

Two-photon absorption and multiphoton excited fluorescence of acetamide-chalcone derivatives: the role of dimethylamine group on the nonlinear optical and photophysical properties

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Supporting Information

1) Compounds

The studied compounds were in powder form and were solubilized in DMSO solution. Compounds $\text{ChN}(\text{CH}_3)_2$ and ChNO_2 presented yellow coloration in solution and the other compounds presented a translucent appearance.

2) Molar absorption coefficient

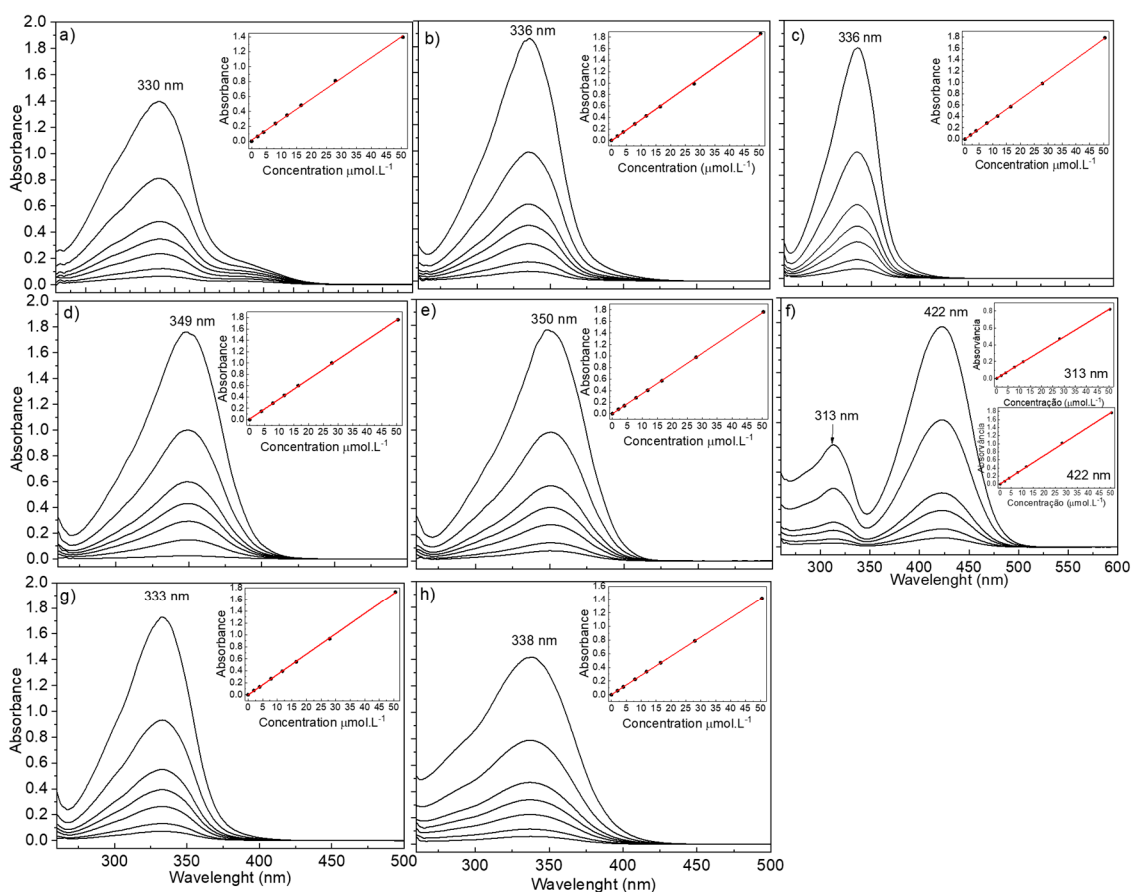


Figure S1 – Graph of absorbance as a function of molar concentration to determine the molar absorption coefficient for a) ChH b) ChCH_3 c) ChCH_2CH_3 d) ChOCH_3 e) $\text{ChOCH}_2\text{CH}_3$ f) $\text{ChN}(\text{CH}_3)_2$ g) ChBr and h) ChNO_2 . The insets show the linear behavior of maximum absorbance with the molar concentration.

3) Gaussian decomposition

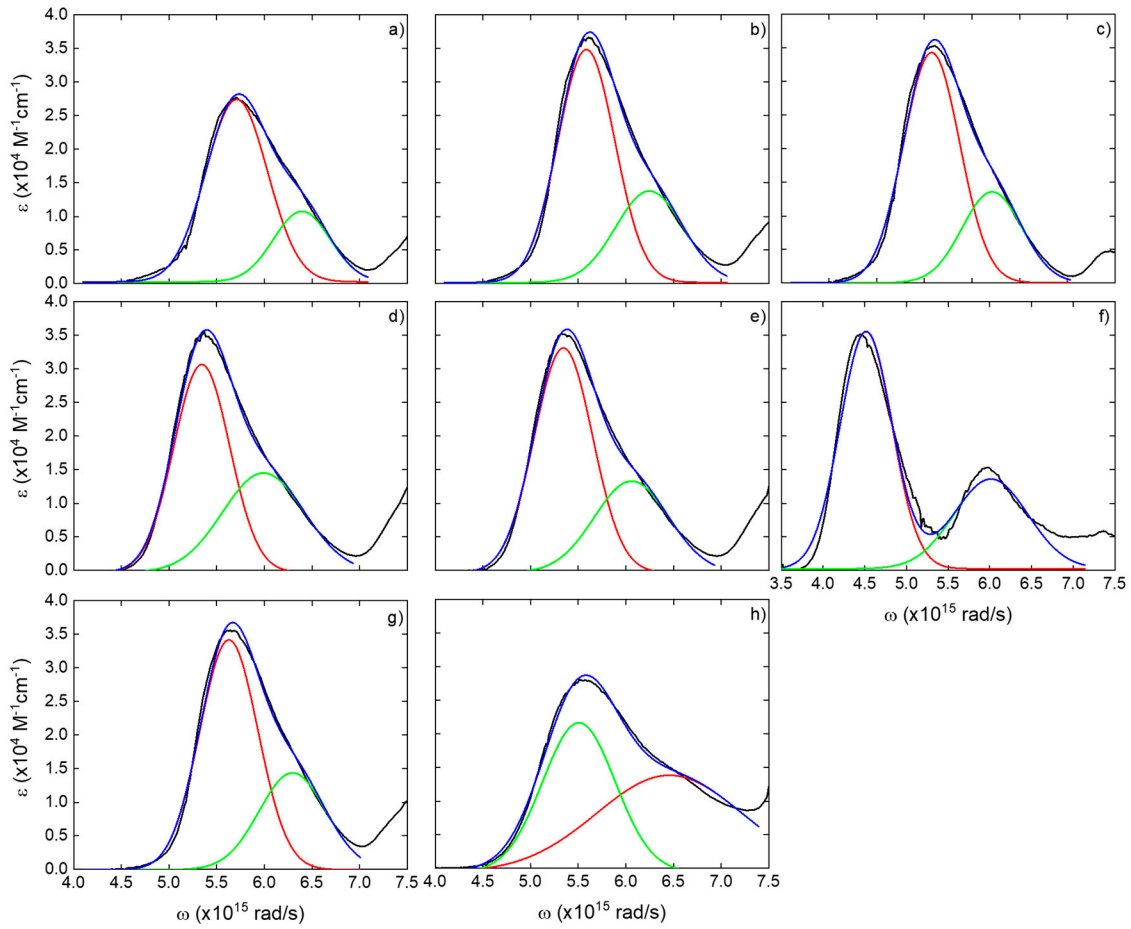


Figure S2 – Gaussian decomposition of of a)ChH b)ChCH3 c)ChCH₂CH₃ d)ChOCH₃ e)ChOCH₂CH₃ f)ChN(CH₃)₂ g)ChBr and h)ChNO₂. The red, green, and blue lines represent the first electronic state, the second electronic state, and the fitting, considering that both are overlapped.

Transition dipole moments from the ground to the first and second excited states were determined through the following equation:

$$|\vec{\mu}_{0n}|^2 = \frac{3 \times 10^3 \ln(10) hc n}{(2\pi)^3 N_A} \frac{1}{L^2} \frac{1}{\omega_{0n}} \int_{\varepsilon_1}^{\varepsilon_f} \varepsilon(\omega) d\omega \quad \text{SI1}$$

in which h is the Planck constant, n is the refractive index of DMSO, L is the Onsager's field factor given by $3n^2/(2n^2+1)$, N_A is the Avogadro number, ω_{0n} is the angular transition frequency of ground (subindex 0) to excited states ($n = 1, 2$) and $\int_{\varepsilon_1}^{\varepsilon_f} \varepsilon(\omega) d\omega$ is the area below each electronic band.

4) Quantum Chemical Calculations

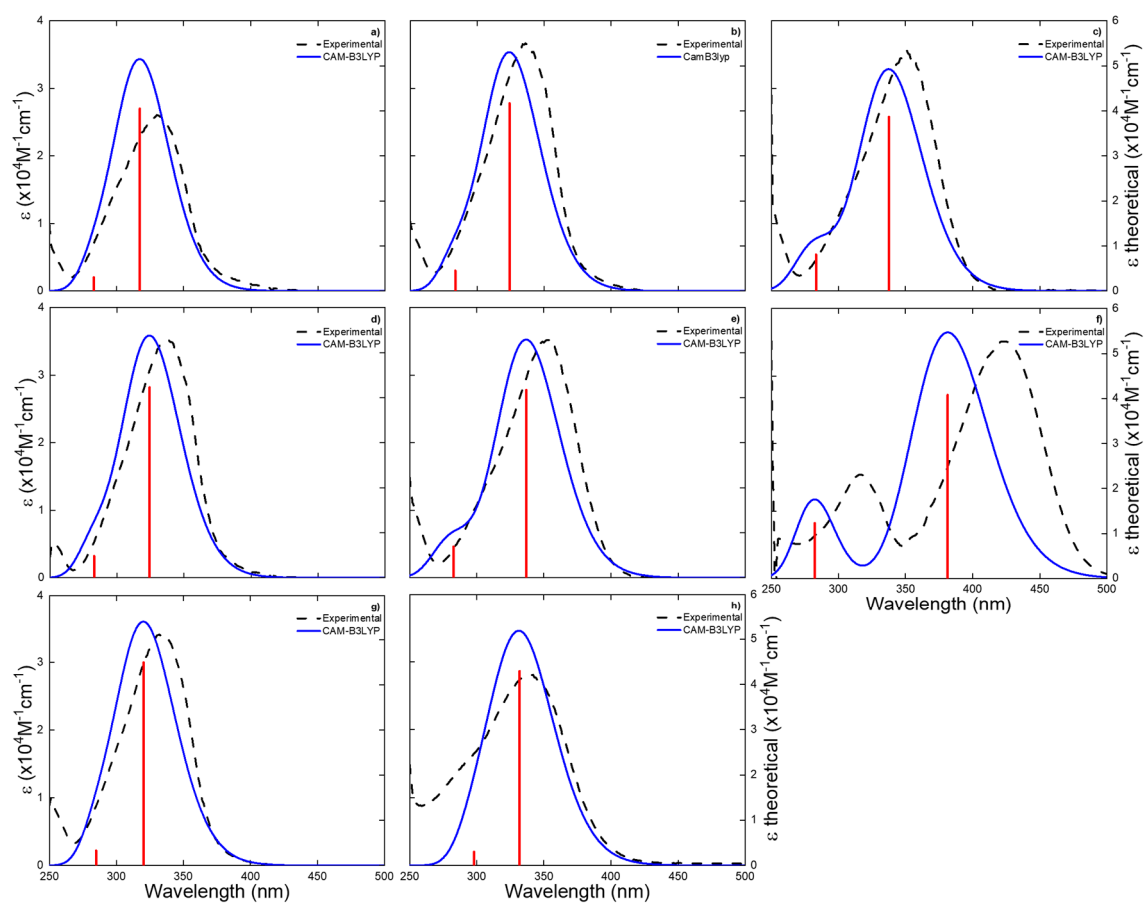


Figure S3 – Experimental (dashed black lines) and simulated (continuous blue lines) one-photon absorption spectra of a) ChH b) ChCH₃ c) ChOCH₃ d) ChCH₂CH₃ e) ChOCH₂CH₃ f) ChN(CH₃)₂ g) ChBr and h) ChNO₂. The vertical red bars represent the oscillator strengths of the electronic transitions as determined via PCM-TD-DFT calculations.

5) Quantum Chemistry Calculations (QCCs)

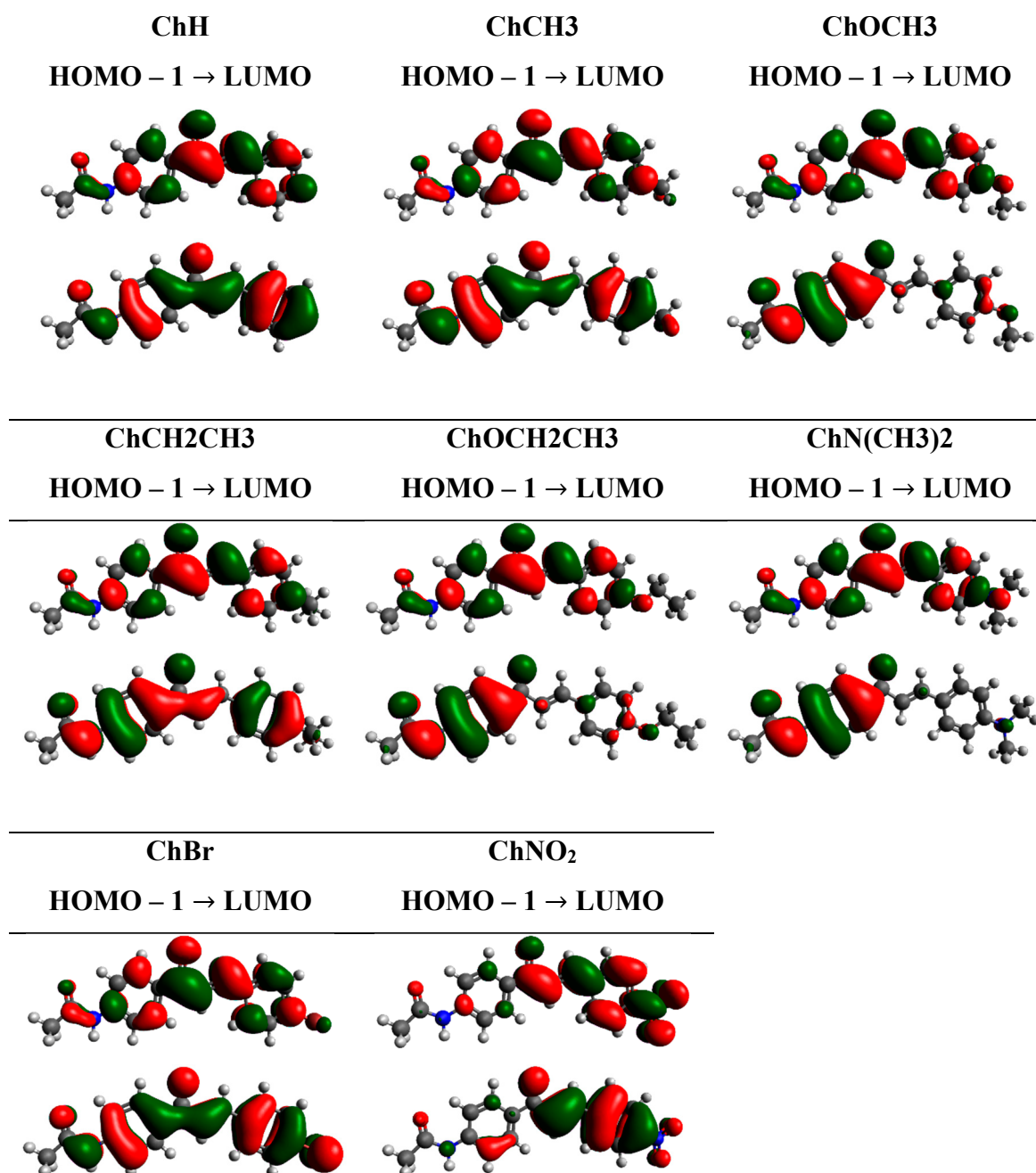


Figure S4 - Frontier Molecular obtained through the PCM-CAM-B3LY/6-311++G(d,p) approach for DMSO medium. The FMOs are involved in the lowest-energy one-photon allowed transition of all studied compounds.

Table S1 – Oscillator strengths and transition wavelengths for all Acetamide-chalcone derivatives obtained by TD-DFT calculations using the PCM-CAM-B3LYP/6-311G++(d,p) approach for DMSO medium.

Compound	$f_{S_0 \rightarrow S_1}$	$\lambda_{S_0 \rightarrow S_1}(nm)$	$f_{S_0 \rightarrow S_2}$	$\lambda_{S_0 \rightarrow S_2}(nm)$
ChH	1.35	317	0.10	283
ChCH3	1.39	324	0.14	284
ChOCH3	1.29	338	0.27	283
ChCH2CH3	1.41	324	0.16	283
ChOCH2CH3	1.39	337	0.23	283
ChN(CH3)2	1.36	381	0.41	282
ChBr	1.50	320	0.11	285
ChNO2	1.43	332	0.10	298

6) Structural analysis

Eight *para*-substituted aceto-amidechalcones were prepared by Claisen-Schmidt reaction with moderated yields (30 -74 %), and their structure was supported by spectroscopic techniques. FTIR spectra of 4-acetamideacetophenone present absorption bands in 3296 cm^{-1} due to stretching (ν) of N-H bond and a large band at 1674 cm^{-1} , related to C=O stretchings of amide and ketone groups. In sequence, ChCH₃ shows similar $\nu(\text{N-H})$ absorption band and, additionally, the $\nu(\text{C=O})$ of carboxylic groups has been split into two new bands, at 1678 cm^{-1} (amide group) cm^{-1} and 1650 cm^{-1} (ketone α,β -insaturated). Furthermore, ChCH₃ exhibits a new band at 808 cm^{-1} relative to C-H bending of *para*-substituted aromatic ring resulting from the connection with 4-methylbenzaldehyde.

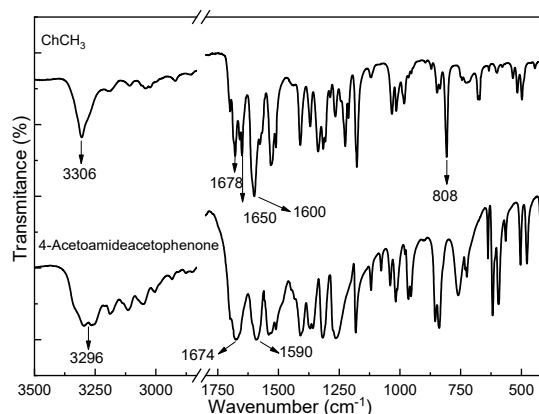


Figure S5 - FTIR Spectra of 4-Acetamideacetophenone and ChCH₃

¹H NMR of all synthesized molecules shows two typical dublets of *trans*-chalcones with coupling constants of 15 Hz. These signals, near 7.4 and 7.7 ppm, are related to the magnetic coupling of α,β -olefinic hydrogens at *E* configuration. Considering the chalcone **ChCH₃** (Fig SI6) are also observed two doublets, with an integral relative to 2 H, at 7.20 and 7.51 ppm ($J = 8.0\text{ Hz}$) associated with the hydrogens bonded to the aromatic carbons C3/C5 and C2/C6, respectively, and at 7.66 and 7.99 ppm associated with hydrogens attached to C3'/C5' and C2'/C6' aromatic carbons. On the other hand, at 2.20 and 2.37 ppm two singlets, with an integral relative to 3 hydrogens, were observed and corresponding to methylenic hydrogens of the methyl group of C8 and C9. The hydrogen of amine group consists of a large singlet at 7.84 ppm.

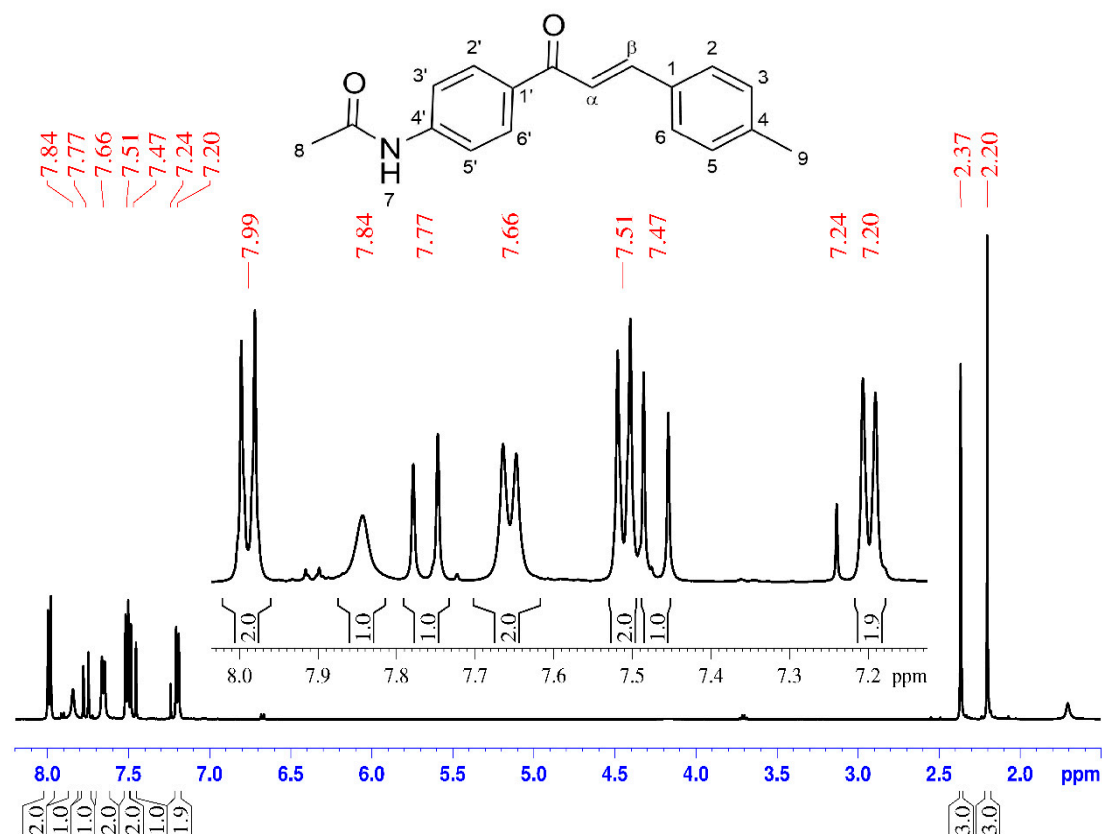


Figure S6 - ^1H NMR spectra, in CDCl_3 (7.24 ppm), of **ChCH3**.

^{13}C NMR spectra of **ChCH3** present signals in 120.8 ppm and 144.7 ppm related to carbons on α and β positions, respectively, in 168.6 ppm associated to carbonyl of amide group and 189.2 to carbonyl group of α,β -unsaturated ketone.

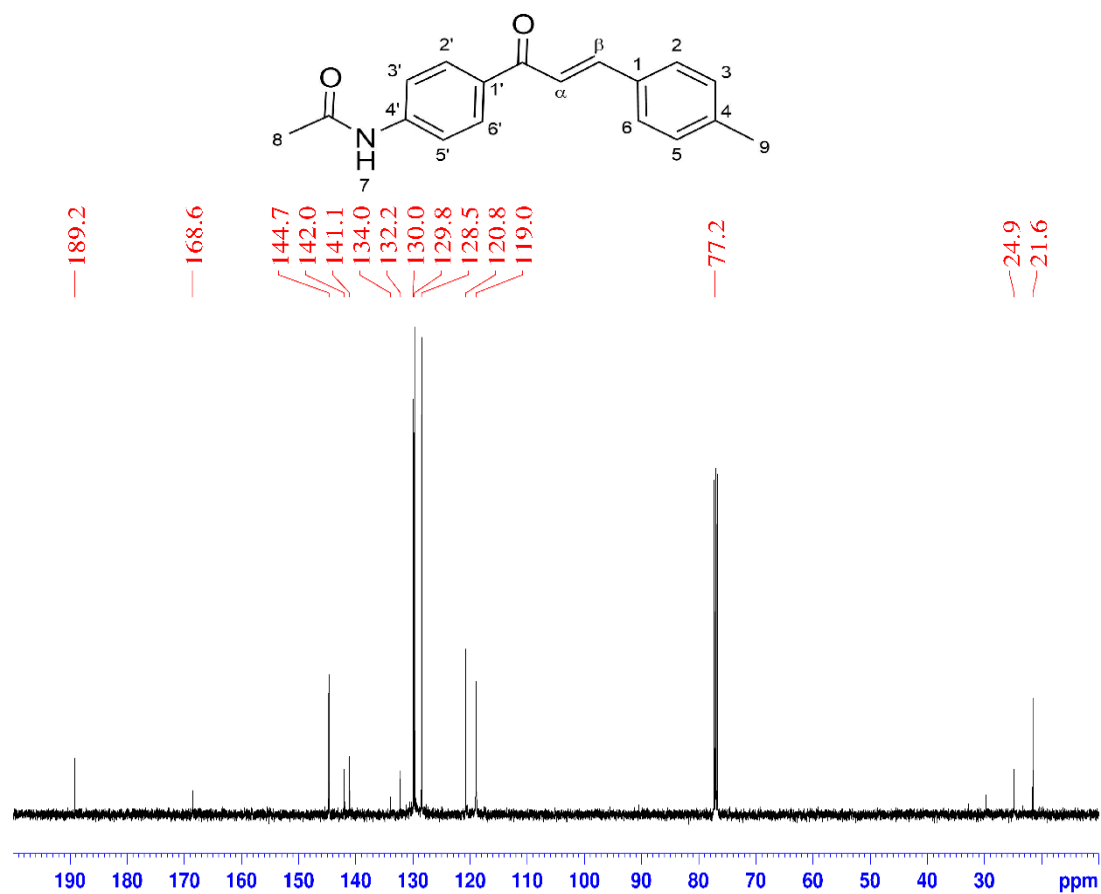


Figure S7 – ^{13}C NMR spectra, in CDCl₃ (77.2 ppm), of ChCH₃.

7) FTIR spectra of all acetamide-chalcones synthesized.

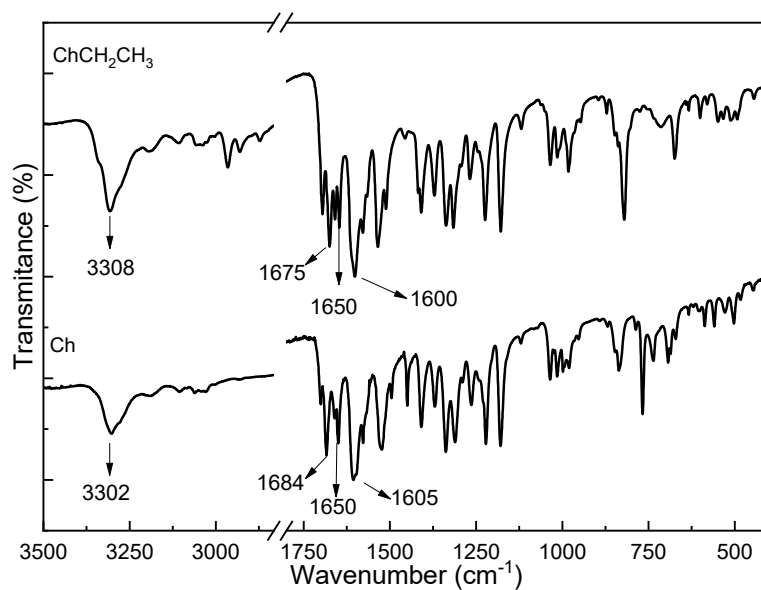


Figure S8 - FTIR Spectra of ChH and ChCH₂CH₃

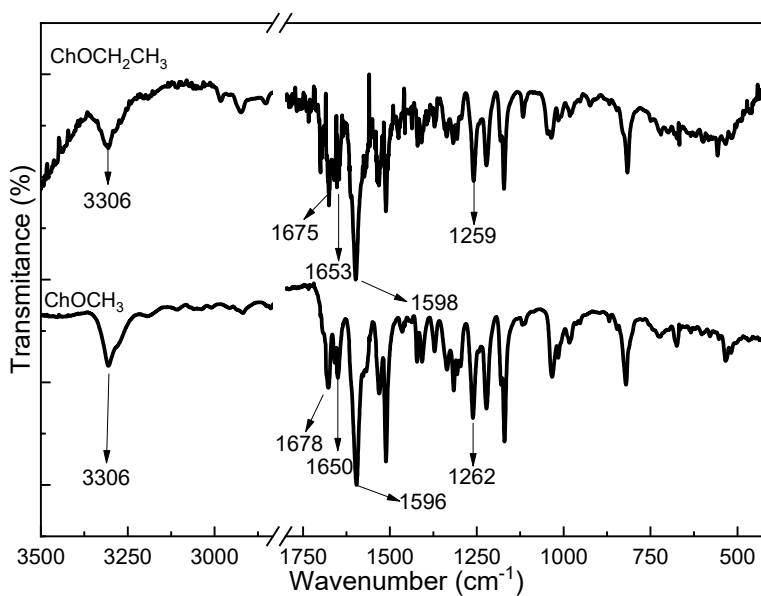


Figure S9 - FTIR Spectra of ChOCH₃ and ChOCH₂CH₃

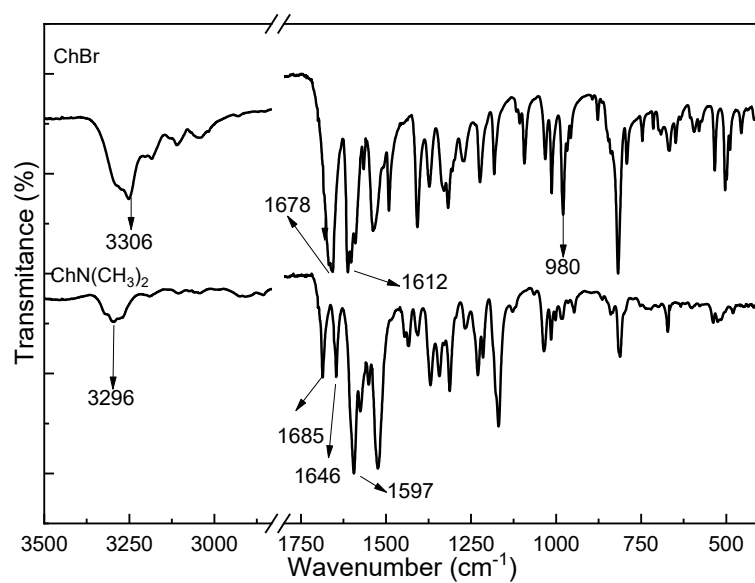


Figure S10 - FTIR Spectra of ChN(CH₃)₂ and ChBr

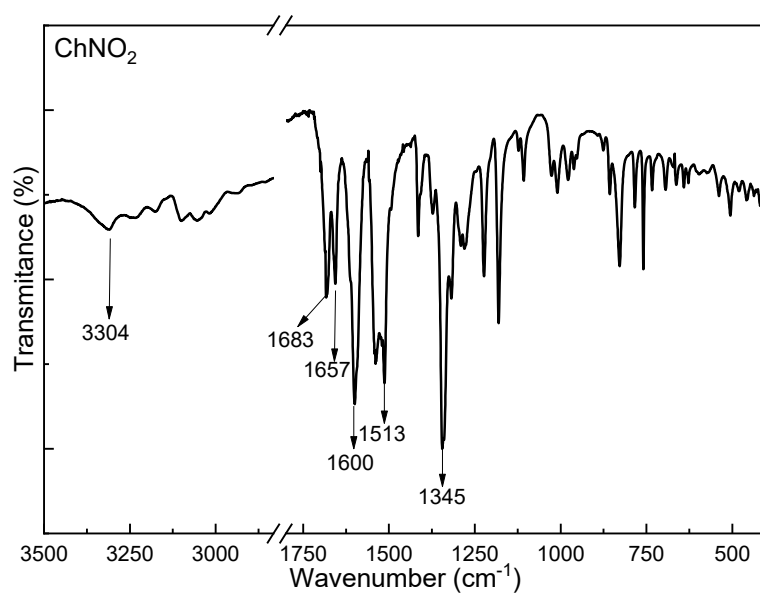


Figure S11 - FTIR Spectra of ChNO₂

8) ^1H NMR Spectra of all studied compounds

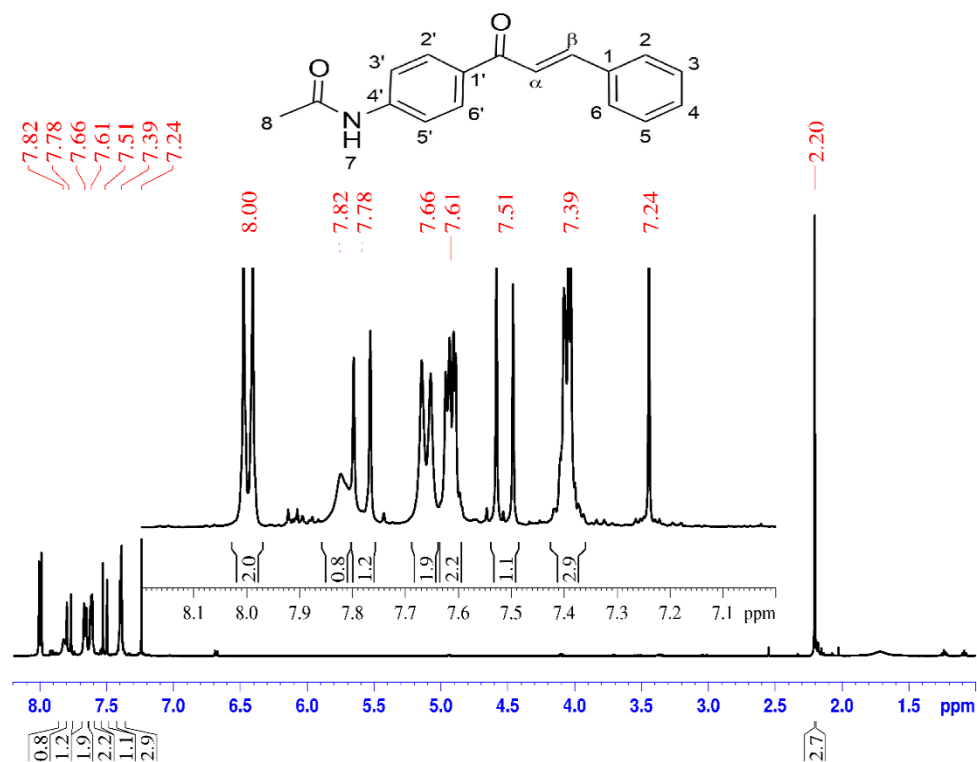


Figure S12 - ^1H NMR spectra, in CDCl_3 (7.24 ppm), of **ChH**.

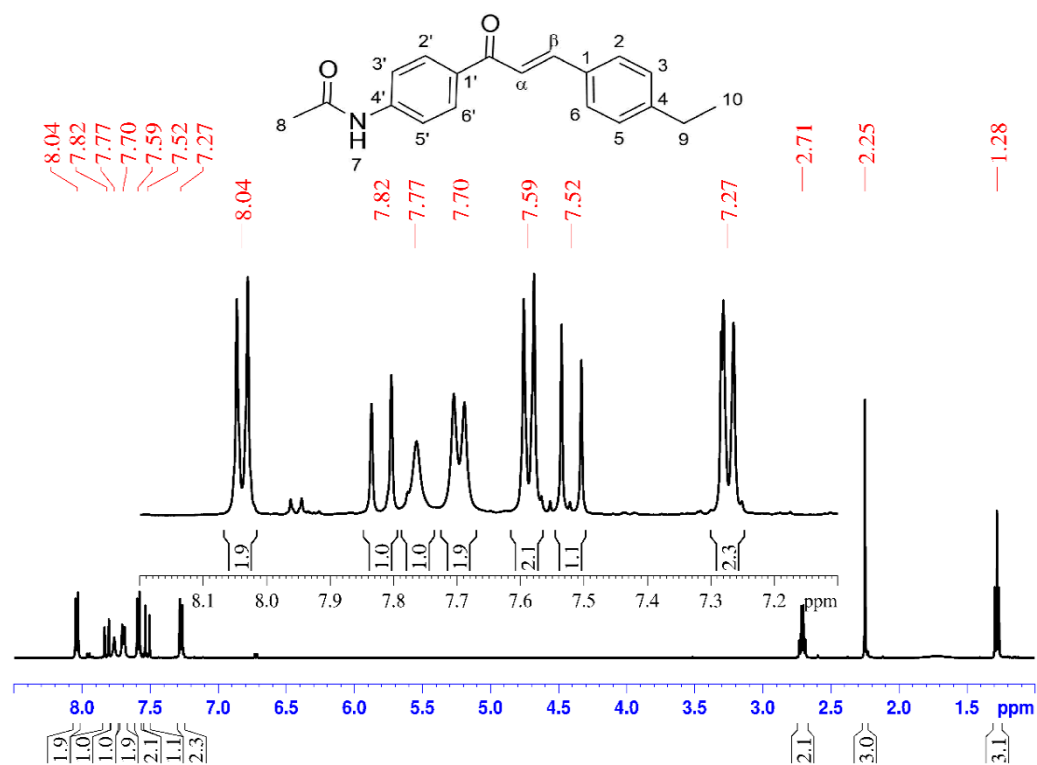


Figure S13 - ^1H NMR spectra, in CDCl_3 (7.24 ppm), of **ChCH₂CH₃**.

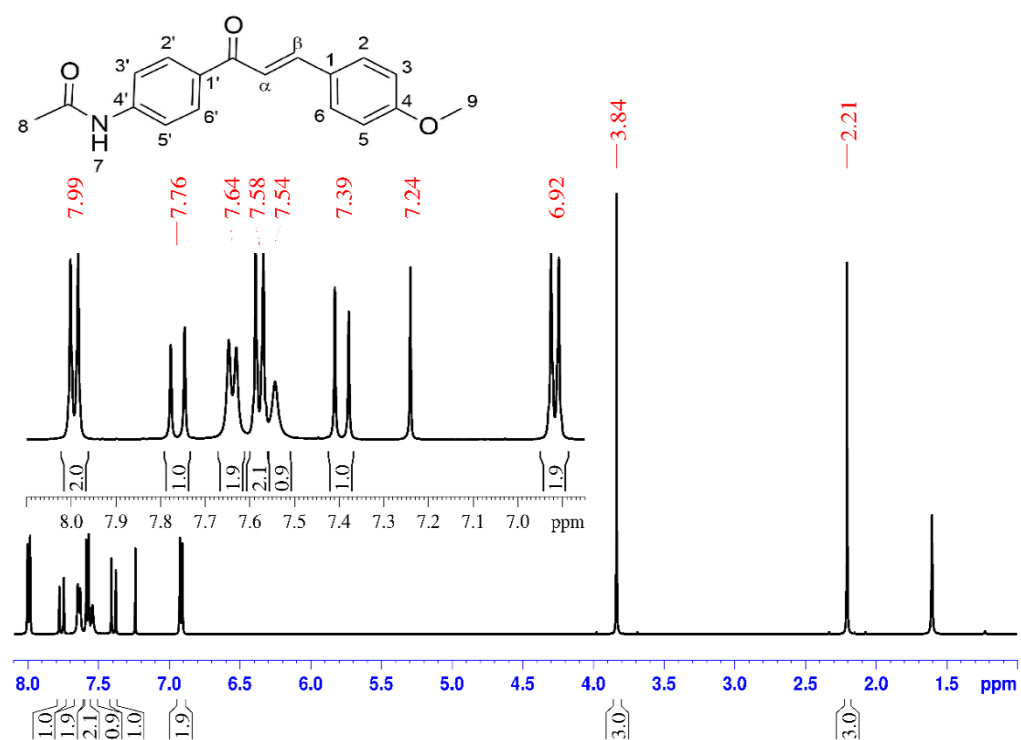


Figure S14 - ^1H NMR spectra, in CDCl_3 (7.24 ppm), of **ChOCH₃**

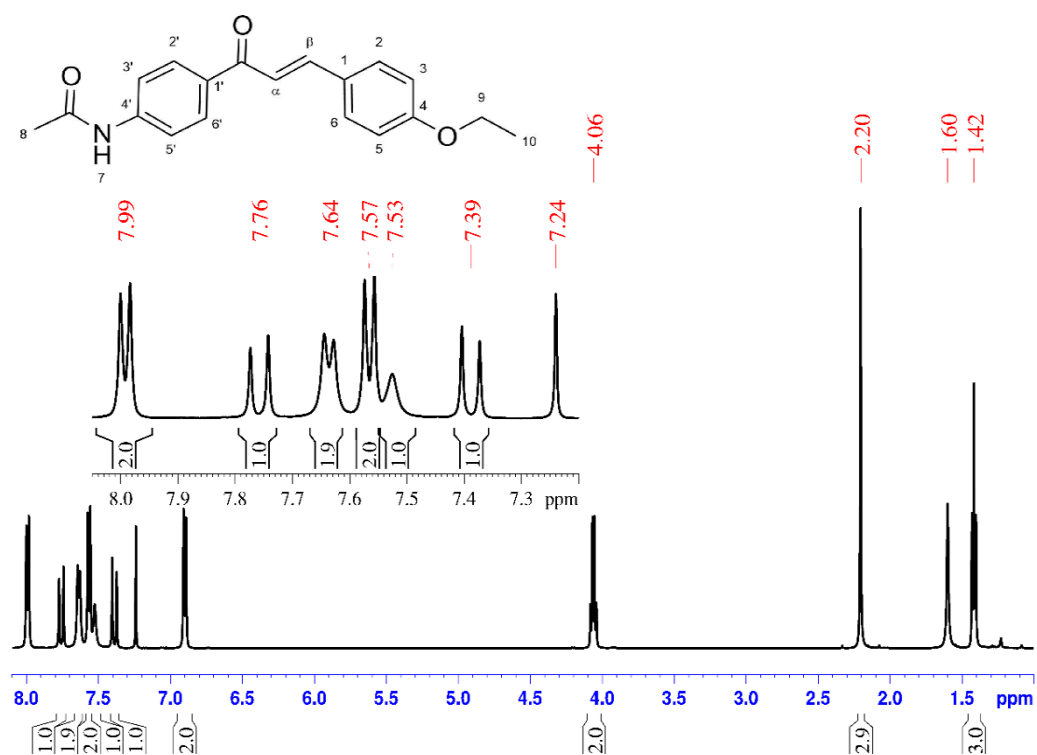


Figure S15 - ^1H NMR spectra, in CDCl_3 (7.24 ppm), of **ChOCH₂CH₃**

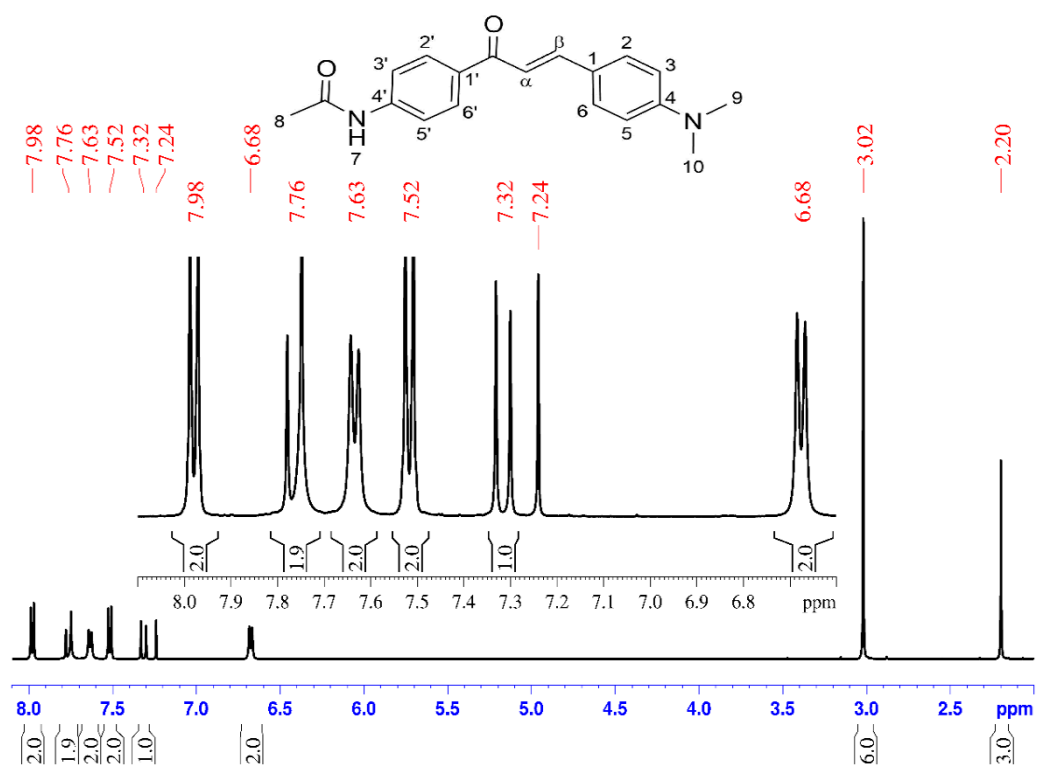


Figure S16 - ¹H NMR spectra, in CDCl₃ (7.24 ppm), of **ChN(CH₃)₂**

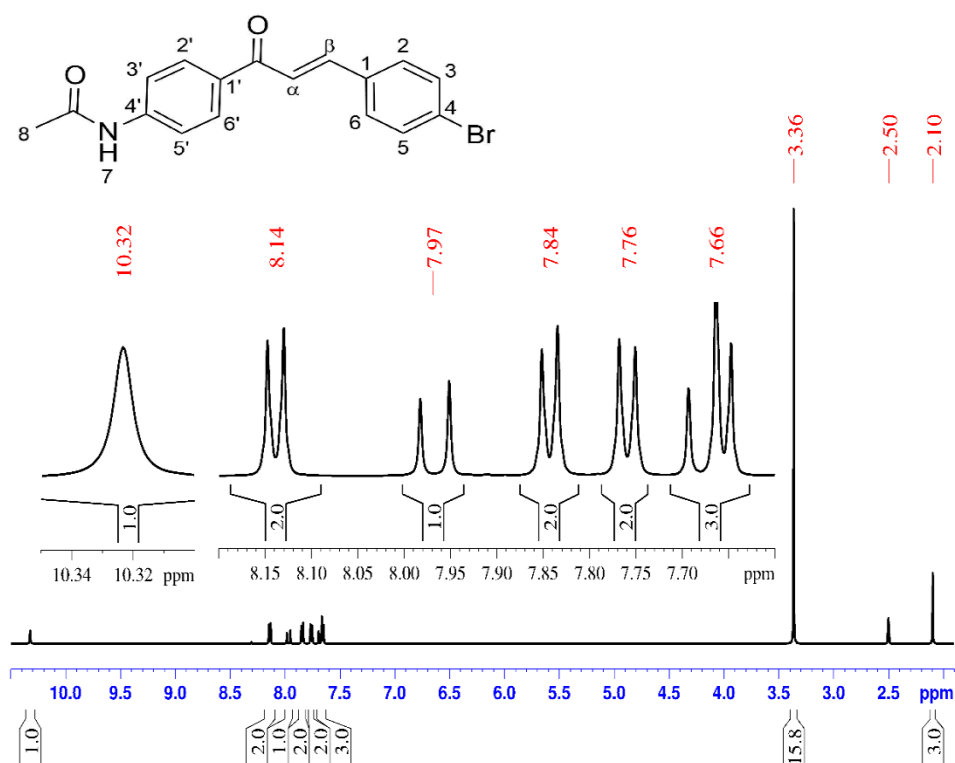


Figure S17 - ¹H NMR spectra, in DMSO-*d*₆ (2.50 ppm), of **ChBr**.

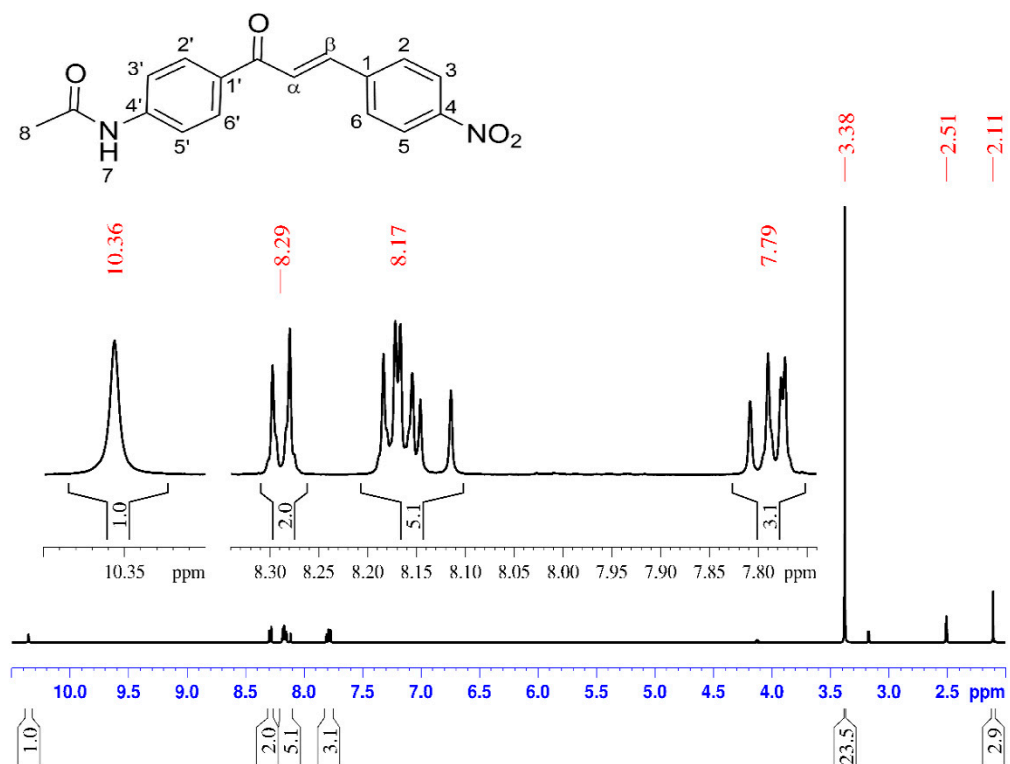


Figure S18 - ¹H NMR spectra, in DMSO-*d*₆ (2.50 ppm), of ChNO2.

9) ¹³C NMR Spectra of all studied compounds.

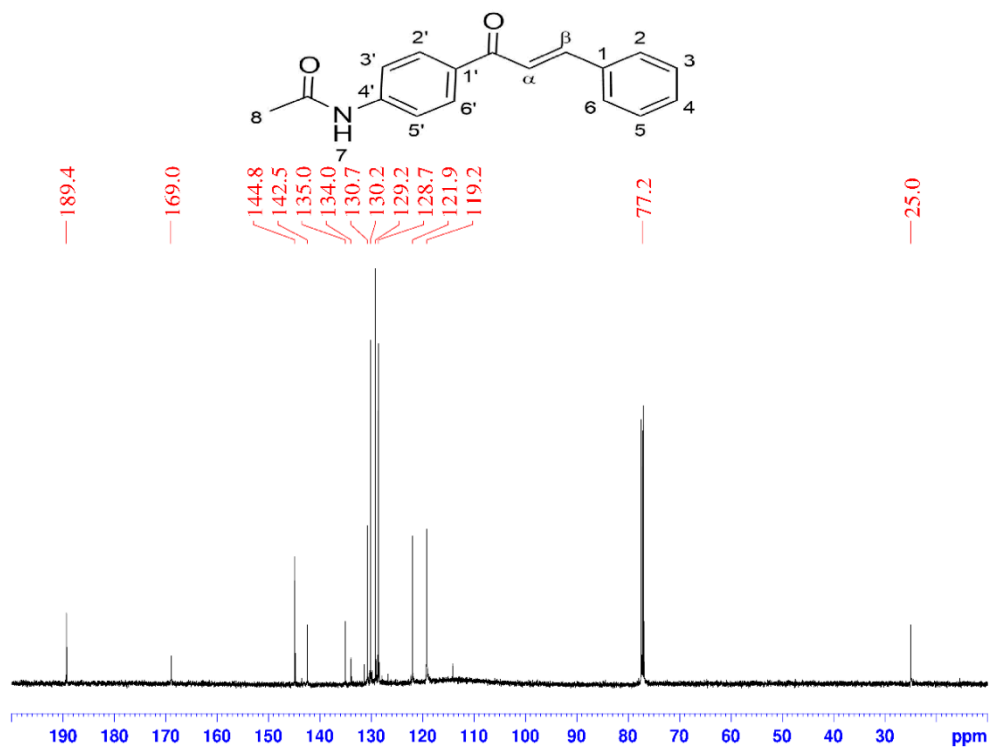


Figure S19 – ^{13}C NMR spectra, in CDCl_3 (77.2 ppm), of ChCH

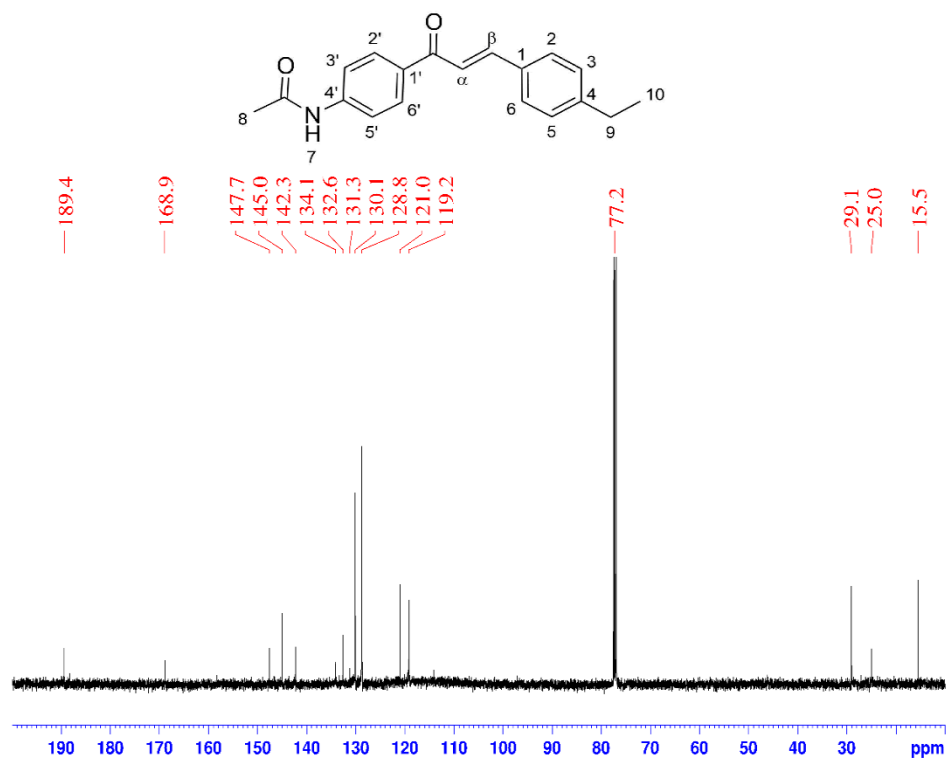


Figure S20 – ^{13}C NMR spectra, in CDCl_3 (77.2 ppm), of ChCH₂CH₃

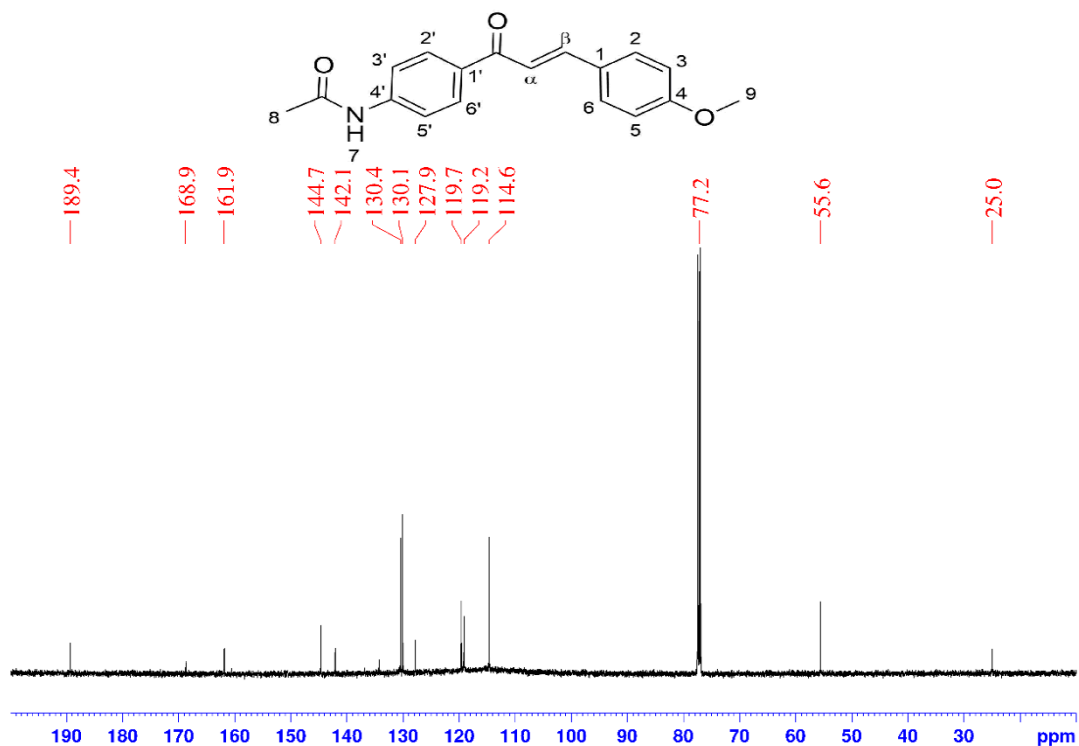


Figure S21 – ^{13}C NMR spectra, in CDCl_3 (77.2 ppm), of **ChOCH3**

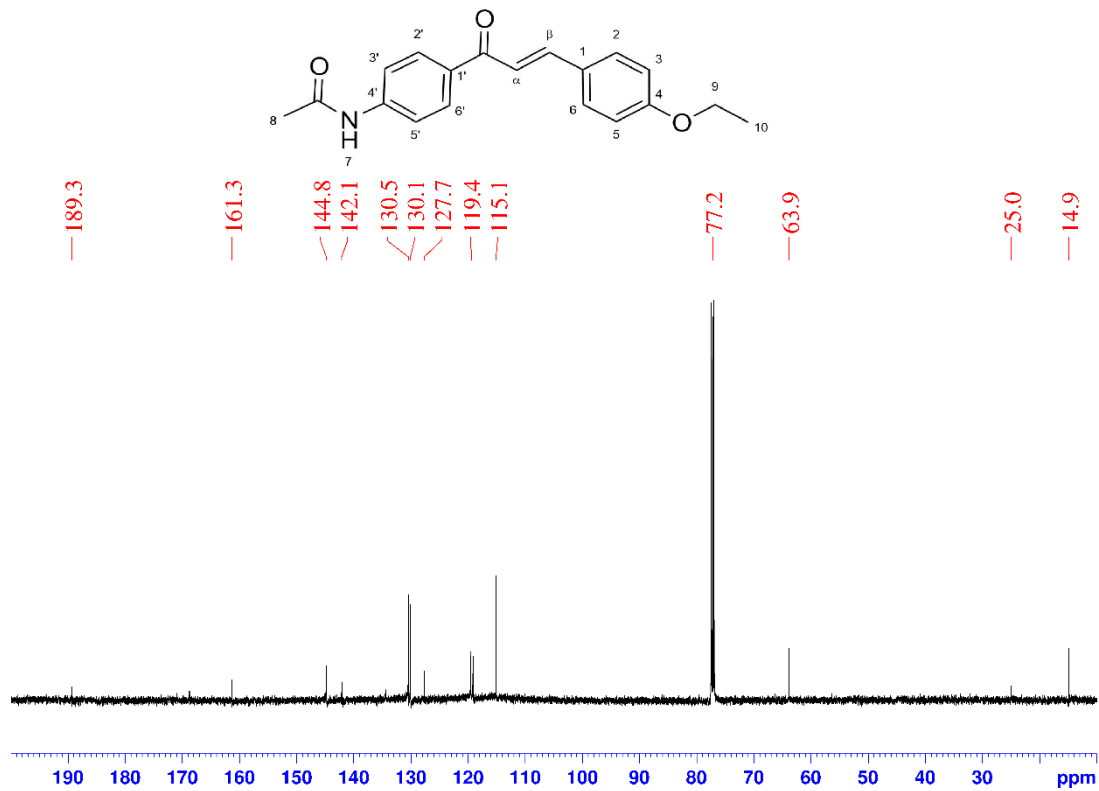


Figure S22 – ^{13}C NMR spectra, in CDCl_3 (77.2 ppm), of **ChOCH₂CH₃**

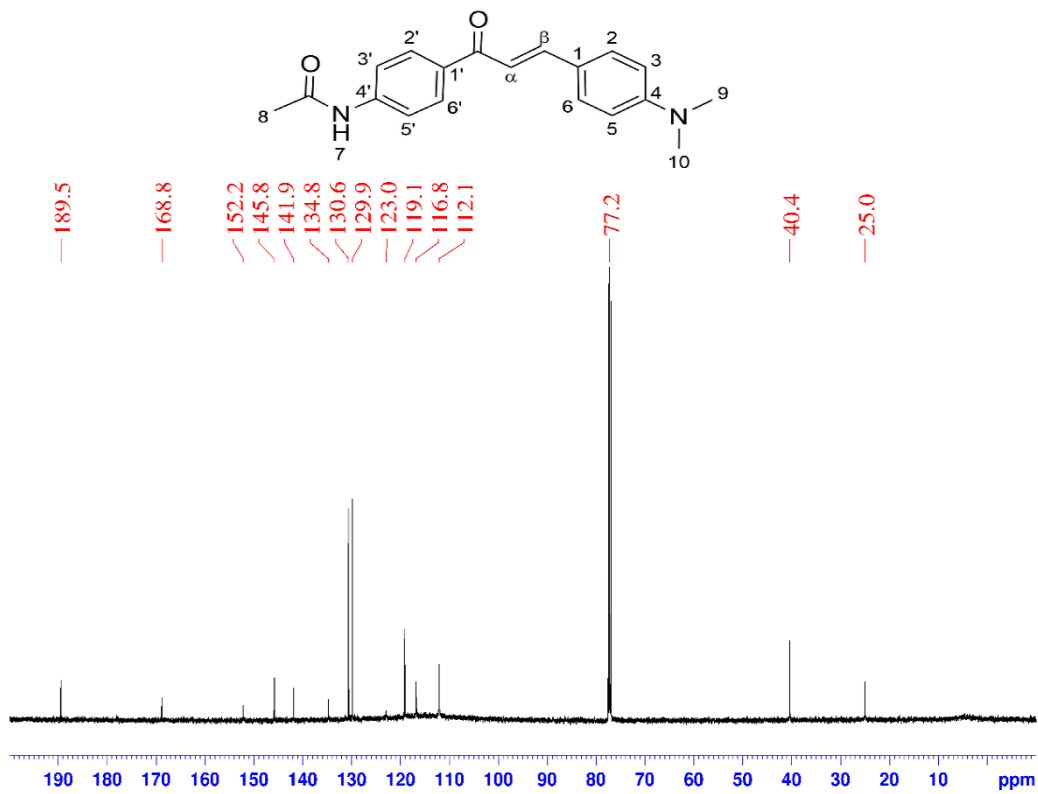


Figure S23 – ^{13}C NMR spectra, in CDCl_3 (77.2 ppm), of $\text{ChN}(\text{CH}_3)_2$

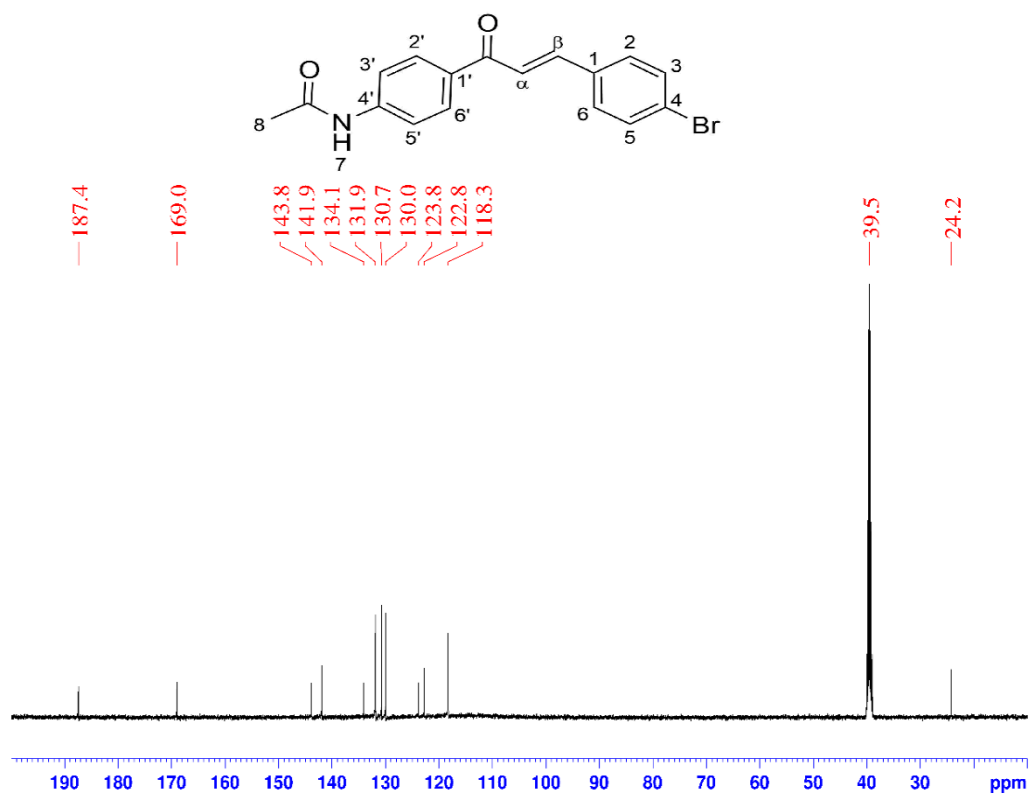


Figure S24 – ^{13}C NMR spectra, in $\text{DMSO}-d_6$ (39.5 ppm), of ChBr

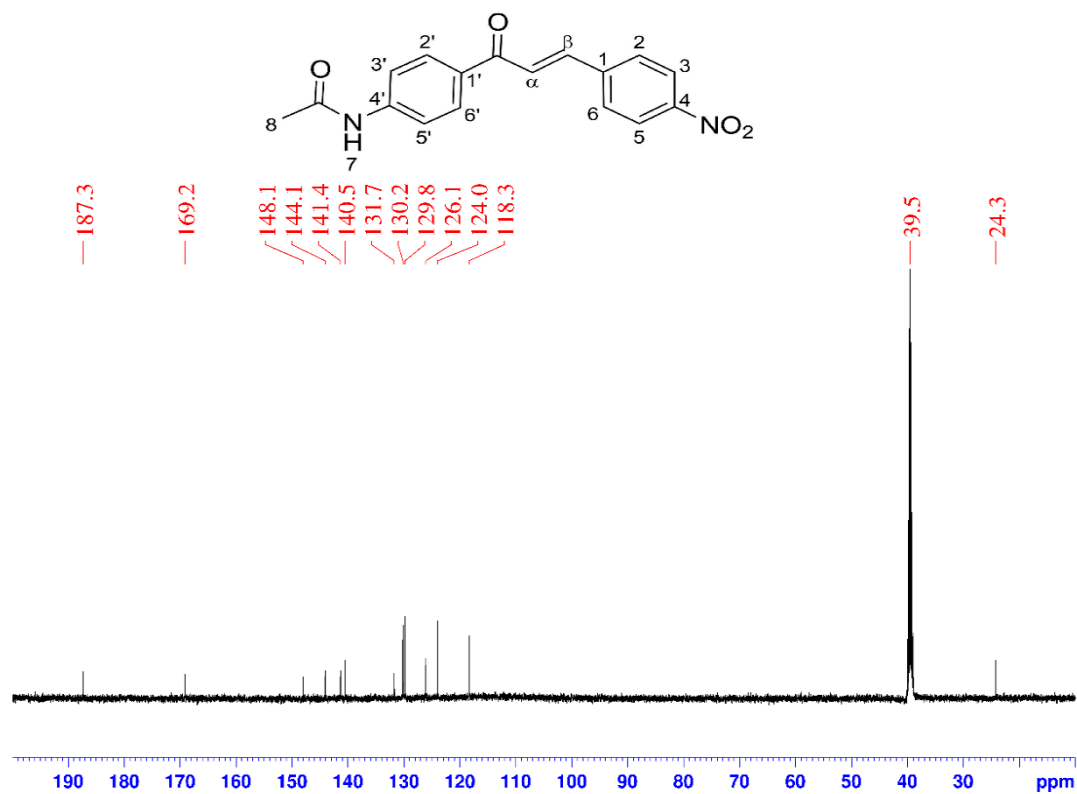


Figure S25 – ^{13}C NMR spectra, in $\text{DMSO-}d_6$ (39.5 ppm), of ChNO2

10) High-Resolution Mass Spectra Data of all studied compounds

Mass spectra were obtained using a Q Exactive hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific, San Jose, U.S.A). All HRESI-MS analyses were performed in positive ionization mode with the capillary temperature maintained at 320 °C, spray voltage at 4.5 kV, S-lens RF level at 60%, resolution at 140 000, three micro scans, and collision energy for MS/MS (higher-energy collisional dissociation – HCD) ranging from 20 to 30 (manufacturer's unit). The spectra were processed using the Xcalibur Analysis software package (version 2.0, Service Release 2, Thermo Electron Corporation). The HRESI-MS spectra are presented in Fig. S26-S32. All synthesized compounds showed low $[\text{M}+\text{H}]^+$ ion mass error, confirming the veracity of the structural proposition of the products.

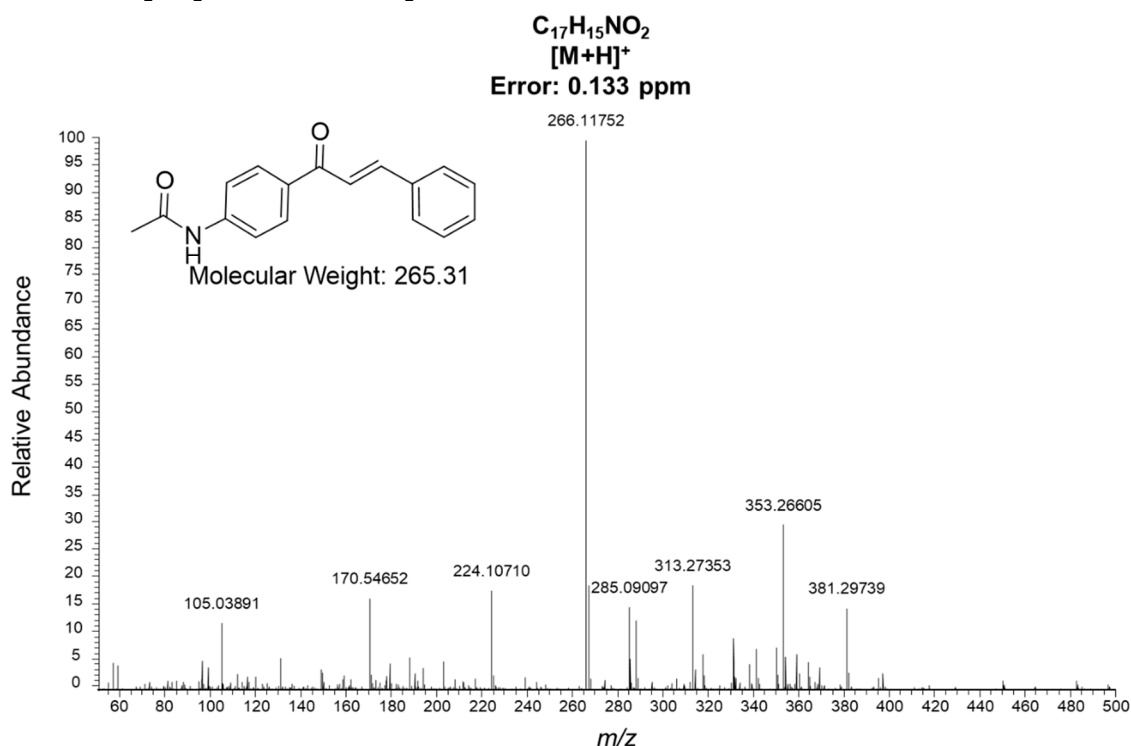


Figure S26 – HRESI-MS spectra of ChH.

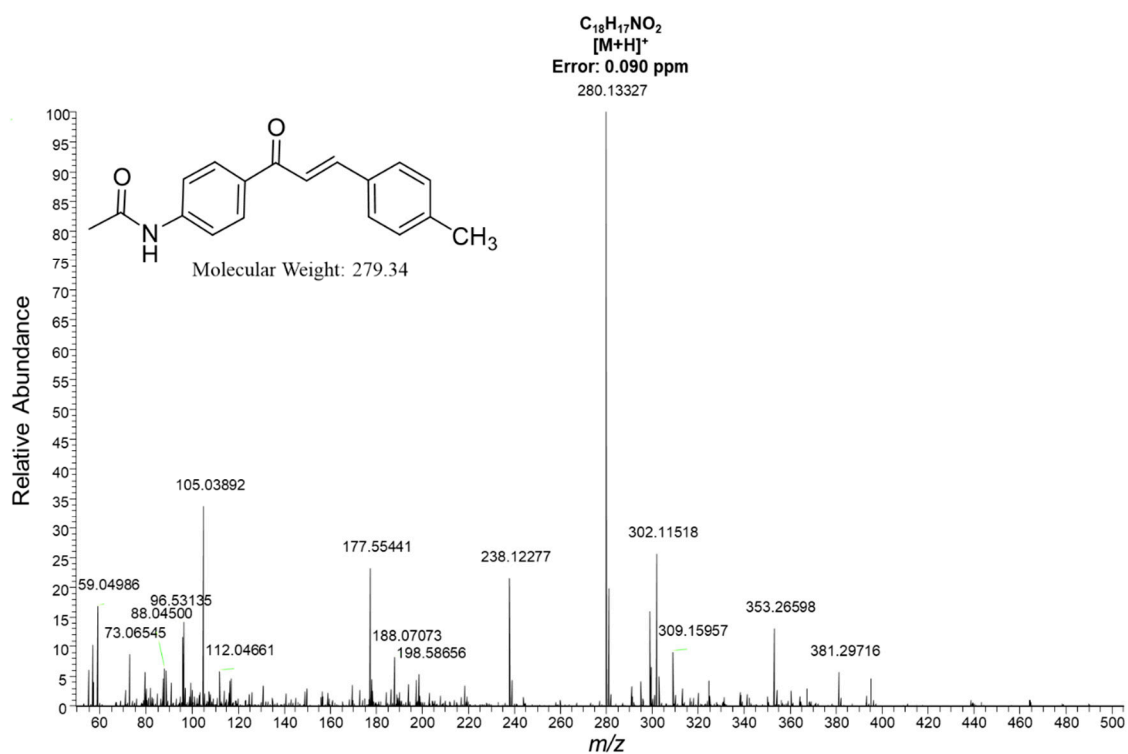


Figure S27 – HRESI-MS spectra of ChCH3.

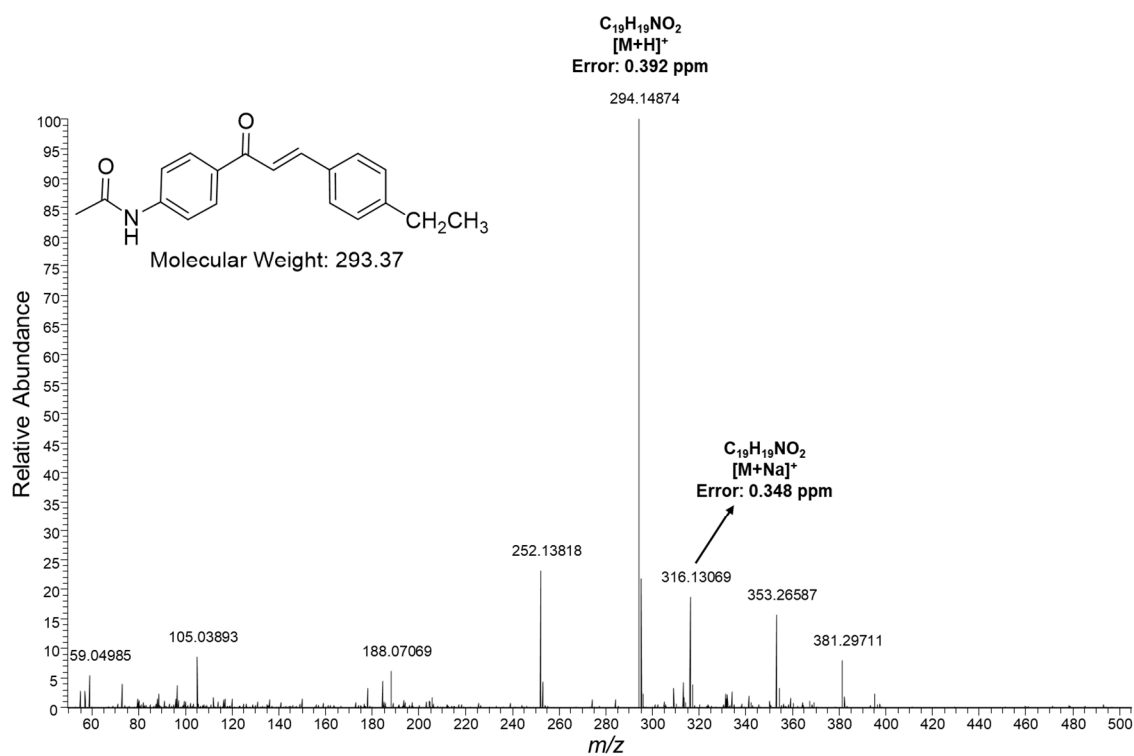


Figure S28 – HRESI-MS spectra of ChCH2CH3.

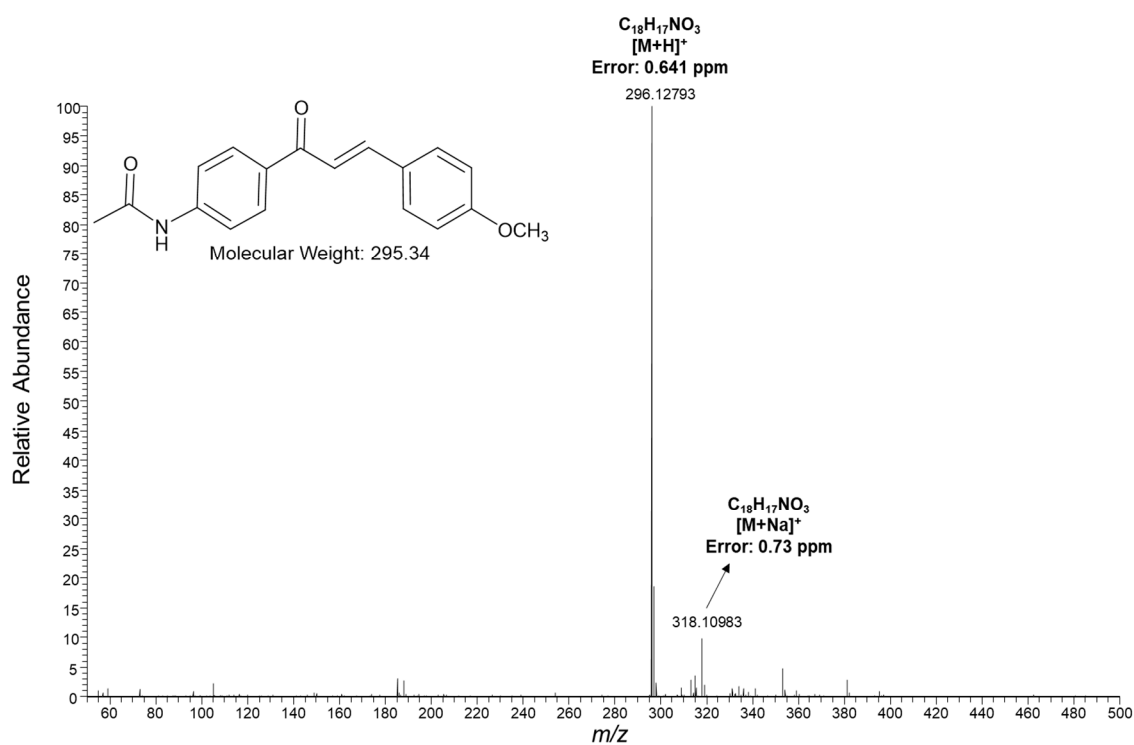


Figure S29 – HRESI-MS spectra of ChOCH3.

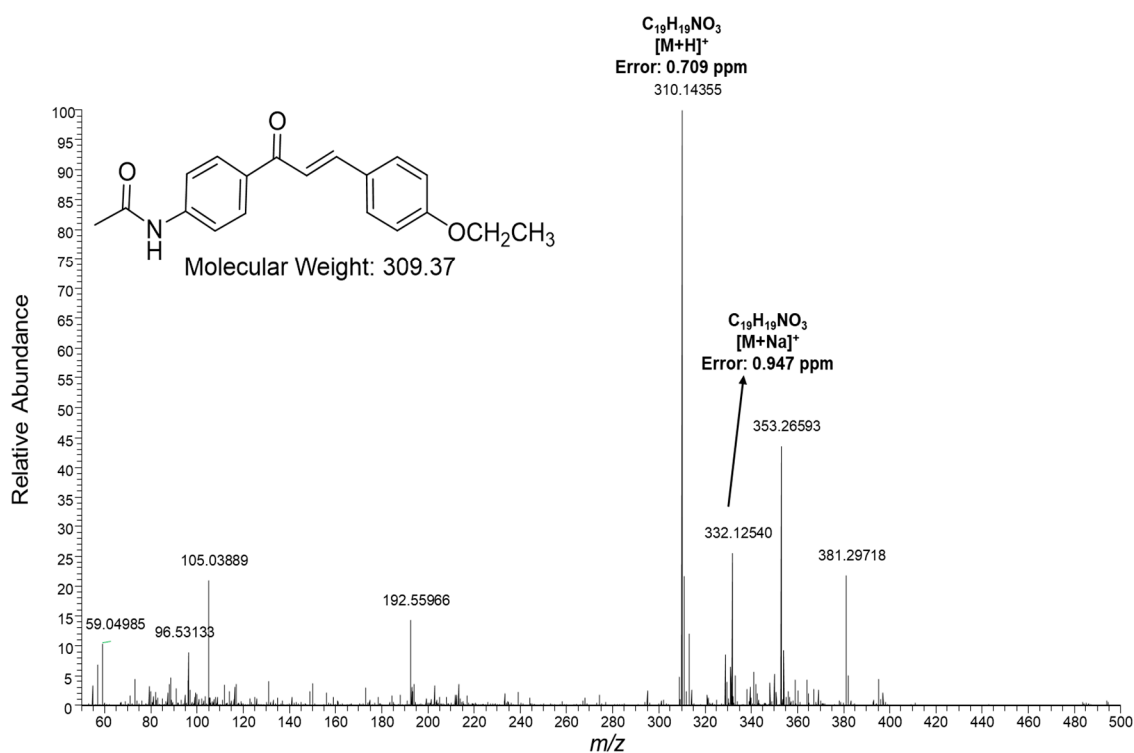


Figure S30 – HRMS spectra of ChOCH2CH3.

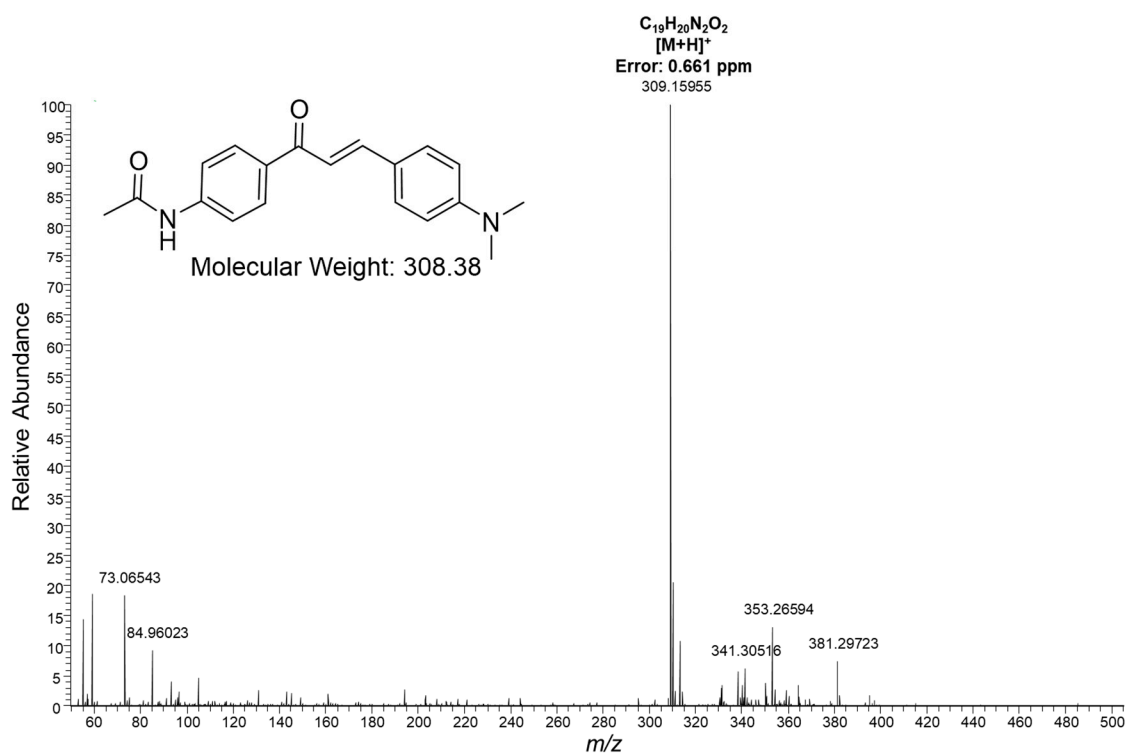


Figure S31 – HRESI-MS spectra of ChN(CH₃)₂.

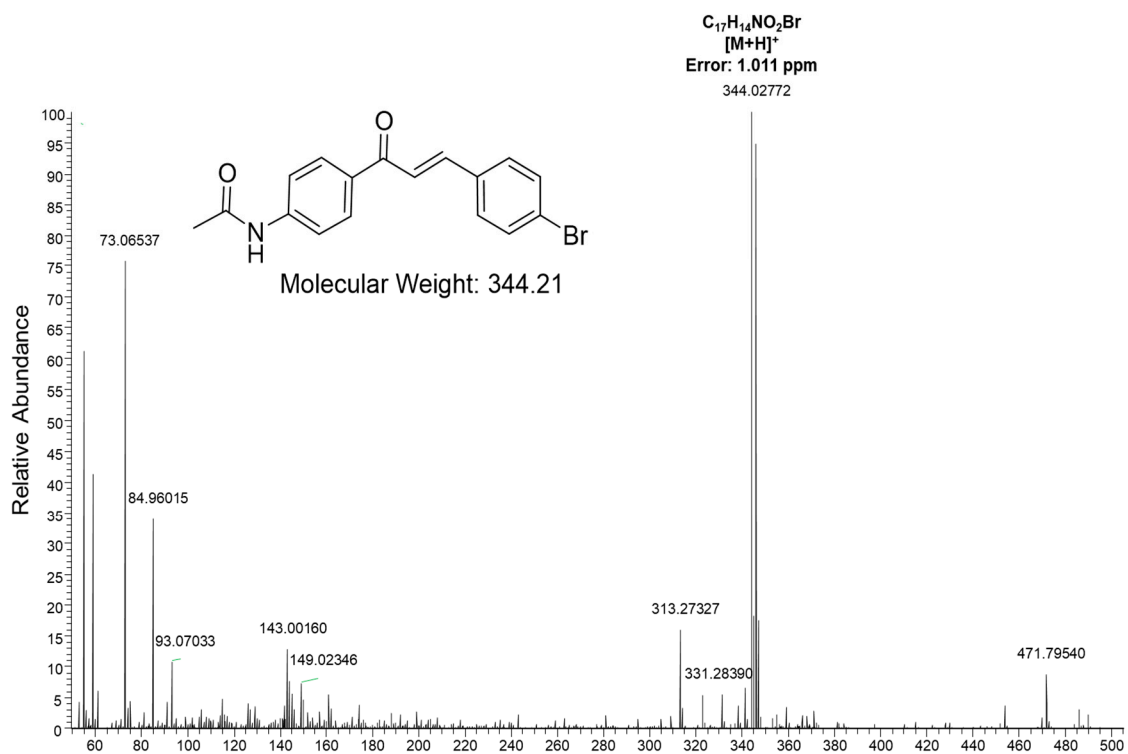


Figure S32 – HRESI-MS spectra of ChBr.

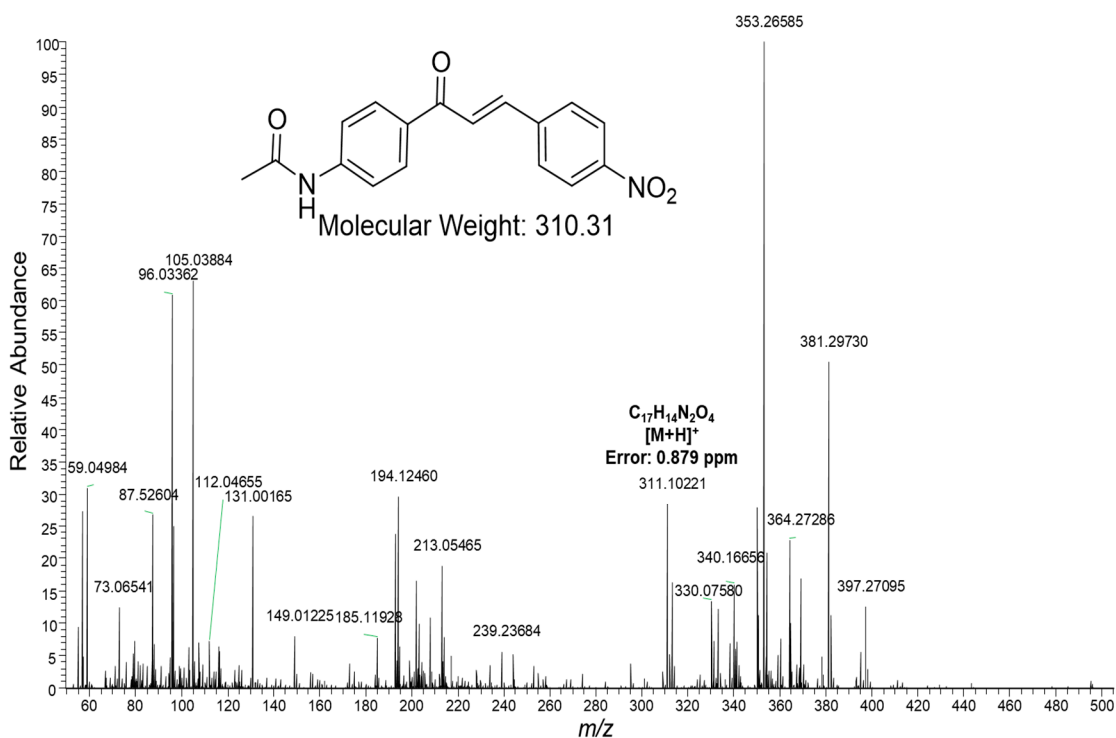


Figure S33 – HRESI-MS spectra of ChNO₂.

11) Additional Structural Information of all studied compounds

a) N-[4-[(2E)-1-Oxo-3-phenyl-2-propen-1-yl]phenyl]acetamide (ChH):
 $C_{17}H_{15}NO_2$; Reaction Yield: 30 %; Molecular Weight: 265,31 g.mol⁻¹; CAS Number:
123456-58-6; ϵ_{DMSO} (330 nm): 27716 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z
266.11752

FTIR (cm⁻¹): 3302 (ν -N-H); 1684 (ν -NHC=O); 1650 (ν C_(α,β) = O); 1605 (ν -
HC_α=C_βH).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 8.00 ppm (d, 8.6 Hz, H-2'/H-6'); 7.82 ppm
(br. s, H-7); 7.78 ppm (d, 15.5 Hz, H-β); 7.66 ppm (d, 8.6 Hz, H-3'/H-5'); 7.61 ppm (m,
H-2/H-6); 7.51 ppm (d, 15.5 Hz, H-α); 7.39 ppm (m, H-3/H-4/H-5); 2.7 ppm (s, 8.6, H-
8).

¹³C NMR 125MHz CDCl₃ (δ ppm): 25.0 ppm (C8)); 121.9 ppm (C_α); 144.8 ppm(C_β);
199.2-142.4 ppm (C_{aromatics}); 169.0 ppm (C=O, amide); 189.4 ppm (C=O, α-β).

b) N-[4-[(2E)-3-(4-Methylphenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide
(ChCH₃): $C_{11}H_{17}NO_2$; Reaction Yield: 72 %; Molecular Weight: 279,34 g.mol⁻¹; CAS
Number: 1015084-94-2; ϵ_{DMSO} (336 nm): 36674 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ =
m/z 280.13327

FTIR (cm⁻¹): 3296 (ν -N-H); 1678 (ν -NHC=O); 1650 (ν C_(α,β) = O); 1600 (ν -HC_α=C_βH).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 7.99 ppm (d, 8.6 Hz, H-2'/H-6'); 7.84 ppm (br. s, H-7); 7.77 ppm (d, 15 Hz, H-β); 7.66 ppm (d, 8.6 Hz, H-3'/H-5'); 7.51 ppm (d, 8.6 Hz, H-2/H-6); 7.47 ppm (d, 15.5 Hz, H-α); 7.20 ppm (d, 8.6 Hz, H-3/H-5); 2.71 ppm (q, 7.4 Hz, H-9); 2.25 ppm (s, H-8); 1.28 ppm (t, 7.6 Hz, H-10)

¹³C NMR 125MHz CDCl₃ (δ ppm): 21.5 ppm (C-9); 24.0 ppm (C-8); 120.8 ppm (C_α); 144.7 ppm (C_β); 129.8-134.0 ppm (C_{aromatics}); 168.0 ppm (C=O, amide); 189.0 ppm (C=O, α-β).

c) N-[4-[(2E)-3-(4-Ethylphenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide

(**ChCH₂CH₃**): C₁₉H₁₉NO₂; Reaction Yield 46 %; Molecular Weight 293,37 g.mol⁻¹; CAS Number: 1993646-89-1; ε_{DMSO} (336 nm): 35303 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 294.14874

FTIR (cm⁻¹): 3308 (ν -N-H); 1675 (ν -NHC=O); 1650 (ν C_(α,β) = O); 1600 (ν -HC_α=C_βH).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 8.04 ppm (d, 8.8 Hz, H-2'/H-6'); 7.77 ppm (br. s, H-7); 7.82 ppm (d, 15 Hz, H-β); 7.77 ppm (d, 8.6 Hz, H-3'/H-5'); 7.59 ppm (d, 8.6 Hz, H-2/H-6); 7.52 ppm (d, 15.5 Hz, H-α); 7.20 ppm (d, H-3/H-5); 2.37 ppm (s, H-8); 2.20 ppm (s, H-8)

¹³C NMR 125MHz CDCl₃ (δ ppm): 25.0 ppm (C-9); 29.1 ppm (C-8); 121.0 ppm (C_α); 145.0 ppm (C_β); 119.2-147.7 ppm (C_{aromatics}); 168.9 ppm (C=O, amide); 189.4 ppm (C=O, α-β).

d) N-[4-[(2E)-3-(4-Methoxyphenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide

(**ChOCH₃**): C₁₈H₁₇NO₃; Reaction Yield 41 %; Molecular Weight: 295,34 g.mol⁻¹. CAS Number: 939047-39-9; ε_{DMSO} (348 nm): 34857 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 296.12793.

FTIR (cm⁻¹): 3306 (ν -N-H); 1678 (ν -NHC=O); 1650 (ν C_(α,β) = O); 1593 (ν -HC_α=C_βH); 1262 (ν C_{Ph} - O).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 7.99 ppm (d, 8.6 Hz, H-2'/H-6'); 7.99 ppm (d, 8.6 Hz, H-2'/H-6'); 7.76 ppm (d, 15.6 Hz, H-β); 7.64 ppm (d, 8.6 Hz, H-3'/H-5'); 7.58 ppm (d, 8.6 Hz, H-2/H-6); 7.54 ppm (br. s, H-7); 7.39 ppm (d, 15.6 Hz, H-α); 6.92 ppm (d, H-3/H-5); 2.37 ppm (s, H-8); 3.84 ppm (s, H-9); 2.06 ppm (s, H-8).

¹³C NMR 125MHz CDCl₃ (δ ppm): 25.0 ppm (C-8); 55.6 ppm (C-9); 119.6 ppm (C_α); 144.7 ppm (C_β); 119.1-142.7 ppm (C_{aromatics}); 169.0 ppm (C=O, amide); 189.4 ppm (C=O, α-β).

e) N-[4-[(2E)-3-(4-Ethoxyphenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide (**ChOCH₂CH₃**): C₁₉H₁₉NO₃; Reaction Yield: 42 %; Molecular Weight: 309,37 g.mol⁻¹; CAS Number: 2378628-58-9; ε_{DMSO}(348nm): 34960 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 310.14355

FTIR (cm⁻¹): 3306 (ν -N-H); 1678 (ν -NHC=O); 1650 (ν C_(α,β) = O); 1593 (ν -HC_α=C_βH); 1259 (ν C_{Ph} - O).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 7.99 ppm (d, 8.3 Hz, H-2'/H-6'); 7.76 ppm (d, 15.5 Hz, H-β); 7.64 ppm (d, 8.3 Hz, H-3'/H-5'); 7.57 ppm (d, 8.3 Hz, H-2/H-6); 7.53 ppm (br. s, H-7); 7.39 ppm (d, 15.5 Hz, H-α); 6.92 ppm (d, 8.3 Hz, H-3/H-5); 4.06 ppm (q, 7.0 Hz, H-9); 3.84 ppm (s, H-9); 2.20 ppm (s, H-8); 1,42 ppm (t, H-10).

¹³C NMR 125MHz CDCl₃ (δ ppm): 25.4 ppm (C-8); 63.9 ppm (C-9); 119.4 ppm (C_α); 144.8 ppm (C_β); 115.1-144.8 ppm (C_{aromatics}); 169.0 ppm (C=O, amide); 189.4 ppm (C=O, α-β).

f) N-[4-[(2E)-3-[4-(Dimethylamino)phenyl]-1-oxo-2-propen-1-yl]phenyl]acetamide (**ChN(CH₃)₂**): C₁₉H₂₀N₂O₂; Reaction Yield: 30 %; Molecular Weight: 308,38 g.mol⁻¹; CAS Number: 1015084-98-6; ε_{DMSO} (313nm): 16331 mol⁻¹.L.cm⁻¹; ε_{DMSO}(422nm): 35169 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 309.15955

FTIR (cm⁻¹): 3296 (ν -N-H); 1685 (ν -NHC=O); 1646 (ν C_(α,β) = O); 1597 (ν -HC_α=C_βH).

¹H NMR 500MHz CDCl₃ (δ ppm, m, J): 7.98 ppm (d, 8.3 Hz, H-2'/H-6'); 7.76 ppm (br. d, 15.6 Hz, H-β/H-7); 7.63 ppm (d, 8.2 Hz, H-3'/H-5'); 7.52 ppm (d, 8.8 Hz, H-2/H-6); 7.32 ppm (d, 15.6 Hz, H-α); 6.68 ppm (d, 8.6 Hz, H-3/H-5); 3.02 ppm (q, 7.0 Hz, H-9/H-10); 2.20 ppm (s, H-8).

¹³C NMR 125MHz CDCl₃ (δ ppm): 25.0 ppm (C-8); 40.4 ppm (C-9;C-10); 119.4 ppm (C_α); 141.9 ppm (C_β); 112.1-152.9 ppm (C_{aromatics}); 168.3 ppm (C=O, amide); 189.5 ppm (C=O, α-β).

g) N-[4-[3-(4-Bromophenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide (**ChBr**): C₁₇H₁₄BrNO₂; Reaction Yield 74 %; Molecular Weight: 344,21 g.mol⁻¹; CAS Number:

690672-56-1; ϵ_{DMSO} (333 nm): 34136 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 344.0272

FTIR (cm⁻¹): 3306 (v -N-H); 1678 (br, v -NHC=O, C_(α , β) = O); 1612 (v -HC α =C β H); 980 (v C_{Ph}-Br).

¹H NMR 500MHz DMSO-*d*₆ (δ ppm, m, J): 10.32 ppm (s, H-7); 8.14 ppm (d, 8.7 Hz, H-2'/H-6'); 7.97 ppm (d, 15.8 Hz, H- β); 7.84 ppm (d, 8.5 Hz, H-3'/H-5'); 7.76 ppm (d, 8.6 Hz, H-3/H-5); 7.66 ppm (m, H-2/H-6/ H- α); 7.52 ppm (d, 8.8 Hz, H-2/H-6); 2.10 ppm (s, H-8).

¹³C NMR 125MHz CDCl₃ (δ ppm): 24.2 ppm (C-8); 118.3 ppm (C α); 143.8 ppm (C β); 122.1-152.9 ppm (C_{aromatics}); 143.8 ppm (C=O, amide); 187.4 ppm (C=O, α - β).

h) N-[4-[(2E)-3-(4-Nitrophenyl)-1-oxo-2-propen-1-yl]phenyl]acetamide

(ChNO₂): C₁₇H₁₄N₂O₄; Reaction Yield: 27 %; Molecular Weight: 310,31 g.mol⁻¹; CAS Number: 1015084-97-5; ϵ_{DMSO} (339 nm): 28055 mol⁻¹.L.cm⁻¹; HRESI-MS: [M+H]⁺ = m/z 311.10221

FTIR (cm⁻¹): 3304 (v -N-H); 1683 (v -NHC=O); 1657 (v C_(α , β) = O); 1600 (v -HC α =C β H); 1513, 1345 (v N-O).

¹H NMR 500MHz DMSO-*d*₆ (δ ppm, m, J): 10.36 ppm (s, H-7); 8.29 ppm (d, 8.8 Hz, H-3/H-5); 8.17 ppm (d, 8.7 Hz, H-2'/H-6'/H-3'/H-5'/H- β); 7.79 ppm (m, H-2/H-6/ H- α); 2.11 ppm (s, H-8).

¹³C NMR 125MHz DMSO-*d*₆ (δ ppm): 24.2 ppm (C-8); 118.3 ppm (C α); 144.1 ppm (C β); 123-148.1 ppm (C_{aromatics}); 169.2 ppm (C=O, amide); 187.3 ppm (C=O, α - β).