Supporting information

for

'Sulfonyl-Azide-Free' (SAFE) Aqueous-Phase Diazo Transfer Reaction for Parallel and Diversity-Oriented Synthesis

Dmitry Dar'in, Grigory Kantin, and Mikhail Krasavin*

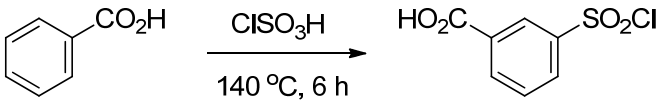
Table of Contents

I. General Information

Substrates for diazo transfer reactions were purchased from commercial sources and used as received or were synthesized according to known procedures. NMR spectroscopic data were recorded with a 400 MHz spectrometer (400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C) in $CDCl_3$ and in DMSO-d_6 and were referenced to residual solvent proton signals (δ_H = 7.26 and δ_H = 2.50, respectively) and solvent carbon signals (δ_C = 77.0 and δ_C = 39.5, respectively). All chemical shifts are reported in parts per million (ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), br (broad), m (multiplet). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Mass spectra were recorded with a HRMS-ESI-qTOF spectrometer (electrospray ionization mode). Melting points were determined with a melting point apparatus Stuart SMP 50 in open capillary tubes. Single crystal X-ray data were obtained using an Agilent Technologies SuperNova Atlas and an Agilent Technologies Xcalibur Eos diffractometers at a temperature of 130 K. Microwave syntheses were performed in Biotage® Initiator+ microwave reactor (4th generation) with the use of Biotage Microwave vials with crimp caps. Flash column chromatography was performed by Biotage® Isolera Prime chromatograph using silica gel Merk grade 60 (0.040−0.063 mm) 230−400 mesh (isocratic or gradient elution as indicated).

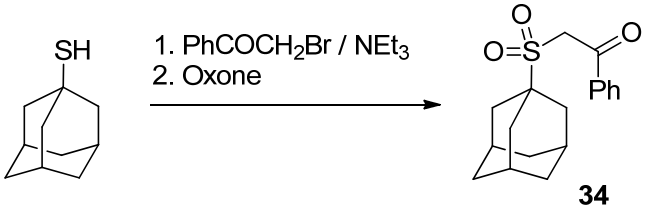
II. Preparation of starting materials

Synthesis of 3-(chlorosulfonyl)benzoic acid



Benzoic acid (36.6 g, 0.3 mol) was added in one portion to chlorosulfonic acid (140 mL) under stirring at room temperature. The mixture was heated at 140 °C for 6 hours. Upon cooling to ambient temperature the resulting viscous solution was slowly poured into finely crushed ice (800 g) maintaining temperature lower then 25 °C. White precipitate was filtered off, washed with cold water (2×150 mL) and dried *in vacuo* (at 40 °C/10 Tor) to afford 58.2 g (88%) of titled compound as white powder. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 11.12 (br.s, 1H), 8.81 (t, *J* = 1.6, 1H), 8.51 (dt, *J* = 7.8, 1.3, 1H), 8.33 (ddd, *J* = 8.0, 2.0, 1.1, 1H), 7.83 (t, *J* = 7.9, 1H). Purity according to ^{1}H NMR is 95%. Presumably the substance contains about 5% *para*-isomer. The prepared sulfonyl chloride was used in diazo transfer reactions without any further purification.

Synthesis of 2-((3s,5s,7s)-adamantan-1-ylsulfonyl)-1-phenylethanone (34)

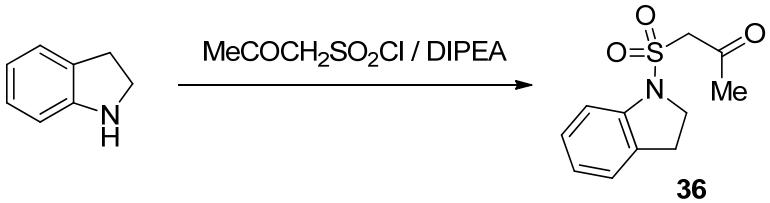


34

To stirred solution of (3s,5s,7s)-adamantane-1-thiol (0.84 g, 5 mmol) and triethylamine (1.39 mL, 10 mmol) in the mixture of 14 mL acetonitrile and 5 mL water was added 2-bromo-1-phenylethanone (1.095 g, 5.5 mmol) in several portions. Reaction mixture was stirred over night at ambient temperature, all volatiles were evaporated *in vacuo*, and the residue was dissolved in mixture of 5 mL chloroform and 5 mL water. Aqueous phase was extracted with 5 mL of chloroform and combined organic phases

were washed with 5 mL of water. After drying over calcium chloride and concentration under reduced pressure semi solid substance was obtained. To a solution of this substance in 20 mL of methanol under ice cooling the solution of Oxone (5.53 g, 9 mmol) in 20 mL of water was added dropwise. The suspension was stirred at room temperature for 4 hours and methanol was removed *in vacuo*. To the residue 50 mL of water were added, undissolved crystals were filtered off and washed with water (2×20 mL). The precipitate was recrystallized from ethanol and dried *in vacuo* (at 40 °C/10 Tor) to afford 0.785 g (49% over two steps) of title compound as white powder, m.p. 165.1–167.7 °C (ethanol). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.11 – 8.05 (m, 2H, *o*-Ph), 7.67 – 7.61 (m, 1H, *p*-Ph), 7.56 – 7.49 (m, 2H, *m*-Ph), 4.52 (s, 2H, CH_2), 2.28 – 2.20 (m, 3H), 2.13 (d, *J* = 2.7, 6H), 1.83 – 1.70 (m, 6H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 188.8, 136.4, 134.2, 129.7, 128.7, 63.9, 54.4, 35.7, 34.8, 28.3. HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{22}N_2NaO_3S$ $[M+Na]^+$: 341.1182, found 341.1190.

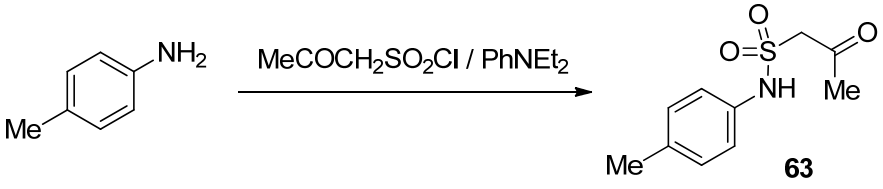
Synthesis of 1-(indolin-1-yl)-2-(methylsulfonyl)ethanone (36)



36

To an ice-salt cooled solution of indoline (1.49 g, 12.5 mmol) and DIPEA (2.13 g, 2.87 mL, 16.5 mmol) in DCM (10 mL) was added dropwise the solution of 2-oxopropane-1-sulfonyl chloride[1] (1.75 g, 11.2 mmol) in DCM (2 mL). The mixture was stirred over night at ambient temperature, then washed twice with 10 mL of 3% HCl and twice with 10 mL of water. After drying over sodium sulphate the solvent was removed *in vacuo*. Resulting dark viscous oil was purified by flash column chromatography on silica (eluent – DCM) to afford 2.21 g (82%) as light beige solid, m.p. 69.4–71.5 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): δ 7.40 (d, *J* = 8.0, 1H), 7.27 – 7.18 (m, 2H), 7.07 (td, *J* = 7.5, 1.1, 1H), 4.07 (t, *J* = 8.5, 2H), 4.06 (s, 2H), 3.19 (t, *J* = 8.5, 2H), 2.43 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$): δ 196.5, 141.1, 131.7, 127.9, 125.6, 124.3, 113.9, 60.1, 50.7, 31.4, 28.0. Exact mass calculated for $C_{11}H_{13}NNaO_3S$ $[M+H]^+$: 262.0508, found 262.0516.

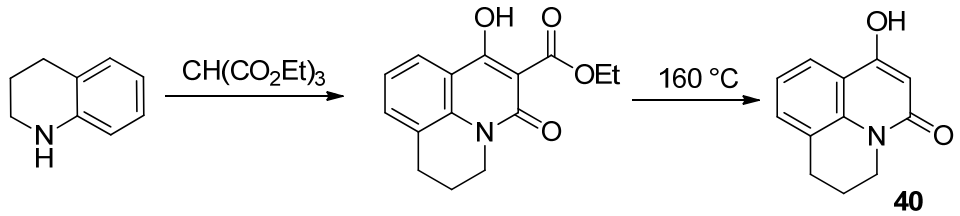
Synthesis of 2-oxo-*N*-(*p*-tolyl)propane-1-sulfonamide (63)



63

To an ice-salt cooled solution of *p*-toluidine (1.177 g, 11 mmol) and *N*,*N*-diethylaniline (1.639 g, 1.76 mL, 11 mmol) in DCM (20 mL) was added dropwise the solution of 2-oxopropane-1-sulfonyl chloride[1] (1.56 g, 10 mmol) in DCM (10 mL). The mixture was stirred over night at ambient temperature, then washed twice with 10 mL of 3% HCl and twice with 10 mL of water. After drying over sodium sulphate the solvent was removed *in vacuo*. Resulting dark viscous oil solidified on standing. Recrystallizing from wet methanol and drying *in vacuo* (at 40 °C/10 Tor) afforded 0.914 g (40%), white crystalls, m.p. 88.1–89.1 °C (MeOH–H_2O). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): δ 7.21 (d, *J* = 8.6, 2H), 7.17 (d, *J* = 8.6, 2H), 6.87 (s, 1H), 4.04 (s, 2H), 2.37 (s, 3H), 2.35 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$): δ 198.1, 136.5, 133.3, 130.2 123.1, 59.4, 31.6, 20.9. HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{13}NNaO_3S$ $[M+Na]^+$: 250.0508, found 250.0517.

Synthesis of 6,7-dihydropyrido[3,2,1-*ij*]quinoline-1,3(2*H*,5*H*)-dione (40)



To heated up 220 °C solution of triethyl methanetricarboxylate (2.32 g, 10 mmol) in diphenyl ether (5 mL) was added 1,2,3,4-tetrahydroquinoline (1.33 g, 10 mmol) dropwise under stirring. Reaction mixture was held at 220 °C during 45 min, cooled to room temperature and combined with 10% potassium carbonate solution (20 mL). After extraction with ethyl acetate (10 mL) the aqueous phase was acidified with concentrated HCl up to pH 1–2. Orange precipitate was filtered off, washed twice with water (10 mL) and dried in air. The obtained substance was mixed with DMSO (12 mL), water (0.24 mL) and heated to 160 °C (suspension was dissolved and gas began to emit). After an hour the reaction mixture was cooled to room temperature, combined with water (10 mL), the formed precipitated was filtered off, washed with water (10 mL), methanol (4 mL) and ether (4 mL). Drying *in vacuo* (at 40 °C/10 Tor) yielded 1.025 g (50% over two steps) of the title compound as light yellow crystals, m.p. 293.9–295.4 °C. NMR ^{1}H (400 MHz, 80 °C, DMSO-d_6, *J*/Hz) δ 10.90 (s, 1H), 7.75 – 7.71 (m, 1H), 7.37 – 7.32 (m, 1H), 7.10 (dd, *J* = 8.0, 7.3 Hz, 1H), 5.87 (s, 1H), 4.06 – 3.92 (m, 2H), 2.94 (t, *J* = 6.2 Hz, 2H), 2.05 – 1.94 (m, 2H). NMR ^{13}C (101 MHz, 80 °C, DMSO-d_6) δ 162.6, 161.4, 137.2, 130.6, 125.0, 121.4, 121.9, 116.3, 98.4, 41.6, 27.7, 20.9. Exact mass calculated for $C_{12}H_{11}NNaO_2$ $[M+Na]^+$: 224.0682, found 224.0689.

III. Preparation of diazo carbonyl compounds

General procedure for the preparation of diazo compounds in *one pot* format (Method A)

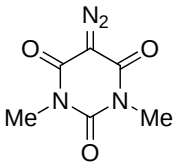
To a stirred solution of sodium azide (195 mg, 3 mmol) and potassium carbonate (552 mg, 4 mmol) in water (4 mL) 3-(chlorosulfonyl)benzoic acid (441 mg, 2 mmol) and corresponding substrate (1.5 mmol) were added (in some cases MeCN (1–2 mL) was additionally added as indicated). The reaction mixture was vigorously stirred at ambient temperature. Upon completion of diazo transfer reaction the product was extracted with chloroform (2×8 mL), organic phase was dried over calcium chloride and evaporated to dryness to afford diazo carbonyl compound. Usually the purity of thus isolated substance was above 95%. In some cases further purification by means of flash chromatography on silica gel or recrystallization was applied as indicated.

General procedure for the preparation of diazo compounds in 'array' format (Method B)

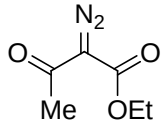
To a stirred solution of sodium azide (0.98 g, 15 mmol) and potassium carbonate (2.76 g, 20 mmol) in water (20 mL) was added 3-(chlorosulfonyl)benzoic acid (2.21 g, 10 mmol) and the mixture was stirred at ambient temperature for 10 minutes to give clear solution. The resulting aqueous solution of 3-(azidosulfonyl)benzoic acid potassium salt was used for diazo transfer reactions.

To the obtained solution taken in a volume containing 1 mmol of sulfonyl azide (1/10 part of whole volume) was added substrate for diazo transfer (0.75 mmol) under stirring at ambient temperature (acetonitrile (0.5–1 mL) was added additionally if indicated). The mixture was stirred for indicated period of time followed by extraction with chloroform (2×4 mL), organic phase was dried over calcium chloride and evaporated to dryness to afford diazo carbonyl compound.

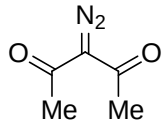
5-Diazo-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione[2] (1'). The title compound was synthesized from 1,3-dimethylbarbituric acid (234 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 248 mg (91%). White solid; m.p. 160.0–161.9 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.34 (s, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 158.2, 150.5, 71.7 ($C{=}N_2$), 28.5 ($2CH_3$).



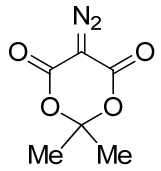
Ethyl 2-diazo-3-oxobutanoate[3] (2'). The title compound was synthesized from ethyl 3-oxobutanoate (390 mg, 3 mmol) according to Method A. Reaction time – 1.5 hour. Yield 370 mg (79%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.30 (q, *J* = 7.1, 2H, $C\underline{H}_2CH_3$), 2.48 (s, 3H, 4-CH_3), 1.33 (t, *J* = 7.1, 3H, $CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.1(C=O), 161.4 (CO_2), 76.3 ($C{=}N_2$), 61.4 ($\underline{C}H_2CH_3$), 28.2 (4-CH_3), 14.3 ($CH_2\underline{C}H_3$).



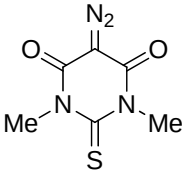
3-Diazopentane-2,4-dione[4] (3'). The title compound was synthesized from acetylacetone (1.2 g, 12 mmol) according to Method A. Reaction time – 1 hour. Yield 1.24 g (82%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 2.42 (s, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 188.2 (2C=O), 84.5 ($C{=}N_2$), 28.4 ($2CH_3$).



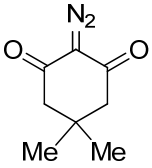
5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione[5] (4'). The title compound was synthesized from Meldrum's acid (216 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 224 mg (88%). Pale yellow solid; m.p. 95–96 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 1.80 (c, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 158.3 (2C=O), 107.1 ($\underline{C}(CH_3)_2$), 64.9 ($C{=}N_2$), 26.8 ($2CH_3$).



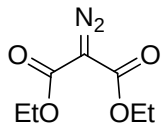
5-Diazo-1,3-dimethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (5'). The title compound was synthesized from 2-thio-1,3-dimethylbarbituric acid (258 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 241 mg (81%). Light lilac solid; m.p. 112.2–113.0 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.72 (s, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 178.9 (C=S), 156.8 (2C=O), 73.9 ($C{=}N_2$), 35.41 ($2CH_3$). HRMS (ESI +ve) Exact mass calculated for $C_6H_6N_4NaO_2S$ $[M+Na]^+$: 221.0104, found 221.0104.



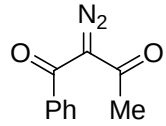
2-Diazo-5,5-dimethylcyclohexane-1,3-dione[6] (6'). The title compound was synthesized from dimedone (210 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 239 mg (96%). Pale yellow solid; m.p. 105.9–107.0 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 2.44 (c, 4H, $2CH_2$), 1.12 (c, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 189.8 (2C=O), 83.6 ($C{=}N_2$), 50.5 ($2CH_2$), 31.1 ($\underline{C}(CH_3)_2$), 28.3 ($2CH_3$).



Diethyl 2-diazomalonate[4] (7'). The title compound was synthesized from diethyl malonate (960 mg, 6.0 mmol) according to Method A. Reaction time – 2 hours. Yield 960 mg (86%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.31 (q, *J* = 7.1, 4H, $2C\underline{H}_2CH_3$), 1.32 (t, *J* = 7.1, 6H, $2CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 161.0 ($2CO_2$), 65.4 ($C{=}N_2$), 61.6 ($2\underline{C}H_2CH_3$), 14.3 ($2CH_2\underline{C}H_3$).

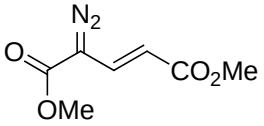


2-Diazo-1-phenylbutane-1,3-dione[7] (8'). The title compound was synthesized from 1-phenylbutane-1,3-dione (243 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 1.5 hour. Yield 259 mg (92%). Pale yellow solid; m.p. 59.4–61.0 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.67 – 7.62 (m, 2H, *o*-Ph), 7.61 – 7.55

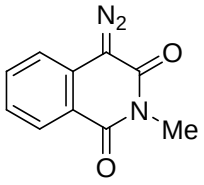


(m, 1H, *p*-Ph), 7.50 (t, *J* = 7.5 Hz, 2H, *t*-Ph), 2.58 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.7, 185.0, 137.4, 132.7, 128.9, 127.3, 83.7 ($C=N_2$), 29.2 (CH_3).

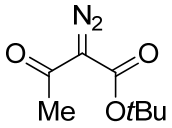
(*E*)-Dimethyl 4-diazopent-2-enedioate[8] (9'). The title compound was synthesized from dimethyl glutaconate (*E/Z* mixture ~ 6:1) (237 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 1.5 hour. Yield 188 mg (68%). Yellow solid; m.p. 68.5–70.5 °C (decomp.). NMR ^1H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.35 (d, *J* = 15.7, 1H), 5.74 (d, *J* = 15.7, 1H), 3.86 (s, 3H), 3.76 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 166.4, 163.5, 131.0, 111.3, 65.2 ($C=N_2$), 52.6, 51.6.



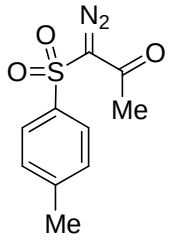
4-Diazo-2-methylisoquinoline-1,3(2*H*,4*H*)-dione[9] (10'). The title compound was synthesized from *N*-methyl homophthalimide (526 mg, 3.0 mmol) according to Method A (with addition of MeCN (4 mL)). Reaction time – 4 hours. Yield 518 mg (86%). Yellow solid; m.p. 146.0–147.5 °C (MeOH). NMR ^1H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.29 (d, *J* = 7.9, 1H), 7.67 (t, *J* = 7.9, 1H), 7.34 (t, *J* = 7.8 1H), 7.13 (d, *J* = 7.9, 1H), 3.46 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.9, 162.7, 134.1, 130.1, 126.4, 125.7, 120.8, 118.6, 68.1($C=N_2$), 27.4 (CH_3).



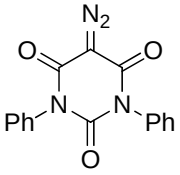
***tert*-Butyl 2-diazo-3-oxobutanoate[10] (11')**. The title compound was synthesized from *tert*-butyl 3-oxobutanoate (1.42 g, 9.0 mmol) according to Method A (with addition of MeCN (6 mL)). Reaction time – 1.5 hour. Yield 1.52 g (92%). Transparent liquid. NMR ^1H (400 MHz, $CDCl_3$, *J*/Hz) δ 2.45 (s, 3H, 4-CH_3), 1.54 (s, 9H, $C(CH_3)_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.5 (C=O), 160.6 (CO_2), 83.1 ($\underline{C}(CH_3)_3$), 77.1 ($C=N_2$), 28.3, 28.3.



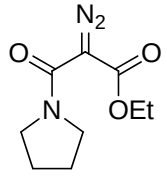
1-Diazo-1-tosylpropan-2-one[11] (12'). The title compound was synthesized from (*p*-tolylsulfonyl)acetone[12] (318 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 1 hour. Yield 328 mg (92%). Yellow solid; m.p. 108.3–109.5 °C. NMR ^1H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.87 (d, *J* = 8.4, 2H), 7.40 (d, *J* = 8.1, 2H), 2.49 (s, 3H), 2.31 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 185.9 (C=O), 145.5, 139.2, 130.1, 127.3, 86.1 ($C=N_2$), 27.0, 21.7.



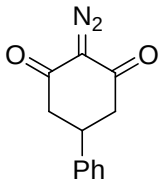
1,3-Diphenyl-5-diazopyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (13'). The title compound was synthesized from 1,3-diphenylbarbituric acid[13] (420 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 1 hour. The obtained substance was purified by flash column chromatography on SiO_2 eluting with DCM. Yield 304 mg (66%). White solid; m.p. 103.4–105.6 °C (decomp.). NMR ^1H (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 3H), 7.34 – 7.29 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 157.9 (4,6-C), 150.0 (2-C), 133.5, 129.4, 129.4, 128.6, 72.7 ($C=N_2$). HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{10}N_4NaO_3$ $[M+Na]^+$: 329.0645, found 329.0657.



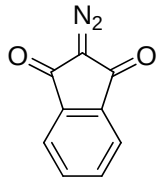
Ethyl 2-diazo-3-oxo-3-(pyrrolidin-1-yl)propanoate[14] (14'). The title compound was synthesized from ethyl 3-oxo-3-(pyrrolidin-1-yl)propanoate (278 mg, 1.5 mmol) according to Method A. Reaction time – 30 hours. Yield 266 mg (84%). Yellow liquid. NMR ^1H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.25 (q, *J* = 7.1, 2H, $C\underline{H}_2CH_3$), 3.52 (t, *J* = 6.8, 4H, $2NCH_2$), 1.94 – 1.83 (m, 4H, $2NCH_2C\underline{H}_2$), 1.30 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.1, 159.6, 66.8 ($C=N_2$), 61.2 ($\underline{C}H_2CH_3$), 47.8 (br.s, $2NCH_2$), 24.8 (br.s, $2NCH_2\underline{C}H_2$), 14.4 ($CH_2\underline{C}H_3$).



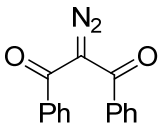
2-Diazo-5-phenylcyclohexane-1,3-dione[15] (15'). The title compound was synthesized from 5-phenylcyclohexane-1,3-dione (282 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 282 mg (88%). Pale yellow solid; m.p. 122.0–122.6 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.39 (t, *J* = 7.4, 2H, *m*-Ph), 7.34 – 7.27 (m, 1H, *p*-Ph), 7.26 – 7.20 (m, 2H, *o*-Ph), 3.44 (tt, *J* = 11.6, 4.2, 1H, C<u>H</u>Ph), 2.90 (dd, *J* = 17.2, 4.2, 2H, 2C<u>H</u>H), 2.79 (dd, *J* = 17.2, 11.7, 2H, 2CH<u>H</u>). NMR ^{13}C (101 MHz, $CDCl_3$) δ 189.2 (2C=O), 141.1, 129.1, 127.5, 126.5, 84.8 (C=N_2), 44.2 (2CH_2), 36.5 (<u>C</u>HPh).



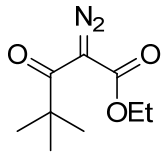
2-Diazo-1*H*-indene-1,3(2*H*)-dione[16] (16'). The title compound was synthesized from 1*H*-indene-1,3(2*H*)-dione (220 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 208 mg (81%). Yellow solid; m.p. 144.9–146.5 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.89 – 7.81 (m, 2H), 7.80 – 7.70 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 182.1 (2C=O), 137.1, 134.8, 122.7, 70.13 (C=N_2).



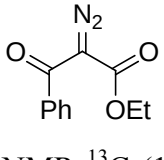
2-Diazo-1,3-diphenylpropane-1,3-dione[17] (17'). The title compound was synthesized from 1,3-diphenylpropane-1,3-dione (336 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 1.5 hours. Yield 322 mg (86%). Pale yellow solid; m.p. 107.8–108.2 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.62 – 7.57 (m, 4H, *o*-Ph), 7.49 – 7.43 (m, 2H, *p*-Ph), 7.37 – 7.31 (m, 4H, *m*-Ph). NMR ^{13}C (101 MHz, $CDCl_3$) δ 186.4 (2C=O), 137.0, 132.6, 128.4, 128.3, 84.4 (C=N_2).



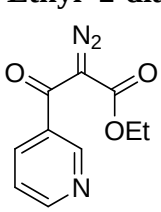
Ethyl 2-diazo-4,4-dimethyl-3-oxopentanoate[18] (18'). The title compound was synthesized from ethyl 4,4-dimethyl-3-oxopentanoate (1.03 g, 6.0 mmol) according to Method A (with addition of MeCN (6 mL)). Reaction time – 2 hours. Yield 1.02 g (86%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.28 (q, *J* = 7.1, 2H, C<u>H</u>$_2$CH$_3$), 1.33 (t, *J* = 7.1, 3H, CH$_2$C<u>H</u>$_3$), 1.30 (s, 9H, C(CH$_3$)$_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 197.3 (C=O), 160.9 (CO_2), 77.5 (C=N_2), 61.3(<u>C</u>H$_2$CH$_3$), 44.3 (<u>C</u>(CH$_3$)$_3$), 25.8 (C(<u>C</u>H$_3$)$_3$), 14.3 (CH$_2$<u>C</u>H$_3$).



Ethyl 2-diazo-3-oxo-3-phenylpropanoate[19] (19'). The title compound was synthesized from ethyl 3-oxo-3-phenylpropanoate (576 mg, 3.0 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 602 mg (92%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.72 – 7.60 (m, 2H, *o*-Ph), 7.55 (t, *J* = 7.4, 1H, *p*-Ph), 7.44 (t, *J* = 7.6, 2H, *m*-Ph), 4.27 (q, *J* = 7.1, 2H, C<u>H</u>$_2$CH$_3$), 1.27 (t, *J* = 7.1, 3H, CH$_2$C<u>H</u>$_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 186.9 (C=O), 161.0 (CO_2), 137.1, 132.2, 128.3, 127.9, 76.2 (C=N_2), 61.6 (<u>C</u>H$_2$CH$_3$), 14.20 (CH$_2$<u>C</u>H$_3$).



Ethyl 2-diazo-3-oxo-3-(pyridin-3-yl)propanoate (20'). The title compound was synthesized from ethyl 3-oxo-3-(pyridin-3-yl)propanoate (290 mg, 1.5 mmol) according to Method A. Reaction time – 2 hours. Yield 292 mg (89%). Transparent viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.84 (d, *J* = 2.2, 1H, 2'-H), 8.74 (dd, *J* = 4.9, 1.6, 1H, 6'-H), 7.93 (dt, *J* = 7.9, 2.0, 1H, 4'-H), 7.38 (dd, *J* = 7.9, 4.9, 1H, 5'-H), 4.26 (q, *J* = 7.1, 2H, C<u>H</u>$_2$CH$_3$), 1.27 (t, *J* = 7.1, 3H, CH$_2$C<u>H</u>$_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 185.1 (C=O), 160.6 (CO_2), 152.5, 149.2, 135.8, 132.9, 122.6, 77.0 (C=N_2), 61.9 (<u>C</u>H$_2$CH$_3$), 14.2 (CH$_2$<u>C</u>H$_3$). HRMS (ESI +ve) Exact mass calculated for $C_{10}H_9N_3NaO_3$ $[M+Na]^+$: 242.0536, found 242.0538.



2-Diazo-3-oxo-3-phenylpropanenitrile[20] (21'). The title compound was synthesized from 3-oxo-3-phenylpropanenitrile (218 mg, 1.5 mmol) according to Method A. Reaction time – 1 hour. Yield 162 mg (63%). Beige solid; m.p. 47.2–48.1 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.93 – 7.88 (m, 2H, 2',6'-H), 7.68 – 7.61 (m, 1H, 4'-H), 7.56 – 7.48 (m, 2H, 3',5'-H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 182.9 (C=O), 134.8, 133.8, 128.9, 128.1, 109.2, 59.0 ($C=N_2$).

2-Diazo-4,4-dimethyl-3-oxopentanenitrile[21] (22'). The title compound was synthesized from 4,4-dimethyl-3-oxopentanenitrile (187 mg, 1.5 mmol) according to Method A. Reaction time – 1.5 hour. Yield 177 mg (78%). Yellow liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 1.33 (s, 9H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 195.3 (C=O), 109.4 (C≡N), 57.03 ($C=N_2$), 44.7 ($\underline{C}(CH_3)_3$), 26.2 ($C(\underline{C}H_3)_3$). HRMS (ESI +ve) Exact mass calculated for $C_7H_9N_3NaO$ $[M+Na]^+$: 174.0638, found 174.0634.

2-Diazo-3-(3-methoxyphenyl)-3-oxopropanenitrile (23'). The title compound was synthesized from 3-(3-methoxyphenyl)-3-oxopropanenitrile[22] (262 mg, 1.5 mmol) according to Method A. Reaction time – 2 hours. Yield 206 mg (68%). Pale orange viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.52 – 7.48 (m, 1H), 7.42 (t, *J* = 8.0, 1H), 7.39 – 7.38 (m, 1H), 7.17 (ddd, *J* = 8.2, 2.6, 0.9, 1H), 3.87 (s, 3H, OCH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 182.7 (C=O), 159.8 (3'-C), 135.7, 129.9, 120.5, 120.4, 112.5, 109.1 (C≡N), 59.1 ($C=N_2$), 55.5 (OCH_3). HRMS (ESI +ve) Exact mass calculated for $C_{10}H_7N_3NaO_2$ $[M+Na]^+$: 224.0430, found 224.0433.

3-((3r,5r,7r)-Adamantan-1-yl)-2-diazo-3-oxopropanenitrile (24'). The title compound was synthesized from 3-((3r,5r,7r)-adamantan-1-yl)-3-oxopropanenitrile[22] (304 mg, 1.75 mmol) according to Method A. Reaction time – 20 hours. Yield 330 mg (96%). Orange solid; m.p. 70.6–71.7 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 2.17 – 2.07 (m, 3H), 2.01 (d, *J* = 2.8, 6H), 1.82 – 1.70 (m, 6H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 194.4 (C=O), 109.6 (C≡N), 57.1 ($C=N_2$), 47.4, 37.7, 36.2, 28.0. HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{15}N_3NaO$ $[M+Na]^+$: 252.1107, found 252.1107.

***tert*-Butyl 2-cyano-2-diazoacetate[23] (25')**. The title compound was synthesized from *tert*-butyl 2-cyanoacetate (212 mg, 1.5 mmol) according to Method A (double amount sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 1 hour. Yield 178 mg (71%). Orange viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 1.54 (s, 9H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 160.1 (C=O), 107.7 (C≡N), 85.6 ($\underline{C}(CH_3)_3$), 51.2 ($C=N_2$), 28.1 ($C(\underline{C}H_3)_3$).

Ethyl 2-cyano-2-diazoacetate[24] (26'). The title compound was synthesized from ethyl 2-cyanoacetate (170 mg, 1.5 mmol) according to Method A (double amount sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 1 hour. Yield 92 mg (44%). Light orange viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.31 (q, *J* = 7.1, 2H, $C\underline{H}_2CH_3$), 1.32 (t, *J* = 7.1, 3H, $CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 161.2 (C=O), 107.3 (C≡N), 63.4 ($\underline{C}H_2CH_3$), 51.1 ($C=N_2$), 14.2 ($CH_2\underline{C}H_3$). HRMS (ESI +ve) Exact mass calculated for $C_5H_5N_3NaO_2$ $[M+Na]^+$: 162.0274, found 162.0273.

1-Diazonaphthalen-2(1*H*)-one[25] (27'). The title compound was synthesized from naphthalen-2-ol (216 mg, 1.5 mmol) according to Method A (double amount sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 2 hours. The obtained substance was purified by flash column chromatography on SiO_2 eluting with DCM. Yield 163 mg (64%). Light brown solid; m.p. 80.8–81.6 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.64 (d, *J* = 9.8, 1H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.32 – 7.24 (m, 2H), 6.67 (d, *J* = 9.8, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 180.2 (C=O), 140.3, 130.0, 129.8, 127.2, 125.9, 125.6, 124.7, 119.7, 77.2 (C=N_2).

2-Diazonaphthalen-1(2*H*)-one[26] (28'). The title compound was synthesized from naphthalen-1-ol (216 mg, 1.5 mmol) according to Method A (double amount sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 1.5 hour. The obtained substance was purified by flash column chromatography on SiO_2 eluting with DCM. Yield 104 mg (41%). Light brown solid; m.p. 74.9–76.3 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.38 – 8.33 (m, 1H), 7.63 (ddd, *J* = 8.0, 7.2, 1.4, 1H), 7.52 – 7.44 (m, 2H), 6.90 (d, *J* = 9.4, 1H), 6.58 (d, *J* = 9.3, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 180.1 (C=O), 137.5, 132.7, 129.6, 128.2, 127.2, 125.4, 117.3, 116.2, 77.2 (C=N_2).

Methyl 2-diazo-2-(4-nitrophenyl)acetate[27] (29'). The title compound was synthesized from methyl 2-(4-nitrophenyl)acetate (296 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 30 hours. Yield 202 mg (61%). Yellow solid; m.p. 143.5–144.0 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.25 (d, *J* = 9.1, 2H), 7.68 (d, *J* = 9.1, 2H), 3.93 (s, 3H, CO_2CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 164.1 (CO_2), 145.1, 133.8, 124.3, 123.1, 64.7 (C=N_2), 52.4 (OCH_3).

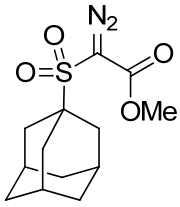
2-Diazo-1-(2,4-dimethylphenyl)-2-(4-nitrophenyl)ethanone (30'). The title compound was synthesized from 1-(2,4-dimethylphenyl)-2-(4-nitrophenyl)ethanone (404 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 372 mg (84%). Yellow solid; m.p. 108.9–109.7 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.27 (d, *J* = 9.1, 2H), 7.77 (d, *J* = 9.1, 2H), 7.30 (d, *J* = 7.8, 1H), 7.13 (s, 1H), 7.09 (d, *J* = 7.8, 1H), 2.41 (s, 3H), 2.39 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 189.3 (C=O), 145.6, 141.3, 135.8, 134.7, 133.9, 132.2, 126.7, 126.6, 124.5, 124.2, 75.1 (C=N_2), 21.4, 19.0. HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{13}N_3NaO_3$ $[M+Na]^+$: 318.0849, found 318.0859.

Diethyl (1-diazo-2-oxopropyl)phosphonate[28] (31'). The title compound was synthesized from diethyl (2-oxopropyl)phosphonate (291 mg, 1.5 mmol) according to Method A. Reaction time – 2 hours. Yield 300 mg (91%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.32 – 4.10 (m, 4H, P(O)($OC\underline{H}_2CH_3$)$_2$), 2.28 (s, 3H, CH_3C=O), 1.38 (td, *J* = 7.1, 0.6, 6H, P(O)($OCH_2C\underline{H}_3$)$_2$), 1.31 (t, *J* = 7.1, 3H, $CO_2CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 190.0 (d, *J* = 13.3, C=O), 64.4 (d, *J* = 218.4, C=N_2), 63.4 (d, *J* = 5.6, , P(O)($O\underline{C}H_2CH_3$)$_2$), 27.13 (d, *J* = 1.5, $\underline{C}H_3C$=O), 16.1 (d, *J* = 6.8, P(O)($OCH_2\underline{C}H_3$)$_2$).

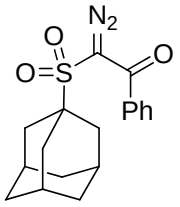
Ethyl 2-diazo-2-(diethoxyphosphoryl)acetate[29] (32'). The title compound was synthesized from ethyl 2-(diethoxyphosphoryl)acetate (336 mg, 1.5 mmol) according to Method A. Reaction time – 50 hours. Yield 304 mg (81%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.27 (q, *J* = 7.1, 2H, $CO_2C\underline{H}_2CH_3$), 4.27 – 4.12 (m, 4H, P(O)($OC\underline{H}_2CH_3$)$_2$), 1.37 (td, *J* = 7.1, 0.6, 6H, P(O)($OCH_2C\underline{H}_3$)$_2$), 1.31 (t, *J* = 7.1, 3H, $CO_2CH_2C\underline{H}_3$). NMR ^{13}C

(101 MHz, $CDCl_3$, *J*/Hz) δ 163.4 (d, *J* = 12.2, CO_2), 63.6 (d, *J* = 5.8, $P(O)(O\underline{C}H_2CH_3)_2$), 61.7 ($CO_2\underline{C}H_2CH_3$), 53.7 (d, *J* = 227.4, $C{=}N_2$), 16.1 (d, *J* = 6.9, $P(O)(OCH_2\underline{C}H_3)_2$), 14.3 ($CO_2CH_2\underline{C}H_3$).

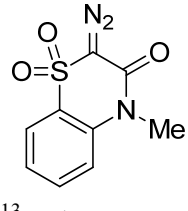
Methyl 2-((3s,5s,7s)-adamantan-1-ylsulfonyl)-2-diazoacetate (33'). The title compound was synthesized from methyl 2-((3s,5s,7s)-adamantan-1-ylsulfonyl)acetate[30] (408 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 6 hours. Yield 388 mg (87%). White solid; m.p. 103.0–105.1 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.87 (c, 3H, OCH_3), 2.25 – 2.20 (m, 3H), 2.08 (d, *J* = 2.9, 6H), 1.81 – 1.69 (m, 6H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 160.8 (CO_2), 68.9 ($C{=}N_2$), 66.6, 52.9, 35.7, 35.2, 28.3. HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{18}N_2NaO_4S$ $[M+Na]^+$: 321.0879, found 321.0882.



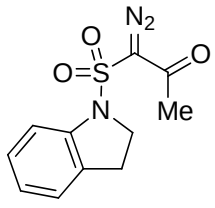
2-((3s,5s,7s)-Adamantan-1-ylsulfonyl)-2-diazo-1-phenylethanone (34'). The title compound was synthesized from 2-((3s,5s,7s)-adamantan-1-ylsulfonyl)-1-phenylethanone (478 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 3 hours. Yield 460 mg (89%). White solid; m.p. 145.3–146.2 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.73 – 7.67 (m, 2H, *o*-Ph), 7.63 – 7.57 (m, 1H, *p*-Ph), 7.50 (t, *J* = 7.5, 2H, *t*-Ph), 2.25 – 2.20 (m, 3H), 2.10 (d, *J* = 2.9, 6H), 1.80 – 1.69 (m, 6H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 183.5 (C=O), 136.4, 132.9, 128.8, 127.7, 67.7, 35.7, 35.4, 28.4. HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{20}N_2NaO_3S$ $[M+Na]^+$: 367.1087, found 367.1089.



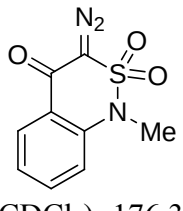
2-Diazo-4-methyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one 1,1-dioxide (35'). The title compound was synthesized from 4-methyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one 1,1-dioxide (316 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 246 mg (69%). Pale orange solid; m.p. 153.3–155.0 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.98 – 7.95 (m, 1H), 7.70 (ddd, *J* = 8.5, 7.4, 1.6, 1H), 7.39 – 7.35 (m, 1H), 7.33 (dd, *J* = 8.4, 0.8, 1H), 3.54 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 158.8 (C=O), 137.0, 134.5, 128.4, 123.9, 122.1, 117.1, 73.7 ($C{=}N_2$), 32.2 (CH_3). HRMS (ESI +ve) Exact mass calculated for $C_9H_7N_3NaO_3S$ $[M+Na]^+$: 260.0100, found 260.0104.



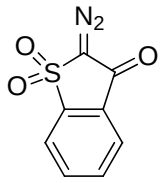
2-Diazo-1-(indolin-1-yl)-2-(methylsulfonyl)ethanone (36'). The title compound was synthesized from 1-(indolin-1-yl)-2-(methylsulfonyl)ethanone (358 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 322 mg (81%). Yellow solid; m.p. 115.4–116.6 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): 7.33 (d, *J* = 7.9, 1H), 7.28 – 7.18 (m, 2H), 7.09 (td, *J* = 7.5, 0.9, 1H), 4.31 (t, *J* = 8.4, 2H), 3.18 (t, *J* = 8.4, 2H), 2.23 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$): 185.9 (C=O), 140.6, 132.3, 127.8, 125.7, 124.7, 114.5, 81.6 ($C{=}N_2$), 51.1 (CH_3), 28.0, 26.8. HRMS (ESI +ve) Exact mass calculated for $C_{11}H_{12}N_3O_3S$ $[M+H]^+$: 266.0594, found 266.0598.



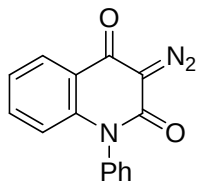
3-Diazo-1-methyl-1*H*-benzo[*c*][1,2]thiazin-4(3*H*)-one 2,2-dioxide (37'). The title compound was synthesized from 1-methyl-1*H*-benzo[*c*][1,2]thiazin-4(3*H*)-one 2,2-dioxide[31] (316 mg, 1.5 mmol) according to Method A. Reaction time – 4 hours. Yield 296 mg (83%). Pale yellow solid; m.p. 114.7–115.5 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): 8.13 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.69 (ddd, *J* = 8.1, 7.5, 1.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 (dd, *J* = 8.1, 0.7 Hz, 1H), 3.37 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$): 176.3 (C=O), 142.4, 135.4, 128.5, 127.0, 125.9, 123.7, 79.34 ($C{=}N_2$), 39.0 (CH_3). HRMS (ESI +ve) Exact mass calculated for $C_9H_7N_3NaO_3S$ $[M+Na]^+$: 260.0100, found 260.0093.



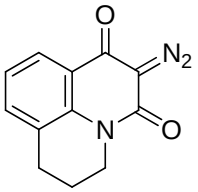
2-Diazobenzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide[32] (38'). The title compound was synthesized from benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide (273 mg, 1.5 mmol) according to Method A. Reaction time – 1.5 hour. Yield 181 mg (58%). Pale yellow solid; m.p. 192.1–193.8 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): 8.05 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.90 – 7.83 (m, 1H). NMR ^{13}C (101 MHz, $CDCl_3$): 173.8 (C=O), 141.5, 136.1, 134.5, 130.1, 124.1, 121.3, 74.5 (C=N_2).



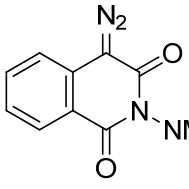
3-Diazo-1-phenylquinoline-2,4(1*H*,3*H*)-dione (39'). The title compound was synthesized from 4-hydroxy-1-phenylquinolin-2(1*H*)-one (356 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 1.5 hour. Yield 332 mg (84%). Beige solid; m.p. 215.1–217.5 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.23 (dd, *J* = 7.9, 1.4, 1H), 7.67 – 7.60 (m, 2H, *t*-Ph), 7.59 – 7.54 (m, 1H, *p*-Ph), 7.45 (ddd, *J* = 8.6, 7.2, 1.7, 1H), 7.35 – 7.30 (m, 2H, *o*-Ph), 7.24 (td, *J* = 7.6, 0.9, 1H), 6.60 (d, *J* = 8.1, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 175.6 (4-C), 159.1 (2-C), 142.5, 136.2, 134.8, 130.4, 129.4, 129.3, 126.4, 123.2, 120.3, 117.0, 79.9 (C=N_2). HRMS (ESI +ve) Exact mass calculated for $C_{15}H_9N_3NaO_2$ $[M+Na]^+$: 286.0587, found 286.0594.



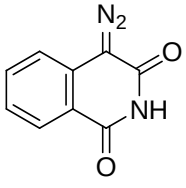
2-Diazo-6,7-dihydropyrido[3,2,1-*ij*]quinoline-1,3(2*H*,5*H*)-dione (40'). The title compound was synthesized from 1-hydroxy-6,7-dihydropyrido[3,2,1-*ij*]quinolin-3(5*H*)-one (302 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2.5 hours. Yield 232 mg (68%). Pale pink solid; m.p. 163.1–164.8 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.02 (ddt, *J* = 7.9, 1.5, 0.6 Hz, 1H), 7.41 (ddt, *J* = 7.4, 1.9, 1.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.00 – 2.92 (m, 2H), 2.13 – 2.02 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 175.7 (1-C), 158.7 (3-C), 137.9, 135.2, 125.8, 124.7, 122.5, 120.5, 79.3 (C=N_2), 42.1 (5-C), 28.0 (7-C), 20.3 (6-C). HRMS (ESI +ve) Exact mass calculated for $C_{12}H_9N_3NaO_2$ $[M+Na]^+$: 250.0587, found 250.0598.



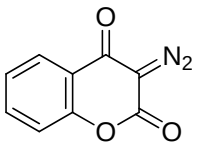
4-Diazo-2-(dimethylamino)isoquinoline-1,3(2*H*,4*H*)-dione[9] (41'). The title compound was synthesized from *N*-(dimethylamino)homophthalimide[9] (306 mg, 1.5 mmol) according to Method A. Reaction time – 20 hours. Yield 310 mg (90%). Pale orange solid; m.p. 130.0–132.1 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.28 (ddd, *J* = 8.0, 1.3, 0.5, 1H), 7.66 (ddd, *J* = 7.9, 7.4, 1.4, 1H), 7.36 – 7.32 (m, 1H), 7.09 (ddd, *J* = 7.9, 1.0, 0.6, 1H), 3.04 (s, 6H, $N(CH_3)_2$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.8, 162.4, 134.2, 130.3, 126.2, 125.7, 121.3, 118.4, 68.5 (C=N_2), 43.7 ($N(CH_3)_2$).



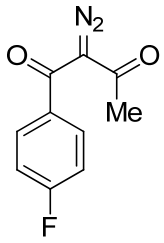
4-Diazoisoquinoline-1,3(2*H*,4*H*)-dione (42'). The title compound was synthesized from homophthalimide[33] (242 mg, 1.5 mmol) according to Method A. Reaction time – 18 hours. After completion of reaction the precipitated product was filtered, washed with water and recrystallized from *i*PrOH–DMF (1:1). Yield 208 mg (74%). Yellow solid; m.p. 237.8–239.5 °C (decomp.) (*i*PrOH–DMF). NMR ^{1}H (400 MHz, DMSO-d_6, *J*/Hz) δ 11.65 (s, 1H), 8.07 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.79 – 7.69 (m, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.31 (m, 1H). NMR ^{13}C (101 MHz, DMSO-d_6) δ 163.4, 163.3, 134.6, 128.9, 128.5, 125.7, 121.0, 120.9, 67.9 (C=N_2). HRMS (ESI +ve) Exact mass calculated for $C_9H_5N_3NaO_2$ $[M+Na]^+$: 210.0274, found 210.0272.



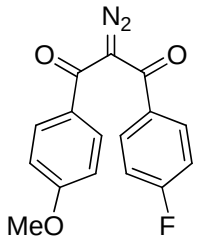
3-Diazochroman-2,4-dione[34] (43'). The title compound was synthesized from 4-hydroxy-2*H*-chromen-2-one (243 mg, 1.5 mmol) according to Method A. Reaction time – 1.5 hour. Yield 175 mg (62%). Beige solid; m.p. 157.6–158.9 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.06 (dd, *J* = 7.9, 1.5, 1H), 7.73 – 7.64 (m, 1H), 7.37 (t, *J* = 7.6, 1H), 7.31 (d, *J* = 8.3, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 174.0 (4-C), 158.0 (2-C), 153.8 (8a-C), 136.1, 125.9, 125.3, 119.0, 117.9, 76.3 (C=N_2).



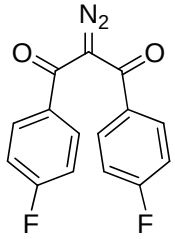
2-Diazo-1-(4-fluorophenyl)butane-1,3-dione[35] (44'). The title compound was synthesized from 1-(4-fluorophenyl)butane-1,3-dione (270 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 300 mg (93%). Yellowish viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.73 – 7.65 (m, 2H), 7.19 (t, *J* = 8.6, 2H), 2.57 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 190.4, 183.6, 165.2 (d, *J* = 254.7), 133.5 (d, *J* = 3.3), 130.04 (d, *J* = 9.2), 116.1 (d, *J* = 22.2), 83.4 (C=N_2), 29.1 (CH_3).



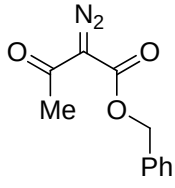
2-Diazo-1-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (45'). The title compound was synthesized from 1-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (408 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 430 mg (96%). Pale yellow solid; m.p. 66.5–67.6 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.63 (dd, *J* = 8.7, 5.3, 2H), 7.60 (d, *J* = 8.8, 2H), 7.03 (t, *J* = 8.6, 2H), 6.85 (d, *J* = 8.9, 2H), 3.84 (s, 3H, OCH_3). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 185.4, 184.6, 165.2 (d, *J* = 254.5), 163.4, 133.3 (d, *J* = 3.1), 131.1 (d, *J* = 9.2), 130.8, 129.3, 115.5 (d, *J* = 22.1), 113.8, 83.5 (C=N_2), 55.5 (OCH_3). HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{11}FN_2NaO_3$ $[M+Na]^+$: 321.0646, found 321.0660.



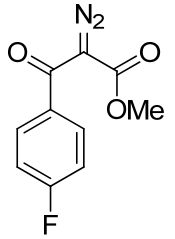
2-Diazo-1,3-bis(4-fluorophenyl)propane-1,3-dione[35] (46'). The title compound was synthesized from 1-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (390 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 398 mg (93%). Pale beige solid; m.p. 101.1–102.1 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.62 (dd, *J* = 8.8, 5.3, 4H), 7.04 (t, *J* = 8.6, 4H). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 184.7 (2C=O), 165.3 (d, *J* = 255.2), 133.1 (d, *J* = 3.2), 131.0 (d, *J* = 9.3), 115.7 (d, *J* = 22.2), 84.3 (C=N_2).



Benzyl 2-diazo-3-oxobutanoate[36] (47'). The title compound was synthesized from benzyl 3-oxobutanoate (288 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 298 mg (91%). Pale yellow solid; m.p. 41.3–43.1 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.43 – 7.36 (m, 5H, Ph(H)), 5.29 (s, 2H, CH_2), 2.51 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.0 (C=O), 161.3 (CO_2), 135.2, 128.8, 128.7, 128.4, 76.4 (C=N_2), 67.0 (CH_2), 28.3 (CH_3).



Methyl 2-diazo-3-(4-fluorophenyl)-3-oxopropanoate[37] (48'). The title compound was synthesized from methyl 3-(4-fluorophenyl)-3-oxopropanoate (294 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 306 mg (92%). Transparent yellowish liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.76 – 7.64 (m, 2H), 7.12 (t, *J* = 8.6, 2H), 3.82 (s, 3H, CO_2CH_3). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 185.3 (C=O), 165.25 (d, *J* = 253.7), 161.4 (CO_2), 133.0 (d, *J* = 3.1), 131.2 (d, *J* = 9.2), 115.1 (d, *J* = 22.1), 76.2 (C=N_2), 52.4 (OCH_3).



Methyl 2-diazo-3-(2-methoxyphenyl)-3-oxopropanoate (49'). The title compound was synthesized from methyl 3-(2-methoxyphenyl)-3-oxopropanoate (312 mg, 1.5 mmol) according to Method A (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 340 mg (97%). Transparent yellowish liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.45 (ddd, *J* = 8.4, 7.5, 1.8, 1H), 7.34 (dd, *J* = 7.5, 1.7, 1H), 7.03 (td, *J* = 7.5, 0.8, 1H), 6.94 (d, *J* = 8.4, 1H), 3.84 (s, 3H), 3.77 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 185.9 (C=O), 161.4 (CO_2), 156.8, 132.5, 128.7, 127.8, 120.7, 110.9, 77.0 (C=N_2), 55.6, 52.2. HRMS (ESI +ve) Exact mass calculated for $C_{11}H_{10}N_2NaO_4$ $[M+Na]^+$: 257.0533, found 257.0541.

2,6-Bis(diazo)cyclohex-4-ene-1,3-dione[34] (50'). The title compound was synthesized from resorcinol (165 mg, 1.5 mmol) according to Method A (double amounts of sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 2 hours. Yield 109 mg (45%). Brown solid; m.p. 77.0–79.3 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.27 (d, *J* = 10.3, 1H), 5.90 (d, *J* = 10.2, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 177.8, 174.0, 129.8, 117.9, 85.5 (C=N_2), 73.8 (C=N_2).

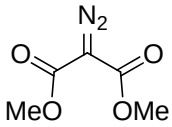
Dimethyl 2,4-bis(diazo)-3-oxopentanedioate[38] (51'). The title compound was synthesized from dimethyl 3-oxopentanedioate (260 mg, 1.5 mmol) according to Method A (double amounts of sulfonyl chloride, sodium azide and potassium carbonate were used). Reaction time – 2 hours. Yield 288 mg (85%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.84 (s, 6H, 2×OCH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 174.3 (C=O), 161.2 (2×CO_2), 74.0 (2×C=N_2), 52.6 (2×OCH_3).

Dimethyl 2-diazosuccinate (52'). The title compound was synthesized from dimethyl 2-acetylsuccinate (282 mg, 1.5 mmol) according to Method A. Reaction time – 2 hours. Yield 183 mg (71%). Yellow liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.79 (s, 3H), 3.75 (s, 3H), 3.34 (s, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 170.0, 167.0, 52.4, 52.2, 28.7 (CH_2). HRMS (ESI +ve) Exact mass calculated for $C_6H_8N_2NaO_4$ $[M+Na]^+$: 195.0376, found 195.0381.

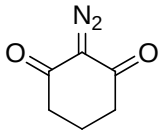
2-Diazo-6-fluoro-2,3-dihydro-1*H*-inden-1-one (53'). The title compound was synthesized from methyl 2-(6-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2-oxoacetate[39] (354 mg, 1.5 mmol) according to Method A (with addition of MeCN (2 mL)). Reaction time – 2 hours. Yield 218 mg (83%). Pale beige solid; m.p. 95.9–97.2 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.46 (dd, *J* = 7.7, 2.5, 1H), 7.42 (dd, *J* = 8.4, 4.5, 1H), 7.29 (td, *J* = 8.6, 2.5, 1H), 4.05 (s, 2H, CH_2). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 187.2 (d, *J* = 3.1, C=O), 162.9 (d, *J* = 248.3), 139.51 (d, *J* = 7.9), 138.5 (d, *J* = 2.4), 126.8 (d, *J* = 8.1), 120.5 (d, *J* = 23.7), 109.3 (d, *J* = 22.9), 61.6 (C=N_2), 28.2 (CH_2). HRMS (ESI +ve) Exact mass calculated for $C_9H_5FN_2NaO$ $[M+Na]^+$: 199.0278, found 199.0269.

1,3-Dicyclohexyl-5-diazopyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (54'). The title compound was synthesized from 1,3-dicyclohexylbarbituric acid[40] (219 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 1.5 hour. Yield 232 mg (97%). Yellow solid; m.p. 111.6–112.9 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.68 (tt, *J* = 12.2, 3.8, 2H), 2.31 (qd, *J* = 12.4, 3.5, 4H), 1.89 – 1.82 (m, 4H), 1.75 – 1.60 (m, 6H), 1.44 – 1.30 (m, 4H), 1.29 – 1.16 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 158.5 (4,6-C), 149.8 (2-C), 72.2 (C=N_2), 55.6, 29.2, 26.4, 25.1. HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{22}N_4NaO_3$ $[M+Na]^+$: 341.1584, found 341.1585.

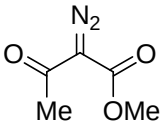
Dimethyl 2-diazomalonate[41] (55'). The title compound was synthesized from diethyl malonate (99 mg, 0.75 mmol) according to Method B. Reaction time – 2 hours. Yield 98 mg (83%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.85 (s, 6H, $2CH_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 161.4 ($2CO_2$), 65.7 ($C{=}N_2$), 52.5 ($2CH_3$).



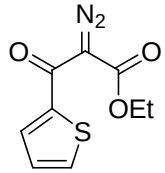
2-Diazocyclohexane-1,3-dione[6] (56'). The title compound was synthesized from cyclohexane-1,3-dione (84 mg, 0.75 mmol) according to Method B. Reaction time – 1.5 hour. Yield 89 mg (86%). Pale yellow solid; m.p. 47.0–48.6 °C. NMR ^{1}H (400 MHz, $CDCl_3$) δ 2.72 – 2.42 (m, 4H, $2CH_2$), 2.11 – 1.95 (m, 2H, 5-CH_2). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.3 (2C=O), 84.9 ($C{=}N_2$), 36.8 ($2CH_2$), 18.6 (5-CH_2).



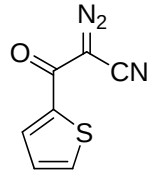
Methyl 2-diazo-3-oxobutanoate[42] (57'). The title compound was synthesized from methyl 3-oxobutanoate (87 mg, 0.75 mmol) according to Method B. Reaction time – 1.5 hour. Yield 88 mg (83%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 3.84 (s, 3H, OCH_3), 2.48 (s, 3H, 4-CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.0 (C=O), 161.8 (CO_2), 76.2 ($C{=}N_2$), 52.2 (OCH_3), 28.14 (4-CH_3).



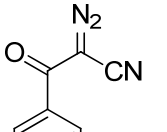
Ethyl 2-diazo-3-oxo-3-(thiophen-2-yl)propanoate[43] (58'). The title compound was synthesized from ethyl 3-oxo-3-(thiophen-2-yl)propanoate (149 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 160 mg (95%). Transparent yellowish liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.08 (dd, *J* = 3.9, 1.1, 1H), 7.68 (dd, *J* = 5.0, 1.1, 1H), 7.13 (dd, *J* = 5.0, 3.9, 1H), 4.35 (q, *J* = 7.1, 2H, $C\underline{H}_2CH_3$), 1.36 (t, *J* = 7.1, 3H, $CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 176.7 (C=O), 160.9 (CO_2), 141.5, 133.9, 133.8, 127.7, 77.1 ($C{=}N_2$), 61.7 ($\underline{C}H_2CH_3$), 14.3 ($CH_2\underline{C}H_3$).



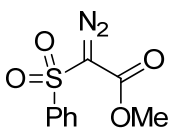
2-Diazo-3-oxo-3-(thiophen-2-yl)propanenitrile (59'). The title compound was synthesized from 3-oxo-3-(thiophen-2-yl)propanenitrile[22] (113 mg, 0.75 mmol) according to Method B. Reaction time – 1.5 hour. Yield 100 mg (75%). Yellow solid; m.p. 94.8–96.0 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.04 (dd, *J* = 4.0, 1.0, 1H), 7.78 (dd, *J* = 5.0, 1.0, 1H), 7.20 (dd, *J* = 5.0, 4.0, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 173.7 (C=O), 139.8, 135.2, 133.0, 128.7, 109.2 (C≡N), 58.6 ($C{=}N_2$). HRMS (ESI +ve) Exact mass calculated for $C_7H_3N_3NaOS$ $[M+Na]^+$: 199.9889, found 199.9889.



2-Diazo-3-(3-fluorophenyl)-3-oxopropanenitrile (60'). The title compound was synthesized from 3-(3-fluorophenyl)-3-oxopropanenitrile[22] (122 mg, 0.75 mmol) according to Method B. Reaction time – 1 hour. Yield 85 mg (60%). Orange viscous liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.71 (ddd, *J* = 7.8, 1.6, 1.0, 1H), 7.59 (ddd, *J* = 9.0, 2.4, 1.9, 1H), 7.51 (td, *J* = 8.0, 5.4, 1H), 7.34 (tdd, *J* = 8.3, 2.6, 0.9, 1H). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) δ 181.6 (d, *J* = 2.6, C=O), 162.6 (d, *J* = 249.5, 3'-C), 136.3 (d, *J* = 7.0), 130.7 (d, *J* = 7.9), 123.8 (d, *J* = 3.2), 120.9 (d, *J* = 21.3), 115.2 (d, *J* = 23.4), 108.8 (C≡N), 59.52 ($C{=}N_2$). HRMS (ESI +ve) Exact mass calculated for $C_9H_4FN_3NaO$ $[M+Na]^+$: 212.0231, found 212.0231.



Methyl 2-diazo-2-(phenylsulfonyl)acetate[44] (61'). The title compound was synthesized from methyl 2-(phenylsulfonyl)acetate[45] (161 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 6 hours. Yield 137 mg (76%). Pale yellow solid; m.p. 67.8–69.9 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.08 – 8.02 (m, 2H, *o*-Ph), 7.71 – 7.66 (m, 1H, *p*-Ph), 7.59 (t, *J* = 7.7, 2H, *t*-Ph), 3.79 (s, 3H, OCH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 160.0 (CO_2), 141.6, 134.1, 129.2, 127.8, 75.8 ($C{=}N_2$), 52.9 (OCH_3).



2-Diazo-1-phenyl-2-tosylethanone[46] (62'). The title compound was synthesized from 1-phenyl-2-tosylethanone[47] (206 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 1.5 hour. Yield 218 mg (97%). Yellow solid; m.p. 96.8–97.6 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.54 (m, 3H), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 2.47 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 182.7 (C=O), 145.4, 138.6, 135.9, 133.0, 129.7, 128.8, 128.2, 127.5, 83.45 (C=N_2), 21.72 (CH_3).

1-Diazo-2-oxo-*N*-(*p*-tolyl)propane-1-sulfonamide (63'). The title compound was synthesized from 2-oxo-*N*-(*p*-tolyl)propane-1-sulfonamide (170 mg, 0.75 mmol) according to Method B (with addition of MeCN (0.5 mL)). Reaction time – 2 hours. Yield 165 mg (87%). Yellow solid; m.p. 123.4–124.2 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz): 7.18 (d, *J* = 8.4 Hz, 2H), 7.15 (br.s, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H), 2.27 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$): 186.1 (C=O), 137.1, 132.6, 130.3, 123.0, 80.1 (C=N_2), 26.4, 20.9. HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{11}N_3NaO_3S$ $[M+Na]^+$: 276.0413, found 276.0416.

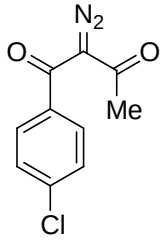
3-Diazo-1-methylquinoline-2,4(1*H*,3*H*)-dione[48] (64'). The title compound was synthesized from 4-hydroxy-1-methylquinolin-2(1*H*)-one (131 mg, 0.75 mmol) according to Method B. Reaction time – 1.5 hour. Yield 140 mg (93%). White solid; m.p. 164.2–165.8 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.20 (dd, *J* = 8.0, 1.7, 1H), 7.68 (ddd, *J* = 8.7, 7.3, 1.7, 1H), 7.32 – 7.23 (m, 2H), 3.59 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 175.5 (4-C), 159.2 (2-C), 141.5, 135.2, 126.6, 123.0, 120.7, 115.0, 79.8 (C=N_2), 29.3 (CH_3).

5-Diazo-1*H*-pyrrolo[3,2,1-*ij*]quinoline-4,6(2*H*,5*H*)-dione (65'). The title compound was synthesized from 6-hydroxy-1*H*-pyrrolo[3,2,1-*ij*]quinolin-4(2*H*)-one[49] (140 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 125 mg (78%). Pale yellow solid; m.p. 168.7–171.1 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.76 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.45 (dq, *J* = 7.3, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.3 Hz, 1H), 4.32 – 4.23 (m, 2H), 3.37 (ddt, *J* = 9.5, 7.6, 1.1 Hz, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 176.7 (6-C), 157.4 (4-C), 144.0, 131.1, 130.3, 123.6, 122.8, 117.3, 80.3 (C=N_2), 46.1 (2-C), 27.3 (1-C). HRMS (ESI +ve) Exact mass calculated for $C_{11}H_8N_3O_2$ $[M+H]^+$: 214.0611, found 214.0612.

4-Diazo-2-(2-morpholinoethyl)isoquinoline-1,3(2*H*,4*H*)-dione[9] (66'). The title compound was synthesized from *N*-(2-morpholinoethyl)homophthalimide[9] (206 mg, 0.75 mmol) according to Method B. Reaction time – 20 hours. Yield 198 mg (88%). Pale orange solid; m.p. 151.1–153.1 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.29 (ddd, *J* = 8.0, 1.3, 0.4, 1H), 7.68 (ddd, *J* = 7.9, 7.4, 1.4, 1H), 7.43 – 7.31 (m, 1H), 7.19 – 7.09 (m, 1H), 4.28 – 4.22 (m, 2H), 3.70 – 3.66 (m, 4H), 2.68 – 2.61 (m, 2H), 2.60 – 2.55 (m, 4H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.7, 162.6, 134.1, 130.2, 126.6, 125.7, 120.9, 118.6, 68.1 (C=N_2), 67.0, 56.0, 53.8, 37.6.

4-Diazo-2-phenylisoquinoline-1,3(2*H*,4*H*)-dione[9] (67'). The title compound was synthesized from *N*-phenylhomophthalimide[9] (178 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 3 hours. Yield 183 mg (93%). Yellow solid; m.p. 184.5–185.3 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.34 (ddd, *J* = 8.0, 1.4, 0.5, 1H), 7.74 (ddd, *J* = 7.9, 7.4, 1.4, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.46 (m,

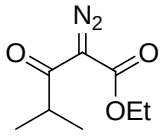
1H), 7.39 (ddd, *J* = 8.0, 7.4, 1.1, 1H), 7.30 – 7.25 (m, 2H), 7.21 (ddd, *J* = 8.0, 1.0, 0.6, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.9 (C=O), 162.6 (C=O), 134.8, 134.5, 130.6, 129.4, 128.9, 128.6, 126.8, 125.8, 121.2, 118.7, 68.6 ($C=N_2$).



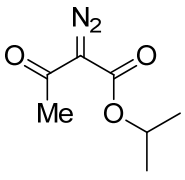
1-(4-Chlorophenyl)-2-diazobutane-1,3-dione[50] (68'). The title compound was synthesized from 1-(4-chlorophenyl)butane-1,3-dione (147 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 150 mg (90%). Pale yellow solid; m.p. 57.1–58.4 °C. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.61 (d, *J* = 8.6, 2H), 7.49 (d, *J* = 8.6, 2H), 2.58 (s, 3H, CH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.3, 183.8, 139.1, 135.6, 129.3, 128.9, 83.6 ($C=N_2$), 29.1 (CH_3).

2-Diazo-4-methyl-1-phenylpentane-1,3-dione (69'). The title compound was synthesized from 4-methyl-1-phenylpentane-1,3-dione (143 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 2 hours. Yield 141 mg (87%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.68 – 7.63 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 3.66 (hept, *J* = 6.8 Hz, 1H, C<u>H</u>$(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C<u>H</u>$_3)_2$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 197.5, 184.9, 137.7, 132.5, 128.9, 127.3, 82.4 ($C=N_2$), 37.8 (<u>C</u>H$(CH_3)_2$), 18.6 (CH(<u>C</u>H$_3)_2$). HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{12}N_2NaO_2$ $[M+Na]^+$: 239.0791, found 239.0802.

2-Diazo-1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (70'). The title compound was synthesized from 1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (191 mg, 0.75 mmol) according to Method B (with addition of MeCN (1 mL)). Reaction time – 4 hours. Yield 195 mg (93%). Pale yellow solid; m.p. 86.4–87.6 °C (decomp.) (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.65 – 7.58 (m, 4H), 7.51 – 7.44 (m, 1H, *p*-Ph), 7.35 (t, *J* = 7.7, 2H, *t*-Ph), 6.83 (d, *J* = 8.9, 2H), 3.83 (s, 3H, OCH_3). NMR ^{13}C (101 MHz, $CDCl_3$) δ 186.7, 184.9, 163.3, 137.1, 132.5, 130.9, 129.4, 128.4, 128.3, 113.6, 83.5 ($C=N_2$), 55.5 (OCH_3). HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{12}N_2NaO_3$ $[M+Na]^+$: 303.0740, found 303.0739.



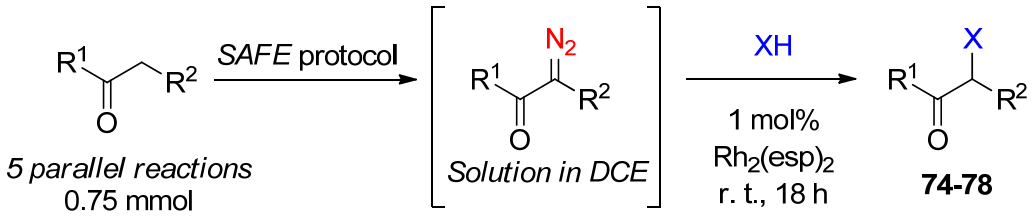
Ethyl 2-diazo-4-methyl-3-oxopentanoate[51] (71'). The title compound was synthesized from ethyl 4-methyl-3-oxopentanoate (119 mg, 0.75 mmol) according to Method B (with addition of MeCN (0.5 mL)). Reaction time – 2 hours. Yield 117 mg (85%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.30 (q, *J* = 7.1, 2H, C<u>H</u>$_2$CH$_3$), 3.58 (hept, *J* = 6.8, 1H, C<u>H</u>$(CH_3)_2$), 1.30 (t, *J* = 7.1, 3H, CH_2C<u>H</u>$_3$), 1.13 (d, *J* = 6.8, 6H, CH(C<u>H</u>$_3)_2$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 197.0 (C=O), 161.1 (CO_2), 75.2 ($C=N_2$), 61.3 (<u>C</u>H$_2$CH$_3$), 36.7 (<u>C</u>H$(CH_3)_2$), 18.5 (CH(<u>C</u>H$_3)_2$), 14.3 (CH_2<u>C</u>H$_3$).



Isopropyl 2-diazo-3-oxobutanoate[2] (72'). The title compound was synthesized from isopropyl 3-oxobutanoate (108 mg, 0.75 mmol) according to Method B (with addition of MeCN (0.5 mL)). Reaction time – 2 hours. Yield 107 mg (84%). Transparent liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 5.16 (hept, *J* = 6.3, 1H, C<u>H</u>$(CH_3)_2$), 2.48 (s, 3H, CH_3CO), 1.32 (d, *J* = 6.3, 6H, CH(C<u>H</u>$_3)_2$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 190.3 (C=O), 161.0 (CO_2), 76.6 ($C=N_2$), 69.4 (<u>C</u>H$(CH_3)_2$), 28.2 (<u>C</u>H$_3$CO), 21.9 (CH(<u>C</u>H$_3)_2$).

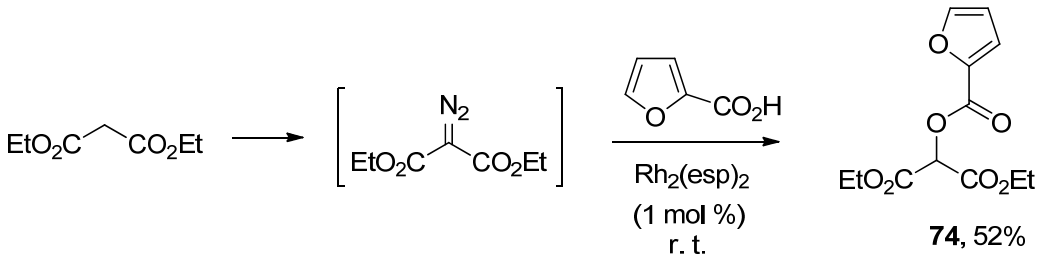
Ethyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate[52] (73'). The title compound was synthesized from ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (167 mg, 0.75 mmol) according to Method B (with addition of MeCN (0.5 mL)). Reaction time – 2 hours. Yield 182 mg (98%). Transparent yellow liquid. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.69 (d, *J* = 8.8, 2H), 6.93 (d, *J* = 8.8, 2H), 4.28 (q, *J* = 7.1, 2H, $C\underline{H}_2CH_3$), 3.88 (s, 3H, OCH_3), 1.30 (t, *J* = 7.1, 3H, $CH_2C\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 185.3 (C=O), 163.2, 161.2, 131.0, 129.4, 113.1, 75.6 (C=N_2), 61.5 ($\underline{C}H_2CH_3$), 55.4 (OCH_3), 14.3 ($CH_2\underline{C}H_3$).

IV. General procedure for the preparation of compounds 74-78



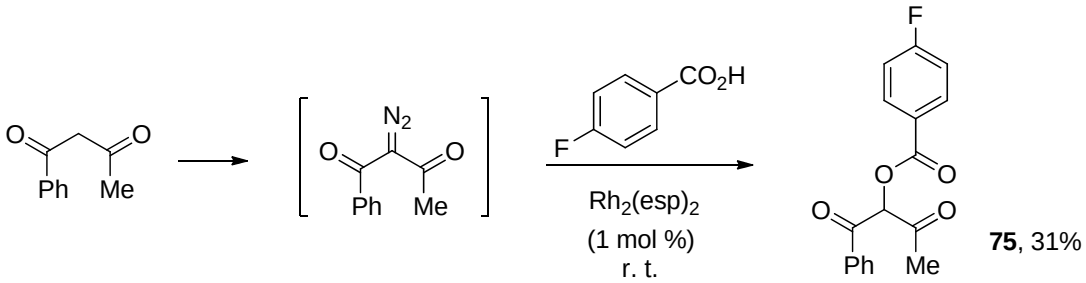
To a stirred solution of sodium azide (0.49 g, 7.5 mmol) and potassium carbonate (1.38 g, 10 mmol) in water (10 mL) was added 3-(chlorosulfonyl)benzoic acid (1.11 g, 5 mmol) and the mixture was stirred at ambient temperature for 10 minutes. The resulting aqueous solution was divided into 5 equal portions. To each portion under stirring the corresponding substrate for diazo transfer and MeCN (1 mL) were added and the mixtures were stirred at ambient temperature for 2 hours. After extraction with DCE (2+1 mL) organic phases were dried over $CaCl_2$ and filtered. To the resulting dry solutions were added the corresponding XH-substrates (0.75 mmol) and $Rh_2(esp)_2$ (5.7 mg, 7.5 μmol, 1 mol %). All reaction mixtures were stirred at ambient temperature overnight, evaporated and subjected to flash column chromatography on SiO_2 using the indicated eluent.

Diethyl 2-((furan-2-carbonyl)oxy)malonate (74)



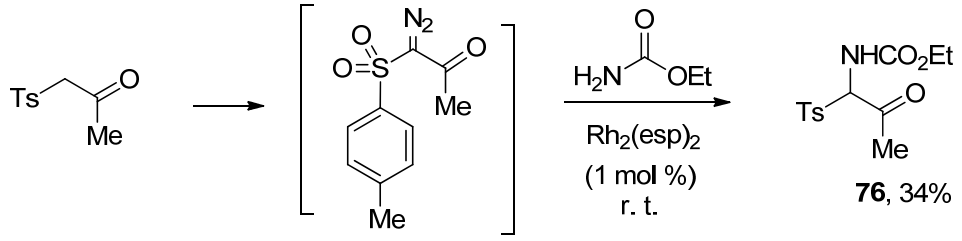
The title compound was synthesized from diethyl malonate (120 mg, 0.75 mmol) and furan-2-carboxylic acid (84 mg, 0.75 mmol); eluent – *n*-hexane–DCM (50:50 to 0:100). Yield 105 mg (52%), transparent colorless oil. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.66 (dd, *J* = 1.7, 0.8, 1H), 7.38 (dd, *J* = 3.6, 0.8, 1H), 6.57 (dd, *J* = 3.6, 1.7, 1H), 5.74 (s, 1H), 4.42 – 4.26 (m, 4H), 1.34 (t, *J* = 7.1, 6H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 164.2, 156.8, 147.4, 143.0, 120.0, 112.1, 71.7, 62.6, 14.0. HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{14}NaO_7$ $[M+Na]^+$: 293.0632, found 293.0636.

1,3-Dioxo-1-phenylbutan-2-yl 4-fluorobenzoate (75)



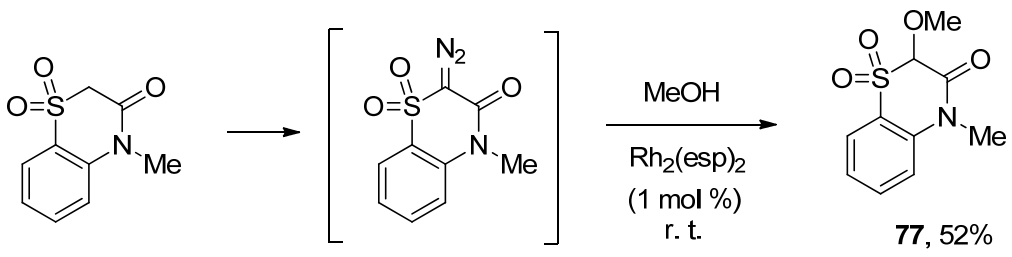
The title compound was synthesized from 1-phenylbutane-1,3-dione (122 mg, 0.75 mmol) and *p*-fluorobenzoic acid (105 mg, 0.75 mmol); eluent – *n*-hexane–acetone (93:7 to 85:15). Yield 70 mg (31%), transparent oil (diketone/ketoenol mixture ~ 8:1). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) (signals of diketone tautomer) δ 8.14 (dd, *J* = 8.9, 5.4, 2H), 8.10 – 8.09 (m, 2H), 7.69 – 7.63 (m, 1H), 7.53 (t, *J* = 7.7, 2H), 7.17 (t, *J* = 8.7, 2H), 6.50 (s, 1H), 2.41 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$, *J*/Hz) (signals of diketone tautomer) δ 199.3, 190.8, 166.3 (d, *J* = 255.6), 164.0, 134.4, 134.4, 132.7 (d, *J* = 9.5), 129.5, 128.8, 124.8 (d, *J* = 3.0), 115.9 (d, *J* = 22.1), 82.6, 27.0. HRMS (ESI +ve) Exact mass calculated for $C_{17}H_{13}FNaO_4$ $[M+Na]^+$: 323.0690, found 323.0675.

Ethyl (2-oxo-1-tosylpropyl)carbamate (76)



The title compound was synthesized from 1-tosylacetone (159 mg, 0.75 mmol) and ethyl carbamate (67 mg, 0.75 mmol); eluent – *n*-hexane–acetone (90:10 to 70:30). Yield 76 mg (34%), white solid; m.p. 121.5–123.2 °C (MeOH–H_2O). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.79 (d, *J* = 8.0, 2H), 7.37 (d, *J* = 8.0, 2H), 5.95 (br.d, *J* = 8.2, 1H), 5.75 (d, *J* = 9.3 Hz, 1H), 3.95 (q, *J* = 7.0, 2H), 2.64 (s, 3H), 2.47 (s, 3H), 1.12 (t, *J* = 7.0, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 195.5, 154.5, 145.9, 133.0, 129.8, 129.7, 78.3, 62.0, 30.5, 21.7, 14.3. HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{17}NNaO_5S$ $[M+Na]^+$: 322.0720, found 322.0711.

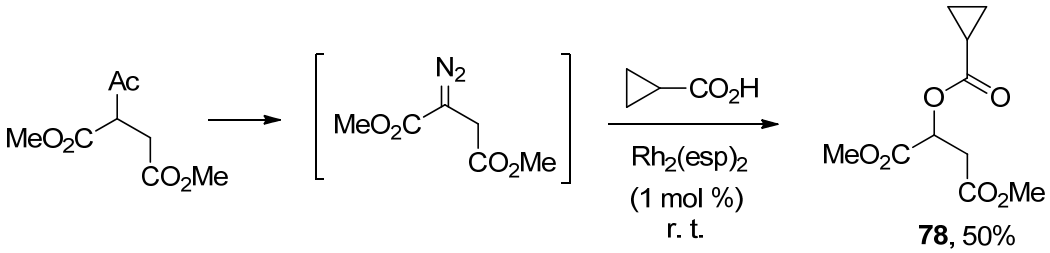
2-Methoxy-4-methyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one 1,1-dioxide (77)



The title compound was synthesized from 4-methyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one 1,1-dioxide (158 mg, 0.75 mmol) and methanol (45 mg, 1.4 mmol); eluent – *n*-hexane–acetone (90:10 to 65:35). Yield 94 mg (52%), white solid; m.p. 135.1–136.7 °C (MeOH). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.00 (dd, *J* = 7.7, 1.6, 1H), 7.71 (ddd, *J* = 8.4, 7.5, 1.6, 1H), 7.36 (td, *J* = 7.6, 0.9, 1H), 7.30 (d, *J* = 8.3, 1H), 4.80 (s, 1H), 3.78 (s, 3H), 3.51 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 162.4, 138.7, 135.2, 126.4,

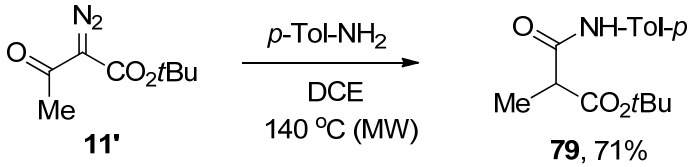
125.8, 124.5, 118.1, 90.4, 61.7, 32.2. HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{11}NNaO_4S$ $[M+Na]^+$: 264.0301, found 264.0306.

Dimethyl 2-((cyclopropanecarbonyl)oxy)succinate (78)

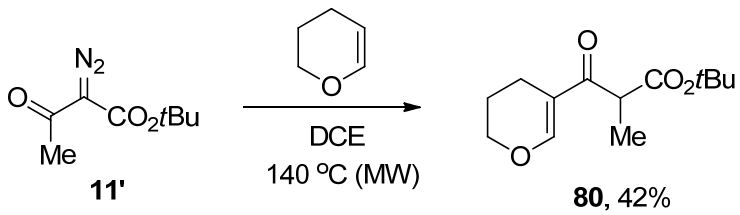


The title compound was synthesized from dimethyl 2-acetylsuccinate (141 mg, 0.75 mmol) and cylopropanecarboxylic acid (65 mg, 0.75 mmol); eluent – *n*-hexane–acetone (98:2 to 90:10). Yield 86 mg (50%), transparent oil. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 5.49 (dd, *J* = 6.5, 5.8, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 2.96 – 2.87 (m, 2H), 1.70 (tt, *J* = 8.0, 4.6, 1H), 1.10 – 1.04 (m, 2H), 0.97 – 0.90 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 173.8, 169.6, 169.5, 68.1, 52.6, 52.1, 36.0, 12.6, 9.0, 8.9. HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{14}NaO_6$ $[M+Na]^+$: 253.0683, found 253.0687.

V. Preparation of compounds 79-83 and 86 from diazo ketoester 11'

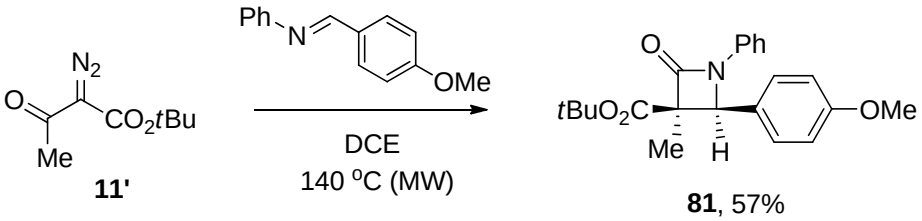


***tert*-Butyl 2-methyl-3-oxo-3-(*p*-tolylamino)propanoate (79)**. A solution of *tert*-butyl 2-diazo-3-oxobutanoate (169 mg, 0.92 mmol) and *p*-toluidine (91 mg, 0.85 mmol) in dry DCE (1.5 mL) was heated in microwave reactor at 140 °C for 1 hour. The residue after evaporation of solvent was purified by flash column chromatorgraphy (*n*-hexane/acetone, gradient from 90:10 to 75:25) to afford the titled compound. Yield 173 mg (71%), white solid; m.p. 147.4–149.7 °C (*n*-hexane–$CHCl_3$). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 8.60 (s, 1H, NH), 7.44 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.35 (q, *J* = 7.3 Hz, 1H, C<u>H</u>CH_3), 2.33 (s, 3H, 4'-CH_3), 1.52 (s, 9H, $C(CH_3)_3$), 1.51 (d, *J* = 7.3 Hz, 3H, $CHC\underline{H}_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 172.1, 167.3, 135.2, 133.9, 129.5, 119.9, 82.5, 48.3, 28.0, 20.8, 15.5. HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{21}NNaO_3$ $[M+Na]^+$: 286.1414, found 286.1408.

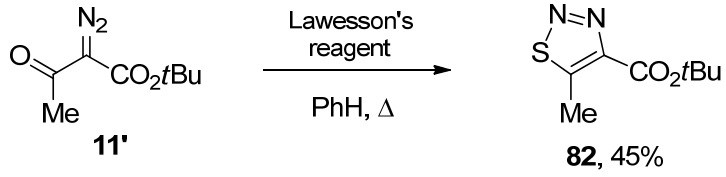


***tert*-Butyl 3-(3,4-dihydro-2*H*-pyran-5-yl)-2-methyl-3-oxopropanoate (80)**. A solution of *tert*-butyl 2-diazo-3-oxobutanoate (169 mg, 0.92 mmol) and *p*-toluidine (419 μL, 4.6 mmol) in dry DCE (1.5 mL) was heated in microwave reactor at 140 °C for 1 hour. The residue after evaporation of solvent was purified by flash column chromatorgraphy (*n*-hexane/acetone, 85:15) to afford the titled compound. Yield 93 mg (42%), transparent oil. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.67 (s, 1H, =CH), 4.08 (t, *J* =

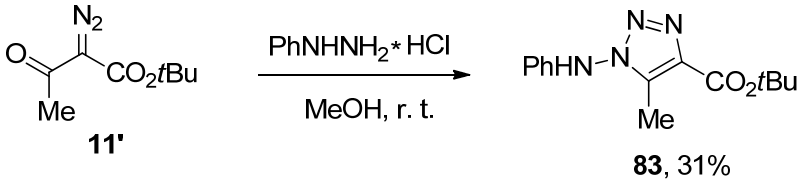
5.3 Hz, 2H), 3.77 (q, *J* = 7.0 Hz, 1H, C<u>H</u>CH$_3$), 2.28 (t, *J* = 6.3 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.42 (s, 9H, C(CH$_3$)$_3$), 1.31 (d, *J* = 7.0 Hz, 3H, CHC<u>H</u>$_3$). NMR ^{13}C (101 MHz, CDCl$_3$) δ 194.4 (C=O), 170.39 (CO$_2$), 157.5 (=CH), 115.9 (<u>C</u>=CH), 81.2, 67.1, 47.8, 27.9, 21.0, 18.6, 13.8. HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{20}NaO_4$ [M+Na]$^+$: 263.1254, found 263.1266.



(2*SR*,3*RS*)-*tert*-Butyl 2-(4-methoxyphenyl)-3-methyl-4-oxo-1-phenylazetidine-3-carboxylate (81). A solution of *tert*-butyl 2-diazo-3-oxobutanoate (169 mg, 0.92 mmol) and *N*-(*p*-methoxybezylidene)aniline (179 mg, 0.85 mmol) in dry DCE (1.5 mL) was heated in microwave reactor at 140 °C for 1 hour. The residue after evaporation of solvent was purified by flash column chromatorgraphy (*n*-hexane/acetone, gradient from 95:5 to 85:15) to afford the titled compound. Yield 177 mg (57%), white solid; m.p. 136.6–138.2 °C (*n*-hexane). NMR ^{1}H (400 MHz, CDCl$_3$, *J*/Hz) δ 7.40 – 7.18 (m, 6H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 4.85 (s, 1H, 4-H), 3.80 (s, 3H, OCH$_3$), 1.76 (s, 3H, 3-CH$_3$), 1.10 (s, 9H, C(CH$_3$)$_3$). NMR ^{13}C (101 MHz, CDCl$_3$) δ 167.1, 164.8, 159.9, 137.6, 129.0, 128.4, 125.8, 124.0, 117.3, 114.0, 82.0, 66.2, 65.9, 55.4, 27.4, 18.1. HRMS (ESI +ve) Exact mass calculated for $C_{22}H_{25}NNaO_4$ [M+Na]$^+$: 390.1676, found 390.1663.

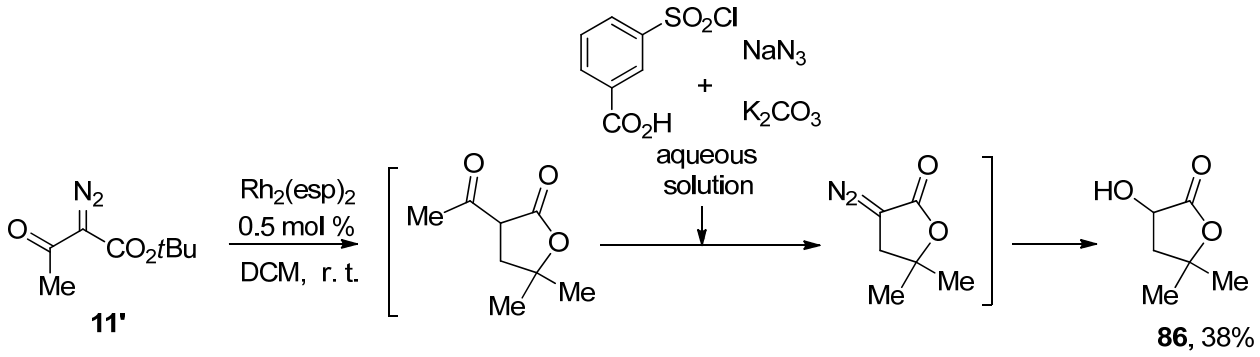


***tert*-Butyl 5-methyl-1,2,3-thiadiazole-4-carboxylate (82)**. To a solution of *tert*-butyl 2-diazo-3-oxobutanoate (169 mg, 0.92 mmol) in 5 mL of dry benzene were added Lawesson's reagent (223 mg, 0.55 mmol) and DIPEA (226 μL, 1.3 mmol) and the mixture was refluxed for 2.5 hours. After evaporation of solvent the residue was purified by flash column chromatorgraphy (*n*-hexane/acetone, gradient from 100:0 to 90:10) to afford the titled compound. Yield 83 mg (45%), yellow oil. NMR ^{1}H (400 MHz, CDCl$_3$, *J*/Hz) δ 2.88 (s, 3H, CH$_3$), 1.68 (s, 9H, C(CH$_3$)$_3$). NMR ^{13}C (101 MHz, CDCl$_3$) δ 160.0 (CO), 158.9, 151.5, 83.3, 28.2, 11.0. HRMS (ESI +ve) Exact mass calculated for $C_8H_{12}N_2NaO_2S$ [M+Na]$^+$: 223.0512, found 223.0510.



***tert*-Butyl 5-methyl-1-(phenylamino)-1*H*-1,2,3-triazole-4-carboxylate (83)**. A solution of *tert*-butyl 2-diazo-3-oxobutanoate (169 mg, 0.92 mmol) and phenylhydrazine hydrochloride (145 mg, 1.0 mmol) in methanol (2 mL) was stirred for 48 hours at room temperature. The residue after removal of solvent was extracted with ether (3×3 mL). Ether washings were evaporated and the crude product was purified by flash column chromatorgraphy (DCM/MeOH, 50:1) to afford the titled compound. Yield 78 mg

(31%), pale beige solid; m.p. 156.1–159.6 °C (decomp.). NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 7.82 (s, 1H, NH), 7.25 – 7.19 (m, 2H), 7.03 – 6.97 (m, 1H), 6.53 – 6.48 (m, 2H), 2.53 (s, 3H, CH_3), 1.66 (s, 9H, $C(CH_3)_3$). NMR ^{13}C (101 MHz, $CDCl_3$) δ 160.6 (CO), 145.1, 139.4, 136.4, 129.5, 122.9, 113.8, 82.3, 28.3, 8.8. HRMS (ESI +ve) Exact mass calculated for $C_{14}H_{18}N_4NaO_2$ $[M+Na]^+$: 297.1322, found 297.1320.



11' **86**, 38%

3-Hydroxy-5,5-dimethyldihydrofuran-2(3*H*)-one (86). To a stirred solution of *tert*-butyl 2-diazo-3-oxobutanoate (339 mg, 1.84 mmol) in 2.5 mL of dry DCM was slowly added the solution of $Rh_2(esp)_2$ (6.8 mg, 0.009 mmol) in 0.5 mL of dry DCM (gas evolution!). The mixture was stirred for 2 hours at room temperature (full conversion of diazo compound was controlled by TLC). The solution prepared as described in Method B (the volume containing 2 mmol of sulfonyl azide) was added and the mixture was vigorously stirred for 2 hours. After extraction with EtOAc (3×6 mL) the organic phase was dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (DCM–acetone, 15:1) to afford the titled compound. Yield 91 mg (38%), transparent colorless oil. NMR ^{1}H (400 MHz, $CDCl_3$, *J*/Hz) δ 4.67 (dd, *J* = 9.9, 8.6 Hz, 1H, 3-H), 3.39 (br.s, 1H, OH), 2.53 (dd, *J* = 12.8, 8.6 Hz, 1H, C<u>H</u>H), 2.08 (dd, *J* = 12.8, 9.9 Hz, 1H, CH<u>H</u>), 1.53 (s, 3H), 1.43 (s, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 177.6 (CO), 82.5 (3-C), 68.8 (5-C), 42.9 (4-C), 29.1 (CH_3), 27.6 (CH_3). HRMS (ESI +ve) Exact mass calculated for $C_6H_{10}NaO_3$ $[M+Na]^+$: 153.0522, found 153.0527.

VI. Crystallographic data for compound 81

X-ray Single Crystal analysis was performed on Agilent Technologies SuperNova HyPix3000 diffractometer with monochromated CuKα radiation. The crystal was kept at 129 K during data collection. Using Olex2[53], the structure was solved with the olex2.solve[54] structure solution program using Charge Flipping and refined with the olex2.refine[54] refinement package using Gauss-Newton minimisation.

