Synthesis of metathesis catalysts with fluorinated unsymmetrical N,N'-diaryl imidazoline-based NHC ligands

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Synthesis of Metathesis Catalysts with Fluorinated Unsymmetrical *N,N'*-Diaryl Imidazoline-based NHC ligands

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Highlights

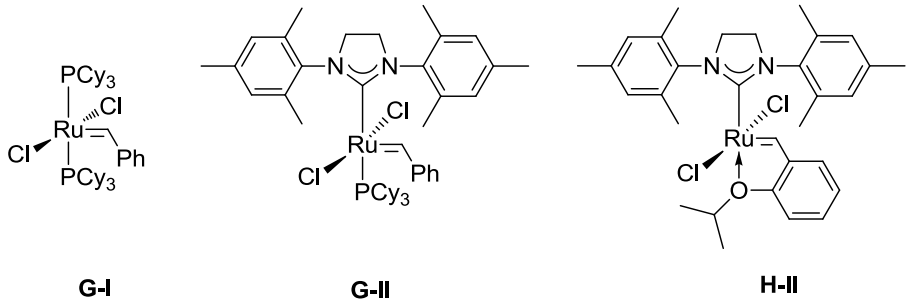
- Fluorinated unsymmetrical N,N'-diaryl imidazolinium salts as new NHC ligand precursors for olefin metathesis catalysts.
- Synthesis of new ruthenium carbene complexes.
- Investigation of catalytic activity of new fluorinated complexes in RCM and CM reactions.

Abstract: New olefin metathesis catalysts bearing unsymmetrical fluorinated NHC ligands with hexafluoroisopropylmethoxy group in *ortho*-positions of *N*-aryl-substituent have been synthesized. The effects of mono-*ortho*-arylsubstitution and the replacement of *para*-methyl *N*-aryl group with more electron-donating methoxy group in unsymmetrical fluorinated NHC ligand on the activity of complexes have been evaluated.

Introduction

Keywords: fluorinated NHC; ; ; , ruthenium complexes, olefin metathesis, catalysis.

N-heterocyclic carbenes (NHCs) have found widespread applications as important auxiliary ligands in modern organometallic and coordination chemistry [1-7]. Their unique steric and electronic properties have made possible the development of effective metal catalysts for various applications with the most outstanding examples in the field of ruthenium-catalyzed olefin metathesis [8-19]. Ruthenium complexes bearing NHC ligands usually demonstrate their superiority over first generation catalysts containing classical phosphine ligands exhibiting higher thermal stability, activity and selectivity (Figure 1) [4,20-23].



G-I **G-II** **H-II**

Figure 1. Commercially available olefin metathesis catalysts

A major advantage of this class of complexes is a possibility to perform a fine-tuning of their catalytic properties by modifying the NHC stereoelectronics [24-28]. In this context, the

importance of unsymmetrical N-heterocyclic carbenes (uNHCs) as ligands in metal catalysis is doubtless, as desymmetrization allows for further fine-tuning. The introduction of functionality, chelation, chirality, and shielding effects can influence the catalyst stability, reactivity, and selectivity, thus motivating the exploration of new tailor-made systems [29].

On the other hand, fluorinated compounds have found extensive applications in pharmaceutical and medicinal chemistry [30-35] or crops [36,37] and material sciences [38,39], due to the unique physicochemical features of fluorine atoms introduced in organic molecules [40]. In the field of ruthenium-alkylidene complexes, the influence of fluorine and fluorinated groups on their catalytic properties has been mainly studied by usage of definitely modified phosphine [41-44], benzylidene [45-56] ligands, as well as by the replacement of one or two chlorine atoms at ruthenium, for example, with perfluoro-carboxylates [57-61] and -alkoxylates [62,63]. Meanwhile, the number of reports on metathesis catalysts decorated with fluorinated NHC ligands is extremely limited [64-67]. For instance, Fürstner *et al.* described an unsymmetrical complex with $C_6F_{13}(CH_2)_2$ group at one of the imidazolyl nitrogen to increase the solubility of the catalyst in supercritical CO_2 [68]. In 2006, Grubbs reported rate acceleration in RCM of diethyl diallylmalonate arising from a Ru···F interaction between one ring of a *N,N'*-bis(2,6-difluorophenyl)imidazol-2-ylidene and the metal center in the Grubbs II catalyst analogue [69,70]. This work has been further extended with studies of synthesis and catalytic activities of closely related non-symmetrical analogues [71,72]. Consequently, the development of new tailor-made NHCs, particularly fluorinated ones, is highly desirable to enable new transformations or to bring established reactions into new reaction media.

At the same time, the variation of the substitution pattern in *N*-aryl moieties of the NHC ligand led to extremely active catalysts for challenging transformations involving metathesis of hindered substrates [4,73-76]. However, it is not always easy to predict how structural and electronic changes at the NHC can affect the catalyst activity. For example, the presence of bulky substituents on nitrogen has been shown to improve catalyst stability limiting decomposition pathways due to C-H bond activation of *N*-aryl rings [77], whereas mono-*ortho*-substituted *N*-aryl groups of the NHC ligand have been recognized as an important feature for successful ring-closing metathesis (RCM) reactions [78]. On the other hand, *N*-*para*-methoxyaryl NHCs [79] have been found to be excellent ligands for palladium catalysts for Buchwald-Hartwig coupling, compared to the corresponding parent NHCs [80,81]. Plenio *et. al.* have recently established that *para*-functionalized *N*-aryl NHC complexes did indeed affect the properties of the transition metal centre [82]. Later Nolan *et. al.* have demonstrated that Ru metathesis catalysts bearing imidazoline-based NHCs with *N*-*para*-methoxyaryl moieties were able to increase the initiation rate in RCM reactions at very low catalyst loadings [83].

Based on our experience in metathesis of different unsaturated fluorine-containing molecules [84-92], we have recently developed an efficient route to novel type of metathesis catalysts comprising unsymmetrical imidazolinylidene ligand with hexafluoroisopropylmethoxy [$(CF_3)_2$(OMe)C-] group in one of the *N*-aryl substituents and have demonstrated their good performance in ring closing olefin metathesis [93] (**1** and **2**, Fig. 2). With the aim of evaluating the effects of mono-*ortho*-arylsubstitution and the replacement of *para*-methyl *N*-aryl group with more electron-donating methoxy group in unsymmetrical fluorinated NHC ligand on the activity of the resulting precatalysts, we now want to disclose the synthesis of the corresponding ruthenium carbene complexes (**3-6**, Fig. 2) and preliminary evaluation of their catalytic activity as well.

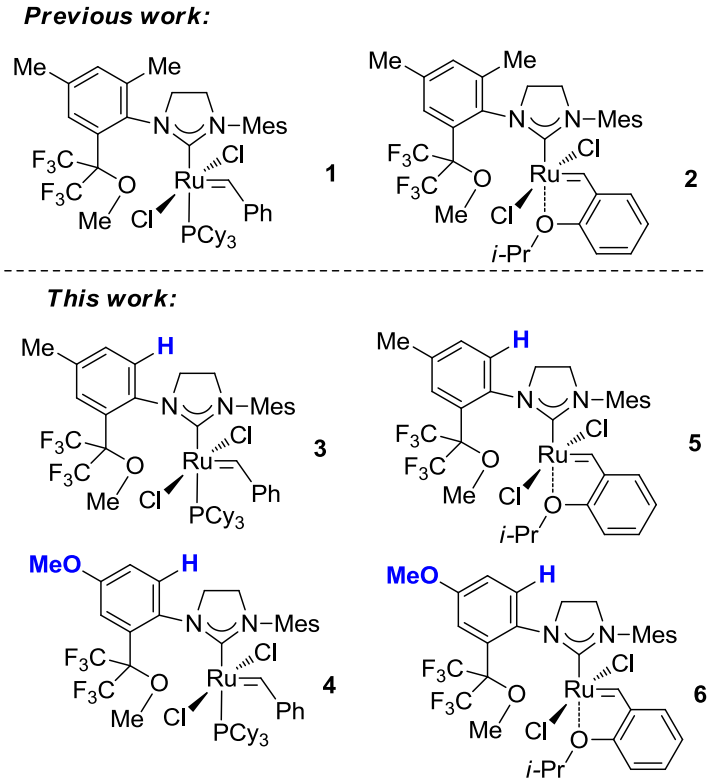
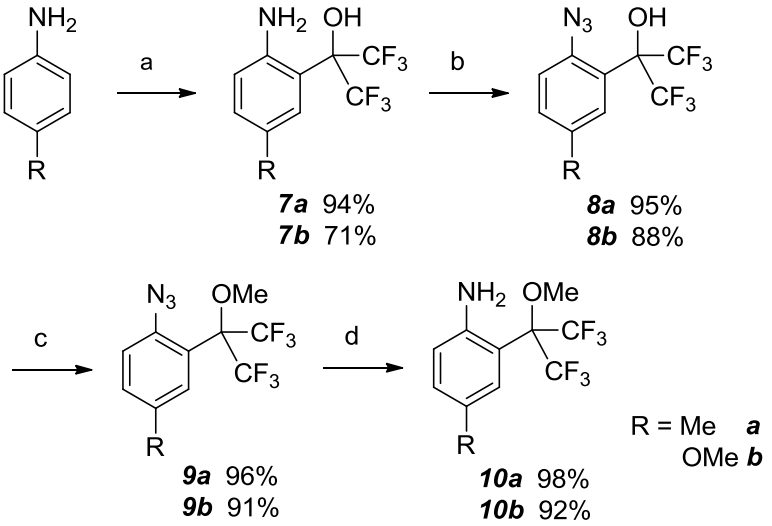


