Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Highly Selective Synthesis of Tetra-substituted Furans and Cyclopropenes: Copper(I)-catalyzed Formal Cycloadditions of Internal Aryl Alkynes and Diazoacetates

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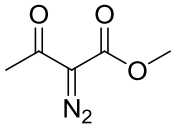
1. General Methods: Chemicals and Instrumentation

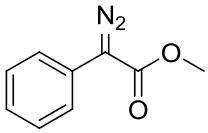
All organic chemicals were ordered from Sigma-Aldrich. Transition metal catalysts were obtained from STREM. Proper storage and handling was followed when they were not in use. Bulk chemicals were obtained from the College of Science at Rochester Institute of Technology. Diethyl ether and hexanes were obtained from Fisher Scientific (20 L) for column chromatography. All chemicals and solvents were used from the storage vessel as is, unless otherwise indicated. All reactions were conducted under dry argon gas. Infrared spectroscopic analyses were performed neat on a Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrometer. High resolution mass spectral (HRMS) samples (<1mg) were dissolved in dichloromethane and sent for analysis on the Thermo Finnigan MAT 95XL Mass Spectrometer at State University of New York at Buffalo's Mass Spectrometry Facility. Nuclear Magnetic Resonance Spectroscopic data was collected on RIT's Bruker Avance DRX-300 MHz NMR spectrometer, or 500MHz as indicated. All samples were dissolved in $CDCl_3$ with a TMS internal standard prior to analysis. Spectra are reported in ppm relative to $CDCl_3$ at 7.26 for ^1H and 77.2 for ^{13}C. X-ray crystallography samples were sent for analysis on a Bruker-AXS SMART Platform diffractometer equipped with an APEX II CCD detector at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester.

2. Diazoacetate Synthesis

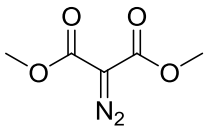


Methyl 2-diazo-3-oxobutanoate (1a) To a solution of *p*-acetamidobenzenesulfonyl azide (30.1 g, 126 mmol), methyl acetoacetate (12.4 mL, 115 mmol), and ACN (500mL) was added Et_3N (17.6 mL, 126 mmol) dropwise via syringe (13.0 mL/hr). The mixture was stirred at 0°C. After addition was complete, stirred mixture at room temperature overnight. The crude was then concentrated *in vacuo* on a rotary evaporator then dissolved in 100mL of 50% Et_2O/hexanes. The mixture was then filtered through celite, washed with 50% Et_2O/hexanes (5 x 50 mL), and reduced *in vacuo* on a rotary evaporator. Purified by column chromatography (SiO_2, 1/1 : Et_2O/hexanes) to afford **1a** (15.2 g, 107 mmol, 92.7 % yield) as a yellow oil. ^1H NMR ($CDCl_3$, 300MHz): δ 3.85 (s, 3H), 2.49 (s, 3H). Compound **1a** is a known compound and the analytical data is consistent with the literature.[1]

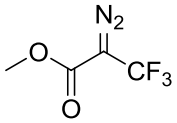
[1] Bagley, M.C.; Buck, R.T.; Hind, S.L.; Moody, C.J *J. Chem. Soc., Perkin Trans. 1* **1998**, 591.



Methyl 2-diazo-2-phenylacetate (1b) To a solution of *p*-acetamidobenzenesulfonyl azide (19.5 g, 81.2 mmol), methyl phenylacetate (10 mL, 62.5 mmol) and ACN (200mL) was added DBU (12.1 mL) dropwise over 1 hour, then stirred at room temperature overnight. The crude was diluted with Et_2O (200 mL) and washed with saturated NH_4Cl (3 x 100 mL), dried with $MgSO_4$, filtered, and reduced *in vacuo* on a rotary evaporator. Purified by column chromatography (SiO_2, 1/5 : Et_2O/hexanes) to afford **1b** (7.06 g, 40.1 mmol, 64.2 % yield) as a red oil. ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.49 (d, *J*= 7.5 Hz, 2H), 7.39 (t, 2H), 7.19 (t, 1H), 3.87 (s, 3H). Compound **1b** is a known compound and the analytical data is consistent with the literature.[2]



Dimethyl 2-diazopropanedioate (1d) To a solution of *p*-acetamidobenzenesulfonyl azide (10.0 g, 41.6 mmol), methyl malonate (5.00 g, 37.8 mmol), and ACN (95.0 mL) was added Et_3N (5.80 mL, 41.6 mmol) dropwise via syringe. The reaction mixture was stirred at 0°C and allowed to stir to room temperature overnight. The crude was then reduced *in vacuo* on a rotary evaporator and dissolved in 100mL of 50% Et_2O/hexanes. The mixture was then filtered through a plug of celite and washed with 50% Et_2O/hexanes (3 x 100 mL). Subsequently, the solvent removed *in vacuo* on a rotary evaporator and purified by column chromatography (SiO_2, 2/3 : Et_2O/hexanes) to afford **1c** (2.59 g, 16.4 mmol, 39.4% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300MHz): δ 3.85 (s, 6H). Compound **1c** is a known compound and the analytical data is consistent with the literature.[3]

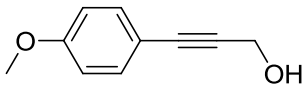


Methyl 2-diazo-3,3,3-trifluoropropanoate (1e) A solution of methyl 3,3,3-trifluropropionate (6.54 mL, 64.1 mmol), tosyl hydrazide (11.9 g, 64.1 mmol), and DCM (120mL) was heated to reflux (15 minutes) then stirred at room temperature 16 hours. Pyridine was added (30 mL) followed by a slow addition of $POCl_3$ (5.97 mL, 64.1 mmol) to allow a gentle reflux. The solution was stirred 20 minutes then H_2O (100

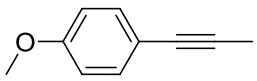
[2] Zhao, W.J.; Yan, M.; Huang, D.; Ji, S-J. *Tetrahedron*, **2005**, *61*, 5585-5593.
[3] Ramachary, D.; Narayana, V.; Ramakumar, K. *Tet. Lett.*, **2008**, *49*, 2704-2709.

mL) was added at which point the phases separated. The aqueous layer was washed with Et_2O (3 x 100 mL). The organic layers were combined and washed with 1M HCl (150 mL), saturated $NaHCO_3$ (100 mL), and then followed by a brine solution (100 mL). The organic phase was dried with ($MgSO_4$). The resultant solution was filtered, reduced *in vacuo* on a rotary evaporator, and distilled by Kugelrohr apparatus (50°C, < 5 mm Hg) to give **1e** (2.17 g, 12.9 mmol, 20.1 % yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300MHz): δ 3.86 (s, 3H). Compound **1e** is a known compound and the analytical data is consistent with the literature.[4]

3. Synthetic Procedure and Characterization of Internal Alkynes



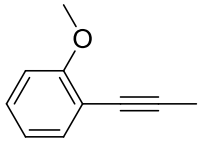
(4-methoxyphenyl)prop-2-yn-1-ol (26) A solution of THF (18.0 mL, degassed) and 4-ethynylanisole (5.0 mL, 37.8 mmol) was cooled to -78°C to which was added 2.0M *n*-BuLi (19.9 mL, 39.7 mmol) dropwise over a 40 minute period after which the reaction stirred 2 hours at -78°C. The reaction was allowed to warm to 0°C. Paraformaldehyde (4.77 g, 30.0 mmol) was added and the reaction was allowed to stir for an additional 2.5 hours. The crude reaction mixture was diluted with Et_2O (50mL) and washed with H_2O and the organic phase was collected. The solvent was removed *in vacuo* on a rotary evaporator and purified by column chromatography (SiO_2, 1/5 - 2/3 : Et_2O/hexanes) to afford **26** (4.33 g, 26.7 mmol, 70.6 % yield) as tan solid. ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.37 (d, *J*= 8.8 Hz, 2H), 6.82 (d, *J*= 8.8 Hz, 2H), 4.47 (s, 2H), 3.79 (s, 3H), 2.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 300MHz): δ 159.8, 133.3, 114.7, 114.0, 86.0, 85.7, 55.4, 51.7. Compound **26** is a known compound and the analytical data is consistent with the literature.[5]



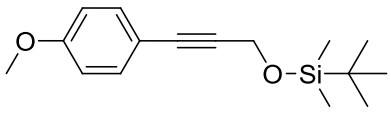
Methoxy-4-prop-1-ynyl-benzene (7) To a -78^{o}C solution of 4-ethynylanisole (5.00 g, 36.7 mmol) in THF (100 mL) was added 2.0M n- BuLi (20.2 mL, 40.4 mmol) dropwise. The reaction was allowed to stir for an additional 1 hour at -78°C. Methyl iodide (22.9 mL, 367 mmol) was added dropwise via syringe pump over 1 hour. The reaction was allowed to stir to room temperature overnight. The reaction mixture was diluted with Et_2O (50mL) washed with saturated aqueous solutions of NH_4Cl (50 mL), $NaHCO_3$ (50 mL), and brine (50 mL). The solvent was removed *in vacuo* on a rotary evaporator and the

[4] Shi, G; Xu, Y. *J. Org. Chem.* **1990**, *55*, 3383.
[5] Tang, B-X.; Wang, F.; Li, J-H, Xie, X-Y.; Zhang, M-B. *J. Org. Chem.* **2007**, *72*, 6294-6297.

resultant oil was purified by Kugelrohr apparatus (115°C, < 5 mm Hg) to afford **7** (4.22 g, 28.9 mmol, 79.0 % yield) as a clear oil. ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.32 (d, *J*= 8.9 Hz, 2H), 6.81 (d, *J*= 8.9 Hz, 2H), 3.79 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 159.2, 133.0, 116.4, 114.0, 84.3, 79.6, 55.4, 4.5. Compound **7** is a known compound and the analytical data is consistent with the literature.[6]

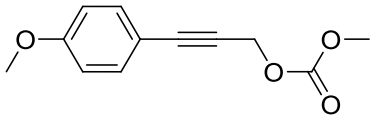


Methoxy-2-prop-1-ynyl-benzene (10) A solution of 2-ethynylanisole (1.00 g, 7.34 mmol) and THF (75 mL) was cooled to -78°C to which was added 2.0M BuLi (4.04 mL, 8.07 mmol) dropwise. The reaction was stirred 30 minutes at -78°C and methyl iodide (4.56 mL, 73.4 mmol) and stirred reaction to room temperature overnight. The solvent was removed *in vacuo* on a rotary evaporator and the crude oil was distilled by Kugelrohr apparatus (100°C, < 5 mm Hg*)* to afford **10** (0.931 g, 6.37 mmol, 87 % yield) as translucent oil. ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.38 – 7.36 (m, 1H), 7.24 - 7.23 (m, 1H), 6.90 - 6.85 (m, 2H), 3.88 (s, 3H), 2.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 300MHz): δ 160.0, 133.8, 129.1, 113.3, 110.7, 90.2, 76.0, 56.0, 5.0. Compound **10** is a known compound and the analytical data is consistent with the literature.[7]

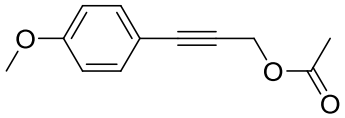


***Tert*-butyl-[3-(4-methoxyphenyl)prop-2-ynoxy]-dimethyl-silane (11)** To a solution of **26** (1.00 g, 6.17 mmol), Et_3N (1.72 mL, 12.3 mmol), and DCM (12.5 mL) was added a solution of TBS-Cl (1.21 g, 8.02 mmol) in DCM (3 mL) dropwise. The reaction was allowed to stir overnight to room temperature. The reaction mixture was concentrated *in vacuo* on a rotary evaporator and purified by column chromatography (SiO_2, 1/10 - 1/5 : Et_2O/hexanes) to afford **11** (1.29 g, 4.66 mmol, 75.5 % yield) as a yellow oil. IR (film) 2932 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.36 (d, *J*= 8.9 Hz, 2H), 6.83 (d, *J*= 8.9 Hz, 2H), 4.53 (s, 2H), 3.80 (s, 3H), 0.94 (s, 9H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 159.8, 133.3, 115.3, 114.1, 86.7, 84.9, 55.5, 52.5, 26.1, 18.6, 0.19, -4.8. Compound **11** is a known compound and the analytical data is consistent with the literature.[8]

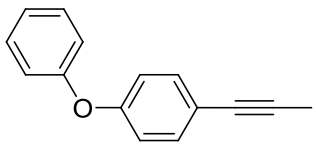
[6] Umeda, R.; Yuasa, T.;Anahara, N.; Nishiyama, Y. *J. Organo. Chem.* **2011**, *696*, 1916-1919.
[7] Cheng C-Y.; Isobe, M. *Tetrahedron* **2011**, *67*, 9957-9965.
[8] Paraskar, A.S. and Sudalai, A. *Tetrahedron*, **2006**, *62*, 5756.



(4-methoxyphenyl)prop-2-ynyl methyl carbonate (12) A solution of **26** (900 mg, 5.55 mmol) and pyridine (15 mL) was cooled to 0°C. Methyl chloroformate (1.05 g, 11.1 mmol) was added over 1 hour and then stirred for overnight at room temperature. The reaction was quenched reaction with H_2O and diluted with Et_2O (100 mL). The crude reaction mixture was washed with H_2O (100 mL x5), then dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* on a rotary evaporator and the concentrated oil was purified by column chromatography (SiO_2, 1/5 : Et_2O/hexanes) to afford **12** (0.502 g, 2.28 mmol, 41.1 % yield) as a yellow oil. IR (film) 1751cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.39 (d, *J*= 8.9 Hz, 2H), 6.84 (d, *J*= 8.9, Hz, 2H), 4.96 (s, 2H), 3.83 (s 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 300MHz): δ 160.0, 155.3, 133.4, 113.9, 113.9, 87.2, 81.0, 56.3, 55.2, 55.1. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}O_4Na$, 243.0628, found 243.0631 $[M+Na]^+$.



(4-methoxyphenyl)prop-2-ynyl acetate (13) A solution of **26** (900 mg, 5.55 mmol) and pyridine (15 mL) was cooled to 0°C. Acetyl chloride (871 mg, 11.1 mmol) was added dropwise over 1 hour and stirred overnight to room temperature. The reaction was quenched reaction with H_2O (1 mL) and diluted with Et_2O (100 mL). The crude reaction mixture was washed with H_2O (5 x 100 mL), dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* on a rotary evaporator and purified by column chromatography (SiO_2, 1/5 : EtOAc/hexanes) to afford **13** (0.935 g, 4.58 mmol, 82.5 % yield) as a pale yellow oil. IR (film) 2978, 1744 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.40 (d, *J*= 8.8 Hz, 2H), 6.84 (d, *J*= 8.9 Hz, 2H), 4.89 (s, 2H), 3.81 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 170.5, 160.2, 133.6, 114.4, 114.1, 86.7, 81.7, 55.4, 53.2, 21.0. HRMS (ESI) *m/z* for $C_{12}H_{12}O_3$, 204.0781, found 204.0788 $[M]^+$.



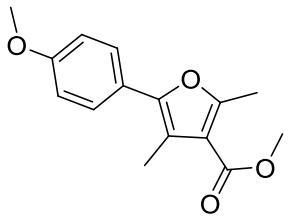
Phenoxy-4-prop-1-ynyl-benzene (15) A solution of 1-ethynyl-4-phenoxy- benzene (1.00 g, 5.15 mmol) in THF (20 mL) was cooled to -78°C. 2.0M BuLi (3.08 mL, 6.18 mmol) was added dropwise and allowed to stir at -78°C for an additional hour. Methyl iodide (3.2 mL, 51.5 mmol) was added dropwise and the reaction was allowed to overnight to room temperature. The reaction was quenched with H_2O (30

mL) and then the organic phase was separated and dried with $MgSO_4$. The solvent was removed from the crude reaction and concentrated *in vacuo* on the rotary evaporator. The residue was distilled on a Kugelrohr apparatus (170°C, < 5 mm Hg) to give **15** (0.793 g, 3.81 mmol, 74.0 % yield) as a translucent oil. ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.36 - 7.32 (m, 4H), 7.13 – 7.10 (m, 1H), 7.02 – 7.00 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 157.1, 156.9, 133.2, 130.0, 123.8, 119.4, 118.9, 118.6, 85.2, 79.4, 4.5. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}O$, 208.0883, found 208.0890 $[M]^+$. Compound **15** is a known compound and the ^{1}H NMR analytical data are consistent with those in the literature.[9]

4. General Procedure for CuI-Catalyzed Cycloaddition

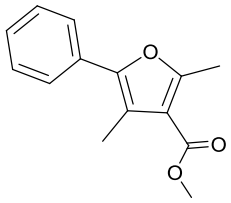
A flame-dried 25-mL one-necked round bottom flask equipped with a Teflon-coated stir bar and reflux condenser was purged with argon gas. Catalyst was quickly added (0.103 mmol, 0.05 eq) and all joints were parafilmed. Internal alkyne (2.05 mmol, 1.00 eq) was added via syringe with a long needle through the reflux condenser. The reaction was heated to 110°C and stirred for 15 minutes. Diazoacetate (13.1 mmol, 6.39 eq) was then added dropwise via syring pump (0.167 mL/hr). The reaction was heated overnight and the crude reaction mixture was purified using column chromatography.

