crystals

MDPI

Article

Structural, Non-Covalent Interaction, and Natural Bond Orbital Studies on Bromido-Tricarbonyl Rhenium(I) Complexes Bearing Alkyl-Substituted 1,4-Diazabutadiene (DAB) Ligands

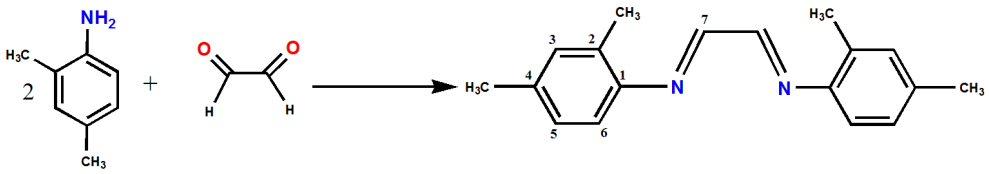
Reza Kia * and Azadeh Kalaghchi

Chemistry Department, Sharif University of Technology, P.O. Box 11155-3516, Tehran, Iran; azade_ka8757@yahoo.com

* Correspondence: Tel.: +98-21-66165332 Fax: +98-21-66029165; rkia@sharif.edu & zsrkk@yahoo.com

Received: 28 February 2020; Accepted: 31 March 2020; Published: date

Content	Page
Figure S1. The ^{1}H-NMR spectrum of complex **L1**.	2
Figure S2. The ^{13}C{^{1}H}-NMR spectrum of complex **L1**.	3
Figure S3. The ^{1}H-NMR spectrum of complex **L2**.	4
Figure S4. The ^{13}C{^{1}H}-NMR spectrum of complex **L2**.	5
Figure S5. The ^{1}H-NMR spectrum of complex **L3**.	6
Figure S6. The ^{13}C{^{1}H}-NMR spectrum of complex **L3**.	7
Figure S7. The ^{1}H-NMR spectrum of complex **L4**.	8
Figure S8. The ^{13}C{^{1}H}-NMR spectrum of complex **L4**.	9
Figure S9. The FTIR spectrum of **1** in KBr pellet.	10
Figure S10. The FTIR spectrum of **2** in KBr pellet.	10
Figure S11. The FTIR spectrum of **3** in KBr pellet.	11
Figure S12. The FTIR spectrum of **4** in KBr pellet.	11
Figure S13. The ^{1}H-NMR spectrum of complex **1**.	12
Figure S14. The ^{13}C{^{1}H}-NMR spectrum of complex **1**.	12
Figure 15. The ^{1}H-NMR spectrum of complex **2**.	13
Figure S16. The ^{13}C{^{1}H}-NMR spectrum of complex **2**.	13
Figure S17. The ^{1}H-NMR spectrum of complex **3**.	14
Figure S18. The ^{13}C{^{1}H}-NMR spectrum of complex **3**.	14
Figure S19. The ^{1}H-NMR spectrum of complex **4**.	15
Figure S20. The ^{13}C{^{1}H}-NMR spectrum of complex **4**.	15
Crystal data and refinement parameters of **1-4**.	16–44



^{1}H-NMR (δ_{ppm} $CDCl_3$): 2.38 (s, 6H, 2-(CH_3)), 2.41(s, 6H, 4-(CH_3)) ,6.97–7.11 (m, 6H, aromatic hydrogens), 8.34 (s, 2H, iminic hydrogens). ^{13}C{^{1}H}-NMR (δ_{ppm} $CDCl_3$): 17.72 (2-CH_3 carbon), 20.97 (4-CH_3 carbon), 116.98 (C6), 127.29 (C5), 131.36 (C3), 133.07 (C2), 137.25 (C4), 146.95 (C1), 158.91 (C7 iminic carbon). FTIR (KBr):.

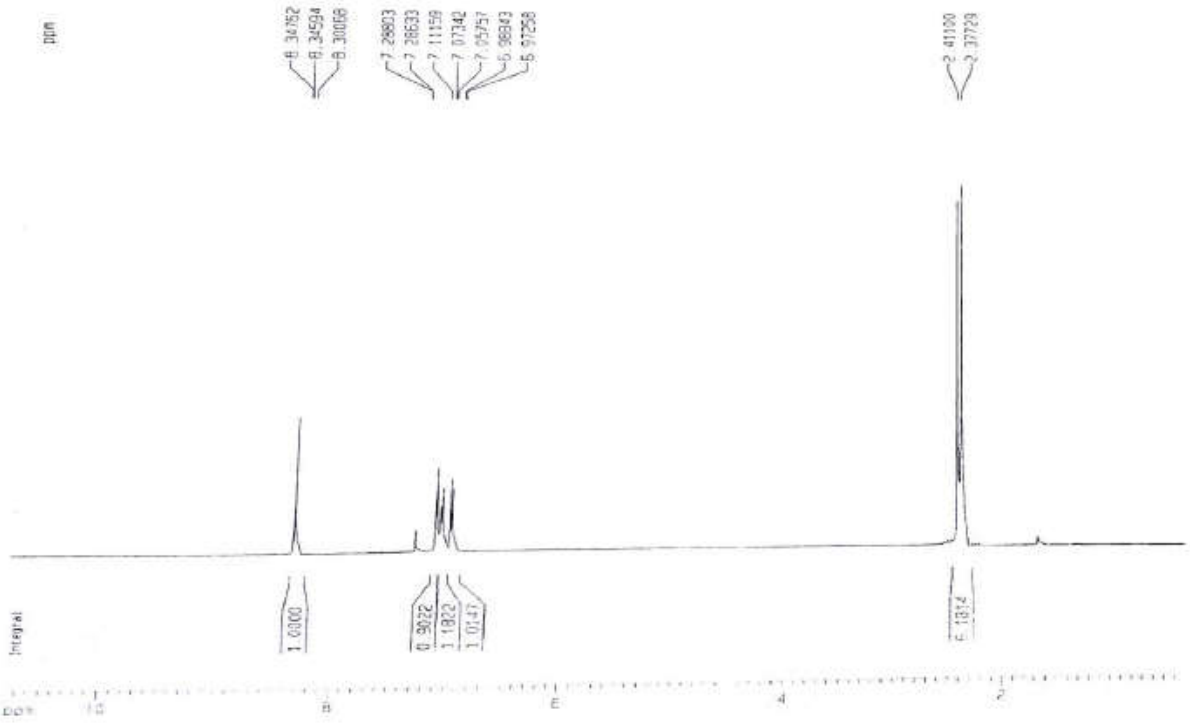


Figure S1. The ^{1}HNMR spectrum of **L1**.

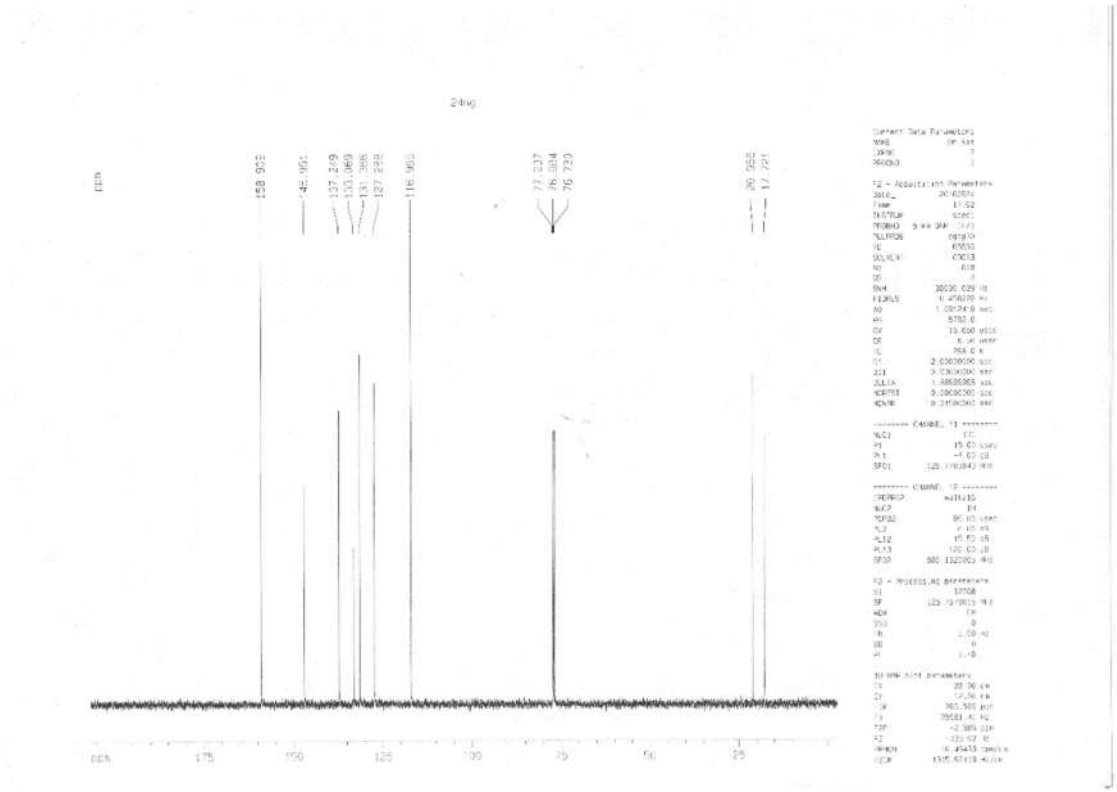
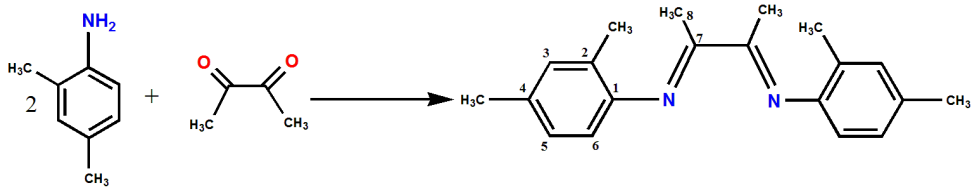


Figure S2. The $^{13}C\{^{1}H\}$ NMR spectrum of **L1**.



^{1}H-NMR (δ_{ppm} $CDCl_3$): **2.18** (s, 6H, 2-CH_3), 2.21 (s, 6H, 4-CH_3), 2.40 (s, 6H, 7-CH_3), 6.62-7.13 (6H, aromatic hydrogens). ^{13}C{^{1}H}-NMR (δ_{ppm} $CDCl_3$): 15.42 (2-CH_3), 17.65 (4-CH_3), 20.75 (7-CH_3), 117.57 (C6), 126.75 (C5), 131.02 (C3,C2), 133.12 (C4), 146.87 (C1), 167.68 (C7 iminic carbon).

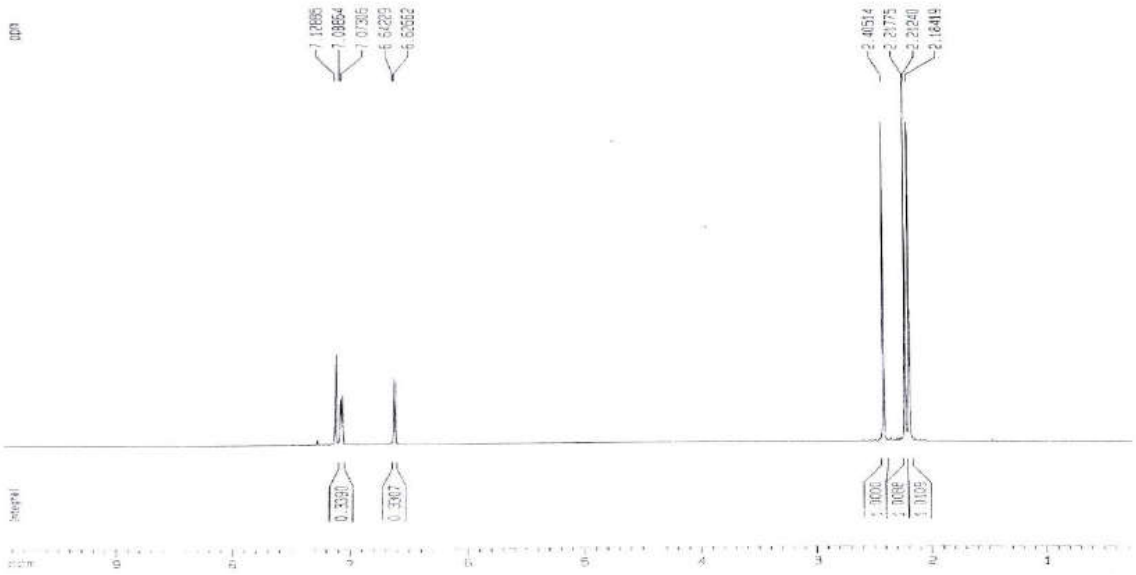


Figure S3. The ^{1}HNMR spectrum of **L2**.

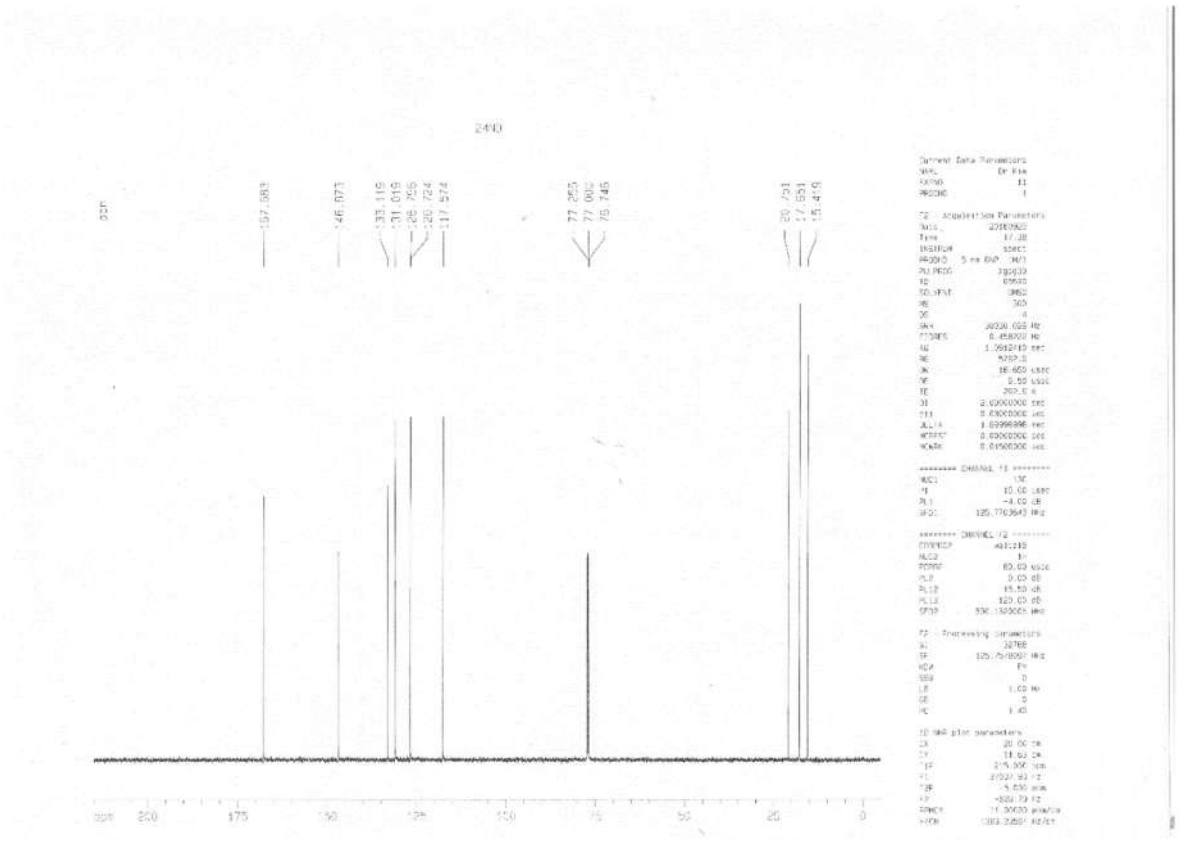
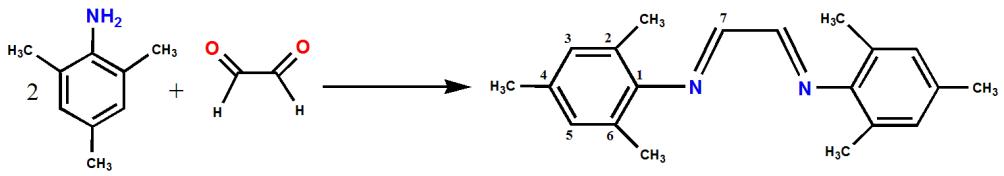


Figure S4. The $^{13}C\{^{1}H\}$ NMR spectrum of **L2**.



شکل 2-3 سنتز لیگاند $^{2,4,6\text{-Me}_3}$DAB

^{1}H-NMR (δ_{ppm} $CDCl_3$): 2.19 (s, 12H, 2,6-$(CH_3)_2$), 2.33 (s,6H, 4-CH_3), 6.95 (s, 4H, aromatic hydrogens), 8.13 (s, 2H, iminic hydrogens). ^{13}C{^{1}H}-NMR (δ_{ppm} $CDCl_3$): 18.13 (2,6-$(CH_3)_2$), 20.54 (4-CH_3), 126.45 (C3, C5), 128.92 (C2, C6), 134.13 (C4), 147.39 (C1), 163.39 (C7 iminic carbon).

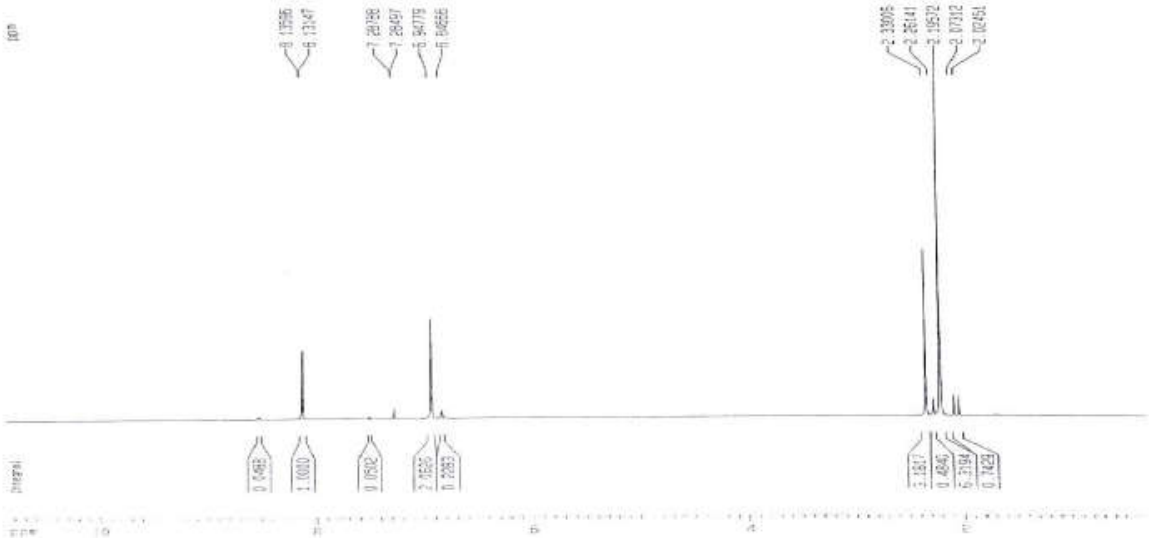


Figure S5. The ^{1}HNMR spectrum of **L3**.

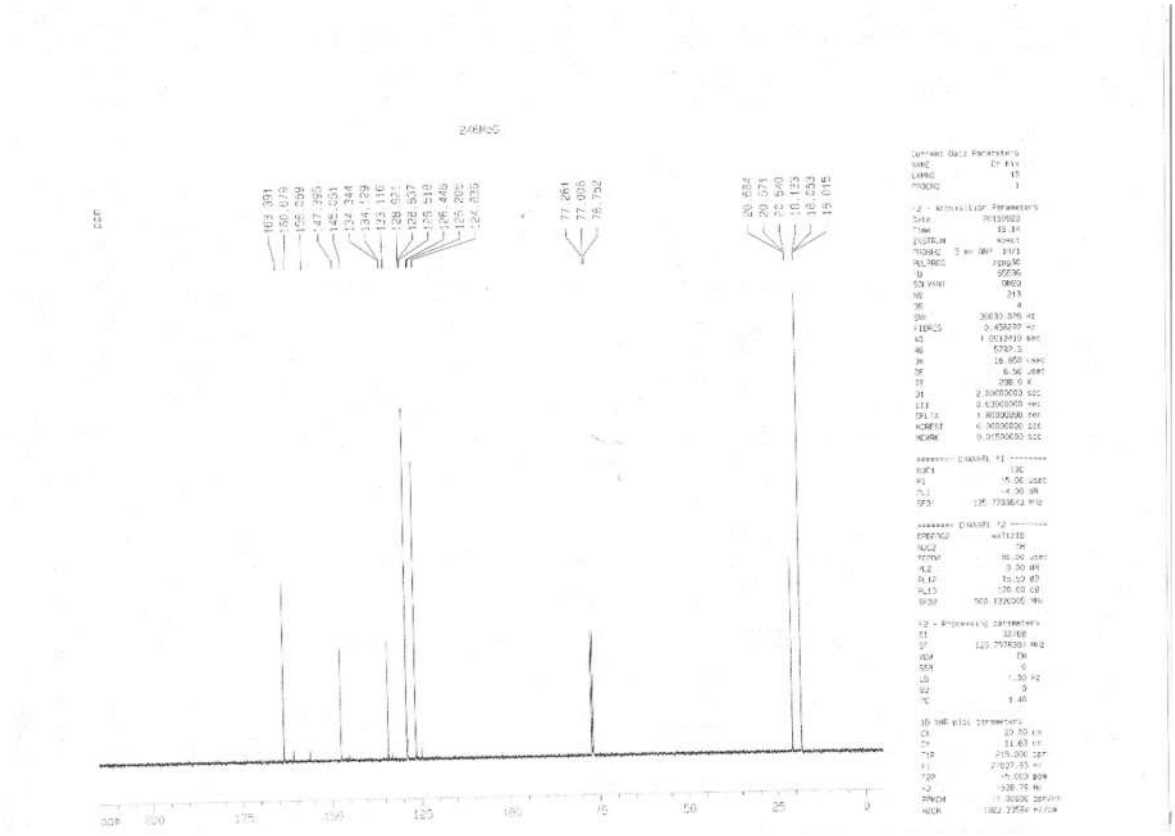
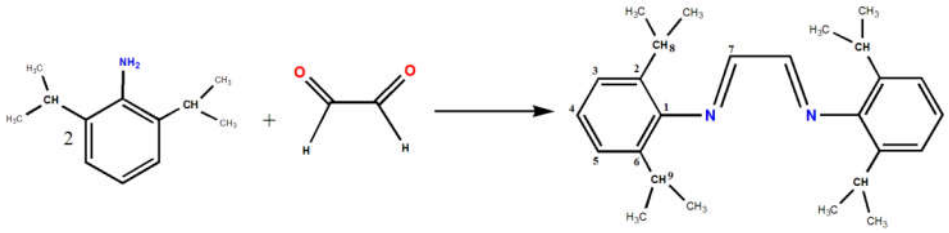


Figure S6. The $^{13}C\{^{1}H\}$ NMR spectrum of **L3**.



^{1}H-NMR (δ_{ppm} $CDCl_3$): 1.30 (s, 12H, 9-CH_3), 1.32 (s, 12H, 8-CH_3), 3.05 (m, 4H, isopropyl hydrogens), 7.22-7.30 (M, 6H, aromatic hydrogens), 8.21 (s, 2H, iminic hydrogens). ^{13}C{^{1}H}-NMR (δ_{ppm} $CDCl_3$): 23.30 (methyls carbon), 27.68(isopropyl carbon (C8, C9), 123.10 (C3,C5), 125.05 (C4), 136.40 (C2,C6), 147.97 (C1), 163.02 (C7 iminic carbon).

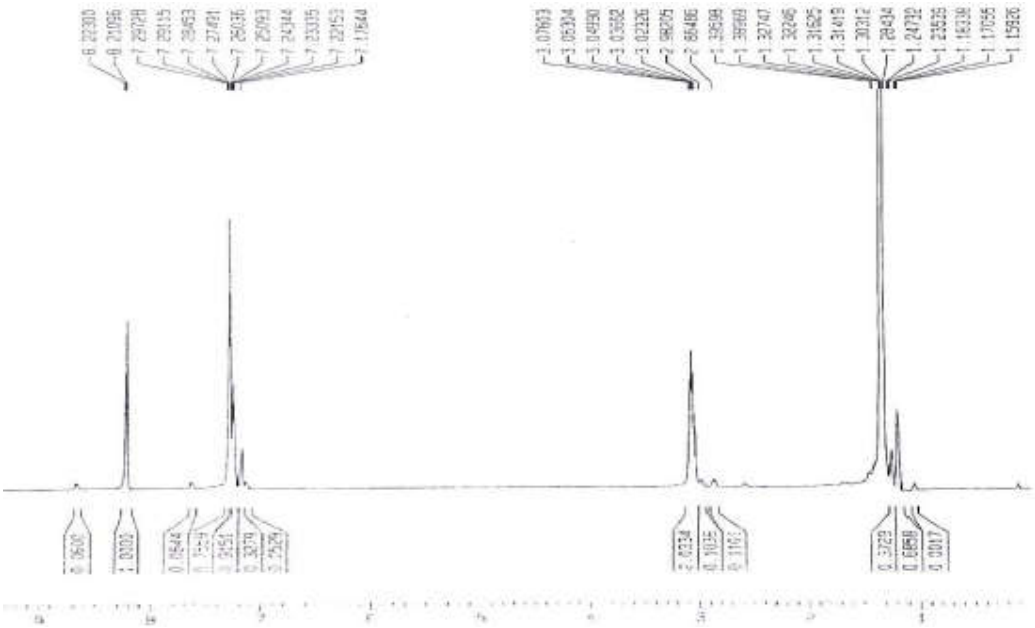


Figure S7. The ^{1}H NMR spectrum of **L4**.

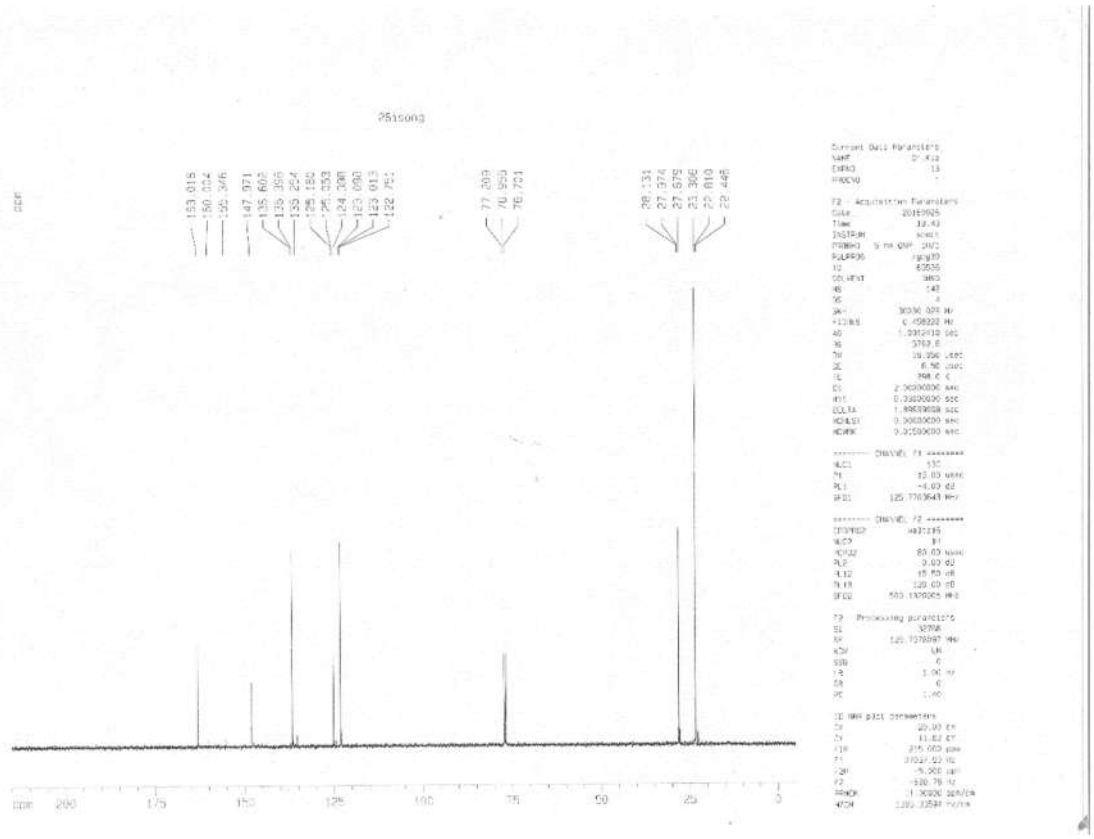


Figure S8. The $^{13}C\{^{1}H\}$ NMR spectrum of **L4**.

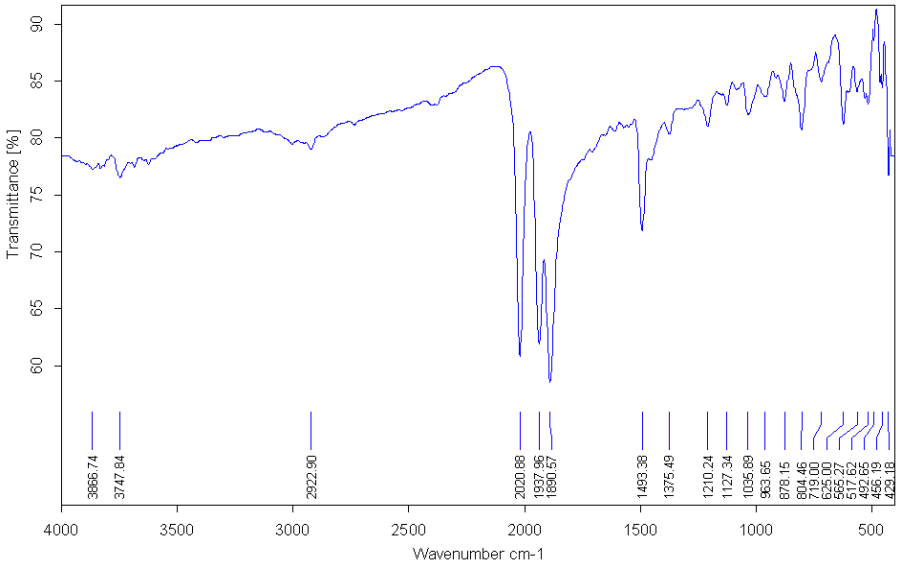


Figure S9. The FTIR spectrum of **1** in KBr pellet.

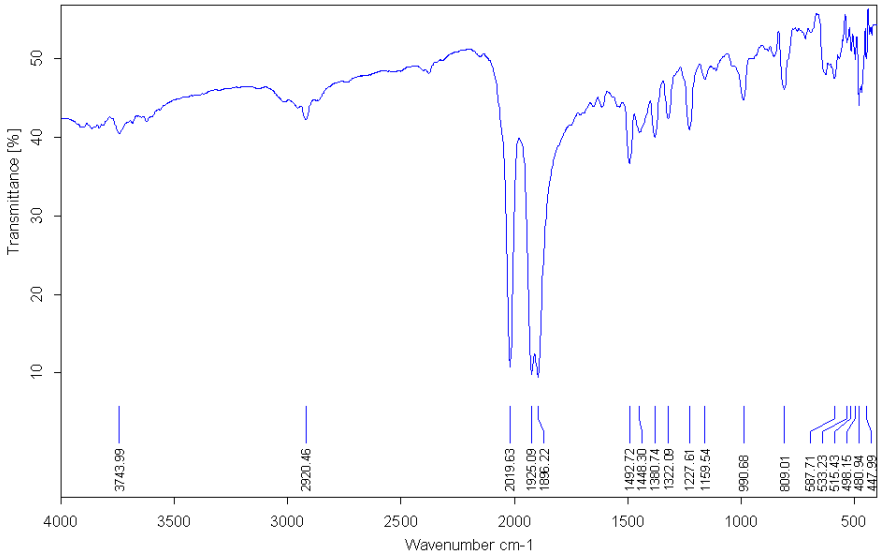


Figure S10. The FTIR spectrum of **2** in KBr pellet.

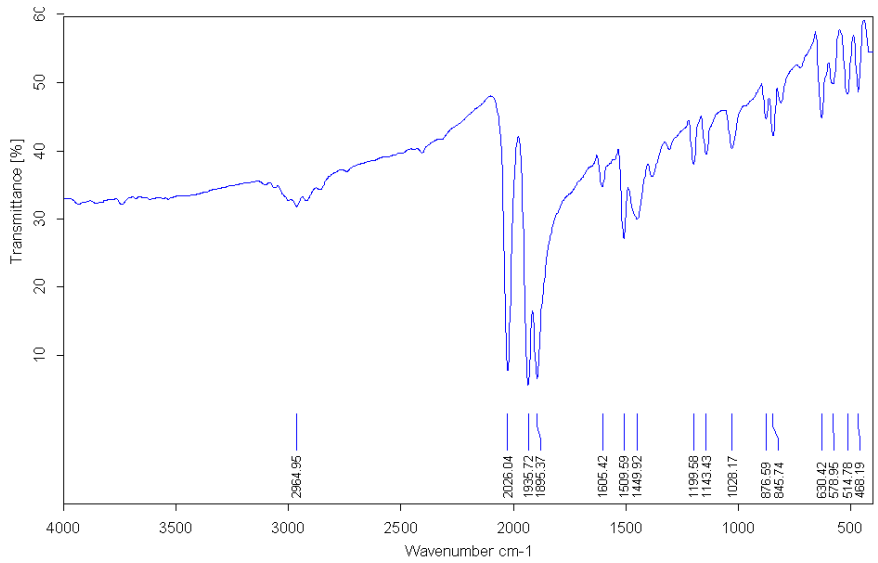


Figure S11. The FTIR spectrum of **3** in KBr pellet.

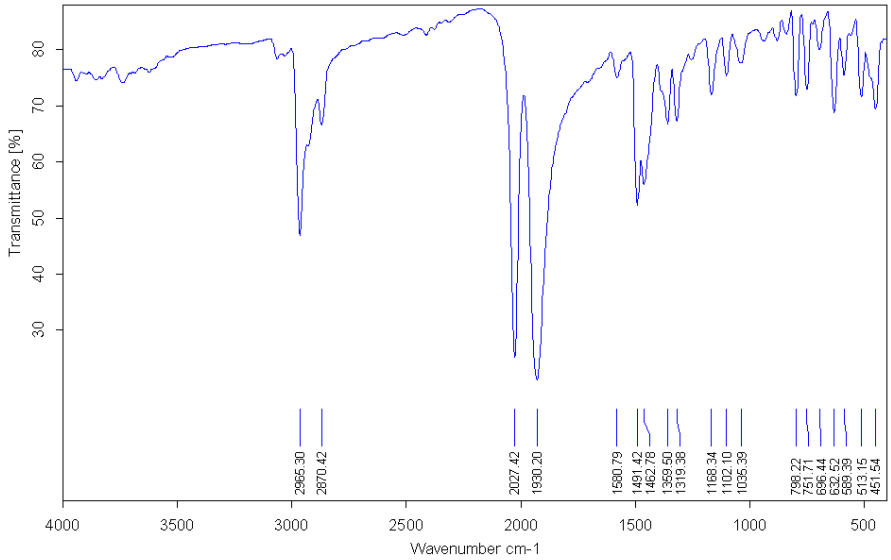


Figure S12. The FTIR spectrum of **4** in KBr pellet.

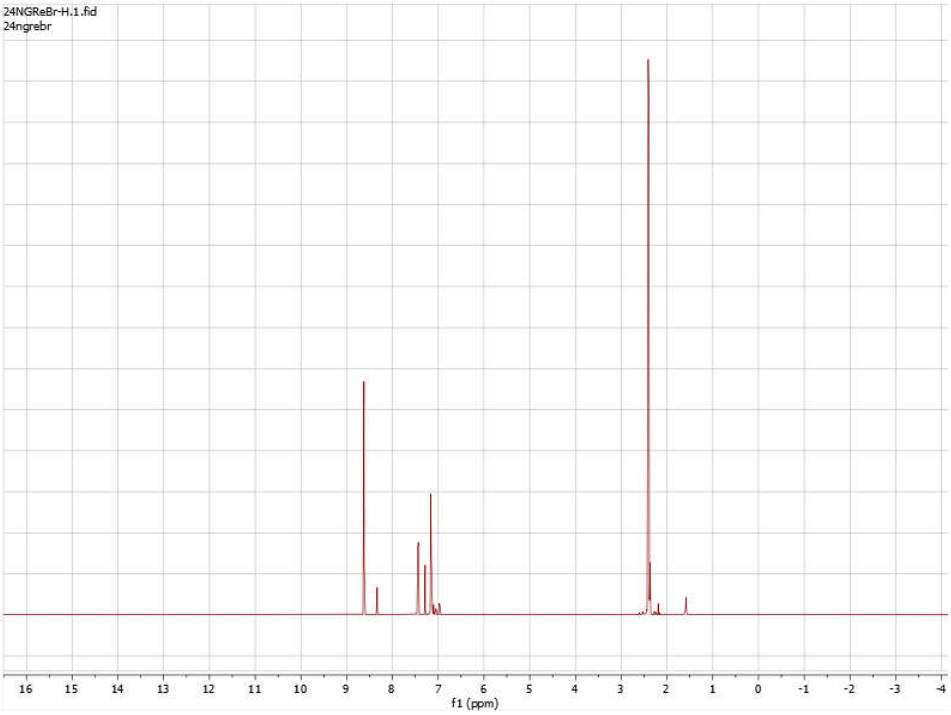


Figure S13. The ^{1}H-NMR spectrum of complex **1**.

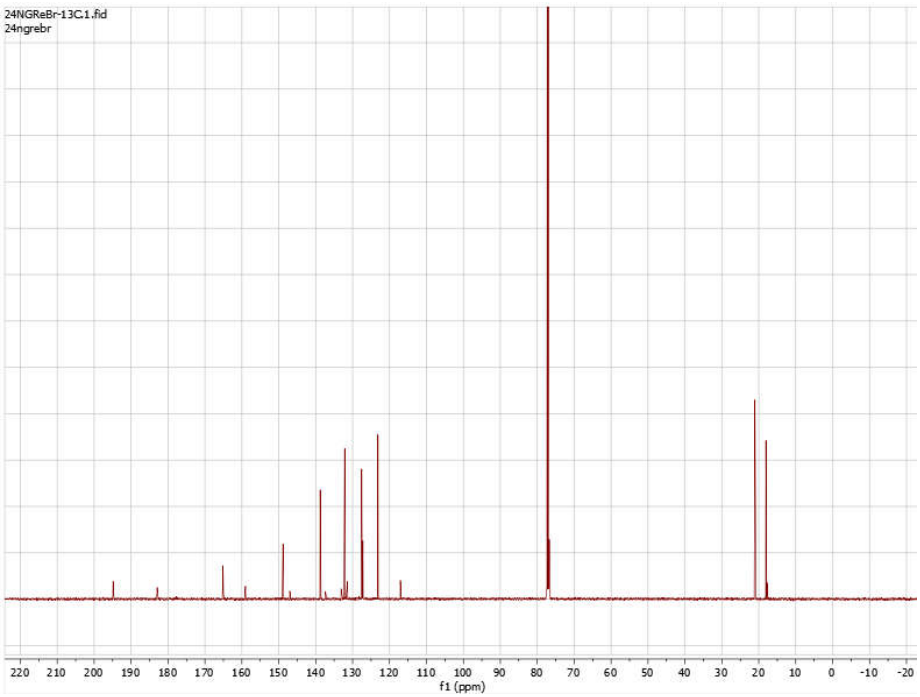


Figure S14. The ^{13}C{^{1}H}-NMR spectrum of complex **1**.

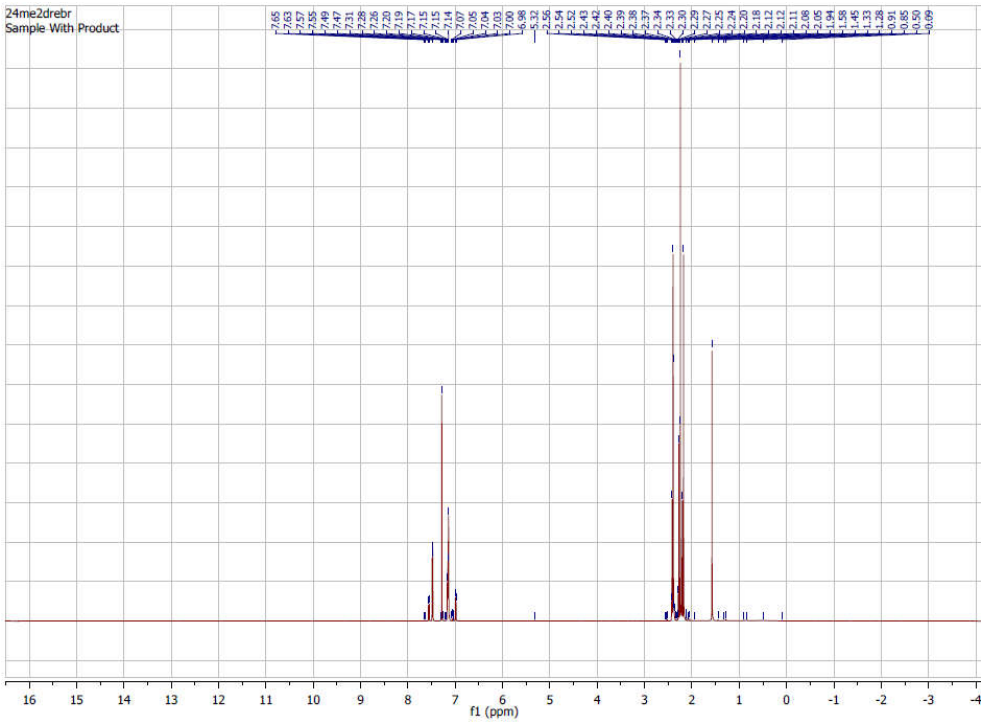


Figure S15. The ^{1}H-NMR spectrum of complex **2**.

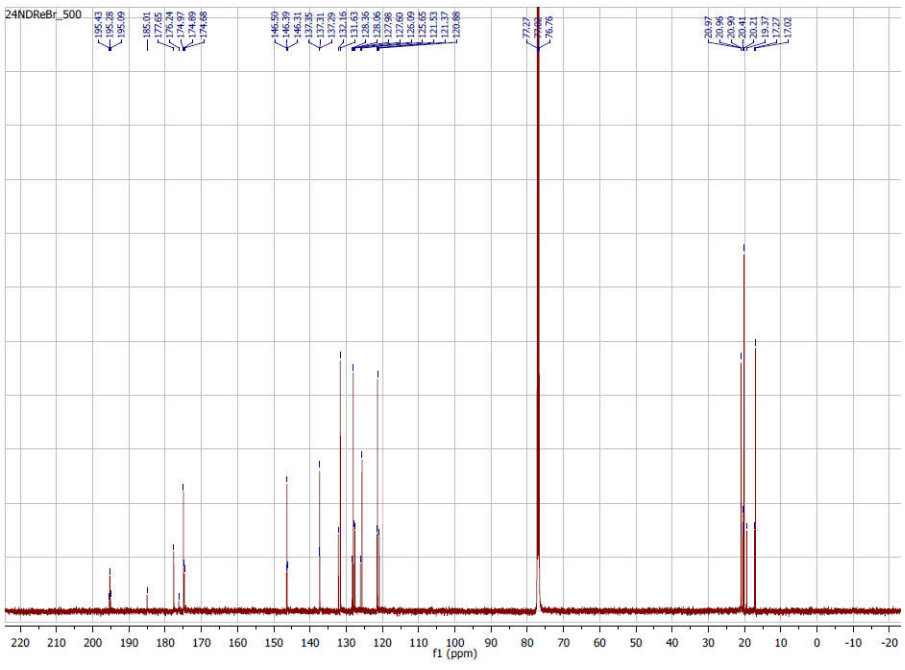


Figure S16. The ^{13}C{^{1}H}-NMR spectrum of complex **2**.

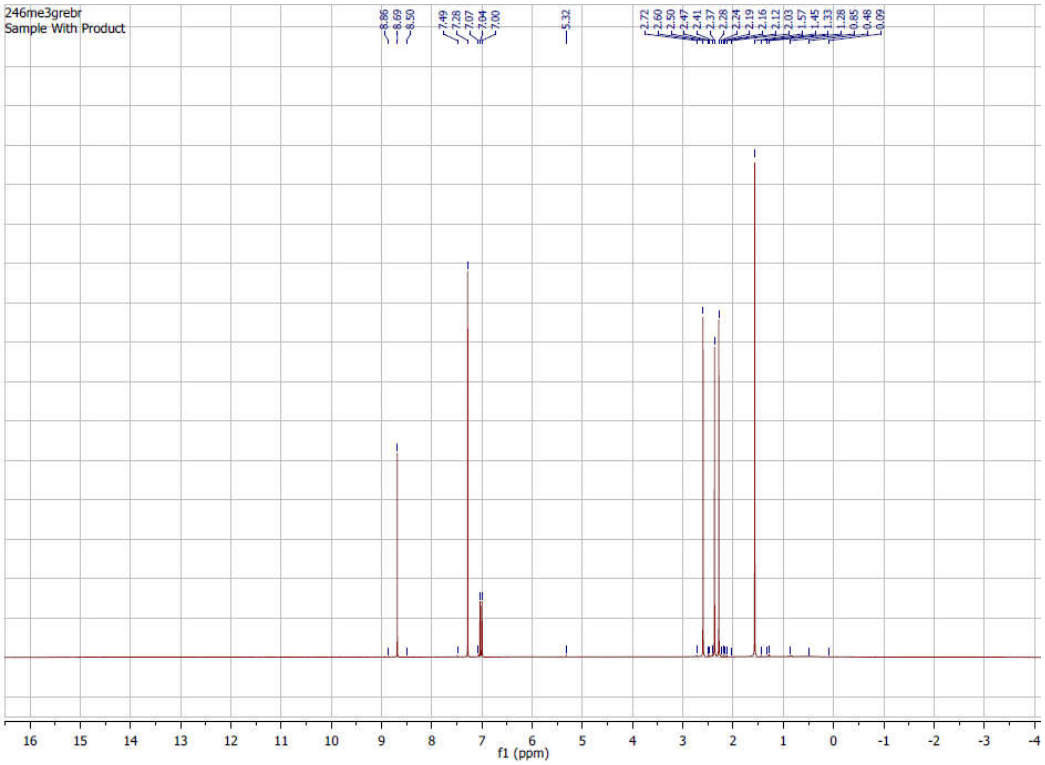


Figure S17. The ^{1}H-NMR spectrum of complex **3**.

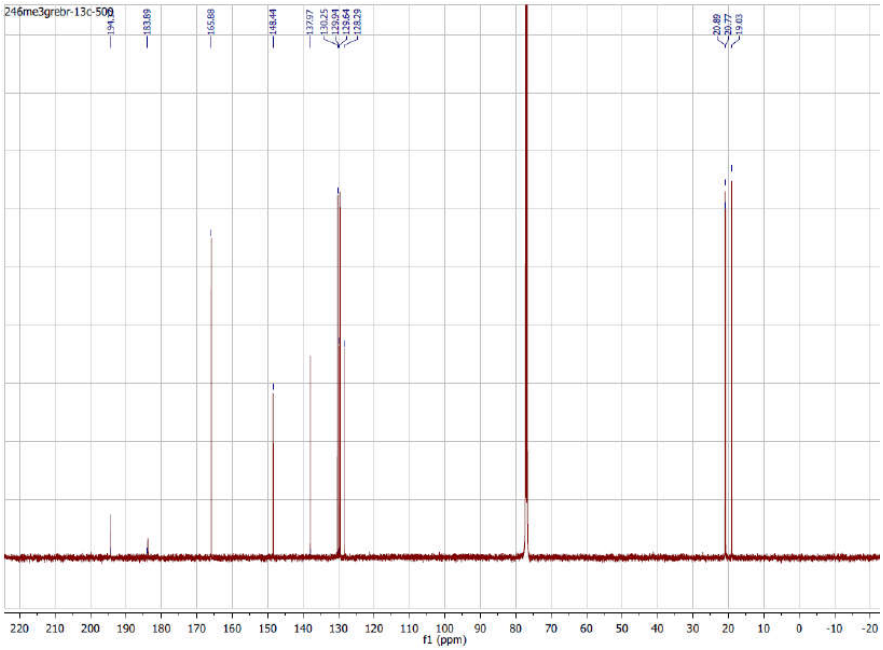


Figure S18. The ^{13}C{^{1}H}-NMR spectrum of complex **3**.

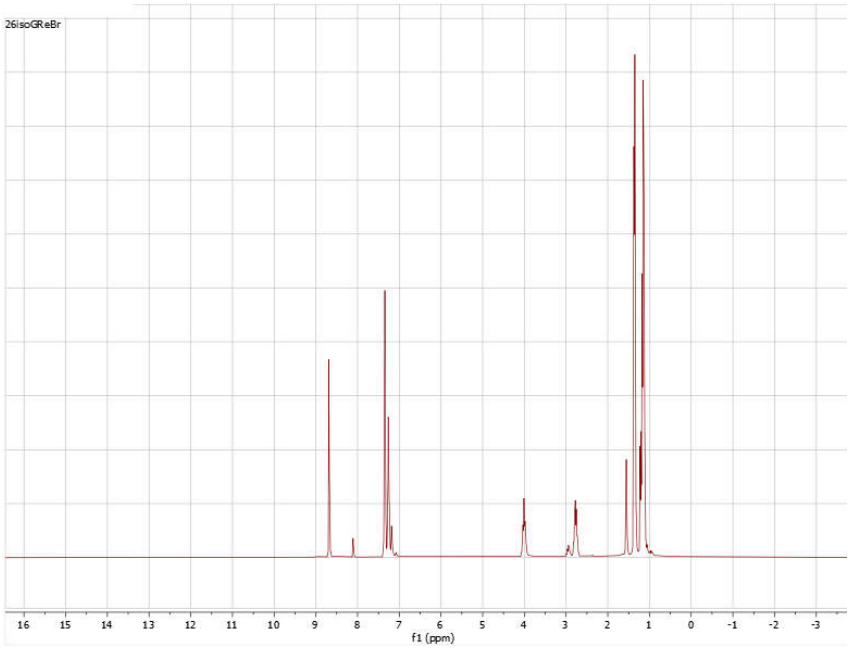


Figure S19. The ^{1}H-NMR spectrum of complex **4**.

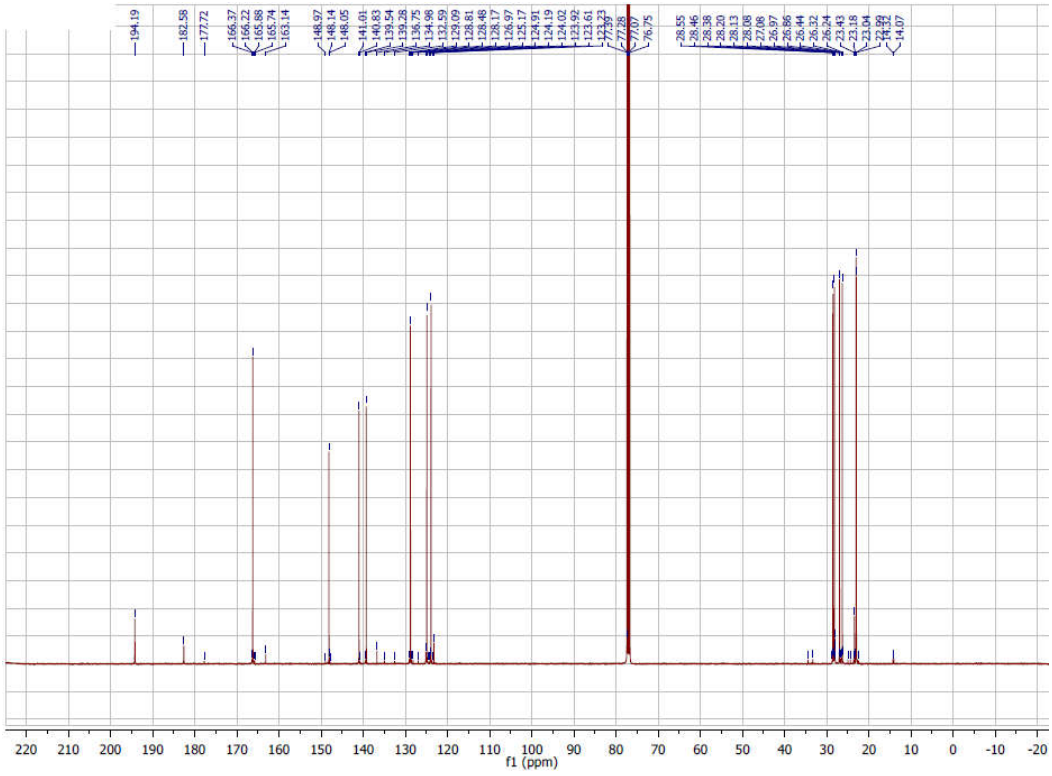


Figure S20. The ^{13}C{^{1}H}-NMR spectrum of complex **4**.

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

Identification code	**1**	
Empirical formula	C21 H18 Br N2 O5 Re	
Formula weight	644.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.5777(4) Å	◎= 90°
	b = 21.4023(14) Å	◎= 93.829(5)°
	c = 13.0644(7) Å	◎ = 90°
Volume	2114.1(2) $Å^3$	
Z	4	
Density (calculated)	2.025 Mg/m^3	
Absorption coefficient	7.673 mm^{-1}	
Theta range for data collection	3.342 to 25.998°	
Index ranges	-6<=h<=9, -21<=k<=26, -15<=l<=16	
Reflections collected	9399	
Independent reflections	4146 [R(int) = 0.0458]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4146 / 3 / 270	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0741	
R indices (all data)	R1 = 0.0668, wR2 = 0.0839	
Largest diff. peak and hole	1.365 and -1.244 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **1**.

