
SUPPLEMENTARY DATA

Unexpected “Ferrate” Compound as Single-Component Catalyst for the Cycloaddition of CO₂ to Epoxides

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General remarks.

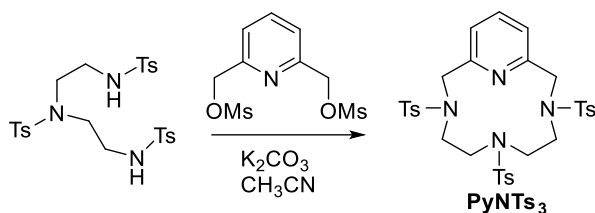
All the reactions that involved the use of reagents sensitive to oxygen or to hydrolysis were carried out under an inert atmosphere. The glassware was previously dried in an oven at 110 °C and was set with cycles of vacuum and nitrogen. All chemicals and solvents were commercially available and used as received except where specified. ¹H NMR analyses were performed with 300 or 400 MHz spectrometers at room temperature. The coupling constants (*J*) are expressed in hertz (Hz), and the chemical shifts (δ) in ppm. Catalytic tests were analysed by ¹H NMR spectroscopy. Low resolution MS spectra were recorded with instruments equipped with electron ionization (EI) and ESI/ion trap sources. The values are expressed as mass-charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. X-ray data collection for the crystal structure determination was carried out by using Bruker Smart APEX II CCD diffractometer with the Mo K radiation ($\lambda = 0.71073$) at 296 K. 2,6-*bis*(methanesulfonyloximethyl)pyridine,¹ ligand **1**² were synthesized as previously reported.

¹ M. Dell'Acqua, B. Castano, C. Cecchini, T. Pedrazzini, V. Pirovano, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 3494-3505.

² N. Panza, A. di Biase, S. Rizzato, E. Gallo, G. Tseberlidis, A. Caselli, *EurJOC* **2020**, *42*, 6635-6644.

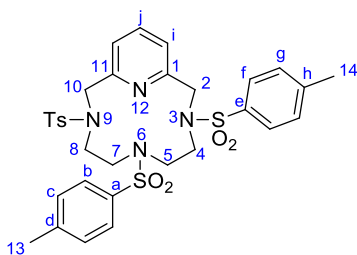
Synthesis of the ligands

Synthesis of Tri-tosyl protected Ligand, PyNTs₃



2,6-bis(methanesulfonyloxymethyl)pyridine (5.3 mmol, 1.57 g) in CH₃CN (40 mL) was added dropwise to a hot suspension of K₂CO₃ (15 mmol, 2.0 g) and *N,N',N''*-tritosyldiethylenetriamine (5.3 mmol, 3.0 g) in CH₃CN (160 mL). The reaction was allowed to react to reflux for 3 hours. The solvent was then evaporated and water was added (50.0 mL). The mixture was washed with DCM (3 x 50.0 mL). The organic phases were concentrated in vacuum and **PyNTs₃** was isolated as a white powder.

Yield: 99%, 3.56 g

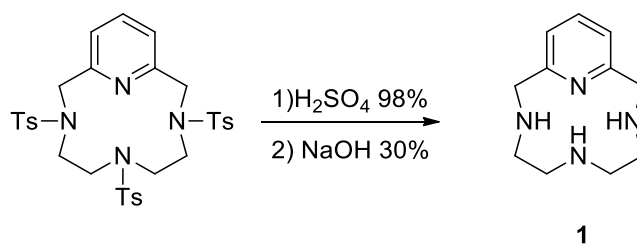


¹H NMR (300 MHz; CDCl₃; T = 300 K) δ 7.80 – 7.69 (m, 7H, H_{Ar}), 7.66 (d, *J* = 8.2 Hz, 2H, H_b), 7.44 (d, *J* = 7.7 Hz, 2H, H_c), 7.36 (d, *J* = 8.1 Hz, 4H, H_g), 7.29 (d, *J* = 7.9 Hz, 2H, H_i), 4.30 (bs, 4H, H_{2,10}), 3.33 (t, *J* = 7.5 Hz, 4H, CH₂), 3.22 – 3.07 (m, 2H, CH₂), 2.77 (bs, 2H, CH₂), 2.46 (s, 6H, H₁₄), 2.42 (s, 3H, H₁₃).

Spectral data are in good agreement with literature values.^{2,3}

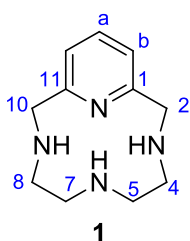
³ J. Serrano-Plana, A. Aguinaco, R. Belda, E. García-España, M. G. Basallote, A. Company, M. Costas, *Angew. Chem. Int. Ed.* **2016**, *55*, 6310-6314.

Synthesis of Ligand 1



PyNTs₃ (17 mmol, 11.37 g) was dissolved in concentrated sulfuric acid (15.0 mL). The mixture was heated to 250°C for 1 h. The mixture was cooled and diluted with water (25 mL) then extracted with DCM (2 x 25.0 mL). To the aqueous phase, NaOH 30% was added until pH > 14. This solution was extracted with DCM (5 x 25.0 mL) and the organic phase was dried with NaSO₄ and evaporated in vacuum. The product was obtained as a yellowish waxy solid.

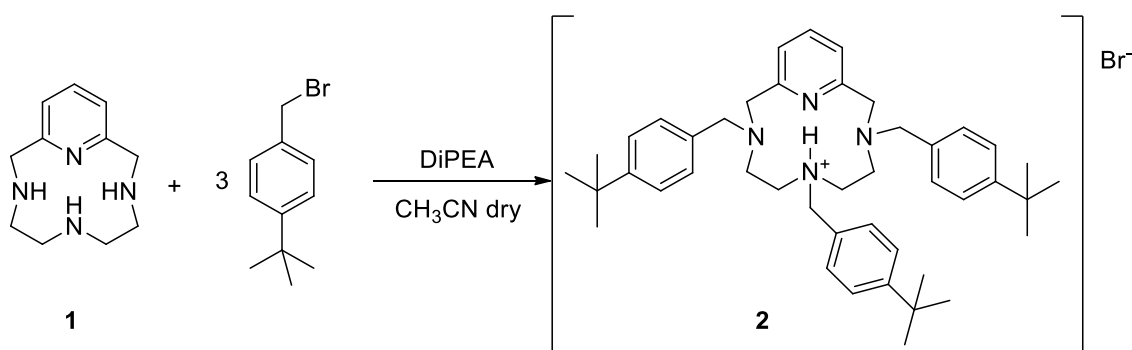
Yield: the yield of the reaction ranged from 60 to 80%



¹H NMR (400 MHz, CDCl₃) δ 7.51 (t, *J* = 7.6 Hz, 1H_a), 6.99 (d, *J* = 7.6 Hz, 2H_b), 3.96 (s, 4H₂₋₁₀), 3.23 (bs, 3H_{NH}), 2.83 – 2.64 (m, 4H₄₋₈), 2.26 (s, 4H₅₋₇).

Spectral data are in good agreement with literature values.^{2,3}

Synthesis of Ligand 2

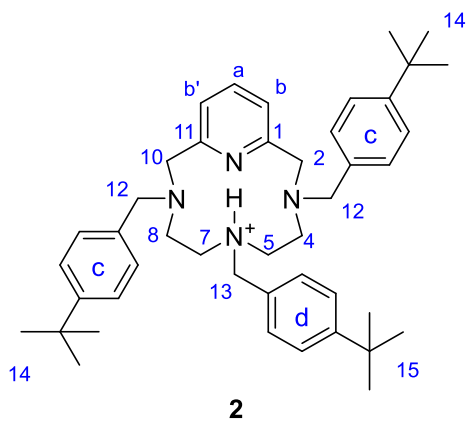


Ligand **1** (2.55 mmol, 525 mg) and 4-^tbutylbenzyl bromide (8.4 mmol, 1.5 mL) were stirred for 5h in dry CH₃CN (15.0 mL) in presence of DiPEA (1.5 mL). After this time, the solvent was evaporated, and cold acetone was added to the resulting oil. A white precipitate of ligand **2** is formed (347 mg). A second crop of the ligand is obtained by leaving the acetone solution at -20 °C (401 mg).

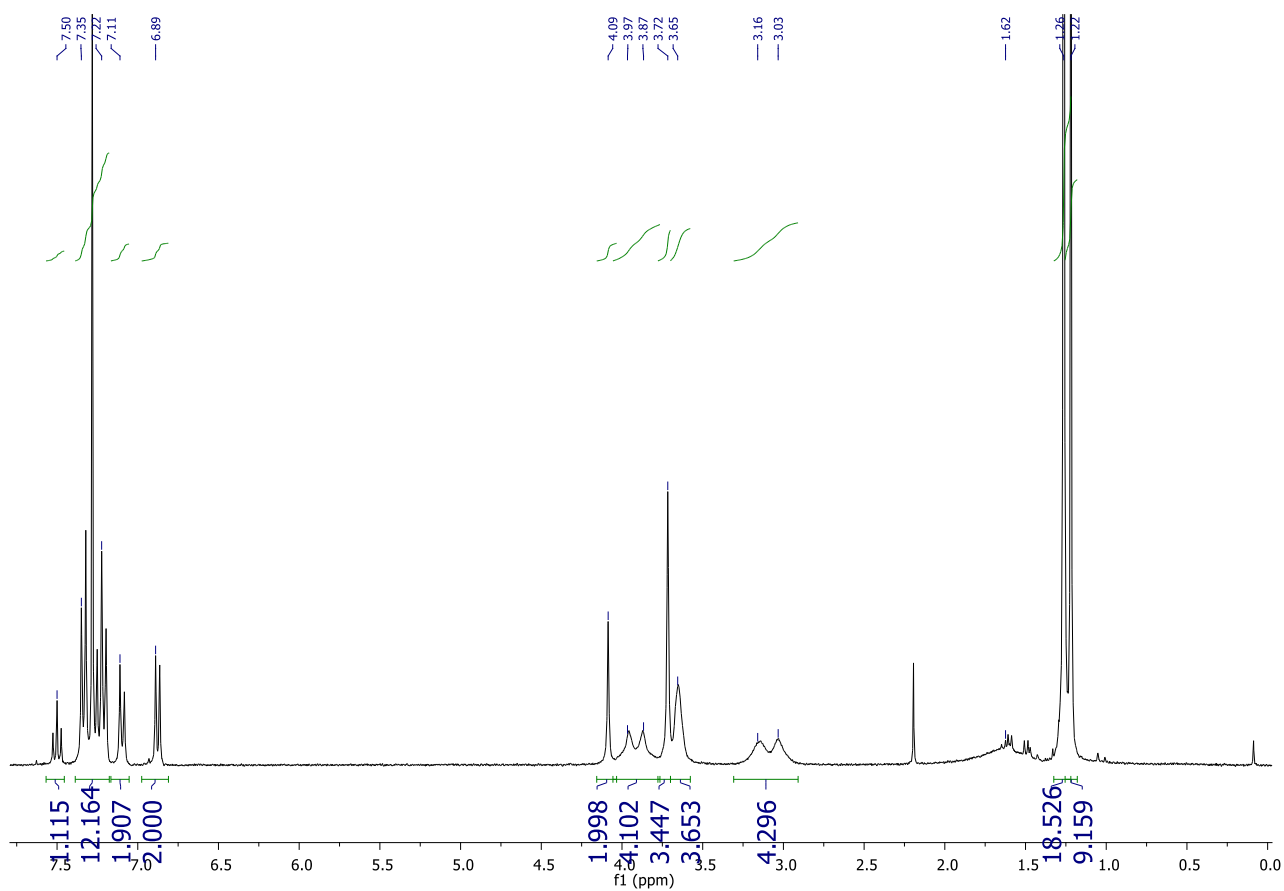
Yield: 41%, 748 mg

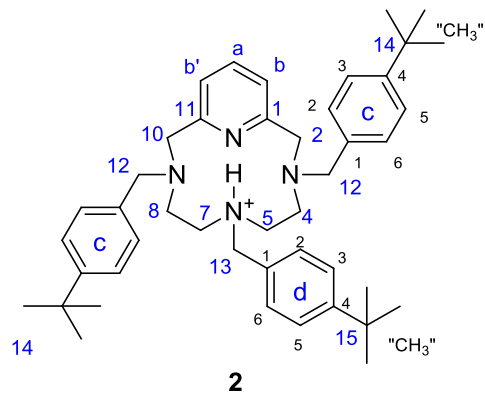
MS (ESI+) m/z (%) = calculated for C₄₄H₆₁N₄ 645.48, found 645.51 (100%, M⁺)

Elemental analysis: calculated for C₄₄H₆₁BrN₄ C, 72.80; H, 8.47; N, 7.72; found C, 72.49; H, 8.43; N, 7.39

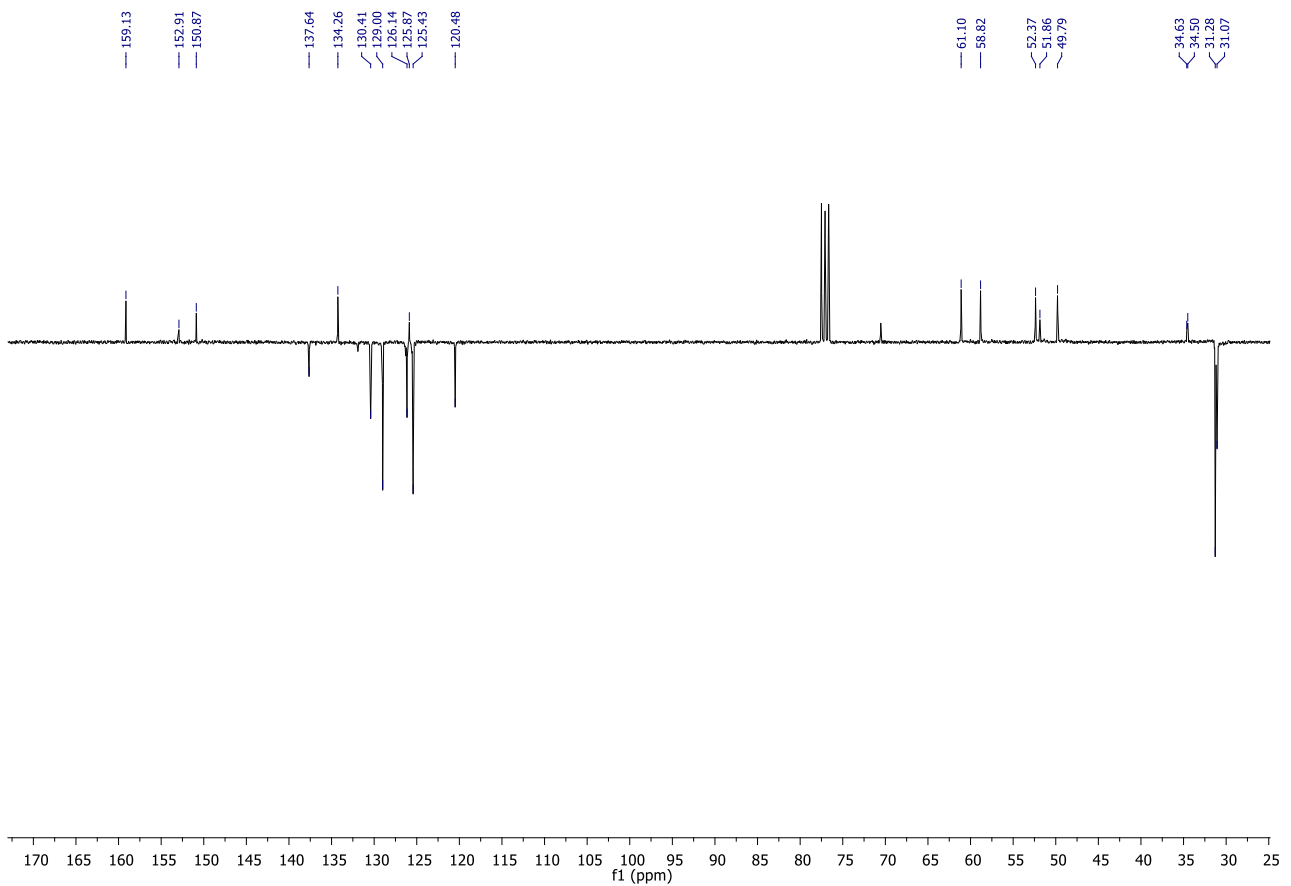


¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, *J* = 7.6 Hz, 1H_a), 7.35-7.22 (dd, 8H_c), 7.11 (dd, 4H_d), 6.89 (d, *J* = 7.6 Hz, 2H_{b,b'}), 4.04 (s, 2H₁₃), 3.97-3.83 (bd, 4H_{2,10}), 3.72 (s, 4H₁₂), 3.65 (bs, 4H₅₋₇), 3.16-2.99 (bd, 4H_{4,8}), 1.26 (s, 18H₁₄), 1.22 (s, 9H₁₅).