CCDC 1897286 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

Table 1 Crystal data and structure refinement for 81.	
Empirical formula	$C_{44}H_{51}N_3O_7$
Formula weight	733.91
Temperature/K	129
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.76130(10)
b/Å	20.9417(3)
c/Å	32.5782(5)
α/°	90
β/°	93.1090(10)
γ/°	90
Volume/Å^3	3924.82(11)
Z	4
ρ_{calc}g/cm^3	1.2419
μ/mm^{-1}	0.676
F(000)	1573.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.02 to 147.74
Index ranges	$-6 \le h \le 7$, $-24 \le k \le 26$, $-40 \le l \le 40$
Reflections collected	23582
Independent reflections	7868 [R_{int} = 0.0453, R_{sigma} = 0.0539]
Data/restraints/parameters	7868/0/497
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0540, wR_2 = 0.1431
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1540
Largest diff. peak/hole / e Å^{-3}	0.47/-0.70

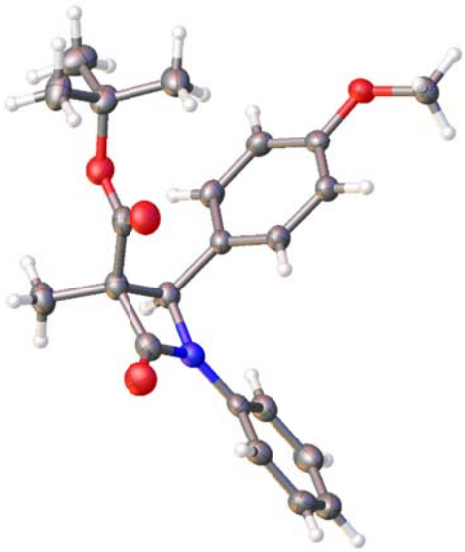


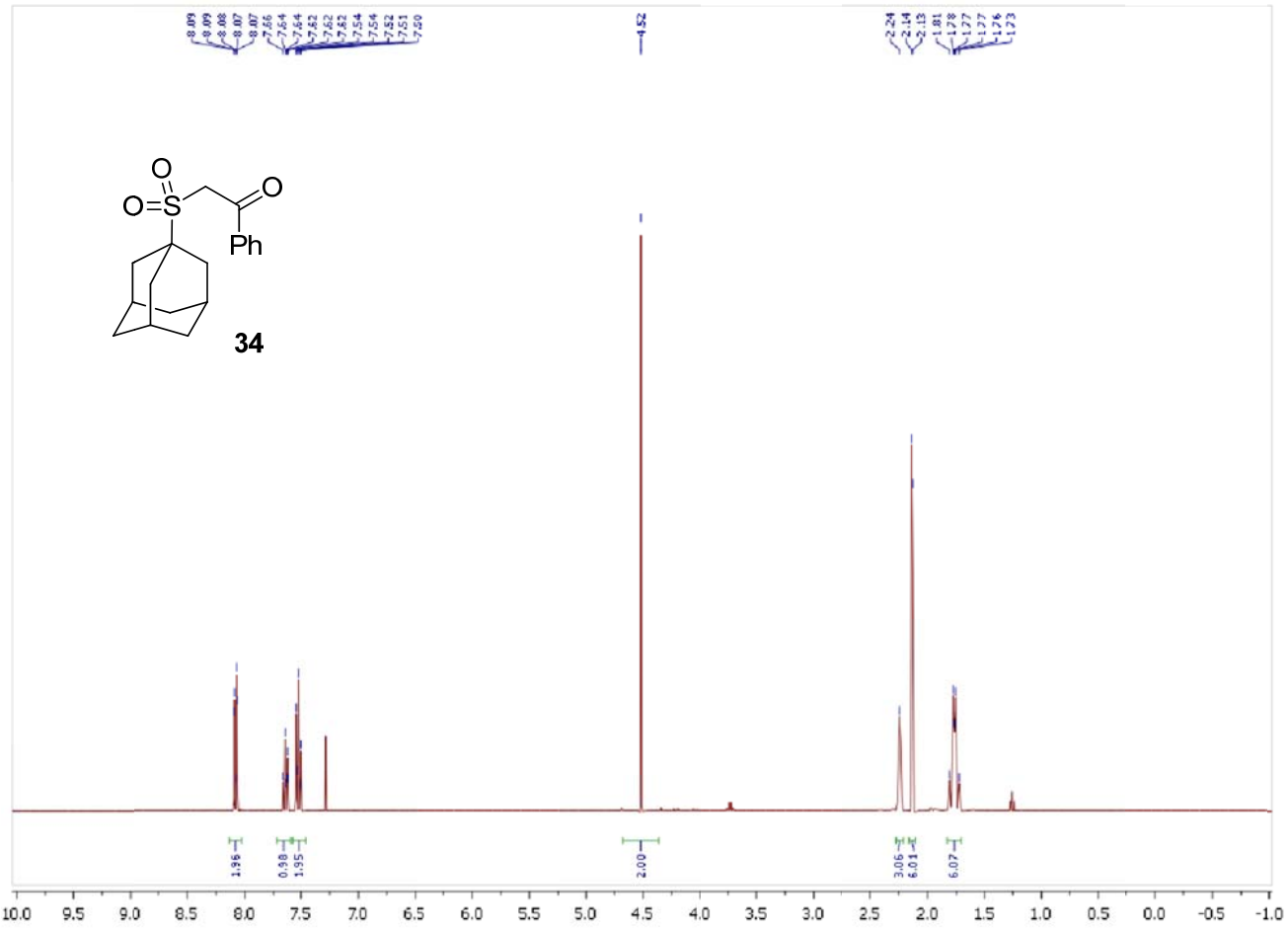
Fig.S1 Crystal structure of compound **81**

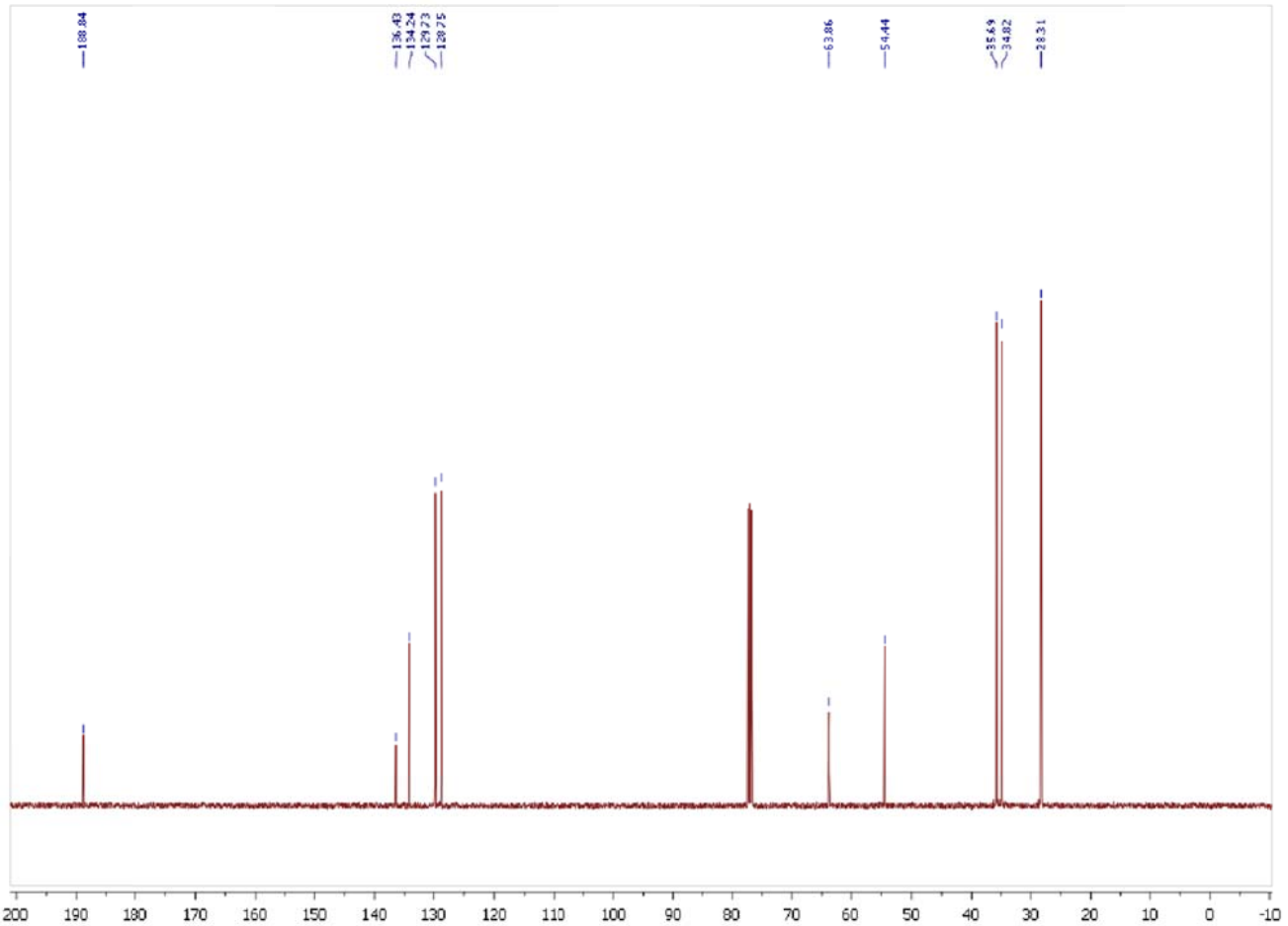
VII. References

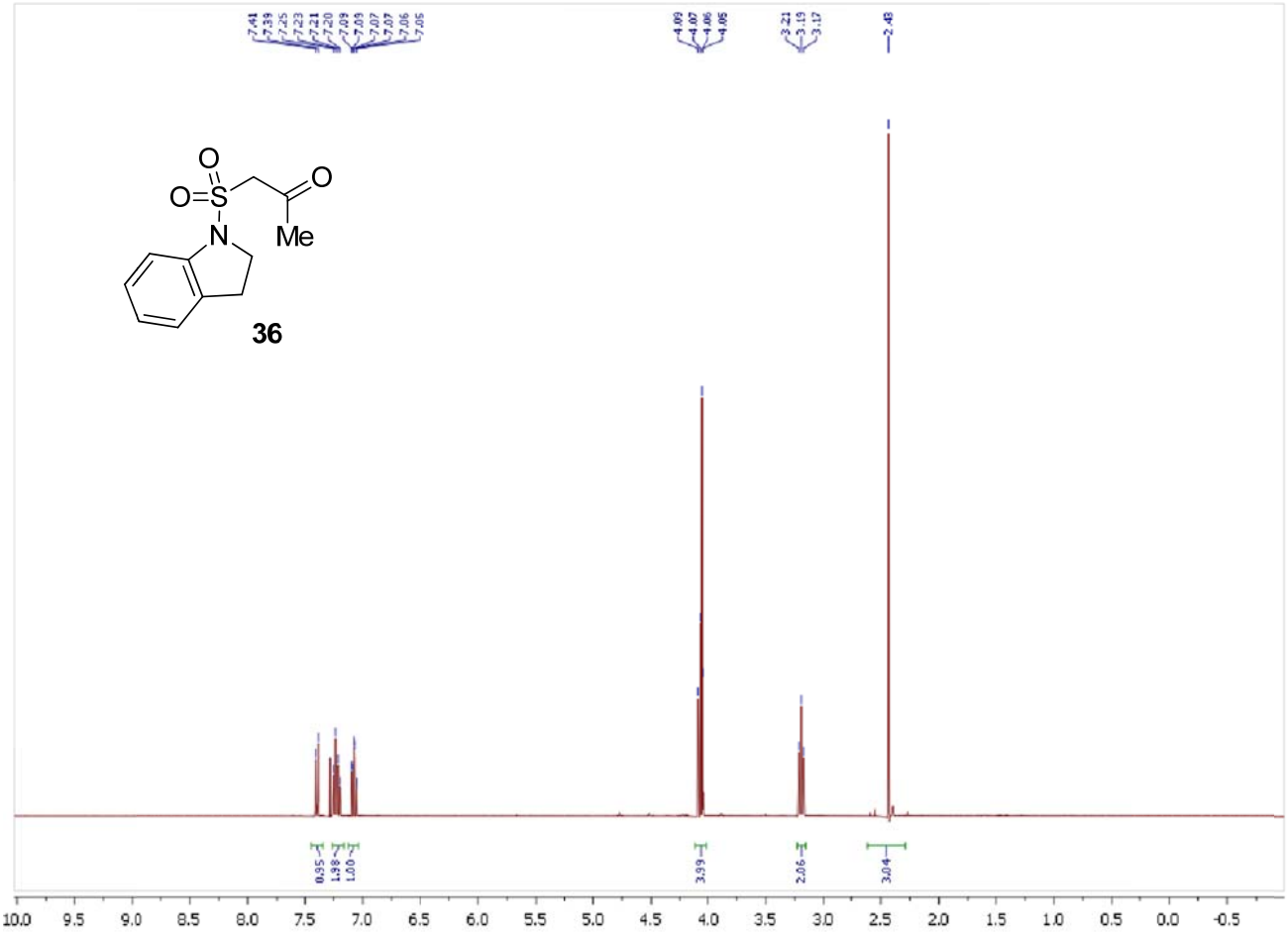
1. Kan He. Novel inhibitors of protein kinases.WO 2017066193 A1.
2. Kokel, B.; Viehe, H. G. *Angew. Chem.* **1980**, *92*(9), 754.
3. Galiullina, S. V.; Zakharova, V. M.; Kantin, G. P.; Nikolaev, V. A. *Rus. J. Org. Chem.* **2007**, *43*(4), 607.
4. Schulze, B.; Nikolaev, Vs. V.; Hennig, L.; Rodina, L. L.; Sieler, J.; Nikolaev, V. A. *Rus. J. Org. Chem.* **2004**, *40*(5), 740.
5. Nikolaev, V. A.; Shevchenko, V. V.; Platz, M. S.; Khimich, N. N. *Rus. J. Org. Chem.* **2006**, *42*(6), 815.
6. Moriarty, R. M.; Bailey, B. R., III; Prakash, O.; Prakash, I. *J. Am. Chem. Soc.* **1985**, *107*(5), 1375.
7. Chen, Z.-B.; Hong, D.; Wang, Y.-G. *J. Org. Chem.* **2009**, *74*(2), 903.
8. Supurgibekov, M. B.; Hennig, L.; Schulze, B.; Nikolaev, V. A. *Rus. J. Org. Chem.* **2008**, *44*(12), 18403.
9. Kantin, G.; Dar'in, D.; Krasavin, M. *Eur. J. Org. Chem.* **2018**, *35*, 4857.
10. Harned, A. M.; Sherrill, W. M.; Flynn, D. L.; Hanson, P. R. *Tetrahedron* **2005**, *61*(51), 12093.
11. Shi, B.; Blake, A. J.; Lewis, W.; Campbell, I. B.; Judkins, B. D.; Moody, C. J. *J. Org. Chem.* **2010**, *75*(1), 152.
12. Swenson, R. E.; Sowin, T. J.; Zhang, H. Q. *J. Org. Chem*., **2002**, *67* (26), 9182.
13. Ingle, V. N.; Gaidhane, P. K.; Hatzade, K. M.; Umare, V. D.; Taile, V. S. *Intern. J. Pharm. Tech. Res.* **2009**, *1*(3), 605.
14. Marcoux, D.; Goudreau, S. R.; Charette, A. B. *J. Org. Chem*. **2009**, *74*(23), 8939.
15. Wheeler, T. N. *J. Org. Chem*. **1979**, *44*(26), 4906.
16. Lu, C.-D.; Chen, Z.-Y.; Liu, H.; Hu, W.-H.; Mi, A.-Q.; Doyle, M. P. *J. Org. Chem*. **2004**, *69*(14), 4856.
17. Qi, H.; Zhang, J.; Xu, J. *Synthesis* **2011,** *6*, 887.
18. Pandit, R. P.; Kim, S. H.; Lee, Y. R. *Adv. Syn. Cat.* **2016**, *358*(22), 3586.
19. Peng, C.; Cheng, J.; Wang, J. *J. Am. Chem. Soc.* **2007**, *129*(28), 8708.
20. Wurz, R. P.; Lin, W.; Charette, A. B. *Tet. Lett*. **2003**, *44*(49), 8845.
21. L'Abbe, G.; Godts, F. *Bull. Soc. Chim. Belges* **1987**, *96*(3), 229.
22. Zheng, C.; Zhang, X.; Ijaz Hussain, M.; Huang, M.; Liu, Q.; Xiong, Y.; Zhu, X. *Tet. Lett*. **2017**, *58*(6), 574.
23. Cui, X.; Xu, X.; Lu, H.; Zhu, S.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc*. **2011**, *133*(10), 3304.
24. Katritzky, A. R.; El Khatib, M.; Bol'shakov, O.; Khelashvili, L.; Steel, P. J. *J. Org. Chem*. **2010**, *75*(19), 6532.
25. Kitamura, M.; Tashiro, N.; Sakata, R.; Okauchi, T. *Synlett* **2010**, *16*, 2503.
26. de Lucas, N. C.; Netto-Ferreira, J. C.; Andraos, J.; Scaiano, J. C. *J. Org. Chem*. **2001**, *66*(15), 5016.
27. Tomioka, H.; Hirai, K.; Tabayashi, K.; Murata, S.; Izawa, Y.; Inagaki, S.; Okajima, T. *J. Am. Chem. Soc*. **1990**, *112*(21), 7692.
28. Harned, A. M.; Sherrill, W. M.; Flynn, D. L.; Hanson, P. R. *Tetrahedron* **2005**, *61*(51), 12093.
29. Lim, H. J.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett*. **2010**, *12*(9), 2162.
30. Peng, H.; Cheng, Y.; Ni, N.; Li, M.; Choudhary, G.; Chou, H. T.; Lu, C.-D.; Tai, P. C.; Wang, B. *ChemMedChem* **2009**, *4*(9), 1457.
31. Volovenko, Y.; Volovnenko, T.; Popov, K. *J. Heterocyclic Chem*. **2007**, *44*(6), 1413.
32. Balli, H.; Loew, R.; Mueller, V.; Rempfler, H.; Sezen-Gezgin, A. *Helv. Chim. Acta* **1978**, *61*(1), 97.
33. Harriman, B. R.; Shelton, R. S.; Van Campen, M. G.; Warren, M. R. *J. Am. Chem. Soc*. **1945,** *67*, 1481.
34. Balli, H.; Mueller, V.; Sezen-Gezgin, A. *Helv. Chim. Acta* **1978**, *61*(1), 104.

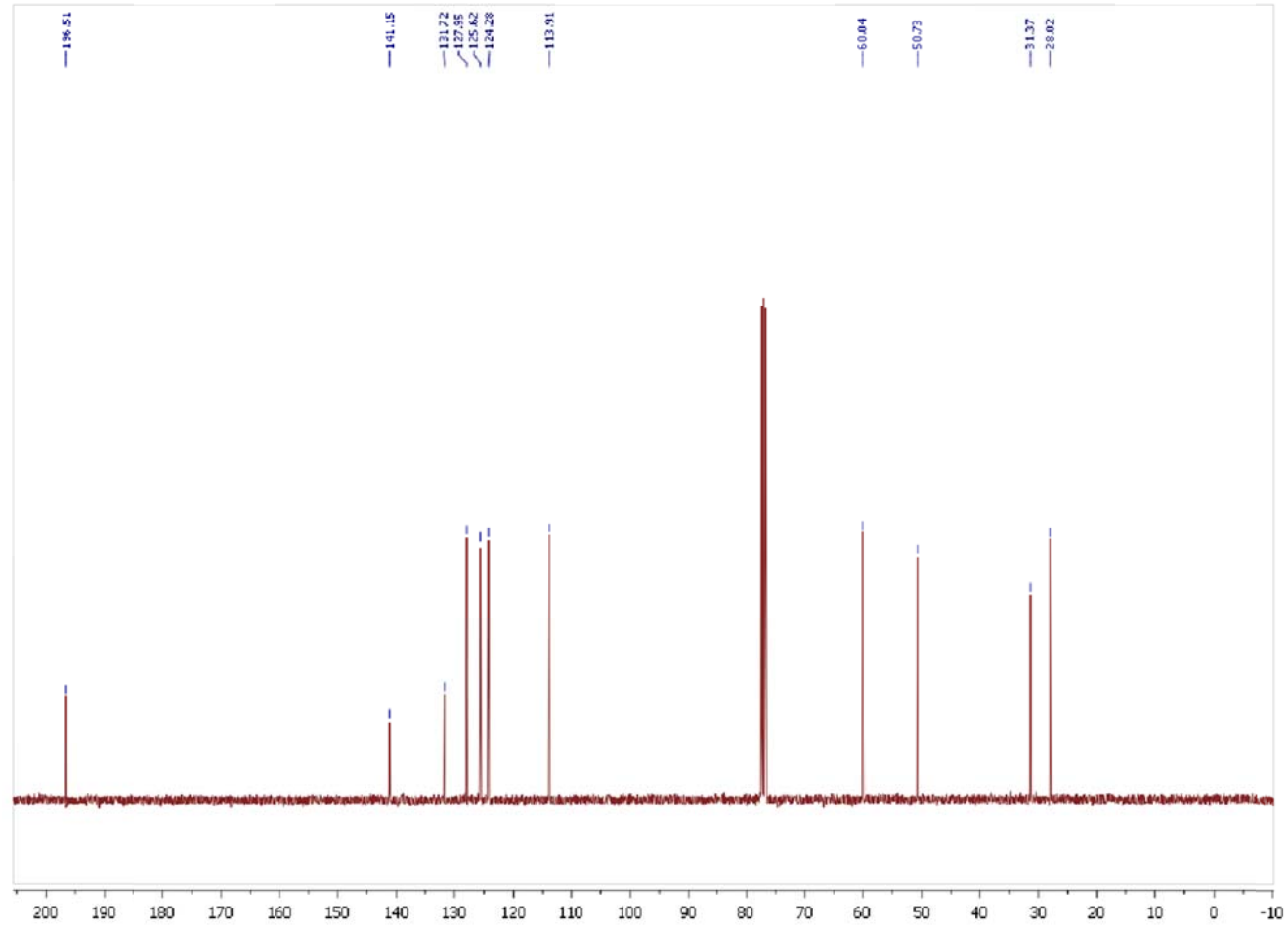
35. Nikolaev, V. A.; Popik, V. V. *Zhurnal Organicheskoi Khimii* **1989**, *25*(1), 222.
36. Deadman, B. J.; O'Mahony, R. M.; Lynch, D.; Crowley, D. C.; Collins, S. G.; Maguire, A. R. *Org. Biomol. Chem*. **2016**, *14*(13), 3423.
37. Marcoux, D.; Goudreau, S. R.; Charette, A. B. *J. Org. Chem*. **2009**, *74*(23), 8939.
38. Ramachary, D. B.; Narayana, V. V.; Ramakumar, K. *Tet. Lett*. **2008**, *49*(17), 2704.
39. Kang, B.-R.; Wang, J.; Li, H.; Li, Y.; Mei, Q.-B.; Zhang, S.-Q. *Med. Chem. Res*., **2014**, *23*(3), 1340.
40. Xia, G.; Benmohamed, R.; Kim, J.; Arvanites, A. C.; Morimoto, R. I.; Ferrante, R. J.; Kirsch, D. R.; Silverman, R. B. *J. Med. Chem*., **2011**, *54* (7), 2409.
41. Chuprakov, S.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*(11), 3714.
42. Brehm, W. J.; Levenson, T. *J. Am. Chem. Soc*. **1954,** *76*, 5389.
43. Pasceri, R.; Bartrum, H. E.; Hayes, C. J.; Moody, C. J. *Chem. Comm*. *(Cambridge, United Kingdom)*, **2012**, *48*(99), 12077.
44. Aitken, R. A.; Armstrong, J. M.; Drysdale, M. J.; Ross, F. C.; Ryan, B. M. *J. Chem. Soc., Perkin Trans. 1* **1999,** *5*, 593.
45. Peng, H.; Cheng, Y.; Ni, N.; Li, M.; Choudhary, G.; Chou, H. T.; Lu, C.-D.; Tai, P. C.; Wang, B. *ChemMedChem* **2009**, *4*(9), 1457.
46. Chan, C.-K.; Wang, H.-S.; Hsu, R.-T.; Chang, M.-Y. *Synthesis* **2017**, *49*(11), 2423.
47. Chang, M.-Y.; Chen, H.-Y.; Chen, Y.-H. *J. Org. Chem*. **2017**, *82*(23), 12631.
48. Shrestha, R.; Lee, G. J.; Lee, Y. R. *RSC Adv*. **2016**, *6*(68), 63782.
49. Ukrainets, V.; Gorokhova, O. V.; Sidorenko, L. V.; Bereznyakova, N. L. *Chem. Heterocyclic Comp*. **2006,** *42*(8), 1032.
50. Regitz, M.; Liedhegener, A. *Chem. Ber*. **1966**, *99*(10), 3128.
51. Sancon, J.; Sweeney, J. B. *Synlett* **2010,** *4*, 664.
52. Erhunmwunse, M. O.; Steel, P. G. *J. Org. Chem*. **2008**, *73*(21), 8675.
53. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst*. 42, 339-341.
54. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

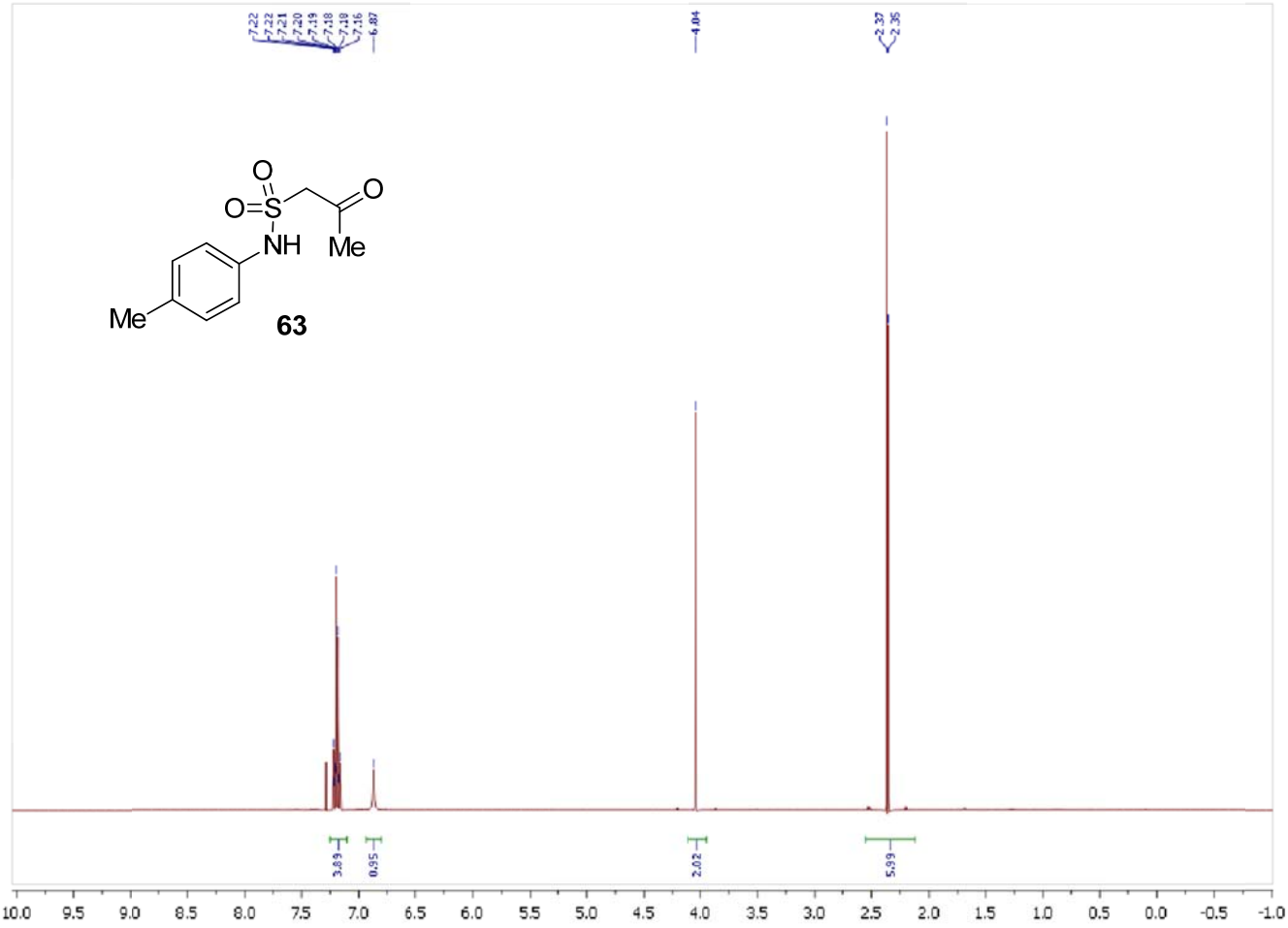
VIII. NMR Spectra

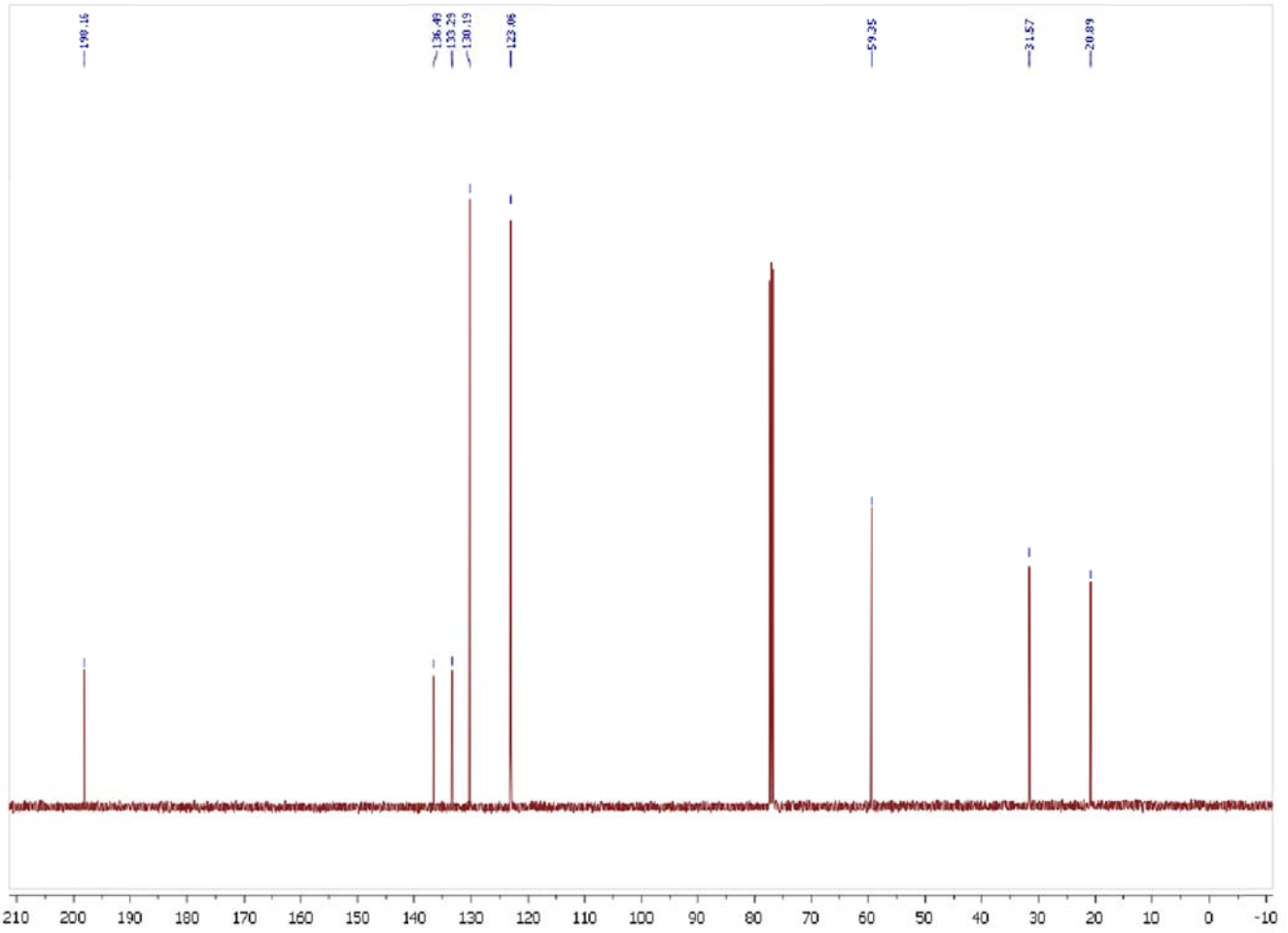


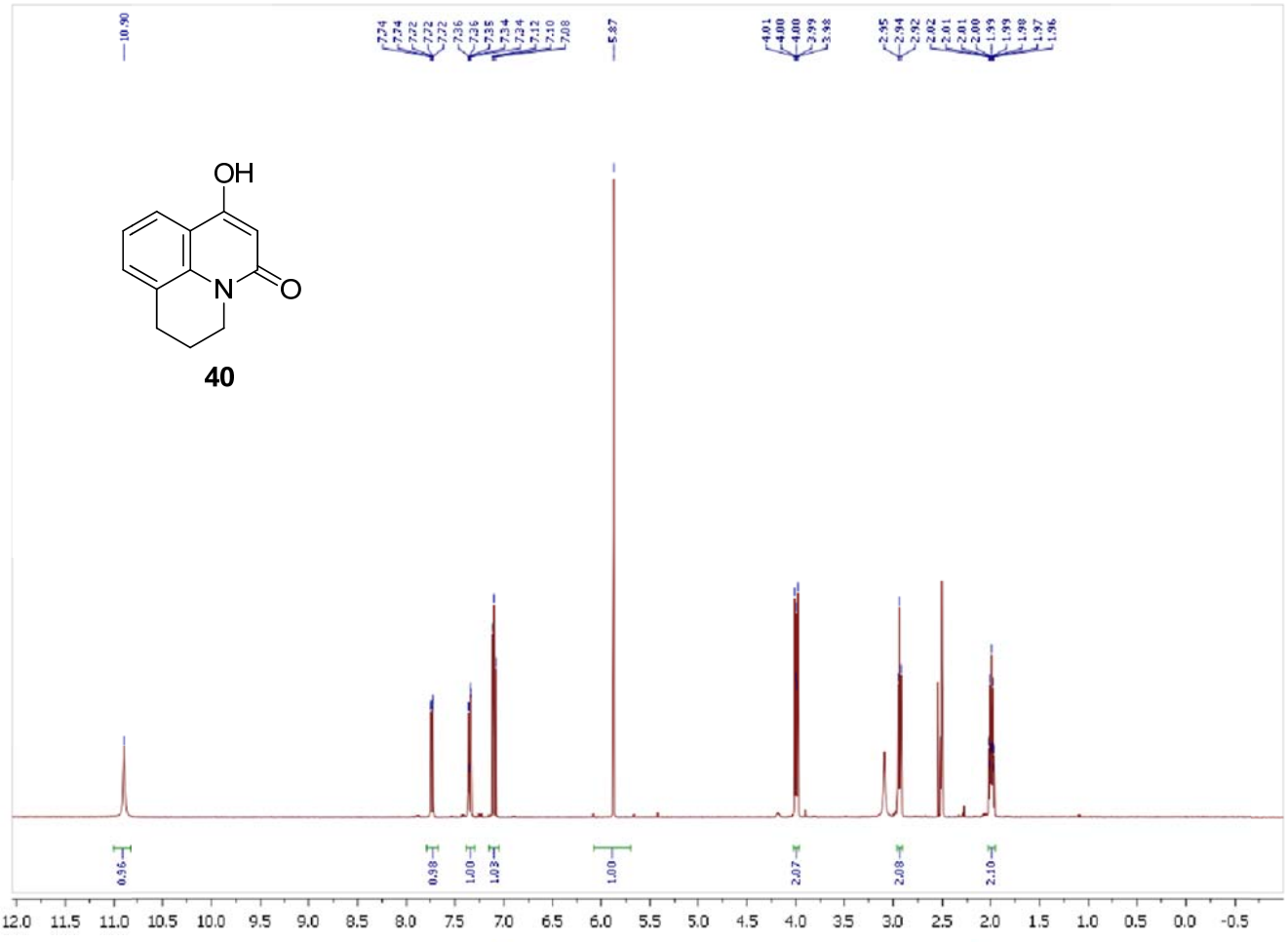



7.41
7.39
7.25
7.23
7.21
7.20
7.09
7.09
7.07
7.07
7.06
7.05
4.09
4.07
4.06
4.06
3.21
3.19
3.17
2.48
O
O=S
N
O
Me
36
0.95
1.98
1.00
3.99
2.06
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

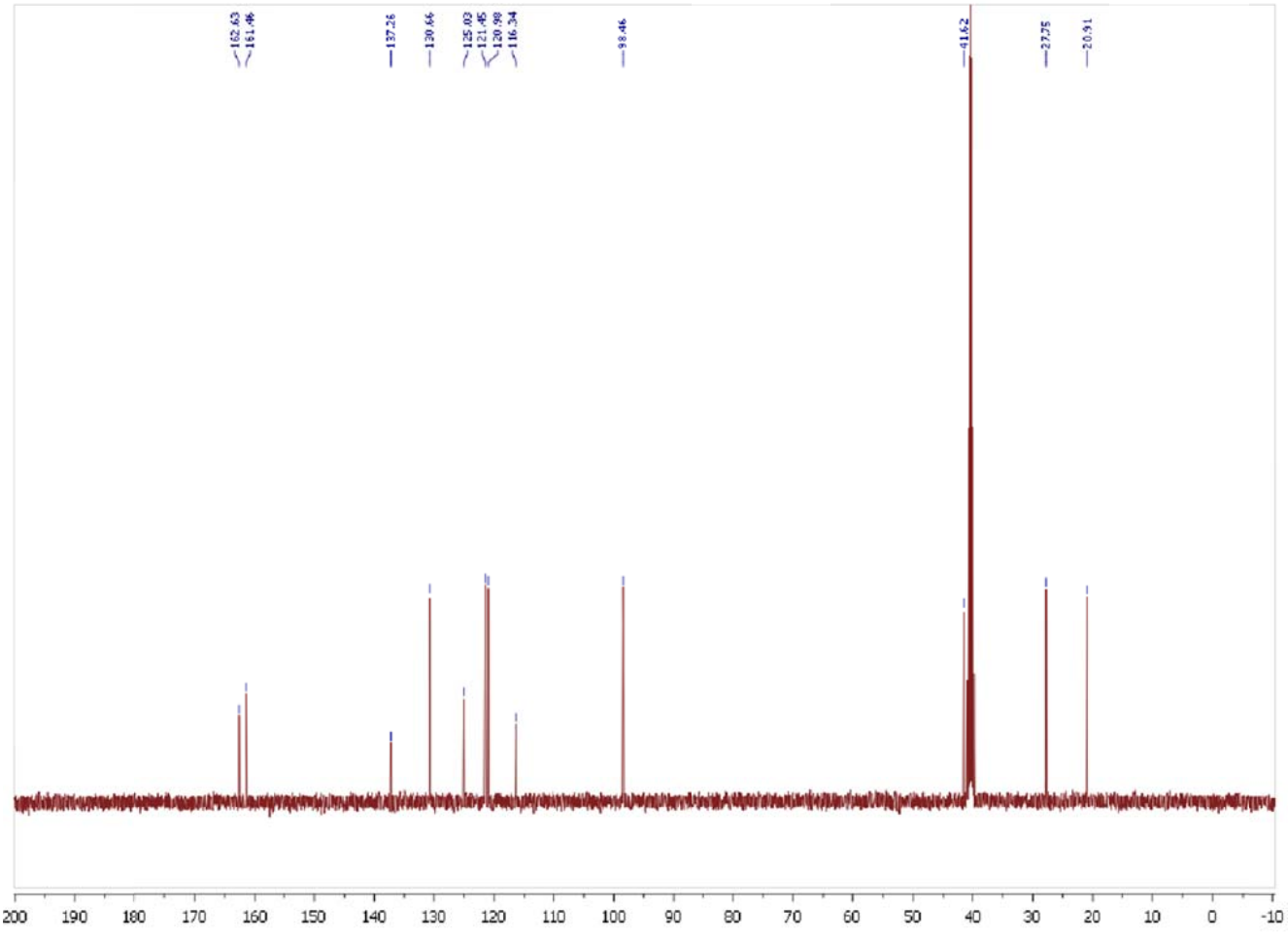

196.51
141.15
131.72
127.95
125.62
124.28
113.91
60.04
50.73
31.37
28.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

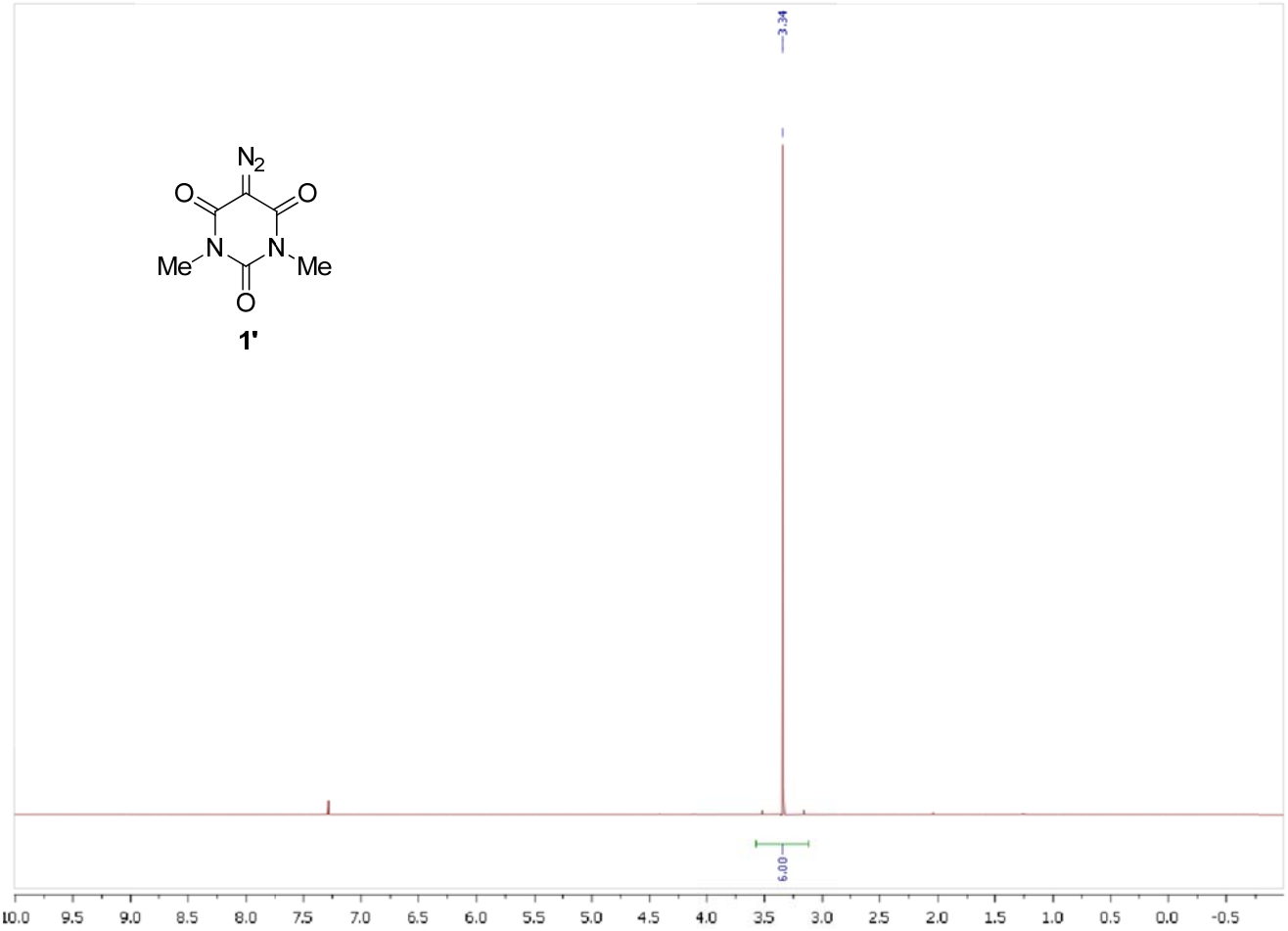

7.22
7.22
7.21
7.20
7.19
7.18
7.18
7.16
6.87
4.04
2.37
2.35
O
O=S
NH
O
Me
Me
63
3.89
0.95
2.02
5.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


190.16
136.49
133.25
130.19
123.06
59.35
31.57
20.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



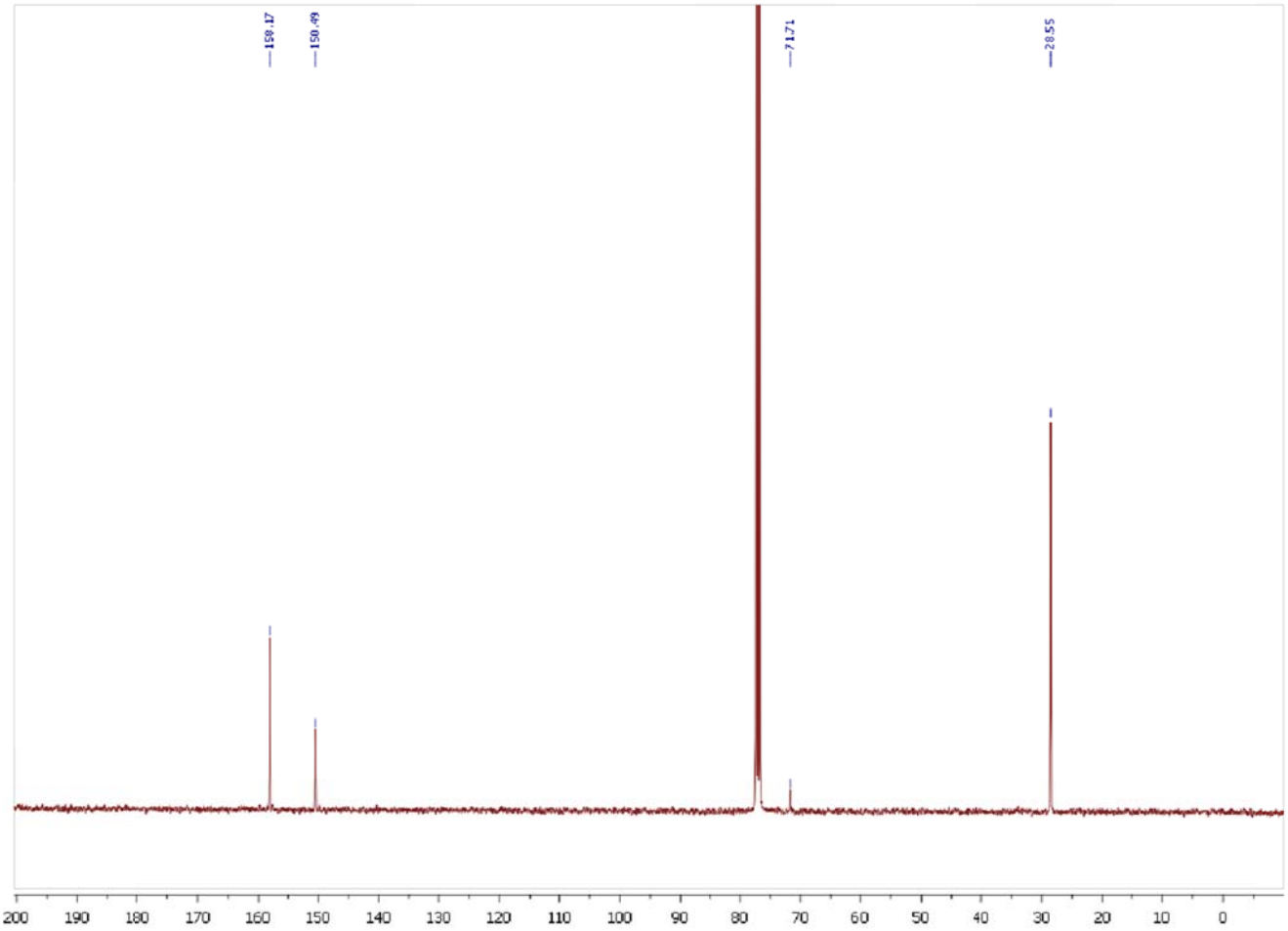
40

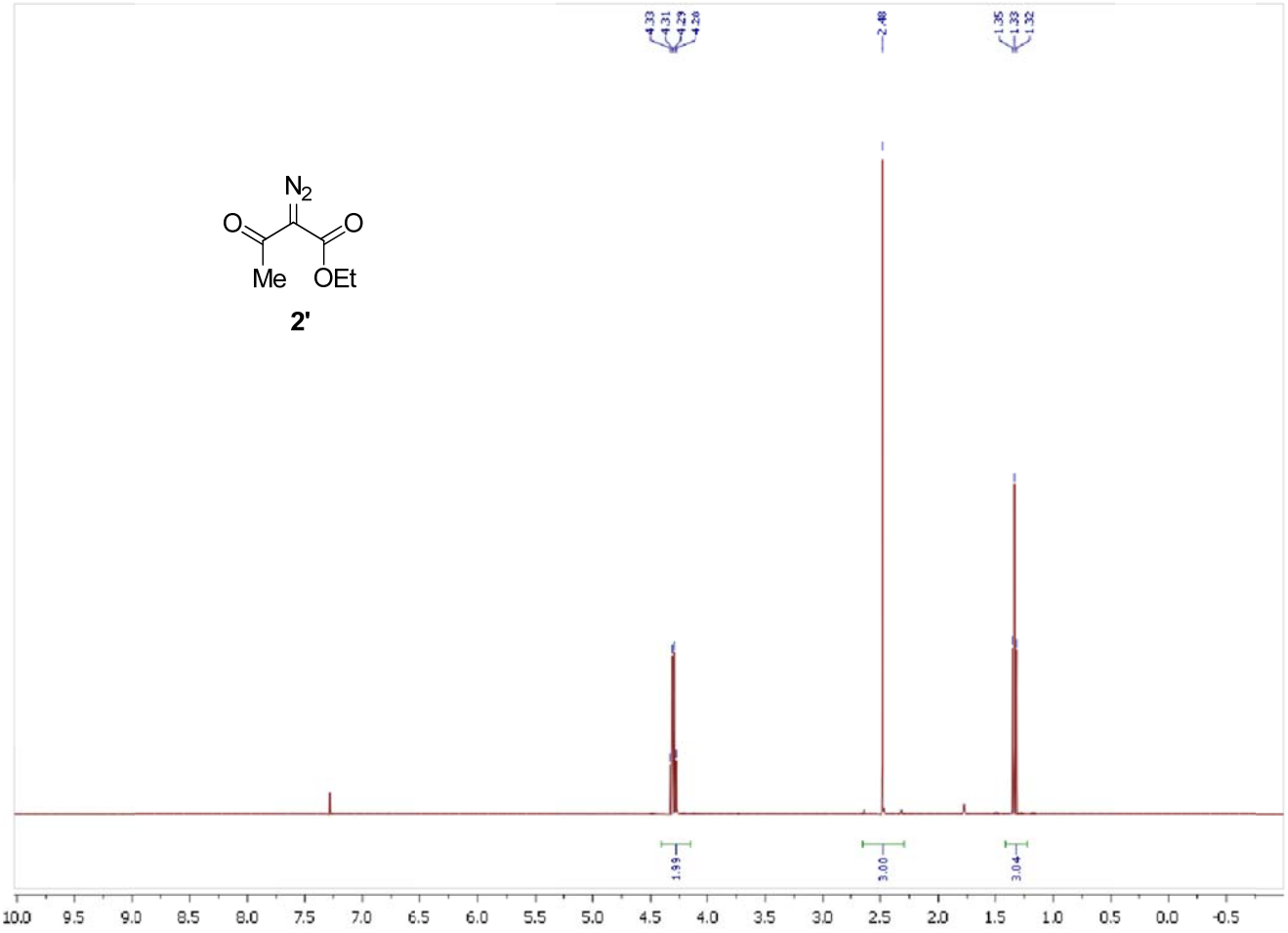



3.34
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

N2
O
O
N
N
Me
Me
O

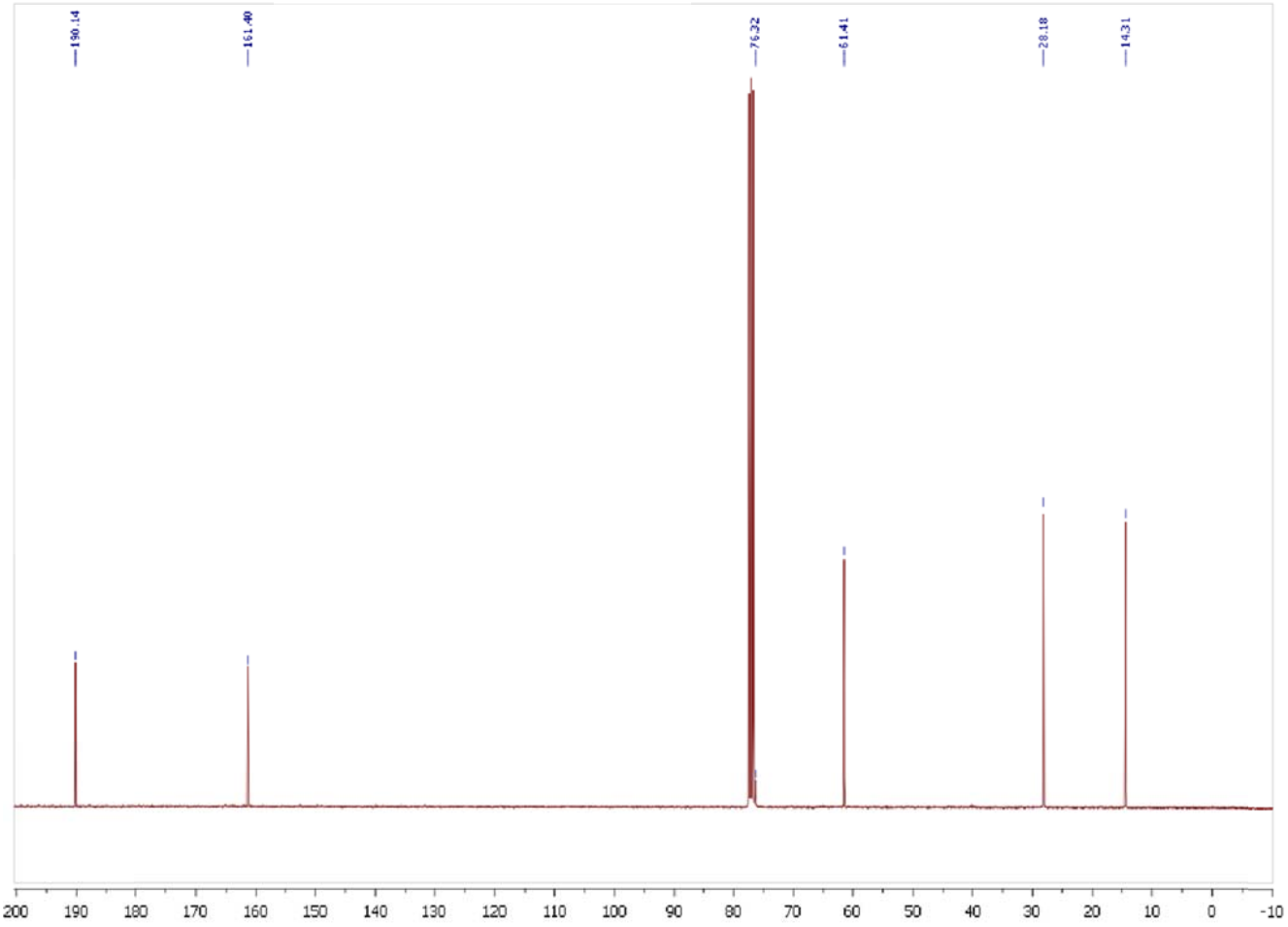
1'

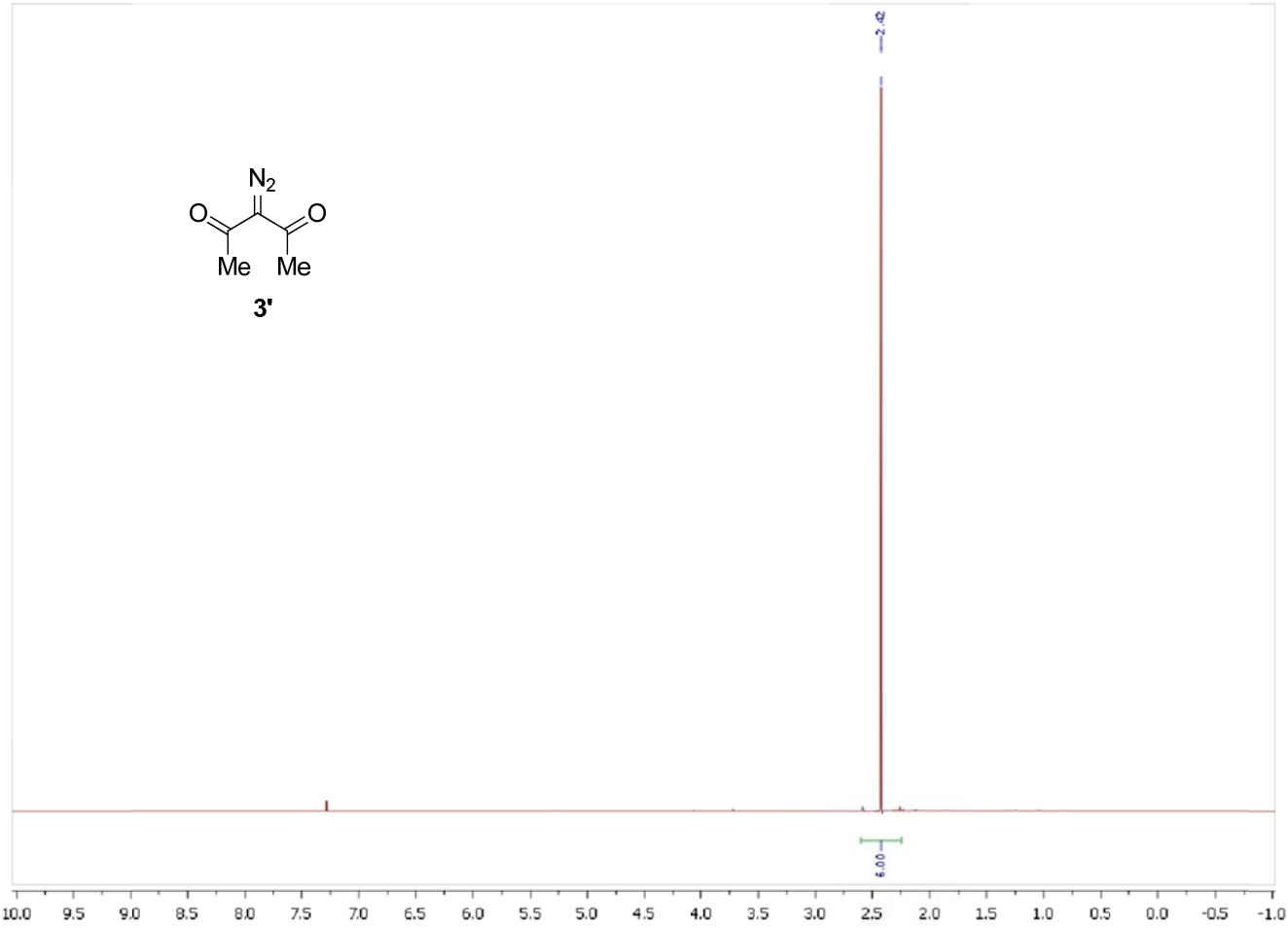

158.17
150.49
71.71
28.55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


4.33
4.31
4.29
4.26
2.48
1.35
1.33
1.32
1.99
3.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

N2
O
O
Me
OEt

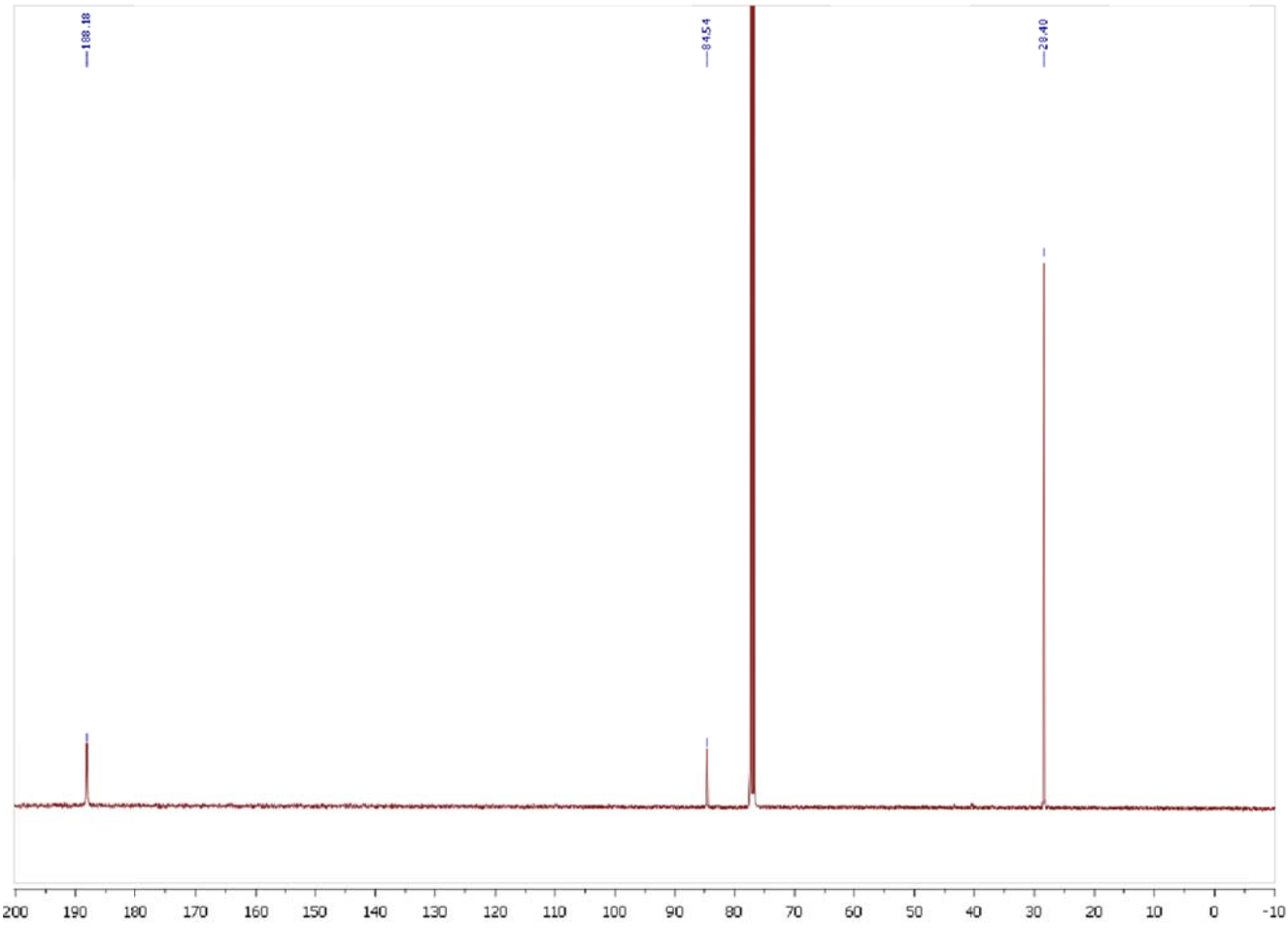
2'

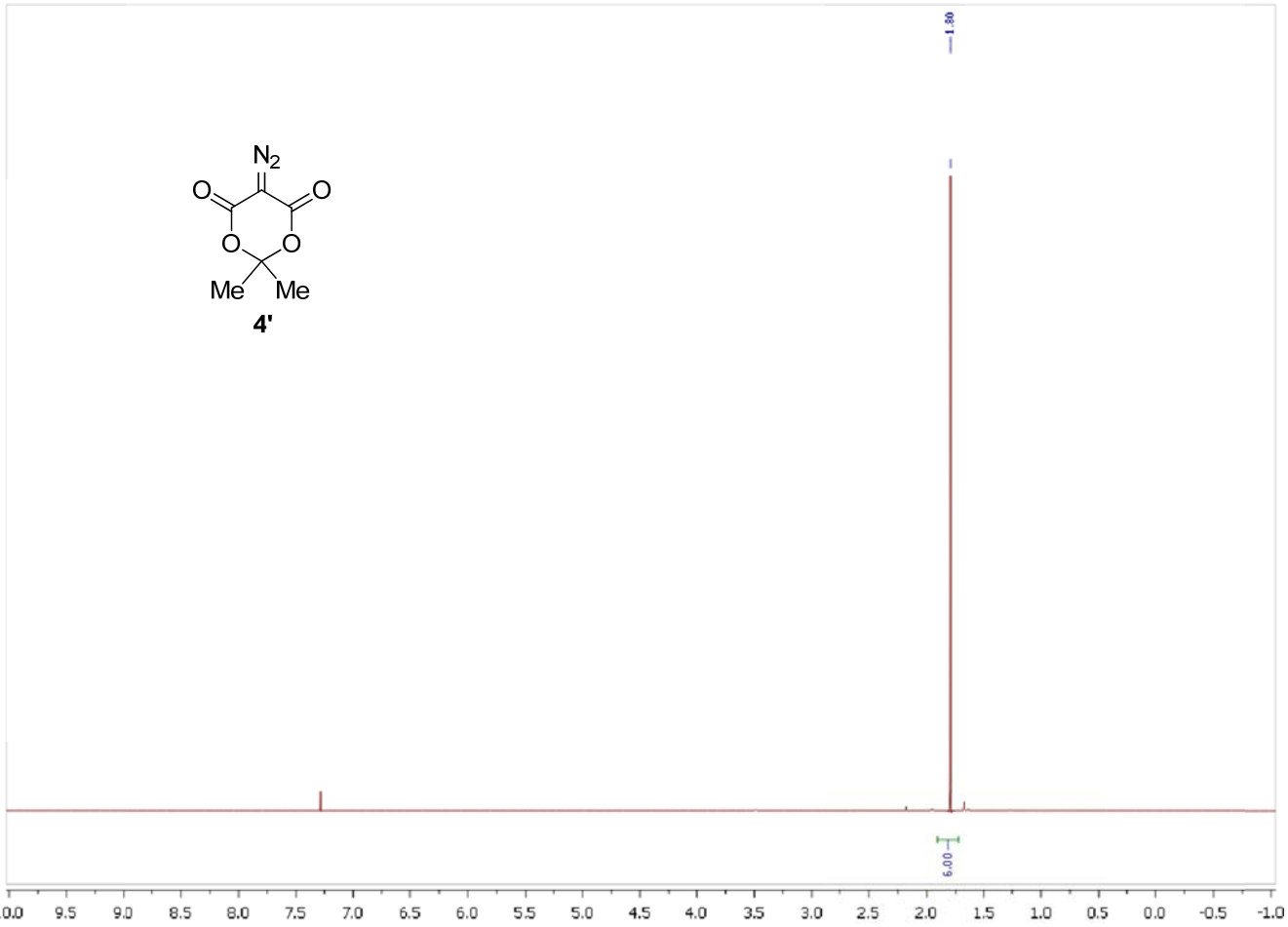

190.14
161.40
76.32
61.41
28.18
14.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

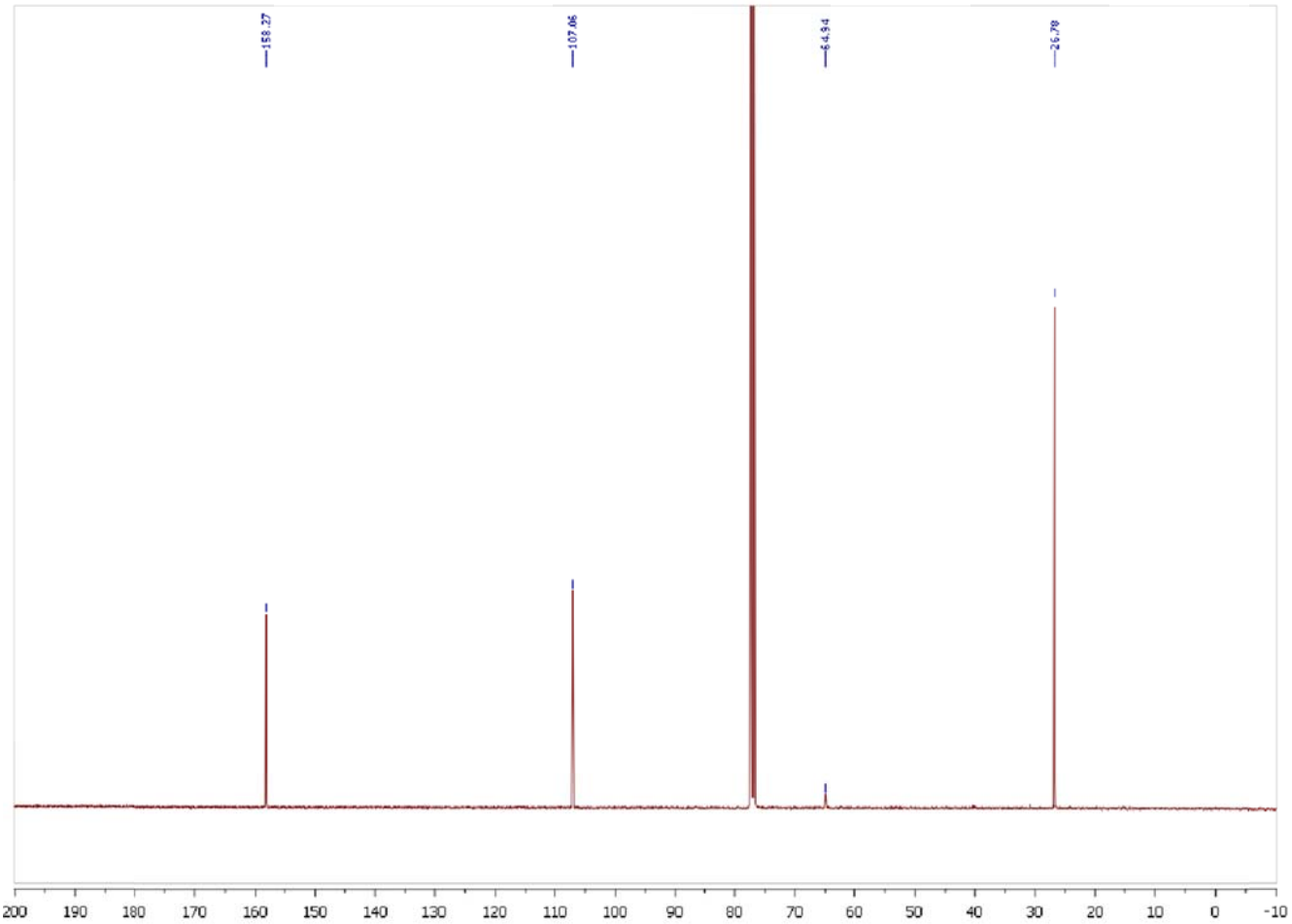

2.42
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

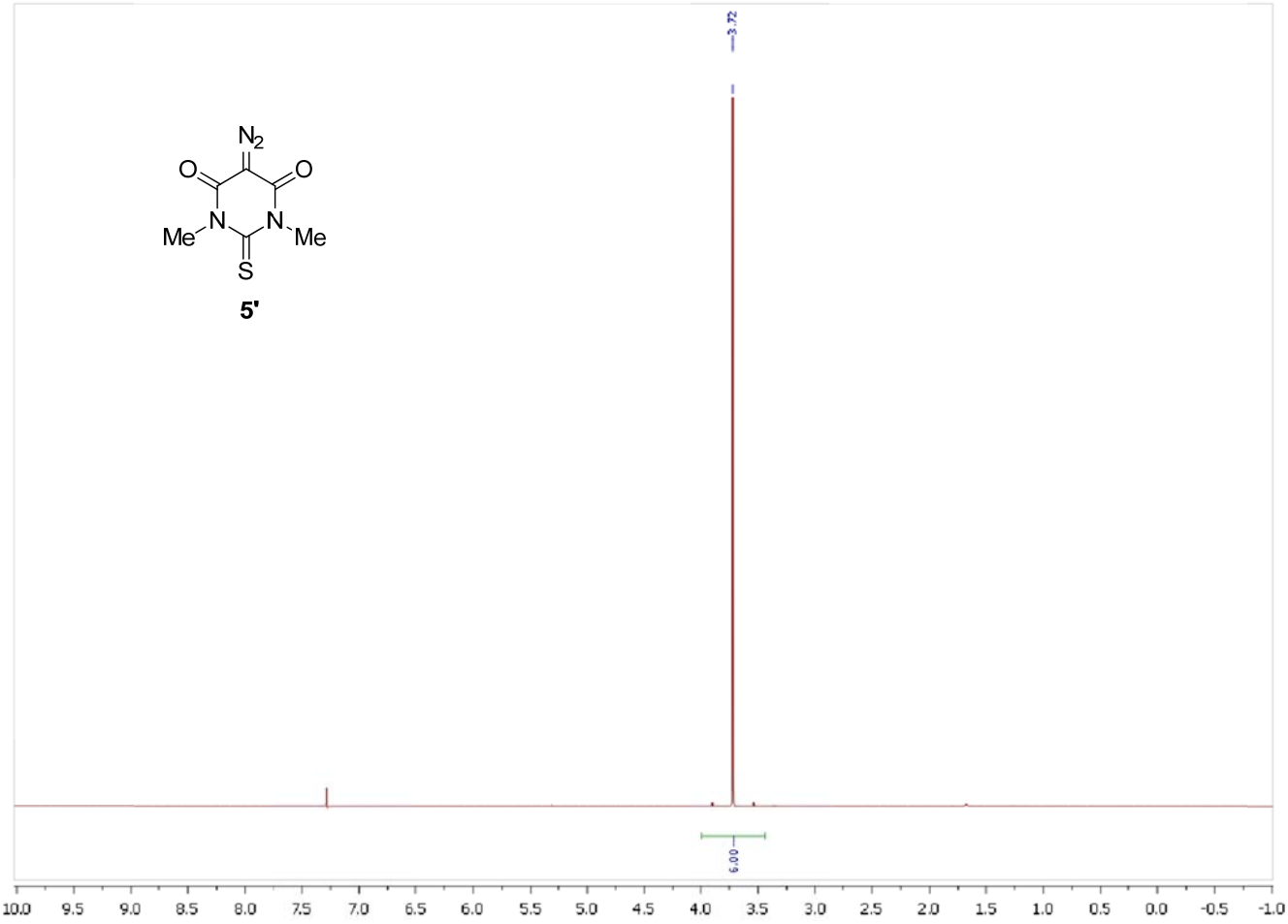
N_2
O O
Me Me

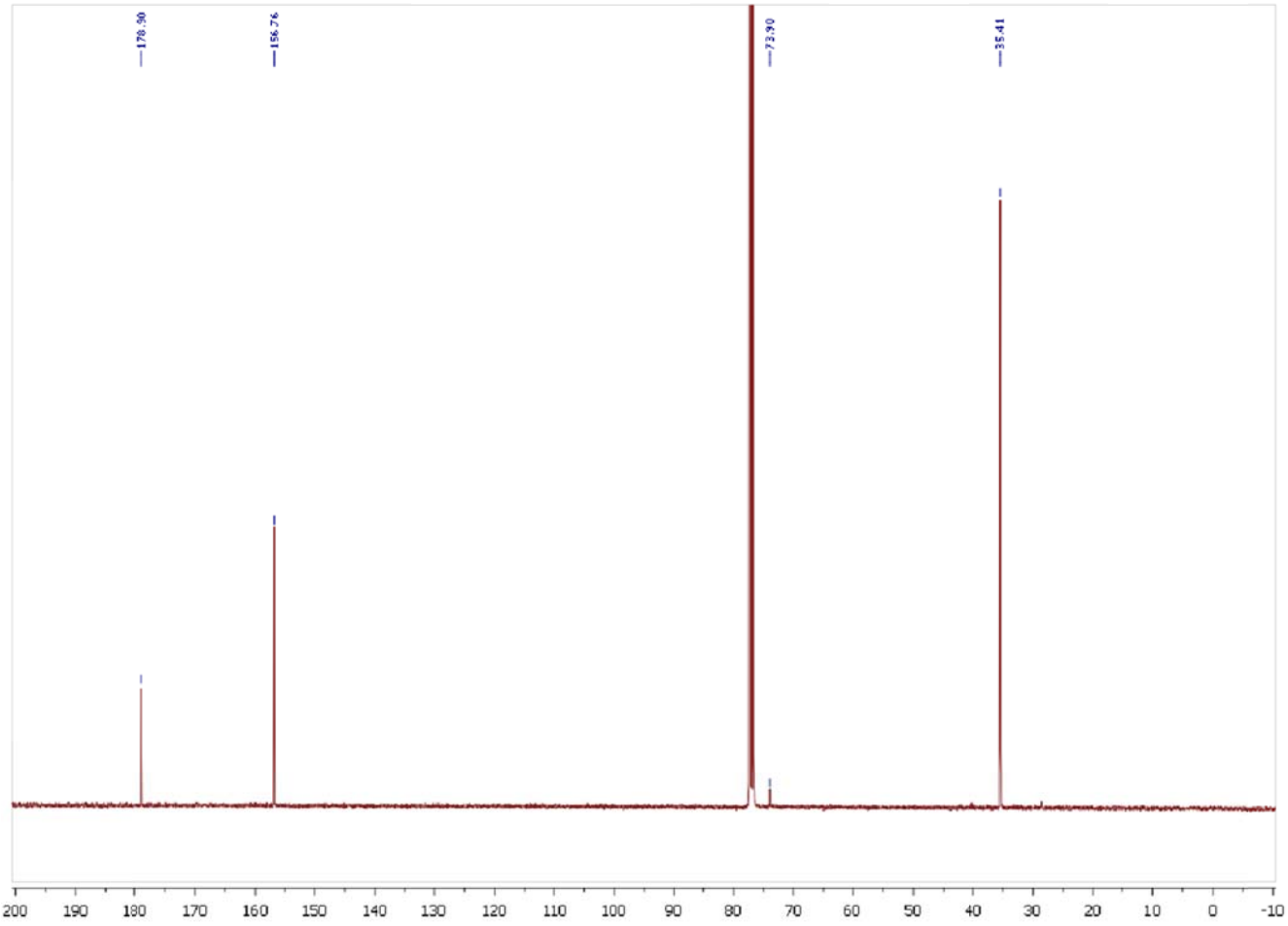
3'


188.18
84.54
29.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

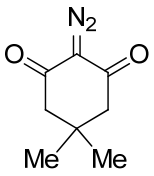

N2
O
O
O
O
Me
Me
4'
1.80
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


158.27
107.06
64.94
26.78
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


3.72
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

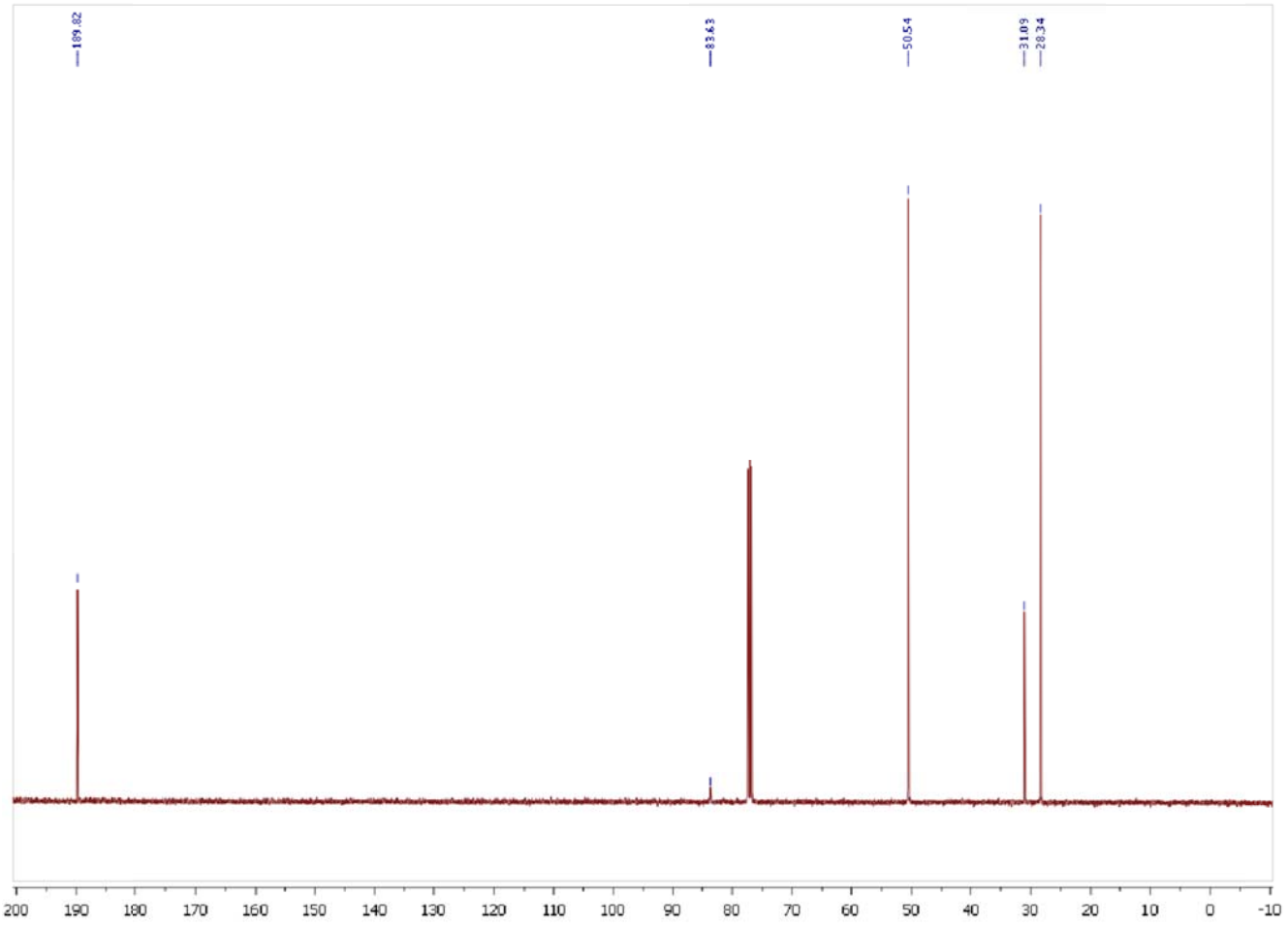

178.90
156.76
73.90
35.41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

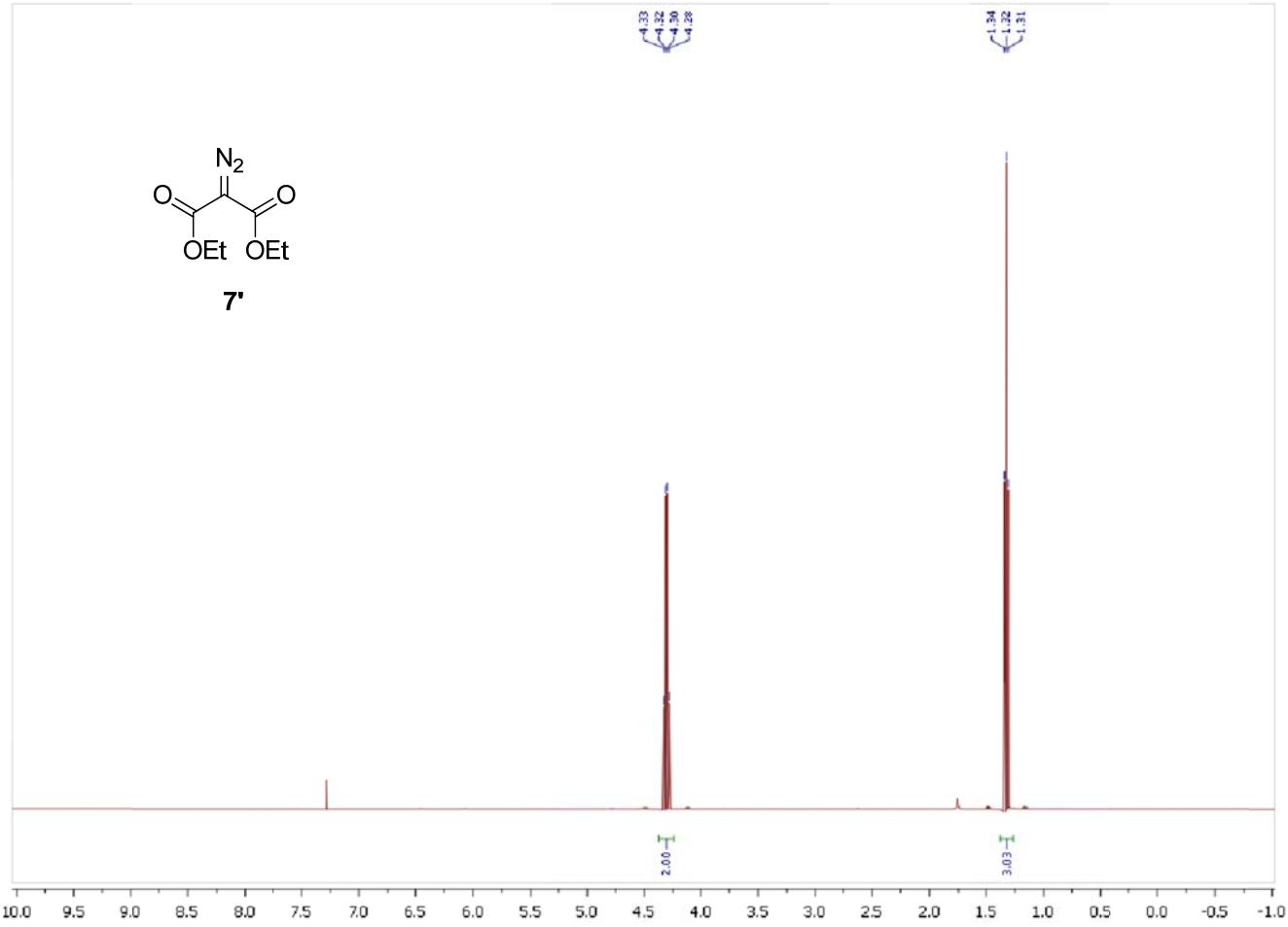
5'


N2
O
O
Me
Me

6'

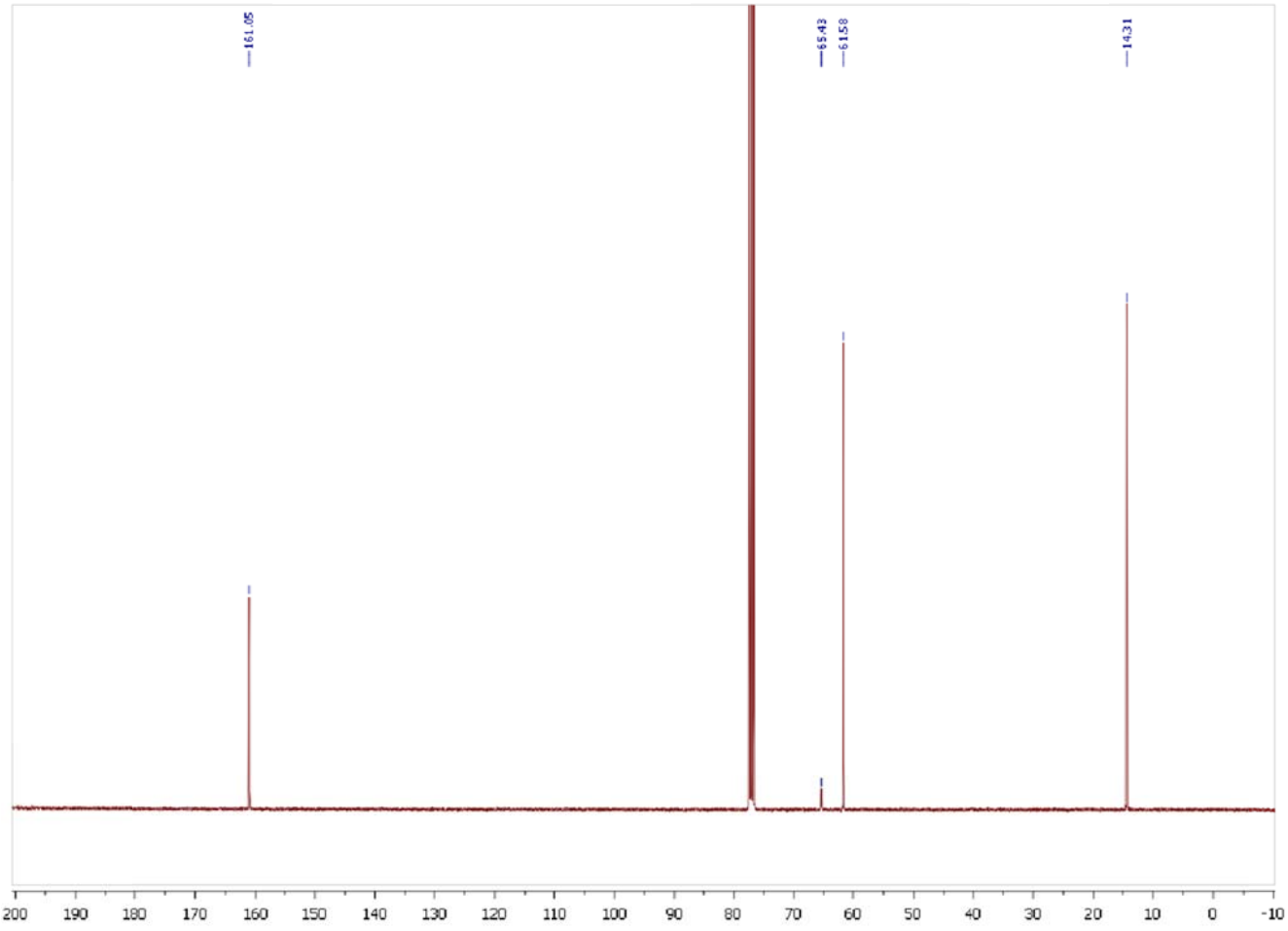
2.44
1.12
4.00
6.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

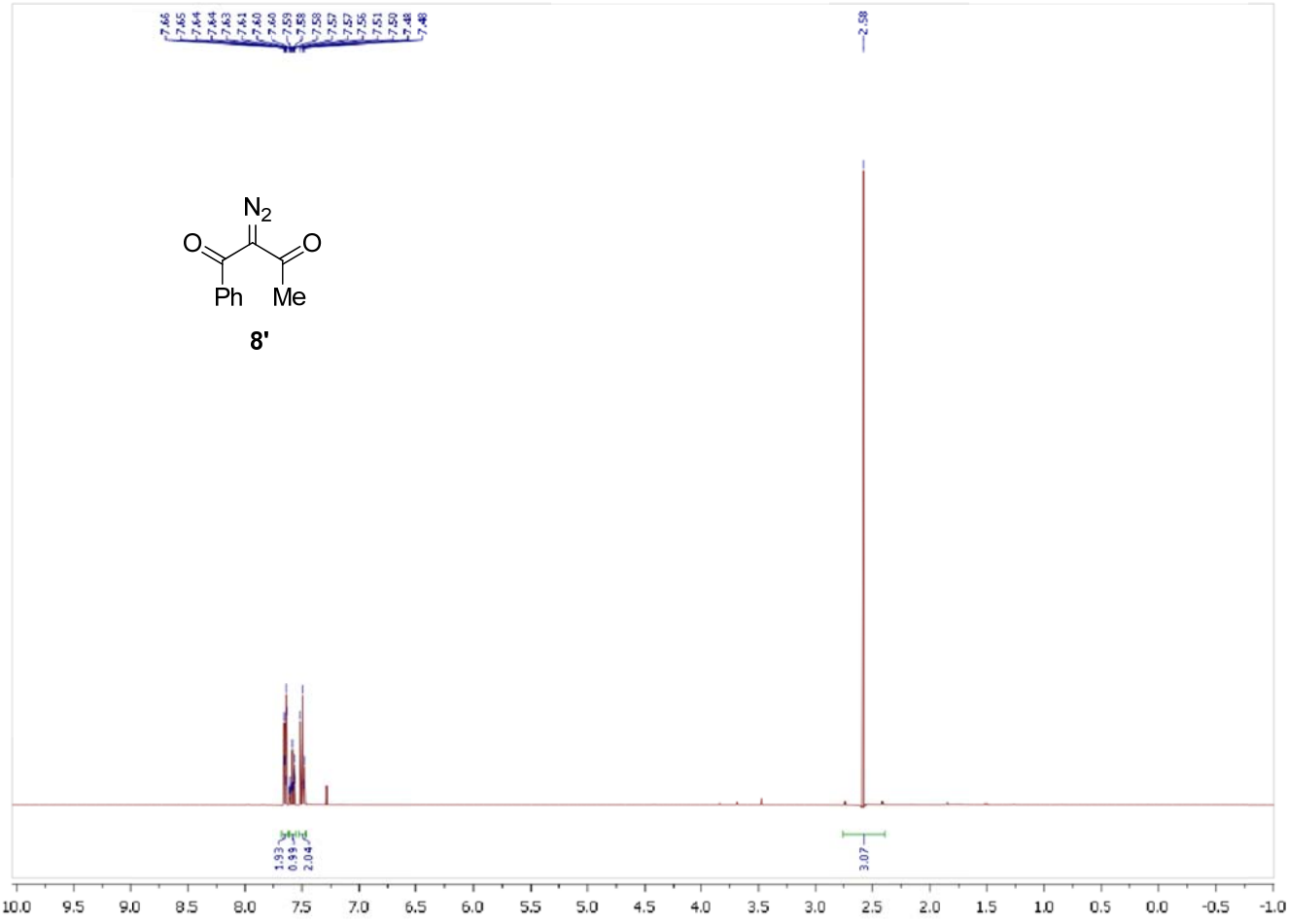

189.82
83.63
50.54
31.09
28.34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


4.33
4.32
4.30
4.28
1.34
1.32
1.31
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

N2
O
O
OEt
OEt

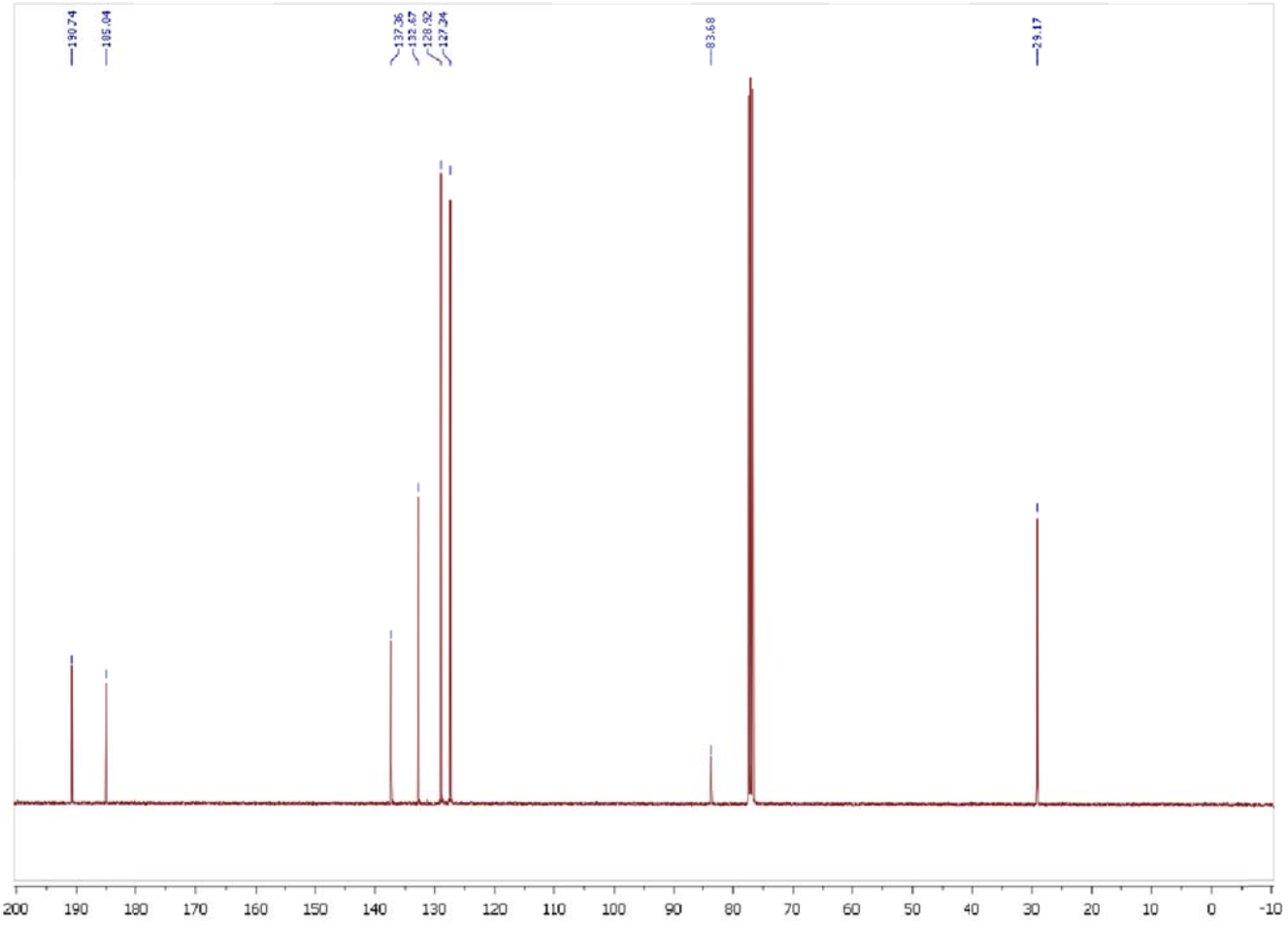
7'

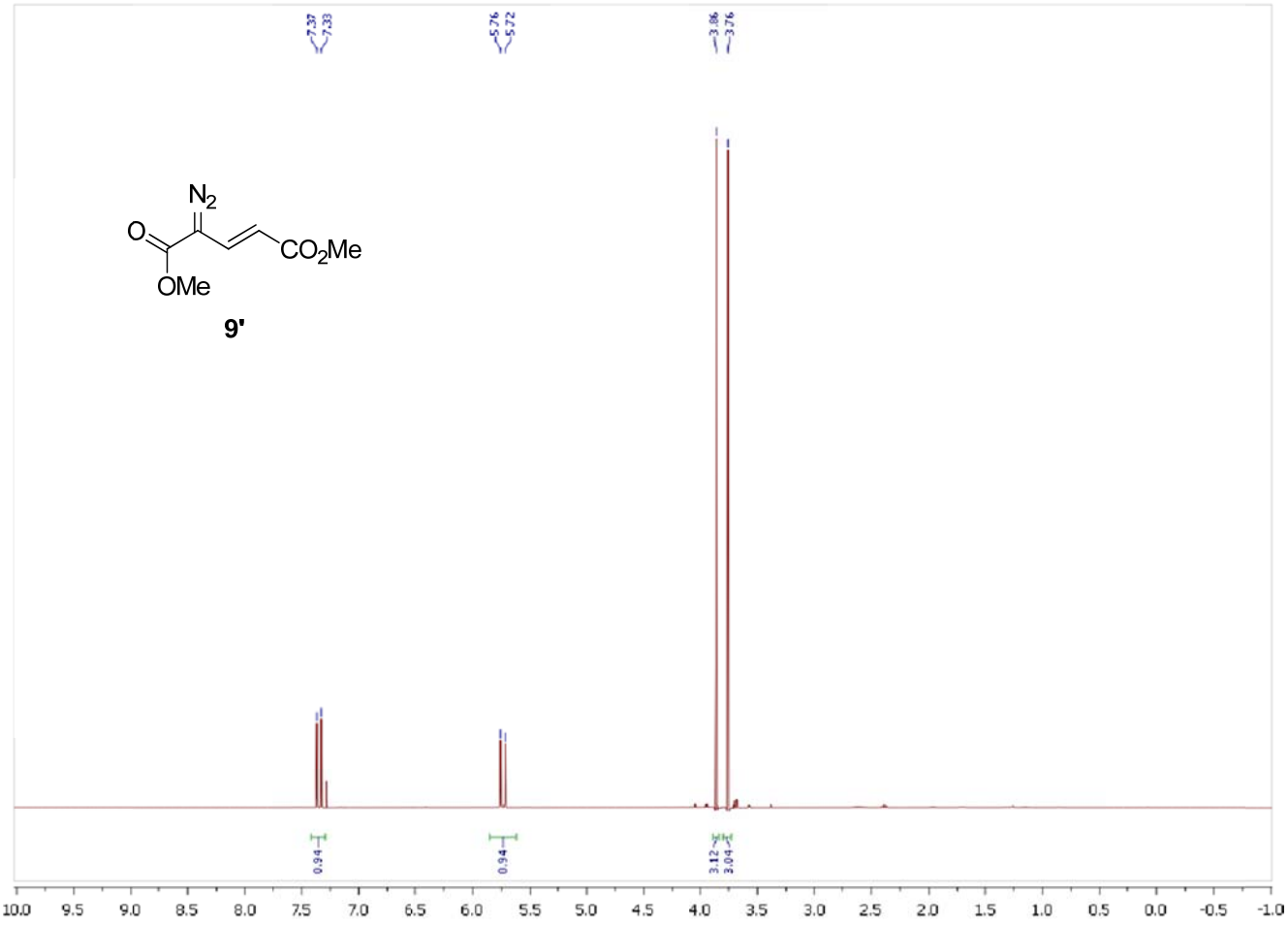

161.05
65.43
61.58
14.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.66
7.65
7.64
7.64
7.63
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.51
7.50
7.48
7.48
2.58
1.93
0.99
2.04
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

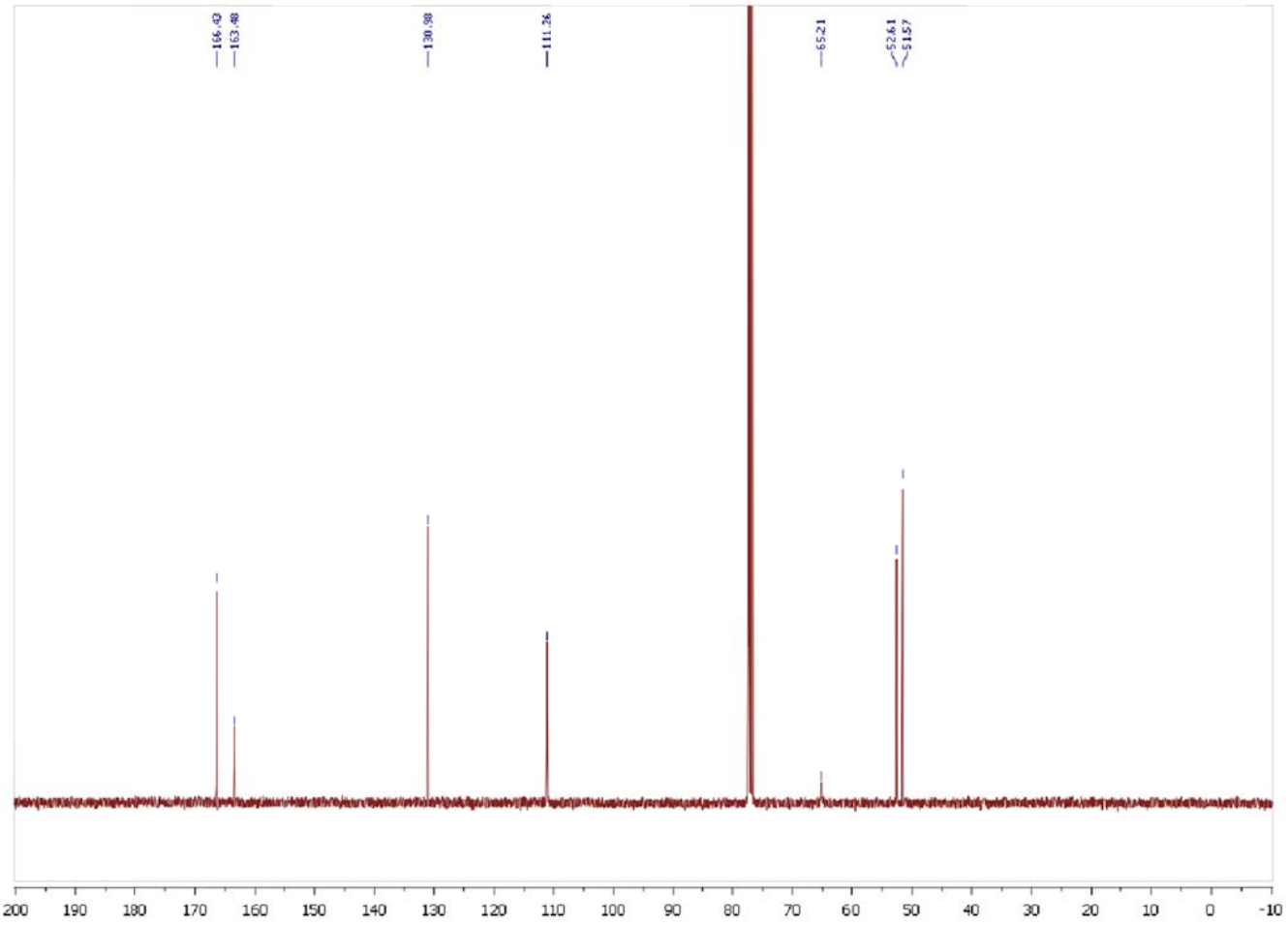
N2
O
O
Ph
Me

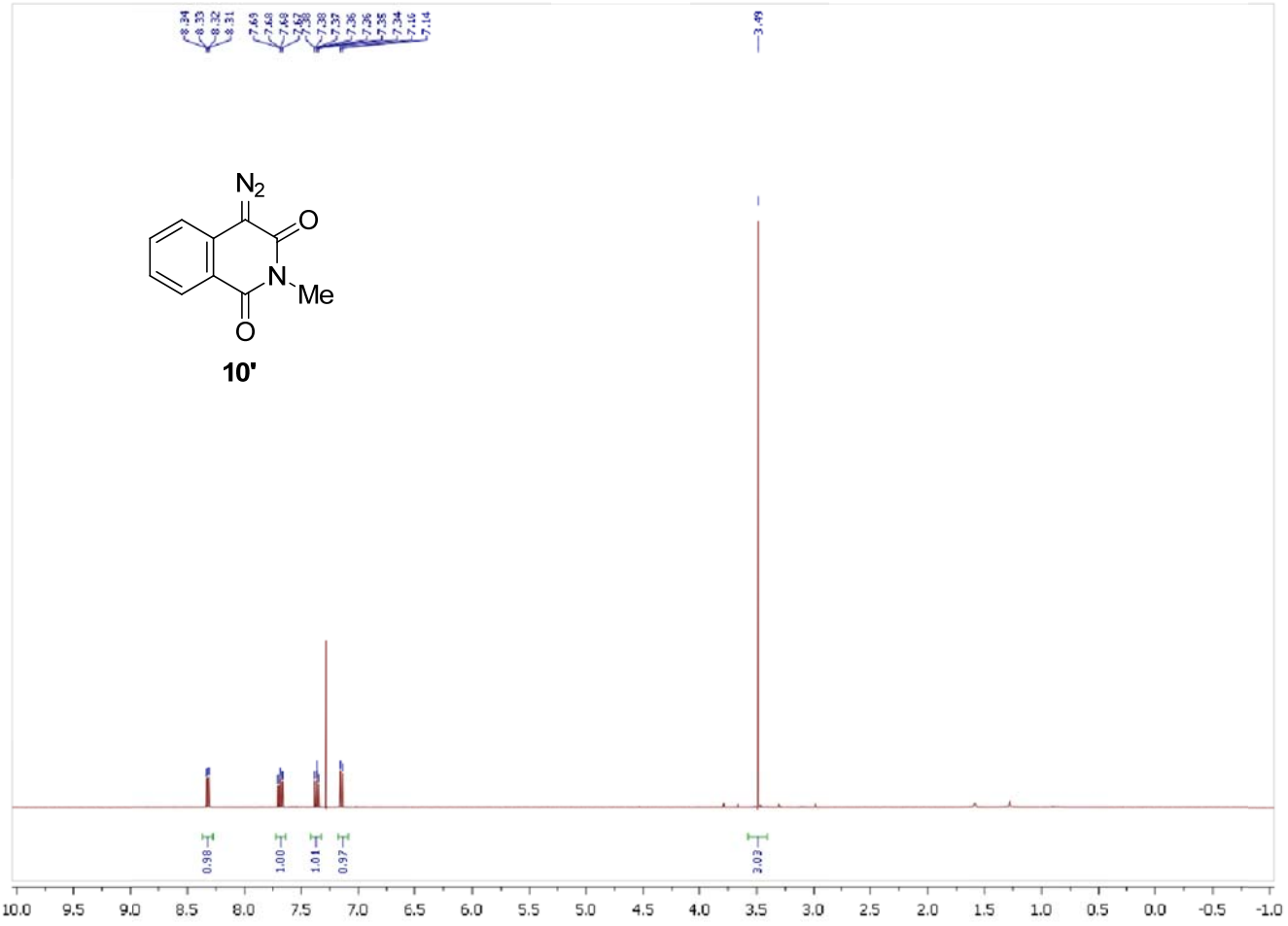
8'


190.74
185.04
137.36
132.67
128.92
127.34
83.68
29.17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.37
7.33
5.76
5.72
3.86
3.76
N2
O
CO2Me
OMe
0.94
0.94
3.12
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

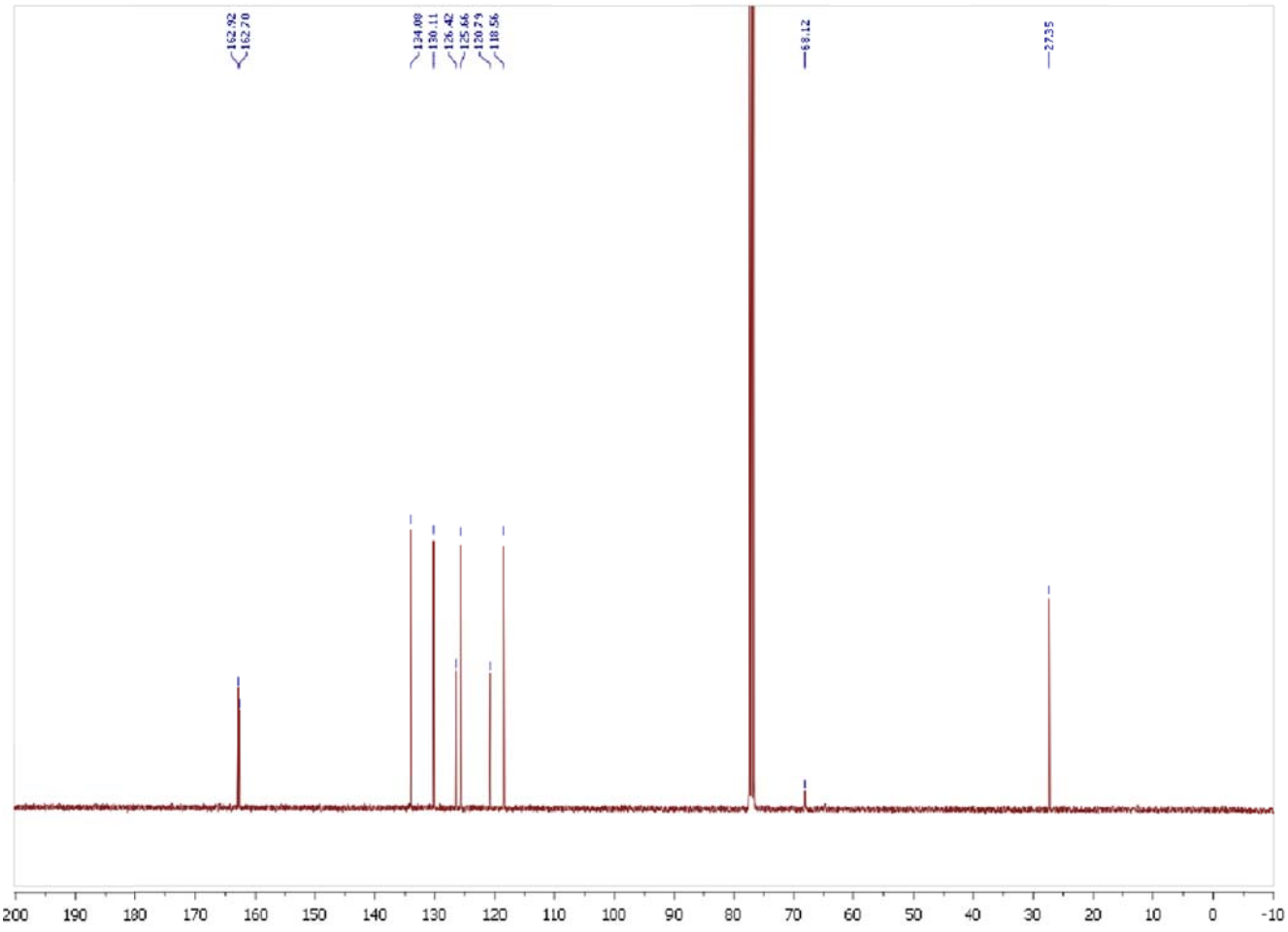
9'

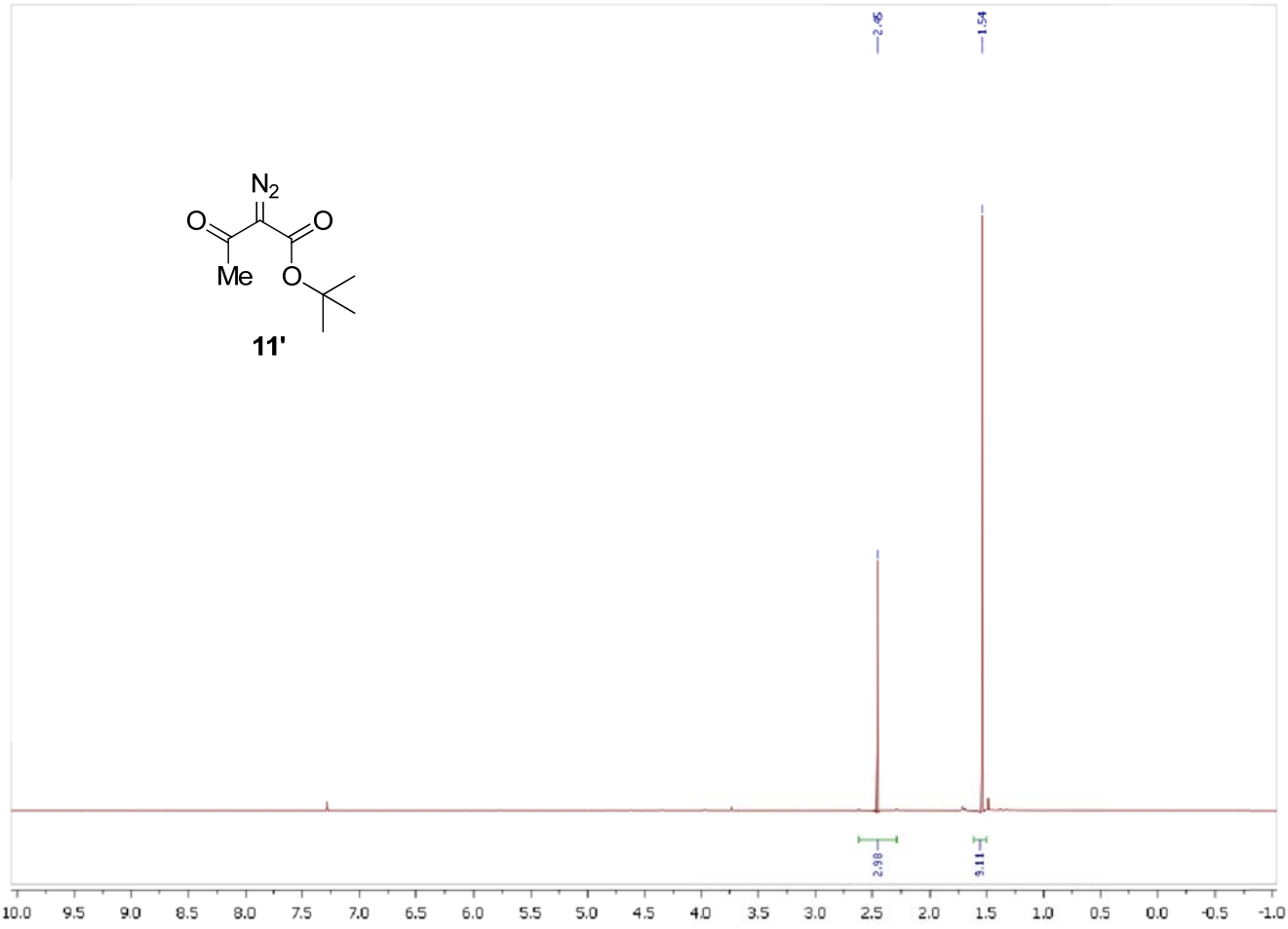

166.42
163.48
130.98
111.26
65.21
52.61
51.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

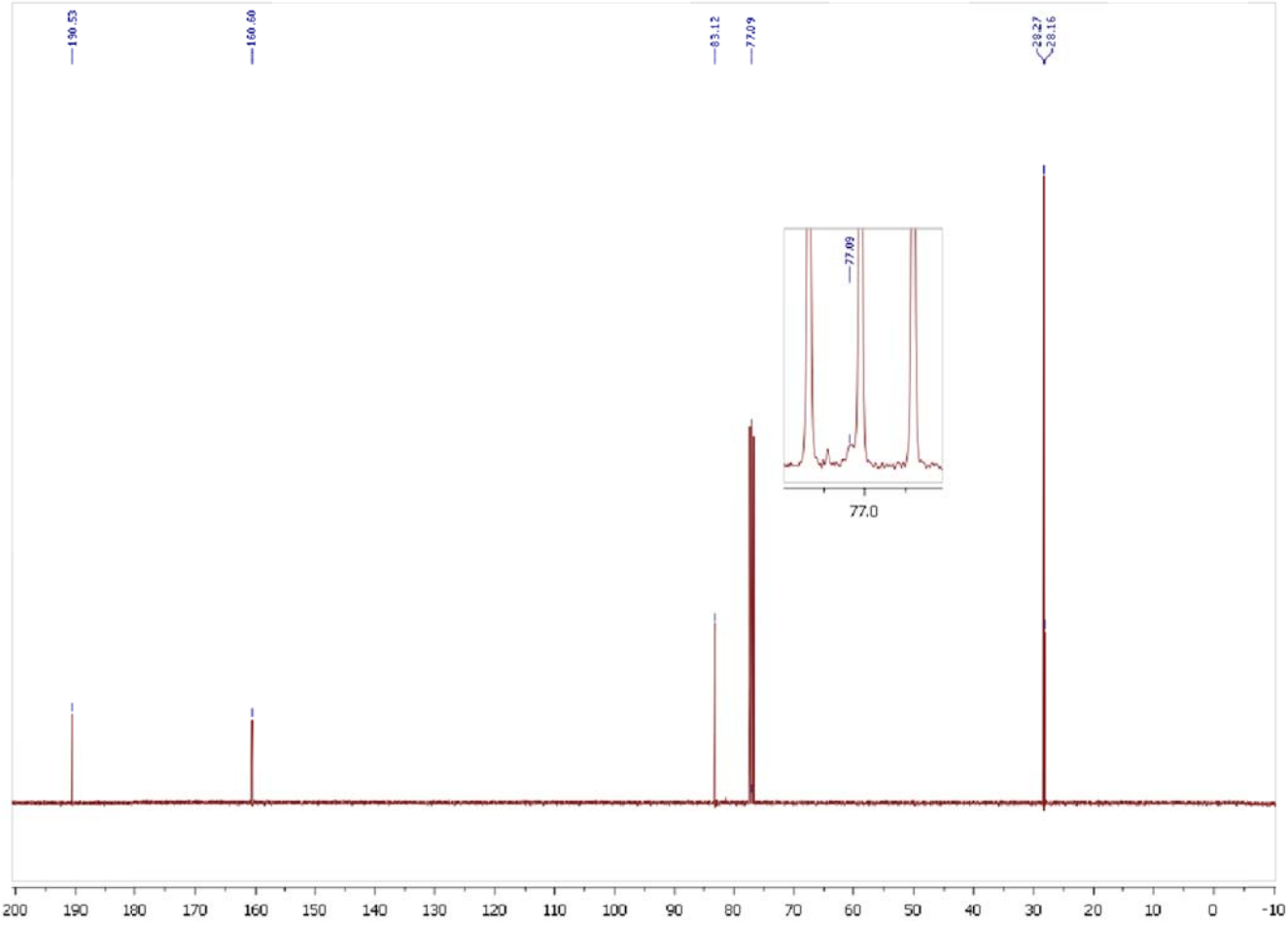

8.34
8.33
8.32
8.31
7.63
7.60
7.49
7.47
7.38
7.37
7.36
7.36
7.35
7.34
7.16
7.14
3.49
0.98
1.00
1.01
0.97
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

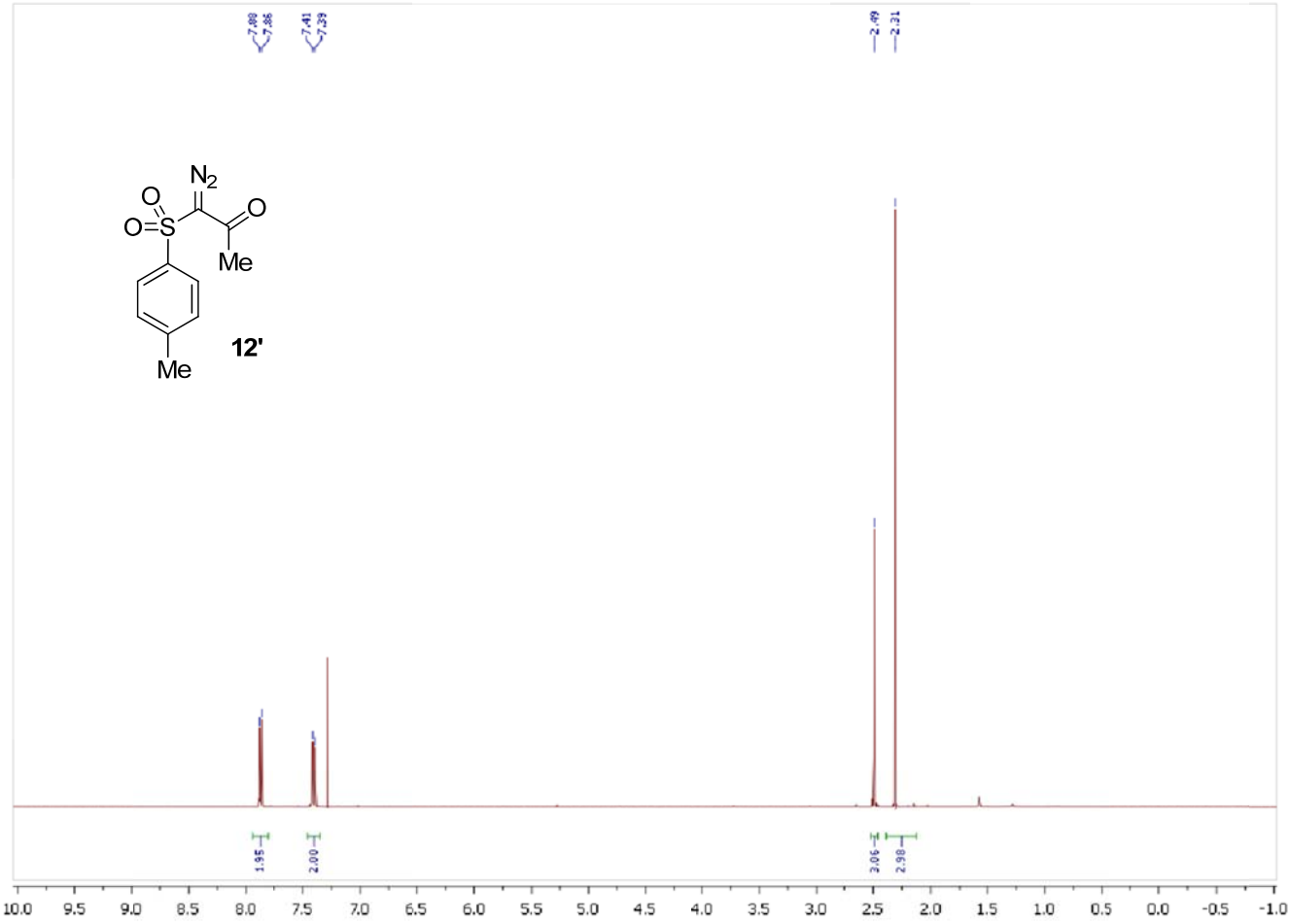
N2
O
N
Me
O

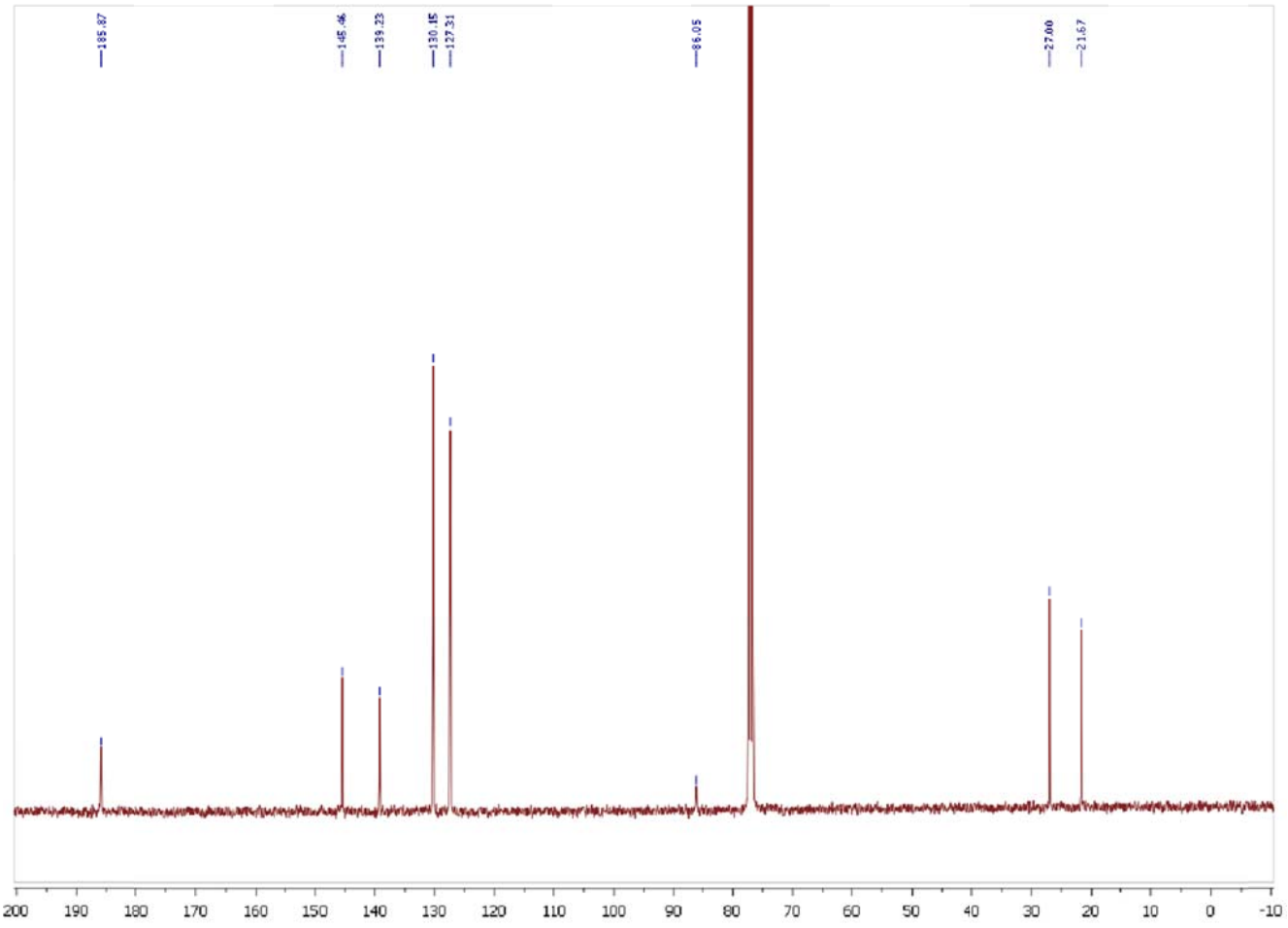
10'

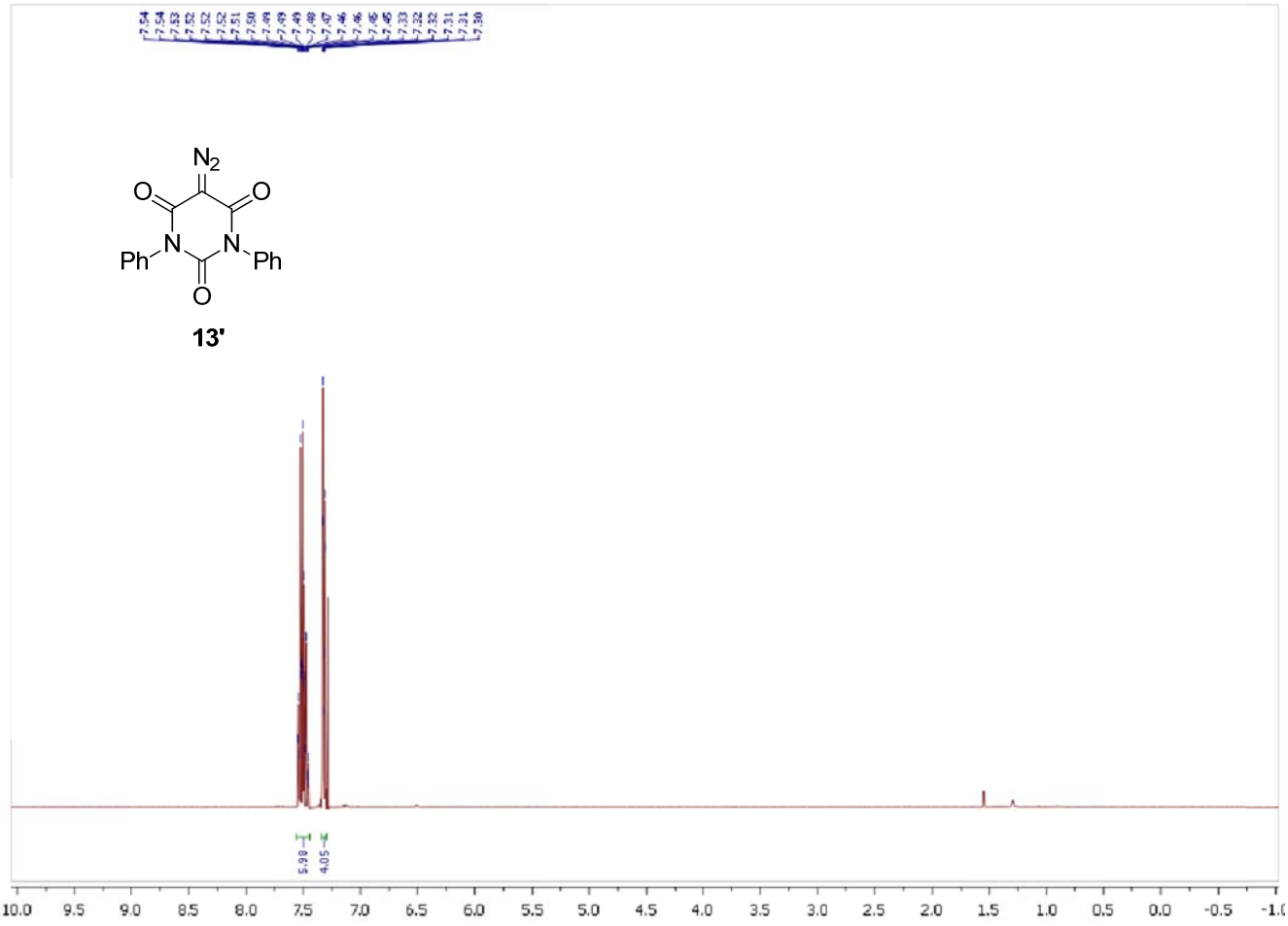

162.92
162.70
134.09
130.11
126.42
125.66
120.79
118.56
68.12
27.35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

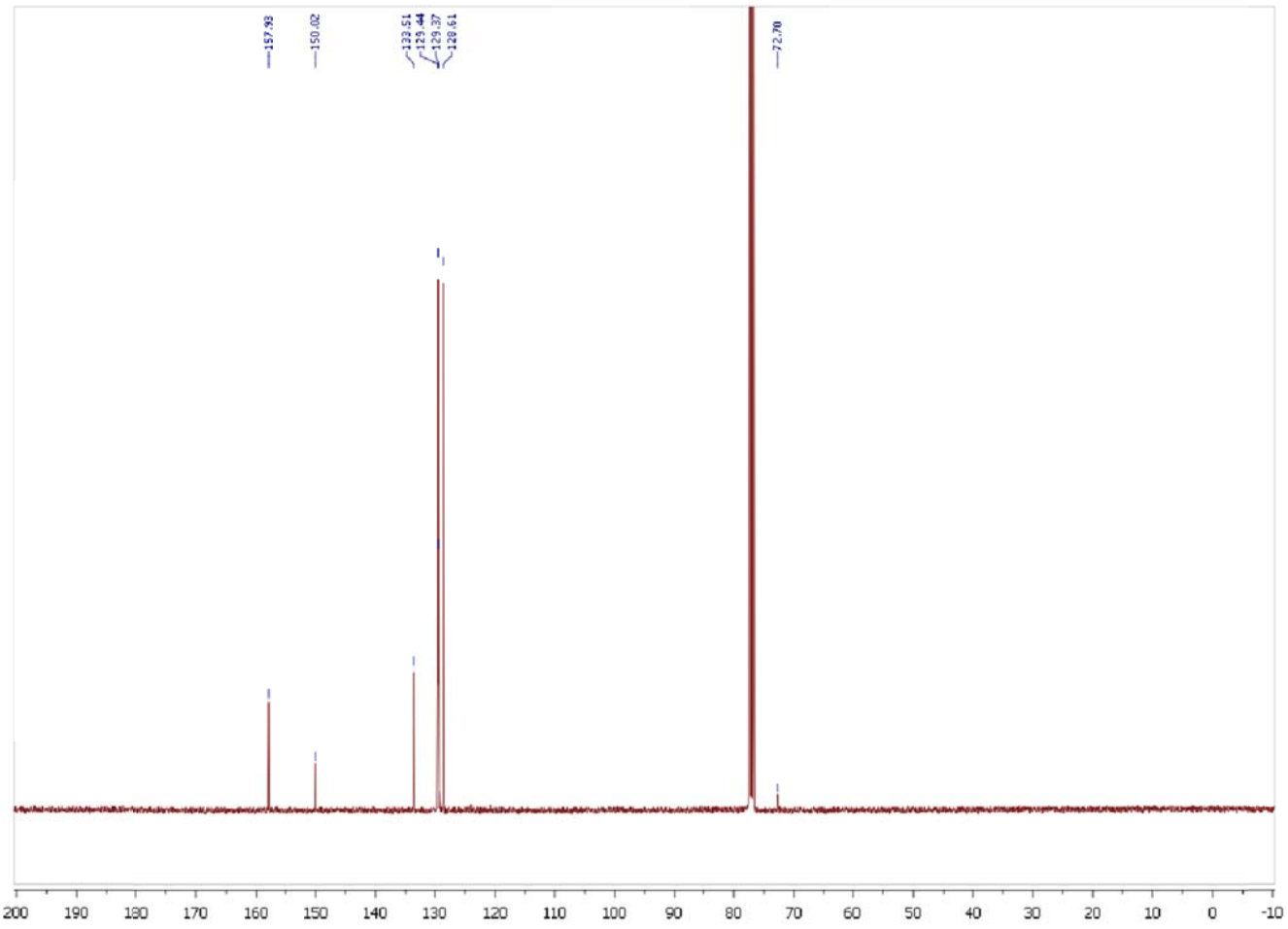

N2
O
O
Me
O
11'
2.48
1.54
2.98
9.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

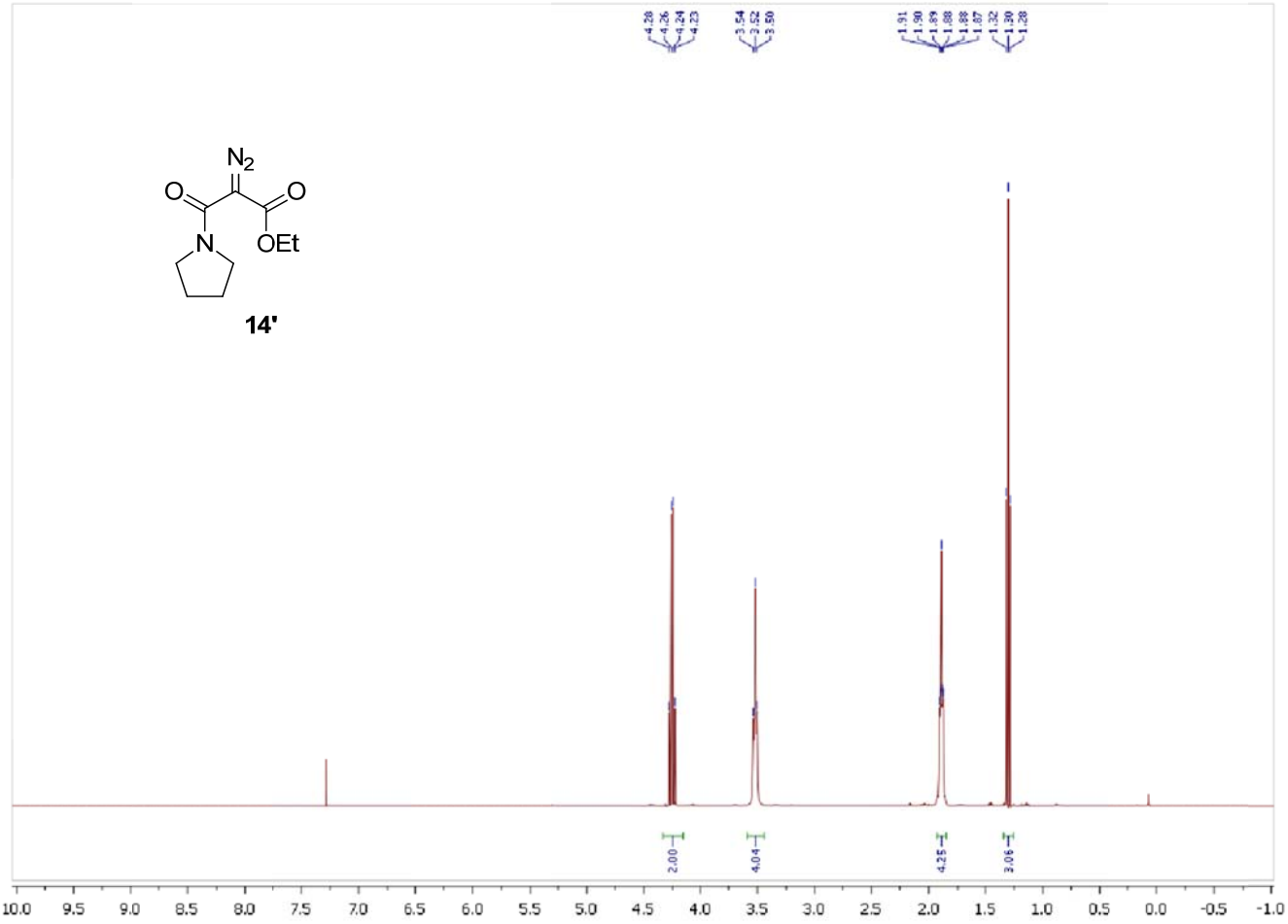

190.53
160.60
83.12
77.09
28.27
28.16
77.09
77.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


N2
O
O=S
O
Me
Me
12'
7.88
7.86
7.41
7.39
2.49
2.31
1.95
2.00
3.06
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


195.87
145.46
139.23
130.15
127.31
86.05
27.00
21.67
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

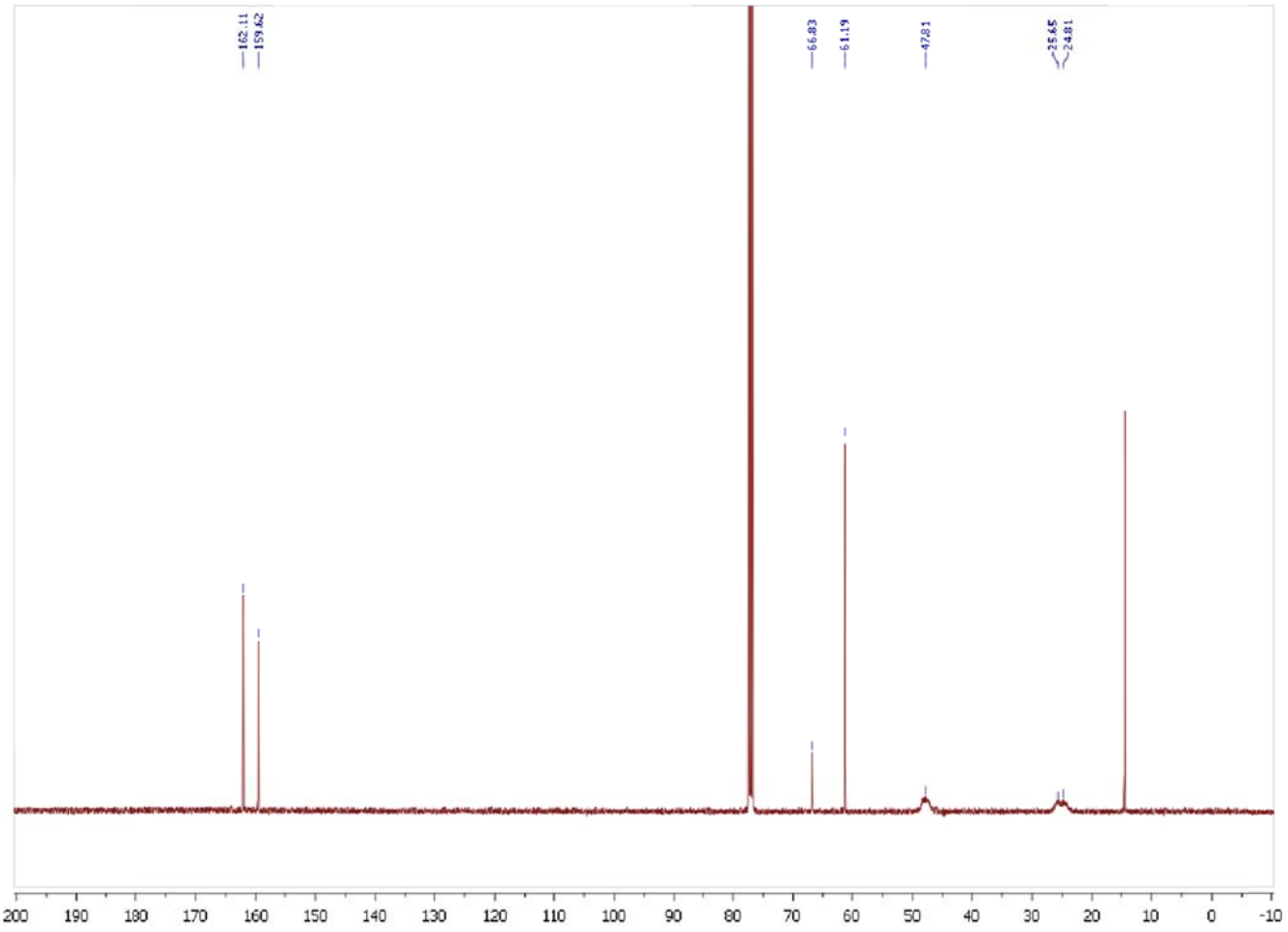

7.54
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.46
7.46
7.46
7.45
7.45
7.33
7.32
7.32
7.31
7.31
7.30
N2
O
O
N
N
Ph
Ph
O
13'
5.98
4.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

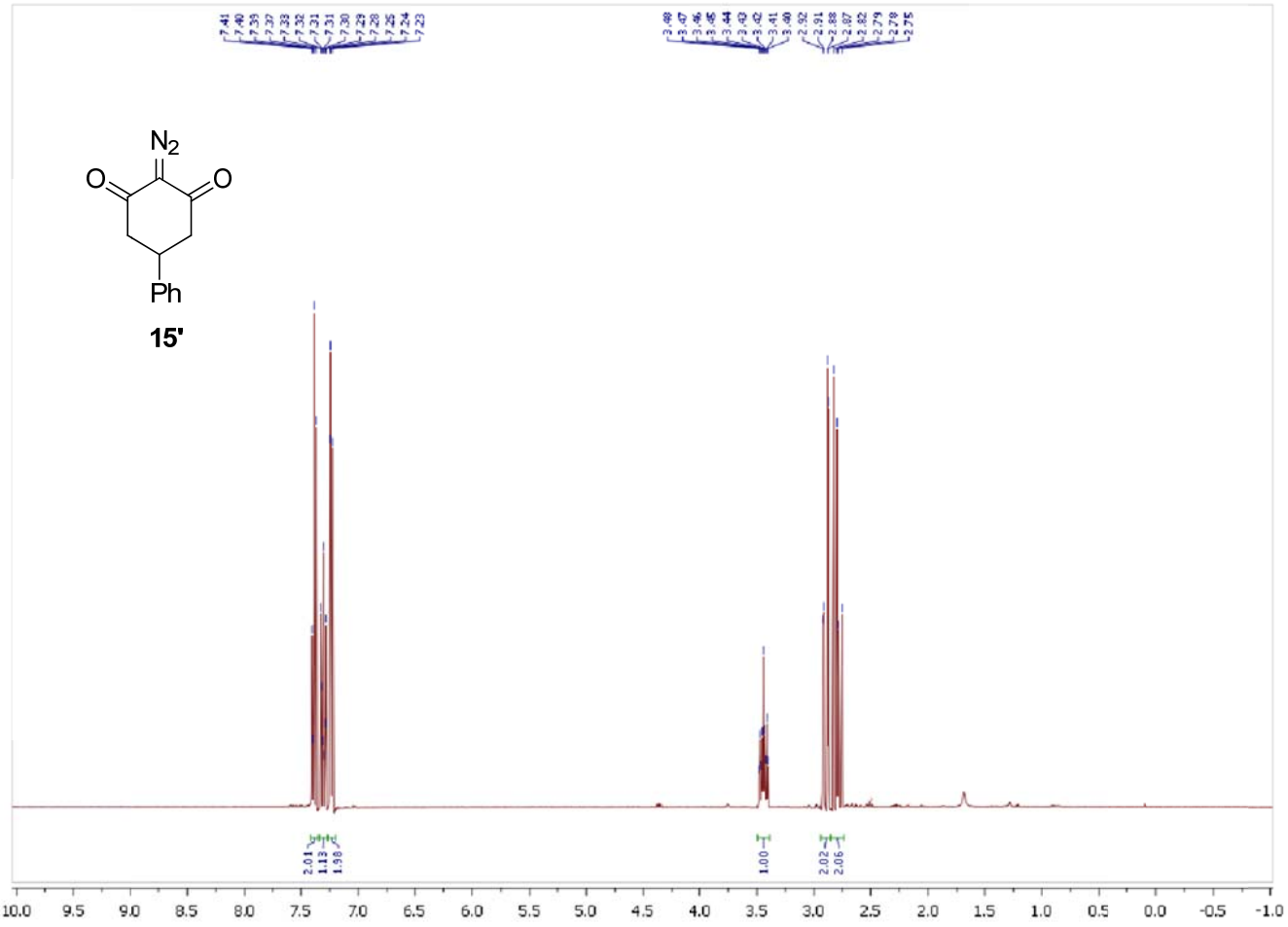

157.93
150.02
132.51
129.44
129.37
128.61
72.70
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

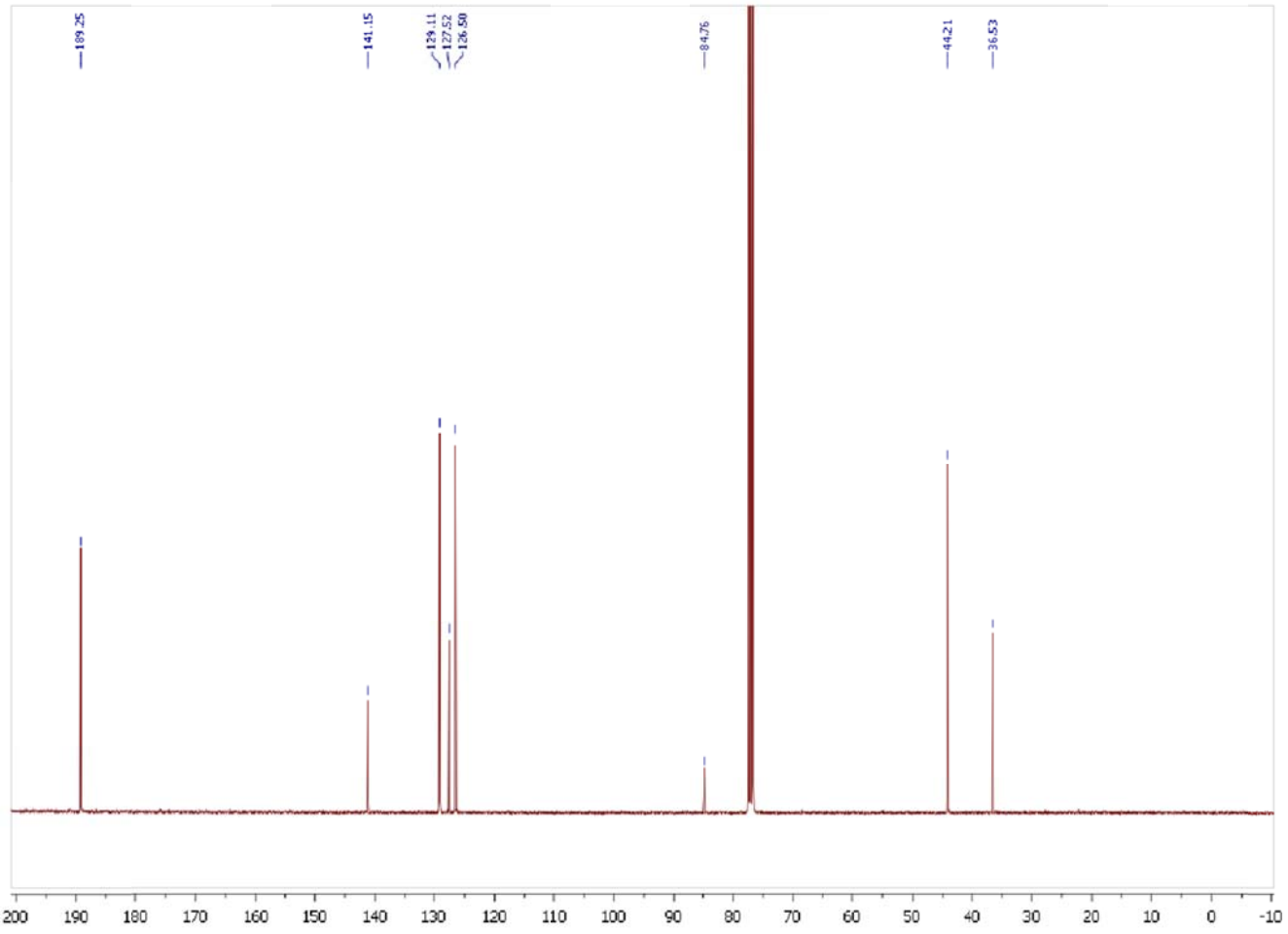

4.28
4.26
4.24
4.23
3.54
3.52
3.50
1.91
1.90
1.89
1.88
1.88
1.87
1.32
1.30
1.28
2.00
4.04
4.25
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

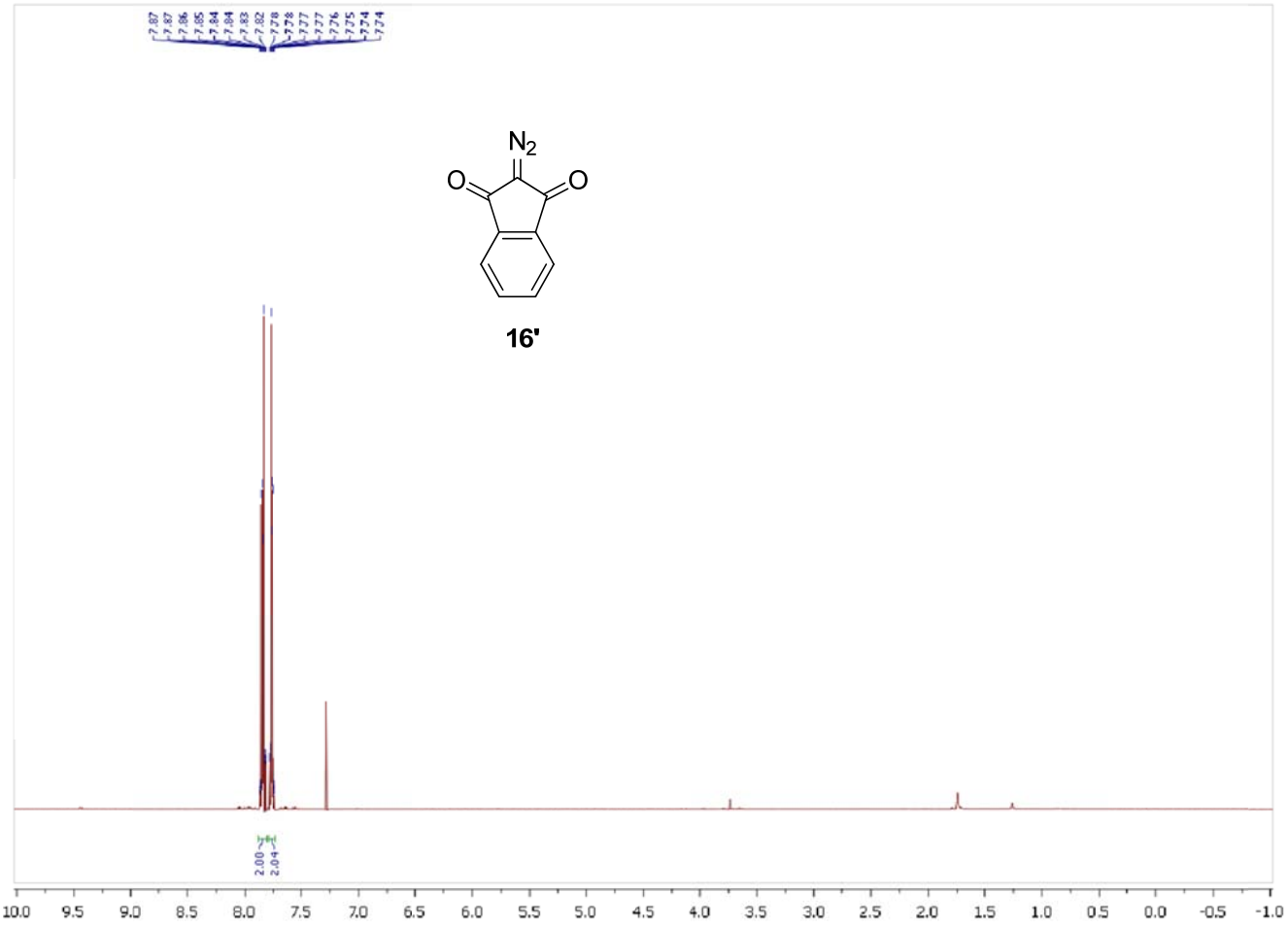
N2
O
O
N
OEt

14'

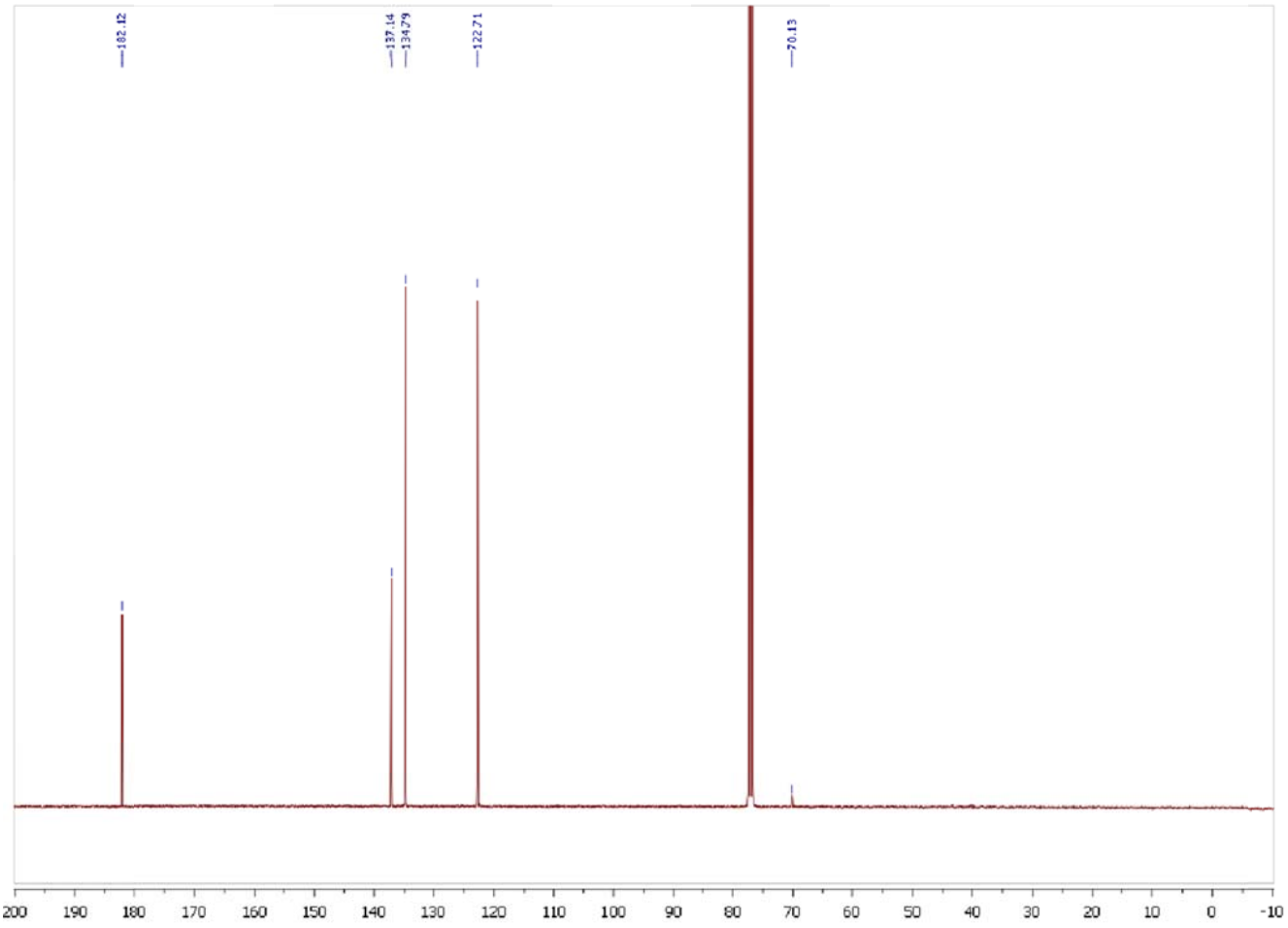

162.11
159.62
66.83
61.19
47.81
25.65
24.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

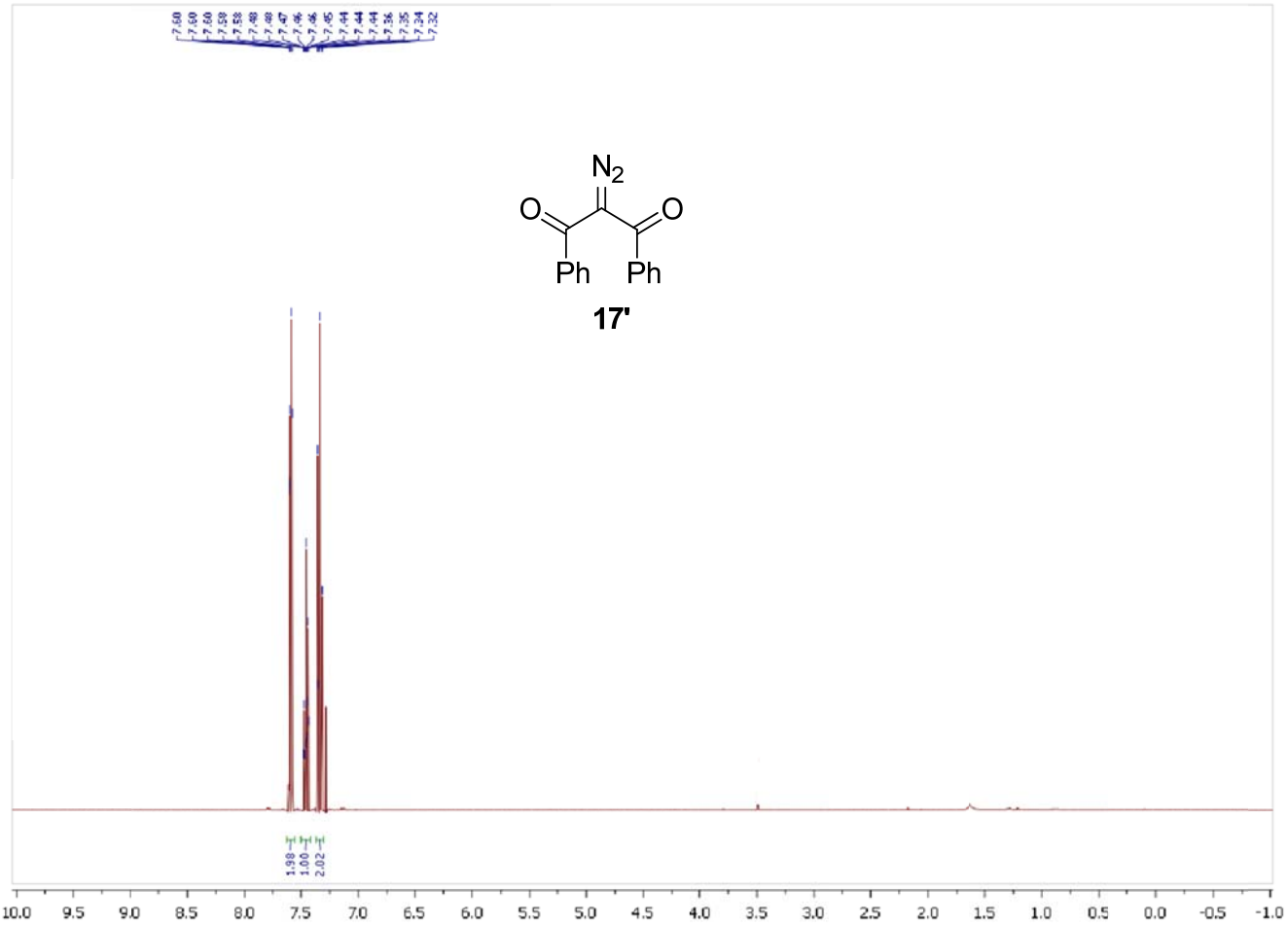

N2
O
O
Ph
15'



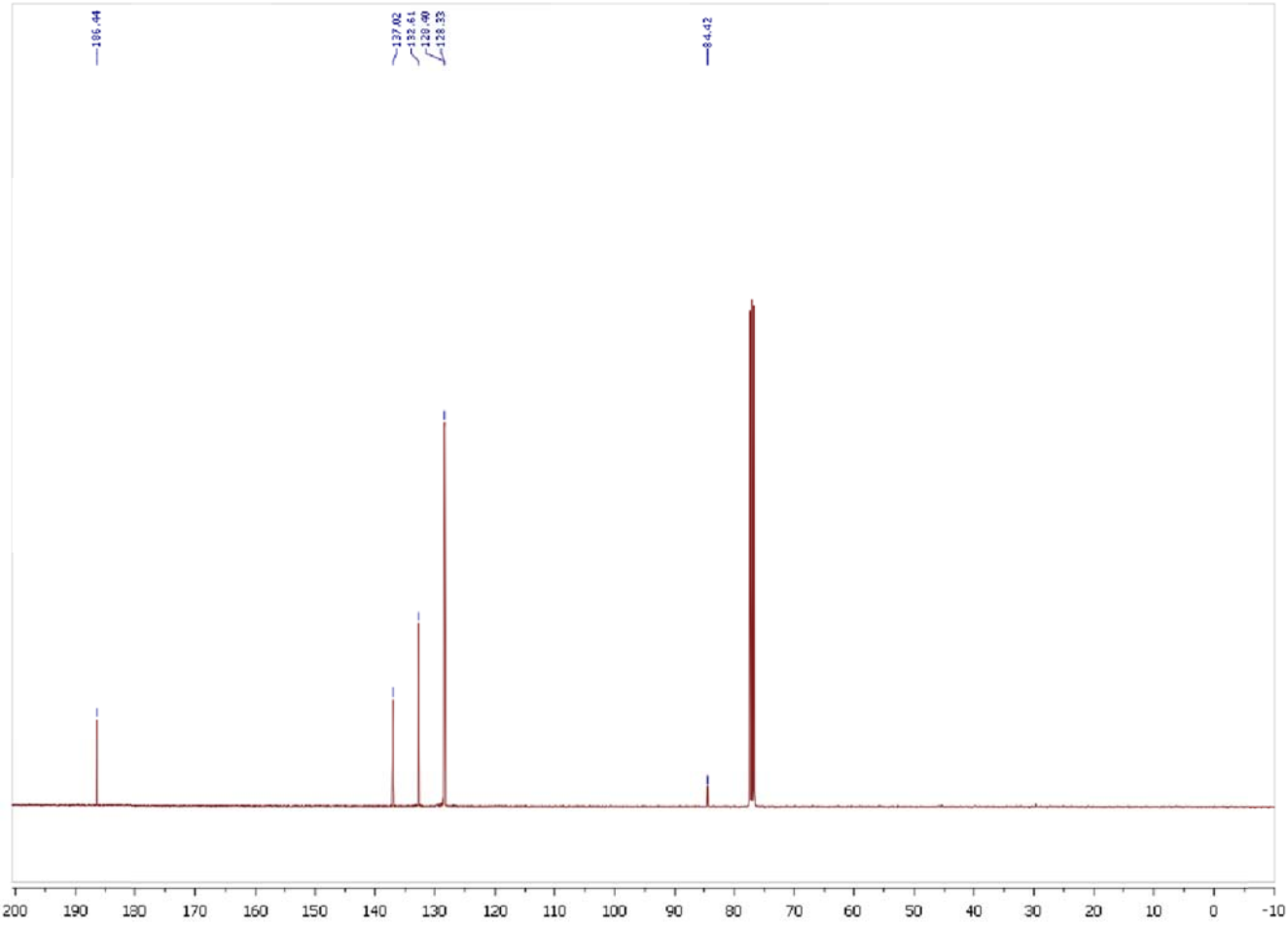

7.87
7.87
7.86
7.85
7.84
7.84
7.84
7.83
7.82
7.78
7.78
7.77
7.77
7.76
7.75
7.74
7.74
O
O
N2
2.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

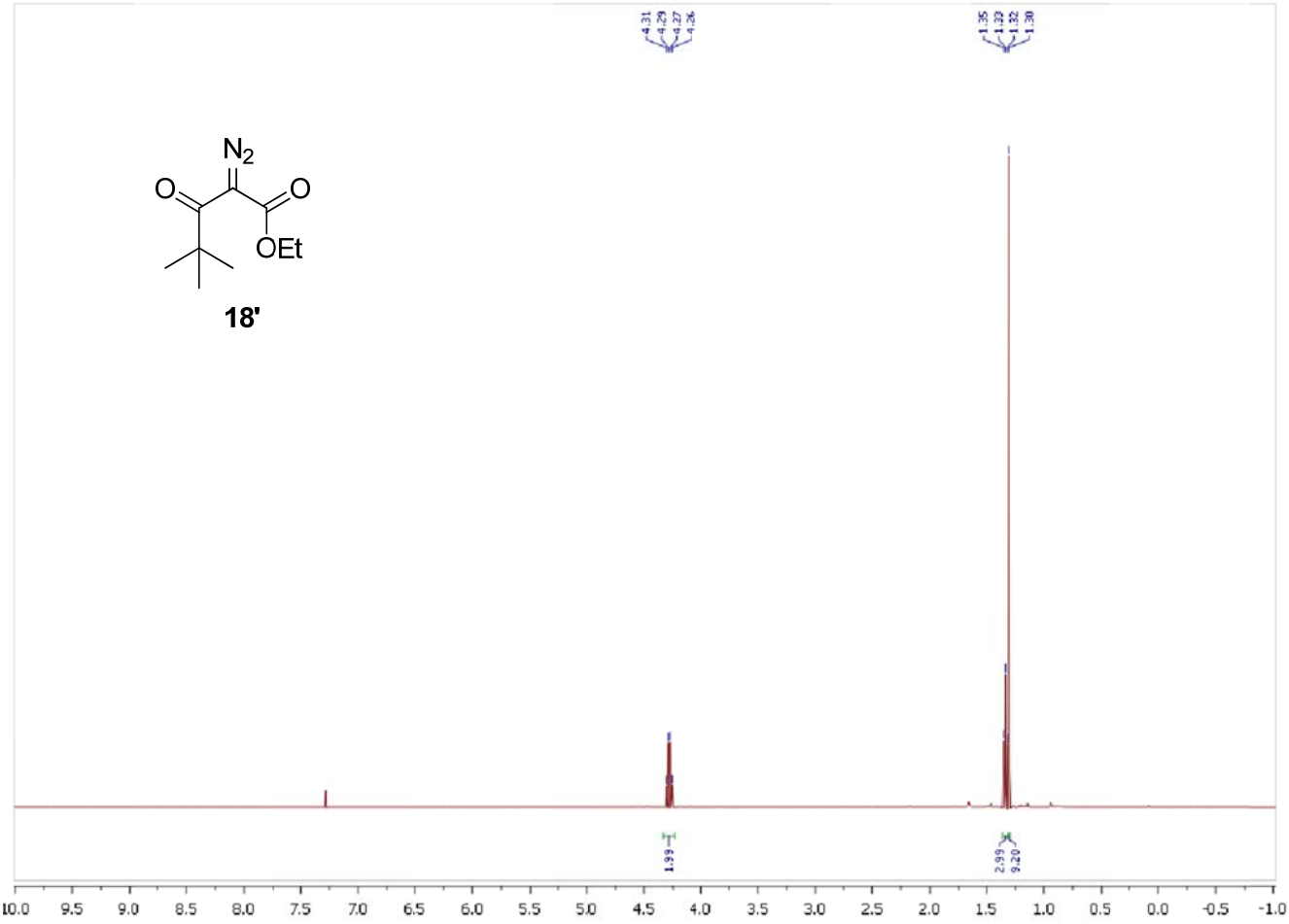
16'

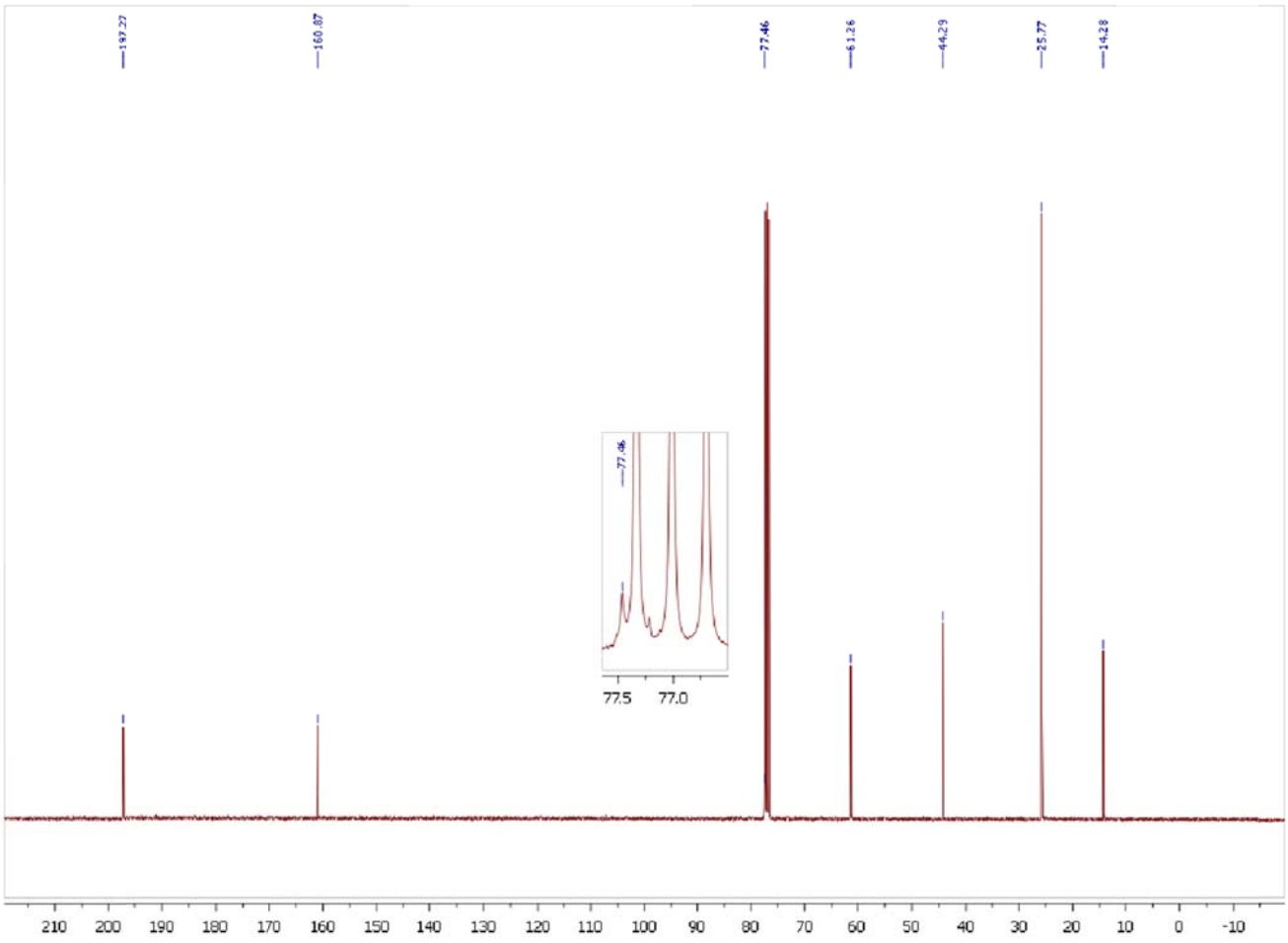

182.12
137.14
134.79
122.71
70.13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

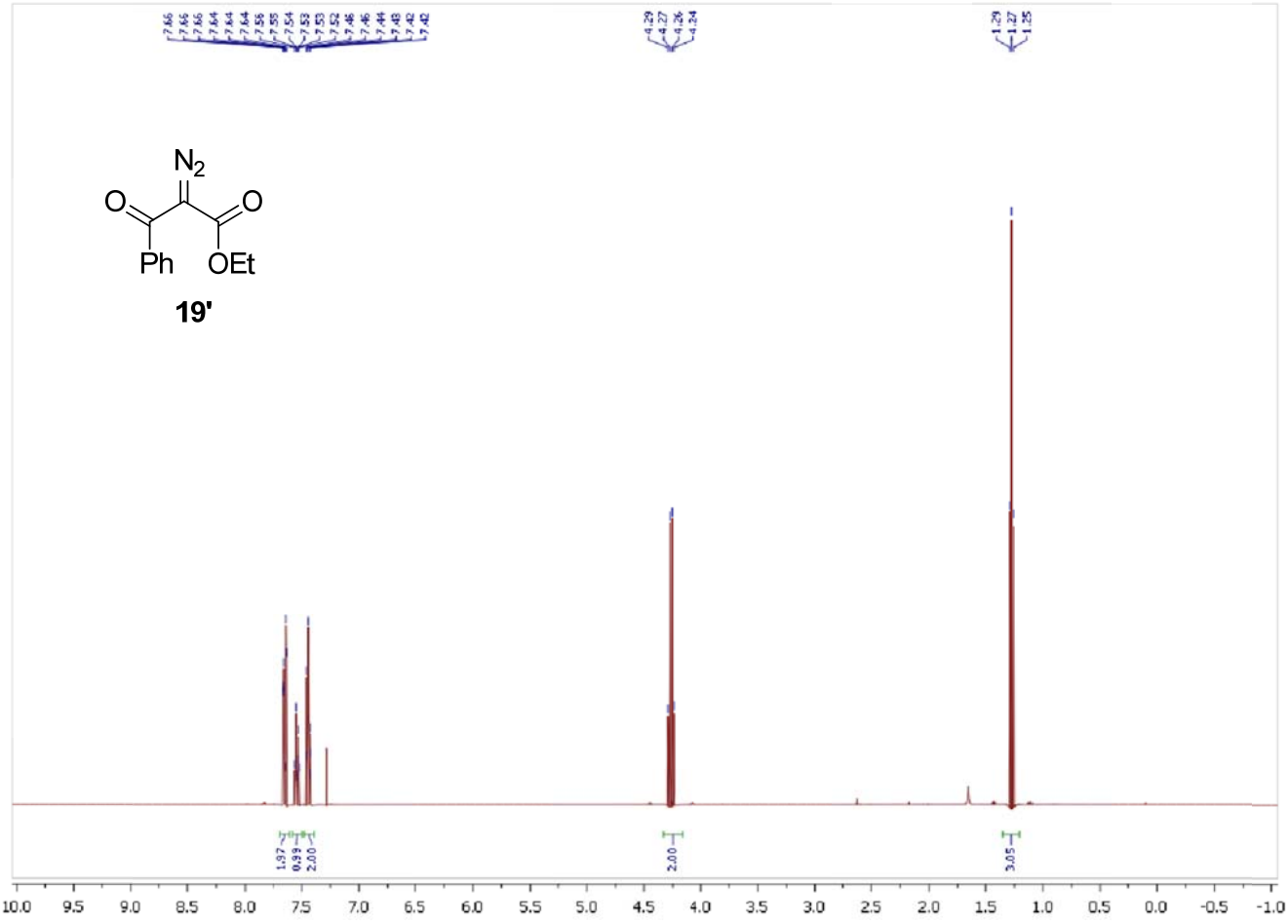

7.60
7.59
7.56
7.55
7.53
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.36
7.35
7.34
7.32
N2
O
O
Ph
Ph
1.98
1.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

17'

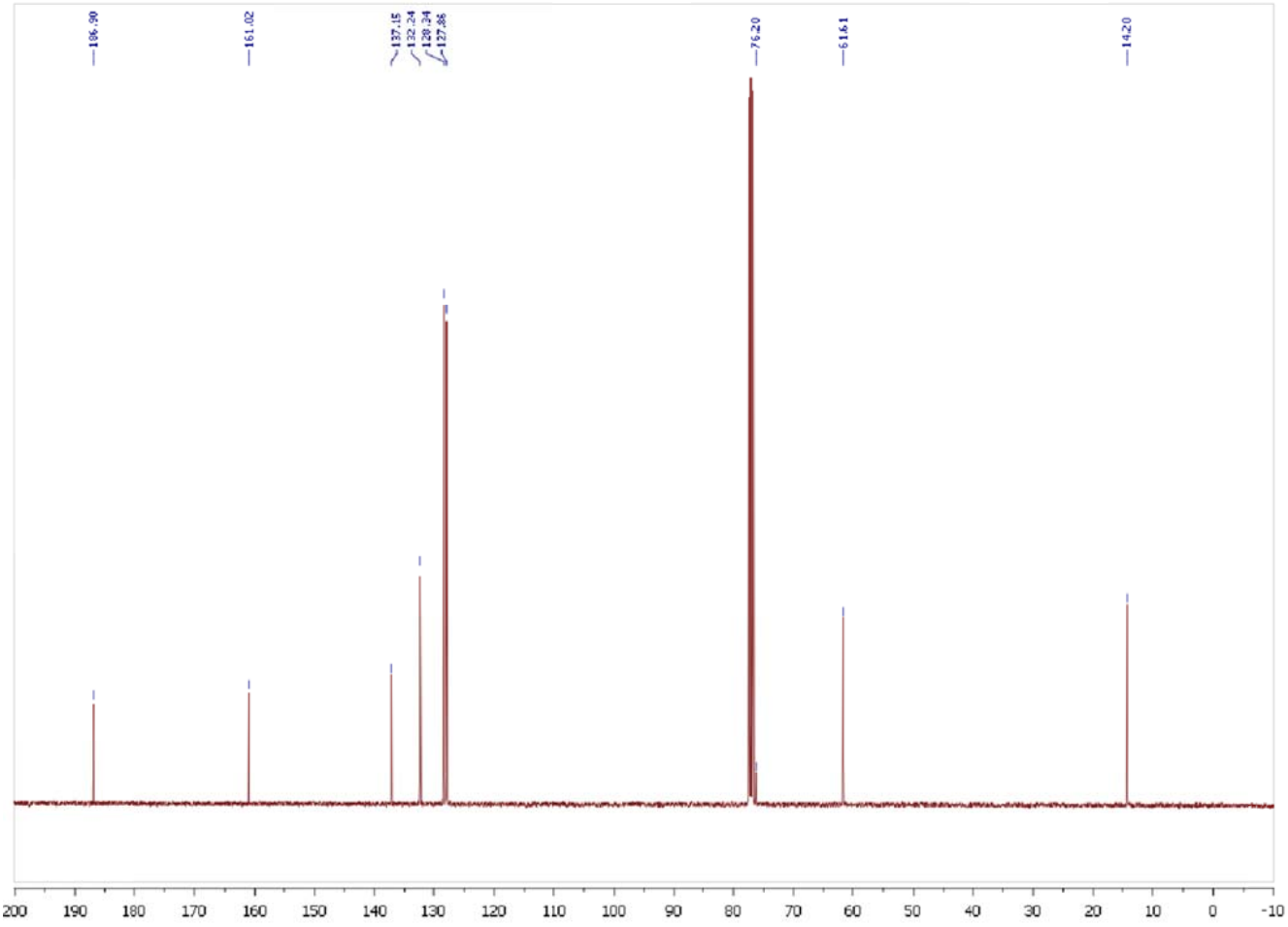

186.44
137.02
133.41
129.49
128.53
84.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

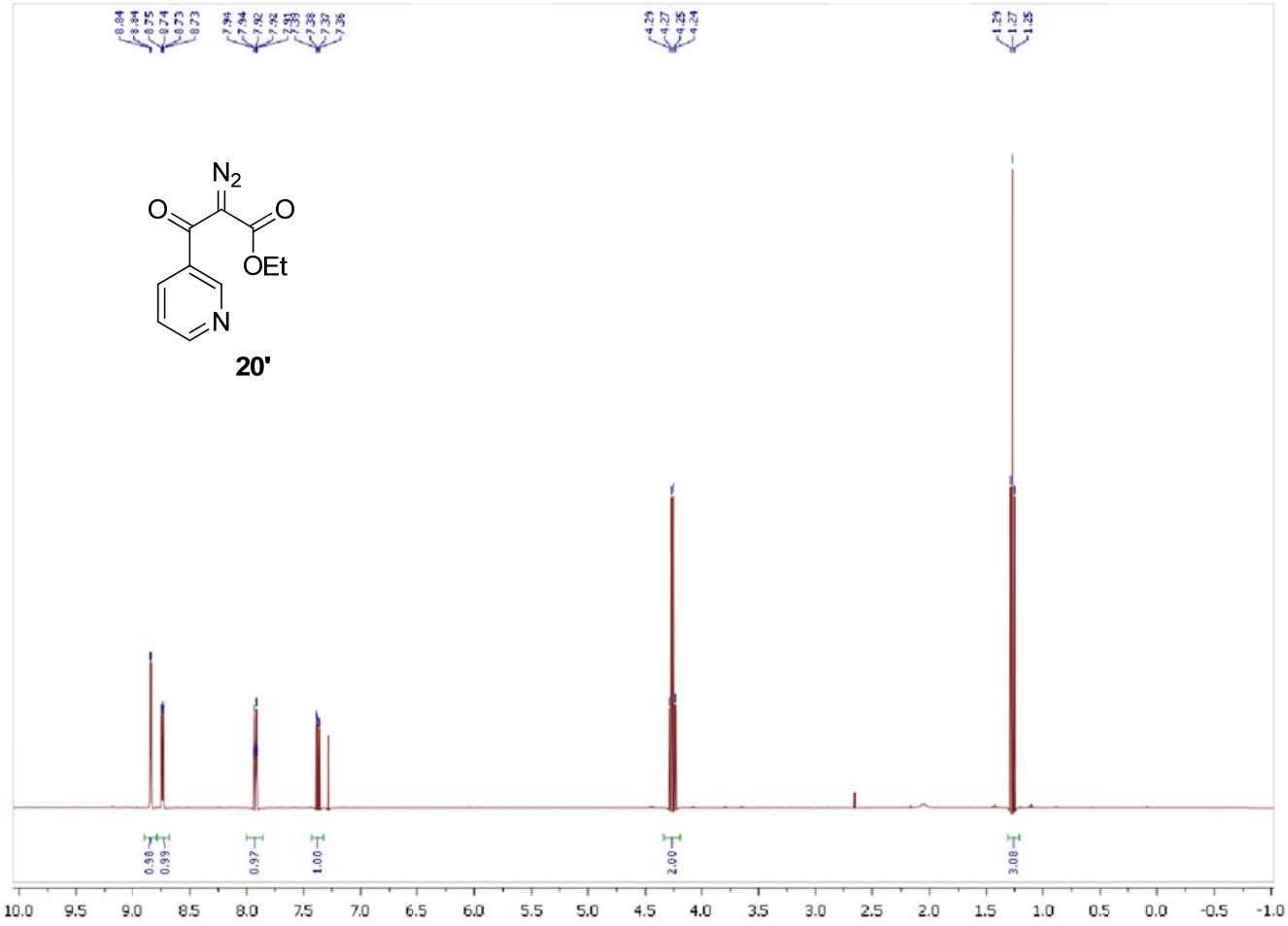

N2
O
O
OEt
18'



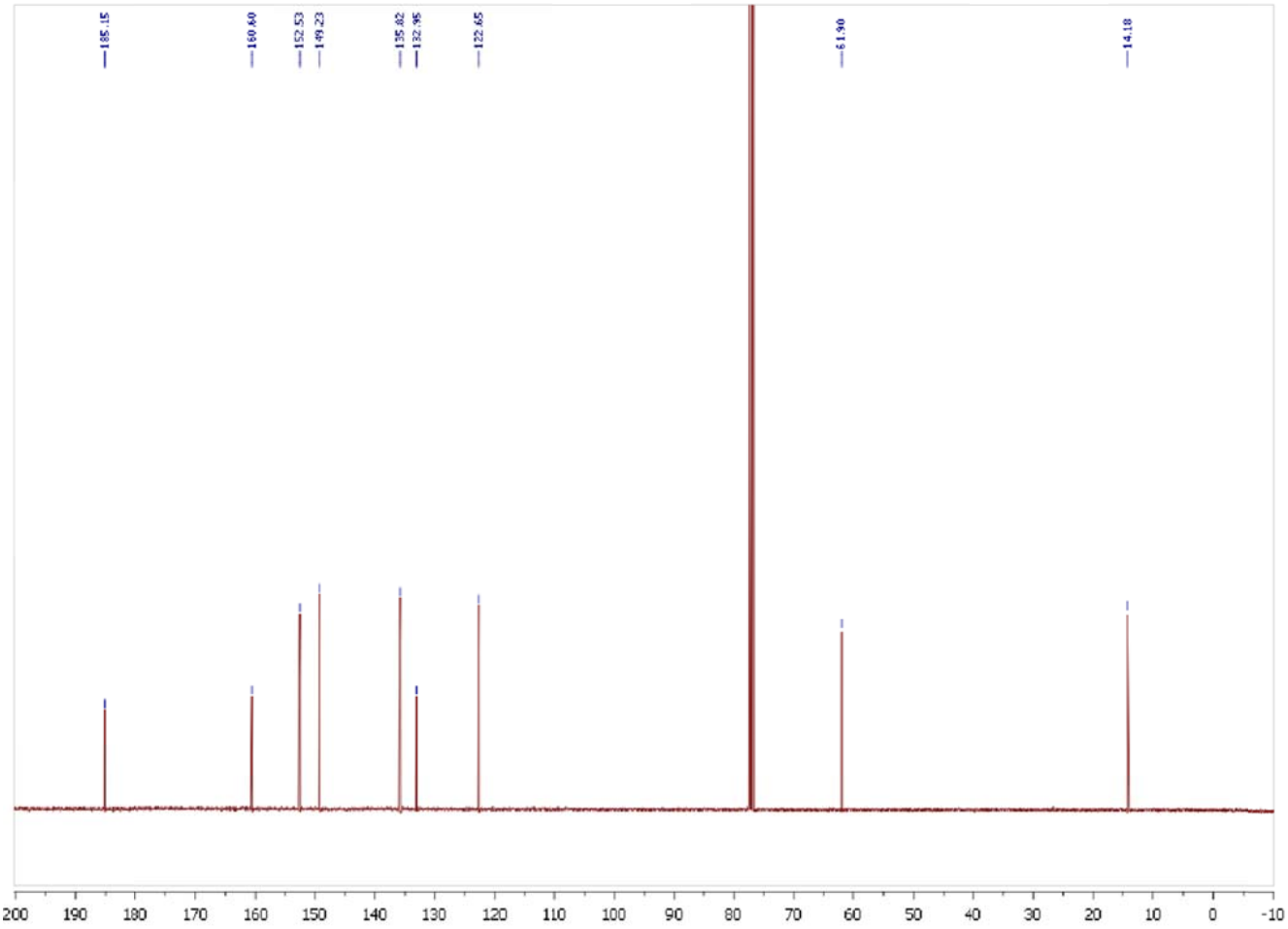


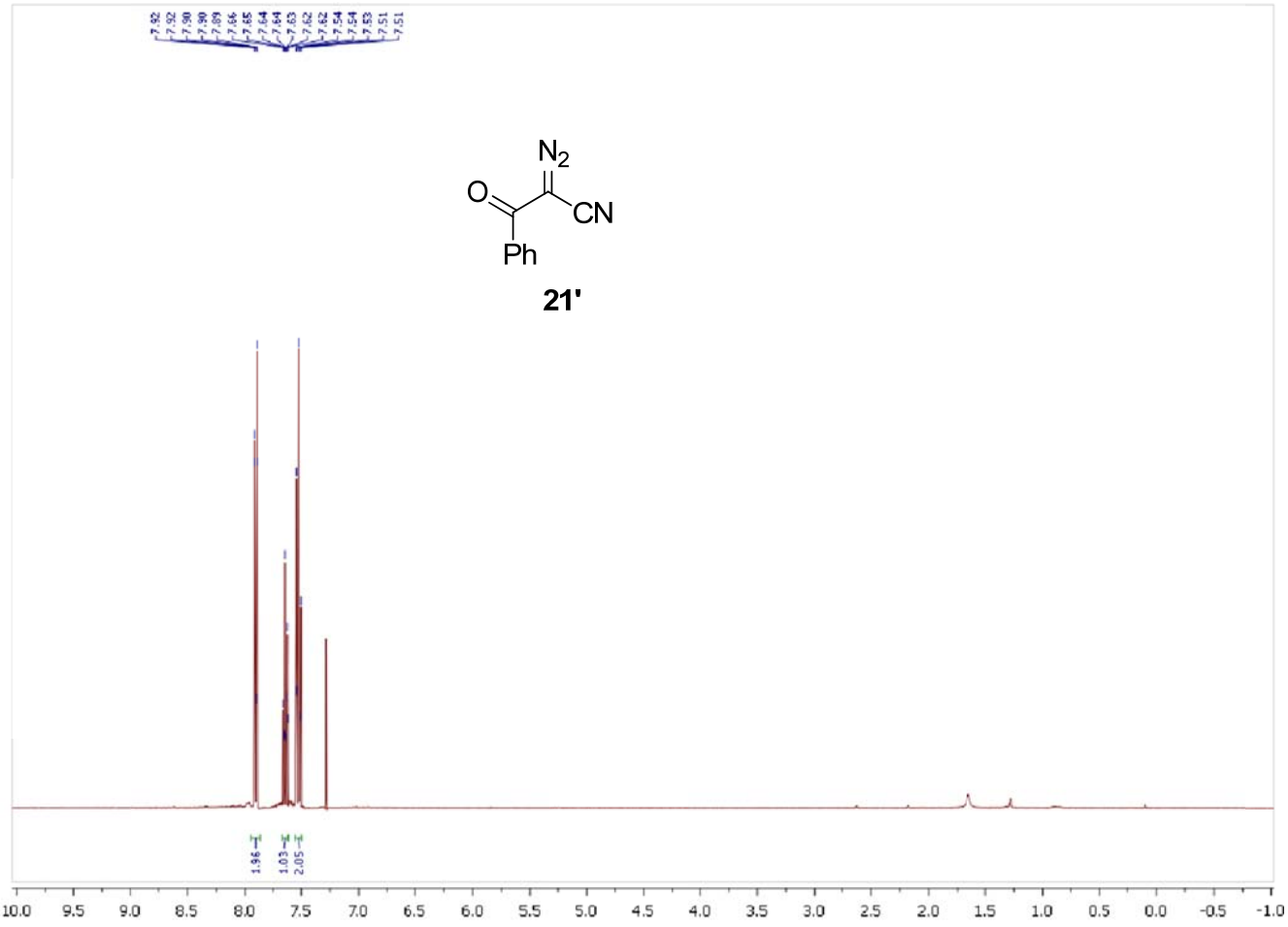
19'



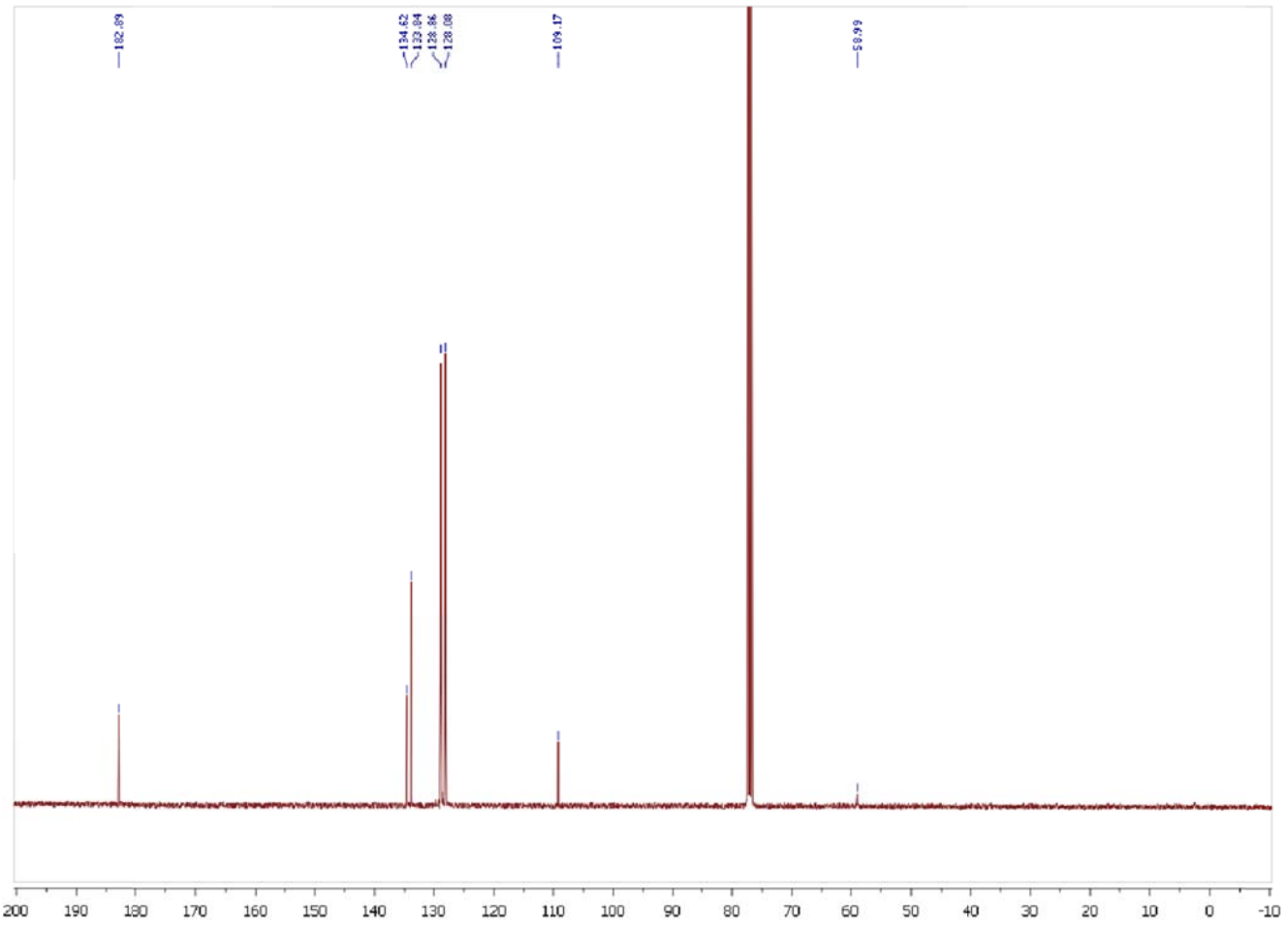

8.84
8.84
8.75
8.74
8.73
8.73
7.94
7.94
7.92
7.92
7.91
7.91
7.38
7.37
7.36
4.29
4.27
4.25
4.24
1.29
1.27
1.25
N2
O
O
OEt
N
0.98
0.99
0.97
1.00
2.00
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

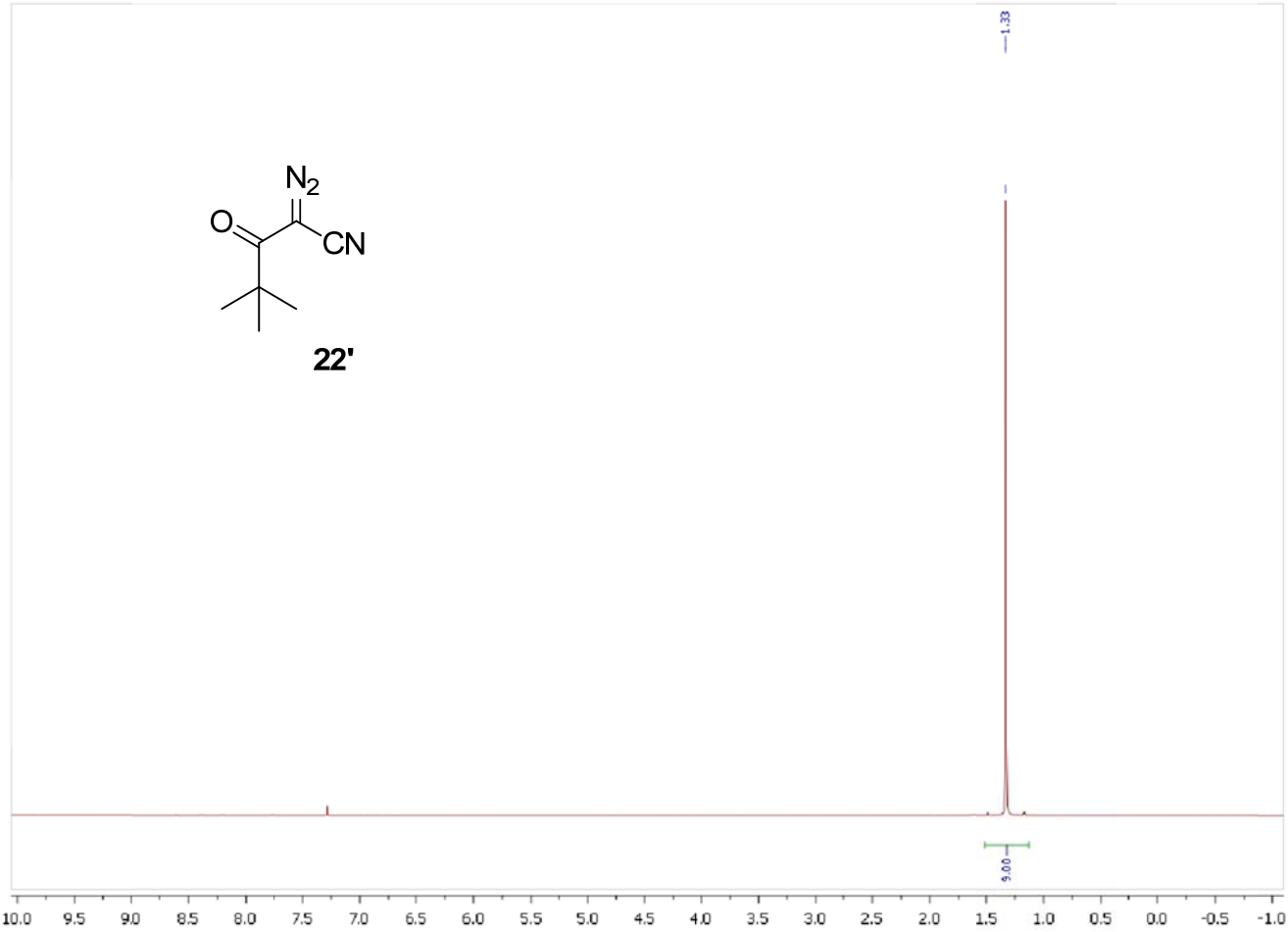
20'

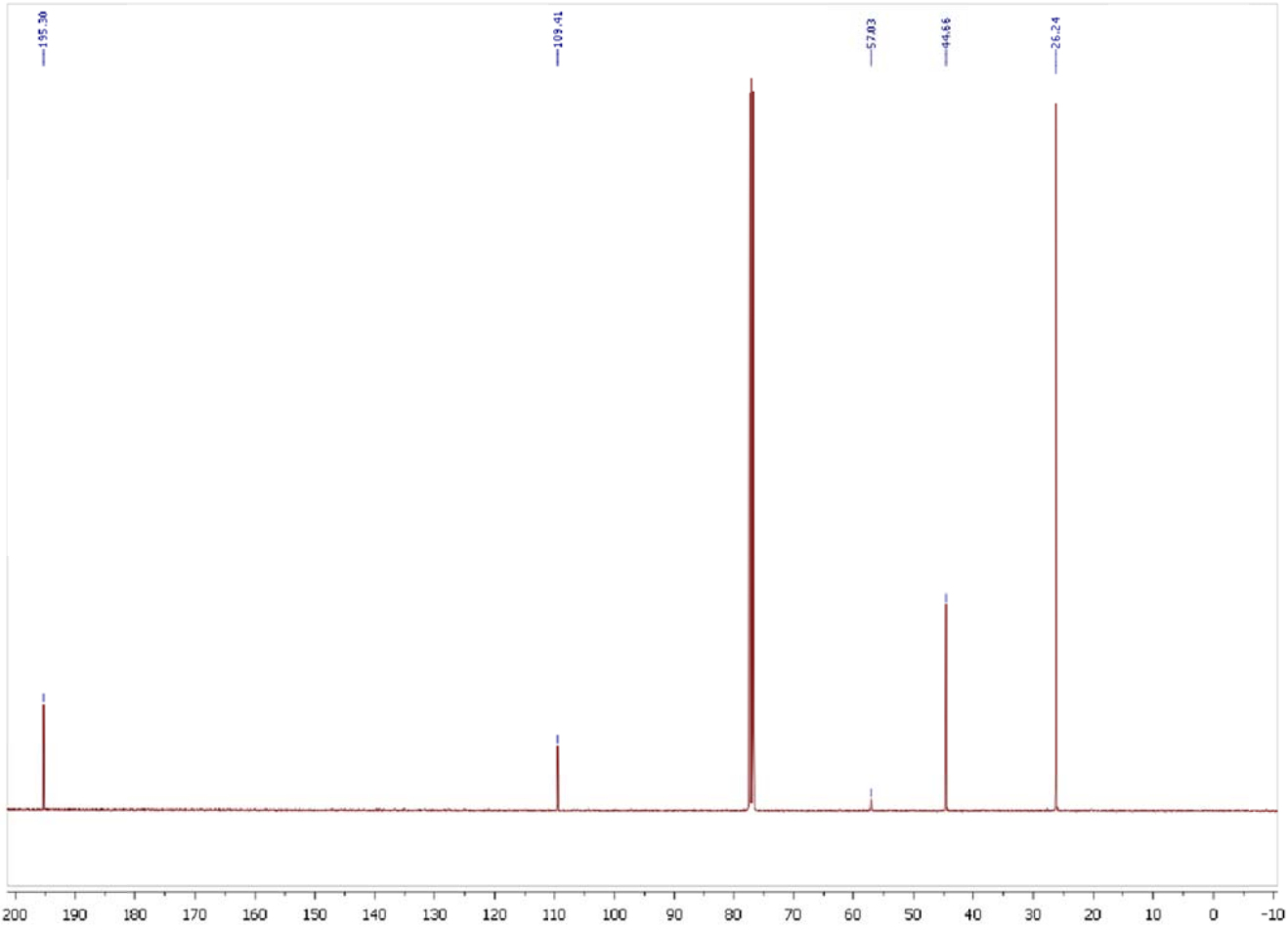

185.15
160.60
152.53
149.23
135.82
132.95
122.65
61.90
14.18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

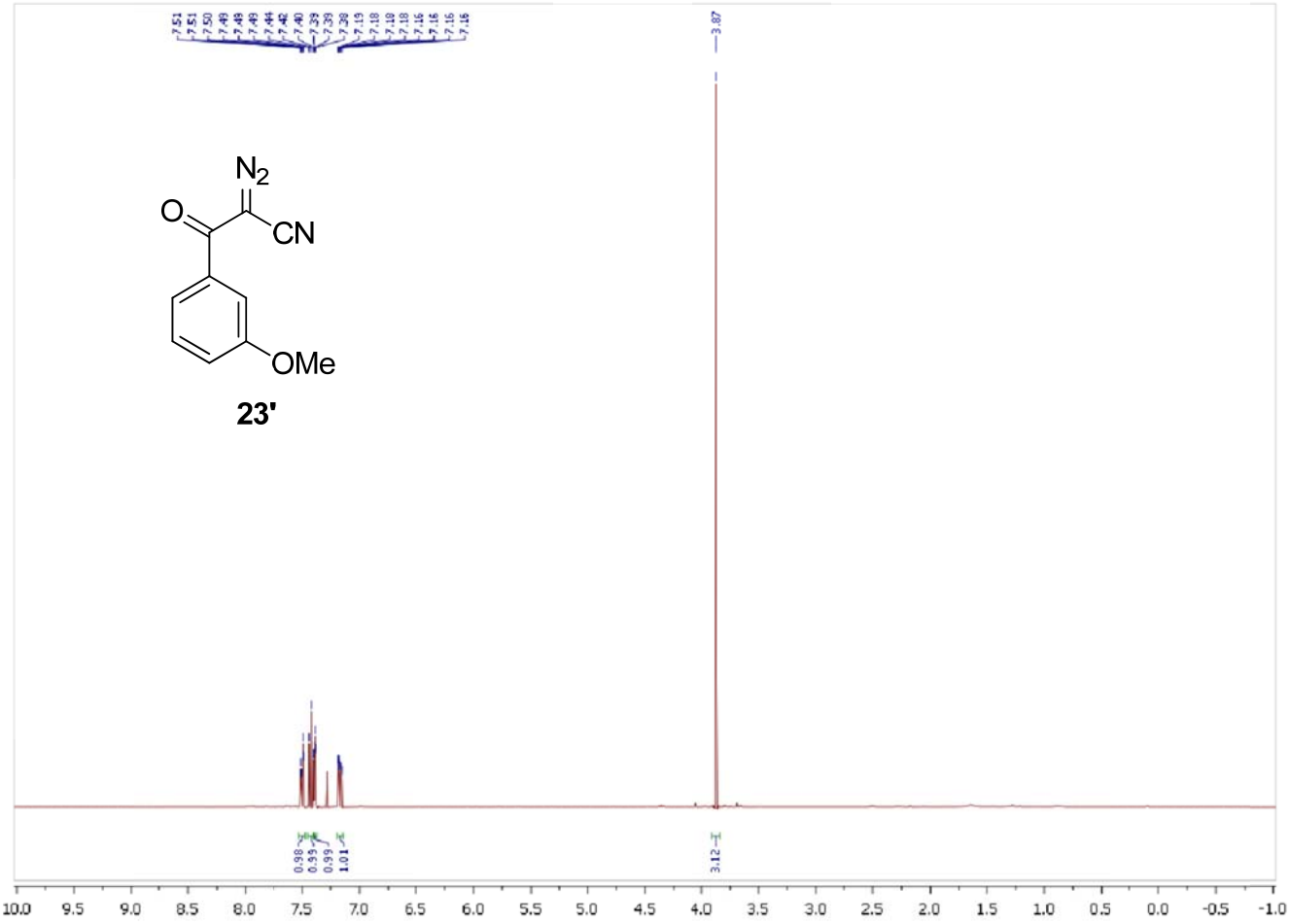

7.92
7.92
7.90
7.90
7.89
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.54
7.54
7.53
7.51
7.51
N2
O
CN
Ph
1.96
1.03
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

21'

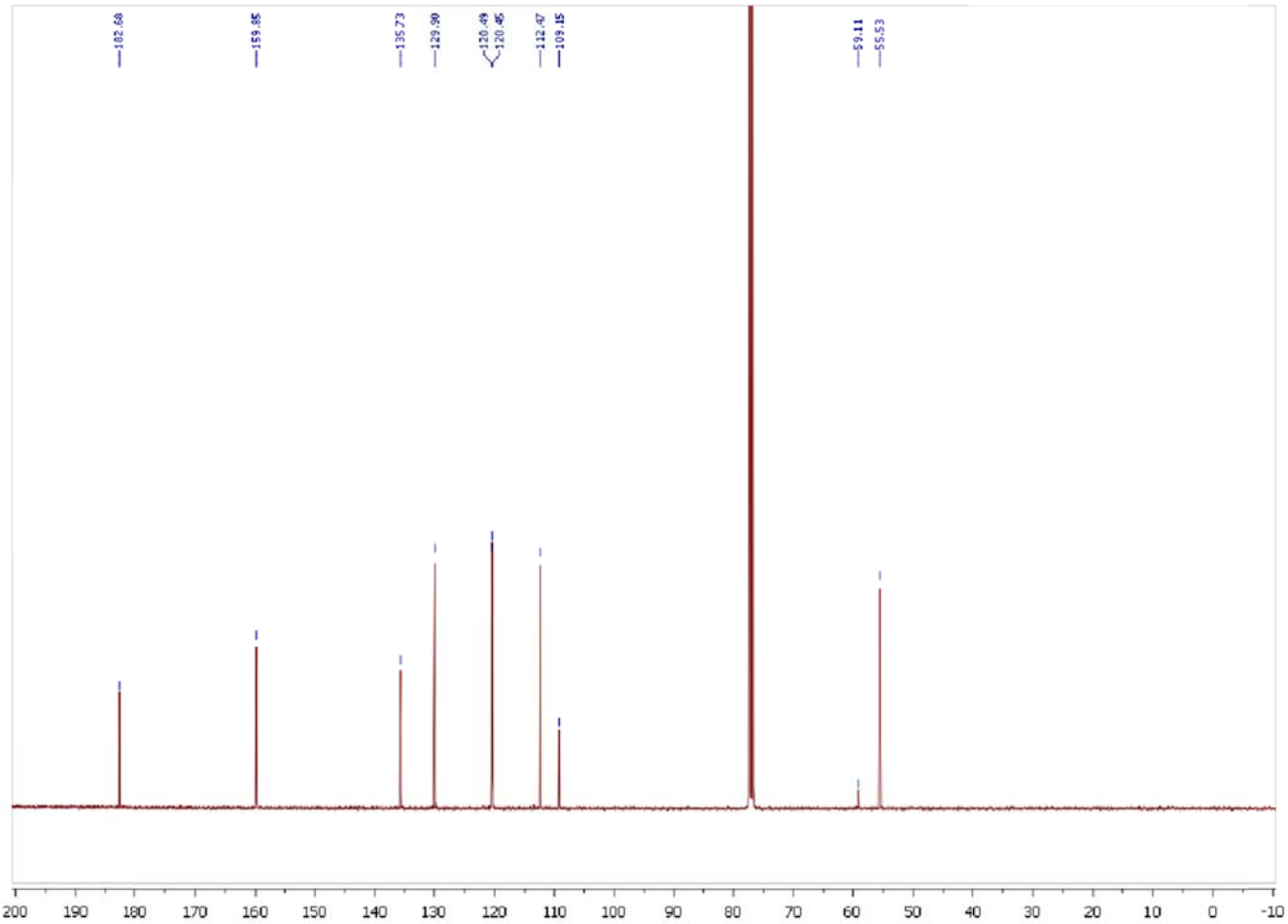

182.89
134.62
133.84
128.86
128.08
109.17
59.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

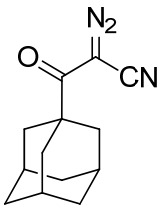

N2
O
CN
22'
1.33
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


195.30
109.41
57.03
44.66
26.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



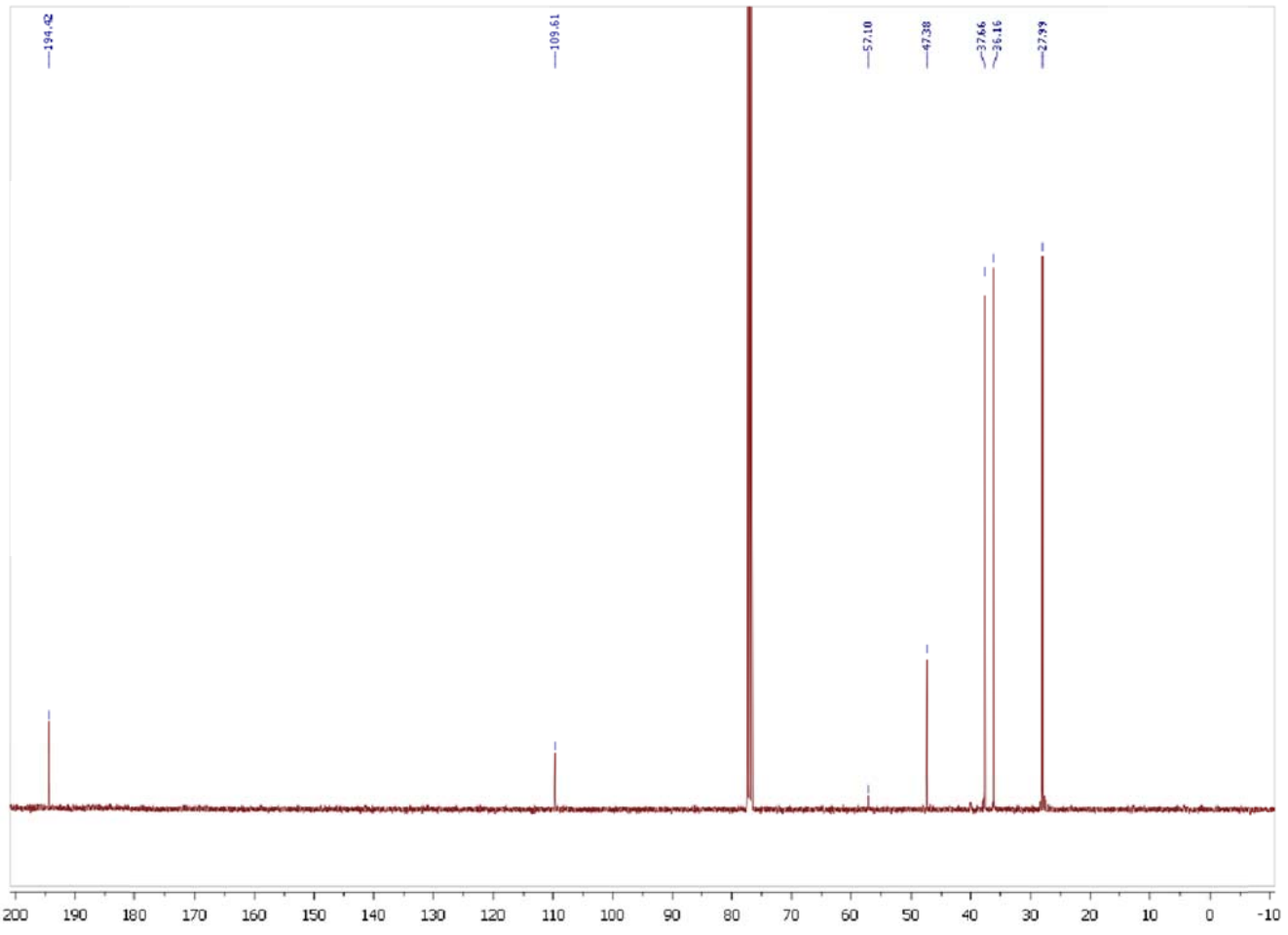
23'

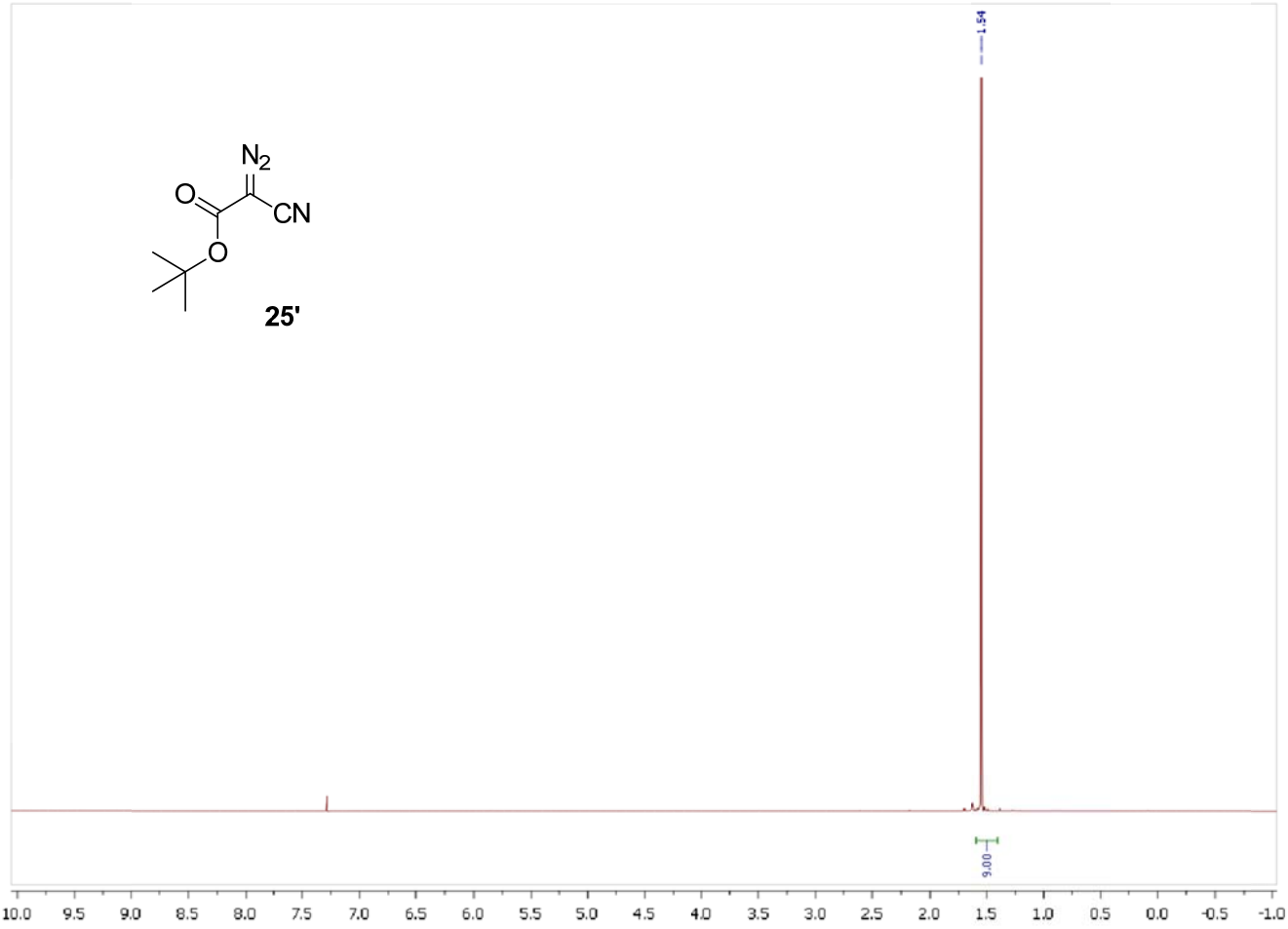


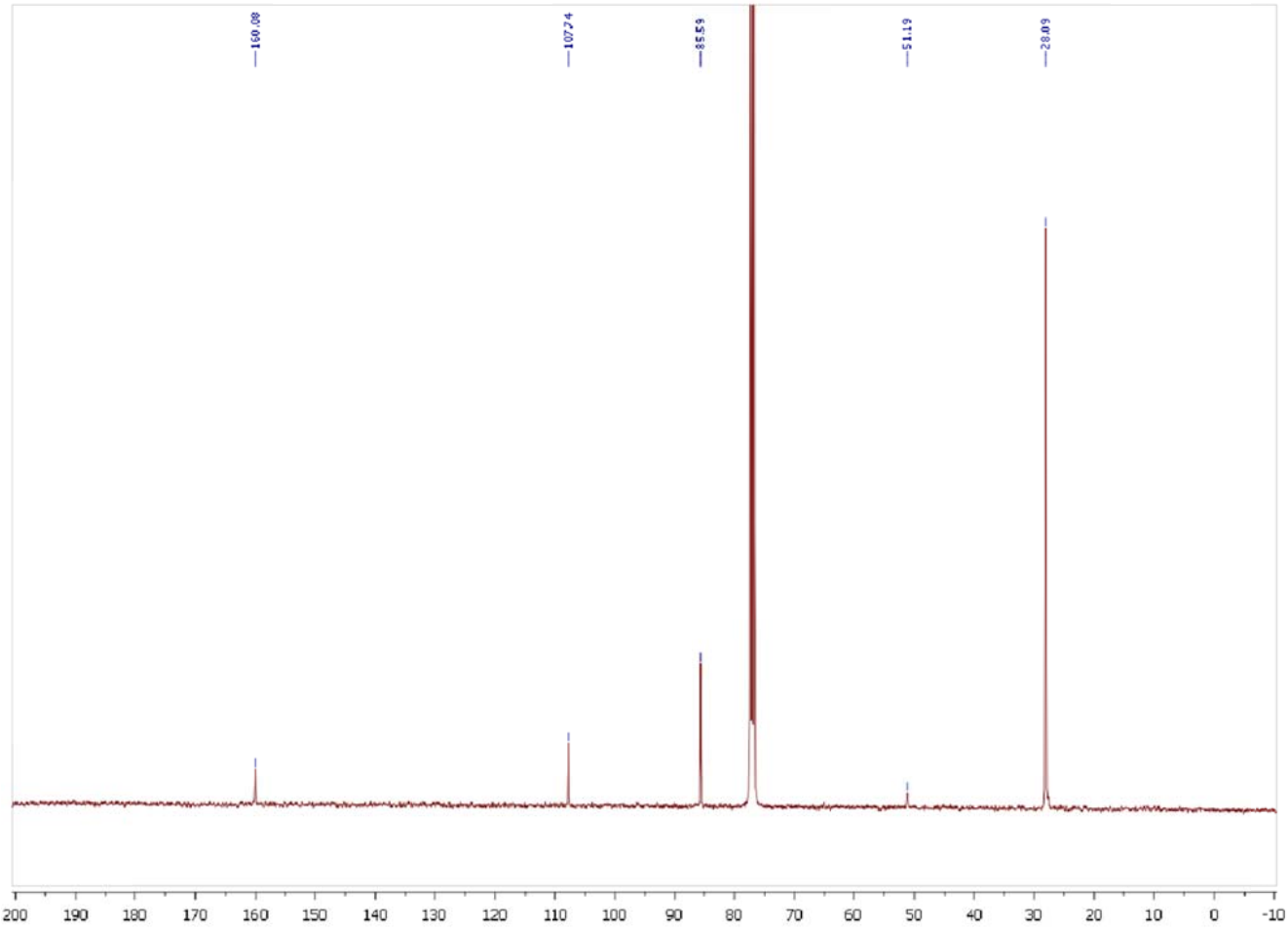

N2
O
CN

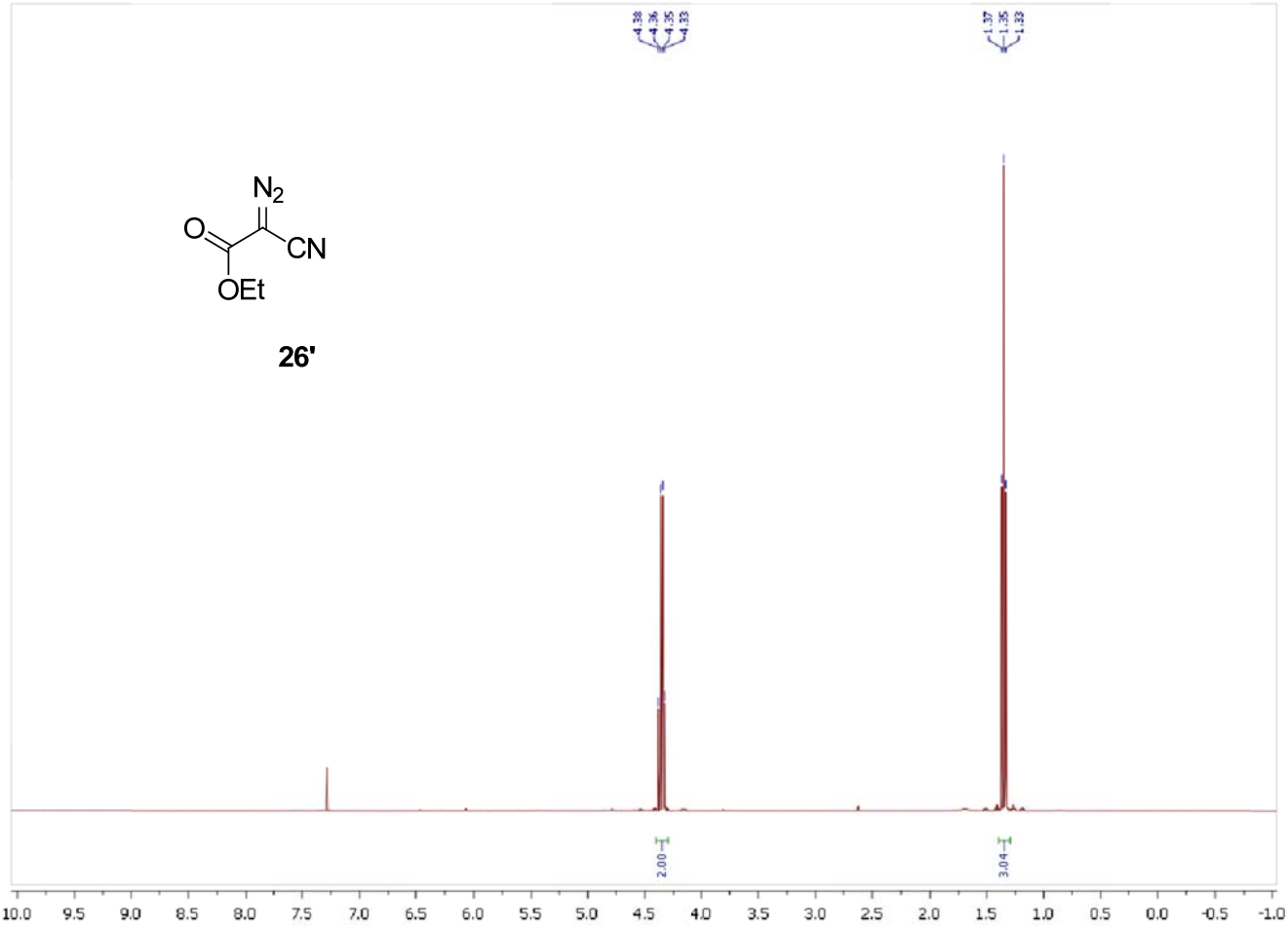
24'

2.12
2.01
2.01
1.80
1.76
1.72
3.12
5.94
6.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


194.42
109.61
57.10
47.38
37.66
36.16
27.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

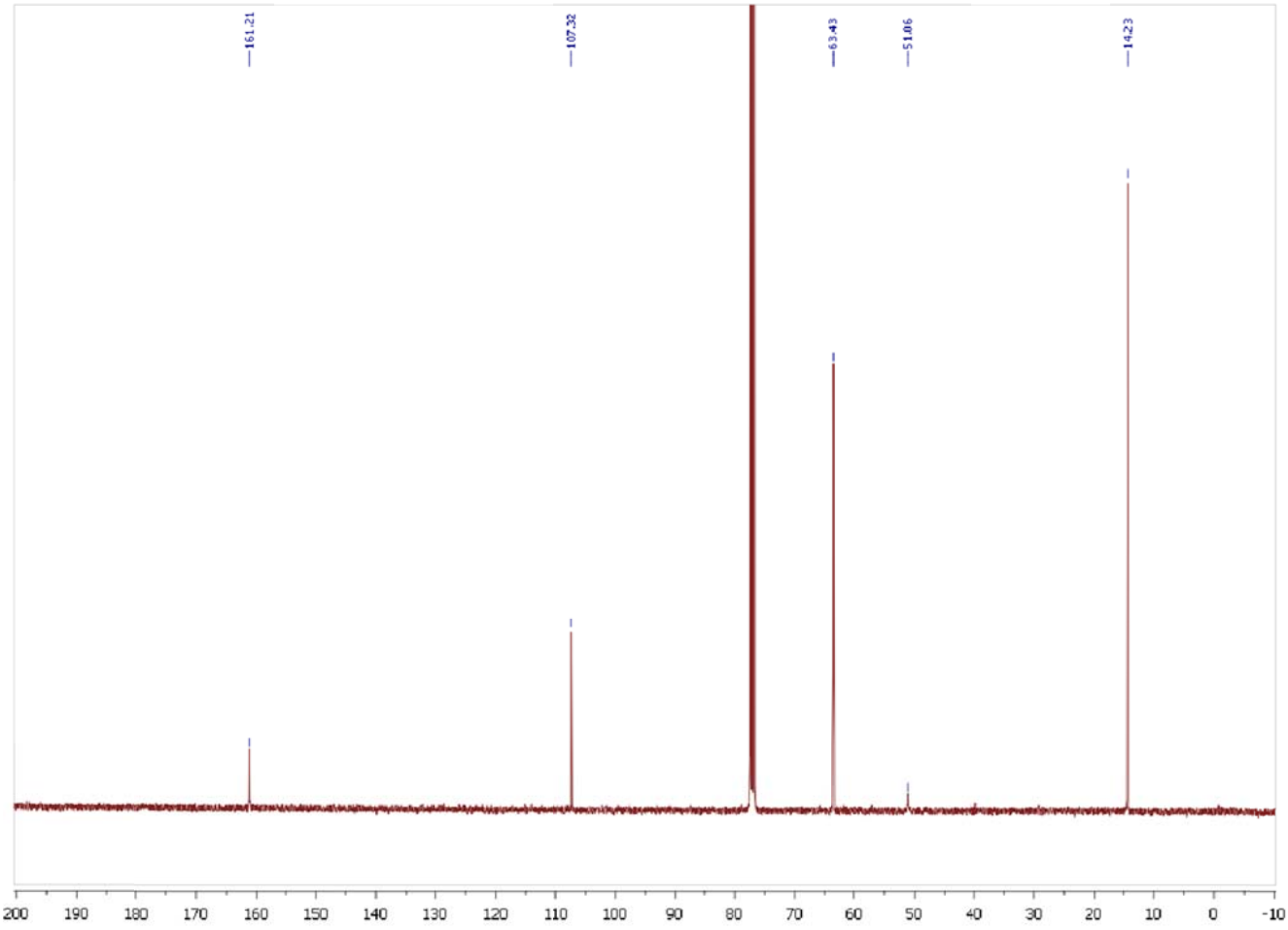

N2
O
CN
O
25'
1.54
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

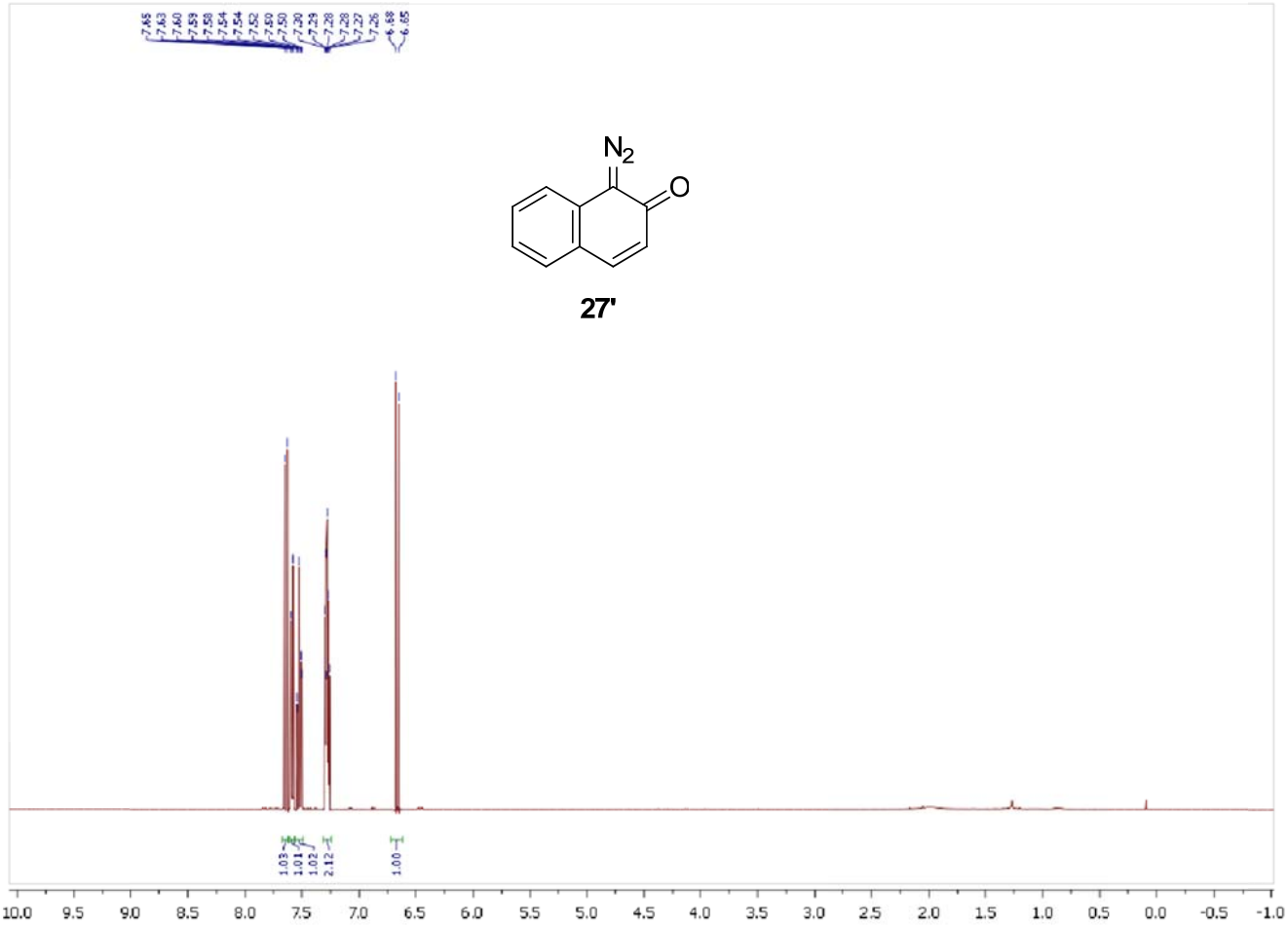

160.08
107.24
85.59
51.19
28.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


4.38
4.36
4.35
4.33
1.37
1.35
1.33
2.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

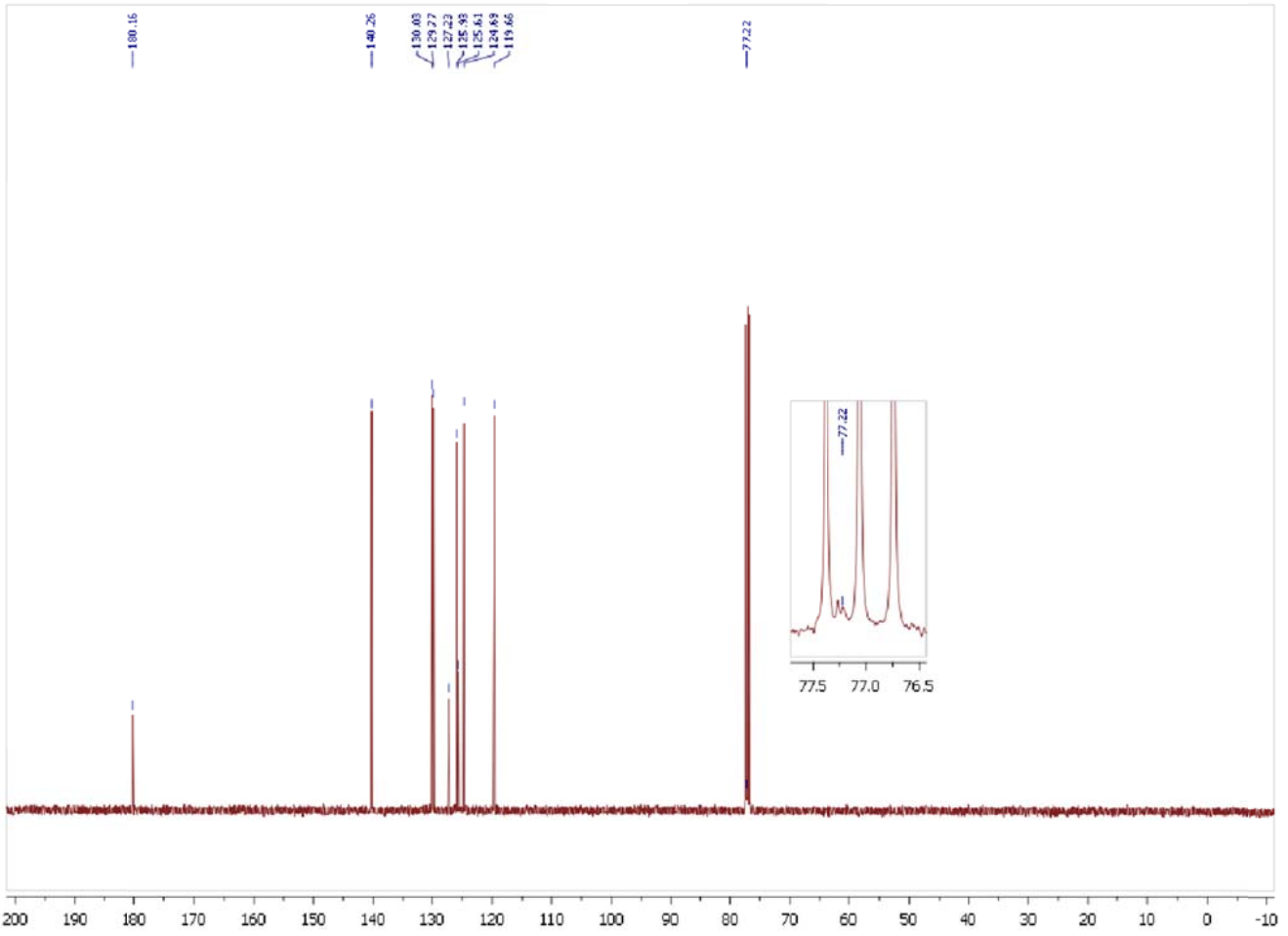
N2
O
CN
OEt

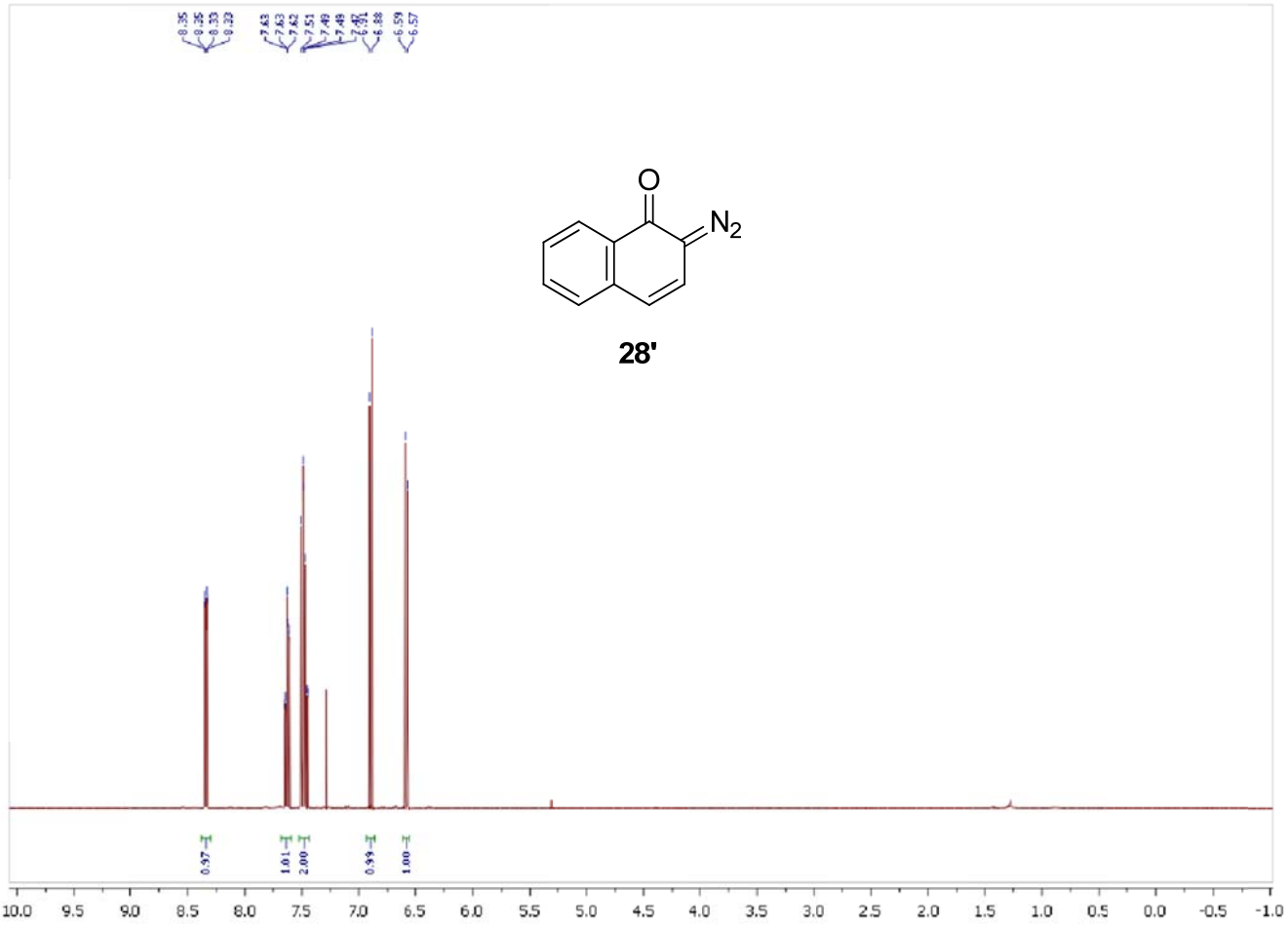
26'

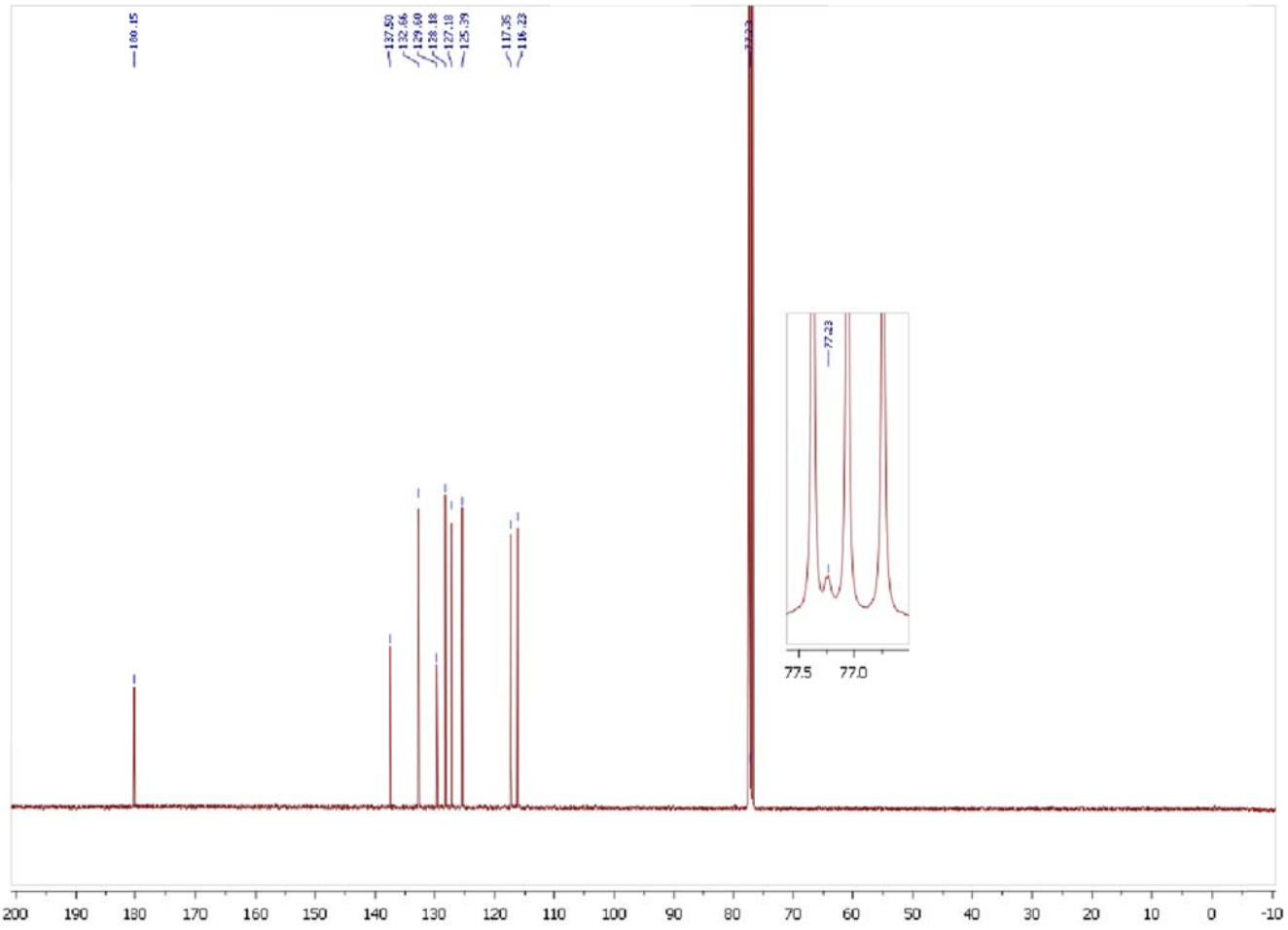

161.21
107.32
63.43
51.06
14.23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

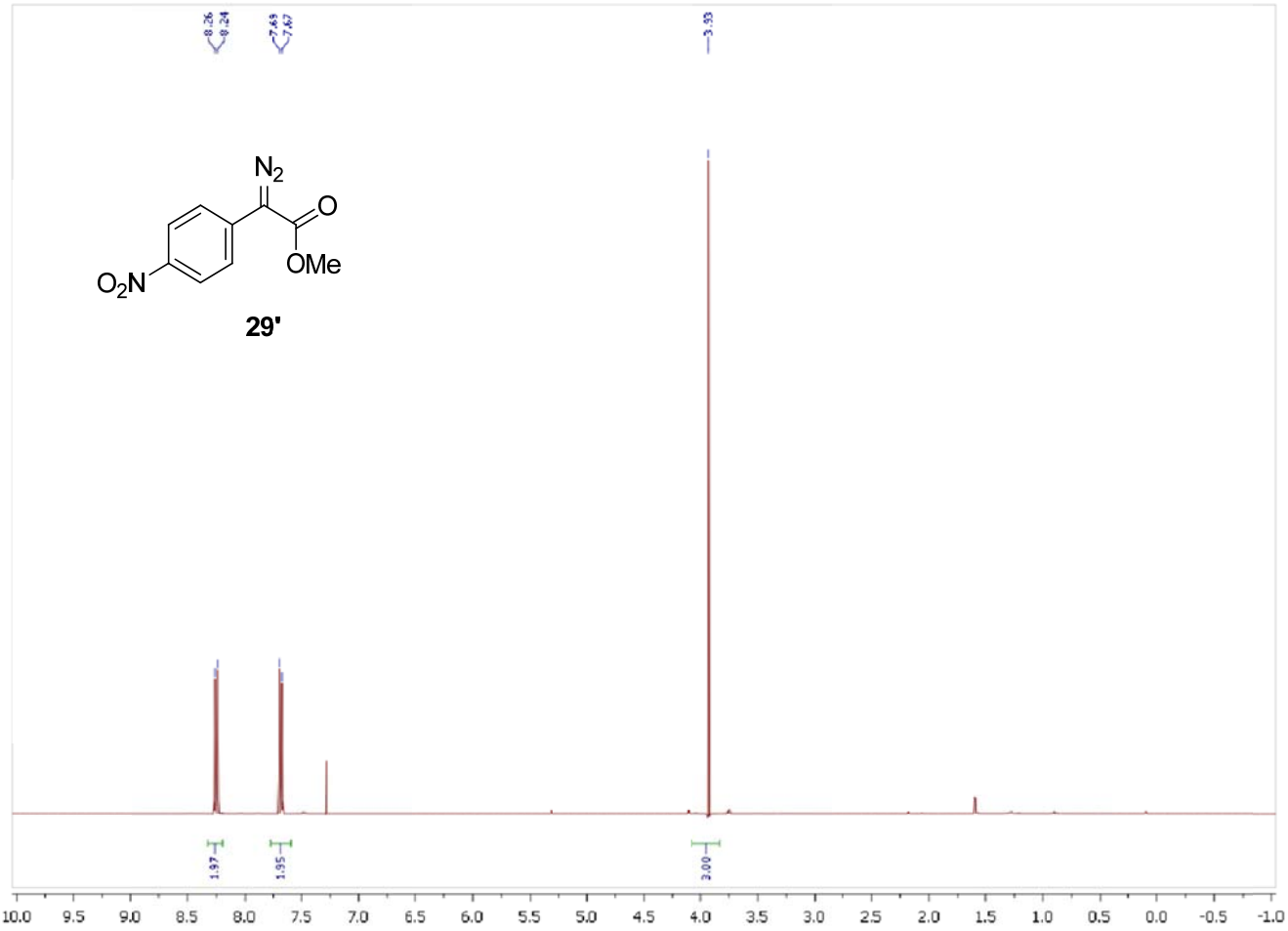

7.65
7.63
7.60
7.59
7.58
7.54
7.52
7.50
7.30
7.29
7.28
7.28
7.27
7.26
6.68
6.65
N2
O
1.03
1.01
1.02
2.12
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

27'

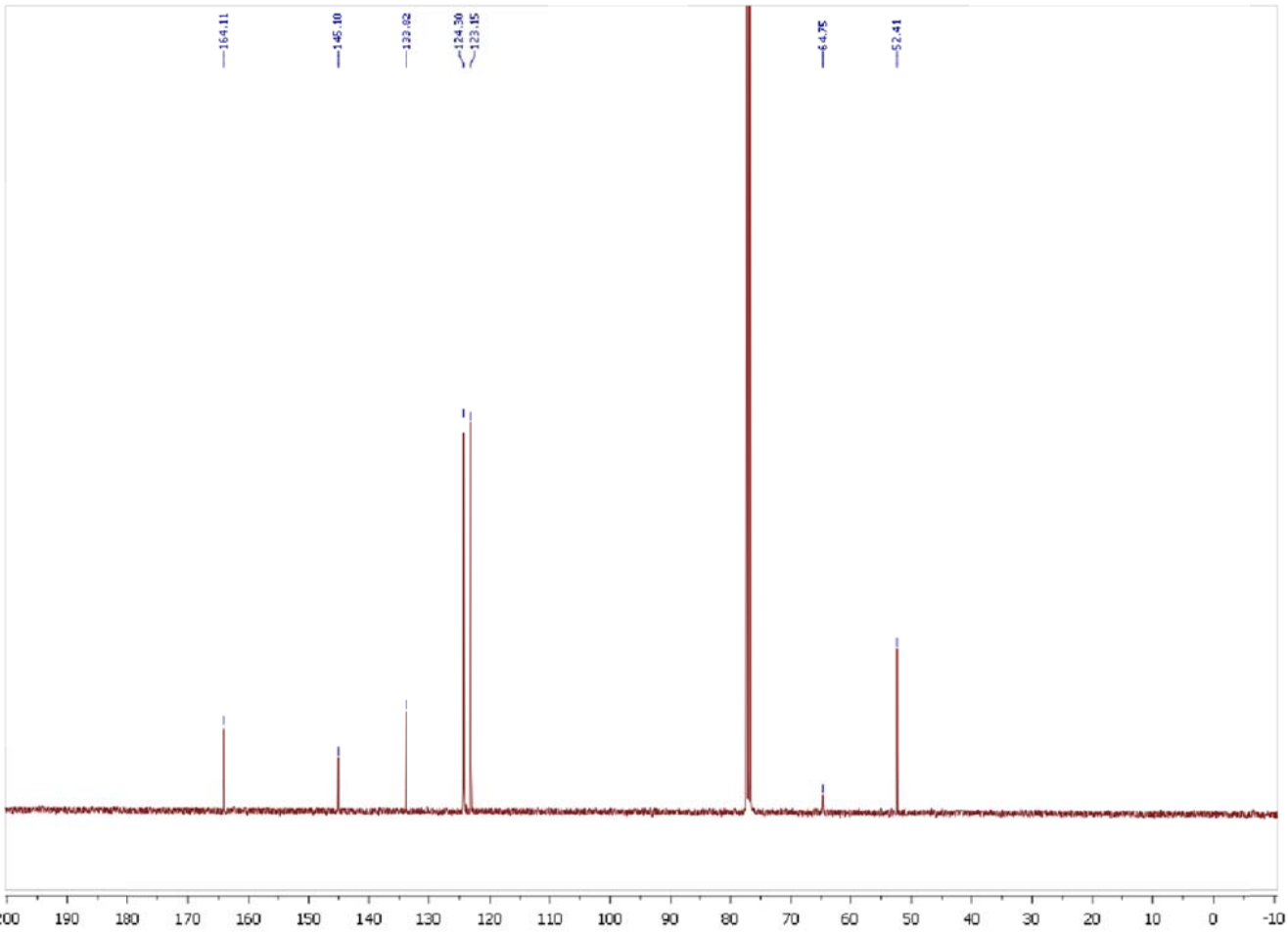

180.16
140.26
130.03
129.77
127.23
125.93
125.61
124.69
119.66
77.22
77.22
77.5
77.0
76.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

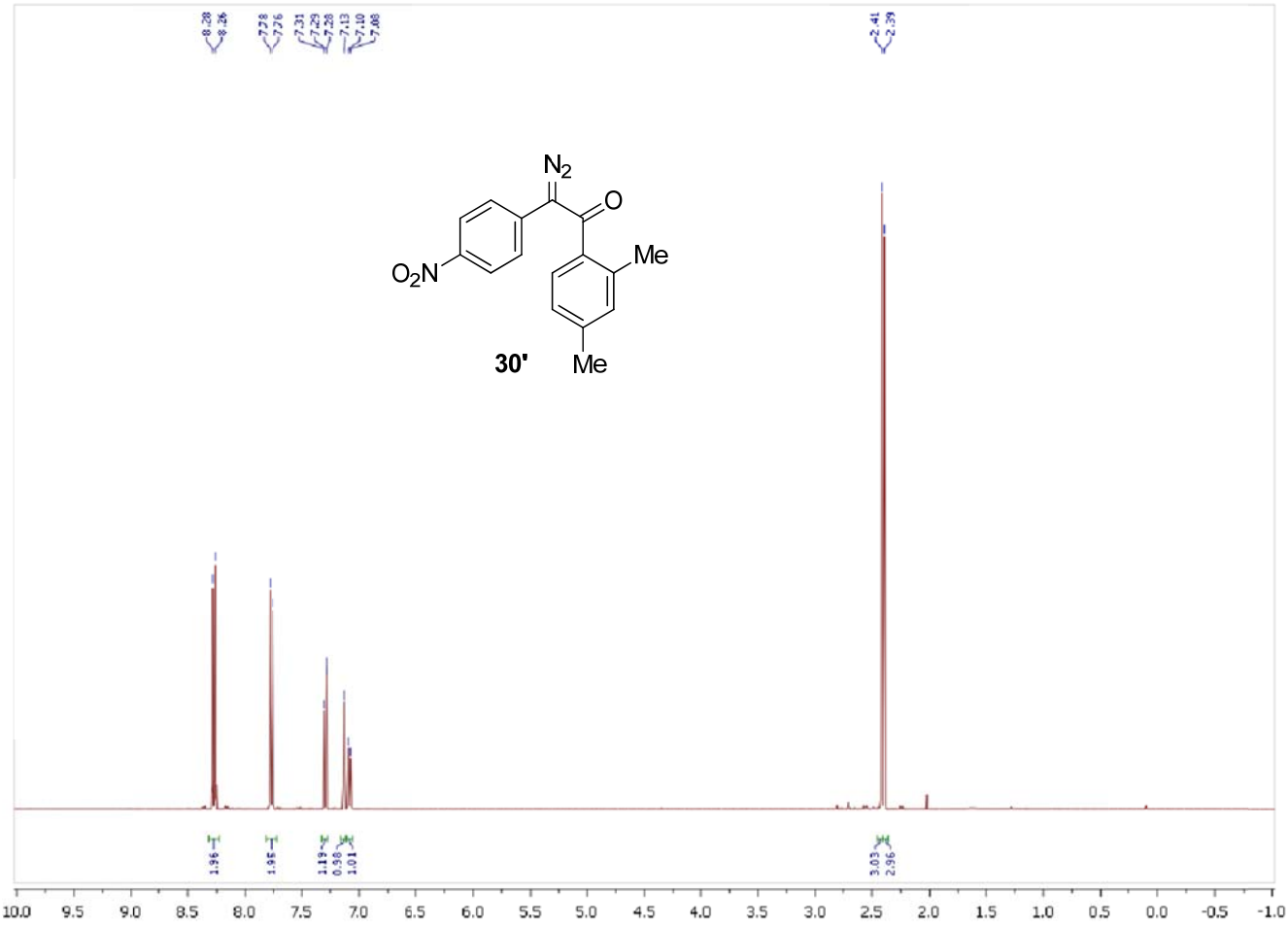

O
N2
28'



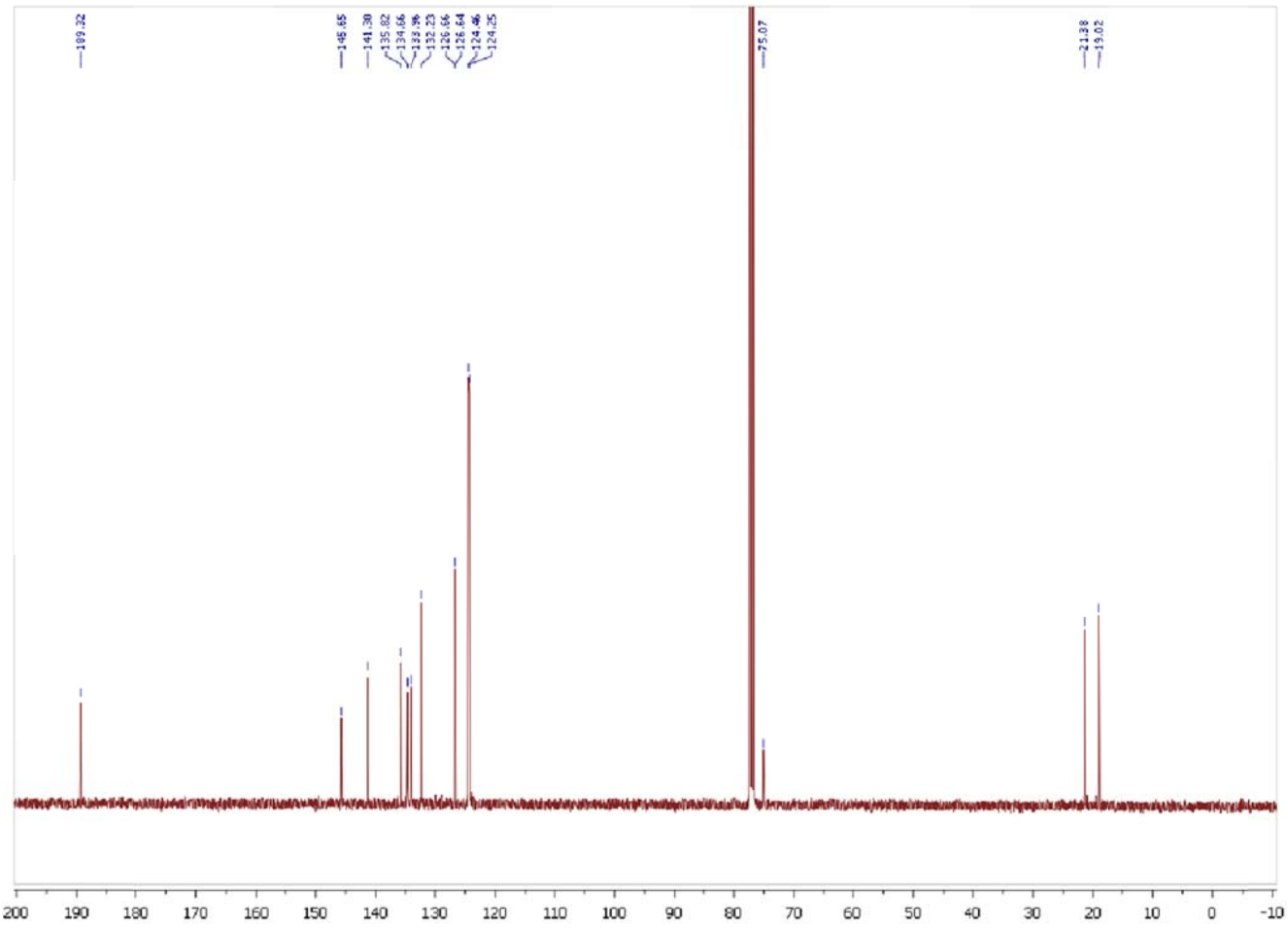

8.26
8.24
7.69
7.67
3.99
N2
O
OMe
O2N
1.97
1.95
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

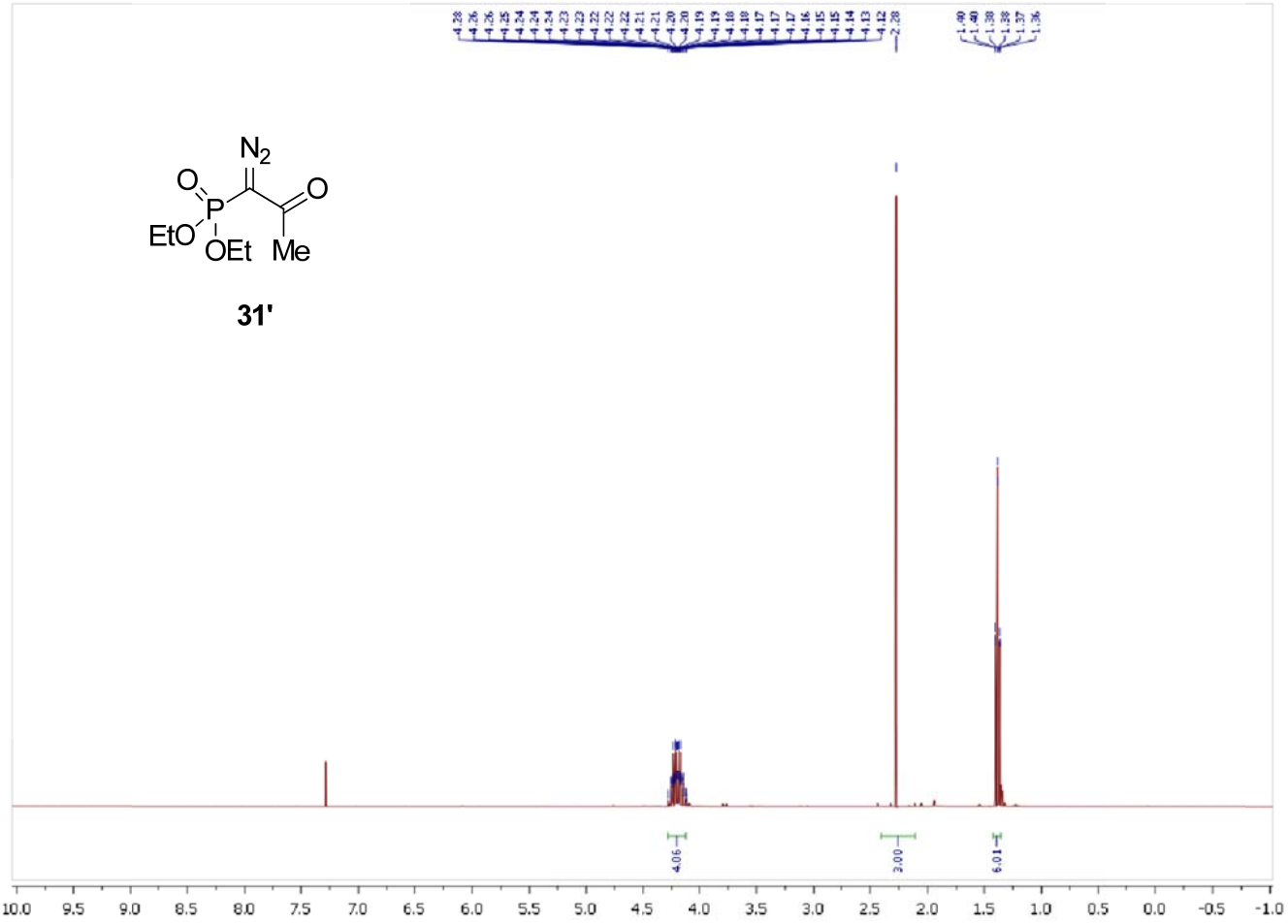
29'


164.11
146.10
133.62
124.30
123.15
64.75
52.41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

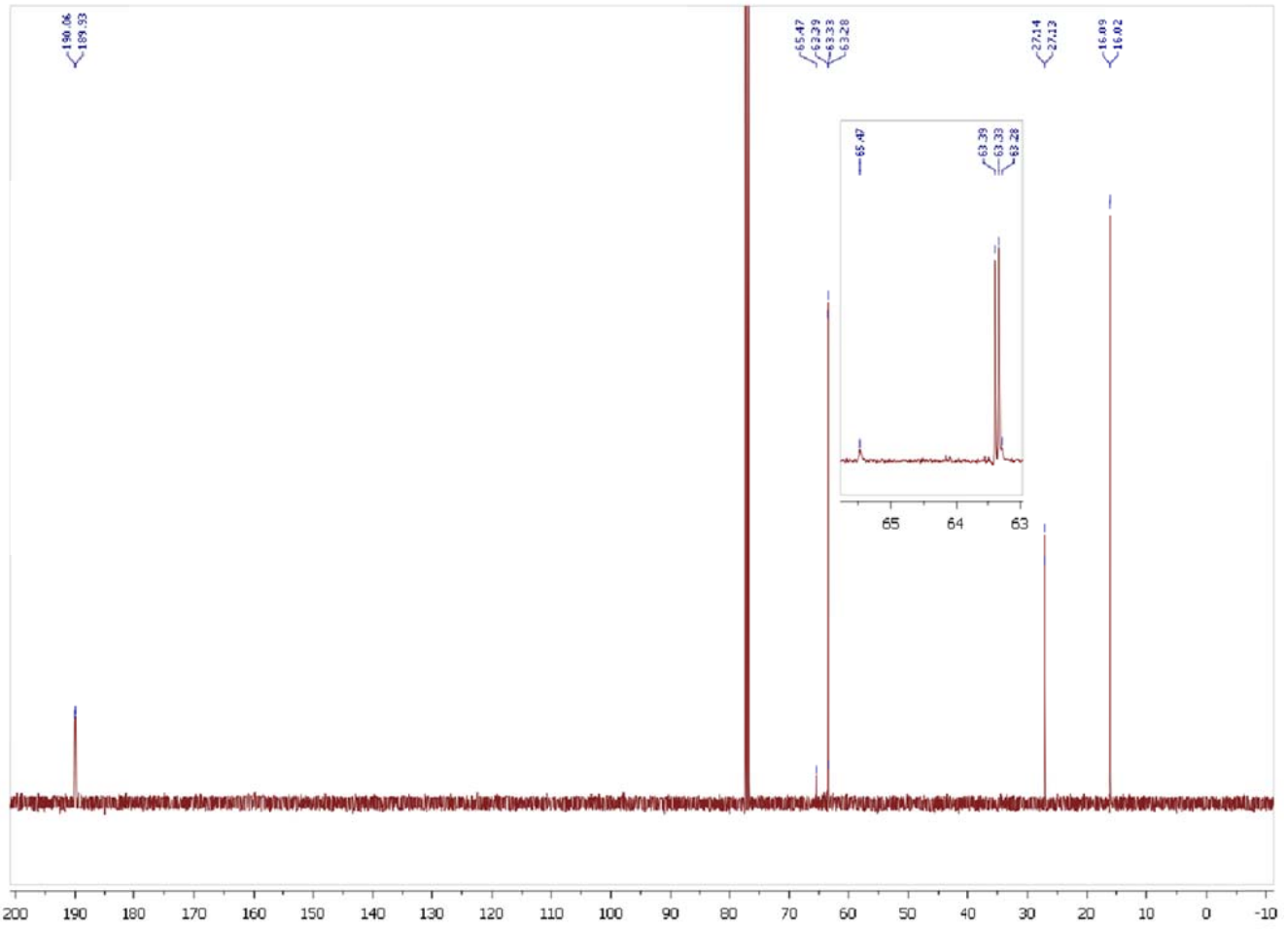

8.28
8.26
7.78
7.76
7.31
7.29
7.28
7.13
7.10
7.08
2.41
2.39
N_2
O
O_2N
Me
Me
1.96
1.96
1.19
0.98
1.01
3.03
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

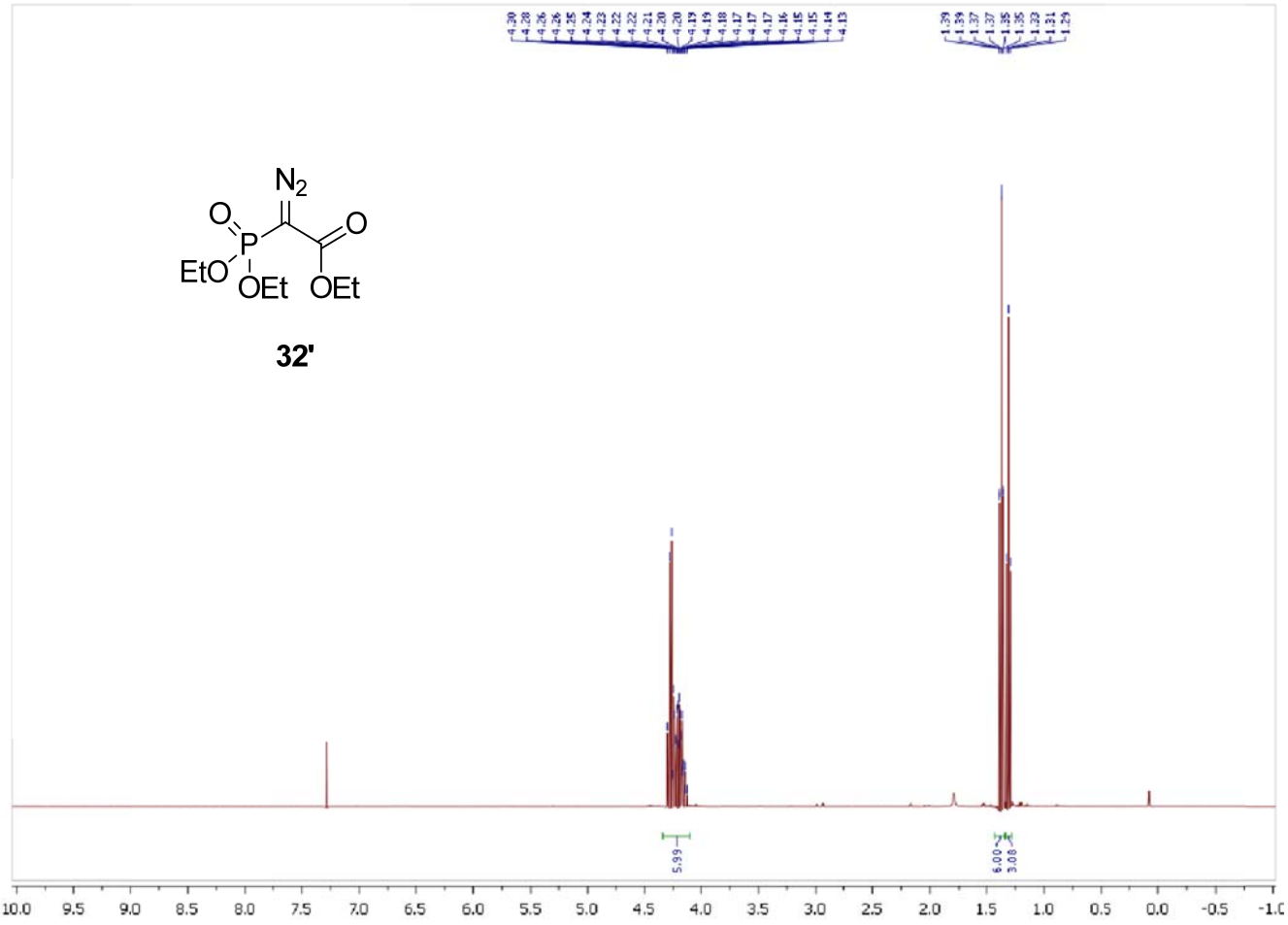
30'

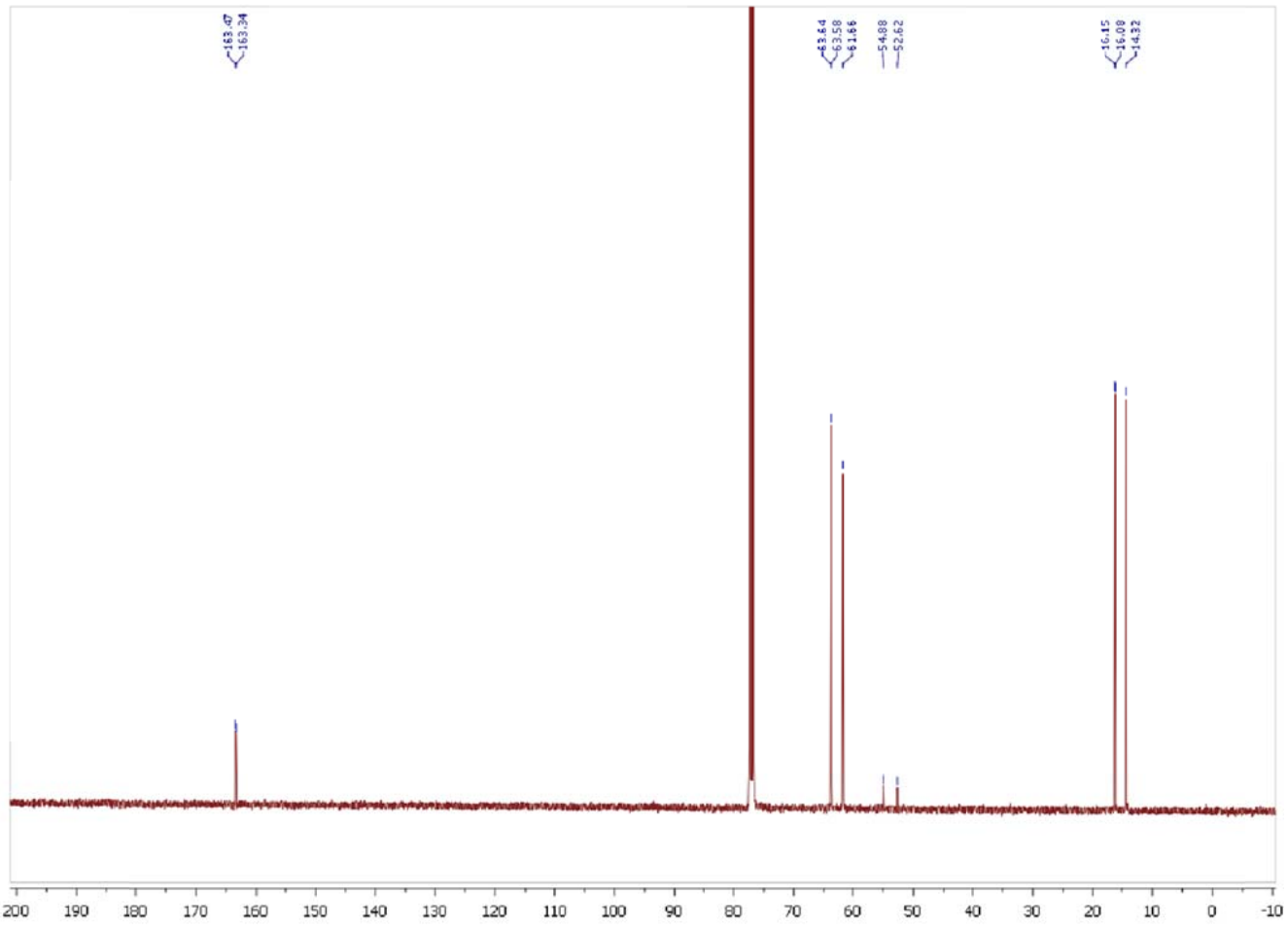

189.22
146.65
141.30
135.82
134.66
133.96
132.23
126.66
126.64
124.46
124.25
75.07
21.88
19.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

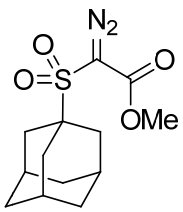


31'



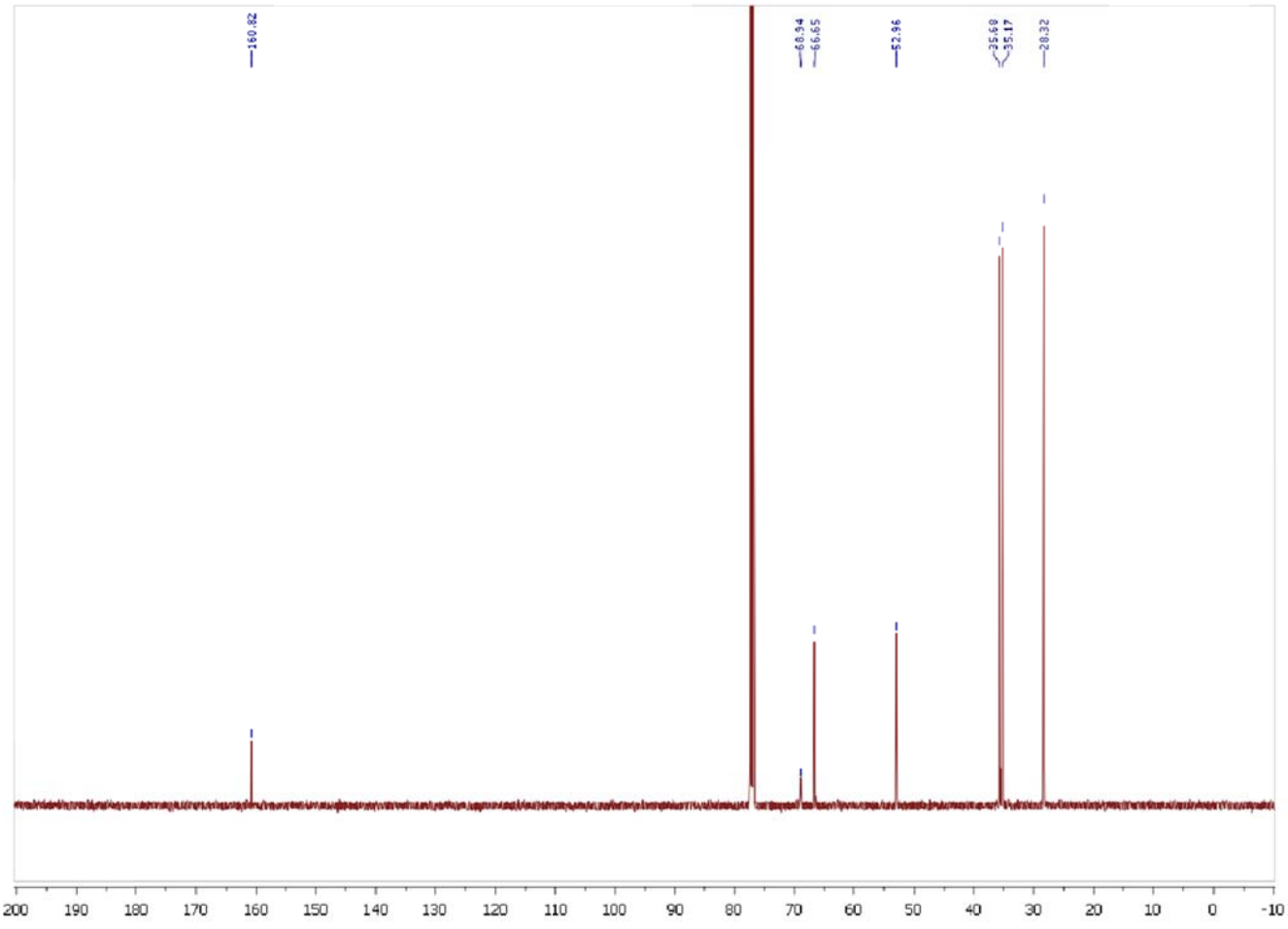

N2
O
P
O
EtO
OEt
OEt
32'

