Electronic Supplementary Material (ESI) for Dalton Transactions.

In vivo and *in vitro* studies of $[M(\eta^6\text{-pseudoerlotinib})_2]^+$ sandwich complexes (M = Re, ^{99m}Tc)

Federica Battistin[a]*, Célia Fernandes[b], Paula. D. Raposinho[b], Olivier Blacque[a], António Paulo[b]*, Roger Alberto[a]

[a] Department of Chemistry, University of Zurich, Winterthurerstr. 190, 8057 Zurich, Switzerland. federica.battistin@chem.uzh.ch

[b] Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Bobadela, Portugal. apaulo@ctn.tecnico.ulisboa.pt

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NMR spectra

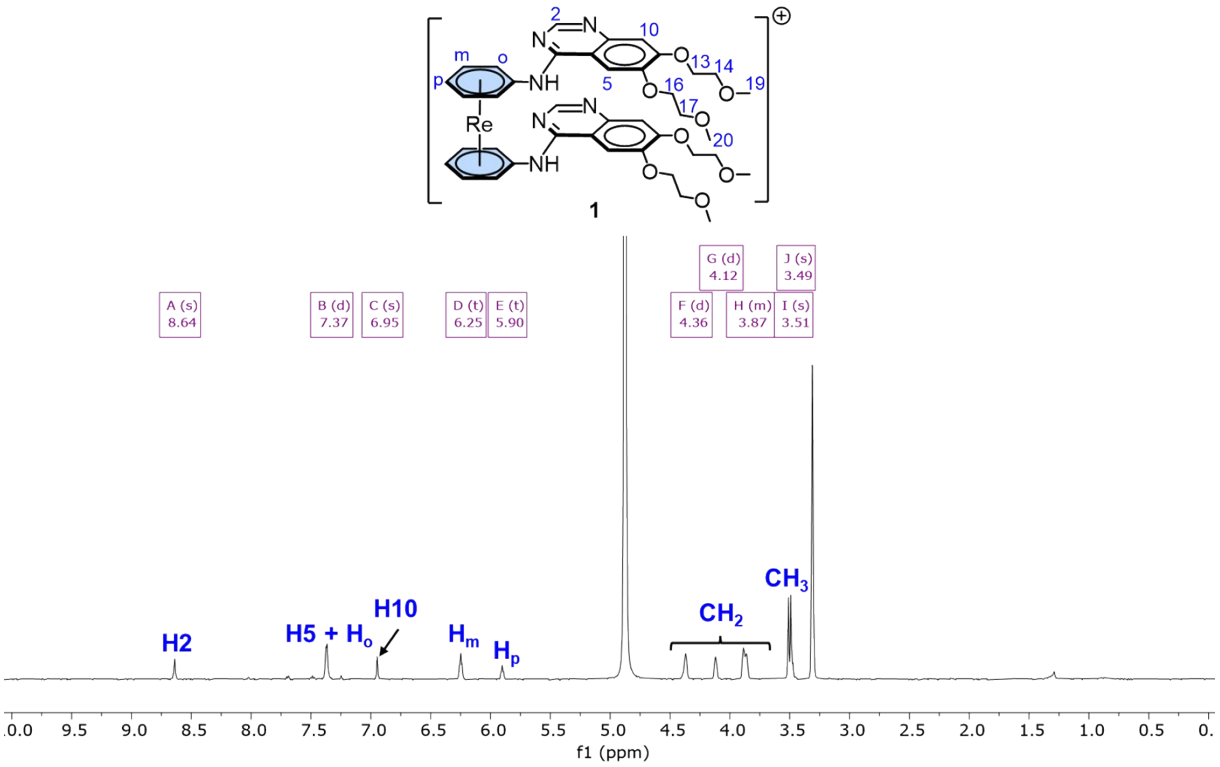

Figure S1. ^{1}H NMR spectrum in CD_3OD of $[Re(\eta^6\text{-pseudoerlotinib})_2]^+$ (**1**).

