Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for:

Ammonium NHC-tagged olefin metathesis catalysts – influence of the counter-ion on the catalytic activity

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1. General Information

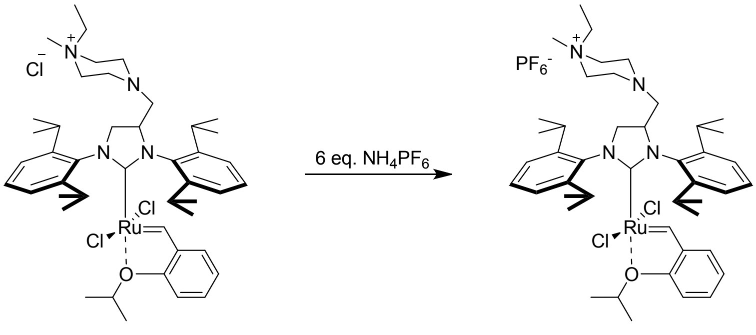
All solvents were ACS grade and used without further purification. DCM and toluene were purchased from VWR. Ethyl Acetate and isopropanol were purchased from Sigma-Aldrich. Cyclopenthyl methyl ether was purchased from Alfa Aesar. DCE was purchased from Roth. All ionic liquids were purchased from Sigma-Aldrich with the following purity: [bmim-Cl] and [bmim-I] 99%, [bmim-BF_4] and [bmim-PF_6] >98.5% (HPLC). No additional treatment was applied to ILs, prior to use.

NMR spectra were recorded on Burker Avance^{TM} 600 Mhz spectrometer in CD_2Cl_2. GC analysis were performed on Perkin Elmer Clarus 680 with FID detector and GL Sciences InertCap 5MS/NP capillary column. High resolution mass spectra was recorded on MaldiSYNAPT G2-S. ICP-MS was analyzed with Perkin Elmer Nexlon 300D.

Catalysts **1a-d**, **2a-b** and **3a** were previously reported[1-3]. Catalysts **1a**, **1d**, **2a**, **2d**, **3a**, **3d**, are commercially available from STREM Chemicals Ltd. Catalysts **4** and **4'** are available from Sigma-Aldrich.

All metathesis substrates and products are known compounds. The identity of metathesis products previously reported by us and authenticated by NMR spectroscopy was confirmed by comparison of GC retention times.

2. Synthesis of catalyst 3d



Solution of ammonium hexafluorophosphate (1.414 g, 8.67 mmol) in 15 ml of water was added under argon to the solution of catalyst **3a** (1.283 g, 1.446 mmol) in dichloromethane (25ml). Reaction mixture was stirred at room temperature for 1h. Aqueous phase was separated and removed. Organic layer was washed with deionized water twice and solvents were evaporated. Catalyst was purified with column chromatography (deactivated aluminum oxide (5% H_2O), MeOH:DCM 5%), recrystallized in DCM/toluene system and dried under reduced pressure. Product was obtained as a pale green powder, 89% yield.

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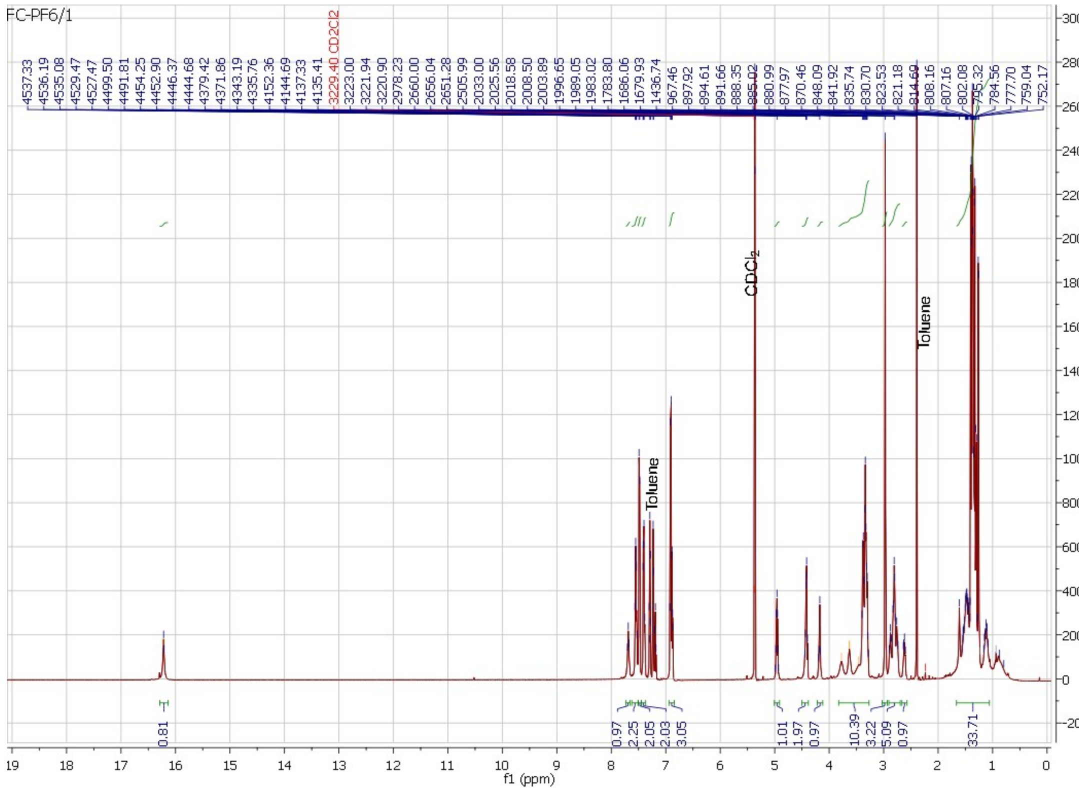
[1] J. Pastva, K. Skowerski, S. J. Czarnocki, N. Zilkova, J. Cejka, Z. Bastl, H. Balcar, *ACS Catal.*, 2014, **4(9)**, 3227.

