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Supporting Information

Heterogenization of Ferrocene Palladacycle Catalysts on ROMP-Derived Monolithic Supports and Application to a Michael Addition

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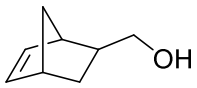
Synthesis of the Functionalized Monomer M2

5-Norbornene-2-methanol (1)[1]

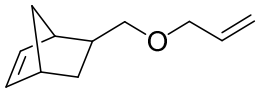


1

A mixture of allyl alcohol (75.0 g, 1.29 mol), cyclopentadiene (94.0 g, 1.42 mol, 1.1 equiv), and a small amount of hydroquinone was heated in an autoclave at 180 °C for 16 h. The resulting mixture was distilled under reduced pressure at 80 °C to afford 5-norbonene-2-methanol **1** as colourless liquid (112 g, 0.90 mol, 70%).

$C_8H_{12}O$, **MW:** 124.18 g mol^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 6.14-5.92 (*m*, 2H, C*H*=C*H*), 3.71-3.18 (*m*, 2H, CH_2O), 2.91 (*s*, 1H), 2.79 (*s*, 1H), 2.34-2.16 (*m*, 1H), 1.84-1.75 (*m*, 2H), 1.45-1.41 (*m*, 1H), 1.30-1.06 (*m*, 2H), 0.53-0.46 (*m*, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** δ = 137.5, 136.9, 136.6, 132.2, 67.5, 66.5, 49.6, 45.0, 43.6, 43.3, 42.3, 41.7, 29.6, 28.9. **GC-MS *m/z*:** calcd. for M^+: 124.09; found: 124. The other analytical data are in accordance with the literature.[1]

5-Allyloxymethylbicyclo[2.2.1]hept-2-ene (5)[1]



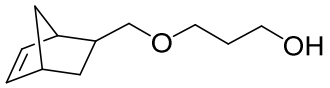
5

Sodium hydride (3.90 g, 160 mmol, 4 equiv) was added to a solution 5-norbornene-2-methanol **1** (5 g, 40 mmol, 1 equiv) in DMF (200 mL) at 0 °C. The reaction mixture was stirred for 5 min, then allyl bromide (19.4 g, 160 mmol, 4 equiv) was added. The reaction mixture was then allowed to stir at room temperature overnight. The reaction was quenched by adding water (50 mL) and extracted with *n*-pentane (3 x 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and then evaporated *in vacuo*. The resulting residue was purified by silica-gel column chromatography using 10% Et_2O in pentane as eluent, yielding 5-allyloxymethylbicyclo[2.2.1]hept-2-ene **5** (5.3 g, 32 mmol, 81%) as pale yellow liquid.

$C_{11}H_{16}O$, **MW:** 164.24 g mol^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 6.13-5.92 (*m*, *J* = 5.6, 3.0, 2H), 5.93-5.85 (*m*, 1H), 5.28-5.14 (*m*, 2H), 4.00-3.88 (*m*, 2H), 3.15 (*dd*, *J* = 9.2, 6.6, 1H),

3.04 (*t*, *J* = 9.1 Hz, 1H), 2.92 (*b*, 1H), 2.76 (*b*, 1H), 2.35 (*m*, 1H), 1.81 (*ddd*, *J* = 11.6, 9.2, 3.8, 1H), 1.44-1.40 (*m*, 1H), 1.32-1.09 (*m*, 1H), 0.49 (*m*, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** δ = 137.3, 136.8, 135.4, 132.6, 116.8, 75.1, 74.2, 72.1, 49.6, 45.1, 44.1, 42.3, 39.1, 29.3. **GC-MS *m/z*:** calcd. for M^+: 164.12; found: 163.9. The other analytical data are in accordance with the literature.[1]

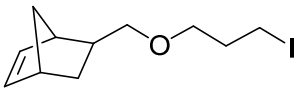
3-(Bicyclo[2.2.1]hept-5-en-2-yl-methoxy)propan-1-ol[1]



To 2-methyl-2-butene (3.1 g, 44 mmol, 2.4 equiv) in THF (200 mL) at –10 °C was added BH_3•THF (22 mL, 1.0 M in THF, 22 mmol, 1.2 equiv) dropwise. The reaction mixture was stirred at 0 °C for 1 h, then 5-allyloxymethylbicyclo[2.2.1]hept-2-ene **5** (3.0 g, 18 mmol, 1 equiv) was added and stirring was continued at 0 °C. After 4 h, the mixture was quenched by adding water and a solution of of NaOH (10%, 40 mL), and H_2O_2 (30% ,40 mL) were added. The reaction mixture was then stirred overnight at room temperature and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, filtered and then evaporated *in vacuo*. The resulting residue was purified by silica-gel column chromatography using 20% EtOAc in pentane as eluent to yield 3-(bicycle[2.2.1]hept-5-en-2-yl-methoxy)propan-1-ol (2.6 g, mmol, 78%) as colourless liquid.

