Advanced Synthesis & Catalysis

Supporting Information

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SUPPORTING INFORMATION

Polystyryl-BEMP as an efficient recyclable catalyst for the nucleophilic addition of nitroalkanes to α,β-unsaturated carbonyls under solvent-free condition

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Experimental Section

GS-MS analyses were carried out by means of the EI technique (70 eV). All ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz, 100.6 MHz respectively, using a convenient deuterated solvent (reported in the characterization charts) and the residual peak as internal standard, or TMS in the case of $CDCl_3$. IR spectra were recorded with FT-IR instrument, using $CHCl_3$ as solvent. Column chromatographies were performed by using silica gel 230-400 mesh and eluting as reported in the following characterization charts. All chemicals were purchased and used without any further purification. PS-BEMP (200-400 mesh, 2% DVB, 2.08 mmol BEMP/g) was purchased by Fluka. Enones **1d**[1] and **1e**[2] were prepared according to the described procedures. Methyl esters **10b-d** were synthesized by refluxing the corresponding acid in MeOH, in the presence of a catalytic amount of sulphuric acid. Nitro derivatives **3a,**[3] **3b,**[4] **3e,**[5] **3h,**[6] **3i,**[7] **5**,[8] **7**,[8] **9**,[8] and **11a**,[10] are known compounds, but essential characterization data (^{1}H NMR, ^{13}C NMR and GC-EIMS) were reported for clarity, whereas adducts **3c**, **3d**, **3f**, **3g**, and **11b-d** are new products.

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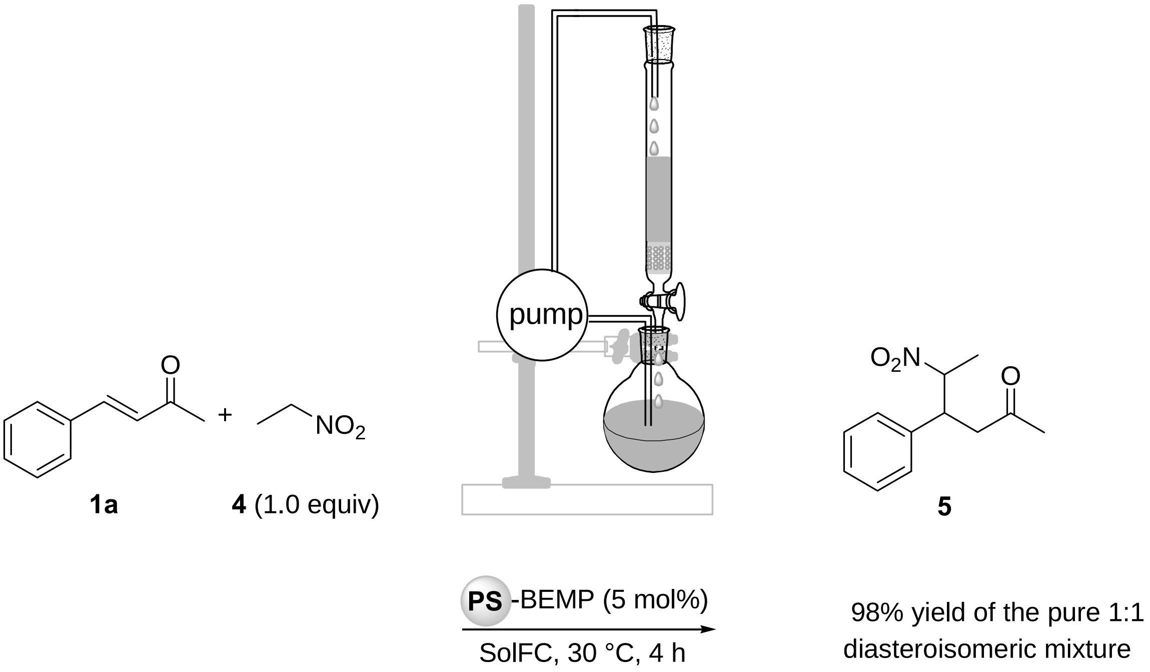
Procedure for the cyclic continuous-flow reactor.

Michael addition of nitroethane (**4**) to (*E*)-benzylidene acetone (**1a**).

PS-BEMP (5 mol%) was charged on a glass column and the pre-mixed solvent-less equimolar mixture of reactants **1a** and **4** was let flowing through it (see Figure). The reaction mixture coming out the column has been then pumped again on the top of glass column at a 1.0 mL/min flow rate, and this cycle was continued for 4 h, to reach the complete conversion of **1a** to **4**. This experiment was run on a 50.0 mmol scale.

At the end of the reaction process, the product **5** was collected into the flask by leaving the pump to work for 10 min without suctioning the reaction mixture. In this way **5** was isolated in a pure form in 90% yield without using any organic solvent. Yield of **5** was improved by cleaning the system with only 10 mL of ethyl acetate (0.2 mL/mmol) (which was cyclically flowed for 5 min at 1 mL/min rate), reaching a 98% yield of pure product



1a **4** (1.0 equiv) **5**

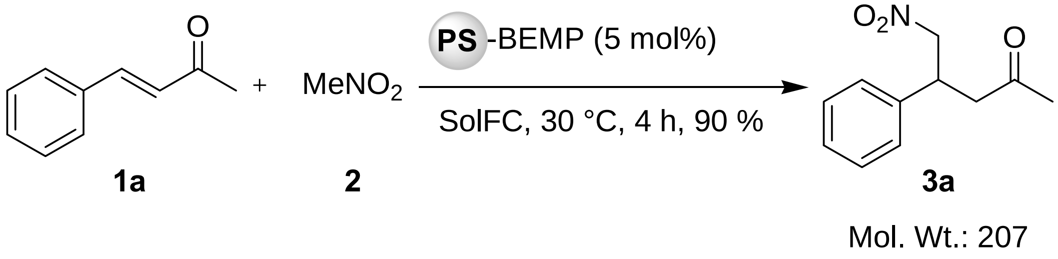
-BEMP (5 mol%)

SolFC, 30 °C, 4 h

98% yield of the pure 1:1
diasteroisomeric mixture

Chem. Name	**5-nitro-4-phenylpentan-2-one (3a)**
Lit. Ref.	*J. Org. Chem.* **1990**, *55*, 4853-4859.