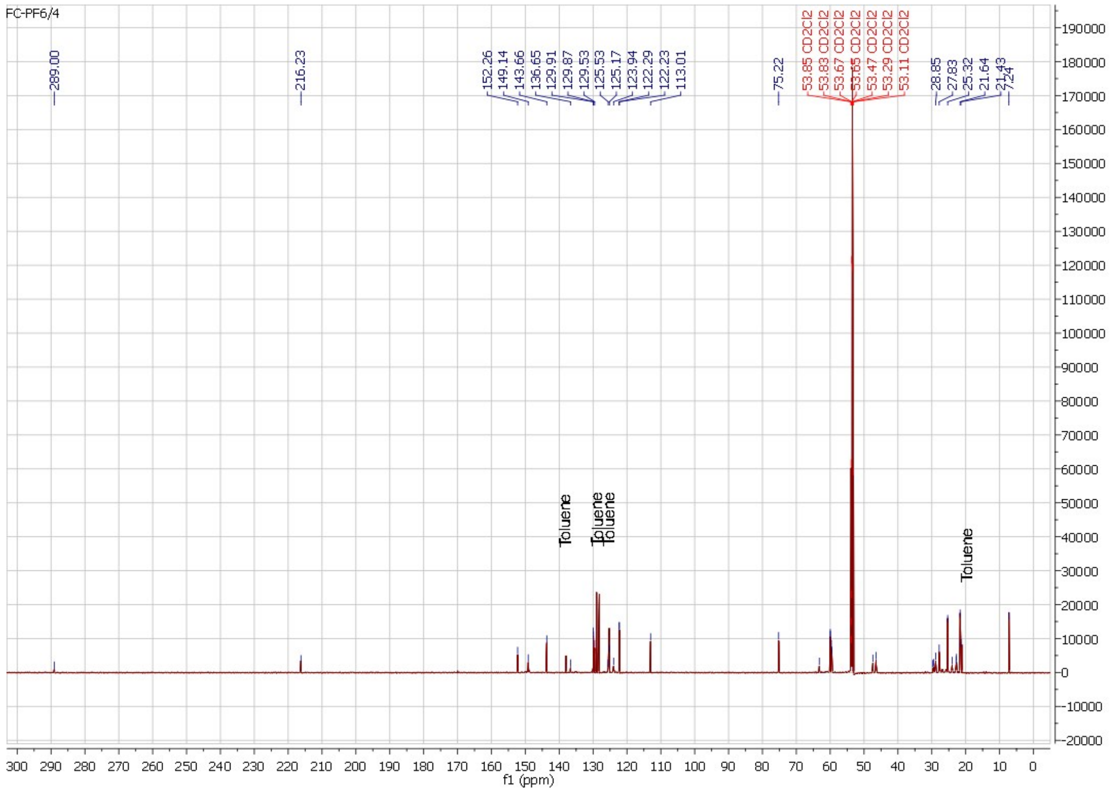
[2] K. Skowerski, C. Wierzbicka, G. Szczepaniak, Ł. Gułajski, M. Bieniek, K. Grela, *Green Chem.*, 2012, **14**, 3264.

[3] K. Skowerski, J. Pastva, S. J. Czarnocki, J. Janoscova, *Org. Process Res. Dev.*, 2015, **19(7)**, 872

