Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *88* (12) S399–S406 (2023) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Synthesis, spectroscopic characterization and DFT analysis of dichlorido(η^6-*p*-cymene)ruthenium(II) complexes with isonicotinate-polyethylene glycol ester ligands

THOMAS EICHHORN[1], DUŠAN DIMIĆ[2], ZORAN MARKOVIĆ[3] and GORAN N. KALUĐEROVIĆ[1]*

[1]*Department of Engineering and Natural Sciences, University of Applied Sciences Merseburg, Eberhard-Leibnitz-Straße 2, 06217 Merseburg, Germany,* [2]*University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia and* [3]*Institute of Information Technologies, University of Kragujevac, Jovana Cvijića bb, 34000 Kragujevac, Serbia*

J. Serb. Chem. Soc. *88* (12) (2023) 1335–1354

ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

2-(2-Methoxyethoxy)ethyl iso-nicotinate hydrochloride (L2·HCl)

Properties: Viscous, hygroscopic oil; soluble in water, methanol, ethanol, *iso*propanol, insoluble in diethyl ether.

^{1}H-NMR (400 MHz, D_2O): δ 3.33 (s, 3H, OCH_3), 3.63, 3.74 (m, 4H, $CH_3OCH_2CH_2$), 3.95 (m, 2H, $COOCH_2CH_2$), 4.63 (m, 2H, $COOCH_2$), 8.59 (d, $^3J_{H,H}$ = 6.8 Hz, 2H, H^3), 9.03 (d, $^3J_{H,H}$ = 6.8 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, D_2O): δ 58.0 (CH_3O), 66.0 (CH_2OOC), 68.1, 69.5, 70.9 (CH_2O), 126.9 (C^3), 142.6 (C^2), 145.9 (C^4), 163.2 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{11}H_{16}NO_4]^+$ 226.10738, *m*/*z* 226.10738 $[M+H]^+$. IR: ν (cm^{-1}) 3068(w), 2877(w), 2400(b), 2100(w), 2022(w), 1916(w), 1731(s), 1635(w), 1605(m), 1501(w), 1450(w), 1282(s), 1239(m), 1198(w), 1100(s), 998(m), 845(m), 754(s), 684(m), 359(w). Yield: 88%.

2-[2-(2-Methoxyethoxy)ethoxy]ethyl iso-nicotinate hydrochloride (L3·HCl)

Properties: Viscous, hygroscopic oil; soluble in water, methanol, ethanol, *iso*propanol, chloroform, and dichloromethane, insoluble in diethyl ether.

^{1}H-NMR (400 MHz, D_2O): δ 3.35 (s, 3H, OCH_3), 3.60, 3.70, 3.72, 3.79 (m, 8H, OCH_2CH_2O), 3.98 (m, 2H, $COOCH_2CH_2$), 4.66 (m, 2H, $COOCH_2$), 8.62 (d, $^3J_{H,H}$ = 6.8 Hz, 2H, H^3), 9.04 (d, $^3J_{H,H}$ = 6.8 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, D_2O): δ 58.0 (CH_3O), 66.1 (CH_2OOC), 68.2, 69.4, 69.5, 69.7, 70.9 (CH_2O), 127.0 (C^3), 142.6 (C^2), 145.9 (C^4), 163.3 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{13}H_{20}NO_5]^+$ 270.13360, *m*/*z* 270.13351 $[M+H]^+$. IR: ν (cm^{-1}) 3073(w), 2875(w), 2400(b), 2100(w), 2026(w), 1916(w), 1730(s), 1635(w), 1607(m), 1500(w), 1450(w), 1282(s), 1239(m), 1198(w), 1098(s), 998(m), 845(m), 758(s), 685(m), 363(w). Yield: 95%.

* Corresponding author. E-mail: goran.kaluderovic@hs-merseburg.de

2-(2-Hydroxyethoxy)ethyl isonicotinate hydrochloride (L4·HCl)

Properties: Viscous, colourless oil; soluble in water, methanol, ethanol, *iso*propanol, acetone, chloroform, and dichloromethane, insoluble in diethyl ether.

