Supporting Information

Synthesis, characterization, and α-glucosidase inhibitory activity of methyl proline derivatives of phenylpropanoid

Weiwei Zhang,*#[a] Huiwen Yang,#[a] Xiangdi Yao,[a] Ruipeng Li,[a] Yao Yao,[a] Wei Ma,[a] Kailiang Ma,[a] Lufei Shao[b] and Pengjuan Zhou[c]

[a] Address here. School of Basic Medical Sciences, Ningxia Medical University, Yinchuan 750004, PR China, E-mail: 20190033@nxmu.edu.cn.

[b] The Neurology department, General Hospital of Ningxia Medical University, Yinchuan 750004, PR China

[c] Institute of Agricultural Resources and Environment, Ningxia Academy of Agriculture and Forestry Science Yinchuan 750004, PR China

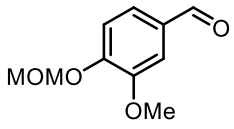
[#] W. Zhang and H. Yang contributed equally to this work.

Content

1. General Information

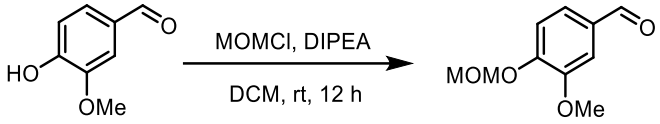
All oxygen and/or moisture-sensitive reactions were carried out under Ar atmosphere. Unless otherwise stated, the materials were obtained from commercial suppliers and used without further purification. During the experiment, reagents such as THF, dichloromethane (DCM), triethyl amine (Et_3N) and *N, N*-Dimethylformamide (DMF) are all purchased highly pure and extra dry reagents, which can be used immediately without further processing. Reactions were monitored using thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates with UV light, and phosphomolybdic acid/heat as developing agents. Silica gel 200-300 mesh was used for column chromatography. NMR spectra were recorded on Bruker 400 MHz spectrometers at 25 °C in suitable deuterated solvents. Chemical shifts are shown in δ ^{13}C NMR spectra were recorded with a complete proton decoupling environment. The chemical shift values are listed as δ_H and δ_C for ^1H and ^{13}C, respectively. Coupling constants (*J*) are reported in hertz (Hz) and the resonance multiplicity abbreviations used are s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; and comp, overlapping multiplets of magnetically non-equivalent protons. Mass spectrometric analysis was performed on an Agilent mass spectrometer (TOF analyzer).

2. Synthetic Procedure and Characterization Data of Products



4

3-methoxy-4-(methoxymethoxy)benzaldehyde (4)

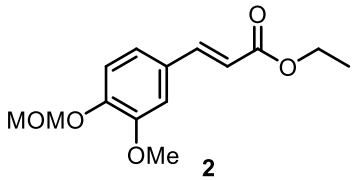


Vanillin **4**

A mixture of vanillin (1.60 g, 39.43 mmol), DIPEA (10.3 mL, 59.15 mmol), and MOMCl (3.0 mL, 39.82 mmol) in CH_2Cl_2 (100 mL) was stirred at 0 °C under Ar. After the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic phases were washed with saturated aqueous NaCl. The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:10) to give compound **4** as a pale yellow oil (7.50 g, 97% yield)

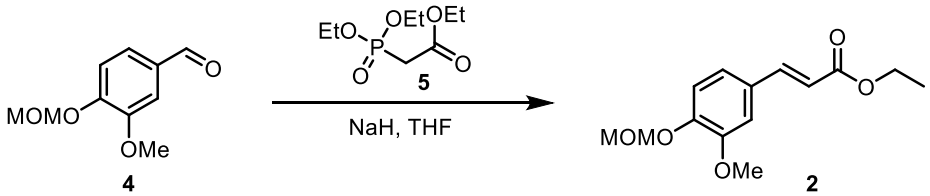
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.46 – 7.40 (m, 2H), 7.27 (d, J = 9.3 Hz, 1H), 5.33 (s, 2H), 3.95 (s, 3H), 3.52 (s, 3H).

HRMS (ESI): calcd for $C_{10}H_{13}O_4$ $[M+H]^+$ 197.0814, found 197.0818.



2

ethyl (*E*)-3-(3-methoxy-4-(methoxymethoxy)phenyl)acrylate (2)



4 **2**

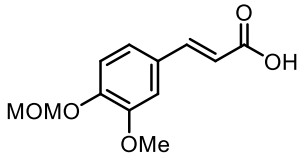
To a stirred suspension of triethyl phosphonoacetate **5** (7.96 mL, 40.14 mmol) in dry THF (100 mL), NaH (2.29 g, 57.35 mmol, 60% in the oil) was added at 0 °C. After the

suspension was stirred for 30 min. A solution of compound **4** (7.50 g, 38.23 mmol) in dry THF (100 mL) was added dropwise at r.t. Then the reaction mixture was stirred for 3-5 h. After reaction was completed (detected by TLC), saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with EtOAc (50 mL × 3). The organic phase was combined and washed with brine, dried over Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:10 to 1:3) to give compound **2** (8.65 g, 85% yield) as a pale yellow solid. mp 55.9-57.3 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 15.8 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.33 (d, J = 15.9 Hz, 1H), 5.26 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 3.51 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H).

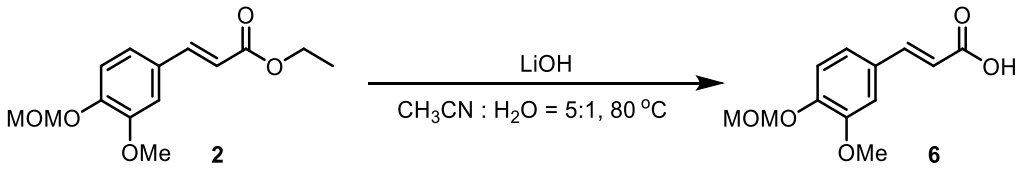
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 149.9, 148.6, 144.5, 129.0, 122.3, 116.7, 116.0, 110.5, 95.3, 60.5, 56.4, 56.0, 14.5.

HRMS (ESI): calcd for $C_{14}H_{18}O_5Na$ $[M+Na]^+$ 289.1052, found 289.1057.



6

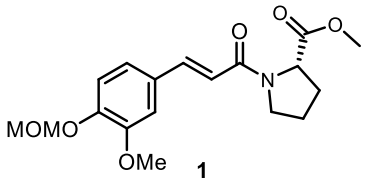
(*E*)-3-(3-methoxy-4-(methoxymethoxy)phenyl)acrylic acid (6)



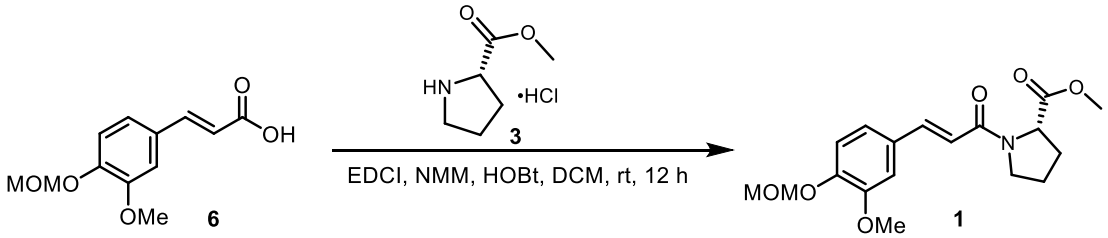
2 **6**

The compound **2** (300.0 mg, 0.54 mmol) was dissolved in 6.0 mL acetonitrile and water mixed solvents and stirred. LiOH (4.34 g, 17.27 mmol) was slowly added to the reaction at 80 ℃ for 3 h. After the mixture was cooled to room temperature, solvent was removed by evaporation under reduced pressure. The combined organic phases were washed with saturated aqueous NaCl. The mixture was extracted with CH_2Cl_2 (50 mL × 3). The organic phase was combined and washed with brine, dried over Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:10 to 1:3) to give compound **6** (96 mg,

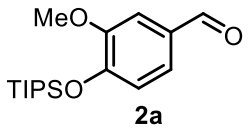
75% yield) as a white powder.



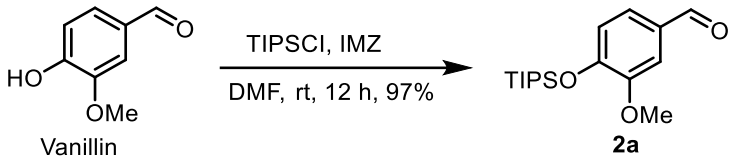
ethyl (*E*)-(3-(3-methoxy-4-(methoxymethoxy)phenyl)acryloyl)-*L*-prolinate (1)



The crude product **6** (0.65 mmol) and **3** (128 mg, 0.72 mmol) was dissolved in CH_2Cl_2 (15 ml) , HOBt (44mg, 0.33mmol), EDCI(187mg, 0.98 mmol), and NMM(0.145 mL, 1.3 mmol) was added. Then the reaction mixture was stirred at r.t. for 12 h. After reaction was completed (detected by TLC), 10 ml water was added to quench the reaction, the aqueous and organic layers were separated; the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3), dried over Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:5 to 2:1) to give compound **1** (183 mg, 77%) as a colorless oil



3-methoxy-4-((triisopropylsilyl)oxy)benzaldehyde（2a）



Under N_2 atmosphere, a mixture of vanillin (6.0 g, 39.43 mmol), imidazole (5.37 g, 78.87 mmol) and 100 ml dry DMF was stirred for 5 min. To this mixture was added TIPSCl (16.88 mL, 78.87 mmol), and the solution was then stirred for 7 h. After reaction was completed (detected by TLC), the reaction was quenched with H_2O and extracted with EtOAc. The combined organic phase was washed with brine, dried over

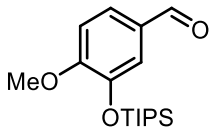
Na_2SO_4, and evaporated under vacuum. The resulting residue was purified by column chromatography over silica gel (gradient eluent of EtOAc/petroleum ether, 1:20 to 1:5) to afford **2a** (11.92 g, 98%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.40 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 1.33 – 1.23 (m, 3H), 1.12 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 152.0, 151.7, 130.7, 126.4, 120.3, 110.1, 55.6, 17.9, 13.0.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1890.

4-methoxy-3-((triisopropylsilyl)oxy)benzaldehyde (3a)



3a

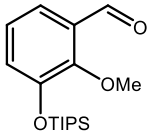
Under the same reaction conditions, compound **3a** (5.77 g, 95%) was obtained as a colorless oil from isovanillin.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.46 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.39 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 3H), 1.32 – 1.23 (m, 3H), 1.13 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 156.7, 146.2, 130.2, 126.3, 119.4, 111.2, 55.7, 18.0, 12.9.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1890.

2-methoxy-3-((triisopropylsilyl)oxy)benzaldehyde (4a)



4a

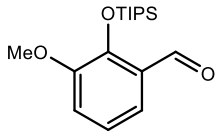
Under the same reaction conditions, compound **4a** (812 mg, 80%) was obtained as a colorless oil from 2-methoxy-3-hydroxybenzaldehyde.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.42 (t, *J* = 5.0 Hz, 1H), 7.13 (t, *J* = 5.0 Hz, 1H), 7.05 (td, *J* = 8.0, 2.6 Hz, 1H), 3.97 (s, 3H), 1.36 – 1.24 (m, 3H), 1.15 – 1.10 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 154.5, 149.9, 130.5, 126.6, 124.3, 120.2, 62.4, 18.0, 12.9.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1888.

3-methoxy-2-((triisopropylsilyl)oxy)benzaldehyde (5a)



5a

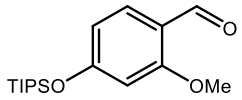
Under the same reaction conditions, compound **5a** (2.49 g, 82%) was obtained as a colorless oil from o-vanillin.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.38 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.94 (td, *J* = 7.9, 0.9 Hz, 1H), 3.83 (s, 3H), 1.35 – 1.24 (m, 3H), 1.11 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 150.6, 150.1, 127.5, 120.8, 119.2, 116.6, 55.2, 18.1, 14.1.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1887.

2-methoxy-4-((triisopropylsilyl)oxy)benzaldehyde (6a)



6a

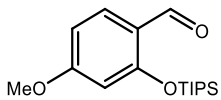
Under the same reaction conditions, compound **6a** (1.3 g, 43%) was obtained as a colorless oil from 4-hydroxy-2-methoxybenzaldehyde.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 6.44 (s, 1H), 3.88 (s, 3H), 1.36 – 1.22 (m, 3H), 1.15 – 0.98 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 163.8, 163.6, 130.6, 119.2, 112.6, 103.2, 55.7, 18.0, 12.8.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1890.

4-methoxy-2-((triisopropylsilyl)oxy)benzaldehyde (7a)



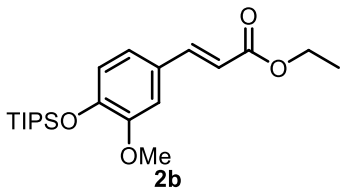
7a

Under the same reaction conditions, compound **7a** (1.89 g, 62%) was obtained as a colorless oil from 2-hydroxy-4-methoxybenzaldehyde.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.79 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 6.37 (s, 1H), 3.83 (s, 3H), 1.41 – 1.29 (m, *J* = 6.7, 5.8 Hz, 3H), 1.19 – 1.10 (m, 18H).

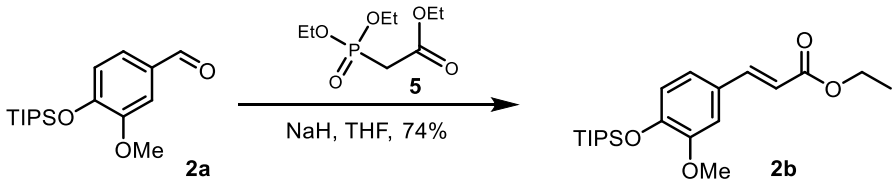
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 165.9, 161.3, 130.1, 121.1, 107.5, 104.8, 55.7, 18.1, 13.1.

HRMS (ESI): calcd for $C_{17}H_{29}O_3Si$ $[M+H]^+$ 309.1886, found 309.1884.



2b

ethyl (*E*)-3-(3-methoxy-4-((triisopropylsilyl)oxy)phenyl)acrylate (2b)



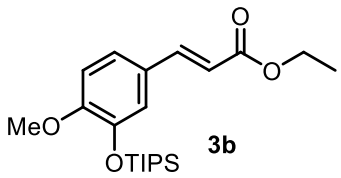
To a stirred suspension of Triethyl phosphonoacetate **5** (4.73 ml, 23.80 mmol) in dry THF (100 ml), NaH (1.36 g, 34.04 mmol) was added at 0 ℃. After the suspension was stirred for 30 min. A solution of compound **2a** (7.0 g, 22.69 mmol) in dry THF (100 ml) was added dropwise at r.t. Then the reaction mixture was stirred for 3-5 h. After reaction was completed (detected by TLC), 50 ml saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with EtOAc (50 ml × 3). The organic phase was combined and washed with brine, dried over Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:20 to 1:5) to give compound **2b** (6.36 g, 74%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.22 (m, 3H), 1.13 – 1.06 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.46, 151.25, 148.15, 144.90, 128.10, 122.32, 120.66, 115.90, 110.94, 60.45, 55.56, 18.00, 14.51, 13.04.

HRMS(ESI) calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2307.

ethyl (*E*)-3-(4-methoxy-3-((triisopropylsilyl)oxy)phenyl)acrylate (3b)



3b

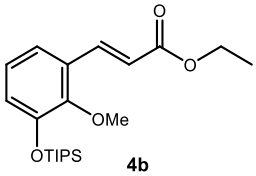
Using the same experimental procedure as described above, compound **3b** (1.2 g, 83%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.9 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.21 (m, 3H), 1.12 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 153.2, 145.7, 144.8, 127.4, 123.0, 119.3, 115.6, 111.7, 60.5, 55.5, 18.0, 14.5, 13.0.

HRMS (ESI): calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2308.

ethyl (*E*)-3-(2-methoxy-3-((triisopropylsilyl)oxy)phenyl)acrylate (4b)



4b

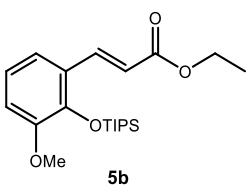
Compound **4b** (850 mg, 58%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.2 Hz, 1H), 7.15 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.48 (d, *J* = 16.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.31 – 1.25 (m, 3H), 1.13 – 1.09 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 150.4, 149.9, 139.8, 129.3, 124.2, 122.3, 120.0, 119.4, 61.3, 60.6, 18.0, 14.5, 12.9.

HRMS (ESI): calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2308.

ethyl (*E*)-3-(3-methoxy-2-((triisopropylsilyl)oxy)phenyl)acrylate (5b)



5b

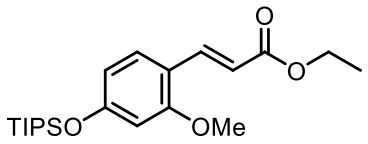
Compound **5b** (1.13 g, 77%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 16.2 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.92 – 6.80 (m, 2H), 6.34 (d, *J* = 16.2 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.24 (m, 3H), 1.11 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 150.5, 145.2, 140.1, 126.1, 120.8, 118.3, 117.9, 112.6, 60.4, 55.0, 18.2, 18.2, 14.5, 14.0.

HRMS (ESI): calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2306.

ethyl (*E*)-3-(2-methoxy-4-((triisopropylsilyl)oxy)phenyl)acrylate (6b)



6b

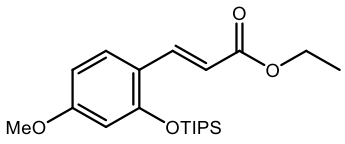
Compound **6b** (960 mg, 60%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.1 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.45 – 6.39 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.23 (m, 3H), 1.14 – 1.08 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 159.9, 159.6, 140.1, 130.3, 116.8, 116.2, 112.2, 103.5, 60.3, 55.5, 18.0, 14.6, 12.8.

HRMS (ESI): calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2307.

ethyl (*E*)-3-(4-methoxy-2-((triisopropylsilyl)oxy)phenyl)acrylate (7b)



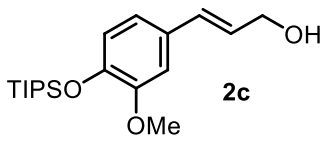
7b

Compound **7b** (1.5 g, 65%) was obtained as a colorless oil.

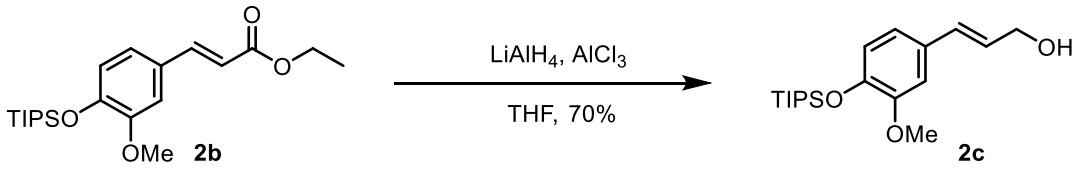
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 16.2 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.37 – 1.28 (m, 6H), 1.16 – 1.12 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 167.7, 162.4, 162.4, 156.5, 139.8, 128.4, 118.8, 118.7, 115.2, 115.1, 107.2, 107.2, 105.3, 105.2, 60.2, 60.2, 55.5, 55.4, 18.1, 18.1, 14.5, 13.0, 13.0.

HRMS (ESI): calcd for $C_{21}H_{35}O_4Si$ $[M+H]^+$ 379.2305, found 379.2309.



(*E*)-3-(3-methoxy-4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (2c)



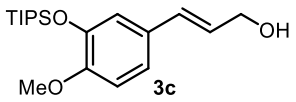
A mixture of compound **2b** (400 mg, 1.056 mmol), $LiAlH_4$ (120.3 mg, 3.17 mmol) and $AlCl_3$ (141 mg, 1.056 mmol) in dry THF (100 ml) was stirred at 0 ℃for 30 min. After reaction was completed (detected by TLC), add 0.12 ml of water, 0.24 ml of 10% sodium hydroxide solution, and 0.36 ml of water slowly in sequence, and quench the reaction in three steps. Filter out the solid impurities through diatomaceous earth to obtain the filtrate, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether , 1:10 to 1:2) to give compound **2c** (248.78 mg, 70%) as a pale yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.82 (d, J = 2.4 Hz, 2H), 6.57 – 6.47 (m, 1H), 6.22 (dt, J = 15.8, 6.0 Hz, 1H), 4.29 (dd, J = 6.0, 1.4 Hz, 2H), 3.81 (s, 3H), 1.29 – 1.20 (m, 3H), 1.12 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 145.73, 131.62, 130.33, 126.41, 120.53, 119.70, 110.02, 64.02, 55.57, 18.02, 13.01.

HRMS(ESI) calcd for C19H33O3Si $[M+H]^+$ 337.2199, found 337.2194.

(*E*)-3-(4-methoxy-3-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (3c)



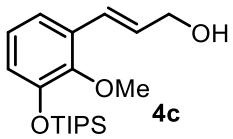
Compound **3c** (673.1 mg, 88%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.23 – 6.13 (m, 1H), 4.29 (d, *J* = 5.2 Hz, 2H), 3.80 (s, 3H), 1.29 – 1.20 (m, 3H), 1.12 – 1.06 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 145.6, 131.4, 129.7, 126.1, 120.3, 118.2, 111.9, 64.1, 55.6, 18.0, 13.0.

HRMS (ESI): calcd for $C_{19}H_{33}O_3Si$ $[M+H]^+$ 337.2199, found 337.2194.

(*E*)-3-(2-methoxy-3-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (4c)



4c

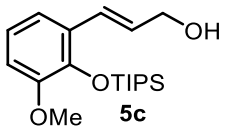
Compound **4c** (370 mg, 49%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.79 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.38 (dt, *J* = 16.1, 5.9 Hz, 1H), 4.34 (dd, *J* = 5.9, 1.5 Hz, 2H), 3.80 (s, 3H), 1.32 – 1.25 (m, 3H), 1.12 – 1.10 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 148.8, 131.3, 129.7, 126.0, 124.0, 119.9, 118.8, 64.3, 60.9, 18.1, 12.9.

HRMS (ESI): calcd for $C_{19}H_{33}O_3Si$ $[M+H]^+$ 337.2199, found 337.2191.

(*E*)-3-(3-methoxy-2-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (5c)



5c

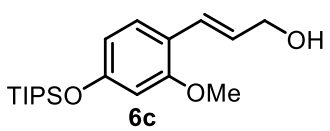
Compound **5c** (606 mg, 60.4%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.84 (t, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.32 – 6.22 (m, 1H), 4.31 (d, *J* = 4.2 Hz, 2H), 3.77 (s, 3H), 1.30 – 1.22 (m, 3H), 1.10 – 1.06 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 143.3, 128.4, 127.0, 120.7, 118.0, 110.4, 64.5, 54.9, 18.2, 14.0.

HRMS (ESI): calcd for $C_{19}H_{33}O_3Si$ $[M+H]^+$ 337.2199, found 337.2203.

(*E*)-3-(2-methoxy-4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (6c)



6c

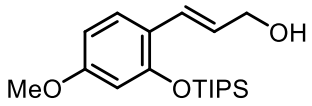
Compound **6c** (715 mg, 84%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.45 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 6.35 – 6.22 (m, 1H), 4.28 (d, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 1.33 – 1.22 (m, 3H), 1.14 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 157.2, 127.7, 127.0, 126.5, 118.8, 112.0, 103.5, 64.7, 55.5, 18.1, 12.8.

HRMS (ESI): calcd for $C_{19}H_{32}O_3NaSi$ $[M+Na]^+$ 359.2018, found 359.2014.

(*E*)-3-(4-methoxy-2-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (7c)



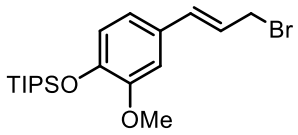
7c

Compound **7c** (1.2 g, 90%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.49 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 6.20 (dt, *J* = 16.0, 6.2 Hz, 1H), 4.29 (t, *J* = 5.0 Hz, 2H), 3.77 (s, 3H), 1.34 – 1.29 (m, 3H), 1.13 – 1.11 (m, 18H).

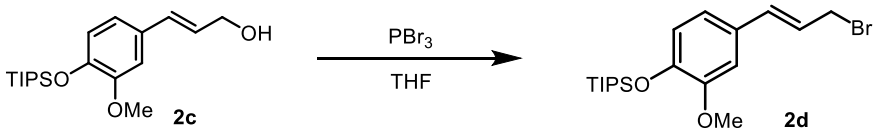
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 154.5, 127.1, 126.9, 126.0, 120.7, 106.6, 105.3, 64.7, 55.4, 18.2, 18.2, 13.1.

HRMS (ESI): calcd for $C_{19}H_{33}O_3Si$ $[M+H]^+$ 337.2199, found 337.2194.

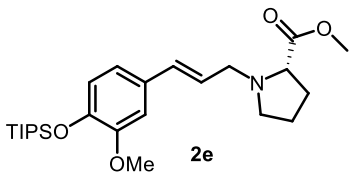


2d

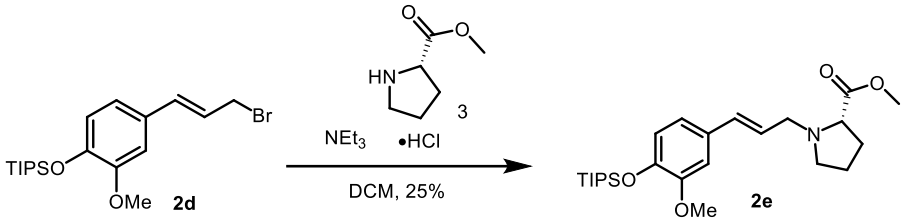
(*E*)-(4-(3-bromoprop-1-en-1-yl)-2-methoxyphenoxy)triisopropylsilane (2d)



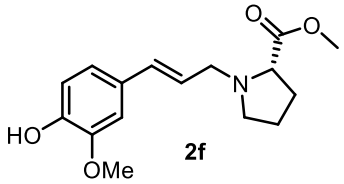
Under Ar_2 atmosphere, to a mixture of compound **2c** (250 mg, 0.74 mmol) and 10 ml dry THF, PBr_3 (0.08 ml, 0.85 mmol) was added slowly at 0 ℃. Then the reaction mixture was stirred for 30 min. After reaction was completed (detected by TLC), 20 ml ice water was added to quench the reaction. The mixture was extracted with EtOAc (20 ml × 3). The organic phase was combined and washed with brine, dried over Na_2SO_4 , evaporated under vacuum to afford crude product **2d**, which was immediately used without further purification.



methyl (*E*)-(3-(3-methoxy-4-((triisopropylsilyl)oxy)phenyl)allyl)-*L*-prolinate (2e)

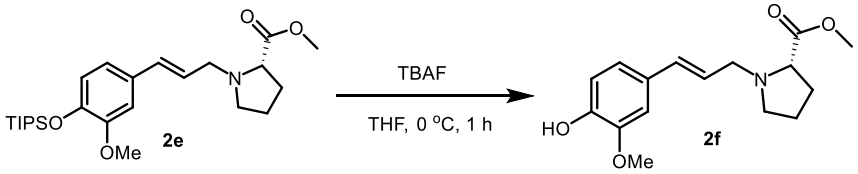


The crude product **2d** (0.74 mmol) was dissolved in CH_2Cl_2 (100 ml) with triethylamine (0.237 ml, 1.702 mmol) and methyl L-prolinate hydrochloride **3** (122.6 mg, 0.74 mmol) was add. Then the reaction mixture was stirred at r.t. for 12 h. After reaction was completed (detected by TLC), 100 ml water was added to quench the reaction, the aqueous and organic layers were separated; the aqueous layer was extracted with CH_2Cl_2 (100 mL × 3), dried over Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:10 to 2:1) to give compound **2e** (82.8 mg, 25%) as a colorless oil



methyl (*E*)-(3-(4-hydroxy-3-methoxyphenyl)allyl)-*L*-prolinate (2f)

previously reported compound：*N-trans*-ferulic-*L*-proline methyl ester



Under Ar_2 atmosphere, to a mixture of **2e** (240 mg, 0.54 mmol) in 10 ml dry THF, tetrabutyl ammonium fluoride solution (1 mol/L in THF) was added slowly at 0 ℃. Then the reaction mixture was stirred for 2 h. After reaction was completed (detected by TLC), 10 ml water was added to quench the reaction. The mixture was extracted with EtOAc. The organic phase was combined and washed with brine, dried over

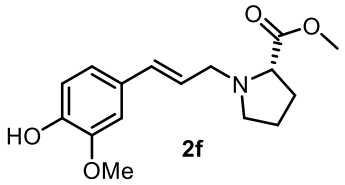
Na_2SO_4, evaporated under vacuum. The residue was purified by chromatography on silica gel (gradient eluent of EtOAc/petroleum ether, 1:10 to 4:1) to afford **2f** (34.6 mg, 22%) as a colourless oil

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (s, 1H), 6.99 (d, J = 1.9 Hz, 1H), 6.78 (dd, J = 8.1, 1.9 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.7 Hz, 1H), 3.77 (s, 3H), 3.57 (s, 3H), 3.39 – 3.35 (m, 1H), 3.23 – 3.13 (m, 2H), 3.02 – 2.93 (m, 1H), 2.45 – 2.34 (m, 1H), 2.10 – 1.97 (m, 1H), 1.85 – 1.70 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 147.7, 146.3, 131.6, 128.3, 124.1, 119.5, 115.4, 109.7, 64.2, 55.9, 55.5, 52.7, 51.3, 28.9, 22.9.

HRMS(ESI) calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1553.

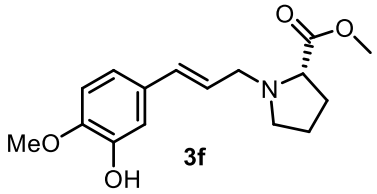
Table S1. Comparison of the ^{1}H NMR (DMSO-d$_6$) and ^{13}C NMR (DMSO-d$_6$) data of natural and our synthetic *N-trans*-ferulic-*L*-proline methyl ester.



2f

No.	^{1}H NMR		^{13}C NMR	
	Natural (600 MHz) δ (*J*, Hz)	Synthetic (400 MHz) δ (*J*, Hz)	Natural (150 MHz) δ	Synthetic (100 MHz) δ
1	3.72 (dd, 12.8, 7.2, H-1a) 3.56 (dd, 12.8, 7.2, H-1b)		56.0	55.9
2	6.11 (dt, 16.0, 7.2)	6.09 (dt, 15.8, 6.7)	118.5	119.5
3	6.58 (d, 16.0)	6.37 (d, 15.8)	136.4	131.6
4			127.4	128.3
5	7.00 (d, 2.0)	6.99 (d, 1.9)	109.2	109.7
6			148.0	147.7
7			147.4	146.3
8	6.72 (d, 8.0)	6.70 (d, 8.0)	115.8	115.4
9	6.81 (dd, 8.0, 2.0)	6.78 (dd, 8.1, 1.9)	120.4	124.1
1’	3.50 (m)	3.39-3.35 (m)	65.1	64.2
2’	2.20 (m, H-2’a); 1.90 (m, H-2’b)	2.10-1.97 (m, 1 H)	30.2	28.9
3’	1.85 (m, H-3’a); 1.68 (m, H-3’b)	1.85-1.70 (m, 3 H)	23.5	22.9
4’	3.41 (m, H-4’a); 2.80 (m, H-4’b)		53.2	52.7
5’	-		169.1	174.0
6-OMe	3.76 (s)	3.77 (s)	55.9	55.5
5’-OMe	3.66 (s)	3.57 (s)	51.5	51.3

methyl (*E*)-(3-(3-hydroxy-4-methoxyphenyl)allyl)-*L*-prolinate (3f)



3f

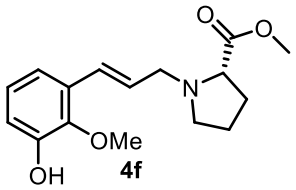
Compound **3f** was obtained as a colorless oil (40 mg, 25% yield)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 1H), 6.88 – 6.81 (m, 2H), 6.76 (dd, J = 8.3, 2.1 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 6.01 (dt, J = 15.6, 6.7 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 3.34 – 3.26 (m, 1H), 3.25 – 3.13 (m, 2H), 3.02 – 2.90 (m, 1H), 2.40 (q, J = 7.9 Hz, 1H), 2.11 – 1.95 (m, 1H), 1.85 – 1.67 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 147.4, 146.5, 131.4, 129.8, 124.7, 117.8, 112.7, 112.1, 64.2, 55.9, 55.6, 52.8, 51.3, 28.9, 22.9.

