Electronic Supplementary Information (ESI) for:

Rhenium Complexes of bidentate, *bis*-bidentate and tridentate N-Heterocyclic Carbene Ligands

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Synthesis

H-Gly-OBzl.TsO: This compound was prepared according to the literature procedure.[1] A mixture of glycine (2.000 g, 26.643 mmol), p-toluene sulfonic acid (5.505 g, 31.971 mmol), benzyl alcohol (13.062 g, 120.791 mmol) in toluene was heated to reflux and the water formed in the reaction was removed using a Dean-Stark receiver. The reaction was judged to be completed when no more water was deposited in the receiver. The mixture was cooled to room temperature and a solid was formed. The solid was collected via filtration and washed with ether. Recrystallization was performed with methanol/ether. A white solid was obtained. (Yield: 4.200 g, 47%) ^{1}H NMR (300MHz) (DMSO-d_6): δ (ppm) 8.26 (s, 2H, NH_2), 7.52-7.49 (d, 2H, $^{3}J_{HH}$ = 7.95 Hz, $H_{Ar\text{-}SO3}$), 7.41-7.36 (m, 5H, $H_{Ar\text{-}CH2O}$), 7.13-7.1 (d, 2H, $^{3}J_{HH}$ = 7.95 Hz, $H_{Ar\text{-}SO3}$), 5.22 (s, 2H, Ar-CH_2-O), 3.89 (s, 2H, CH_2N), 2.28 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) 167.6 C_q, 145.3 C_q, 137.9 C_q, 135.2 C_q, 128.4 $C_{Ar\text{-}CH2O}$, 128.3 $C_{Ar\text{-}CH2O}$, 128.2 $C_{Ar\text{-}CH2O}$, 128.1 $C_{Ar\text{-}SO3}$, 125.5 $C_{Ar\text{-}SO3}$, 66.8 CH$_2$O, 39.5 CH$_2$N, 20.8 CH$_3$.

4.Br_2: A solution of dibromomethane (0.53 g, 3.05 mmol) and 1-methylimidazole (0.50 g, 6.09 mmol) in acetonitrile (15 mL) was heated at 110 °C for 48 h. After cooling to RT the precipitate was collected and washed with ether. The product was obtained as a white crystalline powder. (Yield: 0.83 g, 81%). ^{1}H NMR (500 MHz) (DMSO-d_6): δ (ppm) 9.51 (s, 2H, 2H_{imi} (NCHN)), 8.05 (dd, $^{3}J_{HH}$ = 1.75 Hz, $^{4}J_{HH}$ = 1.75 Hz, 2H, 2H_{imi}), 7.79 (dd, $^{3}J_{HH}$ = 1.75 Hz, $^{4}J_{HH}$ = 1.75 Hz, 2H, 2H_{imi}), 6.74 (s, 2H, CH_2), 3.89 (s, 6H, 2CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) 138.0 2C_{imi} (NCHN), 124.3 2C_{imi}, 121.9 2C_{imi}, 57.9 CH$_2$, 36.2 2CH$_3$.

5.Cl_2: A solution of α,α-dichlorotoluene (3.09 g, 19.19 mmol) and 1-methylimidazole (3.15 g, 38.38 mmol) in PEG 400 (6 mL) was heated at 110 °C for 48 h. After cooling to RT, acetone (10 mL) was added and a brown oil was separated. After carefully decanting the solvent the residual oil was re-suspended in methanol and re-precipitated by the addition of ether. The product was obtained as brown oil. (Yield: 4.75 g, 76%). ^{1}H NMR (500 MHz) (DMSO-d_6): δ (ppm) 9.55 (s, 2H, 2H_{imi} (NCHN)), 8.79

(s, 1H, ArC*H*) 8.05 (dd, $^{3}J_{HH}$ = 1.50 Hz, $^{4}J_{HH}$ = 1.50 Hz, 2H, 2H_{imi}), 7.92 (dd, $^{3}J_{HH}$ = 1.50 Hz, $^{4}J_{HH}$ = 1.50 Hz, 2H, 2H_{imi}), 7.59-7.57 (m, 3H, H_{Ar}), 7.41 (d, $^{3}J_{HH}$ = 7.00 Hz, 2H, H_{Ar}), 3.89 (s, 6H, 2CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) 138.5 2C_{imi} (N*C*HN), 131.6 C_q, 131.5 C_{Ar}, 130.0 2C_{Ar}, 128.0 2C_{Ar}, 125.5 2C_{imi}, 121.5 2C_{imi}, 71.7 Ar*C*H, 36.8 2*C*H_3.

X-ray Crystallography Details:

6.Cl_4: Solved in the triclinic space group *P*-1. The asymmetric unit contains one molecule of the title compound, four chloride anions, two methanol molecules and one water molecule of crystallisation.

12.Cl_3: Solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of the title compound and three Cl^- counter ions. In the case of one of the Cl^- (Cl1) counter ions there is evidence for a mixture of Cl^- and Br^- occupying this position. This mixed anion site was modelled giving a ratio of Cl = 0.73 and Br = 0.27.

14. Solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of the title compound.

Trans-**15**: Solved in the orthorhombic space group *Pnma.* The asymmetric unit contains one half of a molecule of the title compound and one half of a molecule of chloroform. The chloroform molecule is disordered, however aattempts to model the disorder were unsuccessful and as a result the disorder in this solvent molecule was not modelled.

Trans-*trans*-**16**. Solved in the triclinic space group *P*-1. The asymmetric unit contains one molecule of the title compound, one molecule of methanol and one molecule of acetone as solvents of crystallisation.

17.ReO_4 Solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of the title compound and a disordered ReO_4^- counter ion. Disorder was identified in the positions of the Re atom and two of the oxygen atoms for the ReO_4^- counter ion, with each of the disordered atoms occupying two crystallographically independent positions that could be located from the additional residual electron density. Refinement of the site occupancy factors for the disordered atoms gave the value 0.84 and 0.16 respectively.

18: Solved in the triclinic space group *P*-1. The asymmetric unit contains one half of the dinuclear title complex and one acetonitrile molecule of crystallisation. Rotational disorder was identified in the positions of the chlorine ligand and the *trans* carbonyl ligand, with each of these ligands occupying two crystallographically independent positions that could be located from the additional residual electron density. The site occupancy factors for the disordered atoms gave were initially

refined freely and then these were fixed such that one component (Cl and the corresponding trans-CO) was assigned an occupancy of 0.70 and the other 0.30. Additionally, DFIX restraints were placed on all carbonyl CO bond lengths (1.15 ± 0.02 Å) the Re-CO bond lengths (1.94 ± 0.02 Å) and the Re-Cl bond lengths (2.51 ± 0.02 Å).

20: Solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of the title compound and a PF_6^- counter ion.

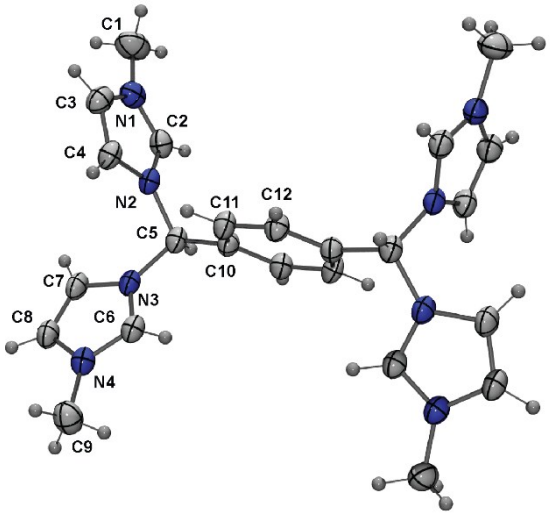

Figure S1. ORTEP structure of **6**.Cl_4. (co-crystallized water and methanol molecules and chloride counter ions omitted for clarity). Thermal ellipsoids are shown at 50% probability.

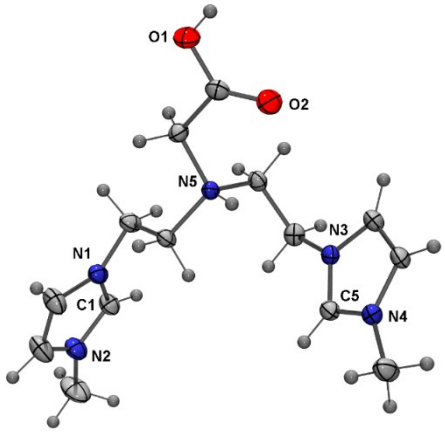

Figure S2. ORTEP structure of **12**.Cl_3.

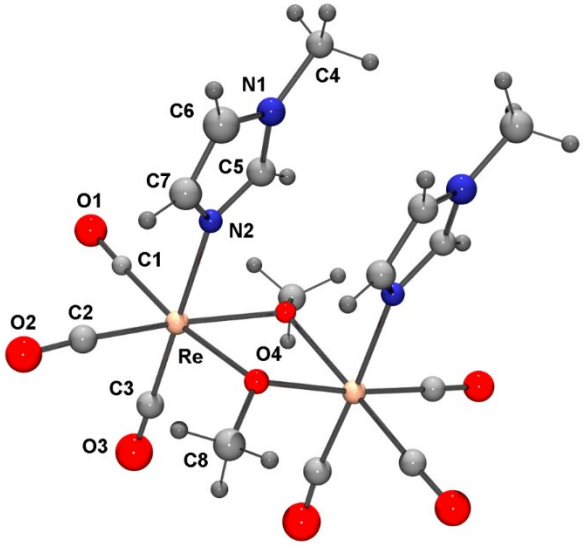

Figure S3. ORTEP structure of the common by-product formed in the synthesis of **15** and **16**.

Table S1 Refinement data

	6.Cl_4	12.Cl_3	14	*trans*-15	*trans-trans*-16	17.ReO_4	18	20
Empirical formula	$C_{26}H_{40}Cl_4N_8O_3$	$C_{14}H_{24}Br_{0.27}Cl_{2.73}N_5O_2$	$C_{12}H_{12}ClN_4O_3Re$	$C_{19}H_{17}Cl_4N_4O_3Re$	$C_{34}H_{36}Cl_2N_8O_8Re_2$	$C_{22}H_{25}N_5O_7Re_2$	$C_{24}H_{28}ClN_6O_3Re$	$C_{19}H_{25}F_6N_5O_5PRe$
Formula weight	654.46	412.85	481.91	677.36	1128.01	843.87	670.17	734.61
Temperature/K	173	173	150	173	172.9	173.02	173.2	173
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$	*P*nma	*P*-1	$P2_1/c$	*P*-1	$P2_1/c$
a/Å	9.8817(3)	10.5678(5)	7.6760(3)	15.0212(4)	9.4195(3)	9.1406(3)	8.0075(3)	9.7542(4)
b/Å	12.7702(6)	18.0774(9)	17.0407(7)	12.3025(4)	13.0035(3)	20.5194(6)	12.8704(5)	18.0646(8)
c/Å	13.4397(5)	10.1355(5)	11.3204(5)	12.4828(3)	16.2478(6)	13.4977(4)	13.4782(5)	13.7100(6)
α/°	107.655(4)	90	90	90	96.224(3)	90	102.922(3)	90
β/°	95.924(3)	106.809(5)	91.879(4)	90	93.276(3)	92.194(3)	100.733(3)	96.253(4)
γ/°	92.500(3)	90	90	90	100.399(2)	90	98.285(3)	90
Volume/$Å^3$	1602.43(11)	1853.54(16)	1479.97(11)	2306.80(10)	1939.91(10)	2529.75(13)	1304.93(9)	2401.41(18)
Z	2	4	4	4	2	4	2	4
$\rho_{calc}g/cm^3$	1.356	1.479	2.163	1.95	1.931	2.216	1.706	2.032
μ/mm^{-1}	3.697	1.06	8.405	5.76	6.432	9.613	4.795	5.216
F(000)	688	860	912	1304	1088	1592	660	1432
Crystal size/mm^3	0.1 × 0.05 × 0.04	0.08 × 0.04 × 0.04	0.1 × 0.08 × 0.08	0.12 × 0.1 × 0.03	0.2 × 0.18 × 0.04	0.2 × 0.15 × 0.15	0.06 × 0.06 × 0.05	0.3 × 0.25 × 0.22
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.954 to 148.09°	6.044 to 52.744°	5.824 to 52.738°	6.33 to 52.742°	5.654 to 60.596°	5.972 to 52.728°	5.66 to 52.744°	5.866 to 52.736°
Index ranges	$-12 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 13$	$-13 \le h \le 13$, $-22 \le k \le 15$, $-9 \le l \le 12$	$-9 \le h \le 8$, $-21 \le k \le 19$, $-8 \le l \le 14$	$-18 \le h \le 18$, $-15 \le k \le 15$, $-14 \le l \le 15$	$-11 \le h \le 13$, $-17 \le k \le 18$, $-22 \le l \le 22$	$-11 \le h \le 11$, $-25 \le k \le 25$, $-16 \le l \le 16$	$-10 \le h \le 9$, $-16 \le k \le 16$, $-16 \le l \le 16$	$-12 \le h \le 11$, $-21 \le k \le 22$, $-17 \le l \le 16$
Reflections collected	11313	9524	7793	19918	20675	14835	11684	13156
Independent reflections	6306 [R_{int} = 0.0210, R_{sigma} = 0.0281]	3783 [R_{int} = 0.0222, R_{sigma} = 0.0289]	3031 [R_{int} = 0.0293, R_{sigma} = 0.0343]	2472 [R_{int} = 0.0301, R_{sigma} = 0.0156]	10178 [R_{int} = 0.0268, R_{sigma} = 0.0420]	5170 [R_{int} = 0.0331, R_{sigma} = 0.0360]	5314 [R_{int} = 0.0231, R_{sigma} = 0.0327]	4904 [R_{int} = 0.0394, R_{sigma} = 0.0463]
Data/restraints/parameters	6306/0/381	3783/0/224	3031/0/192	2472/0/155	10178/0/495	5170/8/337	5314/6/328	4904/0/337
Goodness-of-fit on F^2	1.098	1.084	1.025	1.044	1.035	1.097	1.045	1.09
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1281	R_1 = 0.0289, wR_2 = 0.0739	R_1 = 0.0196, wR_2 = 0.0383	R_1 = 0.0236, wR_2 = 0.0555	R_1 = 0.0284, wR_2 = 0.0591	R_1 = 0.0267, wR_2 = 0.0570	R_1 = 0.0192, wR_2 = 0.0408	R_1 = 0.0281, wR_2 = 0.0610
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1321	R_1 = 0.0365, wR_2 = 0.0779	R_1 = 0.0240, wR_2 = 0.0399	R_1 = 0.0268, wR_2 = 0.0580	R_1 = 0.0403, wR_2 = 0.0648	R_1 = 0.0325, wR_2 = 0.0592	R_1 = 0.0224, wR_2 = 0.0422	R_1 = 0.0356, wR_2 = 0.0646
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.81	0.29/-0.28	1.20/-0.88	2.13/-2.18	1.17/-1.26	0.86/-0.98	0.61/-0.58	0.73/-1.86

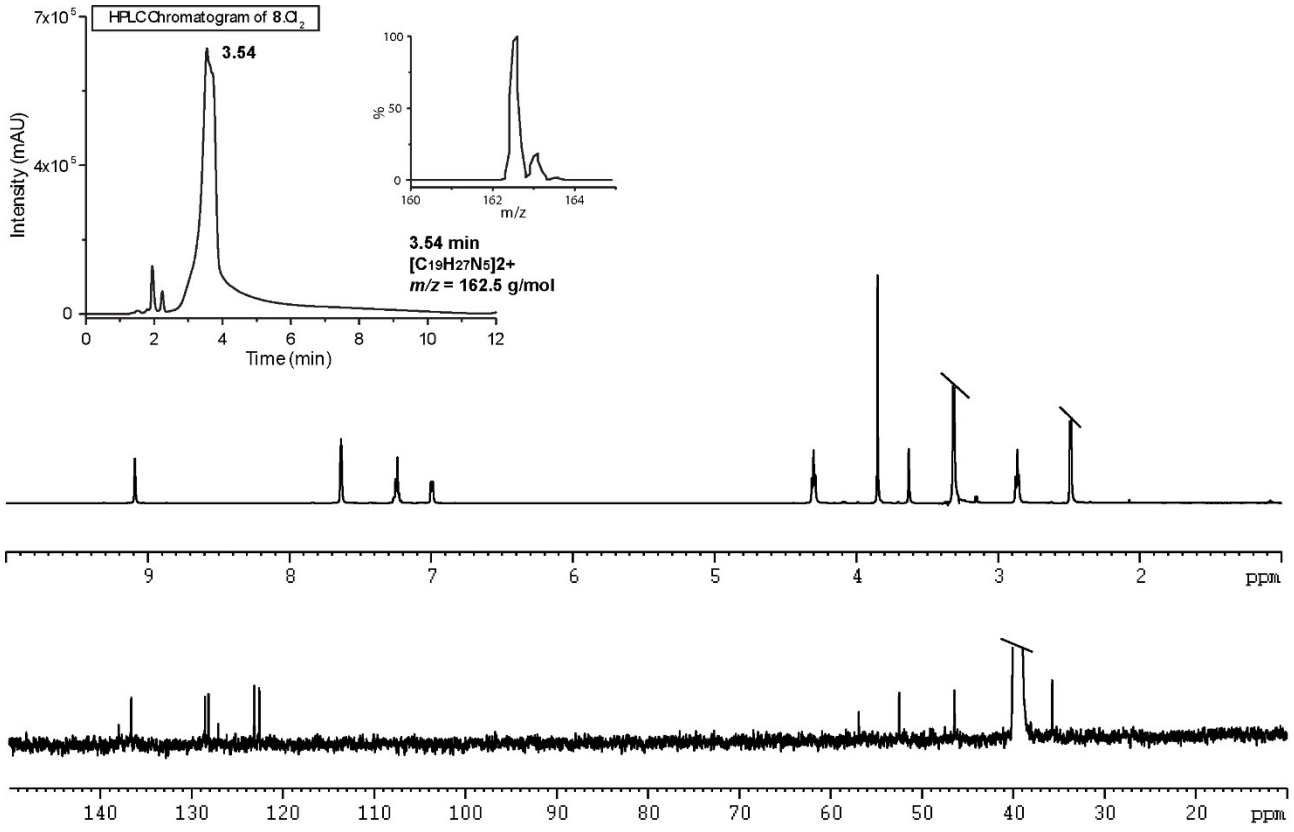

Figure S4. ^{1}H and ^{13}C NMR spectra for **8**.Cl_2. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from a DMSO-d_6 solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **8**.Cl_2 (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

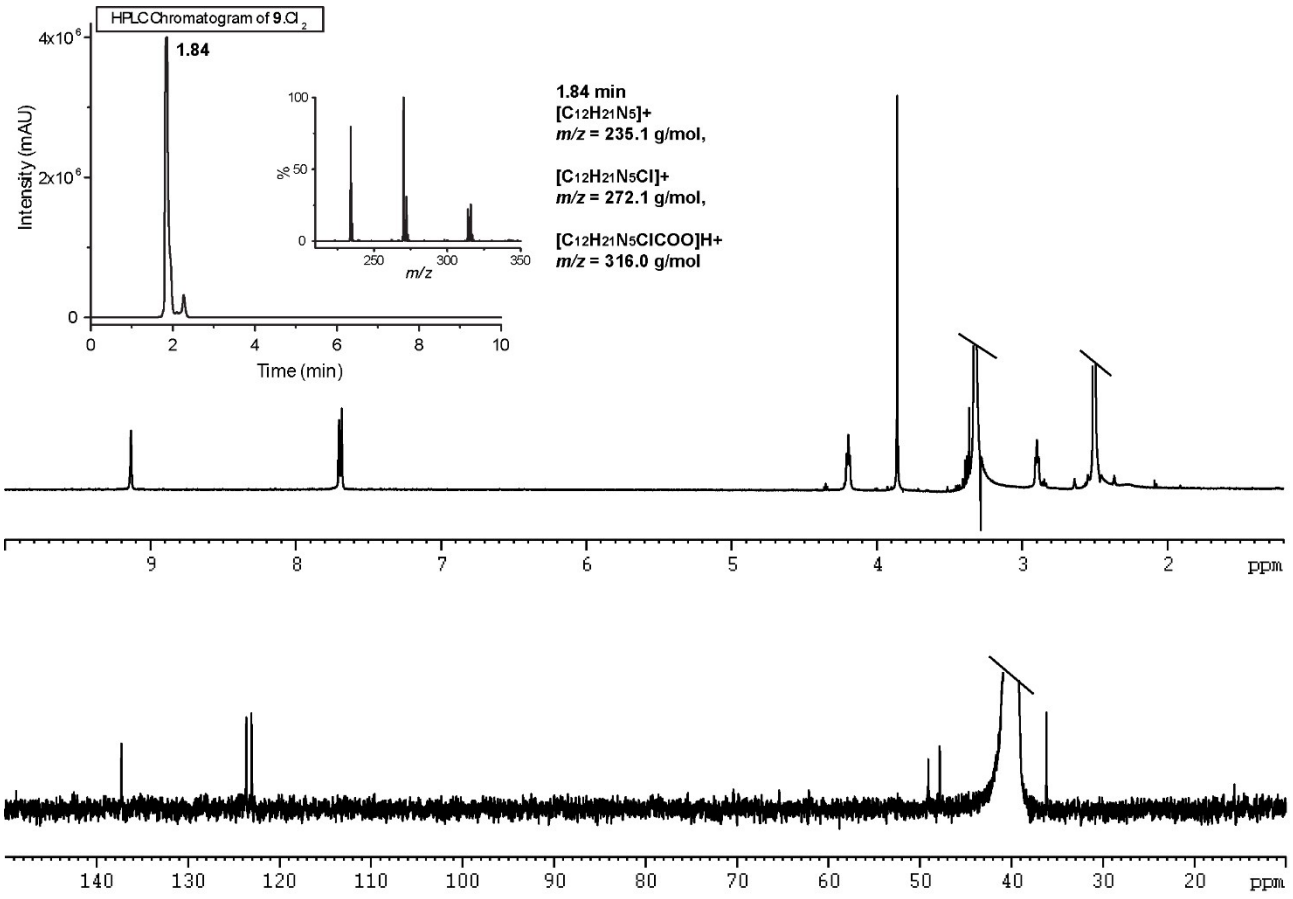

Figure S5. ^{1}H and ^{13}C NMR spectra for **9**.Cl_2. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from s DMSO-d_6 solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **9**.Cl_2 (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