Figure 2

Results and discussion

First, we directed our efforts towards the synthesis of the mono-substituted anilines **10a,b** containing hexafluoroisopropylmethoxy group in the *ortho*-position. For this purpose the commercially available *para*-toluidine and *para*-anisidine were heated with excess of hexafluoroacetone (HFA) hydrate under acid catalysis according to previously elaborated for 2,4-dimethyl derivative protocol [93] to give the corresponding anilines **7a,b** in good to excellent yields. To perform the selective *O*-methylation, they were first transformed into azides **8a,b** *via* successive treatments with sodium nitrite and azide, and then, **8a,b** were methylated with methyl iodide under basic conditions to afford *O*-protected azides **9a,b**. Finally, the reduction of azido group of **9** was performed with sodium borohydride under cobalt dichloride-catalysis in the

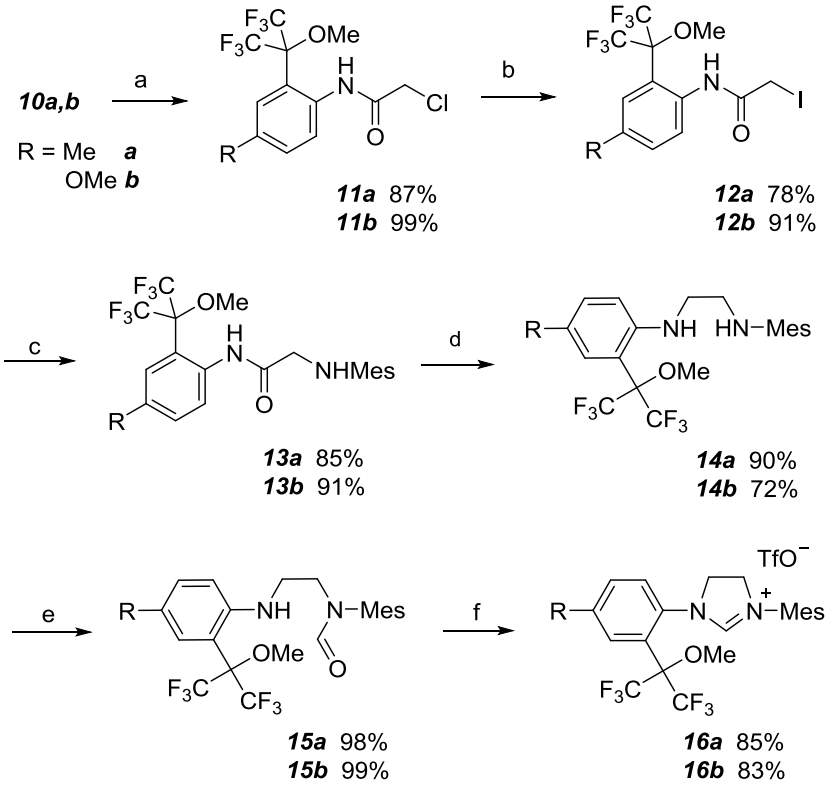
presence of cetyltrimethylammonium bromide to stabilize catalytic Co-species leading to excellent yields of anilines **10a,b** (Scheme 1).



(a) HFA·1.5H_2O, pTSA, 100 °C, 8 h, (b) $NaNO_2$, H_2SO_4, 0 °C, NaN_3, H_2O, rt, 1 h, (c) MeI, K_2CO_3, MeCN, rt, 2 days, (d) $NaBH_4$, $CoCl_2$, CTABr, H_2O/MeOH, rt, 1 h.

Scheme 1

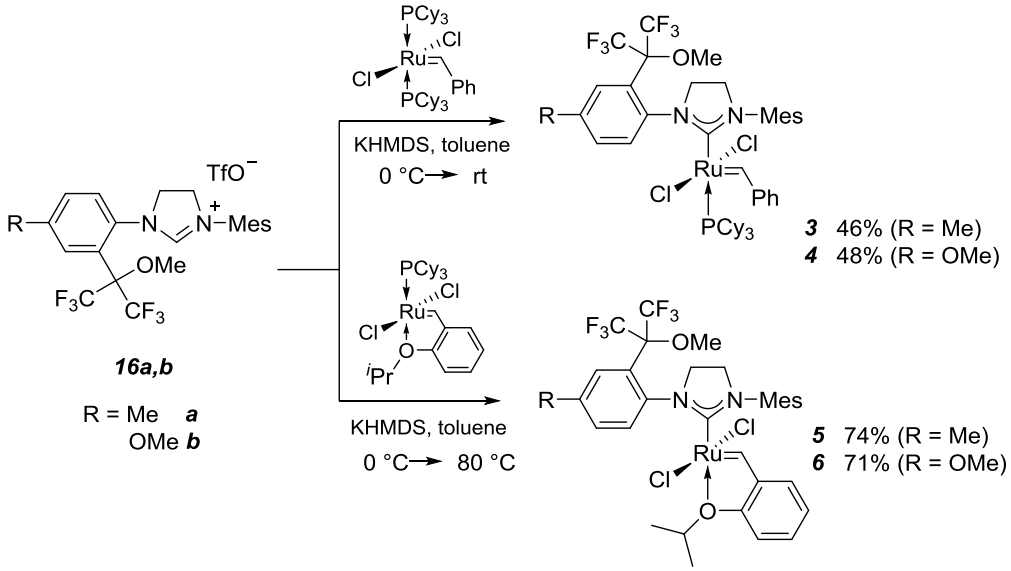
The anilines **10a,b** obtained were further used as the starting materials to construct the desired imidazolinium salts **16a,b.** The synthetic sequence included: (a,b) selective *N*-acylation with chloroacetyl chloride with subsequent halogen exchange with NaI to give the iodides **12a,b** in very good yields for both steps; (c,d) condensation with mesitylamine followed by the reduction of the resulting aminoamides **13a,b** with $BH_3·SMe_2$ to afford the corresponding diamines **14a,b**; and finally (e,f) selective formylation at the more sterically accessible amino group using acetic-formic mixed anhydride followed by heterocyclization *via* the treatment with stoichiometric amounts of triflic acid (TfOH) and triflic anhydride (Tf_2O) to give the target NHC precursors **16a** and **16b** in 85% and 83% yields, respectively (Scheme 2). The last two steps (e,f) were performed using a slightly modified procedure previously developed by us for sterically demanding fluorinated imidazolinium salts [93].



(a) $ClCOCH_2Cl$, AcOH, AcONa, H_2O, rt, 10 min, (b) NaI, acetone, rt, 1 day, (c) $MesNH_2$, rt, 4 days, (d) $BH_3{\cdot}SMe_2$, PhMe, 90 °C, 4 h, (e) AcOCHO, DCM, rt, 5 min., (f) 1. TfOH, rt, 2. Tf_2O, 65 °C, 3. DIPEA, 80 °C, PhMe, 3 h.

