

Ti(IV)-Trisphenolate Catalyst Systems For the Ring-Opening Copolymerization of Cyclohexene Oxide and Carbon Dioxide

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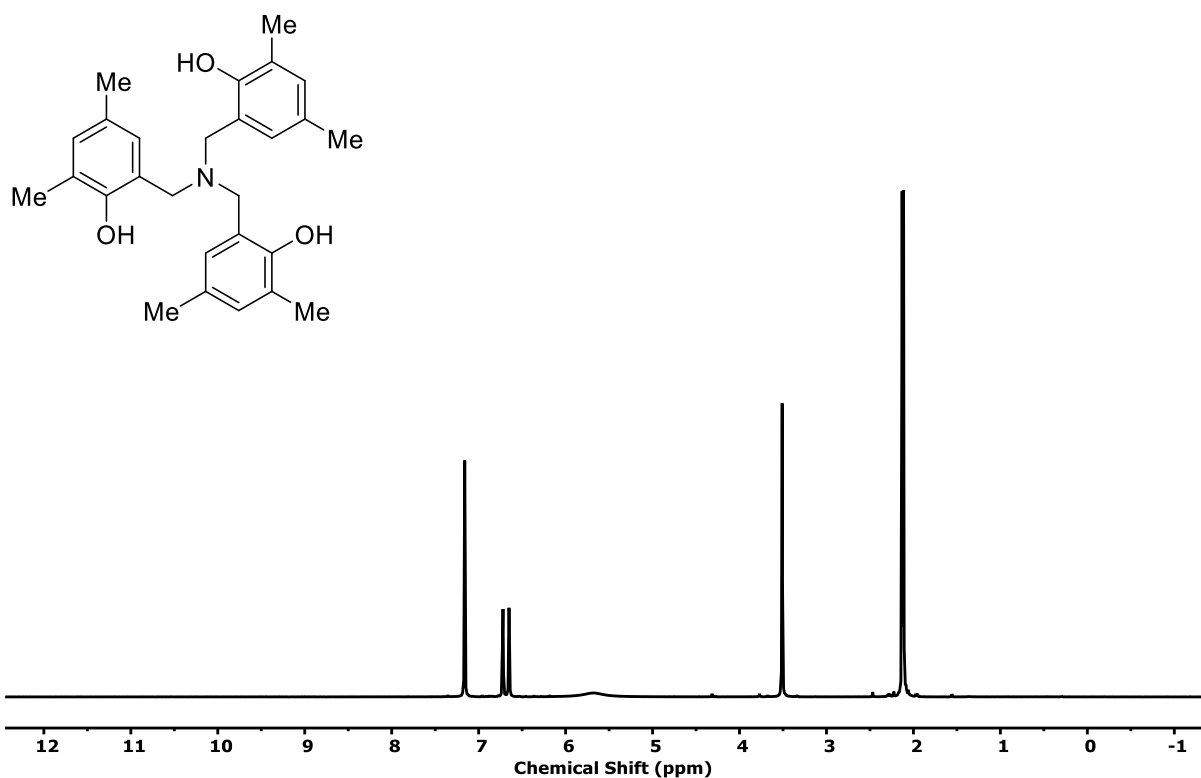


Figure S1: 1H NMR spectrum of H_3L^{Me} ligand (400 MHz, C_6D_6 , 298K)

1H NMR (400 MHz, C_6D_6 , 298K) δ (ppm) 6.72 (s, 3H), 6.65 (s, 3H), 5.65 (br s, 3H), 3.51 (s, 6H), 2.13 (s, 9H), 2.11 (s, 9H).

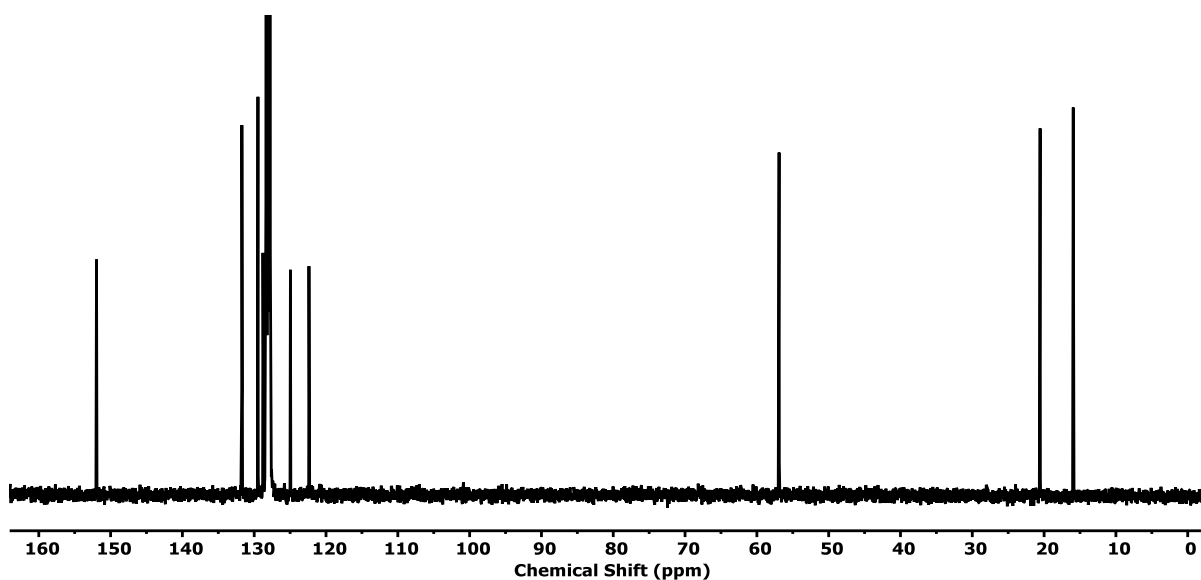


Figure S2: ^{13}C { 1H } NMR spectrum of H_3L^{Me} ligand (101 MHz, C_6D_6 , 298K)

^{13}C { 1H } NMR (101 MHz, C_6D_6 , 298K) δ (ppm) 151.96, 131.72, 129.48, 128.78, 124.96, 122.38, 56.91, 20.56, 15.94.

