

Electronic Supplementary Information

Neutral hydrolysis of poly(ethylene terephthalate) catalysed by highly active terephthalate-based ionic liquids at low loadings

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1. General

Proton Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker DPX 400 MHz using DMSO- d_6 as a solvent and referenced relative to residual DMSO ($\delta = 2.50$ ppm). Chemical shifts are reported in ppm and coupling constants (J) in Hertz. Carbon NMR spectra were recorded on the same instruments (100.6 MHz) with total proton decoupling. Phosphorus NMR spectra were recorded on the same instrument (162 MHz). HSQC, HMBC, TOCSY, NOE, EXSY and ROESY NMR experiments were used to aid assignment of NMR signals when required. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory. ESI mass spectra were acquired using a Waters Micromass LCT- time of flight mass spectrometer (TOF), interfaced to a Waters 2690 HPLC. The instrument was operated in either positive or negative mode as required. Colourless poly(ethylene terephthalate) bottles were purchased from a local large supermarket chain and cut into flakes (*ca.* 5 mm square). Anion exchange resin Amberlite[®] OH IRN78 (Supelco, strongly basic, total exchange capacity (OH) 1.25 eq/L) was purchased from Sigma Aldrich. Anion exchange resin Amberlite[®] IRA-900 chloride form (Supelco, total exchange capacity (Cl) 1.0 eq/L) was purchased from Sigma Aldrich. Unless otherwise noted, all commercially available compounds were used as provided, without any further purification. Compounds **23**, **25** and **26** were made according to literature procedures.¹

2. Neutral PET hydrolysis procedure

Neutral PET hydrolysis using disodium terephthalate as a co-catalyst

A 23 mL Teflon[®] cup was charged with water (10 mL), disodium terephthalate (0.0109 g, 1 mol%),^a catalyst (2 mol%) and poly(ethylene terephthalate) flakes (*ca.* 5 mm squares, 1.000 g). The Teflon[®] cup was then sealed inside a batch hydrothermal autoclave before being placed for 3 h into an oven pre-heated at 200 °C. The batch hydrothermal autoclave was then placed on a ceramic tile for 16 h. To the reaction mixture was then added sodium hydroxide (0.550 g), HPLC-grade water (6 mL) and a stir bar. After 10 min of stirring, the reaction mixture was filtered and the residue was washed with water (10 mL x 2).^b The filtrate was adjusted, with cooling, to pH 2-3 using dilute hydrochloric acid and the precipitate was filtered. The residue was washed with water (10 mL) and the product was dried for 4 h in a vacuum oven at 60 °C.^c

^aMol% of catalyst is related to the number of moles of monomeric units (5.204 mmol) present in 1.000 g of polymer.

^bTo establish catalyst recyclability, the unreacted PET residue was subsequently washed with acetone (2 x 10 mL) and the washings concentrated *in vacuo*.

^cYield calculated based on the mass of recovered TPA after acidification. Correction is made for the the additional TPA derived from protonation of the added disodium terephthalate upon workup. To evaluate purity and provide yield data based on an internal standard – samples of TPA post *in vacuo* drying were added to known amounts of 4-iodoanisole and yield was calculated by ¹H NMR spectroscopy. Spectroscopically obtained yields agreed with those derived from the mass of TPA within 1.1% in all cases.

Neutral PET hydrolysis using an ionic liquid catalyst

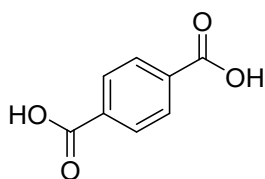
A 23 mL Teflon[®] cup was charged with water (10 mL), catalyst (0.5 - 1 mol%)^a and poly(ethylene terephthalate) flakes (*ca.* 5 mm squares, 1.000 g). The Teflon[®] cup was then sealed inside a batch hydrothermal autoclave before being placed for 3 h into an oven pre-heated at 200 °C. The batch hydrothermal autoclave was then placed on a ceramic tile for 16 h. To the reaction mixture was then added sodium hydroxide (0.550 g), HPLC-grade water (6 mL) and a stir bar. After 10 min of stirring, the reaction mixture was filtered and the residue was washed with water (10 mL x 2).^b The filtrate was adjusted, with cooling, to pH 2-3 using dilute hydrochloric acid and the precipitate was filtered. The residue was washed with water (10 mL) and the product was dried for 4 h in a vacuum oven at 60 °C.

^aMol% of catalyst is related to the number of moles of monomeric units (5.204 mmol) present in 1.000 g of polymer.

^bTo establish catalyst recyclability, the residue was washed with acetone (2 x 10 mL) and the washings concentrated *in vacuo*.

^cYield calculated based on the mass of recovered TPA after acidification. To evaluate purity and provide yield data based on an internal standard – samples of TPA post *in vacuo* drying were added to known amounts of 4-iodoanisole and yield was calculated by ¹H NMR spectroscopy. Spectroscopically obtained yields agreed with those derived from the mass of TPA within 1.1% in all cases.

Terephthalic acid (TPA, **2**)



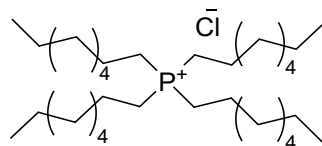
A 23 mL Teflon® cup was charged with water (10 mL), **30** (0.0295 g, 0.026 mmol, 0.5 mol%).^a and polyethylene terephthalate flakes (*ca.* 5 mm squares, 1.000 g). The Teflon® cup was then sealed inside a batch hydrothermal autoclave before being placed into an oven pre-heated at 200 °C for 5 h. The batch hydrothermal autoclave was then placed on a ceramic tile for 16 h. To the reaction mixture was then added sodium hydroxide (0.550 g) and water (6 mL). After 10 min the reaction mixture was filtered and washed with water (10 mL x 2).^b The filtrate was adjusted, with cooling, to pH 2-3 using dilute HCl and the precipitate was filtered. The residue was washed with water (10 mL) and the product was dried for 4 h in a vacuum oven at 60 °C. **2** was isolated as a white solid (0.8353g, 97%) M.p. 299-301 °C (lit. M.p. 300 °C).²

^aMol% of catalyst is related to the number of moles of monomeric units (5.204 mmol) present in 1.000 g of polymer.

δ_H (400 MHz, DMSO-*d*₆): 13.29 (br s, 2H), 8.04 (s, 4H) ppm.

3. Catalyst Synthesis and characterisation

Catalyst 9



A 25 mL round-bottomed flask equipped was charged with tetraoctylphosphonium bromide (1.1276 g, 2 mmol), methanol (30 mL) and Amberlite® IRA-900 chloride form (6 g) and shaken for 18 h at room temperature. The solution was then passed through a column containing Amberlite® IRA-900 chloride form (6 g) and the column was washed with methanol (3 x 30 mL). The solvent was removed under reduced pressure and the product dried *in vacuo* yielding **9** as a yellow oil (1.096 g, 97%).

Spectral data for this compound were consistent with those in literature.³

δ_H (400 MHz, DMSO- d_6): 2.24-2.04 (m, 8H), 1.59-1.20 (m, 48H), 0.91-0.89 (m, 12H) ppm.

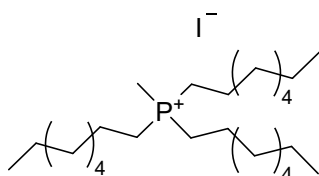
δ_C (101 MHz, DMSO- d_6): 31.7, 30.5 (d, $J = 15.1$), 28.6 (d, $J = 23.1$), 22.5, 21.0, 21.0, 17.9 (d, $J = 47.0$), 14.4 ppm.

δ_P (162 MHz, DMSO- d_6): 33.8 ppm.

HRMS (m/z – ESI⁺): Found: 483.5058 (M⁺) C₃₂H₆₈P⁺ Requires: 483.5053

ν_{max} (neat)/cm⁻¹: 2955, 2923, 2854, 1451, 1378, 1236, 1116, 1030, 720

Catalyst 13



A 25 mL round-bottomed flask equipped with a stirring bar was charged with trioctylphosphine (2.52 mL, 10 mmol), acetonitrile (10 mL) and was cooled in an ice bath. Iodomethane (0.69 mL, 11 mmol) was added dropwise *via* syringe and the heterogeneous mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (2 x 5 mL). The resulting solid was dried *in vacuo* yielding **13** as a colourless gum (3.12 g, 52%).

δ_H (400 MHz, DMSO- d_6): 2.27–2.10 (m, 6H), 1.79 (d, $J = 14.0$, 3H), 1.56–1.17 (m, 36H), 0.93–0.80 (m, 9H) ppm.

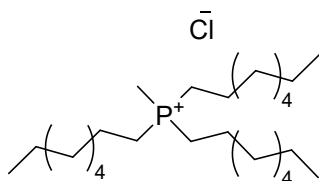
δ_C (101 MHz, DMSO- d_6): 31.2, 30.0 (d, $J = 15.1$), 28.3 (d, $J = 18.8$), 22.4, 22.0, 20.5, 19.1 (d, $J = 51.2$), 13.9, 3.2 (d, $J = 51.2$) ppm.

δ_P (162 MHz, DMSO- d_6): 32.2 ppm.

HRMS (m/z – ESI⁺): Found: 385.3957 (M⁺) C₂₅H₅₄P⁺ Requires: 385.3958

ν_{max} (neat)/cm⁻¹: 2945, 2922, 2854, 1458, 1378, 1305, 1099, 1033, 943, 907, 770, 721

Catalyst 14



A 25 mL round-bottomed flask equipped with a stir bar was charged with **13** (0.5716 g, 1 mmol), methanol (40 mL) and Amberlite® IRA-900 chloride form (6 g) and shaken for 18 h at room temperature. The solution was then passed through a column containing Amberlite® IRA-900 chloride form (6 g) and the column was washed with methanol (3 x 40 mL). The solvent was removed under reduced pressure and the product was dried *in vacuo* yielding **14** as a yellow oil (0.4070 g, 97%).