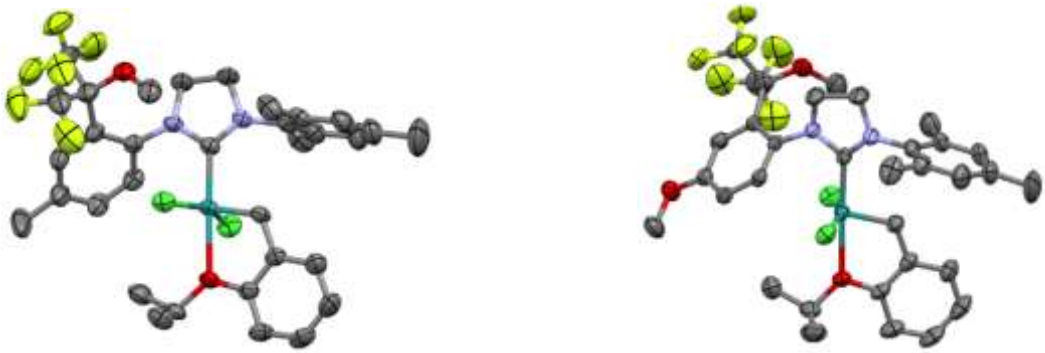
Scheme 2

With these new fluorinated unsymmetrical NHC salts in hand, we prepared the new ruthenium complexes **3**-**6** in moderate to good yields following the conventional route including the reactions of *in situ* generated carbene with commercially available $RuCl_2(PCy_3)_2(=CHPh)$ **G-I** [94] and $RuCl_2(PCy_3)(=CH(o\text{-}^iPrO\text{-}C_6H_4))$ **H-I** [95]. Purification by silica gel chromatography and further recrystallization from a DCM/*n*-pentane mixture afforded dark-brown (**3**, **4**) and dark-green (**5, 6**) air stable solids (Scheme 3).



Scheme 3

The complexes obtained were fully characterized by NMR spectroscopy and elemental analysis. In ^{1}H NMR spectra of both phosphine-containing **3, 4** and phosphine-free **5, 6** complexes measured at room temperature the absorptions of intrinsic benzylidene protons are observed around 19.6 ppm and 16.9 ppm, respectively, as two broad singlets in each case. The doubling of the signals for CF_3-groups takes place in ^{19}F NMR spectra also. This phenomenon could be attributed to the existence of two rotamers due to hindered rotation of bulky fluorinated aryl group around C-N bond. These doublets come together at 60-70 °C under NMR experiment measured in toluene-d_8, which supports the existence of rotamers (see Experimental section). The ^{13}C NMR spectrum of the NHC at 60 °C displays a resonance at 220 ppm for the carbene center, which is in the expected range for aryl-substituted imidazolylidenes (see Experimental section). In addition, single crystals of good quality for X-ray analysis from complexes **5** and **6** (Fig. 3) were obtained by slow diffusion of pentane into a concentrated dichloromethane solution.



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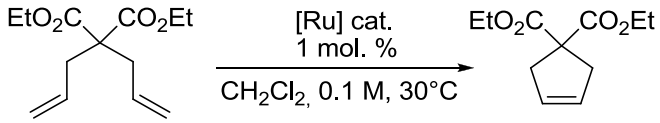
5 **6**

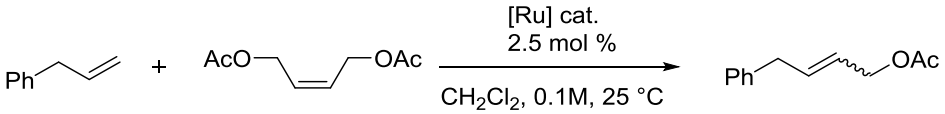
Figure 3. Molecular structure of complexes **5** and **6**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

Catalytic activities of the prepared catalysts **3-6** were investigated in RCM reactions with diethyl diallylmalonate (DEDAM) and in CM reaction of allylbenzene with 1,4-diacetoxybut-2-ene following standard protocols for evaluation of olefin metathesis catalysts [71,72]. The commercially available **G-II** and **H-II** catalysts along with previously obtained **1** and **2** were used as reference catalysts to find out how modulating the electronic and steric changes of the fluoroakyl-substituted aryl ring might affect the catalytic activity.

As a result, we found that initiation rates of the Grubbs type catalyst **3**, **4** in RCM of DEDAM were slightly higher as compared to **G-II** and **1** (Figure 4). On the other hand, the initiation rates of Hoveyda type catalysts **5** and **6** have proved to be in between the corresponding **H-II** and **2** rates (Figure 5), exhibiting some significant initiation period (about 10 min) before they could achieve full conversion in longer reaction times (4 h).



In the cross metathesis of allylbenzene with an excess of 1,3-diacetoxybut-2-ene, the phosphine-containing catalysts **3** and **4** revealed slightly higher reactivity as compared with the *ortho,ortho*-disubstituted analogue **1** and close kinetic profiles to **G-I** catalyst (Figure 6). In the case of phosphine-free complexes **5** and **6** these differences in catalytic activity did not exist and the complexes allowed to reach an equilibrium at 70-80% conversion within 30 min (Figure 7).



as compared to **1, G-II** and **H-II**
as compared to **2, G-II** and **H-II**

In all studied reaction, no significant influence of *para*-methoxyaryl substitution on the catalytic activity of complexes could be found.

Conclusions

In conclusion, the synthesis of new metathesis catalysts bearing unsymmetrical fluorinated NHC ligands with hexafluoroisopropylmethoxy group in *ortho*-position of *N*-aryl-substituent have been developed. The effects of mono-*ortho*-arylsubstitution and the replacement of *para*-methyl *N*-aryl group with more electron-donating methoxy group in unsymmetrical fluorinated NHC ligand on the activity of complexes have been evaluated. As a result, the performance of the new Grubbs type catalysts in olefin metathesis has proved to be similar to the classical Grubbs second generation catalyst. On the other hand, the new Hoveyda type catalysts demonstrate a short latent character before reaching full conversion in RCM of diallylmalonate in longer period in comparison to the commercially available Hoveyda-II catalyst equipped with symmetrical H_2IMes carbene ligand. In all cases, the absence of a methyl group at the other *ortho*-position of the hexafluoroisopropylmethoxy *ortho*-substituted aryl group of the unsymmetrical NHC led to faster initial rates with Grubbs type catalyst (**3**, **4** as compared to **1**) and with Hoveyda type catalysts after the initiation period was completed (**5**, **6** as compared to **2**).

Acknowledgments

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Experimental

4.1. General remarks.

All solvents were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Syntheses of ruthenium complexes were performed under an argon atmosphere using a standard Schlenk technique. Analytical TLC was performed

with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light (254 and 366 nm), spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4 or $KMnO_4$ solution in water. Column chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM) and ethyl acetate/petroleum ether. NMR spectra were recorded, unless otherwise stated, at room temperature on Bruker AV-300, AV-400, AV-500, AV-600 spectrometers operating at 300, 400, 500, and 600 MHz for ^1H; 75, 101, 126, and 151 MHz for ^{13}C; 282, 376, 471, and 564 MHz for ^{19}F ($CFCl_3$ as reference), and 121, 162, 202, and 243 MHz for ^{31}P (85% H_3PO_4 as reference). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks.

*4.2. General procedure for synthesis of **7**.*

A mixture of 6-methylaniline or 6-methoxyaniline (46.7 mmol), hexafluoroacetone sesquihydrate (18.6 g, 112.1 mmol), and PTSA (100 mg, 0.5 mmol) was heated at 100°C for 20 h. After cooling to r.t., water (50 mL) was added and a resulting mixture was extracted with EtOAc (3×30 mL). The combined organic layers were washed with H_2O and brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from petroleum ether to yield a dark solid.

*4.2.1. 2-(2-Amino-5-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**7a**).*

Yield: 94%; brown solid; mp 110-113°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.16 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.97 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 5.57 (br.s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 135.3, 131.3, 129.1, 127.4, 123.5 (q, $^1J_{C,F}$ = 288 Hz), 123.0, 80.0 (p, $^2J_{C,F}$ = 30 Hz), 21.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.14 (s). Anal. Calcd for $C_{10}H_9F_6NO$ (%) C, 43.97; H, 3.32; N, 5.13. Found: C, 43.92; H, 3.38; N, 4.90.

*4.2.2. 2-(2-Amino-5-methoxyphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**7b**).*

Yield: 71%; black solid; mp 104-107°C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.04 (d, $^3J_{H,H}$ = 8.7 Hz, 1H), 6.90 (dd, $J_{H,H}$ = 8.7, 2.7 Hz, 1H), 6.08 (br.s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 133.6, 129.4, 125.0, 123.4 (q, $^1J_{C,F}$ = 289 Hz), 115.8, 114.5–114.3 (m), 81.0 – 79.0 (m), 55.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.33 (s). Anal. Calcd for $C_{10}H_9F_6NO_2$ (%) C, 41.53; H, 3.14; N, 4.84. Found: C, 41.57; H, 3.37; N, 4.65.