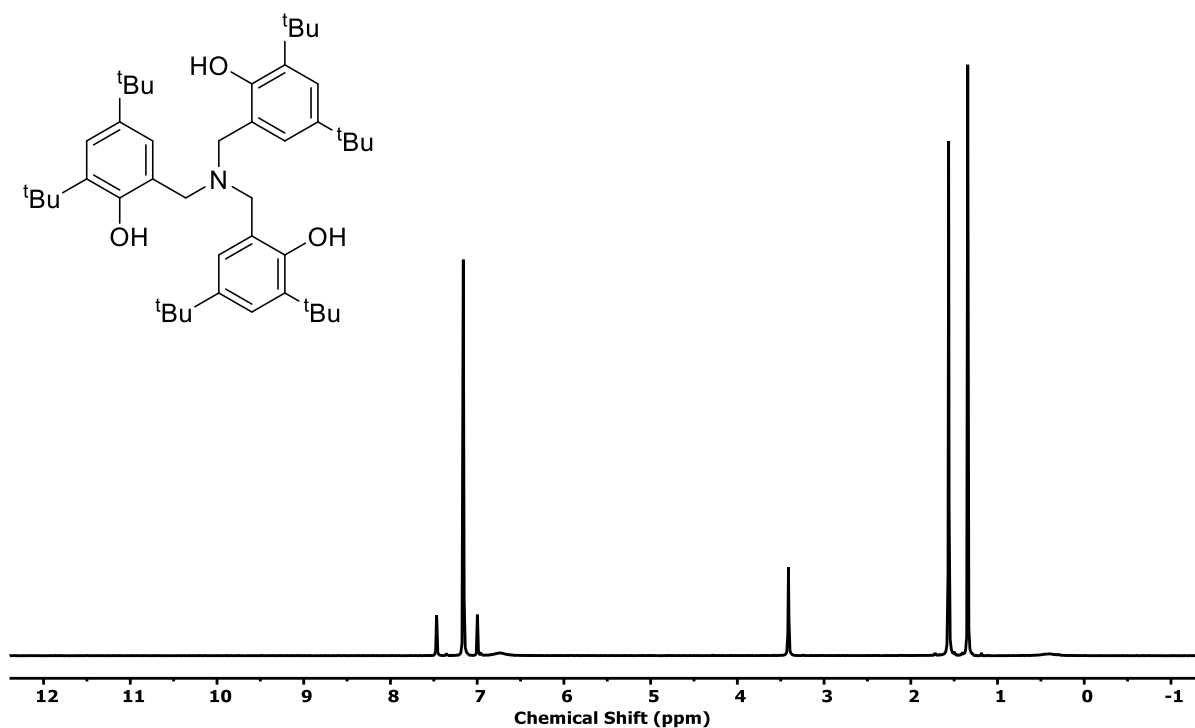


Figure S3: ¹H NMR spectrum of H₃L^{tBu} ligand (400 MHz, C₆D₆, 298K)

¹H NMR (400 MHz, C₆D₆, 298K) δ (ppm) 7.47 (s, 3H) 7.00 (s, 3H), 6.75 (br s, 3H), 3.41 (s, 6H), 1.56 (s, 27H), 1.34 (s, 27H).

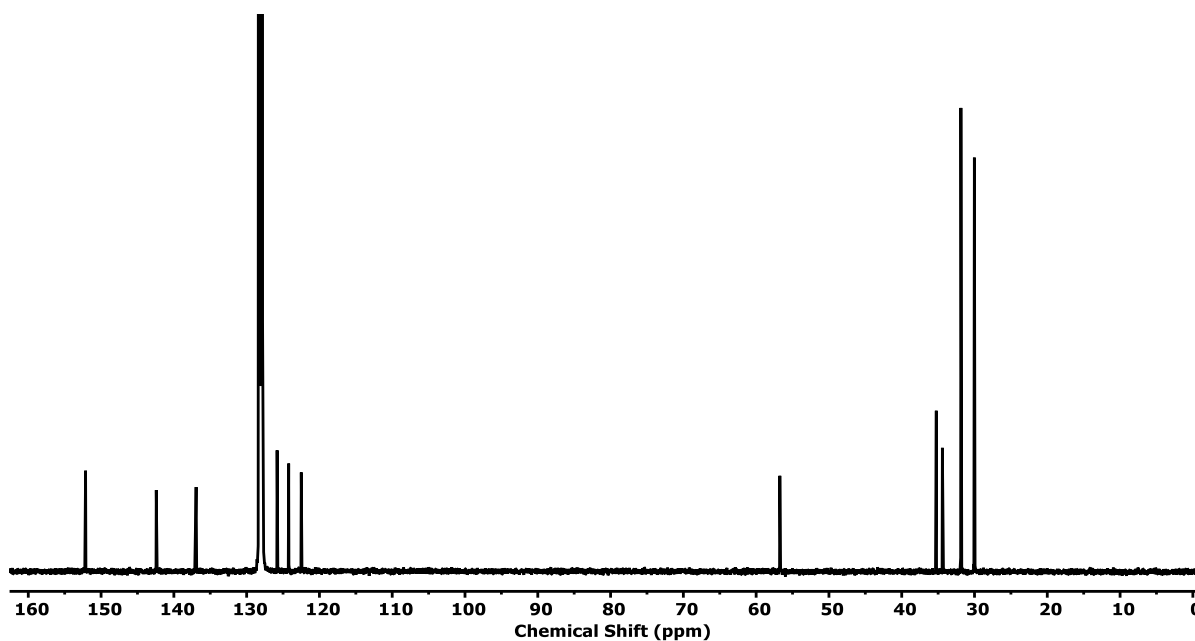


Figure S4: ¹³C {¹H} NMR spectrum of H₃L^{tBu} ligand (126 MHz, C₆D₆, 298K)

¹³C {¹H} NMR (126 MHz, C₆D₆, 298K) δ (ppm) 152.13, 142.42, 136.94, 125.81, 124.23, 122.49, 56.75, 35.25, 33.41, 31.87, 30.02.

