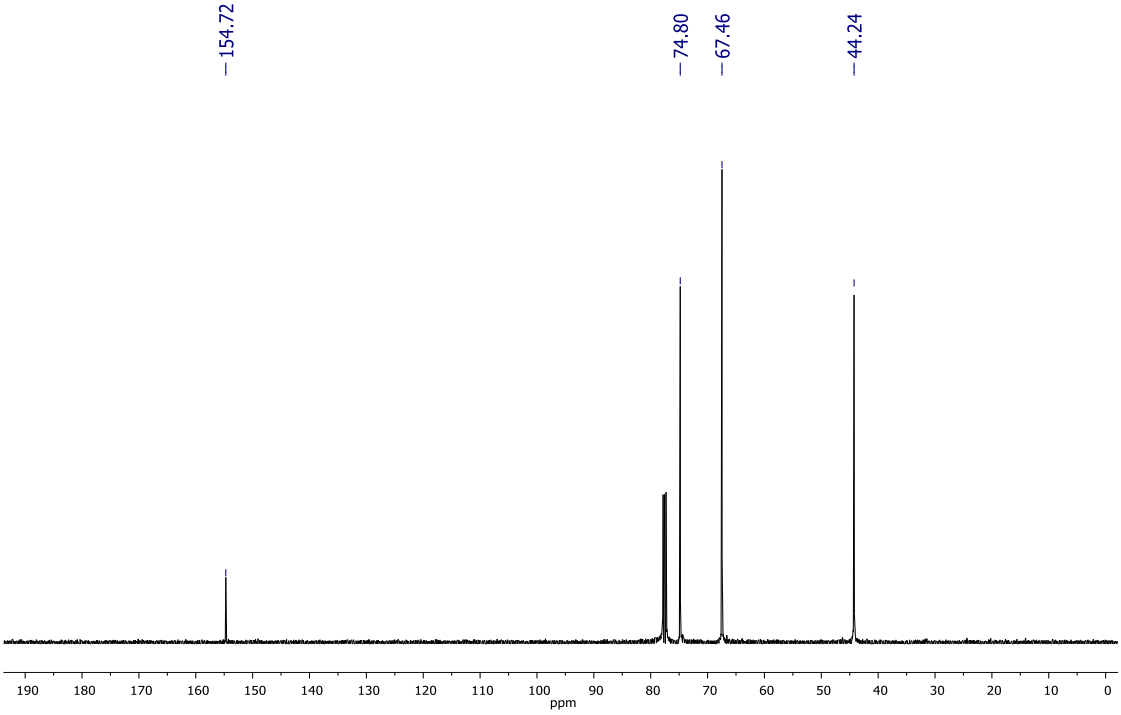


Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (Xg). Obtained as a colourless liquid (315.7 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, 289 K): δ = 5.83 (tt, *J*=52.8, 4.8 Hz, 1H, $CHCF_2$), 4.76-4.81 (m, 1H, OCH), 4.45 (t, *J*=7.6 Hz, 1H, OCH_2), 4.29 (dd, *J*=7.6, 6.0 Hz, 1H, OCH_2), 3.67-3.93 ppm (m, 4H, OCH_2CF_2, OCH_2CH); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 159.9 (C=O), 113.9 (tt, *J*=994.0, 107.6 Hz, $CHCF_2$), 108.2 (tt, *J*=991.6, 138.8 Hz, CF_2), 77.4 (CH), 70,4 (CH_2), 67.4 (t, *J*=112.4 Hz, CH_2), 64.9 ppm (CH_2). ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = (-139.3) - (-139.4) (m, 2F), (-125.1) - (-125.0) ppm (m, 2F).