4.3. *General procedure for synthesis of **8**.*

To a mixture of aniline **7** (20 mmol) in 60 ml of water concentrated sulfuric acid (10.7 mL, 200 mmol) was slowly added. The resulting mixture was cooled to 0°C and solution of $NaNO_2$ (1.59 g, 23.0 mmol) in 6 mL of water was added dropwise and reaction mixture was stirred in an ice bath for 30 min. Then solution of NaN_3 (1.56 g, 24 mmol) in 6 mL of water was added dropwise. After full addition the reaction mixture was allowed to stir at r.t. for 3 hours. Then the reaction mixture was extracted with EtOAc (3×20 mL). Combined organic layer was washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was

purified by flash chromatography using EtOAc/petroleum ether (1:3) as eluent to yield yellowish crystals.

*4.3.1. 2-(2-Azido-5-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**8a**).*

Yield: 95%; mp 64-65°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.33 (d, $^{3}J_{H,H}$= 8.2 Hz, 1H), 7.16 (d, $^{3}J_{H,H}$ = 8.3 Hz, 1H), 7.04 (br.s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 135.4, 132.3, 130.3 (m), 122.7 (q, $^{1}J_{C,F}$= 289 Hz), 119.8, 119.7, 79.9 (p, $^{2}J_{C,F}$ = 30 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.88 (s). Anal. Calcd for $C_{10}H_7F_6N_3O$ (%) C, 40.15; H, 2.36; N, 14.05. Found: C, 39.91; H, 2.39; N, 14.19.

*4.3.2. 2-(2-Azido-5-methoxyphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**8b**).*

Yield: 88%; mp 67-68°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.8 Hz, 2H), 7.19 (s, 1H), 7.07 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.07 (br.s, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 130.3, 122.7 (d, $^{1}J_{C,F}$ = 289 Hz), 121.0, 120.8, 116.9, 115.8 (p, $^{3}J_{C,F}$ = 3 Hz), 79.8 (p, $^{2}J_{C,F}$ = 30 Hz), 55.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.94 (s). Anal. Calcd for $C_{10}H_7F_6N_3O_2$ (%) C, 38.11; H, 2.24; N, 13.33. Found: C, 37.79; H, 2.32; N, 13.45.

*4.4. General procedure for synthesis of **9**.*

A mixture of azide **8** (17.6 mmol), iodomethane (2.2 mL, 35.3 mmol) and anhydrous K_2CO_3 (4.88 g, 35.3 mmol) in 80 mL of acetonitrile was stirred at r.t. for 2 days. After reaction completion the solvent was evaporated under reduced pressure, residual solid was dispersed in EtOAc and filtered. The resulting filtrate was evaporated again and purified by flash chromatography using EtOAc/petroleum ether (1:8) as eluent to yield yellow oil that was crystallized after complete removal of solvent under high vacuum.

*4.4.1. 1-Azido-2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methylbenzene (**9a**).*

Yield: 96%; mp 51-52°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.33 (d, $^{3}J_{H,H}$ = 8.3 Hz, 1H), 7.21 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H), 3.46 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.0, 132.6, 131.8, 122.6 (q, $^{1}J_{C,F}$ = 292 Hz), 120.7, 118.2, 84.3 (p, $^{2}J_{C,F}$ = 29 Hz), 54.6, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.86 (s). Anal. Calcd for $C_{11}H_9F_6N_3O$ (%) C, 42.18; H, 2.90; N, 13.42. Found: C, 42.35; H, 3.11; N, 13.72.

*4.4.2. 1-Azido-2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methoxybenzene (**9b**).*

Yield: 91%; mp 52-53°C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.25 (d, $^{3}J_{H,H}$ = 8.8 Hz, 1H), 7.13 (s, 1H), 7.07 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.83 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 156.8, 132.2, 122.5 (q, $^{1}J_{C,F}$ = 291 Hz), 122.0, 119.6, 117.5-117.3 (m), 117.1, 84.9-83.4 (m), 55.8, 54.7; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -69.87 (s). Anal. Calcd for $C_{11}H_9F_6N_3O_2$ (%) C, 40.13; H, 2.76; N, 12.76. Found: C, 40.41; H, 2.83; N, 12.97.

*4.5. General procedure for synthesis of **10**.*

The azide **9** (13.8 mmol) was dissolved in 4.3 ml of methanol, then $CoCl_2 \cdot 6H_2O$ (290 mg, 1.4 mmol) and cetyltrimethylammonium bromide (CTABr) (426 mg, 1.4 mmol) were added with stirring at r.t. Then a solution of $NaBH_4$ (1.04 g, 27.6 mmol) in 26 ml of water was added dropwise. After full addition the reaction mixture was stirred another 30 min and extracted with Et_2O (3×15 ml). Combined organic layer was washed with 10 ml of water, filtered through cotton wool and evaporated under reduced pressure to yield yellow crystals.

*4.5.1. 2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylaniline (**10a**).*

Yield: 98%; mp 61-63°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.06 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 6.65 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 4.56 (br.s, 2H), 3.56 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 132.1, 130.1 (p, $^3J_{C,F}$ = 2.1 Hz), 127.5, 123.0(q, $^1J_{C,F}$ = 292 Hz), 118.9, 109.4, 85.3 (p, $^2J_{C,F}$ = 28 Hz), 54.8, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.84 (s). Anal. Calcd for $C_{11}H_{11}F_6NO$ (%) C, 46.00; H, 3.86; N, 4.88. Found: C, 45.92; H, 3.97; N, 5.03.

*4.5.2. 2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyaniline (**10b**).*

Yield: 92%; mp 51-53°C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.88 (s, 1H), 6.88 (d, $^3J_{H,H}$ = 9.4 Hz, 1H), 6.69 (d, $^3J_{H,H}$ = 9.4 Hz, 1H), 4.42 (br.s, 2H), 3.75 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 140.4, 123.0 (q, $^1J_{C,F}$ = 292 Hz), 120.0, 118.0, 115.3–115.1 (m), 110.3, 85.9–84.3 (m), 55.9, 54.9; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -69.87 (s). Anal. Calcd for $C_{11}H_{11}F_6NO_2$ (%) C, 43.57; H, 3.66; N, 4.62. Found: C, 43.89; H, 4.01; N, 4.64.

*4.6. General procedure for synthesis of **11**.*

Aniline **10** (10.6 mmol) was added to 6 mL of glacial acetic acid in a round-bottomed flask followed by chloroacetyl chloride (870 µL, 10.9 mmol) and 10.4 mL of half-saturated aqueous sodium acetate. Precipitation of the amide was observed in 10 min. The product is stirred thoroughly with 10 mL of cold water and isolated by filtration. Solid product was dissolved in ethyl acetate and washed with saturated aqueous $NaHCO_3$ and brine, dried above $MgSO_4$. Then solvent was removed under reduced pressure, resulting solid residue was recrystallized in petroleum ether to yield a white solid.

*4.6.1. 2-Chloro-N-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]acetamide (**11a**).*

Yield: 87%; mp 70-71°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.43 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 7.32 (d, $^3J_{H,H}$ = 8.6 Hz, 1H), 7.29 (s, 1H), 4.19 (s, 2H), 3.54 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 134.9, 134.8, 132.2, 130.2 (m), 123.21 (s), 122.5 (q, $^1J_{C,F}$ = 290 Hz), 114.8, 85.1 (p, $^2J_{C,F}$ = 28.6 Hz), 54.7, 43.2, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.57 (s). Anal. Calcd for $C_{13}H_{12}ClF_6NO_2$ (%) C, 42.93; H, 3.33; N, 3.85. Found: C, 43.11; H, 3.67; N, 4.12.

*4.6.2. 2-Chloro-N-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]acetamide (**11b**).*

Yield: 99%; mp 101-102°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.41 (d, $^{3}J_{H,H}$ = 9.9 Hz, 1H), 7.05 (d, $^{3}J_{H,H}$ = 9.9 Hz, 1H), 7.06 (s, 1H), 4.19 (s, 2H), 3.82 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 156.4, 130.1, 125.0, 122.5 (q, $^{1}J_{C,F}$ = 289 Hz), 116.7, 116.4–116.1 (m), 115.9, 84.9 (p, $^{2}J_{C,F}$ = 29 Hz), 55.7, 54.8, 43.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.63 (s). Anal. Calcd for $C_{13}H_{12}ClF_6NO_3$ (%) C, 41.12; H, 3.19; N, 3.69. Found: C, 41.10; H, 3.22; N, 3.43.

*4.7. General procedure for synthesis of **12**.*

Chloroacetamide **11** (9.18 mmol) was dissolved in acetone (90 mL), and then sodium iodide (3.44 g, 23.0 mmol) was added. The reaction mixture was stirred at r.t. for 24 h. After filtration, the mother liquor was concentrated, and the residue was dissolved in EtOAc (20 mL) and washed with a 5% solution of $Na_2S_2O_3$ (10 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). Combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was recrystallized from petroleum ether to yield a brown solid.