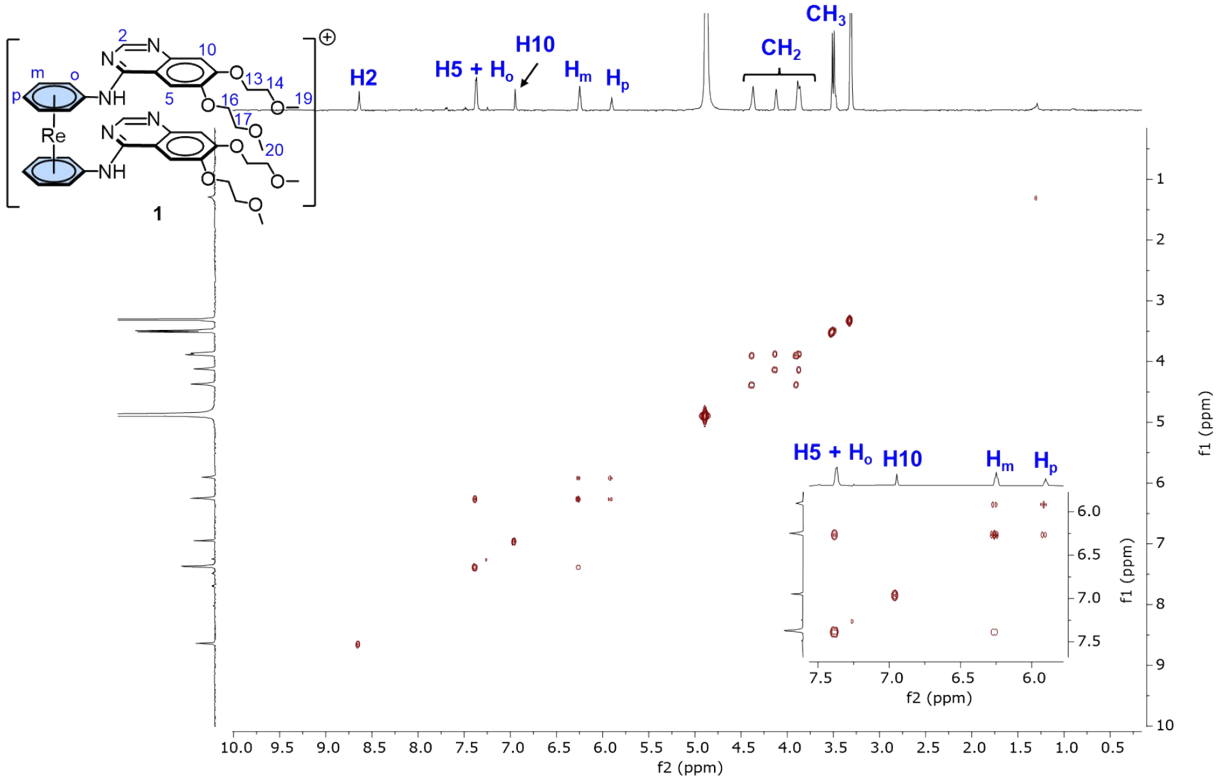

Figure S2. ^{1}H-^{1}H COSY spectrum in CD_3OD of $[Re(\eta^6\text{-pseudoerlotinib})_2]^+$ (**1**).

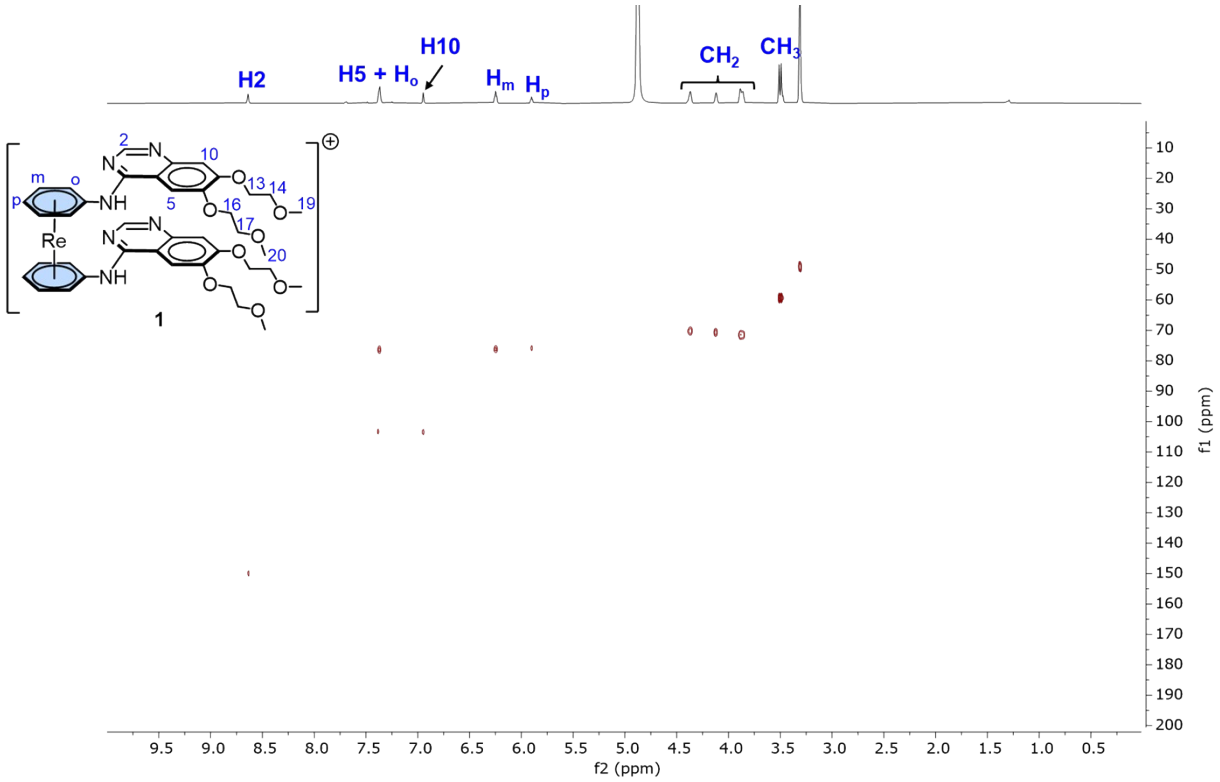

Figure S3. ^{1}H-^{13}C HSQC spectrum in CD_3OD of $[Re(\eta^6\text{-pseudoerlotinib})_2]^+$ (**1**).

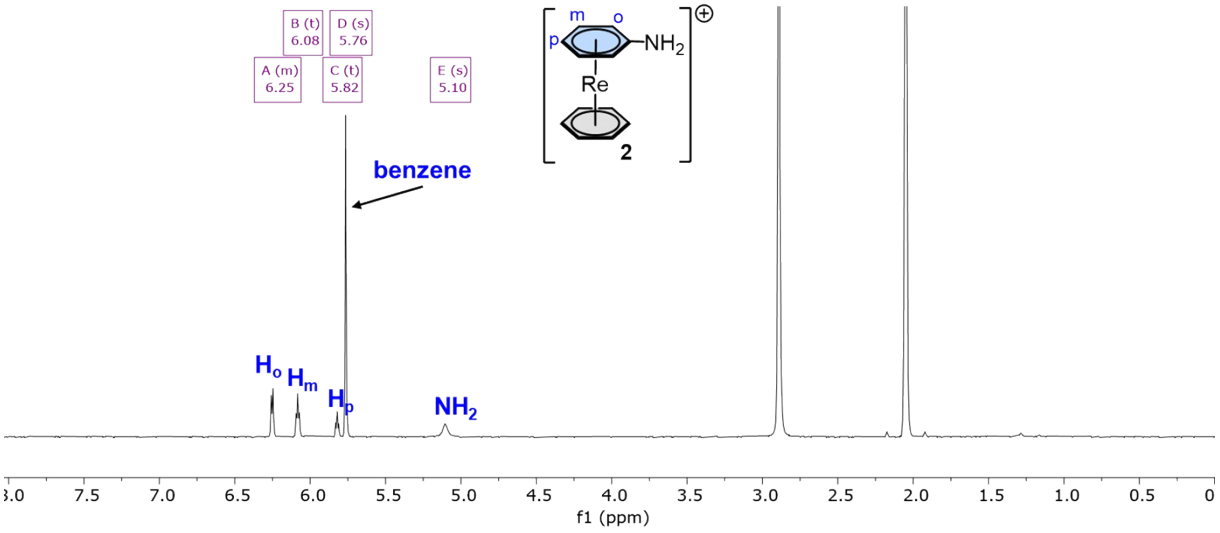

Figure S4. ^{1}H NMR spectrum in acetone-d_6 of $[Re(\eta^6\text{-bz})(\eta^6\text{-aniline})]^+$ (**2**).

