Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Two is Better than One: Difunctional High-affinity PSMA Probes Based on a [CpM(CO)3] (M = Re/99mTc) Scaffold

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Synthetic Procedures and Analytical Data

[^{99m}Tc(OH$_2$)$_3$(CO)$_3$]$^+$: A Biotage microwave vial (2–5 mL) was charged with sodium boranocarbonate (4 mg, 38.5 µmol), sodium tartrate dihydrate (7 mg, 30.4 µmol) and sodium tetraborate decahydrate (7 mg, 18.5 µmol). The vial was sealed and flushed with N$_2$ for 5 min before adding [^{99m}TcO$_4$]$^-$ eluate (1–2 mL) from a commercial generator. The solution was heated by microwave to 110 °C for 7 min. To normalize the overpressure, evolving gases (careful, toxic CO gas is released, handle in a ventilated fume hood) were released with a disposable syringe needle. Excess sodium boranocarbonate was quenched by dropwise addition of 1 m HCl to pH 2 and the solution was subsequently basified by addition of 1 m NaOH to pH 8.

General procedure for the labelling of Cp-Ligands 4 and 5.

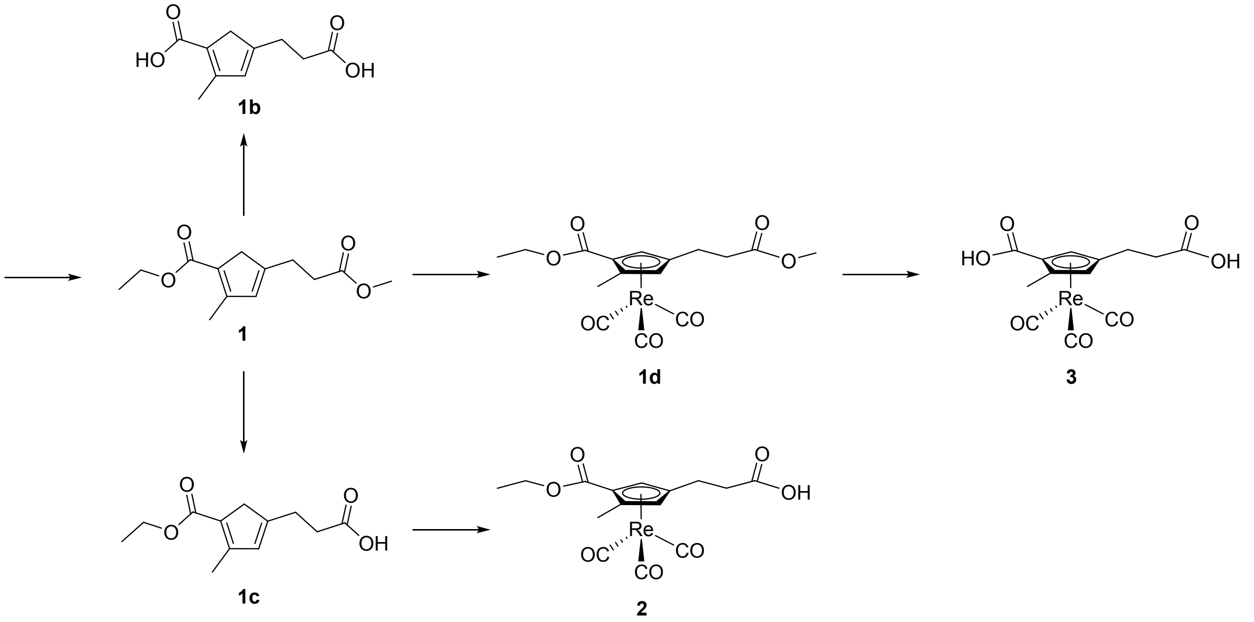
Generally, 0.5 ml of a 5 mM stock solution of the respective ligand in MeOH was added to a Biotage microwave vial (2 – 5 ml). The vial was sealed, and the solvent was removed by passing a stream of N$_2$ through the vial *via* two syringe needles for 30 min.

[^{99m}Tc(OH$_2$)$_3$(CO)$_3$]$^+$ (0.5 ml, typical activity: 50-200 MBq, pH = 13, adjusted with 1 M NaOH) was added to the dried ligand and the solution was heated by microwave to 140 °C for 10 (**5**) or 15 (**4**) min. In order to normalize the overpressure, evolving gases were released with a 1 ml disposable syringe-needle. Reactions were not optimized for yields.

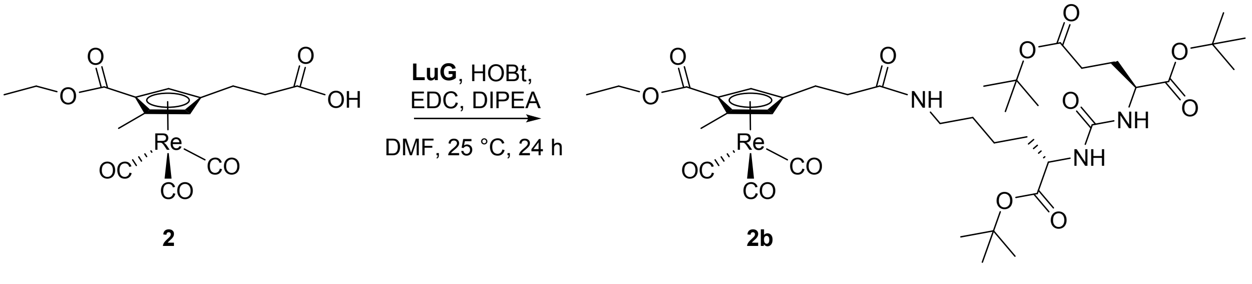
Tc2. Radiochemical Yield (crude reaction, HPLC): 74%

Tc1. Radiochemical Yield (crude reaction, HPLC): 61%

Compounds **1**, **1b**, **1c**, **1d**, **2** and **3** were prepared as reported previously by our group.[1]

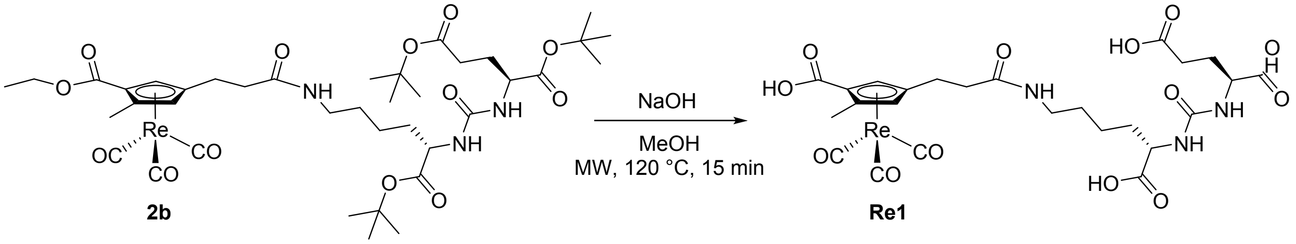


Scheme S1. Overview of the synthetic routes to compounds **1**, **2** and **3**. Synthetic procedures reported elsewhere.[1]



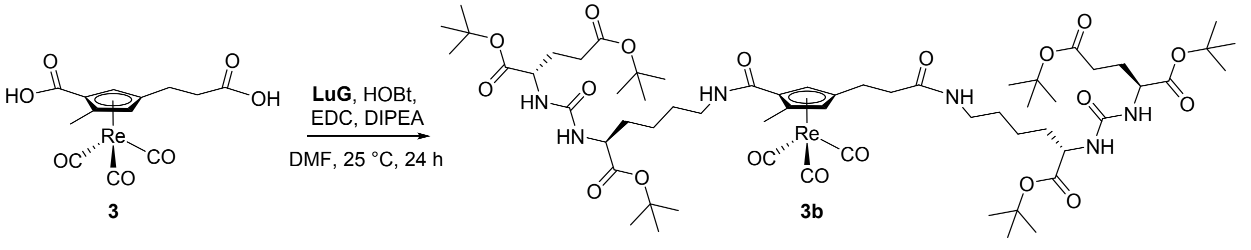
2b. 2 (136 mg, 0.275 mmol) was dissolved in DMF (5 ml). **LuG** (148 mg, 0.3 mmol) and HOBt (41 mg, 0.3 mmol) were added under stirring. After 5 min, EDC (58 mg, 0.3 mmol) and DIPEA (0.105 ml, 0.61 mmol) were added and the solution was stirred for 24 h at 25 °C. The solvent was removed *in vacuo* and the crude was purified by preparative HPLC (Method A) and **2b** was obtained as a pale-yellow oil (79 mg, 0.082 mmol, 30 % overall yield from **1**).

Data for 2b. UPLC (gradient U1): RT = 3.81 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.28 – 1.34 (m, 5H), 1.42 – 1.43 (m, 9H), 1.43 – 1.44 (m, 9H), 1.46 (m, 9H), 1.46 – 1.59 (m, 3H), 1.72 – 1.80 (m, 1H), 1.81 – 1.88 (m, 1H), 2.03 – 2.11 (m, 1H). 2.29 – 2.35 (m, 2H), 2.36 - 2.41 (m, 2H), 2.47 – 2.48 (m, 3H), 2.63 – 2.70 (m, 1H), 2.78 – 2.89 (m, 1H), 3.07 – 3.39 (m, 2H), 4.17 – 4.34 (m, 4H), 5.26 (d, J^3 = 2.1 Hz, 1H), 5.38 (t, J^3 = 7.9 Hz, 1H), 5.53 (t, J^3 = 7.4 Hz, 1H), 5.78 (d, J^3 = 2.1 Hz, 0.5H), 5.84 (d, J^3 = 2.1 Hz, 0.5H), 6.53 – 6.58 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 13.91, 13.96, 14.24, 14.28, 22.61, 22.82, 22.87, 23.79, 23.87, 27.98, 28.11, 28.14, 28.15, 28.18, 28.68, 28.82, 29.84, 31.74, 31.82, 32.48, 32.59, 37.31, 37.67, 39.10, 39.22, 53.31, 53.34, 53.39, 53.54, 61.03, 61.23, 80.81, 80.83, 81.82, 81.87, 82.50, 82.58, 84.39, 84.46, 85.81, 85.97, 86.04, 86.09, 108.19, 108.26, 110.46, 110.64, 157.37, 157.42, 165.06, 165.40, 171.41, 171.43, 172.41, 172.43, 172.47, 173.27, 173.39, 193.69. HR-ESI mass spectrum (MeOH): found 964.36010; calcd. for [$C_{39}H_{58}N_3O_{13}Re+H^+$] 964.35999; found 986.34108; calcd. for [$C_{39}H_{58}N_3O_{13}Re+Na^+$] 986.34194.



Re1. 2b (16 mg, 0.017 mmol) was dissolved in MeOH (2 ml) in an Anton Paar microwave vial (10 ml) and 1 M NaOH was added. The solution was heated by microwave to 120 °C for 15 min. The crude was diluted with H_2O (5 ml) and neutralized to pH = 3 by dropwise addition of 1 M HCl. The solvent was evaporated *in vacuo* and the crude was purified by preparative HPLC, yielding **Re1** as a yellowish oil (10 mg, 0.013 mmol, 76 %).

Data for Re1. UPLC (gradient U1): RT = 2.35 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38 – 1.57 (m, 4H), 1.62 – 1.74 (m, 1H), 1.78 – 1.98 (m, 2H), 2.10 – 2.20 (m, 1H), 2.36 – 2.46 (m, 4H), 2.49 (s, 3H), 2.59 – 2.81 (m, 2H), 3.16 – 3.21 (m, 2H), 4.23 – 4.34 (m, 2H), 5.49 (d, J^3 = 1.96 Hz, 1H), 5.90 (d, J^3 = 1.96 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 14.02, 23.95, 25.10, 28.85, 28.95, 29.89, 29.95, 31.09, 31.11, 33.05, 33.18, 38.57, 40.15, 40.19, 53.56, 53.58, 54.04, 86.11, 87.44, 87.94, 108.95, 112.15, 159.98, 160.12, 168.14, 174.04, 175.90, 176.02, 176.48, 176.56, 176.59, 195.02. HR-ESI mass spectrum (MeOH): found 766.12671; calcd. for [$C_{25}H_{29}N_3O_{13}Re+H^+$] 766.12634.