*4.7.1. N-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-2-iodoacetamide (**12a**).*

Yield: 78%; mp 98-99°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.33 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 7.31 (d, $^{3}J_{H,H}$ = 8.6 Hz, 1H), 3.84 (s, 2H), 3.58 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 135.2, 134.7, 132.2, 130.1, 123.4, 122.6 (q, $^{1}J_{C,F}$ = 292 Hz), 114.6, 85.1 (p, $^{2}J_{C,F}$ = 28.6 Hz), 54.9, 21.2, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.40 (s). Anal. Calcd for $C_{13}H_{12}F_6INO_2$ (%) C, 34.31; H, 2.66; N, 3.08. Found: C, 34.03; H, 2.69; N, 2.78.

*4.7.2. N-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-2-iodoacetamide (**12b**).*

Yield: 91%; mp 87-88°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.31 (d, $^{3}J_{H,H}$ = 8.9 Hz, 1H), 7.04 (d, *J* = 9.1 Hz, 1H), 7.03 (s, 1H), 3.84 (s, 2H), 3.81 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 156.3, 130.5, 125.3, 122.5 (q, $^{1}J_{C,F}$ = 290. Hz), 116.6, 116.2, 115.9, 84.9 (p, $^{2}J_{C,F}$ = 29 Hz), 55.7, 54.9, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.46 (s). Anal. Calcd for $C_{13}H_{12}F_6INO_3$ (%) C, 33.14; H, 2.57; N, 2.97. Found: C, 33.10; H, 2.72; N, 3.18.

*4.8. General procedure for synthesis of **13**.*

A mixture of **12** (4.4 mmol) and mesitylamine (9.3 mL, 65.9 mmol) was stirred at r.t. for 4 days. After reaction completion, the mixture was treated with a 10% solution of $NaHCO_3$ (60 mL) and extracted with EtOAc (3×30 mL). Combined organic layers were washed with brine and water and then dried over $MgSO_4$ and concentrated under reduced pressure. The excess of $MesNH_2$ was removed at 70°C/0.05 mmHg. The residual solid was recrystallized from petroleum ether to yield the corresponding aminoacetamide **7** as a white solid.

*4.8.1. N-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-2-(mesitylamino)-acetamide (**13a**).*

Yield: 85%; mp 160-161°C; ^{1}H NMR (400 MHz, acetone-d_6) δ 10.12 (s, 1H), 8.58 (d, $^{3}J_{H,H}$ = 8.6 Hz, 1H), 7.40 (d, $^{3}J_{H,H}$ = 8.6 Hz, 1H), 7.33 (s, 1H), 6.82 (s, 2H), 4.25 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 3.74 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2H), 3.59 (s, 3H), 2.38 (s, 3H), 2.30 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ 170.3, 143.6, 137.0, 134.5, 132.8, 132.5, 130.5, 130.4, 124.3, 123.6 (d, $^{1}J_{C,F}$ = 291 Hz), 114.9, 85.9 (p, $^{2}J_{C,F}$ = 28 Hz), 55.4, 53.8, 20.9, 20.6, 18.4; ^{19}F NMR (376 MHz, acetone-d_6) δ -69.99 (s). Anal. Calcd for $C_{22}H_{24}F_6N_2O_2$ (%) C, 57.14; H, 5.23; N, 6.06. Found: C, 57.17; H, 5.23; N, 5.71.

*4.8.2. N-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-2-(mesitylamino)-acetamide (**13b**).*

Yield: 91%; mp 137-138°C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.93 (s, 1H), 8.53 (d, $^{3}J_{H,H}$ = 9.2 Hz, 1H), 7.21 (dd, J = 9.2, 2.8 Hz, 1H), 7.02 (s, 1H), 6.82 (s, 2H), 4.24 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1H), 3.85 (s, 3H), 3.73 (d, $^{3}J_{H,H}$ = 7.9 Hz, 2H), 3.59 (s, 3H), 2.30 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ 170.1, 156.7, 143.7, 132.5, 132.2, 130.5, 130.4, 126.5, 123.5 (q, $^{1}J_{C,F}$ = 292 Hz), 116.8, 116.7, 116.3, 86.5–85.0 (m), 56.0, 55.5, 53.7, 20.6, 18.4; ^{19}F NMR (376 MHz, acetone-d_6) δ -70.06 (s). Anal. Calcd for $C_{22}H_{24}F_6N_2O_3$ (%) C, 55.23; H, 5.06; N, 5.86. Found: C, 55.42; H, 5.03; N, 5.96.

*4.9. General procedure for synthesis of **14**.*

Aminoacetamide **13** (3.46 mmol) was dissolved in anhydrous toluene (30 mL), and $BH_3 \cdot SMe_2$ (15.6 mL of 1 M solution in THF, 15.6 mmol) was added dropwise under an argon atmosphere at r.t. The resulting mixture was stirred at 90°C for 3 h. After cooling to r.t., MeOH was slowly added until ceasing of gas evolution. Then, a 10% solution (60 mL) of HCl was added and resulting mixture was extracted with EtOAc (2×20 mL). The aqueous layer was separated, treated with $NaHCO_3$, and extracted with EtOAc (2×20 mL). Combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether to yield a beige solid.

*4.9.1. N^1-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-N^2-mesitylethane-1,2-diamine (**14a**).*

Yield: 90%; mp 53-54°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, $^{3}J_{H,H}$ = 8.9 Hz, 1H), 7.11 (s, 1H), 6.86 (s, 2H), 6.72 (d, $^{3}J_{H,H}$ = 8.4 Hz, 1H), 5.70 (br.s, 1H), 3.54 (s, 3H), 3.46-3.39 (m, 2H), 3.20 (t, $^{3}J_{H,H}$ = 5.9 Hz, 2H), 2.30 (s, 6H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 132.2, 130.8, 130.7, 129.7, 125.6, 123.0 (q, $^{1}J_{C,F}$ = 293 Hz), 112.8, 108.7, 85.7 (p, $^{1}J_{C,F}$ = 28.3 Hz), 54.6, 48.1, 44.7, 20.7, 20.6, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.46 (s). Anal. Calcd for $C_{22}H_{26}F_6N_2O$ (%) C, 58.92; H, 5.84; N, 6.25. Found: C, 58.81; H, 5.87; N, 5.96.

*4.9.2. N^1-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-N^2-mesitylethane-1,2-diamine (**14b**).*

Yield: 72%; mp 56-57°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, $^3J_{H,H}$ = 8.9 Hz, 1H), 6.95 (s, 1H), 6.86 (s, 2H), 6.76 (d, $^3J_{H,H}$ = 8.8 Hz, 1H), 5.54 (s, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 3.37 (dd, $^3J_{H,H}$ = 10.9, 5.3 Hz, 2H), 3.19 (t, $^3J_{H,H}$ = 5.8 Hz, 2H), 2.93 (br.s, 1H), 2.29 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 143.1, 142.9, 132.3, 130.7, 129.7, 122.9 (q, $^1J_{C,F}$ = 292 Hz), 117.5, 116.5, 113.9, 109.6, 85.6 (p, $^2J_{C,F}$ = 28 Hz), 56.0, 54.8, 48.1, 45.5, 20.7, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.50 (s). Anal. Calcd for $C_{22}H_{26}F_6N_2O_2$ (%) C, 56.89; H, 5.64; N, 6.03. Found: C, 57.08; H, 5.65; N, 6.15.

*4.10. General procedure for synthesis of **15**.*

Acetic formic anhydride (360 µL, 4.13 mmol) was added dropwise to the solution of **14** (2.06 mmol) in CH_2Cl_2 (13 mL). After homogenization, the reaction mixture was allowed to stir for 30 min at r.t. Then, 40 mL of water was added and the mixture was extracted with CH_2Cl_2 (2×30 mL). Combined organic layers were washed with a saturated solution of $NaHCO_3$ and water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc/petroleum ether (1:4) as eluent to yield colorless oil.

*4.10.1. N-(2-{[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]amino}ethyl)-N-mesitylformamide (**15a**).*

Yield: 98%; mp 101-102°C; mixture of two rotamers 85:15, signals of major product are given: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.13 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 7.10 (s, 1H), 6.97 (s, 2H), 6.75 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 5.80 (br.s, 1H), 3.81 (t, $^3J_{H,H}$ = 7.0 Hz, 2H), 3.52 (s, 3H), 3.37 (t, $^3J_{H,H}$ = 7.0 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 145.3, 138.7, 136.6, 136.0, 132.4, 130.6, 129.9, 126.2, 123.0 (q, $^1J_{C,F}$ = 292 Hz), 113.1, 109.3, 86.5–84.7 (m), 54.7, 45.7, 42.6, 21.0, 20.6, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.55 (s). Anal. Calcd for $C_{23}H_{26}F_6N_2O_2$ (%) C, 57.98; H, 5.50; N, 5.88. Found: C, 57.69; H, 5.63; N, 6.04.