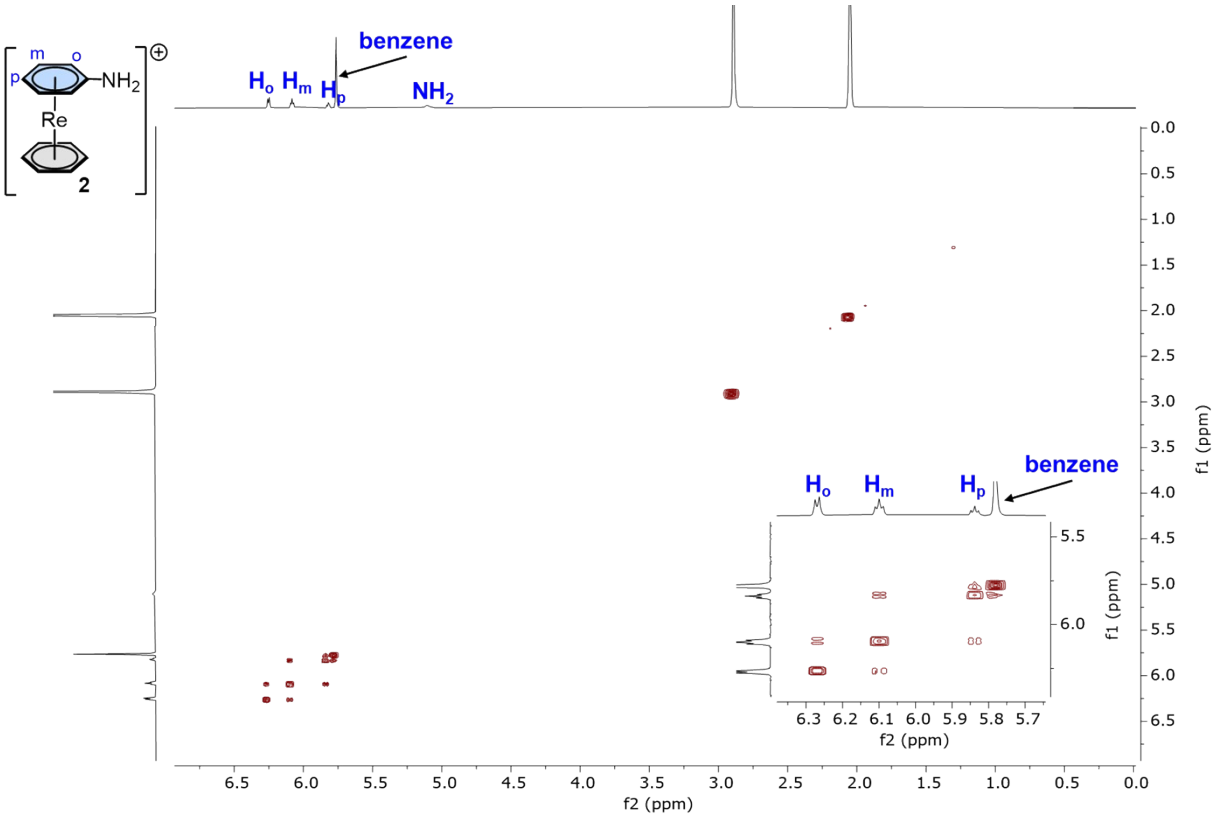

Figure S5. ^{1}H-^{1}H COSY spectrum in acetone-d_6 of [Re(η^6-bz)(η^6-aniline)]$^+$ (**2**).