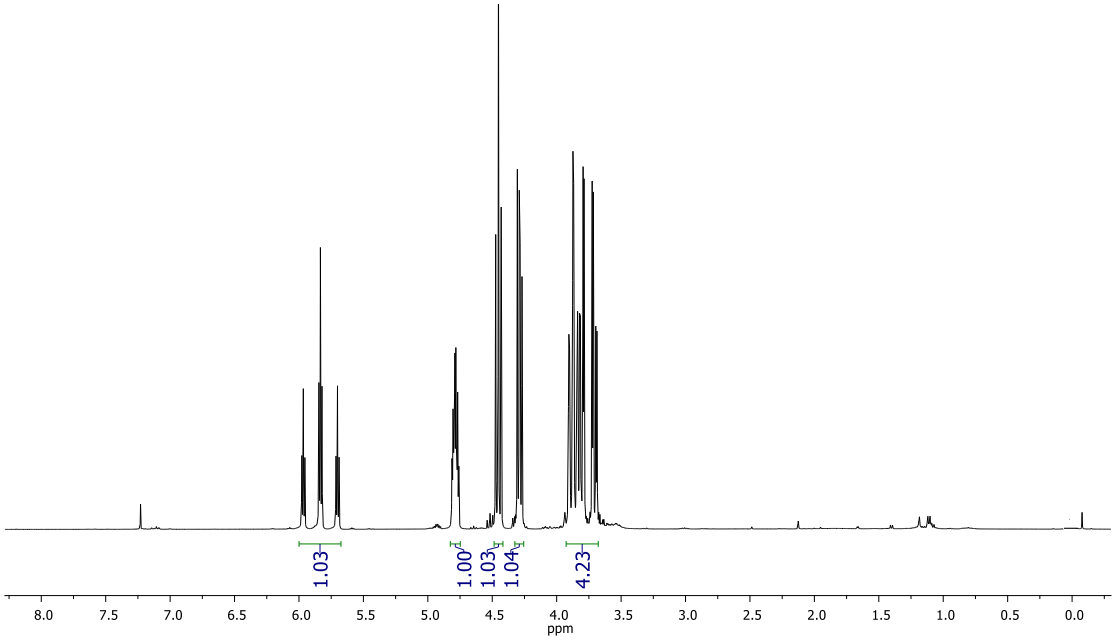


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

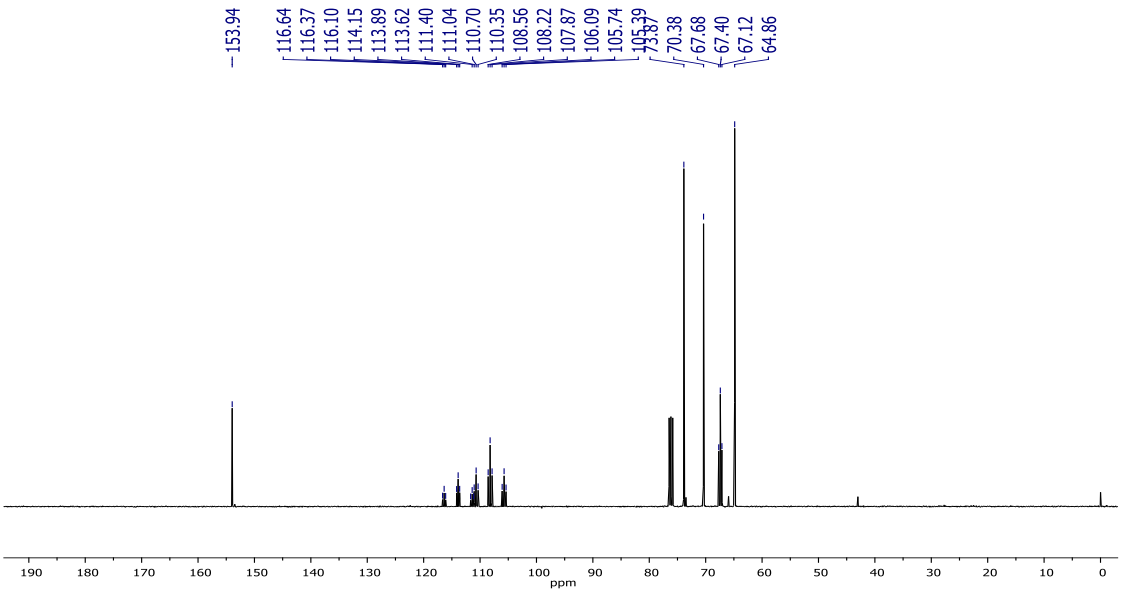


Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

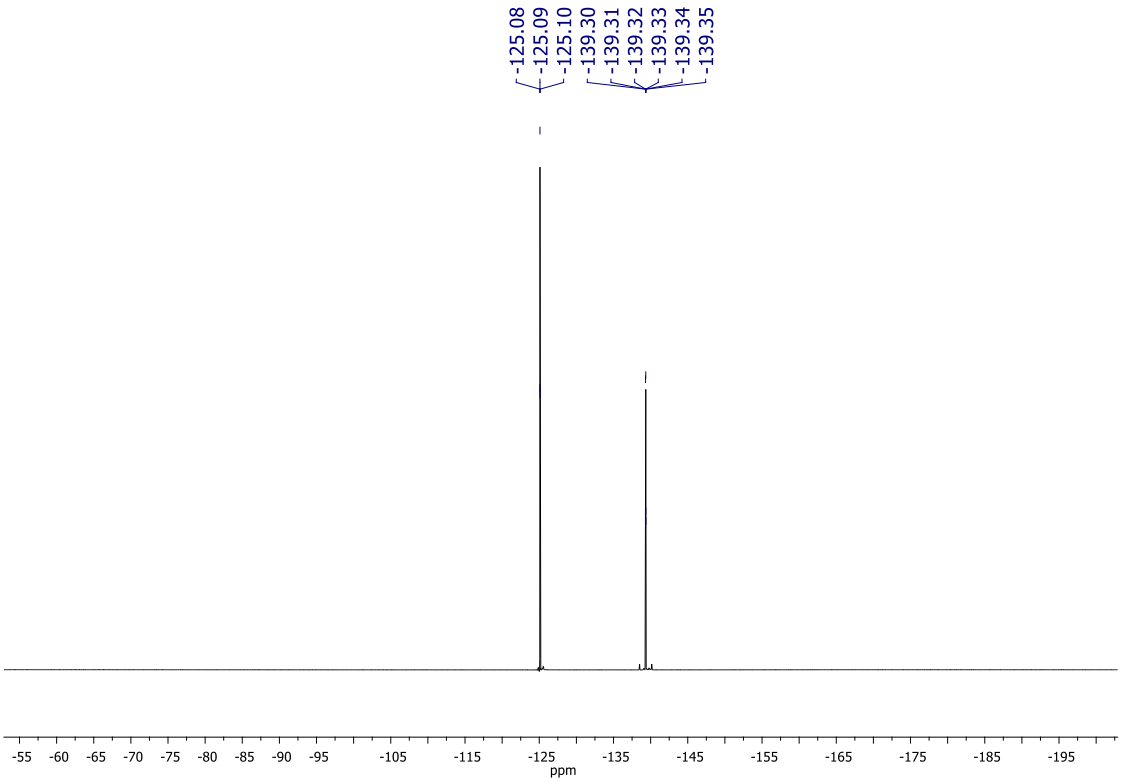


Figure S38. ^{19}**F NMR** (400 MHz, $CDCl_3$, 298 K)

4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan- 2-one (Xh). Obtained as a colourless liquid. (485.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.01 (tt, *J*=52.0, 5.6 Hz, 1H, CHF_2), 4.75-4.83 (m, 1H, OCH), 4.46 (t, *J*=8.8 Hz, 1H, OCH_2), 4.31 (dd, *J*=8.4, 6.0 Hz, 1H, OCH_2), 3.72-4.20 ppm (m, 4H, OCH_2CF_2, OCH_2CH); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 153.8 (C=O), 103.9-117.2 (m, 3 x CF_2), 106.7 (tt, *J*=1009.2, 123.2 Hz, $CHCF_2$), 73.8 (CH), 70,6 (CH_2), 67.3 (t, *J*=102.8 Hz, CH_2), 64.8 ppm (CH_2).^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = (−137.6)–(−136.7) (m, 2F), (−130.4)–(−129.5) (m, 2F), (−125.6)–(−125.7) (m, 2F), (−120.0)– (−120.1) (m, 2F) ppm.