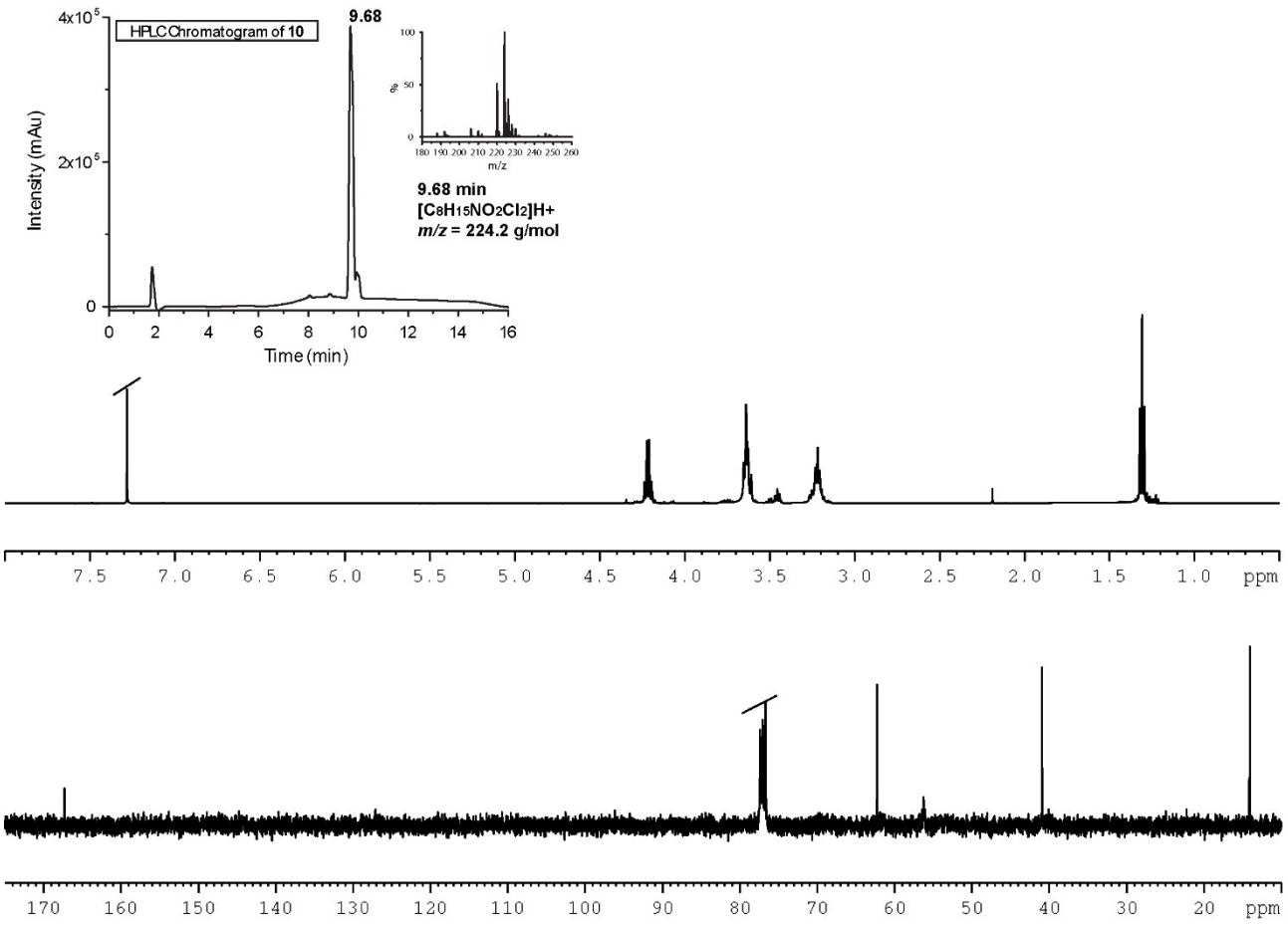

Figure S6. ^{1}H and ^{13}C NMR spectra for **10**. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from a $CDCl_3$ solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **10** (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

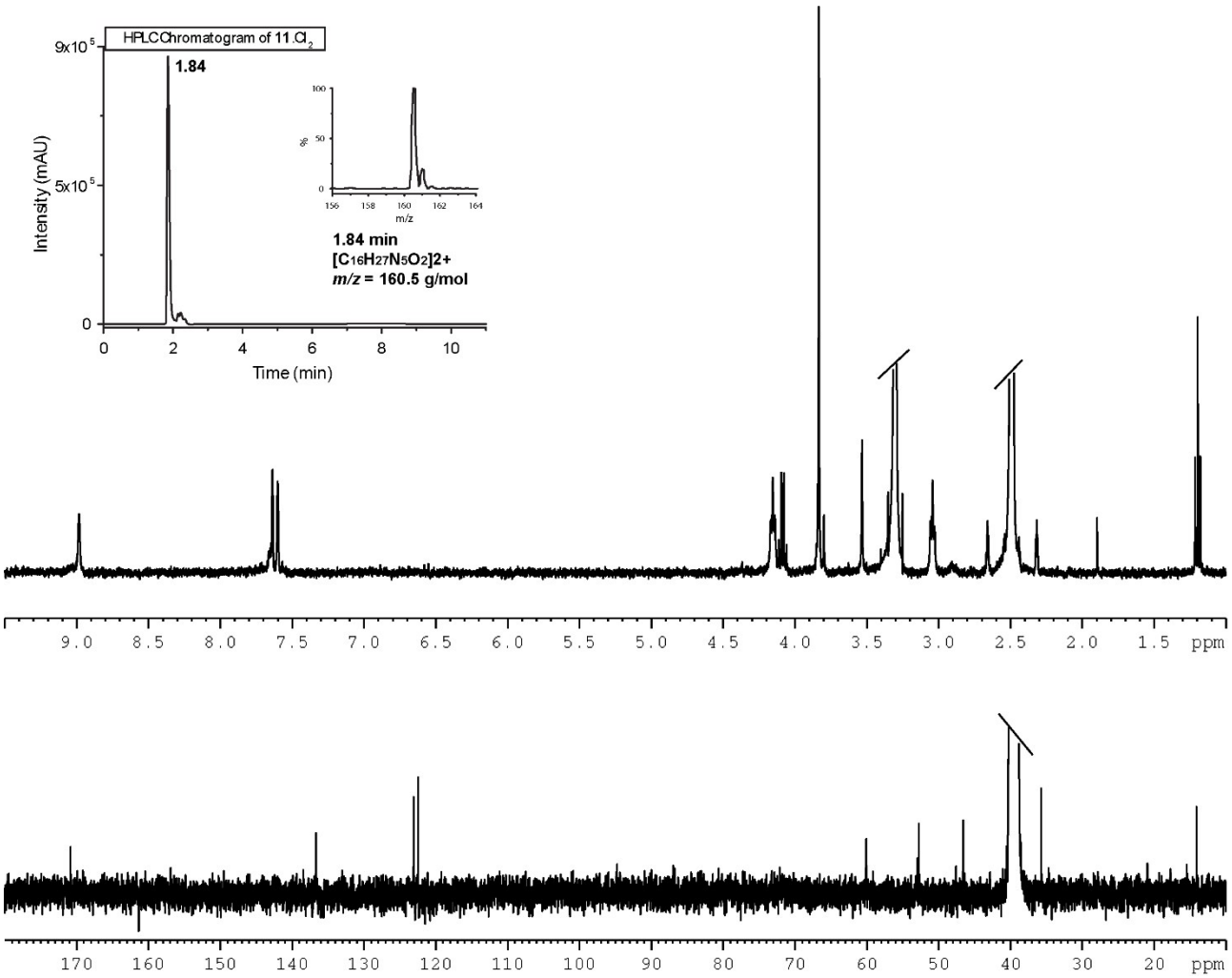

Figure S7. ^{1}H and ^{13}C NMR spectra for **11**.Cl_2. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from a DMSO-d_6 solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **11**.Cl_2 (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