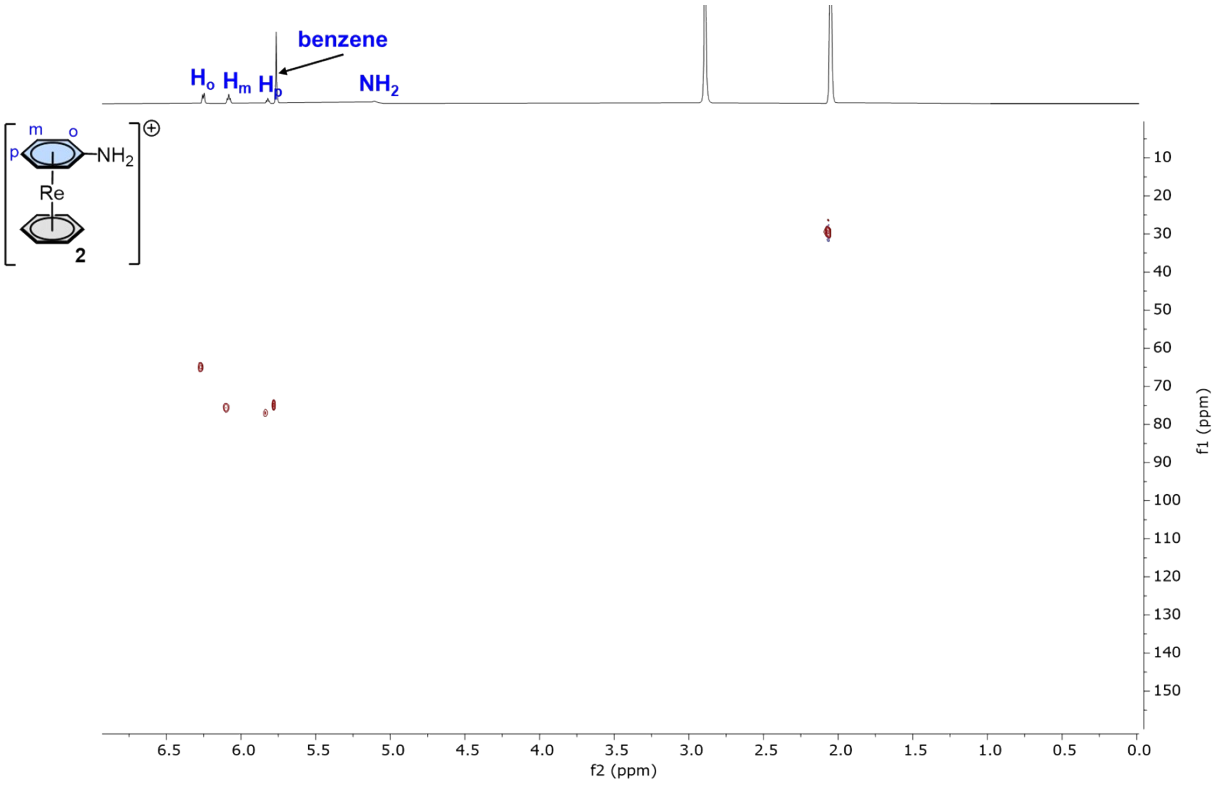

Figure S6. ^{1}H-^{13}C HSQC spectrum in acetone-d_6 of [Re(η^6-bz)(η^6-aniline)]$^+$ (**2**).

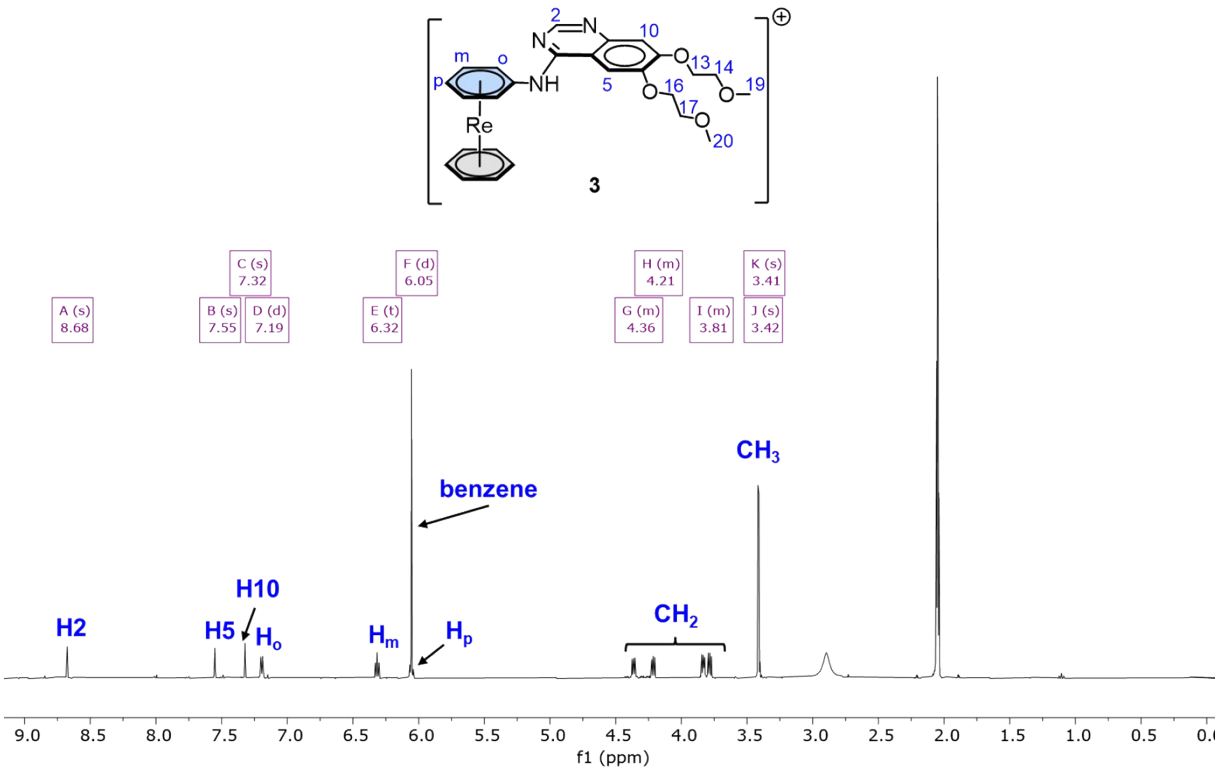

Figure S7. ^{1}H NMR spectrum in acetone-d_6 of [Re(η^6-bz)(η^6-pseudoerlotinib)]$^+$ (**3**).