Scheme



Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), **(**3*E*)-4-phenylbut-3-en-2-one (**1a**) (0.585 g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give, pure 5-nitro-4-phenylpentan-2-one (**3a**) as a white solid (0.745 g, 90% yield).

Mol Formula	$C_{11}H_{13}NO_3$	**m.p.**	99-100°C (EtOH)
Tlc - R_f (eluent)	0.3 (4/1 Etp/EtOAc)		

Elemental Analysis: Calcd. C, 63.76; H, 6.32; N, 6.76. Found C, 63.70; H, 6.35; N, 6.70.

FT-IR ($CHCl_3$, cm^{-1}): 1377, 1555, 1719.

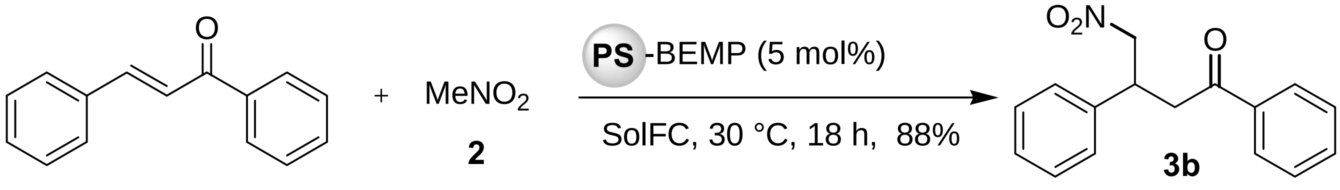
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	2.12	3	*s*	
	2.92	2	*d*	7.0
	3.97-4.03	1	*m*	
	4.60	1	*dd*	12.3, 7.7
	4.69	1	*dd*	12.3, 6.9
	7.20-7.35	5	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 30.4, 39.0, 46.1, 79.4, 127.4, 127.9, 129.1, 138.8, 205.4.

GC-EIMS (m/z, %): 207 (M^+, n.d.), 161(16), 43(100).

Chem. Name	**4-nitro-1,3-diphenylbutan-1-one (3b)**
Lit. Ref.	*Tetrahedron* **2001**, *57*, 8933-8938

Scheme



1b **2** **3b**

Mol. Wt.: 269

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (2*E*)-1,3-diphenylprop-2-en-1-one (**1b**) (0.832 g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 18 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (95/5 Petroleum ether/EtOAc, 100/1 silica/sample) to give pure 4-nitro-1,3-diphenylbutan-1-one (**3b**) as a white solid (0.948 g, 88% yield).

Mol Formula	$C_{16}H_{15}NO_3$	**m.p.**	84-85 °C
Tlc - R_f (eluent)	0.37 (7/3 Petroleum ether/EtOAc)		

Elemental Analysis: Calcd. C, 63.76; H, 6.32; N, 6.76. Found C, 63.70; H, 6.35; N, 6.70.

FT-IR ($CHCl_3$, cm^{-1}): 1378, 1556, 1687.

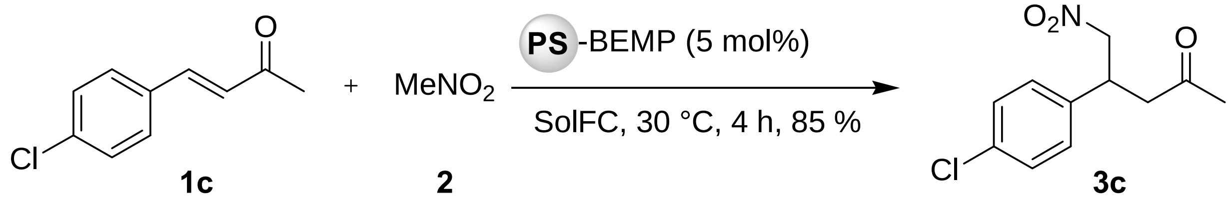
^1H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	3.37-3.51	2	*m*	
	4.22	1	*q*	7.1
	4.67	1	*dd*	12.5, 8.1
	4.82	1	*dd*	12.5, 6.5
	7.22-7.38	5	*m*	
	7.40-7.50	2	*m*	
	7.52-7.60	1	*m*	
	7.90	2	*d*	7.4

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 39.2, 41.4, 79.5, 127.4, 127.8, 127.9, 128.7, 129.0, 133.5, 136.3, 139.1, 196.8.

GC-EIMS (m/z, %): 269 (M^+, n.d.), 77 (33), 105 (100).

Chem. Name	4-(4’-chlorophenyl)-5-nitropentan-2-one (3c)

Scheme



Mol. Wt.: 242

Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (3*E*)-4-(4’-chlorophenyl)but-3-en-2-one (**1c**) (0.720 g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C. After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give, after crystallization (EtOH), pure 4-(4’-chlorophenyl)-5-nitropentan-2-one (**3c**) as a white solid (0.823 g, 85% yield).

Mol Formula	$C_{11}H_{12}ClNO_3$	**m.p.**	67-69°C
Tlc - R_f (eluent)	0.3 (4/1 Etp/EtOAc)		

Elemental Analysis: Calcd. C, 54.67; H, 5.00; N, 5.80. Found C, 54.62; H, 5.03; N, 5.85.

FT-IR ($CHCl_3$, cm^{-1}): 1377, 1557, 1719.