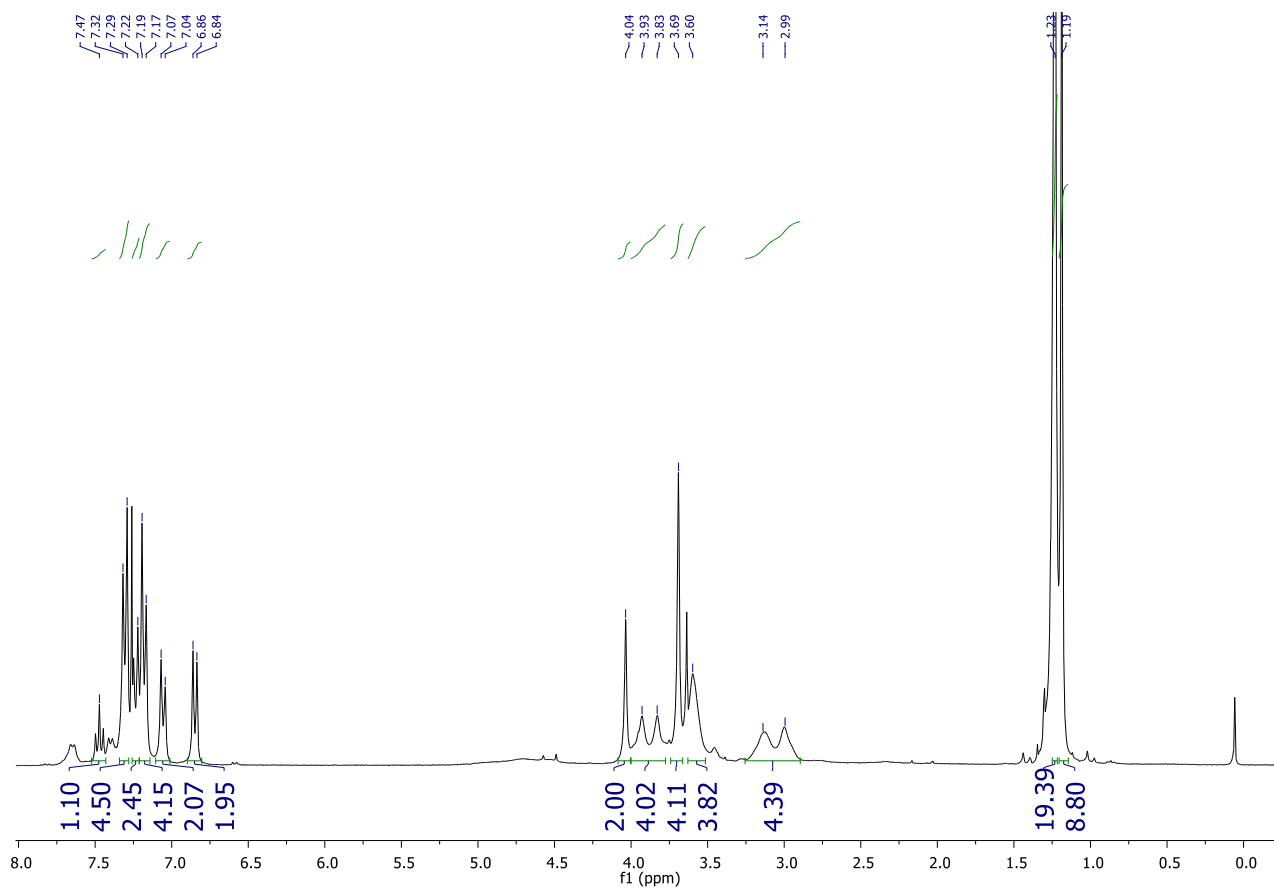




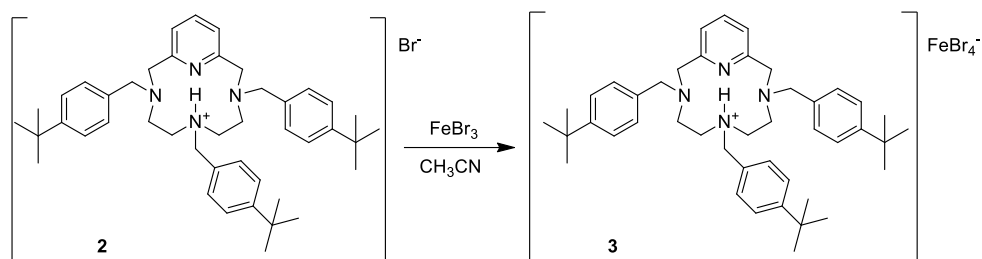
¹³C NMR (75 MHz, CDCl₃) δ 31.07 ("CH₃"₁₅), 31.28 ("CH₃"₁₄), 34.50 (C₁₄), 34.63 (C₁₅), 49.79 (C_{5,7}), 51.76 (C₁₃), 52.27 (C_{4,8}), 58.82 (C_{2,10}), 61.10 (C₁₂), 120.48 (C_b), 125.43 (C_{c2,6}), 125.87 (C_{d4}), 126.14 (C_{d2,6}), 129.00 (C_{c3,5}), 130.41 (C_{d3,5}), 134.26 (C_{c4}), 137.64 (C_a), 150.87 (C_{c1}), 152.91 (C_{d1}), 159.13 (C₁)



The following spectra is referred to the neutral ligand, **2** -H⁺, obtained by column chromatography over deactivated silica (DCM/MeOH(10%NH₄OH)). The broad signal at 1.60 ppm is missing. However, this product is highly hygroscopic and compound **2** was readily formed if the solution is allowed to contact with moisture.

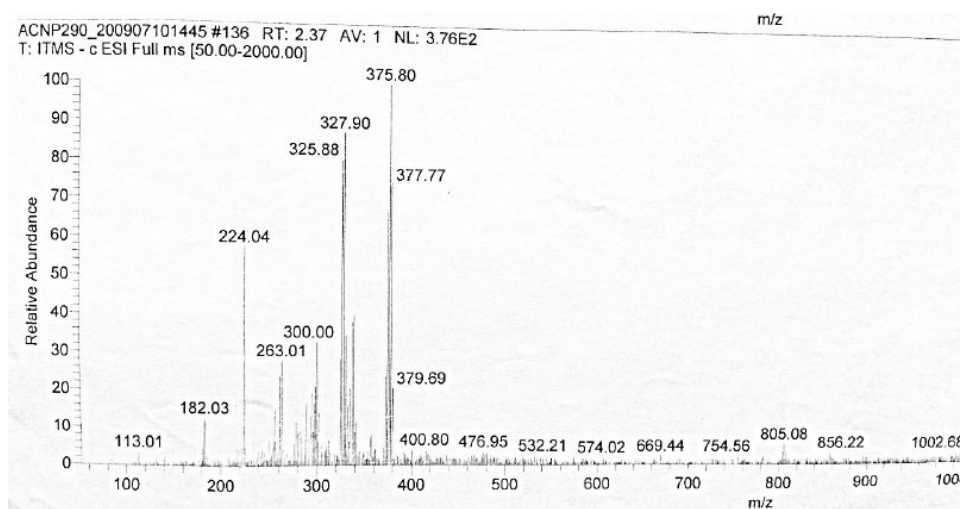
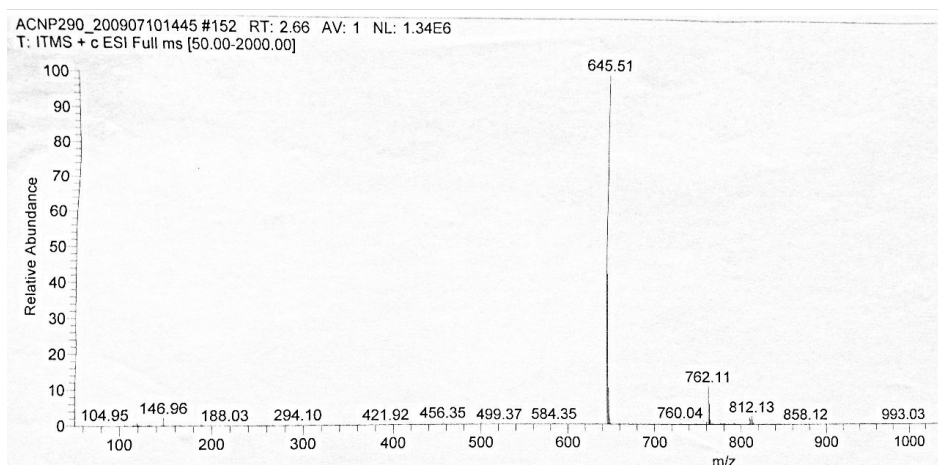


Synthesis of the ferrate compound 3

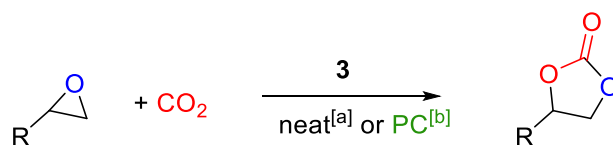


To a stirring solution of ligand **2** (0.17 mmol, 123 mg) in acetonitrile (5.0 mL) at RT, a solution of iron(III) bromide (0.17 mmol, 50 mg) in acetonitrile (3.0 mL) was slowly added and the reaction mixture was left stirring for 1 h. The solvent was evaporated under vacuum and the residue was washed several times with *n*-hexane to yield a bright red powder.

Yield: 3 81% (141 mg) [iron source: FeBr_3 anhydrous]
MS (ESI+) m/z (%) = calculated for $\text{C}_{44}\text{H}_{61}\text{N}_4$ 645.48, found 645.51 (100%, M^+)
MS (ESI-) m/z (%) = calculated for FeBr_4 375.60, found 375,80 (100%, FeBr_4^-)
Elem. An. $\text{C}_{44}\text{H}_{61}\text{Br}_4\text{FeN}_4$ Calcd: C, 51.74; H, 6.02; N, 5.49; found C, 51.41; H, 6.01; N, 5.42



General catalytic procedure:



Method A: A 250 mL stainless steel autoclave reactor was equipped with three 2.5 mL glass vials, containing the catalyst/epoxide mixture (0.25 mol% in 250 μ L of substrate). The vials were equipped with magnetic stirring bars and sealed with specific caps. The autoclave was then charged with 0.5 MPa CO₂ and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO₂ and placed in the heating bath for 4 hours. The reactor was then cooled and the CO₂ released. To each vial the appropriate amount of internal standard (mesitylene) and 1,0 mL of chloroform were added. 300 μ L of the solution were taken and diluted with 350 μ L of CDCl₃ to perform quantitative ¹H NMR analysis.

Method B: A 250 mL stainless steel autoclave reactor was equipped with three 2.5 mL glass vials, containing the catalyst/epoxide mixture (0.25 mol% in 250 μ L of substrate) and 125 μ L of PC as co-solvent. The vials were equipped with magnetic stirring bars and sealed with specific caps. The autoclave was then charged with 0.5 MPa CO₂ and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO₂ and placed in the heating bath for 4 hours. The reactor was then cooled and the CO₂ released. To each vial the appropriate amount of internal standard (mesitylene) and 1.0 mL of chloroform were added. 300 μ L of the solution were taken and diluted with 350 μ L of CDCl₃ to perform quantitative ¹H NMR analysis.

In selected cases, products were isolated by silica flash chromatography (**5b** and **5k**) (*n*-hexane/EtOAc 5:1) or directly collected by filtration as a pure solid from the reaction mixture (**5g**), confirming the NMR calculated yields.

All NMR data of the cyclic carbonates were in agreement with literature.⁴

Scale-up experiment: a 250 mL stainless steel autoclave reactor was equipped with a 50 mL glass vial, containing the catalyst/propylene oxide (PO) mixture (0.25 mol% in 2.5 mL PO) and a magnetic bar. The autoclave was then charged with 0.5 MPa CO₂ and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO₂ and placed in the heating bath set at 100 °C for 4 hours. The reactor was then cooled and the CO₂ released. To the vial the

⁴ Steinbauer J., Werner T., *Green Chem.*, 2017, **19**, 3769-3779

appropriate amount of internal standard (mesitylene) and 10.0 mL of chloroform were added. 300 μL of the solution were taken and diluted with 350 μL of CDCl_3 to perform quantitative ^1H NMR analysis. The mixture was then passed through a silica plug and eluted with *n*-hexane/EtOAc 5:1 and the filtrate was evaporated to dryness in vacuum yielding to pure propylene carbonate (3.03 g, 83%).

Recycling experiment: a 250 mL stainless steel autoclave reactor was equipped with a 50 mL glass vial, containing the catalyst/PO mixture (0.25 mol% in 2.5mL PO) and a magnetic bar. The autoclave was then charged with 0.5 MPa CO_2 and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO_2 and placed in the heating bath set at 100 °C for 4 hours. The reactor was then cooled and the CO_2 released. At this point, 2.5 mL of PO were added in the vial and the autoclave was again charged with CO_2 (0.8 MPa) and placed in the heating bath set at 100 °C for additional 4 hours. This operation repeated a third time, for a total of 7.5 mL of PO. To the vial the appropriate amount of internal standard (mesitylene) and 10.0 mL of chloroform were added. 300 μL of the solution was taken and diluted with 350 μL of CDCl_3 to perform quantitative ^1H NMR analysis (85% conversion, TON = 1020). The mixture was then passed through a silica plug and eluted with *n*-hexane/EtOAc 5:1 and the filtrate was evaporated in vacuum to eliminate residual PO and obtaining pure propylene carbonate (6,76 g, 62%).

Catalyst recovery experiment: a 250 mL stainless steel autoclave reactor was equipped with a 2.5 mL glass vial, containing the catalyst/PO mixture (0.25 mol% in 2.5mL PO) and a magnetic bar. The autoclave was then charged with 0.5 MPa CO_2 and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO_2 and placed in the heating bath set at 100 °C for 4 hours. The reactor was then cooled and the CO_2 released. To each vial the appropriate amount of internal standard (mesitylene) and 1.0 mL of chloroform were added. 300 μL of the solution were taken and diluted with 350 μL of CDCl_3 to perform quantitative ^1H NMR analysis. After that, the product PC and the remaining PO were distilled in vacuum directly from the vial and collected in a Schlenk tube, while the catalyst was recovered and analysed by ESI-MS spectroscopy and reused for a second reaction run to test its robustness. ESI-MS analysis proved the presence of the ferrate anion (relative abundance 100) in the recovered catalyst and the reaction results show a good reproducibility. Yield of PC: 1st run 83%, selectivity 99%, 2nd run 81%, selectivity 99%.

Optimization of the reaction conditions using styrene oxide as reagent.

Table S1. Optimization of the catalyst loading.^[a]

3 mol%	Conversion %	Yield %	Selectivity %	TOF h⁻¹
0.5%	99	79	80	50
0.25%	85	71	83	85
0.1%	23	14	61	57

^[a] Reaction conditions: styrene oxide (SO) 2.19 mmol; T = 100 °C; P = 0.8 MPa; t = 4 h. Conversion and selectivity determined by ¹H NMR using mesitylene as internal standard. Turnover frequency ($\text{mol}_{4\text{a}(\text{converted})} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{reaction time}^{-1}$).

