Electronic Supplementary Information for

Pd(II)/LA-catalyzed acetanilide olefination with dioxygen

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1. Experimental section.

1.1 Materials and analytical methods

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Compounds **1a**-**1s** were synthesized following the literature.[1] The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or $KMnO_4$ as visualizing agents as needed. Flash column chromatography was performed using 200-300 mesh silica gel under increased pressure. The UV–vis spectra were respectively recorded on a Agilent Technologies Cary–8454 UV–vis spectrometer. ^1H and ^{13}C NMR{^1H} spectra were respectively recorded on a Brüker AV-600 spectrometer. Chemical shifts (δ) were expressed in ppm (parts per million) with TMS as the internal standard, and coupling constants (*J*) were reported in hertz (Hz). High resolution mass spectra were obtained on a mass spectrometer by using ESI FT-ICR mass.

1.2 General procedures for the synthesis of acetanilides.[1]

In a typical procedure, the acetanilide (2 mmol, 1.0 equiv.) was dissolved in 20 mL of dichloromethane, and cooled down to 0 °C with an ice bath. Then, Et_3N (3.0 mmol, 1.5 equiv.) was added to the solution followed by adding acetyl chloride or tervaloyl chloride (2.4 mmol, 1.2 equiv.) drop-wise over 30 min. Next, the mixture was stirred at room temperature for 12 h, and washed with 3 × 5 mL of saturated $NaHCO_3$ (aq) and 10 mL saturated NaCl (aq), respectively. The organic layer was dried over $MgSO_4$. After that, the solvent was removed under the reduced pressure. The raw product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate: 4:1 to 1:1) to afford the desired acetanilides as white solids with > 80 % yield.

1.3 General procedure for olefination of acetanilide 1 and acrylate 2 with the $Pd(OAc)_2/Sc(OTf)_3$ catalyst in MeCN.

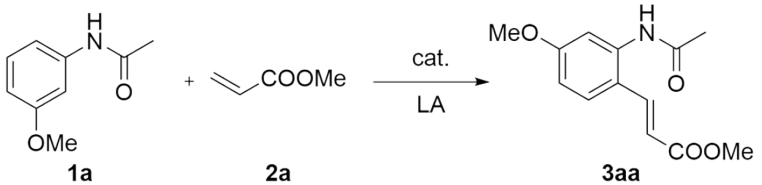
In a typical procedure, $Pd(OAc)_2$ (0.01 mmol, 2.2 mg) and $Sc(OTf)_3$ (0.01 mmol, 4.92 mg) were dissolved in MeCN (1 mL) in a glass tube. After pre-stirring the prepared catalyst solution for 20 min under 60 °C, acetanilide **1** (0.1 mmol, 1.0 equiv.) and acrylate **2** (0.2 mmol, 2.0 equiv.) were added in. The reaction mixture was stirred at 60 °C for 12 h using IKA heating mantle for the desired reaction time with an O_2 balloon as the atmosphere. Then, the mixture was evaporated under reduced pressure, and the residue was purified by column chromatography (petroleum ether/ethyl acetate: 5:1 to 1:1) to give the corresponding olefination product **3**.

1.4 General procedure for UV-vis experiments in MeCN.

In a typical UV–vis kinetic experiment, 3,4-dimethoxyacetanilide (0.1 mmol, 19.6 mg) was dissolved in 10 mL of MeCN in a glass tube. Pd(II) salt (0.1 mmol, 1.0 equiv.) and LA (0.1 mmol, 1 equiv.) were dissolved in MeCN (10 mL) in another glass tube, which was stirred at 60 ^oC in an oil bath for 10 min, then cooled down to room tempreture. Next, the solutions of 3,4-dimithoxyacetanilide and Pd(II)/Sc(III) were mixed together at 60 ^oC for 120 min to generate the palladacycle compound. Then, methyl acrylate (0.1 mmol, 8.6 mg) was dissolved in 10 mL of MeCN in a new glass tube. Next, these mixtures were diluted by 200–folds prior to their use for UV–vis kinetic studies. Upon mixing two prepared solutions together, the formation rate of the olefination product at 60 ^oC was measured by the increase of the absorbance at 329 nm, The rate constants were determined by a least–square curve fit,[2] and all experiments were performed at least three runs.

2. Optimization studies and control experiments of the reaction conditions for the model reaction of 1a and 2a.

Table S1. Control experiments for the model reaction[a]

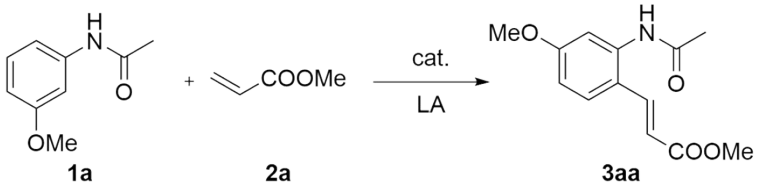


1a **2a** **3aa**

Entry	Cat.	Yield (%)[b]
1[c]	$Pd(OAc)_2$ (10 mol%) + $Cu(OTf)_2$ (10 mol%)	54
2	$Pd(OAc)_2$ (10 mol%) + $Cu(OTf)_2$ (20 mol%)	61
3	$Pd(OAc)_2$ (10 mol%) + $Sc(OTf)_3$ (10 mol%)	73
4	$Pd(OAc)_2$ (10 mol%) + HOTf (5 mol%)	47
5	$Pd(OAc)_2$ (10 mol%) + HOTf (10 mol%)	52
6	$Pd(OAc)_2$ (10 mol%) + HOTf (20 mol%)	31
7	$Pd(OAc)_2$ (10 mol%) + HOTf (40 mol%)	17
8	$Pd(OAc)_2$ (10 mol%) + HOTf (100 mol%)	Trace
9[d]	$Pd(OAc)_2$ (5 mol%) + $Sc(OTf)_3$ (5 mol%)	51

[a]Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), acid, MeCN (1 mL), O_2 balloon, 60 °C, 12 h. [b]Isolated yield. [c]24 h, [d]MeCN (0.5 mL), sealed tube.

Table S2. Different Pd(II) sources for the model reaction[a]



1a **2a** **3aa**

Entry	Cat.	Yield (%)[b]
1	$Pd(TFA)_2$	11
2	$Pd(TFA)_2$/$Sc(OTf)_3$	47
3	$Pd(MeCN)_2Cl_2$	ND
4	$Pd(MeCN)_2Cl_2$/$Sc(OTf)_3$	ND

[a]Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Cat. (0.01 mol), $Sc(OTf)_3$ (0.01 mol), MeCN (1 mL), O_2 balloon, 60 °C, 12 h. [b]Isolated yield, ND = not detected.

Table S3. Ratio of 1a and 2a for the model reaction[a]

Entry	Ratio of **1a/2a**	Yield (%)[b]
1	2:1	19
2	1:1	37
3	1:2	73
4	1:3	71
5	1:4	31
6	1:5	27

[a]Conditions: **1a** (0.1 mmol), **2a**, $Pd(OAc)_2$ (0.01 mol), $Sc(OTf)_3$ (0.01 mol), MeCN (1 mL), O_2 balloon, 60 °C, 12 h. [b]Isolated yield.

Table S4. Ratio and amount of catalyst loading for the model reaction[a]

Entry	Ratio of Cat./LA	Yield (%)[b]
1	2.5%/2.5%	Trace
2	2.5%/5%	Trace
3	5%/5%	38
4	5%/10%	41
5	10%/10%	73
6	10%/20%	71

[a]Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$, $Sc(OTf)_3$, MeCN (1 mL), O_2 balloon, 60 °C, 12 h. [b]Isolated yield.

3. UV–vis and $^{-1}$H NMR studies on $Pd(OAc)_2/Sc(OTf)_3$ species.

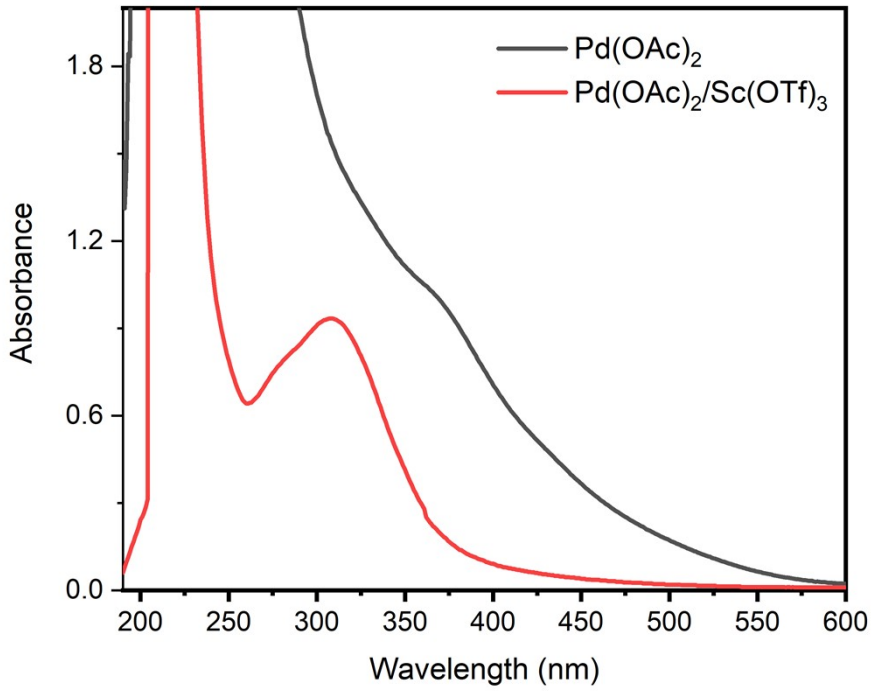


Fig. S1 UV−vis spectra of $Pd(OAc)_2$ in the presence (red) and absence (black) of $Sc(OTf)_3$ in MeCN at room temperature. $[Pd(OAc)_2]$ = 0.1 mM, $[Sc(OTf)_3]$ = 0.1 mM.

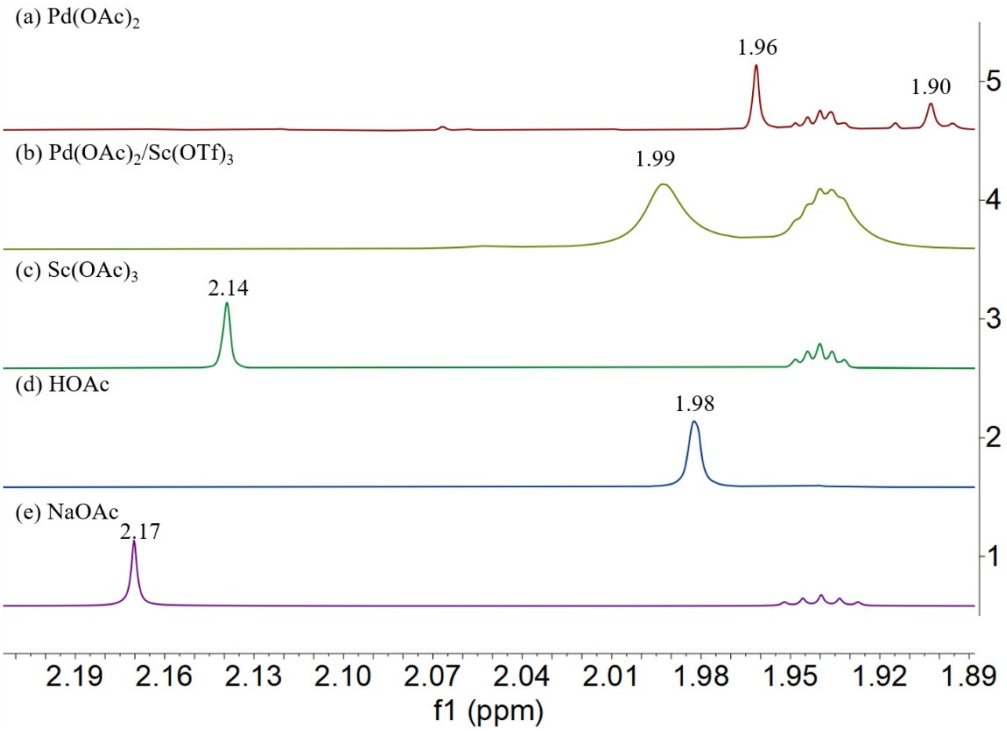


Fig. S2 ^{1}H NMR spectra for the comparison of (a) $Pd(OAc)_2$, (b) $Pd(OAc)_2/Sc(OTf)_3$, (c) $Sc(OAc)_3$, (d) HOAc, and (e) NaOAc in MeCN-d_3 (600 MHz).

4. UV–vis kinetic studies on palladacycle compound and 2a with different LA and internal bases

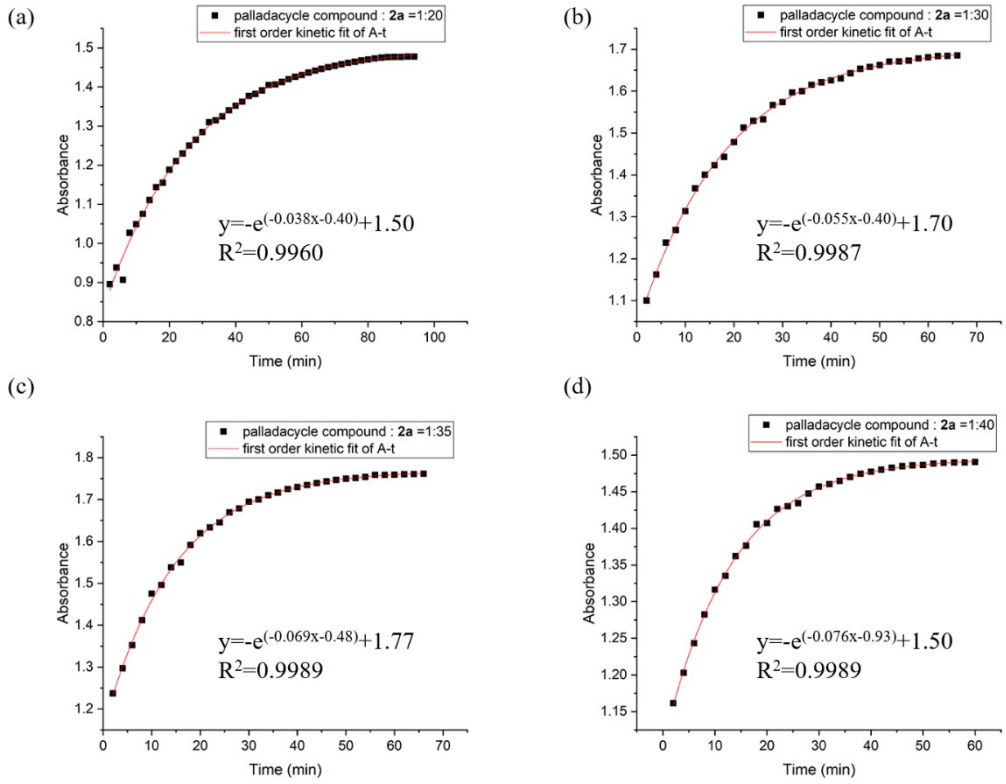


Fig. S3. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4a**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Sc(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4a** and 20 equiv. of **2a**, (b) **4a** and 30 equiv. of **2a**, (c) **4a** and 35 equiv. of **2a**, (d) **4a** and 40 equiv. of **2a**.

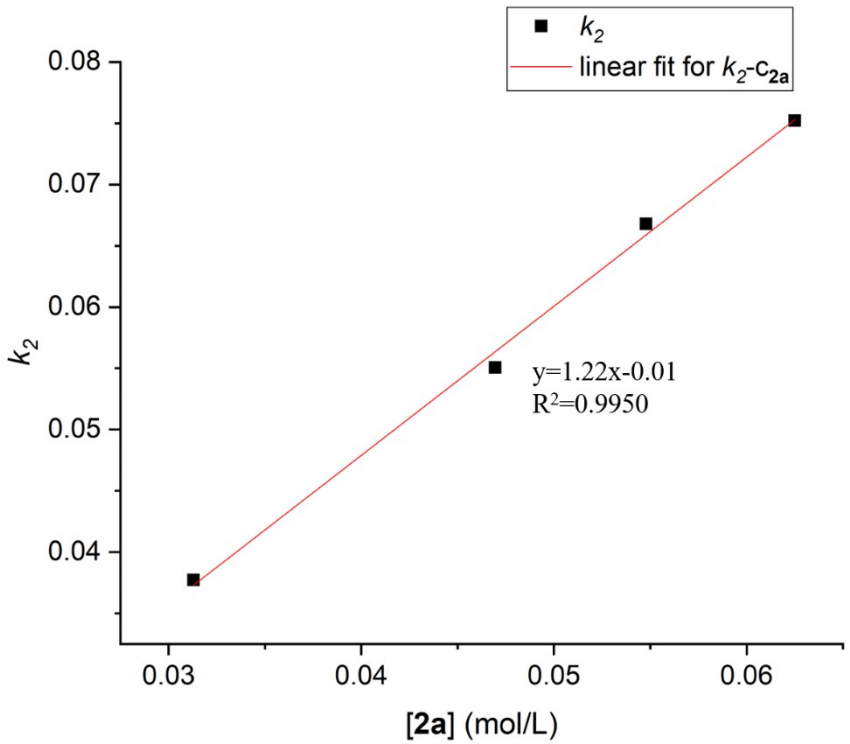


Fig. S4. First–order dependence on [**2a**] with **4a** in MeCN.

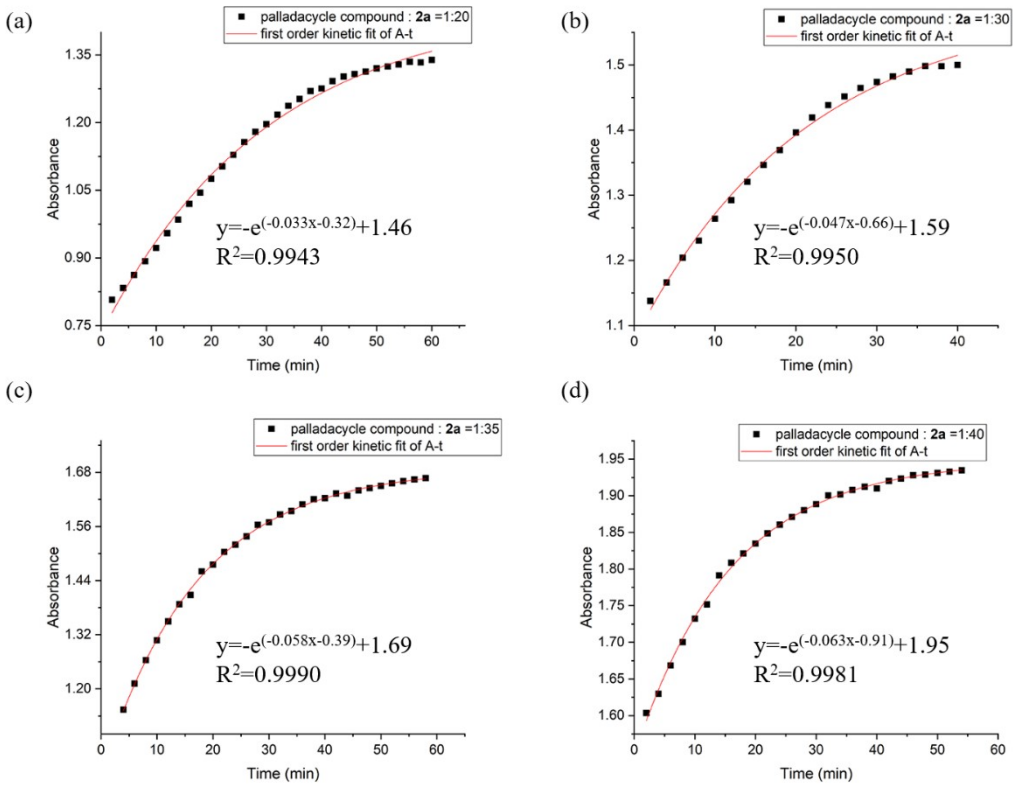


Fig. S5. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4b**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Al(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4b** and 20 equiv. of **2a**, (b) **4b** and 30 equiv. of **2a**, (c) **4b** and 35 equiv. of **2a**, (d) **4b** and 40 equiv. of **2a**.

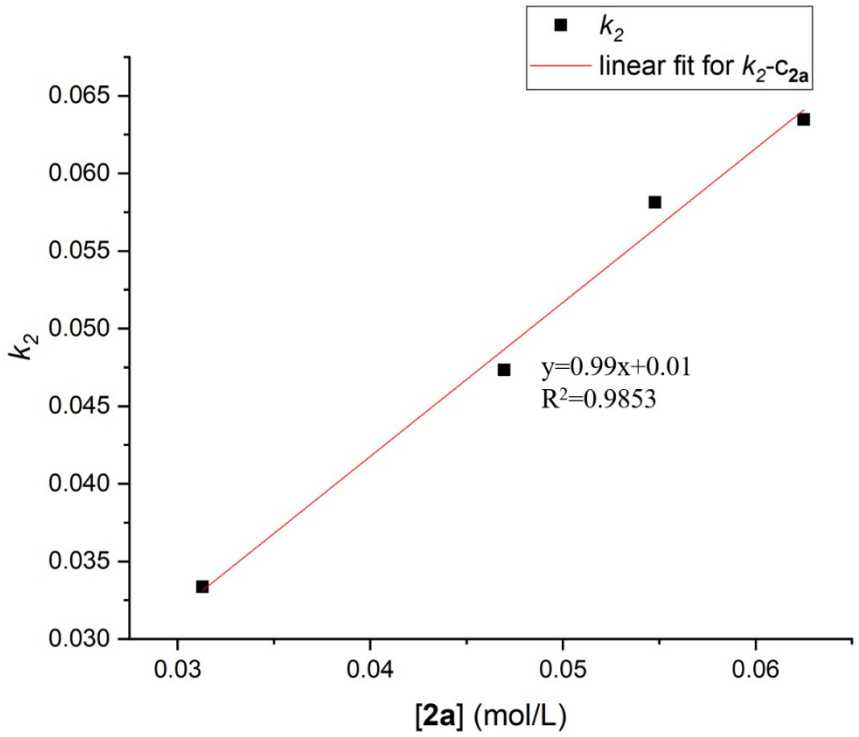


Fig. S6. First–order dependence on [**2a**] with **4b** in MeCN.

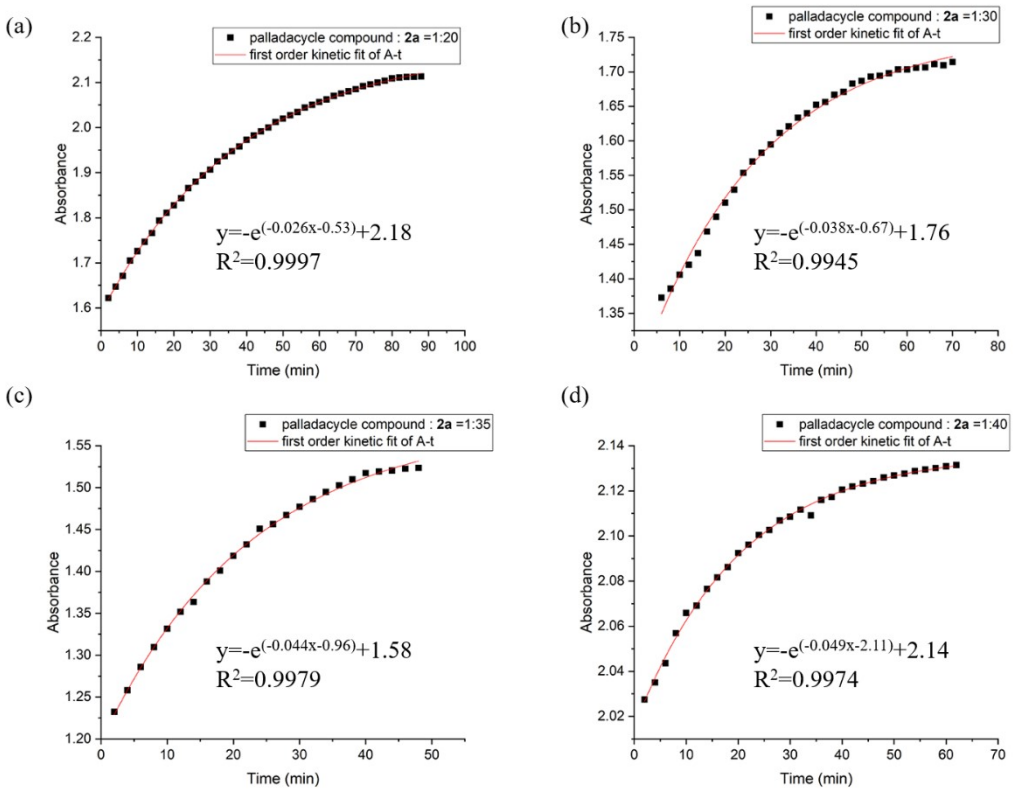


Fig. S7. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4c**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Y(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4c** and 20 equiv. of **2a**, (b) **4c** and 30 equiv. of **2a**, (c) **4c** and 35 equiv. of **2a**, (d) **4c** and 40 equiv. of **2a**.

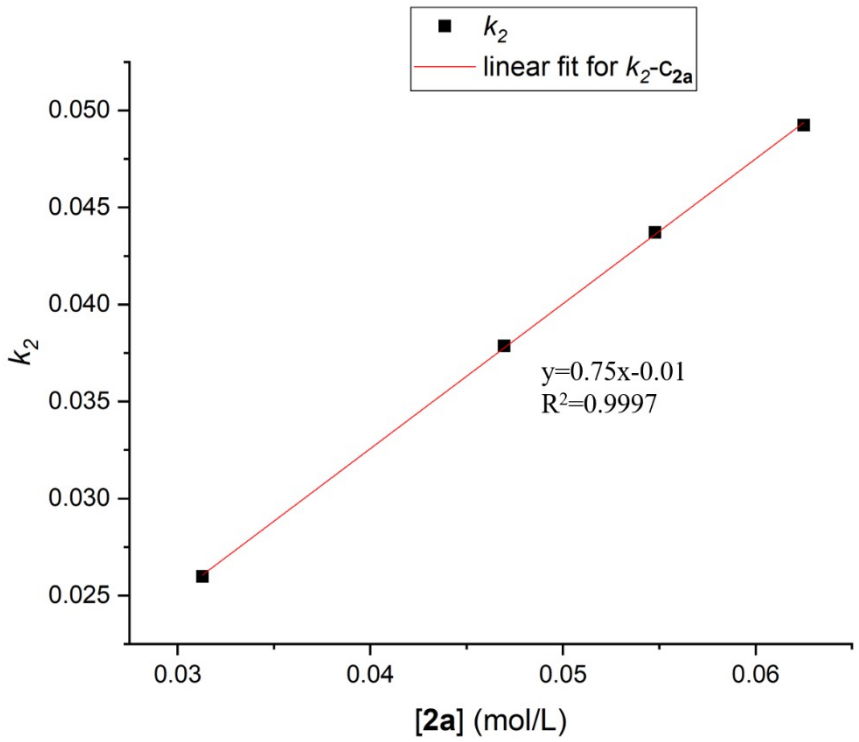


Fig. S8. First–order dependence on [**2a**] with **4c** in MeCN.