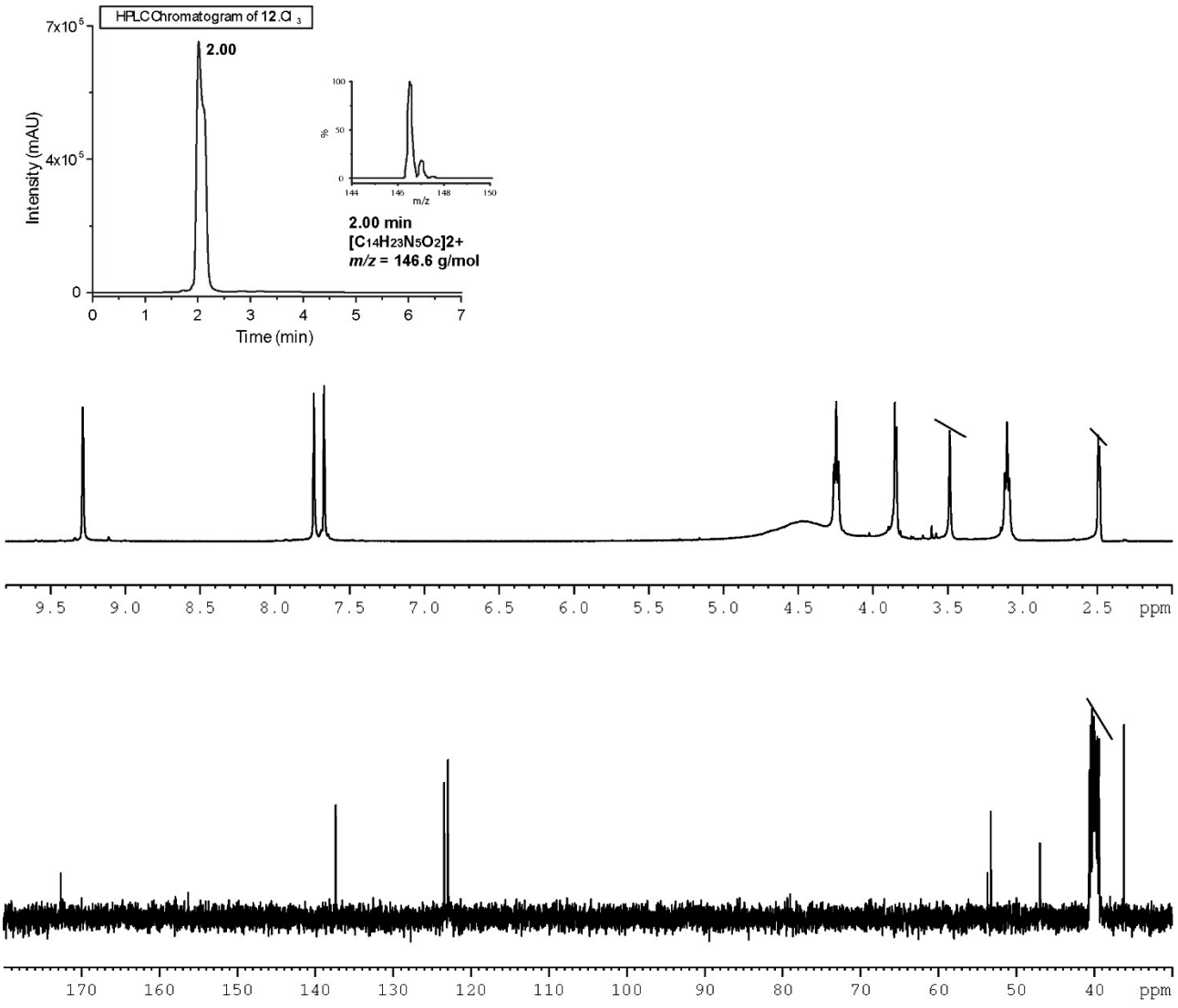

Figure S8. ^{1}H and ^{13}C NMR spectra for **12**.Cl_3. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from a DMSO-d_6 solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **12**.Cl_3 (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

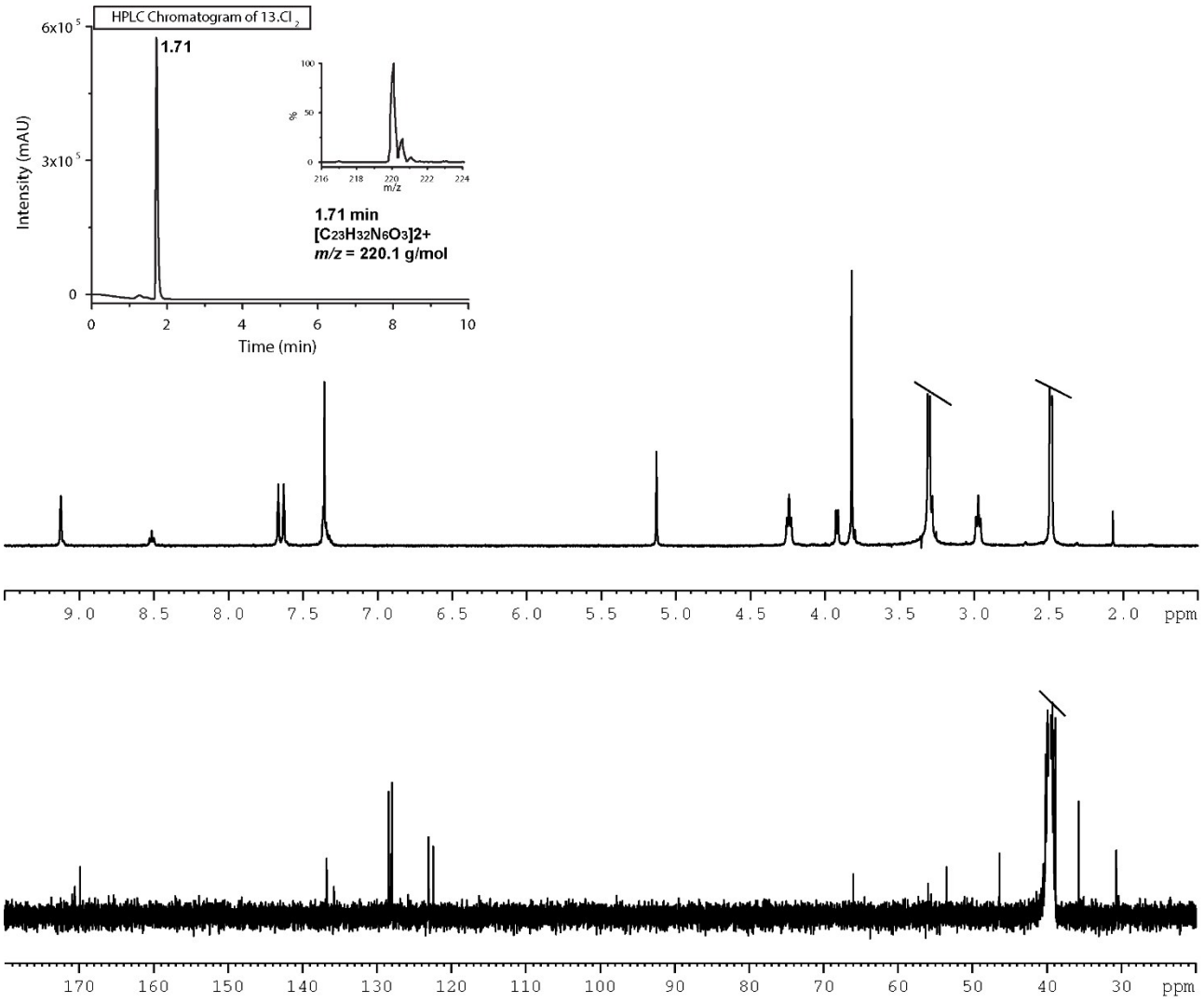

Figure S9. ^{1}H and ^{13}C NMR spectra for **13**.Cl_2. Spectra were recorded at 400.14 MHz for ^{1}H, 100.03 MHz for ^{13}C from a DMSO-d_6 solution and were internally referenced to solvent resonances. (inset) HPLC Chromatogram of **13**.Cl_2 (Eluent: MeOH/H_2O with 0.1% formic acid) and the ESI-MS spectrum corresponding to main peak.

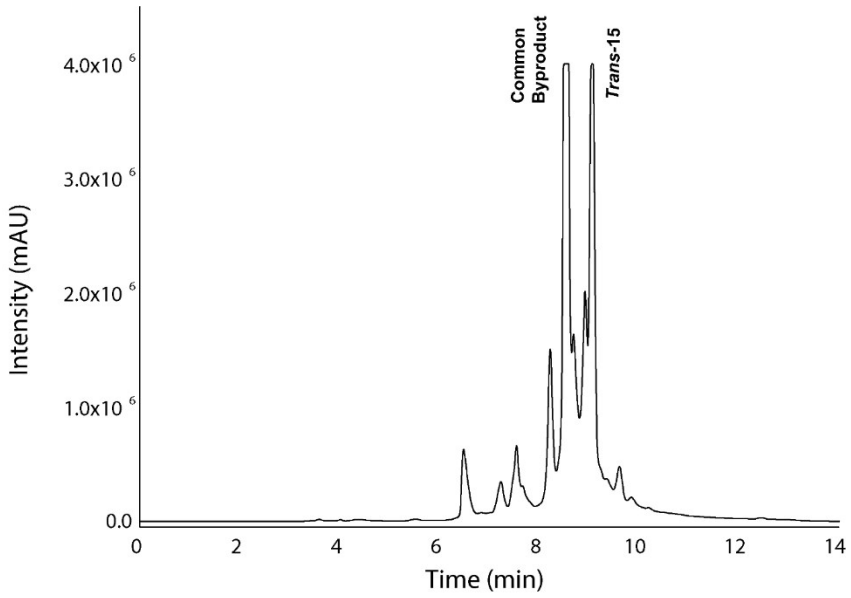

Figure S10. HPLC Chromatogram of the crude reaction product obtained in the synthesis of the Re(I) complex, **15**. The identity of the compounds associated with the main HPLC peaks are labelled.

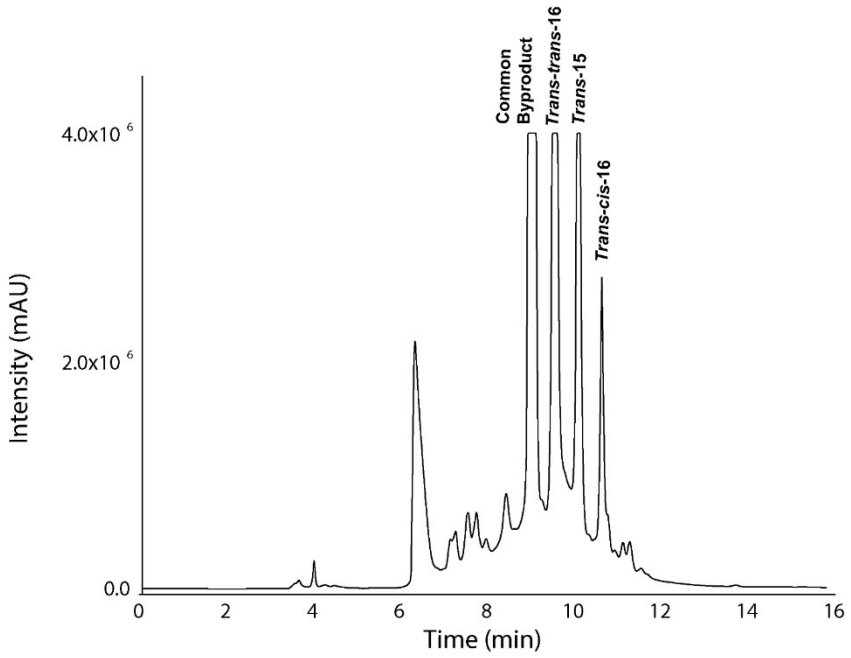

Figure S11. HPLC Chromatogram of the crude reaction product obtained in the synthesis of the Re(I) complex, **16**. The identity of the compounds corresponding to the main HPLC peaks are labelled.

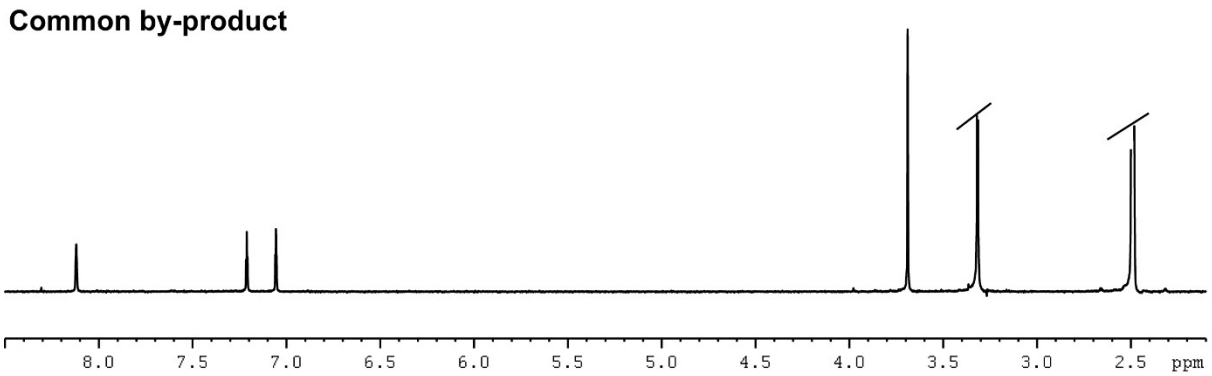

Figure S12. ^{1}H NMR spectrum of the common decomposition product (purified using HPLC) from the silver transmetalation reaction between $Re(CO)_5Cl$ and the imidazolium salts (**5**.Cl_2 and **6**.Cl_4). Spectrum was recorded at 400.14 MHz for ^{1}H, from a DMSO-d_6 solution and was internally referenced to solvent resonance.

