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Ruthenium Complexes of Electronically Coupled Cyclopentadienone Ligands – Catalysts for Transformations of Propargyl Alcohols

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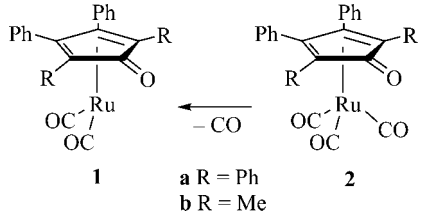
A series of donor- and acceptor-substituted ruthenium cyclopentadienone complexes were synthesized and their catalytic activities towards propargyl alcohols focused on amination reactions have been investigated. It is shown that the substituents of the cyclopentadienone ligand determine the mode of activation of propargyl alcohols by these complexes leading to different central intermediates in catalytic cycles. Catalytic transformations of propargyl alcohols to α- or β-amino ketones, enamino ketones, α,β-unsaturated imines, ketones, alkenes and conjugated enynes could be achieved.

Introduction

Ruthenium complexes of electronically coupled cyclopentadienone ligands catalyze a brought range of homogeneous hydrogen transfer reactions such as disproportionation of aldehydes to esters,[1] reduction of aldehydes and ketones,[2] Oppenauer type oxidations of alcohols and amines,[3,4] racemisation of alcohols and amines[5,6] and the oxidation of alcohols without hydrogen acceptor.[7] The Shov complex $[\{(\eta^5\text{-}Ph_4C_4CO)_2H\}Ru_2(CO)_4(\mu\text{-}H)]$ represents the most famous catalyst of this type.[8] Cyclopentadienone ruthenium(0) species like complex **1** that are also accessible from monomeric complexes of type **2** act as the catalytically active species in the oxidation step (Scheme 1).[9]



Scheme 1. Formation of coordinative unsaturated species **1**.

Due to the electronic coupling of the dienone ligand and its basic coordination site this type of complexes could provide unique features towards catalytic transformations of various substrates.

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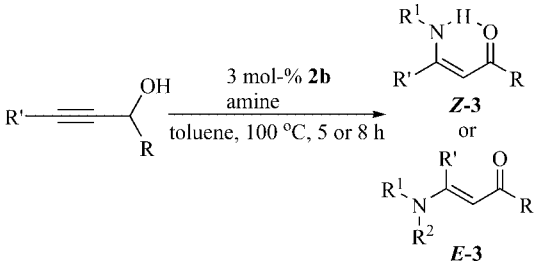
Results and Discussion

In the course of the investigation of ruthenium-catalyzed amination reactions of propargyl alcohols, complexes of type **2** were recently found to be active in enamino ketone formation (Scheme 2, Table 1).[10]



Scheme 2. Ruthenium-catalyzed enamino ketone formation.

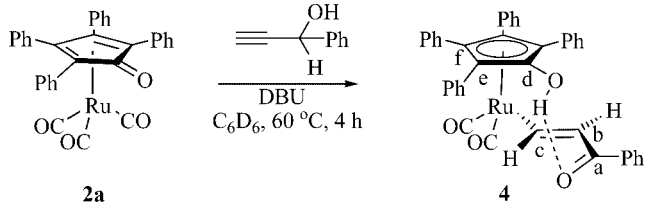
Table 1. Enamino ketone formation from various substrates.

Amines	R	R′	*E*/*Z*	Yield of **3** [%]
Aniline	Ph	H	*Z*	49[a] (**3a**)
Aniline	Me	H	*Z*	47[a] (**3b**)
Aniline	Ph	Me	*Z*	52[a] (**3c**)
Pyrrolidine	Ph	H	*E*	48[b] (**3d**)
L-Proline methyl ester	Ph	H	*E*	65[b] (**3e**)
Allylamine	Ph	H	*Z*	53[b] (**3f**)
Benzhydrylamine	Ph	H	*Z*	39[b] (**3h**)
Benzylamine	Ph	H	*Z*	25[b] (**3i**)
(*R*)-α-Methylbenzylamine	Ph	H	*Z*	14[b] (**3j**)
(*R*)-1-Cyclohexylethylamine	Ph	H	*Z*	20[b] (**3k**)
Tryptamine	Ph	H	*Z*	11[b] (**3l**)
L-Tryptophan methyl ester	Ph	H	*Z*	17[b] (**3m**)
L-Alanine methyl ester	Ph	H	*Z*	16[b] (**3n**)

[a] Reactions were stopped after 5 h. [b] Reactions were stopped after 8 h.

The reactivity of internal propargyl alcohols and the fact that tertiary propargyl alcohols are not converted exclude

the initial formation of vinylidene or allenylidene species by activation of the alkyne terminus. Interestingly, the investigation of the stoichiometrical reaction of 1-phenyl-2-propyn-1-ol with **2a** in the presence of DBU by NMR spectroscopy supports the assumption of the formation of alkenyl complex **4** (Scheme 3, Table 2).



2a **4**

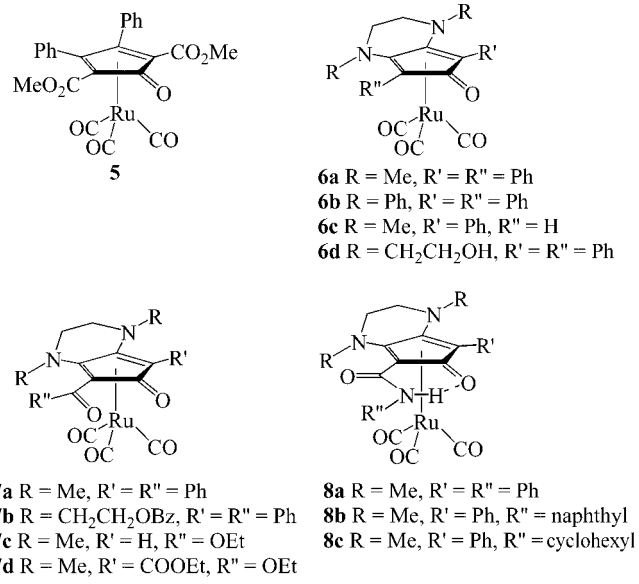
Scheme 3. Formation of a stabilized alkenyl complex.

Table 2. NMR shift data (δ values, ppm) of alkenyl complex **4**.

^{13}C-NMR (50 MHz)		^{1}H-NMR (200 MHz)	
C_a	183.0	H_b	8.34
C_b	125.7	H_c	9.84
C_c	197.6	J_{HbHc}	16.0 Hz
C_d	166.0	O–H	12.50
C_e	85.8		
C_f	103.6		
CO	204.5		

The catalytic enamino ketone formation is probably initiated by base-catalyzed formation of a ruthenium alkenyl complex. Subsequent Michael addition of the amine and β-H elimination give rise to the observed product and a ruthenium(II) hydride which regenerates the active catalyst with elimination of hydrogen (Scheme 4).

By variation of the substituents of the dienone fragment a broad range of new donor- and acceptor-substituted cyclopentadienone complexes has been generated (Figure 1).



5

6a R = Me, R' = R" = Ph
6b R = Ph, R' = R" = Ph
6c R = Me, R' = Ph, R" = H
6d R = CH_2CH_2OH, R' = R" = Ph

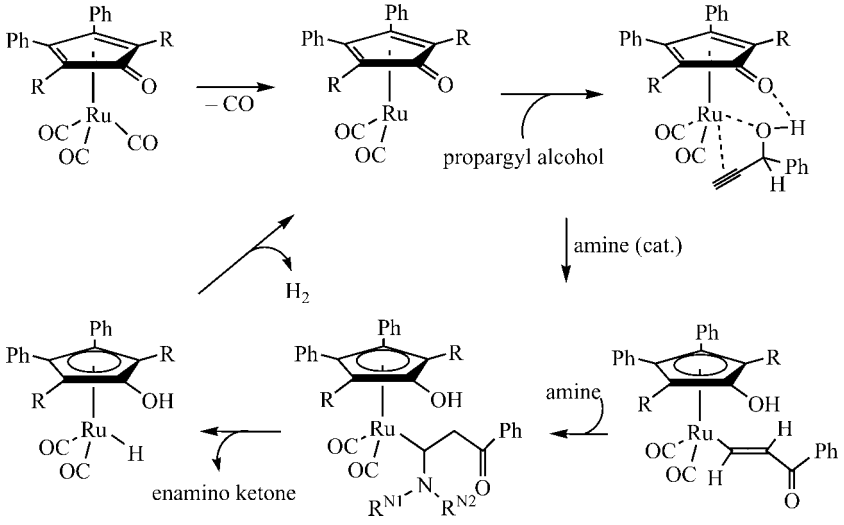
7a R = Me, R' = R" = Ph
7b R = CH_2CH_2OBz, R' = R" = Ph
7c R = Me, R' = H, R" = OEt
7d R = Me, R' = COOEt, R" = OEt

8a R = Me, R' = R" = Ph
8b R = Me, R' = Ph, R" = naphthyl
8c R = Me, R' = Ph, R" = cyclohexyl

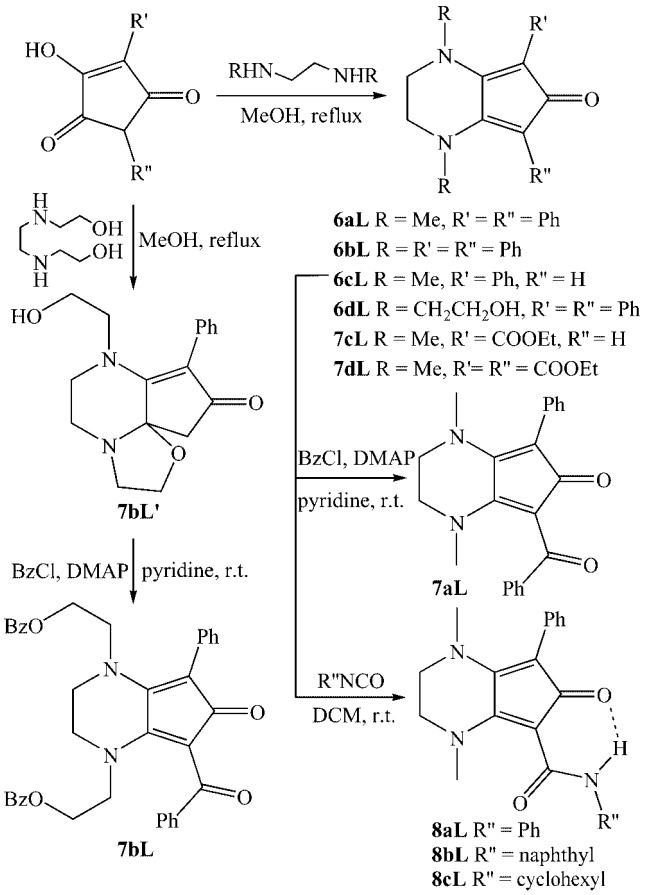
Figure 1. New ruthenium complexes of electronically coupled ligands.

