Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Expedient synthesis of 3-hydroxypyrroles via Bu_3SnH-triggered ionic 5-*exo*-*trig*-cyclization of 5-chloro-3-azamuconoate derivatives

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1. Materials and Methods

Melting points were determined on a melting point apparatus SMP30 and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C). Chemical shifts are reported in parts per million relative to the respective residual solvent peak as an internal standard ($CDCl_3$ [$\delta(^{1}H)$ = 7.28 ppm and $\delta(^{13}C)$ = 77.00 ppm] or DMSO-d_6 [$\delta(^{1}H)$ = 2.50 ppm and $\delta(^{13}C)$ = 39.50 ppm]. The following abbreviations were used: s – singlet, d – doublet, t – triplet, q – quartet, bs – broad singlet, m – multiplet. Electrospray ionization (ESI), positive mode, mass spectra were measured on a Bruker MaXis mass spectrometer using MeOH for dilution of samples. Single crystal X-ray data were collected by means of Agilent Technologies "Xcalibur" diffractometer. Thin-layer chromatography (TLC) was performed using aluminum sheets precoated with SiO_2 ALUGRAM SIL G/UV254. Macherey-Nagel silica gel 60 M (0.04−0.063 mm) was used for column chromatography. All solvents were distilled and dried prior to use. 1,2-Dichloroethane was washed with concentrated H_2SO_4, water, then distilled from P_2O_5 and stored over anhydrous K_2CO_3. *o*-Xylene was distilled and stored over sodium metal. Tributylstannane was purchased from Aldrich and used as received.

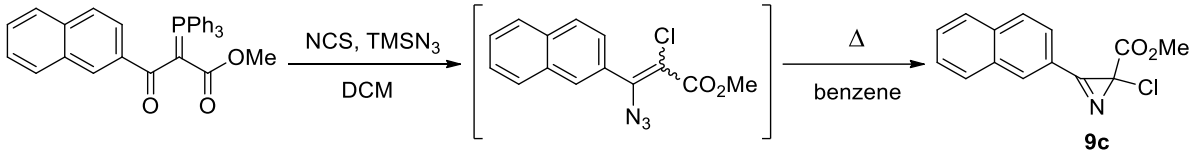
3-Azamuconoates **1b**,**4b**,**6**,[1] azirines **9a**,[2] **9b**,[1] **9e–l**,[3] **11**,[4] diazo compounds **12a**,[1] **12b–d**,**f–h**,[5] **12e**,[6] **12j**,[7] **12k**,**l**,[8] isoxazoles **13a**,**d**,**g**,**i**,[3] **13b**,**e**,[2] are known compounds and were prepared by the reported procedures.

2. Synthesis of 2*H*-Azirines 9

General Procedure

A solution of trimethylsilyl azide (18 mmol) and *N*-chlorosuccinimide (18 mmol) in anhydrous DCM (250 mL) was added dropwise to a stirred solution of the corresponding triphenylphosphoranylidene (12 mmol) in anhydrous DCM (100 mL). The reaction mixture was stirred at room temperature for 24 h, and then the solvent was removed under reduced pressure. The residue was filtered through a pad of silica gel using a hexane/EtOAc mixture (2:1) as an eluent, the solvent was evaporated, the residue was dissolved in anhydrous benzene and heated under reflux for 1 h. Azirines were purified by column chromatography on silica gel using a hexane/EtOAc mixture (from 20:1 to 2:1) as the eluent and followed by crystallization from Et_2O.

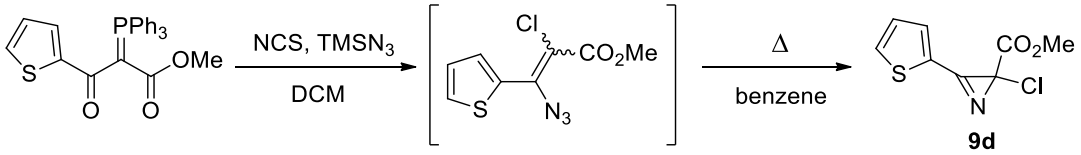
Methyl 2-chloro-3-(naphthalen-2-yl)-2*H*-azirine-2-carboxylate (9c)



9c

Azirine **9c** (1.37 g, 44%) was prepared according to the general procedure from methyl 3-(naphthalen-2-yl)-3-oxo-2-(triphenylphosphoranylidene)propanoate[9] (5.86 g, 12 mmol). White solid, mp 119–120 °C (Et_2O–hexane). ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H), 7.62–7.68 (m, 1H), 7.68–7.75 (m, 1H), 7.93–7.98 (m, 1H), 7.98–8.04 (m, 2H), 8.04–8.09 (m, 1H), 8.41–8.45 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 53.9, 116.8, 124.7, 127.6, 128.2, 129.4, 129.7, 129.75, 129.81, 132.5, 133.6, 136.2, 163.6, 167.9. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{10}{}^{35}ClNNaO_2^+$: 282.0292, found: 282.0295.

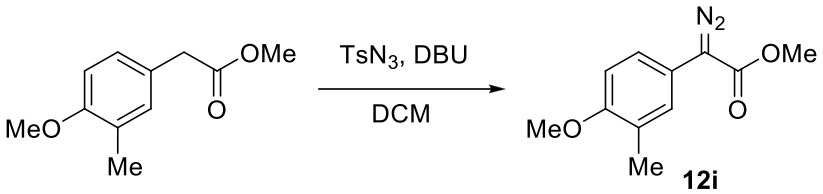
Methyl 2-chloro-3-(thiophen-2-yl)-2*H*-azirine-2-carboxylate (9d)



9d

Azirine **9d** (0.36 g, 14%) was prepared according to the general procedure from methyl 3-oxo-3-(thiophen-2-yl)-2-(triphenylphosphoranylidene)propanoate (5.33 g, 12 mmol). Brown solid, mp 60–62 °C (Et_2O–hexane). ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3H), 7.36 (dd, *J* 5.0, 3.8 Hz, 1H), 7.85 (dd, *J* 3.8, 1.2 Hz, 1H), 8.03 (dd, *J* 5.0, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 54.0, 54.4, 121.2, 129.0, 136.8, 137.6, 157.1, 167.5. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_8H_6{}^{35}ClNNaO_2S^+$: 237.9700, found: 237.9706.

3. Synthesis of methyl 2-diazo-2-(4-methoxy-3-methylphenyl)acetate (12i)



12i

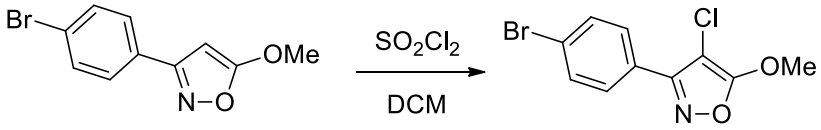
A solution of DBU (3.04 g, 20 mmol) in anhydrous DCM (10 mL) was added dropwise to a stirred solution of methyl 2-(4-methoxy-3-methylphenyl)acetate (1.94 g, 10 mmol) and tosyl azide (2.46 g, 12.5 mmol) in anhydrous DCM (25 mL). The reaction mixture was stirred at room temperature for 3 h, and then the solvent was removed under reduced pressure. Diazo compound **12i** was purified by column chromatography on silica gel (hexane/EtOAc mixture, from 20:1 to 3:1) followed by crystallization from Et_2O/hexane mixture. Orange solid (1.75 g, 90%). mp 71–72 °C. ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 6.85–6.91 (m, 1H), 7.20–7.25 (m, 1H), 7.27–7.33 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 16.3, 51.9, 55.4, 62.2, 110.5, 116.2, 123.5, 127.0, 127.5, 156.4, 166.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{11}H_{13}N_2O_3^+$: 221.0921, found: 221.0927.

4. Synthesis of 4-Chloroisoxazoles 13

General Procedure

To a stirred solution of the corresponding isoxazole (4 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added dropwise SO_2Cl_2 (4 mmol). The mixture was allowed to warm to r.t. and then refluxed for 20 min. The reaction mixture was cooled and washed with $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The isoxazoles were purified by column chromatography on silica gel using hexane–EtOAc as the eluent.

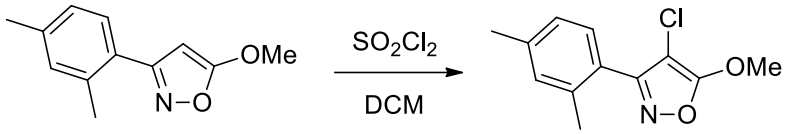
3-(4-Bromophenyl)-4-chloro-5-methoxyisoxazole (13c)



13c

Isoxazole **13c** (0.73 g, 63%) was prepared according to the general procedure from 3-(4-bromophenyl)-5-methoxyisoxazole[9] (1.02 g, 4 mmol). White solid, mp 77–78 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 4.24 (s, 3H), 7.61–7.67 (m, 2H), 7.73–7.78 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 58.6, 82.9, 124.9, 126.9, 129.1, 132.0, 160.5, 168.0. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{10}H_8{}^{79}Br^{35}ClNO_2{}^+$: 287.9421, found: 287.9423.

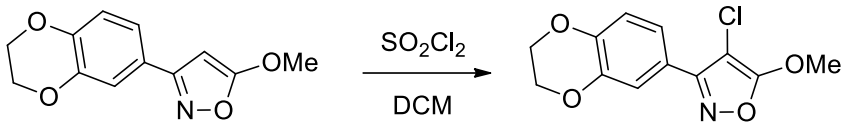
4-Chloro-3-(2,4-dimethylphenyl)-5-methoxyisoxazole (13f)



13f

Isoxazole **13f** (0.33 g, 35%) was prepared according to the general procedure from 3-(2,4-dimethylphenyl)-5-methoxyisoxazole[9] (0.81 g, 4 mmol). White solid, mp 52–53 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 2.40 (s, 3H), 4.25 (s, 3H), 7.09–7.14 (m, 1H), 7.15–7.17 (m, 1H), 7.26–7.31 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 19.8, 21.3, 58.4, 84.3, 124.1, 126.5, 129.7, 131.4, 137.2, 140.1, 163.7, 167.3. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{13}{}^{35}ClNO_2{}^+$: 238.0629, found: 238.0634.

4-Chloro-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5-methoxyisoxazole (13h)

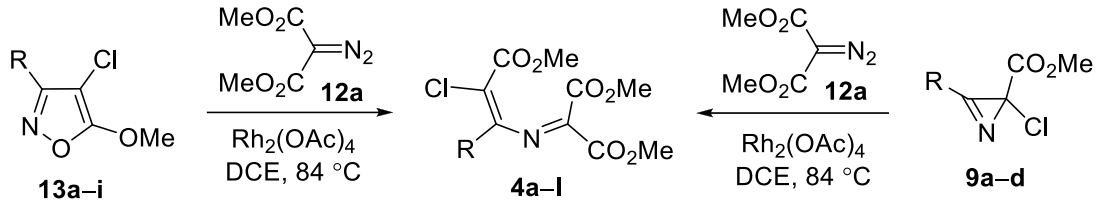


13h

Isoxazole **13h** (0.91 g, 85%) was prepared according to the general procedure from 3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5-methoxyisoxazole[9] (0.93 g, 4 mmol). White solid, mp 65–67 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 4.22 (s, 3H), 4.28–4.36 (m, 4H), 6.97 (d, *J* 8.4 Hz, 1H), 7.38 (dd, *J* 8.4, 2.1 Hz, 1H), 7.42 (d, *J* 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 58.4, 64.2, 64.5, 82.9, 116.8, 117.7, 121.06, 121.11, 143.6, 145.5, 160.8, 167.7. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{11}{}^{35}ClNO_4^+$: 268.0371, found: 268.0369.

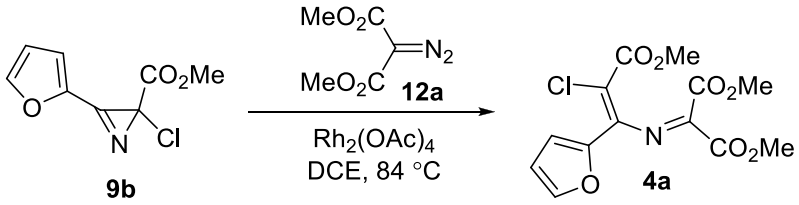
5. Synthesis of 5-Chloro-3-azamuconoates 4

General Procedure



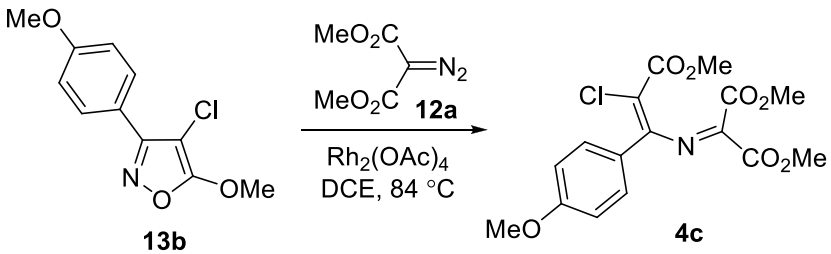
$Rh_2(OAc)_4$ (2 mol% on azirine/isoxazole) was added to a refluxing solution of azirine **9a**–**d** (0.5 mmol) or isoxazole **13a**–**i** (0.5 mmol) and diazo compound **12a** (in amount indicated below) in anhydrous DCE (1.5 mL) under an argon atmosphere. The stirred mixture was heated under reflux until nitrogen evolution had stopped. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using a hexane/EtOAc mixture as the eluent.

Dimethyl (*E*)-2-{[2-chloro-1-(furan-2-yl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4a)



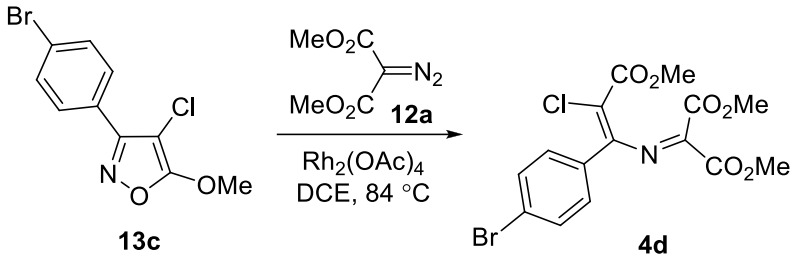
Azamuconoate **4a** (143 mg, 87%) was prepared according to the general procedure from azirine **9b** (100 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (94 mg, 0.6 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3H), 3.97 (bs, 6H), 6.56 (dd, *J* 3.7, 1.8 Hz, 1H), 7.35 (d, *J* 3.7 Hz, 1H), 7.52 (d, *J* 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 52.8, 53.3 (2C), 101.2, 112.3, 117.7, 143.8, 144.0, 144.8, 152.6, 158.7, 161.3, 162.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{13}H_{12}{}^{35}ClNNaO_7^+$: 352.0195, found: 352.0201.

Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl]imino}malonate (4c)



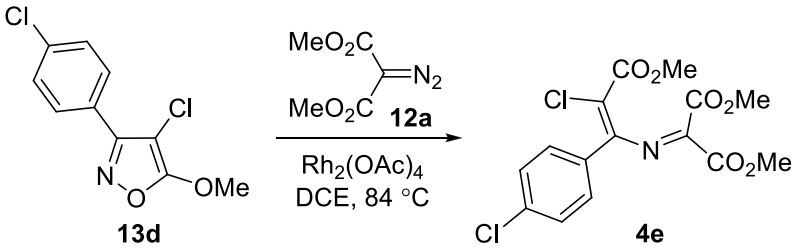
Azamuconoate **4c** (148 mg, 80%) was prepared according to the general procedure from isoxazole **13b** (120 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (126 mg, 0.8 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 3.83 (s, 3H), 3.89 (bs, 6H), 6.90–6.96 (m, 2H), 7.49–7.57 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.8, 53.3, 55.2, 102.4, 113.6, 126.6, 130.4, 149.4, 154.7, 160.5, 160.7, 163.3. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{17}{}^{35}ClNO_7{}^+$: 370.0688, found: 370.0693.

Dimethyl (*E*)-2-{[1-(4-bromophenyl)-2-chloro-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4d)



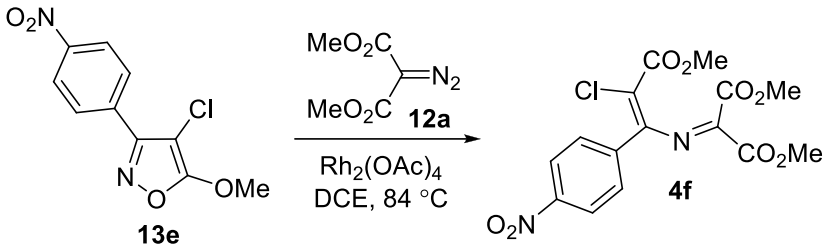
Azamuconoate **4d** (178 mg, 85%) was prepared according to the general procedure from isoxazole **13c** (144 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (126 mg, 0.8 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 3.90 (bs, 6H), 7.43–7.49 (m, 2H), 7.53–7.59 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.9, 53.4, 103.2, 124.3, 130.4, 131.5, 133.3, 149.9, 153.8, 162.9 (two signals of C=O groups are not observed). HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}{}^{79}Br^{35}ClNO_6{}^+$: 417.9688, found: 417.9691.

Dimethyl (*E*)-2-{[2-chloro-1-(4-chlorophenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4e)



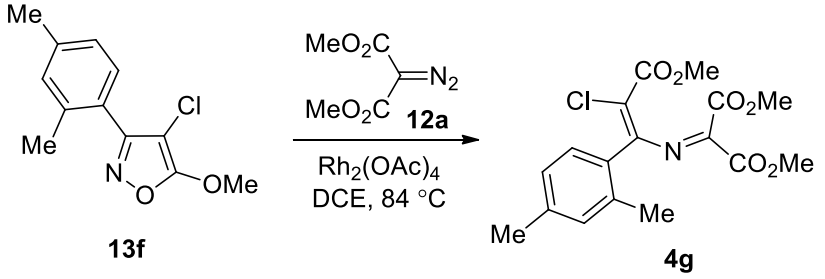
Azamuconoate **4e** (159 mg, 85%) was prepared according to the general procedure from isoxazole **13d** (122 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (126 mg, 0.8 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 3.90 (bs, 6H), 7.37–7.43 (m, 2H), 7.50–7.56 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.9, 53.4, 103.2, 128.6, 130.2, 132.8, 136.0, 149.9, 153.8, 160.1, 162.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}{}^{35}Cl_2NO_6{}^+$: 374.0193, found: 374.0193.

Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(4-nitrophenyl)-3-oxoprop-1-en-1-yl]imino}malonate (4f)



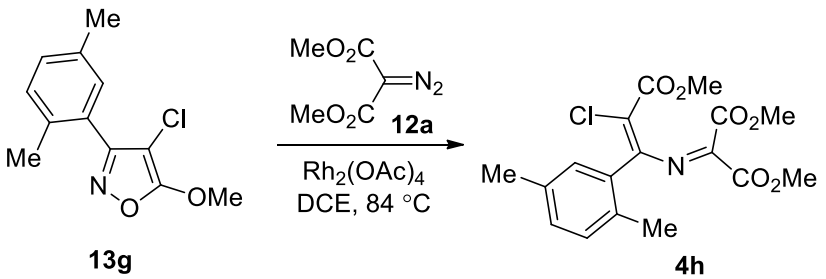
Azamuconoate **4f** (188 mg, 98%) was prepared according to the general procedure from isoxazole **13e** (127 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (111 mg, 0.7 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 3.91 (bs, 6H), 7.74–7.81 (m, 2H), 8.23–8.30 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 53.0, 53.5, 103.9, 123.5, 130.1, 140.4, 148.2, 150.7, 152.8, 158.8, 162.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}{}^{35}ClN_2O_8^+$: 385.0433, found: 385.0431.

Dimethyl (*E*)-2-{[2-chloro-1-(2,4-dimethylphenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4g)



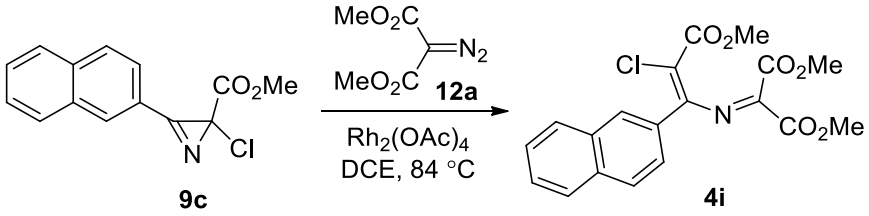
Azamuconoate **4g** (156 mg, 85%) was prepared according to the general procedure from isoxazole **13f** (119 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (111 mg, 0.7 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 2.40 (s, 3H), 3.82 (s, 3H), 3.88 (s, 6H), 7.04–7.08 (m, 1H), 7.09–7.11 (m, 1H), 7.28–7.32 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 19.5, 21.1, 52.8, 53.2, 106.7, 126.5, 128.4, 131.2, 131.3, 136.1, 139.6, 148.4, 154.4, 160.4, 162.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}{}^{35}ClNO_6^+$: 368.0895, found: 368.0899.

Dimethyl (*E*)-2-{[2-chloro-1-(2,5-dimethylphenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4h)



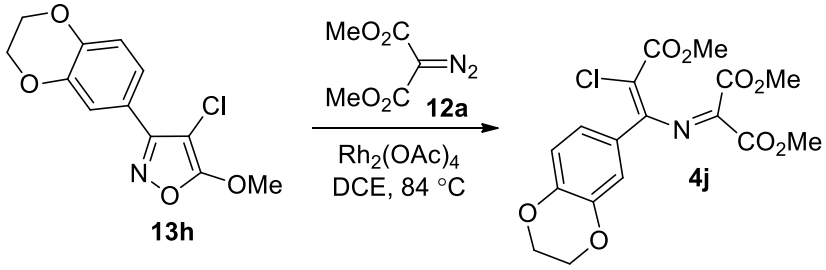
Azamuconoate **4h** (162 mg, 88%) was prepared according to the general procedure from isoxazole **13g** (119 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (111 mg, 0.7 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 2.38 (s, 3H), 3.82 (s, 3H), 3.88 (bs, 6H), 7.11–7.18 (m, 2H), 7.20–7.23 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 19.0, 20.8, 52.8, 53.2, 105.9, 128.7, 130.4 (2C), 133.1, 133.8, 135.3, 148.5, 154.3, 160.5, 162.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}{}^{35}ClNO_6^+$: 368.0895, found: 368.0895.

Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl]imino}malonate (4i)



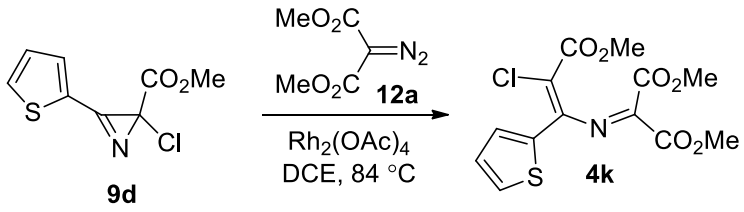
Azamuconoate **4i** (158 mg, 81%) was prepared according to the general procedure from azirine **9c** (130 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (119 mg, 0.75 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H), 3.91 (bs, 6H), 7.50–7.57 (m, 2H), 7.66–7.73 (m, 1H), 7.84–7.94 (m, 3H), 8.07–8.11 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 52.9, 53.3, 103.3, 125.7, 126.5, 127.4, 127.7, 127.8, 128.6, 128.9, 131.9, 132.6, 133.6, 149.6, 155.0, 160.2, 163.2. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}{}^{35}ClNNaO_6^+$: 412.0558, found: 412.0556.

Dimethyl (*E*)-2-{[2-chloro-1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4j)



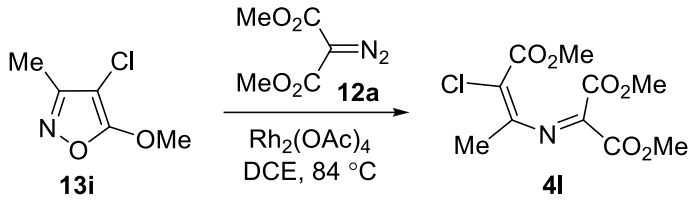
Azamuconoate **4j** (161 mg, 81%) was prepared according to the general procedure from isoxazole **13h** (134 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (111 mg, 0.7 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 3.89 (bs, 6H), 4.24–4.30 (m, 4H), 6.88 (d, *J* 8.4 Hz, 1H), 7.08 (dd, *J* 8.4, 2.1 Hz, 1H), 7.11 (d, *J* 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 52.8, 53.3, 64.2, 64.4, 102.6, 117.0, 118.1, 122.4, 127.3, 143.0, 145.0, 149.4, 154.3, 160.3, 163.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}{}^{35}ClNO_8^+$: 398.0637, found: 398.0631.

Dimethyl (*E*)-2-{[2-chloro-3-methoxy-3-oxo-1-(thiophen-2-yl)prop-1-en-1-yl]imino}malonate (4k)



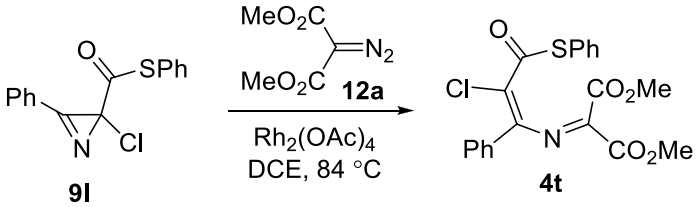
Azamuconoate **4k** (131 mg, 76%) was prepared according to the general procedure from azirine **9d** (108 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (103 mg, 0.65 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 3.89 (bs, 6H), 7.11 (dd, *J* 5.0, 3.9 Hz, 1H), 7.51 (dd, *J* 3.9, 1.2 Hz, 1H), 7.58 (dd, *J* 5.0, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 52.9, 53.4, 102.0, 126.9, 130.8, 131.9, 133.8, 147.8, 152.5, 158.7, 161.3, 163.0. HRMS (ESI) *m/z* $[M+H]^+$ calcd or $C_{13}H_{13}{}^{35}ClNO_6S^+$: 346.0147, found: 346.0146.

Dimethyl (*E*)-2-[(3-chloro-4-methoxy-4-oxobut-2-en-2-yl)imino]malonate (4l)



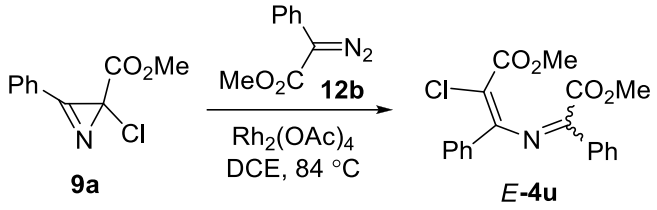
Azamuconoate **4l** (69 mg, 50%) was prepared according to the general procedure from isoxazole **13i** (74 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (111 mg, 0.7 mmol). Yellow solid, mp 69–70 °C (Et_2O–hexane). ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 3.75 (s, 3H), 3.92 (bs, 6H). ^{13}C NMR ($CDCl_3$) δ 21.2, 52.7, 53.4, 102.8, 149.0, 154.5, 160.1, 162.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{10}H_{13}{}^{35}ClNO_6{}^+$: 278.0426, found: 278.0427.

Dimethyl (*E*)-2-{[2-chloro-3-oxo-1-phenyl-3-(phenylthio)prop-1-en-1-yl]imino}malonate (4t)



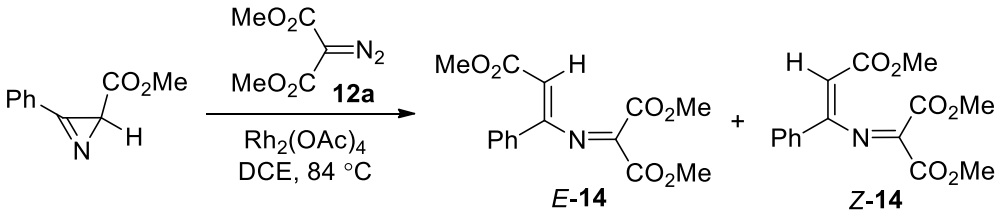
Azamuconoate **4t** (146 mg, 70%) was prepared according to the general procedure from azirine **9l** (144 mg, 0.5 mmol) and diazo compound **12a** (119 mg, 0.75 mmol). Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 7.41–7.49 (m, 8H), 7.56–7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 53.3, 108.7, 128.0, 128.3, 129.0, 129.2, 129.5, 130.1, 134.6, 134.9, 149.6, 151.7, 159.9, 186.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{17}{}^{35}ClNO_5S^+$: 418.0510, found: 418.0512.

Methyl (2*E*)-2-chloro-3-((2-methoxy-2-oxo-1-phenylethylidene)amino)-3-phenylacrylate (*E*-4u)



Azamuconoate *E*-**4u** (170 mg, 95%) was prepared according to the general procedure from azirine **9a** (105 mg, 0.5 mmol) and diazo compound **12b** (97 mg, 0.55 mmol). Yellow solid, mp 77–78 °C. ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 3.89 (s, 3H), 7.39–7.49 (m, 5H), 7.50–7.57 (m, 1H), 7.57–7.67 (m, 2H), 7.76–7.90 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.4, 52.7, 103.7, 128.1, 128.59, 128.62, 132.0, 133.2, 136.0, 156.9, 157.5, 163.0, 163.6. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}{}^{35}ClNNaO_4^+$: 380.0660, found: 380.0665.

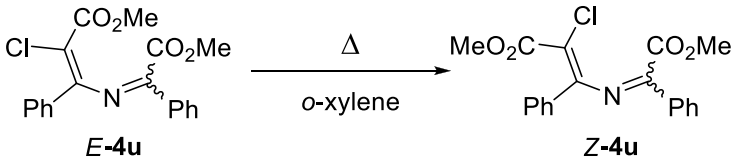
Dimethyl (*E*)-2-[(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)imino]malonate (*E*-14) and dimethyl (*Z*)-2-[(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)imino]malonate (*Z*-14)



Azamuconoates *E*-**14** (75 mg, 49%) and *Z*-**14**[10] (53 mg, 35%) were prepared according to the general procedure from methyl 3-phenyl-2*H*-azirine-2-carboxylate[3] (88 mg, 0.5 mmol) and dimethyl diazomalonate **12a** (95 mg, 0.6 mmol).

Compound *E*-**14**. Yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 3H), 3.90 (bs, 6H), 5.35 (s, 1H), 7.36–7.45 (m, 3H), 7.45–7.54 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 51.2, 52.8, 53.5, 101.9, 127.9, 128.5, 129.8, 132.6, 149.1, 160.8, 161.6, 165.3. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{15}NNaO_6^+$: 328.0792, found: 328.0795.

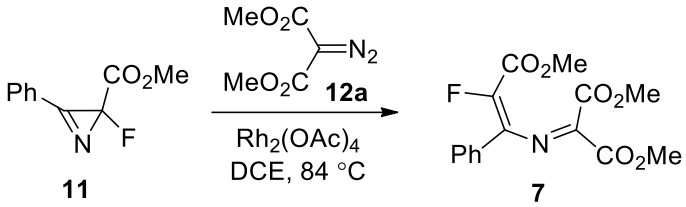
Methyl (2*Z*)-2-chloro-3-[(2-methoxy-2-oxo-1-phenylethylidene)amino]-3-phenylacrylate (*Z*-4u)



A stirred solution of methyl (2*E*)-2-chloro-3-[(2-methoxy-2-oxo-1-phenylethylidene)amino]-3-phenylacrylate *E*-**4u** (179 mg, 0.5 mmol) in *o*-xylene (10 mL) was heated under reflux for 24 h. The

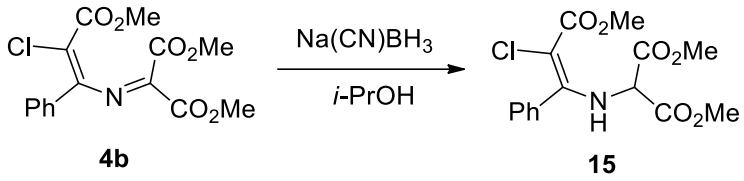
solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using mixture of Et_2O–$CHCl_3$–hexane (1:3:5) as the eluent to give a 8:1 mixture of *Z*-**4u** and *E*-**4u** which was used without further purification. ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3H), 3.90 (s, 3H), 7.37–7.57 (m, 8H), 7.83–7.87 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.4, 52.6, 103.9, 127.9, 128.2, 128.57, 128.62, 129.3, 132.2, 133.0, 135.7, 156.5, 158.1, 162.8, 163.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}{}^{35}ClNNaO_4^+$: 380.0660, found: 380.0663.

6. Synthesis of 5-Fluoro-3-azamuconoate 7



$Rh_2(OAc)_4$ (2 mol% on azirine) was added to a refluxing solution of azirine **11** (97 mg, 0.5 mmol) and diazo compound **12a** (111 mg, 0.7 mmol) in anhydrous DCE (1.5 mL) under an argon atmosphere. The stirred mixture was heated under reflux until nitrogen evolution had stopped. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using a hexane/EtOAc mixture as the eluent to give dimethyl (*E*)-2-[(2-fluoro-1-phenyl-3-methoxy-3-oxoprop-1-en-1-yl)imino]malonate **7** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.75 (bs, 3H), 3.82 (s, 3H), 3.97 (bs, 3H), 7.38–7.43 (m, 3H), 7.52–7.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 52.2, 52.8, 53.5, 128.40, 128.40 (d, *J* 5.5 Hz), 130.1, 131.08 (d, *J* 2.9 Hz), 131.6 (d, *J* 253.9 Hz), 141.5 (d, *J* 24.9 Hz), 152.8 (d, *J* 4.3 Hz), 159.1, 161.04 (d, *J* 31.1 Hz), 161.4. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{14}FNNaO_6^+$: 346.0697, found: 346.0699.

7. Synthesis of Chloroenamine 15



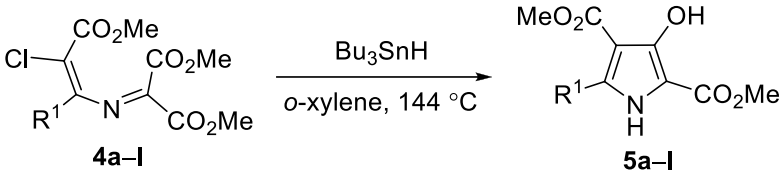
4b **15**

A solution of azamuconoate **4b** (170 mg, 0.5 mmol) and $Na(CN)BH_3$ (94 mg, 1.5 mmol) in isopropyl alcohol (10 mL) was stirred at room temperature for 30 min. The reaction mixture was diluted with water (10 mL) and extracted with DCM (2x10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash-chromatography on silica gel using a hexane/EtOAc mixture (4:1) as the eluent to give dimethyl (*E*)-2-[(2-chloro-3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)amino]malonate **15** as a white solid (68 mg, 40%), mp 83–84 °C (Et_2O/hexane). ^1H NMR ($CDCl_3$) δ 3.75 (s, 6H), 3.88 (s, 3H), 4.40 (d, *J* 9.2 Hz, 1H), 7.18–7.26 (m, 2H), 7.43–7.51 (m, 3H), 9.63 (d, *J* 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 52.2, 53.3, 61.0, 93.5, 128.0, 128.9, 129.7, 133.2, 158.7, 166.7, 167.5. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{16}{}^{35}ClNNaO_6{}^+$: 364.0558, found: 364.0560.

8. Synthesis of 3-Hydroxypyrroles 5

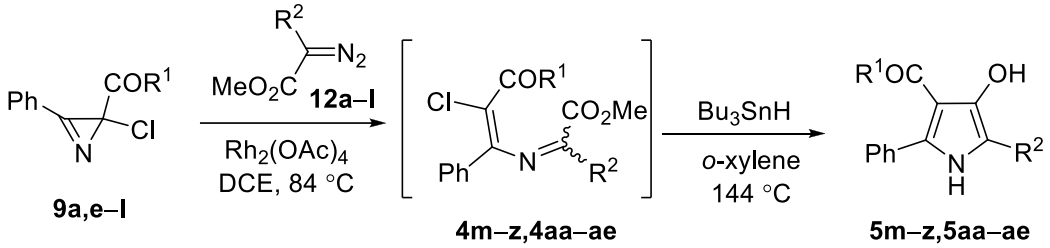
General Procedures

Method A



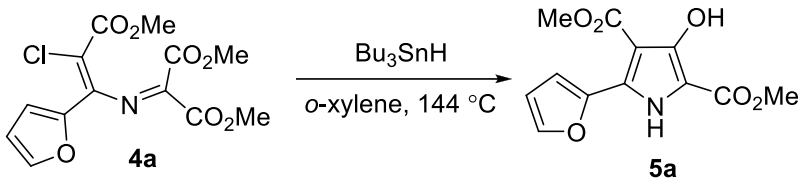
A stirred solution of 3-azamuconoate **4a**–**l** (0.5 mmol) and Bu_3SnH (1 mmol) in anhydrous *o*-xylene (5 mL) was heated under reflux for 10 min under an argon atmosphere. The reaction mixture was treated with saturated NaF solution (15 mL) and the aqueous layer was extracted with DCM (2×5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. The filtrate was concentrated in vacuum and obtained pyrrole **5a**–**l** was recrystallized from EtOAc.

Method B



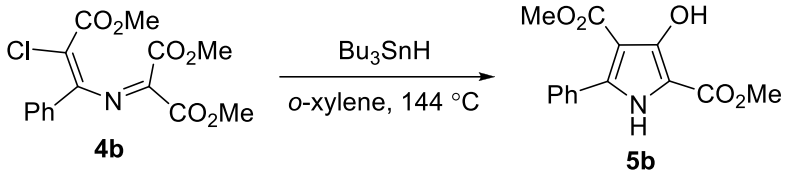
$Rh_2(OAc)_4$ (2 mol% on azirine) was added to a refluxing solution of azirine **9a,e**–**l** (0.5 mmol) and diazo compound **12a**–**l** (in amount indicated below) in anhydrous DCE (1.5 mL) under an argon atmosphere. The stirred mixture was heated under reflux until nitrogen evolution had stopped. The solvent was evaporated under reduced pressure, and the residue was filtrated through a pad of silica gel using a hexane/EtOAc mixture (1:1) as the eluent. The filtrate was concentrated in vacuum. The residue was dissolved in anhydrous *o*-xylene (5 mL) and Bu_3SnH was added in an amount specified below. The stirred solution was heated under reflux for the time indicated below. The reaction mixture was treated with saturated NaF solution (15 mL) and the aqueous layer was extracted with DCM (2×5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$ (for pyrroles **5ad,ae**) or EtOAc/hexane mixture (for pyrroles **5m–z,aa–ac**) as the eluent. The filtrate was concentrated in vacuum and the residue was recrystallized from EtOAc (for pyrroles **5ad,ae**) or Et_2O/hexane mixture (for pyrroles **5m–z,aa–ac**).

Dimethyl 5-(furan-2-yl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5a)



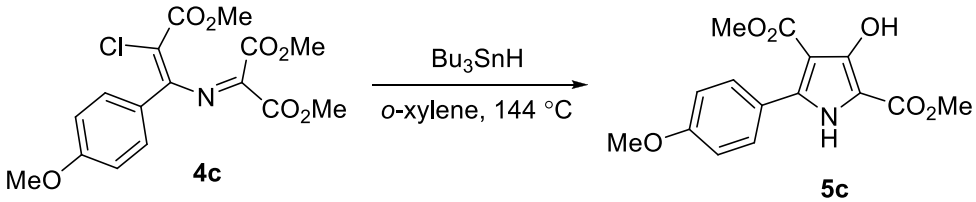
Pyrrole **5a** (77 mg, 58%) was prepared according to method A from azamuconoate **4a** (165 mg, 0.5 mmol). White solid, mp 123–124 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.95 (s, 3H), 4.00 (s, 3H), 6.56 (dd, *J* 3.6, 1.8 Hz, 1H), 7.31 (d, *J* 3.6 Hz, 1H), 7.52 (d, *J* 1.8 Hz, 1H), 9.06 (bs, 1H), 9.22 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.6, 51.7, 98.7, 105.5, 112.4, 112.9, 126.9, 143.1, 144.4, 152.7, 161.0, 166.3. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{12}NO_6^+$: 266.0659, found: 266.0671.

Dimethyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5b)



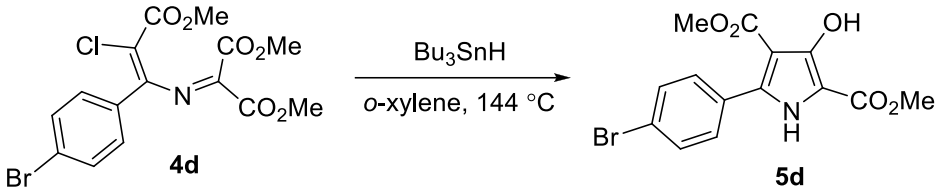
Pyrrole **5b** (105 mg, 76%) was prepared according to method A from azamuconoate **4b** (170 mg, 0.5 mmol). White solid, mp 199–200 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 3.79 (s, 3H), 7.41–7.49 (m, 3H), 7.52–7.60 (m, 2H), 9.36 (s, 1H), 9.43 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 51.3, 51.7, 100.4, 106.2, 128.2, 129.2, 129.4, 130.8, 138.0, 153.0, 161.6, 167.3. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{14}NO_5^+$: 276.0866, found: 276.0866.

Dimethyl 3-hydroxy-5-(4-methoxyphenyl)-1*H*-pyrrole-2,4-dicarboxylate (5c)



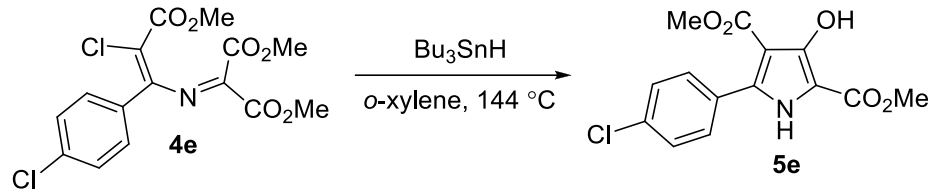
Pyrrole **5c** (111 mg, 73%) was prepared according to method A from azamuconoate **4c** (185 mg, 0.5 mmol). White solid, mp 180–181 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 6.92–6.99 (m, 2H), 7.45–7.53 (m, 2H), 9.31 (bs, 1H), 9.37 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.3, 51.6, 55.3, 100.0, 105.8, 113.6, 123.1, 130.5, 138.1, 153.1, 160.5, 161.6, 167.4. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{16}NO_6^+$: 306.0972, found: 306.0976.

Dimethyl 5-(4-bromophenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5d)



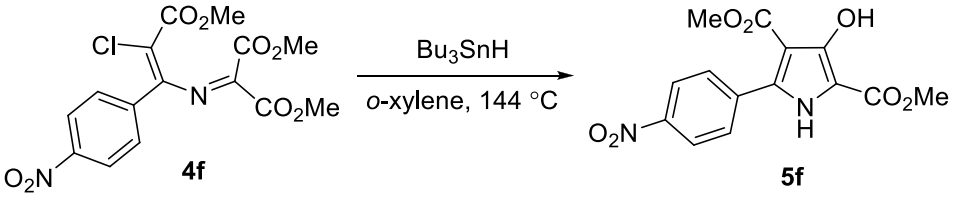
Pyrrole **5d** (127 mg, 72%) was prepared according to method A from azamuconoate **4d** (209 mg, 0.5 mmol). White solid, mp 198–200 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 6H), 7.40–7.46 (m, 2H), 7.56–7.61 (m, 2H), 9.29 (s, 1H), 9.53 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 51.4, 51.8, 100.6, 106.5, 123.9, 129.6, 130.8, 131.4, 136.7, 152.9, 161.6, 167.0. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{12}{}^{79}BrNNaO_5^+$: 375.9791, found: 375.9792.

Dimethyl 5-(4-chlorophenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5e)



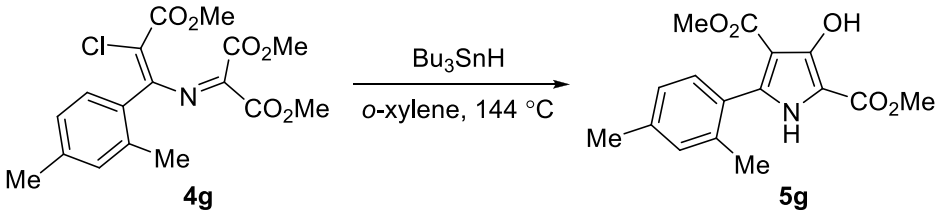
Pyrrole **5e** (116 mg, 75%) was prepared according to method A from azamuconoate **4e** (187 mg, 0.5 mmol). White solid, mp 215–217 °C (EtOAc). ^{1}H NMR (DMSO-d_6) δ 3.65 (s, 3H), 3.77 (s, 3H), 7.42–7.50 (m, 2H), 7.50–7.58 (m, 2H), 8.98 (s, 1H), 12.08 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 50.8, 50.9, 100.8, 106.3, 127.6, 129.3, 131.5, 133.5, 136.7, 151.9, 160.5, 165.0. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{12}{}^{35}ClNNaO_5^+$: 332.0296, found: 332.0294.

Dimethyl 3-hydroxy-5-(4-nitrophenyl)-1*H*-pyrrole-2,4-dicarboxylate (5f)



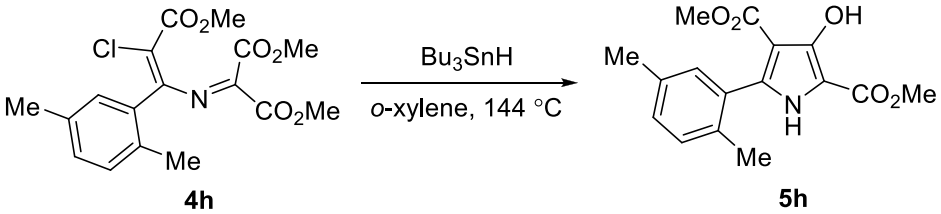
Pyrrole **5f** (138 mg, 86%) was prepared according to method A from azamuconoate **4f** (192 mg, 0.5 mmol). White solid, mp 250–252 °C (EtOAc). ^{1}H NMR (DMSO-d_6) δ 3.66 (s, 3H), 3.79 (s, 3H), 7.73–7.86 (m, 2H), 8.18–8.31 (m, 2H), 9.01 (bs, 1H), 12.35 (bs, 1H). ^{13}C NMR (DMSO-d_6) δ 50.96, 51.02, 101.8, 107.4, 122.6, 131.0, 135.2, 136.9, 147.2, 151.7, 160.5, 164.6. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{12}N_2NaO_7^+$: 343.0537, found: 343.0541.

Dimethyl 5-(2,4-dimethylphenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5g)



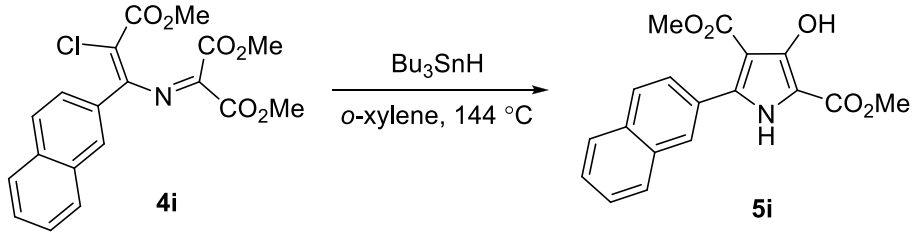
Pyrrole **5g** (91 mg, 60%) was prepared according to method A from azamuconoate **4g** (184 mg, 0.5 mmol). White solid, mp 190–191 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3H), 2.39 (s, 3H), 3.71 (s, 3H), 3.89 (s, 3H), 7.04–7.09 (m, 1H), 7.10–7.12 (m, 1H), 7.13–7.17 (m, 1H), 8.64 (bs, 1H), 9.08 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 19.6, 21.2, 51.3, 51.5, 101.8, 105.6, 126.1, 128.0, 129.8, 130.7, 137.2, 137.8, 139.3, 152.2, 161.6, 167.1. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{18}NO_5^+$: 304.1179, found: 304.1171.

Dimethyl 5-(2,5-dimethylphenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5h)



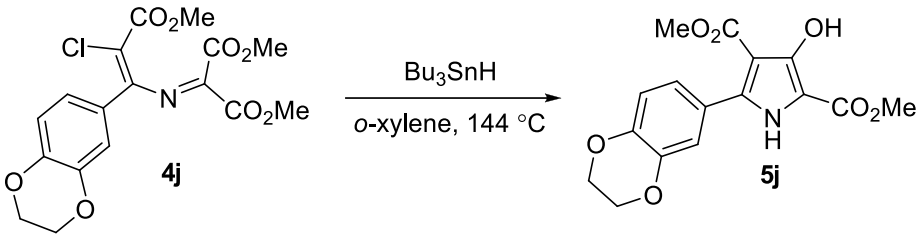
Pyrrole **5h** (62 mg, 41%) was prepared according to method A from azamuconoate **4h** (184 mg, 0.5 mmol). White solid, mp 180–181 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H), 2.34 (s, 3H), 3.67 (s, 3H), 3.68 (s, 3H), 7.02–7.09 (m, 1H), 7.11–7.19 (m, 2H), 9.13 (s, 1H), 9.60 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 19.2, 20.7, 51.3, 51.5, 101.7, 105.6, 129.8, 130.0, 130.3, 130.7, 134.3, 134.7, 138.0, 152.2, 161.7, 167.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{18}NO_5^+$: 304.1179, found: 304.1171.

Dimethyl 3-hydroxy-5-(naphthalen-2-yl)-1*H*-pyrrole-2,4-dicarboxylate (5i)



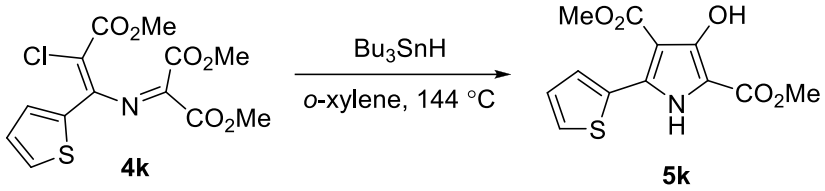
Pyrrole **5i** (91 mg, 56%) was prepared according to method A from azamuconoate **4i** (195 mg, 0.5 mmol). White solid, mp 224–226 °C (EtOAc). ^{1}H NMR (DMSO-d_6) δ 3.65 (s, 3H), 3.80 (s, 3H), 7.51–7.60 (m, 2H), 7.61–7.69 (m, 1H), 7.87–8.02 (m, 3H), 8.05–8.14 (m, 1H), 9.05 (s, 1H), 12.15 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 50.8, 50.9, 100.8, 106.2, 126.3, 126.6, 126.7, 127.45, 127.47, 128.1, 128.2, 128.9, 132.2, 132.8, 138.1, 152.1, 160.5, 165.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_5^+$: 326.1023, found: 326.1023.

Dimethyl 5-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5j)



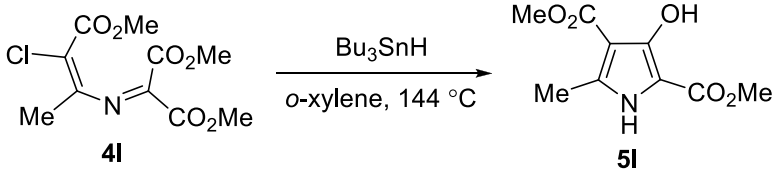
Pyrrole **5j** (120 mg, 72%) was prepared according to method A from azamuconoate **4j** (199 mg, 0.5 mmol). White solid, mp 234–235 °C (EtOAc). ^{1}H NMR (DMSO-d_6) δ 3.66 (s, 3H), 3.76 (s, 3H), 4.21–4.34 (m, 4H), 6.87 (d, *J* 8.4 Hz, 1H), 7.00 (dd, *J* 8.4, 2.1 Hz, 1H), 7.04 (d, *J* 2.1 Hz, 1H), 8.98 (s, 1H), 11.84 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 50.7, 50.9, 64.0, 64.2, 100.2, 105.5, 116.2, 118.4, 123.0, 123.5, 137.8, 142.4, 144.1, 152.1, 160.5, 165.3. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{15}NNaO_7^+$: 356.0741, found: 356.0725.

Dimethyl 3-hydroxy-5-(thiophen-2-yl)-1*H*-pyrrole-2,4-dicarboxylate (5k)



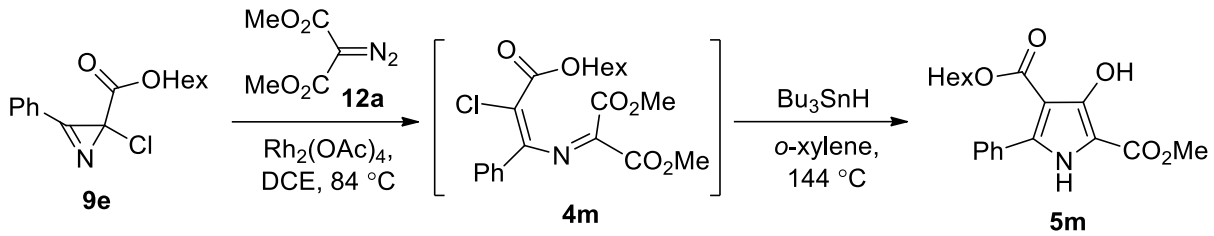
Pyrrole **5k** (98 mg, 70%) was prepared according to method A from azamuconoate **4k** (173 mg, 0.5 mmol). White solid, mp 156–157 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H), 3.89 (s, 3H), 7.12 (dd, *J* 5.2, 3.6 Hz, 1H), 7.46 (dd, *J* 5.2, 1.2 Hz, 1H), 7.50 (dd, *J* 3.6, 1.2 Hz, 1H), 9.18 (bs, 1H), 9.34 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.3, 51.8, 100.5, 106.2, 127.3, 127.9, 129.0, 130.7, 131.5, 152.8, 161.3, 166.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{12}NO_5S^+$: 282.0431, found: 282.0435.

Dimethyl 3-hydroxy-5-methyl-1*H*-pyrrole-2,4-dicarboxylate (5l)



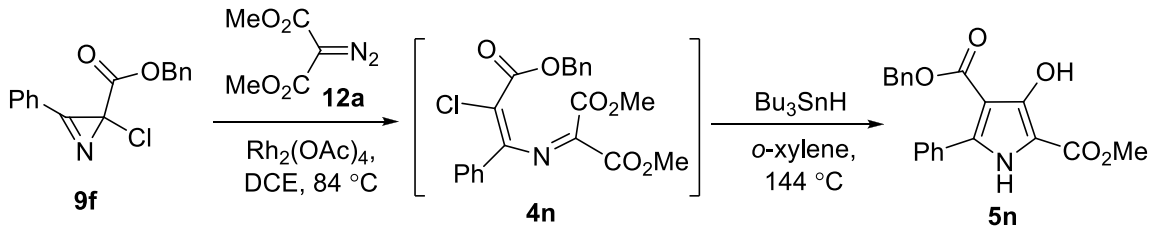
Pyrrole **5l** (40 mg, 38%) was prepared according to method A from azamuconoate **4l** (139 mg, 0.5 mmol). White solid, mp 250–252 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 8.96 (s, 1H), 9.71 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 51.3, 51.6, 101.0, 104.2, 137.1, 152.7, 161.9, 167.5. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_9H_{12}NO_5^+$: 214.0710, found: 214.0706.

4-Hexyl 2-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5m)



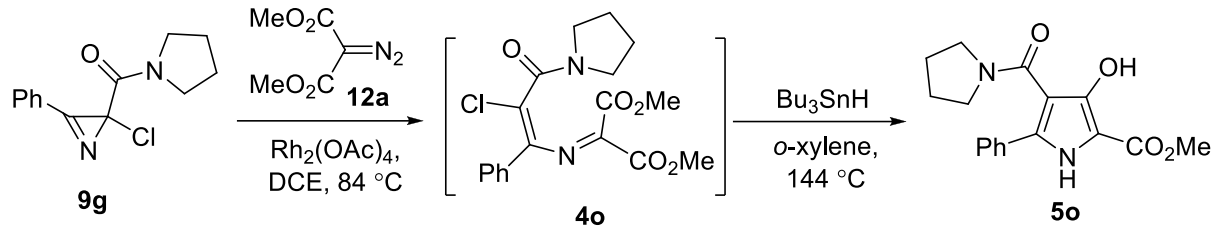
Pyrrole **5m** (122 mg, 71%) was prepared according to method B from azirine **9e** (140 mg, 0.5 mmol), diazo compound **12a** (95 mg, 0.6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 8 min. White solid, mp 144–145 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* 6.9 Hz, 3H), 1.09–1.29 (m, 6H), 1.48–1.60 (m, 2H), 3.80 (s, 3H), 4.20 (t, *J* 6.5 Hz, 2H), 7.38–7.48 (m, 3H), 7.50–7.61 (m, 2H), 9.38 (bs, 1H), 9.45 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.4, 25.6, 28.3, 31.3, 51.7, 64.7, 100.7, 106.1, 128.0, 129.3 (2C), 130.9, 138.0, 153.0, 161.6, 167.2. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{23}NNaO_5^+$: 368.1468, found: 368.1456.

4-Benzyl 2-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5n)



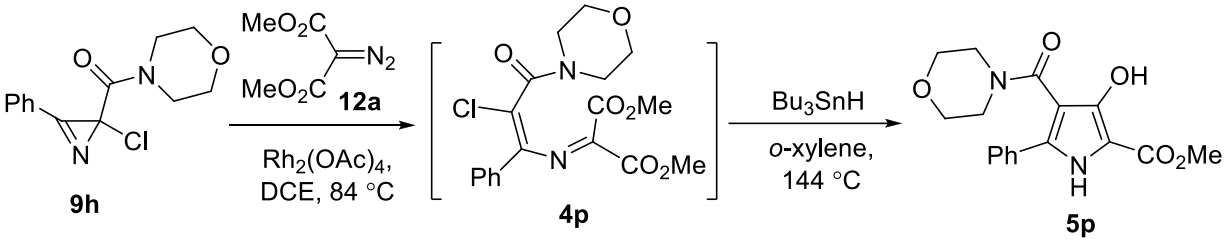
Pyrrole **5n** (98 mg, 56%) was prepared according to method B from azirine **9f** (143 mg, 0.5 mmol), diazo compound **12a** (95 mg, 0.6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 167–168 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 5.25 (s, 2H), 7.10–7.21 (m, 2H), 7.25–7.38 (m, 5H), 7.38–7.44 (m, 1H), 7.48–7.54 (m, 2H), 9.29 (s, 1H), 9.41 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 51.7, 66.1, 100.6, 106.1, 128.07, 128.08, 128.2, 128.4, 129.29, 129.33, 130.7, 135.1, 138.2, 152.9, 161.6, 166.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{18}NO_5^+$: 352.1179, found: 352.1168.

Methyl 3-hydroxy-5-phenyl-4-(pyrrolidine-1-carbonyl)-1*H*-pyrrole-2-carboxylate (5o)



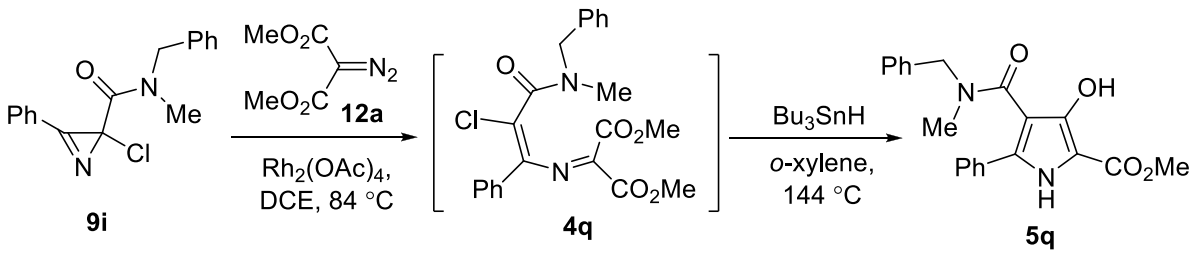
Pyrrole **5o** (111 mg, 71%) was prepared according to method B from azirine **9g** (124 mg, 0.5 mmol), diazo compound **12a** (103 mg, 0.65 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 231–233 °C (EtOAc). ^{1}H NMR (DMSO-d_6) δ 1.75 (bs, 4H), 3.02–3.55 (m, 4H), 3.78 (s, 3H), 7.24–7.46 (m, 3H), 7.47–7.66 (m, 2H), 8.69 (s, 1H), 11.49 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 24.1, 25.1, 50.6, 106.1, 109.1, 126.9, 128.0, 128.4, 130.9, 132.3, 148.3, 161.0, 163.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_4^+$: 315.1339, found: 315.1331.

Methyl 3-hydroxy-4-(morpholine-4-carbonyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (5p)



Pyrrole **5p** (66 mg, 40%) was prepared according to method B from azirine **9h** (132 mg, 0.5 mmol), diazo compound **12a** (119 mg, 0.75 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 200–201 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 8H), 3.87 (s, 3H), 7.34–7.44 (m, 3H), 7.45–7.55 (m, 2H), 7.80 (s, 1H), 9.05 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 45.1, 51.4, 66.6, 105.1, 105.6, 127.1, 129.0, 129.1, 130.6, 134.4, 150.9, 161.9, 164.5. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_5^+$: 331.1288, found: 331.1290.

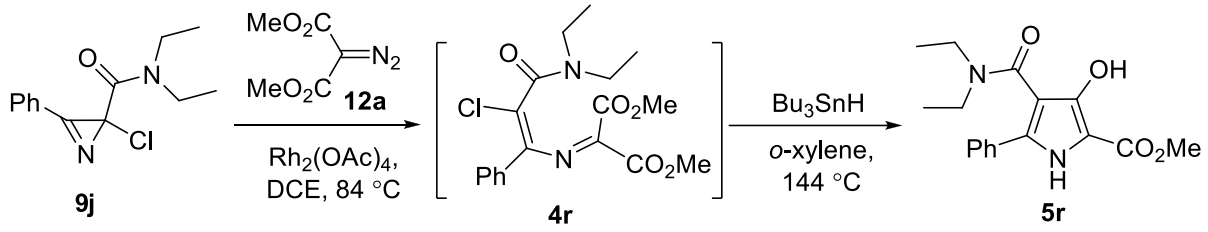
Methyl 4-[benzyl(methyl)carbamoyl]-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5q)



Pyrrole **5q** (76 mg, 42%) was prepared according to method B from azirine **9i** (149 mg, 0.5 mmol), diazo compound **12a** (87 mg, 0.55 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 202–203 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 2.81 (s, 3H), 3.89 (s, 3H), 4.60 (s, 2H), 7.17–7.33 (m, 5H), 7.33–7.42 (m, 3H), 7.46–7.54 (m, 2H), 7.86 (bs, 1H), 8.79 (bs,

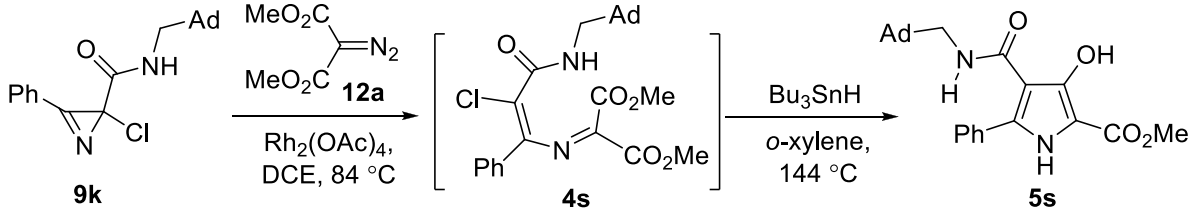
1H). ^{13}C NMR ($CDCl_3$) δ 34.8, 51.4, 52.4, 105.6, 106.3, 126.9, 127.5, 128.0, 128.6, 129.0 (2C), 130.8, 133.9, 136.7, 151.0, 162.0, 166.1. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{21}H_{20}KN_2O_4^+$: 403.1055, found: 403.1055.