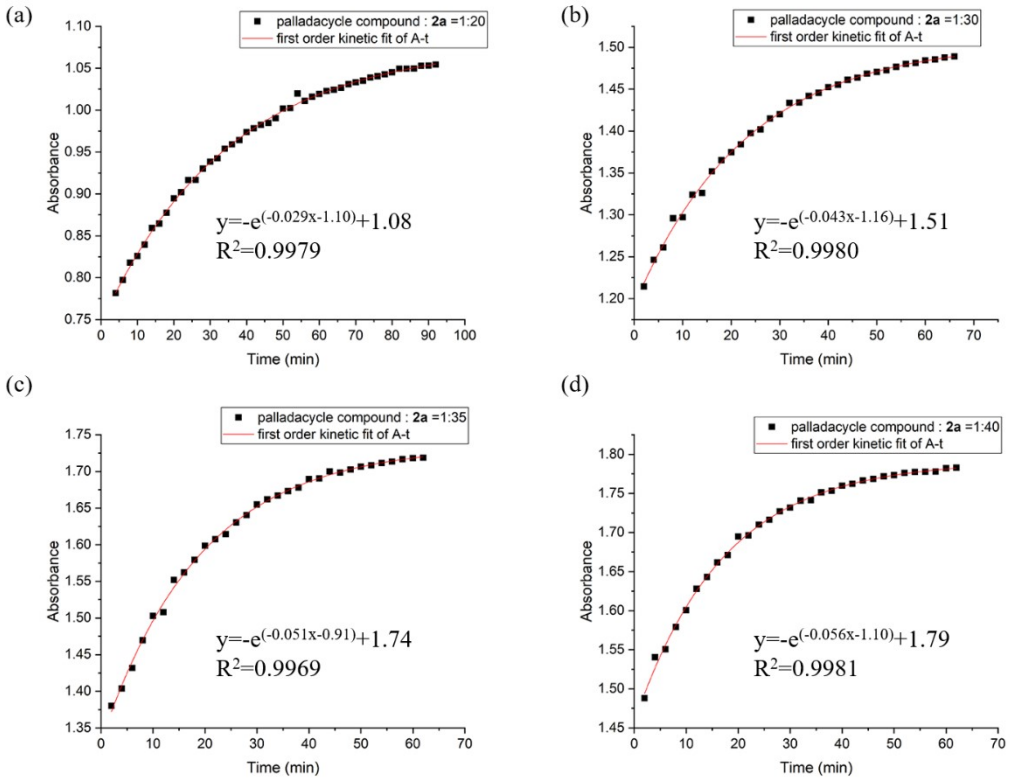


Fig. S9. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4d**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Yb(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4d** and 20 equiv. of **2a**, (b) **4d** and 30 equiv. of **2a**, (c) **4d** and 35 equiv. of **2a**, (d) **4d** and 40 equiv. of **2a**.

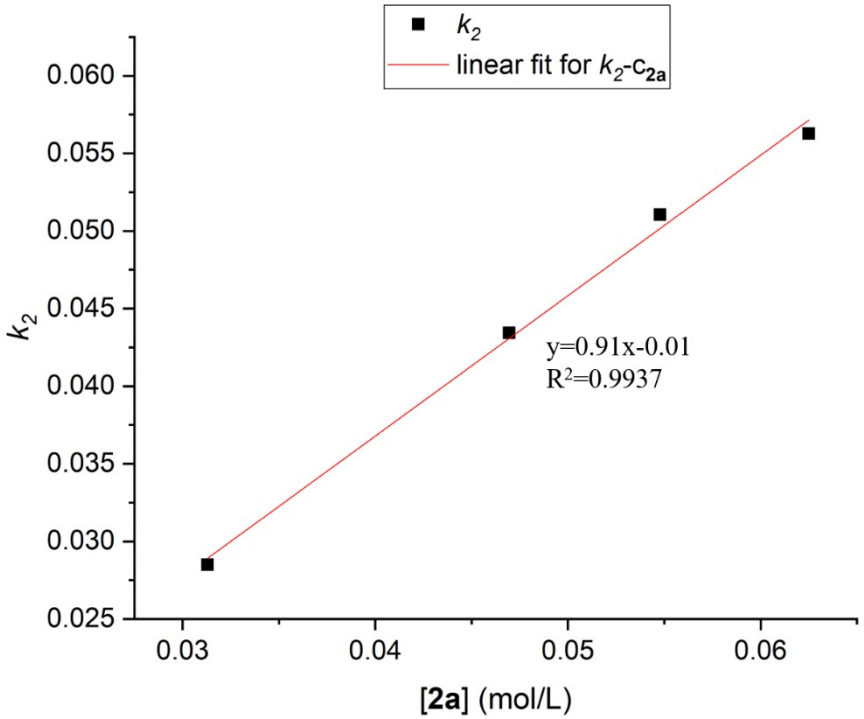


Fig. S10. First–order dependence on [**2a**] with **4d** in MeCN.

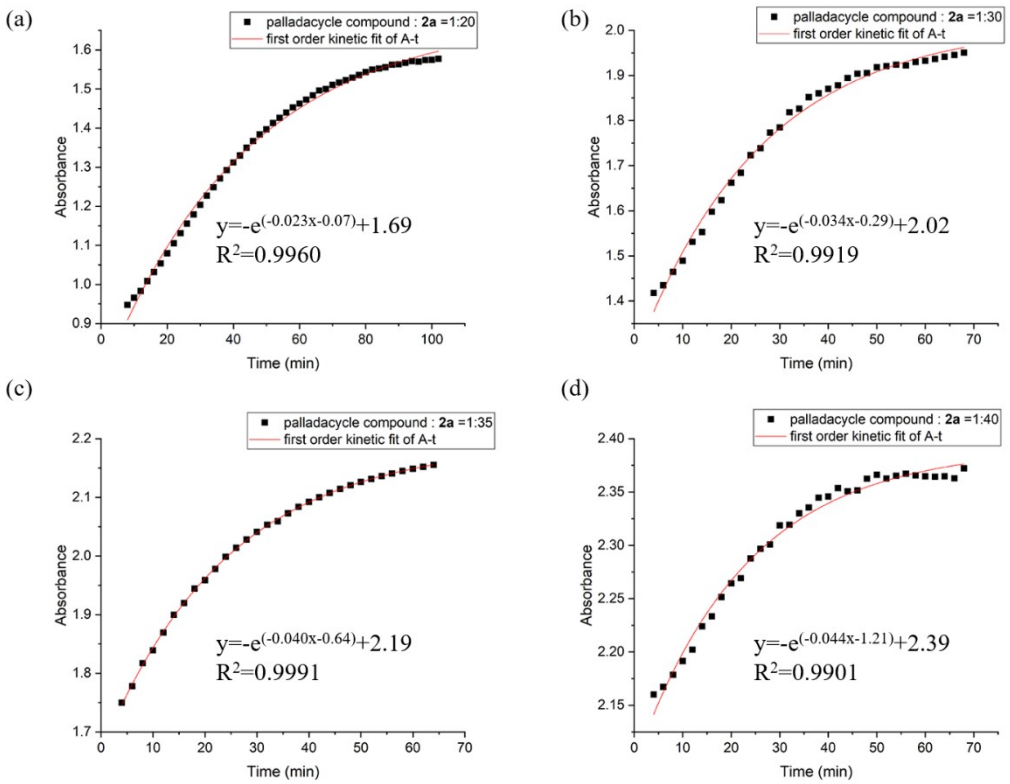


Fig. S11. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4e**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Lu(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4e** and 20 equiv. of **2a**, (b) **4e** and 30 equiv. of **2a**, (c) **4e** and 35 equiv. of **2a**, (d) **4e** and 40 equiv. of **2a**.

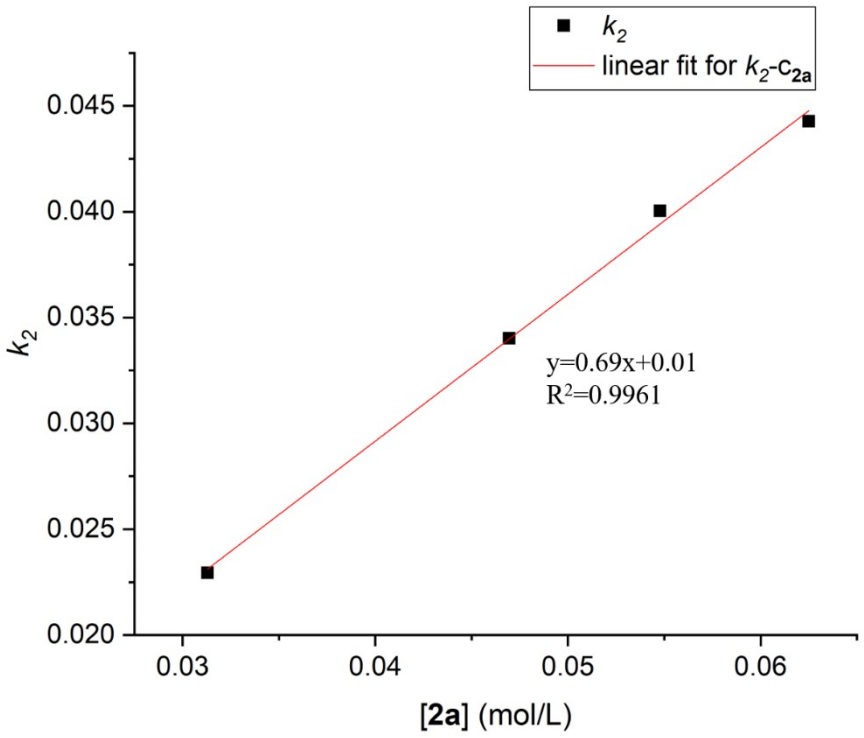


Fig. S12. First–order dependence on [**2a**] with **4e** in MeCN.

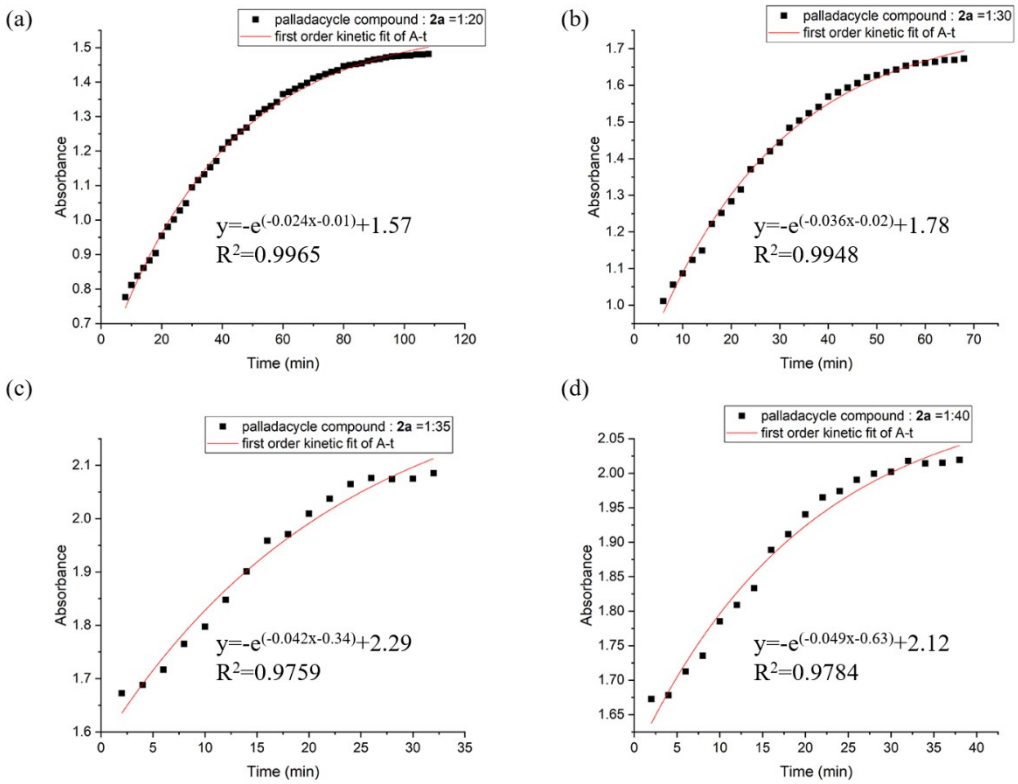


Fig. S13. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4f**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(OAc)_2/Ca(OTf)_2$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4f** and 20 equiv. of **2a**, (b) **4f** and 30 equiv. of **2a**, (c) **4f** and 35 equiv. of **2a**, (d) **4f** and 40 equiv. of **2a**.

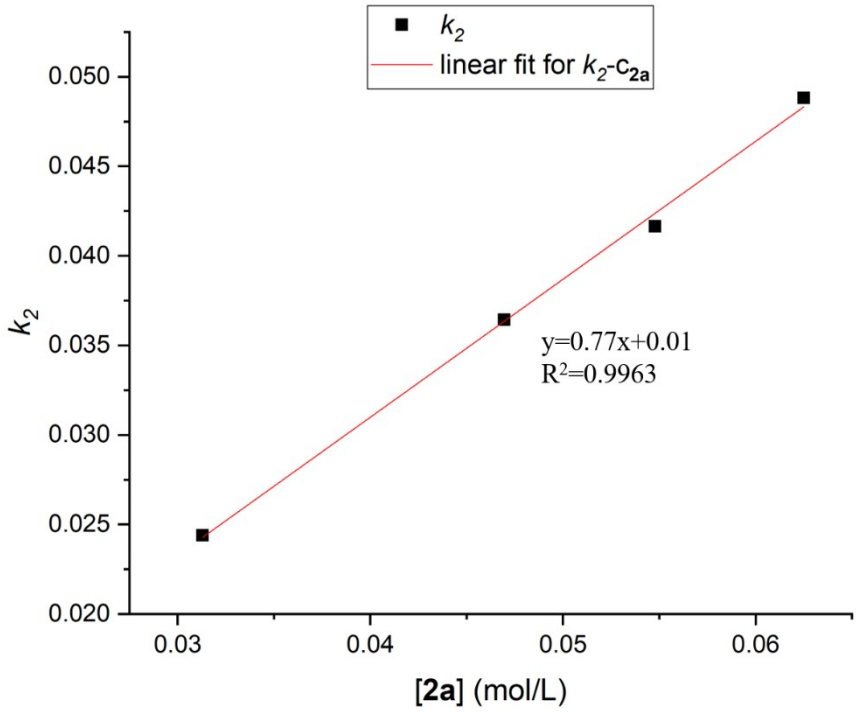


Fig. S14. First–order dependence on [**2a**] with **4f** in MeCN.

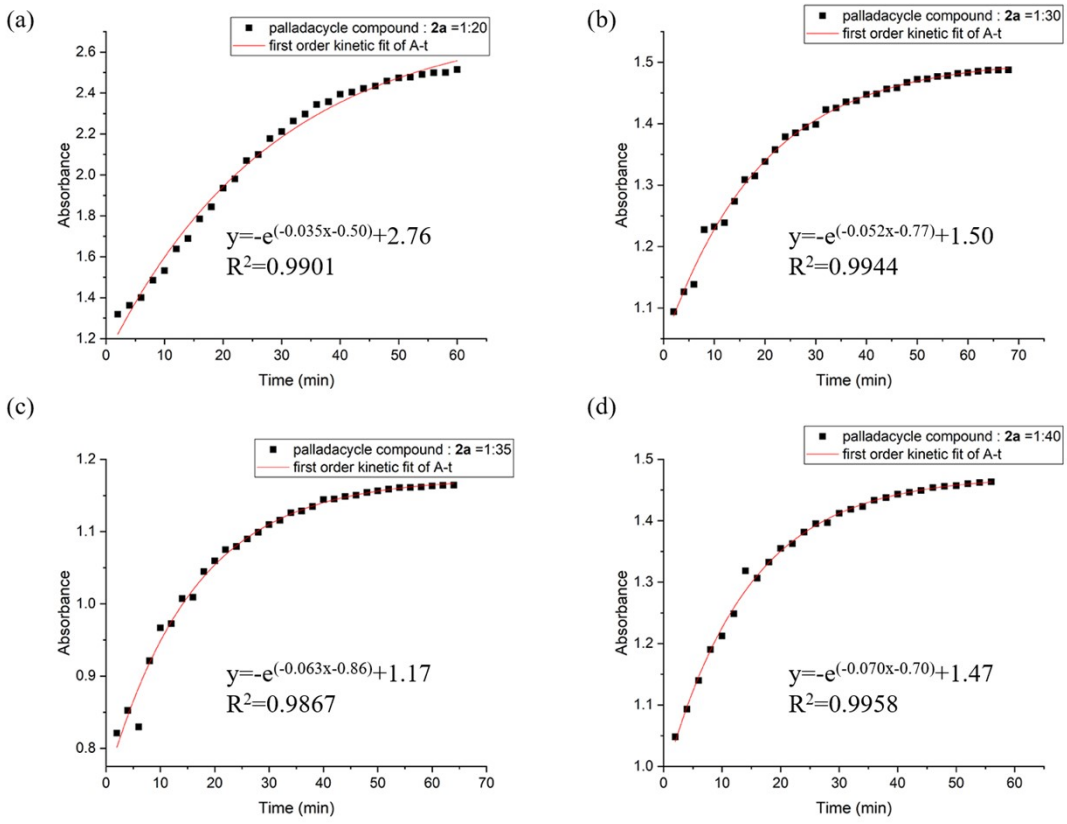


Fig. S15. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4g**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(CClH_2COO)_2/Sc(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4g** and 20 equiv. of **2a**, (b) **4g** and 30 equiv. of **2a**, (c) **4g** and 35 equiv. of **2a**, (d) **4g** and 40 equiv. of **2a**.

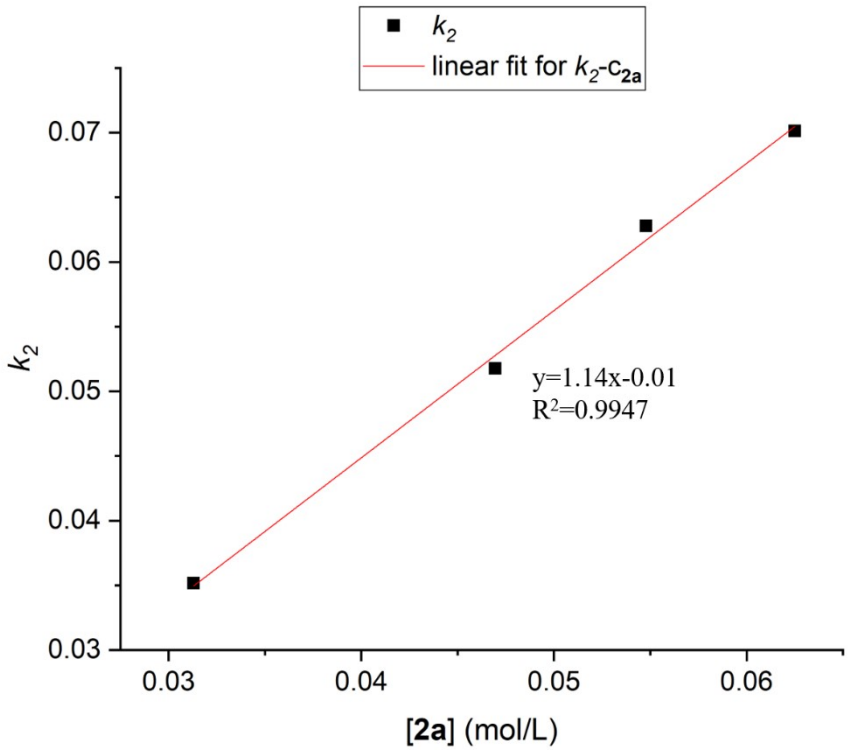


Fig. S16. First–order dependence on [**2a**] with **4g** in MeCN.

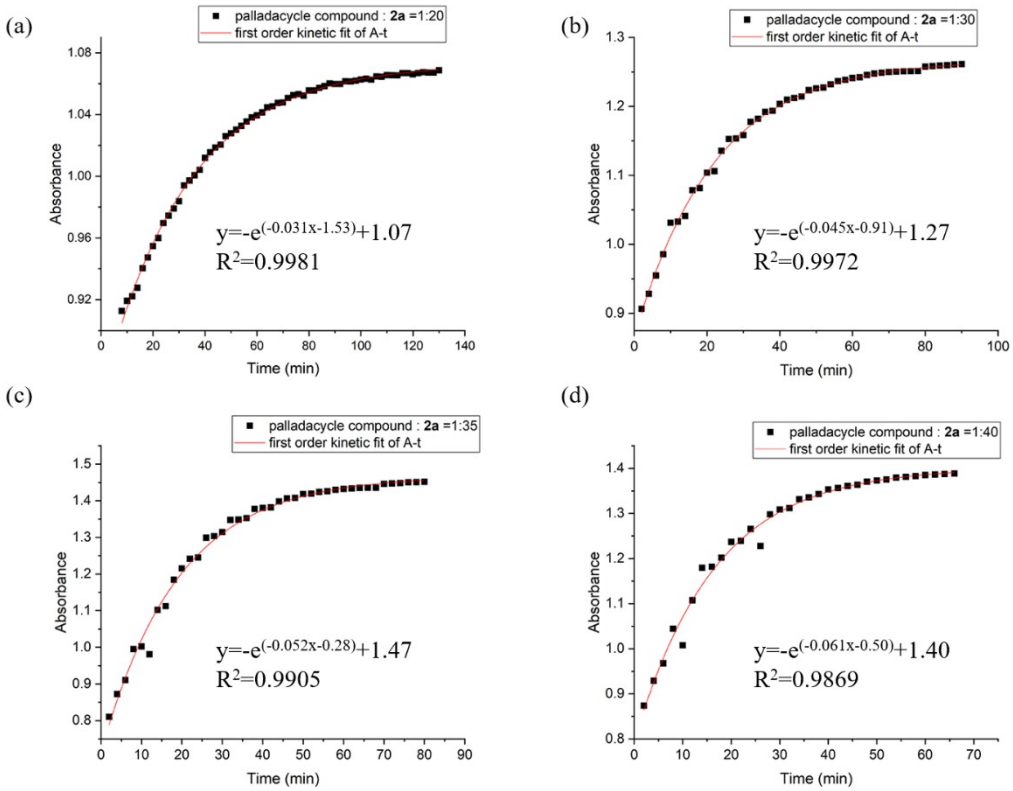


Fig. S17. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4h**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(CCl_2HCOO)_2/Sc(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4h** and 20 equiv. of **2a**, (b) **4h** and 30 equiv. of **2a**, (c) **4h** and 35 equiv. of **2a**, (d) **4h** and 40 equiv. of **2a**.

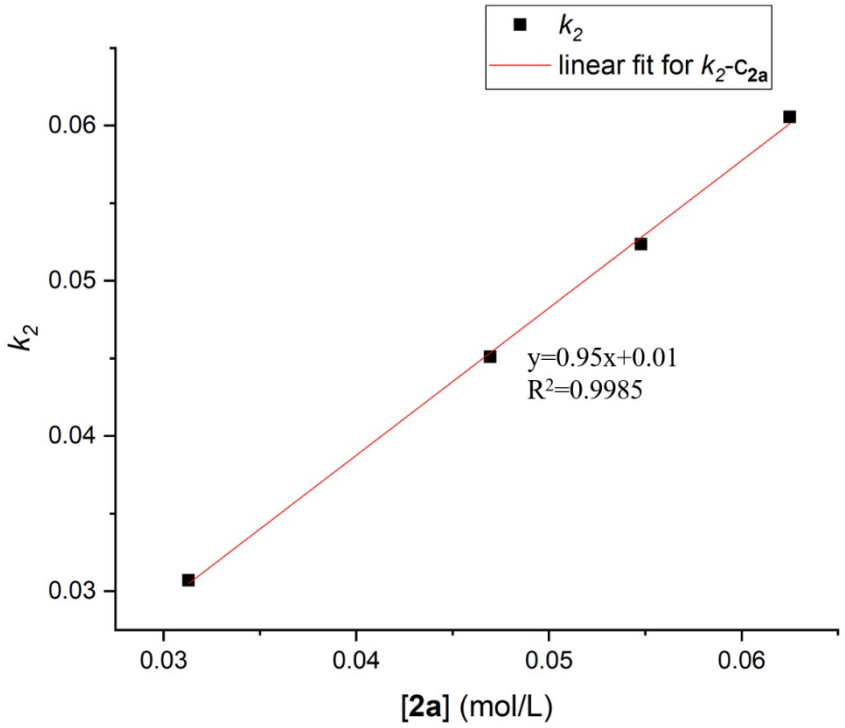


Fig. S18. First–order dependence on [**2a**] with **4h** in MeCN.

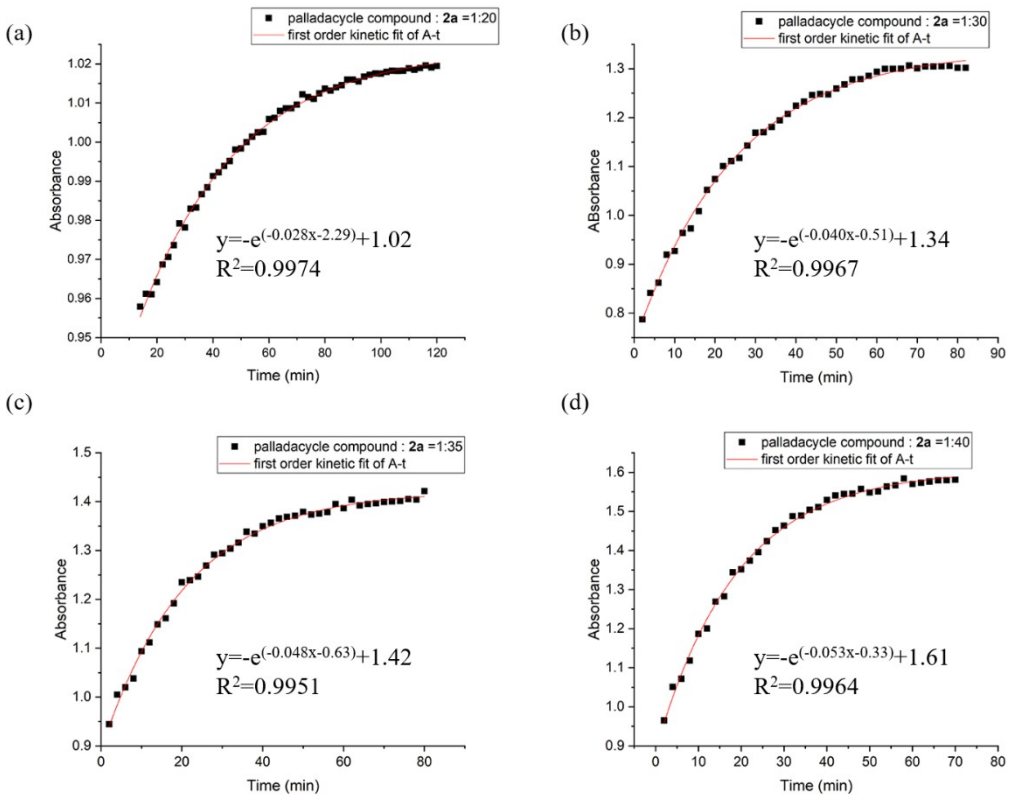


Fig. S19. UV–vis kinetics for the formation of the **3ja** from palladacycle compound (**4i**) from 3,4–dimethoxyacetanilide (**1j**) and $Pd(TFA)_2/Sc(OTf)_3$ with different amount of methyl acrylate (**2a**) in MeCN at 60 °C at 329 nm. First order kinetic fit for (a) **4i** and 20 equiv. of **2a**, (b) **4i** and 30 equiv. of **2a**, (c) **4i** and 35 equiv. of **2a**, (d) **4i** and 40 equiv. of **2a**.