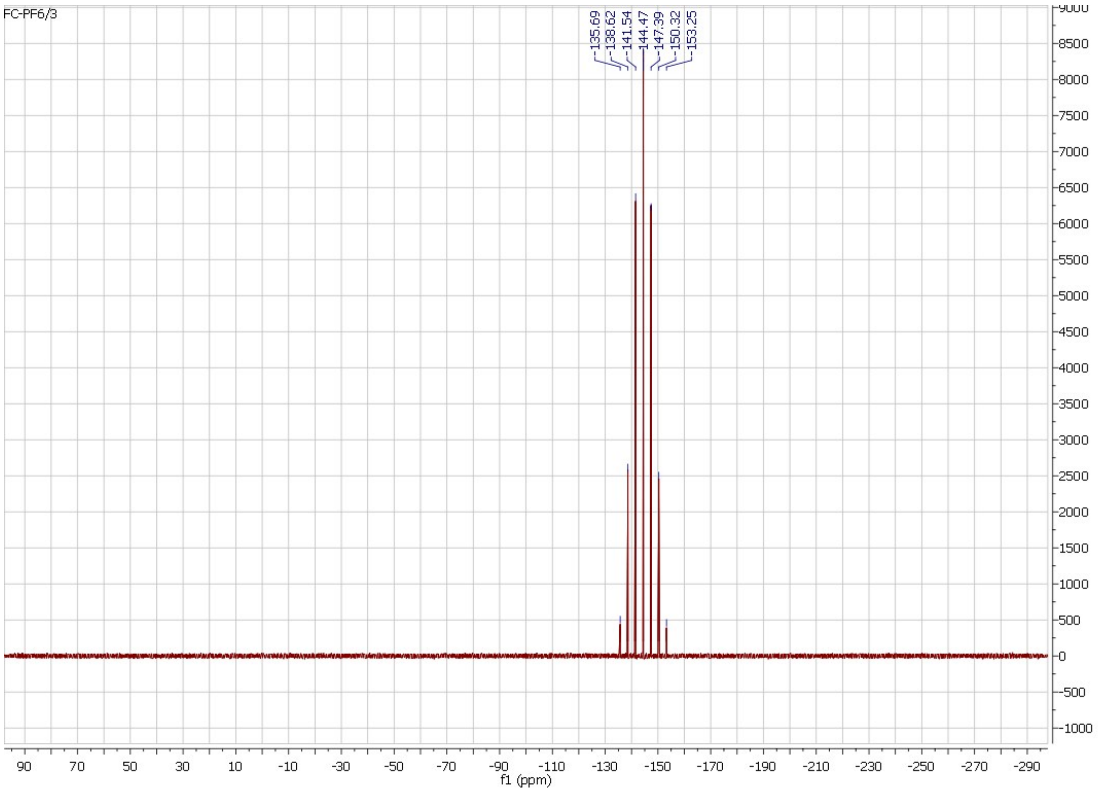
^{1}H NMR (600 MHz, CD_2Cl_2) δ ppm: 16.22 (s, 1H), 7.70 (t, J = 8.5 Hz, 1H), 7.61-7.51(m, 2H), 7.51-7.45 (d, J=7.7 Hz, 2H), 7.45-7.37 (m, 2H), 6.94-6.84 (m, 3H), 5.00-4.91 (septet, J = 6.2 Hz, 1H), 4.50-4.38 (m, 2H), 4.22-4.12 (m, 1H), 3.82-3.26 (m, 10H), 3.02-2.94 (s, 3H), 2.91-2.70 (m, 5H), 2.66-2.57 (m, 1H), 1.66-1.06 (m, 33H)



^{13}C NMR (150 MHz, CD_2Cl_2) δ ppm: 289.0 (Ru=CH), 216.2 (RuCNN), 152.2, 149.1, 143.66, 136.6, 129.9, 129.8, 129.5, 125.5, 125.1, 123.9, 122.3, 122.2, 113.0, 75.2, 63.2, 60.0, 59.9, 59.7, 59.5, 47.4, 46.5, 29.7, 29.4, 28.8, 27.8, 25.3, 24.0, 22.8, 22.7, 21.6, 21.2, 7.2



^{31}P NMR (243 MHz, CD_2Cl_2) δ ppm: 144.5 (septet, J = 711.3 Hz)