5. Compound Characterization of Furans and Cyclopropenes

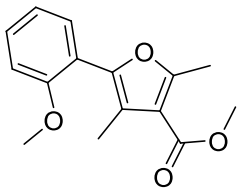


Methyl 5(4-methoxyphenyl)-2,4-dimethyl-furan-3-carboxylate (8a) Purified by column chromatography (SiO_2, 1/10 : Et_2O/hexanes) to afford **8a** as a clear oil (267 mg, 1.0 mmol, 50% yield, 61% conversion). R_f=0.64; 2/3 : Et_2O/hexane. mp = 58 - 61°C; IR (film) 1713 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.50 (d, *J*= 9.0 Hz, 2H), 6.95 (d, *J*= 8.9 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.59 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 165.5, 159.0, 158.2, 148.0, 127.8, 123.9, 115.5, 115.1, 114.2, 5.5, 1.2, 14.6, 11.0. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}O_4$, 260.1043, found 260.1042 $[M]^+$.

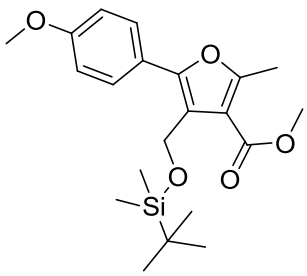
[9] Schmid, G.H.; Nowlan, V.J. *Can. J. Chem.* **1976**, *54*, 695.



Methyl 2,4-dimethyl-5-phenyl-furan-3-carboxylate (16a) Purified by column chromatography (SiO_2, 1/10 : Et_2O/hexanes) to afford a 5:1 regioisomeric mixture of **16a** as a clear oil (40 mg, 0.17 mmol, 8.5% yield). Major isomer: R_f= 0.75; 2/3 : Et_2O/hexane. IR (film) 1715 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.59 - 7.57 (m, 2H), 7.41 (t, 2H), 7.29 (t, 1H), 3.86 (s, 3H), 2.61 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 165.3, 158.6, 147.8, 131.0, 128.5, 127.2, 126.1, 116.9, 115.2, 51.1, 14.5, 10.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}O_3$, 230.0937, found 230.0948 $[M]^+$.

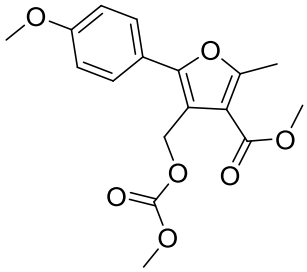


Methyl 5-(2-methoxyphenyl)-2,4-dimethyl-furan-3-carboxylate (17a) Purified by column chromatography (SiO_2, 1/20 - 1/10 : Et_2O/hexanes) to afford **17a** as a clear oil (101 mg, 0.39 mmol, 19% yield, 35% conversion). R_f= 0.60; 1/4 : EtOAc/hexane. IR (film) 1715 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.37-7.32 (m, 2H), 7.03-6.96 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.59 (s, 3H), 2.13 (s, 3H); - ^{13}C NMR ($CDCl_3$, 500MHz): δ 165.6, 159.2, 157.3, 145.6, 131.3, 130.1, 120.6, 120.0, 118.7, 114.7, 111.5, 55.7, 51.2, 14.7, 11.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}O_4$, 260.1043, found 260.1031 $[M]^+$.

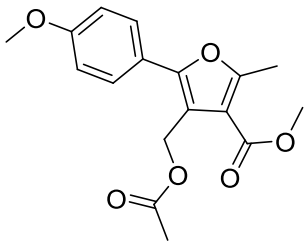


Methyl 4-[[tert-butyl(dimethyl)silyl]oxymethyl]-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (18a) Purified by column chromatography (SiO_2, 1/35 - 1/20 : Et_2O/hexanes) to afford **18a** as a clear oil (306 mg, 0.78 mmol, 38% yield, 59% conversion). R_f= 0.60; 1/4 : Et_2O/hexane. mp = 44 - 47°C; IR (film) 2932, 1713 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.68 (d, *J*= 8.9 Hz, 2H), 6.94 (d, *J*= 8.9, 2H), 4.79 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.60 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 500MHz): δ

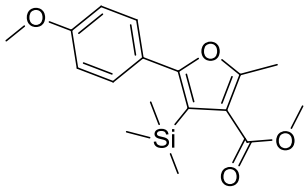
165.0, 159.7, 158.4, 151.5, 128.4, 123.1, 118.4, 114.1, 55.8, 55.5, 51.3, 26.2, 18.7, 14.5, -5.0. HRMS (ESI) *m/z* calcd for $C_{21}H_{30}O_5Si$, 390.1857, found 390.1859 $[M]^+$.



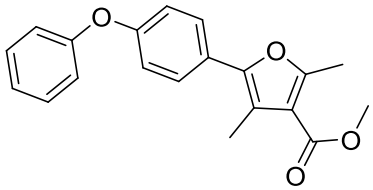
Methyl 4-(methoxycarbonyloxymethyl)-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (19a) Purified by column chromatography (SiO_2, 1/10 - 1/5 : Et_2O/hexanes) to afford **19a** as a clear oil (163 mg, 0.49 mmol, 24% yield, 35% conversion). R_f= 0.58 in 3/2 : Et_2O/hexane. mp = 71 - 74°C; IR (film) 2980, 2970, 2957, 1749, 1717 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.51 (d, *J*= 8.7 Hz, 2H), 6.97 (d, *J*= 8.7 Hz, 2H), 5.32 (s, 2H), 3.85 (s, 6H), 3.81 (s, 3H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 164.3, 160.0, 158.8, 155.6, 152.5, 128.4, 121.9, 114.2, 114.0, 113.0, 61.0, 55.3, 54.7, 51.3, 14.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}O_7Na$, 357.0945, found 357.0930 $[M+Na]^+$.



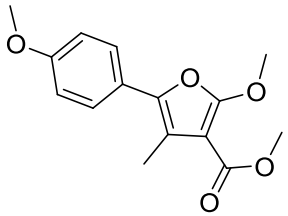
Methyl 4-(acetoxymethyl)-5-(4-methoxyphenyl)-2-methyl-furan-3-carboxylate (20a) Purified by column chromatography (SiO_2, 1/10 - 1/5 : Et_2O/hexanes) to afford **20a** as a yellow oil in (116 mg, 0.36 mmol, 18% yield, 29% conversion). R_f= 0.48 in 1/1 : Et_2O/hexane. mp = 84 - 86°C; IR (film) 1740, 1717 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.49 (d, *J*= 8.9 Hz, 2H), 6.96 (d, *J*= 9.0, 2H), 5.25 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.62 (s,3H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 171.1, 164.6, 160.1, 159.0, 152.2, 128.5, 122.3, 114.4, 114.3, 113.7, 58.0, 55.5, 51.5, 21.2, 14.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}O_6Na$, 341.0996, found 341.0994 $[M+Na]^+$.



Methyl 5-(4-methoxyphenyl)-2-methyl-4-trimethylsilyl-furan-3-carboxylate (21a) Purified by column chromatography (SiO_2, 1/20 - 1/5 : Et_2O/hexanes) to afford **21a** as a clear oil (124 mg, 0.39 mmol, 19% yield, 32% conversion). R_f= 0.79 in 2/3 : Et_2O/hexane. mp = 66 - 70°C; IR (film) 1717 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.33 (d, *J*= 8.7 Hz, 2H), 6.91 (d, *J*= 8.7 Hz, 2H), 3.84 (s, 3H), 3.84 (s, 3H), 2.56 (s, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 165.8, 160.3, 158.8, 158.5, 131.4, 125.1, 118.8, 114.4, 113.5, 55.5, 51.2, 13.9, 0.75. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}O_4Si$, 318.1282, found 318.1288 $[M]^+$.

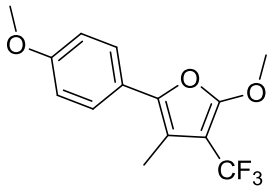


Methyl 2,4-dimethyl-5-(4-phenoxyphenyl)furan-3-carboxylate (22a) Purified by column chromatography (SiO_2, 1/20 - 1/5 : Et_2O/hexanes) to afford **22a** as a clear oil (132 mg, 0.41 mmol, 39% yield, 58% conversion). R_f= 0.78 in 2/3 : Et_2O/hexane). IR (film) 1713 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.53 (d, *J*= 8.7 Hz, 2H), 7.34 (t, 2H), 7.11 (t, 1H), 7.05-7.03 (m, 4H), 3.85 (s, 3H), 2.59 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 165.4, 158.5, 157.1, 156.7, 147.6, 130.0, 127.8, 126.3, 123.7, 119.2, 118.9, 116.3, 115.3, 51.2, 14.6, 11.0. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_4$, 323.1278, found 323.1272 $[M+H]^+$.

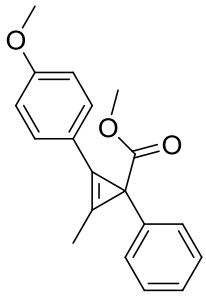


Methyl 2-methoxy-5-(4-methoxyphenyl)- 4-methyl-furan-3-carboxylate (23c) Purified by column chromatography (SiO_2, 1/5 - 1/3 : Et_2O/hexanes) to afford **23c** as a clear oil (79.6 mg, 0.29 mmol, 23% yield, 23% conversion). R_f= 0.49; 1/1 : Et_2O/hexane. IR (film) 2947, 1705 cm^{-1}. ^1H NMR ($CDCl_3$, 500MHz): δ 7.44 (d, *J*= 8.9 Hz, 2H), 6.95 (d, *J*= 9.0 Hz, 2H), 4.14 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H) 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 164.5, 161.9, 158.8, 139.9, 127.4, 123.5, 116.5, 114.2, 93.1, 57.8,

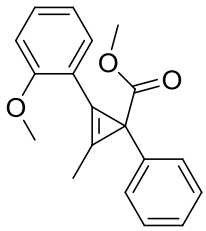
55.5, 51.1, 11.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}O_5Na$, 299.0890, found 299.0891 $[M+Na]^+$.



Methoxy-5-(4-methoxyphenyl)-4-methyl-3-(trifluoromethyl)furan (23d) Purified by column chromatography (SiO_2, 1/30 : Et_2O/hexanes) to afford **23d** as a yellow oil (135 mg, 0.47 mmol, 23% yield, 23% conversion). R_f= 0.64; 2/3 : Et_2O/hexane. IR (film) 1649, 1622, 1601 cm^{-1}. ^1H NMR ($CDCl_3$, 500MHz): δ 7.42 (d, *J*= 9.0 Hz, 2H), 6.95 (d, *J*= 8.9 Hz, 2H), 4.05 (s, 3H), 3.94 (s, 3H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 159.0, 156.7, 140.5, 127.4, 124.4, 123.3, 122.3, 114.3, 114.0, 58.5, 55.5, 10.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}O_3F_3$, 287.0890, found 287.0884 $[M+H]^+$.

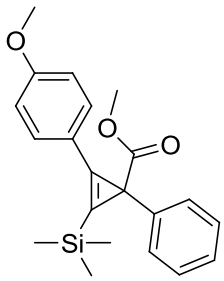


Methyl 2-(4-methoxyphenyl)-3-methyl-1-phenyl-cycloprop-2-ene-1-carboxylate (23b) Purified by column chromatography (SiO_2, 1/20 - 3/20 : Et_2O/hexanes) to afford **23b** as a pale yellow solid (353 mg, 1.2 mmol, 59% yield, 65% conversion). R_f= 0.53; 2/3 : Et_2O/hexane. mp = 69 - 73°C; IR (film) 2947, 1713, 1605 cm^{-1}: ^1H NMR ($CDCl_3$, 500MHz): δ 7.47 (d, *J*= 8.8 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.16 (m, 1H), 6.92 (d, *J*= 8.8 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 175.5, 160.2, 141.5, 130.9, 128.3, 128.2, 126.3, 119.4, 114.6, 108.6, 108.1, 55.5, 52.0, 35.4, 9.7. HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_3Na$, 317.1148, found 317.1153 $[M+Na]^+$.

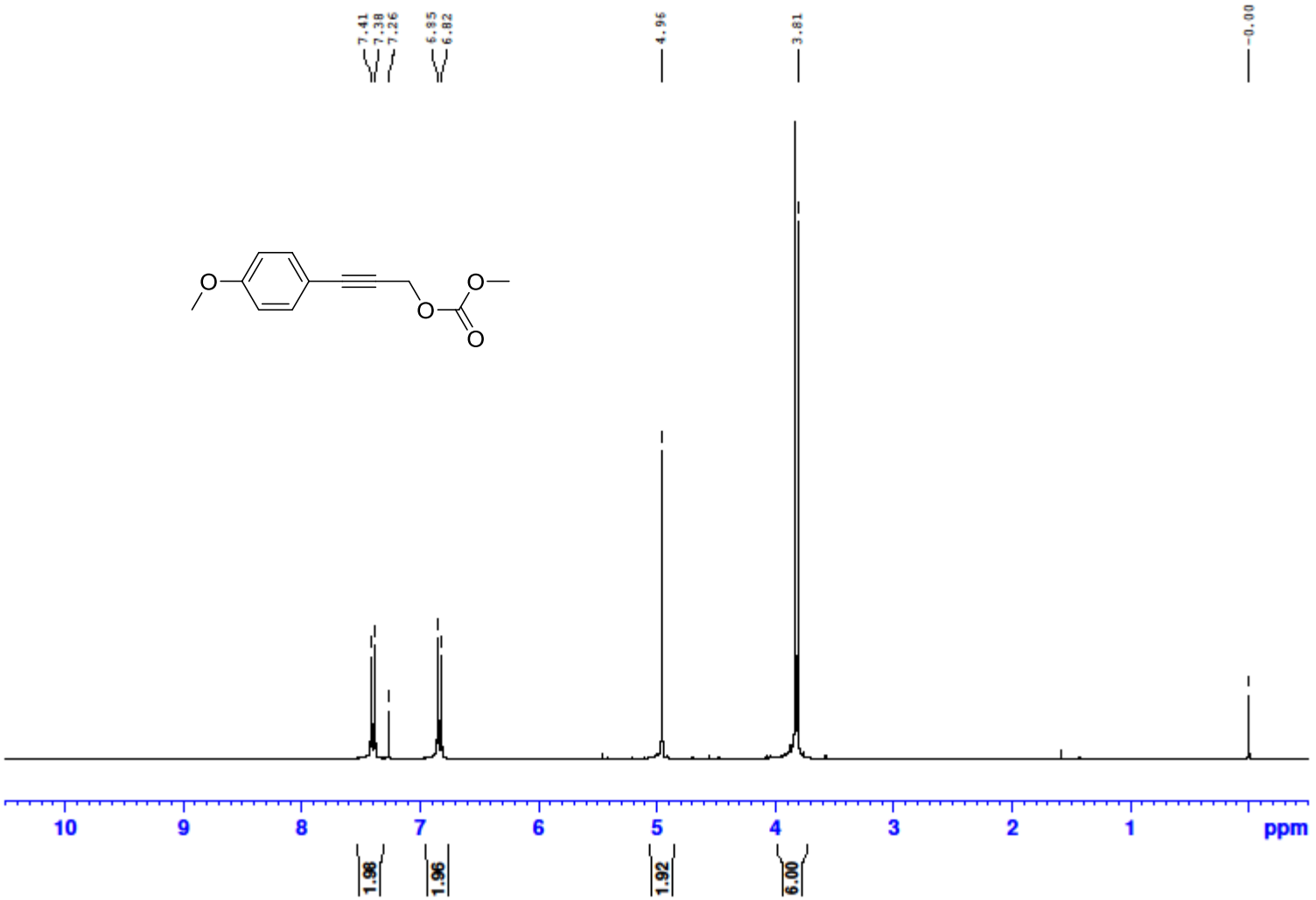


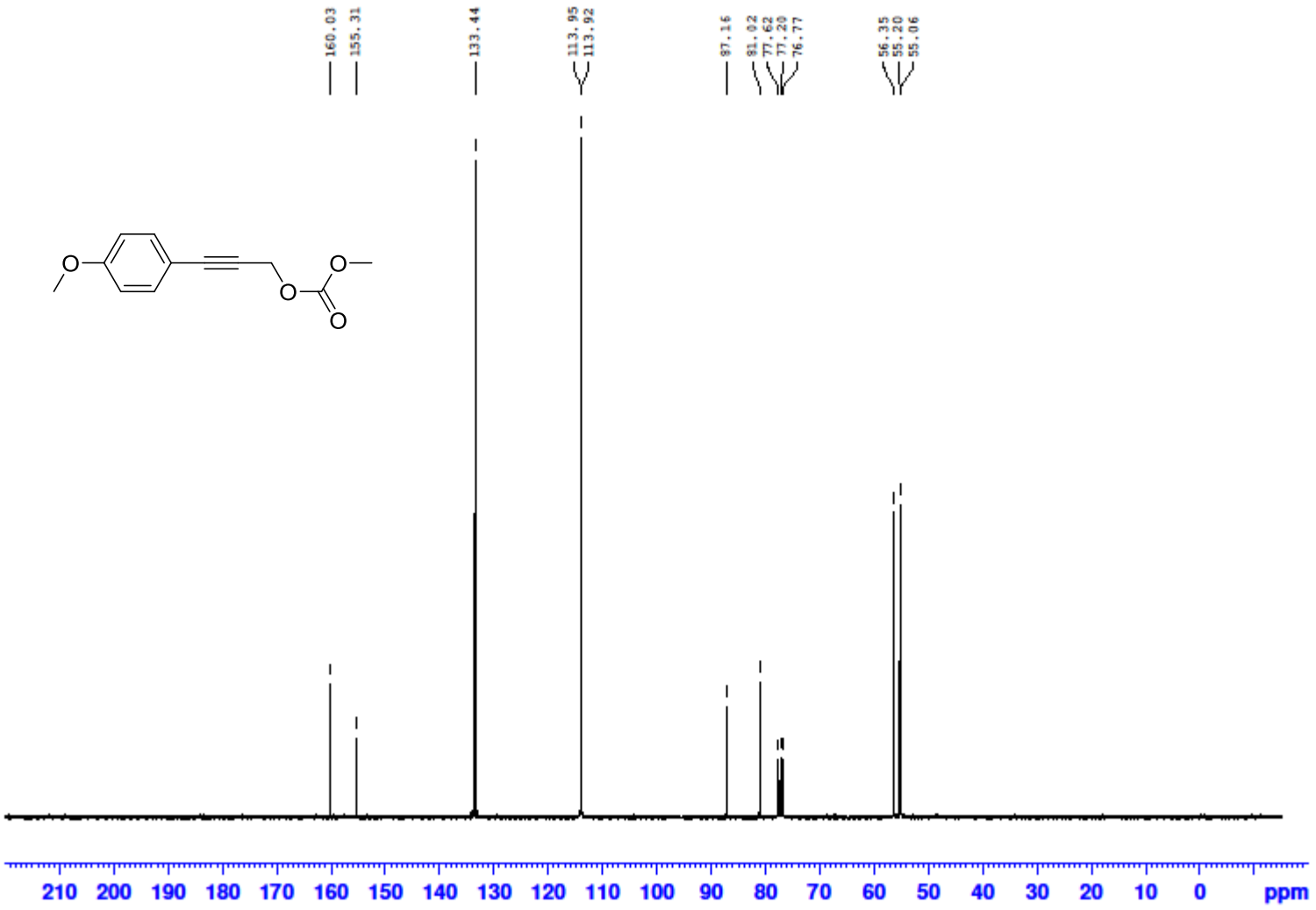
Methyl 2-(2-methoxyphenyl)-3-methyl-1-phenyl-cycloprop-2-ene-1-carboxylate (24b) Purified by column chromatography (SiO_2, 3/20 - 1/3 : Et_2O/hexanes) to afford **24b** as a pale yellow solid (407 mg,