Spectral data for this compound were consistent with those in literature.³

δ_H (400 MHz, DMSO- d_6): 2.20–2.05 (m, 6H), 1.75 (d, $J = 14.2$, 3H), 1.51–1.20 (m, 36H), 0.87–0.82 (m, 9H) ppm.

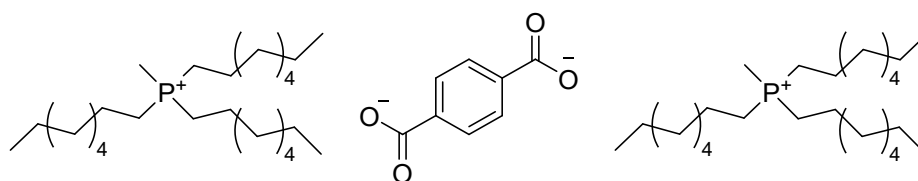
δ_C (101 MHz, DMSO- d_6): 31.7, 30.0 (d, $J = 15.1$), 28.7 (d, $J = 18.8$), 22.5, 21.0, 20.9, 19.5 (d, $J = 51.2$), 14.4, 3.7 (d, $J = 51.2$) ppm.

δ_P (162 MHz, DMSO- d_6): 32.2 ppm.

HRMS (m/z – ESI⁺): Found: 385.3969 (M⁺) C₂₅H₅₄P⁺ Requires: 385.3958

ν_{max} (neat)/cm⁻¹: 2923, 2855, 1727, 1452, 1377, 1305, 1100, 1033, 944, 721

Catalyst **29**



A 25 mL round-bottomed flask equipped was charged with Catalyst **13** (1.0252 g, 2 mmol), methanol (30 mL) and Amberlite®-OH IRN78 (4.4 g) and shaken for 18 h at room temperature. The solution was then passed through a column containing Amberlite®-OH IRN78 (4.4 g) and the column was washed with methanol (3 x 30 mL). The combined washes were placed in a 250 mL round-bottomed flask and were charged with a stir bar and terephthalic acid (0.1661 g, 1 mmol) before being stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the product was dried *in vacuo* yielding **29** as a white wax (0.897 g, 96%).

δ_H (400 MHz, DMSO- d_6): 7.58 (s, 4H), 2.20–2.07 (m, 12H), 1.76 (d, $J = 14.3$, 6H), 1.46–1.25 (m, 72H), 0.87–0.82 (m, 18H) ppm.

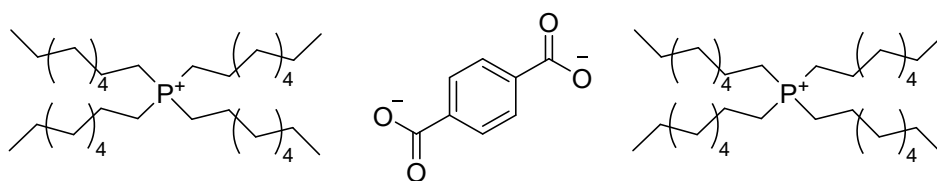
δ_C (101 MHz, DMSO- d_6): 169.0, 142.2, 127.9, 31.7, 30.0 (d, $J = 15.5$), 28.7 (d, $J = 18.3$), 22.5, 21.0, 20.9, 19.5 (d, $J = 47.6$), 14.4, 3.5 (d, $J = 53.4$) ppm.

δ_P (162 MHz, DMSO- d_6): 32.3 ppm.

HRMS (m/z – ESI⁺): Found: 385.3957 (M⁺) C₂₅H₅₄P⁺ Requires: 385.3958

ν_{max} (neat)/cm⁻¹: 2956, 2923, 2865, 1587, 1465, 1349, 1311, 1079, 1017, 945, 890, 801, 753, 721

Catalyst 30



A 25 mL round-bottomed flask equipped was charged with tetrabutylphosphonium bromide (1.1276 g, 2 mmol), methanol (30 mL) and Amberlite[®]-OH IRN78 (4.4 g) and shaken for 18 h at room temperature. The solution was then passed through a column containing Amberlite[®]-OH IRN78 (4.4 g) and the column was washed with methanol (3 x 30 mL). The combined washes were placed in a 250 mL round-bottomed flask and were charged with a stir bar and terephthalic acid (0.1661 g, 1 mmol) before being stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the product was dried *in vacuo* yielding **30** as a colourless gum (1.096 g, 97%).

δ_H (400 MHz, DMSO-*d*₆): 7.62 (s, 4H), 2.34-2.04 (m, 16H), 1.59-1.14 (m, 96H), 0.99-0.74 (m, 24H) ppm.

δ_C (101 MHz, DMSO-*d*₆): 169.0, 142.2, 127.9, 31.7, 30.0 (d, *J* = 15.5), 28.2 (d, *J* = 21.2), 22.0, 21.0, 20.9, 17.4 (d, *J* = 47.1), 14.4 ppm.

δ_P (162 MHz, DMSO-*d*₆): 33.8 ppm.

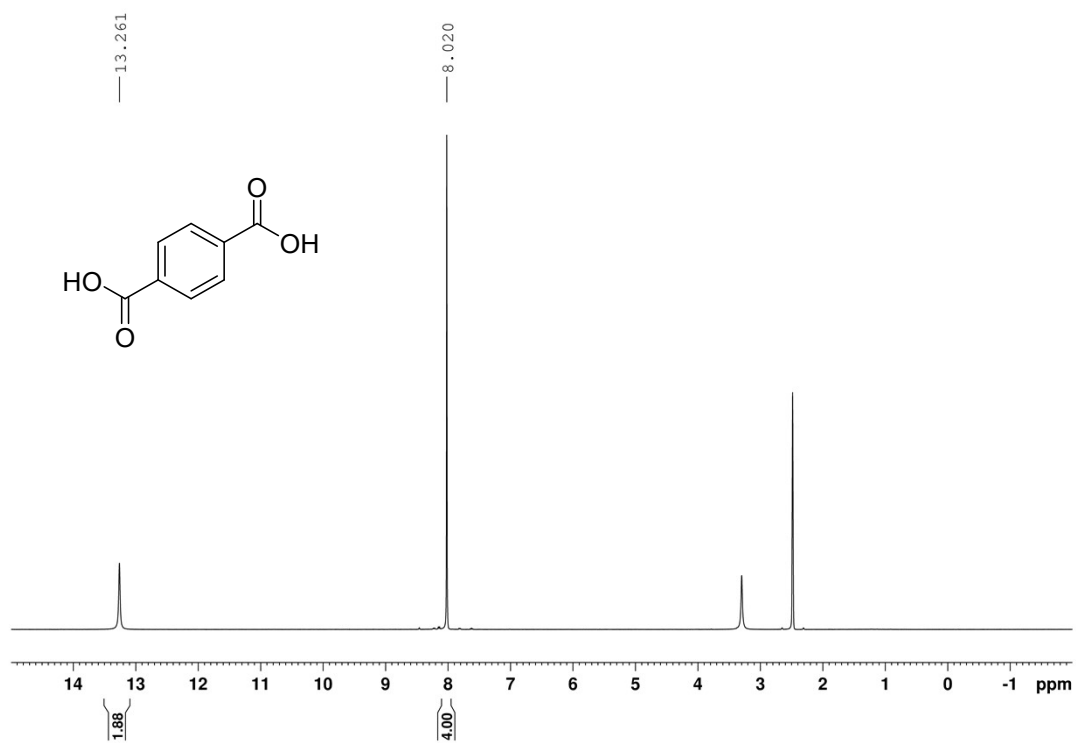
HRMS (*m/z* – ESI⁺): Found: 483.5061 (M⁺) C₃₂H₆₈P⁺ Requires: 483.5053

ν_{max} (neat)/cm⁻¹: 2923, 2854, 1581, 1464, 1350, 1116, 1017, 801, 754, 721

4. NMR Spectra

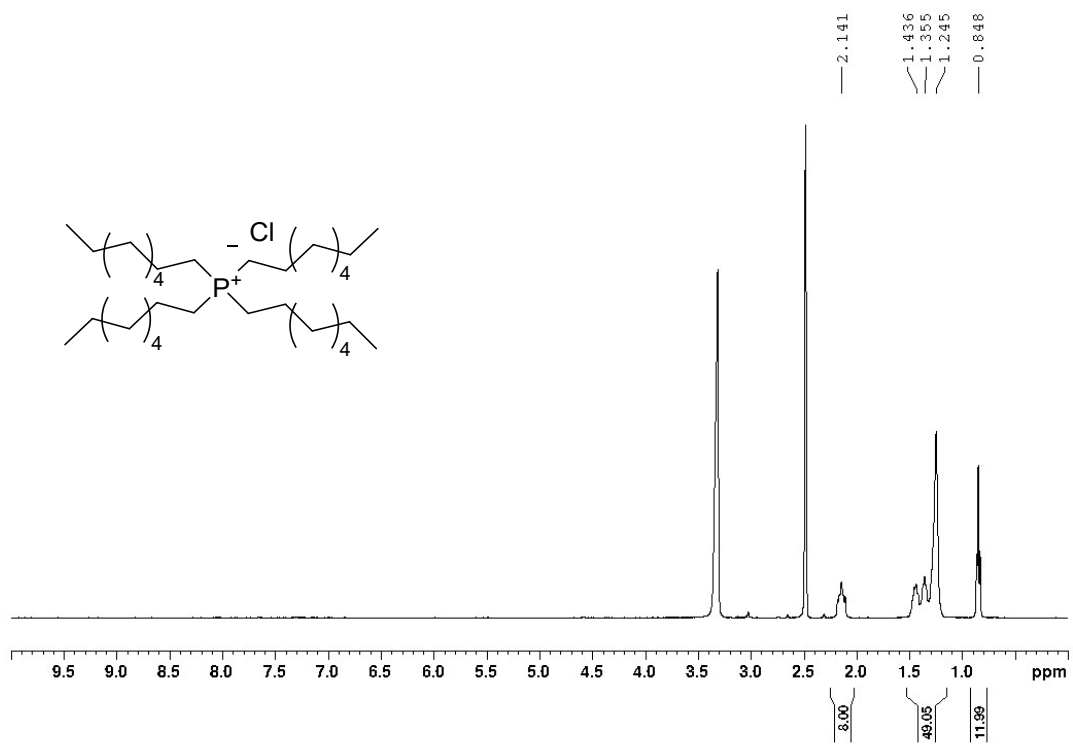
Product of the hydrolysis reaction Terephthalic Acid (TPA).