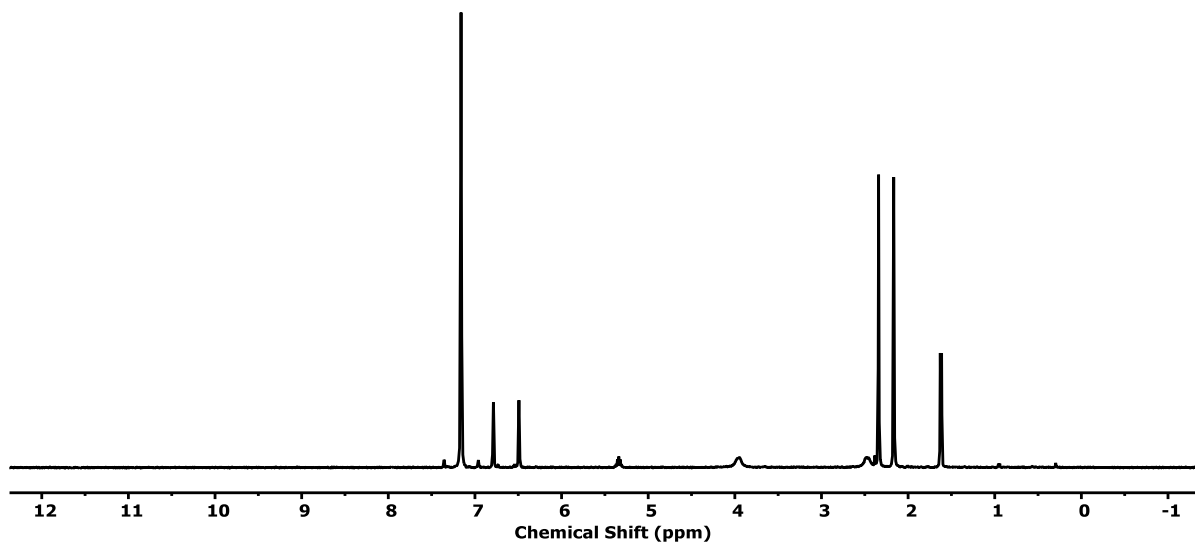
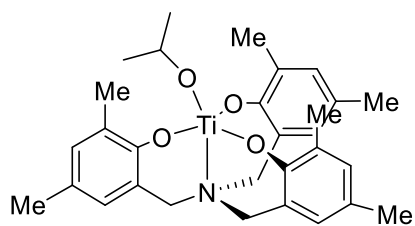


Figure S5: ^1H NMR spectrum of complex 2 ($\text{ATP}^{\text{Me}}\text{TiO}^i\text{Pr}$) (400 MHz, C_6D_6 , 298K)

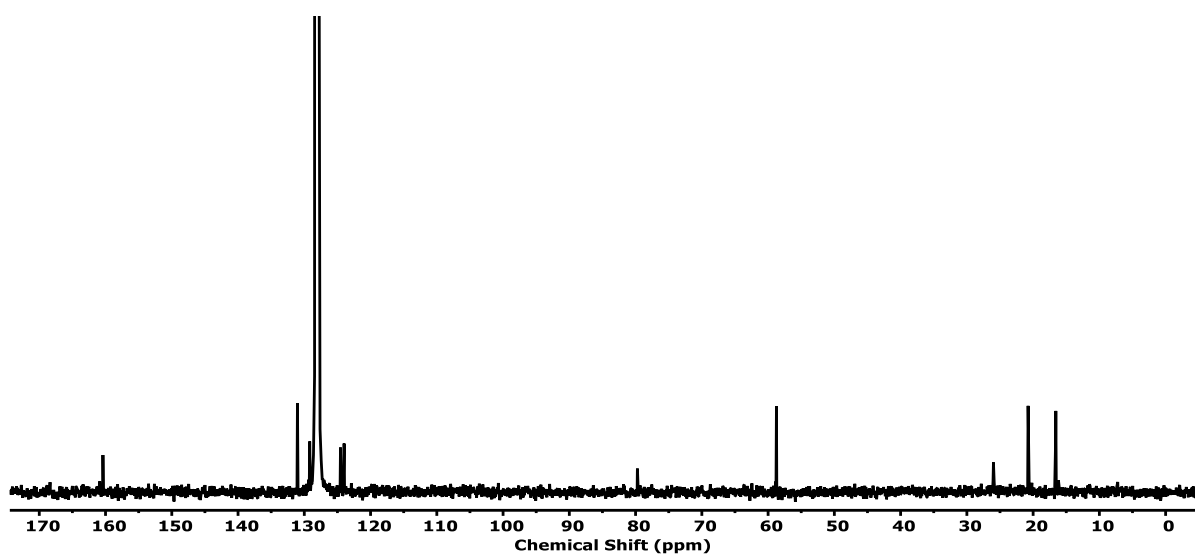


Figure S6: ^{13}C $\{^1\text{H}\}$ NMR spectrum of complex 2 ($\text{ATP}^{\text{Me}}\text{TiO}^i\text{Pr}$) (126 MHz, C_6D_6 , 298K)

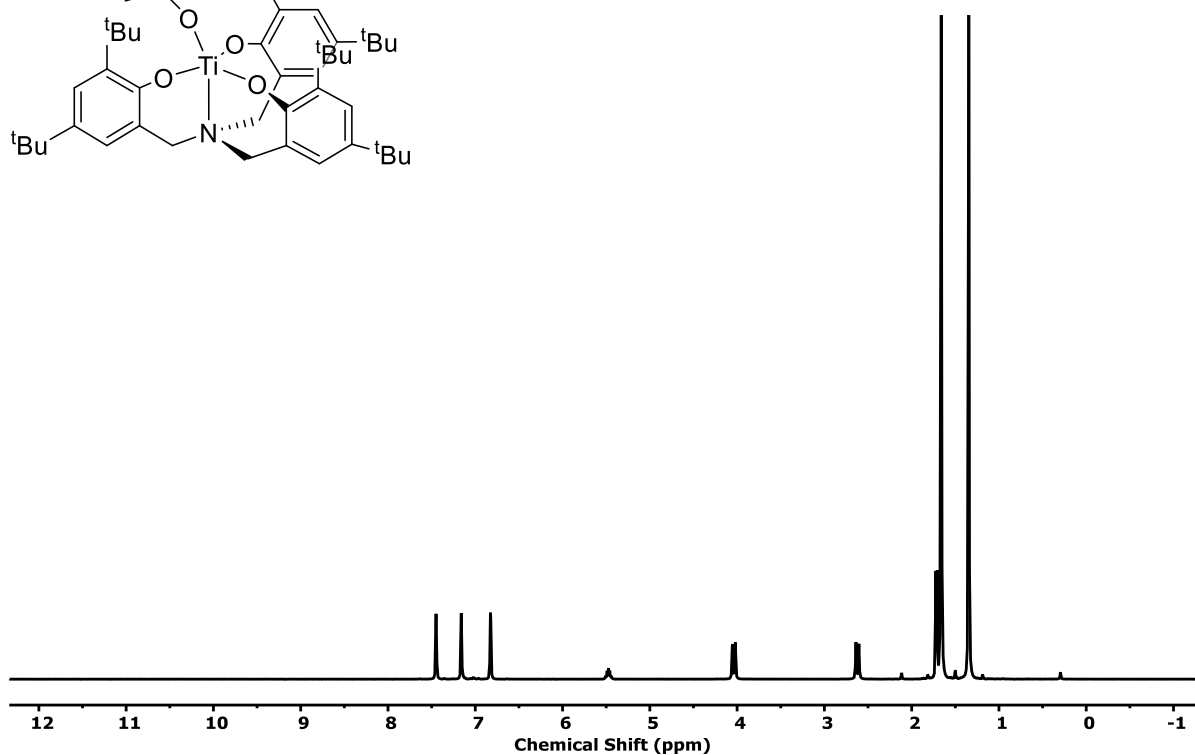
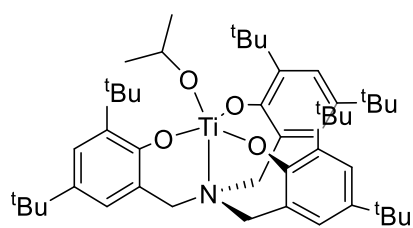