The ruthenium carbonyl complexes were directly obtained from the dienone ligands and $Ru_3(CO)_{12}$. The dienones **5L**,[11a] **6aL** and **6bL**[11b] have already been published by other groups and the dienones **6cL**, **6dL**, **7cL** and **7dL** were synthesized according to these procedures under identical conditions. Since dienone **6cL** exhibits C-nucleophilicity the dienones **7aL**, **8aL**, **8bL** and **8cL** could be obtained by acylation or amidation of **6cL** (Scheme 5).

The new complexes show interesting catalytic activities towards propargyl alcohols. By reacting 1-phenyl-2-propyn-1-ol with aniline in the presence of 3 mol-% of one of the new complexes the α- and β-amino ketone as well as benzylidene aniline are formed besides the enamino ketone in different ratios. By using complexes of type **6** as catalysts the saturated product **9** dominates compared to the unsaturated

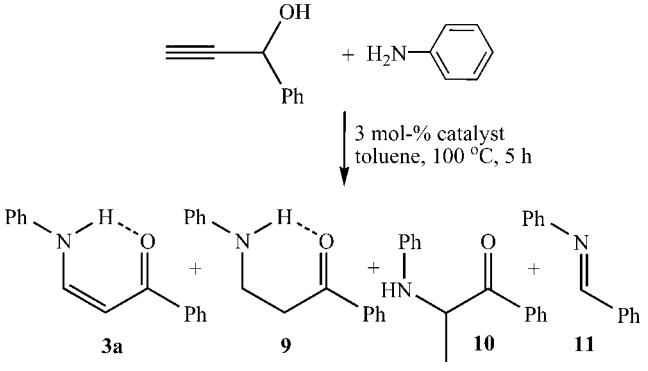


Scheme 4. Postulated catalytic cycle of the enamino ketone formation.



Scheme 5. Synthesis of the ligands **6L**–**8L**.

product **3a**, whereas the asymmetric complex **6c** shows the highest activity. When the acceptor-substituted complex **5** or the donor/acceptor-substituted complexes **7a**–**c** or **8c** are used as catalysts the unsattured product **3a** is formed preferentially. If the reaction is catalyzed by complex **7a**, 3-(phenylallyliden)aniline (**12**) is formed as an additional by-product (9%). The hydrogen-bridged complexes **8a+b** lead to the formation of the imine **11** as major product. The Markownikow hydroamination product **10** is formed in all cases in 19–35% yield (Scheme 6, Table 3).



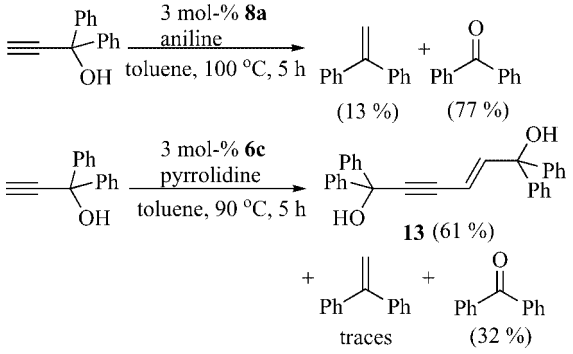
Scheme 6. Catalytic activities of complexes **5**–**8**.

Table 3. Product distributions (%) for catalysts **5**–**8**.[a]

Catalyst	Product **3a**	Product **9**	Product **10**	Product **11**
5	14	< 3	29	< 3
6a	7	15	21	< 3
6b	18	24	30	10
6c	9	59	20	7
6d	11	19	28	8
7a[b]	13	9	19	12
7b	17	11	30	10
7c	14	4	29	11
7d	4	< 3	31	15
8a	5	4	35	40
8b	< 3	< 3	26	31
8c	16	9	21	10

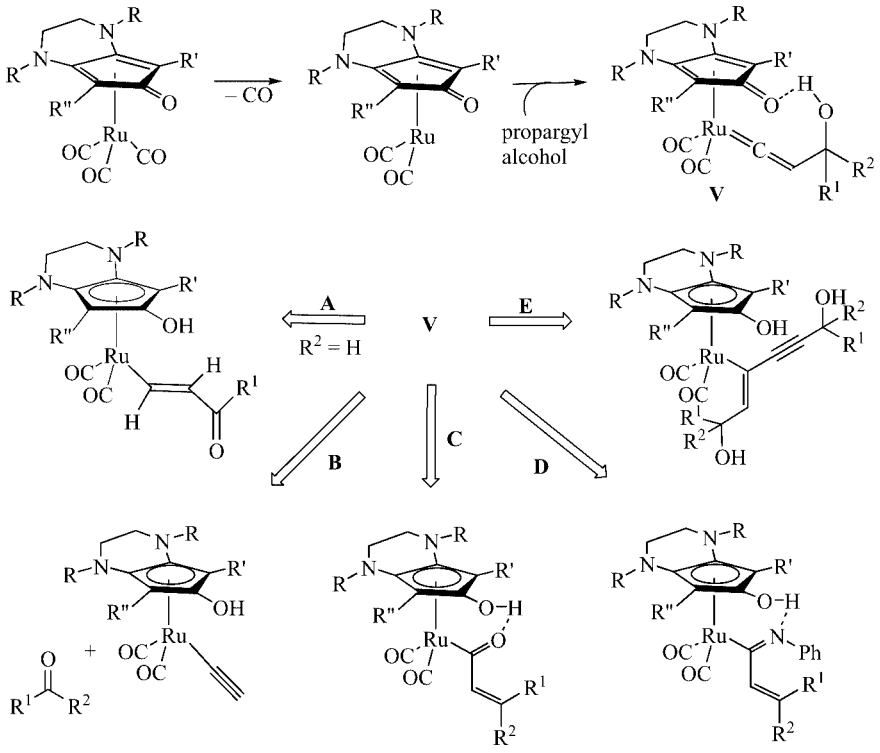
[a] Reactions were stopped after 5 h. [b] 9% 3-(phenylallyliden)-aniline (**12**) as additional product.

The reaction catalyzed by complexes of type **6**–**8** needs to proceed by a different mechanism than that catalyzed by complexes of type **2**. The internal propargyl alcohol 1-phenyl-2-butyn-1-ol shows no reactivity and the tertiary propargyl alcohol 1,1-diphenyl-2-propyn-1-ol is transformed to a mixture of bezophenone and 1,1-diphenylethane in the presence of a catalytic amount of one of the complexes **6**–**8** in presence as well as in absence of the amine. The highest activity regarding this fragmentation is observed with complex **8a**. If a catalytic amount of a strong basic amine like pyrrolidine or DBU is added instead of aniline the enyne **13** is formed as major product (Scheme 7). In the absence of an amine the catalytic fragmentations are also observed with the secondary propargyl alcohol 1-phenyl-2-propyn-1-ol forming benzaldehyde and styrene.

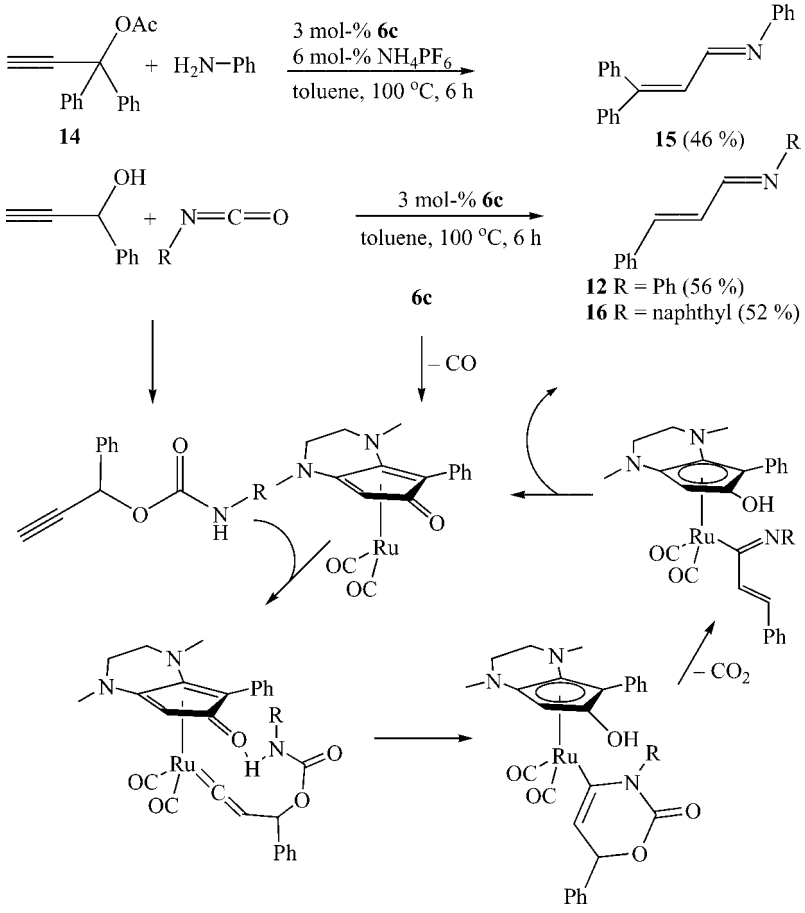


Scheme 7. Reactivity of a tertiary propargyl alcohol.

It is very likely that the initial formation of a ruthenium γ-hydroxyvinylidene complex (**V**) occurs in all cases. Its further transformation depends on the reaction partner and the catalyst used. 1,3-Hydride shift leads to enamino ketones or β-amino ketones by the formation of an alkenyl species in analogy to complex **4**, whereas the product ratio is depending on the ratio of reductive elimination vs. β-hydride elimination (pathway **A**, Scheme 8). Fragmentation to the alkyne complex by elimination of an aldehyde or ketone leads to regeneration of the active catalyst by elimination of acetylene (pathway **B**, Scheme 8). Generation of the alkene can be rationalized by the formation of an allenylidene complex which is attacked in α-position by the initially



Scheme 8. Postulated mechanisms of the observed product formation.



Scheme 9. Catalytic formation of α,β-unsaturated imines.

eliminated water. The resulting acyl complex generates the decarbonylated product under reformation of the tricarbonyl complex (pathway **C**, Scheme 8). The alternative attack of the amine on an allenylidene species or on vinylidene complex **V** combined with a following elimination of water leads to an azadiene complex. The latter regenerates the active catalyst by reductive elimination of the α,β-unsaturated imine (pathway **D**, Scheme 8). In case of the enyne formation a second equivalent of the propargyl alcohol acts as nucleophile. The resulting not donor-stabilized complex undergoes reductive elimination (pathway **E**, Scheme 8).

It is well known that propargyl alcohols form allenylidene species with ruthenium(II) complexes under acidic conditions by elimination of water.[12] In fact, the tertiary propargyl acetate **14** generates with aniline the α,β-unsaturated imine **15** in the presence of a catalytic amount of **6c**. The yield can be increased by adding 6 mol-% of NH_4PF_6. A similar result is observed if the secondary propargyl alcohol 1-phenyl-2-propyn-1-ol is treated with phenyl or naphthyl isocyanate as amine equivalent. Using 3 mol-% **6c** the α,β-unsaturated imines **12** and **16** are obtained in moderate yields (Scheme 9). A plausible mechanism starts again from the initial formation of a vinylidene species that is attacked in α-position. Using an isocyanate that forms a carbamate with the propargyl alcohol this nucleophilic attack occurs intra molecularly. After elimination of the leaving group in β-position the α,β-unsaturated system is reductively eliminated (Scheme 9).

Conclusions

The ligand system used provides a broad range of possible variations. Basicity of the carbonyl group and the degree of electronic coupling can be regulated by the donor- and acceptor-substituents. Donor substituents in 3 and 4 position strongly influences the electron density of the metal centre and its mode of action while acceptor substituents in 2 and 5 position allow the formation of stabilizing hydrogen bridges after oxidative addition of protic nucleophiles. The donor groups in the side chains of complexes **6d** and **7b** could lead to interactions with the metal centre or with metal bonded substrates in intermediates of a catalytic cycle. Finally the chiral complexes **6c**, **7a**–**c** and **8a**–**c** represent interesting motives regarding applications in asymmetric catalysis.

It could be shown that carbonyl(3,4-diaminocyclopentadienone)ruthenium complexes activate the alkyne terminus of propargyl alcohols leading very likely to the formation of (γ-hydroxyvinylidene)ruthenium complexes whereas 3,4-diphenyl-substituted analogues complexes activate the π-system of the triple bond forming alkenyl complexes. These different modes of activation allow several catalytic transformations of propargyl alcohols. Further investigation of catalytic activities, development of broad-ranged catalytic processes and separation of the enantiomers of the chiral complexes are subjects of the actual research.

Experimental Section

All reactions were carried out in a dry atmosphere under argon by using standard Schlenck techniques. The chemicals used were dried and purified according to common procedures. Products were identified by spectroscopic analysis (^{1}H NMR, ^{13}C NMR, IR, MS, HRMS).

General Catalytic Procedure: 1 mmol of the propargyl alcohol and 1 mmol of the amine or amine equivalent were dissolved in 0.5 mL of toluene and 0.03 mmol of the catalyst were added. The mixture was stirred at 100 °C for 5–8 hours under argon. Using allylamine the reaction was performed in a closed tube. Evaporation of the solvent and chromatography on silica furnished the detected products.

***Z*-3a ($C_{15}H_{13}NO$):** 110 mg (49%) yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.94 (d, J = 7.8 Hz, 1 H), 6.99 (t, J = 7.4 Hz, 1 H), 7.01 (d, J = 7.7 Hz, 2 H), 7.25 (dd, J = 8.6, 7.4 Hz, 2 H), 7.33–7.45 (m, 4 H), 7.86 (d, J = 6.7 Hz, 2 H), 12.07 (br. d, J = 11.4 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 93.7 (CH), 116.3 (CH), 123.7 (CH), 127.3 (CH), 128.4 (CH), 129.7 (CH), 131.5 (CH), 139.2 (C), 140.2 (C), 144.9 (CH), 191.0 (C) ppm. IR: $\tilde{\nu}$ = 3053, 2957, 2923, 2854, 1626, 1593, 1579, 1549, 1511, 1493, 1471, 1449, 1356, 1288, 1236, 1215, 1177, 1154, 1074, 1038, 1017, 976, 888, 786, 741, 708, 686 cm^{-1}. MS (EI): *m*/*z* (%) = 223 (52) [M$^+$], 222 (100), 146 (28), 118 (11), 105 (11), 77 (28).

***Z*-3b ($C_{10}H_{11}NO$):** 76 mg (47%) colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3 H), 5.20 (d, J = 6.6 Hz, 1 H), 7.02 (d, J = 7.6 Hz, 2 H), 7.16 (t, J = 7.4 Hz, 1 H), 7.23 (dd, J = 12.0, 4.3 Hz, 1 H), 7.31 (t, J = 7.5 Hz, 2 H), 11.60 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 29.5 (CH_3), 97.4 (CH), 116.1 (CH), 123.4 (CH), 129.6 (CH), 140.4 (C), 143.0 (CH), 198.9 (C) ppm. IR: $\tilde{\nu}$ = 3252, 3038, 2962, 2925, 2869, 1640, 1596, 1567, 1477, 1451, 1356, 1271, 1219, 1199, 1178, 1157, 1075, 1024, 968, 912, 745, 690, 558. MS (EI): *m*/*z* (%) = 161 (60) [M$^+$], 146 (100), 118 (32), 91 (22), 77 (32). HRMS: calcd. 161.08406, found: 161.08404.

***Z*-3c ($C_{16}H_{15}NO$):** 123 mg (52%) yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 5.89 (s, 1 H), 7.14 (dd, J = 7.4, 8.4 Hz, 1 H), 7.17 (d, J = 7.5 Hz, 2 H), (dd, J = 8.6, 7.4 Hz, 2 H), 7.42–7.45 (m, 3 H), 7.92 (dd, J = 7.8, 2.0 Hz, 2 H), 13.11 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 20.1 (CH_3), 93.9 (CH), 124.4 (CH), 125.4 (CH), 126.7 (CH), 127.9 (CH), 128.8 (CH), 130.5 (CH), 138.3 (C), 139.6 (C), 161.8 (C), 188.3 (C) ppm. IR: $\tilde{\nu}$ = 3093, 3057, 3035, 1586, 1544, 1519, 1494, 1431, 1377, 1316, 1281, 1228, 1193, 1167, 1067, 1023, 853, 807, 748, 692, 557. MS (EI): *m*/*z* (%) = 237 (41) [M$^+$], 236 (100), 160 (28), 132 (43), 105 (44), 77 (57). HRMS: calcd. 237.11536, found: 237.11585.

***E*-3d ($C_{13}H_{15}NO$):** 96 mg (48%) yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.81–2.00 (m, 4 H), 3.33–3.46 (m, 4 H), 5.65 (d, J = 12.6 Hz, 1 H), 7.24–7.35 (m, 3 H), 7.81 (dd, J = 8.1, 1.9 Hz, 2 H), 7.92 (d, J = 12.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.1 (CH_2), 47.0 + 52.3 (CH_2), 93.0 (CH), 127.4 (CH), 128.0 (CH), 130.1 (CH), 140.5 (C), 150.0 (CH), 188.5 (C) ppm. IR: $\tilde{\nu}$ = 3060, 2954, 2926, 2874, 1632, 1581, 1542, 1450, 1364, 1341, 1300, 1267, 1245, 1220, 1178, 1142, 1052, 1026, 837, 761, 746, 693, 618, 596, 558, 536 cm^{-1}. MS (EI): *m*/*z* (%) = 201 (100) [M$^+$], 172 (58), 131 (24), 124 (32), 105 (60), 96 (58), 77 (70), 70 (82). HRMS: calcd. 201.11536, found: 201.11492.

***E*-3e ($C_{15}H_{17}NO_3$):** 169 mg (65%) yellow oil (rotamers 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90–2.34 (m, 4 H), 3.50–3.55 (m, 2 H), 3.75 (s, 3 H), 4.16 + 4.29 (t, J = 8.1 Hz, 1 H), 5.67 + 5.77 (d,

J = 12.4 Hz, 1 H), 7.37–7.46 (m, 3 H), 7.87–8.01 (m, 3 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 23.2 + 25.1 (CH_2), 27.5 + 29.7 (CH_2), 45.1 + 46.0 (CH_2), 52.5 (CH_3), 60.4 + 60.9 (CH), 92.9 + 94.8 (CH), 127.4 + 127.5 (CH), 127.9 + 128.0 (CH), 130.6 + 131.0 (CH), 140.0 + 140.5 (C), 149.3 + 149.8 (CH), 166.3 + 172.1, 188.8 (C) ppm. IR: $\tilde{\nu}$ = 3056, 3024, 2956, 2878, 1741, 1662, 1633, 1580, 1539, 1449, 1364, 1340, 1304, 1274, 1209, 1166, 1090, 1051, 1026, 1008, 991, 925, 893, 837, 758, 706, 621, 557 cm^{-1}. MS (EI): *m*/*z* (%) = 259 (45) [M$^+$], 200 (100), 172 (34), 154 (58), 105 (70), 77 (54), 70 (36). HRMS: calcd. 259.12085, found: 259.12007.

***Z*-3f ($C_{12}H_{13}NO$):** 100 mg (53%) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (tt, J = 5.6, 1.6 Hz, 2 H), 5.21 (dq, J = 10.2, 1.4 Hz, 1 H), 5.27 (dq, J = 17.1, 1.7 Hz, 1 H), 5.75 (d, J = 7.5 Hz, 1 H), 5.90 (ddt, J = 17.1, 10.3, 5.1 Hz, 1 H), 6.93 (dd, J = 12.8, 7.5 Hz, 1 H), 7.38–7.44 (m, 3 H), 7.88 (dd, J = 8.2, 1.4 Hz, 2 H), 10.3 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 51.0 (CH_2), 90.7 (CH), 117.1 (CH_2), 127.0 (CH), 128.2 (CH), 130.9 (CH), 134.2 (CH), 139.7 (C), 154.0 (CH), 190.1 (C) ppm. IR: $\tilde{\nu}$ = 3271, 3059, 3027, 2921, 2855, 1627, 1582, 1541, 1499, 1476, 1442, 1363, 1272, 1227, 1205, 1161, 1048, 1021, 988, 922, 867, 734, 699, 554 cm^{-1}. MS (EI): *m*/*z* (%) = 187 (58) [M$^+$], 186 (39), 105 (100), 82 (89), 77 (55). HRMS: calcd. 187.09972, found: 187.09941.