*4.10.2. N-(2-{[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]amino}ethyl)-N-mesitylformamide (**15b**).*

Yield: 99%; mp 115-116°C; mixture of two rotamers 90:10, signals of major product are given: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 6.97 (s, 2H), 6.95 (d, $^3J_{H,H}$ = 9.2 Hz, 1H), 6.91 (s, 1H), 6.81 (d, $^3J_{H,H}$ = 9.0 Hz, 1H), 5.84 (br.s, 1H), 3.80 (t, $^3J_{H,H}$ = 7.0 Hz, 2H), 3.74 (s, 3H), 3.52 (s, 3H), 3.36 (t, $^3J_{H,H}$ = 7.0 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 151.2, 141.8, 138.7, 136.6, 136.0, 129.9, 122.9 (q, $^1J_{C,F}$ = 293 Hz), 117.6, 116.6, 114.3, 110.2, 85.5 (p, $^2J_{C,F}$ = 28 Hz), 56.0, 54.8, 45.8, 43.0, 21.0, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.61 (s). Anal. Calcd for $C_{23}H_{26}F_6N_2O_3$ (%) C, 56.10; H, 5.32; N, 5.69. Found: C, 56.11; H, 5.55; N, 5.91.

*4.11. General procedure for synthesis of **16**.*

Triflic acid (180 µL, 2.0 mmol) was added to the solution of **15** (2.0 mmol) in toluene (50 mL), and the mixture was stirred at r.t. for 15 min. Then, triflic anhydride (340 µL, 2.0 mmol) was added, and the reaction mixture was heated at 65°C for 1.5 h. DIPEA (1.04 mL, 6.0 mmol) was added, and the reaction mixture was heated at 80°C for another 1.5 h. After cooling to r.t., 50 mL of water was added and the mixture was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried using $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether to yield a beige solid.

*4.11.1. 1-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-3-mesityl-4,5-dihydro-1H-imidazol-3-ium triflate (**16a**).*

Yield: 85%; mp 167-169°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.74 (d, $^3J_{H,H}$ = 8.1 Hz, 1H), 7.53 (s, 1H), 7.46 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.95 (s, 2H), 4.64 (t, $^3J_{H,H}$ = 10.6 Hz, 2H), 4.40 (t, $^3J_{H,H}$ = 10.6 Hz, 2H), 3.61 (s, 3H), 2.44 (s, 3H), 2.34 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.9, 141.0, 135.1, 133.9, 132.3, 132.0, 131.6, 130.2, 130.1, 125.0, 122.3 (q, $^1J_{C,F}$ = 290 Hz), 120.7 (q, $^1J_{C,F}$ = 320 Hz), 84.2–82.8 (m), 55.7, 55.1, 51.8, 21.6, 21.1, 17.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.24 (s, 6F), -78.59 (s, 3F). Anal. Calcd for $C_{24}H_{25}F_9N_2O_4S$ (%) C, 47.37; H, 4.14; N, 4.60. Found: C, 47.61; H, 4.14; N, 4.58.

*4.11.2. 1-[2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-3-mesityl-4,5-dihydro-1H-imidazol-3-ium triflate (**16b**).*

Yield: 83%; mp 171-173°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.85 (d, $^3J_{H,H}$ = 8.7 Hz, 1H), 7.25 (s, 1H), 7.15 (dd, $J_{H,H}$ = 8.7, 2.6 Hz, 1H), 6.95 (s, 2H), 4.61 (t, $^3J_{H,H}$ = 10.5 Hz, 2H), 4.39 (t, $^3J_{H,H}$ = 10.4 Hz, 2H), 3.84 (s, 3H), 3.61 (s, 3H), 2.34 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.9, 141.0, 135.1, 133.9, 130.2, 130.1, 126.9, 126.7, 122.3 (q, $^1J_{C,F}$ = 291 Hz), 120.7 (q, $^1J_{C,F}$ = 320 Hz), 118.3, 116.8, 84.2-82.6 (m), 56.0, 55.8, 55.1, 51.8, 21.1, 17.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.27 (s, 6F), -78.55 (s, 3F). Anal. Calcd for $C_{24}H_{25}F_9N_2O_5S$ (%) C, 46.16; H, 4.03; N, 4.49. Found: C, 46.21; H, 4.06; N, 4.51.

*4.12. General procedure for synthesis of Grubbs-type catalysts **3** and **4**.*

In a flame-dried Schlenk flask, imidazolinium salt **16** (0.49 mmol) was mixed with 20 mL of anhydrous toluene. The resulting mixture was cooled to 0°C and degassed three times, and then KHMDS (1 mL of 0.5 M solution in toluene, 0.50 mmol) was added to the mixture under an argon atmosphere. The reaction mixture was stirred for 30 min at r.t.; then Grubbs' catalyst **G-I** (0.33 g, 0.40 mmol) was added and mixture was stirred for 2 h. During this time, the reaction mixture changed color from violet to red-brown. Once complete (TLC-control), solvents were removed from the reaction mixture under reduced pressure, and the resulting substance was purified by column chromatography in a gradient manner using EtOAc/petroleum ether (1:8−1:3) as eluent

under an argon atmosphere. The resulting solid was recrystallized from MeOH to yield **11** as a brown solid.

*4.12.1. Benzylidene(dichloro){1-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-3-mesityl-4,5-dihydroimidazol-2-ylidene}(triphenylphosphine)ruthenium(II) (**3**).*

Yield: 46%; mixture of two rotamers 4:1 at 60°C, signals of major product are given: ^{1}H NMR (400 MHz, toluene-d_8, 60°C) δ 19.62 (s, 1H, C*H*Ar), 9.47 (d, $J_{H,H}$ = 7.9 Hz, 1H, Ar*H*), 8.25 (s, 1H, Ar*H*), 7.74 (s, 1H, Ar*H*), 7.35 (d, $J_{H,H}$ = 7.5 Hz, 1H, Ar*H*), 7.20-7.10 (m, 2H, Ar*H*), 6.94-6.72 (m, 2H, Ar*H*), 6.34 (br.s, 1H, Ar*H*), 6.01 (m, 1H, Ar*H*), 4.43 (s, 1H, CH_2CH$_2$), 4.12 (s, 3H, C(CF$_3$)$_2$OCH_3), 3.78 (s, 1H, CH_2CH$_2$), 3.39 (s, 1H, CH_2CH$_2$), 3.24 (s, 1H, CH_2CH$_2$), 2.48 (s, , CH_3), 2.74-0.92 (m, 42H, PCy$_3$, CH_3); ^{13}C NMR (126 MHz, toluene-d_8, 60°C) δ 298.2, 223.4, 152.4, 139.6, 142.2, 138.9, 138.7, 137.0, 136.7, 135.4, 131.9 (br.s), 130.6, 130.4, 129.7, 129.5, 128.3, 123.6 (q, $^{1}J_{C,F}$ = 289 Hz), 123.4 (q, $^{1}J_{C,F}$ = 290 Hz), 117.6, 117.3, 85.6-84.1 (m), 58.5, 54.9, 52.2, 29.8, 29.5, 29.4, 28.1-28.0 (m), 26.8, 21.0, 19.3, 19.0; ^{19}F NMR (376 MHz, toluene-d_8, 60°C) δ -65.29 (br.s, 3F), -71.15 (br.s, 3F); ^{31}P NMR (202 MHz, toluene-d_8, 60°C) δ 24.2 (s). Anal. Calcd for $C_{48}H_{63}Cl_2F_6N_2OPRu$ (%) C, 57.60; H, 6.34; N, 2.80. Found: C, 57.39; H, 6.47; N, 2.84.

*4.12.2. Benzylidene(dichloro){1-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-3-mesityl-4,5-dihydroimidazol-2-ylidene}(triphenylphosphine)ruthenium(II) (**4**).*

Yield: 48%; mixture of two rotamers 4:1 at 50°C, signals of major product are given: ^{1}H NMR (400 MHz, toluene-d_8, 50°C) δ 19.59 (s, 1H, C*H*Ar), 9.62 (br.s, 1H, Ar*H*), 9.47 (br.s, 1H, Ar*H*), 7.61 (s, 1H, Ar*H*), 7.21 (t, $J_{H,H}$ = 7.3 Hz, 1H, Ar*H*), 7.12 (dd, $J_{H,H}$ = 8.8, 2.6 Hz, 1H, Ar*H*), 7.08-6.86 (m, 4H, Ar*H*), 6.54 (br.s, 1H, Ar*H*), 4.39 (br.s, 1H, CH_2CH$_2$), 4.10 (s, 3H, C(CF$_3$)$_2$OCH_3), 3.76 (br.s, 1H, CH_2CH$_2$), 3.43 (s, 3H, ArOCH_3), 3.38 (br.s, 1H, CH_2CH$_2$), 3.25 (s, 1H, CH_2CH$_2$), 2.77-0.81 (m, 42H, PCy$_3$, CH_3); ^{13}C NMR (126 MHz, toluene-d_8, 50°C) δ 298.2, 223.3, 159.3, 152.4, 139.8, 138.9, 138.7, 137.0, 136.7, 135.4, 132.0 (br.s), 130.6, 130.4, 129.7, 129.5, 128.3, 123.63 (q, $^{1}J_{C,F}$ = 284 Hz), 123.58 (q, $^{1}J_{C,F}$ = 288 Hz), 117.6, 117.3, 85.4-84.1 (m), 58.5, 56.3, 54.9, 52.2, 29.8, 29.4, 28.2-28.1 (m), 26.8, 21.0, 19.3, 18.9; ^{19}F NMR (471 MHz, toluene-d_8, 50°C) δ -65.50 (br.s, 3F), -71.13 (br.s,, 3F); ^{31}P NMR (202 MHz, toluene-d_8, 50°C) δ 24.6 (s). Anal. Calcd for $C_{48}H_{63}Cl_2F_6N_2O_2PRu$ (%) C, 56.69; H, 6.24; N, 2.75. Found: C, 56.68; H, 6.42; N, 2.77.

*4.13. General procedure for synthesis of Hoveyda-Grubbs-type catalysts **5** and **6**.*

In a flame-dried Schlenk flask, imidazolinium salt **16** (0.40 mmol) was mixed with 9 mL of anhydrous toluene. The resulting mixture was cooled to 0°C and degassed three times; then KHMDS (840 µL of 0.5 M solution in toluene, 0.42 mmol) was added to the mixture under an argon atmosphere. The reaction mixture was stirred for 30 min at r.t.; then Hoveyda-Grubbs catalyst first generation **H-I** (0.20 g, 0.30 mmol) was added and mixture was stirred for 40 min at 80°C. During this time, the reaction mixture changed color from brown to dark green. Once

complete, solvents were removed from the reaction mixture under reduced pressure, and the resulting substance was purified by column chromatography using EtOAc/petroleum ether (1:3) as eluent to yield. Hoveyda-type catalyst as a green solid. Suitable for X-ray crystals of **5** and **6** were grown by slow diffusion of hexane vapors in CH_2Cl_2 solution.

*4.13.1. Dichloro{1-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methylphenyl]-3-mesityl-4,5-dihydroimidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (**5**).*

Yield: 74%; ^{1}H NMR (500 MHz, toluene-d_8, 80°C) δ 16.91 (s, 1H, C*H*Ar), 9.14 (br.s, 1H, Ar*H*), 7.78 (s, 1H, Ar*H*), 7.21 (br.s, 1H, Ar*H*), 7.10 (m, 1H, Ar*H*), 6.94 (dd, $J_{H,H}$ = 7.5, 1.1 Hz, 1H, Ar*H*), 6.89 (s, 1H, Ar*H*), 6.82 (s, 1H, Ar*H*), 6.59 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, Ar*H*), 6.43 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, Ar*H*), 4.56 (hept, $^3J_{H,H}$ = 6.3 Hz, 1H, O^{i}Pr, C*H*), 4.51 (m, 1H, H_2I CH_2CH_2), 3.86 (s, 3H, C(CF_3)$_2$OCH_3), 3.69 (q, $J_{H,H}$ = 9.9 Hz, 1H, H_2I CH_2CH_2), 3.48 (q, $J_{H,H}$ = 9.9 Hz, 1H, H_2I CH_2CH_2), 3.42 (q, $J_{H,H}$ = 9.3 Hz, 1H, H_2I CH_2CH_2), 2.51 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.39 (s, 3H, O^{i}Pr CH_3), 1.31 (d, $^3J_{H,H}$ = 6.1 Hz, 3H, O^{i}Pr CH_3); ^{13}C NMR (126 MHz, toluene-d_8, 80°C) δ 294.0, 216.8, 153.3, 145.6, 142.4, 138.8, 138.7, 137.8, 134.1 (br.s), 130.4, 130.1, 130.0, 129.5, 123.8 (q, $^2J_{C,F}$ = 289 Hz), 123.4 (q, $^2J_{C,F}$ = 289 Hz), 122.4, 122.3, 113.4, 85.4 (hept, $^1J_{C,F}$ = 27 Hz), 75.1, 58.0, 54.6 (br.s), 53.1 (br.s), 22.4, 22.2, 22.1, 21.9; ^{19}F NMR (471 MHz, toluene-d_8, 60°C) δ -65.6 (br.s, 3F), -71.7 (br.s, 3F). Anal. Calcd for $C_{33}H_{36}Cl_2F_6N_2O_2Ru$ (%) C, 50.90; H, 4.66; N, 3.60. Found: C, 50.78; H, 4.89; N, 3.42. CCDC 1543696 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

*4.13.2. Dichloro{1-[2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4-methoxyphenyl]-3-mesityl-4,5-dihydroimidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (**6**).*

Yield: 71%; ^{1}H NMR (500 MHz, toluene-d_8, 80°C) δ 16.92 (br.s, 1H, C*H*Ar), 9.13 (br.s, 1H, Ar*H*), 7.61 (s, 1H, Ar*H*), 7.10 (m, 1H, Ar*H*), 6.98 (dd, $J_{H,H}$ = 1.5, 7.4 Hz, 1H, Ar*H*), 6.92 (br.s, 1H, Ar*H*), 6.89 (s, 1H, Ar*H*), 6.83 (s, 1H, Ar*H*), 6.58 (t, $^3J_{H,H}$ = 7.4 Hz, 1H), 6.42 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, Ar*H*), 4.56 (hept, $^3J_{H,H}$ = 6.1 Hz, 1H, O^{i}Pr C*H*), 4.48 (td, $J_{H,H}$ = 9.6, 3.2 Hz, 1H, H_2I CH_2CH_2), 3.85 (s, 3H, C(CF_3)$_2$OCH_3), 3.70 (m, 1H, H_2I CH_2CH_2), 3.48 (m, 1H, H_2I CH_2CH_2), 3.40 (m, 1H, H_2I CH_2CH_2), 3.38 (s, 3H, ArOCH_3), 2.52 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.32 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, O^{i}Pr CH_3); ^{13}C NMR (126 MHz, toluene-d_8, 80°C) δ 294.0, 216.8, 159.7, 153.3, 145.7, 138.8, 138.7, 137.8, 134.7 (br.s), 130.4, 130.1, 129.5, 129.1, 123.8 (q, $^1J_{C,F}$ = 293 Hz), 123.4 (q, $^1J_{C,F}$ = 289 Hz), 122.4, 122.3, 113.4, 85.3 (hept, $^1J_{C,F}$ = 27 Hz), 75.1, 58.0, 55.4, 54.8 (br.s), 53.0 (br.s), 22.3, 22.2, 22.1, 21.9; ^{19}F NMR (282 MHz, toluene-d_8, 60°C) δ -65.89, -70.73. Anal. Calcd for $C_{33}H_{36}Cl_2F_6N_2O_3Ru$ (%) C, 49.88; H, 4.57; N, 3.53. Found: C, 49.91; H, 4.52; N, 3.27. CCDC 1543695 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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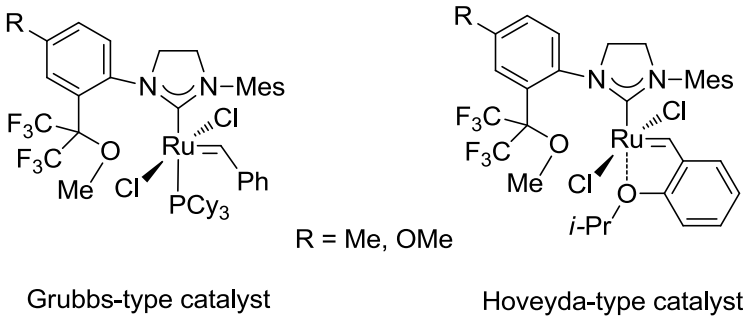
Graphical abstract:



Grubbs-type catalyst

Hoveyda-type catalyst

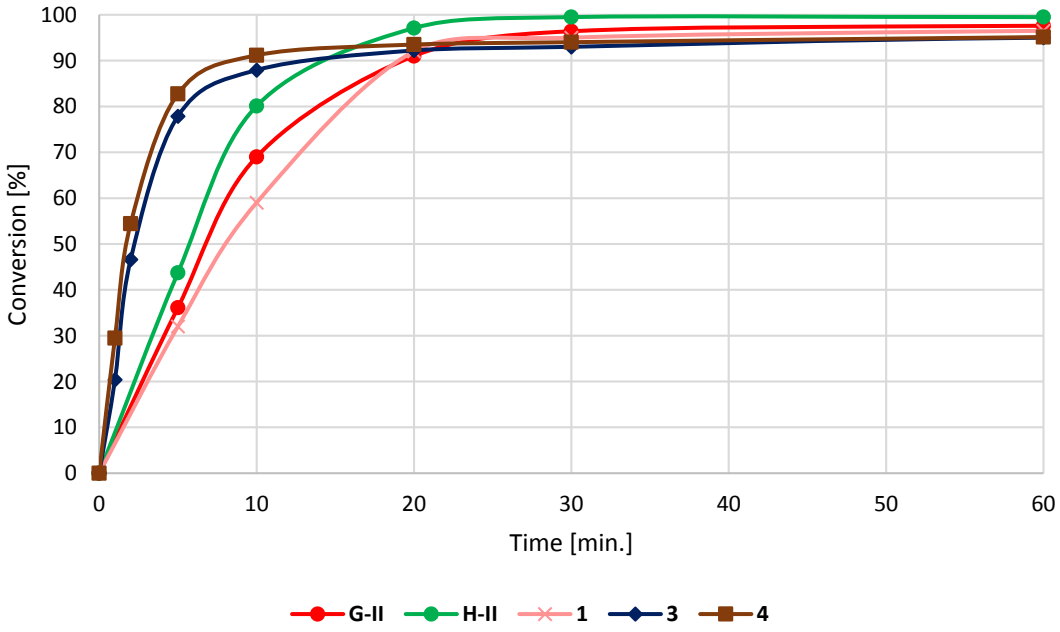


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Figure 4. RCM of DEDAM with catalysts **3**, **4** as compared to **1, G-II** and **H-II**

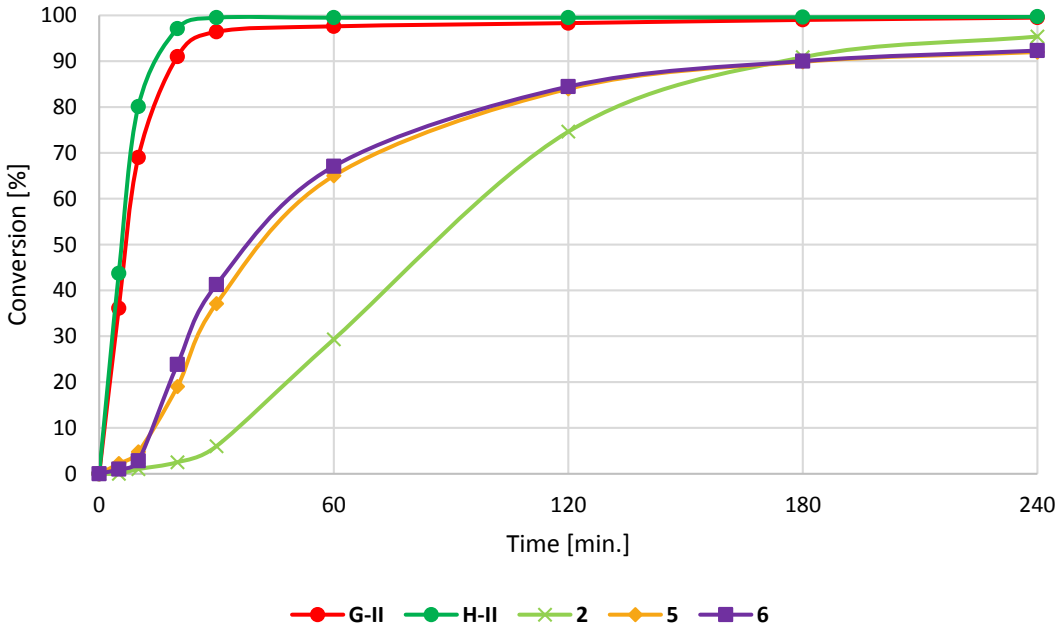

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Figure 5. RCM of DEDAM with catalysts **5**, **6** as compared to **2, G-II** and **H-II**

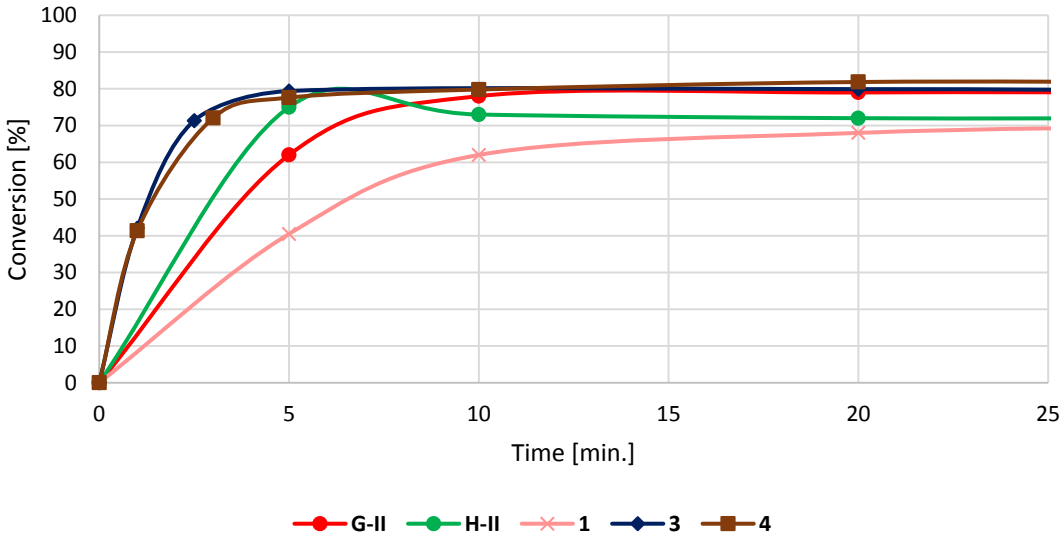

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Figure 6. CM of allylbenzene with 1,3-diacetoxybut-2-ene with catalysts **3, 4**

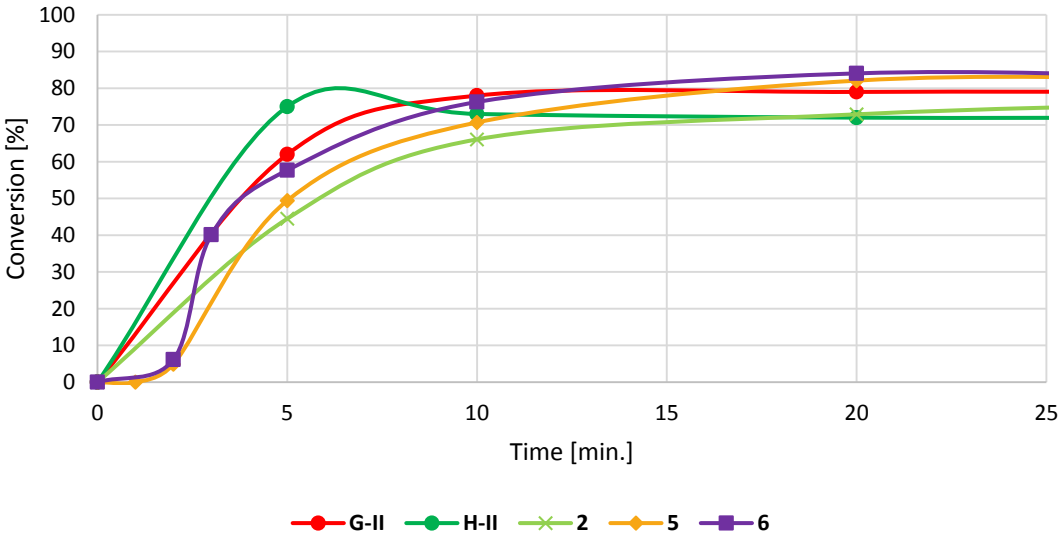

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Figure 7. CM of allylbenzene with 1,3-diacetoxybut-2-ene with catalysts **5, 6**