Electronic Supplementary Material (ESI) for RSC Advances

Eugenol as a renewable feedstock for the production of polyfunctional alkenes via olefin cross-metathesis

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Supplementary Data

General remarks: All the reactions were conducted under an inert atmosphere of argon using standard Schlenk tube techniques. Solvents were dried by distillation prior to use. Dimethyl carbonate and diethyl carbonate were distilled under atmospheric pressure and stored under argon over activated 3Å molecular sieves. Eugenol was purchased from Alfa Aesar and used as received (99%). *O*-eugenol was purchased from Aldrich and used as received (98%). Methyl acrylate and methyl methacrylate were purchased from Acros Organics and stored under argon over activated 3Å molecular sieves prior to use. Acrylonitirile was distilled under atmospheric pressure and stored under argon over activated 3Å molecular sieves. Acrylamide was purchased from Alfa Aesar and used as received (99.9%). Isopropylacrylamide was purchased from Acros Organics and used as received (99%).

General procedure for the cross-metathesis reactions with methyl acrylate

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenol or its derivatives (0.48-0.61 mmol), 4.0 mg of Umicore M51 catalyst **IV** (6.10^{-3} mmol, 1 mol%) or 7.6 mg of Hoveyda catalyst (12.10^{-3} mmol, 2 mol%), 88-106 µl of methyl acrylate (~ 0.97-1.2 mmol, 2 equiv.) or 443 µl of methyl acrylate (4.89 mmol, 10 equiv.), 2.5 -3.3 mg of *para*-benzoquinone (~$22\text{-}30.10^{-3}$ mmol, 5 mol%), or 5.2 mg of *para*-benzoquinone (~49.10^{-3} mmol, 10 mol%), 10 µl of dodecane as internal standard and 2 ml of solvent. The reaction was stirred under the mentioned conditions. After solvent evaporation, the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with methyl methacrylate

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenol or its derivatives (0.48-0.61 mmol), 6.2-7.6 mg of Hoveyda catalyst **II** ($0.97\text{-}12.10^{-3}$ mmol, 2 mol%), 2.5-3.3 mg of *para*-benzoquinone ($\sim 22\text{-}30.10^{-3}$ mmol, 5 mol%), 10 µl of dodecane as internal standard and 2 ml of methyl methacrylate (19 mmol, 31-39 equiv.). The reaction was stirred under the mentioned conditions. If necessary, the reaction mixture was slightly diluted with $CHCl_3$ and poured into 50 ml of pentane to precipitate the poly-MMA formed. After filtration and evaporation the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with acrylonitrile

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenol or its derivatives (0.48-0.61 mmol), 2.5-3.3 mg of *para*-benzoquinone ($\sim 22\text{-}30.10^{-3}$ mmol, 5 mol%), 64-80 µl of acrylonitrile (~ 0.97-1.2 mmol, 2 equiv.), 1.5 ml of solvent and then closed by a rubber septum. Another dry and degassed Schlenk tube was loaded under argon with 6.0-7.6 mg of Hoveyda catalyst **II** (12.10^{-3} mmol, 2 mol%), 10 µl of dodecane as internal standard and 0.5 ml of solvent. The ruthenium catalyst was then taken by a syringe, and was slowly added into the first Schlenk tube through the septum by means of a syringe-pump during 2 h. After addition, the reaction mixture was stirred at 100 °C for additional 3 h. After solvent evaporation, the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with acrylamide

A dry and degassed Schlenk tube was loaded under argon with 125 -157 mg of eugenol or its derivatives (0.76 mmol, 1.25 equiv.), 2.5-3.3 mg of *para*-benzoquinone ($\sim 22\text{-}30.10^{-3}$ mmol, 5 mol%), 43 mg of acrylamide (0.6 mmol, 1 equiv.), 10 µl of dodecane as internal standard and 1.5 ml of solvent and then closed by a rubber septum. Another dry and degassed Schlenk tube was loaded under argon with 7.6 mg of Hoveyda catalyst (12.10^{-3} mmol, 2 mol%), 10 µl of dodecane as internal standard and 0.5 ml of solvent. The ruthenium catalyst was then taken by a syringe, and was slowly added into the first Schlenk tube through the septum by means of a syringe-pump during 2 h. After addition, the reaction mixture was stirred at 80 °C for additional time under the mentioned conditions. After solvent evaporation, the products were

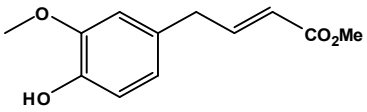
purified by column chromatography on basic alumina gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with isopropylacrylamide

A dry and degassed Schlenk tube was loaded under argon with 125 -157 mg of eugenol or its derivatives (0.76 mmol, 1.25 equiv.), 2.5-3.3 mg of *para*-benzoquinone (~22-30.10^{-3} mmol, 5 mol%), 69 mg of isopropylacrylamide (0.6 mmol, 1 equiv.), 1.5 ml of solvent and then closed by a rubber septum. Another dry and degassed Schlenk tube was loaded under argon with 7.7 mg of Hoveyda catalyst (12.10^{-3} mmol, 2 mol%), 10 µl of dodecane as internal standard and 0.5 ml of solvent. The ruthenium catalyst was then taken by a syringe, and was slowly added into the first Schlenk tube through the septum by means of a syringe-pump during 2 h. After addition, the reaction mixture was stirred at 80 °C for additional time under the mentioned conditions. After solvent evaporation, the products were purified by column chromatography on basic alumina gel using of EtOAc/petroleum ether mixtures.

Synthesis of (E)-methyl 4-(4-hydroxy-3-methoxyphenyl)but-2-enoate **3**

Eugenol (100 mg, 0,6 mmol, 1 equiv.), methyl acrylate (106 µl, 1,2 mmol, 2 equiv), catalyst **IV** (4 mg, 6 10^{-3} mmol, 1 %), DMC, 80 °C, 8 h.



3

Isolated yield: 73%

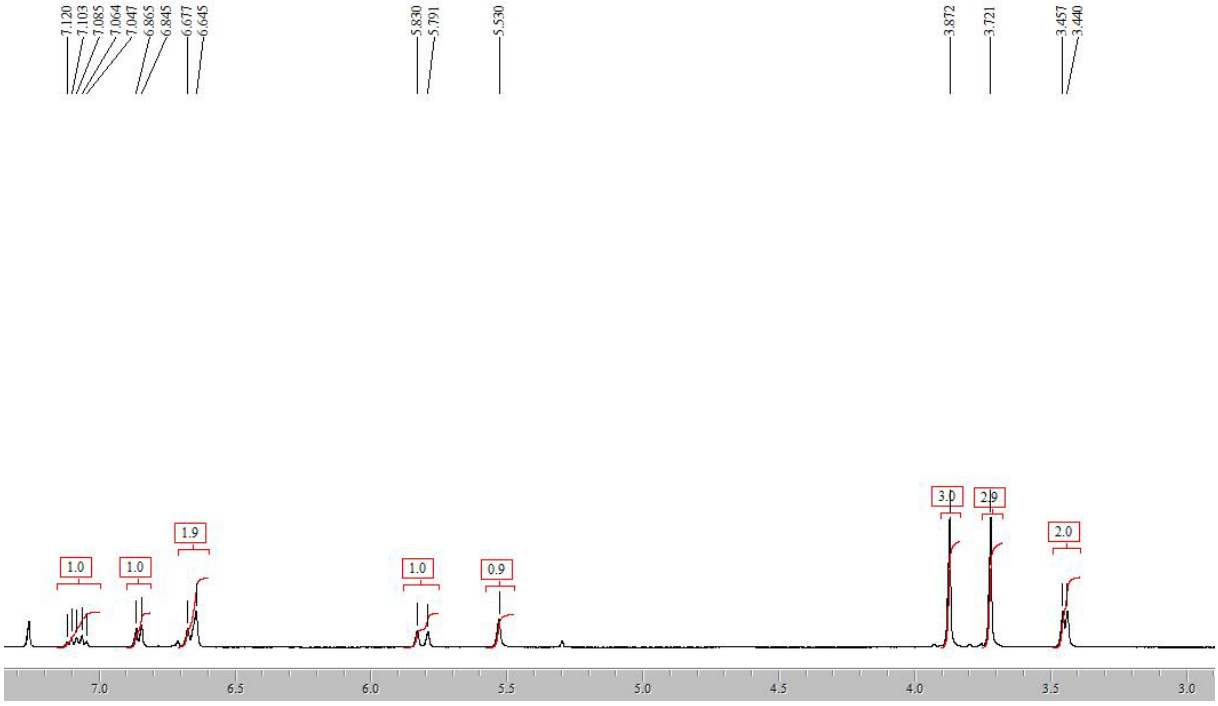
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.44 (d, 6.8 Hz, 2H, CH_2), 3.72 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 5.53 (s, 1H, OH), 5.81 (d, 15.6 Hz, 1H, CH), 6.64-6.67 (m, 2Har, CH), 6.85 (d, 8.0 Hz, 1Har, CH), 7.04-7.12 (m, 1H, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 38.0 (CH_2), 51.3 (CH_3), 55.8 (CH_3), 111.2 (CH), 114.5 (CH), 121.4 (CH), 121.5 (CH), 129.3 (C), 144.3 (C), 146.6 (C), 147.9 (CH), 166.9 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{12}H_{14}O_4Na$) = 245.0789. Measured: 245.0791.

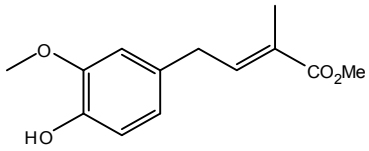
$C_{12}H_{14}O_4$: Theoretical **C** 64.85, **H** 6.35. Experimental **C** 64.52, **H** 6.39.

400 MHz ^{1}H NMR of **3**



Synthesis of (E)-methyl 4-(4-hydroxy-3-methoxyphenyl)-2-methylbut-2-enoate **10**

Eugenol (100 mg, 0,6 mmol, 1 equiv.), methyl methacrylate (2 ml, 19 mmol, 31 equiv.), catalyst **II** (7.6 mg, 12 10^{-3} mmol, 2 %), 90 °C, 16 h.



10

Isolated yield: 60%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.95 (s, 3H, CH_3), 3.45 (d, 7.2 Hz, 2H, CH_2), 3.73 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 5.49 (s, 1H, OH), 6.65-6.68 (m, 2Har, CH), 6.84 (d, 7.6 Hz, 1Har, CH), 6.87-6.91 (m, 1H, CH).

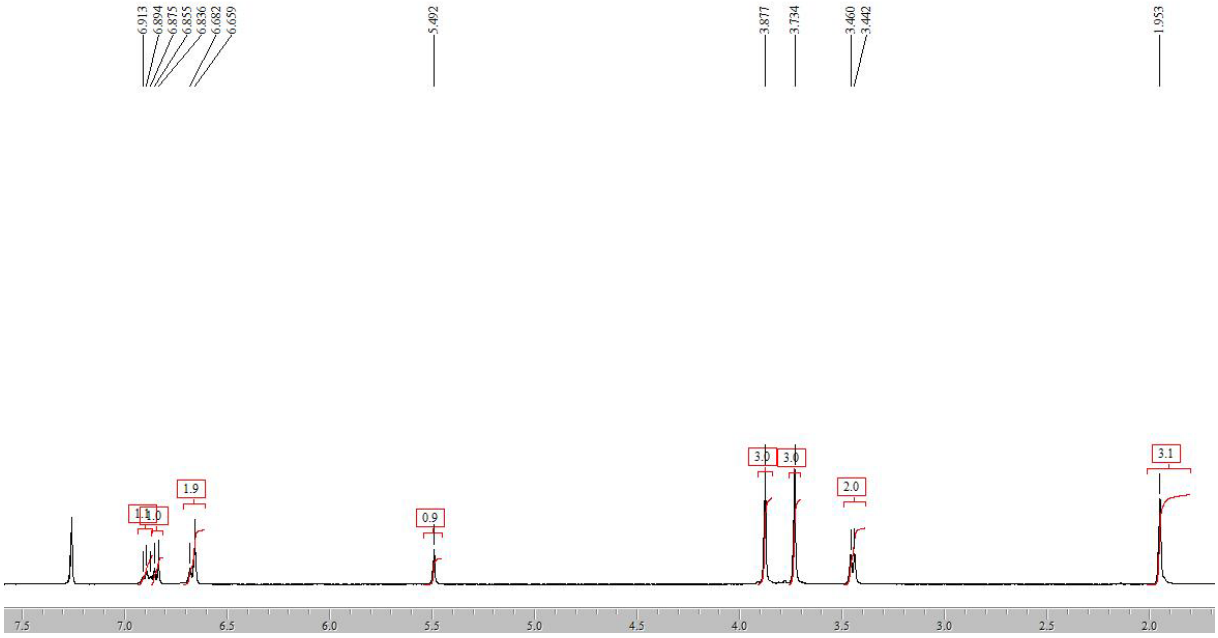
^{13}C NMR (75 MHz, $CDCl_3$, ppm): 12.4 (CH_3), 34.4 (CH_2), 51.7 (CH_3), 55.8 (CH_3), 110.9 (CH), 114.4 (CH), 121.0 (CH), 127.7 (C), 130.6 (C), 140.8 (CH), 144.1 (C), 146.5 (C), 168.5 (C).

The *E* configuration was determined by 2D NOESY (400 MHz). This experiment did not show any cross-peak between the C*H*$_3$ at 1.95 ppm and the *H* at 6.89 ppm whereas a cross-peak was detected between the C*H*$_3$ at 3.73 ppm (CO_2CH_3) and the *H* at 6.89 ppm. A cross-peak was detected between the C*H*$_3$ at 1.95 ppm and the C*H*$_2$ at 3.45 ppm.

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{13}H_{16}O_4Na$) = 259.0946. Measured: 259.0945.

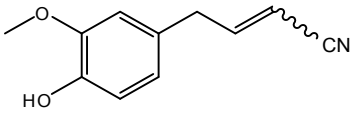
$C_{13}H_{16}O_4$: Theoretical **C** 66.09, **H** 6.83 Experimental **C** 66.31, **H** 6.83.

400 MHz ^{1}H NMR of **10**



Synthesis of 4-(4-hydroxy-3-methoxyphenyl)but-2-enenitrile (Z/E: 2/1) **12**

Eugenol (100 mg, 0,6 mmol, 1 equiv.), acrylonitrile (80 µl, 1,2 mmol, 2 equiv.), catalyst **II** (7.6 mg, 12 10^{-3} mmol, 2 %), DEC, 100 °C, 5 h.



12

Isolated yield: 82%

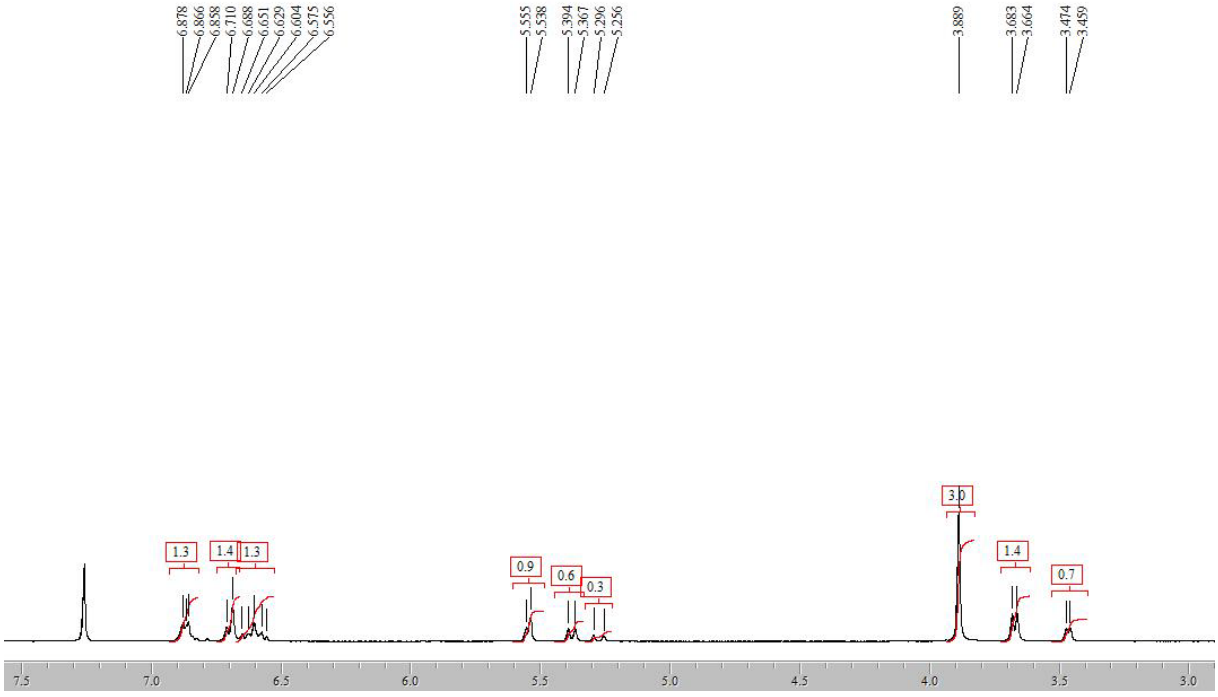
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.46, 3.67 (2d, 6.0 Hz, 7.6 Hz, 2H, CH_2, cis+trans), 3.88 (s, 3H, CH_3), 5.27, 5.38 (2d, 16.0 Hz, 10.8 Hz, 1H, CH, cis+trans), 5.54 (d, 6.8 Hz, 1H, OH), 6.55-6.65 (m, 1H, CH), 6.68-6.71 (m, 2Har, CH), 6.85-6.87 (m, 1Har, CH).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 37.5, 38.9 (CH_2, cis+trans), 55.8 (CH_3), 99.3, 100.3 (CH, cis+trans), 110.9, 111.1 (CH, cis+trans), 114.5, 114.6 (CH, cis+trans), 115.9, 117.2 (C, cis+trans), 121.0, 121.5 (CH, cis+trans), 127.6, 128.5 (C, cis+trans), 144.5, 144.6 (C, cis+trans), 146.6 (C), 153.2, 154.4 (CH, cis+trans).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{11}H_{11}NO_2Na$) = 212.0687. Measured: 212.0689.

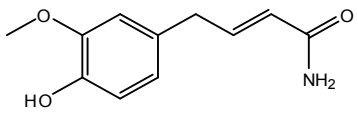
$C_{11}H_{11}NO_2$: Theoretical **C** 69.83, **H** 5.86, **N** 7.40 Experimental **C** 69.03, **H** 5.76, **N** 7.04.

400 MHz ^{1}H NMR of **12**



Synthesis of (E)-4-(4-hydroxy-3-methoxyphenyl)but-2-enamide **14**

Eugenol (125 mg, 0,76 mmol, 1.25 equiv.), acrylamide (43 mg, 0.6 mmol, 1 equiv.), catalyst **II** (7.6 mg, 12 10^{-3} mmol, 2 %), DMC, 80 °C, 4 h.



14

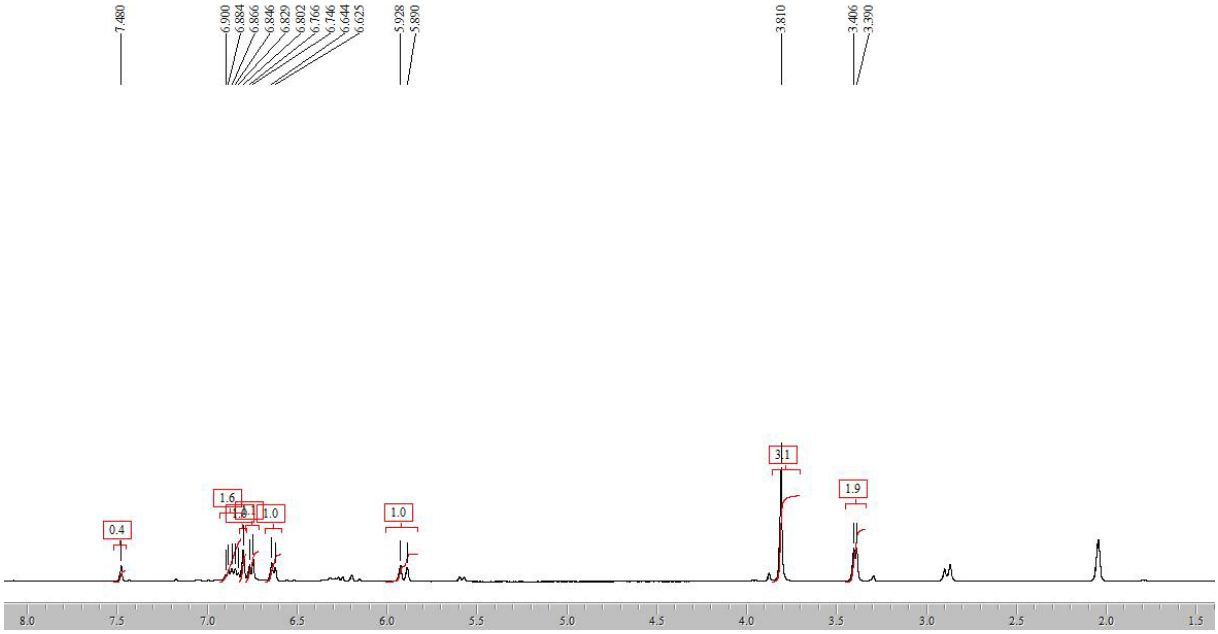
Isolated yield: 62% containing <5% of acrylamide

^{1}H NMR (400 MHz, Acetone-d_6, ppm): 3.39 (d, 6.4 Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 5.90 (d, 15.2 Hz, 1H, CH), 6.63 (d, 7.6 Hz, 1Har, CH), 6.75 (d, 8 Hz, 1Har, CH), 6.80 (bs, 1Har, CH), 6.82-6.90 (m, 2H, CHar, NH), 7.48 (s, 1H, NH). For another example of H splitting in acrylamide derivatives, see; A. Baye, M. E. Maier, *Tetrahedron*, **2004**, *60*, 6665.

^{13}C NMR (100 MHz, Acetone-d_6, ppm): 39.2 (CH_2), 57.2 (CH_3), 114.1 (CH), 116.7 (CH), 123.0 (CH), 126.3 (CH), 131.8 (C), 144.8 (CH), 146.9 (C), 149.3 (C), 168.7 (C).

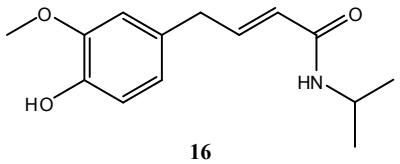
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{11}H_{13}NO_3Na$) = 230.0793. Measured: 230.0794.

400 MHz ^{1}H NMR of **14**



Synthesis of (E)-4-(4-hydroxy-3-methoxyphenyl)-N-isopropylbut-2-enamide **16**

Eugenol (125 mg, 0,76 mmol, 1.25 equiv.), isopropylacrylamide (69 mg, 0.6 mmol, 1 equiv.), catalyst **II** (7.6 mg, 12 10^{-3} mmol, 2 %), DMC, 80 °C, 4 h.



16

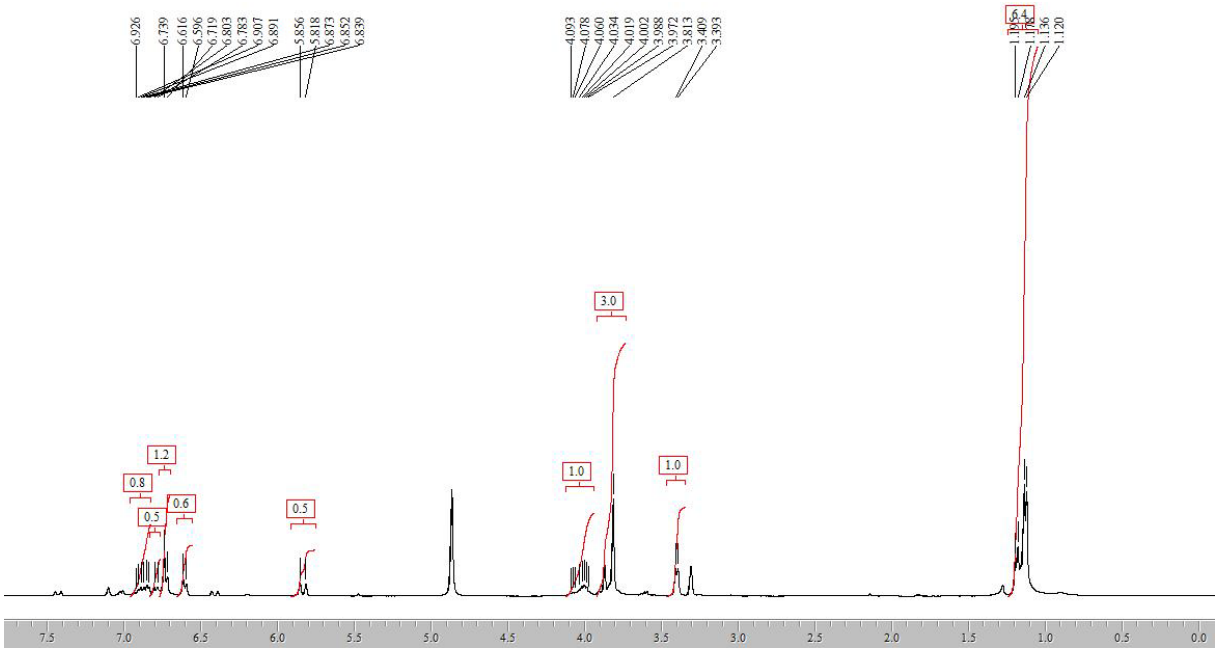
Isolated yield: 70% containing <5% of isopropyl-acrylamide

^{1}H NMR (400 MHz, Methanol-d_4, ppm): 1.12-1.19 (m, 6H, CH_3), 3.40 (d, 6.4 Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.97-4.09 (m, 1H, CH), 5.83 (d, 15.2 Hz, 1H, CH), 6.60 (d, 8.0 Hz, 1Har, CH), 6.72-6.73 (m, 2Har, CH), 6.79 (d, 8.0 Hz, 1H, NH), 6.83-6.92 (m, 1H, CH).

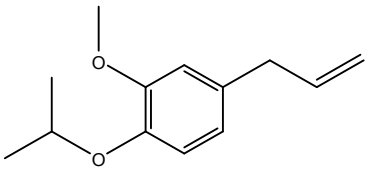
^{13}C NMR (100 MHz, Methanol-d_4, ppm): 22.4 (CH_3), 38.5 (CH_2), 42.1 (CH), 56.1 (CH_3), 113.2 (CH), 116.1 (CH), 122.1 (CH), 125.1 (CH), 130.9 (C), 144.4 (CH), 146.0 (C), 148.8 (C), 167.4 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{14}H_{19}NO_3Na$) = 272.1262. Measured: 272.1262.

400 MHz ^{1}H NMR of **16**



Synthesis of 4-allyl-1-isopropoxy-2-methoxybenzene **17**



17

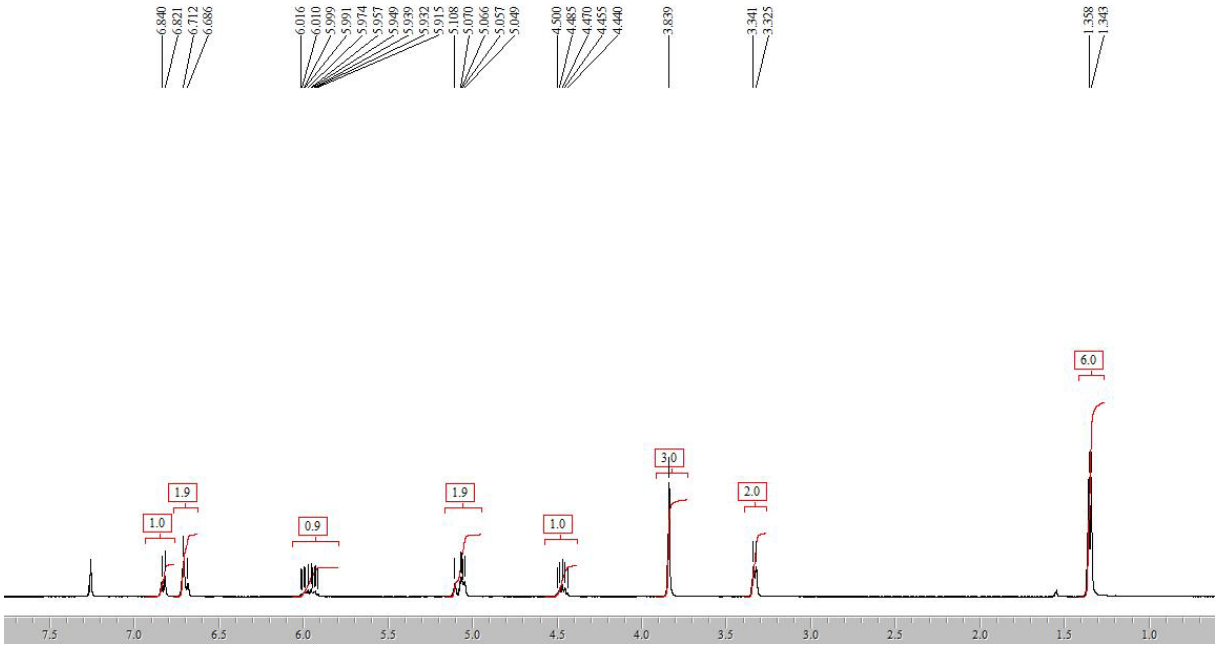
A dry and degassed Schlenk tube was loaded under argon with 1g of eugenol (6.1 mmol), 0.8 ml of 2-bromopropane (8.54 mmol, 1.4 equiv.), 2.52 g K_2CO_3 (18.3 mmol, 3 equiv.) and 20 ml of DMF. The reaction was stirred at 80 °C for 72 h. The product was then extracted with EtOAc, washed with water and finally dried over $MgSO_4$. Solvent was evaporated, and the product was purified by column chromatography on silica gel using of EtOAc/petroleum ether mixture (2/98) to give 960 mg of product (77% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) : 1.35 (d, 6.0 Hz, 6H, CH_3, CH_3), 3.33 (d, 6.4 Hz, CH_2), 3.83 (s, 3H, CH_3), 4.44-4.50 (m, 1H, CH), 5.04-5.10 (m, 2H, CH_2), 5.91-6.01 (m, 1H, CH), 6.68-6.71 (m, 2Har, CH), 6.83 (d, 7.6 Hz, 1Har, CH).

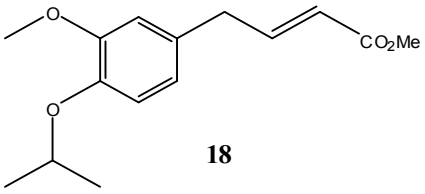
^{13}C NMR (75 MHz, $CDCl_3$, ppm): 22.1 (CH_3), 39.8 (CH_2), 55.8 (CH_3), 71.5 (CH), 112.5 (CH), 115.5 (CH_2), 116.2 (CH), 120.4 (CH), 133.1 (C), 137.6 (CH), 145.5 (C), 150.4 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{13}H_{18}O_2Na$) = 229.1204. Measured: 229.1205.

400 MHz ^{1}H NMR of **17**



Synthesis of (E)-methyl 4-(4-isopropoxy-3-methoxyphenyl)but-2-enoate **18**



18

Isolated yield: 84%

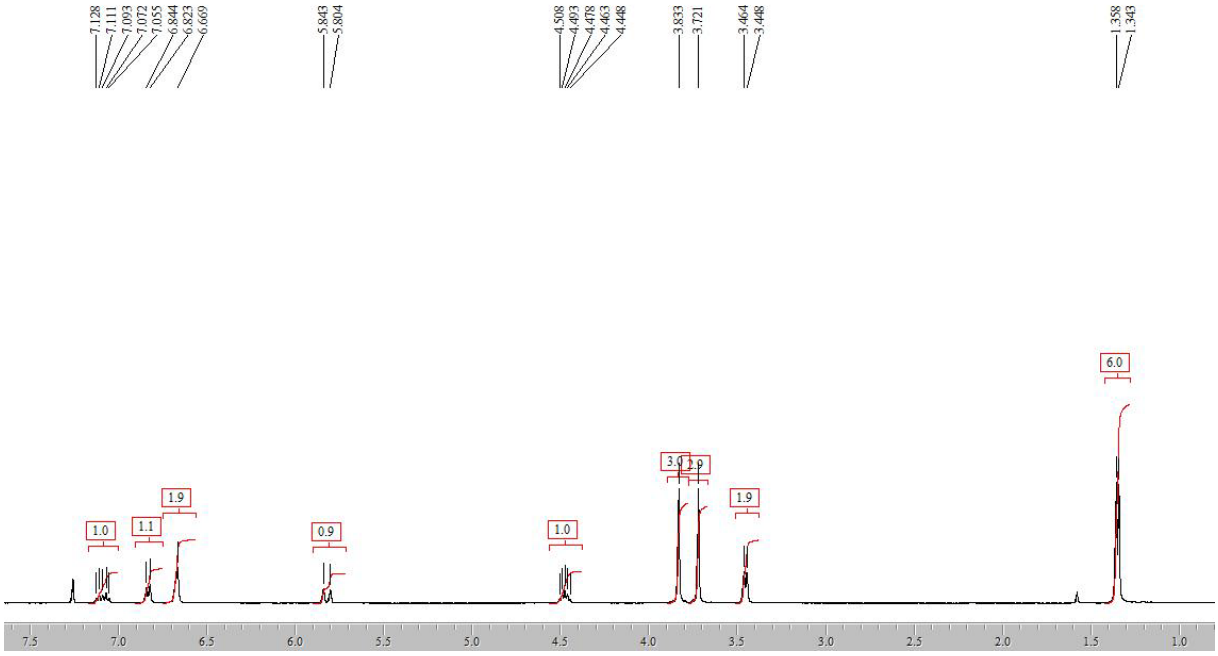
^{1}H NMR (400 MHz, $CDCl_3$, ppm) : 1.35 (d, 6.0 Hz, 6H, CH_3, CH_3), 3,45 (d, 6.4 Hz, 2H, CH_2), 3.72 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.48- 4.50 (m, 1H, CH), 5.82 (d, 15.6 Hz, 1H, CH), 6.66 (bs, 2Har, CH), 6.83 (d, 8.4 Hz, 1Har, CH), 7.05-7.12 (m, 1H, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 22.0 (CH_3), 38.0 (CH_2), 51.3 (CH_3), 55.8 (CH_3), 71.5 (CH), 112.7 (CH), 116.3 (CH), 120.7 (CH), 121.5 (CH), 130.5 (C), 146.0 (C), 147.7 (CH), 150.5 (C), 166.8 (C).

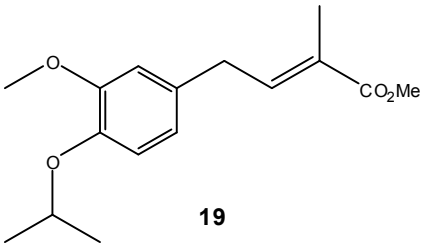
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{15}H_{20}O_4Na$) = 287.1259. Measured: 287.1258.

$C_{15}H_{20}O_4$: Theoretical **C** 68.16, **H** 7.63 Experimental **C** 67.96, **H** 7.55.

400 MHz ^{1}H NMR of **18**



Synthesis of (E)-methyl 4-(4-isopropoxy-3-methoxyphenyl)-2-methylbut-2-enoate **19**



19

Isolated yield: 78%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.35 (d, 6 Hz, 6H, CH_3), 1.95 (s, 3H, CH_3), 3.46 (d, 7.2 Hz, 2H, CH_2), 3.73 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.43-4.49 (m, 1H, CH), 6.67-6.68 (m, 2Har, CH), 6.82 (d, 8.4 Hz, 1Har, CH), 6.89-6.92 (m, 1H, CH).

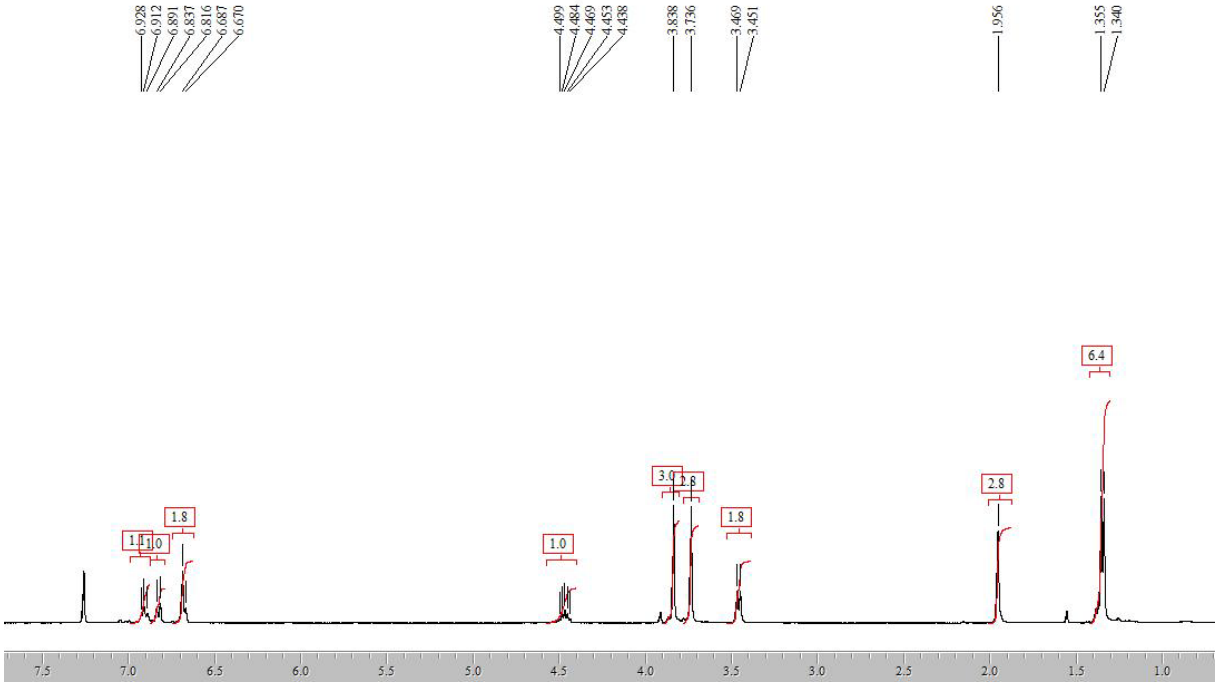
^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.5 (CH_3), 22.0 (CH_3), 34.4 (CH_2), 51.7 (CH_3), 55.9 (CH_3), 71.5 (CH), 112.4 (CH), 116.3 (CH), 120.3 (CH), 127.8 (C), 131.9 (C), 140.6 (CH), 145.8 (C), 150.5 (C), 168.5 (C).

The *E* configuration was determined by 2D NOESY (400 MHz). This experiment did not show any cross-peak between the C*H*$_3$ at 1.95 ppm and the *H* at 6.91 ppm whereas a cross-peak was detected between the C*H*$_3$ at 3.73 ppm (CO_2CH_3) and the *H* at 6.91 ppm. A cross-peak was detected between the C*H*$_3$ at 1.95 ppm and the C*H*$_2$ at 3.46 ppm.

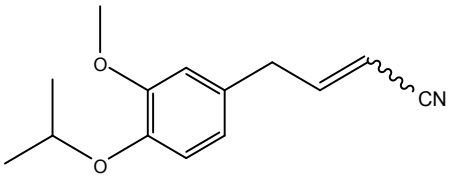
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{16}H_{22}O_4Na$) = 301.1415. Measured: 301.1415.

$C_{16}H_{22}O_4$: Theoretical **C** 69.04, **H** 7.97 Experimental **C** 69.04, **H** 7.91.

400 MHz ^{1}H NMR of **19**



Synthesis of 4-(4-isopropoxy-3-methoxyphenyl)but-2-enenitrile (Z/E: 2/1) **20**



20

Isolated yield: 80%

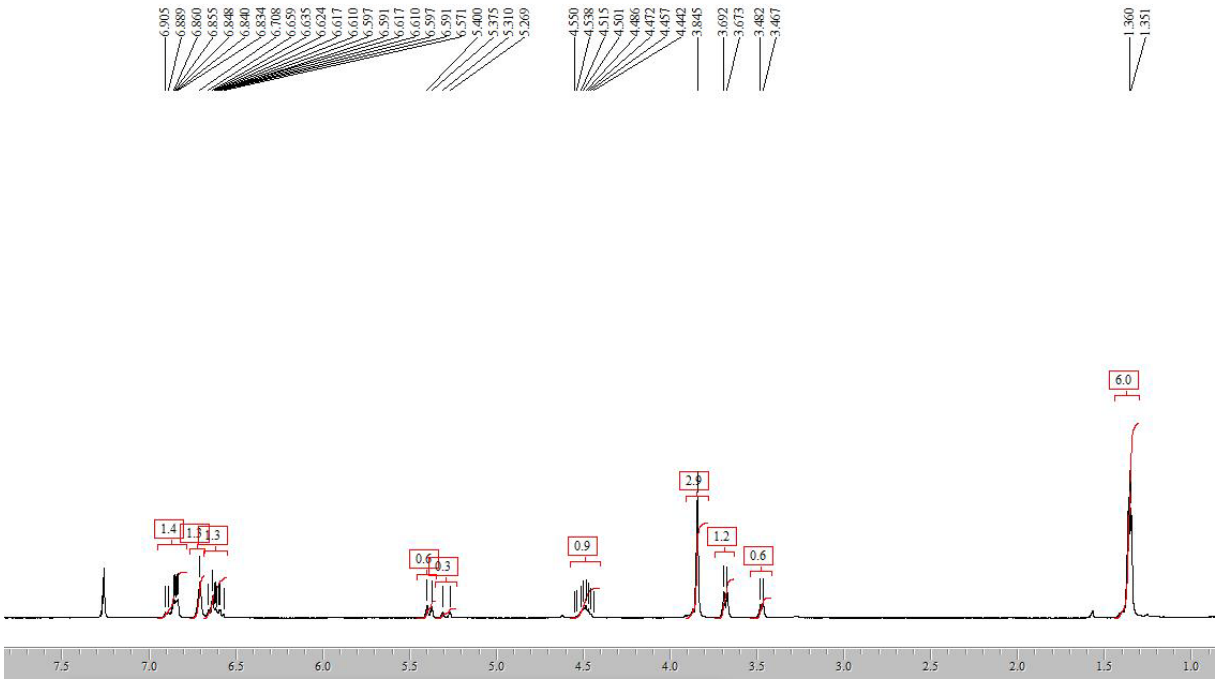
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.35 (d, 3.6 Hz, 6H, CH_3), 3.47, 3.68 (2d, 6.0 Hz, 7.6 Hz, 2H, CH_2, cis+trans), 3.84 (s, 3H, CH_3), 4.44-4.55 (m, 1H, CH), 5.28, 5.38 (2d, 16.4 Hz, 10.0 Hz, 1H, CH, cis+trans), 6.57-6.65 (m, 1H, CH), 6.70 (bs, 2Har, CH), 6.83-6.90 (m, 1Har, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 21.9 (CH_3), 37.4, 38.8 (CH_2, cis+trans), 55.8 (CH_3), 71.4 (CH), 99.4, 100.4 (CH, cis+trans), 112.3, 112.5 (CH, cis+trans), 116.1, 116.2 (CH, cis+trans), 120.4, 120.8 (CH, cis+trans), 128.7 (C), 129.6 (C), 146.2, 146.3 (C, cis+trans), 150.5 (C), 153.0, 154.2 (CH, cis+trans).

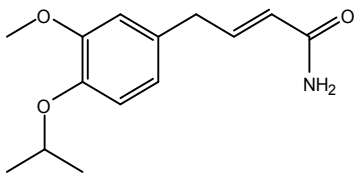
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{14}H_{17}NO_2Na$) = 254.1157. Measured: 254.1155.

$C_{14}H_{17}NO_2$: Theoretical **C** 72.70, **H** 7.41, **N** 6.06 Experimental **C** 72.39, **H** 7.34, **N** 6.01.

400 MHz ^{1}H NMR of **20**



Synthesis of (E)-4-(4-isopropoxy-3-methoxyphenyl)but-2-enamide **21**



21

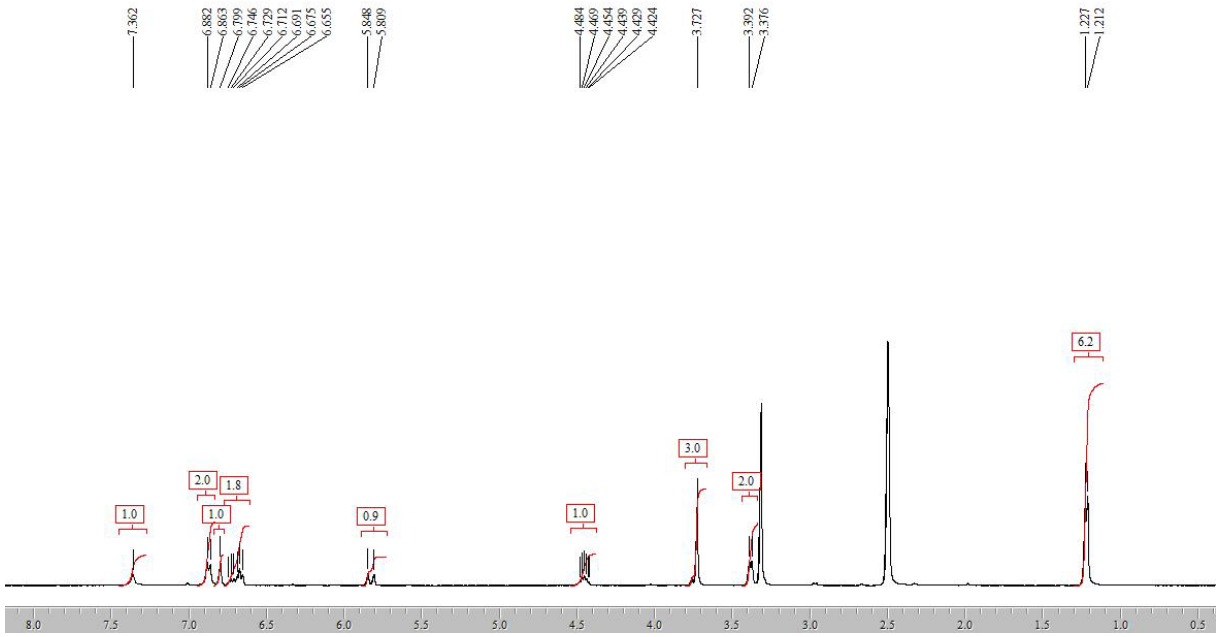
Isolated yield: 57% containing <5% of acrylamide

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 1.22 (d, 6.0 Hz, 6H, CH_3), 3.38 (d, 6.4 Hz, 2H, CH_2), 3.72 (s, 3H, CH_3), 4.42-4.48 (m, 1H, CH), 5.82 (d, 15.6 Hz, 1H, CH), 6.65-6.74 (m, 2Har, CH), 6.79 (s, 1Har, CH), 6.87 (d, 7.6 Hz, 2H, CH, NH), 7.36 (bs, 1H, NH).

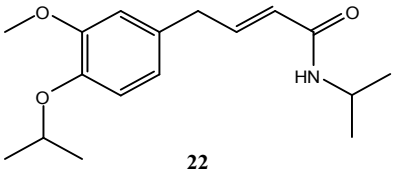
^{13}C NMR (100 MHz, DMSO-d_6, ppm): 21.8 (CH_3), 36.8 (CH_2), 55.3 (CH_3), 70.3 (CH), 112.9 (CH), 116.0 (CH), 120.4 (CH), 124.8 (CH), 131.4 (C), 141.9 (CH), 145.0 (C), 149.9 (C), 166.4 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{14}H_{19}NO_3Na$) = 272.1262. Measured: 272.1259.

400 MHz ^{1}H NMR of **21**



Synthesis of (E)-4-(4-isopropoxy-3-methoxyphenyl)-N-isopropylbut-2-enamide **22**



22

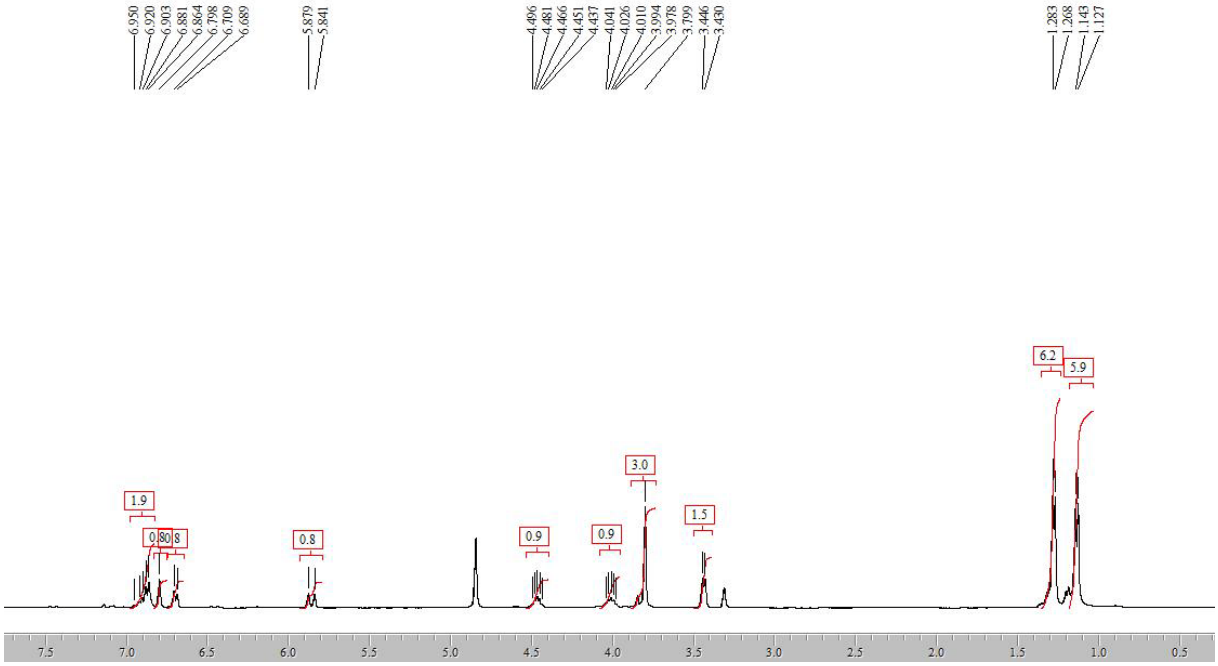
Isolated yield: 52% containing <5% of isopropyl-acrylamide

^{1}H NMR (400 MHz, Methanol-d_4, ppm): 1.13 (d, 6.4 Hz, 6H, CH_3), 1.27 (d, 6.0 Hz, 6H, CH_3), 3.43 (d, 6.4 Hz, 2H, CH_2), 3.79 (s, 3H, CH_3), 3.97-4.04 (m, 1H, CH), 4.43-4.49 (m, 1H, CH), 5.86 (d, 15.2 Hz, 1H, CH), 6.69 (d, 8.0 Hz, 1Har, CH), 6.79 (bs, 1Har, CH), 6.86-6.95 (m, 2H, CHar, CH).

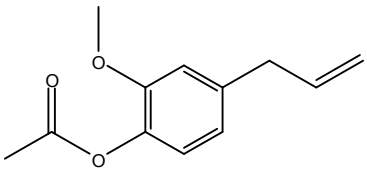
^{13}C NMR (100 MHz, Methanol-d_4, ppm): 22.2 (CH_3), 22.4 (CH_3), 38.4 (CH_2), 42.0 (CH_3), 56.1 (CH), 72.8 (CH), 114.0 (CH), 118.0 (CH), 121.8 (CH), 125.3 (CH), 133.1 (C), 143.8 (CH), 146.6 (C), 151.7 (C), 167.2 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{17}H_{25}NO_3Na$) = 314.1732. Measured: 314.1733.

400 MHz ^{1}H NMR of **22**



Synthesis of 4-allyl-2-methoxyphenyl acetate **23**



23

General procedure

1g of eugenol (6.1 mmol) was dissolved in 10 ml of acetic anhydride. The mixture was reflued at 140 °C for 17 h. After cooling, the product was extracted with EtOAc, washed with water and finally dried over $MgSO_4$. Solvent was evaporated, and the product was purified by column chromatography on silica gel using of EtOAc/petroleum ether mixture (5/95) to give 1 g of product (80% isolated yield).

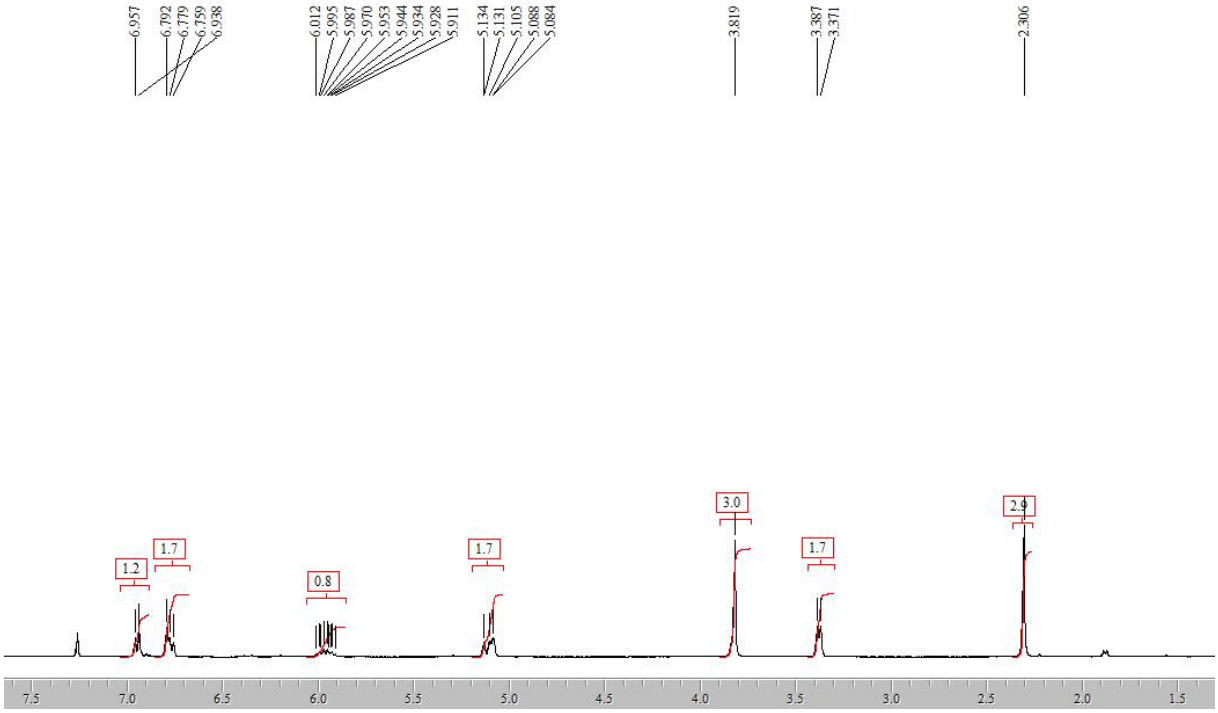
NMR data were consistent with reported data.[1]

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.30 (s, 3H, CH_3), 3.38 (d, 6.4 Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 5.08-5.13 (m, 2H, CH_2), 5.91-6.01 (m, 1H, CH), 6.75-6.79 (m, 2Har, CH), 6.94 (d, 7.6 Hz, 1Har, CH).

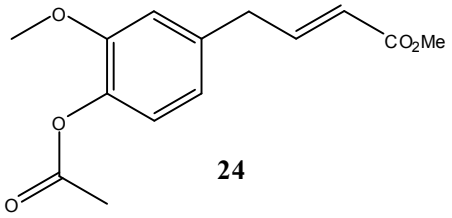
[1] A. L. Dos Santos, G. O. Chierice, K. Alexander, A. Riga, *J. Chem. Crystallogr.*, 2009, **39**, 655

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 20.6 (CH_3), 40.0 (CH_2), 55.7 (CH_3), 112.7 (CH), 116.1 (CH_2), 120.6 (CH), 122.4 (CH), 136.9 (CH), 137.9 (C), 138.9 (C), 150.8 (C), 169.1 (C).

400 MHz ^{1}H NMR of **23**



Synthesis of (E)-methyl 4-(4-acetoxy-3-methoxyphenyl)but-2-enoate **24**



24

Isolated yield: 81%

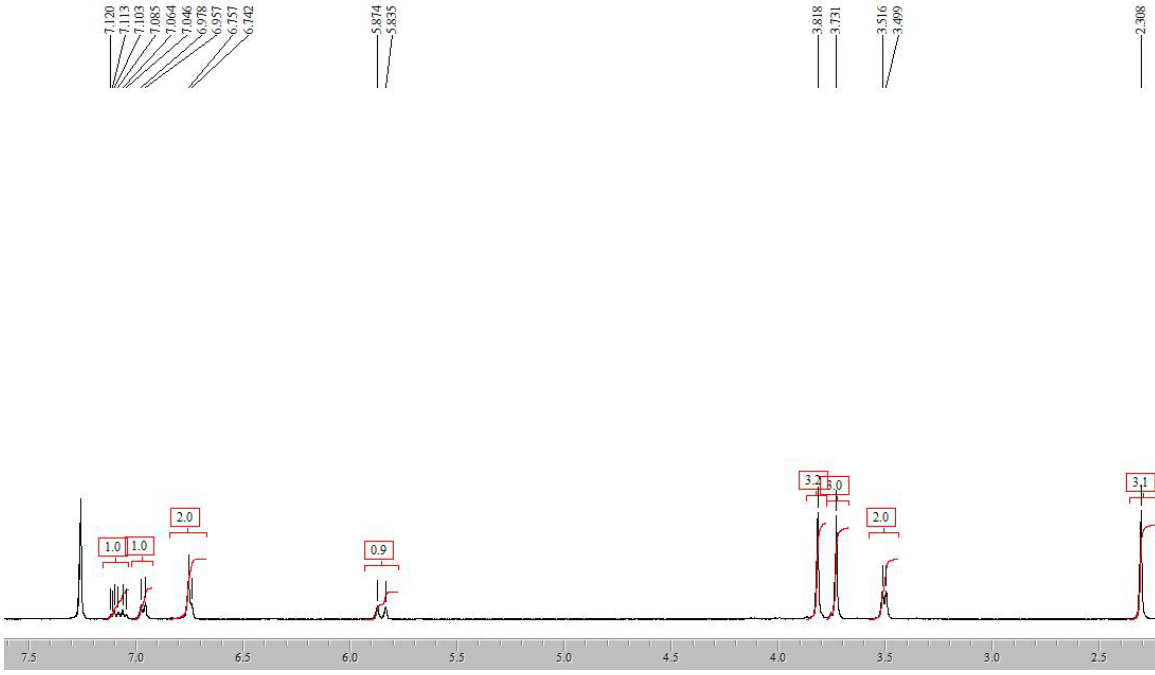
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.30 (s, 3H, CH_3), 3.50 (d, 6.8 Hz, 2H, CH_2), 3.73 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 5.85 (d, 15.6 Hz, 1H, CH), 6.74-6.75 (m, 2Har, CH), 6.96 (d, 8.4 Hz, 1Har, CH), 7.04-7.12 (m, 1H, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 20.5 (CH_3), 38.2 (CH_2), 51.4 (CH_3), 55.7 (CH_3), 112.7 (CH), 120.8 (CH), 122.0 (CH), 122.8 (CH), 136.5 (C), 138.4 (C), 146.9 (CH), 151.0 (C), 166.7 (C), 169.0 (C).

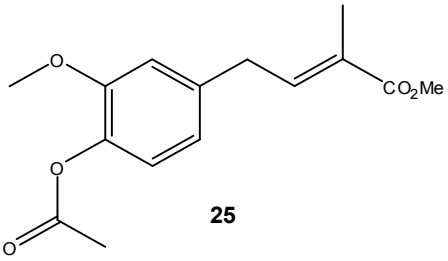
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{14}H_{16}O_5Na$) = 287.0895. Measured: 287.0892.

$C_{14}H_{16}O_5$: Theoretical **C** 63.63, **H** 6.10 Experimental **C** 63.72, **H** 5.80.

400 MHz ^{1}H NMR of **24**



Synthesis of (E)-methyl 4-(4-acetoxy-3-methoxyphenyl)-2-methylbut-2-enoate **25**



25

Isolated yield: 72%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.95 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.50 (d, 7.6 Hz, 2H, CH_2), 3.74 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 6.74-6.76 (m, 2Har, CH), 6.88-6.92 (m, 1H, CH), 6.95 (d, 7.6 Hz, 1Har, CH).

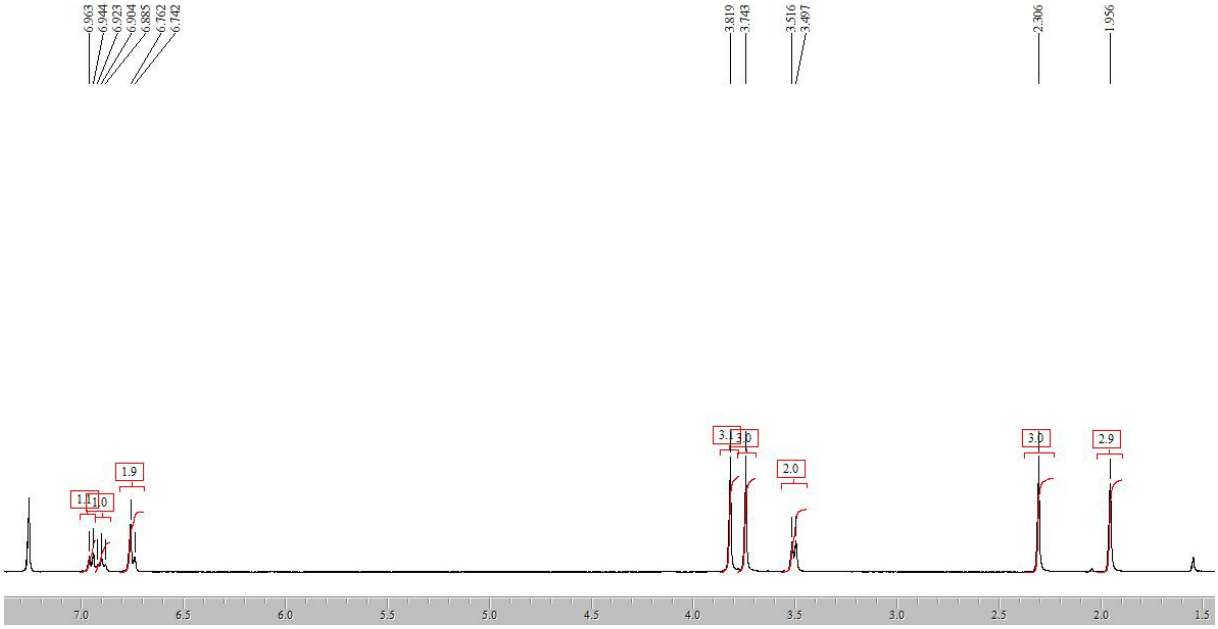
^{13}C NMR (75 MHz, $CDCl_3$, ppm): 12.4 (CH_3), 20.4 (CH_3), 34.5 (CH_2), 51.6 (CH_3), 55.6 (CH_3), 112.4 (CH), 120.4 (CH), 122.6 (CH), 128.2 (C), 137.7 (C), 138.1 (C), 139.8 (CH), 150.9 (C), 168.2 (C), 169.0 (C).

The *E* configuration was determined by 2D NOESY (400 MHz). This experiment did not show any cross-peak between the C*H*$_3$ at 1.95 ppm and the *H* at 6.90 ppm whereas a cross-peak was detected between the C*H*$_3$ at 3.74 ppm (CO_2CH_3) and the *H* at 6.90 ppm. A cross-peak was detected between the C*H*$_3$ at 1.95 ppm and the C*H*$_2$ at 3.50 ppm.

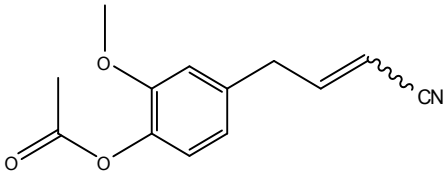
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{15}H_{18}O_5Na$) = 301.1051. Measured: 301.1049.

$C_{15}H_{18}O_5$: Theoretical **C** 64.74, **H** 6.52 Experimental **C** 64.55, **H** 6.55.

400 MHz ^{1}H NMR of **25**



Synthesis of 4-(3-cyanoallyl)-2-methoxyphenyl acetate (Z/E: 3/1) **26**



26

Isolated yield: 79%

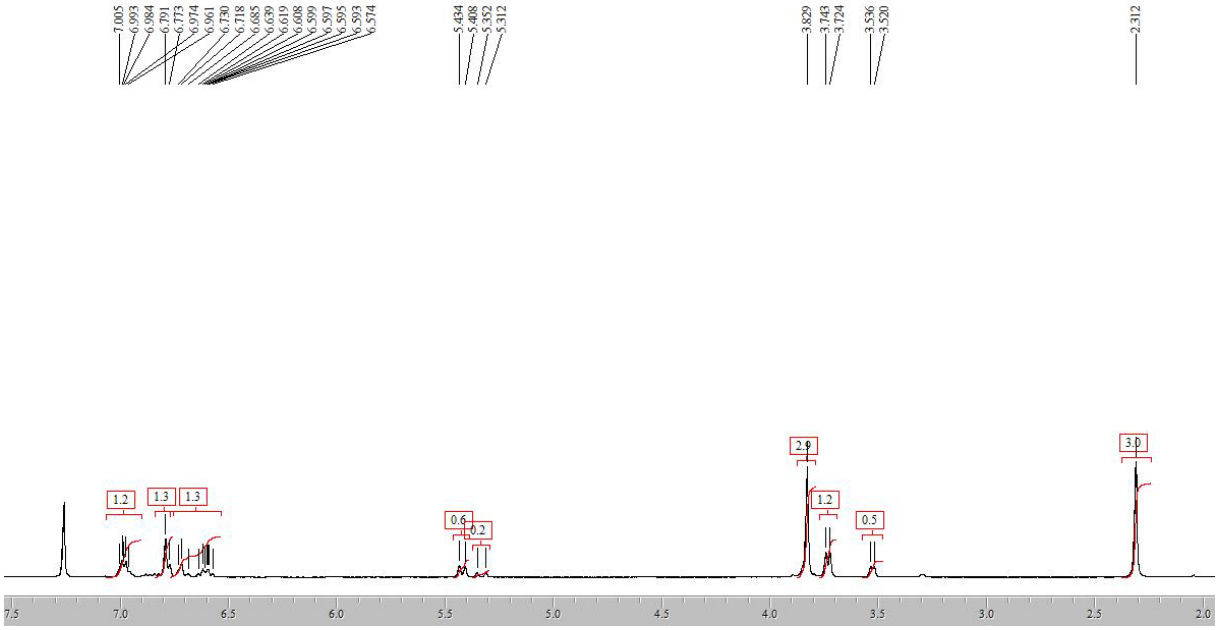
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.31 (s, 3H, CH_3), 3.52, 3.73 (2d, 6.4 Hz, 7.6 Hz, 2H, CH_2, cis+trans), 3.82 (s, 3H, CH_3), 5.33, 5.42 (2d, 16.0 Hz, 10.4 Hz, 1H, CH, cis+trans), 6.57-6.73 (m, 1H, CH), 6.77-6.79 (m, 2Har, CH), 6.96-7.00 (m, 1Har, CH).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 20.5 (CH_3), 37.6, 39.0 (CH_2, cis+trans), 55.7 (CH_3), 100.0, 100.9 (CH, cis+trans), 112.5, 112.6 (CH, cis+trans), 115.7, 117.0 (C, cis+trans), 120.4, 120.8 (CH, cis+trans), 122.9 (CH), 135.6 (C), 138.5 (C), 151.1 (C), 152.3, 153.4 (CH, cis+trans), 168.9 (C).

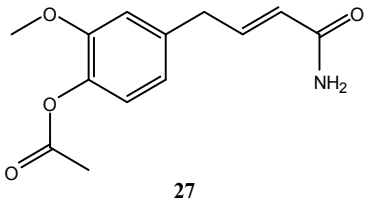
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{13}H_{13}NO_3Na$) = 254.0793. Measured: 254.0793.

$C_{13}H_{13}NO_3$: Theoretical **C** 67.52, **H** 5.67, **N** 6.06 Experimental **C** 67.19, **H** 5.70, **N** 5.55.

400 MHz ^{1}H NMR of **26**



Synthesis of (E)-4-(4-amino-4-oxobut-2-enyl)-2-methoxyphenyl acetate **27**



27

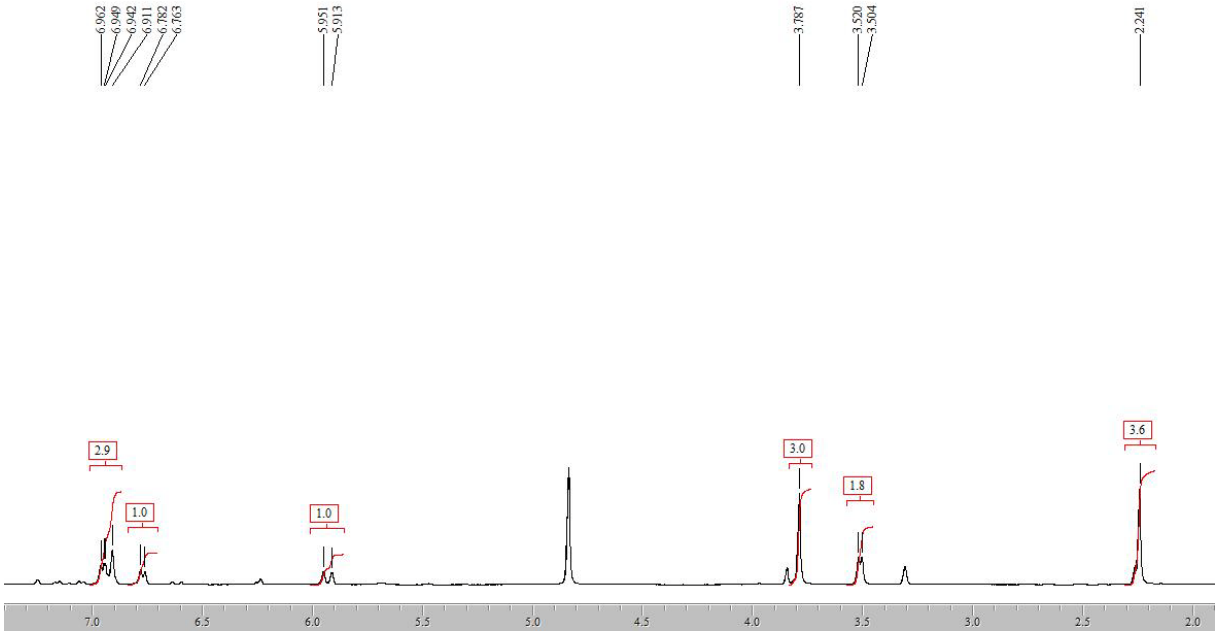
Isolated yield: 65% containing <10% of acrylamide

^{1}H NMR (400 MHz, Methanol-d_4, ppm): 2.24 (s, 3H, CH_3), 3.51 (d, 6.4 Hz, 2H, CH_2), 3.78 (s, 3H, CH_3), 5.93 (d, 15.2 Hz, 1H, CH), 6.77 (d, 7.6 Hz, 1Har, CH), 6.91-6.96 (m, 3H, 2Har, CH).

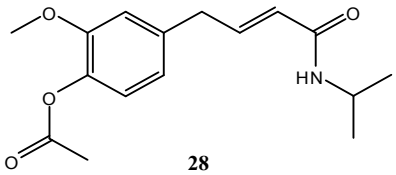
^{13}C NMR (100 MHz, Methanol-d_4, ppm): 20.5 (CH_3), 38.8 (CH_2), 56.3 (CH_3), 114.2 (CH), 121.9 (CH), 123.7 (CH), 125.3 (CH), 138.8 (C), 139.8 (C), 145.0 (CH), 152.6 (C), 170.8 (C), 170.9 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{13}H_{15}NO_4Na$) = 272.0898. Measured: 272.0901.

400 MHz ^{1}H NMR of **27**



Synthesis of (E)-4-(4-(isopropylamino)-4-oxobut-2-enyl)-2-methoxyphenyl acetate **28**



28

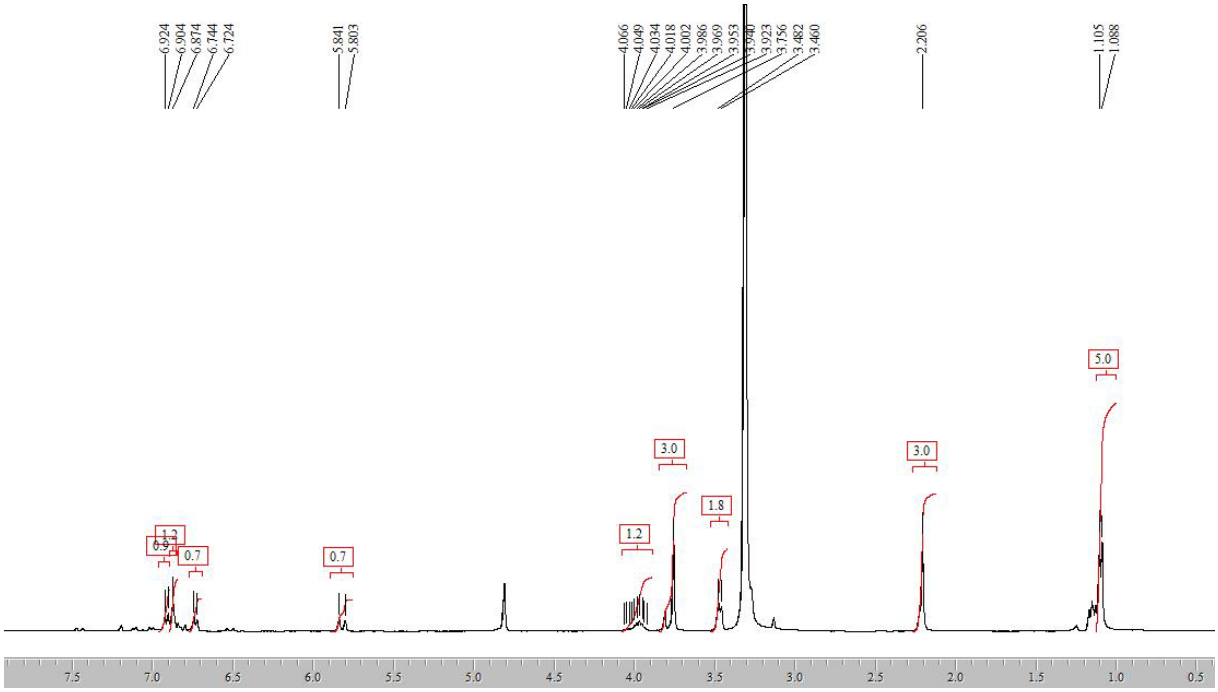
Isolated yield: 53% containing <5% of isopropylacrylamide

^{1}H NMR (400 MHz, Methanol-d_4, ppm): 1.09 (d, 6.8 Hz, 6H, CH_3), 2.20 (s, 3H, CH_3), 3.47 (d, 8.8 Hz, 2H, CH_2), 3.75 (s, 3H, CH_3), 3.92-4.06 (m, 1H, CH), 5.82 (d, 15.2 Hz, 1H, CH), 6.73 (d, 8.0 Hz, 1Har, CH), 6.87 (s, 2Har, CH), 6.91 (d, 8.0 Hz, 1H, CH).

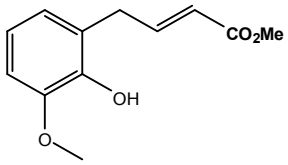
^{13}C NMR (100 MHz, Methanol-d_4, ppm): 20.0 (CH_3), 22.2 (CH_3), 38.4 (CH_2), 42.0 (CH_3), 55.9 (CH), 113.7 (CH), 121.5 (CH), 123.3 (CH), 125.5 (CH), 138.5 (C), 139.4 (C), 143.2 (CH), 152.2 (C), 167.0 (C), 170.5 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{16}H_{21}NO_4Na$) = 314.1368. Measured: 314.1368.

400 MHz ^{1}H NMR of **28**



Synthesis of (E)-methyl 4-(2-hydroxy-3-methoxyphenyl)but-2-enoate **30**



30

Isolated yield: 60%

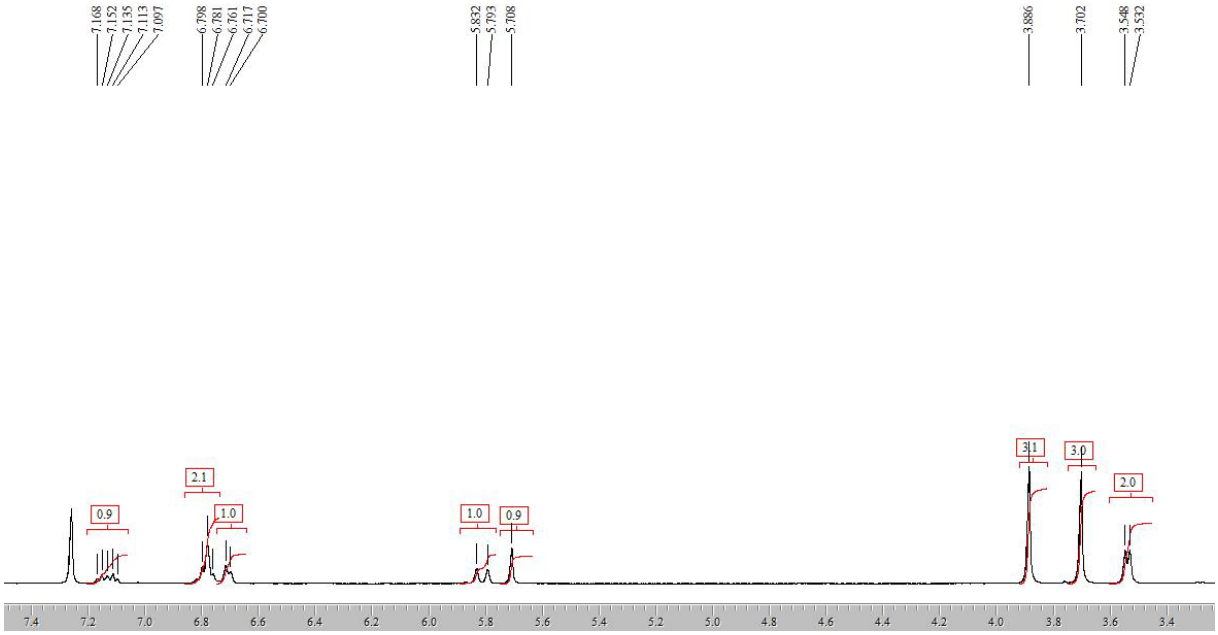
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.54 (d, 6.4 Hz, 2H, CH_2), 3.70 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 5.70 (s, 1H, OH), 5.81 (d, 15.6 Hz, 1H, CH), 6.70 (d, 6.8 Hz, 1Har, CH), 6.76-6.79 (m, 2Har, CH), 7.09-7.16 (m, 1H, CH).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 32.3 (CH_2), 51.3 (CH_3), 55.9 (CH_3), 109.1 (CH), 119.5 (CH), 121.4 (CH), 122.3 (CH), 123.4 (C), 143.5 (C), 146.4 (C), 147.1 (CH), 167.0 (C).

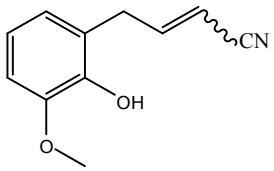
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{12}H_{14}O_4Na$) = 245.0789. Measured: 245.0787.

$C_{12}H_{14}O_4$: Theoretical **C** 64.85, **H** 6.35 Experimental **C** 64.84, **H** 6.37.

400 MHz ^{1}H NMR of **30**



Synthesis of 4-(2-hydroxy-3-methoxyphenyl)but-2-enenitrile (Z/E: 2/1) **31**



31

Isolated yield: 65%

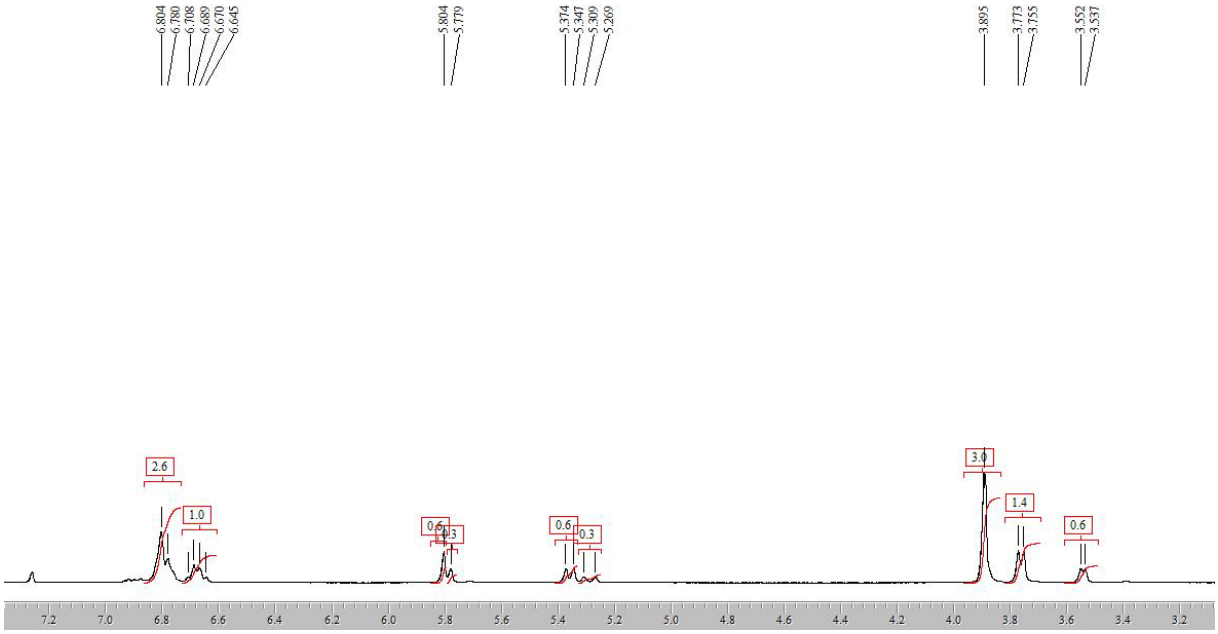
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.54, 3.76 (2d, 6.0 Hz, 7.2 Hz, 2H, CH_2, cis+trans), 3.89 (s, 3H, CH_3), 5.29, 5.36 (2d, 16.0 Hz, 10.8 Hz, 1H, CH, cis+trans), 5.78, 5.80 (2s, 1H, OH, cis+trans), 6.64-6.70 (m, 1H, CH), 6.78-6.80 (m, 3Har, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 32.3, 33.4 (CH_2, cis+trans), 55.9 (CH_3), 99.3, 100.1 (CH, cis+trans), 109.4, 109.5 (CH, cis+trans),116.0, 117.5 (C, cis+trans), 119.7 (CH), 122.0, 122.2 (CH, cis+trans), 122.6 (C), 143.5 (C), 146.4 (C), 152.4, 153.4 (CH, cis+trans).

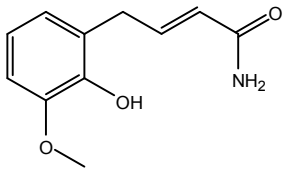
HRMS (ESI): $[M+Na]^+$ calculated for ($C_{11}H_{11}NO_2Na$) = 212.0687. Measured: 212.0688.

$C_{11}H_{11}NO_2$: Theoretical **C** 69.83, **H** 5.86, **N** 7.4 Experimental **C** 69.29, **H** 5.76, **N** 7.03.

400 MHz ^{1}H NMR of **31**



Synthesis of (E)-4-(2-hydroxy-3-methoxyphenyl)but-2-enamide **32**



32

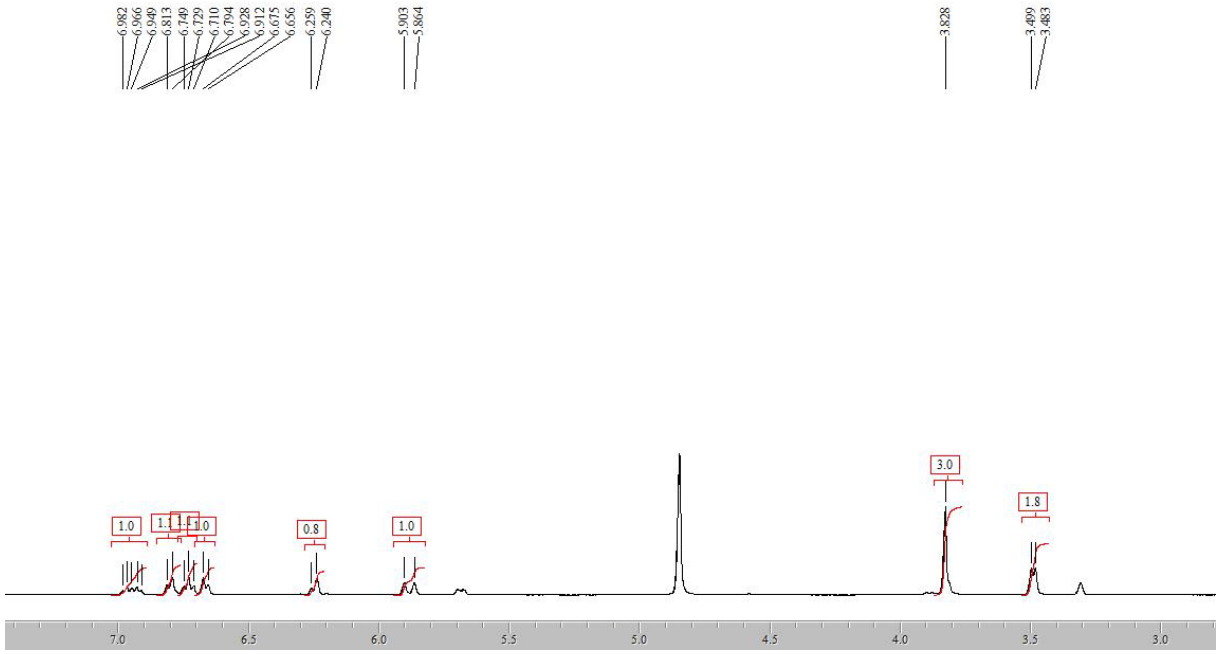
Isolated yield: 56% containing <5% of acrylamide

^{1}H NMR (400 MHz, Methanol-d_4, ppm): 3.49 (d, 6.4 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 5.88 (d, 15.6 Hz, 1H, CH), 6.24-6.26 (m, 1H, OH), 6.66 (d, 7.6 Hz, 1Har, CH), 6.73 (t, 8.0 Hz, 1Har, CH), 6.80 (d, 7.6 Hz, 1Har, CH), 6.91-6.98 (m, 1H, CH).

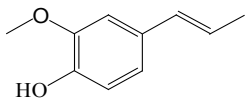
^{13}C NMR (100 MHz, Methanol-d_4, ppm): 33.1 (CH_2), 56.2 (CH_3), 110.7 (CH), 120.1 (CH), 123.0 (CH), 124.2 (CH), 125.6 (C), 144.9 (CH), 145.2 (C), 148.6 (C), 171.0 (C).

HRMS (ESI): $[M+Na]^+$ calculated for ($C_{11}H_{13}NO_3Na$) = 230.0793. Measured: 230.0796.

400 MHz ^{1}H NMR of **32**



Synthesis of (E)-2-methoxy-4-(prop-1-enyl)phenol "isoeugenol"



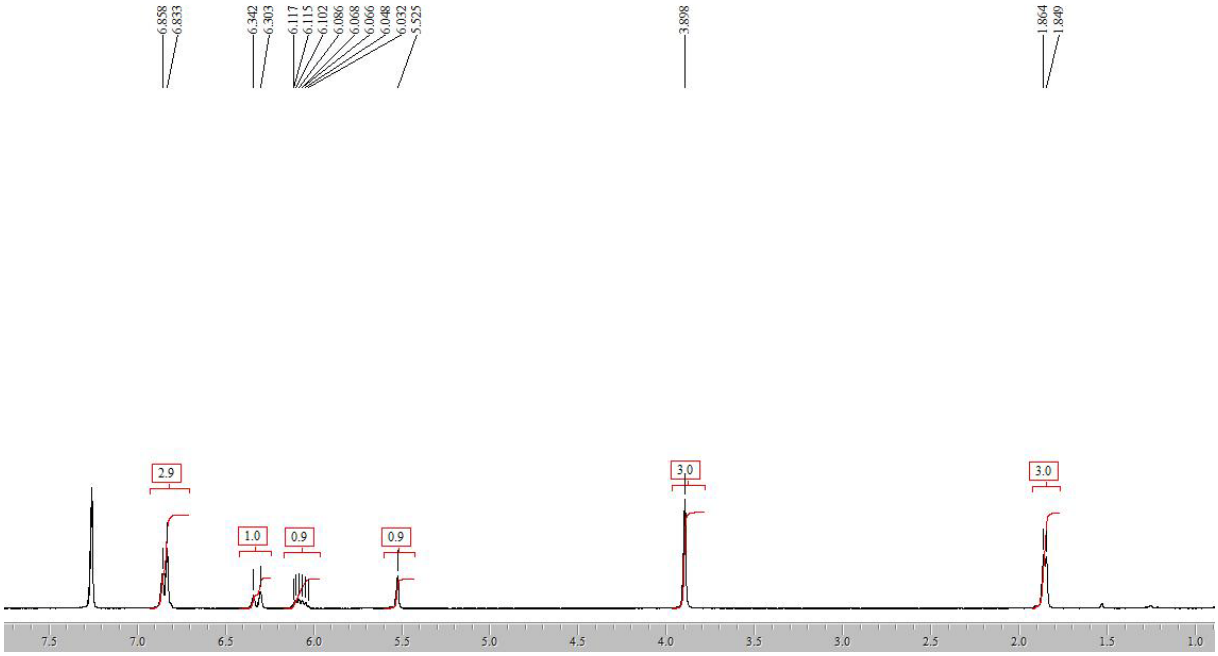
A dry and degassed Schlenk tube was loaded under argon with 300 mg g of eugenol (1.83 mmol) , 35 mg of $RuCl_2(PPh_3)_3$ catalyst ($36.6.10^{-3}$ mmol, 2 mol%) and 2 ml of methanol. The reaction was stirred at 60 °C for 17 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a mixture of EtOAc/petroleum ether (5/95) to give 212 mg of product (71% isolated yield).

NMR data were consistent with Aldrich NMR data.

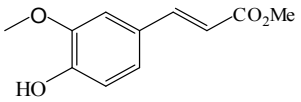
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.85 (d, 6.0 Hz, 3H, CH_3), 3.89 (s, 3H, CH_3), 5.52 (s, 1H, OH), 6.03- 6.11 (m, 1H, CH), 6.32 (d, 15.6 Hz, 1H, CH), 6.83-6.85 (m, 3Har, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 18.2 (CH_3), 55.7 (CH_3), 107.8 (CH), 114.3 (CH), 119.2 (CH), 123.2 (CH), 130.5 (C), 130.6 (CH), 144.6 (C), 146.5 (C).

400 MHz ^{1}H NMR of isoeugenol



Synthesis of (E)-methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate **6**



6

Isolated yield: 60%

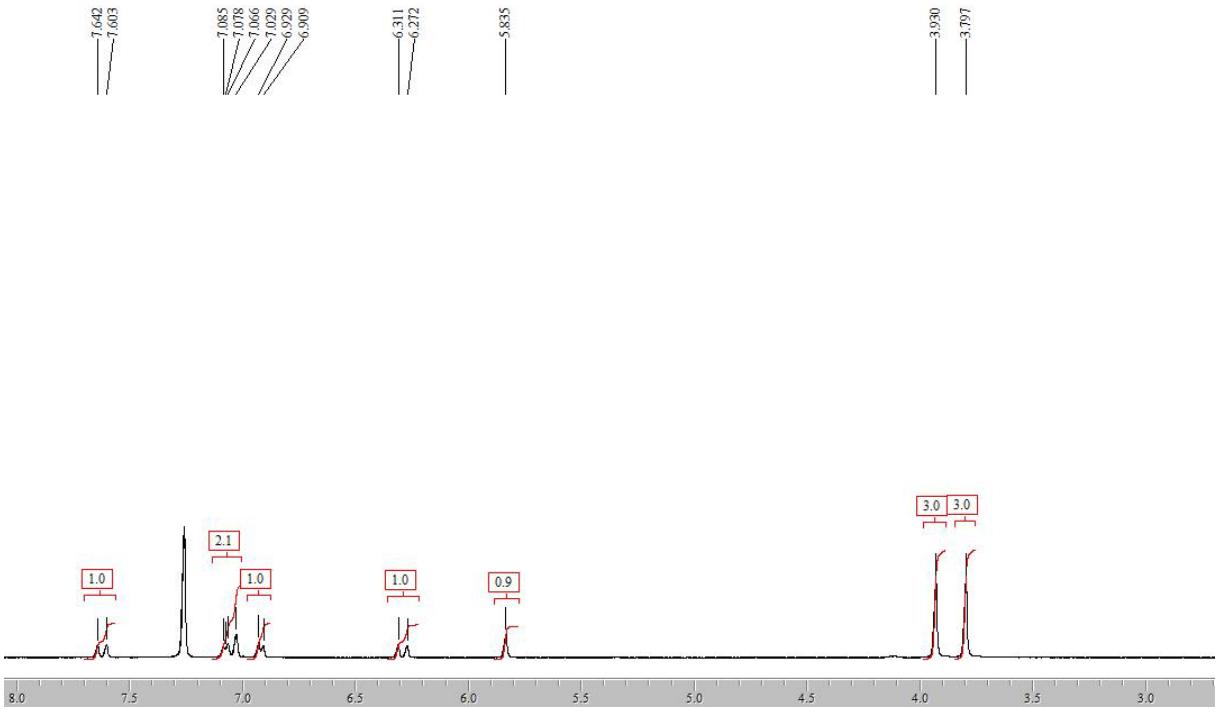
NMR data were consistent with reported data.[2]

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.79 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 5.83 (s, 1H, OH), 6.29 (d, 15.6 Hz, 1H, CH), 6.92 (d, 8.0 Hz, 1Har, CH), 7.02-7.08 (m, 2Har, CH), 7.62 (d, 15.6 Hz, 1H, CH).

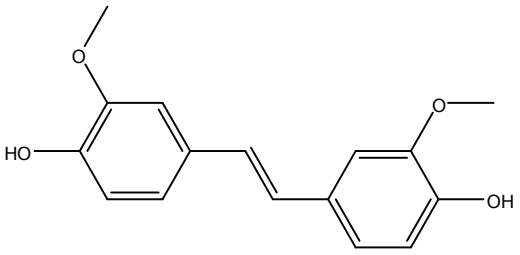
^{13}C NMR (100 MHz, $CDCl_3$, ppm): 51.5 (CH_3), 55.8 (CH_3), 109.3 (CH), 114.7 (CH), 115.0 (CH), 122.9 (CH), 126.8 (C), 144.9 (CH), 146.7 (C), 147.9 (C), 167.7 (C).

[2] F. Saliu, E. L. Tolppa, L. Zoia, M. Orlandi, *Tet. Lett.*, 2011, **52**, 3860

400 MHz ^{1}H NMR of **6**



Synthesis of (E)-4,4'-(ethene-1,2-diyl)bis(2-methoxyphenol) **7**



7

General procedure for the self metathesis without BQ

A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenol (0.61 mmol), 7.6 mg of Hoveyda catalyst (12.10^{-3}mmol, 2 mol%) and 2 ml of DMC. The reaction was stirred at 80 °C for 3 h. After solvent evaporation, the product was purified by column chromatography on silica gel using of EtOAc/petroleum ether mixture (50/50) to give 49 mg of product (60% isolated yield).

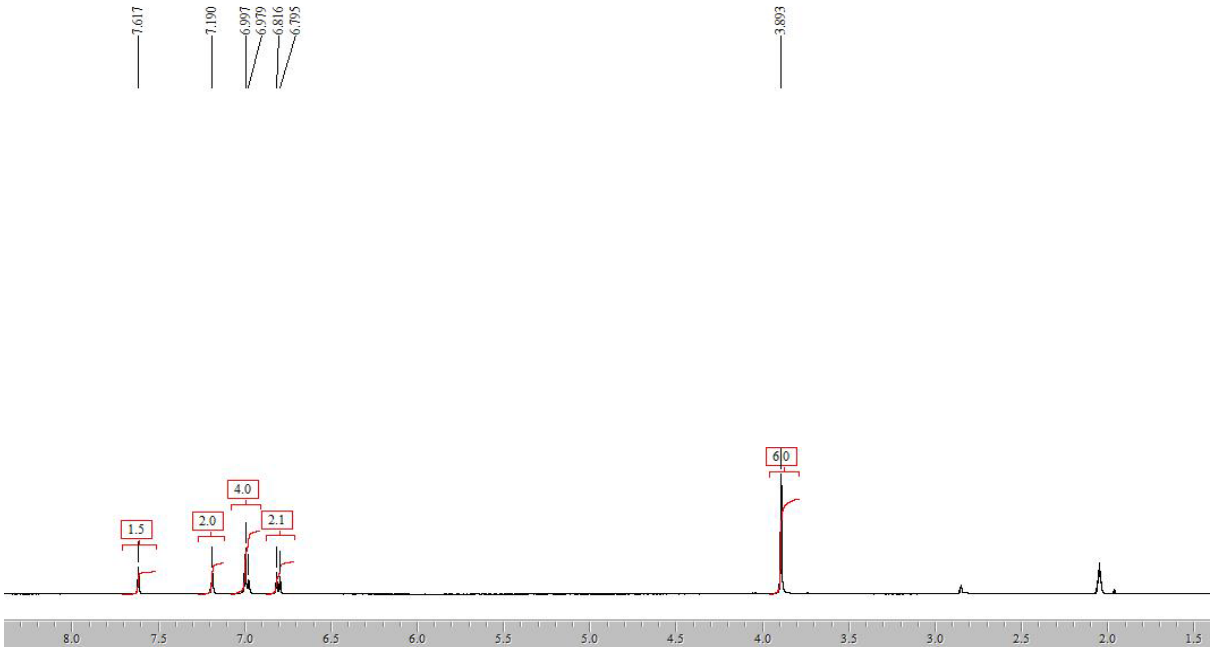
NMR data were consistent with reported data.[3]

[3] Z. Hajdu´, E. Varga, J. Hohmann, A. Kálmán, G. Argay, G. Günther, *J. Nat. Prod.*, 1998, **61**, 1298

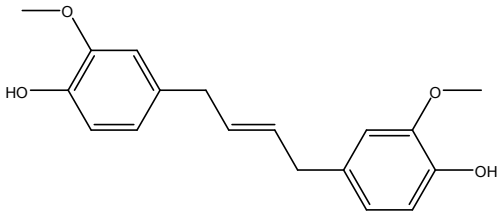
^{1}H NMR (400 MHz, Acetone-d_6, ppm): 3.89 (s, 6H, CH_3), 6.80 (d, 8.4 Hz, 2H, CH), 6.98 (d, 7.2 Hz, 4 Har, CH), 7.19 (s, 2Har, CH), 7.61 (s, 2H, OH).

^{13}C NMR (100 MHz, Acetone-d_6, ppm): 57.2 (CH_3), 110.8 (CH), 116.9 (CH), 121.6 (CH), 127.9 (CH), 131.9 (C), 148.1 (C), 149.5 (C).

400 MHz ^{1}H NMR of **7**



Synthesis of (E)-4,4'-(but-2-ene-1,4-diyl)bis(2-methoxyphenol) **8**



8

General procedure for the self metathesis with BQ

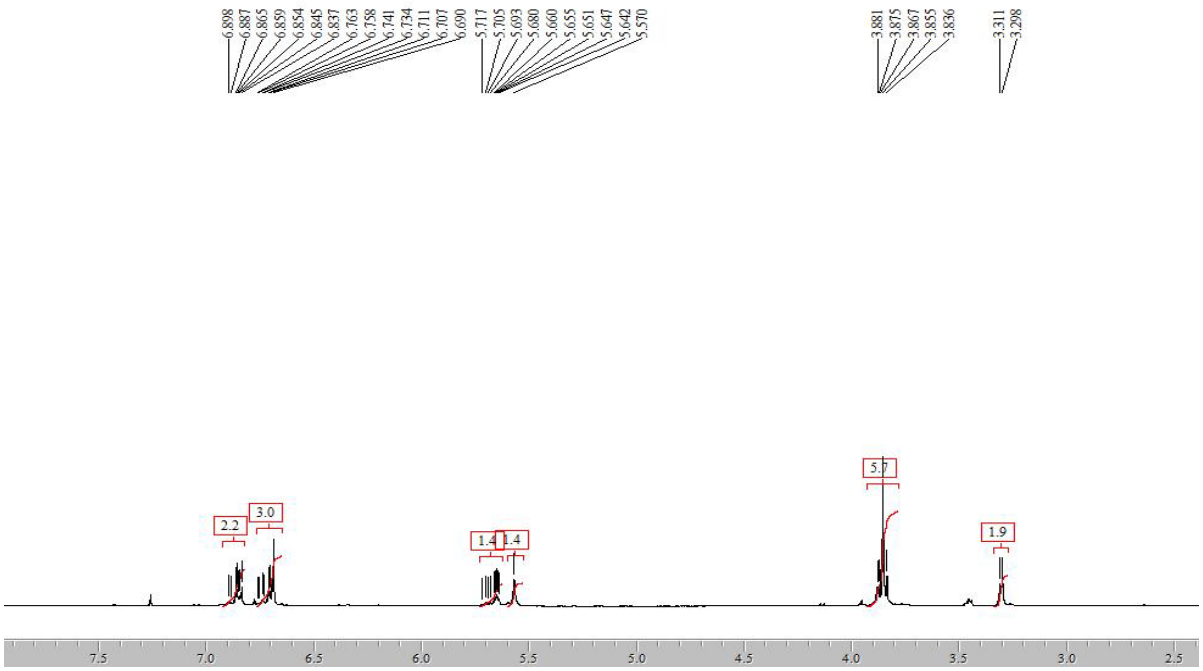
A dry and degassed Schlenk tube was loaded under argon with 100 mg of eugenol (0.61 mmol), 7.6 mg of Hoveyda catalyst (12.10^{-3}mmol, 2 mol%), 3.3 mg of *para*-benzoquinone (30.10^{-3}mmol, 5 mol%) and 2 ml of DMC. The reaction was stirred at 80 °C for 3 h. After solvent evaporation, the product was purified by column chromatography on silica gel using of EtOAc/petroleum ether mixture (50/50) to give 40 mg of product (44% isolated yield).

NMR data were consistent with reported data.[4]

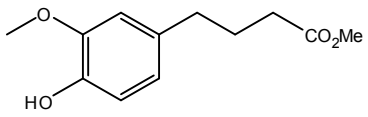
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.30 (d, 5.2 Hz, 2H, CH_2), 3.83-3.88 (m, 6H, CH_3), 5.57 (s, 1H, CH), 5.64-5.71 (m, 1H, CH), 6.69-6.76 (m, 3Har, CH), 6.83-6.89 (m, 3Har, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 38.5 (CH_2), 55.7 (CH_3), 111.0 (CH), 114.1 (CH), 120.9 (CH), 130.5 (CH), 132.6 (C), 143.7 (C), 146.3 (C).

400 MHz ^{1}H NMR of **8**



Synthesis of methyl 4-(4-hydroxy-3-methoxyphenyl)butanoate **5**



5

General procedure

The crude reaction product from the cross metathesis of 100 mg of eugenol (0.61 mmol), 9.4 mg of Grubbs II catalyst (12.10^{-3} mmol, 2mol%), 105 µl of methyl acrylate (12 mmol, 2 equiv.), 2 ml of DMC at 80 °C for 3 h, was transferred into an autoclave and charged with 30

[4] H. E. Blackwell, D. J. O'Leary, A. K. Chatterjee, R. A. Washenfelder, D. A. Bussmann, R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, **122**, 58

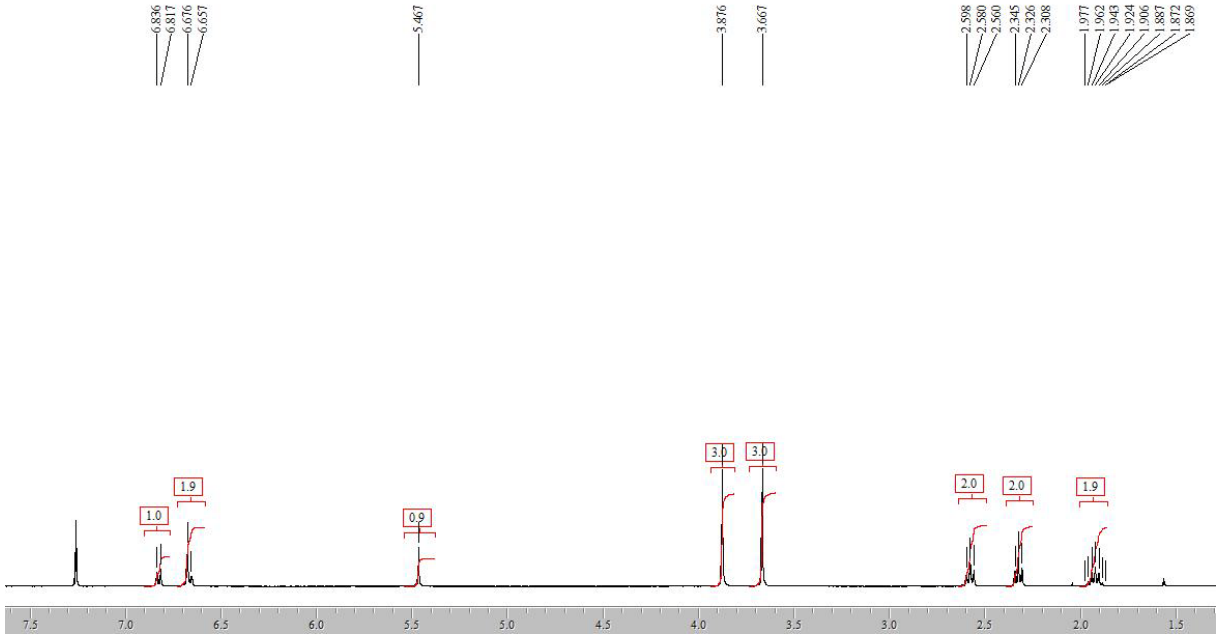
bar of H_2, the reaction was stirred at 80 °C during 17 h. After solvent evaporation, the product was purified by column chromatography on silica gel using of EtOAc/petroleum ether mixture (20/80) to give 87 mg of product (64% isolated yield).

NMR data were consistent with reported data.[5]

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.86-1.97 (m, 2H, CH_2), 2.32 (t, 7.4 Hz, 2H, CH_2), 2.58 (t, 7.6 Hz, 2H, CH_2), 3.66 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 5.46 (s, 1H, OH), 6.65-6.67 (m, 2Har, CH), 6.82 (d, 7.6 Hz, 1Har, CH).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 26.7 (CH_2), 33.2 (CH_2), 34.7 (CH_2), 51.4 (CH_3), 55.7 (CH_3), 110.9 (CH), 114.1 (CH), 120.9 (CH), 133.2 (C), 143.7 (C), 146.3 (C), 173.9 (C).

400 MHz ^{1}H NMR of **5**



[5] T. Chenal, I. Cipres, J. Jenck, P. Kalck, Y. Peres, R. H. Grubbs, *J. Mol. Catal. Chem.*, 1993, **78**, 351