^{1}H-NMR (400 MHz, D_2O): δ 3.77 (m, 4H, HOCH_2CH_2), 4.00 (m, 2H, COOCH_2CH_2), 4.69 (m, 2H, COOCH_2), 8.60 (d, $^{3}J_{H,H}$ = 6.8 Hz, 2H, H^3), 9.04 (d, $^{3}J_{H,H}$ = 6.8 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, D_2O): δ 60.3 (*C*H_2OH), 66.1 (*C*H_2OOC), 68.1 (*C*H_2CH$_2$OOC), 71.8 (*C*H_2CH2OH), 126.9 (C^3), 142.7 (C^2), 145.9 (C^4), 163.4 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{10}H_{14}NO_4]^+$ 212.09173, *m*/*z* 212.09176 $[M+H]^+$. IR: ν (cm^{-1}) 3350(b), 3080(w), 2872(w), 2440(b), 2100(w), 1730(s), 1637(w), 1604(w), 1502(w), 1451(w), 1404(w), 1282(s), 1119(s), 1068(m), 1002(m), 925(w), 889(w), 839(m), 754(s), 678(m), 520(w), 357(w), 255(w).

2-[2-(2-Methylamino-benzoyloxy)ethoxy]ethyl iso-nicotinate (L5)

Properties: Viscous oil, which crystallized upon standing, soluble in methanol, ethanol, *iso*propanol, chloroform, and dichloromethane, and insoluble in diethyl ether and water.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.89 (s, 3H, NCH_3), 3.87 (m, 4H, OCH_2), 4.43, 4.53 (t, $^{3}J_{H,H}$ = 6.8 Hz, 4H, COOCH_2), 6.53 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1H, H^9), 6.65 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H, H^7), 7.37 (ddd, $^{3}J_{H8,H7}$ = 7.8 Hz, $^{3}J_{H8,H9}$ = 7.1 Hz, $^{4}J_{H8,H10}$ = 1.7 Hz, 1H, H^8), 7.84 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2H, H^3), 7.88 (dd, $^{3}J_{H10,H9}$ = 8.0 Hz, $^{4}J_{H10,H8}$ = 1.6 Hz 1H, H^{10}), 8.71 (d, $^{3}J_{H,H}$ = 6.1 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 29.7 (N*C*H$_3$), 63.2, 65.0 (*C*H$_2$OOC), 69.0, 69.4 (*C*H$_2$CH$_2$OOC), 109.7 (C^5), 110.9 (C^7), 114.5 (C^9), 123.4 (C^3), 131.7 (C^{10}), 135.0 (C^8), 138.1 (C^4), 149.8 (C^2), 152.2 (C^6), 164.9, 168.5 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{18}H_{21}N_2O_5]^+$ 345.14450, *m*/*z* 345.14451 $[M+H]^+$. IR: ν (cm^{-1}) 3372(m), 2950(w), 2885(w), 2825(w), 1718(s), 1684(s), 1603(w), 1580(m), 1518(m), 1454(w), 1431(m), 1408(m), 1375(m), 1322(m), 1278(m), 1261(s), 1243(s), 1180(s), 1134(s), 1117(s), 1093(s), 1063(m), 1040(m), 1021(m), 952(m), 894(w), 877(w), 867(w), 850(w), 753(s), 700(s), 675(m), 605(m), 575(m), 533(m), 512(m), 275(m), 217 (w). UV-vis (1.74×10^{-4} M, $CHCl_3$, 298 K): λ_{max} 358 nm (ε = 5747 M^{-1} cm^{-1}).

*Dichlorido(*η^6-p-*cymene)(diethylene glycol monomethyl ether isonicotinate-*κ*N)ruthenium(II) (**2**)*

Properties: Orange powder; soluble in chloroform, dichloromethane, dimethylformamide, acetone, and acetonitrile, moderately soluble in methanol, ethanol, *iso*propanol, and tetrahydrofuran, insoluble in diethyl ether and toluene.