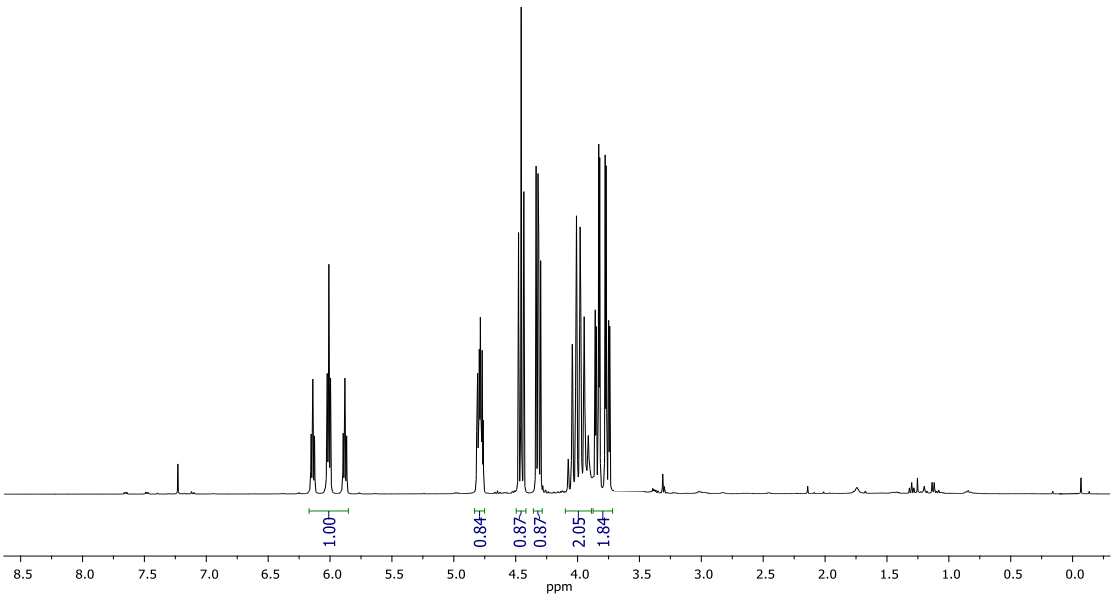


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

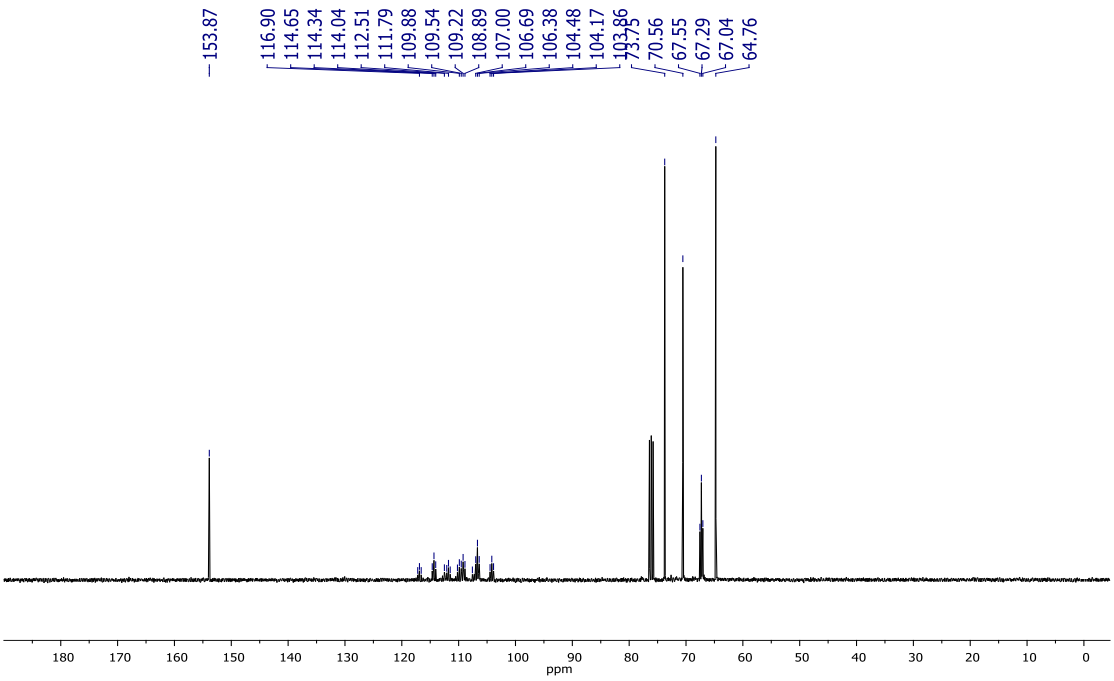