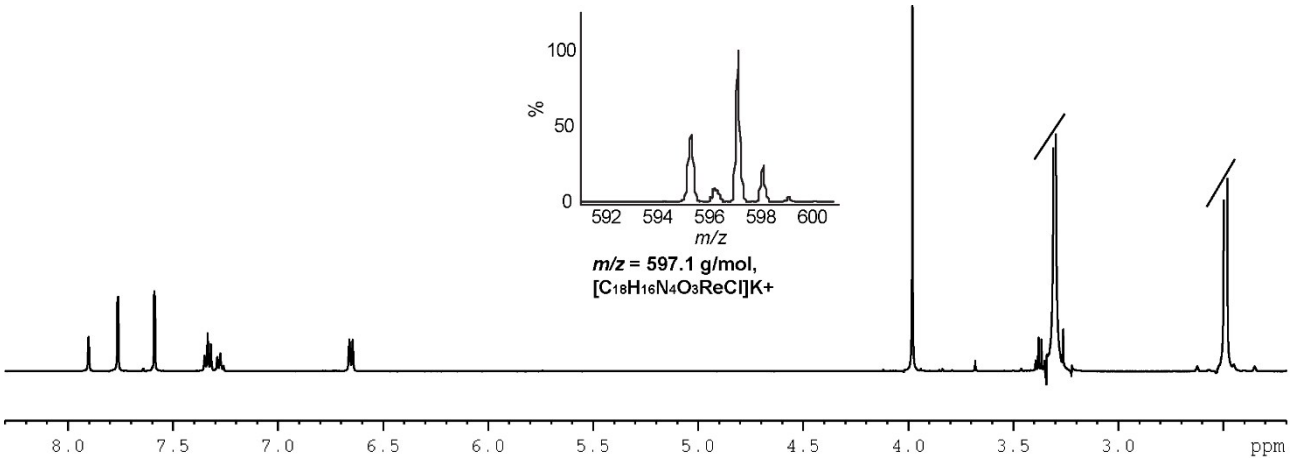

Figure S13. ^{1}H NMR spectrum of *trans*-**15** (purified from the crude reaction product using HPLC) and (inset) the ESI-MS of *trans*-**15**. Spectrum was recorded at 500.13 MHz for ^{1}H, from a DMSO-d_6 solution and was internally referenced to solvent resonance.

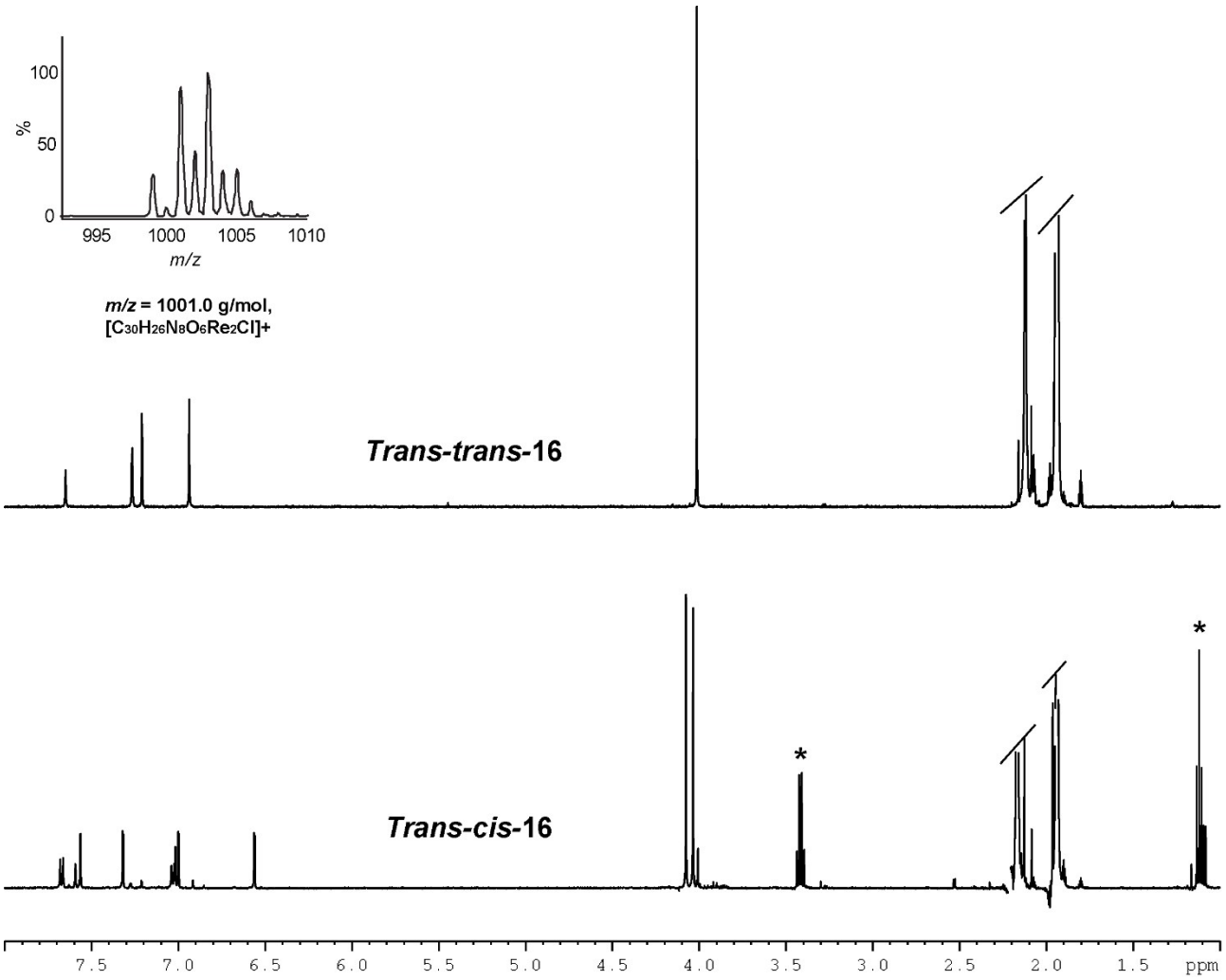

Figure S14. ^{1}H NMR spectrum of *trans-trans*-**16** (top) and *trans-cis*-**16** (bottom). Both compounds gave identical ESI-MS results (inset) and were purified from the crude reaction product using HPLC. Spectra was recorded at 500.13 MHz for ^{1}H, from a CD_3CN solution and were internally referenced to solvent resonances. The signals marked with an asterisk correspond to adventitious diethyl ether.

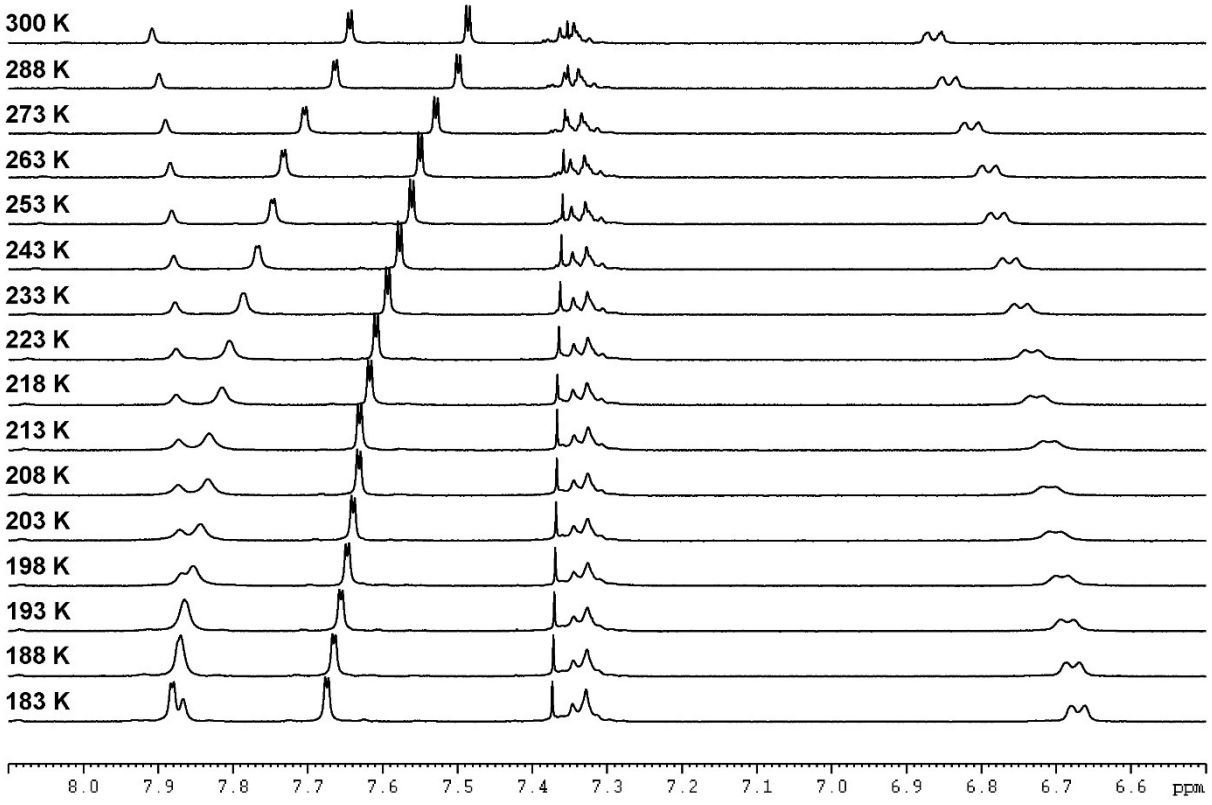

Figure S15. Variable temperature (300 K – 183 K) ^{1}H NMR spectra (400.14 MHz, d_6-acetone) for complex **15**.