EA: Anal. Found: C, 47.00; H, 5.18; N, 2.65. Calcd for $C_{21}H_{29}Cl_2NO_4Ru$ (531.43): C, 47.46; H, 5.50; N, 2.64. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.31 (d, $^{3}J_{H,H}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 2.09 (s, 3H, CCH_3), 2.98 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 3.38 (s, 3H, OCH_3), 3.56, 3.68 (m, 4H, OCH_2), 3.83 (t, $^{3}J_{H,H}$ = 4.7 Hz, 2H, COOCH$_2$CH_2), 4.53 (t, $^{3}J_{H,H}$ = 4.6 Hz, 2H, COOCH_2), 5.23 (d, $^{3}J_{H,H}$ = 5.9 Hz, 2H, C*H*CCH$_3$), 5.45 (d, $^{3}J_{H,H}$ = 5.8 Hz, 2H, C*H*CHCCH$_3$), 7.85 (d, $^{3}J_{H,H}$ = 6.5 Hz, 2H, H^3), 9.23 (d, $^{3}J_{H,H}$ = 6.5 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.4 (C*C*H$_3$), 22.4 (C(*C*H$_3$)$_2$), 30.8 (*C*(CH$_3$)$_2$), 59.2 (*C*H$_3$O), 65.1 (*C*H$_2$OOC), 70.3 (*C*H$_2$O), 82.5, 83.3 (*C*H), 97.5, 103.9 (*C*CH), 123.7 (C^3), 138.7 (C^4), 155.9 (C^2), 163.9 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{21}H_{29}ClNO_4{}^{96}Ru]^+$ 490.08556, *m*/*z* 490.08544 $[M-Cl]^+$. IR: ν (cm^{-1}) 3062(w), 2964(w), 2878(w), 1728(s), 1556(w), 1468(w), 1451(w), 1414(m), 1377(w), 1323(w), 1275(s), 1228(w), 1202(w), 1107(s), 1056(m), 1027(m), 863(m), 769(m), 695(m), 659(w), 451(w), 371(w), 284(s), 232(s).

*Dichlorido(*η^6-p-*cymene)(triethylene glycol monomethyl ether iso-nicotinate-κN)ruthenium(II)* ***(3)***

Properties: Orange powder; soluble in chloroform, dichloromethane, dimethylformamide, acetone, and acetonitrile, moderately soluble in methanol, ethanol, *iso*propanol, and tetrahydrofuran, insoluble in diethyl ether and toluene.

EA: Anal. Found: C, 47.58; H, 5.31; N, 2.47. Calcd for $C_{23}H_{33}Cl_2NO_5Ru$ (575.49): C, 48.00; H, 5.78; N, 2.43. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.31 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.09 (s, 3H, CCH_3), 2.98 (sept, $^3J_{H,H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 3.37 (s, 3H, OCH_3), 3.54, 3.64, 3.67, 3.68 (m, 8H, OCH_2), 3.83 (t, $^3J_{H,H}$ = 4.6 Hz, 2H, COOCH$_2$CH_2), 4.52 (t, $^3J_{H,H}$ = 4.6 Hz, 2H, COOCH_2), 5.23 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CHCCH$_3$), 5.45 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CHCHCCH$_3$), 7.85 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, H^3), 9.22 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.4 (CCH$_3$), 22.4 (C(CH_3)$_2$), 30.8 (C(CH$_3$)$_2$), 59.2 (CH$_3$O), 65.5 (CH$_2$OOC), 69.0, 70.7, 70.8, 70.8, 72.1 (CH$_2$O), 82.5, 83.2 (CH), 97.5, 103.9 (CCH), 123.7 (C^3), 138.8 (C^4), 155.9 (C^2), 163.9 (COO). ESI-HRMS (CH$_3$OH), positive mode: Calcd for $[C_{23}H_{33}ClNO_5{}^{96}Ru]^+$ 534.11178, *m*/*z* 534.11174 [M-Cl]$^+$. IR: ν (cm^{-1}) 3063(w), 2964(w), 2876(w), 1732(s), 1556(w), 1475(w), 1451(w), 1414(m), 1367(w), 1319(w), 1279(s), 1202(w), 1144(m), 1104(s), 1090(s), 1053(m), 1028(m), 947(w), 867(m), 849(m), 802(w), 769(m), 695(m), 659(w), 518(w), 455(w), 371(w), 283(s), 232(s).

*Dichlorido(*η^6-p-*cymene)((3-oxa-5-hydroxy)-pentyl isonicotinate-κN)ruthenium(II)* ***(4)***

Properties: Orange powder; soluble in chloroform, dichloromethane, dimethylformamide, acetone, and acetonitrile, moderately soluble in methanol, ethanol, *iso*propanol, and tetrahydrofuran, insoluble in diethyl ether and toluene.

EA: Anal. Found: C, 45.98; H, 5.16; N, 2.70. Calcd for $C_{20}H_{27}Cl_2NO_4Ru$ (518.21): C, 46.36; H, 5.25; N, 2.70. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.32 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.10 (s, 3H, CCH_3), 2.99 (sept, $^3J_{H,H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 3.64, 3.76, 3.85 (m, 6H, OCH_2), 4.54 (m, 2H, COOCH_2), 5.24 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CHCCH$_3$), 5.46 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, CHCHCCH$_3$), 7.85 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, H^3), 9.24 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.4 (CCH$_3$), 22.4 (C(CH_3)$_2$), 30.8 (C(CH$_3$)$_2$), 61.9, 65.4, 68.9, 72.6 (CH$_2$O), 82.5, 83.2 (CH), 97.6, 104.0 (CCH), 123.7 (C^3), 138.7 (C^4), 156.0 (C^2), 164.0 (COO). ESI-HRMS (CH$_3$OH), positive mode: Calcd for $[C_{20}H_{27}ClNO_4{}^{96}Ru]^+$ 476.06991, *m*/*z* 476.06973 [M-Cl]$^+$. IR: ν (cm^{-1}) 3450(b), 3063(w), 2962(w), 2878(w), 1728(s), 1471(w), 1414(m), 1382(w), 1323(w), 1278(s), 1228(m), 1120(s), 1061(s), 932(w), 866(m), 800(w), 771(s), 698(m), 659(w), 451(w), 400(w), 371(w), 355(w), 286(s), 233(s).

*Dichlorido(*η^6-p-*cymene)[2-{2-(2-methylamino-benzoyloxy)-ethoxy}-ethyl isonicotinate*-κN*]ruthenium(II)* ***(5)***

Properties: Yellow powder; soluble in chloroform, dichloromethane, moderately soluble in methanol, ethanol, *iso*propanol, insoluble in diethyl ether.

EA: Anal. Found: C, 51.83; H, 4.99; N, 4.09. Calcd for $C_{28}H_{34}Cl_2N_2O_5Ru$ (650.56): C, 51.70; H, 5.27; N, 4.31. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.30 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.07 (s, 3H, CCH_3), 2.90 (s, 3H, NCH_3), 2.97 (sept, $^3J_{H,H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 3.86 (m, 4H, OCH_2), 4.43, 4.52 (m, 4H, COOCH_2CH_2), 5.21 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, CHCCH$_3$), 5.44 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, CHCHCCH$_3$), 6.59 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, H^9), 6.69 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, H^7), 7.40 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, H^8), 7.79 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, H^3), 7.90 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H^{10}), 9.17 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, H^2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.3 (CCH$_3$), 22.4 (C(CH_3)$_2$), 29.8 ((b), NCH_3), 30.8 (C(CH$_3$)$_2$), 63.2, 65.3 (CH$_2$OOC), 68.9, 69.4 (CH$_2$OCH_2), 82.5, 83.2 (CH$_{cym}$), 97.5, 103.9 (CCH$_{cym}$), 109.8 ((b),

C[5]), 111.2 ((b), *C*[7]), 114.7 ((b), *C*[9]), 123.6 (*C*[3]), 131.6 (*C*[10]), 135.0 (*C*[8]), 138.6 (*C*[4]), 152.2 ((b), *C*[6]), 155.9 (*C*[2]), 163.9, 168.4 (*C*OO). ESI-HRMS (CH_3OH), positive mode: Calcd for $[C_{28}H_{34}ClN_2O_5{}^{96}Ru]^+$ 609.12267, *m*/*z* 609.12286 $[M\text{-}Cl]^+$. IR: ν (cm^{-1}) 3372(w), 3059(w), 2964(w), 2872(w), 2819(w), 1734(s), 1676(s), 1604(w), 1576(m), 1516(m), 1442(w), 1413(m), 1378(w), 1322(w), 1278(s), 1236(s), 1120(s), 1084(s), 1057(m), 948(w), 858(m), 762(s), 702(s), 662(w), 528(m), 283(s), 234(s). UV-vis (7.01×10^{-5} M, $CHCl_3$, 298 K): λ_{max} 351 nm (ε = 11689 M×cm^{-1}). Fluorescence (7.01×10^{-5} M, $CHCl_3$, 298 K): $\lambda_{max,\ excitation}$ 367 nm, $\lambda_{max,\ emission}$ 418 nm.