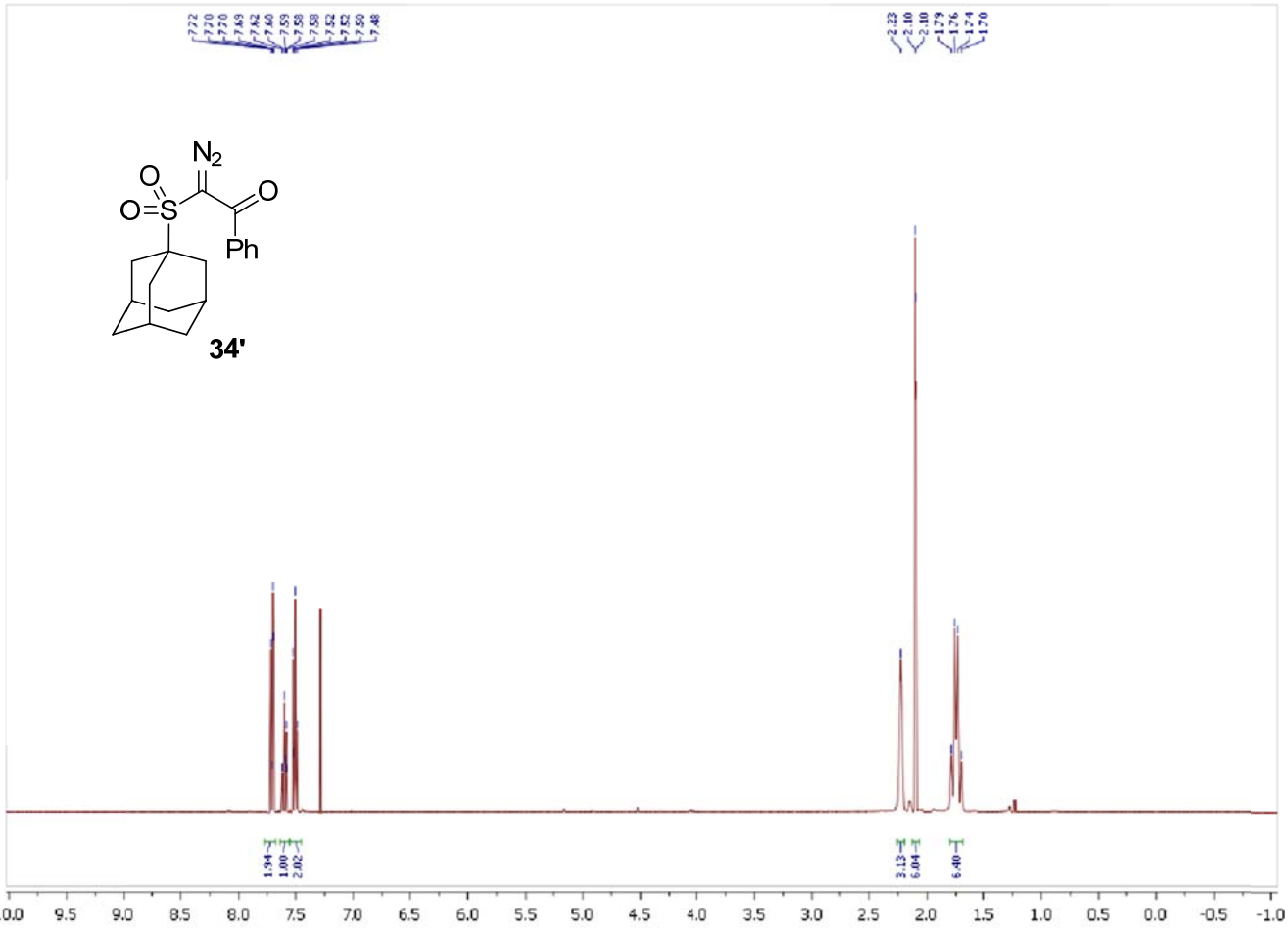


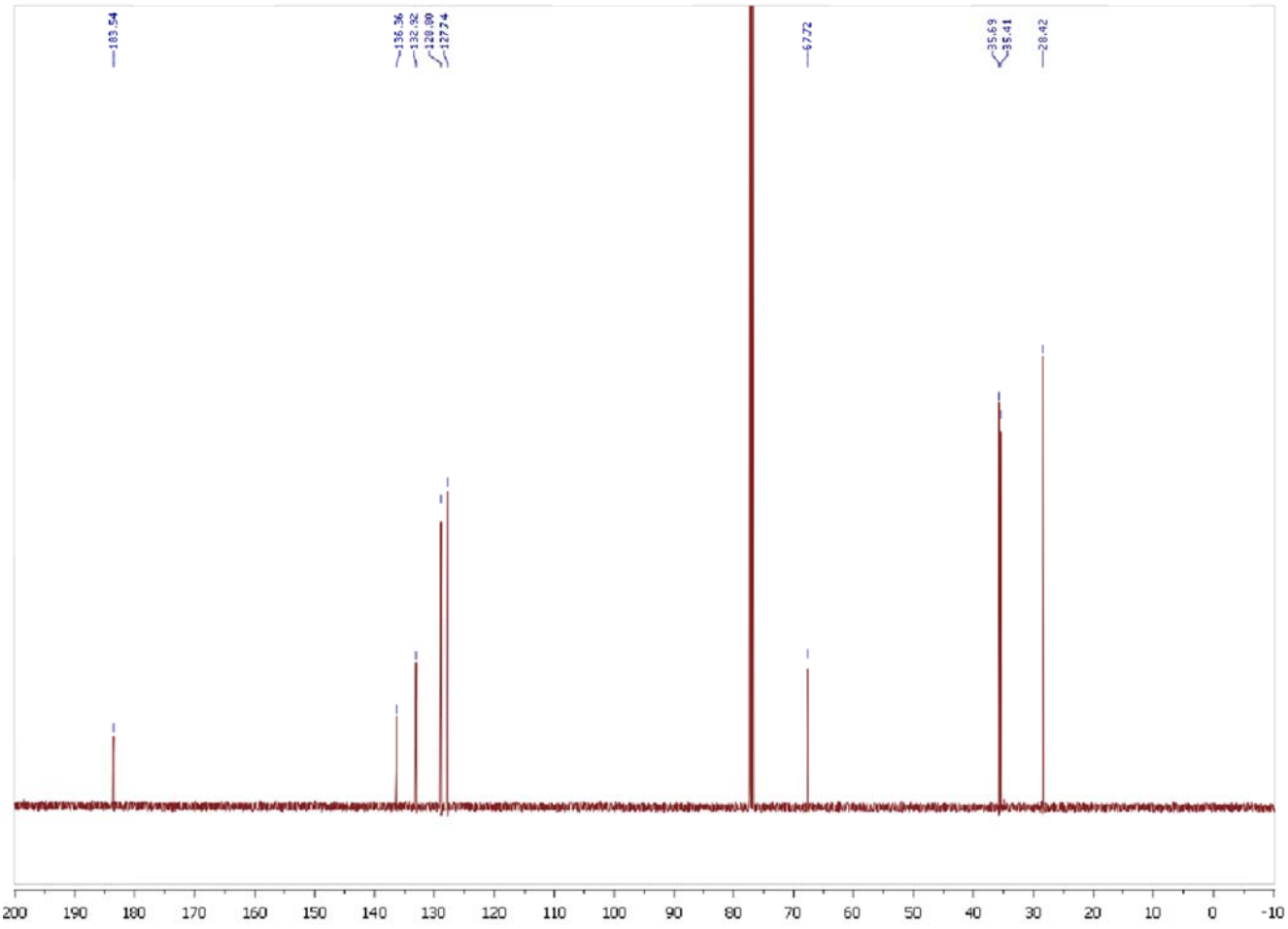

N2
O
O=S
O
OMe

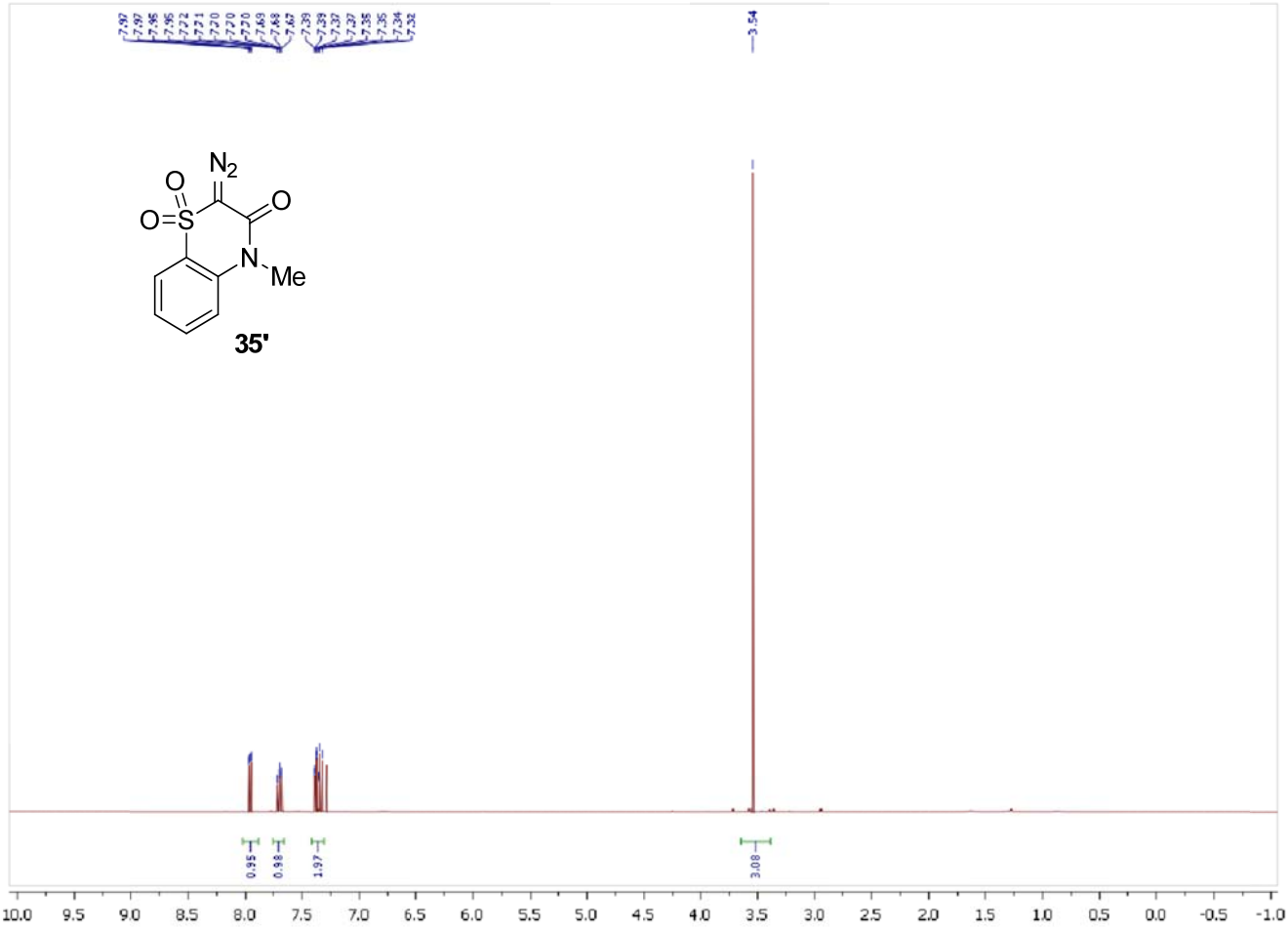
33'

3.87
2.23
2.08
2.07
1.80
1.77
1.74
1.71
2.97
3.04
5.85
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

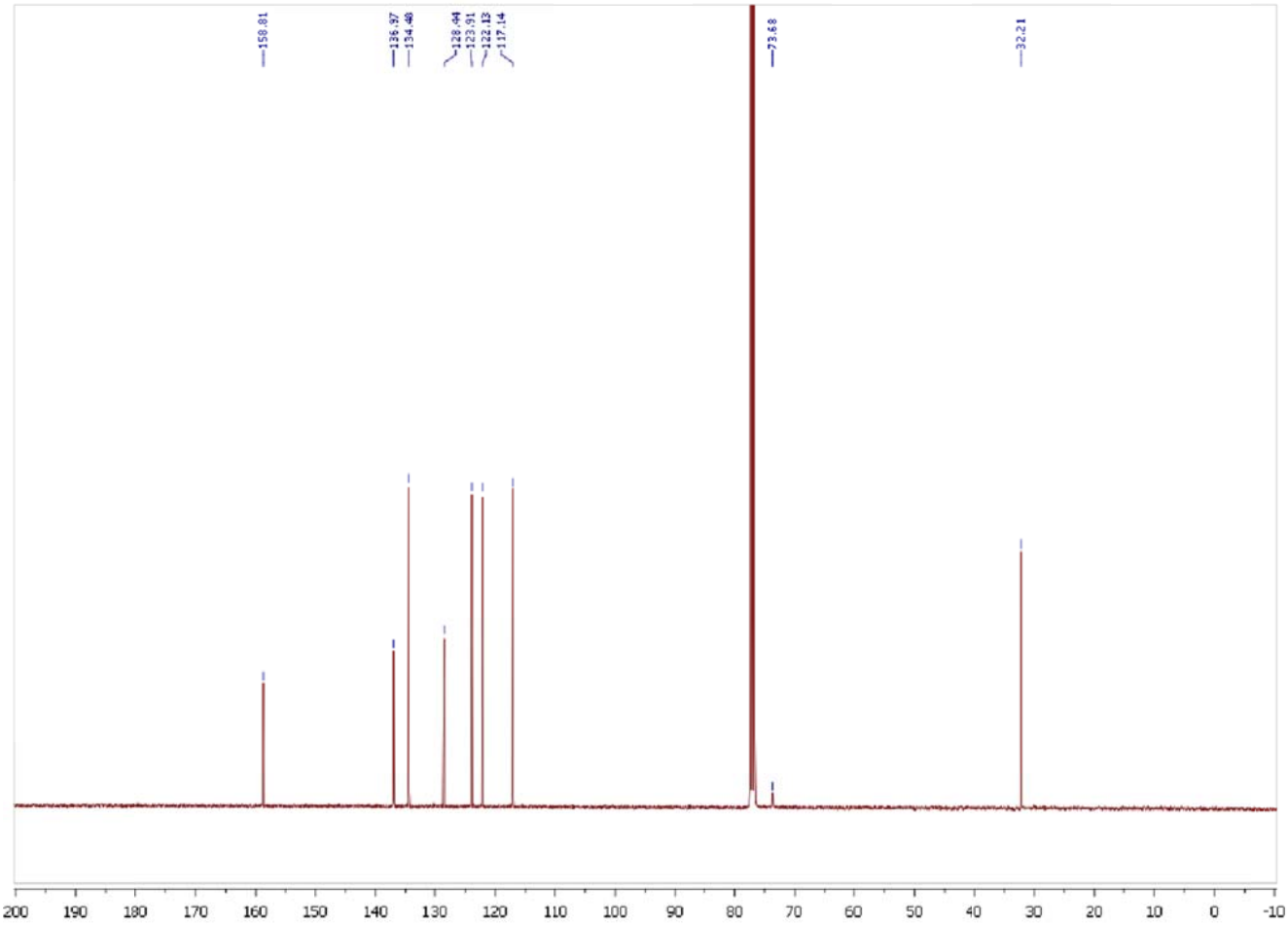

160.82
68.94
66.65
52.96
35.68
35.17
28.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

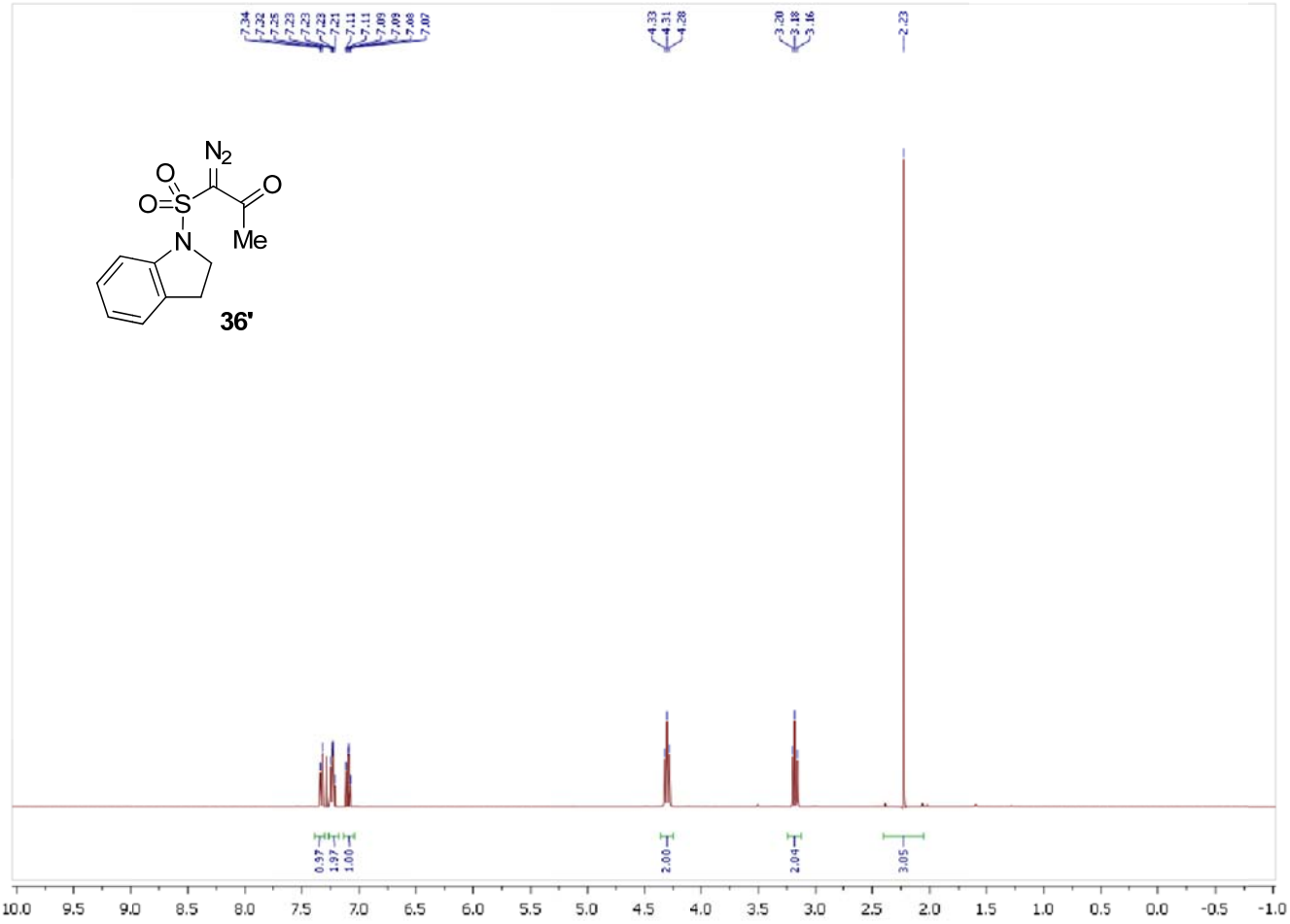

N2
O
O=S
O
Ph
34'



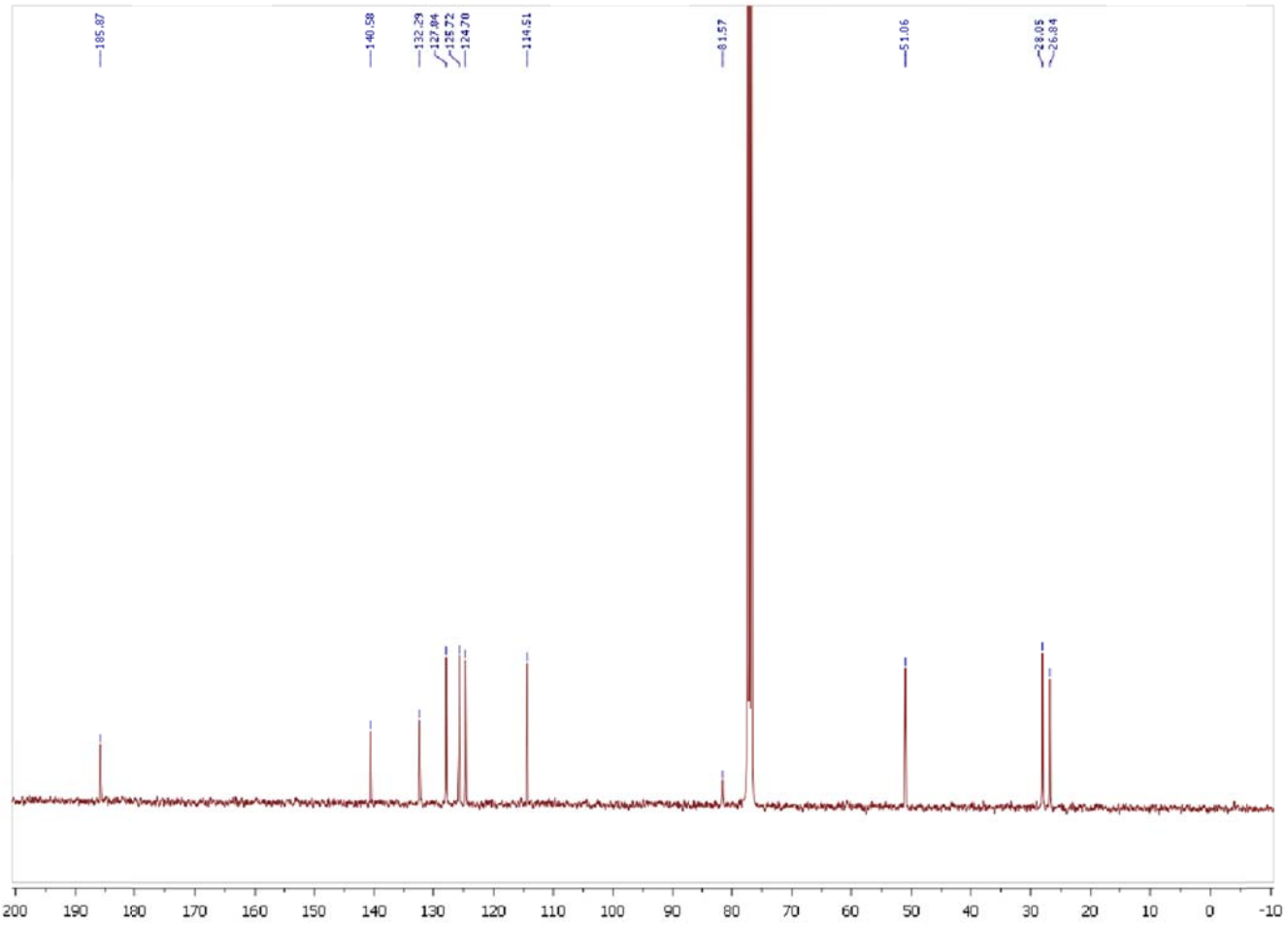

7.97
7.97
7.96
7.95
7.72
7.71
7.70
7.70
7.69
7.68
7.67
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.32
3.54
N2
O
O=S
O
N
Me
0.95
0.88
1.97
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

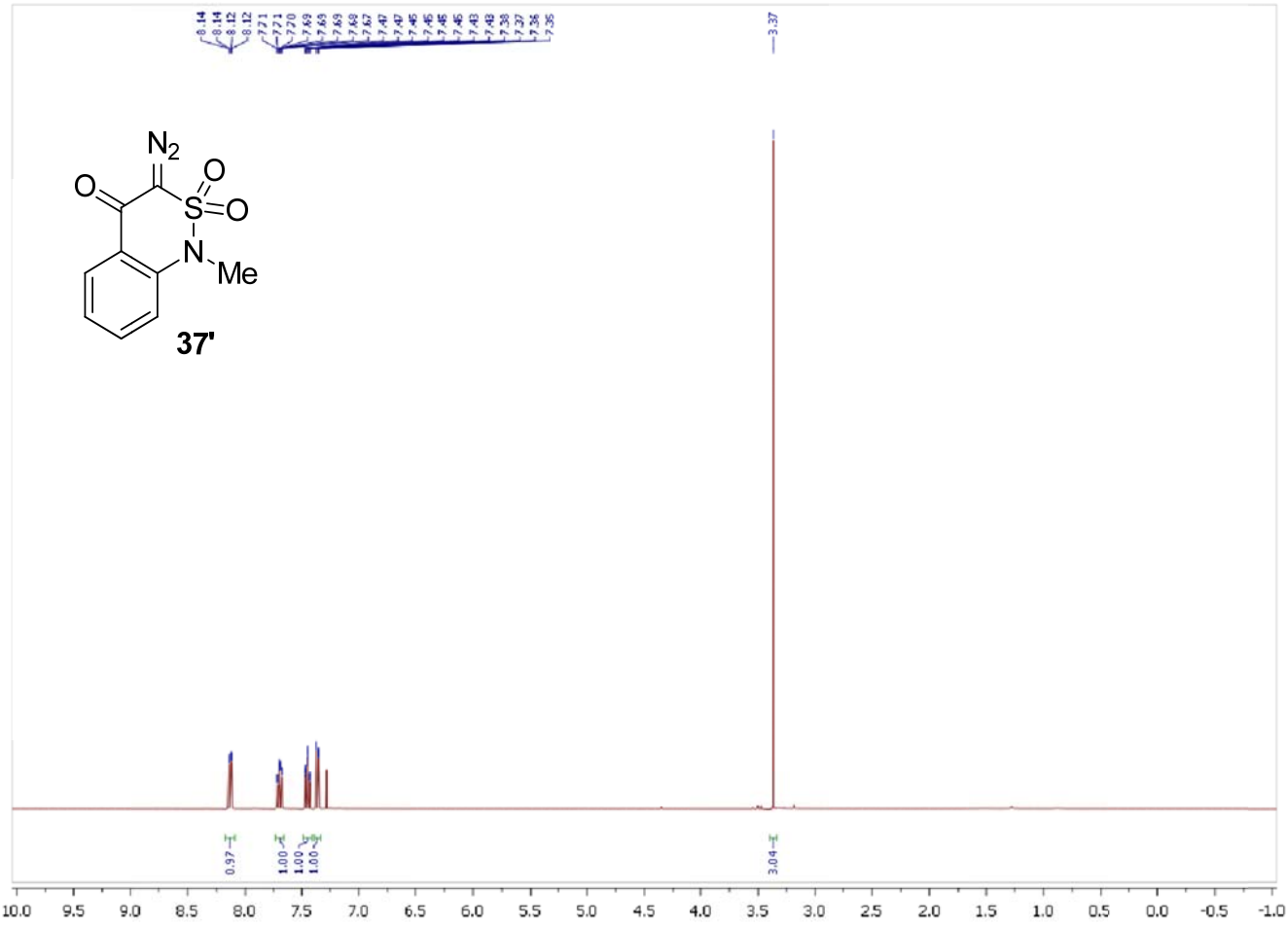
35'

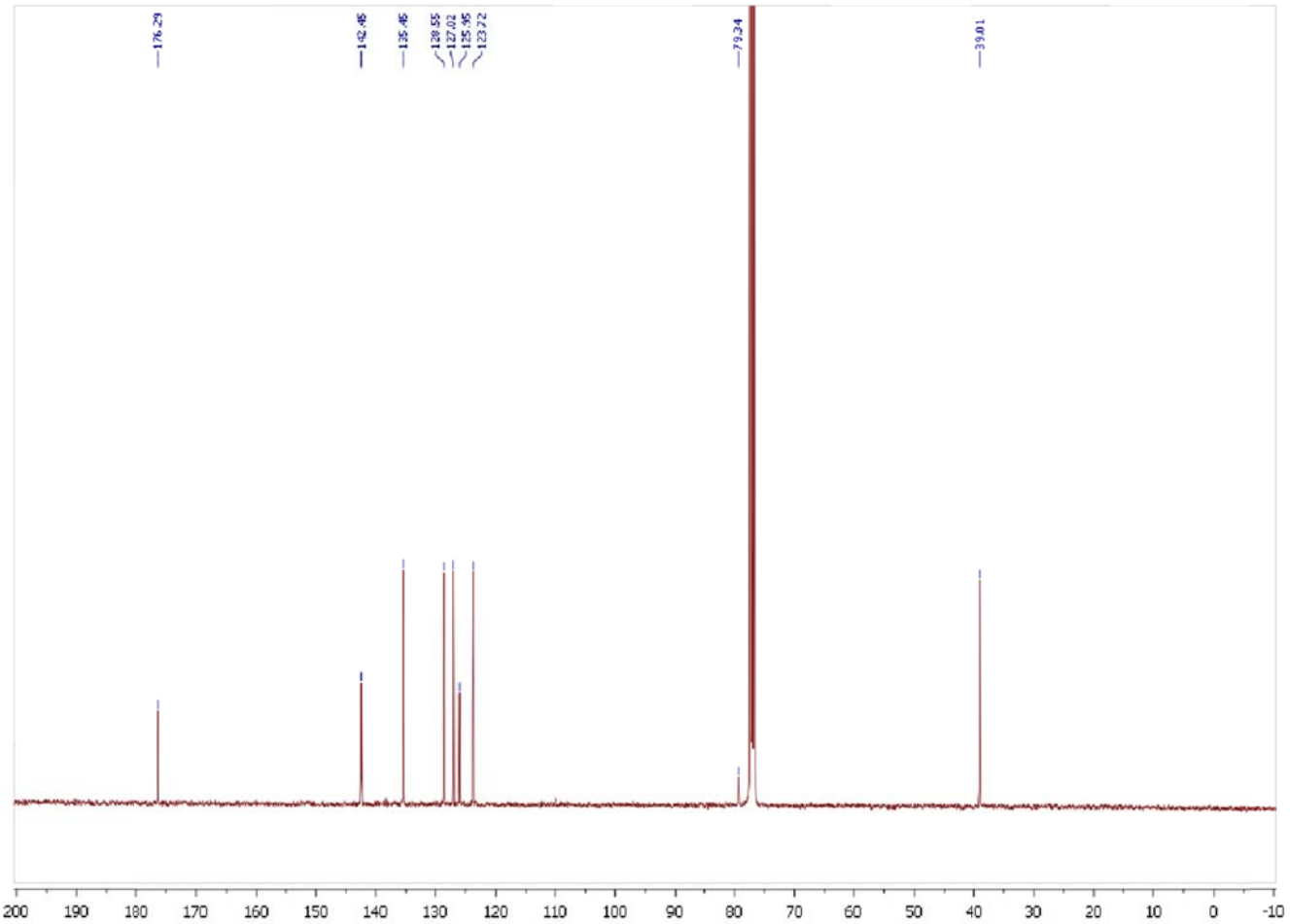

158.81
136.97
134.46
128.44
123.91
122.13
117.14
73.68
32.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

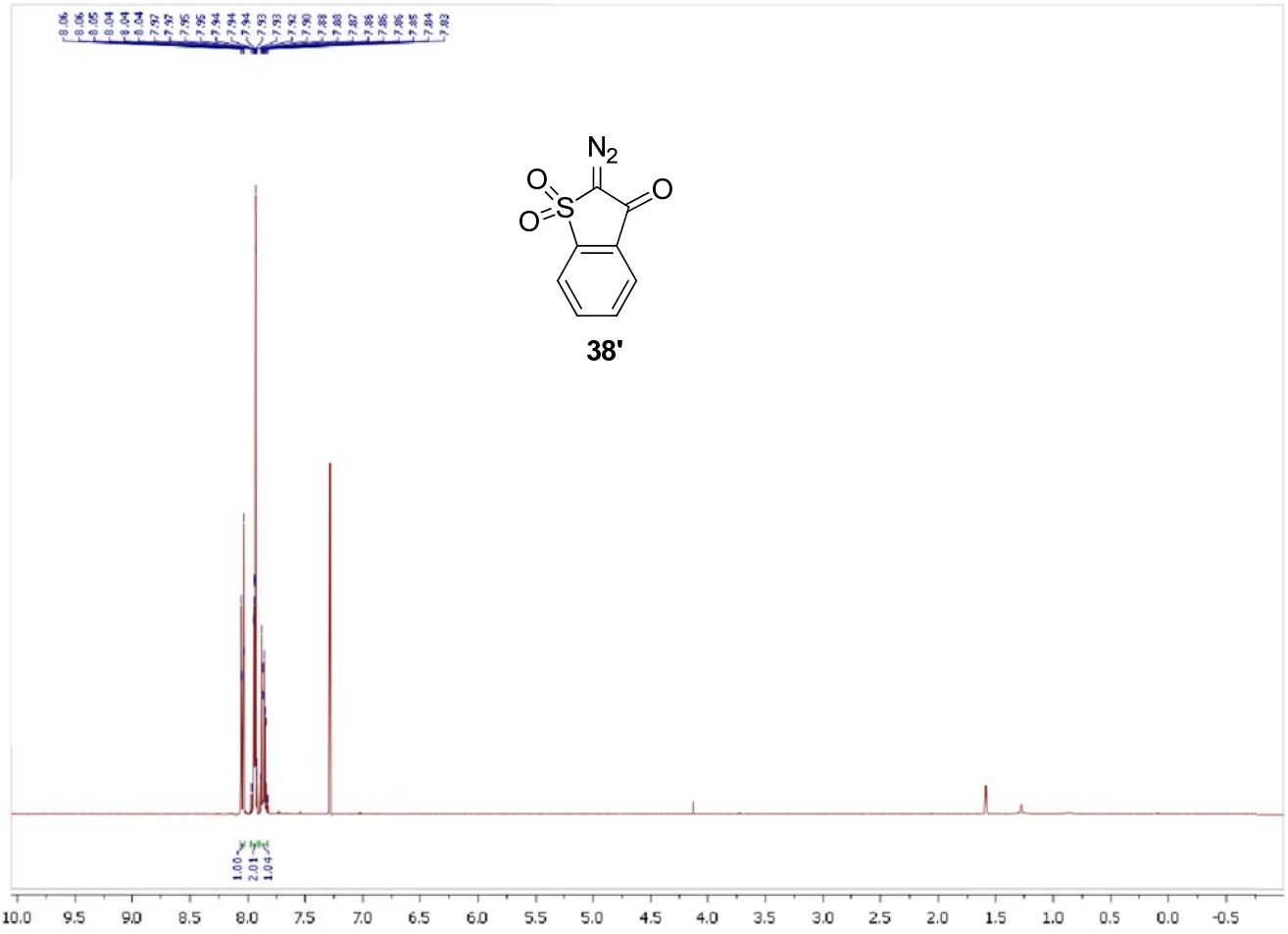

7.34
7.32
7.25
7.23
7.23
7.23
7.23
7.21
7.11
7.11
7.09
7.09
7.08
7.07
4.33
4.31
4.28
3.20
3.18
3.16
2.23
N2
O
O=S
O
N
Me
0.97
1.97
1.00
2.00
2.04
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

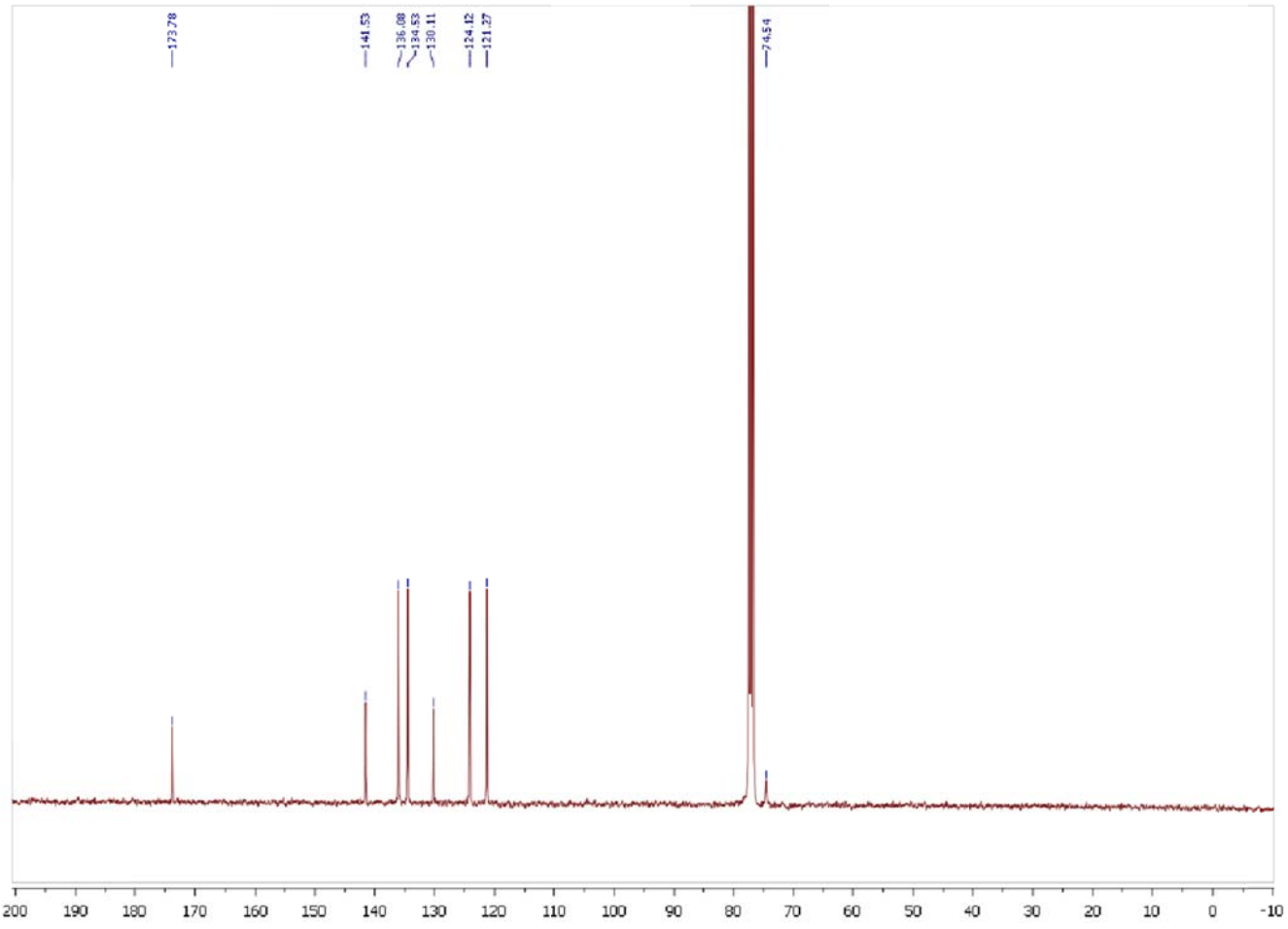
36'

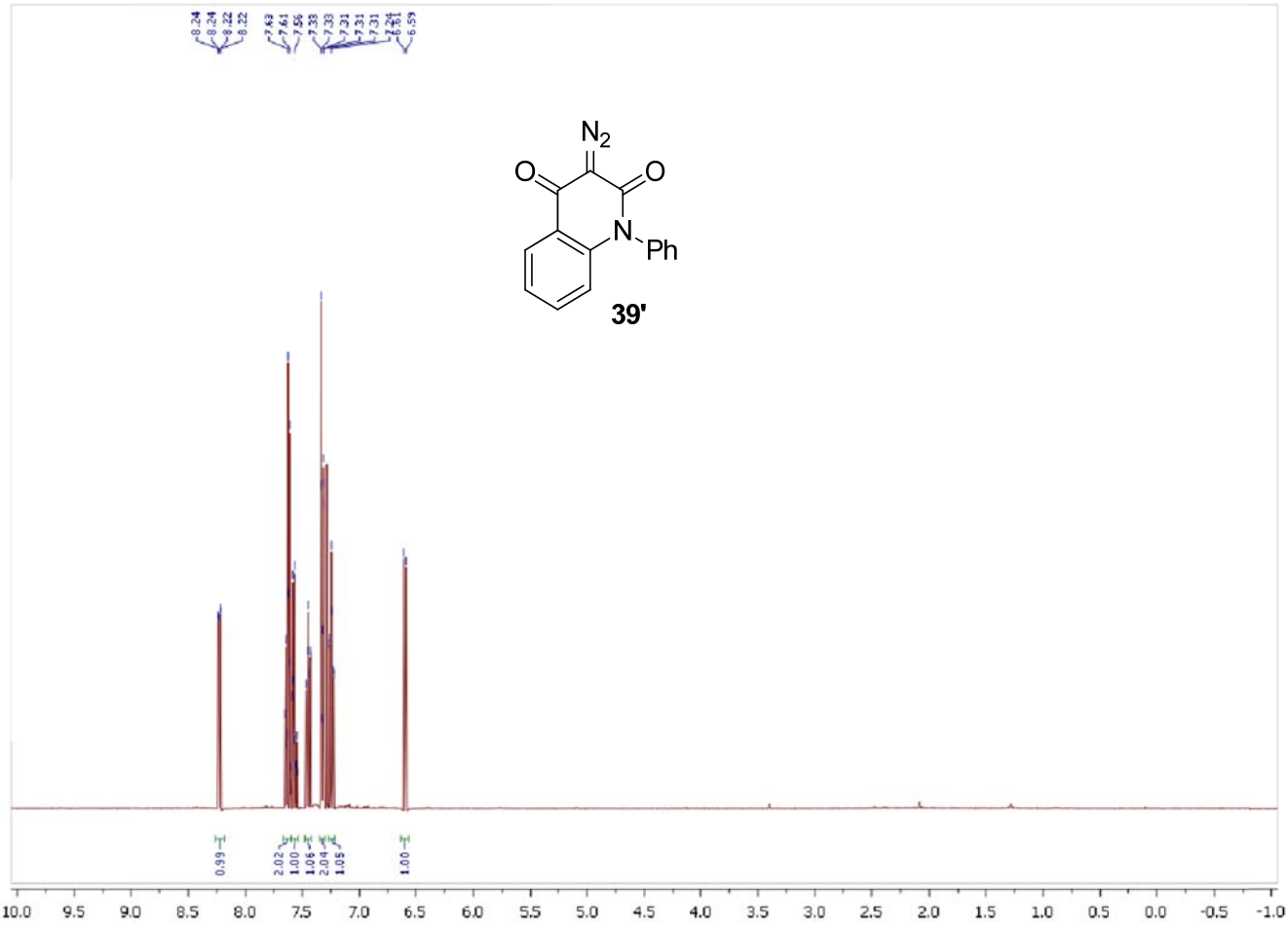

185.87
140.58
132.29
127.84
125.72
124.70
114.51
81.57
51.06
28.05
26.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


N2
O
O
S
O
N
Me
37'

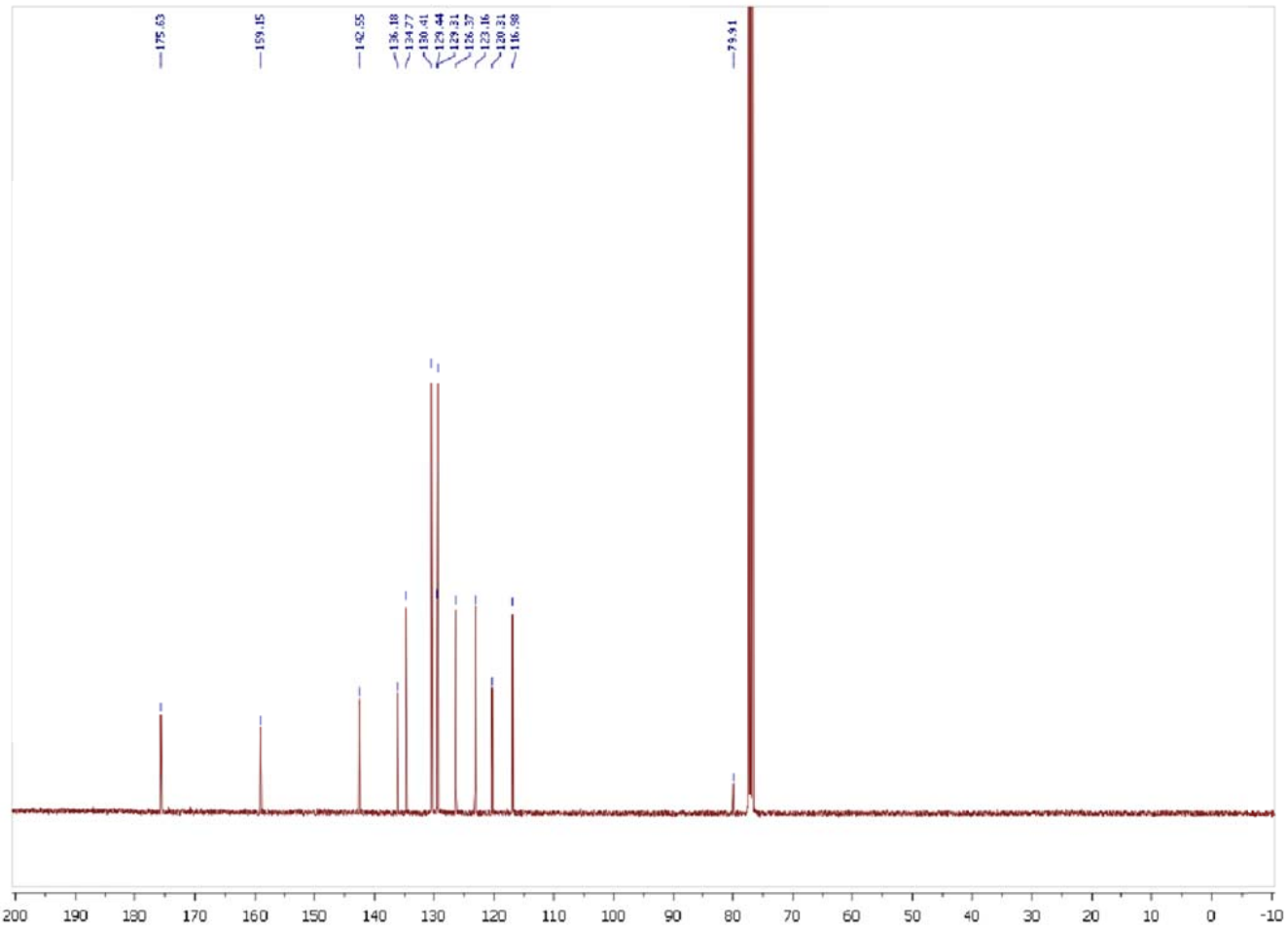


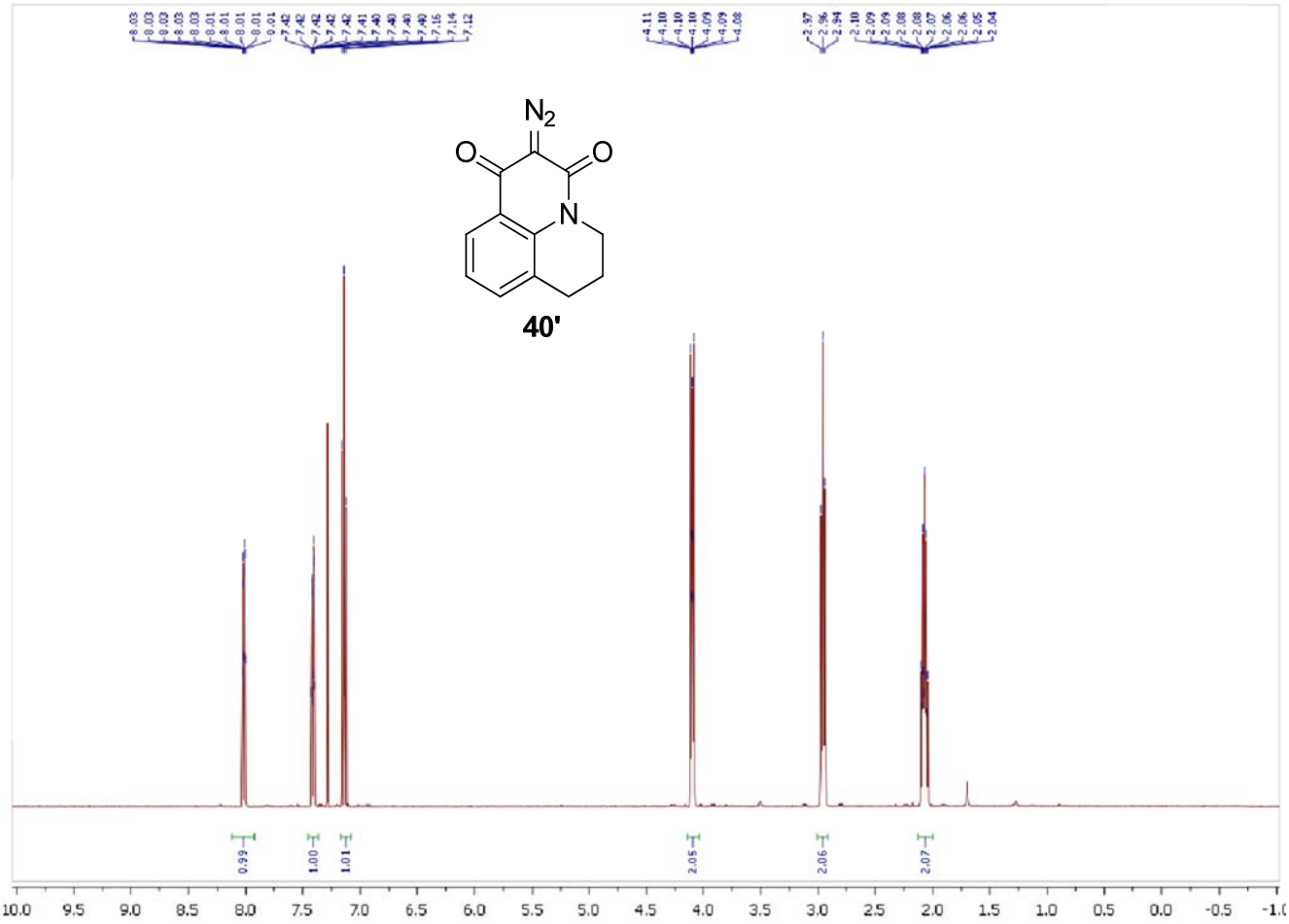

N2
O
O
S
O
38'

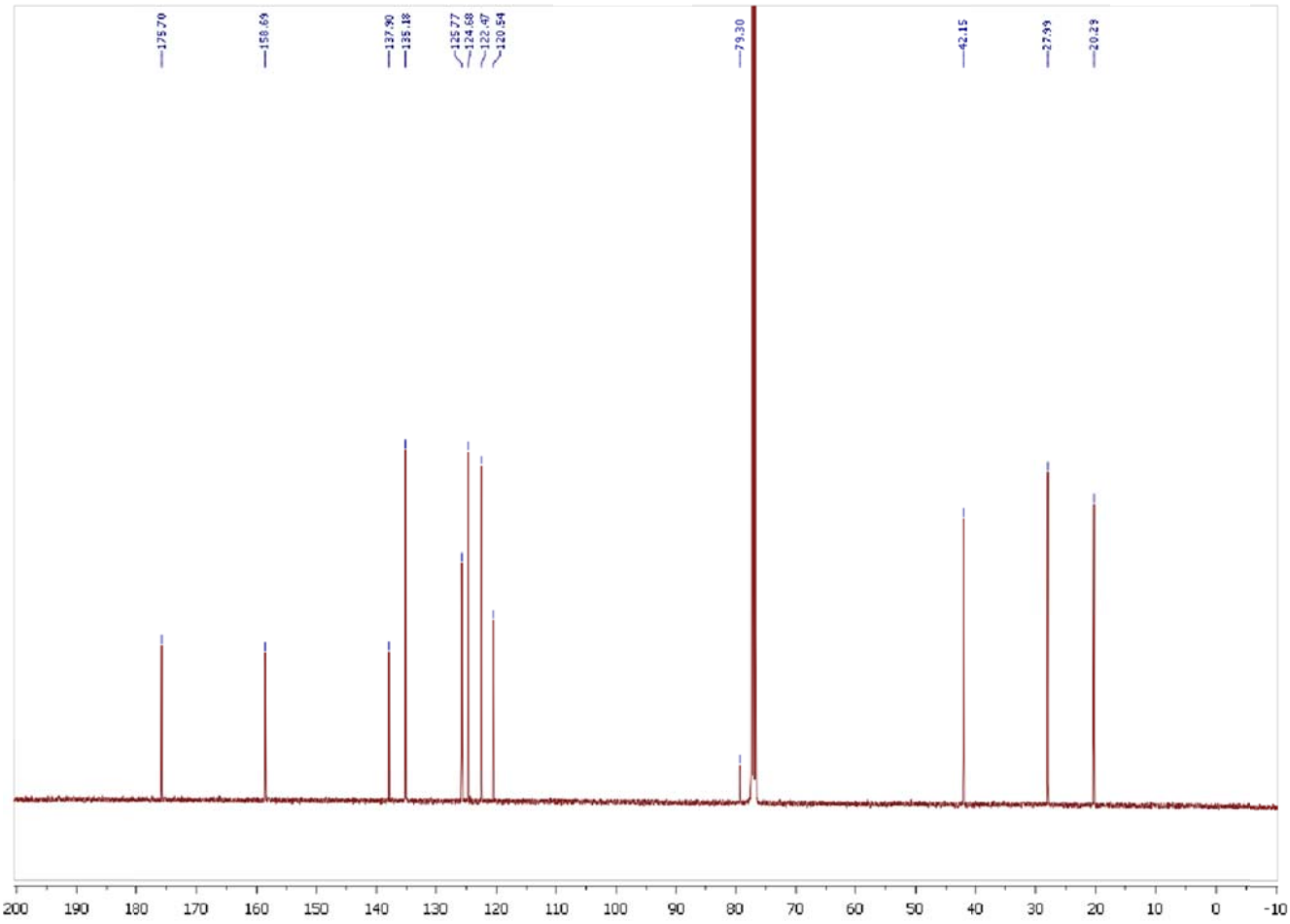


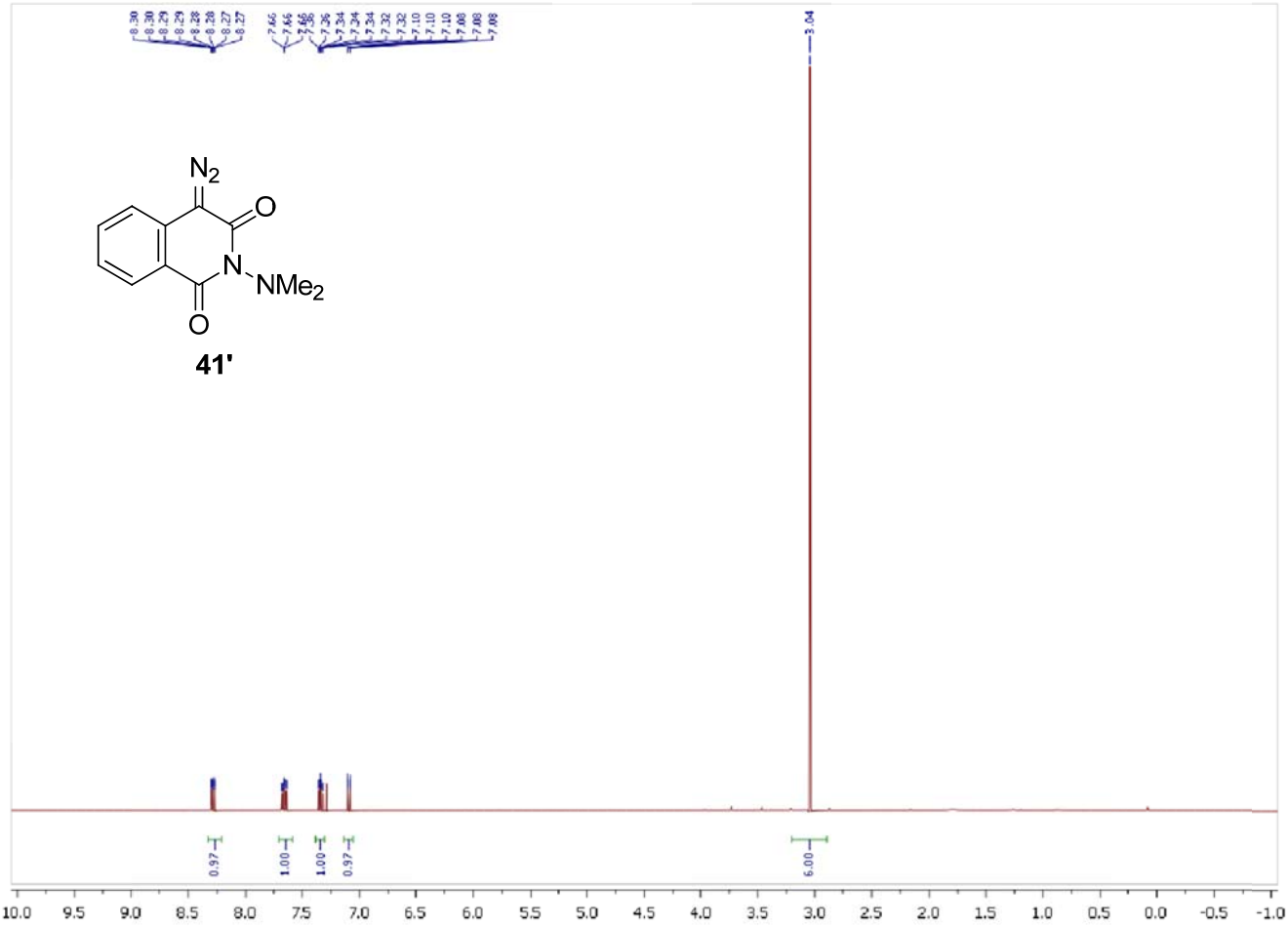

8.24
8.24
8.22
8.22
7.63
7.61
7.56
7.33
7.33
7.31
7.31
7.31
7.31
7.31
6.59
N2
O
O
N
Ph
0.99
2.02
1.00
1.06
2.04
1.05
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

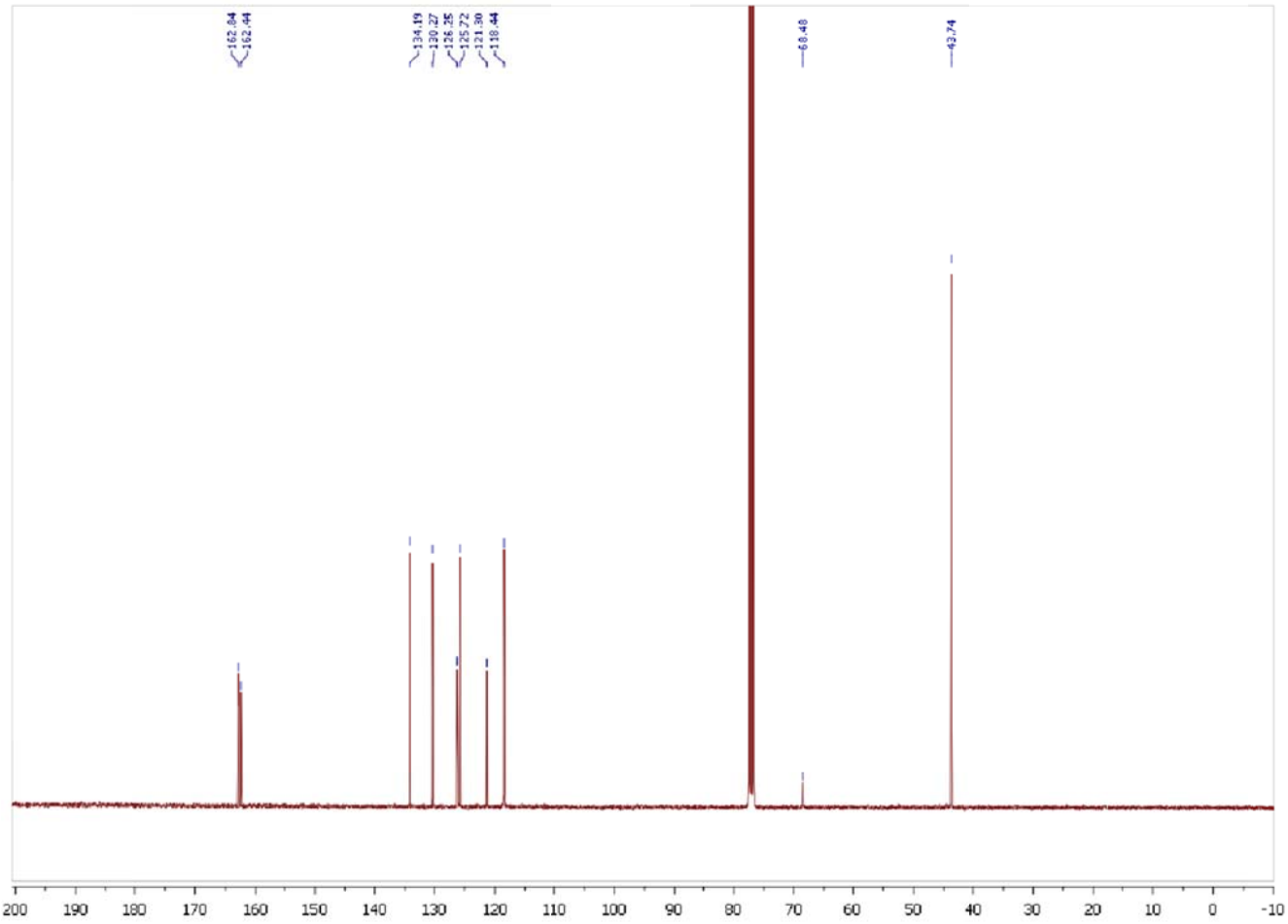
39'

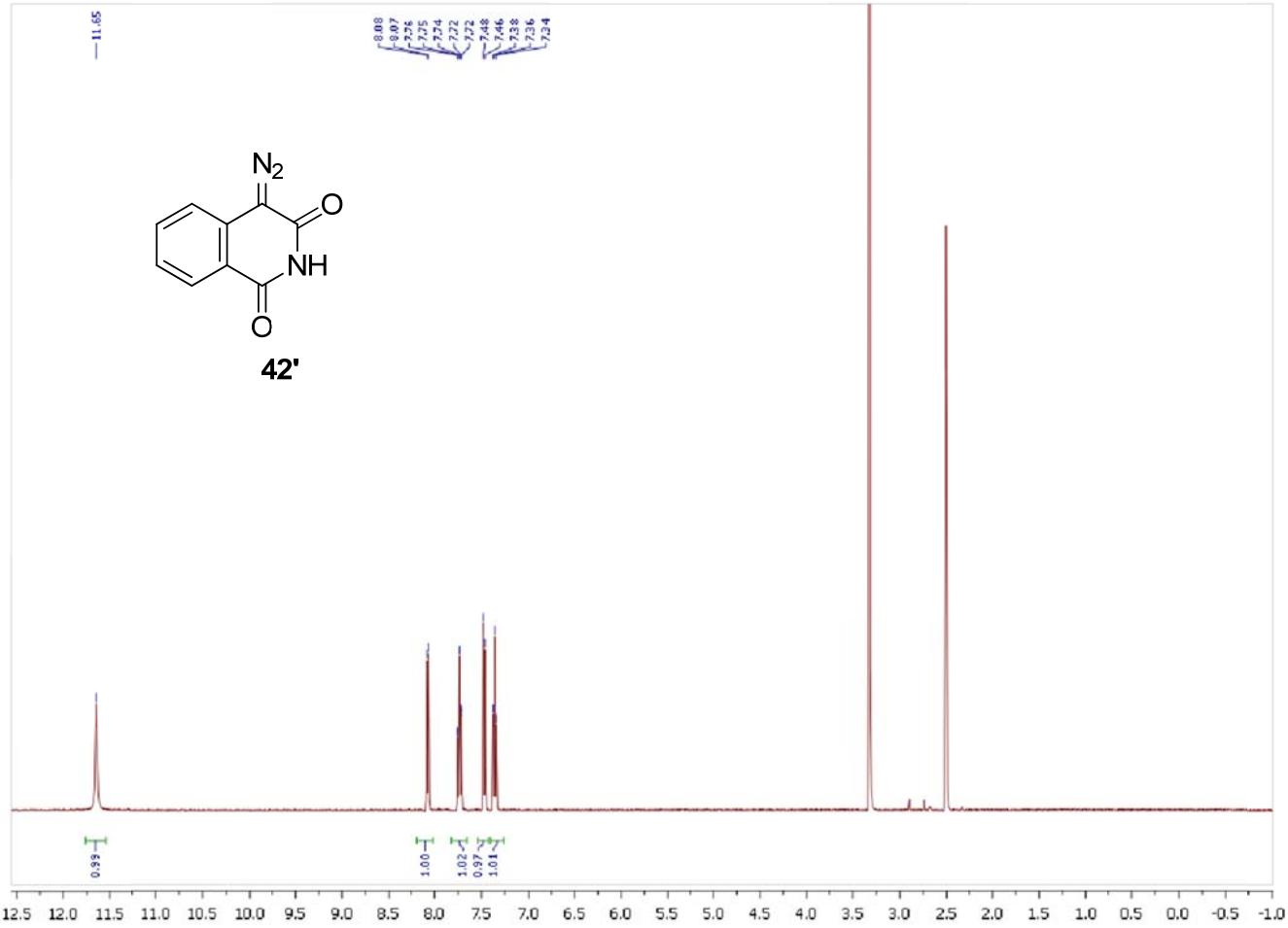

175.63
159.15
142.55
136.18
134.77
130.41
129.44
129.31
126.57
123.16
120.31
116.98
79.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


N2
O
O
N
40'

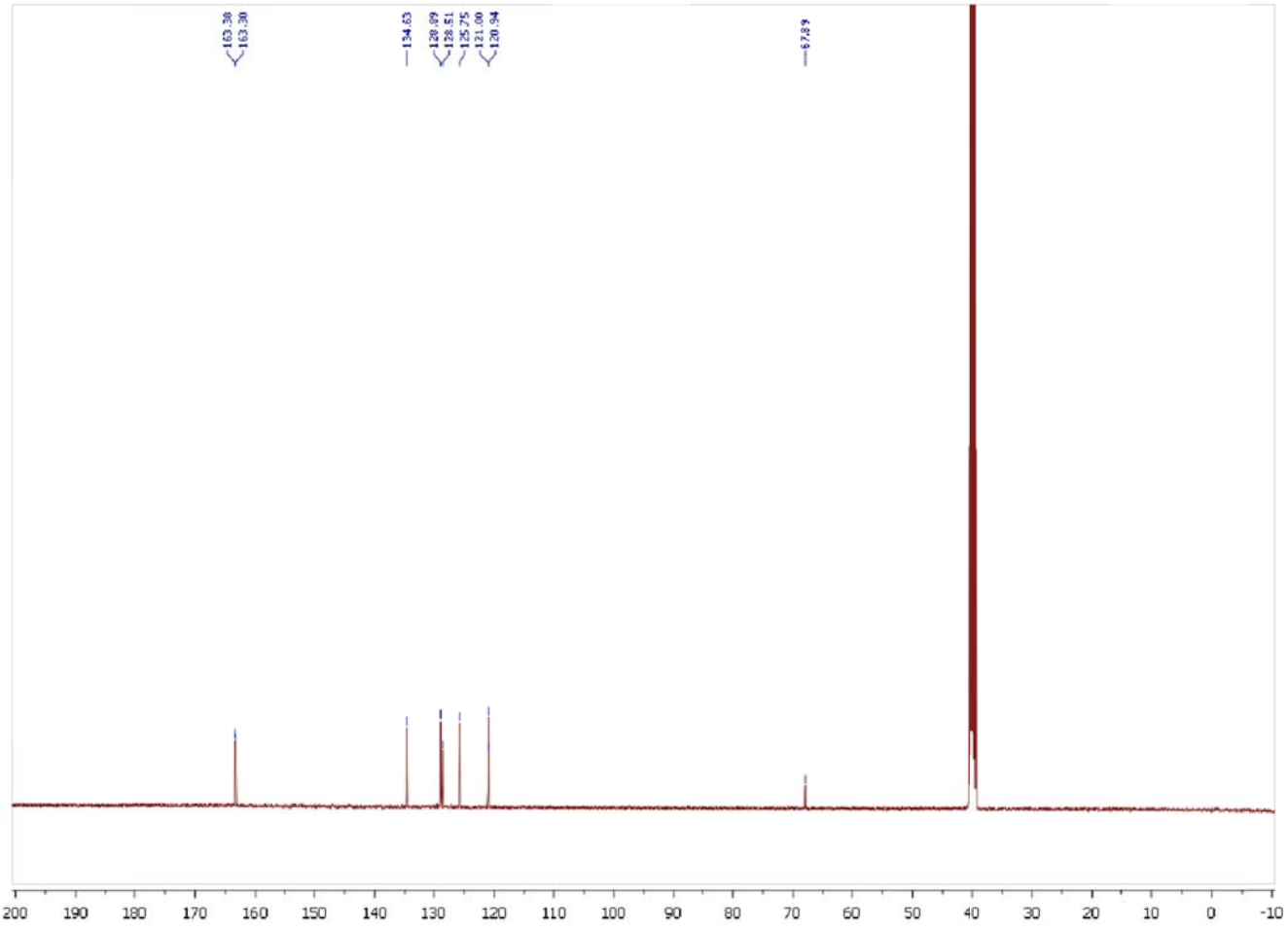


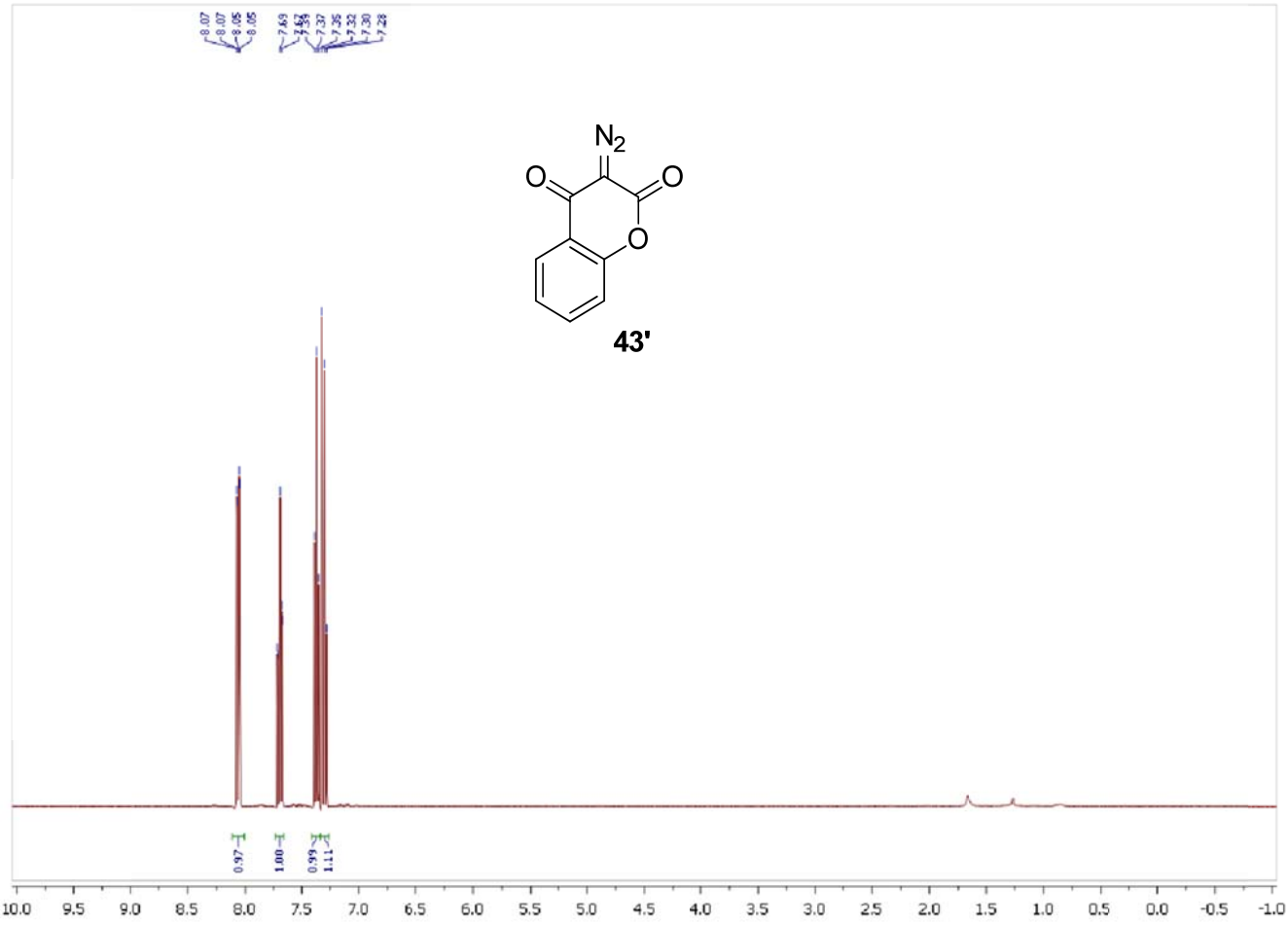

N2
O
N
NMe2
O
41'



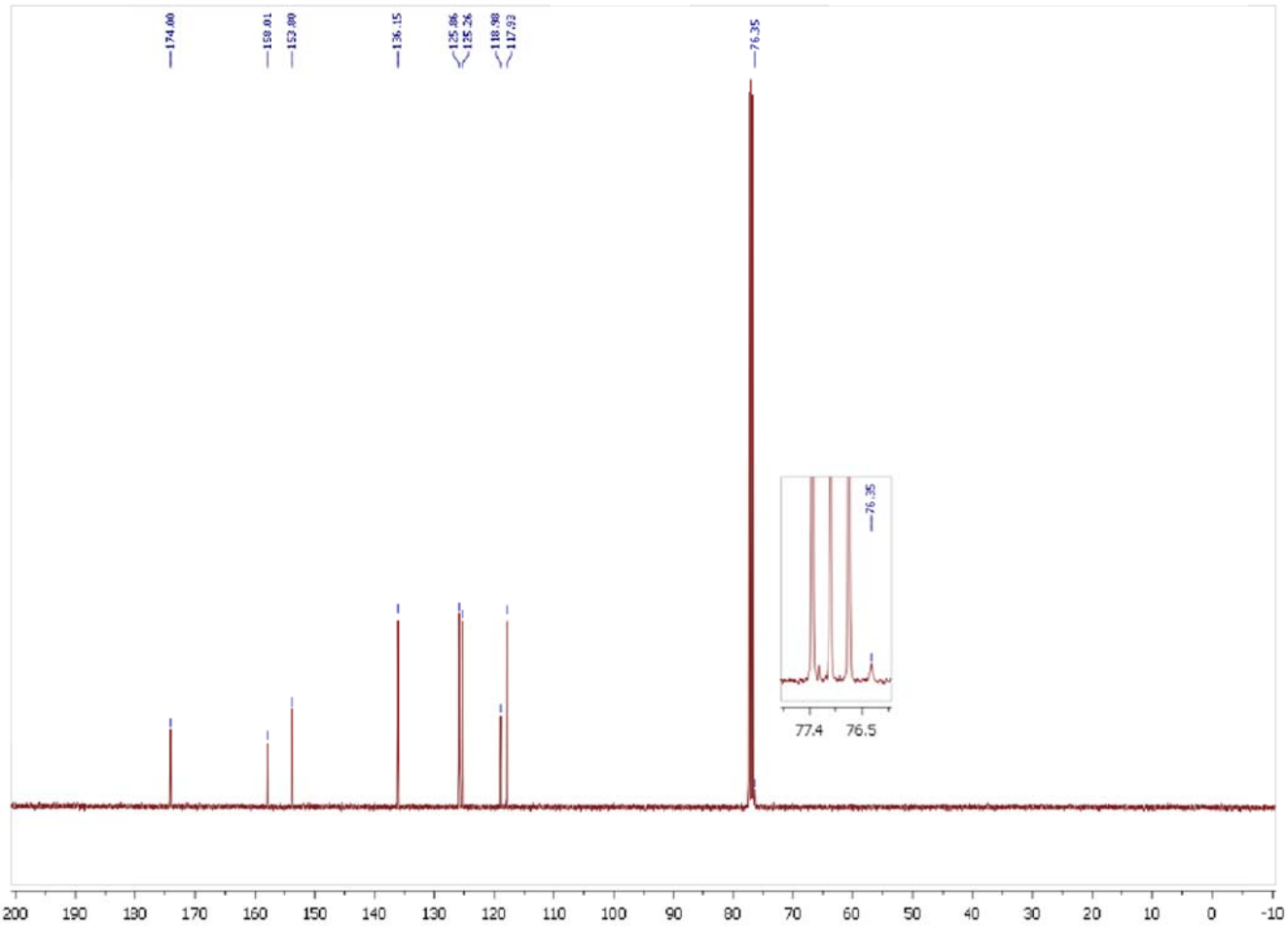

11.65
8.08
8.07
7.75
7.75
7.74
7.72
7.72
7.48
7.46
7.38
7.36
7.34
N2
O
NH
O
0.99
1.00
1.02
0.97
1.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

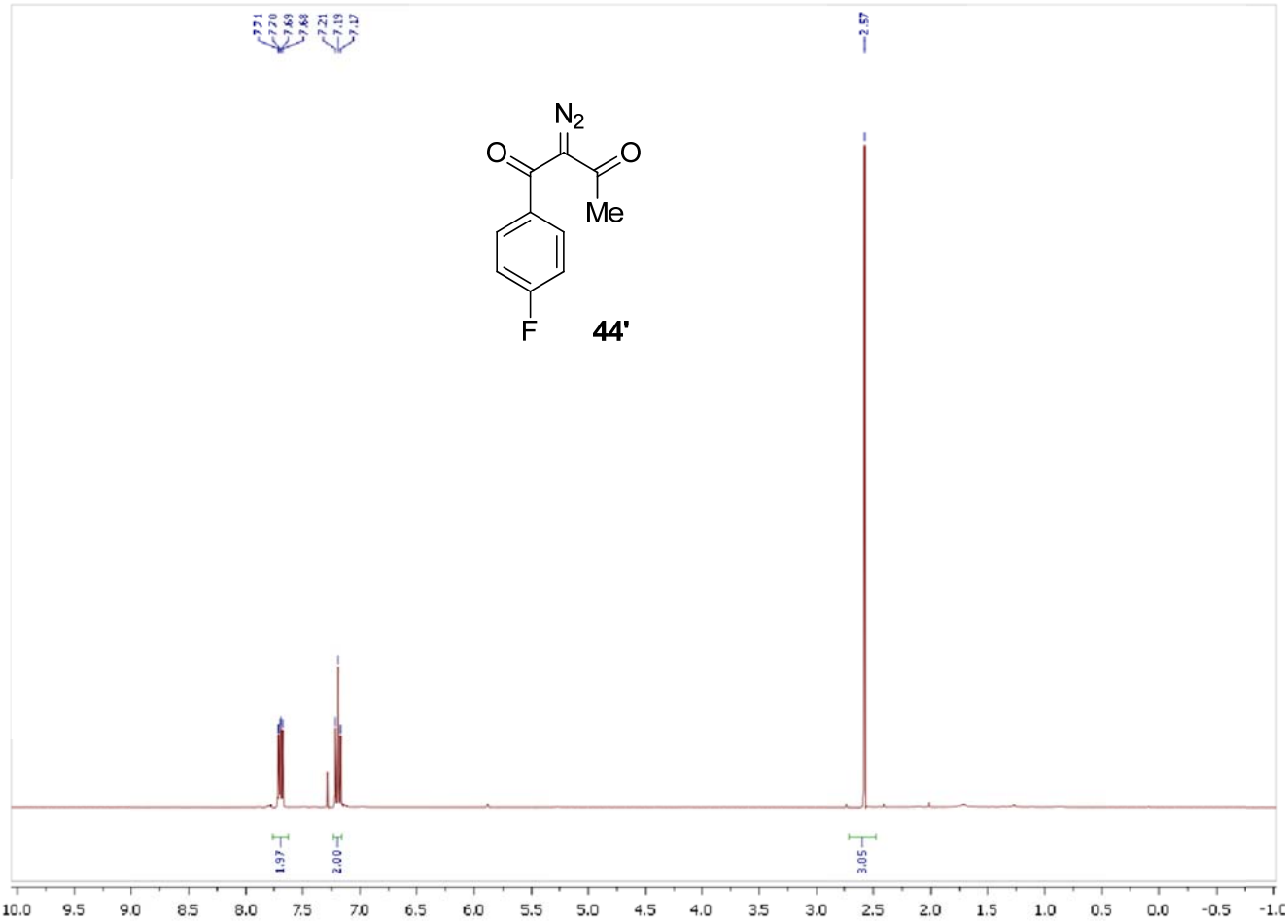
42'

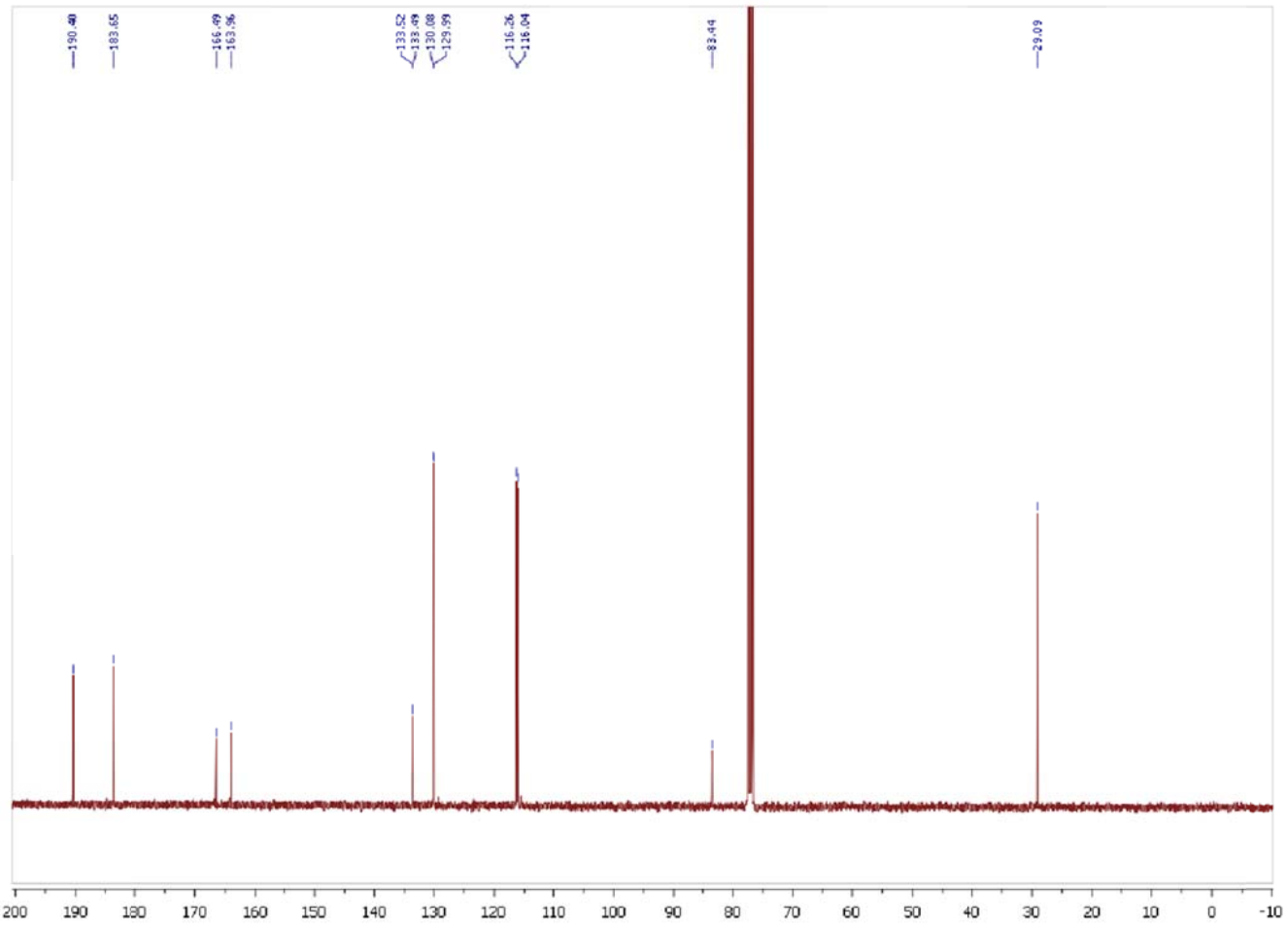

163.38
163.30
134.63
128.89
128.51
125.75
121.06
120.94
67.89
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

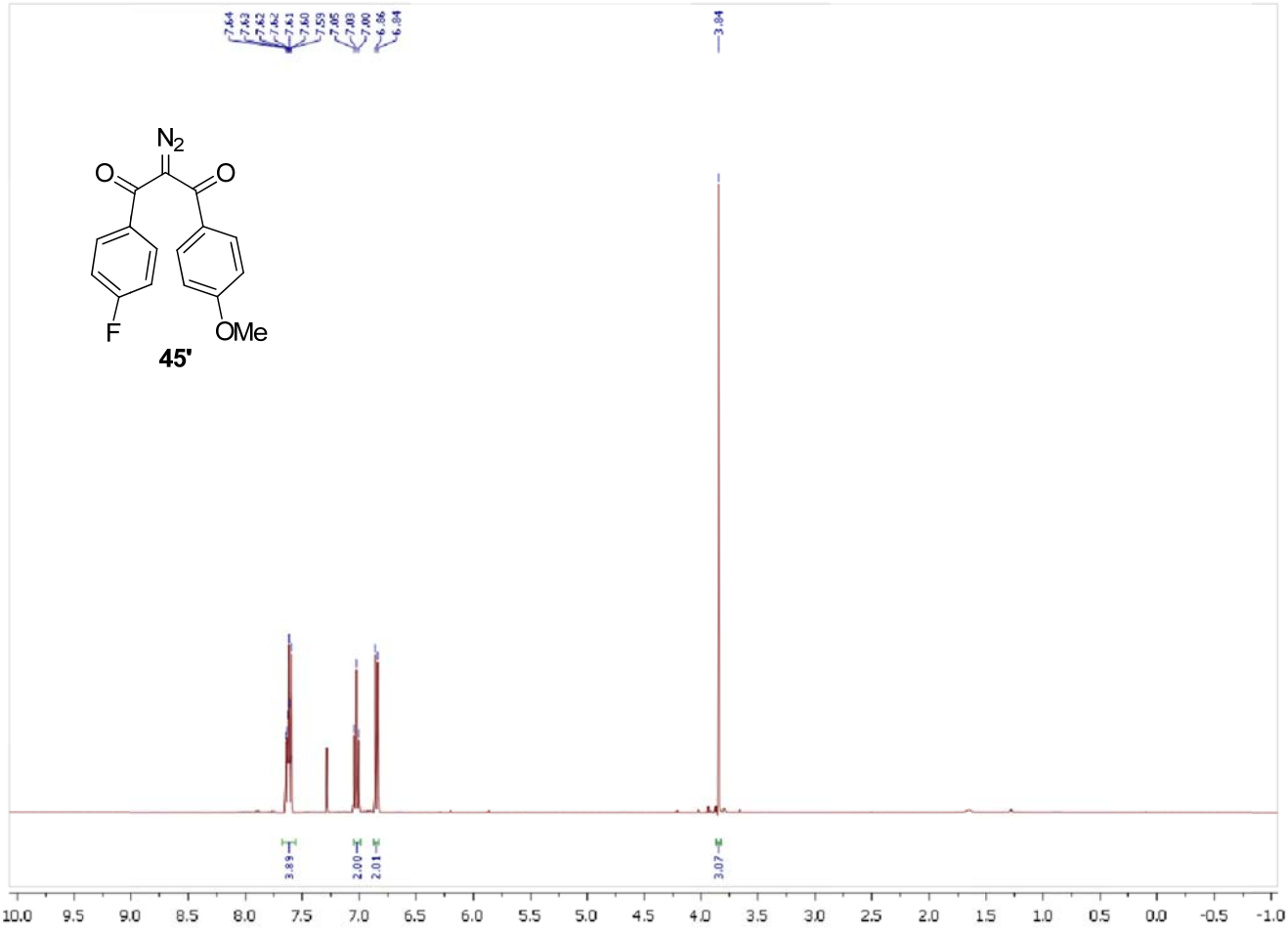

8.07
8.07
8.05
8.05
7.63
7.62
7.39
7.37
7.35
7.32
7.30
7.28
N2
O
O
O
0.97
1.00
0.99
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

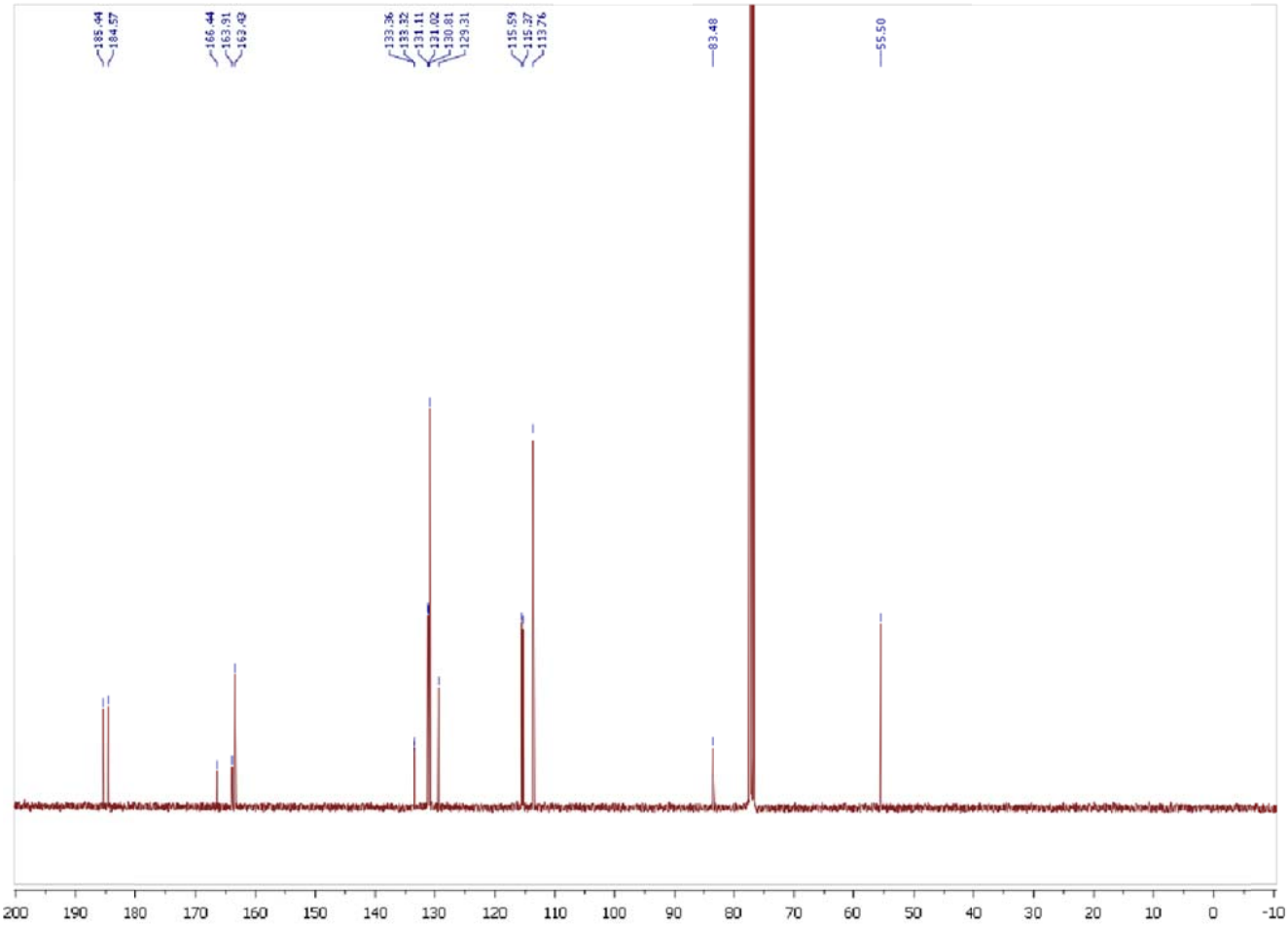
43'