Methyl 4-(diethylcarbamoyl)-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5r)



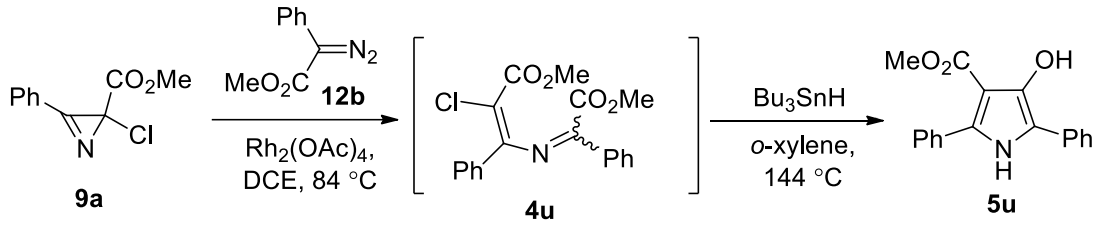
Pyrrole **5r** (46 mg, 36%) was prepared according to method B from azirine **9j** (125 mg, 0.5 mmol), diazo compound **12a** (119 mg, 0.75 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 157–158 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.07 (t, *J* 7.1 Hz, 6H), 3.20–3.52 (m, 4H), 3.86 (s, 3H), 7.30–7.38 (m, 3H), 7.46–7.55 (m, 2H), 7.62 (bs, 1H), 8.98 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 13.2, 41.1, 51.3, 105.4, 107.0, 126.6, 128.7, 128.8, 130.6, 133.1, 150.6, 162.1, 165.1. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{17}H_{20}N_2NaO_4^+$: 339.1315, found: 339.1308.

Methyl 4-[(adamantan-1-ylmethyl)carbamoyl]-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5s)



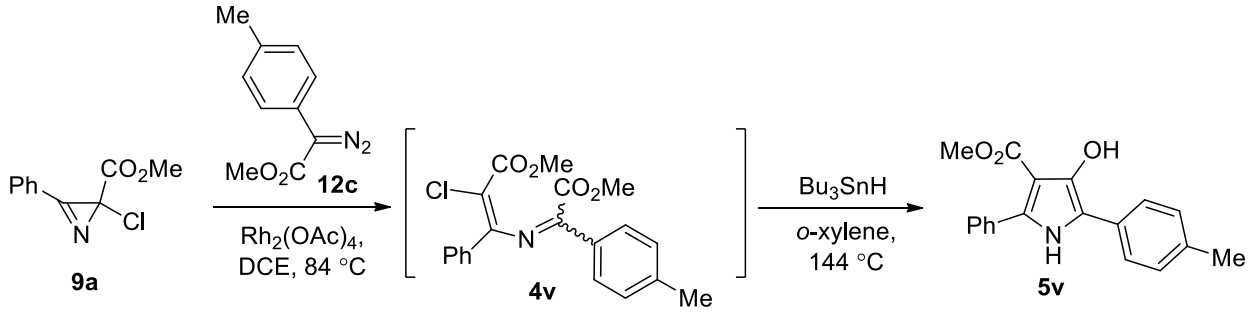
Pyrrole **5s** (127 mg, 62%) was prepared according to method B from azirine **9k** (164 mg, 0.5 mmol), diazo compound **12a** (142 mg, 0.9 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 230–231 °C (EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.22–1.35 (m, 6H), 1.48–1.74 (m, 6H), 1.85–1.97 (m, 3H), 2.87–3.04 (m, 2H), 3.70 (s, 3H), 5.59–5.77 (m, 1H), 7.46–7.66 (m, 5H), 9.56 (bs, 1H), 10.80 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 28.1, 33.1, 36.7, 40.0, 50.4, 51.5, 103.1, 105.8, 129.3, 129.5, 130.0, 131.0, 134.7, 153.1, 162.0, 166.7. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{24}H_{28}N_2NaO_4^+$: 431.1941, found: 431.1941.

Methyl 4-hydroxy-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (5u)



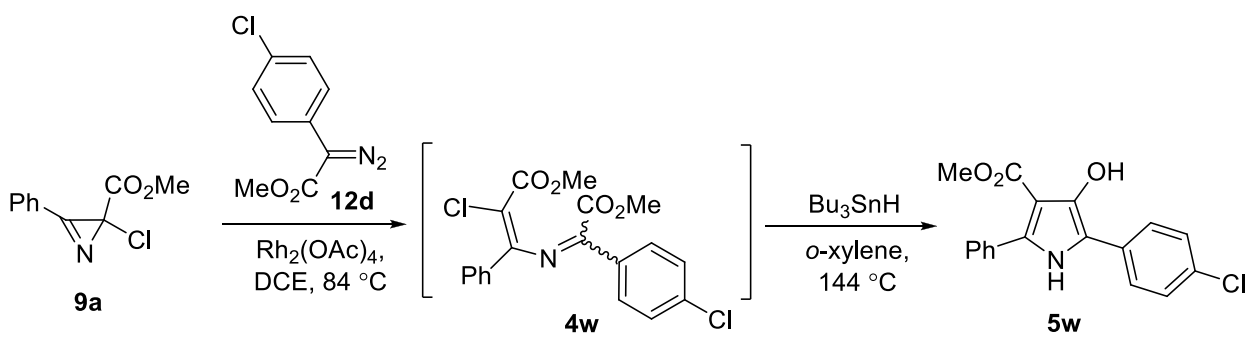
Pyrrole **5u** (125 mg, 85%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12b** (106 mg, 0.6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 2 h. White solid, mp 182–183 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H), 7.16–7.24 (m, 1H), 7.38–7.50 (m, 5H), 7.54–7.61 (m, 2H), 7.65–7.72 (m, 2H), 8.16 (bs, 1H), 8.70 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.1, 100.9, 113.2, 123.3, 125.4, 128.3, 128.5, 128.79, 128.82, 130.8, 131.9, 133.0, 145.2, 167.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{15}NNaO_3^+$: 316.0944, found: 316.0944.

Methyl 4-hydroxy-5-(4-methylphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5v)



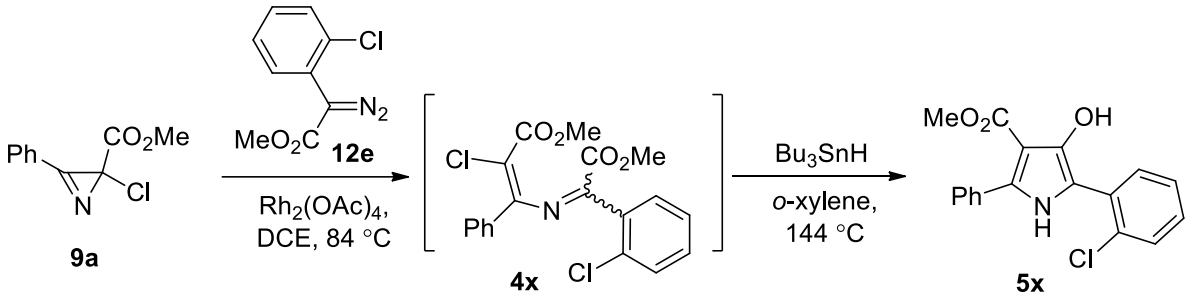
Pyrrole **5v** (140 mg, 91%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12c** (143 mg, 0.75 mmol) and Bu_3SnH (1.16 g, 4 mmol) under reflux in *o*-xylene for 2.5 h. Colorless oil. ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 3.80 (s, 3H), 7.19–7.26 (m, 2H), 7.38–7.49 (m, 3H), 7.53–7.62 (m, 4H), 8.18 (bs, 1H), 8.62 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 21.1, 51.0, 100.8, 113.4, 123.3, 128.1, 128.2, 128.4, 128.8, 129.5, 132.0, 132.6, 135.1, 144.6, 167.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_3^+$: 330.1101, found: 330.1099.

Methyl 5-(4-chlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5w)



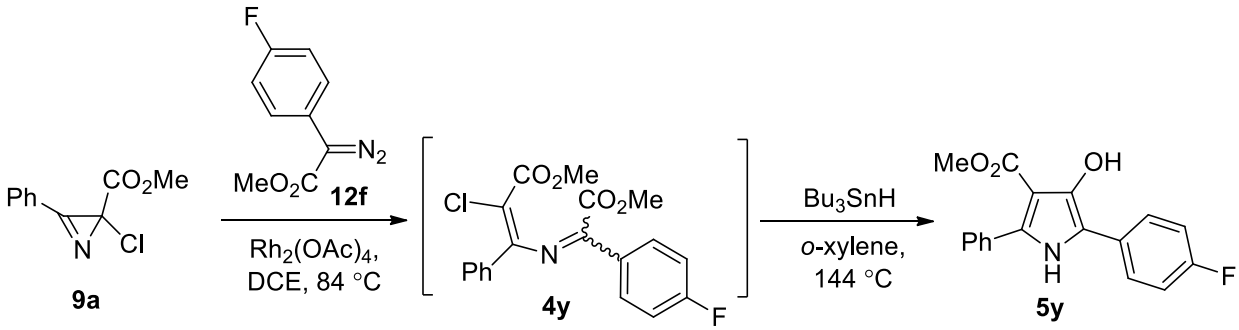
Pyrrole **5w** (147 mg, 90%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12d** (126 mg, 0.6 mmol) and Bu_3SnH (728 mg, 2.5 mmol) under reflux in *o*-xylene for 2 h. White solid, mp 160–161 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.79 (s, 3H), 7.32–7.39 (m, 2H), 7.40–7.50 (m, 3H), 7.53–7.64 (m, 4H), 8.09 (bs, 1H), 8.73 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.2, 101.0, 112.3, 124.4, 128.3, 128.7, 128.8, 128.9, 129.3, 130.7, 131.7, 133.5, 145.5, 167.7. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{14}{}^{35}ClNNaO_3{}^+$: 350.0554, found: 350.0551.

Methyl 5-(2-chlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5x)



Pyrrole **5x** (82 mg, 50%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12e** (126 mg, 0.6 mmol) and Bu_3SnH (1.16 g, 4 mmol) under reflux in *o*-xylene for 2.5 h. White solid, mp 118–119 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 7.17 (td, *J* 7.7, 1.7 Hz, 1H), 7.36 (td, *J* 7.7, 1.4 Hz, 1H), 7.39–7.52 (m, 4H), 7.56–7.65 (m, 2H), 8.09 (dd, *J* 7.9, 1.7 Hz, 1H), 8.89 (s, 1H), 9.02 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 51.1, 99.6, 110.7, 127.0, 127.26, 127.32, 128.56, 128.59, 128.70, 128.73, 128.8, 130.5, 131.9, 132.5, 146.7, 168.0. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{14}{}^{35}ClNNaO_3{}^+$: 350.0554, found: 350.0551.

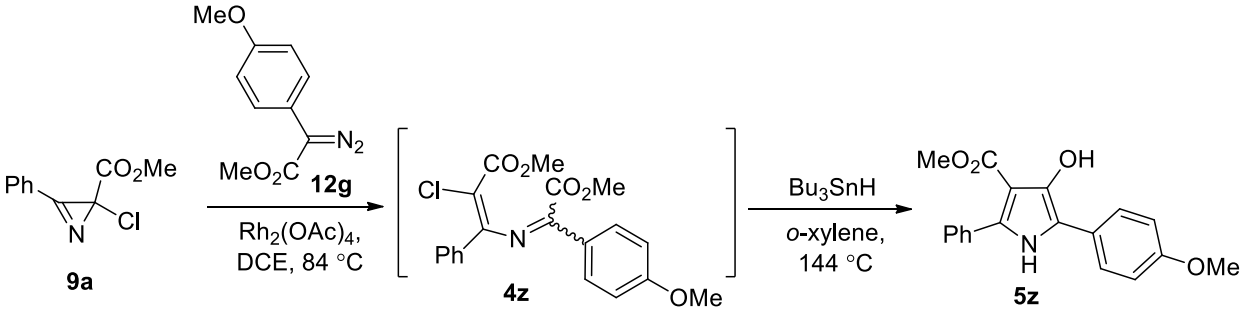
Methyl 5-(4-fluorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5y)



Pyrrole **5y** (92 mg, 59%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12f** (126 mg, 0.65 mmol) and Bu_3SnH (1.16 g, 4 mmol) under reflux in *o*-xylene for 1 h. White solid, mp 167–168 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H), 7.06–7.16 (m, 2H), 7.40–7.49 (m, 3H), 7.53–7.59 (m, 2H), 7.60–7.67 (m, 2H), 8.09 (bs, 1H), 8.64 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.1, 100.9, 112.5, 115.8 (d, *J* 21.4 Hz), 125.0 (d, *J* 7.5 Hz), 127.2 (d, *J* 3.0 Hz),

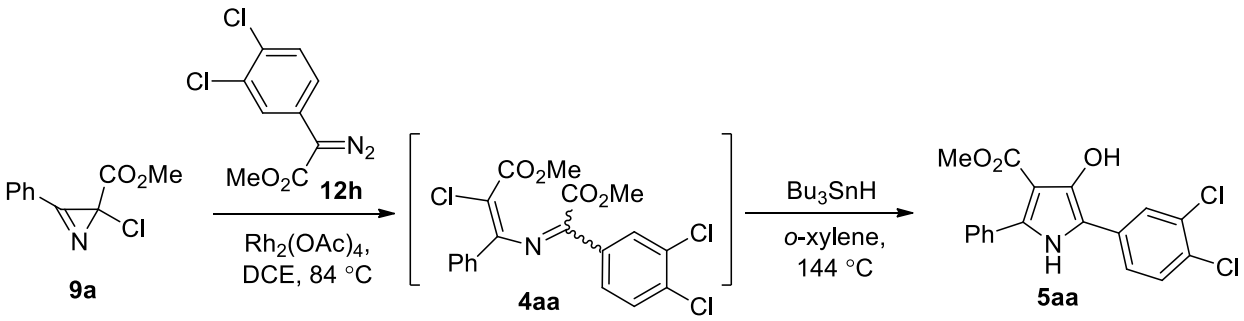
128.3, 128.6, 128.8, 131.9, 133.0, 144.7, 160.7 (d, *J* 245.5 Hz), 167.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{14}FNNaO_3^+$: 334.0850, found: 334.0850.

Methyl 4-hydroxy-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5z)



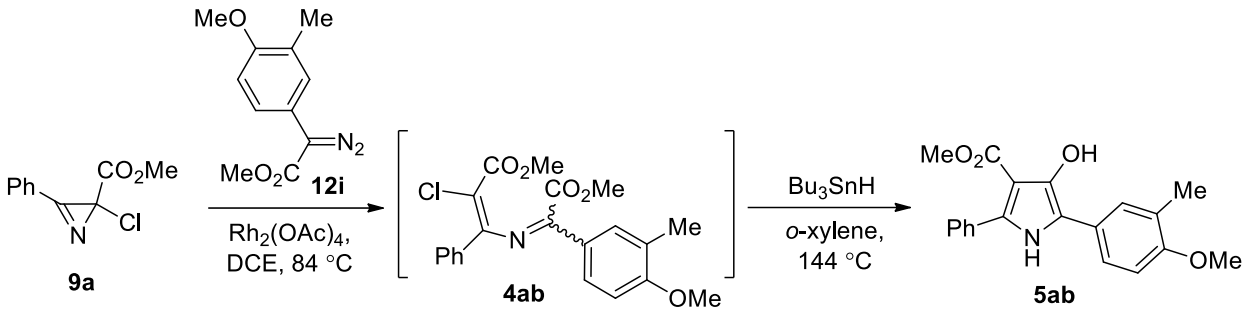
Pyrrole **5z** (144 mg, 89%) was prepared according to method *B* from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12g** (247 mg, 1.2 mmol) and Bu_3SnH (728 mg, 2.5 mmol) under reflux in *o*-xylene for 2 h. White solid, mp 149–150 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H), 3.85 (s, 3H), 6.92–7.02 (m, 2H), 7.37–7.50 (m, 3H), 7.50–7.66 (m, 4H), 8.08 (s, 1H), 8.54 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.1, 55.3, 100.8, 113.2, 114.4, 123.8, 124.8, 128.2, 128.4, 128.8, 132.1, 132.3, 143.9, 157.6, 167.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_4^+$: 346.1050, found: 346.1050.

Methyl 5-(3,4-dichlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5aa)



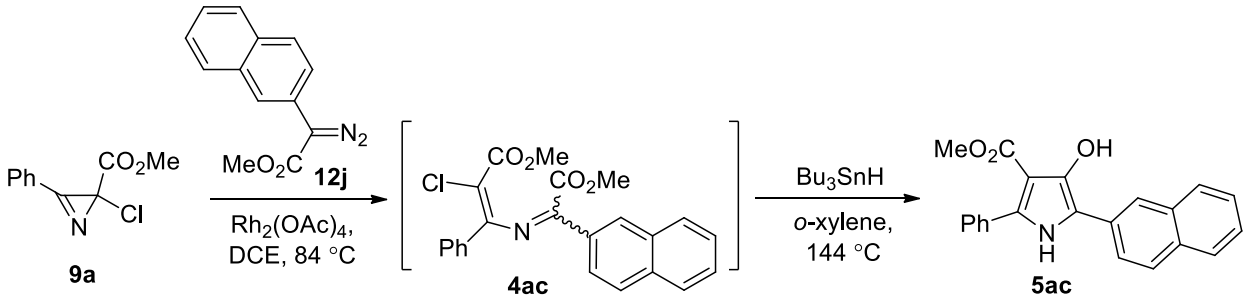
Pyrrole **5aa** (168 mg, 93%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12h** (147 mg, 0.6 mmol) and Bu_3SnH (582 mg, 2 mmol) under reflux in *o*-xylene for 3 h. White solid, mp 154–155 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H), 7.40–7.52 (m, 5H), 7.53–7.60 (m, 2H), 7.71–7.76 (m, 1H), 8.04 (bs, 1H), 8.81 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.3, 101.1, 111.2, 122.3, 124.6, 128.4, 128.5, 128.8, 128.9, 130.7, 130.8, 131.5, 132.9, 134.1, 146.3, 167.6. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{13}{}^{35}Cl_2NNaO_3^+$: 384.0165, found: 384.0160.

Methyl 4-hydroxy-5-(4-methoxy-3-methylphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ab)



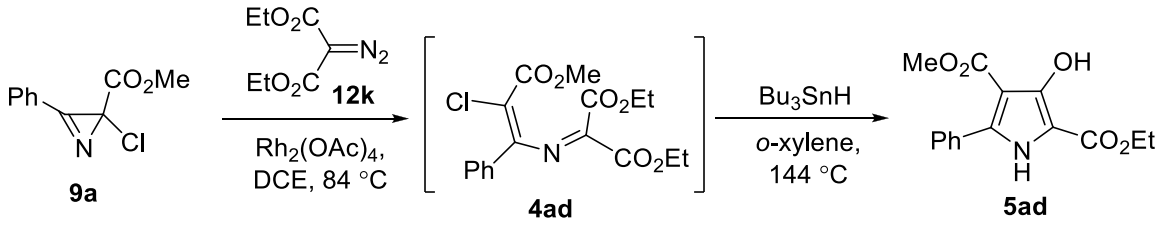
Pyrrole **5ab** (155 mg, 92%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12i** (256 mg, 1.25 mmol) and Bu_3SnH (582 mg, 2 mmol) under reflux in *o*-xylene for 2 h. White solid, mp 138–139 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 6.85–6.93 (m, 1H), 7.32–7.52 (m, 5H), 7.53–7.68 (m, 2H), 8.05 (s, 1H), 8.53 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 16.2, 50.7, 55.2, 100.4, 110.3, 113.7, 122.8, 123.8, 125.2, 126.3, 127.6, 127.7, 129.5, 131.7, 132.4, 142.6, 154.9, 166.5. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{20}H_{19}NNaO_4^+$: 360.1206, found: 360.1206.

Methyl 4-hydroxy-5-(naphthalen-2-yl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ac)



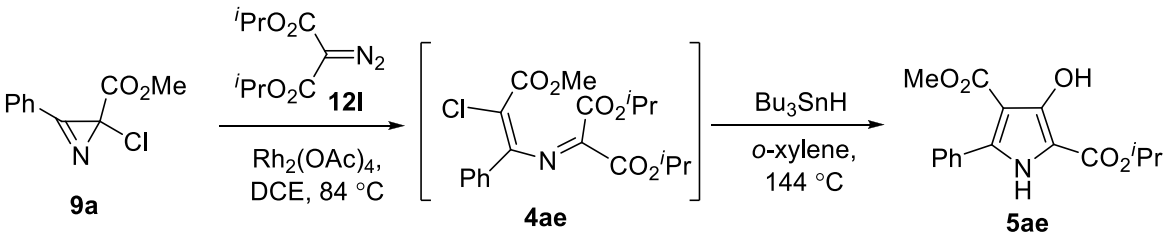
Pyrrole **5ac** (161 mg, 94%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12j** (131 mg, 0.6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 2 h. White solid, mp 151–152 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 7.38–7.54 (m, 5H), 7.57–7.66 (m, 2H), 7.78–7.90 (m, 3H), 7.91–7.97 (m, 1H), 7.98–8.04 (m, 1H), 8.25 (bs, 1H), 8.82 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 51.1, 101.1, 113.4, 120.6, 122.5, 125.2, 126.4, 127.6, 127.7, 128.3, 128.4, 128.5, 128.6, 128.8, 131.5, 131.9, 133.4, 133.8, 145.7, 167.8. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{22}H_{17}NNaO_3^+$: 366.1101, found: 366.1105.

2-Ethyl 4-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5ad)



Pyrrole **5ad** (108 mg, 75%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12k** (126 mg, 0.6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 141–142 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 1.32 (t, *J* 7.1 Hz, 3H), 3.78 (s, 3H), 4.22 (q, *J* 7.1 Hz, 2H), 7.39–7.49 (m, 3H), 7.51–7.60 (m, 2H), 9.25 (s, 1H), 9.45 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ 14.5, 51.3, 60.6, 100.4, 106.4, 128.1, 129.2, 129.3, 130.9, 137.9, 152.9, 161.2, 167.2. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{15}H_{15}KNO_5^+$: 328.0582, found: 328.0581.

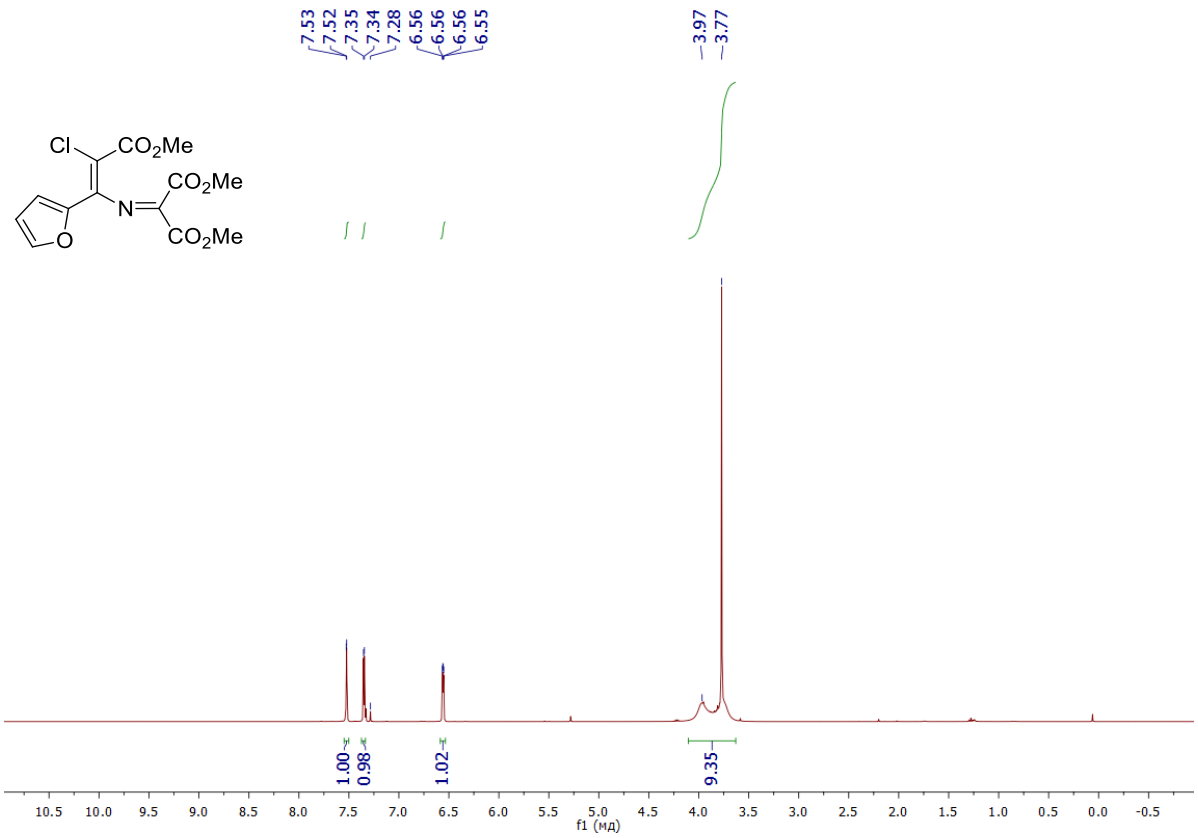
2-Isopropyl 4-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5ae)

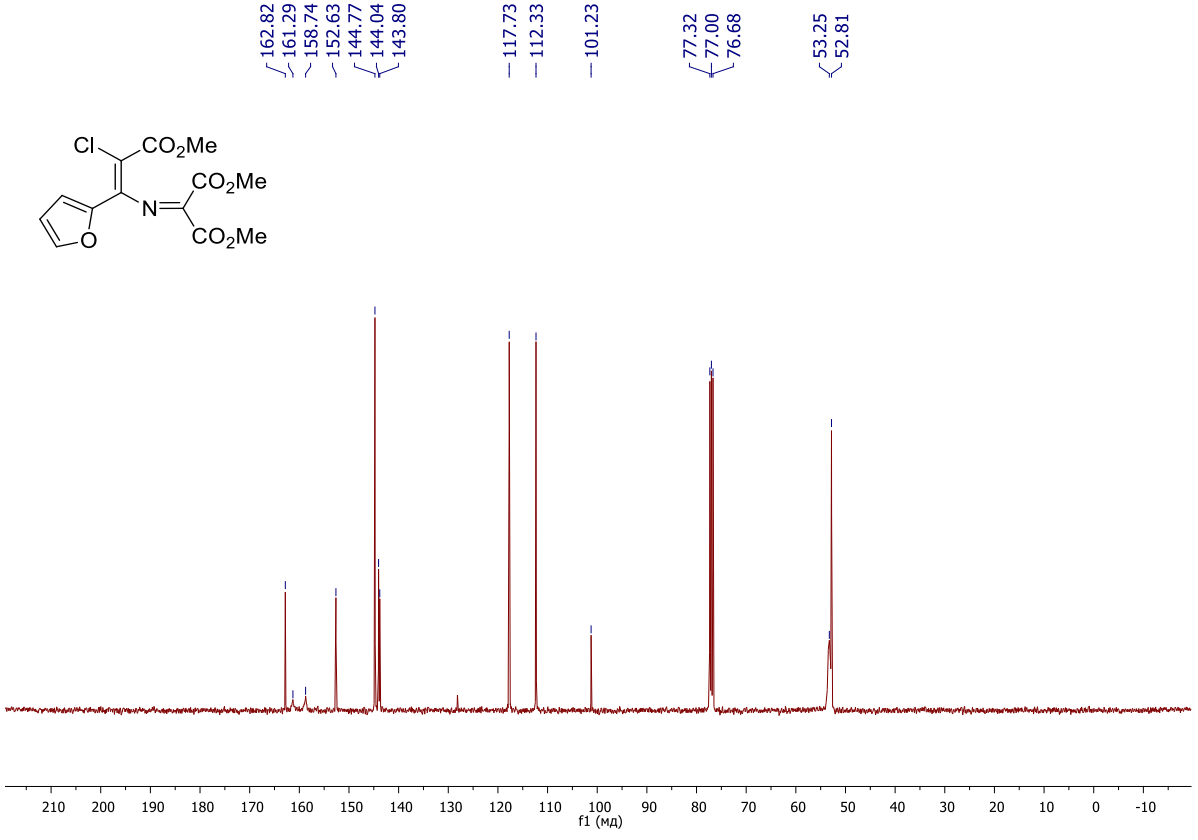


Pyrrole **5ae** (45 mg, 30%) was prepared according to method B from azirine **9a** (105 mg, 0.5 mmol), diazo compound **12l** (1.28 g, 6 mmol) and Bu_3SnH (291 mg, 1 mmol) under reflux in *o*-xylene for 10 min. White solid, mp 138–140 °C (Et_2O–hexane). ^1H NMR ($CDCl_3$) δ 1.33 (d, *J* 6.3 Hz, 6H), 3.78 (s, 3H), 5.11 (sept, *J* 6.3 , 1H), 7.39–7.50 (m, 3H), 7.51–7.61 (m, 2H), 8.94–9.32 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 22.0, 51.3, 68.1, 100.6, 106.6, 128.2, 129.1, 129.3, 131.0, 137.6, 152.9, 160.7, 166.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{18}NO_5^+$: 304.1179, found: 304.1163.

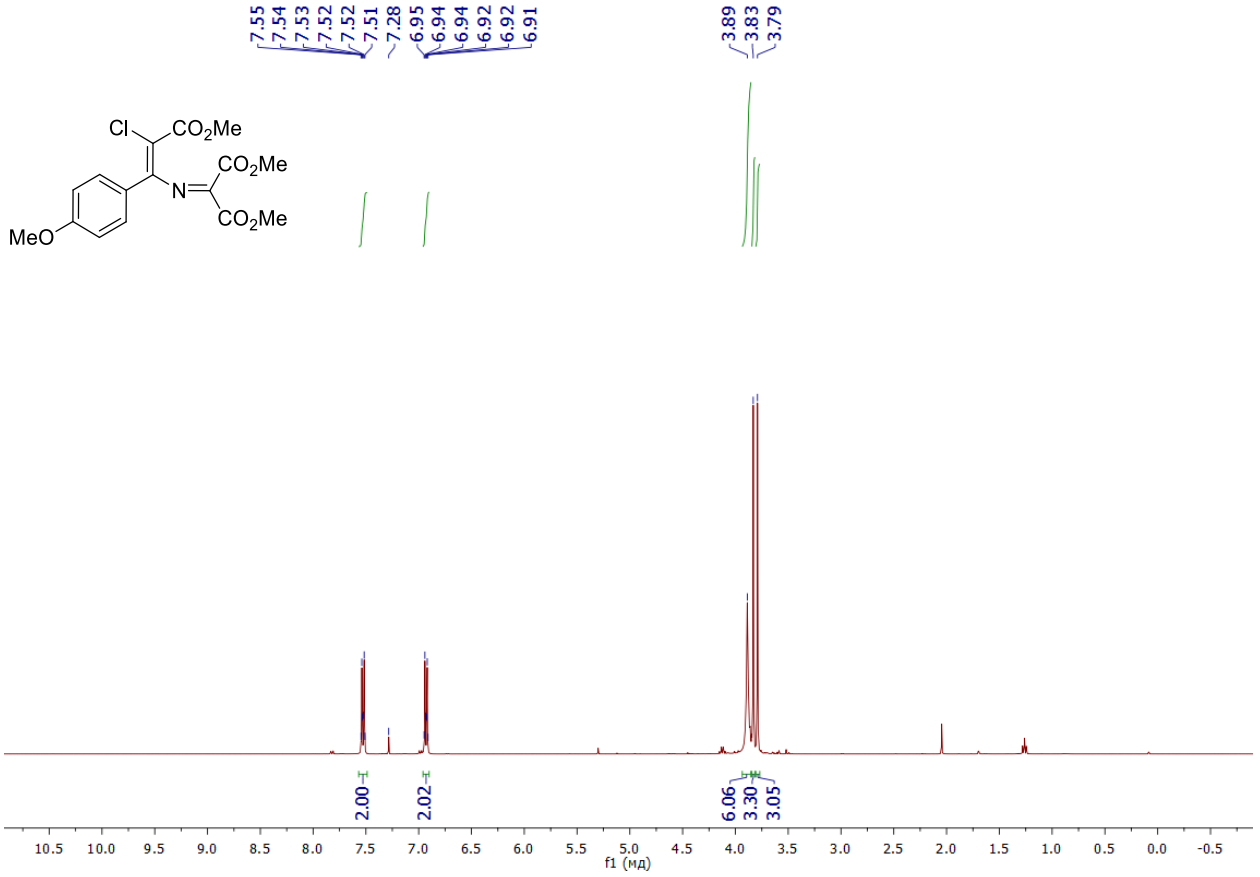
9. NMR Spectra of New Compounds

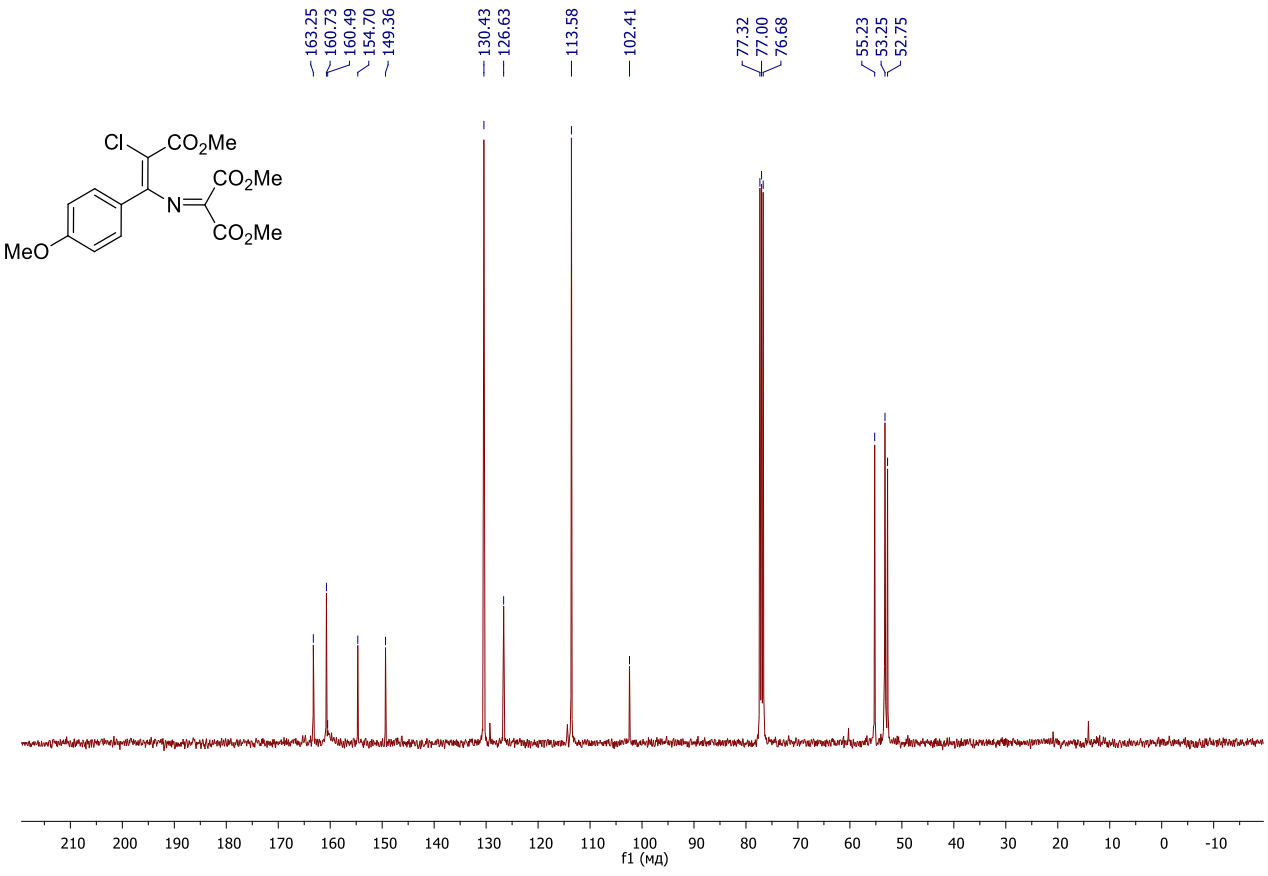
Dimethyl (*E*)-2-{[2-chloro-1-(furan-2-yl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}malonate (4a)



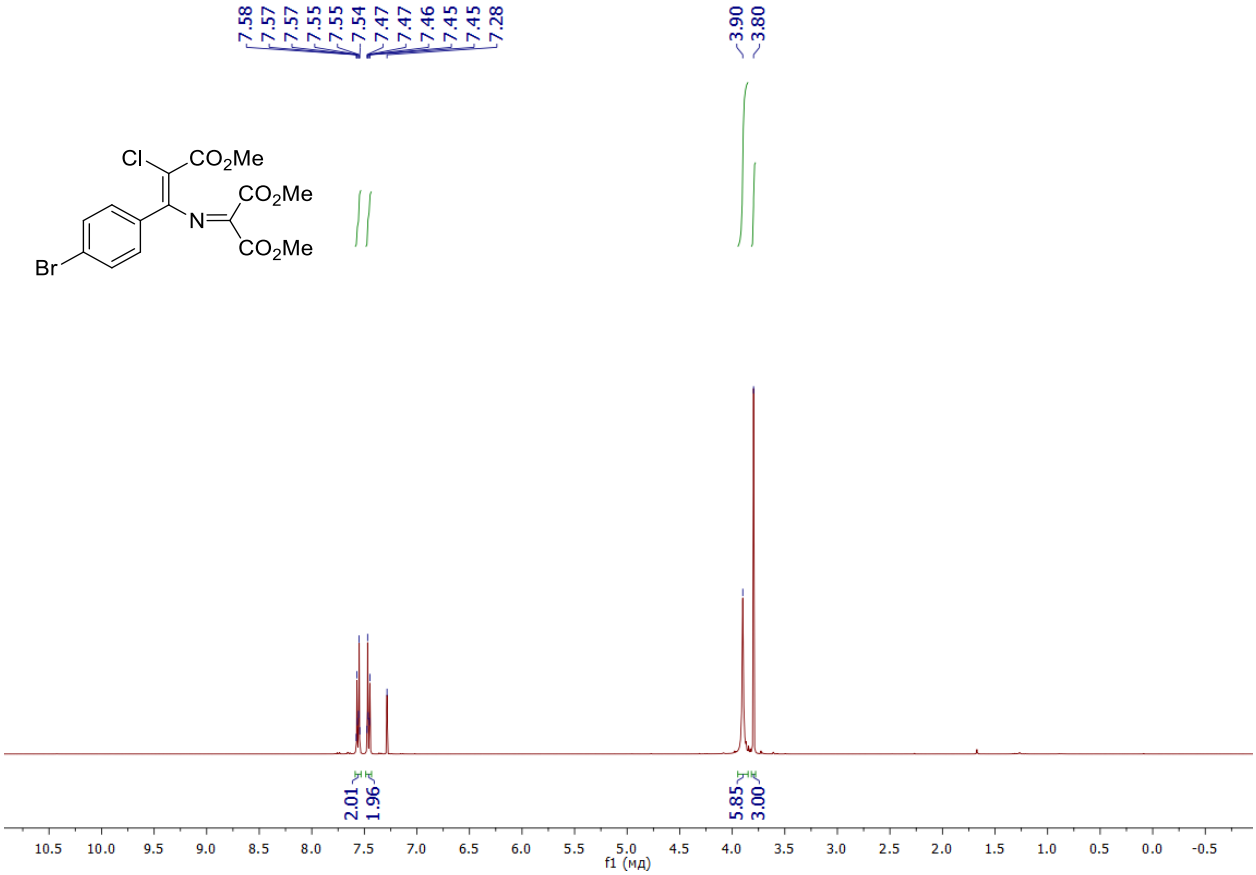


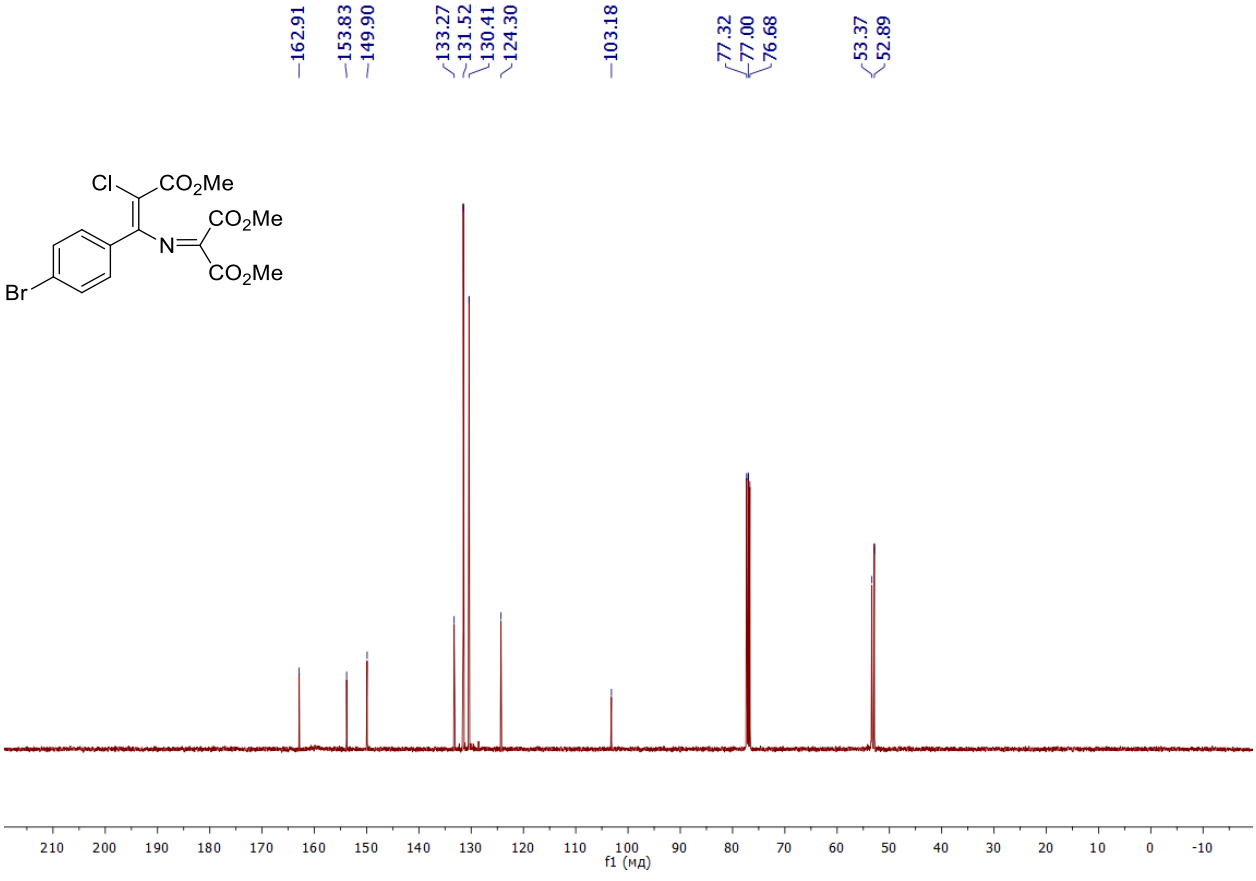
Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl]imino}-malonate (4c)



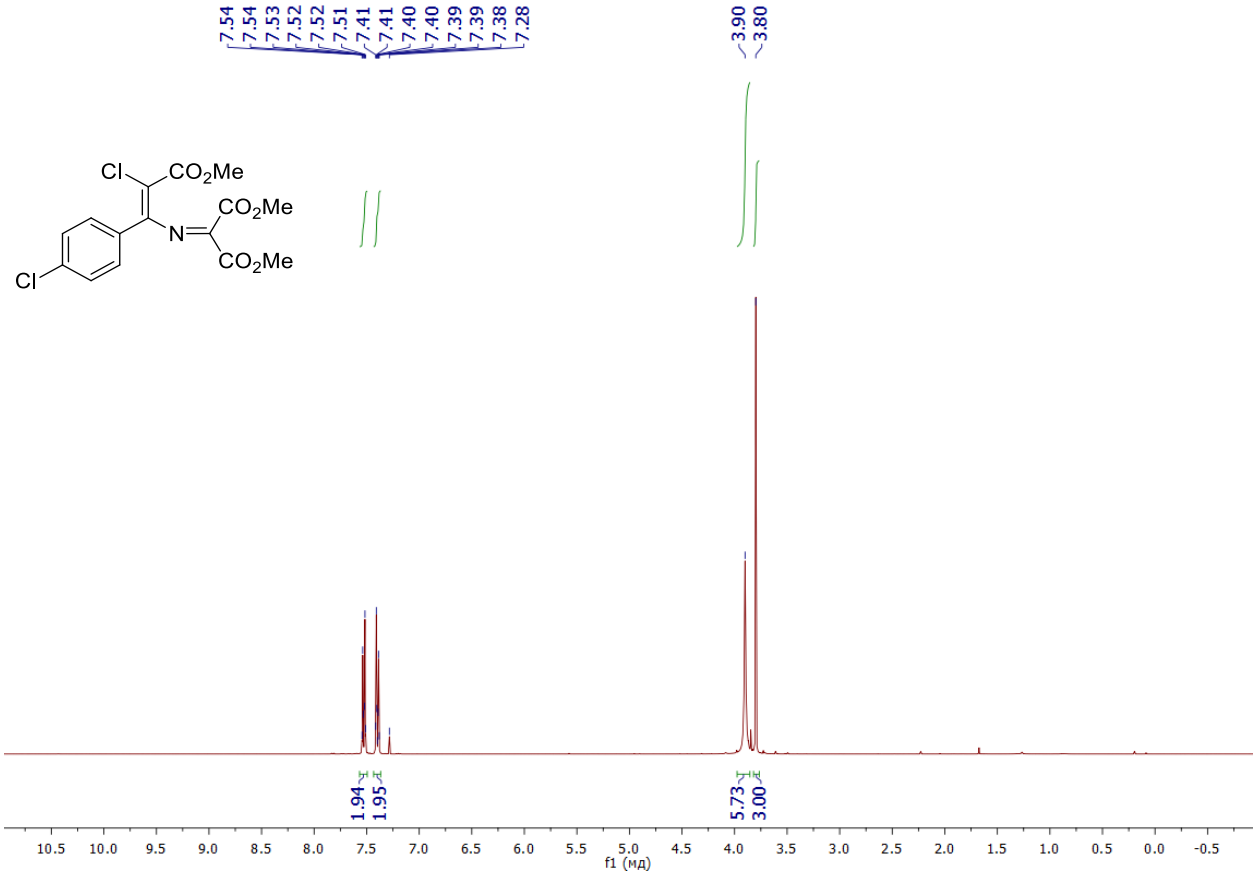


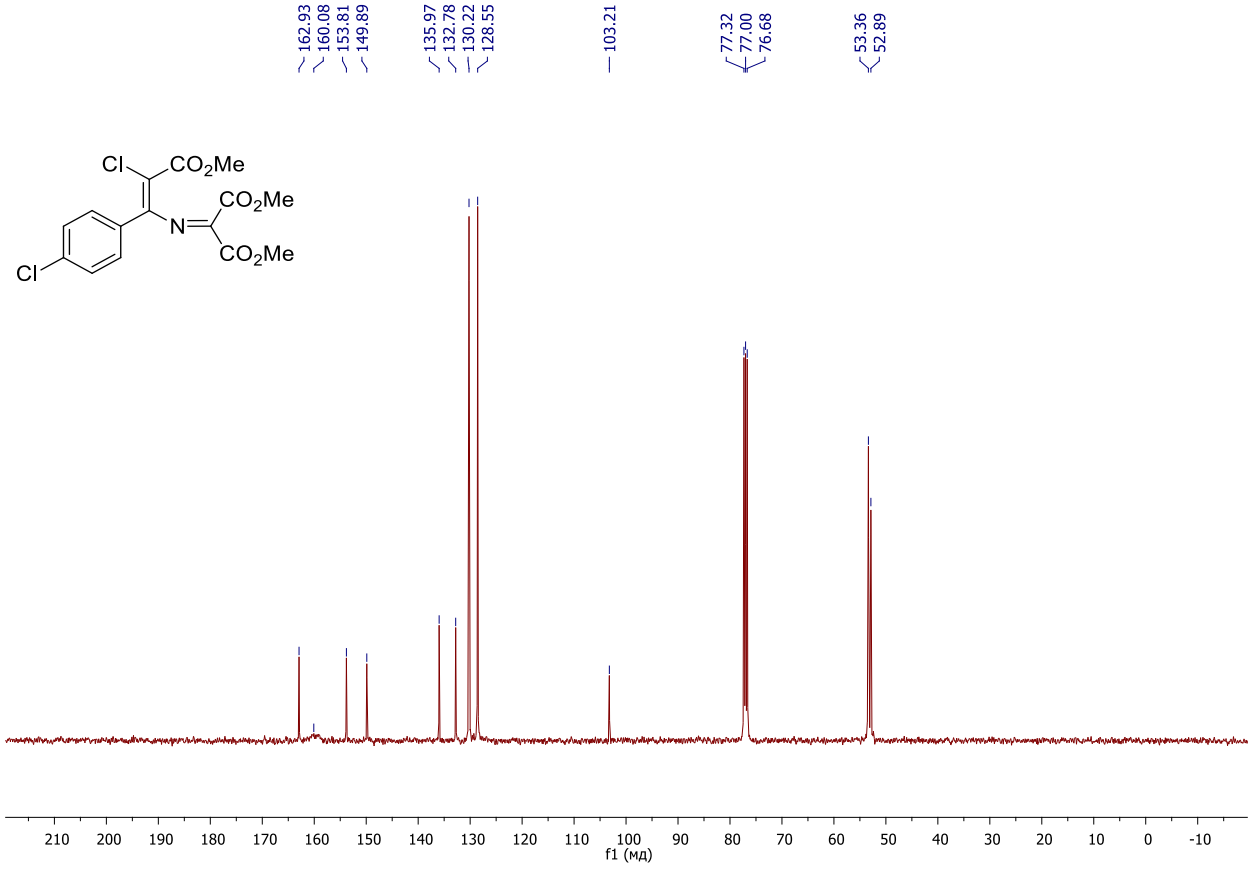
Dimethyl (*E*)-2-{[1-(4-bromophenyl)-2-chloro-3-methoxy-3-oxoprop-1-en-1-yl]imino}-malonate (4d)



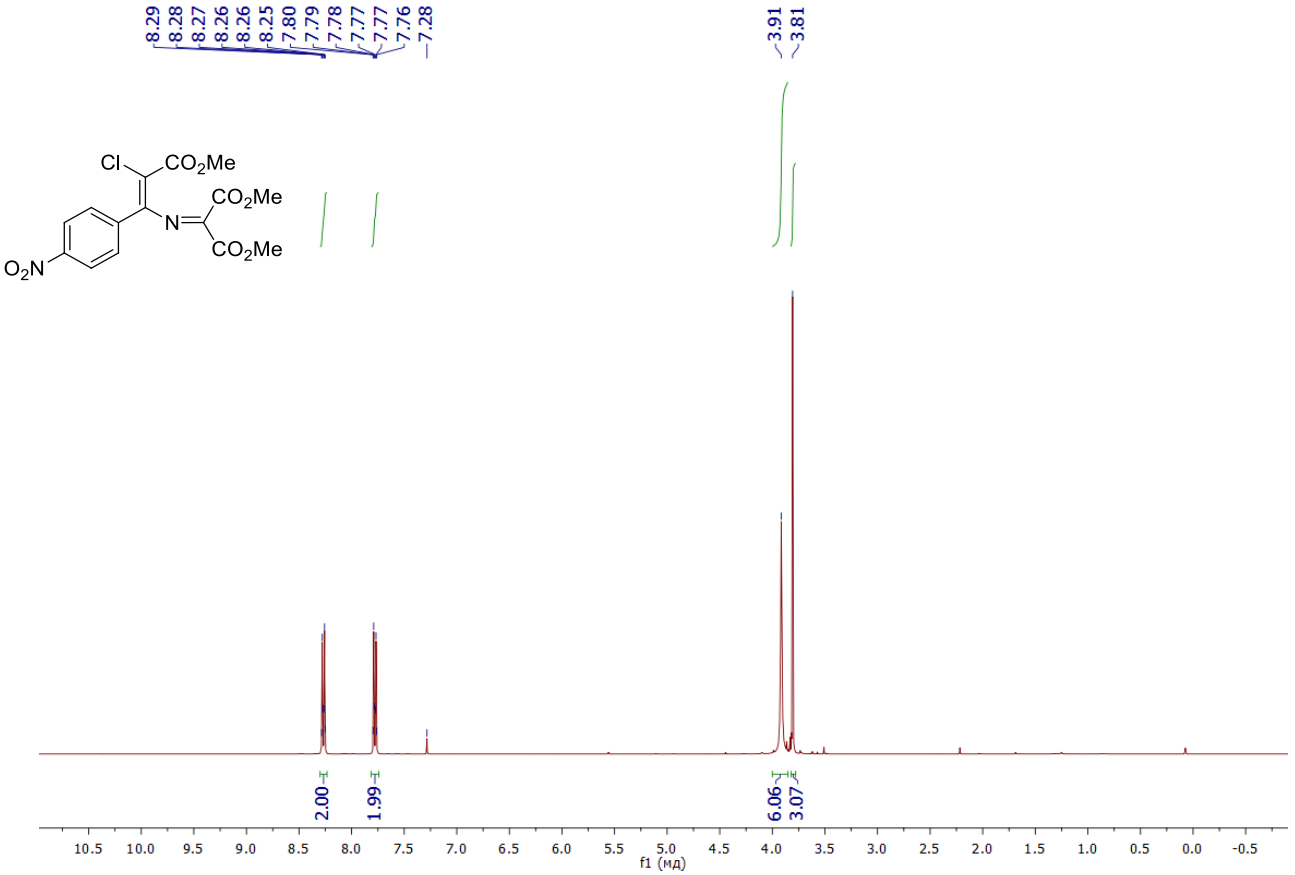


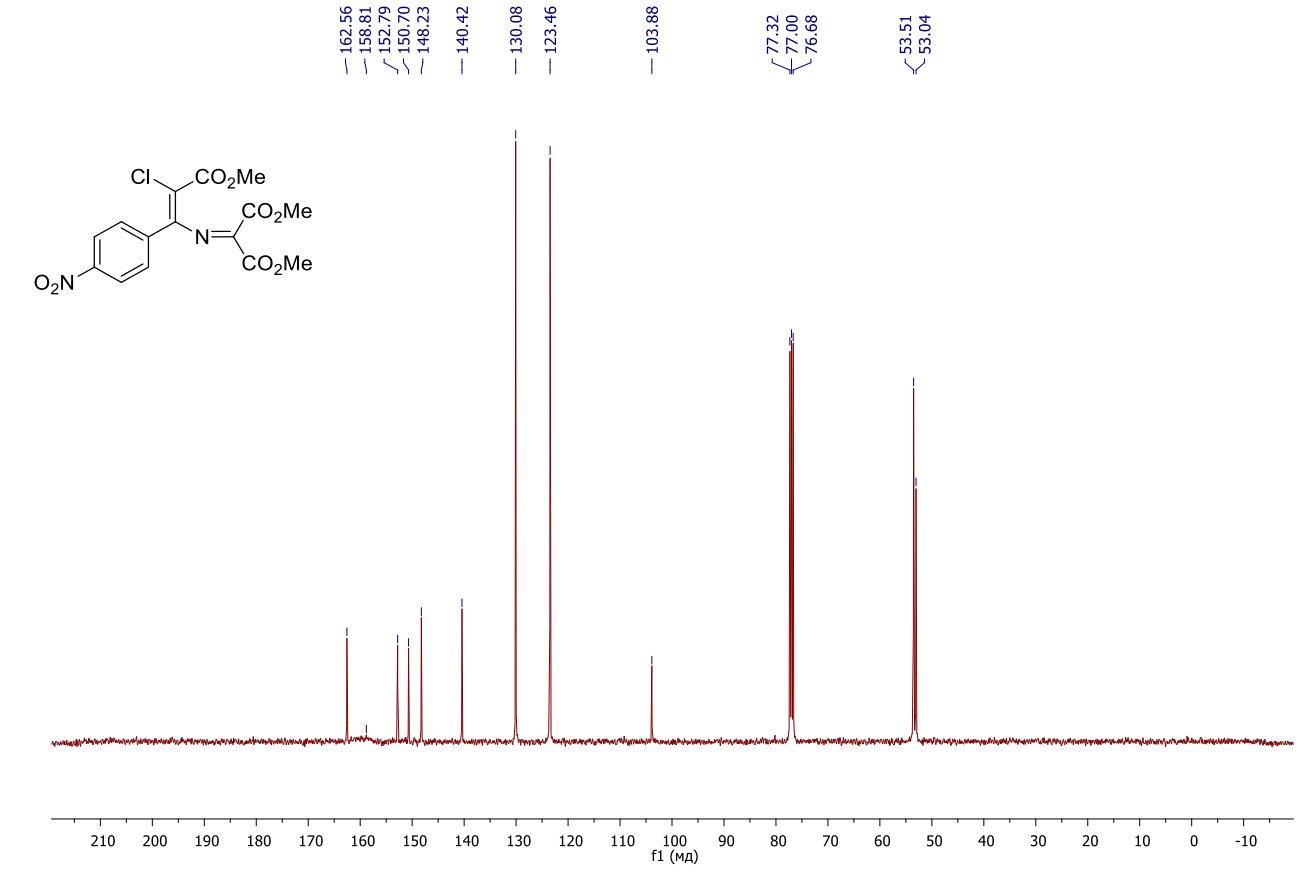
Dimethyl (*E*)-2-{[2-chloro-1-(4-chlorophenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}-malonate (4e)



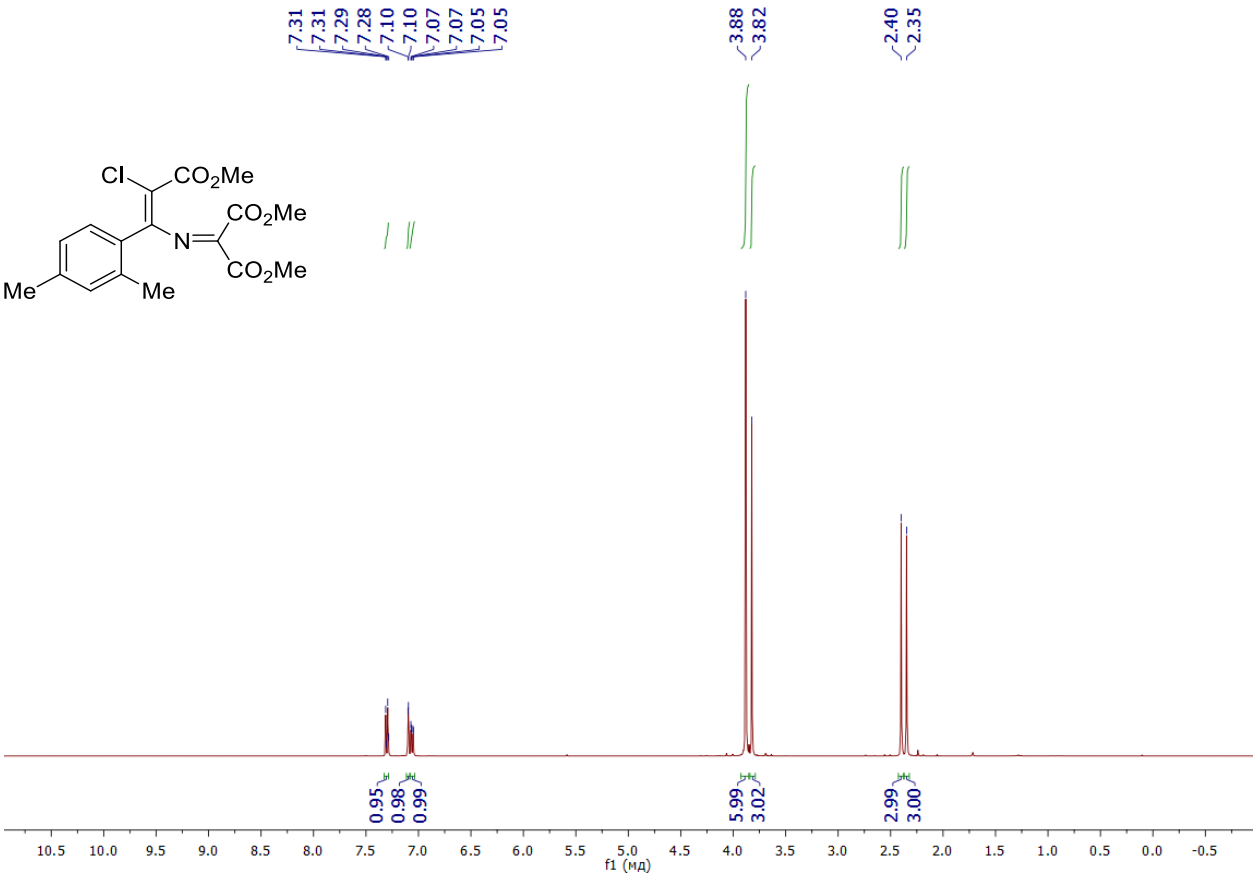


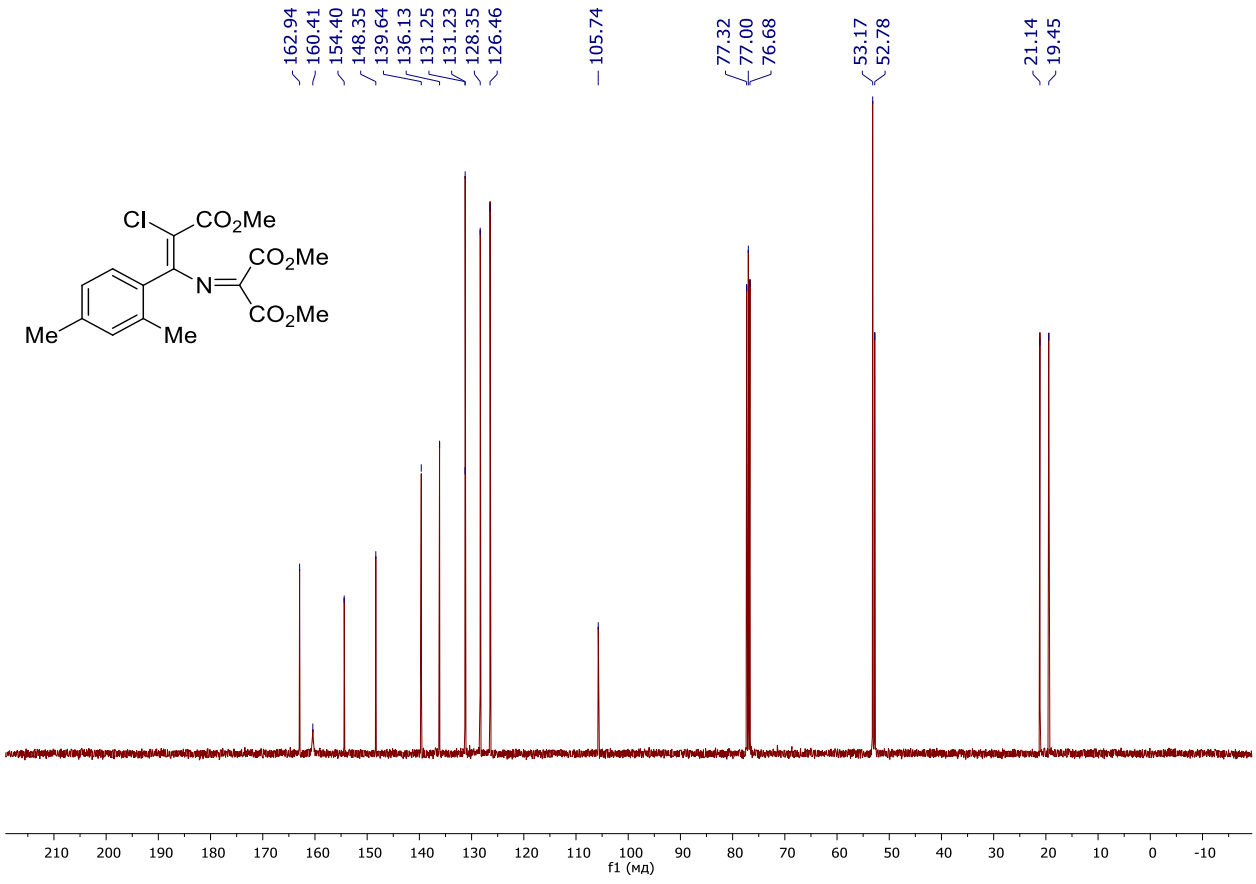
Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(4-nitrophenyl)-3-oxoprop-1-en-1-yl]imino}-malonate (4f)