Table S-I. Second order perturbation theory parameters and occupancies for the selected interactions within investigated ligands and complexes

	L1	
Donor (i)	Acceptor (j)	E2/ kJ mol-1
π(C−C)	π*(C−C)	76
π(C−C)	π*(C−C)	95
π(C−N)	π*(C−C)	60
π(C−C)	π*(C−N)	109
LP(N)	π*(C−C)	41
LP(O)	π*(C−C)	75
LP(O)	π*(C−O)	135
	1	
π(C−C)	π*(C−C)	46
π(C−C)	π*(C−C)	55
π(C−C)	LP*(Ru)	60
π(C−C)	LP*(Ru)	80
LP(N)	σ*(Ru−Cl)	27
π(C−N)	LP*(Ru)	50
LP(Cl)	LP*(Ru)	34
LP(Cl)	LP*(Ru)	75
LP(Cl)	σ(Ru−Cl)	5
	L4	
LP(O)	σ(C−C)	4.8
	L5	
LP(O)	σ(C−C)	71
LP(O)	σ(C−O)	132
LP(O)	π*(C−O)	105

TABLE S-II. Experimental and theoretical ^{13}C-NMR chemical shifts (in ppm) of **L1** and **1**

Carbon atom	Ligand **L1·HCl**		Complex **1**	
	Experimental	Theoretical	Experimental	Theoretical
C^2	142.7	140.8	155.9	148.8
C^3	126.9	127.5	123.7	118.0
C^4	145.7	145.0	138.8	136.2
CH_3O	58.2	62.8	59.2	58.0
CH_2OOC	65.9	73.9	65.5	67.8
CH_2O	69.6	73.7	69.0	69.7
*C*OO	163.4	158.6	163.9	159.2
C*C*H3			18.4	18.9
C(*C*H3)2			22.4	22.7
C(CH3)2			30.8	35.5
C_{arm}			70.8	83.2
C_{arm}			72.1	83.6
C_{arm}			82.5	84.5
C_{arm}			83.3	86.9
*C*H			97.5	99.9
*C*CH			103.9	111.4
	R	0.99	R	0.98
	MAE [ppm]	3.5	MAE [ppm]	4.6

Table S-III. Experimental and theoretical ^{1}H NMR chemical shifts (in ppm) of **L1·HCl** and **1**

Hydrogen atom	Ligand **L1·HCl**		Complex **1**	
	Experimental	Theoretical	Experimental	Theoretical
OCH_3	3.48	3.28	3.42	3.39
OCH_2	3.92	3.60	3.72	3.55
$COOCH_2$	4.67	4.31	4.52	4.17
C^3–*H*	8.62	8.61	7.86	7.62
C^2–*H*	9.05	8.61	9.23	8.64
$CH(CH_3)_2$			1.31	1.31
CCH_3			2.09	1.67
$CH(CH_3)_2$			2.98	3.00
C_{arm}–H			5.23	4.69
C_{arm}–H			5.45	4.95
	R	0.97	R	0.99
	MAE [ppm]	0.27	MAE [ppm]	0.44

Table S-IV. Experimental and theoretical ^{13}C NMR chemical shifts (in ppm) of **L4**·HCl and **4**