Figure S7: ^1H NMR spectrum of complex 1 ($\text{ATP}^{\text{tBu}}\text{Ti}^{\text{oPr}}$) (400 MHz, C_6D_6 , 298K)

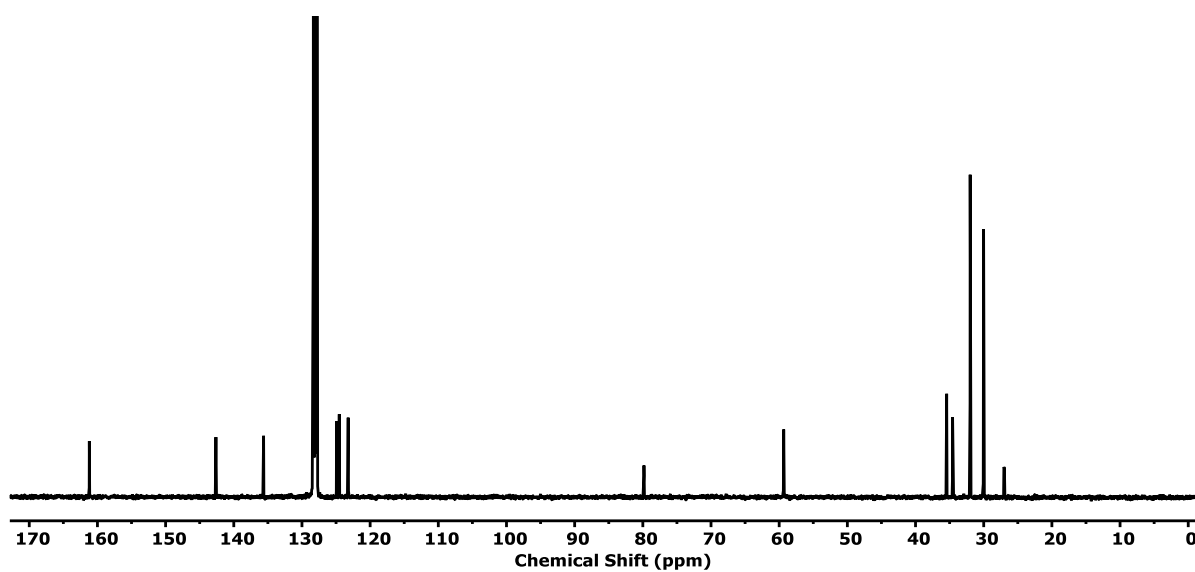


Figure S8: ^{13}C $\{^1\text{H}\}$ NMR spectrum of complex 1 ($\text{ATP}^{\text{tBu}}\text{Ti}^{\text{oPr}}$) (101 MHz, C_6D_6 , 298K)

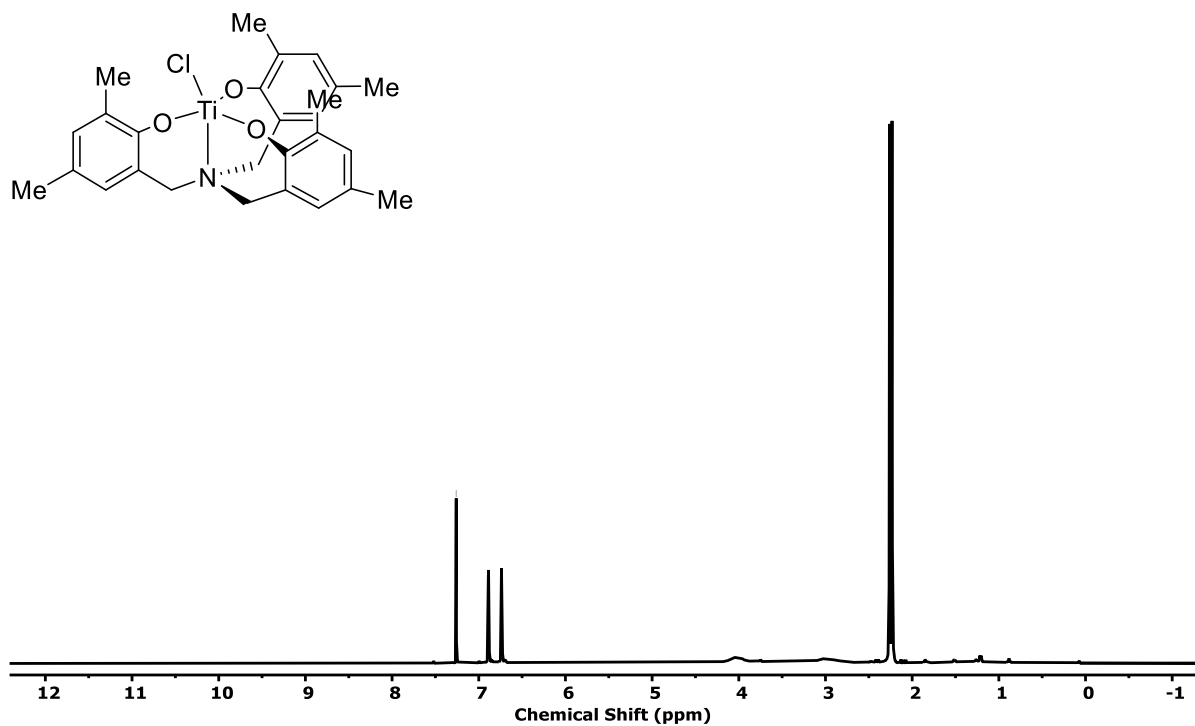


Figure S9: ¹H NMR spectrum of complex 3 (ATP)^{Me}TiCl (500 MHz, CDCl₃, 298K)