***Z*-3g ($C_{15}H_{17}NO_5$):** 143 mg (49%) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (dd, J = 16.9, 7.4 Hz, 1 H), 2.99 (dd, J = 16.9, 5.2 Hz, 1 H), 3.72 (s, 3 H), 3.78 (s, 3 H), 4.31 (ddd, J = 9.4, 7.4, 5.2 Hz, 1 H), 5.81 (d, J = 7.7 Hz, 1 H), 6.96 (dd, J = 12.2, 7.8 Hz, 1 H), 7.38–7.46 (m, 3 H), 7.88 (dd, J = 8.0, 1.3 Hz, 2 H), 10.45 (t br, J = 10.4 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 37.5 (CH_2), 52.2 (CH_3), 52.9 (CH_3), 57.9 (CH), 92.0 (CH), 127.2 (CH), 128.2 (CH), 131.2 (CH), 139.2 (C), 152.6 (CH), 170.3 (C), 170.4 (C), 190.6 (C) ppm. IR: $\tilde{\nu}$ = 3278, 3059, 3028, 3003, 2954, 2849, 1733, 1631, 1584, 1549, 1500, 1476, 1437, 1368, 1270, 1204, 1164, 1045, 1019, 997, 849, 739, 700. MS (EI): *m*/*z* (%) = 291 (12) [M$^+$], 259 (12), 232 (20), 117 (24), 115 (42), 105 (100), 102 (24), 77 (48). HRMS: calcd. 291.11066, found: 291.11046.

***Z*-3h ($C_{22}H_{19}NO$):** 122 mg (39%) yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.61 (d, J = 6.7 Hz, 1 H), 5.80 (d, J = 7.6 Hz, 1 H), 6.99 (dd, J = 12.6, 7.6 Hz, 1 H), 7.29–7.45 (m, 13 H), 7.88 (dd, J = 8.3, 1.7 Hz, 2 H), 11.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 66.3 (CH), 91.4 (CH), 127.2 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 128.9 (CH), 131.1 (CH), 139.6 (C), 141.2 (C), 152.8 (CH), 190.4 (C) ppm. IR: $\tilde{\nu}$ = 3291, 3084, 3048, 3029, 1616, 1580, 1527, 1496, 1475, 1451, 1380, 1278, 1235, 1196, 1179, 1154, 1086, 1051, 1024, 986, 916, 882, 802, 737, 594, 650, 605, 576 cm^{-1}. MS (EI): *m*/*z* (%) = 313 (42) [M$^+$], 167 (100), 165 (40), 152 (25). HRMS: calcd. 313.14667, found: 313.14664.

***Z*-3i ($C_{16}H_{15}NO$):** 60 mg (25%) yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.41 (d, J = 6.2 Hz, 2 H), 5.74 (d, J = 7.5 Hz, 1 H), 6.98 (dd, J = 12.7, 7.5 Hz, 1 H), 7.16–7.43 (m, 8 H), 7.86 (dd, J = 8.2, 1.9 Hz, 2 H), 10.57 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 52.6 (CH_2), 90.8 (CH), 127.0 (CH), 127.4 (CH), 127.7 (CH), 128.3 (CH), 128.7 (CH), 130.9 (CH), 137.6 (C), 139.0 (C), 154.2 (CH), 190.1 (C) ppm. IR: $\tilde{\nu}$ = 3275, 3060, 3029, 2860, 1631, 1581, 1539, 1495, 1450, 1360, 1275, 1204, 1050, 1025, 970, 836, 733, 695, 557. MS (EI): *m*/*z* (%) = 237 (8) [M$^+$], 197 (10), 196 (12), 149 (8), 135 (24), 106 (60), 105 (12), 91 (100), 79 (22), 77 (24). HRMS: calcd. 237.11536, found: 237.11538.

***Z*-3j ($C_{17}H_{17}NO$):** 35 mg (14%) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (d, J = 6.9 Hz, 3 H), 4.52 (quint., J = 6.8 Hz, 1 H), 5.72 (d, J = 7.6 Hz, 1 H), 6.95 (dd, J = 12.8, 7.5 Hz, 1 H), 7.23–7.44 (m, 8 H), 7.88 (dd, J = 7.8, 1.4 Hz, 2 H), 10.68 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 23.7 (CH_3), 57.8 (CH), 90.7 (CH), 126.1 (CH), 127.1 (CH), 127.6 (CH), 128.2 (CH), 128.9 (CH), 130.9 (CH), 139.6 (C), 143.2 (C), 152.7 (CH), 190.0 (C) ppm. IR: $\tilde{\nu}$ = 3274, 3059, 3028, 2972, 2926, 2869, 1627, 1582, 1535, 1496, 1476, 1449, 1376, 1268, 1239, 1205, 1127, 1022, 758, 737, 696, 562, 541 cm^{-1}. MS (EI): *m*/*z* (%) = 251 (10) [M$^+$], 210 (8), 196 (55), 149 (18), 148 (16), 134 (12), 106 (30), 105 (55), 91 (100), 79 (38), 77 (41). HRMS: calcd. 251.13101, found: 251.13111.

***Z*-3k ($C_{17}H_{23}NO$):** 51 mg (20%) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98–1.21 (m, 6 H), 1.25 (d, J = 6.8 Hz, 3 H), 1.65–1.79 (m, 5 H), 3.07 (dquint., J = 8.9, 6.6 Hz, 1 H), 5.67 (d, J = 7.4 Hz, 1 H), 6.96 (dd, J = 12.9, 7.4 Hz, 1 H), 7.34–7.43 (m, 3 H), 7.88 (dd, J = 7.6, 1.5 Hz, 2 H), 10.44 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 19.0 (CH_3), 26.0 (CH_2), 26.1 (CH_2), 26.2 (CH_2), 28.6 (CH_2), 29.5 (CH_2), 44.0 (CH), 60.5 (CH), 89.3 (CH), 127.0 (CH), 128.2 (CH), 130.7 (CH), 139.8 (C), 153.4 (CH), 189.5 (C) ppm. IR: $\tilde{\nu}$ = 3279, 3059, 3029, 2924, 2851, 1627, 1583, 1535, 1501, 1478, 1447, 1380, 1280, 1237, 1154, 1022, 759, 731, 697, 563. MS (EI): *m*/*z* (%) = 257 (20) [M$^+$], 175 (15), 174 (100), 105 (29), 77 (10). HRMS: calcd. 257.17796, found: 257.17796.

***Z*-3l ($C_{19}H_{18}N_2O$):** 32 mg (11%) yellow foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (t, J = 6.8 Hz, 2 H), 3.55 (q, J = 6.6 Hz, 1 H), 5.61 (d, J = 7.4 Hz, 1 H), 6.79 (dd, J = 12.9, 7.4 Hz, 1 H), 7.01 (d, J = 2.4 Hz, 1 H), 7.11 (td, J = 7.7, 1.0 Hz, 1 H), 7.19 (td, J = 7.9, 1.0 Hz, 1 H), 7.33 (d, J = 7.9 Hz, 1 H), 7.35–7.43 (m, 3 H), 7.56 (d, J = 7.8 Hz, 1 H), 7.85 (dd, J = 8.2, 1.5 Hz, 2 H), 8.19 (br. s, 1 H, NH), 10.40 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 27.2 (CH_2), 49.6 (CH_2), 90.0 (CH), 111.3 (CH), 111.9 (C), 118.4 (CH), 119.4 (CH), 122.1 (CH), 122.7 (CH), 126.9 (C), 127.0 (CH), 128.2 (CH), 130.8 (CH), 136.4 (C), 139.9 (C), 154.4 (CH), 189.9 (C) ppm. IR: $\tilde{\nu}$ = 3400, 3270, 3055, 2924, 2853, 1628, 1581, 1526, 1503, 1480, 1453, 1340, 1275, 1228, 1009, 907, 737, 697. MS (EI): *m*/*z* (%) = 290 (4) [M$^+$], 160 (18), 143 (100), 130 (78), 115 (21), 105 (23), 91 (22), 77 (46). HRMS: calcd. 290.14191, found: 290.14114.

***Z*-3m ($C_{21}H_{20}N_2O_3$):** 59 mg (17%) yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (dd, J = 14.6, 8.3 Hz, 1 H), 3.41 (dd, J = 14.6, 4.6 Hz, 1 H), 3.72 (s, 3 H), 4.17 (td, J = 8.6, 4.7 Hz, 1 H), 5.62 (d, J = 7.6 Hz, 1 H), 6.59 (dd, J = 12.6, 7.7 Hz, 1 H), 7.01 (d, J = 2.3 Hz, 1 H), 7.11 (td, J = 7.9, 1.0 Hz, 1 H), 7.18 (td, J = 7.0, 1.0 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 1 H), 7.34–7.43 (m, 3 H), 7.57 (d, J = 8.4 Hz, 1 H), 7.84 (dd, J = 7.9, 1.0 Hz, 2 H), 8.27 (br. s, 1 H, NH), 10.52 (br. dd, J = 12.2, 9.1 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 30.0 (CH_2), 52.6 (CH_3), 62.0 (CH), 91.3 (CH), 109.3 (C), 111.4 (CH), 118.3 (CH), 119.5 (CH), 122.1 (CH), 123.9 (CH), 126.9 (C), 127.2 (CH), 128.2 (CH), 131.1 (CH), 136.2 (C), 139.5 (C), 152.5 (CH), 171.4 (C), 190.5 (C) ppm. IR: $\tilde{\nu}$ = 3397, 3282, 3056, 2950, 2924, 2852, 1736, 1627, 1582, 1533, 1500, 1478, 1454, 1435, 1340, 1304, 1235, 1204, 1172, 1097, 1012, 908, 737, 699. MS (EI): *m*/*z* (%) = 348 (4) [M$^+$], 218 (4), 201 (16), 169 (4), 158 (4), 143 (4), 130 (100), 117 (12), 115 (13), 105 (12), 91 (4), 77 (22). HRMS: calcd. 348.14739, found: 348.14738.

***Z*-3n ($C_{13}H_{15}NO_3$):** 37 mg (16%) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, J = 6.7 Hz, 3 H), 3.71 (s, 3 H), 3.77 (quint., J = 7.0, Hz, 1 H), 5.79 (d, J = 7.6 Hz, 1 H), 6.94 (dd, J = 12.6, 7.6 Hz, 1 H), 7.30 –7.41 (m, 3 H), 7.88 (dd, J = 7.8, 1.8 Hz, 2 H), 10.36 (t br, J = 11.8 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 19.0 (CH_3), 52.7 (CH_3), 55.9 (CH), 91.3 (CH), 126.4 (CH), 128.1 (CH), 131.0 (CH), 139.2 (C), 152.3 (CH), 172.1 (C), 190.1 (C) ppm. IR: $\tilde{\nu}$ = 3293, 3061, 3029, 2983, 2952, 1739,

1632, 1582, 1537, 1449, 1377, 1205, 1159, 1064, 1024, 975, 910, 847, 759, 729, 697, 550. MS (EI): *m*/*z* (%) = 233 (4) [M$^+$], 192 (7), 174 (7), 158 (22), 130 (22), 117 (44), 115 (100), 105 (60), 91 (77), 77 (55). HRMS: calcd. 233.10519, found: 233.10508.