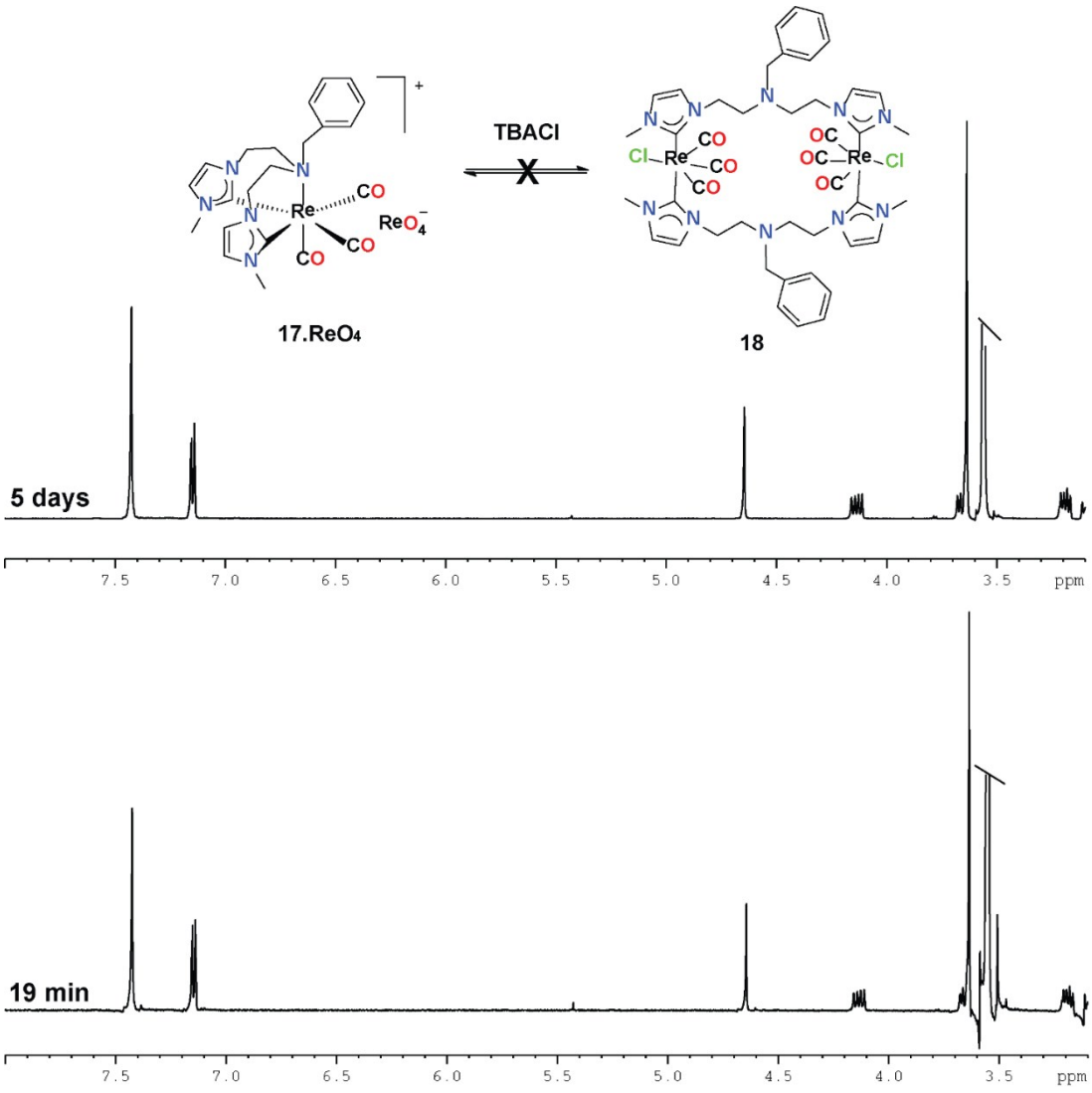

Figure S16. ^{1}H NMR spectra for the reaction of **17**.ReO_4 with 10 molar equivalents of TBACl in CD_3CN. Spectra were recorded 19 min after mixing and 5 days after mixing.

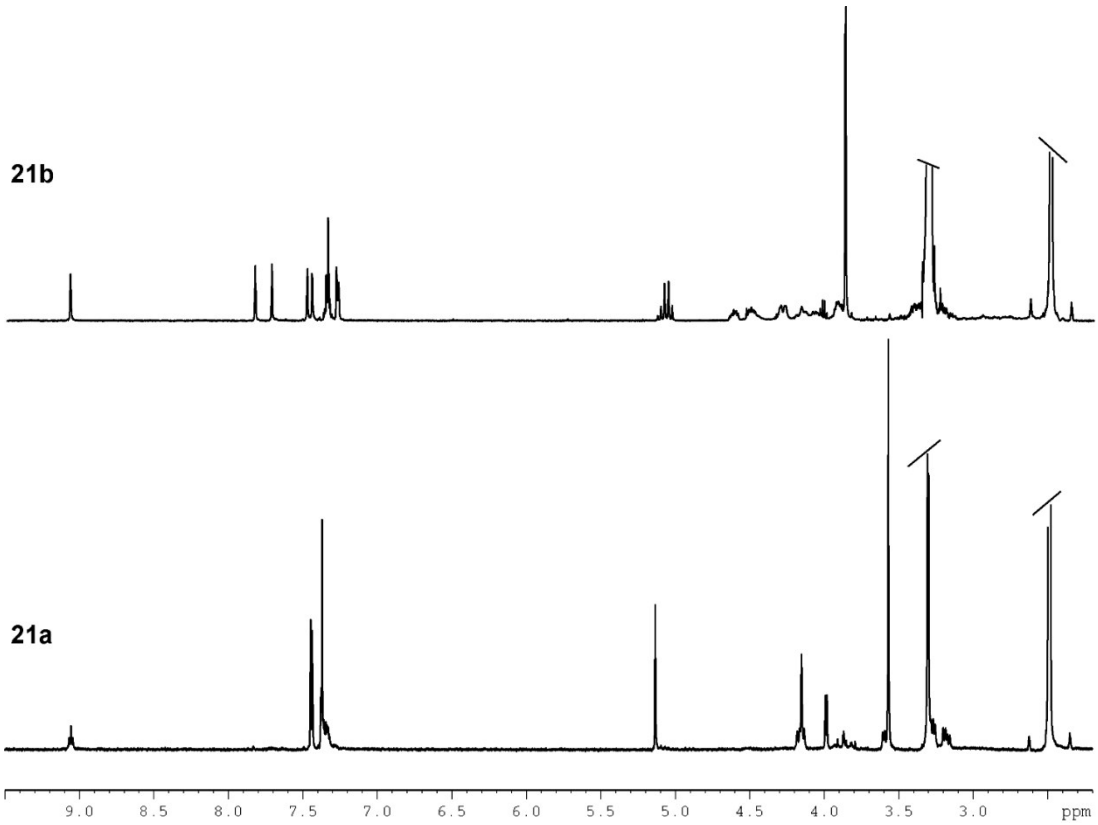

Figure S17. ^{1}H NMR spectra of linkage isomers of Re(I) complexes **21a** (Top) and **21b** (bottom). The spectra were recorded at 500.13 MHz for ^{1}H NMR in a DMSO-d_6 solution and were internally referenced to solvent resonances.

Kinetic analysis of ^{1}H NMR study of the reaction of 14 with CD_3CN to give $[\mathbf{14}CD_3CN]^+ + Cl^-$

NMR experiments. A solution of **14**Cl (0.0152 M) was prepared in 0.60 mL of a solvent mixture consisting of 0.54 mL CD_3CN and 0.06 mL D_2O and the reaction were followed by ^{1}H NMR spectroscopy.

Data analysis. The kinetic analysis of the reaction was undertaken by calculating the relative concentrations of species present at each time point, based on the relative integrals for each of two different proton resonance (these being protons on the imidazolylidene ring) in the ^{1}H NMR spectra (see Figure 7). To fit the experimental data a pseudo first order model was used, in which the complex (**14**Cl) reacts with one mole equivalent of CD_3CN to form the cationic product $[\mathbf{14}CD_3CN]^+$.

The kinetic model is provided below and the forward and reverse rate constants (k_f and k_r) were determined using a non-linear optimization procedure using the program Scientist® (Version 3.0, MicroMath, Inc.).

$$\mathbf{14Cl} + CD_3CN \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\mathbf{14}CD_3CN]^+ + Cl^- \quad (CD_3CN \text{ in large excess}) \qquad (1)$$

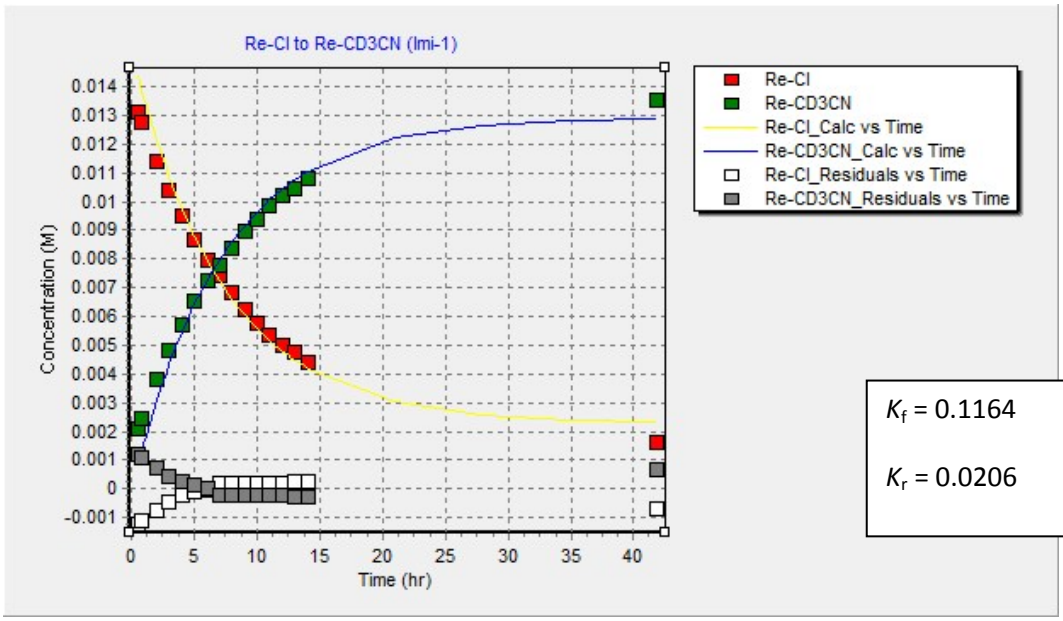

Figure S18. Plot of the time dependence of species (**14**Cl and [**14**CD_3CN]$^+$) observed in the reaction of **14**Cl (0.0152 M) with acetonitrile according to equation (1). Concentrations derived from the integration of one of the imidazolylidene group proton. The curves are computer best fits to the model shown in Scheme S1. The pseudo-first order rate constants for the forward and reverse reactions k_f and k_r are 0.1164 $M^{-1}s^{-1}$ and 0.0206 $M^{-1}s^{-1}$ respectively.