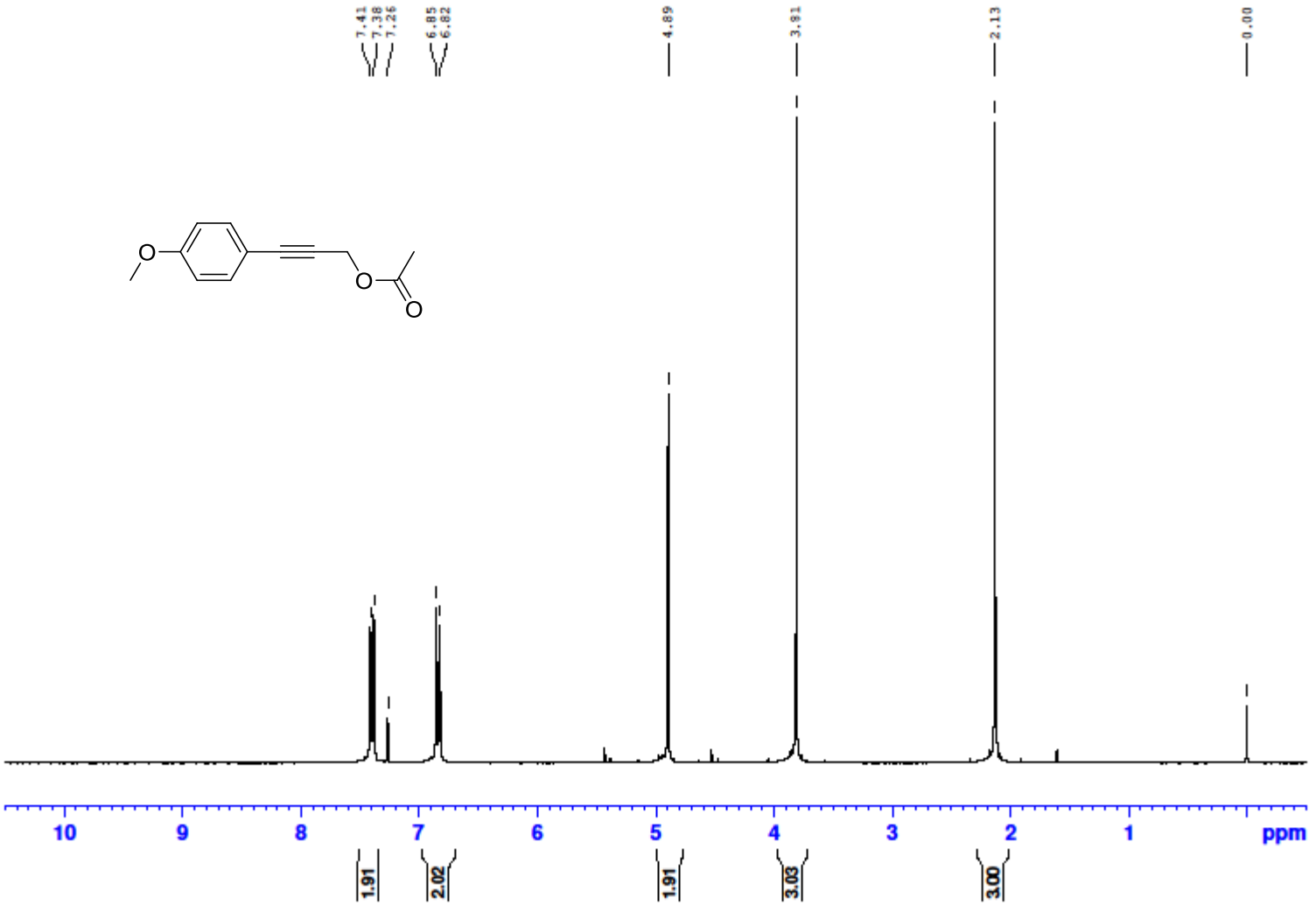
1.4 mmol, 67% yield, 73% conversion). R_f= 0.51; 2/3 : Et_2O/hexane. mp = 100 - 101°C; IR (film) 1717 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.39 - 7.24 (m, 6H), 7.17 (t, 1H), 6.97 – 6.92 (m, 2H), 3.93 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 500MHz): δ 175.6, 158.5, 141.7, 130.5, 130.2, 128.4, 128.1, 126.3, 120.8, 116.0, 112.7, 110.6, 105.2, 55.7, 55.2, 34.6, 10.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_3$, 294.1250, found 294.1254 $[M]^+$.

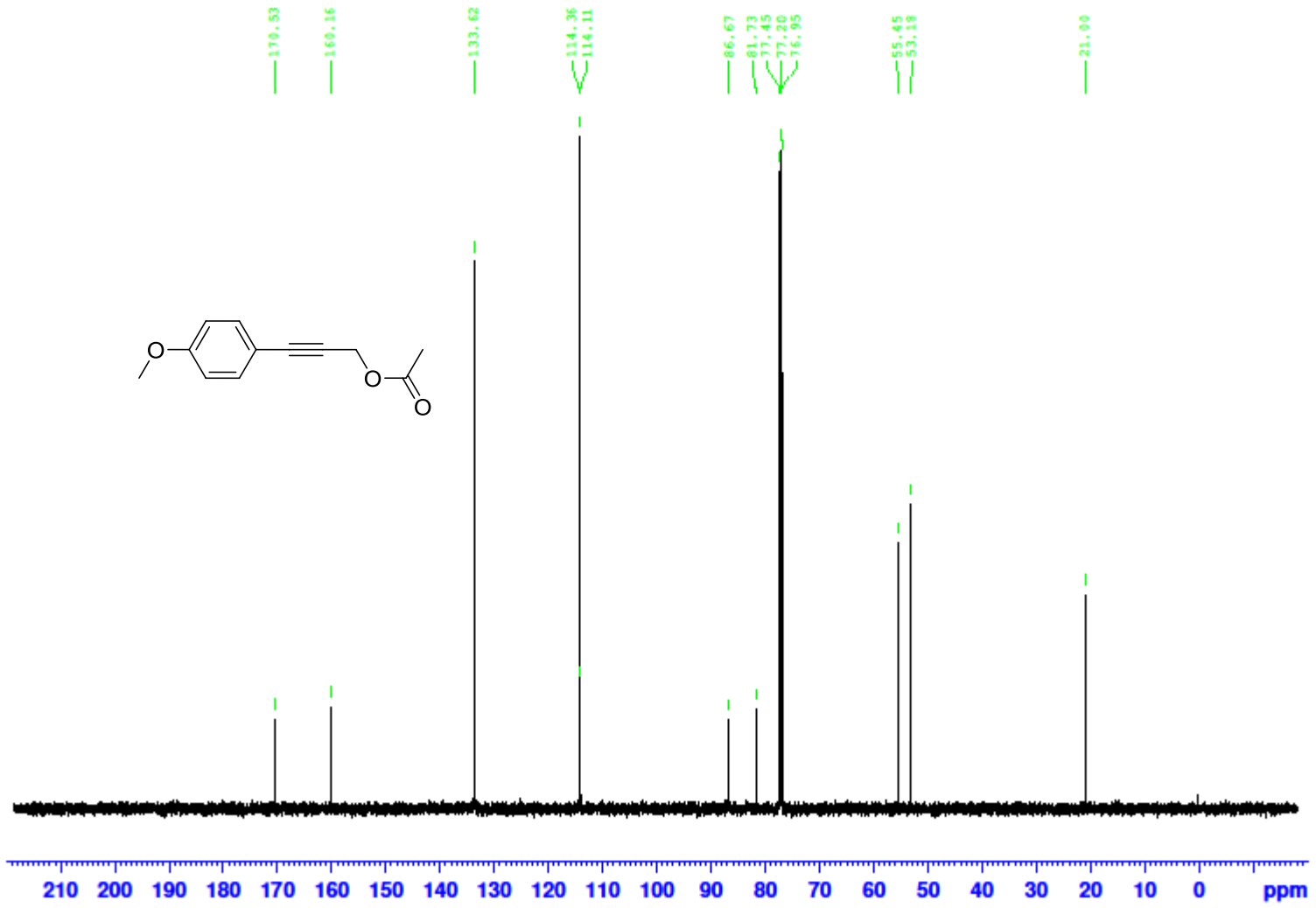


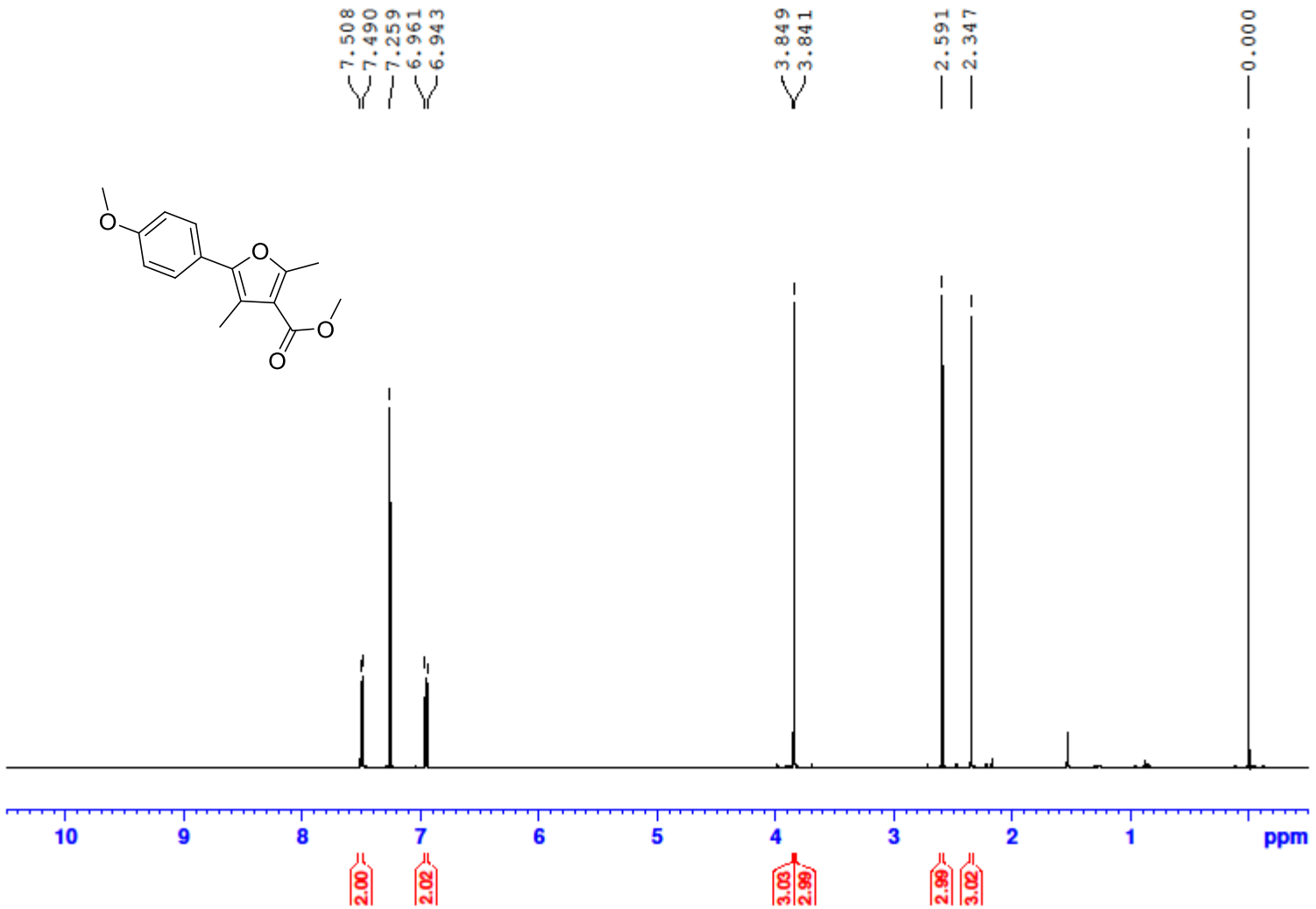
2-(4-Methoxy-phenyl)-1-phenyl-3-trimethylsilanyl-cycloprop-2-enecarboxylic acid methyl ester (25b) Purified by column chromatography (SiO_2, 1/20 - 1/5 : Et_2O/hexanes) to afford **25b** as a yellow solid (331 mg, 0.94 mmol, 46% yield, 49% conversion). R_f= 0.63; 2/3 : Et_2O/hexane. mp = 95 - 97°C; IR (film) 2955, 1713, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ 7.53 (d, *J*= 8.8 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.25 – 7.21 (m, 2 H), 7.14 (t, 1H), 6.94 (d, *J*= 8.8 Hz, 2H), 3.83 (s, 3H), 3.67 (s, 3H), 0.27 (s, 9H); - ^{13}C NMR ($CDCl_3$, 500MHz): δ 175.8, 161.0, 142.4, 131.6, 128.2, 128.0, 126.0, 125.7, 119.9, 114.6, 110.6, 55.6, 51.9, 34.7, -0.8. HRMS (ESI) *m/z* calcd $C_{21}H_{25}O_3Si$, 353.1567, found 353.1562 $[M+H]^+$.