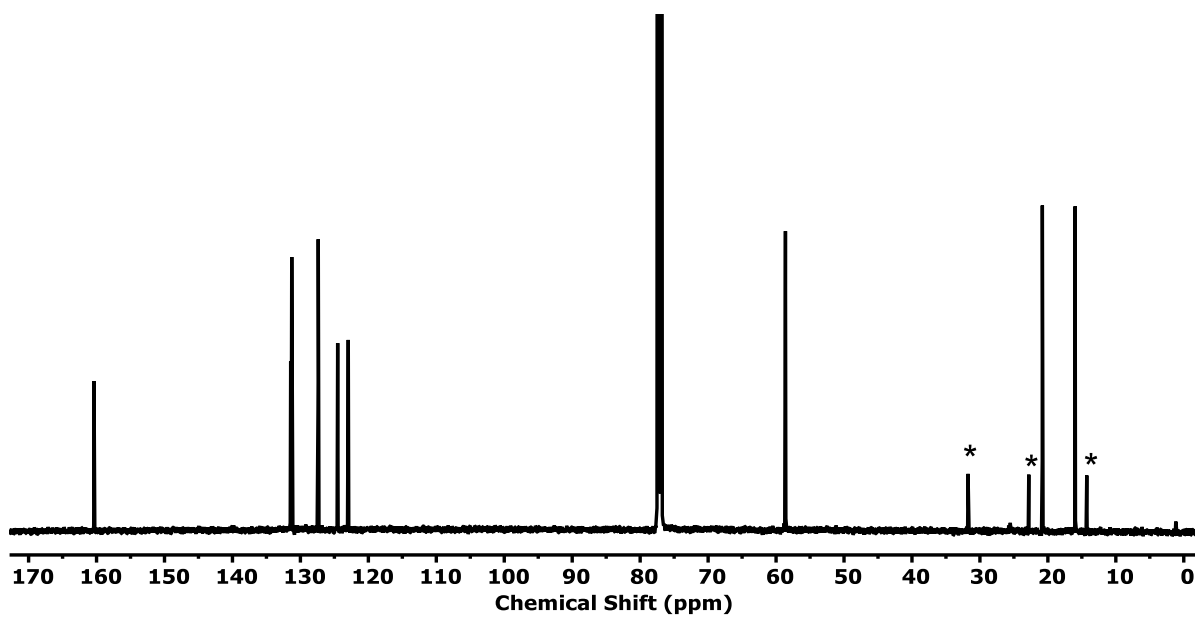


Figure S10: ¹³C {¹H} NMR spectrum of complex 3 (ATP)^{Me}TiCl (126 MHz, CDCl₃, 298K)

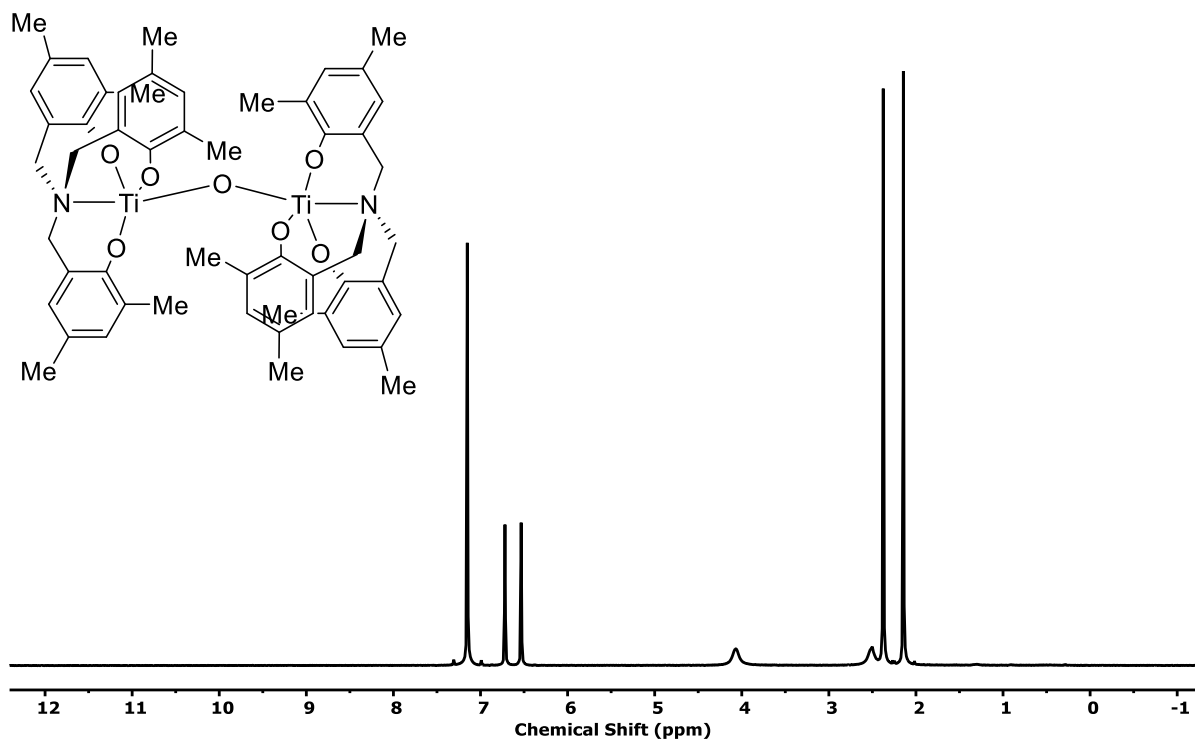


Figure S11: 1H NMR spectrum of dimer $(L^{Me}Ti)_2O$ (400 MHz, C_6D_6 , 298K)