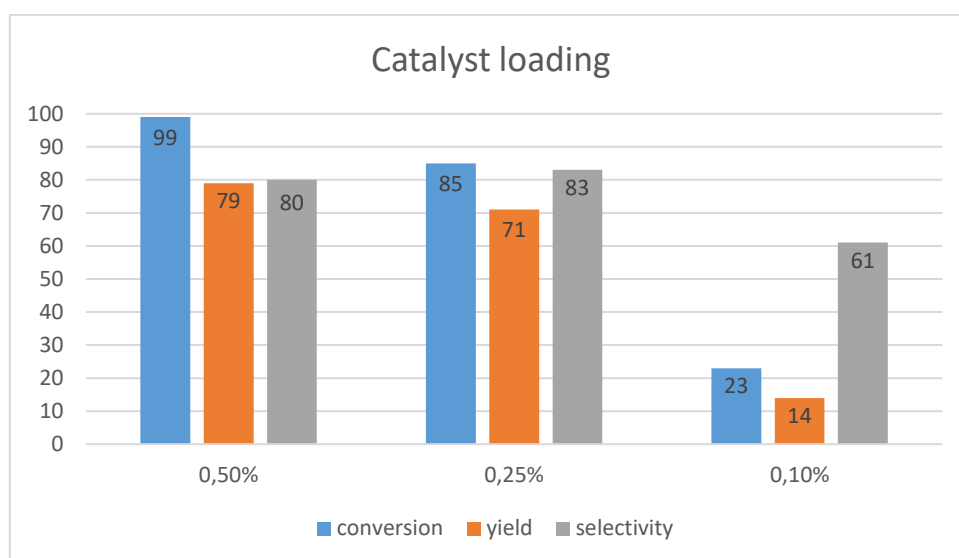


Figure S1. Comparison between different loadings of compound **3**

Table S2. Optimization of the CO₂ pressure.^[a]

pCO ₂ (MPa)	Conversion %	Yield %	Selectivity %	TOF h ⁻¹
0.2	50	26	52	33
0.4	72	52	73	48
0.8	97	80	82	65
1.2	97	86	89	65

^[a] Reaction conditions: styrene oxide (SO) 2.19 mmol; T = 100 °C; Cat 0.5mol%; t = 3 h. Conversion and selectivity determined by ¹H NMR using mesitylene as internal standard. Turnover frequency ($\text{mol}_{\text{a(converted)}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{reaction time}^{-1}$).

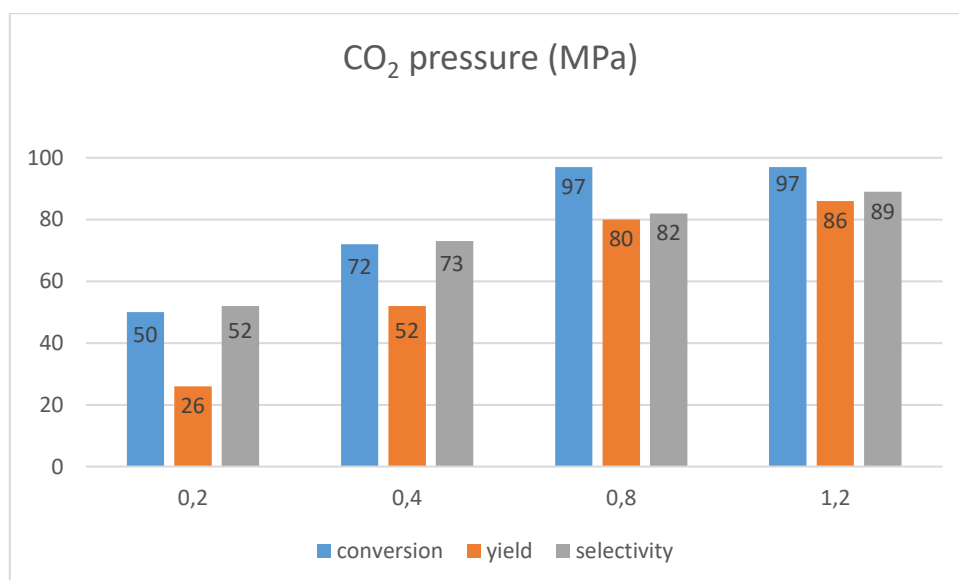
**Figure S2.** Comparison between different reaction pressures

Table S3. Optimization of the temperature.^[a]

T (°C)	Conversion %	Yield %	Selectivity %	TOF h ⁻¹
75	29	22	76	39
100	76	66	87	101
125	99	74	75	132

^[a] Reaction conditions: styrene oxide (SO) 2.19 mmol; P = 0.8 MPa; Cat 0.25mol%; t = 3 h. Conversion and selectivity determined by ¹H NMR using mesitylene as internal standard. Turnover frequency ($\text{mol}_{4\mathbf{a}(\text{converted})} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{reaction time}^{-1}$).

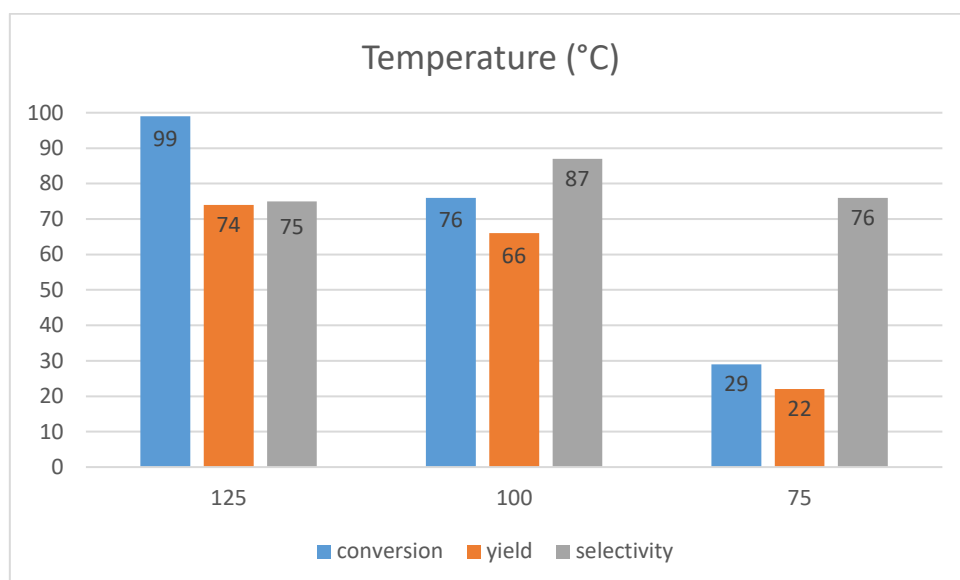


Figure S3. Comparison between different reaction temperatures

Table S4. Optimization of the reaction time.^[a]

t (h)	Conversion %	Yield %	Selectivity %	TOF h ⁻¹
1	21	15	71	84
3	76	66	87	101
4	85	71	83	85
6	99	85	86	66

^[a] Reaction conditions: styrene oxide (SO) 2.19 mmol; P = 0.8 MPa; Cat 0.25 mol%; T = 100 °C. Conversion and selectivity determined by ¹H NMR using mesitylene as internal standard. Turnover frequency ($\text{mol}_{\text{a(converted)}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{reaction time}^{-1}$).

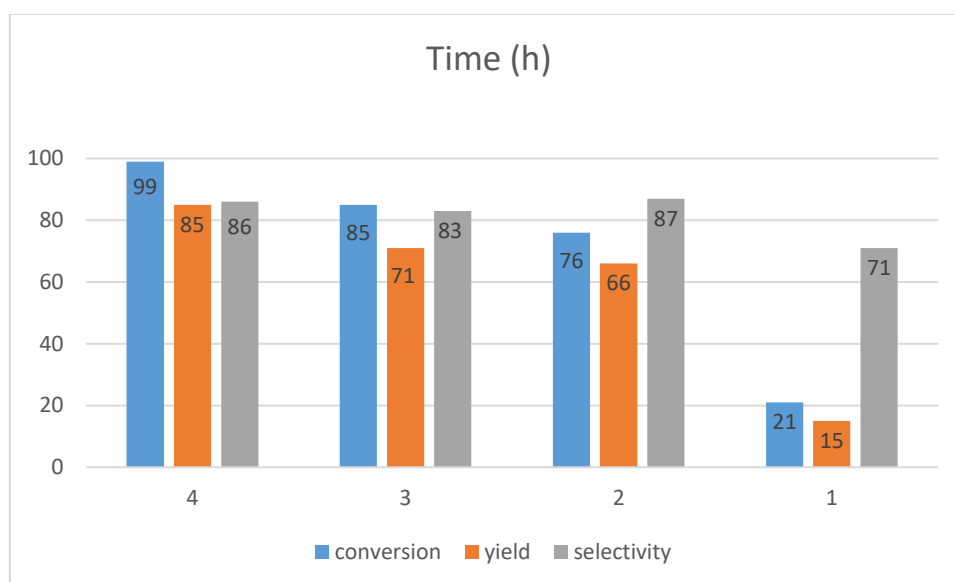
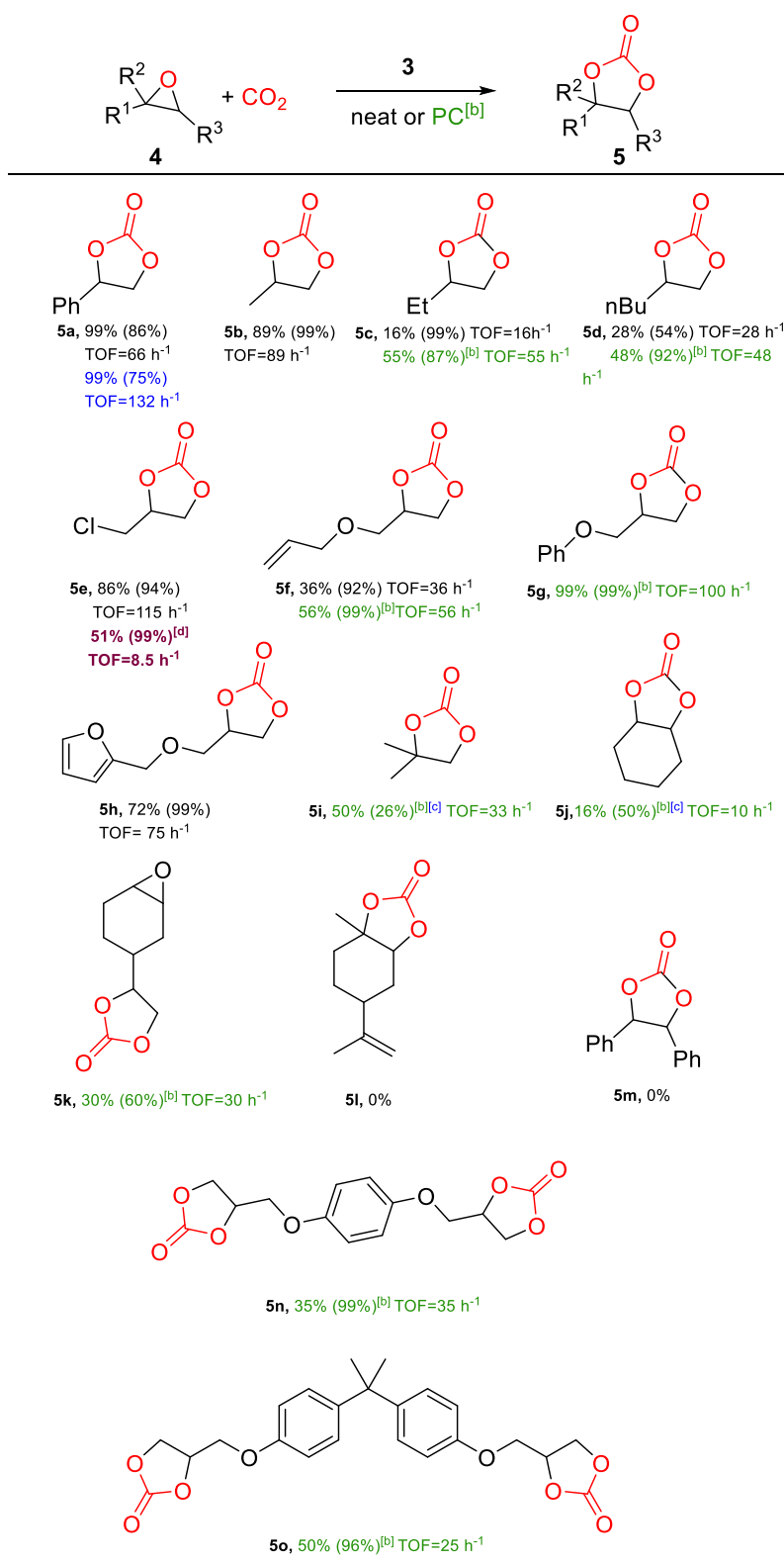


Figure S4. Comparison between different reaction times

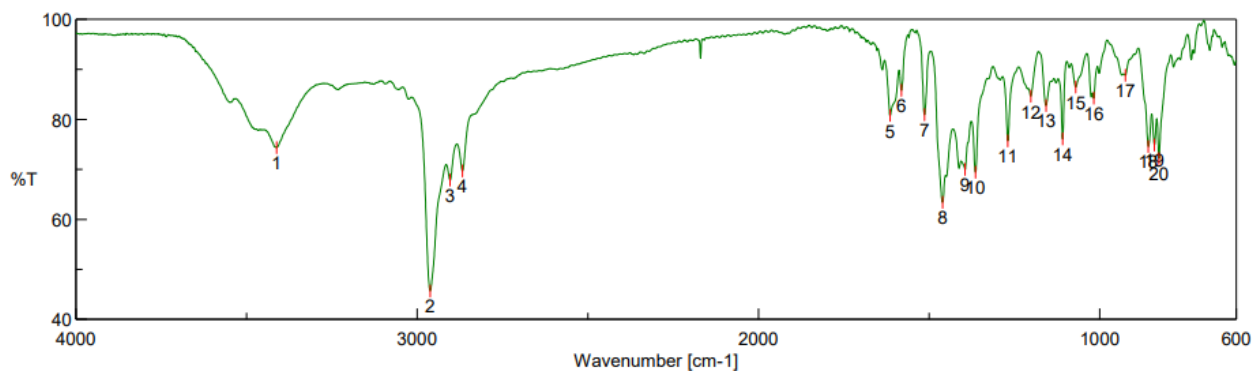
Table S5. Reaction Scope^[a]



substrate	T (°C)	t (h)	conversion %	yield % (isolated yield %)	selectivity %	TON	TOF (h ⁻¹)
4a	100	6	99%	85%	86%	396	66
4a	125	3	99%	74%	75%	396	132
4a ^[c]	125	3	99%	99%	99%	396	132
4a ^[d]	100	24	66%	28%	42%	264	11
4e ^[d]	100	24	51%	51%	99%	204	8.5
4a ^[d]	25	60	38%	25%	66%	152	2.5
4b	100	4	89%	88% (83%)	99%	356	89
4c	100	4	16%	15%	99%	64	16
4c ^[b]	100	4	55%	48%	87%	220	55
4d	100	4	28%	15%	54%	112	28
4d ^[b]	100	4	48%	44%	92%	192	48
4e	100	3	86%	81%	94%	345	115
4f	100	4	36%	33%	92%	144	36
4f ^[b]	100	4	56%	55%	99%	224	56
4g ^[b]	100	4	99%	99% (99%)	99%	400	100
4h	100	4	72%	71%	99%	300	75
4i ^[b]	125	6	50%	13%	26%	198	33
4j ^[b]	125	6	16%	15%	99%	60	10
4k ^[b]	100	4	30%	18% (18%)	60%	120	30
4n ^[b]	100	4	35%	34%	99%	140	35
4o ^[b]	100	4	50%	48%	96%	100	25

^[a] Reaction conditions: Method A, neat; epoxide 250 μ L; **3** = 0.25 mol%; P (CO₂) = 0.8 MPa; conversion, selectivity and yield determined by ¹H NMR using mesitylene as internal standard. Isolated yield in brackets. TOF = mol_{4(converted)}·mol₃⁻¹·reaction time⁻¹. ^[b] Method B, propylene carbonate (PC, 125 μ L) as co-solvent. ^[c] 0.25 mol% TBABr used as co-catalyst. ^[d] P (CO₂) = 0.1 MPa