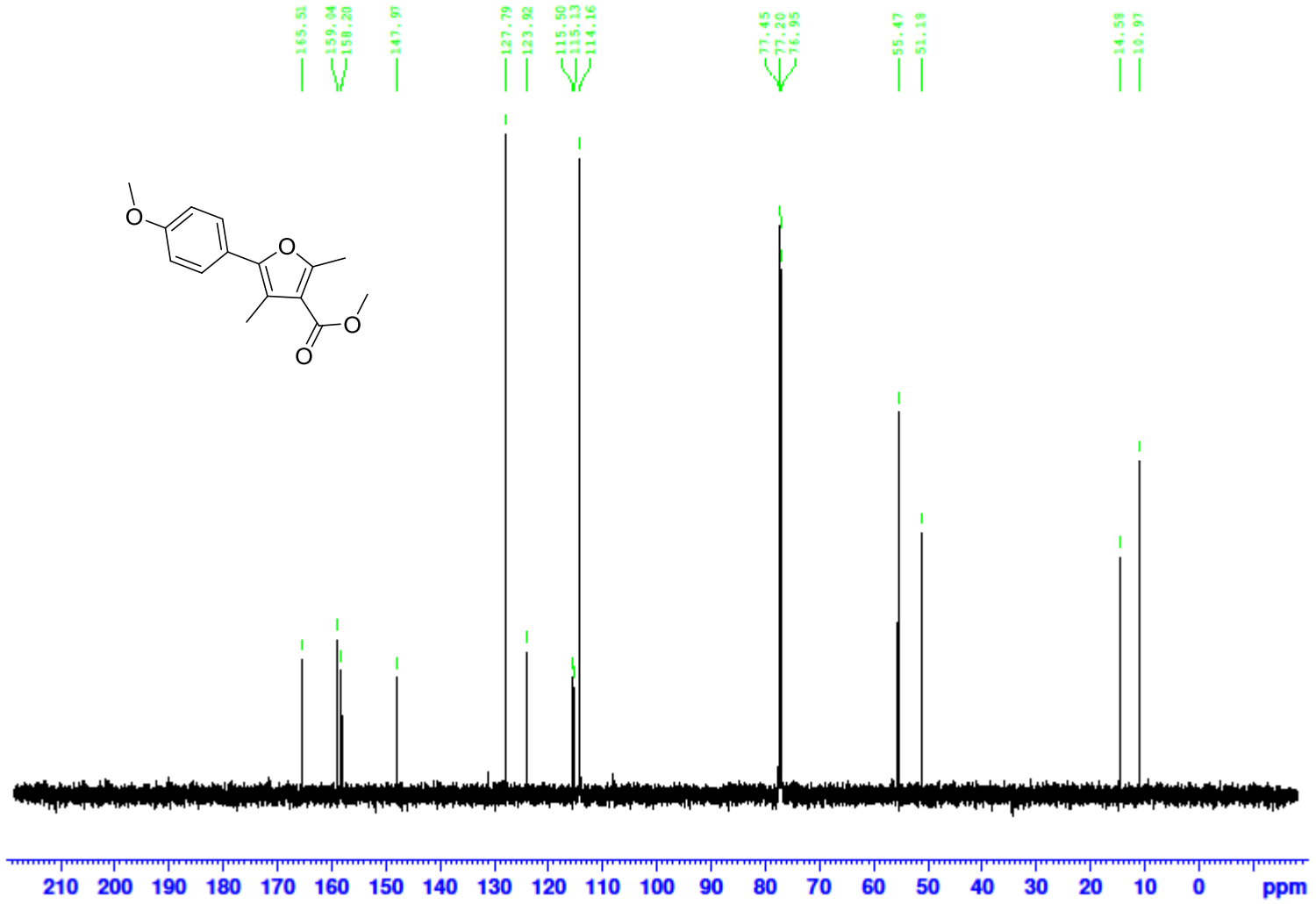


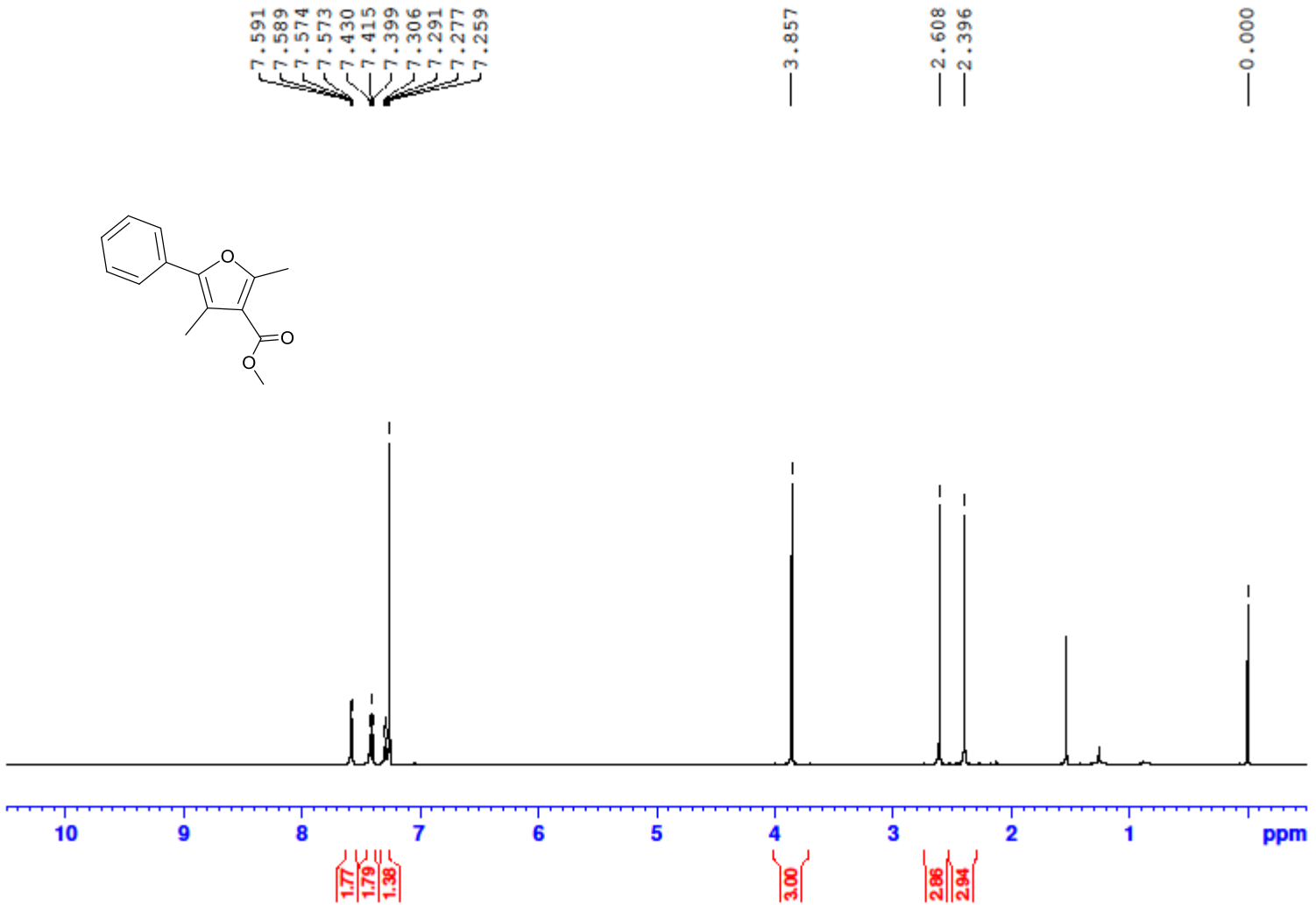


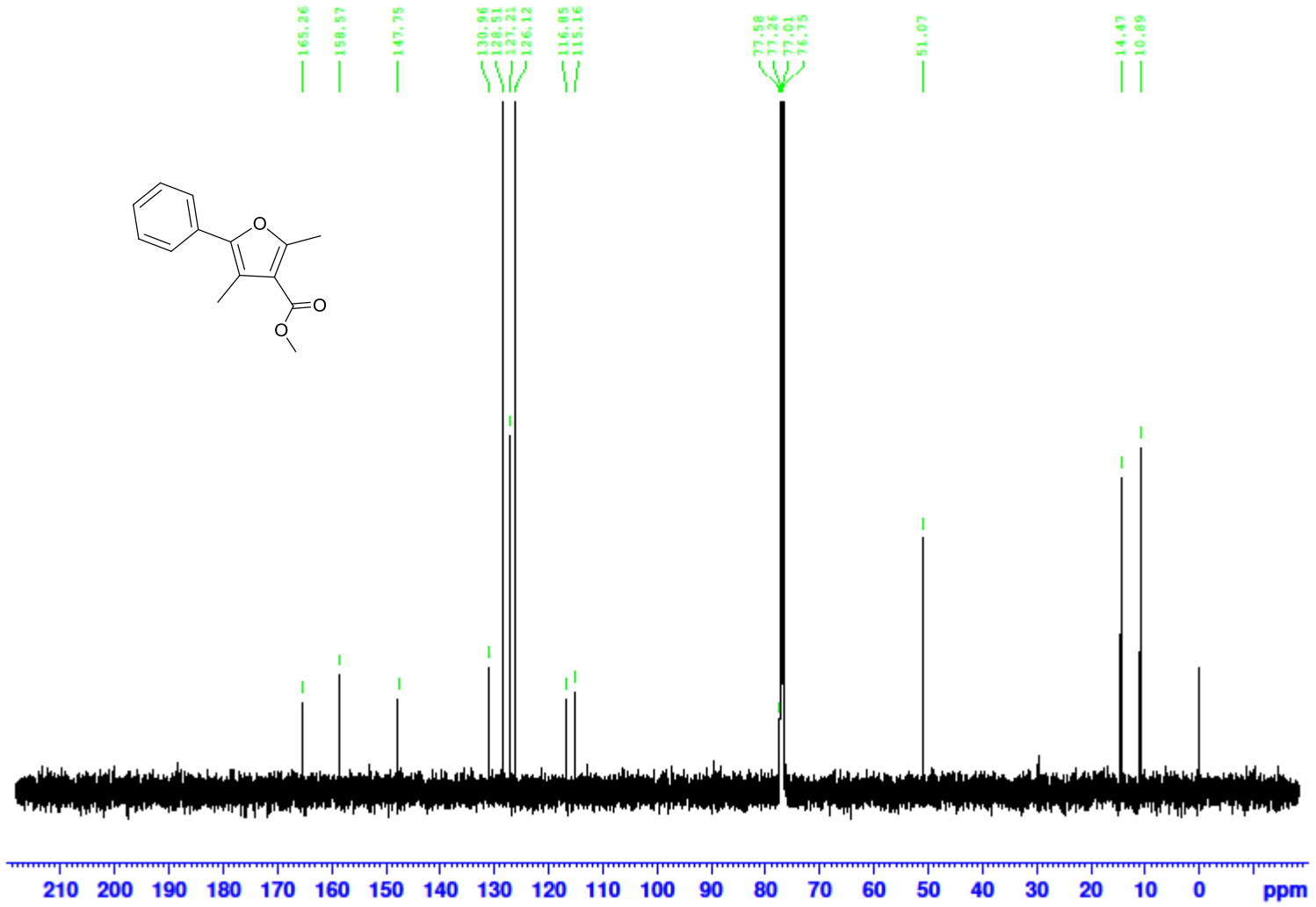


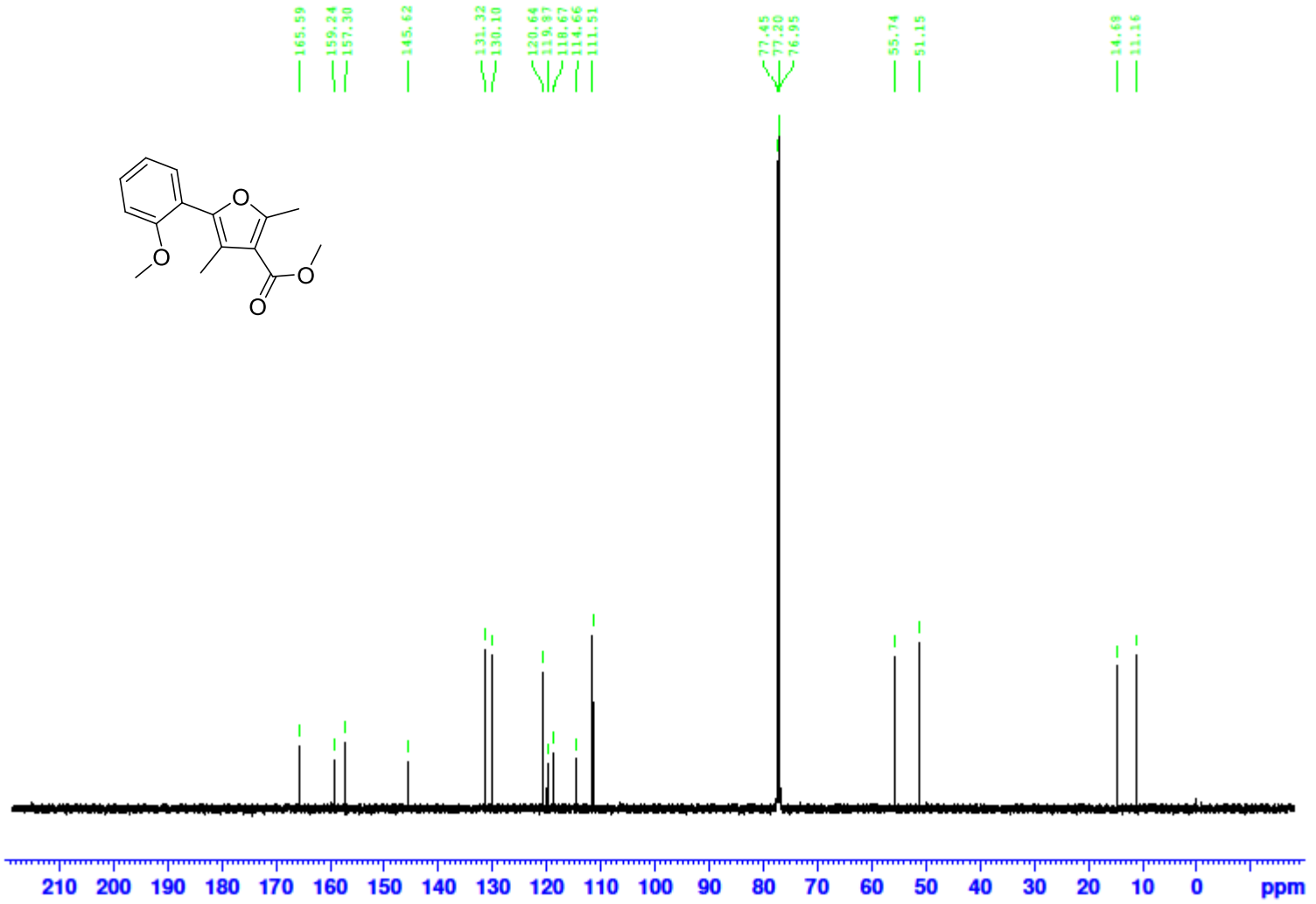


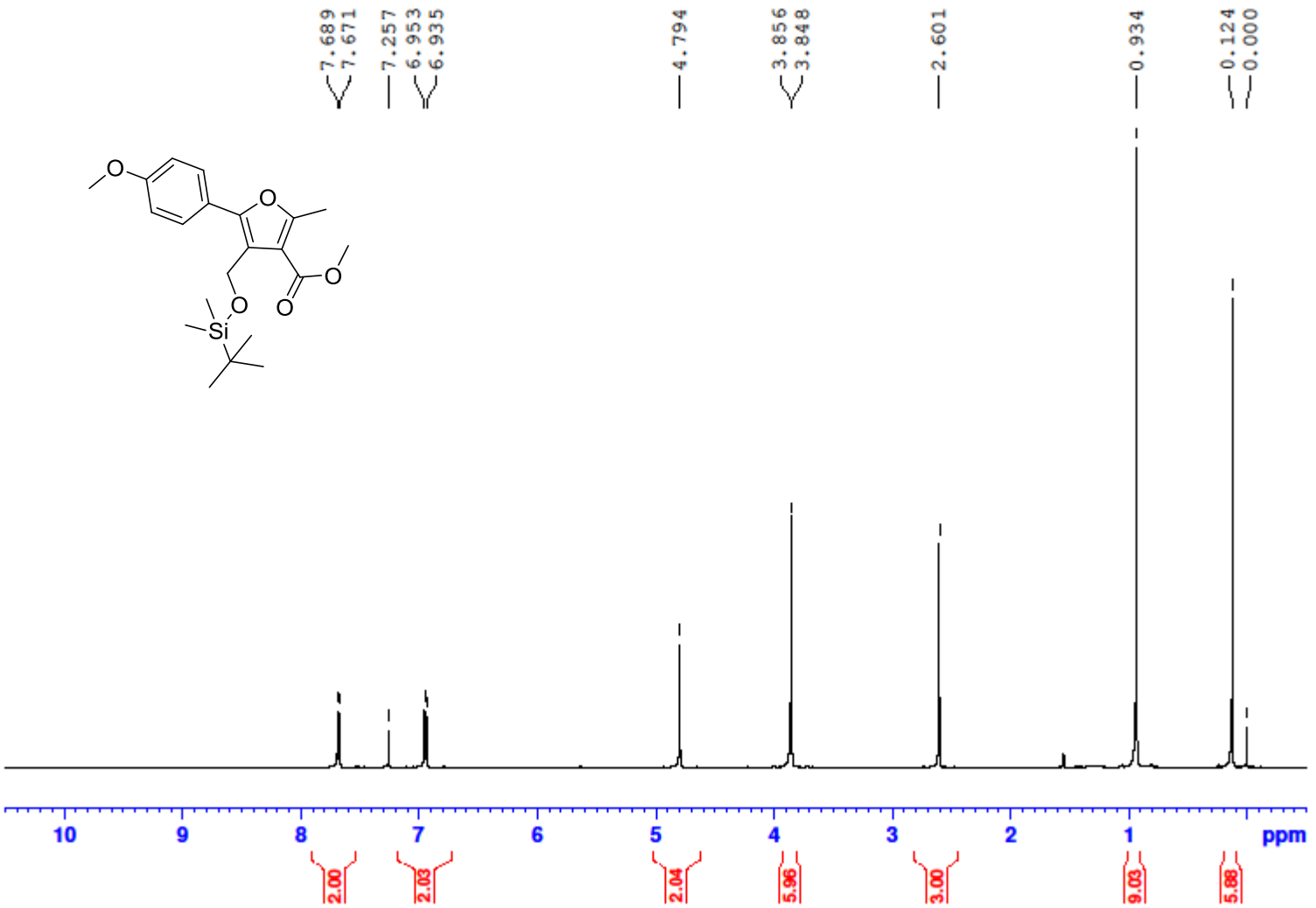