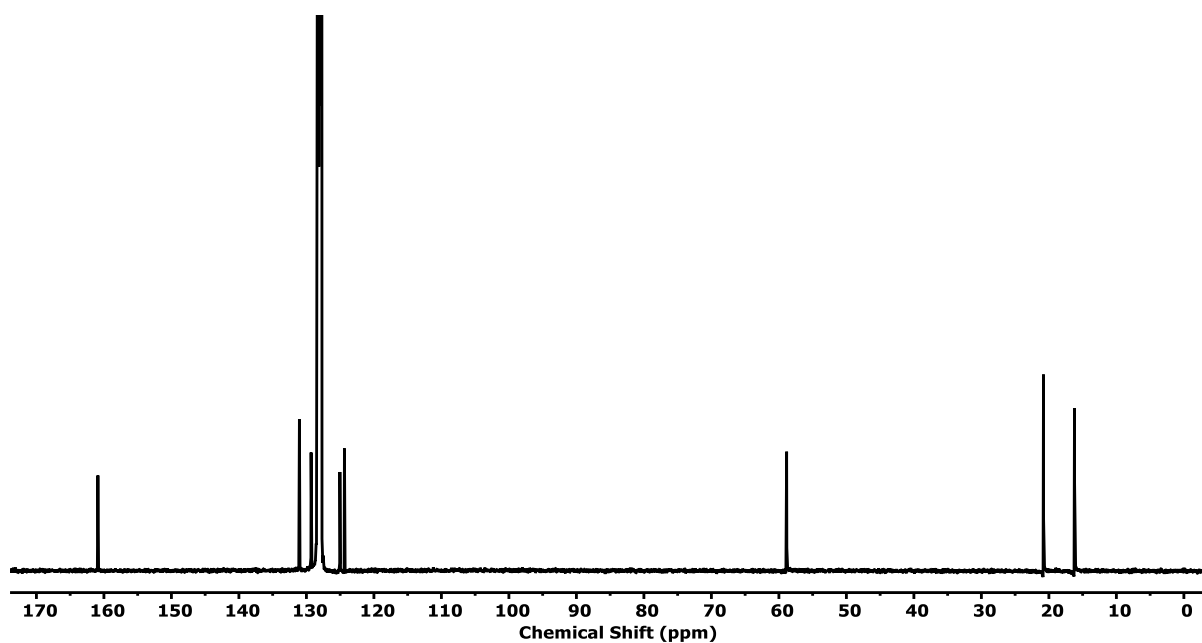


Figure S12: ^{13}C $\{^1H\}$ NMR spectrum of dimer $(L^{Me}Ti)_2O$ (126 MHz, C_6D_6 , 298K)

Table S1. ROCOP of CO₂ and CHO with catalyst precursors.

Entry	Cat	Cocat	Conv. (%)	PCHC(%)	CC(%)	Polyether(%)
1 ^a	Ti(OiPr) ₄	-	8	<1	<1	>99
2 ^b	Ti(OiPr) ₄	PPNCl	18	<1	<1	>99
3 ^c	-	PPNCl	14	<1	>99	<1

Conditions: 80 °C, CO₂ = 40 bar, time = 16 h. ^a[cat]/[cocat]/[CHO] = 1/0/2000,

^b[cat]/[cocat]/[CHO] = 1/1/2000, ^c[cat]/[cocat]/[CHO] = 0/1/2000.

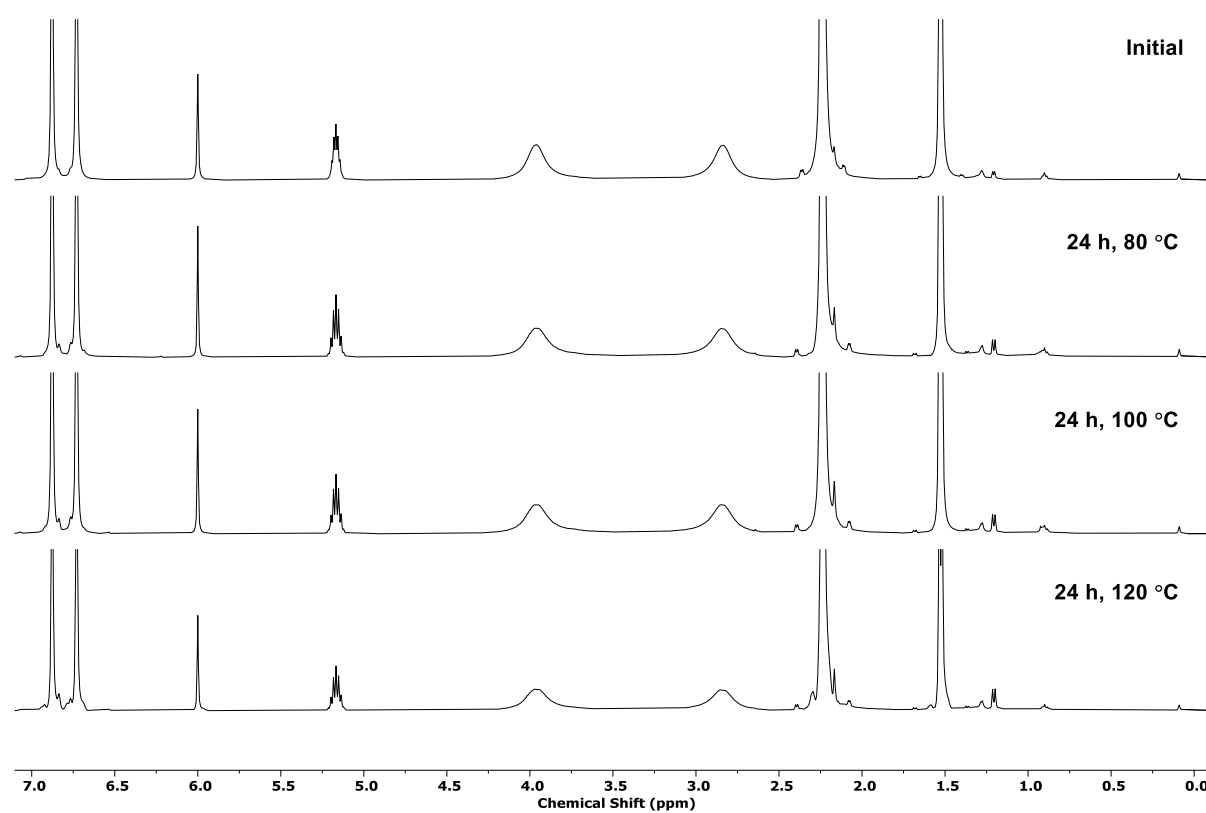


Figure S13: Stacked ¹H NMR Spectra of complex 2 heated for 24 h at temperatures ranging 80-120 °C. (*d*₂-tetrachloroethane)

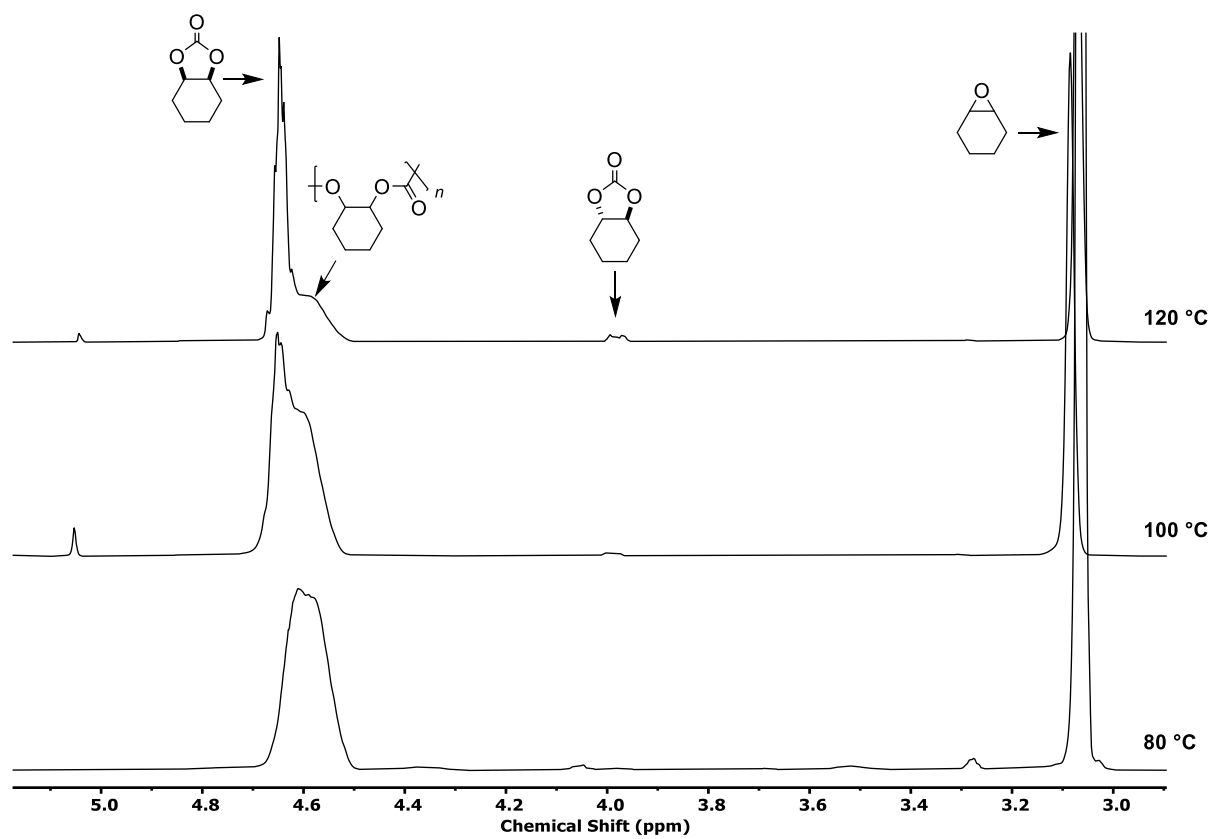


Figure S14: Representative ¹H NMR spectrum (400 MHz, C₆D₆, 298K) of the crude product from the copolymerisation of CO₂ with CHO at different temperatures. Polyether resonances were not observed.

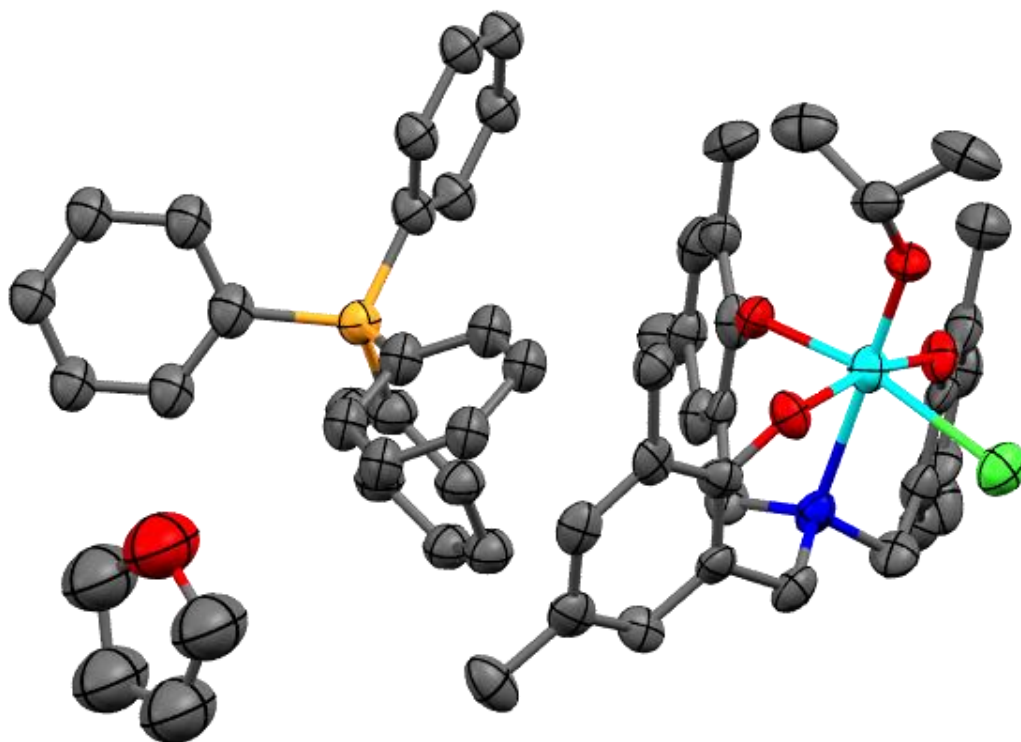


Figure S15: Molecular structure of the product of the reaction between complex 2 and PPh₄Cl. The hydrogen atoms are not illustrated. Titanium (light blue), Oxygen (red), Nitrogen (Dark blue), Chlorine (Green), Phosphorus (Orange).