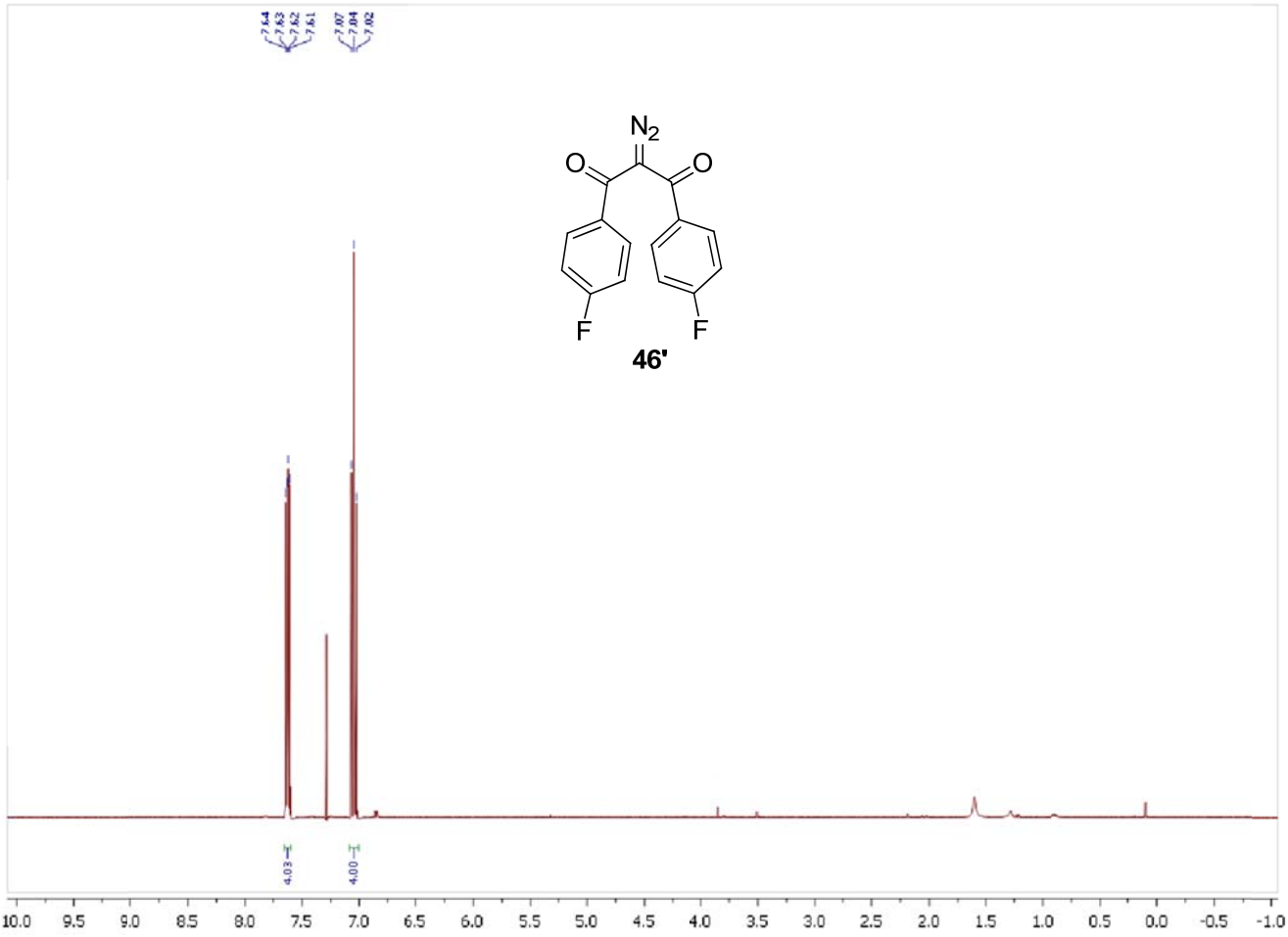

174.60
159.01
152.80
136.15
125.86
125.26
118.98
117.93
76.35
76.35
77.4
76.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.71
7.70
7.69
7.68
7.21
7.19
7.17
2.57
N2
O
O
Me
F
44'
1.97
2.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

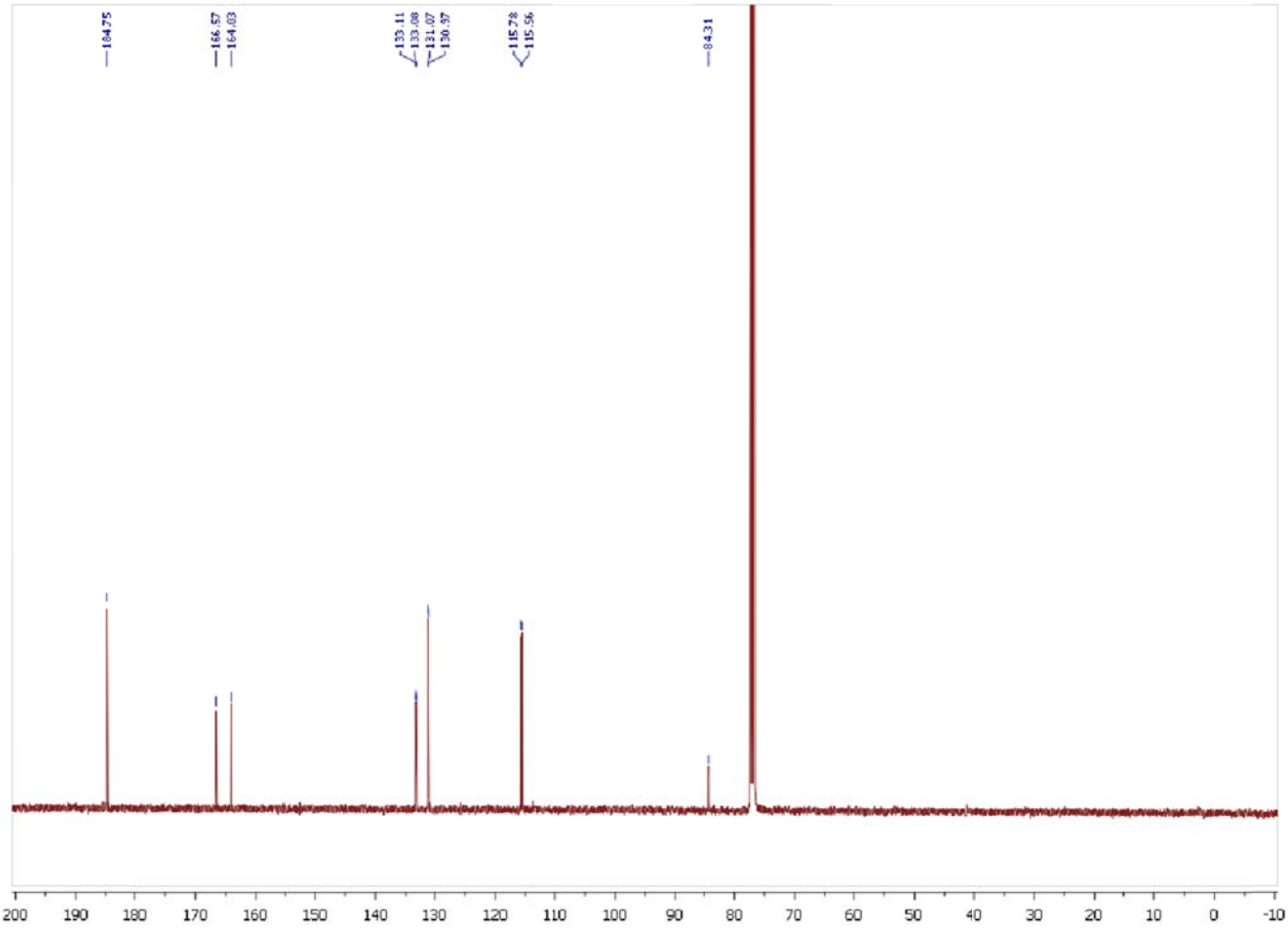

190.40
183.65
166.49
163.96
133.52
133.49
130.08
129.99
116.26
116.04
83.44
29.09
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

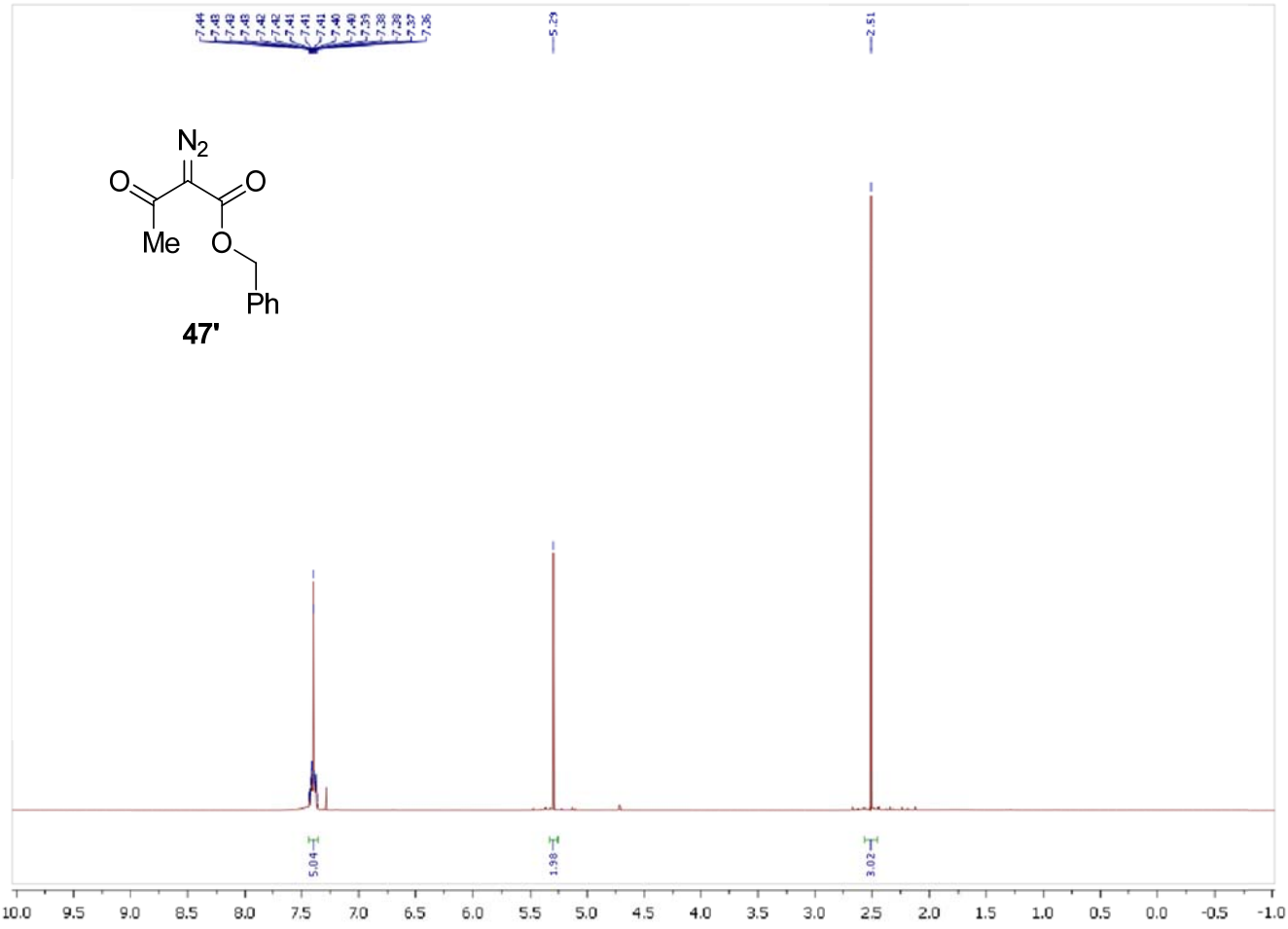

7.64
7.63
7.62
7.62
7.61
7.60
7.59
7.05
7.03
7.00
6.86
6.84
3.84
N2
O
O
F
OMe
45'
3.89
2.00
2.01
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

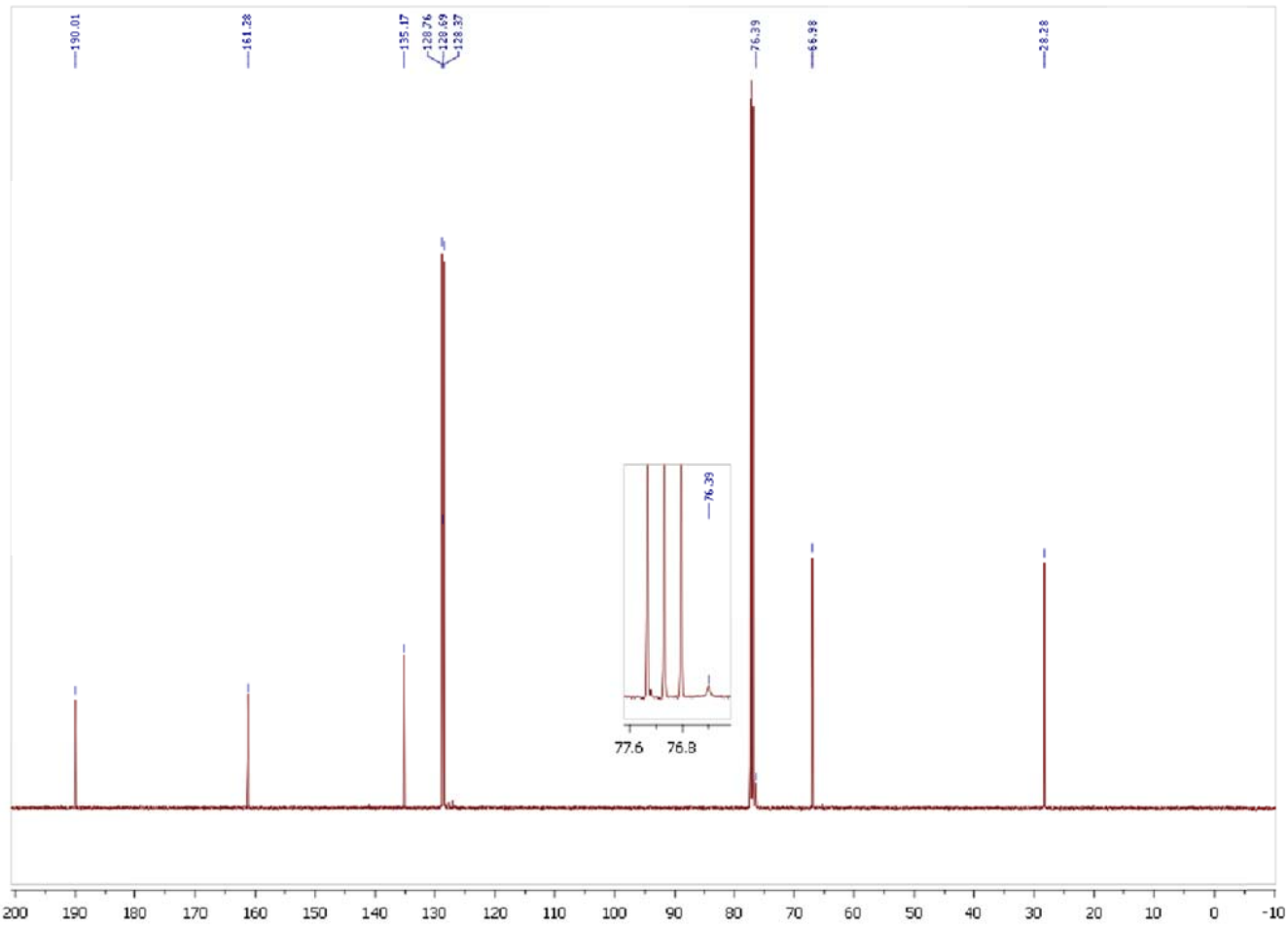

185.44
184.57
166.44
163.91
163.49
133.36
133.32
131.11
131.02
130.81
129.31
115.59
115.37
113.76
83.48
55.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

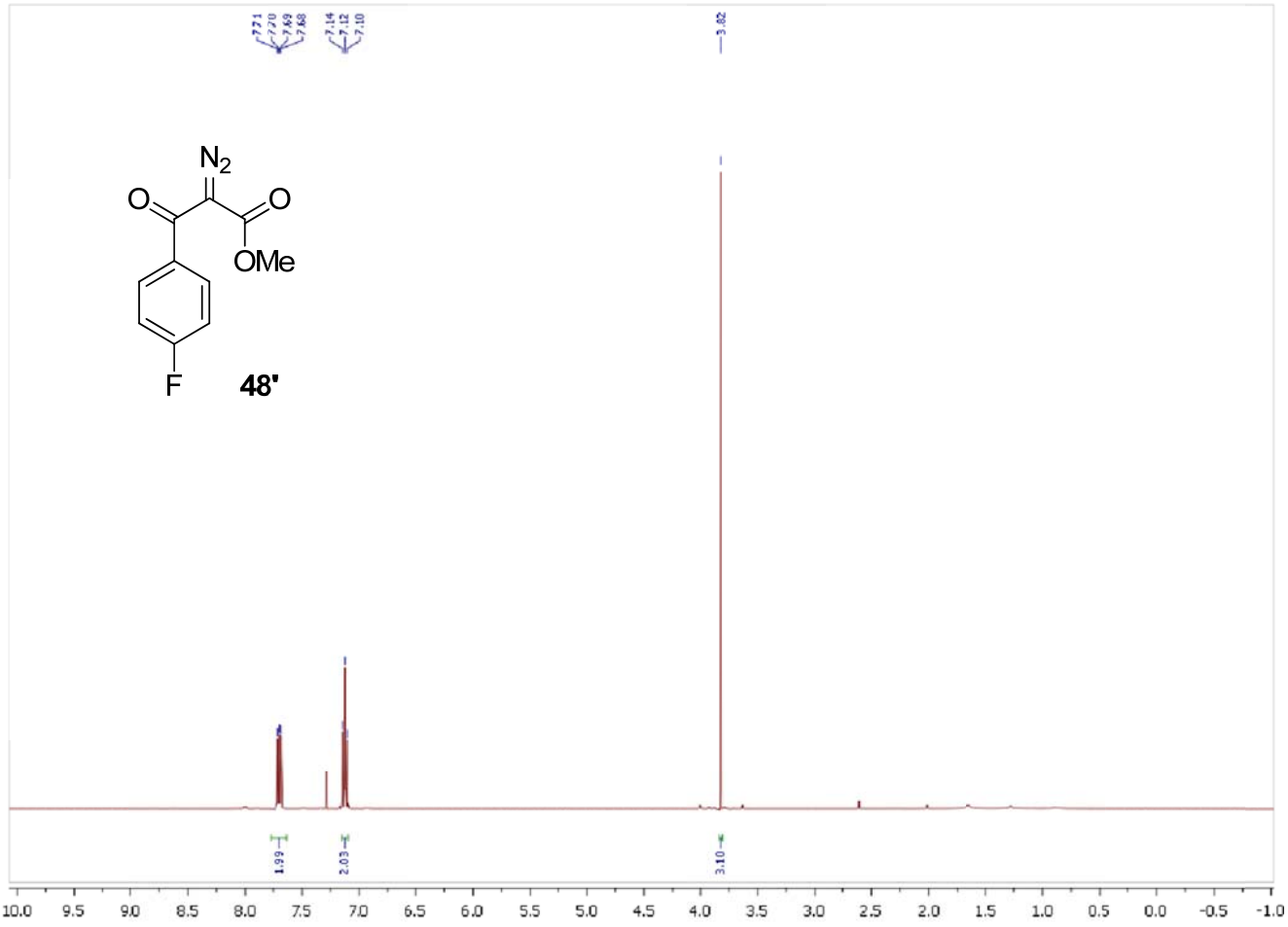

7.64
7.63
7.62
7.61
7.07
7.04
7.02
N2
O
O
F
F
4.03
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

46'


184.75
166.57
164.03
133.11
133.08
131.07
130.97
115.78
115.56
84.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

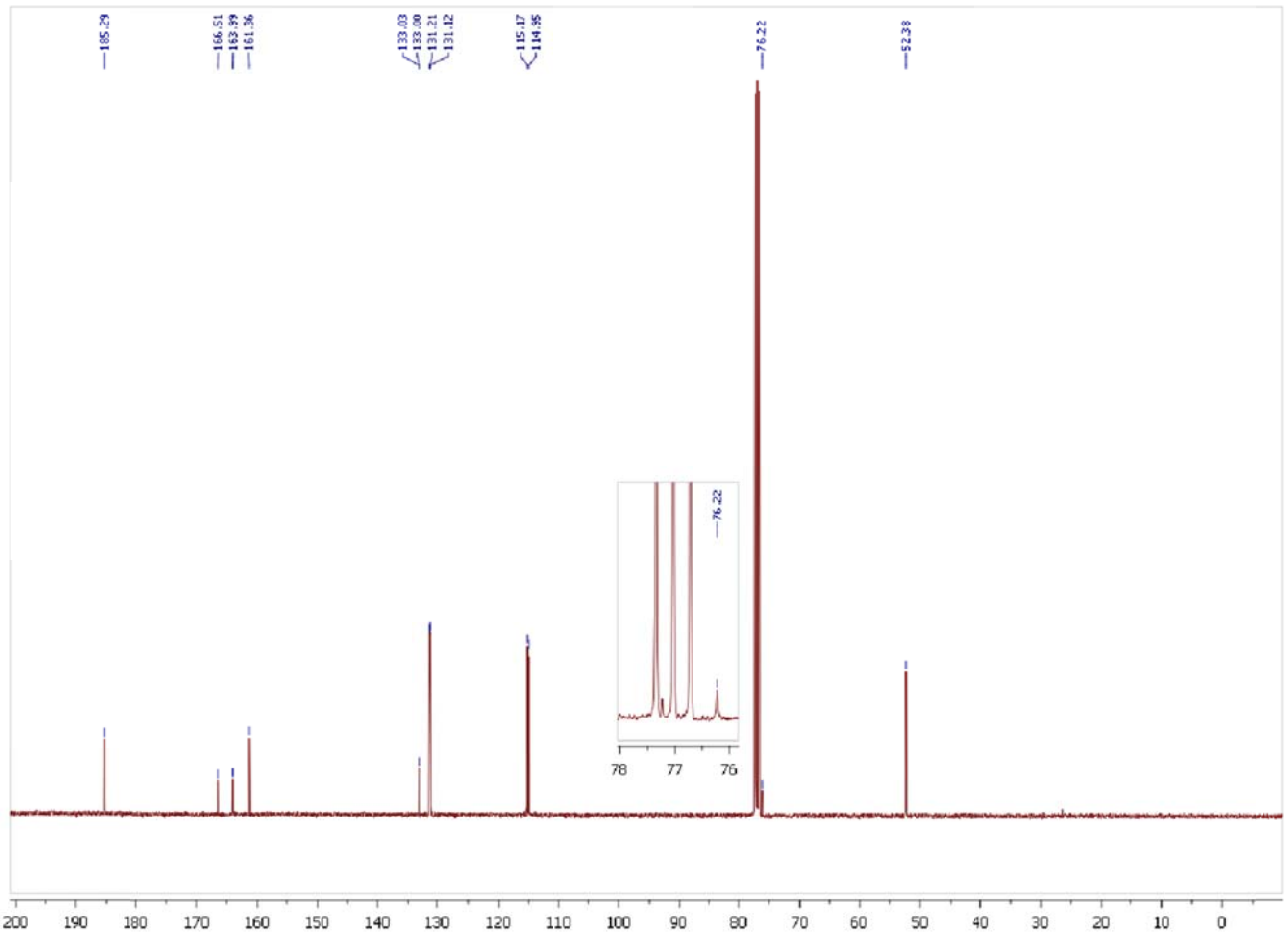

N2
O
O
Me
O
Ph
47'

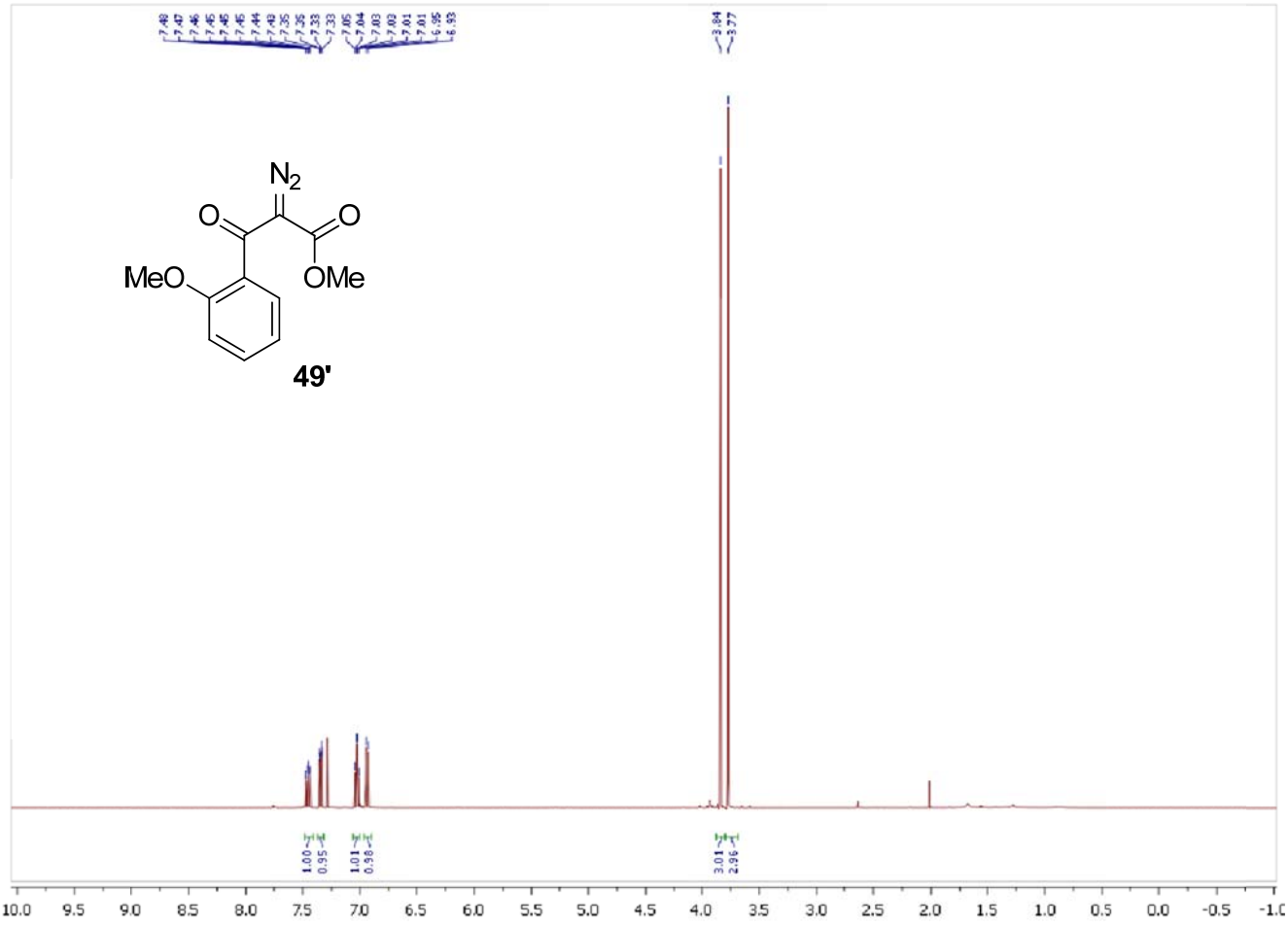



7.71
7.70
7.69
7.68
7.14
7.12
7.10
3.82
1.99
2.03
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

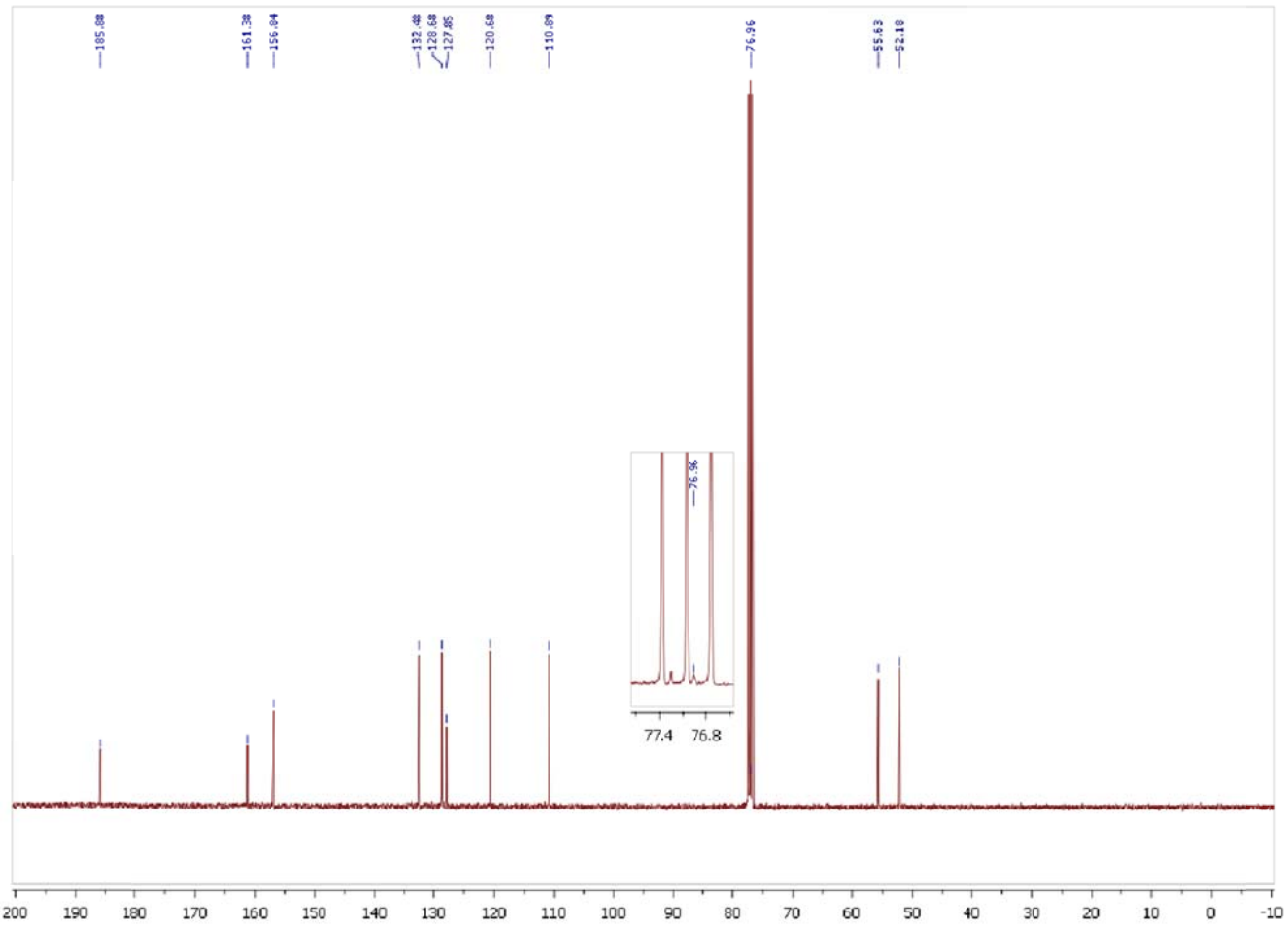
N2
O
O
OMe
F

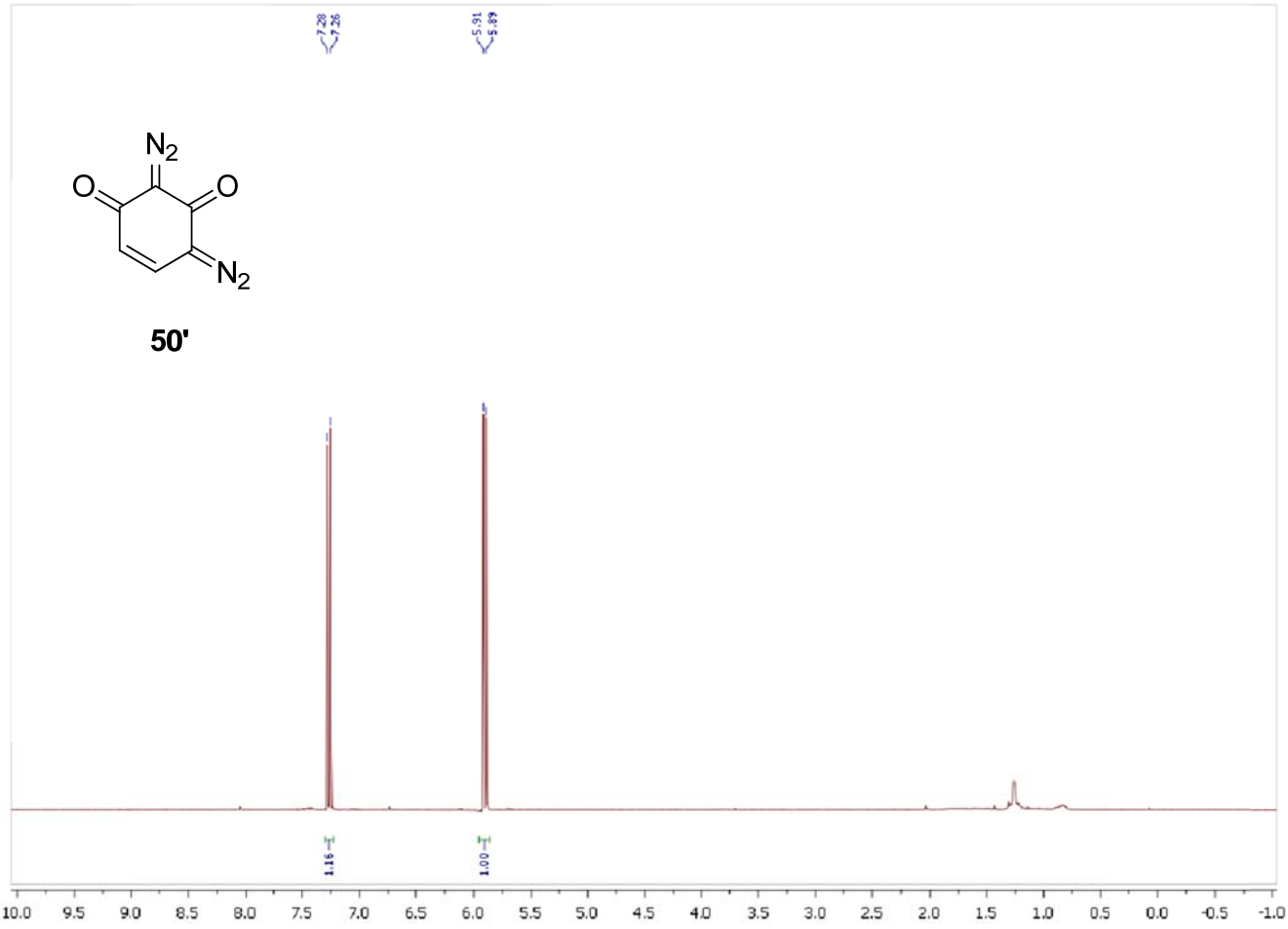
48'


185.29
166.51
163.99
161.36
133.03
133.00
131.21
131.12
115.17
114.95
76.22
52.38
76.22
78 77 76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

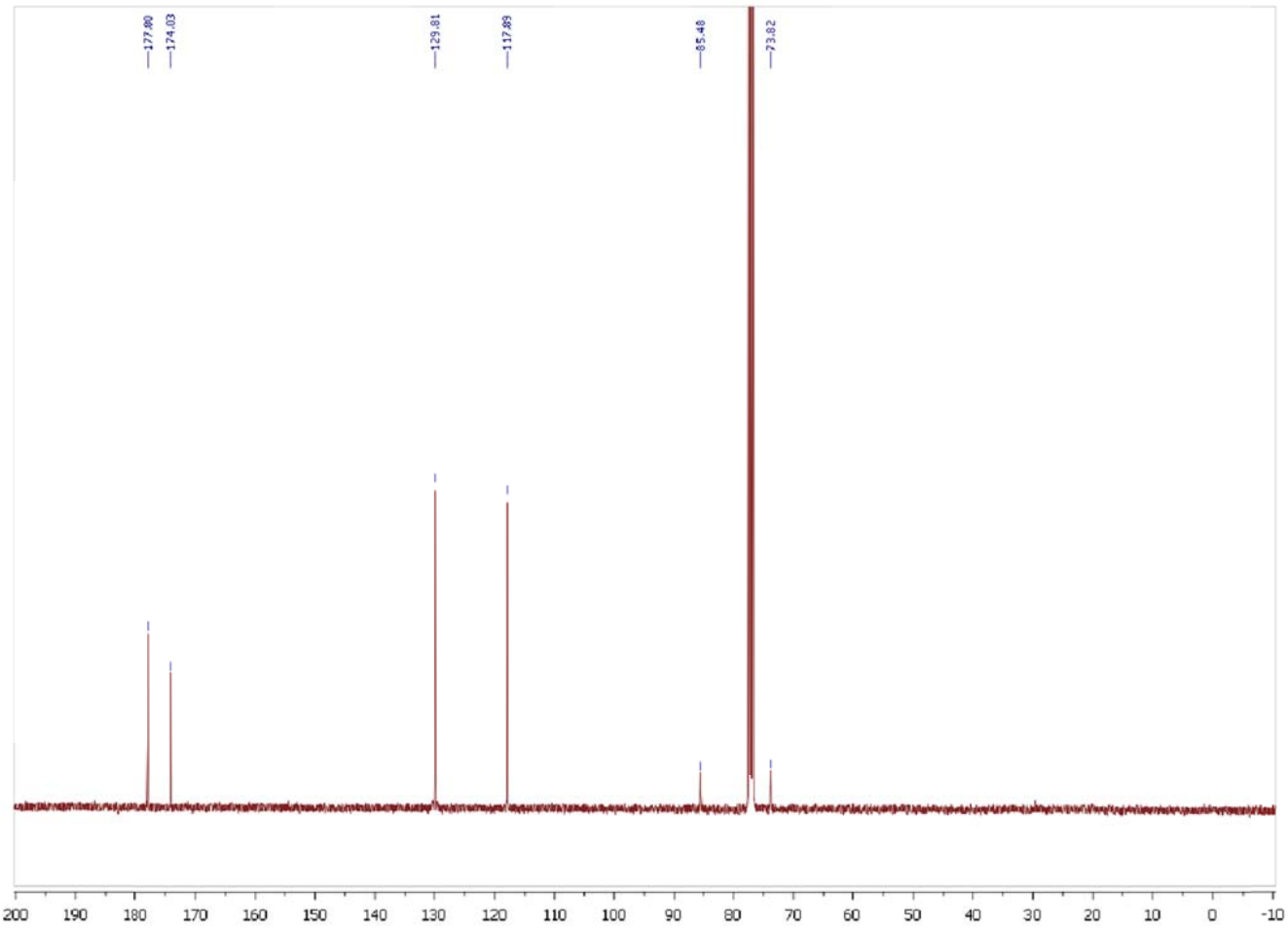


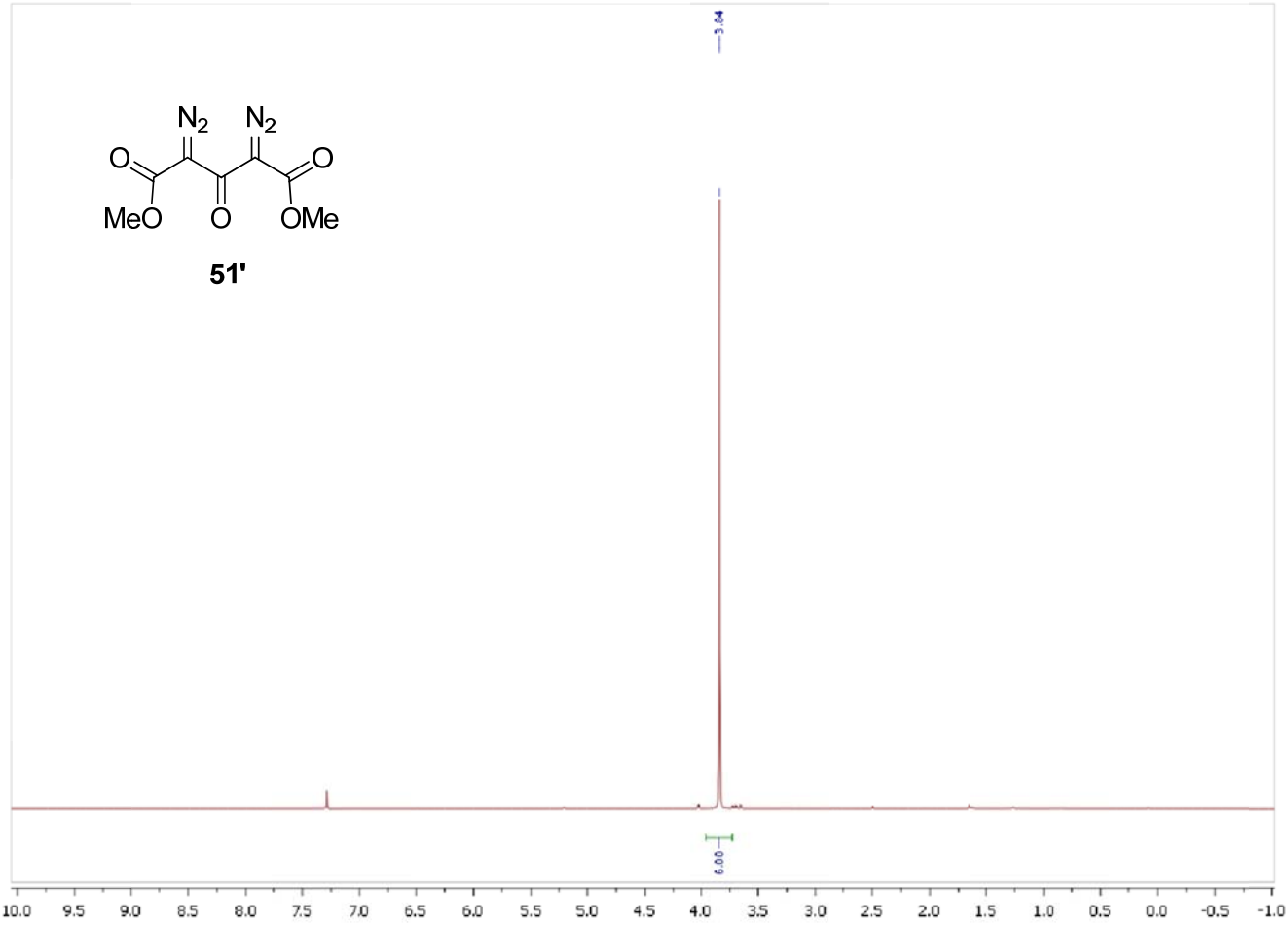
49'




7.28
7.26
5.91
5.89
1.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

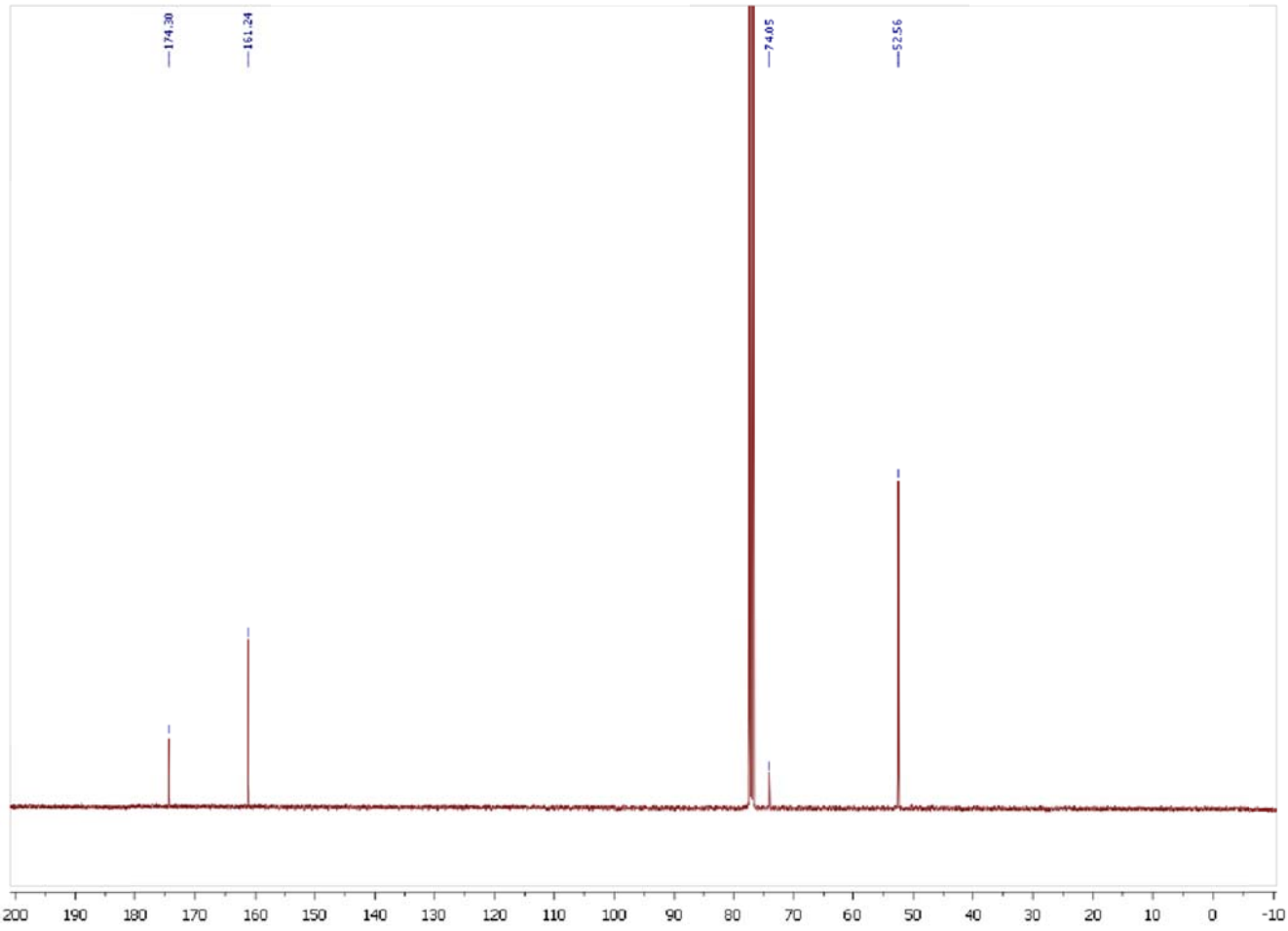
50'

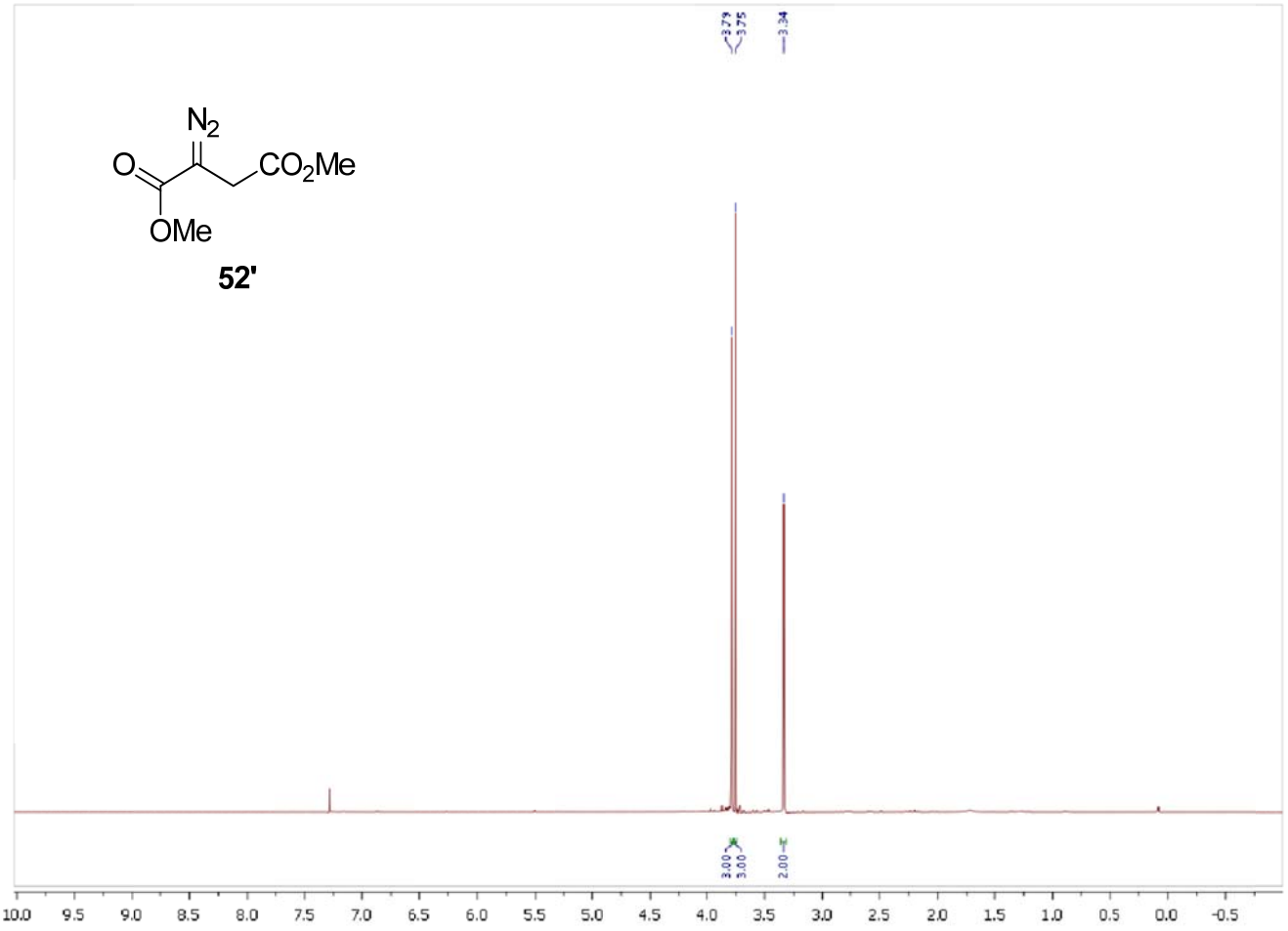

177.90
174.03
129.81
117.89
85.48
73.82
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

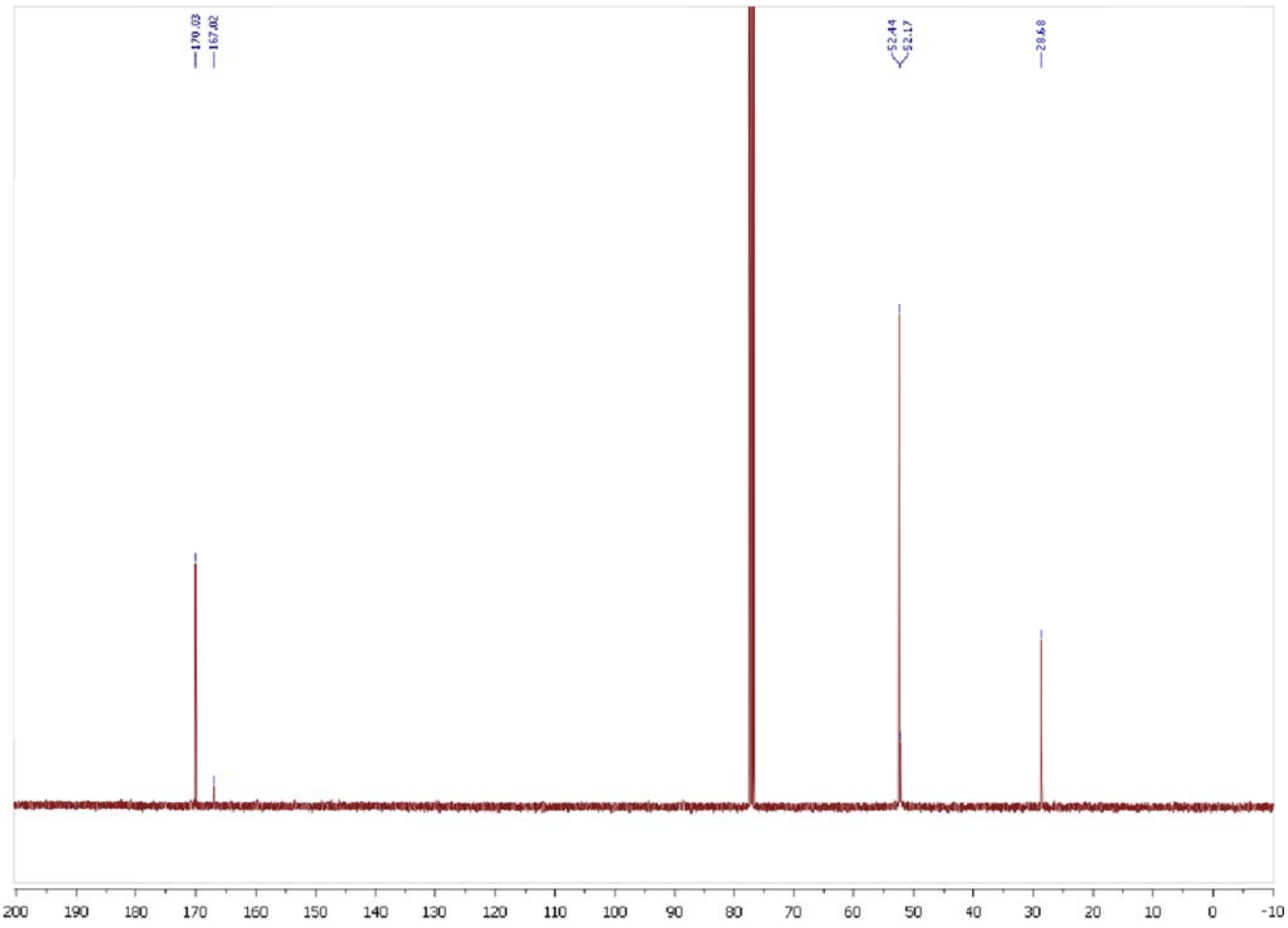


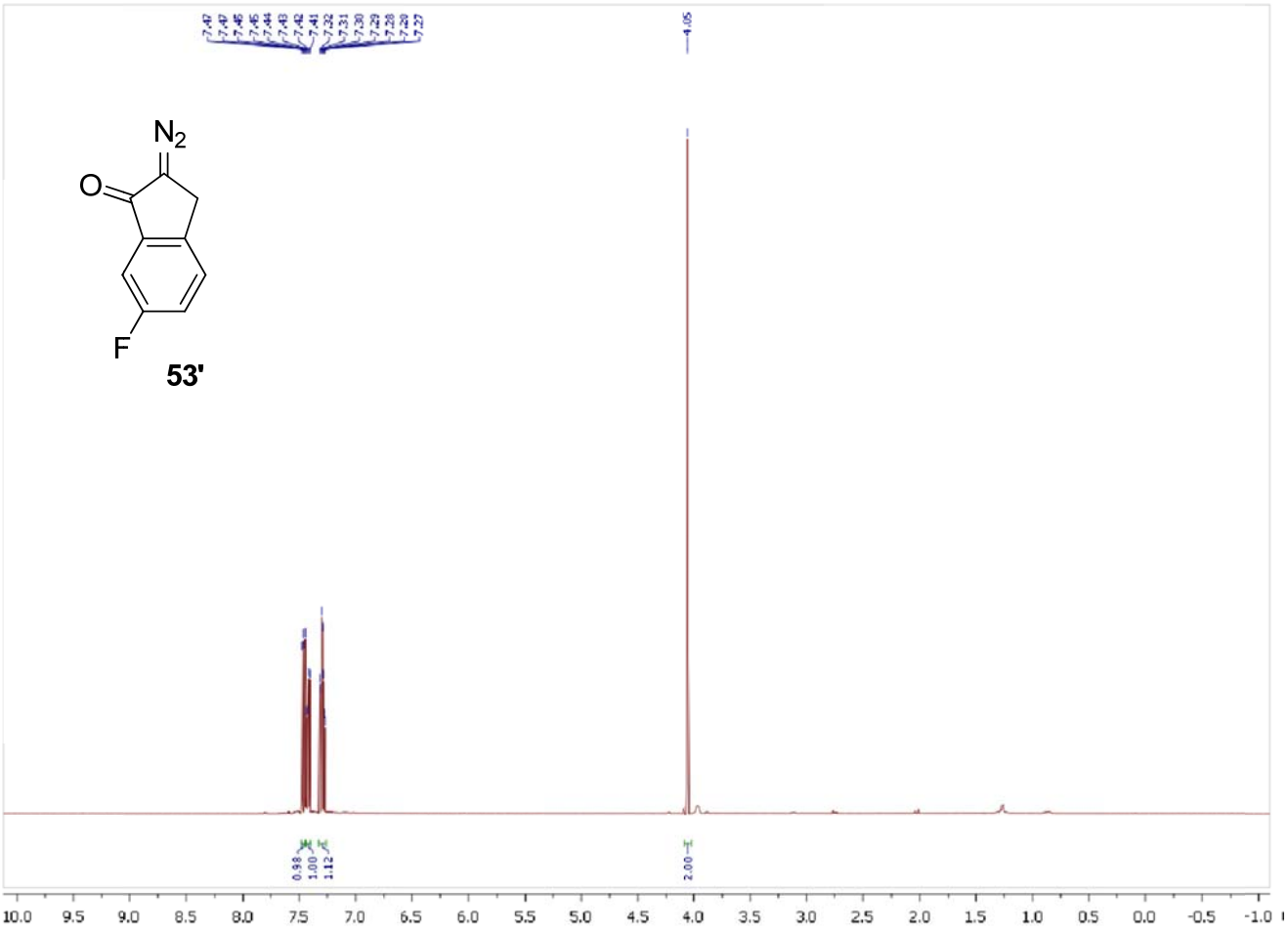
N_2 N_2
O O
MeO O OMe

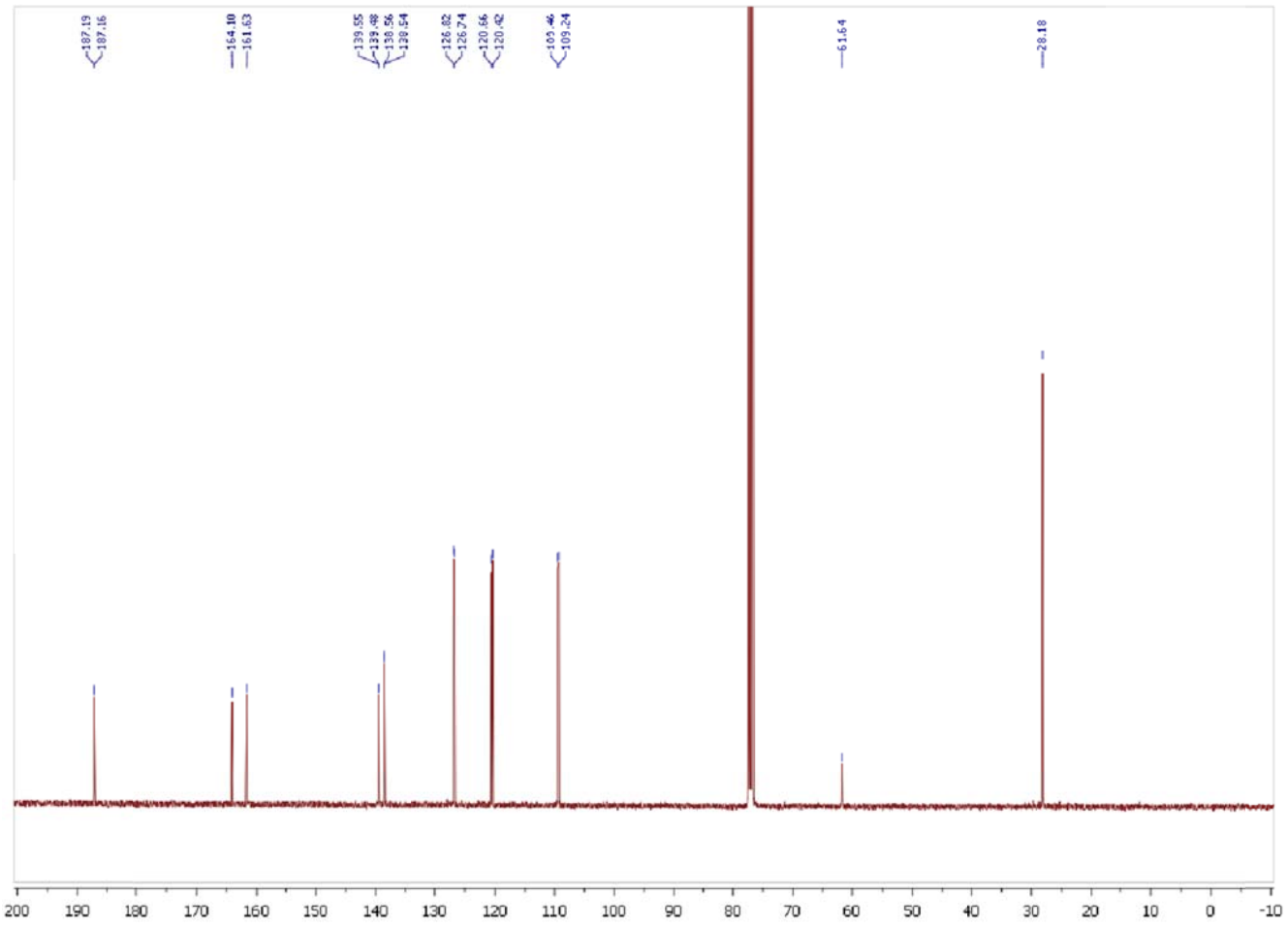
51'

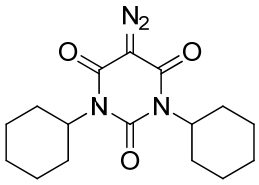



N2
O
CO2Me
OMe
52'

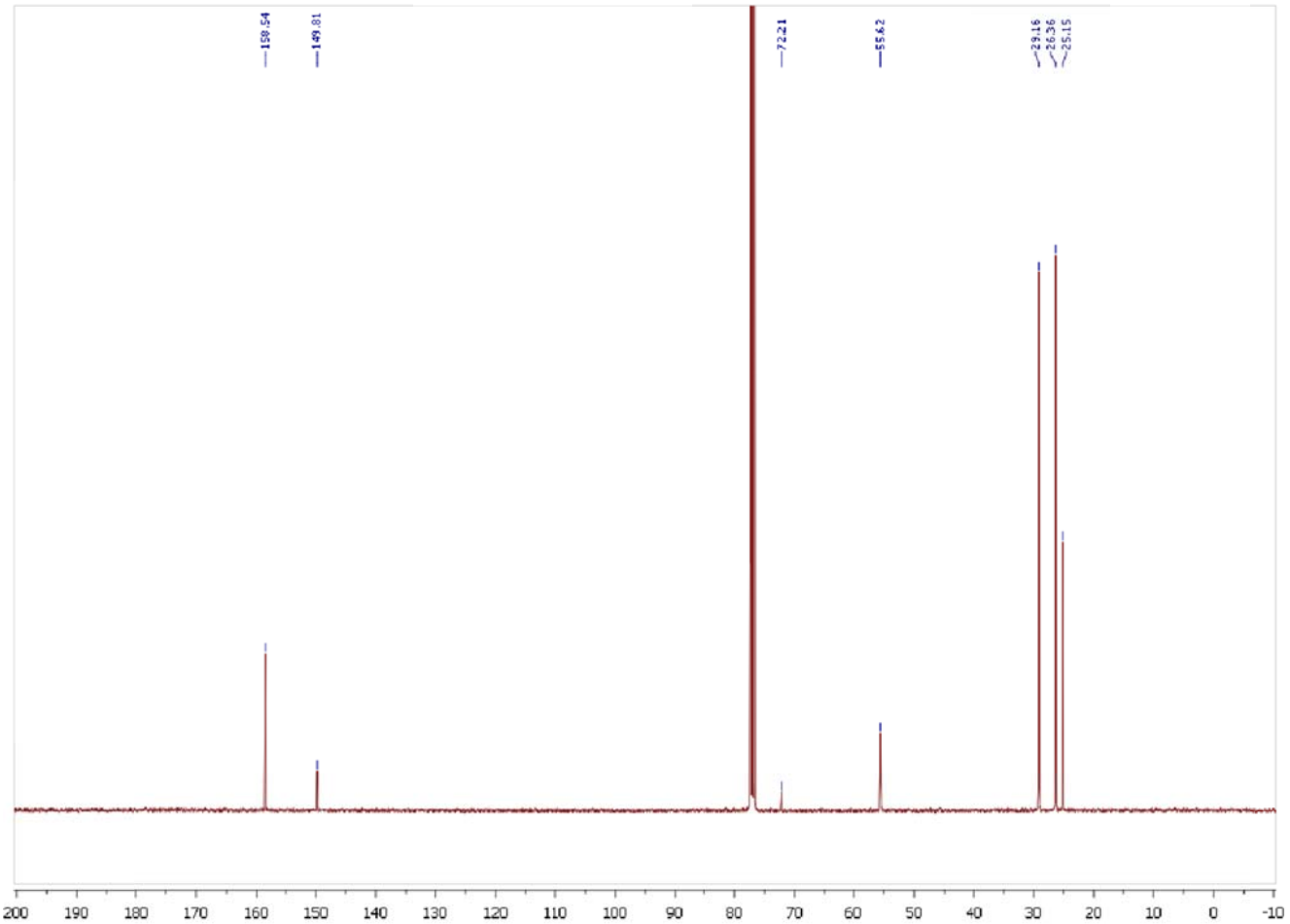


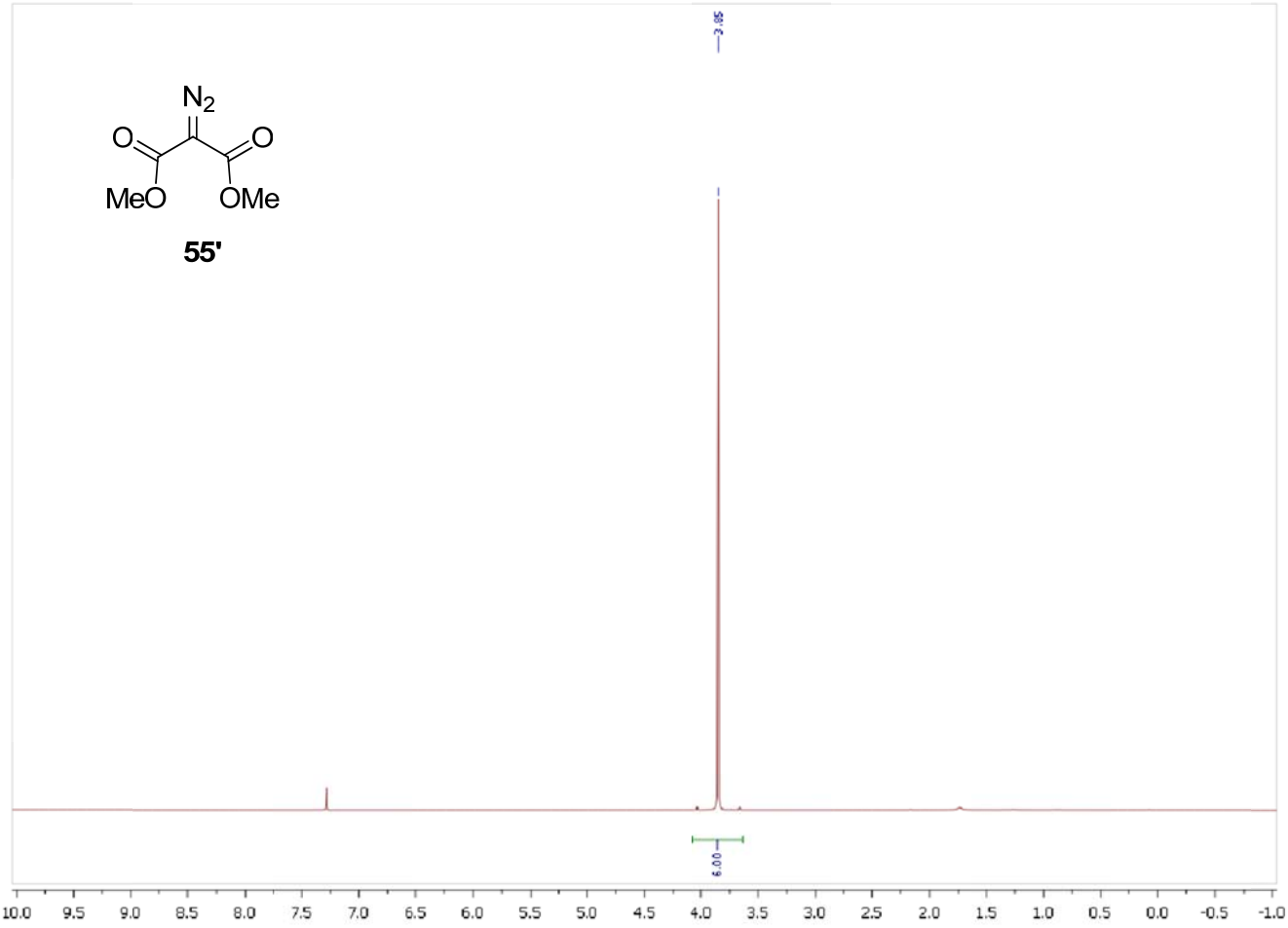

N2
O
F
53'



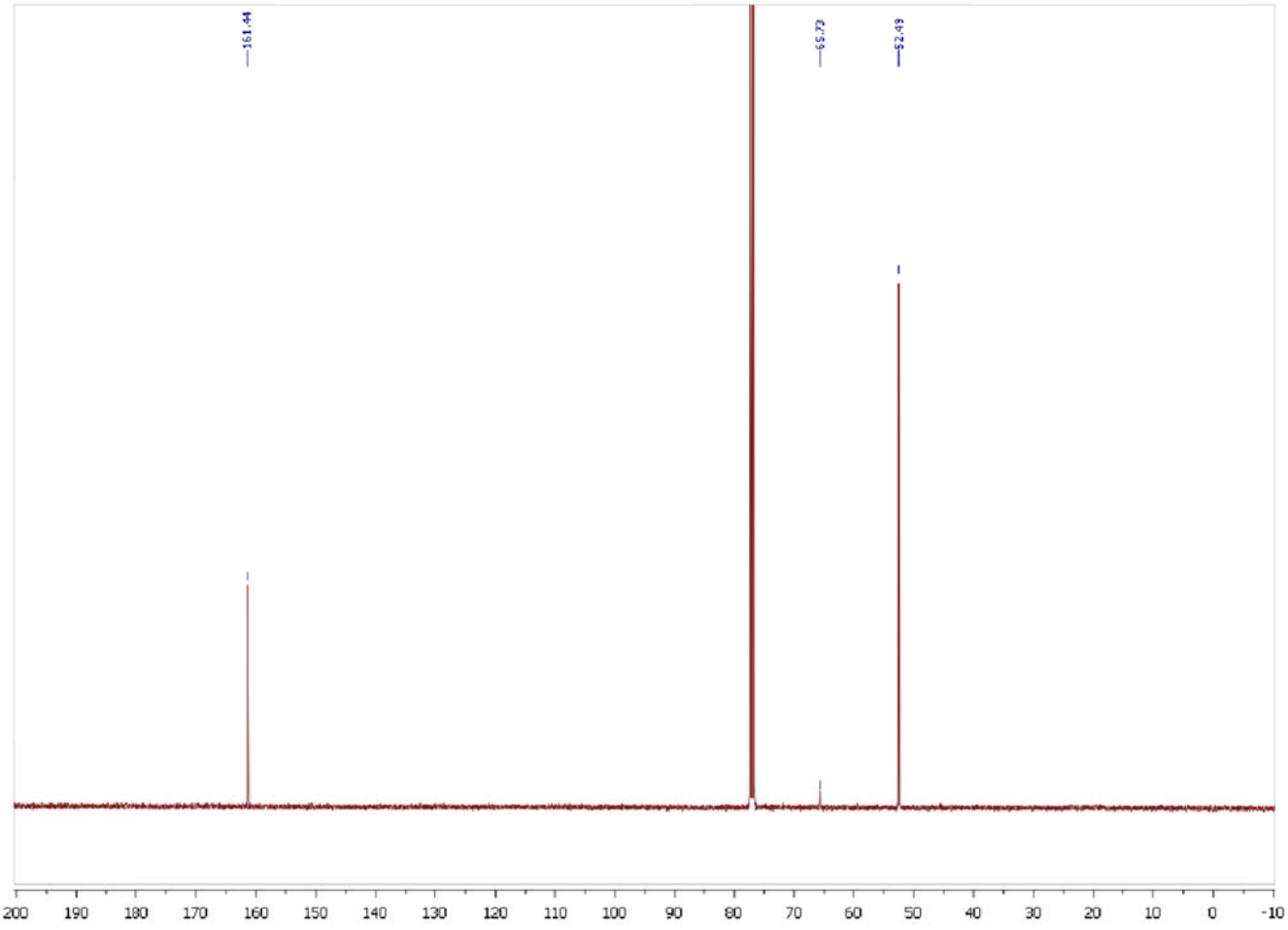


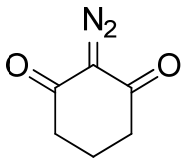
54'




N2
O
O
MeO
OMe
3.85
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

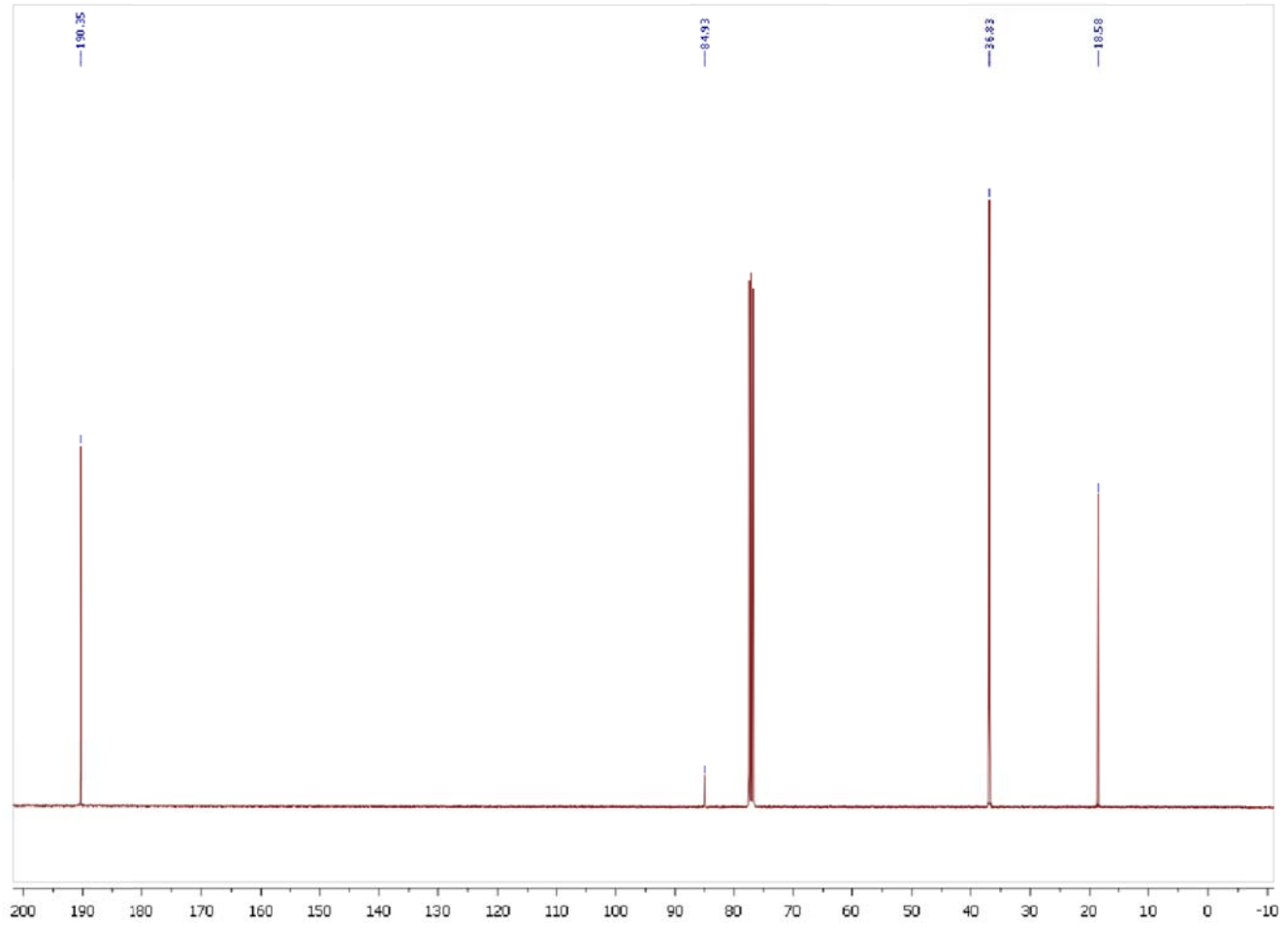
55'

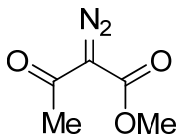

161.44
65.73
52.49
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


N2
O
O

56'

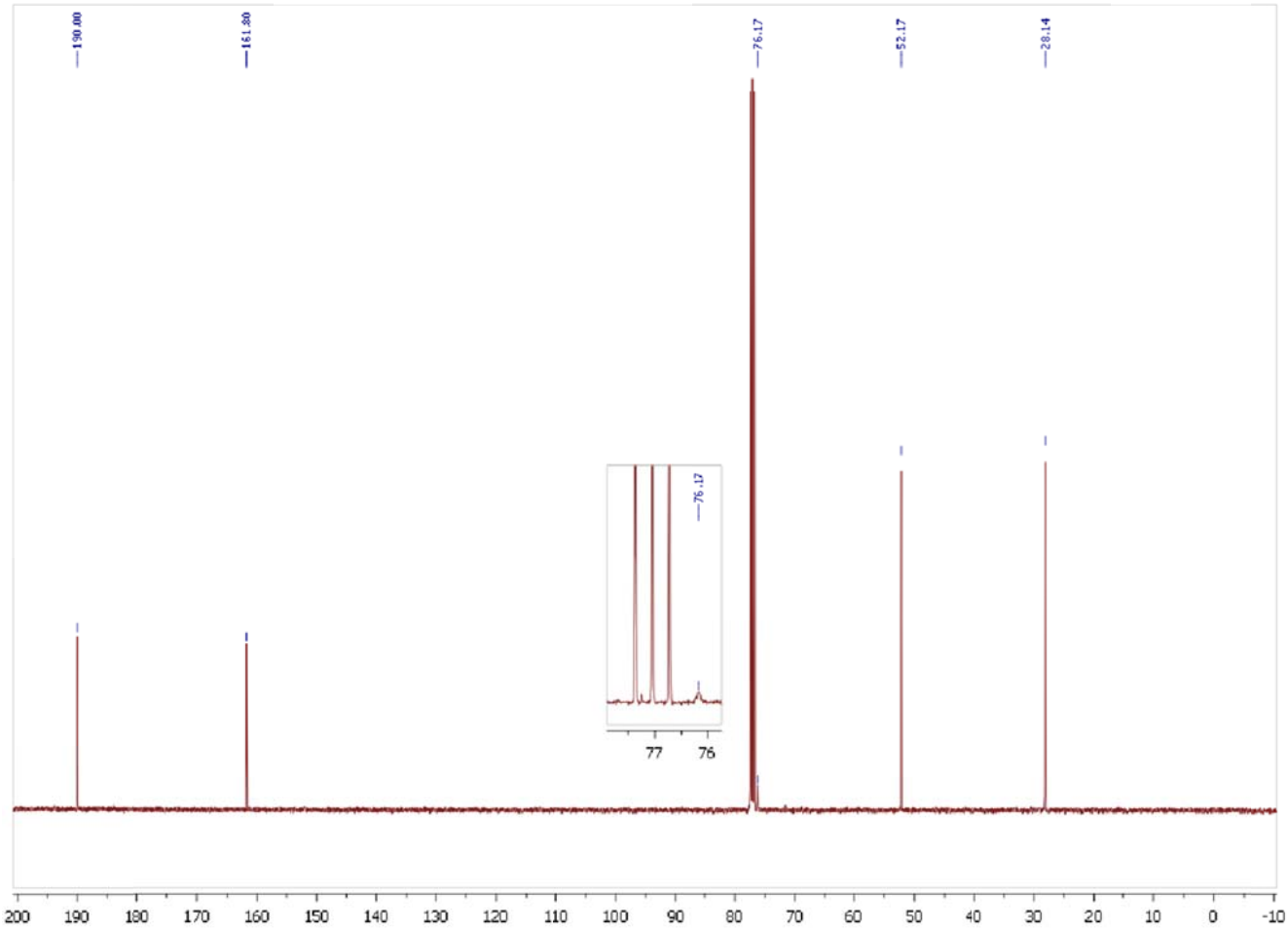
2.59
2.57
2.56
2.54
2.08
2.06
2.04
2.03
2.01
4.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

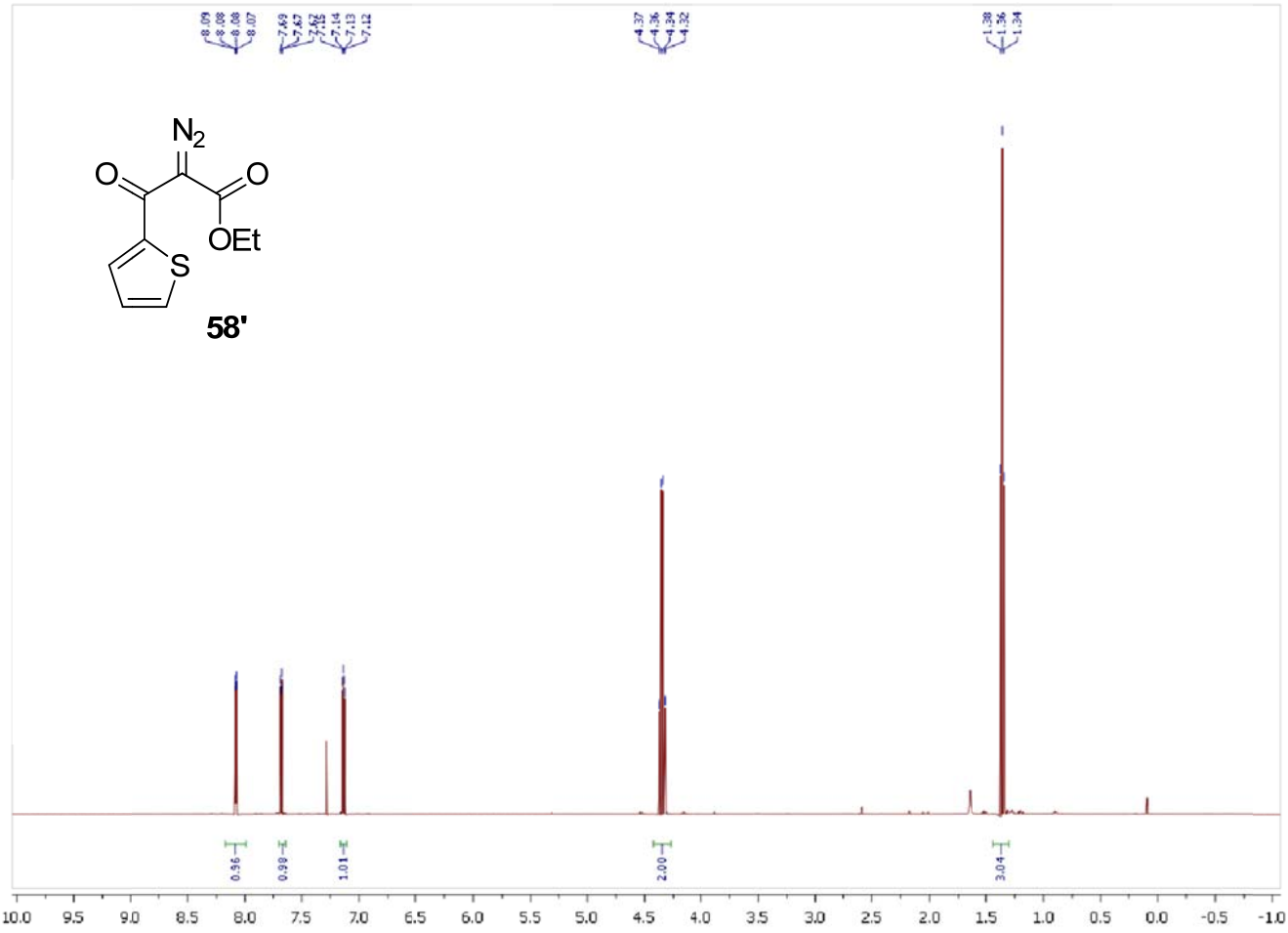

190.35
84.93
36.83
18.58
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


N2
O
O
Me
OMe

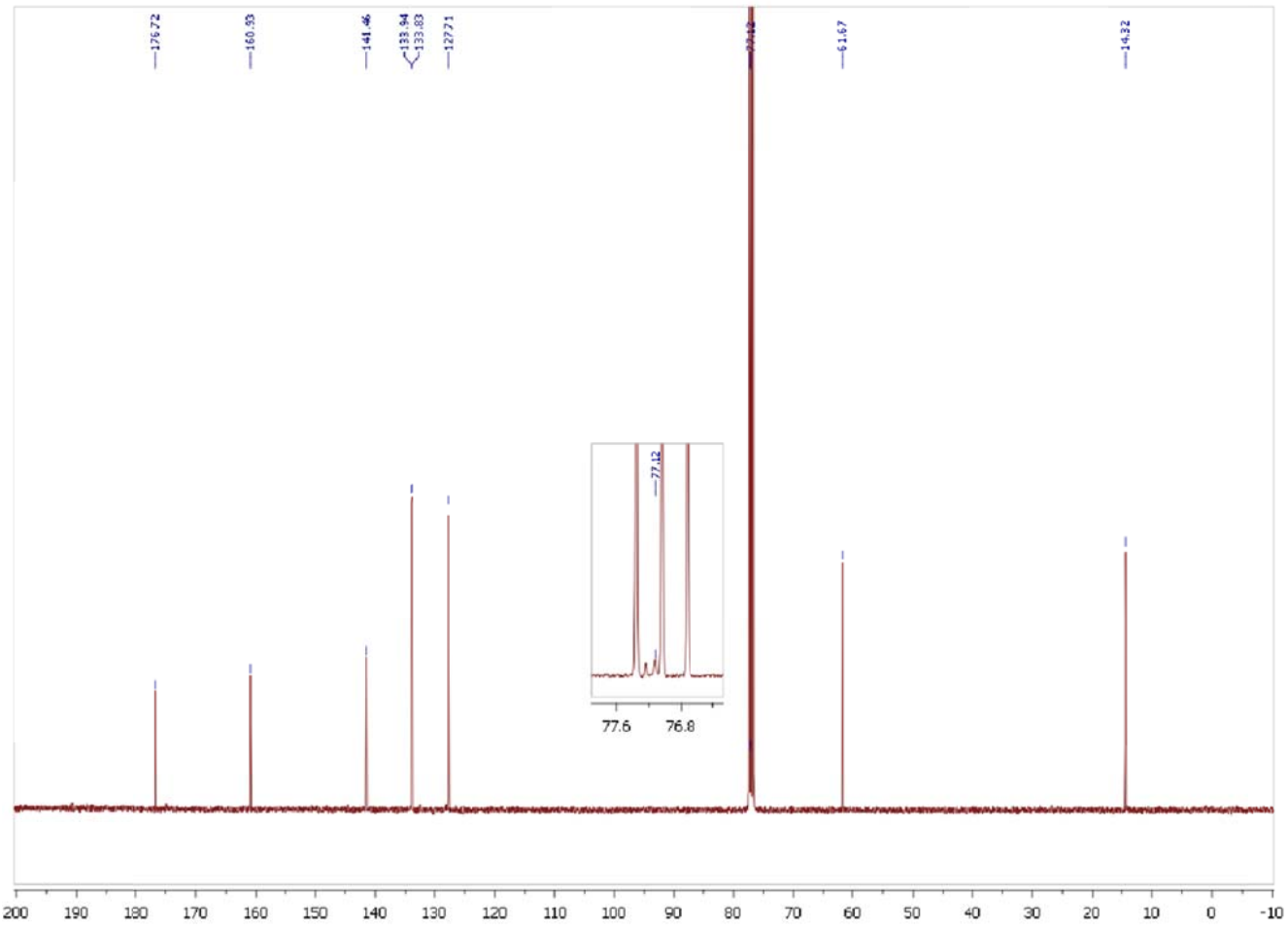
57'

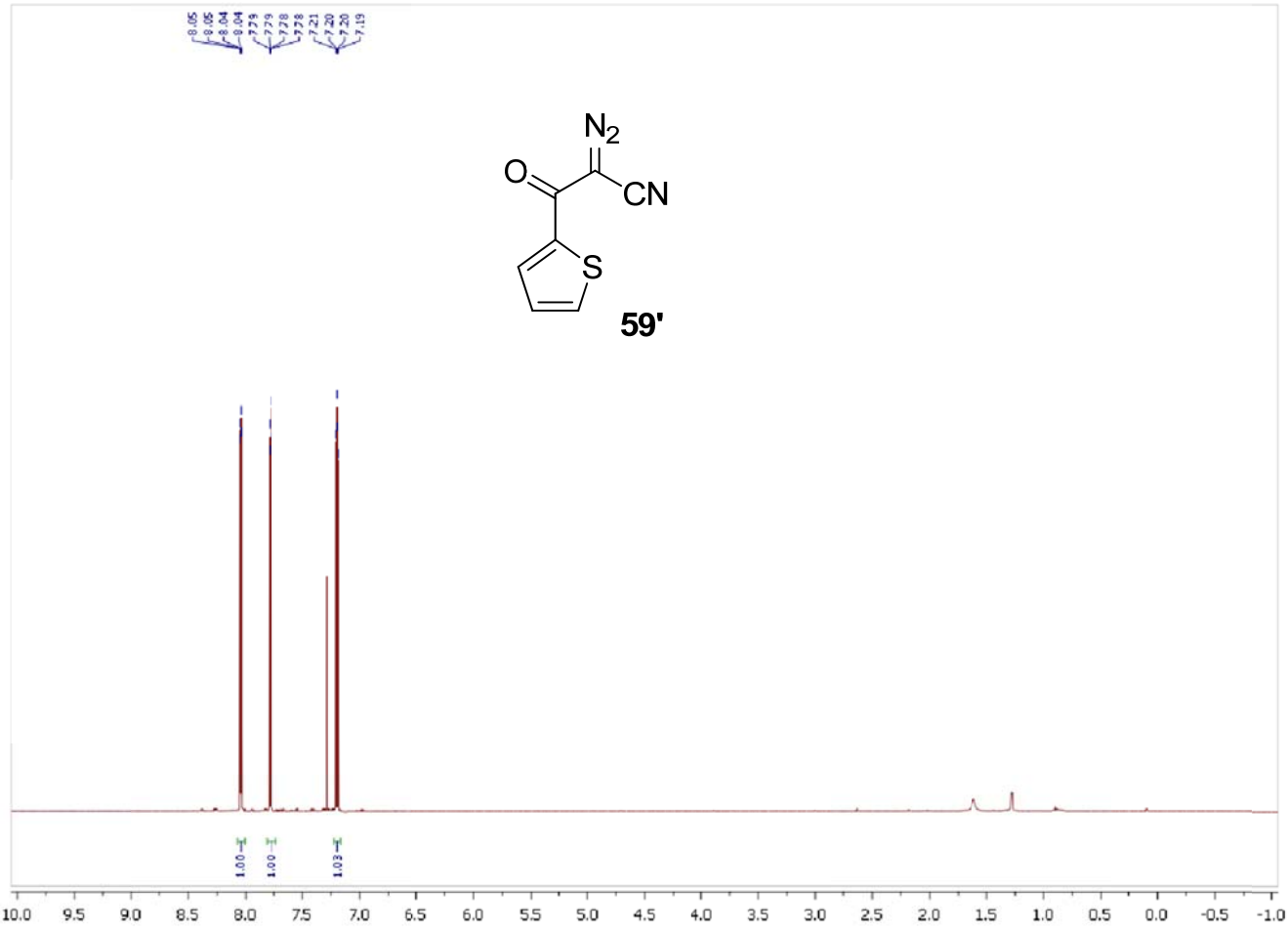
3.84
2.49
3.00
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


190.00
161.80
76.17
52.17
28.14
76.17
77
76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