Compounds **9**–**16** are known and the spectroscopic data was compared with published results. Yields of compounds **9**–**11** depend on the catalyst used and are given in Table 3.

9 ($C_{15}H_{15}NO$): Yellow crystals. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.24 (t, J = 6.0 Hz, 2 H), 3.59 (t, J = 6.0 Hz, 2 H), 3.72 (br., NH), 6.61–6.78 (m, 3 H), 7.09–7.21 (m, 2 H), 7.39–7.58 (m, 3 H), 7.93 (dd, J = 8.2, 1.2 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 37.6 (CH_2), 38.7 (CH_2), 113.0 (CH), 117.5 (CH), 128.0 (CH), 128.6 (CH), 129.3 (CH), 133.2 (CH), 136.7 (C), 147.7 (C), 199.2 (C) ppm.

10 ($C_{15}H_{15}NO$): Yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (d, J = 6.9 Hz, 3 H), 4.66 (br. s, NH), 5.12 (q, J = 6.9 Hz, 1 H), 6.67 (dd, J = 8.6, 1.0 Hz, 2 H), 6.71 (t, J = 7.3 Hz, 1 H), 7.17 (dd, J = 8.5, 7.4 Hz, 2 H), 7.49 (t, J = 7.8 Hz, 2 H), 7.60 (tt, J = 7.4, 1.3 Hz, 1 H), 8.00 (dd, J = 8.6, 1.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 19.5 (CH_3), 53.3 (CH), 113.4 (CH), 117.9 (CH), 128.4 (CH), 128.8 (CH), 129.4 (CH), 133.6 (CH), 134.6 (C), 146.5 (C), 200.6 (C) ppm.

11 ($C_{13}H_{11}NO$): White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.19 (m, 3 H), 7.30–7.35 (m, 2 H), 7.39–7.42 (m, 3 H), 7.82–7.85 (m, 2 H), 8.38 (s, 1 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 121.0 (CH), 126.1 (CH), 128.9 (CH), 128.9 (CH), 129.3 (CH), 131.5 (CH), 136.3 (C), 152.2 (C), 160.6 (CH) ppm.

12 ($C_{15}H_{13}N$): 116 mg (56%) white solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.04–7.25 (m, 5 H), 7.29–7.42 (m, 5 H), 7.48–7.56 (m, 2 H), 8.27 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 120.9 (CH), 126.1 (CH), 127.4 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 129.6 (CH), 135.5 (C), 144.0 (CH), 151.6 (CH), 161.6 (CH) ppm.

13 ($C_{30}H_{24}O_2$): 127 mg (61%) yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.8 (br., 2 H), 5.92 (d, J = 15.8 Hz, 1 H), 6.77 (d, J = 15.8 Hz, 1 H), 7.12–7.35 (m, 16 H), 7.56 (d, J = 7.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 74.6 (C), 79.1 (C), 85.1 (C), 93.2 (C), 108.8 (CH), 126.0 (CH), 126.9 (CH), 127.5 (CH), 127.6 (CH), 128.1 (CH), 128.2 (CH), 144.9 (C), 145.0 (C), 148.4 (CH) ppm. IR: $\tilde{\nu}$ = 3542 (w), 3402 (br.) , 3058 (w), 3026 (w), 3026 (w), 2973 (w), 2874 (w), 1598 (w), 1490 (m), 1446 (m), 1158 (w), 1030 (m), 1001 (m), 907 (m), 756 (m), 732 (m), 695 (s), 641 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 416 [M$^+$] (5), 398 (10), 382 (12), 293 (20), 215 (35), 105 (100), 77 (40).

14 ($C_{17}H_{14}O_2$): White foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3 H), 2.99 (s, 1 H), 7.27 (t, J = 7.4 Hz, 2 H), 7.33 (t, J = 7.6 Hz, 4 H), 7.52 (d, J = 7.1 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 21.8 (CH_3), 78.0 (CH), 79.0 (C), 82.3 (C), 126.1 (CH), 128.0 (CH), 128.3 (CH), 142.0 (C), 168.2 (C) ppm.

15 ($C_{21}H_{17}N$): 130 mg (46%) yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d,J = 8.6 Hz, 2 H), 7.08 (d, J = 9.3 Hz, 1 H), 7.16 (t, J = 7.4 Hz, 1 H), 7.28–7.44 (m, 12 H), 8.13 (d, J = 9.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 121.0 (CH), 126.0 (CH), 127.3 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 129.2 (CH), 130.5 (CH), 138.3 (C), 140.7 (C), 151.9 (C), 154.3 (C), 160.4 (CH) ppm.

16 ($C_{19}H_{15}N$): 134 mg (52%) yellow crystals. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.03 (d, J = 16.2 Hz, 1 H), 7.24 (dd, J = 16.0, 8.0 Hz, 1 H), 7.32–7.87 (m, 10 H), 8.30 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 112.8 (CH), 118.8 (CH), 123.8 (CH), 124.7 (CH), 125.7 (CH), 125.8 (CH), 125.9 (C), 126.2 (CH), 127.4 (CH), 128.4 (CH), 131.2 (CH), 133.9 (C), 134.3 (C), 144.0 (CH), 153.0 (C), 162.0 (CH) ppm.

General Procedure of Ligand Synthesis: 1 mmol of the corresponding 4-hydroxycyclopent-4-ene-1,3-dione and 1 mmol diamine were dissolved in 5 mL of methanol and refluxed for 2 h under argon. After evaporation of the solvent chromatography of the crude products on silica furnished the pure compounds. The procedure was used for the synthesis of ligands **6aL**, **6bL**, **6cL**, **6dL**, **7cL**, **7dL** and precursor **7bL′**. Compounds **7cL** and **7dL** were obtained as an inseparable mixture. Compound **5 L** was prepared according to a published procedure.[12a]

6aL ($C_{21}H_{20}N_2O$): 297 mg (94%) violet foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (s, 6 H), 3.34 (s, 4 H), 7.13–7.17 (m, 2 H), 7.26–7.28 (m, 8 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 42.1 (CH_3), 50.0 (CH_2), 99.0 (C), 125.4 (CH), 127.2 (CH), 131.0 (CH), 133.6 (C), 150.9 (C), 195.2 (C) ppm. IR: $\tilde{\nu}$ = 2926 (w), 2860 (w), 2798 (w), 1586 (s), 1493 (m), 1439 (m), 1409 (m), 1352 (s), 1244 (m), 1175 (w), 1113 (m), 1068 (m), 1025 (w), 942 (m), 914 (w), 839 (w), 804 (w), 774 (m), 727 (m), 698 (s), 648 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 316 [M$^+$] (42), 273 (18), 227 (100), 203 (28), 105 (38), 77 (40). HRMS: calcd. 316.15753, found: 316.15754.

6bL ($C_{31}H_{24}N_2O$): 300 mg (68%) violet powder, poorly soluble: IR: $\tilde{\nu}$ = 3049 (w), 2928 (w), 1659 (m), 1604 (m), 1575 (s), 1492 (s), 1431 (m), 1410 (m), 1356 (s), 1276 (m), 1202 (s), 1132 (w), 1075 (m), 1015 (w), 968 (m), 910 (w), 843 (w), 805 (m), 775 (m), 761 (m), 738 (s), 693 (s), 621 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 440 [M$^+$] (100), 411 (12), 335 (18), 178 (20). HRMS: calcd. 440.18886, found: 440.18867.

6cL ($C_{15}H_{16}N_2O$): 235 mg (98%) dark red foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.73 (s, 3 H), 2.94 (s, 3 H), 3.26–3.34 (m, 4 H), 4.36 (s, 1 H), 7.15 (tt, J = 7.2, 1.4 Hz, 1 H), 7.19–7.22 (m, 2 H), 7.25–7.30 (m, 3 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 39.7 (CH_3), 41.8 (CH_3), 48.7 (CH_2), 50.5 (CH_2), 84.3 (CH), 101.0 (C), 125.8 (CH), 127.5 (CH), 131.4 (CH), 133.9 (C), 148.4 (C), 158.0 (C), 197.0 (C) ppm. IR: $\tilde{\nu}$ = 2920 (w), 2856 (w), 1659 (w), 1588 (s), 1493 (m), 1443 (m), 1409 (m), 1363 (m), 1299 (m), 1232 (m), 1215 (m), 1145 (m), 1112 (m), 1070 (m), 983 (m), 927 (m), 837 (w), 773 (s), 726 (m), 705 (s), 678 (m), 657 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 241 [M$^+$ + 1] (18), 240 [M$^+$] (100), 239 [M$^+$ – 1] (30), 197 (24). HRMS: [M$^+$] calcd. 240.12626, found: 240.12620, [M$^+$ – 1] calcd. 239.11844, found: 239.11836.

6dL ($C_{23}H_{24}N_2O_3$): 332 mg (88%) dark violet crystals, poorly soluble: IR: $\tilde{\nu}$ = 3610 (w), 3356 (br.) , 3052 (w), 2931 (w), 1713 (m), 1649 (w), 1604 (m), 1549 (s), 1494 (s), 1443 (m), 1405 (m), 1358 (m), 1296 (m), 1156 (m), 1072 (m), 1055 (m), 968 (w), 950 (w), 917 (w), 800 (m), 766 (m), 729 (m), 695 (s), 591 (m), 569 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 376 [M$^+$] (100), 346 (35), 332 (30), 301 (64). HRMS: calcd. 376.17869, found: 376.17847.

7bL′ ($C_{13}H_{15}NO$): 175 mg (87%) green foam: ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 47.6 (CH_2), 49.9 (CH_2), 51.8 (CH_2), 53.9 (CH_2), 56.5 (CH_2), 59.8 (CH_2), 63.0 (CH_2), 98.0 (C), 116.3 (C), 127.3 (CH), 128.1 (CH), 130.3 (CH), 132.9 (C), 162.3 (C), 197.4 (C) ppm.

7cL ($C_{12}H_{16}N_2O_3$): 229 mg (84% as 1:1 mixture with **7dL**) red foam. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.1 Hz, 3 H), 2.90 (s, 3 H), 3.08 (s, 3 H), 3.32 (br. s, 4 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.46 (s, 1 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 14.3 (CH_3), 39.2 (CH_3), 43.1 (CH_3), 47.1 (CH_2), 49.1 (CH_2), 60.0 (CH_2), 90.1 (CH), 92.1 (C), 154.2 (C), 159.8 (C), 164.3 (C), 192.3 (C) ppm.

7dL ($C_{15}H_{20}N_2O_5$): 229 mg (84% as 1:1 mixture with **7cL**) red foam. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 6 H), 3.24 (s, 6 H), 3.58 (s, 4 H), 4.22 (q, J = 7.0 Hz, 4 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 14.9 (CH_3), 43.6 (CH_3), 49.7 (CH_2), 60.5 (CH_2), 92.6 (C), 157.4 (C), 164.2 (C), 187.3 (C) ppm.

Synthesis of Ligands 7aL and 7bL: 1 mmol of the ligand precursor (**6cL** for **7aL** and **7bL′** for **7bL**) was dissolved in 3 mL of pyridine. After addition of a catalytic amount of DMAP and 1.5 equiv. (for **7aL**) or 3.5 equiv. (for **7bL**) benzoyl chloride the reaction mixture was stirred at room temp. under argon for 24 h. Aqueous workup and chromatography on silica furnished the ligands **7aL** and **7bL**.

7aL ($C_{22}H_{20}N_2O_2$): 357 mg (97%) dark red foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3 H), 3.17 (s, 3 H), 3.19 (t, J = 6.3 Hz, 2 H), 3.48 (t, J = 6.0 Hz, 2 H), 7.08–7.32 (m, 8 H), 7.67 (d, J = 6.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 41.4 (CH_3), 44.2 (CH_3), 48.5 (CH_2), 50.2 (CH_2), 98.4 (C), 104.3 (C), 126.2 (CH), 127.0 (CH), 127.1 (CH), 129.8 (CH), 130.8 (CH), 131.0 (CH), 132.2 (C), 140.8 (C), 147.6 (C), 164.5 (C), 187.6 (C), 191.2 (C) ppm. IR: $\tilde{\nu}$ = 2929 (w), 1647 (w), 1606 (s), 1581 (s), 1547 (s), 1498 (w), 1445 (m), 1426 (s), 1403 (s), 1364 (s), 1340 (m), 1270 (m), 1250, (m), 1172 (w), 1117 (w), 1074 (w), 1050 (w), 1012 (w), 926 (m), 907 (s), 833 (m), 798 (m), 765 (s), 745 (m), 732 (m), 703 (s), 655 (s) cm^{-1}. MS (EI): m/z (%) = 344 (90) [M$^+$], 253 (100), 105 (40). HRMS (ESI, MeOH): [M$^+$]+Na calcd. 367.14225, found: 367.14208.

7bL ($C_{38}H_{32}N_2O_6$): 570 mg (93%) dark red foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (t, J = 5.8 Hz, 2 H), 3.58 (t, J = 5.0 Hz, 2 H), 3.80 (t, J = 5.6 Hz, 2 H), 4.10 (t, J = 5.2 Hz, 2 H), 4.33 (t, J = 4.9 Hz, 2 H), 4.59 (t, J = 5.1 Hz, 3 H), 7.17–7.23 (m, 3 H), 7.28 (t, J = 7.5 Hz, 2 H), 7.32 (t, J = 7.7 Hz, 2 H), 7.39–7.45 (m, 5 H), 7.55–7.59 (m, 2 H), 7.65 (dd, J = 8.4, 1.4 Hz, 2 H), 7.93 (dd, J = 8.2, 1.4 Hz, 2 H), 8.00 (dd, J = 8.2, 1.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 47.9 (CH_2), 50.8 (CH_2), 51.0 (CH_2), 54.7 (CH_2), 61.1 (CH_2), 61.5 (CH_2), 98.9 (C), 104.67 (C), 127.1 (CH), 127.4 (CH), 127.7 (CH), 128.5 (CH), 128.6 (CH), 129.4 (C), 129.5 (C), 129.5 (CH), 129.6 (CH), 129.7 (CH), 131.1 (CH), 131.2 (CH), 132.0 (C), 133.3 (CH), 133.4 (CH), 141.0 (C), 146.6 (C), 163.3 (C), 166.0 (C), 166.1 (C), 189.1 (C), 191.4 (C) ppm. IR: $\tilde{\nu}$ = 3058 (w), 2927 (w), 2854 (w), 1716 (s), 1668 (w), 1601 (s), 1577 (s), 1551 (m), 1495 (w), 1450 (m), (1422 (m), 1360 (m), 1313 (w), 1265 (s), 1175 (m), 1110 (s), 1097 (s), 1069 (m), 1026 (m), 914 (m), 818 (w), 768 (w), 700 (s), 658 (m), 617 (w) cm^{-1}. MS (EI): m/z (%) = 612 [M$^+$] (10), 490 (55), 149 (33), 122 (50), 105 (100), 77 (47). HRMS: calcd. 612.22604, found: 612.22728.

Synthesis of Ligands 8aL, 8bL and 8cL: 1 mmol of **6cL** was dissolved in 5 mL of DCM. After addition of 1.1 equiv. of the corresponding isocyanate the reaction mixture was stirred at room temp. under argon for 24 h. Aqueous workup and chromatography on silica furnished the ligands **8aL**, **8bL** and **8cL**.

8aL ($C_{22}H_{21}N_3O_2$): 352 mg (98%) violet foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 3 H), 3.31 (dd, J = 6.4, 5.7 Hz, 2 H), 3.53 (dd, J = 6.4, 5.6 Hz, 2 H), 3.64 (s, 3 H), 6.98 (tt, J = 7.4, 1.1 Hz, 1 H), 7.23–7.28 (m, 5 H), 7.31–7.35 (m, 2 H), 7.59–7.62 (m, 2 H), 10.54 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 41.7 (CH_3), 45.3 (CH_3), 48.5 (CH_2), 50.1 (CH_2), 89.8 (C), 103.3 (C), 119.6 (CH), 122.4 (CH), 126.7 (CH), 127.6 (CH), 128.7 (CH), 131.0 (CH), 132.1 (C), 139.7 (C), 148.8 (C), 161.4 (C), 161.6 (C), 195.2 (C) ppm. IR: $\tilde{\nu}$ = 3326 (w), 3230 (w), 3124 (w), 3052 (w), 3025 (w), 2929 (w), 2851 (w), 1658 (m), 1625 (m), 1596 (m), 1569 (s), 1531 (s), 1497 (s), 1436 (s), 1408 (m), 1361 (s), 1305 (m), 1244 (s), 1156 (m), 1111 (w), 1070 (m), 1034 (w), 998 (w), 973 (m), 910 (w), 884 (w), 834 (w), 795 (w), 778 (w), 753 (s), 728 (s), 698 (s), 618 (m) cm^{-1}. MS (EI): m/z (%) = 359 [M$^+$] (38), 267 (100), 240 (30). HRMS: calcd. 359.16339, found: 359.16297.

8bL ($C_{26}H_{23}N_3O_2$): 373 mg (91%) violet foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (s, 3 H), 3.25 (dd, J = 6.4, 5.7 Hz, 2 H), 3.48 (dd, J = 6.4, 5.6 Hz, 2 H), 3.65 (s, 3 H), 7.27–7.30 (m, 3 H), 7.34–7.38 (m, 2 H), 7.41–7.50 (m, 3 H), 7.53 (d, J = 8.2 Hz, 1 H), 7.80 (d, J = 7.9 Hz, 1 H), 8.32 (t, J = 7.6 Hz, 2 H), 11.14 (s, NH) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 41.7 (CH_3), 45.3 (CH_3), 48.5 (CH_2), 50.1 (CH_2), 90.2 (C), 103.4 (C), 117.5 (CH), 121.8 (CH), 122.9 (CH), 125.6 (CH), 125.8 (CH), 125.9 (CH), 126.3 (C), 126.8 (CH), 127.6 (CH), 128.2 (CH), 131.2 (CH), 132.2 (C), 134.1 (C), 134.8 (C), 149.1 (C), 161.6 (C), 161.7 (C), 195.5 (C) ppm. IR: $\tilde{\nu}$ = 3049 (w), 2921 (w), 2855 (w), 2065 (w), 1982 (w), 1643 (m), 1573 (s), 1531 (s), 1496 (s), 1451 (m), 1397 (s), 1357 (s), 1339 (m), 1254 (s), 1206 (w), 1156 (w), 1100 (m), 1070 (w), 1025 (w), 990 (w), 970 (m), 894 (w), 837 (m), 795 (s), 776 (s), 732 (s), 702 (s) cm^{-1}. MS (EI): m/z (%) = 409 (38) [M$^+$], 267 (95), 240 (75), 169 (100), 141 (37), 140 (34). HRMS: calcd. 409.17903, found: 409.17905.

8cL ($C_{22}H_{27}N_3O_2$): 325 mg (89%) violet foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16–1.27 (m, 3 H), 1.30–1.41 (m, 2 H), 1.52–1.57 (m, 1 H), 1.66–1.72 (m, 2 H), 1.88–1.94 (m, 2 H), 2.73 (s, 3 H), 3.30 (dd, J = 6.3, 4.3 Hz, 2 H), 3.51 (dd, J = 6.4 Hz, 2 H), 3.60 (s, 3 H), 7.19–7.23 (m, 3 H), 7.29–7.33 (m, 2 H), 8.30 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 24.7 (CH_2), 25.7 (CH_2), 33.1 (CH_2), 41.7 (CH_3), 44.9 (CH_3), 47.2 (CH), 48.6 (CH_2), 50.0 (CH_2), 89.7 (C), 102.8 (C), 126.4 (CH), 127.4 (CH), 131.0 (CH), 132.4 (C), 148.6 (C), 160.4 (C), 162.7 (C), 195.3 (C) ppm. IR: $\tilde{\nu}$ = 3519 (w), 3294 (w), 2933 (m), 2855 (w), 2231 (w), 1617 (s), 1573 (s), 1518 (s), 1451 (m), 1412 (m), 1358 (m), 1250 (m), 1180 (w), 1113 (m), 1071 (m), 965 (w), 926 (w), 868 (w), 337 (m), 758 (m), 792 (m), 758 (m), 729 (m), 709 (m), 644 (m), 614 (m) cm^{-1}. MS (EI): m/z (%) = 365 [M$^+$] (60), 268 (100), 241 (71). HRMS: calcd. 365.21033, found: 365.21027.

General Procedure of Complex Synthesis: 150 mg dodecacarbonyltriruthenium ($C_{12}O_{12}Ru_3$, 0.23 mmol) and 0.7 mmol of the corresponding ligand were dissolved in 5 mL toluene (for complexes **8d** and **7b** 1 mL MeOH was added) and refluxed for 4–12 h (TLC control). The solvent was evaporated and chromatography on silica furnished the complexes **2** and **5**–**8**.

2a ($C_{32}H_{20}O_4Ru$): 394 mg (98%) white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99–7.04 (m, 6 H), 7.08–7.11 (m, 4 H), 7.14–7.17 (m, 6 H), 7.39–7.42 (m, 4 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 82.0 (C), 107.8 (C), 127.4 (CH), 127.9 (CH), 128.0 (CH), 128.5 (CH), 129.8 (C), 130.7 (CH), 131.5 (C), 132.0 (CH), 173.9 (C), 194.4 (CO) ppm. IR: $\tilde{\nu}$ = 3060, 2075, 2018, 1997, 1633, 1601, 1497, 1445, 1388, 1202, 1185, 1075, 1028, 840, 801, 753, 736, 692, 637, 577, 552, 537 cm^{-1}. MS (EI): m/z (%) = 573, 572, 571, 570, 569, 568, 567, 564 [1:5:2:10:6:4:4:2, distribution of M$^+$ isotopes] (18), 542 (22), 514 (65), 486 (100), 458 (55), 278 (30).

2b ($C_{22}H_{16}O_4Ru$): 300 mg (95%) white powder. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.92 (s, 6 H), 6.83–6.84 (m, 6 H), 6.95–6.98 (m, 4 H) ppm. ^{13}C NMR (100 MHz, DEPT, C_6D_6): δ = 10.7 (CH_3), 77.3 (C), 108.5 (C), 128.2 (CH), 128.5 (CH), 130.7 (C), 131.6 (CH), 176.1 (C), 196.0 (CO) ppm. IR: $\tilde{\nu}$ = 3058, 2066, 2011, 1989, 1767, 1688, 1642, 1501, 1451, 1396, 1180, 1134, 1078, 1036, 1021, 972, 758, 720, 698, 586, 549, 531 cm^{-1}. MS (EI): m/z (%) = 449, 448, 447, 446, 445, 444, 443, 440 [1:5:2:10:6:4:4:2, distribution of M$^+$ isotopes] (10), 418 (40), 362 (100), 332 (35), 328 (30), 260 (25).

5 ($C_{24}H_{16}O_8Ru$): 338 mg (90%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 6 H), 7.20–7.26 (m, 10 H) ppm.

^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 52.6 (CH_3), 71.0 (C), 109.1 (C), 128.1 (CH), 128.6 (C), 129.2 (CH), 130.9 (CH), 165.5 (C), 170.5 (C), 191.5 (CO) ppm. IR: $\tilde{\nu}$ = 3064 (w), 2953 (w), 2101 (s), 2035 (s), 1735 (s), 1707 (s), 1675 (s), 1501 (w), 1436 (m), 1414 (w), 1377 (w), 1347 (s), 1200 (s), 1173 (s), 1123 (m), 1103 (m), 1032 (w), 995 (m), 786 (m), 776 (m), 762 (w), 698 (s), 652 (w), 626 (w), 599 (s), 586 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 538, 537, 536, 535, 534, 533, 532, 529 [1:4:2:8:4:3:3:1, distribution of (M^+ + H) isotopes] (100), 507 [M^+ + H – CO] (39), 479 [M^+ + H – 2 CO] (98).

6a ($C_{24}H_{20}N_2O_4Ru$): 256 mg (72%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 6 H), 2.52 (ddd, *J* = 16.2, 6.6, 4.2 Hz, 2 H), 3.30 (ddd, *J* = 15.9, 6.9, 4.0 Hz, 2 H), 7.18–7.31 (m, 6 H), 7.39–7.41 (m, 4 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 43.5 (CH_3), 50.0 (CH_2), 69.5 (C), 116.6 (C), 127.6 (CH), 128.3 (CH), 132.2 (C), 132.7 (CH), 171.9 (C), 196.2 (CO) ppm. IR: $\tilde{\nu}$ = 2957 (w), 2927 (w), 2866 (w), 2809 (w), 2046 (s), 1963 (s), 1638 (m), 1530 (m), 1493 (m), 1442 (m), 1411 (m), 1359 (m), 1264 (w), 1183 (w), 1115 (w), 1074 (w), 1046 (w), 1004 (w), 946 (m), 848 (w), 753 (m), 723 (m), 697 (s), 655 (w), 606 (m) cm^{-1}. MS (ESI, TBME): *m*/*z* (%) = 506, 505, 504, 503, 502, 501, 500, 497 [1:3:2:7:4:3:2:1, distribution of (M^+ + H) isotopes] (97), 475 [M^+ + H – CO] (86), 317 [M^+ + H – $Ru(CO)_3$] (100).

6b ($C_{34}H_{24}N_2O_4Ru$): 330 mg (75%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76–3.82 (m, 2 H), 3.87–3.93 (m, 2 H), 6.85–7.00 (m, 16 H), 7.43–7.47 (m, 4 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 50.9 (CH_2), 71.9 (C), 110.7 (C), 124.7 (CH), 125.3 (CH), 126.4 (CH), 127.4 (CH), 128.7 (CH), 130.8 (CH), 132.4 (C), 144.1 (C), 171.0 (C), 195.9 (CO) ppm. IR: $\tilde{\nu}$ = 3057 (w), 3020 (w), 2925 (w), 2877 (w), 2044 (s), 1983 (s), 1965 (s), 1646 (s), 1595 (m), 1485 (s), 1438 (m), 1392 (w), 1360 (m), 1306 (m), 1221 (w), 1157 (w), 1125 (w), 1073 (w), 973 (w), 827 (w), 807 (w), 752 (m), 737 (m), 719 (m), 690 (s), 627 (w) cm^{-1}. MS (ESI, TBME): *m*/*z* (%) = 630, 629, 628, 627, 626, 625, 624, 621 [1:5:2:10:6:4:4:2, distribution of (M^+ + H) isotopes] (70), 599 [M^+ + H – CO] (100), 571 [M^+ + H – 2 CO] (22), 543 [M^+ + H – 3 CO] (13), 441 [M^+ + H – $Ru(CO)_3$].

6c ($C_{18}H_{16}N_2O_4Ru$): 268 mg (89%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 2.57 (s, 3 H), 2.59–2.65 (m, 2 H), 3.35–3.46 (m, 2 H), 4.23 (s, 1 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.36 (t, *J* = 7.1 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 39.3 (CH_3), 43.6 (CH_3), 45.5 (CH), 48.1 (CH_2), 51.0 (CH_2), 73.0 (C), 111.2 (C), 121.2 (C), 127.6 (CH), 128.4 (CH), 131.9 (C), 132.5 (CH), 170.6 (C), 196.0 (CO) ppm. IR: $\tilde{\nu}$ = 2959 (w), 2929 (w), 2870 (w), 2805 (w), 2047 (s), 1966 (s), 1621 (s), 1568 (m), 1538 (s), 1496 (m), 1445 (m), 1412 (m), 1361 (m), 1311 (w), 1268 (w), 1202 (w), 1112 (m), 927 (w), 758 (m), 732 (m), 700 (s), 642 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 429, 428, 427, 426, 425, 424, 423, 420 [1:5:2:10:6:4:4:2, distribution of M^+ isotopes] (2), 398 (3) [M^+ – CO], 370 (10) [M^+ – 2 CO], 342 (15) [M^+ – 3 CO], 240 (100) [M^+ – $Ru(CO)_3$].

6d ($C_{26}H_{24}N_2O_6Ru$): 368 mg (93%) yellow powder. ^{1}H NMR (400 MHz, CD_3OD): δ = 2.23–2.31 (m, 2 H), 2.54–2.68 (m, 1 H), 2.80–2.88 (m, 3 H), 3.05–3.17 (m, 1 H), 3.28–3.35 (m, 2 H), 3.45–3.56 (m, 1 H), 3.61–3.68 (m, 2 H), 3.82–3.91 (m, 1 H), 7.13–7.50 (m, 10 H) ppm. ^{13}C NMR (100 MHz, DEPT, CD_3OD): δ = 49.3 (CH_2), 57.4 (CH_2), 60.3 (CH_2), 72.1 (C), 118.2 (C), 129.2 (CH), 129.7 (CH), 133.1 (C), 134.2 (CH), 171.6 (C), 197.0 (CO) ppm. IR: $\tilde{\nu}$ = 3335 (br.) , 3058 (w), 2962 (w), 2926 (w), 2875 (w), 2052 (s), 1971 (s), 1603 (m), 1540 (s), 1495 (m), 1437 (m), 1355 (m), 1260 (m), 1158 (w), 1044 (s), 1028 (s), 910 (w), 799 (m), 752 (m), 725 (s), 697 (s) cm^{-1}. MS (ESI, TBME): *m*/*z* (%) = 566, 565, 564, 563, 562, 561, 560, 557 [1:4:2:8:4:3:2:1, distribution of (M^+ + H) isotopes] (40), 535 [M^+ + H – CO] (40), 507 [M^+ + H – 2 CO] (28).

7a ($C_{25}H_{20}N_2O_5Ru$): 254 mg (68%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 2.23 (s, 3 H), 2.48–2.54 (m, 1 H), 2.59–2.64 (m, 1 H), 3.23–3.29 (m, 1 H), 3.39–3.45 (m, 1 H), 7.14–7.41 (m, 8 H), 7.67 (d, *J* = 7.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 42.8 (CH_3), 43.5 (CH_3), 49.7 (CH_2), 50.2 (CH_2), 69.0 (C), 70.9 (C), 114.3 (C), 114.9 (C), 126.7 (CH), 127.7 (CH), 128.2 (CH), 128.3 (CH), 128.7 (CH), 129.7 (CH), 131.4 (C), 132.6 (CH), 133.4 (CH), 136.7 (C), 169.8 (C), 171.9 (C), 193.2 (CO) ppm. IR: $\tilde{\nu}$ = 2927 (w), 2858 (w), 2057 (s), 1978 (s), 1627 (s), 1581 (s), 1498 (m), 1447 (m), 1401 (m), 1359 (m), 1263 (m), 1211 (w), 1071 (m), 1026 (m), 914 (m), 839 (w), 787 (w), 734 (s), 695 (s) cm^{-1}. MS (ESI, TBME): *m*/*z* (%) = 534, 533, 532, 531, 530, 529, 528, 525 [1:4:2:8:4:3:3:1, distribution of (M^+ + H) isotopes] (8), 497 [M^+ – 2 CO + Na] (5), 469 [M^+ – 3 CO + Na] (4), 367 [M^+ – $Ru(CO)_3$ + Na] (40).

7b ($C_{41}H_{32}N_2O_9Ru$): 360 mg (64%) yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51–2.57 (m, 1 H), 2.66–2.72 (m, 1 H), 2.84–2.90 (m, 1 H), 2.92–2.97 (m, 1 H), 3.12–3.19 (m, 2 H), 3.66–3.75 (m, 3 H), 4.00–4.07 (m, 2 H), 4.15–4.19 (m, 1 H), 7.18–8.04 (m, 20 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 48.1 (CH_2), 48.4 (CH_2), 52.9 (CH_2), 53.8 (CH_2), 61.4 (CH_2), 61.8 (CH_2), 70.1 (C), 70.2 (C), 111.6 (C), 114.5 (C), 128.2 (C), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.0 (C), 129.6 (CH), 129.9 (CH), 131.1 (C), 132.9 (CH), 133.2 (CH), 133.4 (CH), 133.7 (CH), 136.6 (C), 166.0 (C), 166.1 (C), 169.7 (C), 170.2 (C), 192.2 (CO) ppm. IR: $\tilde{\nu}$ = 3060 (w), 2928 (w), 2855 (w), 2064 (s), 1985 (s), 1718 (s), 1603 (m), 1580 (s), 1496 (w), 1452 (s), 1362 (m), 1316 (w), 1267 (s), 1177 (m), 1111 (s), 1071 (s), 1028 (m), 820 (w), 710 (s) cm^{-1}. MS (ESI, TBME): *m*/*z* (%) = 802, 801, 800, 799, 798, 797, 796, 793 [1:3:2:6:4:3:2:1, distribution of (M^+ + H) isotopes] (90), 771 [M^+ + H – CO] (30), 743 [M^+ + H – 2 CO] (10), 715 [M^+ + H – 3 CO] (42), 613 [M^+ + H – $Ru(CO)_3$] (100).

7c ($C_{15}H_{16}N_2O_6Ru$): 134 mg (45%) yellow powder. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.23 (t, *J* = 7.1 Hz, 3 H), 2.49 (s, 3 H), 2.51 (s, 3 H), 2.56–2.67 (m, 2 H), 3.29–3.40 (m, 2 H), 4.12–4.25 (m, 2 H), 4.35 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, CD_3OD): δ = 14.4 (CH_3), 39.5 (CH_3), 43.4 (CH_3), 48.0 (CH), 48.9 (CH_2), 51.9 (CH_2), 63.1 (CH_2), 64.1 (C), 109.9 (C), 123.1 (C), 167.6 (C), 168.9 (C), 196.1 (CO) ppm. IR: $\tilde{\nu}$ = 2962 (w), 2923 (w), 2873 (w), 2810 (w), 2056 (s), 1987 (s), 1718 (m), 1638 (s), 1592 (s), 1544 (s), 1446 (m), 1416 (s), 1326 (s), 1311 (m), 1267 (m), 1214 (s), 1176 (s), 1115 (m), 1044 (s), 941 (m), 856 (w), 792 (w), 739 (m), 706 (m), 641 (w), 565 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 422 [M^+] (5), 397, 396, 395, 394, 393, 392, 391, 388 [1:5:2:10:5:4:4:1, distribution of (M^+ – CO) isotopes], 236 [M^+ – 3 CO].

7d ($C_{18}H_{20}N_2O_8Ru$): 157 mg (45%) yellow powder. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.23 (t, *J* = 7.1 Hz, 6 H), 2.51 (s, 6 H), 2.67 (dd, *J* = 6.8, 3.7 Hz, 1 H), 2.71 (dd, *J* = 6.4, 4.0 Hz, 1 H), 3.36 (dd, *J* = 6.8, 4.0 Hz, 1 H), 3.41 (dd, *J* = 6.8, 3.7 Hz, 1 H), 4.19 (q, *J* = 7.1 Hz, 1 H), 4.20 (q, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, CD_3OD): δ = 14.3 (CH_3), 42.8 (CH_3), 50.7 (CH_2), 62.4 (C), 63.3 (CH_2), 115.0 (C), 167.1 (C), 170.0 (C), 195.5 (CO) ppm. IR: $\tilde{\nu}$ = 2981 (w), 2932 (w), 2873 (w), 2064 (s), 1986 (s), 1710 (s), 1643 (s), 1538 (m), 1515 (m), 1415 (m), 1381 (m), 1361 (m), 1324 (m), 1265 (m), 1208 (m), 1176 (m), 1088 (m), 1055 (m), 1018 (m), 974 (m), 844 (w), 755 (w), 699 (w), 617 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 494 [M^+] (5), 469, 468, 467, 466, 465, 464, 463, 460 [1:5:9:5:4:3:2:1, distribution of (M^+ – CO) isotopes] (71), 308 [M^+ – $Ru(CO)_3$] (100).

8a ($C_{25}H_{21}N_3O_5Ru$): 380 mg (99%) yellow powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3 H), 2.61 (ddd, J = 12.0, 10.4, 2.9 Hz, 1 H), 3.01 (dt, J = 13.3, 3.0 Hz, 1 H), 3.14 (dt, J = 12.0, 3.0 Hz, 1 H), 3.15 (s, 3 H), 3.56 (ddd, J = 13.2, 10.3, 2.9 Hz, 1 H), 7.05 (t, J = 7.4 Hz, 1 H), 7.26–7.30 (m, 3 H), 7.36–7.43 (m, 4 H), 7.61–7.64 (m, 2 H), 11.55 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 42.4 (CH_3), 47.7 (CH_3), 48.7 (CH_2), 50.4 (CH_2), 54.7 (C), 72.7 (C), 114.9 (C), 118.6 (C), 120.1 (CH), 123.6 (CH), 128.3 (CH), 128.8 (CH), 128.8 (CH), 131.1 (C), 132.5 (CH), 138.7 (C), 164.3 (C), 170.7 (C), 194.2 (CO) ppm. IR: $\tilde{\nu}$ = 3028 (w), 2927 (w), 2858 (w), 2058 (s), 1982 (s), 1676 (m), 1588 (s), 1536 (s), 1495 (s), 1443 (s), 1410 (m), 1359 (s), 1331 (m), 1309 (w), 1252 (m), 1117 (w), 1069 (w), 1028 (w), 962 (w), 890 (w), 850 (w), 754 (s), 732 (s), 693 (s), 626 (w) cm^{-1}. MS (ESI, TBME): m/z (%) = 549, 548, 547, 546, 545, 544, 543, 540 [1:4:2:8:4:3:3:2, distribution of (M^+ + H) isotopes] (100), 518 [M^+ + H – CO] (45), 490 [M^+ + H – 2 CO] (22), 462 [M^+ + H – 3 CO] (50).

8b ($C_{29}H_{23}N_3O_5Ru$): 177 mg (42%) yellow powder. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.60 (ddd, J = 12.0, 10.5, 2.7 Hz, 1 H), 2.99 (dt, J = 13.2, 2.9 Hz, 1 H), 3.10 (dt, J = 12.0, 3.0 Hz, 1 H), 3.17 (s, 3 H), 3.56 (ddd, J = 13.2, 10.4, 2.8 Hz, 1 H), 7.42–7.49 (m, 8 H), 7.61 (d, J = 8.2 Hz, 1 H), 7.79–7.82 (m, 1 H), 8.18–8.21 (m, 1 H), 8.38 (dd, J = 7.6, 1.1 Hz, 1 H), 12.07 (s, 1 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 42.4 (CH_3), 47.6 (CH_3), 48.8 (CH_2), 50.4 (CH_2), 55.0 (C), 72.8 (C), 115.3 (C), 118.4 (C), 118.5 (CH), 121.5 (CH), 124.2 (CH), 125.7 (CH), 125.8 (CH), 126.1 (C), 126.3 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 131.2 (C), 132.7 (CH), 133.7 (C), 134.0 (C), 164.7 (C), 171.1 (C), 194.3 (CO) ppm. IR: $\tilde{\nu}$ = 3052 (w), 2957 (w), 2924 (w), 2855 (w), 2059 (s), 1982 (s), 1679 (s), 1535 (s), 1500 (s), 1442 (m), 1407 (m), 1359 (s), 1330 (m), 1255 (w), 1118 (w), 1058 (w), 1028 (w), 960 (w), 796 (s), 770 (s), 732 (s), 696 (s) cm^{-1}. MS (ESI, TBME): m/z (%) = 599, 598, 597, 596, 595, 594, 593, 590 [1:4:2:8:5:4:3:1, distribution of (M^+ + H) isotopes] (100), 568 [M^+ + H – CO] (35), 540 [M^+ + H – 2 CO] (42), 512 [M^+ + H – 3 CO] (37).

8c ($C_{25}H_{27}N_3O_5Ru$): 132 mg (34%) yellow powder. ^1H NMR (400 MHz, CD_3OD): δ = 1.25–1.31 (m, 3 H), 1.32–1.45 (m, 2 H), 1.55–1.62 (m, 1 H), 1.68–1.74 (m, 2 H), 1.86–1.90 (m, 2 H), 2.06 (s, 3 H), 2.60 (ddd, J = 12.5, 9.5, 3.2 Hz, 1 H), 2.98 (s, 3 H), 3.01 (dt, J = 13.3, 3.3 Hz, 1 H), 3.26 (dt, J = 12.4, 3.7 Hz, 1 H), 3.54 (ddd, J = 12.8, 9.6, 3.3 Hz, 1 H), 3.78–3.85 (m, 1 H), 7.40–7.44 (m, 5 H) ppm. ^{13}C NMR (100 MHz, DEPT, CD_3OD): δ = 25.4 (CH_2), 25.5 (CH_2), 26.7 (CH_2), 33.3 (CH_2), 33.6 (CH_2), 43.0 (CH_3), 45.2 (CH_3), 49.5 (CH), 50.7 (CH_2), 51.1 (CH_2), 58.6 (C), 73.8 (C), 115.6 (C), 120.6 (C), 129.4 (CH),129.8 (CH), 132.7 (C), 134.0 (CH), 166.6 (C), 171.0 (C), 196.3 (CO) ppm. IR: $\tilde{\nu}$ = 2928 (m), 2853 (w), 2056 (s), 1975 (s), 1649 (s), 1612 (s), 1575 (s), 1435 (s), 1411 (s), 1357 (s), 1256 (w), 1108 (m), 1069 (m), 1026 (m), 957 (w), 770 (s), 734 (m), 698 (w), 622 (m) cm^{-1}. MS (ESI, TBME): m/z (%) = 556, 555, 554, 553, 552, 551, 550, 547 [1:4:3:8:6:4:4:1, distribution of (M^+ + 2 H) isotopes] (100), 525 [M^+ + 2 H – CO] (78), 495 [M^+ – 2 CO] (12), 367 [M^+ + 2 H – $Ru(CO)_3$] (45).

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