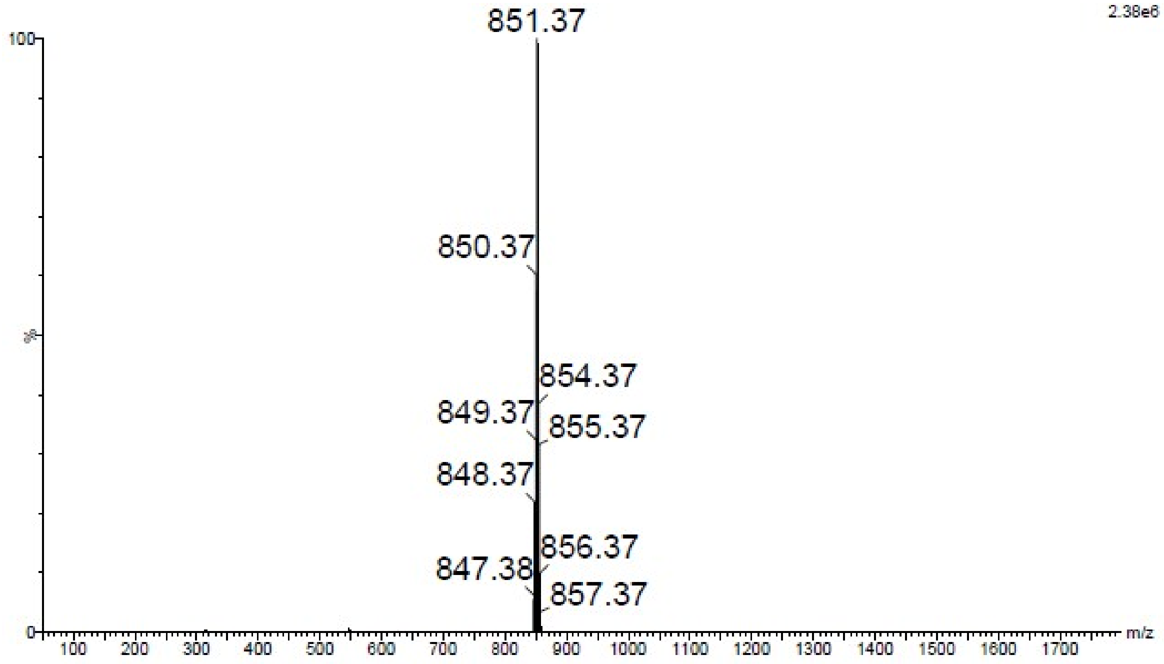


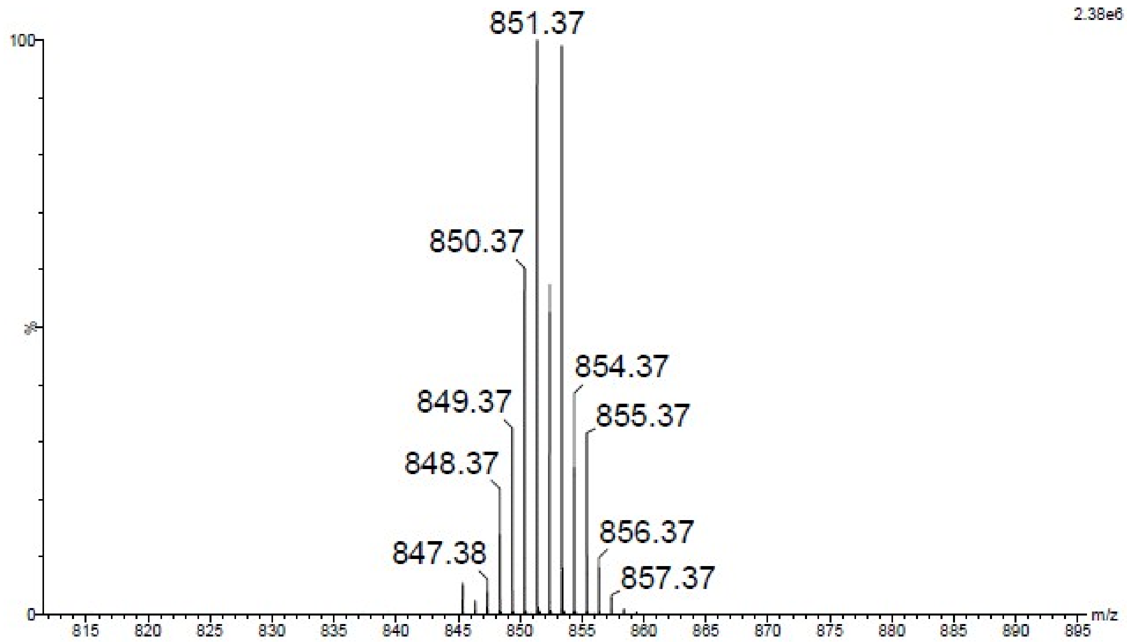
HRMS (ESI) – calculated for $C_{45}H_{67}Cl_2N_4ORu$ ($[M-PF_6]^+$) m/z 851.3735. Found 851.3724.

Elements Used:
C: 0-100 H: 0-100 N: 0-4 O: 0-1 Cl: 0-2 Ru: 1-1

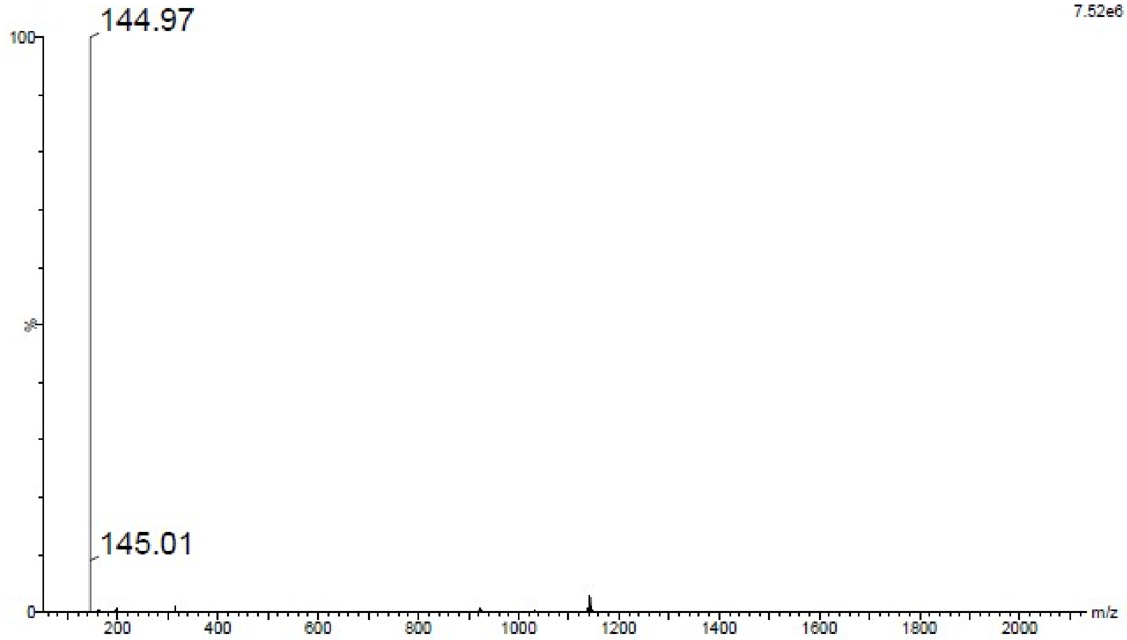
Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	Cl	Ru
851.3724	851.3735	-1.1	-1.3	13.5	C45 H67 N4 O Cl2 Ru	811.6	n/a	n/a	45	67	4	1	2	1

Positive ions mass spectra:





Negative ions mass spectra:



3. Olefin metathesis reactions

3.1 Procedures

General procedure for metathesis in green solvents

Substrate (1 mmol) was placed in a round-bottom flask and diluted with an appropriate solvent (C = 0.2 M). The reaction vessel was placed in an oil bath and it was thermostated at 40^{o}C for 15 minutes. Catalyst was added in a DCM solution (50µl) in one portion. Reaction was conducted under argon flow for ethylene removal. After 2 h reaction was quenched with ethyl vinyl ether and analyzed with GC.