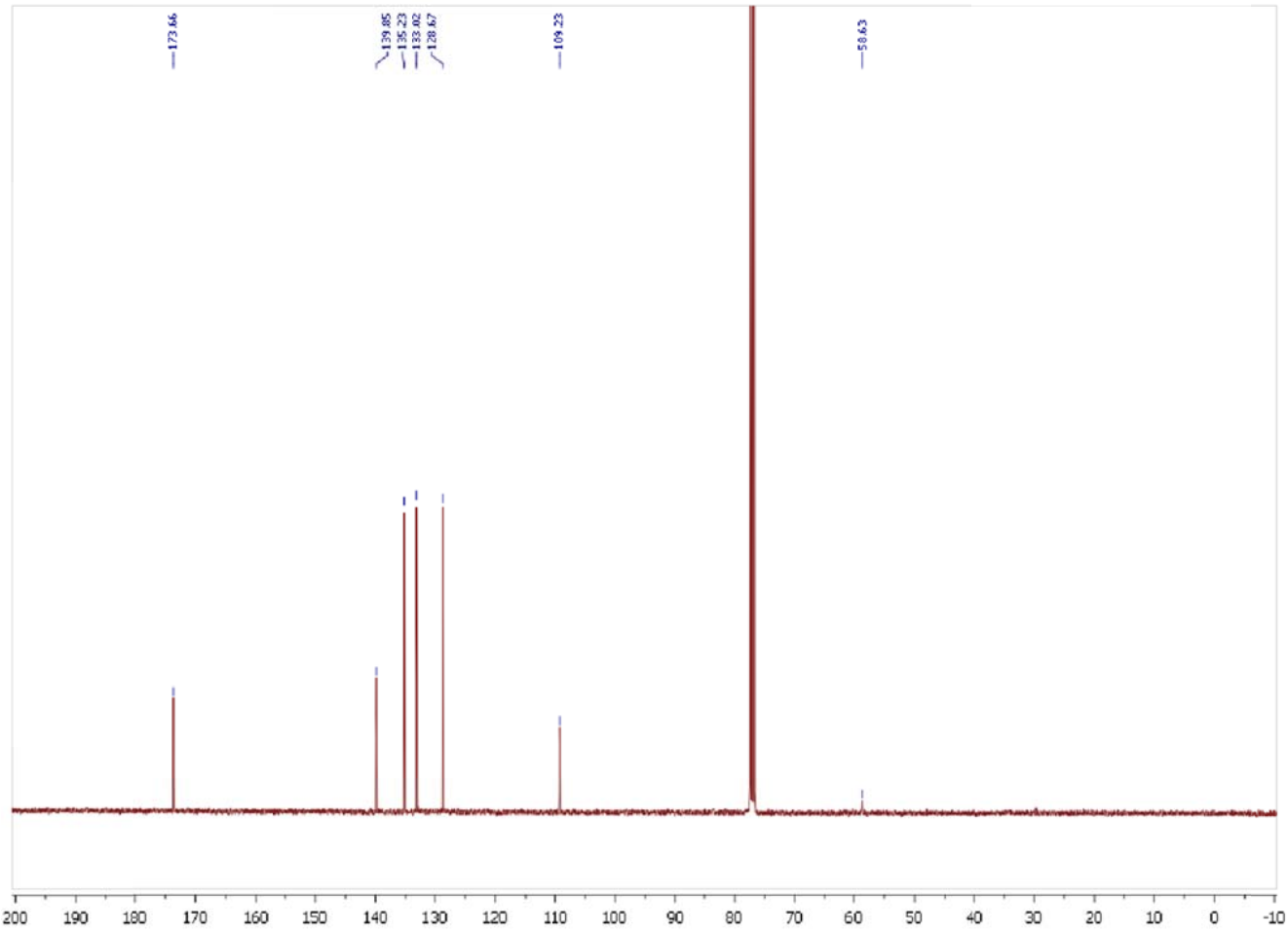

8.09
8.08
8.08
8.07
7.69
7.67
7.62
7.15
7.14
7.13
7.12
4.37
4.36
4.34
4.32
1.38
1.36
1.34
N2
O
O
OEt
S
0.96
0.99
1.01
2.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

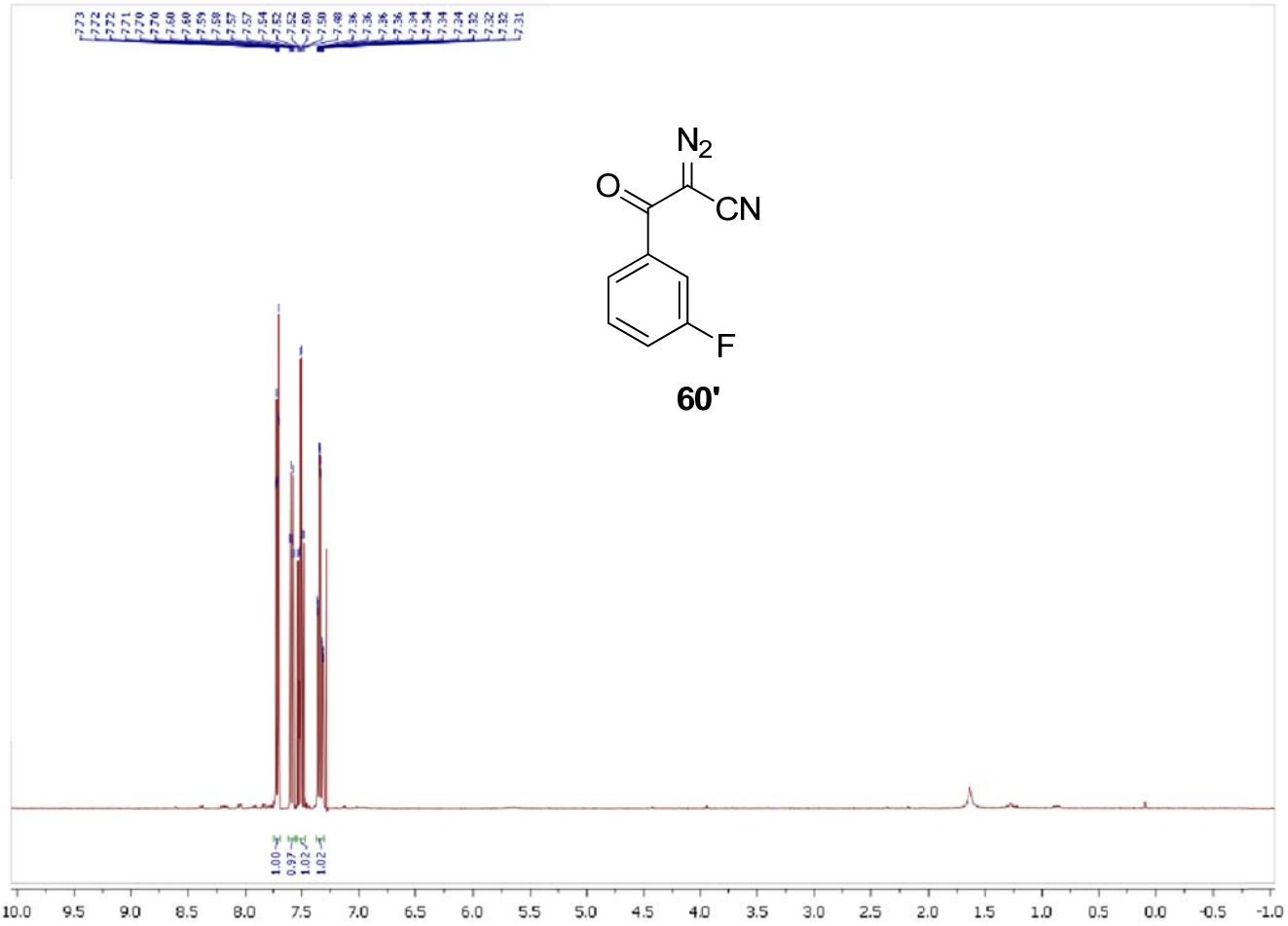
58'

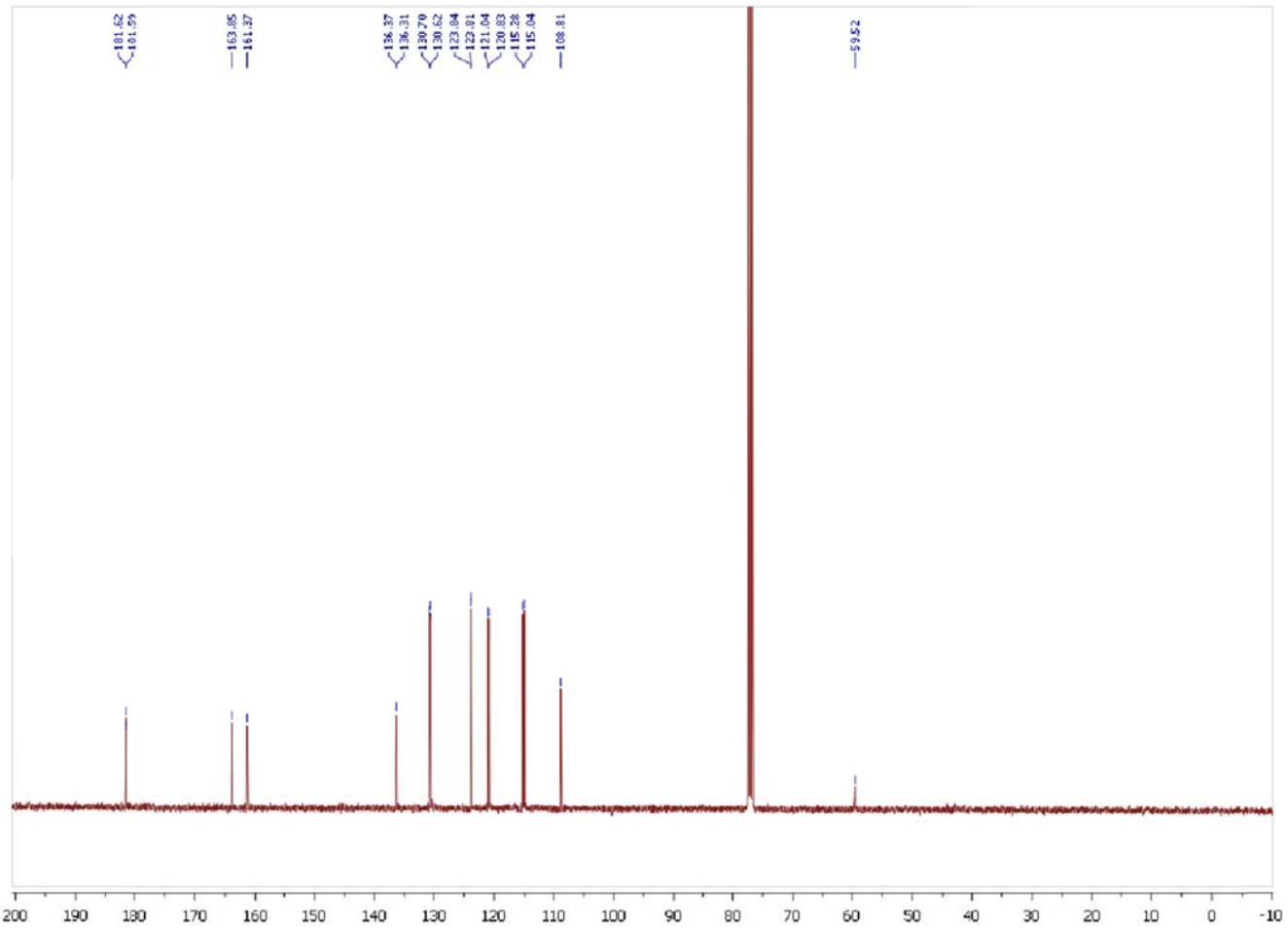

176.72
160.93
141.46
133.94
133.83
127.71
77.12
61.67
14.32
77.6
76.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

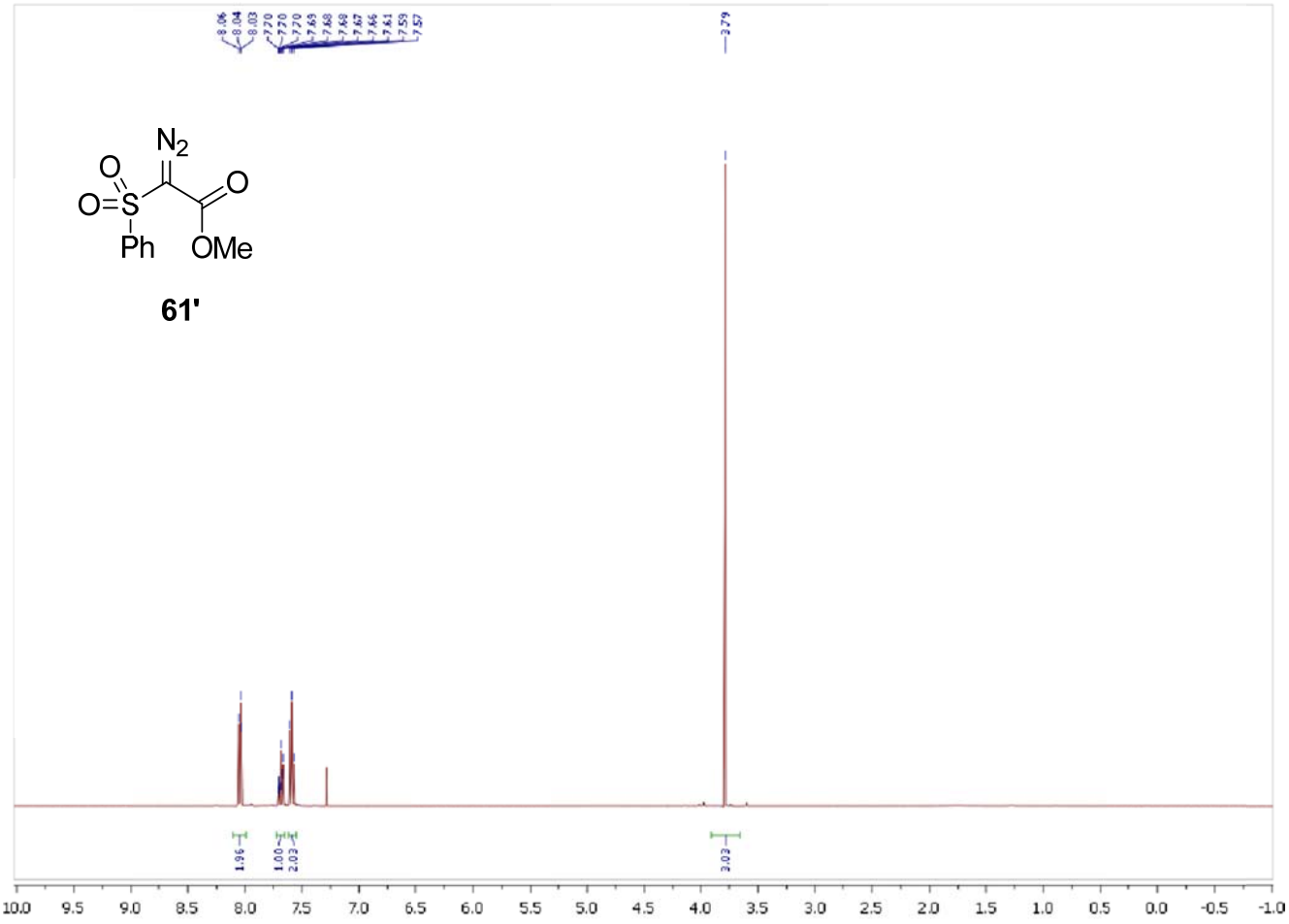

8.05
8.05
8.04
8.04
7.79
7.79
7.78
7.78
7.21
7.20
7.20
7.19
N2
O
CN
S
1.00
1.00
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

59'

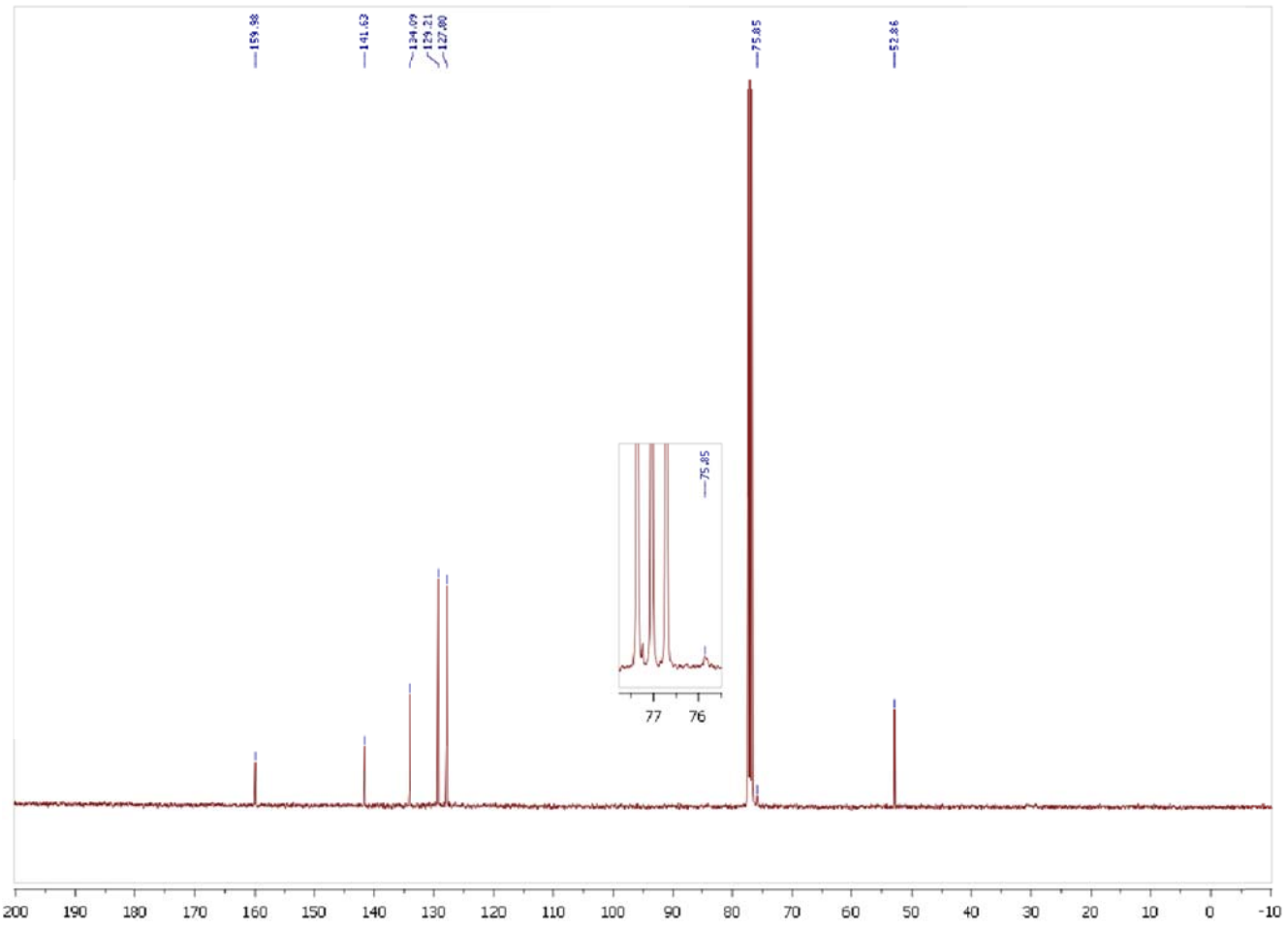

173.66
139.85
135.23
133.02
128.67
109.23
59.63
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

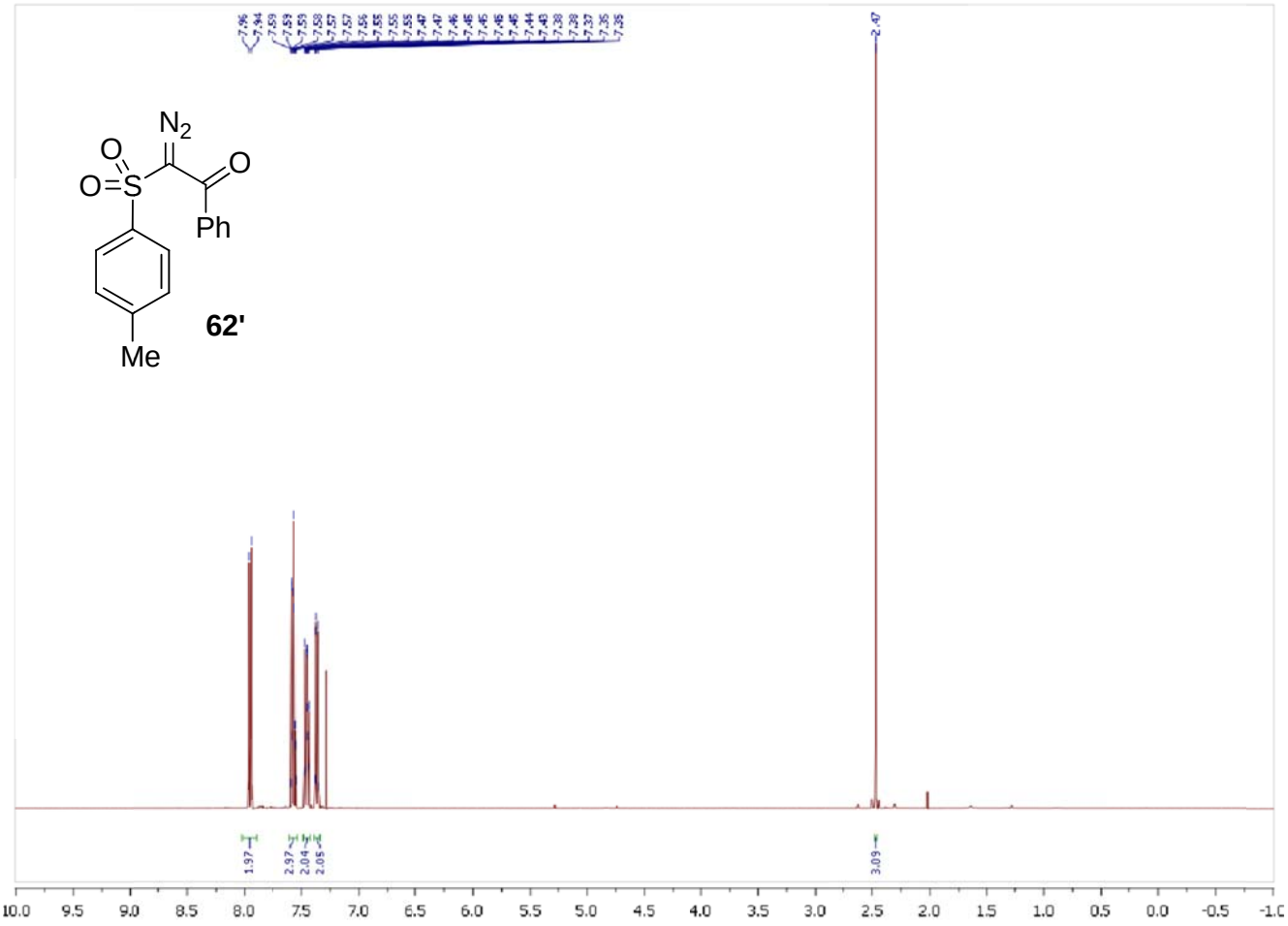

N2
O
CN
F
60'

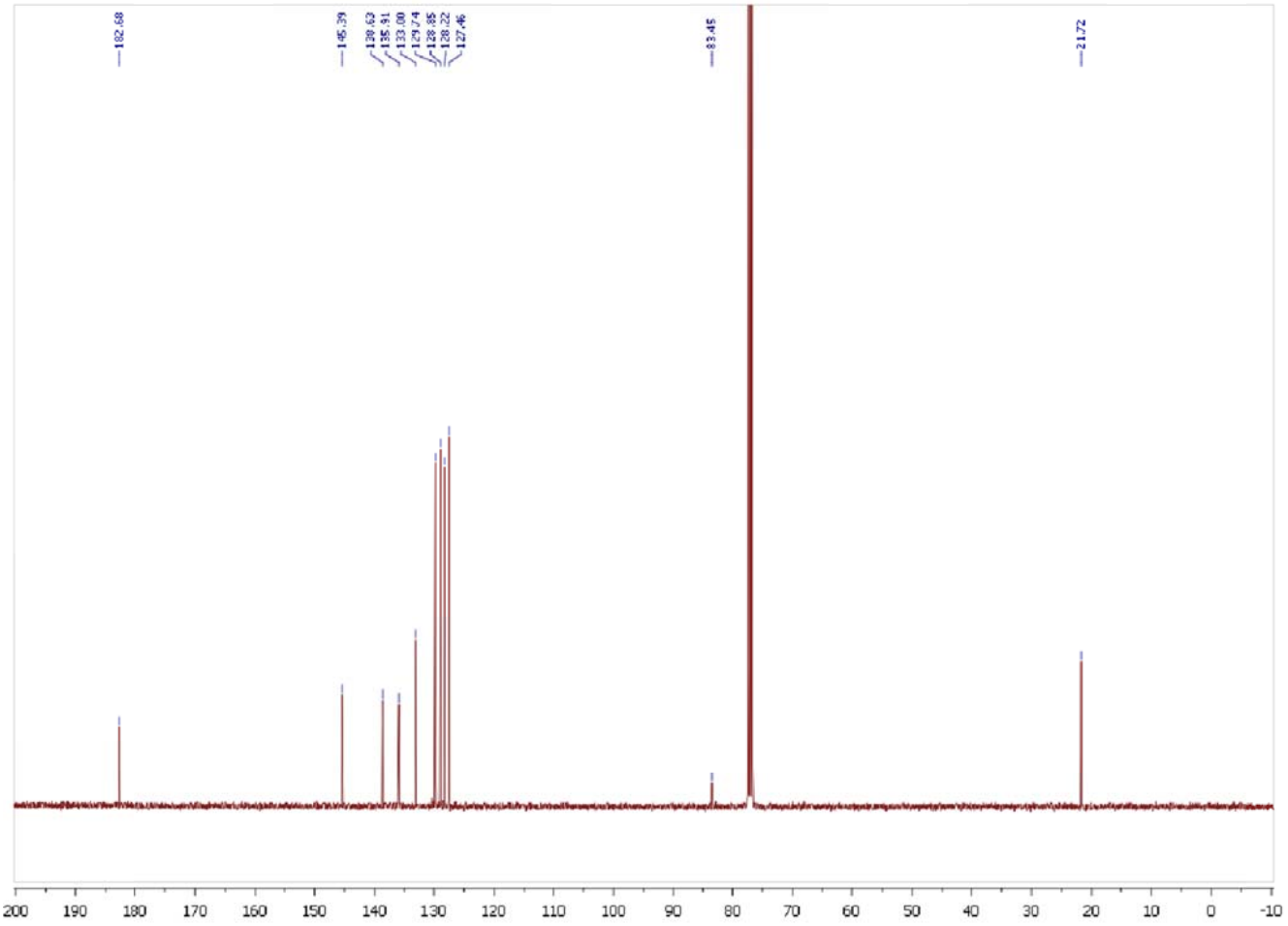


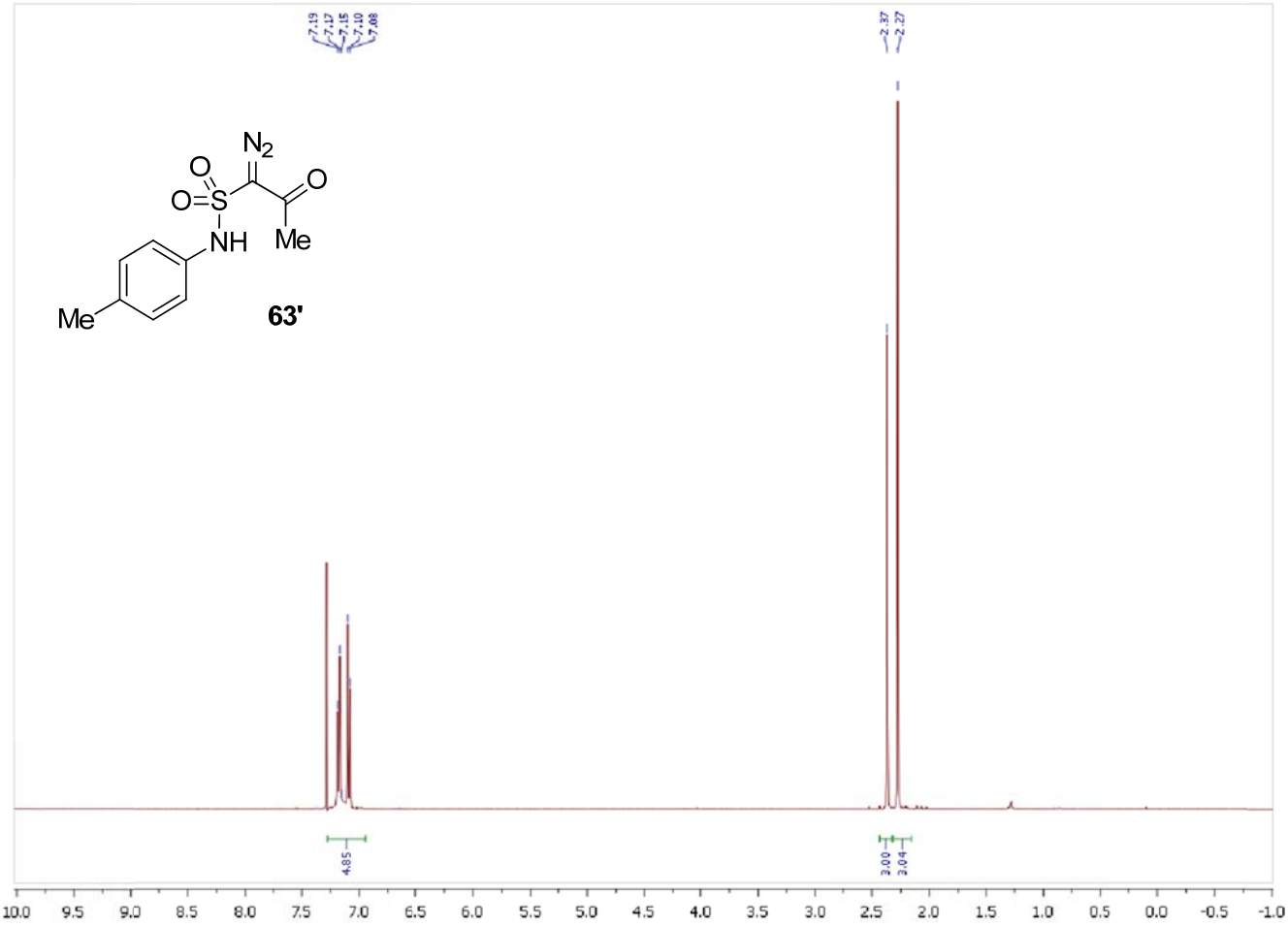


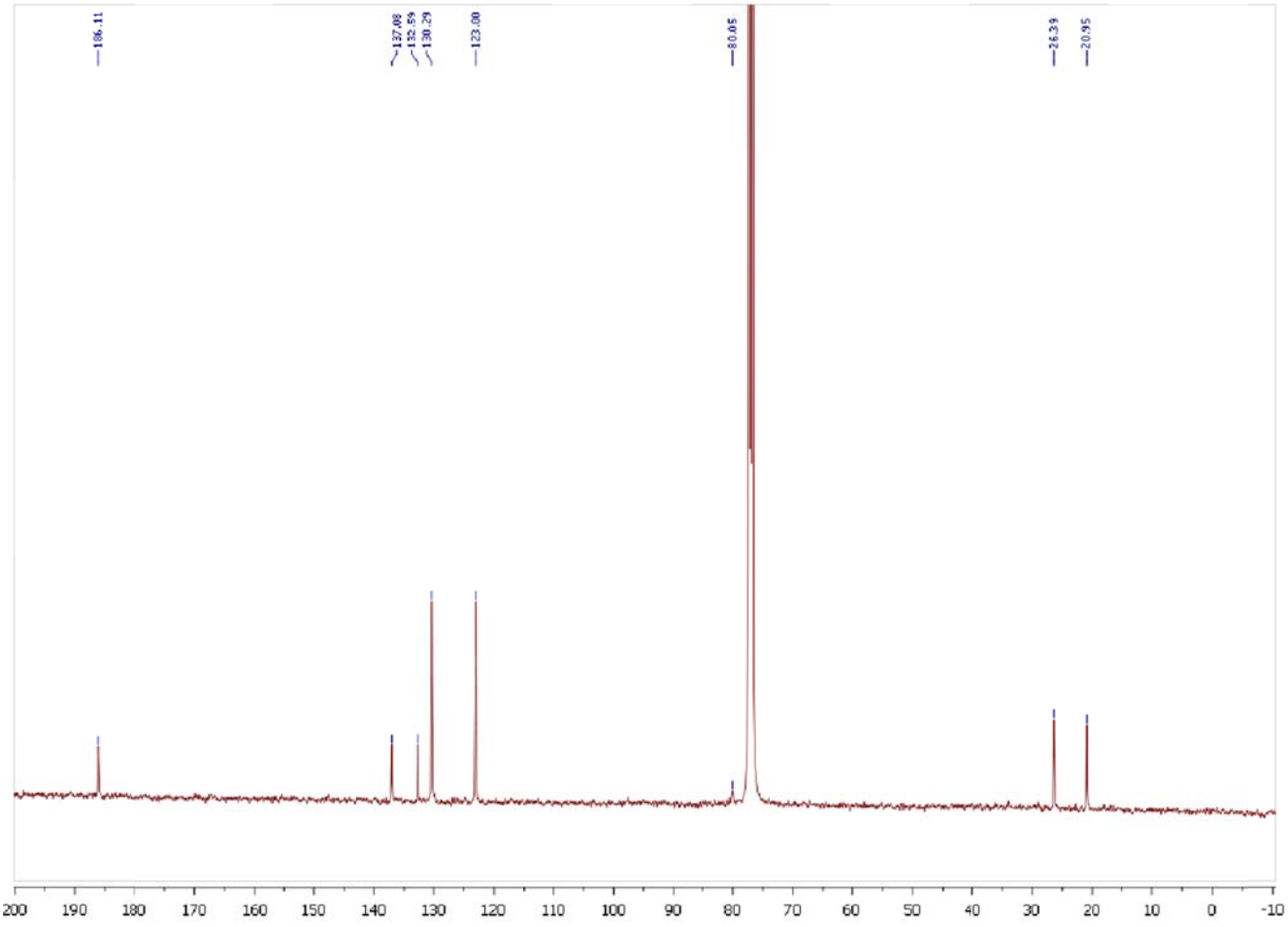
61'

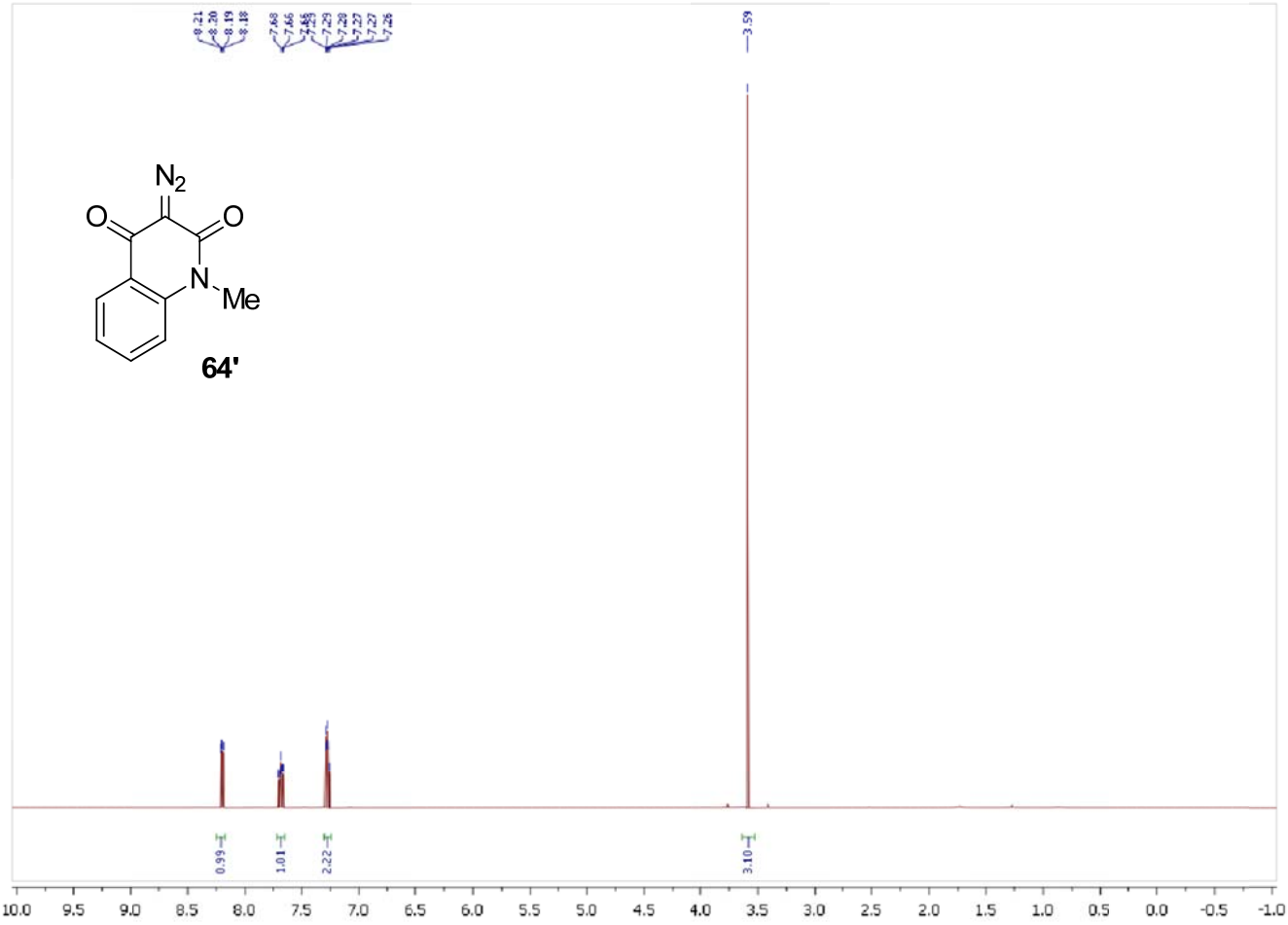


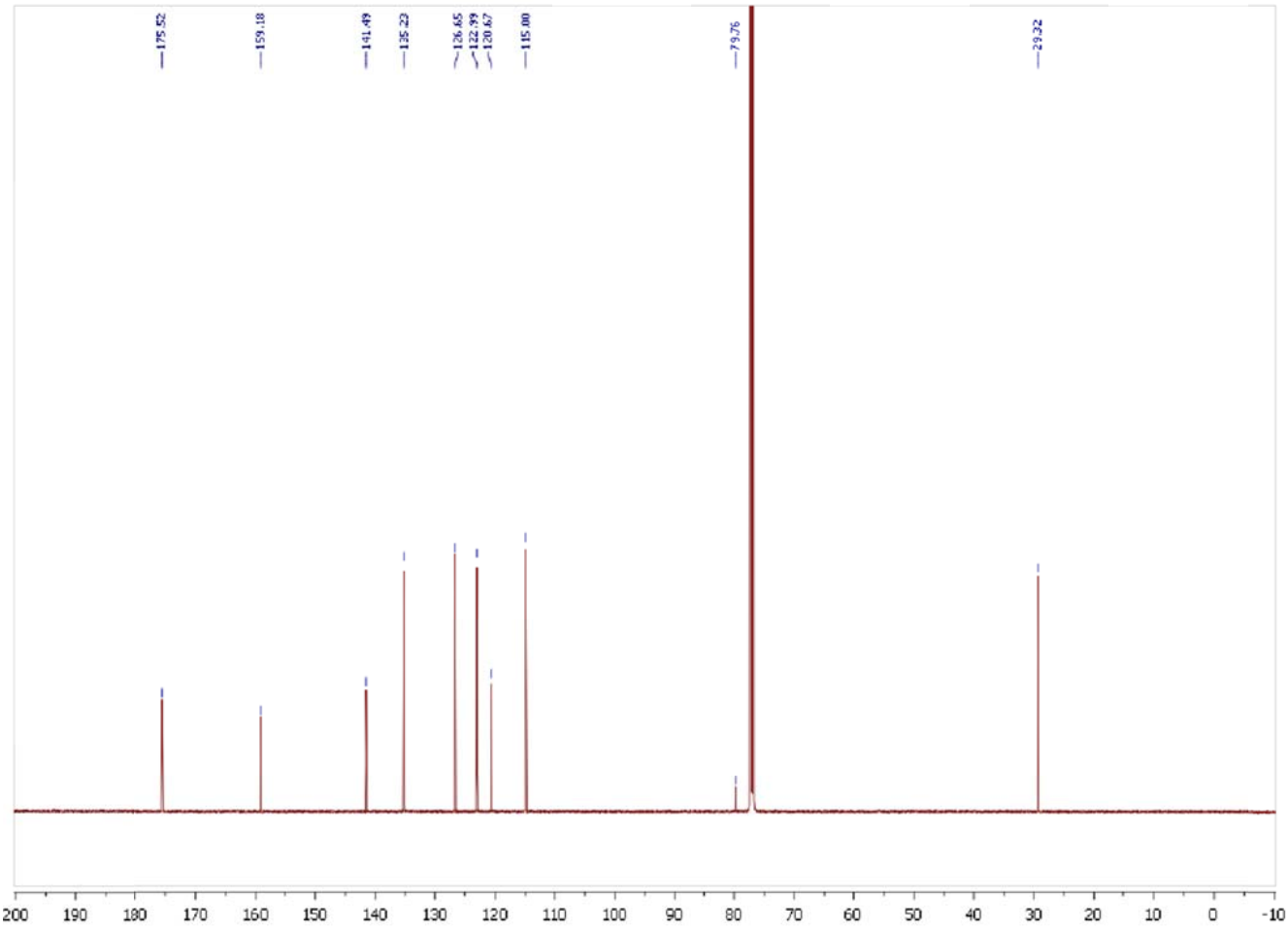

N2
O
O=S
O
Ph
Me
62'

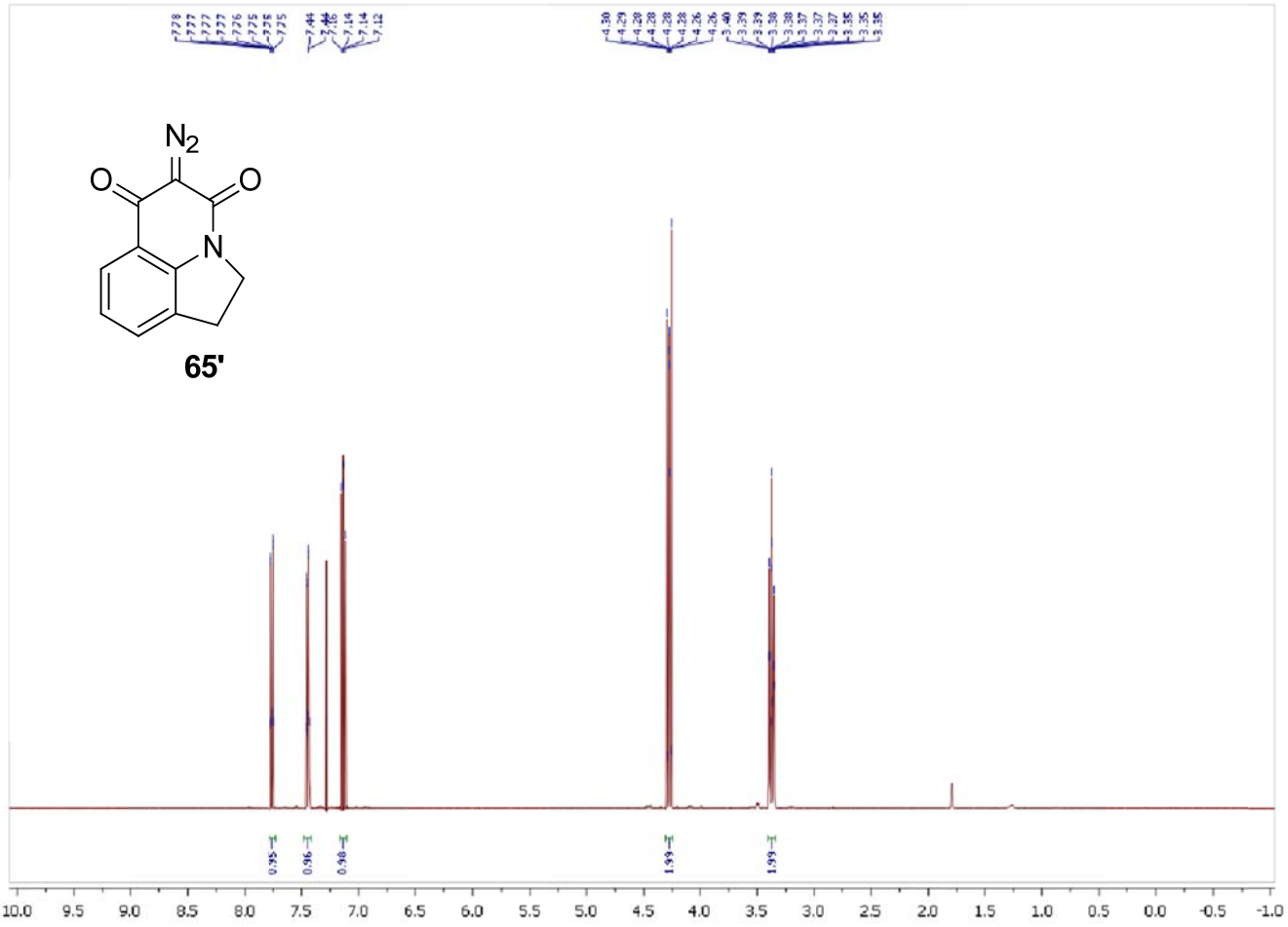


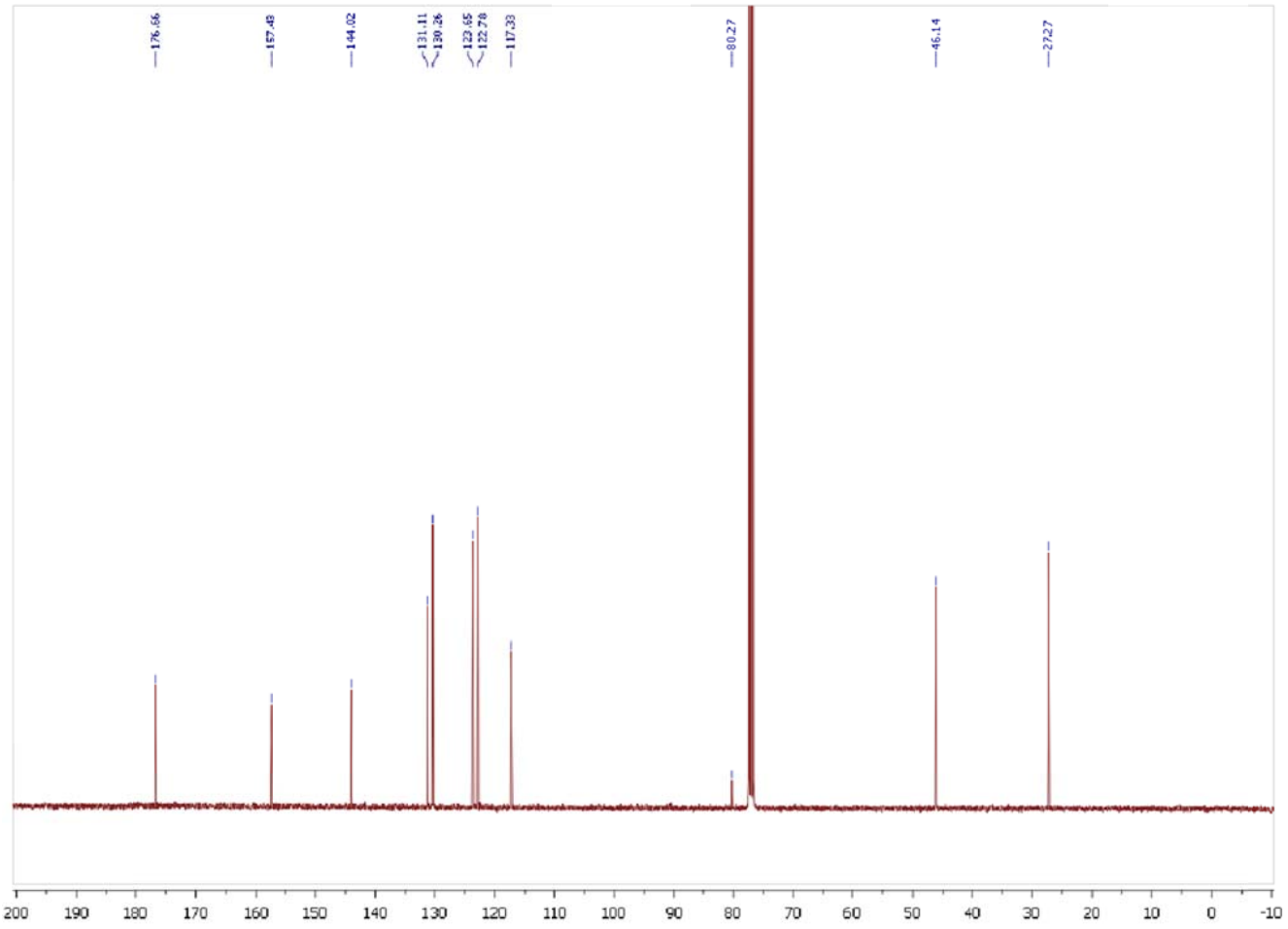

7.19
7.17
7.15
7.10
7.08
2.37
2.27
N2
O
O=S
O
NH
Me
Me
63'
4.85
3.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

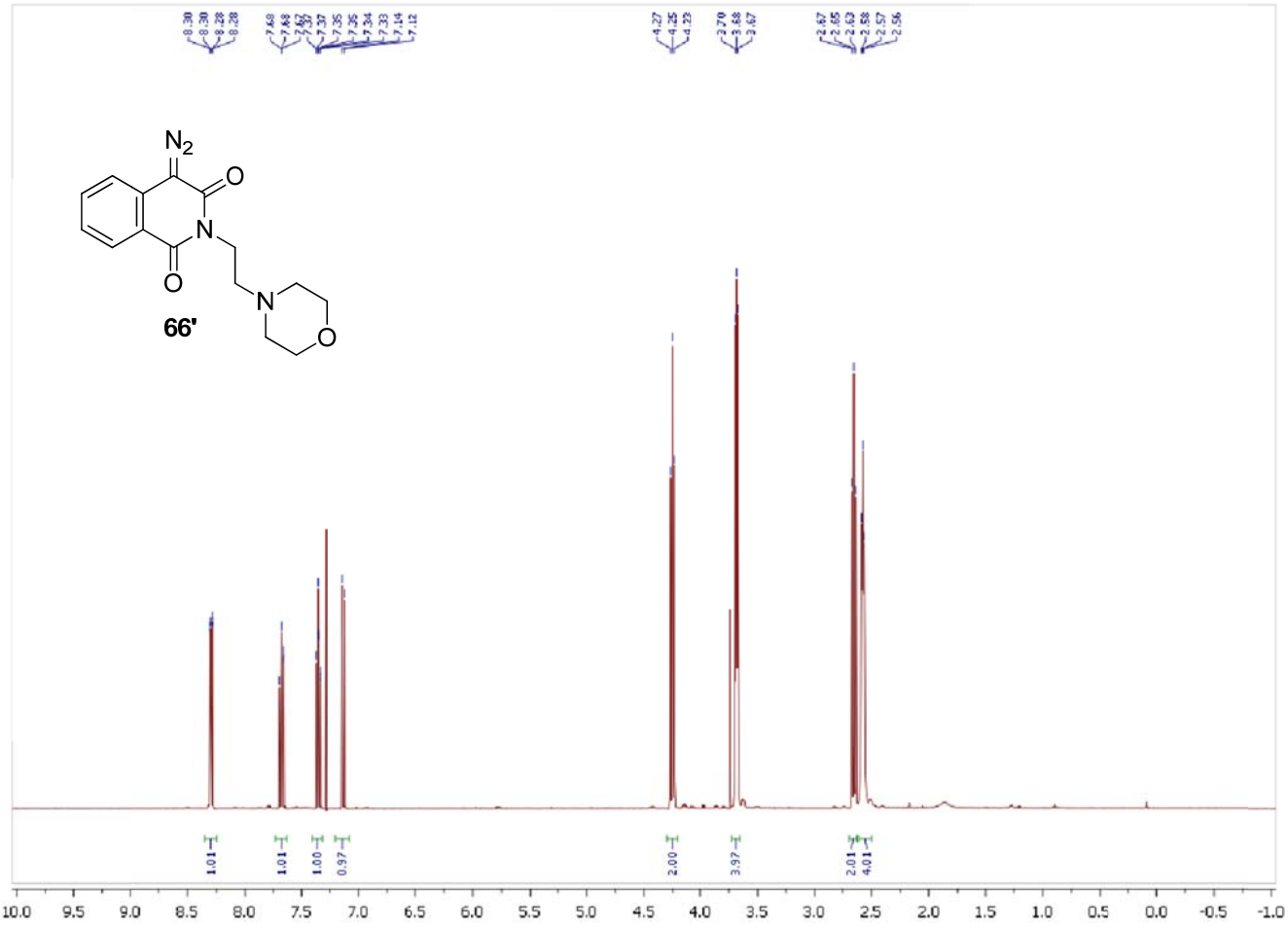

186.11
137.08
132.59
130.29
123.00
80.05
26.39
20.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

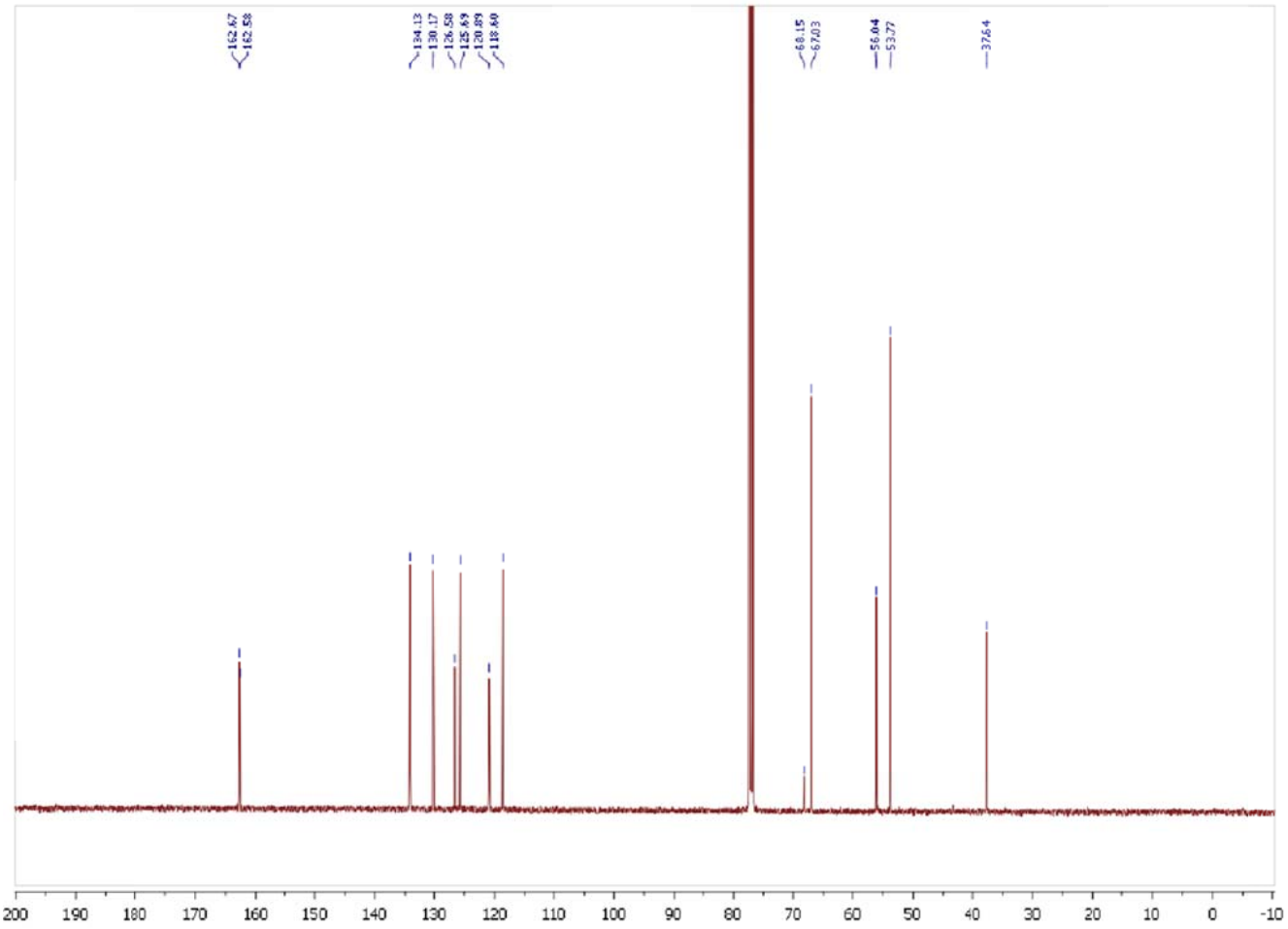

N2
O
O
N
Me
64'

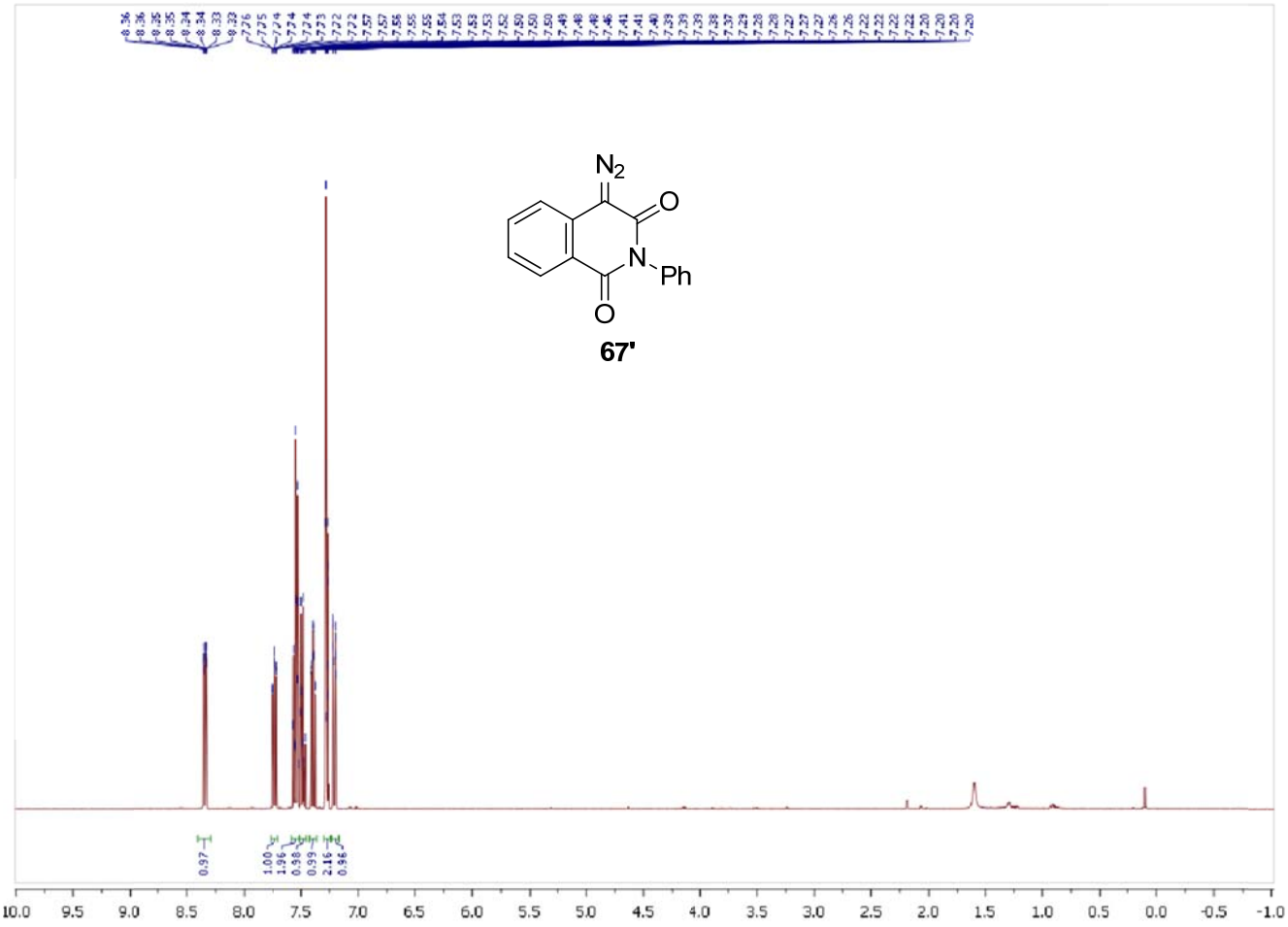



N2
O
O
N
65'

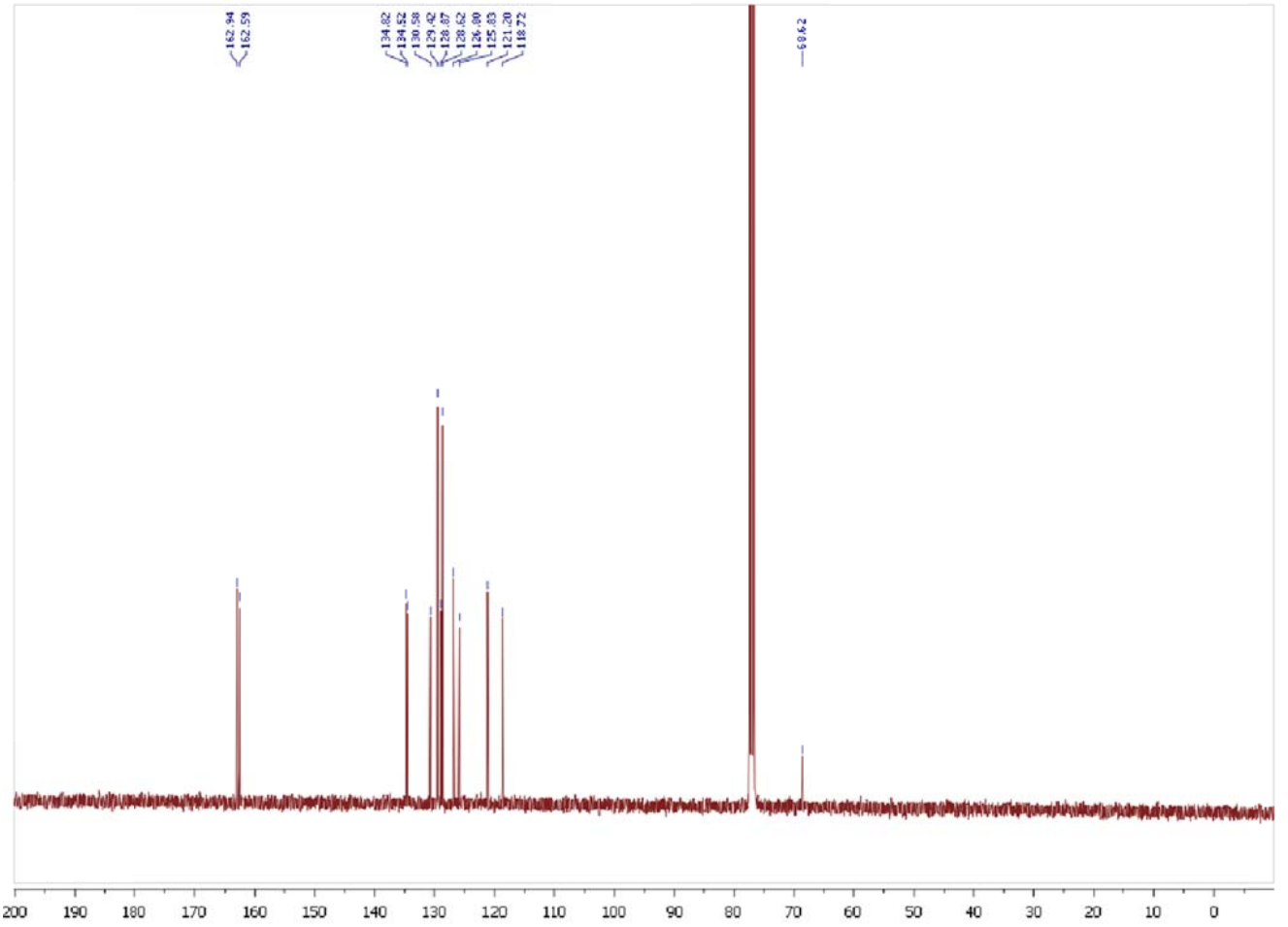


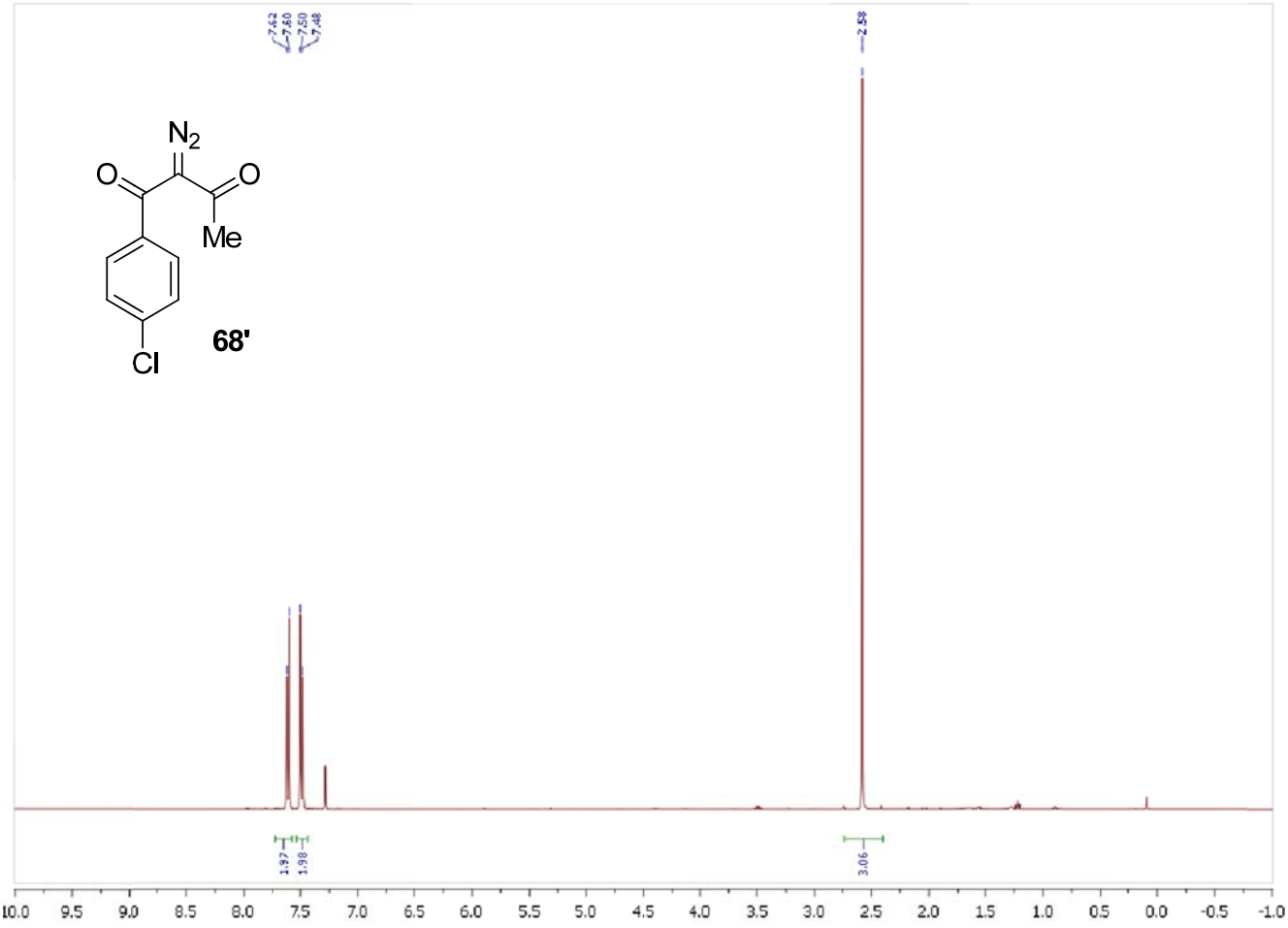

N2
O
N
O
N
O
66'

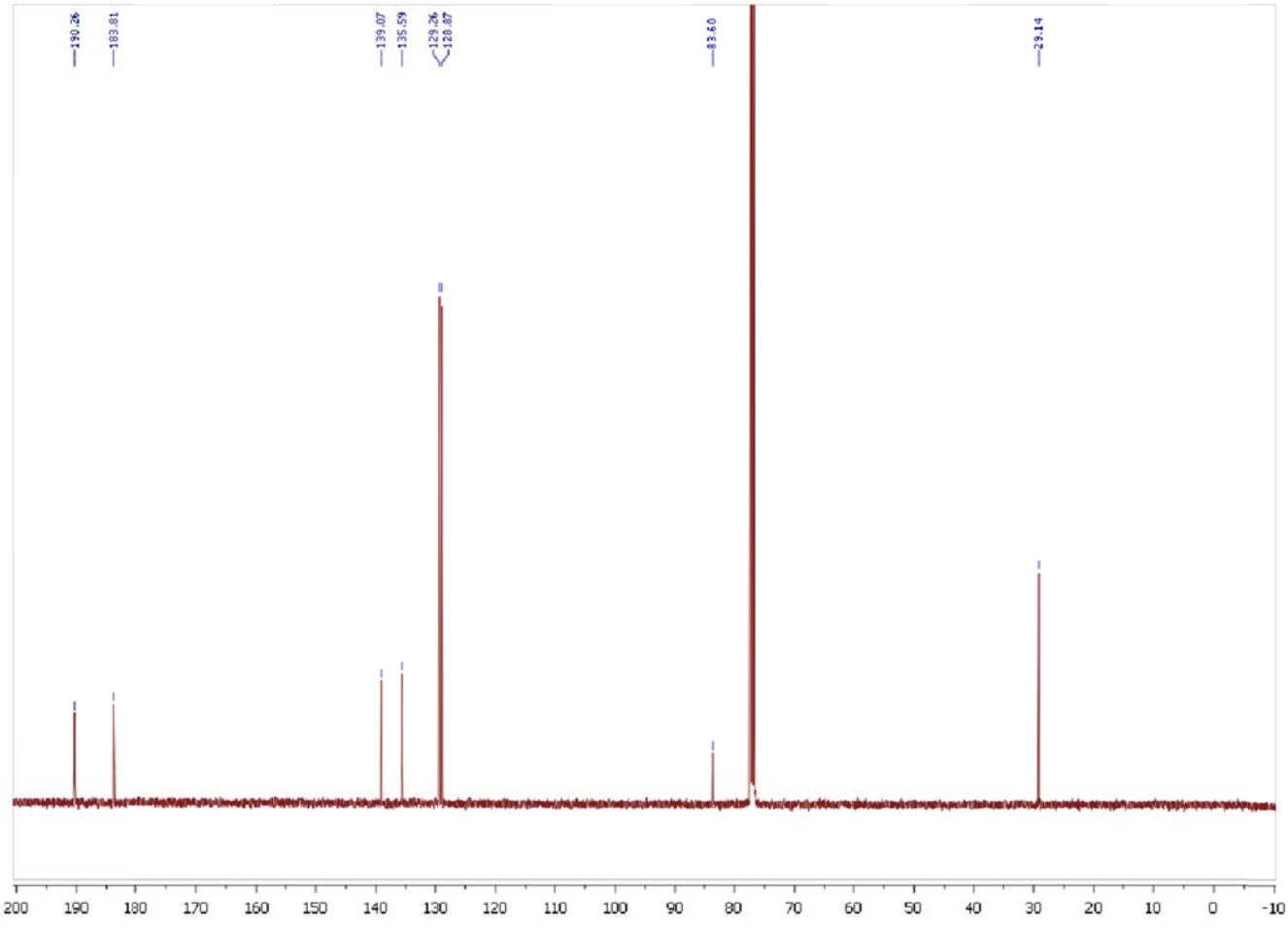


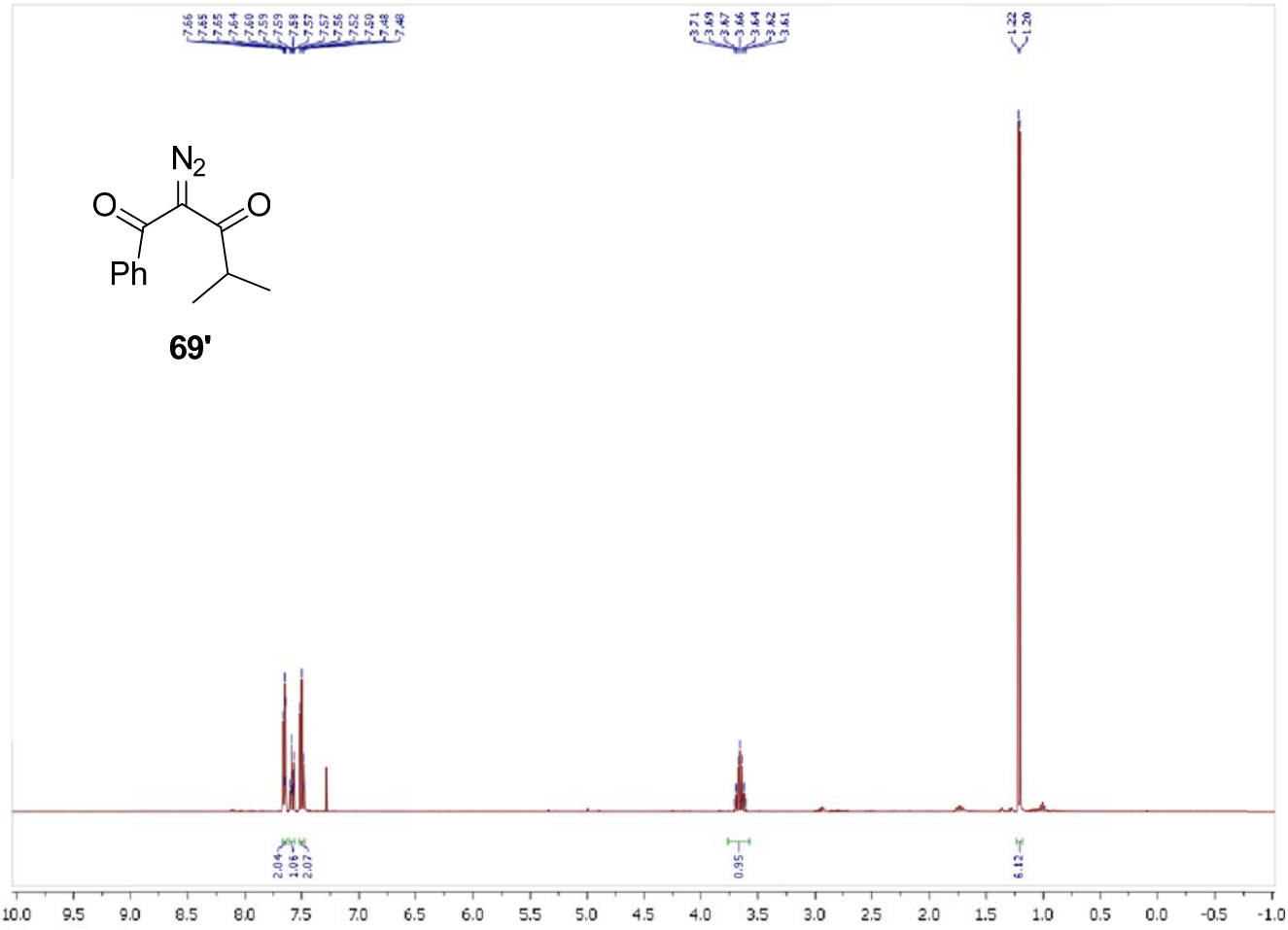

8.36
8.36
8.35
8.35
8.34
8.34
8.33
8.33
7.76
7.75
7.74
7.74
7.74
7.73
7.73
7.72
7.72
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.50
7.50
7.50
7.49
7.48
7.48
7.46
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.22
7.22
7.22
7.20
7.20
7.20
7.20
N2
O
N
Ph
O
0.97
1.00
1.96
0.98
0.99
2.16
0.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

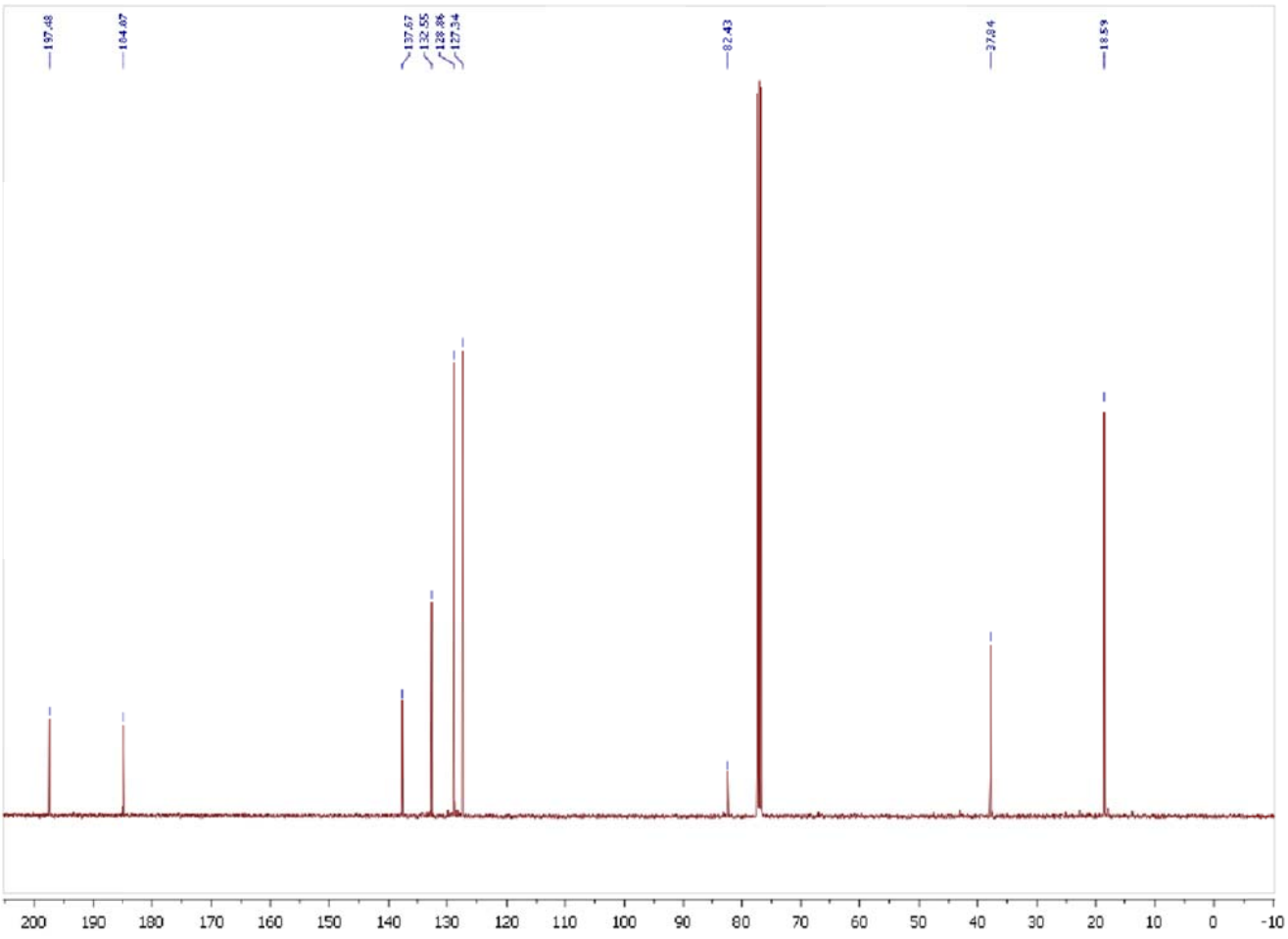
67'


162.94
162.59
134.82
134.52
130.58
129.42
128.87
128.62
126.00
125.83
121.20
118.72
69.62
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.62
7.60
7.50
7.48
2.58
1.97
1.98
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

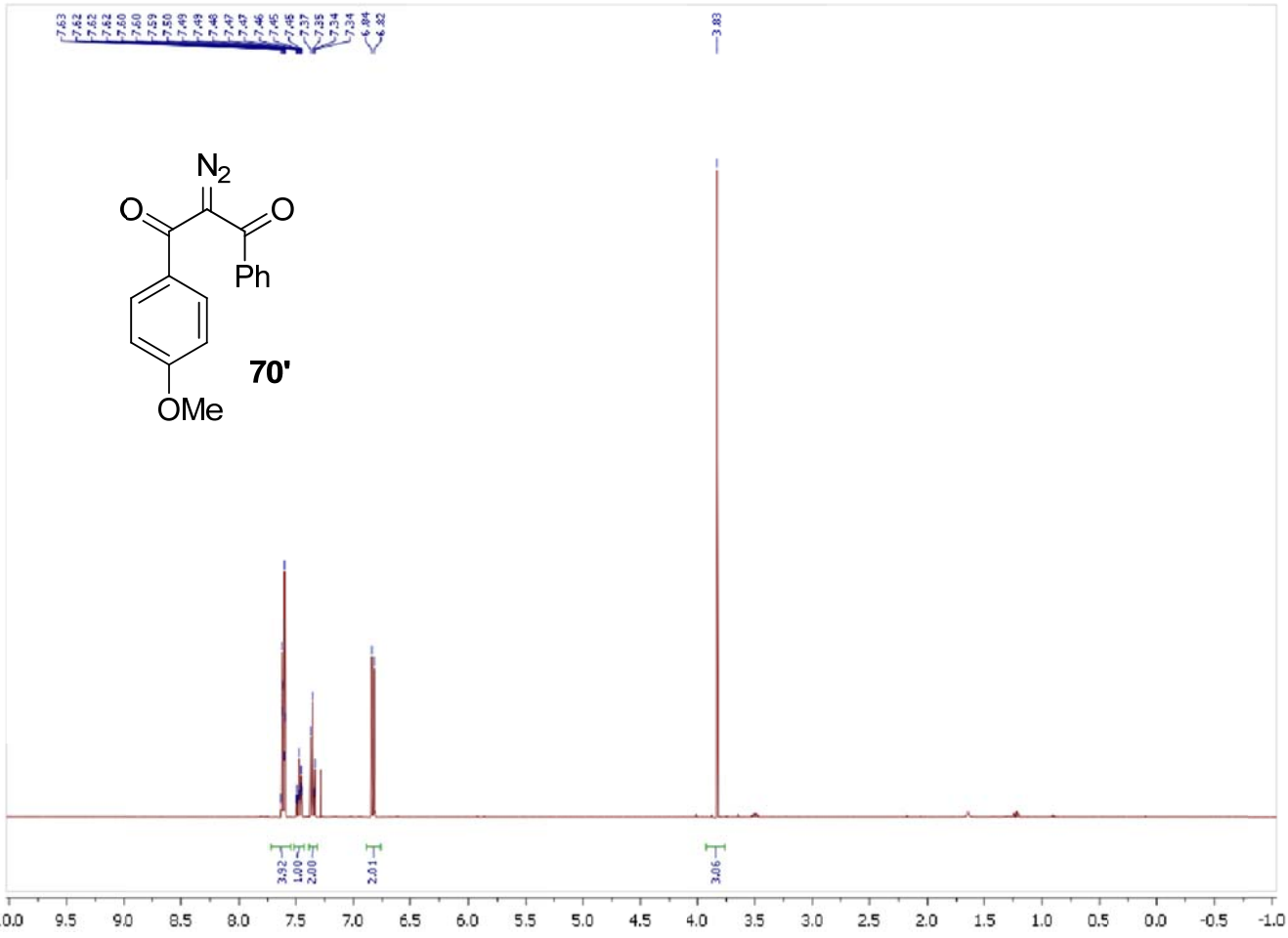

190.26
183.81
139.07
135.59
129.26
128.87
83.60
29.14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

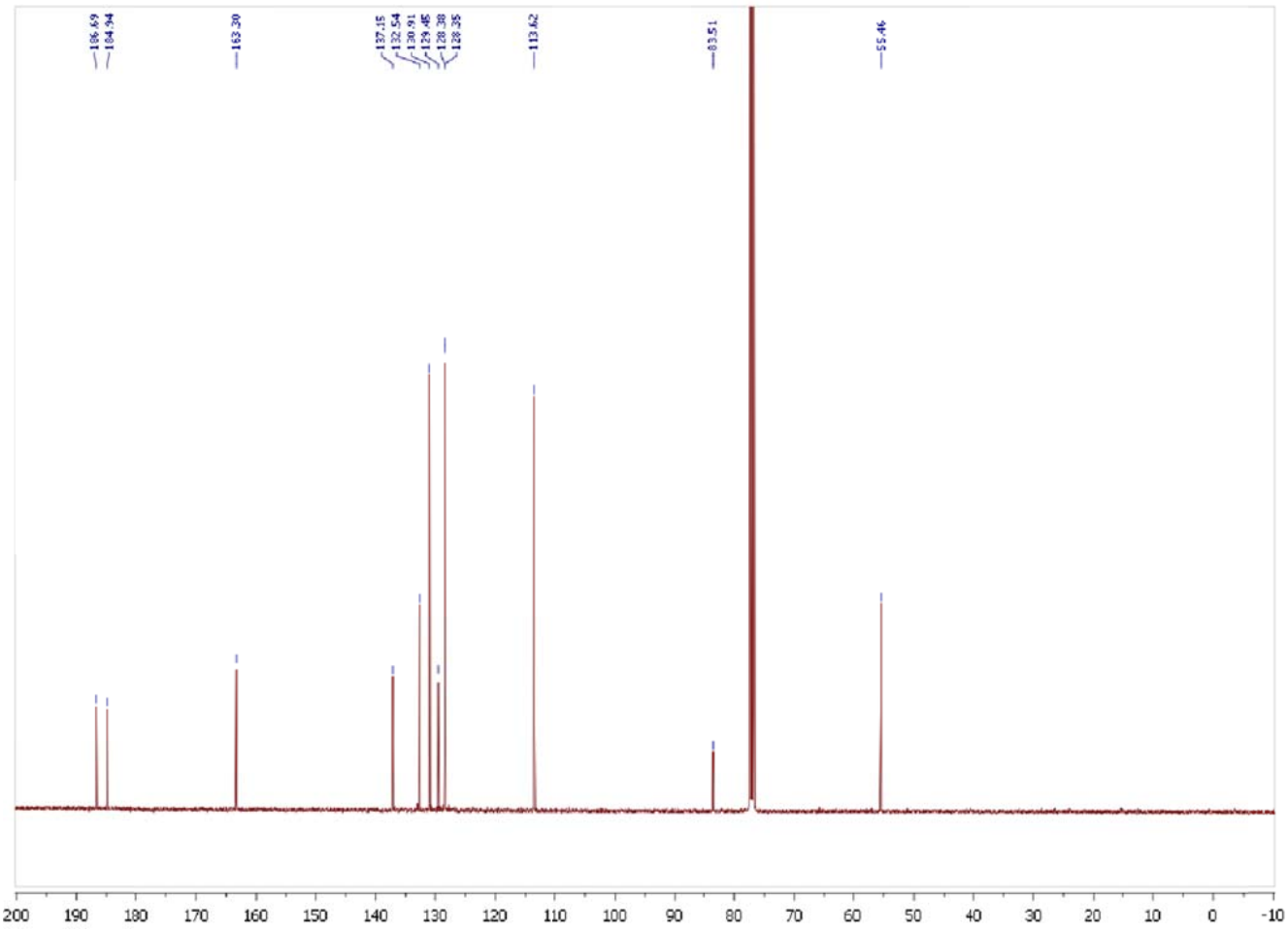

7.66
7.65
7.65
7.64
7.60
7.59
7.59
7.58
7.57
7.57
7.56
7.52
7.50
7.48
7.48
3.71
3.69
3.67
3.66
3.64
3.62
3.61
1.22
1.20
2.04
1.06
2.07
0.95
6.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

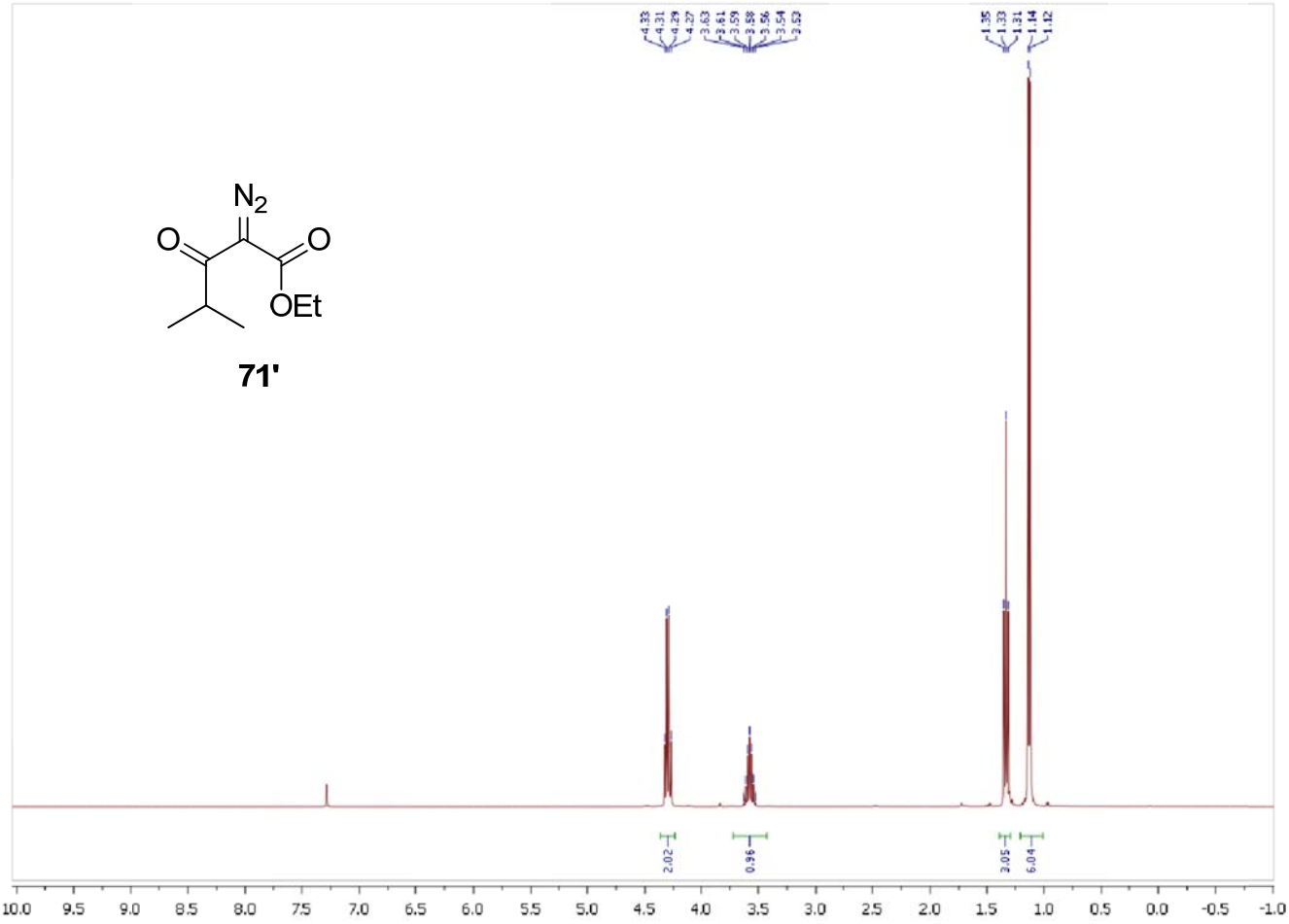

197.48
184.67
137.67
132.55
128.86
127.34
82.43
37.84
18.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

N2
O
O
Ph

69'

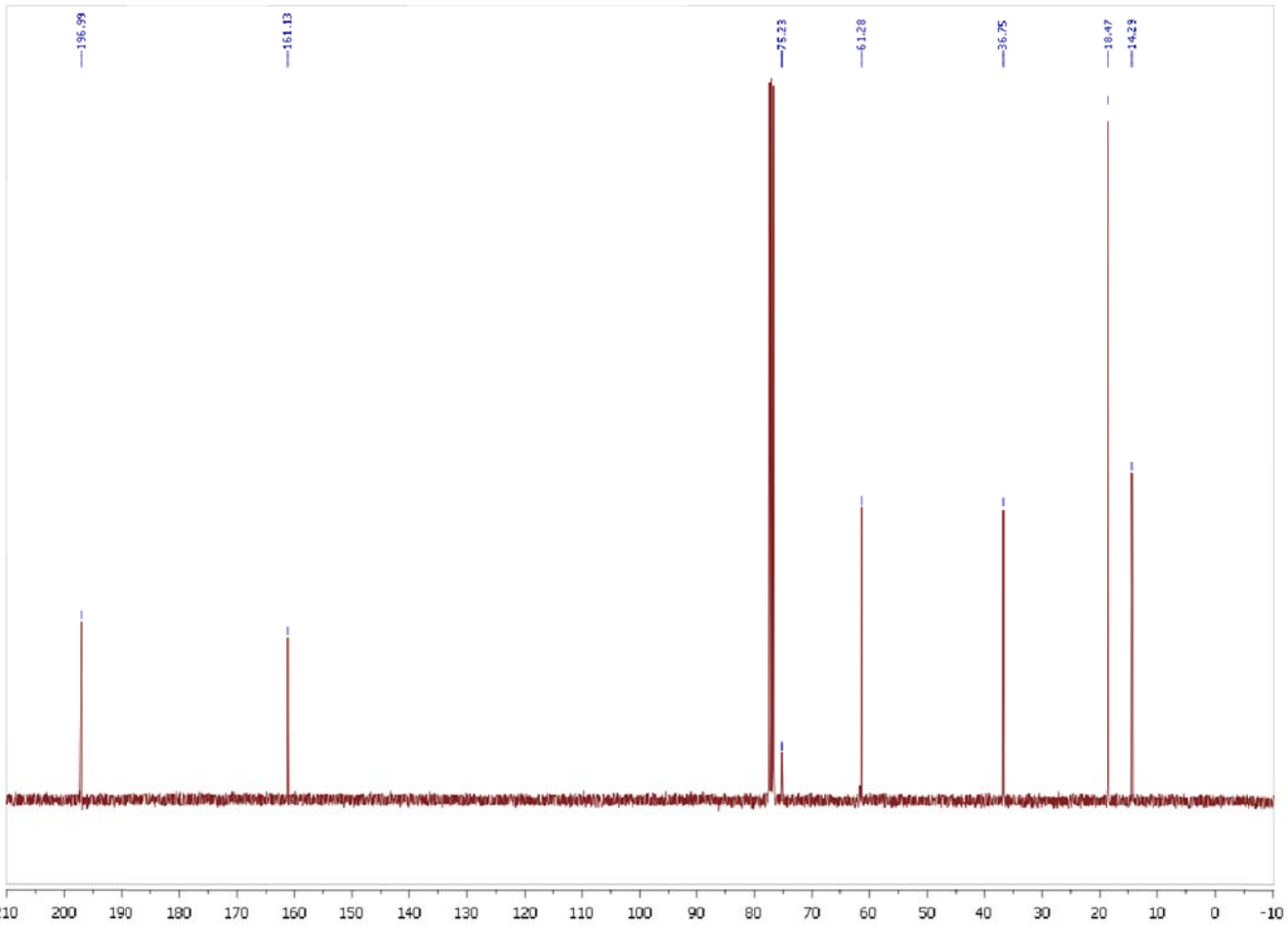

N2
O
O
Ph
OMe
70'

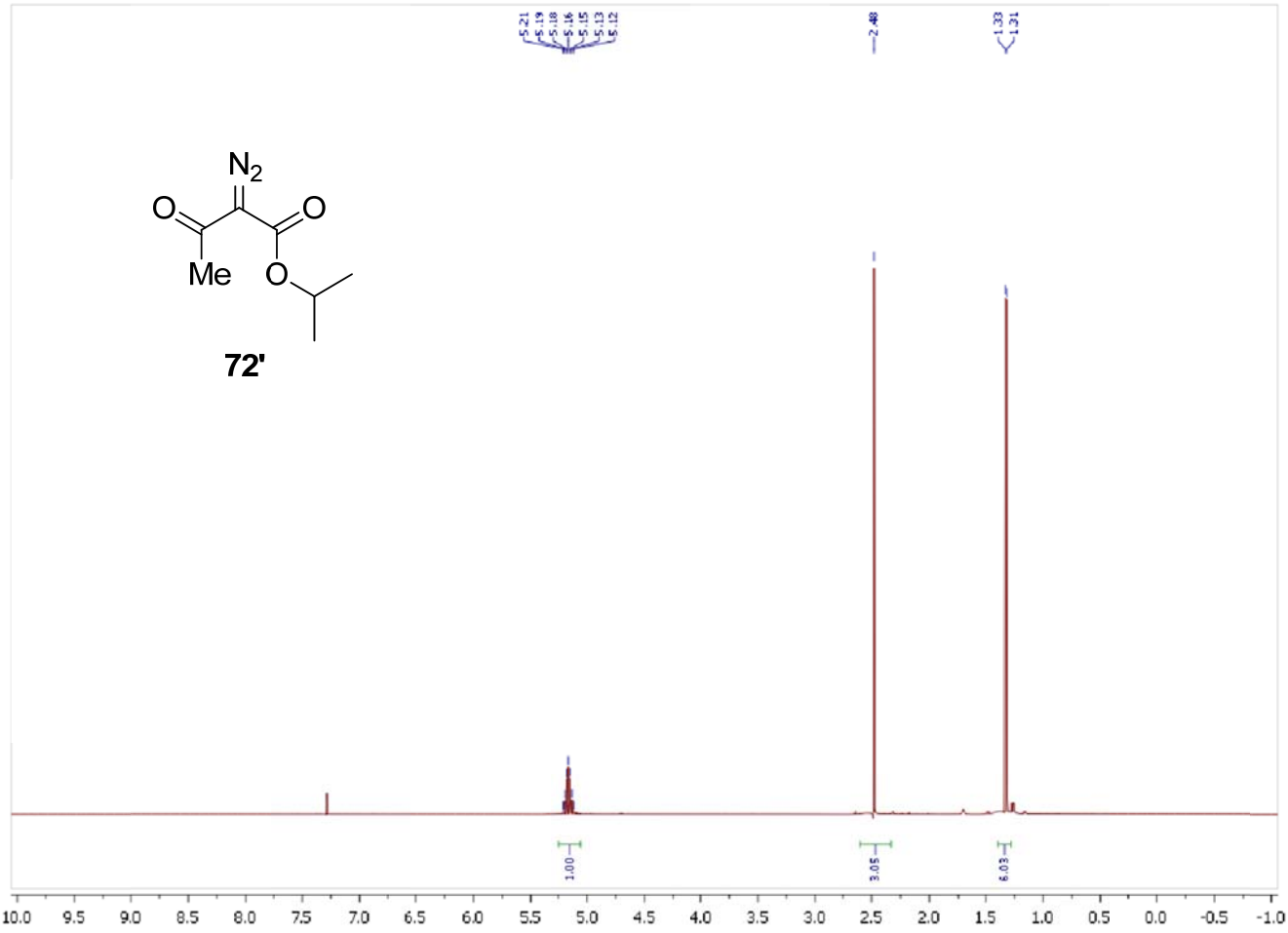



4.33
4.31
4.29
4.27
3.63
3.61
3.59
3.58
3.56
3.54
3.53
1.35
1.33
1.31
1.14
1.12
2.02
0.96
3.05
6.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

N2
O
O
OEt

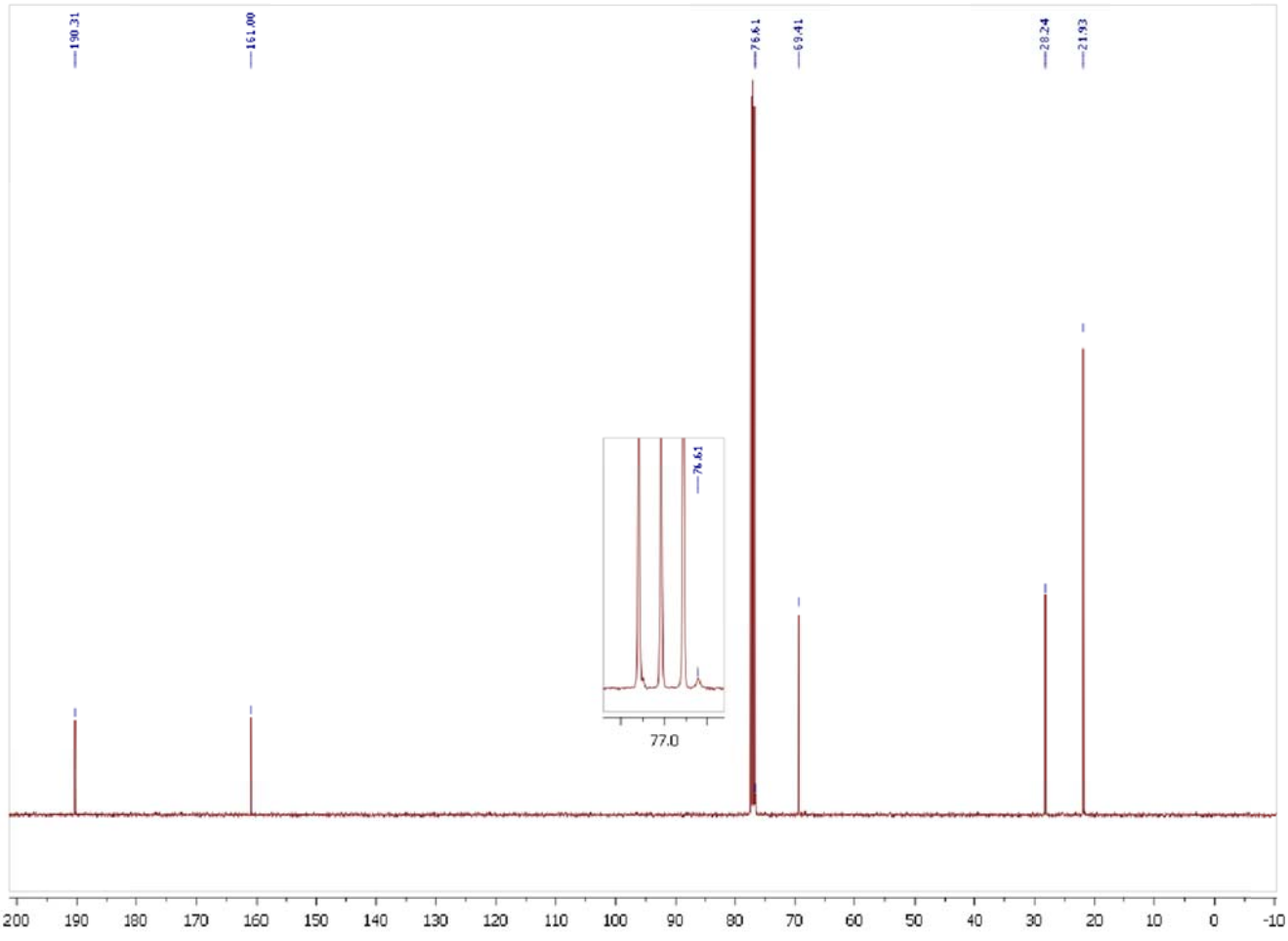
71'

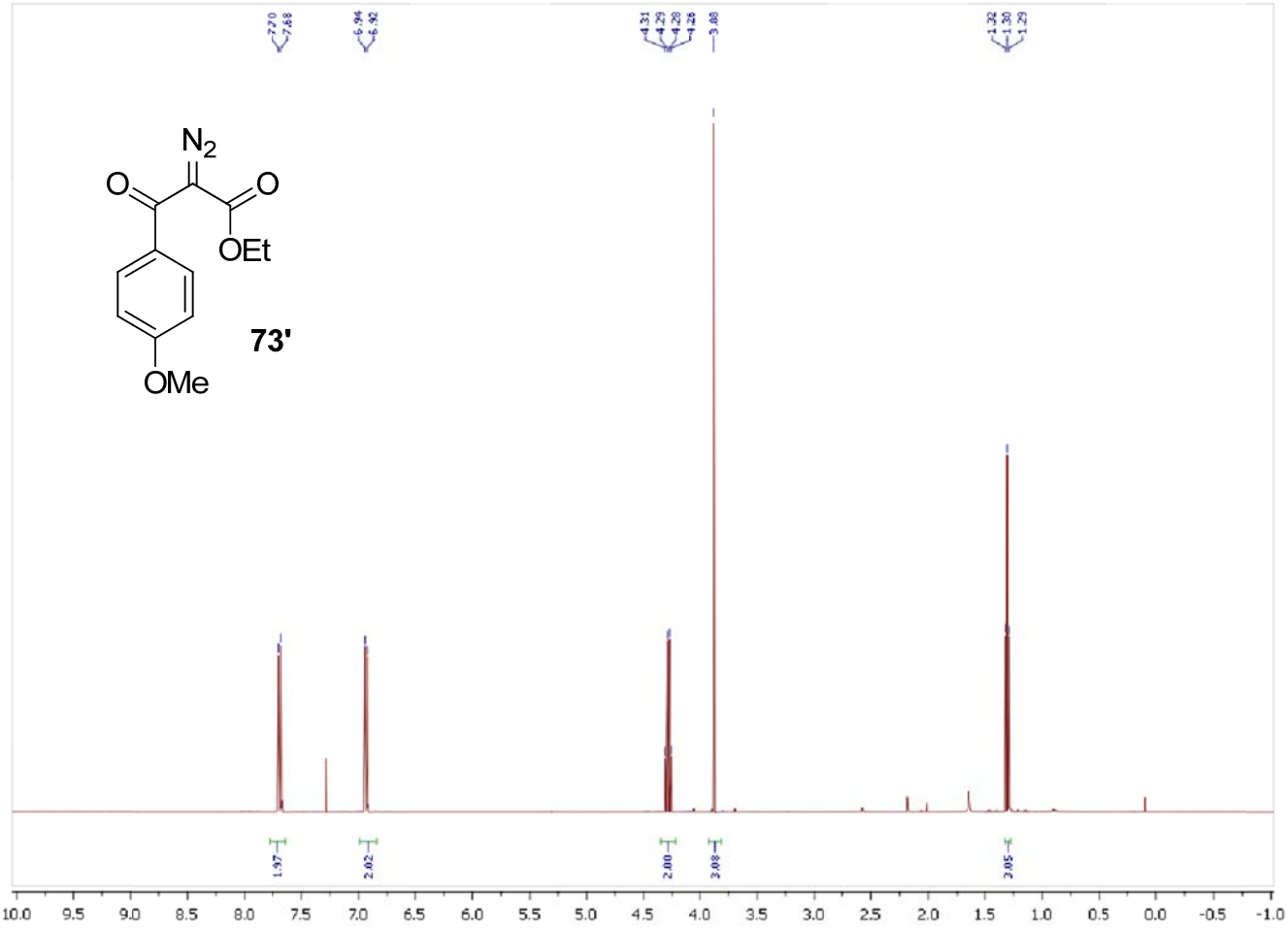

196.99
161.13
75.23
61.28
36.75
18.47
14.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

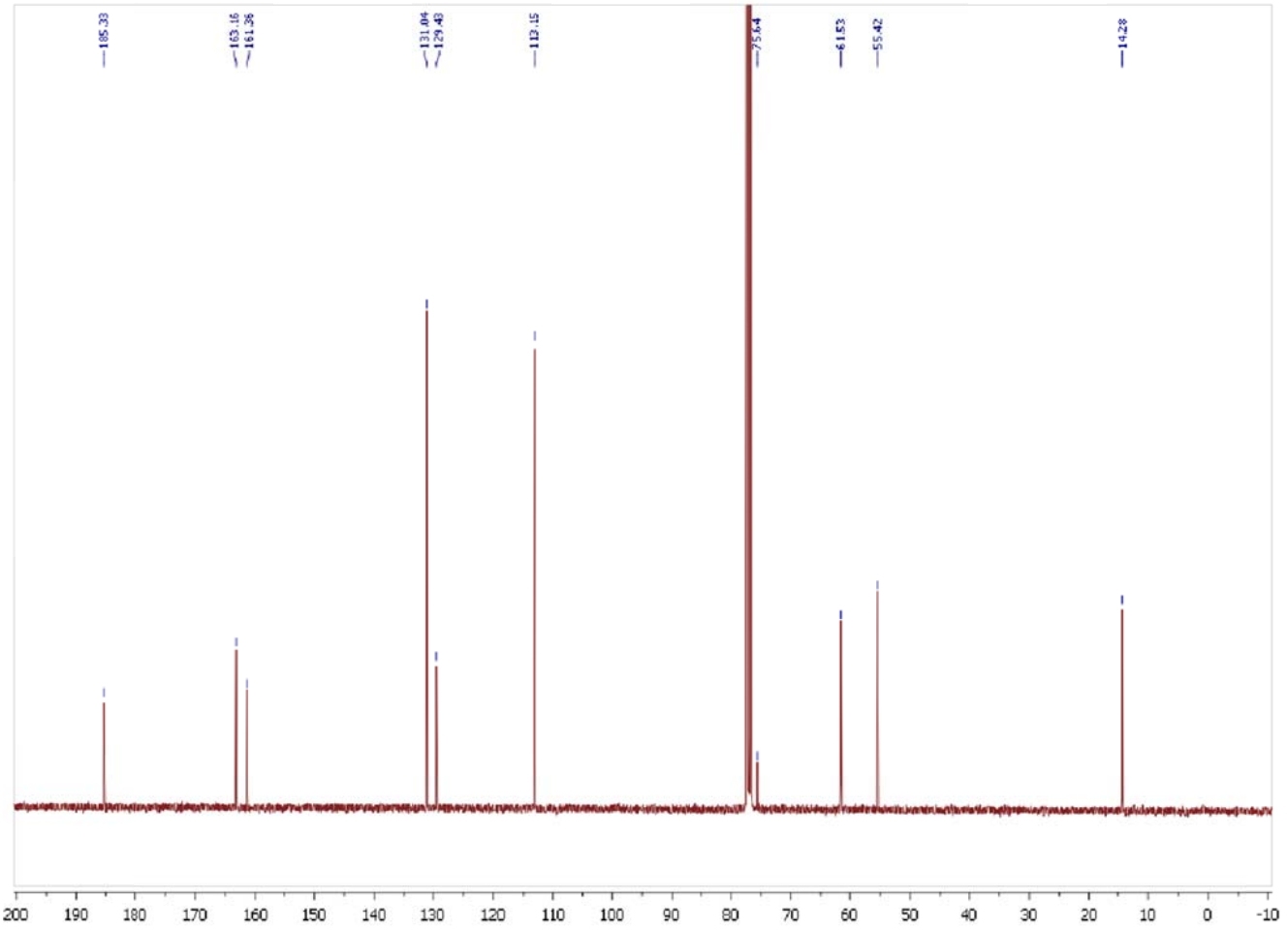

5.21
5.19
5.18
5.16
5.15
5.13
5.12
2.48
1.33
1.31
1.00
3.05
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

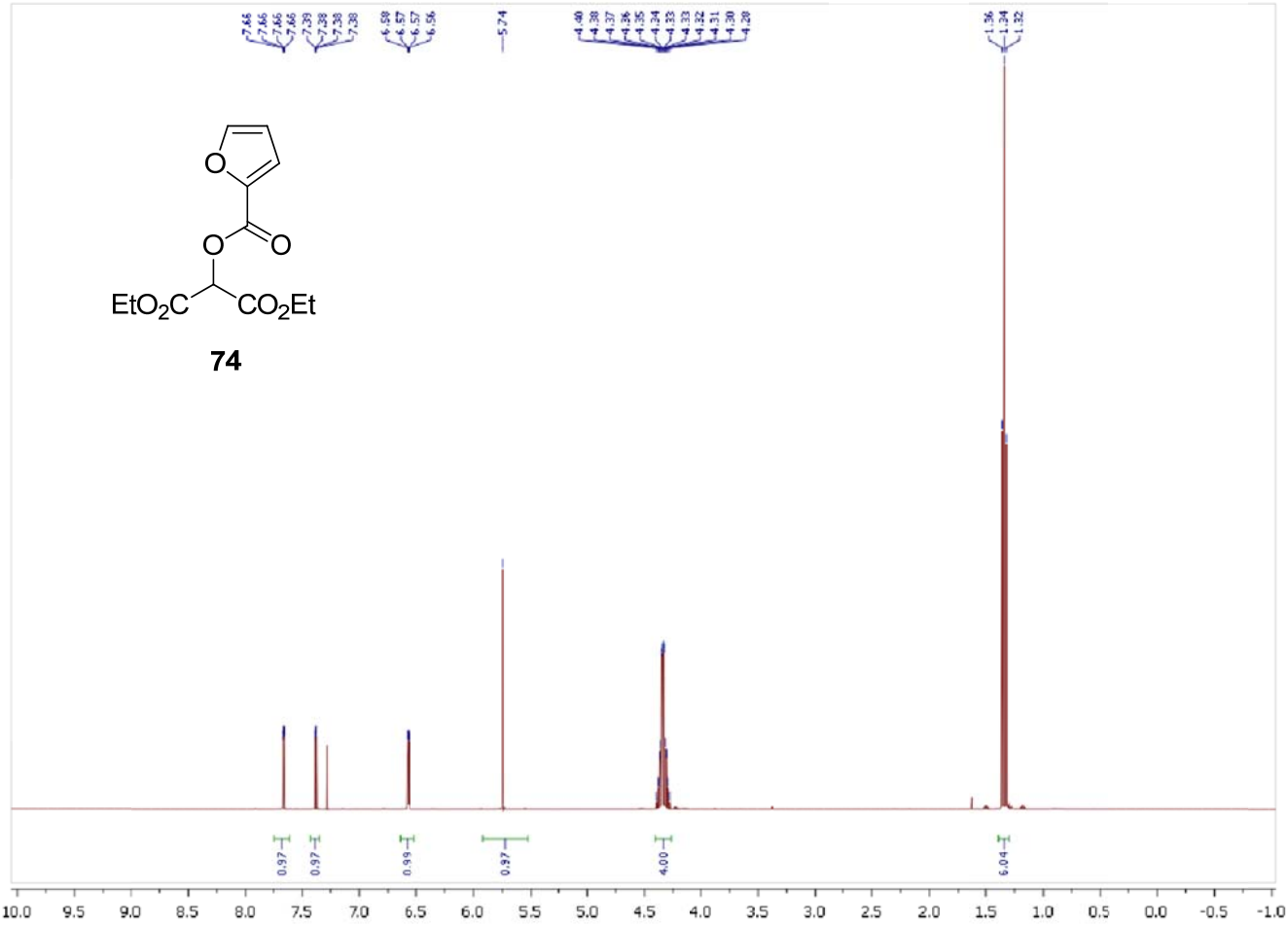
N2
O
O
Me
O

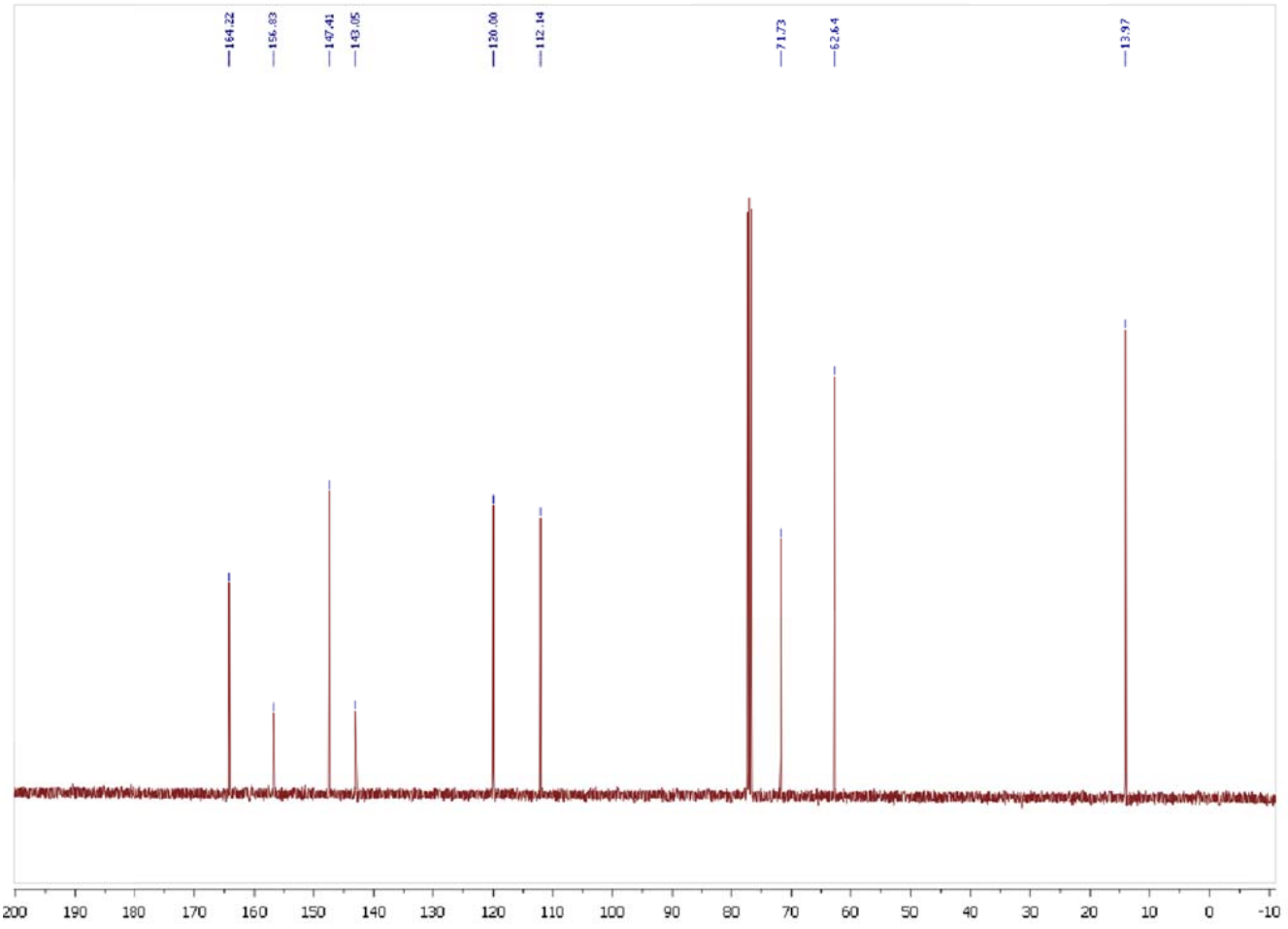
72'

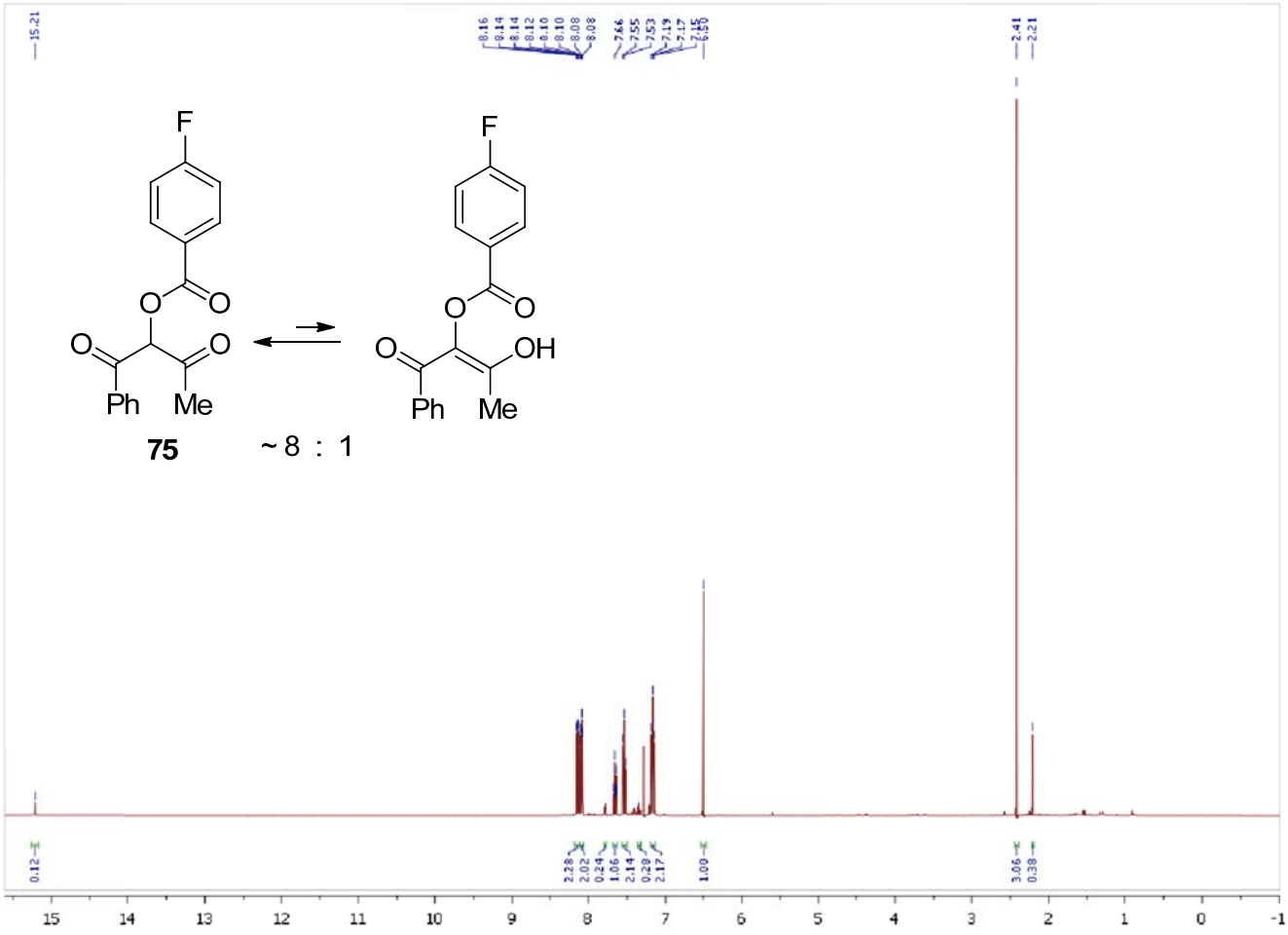

190.31
161.00
76.61
69.41
28.24
21.93
76.61
77.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.70
7.68
6.94
6.92
4.31
4.29
4.28
4.26
3.88
1.32
1.30
1.29
N2
O
O
OEt
OMe
73'
1.97
2.02
2.00
3.08
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

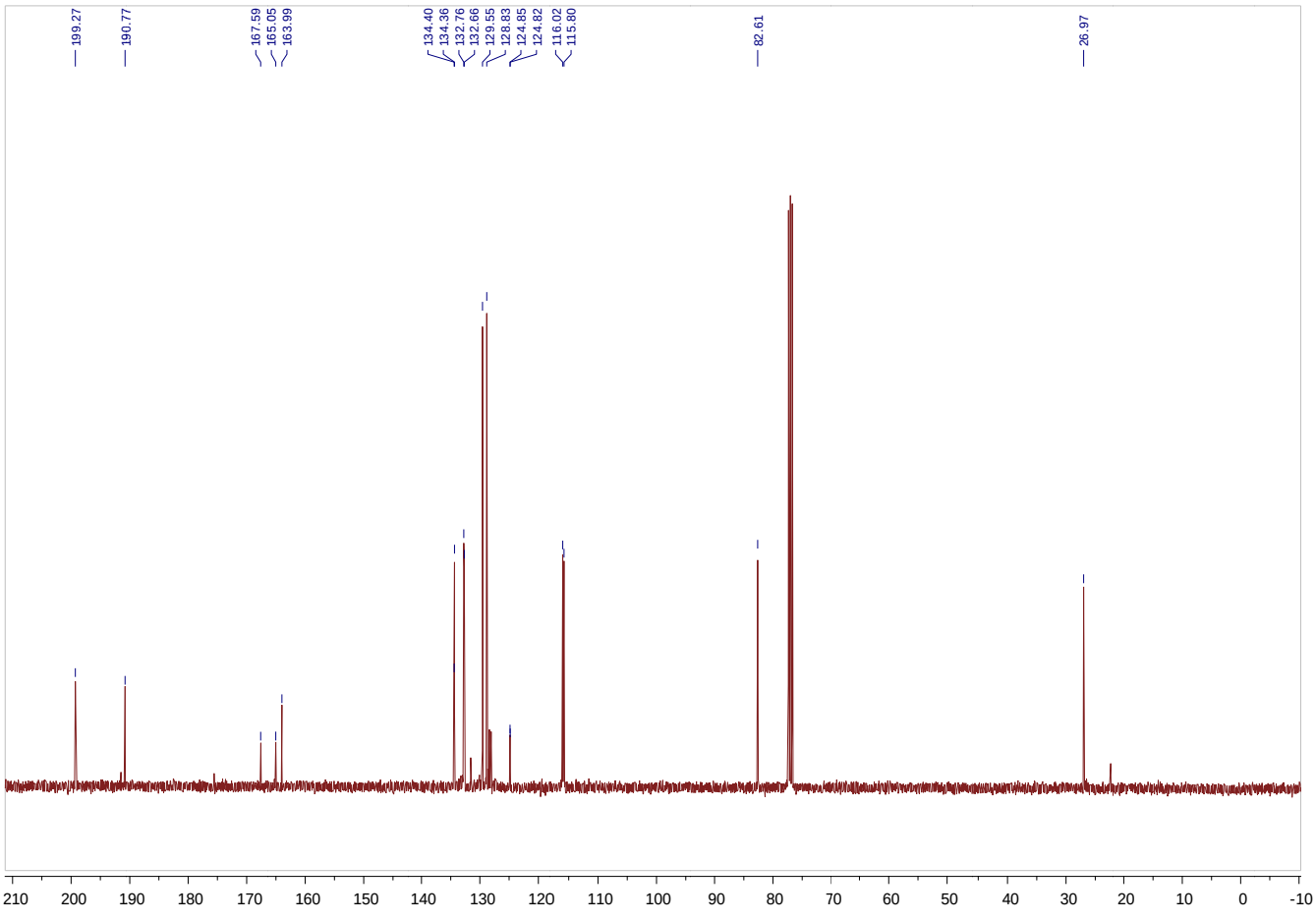

185.33
163.16
161.36
131.04
129.48
112.15
75.64
61.53
55.42
14.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

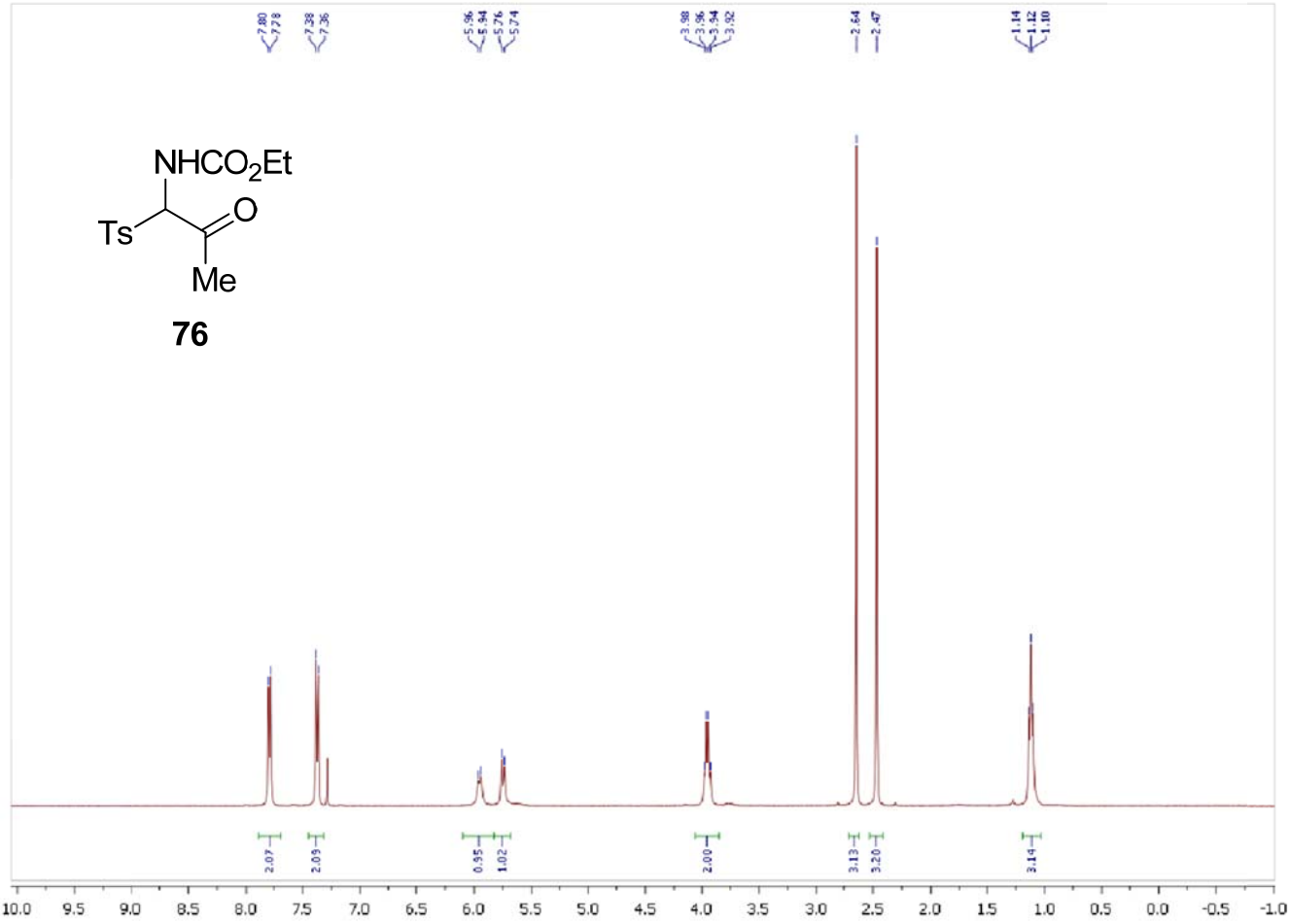

7.66
7.66
7.66
7.66
7.39
7.38
7.38
7.38
6.59
6.57
6.57
6.56
5.74
4.40
4.38
4.37
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.30
4.28
1.36
1.34
1.32
O
O
O
O
EtO2C
CO2Et
74
0.97
0.97
0.99
0.97
4.00
6.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

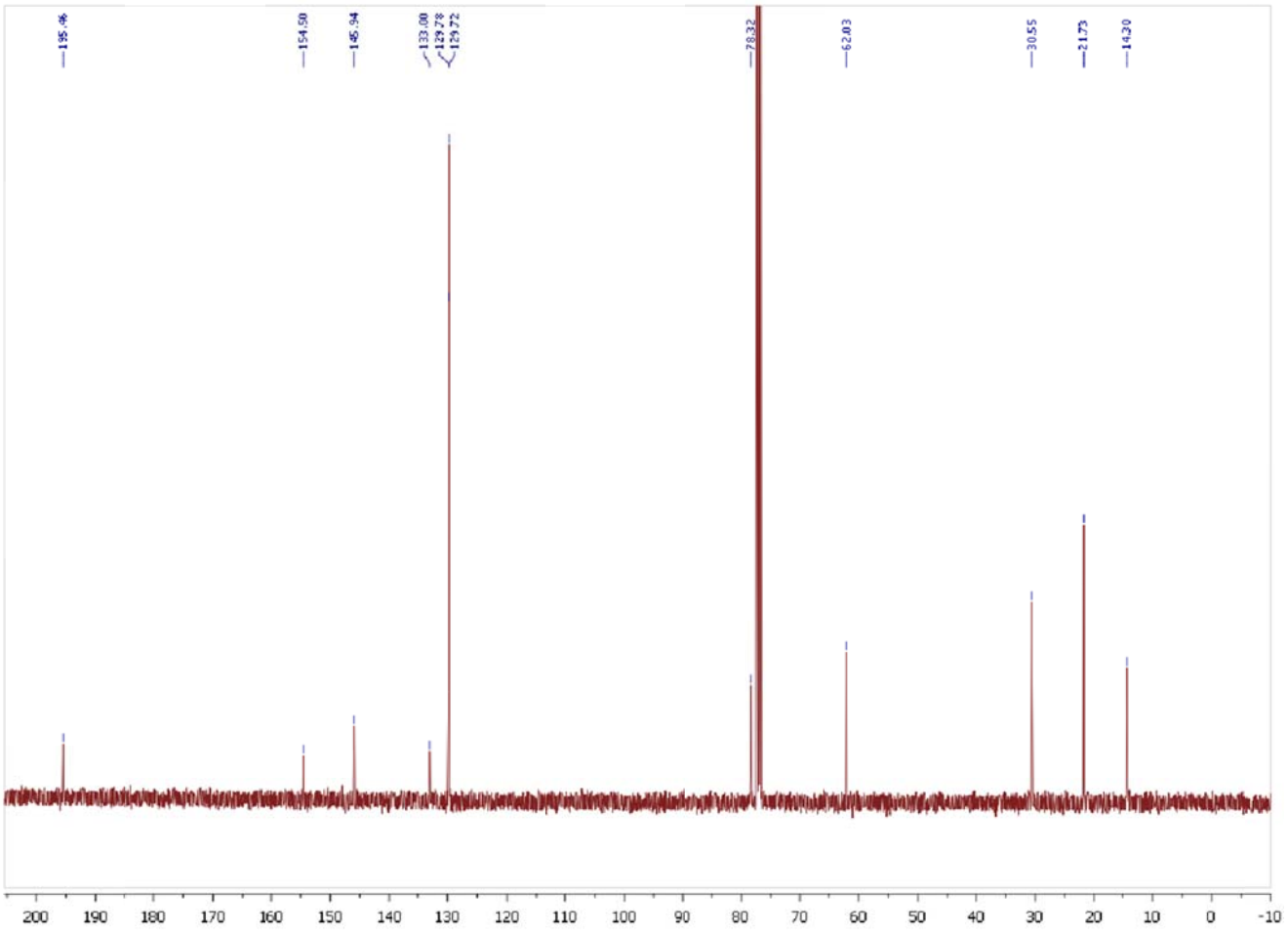

164.22
156.83
147.41
143.05
120.00
112.14
71.73
62.64
13.97
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

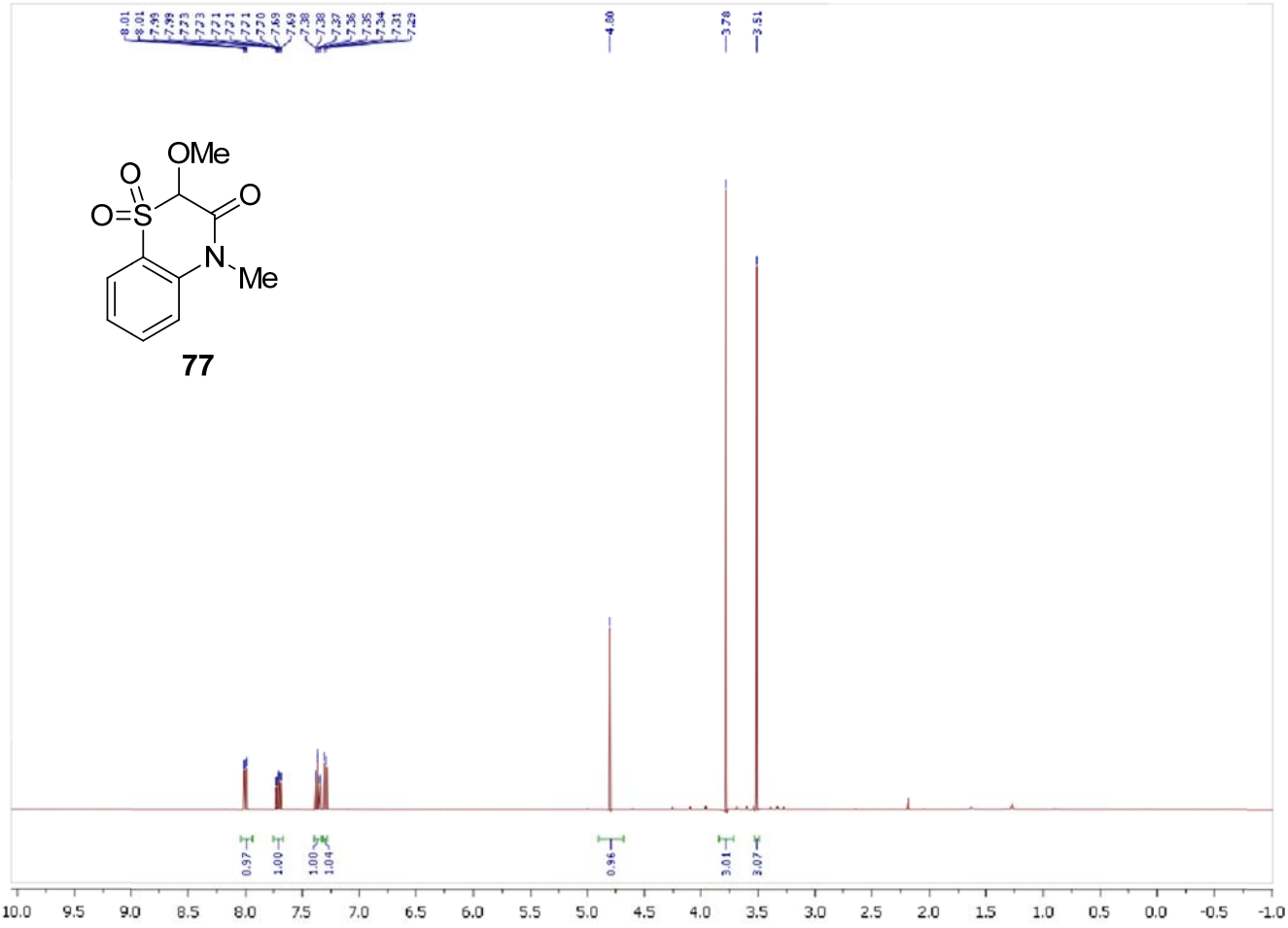


75 ~ 8 : 1

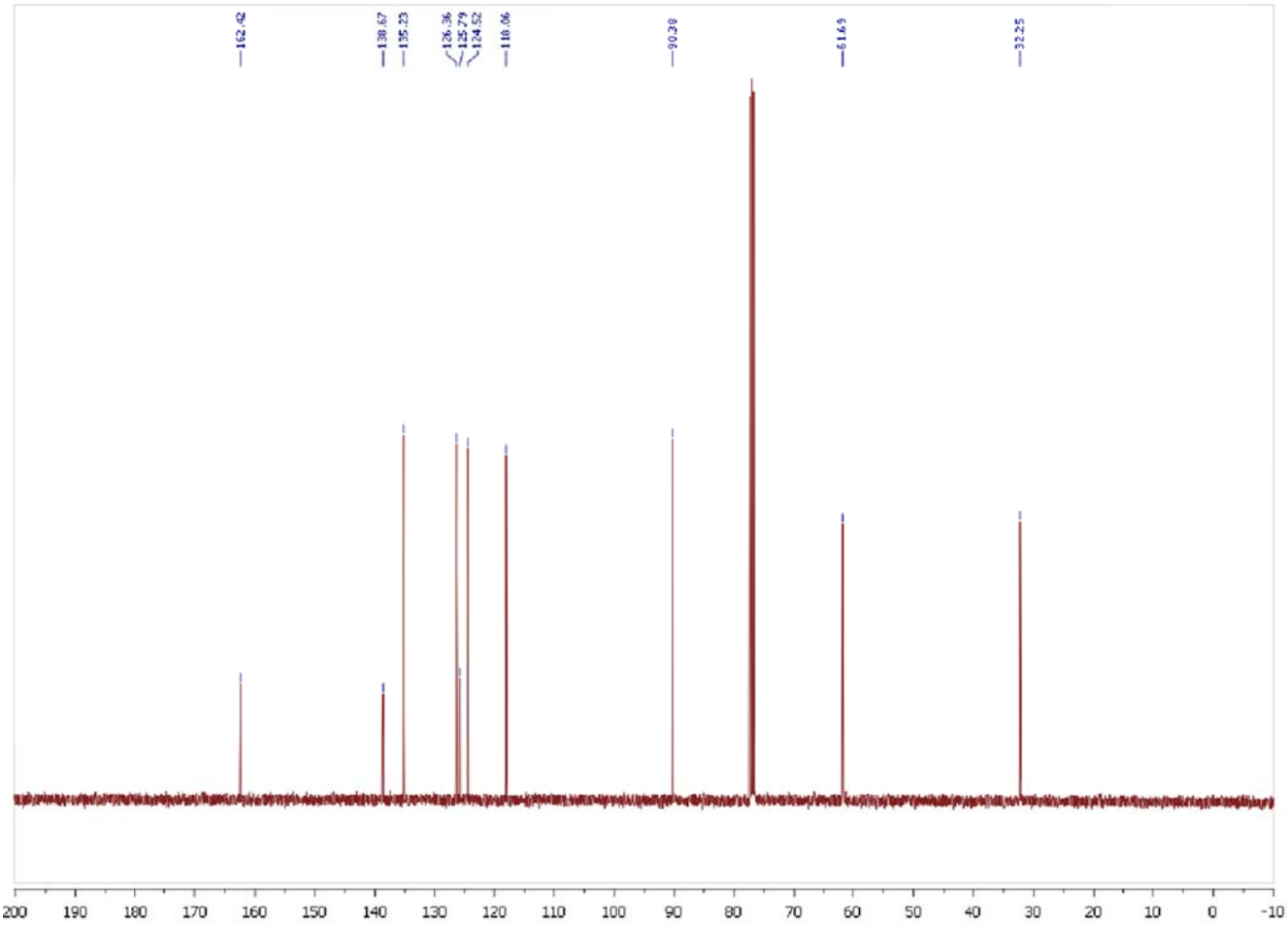


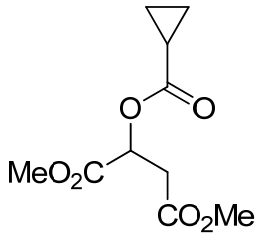

NHCO2Et
Ts
O
Me
76





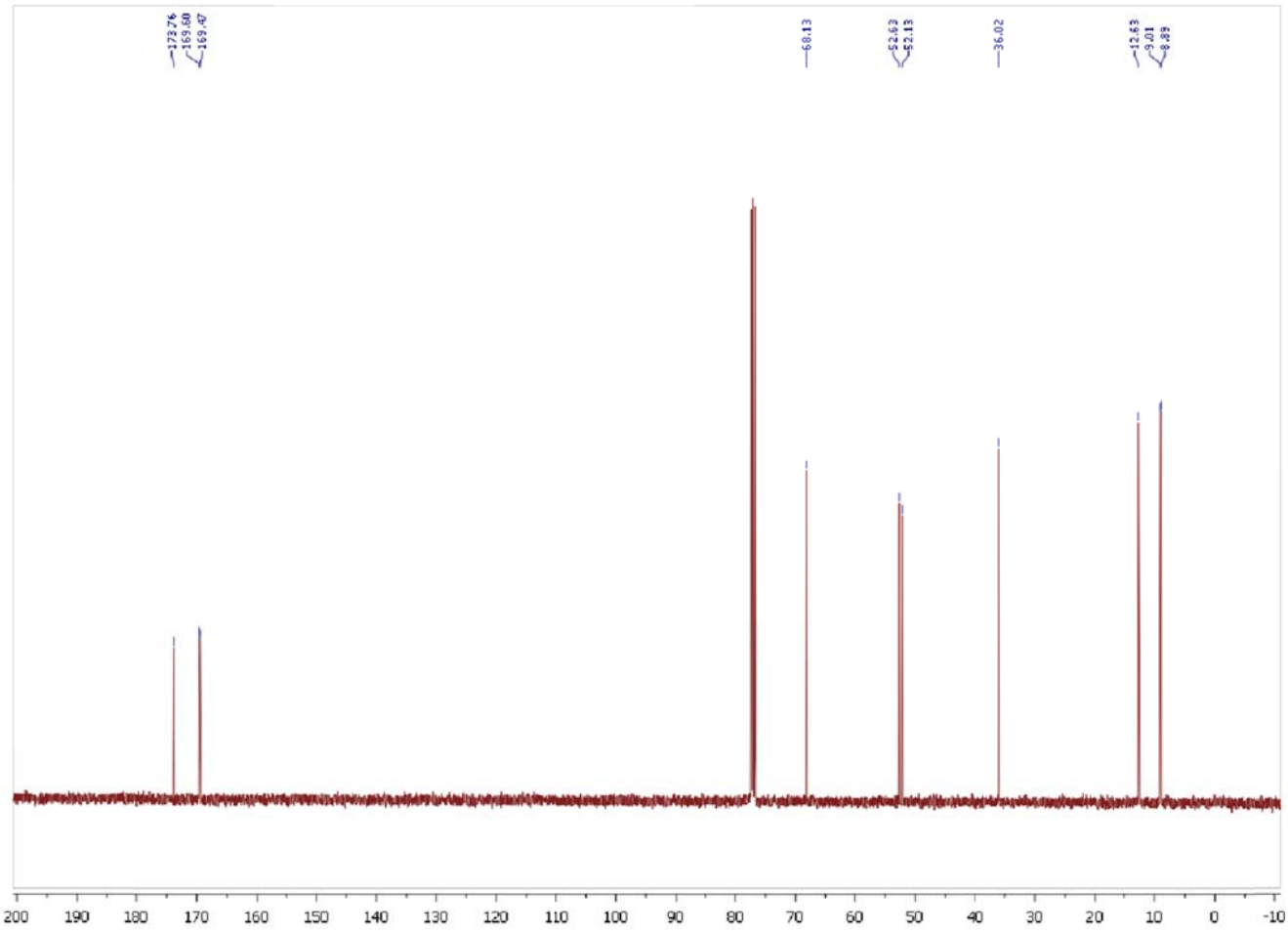
77

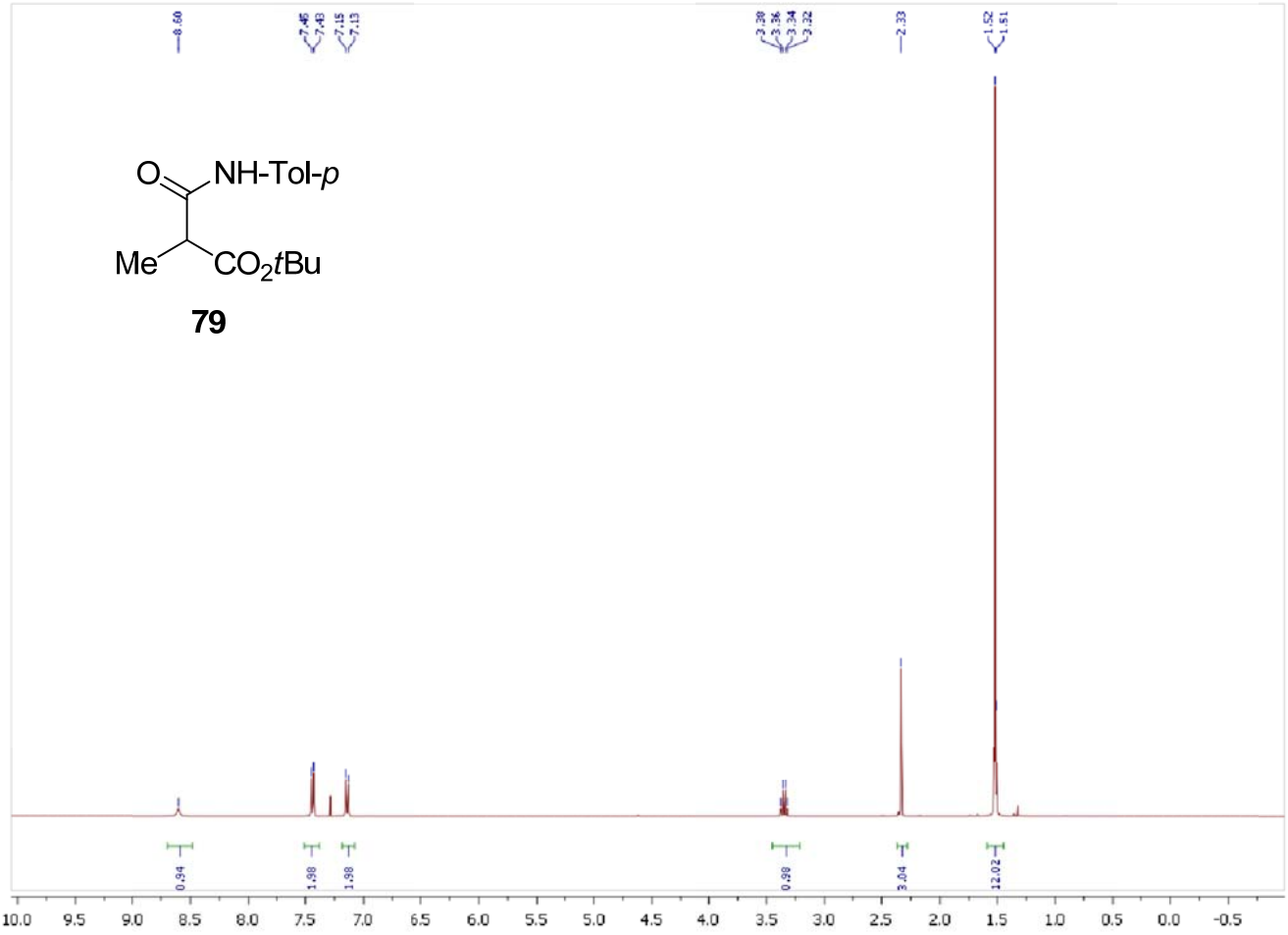


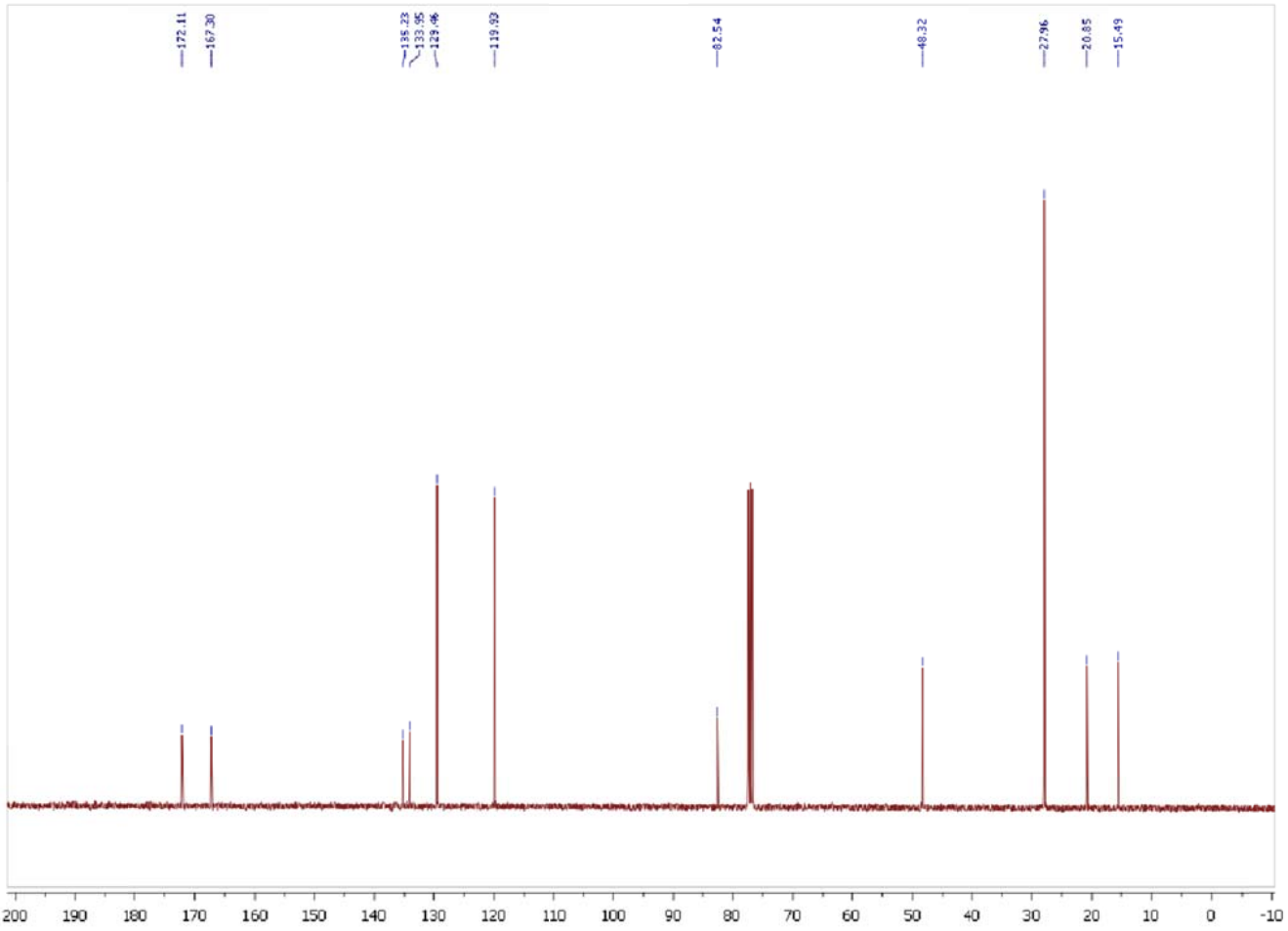

O
O
MeO2C
CO2Me

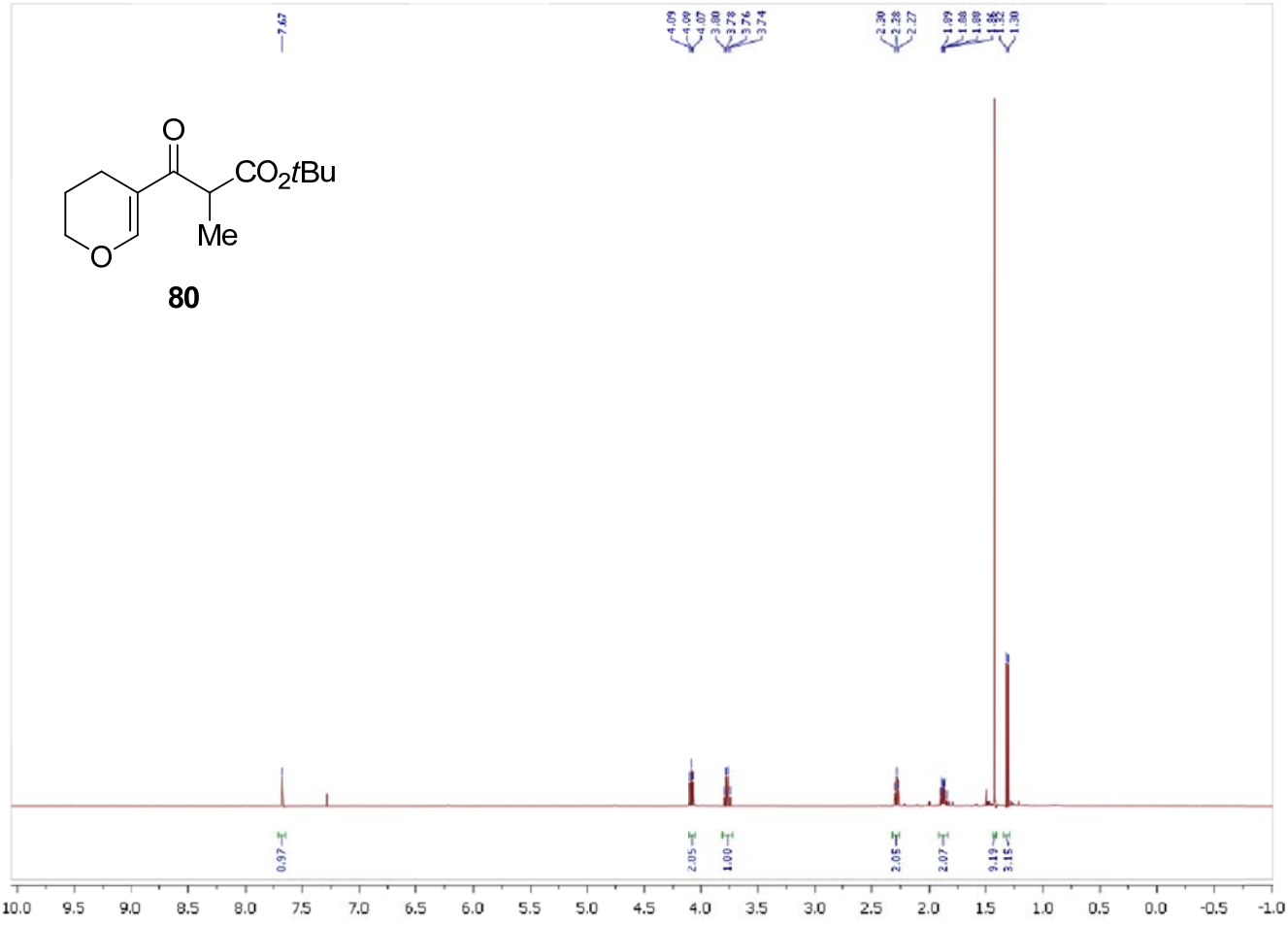
78

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

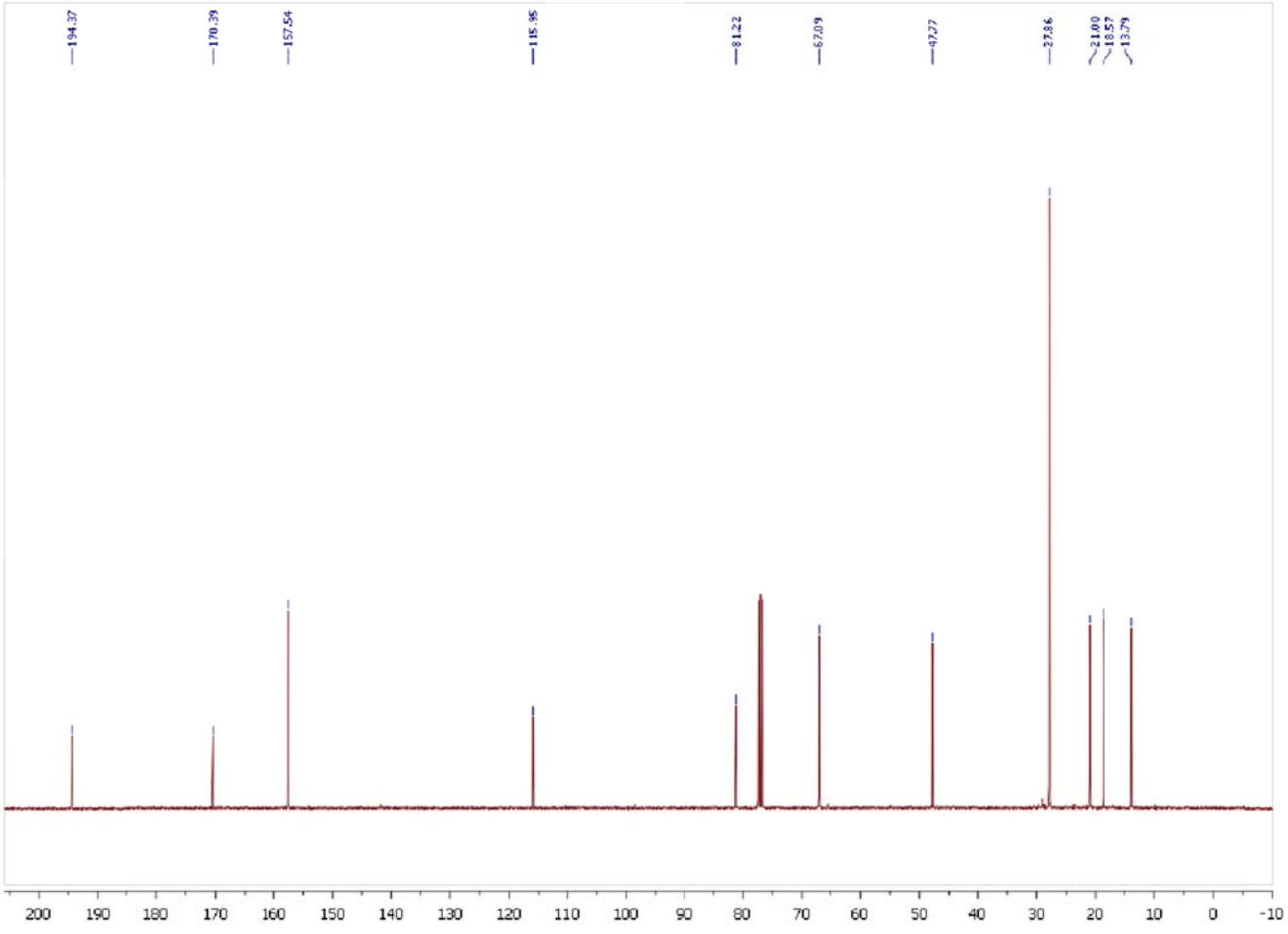

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

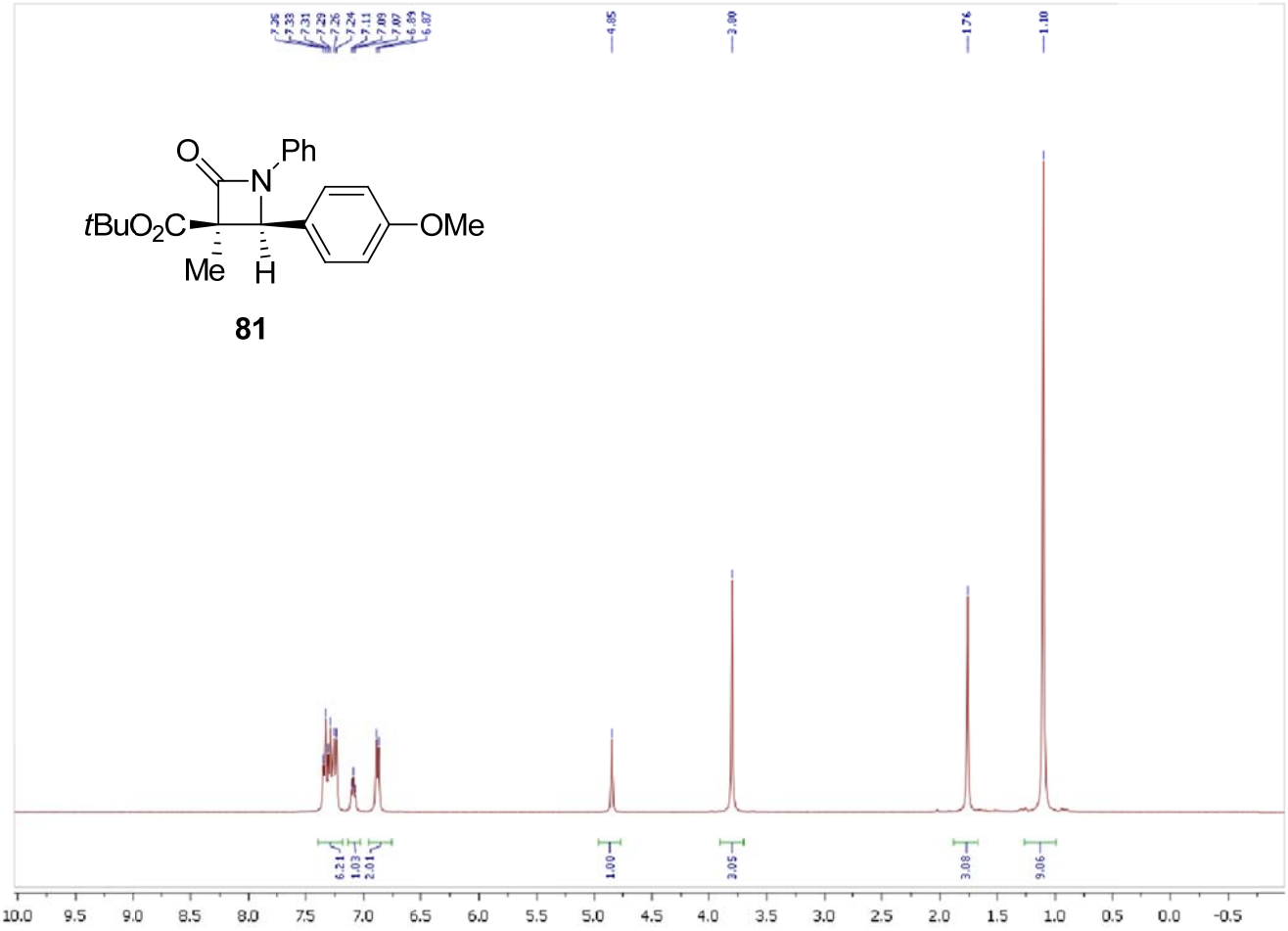

8.60
7.46
7.43
7.15
7.13
3.39
3.36
3.34
3.32
2.33
1.52
1.51
O
NH-Tol-p
Me
CO2tBu
79
0.94
1.98
1.98
0.98
3.04
12.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


172.11
167.30
135.23
133.95
129.46
119.93
82.54
48.32
27.96
20.85
15.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

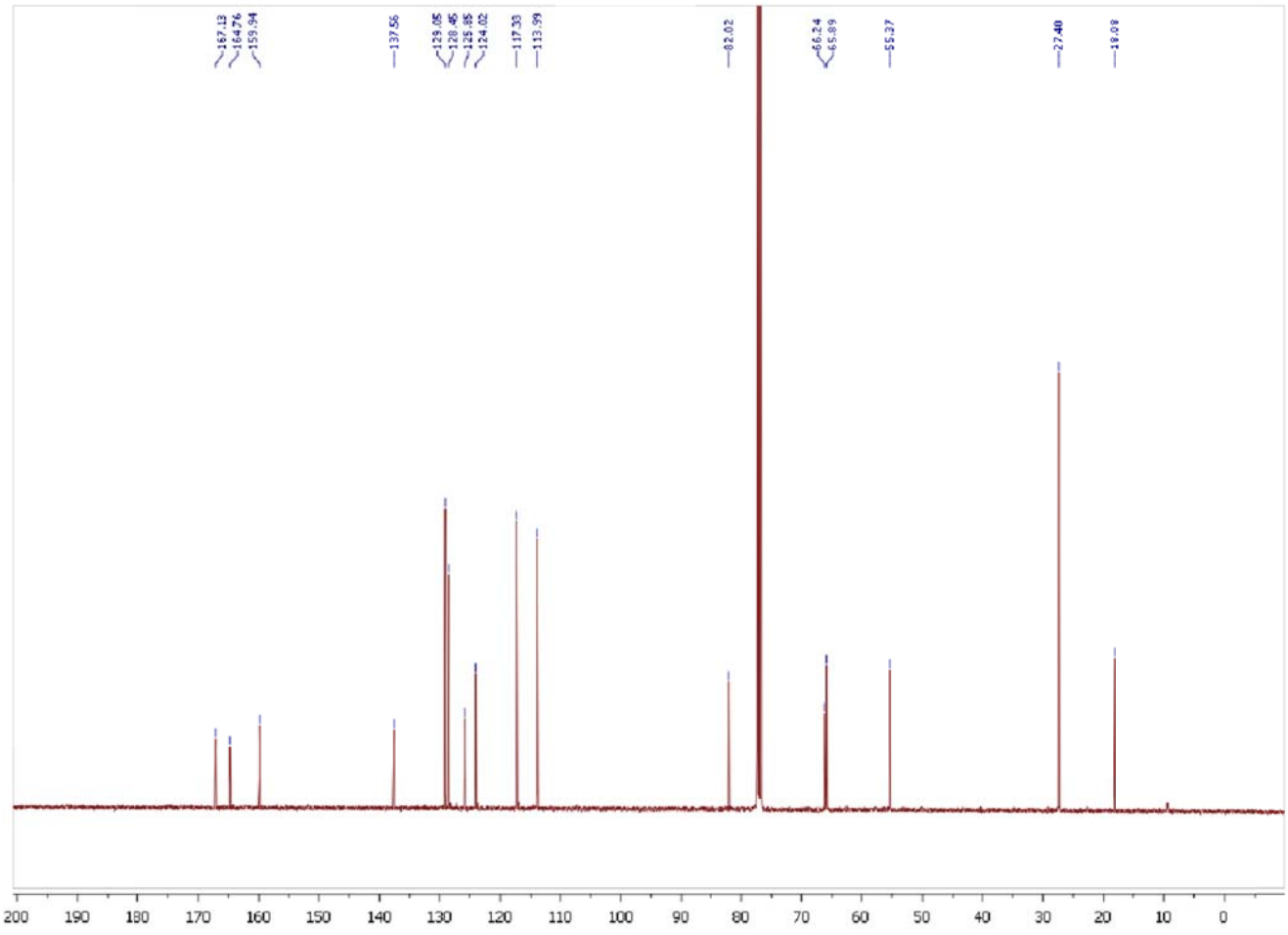


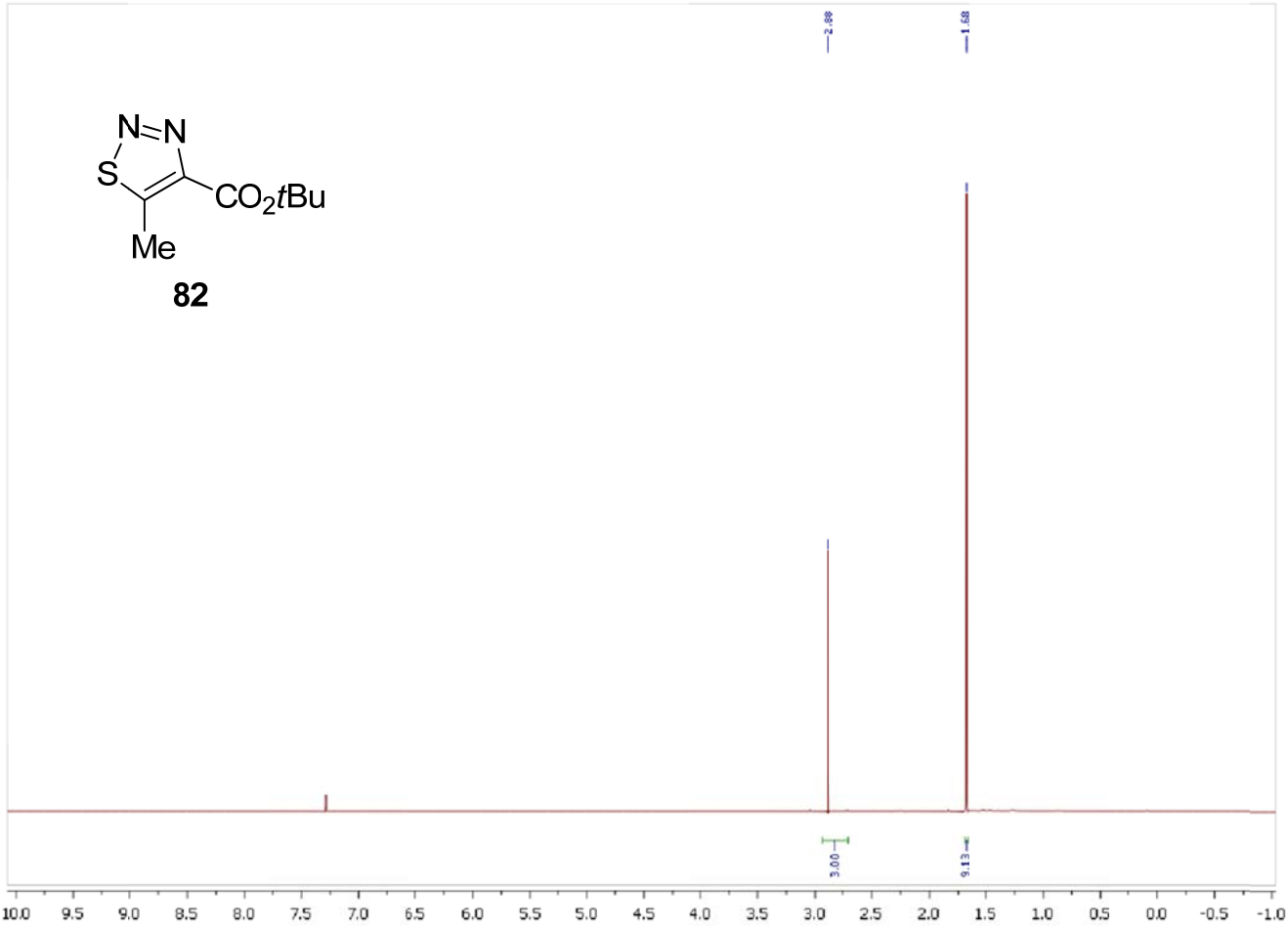
80



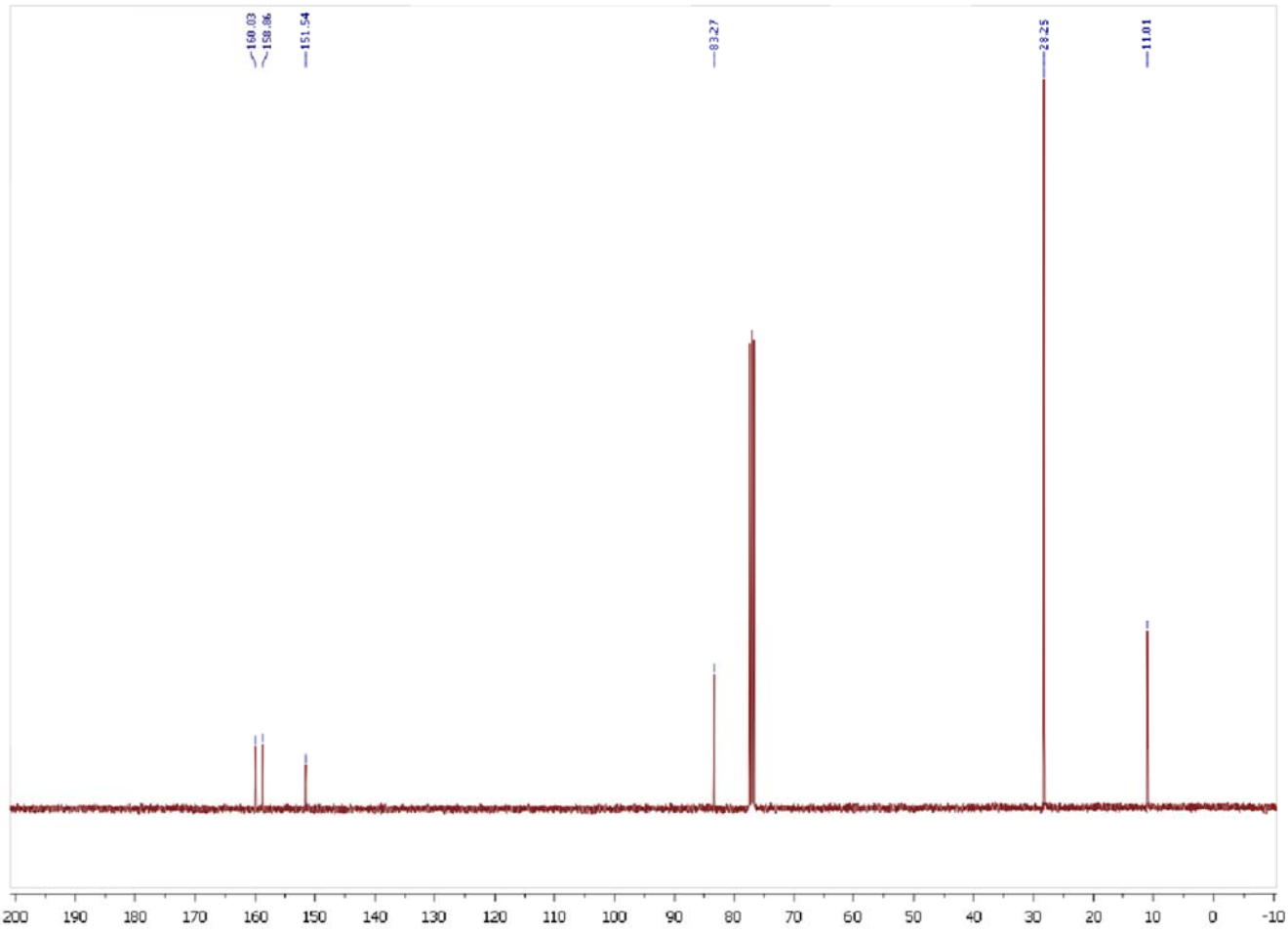


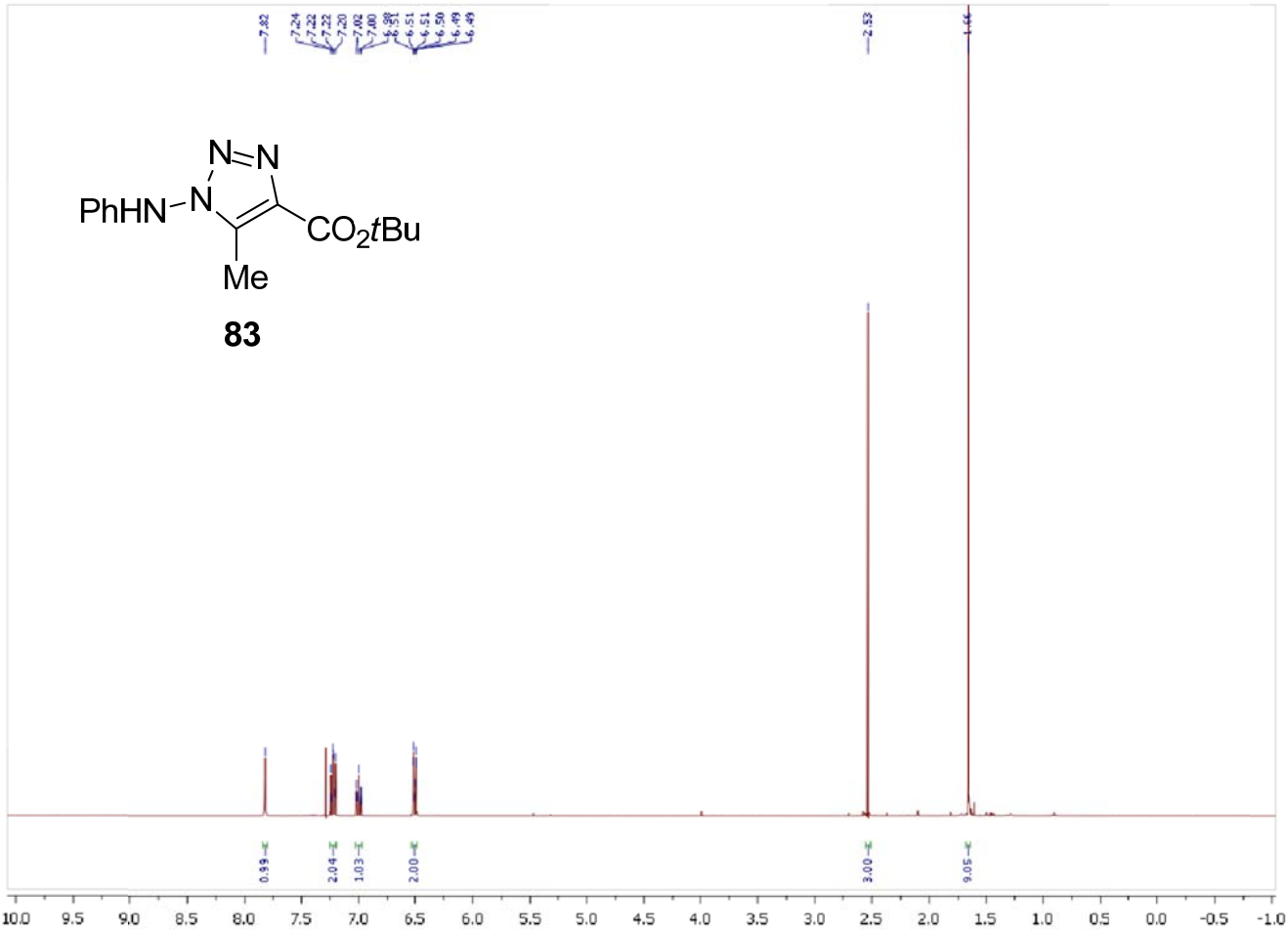
81



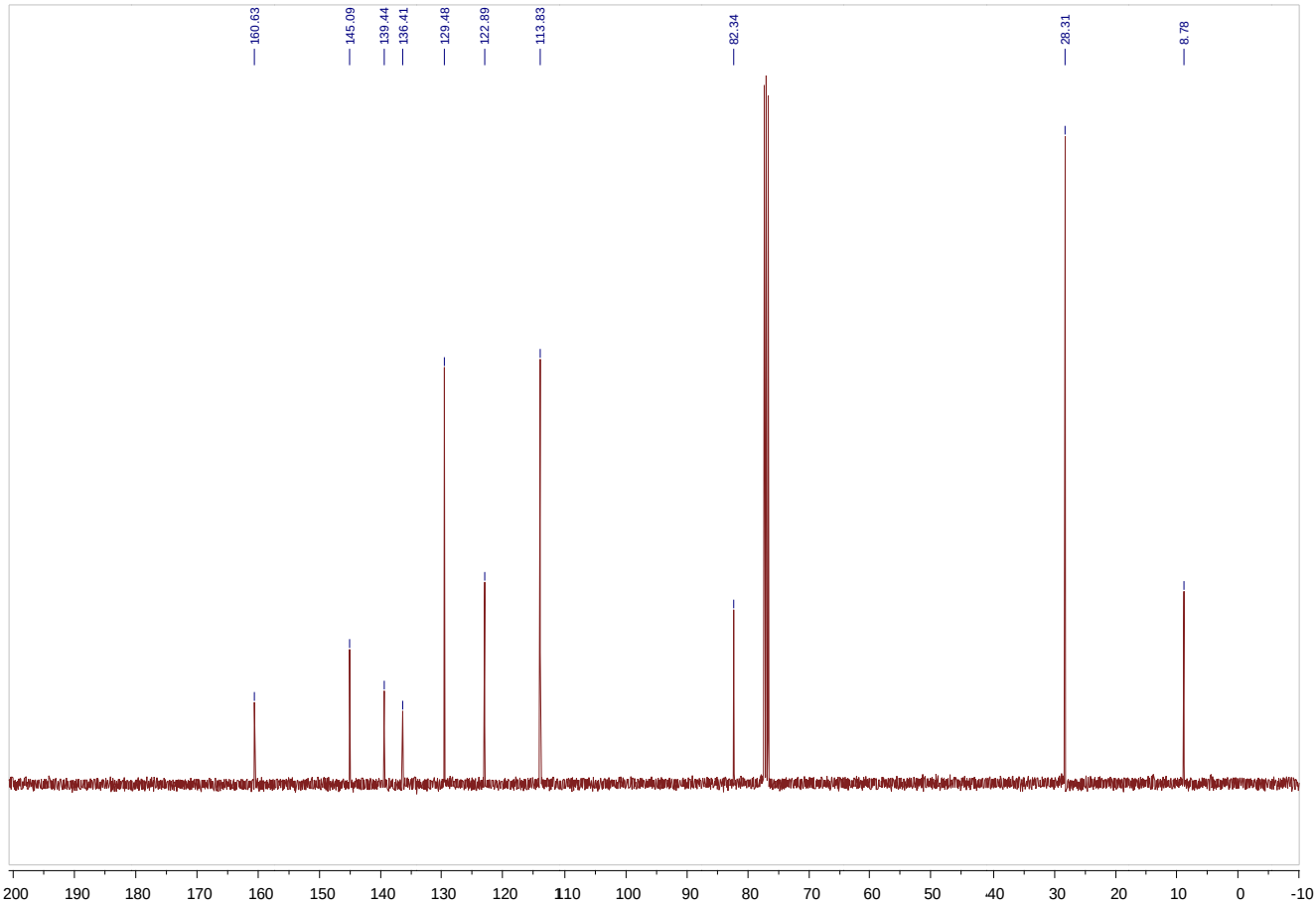

N
N
S
CO2tBu
Me
2.88
1.68
3.00
9.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

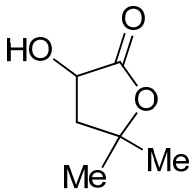
82


160.03
158.86
151.54
83.27
28.25
11.01
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



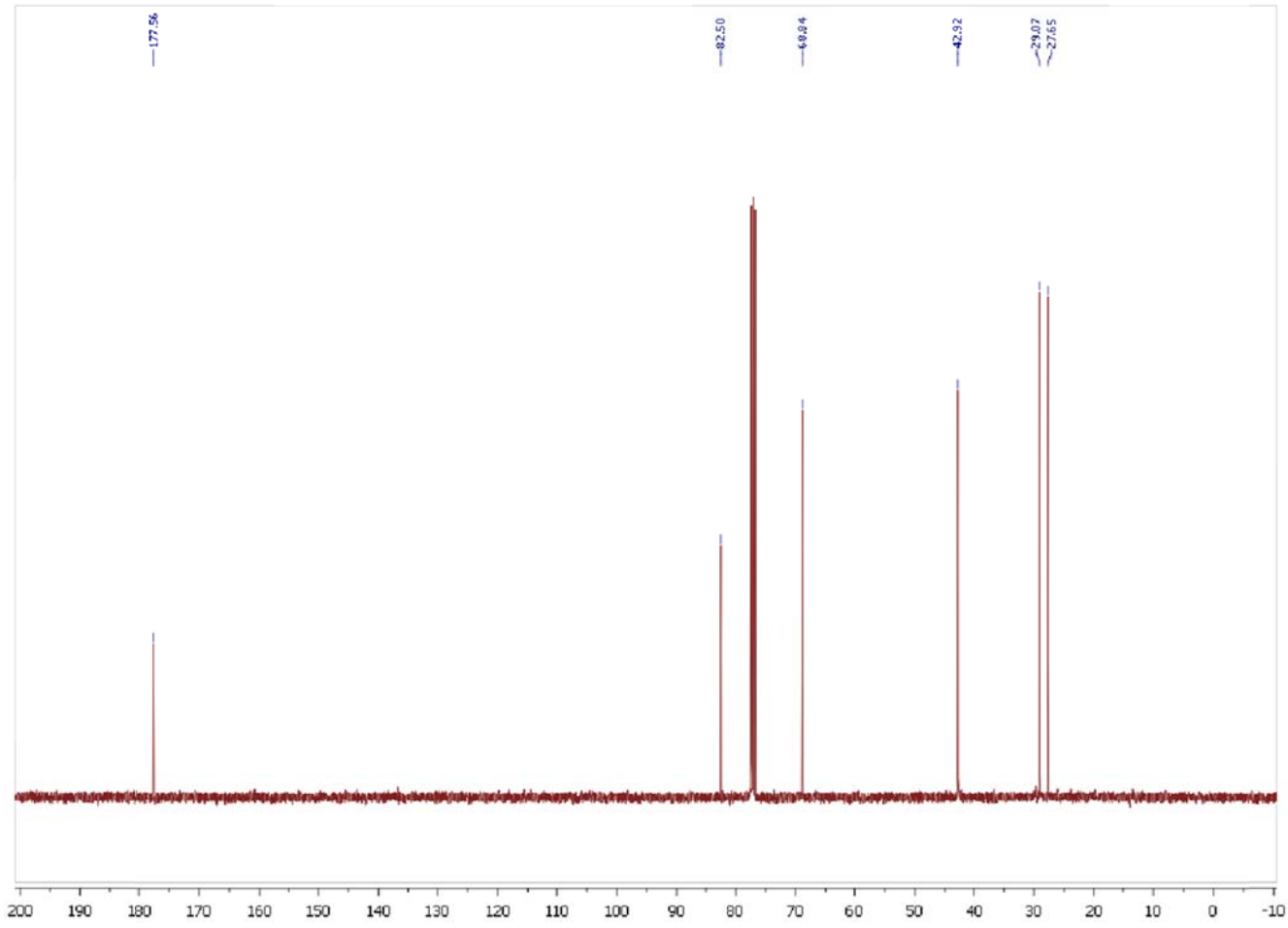
83




HO
O
O
Me
Me

86

4.69
4.67
4.67
4.64
3.39
2.55
2.53
2.52
2.50
2.11
2.09
2.08
2.05
1.53
1.43
1.00
0.93
1.04
1.02
3.09
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


177.56
82.50
69.84
42.92
29.07
27.65
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10