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)

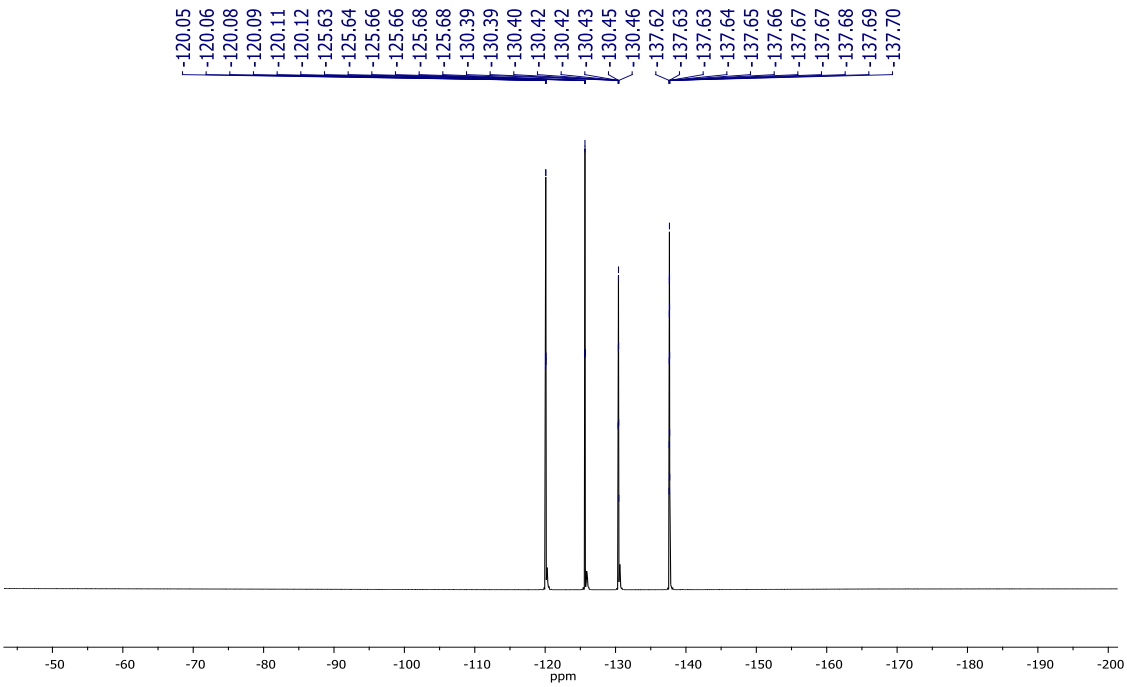
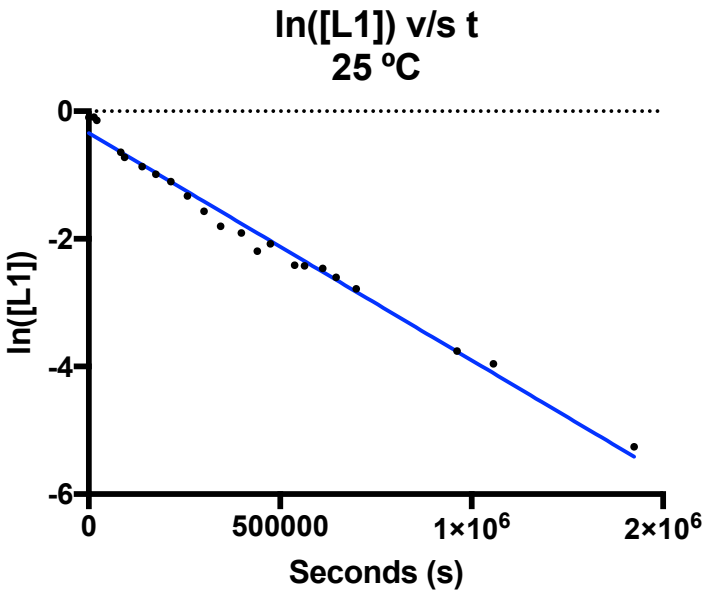