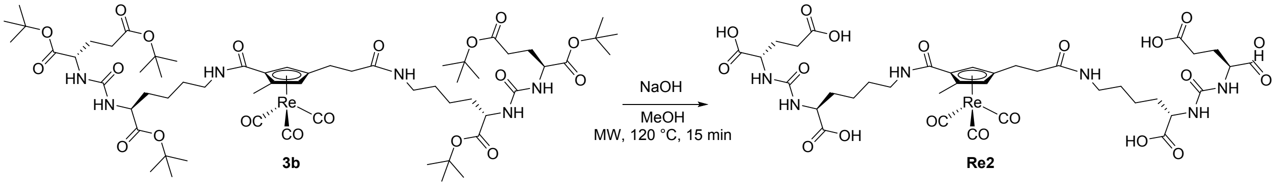


3b. 3 (78 mg, 0.168 mmol) was dissolved in DMF (5 ml). **LuG** (164 mg, 0.34 mmol) and HOBt (50 mg, 0.37 mmol) were added under stirring. After 5 min, EDC (71 mg, 0.37 mmol) and DIPEA (0.129 ml, 0.74 mmol) were added and the solution was stirred for 24 h at 25 °C. The solvent was removed *in vacuo* and the crude was purified by preparative HPLC (Method A) and the two diastereoisomers of **3b** (**3b'** and **3b''**) were obtained as a pale-yellow oil (**3b'**, 38.3 mg, 0.027 mmol; **3b''**, 35.9 mg, 0.026 mmol; yield: 31 %).

Data for 3b'. UPLC (gradient U1): RT = 4.11 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.35 – 1.50 (m, 58H), 1.50 – 1.64 (m, 5H), 1.72 – 1.96 (m, 5H), 2.01 – 2.14 (m, 2H), 2.25 – 2.43 (m, 6H), 2.49 (s, 3H), 2.57 – 2.68 (m, 1H), 2.83 – 2.93 (m, 1H), 3.09 – 3.20 (m, 1H), 3.27 – 3.38 (m, 3H), 4.23 – 4.38 (m, 4H), 5.19 (s, 1H), 5.33 – 5.39 (m, 1H), 5.45 – 5.51 (m, 1H), 5.54 – 5.60 (m, 1H), 5.66 – 5.71 (m, 1H), 5.89 (s, 1H), 6.59 – 6.63 (m, 1H), 6.68 – 6.74 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 13.93, 22.16, 22.58, 23.92, 28.16, 28.18, 28.22, 28.45, 28.80, 31.69, 31.82, 32.66, 32.78, 37.50, 38.98, 39.42, 53.20, 53.25, 53.35, 53.48, 80.84, 80.88, 81.89, 82.01, 82.42, 82.45, 82.95, 85.19, 90.93, 107.85, 109.04, 157.45, 157.71, 164.47, 171.62, 172.53, 172.59, 172.63, 172.65, 172.87, 173.21, 194.31, 194.39. HR-ESI mass spectrum (MeOH): found 1405.64555; calcd. for [$C_{61}H_{97}N_6O_{19}Re+H^+$] 1405.64388; found 1427.62612; calcd. for [$C_{61}H_{97}N_6O_{19}Re+Na^+$] 1427.62582.

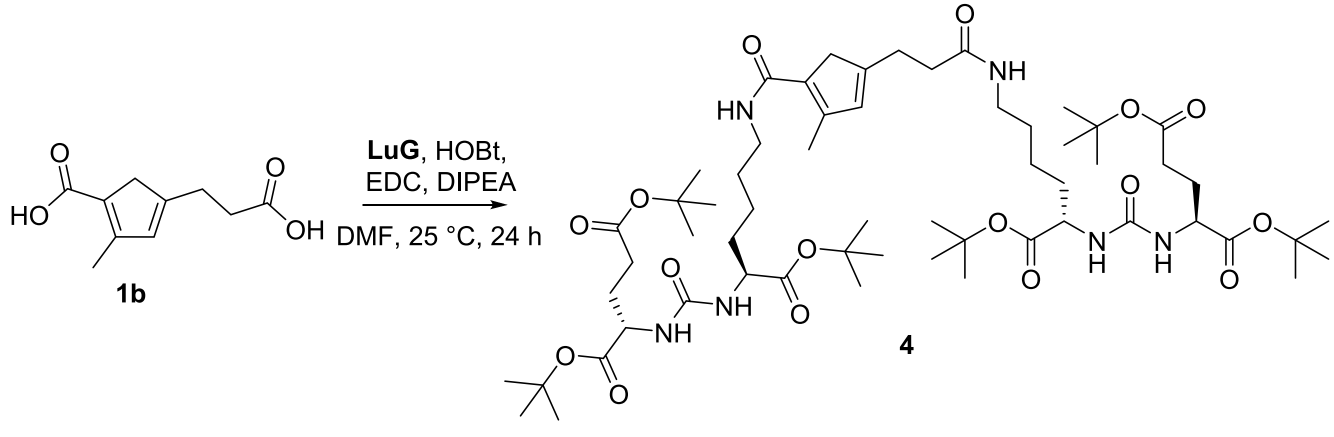
Data for 3b''. UPLC (gradient U1): RT = 4.13 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.35 – 1.50 (m, 58H), 1.50 – 1.64 (m, 5H), 1.72 – 1.96 (m, 5H), 2.01 – 2.14 (m, 2H), 2.25

– 2.43 (m, 6H), 2.49 (s, 3H), 2.64 – 2.76 (m, 2H), 3.09 – 3.20 (m, 1H), 3.27 – 3.38 (m, 3H), 4.23 – 4.38 (m, 4H), 5.16 (m, 1H), 5.58 – 5.62 (m, 2H), 5.73 (m, 1H), 5.89 – 5.91 (m, 2H), 6.77 – 6.82 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 13.41, 13.73, 18.03, 22.13, 22.30, 22.90, 23.55, 27.41, 27.61, 27.63, 27.65, 27.70, 28.11, 28.97, 29.04, 29.24, 29.27, 29.32, 29.35, 31.19, 31.26, 31.54, 32.19, 32.51, 33.06, 37.19, 38.73, 38.82, 52.60, 52.73, 52.94, 80.24, 80.34, 81.30, 81.64, 81.87, 81.98, 82.97, 84.32, 90.32, 106.62, 108.70, 157.18, 163.90, 171.14, 171.87, 171.97, 172.21, 172.33, 172.37, 172.88, 193.77. HR-ESI mass spectrum (MeOH): found 1405.64572; calcd. for [$C_{61}H_{97}N_6O_{19}Re+H^+$] 1405.64388.



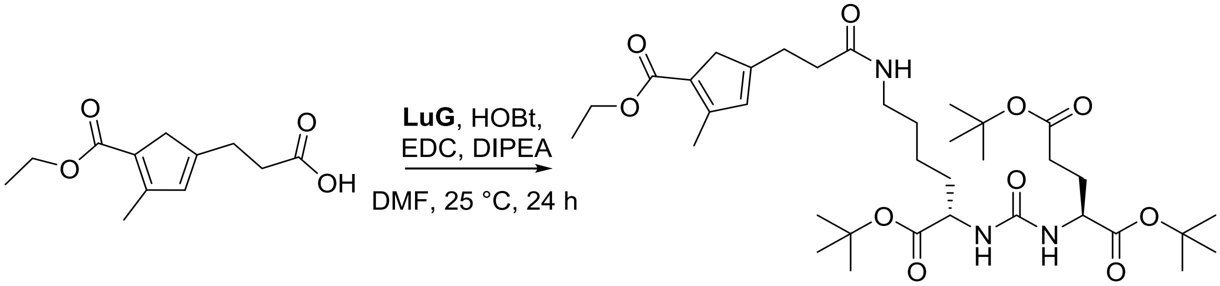
Re2. A 1:1 mixture of **3b'** and **3b''** (60 mg, 0.043 mmol) was dissolved in MeOH (2 ml) and 1 M NaOH (1 ml) in an Anton Paar microwave vial (10 ml) and was heated by microwave to 120 °C for 15 min. The solution was adjusted to pH = 3 by addition of 1 M HCl. The solvent was evaporated *in vacuo* and the crude was purified by preparative HPLC (Method A), yielding **Re2** as a yellowish oil (25.7 mg, 0.024 mmol, 56 %).

Data for Re2. UPLC (gradient U1): RT = 2.16 min. ^{1}H NMR (500 MHz, CD_3OD): δ (ppm) 1.39 – 1.74 (m, 10H), 1.79 – 1.96 (m, 4H), 2.10 - 2.19 (m, 2H), 2.36 – 2.46 (m, 6H), 2.50 (s, 3H), 2.62 – 2.74 (m, 2H), 3.15 – 3.27 (m, 4H), 4.23 – 4.28 (m, 2H), 4.30 – 4.35 (m, 2H), 5.43 (m, 1H), 5.99 (m, 1H). HR-ESI mass spectrum (MeOH): found 1067.25684; calcd. for [$C_{37}H_{48}N_6O_{19}Re-H^+$] 1067.25372.



4. 1b (41 mg, 0.210 mmol) was dissolved in DMF (5 ml). **LuG** (225 mg, 0.462 mmol) and HOBt (62 mg, 0.462 mmol) were added under stirring. After 5 min, EDC (89 mg, 0.462 mmol) and DIPEA (0.161 ml, 0.924 mmol) were added and the solution was stirred for 24 h at 25 °C. The solvent was removed *in vacuo* and the crude was purified by preparative HPLC (Method A) and **4** was obtained as a pale-yellow oil (36 mg, 0.032 mmol, 15 % overall yield from **1**).

Data for 4. UPLC (gradient U1): RT = 3.78 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.18 – 1.29 (m, 4H), 1.31 – 1.38 (m, 54H), 1.38 - 1.57 (m, 6H), 1.60 – 1.80 (m, 4H), 1.92 – 2.03 (m, 2H), 2.12 (s, 3H), 2.17 – 2.28 (m, 4H), 2.28 – 2.40 (m, 2H), 2.51 – 2.60 (m, 1H), 2.67 – 2.75 (m, 1H), 2.83 – 2.96 (m, 2H), 3.03 – 3.11 (m, 1H), 3.19 – 3.32 (m, 3H), 4.14 – 4.27 (m, 4H), 5.30 – 5.36 (m, 1H), 5.36 - 5.40 (m, 1H), 5.49 – 5.56 (m, 1H), 5.86 – 5.93 (m, 1H), 5.95 (s, 1H), 5.97 – 6.00 (m, 1H), 6.50 – 6.57 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 15.73, 22.41, 23.21, 27.50, 28.38, 28.60, 28.62, 28.67, 28.68, 29.01, 29.80, 30.29, 32.21, 32.37, 32.89, 33.11, 36.57, 39.17, 39.60, 44.15, 53.55, 53.62, 53.81, 54.02, 81.14, 81.16, 82.05, 82.20, 82.53, 82.63, 131.41, 133.78, 149.43, 151.01, 157.76, 158.13, 166.96, 172.89, 172.92, 173.01, 173.04, 173.12, 173.15, 173.96. HR-ESI mass spectrum (MeOH): found 1135.71147; calcd. for [$C_{58}H_{99}N_6O_{16}Re+H^+$] 1135.71121; found 1157.69285; calcd. for [$C_{58}H_{99}N_6O_{16}Re+Na^+$] 1157.69315.



5. 1c (57 mg, 0.253 mmol) was dissolved in DMF (5 ml). **LuG** (136 mg, 0.278 mmol) and HOBt (38 mg, 0.278 mmol) were added under stirring. After 5 min, EDC (53 mg, 0.278 mmol) and DIPEA (0.097 ml, 0.557 mmol) were added and the solution was stirred for 24 h at 23 °C. The solvent was removed *in vacuo* and the crude was purified by preparative HPLC (Method A) and **5** was obtained as a pale-yellow oil (30 mg, 0.043 mmol, 17 % overall yield from **1**).

Data for 5. UPLC (gradient U1): RT = 3.48 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.27 – 1.40 (m, 3H), 1.38 – 1.53 (m, 31H), 1.74 – 1.92 (m, 3 H), 2.03 – 2.11 (m, 1H), 2.27 (s, 3H), 2.32 – 2.38 (m, 2H), 2.40 – 2.53 (m, 2H), 2.65 - 2.72 (m, 1H), 2.81 – 2.88 (m, 1H), 2.97 – 3.05 (m, 1H), 3.16 – 3.25 (m, 1H), 3.36 – 3.45 (m, 2H), 4.19 – 4.36 (m, 4H), 5.30 – 5.36 (m, 1H), 5.58 – 5.64 (m, 1H), 6.12 (s, 1H), 6.39 – 6.44 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 14.53, 15.70, 22.28, 27.02, 27.92, 28.08, 28.11, 28.16, 28.66, 31.82, 32.45, 35.63, 38.88, 44.17, 50.77, 53.21, 53.36, 59.83, 80.78, 81.72, 82.29, 127.05, 133.14, 154.08, 155.91, 157.52, 165.84, 172.40, 172.52, 172.56, 173.35. HR-ESI mass spectrum (MeOH): found 694.42714; calcd. for $[C_{36}H_{59}N_3O_{10}+H^+]$ 694.42732.