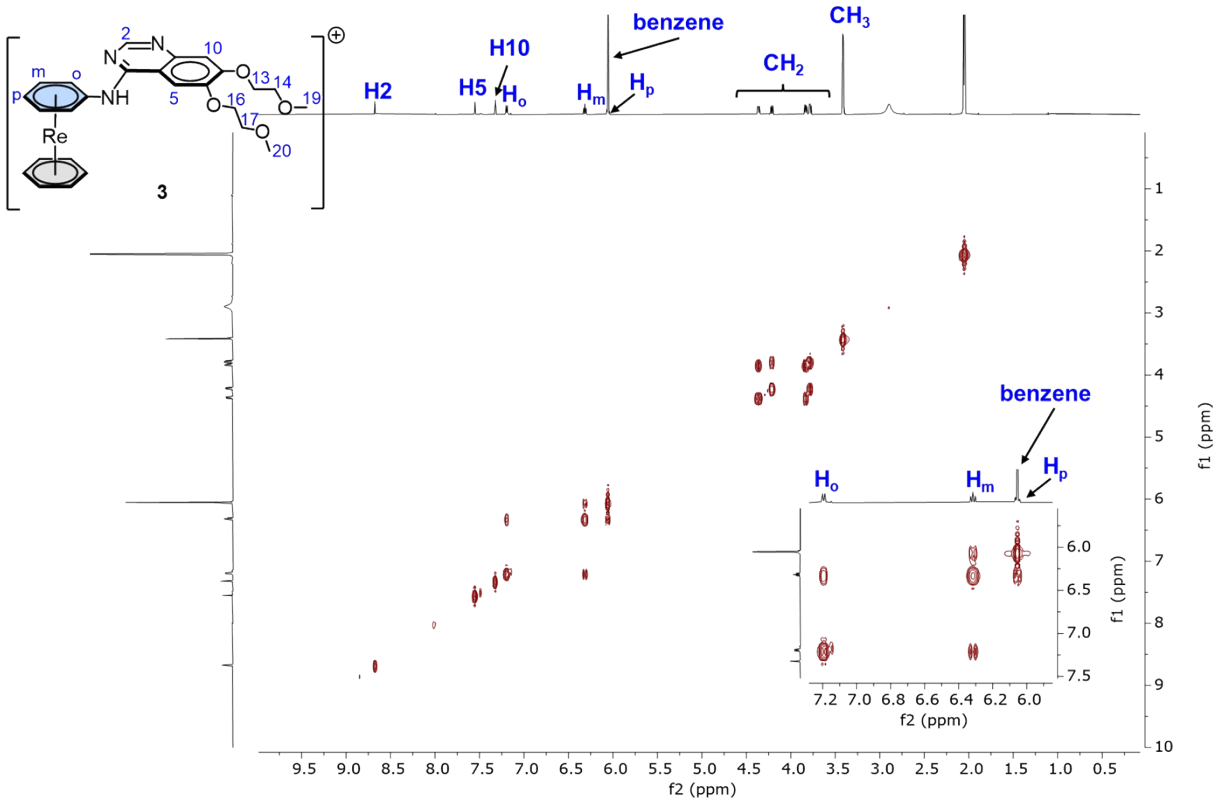

Figure S8. ^{1}H-^{1}H COSY spectrum in acetone-d_6 of [Re(η^6-bz)(η^6-pseudoerlotinib)]$^+$ (**3**).

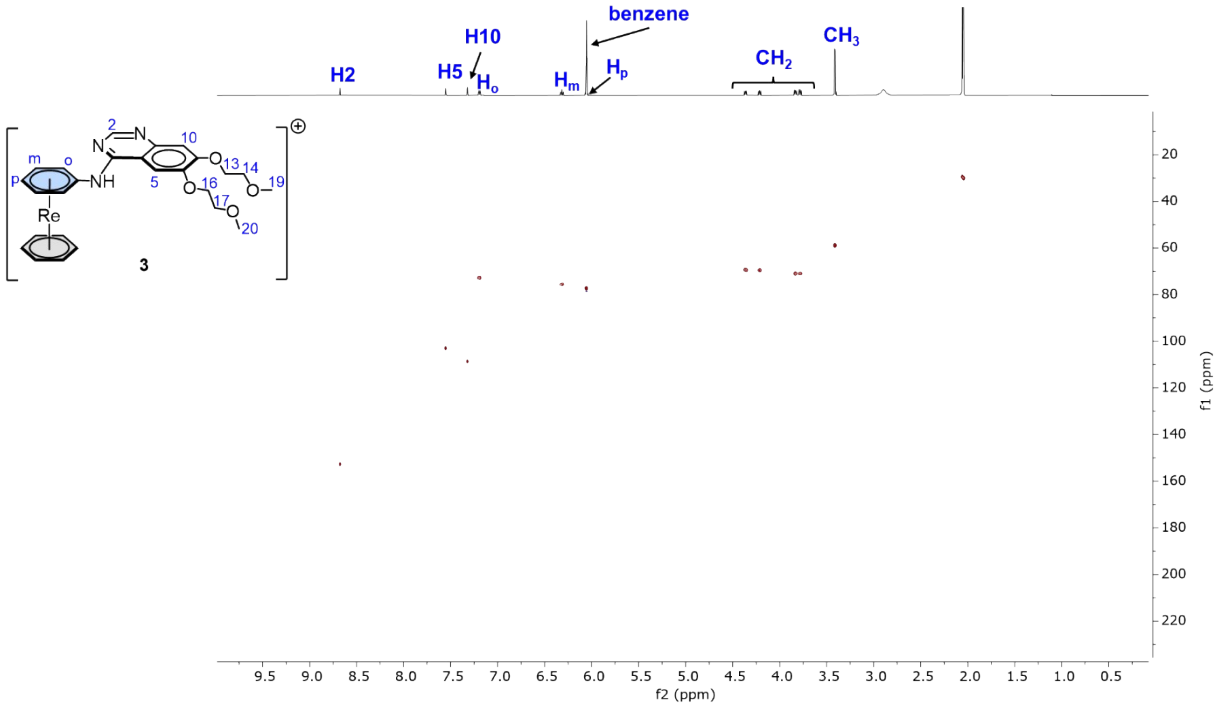

Figure S9. ^{1}H-^{13}C HSQC spectrum in acetone-d_6 of $[Re(\eta^6\text{-bz})(\eta^6\text{-pseudoerlotinib})]^+$ (**3**).