Figure S41. ^{19}**F NMR** (400 MHz, $CDCl_3$, 298 K)

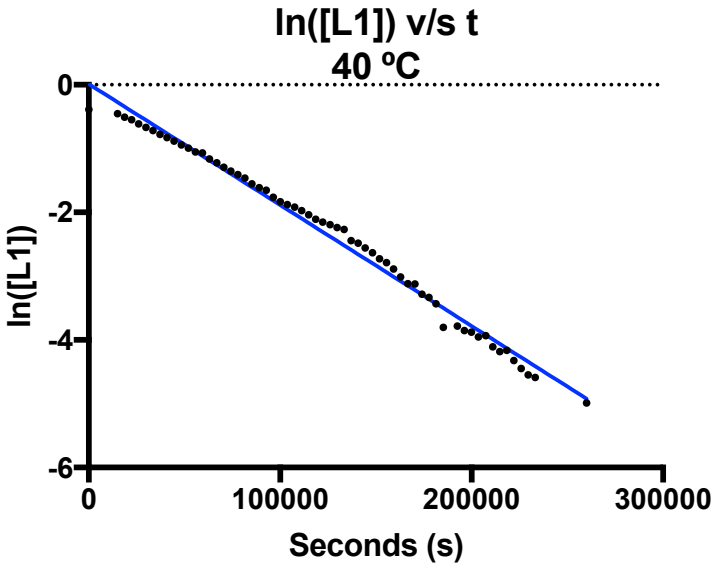
Intramolecular cyclization kinetic study



$$y = -3.56x10^{-6}x - 0.3411$$

$$r^2 = 0.9864$$

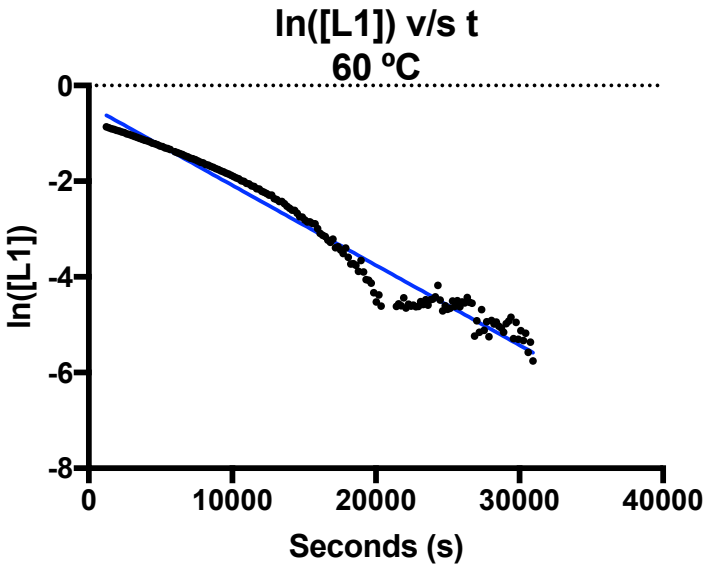
Figure S42. First order rate plot (ln([**L1**]) vs t) at 25 °C.