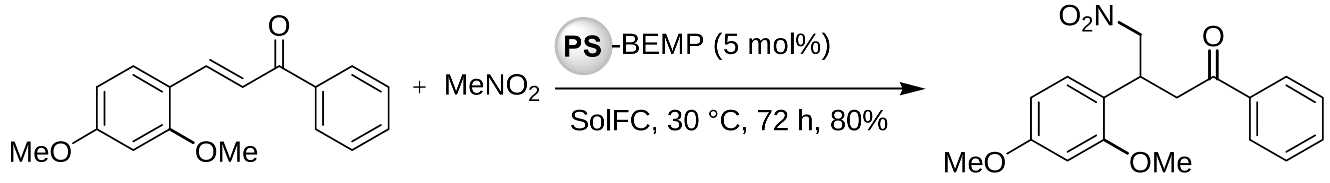
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	2.13	3	*s*	
	2.89	2	*d*	7.0
	3.97-4.03	1	*m*	
	4.57	1	*dd*	12.4, 7.9
	4.68	1	*dd*	12.4, 6.6
	7.15	2	*d*	8.5
	7.30	2	*d*	8.5

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 30.4, 38.4, 46.0, 79.2, 128.8, 129.3, 133.8, 137.3, 205.0.

GC-EIMS (m/z, %): 242 (M^+, n.d.), 194(12), 43(100).

Chem. Name	**3-(2’,4’-dimethoxyphenyl)-4-nitro-1-phenylbutan-1-one (3d)**

Scheme



1d **2** **3d**

Mol. Wt.: 329

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (2*E*)-3-(2’,4’-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**1d**) (1.072g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 72 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (95/5 Petroleum ether/EtOAc, 100/1 silica/sample) to give pure 3-(2’,4’-dimethoxyphenyl)-4-nitro-1-phenylbutan-1-one (**3d**) as a white solid (1.053 g, 80% yield).

Mol Formula	$C_{18}H_{19}NO_5$	**m.p.**	100-101 °C
Tlc - R$_f$ (eluent)	0.45 (6/4 Petroleum ether/EtOAc)		

Elemental Analysis: Calcd. C, 65.64; H, 5.81; N, 4.25. Found C, 65.61; H, 5.78; N, 4.27.

FT-IR (CHCl$_3$, cm^{-1}): 1379, 1553, 1686.

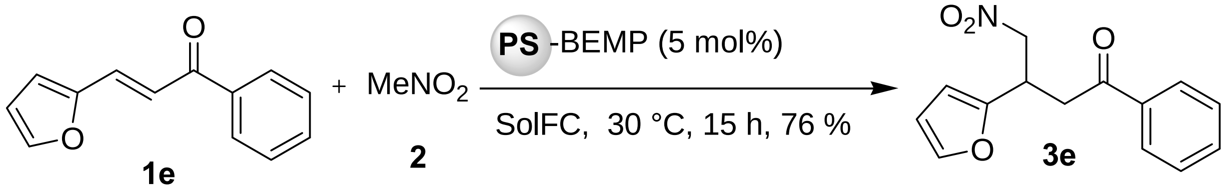
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	3.47	2	*m*	
	3.72	3	*s*	
	3.79	3	*s*	
	4.32	1	*q*	6.9
	4.79	2	*d*	7.0
	6.38	1	*dd*	8.3, 2.3
	6.43	1	*d*	2.3
	7.08	1	*d*	8.3
	7.39-7.45	2	*m*	
	7.50-7.56	1	*m*	
	7.90	2	*d*	7.4

^{13}C NMR (100.6 MHz, CDCl$_3$) δ : 35.4, 39.7, 55.0, 55.1, 77.9, 98.8, 104.2, 118.8, 127.8, 128.4, 129.8, 133.1, 136.4, 158.0, 160.2, 197.6.

GC-EIMS (m/z, %): 329 (M$^+$, n.d.), 254 (10), 282 (10), 77 (32), 105 (100).

Chem. Name	**3-(2'-furyl)-4-nitro-1-phenylbutan-1-one**
Lit. Ref.	*Tetrahedron Lett.* **2000**, *41*, 5683-5687

Scheme:



Mol. Wt.: 259

Method:

In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (2E)-3-(2'-furyl)-1-phenylprop-2-en-1-one (**1e**) (0.792 g, 4.0 mmol) and nitromethane (**2**) (0.651 mL, 12.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 15 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (95/5 Petroleum ether/EtOAc, silica/sample 100:1) to give pure 3-(2'-furyl)-4-nitro-1-phenylbutan-1-one (**3e**) as an oil (0.788 g, 76 % yield).

Mol Formula	$C_{14}H_{13}NO_4$	**m.p.**	Oil
Tlc - R$_f$ (eluent)	0,52 (6/4 Petroleum ether/EtOAc)		

Elemental Analysis: Calcd. C, 64.86; H, 5.05; N, 5.40. Found C , 64.82; H, 5.01; N, 5.36.

FT-IR (CHCl$_3$, cm^{-1}): 1377, 1557, 1687.

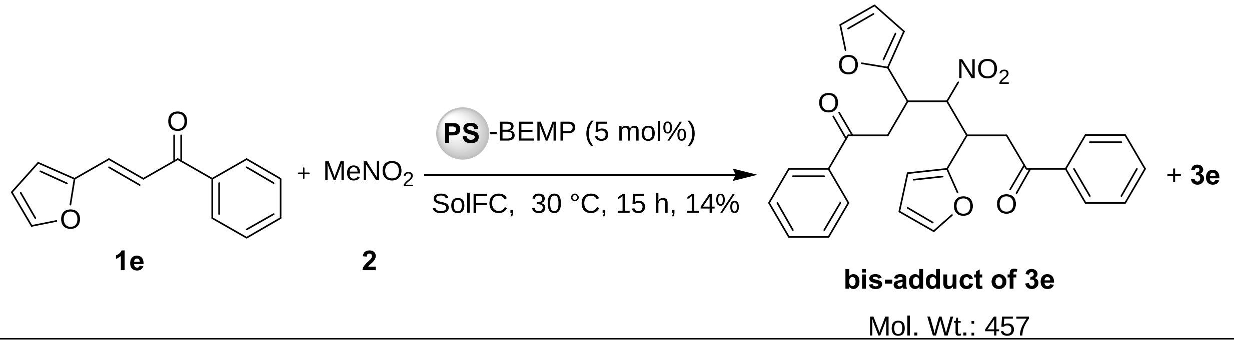
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	3.43	1	*dd*	17.8, 7.5
	3.52	1	*dd*	17.8, 6.1
	4.34	1	*q*	6.7
	4.75	1	*dd*	12.6, 7.2
	4.81	1	*dd*	12.6, 6.1
	6.19	1	*d*	3.3
	6.29	1	*dd*	3.1, 1.9
	7.34	1	*dd*	1.9, 0.8
	7.44-7.51	2	*m*	
	7.59	1	*t*	7.4
	7.94	1	*d*	1.3
	7.96	1	*d*	0.7

^{13}C NMR (100.6 MHz, CDCl$_3$) δ : 33.1, 38.9, 77.2, 107.1, 110.4, 128.0, 128.7, 133.6, 136.2, 142.2, 151.9, 196.5.

GC-EIMS (m/z, %): 259 (M$^+$, n.d.), 184 (16), 77 (37), 105 (100).

Chem. Name	**3,5-di(furan-2’-yl)-4-nitro-1,7-diphenylheptane-1,7-dione (bis-adduct of 3e)**
Lit. Ref.	*Tetrahedron Lett.* **2000**, *41*, 5683-5687

Scheme



Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (2E)-3-(2’-furyl)-1-phenylprop-2-en-1-one (**1e**) (0.792 g, 1 mmol) and nitromethane (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 15 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (95/5 Petroleum ether/EtOAc, silica/sample 100:1) to give pure 3,5-di(furan-2’-yl)-4-nitro-1,7-diphenylheptane-1,7-dione as white solid (0.256 g, 14% yield).

Mol Formula	$C_{27}H_{23}NO_6$	**m.p.**	oil
Tlc - R_f (eluent)	0.50 (6/4 Petroleum ether/AcOEt)		

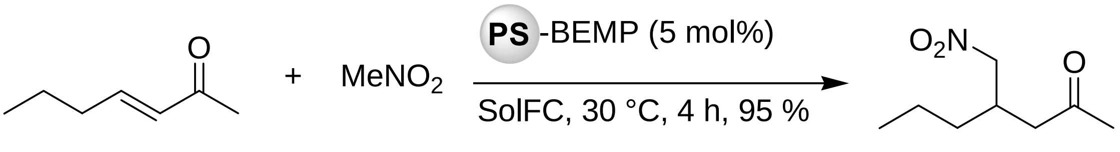
Elemental Analysis: Calcd. C, 70.89; H, 5.07; N, 3.06. Found: C, 71.36; H, 5.40; N, 3.05.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	3.09	1	*dd*	16.9, 2.9
	3.45	1	*dd*	18.0, 6.5
	3.52-3.66	2	*m*	
	3.99	1	*dt*	6.9, 4.4
	4.33	1	*dt*	10.0, 2.8
	5.35	1	*dd*	9.9, 4.4
	6.20	1	*d*	3.2
	6.28-6.33	2	*m*	
	6.35	1	*d*	2.9
	7.34	1	*dd*	1.8, 0.7
	7.37-7.50	5	*m*	
	7.51-7.62	2	*m*	
	7.83	1	*d*	1.4
	7.85	1	*s*	
	7.93	1	*d*	1.3
	7.94	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 35.4, 36.0, 38.7, 39.0, 90.8, 108.8, 109.4, 110.4, 110.6, 127.9, 128.0, 128.1, 128.6, 128.7, 133.3, 133.5, 136.3, 136.4, 142.4, 142.5, 150.4, 150.8, 196.3, 196.5.

Chem. Name	**4-(nitromethyl)heptan-2-one (3f)**

Scheme



1f **2** **3f**

Mol. Wt.: 173

Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (3*E*)-hept-3-en-2-one (**1f**) (0.448g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.

After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give, pure 4-(nitromethyl)heptan-2-one (**3f**) as a colourless oil (0.657 g, 95% yield).

Mol Formula	$C_8H_{15}NO_3$	**m.p.**	Colourless oil
Tlc - R_f (eluent)	0.3 (8/2 Etp/EtOAc)		

Elemental analysis: Calcd. C, 55.47; H, 8.73; N, 8.09. Found: C, 55.43; H, 8.77; N, 8.02.

FT-IR ($CHCl_3$, cm^{-1}): 1371, 1552, 1715.

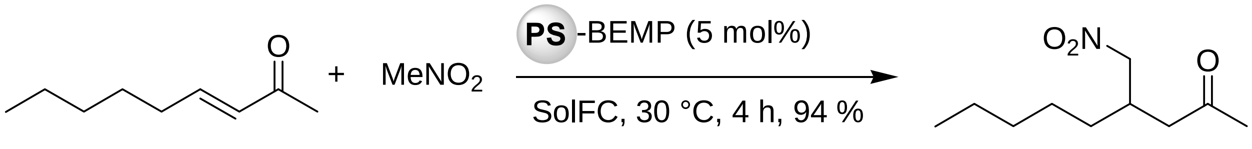
^1H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.85-0.95	3	*m*	
	1.35-1.45	4	*m*	
	2.17	3	*s*	
	2.50-2.65	3	*m*	
	4.45	2	*d*	5.4

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 13.8, 19.7, 30.3, 32.7, 33.5, 44.5, 78.3, 206.6.

GC-EIMS (m/z, %): 173 (M^+, n.d.), 43(73), 55(92), 69(100).

Chem. Name	**4-(nitromethyl)nonan-2-one (3g)**

Scheme



1g **2** **3g**

Mol. Wt.: 201

Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (3*E*)-non-3-en-2-one (**1g**) (0.560g, 4.0 mmol) and nitromethane (**2**) (0.217 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give, pure 4-(nitromethyl)nonan-2-one (**3g**) as a colourless oil (0.756 g, 94% yield).

Mol Formula	$C_{10}H_{19}NO_3$	**m.p.**	Colourless oil

Elemental analysis: Calcd. C, 59.68; H, 9.52; N, 6.96. Found: C, 59.63; H, 9.50; N, 6.92.

FT-IR ($CHCl_3$, cm^{-1}): 1372, 1551, 1716.

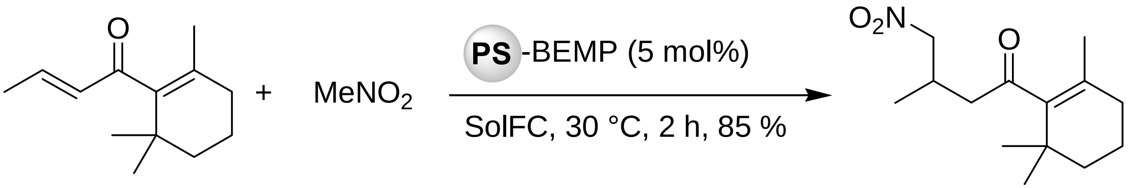
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.85-0.89	3	*m*	
	1.27-1.35	8	*m*	
	2.17	3	*s*	
	2.50-2.65	3	*m*	
	4.43	2	*d*	5.4

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 13.8, 22.3, 26.2, 30.4, 31.3, 31.5, 32.9, 44.5, 78.3, 206.6.

GC-EIMS (m/z, %): 201 (M$^+$, n.d.), 69(34), 58(43), 55(52), 43(100).

Chem. Name	**3-methyl-4-nitro-1-(2’,6’,6’-trimethylcyclohex-1-en-1-yl)butan-1-one (3h)**
Lit. Ref.	*Eur. J. Med. Chem.* **1990**, *25*, 279-284.

Scheme



1h **2** **3h**

Mol. Wt.: 253

Method:

In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (2*E*)-1-(2’,6’,6’-trimethylcyclohex-1-en-1-yl)but-2-en-1-one (**1h**) (0.768 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.

After 2 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (98/2 Etp/EtOAc, 30/1 silica/sample) to give pure 3-methyl-4-nitro-1-(2’,6’,6’-trimethylcyclohex-1-en-1-yl)butan-1-one (**3h**) as a colourless oil (0.860 g, 85% yield).

Mol Formula	$C_{14}H_{23}NO_3$	**m.p.**	Colourless Oil
Tlc - R_f (eluent)	0.6 (9/1 Etp/EtOAc)		

Elemental analysis: Calcd. C, 66.37; H, 9.15; N, 5.53. Found: C, 66.32; H, 9.11; N, 5.50.

FT-IR ($CHCl_3$, cm^{-1}): 1382, 1552, 1687.

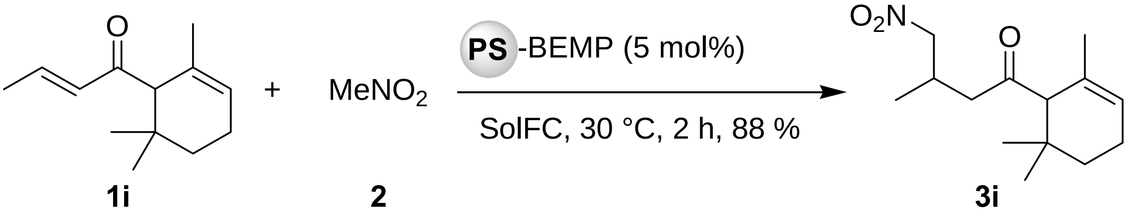
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.05	6	*s*	
	1.11	3	*d*	6.8
	1.42-1.45	2	*m*	
	1.56	3	*s*	
	1.63-1.70	2	*m*	
	1.95	2	*t*	6.4
	2.62	1	*dd*	19.2, 6.6
	2.71	1	*dd*	19.2, 6.1
	2.86	1	*m*	
	4.39	1	*dd*	11.9, 6.8
	4.53	1	*dd*	11.9, 6.1

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 17.4, 18.7, 20.7, 28.0, 28.6, 31.1, 33.2, 38.7, 48.5, 80.4, 129.6, 142.5, 208.9.

GC-EIMS (m/z, %): 253(M^+, 1), 81(34), 123(47), 151(100).

Chem. Name	**3-methyl-4-nitro-1-(2’,6’,6’-trimethylcyclohex-2-en-1-yl)butan-1-one (3i)**
Lit. Ref.	*Tetrahedron* **1989**, *45*, 1517-1532.

Scheme



1i **2** **3i**

Mol. Wt.: 253

Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), (±)-(2*E*)-1-(2’,6’,6’-trimethylcyclohex-2-en-1-yl)but-2-en-1-one (**1i**) (0.768 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.

After 2 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (98/2 Etp/EtOAc, 30/1 silica/sample) to give 3-methyl-4-nitro-1-(2,6,6-trimethylcyclohex-2-en-1-yl)butan-1-one (**5i**) as a colourless oil (0.614 g, 88% yield).

(2*E*)-1-(2’,6’,6’-trimethylcyclohex-2-en-1-yl)butan-1-one (**1i**) is commercially available in a ca. 90/10 mixture with its isomer **1h**. Product **3i** was isolated as 93/7 mixture with **3h**.

Mol Formula	$C_{14}H_{23}NO_3$	**m.p.**	Colourless Oil
Tlc - R_f (eluent)	0.6 (9/1 Etp/AcOEt)		

FT-IR ($CHCl_3$, cm^{-1}): 1382, 1553, 1670, 1711.

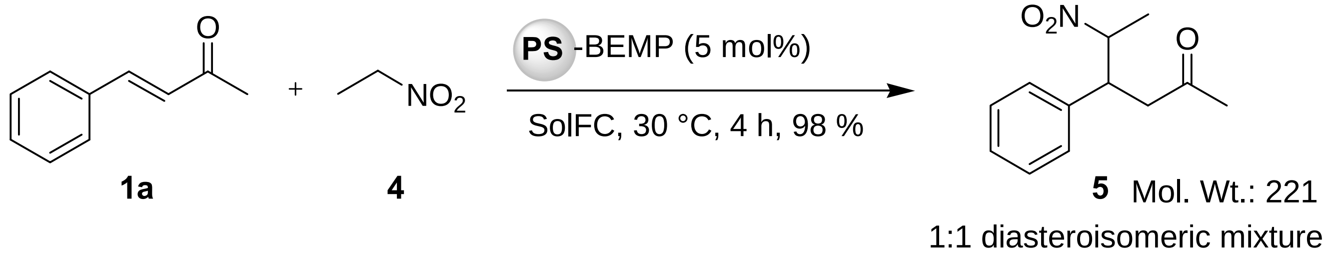
^1H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.89	3	*s*	
	0.92	3	*s*	
	1.05-1.08	3	*m*	
	1.59	3	*s*	
	1.65-1.76	2	*m*	
	2.05-2.20	2	*m*	
	2.60-2.81	4	*m*	
	4.30-4.50	2	*m*	
	5.59	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 17.3, 22.5, 23.4, 27.6, 27.8, 28.0, 28.1, 30.5, 32.5, 48.7, 48.8, 63.4, 80.17, 80.22, 123.8, 123.9, 129.6, 129.7, 211.3.

GC-EIMS (m/z, %): 253(M^+, 1), 55 (19), 81 (43), 123 (100).

Chem. Name	**5-nitro-4-phenylhexan-2-one (5)**
Lit. Ref.	*J. Org. Chem.* **2002**, *67*, 8331-8338

Scheme



Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.024 g, 0.05 mmol, 2.08 mmol/g), **(**3*E*)-4-phenylbut-3-en-2-one (**1a**) (0.584 g, 4.0 mmol) and nitroethane (**4**) (0.288 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C. After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give a 52/48 mixture of two diastereoisomers of 5-nitro-4-phenylhexan-2-one (**5**) as a colourless oil (0.866 g, 98 % yield).

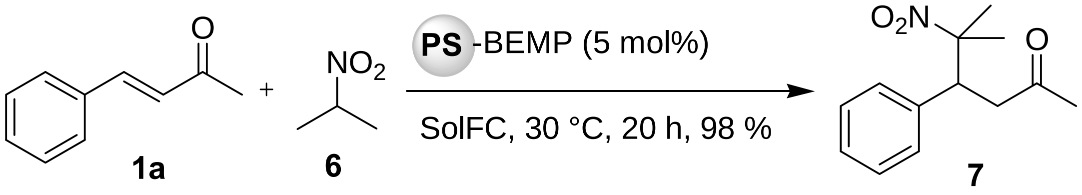
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	Diastereoisomer A			
	1.32	3	*d*	6.6
	2.01	3	*s*	
	2.74	1	*dd*	17.0, 4.3
	2.97	1	*dd*	17.0, 9.6
	3.66-3.77	1	*m*	
	4.71-4.81	1	*m*	
	7.18	1	*s*	
	7.20	1	*d*	1.5
	7.23-7.38	3	*m*	
	Diastereoisomer B			
	1.48	3	*d*	6.7
	2.12	3	*s*	
	2.90	1	*dd*	17.5, 7.6
	3.05	1	*dd*	17.5, 6.7
	3.66-3.77	1	*m*	
	4.88	1	*q*	6.6
	7.13	1	*d*	1.4
	7.15	1	*d*	1.7
	7.23-7.38	3	*m*	

^{13}C NMR (100.6 MHz, CDCl$_3$) δ : Diastereoisomer A: 17.6, 30.3, 45.2, 46.1, 87.0, 127.8, 128.1, 128.9, 138.2, 204.9. Diastereoisomer B: 16.6, 30.4, 44.5, 44.6, 85.8, 127.8, 128.0, 128.6, 137.8, 205.6.

GC-EIMS (m/z, %): Diastereoisomer A: 221 (M$^+$, n.d.), 174 (32), 43 (100). Diastereoisomer B: 221 (M$^+$, n.d.), 174 (33), 43 (100).

Chem. Name	**5-methyl-5-nitro-4-phenylhexan-2-one (7)**
Lit. Ref.	*J. Org. Chem.* **2002**, *67*, 8331-8338

Scheme



Mol. Wt.: 235

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.096 g, 2.08 mmol/g), **(**3*E*)-4-phenylbut-3-en-2-one (**1a**) (0.584g, 4.0 mmol) and 2-nitropropane (**6**) (0.374 mL, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 20 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent and the residual nitroalkane were evaporated under vacuum to give pure 5-methyl-5-nitro-4-phenylhexan-2-one (**7**) as a white solid (0.921 g, 98 % yield).

Mol Formula	$C_{13}H_{17}NO_3$	**m.p.**	61-62 °C
Tlc - R_f (eluent)	0.37 (7/3 Petroleum ether/EtOAc)		

Elemental analysis: Calcd. C, 66.36; H, 7.28; N, 5.95. Found: C, 66.38; H, 7.22; N, 5.90.

FT-IR ($CHCl_3$, cm^{-1}): 1374, 1535, 1721.

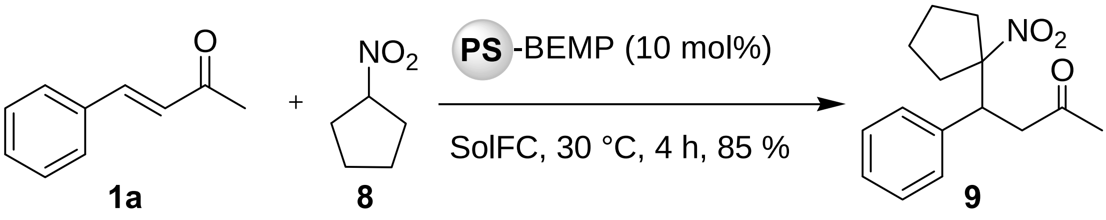
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.48	3	*s*	
	1.55	3	*s*	
	2.02	3	*s*	
	2.71	1	*dd*	17.0, 3.5
	3.09	1	*dd*	17.0, 10.6
	3.93	1	*dd*	10.6, 3.5
	7.17-7.22	2	*m*	
	7.24-7.33	3	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 22.4, 25.8, 30.3, 44.0, 48.8, 91.0, 127.8, 128.5, 129.1, 137.6, 205.0.

GC-EIMS (m/z, %): 235 (M^+, n.d.), 145 (30), 91 (36), 131 (57), 43 (100).

Chem. Name	**4-(1’-nitrocyclopentyl)-4-phenylbutan-2-one (9)**
Lit. Ref.	*J. Org. Chem.* **2002**, *67*, 8331-8338

Scheme



Mol. Wt.: 261

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.192 g, 2.08 mmol/g), (3*E*)-4-phenylbut-3-en-2-one (**1a**) (0.584 g, 4.0 mmol) and nitrocyclopentane (**8**) (0.636 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 4 h, ethyl acetate was added, the catalyst was recovered by filtration, the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (Hexane/Et_2O from 95/5 to 20/80, silica gel/sample 4/1) to give 4-(1’-nitrocyclopentyl)-4-phenylbutan-2-one (**9**) as a white solid (0.887 g, 85 % yield).

Mol Formula	$C_{15}H_{19}NO_3$	**m.p.**	72-73 °C
Tlc - R_f (eluent)	0.39 (6/4 Et_2O/Petroleum ether)		

Elemental analysis: Calcd. C, 68.94; H, 7.33; N, 5.36. Found: C, 68.90; H, 7.34; N, 5.31.

FT-IR ($CHCl_3$, cm^{-1}): 1358, 1535, 1720.

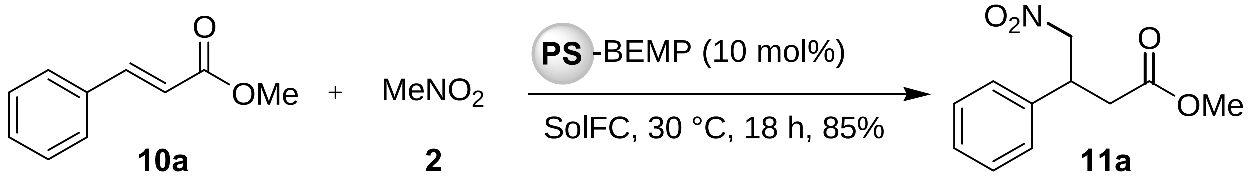
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.53-1.71	4	*m*	
	1.76-1.90	2	*m*	
	2.04	3	*s*	
	2.44-2.59	2	*m*	
	2.93	1	*dd*	17.3, 3.7
	3.14	1	*dd*	17.3, 10.2
	3.87	1	*dd*	10.2, 3.7
	7.11-7.16	2	*m*	
	7.22-7.32	3	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 23.0, 23.1, 30.5, 34.0, 36.5, 45.2, 47.4, 103.8, 127.8, 128.5, 128.7, 138.3, 205.6.

GC-EIMS (m/z, %): 261 (M^+, n.d.), 91 (37), 129 (63), 43 (71), 157 (100).

Chem. Name	**Methyl 4-nitro-3-phenylbutanoate (11a)**
Lit. Ref.	*Tetrahedron:* Asymmetry **2005**, *16*, 1341-1345

Scheme



Mol. Wt.: 223

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.192 g, 2.08 mmol/g), methyl (2*E*)-3-phenylacrylate (**10a**) (0.648 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 15 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (98/2 Petroleum ether/EtOAc gradient, 100/1 silica/sample) to give pure methyl 4-nitro-3-phenylbutanoate (**11a**) as a white solid (0.758 g, 85% yield).

Mol Formula	$C_{11}H_{13}NO_4$	**m.p.**	35-36°C
Tlc - R_f (eluent)	0.35 (7/3 Petroleum ether/EtOAc)		

Elemental analysis: Calcd. C, 59.19; H, 5.87; N, 6.27. Found: C, 59.17; H, 5.82; N, 6.22.

FT-IR ($CHCl_3$, cm^{-1}): 1378, 1557, 1736.

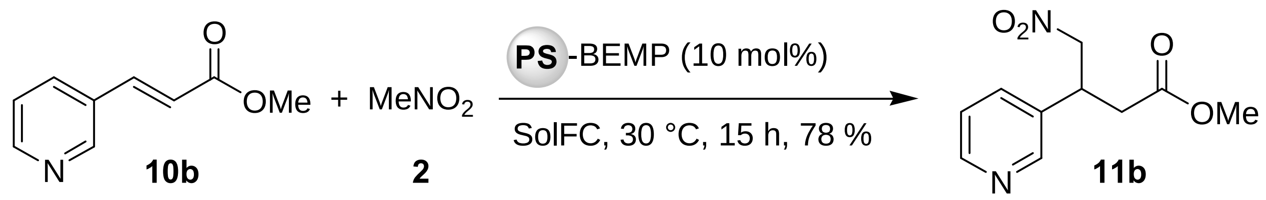
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	2.78	2	*d*	7.3
	3.63	3	*s*	
	3.99	1	*q*	7.4
	4.64	1	*dd*	12.6, 7.9
	4.74	1	*dd*	12.6, 7.0
	7.20-7.25	2	*m*	
	7.25-7.37	3	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 37.5, 40.1, 51.9, 79.3, 127.2, 128.0, 129.0, 138.2, 171.0.

GC-EIMS (m/z, %): 223 (M^+, n.d.), 115 (40), 91 (41), 135 (41), 104 (43), 118 (92), 176 (96), 117 (100).

Chem. Name	**Methyl 4-nitro-3-pyridin-3’-ylbutanoate (11b)**

Scheme



Mol. Wt.: 224

Method: In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.048 g, 0.1 mmol, 2.08 mmol/g), methyl (2*E*)-3-pyridin-3’-ylacrylate (**10b**) (0.672 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.

After 15 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (5/20/75 MeOH/EtOAc/Etp, 100/1 silica/sample) to give pure methyl 4-nitro-3-pyridin-3’-ylbutanoate (**11b**) as a yellow oil (0.699 g, 78% yield).

Mol Formula	$C_{10}H_{12}N_2O_4$	**m.p.**	Yellow oil
Tlc - R$_f$ (eluent)	0.38 (1/5/4 MeOH/EtOAc/Etp)		

Elemental analysis: Calcd. C, 53.57; H, 5.39; N, 12.49. Found: C, 53.52; H, 5.37; N, 12.44.

FT-IR (CHCl$_3$, cm^{-1}): 1376, 1557, 1736.

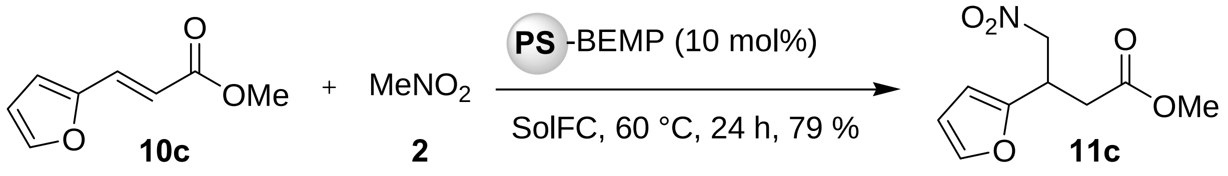
^{1}H NMR 400 MHz CDCl$_3$	**□ value**	**No. H**	**Mult.**	**j value/Hz**	
	2.78	2	*m*		
	3.62	3	*s*		
	3.97-4.03	1	*m*		
	4.66	1	*dd*	12.9, 8.2	
	4.77	1	*dd*	12.9, 6.6	
	7.28-7.32	1	*m*		
	7.58-7.62	1	*m*		
	8.56	2	*s, bs*		

^{13}C NMR (100.6 MHz, CDCl$_3$) δ : 37.0, 37.7, 52.0, 78.5, 123.8, 134.0, 135.0, 148.9, 149.3, 170.5.

GC-EIMS (m/z, %): 224 (M$^+$, n.d.), 105 (41), 59 (44), 136 (47), 117 (48), 119 (52), 162 (57), 118 (100).

Chem. Name	**Methyl 3-(2’-furyl)-4-nitrobutanoate (11c)**

Scheme:



Mol. Wt.: 213

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.192 g, 2.08 mmol/g), methyl (2*E*)-3-(2’-furyl)acrylate (**10c**) (0.608 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C.
After 24 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (15/1 Petroleum ether/EtOAc, silica/sample 100:1) to give pure methyl 3-(2’-furyl)-4-nitrobutanoate (**11c**) as an oil (0.673 g, 79% yield).

Mol Formula	$C_9H_{11}NO_5$	**m.p.**	Oil
Tlc - R_f (eluent)	0,41 (6/4 Petroleum ether/EtOAc)		

Elemental analysis: Calcd. C, 50.70; H, 5.20; N, 6.57. Found: C, 50.72; H, 5.23; N, 6.54.

FT-IR ($CHCl_3$, cm^{-1}): 1377, 1558, 1737.

^{1}H NMR 400 MHz $CDCl_3$

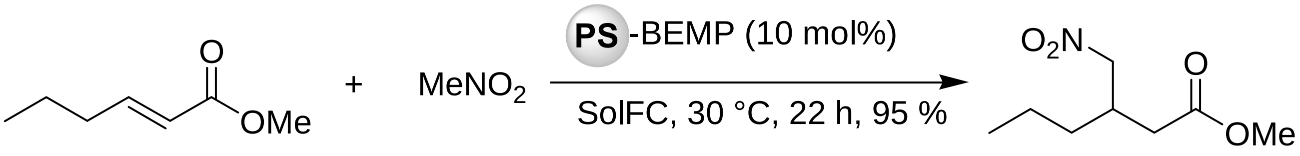
δ value	No. H	Mult.	j value/Hz
2.76	1	*dd*	16.5, 7.2
2.83	1	*dd*	16.5, 7.0
3.68	3	*s*	
4.09	1	*q*	7.0
4.72	2	*d*	6.9
6.16-6.19	1	*m*	
6.28-6.32	1	*m*	
7.32-7.36	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 33.9, 34.9, 51.9, 76.9, 107.0, 110.4, 142.4, 151.2, 170.8.

GC-EIMS (m/z, %): 213 (M^+, n.d.), 79 (31), 107 (35), 94 (55), 166 (66), 108 (100).

Chem. Name	**Methyl 3-(nitromethyl)hexanoate (11d)**

Scheme



10d **2** **11d**

Mol. Wt.: 189

Method:
In a screw capped vial equipped with a magnetic stirrer PS-BEMP (0.192 g, 2.08 mmol/g), methyl (2*E*)-hex-2-enoate (**10d**) (0.512 g, 4.0 mmol) and nitromethane (**2**) (0.326 mL, 6.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C.
After 22 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give, pure methyl 3-(nitromethyl)hexanoate (**11d**) as a colourless oil (0.718 g, 95% yield).

Mol Formula	$C_8H_{15}NO_4$	**m.p.**	Colourless oil
Tlc - R_f (eluent)	0.41 (9/1 Etp/EtOAc)		-

Elemental analysis: Calcd. C, 50.78; H, 7.99; N, 7.40. Found: C, 50.72; H, 7.93; N, 7.42.

FT-IR ($CHCl_3$, cm^{-1}): 1381, 1553, 1734.

^1H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.91-0.95	3	*m*	
	1.35-1.43	4	*m*	
	2.46	2	*d*	6.6
	2.60-2.70	1	*m*	
	3.70	3	*s*	
	4.45	1	*dd*	12.3, 6.0
	4.51	1	*dd*	12.3, 6.5

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.7, 19.5, 33.4, 33.8, 35.5, 51.6, 78.4, 171.9.

GC-EIMS (m/z, %): 189 (M^+, n.d.), 43 (45), 59 (70), 69 (73), 83 (73), 55 (100).