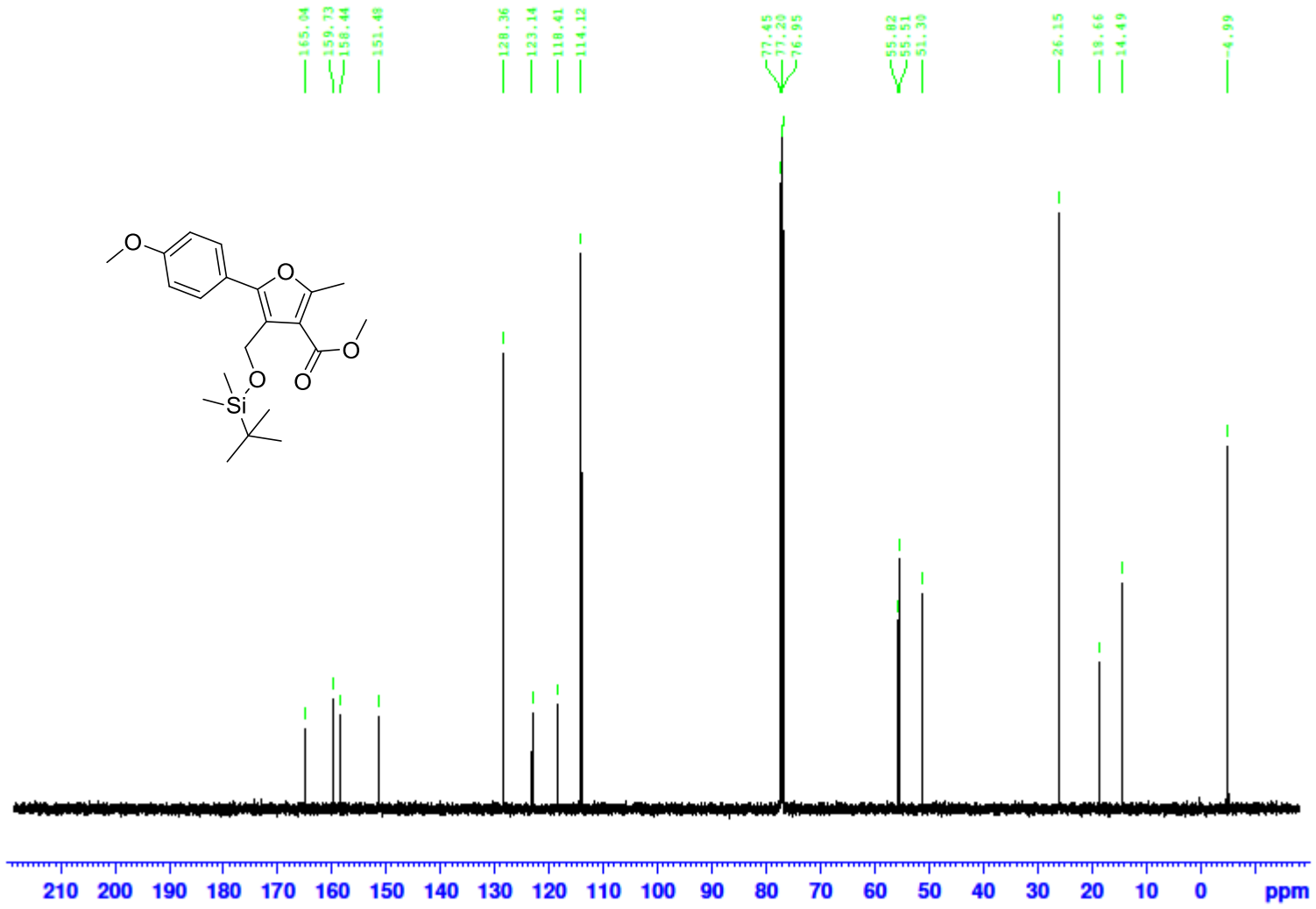


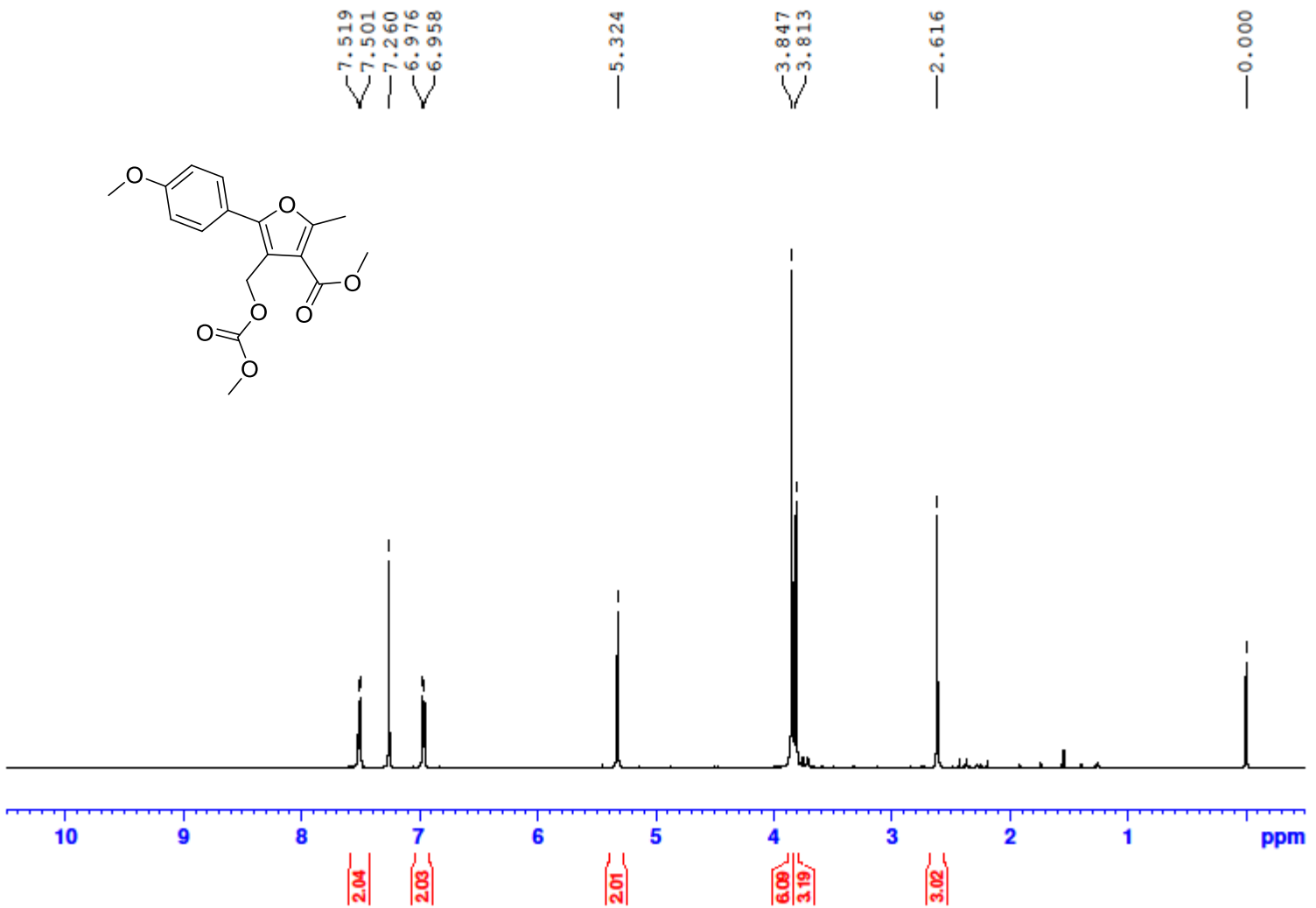


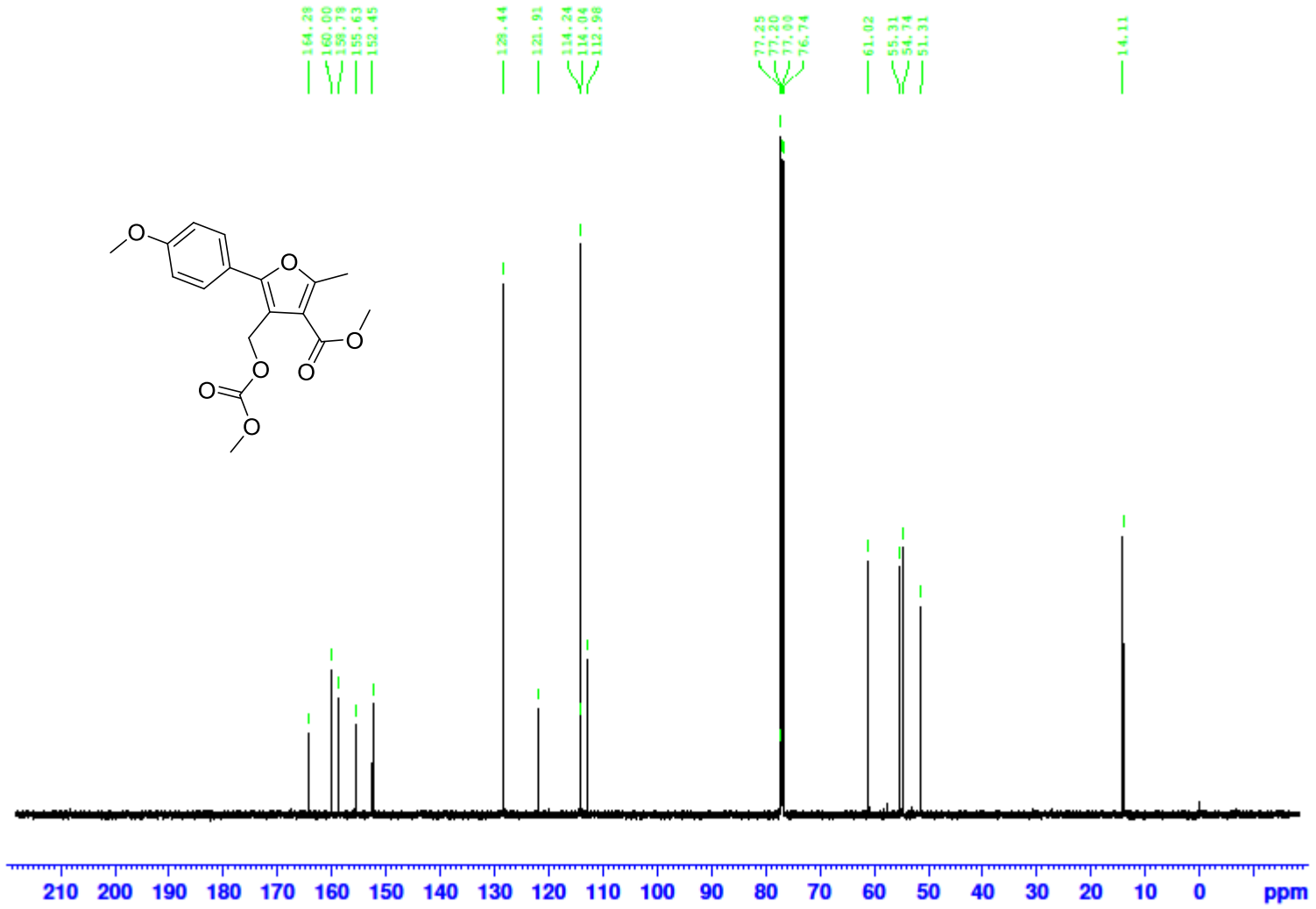


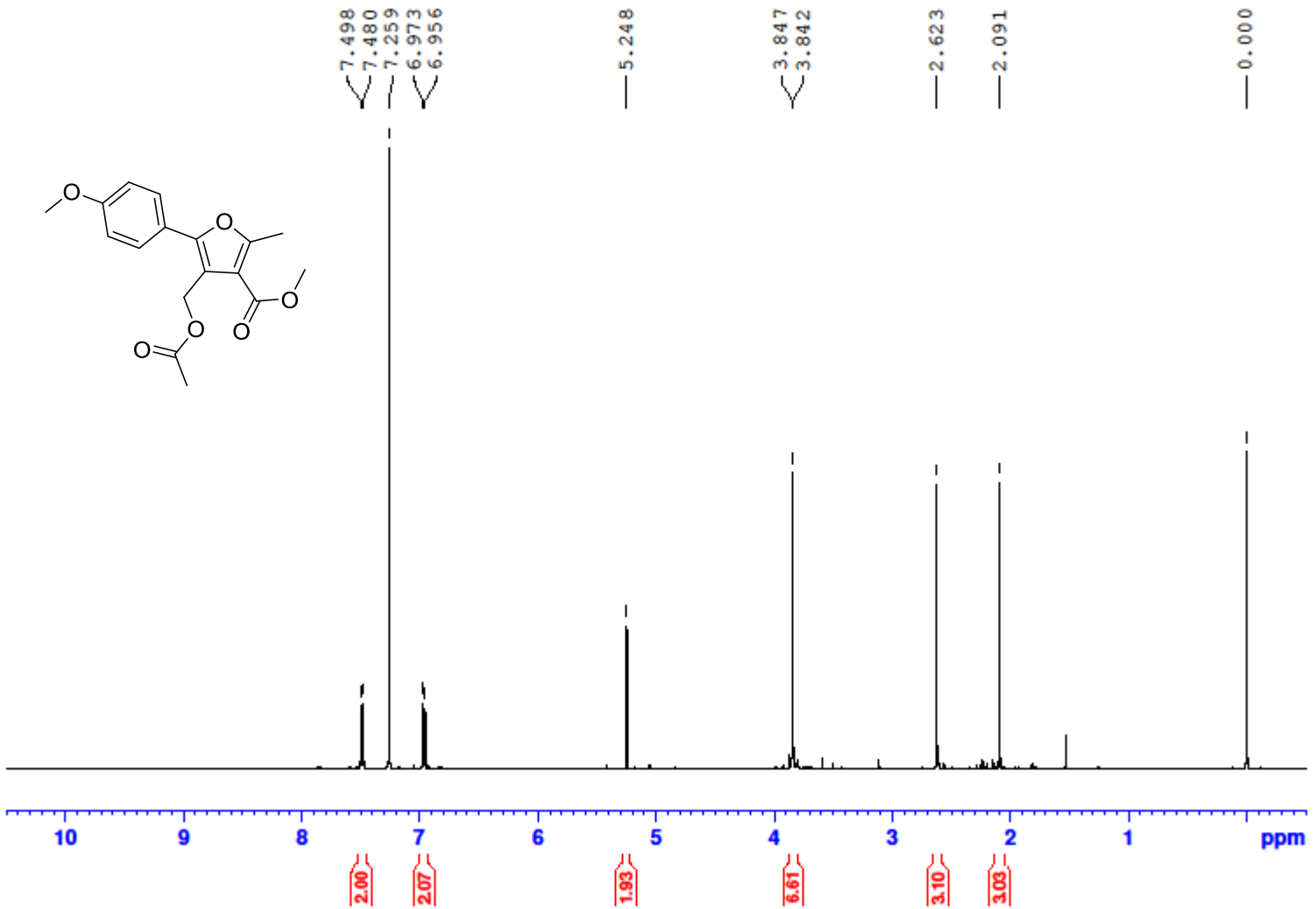


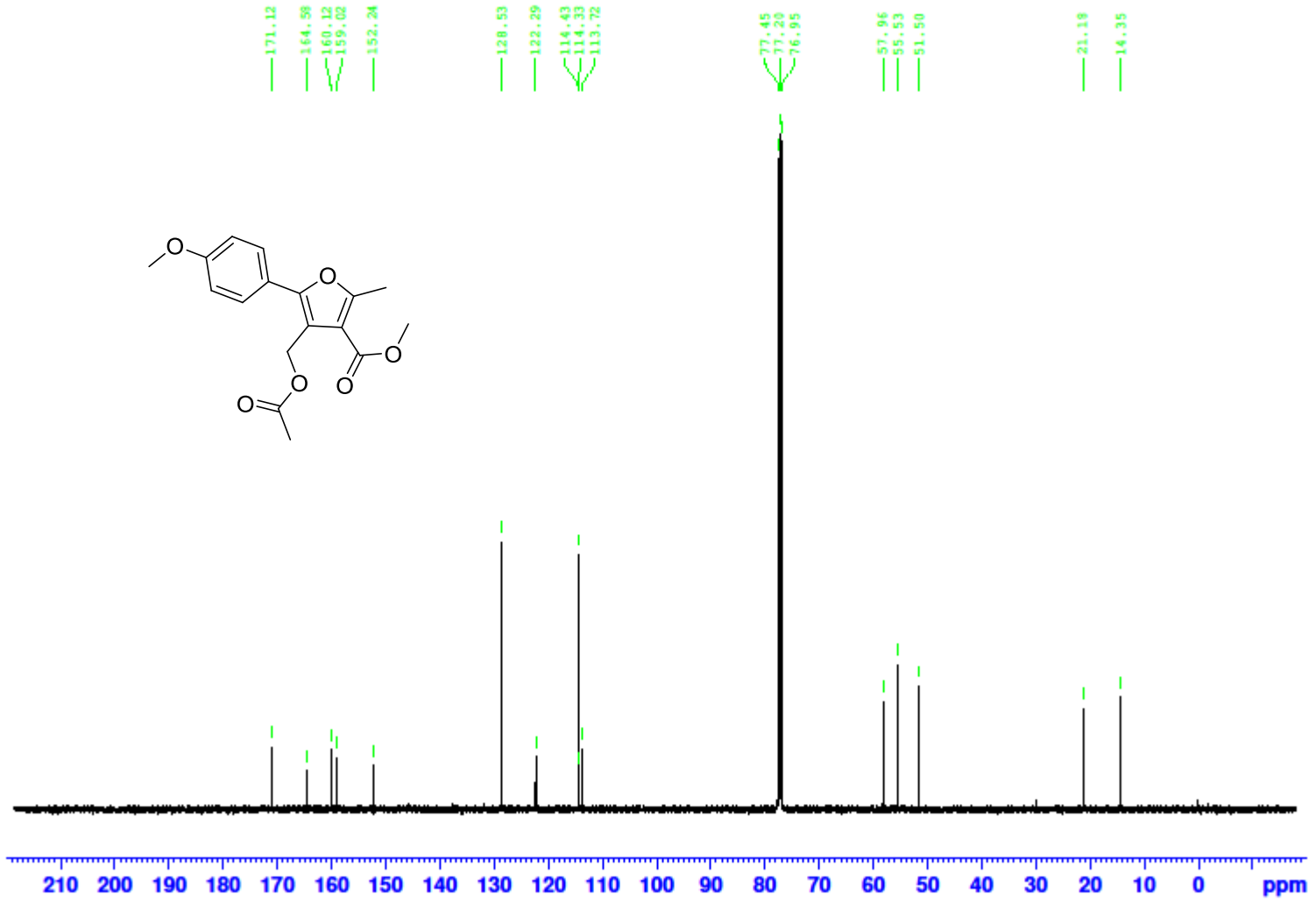