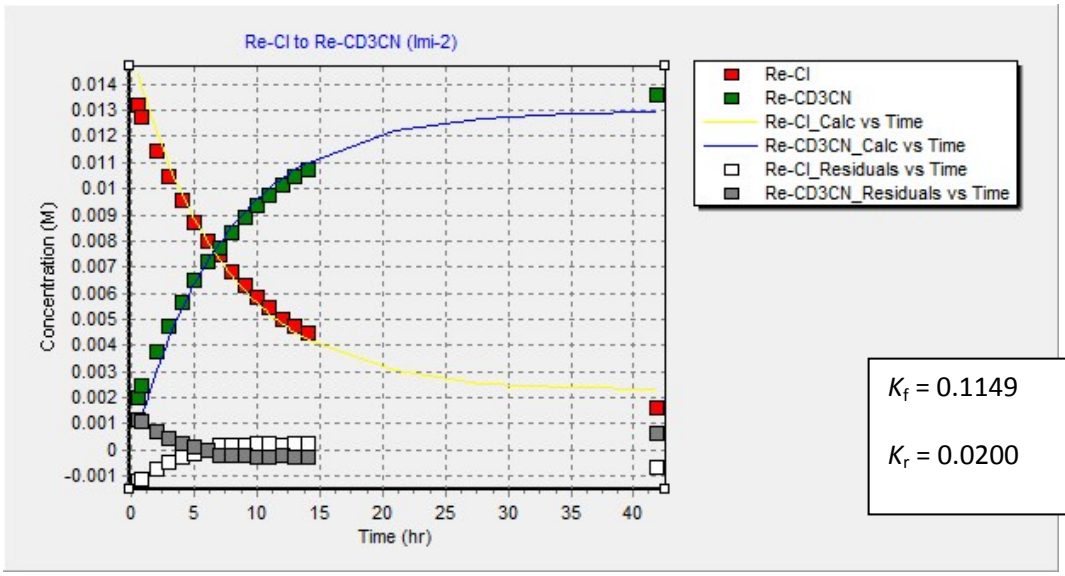

Figure S19. Plot of the time dependence of species (**14**Cl and [**14**CD_3CN]$^+$) observed in the reaction of **14**Cl (0.0152 M) with acetonitrile according to equation (1). Concentrations derived from the integration of the second imidazolylidene group proton. The curves are computer best fits to the model shown in Scheme S1. The pseudo-first order rate constants for the forward and reverse reactions k_f and k_r are 0.1149 $M^{-1}s^{-1}$ and 0.0200 $M^{-1}s^{-1}$ respectively.

Scheme S1: Scientist® model: Reaction of 14Cl with CD_3CN

// MicroMath Scientist Model File
IndVars: T
DepVars: A, P
Params: AO, PO, KF, KR
A = (KR*(AO+PO)+(KF*AO-KR*PO)*EXP((-(KF+KR))*T))/(KF+KR)
P = (KF*(AO+PO)-(KF*AO-KR*PO)*EXP((-(KF+KR))*T))/(KF+KR)
// Representative Initial conditions
T=30 min, AO=0.0152 M, PO=0 M
KF= K_f
KR= K_r
T=first time point
AO=initial concentration of Re-Cl
PO=initial concentration of Re-CD_3CN

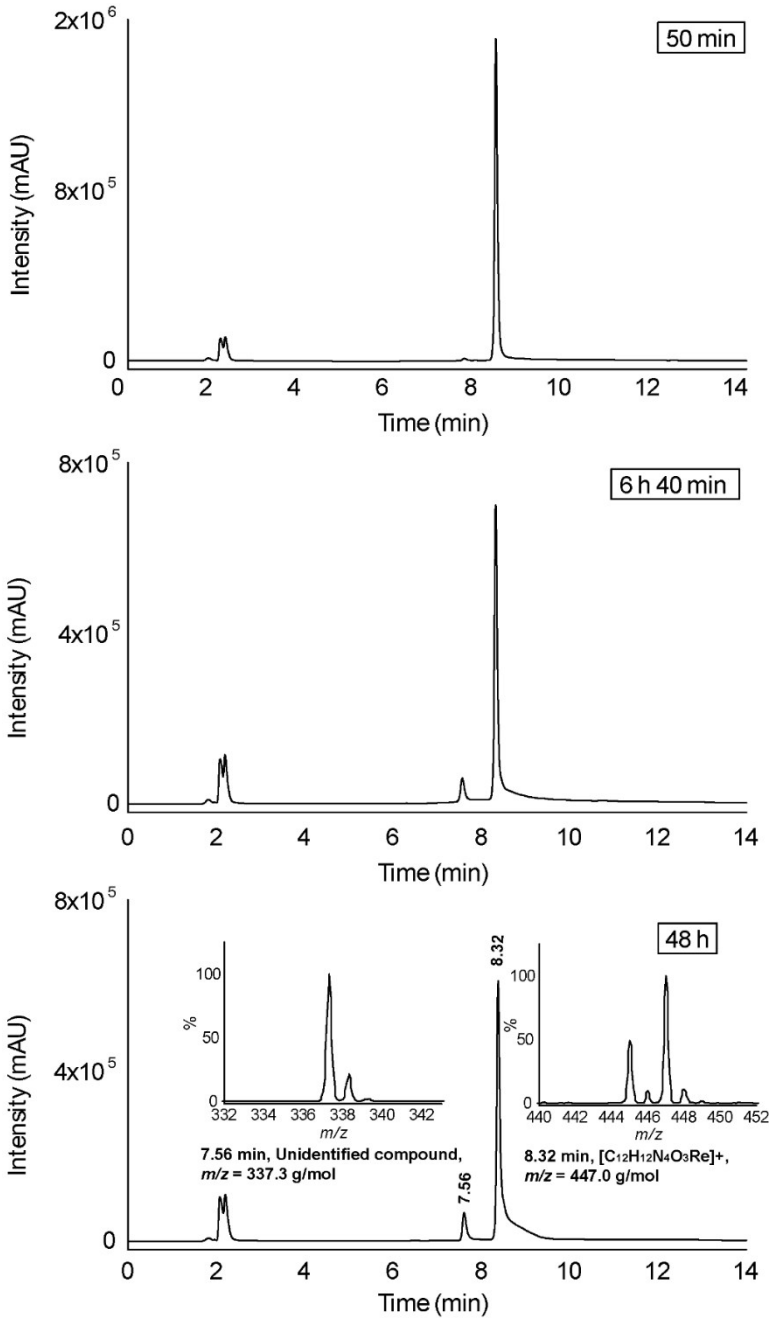

Figure S20. HPLC chromatograms obtained for complex **14** (3.33 mM) in phosphate buffered saline (PBS), recorded at 50 min, 6 h 40 min and 48 h after mixing. Insets in lower panel: ESI-mass spectra corresponding to main peaks.

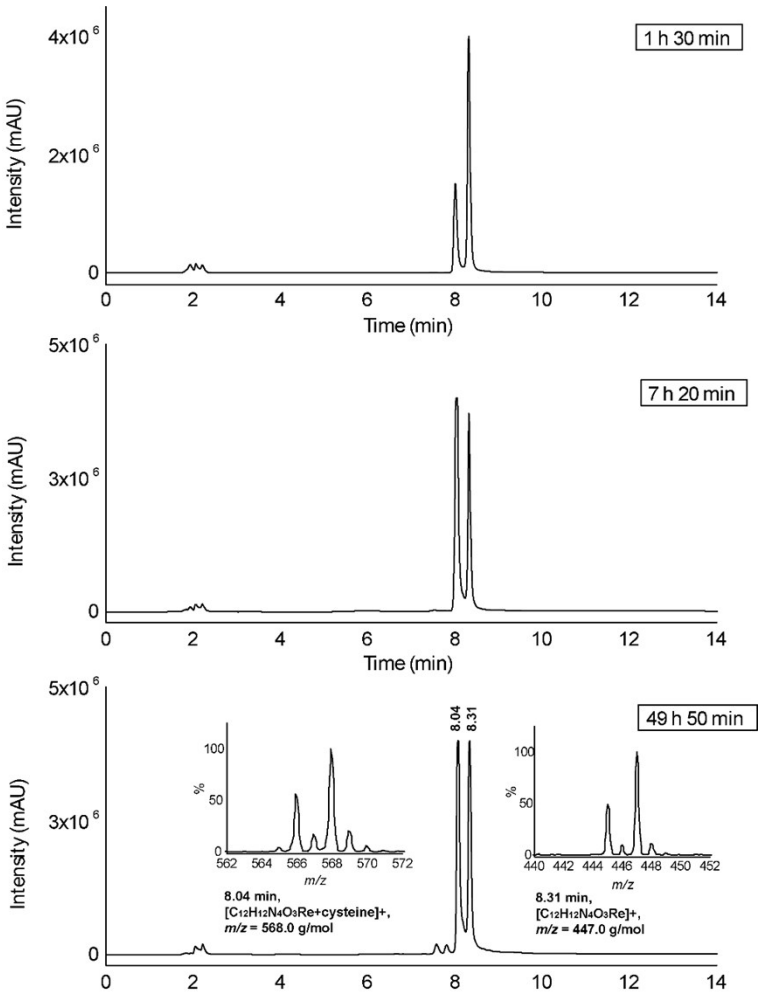

Figure S21. HPLC chromatograms obtained for complex **14** (5 mM) in phosphate buffered saline (PBS) containing cysteine (100 mM), recorded at 1 h 30 min, 7 h 20 min and 49 h 50 min after mixing. Insets in lower panel: ESI-mass spectra corresponding to main peaks.

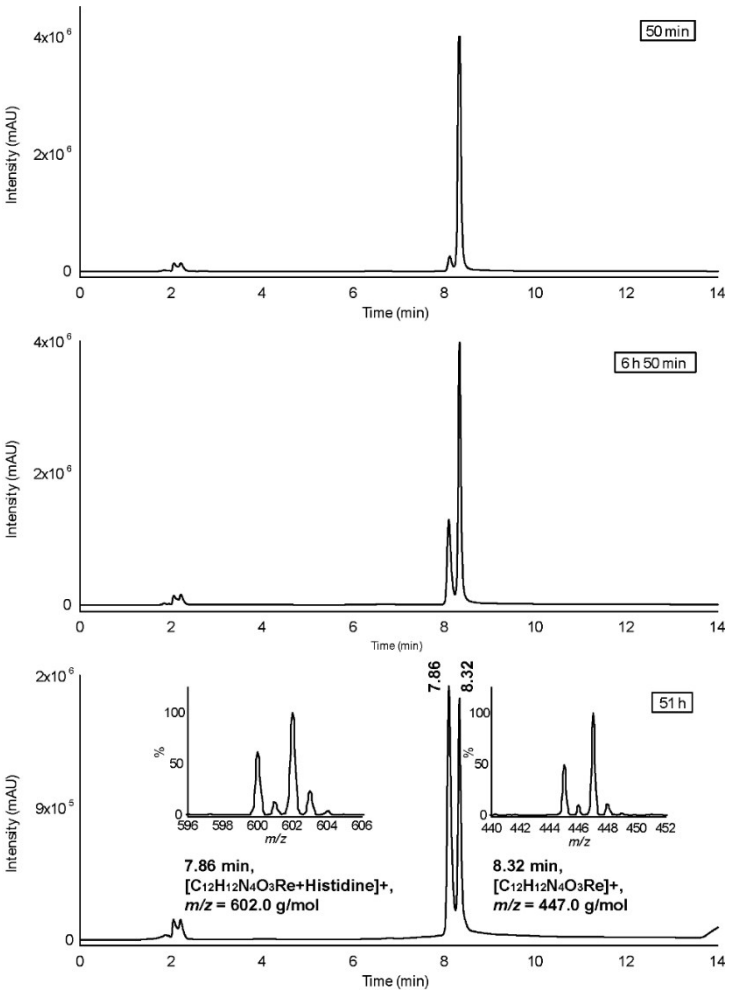

Figure S22. HPLC chromatograms obtained for complex **14** (5 mM) in phosphate buffered saline (PBS) containing histidine (100 mM), recorded at 50 min, 6 h 50 min and 51 h after mixing. Insets in lower panel: ESI-mass spectra corresponding to main peaks.

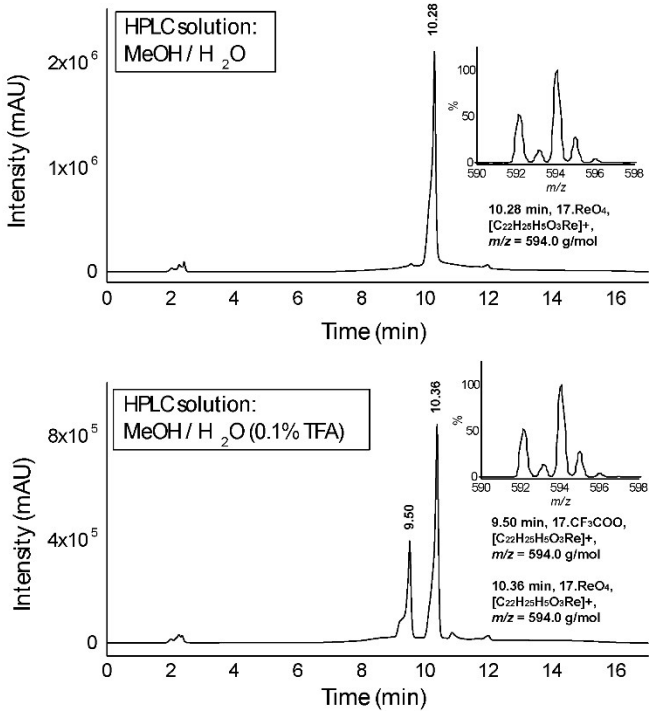

Figure S23. HPLC chromatograms for **17**.ReO_4 with the eluents methanol and water (upper chromatogram) and methanol and water with 0.1% trifluoroacetic acid (lower chromatogram). When the modifier TFA was added to the eluent two complex containing peaks eluted; the first (9.5 min) corresponds to the cation **17**$^+$ and ReO_4^- anion ion pair while the second (9.5 min) corresponds to the cation **17**$^+$ and $CF_3CO_2^-$ anion ion pair.

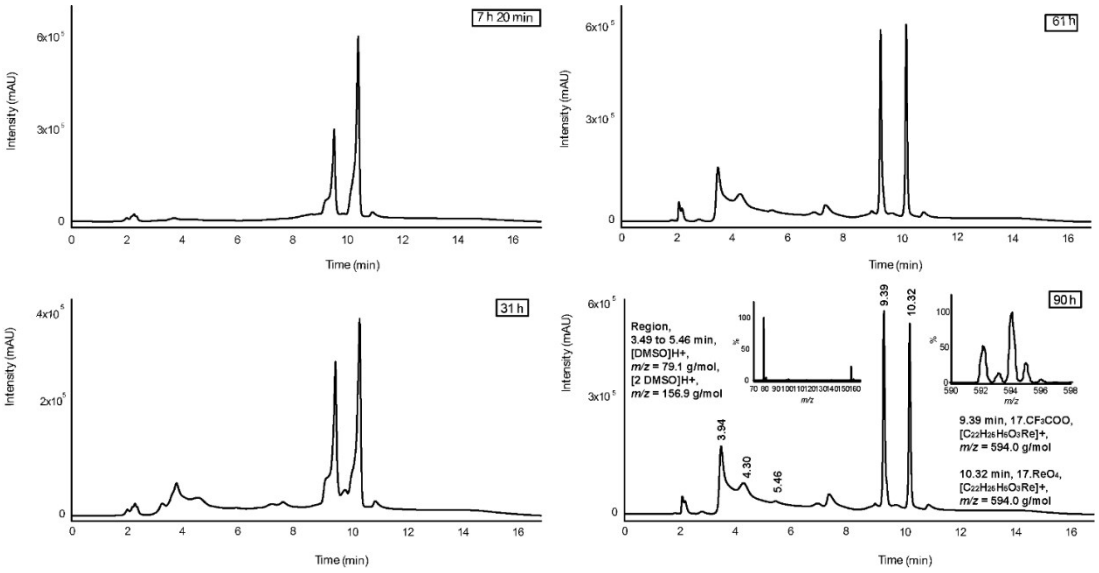

Figure S24. HPLC chromatograms obtained for **17**.ReO_4 (5 mM) in phosphate buffered saline (PBS), recorded at 7.2 h, 31 h and 61 h and 90 h after mixing. Insets in lower right panel: ESI-mass spectra corresponding to main peaks.

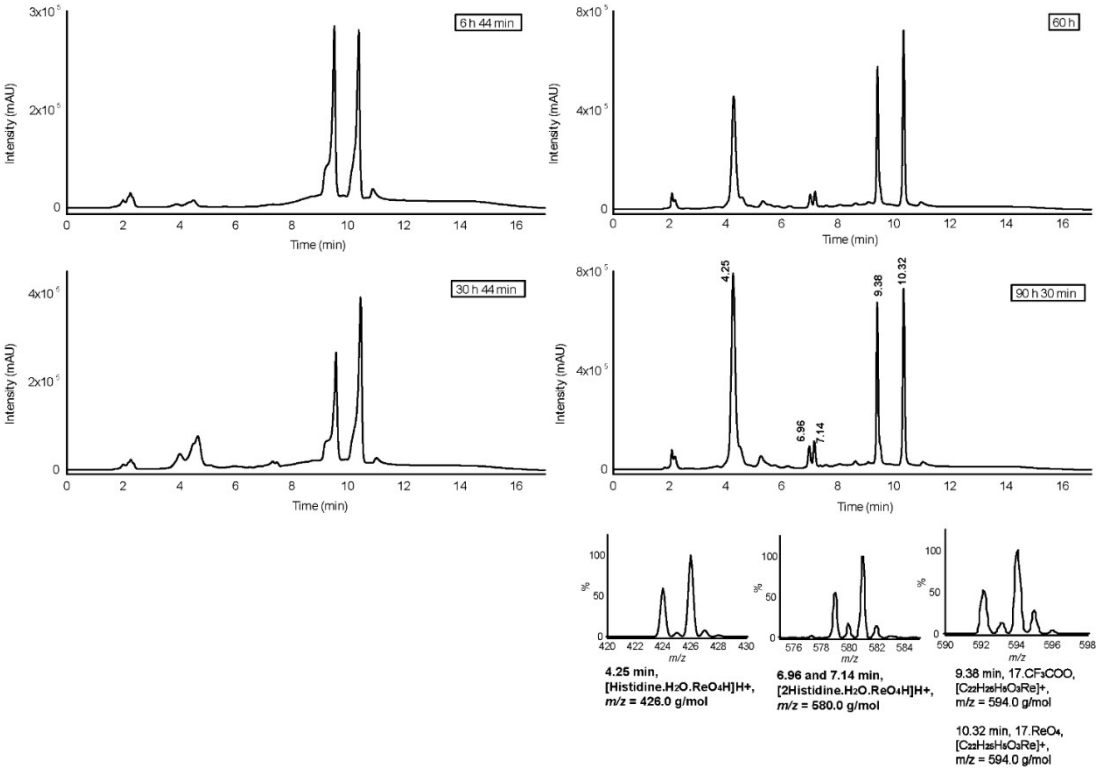

Figure S25. HPLC chromatograms obtained for **17**.ReO_4 (5 mM) in phosphate buffered saline (PBS) containing histidine (100 mM), recorded at 6 h 44 min, 30 h 44 min, 60 h and 90 h 30 min after mixing. Insets in lower right panel: ESI-mass spectra corresponding to main peaks.

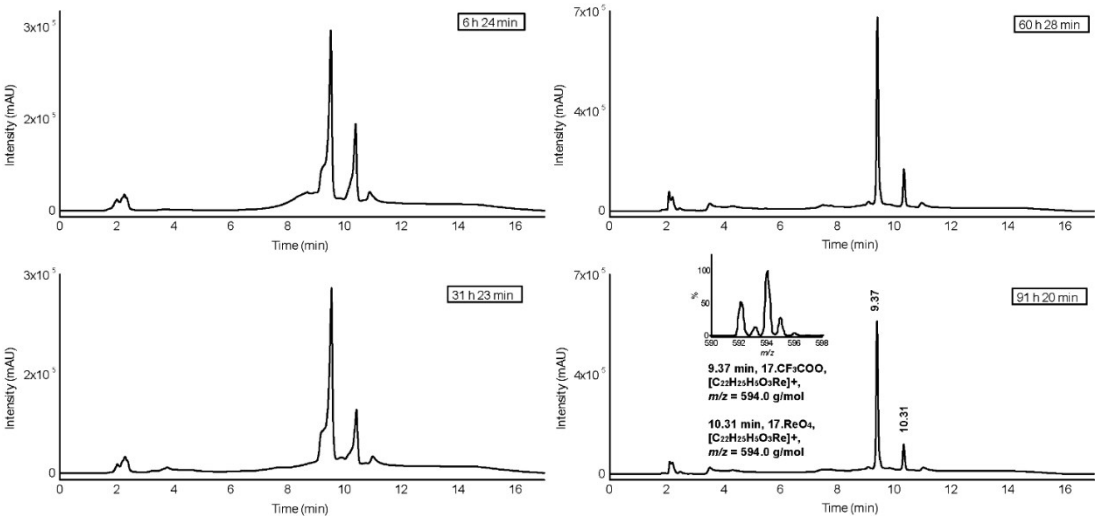

Figure S26. HPLC chromatograms obtained for **17**.ReO_4 (5 mM) in phosphate buffered saline (PBS) containing cysteine (100 mM), recorded at 6 h 24 min, 31 h 23 min, 60 h 23 min and 91 h 20 min after mixing. Insets in lower right panel: ESI-mass spectra corresponding to main peaks.

References

1. Bodanszky, M.; Bodanszky, A., *The practice of peptide synthesis*. 2nd ed.; Springer-Verlag: Berlin and New York, 1994.