The molecular structure of **2.PPh₄Cl** was solved using SHELXT¹ and least-square refined using SHELXL² in Olex2.³ This structure is included as connectivity only and therefore bond lengths should not be considered as accurate. Hydrogen atoms were treated by constrained refinement. Displacement parameters were added using the EADP command for the PPh₄ counter ion and one highly disordered solvent molecule of THF. In addition 81.6 electrons were excluded from the lattice using the Olex solvent mask feature,⁴ which was believed to be two highly disordered THF molecules.

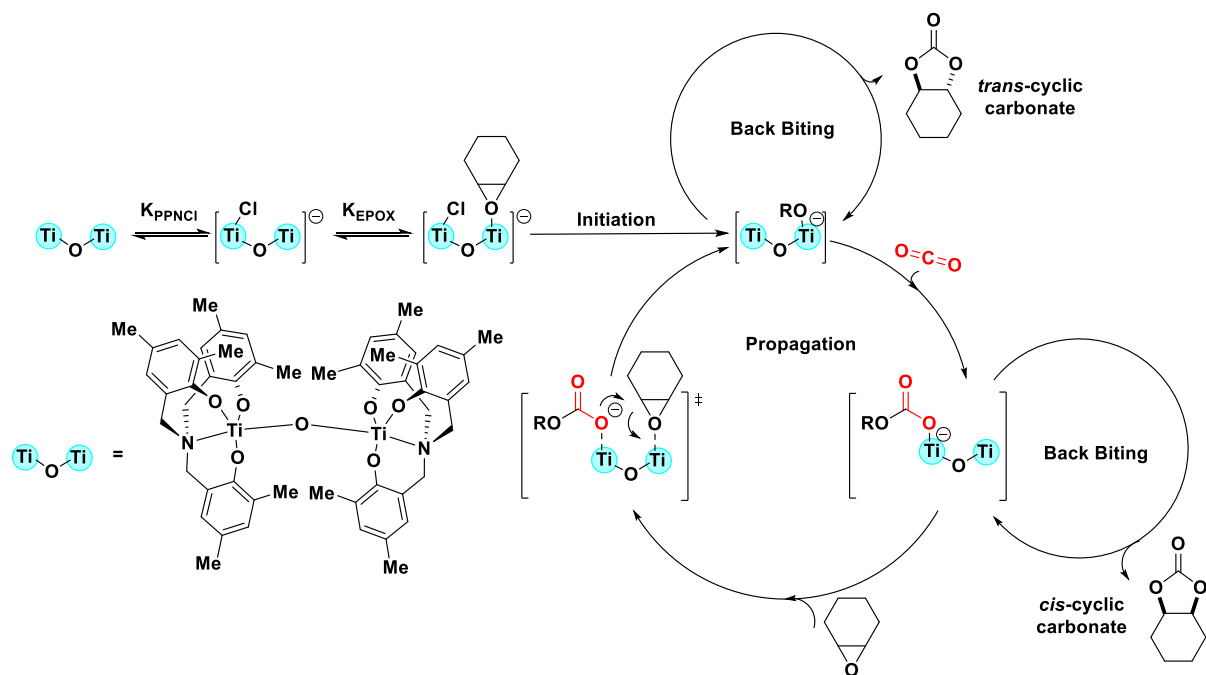


Figure S16: Illustrates a possible catalytic cycle, involving the Ti(IV) dimer complex (4) to rationalize the formation of PCHC and cyclic carbonates.

Table S2: Experimental details

Local code	002rwwk19
Chemical formula	C ₃₀ H ₃₇ ClNO ₄ Ti·C ₂₄ H ₂₀ P·C ₄ H ₈ O
<i>M_r</i>	970.43
Crystal system, space group	Monoclinic, <i>P2₁</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.7978 (4), 20.5515 (5), 12.6554 (4)
β (°)	115.944 (4)
<i>V</i> (Å ³)	2759.23 (17)
<i>Z</i>	2
Radiation type	Cu Kα
μ (mm ⁻¹)	2.39
Crystal size (mm)	0.137 × 0.090 × 0.018
Diffractometer	SuperNova, Dual, Cu at home/near, Atlas
Absorption correction	Multi-scan <i>CrysAlis PRO</i> 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T_{min}</i> , <i>T_{max}</i>	0.867, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11705, 5557, 4162
<i>R_{int}</i>	0.060
θ _{max} (°)	51.8
(sin θ/λ) _{max} (Å ⁻¹)	0.510
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.072, 0.189, 1.02
No. of reflections	5557
No. of parameters	459
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.52, -0.70
Absolute structure	Flack <i>x</i> determined using 1287 quotients [(<i>I</i> ⁺)-(<i>I</i> ⁻)]/[(<i>I</i> ⁺)+(<i>I</i> ⁻)] (Parsons, Flack and Wagner, <i>Acta Cryst. B</i> 69 (2013) 249-259).
Absolute structure parameter	-0.032 (10)

Computer programs: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov et al., 2009).

1. G. Sheldrick., *SHELXT* – Integrated Space-Group And Crystal-Structure Determination. *Acta Cryst. A*, **2015**, 71, 3-8.
2. G. Sheldrick., Crystal Structure Refinement With *SHELXL*. *Acta Cryst. C*, **2015**, 71, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann., *OLEX2*: A Complete Structure Solution, Refinement And Analysis Program. *J. Appl. Crystallogr.*, **2009**, 42, 339-341.
4. A. Spek., *PLATON SQUEEZE*: A Tool For The Calculation Of The Disordered Solvent Contribution To The Calculated Structure Factors. *Acta Cryst. C*. **2015**, 71, 9-18.