C(1)-C(2)	1.370(8)
C(1)-C(6)	1.391(9)
C(1)-N(1)	1.460(8)
C(2)-C(3)	1.395(9)
C(2)-H(2)	0.9300
C(3)-C(4)	1.385(9)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(8)
C(4)-C(15)	1.509(9)
C(5)-C(6)	1.397(9)
C(5)-H(5)	0.9300
C(6)-C(16)	1.517(8)
C(7)-N(1)	1.297(8)
C(7)-C(8)	1.444(9)
C(7)-H(7)	0.9300
C(8)-N(2)	1.283(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.377(9)
C(9)-C(14)	1.398(9)
C(9)-N(2)	1.444(8)
C(10)-C(11)	1.407(9)
C(10)-H(10)	0.9300
C(11)-C(12)	1.370(10)
C(11)-H(11)	0.9300
C(12)-C(13)	1.375(9)
C(12)-C(17)	1.517(9)
C(13)-C(14)	1.399(9)
C(13)-H(13)	0.9300
C(14)-C(18)	1.501(9)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600

C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-O(1)	1.145(7)
C(19)-Re(1)	1.922(7)
C(20)-O(2)	1.141(8)
C(20)-Re(1)	1.930(7)
C(21)-O(3)	1.157(8)
C(21)-Re(1)	1.893(7)
N(1)-Re(1)	2.147(5)
N(2)-Re(1)	2.179(5)
Re(1)-O(4)	2.1430(10)
Re(1)-Br(1)	2.591(3)
O(4)-N(3)	1.2931(10)
O(5)-N(3)	1.2339(10)

C(2)-C(1)-C(6)	121.8(6)
C(2)-C(1)-N(1)	118.0(6)
C(6)-C(1)-N(1)	120.2(6)
C(1)-C(2)-C(3)	120.1(6)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	119.9(6)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(5)-C(4)-C(3)	118.6(6)
C(5)-C(4)-C(15)	119.5(6)
C(3)-C(4)-C(15)	121.9(6)
C(4)-C(5)-C(6)	123.1(6)
C(4)-C(5)-H(5)	118.4
C(6)-C(5)-H(5)	118.4
C(1)-C(6)-C(5)	116.5(6)
C(1)-C(6)-C(16)	123.7(6)
C(5)-C(6)-C(16)	119.8(6)
N(1)-C(7)-C(8)	116.7(7)
N(1)-C(7)-H(7)	121.6
C(8)-C(7)-H(7)	121.6
N(2)-C(8)-C(7)	117.9(6)

N(2)-C(8)-H(8)	121.1
C(7)-C(8)-H(8)	121.1
C(10)-C(9)-C(14)	121.1(6)
C(10)-C(9)-N(2)	117.4(6)
C(14)-C(9)-N(2)	121.5(6)
C(9)-C(10)-C(11)	119.9(7)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.2(7)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	119.0(7)
C(13)-C(12)-C(17)	119.9(7)
C(11)-C(12)-C(17)	121.1(7)
C(12)-C(13)-C(14)	123.0(7)
C(12)-C(13)-H(13)	118.5
C(14)-C(13)-H(13)	118.5
C(13)-C(14)-C(9)	116.9(7)
C(13)-C(14)-C(18)	120.9(6)
C(9)-C(14)-C(18)	122.1(6)
C(4)-C(15)-H(15A)	109.5
C(4)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(4)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(6)-C(16)-H(16A)	109.5
C(6)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(6)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5

C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(1)-C(19)-Re(1)	179.0(6)
O(2)-C(20)-Re(1)	179.5(7)
O(3)-C(21)-Re(1)	177.1(5)
C(7)-N(1)-C(1)	116.3(5)
C(7)-N(1)-Re(1)	115.4(4)
C(1)-N(1)-Re(1)	128.3(4)
C(8)-N(2)-C(9)	116.3(5)
C(8)-N(2)-Re(1)	114.0(4)
C(9)-N(2)-Re(1)	128.7(4)
C(21)-Re(1)-C(19)	86.2(3)
C(21)-Re(1)-C(20)	90.9(3)
C(19)-Re(1)-C(20)	88.6(3)
C(21)-Re(1)-O(4)	169.0(3)
C(19)-Re(1)-O(4)	100.7(3)
C(20)-Re(1)-O(4)	97.7(3)
C(21)-Re(1)-N(1)	92.8(3)
C(19)-Re(1)-N(1)	100.0(2)
C(20)-Re(1)-N(1)	170.9(2)
O(4)-Re(1)-N(1)	77.7(3)
C(21)-Re(1)-N(2)	99.5(2)
C(19)-Re(1)-N(2)	172.4(3)
C(20)-Re(1)-N(2)	96.4(2)
O(4)-Re(1)-N(2)	72.9(3)
N(1)-Re(1)-N(2)	74.8(2)
C(21)-Re(1)-Br(1)	169.74(18)
C(19)-Re(1)-Br(1)	84.0(2)
C(20)-Re(1)-Br(1)	85.9(2)
N(1)-Re(1)-Br(1)	91.79(15)
N(2)-Re(1)-Br(1)	90.57(15)
N(3)-O(4)-Re(1)	130.6(8)
O(5)-N(3)-O(4)	107.7(11)

Symmetry transformations used to generate equivalent atoms:.

Table 3. Torsion angles [°] for **1**.

C(6)-C(1)-C(2)-C(3)	-1.3(11)
N(1)-C(1)-C(2)-C(3)	178.8(6)
C(1)-C(2)-C(3)-C(4)	-1.0(11)
C(2)-C(3)-C(4)-C(5)	2.9(10)
C(2)-C(3)-C(4)-C(15)	-178.8(7)
C(3)-C(4)-C(5)-C(6)	-2.6(11)
C(15)-C(4)-C(5)-C(6)	179.1(7)
C(2)-C(1)-C(6)-C(5)	1.6(10)
N(1)-C(1)-C(6)-C(5)	-178.5(6)
C(2)-C(1)-C(6)-C(16)	-176.8(7)
N(1)-C(1)-C(6)-C(16)	3.1(11)
C(4)-C(5)-C(6)-C(1)	0.3(11)
C(4)-C(5)-C(6)-C(16)	178.8(7)
N(1)-C(7)-C(8)-N(2)	3.2(10)
C(14)-C(9)-C(10)-C(11)	-0.2(10)
N(2)-C(9)-C(10)-C(11)	-178.2(6)
C(9)-C(10)-C(11)-C(12)	1.4(10)
C(10)-C(11)-C(12)-C(13)	-1.4(10)
C(10)-C(11)-C(12)-C(17)	177.6(6)
C(11)-C(12)-C(13)-C(14)	0.4(10)
C(17)-C(12)-C(13)-C(14)	-178.7(6)
C(12)-C(13)-C(14)-C(9)	0.8(10)
C(12)-C(13)-C(14)-C(18)	177.6(6)
C(10)-C(9)-C(14)-C(13)	-0.8(9)
N(2)-C(9)-C(14)-C(13)	177.1(5)
C(10)-C(9)-C(14)-C(18)	-177.7(6)
N(2)-C(9)-C(14)-C(18)	0.2(9)
C(8)-C(7)-N(1)-C(1)	-171.7(6)
C(8)-C(7)-N(1)-Re(1)	5.8(8)
C(2)-C(1)-N(1)-C(7)	-125.4(7)
C(6)-C(1)-N(1)-C(7)	54.7(9)
C(2)-C(1)-N(1)-Re(1)	57.5(8)
C(6)-C(1)-N(1)-Re(1)	-122.4(6)
C(7)-C(8)-N(2)-C(9)	179.8(6)
C(7)-C(8)-N(2)-Re(1)	-10.2(8)
C(10)-C(9)-N(2)-C(8)	58.0(8)
C(14)-C(9)-N(2)-C(8)	-119.9(7)

C(10)-C(9)-N(2)-Re(1)	-110.2(6)
C(14)-C(9)-N(2)-Re(1)	71.9(8)
Re(1)-O(4)-N(3)-O(5)	13(3)

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

Identification code	**2**	
Empirical formula	C20 H20 Br N2 O3 Re	
Formula weight	602.49	
Temperature	293(2) K	
Wavelength	0.71073 ¦	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 8.1105(3) ¦	◎= 93.857(4)°.
	b = 8.3373(4) ¦	◎= 97.380(4)°.
	c = 18.3651(11) ¦	◎ = 104.588(4)°.
Volume	1185.41(10) ^{3}¦	
Z	3	
Density (calculated)	2.532 Mg/m^{3}	
Absorption coefficient	10.244 mm^{-1}	
F(000)	864	
Theta range for data collection	3.286 to 30.429°	
Index ranges	-11<=h<=11, -11<=k<=11, -25<=l<=25	
Reflections collected	23113	
Independent reflections	6361 [R(int) = 0.0674]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	6361 / 0 / 282	
Goodness-of-fit on F^{2}	1.184	
Final R indices [I>2sigma(I)]	R1 = 0.0783, wR2 = 0.1603	
R indices (all data)	R1 = 0.0981, wR2 = 0.1678	
Largest diff. peak and hole	3.455 and -3.289 e.$^{3-}$¦	

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

C(1)-O(1)	1.168(18)
C(1)-Re(1)	1.871(15)
C(2)-O(2)	1.146(18)
C(2)-Re(1)	1.923(15)
C(3)-O(3)	1.135(14)
C(3)-Re(1)	1.921(12)
C(4)-C(5)	1.33(2)
C(4)-C(9)	1.39(2)
C(4)-N(1)	1.469(13)
C(5)-C(6)	1.416(18)
C(5)-H(5)	0.9300
C(6)-C(7)	1.34(2)
C(6)-H(6)	0.9300
C(7)-C(8)	1.35(2)
C(7)-C(19)	1.532(19)
C(8)-C(9)	1.422(19)
C(8)-H(8)	0.9300
C(9)-C(20)	1.52(2)
C(10)-N(1)	1.284(14)
C(10)-C(11)	1.482(14)
C(10)-C(23)	1.485(15)
C(11)-N(2)	1.295(14)
C(11)-C(24)	1.490(16)
C(12)-C(13)	1.378(17)
C(12)-C(17)	1.396(15)
C(12)-N(2)	1.441(13)
C(13)-C(14)	1.378(17)
C(13)-C(22A)	1.51(6)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.409(19)
C(14)-H(14)	0.9300
C(15)-C(16)	1.365(18)
C(15)-C(21)	1.493(16)
C(16)-C(17)	1.399(15)
C(16)-H(16)	0.9300
C(17)-C(22)	1.610(19)
C(17)-H(17A)	0.9300

C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
N(1)-Re(1)	2.170(9)
N(2)-Re(1)	2.159(9)
Br(1)-Re(1)	2.6166(17)
C(22A)-H(22D)	0.9600
C(22A)-H(22E)	0.9600
C(22A)-H(22F)	0.9600

O(1)-C(1)-Re(1)	176.1(14)
O(2)-C(2)-Re(1)	176.3(18)
O(3)-C(3)-Re(1)	177.3(12)
C(5)-C(4)-C(9)	122.8(12)
C(5)-C(4)-N(1)	118.1(12)
C(9)-C(4)-N(1)	119.0(12)
C(4)-C(5)-C(6)	118.7(15)
C(4)-C(5)-H(5)	120.7
C(6)-C(5)-H(5)	120.7
C(7)-C(6)-C(5)	121.0(16)
C(7)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5
C(6)-C(7)-C(8)	119.7(13)
C(6)-C(7)-C(19)	118.7(18)