$C_{11}H_{18}O_2$, MW: 182.26 g mol^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 6.12-5.90 (*m*, *J* = 5.7, 3.0, 2H), 3.76 (*m*, 2H), 3.62-3.53 (*m*, 2H), 3.15 (*dd*, *J* = 9.2, 6.7, 1H), 3.04 (*m*, 1H), 2.85 (*b*, 1H), 2.77 (*b*, 1H), 2.63 (*b*, 1H), 2.32 (*m*, 1H), 1.83-1.76 (*m*, 3H), 1.42-1.06 (*m*, 2H), 0.48 (*m*, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** δ = 137.3, 132.4, 75.1, 70.7, 62.6, 49.5, 44.1, 41.6, 38.8, 32.1, 29.2. **GC-MS *m/z*:** calcd. for M^+: 182.13; found: 182.1. The other analytical data are in accordance with the literature.[1]

5-(3-Iodopropoxymethyl)bicyclo[2.2.1]hept-2-ene (6)[1]

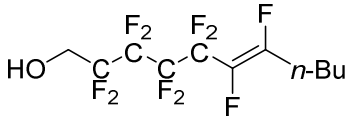


6

To a mixture of 3-(bicycle[2.2.1]hept-5-en-2-yl-methoxy)propan-1-ol (1.0 g, 5.5 mmol, 1 equiv) and Et_3N (2.2 g, 22 mmol, 4 equiv) in CH_2Cl_2 (30 mL) was added dropwise mesyl chloride (0.95 g, 8.3 mmol, 1.5 equiv) at 0 °C over a period of 5 min. The reaction mixture was stirred for 30 min and then quenched by adding water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was dissolved in acetone (30 mL) then NaI (2.5 g, 16.5 mmol, 3 equiv) was added. The mixture was refluxed for 3 h. After cooling to room temperature, the mixture was diluted with diethyl ether (150 mL) and washed with $Na_2S_2O_3$ (10%) and water. The organic layer was dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by silica-gel column chromatography using 20% Et_2O in pentane as eluent to afford 5-(3-iodopropoxymethyl]bicycle[2.2.1]hept-2-ene **6** (1.4 g, 4.8 mmol, 86%) as pale yellow liquid.

$C_{11}H_{17}IO$, MW: 292.16. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 6.13-5.93 (*m*, *J* = 5.6, 3.0, 2H), 3.51-3.38 (*m*, 2H), 3.33-3.27 (*m*, 2H), 3.16 (*dd*, *J* = 9.2, 5.9, 1H), 2.02 (*m*, 1H), 2.89 (*b*, 1H), 2.78 (*b*, 1H), 2.33 (*m*, 1H), 2.02-1.99 (*m*, 2H), 1.80 (*ddd*, *J* = 9.9, 8.6, 3.8, 1H), 1.41 (*m*, 1H), 1.31-1.23 (*m*, 1H), 0.48 (*m*,1H). **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** δ = 137.3, 132.6, 74.9, 70.1, 49.5, 44.1, 42.3, 38.9, 33.6, 29.2, 3.8. **GC-MS *m/z*:** calcd. for M^+: 292.03; found: 292.0. The other analytical data are in accordance with the literature.[1]

2,2,3,3,4,4,5,5,6,7-Decafluoroundec-6-en-1-ol[2]

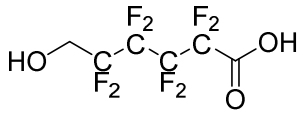


1*H*,1*H*,7*H*-Dodecafluoro-1-heptanol (3.0 g, 9.0 mmol, 1 equiv) was dissolved in Et_2O (60 mL). A solution of *n*-buthyllithium (19.2 mL, 1.60 M in hexanes, 30.7 mmol, 3.4 equiv) was added drop-wise over 30 min at −78 °C. The mixture was stirred for 1.5 h at room temperature and then the reaction was quenched by the addition of aqueous HCl (1M). The organic phase was separated, washed with water (2 x 20 mL), dried over Na_2SO_4, filtered and the solvent was

evaporated *in vacuo*. The residue was distilled under reduced pressure (110-120°C bath temperature, 13 mbar) to yield 2,2,3,3,4,4,5,5,6,7-decafluoroundec-6-en-1-ol (1.9 g, 5.4 mmol, 60%) as colourless liquid**.**

$C_{11}H_{12}F_{10}O$, MW: 350.20 g mol^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 4.08 (*t*, 2H), 2.53-2.36 (*m*, 2H), 1.97 (*b*, 1H), 1.63-1.55 (*m*, 2H), 1.44-1.35 (*m*, 2H), 0.93 (*m*, 3H). **^{19}F NMR (235 MHz, $CDCl_3$, 25 °C):** *δ* = −115.1, −115.3, −117.1, −122.6, −124.2, −137.3, −156.3, −171.3. **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** *δ* = 160.3, 157.5, 138.3, 115.6, 114.1, 109.3, 60.9, 27.2, 21.9, 13.7. **GC-MS *m/z*:** calcd. for $[M - HF]^+$: 330.06; found: 330.0. The other analytical data are in accordance with the literature.[2]

2,2,3,3,4,4,5,5-Octafluoro-6-hydroxyhexanoic acid (7)[3]

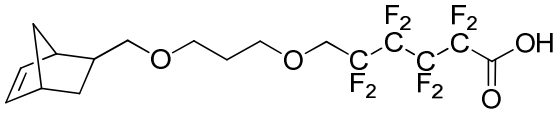


7

To a stirred solution of 2,2,3,3,4,4,5,5,6,7-decafluoroundec-6-en-1-ol (0.8 g, 2.3 mmol, 1 equiv) in acetone (20 mL) was added $KMnO_4$ (0.8 g, 5.1 mmol, 2.2 equiv). The temperature of the reaction was maintained at 20 to 30 °C. After 20 h, the reaction mixture was clarified with aqueous $NaHSO_3$ solution and acidified with dilute sulphuric acid. The clear solution was saturated with NaCl and extracted with diethyl ether (2 x 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent evaporated *in vacuo*. The residue was recrystallized from warm $CHCl_3$ to afford 2,2,3,3,4,4,5,5-octafluoro-6-hydroxyhexanoic acid **7** (0.32 g, 1.2 mmol, 52%) as a white solid.

$C_6H_4F_8O_3$, MW: 276.08. **^{1}H NMR (400 MHz, DMSO-D_6, 25 °C):** δ = 3.95. **^{19}F NMR (235 MHz, $CDCl_3$, 25 °C):** *δ* = −118.4, −121.0, −123.0. **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** *δ* = 159.6, 116.4, 113.9, 110.7, 108.1, 58.9. The other analytical data are in accordance with the literature.[3]

6-(3-Bicyclo[2.2.1]hept-5-en-2ylmethoxy)propoxy)-2,2,3,3,4,4,5,5-octa-fluorohexanoic acid (M2)



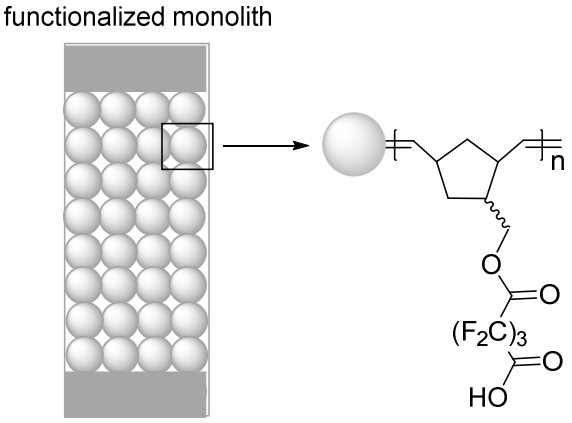
M2

Sodium hydride (60% dispersion in oil, 38.3 mg, 1.09 mmol, 3 equiv) was added to a solution of 2,2,3,3,4,4,5,5-octafluoro-6-hydroxyhexanoic acid **7** (100 mg, 0.36 mmol, 1 equiv) in anhydrous DMF (5 mL) at 0 °C. After stirring for 15 min 5-(3-iodopropoxymethyl)bicyclo[2.2.1]hept-2-ene **6** (159 mg, 0.54 mmol, 1.5 equiv) was added drop-wise. The reaction mixture was then stirred at room temperature. After 3h the reaction was quenched by adding water (20 mL) and washed with pentane twice. The aqueous layers were acidified with a aqueous HCl (1M) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and the solvent evaporated *in vacuo* to afford the desired product **M2** (110 mg, 0.25 mmol, 70 %) as pale yellow viscous liquid containing DMF for stability.

$C_{17}H_{20}F_8O_4$, MW: 440.33 g mol^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 9.66 (*b*, 1H), 6.14-5.89 (*m*, *J* = 5.7, 3.1, 2H), 4.08 (*t*, *J* = 14.6, 4H), 3.92 (*t*, *J* = 14.0, 2H), 3.68 (*t*, *J* = 5.7, 4H), 3.60-3.52 (*m*, 2H), 3.21 (*dd*, *J* = 9.2, 5.9, 1H), 3.12 (*t*, *J* = 9.2, 1H), 3.02 (*m*, 1H), 2.88 (*b*, 1H), 2.79 (*b*, 1H), 2.35 (*m*, 1H), 1.99-1.78 (*m*, 3H), 1.44-1.41 (*m*, 1H), 1.29-1.07 (*m*, 2H), 0.48 (*m*, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):** *δ* = 160.6, 137.6, 132.3, 115.7, 112.3, 108.8, 108.5, 76.0, 75.0, 69.9, 68.1, 67.4, 60.8, 49.6, 44.1, 42.3, 38.5, 29.6, 29.3. **^{19}F NMR (235 MHz, $CDCl_3$, 25 °C):** *δ* = −119.2 (*m*), −119.9 (*t*), −122.6 (*t*), −123.0 (*m*), −123.4 (*m*), −123.6 (*m*). **HRMS (ESI) *m/z*:** calcd. for $[M+H]^+$: 441.1307; found: 441.1302.

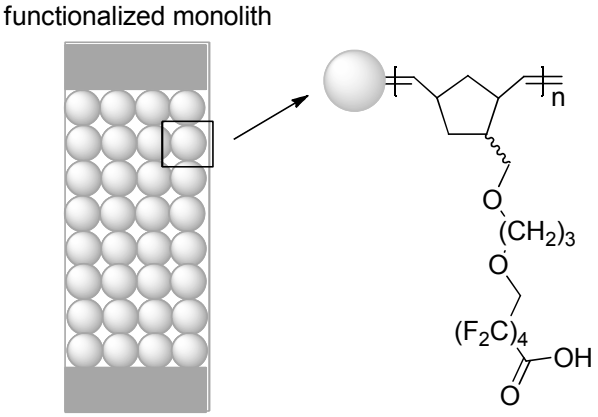
Monolithic Supports and Catalysis

Monolithic Support with Functionalized Monomer M1



Preparation of the monolithic support inside a PEEK column (100 x 7 mm i.d.) and grafting of functionalized monomer **M1** (~ 120 µmol) to the monolithic support was performed according to literature procedures.[4]