HRMS (ESI): calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1550.

methyl (*E*)-(3-(3-hydroxy-2-methoxyphenyl)allyl)-*L*-prolinate (4f)



4f

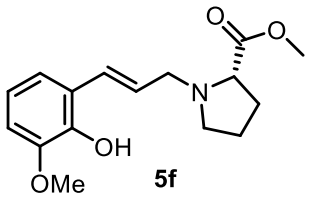
Compound **4f** was obtained as a colorless oil (44 mg, 28% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 7.7 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 14.0, 6.4 Hz, 1H), 3.66 (s, 3H), 3.56 (s, 3H), 3.42 – 3.38 (m, 1H), 3.29 – 3.18 (m, 2H), 3.02 – 2.93 (m, 1H), 2.43 (q, J = 8.1 Hz, 1H), 2.11 – 1.96 (m, 1H), 1.84 – 1.68 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 150.4, 145.0, 130.5, 128.2, 126.0, 124.1, 116.4, 115.7, 64.2, 60.1, 56.2, 52.8, 51.4, 29.0, 23.0.

HRMS (ESI): calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1553.

methyl (*E*)-(3-(2-hydroxy-3-methoxyphenyl)allyl)-*L*-prolinate (5f)



5f

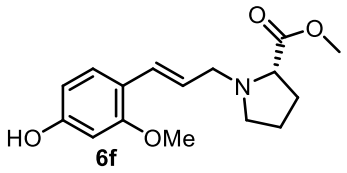
Compound **5f** was obtained as a colorless oil (36 mg, 23% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 1H), 6.99 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 7.9 Hz, 1H), 6.77 – 6.67 (m, 2H), 6.21 (dt, J = 15.1, 6.8 Hz, 1H), 3.78 (s, 3H), 3.56 (s, 3H), 3.37 – 3.34 (m, 1H), 3.26 – 3.15 (m, 2H), 3.02 – 2.91 (m, 1H), 2.40 (q, J = 8.0 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.84 – 1.67 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 147.8, 143.6, 126.9, 126.4, 123.8, 118.8, 118.2, 110.5, 64.2, 56.5, 55.8, 52.8, 51.4, 28.9, 23.0.

HRMS (ESI): calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1552.

methyl (*E*)-(3-(4-hydroxy-2-methoxyphenyl)allyl)-*L*-prolinate (6f)



6f

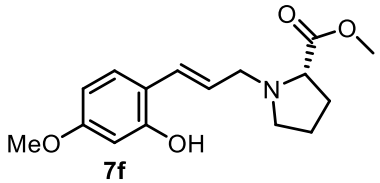
Compound **6f** was obtained as a colorless oil (31 mg, 20% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.22 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 15.9 Hz, 1H), 6.37 (d, J = 2.3 Hz, 1H), 6.32 (dd, J = 8.4, 2.3 Hz, 1H), 6.02 (dt, J = 16.0, 6.8 Hz, 1H), 3.73 (s, 3H), 3.56 (s, 3H), 3.32 – 3.29 (m, 1H), 3.21 – 3.13 (m, 2H), 2.98 – 2.92 (m, 1H), 2.39 (q, J = 8.2 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.81 – 1.69 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 174.0, 158.3, 157.3, 127.2, 126.1, 124.0, 116.3, 107.4, 98.9, 64.1, 56.5, 55.2, 52.7, 51.3, 28.9, 22.9.

HRMS (ESI): calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1542.

methyl (*E*)-(3-(2-hydroxy-4-methoxyphenyl)allyl)-*L*-prolinate (7f)



7f

Compound **7f** was obtained as a colorless oil (47 mg, 30% yield).

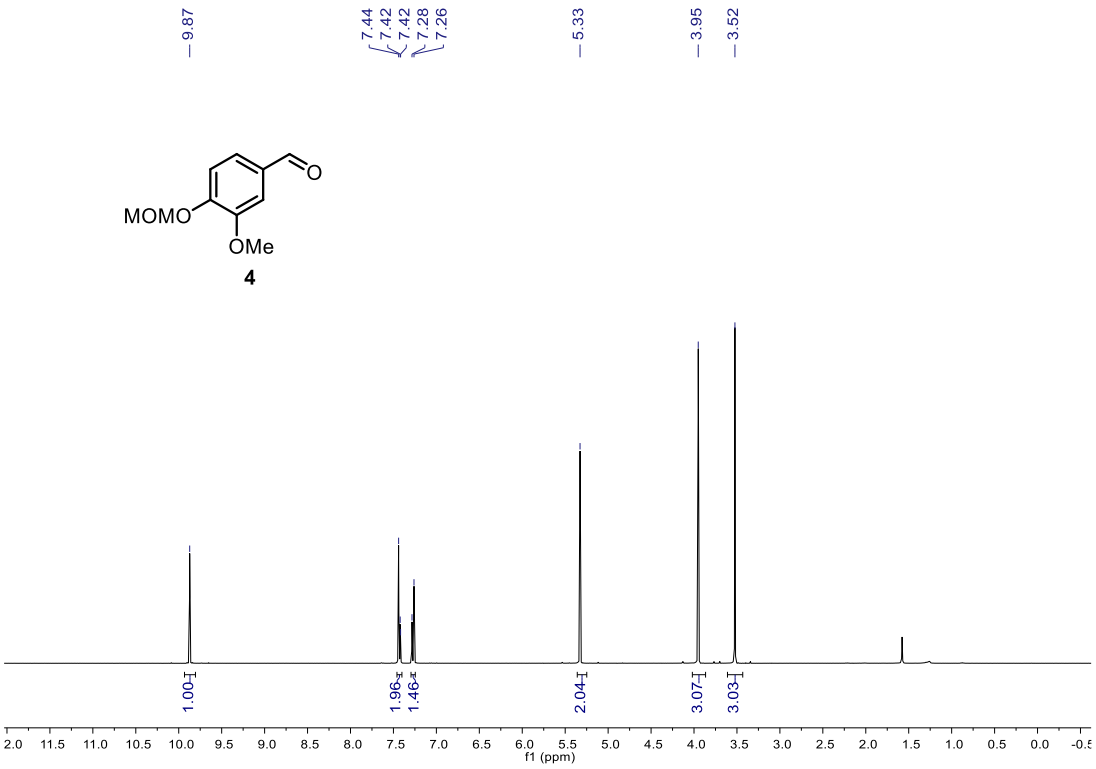
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.27 (dd, J = 8.5, 1.7 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.36 (dd, J = 10.7, 2.2 Hz, 2H), 6.08 (ddd, J = 16.9, 7.7, 6.0 Hz, 1H), 3.68 (s, 3H), 3.57 (s, 3H), 3.34 – 3.29 (m, 1H), 3.22 – 3.12 (m, 2H), 3.00 – 2.92 (m, 1H), 2.43 – 2.34 (m, 1H), 2.09 – 1.98 (m, 1H), 1.83 – 1.66 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 159.5, 155.6, 127.4, 126.4, 124.1, 116.6, 105.1, 101.1, 64.2, 56.6, 54.9, 52.7, 51.3, 28.9, 22.9.

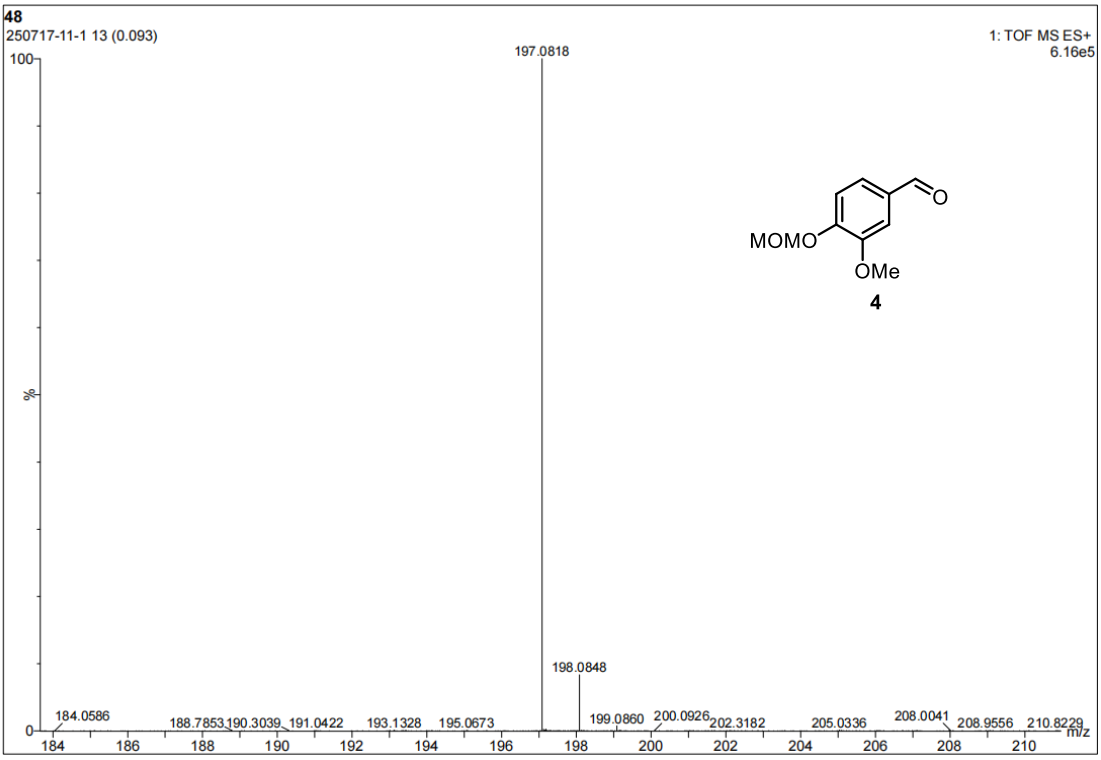
HRMS (ESI): calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1549, found 292.1543.

3. Spectra

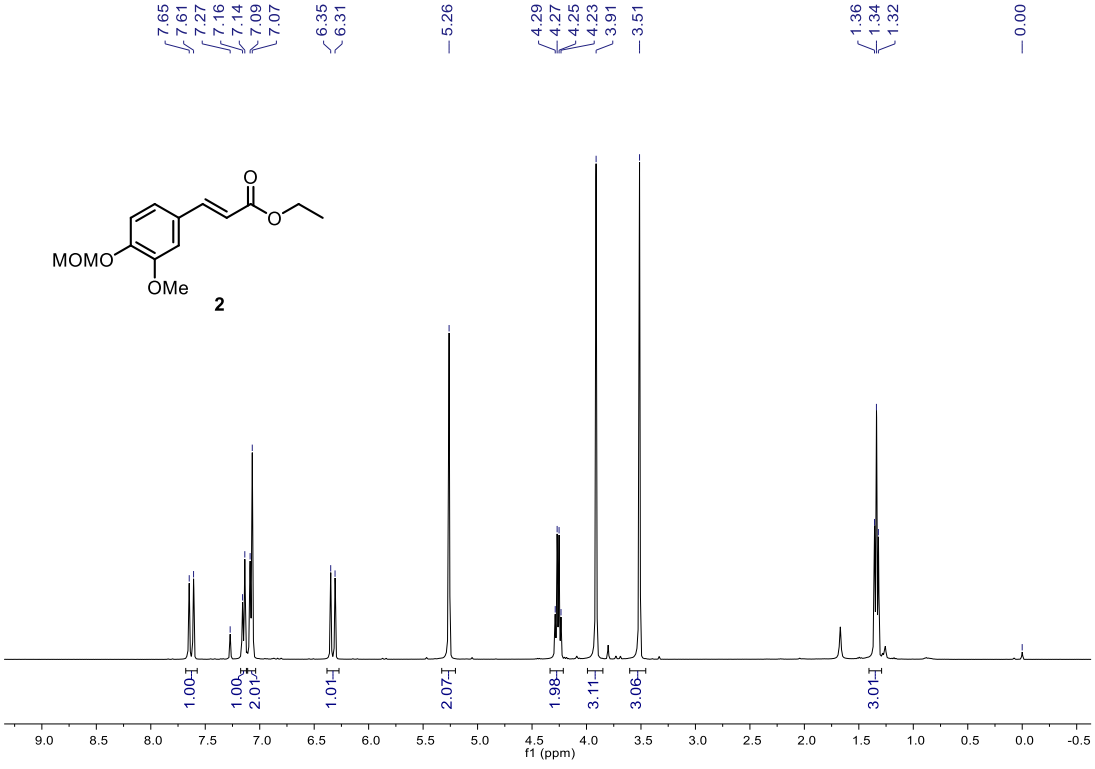
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4



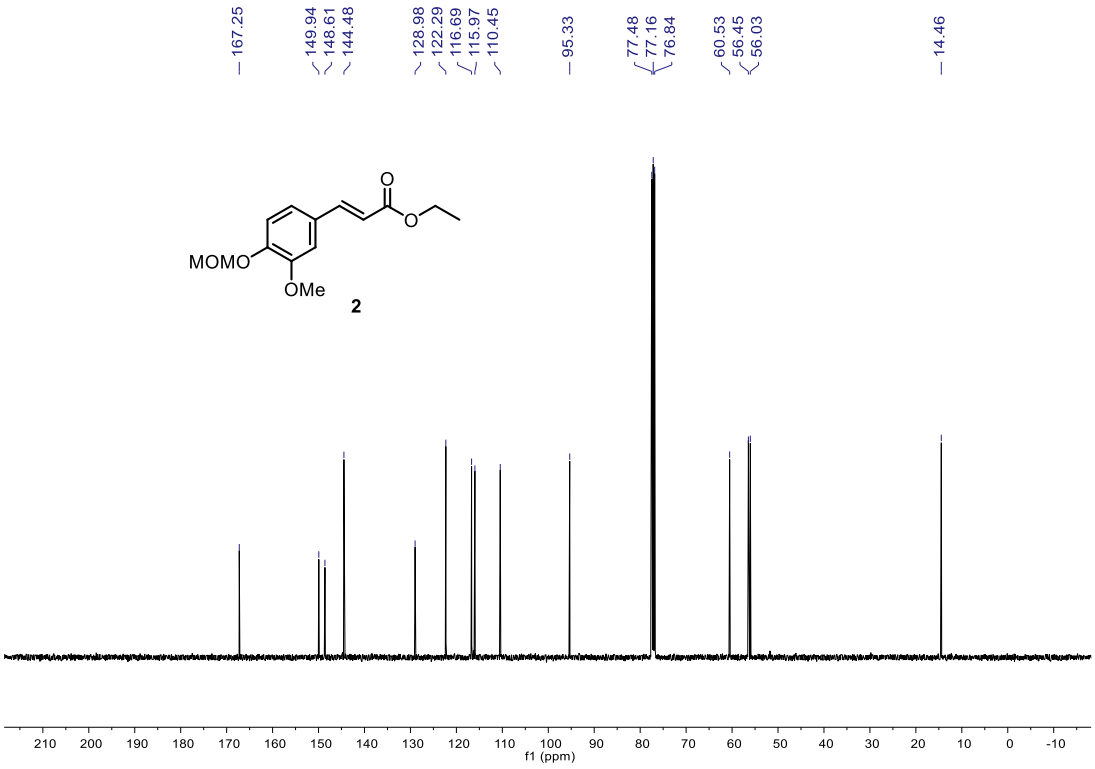
HRMS of 4


48
250717-11-1 13 (0.093)
1: TOF MS ES+
6.16e5
100
%
0
197.0818
198.0848
184.0586
188.7853
190.3039
191.0422
193.1328
195.0673
199.0860
200.0926
202.3182
205.0336
208.0041
208.9556
210.8229
184
186
188
190
192
194
196
198
200
202
204
206
208
210
m/z
MOMO
OMe
O
4

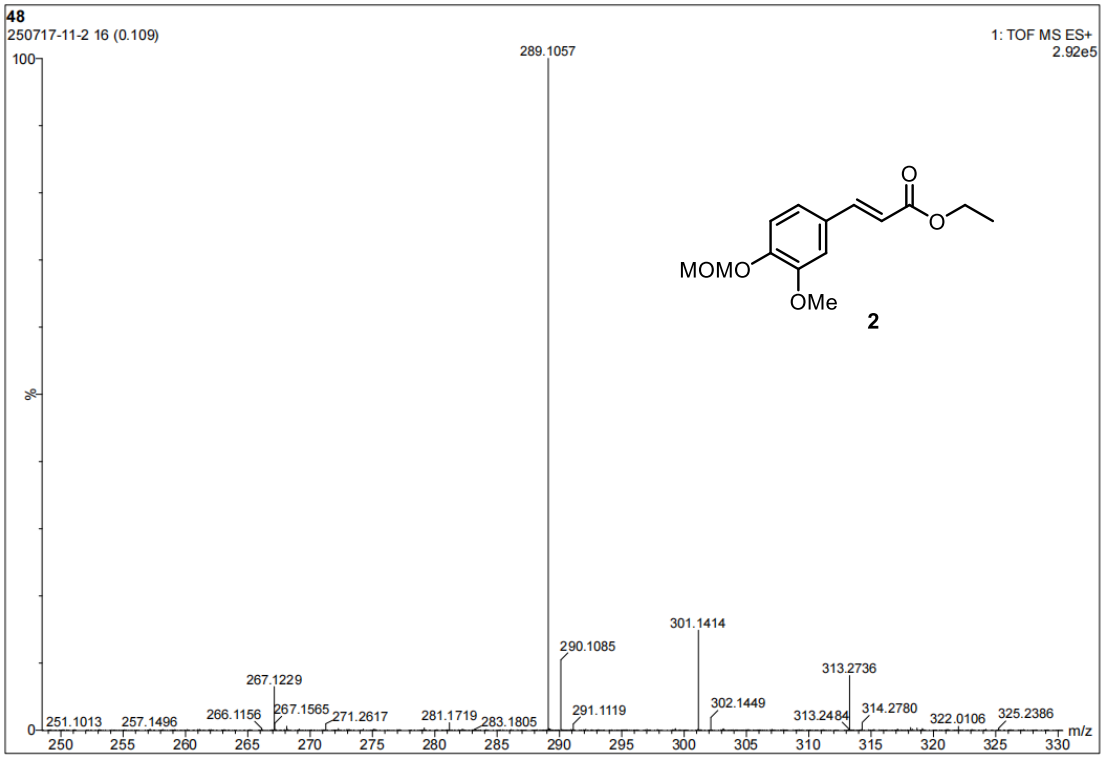
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 2



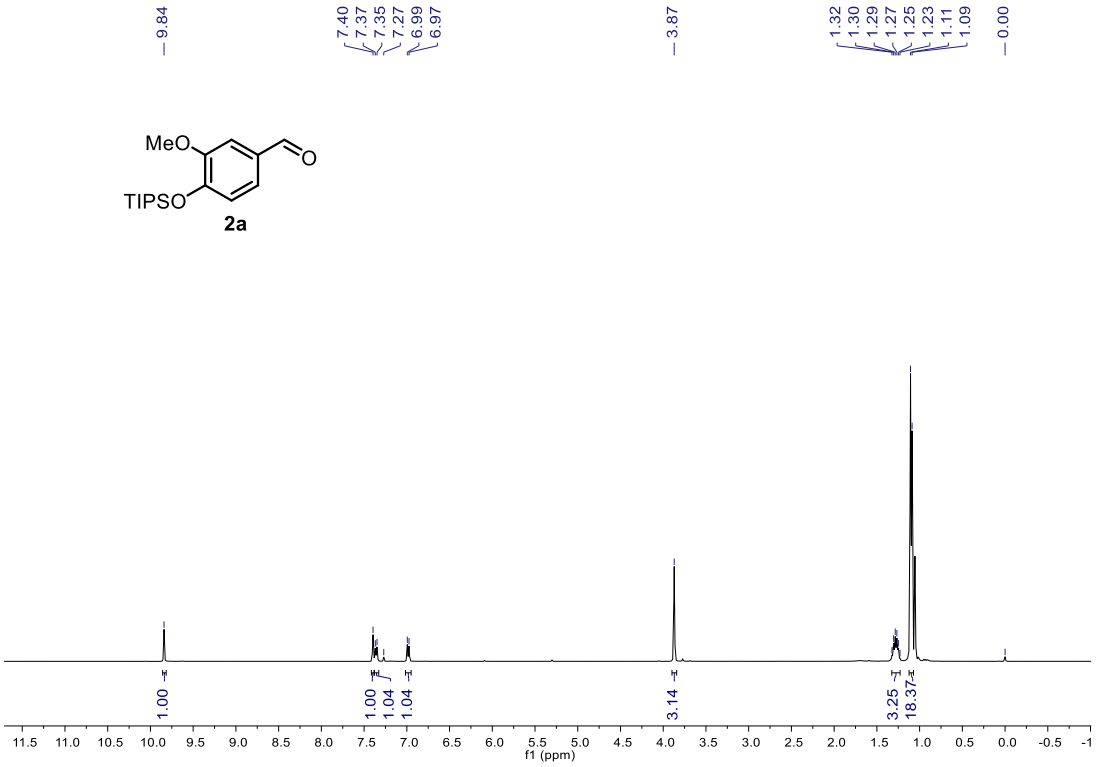
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 2



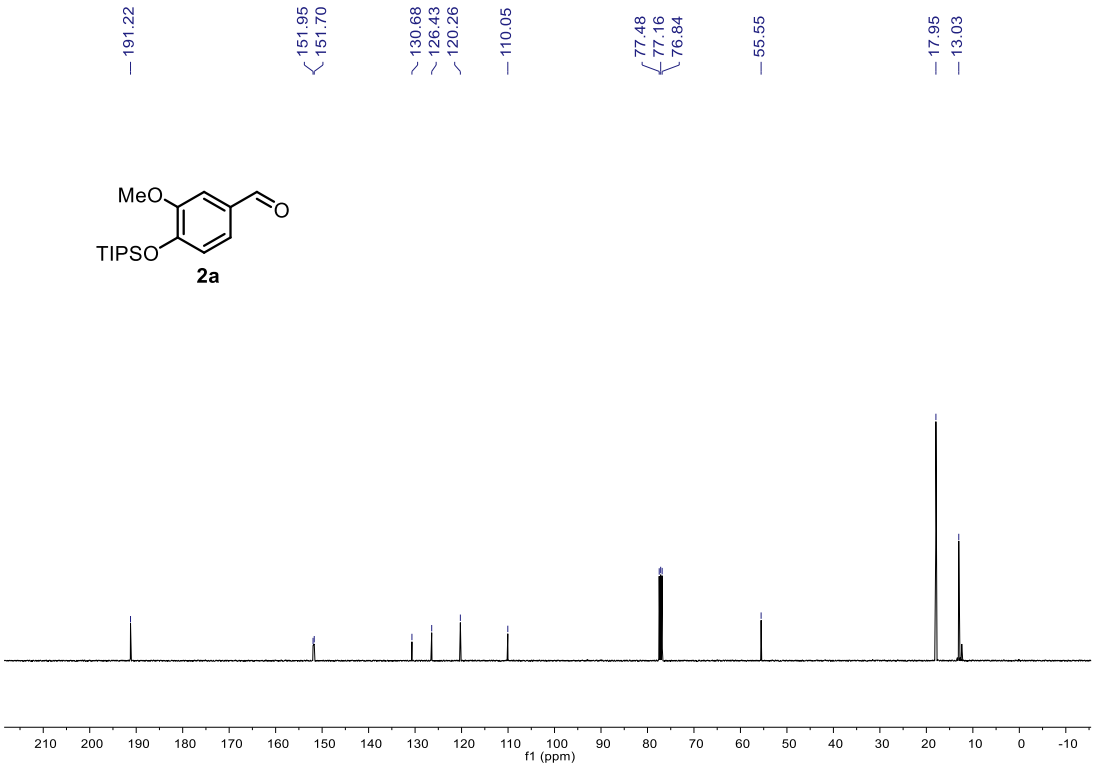
HRMS of 2


48
250717-11-2 16 (0.109)
1: TOF MS ES+
2.92e5
100
%
0
289.1057
301.1414
290.1085
313.2736
267.1229
302.1449
267.1565
314.2780
266.1156
271.2617
281.1719
283.1805
291.1119
313.2484
322.0106
325.2386
251.1013
257.1496
250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330
m/z
O
O
MOMO
OMe
2

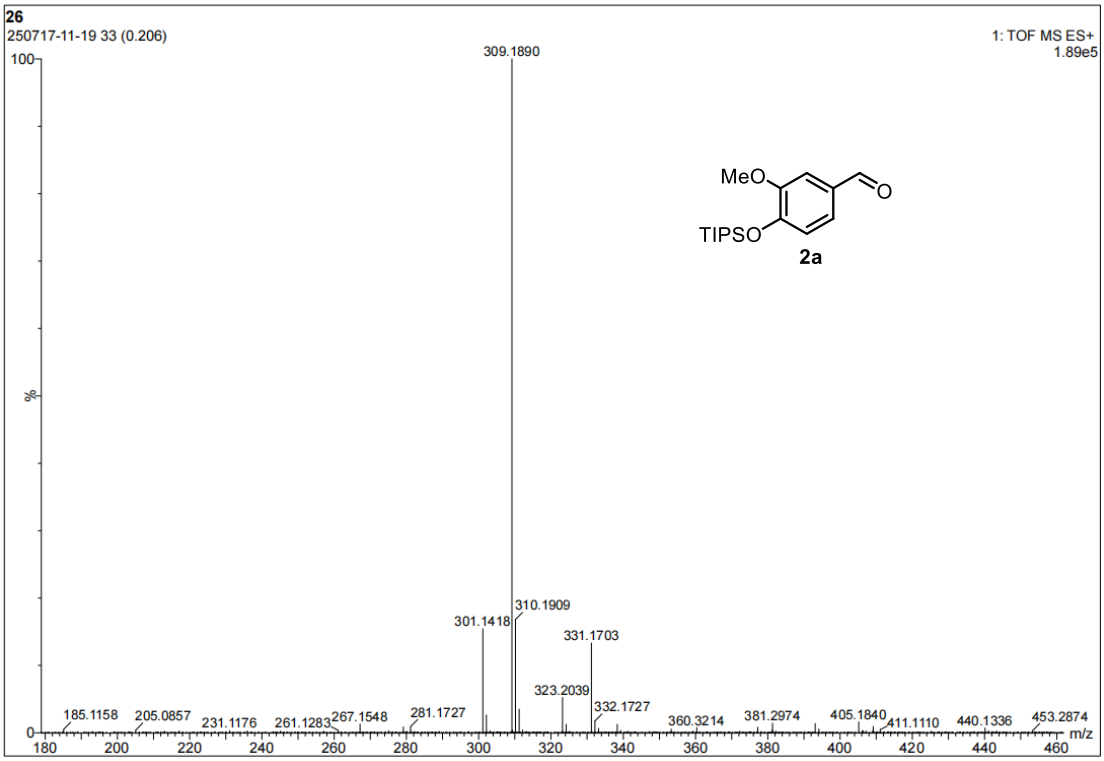
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 2a



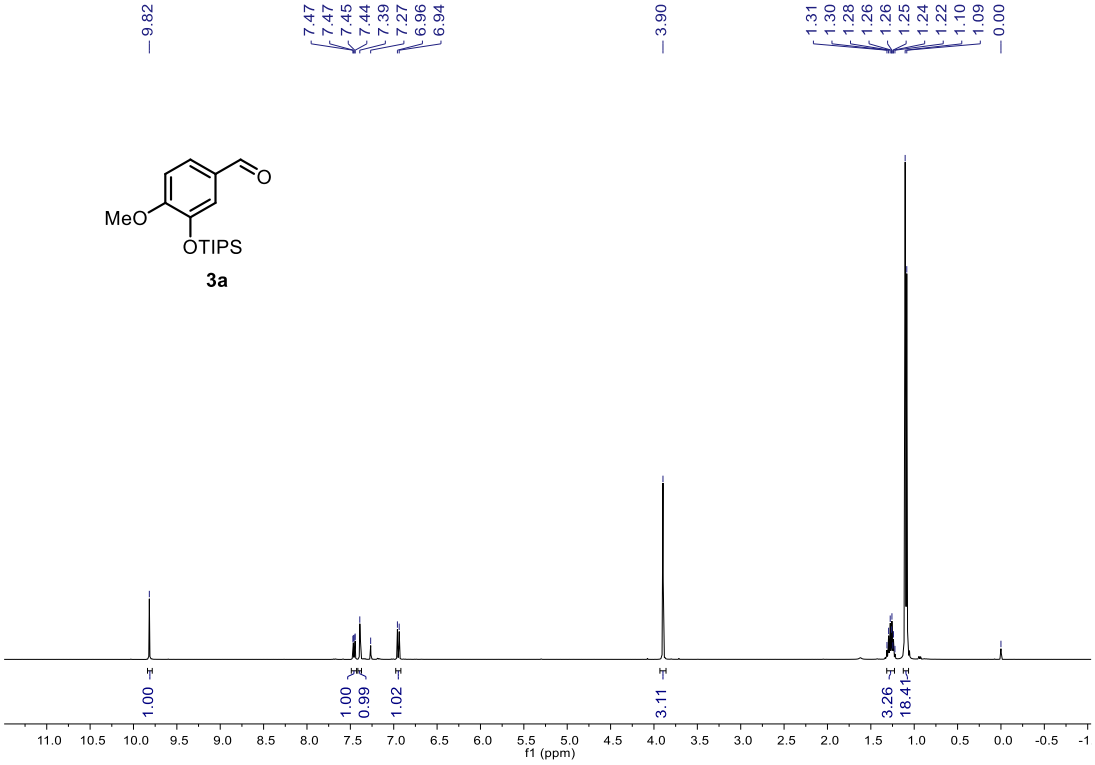
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 2a



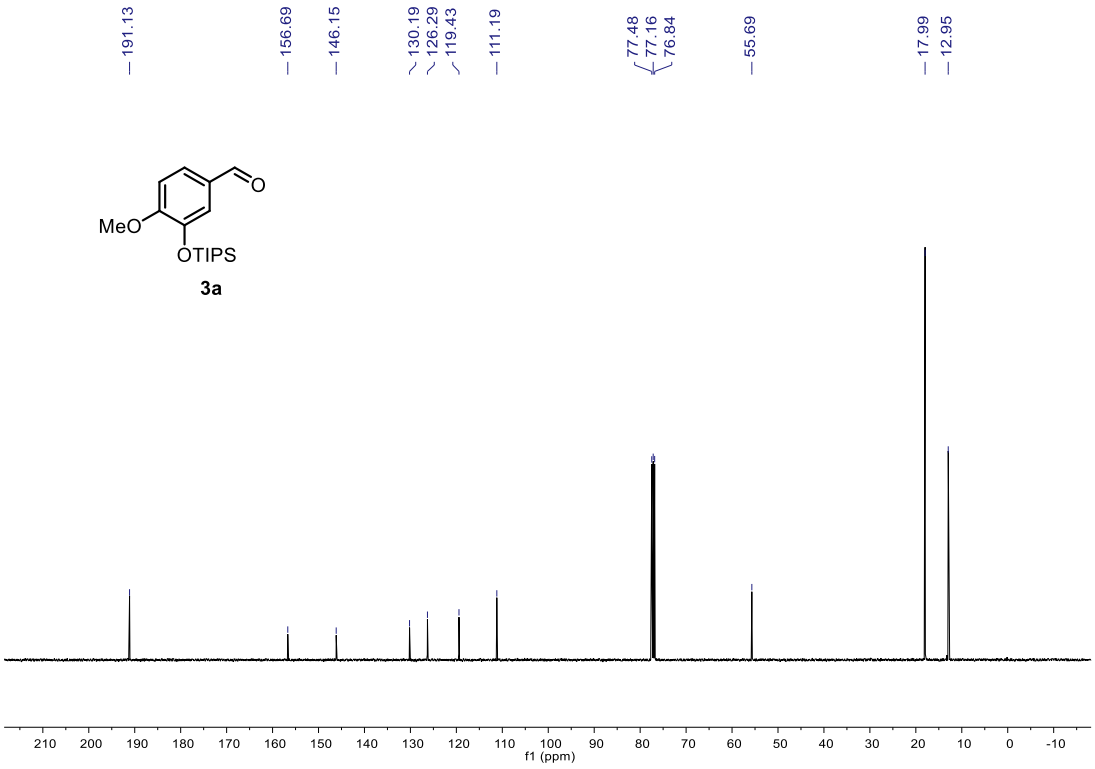
HRMS of 2a


26
250717-11-19 33 (0.206)
1: TOF MS ES+
1.89e5
100
%
0
309.1890
310.1909
301.1418
331.1703
323.2039
332.1727
185.1158
205.0857
231.1176
261.1283
267.1548
281.1727
360.3214
381.2974
405.1840
411.1110
440.1336
453.2874
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
m/z
MeO
TIPSO
O
2a