C(8)-C(7)-C(19)	121.5(17)
C(7)-C(8)-C(9)	121.9(15)
C(7)-C(8)-H(8)	119.1
C(9)-C(8)-H(8)	119.1
C(4)-C(9)-C(8)	115.8(15)
C(4)-C(9)-C(20)	123.9(12)
C(8)-C(9)-C(20)	120.3(14)
N(1)-C(10)-C(11)	115.3(9)
N(1)-C(10)-C(23)	125.7(10)
C(11)-C(10)-C(23)	118.9(10)
N(2)-C(11)-C(10)	115.2(10)
N(2)-C(11)-C(24)	124.6(10)
C(10)-C(11)-C(24)	120.2(10)
C(13)-C(12)-C(17)	121.2(11)
C(13)-C(12)-N(2)	120.8(11)
C(17)-C(12)-N(2)	118.0(10)
C(12)-C(13)-C(14)	119.5(13)
C(12)-C(13)-C(22A)	124(3)
C(14)-C(13)-C(22A)	113(3)
C(12)-C(13)-H(13A)	120.2
C(14)-C(13)-H(13A)	120.2
C(13)-C(14)-C(15)	121.3(12)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-H(14)	119.3
C(16)-C(15)-C(14)	117.3(11)
C(16)-C(15)-C(21)	121.1(13)
C(14)-C(15)-C(21)	121.6(13)
C(15)-C(16)-C(17)	123.3(11)
C(15)-C(16)-H(16)	118.4
C(17)-C(16)-H(16)	118.4
C(12)-C(17)-C(16)	117.3(11)
C(12)-C(17)-C(22)	125.0(10)
C(16)-C(17)-C(22)	117.6(10)
C(12)-C(17)-H(17A)	121.3
C(16)-C(17)-H(17A)	121.3
C(7)-C(19)-H(19A)	109.5
C(7)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(7)-C(19)-H(19C)	109.5

H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(9)-C(20)-H(20A)	109.5
C(9)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(9)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(15)-C(21)-H(21A)	109.5
C(15)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(15)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(17)-C(22)-H(22A)	109.5
C(17)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(17)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(10)-C(23)-H(23A)	109.5
C(10)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(10)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(11)-C(24)-H(24A)	109.5
C(11)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(11)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(10)-N(1)-C(4)	118.1(9)
C(10)-N(1)-Re(1)	117.8(7)
C(4)-N(1)-Re(1)	123.9(7)
C(11)-N(2)-C(12)	120.2(9)
C(11)-N(2)-Re(1)	117.7(7)
C(12)-N(2)-Re(1)	122.0(7)
C(1)-Re(1)-C(3)	89.6(5)

C(1)-Re(1)-C(2)	89.0(7)
C(3)-Re(1)-C(2)	89.2(5)
C(1)-Re(1)-N(2)	98.1(5)
C(3)-Re(1)-N(2)	96.3(4)
C(2)-Re(1)-N(2)	171.0(6)
C(1)-Re(1)-N(1)	95.4(5)
C(3)-Re(1)-N(1)	168.9(4)
C(2)-Re(1)-N(1)	100.7(5)
N(2)-Re(1)-N(1)	73.3(3)
C(1)-Re(1)-Br(1)	177.8(4)
C(3)-Re(1)-Br(1)	91.7(4)
C(2)-Re(1)-Br(1)	89.3(6)
N(2)-Re(1)-Br(1)	83.5(2)
N(1)-Re(1)-Br(1)	83.6(3)
C(13)-C(22A)-H(22D)	109.5
C(13)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22E)	109.5
C(13)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for **2**.

C(9)-C(4)-C(5)-C(6)	-5(2)
N(1)-C(4)-C(5)-C(6)	176.6(12)
C(4)-C(5)-C(6)-C(7)	4(2)
C(5)-C(6)-C(7)-C(8)	-1(2)
C(5)-C(6)-C(7)-C(19)	-177.3(14)
C(6)-C(7)-C(8)-C(9)	0(2)
C(19)-C(7)-C(8)-C(9)	175.8(14)
C(5)-C(4)-C(9)-C(8)	3(2)
N(1)-C(4)-C(9)-C(8)	-178.1(11)
C(5)-C(4)-C(9)-C(20)	-177.9(14)
N(1)-C(4)-C(9)-C(20)	1(2)
C(7)-C(8)-C(9)-C(4)	-1(2)
C(7)-C(8)-C(9)-C(20)	-179.6(15)
N(1)-C(10)-C(11)-N(2)	3.1(16)
C(23)-C(10)-C(11)-N(2)	-177.4(11)
N(1)-C(10)-C(11)-C(24)	-176.9(11)
C(23)-C(10)-C(11)-C(24)	2.6(17)
C(17)-C(12)-C(13)-C(14)	0(2)
N(2)-C(12)-C(13)-C(14)	178.3(12)
C(17)-C(12)-C(13)-C(22A)	158(3)
N(2)-C(12)-C(13)-C(22A)	-23(3)
C(12)-C(13)-C(14)-C(15)	1(2)
C(22A)-C(13)-C(14)-C(15)	-160(3)
C(13)-C(14)-C(15)-C(16)	-1(2)
C(13)-C(14)-C(15)-C(21)	178.6(14)
C(14)-C(15)-C(16)-C(17)	0.3(19)
C(21)-C(15)-C(16)-C(17)	-179.2(12)
C(13)-C(12)-C(17)-C(16)	-0.4(17)
N(2)-C(12)-C(17)-C(16)	-178.9(10)
C(13)-C(12)-C(17)-C(22)	-176.3(12)
N(2)-C(12)-C(17)-C(22)	5.2(16)
C(15)-C(16)-C(17)-C(12)	0.4(18)
C(15)-C(16)-C(17)-C(22)	176.6(11)
C(11)-C(10)-N(1)-C(4)	179.6(10)
C(23)-C(10)-N(1)-C(4)	0.2(18)
C(11)-C(10)-N(1)-Re(1)	3.6(13)
C(23)-C(10)-N(1)-Re(1)	-175.8(10)

C(5)-C(4)-N(1)-C(10)	-96.6(15)
C(9)-C(4)-N(1)-C(10)	84.6(14)
C(5)-C(4)-N(1)-Re(1)	79.1(13)
C(9)-C(4)-N(1)-Re(1)	-99.6(12)
C(10)-C(11)-N(2)-C(12)	174.2(10)
C(24)-C(11)-N(2)-C(12)	-5.8(18)
C(10)-C(11)-N(2)-Re(1)	-8.3(13)
C(24)-C(11)-N(2)-Re(1)	171.6(10)
C(13)-C(12)-N(2)-C(11)	95.6(15)
C(17)-C(12)-N(2)-C(11)	-85.9(13)
C(13)-C(12)-N(2)-Re(1)	-81.7(13)
C(17)-C(12)-N(2)-Re(1)	96.8(11)

Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	C23 H24 Br N2 O3 Re	
Formula weight	642.55	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 14.0730(2) Å	◎= 90°.
	b = 13.8361(2) Å	◎= 90°.
	c = 23.2653(3) Å	◎ = 90°.
Volume	4530.11(11) $Å^3$	
Z	8	
Density (calculated)	1.884 Mg/m^3	
Absorption coefficient	12.775 mm^{-1}	
F(000)	2480	
Theta range for data collection	3.800 to 72.915°	
Index ranges	-17<=h<=11, -14<=k<=17, -28<=l<=28	
Reflections collected	21739	
Independent reflections	4448 [R(int) = 0.0298]	
Completeness to theta = 67.684°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4448 / 0 / 277	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0714	
R indices (all data)	R1 = 0.0306, wR2 = 0.0726	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.474 and -0.982 $e.Å^{-3}$	

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

C(1)-O(1)	1.003(5)
C(1)-Re(1)	1.994(5)
C(2)-O(2)	1.143(5)
C(2)-Re(1)	1.933(4)
C(3)-O(3)	1.145(5)
C(3)-Re(1)	1.924(4)
C(4)-C(5)	1.393(6)
C(4)-C(9)	1.401(6)
C(4)-N(1)	1.456(5)
C(5)-C(6)	1.399(6)
C(5)-C(20)	1.508(6)
C(6)-C(7)	1.380(7)
C(6)-H(6)	0.9300
C(7)-C(8)	1.393(6)
C(7)-C(19)	1.502(6)
C(8)-C(9)	1.388(5)
C(8)-H(8)	0.9300
C(9)-C(18)	1.502(6)
C(10)-N(1)	1.298(5)
C(10)-C(11)	1.456(5)
C(10)-H(10)	0.9300
C(11)-N(2)	1.284(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.391(6)
C(12)-C(17)	1.402(6)
C(12)-N(2)	1.453(5)
C(13)-C(14)	1.399(6)
C(13)-C(23)	1.500(6)
C(14)-C(15)	1.378(6)
C(14)-H(14)	0.9300
C(15)-C(16)	1.388(6)
C(15)-C(22)	1.517(6)
C(16)-C(17)	1.399(6)
C(16)-H(16)	0.9300
C(17)-C(21)	1.514(6)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600

C(18)-H(18C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
Br(1)-Re(1)	2.6160(5)
N(1)-Re(1)	2.182(3)
N(2)-Re(1)	2.179(3)

O(1)-C(1)-Re(1)	175.3(4)
O(2)-C(2)-Re(1)	179.7(4)
O(3)-C(3)-Re(1)	177.3(4)
C(5)-C(4)-C(9)	122.1(4)
C(5)-C(4)-N(1)	120.2(4)
C(9)-C(4)-N(1)	117.6(3)
C(4)-C(5)-C(6)	117.2(4)
C(4)-C(5)-C(20)	124.4(4)
C(6)-C(5)-C(20)	118.4(4)
C(7)-C(6)-C(5)	122.9(4)
C(7)-C(6)-H(6)	118.6
C(5)-C(6)-H(6)	118.6
C(6)-C(7)-C(8)	117.6(4)
C(6)-C(7)-C(19)	121.6(4)
C(8)-C(7)-C(19)	120.7(4)
C(9)-C(8)-C(7)	122.5(4)
C(9)-C(8)-H(8)	118.7
C(7)-C(8)-H(8)	118.7
C(8)-C(9)-C(4)	117.6(4)

C(8)-C(9)-C(18)	119.8(4)
C(4)-C(9)-C(18)	122.5(3)
N(1)-C(10)-C(11)	116.5(4)
N(1)-C(10)-H(10)	121.7
C(11)-C(10)-H(10)	121.7
N(2)-C(11)-C(10)	117.3(4)
N(2)-C(11)-H(11)	121.3
C(10)-C(11)-H(11)	121.3
C(13)-C(12)-C(17)	122.0(4)
C(13)-C(12)-N(2)	119.6(4)
C(17)-C(12)-N(2)	118.4(4)
C(12)-C(13)-C(14)	117.6(4)
C(12)-C(13)-C(23)	122.1(4)
C(14)-C(13)-C(23)	120.3(4)
C(15)-C(14)-C(13)	122.5(4)
C(15)-C(14)-H(14)	118.7
C(13)-C(14)-H(14)	118.7
C(14)-C(15)-C(16)	118.2(4)
C(14)-C(15)-C(22)	120.5(4)
C(16)-C(15)-C(22)	121.2(4)
C(15)-C(16)-C(17)	122.0(4)
C(15)-C(16)-H(16)	119.0
C(17)-C(16)-H(16)	119.0
C(16)-C(17)-C(12)	117.6(4)
C(16)-C(17)-C(21)	119.3(4)
C(12)-C(17)-C(21)	123.1(4)
C(9)-C(18)-H(18A)	109.5
C(9)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(9)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(7)-C(19)-H(19A)	109.5
C(7)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(7)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(5)-C(20)-H(20A)	109.5

C(5)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(5)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(15)-C(22)-H(22A)	109.5
C(15)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(15)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(13)-C(23)-H(23A)	109.5
C(13)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(13)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(10)-N(1)-C(4)	116.6(3)
C(10)-N(1)-Re(1)	115.3(3)
C(4)-N(1)-Re(1)	127.9(2)
C(11)-N(2)-C(12)	117.1(3)
C(11)-N(2)-Re(1)	115.8(3)
C(12)-N(2)-Re(1)	126.8(2)
C(3)-Re(1)-C(2)	89.49(17)
C(3)-Re(1)-C(1)	88.03(16)
C(2)-Re(1)-C(1)	88.88(16)
C(3)-Re(1)-N(2)	99.31(15)
C(2)-Re(1)-N(2)	171.19(15)
C(1)-Re(1)-N(2)	91.77(14)
C(3)-Re(1)-N(1)	169.76(15)
C(2)-Re(1)-N(1)	97.14(15)
C(1)-Re(1)-N(1)	99.85(13)
N(2)-Re(1)-N(1)	74.09(12)

C(3)-Re(1)-Br(1)	86.02(12)
C(2)-Re(1)-Br(1)	88.58(12)
C(1)-Re(1)-Br(1)	173.55(11)
N(2)-Re(1)-Br(1)	91.65(9)
N(1)-Re(1)-Br(1)	86.36(9)

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for **3**.