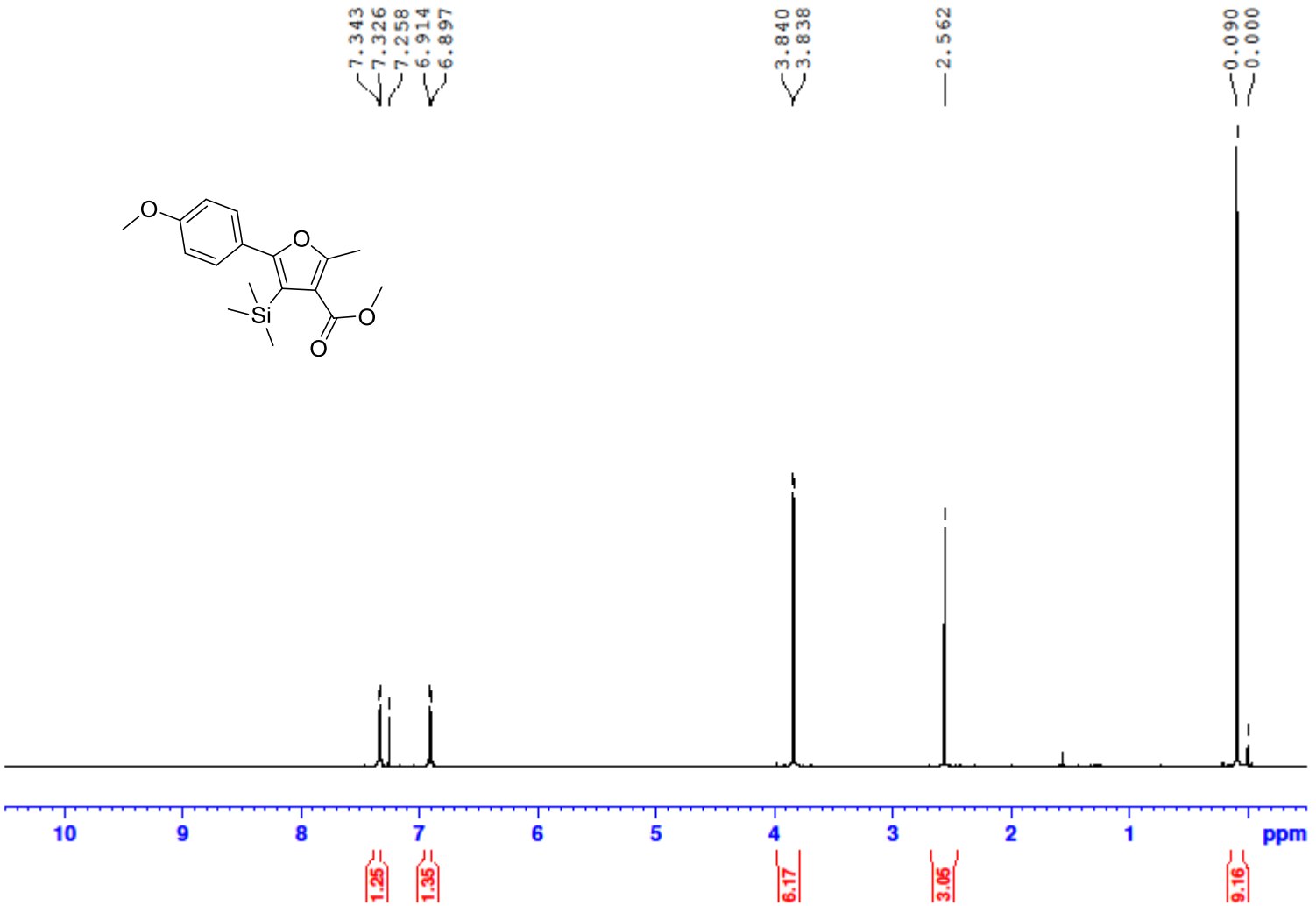


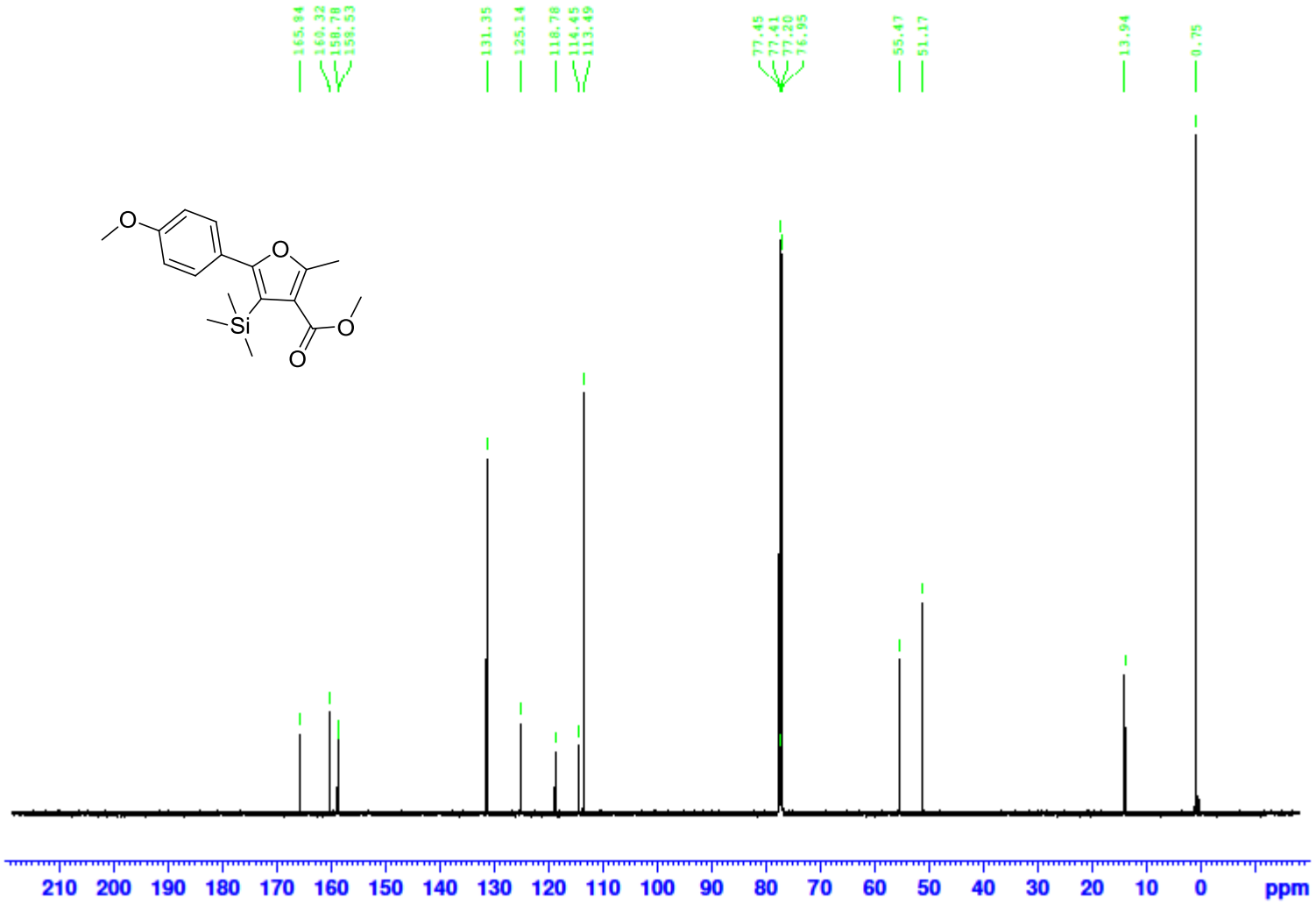


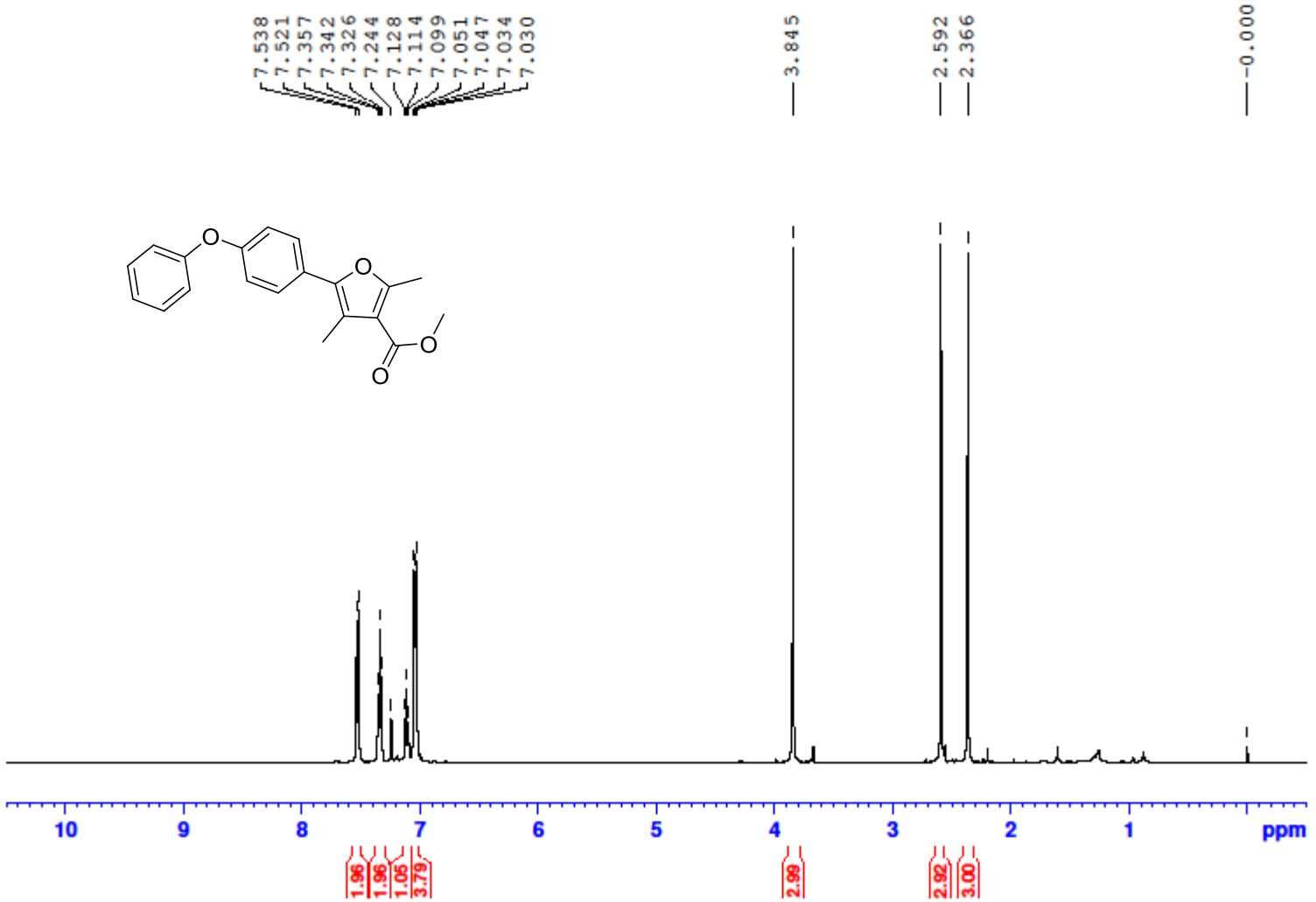


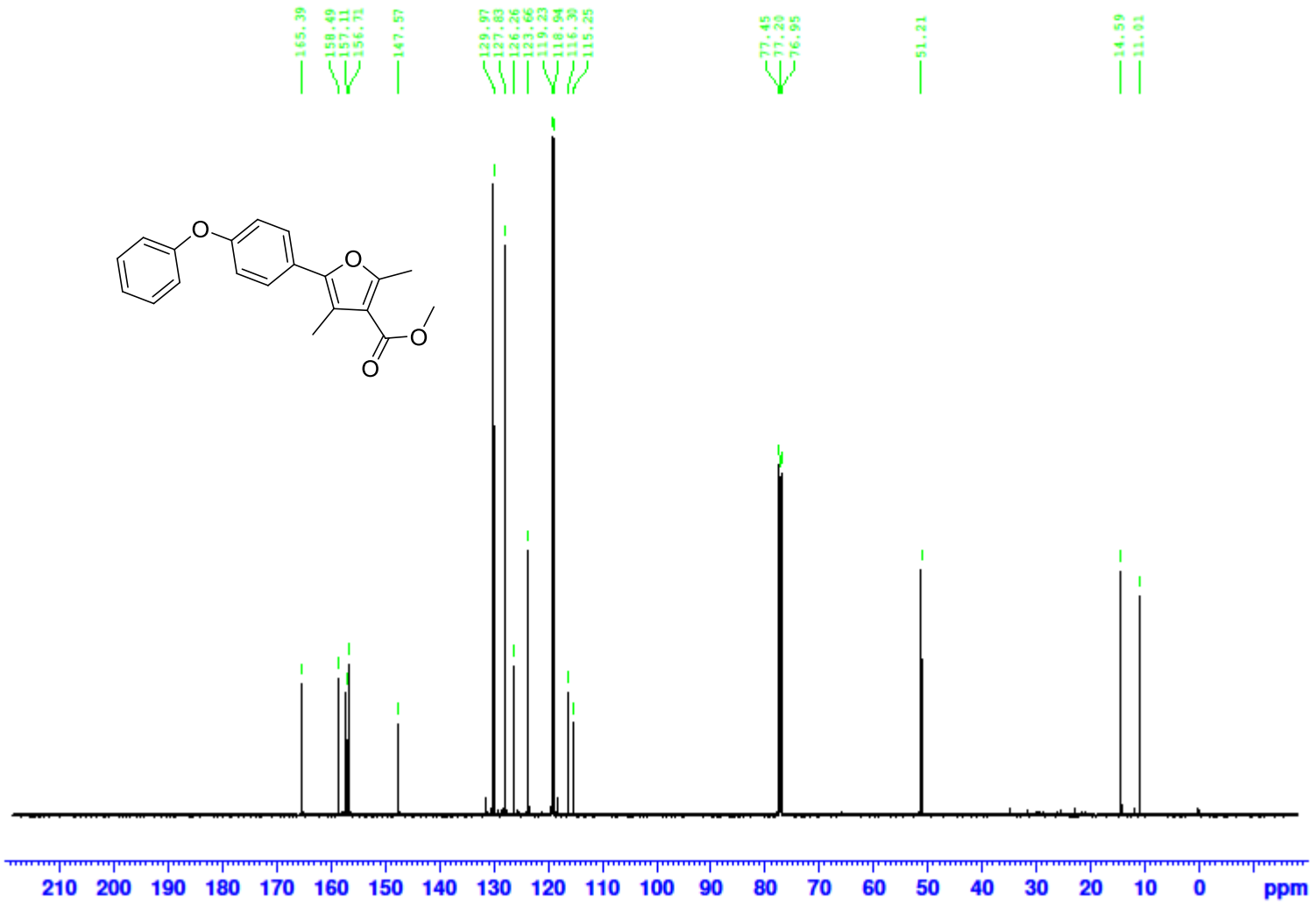


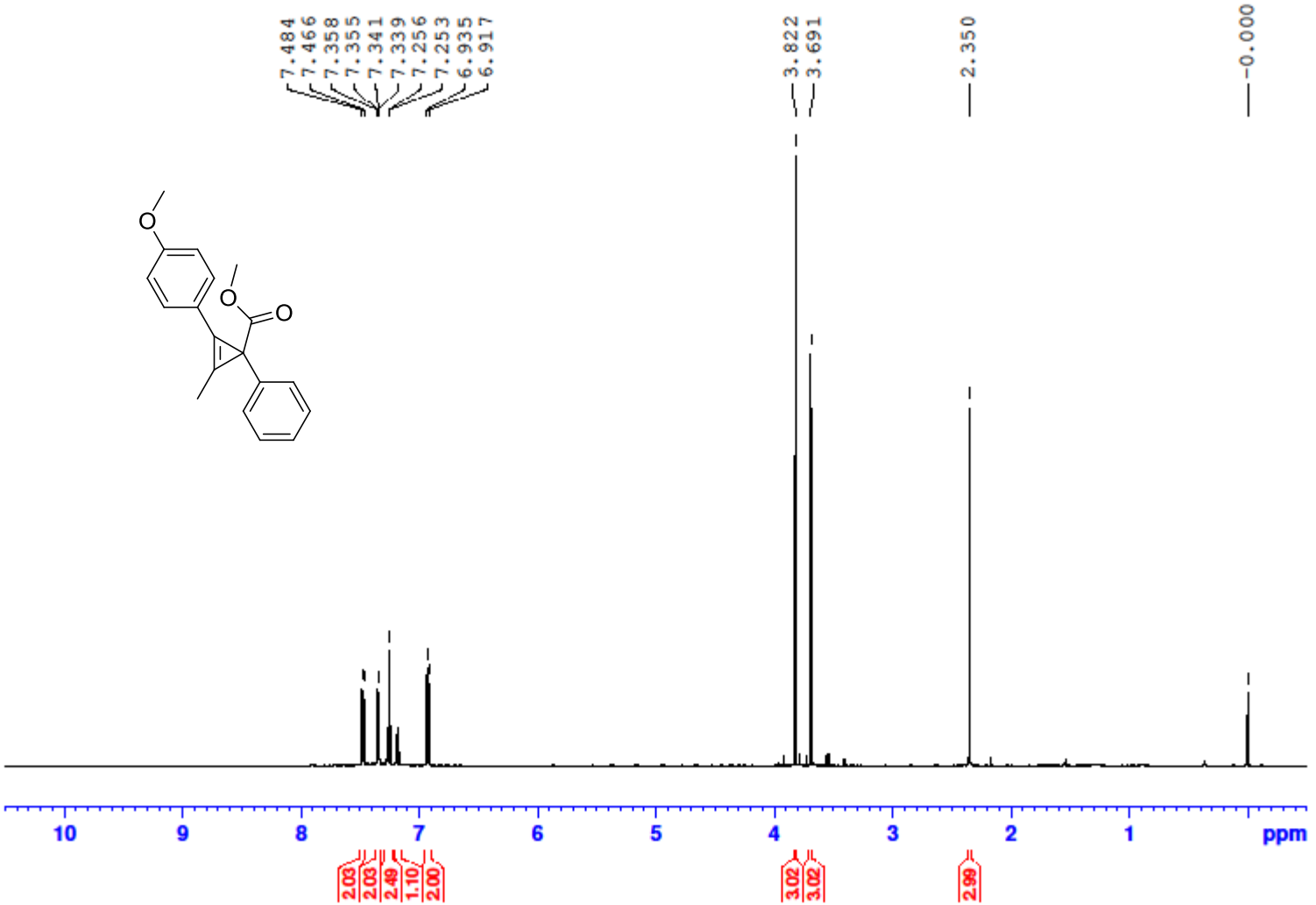