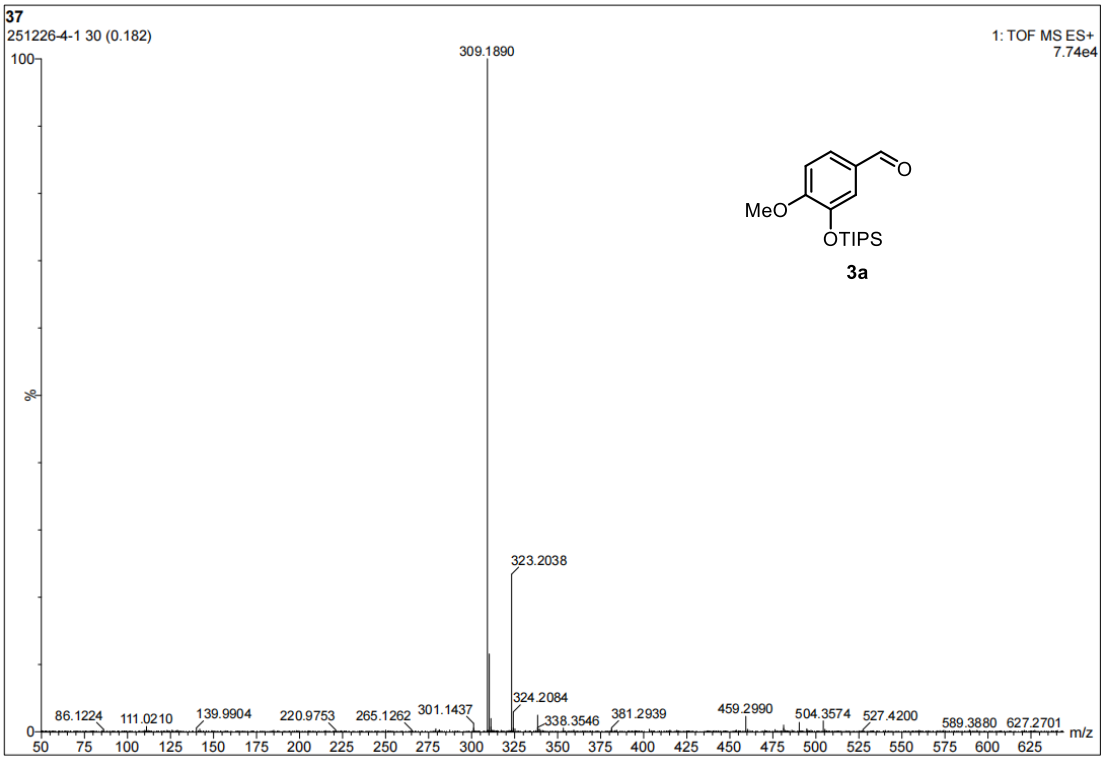
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3a



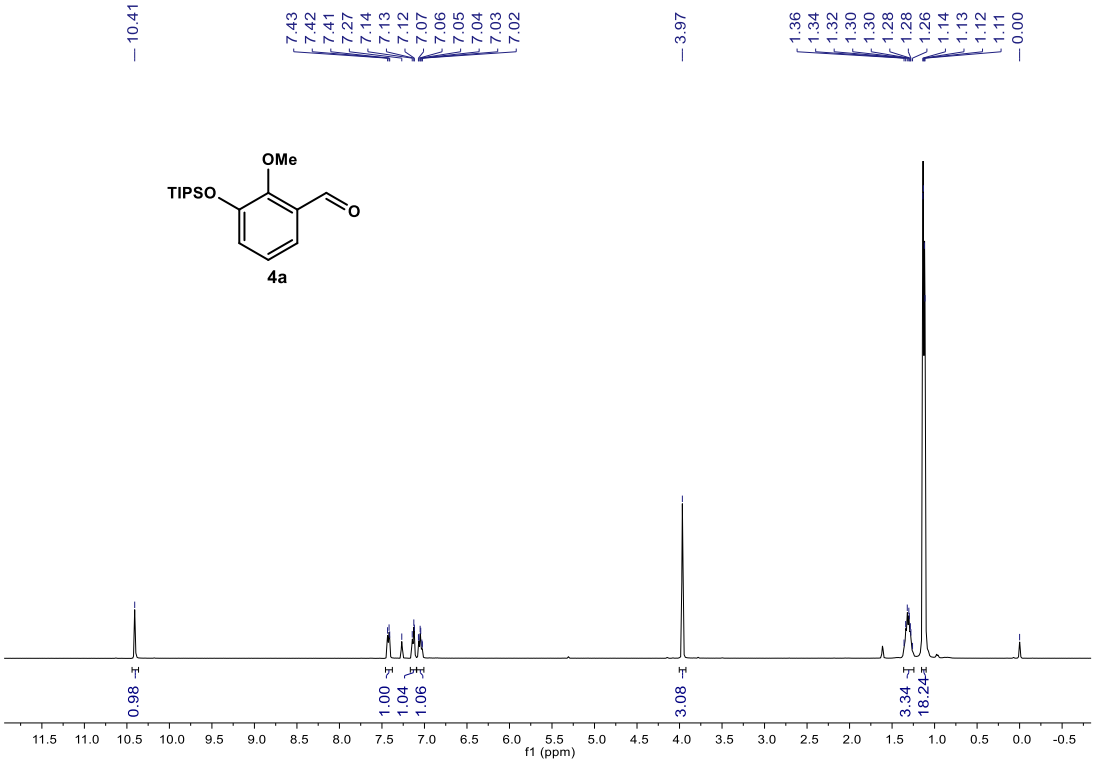
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3a



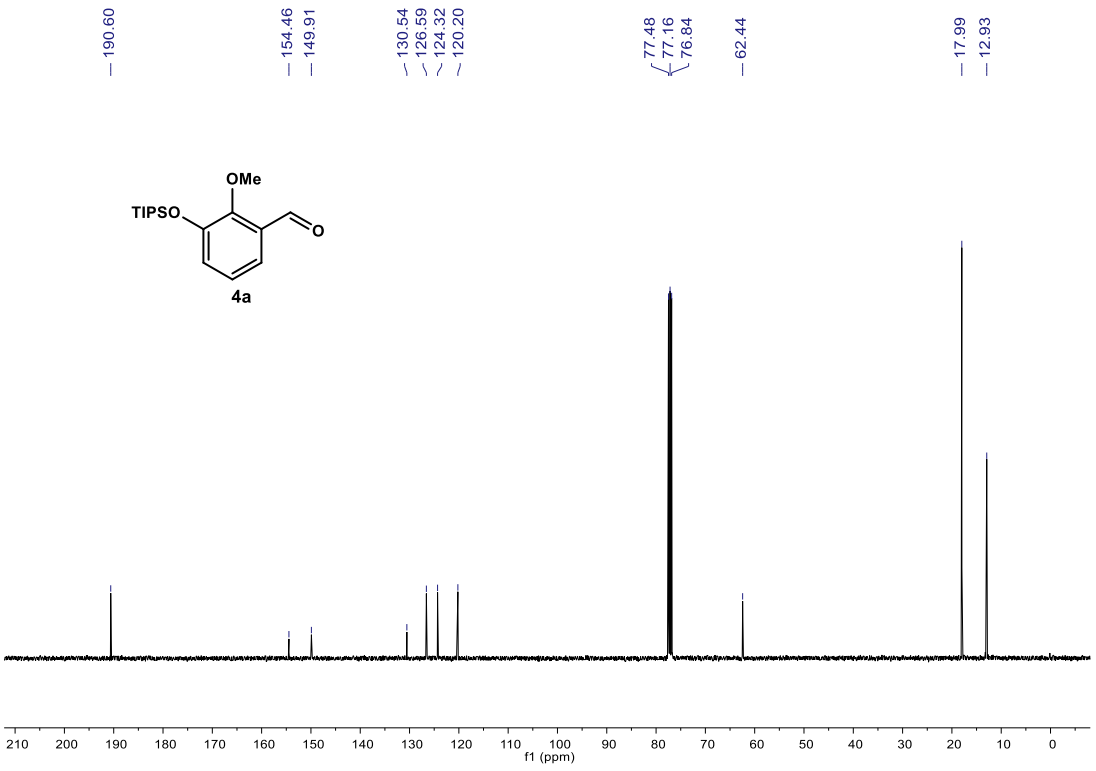
HRMS of 3a


37
251226-4-1 30 (0.182)
1: TOF MS ES+
7.74e4
100
%
0
309.1890
323.2038
324.2084
86.1224
111.0210
139.9904
220.9753
265.1262
301.1437
338.3546
381.2939
459.2990
504.3574
527.4200
589.3880
627.2701
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625
m/z
MeO
OTIPS
O
3a

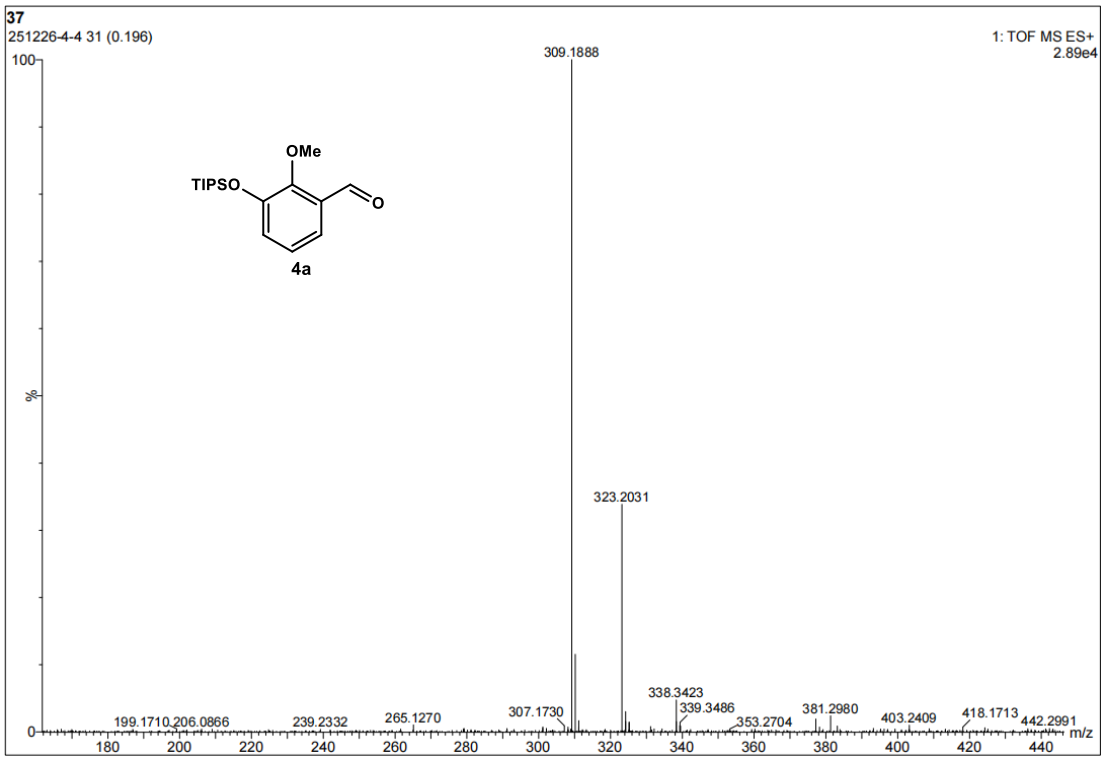
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



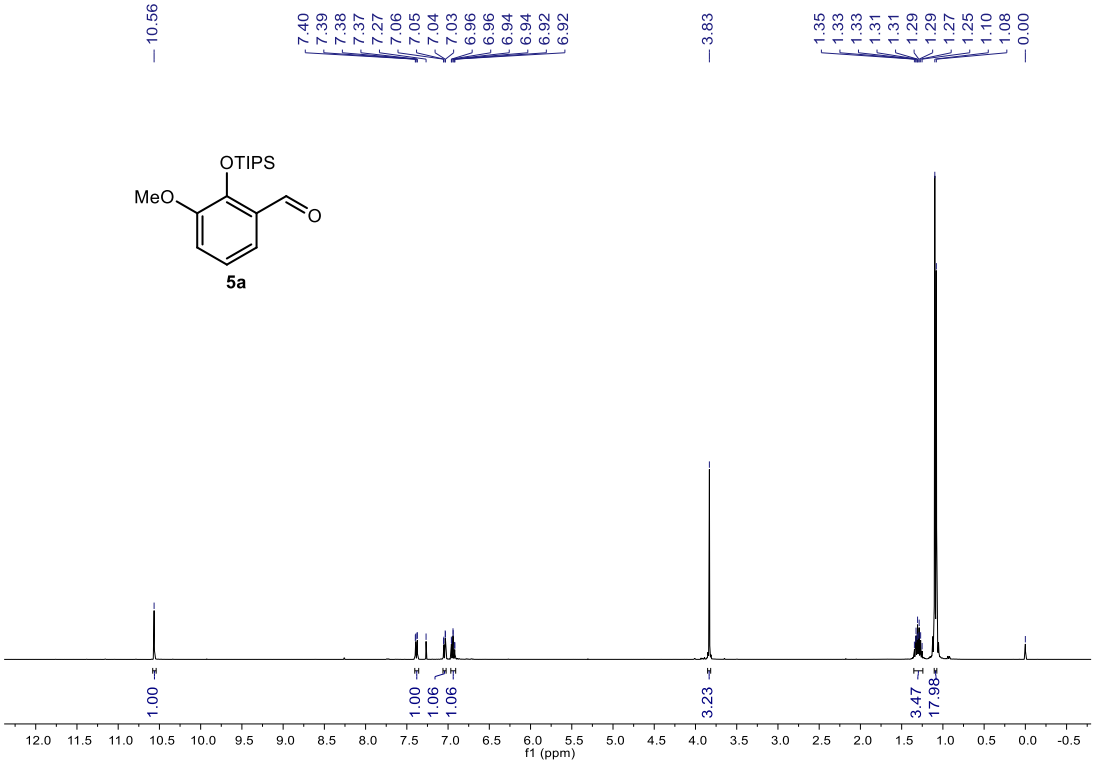
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4a



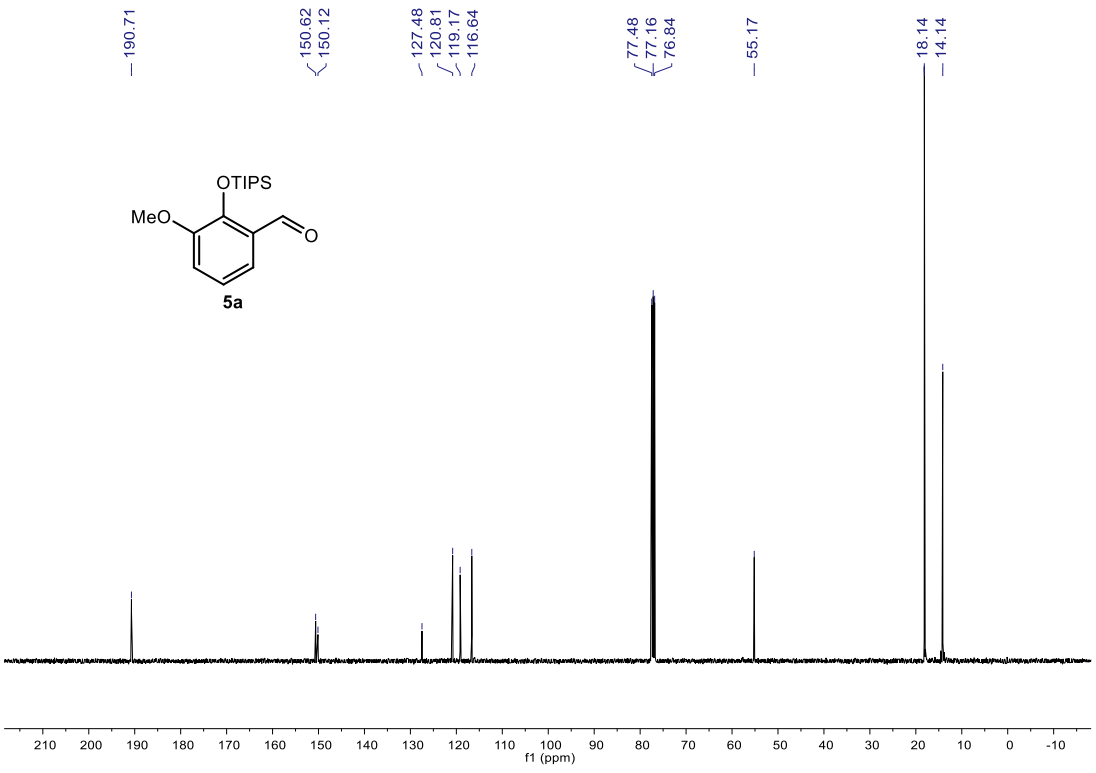
HRMS of 4a


37
251226-4-4 31 (0.196)
1: TOF MS ES+
2.89e4
100
%
0
309.1888
323.2031
338.3423
339.3486
307.1730
199.1710
206.0866
239.2332
265.1270
353.2704
381.2980
403.2409
418.1713
442.2991
m/z
180
200
220
240
260
280
300
320
340
360
380
400
420
440
OMe
TIPSO
O
4a

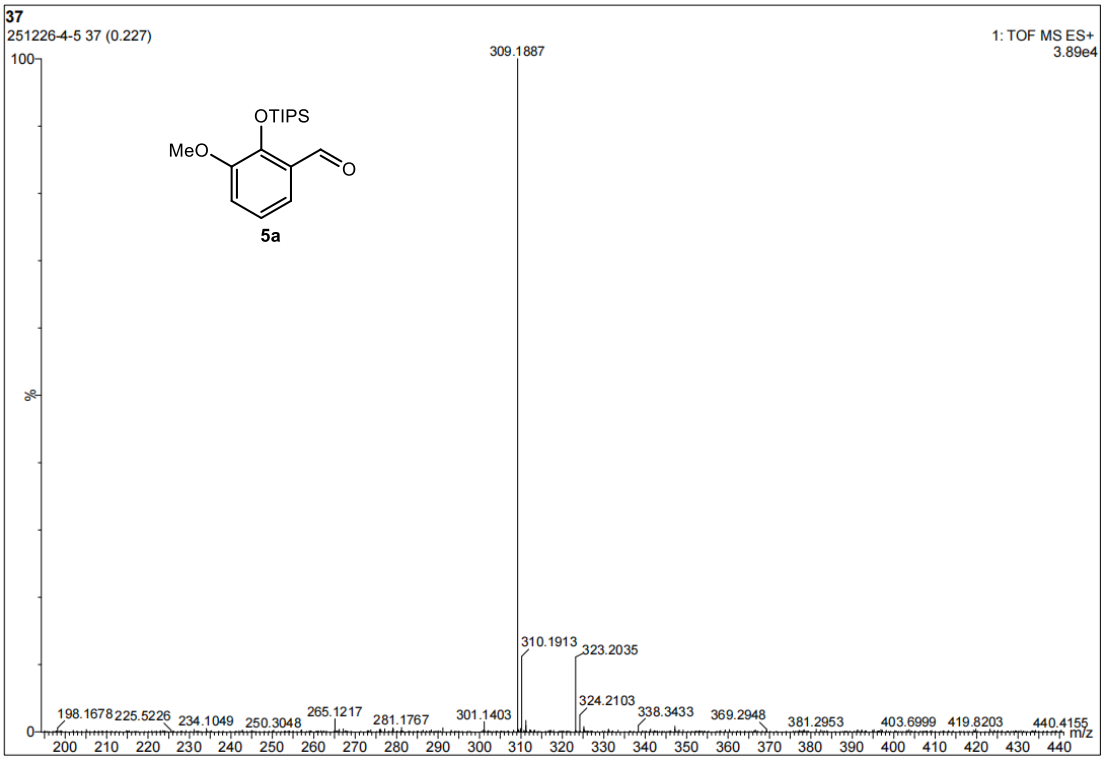
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5a



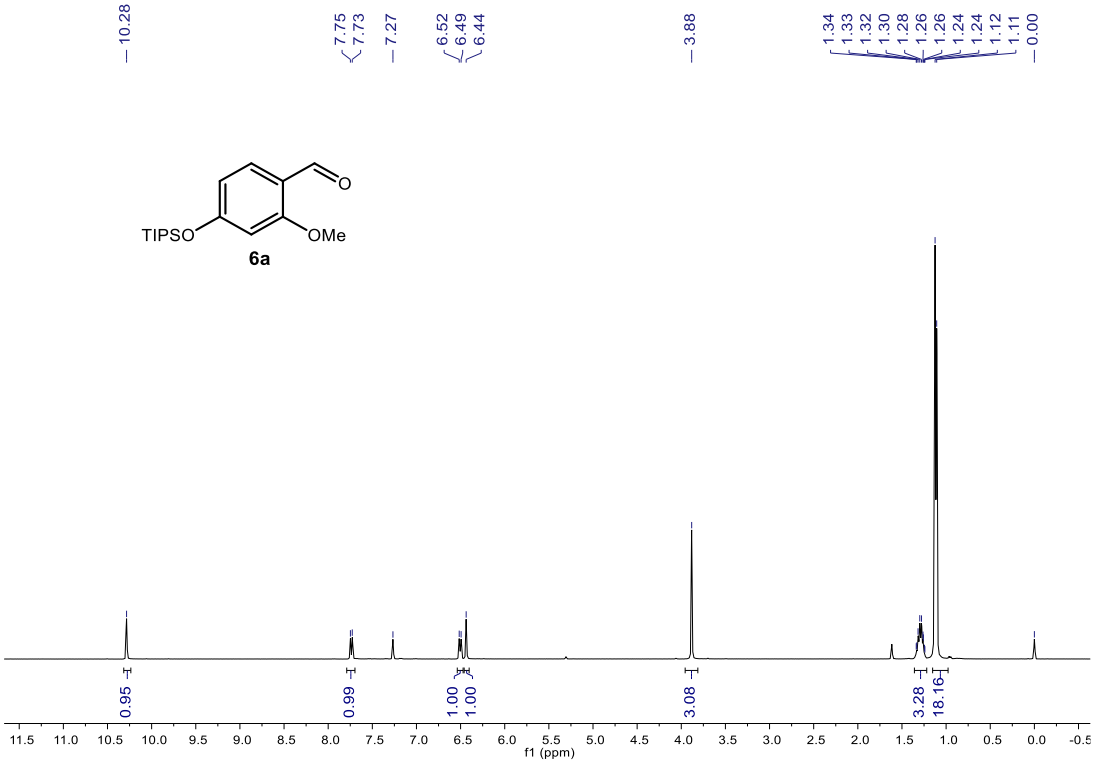
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5a



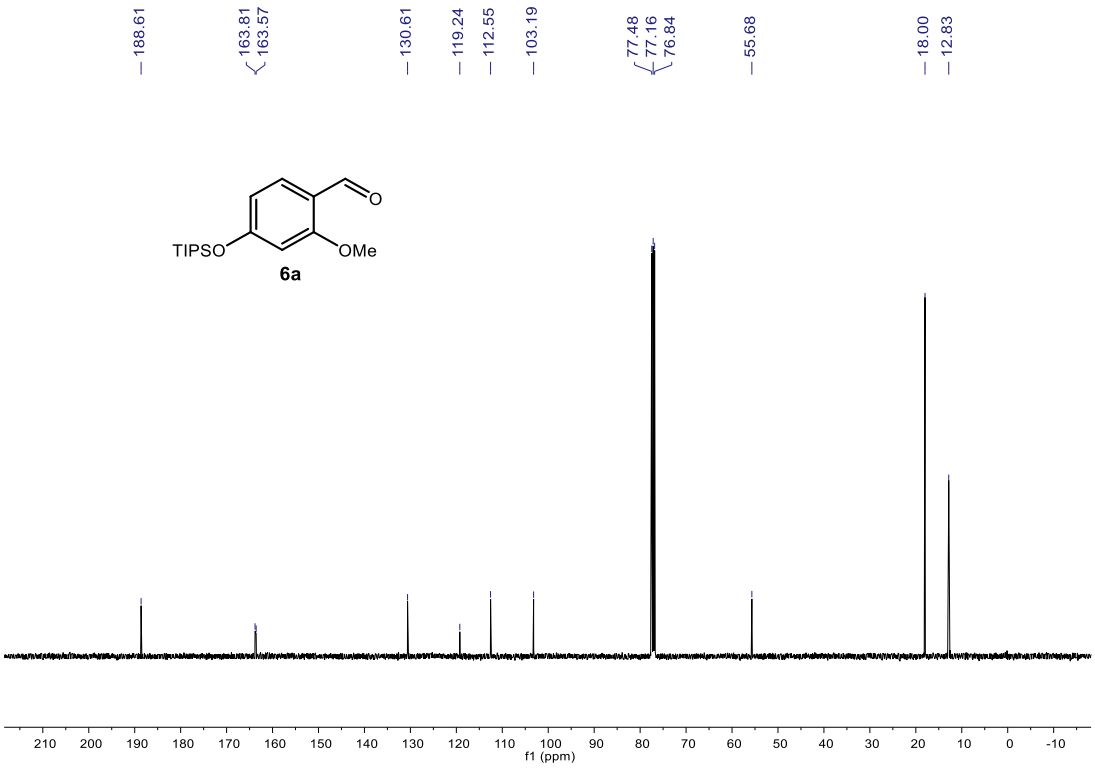
HRMS of 5a


37
251226-4-5 37 (0.227)
1: TOF MS ES+
3.89e4
100
%
0
309.1887
310.1913
323.2035
324.2103
198.1678
225.5226
234.1049
250.3048
265.1217
281.1767
301.1403
338.3433
369.2948
381.2953
403.6999
419.8203
440.4155
m/z
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440
OTIPS
MeO
O
5a

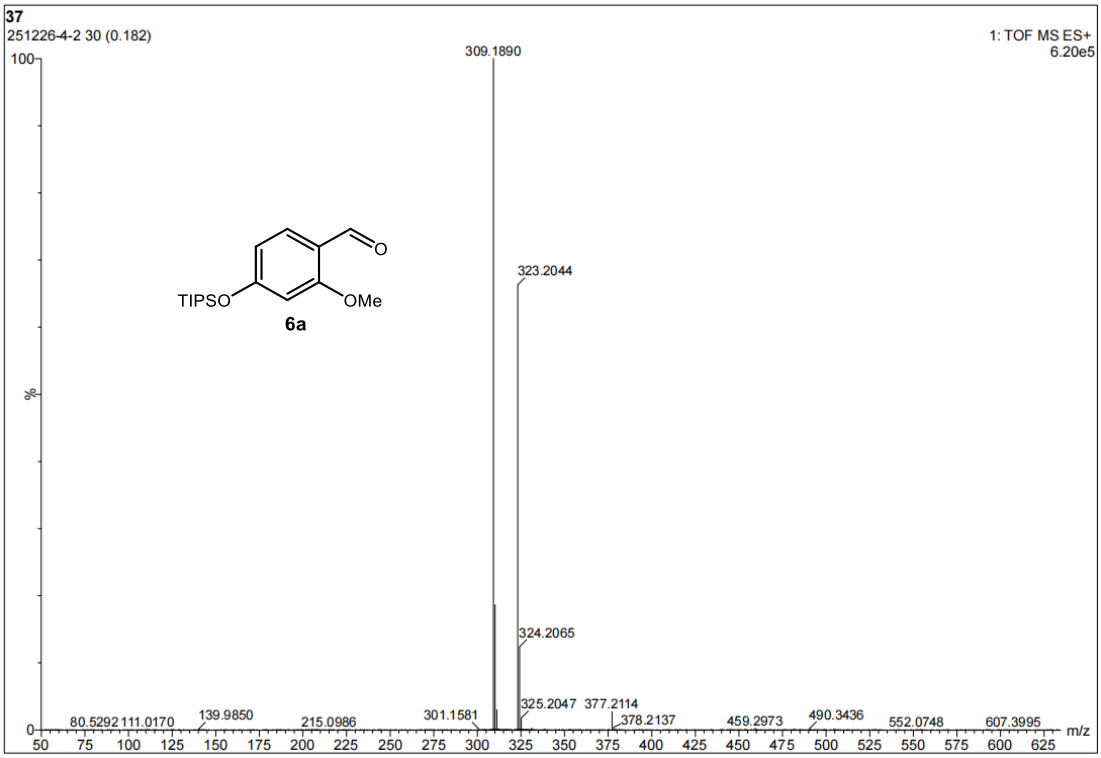
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 6a



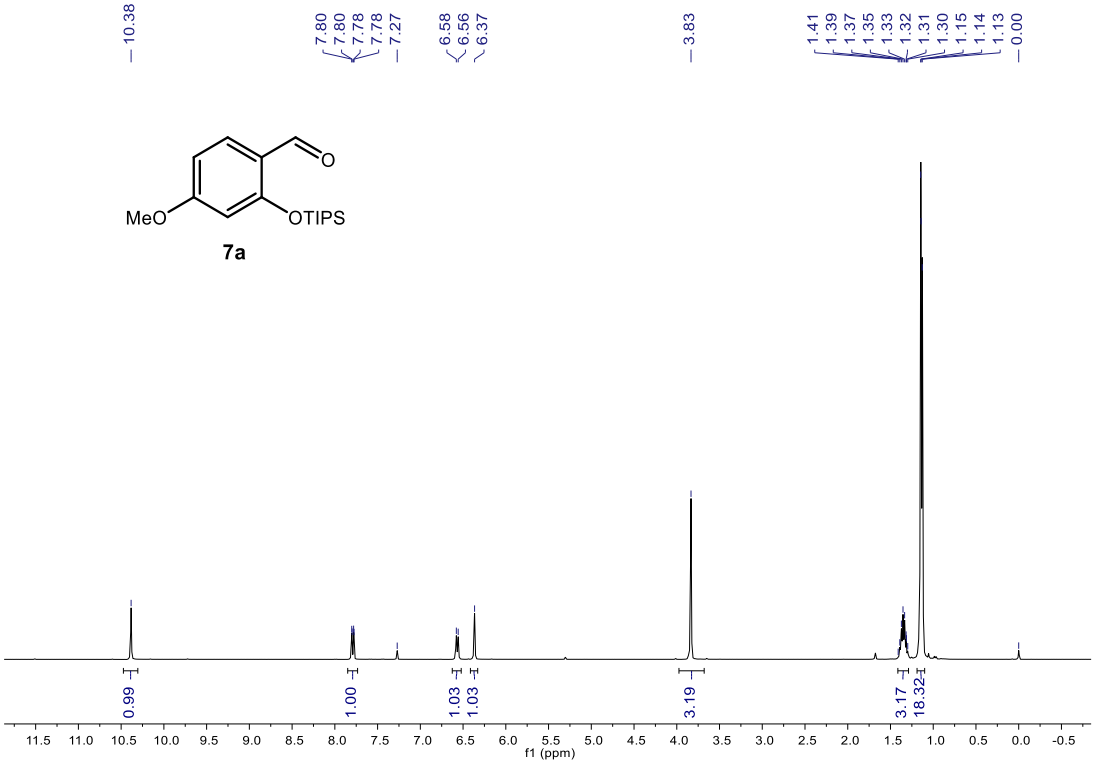
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 6a



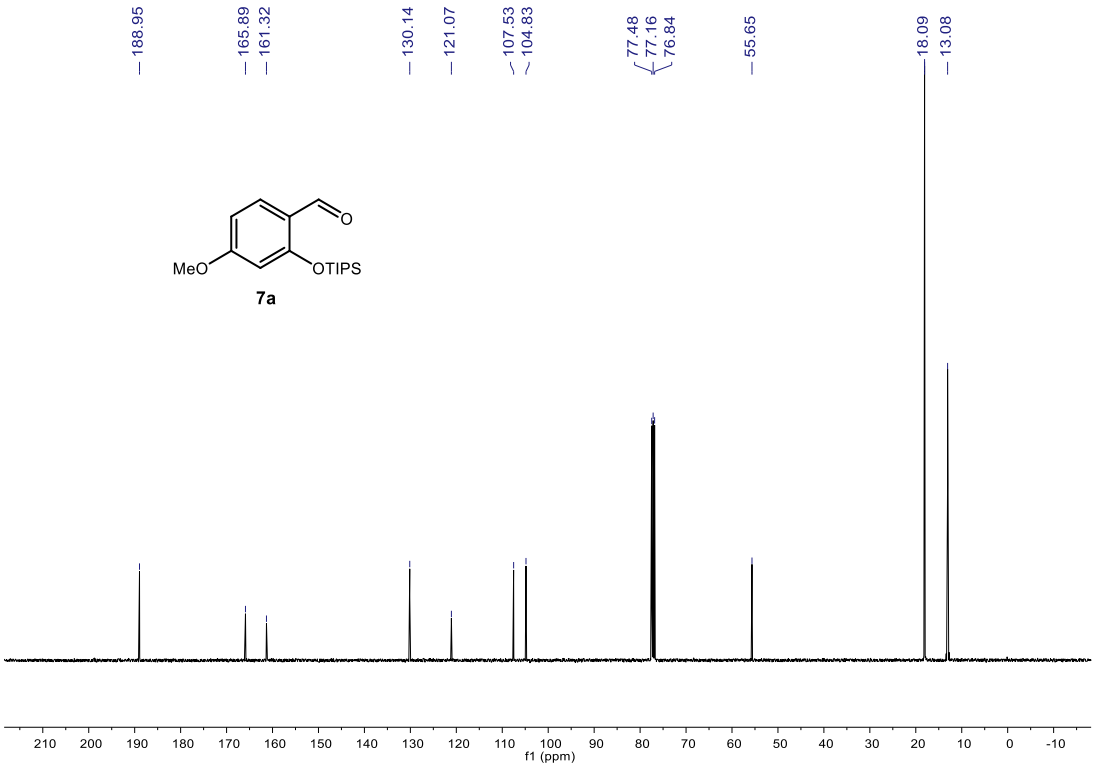
HRMS of 6a


37
251226-4-2 30 (0.182)
1: TOF MS ES+
6.20e5
100
%
0
309.1890
323.2044
324.2065
325.2047
377.2114
378.2137
80.5292
111.0170
139.9850
215.0986
301.1581
459.2973
490.3436
552.0748
607.3995
m/z
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625
TIPSO
OMe
O
6a

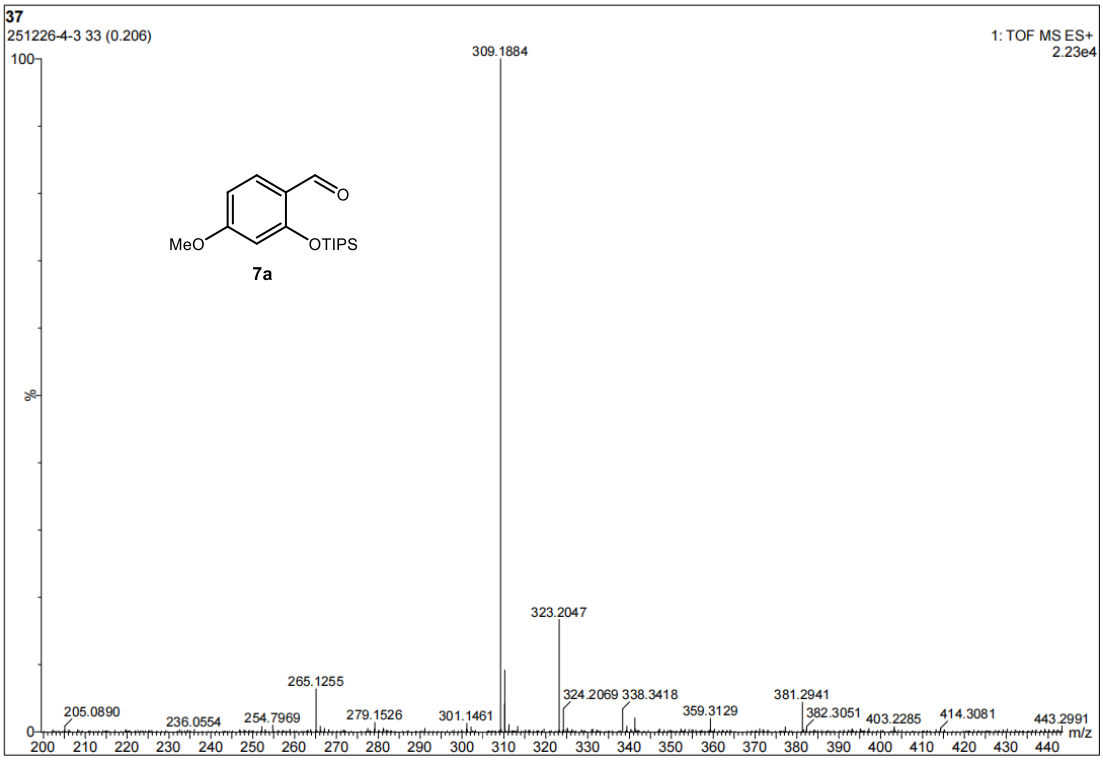
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 7a



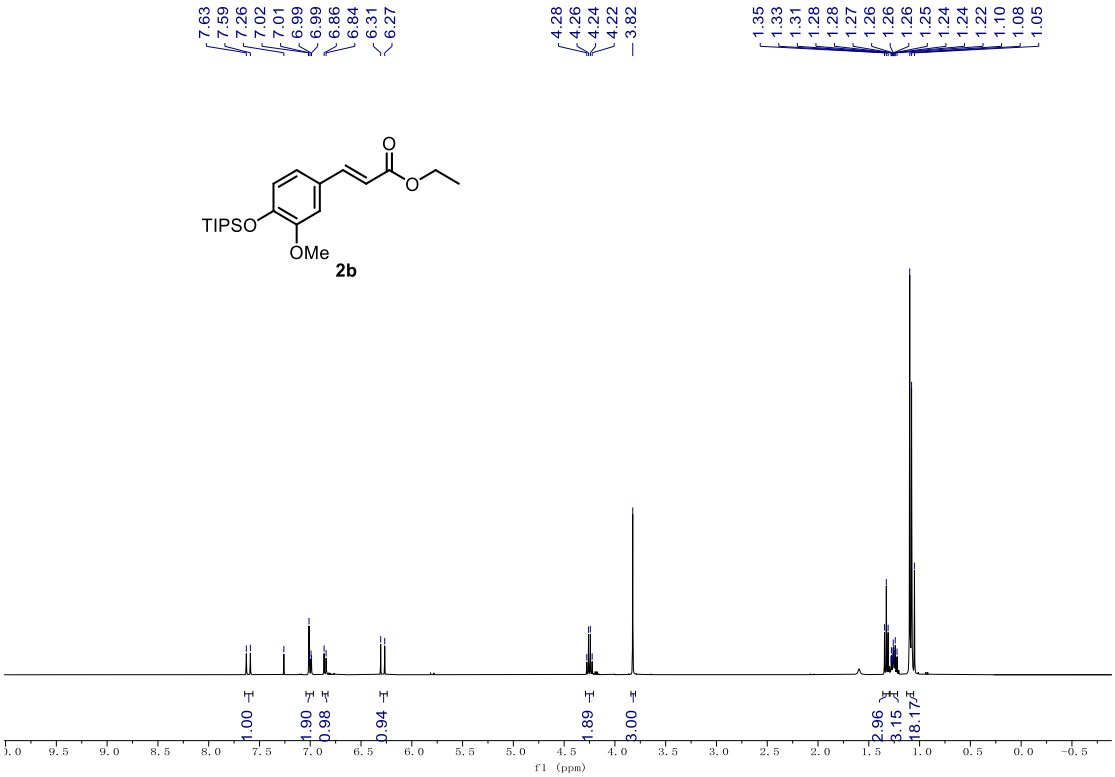
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 7a



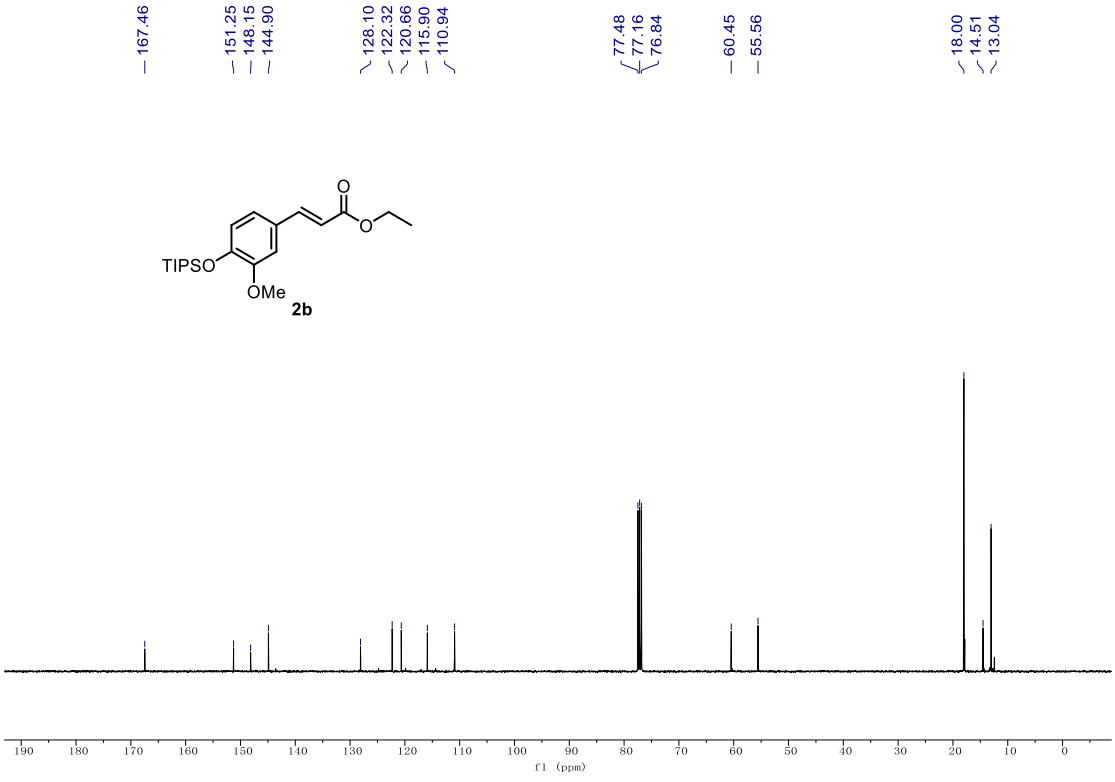
HRMS of 7a


37
251226-4-3 33 (0.206)
1: TOF MS ES+
2.23e4
100
%
0
309.1884
323.2047
265.1255
205.0890
236.0554
254.7969
279.1526
301.1461
324.2069
338.3418
359.3129
381.2941
382.3051
403.2285
414.3081
443.2991
m/z
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440
MeO
OTIPS
O
7a

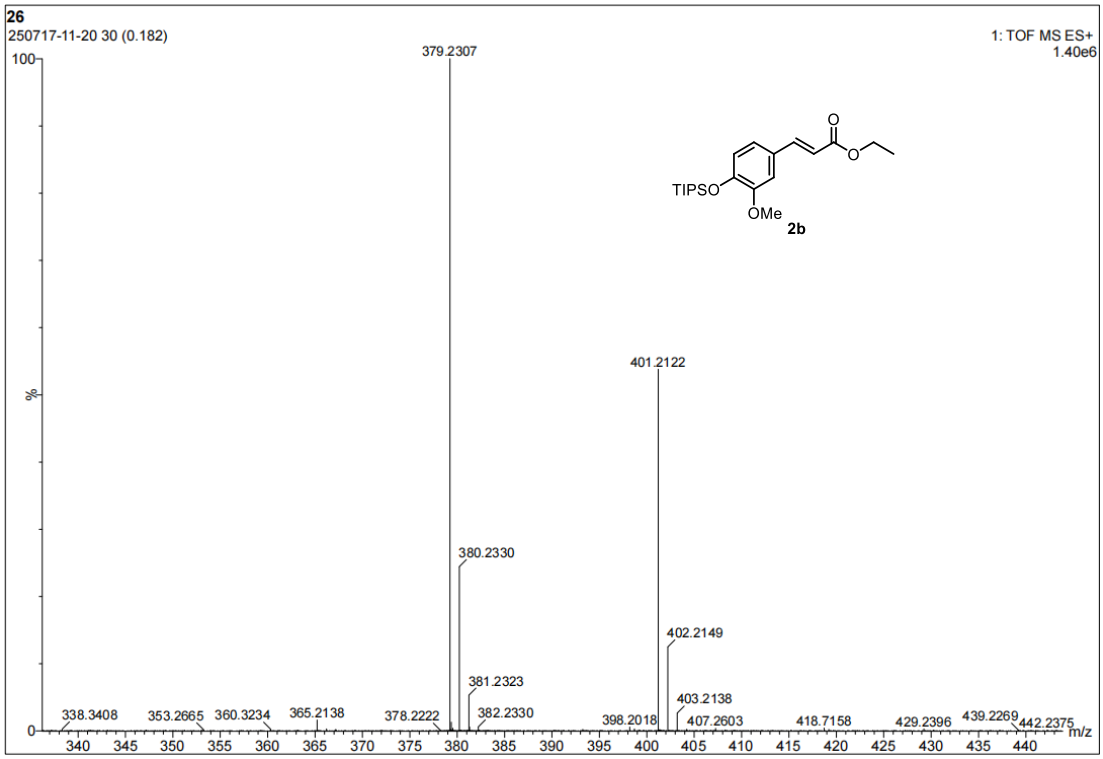
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 2b



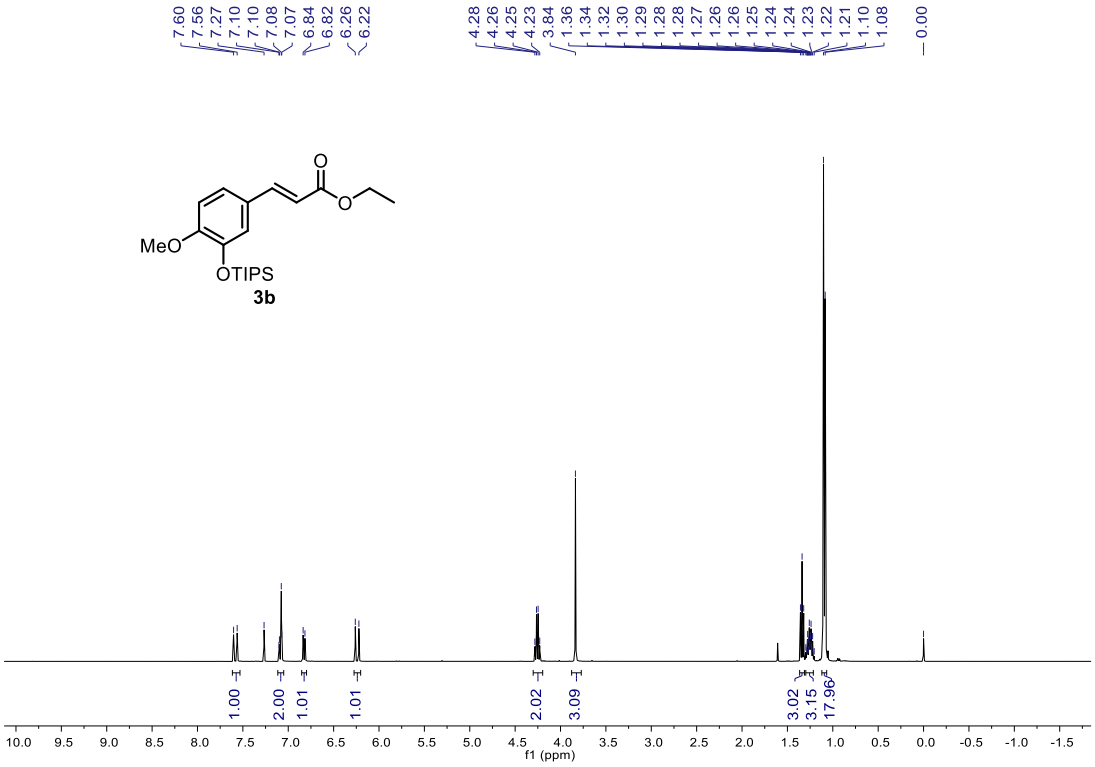
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 2b



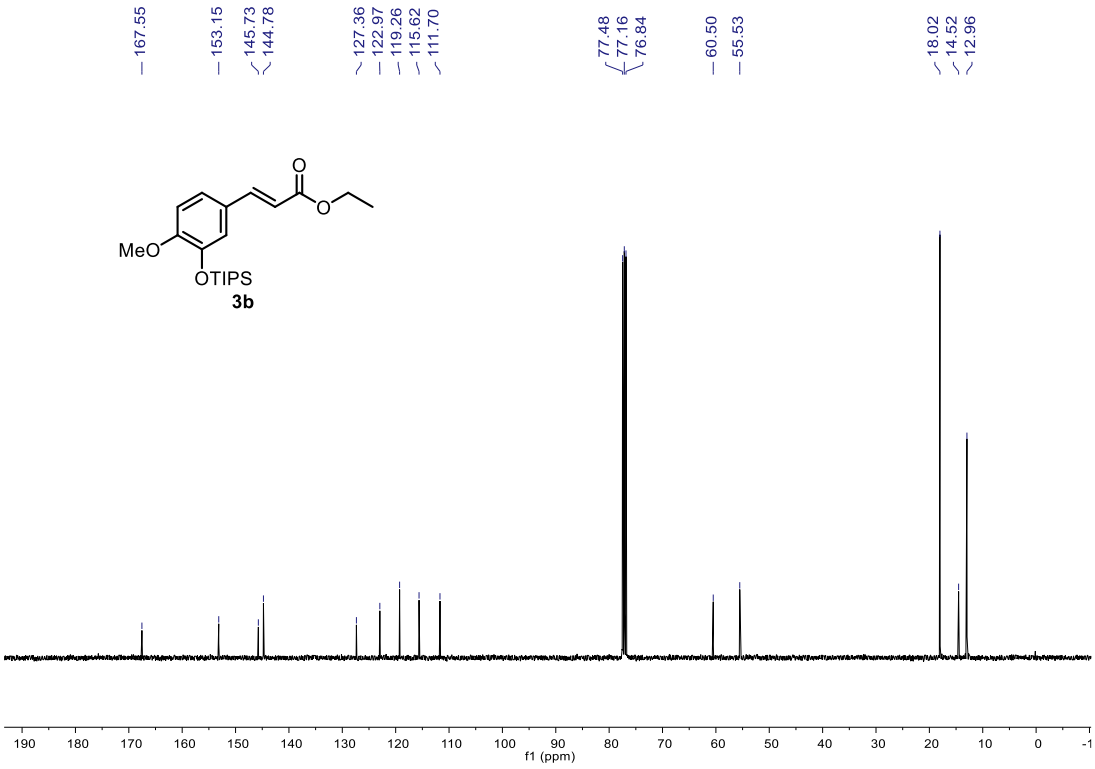
HRMS of 2b


26
250717-11-20 30 (0.182)
1: TOF MS ES+
1.40e6
100
%
0
379.2307
401.2122
380.2330
402.2149
381.2323
403.2138
338.3408
353.2665
360.3234
365.2138
378.2222
382.2330
398.2018
407.2603
418.7158
429.2396
439.2269
442.2375
m/z
340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440
TIPSO
OMe
O
O
2b

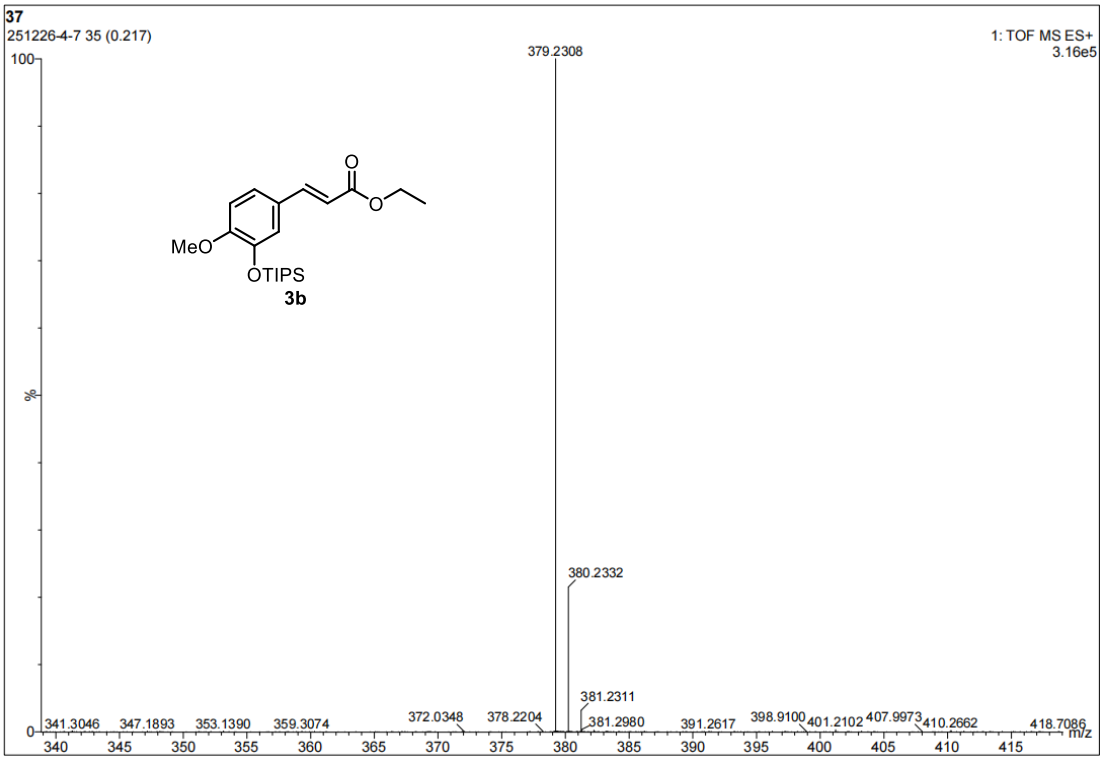
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3b



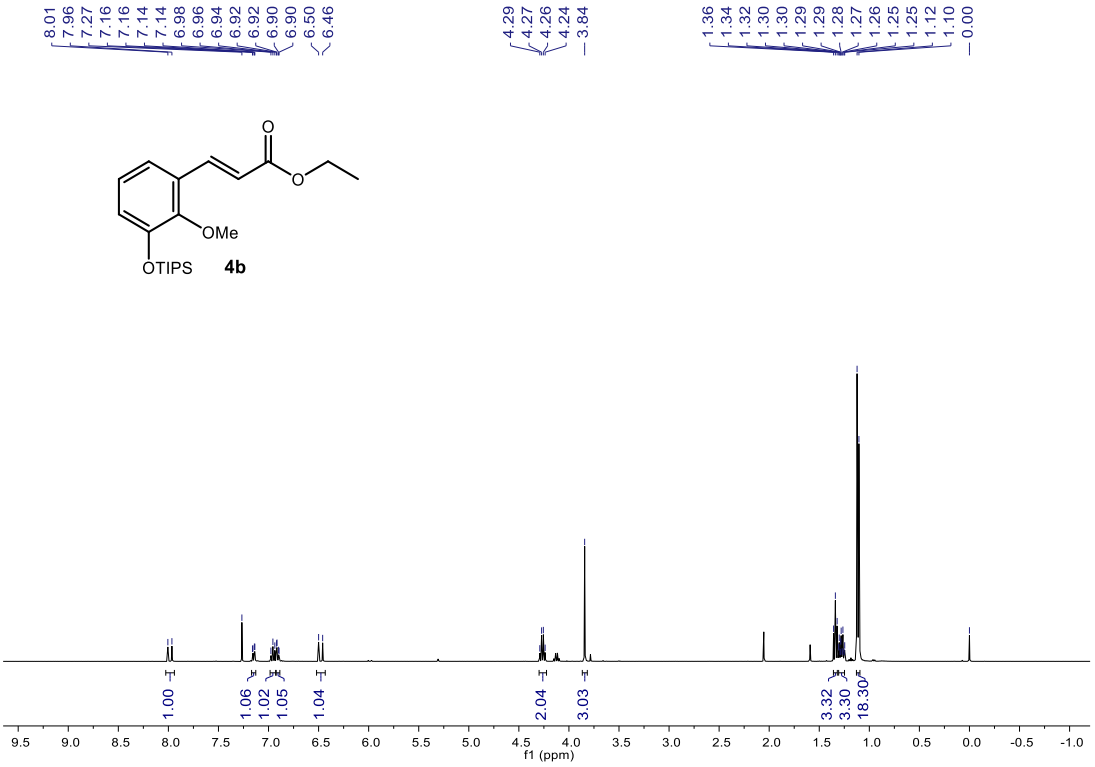
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3b



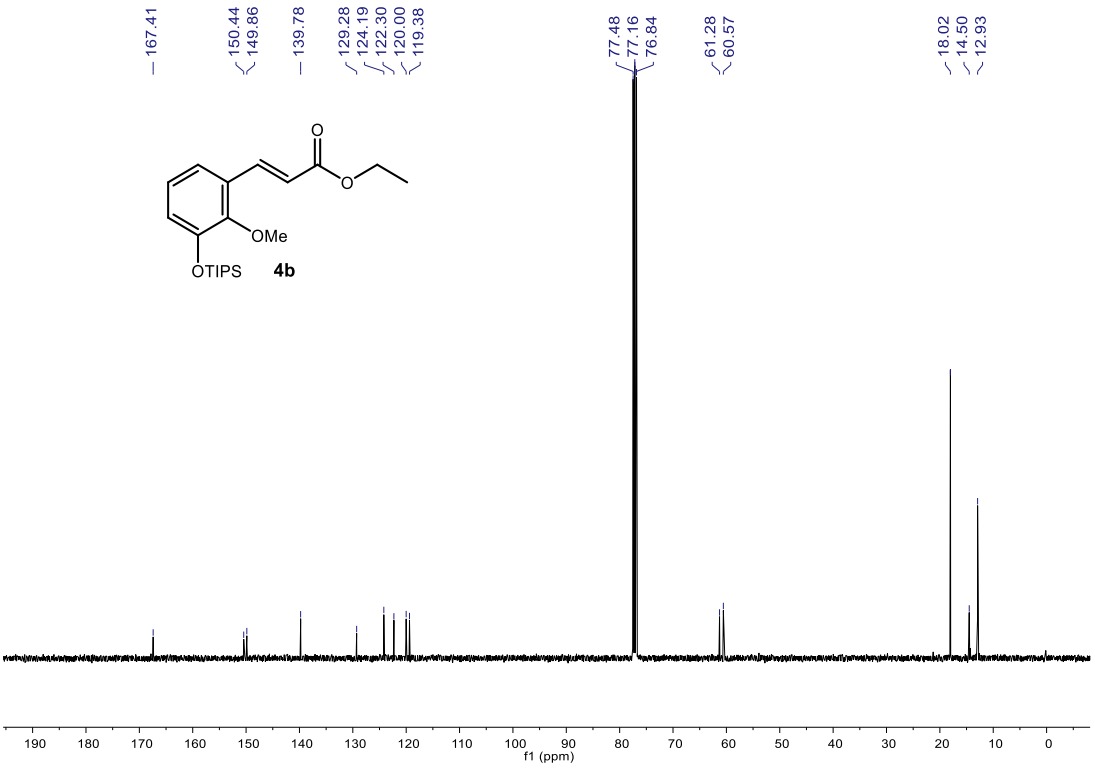
HRMS of 3b


37
251226-4-7 35 (0.217)
1: TOF MS ES+
3.16e5
379.2308
100
%
0
MeO
OTIPS
O
O
3b
380.2332
381.2311
341.3046
347.1893
353.1390
359.3074
372.0348
378.2204
381.2980
391.2617
398.9100
401.2102
407.9973
410.2662
418.7086
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
m/z

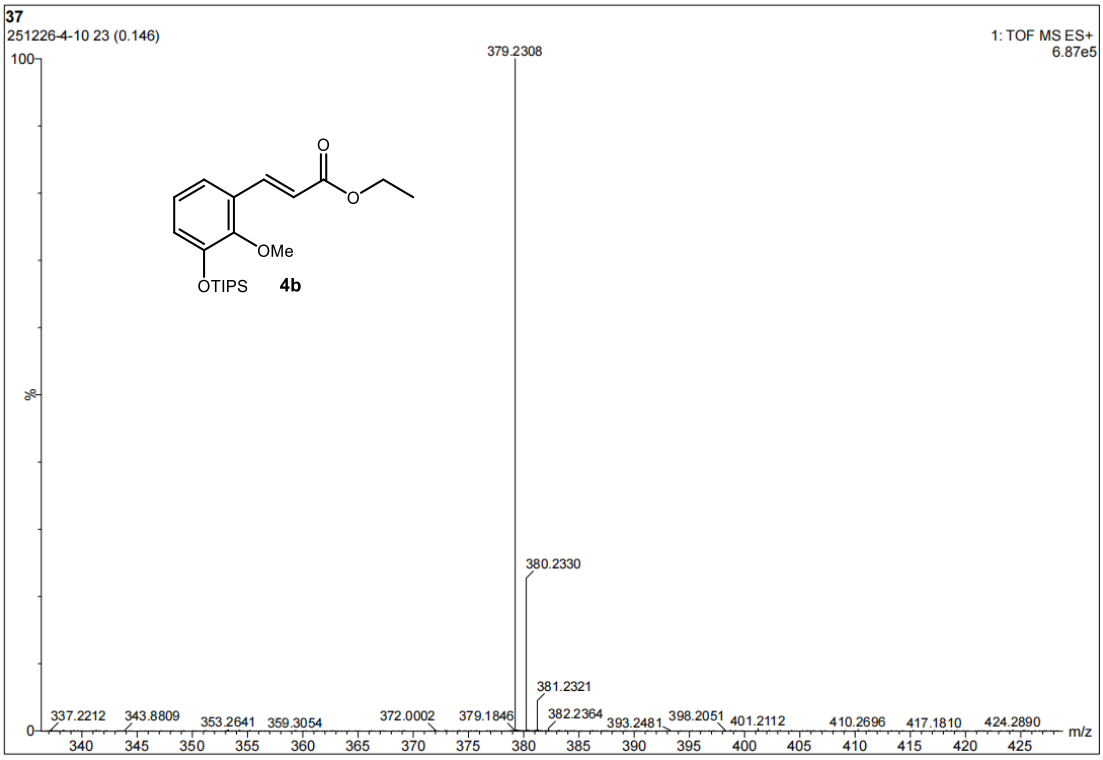
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4b



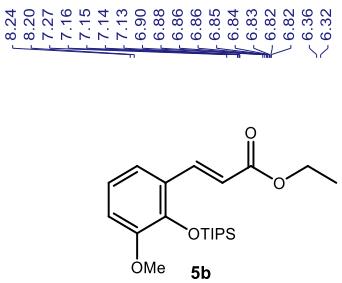
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4b



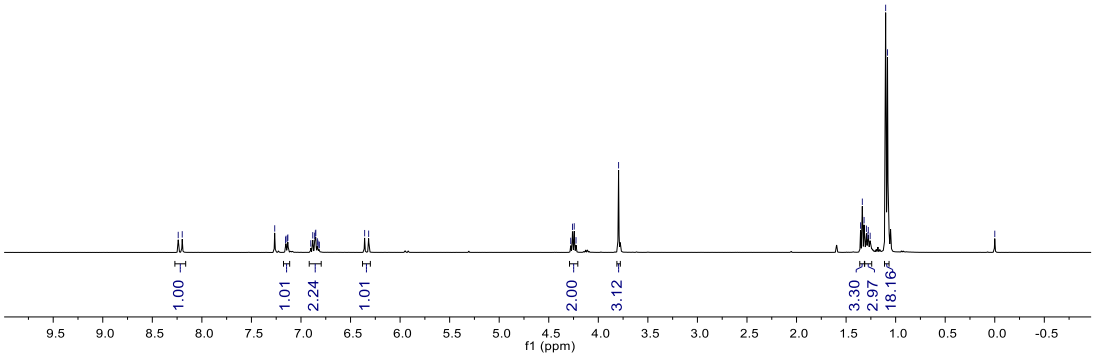
HRMS of 4b


37
251226-4-10 23 (0.146)
1: TOF MS ES+
6.87e5
100
%
0
379.2308
380.2330
381.2321
337.2212
343.8809
353.2641
359.3054
372.0002
379.1846
382.2364
393.2481
398.2051
401.2112
410.2696
417.1810
424.2890
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
m/z
OMe
OTIPS
4b