$$y = -1.897x10^{-5}x - 0.01319$$

$$r^2 = 0.9896$$

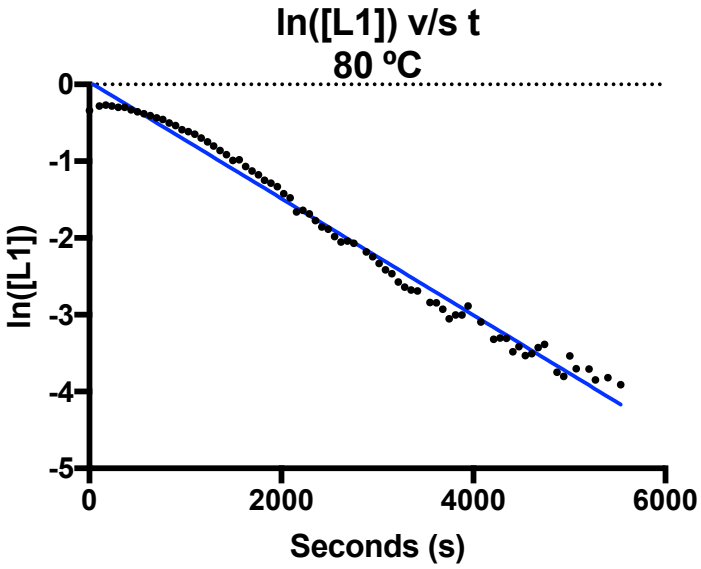
Figure S43. First order rate plot (ln([**L1**]) vs t) at 40 °C.



$$y = -1.67x10^{-4}x - 0.4141$$

$$r^2 = 0.9733$$

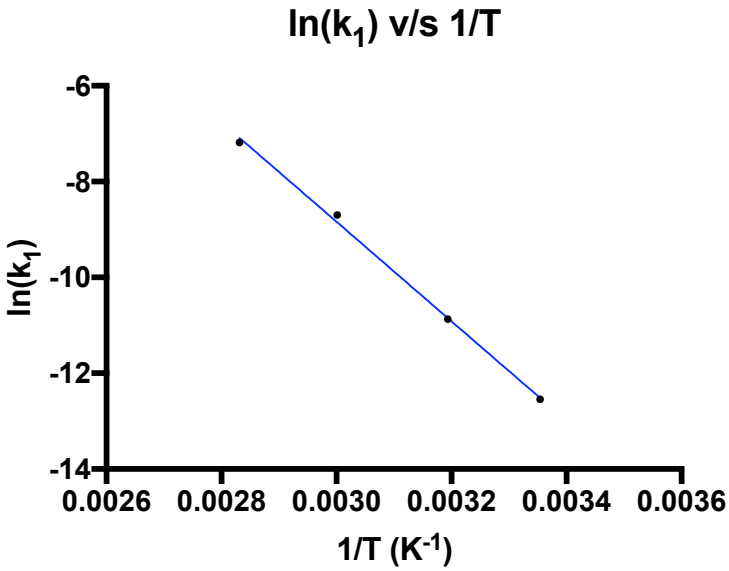
Figure S44. First order rate plot (ln([**L1**]) vs t) at 60 °C.



$$y = -7.59x10^{-4}x - 0.03329$$

$$r^2 = 0.9880$$

Figure S45. First order rate plot (ln([**L1**]) vs t) at 80 °C.



$$y = -10390x + 22.33$$

$$r^2 = 0.9979$$

$$Arrhenius\ equation:$$

$$ln(k_1) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

$$E_a = 20.6\ {}^{kcal}/_{mol}$$

Figure S46. Arrhenius plot ($Ln(k_1)$ vs 1/T) for the intramolecular cyclization of **L1**.