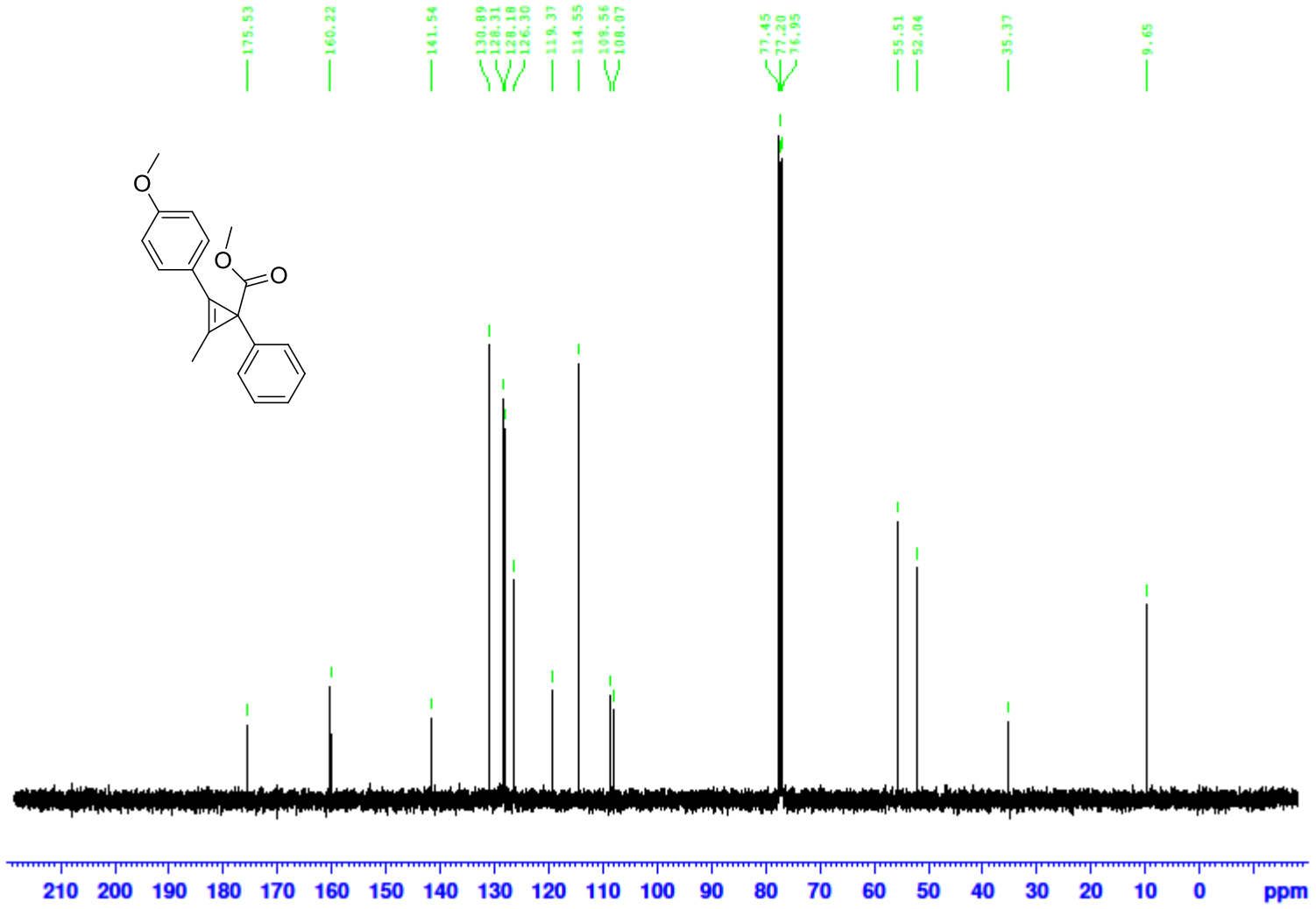


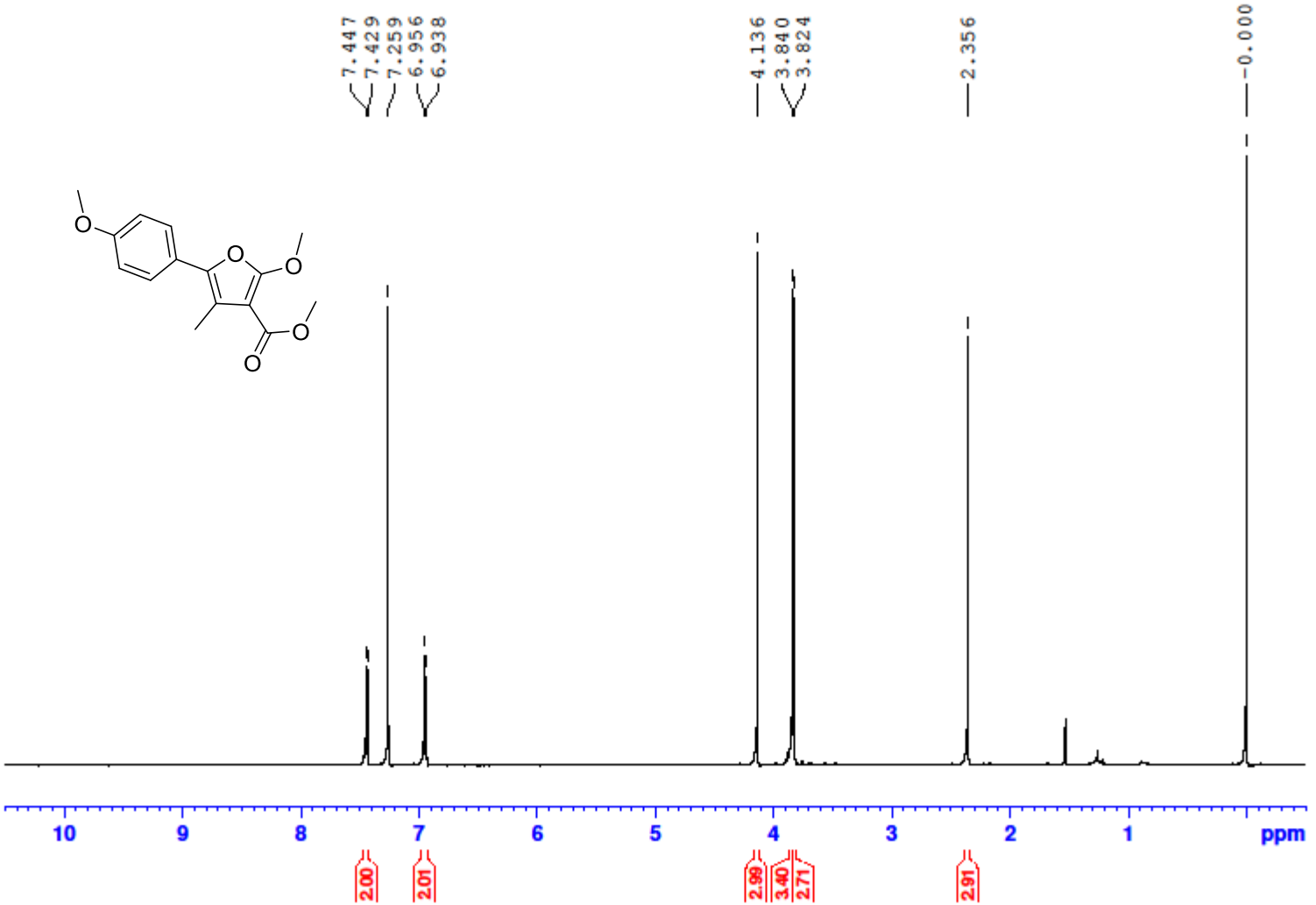


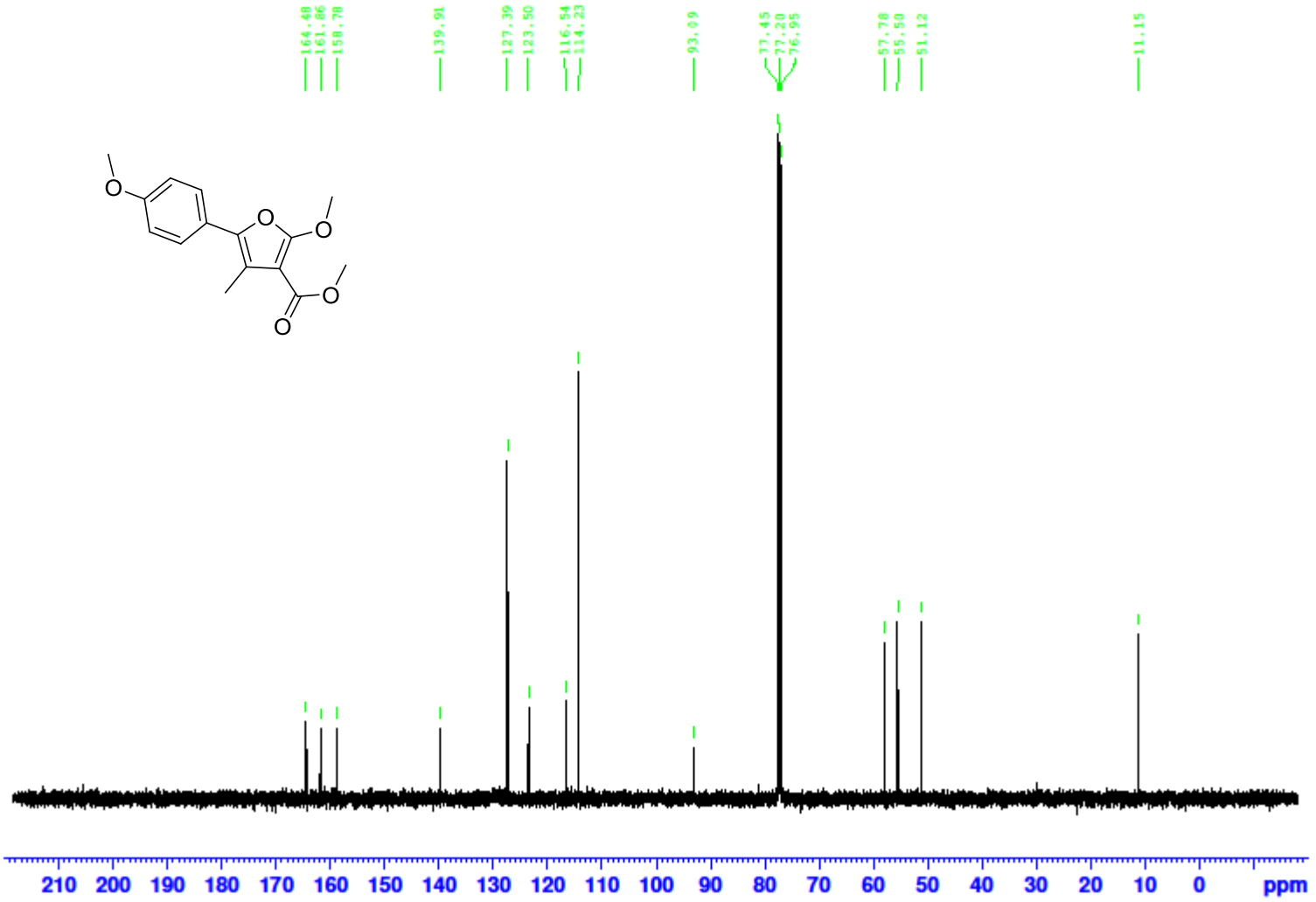


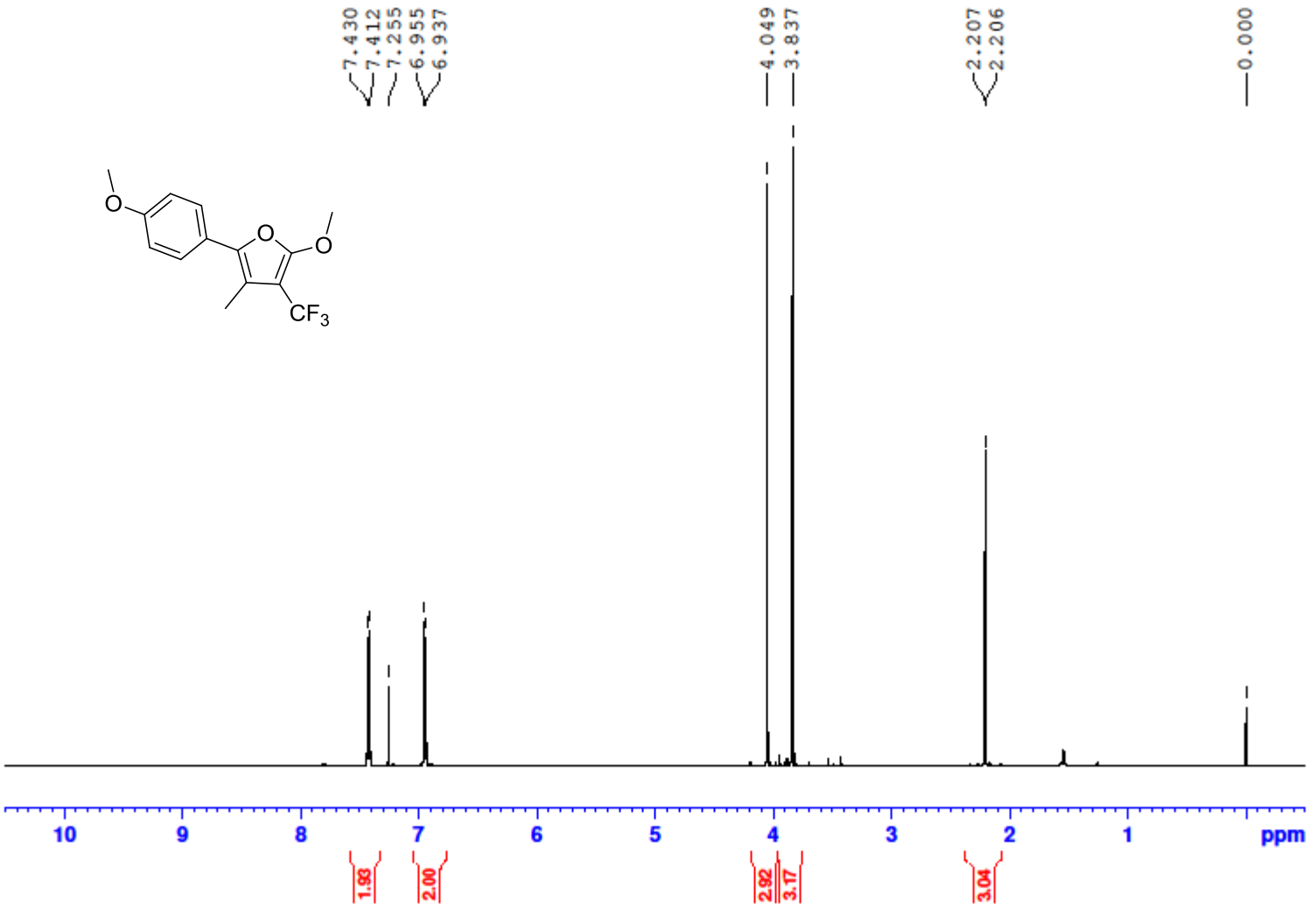


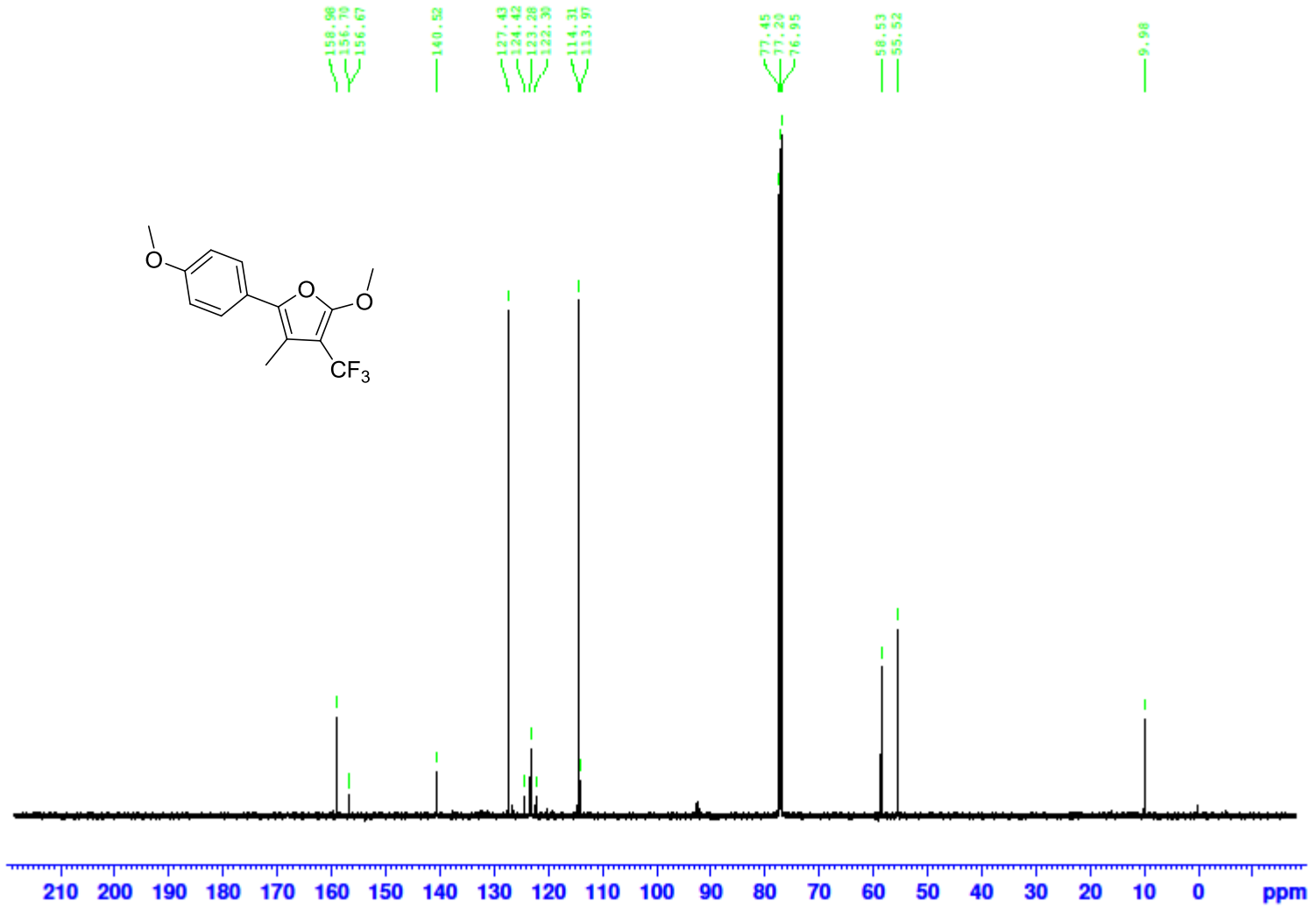