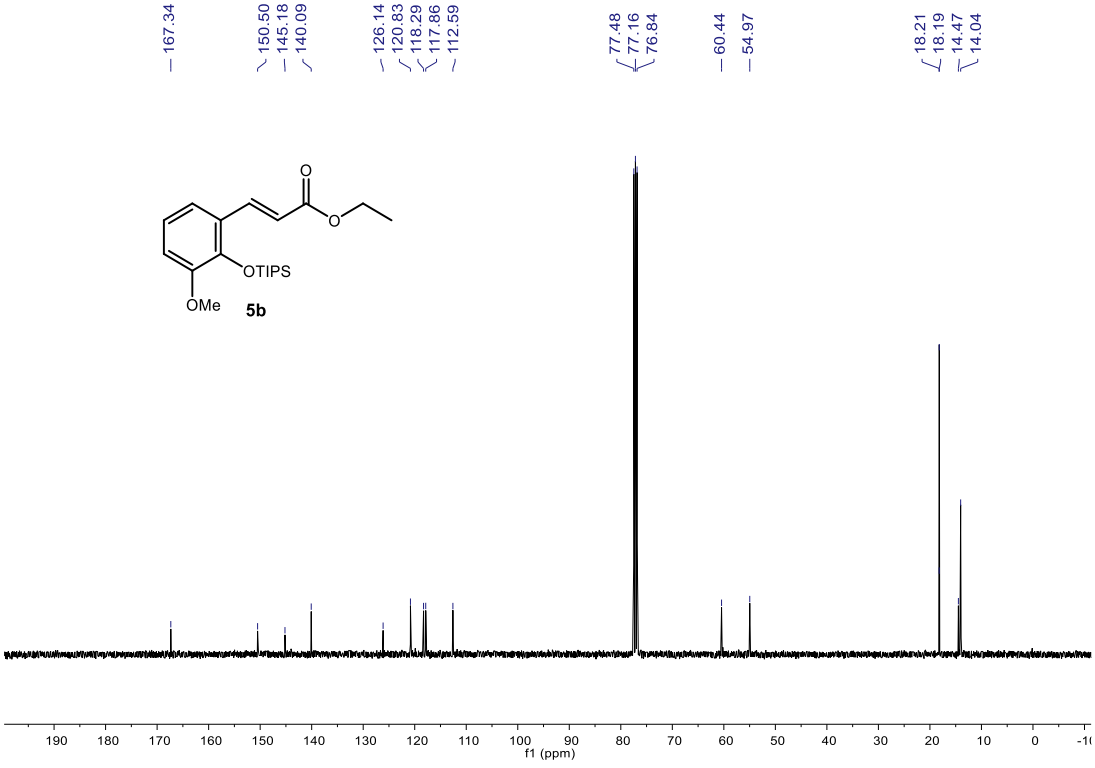
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5b



5b

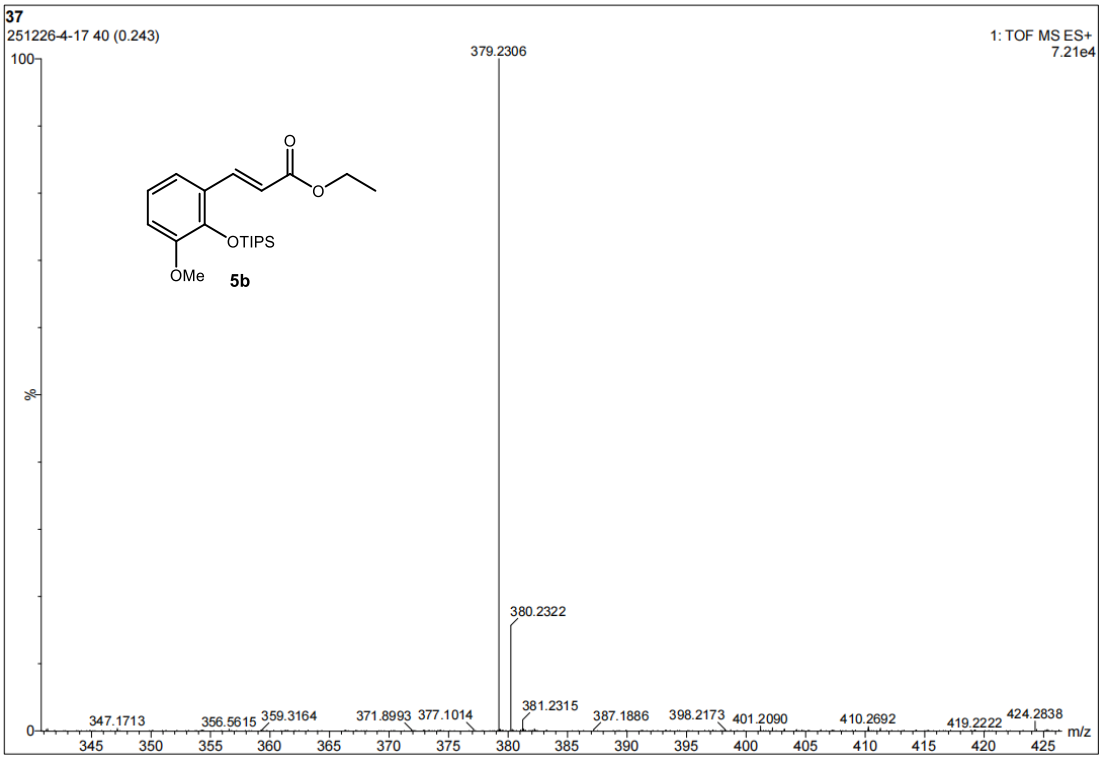


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5b



5b

HRMS of 5b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251226-4-17 40 (0.243)
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%
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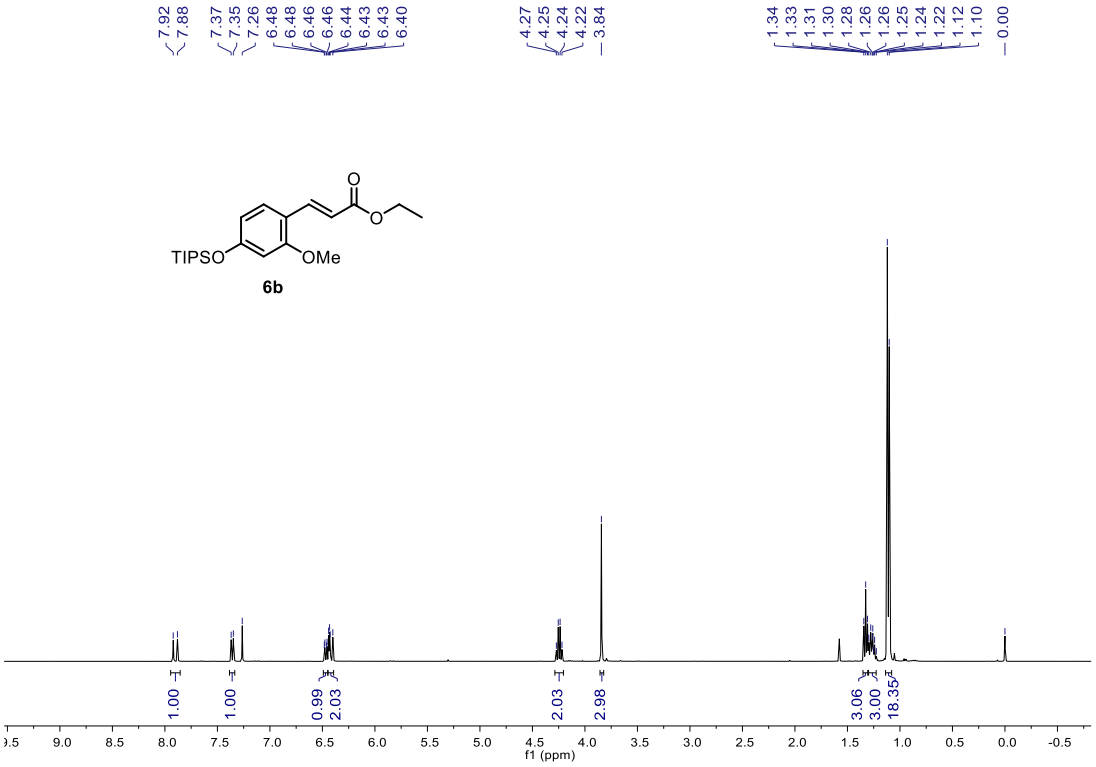
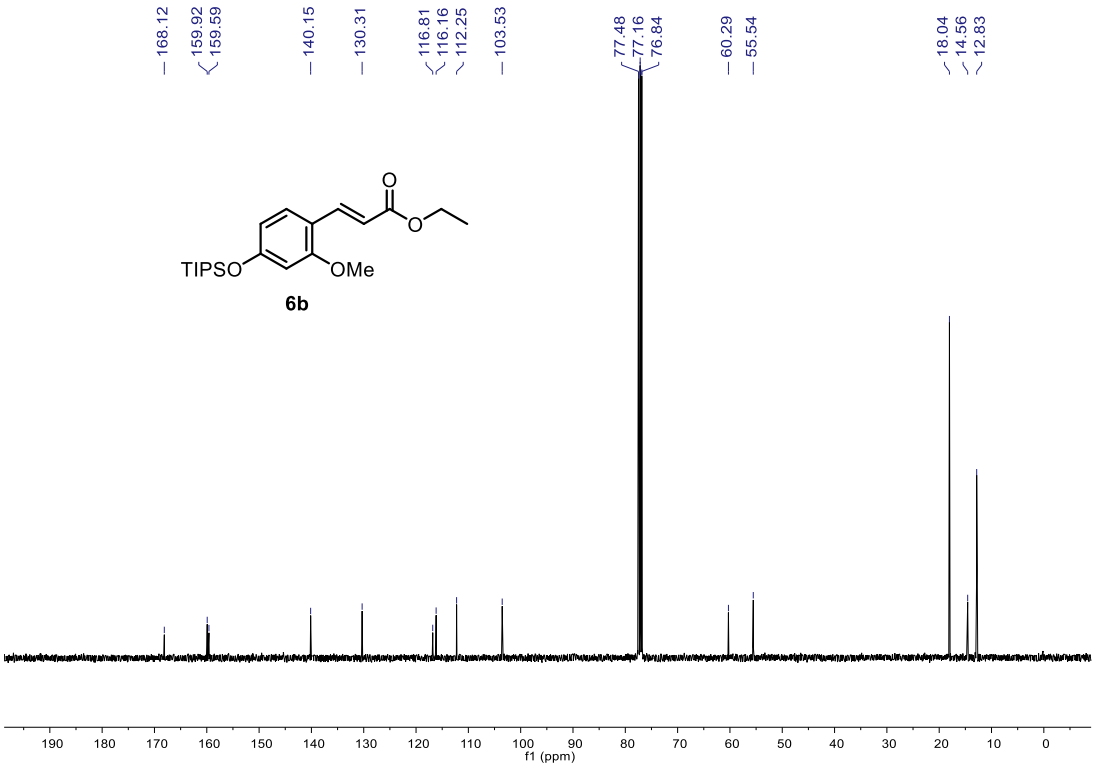
380.2322
381.2315
347.1713
356.5615
359.3164
371.8993
377.1014
387.1886
398.2173
401.2090
410.2692
419.2222
424.2838
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
m/z
O
O
OTIPS
OMe
5b

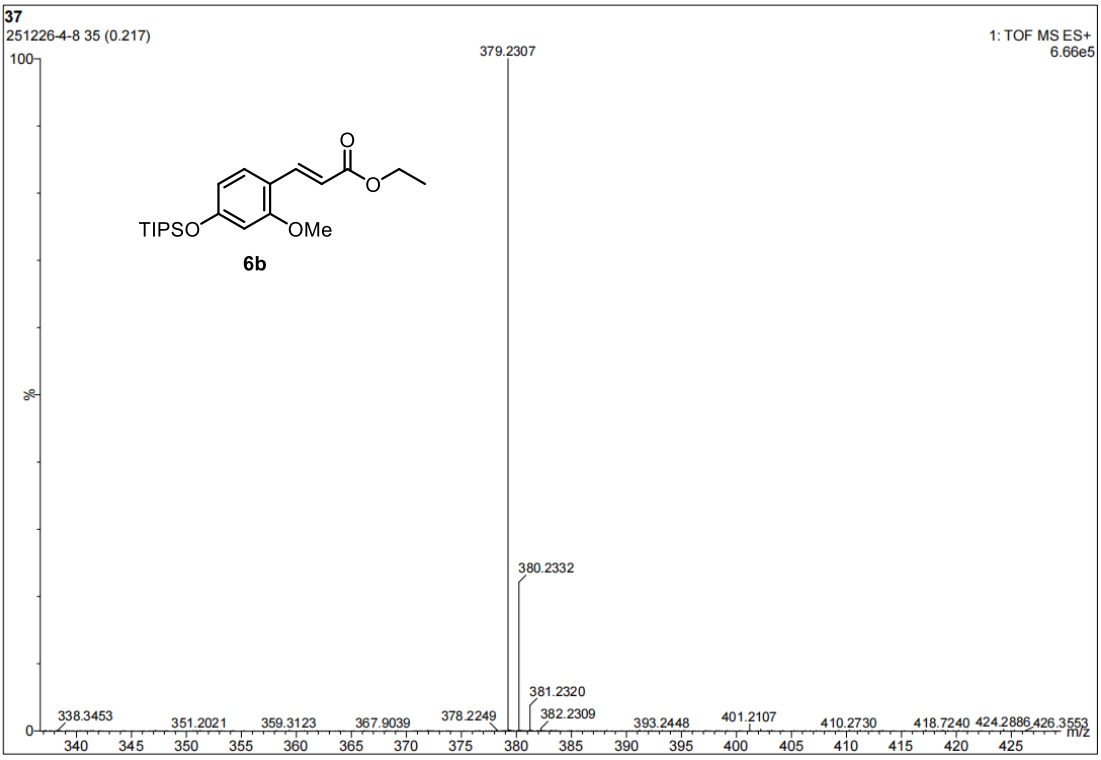
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 6b



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 6b



HRMS of 6b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381.2320
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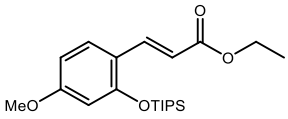
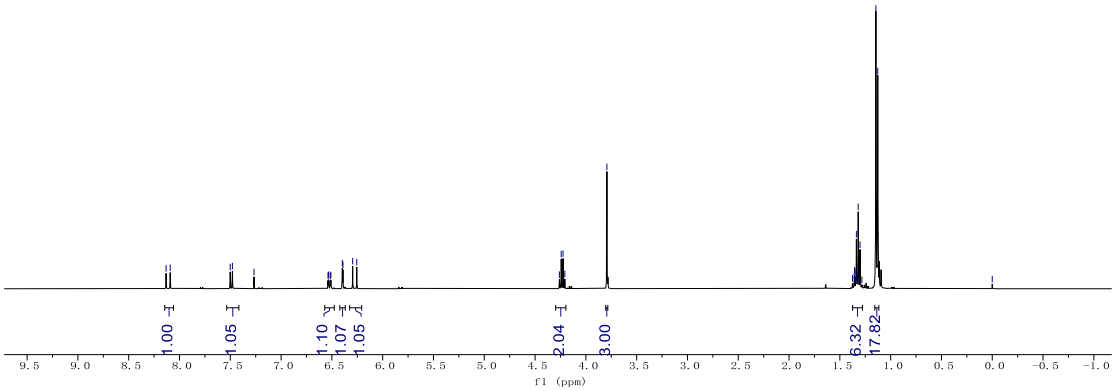
359.3123
367.9039
378.2249
393.2448
401.2107
410.2730
418.7240
424.2886
426.3553
TIPSO
OMe
6b
%
m/z

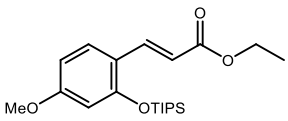
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 7b



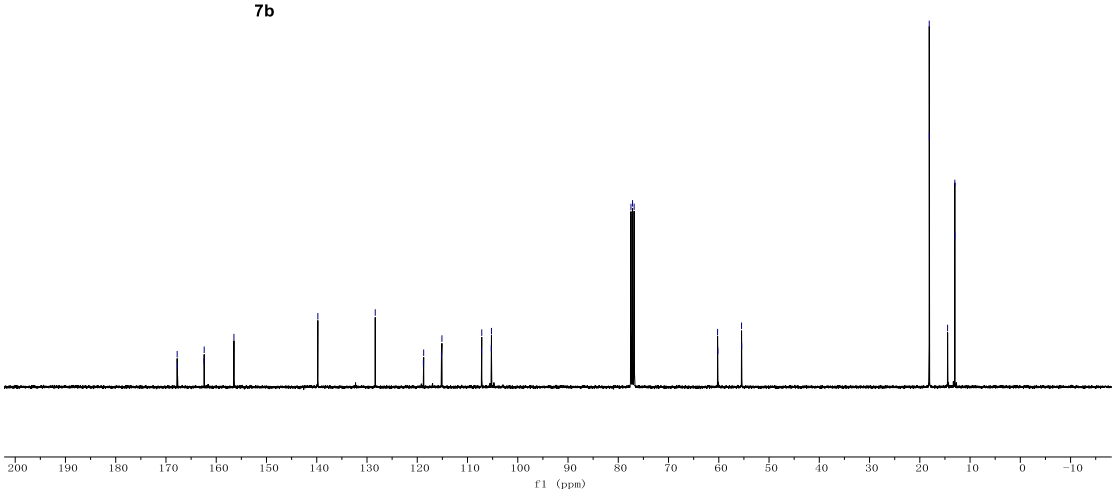
7b



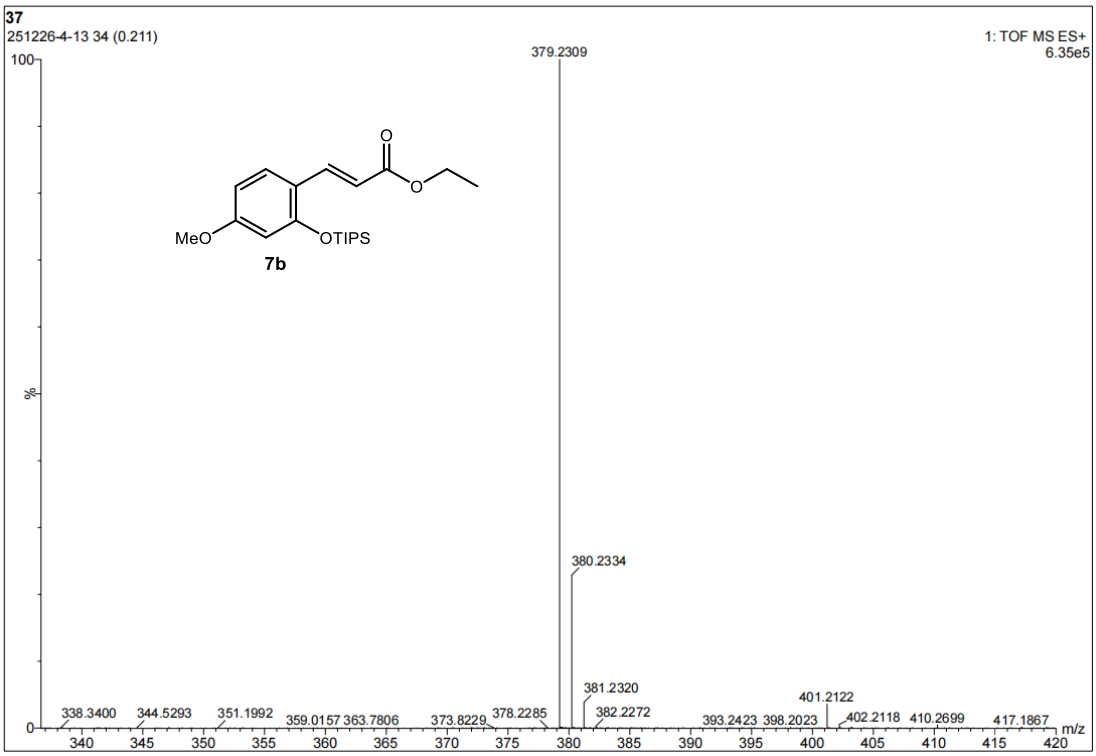
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 7b



7b



HRMS of 7b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%
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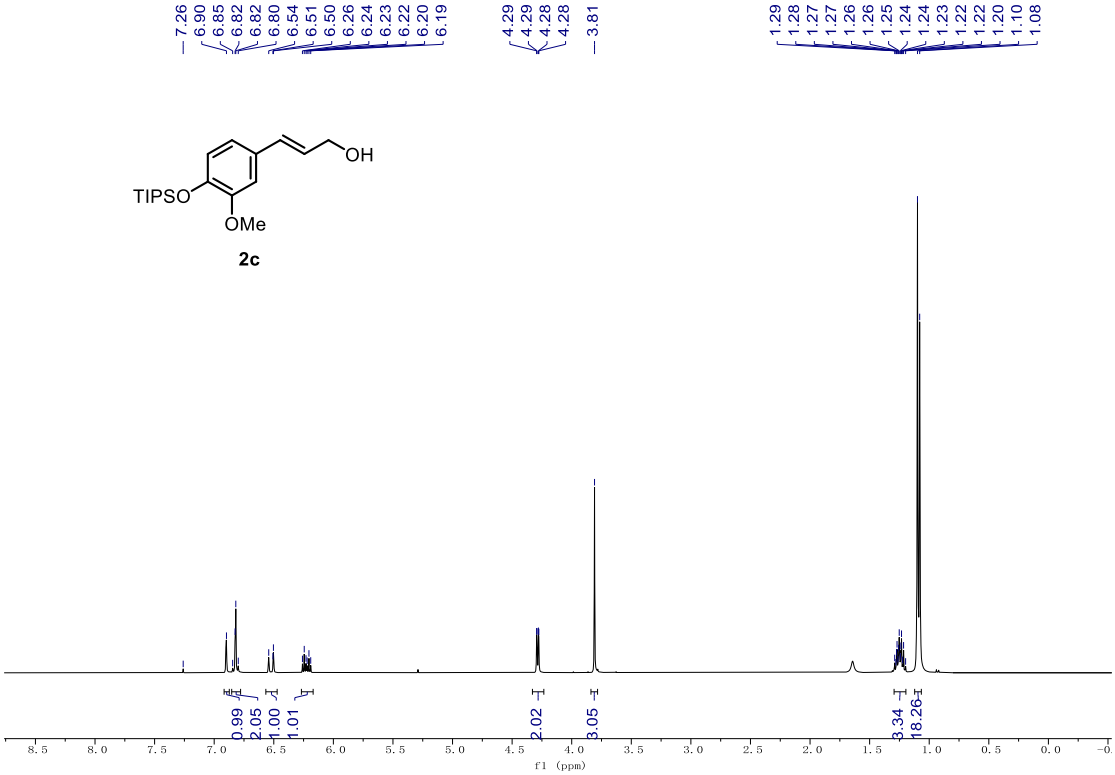
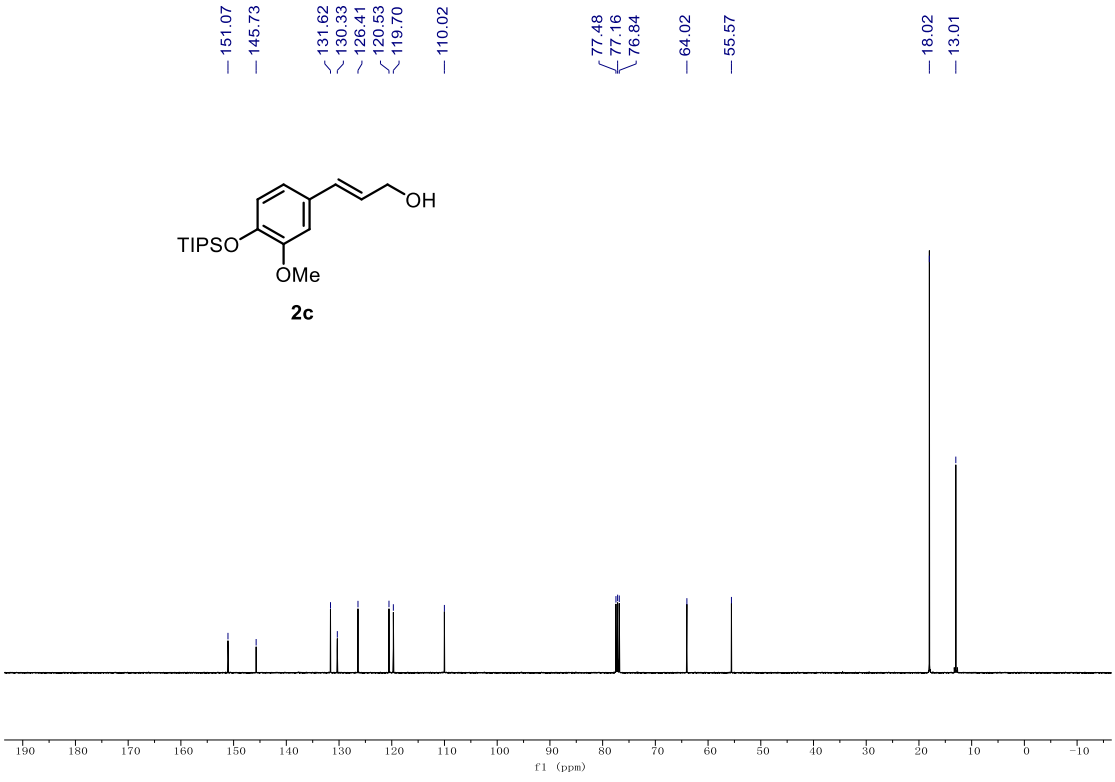
381.2320
382.2272
338.3400
344.5293
351.1992
359.0157
363.7806
373.8229
378.2285
393.2423
398.2023
401.2122
402.2118
410.2699
417.1867
m/z
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
O
O
MeO
OTIPS
7b

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 2c



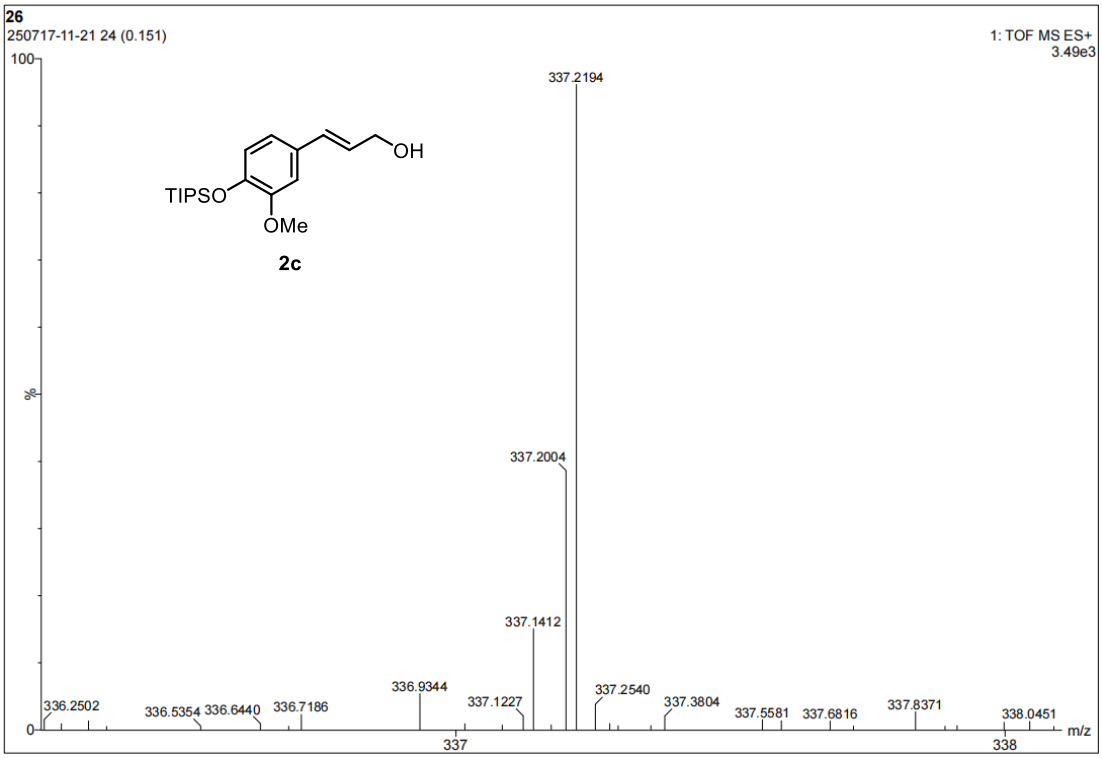
2c

^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 2c



2c

HRMS of 2c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100
%
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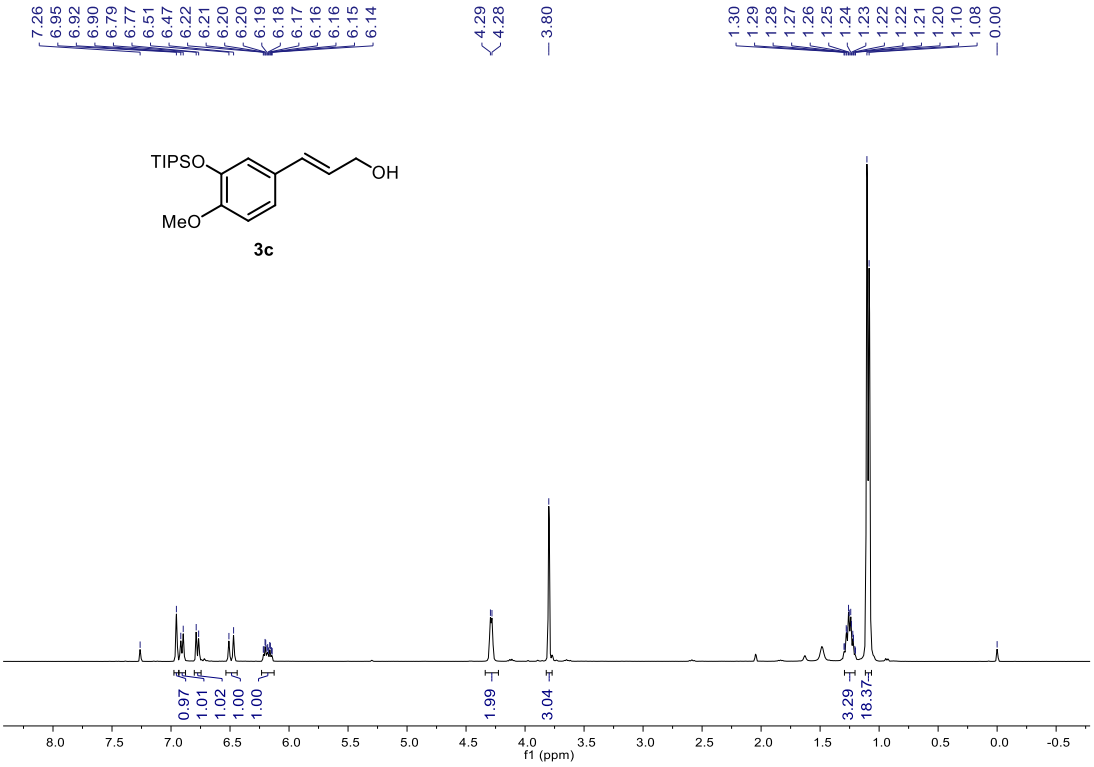
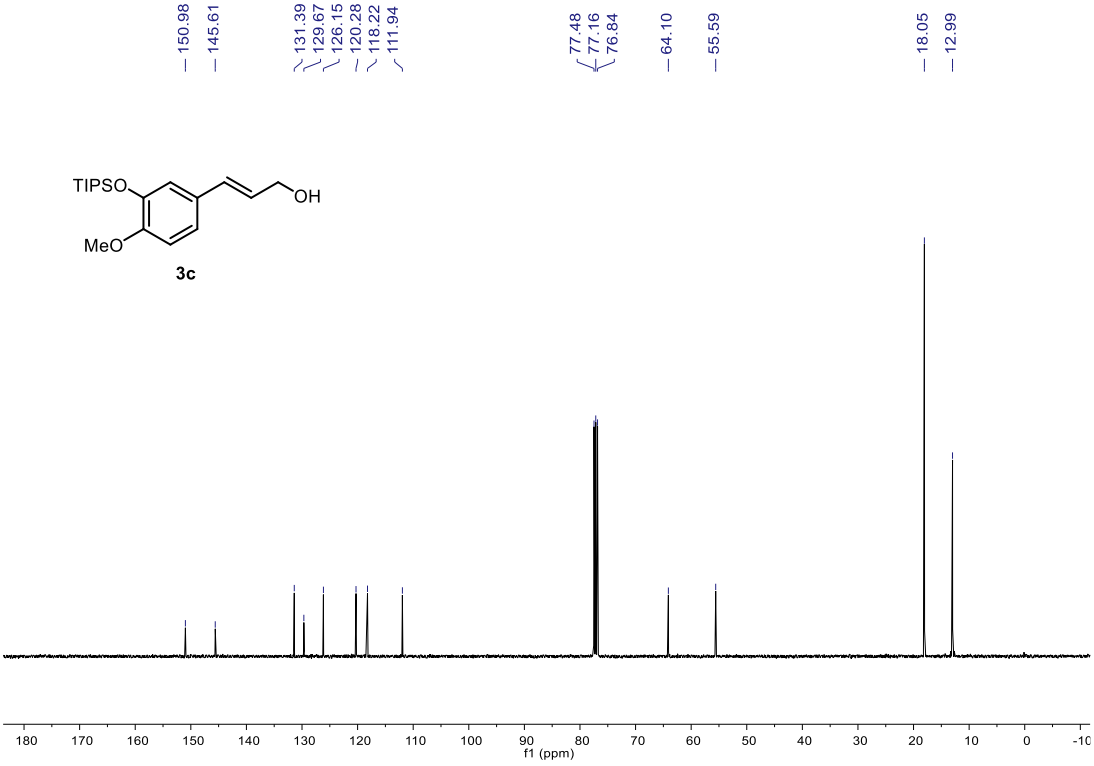
336.9344
337.1227
337.2540
337.3804
336.2502
336.5354
336.6440
336.7186
337.5581
337.6816
337.8371
338.0451
337
338
m/z
OH
TIPSO
OMe
2c