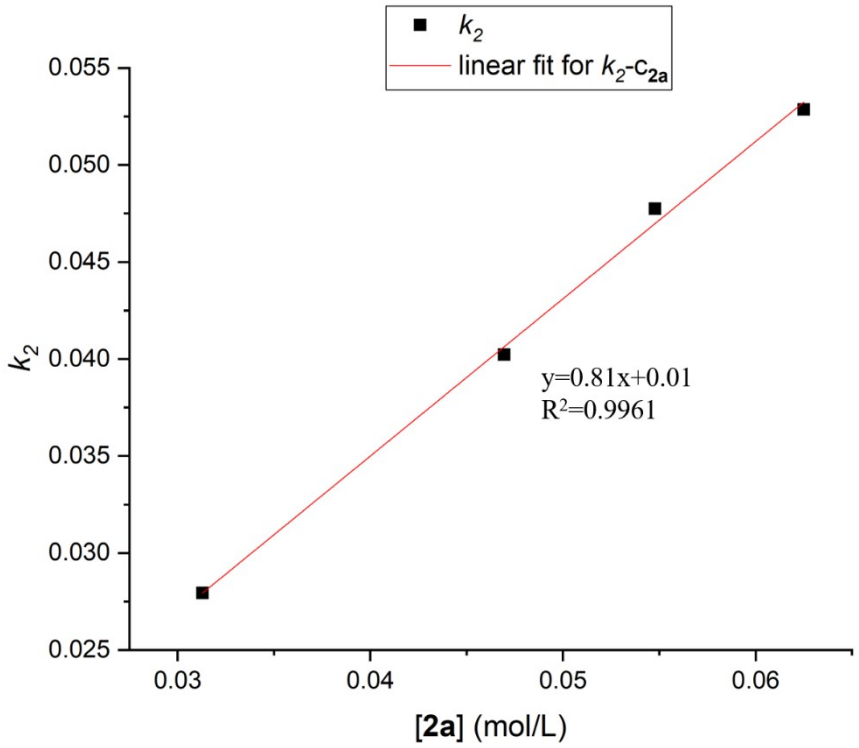


Fig. S20. First–order dependence on [**2a**] with **4i** in MeCN.

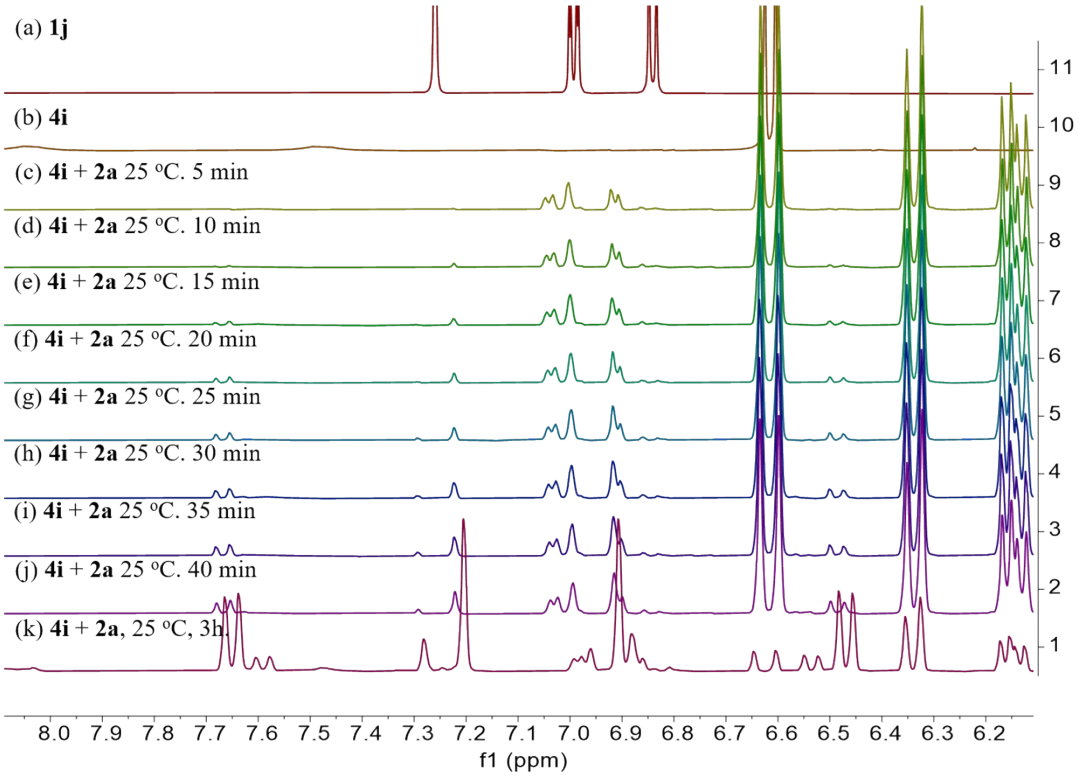


Fig. S21 ^{1}H NMR kinetics of Olefination of palladacycle compound **4i** (0.05 mM) from 3,4-dimethoxyacetanilide (**1j**) by $Pd(TFA)_2/Sc(OTf)_3$ (0.05 mM/0.05 mM) in MeCN-d_3 (0.5 ml) at 25 °C (600 MHz).

5. Experimental characterization data for products

methyl (E)-3-(2-acetamido-4-methoxyphenyl)acrylate(3aa): gray solid (73% yield, 18.2 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 15.7 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.49 – 7.34 (m, 1H), 7.28 (s, 0H), 6.82 – 6.74 (m, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.26 (s, 3H).^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 170.1, 169.3, 167.5, 161.5, 152.3, 140.5, 139.2, 127.9, 115.5, 113.8, 111.6, 55.9, 51.8, 23.8. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{13}H_{16}NO_4^+$, 250.1074; found, 250.1073.

methyl (E)-3-(2-acetamidophenyl)acrylate (3ba): gray solid (17% yield, 3.8 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.84 (s, 1H), 7.87 – 7.74 (m, 2H), 7.40 (d, *J* = 4.2 Hz, 2H), 7.23 (q, *J* = 6.9, 5.1 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 3.73 (s, 1H), 2.08 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.26, 167.20, 140.81, 137.54, 131.04, 128.94, 127.30, 118.87, 51.98, 23.64.

methyl (E)-3-(2-acetamido-5-methoxyphenyl)acrylate (***3ca***): brown solid (47% yield, 11.7 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.70 (d, *J* = 15.9 Hz, 1H), 7.33 (d, *J* = 2.9 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 4H), 2.05 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.35, 167.24, 157.54, 140.69, 130.74, 130.53, 128.97, 119.27, 117.72, 110.87, 55.94, 52.00, 23.45.

methyl (E)-3-(2-acetamido-5-cyanophenyl)acrylate (3da): brown solid (17% yield, 4.2 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.52 (d, *J* = 2.7 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 4H), 2.05 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 170.43, 165.75, 158.62, 141.76, 129.25, 127.47, 117.78, 116.22, 109.38, 105.16, 57.01, 50.51, 24.53.

methyl (E)-3-(2-acetamido-4-(tert-butyl)phenyl)acrylate (3ea): brown solid (73% yield, 20.1 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.81 – 7.67 (m, 2H), 7.39 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 2H), 2.08 (s, 3H), 1.27 (s, 9H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.27, 167.32, 154.09, 140.86, 128.74, 127.04, 123.78, 120.40, 117.90, 116.44, 51.92, 35.03, 31.26, 23.67. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{16}H_{21}NO_3^+$, 276.1594; found, 276.1594.

methyl (E)-3-(2-acetamido-4-methylphenyl)acrylate (3fa): brown solid (37% yield, 8.6 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.80 (s, 1H), 7.77 – 7.56 (m, 2H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.05 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 3.72 (s, 3H), 2.30 (s, 3H), 2.07 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.23, 167.33, 141.13, 140.75, 137.50, 127.48, 127.14, 127.10, 126.17, 117.73, 51.92, 23.66, 21.39. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{13}H_{15}NO_3^+$, 234.1125; found, 234.1124

methyl (E)-3-(2-acetamido-3-methylphenyl)acrylate (3ga): brown solid (47% yield, 11.0 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H), 7.61 (d, *J* = 2.9 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 6.62 (s, 1H), 3.73 (d, *J* = 2.7 Hz, 3H), 2.20 (s, 3H), 2.09 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 167.86, 165.62, 138.91, 138.35, 137.04, 132.32, 127.02, 125.20, 117.83, 98.60, 50.04, 22.56, 16.95.

methyl (E)-3-(2-acetamido-3-iodophenyl)acrylate (3ha): black solid (47% yield, 16.2 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 7.61 (d, *J* = 2.9 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 6.60 (s, 0H), 3.73 (d, *J* = 2.7 Hz, 3H), 2.09 (s, 2H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.11, 166.87, 141.69, 141.07, 139.76, 135.04, 129.74, 127.92, 120.55, 101.32, 52.75, 23.81.

methyl (E)-3-(2-acetamido-4-methoxy-5-methylphenyl)acrylate (3ia): brown solid (69% yield, 18.2 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.80 (s, 1H), 7.73 (d, *J* = 15.9 Hz, 1H), 7.65 (s, 1H), 7.00 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.24, 167.53, 159.62, 140.59, 137.31, 128.62, 124.18, 120.71, 115.75, 108.65, 55.95, 51.79, 23.71, 16.03.

methyl (E)-3-(2-acetamido-4,5-dimethoxyphenyl)acrylate (3ja): brown solid (74% yield, 20.6 mg) ^{1}H NMR (600 MHz, MeCN-d_3) δ 8.15 (s, 1H), 7.72 (d, *J* = 15.9 Hz, 1H), 7.16 (s, 1H), 6.98 (s, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 2.09 (s, 3H). ^{13}C NMR{^{1}H} (151 MHz, MeCN-d_3) δ 170.3, 168.2, 152.2, 148.4, 140.7, 132.0, 122.4, 117.2, 110.9, 109.3, 56.5 (d, *J* = 20.5 Hz), 52.0, 23.5.

methyl (E)-3-(2-acetamido-5-(tert-butyl)-4-methoxyphenyl)acrylate (3ka): brown solid (71% yield, 21.7 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.51 (s, 1H), 7.06 (s, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.08 (s, 3H), 1.34 (s, 10H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.29, 167.48, 160.44, 140.99, 137.48, 135.64, 124.76, 120.29, 115.78, 110.10, 55.90, 51.79, 34.88, 29.94, 23.73.

methyl (E)-3-(2-acetamido-5-chloro-4-methoxyphenyl)acrylate (3la): brown solid (21% yield, 6.1 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.93 (s, 1H), 7.94 (s, 1H), 7.68 (d, *J* = 15.9 Hz, 1H), 7.26 (s, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 2.10 (s, 4H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.40, 167.30, 156.22, 139.17, 138.00, 128.13, 121.98, 119.00, 117.74, 110.50, 56.80, 51.92, 23.78.

methyl (E)-3-(7-acetamido-2,3-dihydrobenzo[b][1,4]dioxin-6-yl)acrylate (3ma): brown solid (74% yield, 20.5 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.65 (d, *J* = 15.9 Hz, 1H), 7.34 (s, 1H), 6.87 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 4.26 (dt, *J* = 16.8, 4.3 Hz, 5H), 3.70 (s, 3H), 2.04 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.28, 167.41, 145.80, 141.95, 140.22, 131.69, 122.58, 116.86, 115.62, 114.70, 64.91, 64.40, 51.83, 23.54.

methyl (E)-3-(2-acetamido-4,5-dimethylphenyl)acrylate (3na): brown solid (41% yield, 11.6 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.71 (s, 1H), 7.79 – 7.68 (m, 1H), 7.62 (s, 1H), 7.16 (s, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 1H), 2.22 (d, *J* = 4.9 Hz, 5H), 2.06 (s, 2H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.22, 167.37, 140.85, 140.03, 135.36, 134.60, 128.20, 127.75, 126.52, 117.46, 51.91, 23.58, 19.86, 19.28. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{14}H_{18}NO_3^+$, 248.1281; found, 248.1281.

methyl (E)-3-(2-acetamido-5-methoxy-4-methylphenyl)acrylate (3oa): brown solid (47% yield, 12.4 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.70 (d, *J* = 15.9 Hz, 1H), 7.28 (s, 1H), 7.11 (s, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.32, 167.41, 155.80, 140.80, 130.50, 129.72 (d, *J* = 3.2 Hz), 127.98, 118.07, 107.62, 56.11, 51.92, 23.45, 16.52.

methyl (E)-3-(2-acetamido-4,6-dimethoxyphenyl)acrylate (3pa): brown solid (82% yield, 22.9 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.61 (d, *J* = 16.0 Hz, 1H), 6.62 (s, 0H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 2.04 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.16, 168.38, 161.83, 161.21, 140.48, 137.46, 118.23, 111.34, 104.87, 96.75, 56.39, 55.96, 51.69, 23.65.

methyl (E)-3-(6-acetamido-2,3,4-trimethoxyphenyl)acrylate (3qa): brown solid (79% yield, 24.4 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.57 (d, *J* = 16.2 Hz, 1H), 6.84 (s, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 6H), 3.72 (s, 3H), 2.02 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz,

DMSO–d_6) ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) δ 169.26, 167.02, 140.89, 139.69, 135.01, 134.25, 128.23, 127.40, 126.18, 117.49, 61.16, 60.89, 60.39, 51.94, 23.23.

methyl (E)-3-(5-acetamidobenzo[b]thiophen-6-yl)acrylate (3ra): purple solid (47% yield, 11.83 mg) ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 9.90 (s, 1H), 8.56 (s, 1H), 7.86 (td, *J* = 17.9, 16.2, 11.7 Hz, 5H), 7.52 – 7.35 (m, 2H), 6.86 – 6.65 (m, 1H), 3.75 (d, *J* = 2.7 Hz, 3H), 2.12 (s, 2H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) 180.89, 180.08, 157.98, 152.98, 143.99, 136.53, 128.14, 123.81, 122.15, 119.02, 112.56, 111.29, 50.83, 35.64, 29.18, 15.39, 21.06. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{14}H_{14}NO_3S^+$, 276.0689; found, 276.0689.

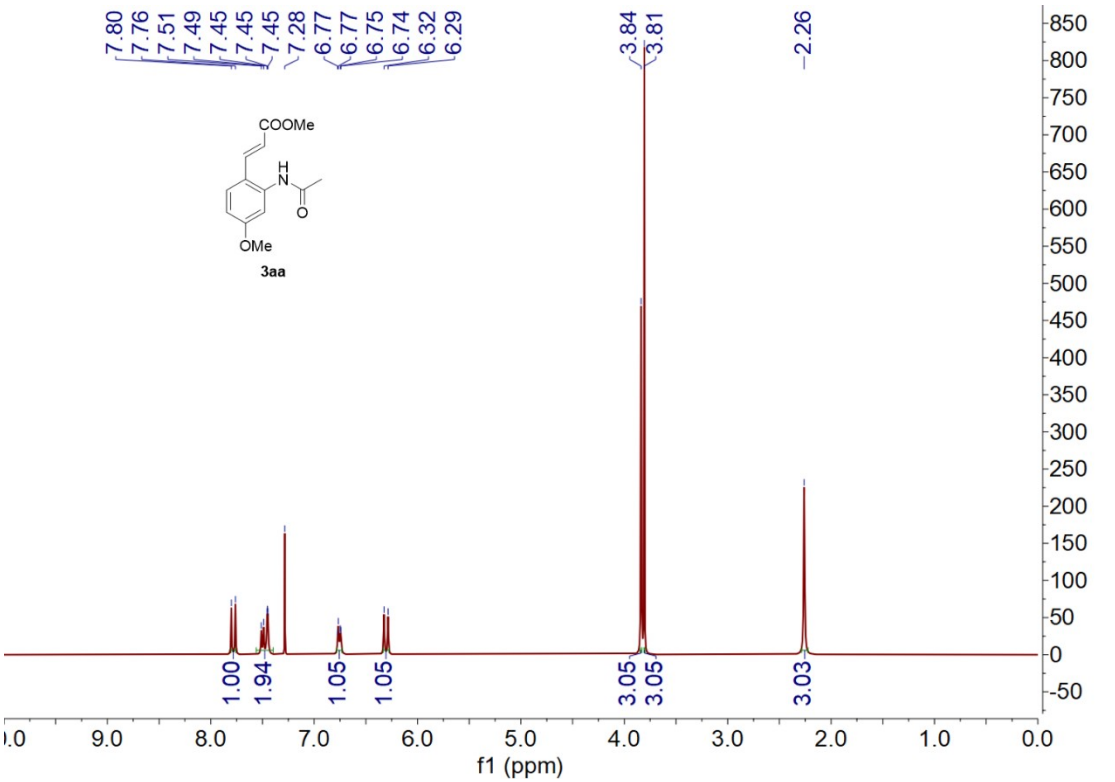
methyl (E)-3-(4-methoxy-2-pivalamidophenyl)acrylate (3sa): brown solid (61% yield, 11.7 mg) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 15.9 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 1.25 (s, 9H). ^{13}C NMR{^{1}H} (101 MHz, DMSO–d_6) ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.55, 167.48, 161.52, 140.89, 139.70, 128.44, 123.41, 115.76, 113.35 (d, *J* = 2.4 Hz), 55.94, 51.77, 27.72. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{16}H_{22}NO_4^+$, 292.1543; found, 292.1543.

ethyl (E)-3-(2-acetamido-4-methoxyphenyl)acrylate (3ab) brown solid (71% yield, 18.7 mg) ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 9.85 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 15.9 Hz, 0H), 7.04 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 17.0 Hz, 1H), 4.18 (d, *J* = 9.4 Hz, 2H), 3.78 (s, 3H), 2.09 (s, 3H), 1.26 (t, *J* = 8.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) 167.01, 166.14, 161.50, 140.39, 139.71, 131.72, 128.64, 116.53, 112.51, 111.91, 60.29, 55.86, 23.62, 14.72. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{14}H_{18}NO_4^+$, 264.1230; found, 264.1230.

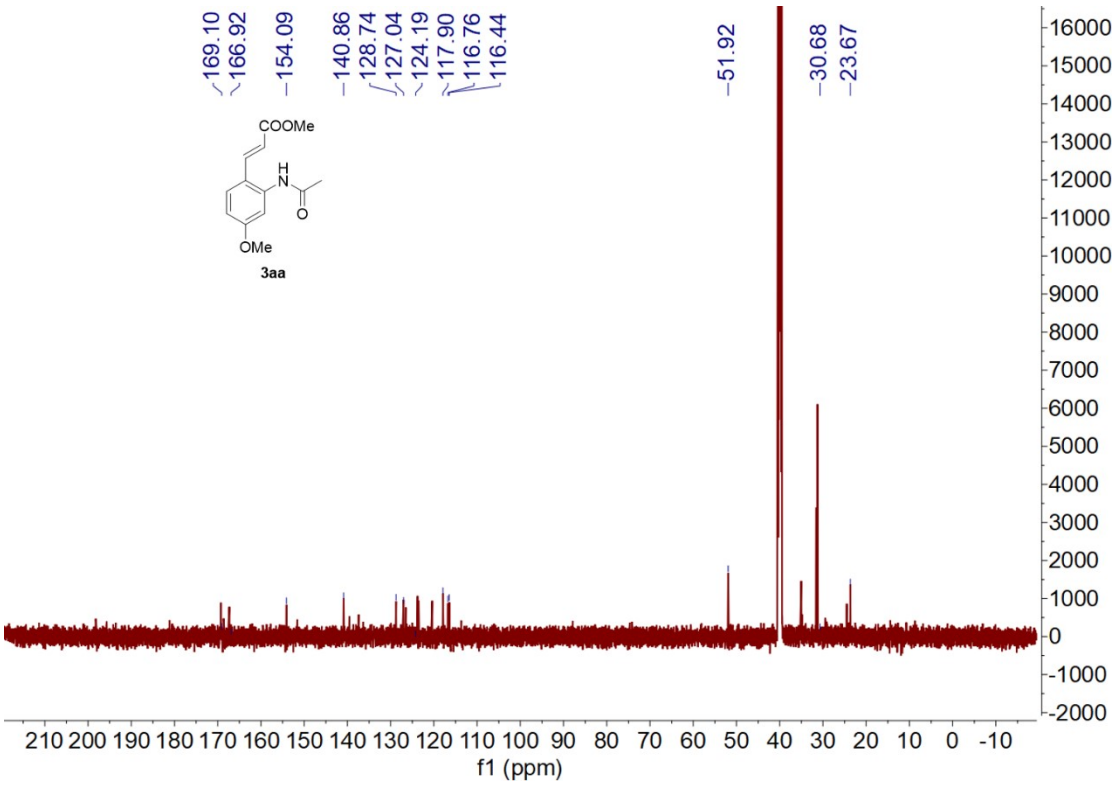
butyl (E)-3-(2-acetamido-4-methoxyphenyl)acrylate (3ac) brown solid (69% yield, 20.1 mg) ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 9.84 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 15.9 Hz, 1H), 7.02 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 4.14 (s, 2H), 3.78 (s, 3H), 2.09 (s, 3H), 1.64 (s, 2H), 1.39 (q, *J* = 7.6 Hz, 2H), 0.97 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) 166.26, 159.15, 141.74, 136.76, 131.93, 128.45, 118.63, 114.26, 109.97, 104.06, 61.24, 55.19, 32.03, 27.63, 20.39, 13.13. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{16}H_{22}NO_4^+$, 292.1543; found, 292.1543

6. The ^{1}H NMR and ^{13}C NMR{^{1}H} spectra of the synthesized compounds

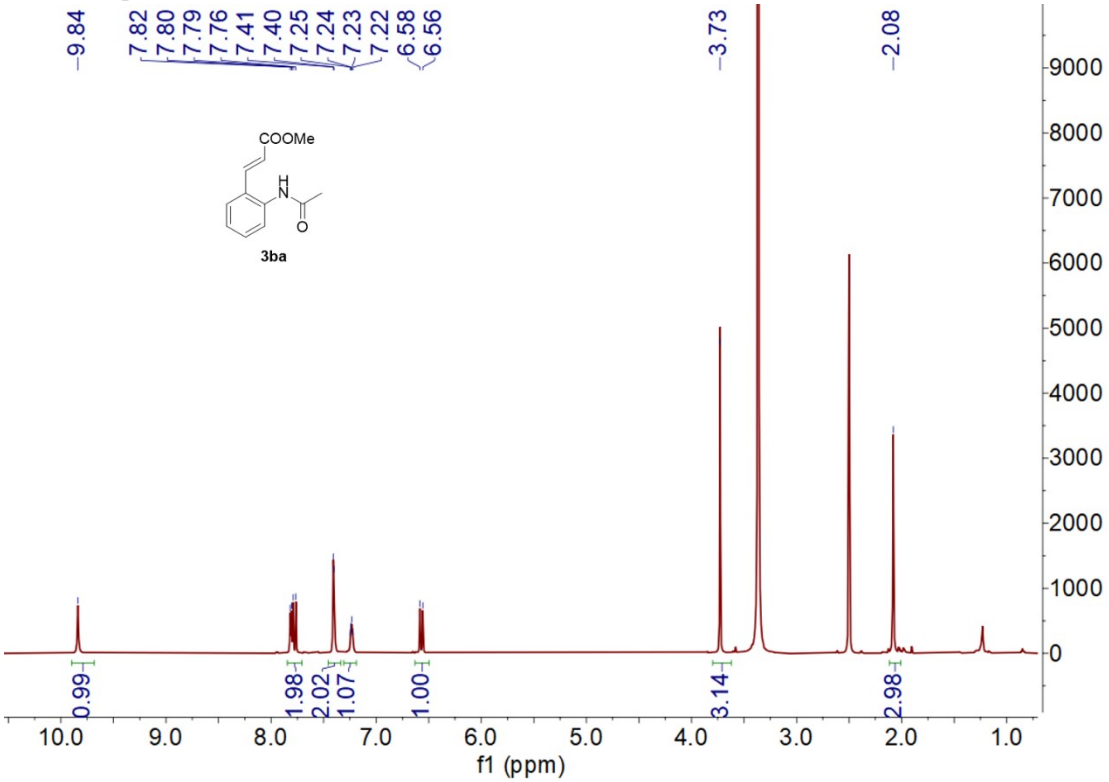
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aa**



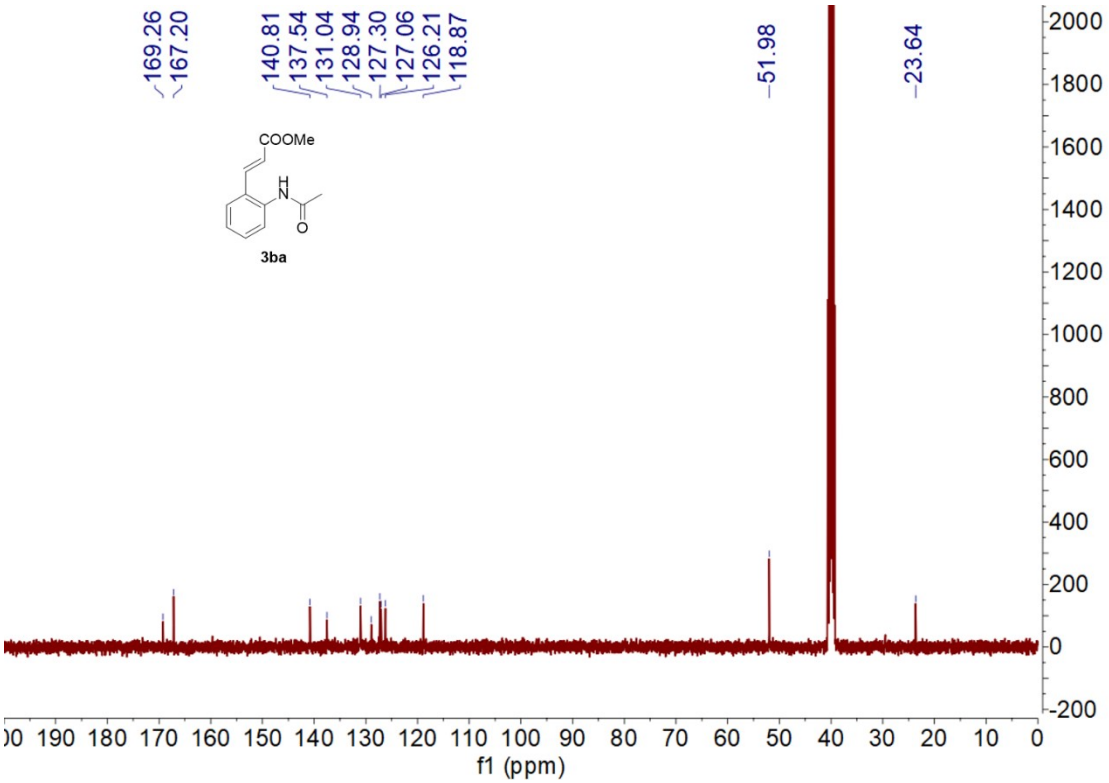
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3aa**