^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of TPA.

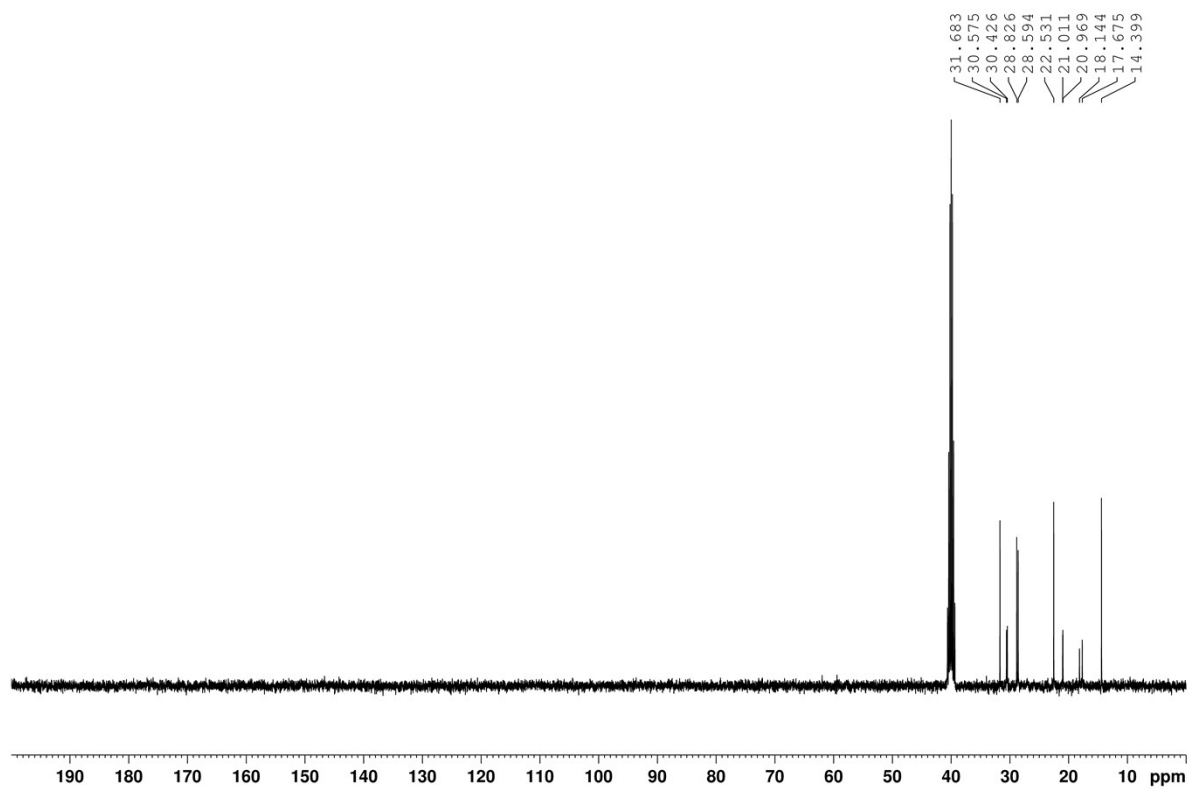


Catalyst 9

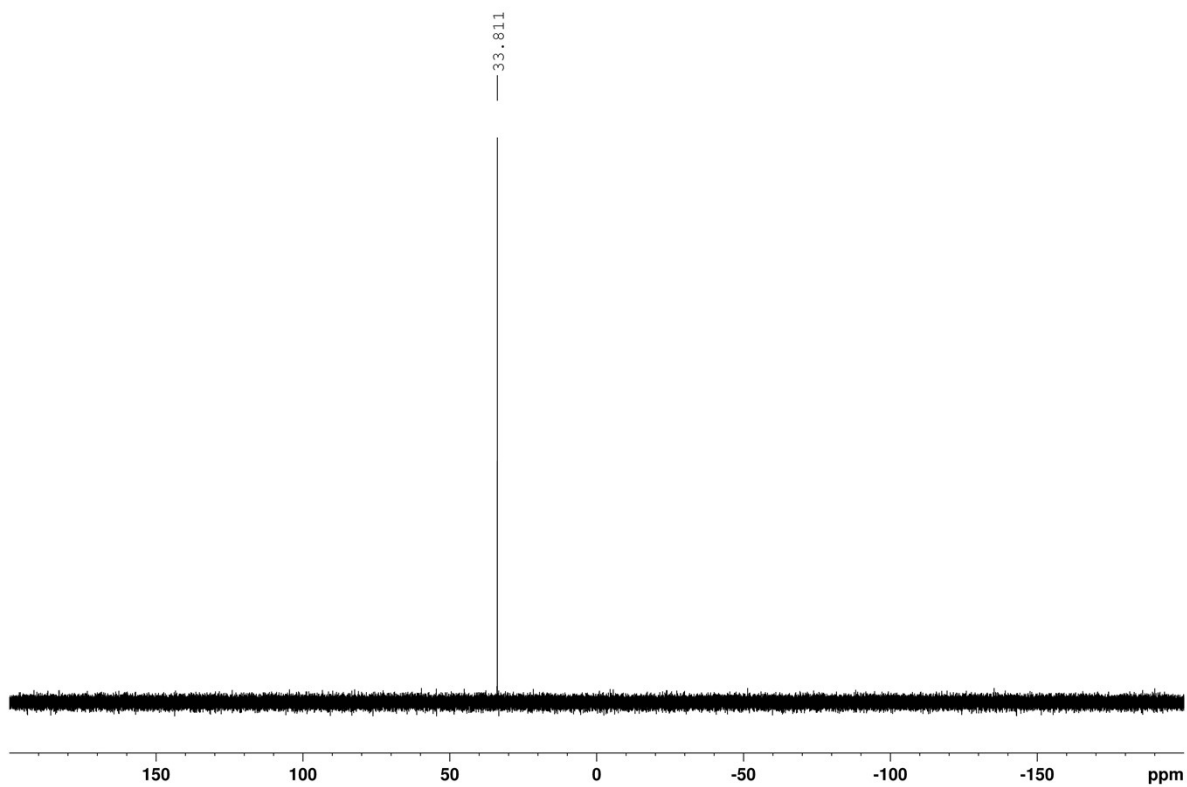
^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **9**.



^{13}C NMR spectrum (101 MHz, $\text{DMSO-}d_6$) of **9**.

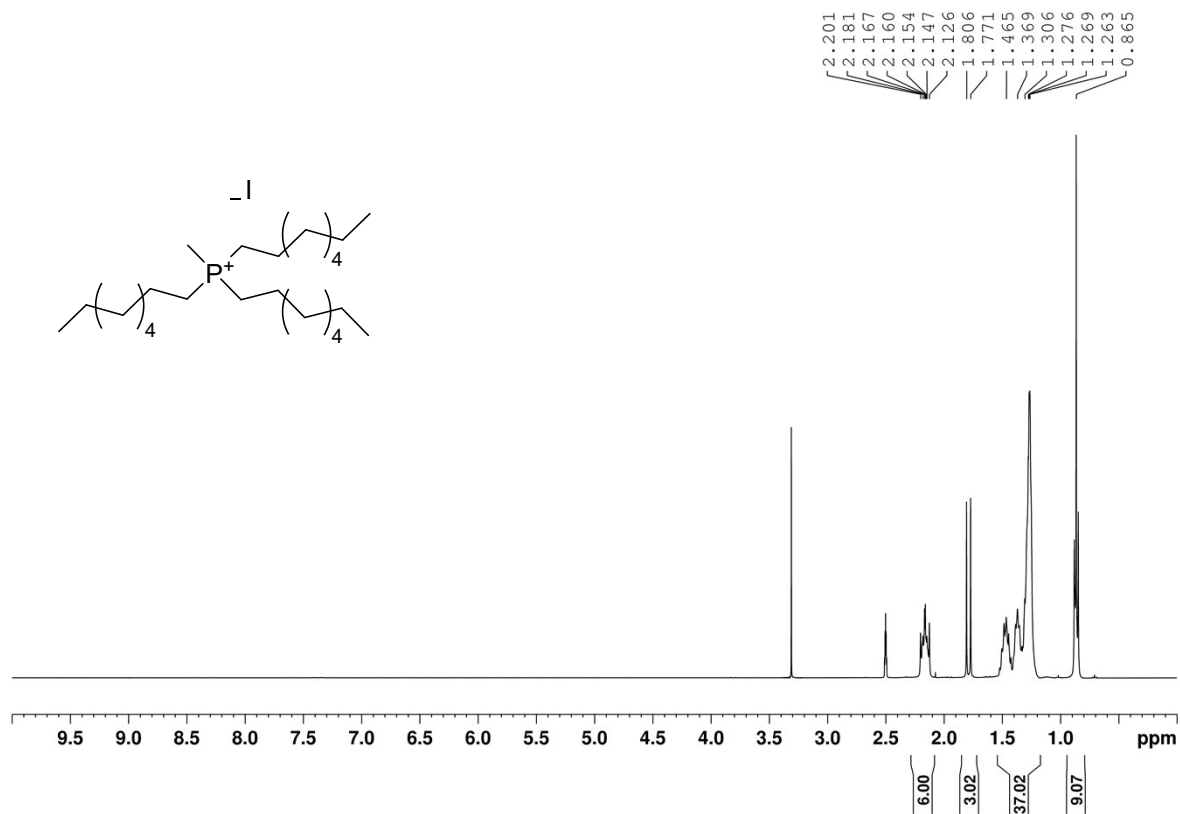


^{31}P NMR spectrum (164 MHz, $\text{DMSO-}d_6$) of **9**.