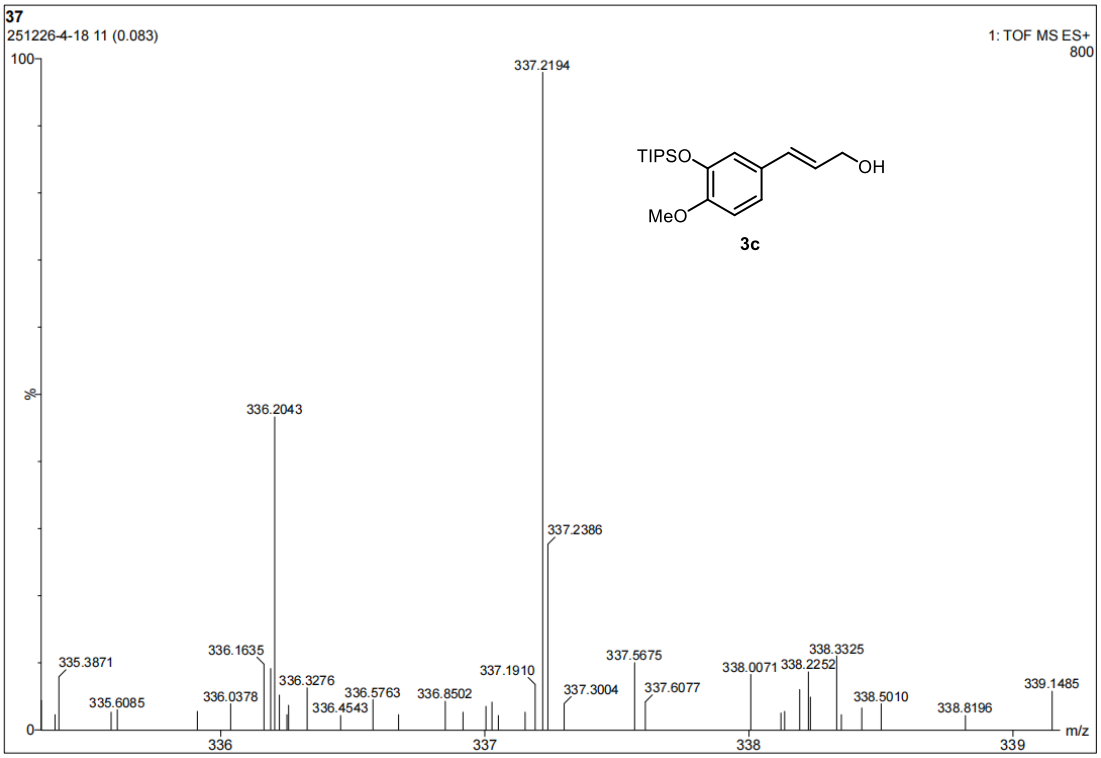
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3c



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3c



HRMS of 3c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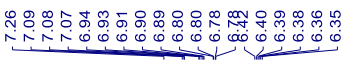
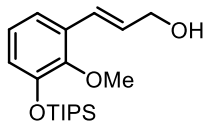
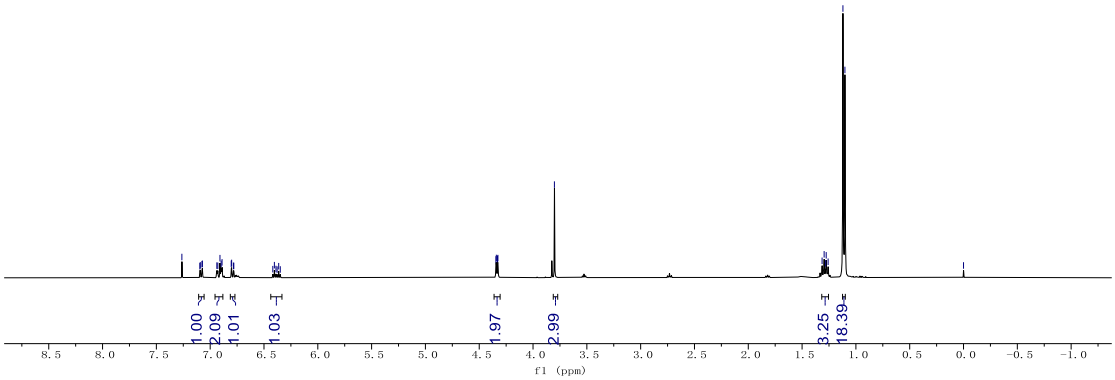
336.3276
335.6085
336.0378
336.5763
336.4543
336.8502
337.1910
337.3004
337.5675
337.6077
338.0071
338.3325
338.2252
338.5010
338.8196
339.1485
336
337
338
339
m/z
TIPSO
MeO
OH
3c

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4c

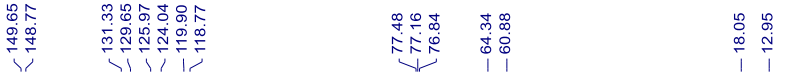


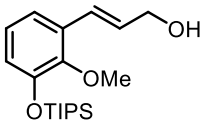


4c

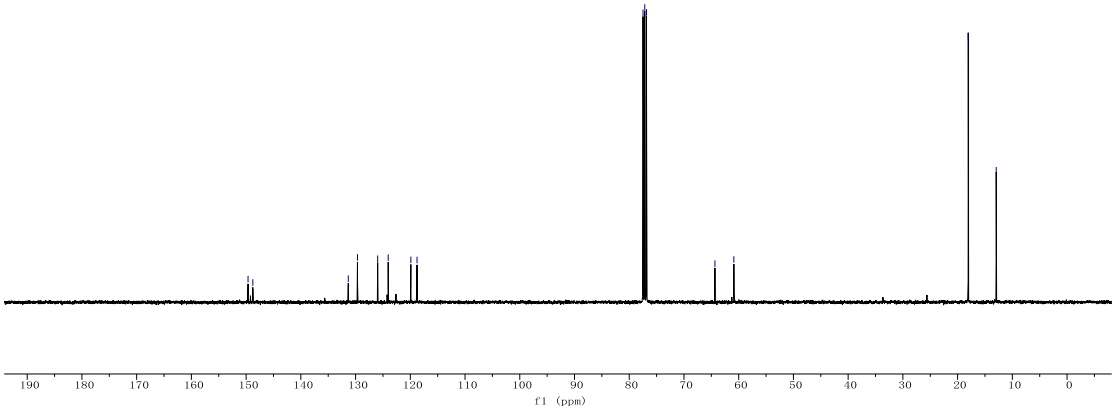


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4c

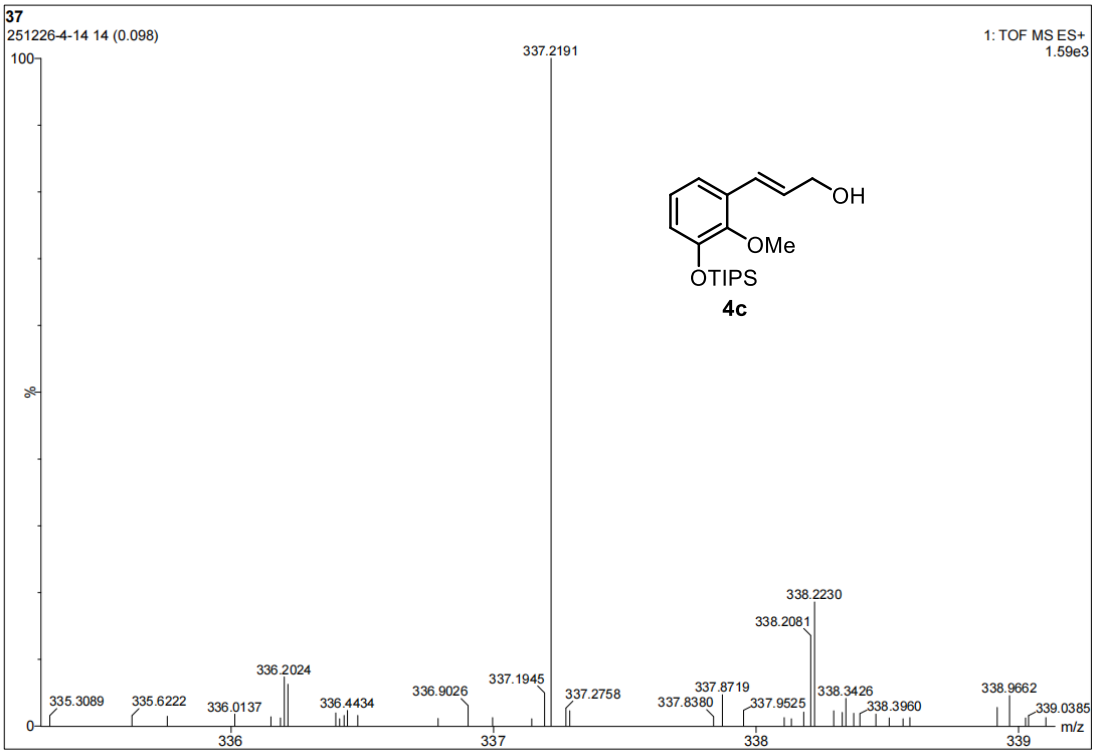




4c



HRMS of 4c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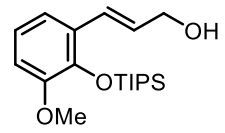
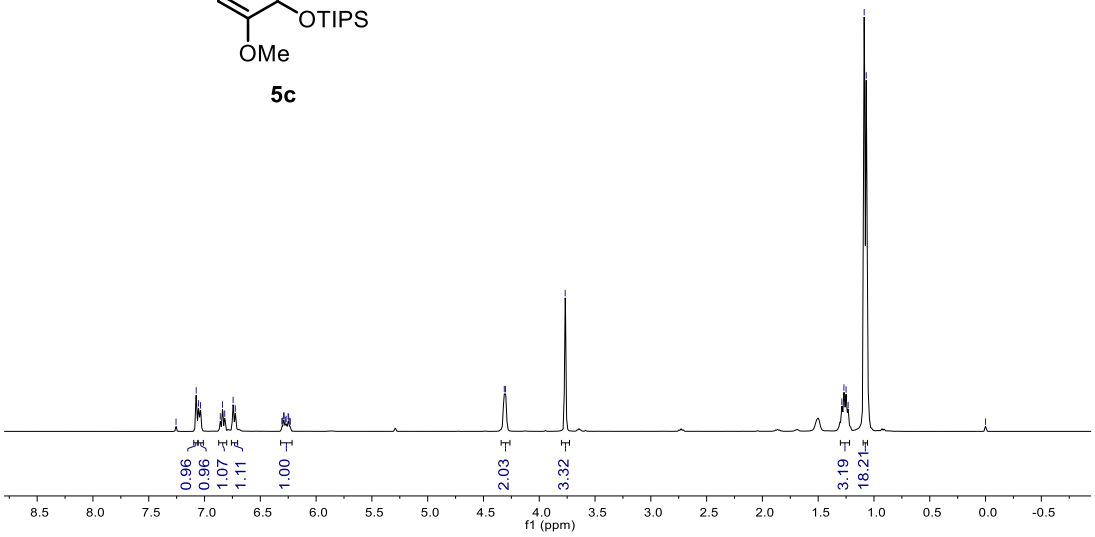
337.8380
337.9525
338.3426
338.3960
338.9662
339.0385
335.3089
335.6222
336.0137
336.4434
336
337
338
339
m/z
OH
OMe
OTIPS
4c

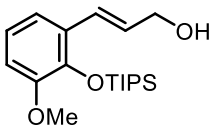
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5c



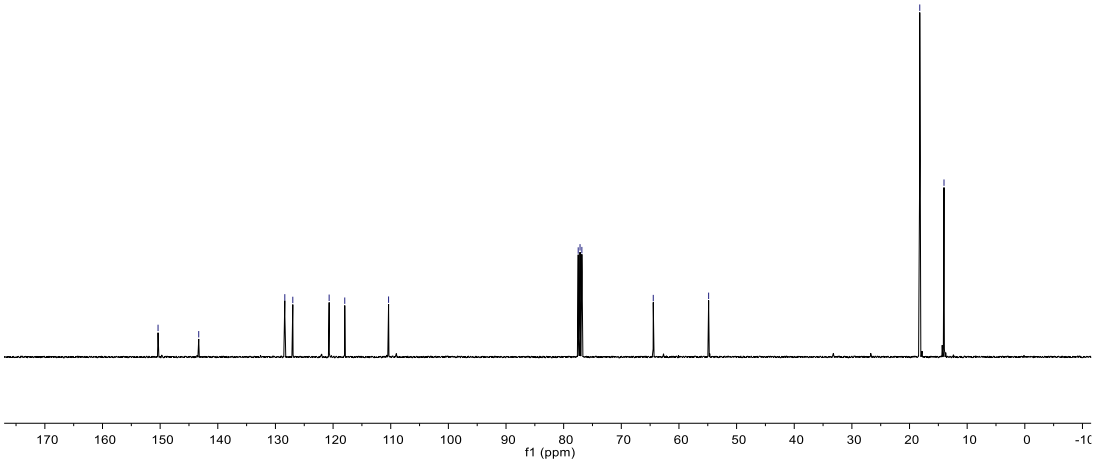
5c



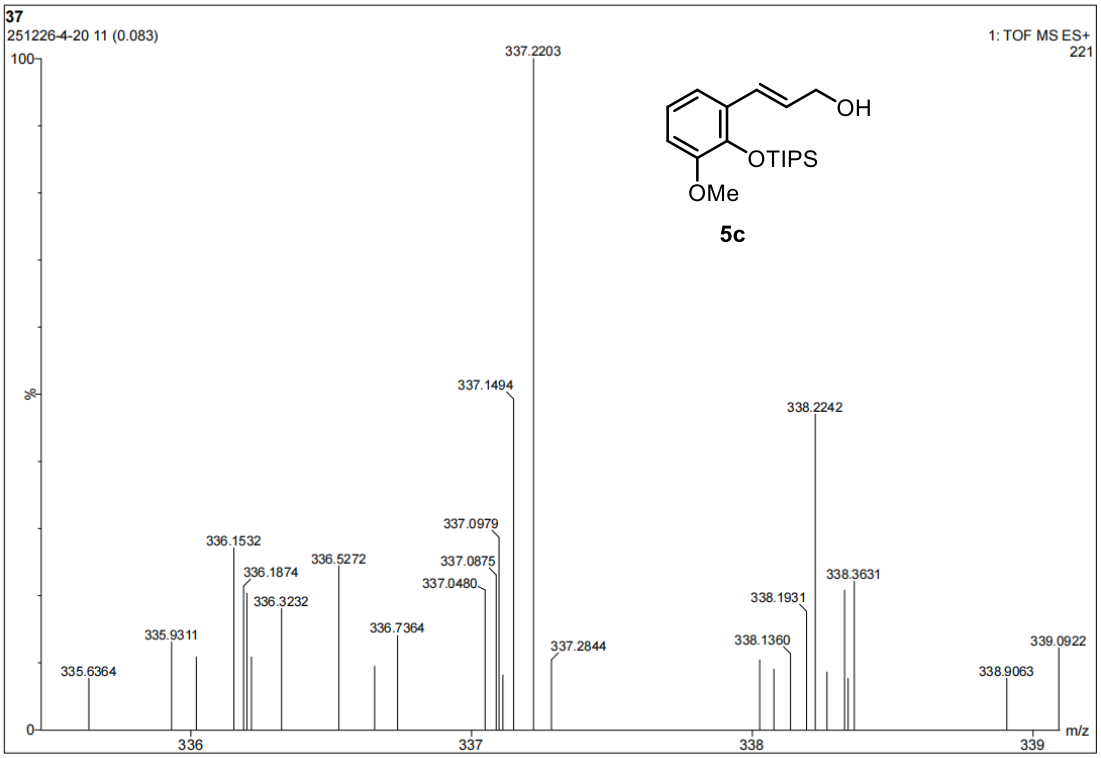
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5c



5c



HRMS of 5c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337.0979
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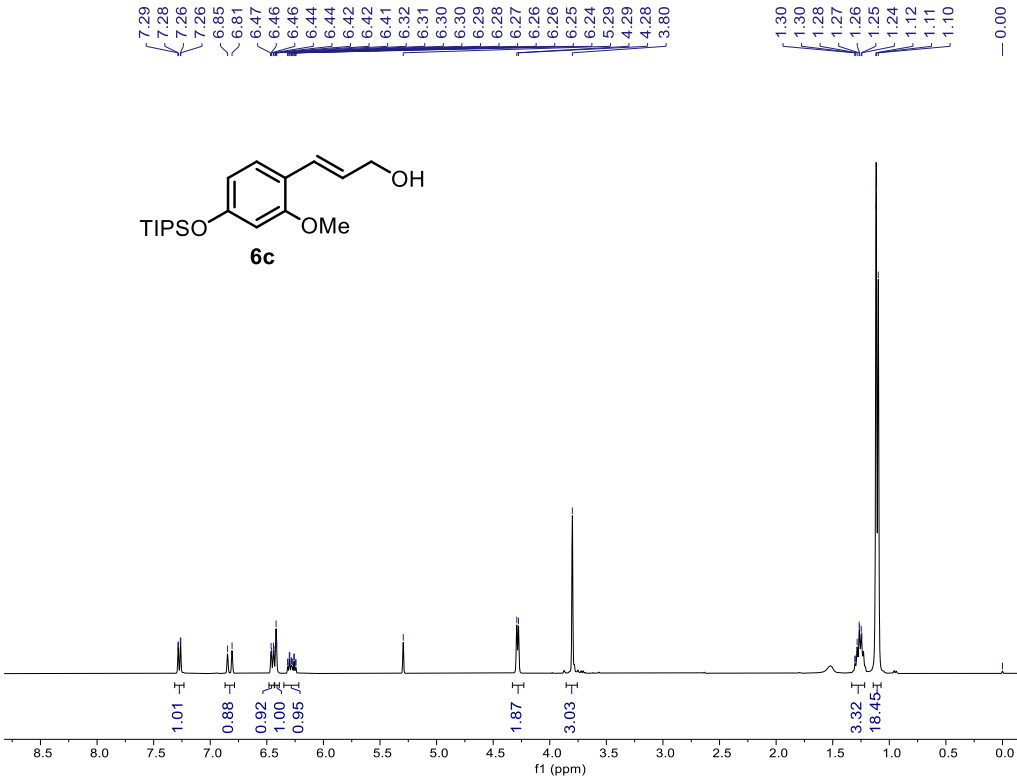
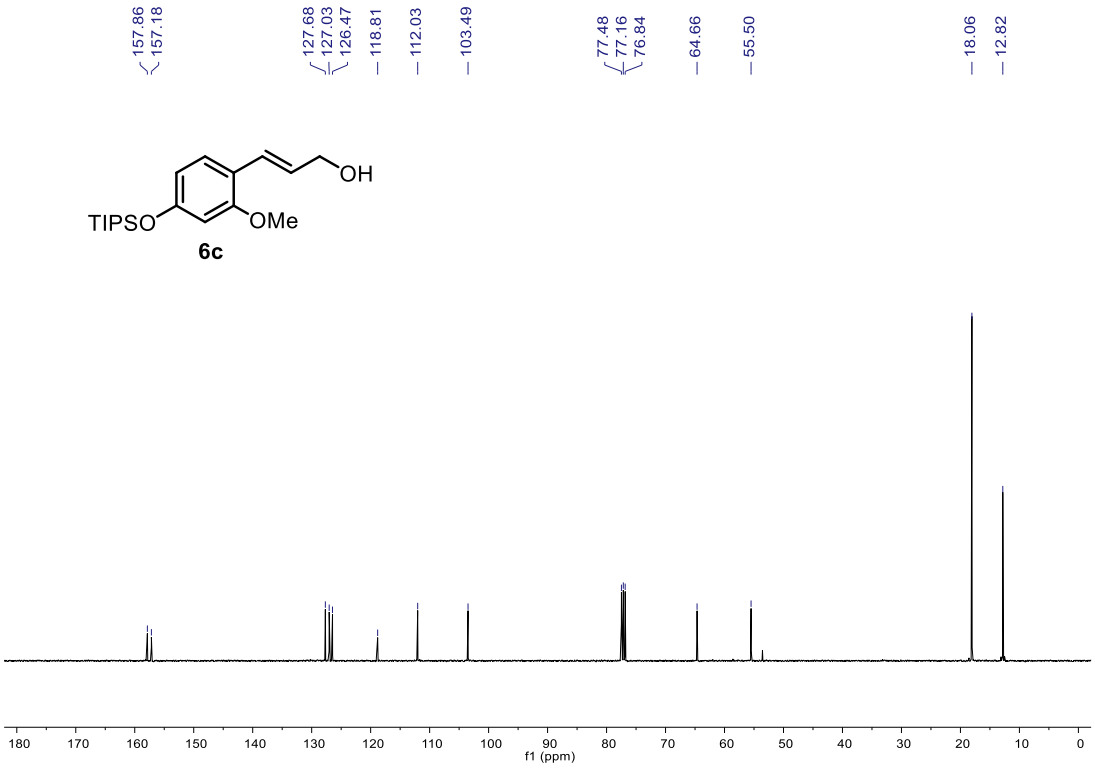
337.0875
336.5272
336.1874
337.0480
338.3631
336.3232
338.1931
335.9311
336.7364
337.2844
338.1360
339.0922
335.6364
338.9063
336
337
338
339
m/z
OH
OTIPS
OMe
5c

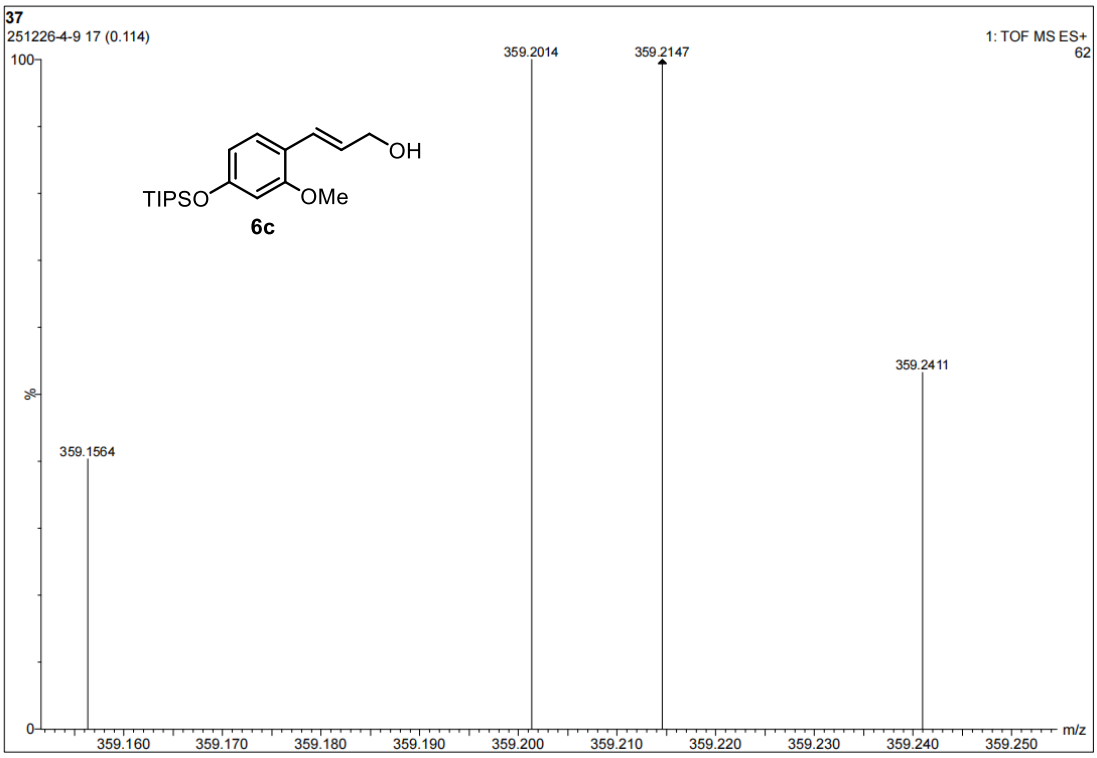
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 6c



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 6c



HRMS of 6c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%
0
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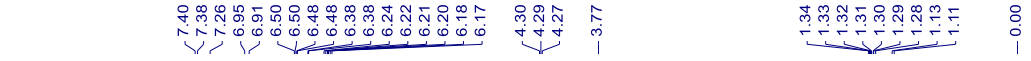
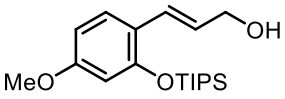
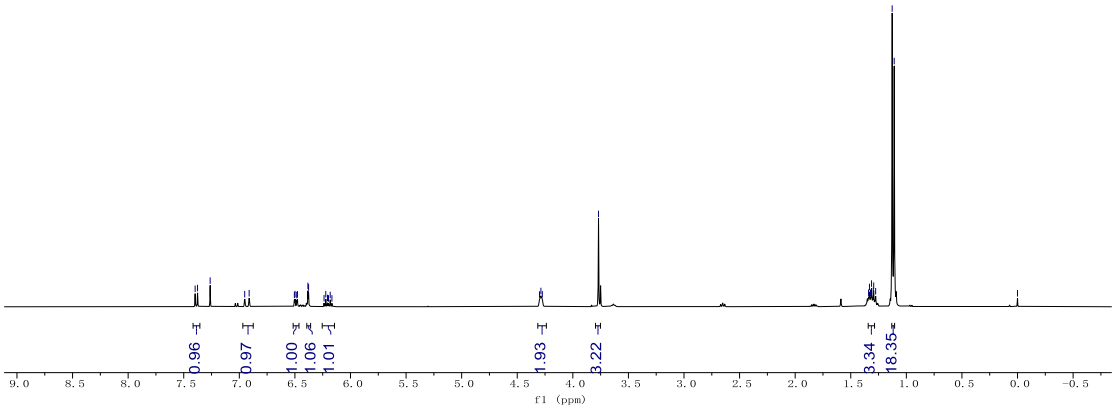
359.1564
OH
TIPSO
OMe
6c
359.160
359.170
359.180
359.190
359.200
359.210
359.220
359.230
359.240
359.250
m/z

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 7c

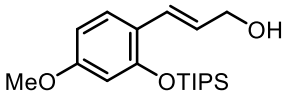




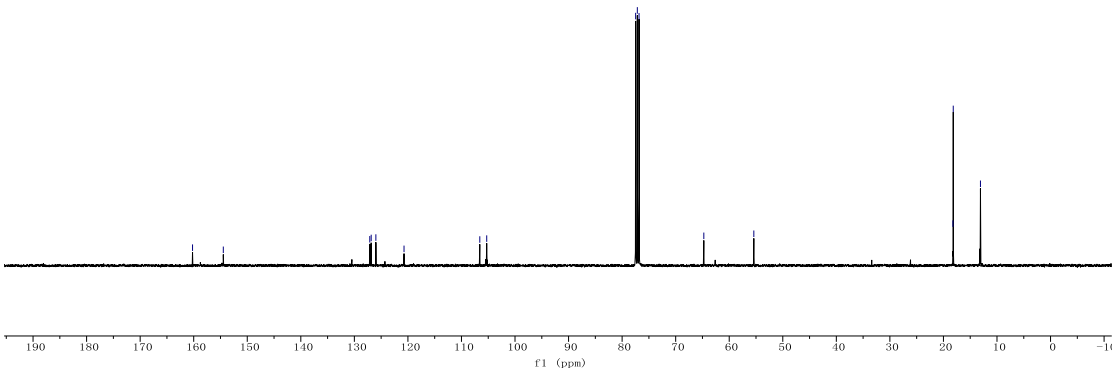
7c



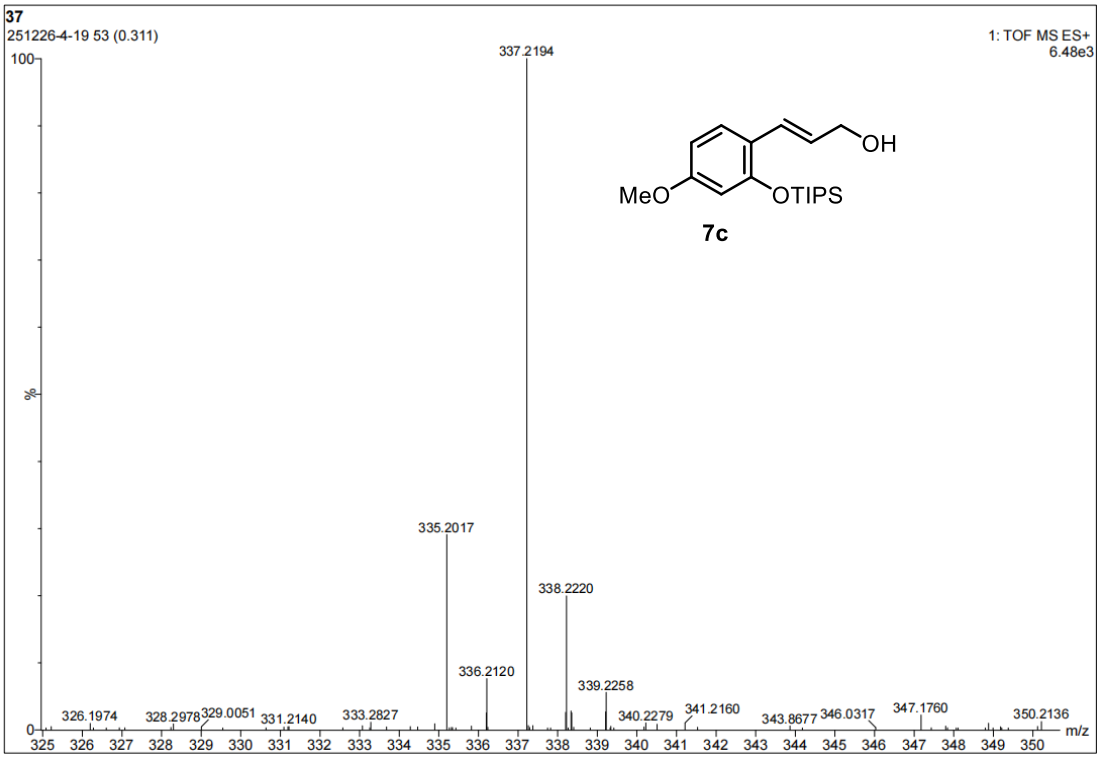
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 7c