Carbon atom	**L4·HCl**		**4**	
	Experimental	Theoretical	Experimental	Theoretical
C^2	142.7	155.2	156.0	150.9
C^3	126.9	127.5	138.7	119.5
C^4	145.9	141.1	123.7	134.3
CH_2CH_2OH	71.8	67.4	72.6	73.4
CH_2CH_2OOC	68.1	63.8	65.4	66.7
CH_2OOC	66.1	62.9	68.9	68.5
CH_2OH	60.3	59.2	61.9	60.4
COO	163.4	161.7	164.0	161.4
CCH3			18.4	18.8
C(CH3)2			22.4	27.2
C(CH3)2			30.8	35.9
C_{arm}			82.5	84.4
C_{arm}			82.5	85.34
C_{arm}			83.2	85.9
C_{arm}			83.2	87.0
CH			97.6	100.6
CCH			104.0	114.1
	R	0.98	R	0.98
	MAE [ppm]	4.1	MAE [ppm]	4.5

Table S-V. Experimental and theoretical ^1H NMR chemical shifts (in ppm) of **L4**·HCl and **4**

Hydrogen atom	**L4·HCl**		**4**	
	Experimental	Theoretical	Experimental	Theoretical
OCH_2	3.77	3.71	3.85	3.96
$HOCH_2CH_2$	3.77	3.55	3.64	3.93
$COOCH_2CH2$	4.00	3.74	3.76	3.87
$COOCH_2$	4.69	44.26	4.54	4.45
C^3-*H*	8.60	8.64	9.24	9.13
C^2-*H*	9.04	9.45	7.85	8.09
$CH(CH_3)_2$			1.32	1.38
CCH_3			2.10	1.81
$CH(CH_3)_2$			2.99	3.21
C_{arm}-H			5.24	5.01
C_{arm}-H			5.46	5.21
	R	0.99	R	0.99
	MAE [ppm]	0.24	MAE [ppm]	0.18

Table S-VI. Experimental and theoretical ^{13}C NMR chemical shifts (in ppm) of **L5** and **5**

Carbon atom	**L5**		**5**	
	Experimental	Theoretical	Experimental	Theoretical
C^2	149.8	148.5	155.9	151.1
C^3	123.4	123.4	123.6	119.7
C^4	138.1	136.2	138.6	134.4
C^5	109.7	127.6	109.8	128.7
C^6	152.2	150.9	152.2	126.0
C^7	110.9	110.3	111.2	125.1
C^8	135.0	135.7	135.0	127.7
C^9	114.5	130.8	114.7	123.9
C^{10}	131.7	129.6	131.6	122.7
N*C*H3	29.7	29.1	29.8	29.7
CH_2CH_2OOC	69.4	67.2	69.4	68.6
CH_2OOC	65.0	64.0	65.3	67.3
CH_2CH_2OOC	69.0	62.8	68.9	72.3
CH_2OOC	63.2	61.1	63.2	69.3
*C*OO	168.5	164.2	168.4	169.4
*C*OO	164.9	156.2	163.9	161.7
C*C*H_3			18.3	19.1
C(*C*H_3)$_2$			22.4	22.8
C(CH_3)$_2$			30.8	36.3
C_{arm}			82.5	85.2
C_{arm}			82.5	85.2
C_{arm}			83.2	85.8
C_{arm}			83.2	88.3
*C*H			97.5	114.3
*C*CH			103.9	102.5
	R	0.96	R	0.95
	MAE [ppm]	4.2	MAE [ppm]	6.0

Table S-VII. Experimental and theoretical ^{1}H NMR chemical shifts (in ppm) of **L5** and **5**

Hydrogen atom	**L5**		**5**	
	Experimental	Theoretical	Experimental	Theoretical
NCH_3	2.89	2.53	2.90	2.69
OCH_2	3.87	3.88	3.86	2.85
$COOCH_2CH_2$	4.43	3.44	4.43	3.27
$COOCH_2CH_2$	4.53	3.51	4.52	3.40
C^3-*H*	7.84	8.23	7.79	7.07
C^2-*H*	8.71	9.05	9.17	8.16
C^7-*H*	6.65	6.81	6.69	6.74
C^8-*H*	7.37	7.68	7.40	6.89
C^9-*H*	6.53	6.81	6.59	6.74
C^{10}-*H*	7.88	7.73	7.90	6.74
$CH(CH_3)_2$			1.30	0.30
CCH_3			2.07	0.79
$CH(CH_3)_2$			2.97	2.09
	R	0.95	R	0.94
	MAE [ppm]	0.40	MAE [ppm]	0.79