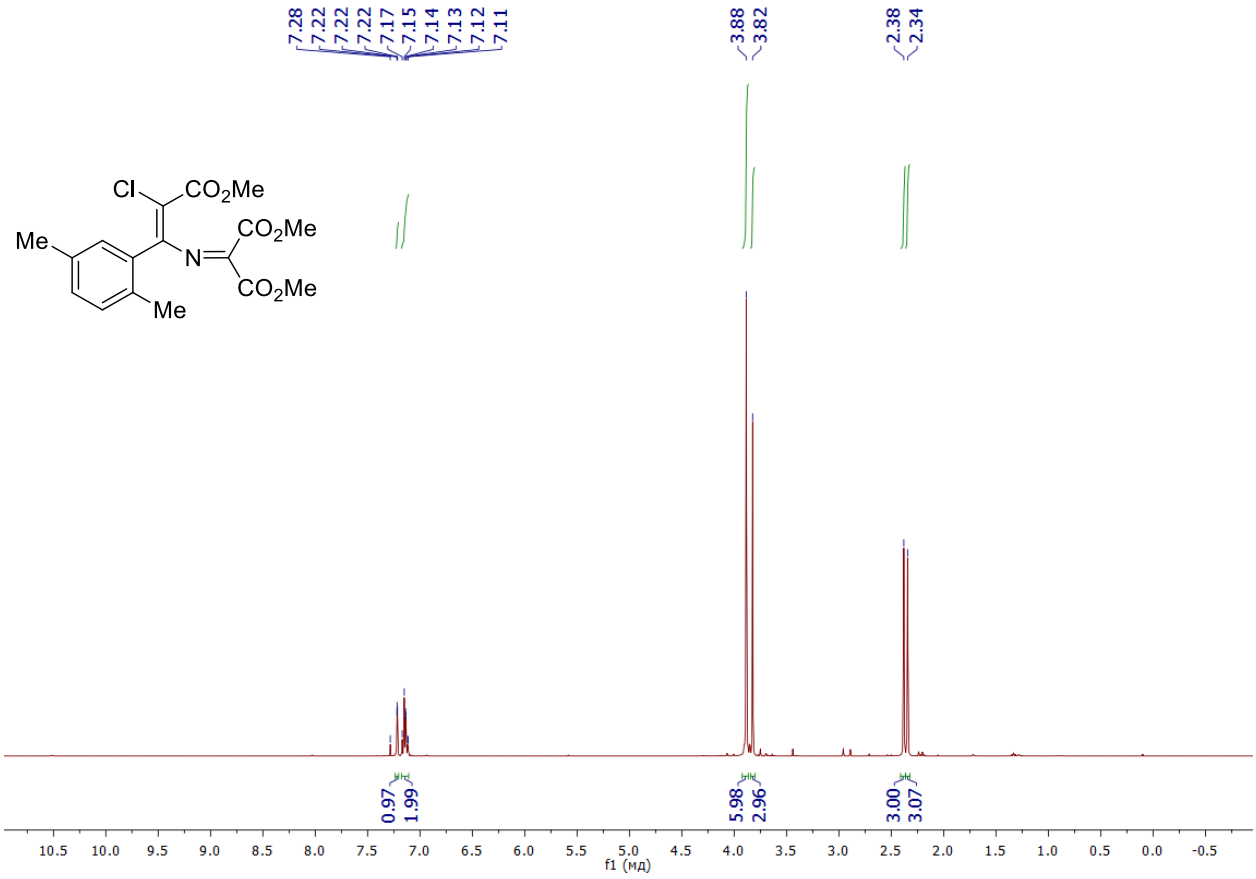


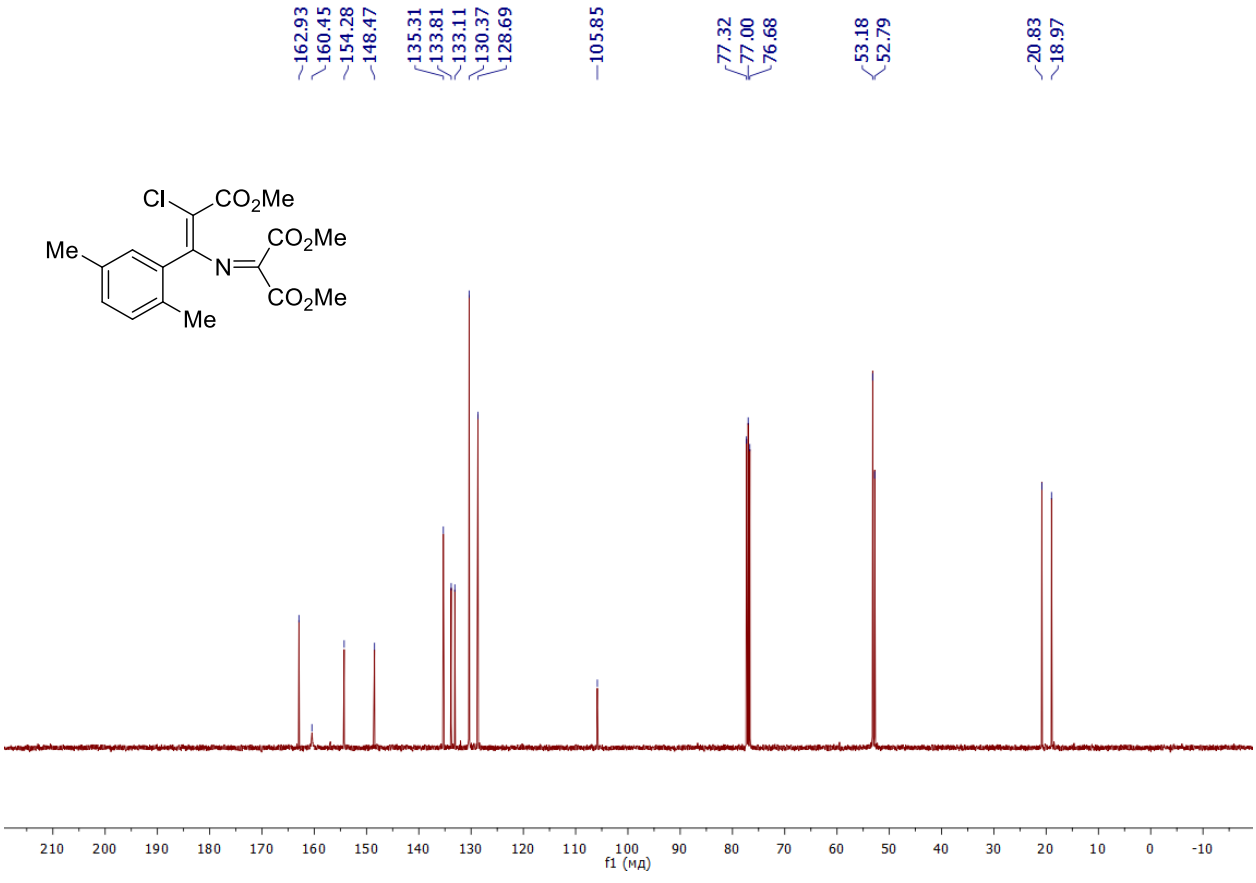
Dimethyl (*E*)-2-{[2-chloro-1-(2,4-dimethylphenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}-malonate (4g)



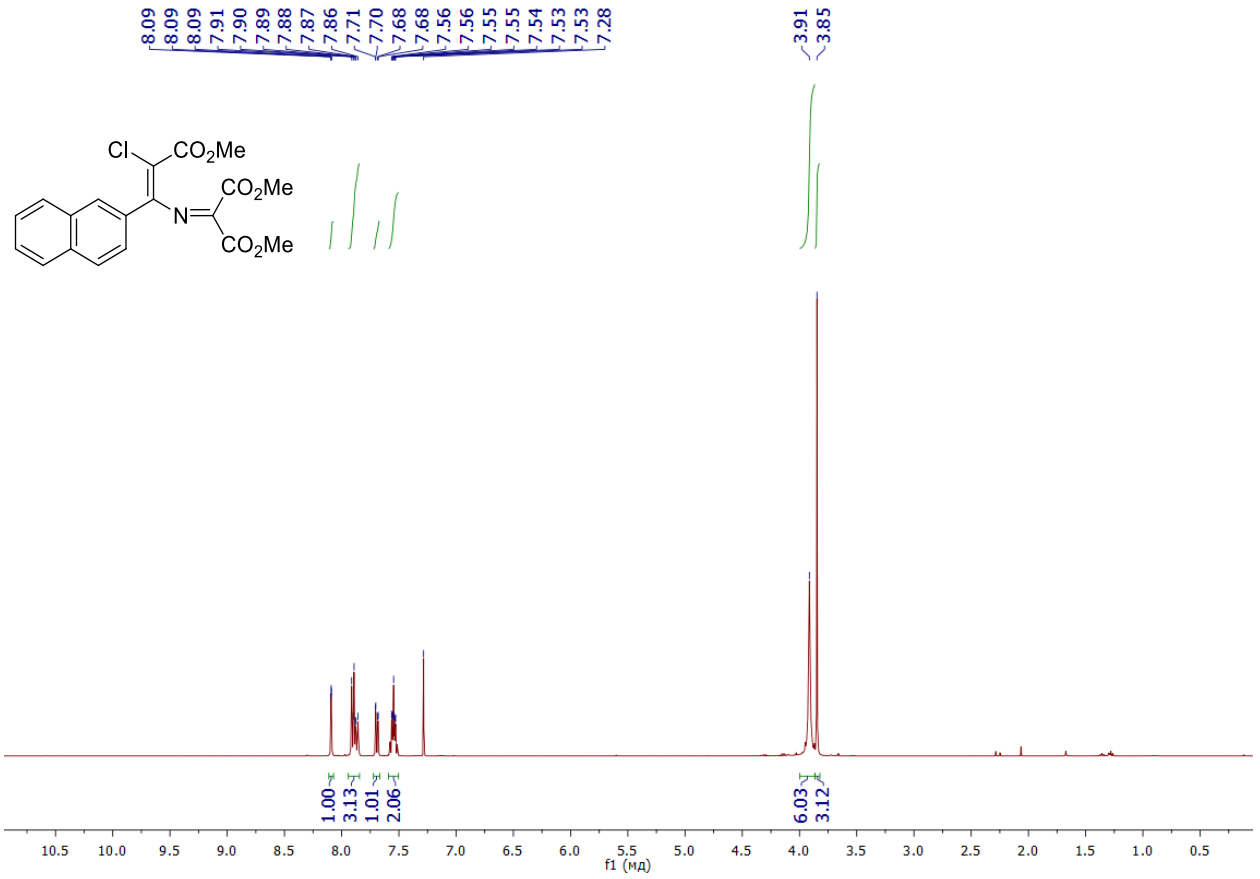


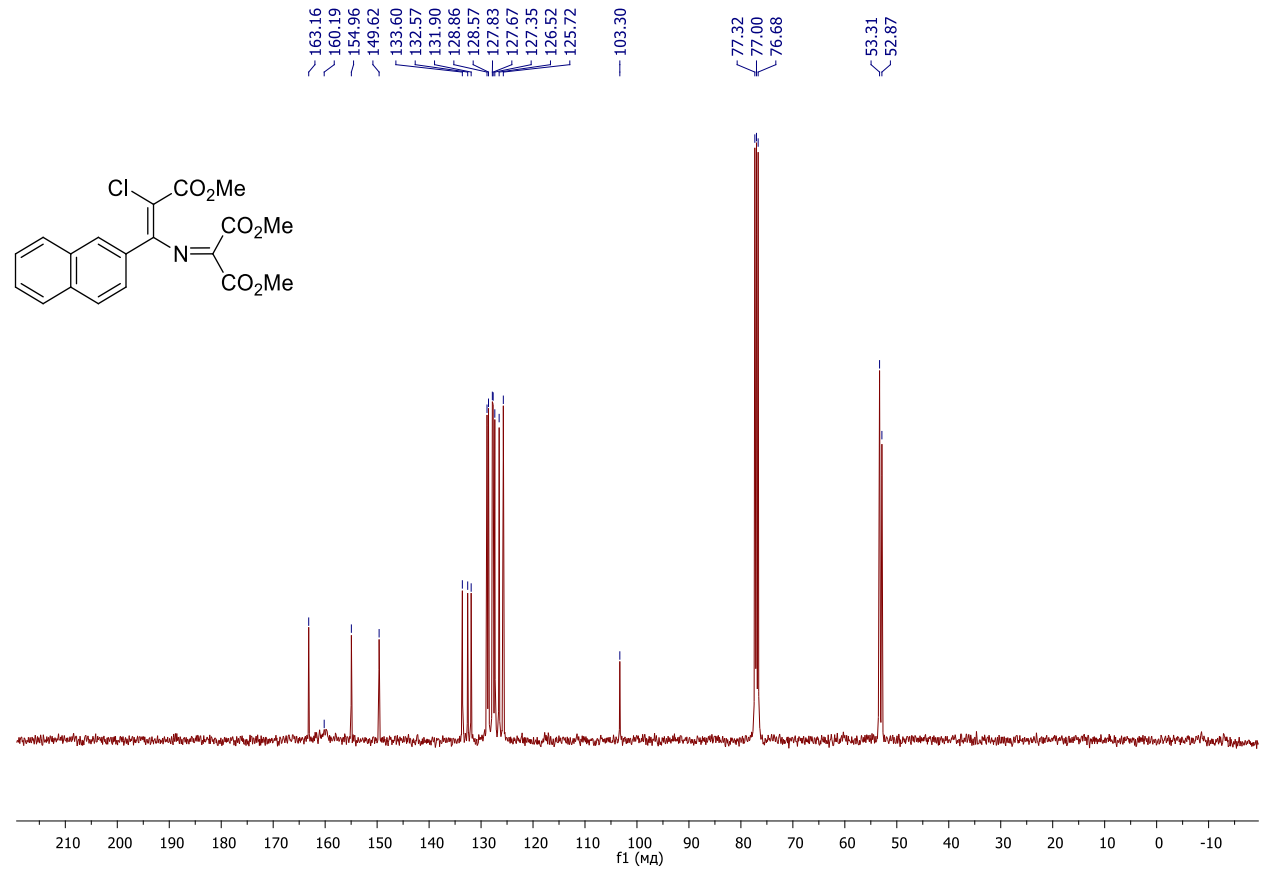
Dimethyl (*E*)-2-{[2-chloro-1-(2,5-dimethylphenyl)-3-methoxy-3-oxoprop-1-en-1-yl]imino}-malonate (4h)



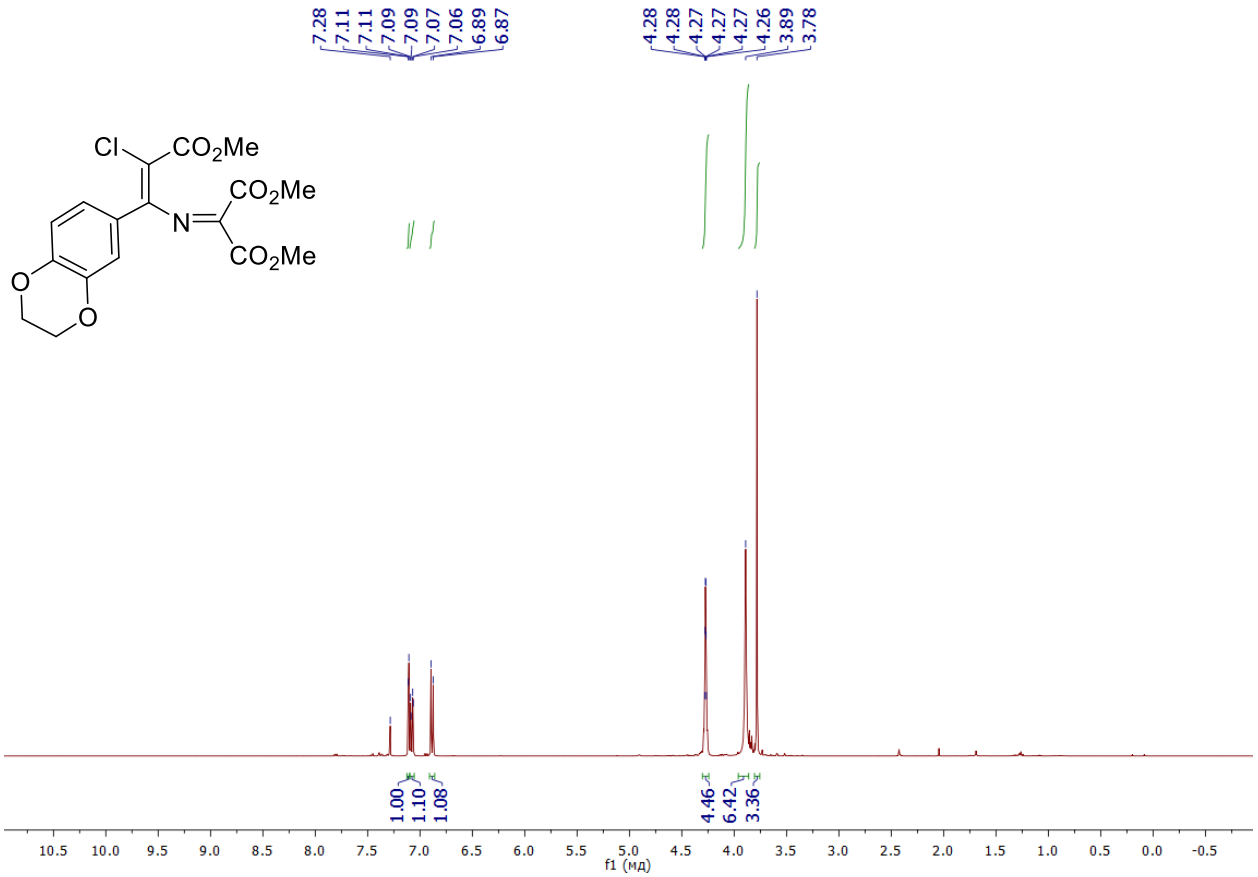


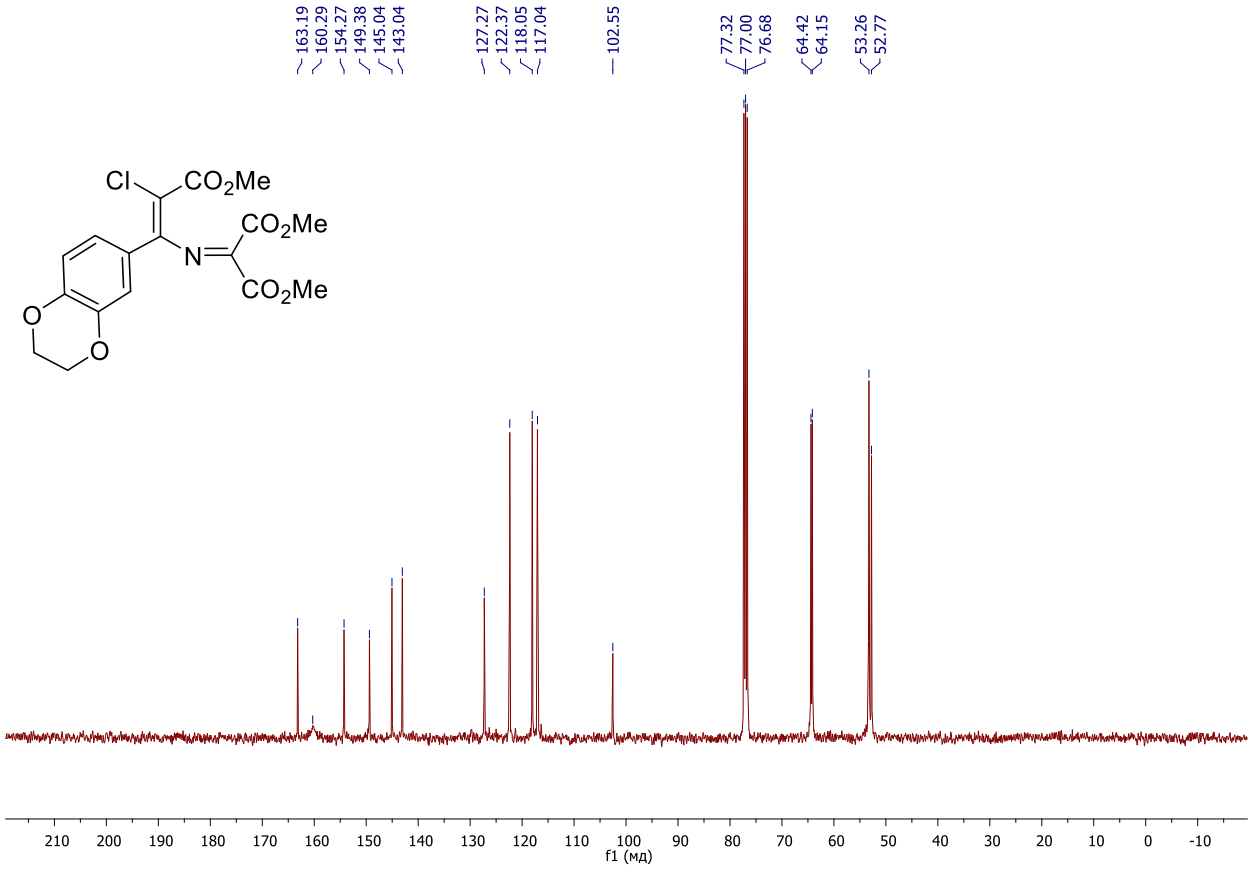
Dimethyl (*E*)-2-{[2-chloro-3-methoxy-1-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl]imino}-malonate (4i)



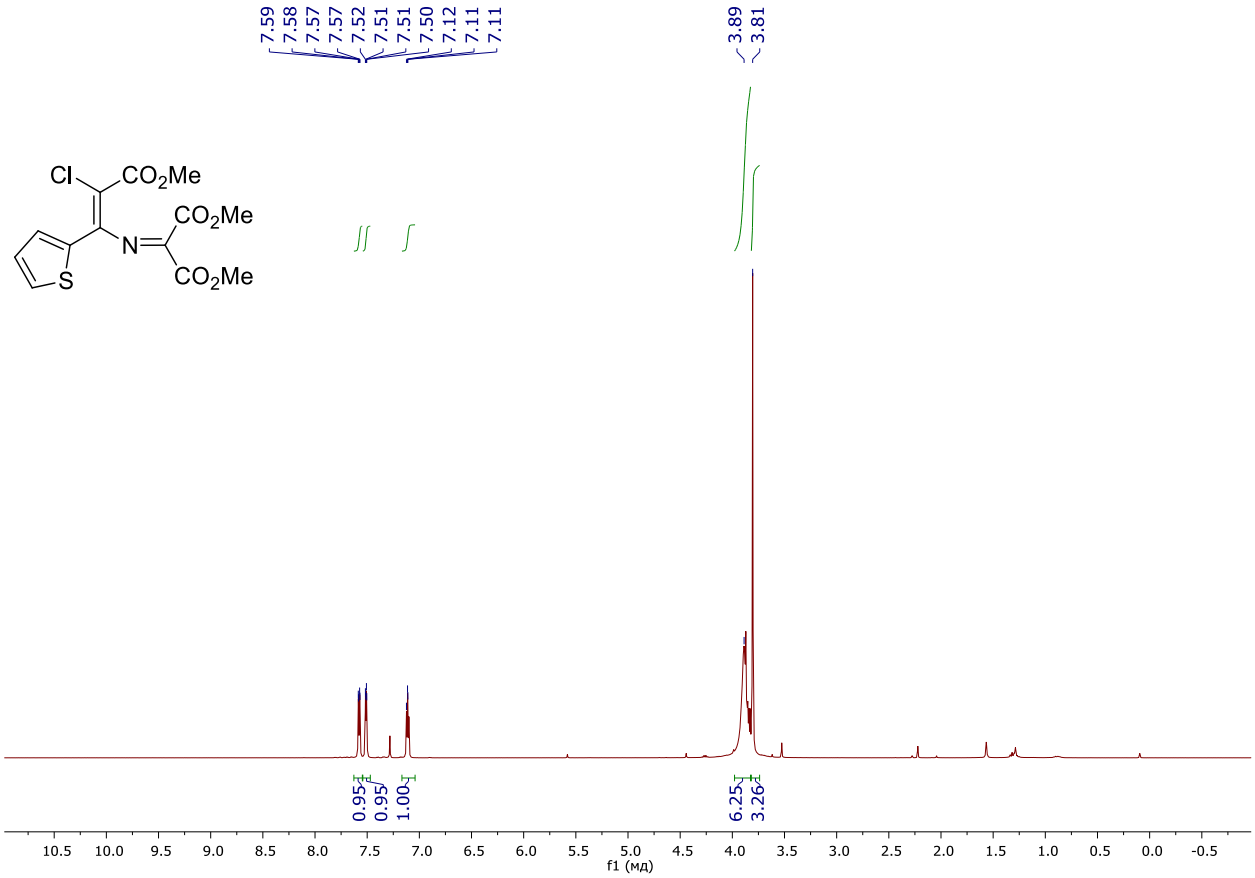


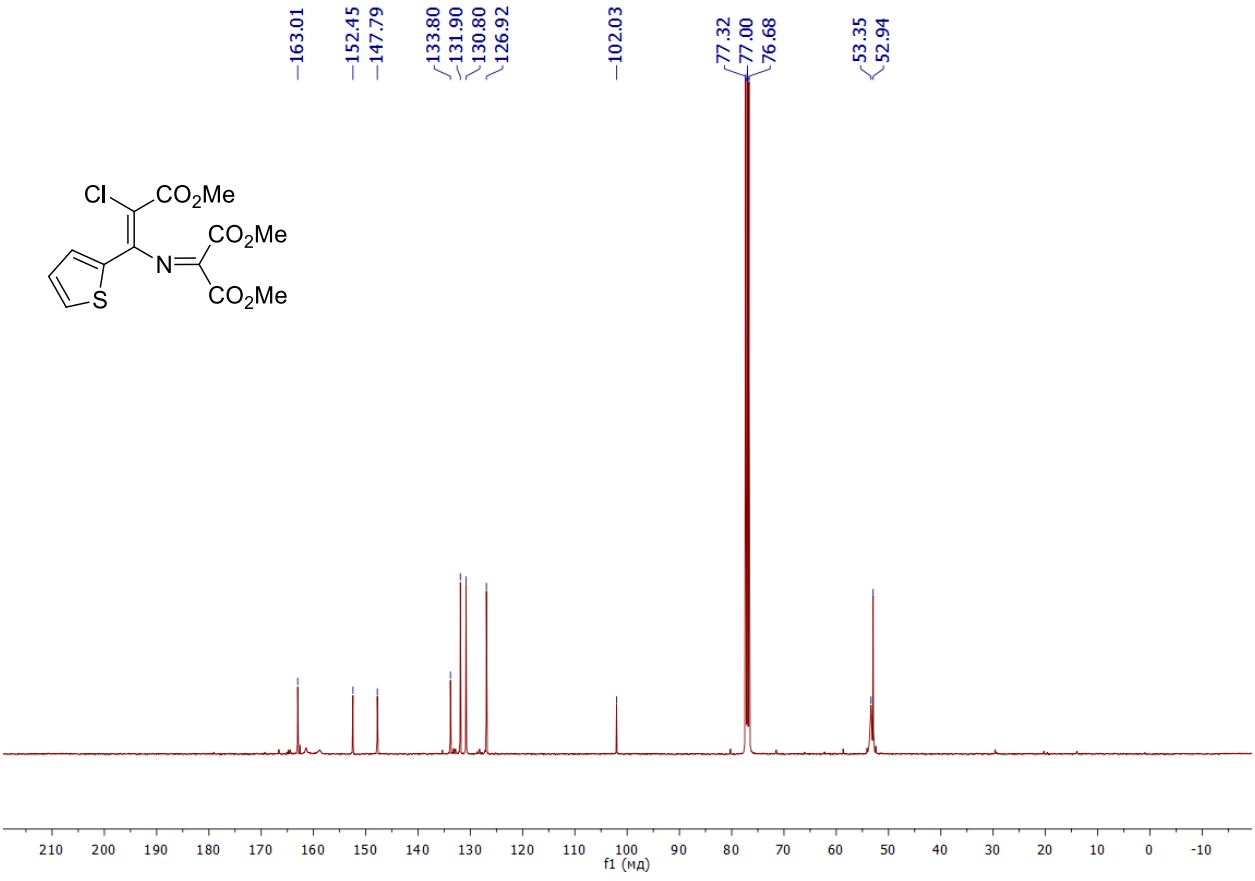
Dimethyl (*E*)-2-{[2-chloro-1-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl]-3-methoxy-3-oxoprop-1-en-1-yl}imino)malonate (4j)



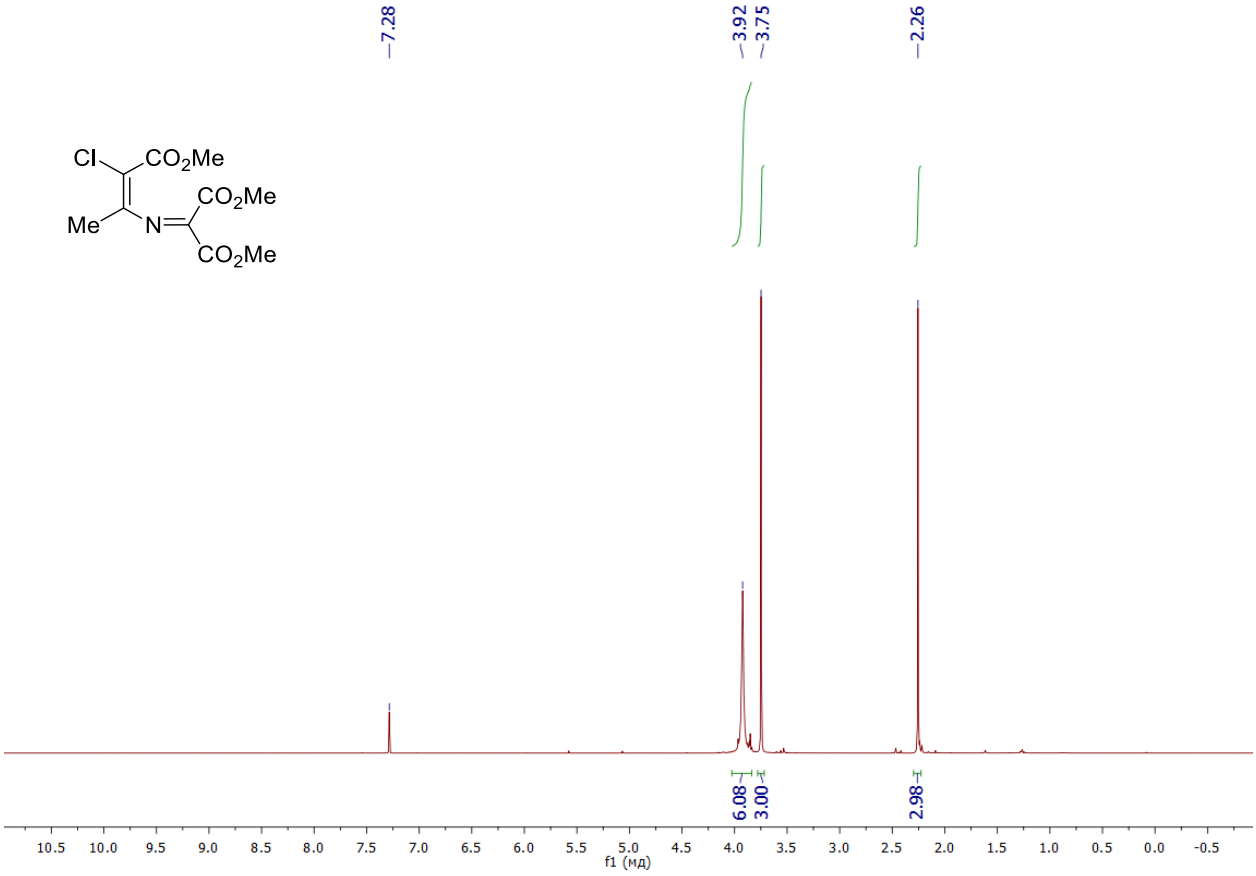


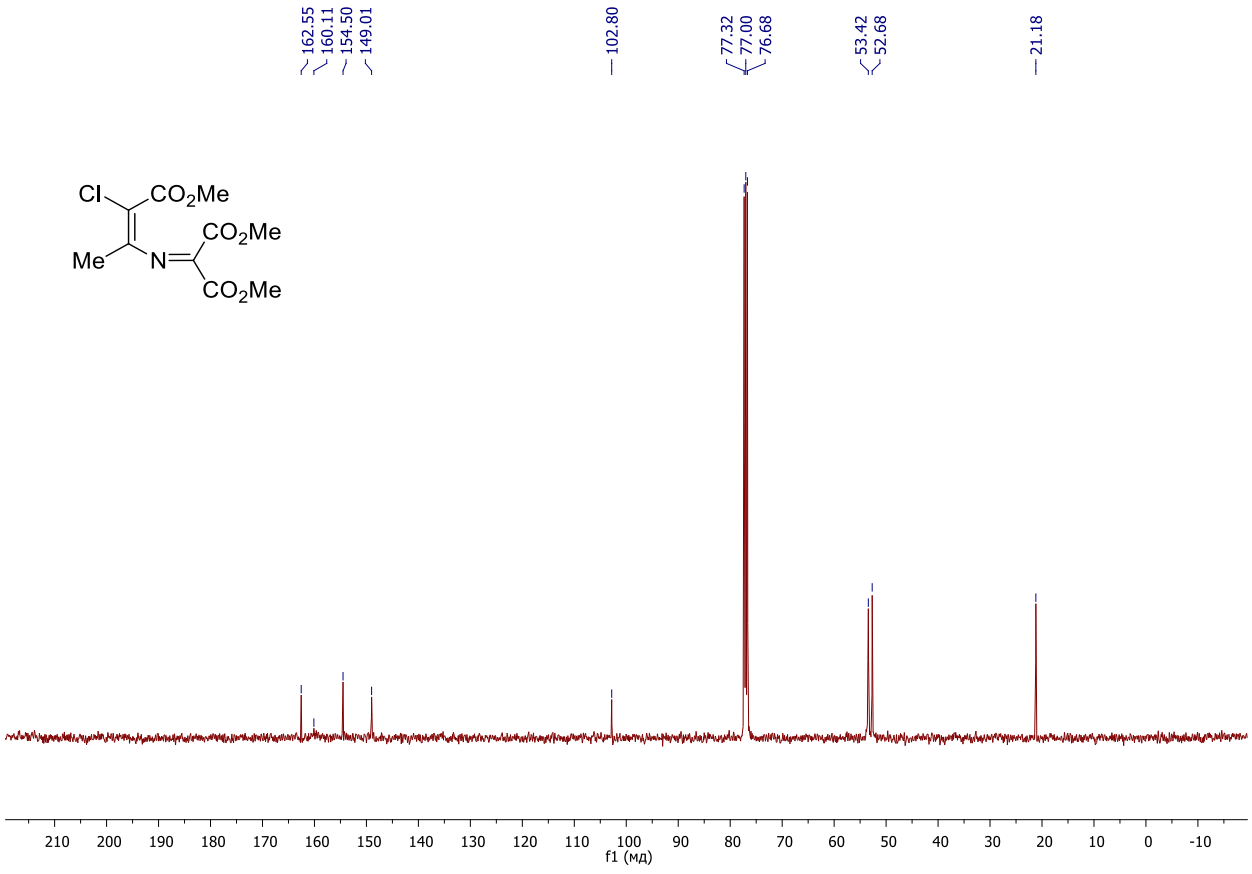
Dimethyl (*E*)-2-{]2-chloro-3-methoxy-3-oxo-1-(thiophen-2-yl)prop-1-en-1-yl]imino}-malonate (4k)



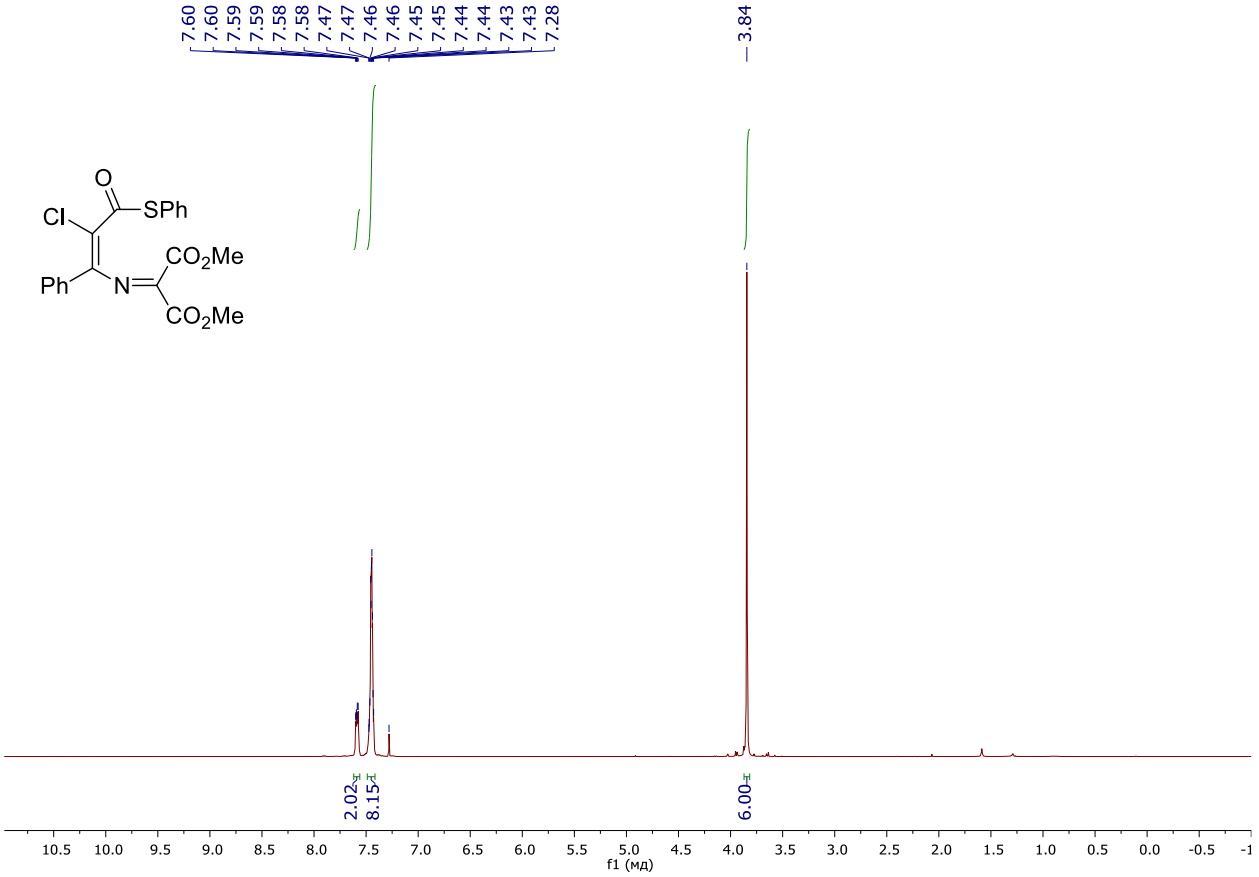


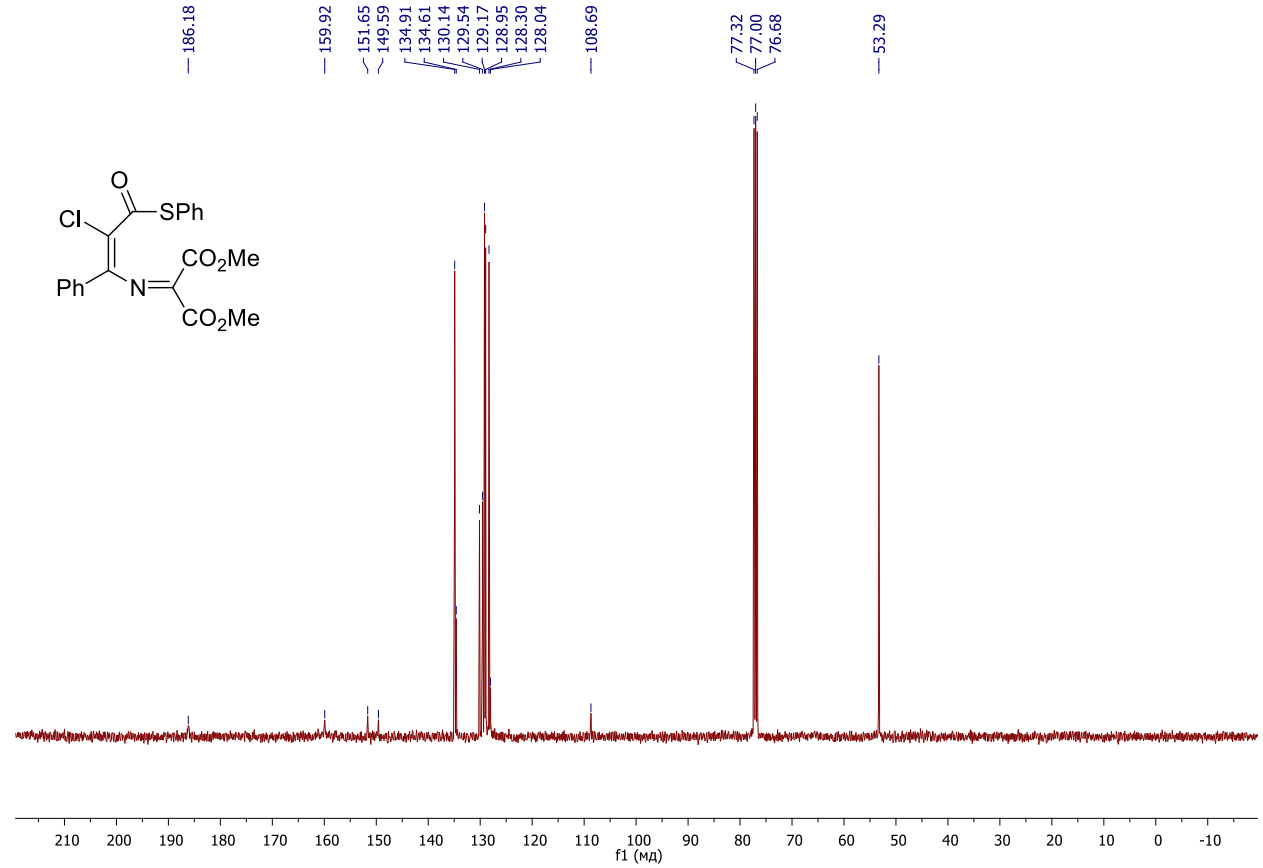
Dimethyl (*E*)-2-[(3-chloro-4-methoxy-4-oxobut-2-en-2-yl)imino]malonate (4l)



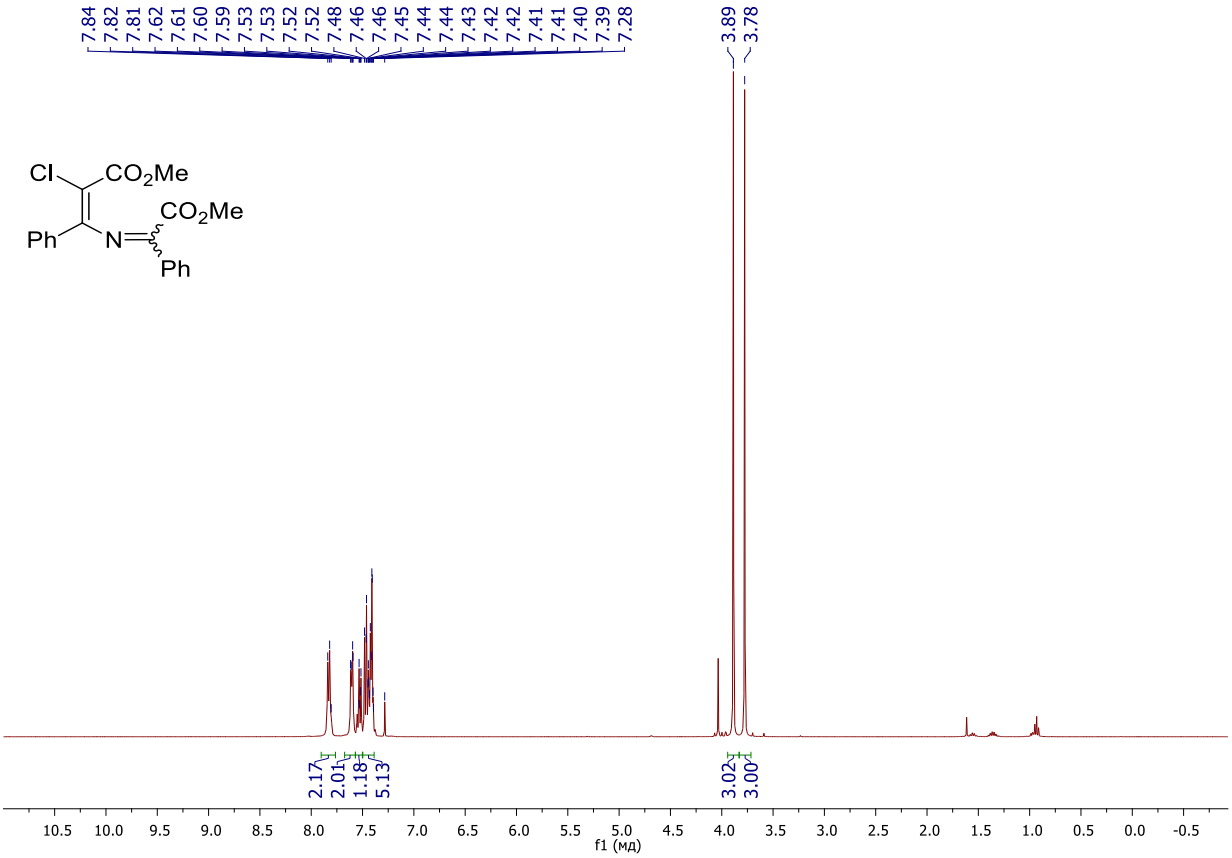


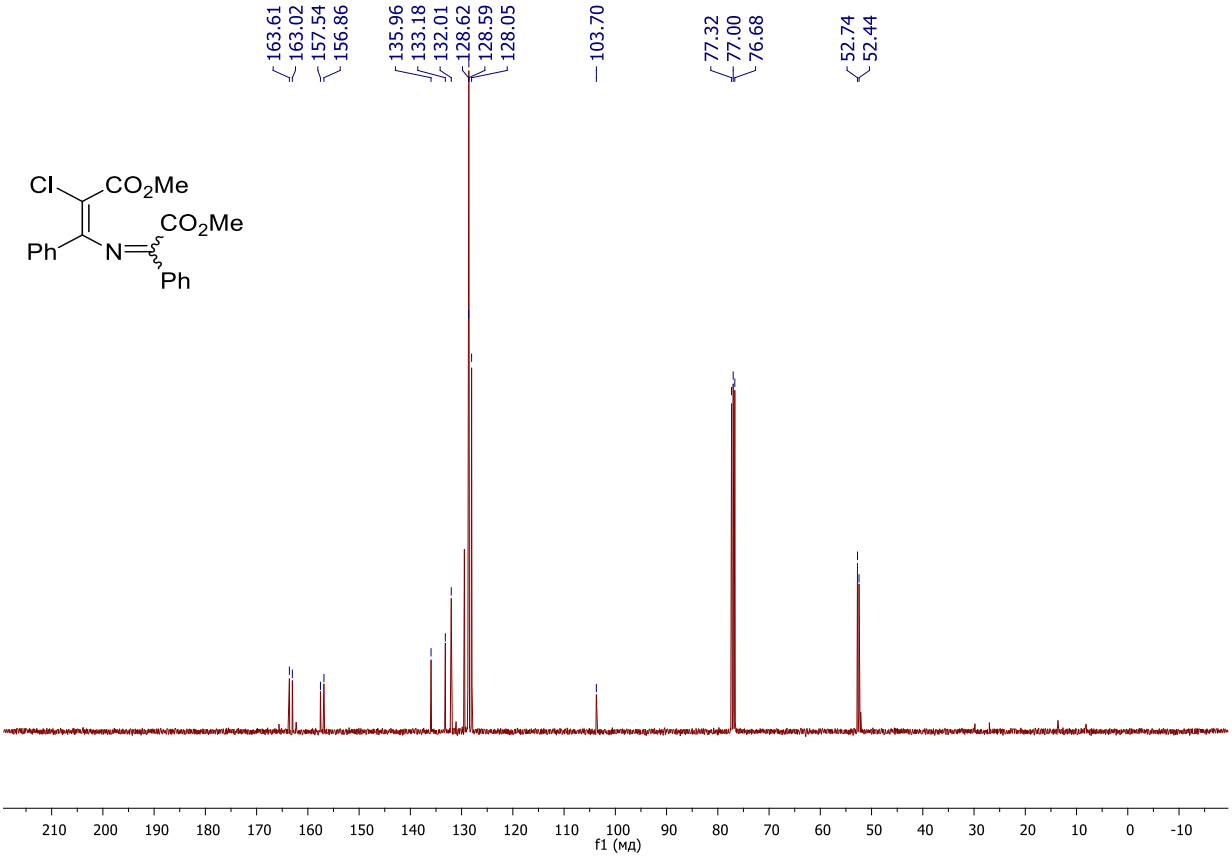
Dimethyl (*E*)-2-{[2-chloro-3-oxo-1-phenyl-3-(phenylthio)prop-1-en-1-yl]imino}malonate (4t)



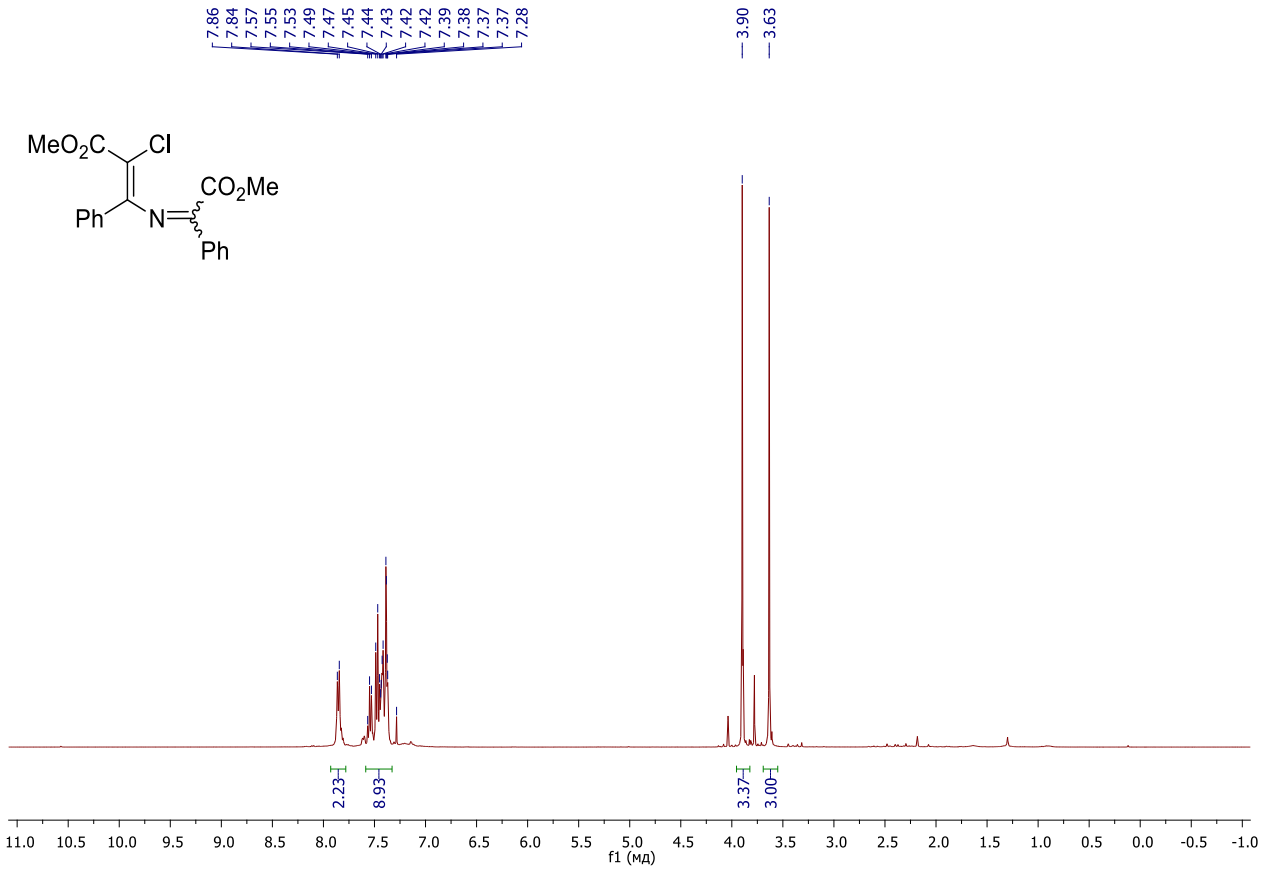


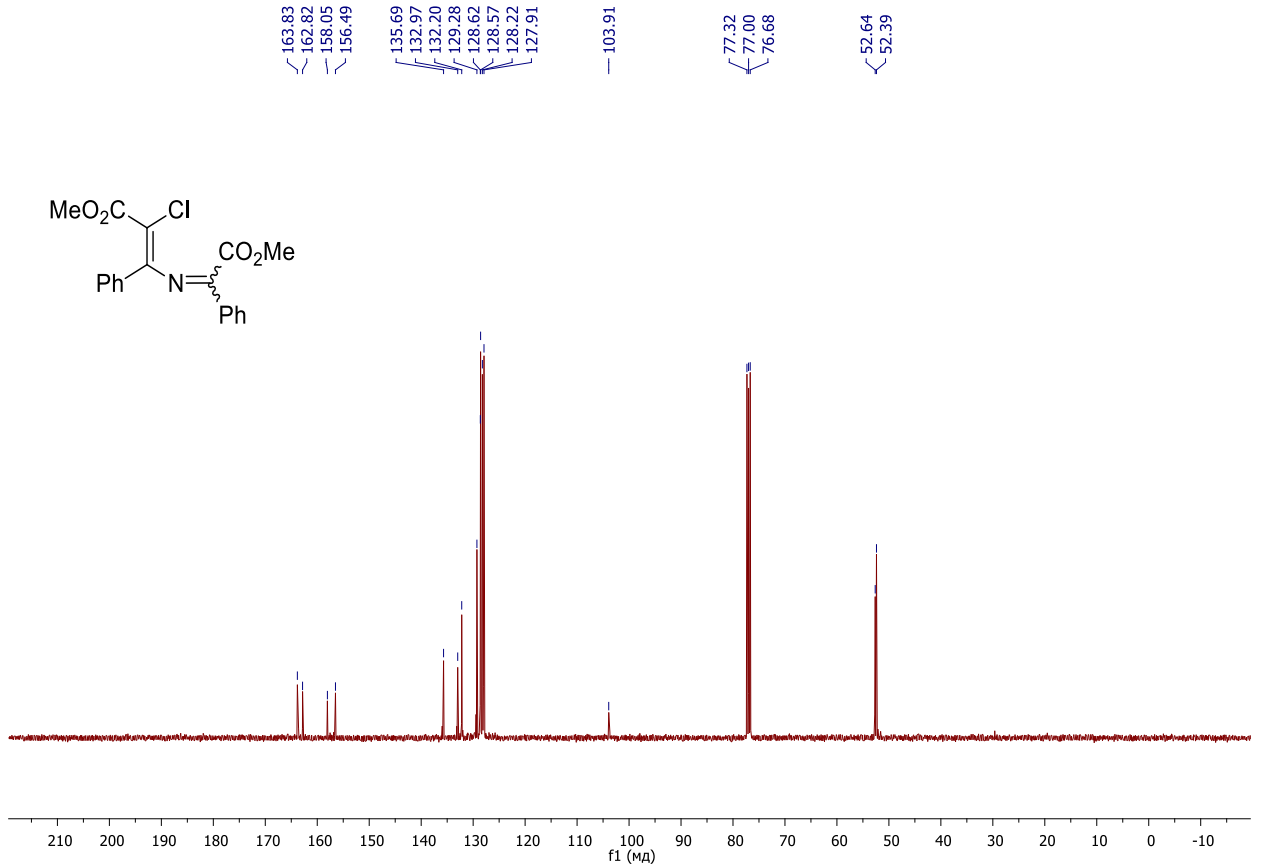
Methyl (2*E*)-2-chloro-3-[(2-methoxy-2-oxo-1-phenylethylidene)amino]-3-phenylacrylate (*E*-4u)



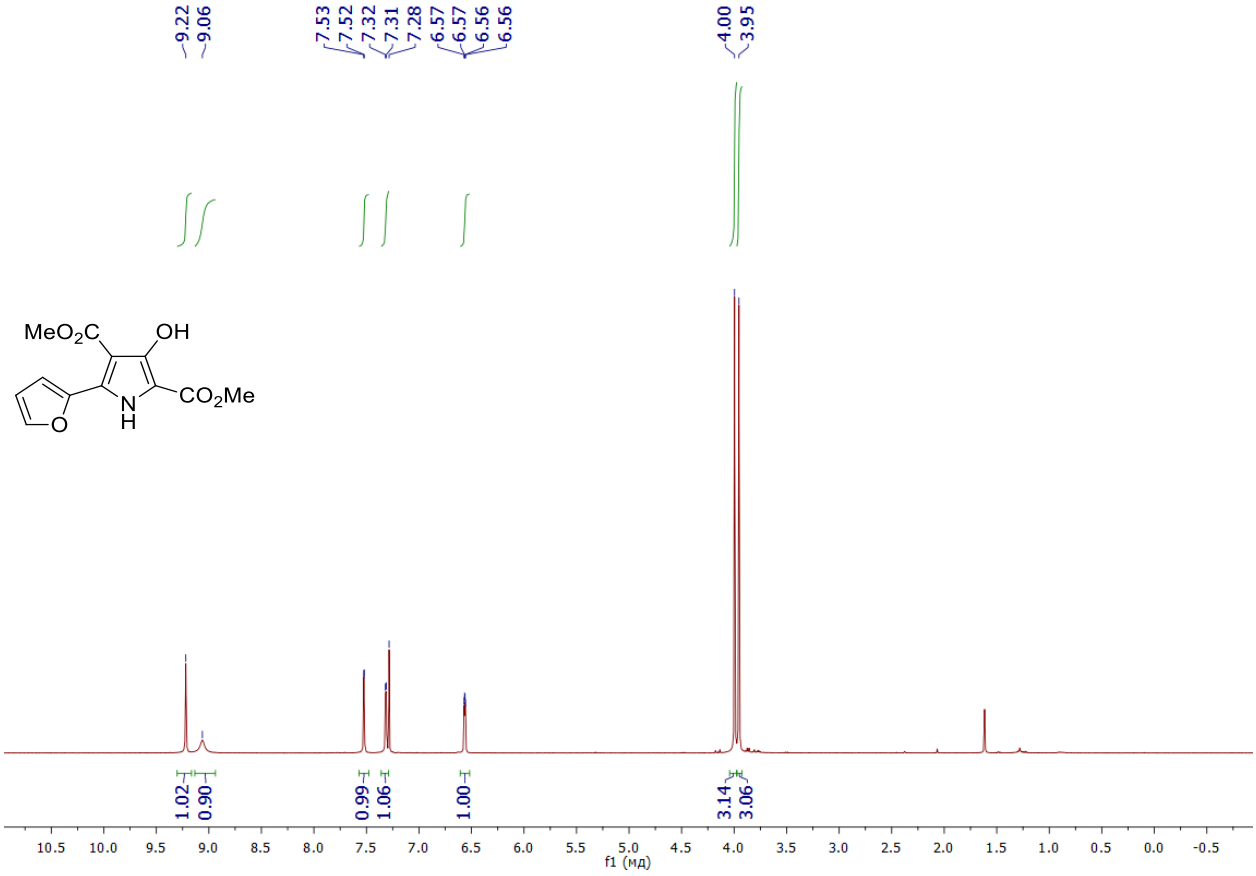


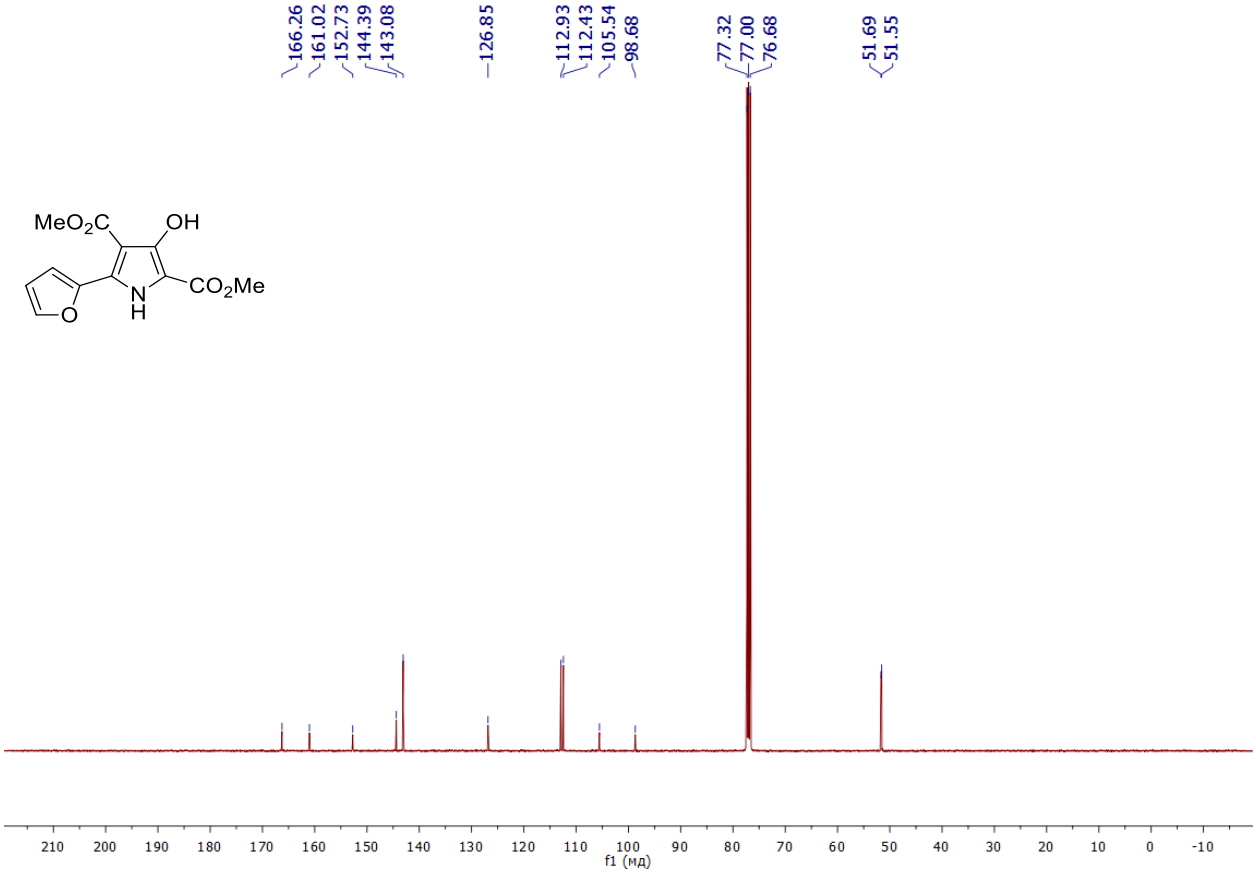
Methyl (2*Z*)-2-chloro-3-[(2-methoxy-2-oxo-1-phenylethylidene)amino]-3-phenylacrylate (*Z*-4u)



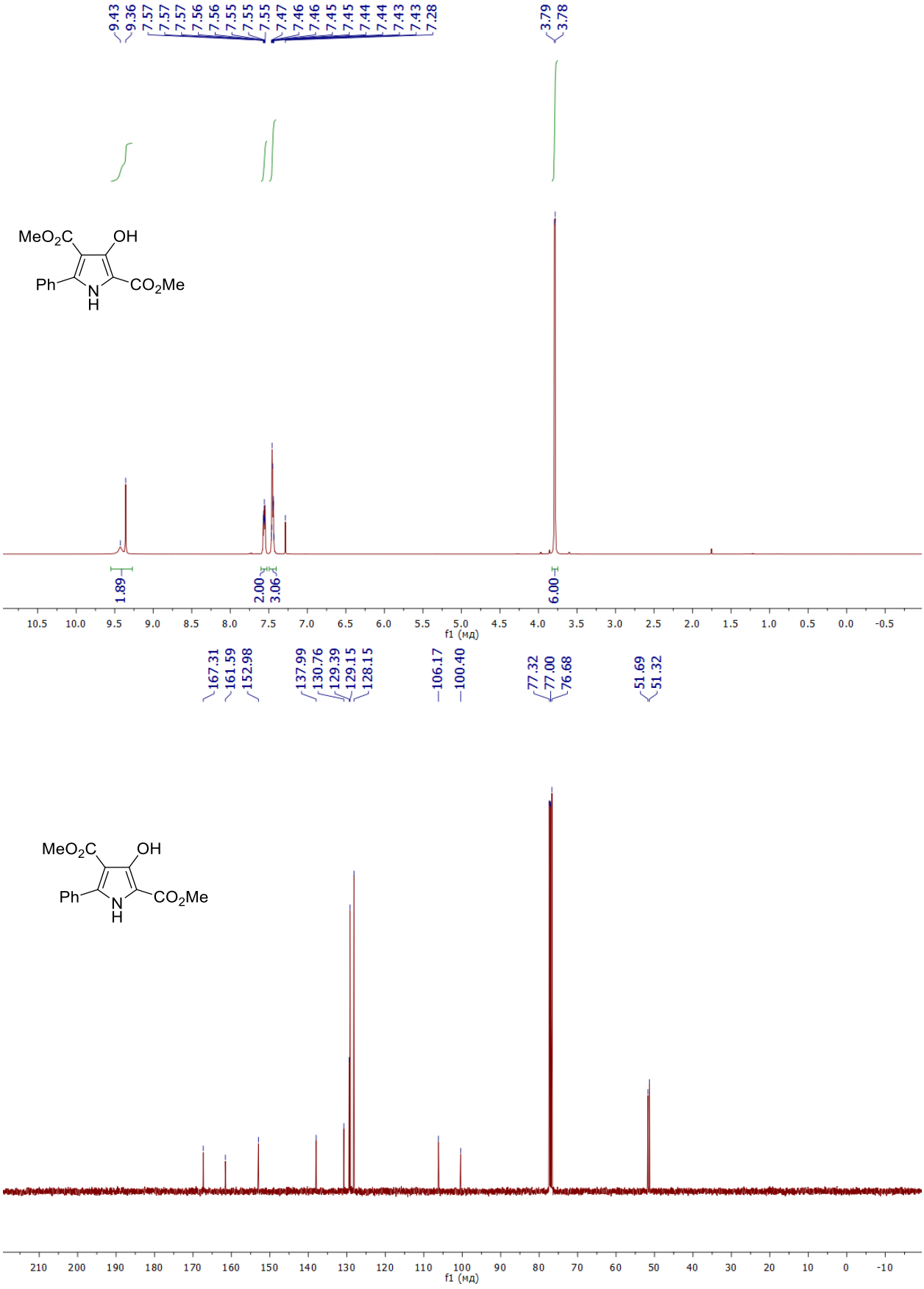


Dimethyl 5-(furan-2-yl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5a)

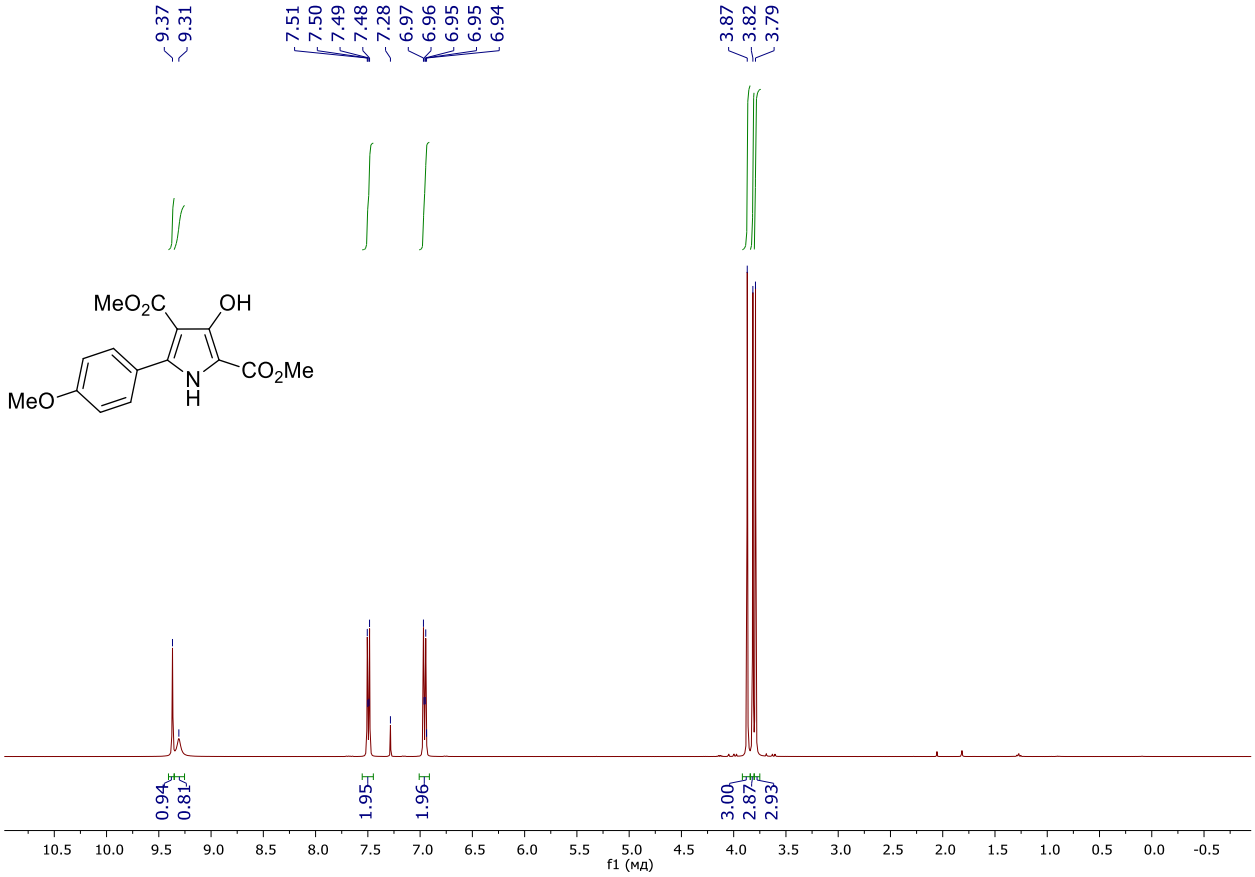


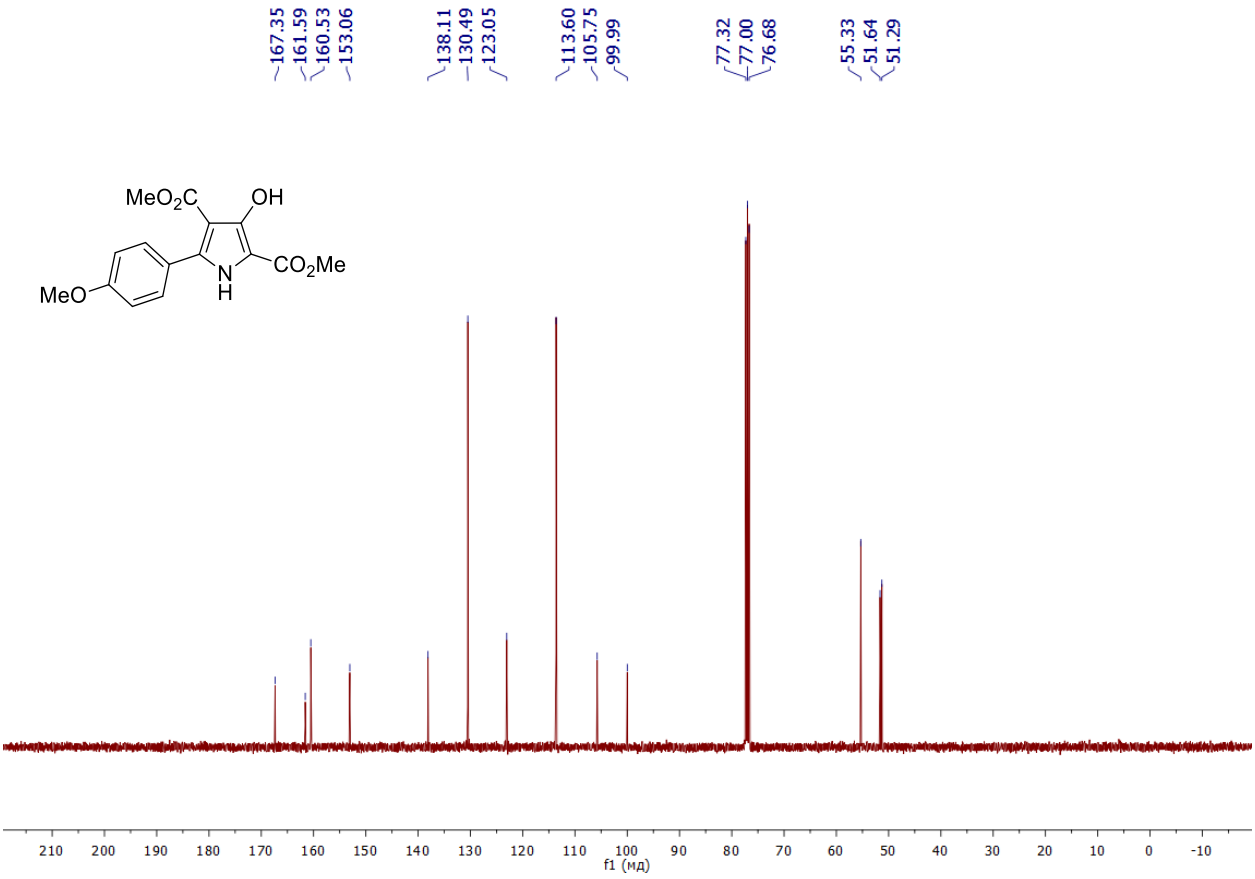


Dimethyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5b)

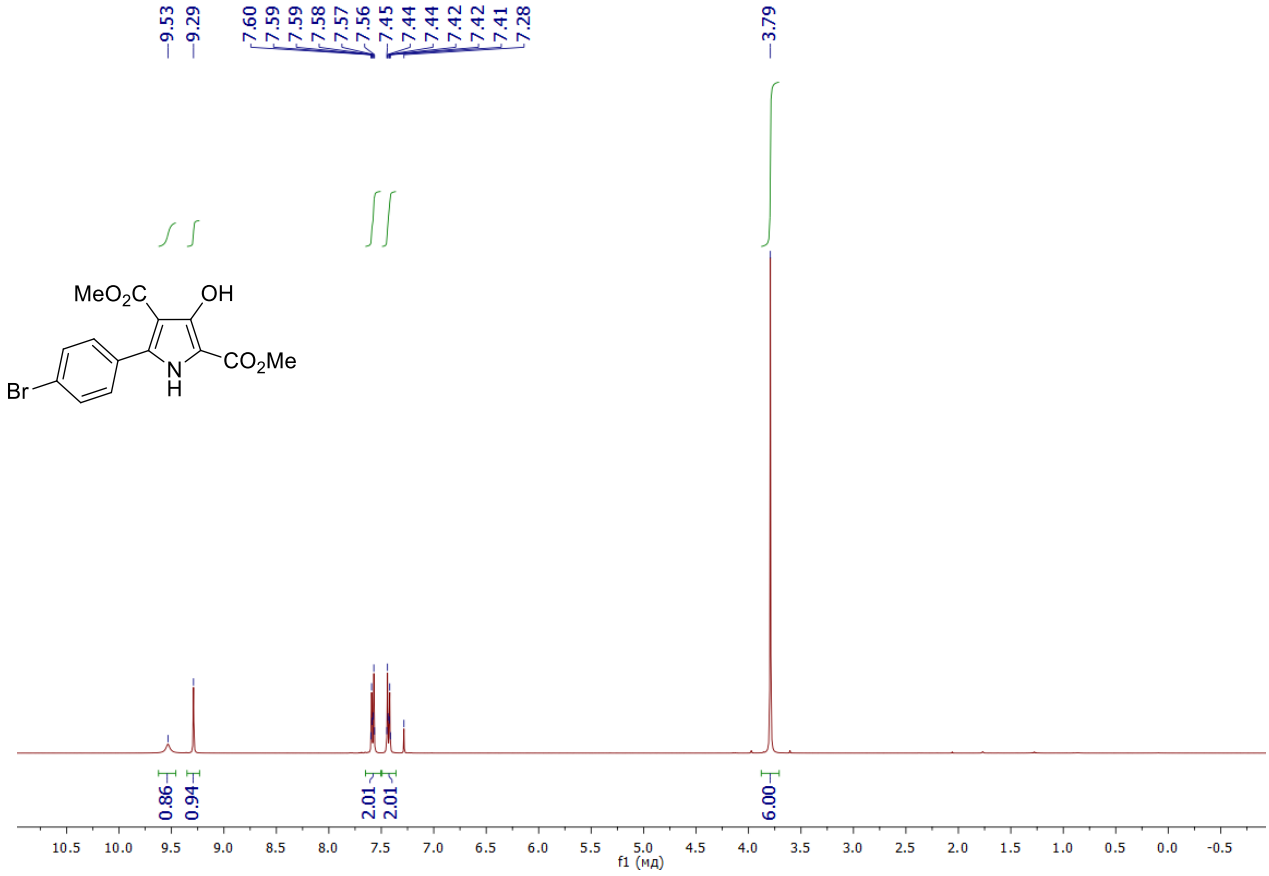


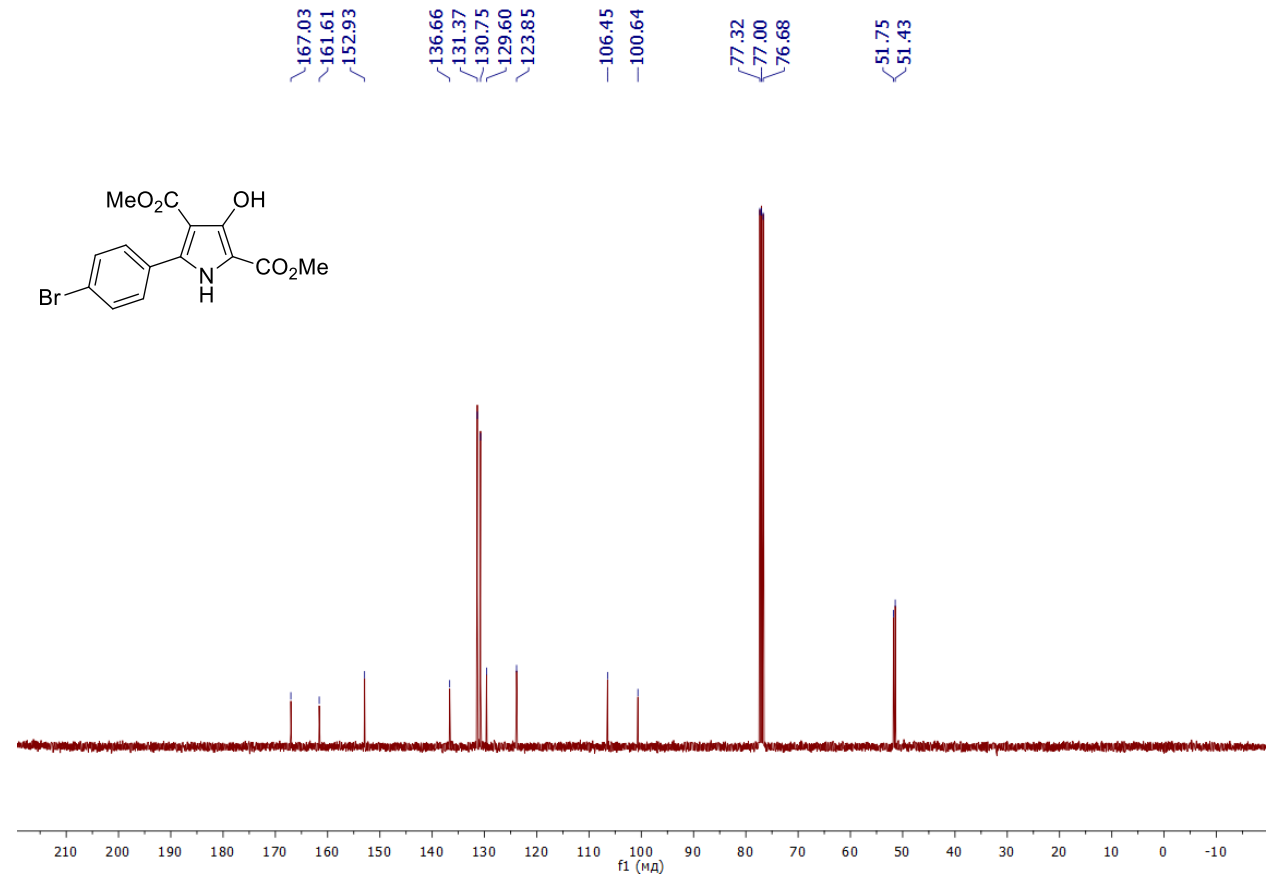
Dimethyl 3-hydroxy-5-(4-methoxyphenyl)-1*H*-pyrrole-2,4-dicarboxylate (5c)



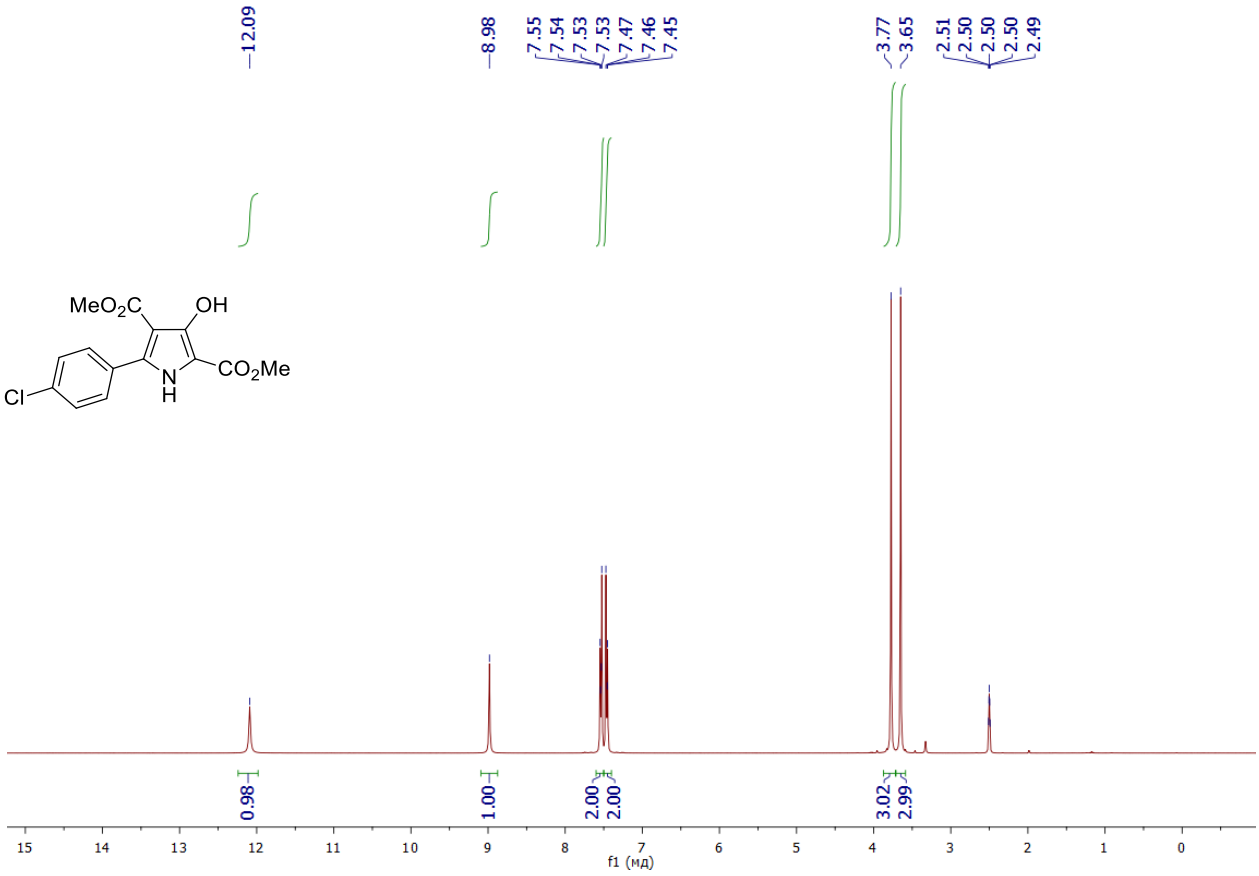


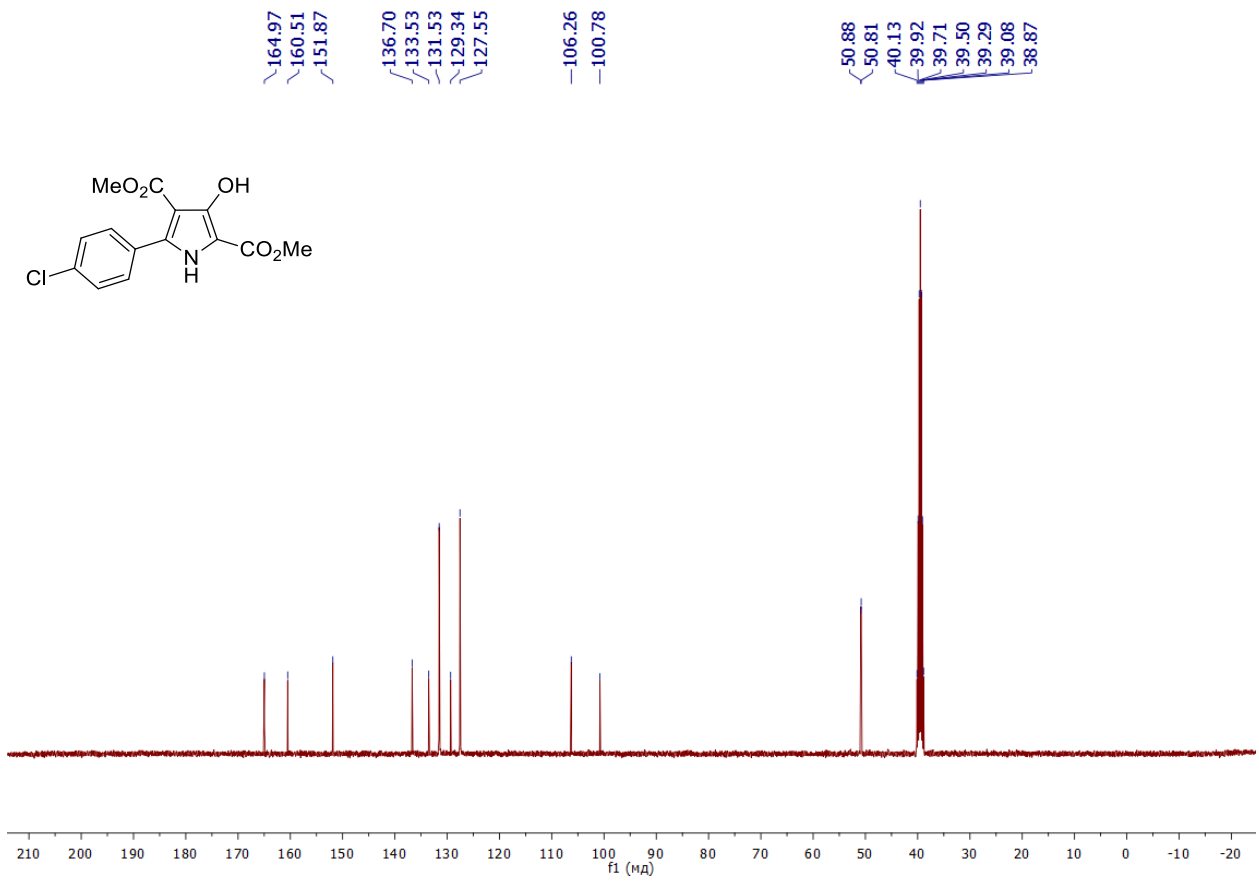
Dimethyl 5-(4-bromophenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5d)



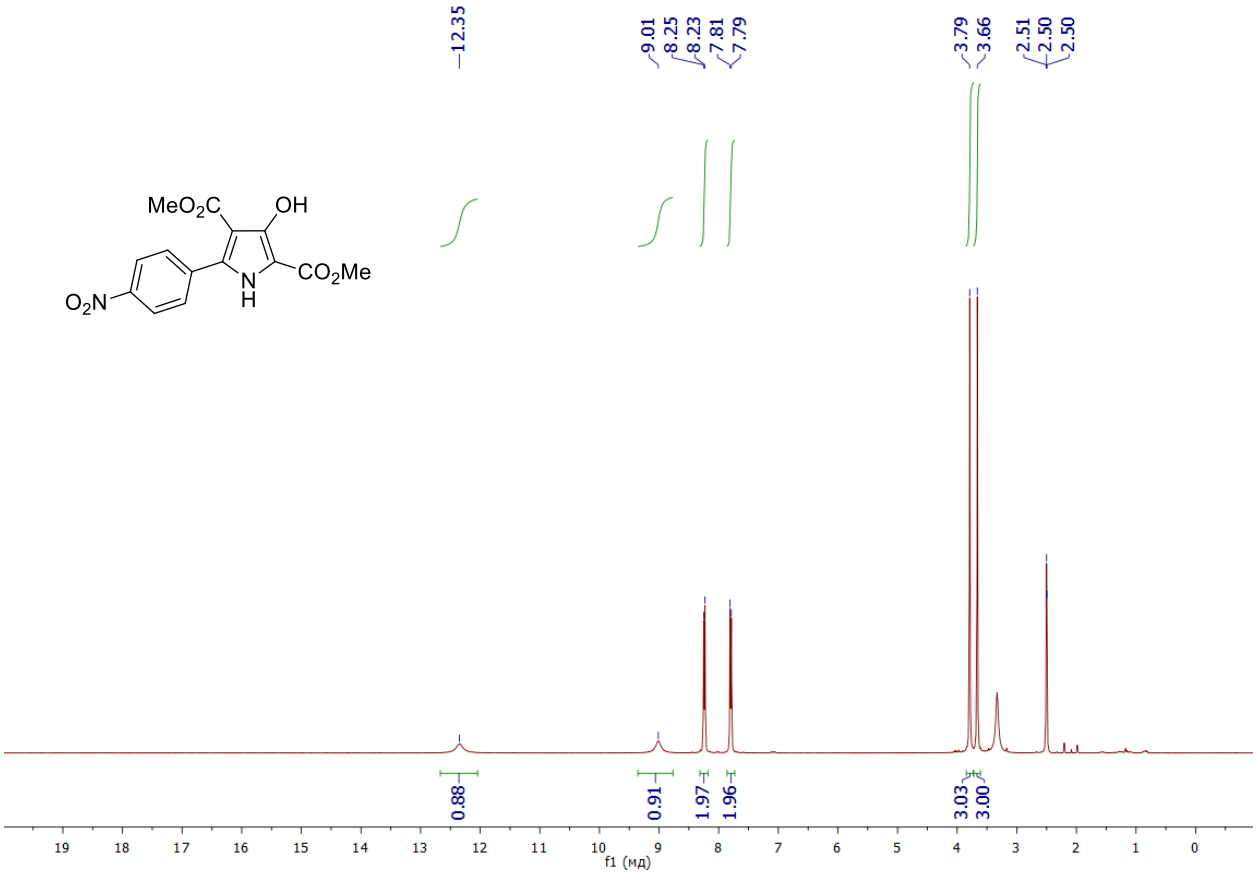


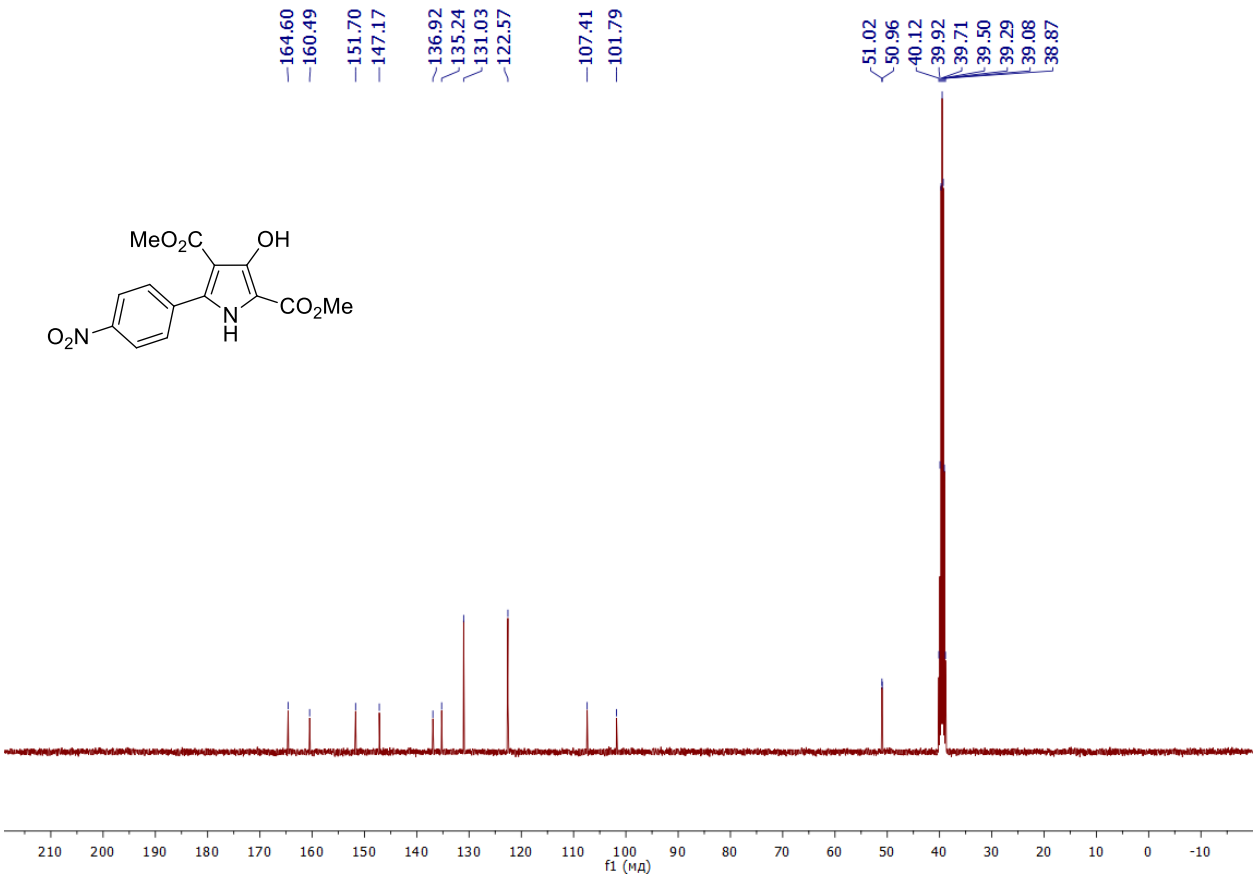
Dimethyl 5-(4-chlorophenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5e)



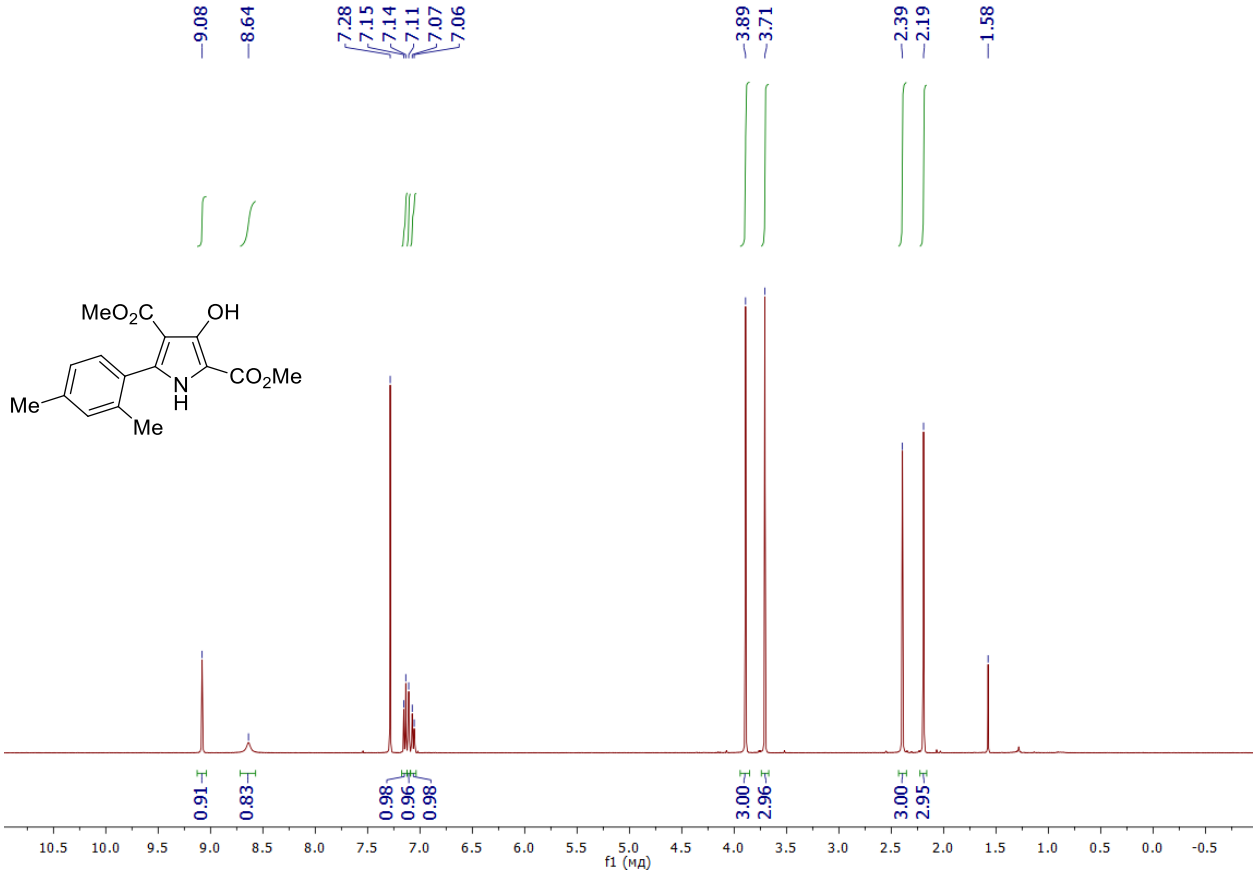


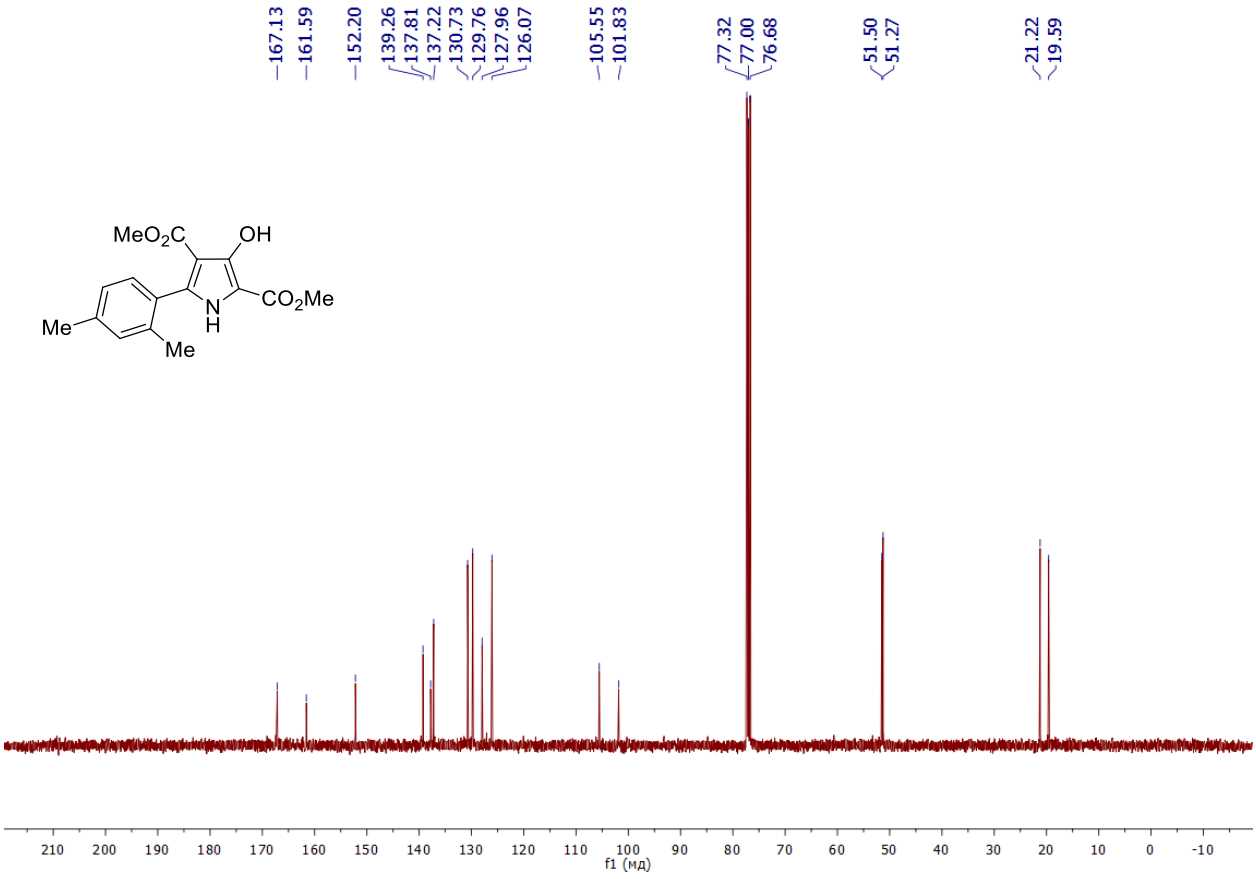
Dimethyl 3-hydroxy-5-(4-nitrophenyl)-1*H*-pyrrole-2,4-dicarboxylate (5f)



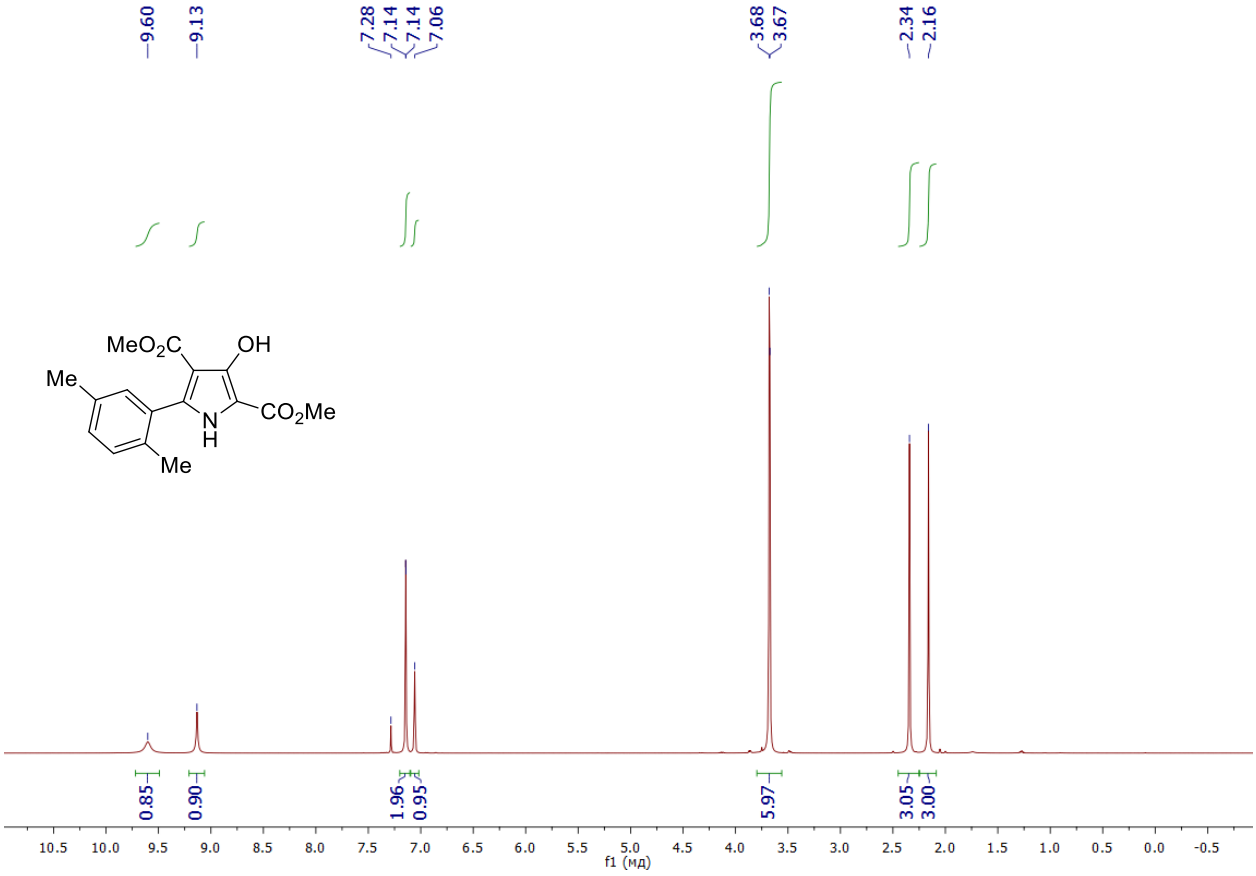


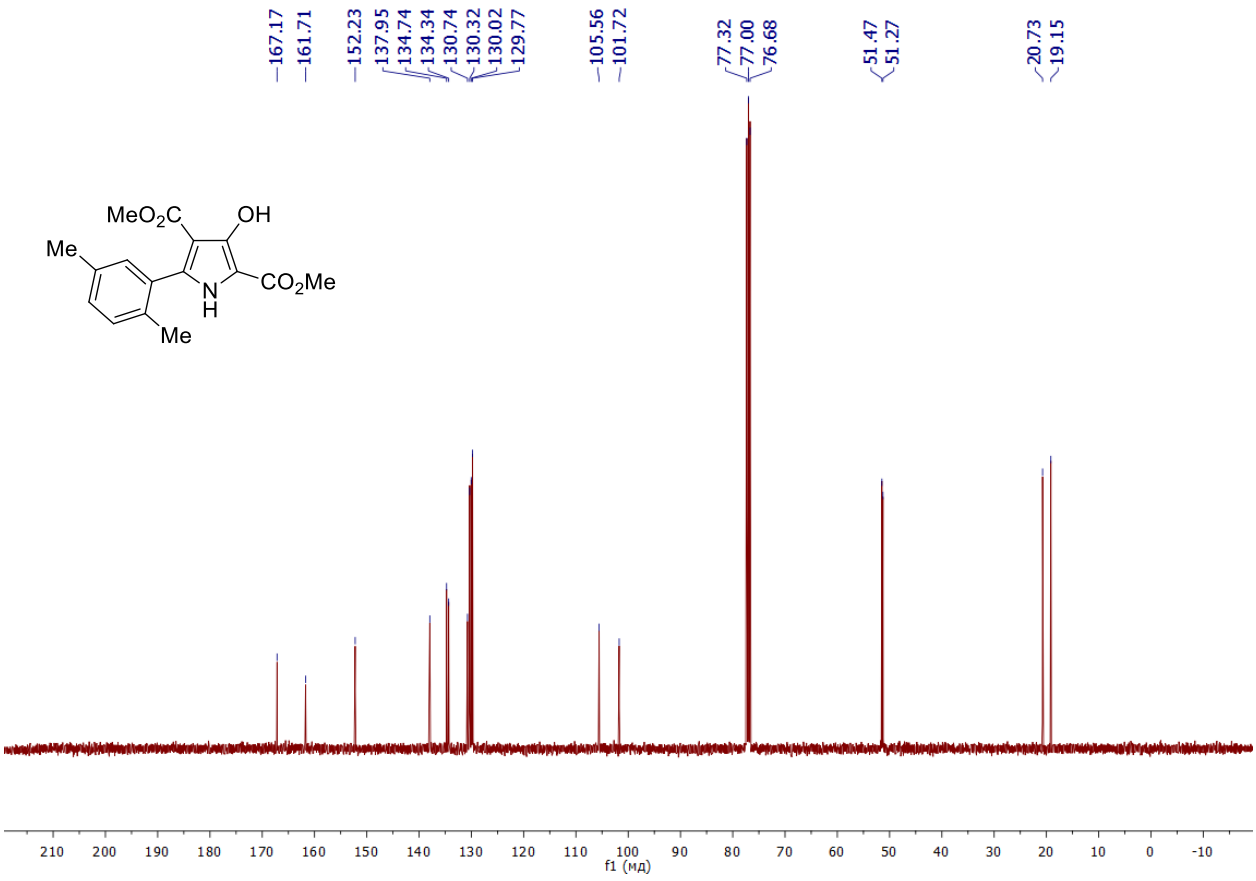
Dimethyl 5-(2,4-dimethylphenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5g)



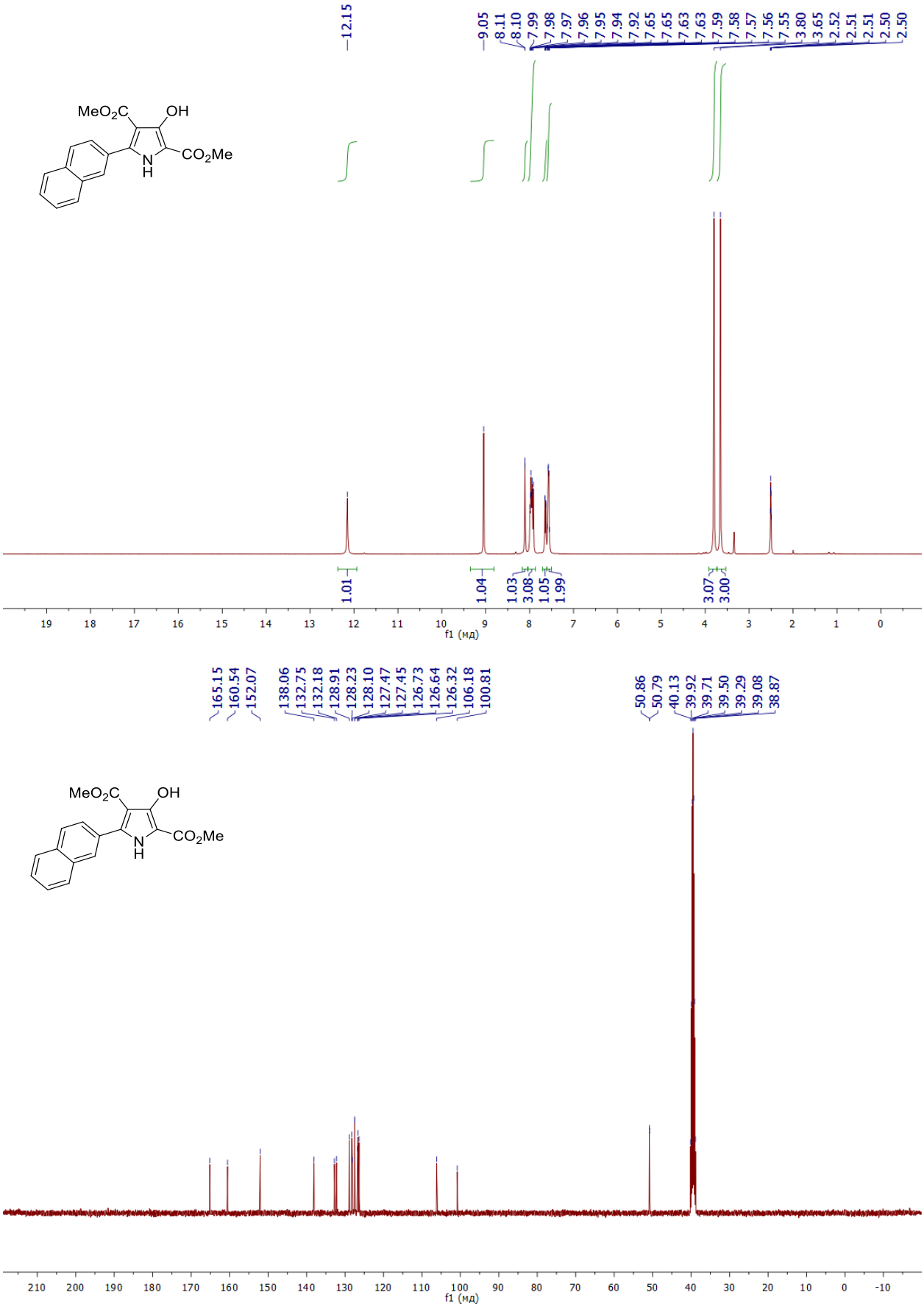


Dimethyl 5-(2,5-dimethylphenyl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5h)

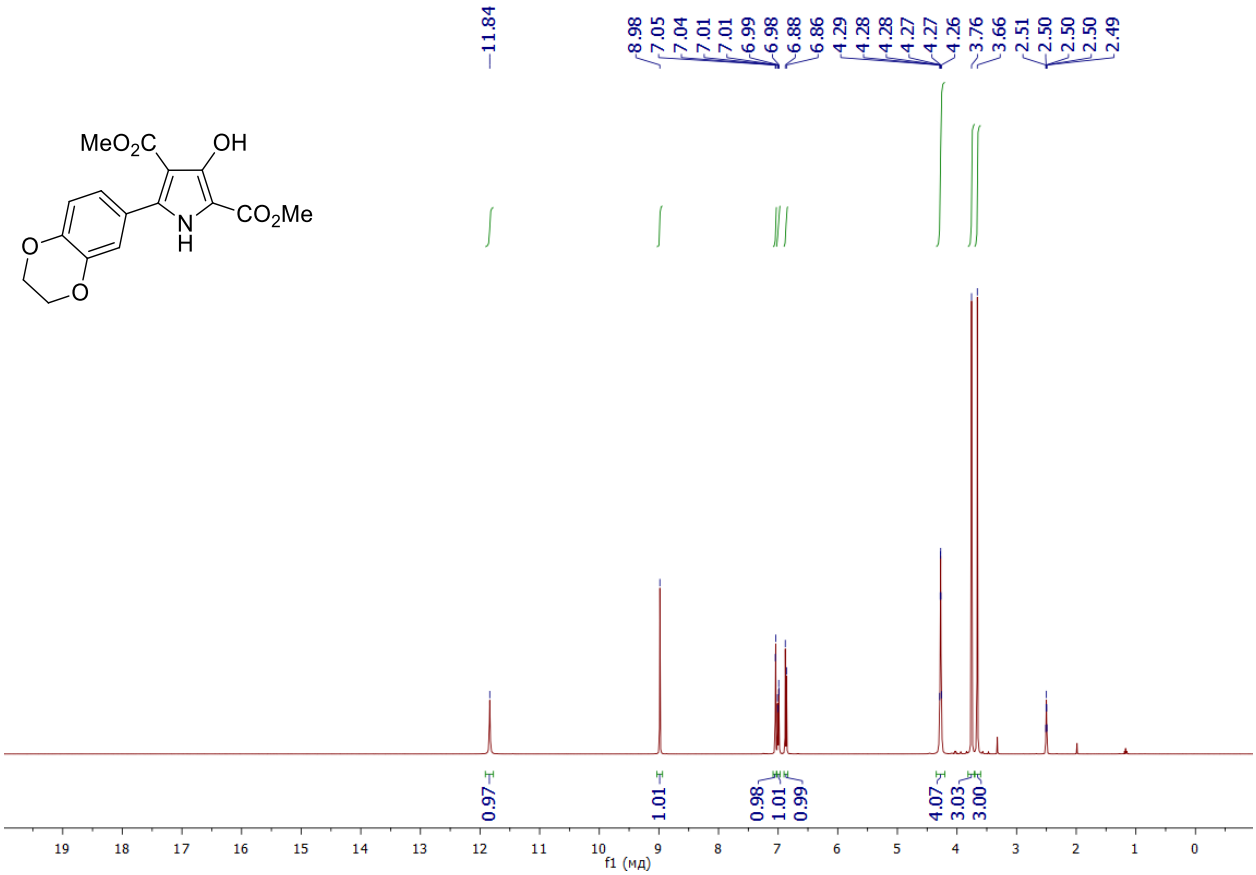


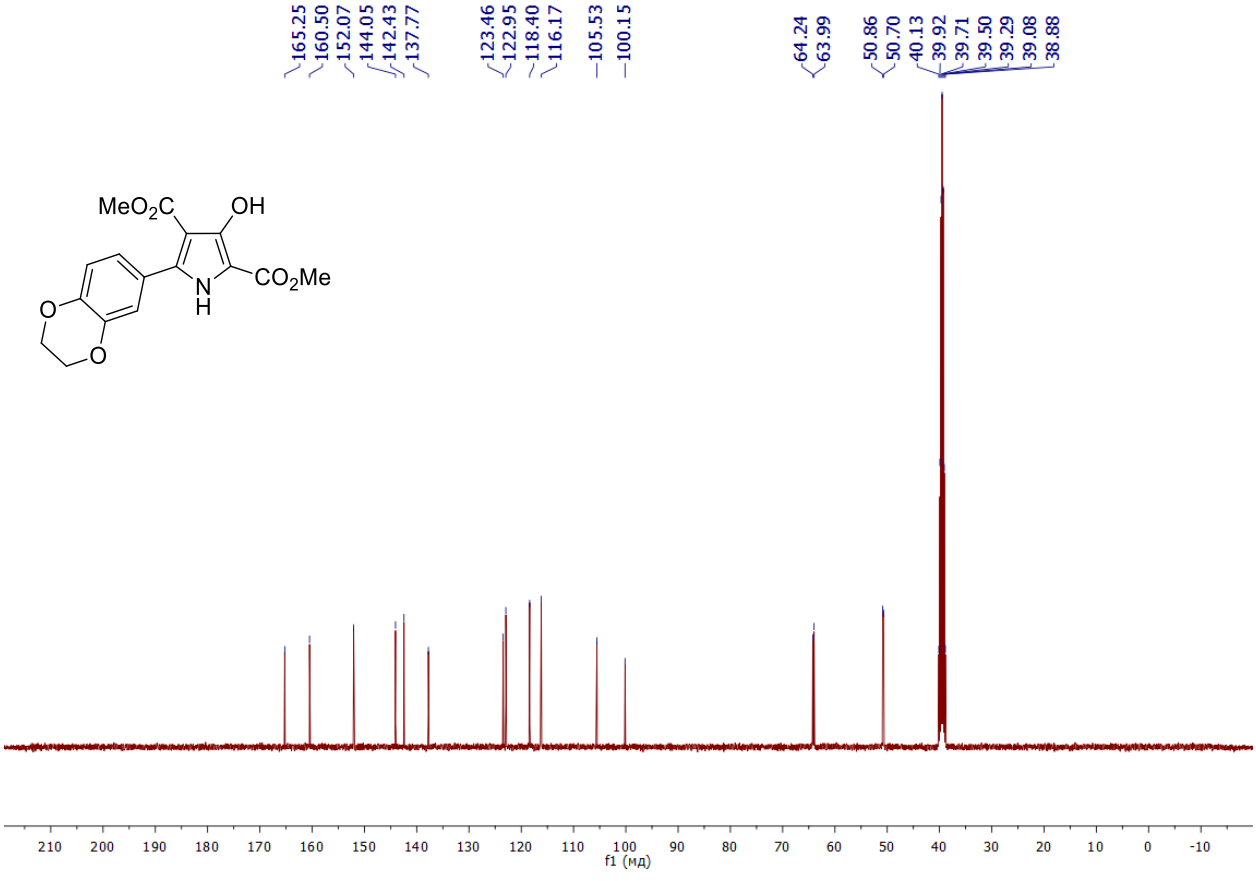


Dimethyl 3-hydroxy-5-(naphthalen-2-yl)-1*H*-pyrrole-2,4-dicarboxylate (5i)

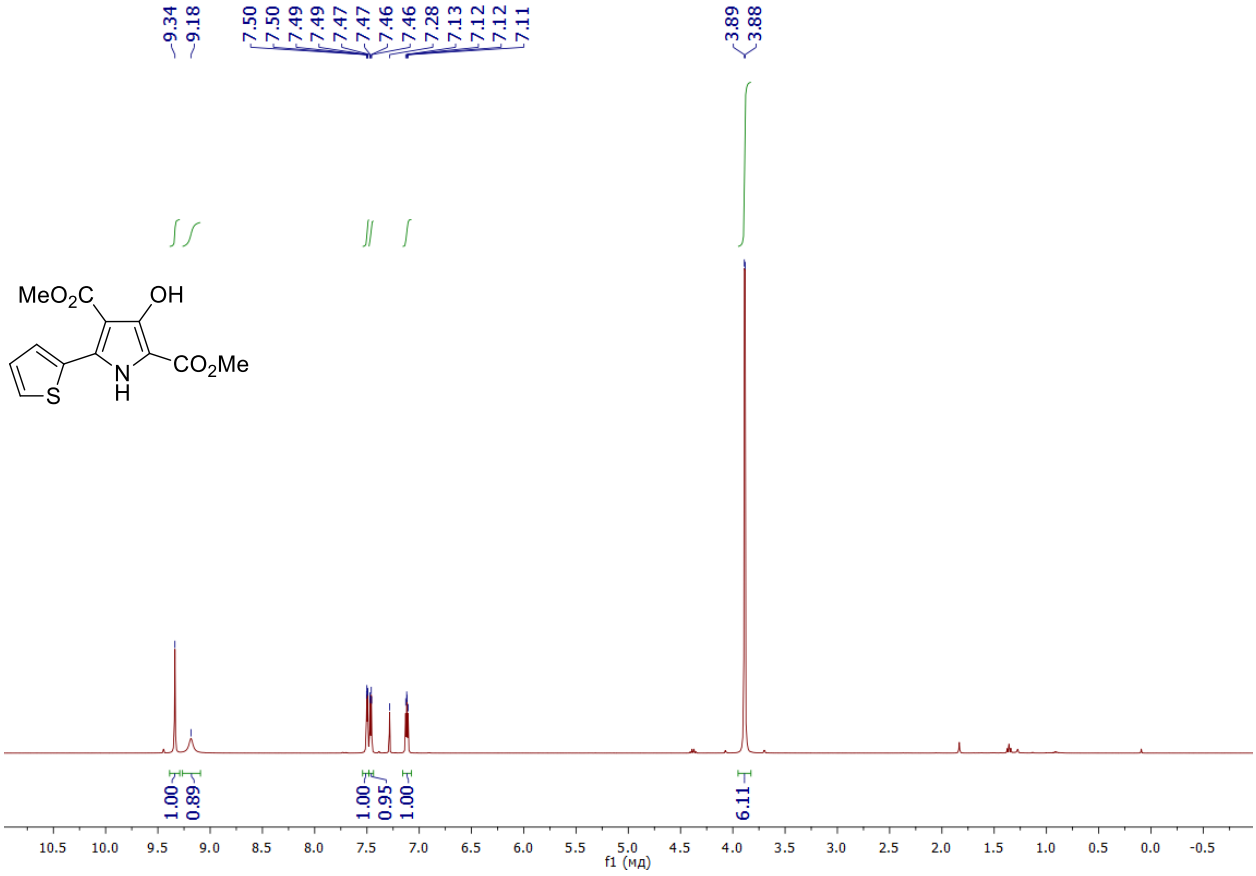


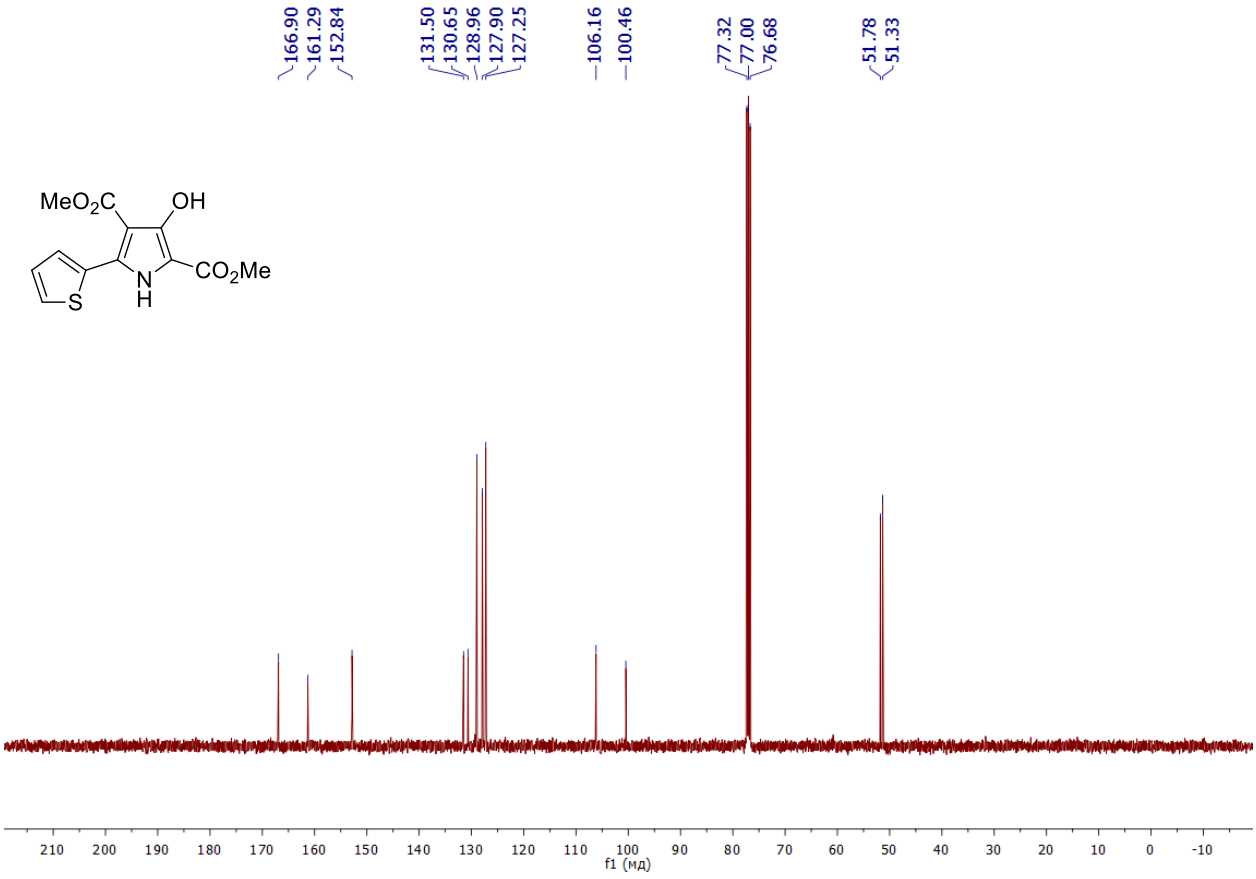
Dimethyl 5-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-hydroxy-1*H*-pyrrole-2,4-dicarboxylate (5j)



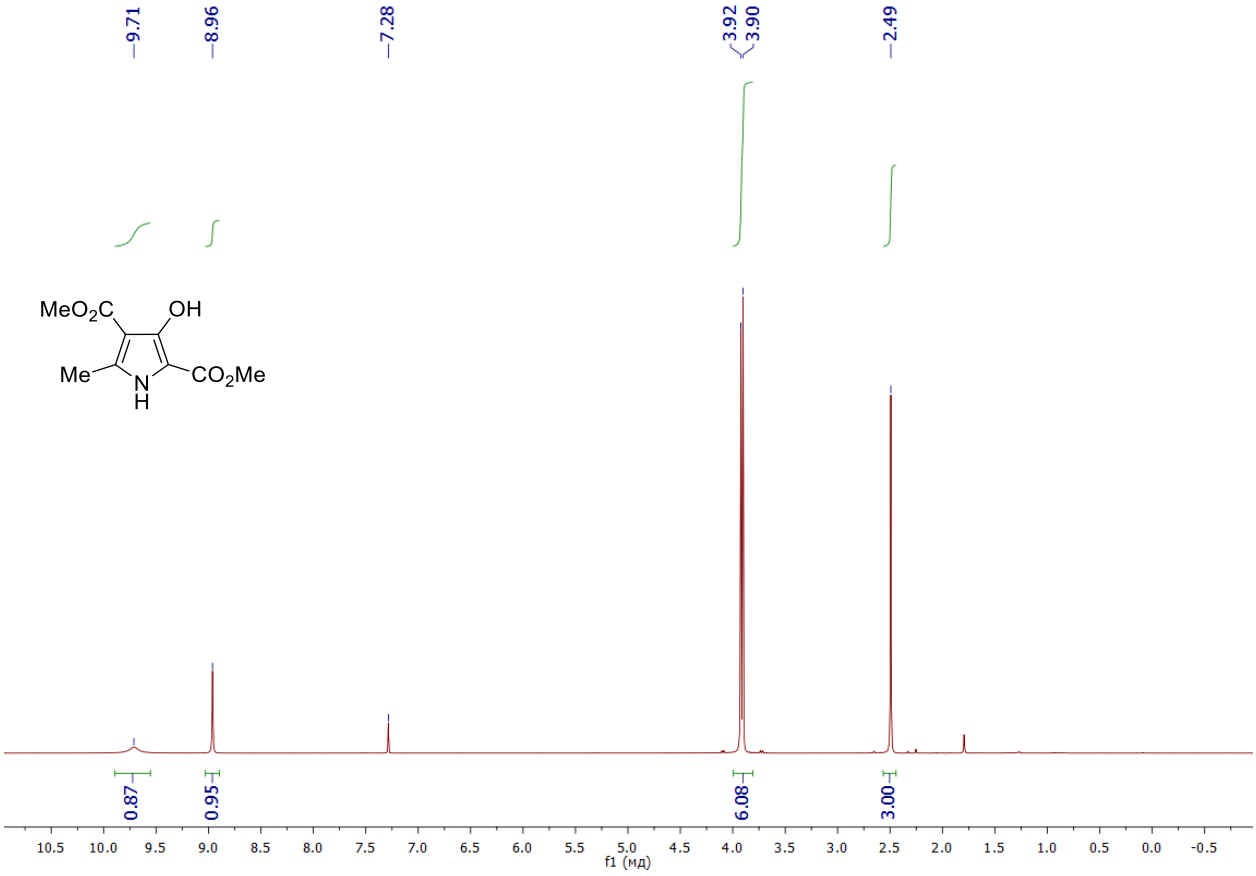


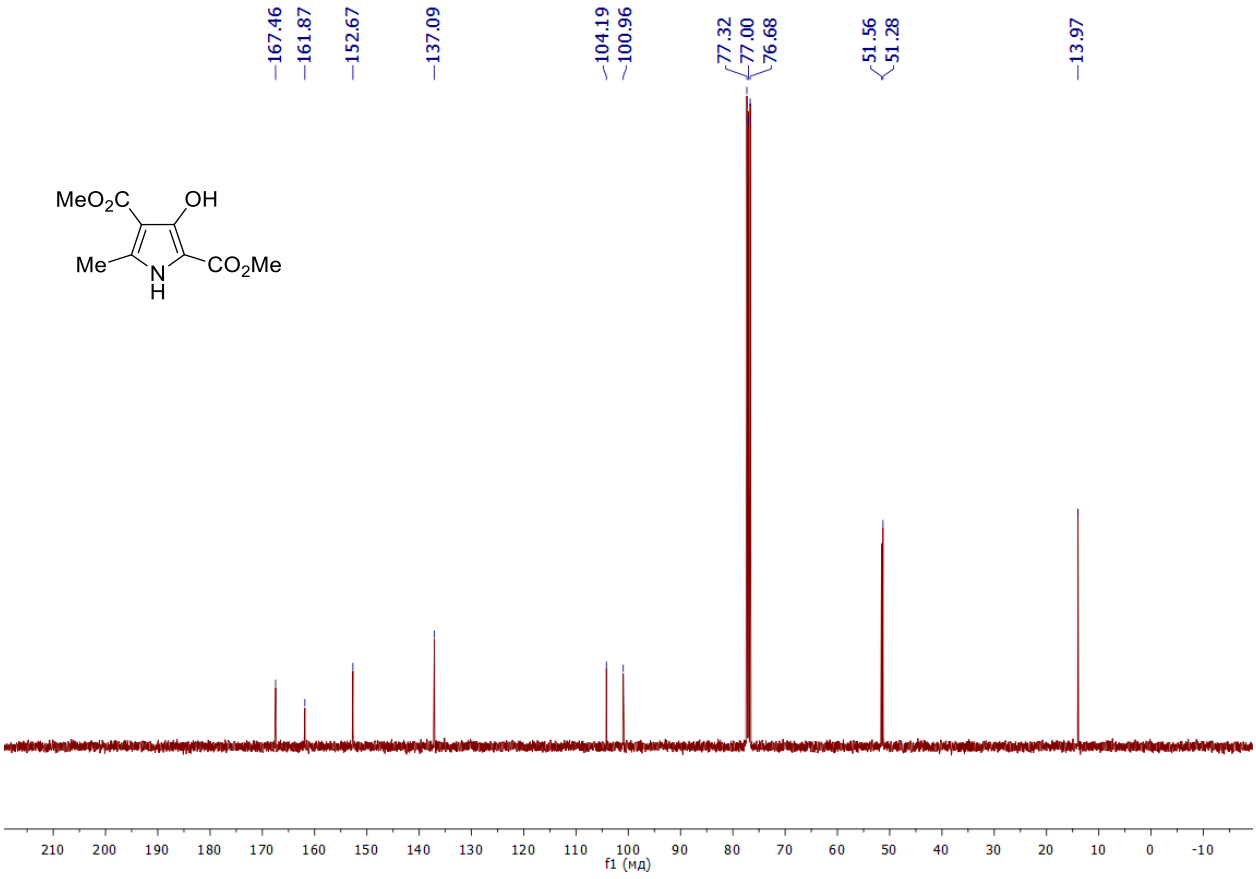
Dimethyl 3-hydroxy-5-(thiophen-2-yl)-1*H*-pyrrole-2,4-dicarboxylate (5k)



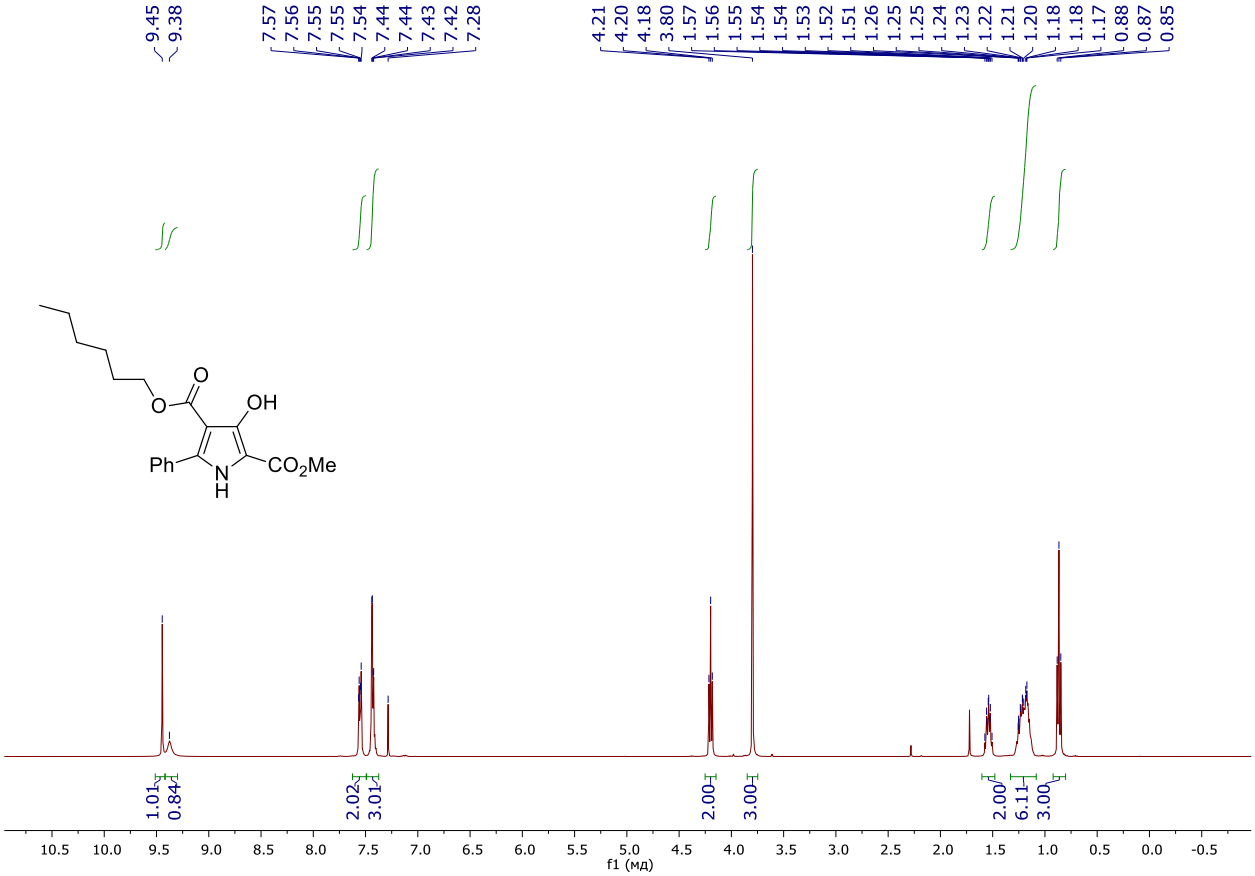


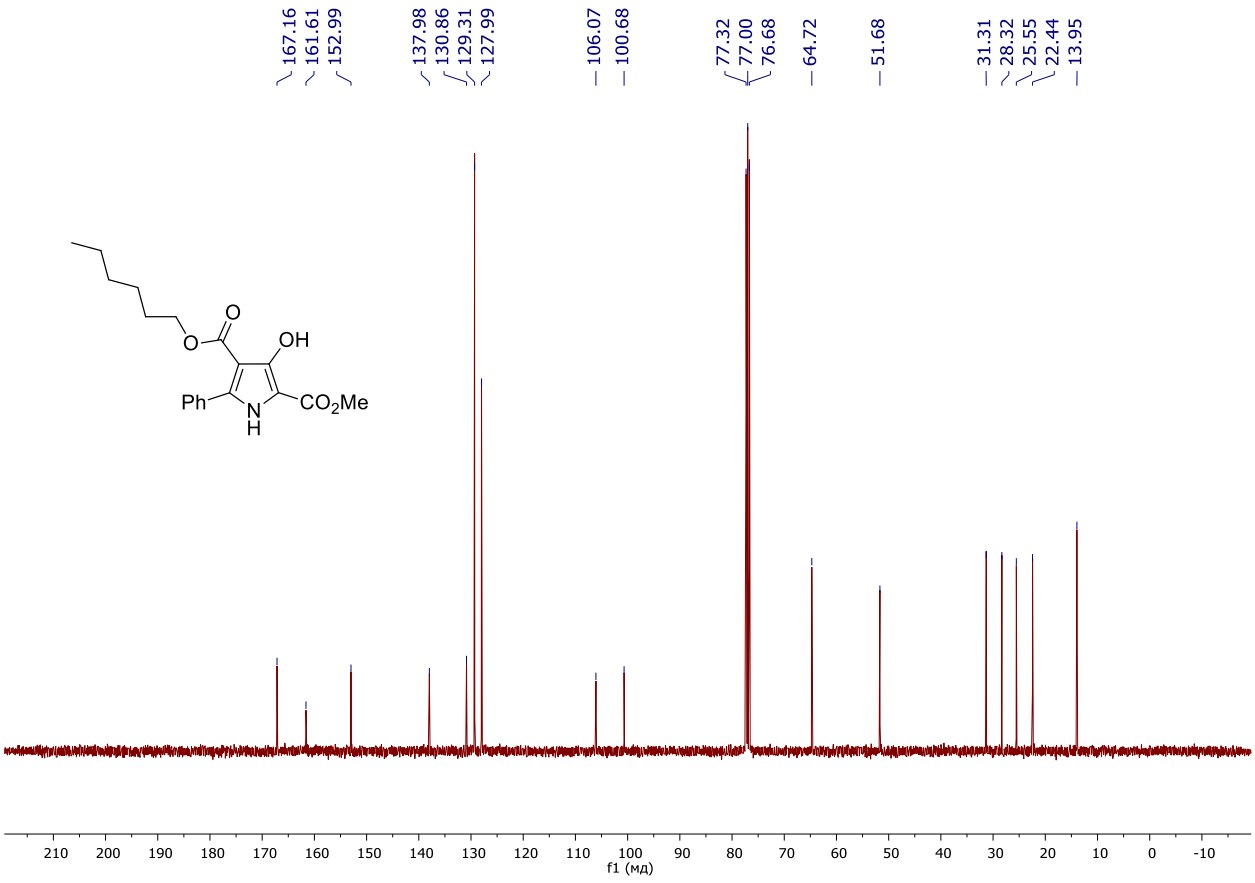
Dimethyl 3-hydroxy-5-methyl-1*H*-pyrrole-2,4-dicarboxylate (5l)



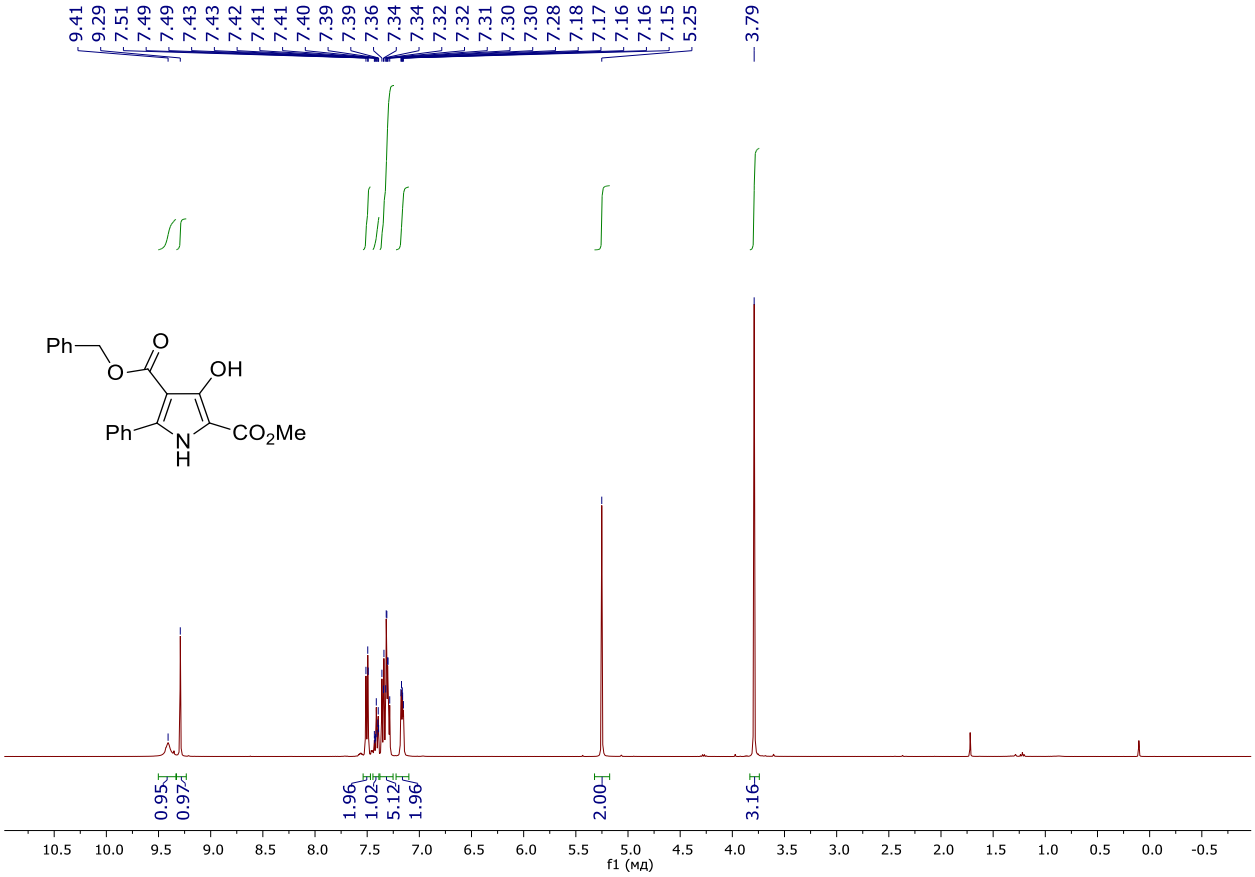


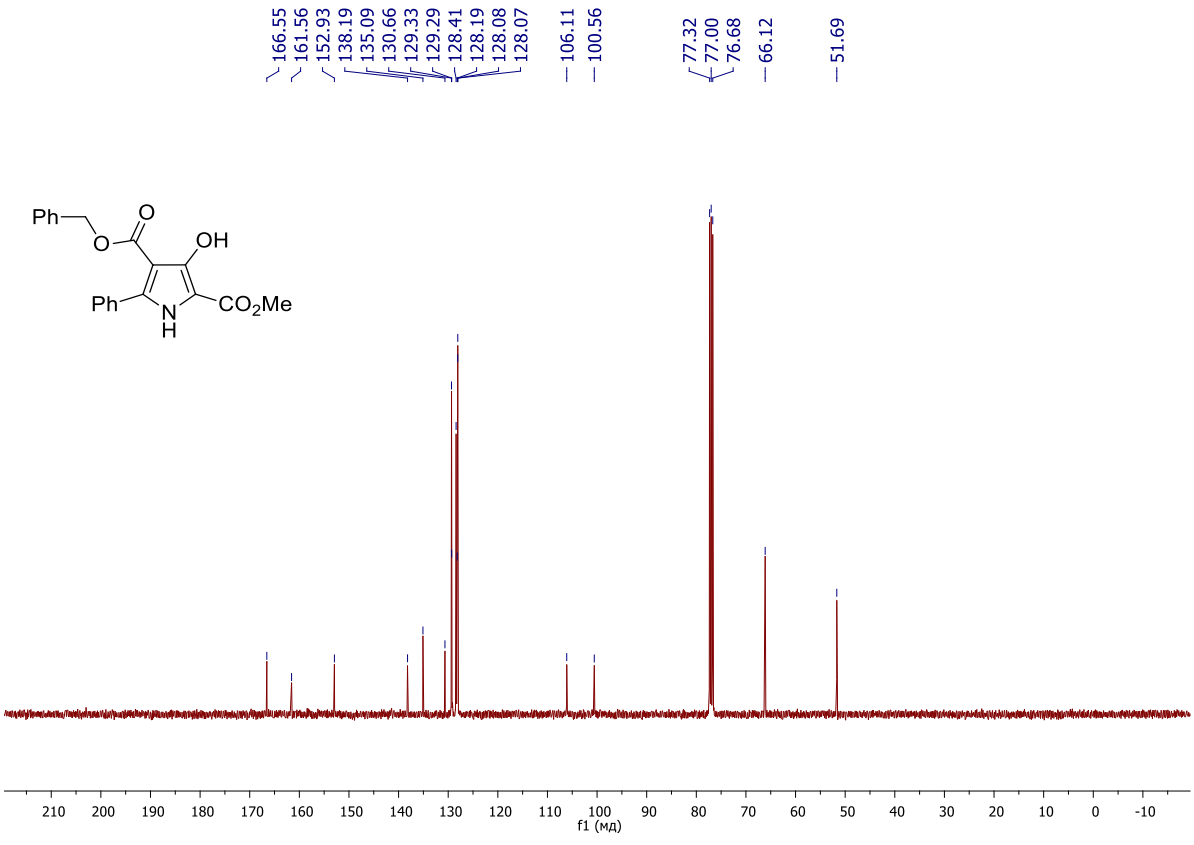
4-Hexyl 2-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5m)



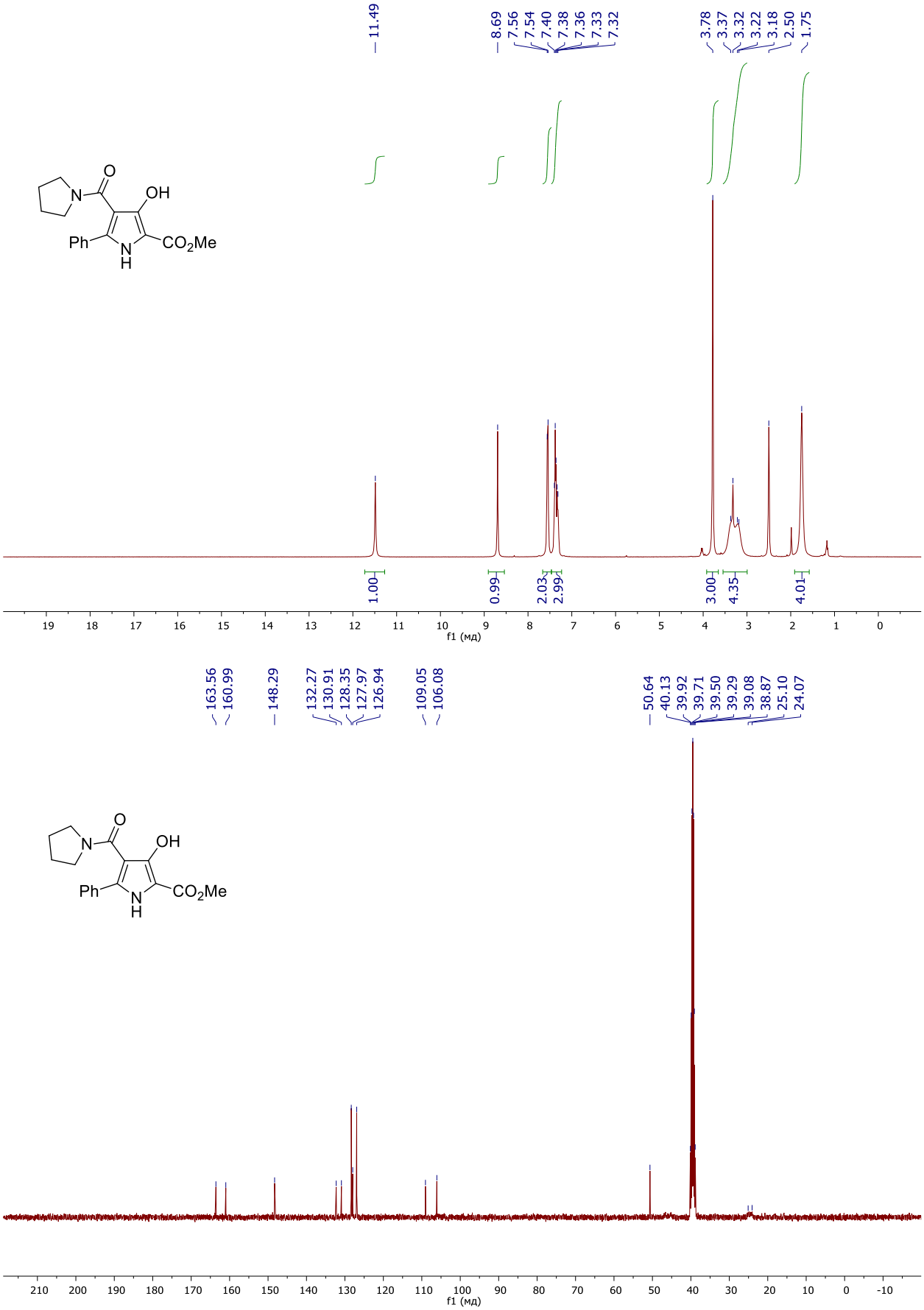


4-Benzyl 2-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5n)

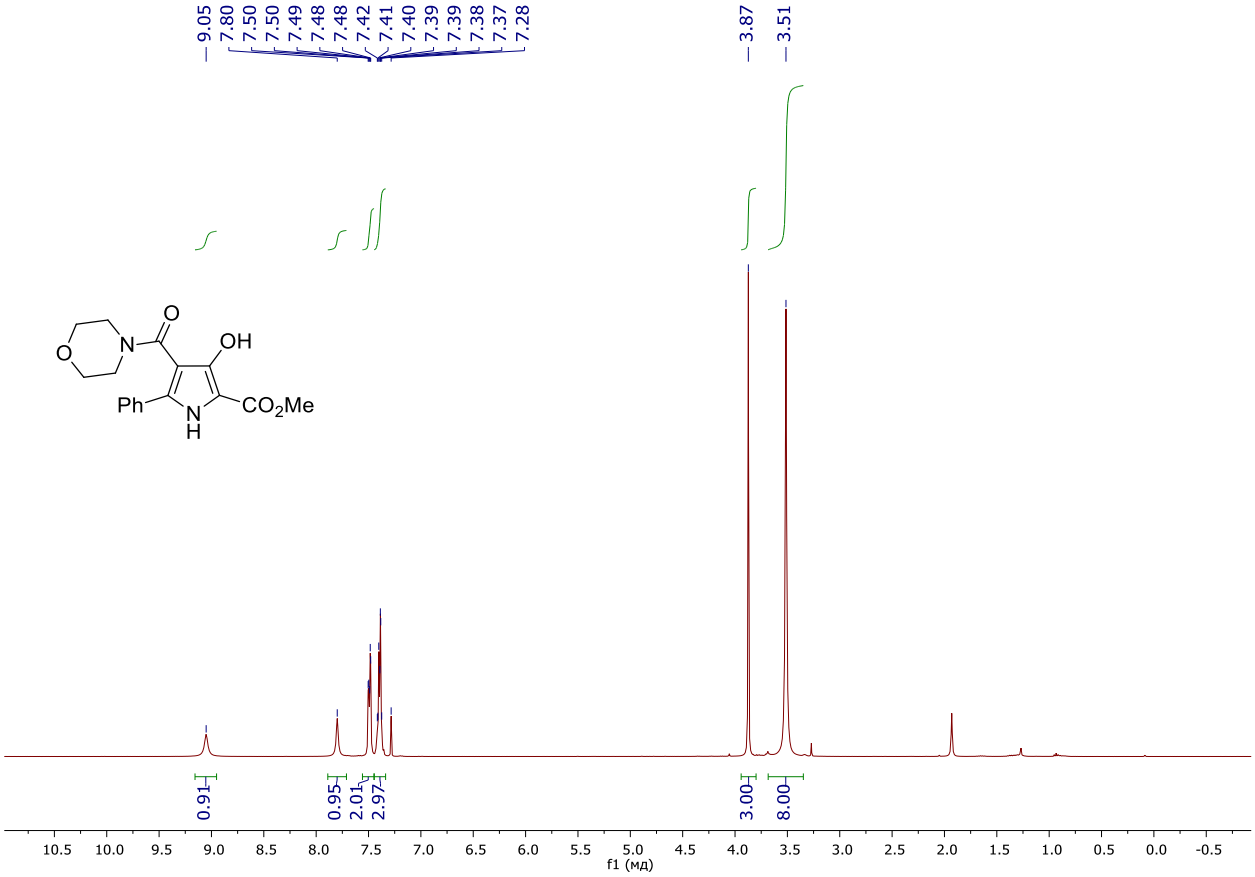


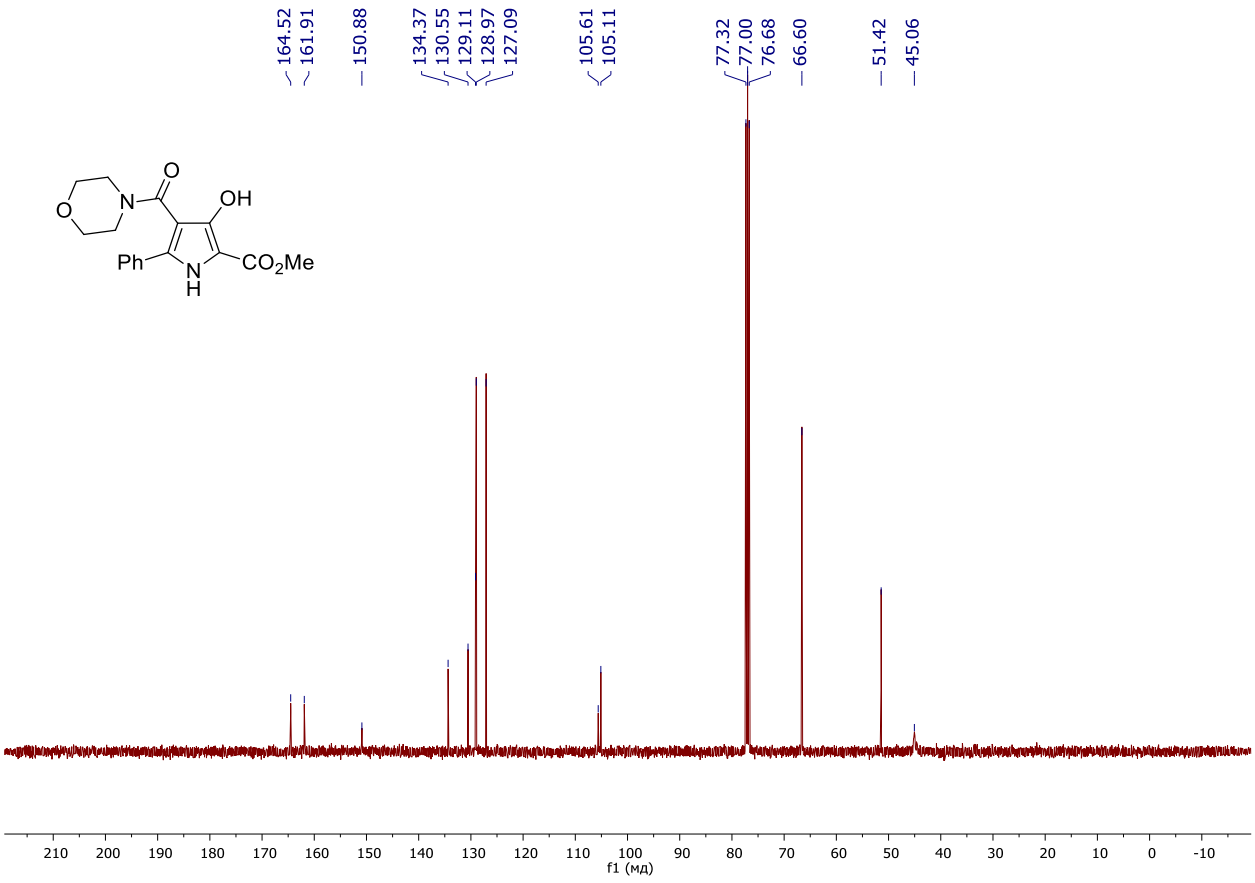


Methyl 3-hydroxy-5-phenyl-4-(pyrrolidine-1-carbonyl)-1*H*-pyrrole-2-carboxylate (5o)

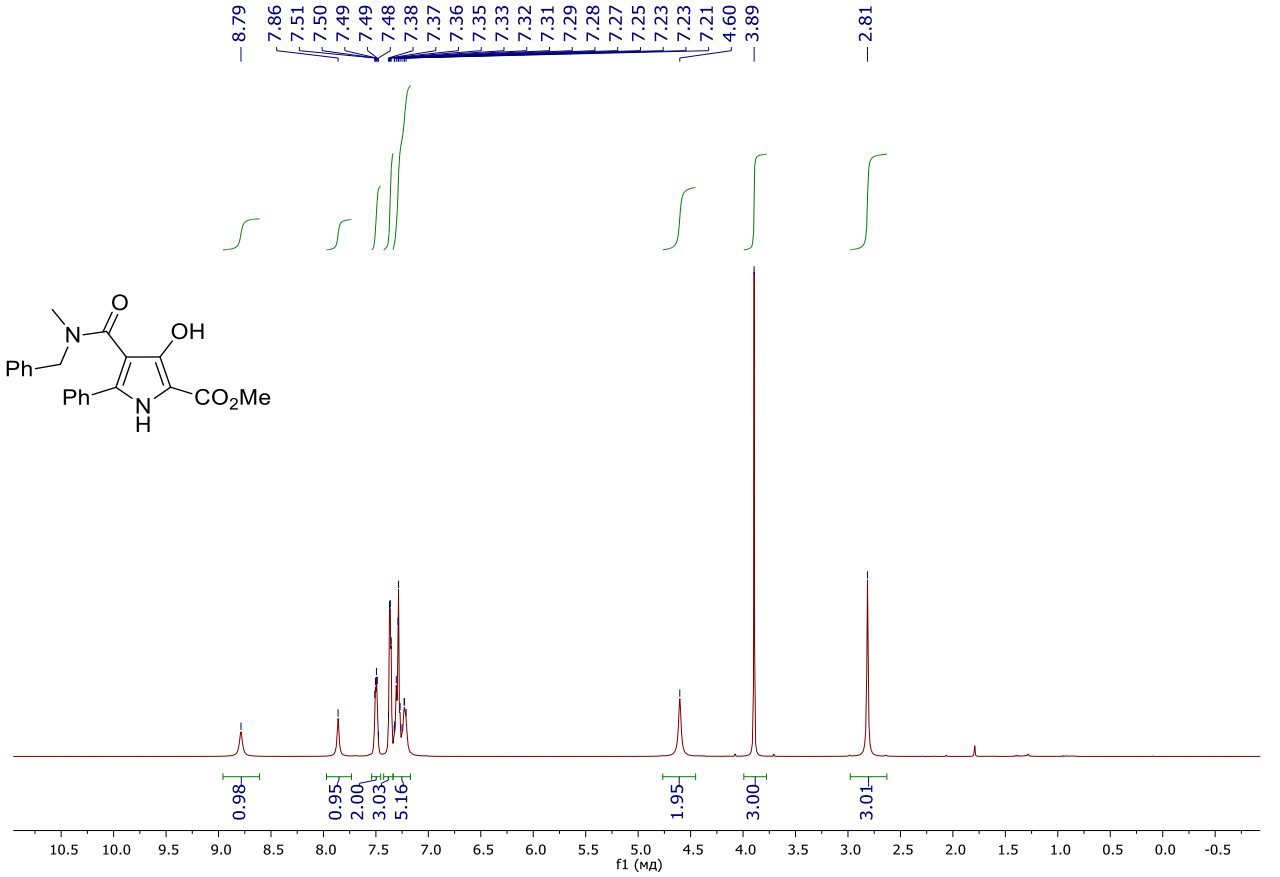


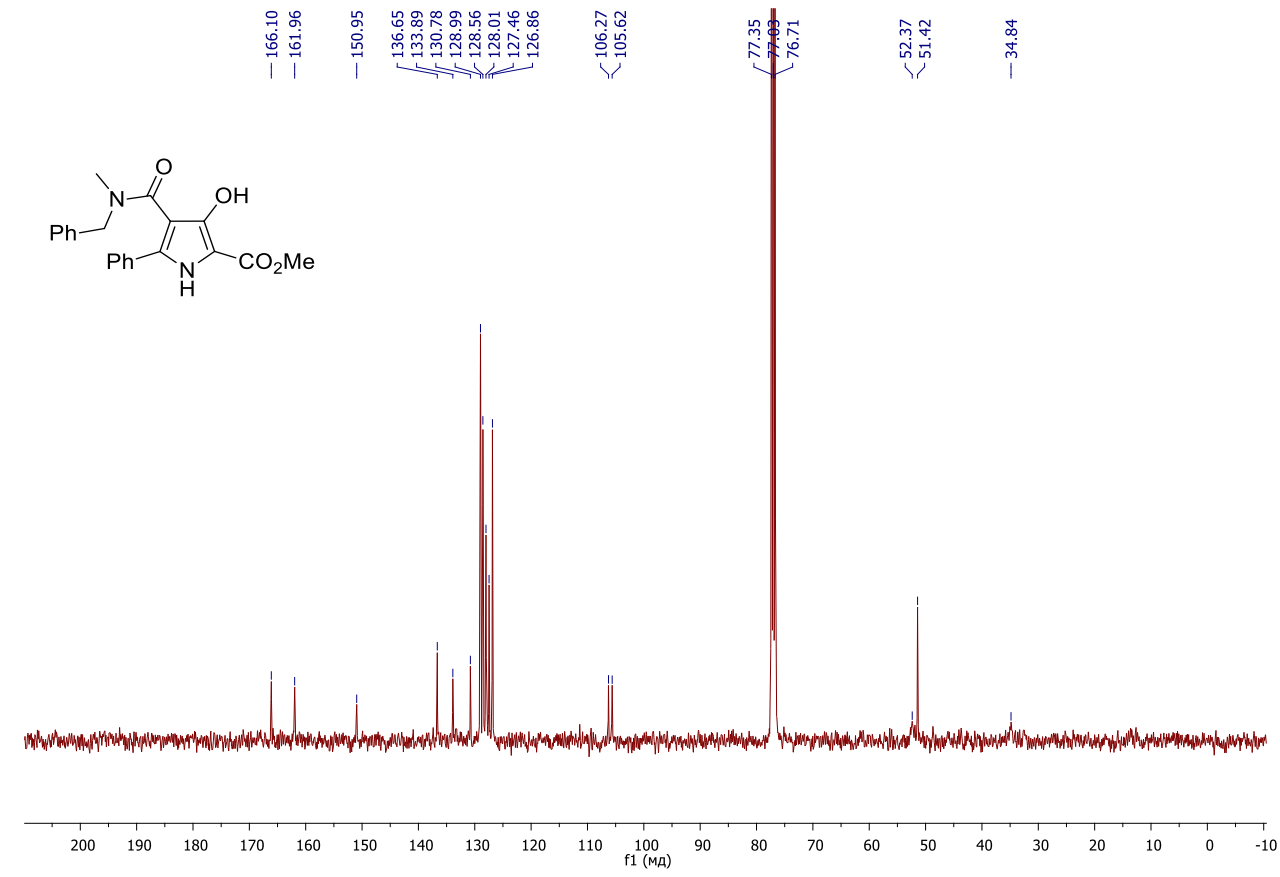
Methyl 3-hydroxy-4-(morpholine-4-carbonyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (5p)



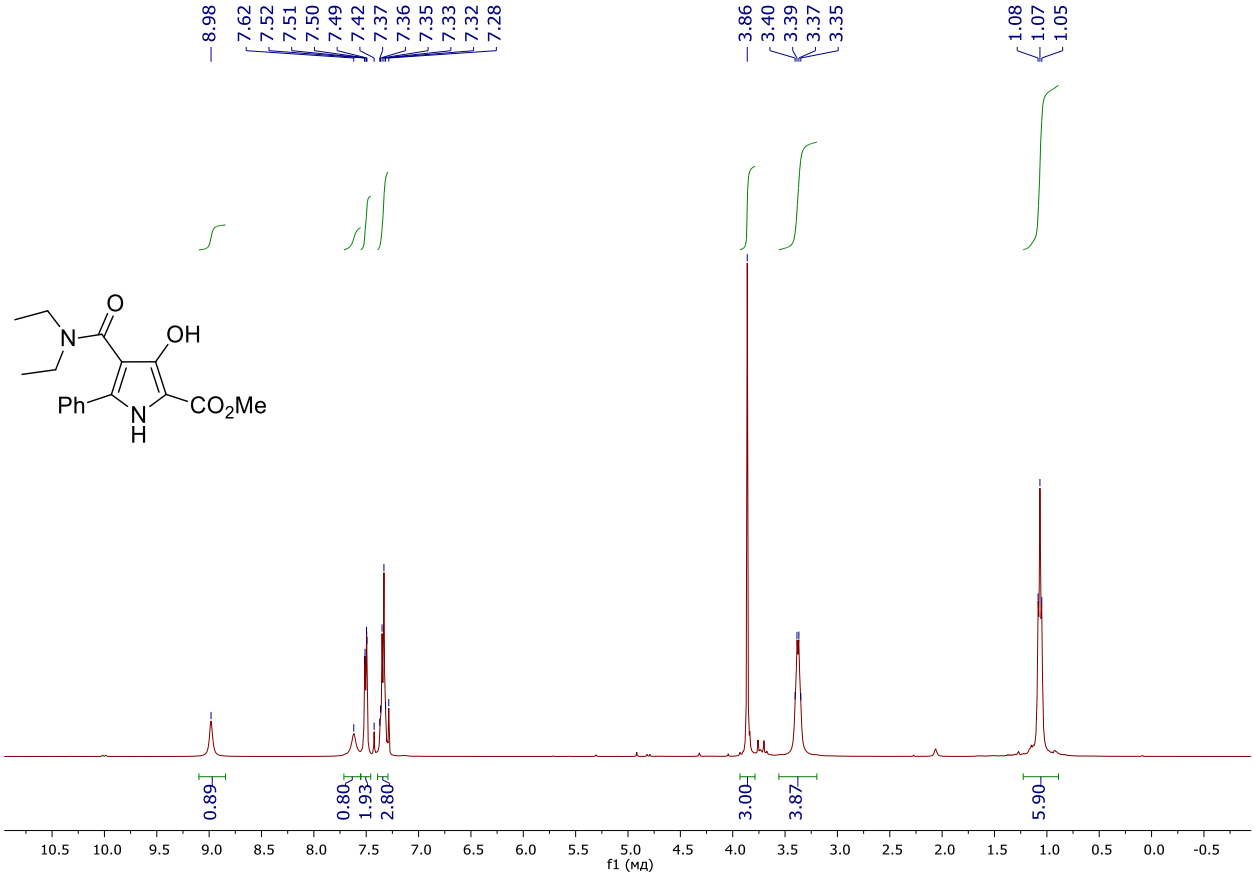


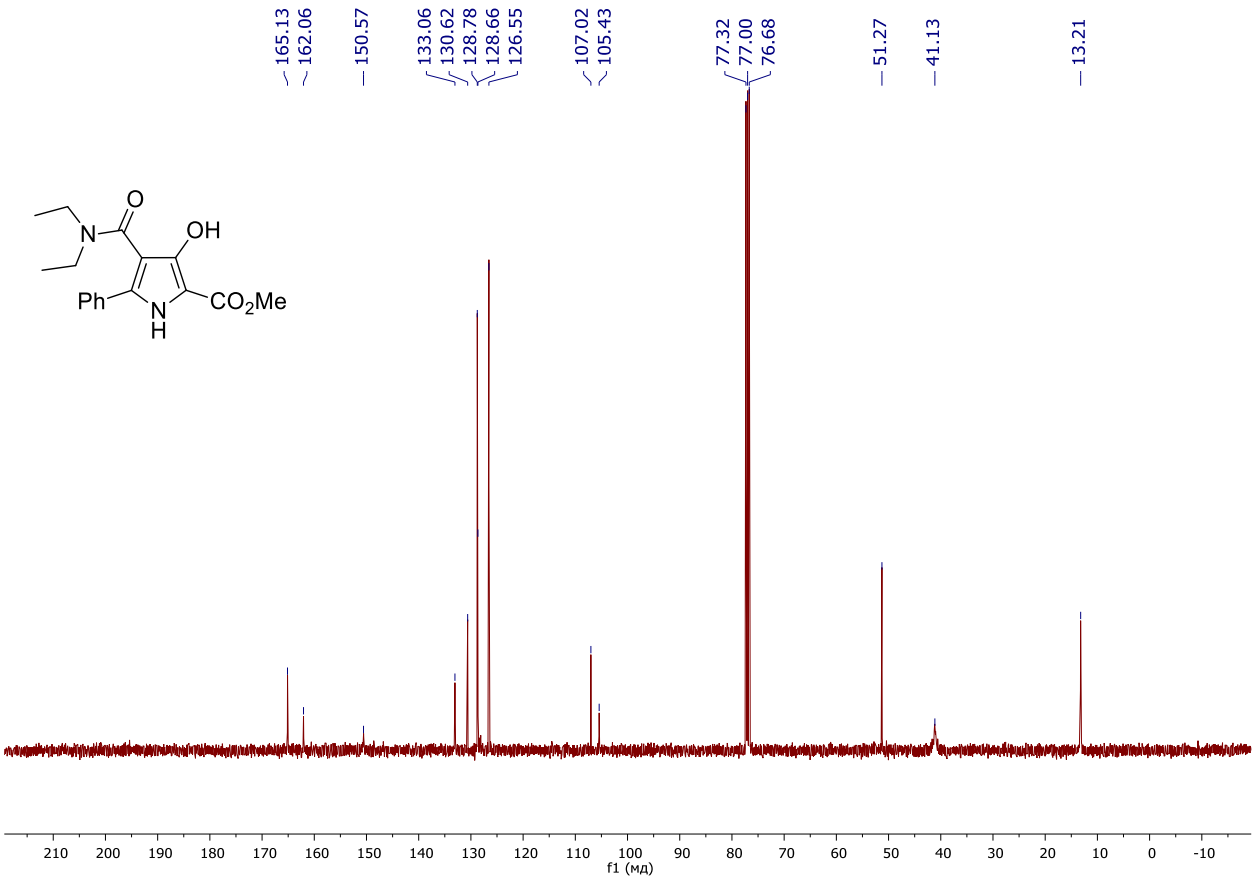
Methyl 4-(benzyl(methyl)carbamoyl)-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5q)



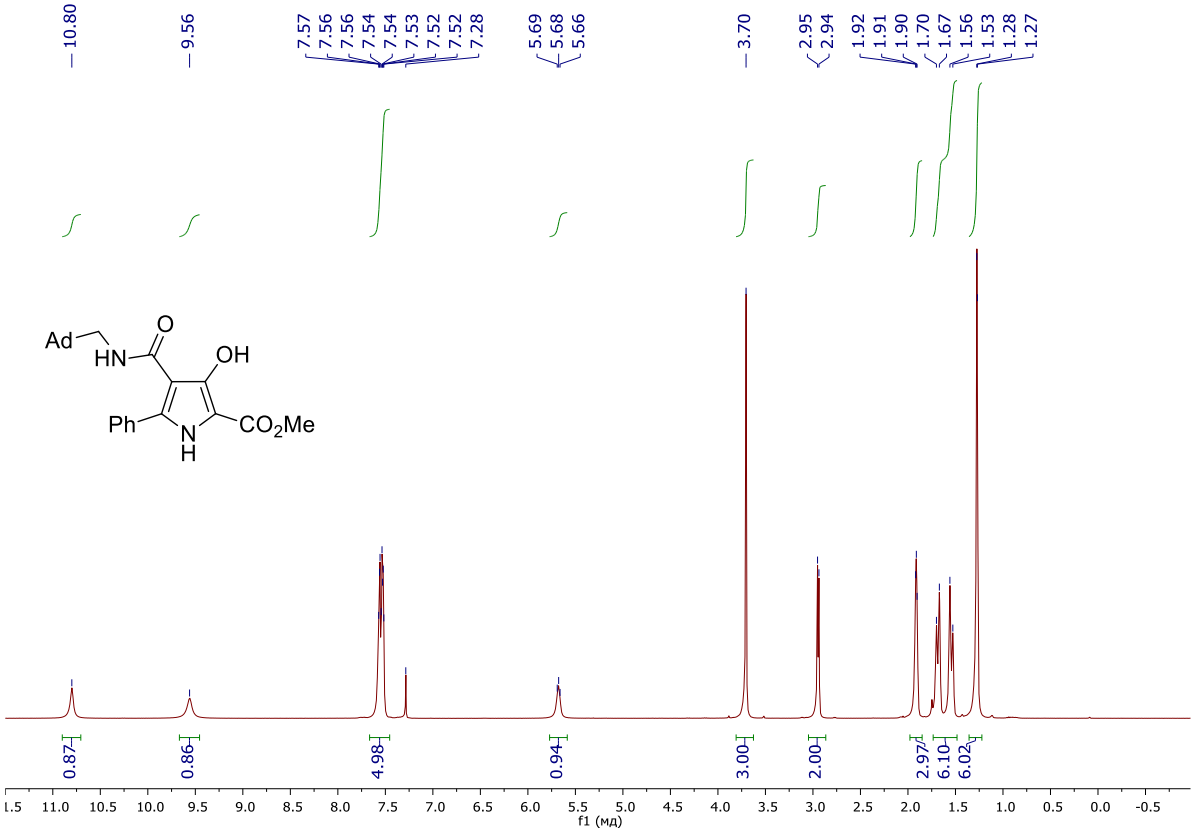


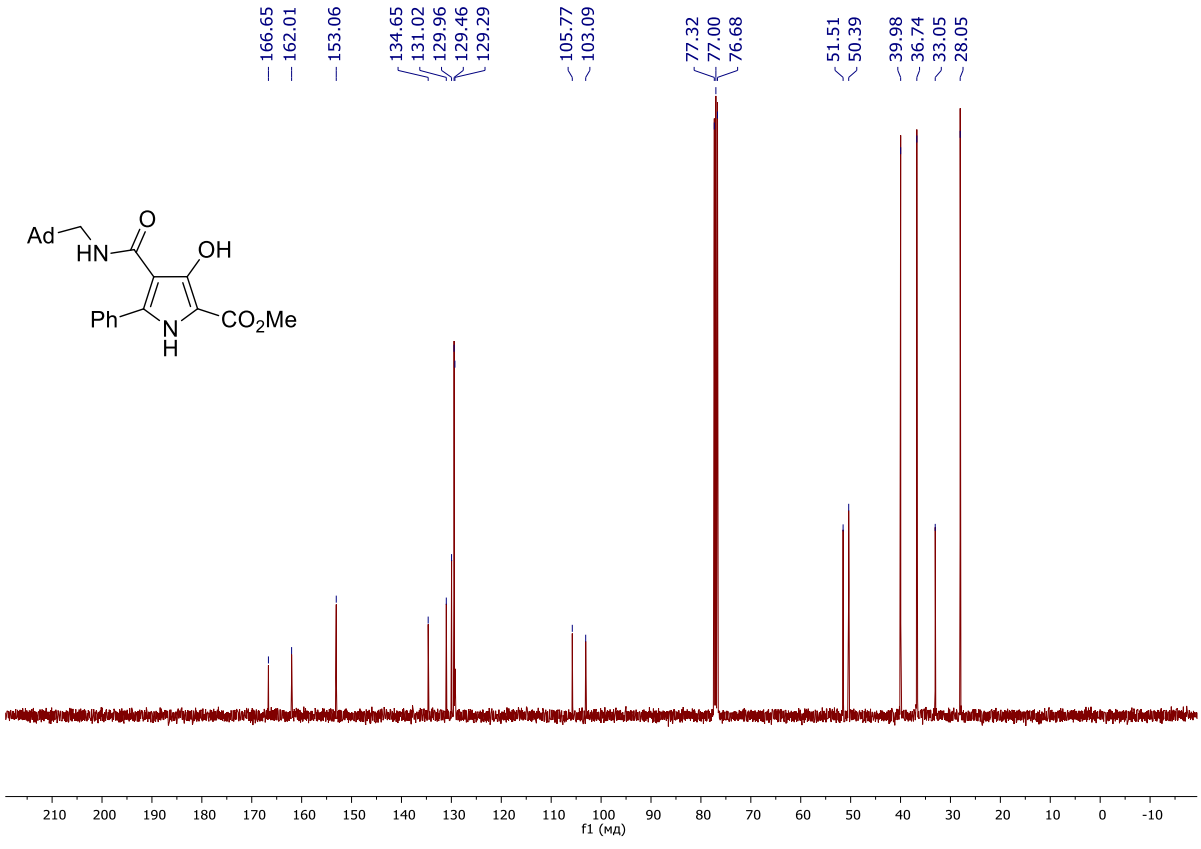
Methyl 4-(diethylcarbamoyl)-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5r)



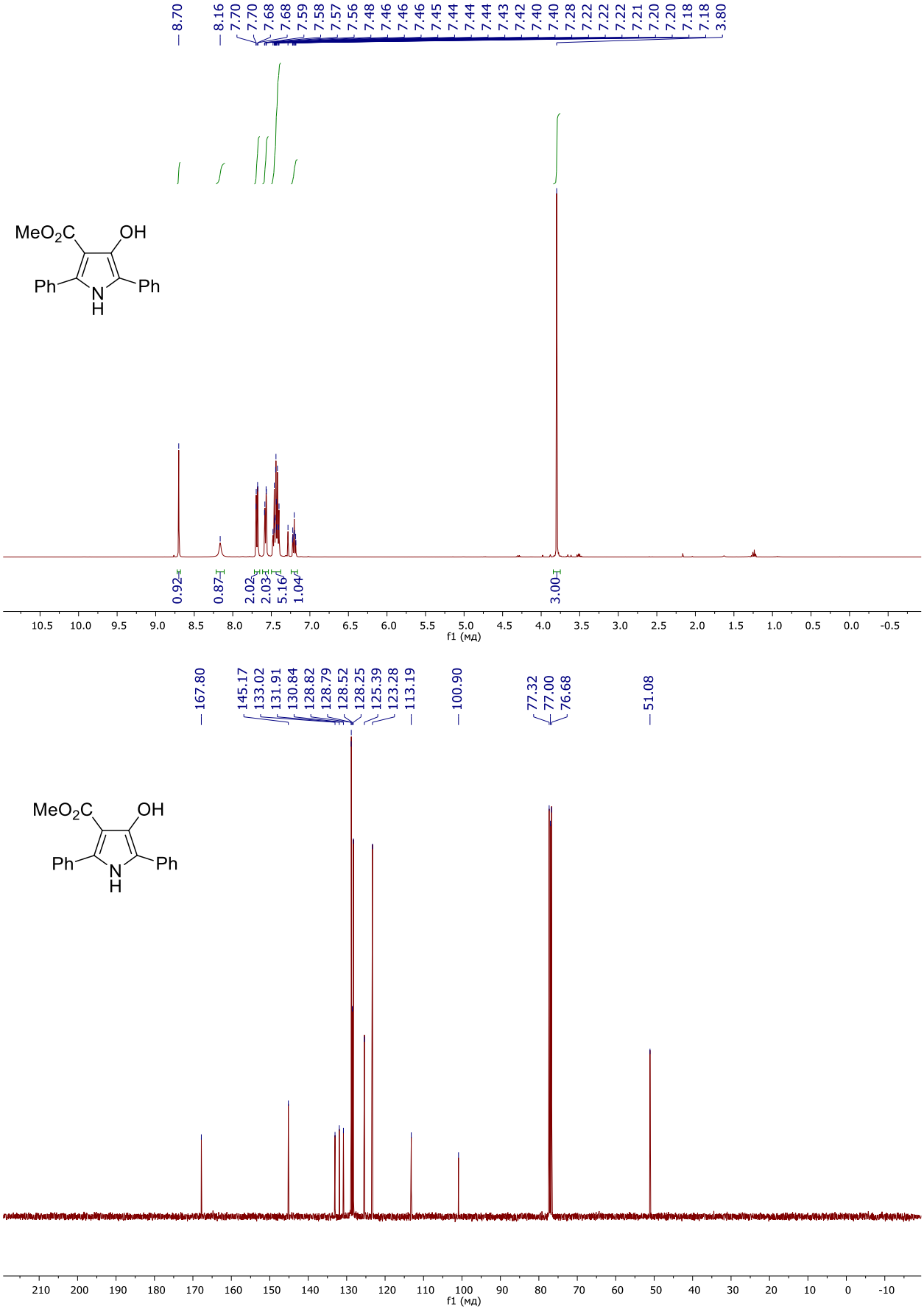


Methyl 4-((adamantan-1-ylmethyl)carbamoyl)-3-hydroxy-5-phenyl-1*H*-pyrrole-2-carboxylate (5s)

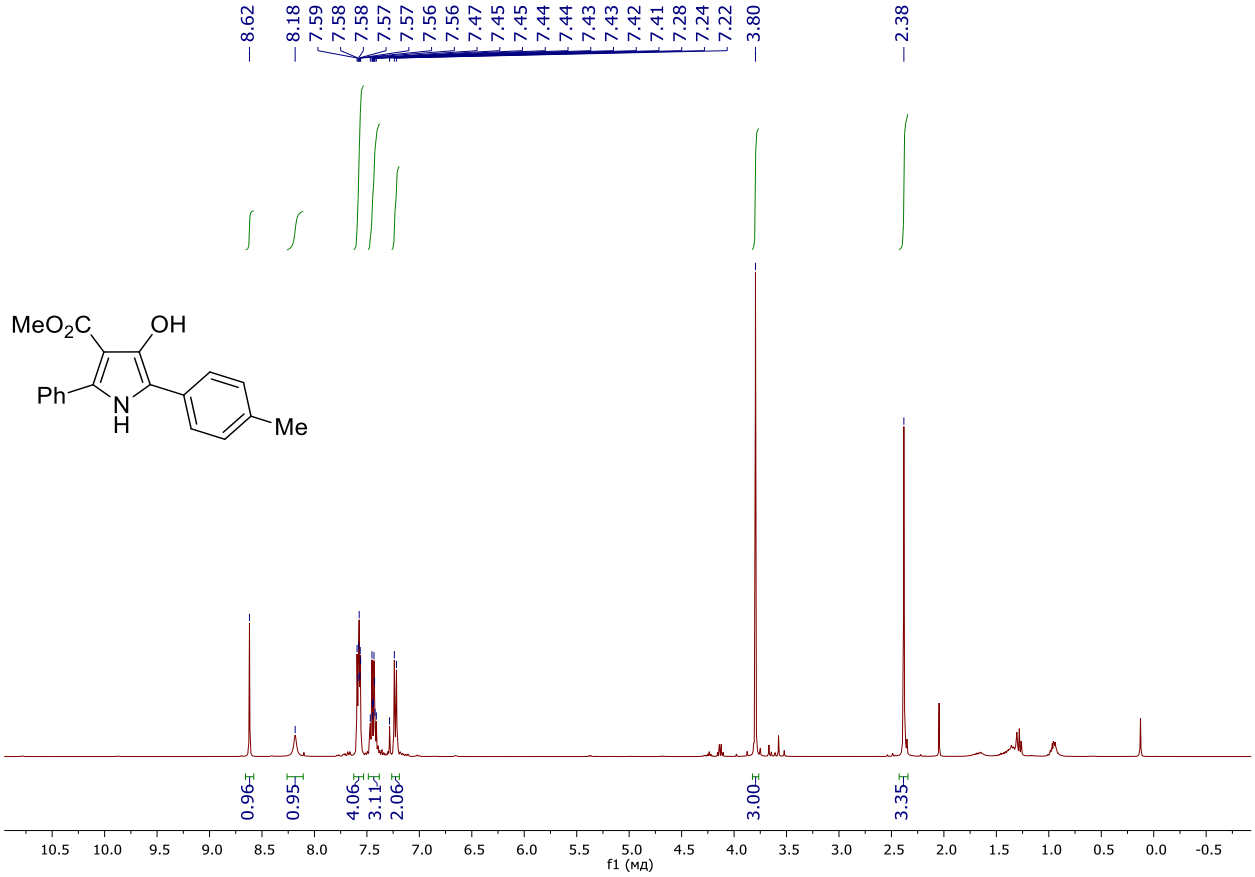


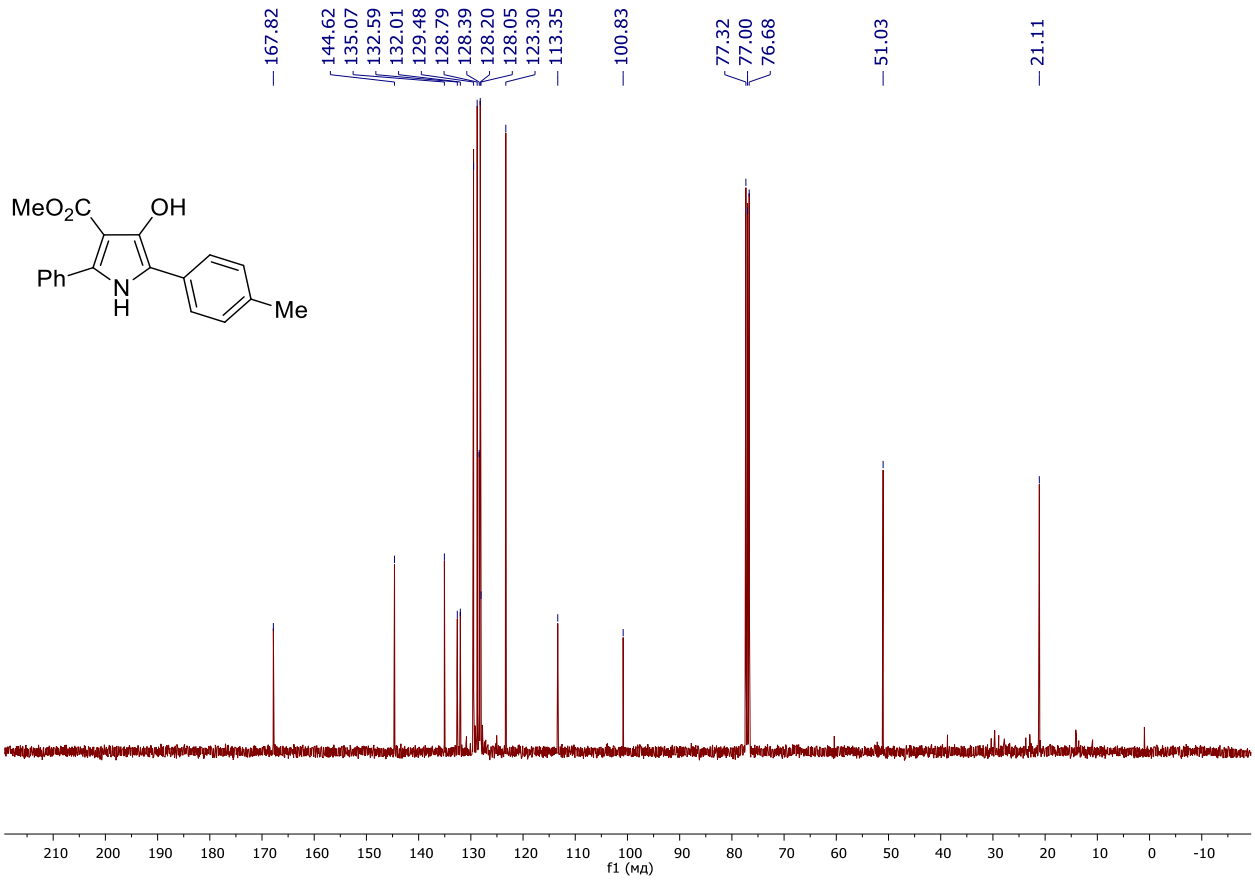


Methyl 4-hydroxy-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (5u)

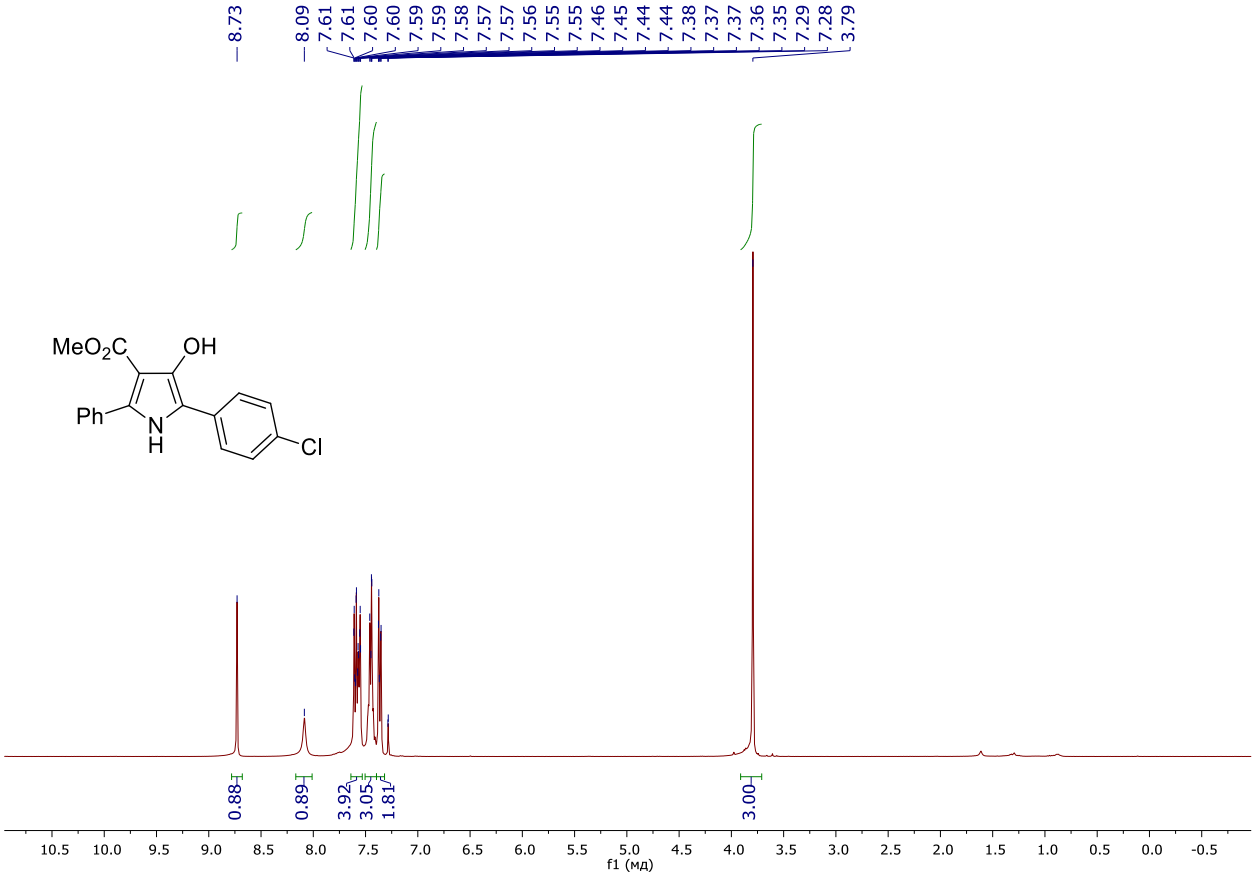


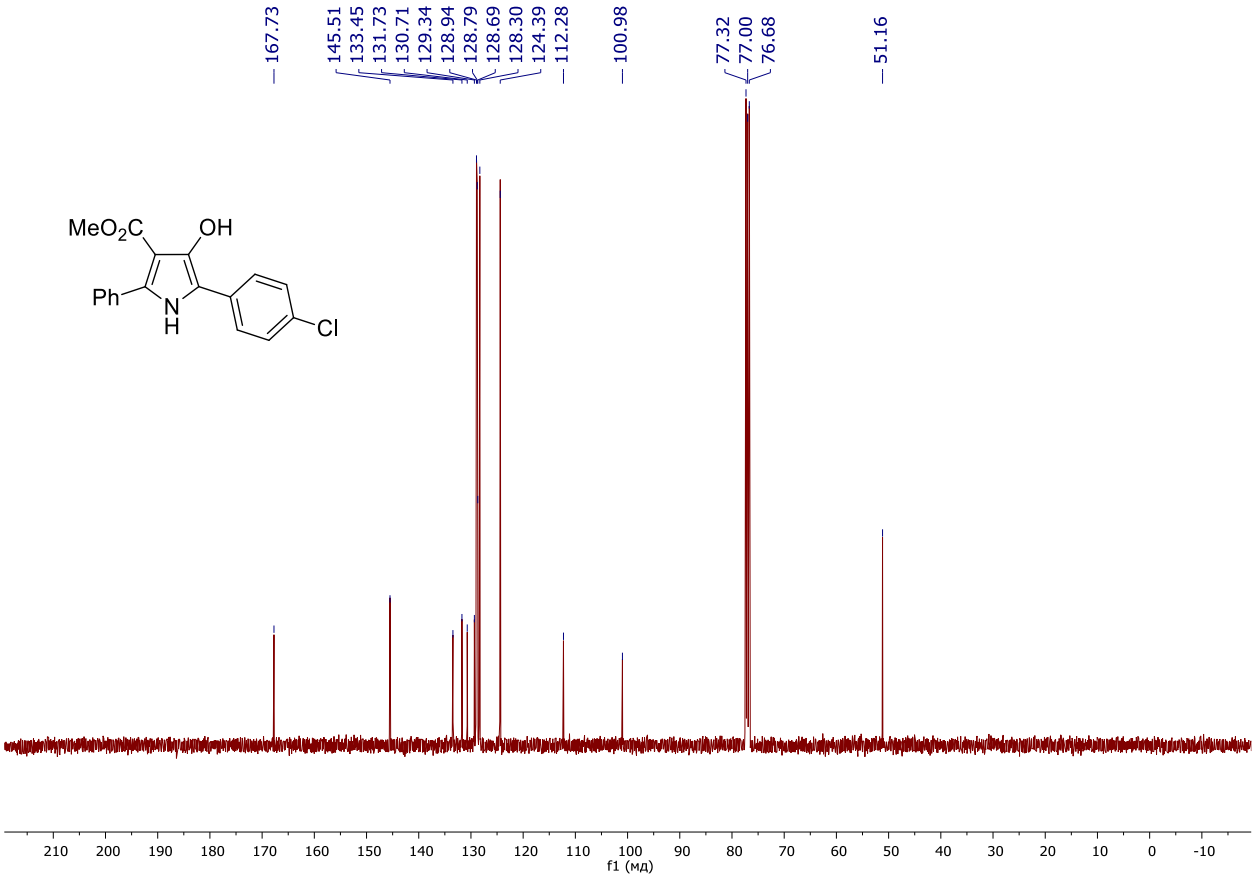
Methyl 4-hydroxy-5-(4-methylphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5v)



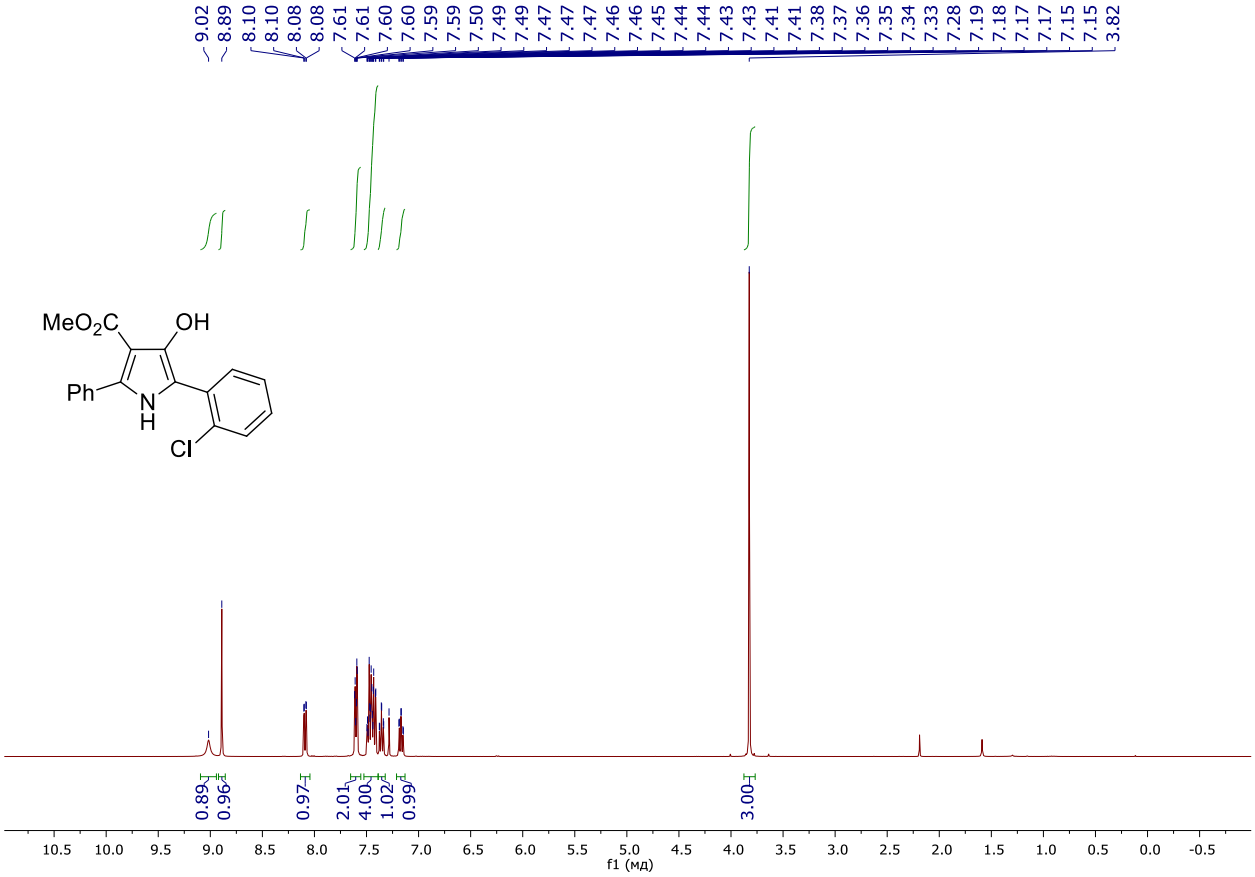


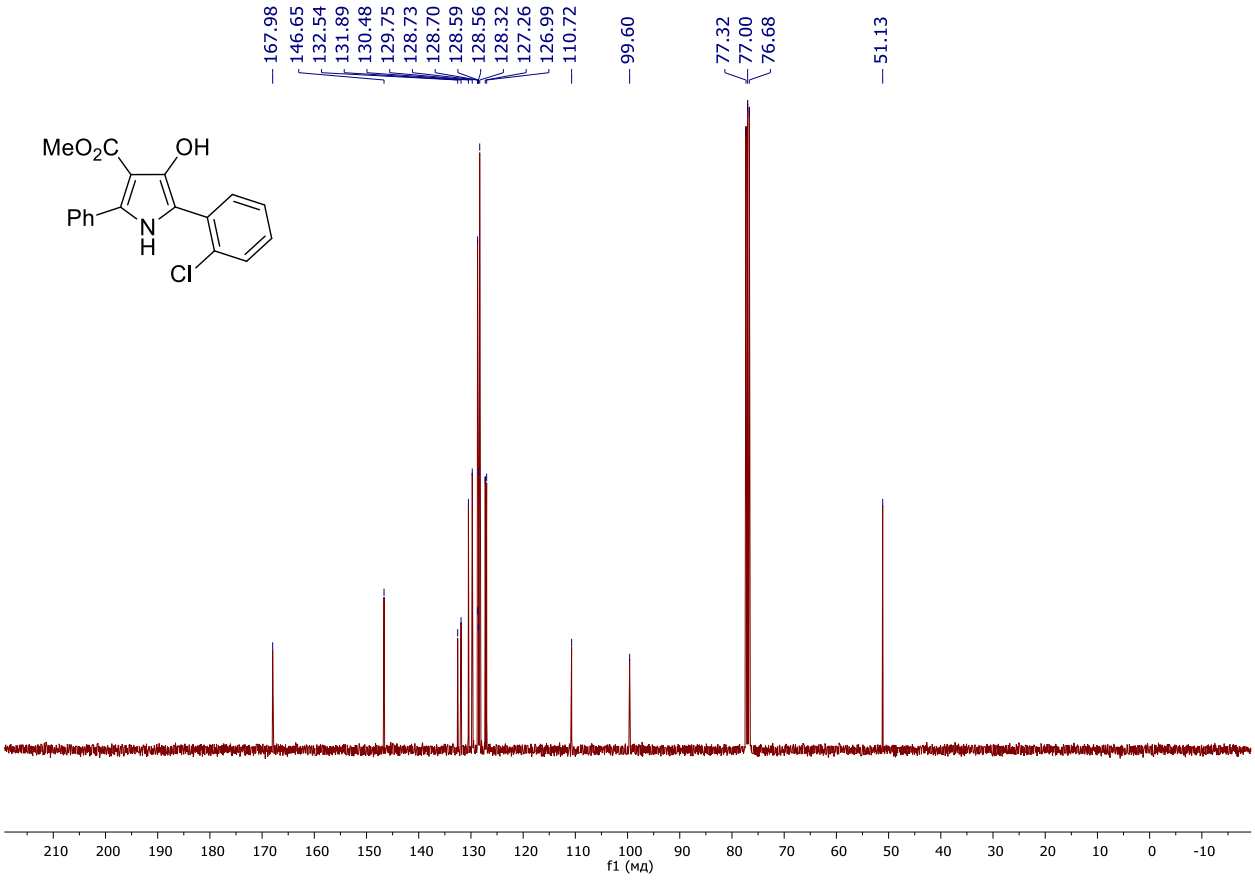
Methyl 5-(4-chlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5w)



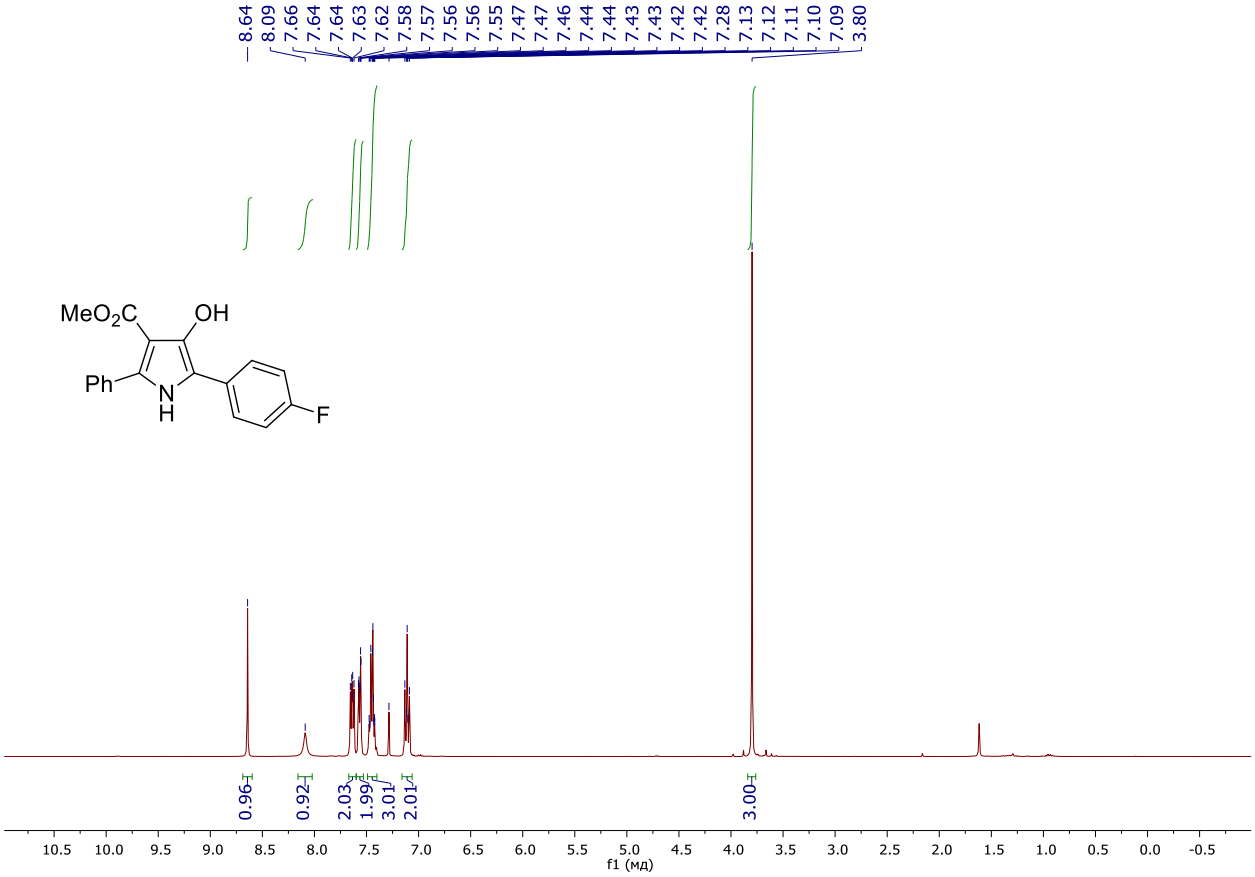


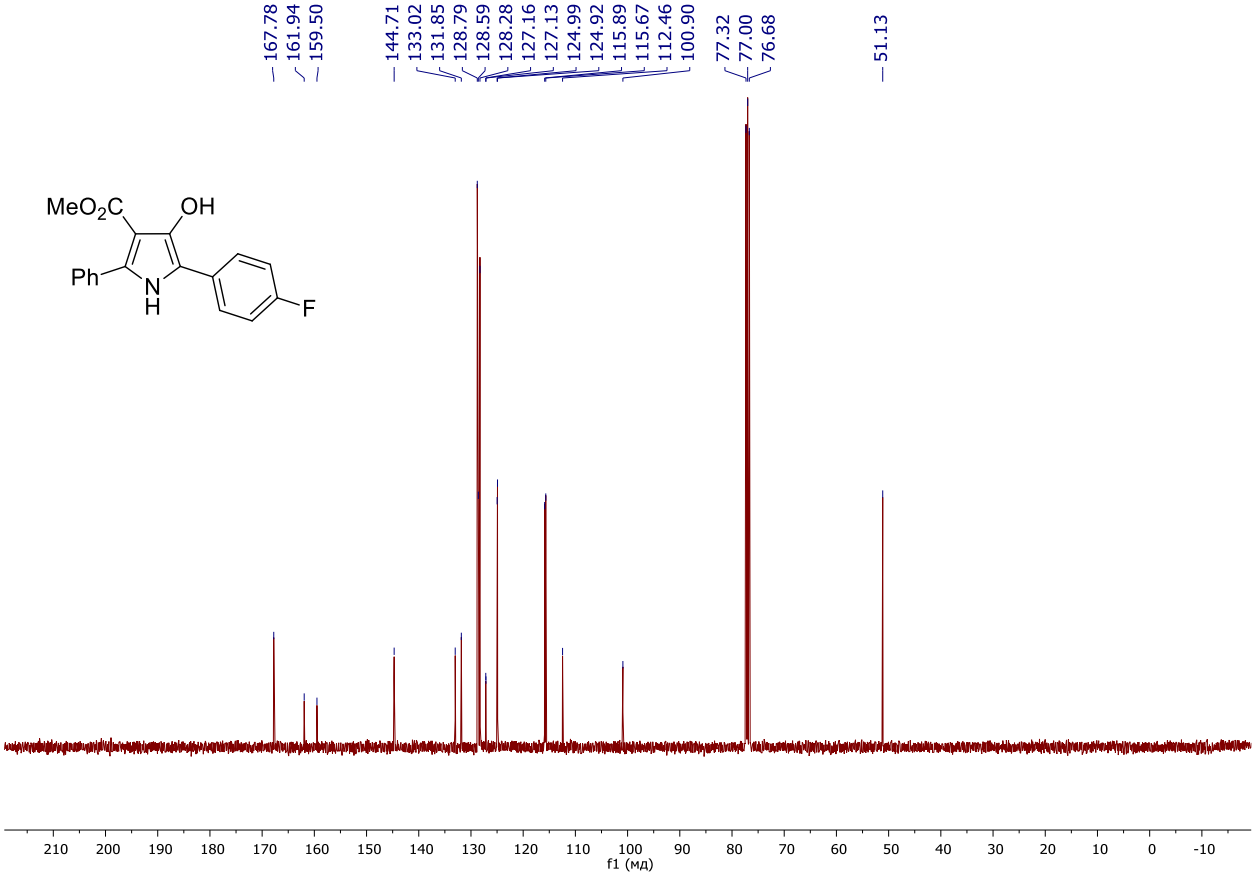
Methyl 5-(2-chlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5x)



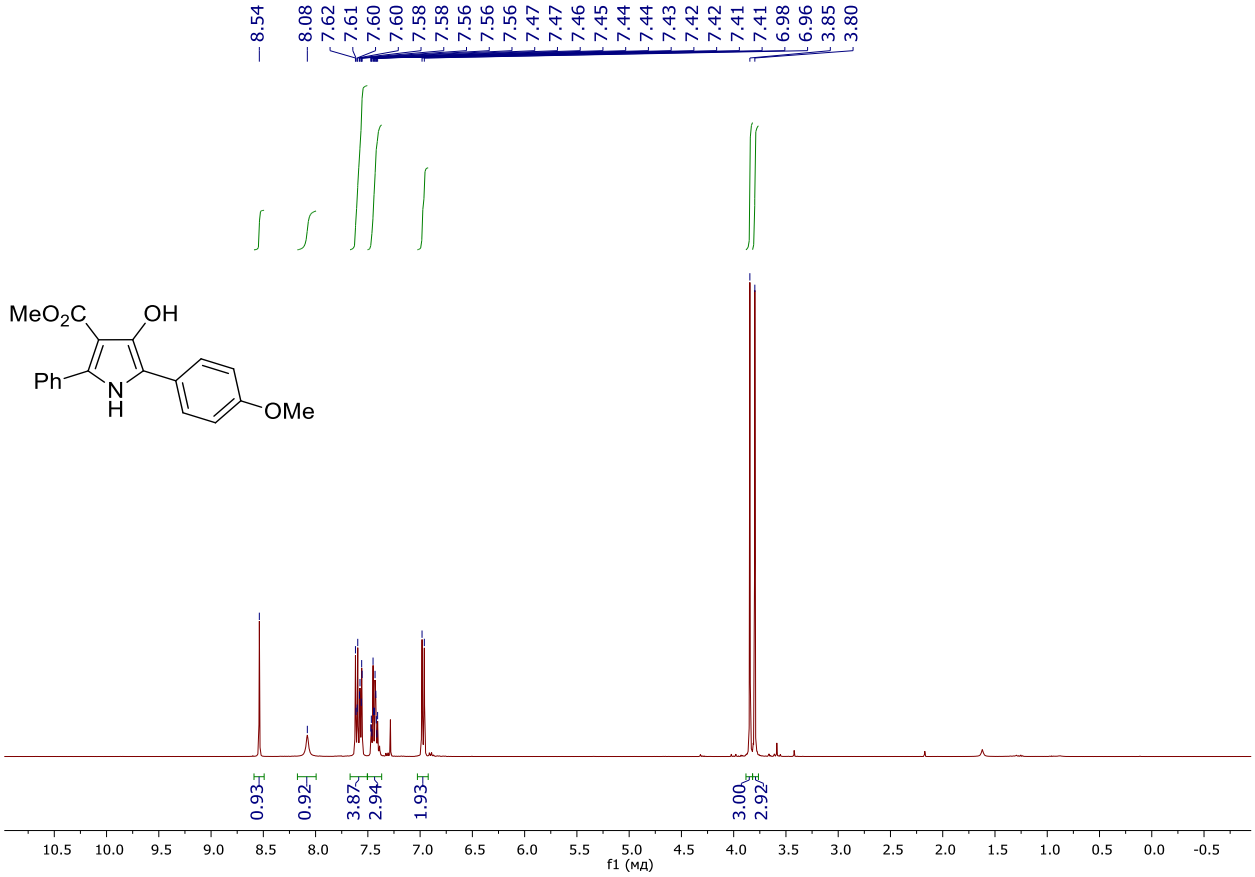


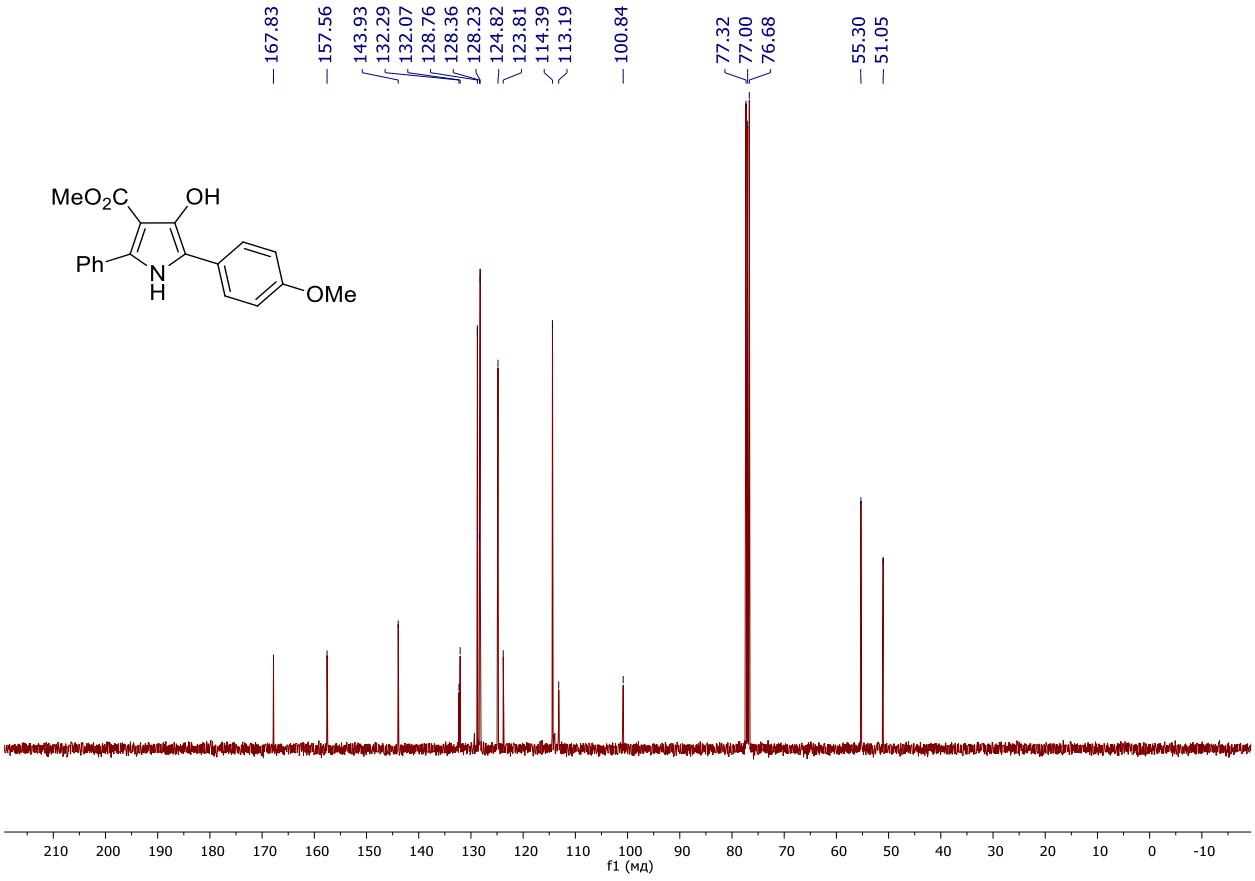
Methyl 5-(4-fluorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5y)



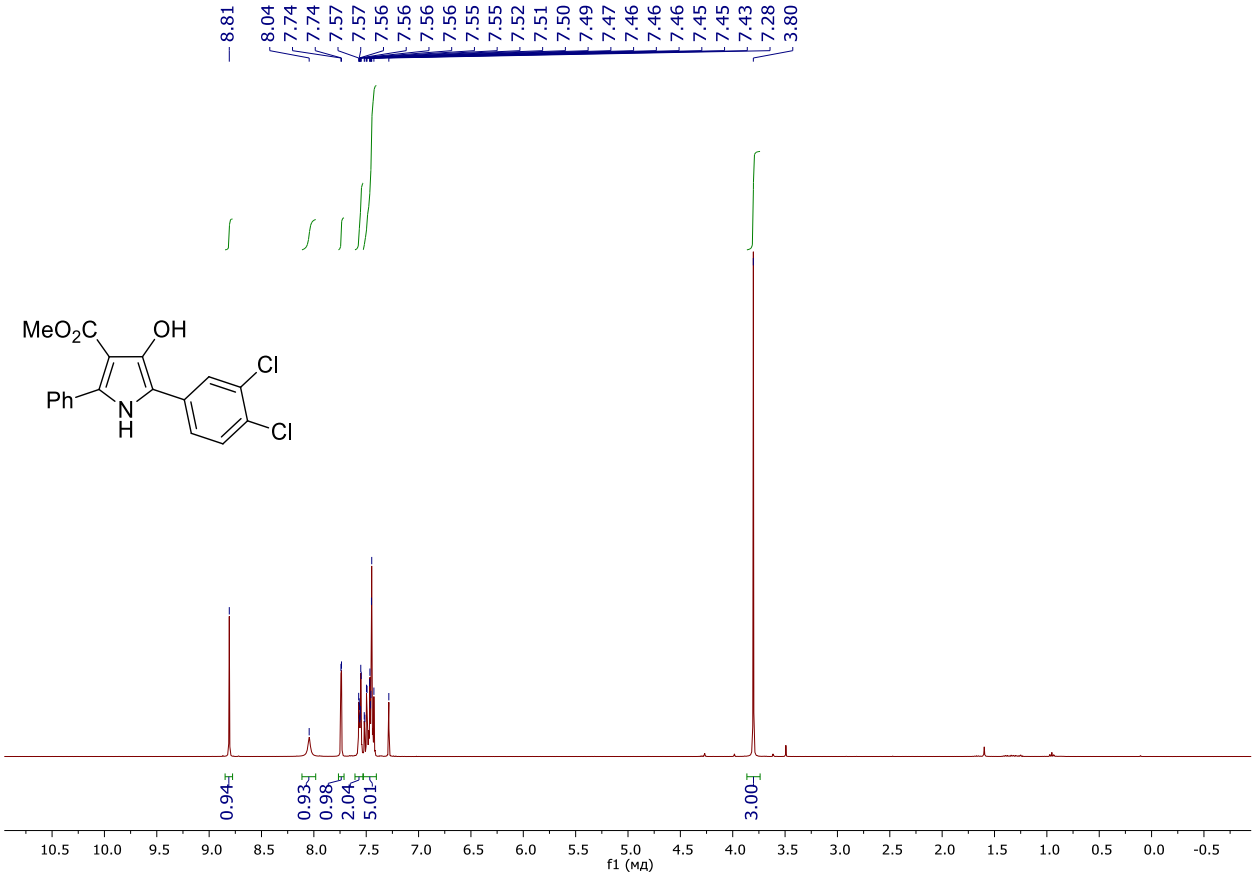


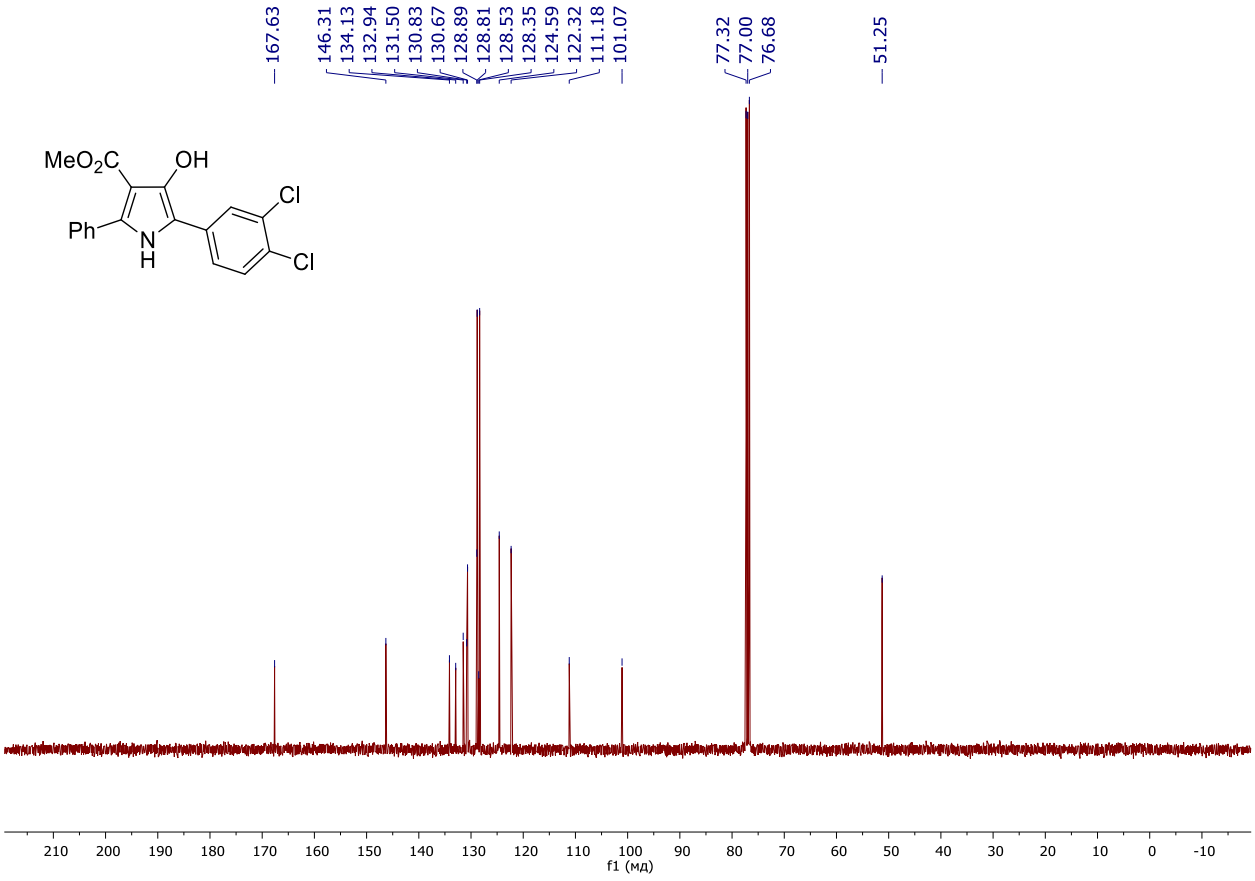
Methyl 4-hydroxy-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5z)



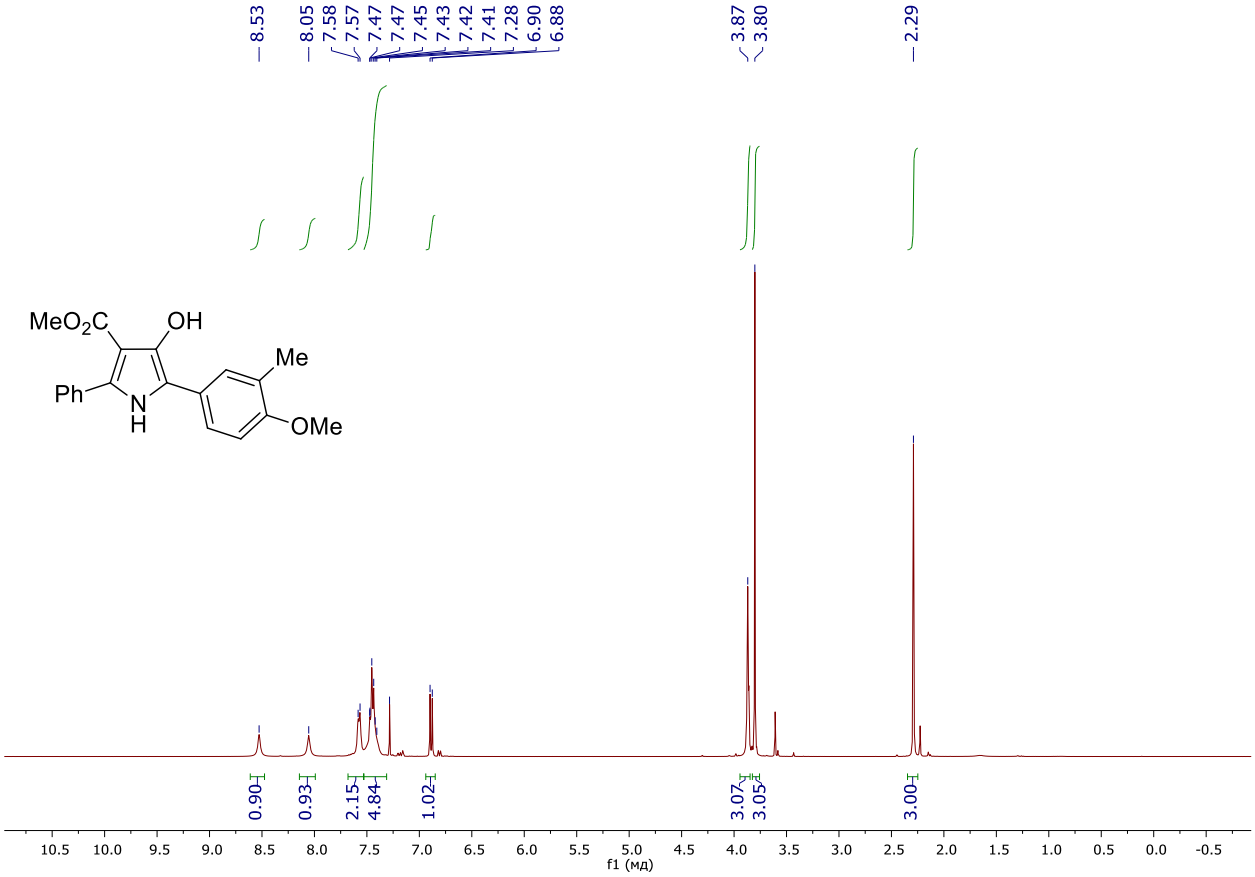


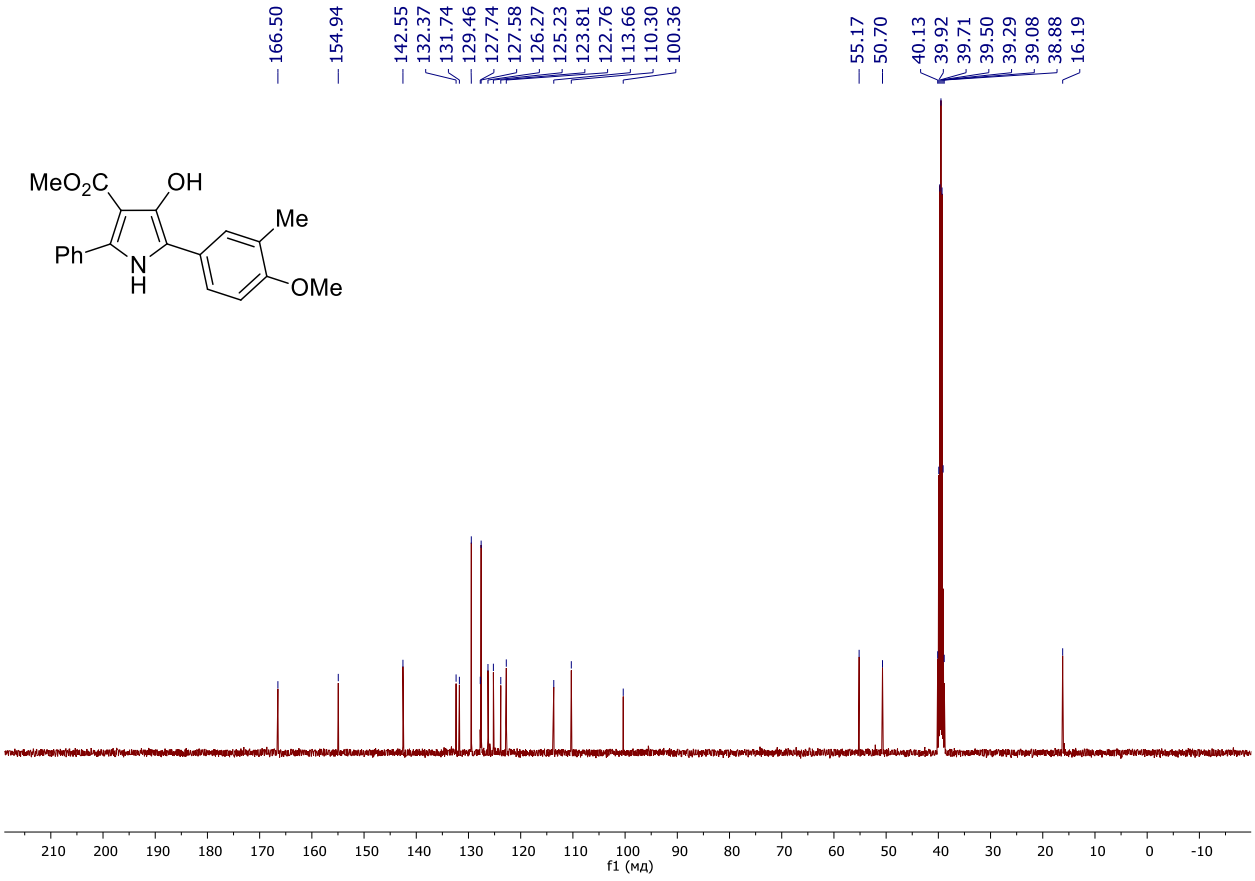
Methyl 5-(3,4-dichlorophenyl)-4-hydroxy-2-phenyl-1*H*-pyrrole-3-carboxylate (5aa)



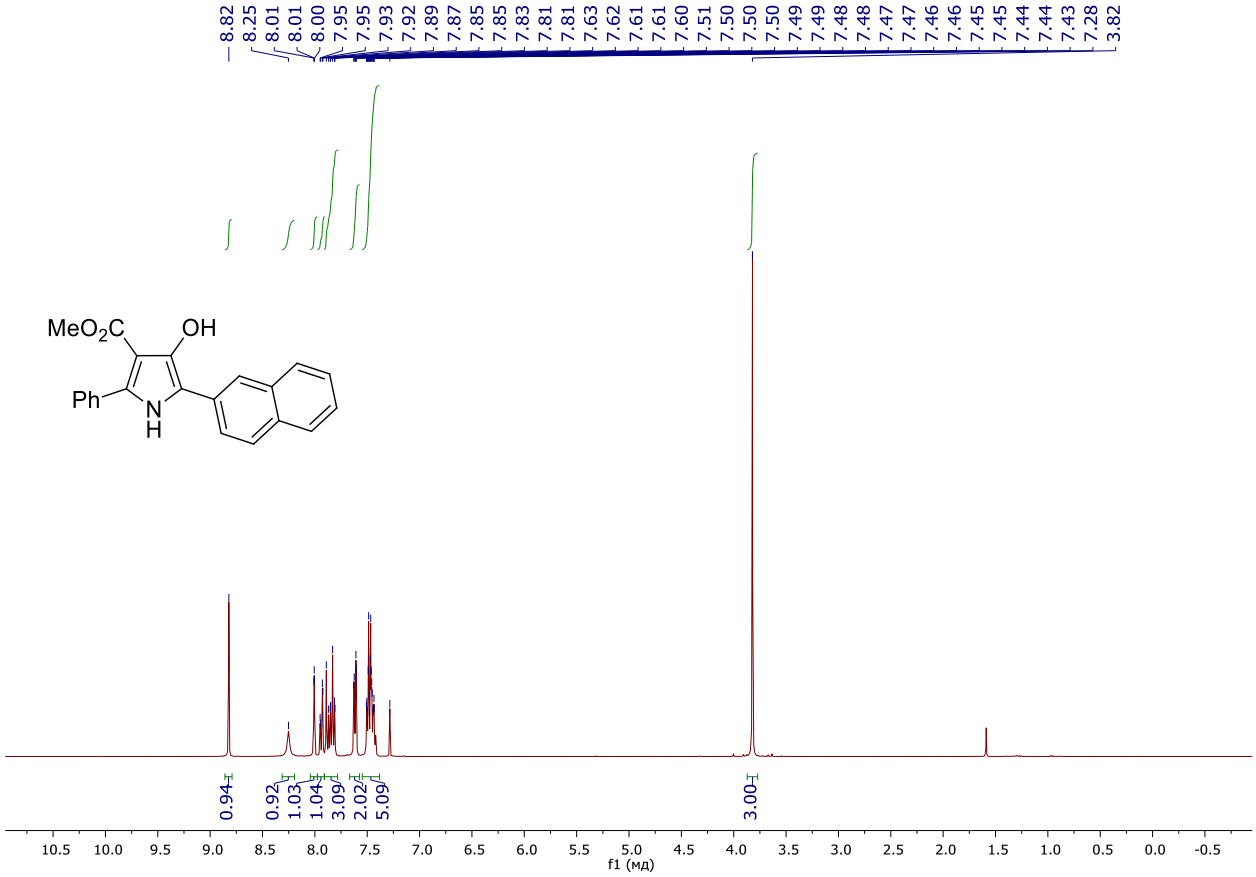


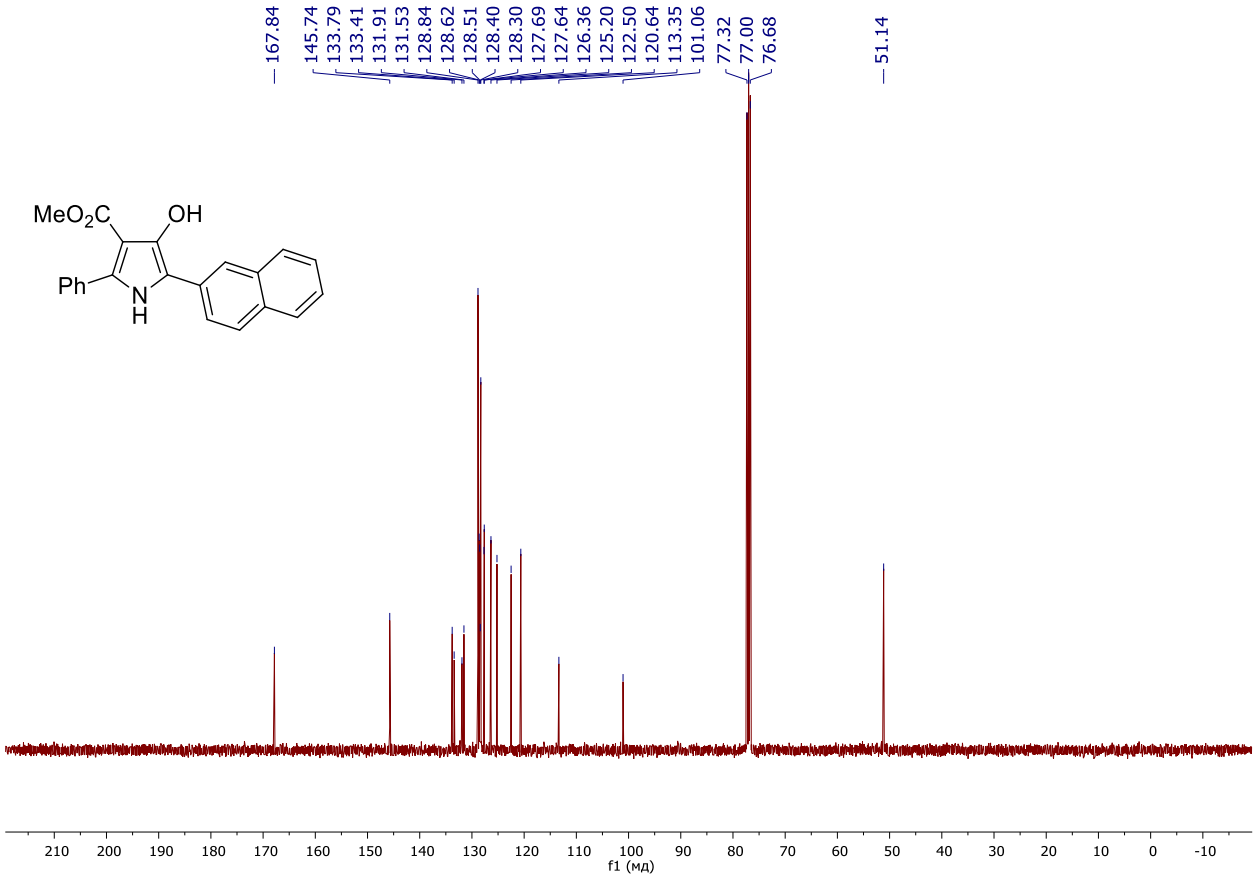
Methyl 4-hydroxy-5-(4-methoxy-3-methylphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ab)



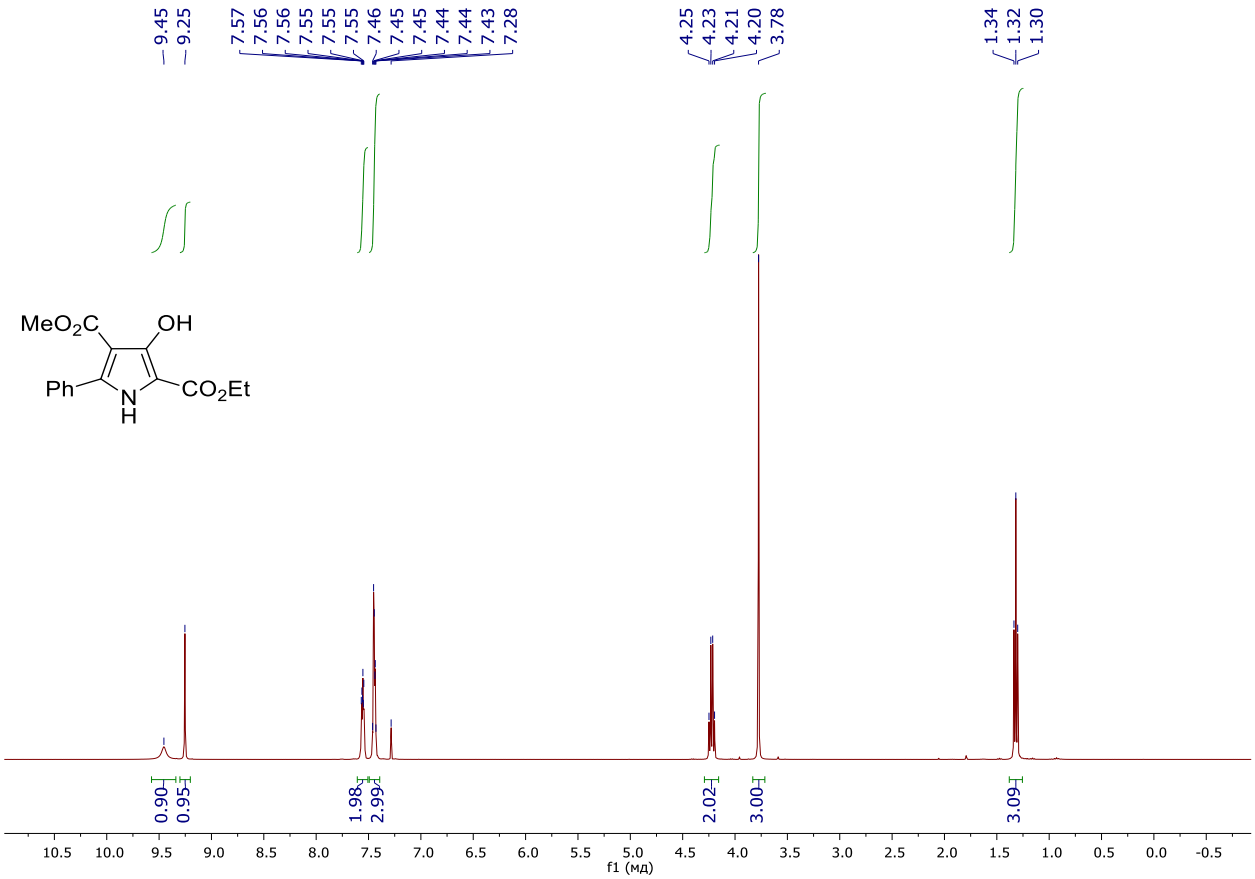


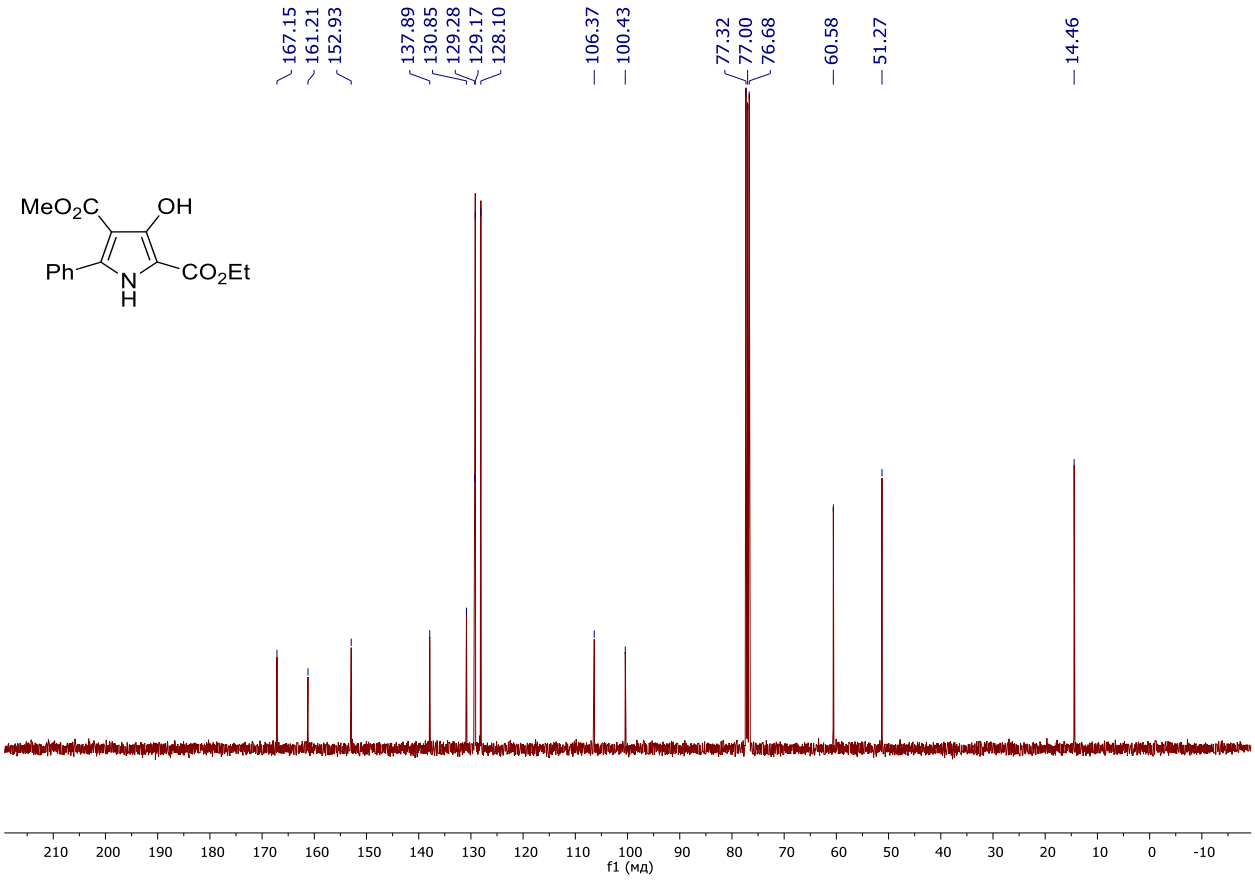
Methyl 4-hydroxy-5-(naphthalen-2-yl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ac)



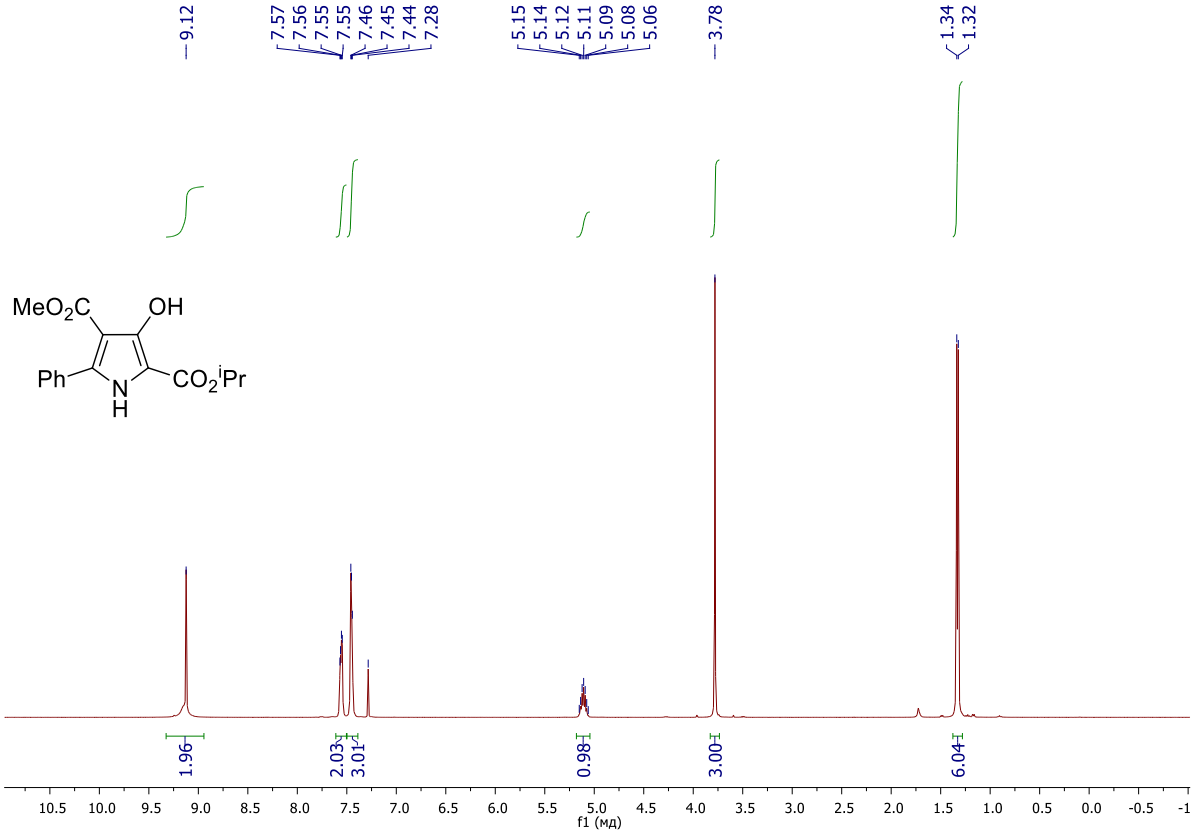


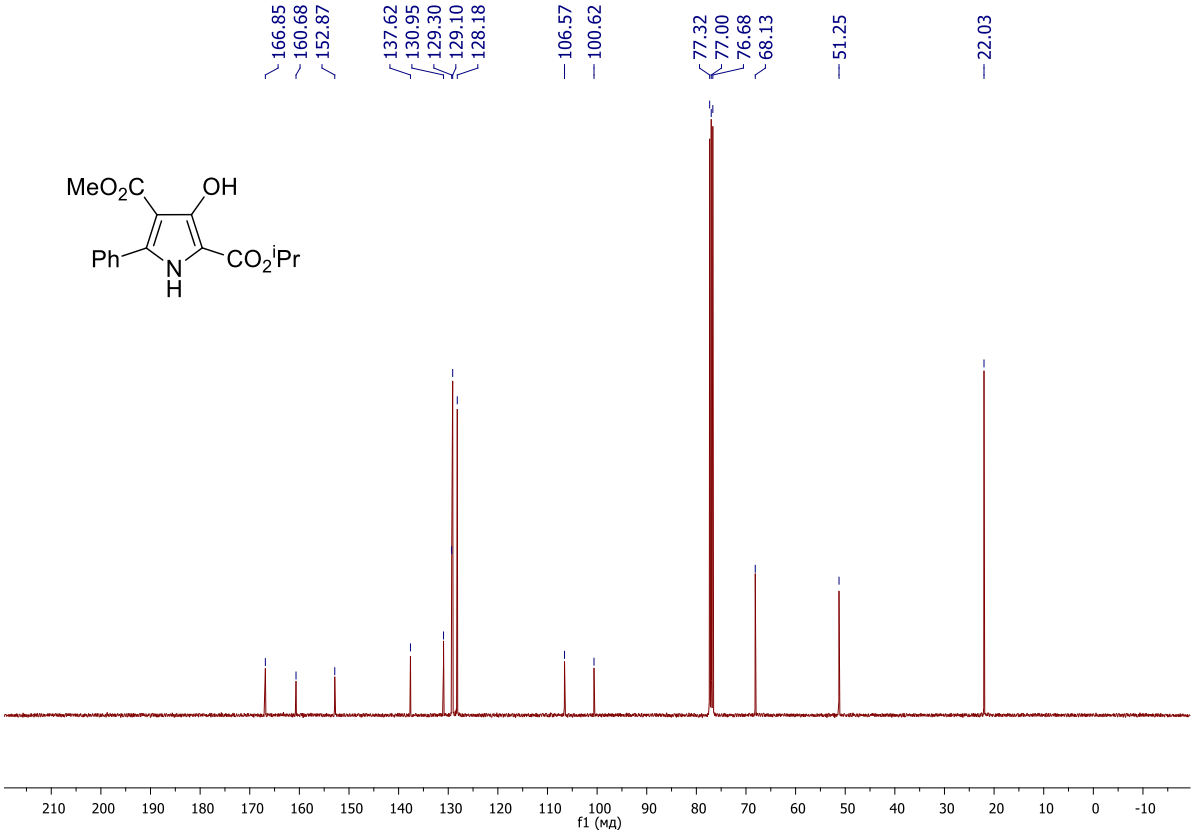
2-Ethyl 4-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5ad)



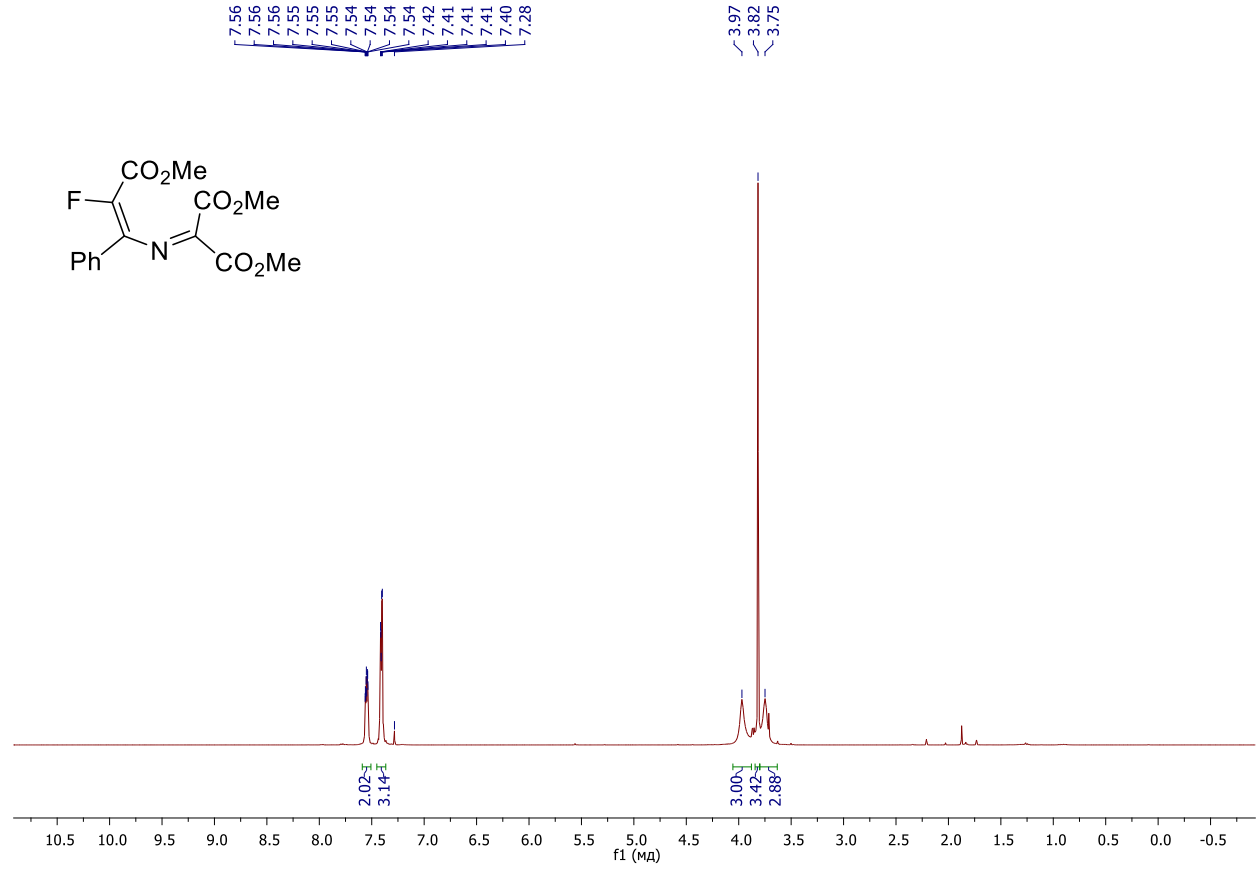


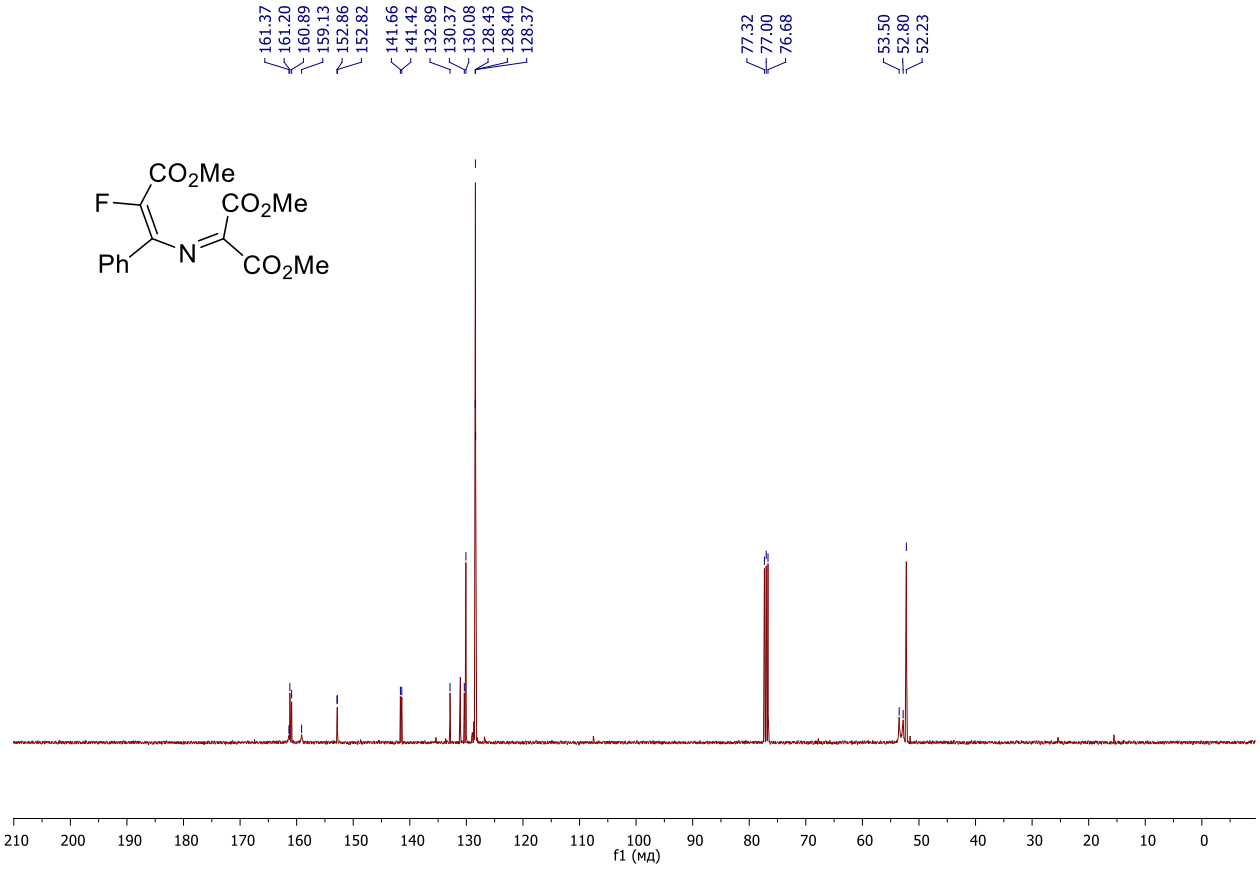
2-Isopropyl 4-methyl 3-hydroxy-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (5ae)



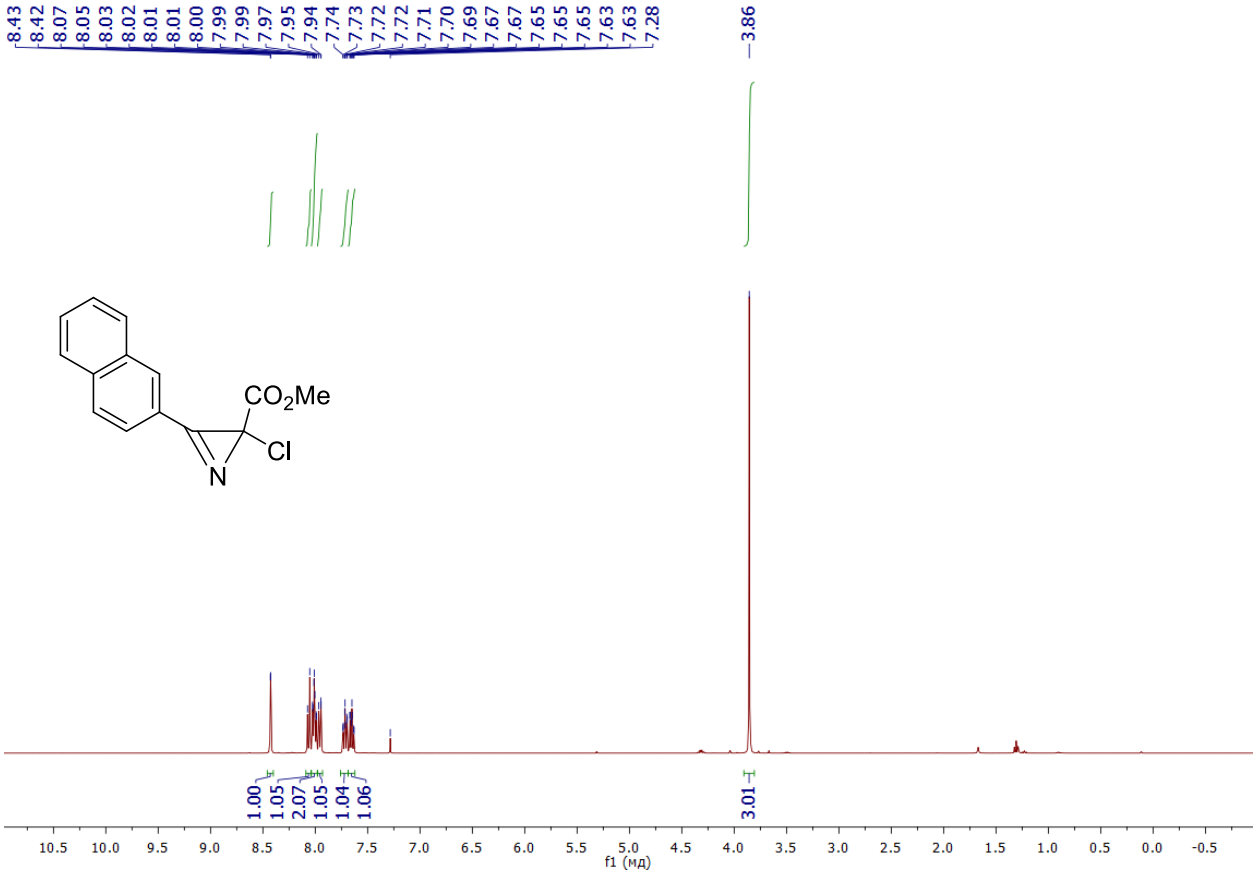


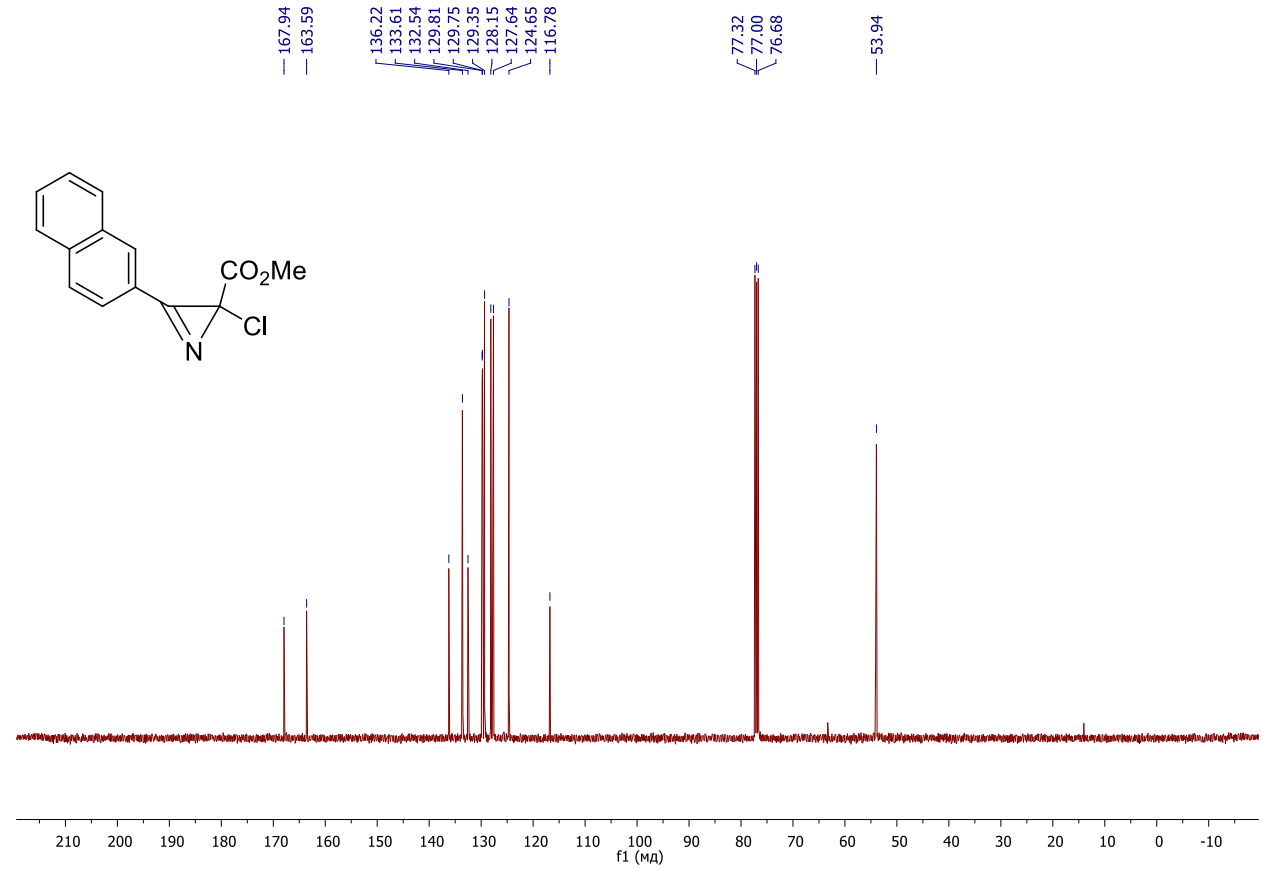
(*E*)-2-[(2-fluoro-1-phenyl-3-methoxy-3-oxoprop-1-en-1-yl)imino]malonate (7)



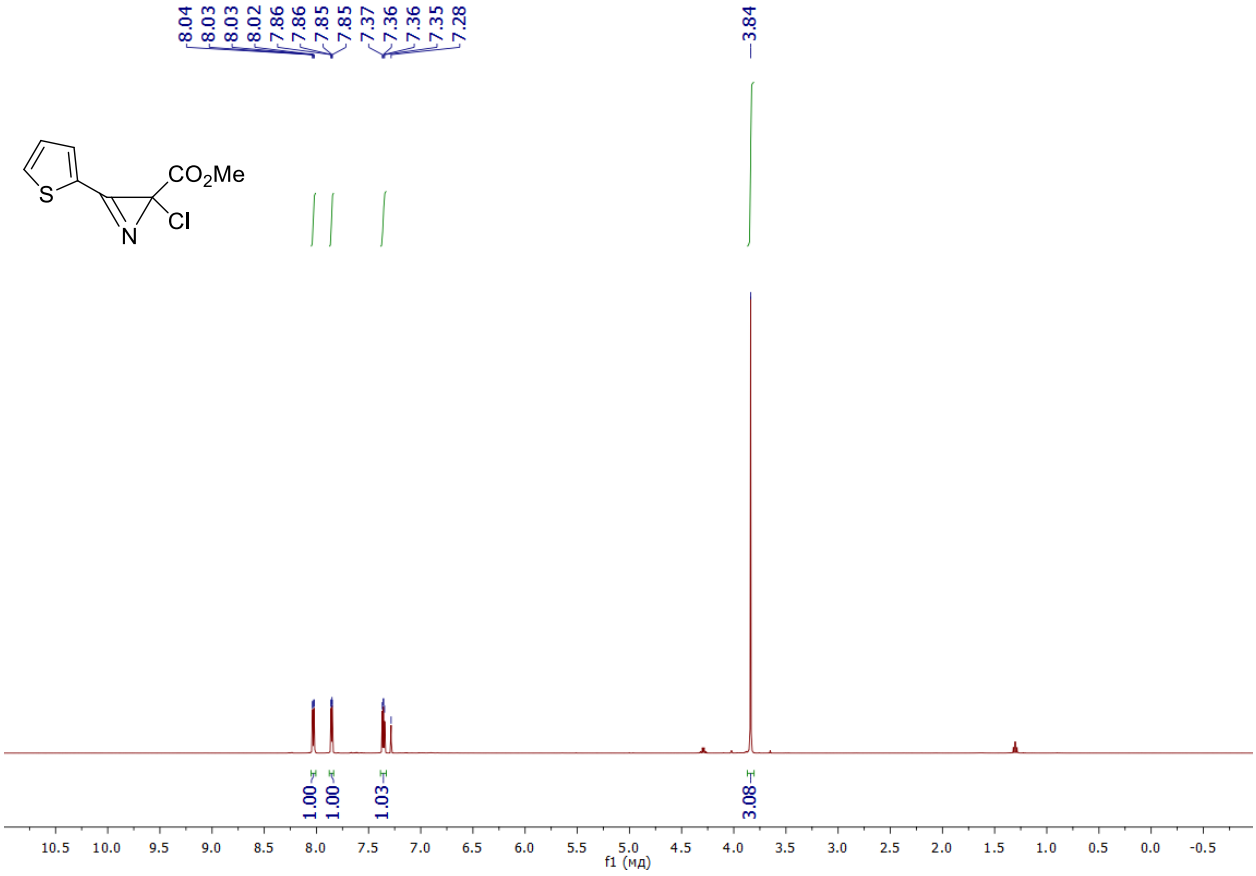


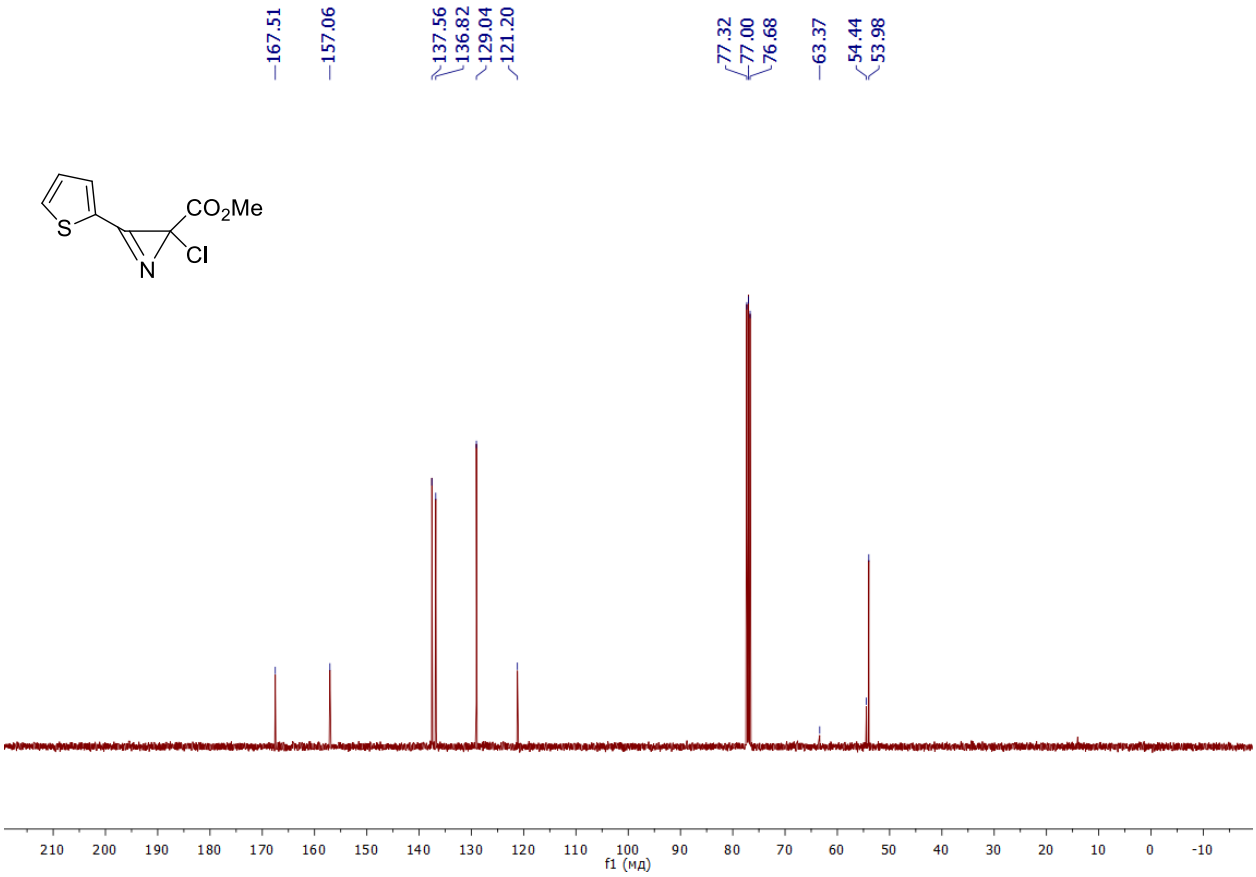
Methyl 2-chloro-3-(naphthalen-2-yl)-2*H*-azirine-2-carboxylate (9c)



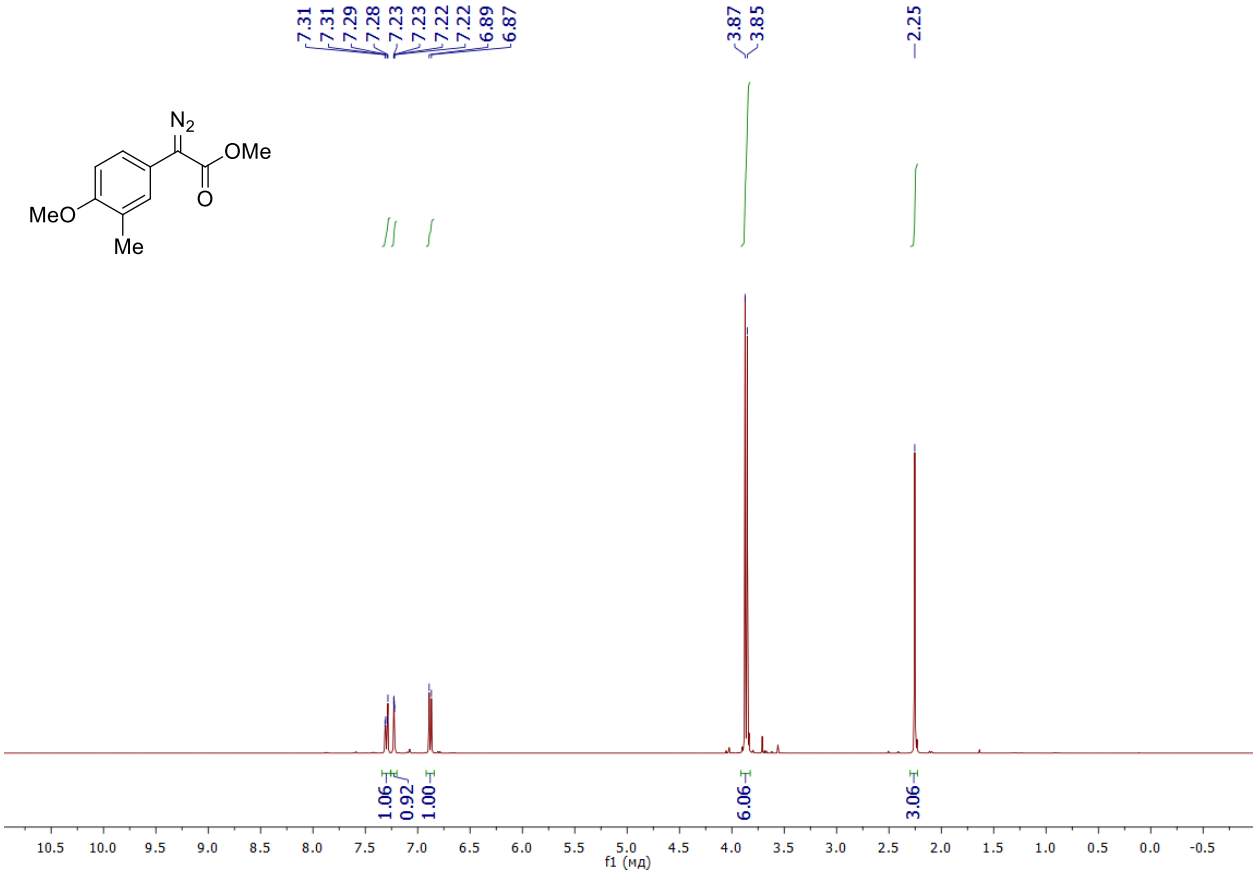


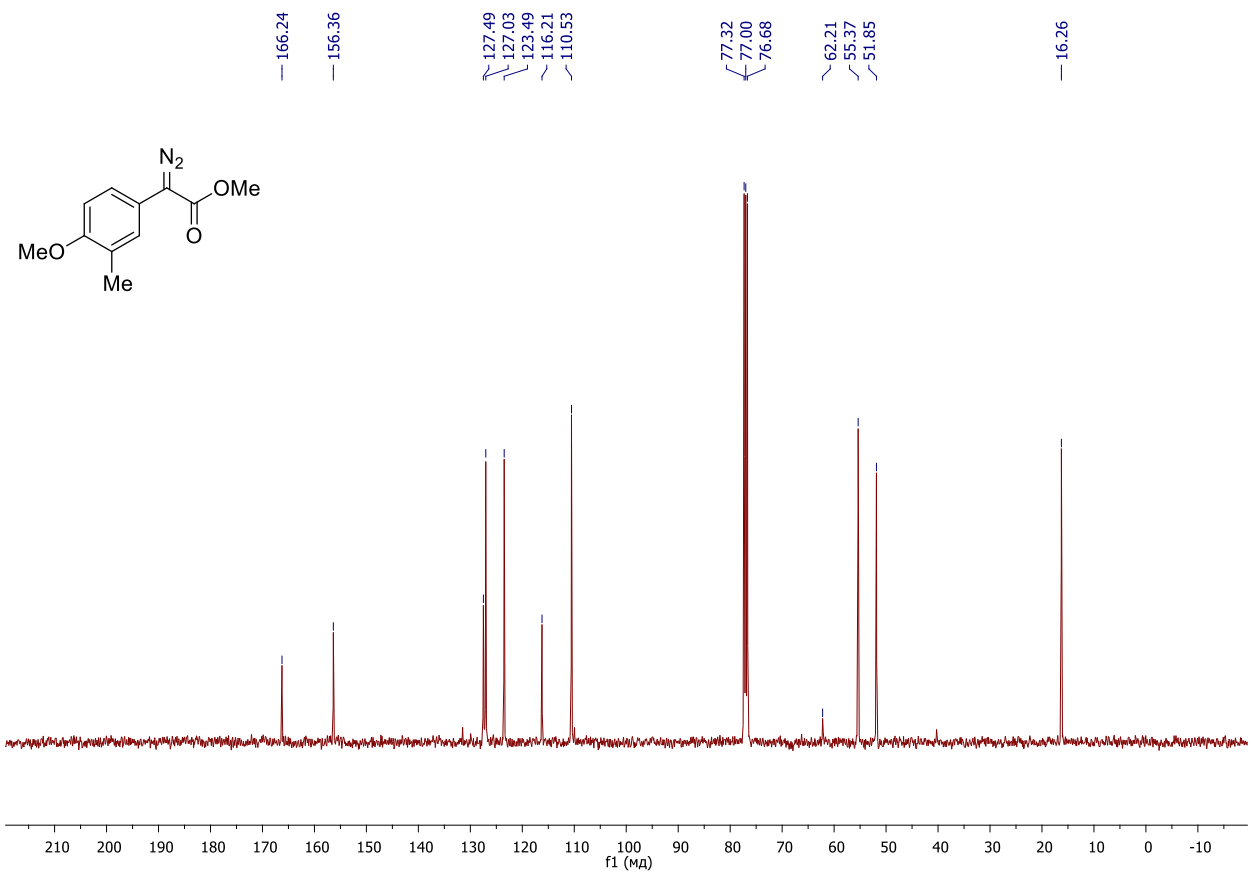
Methyl 2-chloro-3-(thiophen-2-yl)-2*H*-azirine-2-carboxylate (9d)



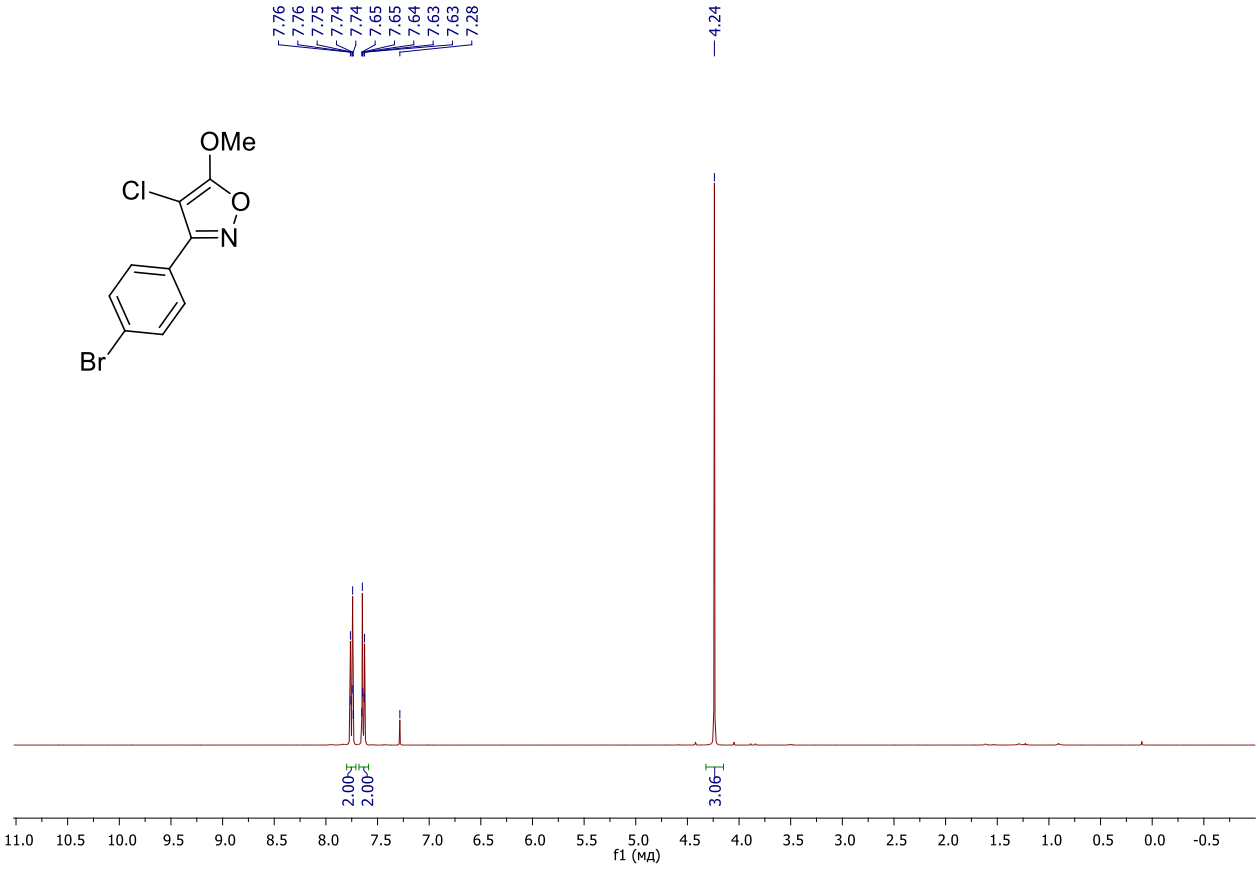


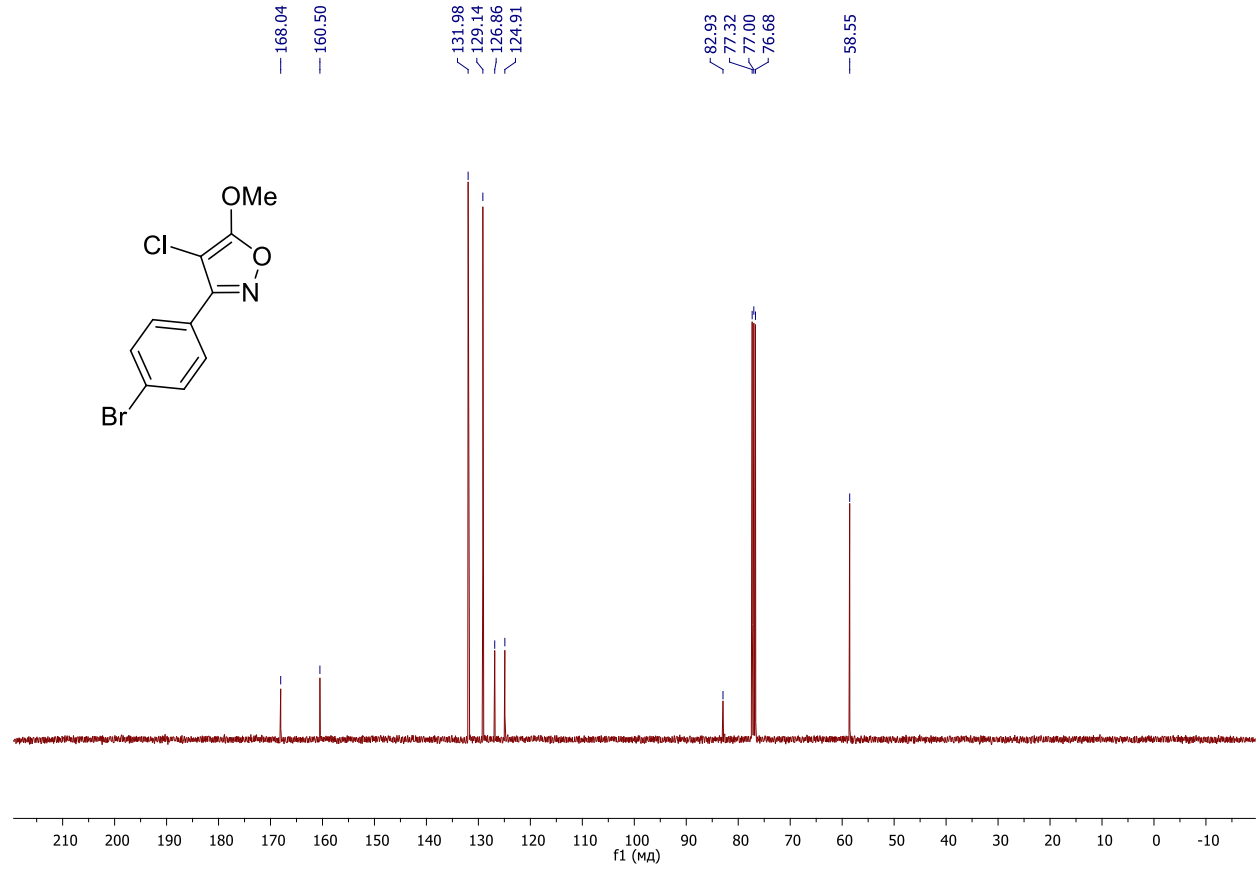
Methyl 2-diazo-2-(4-methoxy-3-methylphenyl)acetate (12i)



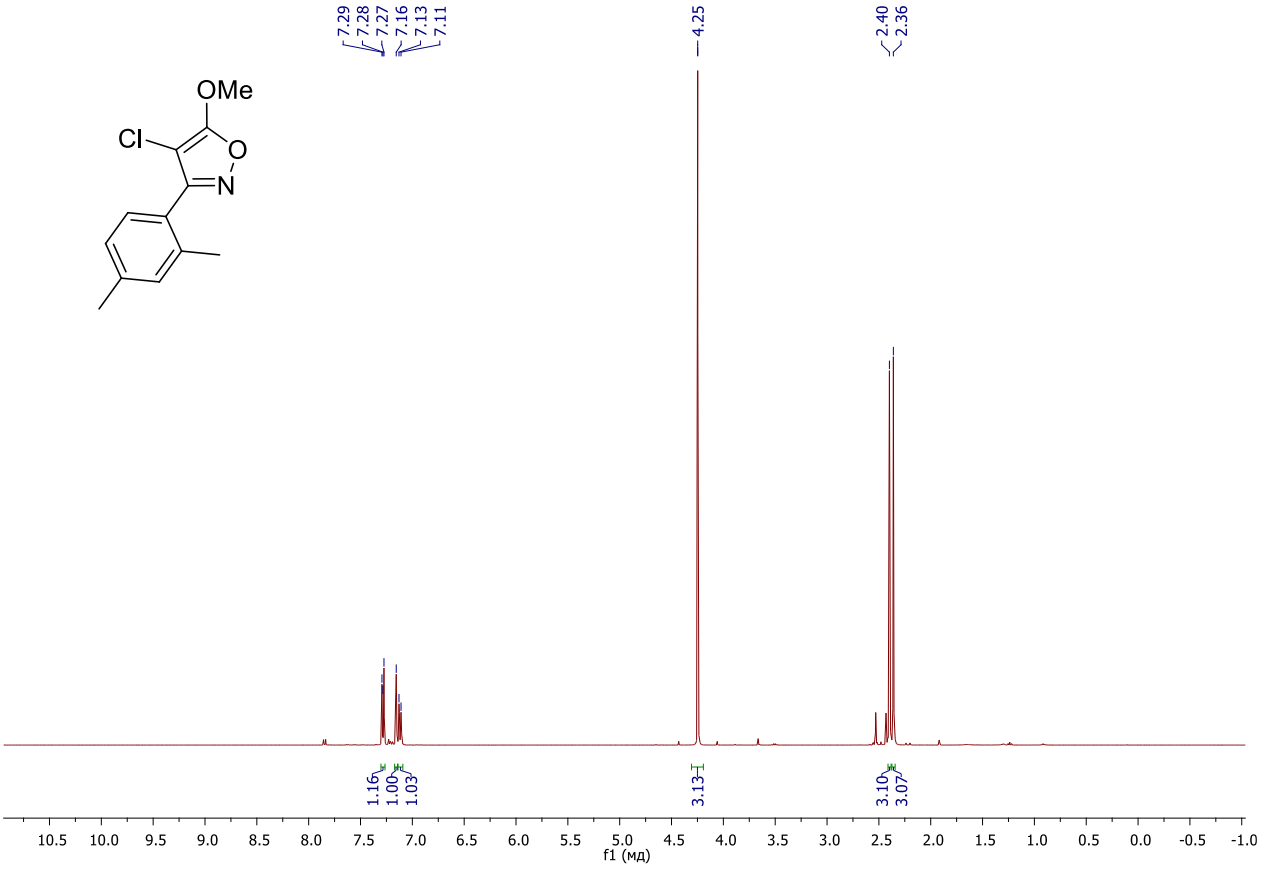


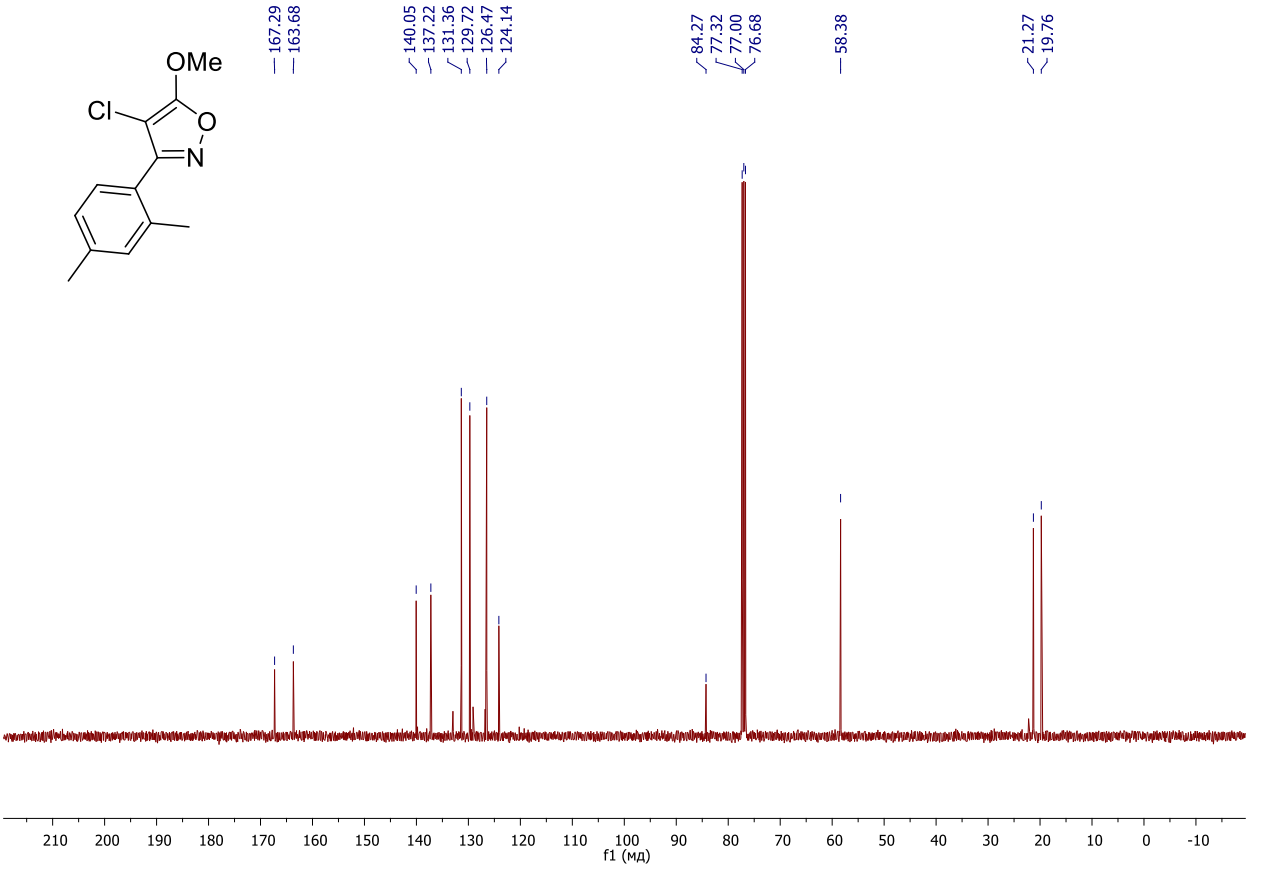
3-(4-Bromophenyl)-4-chloro-5-methoxyisoxazole (13c)



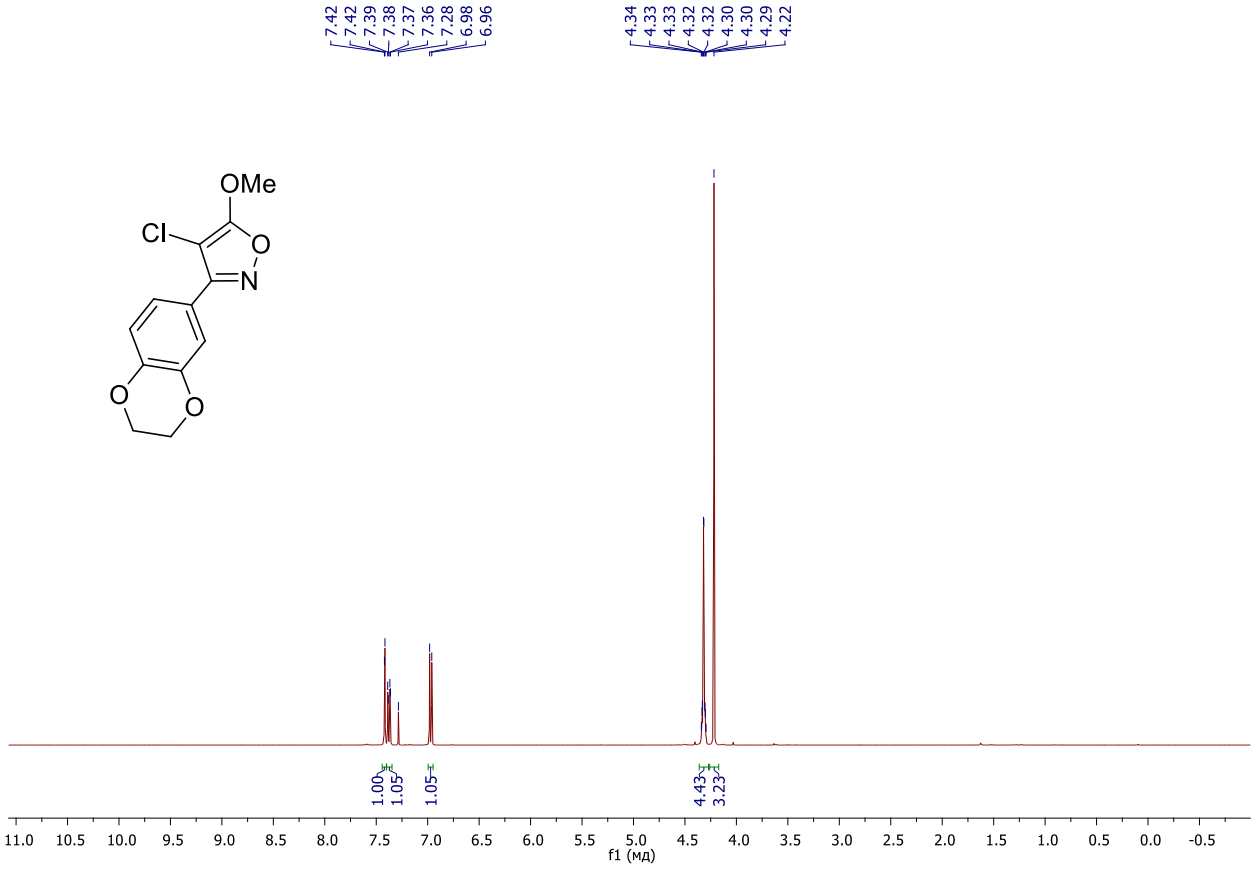


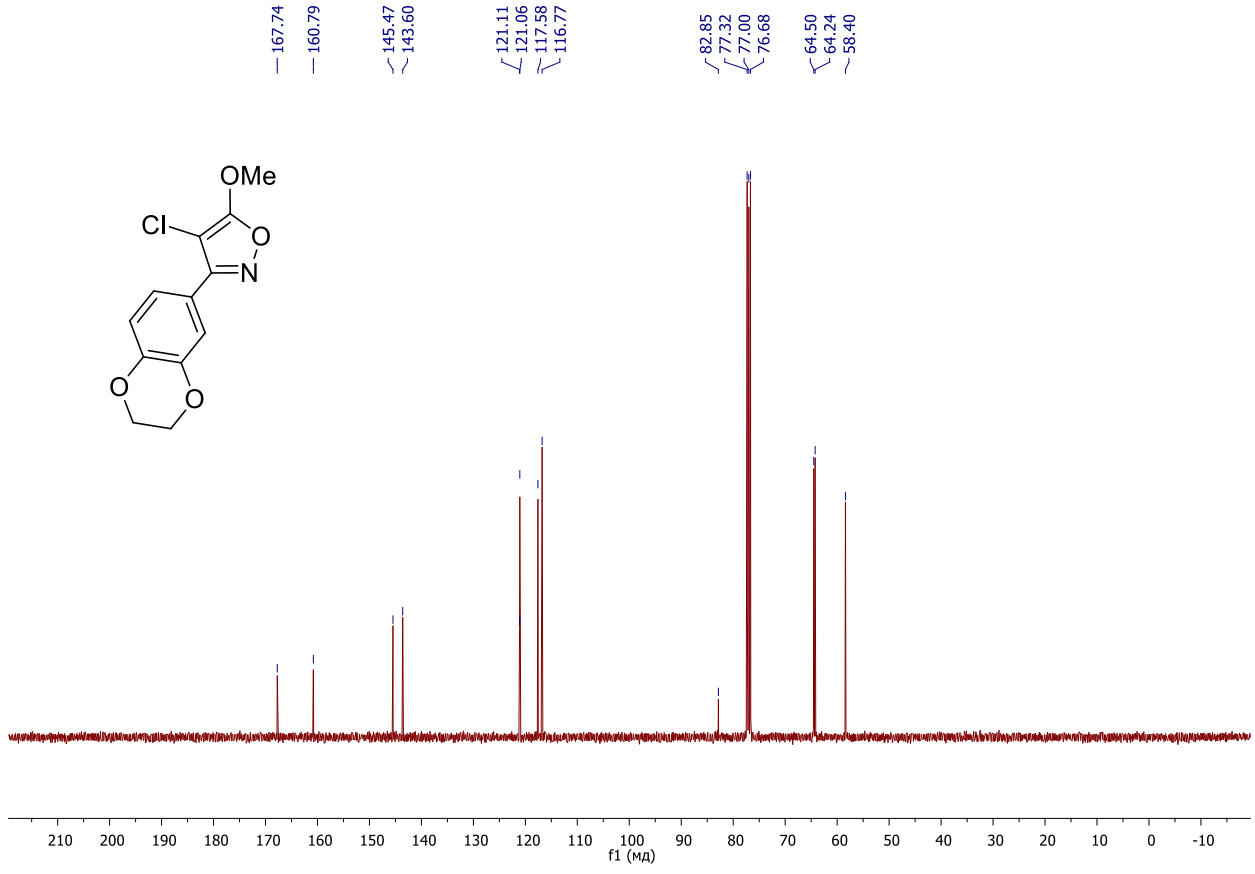
4-Chloro-3-(2,4-dimethylphenyl)-5-methoxyisoxazole (13f)



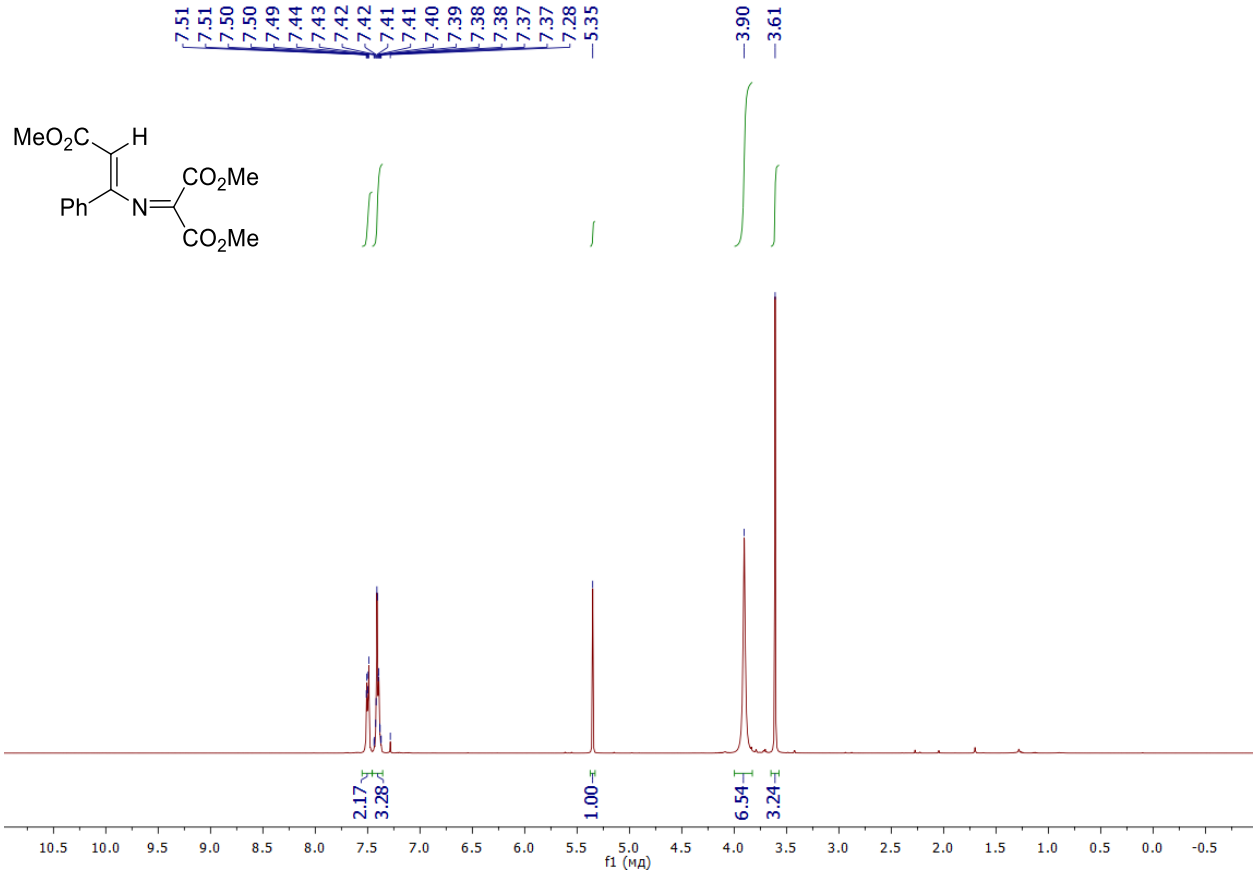


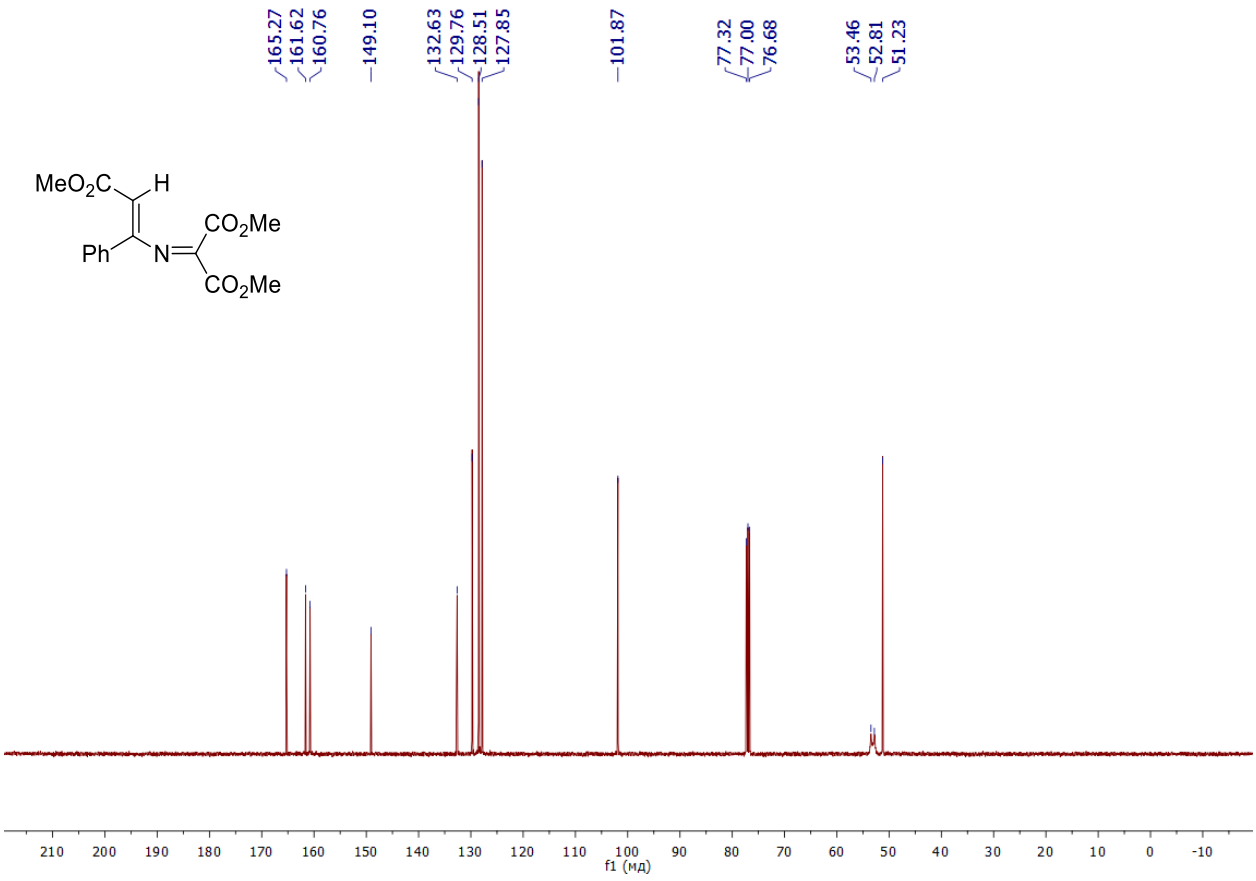
4-Chloro-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5-methoxyisoxazole (13h)



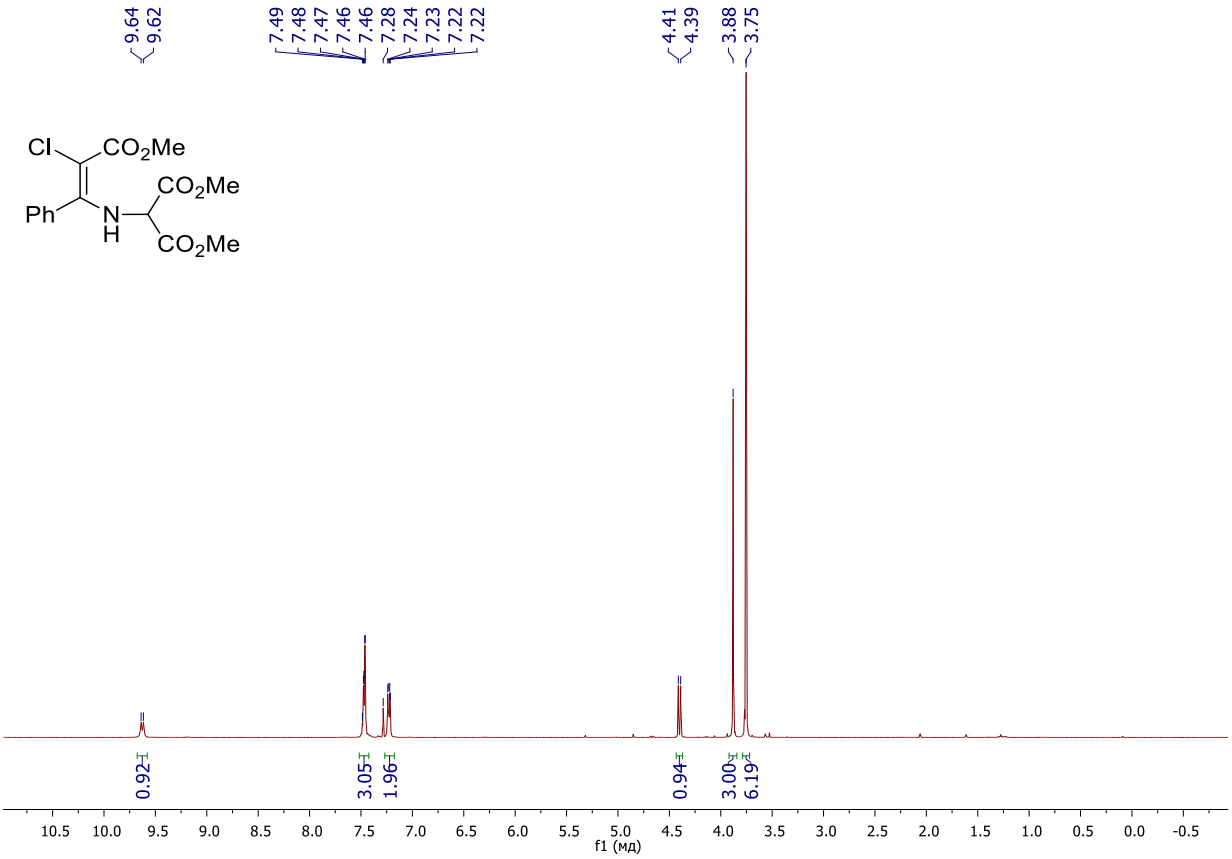


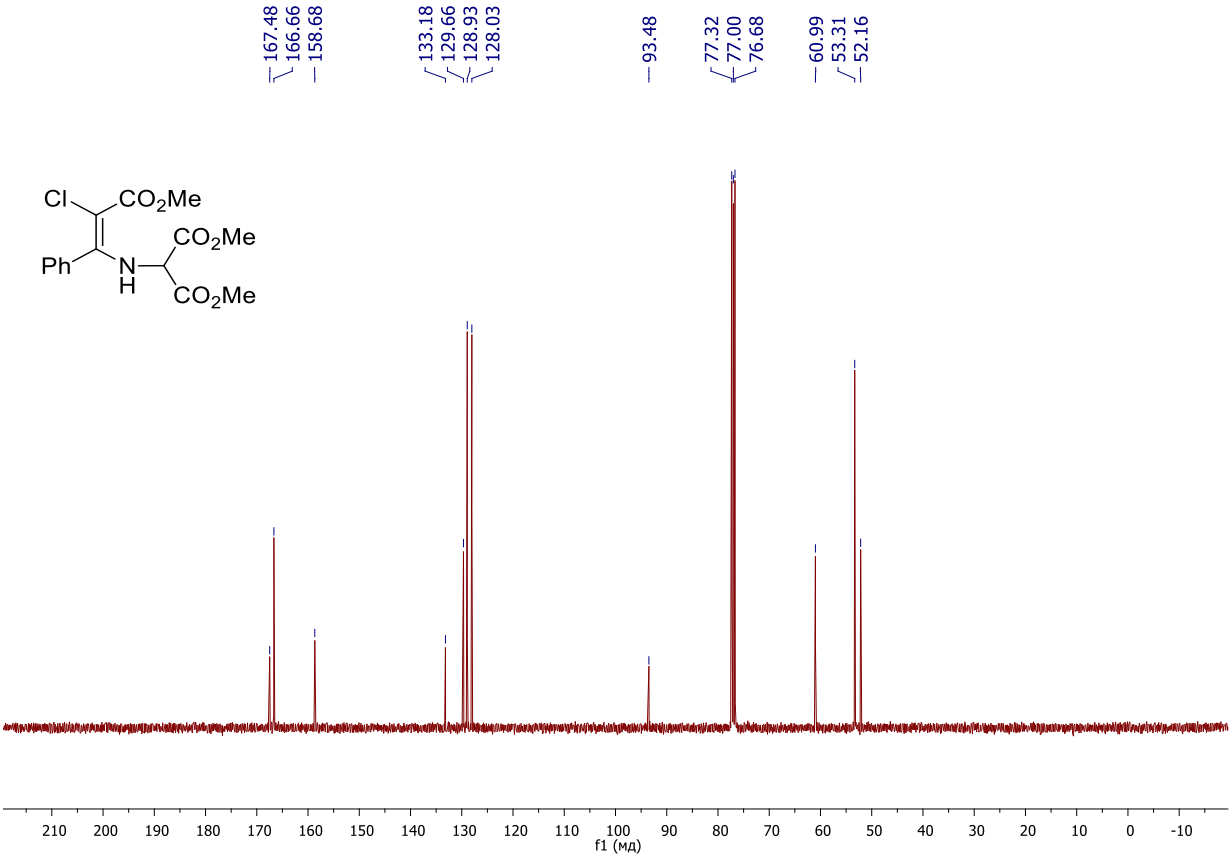
Dimethyl (*E*)-2-[(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)imino]malonate (*E*-14)





Dimethyl (*E*)-2-[(2-chloro-3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)amino]malonate (15)





10. X-Ray Data of Compound 5b

Figure S-1. X-Ray Crystal Structure of Compound **5b** with 50% Ellipsoid Probability (CCDC 1547356)

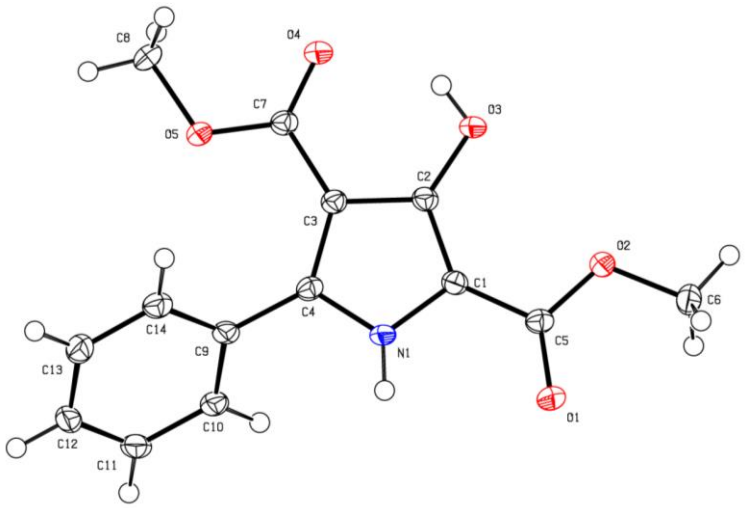


Table S-1. Crystal data and structure refinement for Compound **5b**

Identification code	smi13
Empirical formula	$C_{14}H_{13}NO_5$
Formula weight	275.25
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.5316(8)
b/Å	10.4595(15)
c/Å	10.4693(14)
α/°	62.167(14)
β/°	83.427(11)
γ/°	87.651(11)
Volume/Å^3	628.27(16)
Z	2
ρ_{calc}g/cm^3	1.455
μ/mm^{-1}	0.942
F(000)	288.0
Crystal size/mm^3	0.36 × 0.26 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.562 to 139.974
Index ranges	$-4 \le h \le 7$, $-12 \le k \le 12$, $-12 \le l \le 12$
Reflections collected	4180
Independent reflections	2360 [R_{int} = 0.0322, R_{sigma} = 0.0368]
Data/restraints/parameters	2360/0/184
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1193
Largest diff. peak/hole / e Å^{-3}	0.31/-0.25

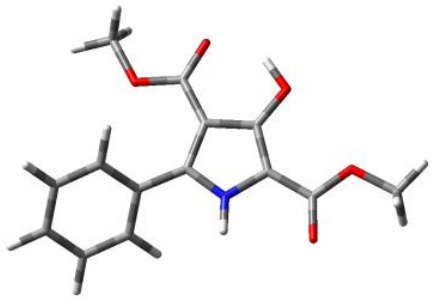
11. Calculation Details

All calculations were performed by using the Gaussian 09 suite of quantum chemical programs.[10] Geometry optimizations of Me_3SnH, Me_3SnOMe, Me_3SnCl, MeOH, compounds **4b**, **5b**, **16–22** and transition states TS1−TS7 were performed at the DFT B3LYP/6-31+G(d,p) level using PCM model for toluene. Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the frequency indeed pertains to the desired reaction coordinate. Single point calculations of Gibbs free energies for stationary points were carried out at the DFT wB97XD level using LANL2DZ basis set for chlorine and tin atoms and cc-pVTZ basis set for other atoms (PCM solvation model for toluene). Thermal corrections to Gibbs free energies obtained in optimization calculations were used.

Table S-2. Energies (au) and cartesian coordinates of stationary points for Me_3SnH, Me_3SnOMe, Me_3SnCl, MeOH, compounds **4b**, **5b**, **16–22** and transition states TS1–TS7 (B3LYP/6-31+G(d,p), a.u., PCM, toluene, 383 K), and Gibbs free energies (G′, au) for these compounds calculated at wB97XD/cc-pVTZ/LANL2DZ level (PCM, toluene).

1*H*-Pyrrole **5b**

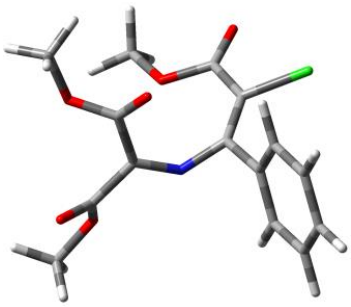
Zero-point correction = 0.254225
Thermal correction to Gibbs Free Energy = 0.206467
E_0 = -972.032298, E = -972.013882, H = -972.012938
G = -972.080056, G′ = -972.0436387.
Imaginary frequency = 0.



C	-0.31630932	0.75208100	-0.00345466
C	-0.73923532	-0.59839800	-0.00579566
N	0.38076368	-1.35494700	-0.01360666
C	1.53876068	-0.58228500	-0.00137266
C	-2.06388332	-1.24306900	0.00300934
C	2.82148768	-1.25746600	0.01391634
C	1.11904668	0.74491100	0.00244234
O	2.93157768	-2.48189600	0.01480834
O	3.86757268	-0.41042500	0.02849734
O	1.90095268	1.83239900	-0.01053666
C	5.17473868	-1.01743700	0.04781134
C	-1.03669532	2.00921600	-0.10889466
O	-0.45094832	3.10019600	-0.10282766
O	-2.36782732	1.91295600	-0.22930166
C	-3.09494232	3.15363500	-0.36627466
C	-2.31143432	-2.33741700	-0.84605866
C	-3.54117832	-2.99740700	-0.81237866
C	-4.53966032	-2.57498100	0.06921834
C	-4.30132732	-1.48808000	0.91690534
C	-3.07441932	-0.82575100	0.88597534
H	5.87592268	-0.18398400	0.05363434
H	5.29814268	-1.63005800	0.94386534
H	5.32126568	-1.63730100	-0.83966666
H	-4.14069132	2.86138400	-0.44961866
H	-2.77056732	3.68547100	-1.26297966
H	-2.93773332	3.78517500	0.51047834
H	-1.54895332	-2.65599800	-1.55126166
H	-3.71974932	-3.83539400	-1.47950966
H	-5.49638932	-3.08801000	0.09609834
H	-5.07057132	-1.15981200	1.60968534
H	-2.89154632	0.00928500	1.55243034
H	0.40988768	-2.36401700	0.05489534
H	1.28869768	2.60480800	-0.02940566

Azamuconoate **4b**

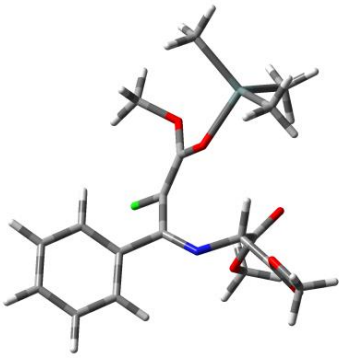
Zero-point correction = 0.273109
Thermal correction to Gibbs Free Energy = 0.191292
E_0 = -1100.808713, E = -1100.772591 H = -1100.771378
G = -1100.890530, G′ = -1100.8855592.
Imaginary frequency = 0.



C	1.29902180	1.92844449	-0.48062477
C	1.22871080	0.57178449	-0.41797677
N	0.08893080	-0.16970551	-0.73984577
C	-0.88071420	-0.46867951	0.01913623
C	2.40275880	-0.32632551	-0.20042877
C	-1.92502020	-1.44503051	-0.48168877
C	-1.01353720	0.01451549	1.45643523
O	-2.32522720	-2.35856551	0.21322023
O	-2.29900120	-1.20128251	-1.73615277
O	-0.06191820	0.21733549	2.18010323
C	-3.24340420	-2.13626251	-2.31244177
O	-2.29301520	0.21041549	1.77691223
C	-2.55624720	0.68275149	3.12119123
C	0.21249480	2.90695449	-0.72271377
O	0.38641580	4.09178749	-0.94014877
O	-1.01348820	2.34046749	-0.67544377
C	-2.12240420	3.22112149	-0.95745977
C	3.13780380	-0.26515251	0.99290823
C	4.20746480	-1.13736051	1.19641523
C	4.55313980	-2.07215351	0.21424623
C	3.81730180	-2.13983651	-0.97217377
C	2.73752980	-1.27786451	-1.17702177
H	-3.43494120	-1.76394451	-3.31722077
H	-2.80486120	-3.13564351	-2.34461477
H	-4.16123020	-2.15420151	-1.72115977
H	-3.63803220	0.78709449	3.18006723
H	-2.19606320	-0.04959051	3.84626423
H	-2.06071120	1.64194549	3.28377423
H	-3.01041320	2.59463849	-0.88260377
H	-2.02753920	3.63827649	-1.96223777
H	-2.15669620	4.03276649	-0.22747577
H	2.86259080	0.45287949	1.75703823
H	4.77024280	-1.08756651	2.12390423
H	5.38973680	-2.74589851	0.37540023
H	4.08026380	-2.86325451	-1.73832877
H	2.16222780	-1.33043251	-2.09576177
Cl	2.91181780	2.71880149	-0.37730277

Intermediate **16**

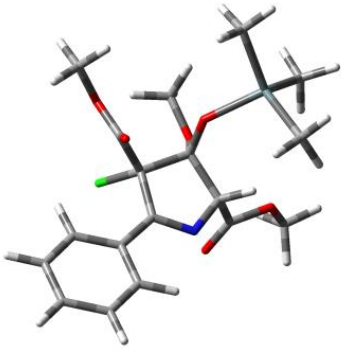
Zero-point correction = 0.394188
Thermal correction to Gibbs Free Energy = 0.292065
E_0 = -1224.454014, E = -1224.403449, H = -1224.402235
G = -1224.556138, G′ = -1224.5630404.
Imaginary frequency = 0.



C	-0.74036824	-0.12966078	-0.83076996
C	-1.70622424	-0.87928178	0.00839204
N	-1.64711124	-2.13630578	0.28595704
C	-0.61889324	-2.99081578	-0.27008696
C	-2.85668124	-0.12077578	0.59074004
C	-0.87054624	-4.42681278	0.20905704
C	-0.46032524	-3.00890878	-1.79760896
O	-1.18363724	-5.35717578	-0.50856096
O	-0.68894824	-4.52651778	1.53285204
O	0.60831676	-3.21125578	-2.34434596
C	-0.95820124	-5.81851478	2.11844904
O	-1.61630224	-2.82494278	-2.43859696
C	-1.56459924	-2.86764878	-3.88117396
C	0.59951076	-0.01464178	-0.62840696
O	1.21676376	-0.66471278	0.34205804
O	1.43275576	0.72120422	-1.42702796
C	1.34285276	2.16282822	-1.35562096
C	-4.06808024	-0.77920178	0.86019004
C	-5.13259124	-0.09291778	1.44443104
C	-5.00141824	1.26135422	1.77329204
C	-3.79932824	1.92471522	1.50929204
C	-2.73735324	1.23997422	0.91454804
H	-0.76680924	-5.69687578	3.18378204
H	-1.99856524	-6.10142678	1.94326004
H	-0.29641524	-6.57441578	1.68951704
H	-2.58692324	-2.68600278	-4.20955296
H	-0.89533424	-2.09091278	-4.25650296
H	-1.21862524	-3.84879378	-4.21365096
H	2.19374476	2.53599922	-1.92646296
H	1.41736776	2.49763622	-0.31612896
H	0.41334076	2.51771422	-1.80287396
H	-4.15937224	-1.82900678	0.60338004
H	-6.06655424	-0.61242978	1.63977604
H	-5.83076624	1.79546322	2.22857404
H	-3.68859724	2.97495322	1.76418504
H	-1.80603724	1.75938922	0.71127504
Cl	-1.49543424	0.75051222	-2.23477796
Sn	3.24655976	-0.82582978	0.45831804
C	3.32575076	-2.23283278	2.05829504
H	4.35356576	-2.34472678	2.41758104
H	2.70218376	-1.89434278	2.89050004
H	2.96652776	-3.21201878	1.73029904
C	3.97883876	1.09879822	1.02868304
H	4.01060776	1.77948222	0.17450204
H	3.34090476	1.53219522	1.80457604

Pyrroline **17**

Zero-point correction = 0.395504
Thermal correction to Gibbs Free Energy = 0.298088
E_0 = -1224.467687, E = -1224.418412, H = -1224.417198
G = -1224.565103, G′ = -1224.5787373.
Imaginary frequency = 0.



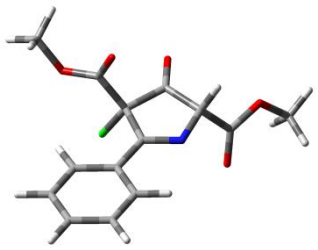
C	-0.65000990	-0.17282620	0.76687814
C	-1.37156790	0.45869780	-0.42393386
N	-0.67367390	1.32373980	-1.06627786
C	0.64028010	1.50033380	-0.48404786
C	-2.76397390	0.15013380	-0.83090686
C	0.78293310	2.91410480	0.08753514
C	0.85504510	0.36220980	0.58251614
O	-0.10936590	3.56514980	0.58477714
O	2.04994710	3.35167180	-0.05610186
O	1.56918010	-0.70664320	0.09033714
C	2.33441610	4.65317680	0.49958314
O	1.43333210	0.94740780	1.71477614
C	1.86467610	0.08420780	2.77421814
C	-0.69206990	-1.70454120	0.75828914
O	-0.91048090	-2.33949220	-0.25283186
O	-0.43771590	-2.24849420	1.95175714
C	-0.40597390	-3.69195420	1.99539114
C	-3.23578090	0.65504080	-2.05721486
C	-4.53924590	0.39934680	-2.47714086
C	-5.40009390	-0.36207020	-1.67792786
C	-4.94393790	-0.86339920	-0.45649286
C	-3.63642890	-0.61142820	-0.03621086
H	3.38885910	4.83280080	0.29274114
H	1.71231510	5.41285980	0.02110214
H	2.14619810	4.65164980	1.57555614
H	2.25528610	0.74903980	3.54630914
H	1.03474010	-0.49960820	3.17850214
H	2.65755610	-0.59147020	2.43976814
H	0.38242310	-4.07015920	1.34114014
H	-1.36930390	-4.10013320	1.68230414
H	-0.20068190	-3.94217520	3.03527814
H	-2.56555790	1.24674080	-2.67046986
H	-4.88468190	0.79355680	-3.42857186
H	-6.41687690	-0.56094920	-2.00461586
H	-5.60520490	-1.45034720	0.17423414
H	-3.31347490	-0.99818420	0.92283014
Cl	-1.43445290	0.50462880	2.33095814
Sn	3.30479710	-0.89052720	-0.87829186
C	2.92931410	-0.39713520	-2.92672386
H	2.97049210	0.68272880	-3.09462486
H	3.68110310	-0.87158220	-3.56565886
H	1.94266110	-0.76202620	-3.22633386
C	3.67050910	-2.96848920	-0.57227486
H	4.58509110	-3.27928120	-1.08666186
H	3.78239110	-3.18580620	0.49368314

H	4.99157476	1.00383822	1.43316104
C	3.94661276	-1.57597478	-1.41009596
H	4.83304276	-2.19872278	-1.25606696
H	3.16606376	-2.18466778	-1.87512496
H	4.20110376	-0.75539178	-2.08509896
H	0.42878876	-2.67344278	0.14934504

H	2.83563810	-3.55631520	-0.96381086
C	4.72607810	0.40384880	0.05921814
H	5.64281210	0.44842280	-0.53707886
H	4.31577010	1.41332780	0.14689114
H	4.98047810	0.04133380	1.05903414
H	1.39406010	1.39580780	-1.26936086

Pyrroline **18**

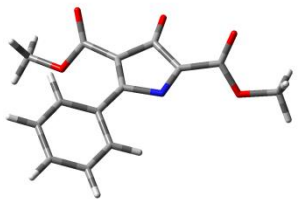
Zero-point correction = 0.242121
Thermal correction to Gibbs Free Energy = 0.168020
E_0 = -986.319403, E = -986.288422, H = -986.287209
G = -986.393504, G′ = -986.3894945.
Imaginary frequency = 0.



C	-0.49020609	-0.86379169	0.46303055
C	-0.77742809	0.58022331	0.04222255
N	0.23381191	1.19297731	-0.46323545
C	1.41433191	0.35644131	-0.52440145
C	-2.09883909	1.22531931	0.17329455
C	2.59084291	0.96581031	0.24821655
C	1.00488691	-1.01312269	0.04581255
O	2.47358391	1.68804431	1.21380255
O	3.75269791	0.56202231	-0.27963145
O	1.66806491	-2.01184069	0.13589955
C	4.95241891	0.99478631	0.40523355
C	-1.32208509	-1.89694869	-0.29389245
O	-1.32265809	-1.87181869	-1.51032245
O	-1.96820809	-2.77226669	0.46226755
C	-2.72493809	-3.78862269	-0.24443645
C	-2.27082609	2.53524431	-0.31412145
C	-3.50757709	3.16663131	-0.21591245
C	-4.59342209	2.50310731	0.36963455
C	-4.43179209	1.20454131	0.85773155
C	-3.19234409	0.56800231	0.76244555
H	5.77540891	0.55257331	-0.15361745
H	5.01615491	2.08473731	0.39453755
H	4.94490591	0.63471131	1.43597155
H	-2.05300109	-4.38299269	-0.86593045
H	-3.48937309	-3.31838469	-0.86562345
H	-3.17509609	-4.39803469	0.53675955
H	-1.42583709	3.04132031	-0.76732145
H	-3.62769309	4.17678531	-0.59603945
H	-5.55751609	2.99760631	0.44533755
H	-5.26716009	0.68564531	1.31808055
H	-3.08536909	-0.43219369	1.16643855
Cl	-0.54890509	-1.03820869	2.31478055
H	1.72977491	0.21157231	-1.56482245

Pyrrolidone **19**

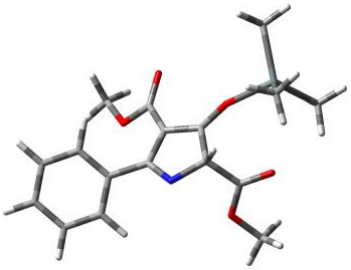
Zero-point correction = 0.228446
Thermal correction to Gibbs Free Energy = 0.158062
E_0 = -970.779444, E = -970.750838, H = -970.749624,
G = -970.849828, G′ = -970.8058001.
Imaginary frequency = 0.



C	-0.64317682	1.64838746	0.52765661
C	-0.73758282	0.28537146	0.49983661
N	0.58352218	-0.34832354	0.46880161
C	1.45867818	0.57794846	0.55357961
C	-1.87115982	-0.62541754	0.54587961
C	2.93035118	0.33464146	0.65823261
C	0.80253118	1.97218646	0.59158361
O	3.60927018	0.87807646	1.50632661
O	3.37257518	-0.52869854	-0.25946439
O	1.37367518	3.04098646	0.58655961
C	4.78623918	-0.84267254	-0.20766639
C	-1.66918182	2.71262846	0.48610561
O	-1.65465482	3.69396246	1.20552961
O	-2.60058982	2.49310646	-0.46402439
C	-3.64442782	3.48681046	-0.56986439
C	-1.69910882	-1.96116454	0.12097061
C	-2.76904382	-2.85330454	0.14697861
C	-4.01655282	-2.43903254	0.62214161
C	-4.19214682	-1.12405854	1.07312161
C	-3.13359782	-0.22354854	1.03380361
H	4.95576318	-1.52685354	-1.03692739
H	5.37622418	0.06815546	-0.32604039
H	5.02702818	-1.31815154	0.74509961
H	-4.29192282	3.13684546	-1.37241339
H	-3.21508482	4.46029246	-0.81495339
H	-4.19645382	3.55899146	0.37020061
H	-0.72641582	-2.28066154	-0.23273239
H	-2.62706082	-3.87374754	-0.19497739
H	-4.84705682	-3.13803554	0.65285361
H	-5.15409782	-0.80694754	1.46366161
H	-3.27754482	0.78312146	1.40669361

2*H*-Pyrrole **20**

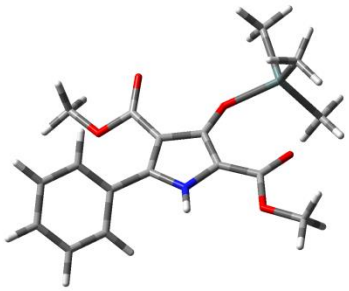
Zero-point correction = 0.350084
Thermal correction to Gibbs Free Energy = 0.259515
E_0 = -1094.442807, E = -1094.399991, H = -1094.398777
G = -1094.533376, G′ = -1094.5198799.
Imaginary frequency = 0.



C	-0.28924343	0.10412756	-0.29189209
C	-1.22038843	-0.93717144	0.18510991
N	-0.63223243	-2.02401744	0.59963391
C	0.79639157	-1.82516844	0.45062791
C	-2.69564143	-0.82338344	0.29861591
C	1.51902457	-2.83628644	-0.43355209
C	0.98045557	-0.40949244	-0.11808509
O	2.73573857	-2.94066944	-0.43024609
O	0.70781857	-3.54217144	-1.21894209
O	2.11885957	0.12940256	-0.43059909
C	1.34067157	-4.48996544	-2.10937709
C	-0.55429143	1.39533456	-0.94076609
O	0.19480457	2.36143256	-0.92113309
O	-1.72999943	1.40046656	-1.61628609
C	-2.07899243	2.63256456	-2.27288509
C	-3.49613643	-1.94172344	0.01550091
C	-4.88238643	-1.87757344	0.16789591
C	-5.48529943	-0.70038544	0.62337591
C	-4.69307143	0.41285956	0.92287291
C	-3.30828743	0.35461556	0.75447591
H	0.52142957	-4.97017144	-2.64215709
H	2.00271857	-3.96942944	-2.80468509
H	1.91170957	-5.22223544	-1.53486009
H	-3.05534143	2.45320156	-2.72257309
H	-1.34143243	2.87876456	-3.04081009
H	-2.13268243	3.45164756	-1.55096909
H	-3.01958243	-2.85514744	-0.32476209
H	-5.49115743	-2.74672644	-0.06525109
H	-6.56361943	-0.65127444	0.74656791
H	-5.15309743	1.32678556	1.28812691
H	-2.70255443	1.22245156	0.99561591
Sn	4.07621957	0.01262256	0.08354791
C	5.04333057	-0.86122744	-1.60030309
H	6.12898957	-0.75882144	-1.50550609
H	4.78547257	-1.91901444	-1.67364309
H	4.72712457	-0.34835744	-2.51325909
C	4.20183657	-1.01083244	1.95240591
H	3.44589757	-0.63036344	2.64603191
H	4.05937457	-2.08394044	1.81286691
H	5.18674257	-0.83574444	2.39697991
C	4.48006157	2.09931356	0.26452391
H	5.55074857	2.27352856	0.41225291
H	4.16247457	2.62129556	-0.64226109
H	3.93673857	2.52343056	1.11335291
H	1.27689157	-1.89752944	1.43563191

1*H*-Pyrrole **21**

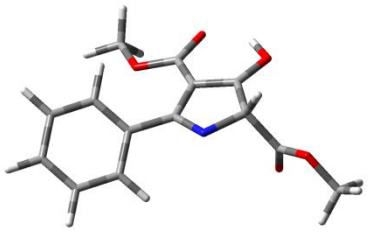
Zero-point correction = 0.350645
Thermal correction to Gibbs Free Energy = 0.259801
E_0 = -1094.474161, E = -1094.431092, H = -1094.429879
G = -1094.565006, G′ = -1094.5491417.
Imaginary frequency = 0.



C	1.17160853	-0.52317821	-0.08724318
C	2.07726153	0.55547479	-0.04792818
N	1.35524953	1.70312779	-0.07121618
C	-0.01054447	1.43121079	-0.10531218
C	3.54413853	0.61974379	0.07211582
C	-1.02086047	2.44405779	-0.14706818
C	-0.15766447	0.03079279	-0.11811518
O	-2.23461247	2.22242879	-0.17296718
O	-0.50836647	3.70286779	-0.15088018
O	-1.25818047	-0.67994721	-0.21865918
C	-1.46153547	4.78304179	-0.18409818
C	1.47087153	-1.95901921	-0.17055418
O	0.74918853	-2.85528621	0.23701882
O	2.65927253	-2.20392721	-0.78123318
C	3.05100053	-3.58578421	-0.86814918
C	4.27256753	1.54510279	-0.69701618
C	5.65809053	1.65261779	-0.55496918
C	6.33575453	0.83805979	0.35637582
C	5.61847453	-0.08484221	1.12611582
C	4.23488453	-0.19379521	0.98719782
H	-0.86411347	5.69432179	-0.17992318
H	-2.06972647	4.72813579	-1.08997818
H	-2.11113047	4.74711079	0.69360382
H	4.02302353	-3.57992621	-1.36122418
H	2.32578453	-4.15307721	-1.45674018
H	3.12848653	-4.02822021	0.12855182
H	3.75683653	2.16220979	-1.42779618
H	6.20688453	2.36600079	-1.16305818
H	7.41312653	0.92033379	0.46663482
H	6.13704853	-0.71618521	1.84196782
H	3.68338853	-0.89981621	1.59956182
Sn	-3.23924147	-0.45636421	0.06009882
C	-4.14271047	0.34406179	-1.70299418
H	-5.07446847	-0.18625121	-1.92351718
H	-4.34385047	1.41015079	-1.58453118
H	-3.46142947	0.21045479	-2.54915418
C	-3.62435147	0.44464479	1.95983982
H	-2.72572647	0.38528779	2.58187782
H	-3.89597947	1.49501579	1.83957382
H	-4.43159247	-0.08808821	2.47213682
C	-3.65763447	-2.55589321	0.16036482
H	-4.73169847	-2.73128621	0.28733682
H	-3.33243847	-3.05375621	-0.75813318
H	-3.12799347	-3.01392821	1.00071182
H	1.73660053	2.62588779	0.08086982

2*H*-Pyrrole **22**

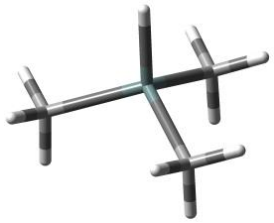
Zero-point correction = 0.253064
Thermal correction to Gibbs Free Energy = 0.204062
E_0 = -972.000401, E = -971.981993, H = -971.981049
G = -972.049404, G′ = -972.013619.
Imaginary frequency = 0.



C	-0.01814200	1.01853100	0.31070900
C	-0.27277200	-0.44065800	0.37834400
N	0.79580800	-1.13280900	0.65092900
C	1.91551300	-0.19671100	0.80727500
C	-1.56703000	-1.13939300	0.19660100
C	3.02098100	-0.54239900	-0.19839100
C	1.32265000	1.16292700	0.57422200
O	2.95840500	-0.31256900	-1.38765600
O	4.04613700	-1.15595900	0.40814200
O	2.03592000	2.27018800	0.60714800
C	5.12803600	-1.58945300	-0.44988700
C	-0.78191000	2.19982000	-0.06567400
O	-0.27103700	3.33097700	-0.03116200
O	-2.03633600	1.99354500	-0.47031900
C	-2.78428600	3.15817400	-0.88958300
C	-1.59114000	-2.35769300	-0.50297600
C	-2.78377300	-3.06719500	-0.64536900
C	-3.96361600	-2.57838800	-0.07512900
C	-3.94432300	-1.37423300	0.63482000
C	-2.75543500	-0.65401700	0.76411700
H	5.85125800	-2.05675600	0.21623200
H	4.75737200	-2.30641900	-1.18503400
H	5.56789700	-0.73081300	-0.96087600
H	-3.76379000	2.77689200	-1.17331900
H	-2.29289700	3.63429000	-1.74016300
H	-2.86734900	3.87053800	-0.06649900
H	-0.66970700	-2.73538800	-0.93313600
H	-2.79196400	-4.00170800	-1.19870700
H	-4.89149000	-3.13289400	-0.18199500
H	-4.85505900	-0.99487500	1.08906900
H	-2.75032000	0.27832000	1.31726700
H	2.32345600	-0.28349900	1.82084800
H	1.39870300	3.00664200	0.39612200

Me_3SnH

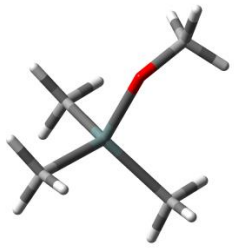
Zero-point correction = 0.114664
Thermal correction to Gibbs Free Energy = 0.068125
E_0 = -123.614336, E = -123.601427, H = -123.600214
G = -123.660874, G′ = -123.6585904.
Imaginary frequency = 0.



Sn	-0.00007500	-0.00003900	-0.23086800
C	0.57586500	1.95426900	0.45844700
H	0.58831100	1.98964900	1.55239800
H	1.57545800	2.21282300	0.09548900
H	-0.12594600	2.71309100	0.09872400
C	1.40492000	-1.47555900	0.45852800
H	1.12731800	-2.47122500	0.09888700
H	2.41216800	-1.24877200	0.09550000
H	1.43251700	-1.50133700	1.55244800
C	-1.98048400	-0.47853000	0.45857300
H	-2.01674600	-0.48622100	1.55251300
H	-2.70423700	0.25838500	0.09674500
H	-2.28719800	-1.46531400	0.09822700
H	0.00031700	-0.00022600	-1.95082300

Me_3SnOMe

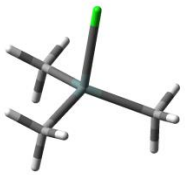
Zero-point correction = 0.148881
Thermal correction to Gibbs Free Energy = 0.092608
E_0 = -238.145602, E = -238.127730, H = -238.126516
G = -238.201875, G′ = -238.1989707.
Imaginary frequency = 0.



O	-1.46138960	-0.10337661	-0.89031024
C	-2.72223460	-0.10458861	-0.24694224
H	-3.50612860	-0.10335461	-1.01438824
H	-2.87236060	-0.99719261	0.38154976
H	-2.87252760	0.78585339	0.38456976
Sn	0.25905840	-0.10536461	0.06440776
C	1.67145640	-0.10263561	-1.53583524
H	2.69732440	-0.10187761	-1.15472124
H	1.53437240	-0.98944761	-2.16125224
H	1.53248540	0.78500539	-2.15966324
C	0.34469740	-1.88088661	1.26738476
H	-0.44070860	-1.87634561	2.02929376
H	0.21685440	-2.77046061	0.64349276
H	1.31183840	-1.95220261	1.77556976
C	0.34532440	1.66582339	1.27372276
H	1.31136940	1.73338339	1.78449976
H	0.22076140	2.55786039	0.65269776
H	-0.44192760	1.66016239	2.03371776

Me_3SnCl

Zero-point correction = 0.109490
Thermal correction to Gibbs Free Energy = 0.058535
E_0 = -138.035553, E = -138.020786, H = -138.019572
G = -138.086509, G′ = -138.0945855.
Imaginary frequency = 0.



Cl	1.80415802	-0.61196383	-0.15140939
Sn	-0.65782298	-0.61175783	-0.15134339
C	-1.16571798	-2.40346983	-1.18997639
H	-2.25311498	-2.51255383	-1.25120539
H	-0.75759398	-2.38072883	-2.20374139
H	-0.75461398	-3.27149383	-0.66805739
C	-1.16518498	1.18411517	-1.18299939
H	-0.75540698	2.05021617	-0.65676839
H	-0.75536198	1.16568117	-2.19619639
H	-2.25252898	1.29316517	-1.24565639
C	-1.16502998	-0.61569183	1.91972161
H	-2.25236598	-0.62261083	2.04534861
H	-0.74976198	-1.50111783	2.40803061
H	-0.76076298	0.27436817	2.40893561

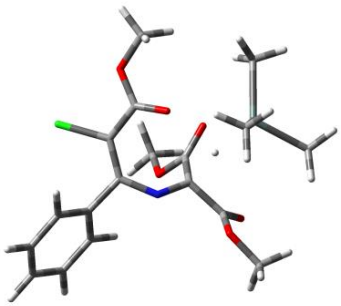
MeOH

Zero-point correction = 0.051223
Thermal correction to Gibbs Free Energy = 0.020538
E_0 = -115.686484, E = -115.681839, H = -115.680626
G = -115.717168, G′ = -115.7127995.
Imaginary frequency = 0.

C	-0.53034143	-0.31602658	-0.25507817
H	-0.88830843	-0.84252158	0.63935183
H	-0.88834043	-0.84268658	-1.14939817
H	-0.94659643	0.69350142	-0.25516617
O	0.89107057	-0.17273258	-0.25512417
H	1.29332057	-1.05051058	-0.25507917

TS1

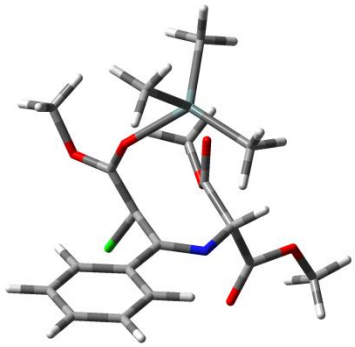
Zero-point correction = 0.387370
Thermal correction to Gibbs Free Energy = 0.285779
E_0 = -1224.397719, E = -1224.347157, H = -1224.345944
G = -1224.499310, G′ = -1224.5038208.
Imaginary frequency = 1.



C	1.65258600	1.54900200	-0.14281900
C	1.91830000	0.21459600	-0.36190900
N	1.00298300	-0.79907000	-0.46025900
C	0.01422100	-1.03796600	0.37710200
C	3.31534300	-0.28473100	-0.59003900
C	-0.53634700	-2.46250700	0.33793000
C	0.00411400	-0.47173300	1.82016000
O	-0.82625500	-3.06873700	1.35275500
O	-0.65125700	-2.93916700	-0.89924100
O	-0.91906000	0.12727500	2.33077000
C	-1.09795700	-4.30987300	-1.01583300
O	1.16036100	-0.75055200	2.42703100
C	1.29260700	-0.29627500	3.79587100
C	0.35688200	2.21440900	-0.27873900
O	-0.61658300	1.70742000	-0.83767500
O	0.34038500	3.46561800	0.21383700
C	-0.85724300	4.23418500	-0.00095300
C	3.81252100	-1.33453400	0.19600700
C	5.08971200	-1.84876800	-0.03945000
C	5.87010800	-1.33869300	-1.08128700
C	5.36975000	-0.30716400	-1.88294900
C	4.10250700	0.22276300	-1.63458500
H	-1.13170900	-4.50829300	-2.08589300
H	-0.38833700	-4.97661000	-0.52156800
H	-2.08630000	-4.42599700	-0.56614300
H	2.28949700	-0.60722100	4.10370900
H	1.19393800	0.79005300	3.83983600
H	0.52800000	-0.76597300	4.41771700
H	-0.61328400	5.24147800	0.33512800
H	-1.68103600	3.82632400	0.58725900
H	-1.12595100	4.23602700	-1.05995500
H	3.19854300	-1.73863200	0.99420700
H	5.47048500	-2.65217900	0.58476500
H	6.85970800	-1.74476100	-1.27102600
H	5.96613400	0.08634300	-2.70115200
H	3.71909400	1.02554200	-2.25628900
Cl	3.04572700	2.65859000	0.22134100
Sn	-3.00737000	0.11103700	-0.44952700
C	-4.11926100	-1.65642500	0.08988700
H	-5.19119800	-1.44035500	0.01875800
H	-3.89228400	-2.48717700	-0.58421300
H	-3.89702000	-1.96482700	1.11510900
C	-3.05631200	0.40622300	-2.56950100
H	-2.41863200	1.24955500	-2.84177100
H	-2.69749300	-0.48839900	-3.08581900
H	-4.08260700	0.60863900	-2.89406700

TS2

Zero-point correction = 0.393639
Thermal correction to Gibbs Free Energy = 0.296459
E_0 = -1224.437700, E = -1224.388668, H = -1224.387454
G = -1224.534880, G′ = -1224.5458267.
Imaginary frequency = 1.



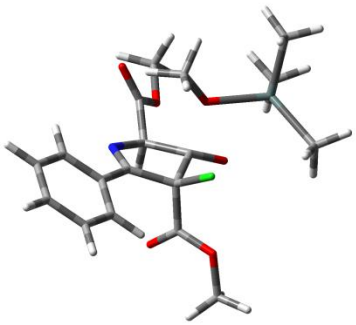
C	0.53832534	1.43479708	1.32338538
C	0.71417534	2.15793908	0.01783438
N	1.28152534	1.56122108	-0.96826962
C	1.71188634	0.20454008	-0.73354562
C	0.24373934	3.56090608	-0.14971662
C	3.24256034	0.14361508	-0.63201162
C	0.99101834	-0.48192892	0.46770238
O	3.95918334	1.03309908	-0.22966762
O	3.68728034	-1.04452592	-1.08363062
O	-0.12915166	-1.04653592	0.27268638
C	5.11107434	-1.26399592	-0.99432362
O	1.86805834	-1.02568292	1.34358138
C	1.34210834	-1.92679792	2.33150938
C	-0.76022466	1.18190508	1.81860338
O	-1.73645366	0.93701708	1.03637938
O	-0.94291266	1.11506108	3.13862538
C	-2.24362566	0.71686308	3.62145438
C	0.31424234	4.17637008	-1.41420162
C	-0.12444166	5.48658308	-1.58978362
C	-0.63822366	6.20999108	-0.50580962
C	-0.70675566	5.61127408	0.75413738
C	-0.27018866	4.29589708	0.93118038
H	5.27500234	-2.26373292	-1.39475362
H	5.64665534	-0.51820592	-1.58593562
H	5.43606534	-1.20641392	0.04705038
H	2.20636634	-2.26188792	2.90447438
H	0.64114534	-1.40418992	2.98834738
H	0.84299134	-2.77280692	1.85390138
H	-2.46215966	-0.31253292	3.32803038
H	-3.01599866	1.38526508	3.23639038
H	-2.17387566	0.79401108	4.70558538
H	0.71693034	3.61215408	-2.24784462
H	-0.06632666	5.94671108	-2.57213762
H	-0.97839066	7.23239808	-0.64397662
H	-1.09539766	6.16677808	1.60266538
H	-0.31316066	3.85292508	1.92022838
Cl	1.79489434	1.89458708	2.56758038
Sn	-2.24303066	-0.45494692	-0.52709462
C	-4.06652166	0.69083808	-0.66657562
H	-3.85207766	1.72919908	-0.93743562
H	-4.71632666	0.26045808	-1.43734362
H	-4.60901466	0.68783408	0.28368338
C	-2.76449766	-2.36996992	0.26431838
H	-3.75188566	-2.66981892	-0.10028862
H	-2.02590966	-3.12094192	-0.02460362

C	-3.71705400	1.76239700	0.71132700
H	-4.73580800	1.54990300	1.05052100
H	-3.08180500	1.90537300	1.58850200
H	-3.72715400	2.67887000	0.11662300
H	-1.29209200	-0.41636500	-0.03002200

H	-2.80097866	-2.32565292	1.35715238
C	-1.35097066	-0.32238192	-2.46807862
H	-2.14643066	-0.27356192	-3.21857662
H	-0.73957066	0.57976908	-2.55791962
H	-0.72416266	-1.19561092	-2.66580762
H	1.43643734	-0.39600892	-1.60655462

TS3

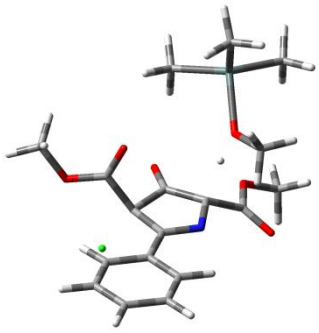
Zero-point correction = 0.393651
Thermal correction to Gibbs Free Energy = 0.298125
E_0 = -1224.444573, E = -1224.395664, H = -1224.394451
G = -1224.540100, G′ = -1224.5532914.
Imaginary frequency = 1.



C	1.09863854	-0.03360201	0.32610255
C	1.96884654	1.19580499	0.08059855
N	1.43947254	2.29229799	0.49258955
C	0.15611454	2.05310399	1.12672755
C	3.31001654	1.17514599	-0.54166445
C	-0.81830946	3.20222499	0.91603055
C	-0.31313546	0.63831199	0.65569055
O	-0.75394746	4.02853899	0.02852655
O	-1.76174446	3.19808699	1.87331055
O	-1.24525446	-0.01388201	1.16695655
C	-2.74712546	4.25035199	1.80278055
O	-1.07091146	0.98299799	-0.94451045
C	-0.54261646	1.64226099	-2.11136745
C	1.51271954	-0.76539901	1.61274255
O	1.89516154	-0.13670501	2.58233155
O	1.36032154	-2.08362601	1.57355155
C	1.64790954	-2.79089601	2.80417755
C	3.83852654	2.37276599	-1.05845445
C	5.11498554	2.39902699	-1.61586545
C	5.88821754	1.23242899	-1.65903645
C	5.37391154	0.04016099	-1.14292345
C	4.09089054	0.00869999	-0.59220745
H	-3.43063946	4.06150199	2.62927755
H	-2.26464846	5.22403499	1.91433755
H	-3.27585046	4.21448099	0.84778755
H	0.12427454	0.97040999	-2.65938945
H	-1.37345446	1.93982599	-2.75553345
H	-0.00925446	2.54045899	-1.79799545
H	0.98124354	-2.44358901	3.59572555
H	2.68704954	-2.62752201	3.09661155
H	1.46791854	-3.83988601	2.57552555
H	3.23590354	3.27347699	-1.01278745
H	5.50847454	3.32868799	-2.01664145
H	6.88404454	1.25385299	-2.09240145
H	5.96889354	-0.86794001	-1.16915845
H	3.70766854	-0.92788701	-0.20283745
Cl	1.02241454	-1.19457901	-1.11631245
Sn	-2.84703346	-0.11573201	-0.80840645
C	-4.24149646	0.82867899	0.50401455
H	-4.29212046	1.90230299	0.30232855

TS4

Zero-point correction = 0.388345
Thermal correction to Gibbs Free Energy = 0.285982
E_0 = -1224.453686, E = -1224.403298, H = -1224.402085
G = -1224.556049, G′ = -1224.5569176.
Imaginary frequency = 1.



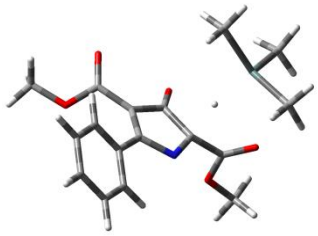
C	1.67922991	0.26446217	-0.96490355
C	2.01285991	0.86265817	0.39700245
N	1.10897591	1.68741217	0.80601645
C	0.00070091	1.75738317	-0.08869655
C	3.22337491	0.55549017	1.18105445
C	-0.71934609	3.04888217	-0.13259255
C	0.28989591	0.95237217	-1.28163255
O	-0.53446409	3.98871817	0.62581145
O	-1.67944109	3.05883417	-1.09151155
O	-0.34307909	0.73977717	-2.30009255
C	-2.42027209	4.28521117	-1.22503155
C	1.50477291	-1.24542983	-0.96394155
O	0.71155791	-1.76116483	-0.19470355
O	2.24079691	-1.90934083	-1.85026155
C	2.05852291	-3.34407583	-1.88573355
C	3.41804591	1.18357017	2.42742045
C	4.54954991	0.90922217	3.19122445
C	5.51234991	0.00190817	2.72948945
C	5.33070691	-0.62419683	1.49436345
C	4.19728791	-0.34972683	0.72431245
H	-3.11561309	4.11373117	-2.04675355
H	-2.96192809	4.51252517	-0.30302655
H	-1.74983909	5.11524317	-1.46088755
H	1.02458491	-3.58209883	-2.14300955
H	2.30910091	-3.77853283	-0.91571655
H	2.73995291	-3.69689483	-2.65800955
H	2.67170491	1.88842717	2.77739545
H	4.68451891	1.40513017	4.14845045
H	6.39513591	-0.20987683	3.32600445
H	6.07367391	-1.32416183	1.12273545
H	4.08927791	-0.83303583	-0.24038255
Cl	2.88455391	0.87922217	-2.25411555
H	-1.04271309	0.94683317	0.61463245
O	-1.79788609	0.40831617	1.29212345
C	-1.56257409	0.74272717	2.68178245
H	-0.64853709	1.33714417	2.72864145
H	-2.39944809	1.32691617	3.07556245
H	-1.43191209	-0.17422583	3.26166445

H	-5.23747146	0.40454099	0.33747455
H	-3.95093846	0.67540399	1.54468155
C	-2.61183446	-2.22663501	-0.59780245
H	-2.48171946	-2.49043601	0.45338655
H	-3.49890746	-2.73058101	-0.99582845
H	-1.73578746	-2.56790701	-1.15430545
C	-3.48841946	0.26186899	-2.83185245
H	-3.67675246	1.32423099	-3.01440045
H	-2.76002746	-0.09581201	-3.56580545
H	-4.42707946	-0.27842801	-2.99968545
H	0.31068254	1.94866999	2.20855855

Sn	-3.39842409	-0.72623483	0.63943745
C	-2.75380609	-1.47004983	-1.23991455
H	-3.59614109	-1.94854683	-1.74888455
H	-2.37462309	-0.65795183	-1.86517255
H	-1.95674909	-2.20319783	-1.09710755
C	-4.98661509	0.69685317	0.57774645
H	-5.14858509	1.14509217	1.56198745
H	-4.75089509	1.48935317	-0.13725555
H	-5.91559409	0.21084317	0.26330045
C	-3.57209809	-2.16789883	2.20266345
H	-4.31450109	-2.92312883	1.92606145
H	-2.61477409	-2.67123283	2.36367645
H	-3.89158909	-1.70165183	3.13857745

TS5^{C}

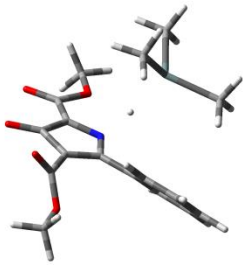
Zero-point correction = 0.342346
Thermal correction to Gibbs Free Energy = 0.247790
E_0 = -1094.365116, E = -1094.321632 H = -1094.320419
G = -1094.459672, G′ = -1094.4368497.
Imaginary frequency = 1.



C	-0.73985504	0.49290134	0.78255408
C	-0.95446404	0.30441634	-0.57751592
N	0.10724396	0.75932434	-1.38411692
C	1.09366996	1.08229434	-0.57206792
C	-2.07550404	-0.32993866	-1.27833792
C	2.19975096	2.00977334	-1.03805392
C	0.58876396	1.09684634	0.90822908
O	3.34144396	1.67732434	-1.29154692
O	1.73375596	3.25796034	-1.10801692
O	1.18829296	1.57427734	1.85395708
C	2.68177796	4.27965834	-1.50195492
C	-1.61273304	0.30256834	1.95155508
O	-1.21896904	-0.03569766	3.05630608
O	-2.91052604	0.58558234	1.68931708
C	-3.83027804	0.41269034	2.78534008
C	-2.34708504	0.04192534	-2.61060192
C	-3.39729204	-0.55146866	-3.30984592
C	-4.17016104	-1.54727566	-2.70359792
C	-3.88947104	-1.94552766	-1.39099992
C	-2.85572304	-1.33897366	-0.68074392
H	2.11761796	5.21057234	-1.48883292
H	3.50824896	4.31543334	-0.78949592
H	3.06217096	4.06826834	-2.50327392
H	-4.81020304	0.66432134	2.38066708
H	-3.57040404	1.08159534	3.60901608
H	-3.81380704	-0.62066966	3.14123508
H	-1.73283004	0.80286834	-3.07817292
H	-3.60719204	-0.24369966	-4.32996992
H	-4.98121604	-2.01726166	-3.25250992
H	-4.47395704	-2.73273866	-0.92408492
H	-2.63648604	-1.66727066	0.32863508
Sn	3.36044196	-1.34940666	-0.12205592
C	3.95734796	-1.77747966	-2.13280992
H	4.72158696	-2.56156466	-2.13558792
H	3.10344296	-2.12229366	-2.72234192

TS5^{N}

Zero-point correction = 0.341478
Thermal correction to Gibbs Free Energy = 0.247804
E_0 = -1094.351331, E = -1094.307690, H = -1094.306476
G = -1094.445005, G′ = -1094.4212682.
Imaginary frequency = 1.



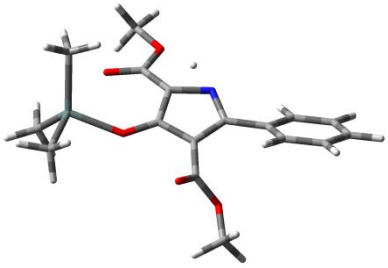
C	1.82753600	1.31602500	-0.23796500
C	1.14655300	0.36505900	0.44723400
N	-0.13626000	0.88739400	0.91079300
C	-0.25878300	2.13206400	0.46522000
C	1.50748100	-1.00495400	0.82617800
C	-1.41697200	2.97411000	0.78341300
C	0.95049100	2.53337500	-0.30861100
O	-1.51528700	4.16012400	0.51622000
O	-2.39481200	2.26174000	1.39688400
O	1.23456400	3.62421800	-0.77668600
C	-3.57795000	3.00550900	1.75080500
C	3.18667900	1.28216800	-0.82409200
O	3.42860100	1.57645800	-1.98035600
O	4.12140100	0.91404500	0.07222500
C	5.47980600	0.85073000	-0.41528800
C	1.08858700	-1.51279900	2.07061600
C	1.45745000	-2.79844300	2.46643600
C	2.23652000	-3.59887600	1.62410100
C	2.64542700	-3.10599200	0.37999500
C	2.28629900	-1.81803300	-0.01743200
H	-4.24454600	2.28223400	2.21926800
H	-3.32740800	3.80677600	2.45007700
H	-4.04017500	3.43596600	0.85924300
H	6.07840700	0.55001500	0.44344900
H	5.79425400	1.82943400	-0.78368200
H	5.55979700	0.11515200	-1.21929700
H	0.48990600	-0.88800400	2.72558300
H	1.13870900	-3.17486300	3.43400600
H	2.52000500	-4.60071400	1.93294300
H	3.23988200	-3.72686900	-0.28370400
H	2.59040000	-1.45133900	-0.99300700
Sn	-2.00446200	-1.26680100	-0.70896300
C	-4.03825900	-0.56352200	-0.67132700
H	-4.65200300	-1.18470500	-1.33286000

H	4.36792196	-0.87808466	-2.59729792
C	2.46010896	-3.04573066	0.84123708
H	2.07114696	-2.76728366	1.82425408
H	1.63933196	-3.44347466	0.23807908
H	3.20862296	-3.83460466	0.97266808
C	4.86856396	-0.42705866	1.08210708
H	5.62971496	-1.16593166	1.35314008
H	5.34061296	0.38767834	0.52857708
H	4.43098896	-0.02446066	1.99944008
H	1.97576096	-0.15230566	-0.28799692

H	-4.44572300	-0.62101100	0.34135900
H	-4.09500700	0.47280000	-1.01419300
C	-1.84037400	-3.25579700	0.09169300
H	-0.79238700	-3.55142700	0.18111700
H	-2.30643000	-3.31310000	1.07904500
H	-2.34993200	-3.95838600	-0.57682700
C	-1.16413800	-1.11276500	-2.68371400
H	-1.77726200	-1.68983500	-3.38466900
H	-1.14450100	-0.07244500	-3.01968200
H	-0.14474000	-1.50654000	-2.70727900
H	-1.00817600	-0.04469000	0.41181100

TS6

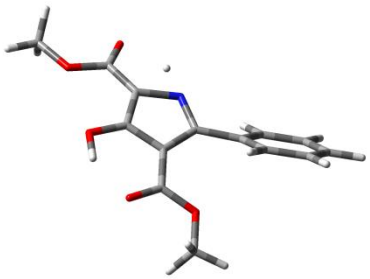
Zero-point correction = 0.345224
Thermal correction to Gibbs Free Energy = 0.254416
E_0 = -1094.393305, E = -1094.350538, H = -1094.349325
G = -1094.484113, G′ = -1094.4686837.
Imaginary frequency = 1.



C	0.02355441	-0.48872027	0.05009780
C	0.91072641	0.60964073	0.18405980
N	0.25734541	1.79416873	0.24551780
C	-1.17290859	1.43604773	0.24839880
C	2.37950341	0.59910373	0.34021880
C	-2.21885359	2.40287073	-0.09307520
C	-1.29714559	0.00785973	0.10430680
O	-3.40031959	2.08252173	-0.21090220
O	-1.77838559	3.65815373	-0.24110920
O	-2.38154259	-0.71384727	-0.02371520
C	-2.77861659	4.65810673	-0.53390020
C	0.34648641	-1.92251127	-0.13438120
O	-0.17042759	-2.83918527	0.48085580
O	1.28025941	-2.10829627	-1.09258820
C	1.69233641	-3.47019827	-1.32436820
C	3.14020541	1.67144273	-0.15928520
C	4.52656941	1.69205773	-0.00192820
C	5.17590441	0.64573373	0.66210980
C	4.42715841	-0.41968027	1.17175980
C	3.04032141	-0.44350827	1.01265180
H	-2.22896359	5.59513073	-0.61020420
H	-3.28054159	4.42752473	-1.47594120
H	-3.51439159	4.70638873	0.27206580
H	2.44977441	-3.41305427	-2.10535320
H	0.84321041	-4.07359727	-1.65362220
H	2.11161241	-3.90210427	-0.41217420
H	2.63472341	2.48086673	-0.67577620
H	5.10071941	2.52384873	-0.40027220
H	6.25516441	0.66223773	0.78439380
H	4.92128941	-1.22954027	1.70101380
H	2.46970541	-1.26418427	1.43647580
Sn	-4.37092059	-0.54423927	0.29749980
C	-5.33842159	0.06995473	-1.50303020
H	-6.27455159	-0.48230327	-1.63133420
H	-5.54259159	1.14178373	-1.49030120
H	-4.68835559	-0.15152227	-2.35517520

TS7

Zero-point correction = 0.248406
Thermal correction to Gibbs Free Energy = 0.179959
E_0 = -971.946587, E = -971.918185, H = -971.916971
G = -972.015035, G′ = -971.9788723.
Imaginary frequency = 1.



C	-0.18568173	0.75978617	0.22920496
C	-0.63419673	-0.59453283	0.20976796
N	0.40562327	-1.45574683	0.24510896
C	1.61698927	-0.63336383	0.40869396
C	-2.00085573	-1.15660883	0.20400696
C	2.93753927	-1.25368883	0.14114896
C	1.21877327	0.73294717	0.37456096
O	3.10909627	-2.43638283	-0.08941404
O	3.92434427	-0.34302883	0.21047996
O	2.02659327	1.78803217	0.44264796
C	5.26050127	-0.83862283	-0.02099504
C	-0.85715773	2.04986817	0.05528296
O	-0.24146773	3.11776317	0.16177996
O	-2.15182873	1.99432417	-0.25685204
C	-2.82287273	3.25680217	-0.47803504
C	-2.25976573	-2.31650383	-0.54801204
C	-3.52694473	-2.90006683	-0.53752304
C	-4.55161573	-2.34092183	0.23225596
C	-4.29962173	-1.19528783	0.99331996
C	-3.03515073	-0.60505183	0.97844696
H	5.90593827	0.03449417	0.06173596
H	5.52286627	-1.58629483	0.73074496
H	5.33365927	-1.28082583	-1.01680904
H	-3.85278973	2.99147217	-0.71026304
H	-2.36103473	3.78617017	-1.31355504
H	-2.77320073	3.87361117	0.42134196
H	-1.46132073	-2.75096183	-1.14029804
H	-3.71344273	-3.79082883	-1.13018204
H	-5.53761173	-2.79628883	0.24234796
H	-5.08674073	-0.76359083	1.60474496
H	-2.84766073	0.27652217	1.58109996
H	1.05623327	-1.31879183	1.33555196
H	1.43988127	2.58249917	0.38798896

C	-4.73016359	0.51060373	2.12078680	
H	-3.81071959	0.54988573	2.71321780	
H	-5.05995359	1.53164473	1.91960380	
H	-5.49242759	-0.01019627	2.70829280	
C	-4.69128059	-2.64195827	0.58712180	
H	-5.75216959	-2.85058427	0.76360880	
H	-4.37210959	-3.20180927	-0.29710620	
H	-4.11812859	-3.00473927	1.44520680	
H	-0.51678859	1.82711673	1.27045880	

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