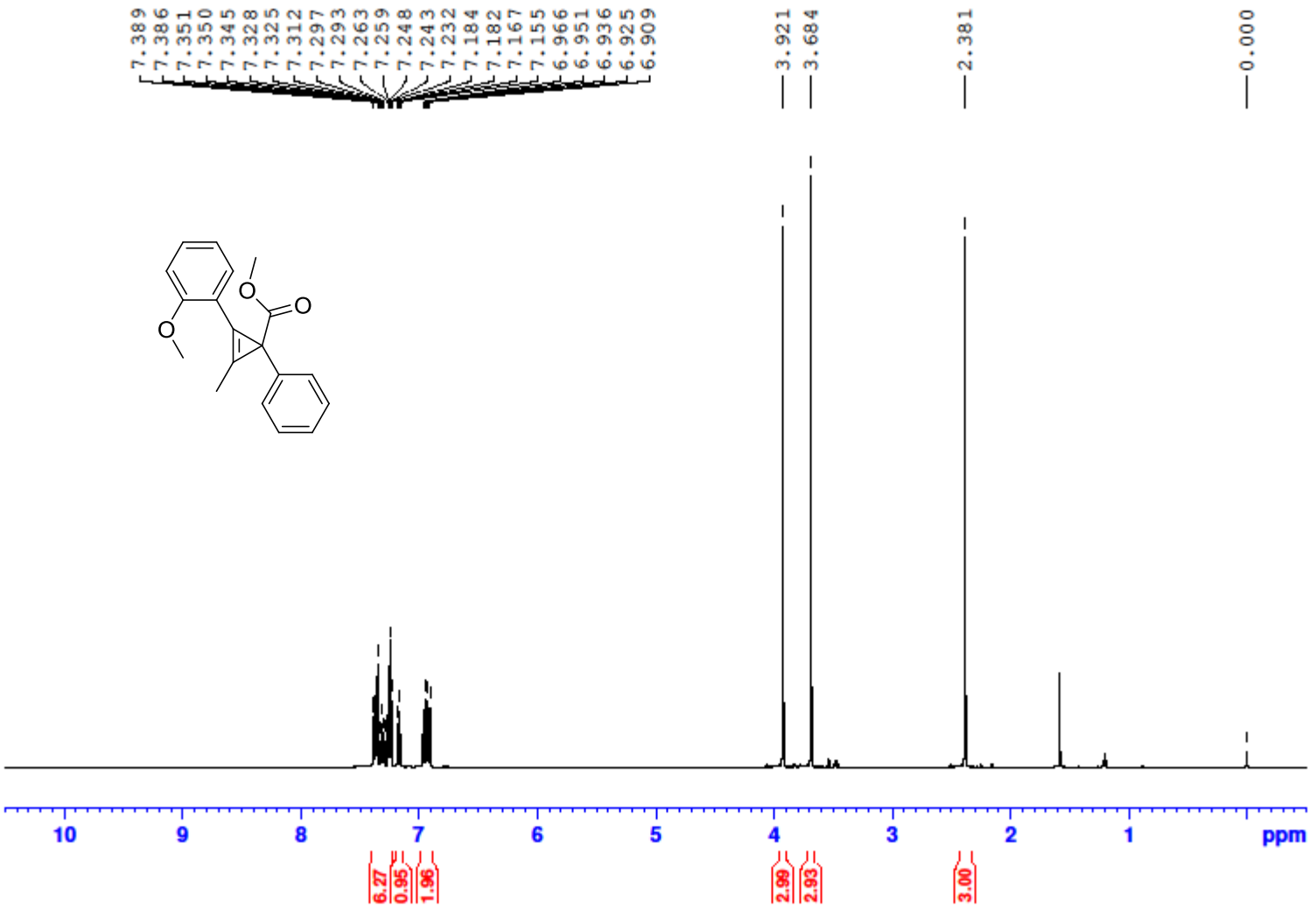


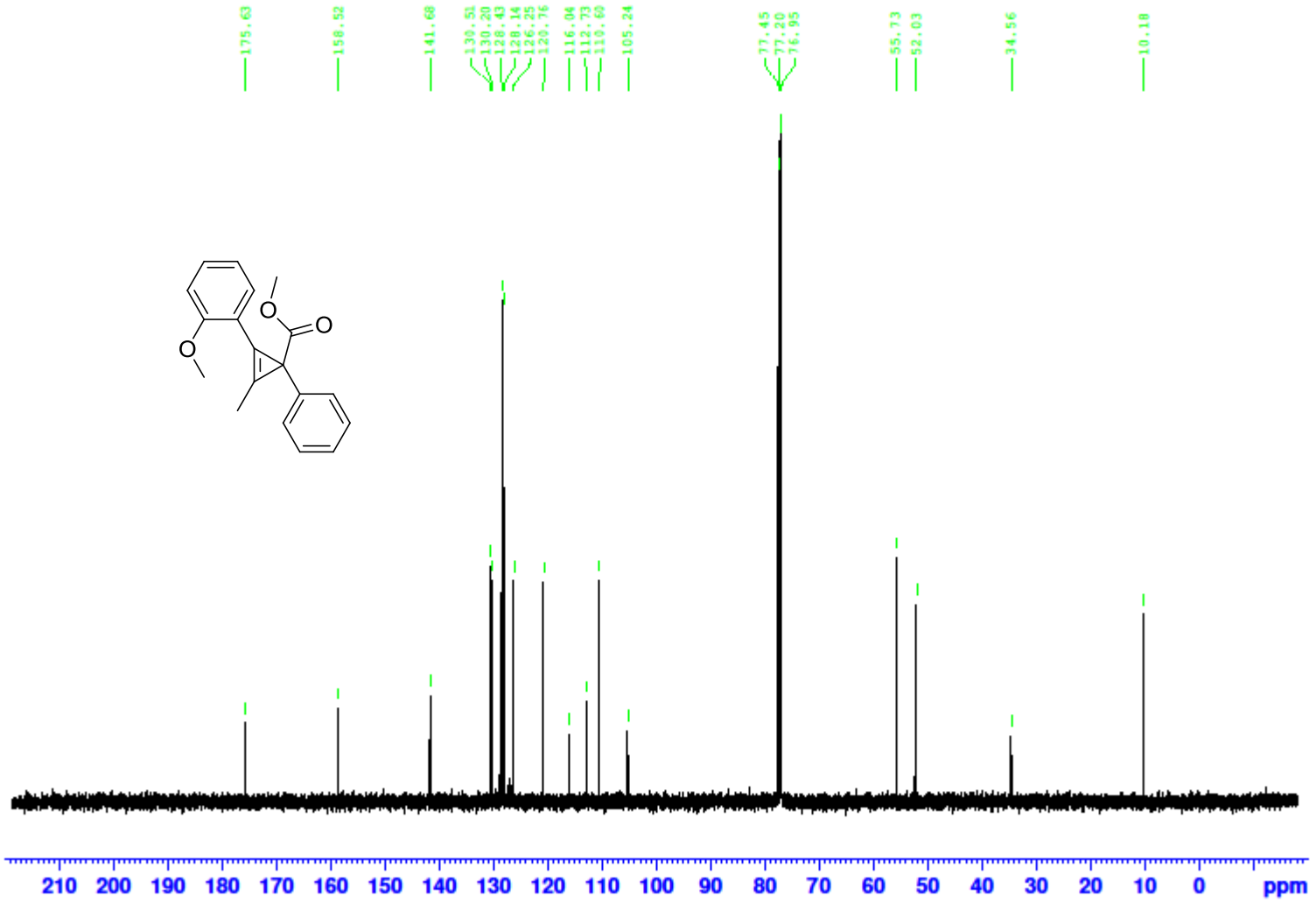


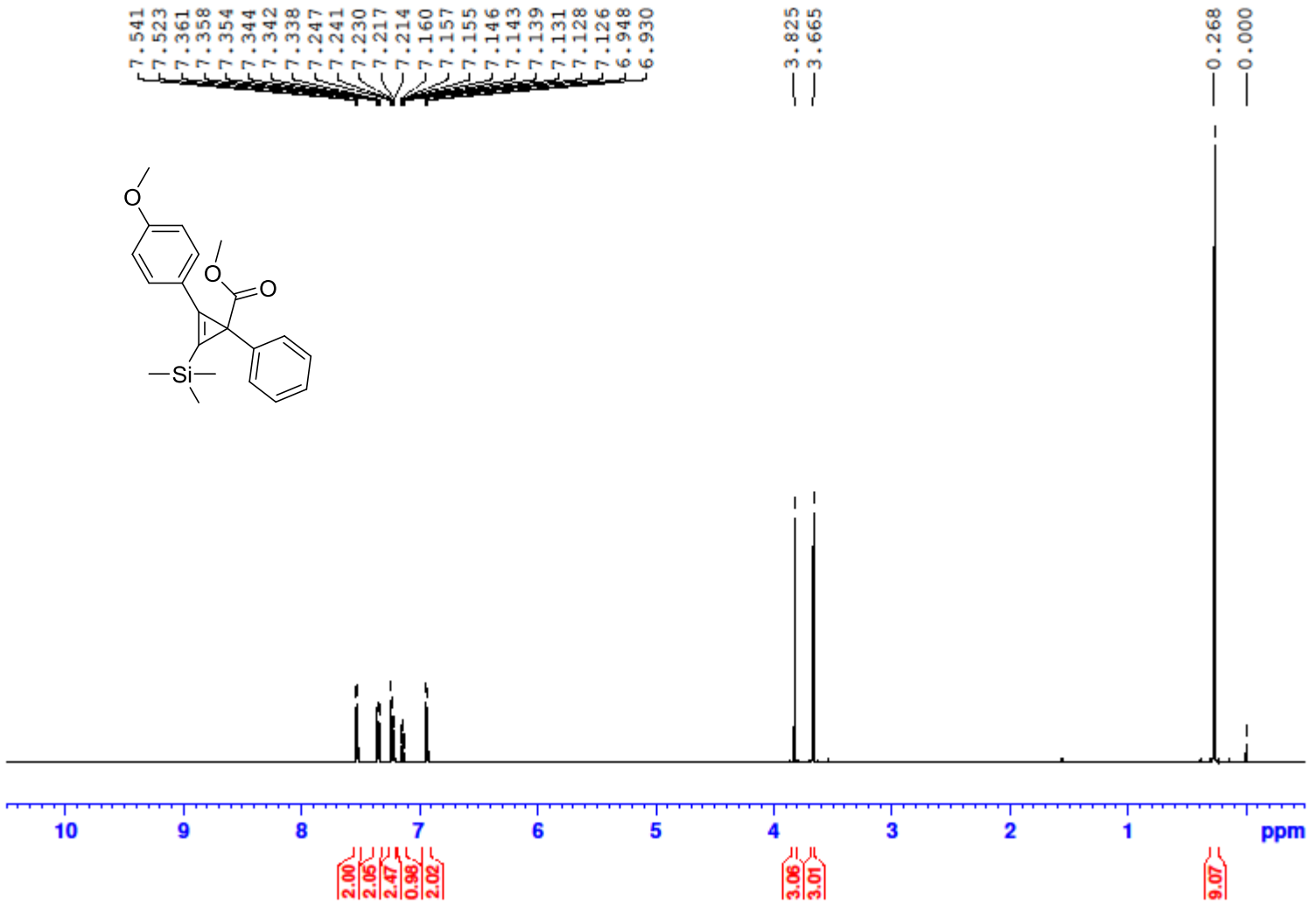


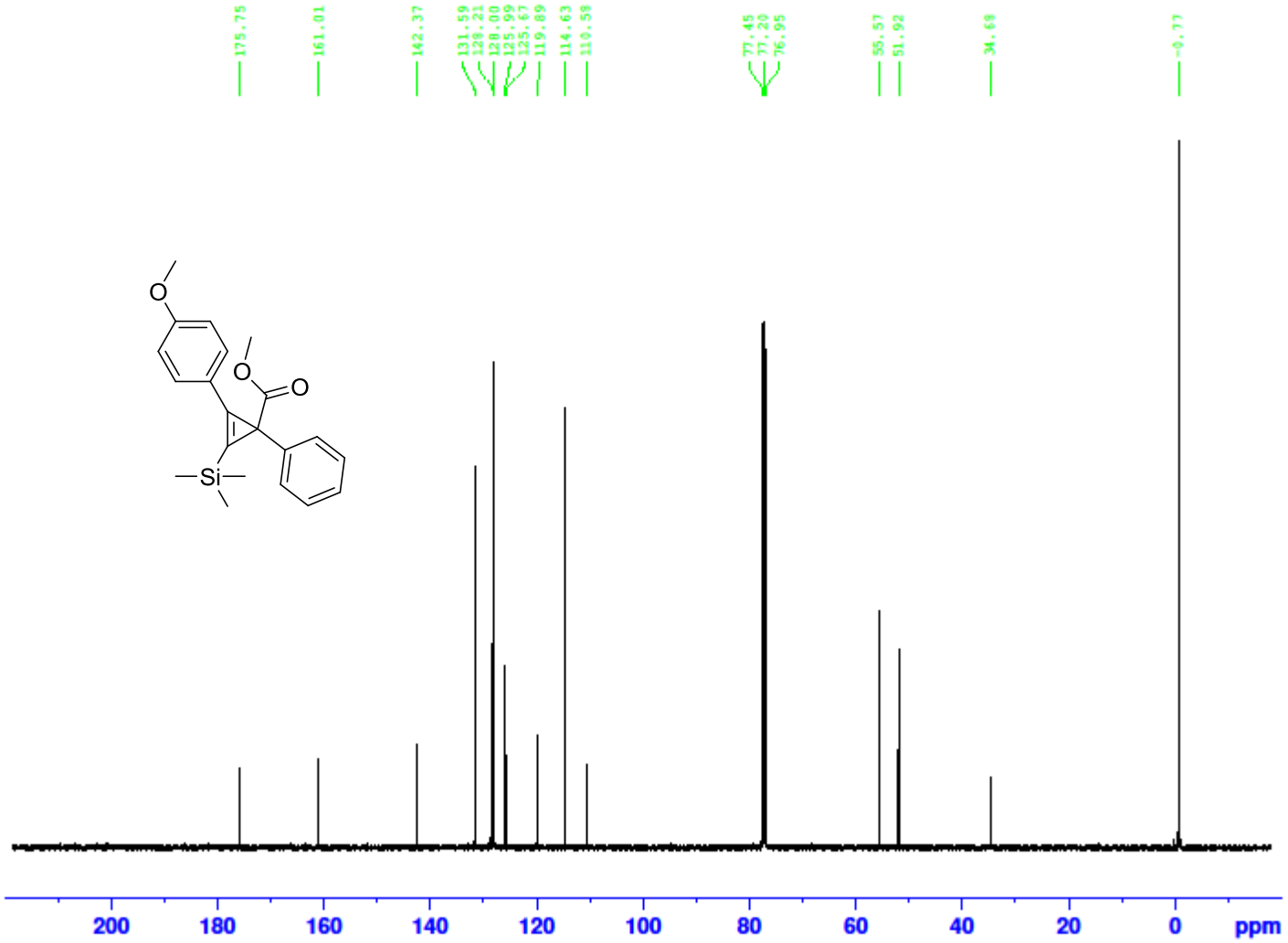












Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry