Supplementary Information
Deoxydehydration of vicinal diols and polyols catalysed by pyridinium perrhenate salts

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1. General Procedures

^{1}H-NMR spectra were recorded on a Bruker AVA400 spectrometer operating at 399.90 MHz, a Bruker AVA500 or Bruker PRO500 operating at 500.12 MHz or a Bruker AVA600 spectrometer operating at 599.81 MHz.^{13}C{^{1}H}-NMR spectra were recorded on a Bruker AVA500 or Bruker PRO500 operating at 125.76 MHz.^{19}F{^{1}H}-NMR spectra were recorded on a Bruker AVA500 spectrometer operating at 470.59 MHz. Chemical shifts are reported in parts per million (ppm). ^{1}H- and ^{13}C{^{1}H}-NMR spectra are referenced to residual solvent resonances calibrated against an external standard, $SiMe_4$ (δ = 0 ppm). ^{19}F{^{1}H}-NMR spectra are referenced to an external standard, CCl_3F (δ = 0 ppm). All spectra were recorded at 298 K unless otherwise specified. IR spectra were recorded on a Bruker Alpha II FTIR ATR spectrometer.

X-ray crystallographic data were collected at 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-Kα radiation equipped with an Eos CCD detector (λ = 0.71073 Å). Structures were solved using SHELXT Intrinsic Phasing and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-2015. All programs are used within the Olex2 suite. All non-hydrogen atoms refined with anisotropic displacement parameters and H-atom parameters were constrained to parent atoms and refined using a riding model unless otherwise stated.

Elemental analyses were measured in duplicate by Mr Stephen Boyer at London Metropolitan University.

Commercial materials and solvents were reagent grade and used as received. Catalysts **1** and **13** and substrates **17a**-**20a** were synthesized according to literature procedures.[1],[2]

[1] M. Cokoja, I. I. E. Markovits, M. H. Anthofer, S. Poplata, A. Pöthig, D. S. Morris, P. A. Tasker, W. A. Herrmann, F. E. Kühn, J. B. Love, *Chem. Commun.* **2015**, *51*, 3399-3402; D. S. Morris, C. Weetman, J. T. C. Wennmacher, M. Cokoja, M. Drees, F. E. Kühn, J. B. Love, *Catal. Sci. Technol.*, **2017**, *7*, 2838-2845

[2] P. Mahajabeen, A. Chadha, *Tetrahedron: Asymmetry* **2011**, *22*, 2156−2160.

2. Synthetic procedures

Synthesis of 2,6-di-tert-butyl-4-methylpyridinium perrhenate, 2

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to as solution of 2,6-di-*tert*-butyl-4-methylpyridine (205 mg, 1.0 mmol) in CH_2Cl_2 (1.0 mL) and the resulting mixture was stirred at RT for 16 h with formation of a white precipitate. After removal of the solvents under reduced pressure, the white solid was dissolved in acetonitrile (1.0 mL), passed through a pad of $MgSO_4$ and the filtrate removed under reduced pressure to obtain 443 mg, 97% **2** as a white solid. ^{1}H NMR (500 MHz, Acetonitrile-d_3): δ_H 10.85 (m, 1H, N*H*), 7.72 (s, 2H, *m*-C4*H*), 2.61 (s, 3H, *p*-C6H_3), 1.50 (s, 18H, CC1H_3); ^{13}C{^{1}H} NMR (500 MHz, Acetonitrile-d_3): δ_C 163.02 (*o-C3*), 162.94 (*p-C5*), 124.13 (*m-C4*H), 37.34 (*C2*CH_3), 28.93 (C*C1*H_3), 22.70 (*p-C6*H_3). Analysis. Found: C, 36.72; H, 5.21; N, 2.96 %. $C_{14}H_{24}NO_4Re$ requires: C, 36.83; H, 5.30; N, 3.07 %. HRMS (ESI+, m/z): found 663.3126; $C_{28}H_{48}N_2O_4Re^+$ requires 663.3166. FTIR (ATR, cm^{-1}): ν 3380 (sh, m, NH), 897 (br, s, ReO).

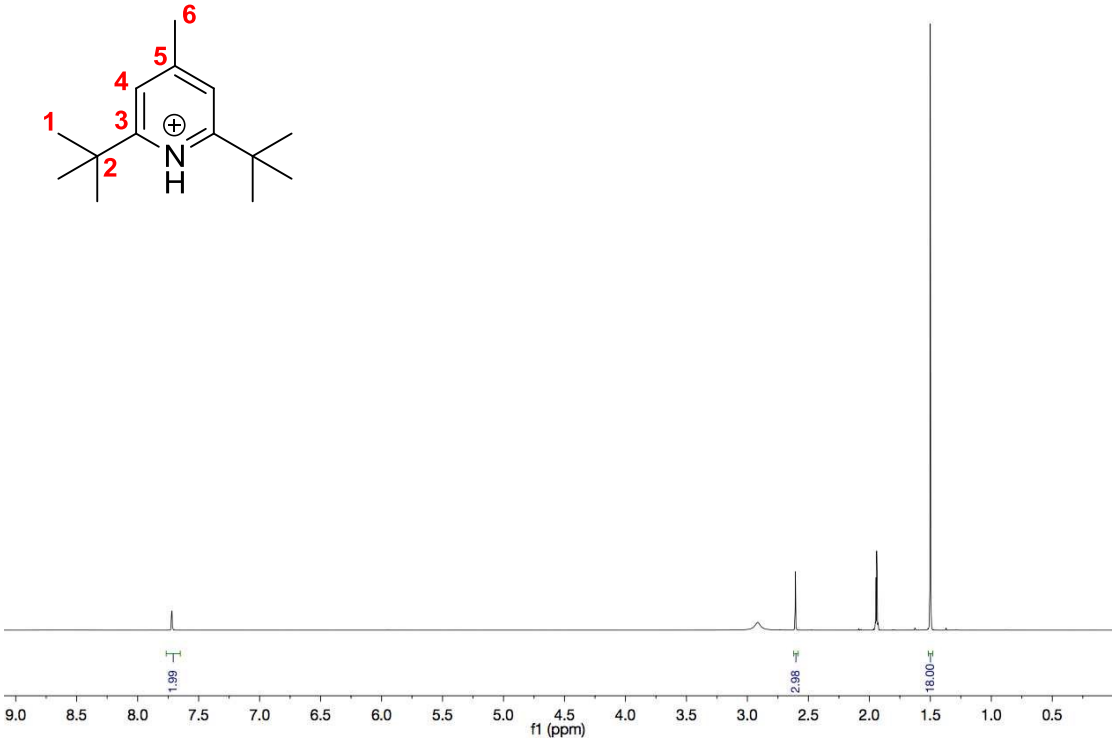


Figure S1. ^{1}H NMR spectrum of **2** in CD_3CN.

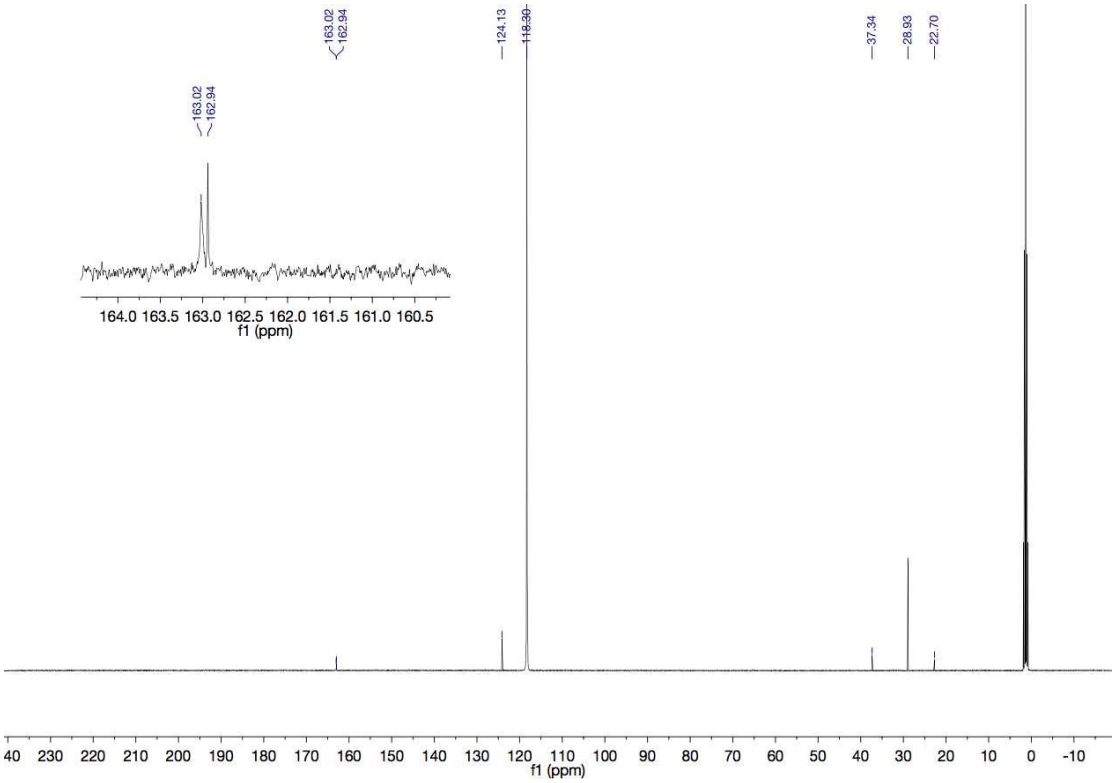


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in CD_3CN.

Synthesis of 2,6-lutidinium perrhenate, 3

An aqueous solution of perrhenic acid (0.420 mL, 2.79 mmol) was added to a solution 2,6-lutidine (0.325 mL, 2.79 mmol) in toluene (3.0 mL) and the resulting mixture was stirred at RT for 16 h. After dilution with additional toluene and washing with water, the aqueous phase was extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent removed under reduced pressure to obtain 1.0 g, >99 % of **3** as a white solid. ^{1}H NMR (601 MHz, $CDCl_3$): δ_H 13.68 (bs, 1H, N*H*), 8.26 (t, J = 7.9 Hz, 1H, *p*-C4*H*), 7.61 (d, J = 8.0 Hz, 2H, *m*-C3*H*), 2.81 (s, 6H, C1H_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ_C 153.51 (*C2*CH_3), 146.19 (*p-C4*H), 125.11 (*m-C3*H), 20.07 (*C1*H_3). Analysis. Found: C, 23.55; H, 2.91; N, 3.95 %. $C_7H_{10}NO_4Re$ requires: C, 23.46; H, 2.81; N, 3.91 %. HRMS (ESI+, m/z): found 467.0975; $C_{14}H_{20}N_2O_4Re^+$ requires 467.0970. FTIR (ATR, cm^{-1}): ν 3289 (m, NH), 883 (br, s, ReO).

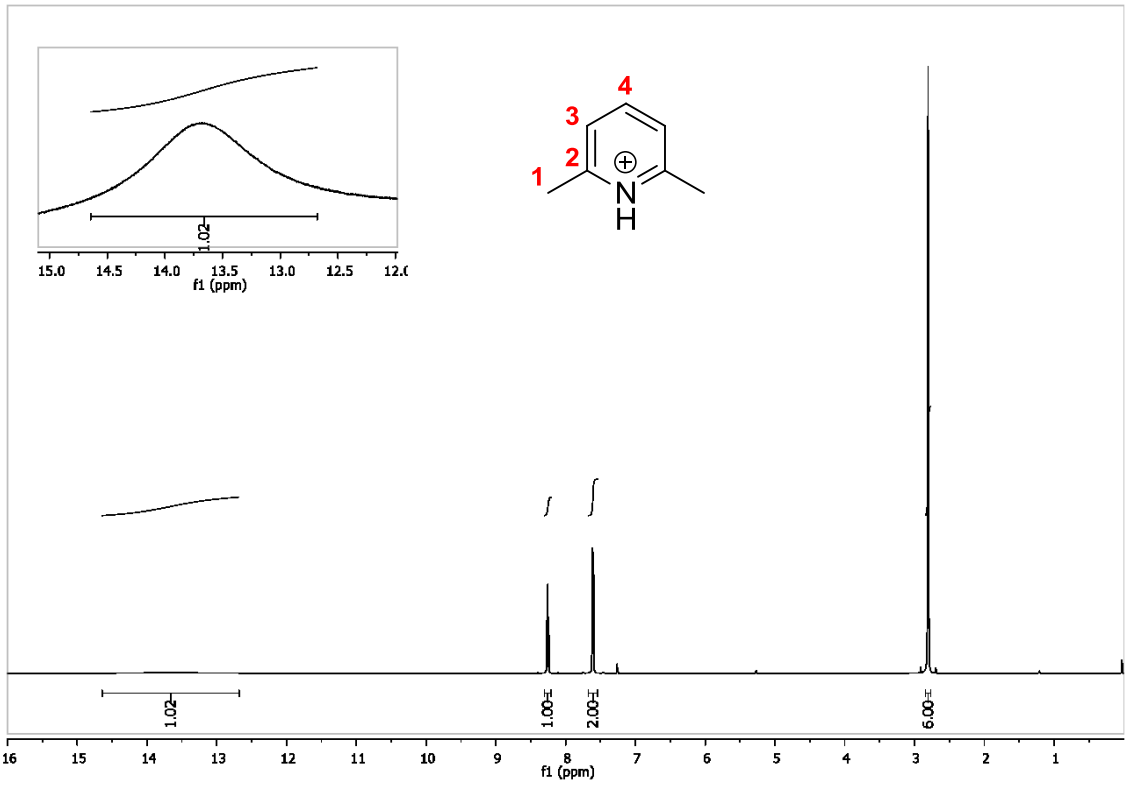


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$.

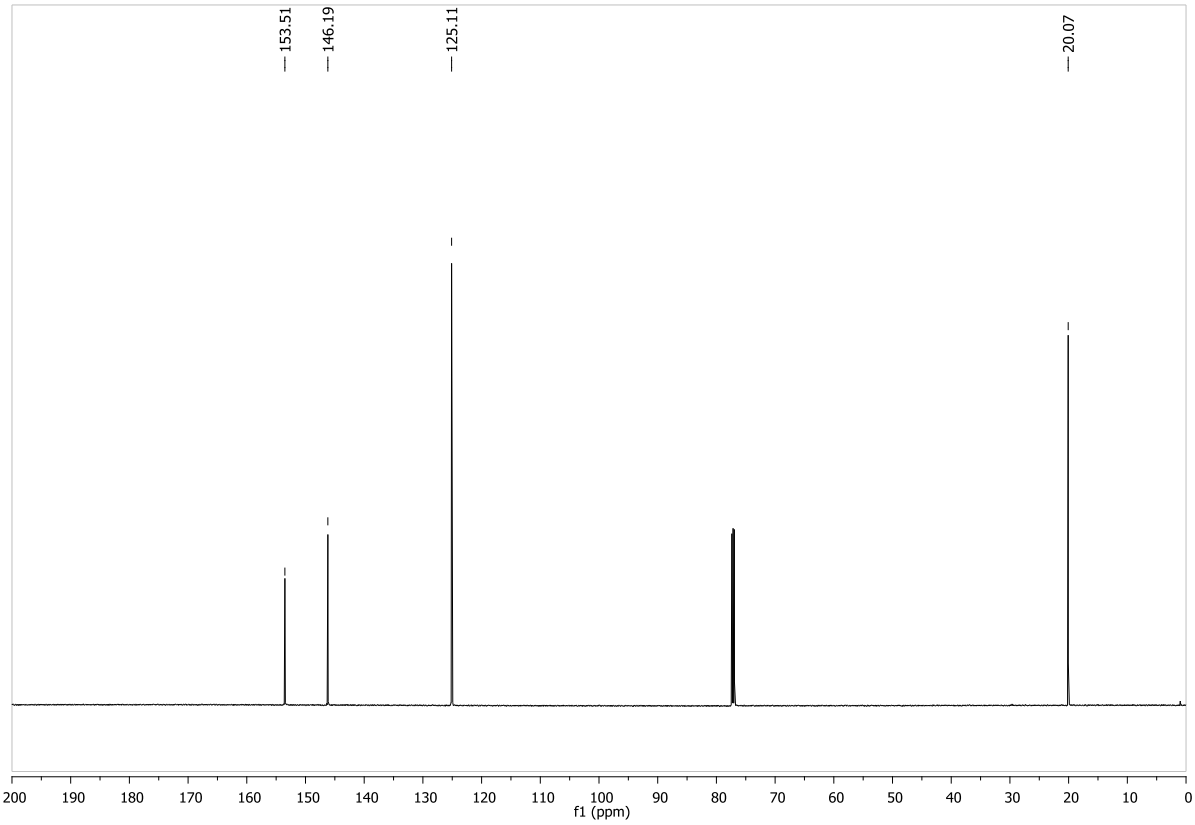


Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

Synthesis of 2-chloropyridinium perrhenate, 4

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to a DCM solution (1 mL) of 2-chloropyridine (113 mg, 1.0 mmol) and the resulting mixture was stirred at rt for 16 h with formation of a white precipitate. After removal of DCM under reduced pressure, the white solid was dissolved in acetonitrile (1.0 mL), passed through a short pad of $MgSO_4$ and the solvent removed under reduced pressure to obtain **4** as a white solid (358 mg, 98%). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 9.78 (s, 1H, N*H*), 8.65 (dd, *J* = 6.0, 1.8 Hz, 1H, C3*H*), 8.58 – 8.50 (m, 1H, C5*H*), 8.05 (dt, *J* = 8.4, 0.8 Hz, 1H, C6*H*), 7.96 (ddd, *J* = 7.3, 6.0, 1.2 Hz, 1H, C4*H*). ^{13}C NMR (500 MHz, Acetonitrile-d_3) δ 150.15 (*C*5H), 145.95 (*C*2Cl), 144.63 (*C*3H), 129.69 (*C*6H), 126.86 (*C*4H). Anal. calcd. for $C_5H_5ClNO_4Re$: C, 16.46; H, 1.38; N, 3.84 %. Found: C, 16.40; H, 1.26; N, 3.89 %. HRMS (ESI+, m/z): $C_{10}H_{10}Cl_2N_2O_4Re^+$ requires 478.9554, found 478.9564.

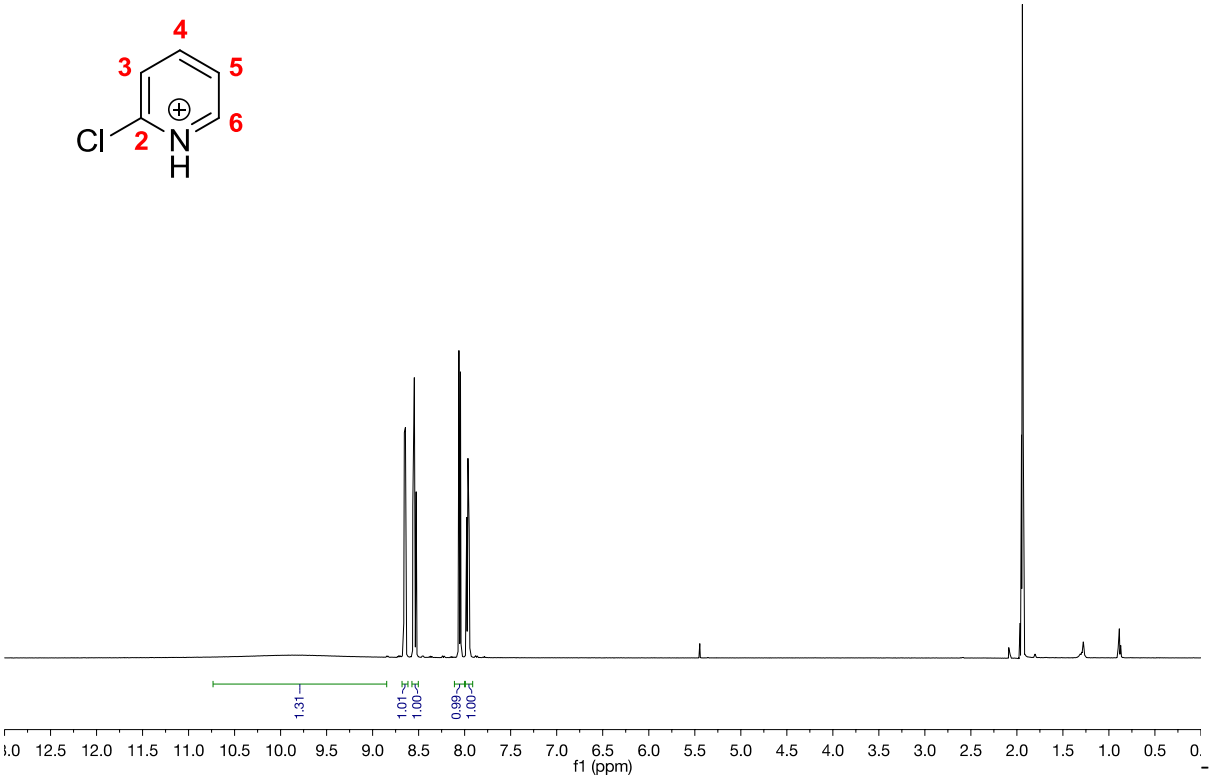


Figure S5. ^{1}H NMR spectrum of compound **4**.

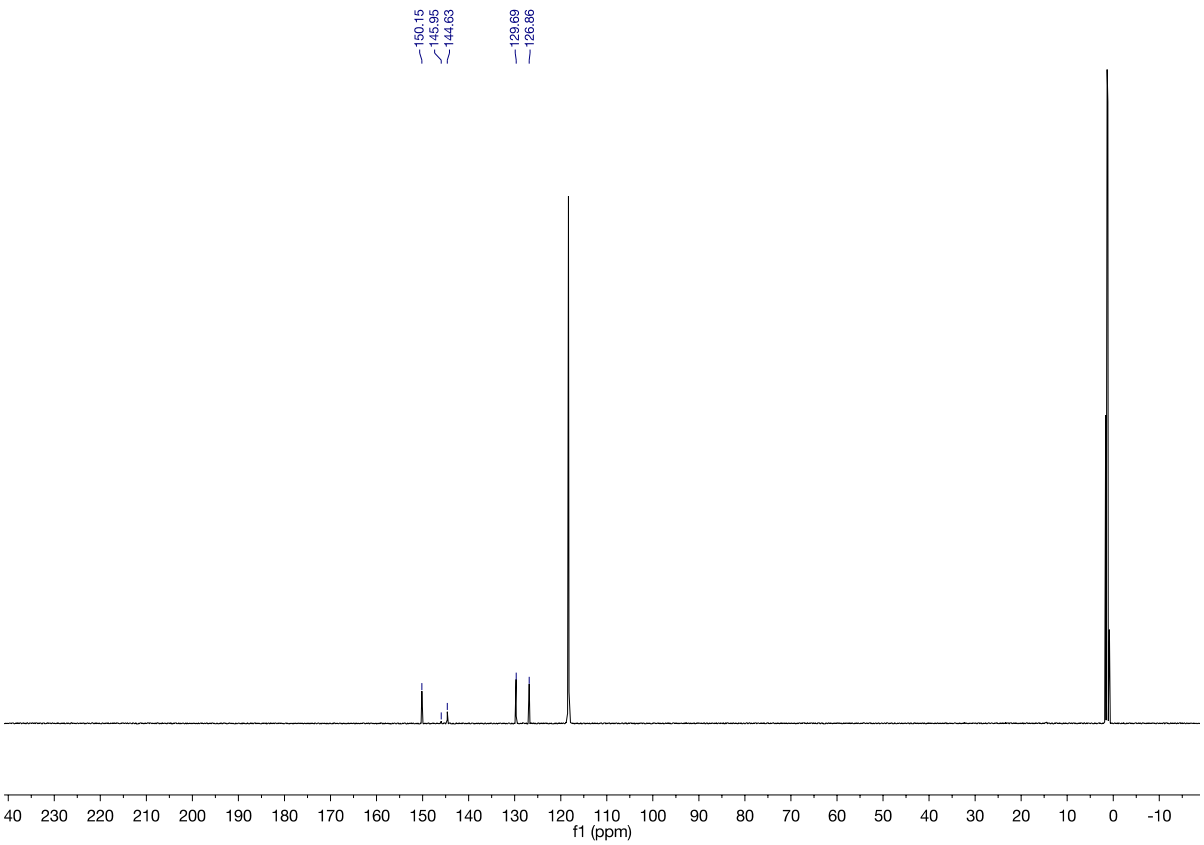


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4**.

Synthesis of 2-methoxypyridinium perrhenate, 5

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to a DCM solution (1 mL) of 2-methoxypyridine (109 mg, 1.0 mmol) and the resulting mixture was stirred at rt for 16 h. Crystallization at -30 °C and washing with DCM provided **5** in a white solid (302 mg, 84%). ^{1}H NMR (400 MHz, Dimethylsulfoxide-d_6) δ 8.20 (dd, *J* = 5.1, 1.3 Hz, 1H, C6*H*), 7.79 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H, C4*H*), 7.03 (ddd, *J* = 7.1, 5.2, 0.8 Hz, 1H, C5*H*), 6.91 (d, *J* = 8.4 Hz, 1H, C3*H*), 6.67 (s, 1H, N*H*), 3.88 (s, 2H, OC*H*$_3$). ^{13}C NMR (400 MHz, Dimethylsulfoxide-d_6) δ 163.13 (*C2*), 145.93 (*C6*H), 140.21 (*C4*H), 117.16 (*C5*H), 110.63 (*C3*H), 53.59 (O*C*H$_3$). Anal. calcd. for $C_6H_8NO_5Re$: C, 20.00; H, 2.24; N, 3.89 %. Found: C, 20.11; H, 2.18; N, 4.02 %. HRMS (ESI+, m/z): $C_{12}H_{16}N_2O_6Re^+$ requires 471.0561, found 471.0554. FTIR (ATR, cm^{-1}): ν 3123 (w, NH), 902, 882, 866 (s, ReO).

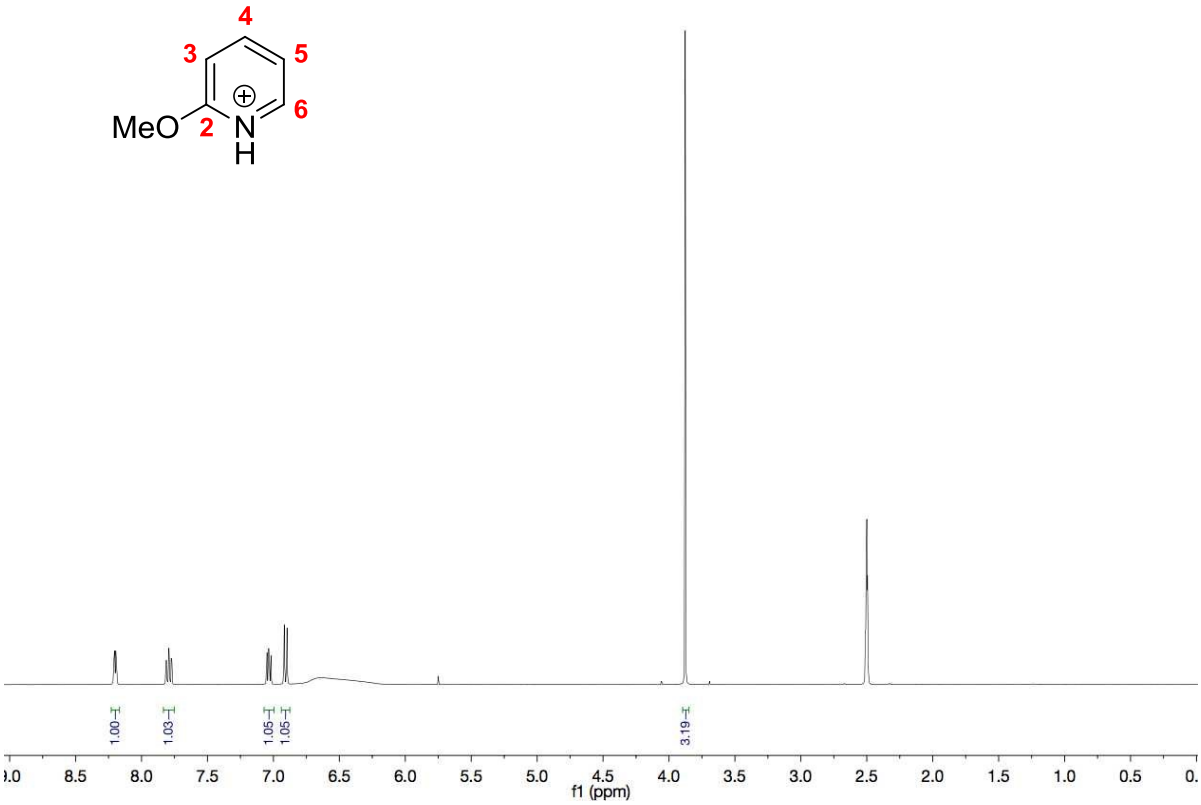


Figure S7. ^{1}H NMR spectrum of compound **5**.

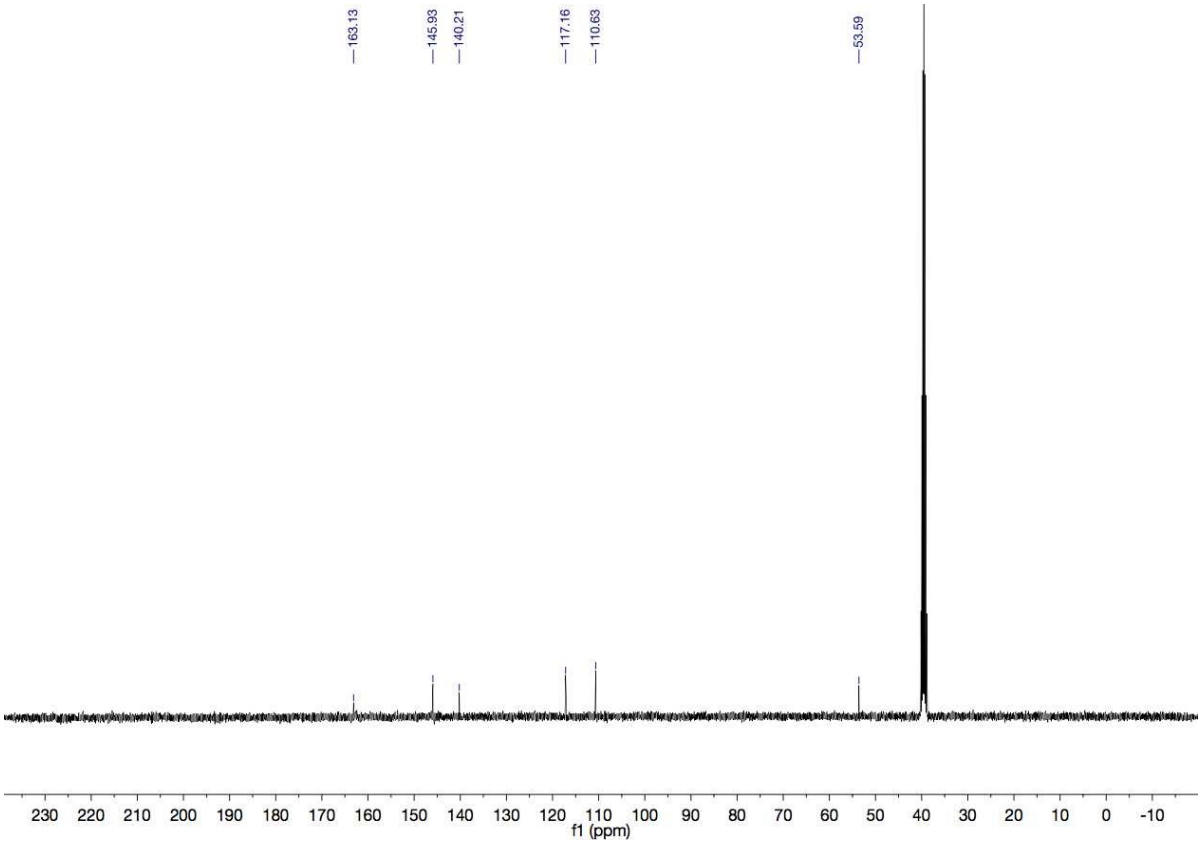


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5**.

Synthesis of 3-bromopyridinium perrhenate, 6

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to a MeCN solution (1 mL) of 3-bromopyridine (158 mg, 1.0 mmol) and the resulting mixture was stirred at rt for 16 h. After dilution with additional acetonitrile, the solution was dried over $MgSO_4$ and the solvent removed under reduced pressure to obtain **6** as a white solid (397 mg, 97%). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.88 (d, *J* = 2.1 Hz, 1H, C2*H*), 8.71 (d, *J* = 5.7 Hz, 1H, C6*H*), 8.68 (s, 1H, N*H*) 8.66 (ddd, *J* = 8.4, 2.2, 1.3 Hz, 1H, C4*H*), 7.89 (dd, *J* = 8.4, 5.8 Hz, 1H, C5*H*). ^{13}C NMR (600 MHz, Acetonitrile-d_3) δ 211.28 (*C*2H), 205.22 (*C6*H), 202.82 (*C4*H), 190.05 (*C5*H), 183.92 (*C3*H). Anal. calcd. for $C_5H_5BrNO_4Re$: C, 14.68; H, 1.23; N, 3.42 %. Found: C, 14.55; H, 1.19; N, 3.36 %. HRMS (ESI+, m/z): $C_{10}H_{10}Br_2N_2O_4Re^+$ requires 568.8539, found 568.8521. FTIR (ATR, cm^{-1}): ν 3210 (br, w, NH); 892 (br, s, ReO).

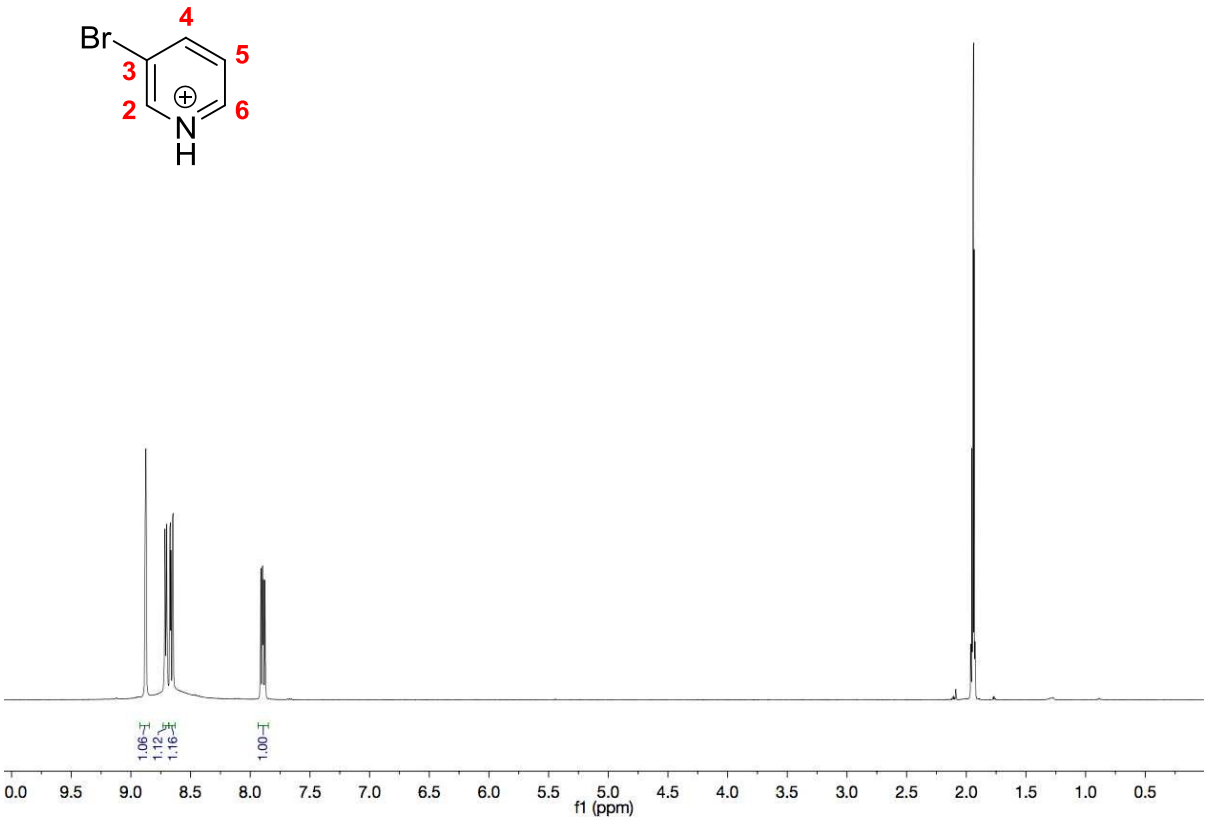


Figure S9. ^{1}H NMR spectrum of compound **6**.

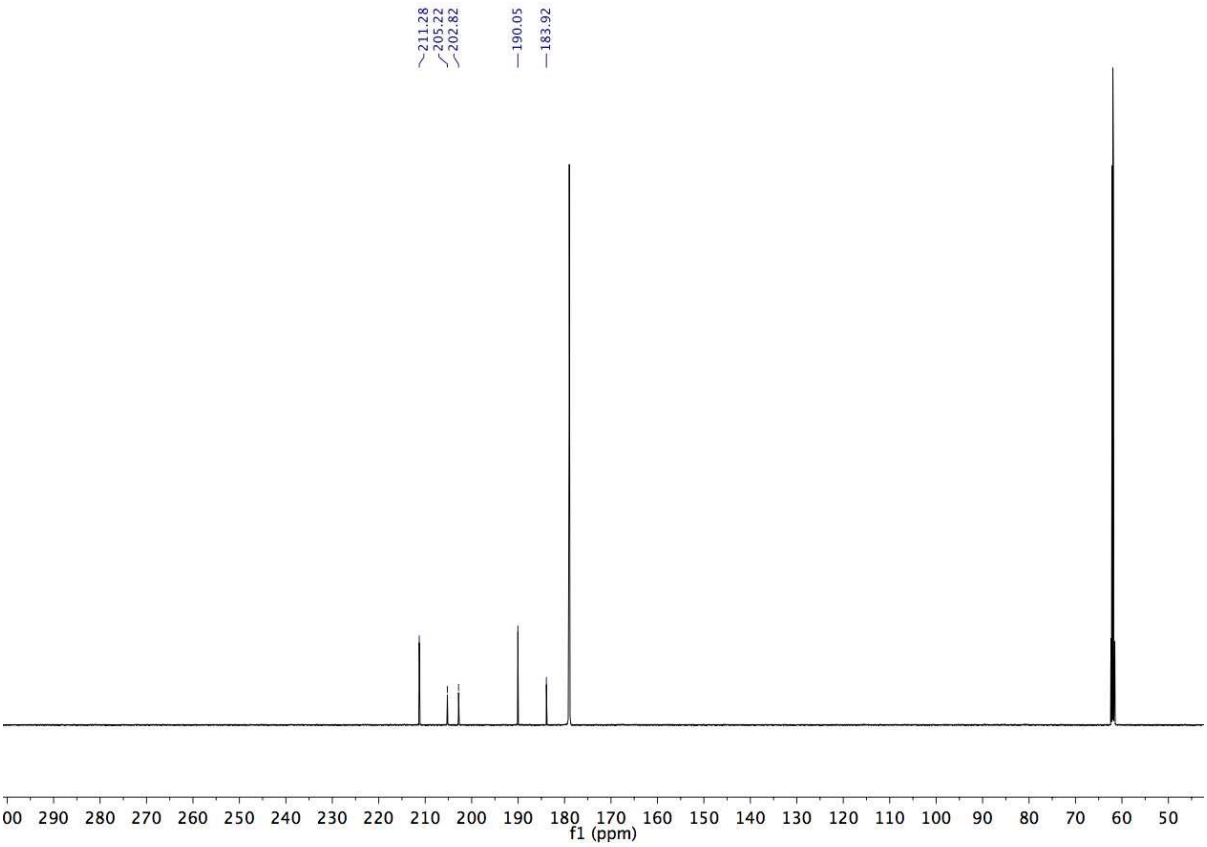


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6**.

Synthesis of 2-fluoropyridinium perrhenate, 7

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to an acetonitrile solution (1 mL) of 2-fluoropyridine (97 mg, 1.0 mmol) and the resulting mixture was stirred at rt for 4 h. Overnight crystallization at -30 °C and washing with cold acetonitrile provided **7** as a white crystalline solid (299 mg, 86%). ^{1}H NMR (500 MHz, Dimethylsulfoxide-d_6) δ 10.32 (s, 1H, N*H*), 8.26 (ddt, *J* = 5.0, 1.9, 0.9 Hz, C6*H*), 8.00 (tdd, *J* = 8.4, 7.2, 2.1 Hz, C4*H*), 7.36 (dddd, *J* = 7.5, 4.9, 2.7, 0.9 Hz, C5*H*), 7.18 (ddt, *J* = 8.3, 2.5, 0.8 Hz, C3*H*). ^{13}C NMR (500 MHz, Dimethylsulfoxide-d_6) δ 163.02 (d, *J*=935, *C2*H), 147.73 (d, *J*=55, *C6*H), 142.22 (d, *J*=30, *C4*H), 122.06 (d, *J*=15, *C5*H), 109.71 (d, *J*=145, *C3*H). ^{19}F NMR (500 MHz, Dimethylsulfoxide-d_6) δ -68.05 (C1*F*). Anal. calcd. for $C_5H_5FNO_4Re$: C, 17.24; H, 1.45; N, 4.02 %. Found: C, 17.05; H, 1.33; N, 4.04 %. HRMS (ESI+, m/z): $C_{10}H_{10}F_2N_2O_4Re^+$ requires 509.9774, found 510.0112. FTIR (ATR, cm^{-1}): ν 3398 (br, w, NH), 862 (br, s, ReO).

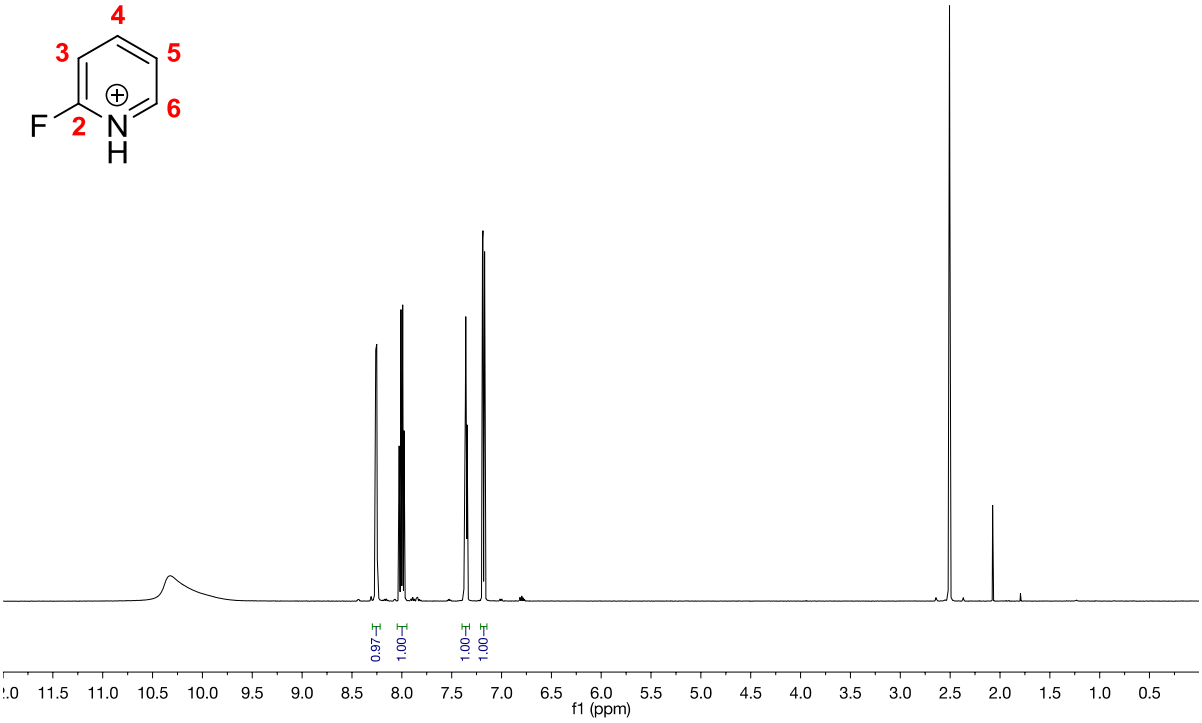


Figure S11. ^{1}H NMR spectrum of compound **7**.

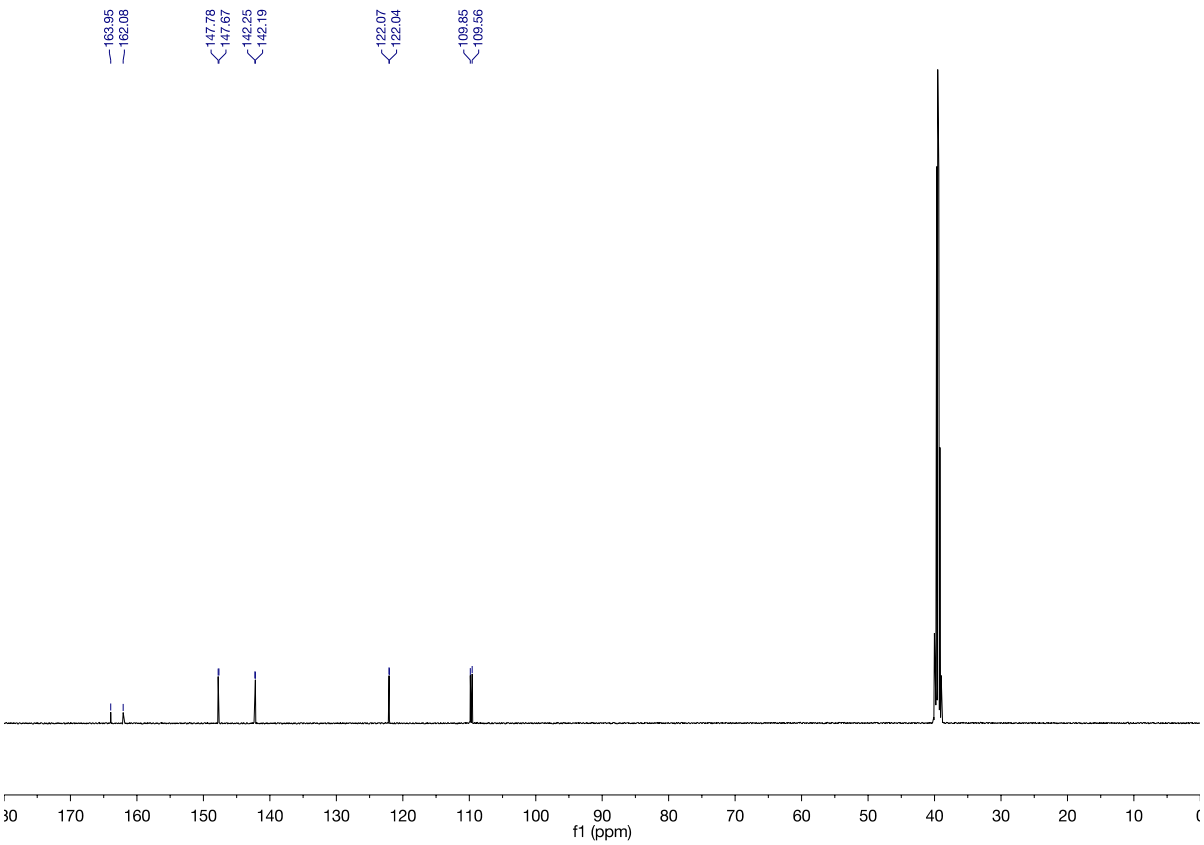


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7**.

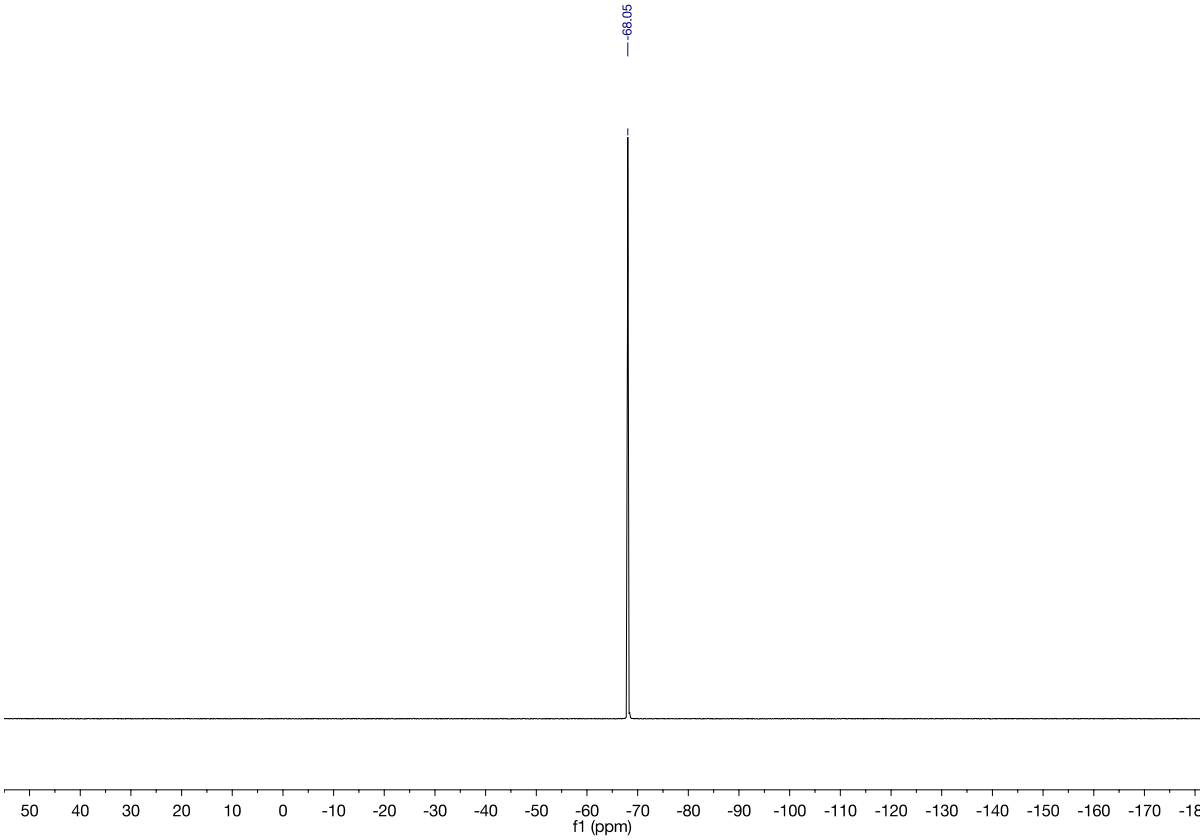


Figure S13. ^{19}F NMR spectrum of compound **7**.

Synthesis of N-methylpiperidinium perrhenate, 8

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to a DCM solution (1.0 mL) of *N*-methylpiperidine (0.12 mL, 1.0 mmol) and the resulting mixture was stirred at rt for 16 h. After dilution with additional dichloromethane, the solution was dried over $MgSO_4$ and the solvent removed under reduced pressure to obtain **8** as a white solid (0.35 g, >99%). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 6.93 (t, 1H, N*H*), 3.41(m, 2H, *m*-C3H_2), 2.87 (tdd, *J* = 12.6, 9.9, 3.1 Hz, 2H, *m*-C3H_2), 2.77 (d, *J* = 5.2 Hz, 3H, NC1H_3), 1.90 (d, *J* = 15.0 Hz, 2H, *o*-C2H_2), 1.76 (m, 1H, *p*-C4H_2), 1.68 (m, 2H, *o*-C2H_2), 1.42 (dddd, *J* = 16.2, 13.3, 8.5, 3.9 Hz, 1H, *p*-C4H_2). ^{13}C NMR (500 MHz, Acetonitrile-d_3) δ 56.24 (*m-C3*H_2), 44.46 (N*C1*H_3), 23.98 (*o-C2*H_2), 21.65 (*p-C4*H_2). Anal. calcd. for $C_6H_{14}NO_4Re$: C, 20.57; H, 4.03; N, 4.00 %. Found: C, 20.61; H, 3.99; N, 3.95 %. HRMS (ESI+, m/z): $C_{12}H_{28}N_2O_4Re^+$ requires 451.1601, found 451.1602. FTIR (ATR, cm^{-1}): ν 3380 (vbr, m, NH), 884 (br, s, ReO).

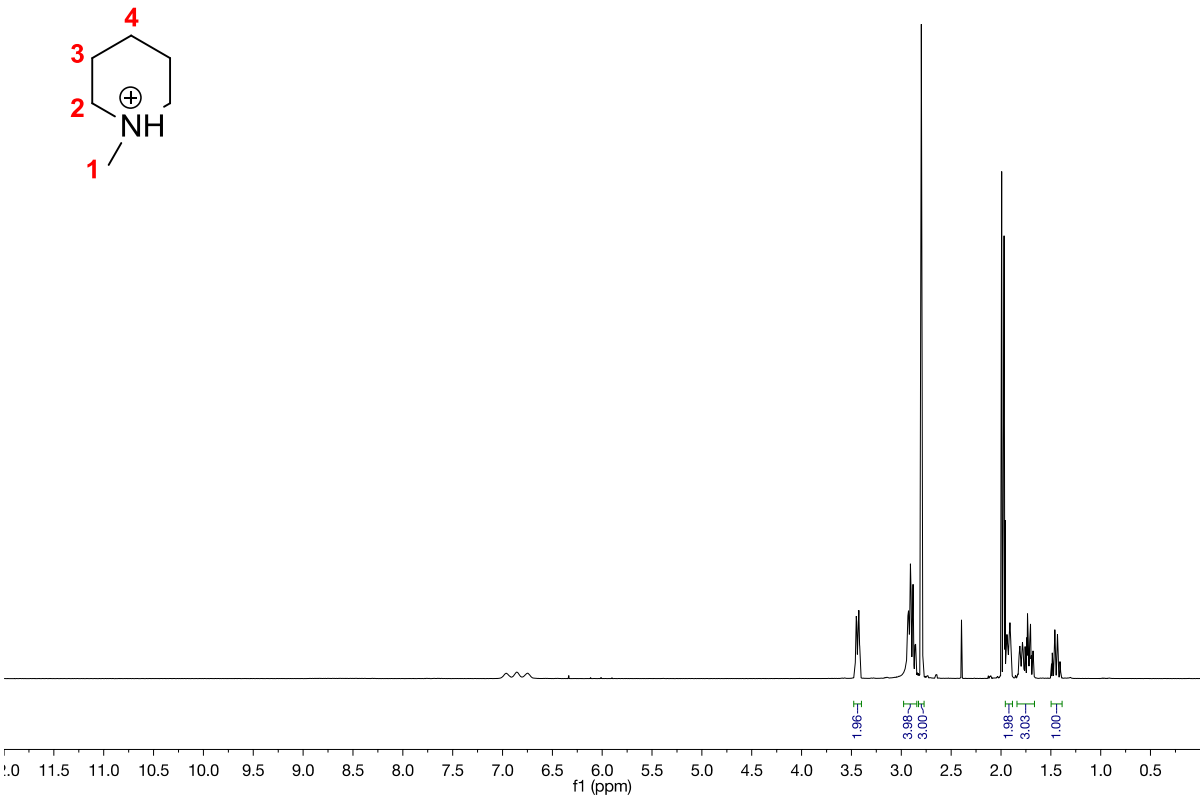


Figure S14. ^{1}H NMR spectrum of compound **8**.

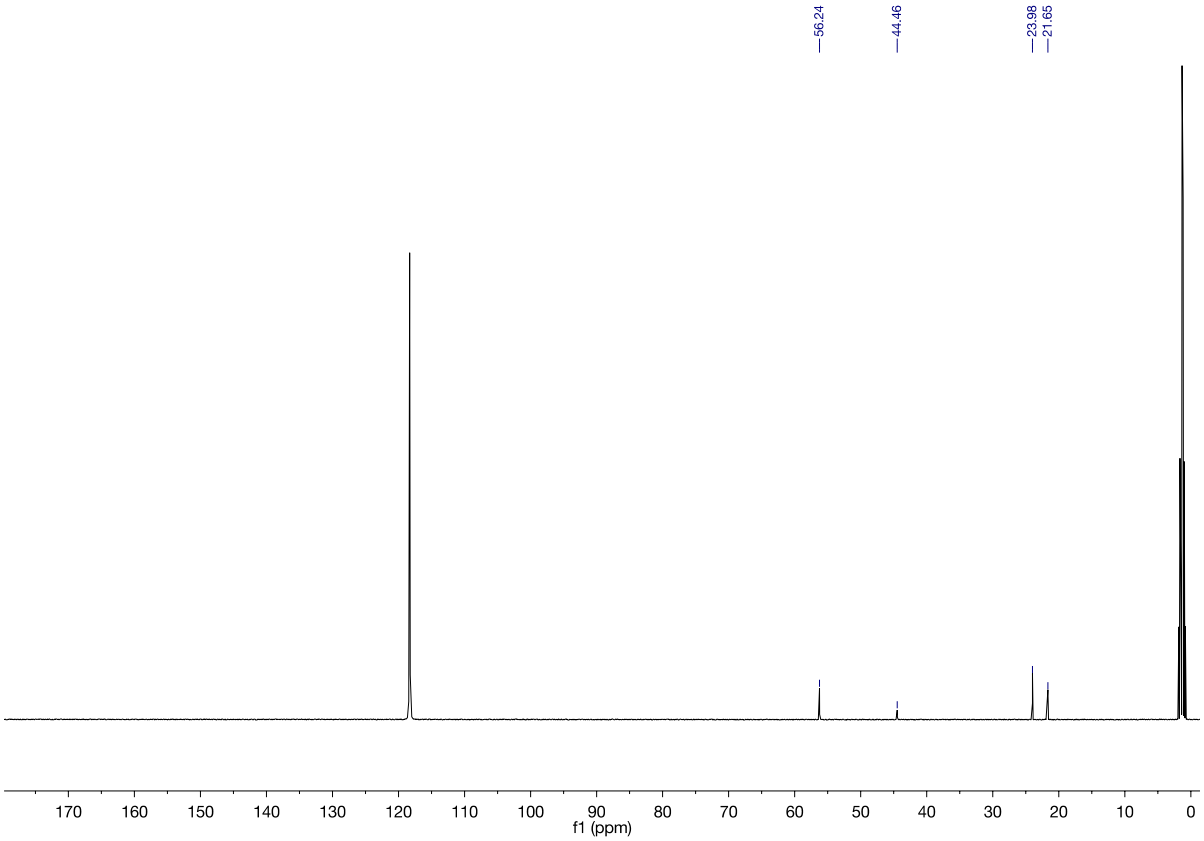


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8**.

Synthesis of N,N-dimethylanilinium perrhenate, 9

An aqueous solution of perrhenic acid (0.15 mL, 1.0 mmol) was added to a DCM solution (1.0 mL) of *N*,*N*-dimethylaniline (121 mg, 1.0 mmol) and the resulting mixture was stirred at rt for 16 h. After dilution with additional dichloromethane, the solution was dried over $MgSO_4$ and the solvent removed under reduced pressure to obtain **9** as a white solid (361 mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65-7.56 (m, 5H, *m*-C3H, *o*-C4*H*, *p*-C5*H*), 3.29 (s, 6H, NC1H_3). ^{13}C NMR (400 MHz, Chloroform-*d*) δ 142.00 (*C*2H), 131.13 (*o*-*C*4H), 130.96 (*p*-*C*5H), 120.12 (*m*-*C*3H), 47.82 (N*C*1H). Anal. calcd. for $C_8H_{12}NO_4Re$: C, 25.80; H, 3.25 %; N, 3.76. Found: C, 25.95; H, 3.36; N, 3.62 %. HRMS (ESI+, m/z): $C_{16}H_{24}N_2O_4Re^+$ requires 495.1288, found 495.1285. FTIR (ATR, cm^{-1}): ν 881 (br, s, ReO).

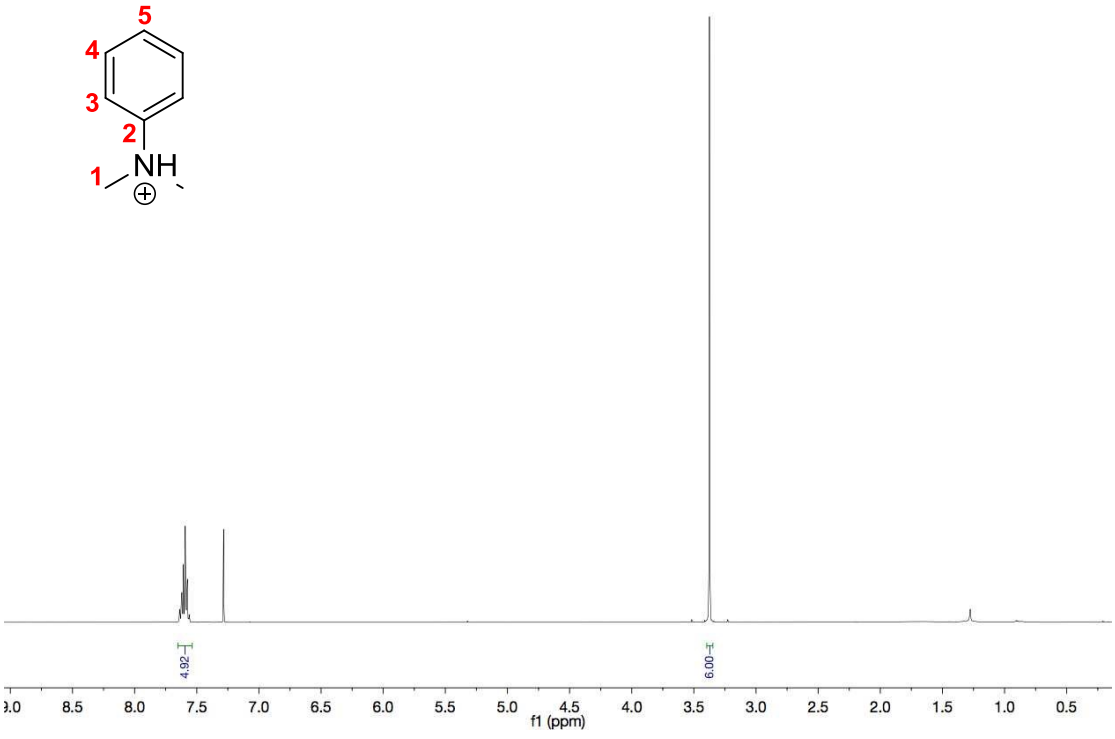


Figure S16. ^{1}H NMR spectrum of compound **9**.

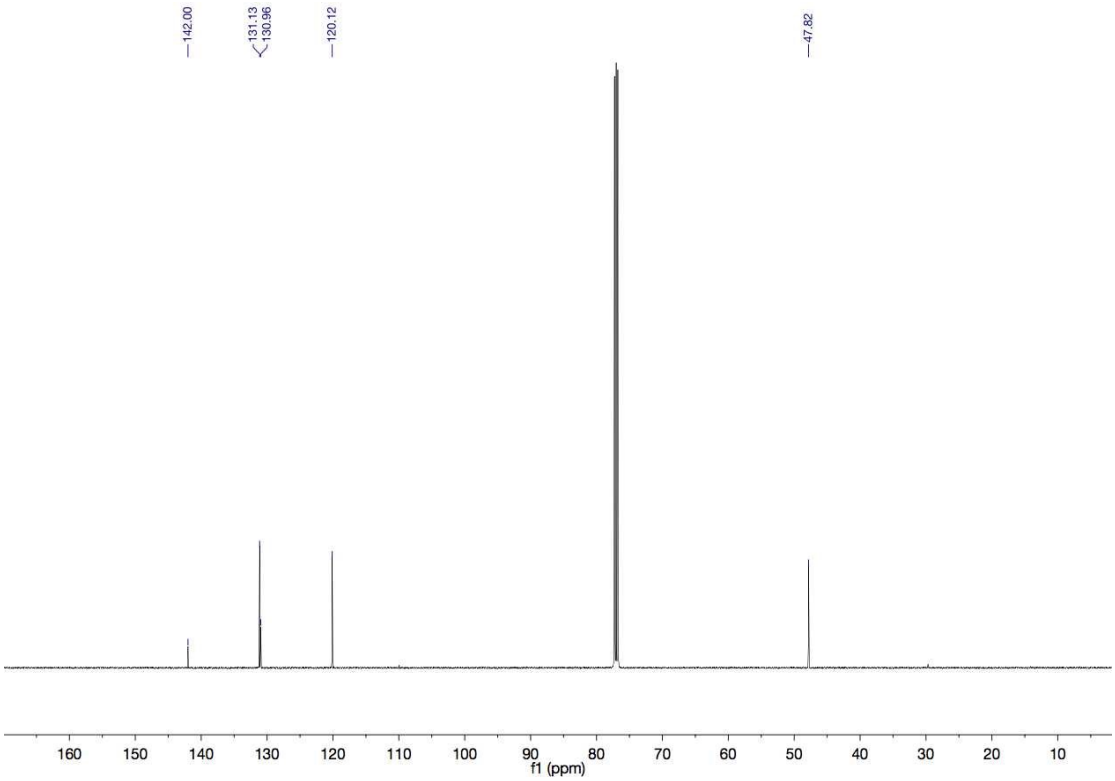


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9**.

Synthesis of *n*-hexylammonium perrhenate, 10

An aqueous solution of perrhenic acid (0.30 mL, 2 mmol) was added to neat *n*-hexylamine (204 mg, 2 mmol) which immediately reacted to give a solid. This product was suspended in hexane (10 mL), filtered, washed with hexane (3 x 5 mL) and dried under reduced pressure to give **10** as a white solid (551 mg, 78 %). ^{1}H NMR (500.12 MHz; CD_3CN): δH (ppm) 6.35 (t, *J* = 53 Hz, 3 H, N*H*$_3$), 2.95 (m, 2 H, C1*H*$_2$), 1.61 (quint, 2 H, C2*H*$_2$), 1.31 (m, 6 H, C3,4,5*H*$_2$), 0.90 (t, 3 H, C6*H*$_3$); ^{13}C NMR (500 MHz, Acetonitrile-*d*$_3$) δ 41.38 (*C1*H$_2$), 31.82 (*C3,4,5*H$_2$), 27.72 (*C2*H$_2$), 26.54 (*C3,4,5*H$_2$), 23.09 (*C3,4,5*H$_2$), 14.23 (*C6*H$_3$). Anal. calcd. for $C_6H_{16}NO_4Re$: C, 20.45; H, 4.58; N, 3.97 %. Found: C, 20.51; H, 4.62; N, 4.01 %.

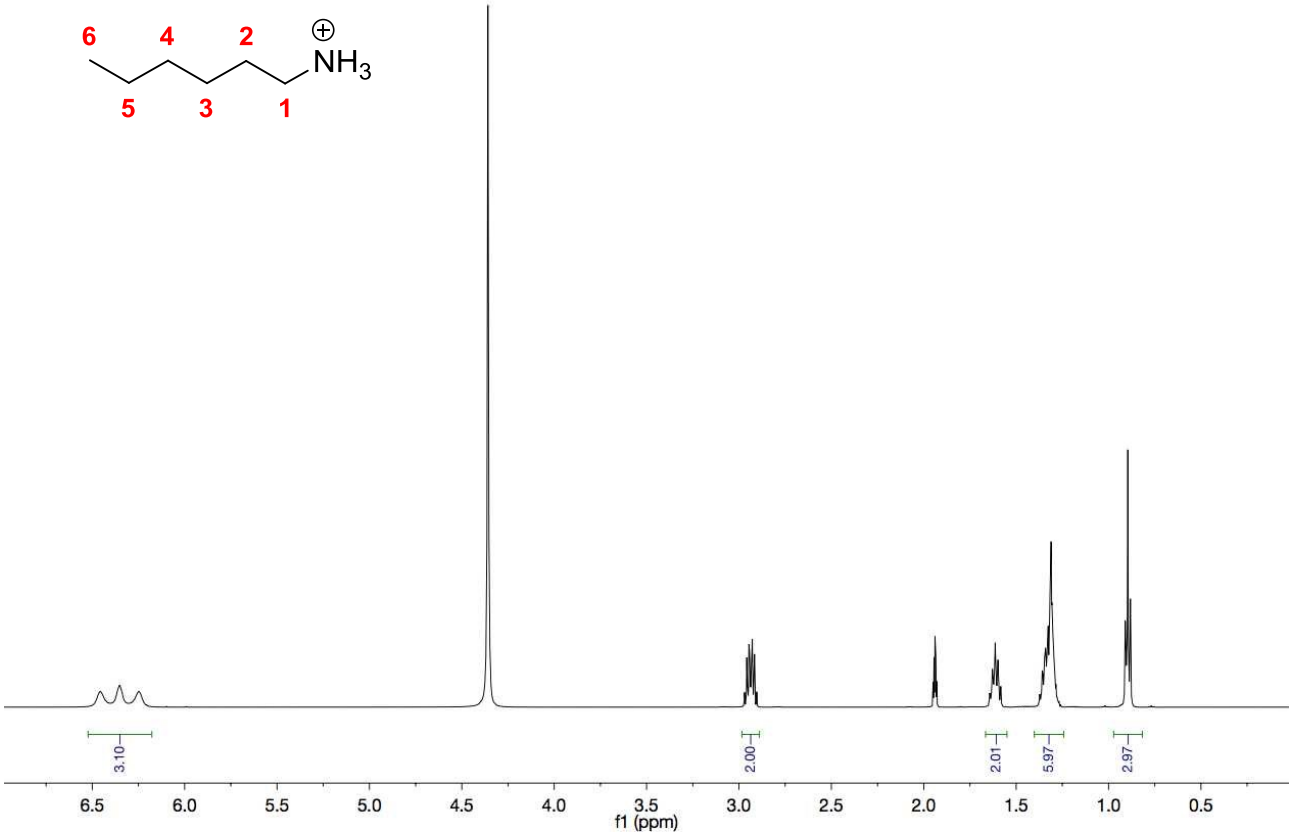


Figure S18. ^{1}H NMR spectrum of compound **10**.

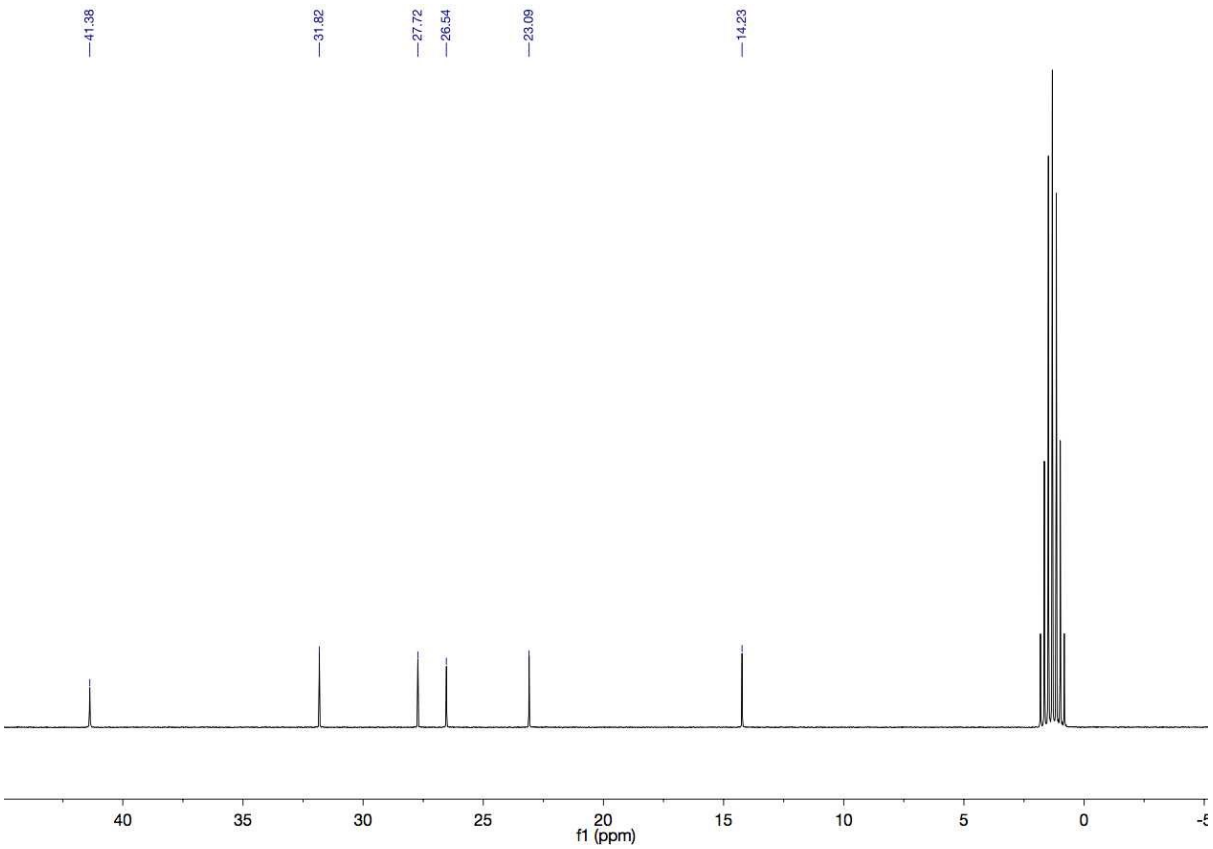


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10**.

Synthesis of di-n-hexylammonium perrhenate, 11

An aqueous solution of perrhenic acid (0.15 mL, 1 mmol) was added to neat di-*n*-hexylamine (194 mg, 1 mmol) which immediately reacted to give a solid. This product was suspended in hexane (10 mL), filtered, washed with hexane (2 x 5 mL) and dried under reduced pressure to give **11** as an off- white solid (284 mg, 62 %). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 6.59 (t, J = 44.2 Hz, 2H, NH_2), 3.18 – 2.69 (m, 4H, C1H_2), 1.64 (p, J = 7.5 Hz, 4H, C2H_2), 1.45 – 1.19 (m, 12H, C3,4,5H_2), 1.07 – 0.68 (m, 3H, C6H_2). ^{13}C NMR (500 MHz, Acetonitrile-d_3) δ 49.24 ($C1$H$_2$), 31.83 ($C3,4,5$H$_2$), 26.67 ($C2$H$_2$), 26.65 ($C3,4,5$H$_2$), 23.08 ($C3,4,5$H$_2$), 14.23 ($C6$H$_2$). Anal. calcd. for $C_{12}H_{28}NO_4Re$: C, 33.01; H, 6.46; N, 3.21 %. Found: C, 33.26; H, 6.30; N, 3.32 %. FTIR (ATR, cm^{-1}): ν 888 (br, s, ReO).

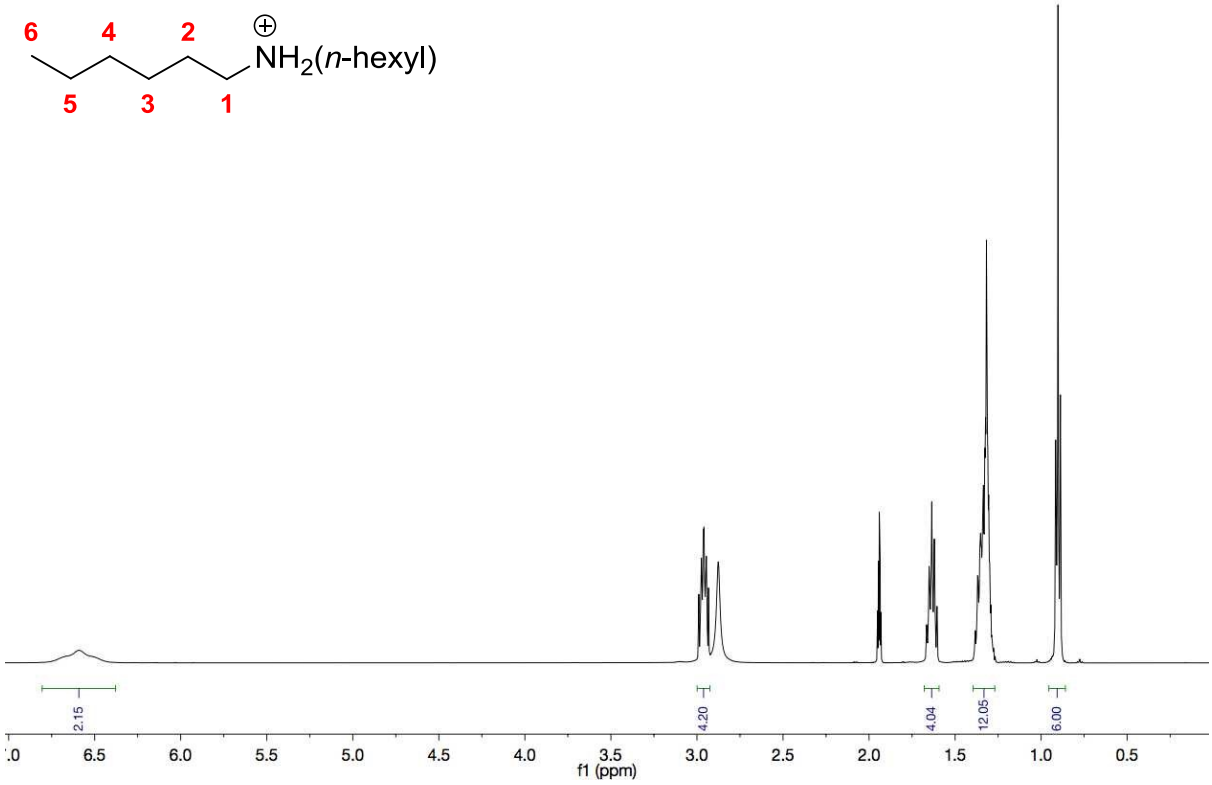


Figure S20. ^{1}H NMR spectrum of compound **11**.

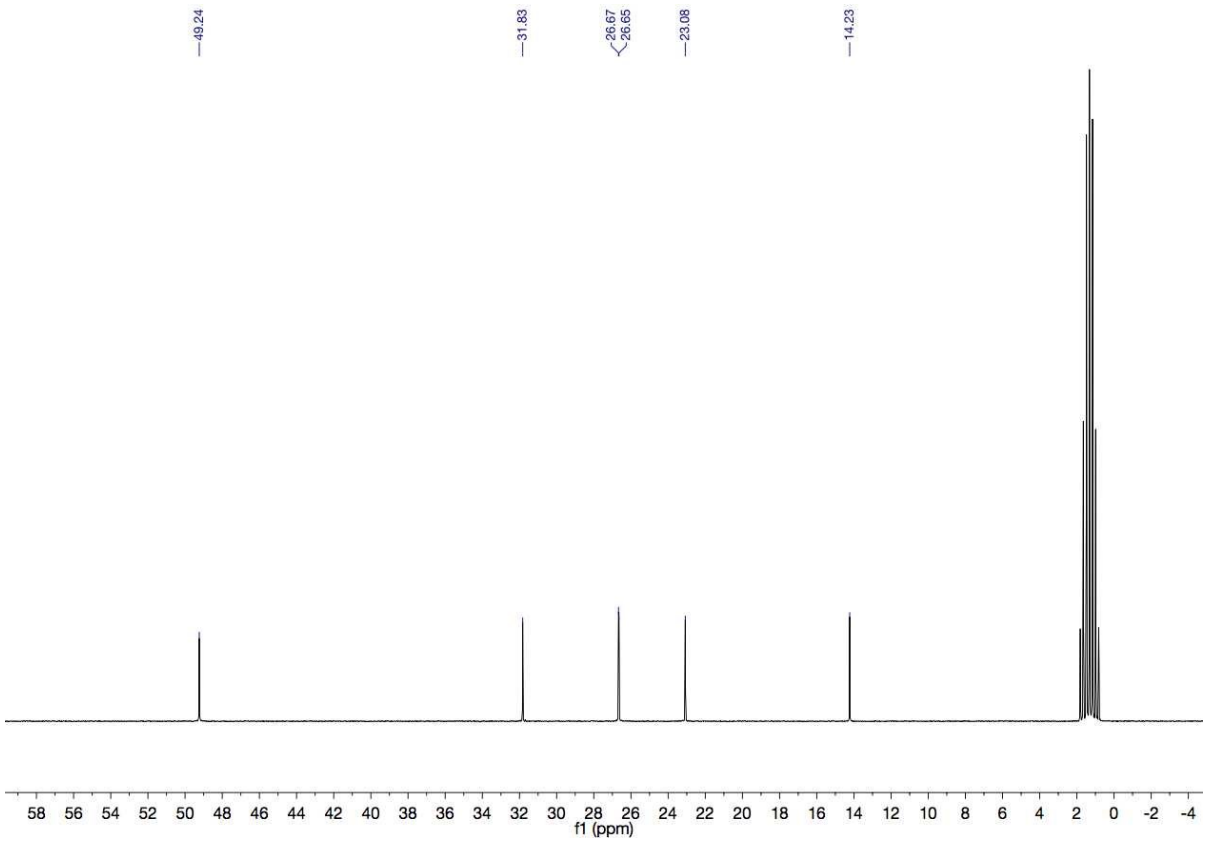


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of compound **11**.

Synthesis of tri-n-hexylammonium perrhenate, 12

An aqueous solution of perrhenic acid (0.15 mL, 1 mmol) was added to neat tri-*n*-hexylamine (272 mg, 1 mmol), then dissolved in toluene (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford **12** as a colorless oil (352 mg, 68 %). ^{1}H NMR (500.12 MHz; CD_3CN): ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 6.59 (s, 3H, NH_3), 2.99 – 2.92 (m, 6H, C1H_2), 1.64 (p, J = 7.5 Hz, 6H, C2H_2), 1.39 – 1.28 (m, 18H, C3,4,5H_2), 0.93 – 0.87 (m, 9H, C6H_3. ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 49.24 (C1H_2), 31.83 (C2H_2), 26.67 (C3H_2), 26.65 (C4H_2), 23.08 (C5H_2), 14.23 (C6H_3). Anal. calcd. for $C_{18}H_{40}NO_4Re$: C, 41.52; H, 7.74; N, 2.69 %. Found: C, 41.78; H, 7.64; N, 2.55 %.

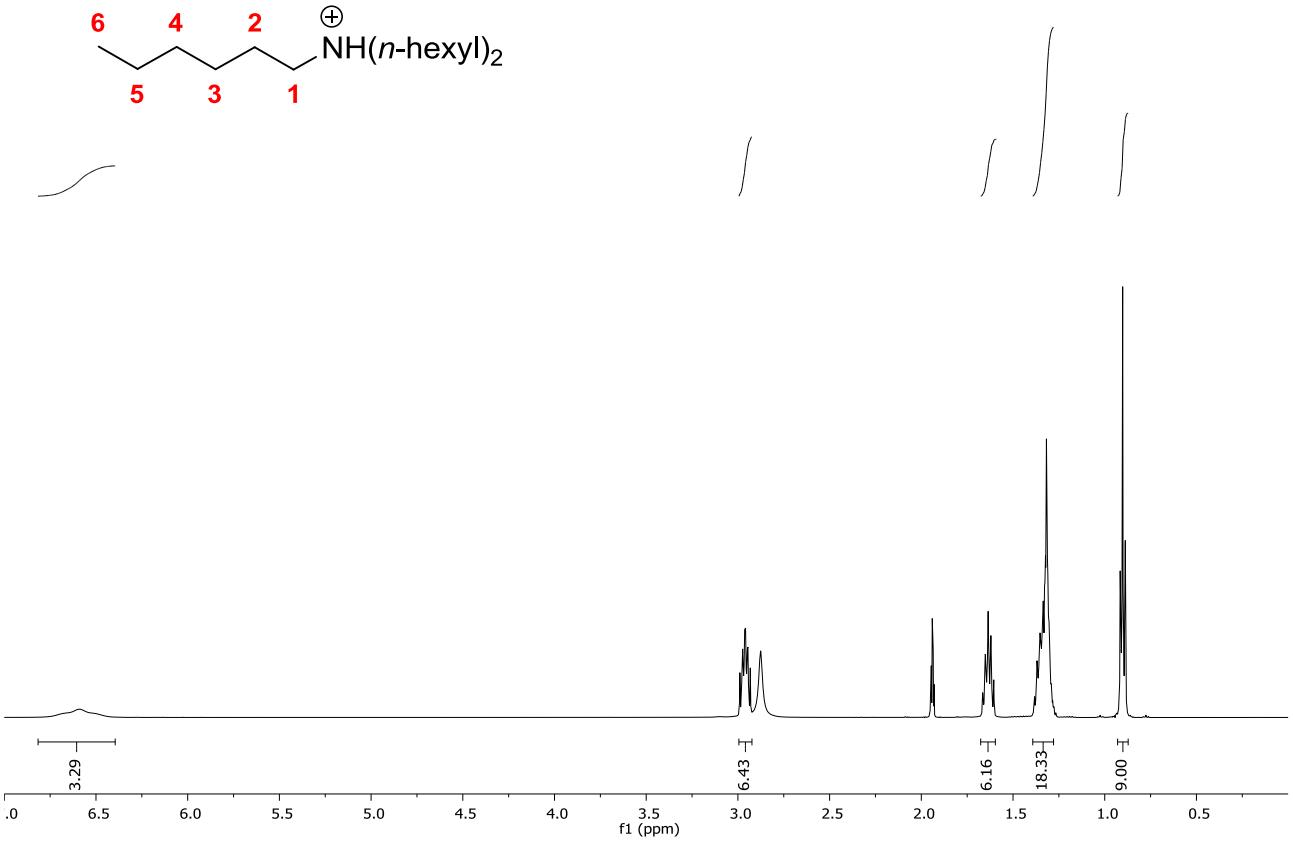


Figure S22. ^{1}H NMR spectrum of compound **12**.

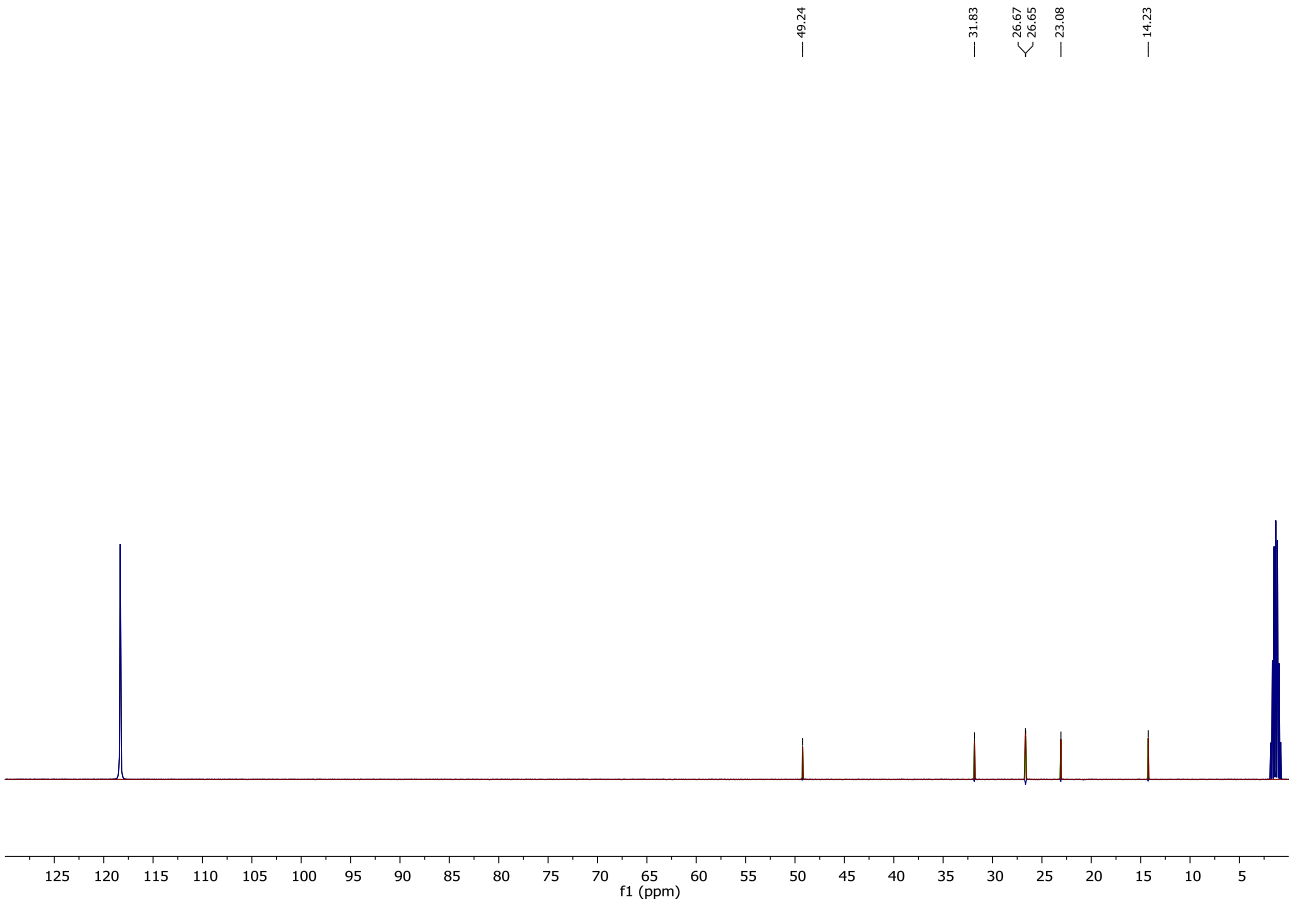


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of compound **13**.

Synthesis of tetra-n-hexylammonium perrhenate, 13

An aqueous solution of ammonium perrhenate (1.26 g, 4.7 mmol) was added to a solution of tetra-*n*-hexylammonium bromide (2 g, 4.6 mmol) in chloroform (35 mL) and stirred for 6 h at room temperature after which the two layers were separated and the aqueous layer extracted with chloroform (2 x 10 mL). The combined chloroform extracts were dried over magnesium sulfate and the solvent evaporated under reduced pressure to give **13** as a colorless solid (2.1 g, 75 %). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 3.11 – 3.02 (m, 8H, C1H_2), 1.60 (tt, J = 10.1, 6.6 Hz, 8H, C2H_2), 1.33 (q, J = 5.9, 4.3 Hz, 24H, C3,4,5H_2), 0.99 – 0.85 (m, 12H, C6H_3). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 59.53, 59.51, 59.49, 31.83, 26.57, 26.55, 23.08, 22.34, 14.19. Anal. Calcd. for $C_{24}H_{52}NO_4Re$: C, 47.66; H, 8.67; N, 2.32. Found: C, 47.55; H, 8.72; N, 2.38. FTIR: ν(ReO) 902 cm^{-1}. FTIR (ATR, cm^{-1}): ν 889 (br, s, ReO)

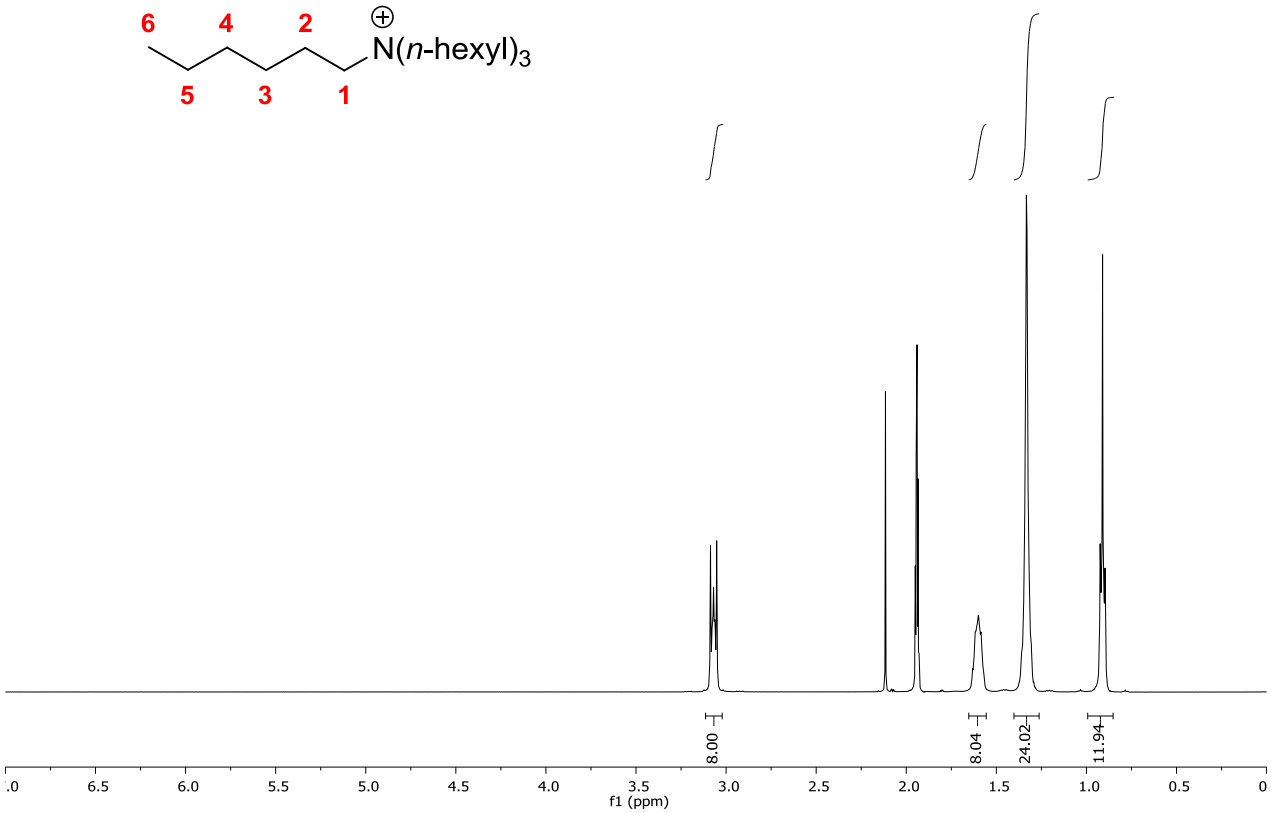


Figure S24. ^{1}H NMR spectrum of compound **13**.

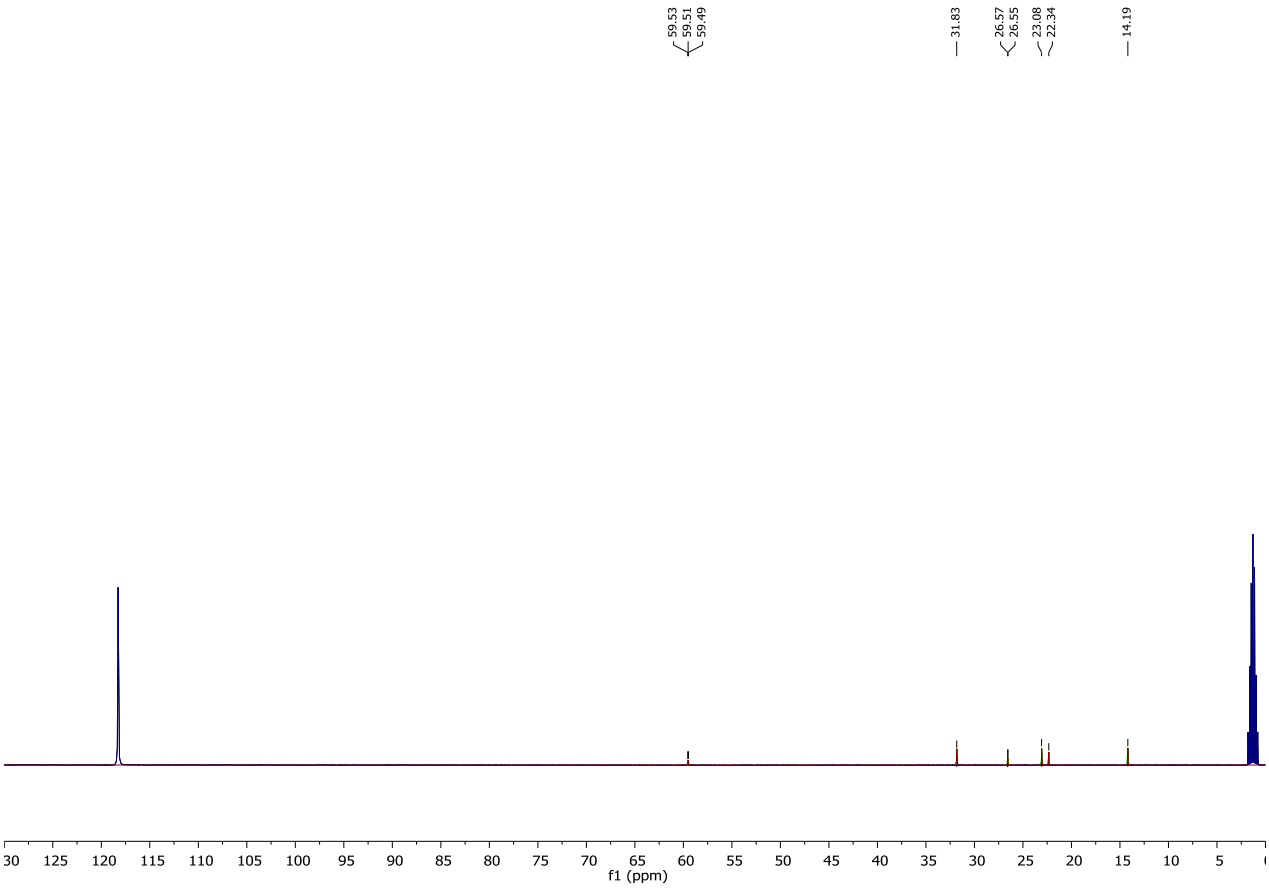
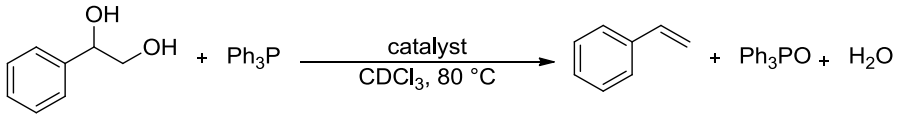


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of compound **13**.

3. Optimization of the reaction conditions

General procedure: Styrene glycol (38.55 mg, 0.279 mmol), reducing agent (0.307mmol), **3** (X mmol) and triphenylmethane (34.00 mg, 0.140 mmol) were dissolved in 500 µL of the appropriate deuterated solvent, transferred to a Teflon Tapped NMR tube and left to react at 80 °C for 16 h, unless otherwise stated.

4. Catalyst screening



General procedure: Styrene glycol (38.55 mg, 0.279 mmol), triphenylphosphine (80.50 mg, 0.307mmol), catalyst (0.014 mmol), and triphenylmethane (34.00 mg, 0.140 mmol) were dissolved in the appropriate deuterated solvent (500 µL), transferred to a Teflon-tapped NMR tube and left to react at 80 °C for the required time, unless otherwise specified. The product olefin peaks were used to measure the conversion. All reactions were carried out in triplicate.

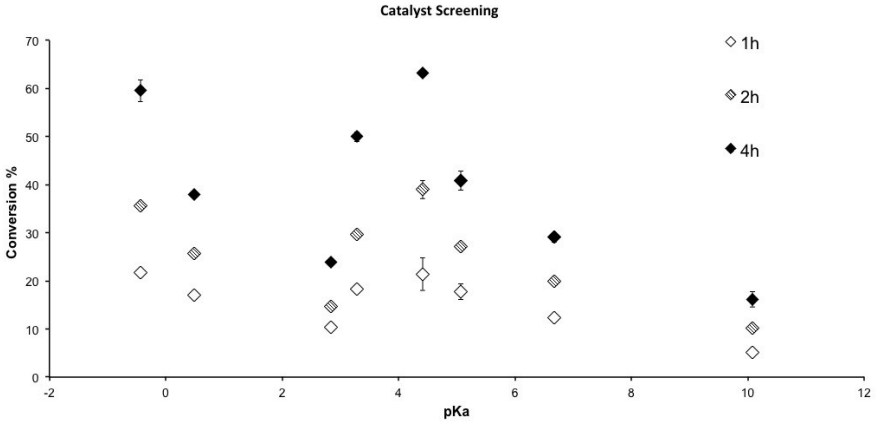


Figure S26. Monitored conversions of styrene glycol at 1, 2 and 4 h (Table S1).

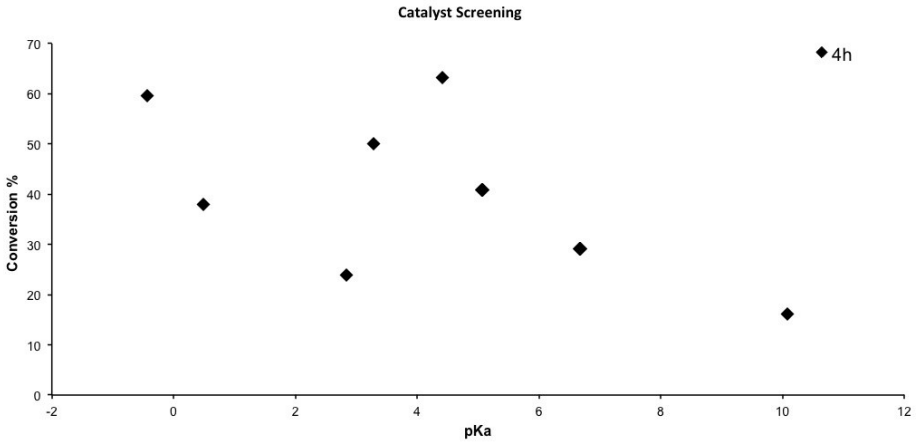
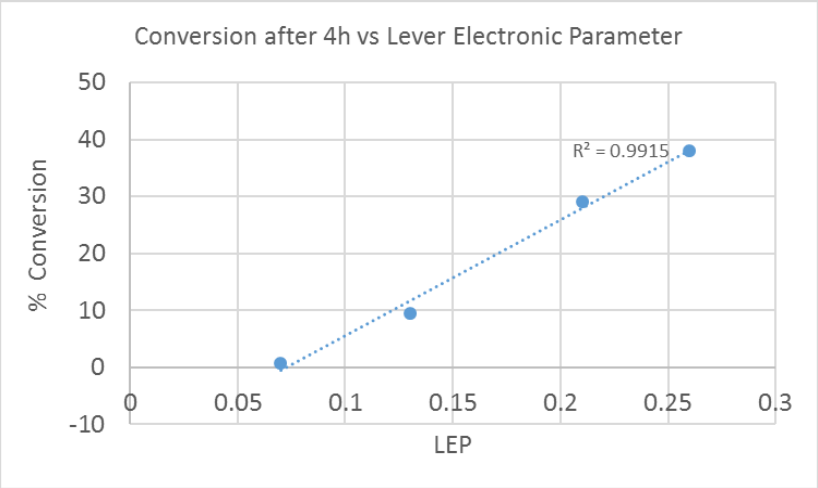


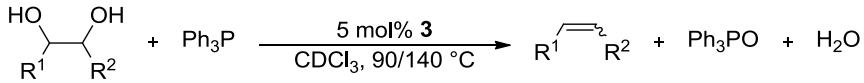
Figure S27. Monitored conversion of styrene glycol at 4 h (Table S1).



Amine/py[a]	LEP	Conversion
p-Cl py	0.26	38
Lutidine	0.21	29
$BuNH_2$	0.13	9.5[b]
NH_3	0.07	0.75[b]

Figure S28. Conversion vs. Lever Electronic Parameter (LEP). [a] nearest derivative to those used in catalytic study. [b] extrapolated from yields after 16 h

5. Substrate screening

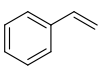
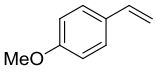
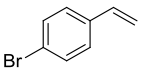
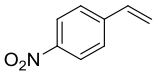
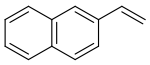
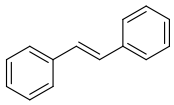
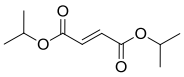
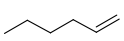
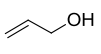


General procedure: The substrate (0.279 mmol), triphenylphosphine (80.50 mg, 0.307 mmol), **3** (5.00 mg, 0.014 mmol), and triphenylmethane (34.00 mg, 0.140 mmol) were dissolved in $CDCl_3$ (500 µL), transferred into a Teflon-tapped ampule and reacted at 90 or 140 °C for 4 or 16 h, unless otherwise specified. The reaction mixture was analysed by ^{1}H NMR spectroscopy. The product olefin peaks were used to measure the yield.

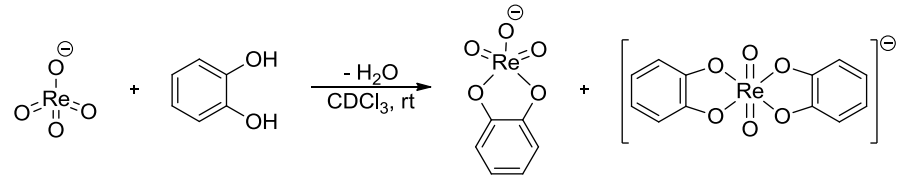
Product identification

Product ^{1}H NMR peaks are reported in table S2. The product olefin peaks were used to measure the yield with triphenylmethane as internal standard: ^{1}H-NMR (triphenylmethane) (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 6H), 7.25-7.21 (m, 3H), 7.16-7.12 (m, 6H), 5.57 (s, 1H, used for quantification).

Table S1. Characterization of the DODH products.

Entry	Product	TOF (h^{-1})	Structure	NMR data
1	Styrene (**p1**)	5.0		^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.5-5.1 (m, 5H) 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.26 (dd, *J* = 10.9, 0.7 Hz, 1H).
2	1-methoxy-4-vinylbenzene (**p2**)	4.0		^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 6.93 – 6.87 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.65 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.16 (dd, *J* = 10.9, 0.8 Hz, 1H), 3.82 (s, 3H).
3	1-bromo-4-vinylbenzene (**p3**)	5.0		^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.12 (m, 2H), 6.61 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H)
4	1-nitro-4-vinylbenzene (**p4**)	0.7		^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 7.56 (m, 2H), 6.82 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.97 (d, *J* = 17.6 Hz, 1H), 5.54 (d, *J* = 10.9 Hz, 1H)
5	2-vinylnaphthalene (**p5**)	5.0		^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 3H), 7.66 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.54 (tq, *J* = 6.9, 1.3 Hz, 3H), 6.91 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H).
6	(*E*)-1,2-diphenylethene (**p6**)	4.9		^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53-7.29(m, 10H), 7.13 (s, 2H).
7	diisopropyl fumarate (**p7**)	1.3		^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 5.03 (p, *J* = 6.3 Hz, 2H), 1.20 (d, *J* = 6.3 Hz, 12H).
8	2,5-dihydrofuran (**p8**)	1.0		^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.90 (s, 2H), 4.67 (s, 4H).
9	hex-1-ene (**p9**)	0.5		^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 2.09 (q, *J* = 6.9 Hz, 2H), 1.61 – 1.23 (m, 4H), 1.01 – 0.84 (m, 3H).
10	prop-2-en-1-ol (**p10**)	0.3		^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.14 – 5.96 (m, 1H), 5.37 – 5.28 (m, 1H), 5.22 – 5.11 (m, 1H), 4.18 (d, *J* = 5.0 Hz, 2H), 2.68 (s, 1H).

6. Synthesis of [2,6-dimethylpyridinium][rhenium(VII)catecholate]



A mixture of **3** (50 mg, 0.140 mmol) and catechol (15.34 mg, 0.140 mmol) in $CDCl_3$ (500 µL) was stirred at room temperature over 4 Å molecular sieves. The mixture turned dark purple immediately and was stirred for ~7 days. A sample of the dark oily product was analyzed by mass spectrometry and confirmed the formation of rhenium(VII)catecholate species. The dark precipitate was redissolved in deuterated acetonitrile and characterised by ^{1}H-NMR. The latter confirmed the formation of a mixture of [2,6-dimethylpyridinium][$Re^{VII}O_3(C_6H_4O_2)$] and [2,6-dimethylpyridinium][$Re^{VII}O(C_6H_4O_2)_2$].

^{1}H NMR (600 MHz, Acetonitrile-d_3) δ 8.11 (t, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 6.80 (dd, *J* = 7.9, 1.4 Hz, 1.5H), 6.65 (td, *J* = 7.7, 1.4 Hz, 1.5H), 6.52 (td, *J* = 7.7, 1.4 Hz, 1.5H), 6.47 (dd, *J* = 7.9, 1.3 Hz, 1.5H). HRMS (ESI-, m/z): ReO_4 ($[ReO_4]^-$) requires 250.9354, found 250.9474; $C_6H_4O_5Re$ ($[ReO_3(C_6H_4O_2)]^-$) requires 342.9616, found 342.9597; $C_{12}H_8O_6Re$ ($[ReO_2(C_6H_4O_2)_2]^-$) requires 434.9878, found 434.9859.

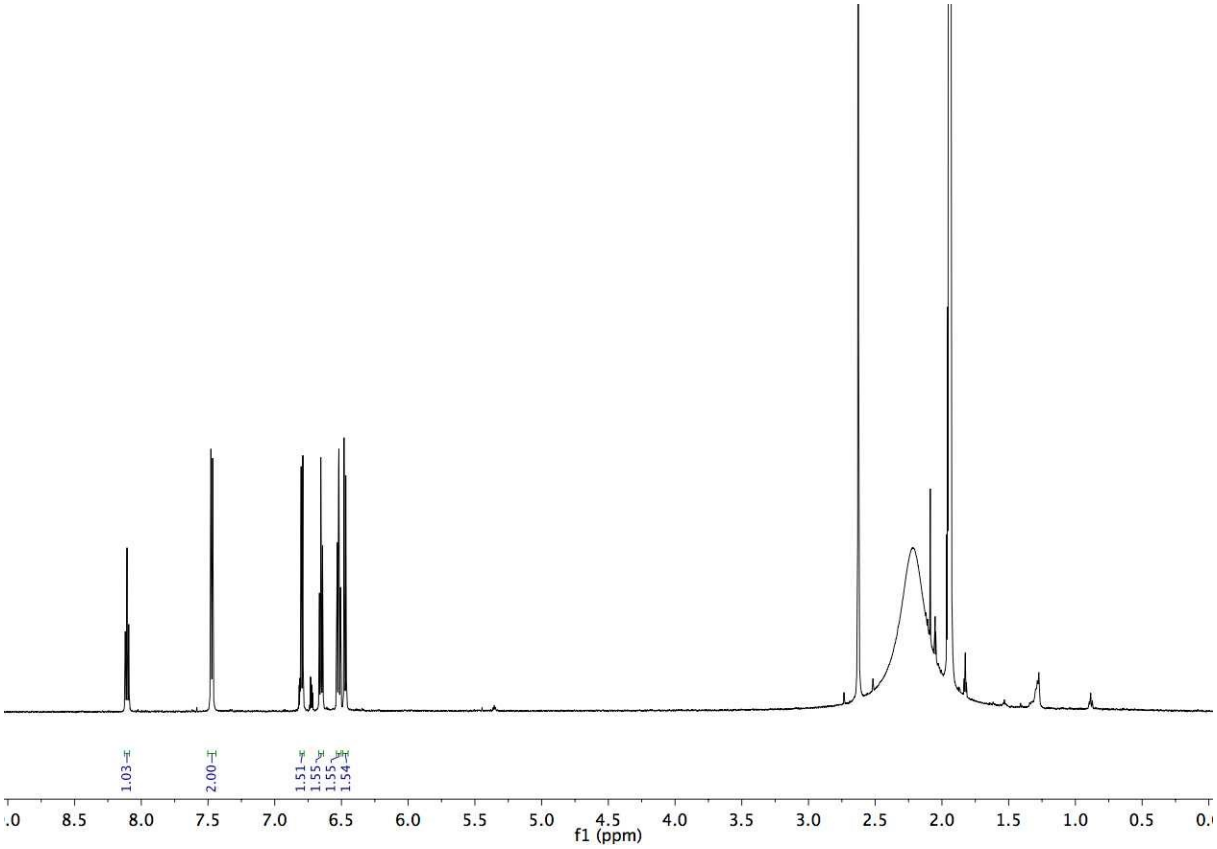
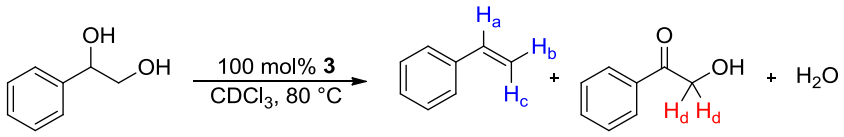


Figure S29. ^{1}H-NMR of the mixture containing [2,6-dimethylpyridinium][$Re^{VII}O_3(C_6H_4O_2)$] and [2,6-dimethylpyridinium][$Re^{VII}O(C_6H_4O_2)_2$].

7. Reaction monitoring by ^{1}H NMR spectroscopy at 80 °C



A mixture of styrene glycol (38.55 mg, 0.279 mmol) and **3** (0.279 mmol) in $CDCl_3$ (500 µL) was heated in a Teflon-Tapped NMR tube at 80 °C for 120 min. The ^{1}H NMR spectrum was recorded at 1 min intervals.

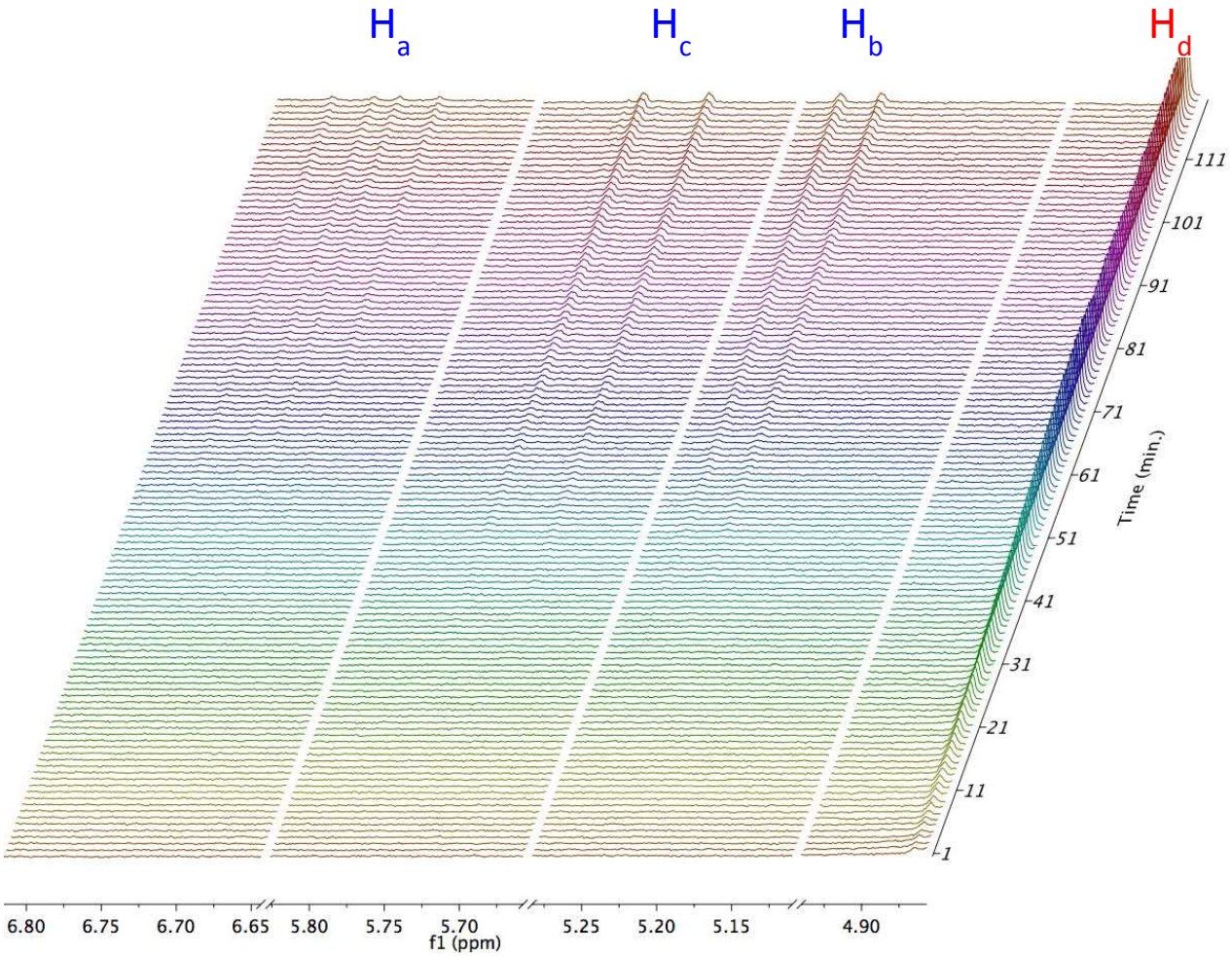


Figure S30. Portions of the ^{1}H NMR spectrum in $CDCl_3$ for the DODH reaction of styrene diol catalysed by **3** in the absence of PPh_3.

8. Crystallographic data

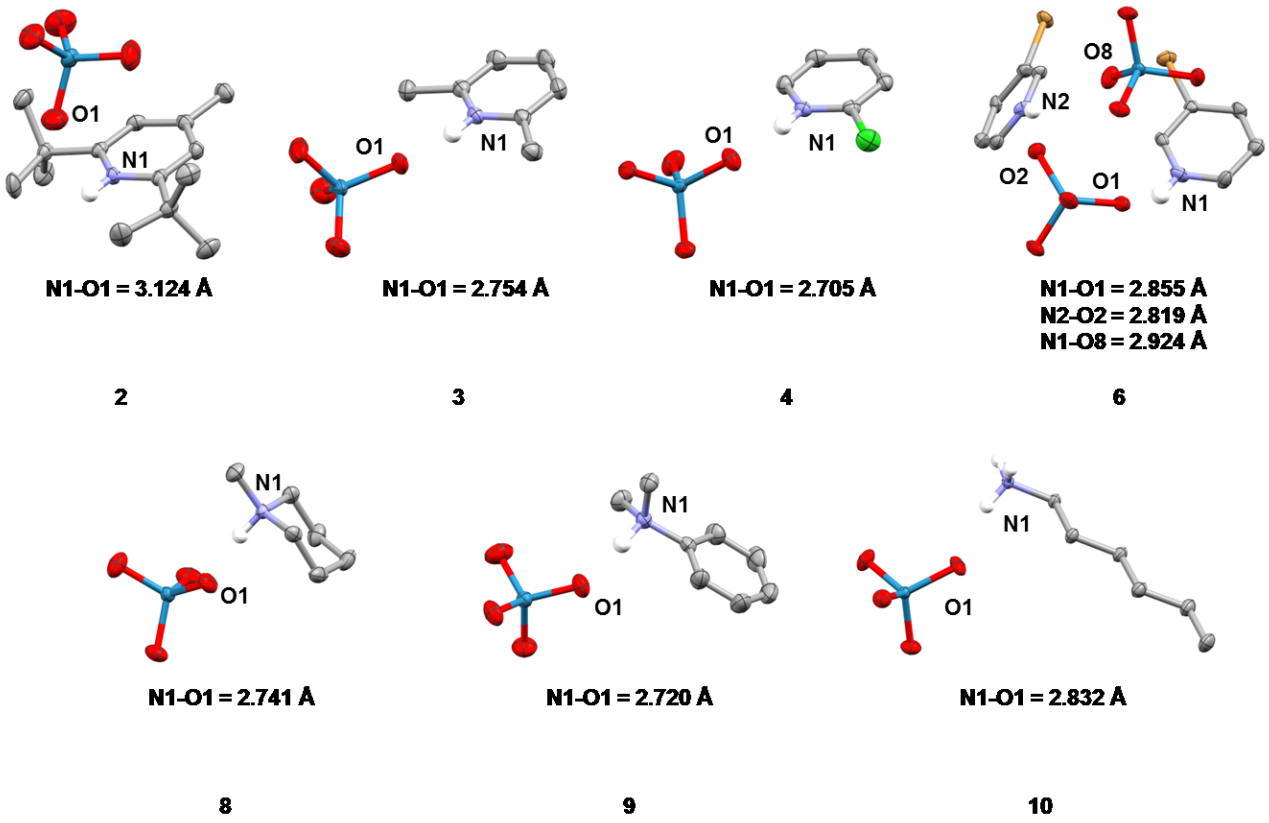


Figure S31. Solid-state structures for **2**, **3**,**4**, **6**, **8**, **9** and **10** (displacement ellipsoids are drawn at 50% probability). For clarity, all hydrogen atoms except ammonium/pyridinium-N hydrogen atoms are omitted.

Table S2. Crystallographic data for **2** and **3**.

	2	**3**
Chemical formula	$O_4Re{\cdot}C_{14}H_{24}N$	$O_4Re{\cdot}C_7H_{10}N$
M_r	456.54	358.36
Crystal system, space group	Monoclinic, $P12_1/m1$	Monoclinic, $P2_1/c$
Temperature (K)	170	170
a, b, c (Å)	8.9052 (2), 8.4384 (1), 10.9159 (2)	9.6740 (1), 12.4192 (1), 8.5156 (1)
β (°)	90.016 (2)	108.736 (1)
V (Å^3)	820.28 (3)	968.88 (2)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	7.42	12.52
Crystal size (mm)	0.35 × 0.23 × 0.14	0.24 × 0.16 × 0.08
Diffractometer	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Analytical numeric absorption correction using a multifaceted crystal model based on Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01) Analytical numeric absorption correction using a multifaceted crystal model based on Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.753, 0.857	0.995, 0.998
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8547, 1608, 1572	65584, 2219, 2174
R_{int}	0.018	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.045, 1.31	0.015, 0.033, 1.25
No. of reflections	1608	2219
No. of parameters	128	120
No. of restraints	6	
H-atom treatment	mixture of independent and constrained refinement	constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.78, -0.35	0.52, -1.07

Table S3. Crystallographic data for **4** and **6**.

	4	**6**
Chemical formula	$2(O_4Re)\cdot2(C_5H_5ClN)$	$2(O_4Re)\cdot2(C_5H_5BrN)$
M_r	729.50	818.42
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P^{-}1$
Temperature (K)	170	293
a, b, c (Å)	5.2446 (1), 12.7123 (2), 12.8020 (2)	8.3466 (3), 10.4128 (4), 10.9082 (6)
β (°)	95.597 (1)	113.523 (4), 92.589 (4), 97.987 (3)
V (Å^3)	849.45 (2)	855.53 (7)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	14.59	18.85
Crystal size (mm)	0.46 × 0.26 × 0.04	0.61 × 0.34 × 0.18
Diffractometer	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.320, 0.861	0.012, 0.087
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25488, 2201, 2076	14803, 4109, 3671
R_{int}	0.036	0.047
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.690	0.688
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.018, 0.048, 1.09	0.042, 0.109, 1.11
No. of reflections	2201	4109
No. of parameters	109	217
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.01, -1.62	2.12, -3.77

Table S4. Crystallographic data for **8** and **9**.

	8	**9**
Chemical formula	$4(O_4Re)\cdot4(C_6H_{14}N)$	$O_4Re\cdot C_8H_{12}N$
M_r	1401.52	372.39
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, $P2_1/c$
Temperature (K)	170	170
a, *b*, *c* (Å)	13.0504 (2), 12.1955 (2), 12.2542 (2)	12.2151 (2), 10.4607 (1), 8.8902 (1)
β (°)	95.553 (2)	105.704 (2)
V (Å^3)	1941.18 (5)	1093.57 (3)
Z	2	4
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	12.50	11.10
Crystal size (mm)	0.31 × 0.25 × 0.16	0.25 × 0.15 × 0.01
Diffractometer	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.783, 0.877	0.994, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17336, 1783, 1695	26146, 3038, 2665
R_{int}	0.042	0.041
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.709
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.016, 0.034, 1.16	0.021, 0.041, 1.08
No. of reflections	1783	3038
No. of parameters	111	129
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.64, -0.61	0.73, -0.92

Table S5. Crystallographic data for **10**.

	10
Chemical formula	$O_4Re{\cdot}C_6H_{16}N$
M_r	352.40
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	14.9581 (4), 7.5570 (2), 9.3623 (3)
β (°)	107.339 (3)
V (Å^3)	1010.21 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	12.01
Crystal size (mm)	0.81 × 0.11 × 0.06
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.950, 0.994
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18942, 2314, 2147
R_{int}	0.044
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.038, 1.09
No. of reflections	2314
No. of parameters	111
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.70, -1.01

Computer programs: *CrysAlis PRO* 1.171.38.42b (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

9. Computational Analysis

Density functional theory (DFT) calculations were performed with Gaussian 09 E.01.[1] Geometry optimizations and frequency calculations were performed at the (dispersion-corrected) B3LYP-D3(BJ)/6-31+G* level of theory and the rhenium centre was described using the Stuttgart–Dresden (SDD) effective core potentials.[2] Similar methodologies have been applied to the study of rhenium-based catalytic deoxydehydration.[3] For each system two different conformations were explored, each of them having the pyridinium/ammonium group either *cis* or *trans* to the benzyl group of the alcohol. In most cases *cis*-conformation was found to be favoured. Stationary points were characterized *via* frequency analysis at the same level of theory and connected to their respective minima via intrinsic reaction coordinate (IRC) calculations.[4] In all cases, a quasi-rigid-rotor-harmonic-oscillator (RRHO) approximation was used in which the treatment of vibrational entropies switches from the standard RRHO model to a free rotor description for frequencies below 100 cm^{-1}, as first proposed by Grimme,[5] and implemented in Python.[6] Single point corrections with the SMD continuum solvation model[7] were applied to include the effect of chloroform on the computed Gibbs energy profile at the SMD($CHCl_3$)B3LYP-D3(BJ)/Def2QZVP level of theory and Gibbs free energies in chloroform solution were estimated from the equation $G_{solv} = E_{solv} + (G_{gas} - E_{gas})$ at 353 K.

Pathway B: Condensation-Reduction-elimination

The relative Gibbs free energy profile for Path B is shown in **Figure S32** along with the corresponding transition states and intermediate structures. In all cases, the energy reference was taken as the energy of the separate reagents $[ReO_4]^-$+ RNH_3^+ + PPh_3+diol. In this case the reaction is initiated with activation of diol *via* transition state TS_1 (24.1 kcal mol^{-1}). In this step, one H atom of the diol is transferred to one oxo group land a new Re-O bond is form. This leads to the high energy intermediate **B** (18.7 kcal mol^{-1}). Following from this, a second H transfer takes place eventually leading to formation of water and the formation of a second Re-O bond. The next step is reduction of the metal center, which is substantially higher in energy (50.8 kcal mol^{-1}) than the analogous step found for Path A. The common final step is styrene extrusion, which has a very small activation barrier and is thermodynamically favorable. These data support pathway A as the preferred mechanism for the reaction under study.

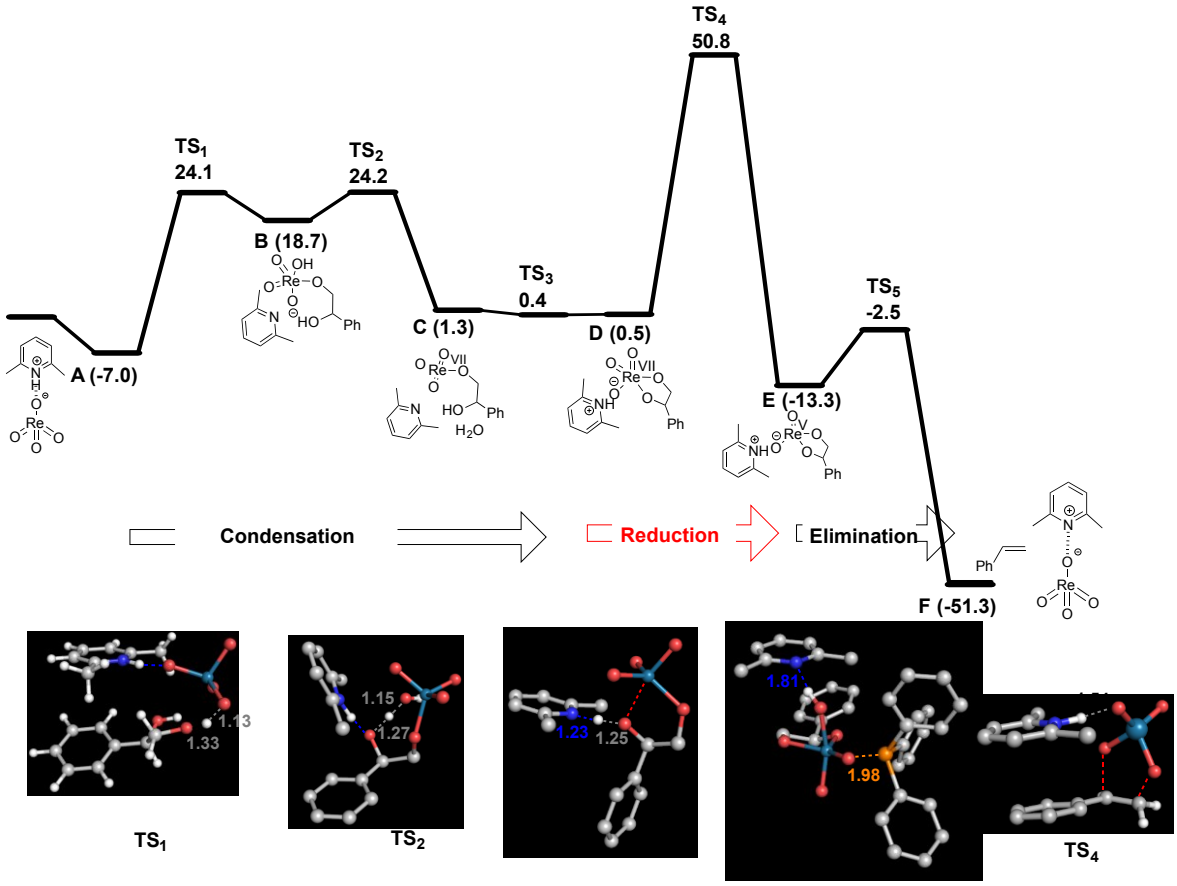


Figure S32. Structures and relative free energies (ΔG, in kcal mol^{-1}; selected distances in Å) of stationary points involved in the catalytic cycle for the DODH reaction of styrene diol by **3** proceeding via condensation, reduction and extrusion steps. Energy values were calculated at the SMD($CHCl_3$)B3LYP-D3(BJ)/Def2QZVP//B3LYP-D3(BJ)/6-31G+(d) level of theory relative to the separated species.)

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Absolute Energies

Table S6. Absolute electronic energies (E_{el}), zero point energy (ZPE), enthalpy (H), quasi-harmonic entropies (Tqh-S), quasi-harmonic Gibbs energy (qh-G) (in atomic units) and the lowest frequency value (ν, cm^{-1}) for **Pathway A with Lutidinium salt**. Reaction free energies are given in kcal mol^{-1} relative to the independent species at 353 K. Calculations were carried out at the SMD($CHCl_3$)B3LYP-D3(BJ)/Def2QZVP//B3LYP-D3(BJ)/6-31G+(d) level of theory.

	B3LYP-D3(BJ)/6-31G+(d)					SMD($CHCl_3$)-B3LYP-D3(BJ)/Def2QZVP			ν (cm^{-1})
	E_{el}	ZPE	H	Tqh-S	qh-G	E_{corr}	H_{corr}	G_{corr}	
ReO_4^-	–379.44341	0.01209	0.04426	–379.42377	–379.46803	–379.66852	–379.64887	–379.69314	322.4
3	–327.34608	0.15790	0.05192	–327.17624	–327.22816	–327.56109	–327.39125	–327.44317	33.3
H_2O	–76.42315	0.02109	0.02615	–76.39758	–76.42372	–76.47972	–76.45415	–76.48030	1662.5
Diol	-461.35064	0.16604	0.05699	-461.17044	-461.22743	-461.57394	-461.39375	-461.45074	42.9
Styrene	–309.68884	0.13364	0.04837	–309.54482	–309.59319	–309.82507	–309.68106	–309.72942	52.4
PPh_3	–1036.41025	0.27439	0.07582	–1036.11295	–1036.18877	–1036.74543	–1036.44812	–1036.52394	25.5
$OPPh_3$	–1111.67022	0.27913	0.07902	–1111.36688	–1111.44591	–1112.05986	–1111.75652	–1111.83554	12.7
A	–706.93305	0.17107	–706.74205	0.07155	–706.81360	–707.26687	–707.07587	–707.14742	31.9
TS_1	–1743.31401	0.44420	–1742.82622	0.11891	–1742.94513	–1743.98123	–1743.49344	–1743.61234	–258.4
B	-631.65538	0.16652	-631.46956	0.07149	-631.54106	-631.95047	-631.76465	-631.83615	9.9
TS_2	–1092.99407	0.33145	–1092.63036	0.09744	–1092.72780	–1093.50564	–1093.14193	–1093.23937	–1333.9
C	–1093.03260	0.33600	–1092.66411	0.09758	–1092.76169	–1093.54287	–1093.17439	–1093.27197	9.8
TS_3	–1093.01585	0.33147	–1092.65314	0.09319	–1092.74633	–1093.52293	–1093.16022	–1093.25341	–898.7
D	–1016.60751	0.30972	–1016.26854	0.08976	–1016.35830	–1017.06560	–1016.72663	–1016.81639	23.5
TS_4	–1016.58371	0.30629	–1016.24778	0.09055	–1016.33833	–1017.04446	–1016.70852	–1016.79907	-407.2
$TS_{off\text{-}cycle}$	–1016.58894	0.30800	–1016.25168	0.09087	–1016.34255	–1017.04250	–1016.70524	–1016.79611	–99.0
$PS_{off\text{-}cycle}$	–1016.61500	0.31050	–1016.27552	0.08888	–1016.36440	–1017.07220	–1016.73272	–1016.8216	17.8
	$\Delta E^{\ddagger}_{el}$	ZPE	$\Delta H^{\ddagger}$	$T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}_{corr}$	$\Delta H^{\ddagger}_{corr}$	$\Delta G^{\ddagger}_{corr}$	
ReO_4^-**+3**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
A	–90.1	0.7	–15.5	–89.1	–73.7	–23.4	–22.4	–7.0	
TS_1	–71.7	-0.1	–71.1	–33.3	–37.8	–3.9	–3.3	30.1	
B	–79.0	0.8	–77.5	–13.5	-64.0	–22.1	–20.7	–7.2	
TS_2	–71.5	0.1	–71.4	–33.0	–38.5	–10.4	–10.3	22.6	
C	–95.7	2.9	–92.6	–32.9	-59.7	–33.7	–30.7	2.2	
TS_3	–85.1	0.1	–85.7	–35.6	-50.1	–21.2	–21.8	13.8	
D	–94.4	-0.3	–21.4	–93.9	–72.5	–35.3	–34.7	–13.3	
TS_4	–79.5	–2.5	–20.9	–80.9	-60.0	–22.0	–23.3	–2.5	
E	–103.5	–3.5	–2.4	–105.4	–102.9	-51.8	-53.7	-51.3	
$TS_{off\text{-}cycle}$	–82.8	–1.4	–83.3	–20.7	-62.6	–20.8	–21.3	-0.6	
$PS_{off\text{-}cycle}$	–99.1	0.2	–98.3	–21.9	–76.3	–39.4	–38.5	–16.6	

Table S7. Absolute electronic energies (E_{el}), zero point energy (ZPE), enthalpy (H), quasi-harmonic entropies (Tqh-S), quasi-harmonic Gibbs energy (qh-G) (in atomic units) and the lowest frequency value (ν, cm^{-1}) for **Pathway A with ammonium salt 15**. Reaction free energies are given in kcal mol^{-1} relative to the independent species at 353 K. Calculations were carried out at the SMD($CHCl_3$)B3LYP-D3(BJ)/Def2QZVP//B3LYP-D3(BJ)/6-31G+(d) level of theory.

	B3LYP-D3(BJ)/6-31G+(d)					SMD($CHCl_3$)-B3LYP-D3(BJ)/Def2QZVP			ν (cm^{-1})
	E_{el}	ZPE	H	Tqh-S	qh-G	E_{corr}	H_{corr}	G_{corr}	
ReO_4^-	–379.44341	0.01209	0.04426	–379.42377	–379.46803	–379.66852	–379.64887	–379.69314	322.4
15	–327.34608	0.15790	0.05192	–327.17624	–327.22816	–327.56109	–327.39125	–327.44317	33.3
H_2O	–76.42315	0.02109	0.02615	–76.39758	–76.42372	–76.47972	–76.45415	–76.48030	1662.5
Diol	-461.35064	0.16604	0.05699	-461.17044	-461.22743	-461.57394	-461.39375	-461.45074	42.9
Styrene	–309.68884	0.13364	0.04837	–309.54482	–309.59319	–309.82507	–309.68106	–309.72942	52.4
PPh_3	–1036.41025	0.27439	0.07582	–1036.11295	–1036.18877	–1036.74543	–1036.44812	–1036.52394	25.5
$OPPh_3$	–1111.67022	0.27913	0.07902	–1111.36688	–1111.44591	–1112.05986	–1111.75652	–1111.83554	12.7
A	-436.51390	0.06311	-436.43925	0.05273	-436.49199	-436.74436	-436.66971	-436.72244	55.3
TS_1	–1472.90502	0.33683	–1472.53295	0.10169	–1472.63464	–1473.46262	–1473.09055	–1473.19224	–261.7
B	–822.61589	0.22896	–822.36206	0.08206	–822.44411	–823.02061	–822.76678	–822.84883	16.6
TS_2	–822.57310	0.22313	–822.32621	0.07976	–822.40597	–822.98125	–822.73437	–822.81412	–1420.0
C	–822.61818	0.22605	–822.36757	0.08064	–822.44821	–823.01494	–822.76433	–822.84497	18.6
TS_3	–822.60761	0.22481	–822.36046	0.07494	–822.43540	–823.00472	–822.75757	–822.83251	–885.4
D	–746.19380	0.20314	–745.97013	0.07161	–746.04175	–746.54378	–746.32011	–746.39173	49.0
TS_4	–746.17276	0.19997	–745.95208	0.07181	–746.02389	–746.52435	–746.30367	–746.37548	–328.3
$TS_{off\text{-}cycle}$	–746.17850	0.19968	–745.95751	0.07399	–746.03150	–746.524425	–746.30344	–746.37743	–140.6
$PS_{off\text{-}cycle}$	–746.204313	0.202508	–745.98083	0.07304	–746.053875	–746.5578846	–746.33440	–746.40745	27.6
	$\Delta E^{\ddagger}_{el}$	**ZPE**	**$\Delta H^{\ddagger}$**	**$T\Delta S^{\ddagger}$**	**$\Delta G^{\ddagger}$**	**$\Delta E^{\ddagger}_{corr}$**	**$\Delta H^{\ddagger}_{corr}$**	**$\Delta G^{\ddagger}_{corr}$**	
ReO_4^-+15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
A	–109.2	0.7	–108.9	–10.9	–98.0	–23.2	–22.9	–12.0	
TS_1	–97.2	0.2	–96.8	–27.7	-69.1	-6.1	-5.7	22.0	
B	–116.3	3.5	–112.8	–26.2	–86.6	–33.7	–30.2	-4.0	
TS_2	–89.4	-0.1	–90.3	–27.7	-62.7	–9.0	–9.9	17.8	
C	–117.7	1.7	–116.3	–27.1	–89.2	–30.1	–28.7	–1.6	
TS_3	–111.1	0.9	–111.8	–30.7	–81.1	–23.7	–24.4	6.2	
D	–117.0	0.6	–116.4	–16.4	–100.0	–35.5	–34.9	–18.5	
TS_4	–103.8	–1.4	–105.0	–16.2	–88.8	–23.3	–24.6	–8.3	
E	–122.6	–3.5	–125.1	2.1	–127.2	-51.6	-54.1	-56.3	
$TS_{off\text{-}cycle}$	–107.4	–1.6	–108.4	–14.9	–93.6	–23.4	–24.4	–9.6	
$PS_{off\text{-}cycle}$	–123.6	0.2	–123.1	–15.5	–107.6	-44.4	-43.9	–28.4	

Table S8. Absolute electronic energies (E_{el}), zero point energy (ZPE), enthalpy (H), quasi-harmonic entropies (Tqh-S), quasi-harmonic Gibbs energy (qh-G) (in atomic units) and the lowest frequency value (ν, cm^{-1}) for **Pathway B with Lutidinium salt**. Reaction free energies are given in kcal mol^{-1} relative to the independent species at 353 K. Calculations were carried out at the SMD($CHCl_3$)B3LYP-D3(BJ)/Def2QZVP//B3LYP-D3(BJ)/6-31G+(d) level of theory.

	B3LYP-D3(BJ)/6-31G+(d)					SMD($CHCl_3$)-B3LYP-D3(BJ)/Def2QZVP			ν (cm^{-1})
	E_{el}	ZPE	H	Tqh-S	qh-G	E_{corr}	H_{corr}	G_{corr}	
ReO_4^-	–379.44341	0.01209	0.04426	–379.42377	–379.46803	–379.66852	–379.64887	–379.69314	322.4
3	–327.34608	0.15790	0.05192	–327.17624	–327.22816	–327.56109	–327.39125	–327.44317	33.3
H_2O	–76.42315	0.02109	0.02615	–76.39758	–76.42372	–76.47972	–76.45415	–76.48030	1662.5
Diol	-461.35064	0.16604	0.05699	-461.17044	-461.22743	-461.57394	-461.39375	-461.45074	42.9
Styrene	–309.68884	0.13364	0.04837	–309.54482	–309.59319	–309.82507	–309.68106	–309.72942	52.4
PPh_3	–1036.41025	0.27439	0.07582	–1036.11295	–1036.18877	–1036.74543	–1036.44812	–1036.52394	25.5
$OPPh_3$	–1111.67022	0.27913	0.07902	–1111.36688	–1111.44591	–1112.05986	–1111.75652	–1111.83554	12.7
A	–706.93305	0.17107	0.07155	–706.74205	–706.81360	–707.26687	–707.07587	–707.14742	31.9
TS_1	–1168.27265	0.33590	0.09846	–1167.90342	–1168.00188	–1168.81934	–1168.45010	–1168.54856	–870.4
B	–1168.28467	0.34027	0.09852	–1167.91080	–1168.00932	–1168.83264	–1168.45878	–1168.55730	21.2
TS_2	–1168.27734	0.33522	0.09642	–1167.90940	–1168.00582	–1168.81996	–1168.45202	–1168.54844	-571.8
C	–1091.86144	0.31307	0.09449	–1091.51726	–1091.61174	–1092.35441	–1092.01023	–1092.10471	16.8
TS_3	–1091.85816	0.30957	0.09263	–1091.51816	–1091.61079	–1092.35341	–1092.01341	–1092.10603	-576.8
D	–1091.85865	0.31280	0.09338	–1091.51511	–1091.60848	–1092.35613	–1092.01259	–1092.10596	20.0
TS_4	–2128.21771	0.58906	0.13723	–2127.57494	–2127.71216	–2129.05530	–2128.41252	–2128.54975	–252.6
E	–1016.60751	0.30972	0.08976	–1016.26854	–1016.35830	–1017.06560	–1016.72663	–1016.81639	23.5
TS_5	–1016.58371	0.30629	0.09055	–1016.24778	–1016.33833	–1017.04446	–1016.70852	–1016.79907	-407.2
	$\Delta E^{\ddagger}_{el}$	ZPE	$\Delta H^{\ddagger}$	$T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}_{corr}$	$\Delta H^{\ddagger}_{corr}$	$\Delta G^{\ddagger}_{corr}$	
ReO_4^-+**3**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
A	–90.1	0.7	–15.5	–89.1	–73.7	–23.4	–22.4	–7.0	
TS_1	–83.2	-0.1	–34.3	–83.4	-49.1	–9.9	–10.2	24.1	
B	–90.7	2.7	–34.3	–88.1	-53.8	–18.3	–15.6	18.7	
TS_2	–86.1	-0.5	–35.6	–87.2	-51.6	–10.3	–11.4	24.2	
C	–90.6	–1.2	–20.4	–90.6	–70.2	–19.2	–19.1	1.3	
TS_3	–88.6	–3.4	–21.6	–91.2	-69.6	–18.6	–21.1	0.4	
D	–88.9	–1.4	–21.1	–89.3	-68.1	–20.3	–20.6	0.5	
TS_4	-56.8	-0.2	-41.2	-55.9	–14.7	8.8	9.6	50.8	
E	–94.4	-0.3	–21.4	–93.9	–72.5	–35.3	–34.7	–13.3	
TS_5	–79.5	–2.5	–20.9	-80.9	-60.0	–22.0	–23.3	–2.5	
F	–103.5	–3.5	–2.4	–105.4	–102.9	-51.8	-53.7	-51.3	

A. Optimized Cartesian Coordinates (Independent species)

1) $ReO4^-$

Re	0.00025300	0.00003700	0.00003800
O	-0.58318900	-0.56373500	-1.55422500
O	-0.60306700	-1.05249600	1.26574500
O	-0.56941900	1.63455500	0.27909100
O	1.75330100	-0.01867500	0.00903500

2) 3

C	-1.21103800	0.22584400	-0.00000500
N	0.00000000	0.84862000	-0.00000600
C	1.21103800	0.22584500	-0.00000400
C	1.21252400	-1.16278900	0.00000000
C	0.00000000	-1.85569200	0.00000300
C	-1.21252400	-1.16278900	-0.00000100
H	0.00000000	1.86709300	-0.00001000
C	2.43537300	1.08648700	0.00000300
H	2.15907300	-1.69074900	0.00000000
H	0.00000000	-2.94145400	0.00000500
H	-2.15907300	-1.69074900	-0.00000200
H	2.46422100	1.72980800	-0.88786200
H	3.33454200	0.46809200	-0.00007800
H	2.46429400	1.72967900	0.88796100
C	-2.43537400	1.08648700	0.00000400
H	-2.46430200	1.72966400	0.88797200
H	-3.33454200	0.46809200	-0.00009600
H	-2.46421300	1.72982200	-0.88785100

3) Diol

O	-3.39436500	-0.40395800	-0.68459900
O	-1.72066900	1.05340600	1.13153000
C	-1.98922200	-0.26914000	-0.83335700
C	-1.23085300	-0.12306800	0.49071700
C	0.26444100	-0.07304700	0.24190900
C	0.86236500	1.10057900	-0.23825100
C	2.23173900	1.13711700	-0.50646800
C	3.01956900	0.00048200	-0.30024100
C	2.43089300	-1.17227600	0.17886200
C	1.06057500	-1.20552500	0.44917000
H	-3.58183000	-1.16225300	-0.10944900
H	-1.83908000	0.63434000	-1.43110700
H	-1.56249200	-1.12153300	-1.38327600
H	-1.45387300	-1.00732800	1.11366100
H	-1.20309600	1.19929400	1.93913800
H	0.24922500	1.98433600	-0.39051300
H	2.68471800	2.05286300	-0.87712100
H	4.08576000	0.03045000	-0.50780100
H	3.03763700	-2.05782700	0.34825300
H	0.60626400	-2.11865700	0.82872600

4) Styrene

C	-0.51521800	-0.22276100	-0.00000400

C	-0.01216700	1.09156700	-0.00000200
C	1.35945700	1.33158600	0.00000300
C	2.26540200	0.26439300	0.00000600
C	1.78278300	-1.04548000	0.00000400
C	0.40739000	-1.28308200	-0.00000200
C	-1.95392300	-0.53238700	-0.00000900
H	-0.69847200	1.93307400	-0.00000500
H	1.72580000	2.35486000	0.00000500
H	3.33511300	0.45485100	0.00001000
H	2.47533600	-1.88300300	0.00000600
H	0.03742200	-2.30598000	-0.00000300
C	-2.97557700	0.33664000	0.00000300
H	-2.18718900	-1.59729400	-0.00002400
H	-2.83349000	1.41414700	0.00001800
H	-4.00339900	-0.01350700	-0.00000200

5) PPh_3

P	-0.00036900	-0.00050800	-1.27440700
C	0.38056500	1.60665900	-0.44497400
C	1.40808600	2.38677800	-1.00032700
C	-0.29246400	2.08544200	0.68842400
C	1.77069300	3.60517700	-0.42447100
H	1.92813700	2.03420500	-1.88837000
C	0.06101100	3.31185700	1.25779300
H	-1.09361400	1.50023100	1.12899100
C	1.09523500	4.07237700	0.70700400
H	2.57234100	4.19337300	-0.86357200
H	-0.47122900	3.67029400	2.13533000
H	1.36957300	5.02515300	1.15203300
C	-1.58252900	-0.47391000	-0.44472800
C	-2.77189800	0.02600700	-1.00001800
C	-1.66042900	-1.29605000	0.68867200
C	-4.00828800	-0.26923300	-0.42407700
H	-2.72662600	0.65267100	-1.88807000
C	-2.89920600	-1.60330000	1.25808300
H	-0.75255700	-1.69678800	1.12857900
C	-4.07501500	-1.08803300	0.70723500
H	-4.91857500	0.13092000	-0.86303000
H	-2.94358100	-2.24323900	2.13576700
H	-5.03725800	-1.32682300	1.15239600
C	1.20108600	-1.13361800	-0.44460900
C	1.36321500	-2.41373400	-0.99938500
C	1.95250800	-0.78894900	0.68805500
C	2.23815400	-3.33599000	-0.42366500
H	0.79697200	-2.68878900	-1.88657500
C	2.83887900	-1.70731300	1.25739600
H	1.84536500	0.19785000	1.12760100
C	2.98105100	-2.98341400	0.70707600
H	2.34709100	-4.32447200	-0.86237100
H	3.41581900	-1.42480400	2.13440800
H	3.66975100	-3.69667400	1.15209400

6) $OPPh_3$

O	-0.00066300	-0.00149200	2.47482700
P	-0.00096200	-0.00070000	0.96904300
C	1.17389500	-1.19728600	0.25006300
C	1.40875600	-2.37961000	0.96680000
C	1.82408800	-0.98697300	-0.97340600
C	2.27408500	-3.34764900	0.45548600
H	0.92192200	-2.52410800	1.92707000
C	2.68906200	-1.95808100	-1.48322200
H	1.66629900	-0.06292100	-1.52213600
C	2.91208100	-3.13953600	-0.77123100
H	2.45536500	-4.26079000	1.01597300
H	3.19368500	-1.78822800	-2.43062300
H	3.58794800	-3.89285400	-1.16719800
C	0.44975900	1.61519200	0.25141900
C	1.36977700	2.40047400	0.96124800
C	-0.06767200	2.08165600	-0.96447500
C	1.77880900	3.63290100	0.45043100
H	1.74643300	2.04480300	1.91606100
C	0.34408300	3.31554900	-1.47377900
H	-0.79911200	1.49025300	-1.50764500
C	1.26927600	4.08987200	-0.76894500
H	2.48962000	4.23910500	1.00548800
H	-0.06297400	3.67417500	-2.41546600
H	1.58648700	5.05101200	-1.16476600
C	-1.62553500	-0.41832600	0.25124400
C	-2.76556300	-0.01978500	0.96434400
C	-1.77098500	-1.09548600	-0.96698500
C	-4.03750100	-0.28329200	0.45456000
H	-2.64560100	0.48086300	1.92088400
C	-3.04553300	-1.35749200	-1.47514300
H	-0.89316700	-1.42875800	-1.51297300
C	-4.17869500	-0.94911500	-0.76691800
H	-4.91782100	0.02475500	1.01220900
H	-3.15268700	-1.88649600	-2.41839900
H	-5.16978100	-1.15645100	-1.16168200

B. Optimized Cartesian Coordinates for Pathway A with Lutidinium salt

1) A

Re	-1.49576400	0.00000300	-0.07873800
O	-3.19175300	0.00024800	0.27455200
O	-1.04229600	1.42053100	-0.98632200
O	-1.04267100	-1.42070900	-0.98621300
O	-0.53232100	-0.00006000	1.42314100
C	2.50120500	-1.20125000	0.26036800
N	1.96067100	0.00001000	0.57184400
C	2.50125400	1.20124900	0.26036500
C	3.73339600	1.21121400	-0.38789000
C	4.34922500	-0.00003700	-0.70613700
C	3.73335000	-1.21125900	-0.38789000
H	0.99907200	0.00001900	1.03109200
C	1.70131600	2.41829500	0.60252400
H	4.19077000	2.15943100	-0.64625500
H	5.30919200	-0.00005800	-1.21431200
H	4.19068000	-2.15949700	-0.64626100
H	0.78693300	2.43744600	-0.00745800
H	2.27985000	3.32466800	0.41177000
H	1.39050400	2.40288900	1.65241300
C	1.70123500	-2.41827300	0.60254600
H	1.39050400	-2.40288000	1.65245900
H	2.27972100	-3.32466000	0.41172500
H	0.78679800	-2.43738600	-0.00736000

2) TS_1

C	3.66989400	0.77594000	1.19498600
C	4.80259700	1.58620100	1.07631000
C	5.35203600	1.79506100	-0.18761400
C	4.76055800	1.19512600	-1.29714500
C	3.62731200	0.39517800	-1.11471800
H	5.24006900	2.03945000	1.96023600
H	6.23319000	2.42006600	-0.30635500
H	5.16537100	1.33850900	-2.29393800
N	3.11221400	0.20356800	0.11317300
C	3.01673400	0.49159100	2.52037600
C	2.93016800	-0.28489400	-2.25942000
O	-1.37715400	-1.47429100	-0.70952500
O	0.91243300	-3.02062400	-1.73168700
P	-1.25375700	0.55870400	-0.08929600
H	1.97795100	0.83694900	2.51488600
H	2.99792100	-0.58649900	2.71586000
H	3.54697600	0.98724200	3.33837700
H	2.87741700	-1.36777600	-2.10627300
H	1.89739500	0.07024300	-2.33921000
H	3.43952200	-0.08702000	-3.20666600
H	1.71034700	-0.53281600	0.29892800
Re	0.07888400	-2.48588800	-0.31060300
O	-0.23316200	-3.67406300	0.90607900
O	0.74282600	-0.87024900	0.43375000
C	-2.62740300	1.15684700	-1.14136700

C	-3.55880900	0.22932600	-1.64047100
C	-2.79845900	2.52054000	-1.43502700
C	-4.63807400	0.66217400	-2.41311900
H	-3.42687700	-0.82445800	-1.42525900
C	-3.87673500	2.94775500	-2.21208100
H	-2.09220000	3.25051700	-1.05324900
C	-4.79962800	2.01978900	-2.70302300
H	-5.35028200	-0.06516100	-2.79339300
H	-3.99630200	4.00581900	-2.43013700
H	-5.63855300	2.35292400	-3.30825200
C	-0.05412700	1.94347100	-0.14279300
C	0.52923400	2.26838400	-1.37958400
C	0.41355200	2.58018800	1.01589700
C	1.56308900	3.19988200	-1.45412600
H	0.17137800	1.78668200	-2.28641100
C	1.45191700	3.51128100	0.93850500
H	-0.03473300	2.34990000	1.97727000
C	2.03484200	3.81987200	-0.29245000
H	2.00795000	3.43510500	-2.41731600
H	1.80611700	3.99554100	1.84500900
H	2.85112500	4.53430200	-0.34749600
C	-1.93601700	0.56246200	1.60689800
C	-1.24228300	-0.10082900	2.63336400
C	-3.15444400	1.19511000	1.90140000
C	-1.75160600	-0.11208900	3.93273500
H	-0.31235700	-0.60899300	2.40660200
C	-3.66134700	1.17705700	3.20225400
H	-3.70694900	1.70110400	1.11691100
C	-2.96082200	0.52639100	4.22147000
H	-1.20793100	-0.63296500	4.71626200
H	-4.60533700	1.67079700	3.41725900
H	-3.35926900	0.50954000	5.23232300

3) B

Re	-1.65377700	-0.00246100	-0.05062400
O	-3.28249100	0.56389500	-0.13870900
O	-1.11232600	-1.26785100	-1.10848800
O	-0.47400100	0.67004200	1.09812600
H	0.98311600	0.30796800	0.76892300
N	1.98523400	0.13378200	0.41341600
C	2.68216200	1.22162900	0.01123600
C	3.96695800	1.03326500	-0.48927900
C	4.48640700	-0.26035900	-0.56740700
C	3.72214700	-1.35063000	-0.15300900
C	2.43676800	-1.13905000	0.34265000
C	1.99681000	2.54891800	0.12541200
H	4.54332300	1.89147800	-0.81574300
H	5.48778600	-0.41852400	-0.95721700
H	4.10630200	-2.36239500	-0.21638300
C	1.50411000	-2.22842700	0.76878400
H	2.03186500	-3.18265100	0.83131800
H	0.68366300	-2.31482700	0.04334800
H	1.05072100	-2.00314000	1.73954900

H	2.65840500	3.35213900	-0.20597700
H	1.68610300	2.73941500	1.15823800
H	1.08370700	2.55787000	-0.48092600

4) TS_2

Re	-1.13682500	-1.64867400	-0.16646500
O	-0.52615400	-3.24565100	-0.83556000
O	-0.84176100	-0.37601800	1.05080800
O	-2.65113200	-1.26733600	-0.89199100
O	1.06996800	-1.97195000	0.12236800
C	2.17861400	-1.19820000	-0.28300500
C	2.69728300	-0.33731700	0.88268600
C	3.94285000	0.41052200	0.46067600
C	3.89420400	1.75548500	0.07659900
C	5.04789600	2.41081800	-0.36331400
C	6.26541900	1.72874000	-0.42812900
C	6.32328500	0.38593900	-0.04202300
C	5.17011500	-0.26415700	0.40107700
H	2.95145200	2.28651500	0.14491200
H	4.99639000	3.45794900	-0.65194100
H	7.16245900	2.23910400	-0.76875800
H	7.26686100	-0.15234000	-0.07905700
H	5.22325300	-1.30588500	0.71091300
H	2.94901100	-1.02197400	1.70774600
H	1.91265400	-0.53633100	-1.12200000
H	2.98321700	-1.86590300	-0.61885900
O	1.70833900	0.58640000	1.31659800
H	0.85782100	0.10285500	1.40838400
H	0.57073600	-2.95776800	-0.50604400
N	-2.17435100	1.78705200	0.33216000
H	-1.63141800	0.93487300	0.66462000
C	-1.52762700	2.68452600	-0.44683300
C	-3.47806400	1.86430700	0.68495200
C	-2.24198000	3.79657200	-0.88787700
H	-1.74495900	4.53361000	-1.50834400
C	-3.58404000	3.93557100	-0.53431800
H	-4.14685900	4.79888200	-0.87737700
C	-4.20968800	2.96544800	0.25042200
H	-5.25544200	3.05068400	0.52289300
C	-0.10642900	2.39123000	-0.80973800
H	0.36238700	3.27136800	-1.25610600
C	-4.03213200	0.73220000	1.49121500
H	-5.05269800	0.95083700	1.81260300
H	-0.07715400	1.57181300	-1.53973200
H	0.48373000	2.05511300	0.05012200
H	-3.41088900	0.53454000	2.37101600
H	-4.03056400	-0.18045600	0.88263400

5) C

Re	-0.97086000	-1.77274600	-0.03613400
O	-0.92219000	-3.54060500	0.77005400
O	-1.37820600	-0.44022000	1.08487300
O	-1.68447000	-1.76910600	-1.60924000

O	0.94442100	-2.20003100	0.00652200
C	1.92500100	-1.29866600	-0.47866900
C	2.44560600	-0.36849600	0.63221000
C	3.61999600	0.43803500	0.13033800
C	3.41779000	1.60735400	-0.61438900
C	4.50520600	2.31761100	-1.12735200
C	5.80953000	1.86501100	-0.90552300
C	6.01880400	0.69870300	-0.16475000
C	4.92872100	-0.00723800	0.35047000
H	2.40385300	1.95926300	-0.77709200
H	4.33566600	3.22503600	-1.70170400
H	6.65570500	2.41851200	-1.30396200
H	7.02910500	0.34211500	0.01797700
H	5.09509200	-0.91061300	0.93332800
H	2.76760100	-1.00104500	1.47242500
H	1.53278700	-0.68796200	-1.30405700
H	2.76289000	-1.89912300	-0.85709600
O	1.43144300	0.53502000	1.08085900
H	0.60525000	0.03932800	1.23440200
H	0.01160000	-3.84516100	0.78626000
N	-2.20943800	1.94133600	0.37274100
H	-1.90913300	0.95705300	0.67964800
C	-1.61618400	2.99676100	0.98040400
C	-3.13316000	2.04275300	-0.61400000
C	-1.96582800	4.27866000	0.56067000
H	-1.50216300	5.13585100	1.03558700
C	-2.90300300	4.43583200	-0.45969600
H	-3.17918900	5.43194400	-0.79334900
C	-3.49343700	3.31666300	-1.04696300
H	-4.23097300	3.41903600	-1.83479900
C	-0.61525500	2.71245800	2.05500900
H	-0.39730600	3.62202300	2.61974000
C	-3.70907200	0.77756600	-1.16788400
H	-4.49442400	1.00544700	-1.89197900
H	0.31913800	2.32906900	1.62500900
H	-0.98457200	1.94239600	2.74001800
H	-4.13393400	0.16220900	-0.36709500
H	-2.94270000	0.16267600	-1.65619800

6) TS3

Re	1.99732200	-0.55112700	-0.19832000
O	0.43997800	-1.26309700	-0.65267900
O	3.14533700	0.19300800	1.50797700
O	3.32478800	-1.55271500	-0.62191000
O	2.09908600	1.30071900	-0.88850600
C	1.81502800	2.41553200	-0.05121300
C	0.65071100	2.06971400	0.88258900
C	-0.71916500	2.08046200	0.22733300
C	-0.89716800	1.96748900	-1.15807600
C	-2.18093900	1.97014400	-1.70975400
C	-3.30567300	2.05920300	-0.88612500
C	-3.13859600	2.15423100	0.49883300
C	-1.85412900	2.17281000	1.04472700

H	-0.02922300	1.86466600	-1.80111900
H	-2.30093900	1.89679900	-2.78773100
H	-4.30327700	2.05932500	-1.31773200
H	-4.00603600	2.22593000	1.15003400
H	-1.72472000	2.25680100	2.12169000
H	0.63390400	2.77668300	1.72574700
H	1.57601200	3.26737600	-0.70062400
H	2.69198000	2.70159300	0.55025100
O	0.89848900	0.75682600	1.40185900
H	2.04881100	0.66291900	1.75611200
H	3.79266000	0.86879700	1.24369100
H	-0.98287600	-1.22513400	-0.18231800
N	-2.03707800	-1.25481900	0.06079300
C	-2.89766000	-1.29367100	-0.97856400
C	-4.26391300	-1.31820600	-0.70975500
C	-4.69821400	-1.30746100	0.61443900
C	-3.77032900	-1.27234700	1.65464500
C	-2.40823900	-1.24942200	1.36146200
C	-2.31083000	-1.35369400	-2.35620200
H	-4.96789500	-1.34278200	-1.53413800
H	-5.76143100	-1.32480500	0.83678100
H	-4.08863400	-1.26563200	2.69108700
C	-1.32146700	-1.24217300	2.38596900
H	-0.61494900	-0.42204300	2.20097900
H	-0.74059300	-2.17110700	2.32698300
H	-1.74332300	-1.15506100	3.39021400
H	-2.09020600	-2.39549300	-2.62159800
H	-1.37115100	-0.80054400	-2.40647700
H	-3.01561600	-0.95361300	-3.08918700

7) D

Re	2.02491400	-0.47587100	0.05174100
O	0.79778600	-1.74400300	-0.19038500
O	3.62669200	-0.89370900	0.51330800
O	2.05052000	0.93456200	-1.31361900
O	1.20867800	1.00373800	1.05513500
C	1.85329700	2.27557800	-0.84305800
C	0.88377200	2.21855800	0.32360600
C	-0.58226300	2.17763200	-0.05958300
C	-1.01891800	1.60289100	-1.26362200
C	-2.38028000	1.53843200	-1.56640800
C	-3.32958400	2.03285200	-0.66728000
C	-2.90595400	2.60189200	0.53653900
C	-1.54234900	2.67406700	0.83225400
H	1.48156600	2.87964900	-1.67915900
H	2.81516400	2.69234700	-0.51315900
H	1.04832200	3.04813100	1.02174800
H	-0.28516100	1.20607700	-1.95914400
H	-2.70239100	1.10340100	-2.50969100
H	-4.38871000	1.98105700	-0.90605600
H	-3.63497500	2.99700300	1.23981000
H	-1.21400700	3.12199100	1.76761100
H	-0.66672600	-1.52136400	0.03839400

N	-1.73650200	-1.42674000	0.17149800
C	-2.50775700	-1.76602900	-0.88466500
C	-3.88939900	-1.69539500	-0.74589500
C	-4.43005900	-1.25993900	0.46509400
C	-3.59219600	-0.90005300	1.51770300
C	-2.20954200	-0.99444000	1.36059200
C	-1.79626000	-2.17047900	-2.13948100
H	-4.52505500	-1.96918900	-1.58053000
H	-5.50776400	-1.19376800	0.58396700
H	-3.99421200	-0.54744600	2.46054900
C	-1.21184400	-0.66446300	2.42362000
H	-1.71691100	-0.27349000	3.30983400
H	-0.47954500	0.07066200	2.06437100
H	-0.64610600	-1.56089500	2.70478400
H	-2.50300300	-2.56208600	-2.87464200
H	-1.02760300	-2.92094100	-1.93115700
H	-1.27932300	-1.30492700	-2.57056000

8) TS_4

Re	2.02830600	-0.45765000	0.09837500
O	0.85333400	-1.77805500	-0.14881800
O	3.59664100	-0.88198800	0.69116100
O	2.12580300	0.70979700	-1.34199600
O	1.25232100	0.84308900	1.06439200
C	1.74813100	2.29361100	-1.16687600
C	0.85639600	2.51349800	-0.06204800
C	-0.58212300	2.35336300	-0.19873800
C	-1.15982200	1.65702000	-1.28475200
C	-2.54122900	1.50549200	-1.38822800
C	-3.39045900	2.01613600	-0.40081000
C	-2.83404400	2.68833700	0.69438300
C	-1.45429800	2.85267100	0.79310800
H	1.33435300	2.46049800	-2.15991400
H	2.72670600	2.75782200	-1.05802100
H	1.20204900	3.10855500	0.77445200
H	-0.51401300	1.23307000	-2.04836700
H	-2.96034200	0.98261900	-2.24504400
H	-4.46710200	1.89471300	-0.48381900
H	-3.48071300	3.09317800	1.46947700
H	-1.03077700	3.37900900	1.64520800
H	-0.64891500	-1.52237000	0.06783900
N	-1.71592700	-1.44768400	0.15890300
C	-2.43790200	-1.84219500	-0.91378700
C	-3.82484600	-1.81974500	-0.82153700
C	-4.42232900	-1.37521800	0.35910100
C	-3.63441400	-0.94970300	1.42531000
C	-2.24516600	-0.99352500	1.31592800
C	-1.67190400	-2.24476700	-2.13645100
H	-4.42108800	-2.13870600	-1.66910800
H	-5.50508600	-1.34866700	0.44118300
H	-4.08040000	-0.58168800	2.34196400
C	-1.29774300	-0.58100900	2.39485400
H	-1.84457500	-0.15471000	3.23854700

H	-0.57493200	0.15395200	2.01882000
H	-0.72090800	-1.44501700	2.74700300
H	-2.33260400	-2.71498500	-2.86834800
H	-0.85468700	-2.92683100	-1.88399400
H	-1.21270500	-1.35939500	-2.59297200

9) **$TS_{off\text{-}cycle}$**

Re	-0.21686900	-0.17001700	-0.36055200
O	-0.68277600	-1.25846500	0.86770600
O	-1.07467300	0.16289500	-2.01423600
O	0.39709300	1.44362500	0.51042100
C	1.81301400	1.48713300	0.76808000
C	2.52221500	0.75405200	-0.36177500
C	3.88248200	0.23199400	0.01807900
C	4.00633400	-0.91372100	0.81590000
C	5.26690300	-1.36596400	1.20742600
C	6.41764100	-0.67621400	0.81017500
C	6.30048800	0.46413600	0.01200500
C	5.03734200	0.91140400	-0.38526600
H	3.11277200	-1.45622800	1.11023700
H	5.35303900	-2.25925100	1.82047500
H	7.39864800	-1.03007300	1.11568400
H	7.18971900	1.00035200	-0.30869000
H	4.94815600	1.79280900	-1.01683900
H	2.60703000	1.41320300	-1.23594100
H	2.01293700	0.99579000	1.72945500
H	2.11057600	2.53849100	0.83740000
O	1.65249500	-0.34734300	-0.74615300
H	-2.04954900	0.11161100	-1.83977500
N	-3.30096600	0.06664100	-0.34591000
C	-3.63160300	1.22390300	0.26450300
C	-4.63116000	1.26723500	1.24186800
C	-5.29231400	0.09037800	1.58770300
C	-4.94404700	-1.09831500	0.94965600
C	-3.93458700	-1.07698100	-0.01734800
C	-2.86540600	2.45822700	-0.13209800
H	-4.88037100	2.21003800	1.71843800
H	-6.07239400	0.10011700	2.34426900
H	-5.44044100	-2.03208600	1.19433300
C	-3.48188400	-2.33347300	-0.71066500
H	-2.55084000	-2.69240200	-0.25514900
H	-3.28464800	-2.14776800	-1.77142900
H	-4.23052200	-3.12669100	-0.62689400
H	-3.36325300	3.36191600	0.23171300
H	-2.76760800	2.52447400	-1.22047100
H	-1.85093700	2.43203800	0.28457300

10) **$PS_{off\text{-}cycle}$**

Re	0.43300800	-0.54562700	0.20469200
O	0.27011700	-2.16449500	-0.27082600
O	0.84894000	-0.46625000	2.14258500
O	0.02388100	0.65432500	-1.30536100
C	-1.38332700	0.83563500	-1.46616400

C	-2.01105100	0.97703400	-0.07205500
C	-3.46837000	0.58149400	-0.05834900
C	-3.84683400	-0.74417300	0.18760600
C	-5.19208000	-1.11364700	0.13015900
C	-6.17270200	-0.16453300	-0.17544400
C	-5.80055400	1.16077500	-0.41670200
C	-4.45452400	1.53027400	-0.35362600
H	-3.08384800	-1.47410800	0.43833100
H	-5.47609600	-2.14377600	0.32937900
H	-7.21939700	-0.45405000	-0.21745400
H	-6.55670300	1.90734500	-0.64559900
H	-4.16827000	2.56536800	-0.53026000
H	-1.91562500	2.01897400	0.26881900
H	-1.80803700	-0.03458600	-1.98650000
H	-1.56368300	1.72807800	-2.07813500
O	-1.24782400	0.17014900	0.83398600
H	1.80516100	-0.48700000	2.31875600
N	2.42770600	0.19400400	-0.06524500
C	2.67424300	1.49781400	0.27559800
C	3.94646700	2.04473900	0.11161900
C	4.98280100	1.27535200	-0.40415700
C	4.71440800	-0.04567200	-0.74891600
C	3.43628500	-0.57419000	-0.57813100
C	1.55290300	2.34770600	0.80975200
H	4.10574100	3.07984900	0.39380300
H	5.97608100	1.69389700	-0.53484400
H	5.49054800	-0.68475800	-1.15555700
C	3.15027300	-1.99479000	-0.96302000
H	2.37511400	-2.04380700	-1.73487200
H	2.78323500	-2.57741200	-0.11154900
H	4.05783700	-2.46784100	-1.34527900
H	1.94785300	3.30390100	1.16185900
H	1.03206100	1.86123100	1.64205500
H	0.81996700	2.53997200	0.01980800

C. Optimized Cartesian Coordinates for Pathway B with Lutidinium salt

1) A (Same as in Pathway A)

2) TS_1

Re	2.55335500	-0.00986700	0.15030000
O	3.78748800	1.01715200	0.77492200
O	3.27746900	-1.68470400	0.45652200
O	2.34524300	0.45080900	-1.50718300
O	1.10487300	0.40794000	1.07100500
O	1.21783500	-1.93675700	-0.55576600
C	-0.06223200	-2.20628000	-0.07476500
C	-1.07622100	-1.83138800	-1.18317400
C	-2.50036200	-1.71860900	-0.69049300
C	-3.32235000	-0.65965500	-1.09660900
C	-4.63642800	-0.55772400	-0.63233600
C	-5.15217700	-1.51164900	0.24794200
C	-4.34295200	-2.57954200	0.65017500
C	-3.03171200	-2.68319200	0.18097300
H	-2.92074400	0.08166600	-1.77837900
H	-5.25913000	0.27052400	-0.96193500
H	-6.17478900	-1.43342200	0.60754700
H	-4.73368500	-3.33466900	1.32730000
H	-2.41846100	-3.52156900	0.49875600
H	-1.02624100	-2.61235700	-1.95987700
H	-0.28115000	-1.62086600	0.83388700
H	-0.17255900	-3.27200000	0.17742800
O	-0.67474800	-0.59100500	-1.76326200
H	0.29712500	-0.67886900	-1.85758000
H	2.38237400	-2.22646300	0.05792600
N	-1.21588800	1.60241700	0.43501200
C	-1.27614000	2.49117000	-0.58602700
C	-2.45728600	3.20551000	-0.75570500
C	-3.52194600	2.99907300	0.12373800
C	-3.40496800	2.07572200	1.15826900
C	-2.22061900	1.35752300	1.30408300
H	-0.31921500	1.07535100	0.57444500
H	-2.52938300	3.92132600	-1.56657600
H	-4.44425900	3.55877400	-0.00230900
H	-4.22368800	1.88710500	1.84291800
C	-0.06383400	2.64901900	-1.44467100
H	0.80054800	2.95985500	-0.84759800
H	0.19682600	1.69766200	-1.91610100
H	-0.24133800	3.39826800	-2.21920800
C	-2.01103200	0.30201800	2.34305800
H	-2.40929500	-0.64971600	1.97049200
H	-0.94991800	0.16406600	2.56393700
H	-2.54718400	0.55897300	3.26072500

3) B

Re	2.43329400	-0.08705000	0.09627500

O	3.71158900	0.96409200	0.60290500
O	3.68113500	-1.56328900	0.28560700
O	2.11087400	0.37614700	-1.55067300
O	1.10124800	0.51455300	1.11084800
O	1.31132700	-1.84285600	-0.01807800
C	-0.05253800	-1.96164700	0.24337900
C	-0.91320900	-1.73633600	-1.02265200
C	-2.38902900	-1.77731000	-0.68436300
C	-3.22923400	-0.69689200	-0.98142200
C	-4.57911000	-0.72174800	-0.61966100
C	-5.11258300	-1.82705000	0.04660900
C	-4.28532400	-2.91819700	0.33281900
C	-2.93867200	-2.89448400	-0.03477200
H	-2.81314200	0.15701100	-1.50284400
H	-5.21605700	0.12493800	-0.86462400
H	-6.16218600	-1.84690100	0.32769800
H	-4.69000800	-3.79127100	0.83792400
H	-2.31333400	-3.75584700	0.18313200
H	-0.67703800	-2.53923300	-1.73851300
H	-0.35830100	-1.24065700	1.01321400
H	-0.25401200	-2.97152100	0.62907900
O	-0.62286700	-0.47629600	-1.62092800
H	0.33210800	-0.44202600	-1.82022200
H	3.15563300	-2.38404300	0.20920500
N	-1.17957700	1.76018600	0.53456000
C	-1.16175400	2.66687500	-0.47277000
C	-2.34135200	3.34612000	-0.75993400
C	-3.48757700	3.08940000	-0.00565100
C	-3.44875900	2.15628900	1.02623900
C	-2.26264500	1.47471100	1.28926100
H	-0.28210300	1.23657400	0.73223900
H	-2.34941100	4.07363400	-1.56349400
H	-4.41005600	3.61948400	-0.22451000
H	-4.32778200	1.93290400	1.61972600
C	0.12932600	2.88660600	-1.19176000
H	0.91817800	3.18297400	-0.49118600
H	0.46932700	1.96678100	-1.67685600
H	0.01570400	3.66858200	-1.94564800
C	-2.13878400	0.41684400	2.34062100
H	-2.49409600	-0.53767000	1.93319000
H	-1.10255500	0.28845200	2.66157300
H	-2.75984900	0.66742500	3.20526100

4) TS_2

O	-0.32557300	-1.64192000	-0.03371100
O	-1.34813300	-0.01171400	1.86061800
C	0.28179500	-2.23061500	1.11129400
H	-0.44979000	-2.33218100	1.91884200
H	0.59822200	-3.24003900	0.82555800
C	1.46841100	-1.39743600	1.62159200
H	1.78851000	-1.90414900	2.55312300
O	-2.21675100	-1.27718400	-1.86514400
H	-1.87920500	-0.43491900	2.55059400

O	1.05795700	-0.08553200	1.92741700
H	-0.20776600	-0.06964600	2.03272000
Re	-1.95563100	-0.64300300	-0.27928500
O	-1.77586200	1.05743100	-0.56774300
O	-3.41918400	-1.02343400	0.56002600
C	2.67795400	-1.37388600	0.68927500
C	3.67098300	-0.41045200	0.92456900
C	2.85427600	-2.26234000	-0.37819500
C	4.80285000	-0.32954200	0.11196200
H	3.53915000	0.28404700	1.74871000
C	3.98465800	-2.18275600	-1.19801700
H	2.09841100	-3.00657700	-0.60487500
C	4.96315000	-1.21574900	-0.95894400
H	5.56035300	0.42379300	0.31380700
H	4.09300100	-2.87385300	-2.02988300
H	5.84074300	-1.15348600	-1.59682300
H	1.09395500	1.00771800	0.81438200
C	0.31866500	4.17186600	-1.17145600
C	0.79312700	3.04487300	-1.83763900
C	1.09489700	1.89278000	-1.11674100
C	0.44705900	2.97267300	0.90971400
C	0.14445400	4.13721500	0.21018800
H	0.07315600	5.07094900	-1.72930100
H	0.91623000	3.03923800	-2.91464400
H	-0.24064500	4.99449000	0.75084400
N	0.93052200	1.90868000	0.22659100
C	0.22133900	2.81883500	2.38165200
H	1.03118900	2.25691100	2.85440600
H	0.11939600	3.79830900	2.85533600
H	-0.69955400	2.24398100	2.53871100
C	1.59588100	0.64144500	-1.76359400
H	1.45599000	0.69972400	-2.84540900
H	2.66126200	0.49518200	-1.55487500
H	1.06942800	-0.23763300	-1.38666700

5) C

Re	2.11718000	-0.40986900	0.01881200
O	1.72059800	0.75664000	-1.19804600
O	2.00740700	0.29593200	1.59268400
O	3.78755700	-0.75574500	-0.20867600
O	1.50134400	-2.20396700	-0.29493700
C	0.15564800	-2.65936400	-0.19809400
C	-0.78605200	-1.49119300	-0.49304600
C	-2.22788700	-1.78962300	-0.16255300
C	-2.67646900	-1.74384900	1.16399000
C	-4.00284600	-2.05210300	1.46863300
C	-4.89290500	-2.41208800	0.45111000
C	-4.45052700	-2.45895100	-0.87318600
C	-3.12299900	-2.14528700	-1.17729100
H	-1.98330000	-1.45316300	1.94780900
H	-4.34373500	-2.01021600	2.49963400
H	-5.92584100	-2.65028800	0.68942100
H	-5.13792700	-2.73159600	-1.66930300

H	-2.78179800	-2.17193300	-2.21018100
H	-0.69379300	-1.22313300	-1.55520300
H	-0.01987200	-3.03648900	0.81663800
H	0.02472800	-3.47455000	-0.91649700
O	-0.24235200	-0.45282800	0.31347200
H	-0.66470500	0.47144300	0.12771300
N	-1.15352700	1.98810900	-0.00966000
C	-1.60402200	3.92398100	-1.33128500
C	-1.62082500	4.70801400	-0.17861800
C	-1.39730600	4.10821200	1.05927800
C	-1.16084000	2.73063900	1.11352700
C	-1.36103800	2.55270000	-1.21284300
H	-1.76951400	4.36247900	-2.31013300
H	-1.80411300	5.77707300	-0.24515100
H	-1.39888100	4.69257600	1.97378600
C	-0.89450900	2.00917700	2.40688700
H	0.10142300	1.55200500	2.39343300
H	-0.95900100	2.69187800	3.25872600
H	-1.62056400	1.20070300	2.54983200
C	-1.30362600	1.63800100	-2.40580500
H	-0.30477100	1.19349100	-2.48077700
H	-2.03254300	0.82551400	-2.30103400
H	-1.51881700	2.17778600	-3.33216500

6) **TS_3**

Re	-2.10330000	-0.24469600	-0.03755000
O	-1.81083900	0.79764500	1.32102800
O	-1.88088400	0.62634500	-1.52113200
O	-3.79755500	-0.56802600	0.01909200
O	-1.68289900	-2.12837900	0.19231300
C	-0.36703800	-2.65822300	0.13811600
C	0.61033300	-1.54755400	0.53739900
C	2.04931400	-1.86011000	0.20103000
C	2.49113100	-1.80740000	-1.12848600
C	3.81492200	-2.11214200	-1.44627300
C	4.71445500	-2.47560000	-0.43756800
C	4.28088700	-2.53200900	0.88894800
C	2.95413000	-2.22294000	1.20439000
H	1.78907900	-1.51989200	-1.90565200
H	4.14679500	-2.06849900	-2.48039600
H	5.74562200	-2.71224600	-0.68527700
H	4.97376000	-2.81126600	1.67822400
H	2.61916800	-2.26202500	2.23898700
H	0.51726200	-1.38118700	1.62340500
H	-0.15582700	-2.99600700	-0.88475900
H	-0.31650900	-3.51532800	0.81877000
O	0.13034300	-0.42682100	-0.17313900
H	0.72153300	0.66544900	-0.02936800
N	1.20330200	1.79372000	0.03052500
C	1.38535200	2.46554300	-1.12589000
C	1.43780600	2.34135900	1.24062900
C	1.89577100	3.65601600	1.32260200
C	2.09625100	4.38043800	0.14794300

C	1.84159400	3.78374500	-1.08585700
H	2.08305900	4.09888700	2.29479400
H	2.44757000	5.40745000	0.19431100
H	1.98638600	4.32781000	-2.01292500
C	1.07772700	1.73688100	-2.40034900
H	0.04494000	1.37088600	-2.38939200
H	1.22287800	2.39203600	-3.26294200
H	1.73276400	0.86484500	-2.50574200
C	1.17850900	1.47934700	2.44066000
H	0.13582300	1.14214900	2.43617400
H	1.82331000	0.59280000	2.42134000
H	1.37454600	2.03008600	3.36392600

7) D

Re	2.04222500	-0.31644400	0.04630300
O	1.85185800	0.67720000	-1.36923100
O	1.81804300	0.64288700	1.47929000
O	3.72487300	-0.71134200	0.07251700
O	1.61918300	-2.21488500	-0.15792000
C	0.29372500	-2.71557500	-0.12268500
C	-0.64533500	-1.57827200	-0.54473900
C	-2.09646200	-1.83262800	-0.20899800
C	-2.54295200	-1.71980900	1.11546300
C	-3.87825600	-1.96627800	1.43622900
C	-4.78636900	-2.33068000	0.43538900
C	-4.34890700	-2.44704500	-0.88595800
C	-3.01020500	-2.19640000	-1.20407300
H	-1.83267200	-1.43357400	1.88562500
H	-4.21271200	-1.87773000	2.46680400
H	-5.82637400	-2.52242200	0.68523200
H	-5.04774100	-2.72842000	-1.66933900
H	-2.67188300	-2.28265800	-2.23479600
H	-0.54566700	-1.43955000	-1.63600400
H	0.05460700	-3.04192900	0.89852800
H	0.23320600	-3.57657100	-0.79849500
O	-0.13977200	-0.46103600	0.14175200
N	-1.10826400	1.88034300	-0.03180900
H	-0.75249500	0.82831500	0.02179700
C	-1.81000900	4.50694000	-0.17493200
C	-1.62439900	3.90222000	1.06788600
C	-1.26366800	2.55713700	1.12754800
C	-1.27784300	2.42498600	-1.25648200
C	-1.63967000	3.76715200	-1.34534600
H	-2.08672900	5.55586900	-0.23174100
H	-1.75002000	4.46063800	1.98875500
H	-1.77698300	4.21895700	-2.32136200
C	-1.03061600	1.80329100	2.39955700
H	-1.73874700	0.97110600	2.48199700
H	-0.02059900	1.37638900	2.40093700
H	-1.15457200	2.46126800	3.26288600
C	-1.05381000	1.53168700	-2.43729200
H	-0.03049300	1.13820900	-2.41193100
H	-1.74409400	0.68045300	-2.41019600

H	-1.20990300	2.07959200	-3.36944900

8) TS_4

Re	0.29429700	-1.12521700	-1.05594600
O	1.90860000	-1.86112300	-0.46499000
O	0.91431000	-0.72368100	-2.63123500
O	-0.37753900	-2.17891700	0.44944100
O	-1.44904300	-1.64171800	-1.85568000
O	-0.78157900	0.45586500	-0.70447200
C	-2.45197900	-0.65757500	-1.99855700
C	-1.84289600	0.70669600	-1.63021100
C	-2.82461000	1.69015200	-1.03160800
C	-2.47339800	2.46672300	0.07714400
C	-3.38733000	3.36501200	0.63062000
C	-4.66687500	3.49715100	0.08481700
C	-5.02254000	2.72691900	-1.02630000
C	-4.10561600	1.83181900	-1.58160600
H	-3.29671800	-0.89013000	-1.34123200
H	-2.81015700	-0.65697500	-3.03742800
H	-1.37664400	1.14143200	-2.52911900
H	-1.48754100	2.35615300	0.50709400
H	-3.09664500	3.96029000	1.49292000
H	-5.37941300	4.19464600	0.51748900
H	-6.01427800	2.82109900	-1.46114100
H	-4.39634600	1.23665500	-2.44372300
P	2.10416500	-0.00212900	0.19964000
N	-3.04657100	-1.79504200	1.14351000
H	-1.35974800	-2.17916700	0.61411100
C	1.52434100	1.72019900	0.57977300
C	1.13737100	2.10973500	1.86785200
C	1.34921200	2.61899100	-0.48581500
C	0.63301900	3.39472200	2.09631700
H	1.23719800	1.41971400	2.69896200
C	0.85104800	3.89948000	-0.25807000
H	1.60506100	2.31366200	-1.49690300
C	0.49733500	4.29385000	1.03760700
H	0.34764900	3.68779500	3.10328600
H	0.72429700	4.58561800	-1.09085700
H	0.10325500	5.29090700	1.21423400
C	3.59476500	0.32361200	-0.81331100
C	4.34473800	1.49036100	-0.59226700
C	4.01765500	-0.59207300	-1.78693200
C	5.50772900	1.72941900	-1.32574700
H	4.01952900	2.22266500	0.13829000
C	5.17357200	-0.34113400	-2.52672700
H	3.43454100	-1.48827700	-1.95753500
C	5.92381200	0.81491600	-2.29629600
H	6.08068100	2.63427000	-1.14250900
H	5.48550100	-1.05242400	-3.28625300
H	6.82485200	1.00499900	-2.87329900
C	2.58105200	-0.62436400	1.85037400
C	3.62153400	0.02777800	2.52794100
C	1.92443000	-1.70694400	2.44914600

C	4.00369500	-0.39872700	3.80051600
H	4.13924300	0.86365200	2.06870700
C	2.30618800	-2.11949100	3.72827700
H	1.12689500	-2.21368900	1.91559900
C	3.34227300	-1.47133100	4.40548300
H	4.81665800	0.10610000	4.31520400
H	1.79215500	-2.95742000	4.19143400
H	3.63764400	-1.80249900	5.39754700
C	-5.34913700	-1.77419800	0.49616900
C	-4.08485800	-2.37326000	0.51446600
C	-3.20379300	-0.61703600	1.77250800
C	-4.43726600	0.04458700	1.77916000
C	-5.51971600	-0.54338900	1.13022600
H	-6.17271400	-2.25792100	-0.02039300
H	-4.53203600	1.01061700	2.26271400
H	-6.48452200	-0.04368800	1.11177800
C	-3.79265700	-3.66743200	-0.19655900
H	-3.03761600	-3.50048600	-0.97434200
H	-3.37990500	-4.40332000	0.50282800
H	-4.69294900	-4.08514100	-0.65730600
C	-1.98480900	-0.03921800	2.43979600
H	-1.24688900	0.24117100	1.68296800
H	-2.23754300	0.85027900	3.02405900
H	-1.51796500	-0.78125000	3.09597100