General procedure for RCM of 14 and metathesis of 15.

Substrate (0.25 mmol) was placed in a round-bottom flask and diluted with toluene or DCE to a desired concentration (15 mM, 25 mM or 35 mM). The solution was kept in oil bath at the temperature of 70^{o}C for 15 min. Catalyst was added in DCM solution (50-100 µl) in one portion. Reaction was stirred for 2 or 4 hours under continuous flow of argon. Reaction was quenched with ethyl vinyl ether and analyzed with GC. Reaction yield was calculated with respect to external standard of **15**.

Metathesis in neat ionic liquids

Solution of catalyst (1.313 µmol) in DCM was added to ionic liquid under argon atmosphere. DCM was removed under reduced pressure and the solution was heated up to 40^{o}C. Substrate (0.875 mmol) was added and the reaction was stirred for 2 h under reduced pressure to ensure ethylene removal. Reaction was quenched with ethyl vinyl ether and washed with toluene. Extracted product was analyzed with GC.

Metathesis in biphasic system

Substrate (1.313 mmol) was placed in a round-bottom flask and diluted with toluene to 1M concentration and heated up to 40^{o}C. The catalyst (0.262 µmol) was added to ionic liquid (0.2 ml) in DCM solution. DCM was evaporated under reduced pressure and 0.1 ml of ionic liquid with immobilized catalyst was added to the substrate solution. Reaction was stirred under the flow of argon. Reaction was quenched with ethyl vinyl ether after 2 h and cooled down to room temperature. Upper layer was separated from the ionic liquid and analyzed with GC.

Metathesis with extraction of residual ruthenium

Route A: Substrate **5** (0.796 mmol, 0.2g) was diluted with DCM to 0.25 M concentration. Catalyst **2a** was added in a DCM solution and the reaction was stirred for 1h in 40^{o}C. The solution was washed 3 times with 4 ml of D_2O, slowly stirring the mixture for 10 min after each portion. The organic layer was separated, and a sample (1 ml) collected for ICP-MS. To 3 ml green from the merged aqueous solutions (12ml) substrate **7** was added (0.200 mmol, C = 0.066 M) and the reaction stirred in 40^{o}C for 2h (46% conversion). NH_4BF_4 or NH_4PF_6 (0.06 mmol) was added and the mixture was stirred for additional 15 min. Aqueous solution was washed 3 times with 4 ml of DCM, separated from the organic layer and a sample collected for ICP-MS.

Route B: Substrate **5** (0.796 mmol, 0.2g) was diluted with DCM to 0.25 M concentration. Catalyst **2a** was added in a DCM solution and the reaction was stirred for 1h in 40^{o}C. The solution was washed 3 times with 4 ml of deionized water, and the organic layer separated. To 3 ml of the merged aqueous solutions NH_4BF_4 or NH_4PF_6 was added (0.06 mmol) and stirred for 15 min. in room temperature. The solution was washed 3 times with 4 ml of DCM. A sample for ICP-MS was collected from the aqueous layer. To the merged DCM solutions substrate **5** was added (0.20 mmol) and reaction was stirred in 40^{o}C, and after 2h analyzed with GC (89% conversion).

3.2 Additional results

Reactions in neat [bmim-Cl] and [bmim-I]

Table 1. Catalytic activity of **1a-d** with substrate **5** (C = 1 M, 2 h) in neat [bmim-Cl] and [bmim-I]. a) Reactions in [bmim-Cl] were conducted in elevated temperature due to its higher melting point (~70^{o}C).

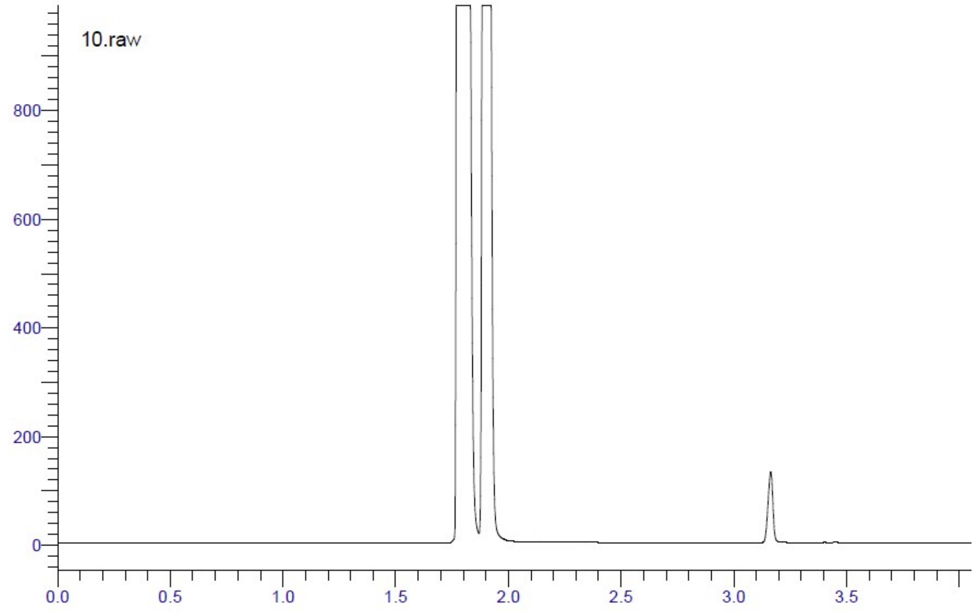
[Ru]	Loading [ppm]	Temp. [^{o}C]	IL	Conversion
1a	1500	80^a	[bmim-Cl]	3,4
1b	1500	80^a	[bmim-Cl]	4,6
1c	1500	80^a	[bmim-Cl]	3,0
1d	1500	80^a	[bmim-Cl]	3,6
1a	1500	40	[bmim-I]	1,2
1b	1500	40	[bmim-I]	0,9
1c	1500	40	[bmim-I]	1,0
1d	1500	40	[bmim-I]	1,1