C(9)-C(4)-C(5)-C(6)	3.9(6)
N(1)-C(4)-C(5)-C(6)	179.8(4)
C(9)-C(4)-C(5)-C(20)	-173.4(4)
N(1)-C(4)-C(5)-C(20)	2.5(6)
C(4)-C(5)-C(6)-C(7)	-3.6(7)
C(20)-C(5)-C(6)-C(7)	173.8(5)
C(5)-C(6)-C(7)-C(8)	1.0(7)
C(5)-C(6)-C(7)-C(19)	-176.1(5)
C(6)-C(7)-C(8)-C(9)	1.5(7)
C(19)-C(7)-C(8)-C(9)	178.7(5)
C(7)-C(8)-C(9)-C(4)	-1.3(7)
C(7)-C(8)-C(9)-C(18)	-179.5(4)
C(5)-C(4)-C(9)-C(8)	-1.6(6)
N(1)-C(4)-C(9)-C(8)	-177.6(4)
C(5)-C(4)-C(9)-C(18)	176.6(4)
N(1)-C(4)-C(9)-C(18)	0.6(6)
N(1)-C(10)-C(11)-N(2)	-4.6(6)
C(17)-C(12)-C(13)-C(14)	-3.1(6)
N(2)-C(12)-C(13)-C(14)	177.7(4)
C(17)-C(12)-C(13)-C(23)	173.9(4)
N(2)-C(12)-C(13)-C(23)	-5.3(6)
C(12)-C(13)-C(14)-C(15)	0.6(6)
C(23)-C(13)-C(14)-C(15)	-176.4(4)
C(13)-C(14)-C(15)-C(16)	1.7(7)
C(13)-C(14)-C(15)-C(22)	-178.7(4)
C(14)-C(15)-C(16)-C(17)	-1.7(6)
C(22)-C(15)-C(16)-C(17)	178.6(4)
C(15)-C(16)-C(17)-C(12)	-0.6(6)
C(15)-C(16)-C(17)-C(21)	179.5(4)
C(13)-C(12)-C(17)-C(16)	3.0(6)
N(2)-C(12)-C(17)-C(16)	-177.7(4)
C(13)-C(12)-C(17)-C(21)	-177.0(4)
N(2)-C(12)-C(17)-C(21)	2.2(6)
C(11)-C(10)-N(1)-C(4)	-174.2(4)
C(11)-C(10)-N(1)-Re(1)	10.2(5)
C(5)-C(4)-N(1)-C(10)	-71.0(5)
C(9)-C(4)-N(1)-C(10)	105.1(4)

C(5)-C(4)-N(1)-Re(1)	103.9(4)
C(9)-C(4)-N(1)-Re(1)	-80.0(4)
C(10)-C(11)-N(2)-C(12)	170.5(4)
C(10)-C(11)-N(2)-Re(1)	-3.5(5)
C(13)-C(12)-N(2)-C(11)	98.2(5)
C(17)-C(12)-N(2)-C(11)	-81.0(5)
C(13)-C(12)-N(2)-Re(1)	-88.4(4)
C(17)-C(12)-N(2)-Re(1)	92.3(4)

Table 1. Crystal data and structure refinement for **4**.

Identification code	**4**	
Empirical formula	C29 H36 Br N2 O3 Re	
Formula weight	726.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnma*	
Unit cell dimensions	a = 13.3103(5) Å	◎= 90°.
	b = 21.7931(9) Å	◎= 90°.
	c = 10.3165(5) Å	◎ = 90°.
Volume	2992.5(2) $Å^3$	
Z	4	
Density (calculated)	1.613 Mg/m^3	
Absorption coefficient	5.426 mm^{-1}	
F(000)	1432	
Theta range for data collection	3.430 to 29.387°	
Index ranges	-18<=h<=15, -27<=k<=18, -13<=l<=8	
Reflections collected	8882	
Independent reflections	3587 [R(int) = 0.0467]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3587 / 0 / 173	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0656	
R indices (all data)	R1 = 0.0529, wR2 = 0.0709	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.370 and -1.589 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **4**.

C(1)-C(2)	1.382(6)
C(1)-C(6)	1.407(6)
C(1)-C(8)	1.522(6)
C(2)-C(3)	1.378(7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.368(7)
C(3)-H(3)	0.9300
C(4)-C(5)	1.392(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.401(6)
C(5)-C(11)	1.512(6)
C(6)-N(1)	1.464(5)
C(7)-N(1)	1.297(5)
C(7)-C(7)#1	1.450(8)
C(7)-H(7)	0.9300
C(8)-C(10)	1.529(6)
C(8)-C(9)	1.533(6)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(13)	1.520(6)
C(11)-C(12)	1.531(6)
C(11)-H(11)	0.9800
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-O(1)	1.147(5)
C(14)-Re(1)	1.919(5)
C(15)-O(2)	1.166(8)
C(15)-Re(1)	1.893(7)

N(1)-Re(1)	2.176(3)
Br(1)-Re(1)	2.6121(7)
Re(1)-C(14)#1	1.919(5)
Re(1)-N(1)#1	2.176(3)

C(2)-C(1)-C(6)	117.0(5)
C(2)-C(1)-C(8)	119.1(4)
C(6)-C(1)-C(8)	123.9(4)
C(3)-C(2)-C(1)	121.9(5)
C(3)-C(2)-H(2)	119.1
C(1)-C(2)-H(2)	119.1
C(4)-C(3)-C(2)	119.8(5)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	121.9(5)
C(3)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(4)-C(5)-C(6)	116.9(4)
C(4)-C(5)-C(11)	119.8(5)
C(6)-C(5)-C(11)	123.4(4)
C(5)-C(6)-C(1)	122.6(4)
C(5)-C(6)-N(1)	120.9(4)
C(1)-C(6)-N(1)	116.5(4)
N(1)-C(7)-C(7)#1	118.0(2)
N(1)-C(7)-H(7)	121.0
C(7)#1-C(7)-H(7)	121.0
C(1)-C(8)-C(10)	111.6(4)
C(1)-C(8)-C(9)	111.1(4)
C(10)-C(8)-C(9)	110.4(4)
C(1)-C(8)-H(8)	107.9
C(10)-C(8)-H(8)	107.9
C(9)-C(8)-H(8)	107.9
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5

C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(5)-C(11)-C(13)	111.6(4)
C(5)-C(11)-C(12)	111.1(4)
C(13)-C(11)-C(12)	109.6(4)
C(5)-C(11)-H(11)	108.2
C(13)-C(11)-H(11)	108.2
C(12)-C(11)-H(11)	108.2
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(1)-C(14)-Re(1)	179.6(4)
O(2)-C(15)-Re(1)	174.6(5)
C(7)-N(1)-C(6)	116.9(3)
C(7)-N(1)-Re(1)	113.2(3)
C(6)-N(1)-Re(1)	129.8(2)
C(15)-Re(1)-C(14)#1	87.4(2)
C(15)-Re(1)-C(14)	87.4(2)
C(14)#1-Re(1)-C(14)	88.5(3)
C(15)-Re(1)-N(1)#1	96.54(17)
C(14)#1-Re(1)-N(1)#1	172.66(16)
C(14)-Re(1)-N(1)#1	97.85(16)
C(15)-Re(1)-N(1)	96.54(17)
C(14)#1-Re(1)-N(1)	97.85(16)
C(14)-Re(1)-N(1)	172.66(16)
N(1)#1-Re(1)-N(1)	75.59(18)
C(15)-Re(1)-Br(1)	176.12(18)

C(14)#1-Re(1)-Br(1)	89.84(15)
C(14)-Re(1)-Br(1)	89.84(15)
N(1)#1-Re(1)-Br(1)	86.52(9)
N(1)-Re(1)-Br(1)	86.52(9)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table 3. Torsion angles [°] for **4**.

C(6)-C(1)-C(2)-C(3)	1.0(7)
C(8)-C(1)-C(2)-C(3)	-178.0(4)
C(1)-C(2)-C(3)-C(4)	0.3(8)
C(2)-C(3)-C(4)-C(5)	-1.1(8)
C(3)-C(4)-C(5)-C(6)	0.4(7)
C(3)-C(4)-C(5)-C(11)	-178.8(4)
C(4)-C(5)-C(6)-C(1)	1.0(6)
C(11)-C(5)-C(6)-C(1)	-179.8(4)
C(4)-C(5)-C(6)-N(1)	-178.0(4)
C(11)-C(5)-C(6)-N(1)	1.2(6)
C(2)-C(1)-C(6)-C(5)	-1.7(6)
C(8)-C(1)-C(6)-C(5)	177.3(4)
C(2)-C(1)-C(6)-N(1)	177.4(4)
C(8)-C(1)-C(6)-N(1)	-3.6(6)
C(2)-C(1)-C(8)-C(10)	-69.4(6)
C(6)-C(1)-C(8)-C(10)	111.6(5)
C(2)-C(1)-C(8)-C(9)	54.2(5)
C(6)-C(1)-C(8)-C(9)	-124.7(5)
C(4)-C(5)-C(11)-C(13)	63.4(6)
C(6)-C(5)-C(11)-C(13)	-115.7(5)
C(4)-C(5)-C(11)-C(12)	-59.2(6)
C(6)-C(5)-C(11)-C(12)	121.7(5)
C(7)#1-C(7)-N(1)-C(6)	166.1(2)
C(7)#1-C(7)-N(1)-Re(1)	-10.7(3)
C(5)-C(6)-N(1)-C(7)	96.5(4)
C(1)-C(6)-N(1)-C(7)	-82.6(5)
C(5)-C(6)-N(1)-Re(1)	-87.3(4)
C(1)-C(6)-N(1)-Re(1)	93.6(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z