Monolithic Support with Functionalized Monomer M2



The monolith was prepared inside a PEEK column (100 x 7 mm i.d.) according to previously published procedures.[4] Briefly, two solutions A and B were prepared. Solution A consisted of NBE (20 wt.-%), $(NBE\text{-}CH_2O)_3SiCH_3$ (20 wt.-%) and 2-propanol (45.7 wt.-%), solution B consisted of $RuCl_2(CHPh)(PCy_3)_2$ (0.4 wt.-%) in toluene (13.9 wt.-%). Both solutions A and B were cooled to −20 °C, mixed and rapidly transferred to the PEEK column. The column was kept at 0 °C for 30 min and then the polymerization was allowed to proceed for another 30 min at room temperature. The column was flushed with freshly distilled toluene for 30 min at a flow rate of 0.2 mL min^{-1}. Argon was passed through the monolith for 10 min to elute the solvent.

For the grafting, a solution of the functionalized monomer **M2** (22 mg, 50 µmol) in CH_2Cl_2 (1.5 mL) was introduced into the monolith at a flow rate of 0.1 mL min^{-1}. The column was then sealed and kept at 40 °C overnight. Then the monolith was flushed with a mixture of DMSO/THF/ethyl vinyl ether (40/40/20) to remove the initiator and then with THF each for 30 min. Finally the monolith was flushed with CH_2Cl_2 for 30 min at a flow rate of 0.1 mL min^{-1}. The grafted monolith was then directly used for the immobilization.

Quantification of Carboxylate Groups on the Functionalized Monoliths

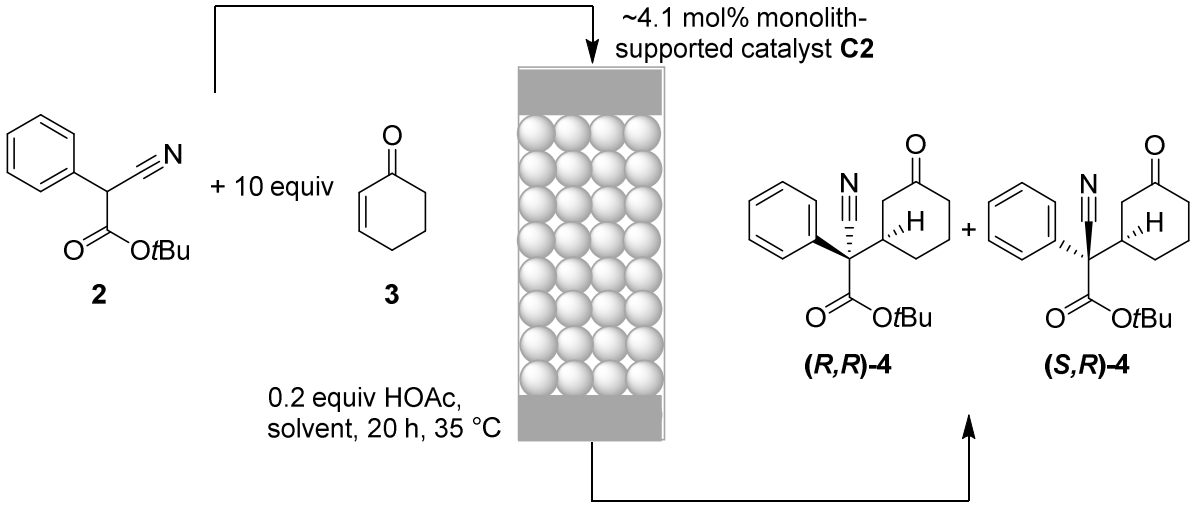
The amount of carboxylate groups in the monolith was determined by acid-base titration. For this purpose, the functional monolith was flushed with water for 30 min at a flow rate of 0.2 mL min^{-1}. A known volume of an aqueous KOH solution (10 mL, 5.2 mM) was passed through the monolith at a flow rate of 0.1 mL min^{-1}, followed by water until reaching a neutral eluent. The amount of carboxylate groups was then quantified by comparing the molarity of the flow through solution with standard KOH solution. The molarities of both the solutions were determined by titrating against standard HCl solution (1 mM) using phenolphthalein as indicator. The results of the three columns are shown in the following Table.

Amount of carboxylic acid groups on the functionalized monoliths.

#	column	amount of carboxylic acid groups
1	C1	117 µmol
2	C2	50 µmol
3	C3	50 µmol

Solvent Screening in the Michael Addition with Monolith-Supported Catalyst C2

Further solvents and solvent mixture have been tested and the results are summarized in the following table:



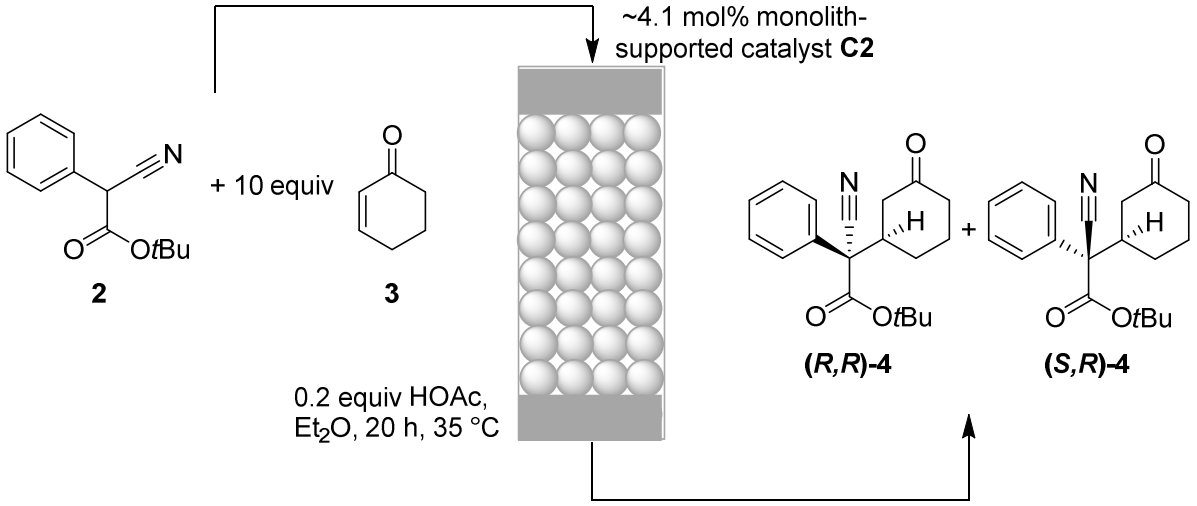
entry	solvent	yield [%][b]	$ee_{(R,R)}$ [%][c]	$ee_{(S,R)/(R,S)}$ [%][c,d]	dr[c,e]
1	glyme	10	12	n.d.	52:48
2	diethyleneglycol diethyl ether	25	9	-23	59:41
3	$CHCl_3$	3	57	-10	53:47
4	hexafluorobenzene	46	18	-6	57:43
5	benzyltrifluorid	21	33	-11	48:52
6	benzene	10	51	-6	52:48
7	tetrahydrofuran	9	32	1	54:46
8	1,3,5-trifluorobenzene	9	41	3	57:43
9	toluene	18	18	-3	60:40
10	methyl *tert*-butyl ether	19	29	-2	62:38
11	acetone	12	54	3	56:44
12	1,2-dichloroethane	28	33	5	57:43
13	di-*iso*propyl ether	18	42	4	62:38
14	CH_2Cl_2:Et_2O (1:3)	9	46	5	64:36
15	CH_2Cl_2:EtOAc (1:1)	5	45	5	60:40
16	CH_2Cl_2:MTBE (1:3)	8	32	1	63:37
17	$CHCl_3$:Et_2O (1:3)	15	48	-1	62:38
18	CH_2Cl_2:EtOAc:Et_2O (0.1:1:1)	28	31	2	61:39
19	$CHCl_3$:MTBE (1:3)	5	34	-9	58:42

20	$CHCl_3$:EtOAc (1:3)	6	50	10	62:38
21	EtOAc:Et_2O (1:1)	9	35	6	57:43
22	EtOAc:MTBE (1:1)	7	21	27	51:49
23	$CHCl_3$:EtOAc (1:10)	21	18	6	63:37
24	CH_2Cl_2:Et_2O (1:10)	6	33	21	56:44
25	$CHCl_3$:Et_2O (1:10)	23	18	5	66:34

[a] Conditions: 92 µmol of **2**, 10 equiv. of **3**, 0.2 equiv. of HOAc, 0.2 mL of solvent. [b] Determined by ^{1}H NMR spectroscopy using an internal standard. [c] Determined by HPLC. [d] A minus sign indicates that the (*R*,*S*)-enantiomer has been formed in excess. [e] (*R*,*R*+*S*,*S*):(*S*,*R*+*R*,*S*).

Further Michael Addition Reactions using Diethyl Ether and Supported Catalyst C2

Further results of the Michael addition reactions carried out by using diethylether and the supported catalyst **C2** under otherwise identical reaction conditions resulted in good yield and diastereoselectivity, but with rather poor enantioselectivity for both diastereomers, see the following table:



entry	yield [%][b]	$ee_{(R,R)}$ [%][c]	$ee_{(S,R)}$ [%][c]	dr[c,d]
1	51	25	4	60:40
2	48	22	5	62:38
3	94	25	4	59:41
4	35	23	4	60:40
5	36	24	9	59:41
6	89	11	7	57:43
7	13	20	11	49:51
8	89	11	1	37:63
9	39	29	9	53:47
10	19	26	19	54:46

[a] Conditions: 92 µmol of **2**, 10 equiv. of **3**, 0.2 equiv. of HOAc, 0.2 mL of Et_2O. [b] Determined by ^1H NMR spectroscopy using an internal standard. [c] Determined by HPLC. [d] (*R*,*R*+*S*,*S*):(*S*,*R*+*R*,*S*).

Determination of Metal Amounts

Experimental

Pd- (340.458 nm) and Fe-amounts (259.941 nm) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Samples (concentrations between 1 and 5 mg L^{-1} metal) were prepared by dissolution of the organic substance in *aqua regia* (5 mL, 20 h, 80 °C). After cooling to room temperature the mixture was filtered and diluted with demineralized water (factor 25 for catalysis samples, factor 250 to 1000 for the monolithic material). Standardization was carried out with Pd- and Fe- standard solutions (0, 0.1, 1.0, 2.5 and 5.0 mg L^{-1}, limit of detection for Pd: 0.0314 mg L^{-1} and for Fe: 0.0015 mg L^{-1}).

Pd-Amount of Monolith-Supported Catalyst C2 and C3

The amount of immobilized catalyst on the functionalized columns **C2** and **C3** after the performed catalysis reactions was calculated from the palladium amount in the monolith, determined by ICP-OES. The results are shown in the following table.

Pd-amount of monolith-supported catalyst C2 and C3.

#	monolith-supported catalyst	Catalyst	Pd (wt.-%)	Pd (µmol)
1	**C2**	**FBIP-$O_2CC_3F_7$**	0.610	7.33
2	**C3**	**FIP-$O_2CC_3F_7$**	0.039	1.71
3	*blank test*	-	*bld.*	-

bld.: below limit of detection.

Pd- and Fe-Amounts of Product Samples Prepared with Monolith-Supported Catalyst C2 and C3

The leaching behavior of the immobilized catalyst was investigated by quantification of the Pd-amount in the catalysis samples. The measurements show, that no Pd is detected in the samples and therefore no catalyst is washed from the monolith (see following table). The blank test (#18) was prepared in analogy to the samples and already shows a certain Fe-amount. Therefore the Fe-amount cannot be used for detection of the catalyst decomposition and possible ligand leaching.

Pd- and Fe-amounts of product samples prepared with monolith-supported catalyst C2 and C3.

#	Monolith-supported catalyst	Run	Pd (wt.-%)	Fe (mg L^{-1})$^{\alpha}$	Fe (wt.-%)	Pd (µmol)
1	**C2**	1	*bld.*	0.1080	0.087	-
2	**C2**	2	*bld.*	0.0928	0.070	-
3	**C2**	3	*bld.*	0.1189	0.142	-
4	**C2**	4	*bld.*	0.1288	0.189	-
5	**C2**	5	*bld.*	0.1018	0.034	-
6	**C2**	6	*bld.*	0.0961	0.096	-
7	**C2**	7	*bld.*	0.0884	0.096	-
8	**C2**	8	*bld.*	0.0814	0.055	-
9	**C2**	9	*bld.*	0.0882	0.067	-
10	**C2**	10	*bld.*	0.0855	0.049	-
11	**C3**	1	*bld.*	0.0960	0.160	-
12	**C3**	2	*bld.*	0.0943	0.262	-
13	**C3**	3	*bld.*	0.0924	0.077	-
14	**C3**	4	*bld.*	0.0834	0.091	-
15	**C3**	5	*bld.*	0.0988	0.042	-
16	**C3**	6	0.016	0.1882	0.025	0.03
17	**C3**	7	*bld.*	0.0913	0.190	-
18	*blank test*	-	*bld.*	0.1124	-	-

bld.: below limit of detection. $^{\alpha}$: For comparsion with the blank test, total volume of each sample: 25 mL.

References

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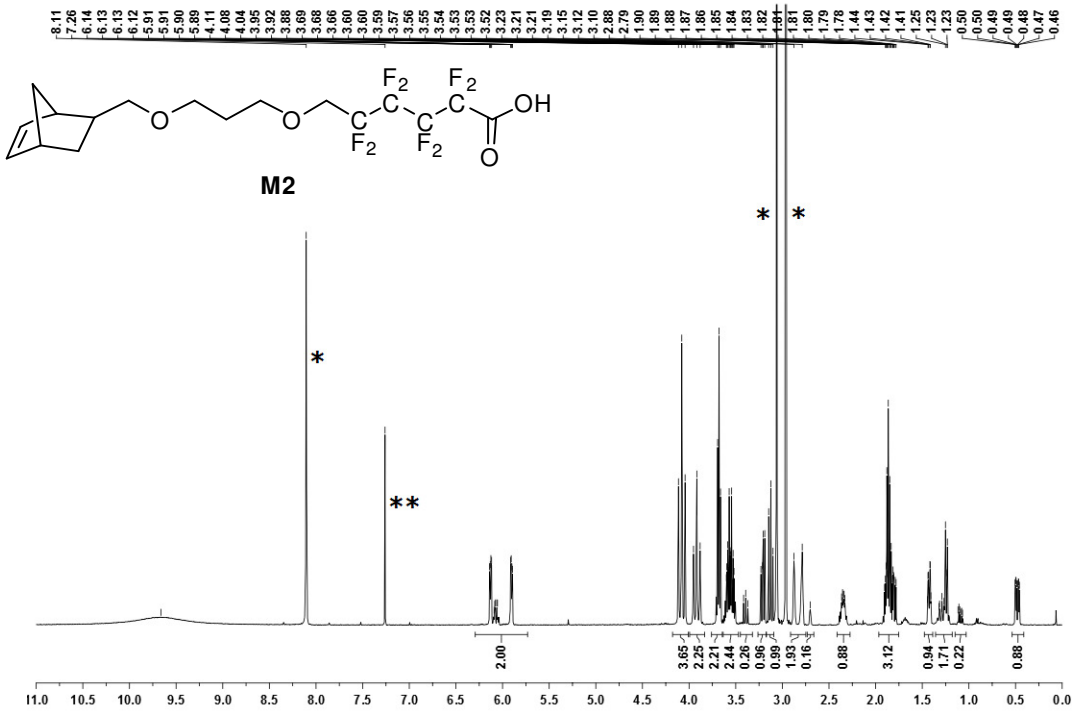
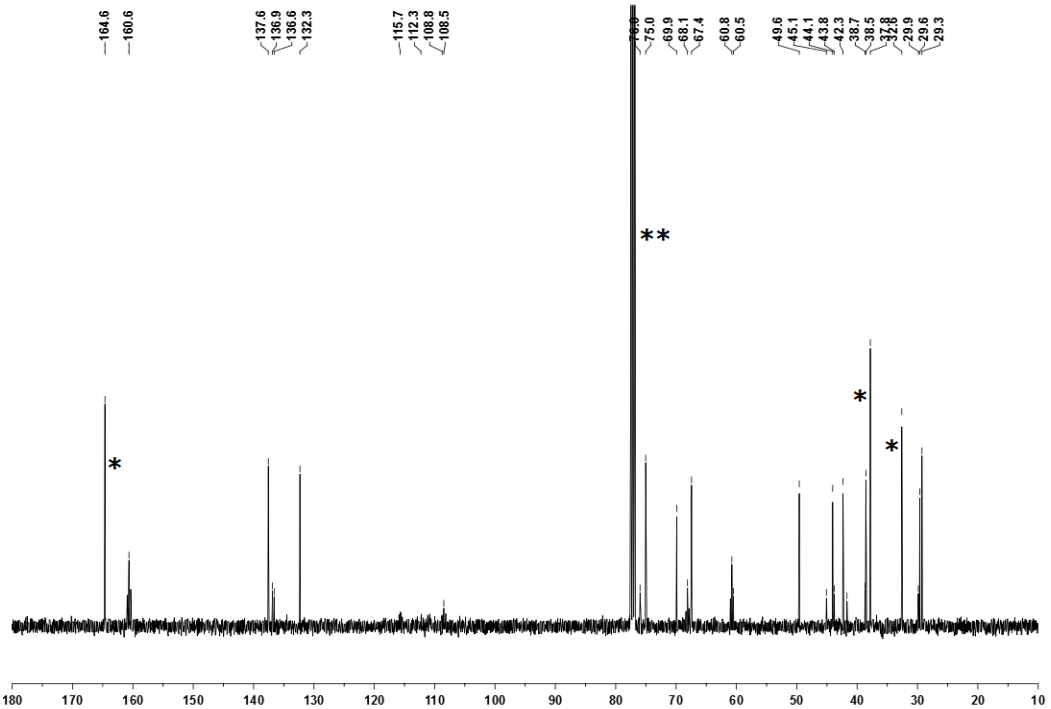
NMR spectra of new compounds

6-(3-Bicyclo[2.2.1]hept-5-en-2ylmethoxy)propoxy)-2,2,3,3,4,4,5,5-octa-fluorohexanoic acid (M2)

^{1}H NMR: * denotes DMF and ** denotes $CDCl_3$



^{13}C NMR: * denotes DMF and ** denotes $CDCl_3$



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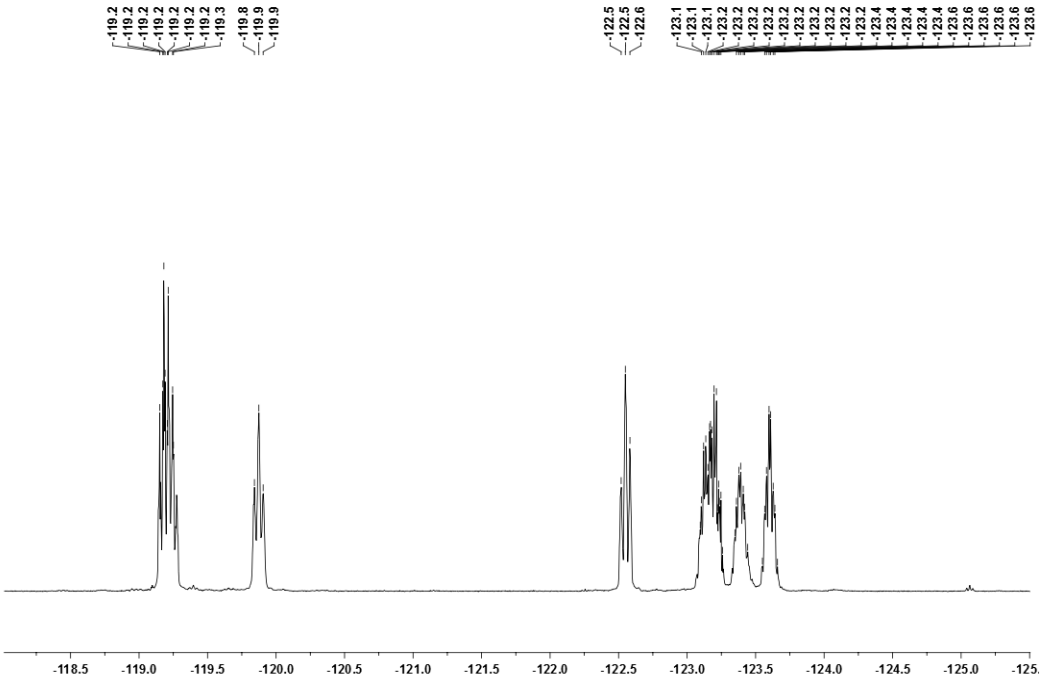
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FBIP-BF_4

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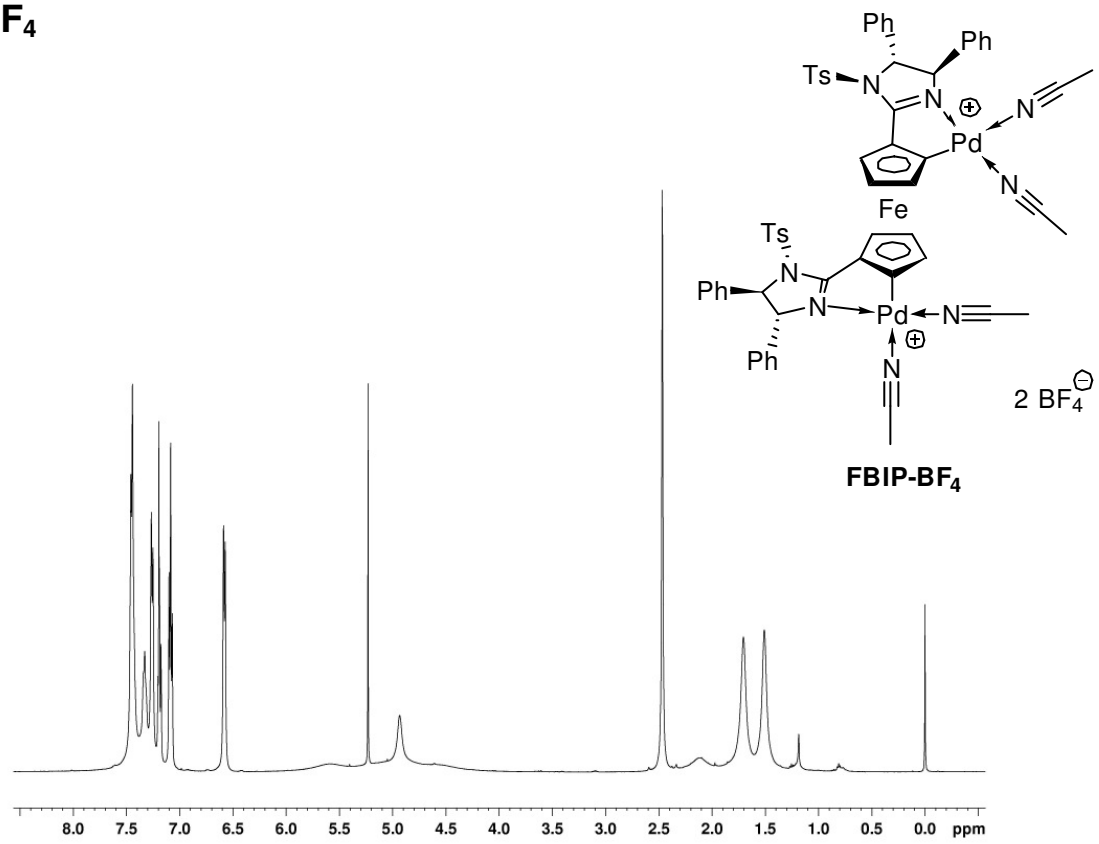

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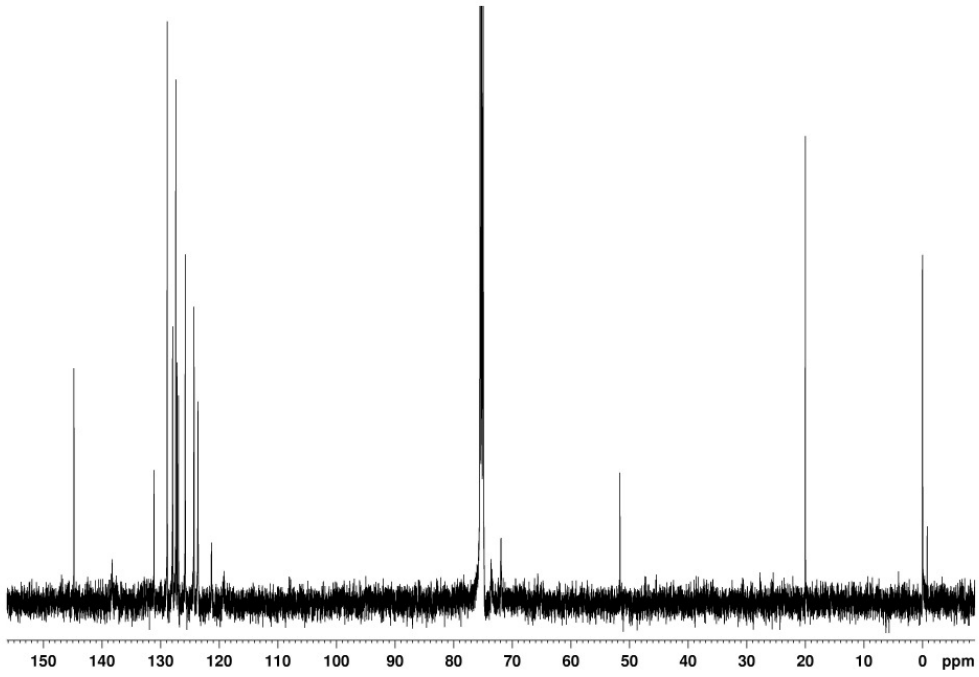

^{19}F NMR: