

ELECTRONIC SUPPORTING INFORMATION

Biomass-derived safer medium to replace toxic dipolar solvents and access cleaner Heck coupling

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Experimental Section

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources without further purification. GLC analyses were performed by using Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and hydrogen as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (¹H at 400 MHz and ¹³C at 100.6 MHz) in CDCl₃ using TMS as the internal standard. Elemental Analyses were conducted on a Fisons EA1108CHN. Melting points were measured on a Büchi 510. ICP-OES 710 Agilent Technology.

Preparation of the samples for ICP

The compounds (ca. 100 mg) were dissolved in ca. 3 mL of aqua regia and stirred for 10 minutes at room temperature. Water was added to reach a final volume of 10 mL. If present, residual solid was filtered off and the sample was taken to the ICP analyzer.

Compounds **3a**¹, **3b**¹, **3c**², **3d**³, **3e**⁴, **3f**³, **3g**¹, **3h**⁵, **3i**⁶, **3j**⁶, **3k**⁶, **3l**⁶, **5a**¹, **5b**³, **5c**⁷, **5d**⁷, **5e**⁸, **5f**⁹, **5g**¹⁰, **5h**¹¹ are known compounds.

Characterization data and copies of the ¹H and ¹³C NMR are reported below.

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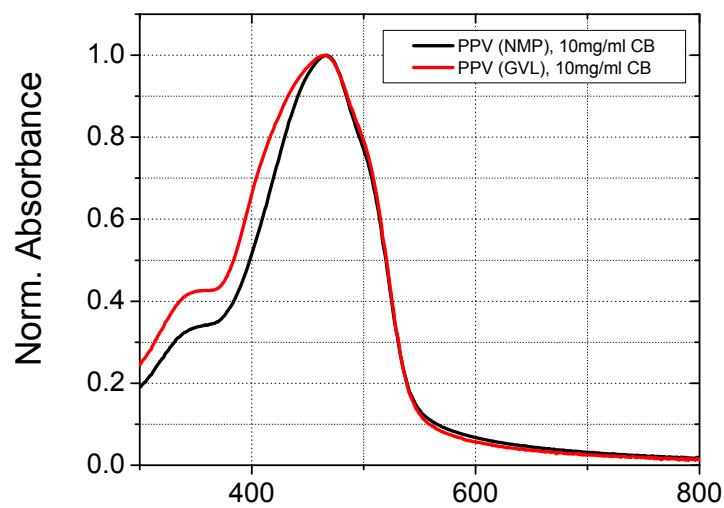


Figure S1. Normalized absorption spectra of PPV derivative **1** through NMP-based protocol (black line) and GVL-based protocol (red line) in thin film.

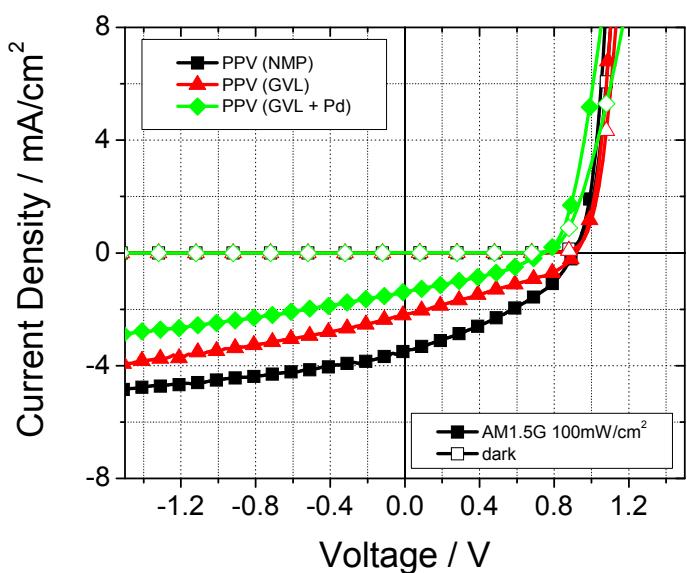


Figure S2. J-V characteristics of **1**/PCBM based OPVs.

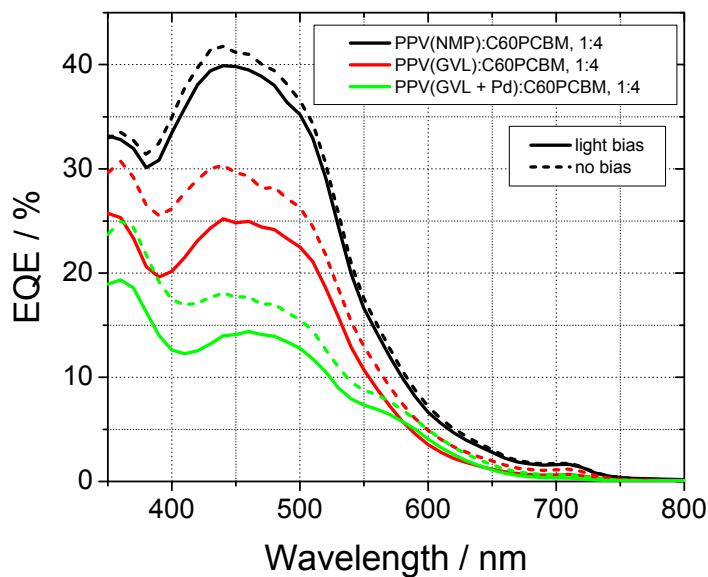


Figure S3. EQE spectra of BHJ **1** / PCBM. Black curves represent data using polymer **1** through NMP-based protocol. Red curves represent data using pure **1** through GVL-based protocol, while green curves represent data obtained using contaminated **1** through GVL-based protocol.

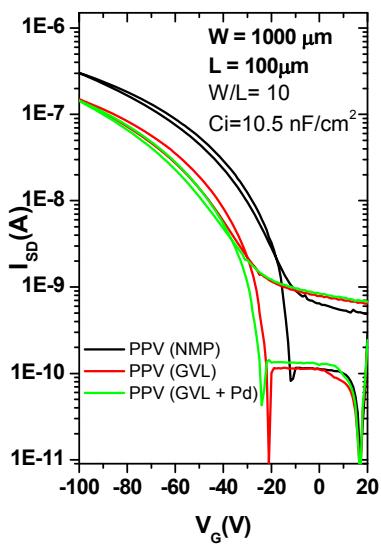


Figure S4. Typical transfer plot for spin-coated **1** OFETs. Black curves represent data using polymer **1** through NMP-based protocol. Red curves represent data using pure **1** through GVL-based protocol, while green curves represent data obtained using contaminated **1** through GLV-based protocol.

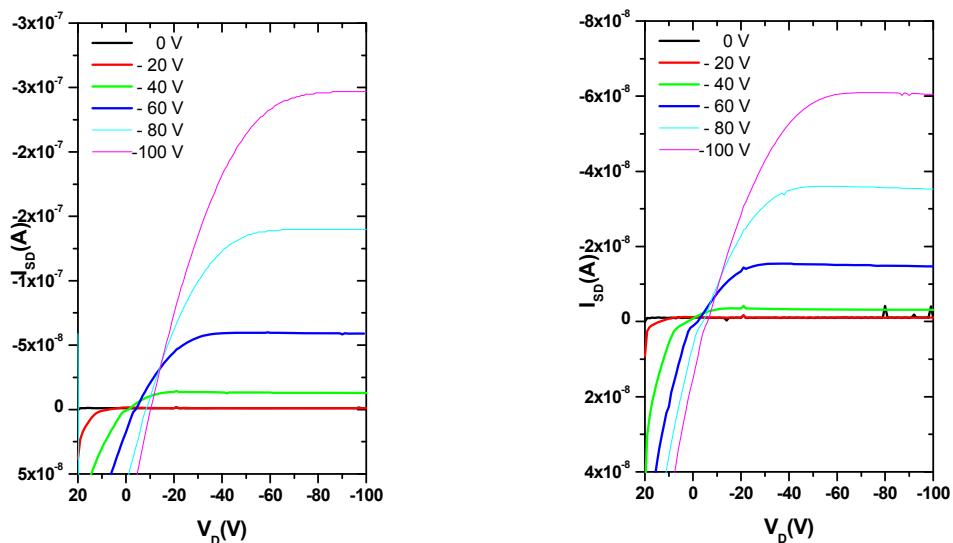
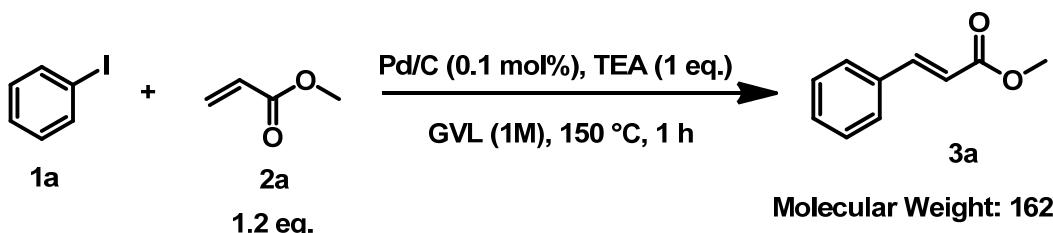


Figure S5. Typical output plot for spin-coated **1** OFETs through a) NMP-based and b) GVL based protocol.

Chem. Name	Methyl cinnamate (3a)	
Lit. Ref.	<i>J. Org. Chem.</i> , 2006, 71, 4339-4342	



METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene (**1a**) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and methyl acrylate (**2a**) (207 mg, 0.216 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3a** was obtained as a pale yellow solid (266 mg, 82% yield).

Mol Formula	C ₁₀ H ₁₀ O ₂	m.p.	38 °C
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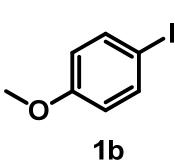
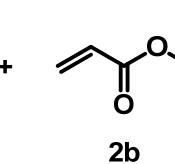
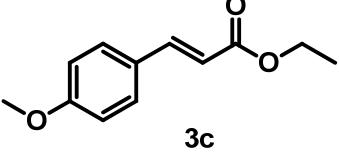
Elemental Analysis: Calc.: C: 74.06; H: 6.21; found: C: 74.10; H: 6.23

¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz	
	3.80	3	s		
	6.44	1	d	16	
	7.37 – 7.38	3	m		
	7.51 – 7.52	2	m		
	7.70	1	d	16	

¹³C NMR (100.6 MHz, CDCl₃) δ : 51.6, 117.7, 128.0, 128.8, 130.2, 134.3, 144.8, 167.4

GC-EIMS (m/z, %): 51 (30), 77 (53), 102 (25), 103 (93), 131 (100), 132 (16), 161 (44), 162 (M⁺, 86)

Chem. Name	(E)-methyl 3-(4methoxyphenyl)acrylate (3b)				
Lit. Ref.	<i>J. Org. Chem.</i> , 2006, 71, 4339-4342				
 1b + 2a $\xrightarrow[\text{GVL (1M), 150 } ^\circ\text{C, 2 h}]{\text{Pd/C (0.1 mol%), TEA (1 eq.)}}$ 3b					
				Molecular Weight: 192	
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole (1b) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and methyl acrylate (2a) (207 mg, 0.216 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way 3b was obtained as a slightly yellow solid (315 mg, 82% yield).					
Mol Formula	C₁₁H₁₂O₃		m.p.	90-91 °C	
Elemental Analysis: Calc.: 68.74; H: 6.29; found: C: 68.82; H: 6.34					
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz	
	3.78	3	s		
	3.82	3	s		
	6.30	1	d	16	
	6.89	2	d	8.8	
	7.46	2	d	8.8	
	7.64	1	d	16	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 51.5, 55.3, 114.2, 115.1, 127.0, 130.0, 144.4, 161.2, 167.7					
GC-EIMS (m/z, %): 63 (15), 89 (25), 90 (16), 118 (17), 133 (34), 134 (16), 161 (100), 192 (M ⁺ , 70)					

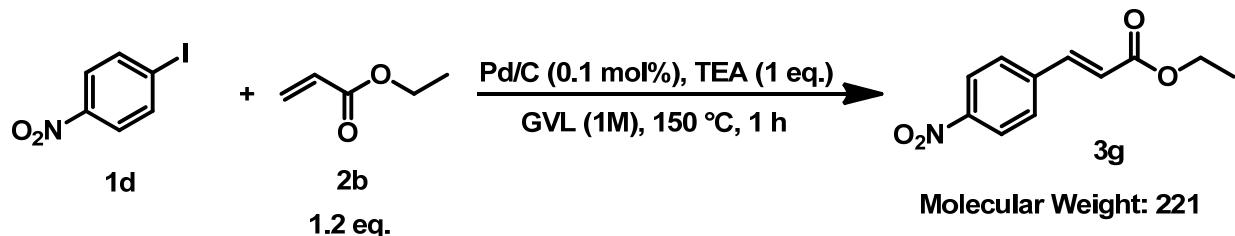
Chem. Name	(E)-ethyl 3-(4methoxyphenyl)acrylate (3c)			
Lit. Ref.	<i>J. Org. Chem.</i> , 2005, 70, 6111-6113			
 1b	 2b 1.2 eq.	$\xrightarrow[\text{GVL (1M), 150 } ^\circ\text{C, 2 h}]{\text{Pd/C (0.1 mol%), TEA (1 eq.)}}$	 3c Molecular Weight: 206	
METHOD:				
<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole (1b) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and ethyl acrylate (2b) (240 mg, 0.264 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way 3c was obtained as a white solid (371 mg, 90% yield).</p>				
Mol Formula	$C_{12}H_{14}O_3$	m.p.	49 °C	
Elemental Analysis: Calc.: C: 69.88; H: 6.84; found: C: 69.92; H: 6.78				
$^1\text{H NMR}$ 400 MHz CDCl_3	δ value	No. H	Mult.	j value/Hz
	1.30	3	<i>t</i>	7.0
	3.79	3	<i>s</i>	
	4.22	2	<i>q</i>	7.2
	6.86	2	<i>d</i>	8.8
	7.44	2	<i>d</i>	8.4
	7.61	1	<i>d</i>	16
$^{13}\text{C NMR (100.6 MHz, CDCl}_3\text{)}$ δ : 14.3, 55.2, 60.2, 114.2, 115.6, 127.0, 129.6, 144.1, 161.1, 167.3				
GC-EIMS (m/z, %): 63 (15), 89 (24), 90 (18), 118 (17), 133 (36), 134 (16), 161 (100), 192 (M ⁺ , 71)				

Chem. Name	(E)-methyl 3-(4-acetoxyphenyl) acrylate (3d)					
Lit. Ref.	<i>Adv. Synth. & Cat.</i> , 2008, 350, 2551-2558					
<p style="text-align: center;"> <chem>CC(=O)c1ccc(I)cc1</chem> + <chem>CC(=O)OC</chem> $\xrightarrow[\text{GVL (1M), 150 } \text{°C, 1.5 h}]{\text{Pd/C (0.1 mol%), TEA (1 eq.)}}$ <chem>CC(=O)c1ccc(CC=CC(=O)OC)cc1</chem> 1c 2a 3d 1.2 eq. </p> <p style="text-align: center;">Molecular Weight: 204</p>						
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone (1c) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and methyl acrylate (2a) (207 mg, 0.216 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way 3d was obtained as a white solid (355 mg, 87% yield).						
Mol Formula	C₁₀H₁₀O₃		m.p.			
Elemental Analysis: Calc.: C: 70.57; H: 5.92; found: C: 70.63; H: 5.95						
¹H NMR 400 MHz CDCl₃	δ value	No. H	Mult.	j value/Hz		
	2.58	3	s			
	3.78	3	s			
	6.48	1	d	16		
	7.56	2	d	8		
	7.66	1	d	16		
	7.93	2	d	8		
¹³C NMR (100.6 MHz, CDCl₃) δ : 26.6, 51.8, 120.2, 128.0, 128.8, 137.9, 138.5, 143.1, 166.8, 197.2						
GC-EIMS (m/z, %): 43 (26), 76 (10), 102 (25), 161 (15), 189 (100), 190 (13), 204 (M ⁺ , 29)						

Chem. Name	(E)-ethyl 3-(4-acetoxyphenyl) acrylate (3e)					
Lit. Ref.	<i>J. Am. Chem. Soc.</i> , 2003, 125, 6034-6035					
<p style="text-align: center;">1c + 2b $\xrightarrow[\text{1.2 eq.}]{\text{Pd/C (0.1 mol%), TEA (1 eq.)}}$ 3e</p> <p style="text-align: center;">GVL (1M), 150 °C, 1.5 h</p> <p style="text-align: center;">Molecular Weight: 218</p>						
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone (1c) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and ethyl acrylate (2b) (240 mg, 0.264 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way 3e was obtained as a slightly yellow solid (371 mg, 85% yield).						
Mol Formula	C₁₃H₁₄O₃	m.p.	46 °C			
Elemental Analysis: Calc.: C: 71.54; H: 6.47; found: C: 7.63; H: 6.51						
¹H NMR 400 MHz CDCl₃	δ value	No. H	Mult.	j value/Hz		
	1.33	3	<i>t</i>	7.0		
	2.6	3	<i>s</i>			
	4.26	2	<i>q</i>	7.0		
	6.50	1	<i>d</i>	16		
	7.59	2	<i>d</i>	8		
	7.68	1	<i>d</i>	16		
	7.95	2	<i>d</i>	8.4		
¹³C NMR (100.6 MHz, CDCl₃) δ : 14.2, 26.6, 60.7, 120.7, 128.0, 128.7, 137.8, 138.7, 142.9, 166.4, 197.2						
GC-EIMS (m/z, %): 43 (10), 76 (17), 102 (36), 131 (19), 173 (20), 175 (31), 203 (100), 204 (15), 218 (M ⁺ , 33)						

Chem. Name	(E)-methyl 3-(4-nitrophenyl) acrylate (3f)			
Lit. Ref.	Adv. Synth. & Cat., 2008, 350, 2559-2565			
	<p style="text-align: center;"> <chem>Ic1ccc([N+](=O)[O-]c1)C</chem> 1d + <chem>CC(=O)OC</chem> 2a $\xrightarrow[\text{1.2 eq.}]{\text{Pd/C (0.1 mol%), TEA (1 eq.), GVL (1M), 150 }^\circ\text{C, 1 h}}$ <chem>CC(=O)OCc1ccc([N+](=O)[O-]c1)C</chem> 3f </p> <p style="text-align: right;">Molecular Weight: 207</p>			
METHOD:				
Mol Formula		C ₁₀ H ₉ NO ₄	m.p.	161 °C
Elemental Analysis: Calc.: C: 57.97; H: 4.38; N: 6.76; found: C: 57.91; H: 4.43; N: 6.83				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	3.84	3	s	
	6.57	1	d	14.8
	7.67-7.74	3	m	
	8.27	2	d	8.8
¹³C NMR (100.6 MHz, CDCl₃) δ : 52.2, 122.0, 124.1, 128.6, 140.4, 141.8, 148.4, 166.4				
GC-EIMS (m/z, %): 50 (26), 51 (22), 63 (21), 74 (19), 75 (22), 76 (38), 89 (22), 90 (31), 102 (61), 118 (26), 130 (38), 176 (100), 207 (M ⁺ , 57)				