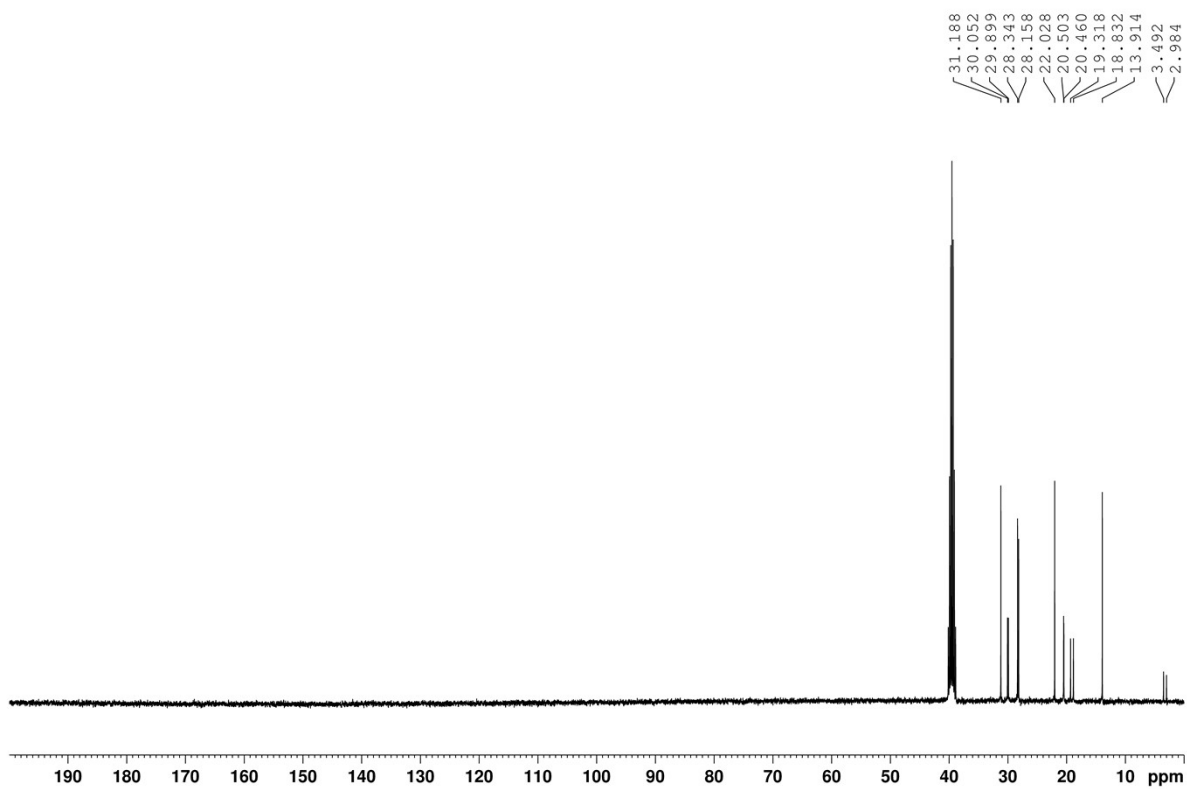


Catalyst 13

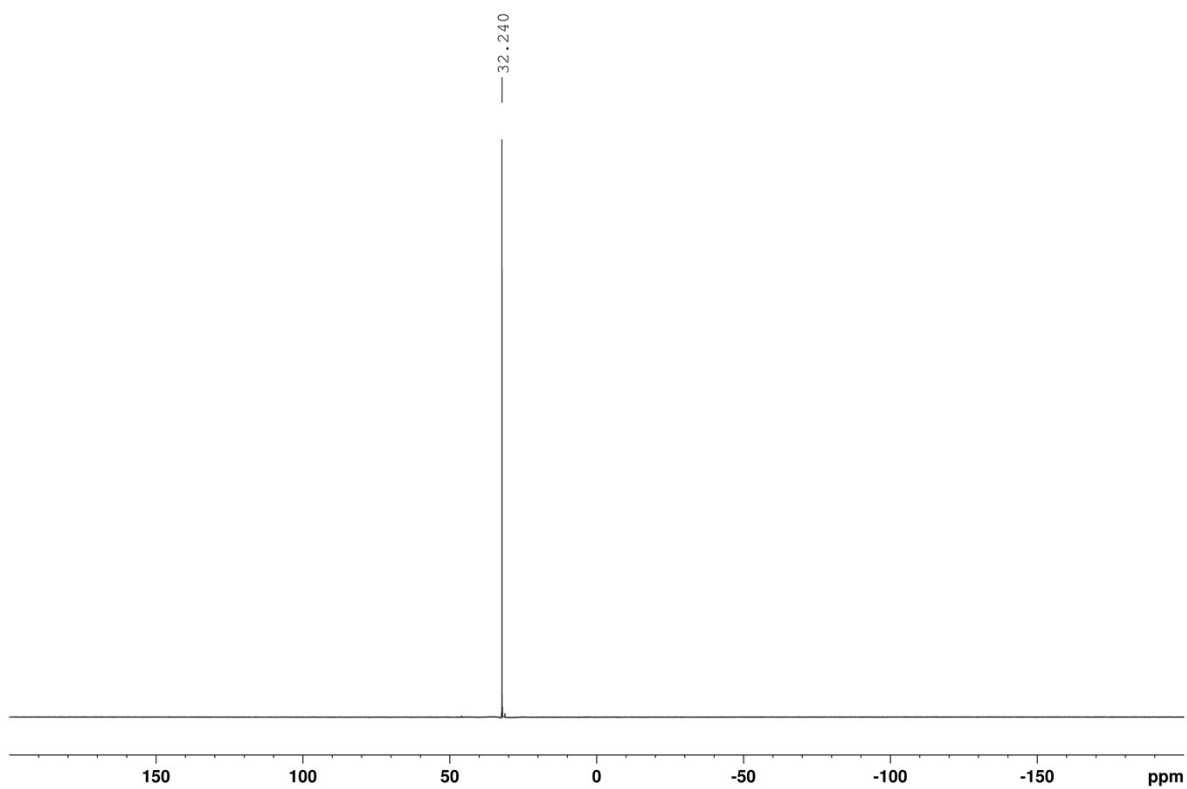
¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **13**.



^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$) of **13**.

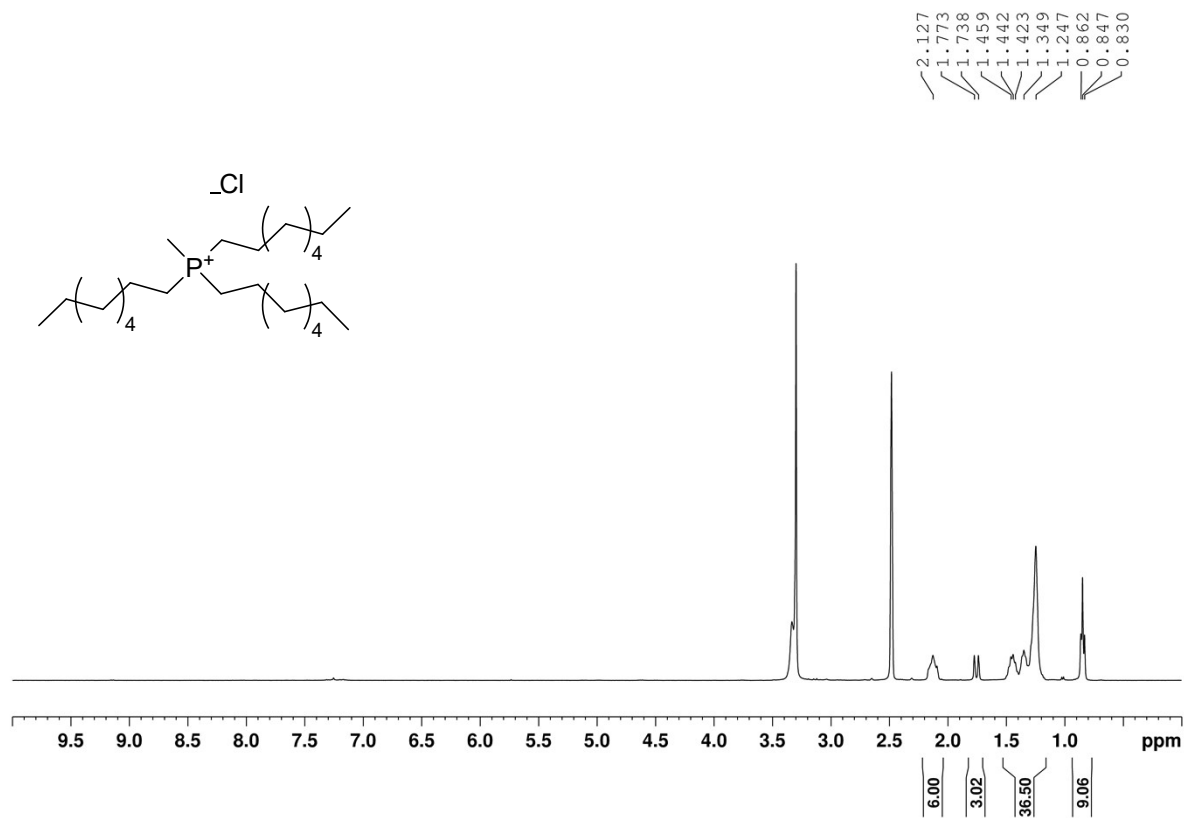


^{31}P NMR spectrum (164 MHz, $\text{DMSO-}d_6$) of **13**.

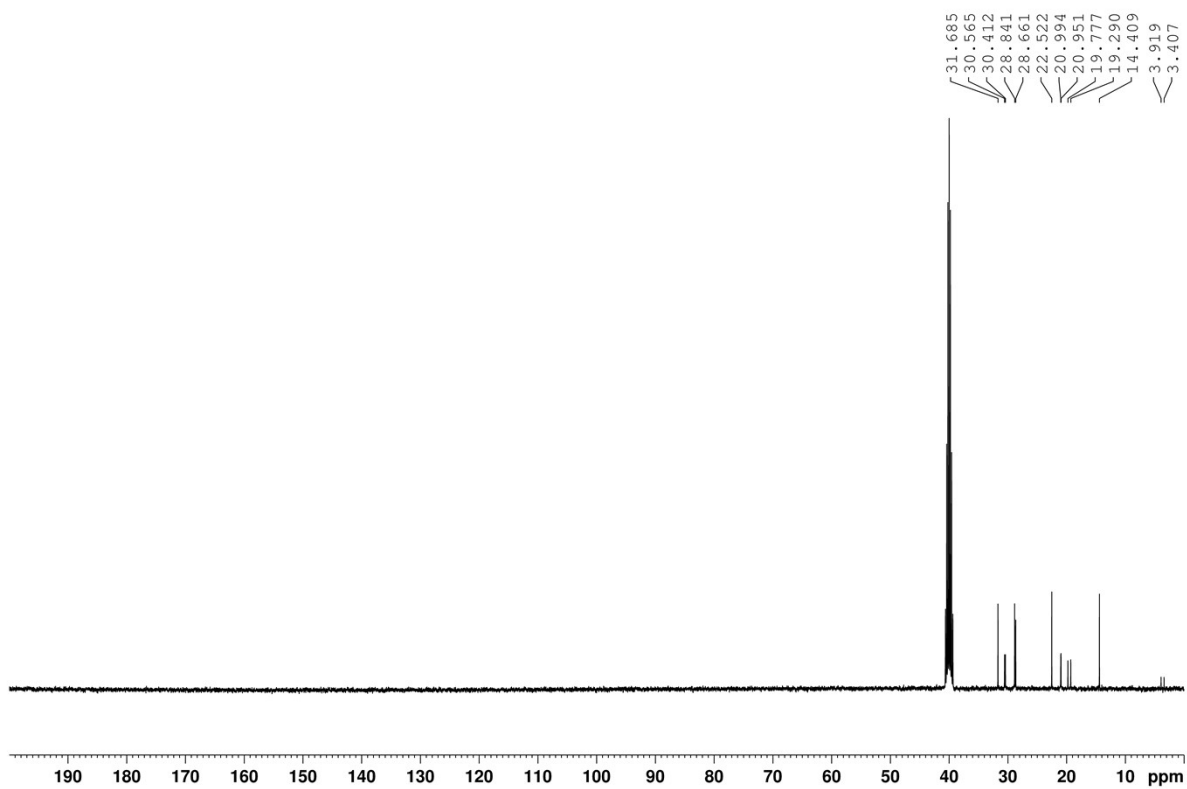


Catalyst 14

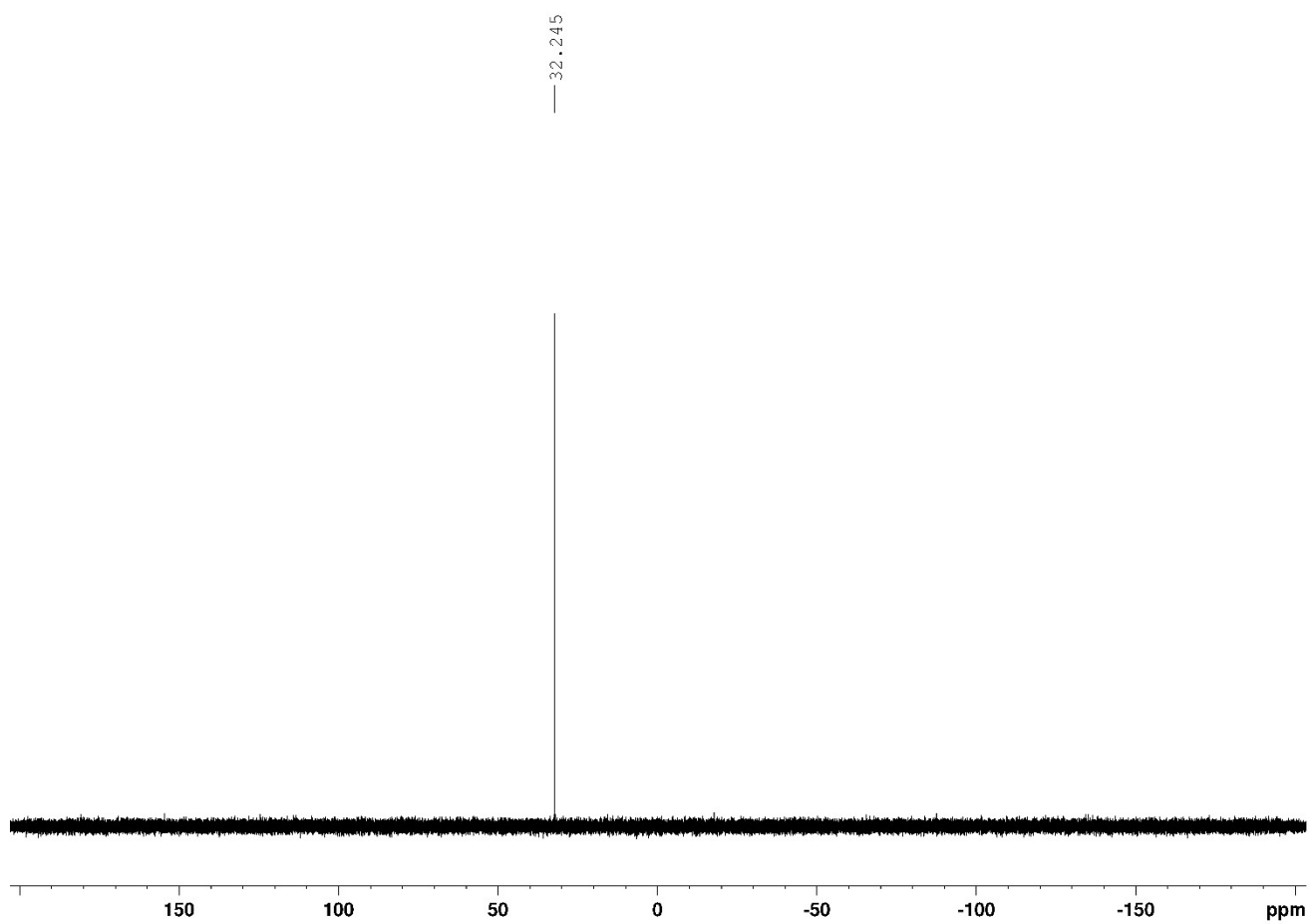
^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **14**.



^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$) of **14**.

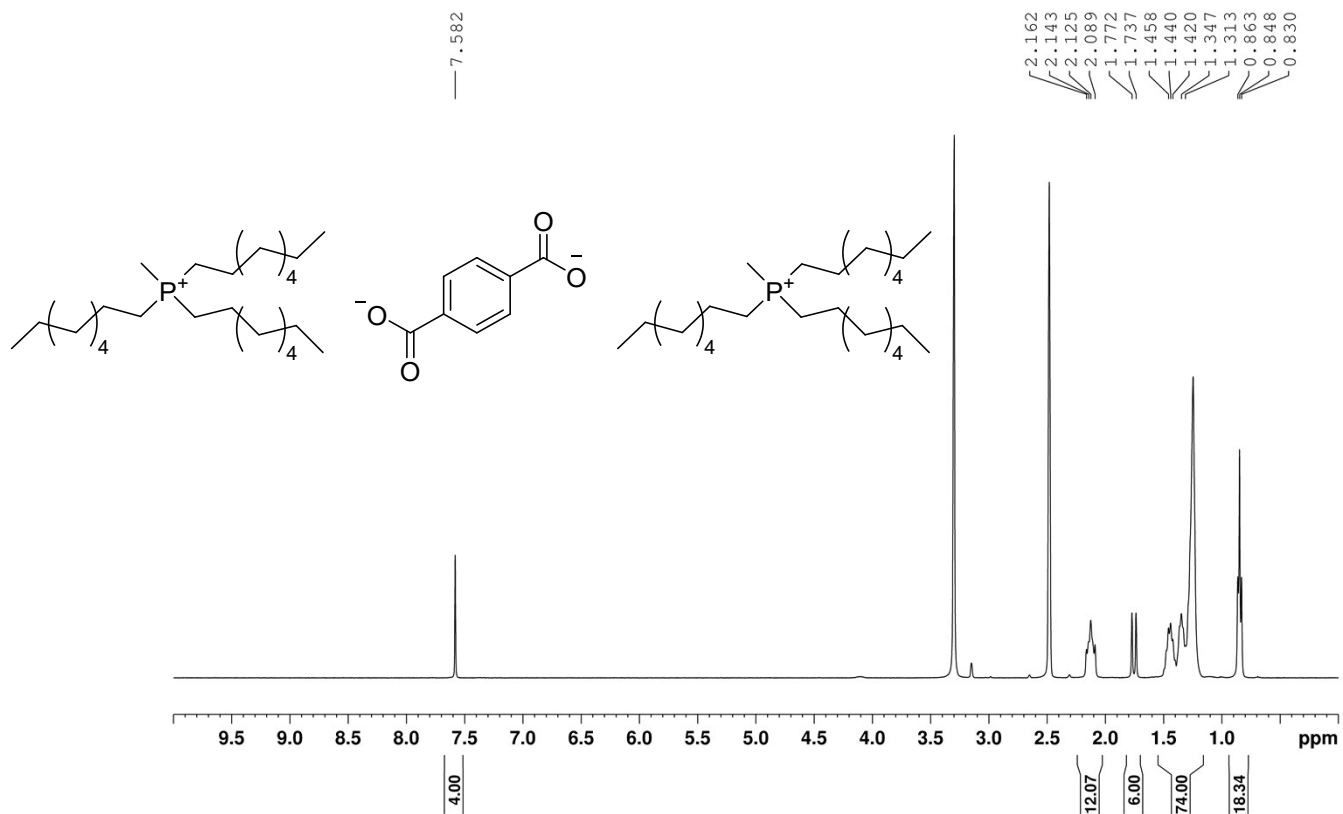


^{31}P NMR spectrum (164 MHz, $\text{DMSO-}d_6$) of **14**.

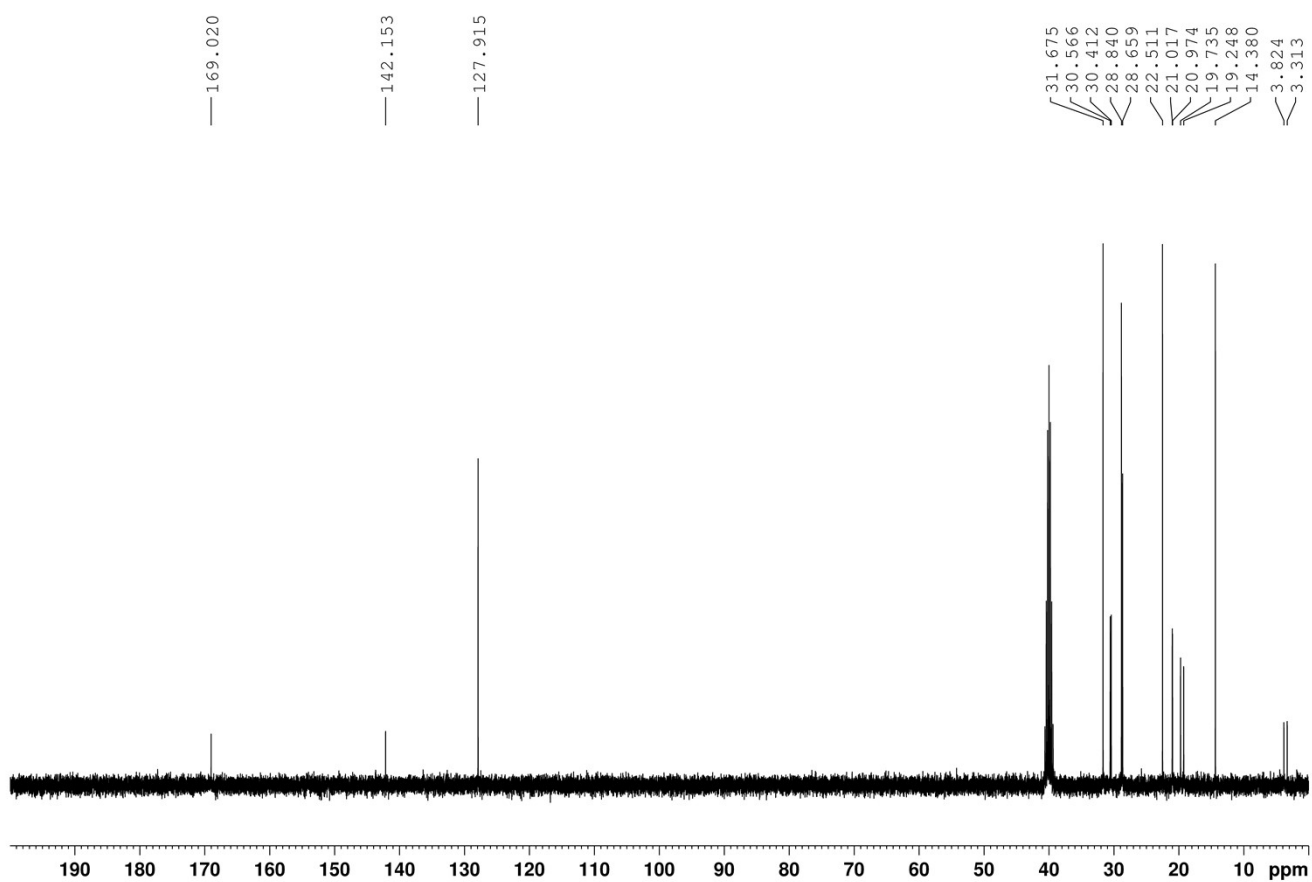


Catalyst 29

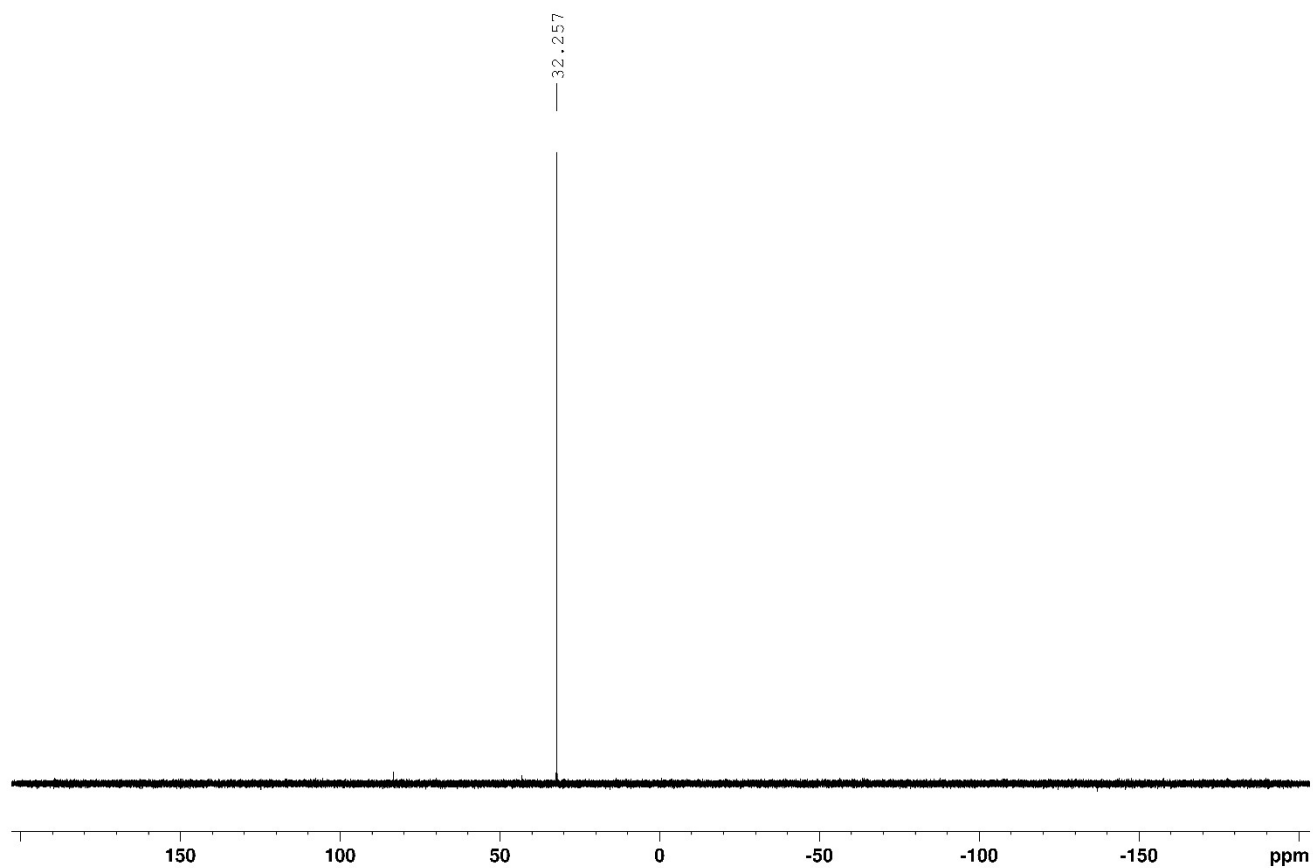
^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **29**.



^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$) of **29**.

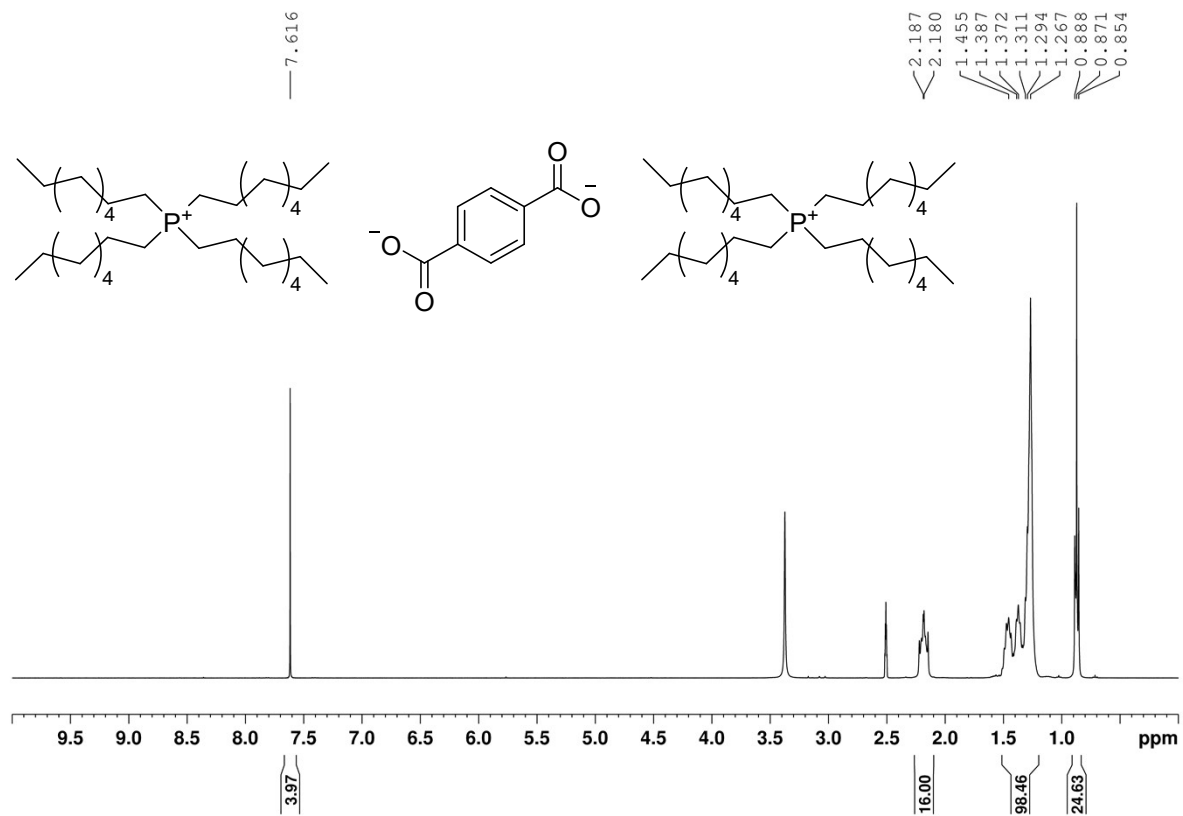


^{31}P NMR spectrum (164 MHz, $\text{DMSO-}d_6$) of **29**.

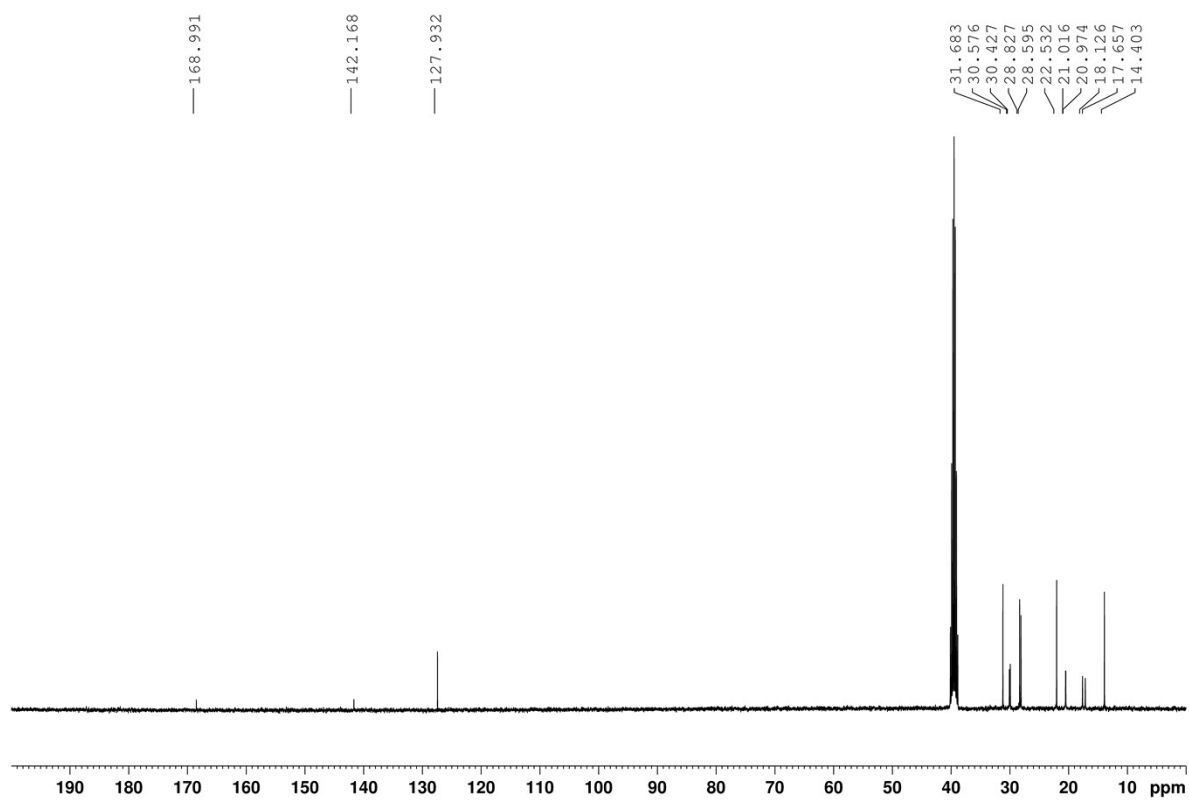


Catalyst 30

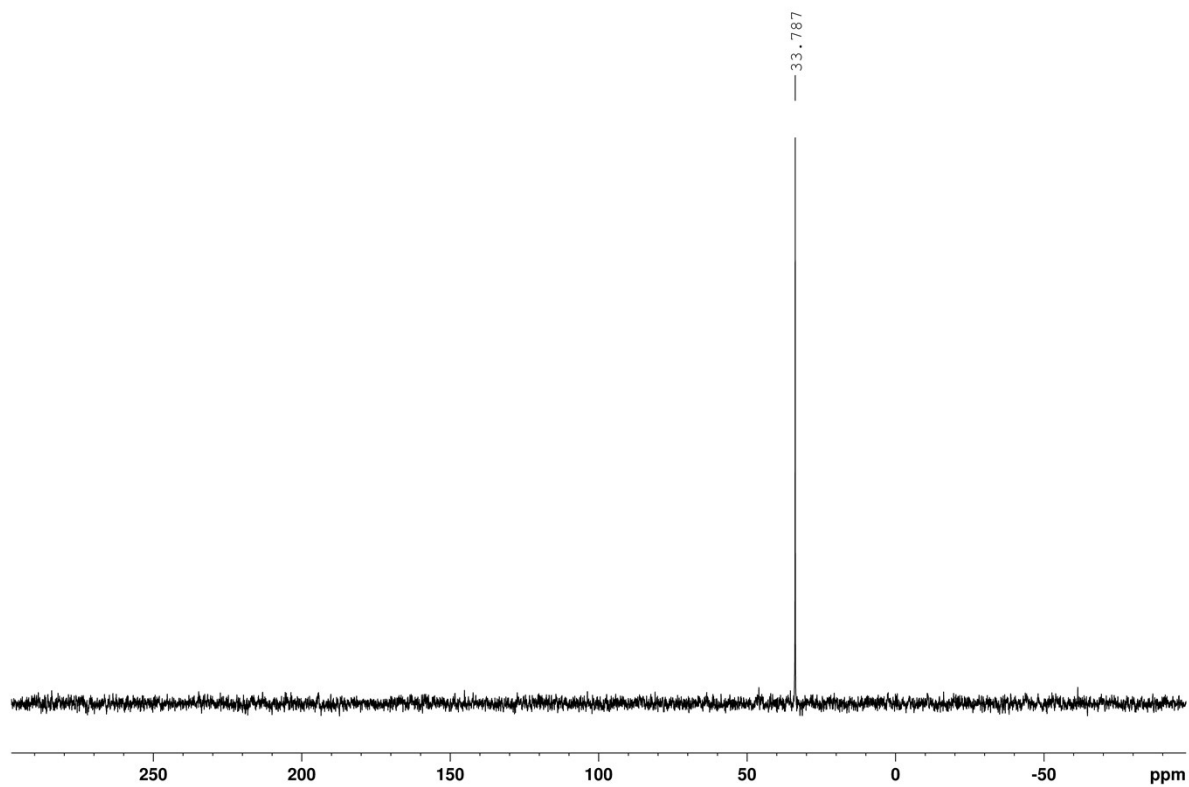
^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **30**.



^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$) of **30**.

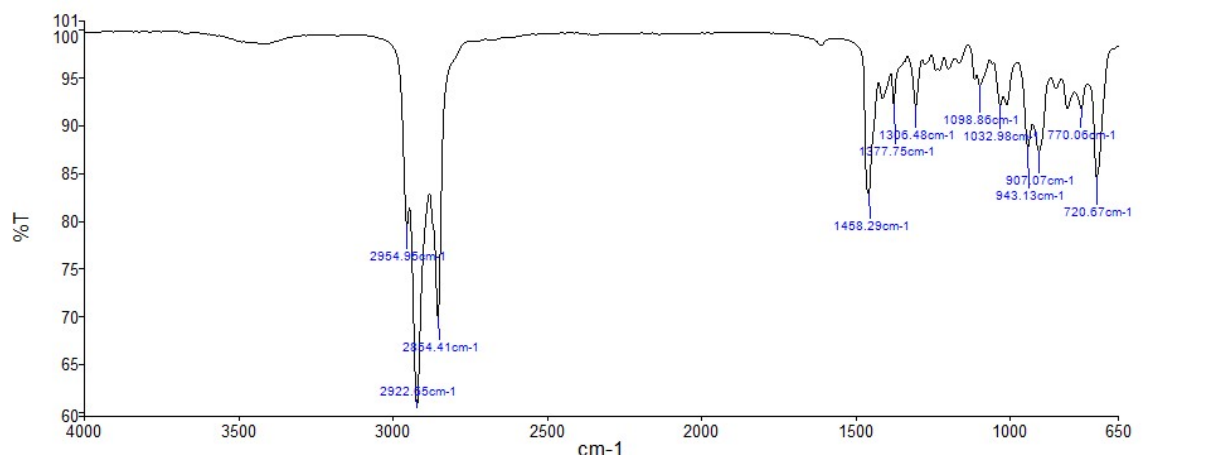


^{31}P NMR spectrum (164 MHz, $\text{DMSO-}d_6$) of **30**.



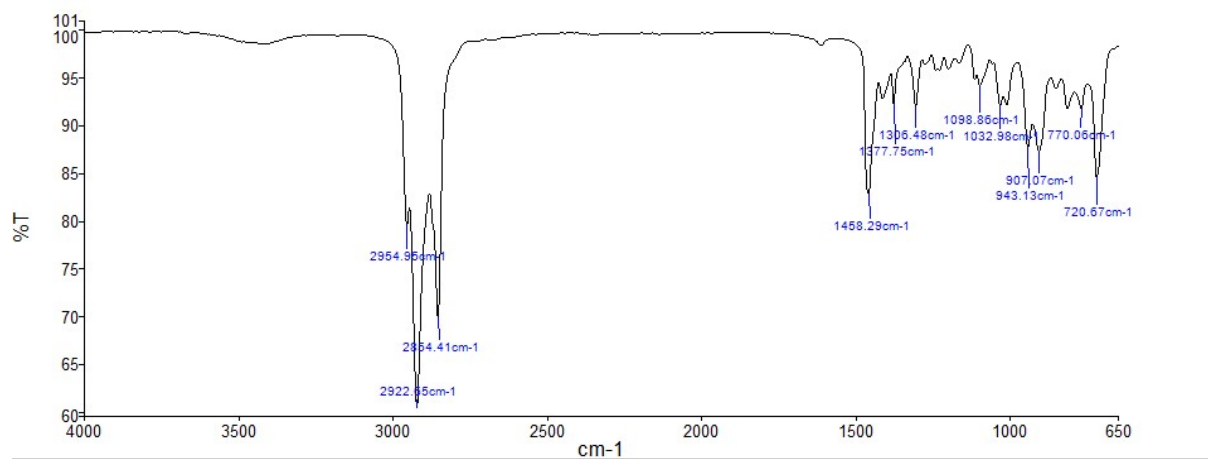
5. FT-IR Spectra

FT-IR spectrum of **9**.



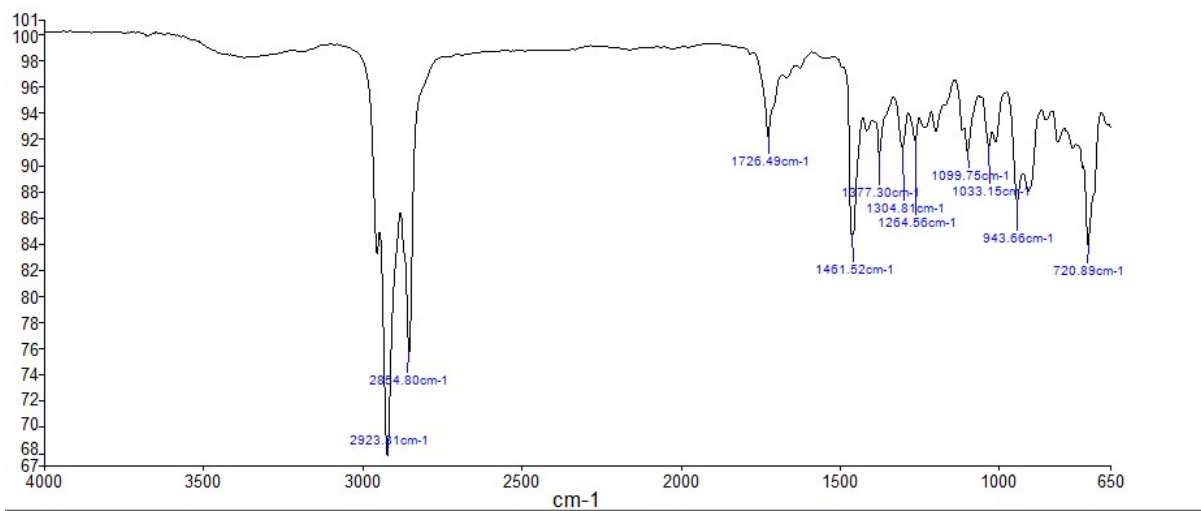
Catalyst **13**

FT-IR spectrum of **13**.



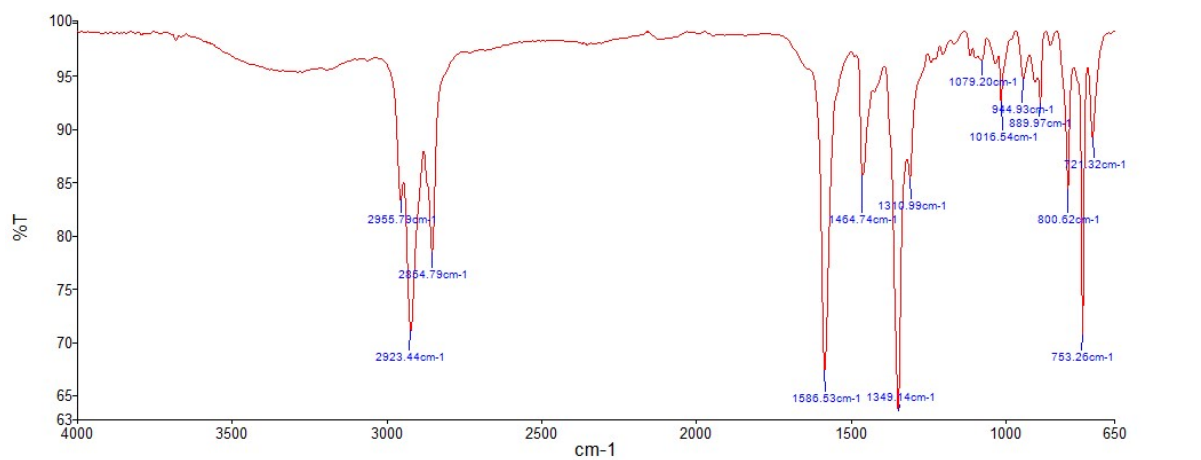
Catalyst 14

FT-IR spectrum of 14.



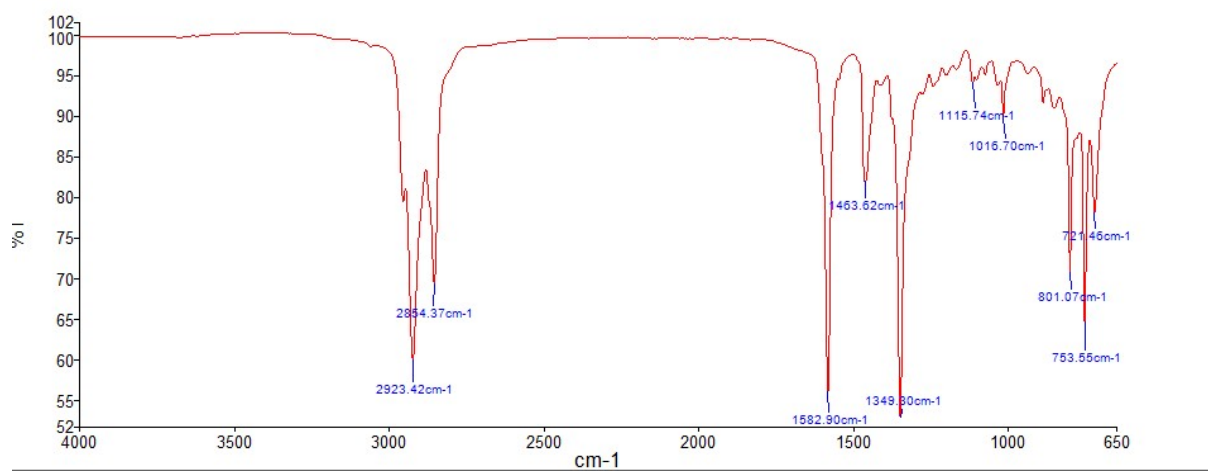
Catalyst 29

FT-IR spectrum of 29.



Catalyst 30

FT-IR spectrum of 30.



6. References

1. L. B. Anderson, C. Molloy, L. Pedrini, I. L. Martin and S. J. Connon, *Green Chem.*, 2024, DOI: 10.1039/D4GC05070C.
2. X. Wang, C. Wang, Y. Liu and J. Xiao, *Green Chem.*, 2016, **18**, 4605-4610.
3. G. Adamová, R. L. Gardas, L. P. N. Rebelo, A. J. Robertson and K. R. Seddon, *Dalton Trans.*, 2011, **40**, 12750-12764.