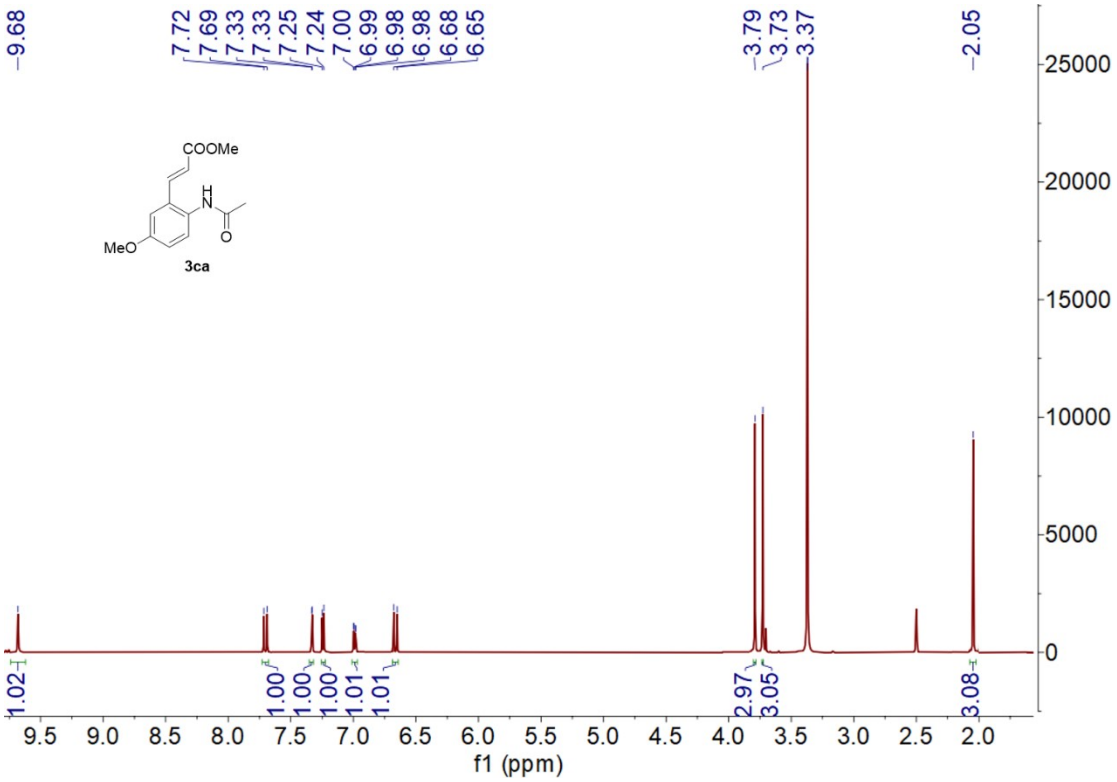
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ba**



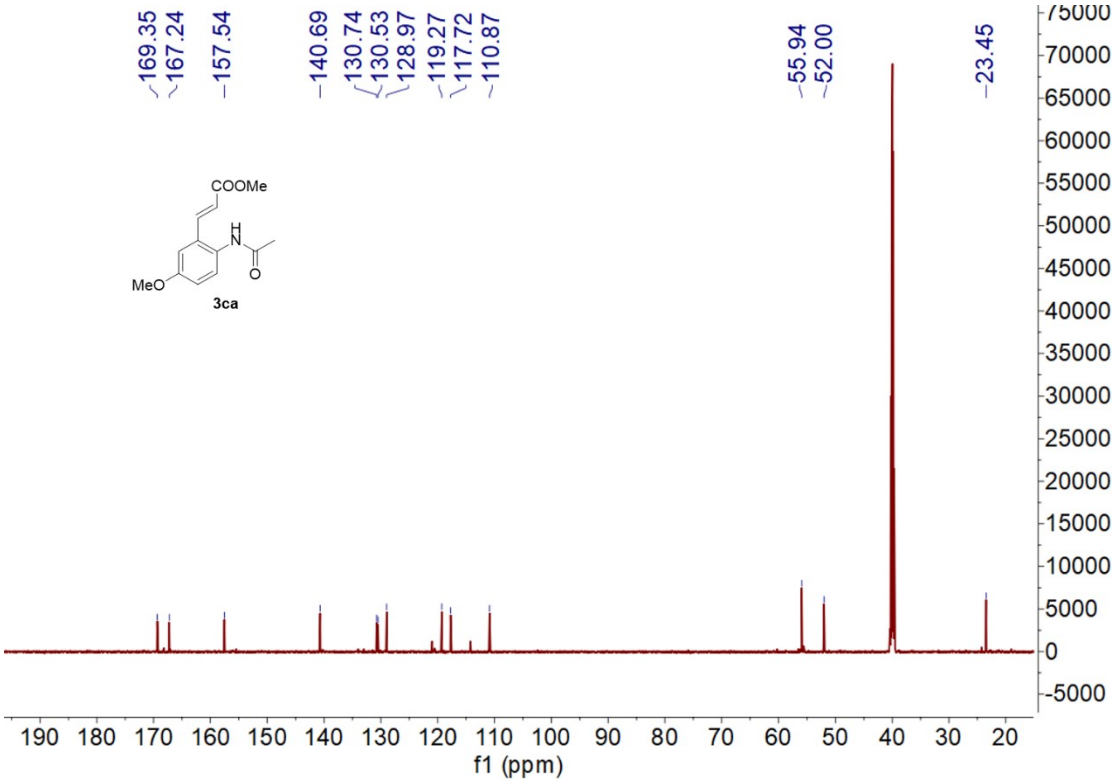
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ba**



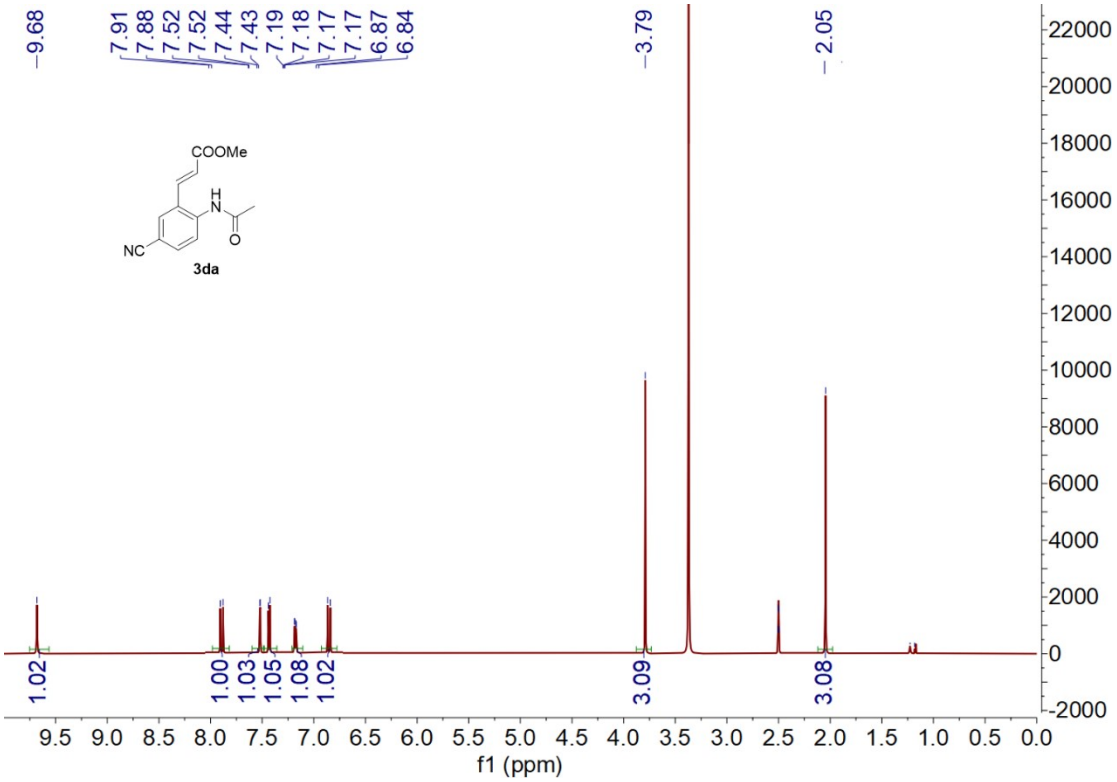
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ca**



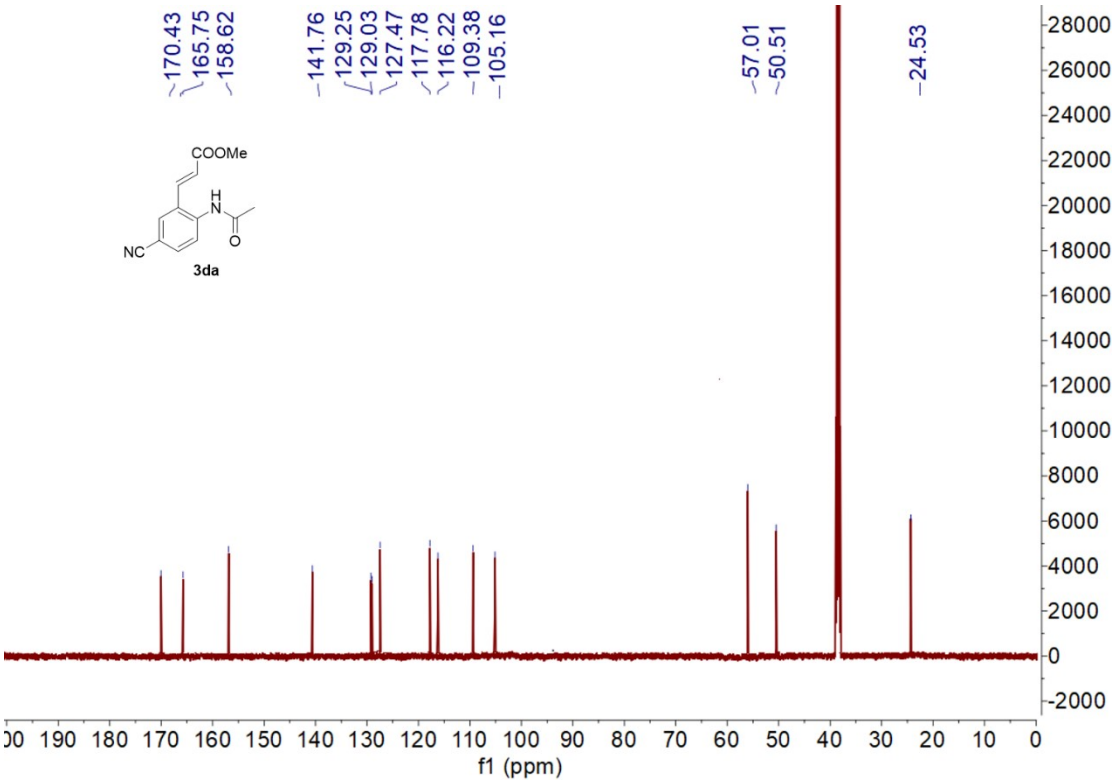
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ca**



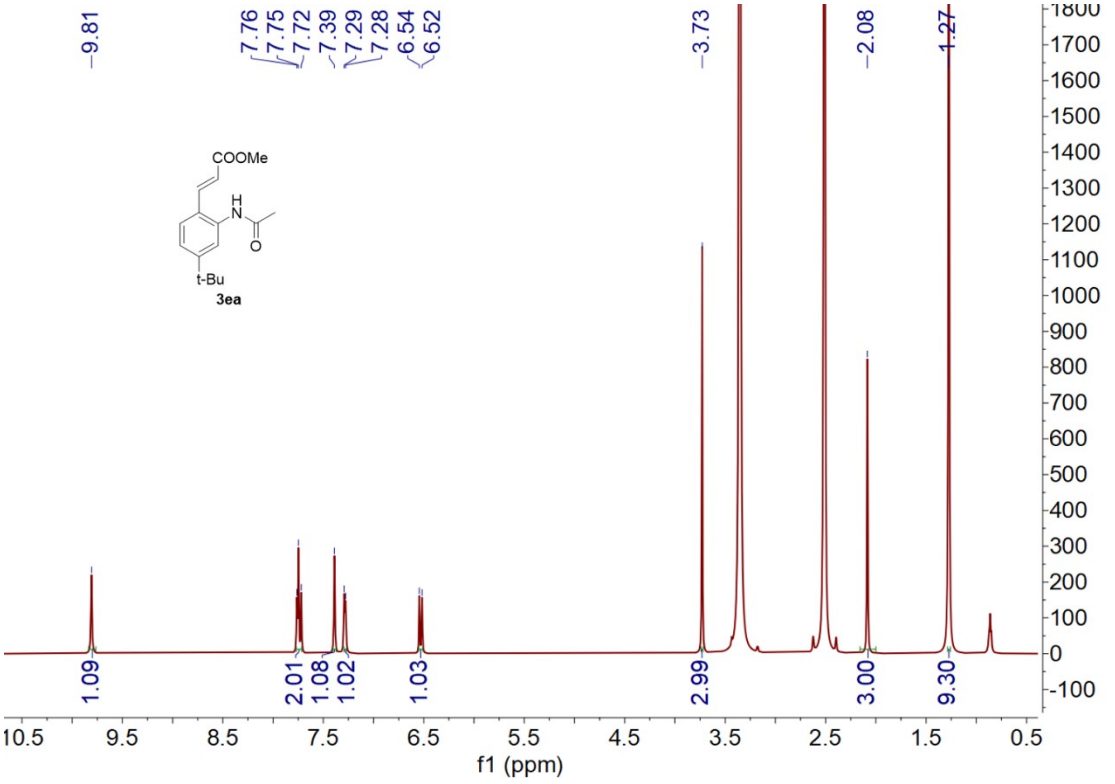
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3da**



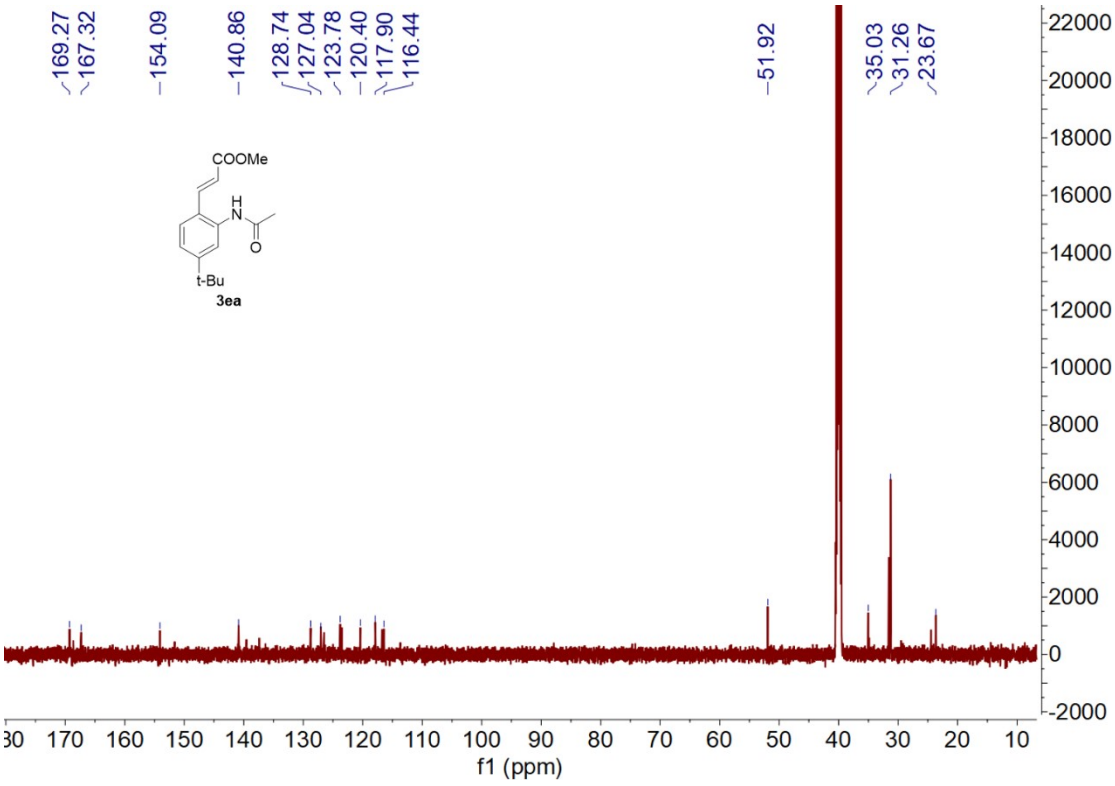
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3da**



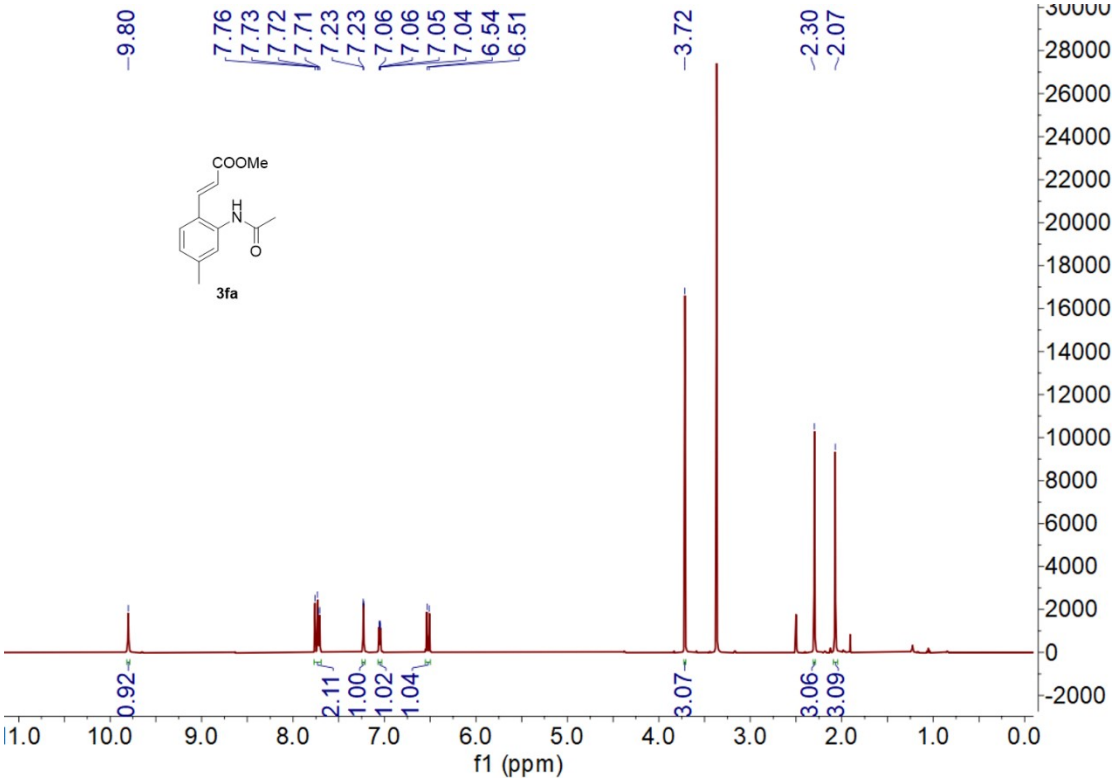
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ea**



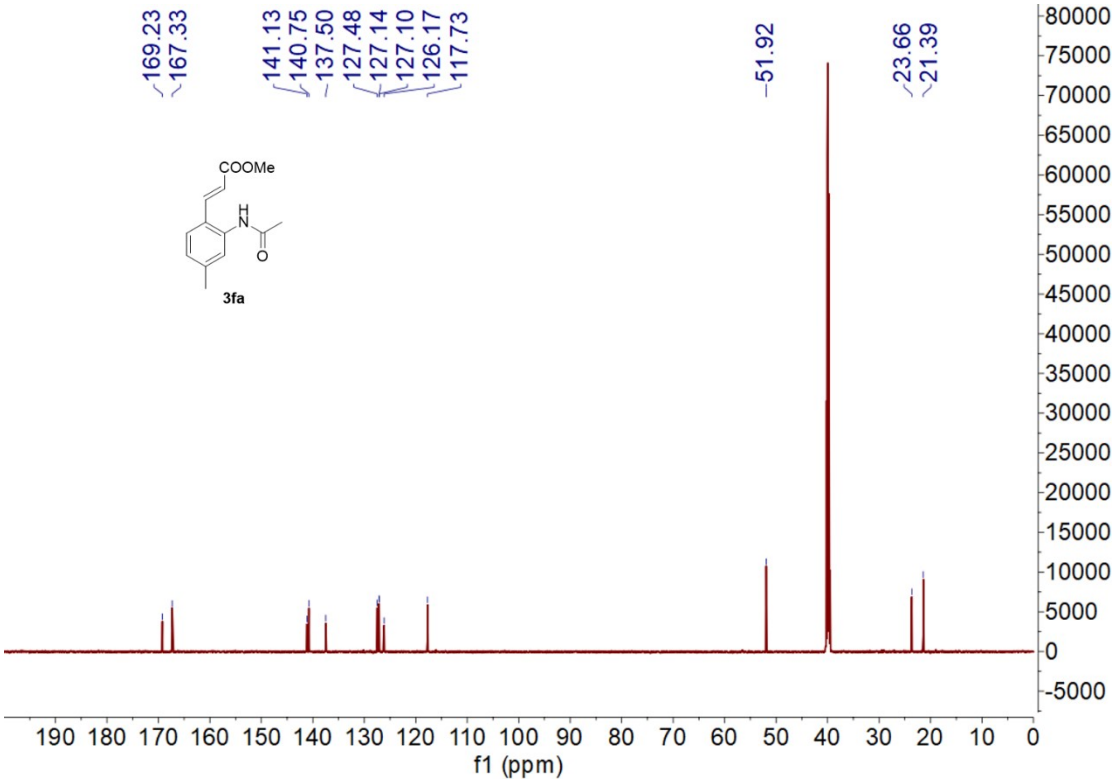
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ea**



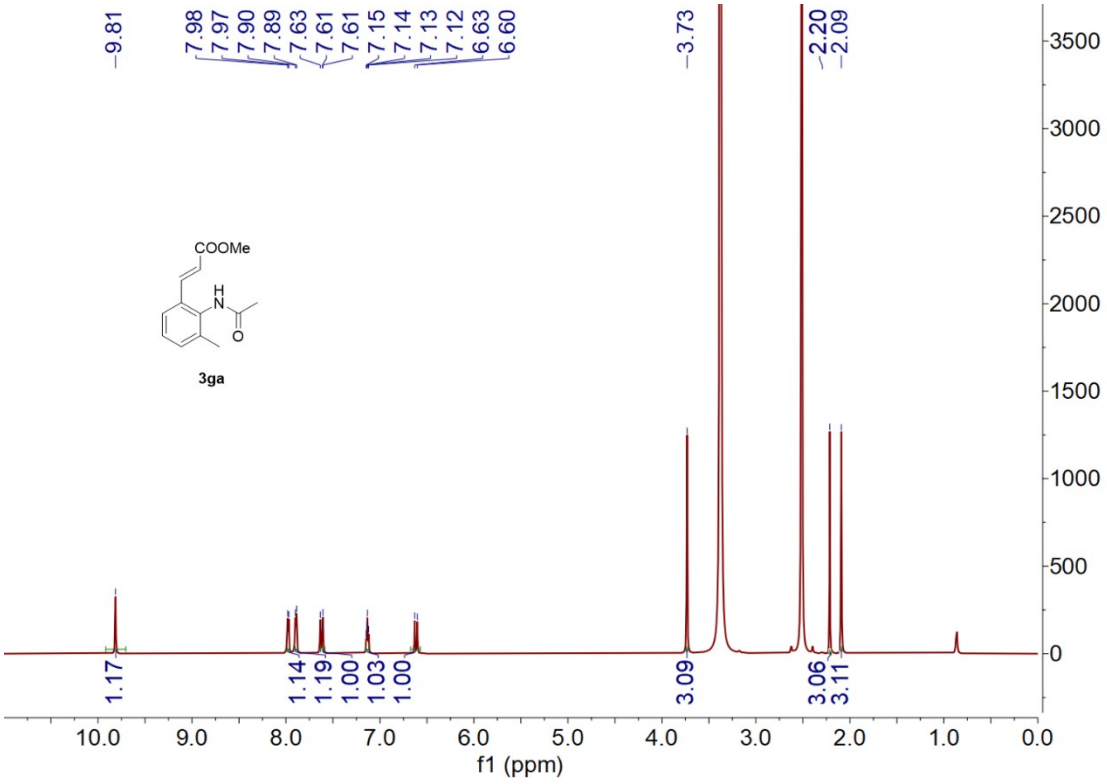
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3fa**



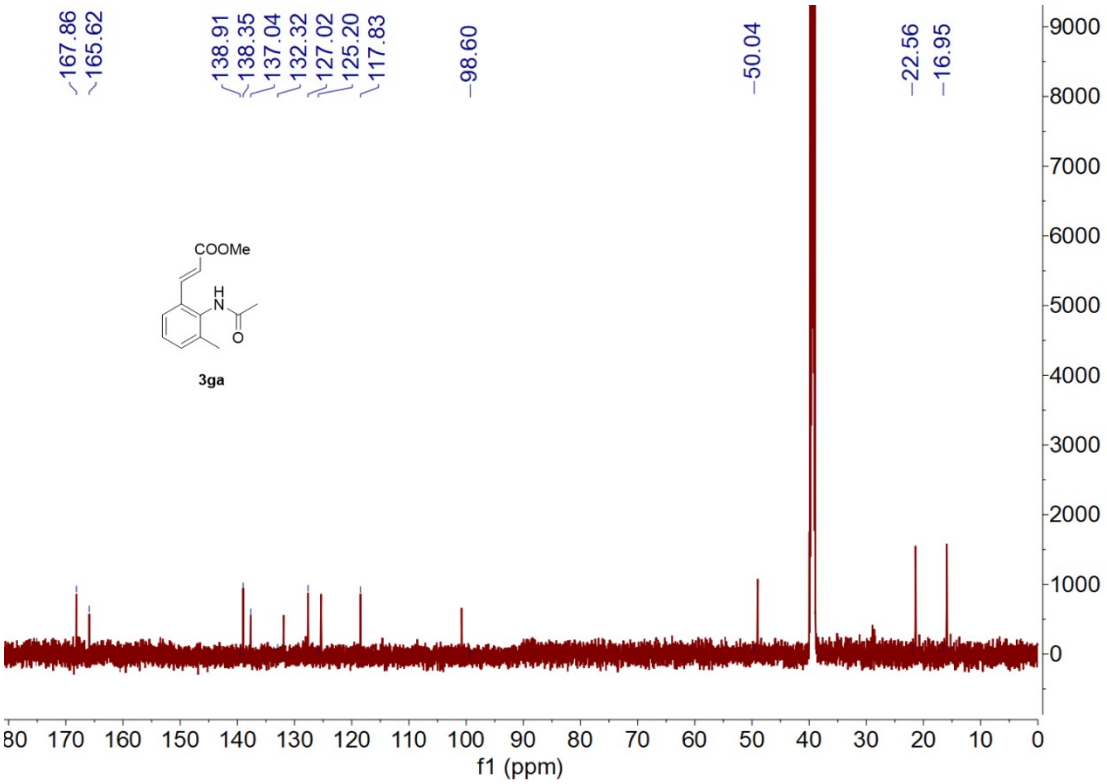
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3fa**