Chem. Name	(E)-ethyl 3-(4-nitrophenyl) acrylate (3g)
Lit. Ref.	<i>J. Org. Chem.</i> , 2006 , 71, 4339-4342



METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (**1d**) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and ethyl acrylate (**2b**) (240 mg, 0.264 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3q** was obtained as a slightly yellow solid (380 mg, 86% yield).

Mol Formula	C ₁₁ H ₁₁ NO ₄	m.p.	135 °C
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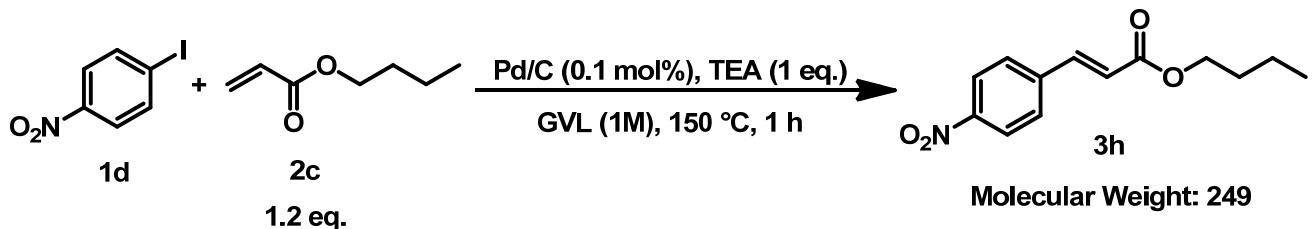
Elemental Analysis: Calc.: C: 59.73; H: 5.01; N: 6.33; found: C: 59.81; H: 5.10; N: 6.24

¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz	
	1.35	3	<i>t</i>	7.0	
	4.29	2	<i>q</i>	7.0	
	6.56	1	<i>d</i>	16	
	7.66-7.72	3	<i>m</i>		
	8.25	2	<i>d</i>	8.8	

¹³C NMR (100.6 MHz, DMSO) δ : 14.5, 60.8, 122.8, 124.3, 129.8, 140.8, 142.2, 148.4, 166.0

GC-EIMS (m/z, %): 50 (17), 51 (16), 75 (19), 76 (35), 102 (60), 130 (47), 176 (100), 193 (46), 221 (M⁺, 22)

Chem. Name	(E)-butyl 3-(4-nitrophenyl) acrylate (3h)	
Lit. Ref.	Adv. Synth. & Cat., 2002, 344, 495-498	



METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (**1d**) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and butyl acrylate (**2c**) (311 mg, 0.348 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3h** was obtained as a slightly yellow solid (408 mg, 82% yield).

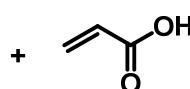
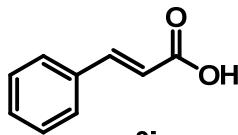
Mol Formula	C ₁₃ H ₁₅ NO ₄	m.p.	64-65 °C
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Elemental Analysis: Calc.: C: 62.64; H: 6.07; N: 5.62; found: C: 62.72; H: 6.12; N: 5.68

¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	\jmath value/Hz
	0.939	3	<i>t</i>	7.4
	1.37-1.46	2	<i>m</i>	
	1.64-1.71	2	<i>m</i>	
	4.21	2	<i>t</i>	6.6
	6.54	1	<i>d</i>	16
	7.64-7.69	3	<i>m</i>	
	8.21	2	<i>d</i>	8.0

¹³C NMR (100.6 MHz, DMSO) δ : 14.5, 60.8, 122.8, 124.3, 129.8, 140.8, 142.2, 148.4, 166.0

GC-EIMS (m/z, %): 56 (47), 76 (29), 90 (21), 102 (66), 130 (38), 176 (100), 177 (21), 193 (39), 194 (48)

Chem. Name	Cinnamic Acid (3i)		
Lit. Ref.	<i>J. Org. Chem.</i> 2004 , 69, 8805-8807		
 1a	 2d 1.5 eq.	Pd/C (0.1 mol%), TEA (1 eq.) GVL (1M), 150 °C, 1 h	 3i Molecular Weight: 148

METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene (**1a**) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (**2d**) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3i** was obtained as a white solid (249 mg, 84% yield).

Mol Formula	C ₉ H ₈ O ₂	m.p.	132-135 °C
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Elemental Analysis: Calc.: C: 72.96; H: 5.44; found: C: 73.04; H: 5.38

¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz	
	6.57	1	<i>d</i>	16	
	7.45-7.46	3	<i>m</i>		
	7.63	1	<i>d</i>	16	
	7.72-7.74	2	<i>m</i>		

¹³C NMR (100.6 MHz, CDCl₃) δ : 117.2, 128.3, 128.9, 130.7, 133.9, 147.0, 128.8, 172.4

GC-EIMS (m/z, %): 43 (22), 45 (21), 50 (29), 51 (45), 77 (65), 91 (37), 102 (40), 103 (66), 131 (32), 147 (100), 148 (67), 207 (M⁺, 15)

Chem. Name	(E)-3-(4-methoxyphenyl)acrylic acid (3j)		
Lit. Ref.	<i>J. Org. Chem.</i> , 2004 , 69, 8805-8807		
	<p style="text-align: center;">1.5 eq.</p>	3j	Molecular Weight: 178

METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole (**1b**) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (**2d**) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3j** was obtained as a white solid (285 mg, 80 % yield).

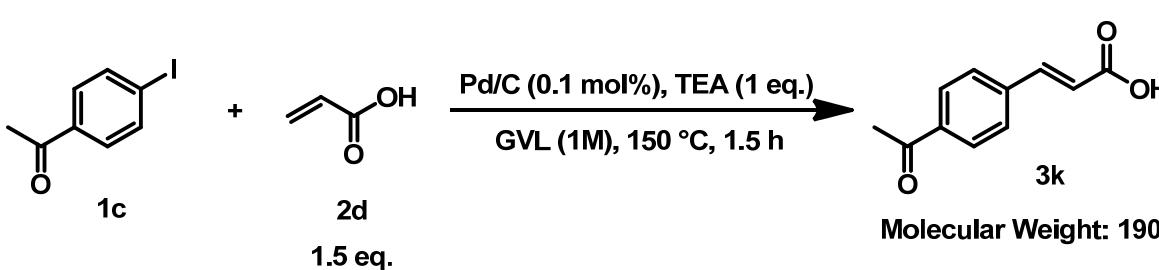
Mol Formula	C ₁₀ H ₁₀ O ₃	m.p.	172-173 °C
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Elemental Analysis: Calc.: C: 67.41; H: 5.66; found: C: 67.34; H: 5.45

¹ H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz	
	3.83	3	s		
	6.41	1	d	16	
	7.01	2	d	8.4	
	7.58	1	d	16	
	7.68	2	d	8.4	

¹³C NMR (100.6 MHz, DMSO) δ : 55.7, 114.7, 116.8, 127.1, 130.3, 144.1, 161.3, 168.2

GC-EIMS (m/z, %): 63 (20), 77 (31), 79 (16), 89 (30), 90 (15), 132 (22), 133 (26), 161 (44), 177 (26), 178 (M⁺, 100)

Chem. Name	(E)-methyl 3-(4-acetylphenyl) acrylic acid (3k)		
Lit. Ref.	<i>J. Org. Chem.</i> , 2004 , 69, 8805-8807		
			

METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone (**1c**) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (**2d**) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3k** was obtained as a yellowish solid (323 mg, 85 % yield).

Mol Formula	C ₁₁ H ₁₀ O ₃	m.p.	224-225 °C
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Elemental Analysis: Calc.: C: 69.46; H: 5.30; found: C: 69.51; H: 5.22

¹ H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz	
	2.59	3	s		
	6.67	1	d	16	
	7.64	1	s	16	
	77.83	2	d	8	
	7.96	2	d	8.4	

¹³C NMR (100.6 MHz, DMSO) δ : 27.2, 122.1, 128.8, 129.0, 137.9, 138.9, 142.9, 167.7, 197.8

GC-EIMS (m/z, %): Not performed

Chem. Name	(E)-3-(4-nitrophenyl) acrylic acid (3I)		
Lit. Ref.	<i>J. Org. Chem.</i> , 2004, 69, 8805-8807		
	<p style="text-align: center;">1.5 eq.</p>	<p style="text-align: right;">Molecular Weight: 193</p>	

METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (**1d**) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (**2d**) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3I** was obtained as a yellowish solid (320 mg, 83% yield).

Mol Formula	C ₉ H ₇ NO ₄	m.p.	286-287 °C
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Elemental Analysis: Calc.: C: 55.96; H: 3.65; N: 7.25; found: C: 55.89; H: 3.61; N: 7.29

¹ H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz	
	6.76-6.84	1	<i>m</i>		
	7.71-7.77	1	<i>m</i>		
	7.67-7.74	3	<i>m</i>		
	7.97	2	<i>d</i>	8.4	
	8.23	2	<i>d</i>	8.4	

¹³C NMR (100.6 MHz, DMSO) δ : 124.0, 124.3, 129.7, 141.1, 141.7, 148.4, 167.4

GC-EIMS (m/z, %): Not performed

Chem. Name	(E)-1,2-diphenylethene (5a)				
Lit. Ref.	<i>J. Org. Chem.</i> , 2006, 71, 4339-4342				
 1a 4a 1 eq.	Pd/C (0.1 mol%), TEA (1 eq.) GVL (1M), 150 °C, 2 h	 5a	 5a'		
Molecular Weight: 180					
Mol Formula C₁₄H₁₂ m.p. 126-127 °C					
Elemental Analysis: Calc.: C: 93.29; H: 6.71; found: 93.38; H: 6.61					
¹H NMR 400 MHz CDCl₃	δ value	No. H	Mult.	J value/Hz	
	7.13	2	s		
	7.28-7.30	2	m		
	7.36-7.40	4	m		
	7.53-7.55	4	m		
¹³C NMR (100.6 MHz, CDCl₃) δ : 126.6, 127.7, 128.8, 137.4					
GC-EIMS (m/z, %): 89 (15), 152 (17), 165 (52), 178 (64), 179 (99), 180 (M ⁺ , 100), 181 (14)					

Chem. Name	(E)-1-methoxy-4-styrylbenzene (5b)			
Lit. Ref.	<i>Adv. Synth. & Cat.</i> , 2008 , 350, 2551-2558			
<p style="text-align: center;">Molecular Weight: 210</p>				
METHOD:	<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole (1b) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene (4a) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 95:5 mixture of 5b and 5b' (344 mg, 82% yield).</p>			
Mol Formula	C ₁₅ H ₁₄	m.p.	138 °C	
Elemental Analysis: Calc.: C: 85.68; H: 6.71; found: C: 85.71; H: 6.65				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	3.84	3	s	
	6.90-7.09	4	m	
	7.22-7.24	2	m	
	7.33-7.37	2	m	
	7.45-7.50	4	m	
¹³C NMR (100.6 MHz, CDCl₃) δ : 55.2, 114.6, 126.2, 126.5, 127.1, 127.6, 128.1, 128.5, 130.1, 137.6, 159.2				
GC-EIMS (m/z, %): 152 (33), 165 (51), 166 (19), 167 (38), 179 (16), 195 (29), 209 (27), 210 (M ⁺ , 100), 211 (25)				

Chem. Name	(E)-1-(4-styrylphenyl) ethanone (5c)			
Lit. Ref.	<i>Eur. J. Org. Chem.</i> , 2007, 13, 2197-2201			
<p style="text-align: center;">Molecular Weight: 222</p>				
METHOD:	<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone (1c) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene (4a) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 99:1 mixture of 5c and 5c' (382 mg, 86% yield).</p>			
Mol Formula	$C_{15}H_{14}$	m.p.	140-144 °C	
Elemental Analysis: Calc.: C: 86.45; H: 6.35; found: C: 86.39; H: 6.31				
^1H NMR 400 MHz CDCl_3	δ value	No. H	Mult.	j value/Hz
	2.61	3	s	
	7.12-7.22	2	m	
	7.33-7.29	1	m	
	7.37-7.41	2	m	
	7.54-7.60	4	m	
	7.96	2	d	8
^{13}C NMR (100.6 MHz, CDCl_3) δ : 26.6, 126.4, 126.7, 127.3, 128.3, 128.7, 128.8, 131.4, 135.8, 136.6, 141.9, 197.5				
GC-EIMS (m/z, %): 152 (18), 176 (15), 178 (70), 179 (24), 207 (100), 208 (17), 222 (M^+ , 64)				

Chem. Name	(E)-1-nitro-4-styrylbenzene (5d)					
Lit. Ref.	<i>Eur. J. Org. Chem.</i> , 2007, 13, 2197-2201					
<p style="text-align: center;">Molecular Weight: 225</p>						
METHOD:						
<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (1d) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene (4a) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a yellowish solid consisting in a 99:1 mixture of 5d and 5d' (378 mg, 84% yield).</p>						
Mol Formula	C ₁₅ H ₁₄		m.p.			
158-159 °C						
Elemental Analysis: Calc.: C: 74.65; H: 4.92; N: 6.22; found: C: 74.72; H: 4.87; N: 6.28						
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz		
	7.15	1	<i>d</i>	16.4		
	7.30-7.44	4	<i>m</i>			
	7.56-7.65	4	<i>m</i>			
	8.23	2	<i>d</i>	8.4		
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 124.1, 126.2, 126.8, 127.0, 128.8, 133.2, 136.1, 143.8, 146.6						
GC-EIMS (m/z, %): 151 (14), 152 (36), 165 (18), 176 (20), 177 (19), 178 (100), 179 (36), 225 (M ⁺ , 70)						

Chem. Name	(E)-1-methyl-4-styrylbenzene (5e)			
Lit. Ref.	<i>Tetrahedron</i> , 2013, 69, 7925-7930			
<p style="text-align: center;"> <chem>Ic1ccccc1</chem> (1e) + <chem>C=Cc1ccccc1</chem> (4a) $\xrightarrow[\text{GVL (1M), 150 } \text{°C, 2.5 h}]{\text{Pd/C (0.1 mol%), TEA (1 eq.)}}$ <chem>C=Cc1ccccc1Cc2ccccc2</chem> (5e) + <chem>C=Cc1ccccc1C(=O)c2ccccc2</chem> (5e') Molecular Weight: 194 </p>				
METHOD:				
Mol Formula	C ₁₅ H ₁₄	m.p.	124 °C	
Elemental Analysis: Calc.: C: 85.68; H: 6.71; found: C: 85.71; H: 6.65				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	2.36	3	s	
	7.07-7.08	2	m	
	7.16-7.18	2	m	
	7.23-7.25	1	m	
	7.33-7.37	2	m	
	7.41-7.43	2	m	
	7.50-7.52	2	m	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 21.4, 126.5, 126.6, 127.5, 127.8, 128.7, 128.8, 129.5, 134.6, 137.6, 137.7				
GC-EIMS (m/z, %): 89 (12), 115 (23), 152 (15), 165 (18), 178 (82), 179 (100), 180 (16), 193 (19), 194 (M ⁺ , 94), 195 (19)				

Chem. Name	(E)-1-chloro-4-styrylbenzene (5f)			
Lit. Ref.	Green Chem., 2012, 14, 2513-2522			
<p>1a + 4b → 5f + 5f'</p> <p>Molecular Weight: 214</p>				
METHOD:				
<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene (1a) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and 4-chlorostyrene (4b) (286 mg, 0.247 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this a white solid consisting in a 92:8 mixture of 5f and 5f' (385 mg, 90% yield).</p>				
Mol Formula	C ₁₄ H ₁₁ Cl	m.p.	127-129°C	
Elemental Analysis: Calc.: C: 78.32; H: 5.16; found: 78.64; H: 5.08.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	J value/Hz
	7.07	2	<i>m</i>	
	7.26-7.39	5	<i>m</i>	
	7.44	2	<i>d</i>	8.4
	7.51	2	<i>d</i>	7.6
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 126.7, 127.5, 127.8, 128.0, 128.9, 129.0, 129.4, 133.3, 135.9, 137.1				
GC-EIMS (m/z, %): 50 (17), 51 (21), 63 (18), 75 (20), 76 (27), 89 (24), 152 (17), 176 (24), 178 (100), 179 (94), 214 (70), 216 (23).				

Chem. Name	(E)-1-chloro-4-(4-methoxystyryl)benzene (5g)			
Lit. Ref.	<i>J. Mol. Cat. A: Chem.</i> , 2006 , 254, 58-63			
<p style="text-align: center;">Molecular Weight: 245</p>				
METHOD:	<p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole (1b) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and 4-chlorostyrene (4b) (286 mg, 0.247 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this a white solid consisting in a 90:10 mixture of 5g and 5g' (441 mg, 90% yield).</p>			
Mol Formula	$C_{15}H_{13}ClO$	m.p.	193-194°C	
Elemental Analysis: Calc.: C: 73.62; H: 5.35; found: 74.01; H: 5.37.				
¹ H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	J value/Hz
	3.84	3	s	
	6.89-6.94	3	m	
	7.03	1	d	16.4
	7.30-7.32	2	m	
	7.40-7.46	4	m	
¹³ C NMR (100.6 MHz, $CDCl_3$) $δ$: 55.4, 114.3, 125.3, 127.5, 127.9, 128.9, 129.8, 132.8, 136.2, 159.5				
GC-EIMS (m/z, %): 165 (91), 166 (54), 229 (20), 244 (100), 245 (17), 246 (34)				

Chem. Name	(E)-1-(4-(4-chlorostyryl)phenyl)ethanone (5h)							
Lit. Ref.	Tetrahedron Lett., 2012, 53, 5961-5965							
<p style="text-align: center;">Molecular Weight: 257</p>								
METHOD:								
Mol Formula	C ₁₆ H ₁₃ ClO	m.p.						
Elemental Analysis: Calc.: C: 74.85; H: 5.10; found: 75.03; H: 5.12.								
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	J value/Hz				
	2.61	3	s					
	7.07-7.19	2	m					
	7.34	2	d	8.4				
	7.46	2	d	8.4				
	7.57	2	d	8.4				
	7.95	2	d	8.4				
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 26.7, 126.6, 128.0, 128.1, 129.0, 129.1, 130.2, 134.0, 135.3, 136.2, 141.7								
GC-EIMS (m/z, %): 43 (25), 176 (29), 177 (18), 178 (56), 241 (100), 243 (36), 256 (74), 258 (24).								