HR-ESI spectra

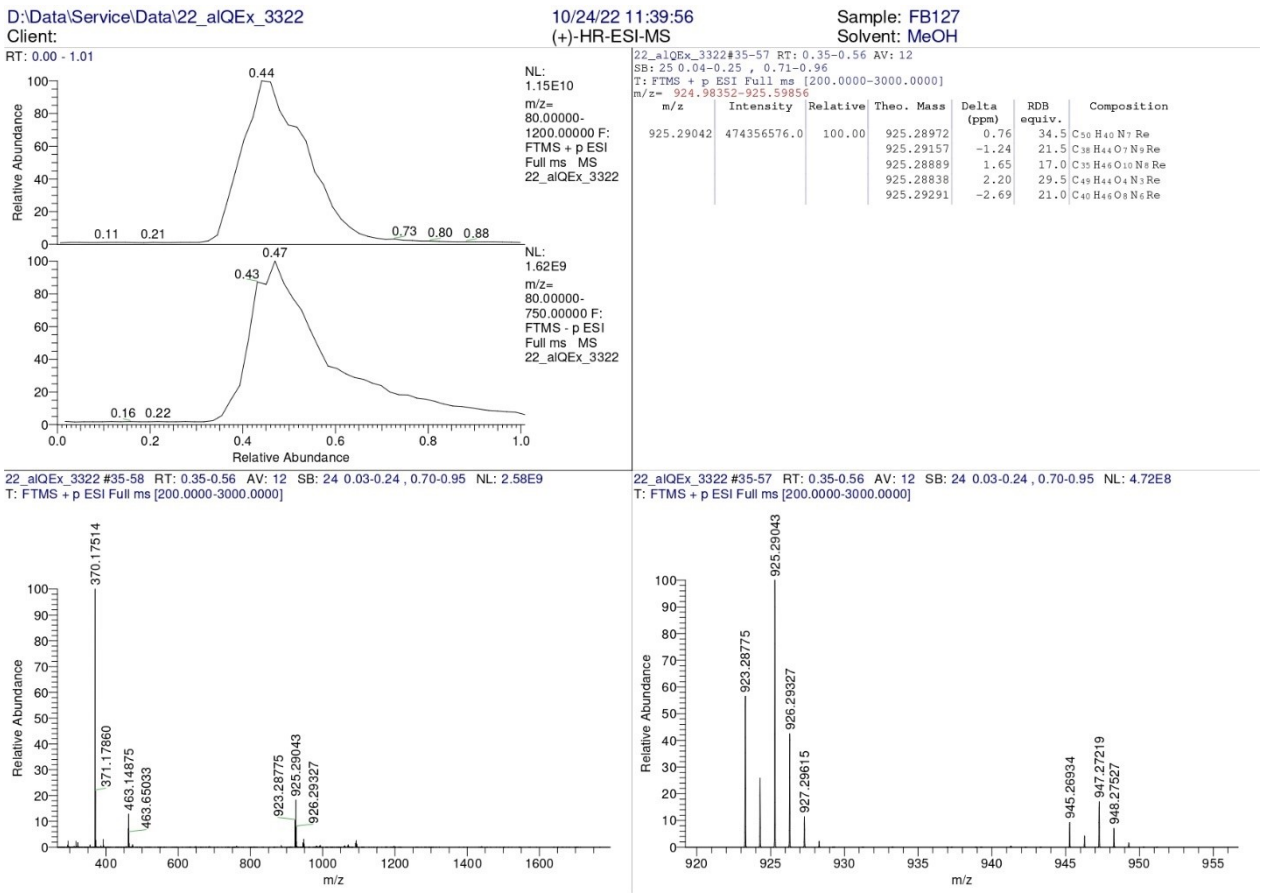

Figure S10. HR-ESI-MS spectrum of $[Re(\eta^6\text{-pseudoerlotinib})_2]^+$ (**1**).