7c



HRMS of 7c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%
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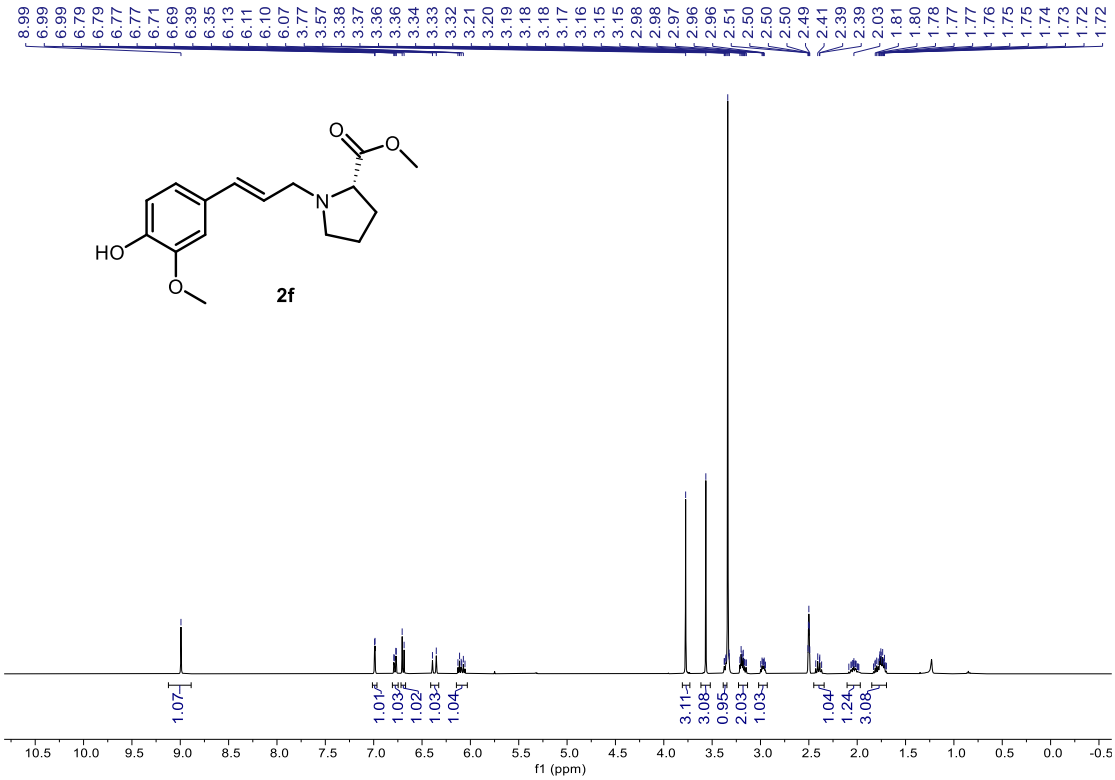
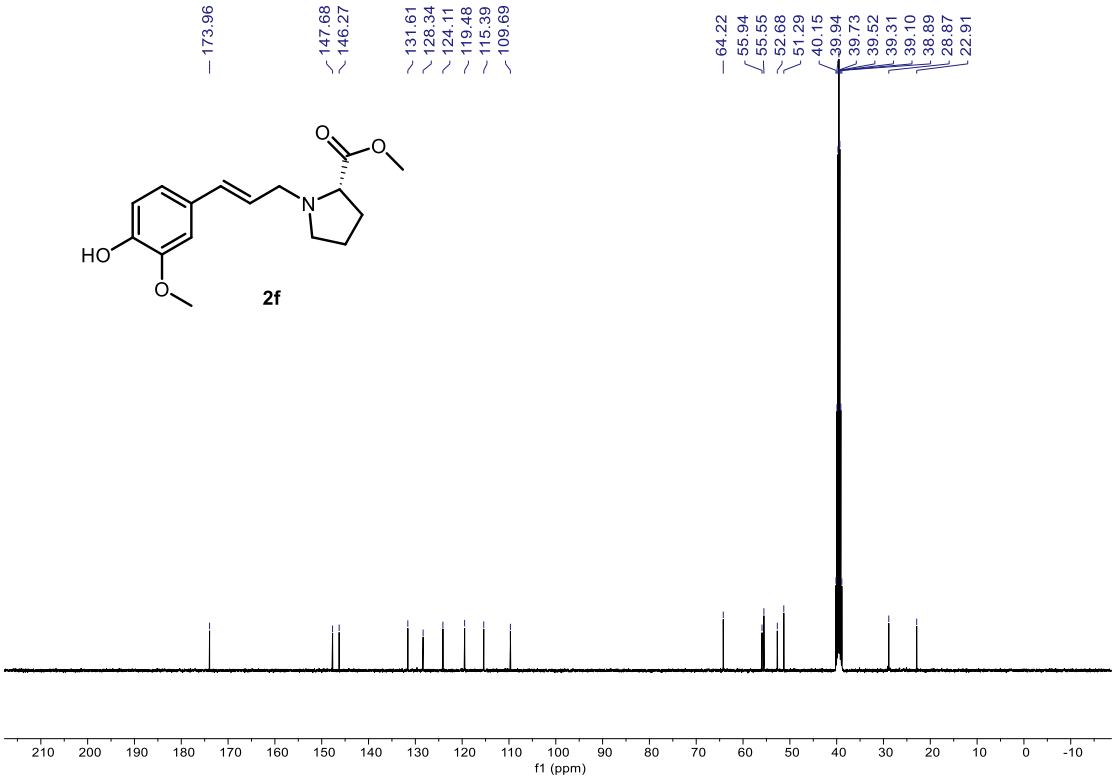
336.2120
339.2258
326.1974
328.2978
329.0051
331.2140
333.2827
340.2279
341.2160
343.8677
346.0317
347.1760
350.2136
m/z
325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350
OH
MeO
OTIPS
7c

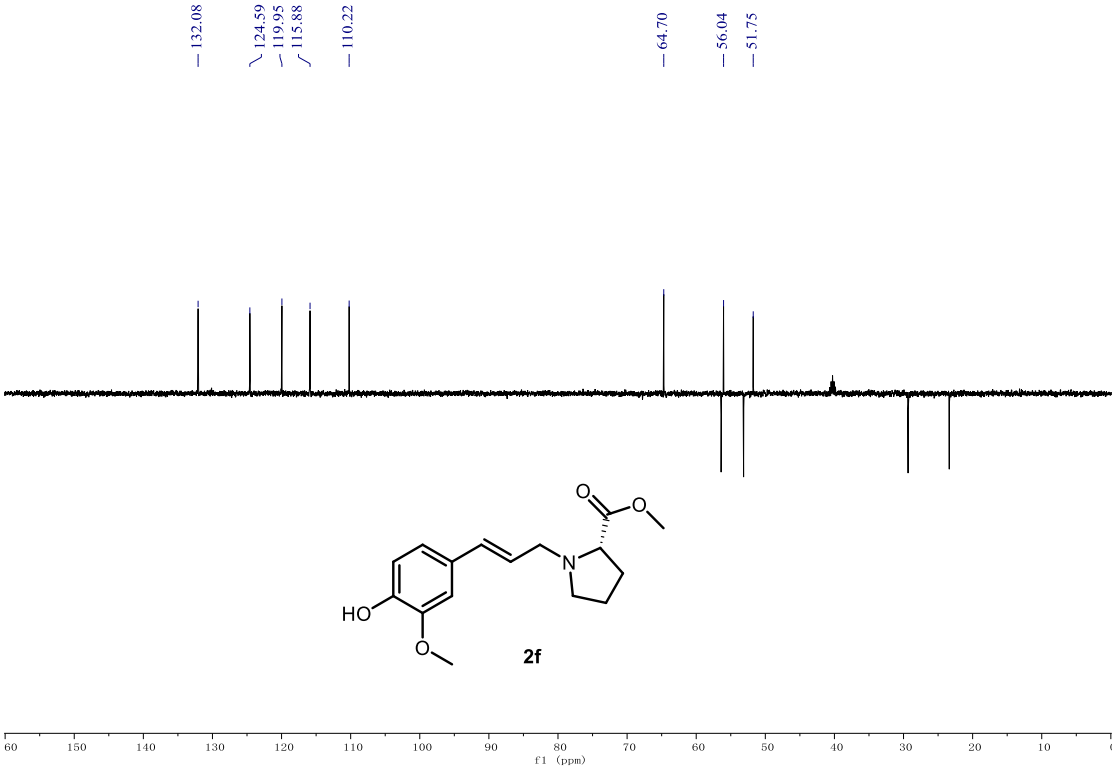
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of 2f



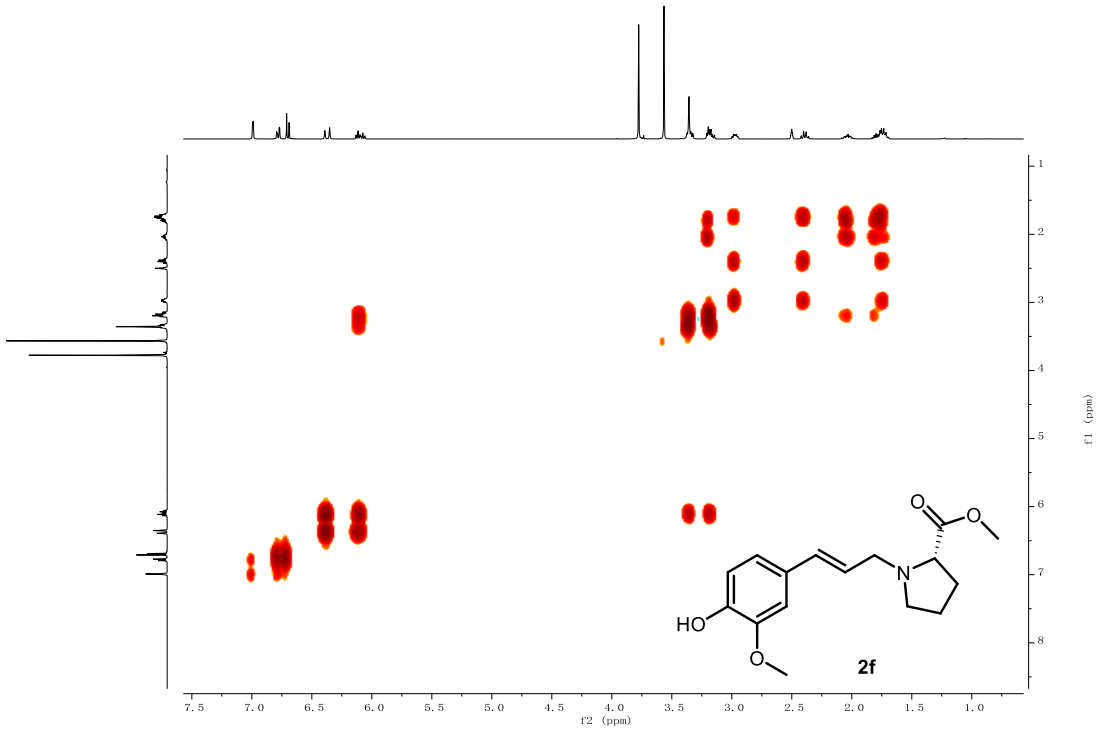
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of 2f



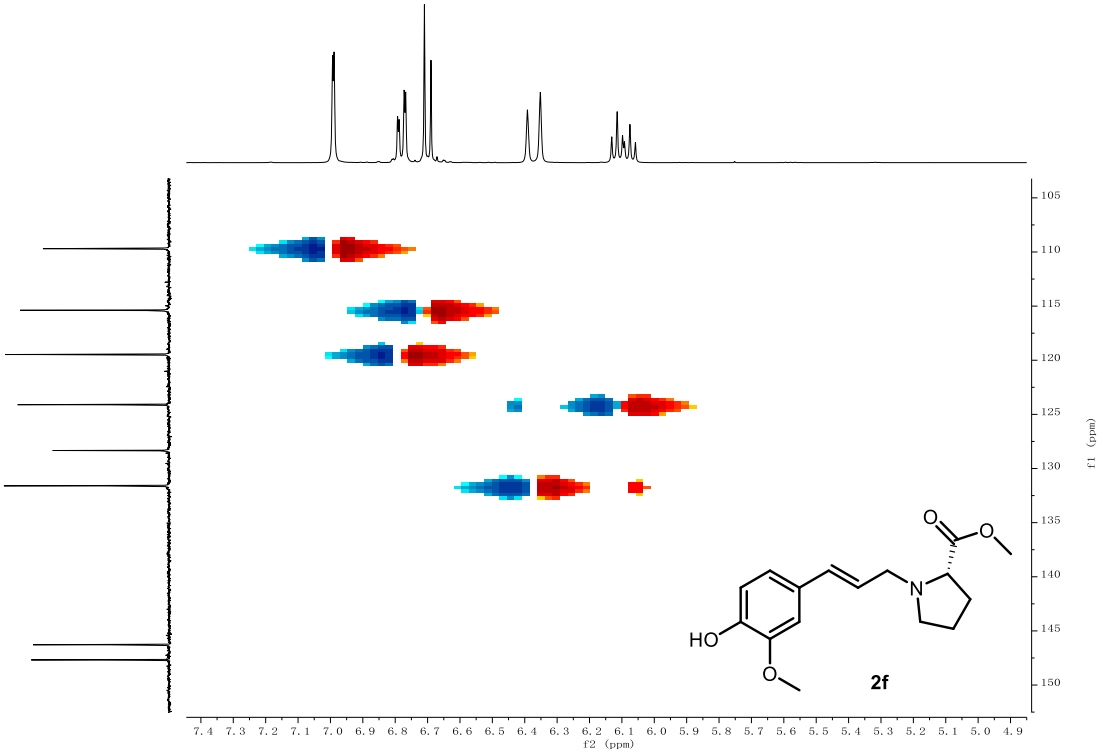
DEPT135 (400 MHz, DMSO-d_6) Spectrum of 2f



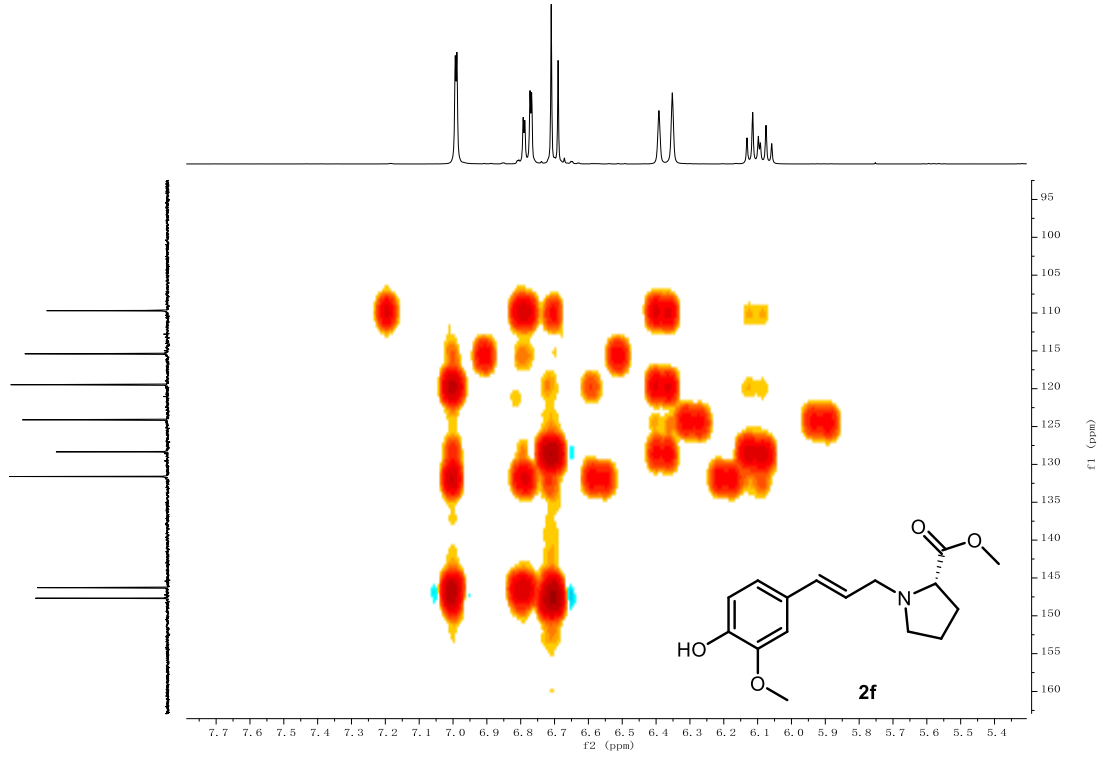
^{1}H-^{1}H COSY (400 MHz, DMSO-d_6) Spectrum of 2f



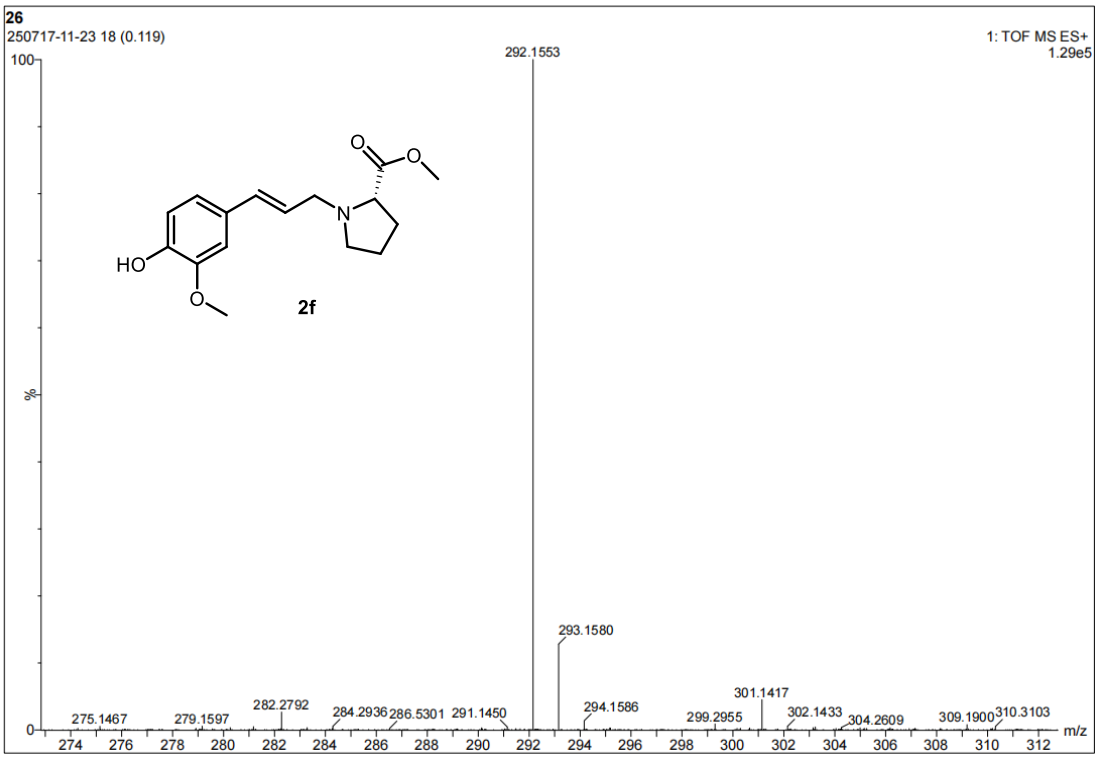
HSQC (400 MHz, DMSO-d_6) Spectrum of 2f



HMBC (400 MHz, DMSO-d_6) Spectrum of 2f



HRMS of 2f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%
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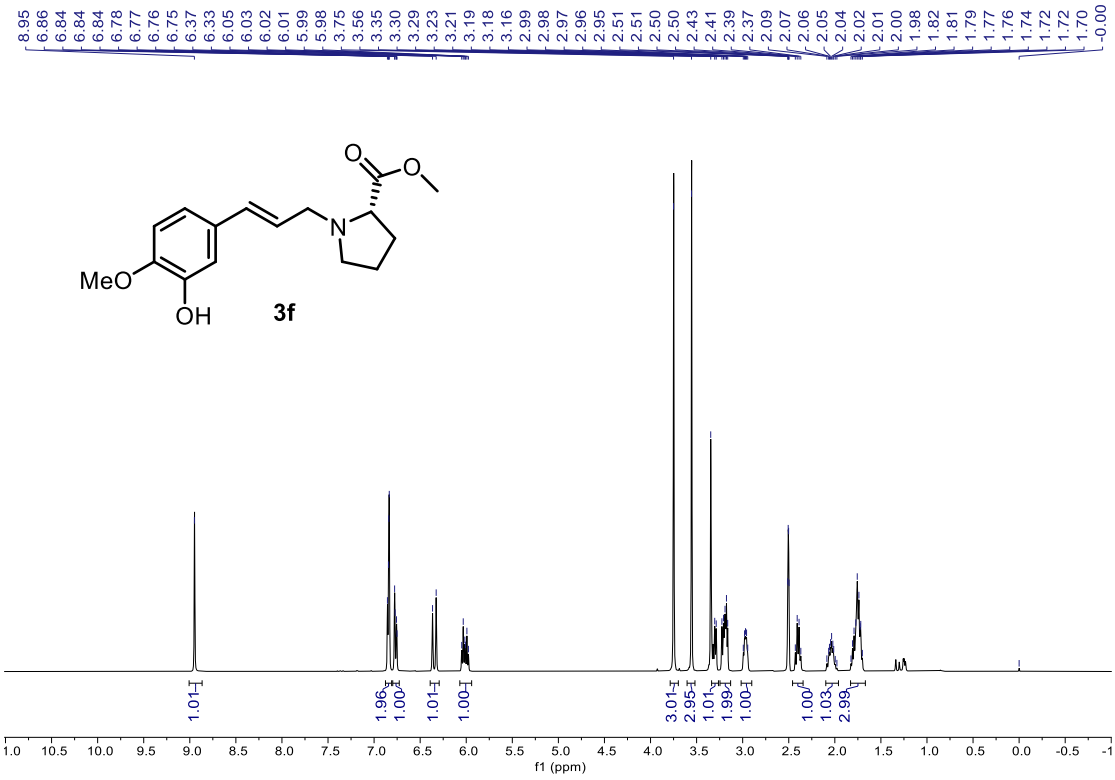
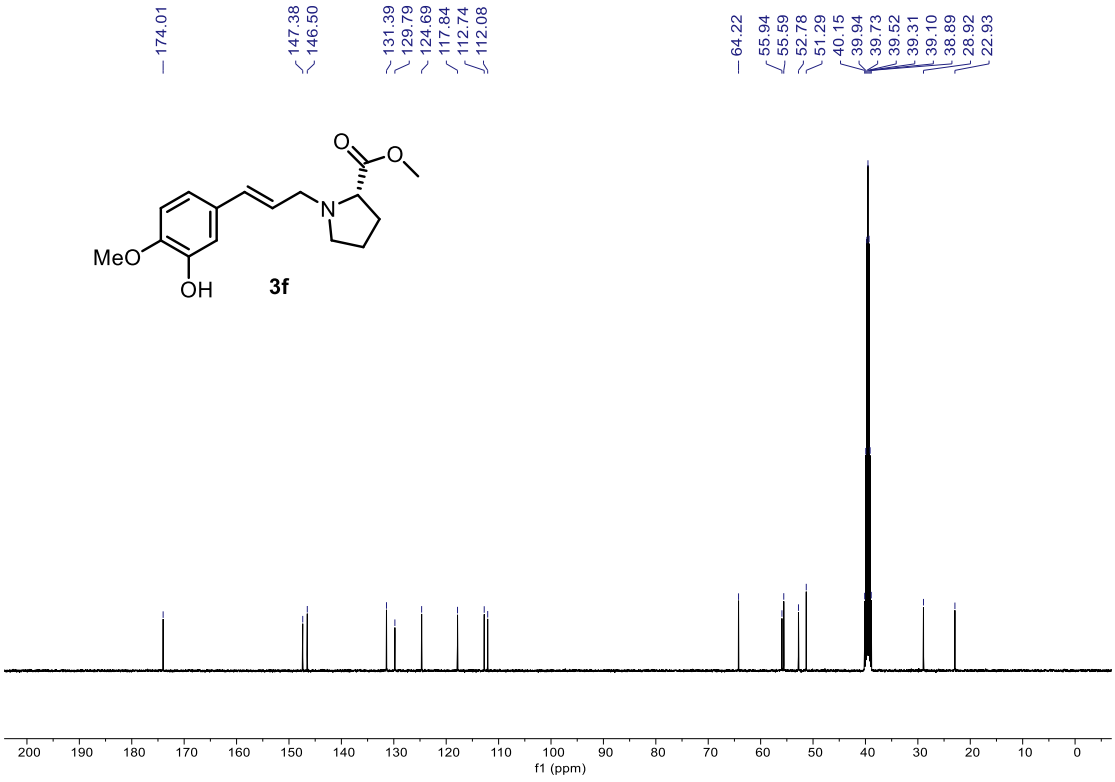
293.1580
301.1417
275.1467
279.1597
282.2792
284.2936
286.5301
291.1450
294.1586
299.2955
302.1433
304.2609
309.1900
310.3103
274
276
278
280
282
284
286
288
290
292
294
296
298
300
302
304
306
308
310
312
m/z
HO
O
O
N
O
2f

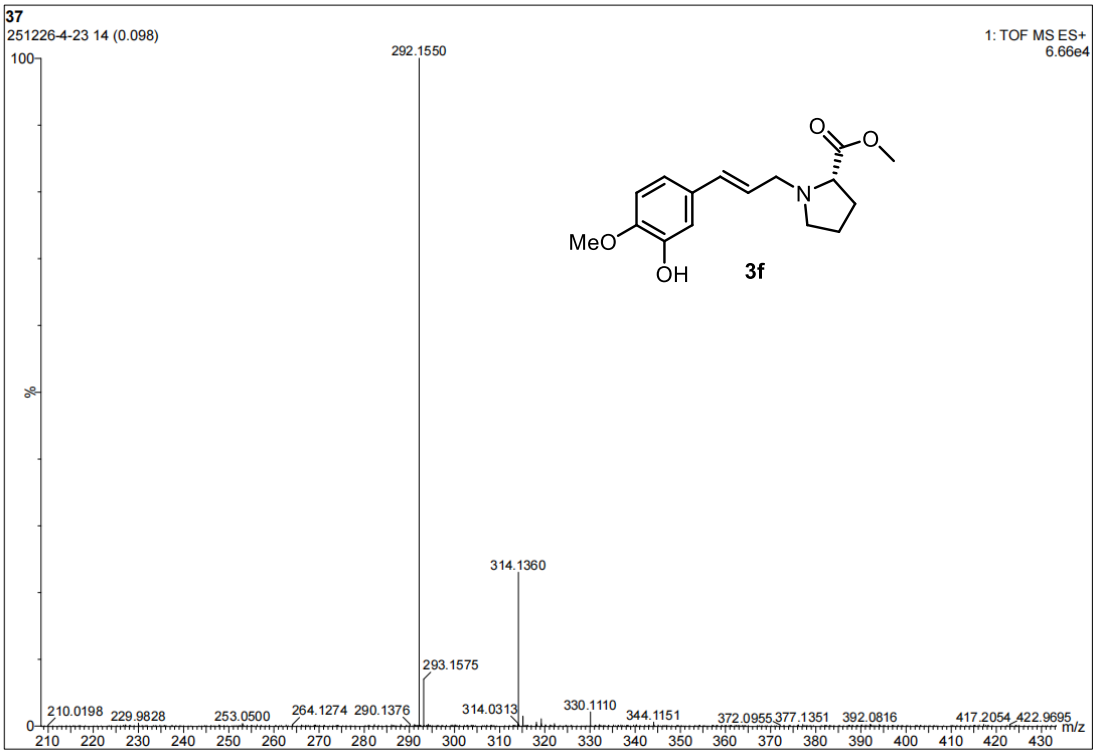
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of 3f



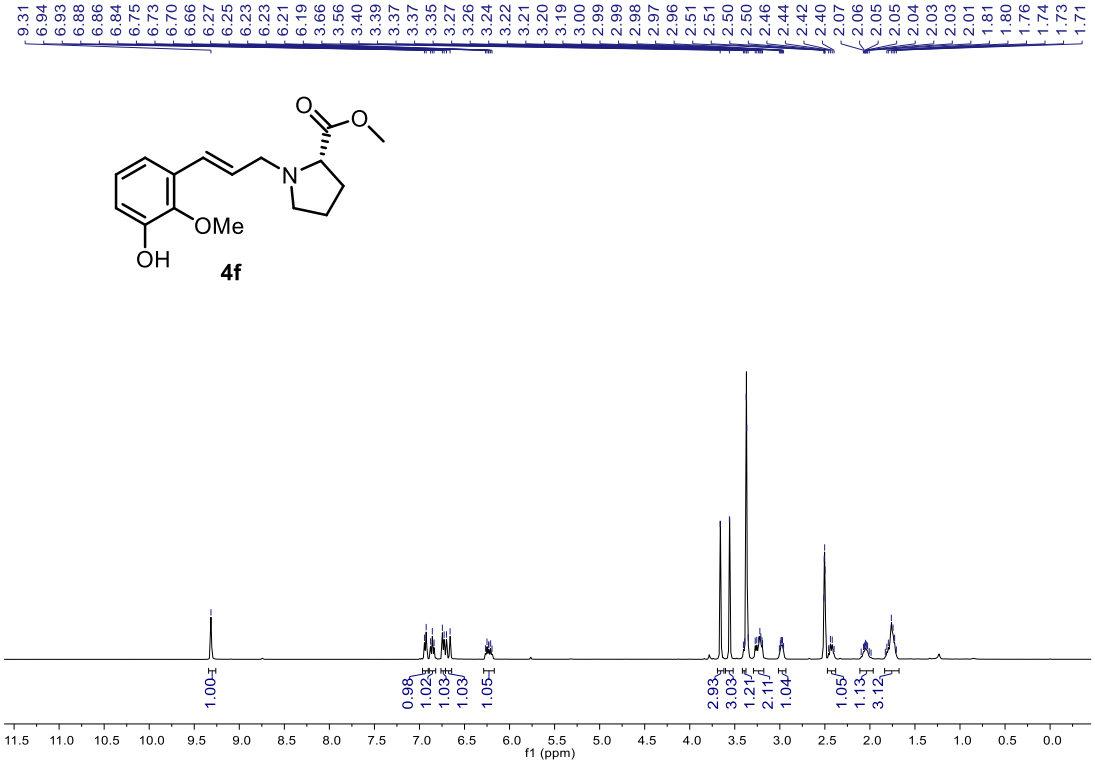
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of 3f



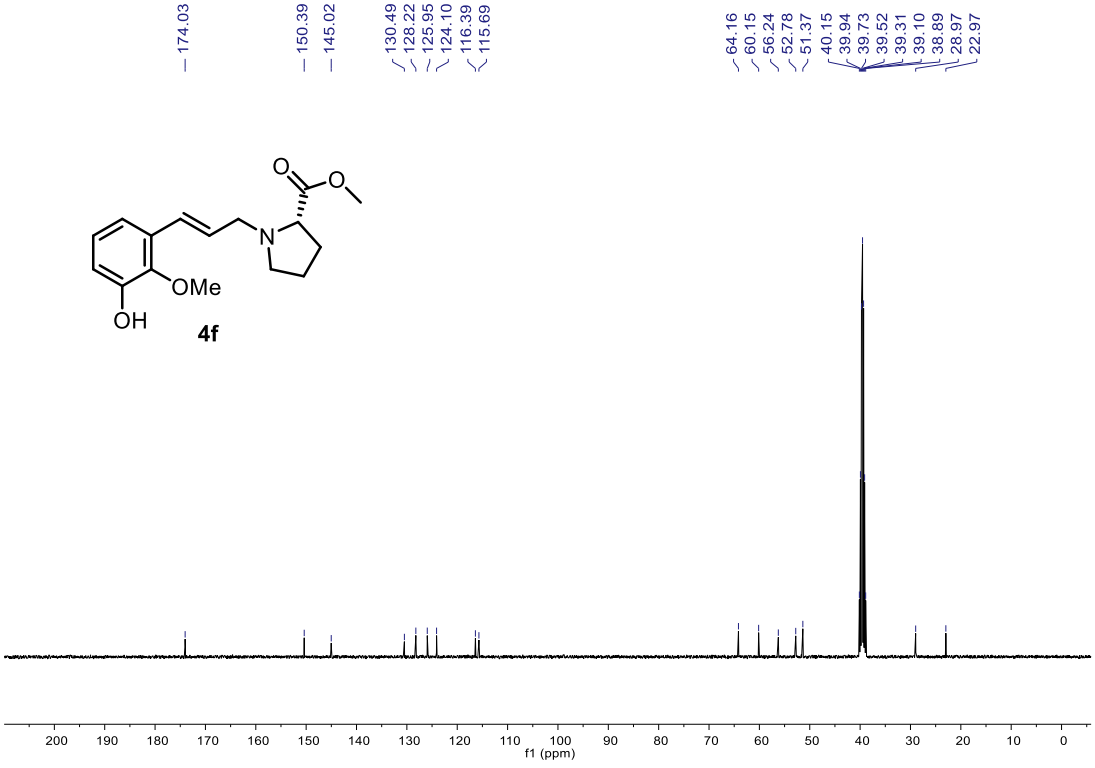
HRMS of 3f


37
251226-4-23 14 (0.098)
1: TOF MS ES+
6.66e4
100
%
0
292.1550
314.1360
293.1575
210.0198
229.9828
253.0500
264.1274
290.1376
314.0313
330.1110
344.1151
372.0955
377.1351
392.0816
417.2054
422.9695
m/z
210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430
MeO
OH
N
O
O
3f

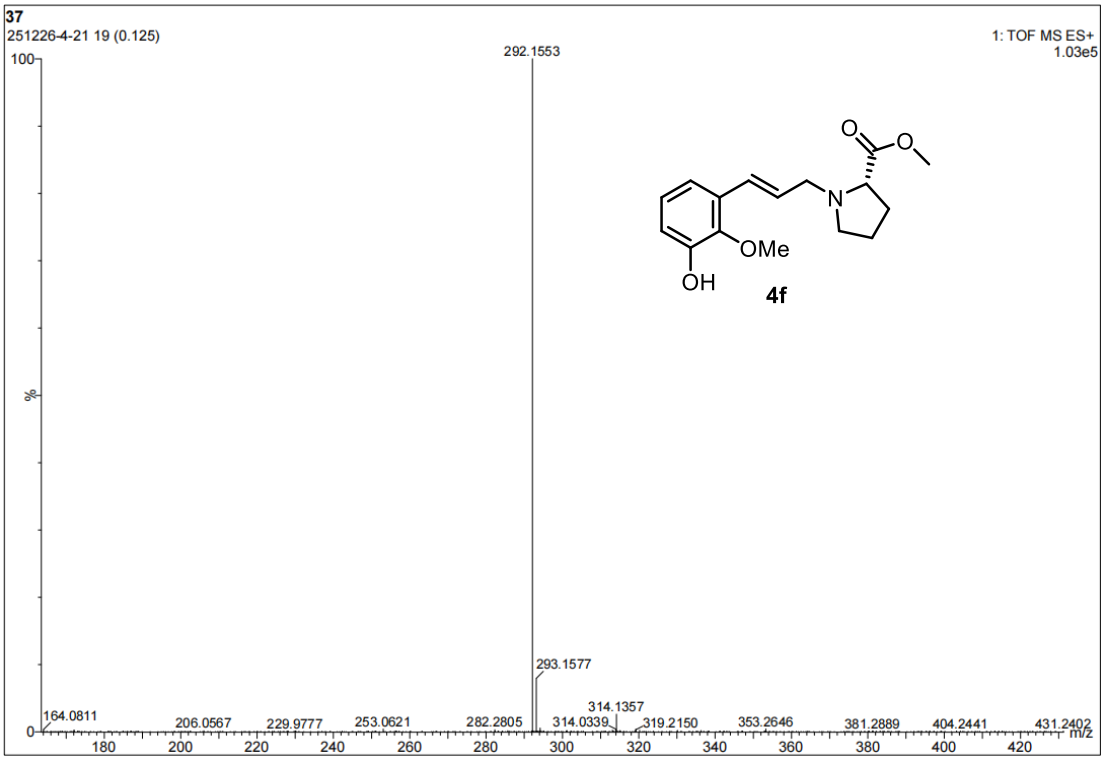
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of 4f



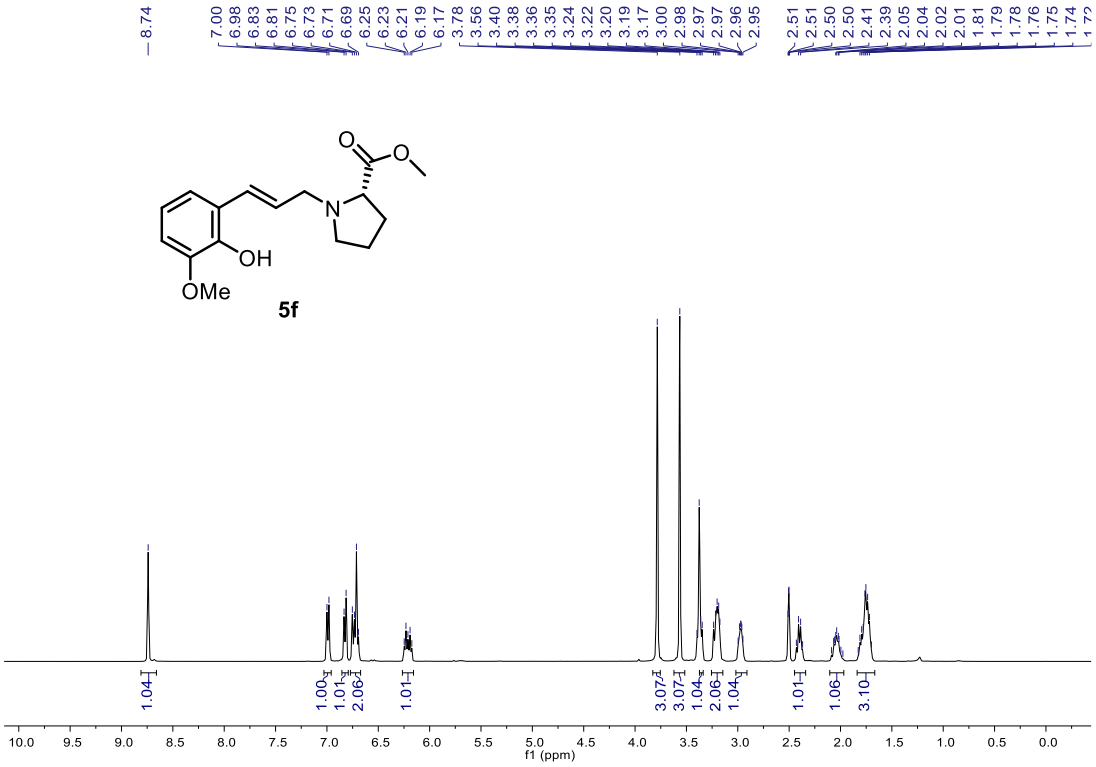
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of 4f



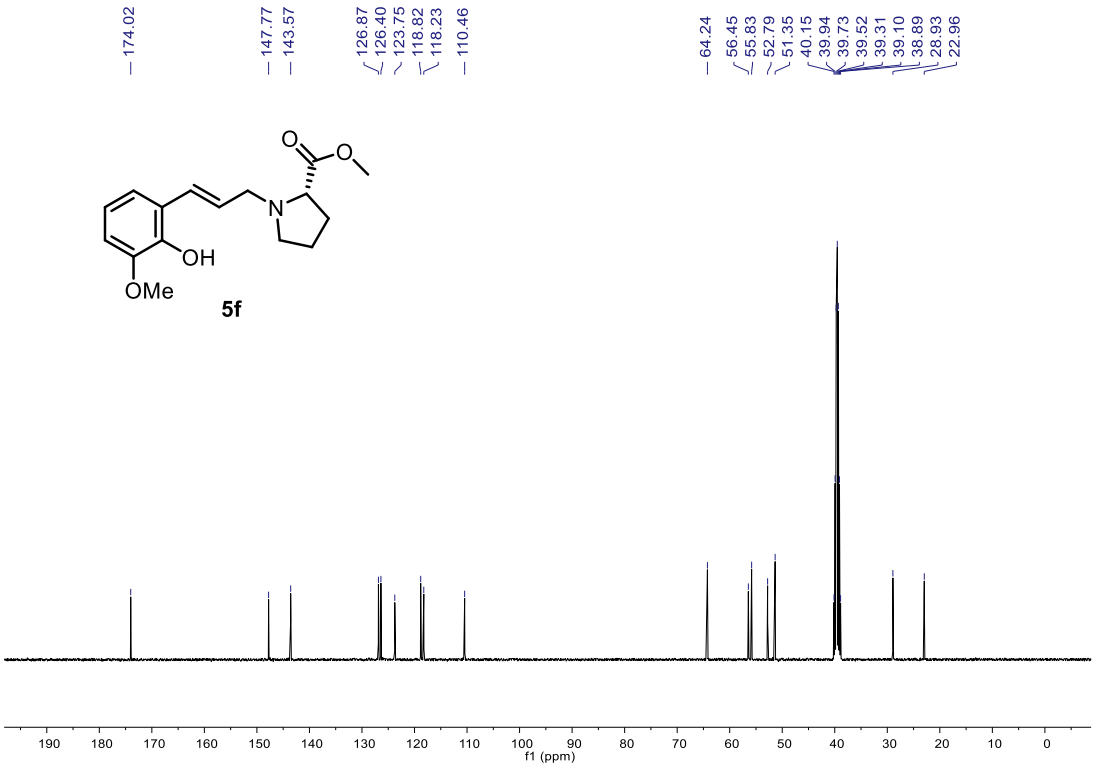
HRMS of 4f


37
251226-4-21 19 (0.125)
1: TOF MS ES+
1.03e5
100
%
0
292.1553
293.1577
314.1357
164.0811
206.0567
229.9777
253.0621
282.2805
314.0339
319.2150
353.2646
381.2889
404.2441
431.2402
180
200
220
240
260
280
300
320
340
360
380
400
420
m/z
O
O
N
OMe
OH
4f

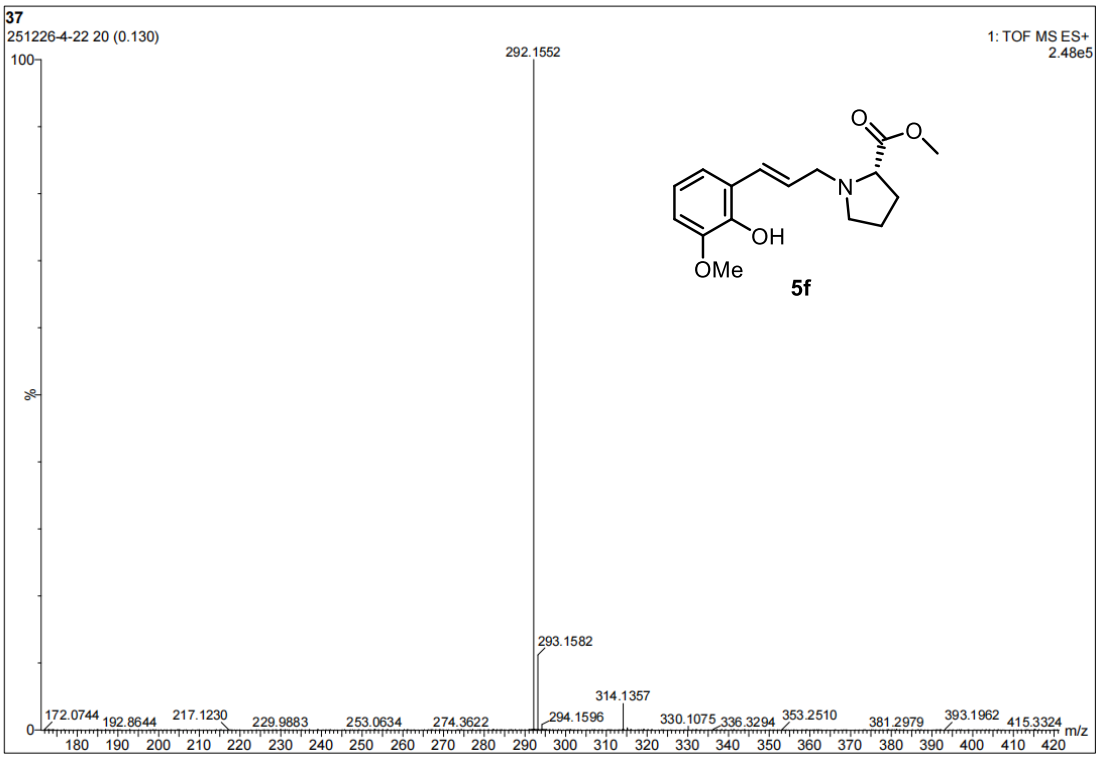
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of 5f



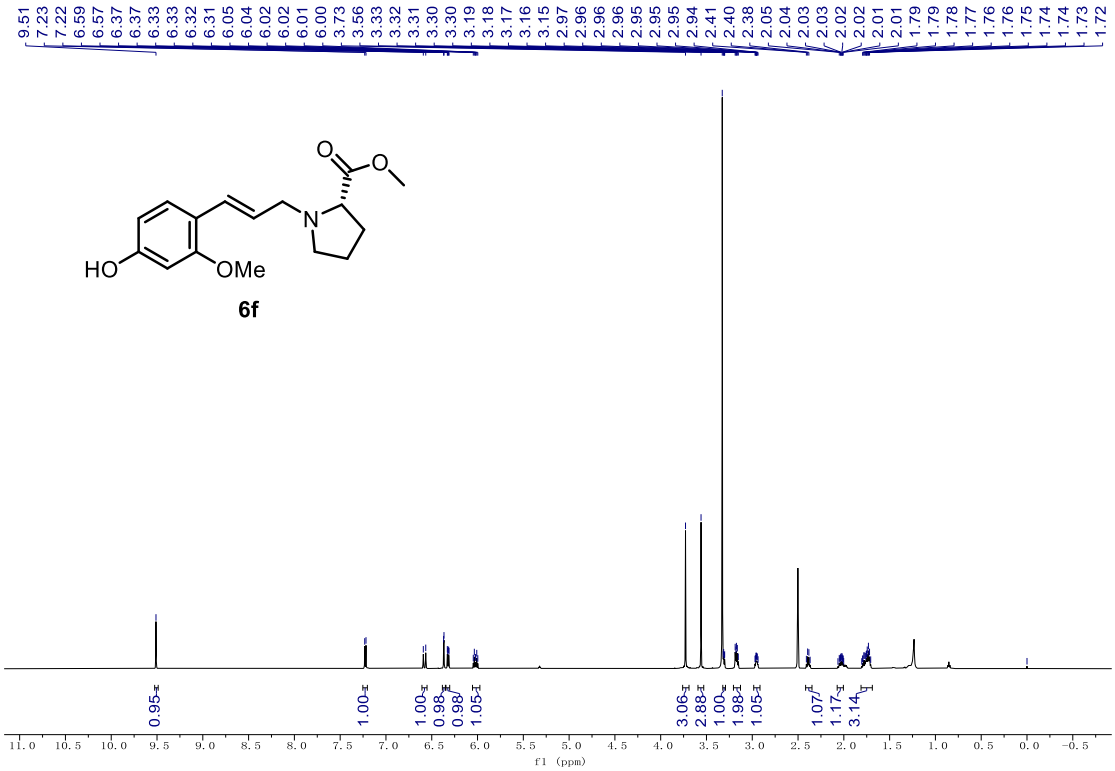
^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of 5f



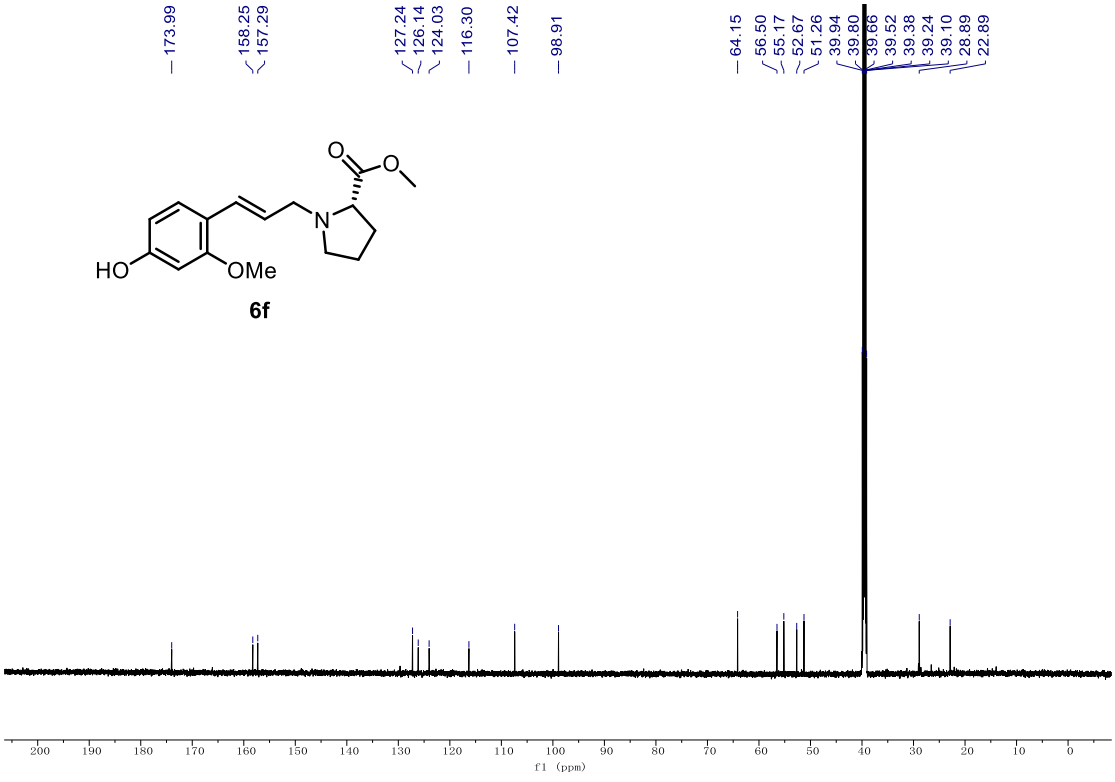
HRMS of 5f


37
251226-4-22 20 (0.130)
1: TOF MS ES+
2.48e5
100
%
0
292.1552
293.1582
314.1357
172.0744
192.8644
217.1230
229.9883
253.0634
274.3622
294.1596
330.1075
336.3294
353.2510
381.2979
393.1962
415.3324
180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420
m/z
O
O
N
OH
OMe
5f

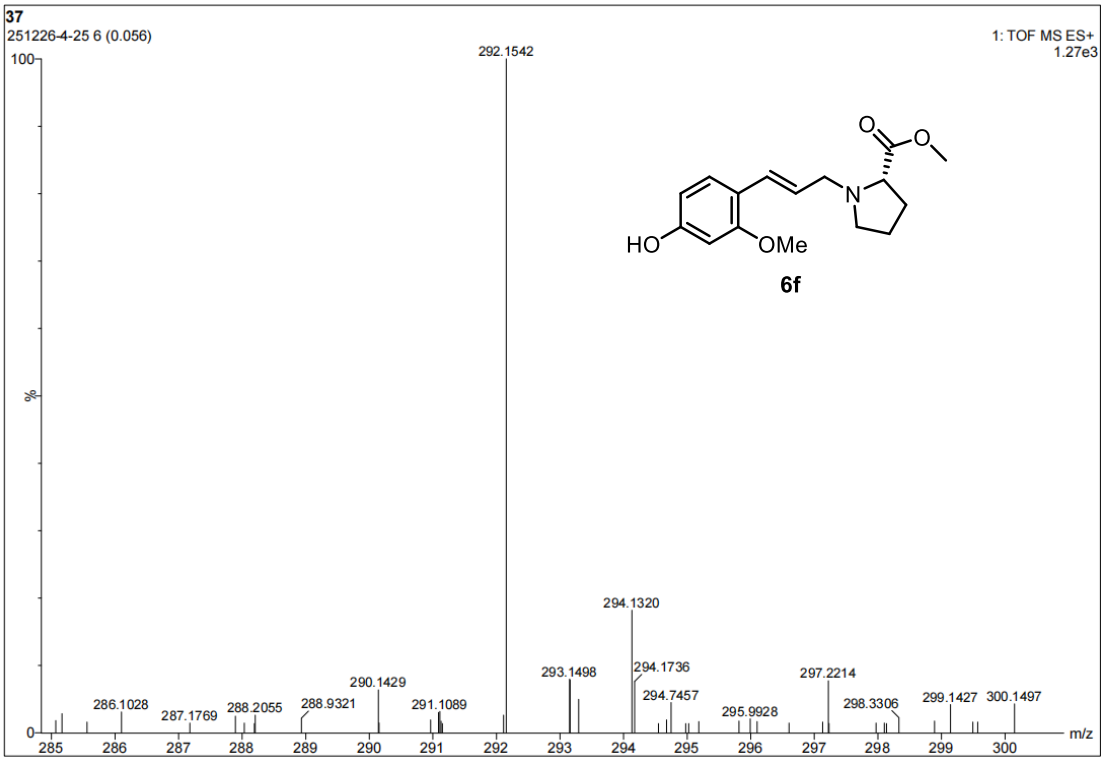
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of 6f



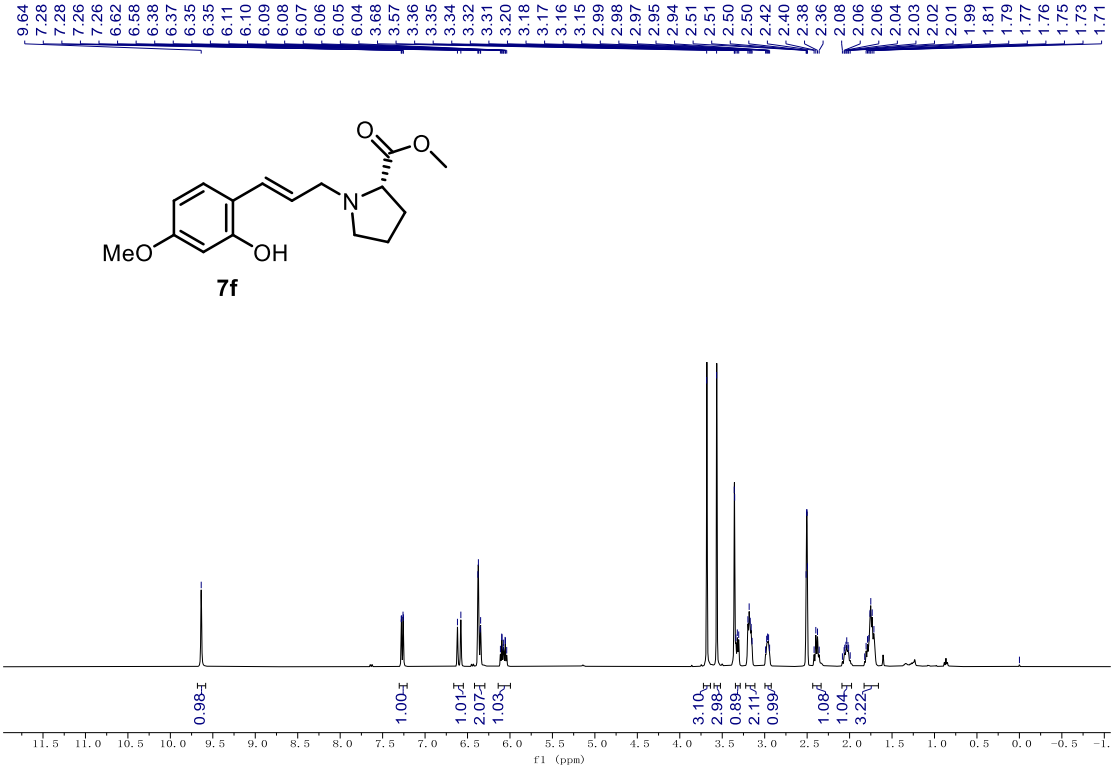
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of 6f



HRMS of 6f

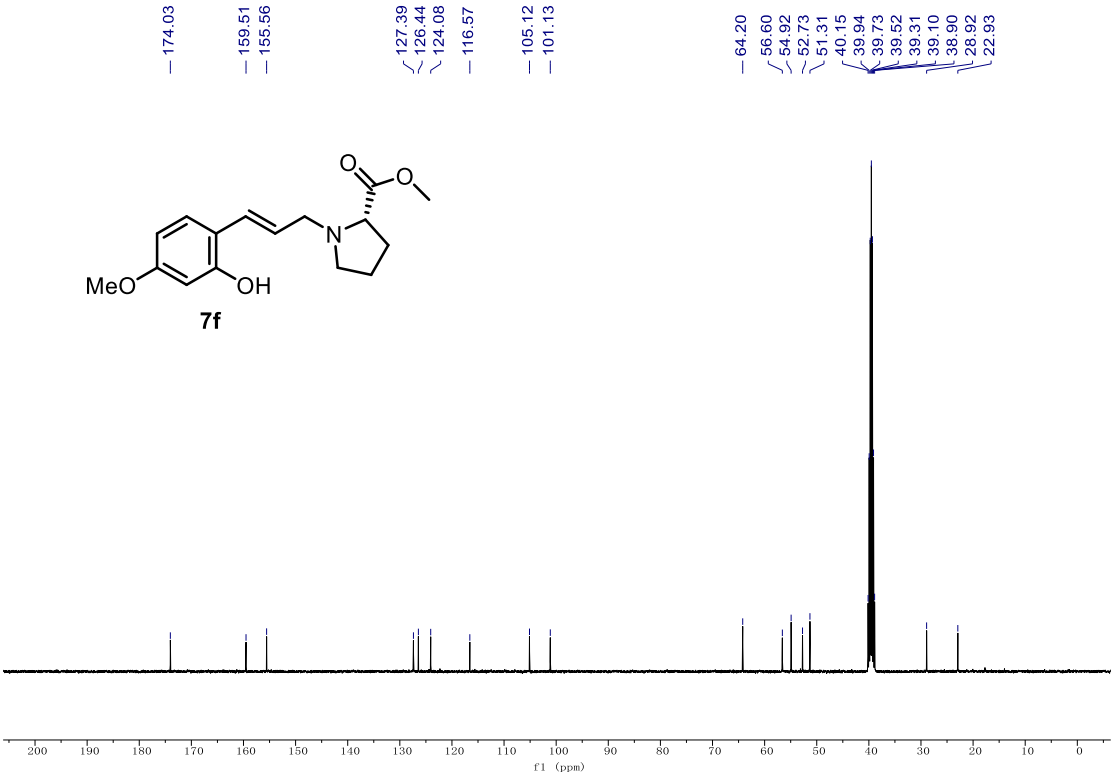

37
251226-4-25 6 (0.056)
1: TOF MS ES+
1.27e3
100
%
0
292.1542
294.1320
294.1736
293.1498
294.7457
290.1429
297.2214
286.1028
288.2055
288.9321
291.1089
287.1769
295.9928
298.3306
299.1427
300.1497
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
m/z
HO
OMe
N
O
O
6f

^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of 7f



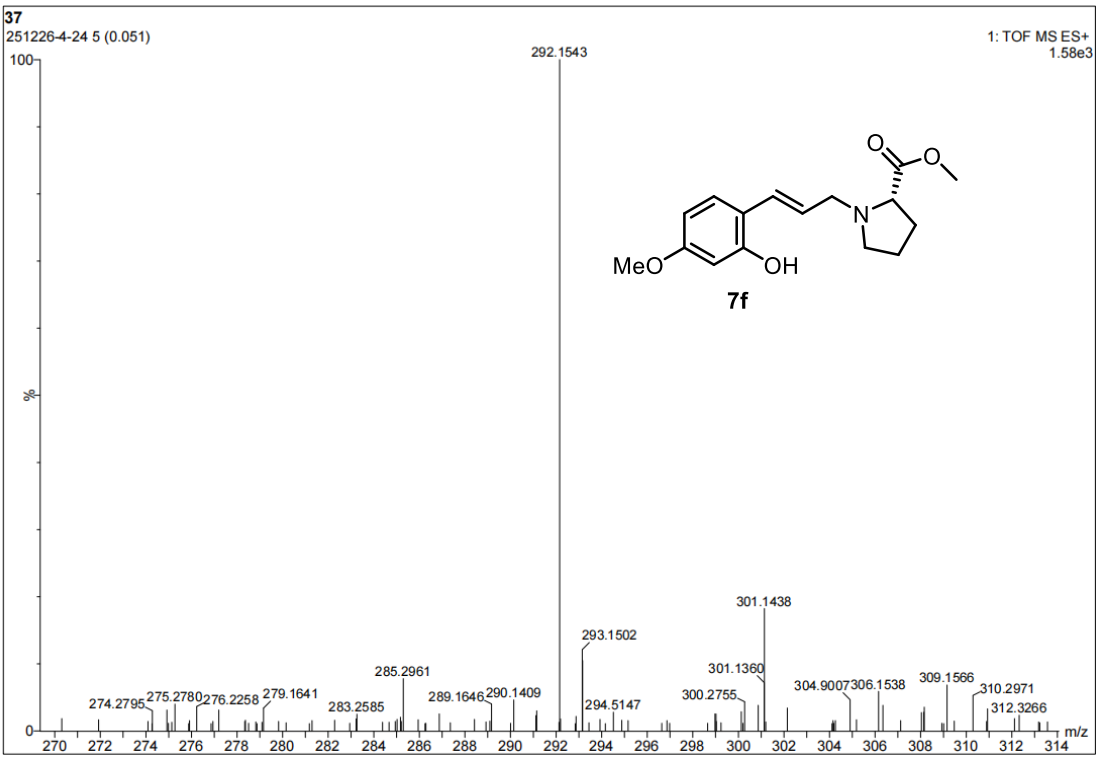
7f

^{13}C NMR (101 MHz, DMSO-d_6) Spectrum of 7f

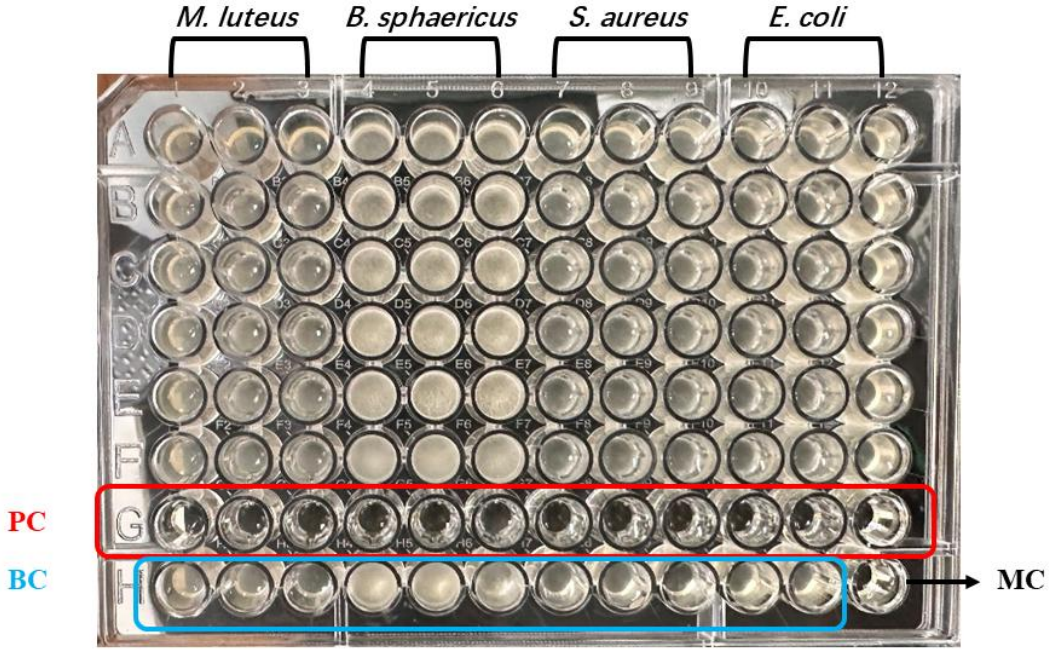


7f

HRMS of 7f


37
251226-4-24 5 (0.051)
1: TOF MS ES+
1.58e3
100
%
0
292.1543
301.1438
293.1502
285.2961
301.1360
304.9007
306.1538
309.1566
310.2971
312.3266
274.2795
275.2780
276.2258
279.1641
283.2585
289.1646
290.1409
294.5147
300.2755
270 272 274 276 278 280 282 284 286 288 290 292 294 296 298 300 302 304 306 308 310 312 314
m/z
O
O
N
MeO
OH
7f

4. Antimicrobial Susceptibility Testing



Positive Control (PC)： A sample known to produce a positive result, used to verify that the testing method itself is valid and functioning properly.

Bacterial Control (BC): Containing bacterial inoculum only, without any drug/treatment.

Medium Control (MC) / Uninoculated Control: Containing sterile medium only, without bacterial inoculum.