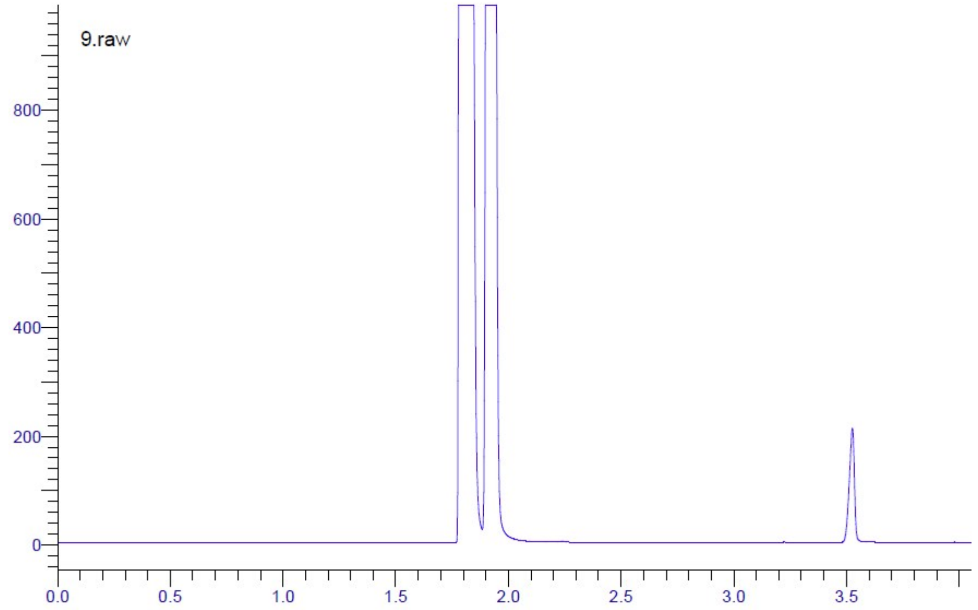
4. Metathesis products analysis

RCM of diethyl diallylmalonate:

GC method: experimental time: 4.05 min; initial temperature: 160 deg for 0.1 min; Ramp 1: 8.0 deg/min to 190 deg, hold for 0.2 min.

Retention times: substrate **9** - 3.52 min, product **10** - 3.16 min.