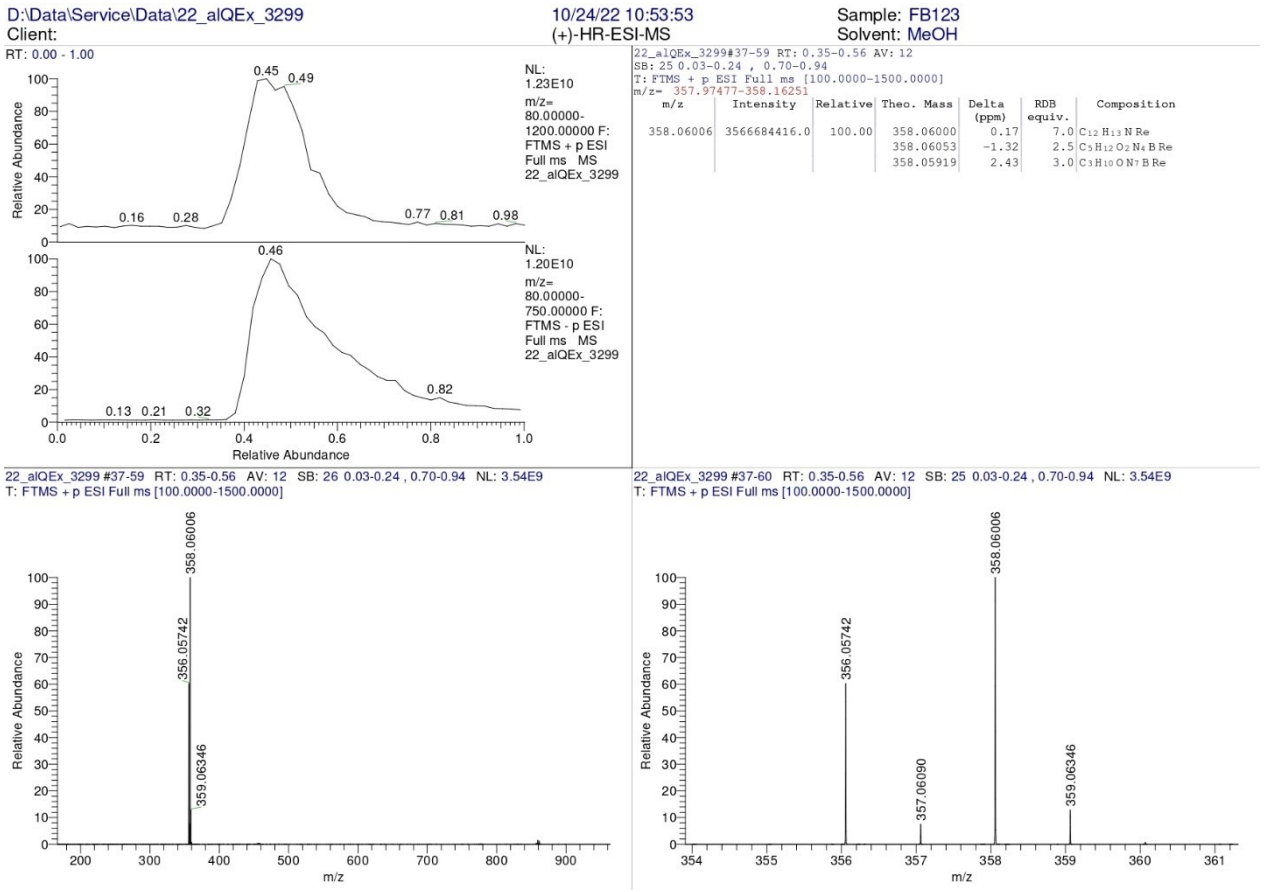

Figure S11. HR-ESI-MS spectrum of $[Re(\eta^6\text{-bz})(\eta^6\text{-aniline})]^+$ (**2**).

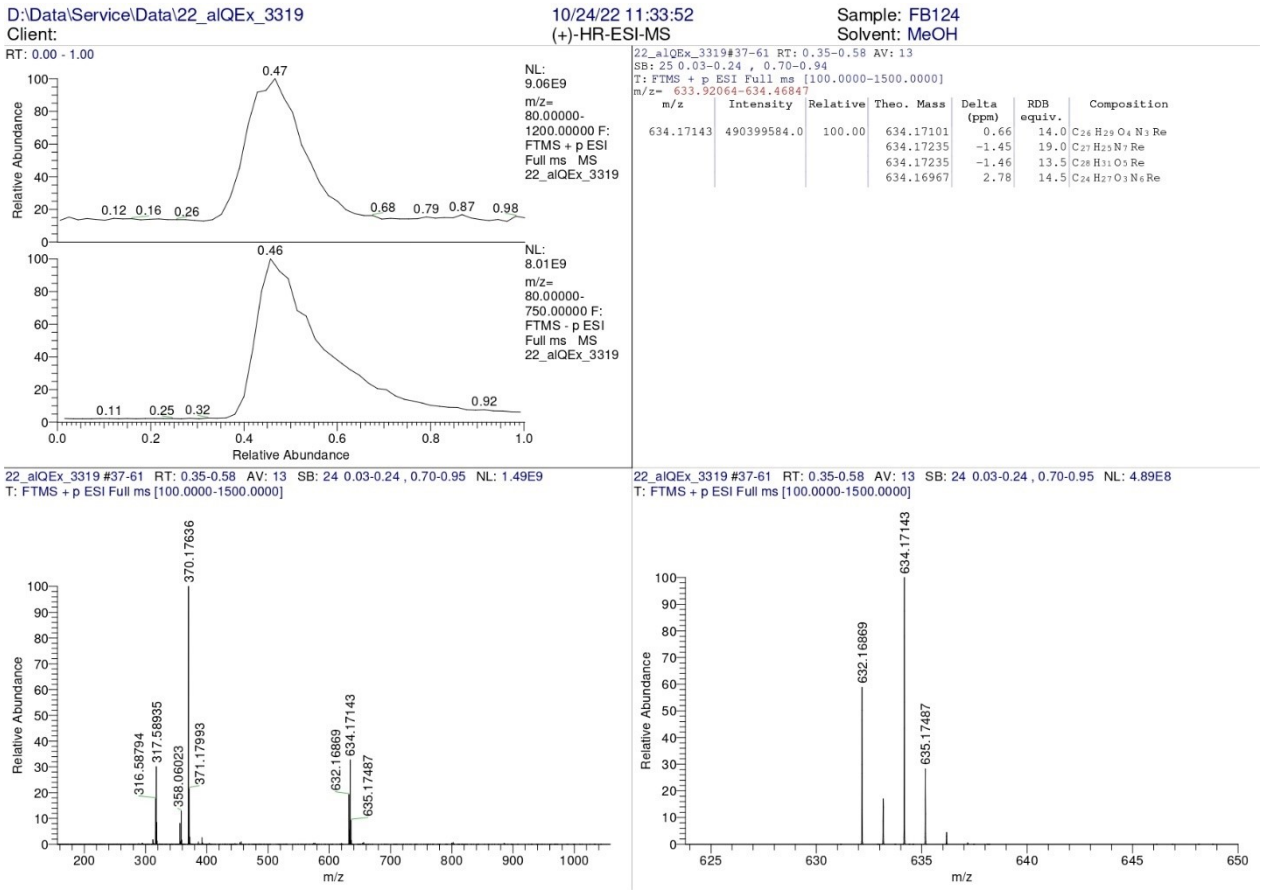

Figure S12. HR-ESI-MS spectrum of $[Re(\eta^6\text{-bz})(\eta^6\text{-pseudoerlotinib})]^+$ (**3**).