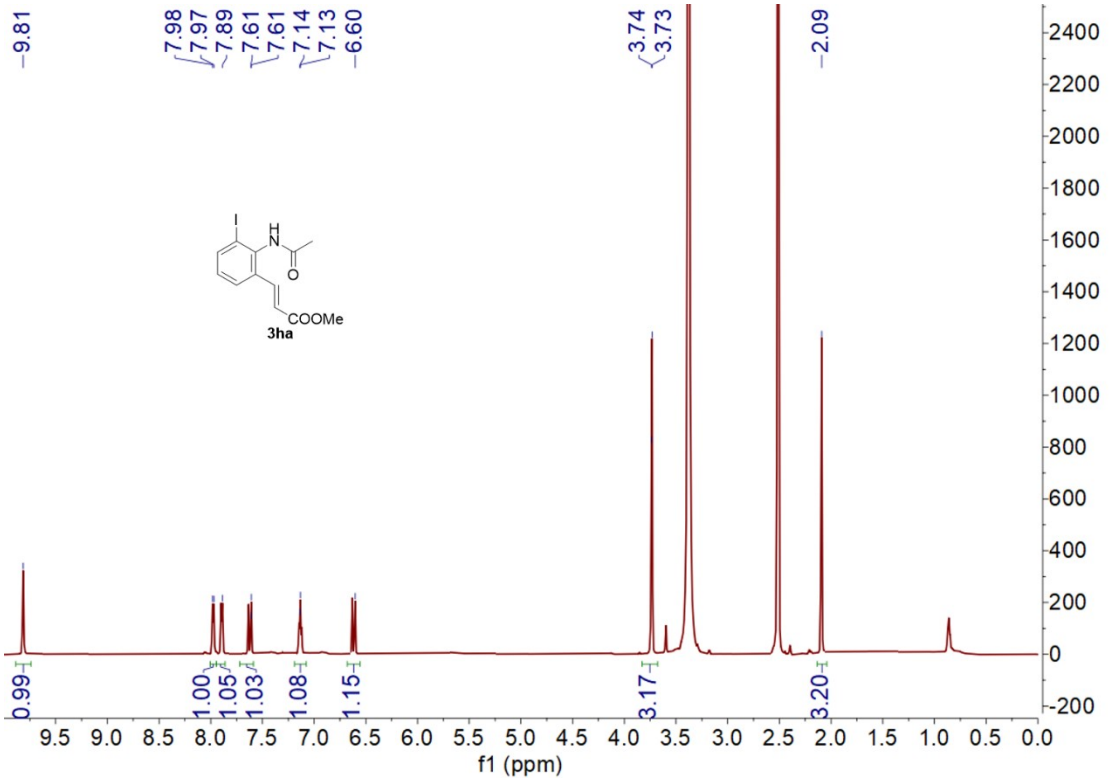
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ga**



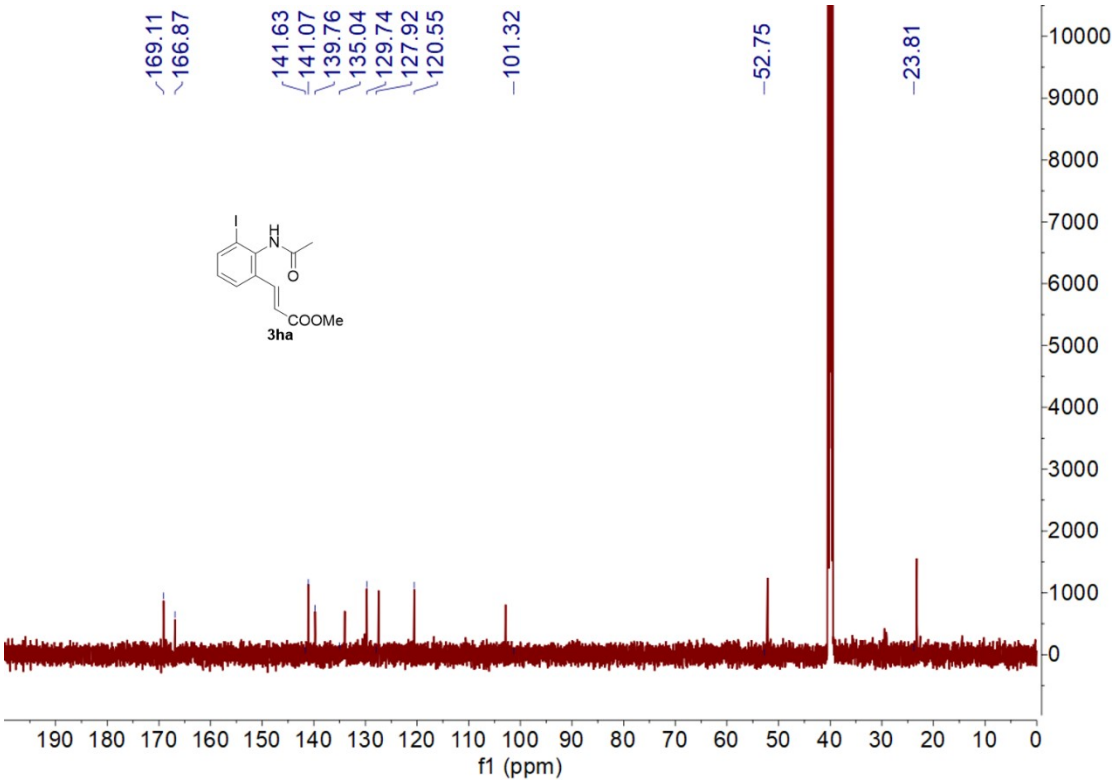
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ga**



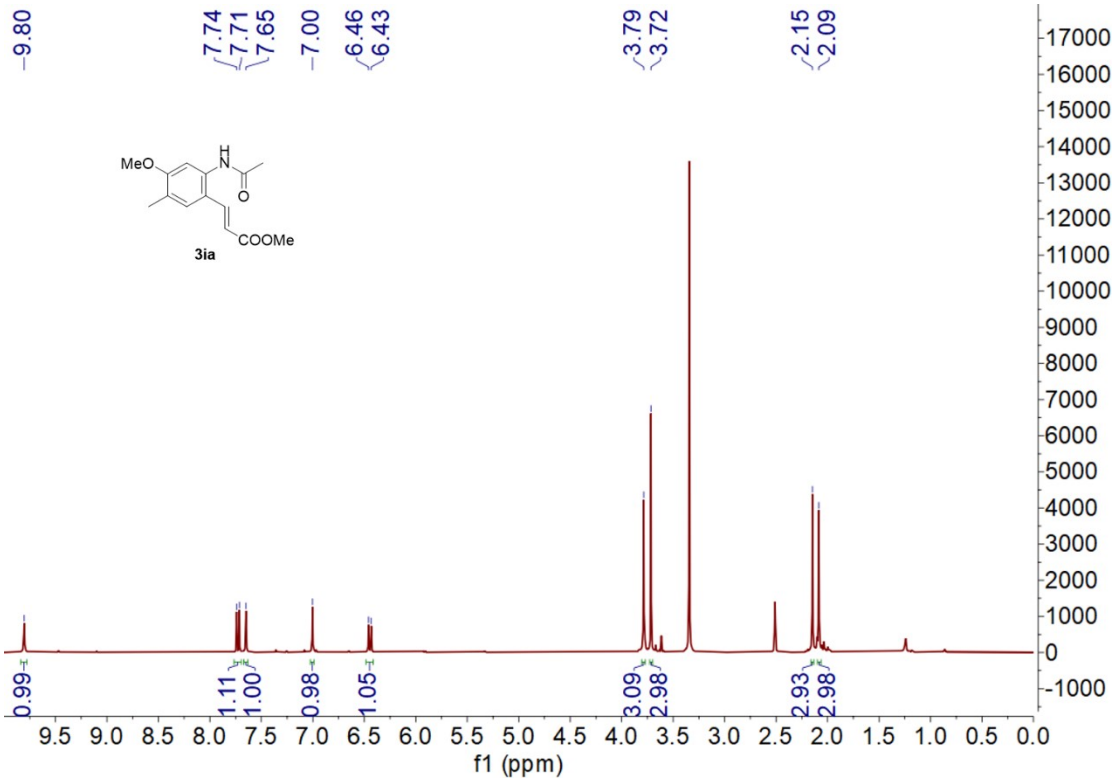
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ha**



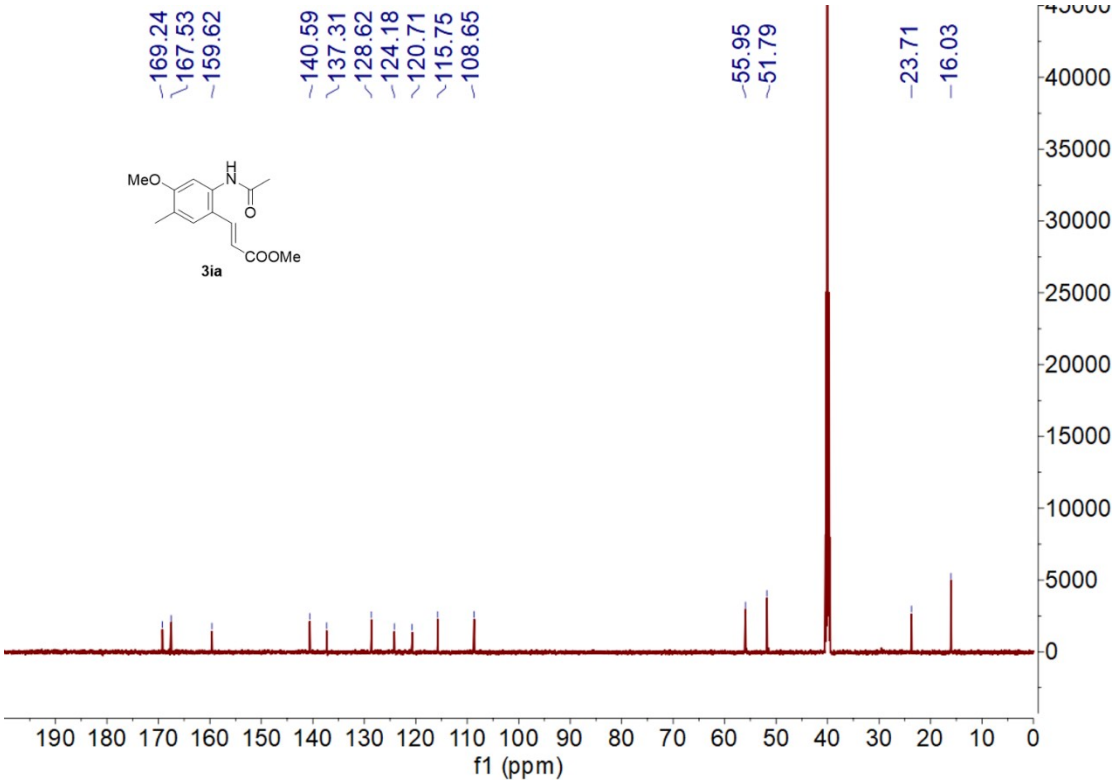
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ha**



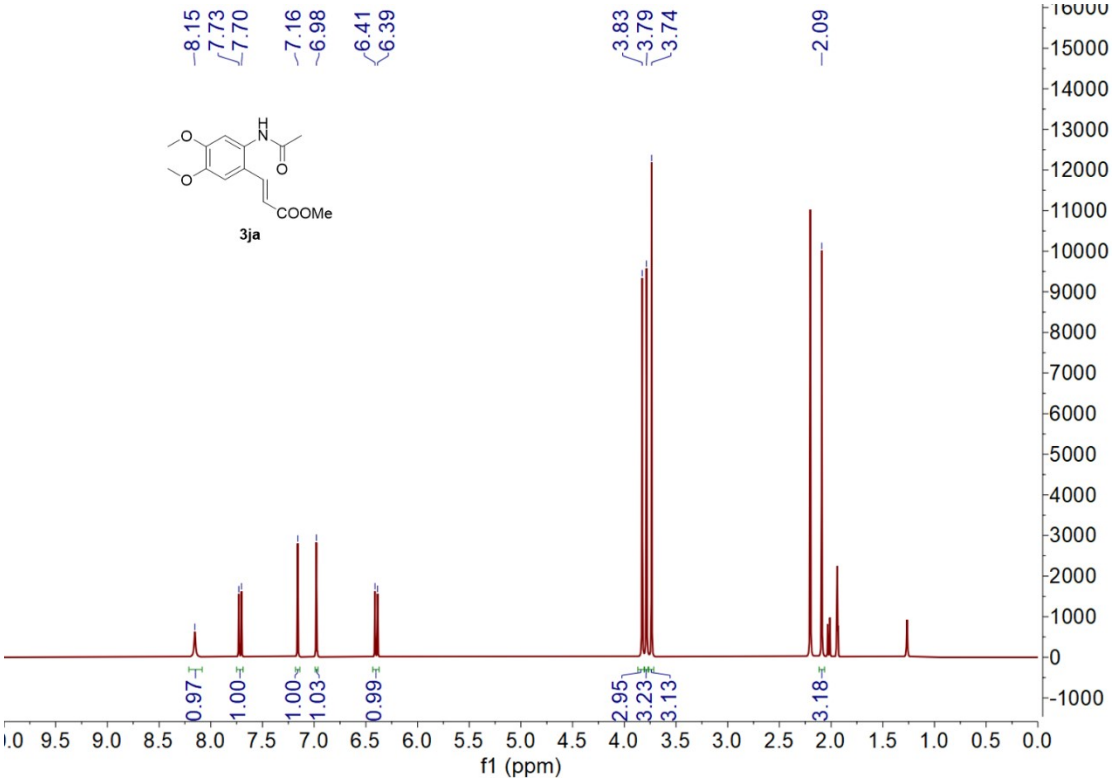
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ia**



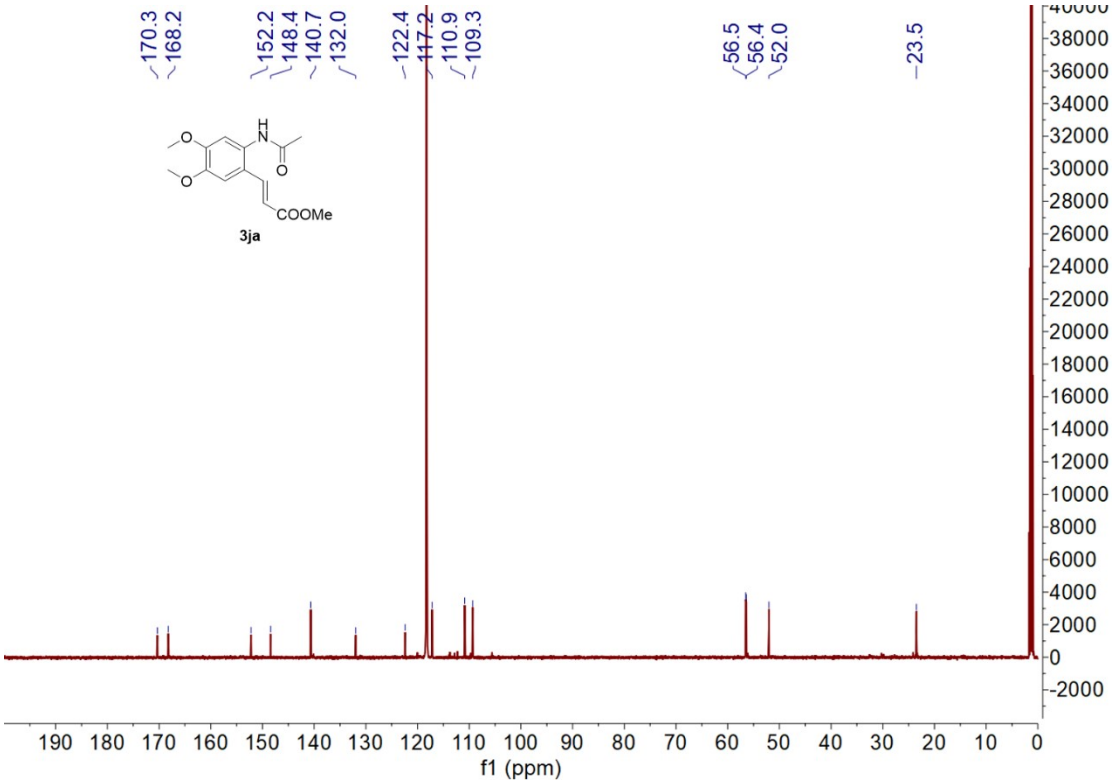
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ia**



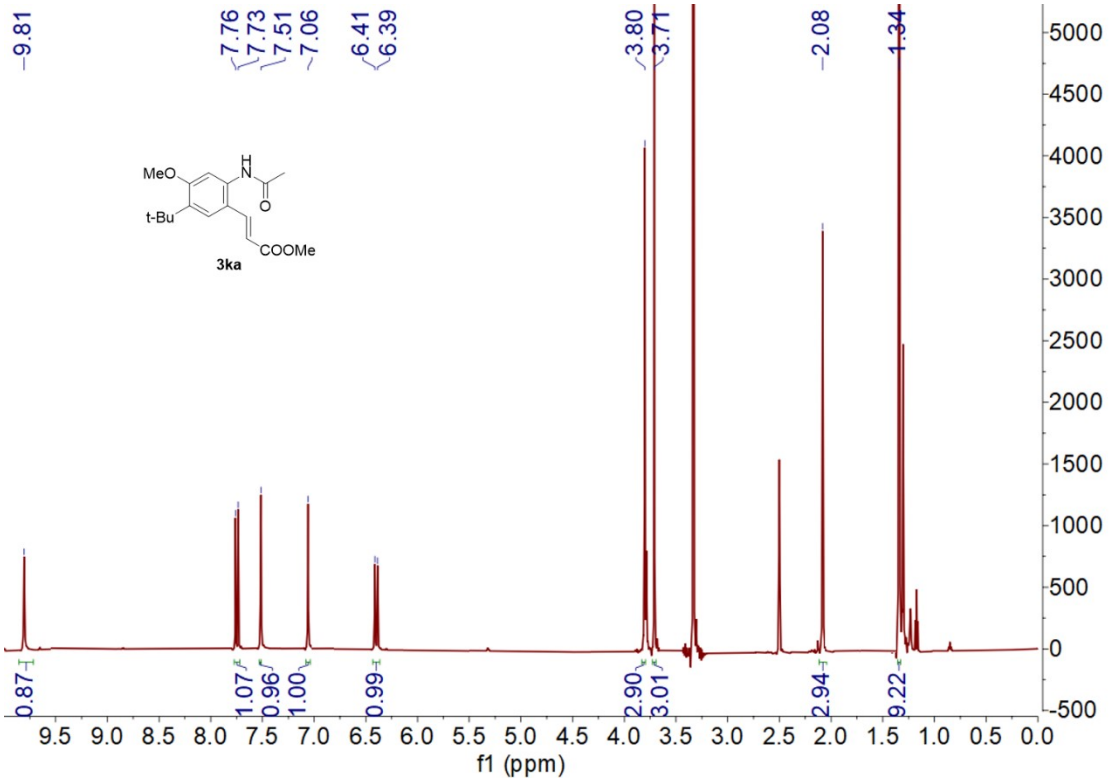
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ja**



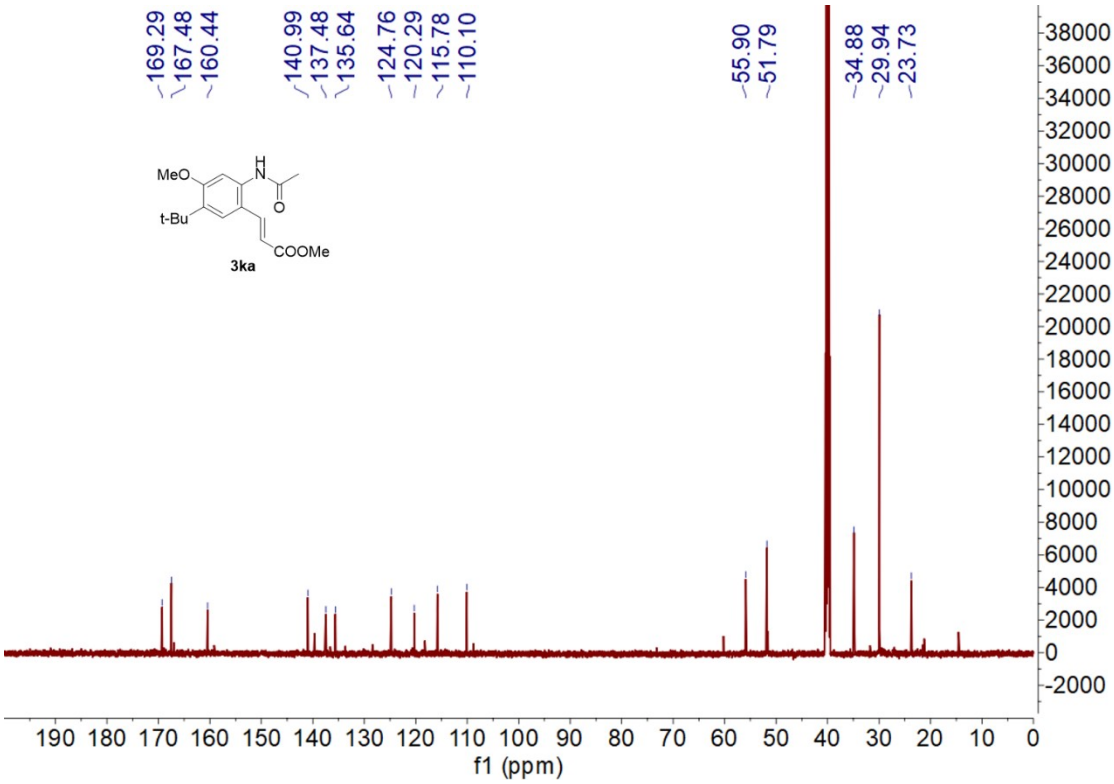
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ja**



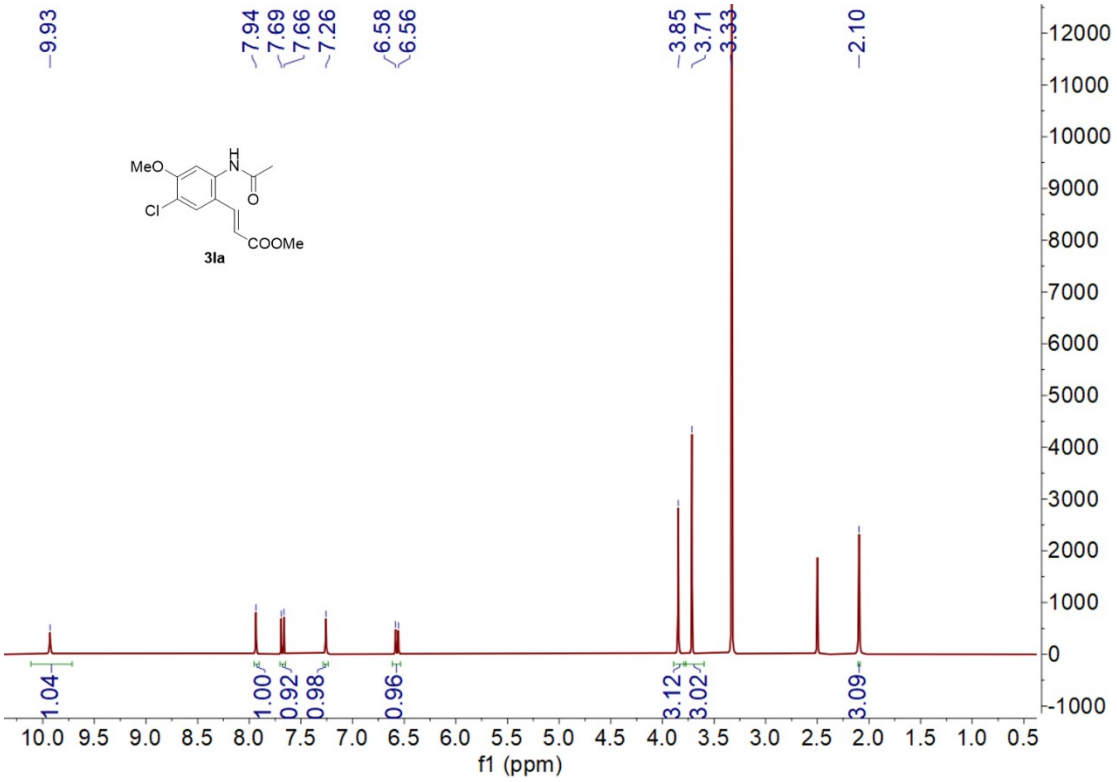
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ka**



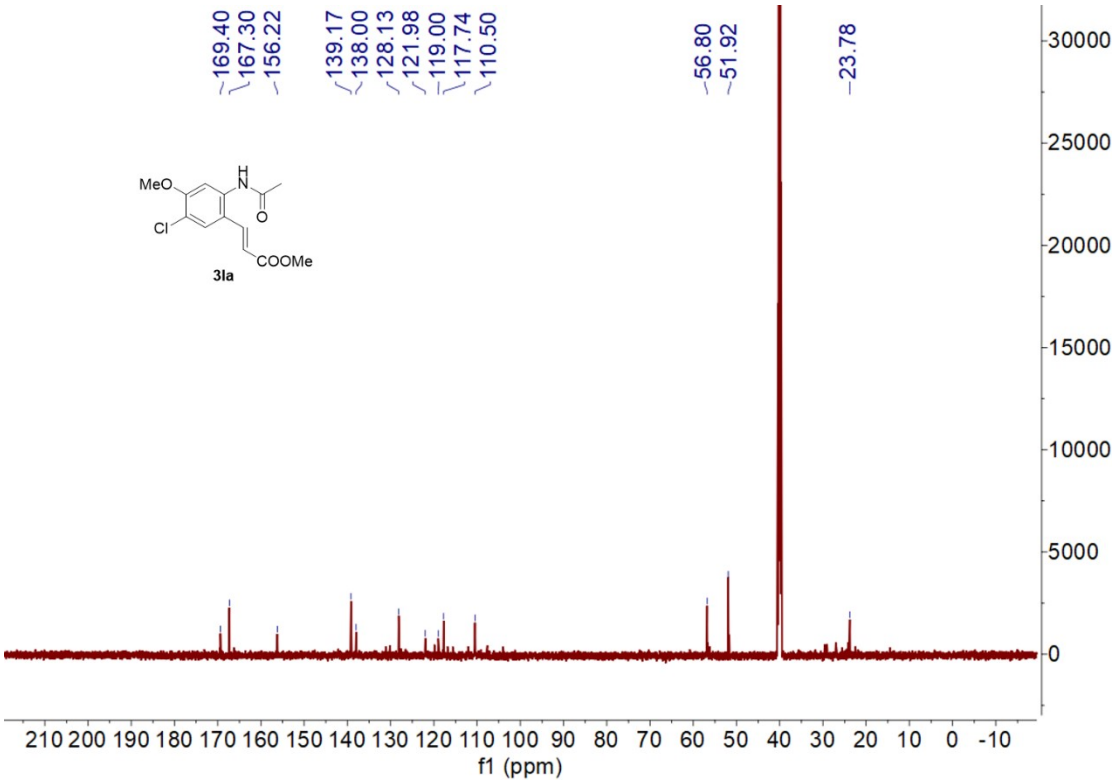
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ka**