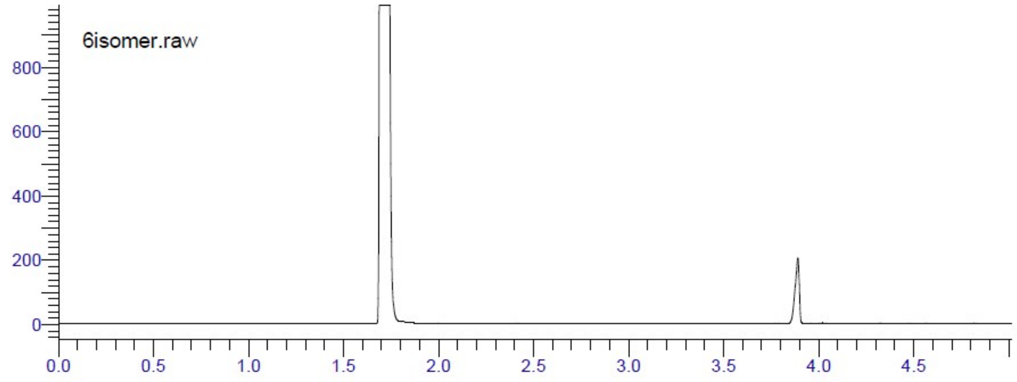


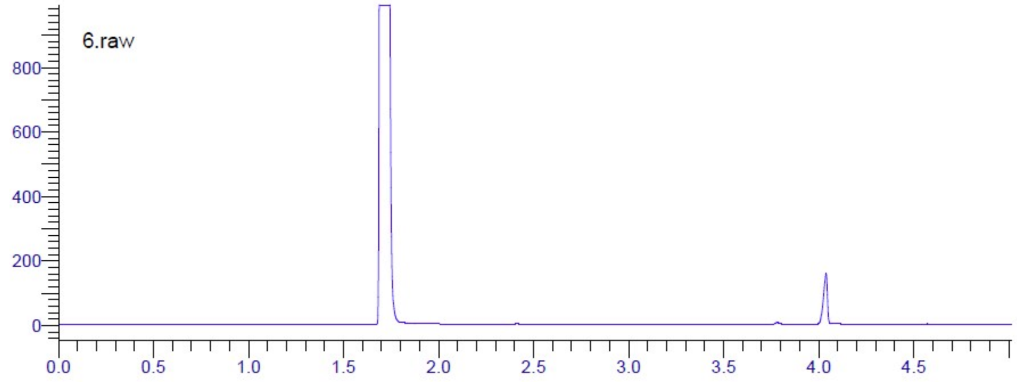


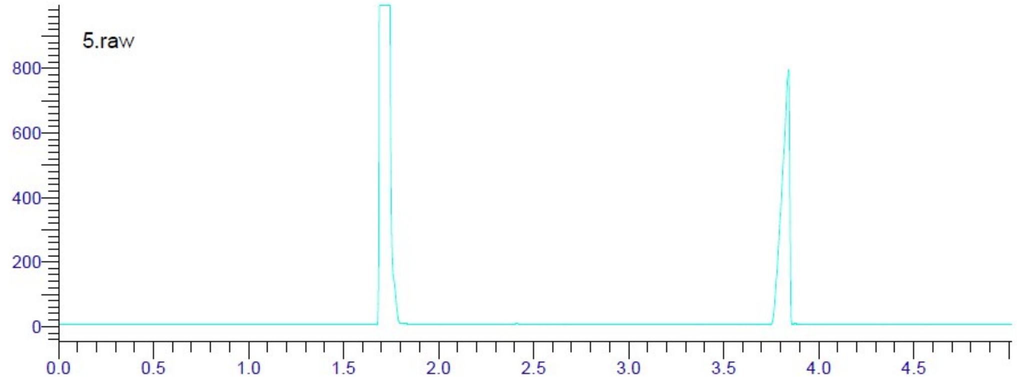
RCM of diallyl N-tosylamide:

GC method: experimental time: 5.01 min; initial temperature: 195 deg for 0.1 min; Ramp 1: 17.0 deg/min to 270 deg, hold for 0.5 min.

Retention times: substrate **5 -** 3.84 min, product **6** - 4.04 min, isomer **6’** - 3.89 min, isomer **6’’** - 4.57 min.

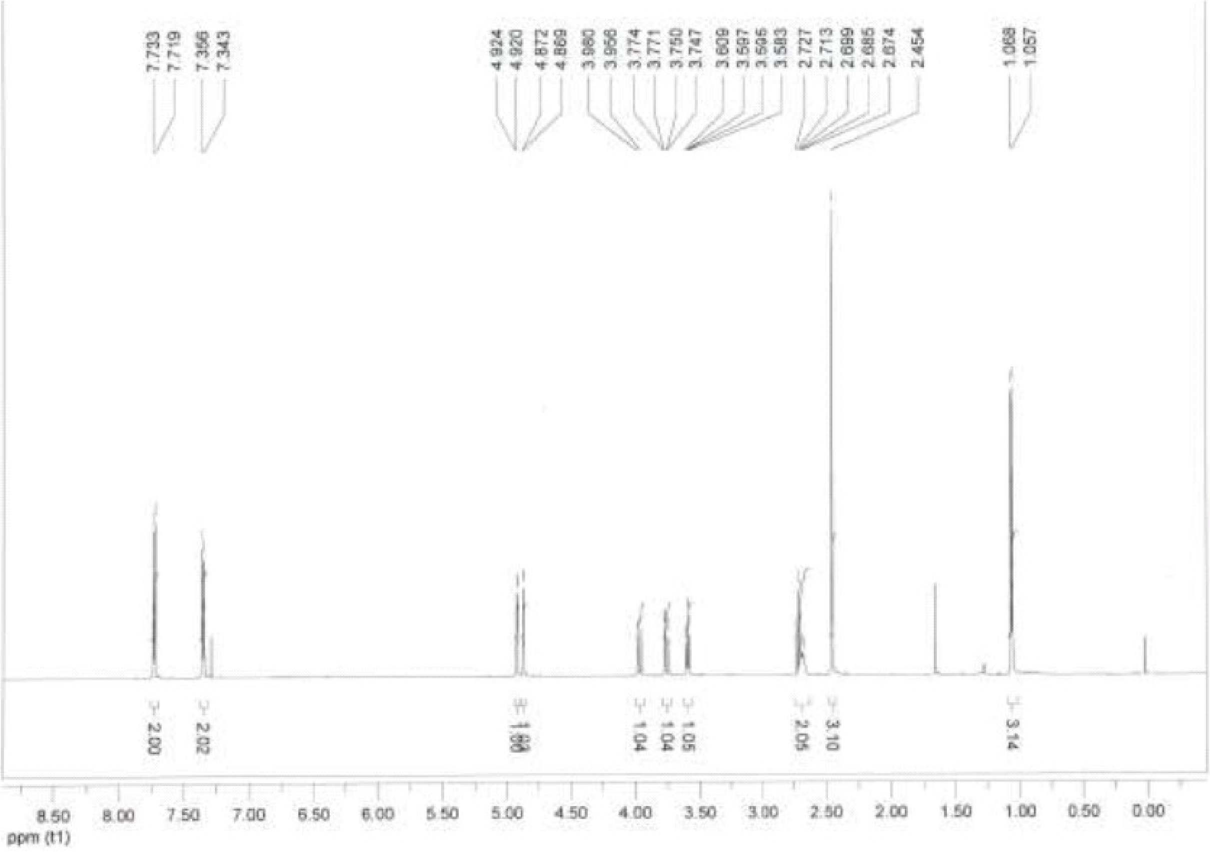






Characterization of *3-Methyl-4-methylene-1-[(4-methylphenyl)sulfonyl]pyrrolidin* (6''):