***in vitro* stability of [^{99m}Tc]1**

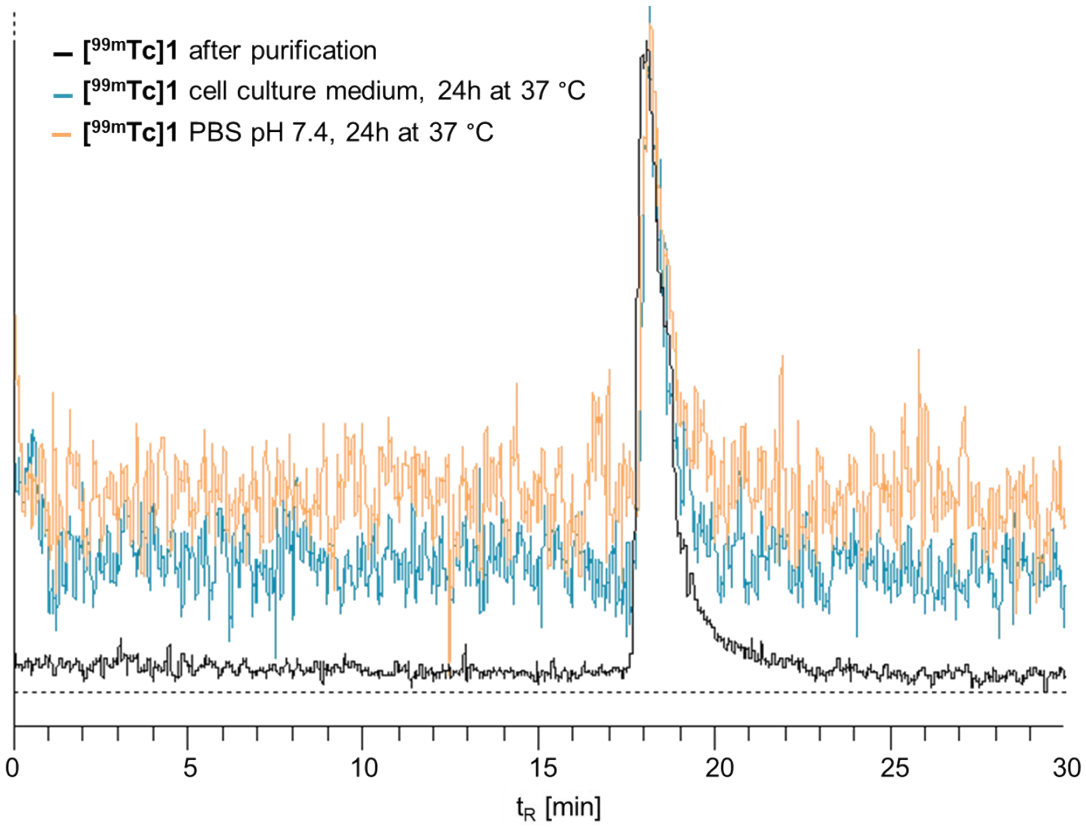

Figure S13. γ-traces of **[^{99m}Tc]1** after purification (black line), after incubation in cell culture medium for 24h at 37 °C (blue line), after incubation in PBS at pH 7.4 for 24h at 37 °C (blue line).

X-ray crystallography

Single-crystal X-ray diffraction data of **1**, **2**, **3** were collected at 160(1) K on a Rigaku OD XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer using a single wavelength X-ray source (Cu Kα radiation: λ= 1.54184Å) using the copper X-ray radiation (λ = 1.54184 Å) from a dual wavelength X-ray source and an Oxford Instruments Cryojet XL cooler. The selected suitable single crystal was mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction[1] were performed with the program suite CrysAlisPro.[2] Using Olex2,[3] the structure was solved with the SHELXT[4] small molecule structure solution program and refined with the SHELXL2018/3 program package[5] by full-matrix least-squares minimization on F2. PLATON[6] was used to check the result of the X-ray analysis. CCDC 2293185-2293187 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data and data collection of complexes [**1**]$(PF_6)Cl_2$, [**2**](PF_6), and [**3**](TFA).

	[Re(η⁶-pseudoerlotinib)$_2$] $(PF_6)Cl_2$2(H_2O) ([1]$PF_6Cl_2$2(H_2O))	**[Re(η⁶-bz)(η⁶-aniline)]PF_6 ([2]PF_6)**	**4[Re(η⁶-bz)(η⁶-pseudoerlotinib)] 4(PF_6)2.25(H_2O) 0.667(CH_2Cl_2) (4[3](PF_6)2.25(H_2O)0.667(CH_2Cl_2))**
Empirical formula	$C_{40}H_{52}Cl_2F_6N_6O_{10}PRe$	$C_{12}H_{13}F_6NPRe$	$C_{104.67}H_{120.43}Cl_{1.33}F_{24}N_{12}O_{17.55}P_4Re_4$
Formula weight	1178.94	502.40	3199.22
Temperature/K	160(1)	160(1)	160.0(1)
Crystal system	triclinic	orthorhombic	triclinic
Space group	P-1	Immm	P-1
a/Å	11.06150(10)	8.09180(10)	11.04098(7)
b/Å	13.8305(3)	12.2476(2)	14.03029(9)
c/Å	16.0904(3)	7.01550(10)	19.54390(14)
α/°	73.359(2)	90	77.5660(6)
β/°	71.7530(10)	90	84.5485(6)
γ/°	75.7690(10)	90	83.5136(5)
Volume/Å^3	2206.68(7)	695.272(17)	2929.77(4)
Z	2	2	1
ρ_{calc}g/cm^3	1.774	2.400	1.813
μ/mm^{-1}	7.636	18.792	9.607
F(000)	1184.0	472.0	1571.0
Crystal size/mm^3	0.15 × 0.04 × 0.03	0.18 × 0.12 × 0.09	0.15 × 0.09 × 0.01
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.94 to 148.998	13.114 to 148.64	7.15 to 149.004
Index ranges	-12 ≤ h ≤ 13, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -8 ≤ l ≤ 8	-13 ≤ h ≤ 13, -17 ≤ k ≤ 14, -23 ≤ l ≤ 24
Reflections collected	46323	3744	61434
Independent reflections	8981 [R_{int} = 0.0251, R_{sigma} = 0.0172]	436 [R_{int} = 0.0280, R_{sigma} = 0.0112]	11918 [R_{int} = 0.0237, R_{sigma} = 0.0171]
Data/restraints/parameters	8981/0/627	436/108/72	11918/409/832
Goodness-of-fit on F^2	1.130	1.172	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0287, wR_2 = 0.0690	R_1 = 0.0162, wR_2 = 0.0396	R_1 = 0.0293, wR_2 = 0.0755
Final R indexes [all data]	R_1 = 0.0292, wR_2 = 0.0692	R_1 = 0.0162, wR_2 = 0.0396	R_1 = 0.0306, wR_2 = 0.0764
Largest diff. peak/hole / e Å^{-3}	1.30/-1.61	0.47/-0.70	1.09/-1.52
CCDC Nr.	2293186	2293185	2293187

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(2) CrysAlisPro (version 1.171.42.57a). Rigaku Oxford Diffraction Ltd. Yarnton, Oxfordshire, England, 2022.

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