IR spectra



No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3411.94	74.3222	2	2962.13	45.675	3	2903.79	67.8421
4	2867.63	69.6571	5	1614.61	80.7626	6	1581.34	85.8041
7	1513.36	80.8935	8	1460.81	63.4006	9	1394.76	69.9577
10	1363.91	69.4193	11	1269.41	75.7067	12	1201.92	84.6404
13	1157.56	82.7553	14	1108.87	76.0807	15	1070.3	86.4521
16	1017.75	84.2166	17	925.182	88.8214	18	857.686	74.5506
19	839.847	74.8774	20	826.348	72.1585			

Figure S5. IR spectra of **3** (KBr)

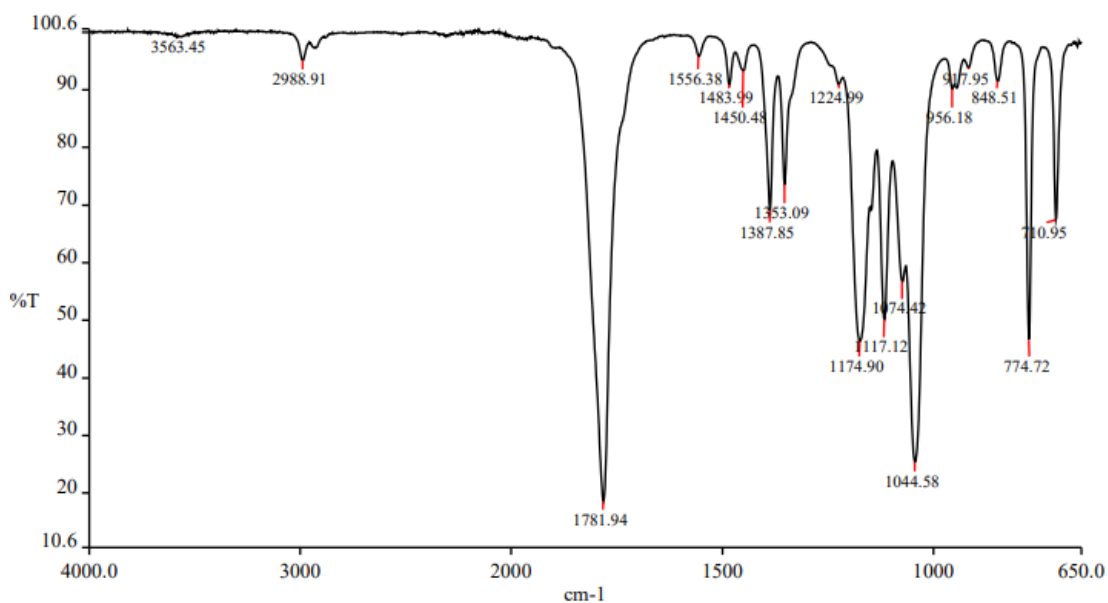
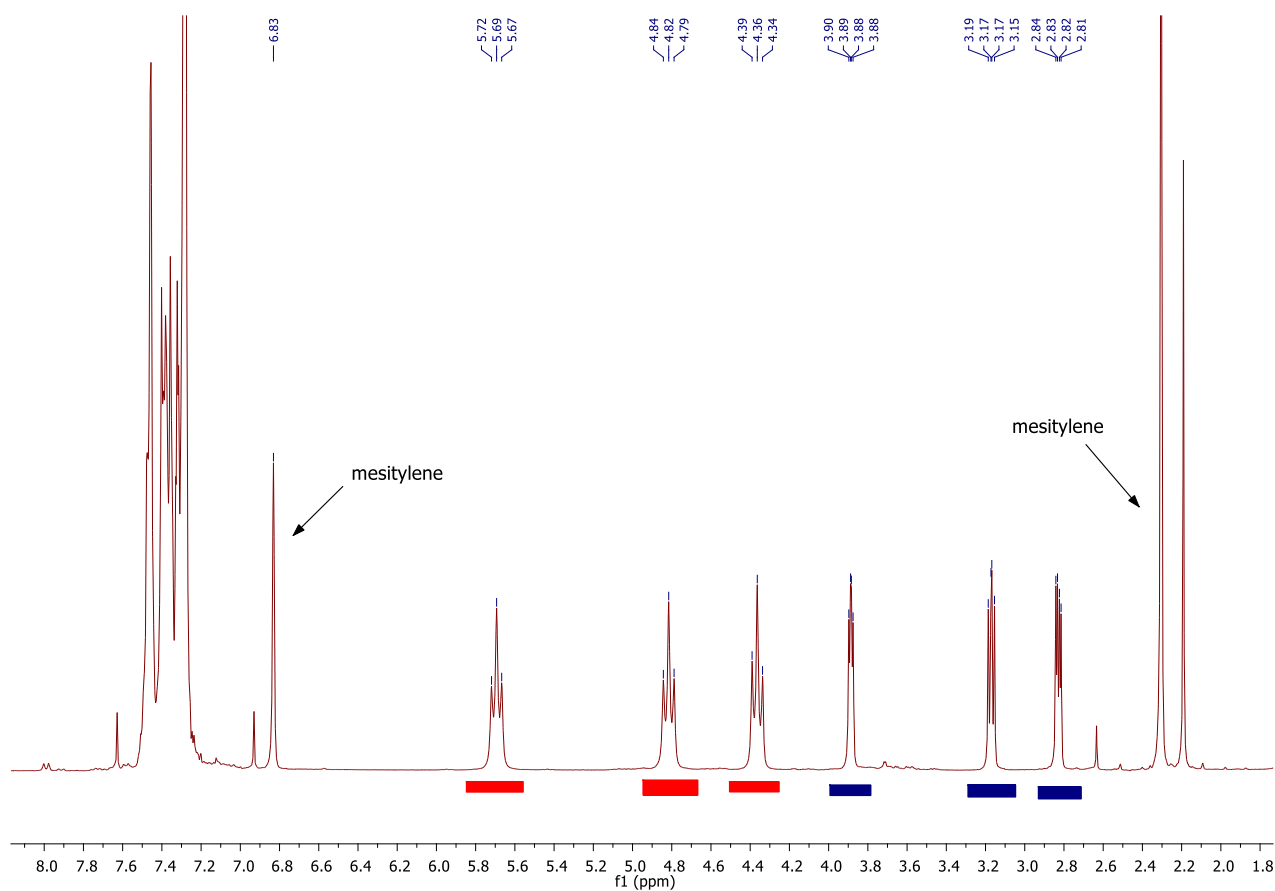
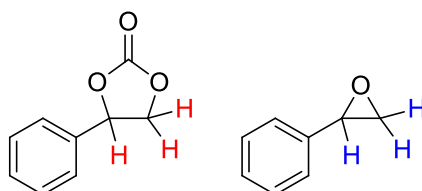


Figure S6. IR spectra of isolated product from scale-up synthesis of propylene carbonate (ATR-IR)

¹H NMR of selected reactions:



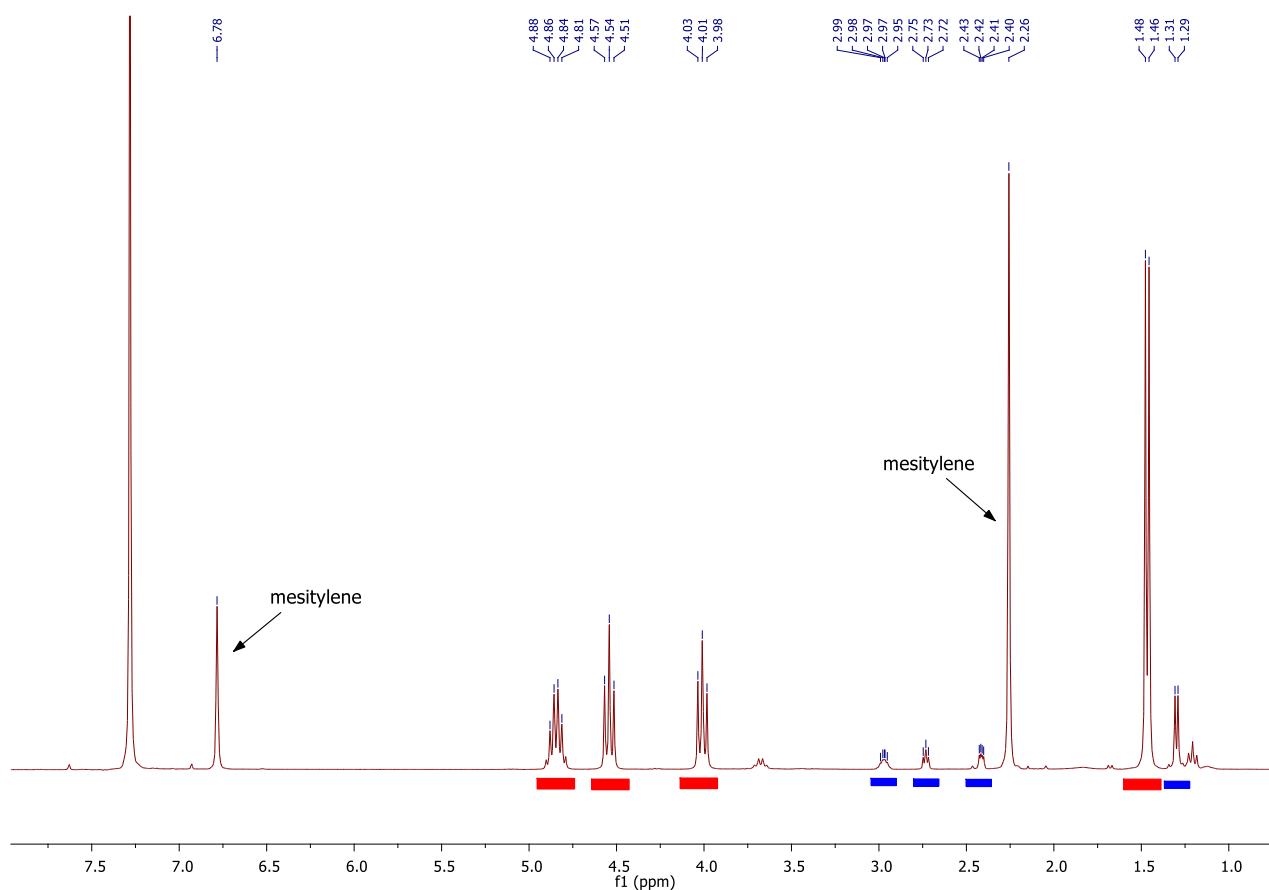
Reaction crude of the synthesis of compound **5a**



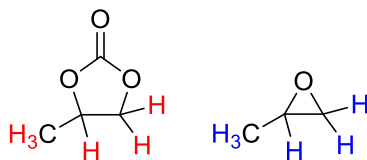
Styrene carbonate **5a**

¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.33 (m, 5H), 5.68 (t, 1H), 4.81 (t, 1H), 4.35 (t, 1H).

*NMR data of the product were in agreement with literature data.*⁴



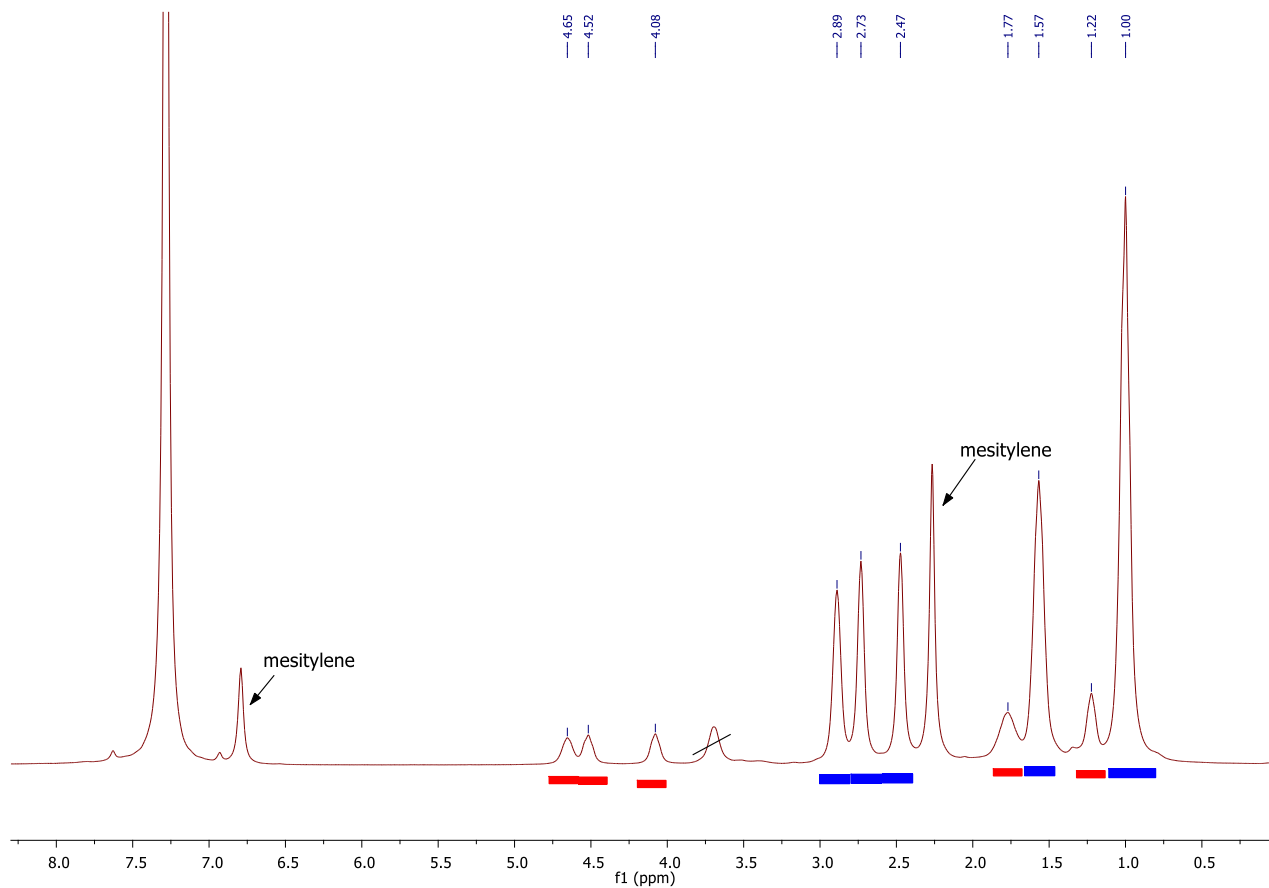
Reaction crude of the synthesis of compound **5b**



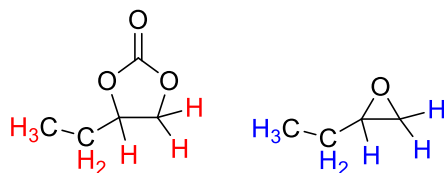
Propylene carbonate **5b**

¹H NMR (400 MHz, CDCl₃) δ 4.85 (m, 1H), 4.54 (t, 1H), 4.01 (t, 1H), 1.47 (dd, 3H).

*NMR data of the product were in agreement with literature data.*⁴



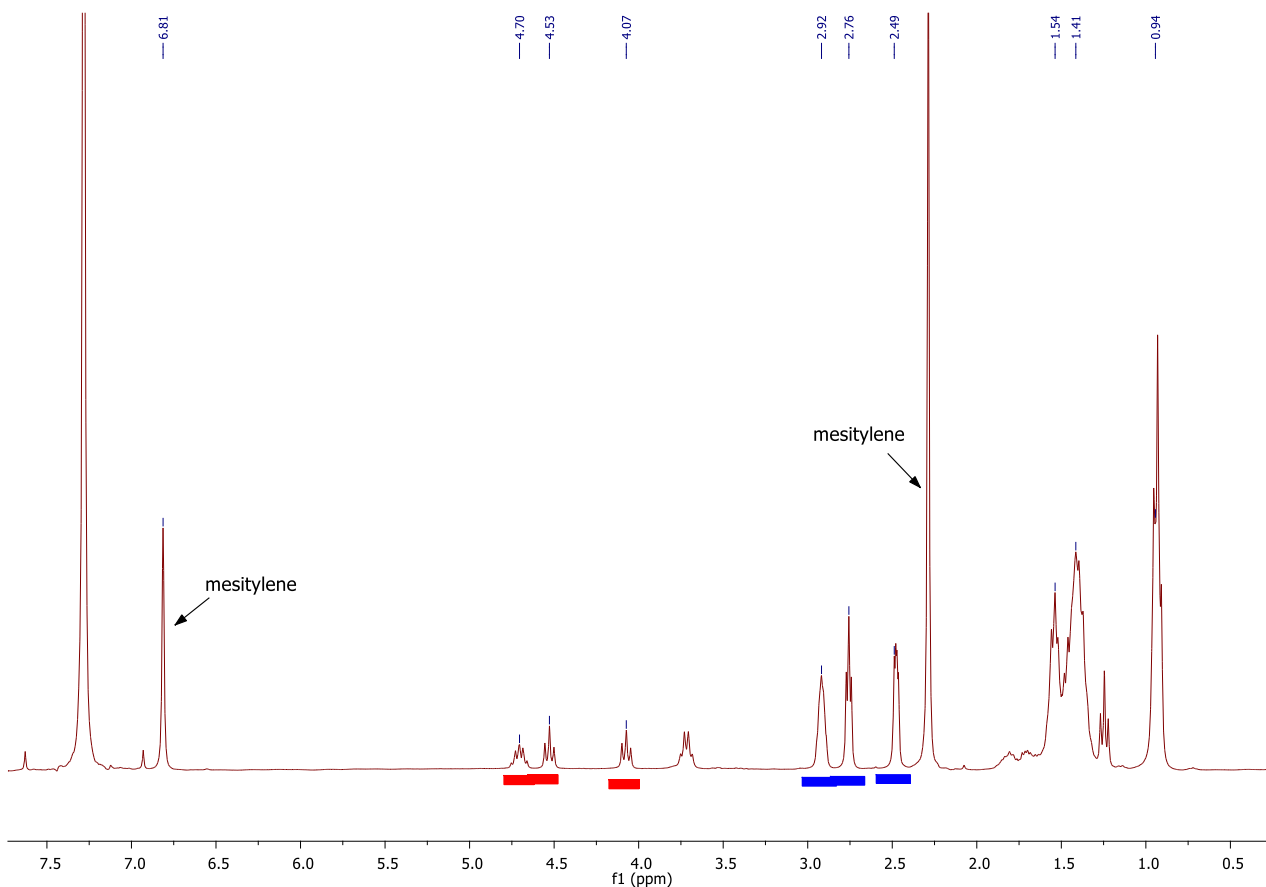
Reaction crude of the synthesis of compound **5c**-(*paramagnetic broadening of signals*)



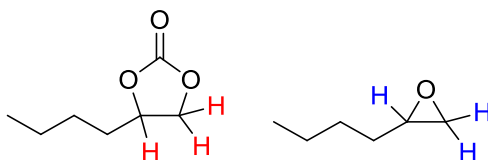
Butylene carbonate **5c**

¹H NMR (400 MHz, CDCl₃) δ 4.65 (1H), 4.52 (1H), 4.08 (1H), 1.77 (2H), 1.22 (3H).

*NMR data of the product were in agreement with literature data.*⁴



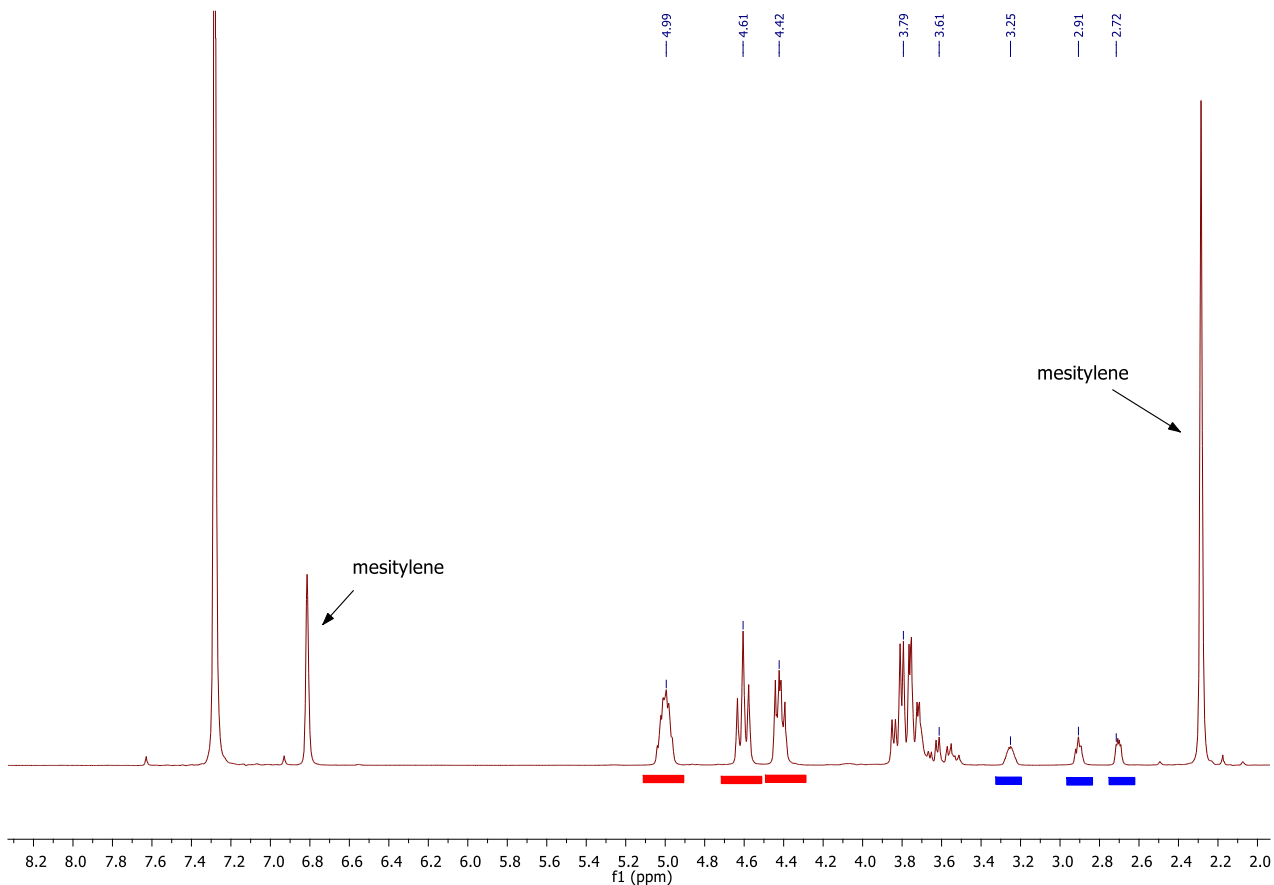
Reaction crude of the synthesis of compound **5d**



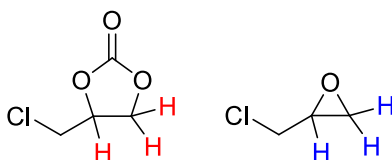
4-butyl-1,3-dioxolan-2-one 5d

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.70 (1H), 4.51 (1H), 4.07 (1H), 1.88-1.33 (6H), 0.93 (3H).

*NMR data of the product were in agreement with literature data.*⁴



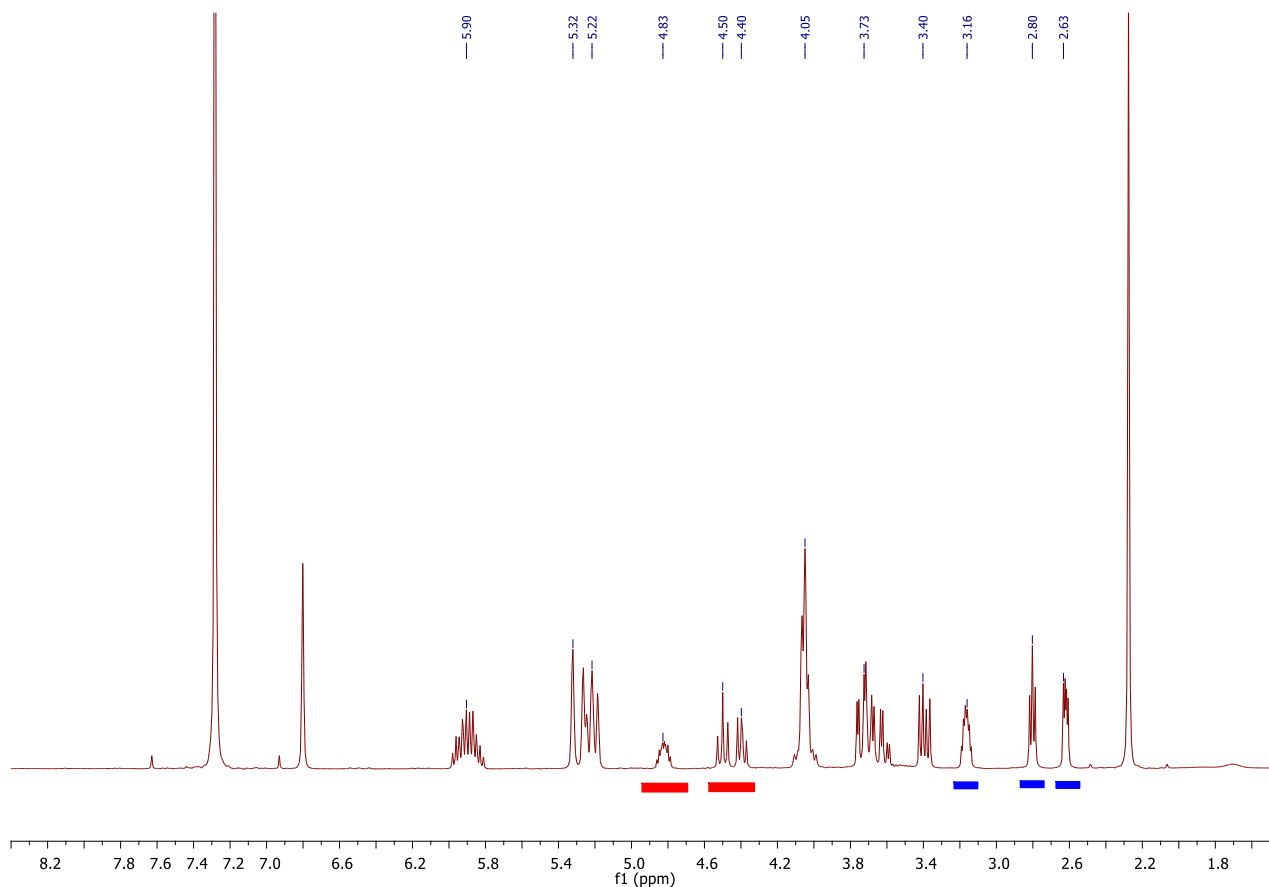
Reaction crude of the synthesis of compound **5e**



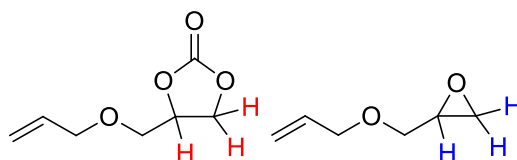
4-(Chloromethyl)-1,3-dioxolan-2-one **5e**

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.99 (1H), 4.61 (1H), 4.42 (1H), 3.79 (2H).

*NMR data of the product were in agreement with literature data.*⁴



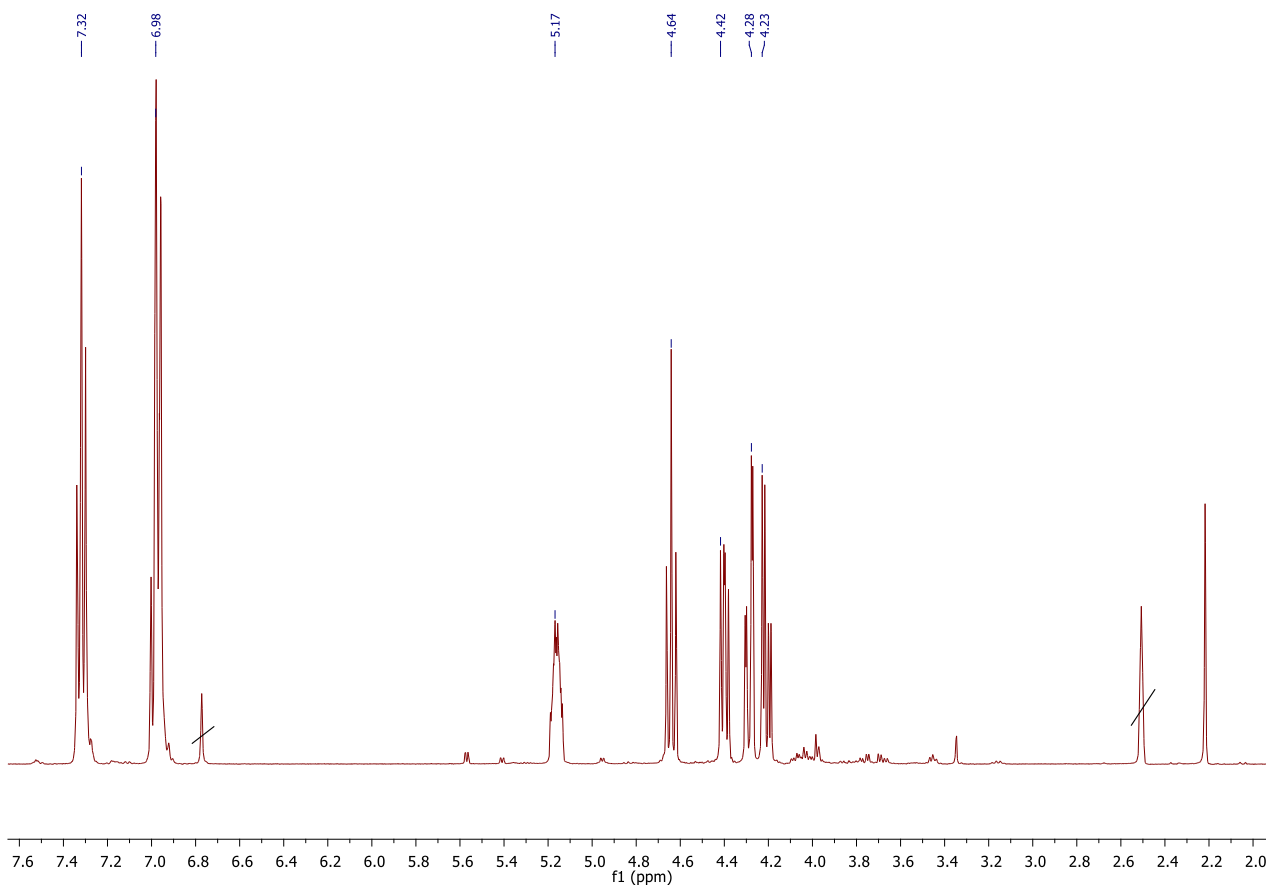
Reaction crude of the synthesis of compound **5f**



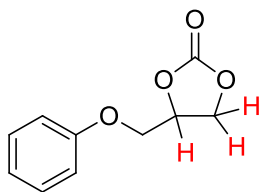
4-((Allyloxy)methyl)-1,3-dioxolan-2-one **5f**

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.90 (1H), 5.35-5.20 (2H), 4.83 (1H), 4.50 (1H), 4.40 (1H), 4.05 (2H), 3.73 (2H).

*NMR data of the product were in agreement with literature data.*⁴



Isolated product **5g** (white solid)

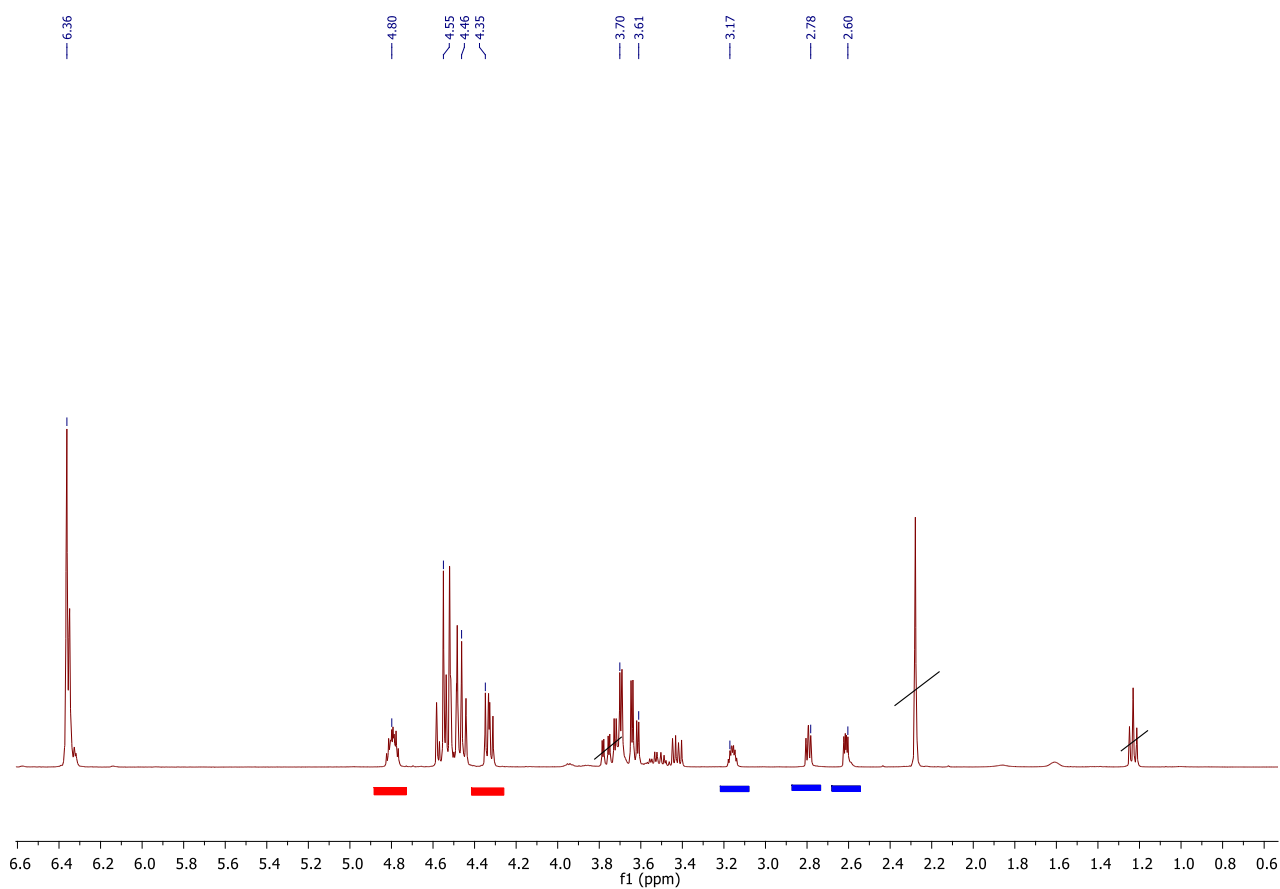


4-Phenoxyethyl-1,3-dioxolan-2-one 5g

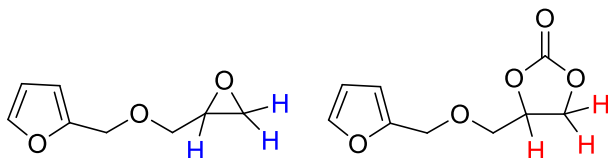
¹H NMR (400 MHz, CDCl₃) δ 7.32 (2H), 6.98 (3H), 5.17 (1H), 4.64 (1H), 4.42 (1H), 4.28 (1H), 4.23 (1H).

Isolated yield : 212 mg , 99%

*NMR data of the product were in agreement with literature data.*⁴



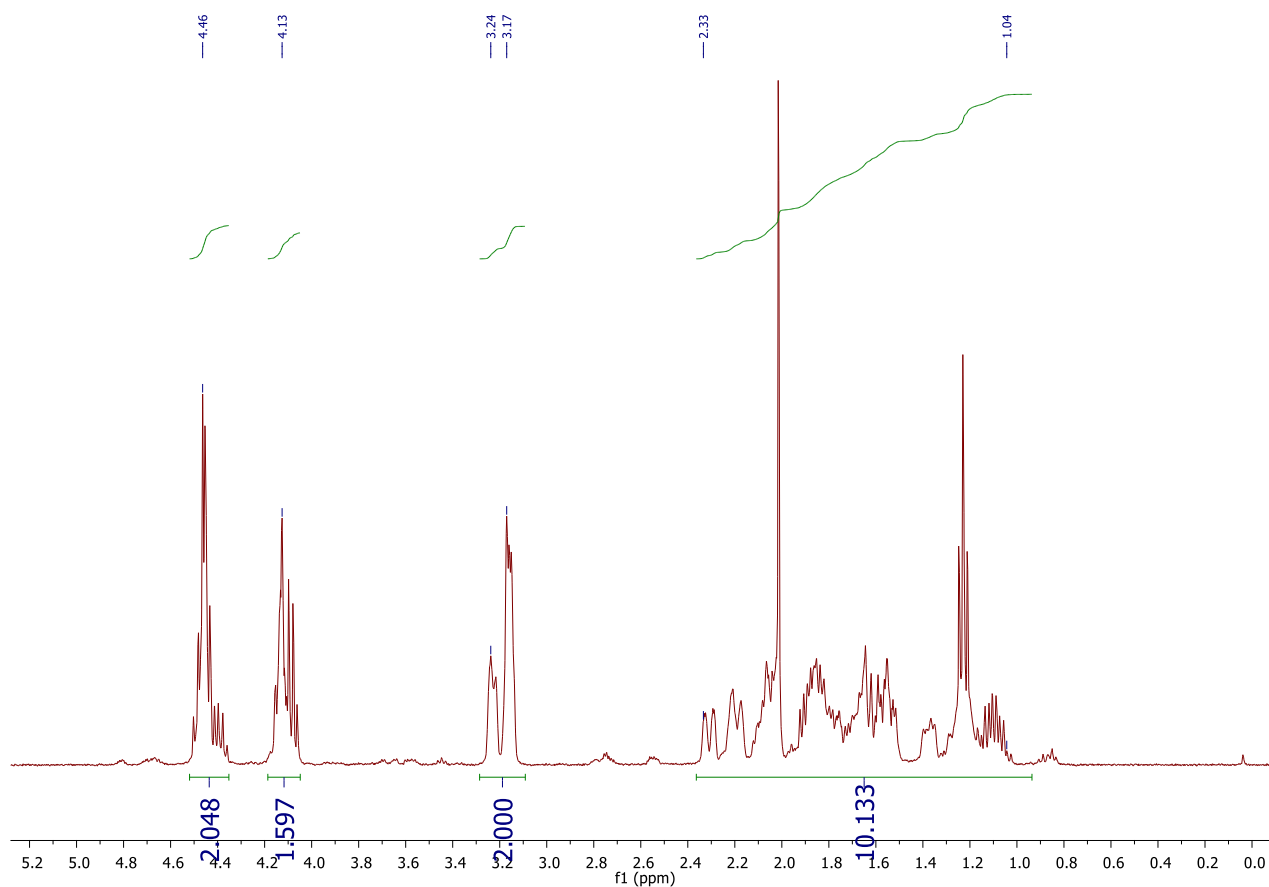
Reaction crude of the synthesis of compound **5h**



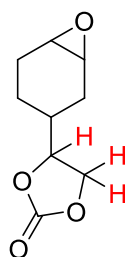
Furfuryl glycidyl carbonate **5h**

¹H NMR (400 MHz, CDCl₃) δ 6.36 (3H), 4.80 (1H), 4.55 (2H), 4.46 (3H), 4.35 (1H).

*NMR data of the product were in agreement with literature data.*⁴



Isolated compound **5k**

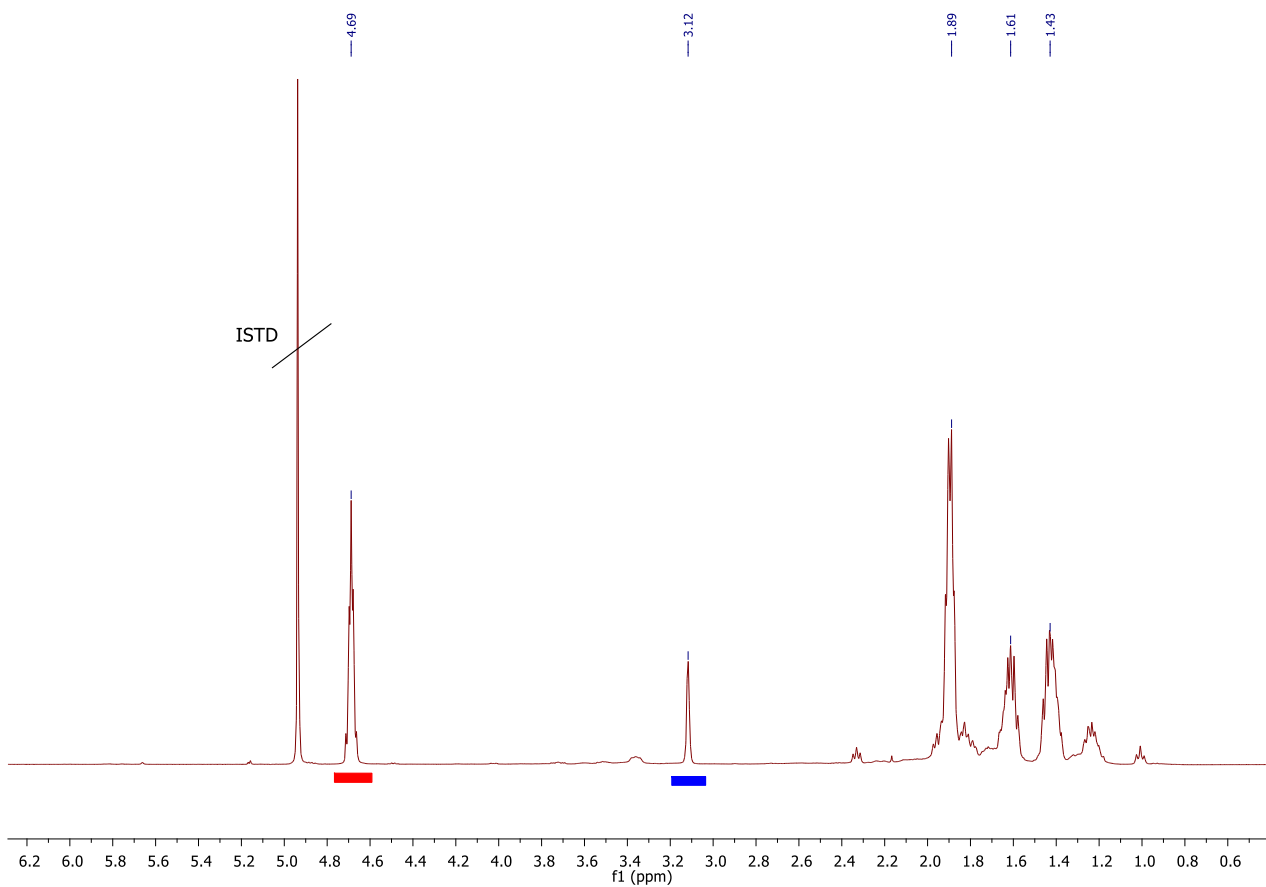


4-(7-Oxabicyclo[4.1.0]hept-3-yl)-1,3-dioxolan-2-one **5k**

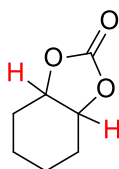
¹H NMR (400 MHz, CDCl₃) δ 4.46 (2H), 4.15 (1H), 3.24 (1H), 3.17 (1H), 2.33 – 1.04 (m, 9H).

Isolated yield: 65 mg, 18%

*NMR data of the product were in agreement with literature data.*⁴



Reaction crude of the synthesis of compound **5j**



Cyclohexene carbonate **5j**

¹H NMR (400 MHz, CDCl₃) δ 4.69 (2H), 1.89 (4H), 1.61 (2H), 1.43 (2H).

*NMR data of the product were in agreement with literature data.*⁴

Crystal structure determination

Block colourless crystals of compound **2** suitable for X-ray analysis were grown by slow diffusion of water in an ethanolic solution of compound **3**. Single crystal X-ray diffraction experiment was performed on a Bruker Smart APEX II diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω -scan mode, within the limits $2.8^\circ < 2\theta < 46.5^\circ$. The frames were integrated and corrected for Lorentz-polarization effects with the Bruker SAINT software package⁵. The intensity data were then corrected for absorption by using SADABS⁶. No decay correction was applied. The structure was solved by direct methods (SIR-97)⁷ and refined by iterative cycles of full-matrix least-squares on F_o^2 and Fourier-difference synthesis with SHELXL-97⁸ within the WinGX interface⁹.

Crystal data for **2**: $(C_{44}H_{61}N_4)^+ (Br)^- \cdot H_2O$, monoclinic space group $P 2_1/c$ ($n^\circ 14$), $Z = 8$, $a = 18.822(2)$, $b = 18.654(2)$, $c = 24.150(2) \text{ \AA}$, $\alpha = 90$, $\beta = 100.100(1)$, $\gamma = 90^\circ$, $V = 8348(2) \text{ \AA}^3$. $D_c = 1.179 \text{ g}\cdot\text{cm}^{-3}$, $F(000) = 3160$, $T = 298(2) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 1.021 \text{ mm}^{-1}$. Total number of reflections recorded to $\vartheta_{\text{max}} = 23.255^\circ$, was 46762 of which 11992 were unique ($R_{\text{int}} = 0.0327$); 8943 were 'observed' with $I > 2\sigma(I)$. Final R -values: $wR_2 = 0.1521$ and $R_1 = 0.0764$ for all data; $R_1 = 0.0543$ for the 'observed' data.

There are two crystallographically independent formula units in the asymmetric unit having the same structure. All atoms are in general position and refined anisotropically, except those of the disordered parts of the molecules. Five out of the six *ter*-butyl groups were found to be disordered over two positions which were refined isotropically with occupation factors constrained to sum to unity. Final occupancies are 0.51/0.49, 0.62/0.38, 0.68/0.32, 0.61/0.39 and 0.62/0.48. An orientational disorder of a benzene ring is also observed and refined over two orientations with refined-site occupancy factors of 0.57 and 0.43. All hydrogen atoms attached to carbon atoms were placed in geometrically calculated positions and then refined using a riding model based on the positions of the parent atoms with $U_{\text{iso}} = 1.2 U_{\text{eq}}$ ($1.5 U_{\text{eq}}$ in the case of methyl groups). The hydrogen atoms bound to N4 and N7 (protonated nitrogens) were located from a difference Fourier map and refined isotropically, whereas it was not possible to determine and obtain a satisfactory refinement for the position of the hydrogens bound to O1 and O2 (water molecules). Some restraints were applied to the bond distances in the disordered *ter*-butyl moieties in order to ensure reasonable values of the C-C bond lengths.

CCDC-2071881 contains 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/data_request/cif.

⁵ Bruker AXS Inc. SAINT. Madison, WI, USA 2007

⁶ Bruker AXS Inc. "SADABS Area-Detector Absorption Correction Program." Madison, WI, USA 2001

⁷ A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, **1999**, 32, 115-119

⁸ G. M. Sheldrick, *Acta Cryst C*, **2015**, 71, 3-8

⁹ L. J. Farrugia, *J. Appl. Cryst.*, **1999**, 32, 837-838

Table 1. Crystal data and structure refinement for compound **2**.

Identification code	ACDR29	
Empirical formula	C ₄₄ H ₆₃ Br N ₄ O	
Formula weight	743.87	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 24.150(2) Å	α = 90°.
	b = 18.654(2) Å	β = 100.100(1)°.
	c = 18.822(2) Å	γ = 90°.
Volume	8347.8(14) Å ³	
Z	8	
Density (calculated)	1.181 Mg/m ³	
Absorption coefficient	1.021 mm ⁻¹	
F(000)	3168	
Crystal size	0.250 x 0.212 x 0.131 mm ³	
Theta range for data collection	1.387 to 23.255°.	
Index ranges	-26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -20 ≤ l ≤ 20	
Reflections collected	46762	
Independent reflections	11992 [R(int) = 0.0327]	
Completeness to theta = 23.255°	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11992 / 75 / 896	
Goodness-of-fit on F ²	1.054	
Final R indices [I > 2σ(I)]	R1 = 0.0543, wR2 = 0.1454	
R indices (all data)	R1 = 0.0764, wR2 = 0.1621	
Largest diff. peak and hole	0.831 and -0.612 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for acdr29_2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	3976(1)	7550(2)	7283(2)	48(1)
C(2)	4306(2)	7744(2)	6780(2)	58(1)
C(3)	4309(2)	7312(3)	6193(2)	64(1)
C(4)	3998(2)	6692(2)	6119(2)	57(1)
C(5)	3677(1)	6529(2)	6639(2)	47(1)
C(6)	3318(2)	5863(2)	6561(2)	57(1)
C(7)	3703(2)	5097(2)	7573(2)	53(1)
C(8)	4211(2)	5529(2)	7909(2)	50(1)
C(9)	4531(2)	6626(2)	8606(2)	56(1)
C(10)	4349(2)	7284(2)	8971(2)	58(1)
C(11)	3954(2)	8010(2)	7929(2)	59(1)
C(12)	3948(2)	5722(2)	9120(2)	52(1)
C(13)	3468(1)	6056(2)	9418(2)	45(1)
C(14)	2941(2)	6111(3)	9013(2)	72(1)
C(15)	2508(2)	6429(3)	9292(2)	72(1)
C(16)	2580(2)	6694(2)	9986(2)	48(1)
C(17)	3107(2)	6606(2)	10393(2)	54(1)
C(18)	3542(2)	6295(2)	10115(2)	52(1)
C(19)	2118(2)	7105(2)	10275(2)	56(1)
C(23)	3592(2)	8101(2)	9045(2)	58(1)
C(24)	3020(2)	8373(2)	8722(2)	51(1)
C(25)	2648(2)	7982(2)	8223(2)	59(1)
C(26)	2101(2)	8216(2)	7989(2)	64(1)
C(27)	1904(2)	8855(2)	8241(2)	63(1)
C(28)	2283(2)	9249(2)	8721(3)	67(1)
C(29)	2830(2)	9016(2)	8952(2)	62(1)
C(30)	1290(2)	9072(3)	8009(3)	83(2)
C(34)	2729(2)	5055(2)	7066(2)	60(1)
C(35)	2184(2)	5432(2)	6792(2)	57(1)
C(36)	1874(2)	5283(3)	6122(3)	77(1)
C(37)	1350(2)	5565(3)	5892(3)	82(1)
C(38)	1097(2)	6015(2)	6318(3)	63(1)
C(39)	1421(2)	6202(3)	6953(3)	97(2)
C(40)	1950(2)	5919(3)	7188(3)	98(2)

C(41)	497(2)	6288(3)	6090(3)	81(1)
C(45)	6223(1)	7552(2)	8091(2)	43(1)
C(46)	5924(2)	7841(2)	8586(2)	54(1)
C(47)	5923(2)	7482(2)	9223(2)	61(1)
C(48)	6210(2)	6848(2)	9346(2)	58(1)
C(49)	6506(2)	6592(2)	8837(2)	46(1)
C(50)	6846(2)	5918(2)	8982(2)	61(1)
C(51)	6448(2)	5058(2)	8059(2)	61(1)
C(52)	5955(2)	5478(2)	7656(2)	52(1)
C(53)	5664(2)	6500(2)	6848(2)	51(1)
C(54)	5856(2)	7109(2)	6426(2)	53(1)
C(55)	6238(2)	7933(2)	7392(2)	52(1)
C(56)	7431(2)	5044(2)	8545(3)	74(1)
C(57)	7974(2)	5446(2)	8738(3)	65(1)
C(60)	9055(2)	6074(2)	9036(3)	69(1)
C(63)	9648(2)	6375(3)	9172(3)	88(2)
C(67)	6603(2)	7902(2)	6279(2)	50(1)
C(68)	7171(2)	8219(2)	6570(2)	47(1)
C(69)	7351(2)	8824(2)	6253(2)	58(1)
C(70)	7898(2)	9071(2)	6436(3)	70(1)
C(71)	8289(2)	8726(3)	6952(3)	66(1)
C(72)	8094(2)	8144(2)	7287(2)	62(1)
C(73)	7553(2)	7895(2)	7107(2)	55(1)
C(74)	8911(2)	8925(3)	7137(3)	98(2)
C(78)	6261(2)	5527(2)	6462(2)	60(1)
C(79)	6689(2)	5863(2)	6071(2)	47(1)
C(80)	7202(2)	6094(2)	6438(2)	54(1)
C(81)	7599(2)	6388(2)	6081(2)	55(1)
C(82)	7504(2)	6460(2)	5335(2)	48(1)
C(83)	6993(2)	6204(2)	4968(2)	56(1)
C(84)	6593(2)	5913(2)	5332(2)	56(1)
C(85)	7941(2)	6831(2)	4960(2)	55(1)
N(1)	3660(1)	6952(2)	7209(2)	48(1)
N(2)	3225(1)	5531(2)	7231(2)	46(1)
N(3)	3844(1)	7621(2)	8568(2)	49(1)
N(4)	4073(1)	6079(2)	8441(2)	44(1)
N(5)	6518(1)	6942(2)	8220(2)	45(1)
N(6)	6931(1)	5508(2)	8345(2)	55(1)
N(7)	6118(1)	5958(2)	7087(2)	46(1)

N(8)	6359(1)	7476(2)	6804(2)	45(1)
O(1)	5536(1)	5320(2)	9240(2)	84(1)
O(2)	4939(2)	6080(2)	5128(2)	126(2)
Br(1)	4775(1)	3893(1)	9290(1)	69(1)
Br(2)	5251(1)	5274(1)	3697(1)	86(1)
C(86)	8509(2)	6460(3)	5155(3)	95(2)
C(87)	7983(3)	7614(3)	5193(3)	91(2)
C(88)	7774(2)	6830(3)	4134(2)	84(1)
C(58A)	8080(4)	6086(5)	8433(5)	60(3)
C(59A)	8612(4)	6389(6)	8551(5)	63(3)
C(61A)	8922(5)	5508(7)	9365(8)	84(4)
C(62A)	8389(5)	5198(7)	9239(7)	73(4)
C(58B)	8192(5)	5878(8)	8207(9)	73(4)
C(59B)	8716(6)	6175(9)	8392(9)	85(5)
C(61B)	8846(5)	5598(7)	9569(8)	61(4)
C(62B)	8327(6)	5322(7)	9420(9)	64(4)
C(20A)	2277(5)	7898(4)	10280(7)	67(3)
C(21A)	2024(6)	6840(7)	10984(6)	76(4)
C(22A)	1540(4)	7009(7)	9749(7)	78(4)
C(21B)	2235(5)	7121(7)	11132(5)	68(3)
C(22B)	1548(4)	6787(8)	10048(9)	91(4)
C(20B)	2115(6)	7876(5)	10023(8)	70(3)
C(31A)	1119(4)	9100(7)	7191(4)	89(3)
C(32A)	914(4)	8465(6)	8261(6)	99(4)
C(33A)	1125(6)	9758(6)	8326(8)	130(5)
C(31B)	1015(9)	8788(14)	7262(9)	132(8)
C(32B)	984(7)	8926(11)	8621(9)	116(7)
C(33B)	1267(8)	9923(7)	7938(12)	115(6)
C(42A)	331(4)	6335(5)	5259(4)	100(3)
C(43A)	90(4)	5752(5)	6326(6)	110(3)
C(44A)	423(5)	7040(5)	6389(7)	119(4)
C(42B)	126(12)	5748(16)	5606(17)	193(15)
C(43B)	156(7)	6139(11)	6721(9)	95(6)
C(44B)	470(10)	7098(7)	5999(14)	118(8)
C(64A)	10033(4)	5849(6)	8889(6)	108(4)
C(65A)	9884(5)	6441(7)	9998(5)	117(4)
C(66A)	9679(5)	7121(6)	8836(8)	133(5)
C(64B)	9903(8)	6285(12)	8469(9)	128(7)
C(65B)	10079(10)	5994(15)	9734(14)	186(11)

C(66B)	9633(8)	7171(7)	9305(12)	120(7)
C(75A)	9268(3)	8259(5)	6966(7)	86(4)
C(76A)	9091(6)	9106(9)	7930(4)	107(5)
C(77A)	9063(8)	9598(7)	6746(10)	133(7)
C(75B)	9211(7)	8569(11)	6573(10)	100(7)
C(76B)	9109(8)	8882(12)	7974(4)	79(6)
C(77B)	8960(14)	9715(9)	6879(17)	136(11)

Table 3. Bond lengths [Å] and angles [°] for compound 2.

C(1)-N(1)	1.345(5)	C(24)-C(25)	1.388(5)
C(1)-C(2)	1.388(5)	C(25)-C(26)	1.387(6)
C(1)-C(11)	1.497(6)	C(26)-C(27)	1.397(6)
C(2)-C(3)	1.368(6)	C(27)-C(28)	1.380(6)
C(3)-C(4)	1.373(6)	C(27)-C(30)	1.525(6)
C(4)-C(5)	1.385(5)	C(28)-C(29)	1.387(6)
C(5)-N(1)	1.340(5)	C(30)-C(33A)	1.496(10)
C(5)-C(6)	1.507(6)	C(30)-C(32B)	1.500(12)
C(6)-N(2)	1.458(5)	C(30)-C(31A)	1.523(9)
C(7)-N(2)	1.465(5)	C(30)-C(31B)	1.540(13)
C(7)-C(8)	1.511(5)	C(30)-C(32A)	1.575(9)
C(8)-N(4)	1.510(5)	C(30)-C(33B)	1.593(12)
C(9)-N(4)	1.497(5)	C(34)-N(2)	1.479(5)
C(9)-C(10)	1.510(5)	C(34)-C(35)	1.503(6)
C(10)-N(3)	1.461(5)	C(35)-C(40)	1.360(6)
C(11)-N(3)	1.469(5)	C(35)-C(36)	1.377(6)
C(12)-C(13)	1.510(5)	C(36)-C(37)	1.370(7)
C(12)-N(4)	1.516(5)	C(37)-C(38)	1.374(7)
C(13)-C(18)	1.368(5)	C(38)-C(39)	1.354(7)
C(13)-C(14)	1.368(5)	C(38)-C(41)	1.525(6)
C(14)-C(15)	1.384(6)	C(39)-C(40)	1.383(7)
C(15)-C(16)	1.379(6)	C(41)-C(44B)	1.521(13)
C(16)-C(17)	1.376(5)	C(41)-C(43A)	1.522(9)

C(16)-C(19)	1.530(5)	C(41)-C(44A)	1.534(9)
C(17)-C(18)	1.381(5)	C(41)-C(42B)	1.537(15)
C(19)-C(21A)	1.477(9)	C(41)-C(42A)	1.547(8)
C(19)-C(22B)	1.491(10)	C(41)-C(43B)	1.585(12)
C(19)-C(20B)	1.515(9)	C(45)-N(5)	1.341(4)
C(19)-C(20A)	1.526(9)	C(45)-C(46)	1.384(5)
C(19)-C(22A)	1.574(9)	C(45)-C(55)	1.501(5)
C(19)-C(21B)	1.588(9)	C(46)-C(47)	1.375(6)
C(23)-N(3)	1.472(5)	C(47)-C(48)	1.370(6)
C(23)-C(24)	1.497(5)	C(48)-C(49)	1.376(5)
C(24)-C(29)	1.381(5)	C(49)-N(5)	1.337(5)
C(49)-C(50)	1.502(5)	C(74)-C(76A)	1.518(7)
C(50)-N(6)	1.465(5)	C(74)-C(77A)	1.532(7)
C(51)-N(6)	1.462(5)	C(74)-C(75B)	1.536(8)
C(51)-C(52)	1.513(5)	C(74)-C(77B)	1.564(8)
C(52)-N(7)	1.501(5)	C(74)-C(76B)	1.566(8)
C(53)-N(7)	1.501(5)	C(74)-C(75A)	1.576(7)
C(53)-C(54)	1.506(5)	C(78)-C(79)	1.505(5)
C(54)-N(8)	1.467(5)	C(78)-N(7)	1.515(5)
C(55)-N(8)	1.466(5)	C(79)-C(84)	1.373(5)
C(56)-N(6)	1.479(5)	C(79)-C(80)	1.377(5)
C(56)-C(57)	1.499(6)	C(80)-C(81)	1.377(5)
C(57)-C(62A)	1.334(11)	C(81)-C(82)	1.390(5)
C(57)-C(58A)	1.369(9)	C(82)-C(83)	1.388(5)
C(57)-C(62B)	1.430(14)	C(82)-C(85)	1.535(5)

C(57)-C(58B)	1.451(14)	C(83)-C(84)	1.388(6)
C(60)-C(61A)	1.292(13)	C(85)-C(86)	1.523(6)
C(60)-C(59B)	1.352(15)	C(85)-C(87)	1.524(6)
C(60)-C(59A)	1.406(10)	C(85)-C(88)	1.537(6)
C(60)-C(61B)	1.492(15)	C(58A)-C(59A)	1.386(11)
C(60)-C(63)	1.518(7)	C(61A)-C(62A)	1.393(16)
C(63)-C(66B)	1.508(13)	C(58B)-C(59B)	1.370(17)
C(63)-C(64A)	1.511(9)	C(61B)-C(62B)	1.338(17)
C(63)-C(65B)	1.524(14)		
C(63)-C(66A)	1.535(10)	N(1)-C(1)-C(2)	121.9(4)
C(63)-C(64B)	1.562(13)	N(1)-C(1)-C(11)	117.3(3)
C(63)-C(65A)	1.566(10)	C(2)-C(1)-C(11)	120.8(4)
C(67)-N(8)	1.468(4)	C(3)-C(2)-C(1)	118.8(4)
C(67)-C(68)	1.507(5)	C(2)-C(3)-C(4)	119.9(4)
C(68)-C(73)	1.381(5)	C(3)-C(4)-C(5)	118.5(4)
C(68)-C(69)	1.382(5)	N(1)-C(5)-C(4)	122.4(4)
C(69)-C(70)	1.384(6)	N(1)-C(5)-C(6)	117.8(3)
C(70)-C(71)	1.388(7)	C(4)-C(5)-C(6)	119.8(4)
C(71)-C(72)	1.380(6)	N(2)-C(6)-C(5)	116.1(3)
C(71)-C(74)	1.528(7)	N(2)-C(7)-C(8)	114.1(3)
C(72)-C(73)	1.372(6)	N(4)-C(8)-C(7)	112.6(3)
N(4)-C(9)-C(10)	112.6(3)	C(27)-C(28)-C(29)	121.6(4)
N(3)-C(10)-C(9)	113.4(3)	C(24)-C(29)-C(28)	121.7(4)
N(3)-C(11)-C(1)	114.9(3)	C(33A)-C(30)-C(31A)	109.3(7)
C(13)-C(12)-N(4)	114.3(3)	C(33A)-C(30)-C(27)	115.2(6)

C(18)-C(13)-C(14)	117.6(3)	C(32B)-C(30)-C(27)	108.5(8)
C(18)-C(13)-C(12)	120.8(3)	C(31A)-C(30)-C(27)	112.1(5)
C(14)-C(13)-C(12)	121.6(3)	C(32B)-C(30)-C(31B)	116.6(12)
C(13)-C(14)-C(15)	120.8(4)	C(27)-C(30)-C(31B)	114.4(9)
C(16)-C(15)-C(14)	122.3(4)	C(33A)-C(30)-C(32A)	106.6(7)
C(17)-C(16)-C(15)	115.9(3)	C(31A)-C(30)-C(32A)	105.1(7)
C(17)-C(16)-C(19)	121.5(3)	C(27)-C(30)-C(32A)	107.8(5)
C(15)-C(16)-C(19)	122.6(3)	C(32B)-C(30)-C(33B)	103.2(10)
C(16)-C(17)-C(18)	122.0(4)	C(27)-C(30)-C(33B)	107.9(8)
C(13)-C(18)-C(17)	121.3(3)	C(31B)-C(30)-C(33B)	105.3(12)
C(22B)-C(19)-C(20B)	109.5(7)	N(2)-C(34)-C(35)	114.7(3)
C(21A)-C(19)-C(20A)	113.4(7)	C(40)-C(35)-C(36)	115.2(4)
C(21A)-C(19)-C(16)	113.0(5)	C(40)-C(35)-C(34)	123.2(4)
C(22B)-C(19)-C(16)	113.1(6)	C(36)-C(35)-C(34)	121.6(4)
C(20B)-C(19)-C(16)	109.1(5)	C(37)-C(36)-C(35)	122.4(5)
C(20A)-C(19)-C(16)	106.9(5)	C(36)-C(37)-C(38)	122.0(5)
C(21A)-C(19)-C(22A)	105.7(6)	C(39)-C(38)-C(37)	115.2(4)
C(20A)-C(19)-C(22A)	107.9(6)	C(39)-C(38)-C(41)	122.3(5)
C(16)-C(19)-C(22A)	109.9(5)	C(37)-C(38)-C(41)	122.4(4)
C(22B)-C(19)-C(21B)	106.8(7)	C(38)-C(39)-C(40)	122.8(5)
C(20B)-C(19)-C(21B)	107.0(6)	C(35)-C(40)-C(39)	121.9(5)
C(16)-C(19)-C(21B)	111.1(5)	C(44B)-C(41)-C(38)	112.5(10)
N(3)-C(23)-C(24)	114.1(3)	C(43A)-C(41)-C(38)	109.2(5)
C(29)-C(24)-C(25)	117.2(4)	C(43A)-C(41)-C(44A)	111.8(7)
C(29)-C(24)-C(23)	120.0(4)	C(38)-C(41)-C(44A)	111.6(6)

C(25)-C(24)-C(23)	122.6(3)	C(44B)-C(41)-C(42B)	125.2(16)
C(26)-C(25)-C(24)	121.1(4)	C(38)-C(41)-C(42B)	112.0(13)
C(25)-C(26)-C(27)	121.6(4)	C(43A)-C(41)-C(42A)	105.5(6)
C(28)-C(27)-C(26)	116.7(4)	C(38)-C(41)-C(42A)	111.6(5)
C(28)-C(27)-C(30)	123.1(4)	C(44A)-C(41)-C(42A)	107.0(6)
C(26)-C(27)-C(30)	120.1(4)	C(44B)-C(41)-C(43B)	103.9(12)
C(38)-C(41)-C(43B)	108.9(7)	C(60)-C(63)-C(66A)	112.2(6)
C(42B)-C(41)-C(43B)	90.2(15)	C(66B)-C(63)-C(64B)	105.7(11)
N(5)-C(45)-C(46)	122.1(3)	C(60)-C(63)-C(64B)	108.6(8)
N(5)-C(45)-C(55)	117.8(3)	C(65B)-C(63)-C(64B)	102.5(13)
C(46)-C(45)-C(55)	120.0(3)	C(64A)-C(63)-C(65A)	105.1(7)
C(47)-C(46)-C(45)	118.6(4)	C(60)-C(63)-C(65A)	111.3(6)
C(48)-C(47)-C(46)	119.3(4)	C(66A)-C(63)-C(65A)	107.6(8)
C(47)-C(48)-C(49)	119.4(4)	N(8)-C(67)-C(68)	114.5(3)
N(5)-C(49)-C(48)	121.9(4)	C(73)-C(68)-C(69)	117.0(4)
N(5)-C(49)-C(50)	118.2(3)	C(73)-C(68)-C(67)	122.8(3)
C(48)-C(49)-C(50)	119.8(4)	C(69)-C(68)-C(67)	119.9(3)
N(6)-C(50)-C(49)	116.0(3)	C(68)-C(69)-C(70)	121.5(4)
N(6)-C(51)-C(52)	113.2(3)	C(69)-C(70)-C(71)	121.5(4)
N(7)-C(52)-C(51)	112.7(3)	C(72)-C(71)-C(70)	116.1(4)
N(7)-C(53)-C(54)	113.0(3)	C(72)-C(71)-C(74)	119.2(5)
N(8)-C(54)-C(53)	113.6(3)	C(70)-C(71)-C(74)	124.6(4)
N(8)-C(55)-C(45)	115.2(3)	C(73)-C(72)-C(71)	122.6(4)
N(6)-C(56)-C(57)	114.2(3)	C(72)-C(73)-C(68)	121.1(4)
C(62A)-C(57)-C(58A)	115.3(7)	C(76A)-C(74)-C(71)	112.2(7)

C(62B)-C(57)-C(58B)	118.4(8)	C(76A)-C(74)-C(77A)	103.8(10)
C(62A)-C(57)-C(56)	121.0(6)	C(71)-C(74)-C(77A)	113.5(8)
C(58A)-C(57)-C(56)	123.7(5)	C(71)-C(74)-C(75B)	107.6(7)
C(62B)-C(57)-C(56)	119.7(7)	C(71)-C(74)-C(77B)	106.4(13)
C(58B)-C(57)-C(56)	121.3(6)	C(75B)-C(74)-C(77B)	97.0(15)
C(61A)-C(60)-C(59A)	115.3(7)	C(71)-C(74)-C(76B)	109.4(8)
C(59B)-C(60)-C(61B)	117.6(9)	C(75B)-C(74)-C(76B)	125.1(11)
C(61A)-C(60)-C(63)	121.8(7)	C(77B)-C(74)-C(76B)	109.5(15)
C(59B)-C(60)-C(63)	120.2(8)	C(76A)-C(74)-C(75A)	107.7(8)
C(59A)-C(60)-C(63)	122.8(6)	C(71)-C(74)-C(75A)	108.3(5)
C(61B)-C(60)-C(63)	121.9(6)	C(77A)-C(74)-C(75A)	111.2(8)
C(66B)-C(63)-C(60)	110.1(8)	C(79)-C(78)-N(7)	115.3(3)
C(64A)-C(63)-C(60)	108.7(5)	C(84)-C(79)-C(80)	117.6(3)
C(66B)-C(63)-C(65B)	112.2(14)	C(84)-C(79)-C(78)	121.0(3)
C(60)-C(63)-C(65B)	116.9(11)	C(80)-C(79)-C(78)	121.3(4)
C(64A)-C(63)-C(66A)	111.5(7)	C(81)-C(80)-C(79)	121.5(4)
C(80)-C(81)-C(82)	121.7(4)	C(55)-N(8)-C(67)	110.5(3)
C(83)-C(82)-C(81)	116.4(4)	C(54)-N(8)-C(67)	108.7(3)
C(83)-C(82)-C(85)	123.3(3)	C(57)-C(58A)-C(59A)	121.6(7)
C(81)-C(82)-C(85)	120.2(3)	C(58A)-C(59A)-C(60)	120.8(8)
C(82)-C(83)-C(84)	121.5(4)	C(60)-C(61A)-C(62A)	123.9(11)
C(79)-C(84)-C(83)	121.3(4)	C(57)-C(62A)-C(61A)	122.3(10)
C(86)-C(85)-C(87)	110.8(4)	C(59B)-C(58B)-C(57)	118.8(11)
C(86)-C(85)-C(82)	110.3(4)	C(60)-C(59B)-C(58B)	123.9(13)
C(87)-C(85)-C(82)	108.5(3)	C(62B)-C(61B)-C(60)	120.2(11)

C(86)-C(85)-C(88)	107.9(4)	C(61B)-C(62B)-C(57)	121.0(12)
C(87)-C(85)-C(88)	106.6(4)		
C(82)-C(85)-C(88)	112.7(4)		
C(5)-N(1)-C(1)	118.4(3)		
C(6)-N(2)-C(7)	112.6(3)		
C(6)-N(2)-C(34)	108.4(3)		
C(7)-N(2)-C(34)	107.8(3)		
C(10)-N(3)-C(11)	112.5(3)		
C(10)-N(3)-C(23)	110.0(3)		
C(11)-N(3)-C(23)	110.7(3)		
C(9)-N(4)-C(8)	111.0(3)		
C(9)-N(4)-C(12)	112.0(3)		
C(8)-N(4)-C(12)	111.1(3)		
C(49)-N(5)-C(45)	118.7(3)		
C(51)-N(6)-C(50)	112.6(3)		
C(51)-N(6)-C(56)	108.7(3)		
C(50)-N(6)-C(56)	108.8(3)		
C(53)-N(7)-C(52)	110.3(3)		
C(53)-N(7)-C(78)	112.3(3)		
C(52)-N(7)-C(78)	111.2(3)		
C(55)-N(8)-C(54)	112.3(3)		

Table 4. Selected bond lengths [\AA] for compound **2**.

N(1)···H(41)	2.26(4)	N(5)···H(71)	2.24(4)
N(2)···H(41)	2.53(4)	N(6)···H(71)	2.53(3)
N(3)···H(41)	2.59(4)	N(5)···H(71)	2.56(4)

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for acdr29_2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	37(2)	51(2)	57(2)	14(2)	14(2)	3(2)
C(2)	40(2)	66(3)	68(3)	25(2)	10(2)	-3(2)
C(3)	50(2)	92(3)	54(3)	26(2)	18(2)	6(2)
C(4)	48(2)	79(3)	44(2)	10(2)	10(2)	8(2)
C(5)	39(2)	60(2)	42(2)	8(2)	7(2)	7(2)
C(6)	55(2)	69(3)	46(2)	0(2)	8(2)	1(2)
C(7)	51(2)	53(2)	55(2)	-1(2)	12(2)	10(2)
C(8)	43(2)	56(2)	53(2)	2(2)	13(2)	14(2)
C(9)	38(2)	62(2)	66(3)	4(2)	6(2)	3(2)
C(10)	44(2)	58(2)	68(3)	-3(2)	-1(2)	1(2)
C(11)	57(2)	49(2)	75(3)	9(2)	20(2)	-3(2)
C(12)	55(2)	57(2)	46(2)	7(2)	14(2)	16(2)
C(13)	40(2)	49(2)	45(2)	2(2)	9(2)	7(2)
C(14)	53(3)	111(4)	50(2)	-21(2)	5(2)	16(2)
C(15)	41(2)	114(4)	57(3)	-8(3)	1(2)	17(2)
C(16)	47(2)	47(2)	54(2)	4(2)	18(2)	2(2)
C(17)	52(2)	65(3)	45(2)	-7(2)	10(2)	3(2)
C(18)	40(2)	69(3)	46(2)	0(2)	4(2)	10(2)
C(19)	50(2)	55(2)	67(3)	4(2)	23(2)	9(2)
C(23)	60(2)	55(2)	57(2)	-8(2)	8(2)	1(2)
C(24)	56(2)	42(2)	57(2)	-2(2)	17(2)	0(2)
C(25)	60(3)	51(2)	66(3)	-12(2)	13(2)	7(2)
C(26)	56(3)	73(3)	64(3)	-7(2)	9(2)	4(2)
C(27)	66(3)	61(3)	70(3)	13(2)	29(2)	16(2)
C(28)	79(3)	44(2)	85(3)	-1(2)	33(3)	11(2)
C(29)	71(3)	42(2)	75(3)	-7(2)	20(2)	-2(2)
C(30)	70(3)	95(4)	90(4)	21(3)	35(3)	33(3)
C(34)	52(2)	52(2)	75(3)	1(2)	9(2)	-4(2)
C(35)	45(2)	52(2)	74(3)	-3(2)	8(2)	-8(2)
C(36)	68(3)	71(3)	87(3)	-19(3)	2(3)	7(2)
C(37)	68(3)	82(3)	86(3)	-5(3)	-11(3)	1(3)
C(38)	43(2)	60(3)	85(3)	12(2)	7(2)	-7(2)
C(39)	70(3)	118(5)	98(4)	-31(3)	4(3)	27(3)
C(40)	64(3)	134(5)	88(4)	-40(4)	-12(3)	20(3)

C(41)	54(3)	77(3)	112(4)	26(3)	16(3)	-5(2)
C(45)	36(2)	46(2)	48(2)	-7(2)	9(2)	-4(2)
C(46)	47(2)	58(2)	57(2)	-13(2)	9(2)	3(2)
C(47)	53(2)	82(3)	50(2)	-21(2)	17(2)	-9(2)
C(48)	60(2)	68(3)	44(2)	-3(2)	7(2)	-12(2)
C(49)	43(2)	50(2)	44(2)	-5(2)	4(2)	-9(2)
C(50)	63(3)	61(3)	57(2)	8(2)	0(2)	-1(2)
C(51)	59(3)	50(2)	72(3)	5(2)	4(2)	-10(2)
C(52)	45(2)	54(2)	58(2)	1(2)	11(2)	-11(2)
C(53)	41(2)	50(2)	62(2)	-2(2)	5(2)	-1(2)
C(54)	47(2)	50(2)	60(2)	3(2)	4(2)	0(2)
C(55)	56(2)	44(2)	60(2)	0(2)	18(2)	3(2)
C(56)	62(3)	50(2)	106(4)	9(2)	1(3)	8(2)
C(57)	47(2)	56(3)	87(3)	4(2)	3(2)	10(2)
C(60)	50(2)	69(3)	85(3)	-19(2)	5(2)	5(2)
C(63)	66(3)	92(4)	108(4)	-26(3)	20(3)	0(3)
C(67)	52(2)	53(2)	46(2)	6(2)	10(2)	-1(2)
C(68)	55(2)	46(2)	42(2)	-1(2)	15(2)	-1(2)
C(69)	74(3)	48(2)	55(2)	4(2)	19(2)	-2(2)
C(70)	88(4)	54(3)	77(3)	-8(2)	39(3)	-20(2)
C(71)	62(3)	73(3)	71(3)	-29(3)	30(2)	-18(2)
C(72)	51(2)	74(3)	60(3)	-11(2)	6(2)	-1(2)
C(73)	59(3)	55(2)	51(2)	3(2)	10(2)	-3(2)
C(74)	79(3)	107(4)	119(5)	-51(4)	49(3)	-26(3)
C(78)	65(3)	51(2)	67(3)	-10(2)	25(2)	-7(2)
C(79)	47(2)	42(2)	54(2)	-7(2)	12(2)	1(2)
C(80)	57(2)	64(3)	41(2)	2(2)	8(2)	-1(2)
C(81)	47(2)	64(2)	51(2)	-5(2)	4(2)	-4(2)
C(82)	53(2)	44(2)	48(2)	-3(2)	12(2)	8(2)
C(83)	57(2)	68(3)	43(2)	-5(2)	7(2)	6(2)
C(84)	47(2)	64(3)	57(3)	-12(2)	5(2)	-4(2)
C(85)	58(2)	57(2)	56(2)	-6(2)	23(2)	2(2)
N(1)	40(2)	54(2)	51(2)	9(2)	16(1)	1(2)
N(2)	41(2)	49(2)	48(2)	4(1)	9(1)	1(1)
N(3)	47(2)	47(2)	53(2)	0(2)	10(1)	2(1)
N(4)	35(2)	51(2)	46(2)	5(2)	8(1)	13(2)
N(5)	41(2)	45(2)	49(2)	-3(1)	11(1)	-2(1)
N(6)	48(2)	44(2)	70(2)	2(2)	3(2)	2(1)
N(7)	39(2)	44(2)	55(2)	-5(2)	9(2)	-9(2)

N(8)	47(2)	42(2)	47(2)	-1(1)	12(1)	0(1)
O(1)	82(2)	75(2)	103(2)	11(2)	34(2)	-6(2)
O(2)	168(4)	116(3)	97(3)	-19(2)	36(3)	35(3)
Br(1)	60(1)	56(1)	88(1)	-18(1)	7(1)	-4(1)
Br(2)	83(1)	99(1)	83(1)	-32(1)	35(1)	-34(1)
C(86)	67(3)	124(5)	100(4)	14(4)	32(3)	5(3)
C(87)	124(4)	68(3)	93(4)	-13(3)	54(3)	-27(3)
C(88)	106(4)	89(4)	64(3)	0(3)	34(3)	-8(3)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **2** (only the hydrogens located from the difference Fourier map and refined isotropically are listed).

	x	y	z	U(eq)
H(41)	3793(16)	6280(20)	8220(20)	46(11)
H(71)	6396(16)	6188(19)	7281(19)	42(10)