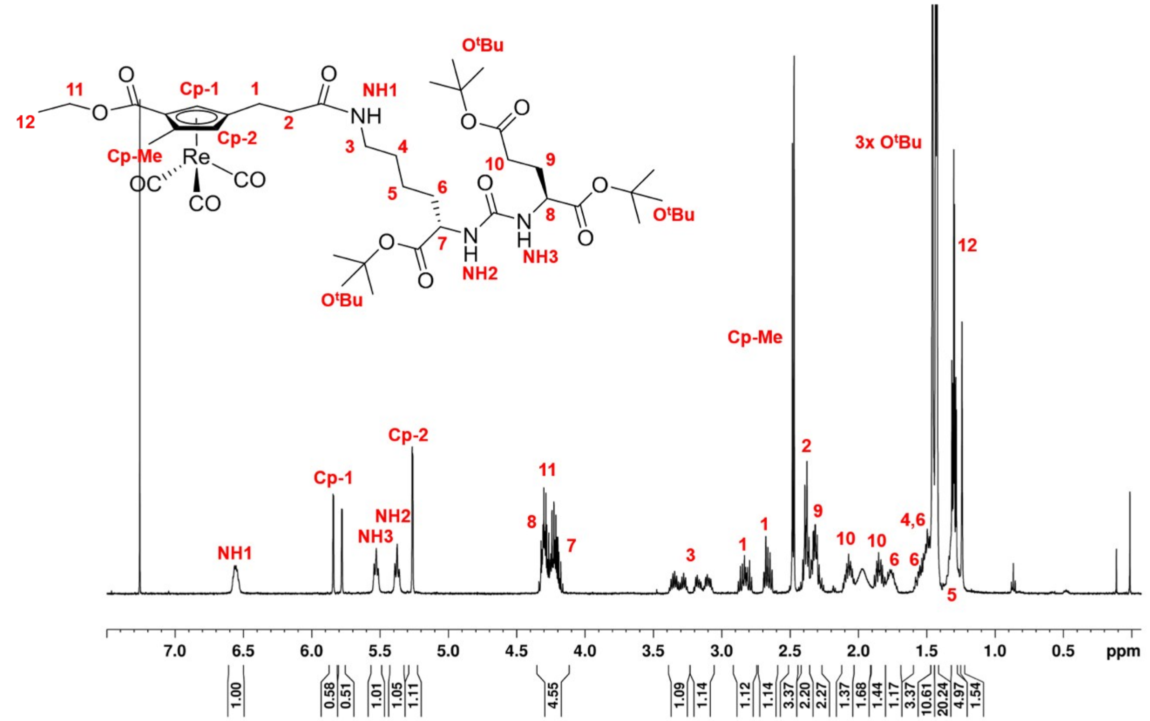


Figure S1. ^{1}H NMR of **2b** in $CDCl_3$ with assigned proton signals.

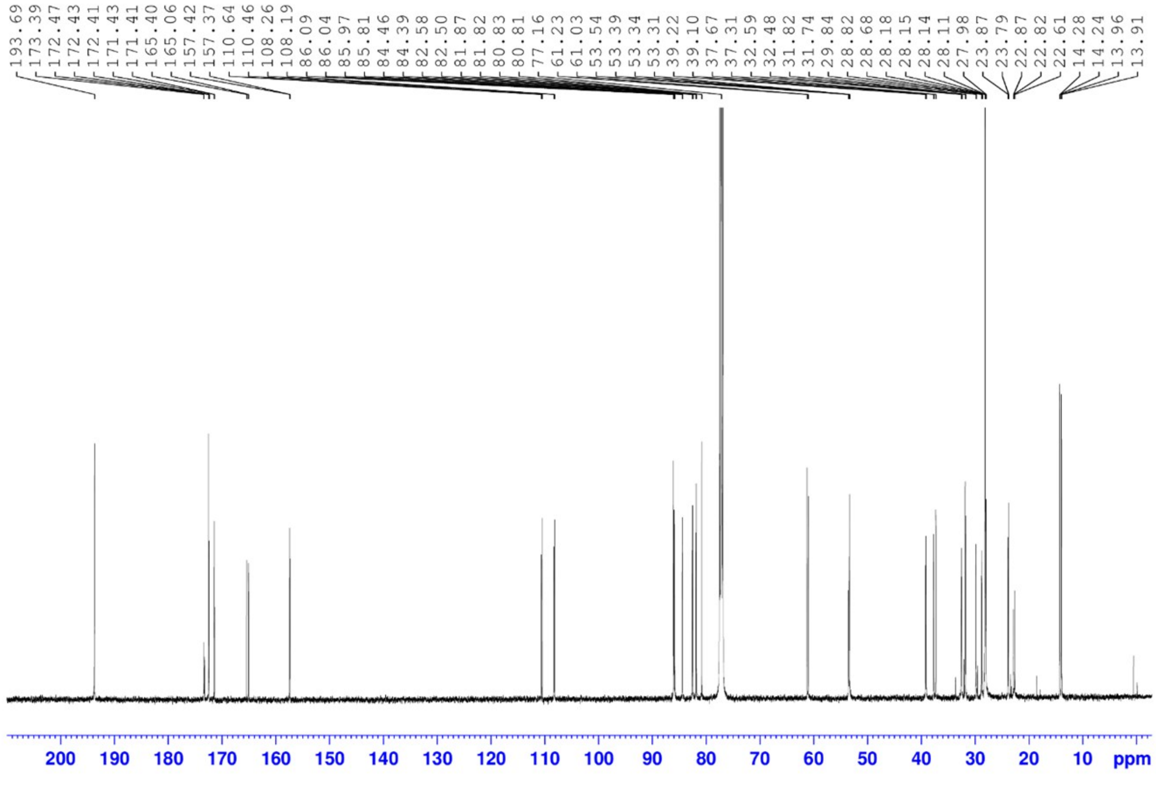


Figure S2. ^{13}C NMR of **2b** in $CDCl_3$.

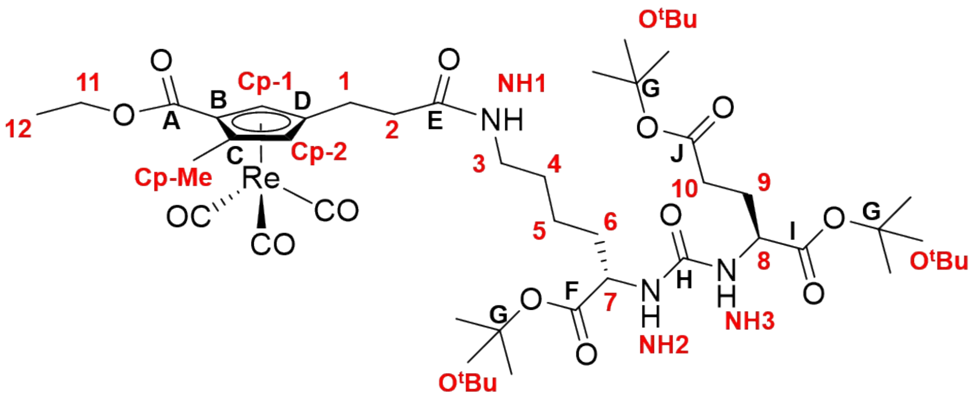


Figure S3. Carbon label reference for carbon atoms on **2b**.

Number	δ	Carbon Ref.
1	13.91	Cp-Me
2	13.96	Cp-Me
3	14.24	12
4	14.28	12
5	22.61	5
6	22.82	-
7	22.87	5
8	23.79	1
9	23.87	1
10	27.98	10*
11	28.11	tertbutyl-CH_3**
12	28.14	tertbutyl-CH_3**
13	28.15	tertbutyl-CH_3**
14	28.18	tertbutyl-CH_3**
15	28.68	4
16	28.82	4
17	29.84	-
18	31.74	9
19	31.82	9
20	32.48	6
21	32.59	6
22	37.31	2
23	37.67	2
24	39.1	3
25	39.22	3
26	53.31	7 or 8
27	53.34	7 or 8
28	53.39	7 or 8

29	53.54	7 or 8
30	61.03	11
31	61.23	11
32	80.81	tertbutyl-C_q (G)
33	80.83	tertbutyl-C_q (G)
34	81.82	tertbutyl-C_q (G)
35	81.87	tertbutyl-C_q (G)
36	82.5	tertbutyl-C_q (G)
37	82.58	tertbutyl-C_q (G)
38	84.39	B
39	84.46	B
40	85.81	Cp-1 or Cp-2
41	85.97	Cp-1 or Cp-2
42	86.04	Cp-1 or Cp-2
43	86.09	Cp-1 or Cp-2
44	108.19	C or D
45	108.26	C or D
46	110.46	C or D
47	110.64	C or D
48	157.37	H
49	157.42	H
50	165.06	A
51	165.4	A
52	171.41	E
53	171.43	F
54	172.41	F
55	172.43	J
56	172.47	J
57	173.27	I
58	173.39	I
59	193.69	CO

Table S1. Carbon signal assignment for **2b** (*all ^{13}C occur distinctly double due to the presence of two diastereoisomers, except 10; **Overlap of signals makes it impossible to distinguish the expected 6 peaks)

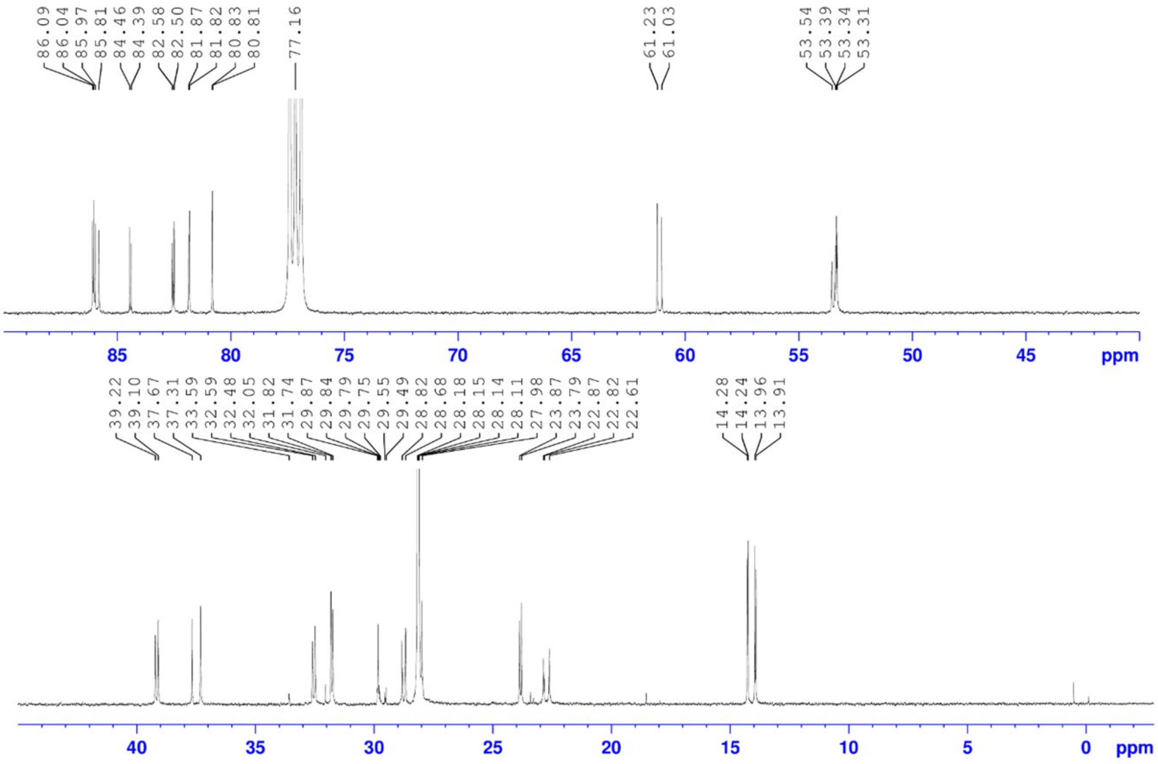


Figure S4, ^{13}C NMR (magnified) of **2b** in $CDCl_3$.

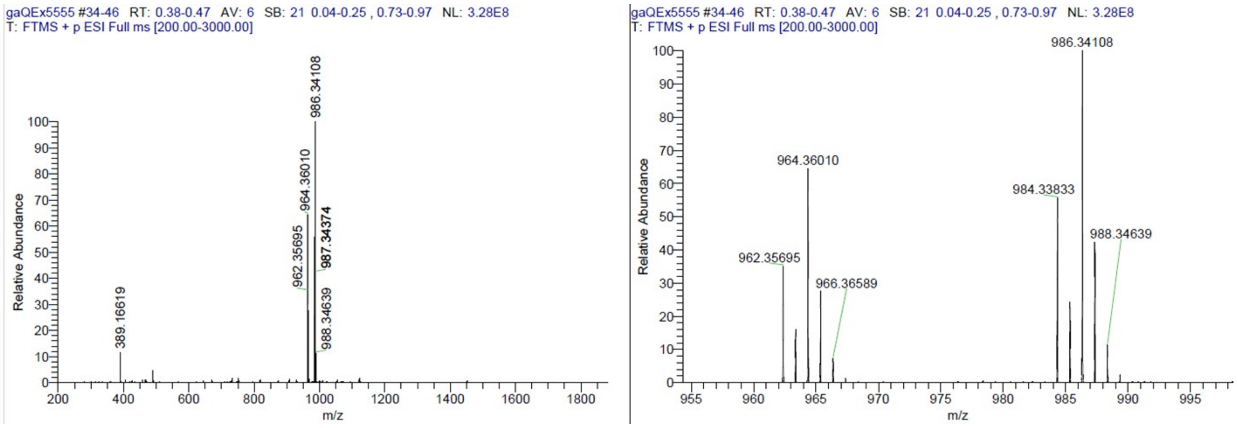


Figure S5. HR-ESI MS of **2b** (MeOH).

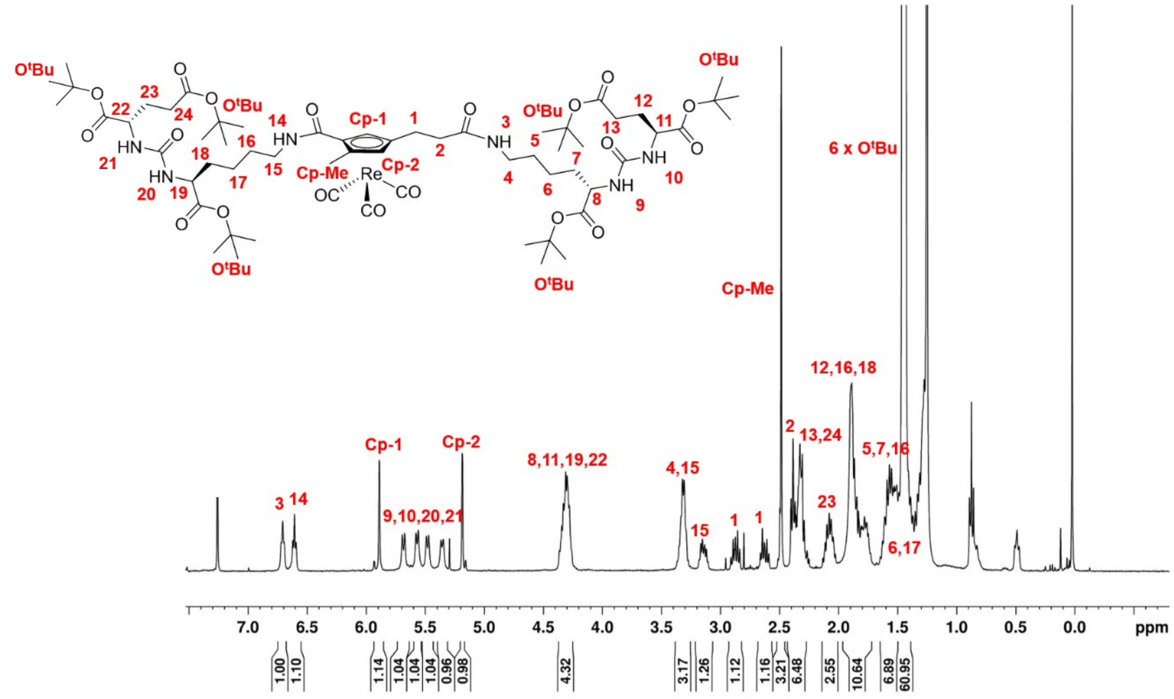


Figure S6. ^{1}H NMR of **3b'** in $CDCl_3$ with assigned proton signals.

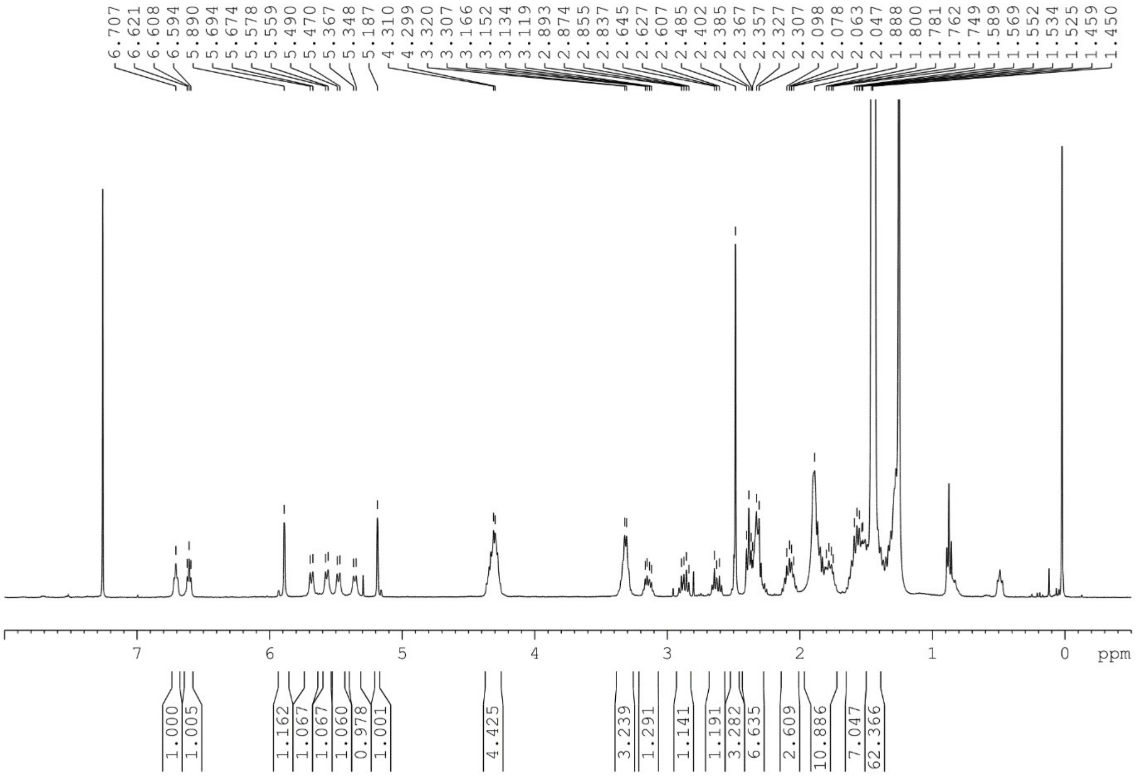


Figure S7. ^{1}H NMR of **3b'** in $CDCl_3$.

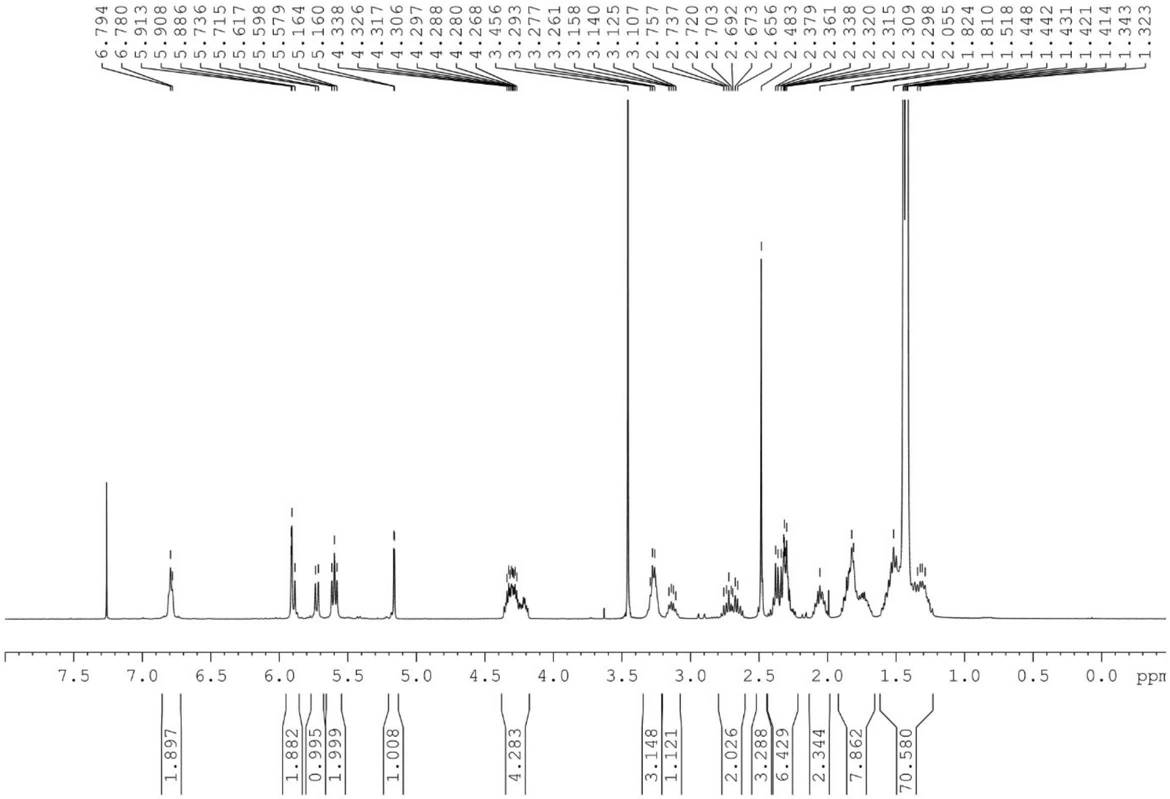


Figure S8. ^{1}H NMR of **3b''** in $CDCl_3$.

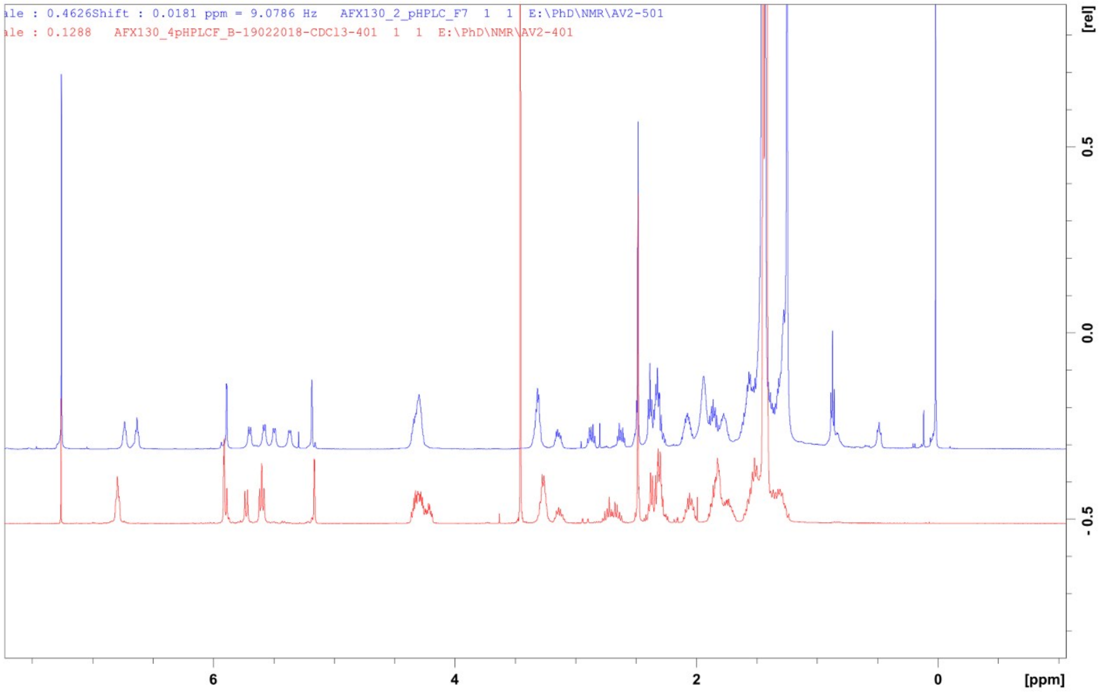


Figure S9. ^{1}H NMR of **3b'** and **3b''** overlaid ($CDCl_3$).

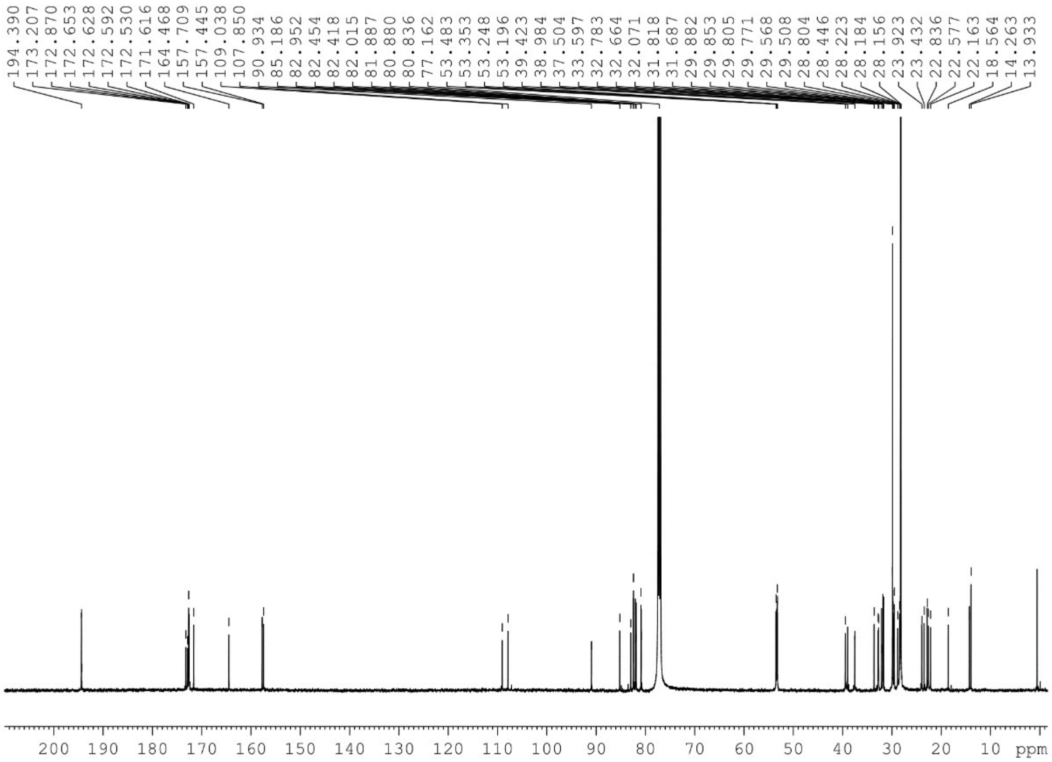


Figure S10. ^{13}C NMR of **3b’** in $CDCl_3$.

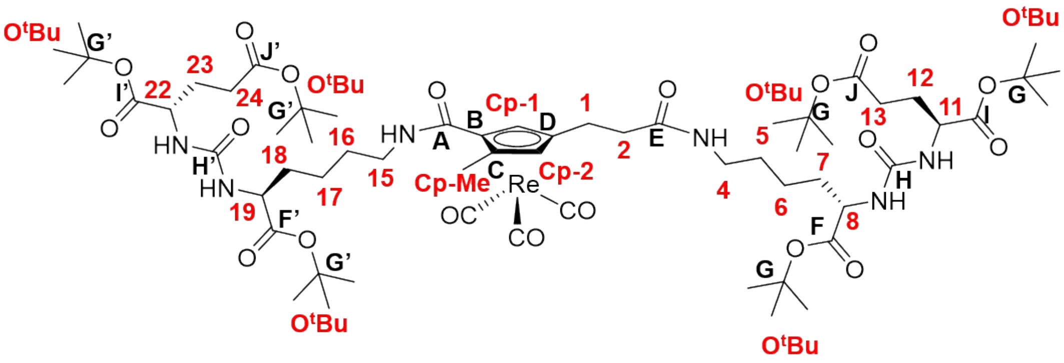


Figure S11. Carbon label reference for carbon atoms on **3b**.

Number	δ	Carbon Ref.
1	13.93	Cp-Me
2	22.16	5,7,16 or 18
3	22.58	5,7,16 or 18
4	22.84	5,7,16 or 18
5	23.43	5,7,16 or 18
6	23.92	1
7	28.16	tertbutyl-CH_3
8	28.18	tertbutyl-CH_3

9	28.22	tertbutyl-CH$_3$
10	28.45	12,13,23 or 24
11	28.8	12,13,23 or 24
12	31.69	12,13,23 or 24
13	31.82	12,13,23 or 24
14	32.66	6 or 17
15	32.78	6 or 17
16	37.5	2
17	38.98	4 or 15
18	39.42	4 or 15
19	53.2	8,11,19 or 22
20	53.25	8,11,19 or 22
21	53.35	8,11,19 or 22
22	53.48	8,11,19 or 22
23	80.84	tertbutyl-C$_q$ (G)
24	80.88	tertbutyl-C$_q$ (G)
25	81.89	tertbutyl-C$_q$ (G)
26	82.01	tertbutyl-C$_q$ (G)
27	82.42	tertbutyl-C$_q$ (G)
28	82.45	tertbutyl-C$_q$ (G)
29	82.95	Cp-1
30	85.19	Cp-2
31	90.93	B
32	107.85	C or D
33	109.04	C or D
34	157.45	H or H’
35	157.71	H or H’
36	164.47	A
37	171.62	E
38	172.53	F,F’,I,I’,J or J’
39	172.59	F,F’,I,I’,J or J’
40	172.63	F,F’,I,I’,J or J’
41	172.65	F,F’,I,I’,J or J’
42	172.87	F,F’,I,I’,J or J’
43	173.21	F,F’,I,I’,J or J’
44	194.31	CO
45	194.39	CO

Table S2. Carbon signal assignment for **3b’** (*Overlap of signals makes it impossible to distinguish the expected 6 peaks).

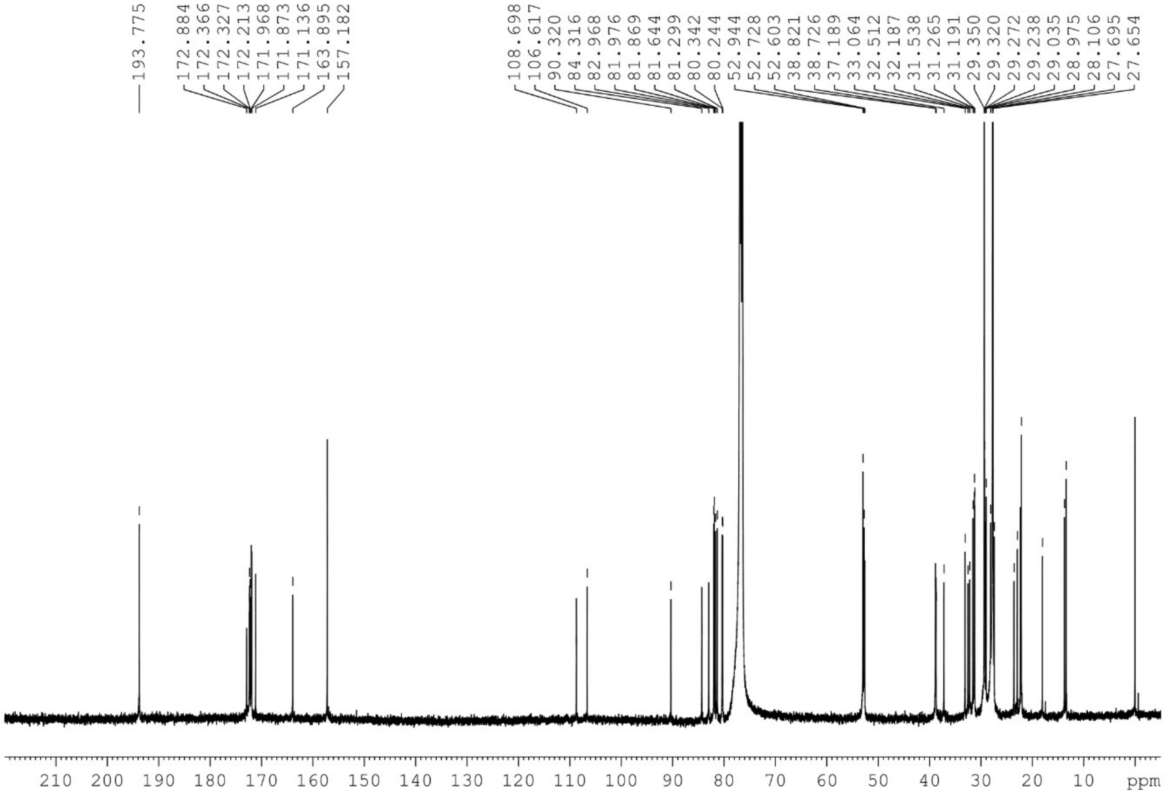


Figure S12. ^{13}C NMR of **3b''** in $CDCl_3$.

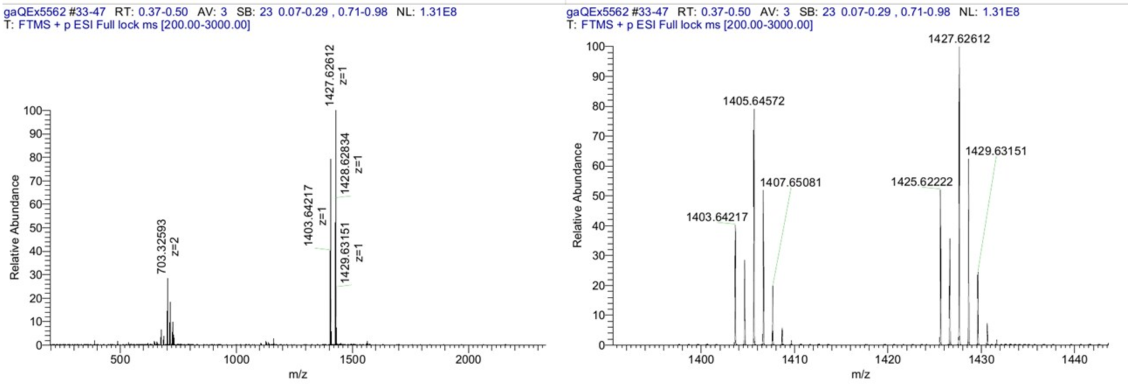


Figure S13. HR-ESI MS of **3b** (MeOH).

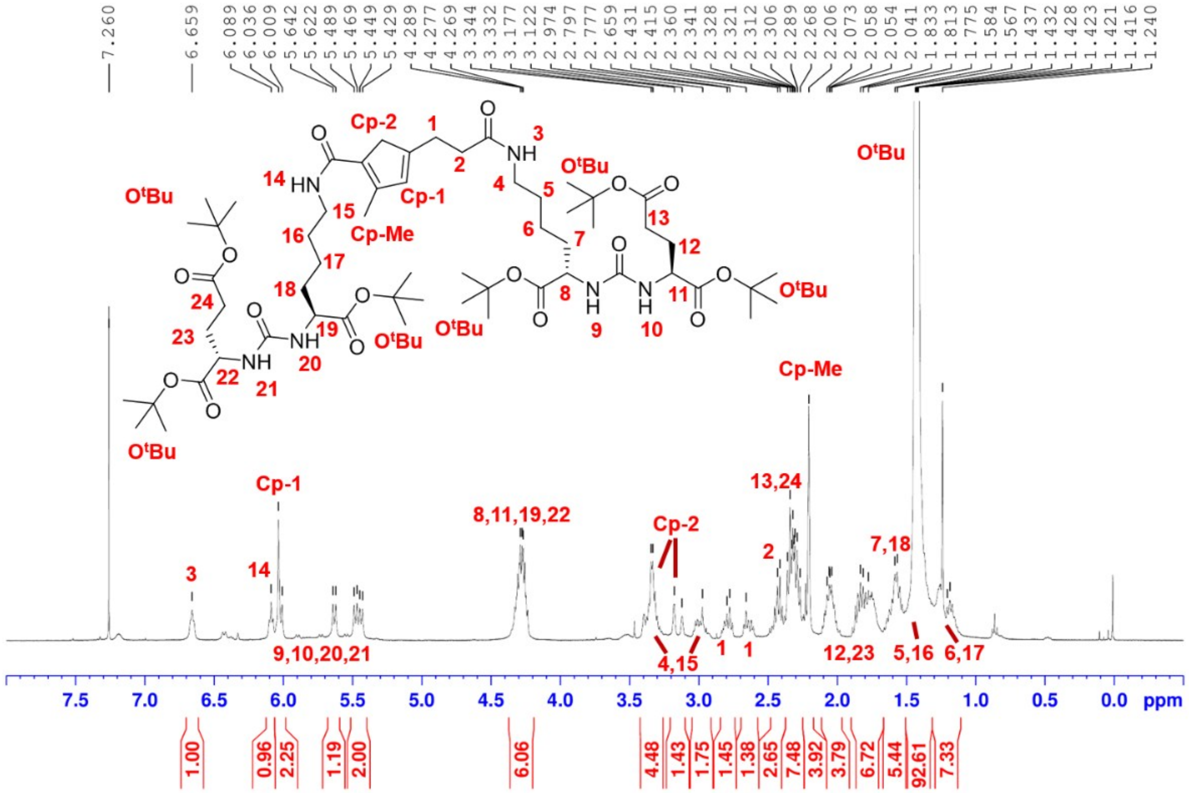


Figure S14. ^{1}H NMR of **4** in $CDCl_3$ with assigned proton signals.

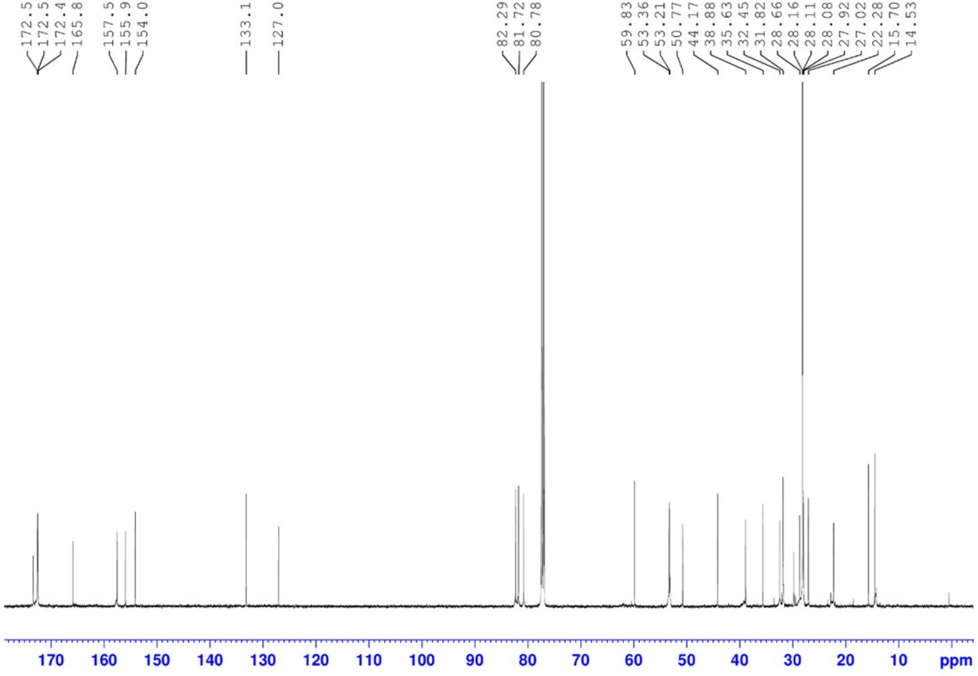


Figure S15. ^{13}C NMR of **4** in $CDCl_3$.

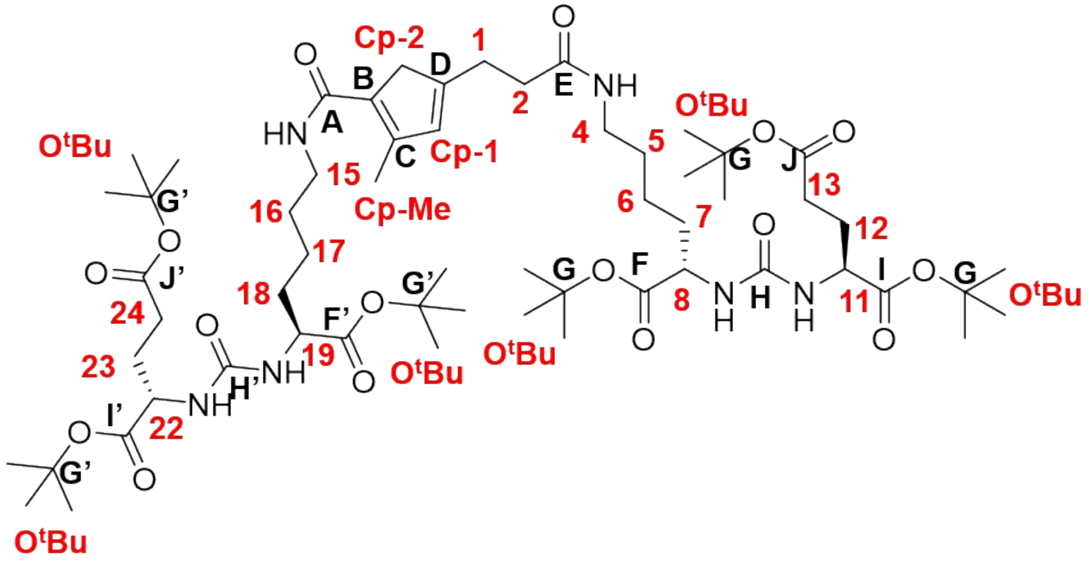


Figure S16. Carbon label reference for carbon atoms on **4**.

Number	δ	Carbon Ref.
1	15.73	Cp-Me
2	22.41	6 or 17
3	23.21	6 or 17
4	27.5	1
5	28.38	tertbutyl-CH_3
6	28.6	tertbutyl-CH_3
7	28.62	tertbutyl-CH_3
8	28.67	tertbutyl-CH_3
9	28.68	tertbutyl-CH_3
10	29.01	tertbutyl-CH_3
11	29.8	5 or 16
12	30.29	5 or 16
13	32.21	13 or 24
14	32.37	13 or 24
15	32.89	7 or 18
16	33.11	7 or 18
17	36.57	2
18	39.17	4 or 19
19	39.6	4 or 19
20	44.15	Cp-2
21	53.55	8,11,19 or 22
22	53.62	8,11,19 or 22
23	53.81	8,11,19 or 22
24	54.02	8,11,19 or 22

25	81.14	tertbutyl-C_q (G or G’)
26	81.16	tertbutyl-C_q (G or G’)
27	82.05	tertbutyl-C_q (G or G’)
28	82.2	tertbutyl-C_q (G or G’)
29	82.53	tertbutyl-C_q (G or G’)
30	82.63	tertbutyl-C_q (G or G’)
31	131.41	B
32	133.78	Cp-1
33	149.43	C
34	151.01	D
35	157.76	H or H’
36	158.13	H or H’
37	166.96	A
38	172.89	E,F,F’,I,I’,J or J’
39	172.92	E,F,F’,I,I’,J or J’
40	173.01	E,F,F’,I,I’,J or J’
41	173.04	E,F,F’,I,I’,J or J’
42	173.12	E,F,F’,I,I’,J or J’
43	173.15	E,F,F’,I,I’,J or J’
44	173.96	E,F,F’,I,I’,J or J’

Table S4. Carbon signal assignment for **4**.

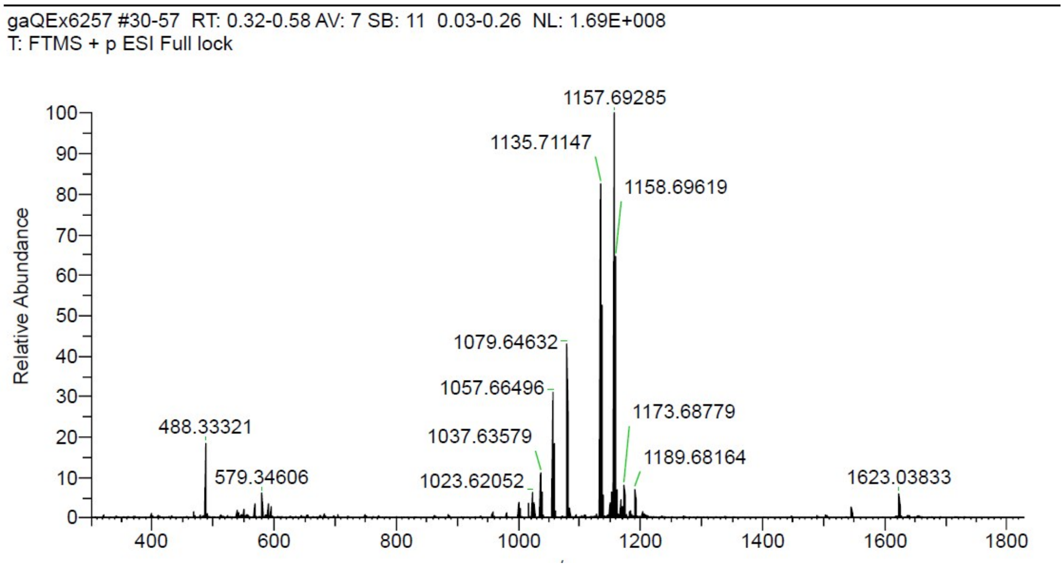


Figure S17. HR-ESI MS of **4** (MeOH).

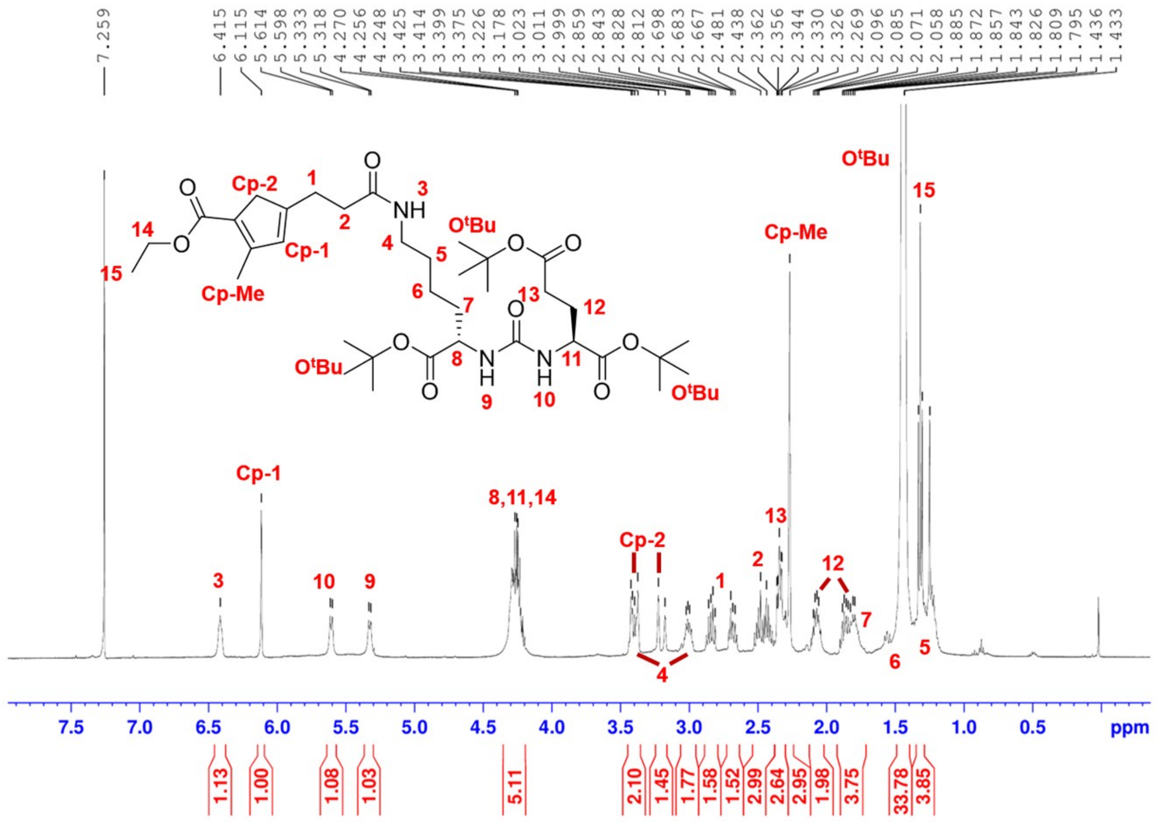


Figure S18. ^{1}H NMR of **5** in $CDCl_3$ with assigned proton signals.

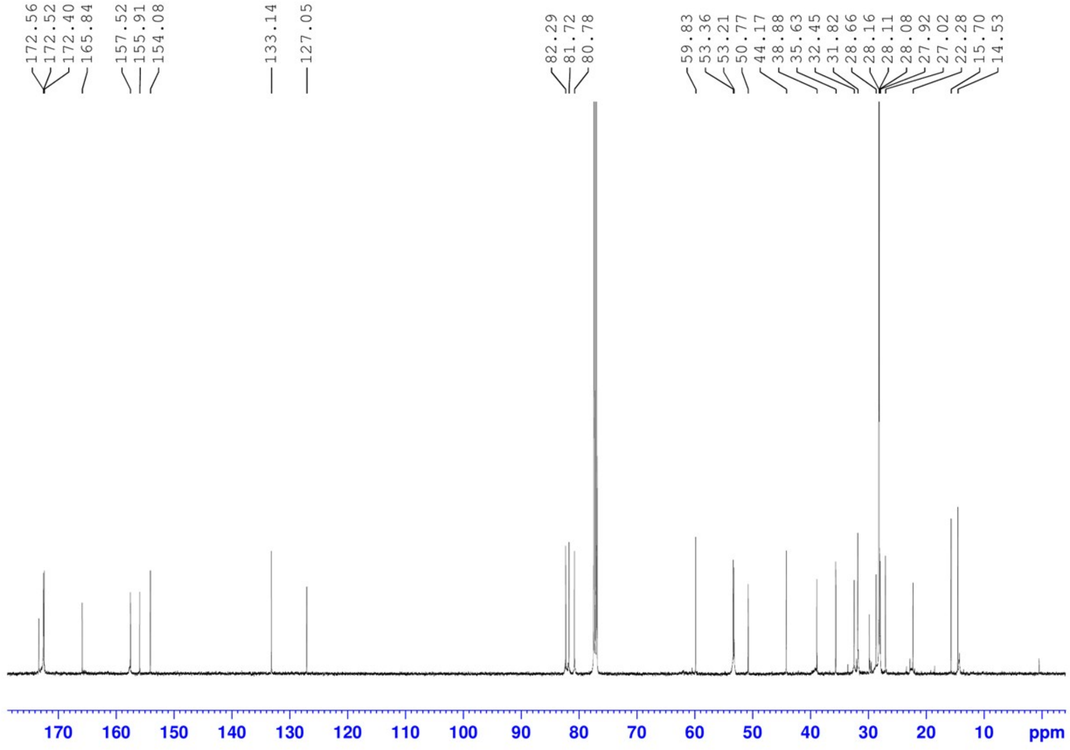


Figure S19. ^{13}C NMR of **5** in $CDCl_3$.

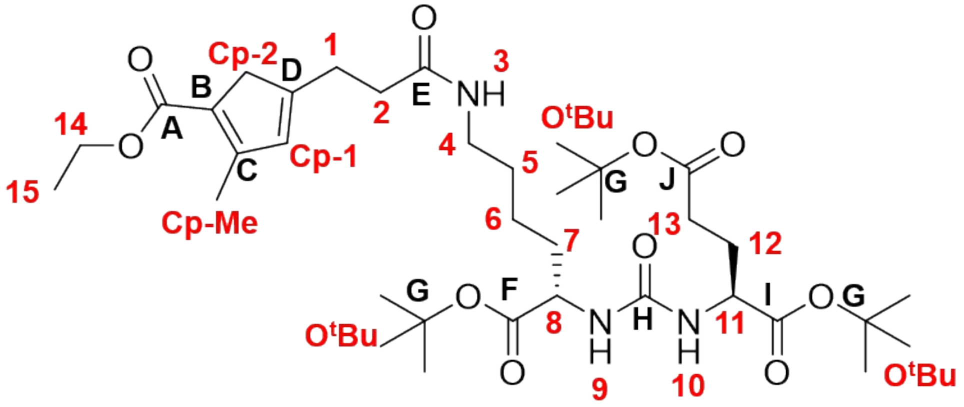


Figure S20. Carbon label reference for carbon atoms on **5**.

Number	δ	Carbon Ref.
1	14.53	15
2	15.7	Cp-Me
3	22.28	6
4	27.02	1
5	27.92	12
6	28.08	tertbutyl-CH_3
7	28.11	tertbutyl-CH_3
8	28.16	tertbutyl-CH_3
9	28.66	5
10	31.82	13
11	32.45	7
12	35.63	2
13	38.88	4
14	44.17	Cp-2
15	50.77	-
16	53.21	8 or 11
17	53.36	8, or 11
18	59.83	14
19	80.78	tertbutyl-C_q (G)
20	81.72	tertbutyl-C_q (G)
21	82.29	tertbutyl-C_q (G)
22	127.05	B
23	133.14	Cp-1
24	154.08	D
25	155.91	C
26	157.52	H
27	165.84	A

28	172.4	E,F or I
29	172.52	E,F or I
30	172.56	E,F or I
31	173.35	J

Table S4. Carbon signal assignment for **5**.

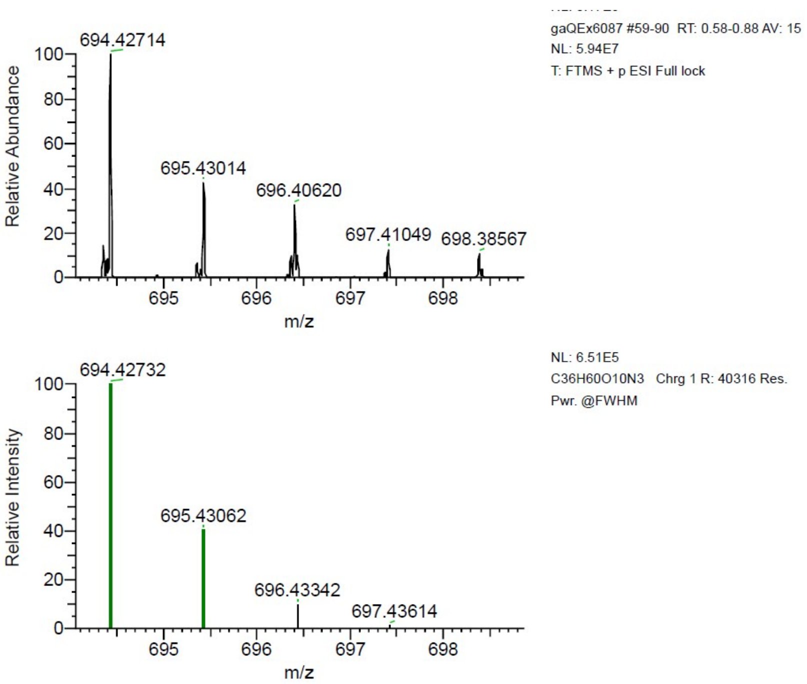


Figure S21. HR-ESI MS of 5 (MeOH).

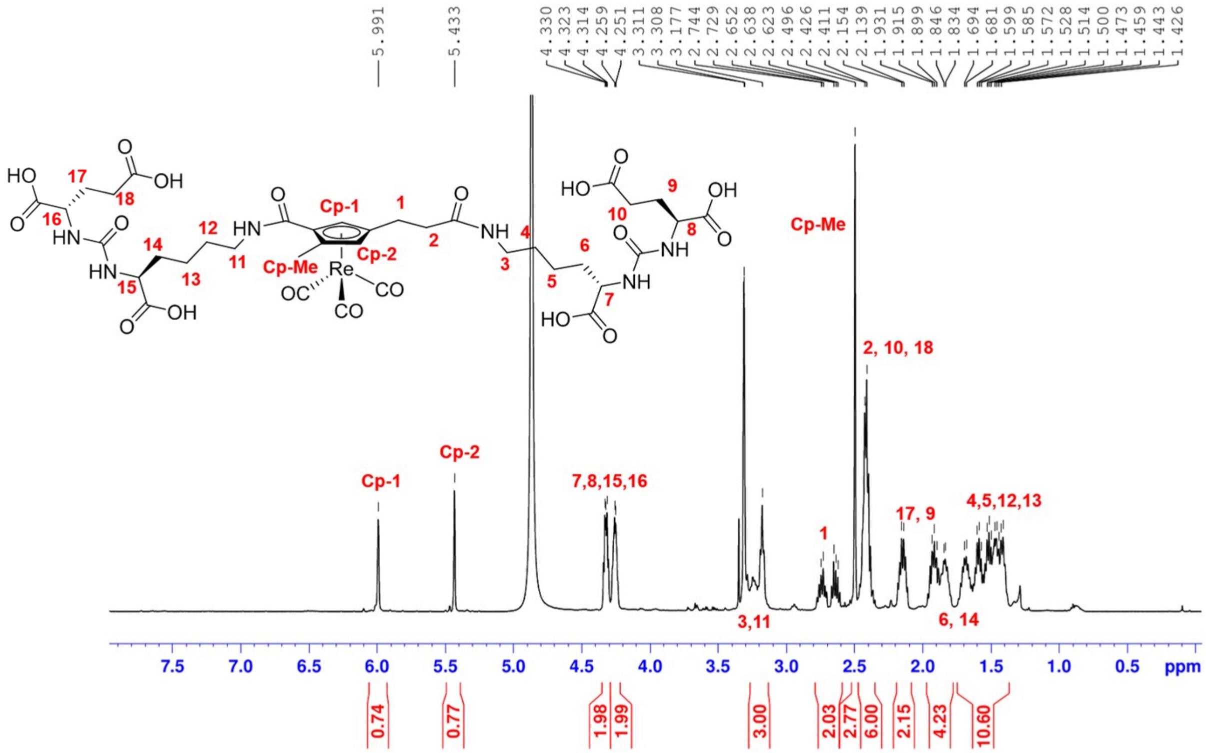


Figure S22. ¹H NMR of **Re2** in MeOD with assigned proton signals.

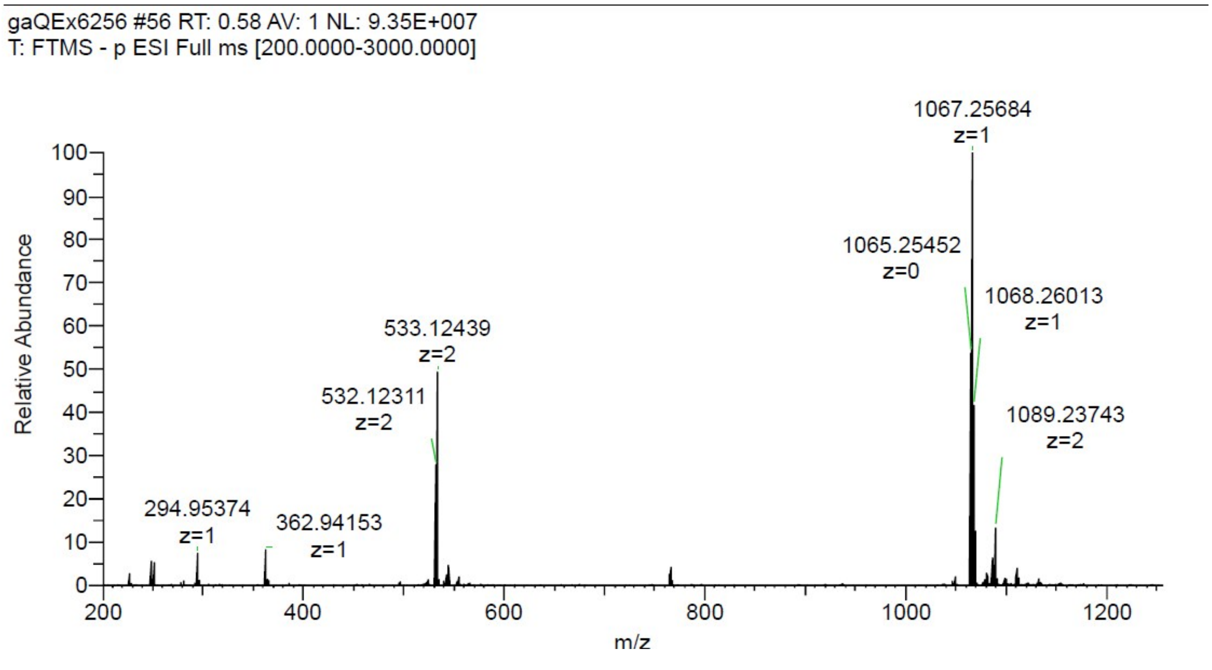


Figure S19. HR-ESI MS of **Re2** (MeOH).

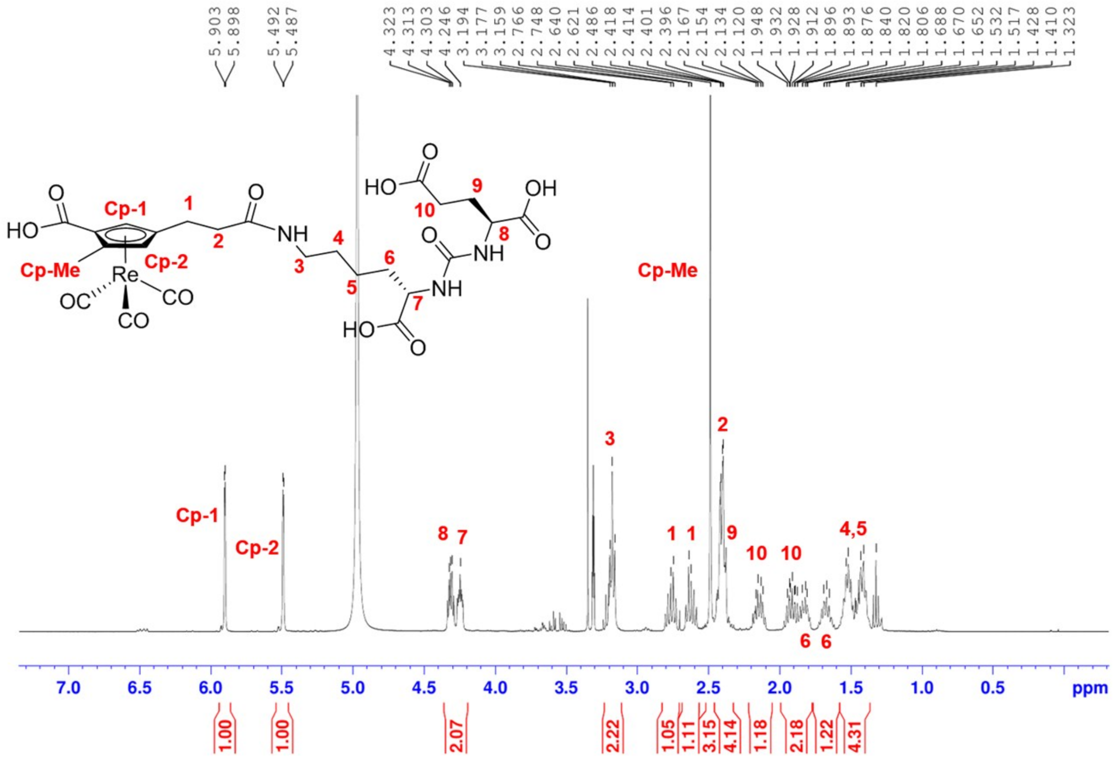


Figure S23. ^{1}H NMR of **Re1** in MeOD with assigned proton signals (assignments based on DEPT, COSY, HSQC and HMBC experiments).

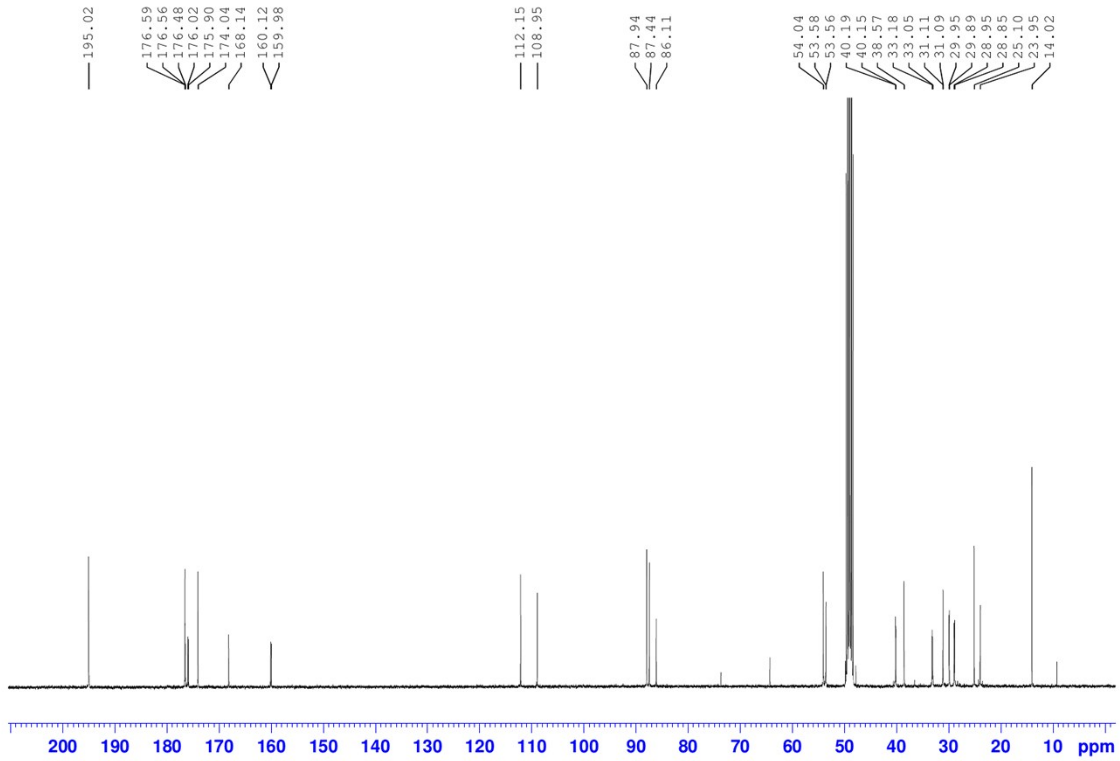


Figure S24. ^{13}C NMR of **Re1** in MeOD.

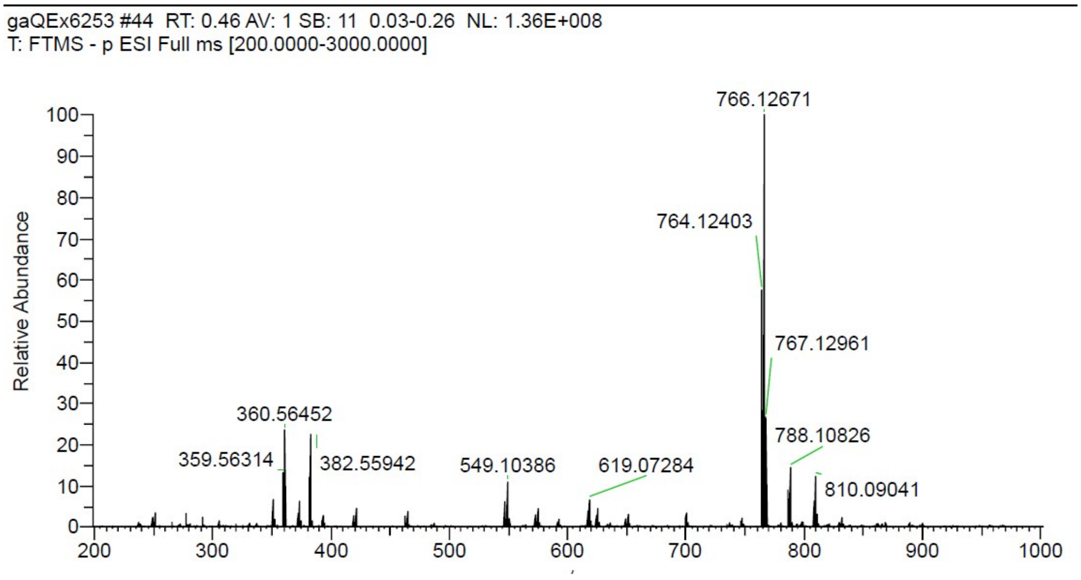


Figure S25. HR-ESI MS of **Re1** (MeOH).

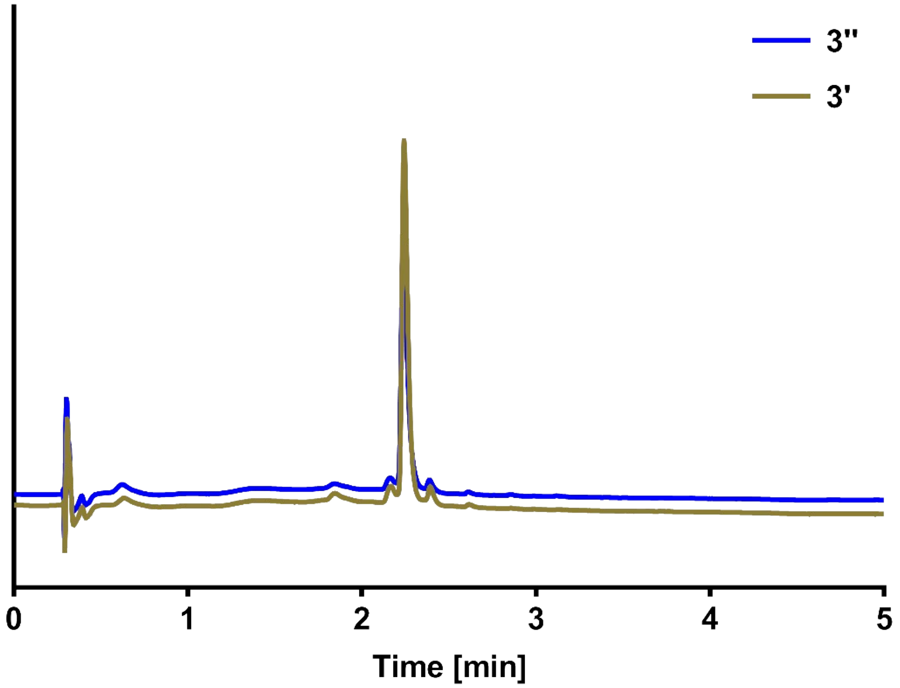


Figure S26. Overlay of UPLC traces of **Re2'** and **Re2''**.

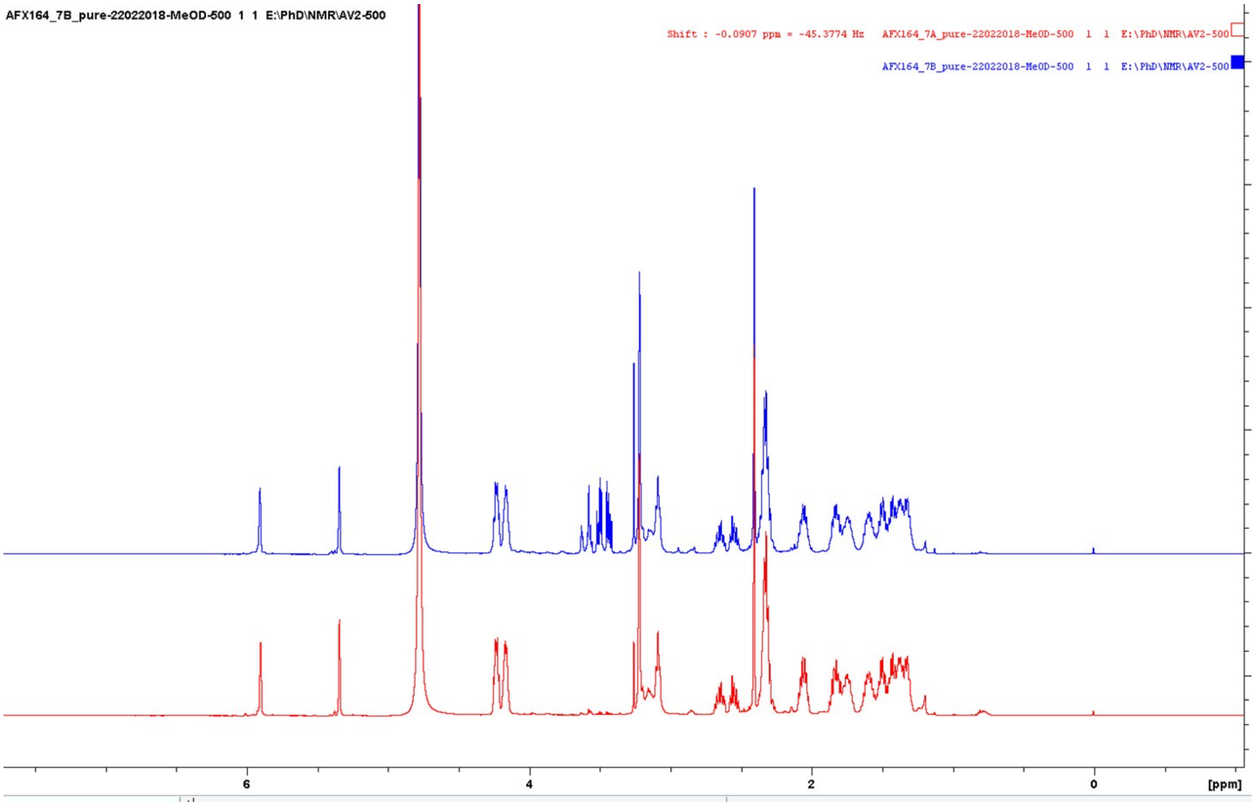


Figure S27. Overlay of ^{1}H NMR spectra of **Re2'** and **Re2''** in CD_3OD (peaks between 3.4 – 3.65 in blue graph represent an impurity).

References

[1] A. Frei, B. Spingler, R. Alberto, *Chem. - Eur. J.* **2018**, *24*, 10156-10164.