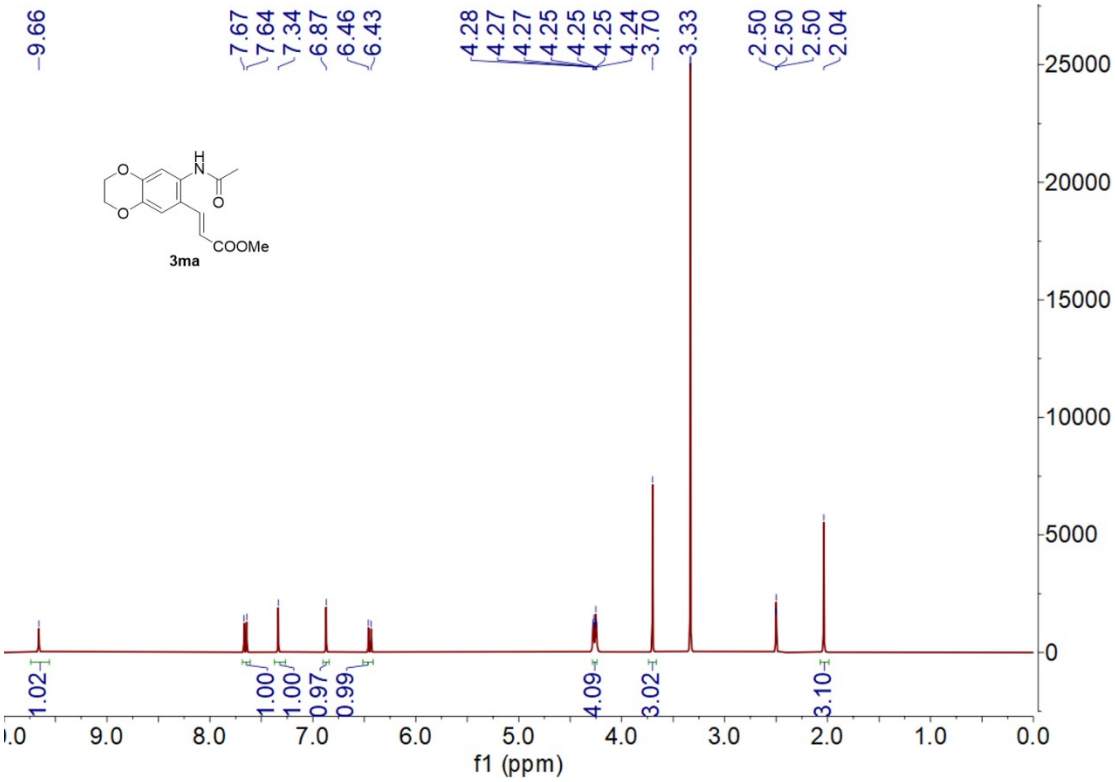
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3la**



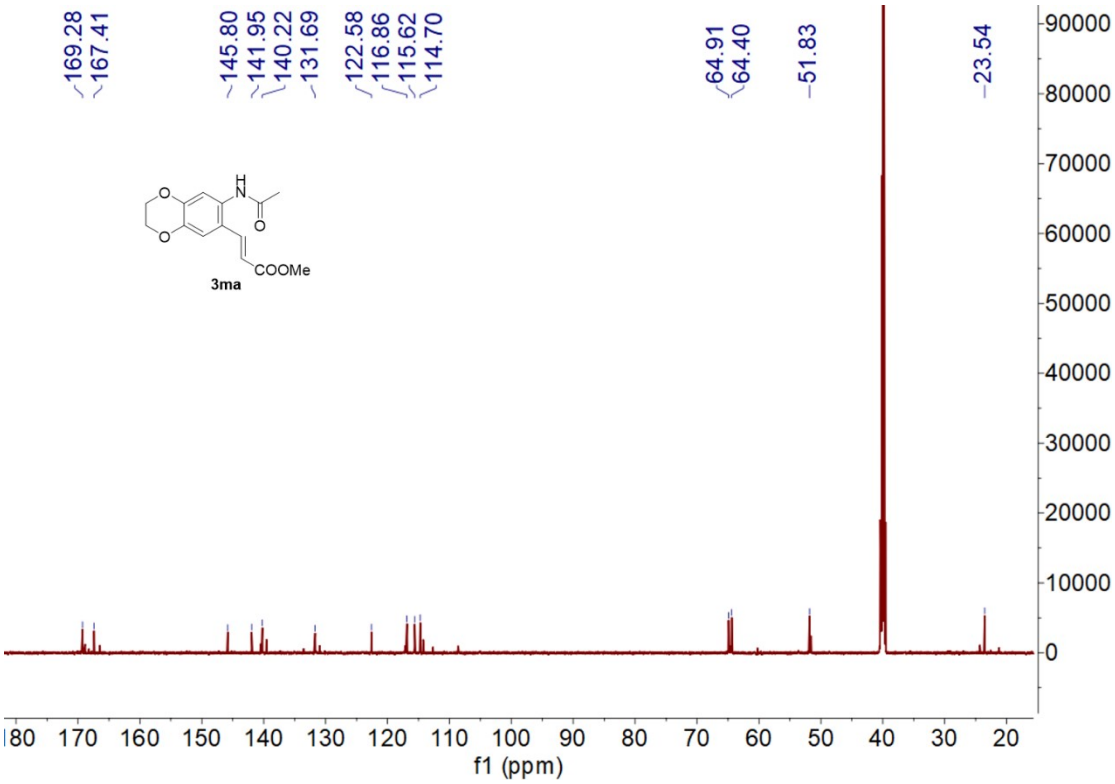
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3la**



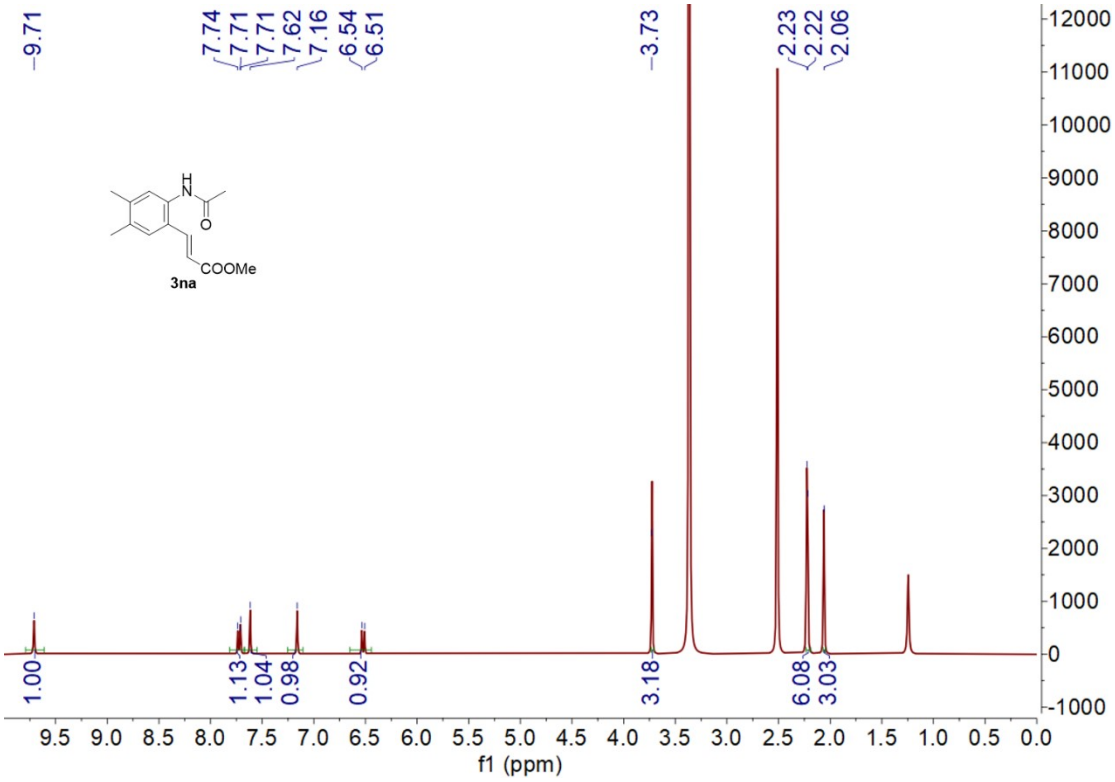
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ma**



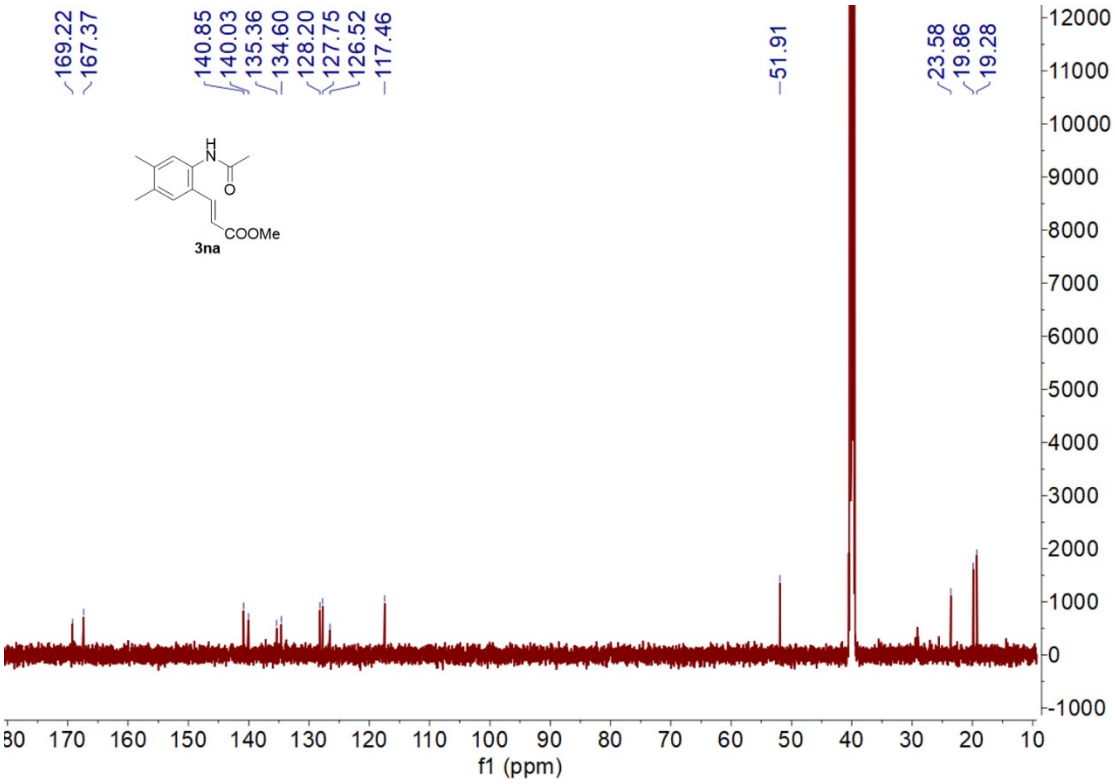
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ma**



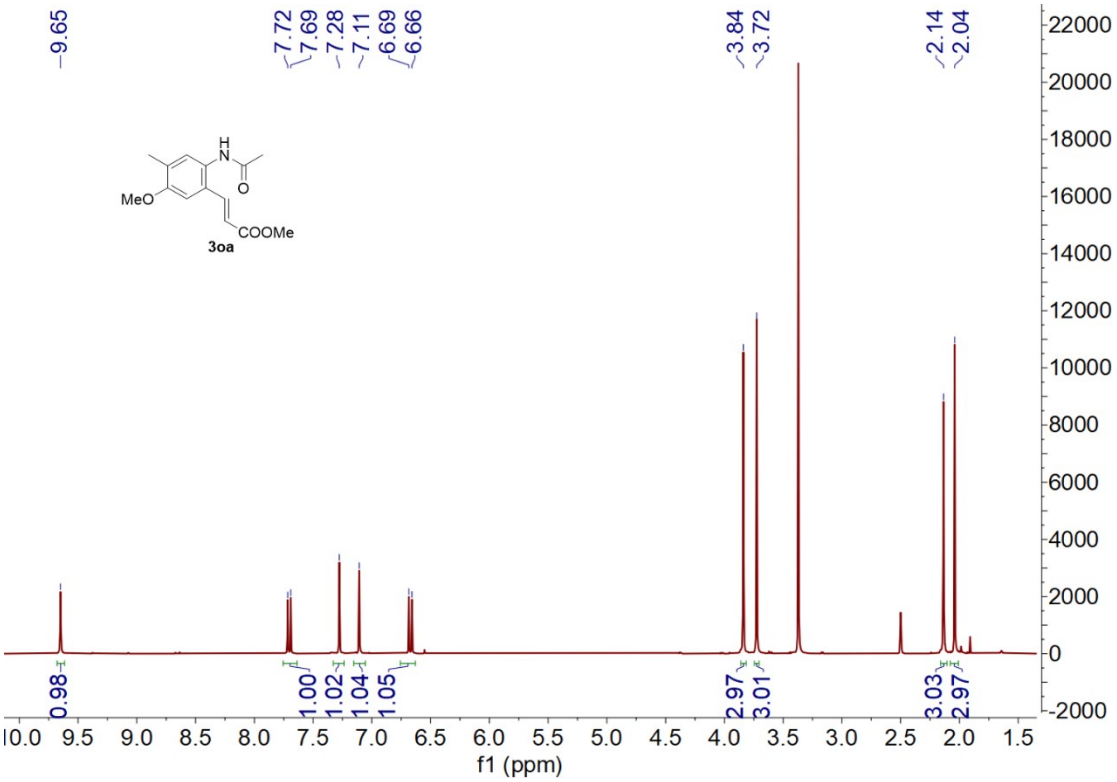
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3na**



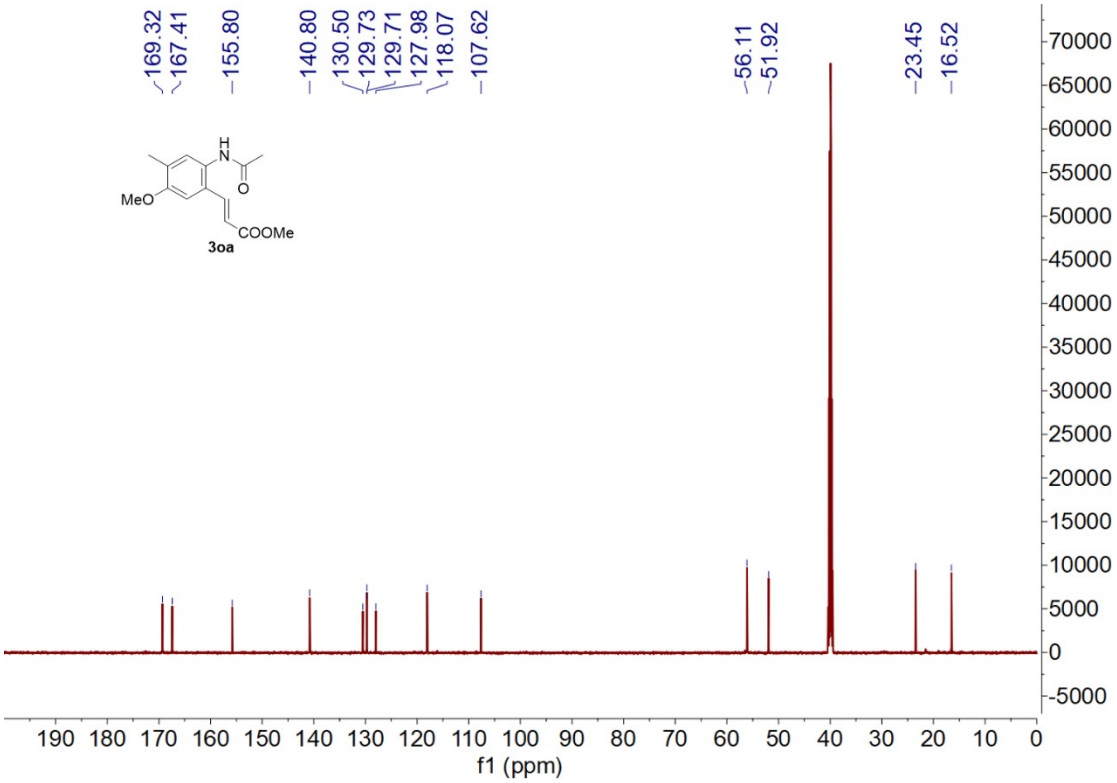
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3na**



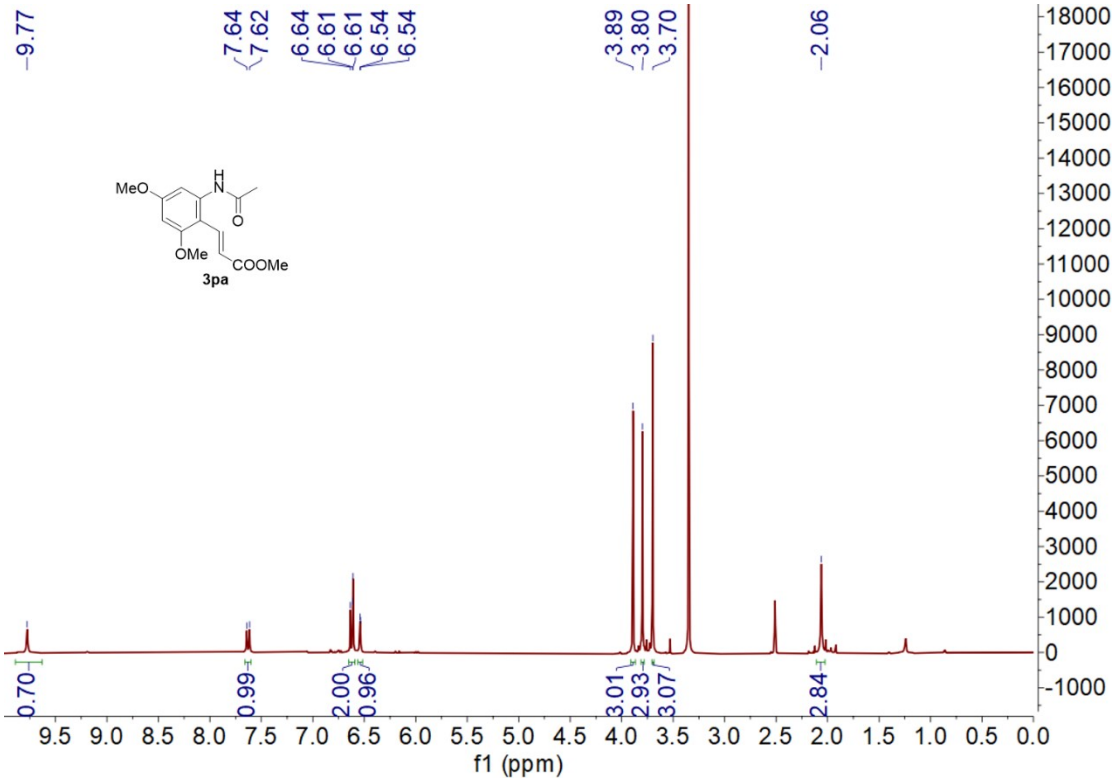
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3oa**



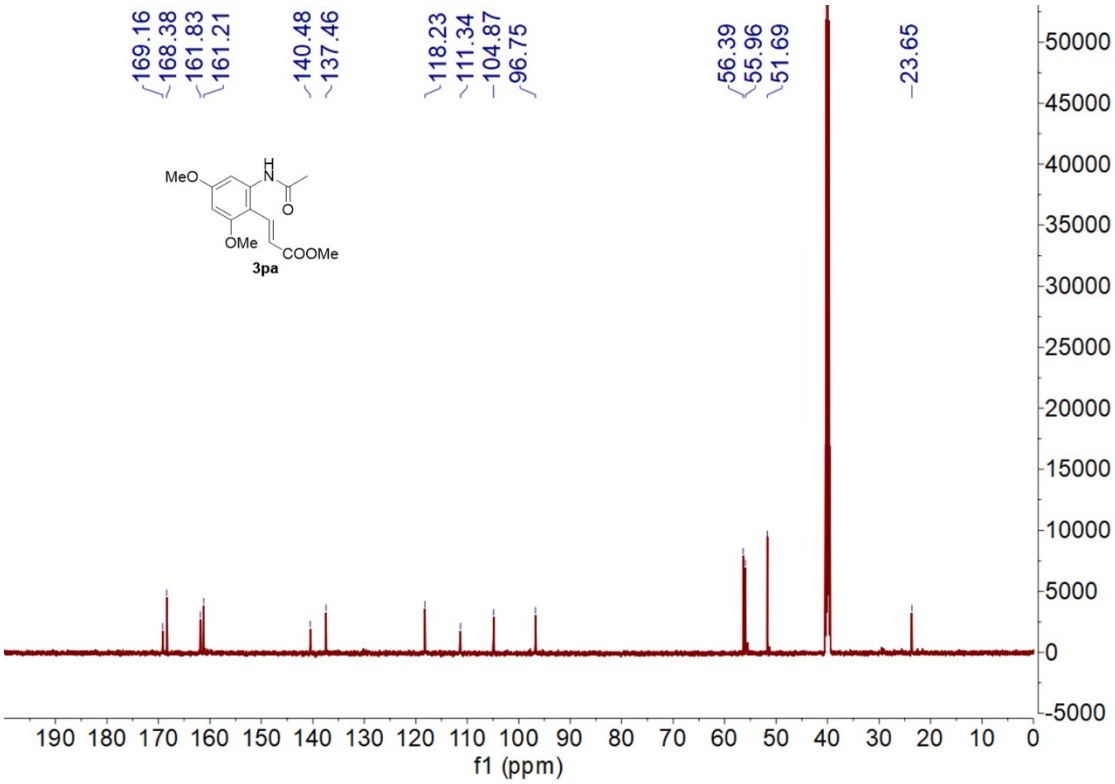
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3oa**



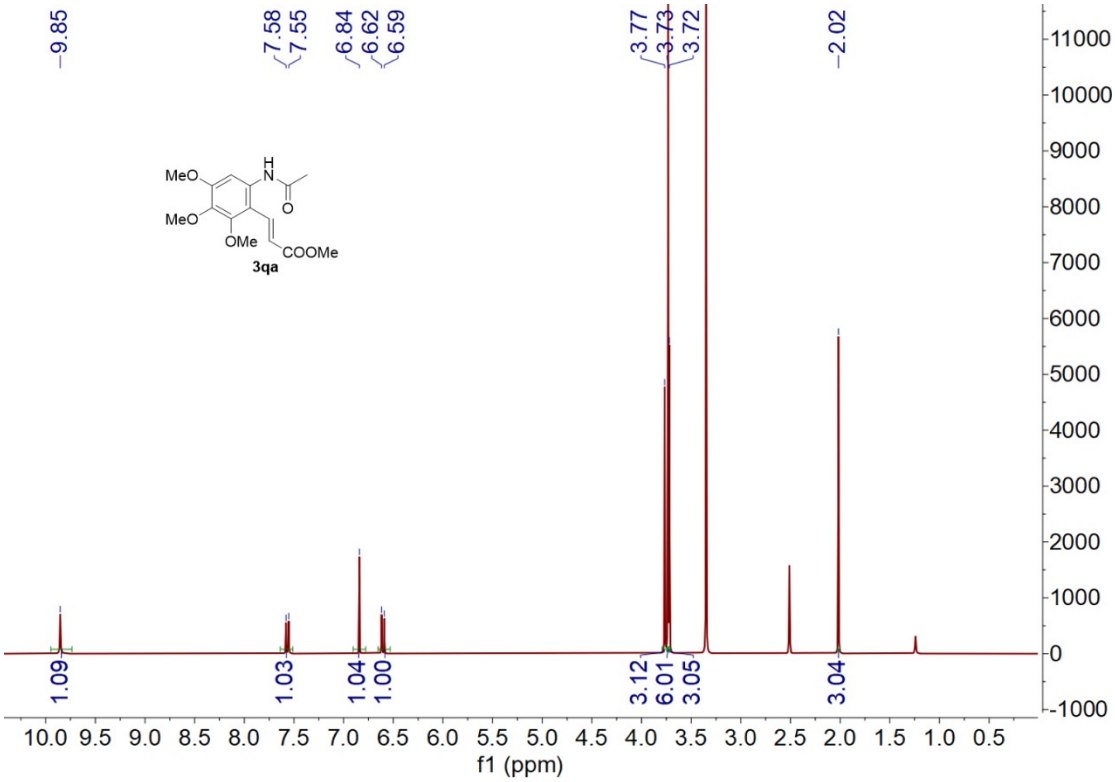
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3pa**



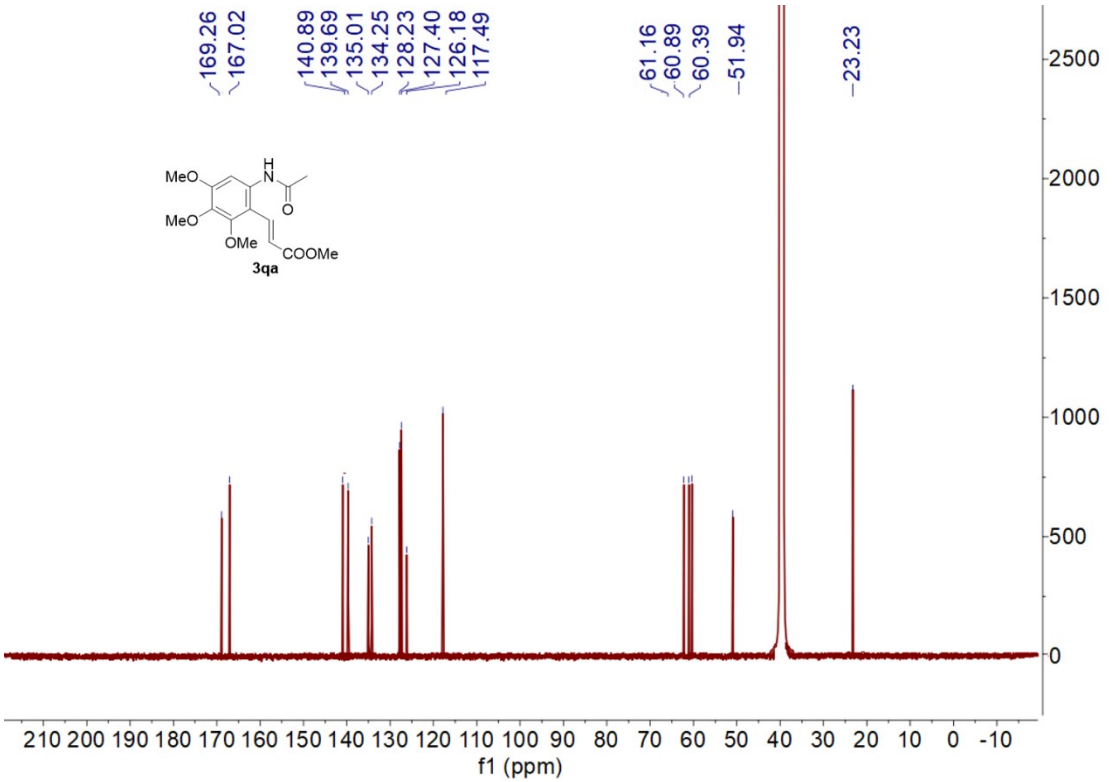
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3pa**



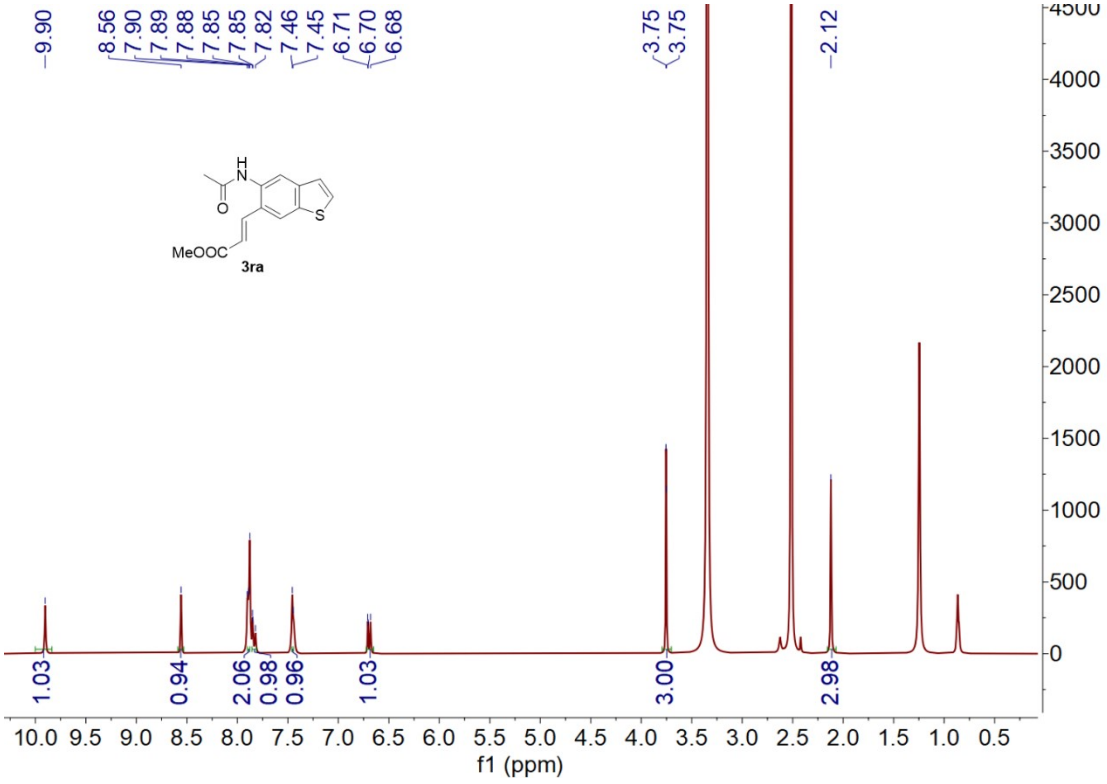
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3qa**



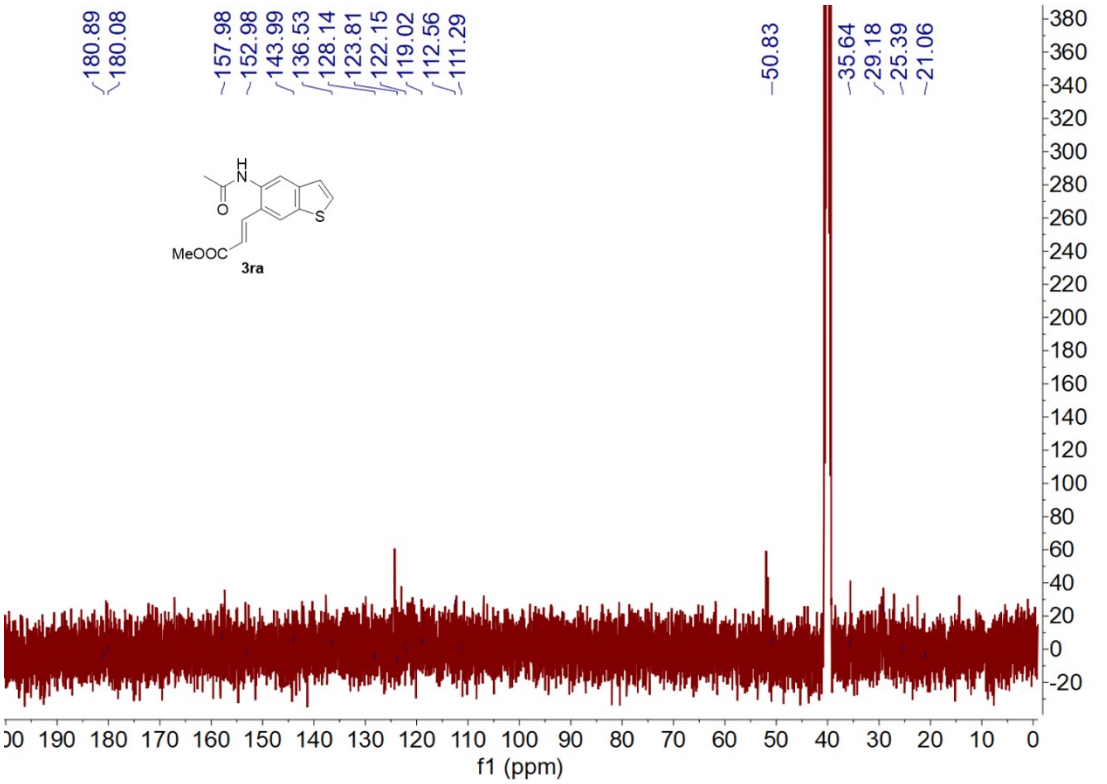
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3qa**



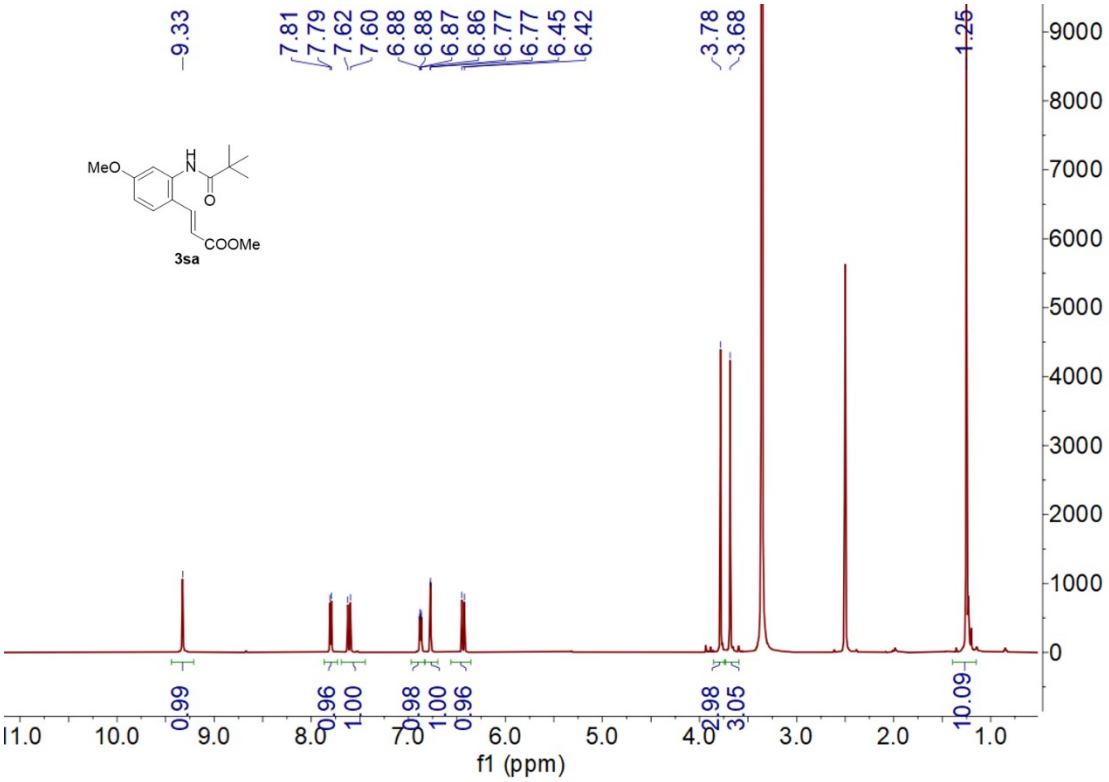
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ra**



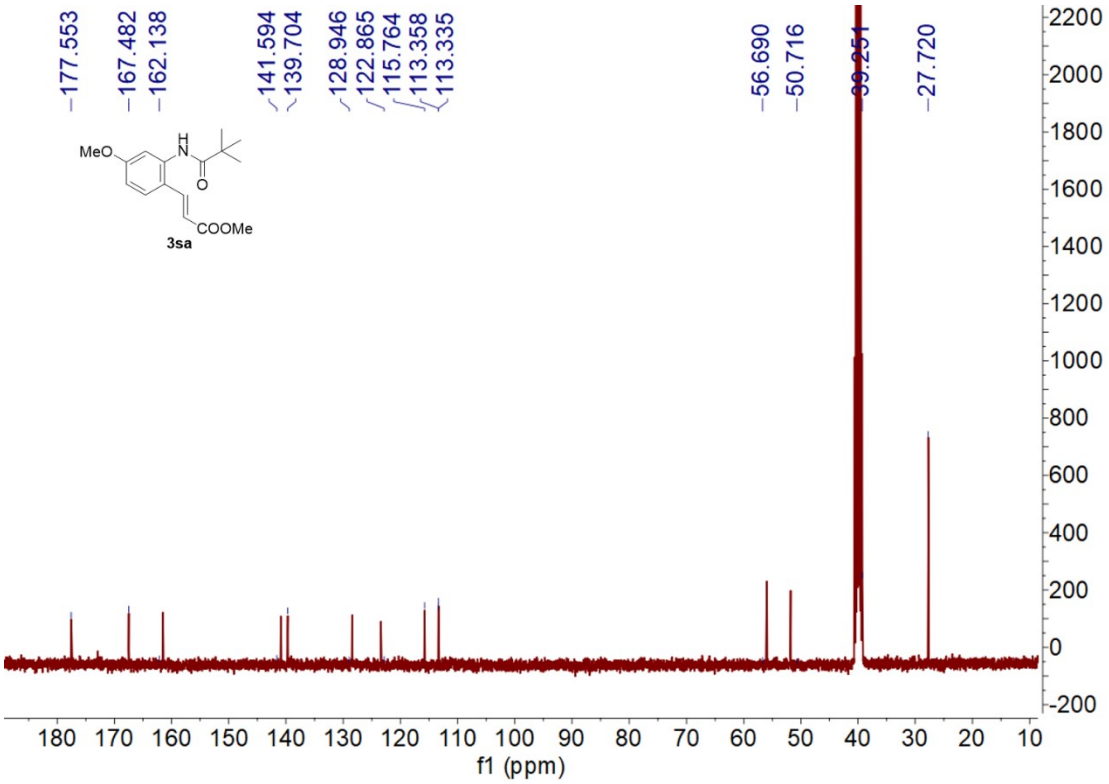
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ra**



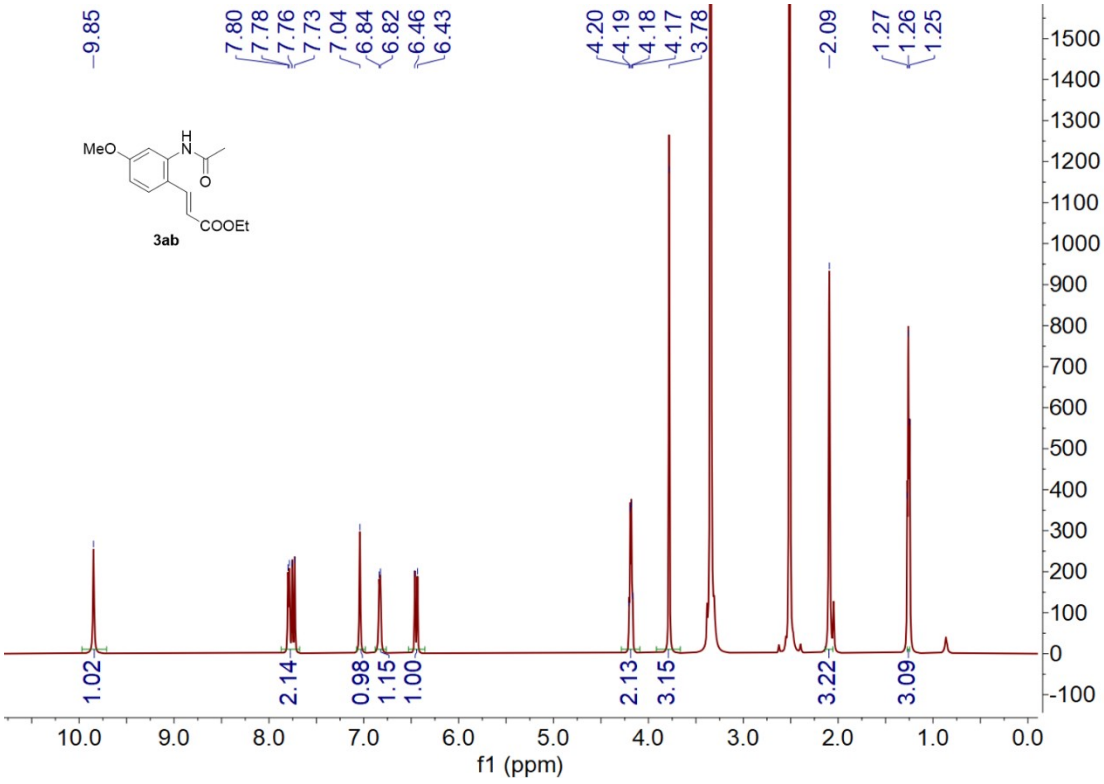
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3sa**



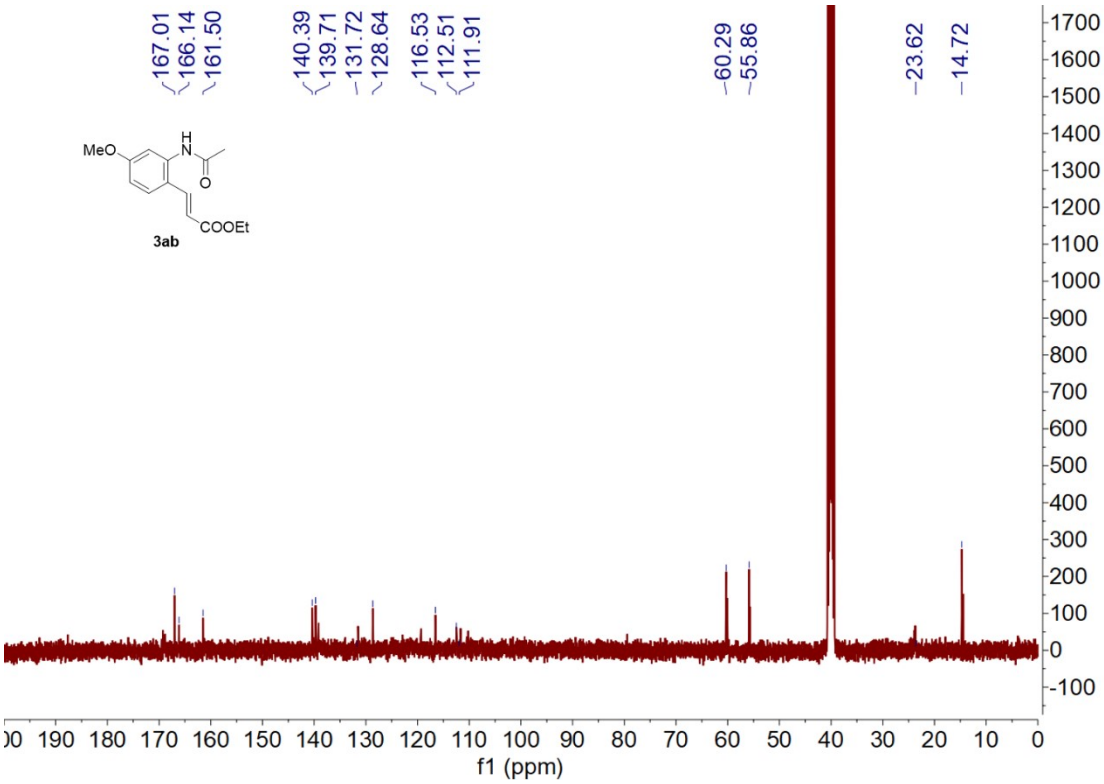
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3sa**



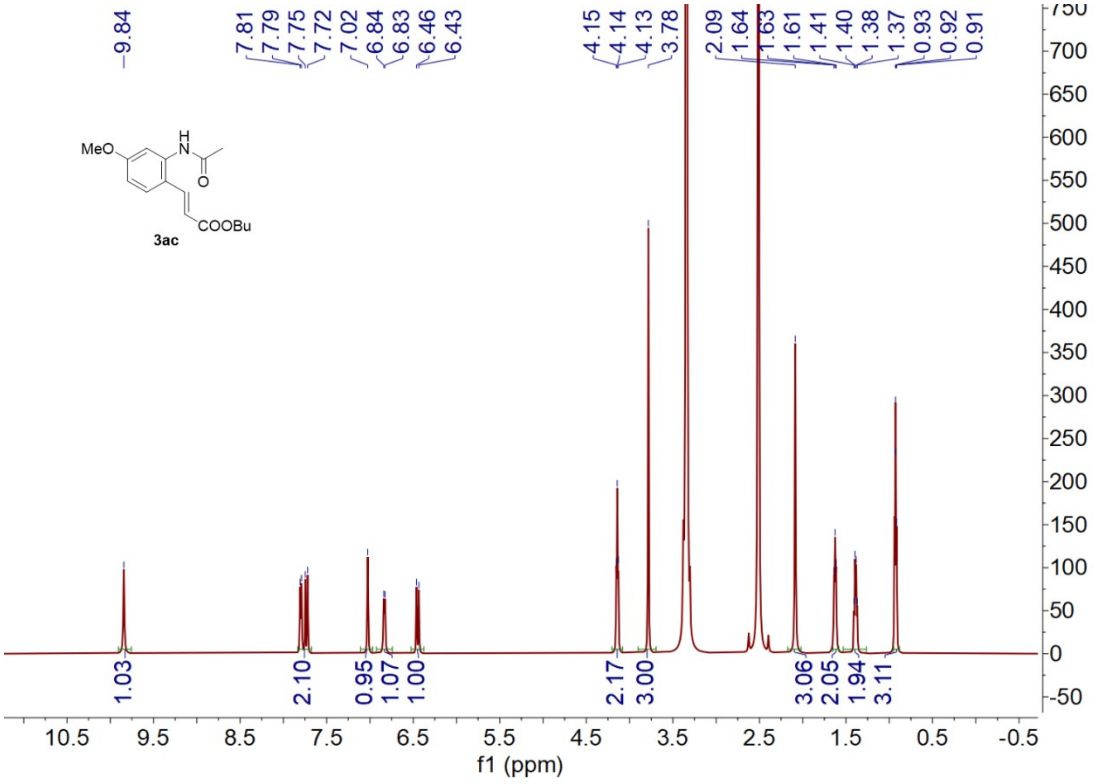
^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ab**



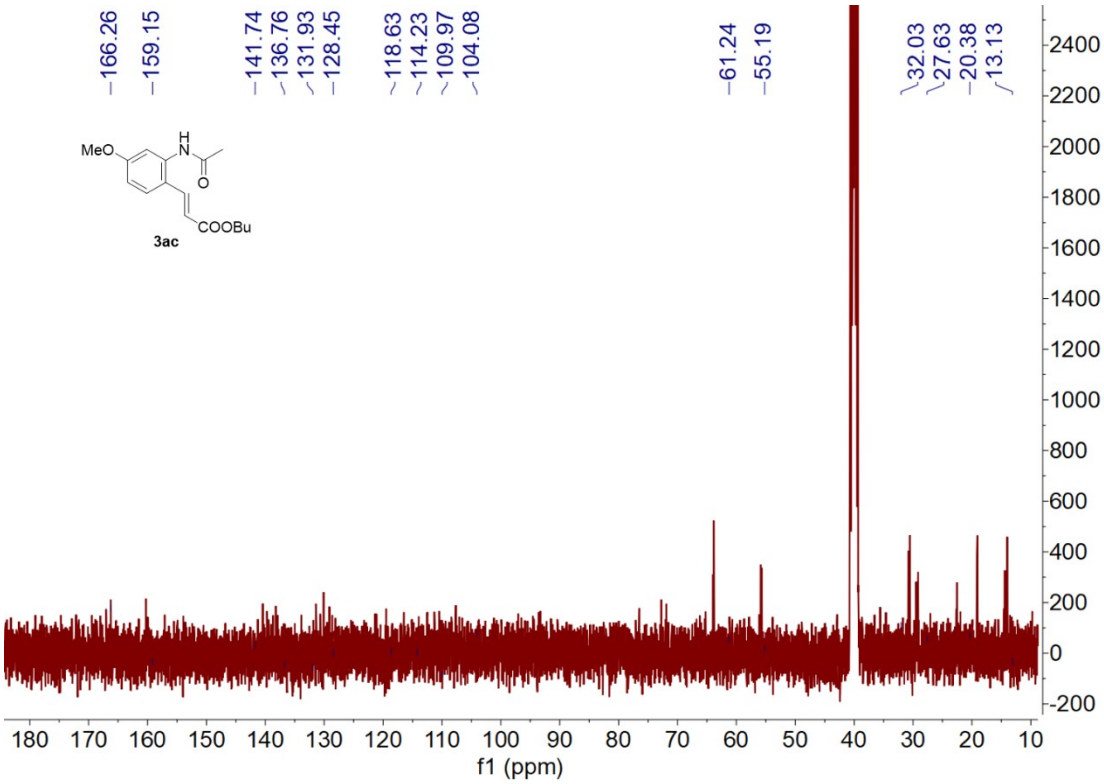
^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ab**



^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **3ac**

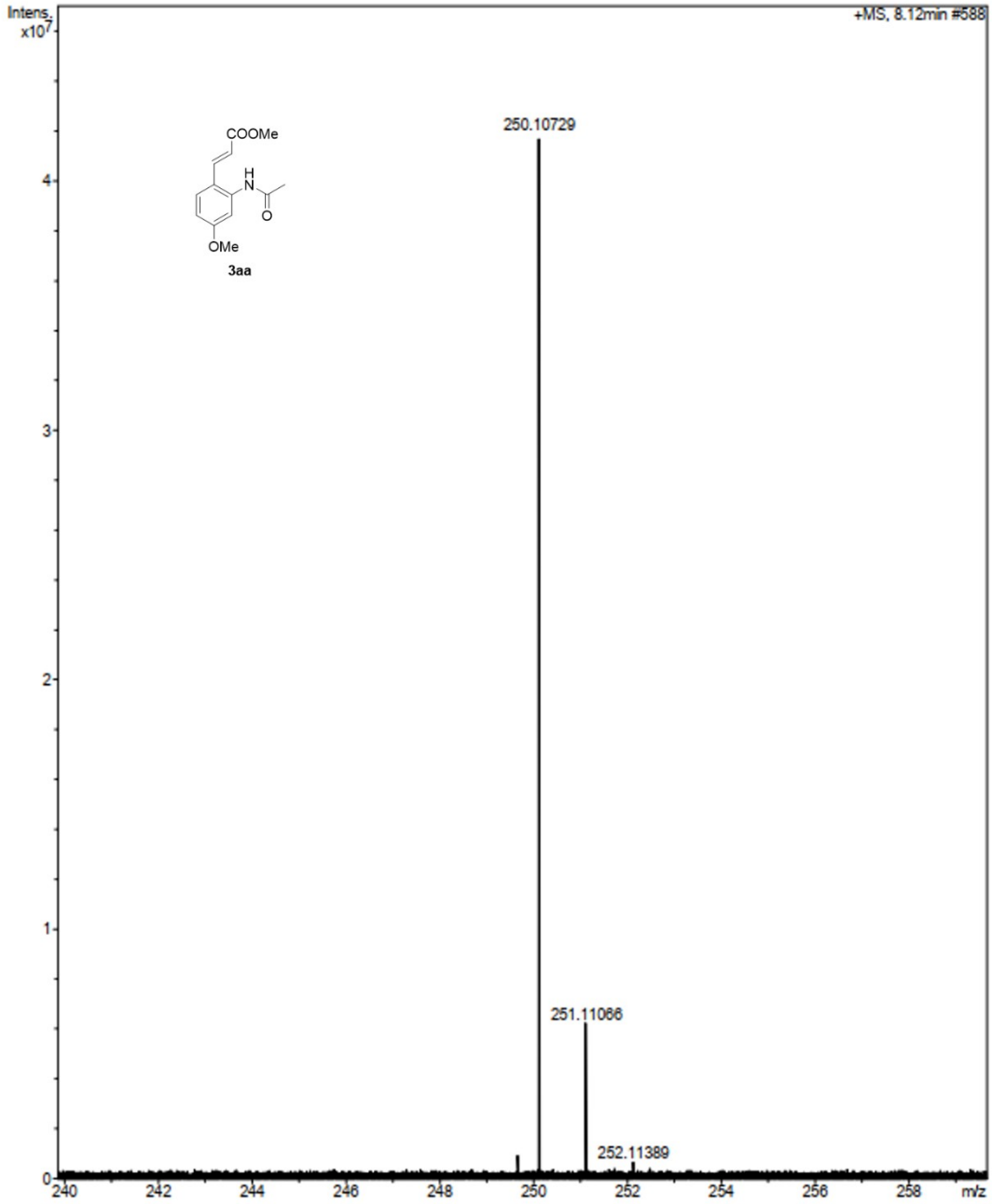


^{13}C NMR{1H} spectrum (100 MHz, DMSO-d_6) of **3ac**

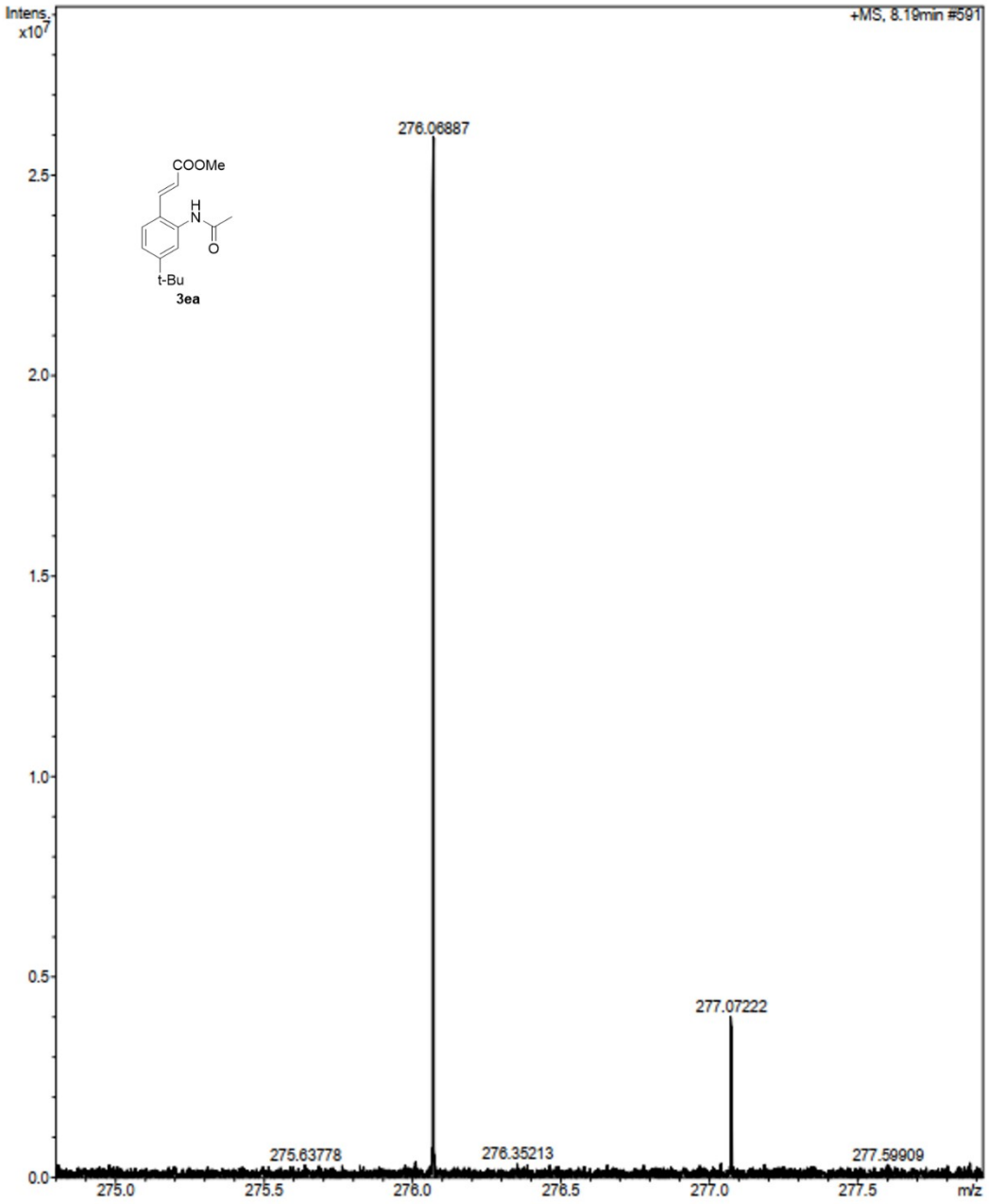


7. The HRMS spectra of the new compounds

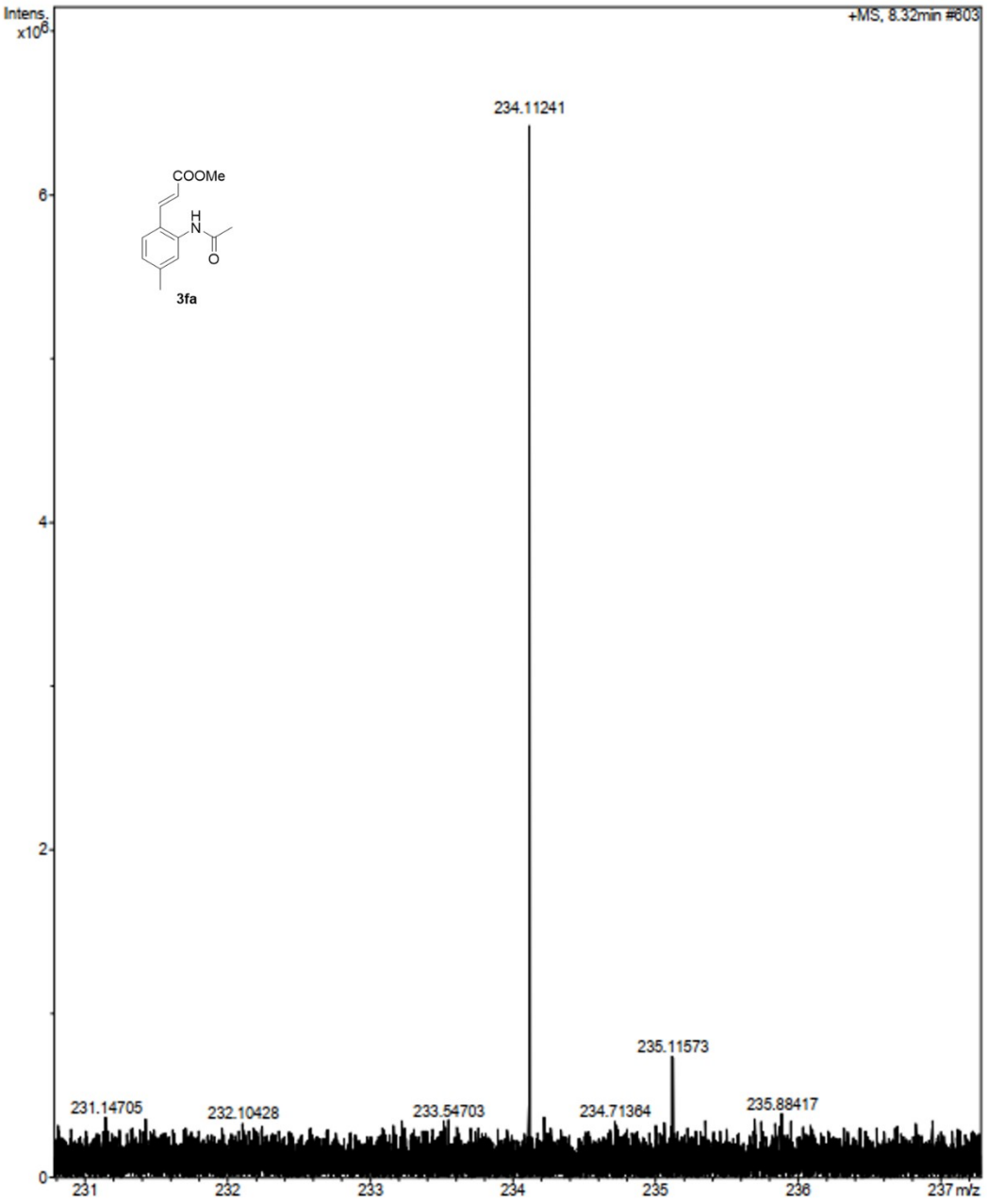
HRMS (ESI-TOF) spectrum of **3aa**



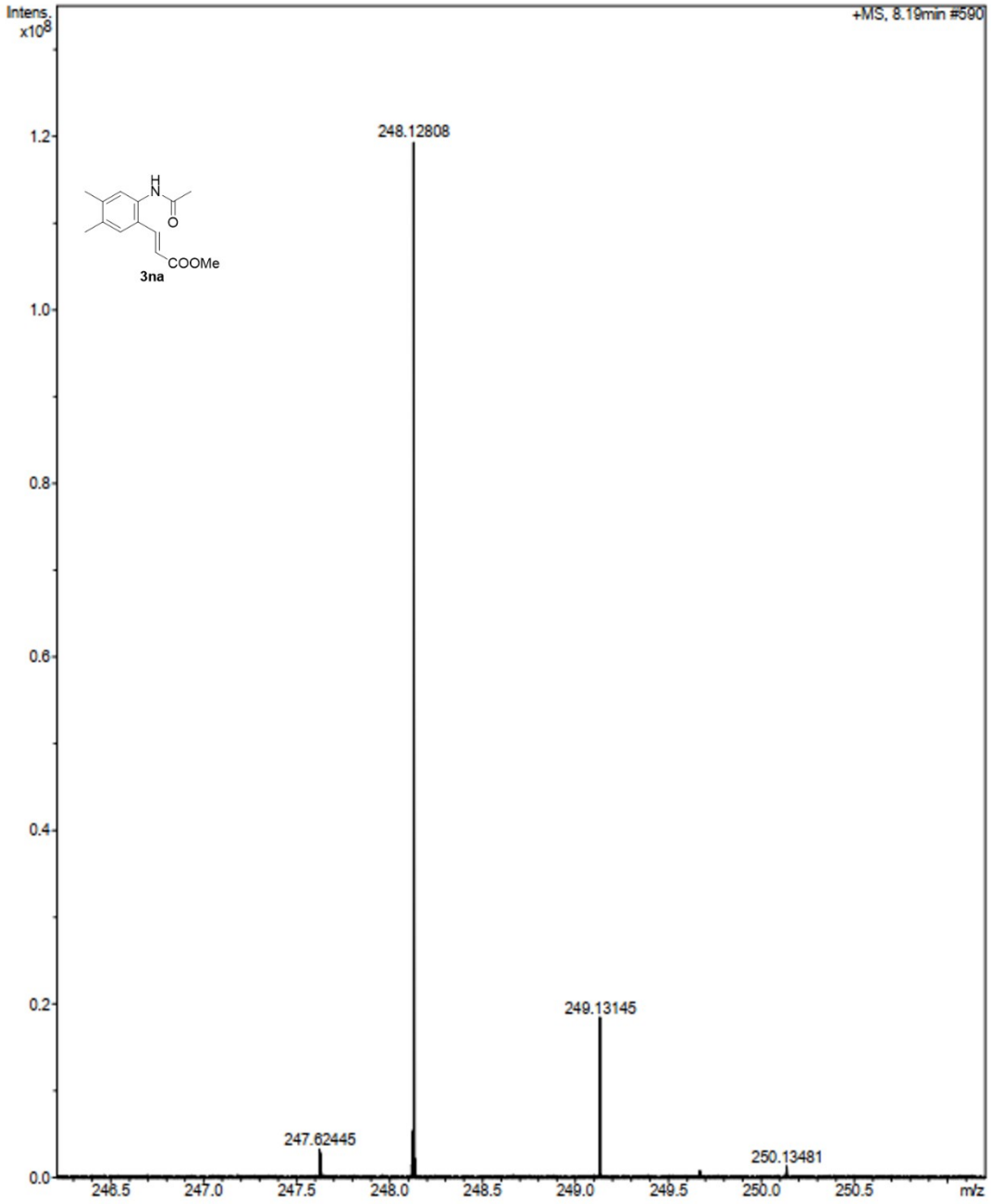
HRMS (ESI-TOF) spectrum of **3ea**



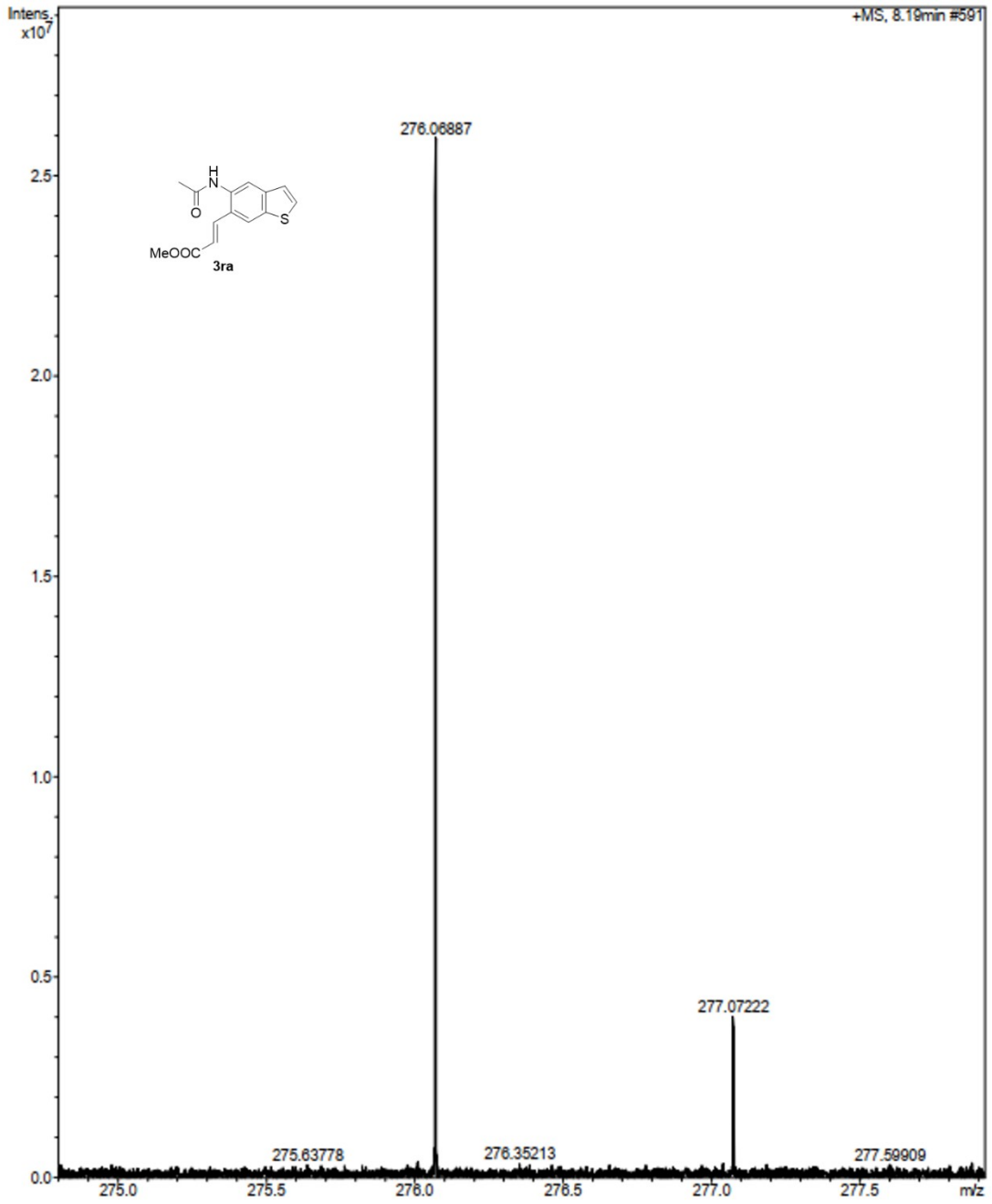
HRMS (ESI-TOF) spectrum of **3fa**



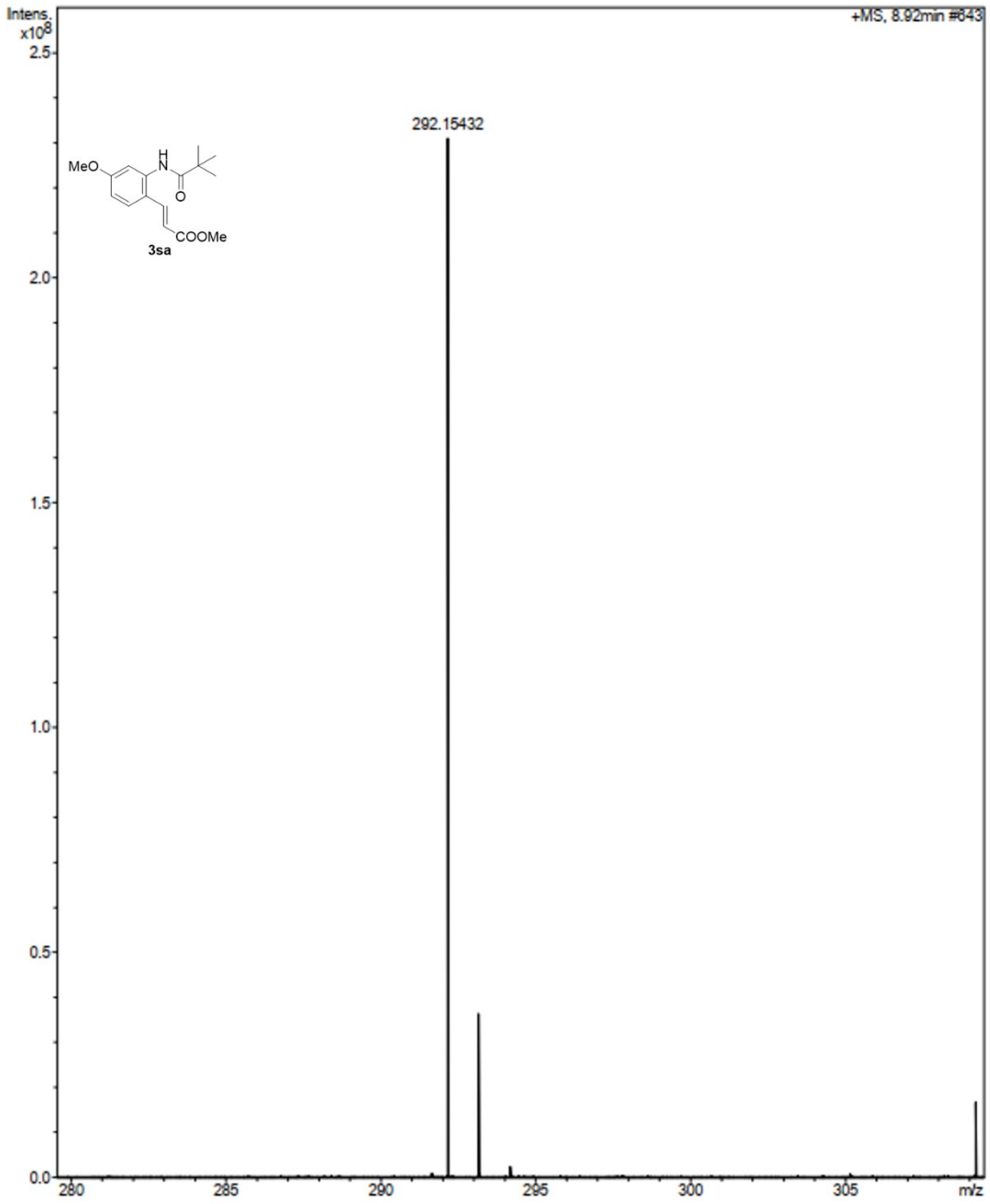
HRMS (ESI-TOF) spectrum of **3na**



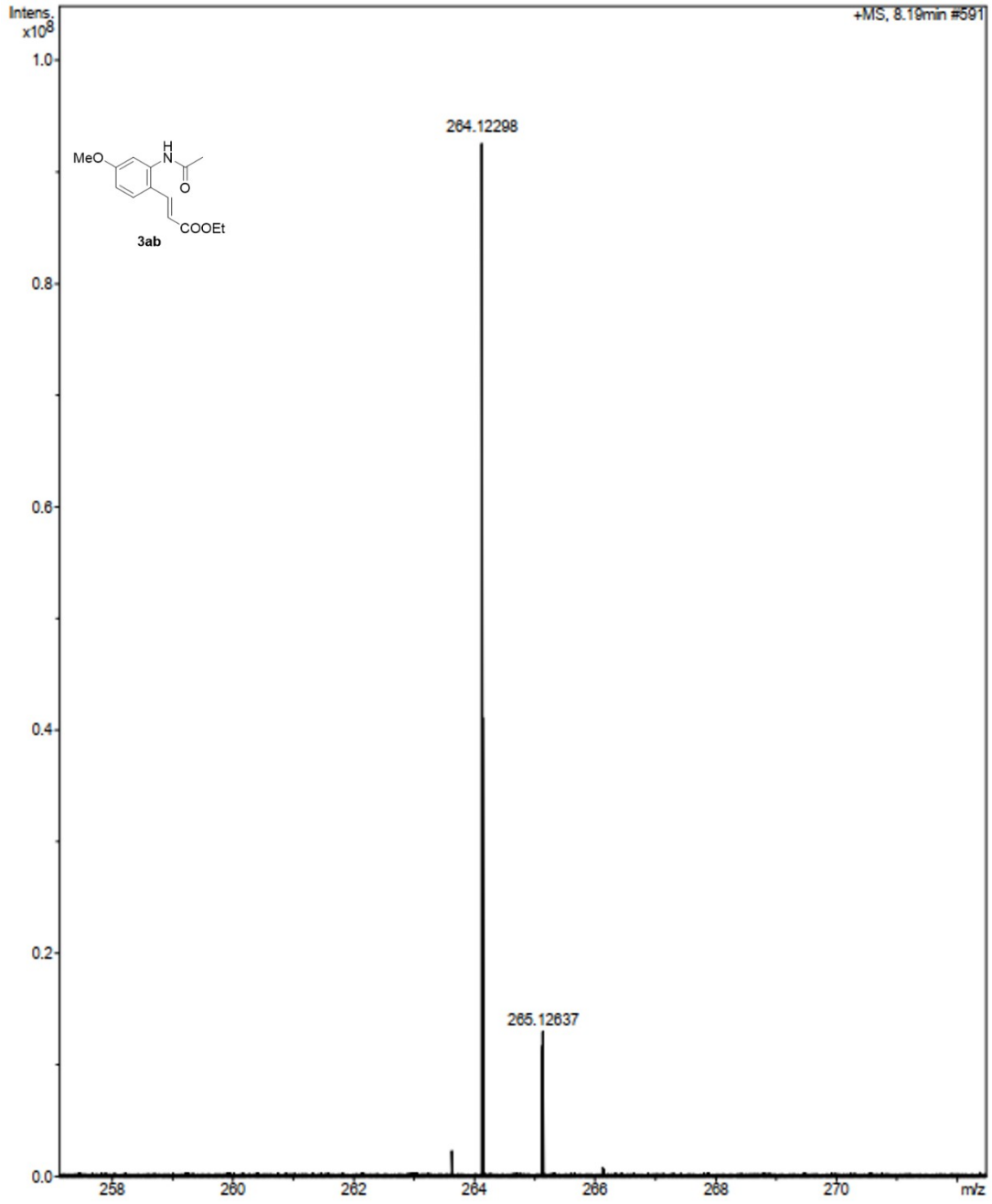
HRMS (ESI-TOF) spectrum of **3ra**



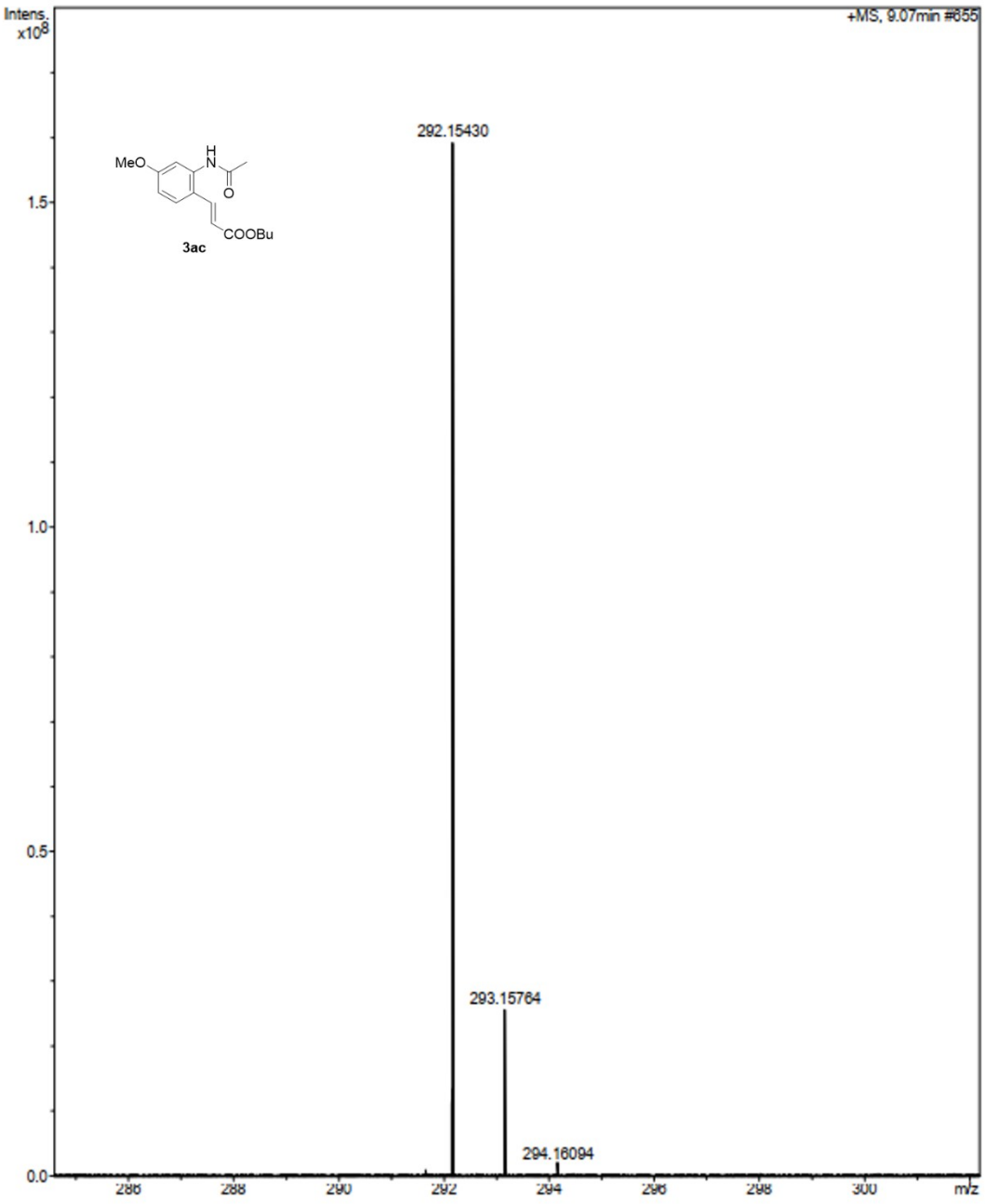
HRMS (ESI-TOF) spectrum of **3ra**



HRMS (ESI-TOF) spectrum of **3ab**



HRMS (ESI-TOF) spectrum of **3ac**



8. Reference

1 Y. Li, Y. Zhu, G. Tu, J. Zhang, Y. Zhao. Silver-catalyzed direct benzylation of acetanilide: a highly efficient approach to unsymmetrical triarylmethanes. RSC Adv, 2018, 8, 30374-30378

2 S. Lee, Y. You, K. Ohkubo, S. Fukuzumi, W. Nam. Highly efficient cycloreversion of photochromic dithienylethene compounds using visible light-driven photoredox catalysis. Chem. Sci., 2014, 5, 1463-1474.