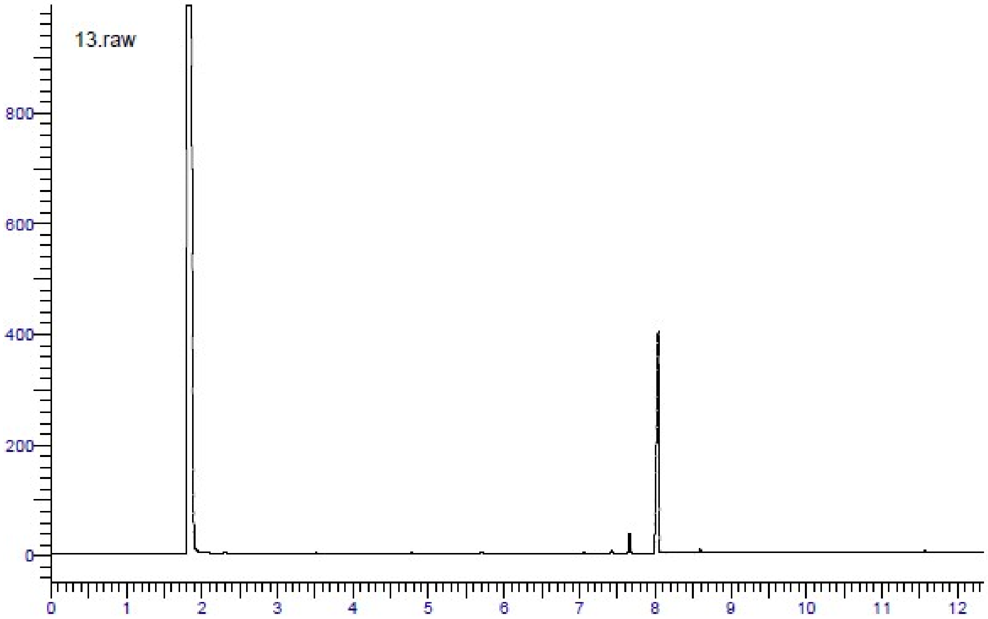
^{1}H-NMR (600 MHz, $CDCl_3$) δ ppm: 7.71 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.91 (d, J = 2.0 Hz, 1H), 4.85 (d, J = 2.2 Hz, 1H), 3.96 (d, J = 14.0 Hz, 1H), 3,73 (d, J = 15.8 Hz, 1H), 3.60-3.58 (m, 1H), 2.72-2.67 (m, 2H), 2.45 (s, 3H), 1.05 (d, J = 6.4, 3H).

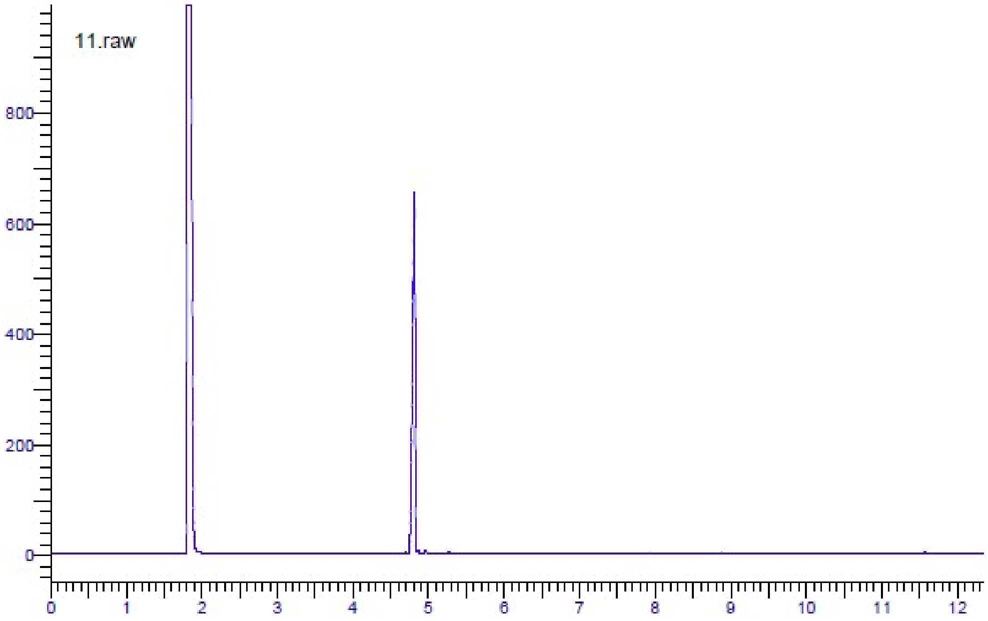


CM of ethyl undecenoate and methyl acrylate:

GC method: experimental time: 12.34 min; initial temperature: 145 deg for 0.1 min; Ramp 1: 9.0 deg/min to 180 deg, hold for 0.1 min; Ramp 2: 20.0 deg/min to 305 deg, hold for 2 min.

Retention times: substrate **11** - 4.81 min, product **13(*Z*)** - 7.66 min, product **13(*E*)** - 8.04 min.





mRCM:

GC method: experimental time: 17.0 min; initial temperature: 160 deg for 7.0 min; Ramp 1: 4.0 deg/min to 200 deg, hold for 0 min.

Retention times: substrate **14** – 15.30 min, product **15(*E*)** - 14.53 min, product **15(*Z*)** – 14.88 min