Electronic Supporting Information

Lactic acid as an invaluable bio-based solvent for organic reactions

Jie Yang,[a] Jia-Neng Tan[a] and Yanlong Gu*[a,b]

[a] Institute of Physical Chemistry and Industrial Catalysis, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu road, Hongshan District, Wuhan 430074, China. Fax: (0)86-(0)27-87 54 45 32; E-mail: klgyl@hust.edu.cn

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou, 730000, China.

General remarks:

α-Methylstyrene, 4-methoxystyrene, 4-chloro-α-methylstyrene, 4-fluoro-α-methylstyrene, 4-methylstyrene, 4-chlorostyrene, 4-bromostyrene, 4-tert-butylstyrene, styrene, 4-hydroxy-6-methyl-2-pyrone, 2-hydroxy-1,4-naphthoquinone, 4-hydroxy coumarin, 6-bromo-2-naphthol, 2-hydroxy-1,4-naphthoquinone, N,N-diethylacetoacetamide, 4-(trifluoromethyl)benzaldehyde, 4-acetoxybenzaldehyde, 4-chlorobenzaldehyde, p-tolualdehyde, 2-hydroxy-3-methoxybenzaldehyde, salicyaldehyde, 3-ethoxysalicylaldehyde, 5-bromosalicyladehyde, 4-(diethylamino)salicylaldehyde, p-anisidine, 2-methoxyethyl acetoacetate, trifluoroacetylacetone, 5-methyl-1,3-cyclohexanedione, 5,5-dimethyl-1,3-cyclohexanedione, tetronic acid, 1,3-indanedion, 2-aminoacetophenone and chloroform-*d* were purchased from Alfa Aesar Chemical Company. Sesamol，formaldehyde aqueous solution, 2-naphthol, methyl acetoacetate, acetoacetone, ethyl acetoacetate, 1,3-cyclohexanedione, aniline, 4-nitroaniline, 4-methylaniline, diethyl acetylenedicarboxylate, lactic acid, glacial acetic acid, citric acid, trifluoroacetic acid, glycerol, 1,2-dichloroethane, acetonitrile, nitromethane, ethanol, ethyl acetate, and petroleum ether were purchased from Sinopharm Chemical Reagent Co., Ltd. The purity of lactic acid is about 85% with less than 5 wt% of water. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are

expressed in ppm relative to Me_4Si in $CDCl_3$. IR spectra were recorded on a FT-IR Bruker (VERTEX 70) using KBr technology.

A typical procedure for the synthesis of 1-piperidin-1-yl-butane-1,3-dione: All reactions were conducted in a 100 mL of two-necked round bottomed flask equipped with triangle magnetic stirring. In a typical reaction, toluene (40.0 ml) was mixed with methyl acetoacetate (4.64 g, 40.0 mmol) and piperidine (5.10 g, 60.0 mmol) for 12 hours at 100 ^oC. After completion of the reaction, the mixture was cooled to room temperature, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using the mixture of dichloromethane and ethanol (60/1, v/v) as the eluting solvent to give acetoacetopiperidine 4.70 g, yield = 70 %. The synthesis of 1-(4-methyl-piperidin-1-yl)-butane-1,3-dione and N,N-dibutyl-3-oxo-butyramide were preformed with an analogous procedure.

A typical procedure for the reaction of formaldehyde, sesamol and 4-methylstyrene: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with formaldehyde (105 mg, 1.3 mmol), sesamol (135 mg, 0.98 mmol) and 4-methylstyrene (76 mg, 0.65 mmol) for 3 h at 100 ^oC. After completion of the reaction, the mixture was cooled to room temperature and extracted with the mixture of petroleum ether and ethyl acetate (PE/EA = 2/1, 5 × 2 ml). The obtained organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by preparative TLC using the mixture of petroleum ether and ethyl acetate (8/1, v/v) as the eluting solvent to give the desired product, **3a**, 127 mg, yield = 73 %. Tests for substrate scope were all performed with an analogous procedure. The recovered lactic acid was treated at 60 ^oC under vacuum condition (15 mmHg) for 20 minutes. Then, it was subjected to the next run.

A typical procedure for one-pot three-component reaction of N,N-diethylacetoacetamide, formaldehyde and α-methylstyrene: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with N,N-diethylacetoacetamide (204.4 mg, 1.3 mmol), formaldehyde (131.7 mg, 1.63 mmol) and α-methylstyrene (76 mg, 0.65 mmol) for 24 hours at 80 ^oC. After completion of the reaction, the mixture was cooled to room temperature and extracted with a mixture of petroleum ether and ethyl

acetate (PE/EA = 1/1) until **6a** in lactic acid phase could be hardly detected by TLC. The obtained organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluting solvent (the ratio of EA/PE is 1/4) to give the desired product, **6a**, 103 mg, yield = 55 %. Tests for substrate scope were all performed with an analogous procedure.

A typical procedure for one-pot three-component reaction of diethyl acetylenedicarboxylate, aniline and 4-chlorobenzaldehyde: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with diethyl acetylenedicarboxylate (170 mg, 1.0 mmol), aniline (93 mg, 1.0 mmol) and 4-chlorobezaldehyde (141 mg, 1.0 mmol) for 2 hours at 30 ^{o}C. After completion of the reaction, cold ethanol (2.0 ml) was added and the mixture was stirred for 1 minute. Then, the mixture was filtered and the solid was washed with cold ethanol (5.0 ml * 3). The solid was dried under vacuum oven at 50 ^{o}C for 12 hours. The desired product, **8d**, was obtained, 272 mg, yield = 76 %. Tests for substrate scope were all performed with an analogous procedure.

A typical procedure for the aniline-catalyzed reaction of diethyl acetylenedicarboxylate and 3-methoxylsalicylaldehyde: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with diethyl acetylenedicarboxylate (172 mg, 1.0 mmol), 3-methoxysalicylaldehyde (152 mg, 1.0 mmol) and aniline (18.6 mg 0.2 mmol) for 24 hours at 30 ^{o}C. After completion of the reaction, brine (3.0 ml) was added and the mixture was stirred for 1 minute. Then, the mixture was filtered and the solid was washed with brine (5.0 ml * 3) and petroleum ether (5.0 ml * 3). The solid was dried under vacuum oven at 50 ^{o}C for 24 h. The desired product, **9a**, was obtained, 296 mg, yield = 92 %. Test for 3-ethoxysalicylaldehyde was performed with an analogous procedure. As for salicylaldehyde, 5-bromosalicyladehyde and 4-(diethylamino)salicylaldehyde, after completion of the reaction, the mixture was extracted with the mixture of petroleum ether and ethyl acetate (PE/EA = 1/1) until product in lactic acid phase could be hardly detected by TLC. The obtained organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluting

solvent (normally, the ratio of EA/PE is 1/6).

The procedure for one-pot three-component reaction of 4-nitroaniline, diethyl acetylenedicarboxylate and salicylaldehyde: The reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with diethyl acetylenedicarboxylate (172 mg, 1.0 mmol), salicylaldehyde (122 mg, 1.0 mmol) and 4-nitroaniline (138 mg, 1.0 mmol) for 24 hours at 30 ^{o}C. After completion of the reaction, brine (3.0 ml) was added and the mixture was stirred for 1 minute. Then, the mixture was filtered and the solid was washed with brine (5.0 ml * 3) and petroleum ether (5.0 ml * 3). The solid was dried under vacuum oven at 50 ^{o}C for 24 h. The desired product, **10a**, was obtained, 384 mg, yield = 89 %.

The procedure for one-pot step-wise preparation of 9b: The reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with diethyl acetylenedicarboxylate (172 mg, 1.0 mmol), salicylaldehyde (122 mg, 1.0 mmol) and 4-nitroaniline (138 mg, 1.0 mmol) for 24 hours at 30 ^{o}C. Then, the mixture was stirred at 100 ^{o}C for another 6 hours. After completion of the reaction, the mixture was cooled to room temperature and extracted with the mixture of petroleum ether and ethyl acetate (PE/EA = 1/1). The obtained organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The product **9b** was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluting solvent (the ratio of EA/PE is 1/5), 220 mg, yield = 75 %.

A typical procedure for the reaction of acetylacetone and 2'-aminoacetophenone: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, lactic acid (1.0 ml) was mixed with 2'-aminoacetophenone (135 mg, 1.0 mmol) and acetylacetone (120 mg, 1.2 mmol) for 2.5 hours at 80 ^{o}C. After completion of the reaction, the mixture was cooled to room temperature, poured into ethyl acetate (3.0 ml) and neutralized with an aqueous solution of NaOH (1N). The upper organic layer was separated, and the bottom aqueous layer was extracted with ethyl acetate (3.0 ml * 2). The obtained organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluting solvent (the ratio

of EA/PE is 1/8) to give the desired product, **13a**, 189 mg, yield = 95 %. Tests for substrate scope were all performed with an analogous procedure. As for tetronic acid and 1,3-indanedione, the solvent was mixture of lactic acid and water (9/1, v/v). After completion of the reaction, the mixture was cooled to room temperature and the precipitate was formed. Then, brine (3.0 ml) was added and the mixture was stirred for 1 minute. Then, the mixture was filtered and the solid was washed with brine (5.0 ml * 3) and petroleum ether (5.0 ml * 3). The solid was dried under vacuum oven at 50 ^{o}C for 24 h. The desired product was obtained.

Spectroscopic data of known compounds

3-(p-tolyl)-2,3-dihydro-1H-benzo[f]chromene (**4c**)[1]: yellow solid, mp: 105-107 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.11-2.23 (m, 1H), 2.27-2.33 (m, 1H), 2.35 (s, 3H), 3.06-3.13 (m, 2H), 5.03 (dd, J_a = 2.4 Hz, J_b = 10.4 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.30-7.36 (m, 3H), 7.46 (td, J_a = 1.2 Hz, J_b = 7.2 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.76 (dd, J_a = 8.4 Hz, J_b = 12.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): 21.3, 21.9, 29.7, 77.5, 113.7, 119.4, 122.1, 123.3, 126.2, 126.4, 127.8, 128.5, 129.1, 129.3, 133.1, 137.7, 138.7, 152.9; HRMS *m/z* (ESI) calcd for $C_{20}H_{18}NaO$ $[M + Na]^+$ 297.1255 found 297.1250.

8-Bromo-3-methyl-3-phenyl-2,3-dihydro-1H-benzo[f]chromene (**4d**)[1]: pale yellow liquid**;** ^{1}H NMR ($CDCl_3$): 1.67 (s, 3H), 2.12-2.23 (m, 1H), 2.48-2.64 (m, 2H), 2.89-3.00 (m, 1H), 7.18 (tt, J_a = 1.2 Hz, J_b = 7.6 Hz, 1H), 7.23 (dd, J_a = 2.0 Hz, J_b = 9.2 Hz, 2H), 7.27 (dd, J_a = 2.0 Hz, J_b = 6.8 Hz, 1H), 7.35-7.40 (m, 2H), 7.43 (dd, J_a = 2.0 Hz, J_b = 8.8 Hz, 1H), 7.52 (t, J = 9.2 Hz, 2H), 7.85 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): 19.4, 30.1, 32.6, 78.5, 113.8, 116.8, 120.6, 123.9, 124.9, 127.0, 127.1, 128.5, 129.4, 130.1, 130.3, 131.6, 145.2, 151.8; HRMS *m/z* (ESI) calcd for $C_{20}H_{17}BrNaO$ $[M + Na]^+$ 375.0360 found 375.0355

2-(p-tolyl)-3,4-dihydro-2H-benzo[g]chromene-5,10-dione (**4f**)[1]**:** yellow solid, mp: 134-136 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.01-2.12 (m, 1H), 2.25-2.33 (m, 1H), 2.36 (s, 3H), 2.58-2.78 (m, 2H), 5.17 (dd, J_a = 2.8 Hz, J_b = 9.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.63-7.72 (m, 2H), 8.00-8.11 (m, 2H); ^{13}C NMR ($CDCl_3$): 18.6, 21.2, 27.8, 79.0, 121.6, 125.9, 126.0, 126.3, 129.3, 131.0, 132.0, 133.1, 133.9, 136.4, 138.1, 155.5, 179.4, 184.2; HRMS *m/z* (ESI) calcd for $C_{20}H_{16}NaO_3$ $[M + Na]^+$ 327.0997 found 327.0991.

N,N-Dibutyl-3-oxo-butyramide (**5b**)[2]: pale yellow liquid; ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 7.2 Hz,

3H), 0.91 (t, J = 7.2 Hz, 3H), 1.21-1.34 (m, 4H), 1.43-1.55 (m, 4H), 1.90 (s, 0.80H), 2.24 (s, 2.17H), 3.15 (t, J = 8.0 Hz, 2H), 3.28 (t, J = 8.0 Hz, 2H), 3.45 (s, 1.46 H), 5.01 (s, 0.20H), 14.94 (s, 0.19H); ^{13}C NMR ($CDCl_3$): 13.7, 13.8, 20.0, 20.1, 20.1, 22.0, 29.6, 30.1, 31.0, 45.6, 45.7, 47.6, 48.2, 49.9, 87.1, 166.1, 171.5, 174.4, 202.8; HRMS *m/z* (ESI) calcd for $C_{12}H_{23}NNaO_2$ $[M + Na]^+$ 236.1626 found 236.1622.

1-Piperidin-1-yl-butane-1,3-dione (**5d**)[3]: yellow liquid; ^{1}H NMR ($CDCl_3$): 1.47-1.55 (m, 4H), 1.55-1.64 (m, 2H), 1.90 (s, 0.37H), 2.22 (s, 2.52H), 3.30 (t, J = 4.2 Hz, 2H), 3.36-3.58 (m, 4H), 5.11 (s, 0.12H), 14.7 (s, 0.10H); ^{13}C NMR ($CDCl_3$): 22.0, 24.3, 24.5, 25.4, 26.3, 30.0, 42.8, 47.4, 50.2, 86.4, 164.7, 170.3, 174.8, 202.5; HRMS *m/z* (ESI) calcd for $C_9H_{15}NNaO_2$ $[M + Na]^+$ 192.1000 found 192.0998.

6-Bromo-2-hydroxy-2H-chromene-2,3-dicarboxylic acid diethyl ester (**9d**)[4]: white solid, mp: 96-98 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.27 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 4.21-4.39 (m, 4H), 5.38 (s, 1H), 6.84 (d, J = 8.8 Hz, 1H), 7.38 (dd, J_a = 2.4 Hz, J_b = 8.8 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$): 13.8, 14.1, 61.3, 63.5, 93.2, 114.3, 118.6, 119.9, 122.8, 131.1, 133.7, 134.9, 150.3, 163.6, 168.8; HRMS *m/z* (ESI) calcd for $C_{15}H_{15}BrNaO_6$ $[M + Na]^+$ 370.0052 found 370.0050**.**

1-(2,4-Dimethyl-quinolin-3-yl)-ethanone (**13a**)[5]: pale yellow liquid; ^{1}H NMR ($CDCl_3$): 2.47 (s, 3H), 2.50 (s, 3H), 2.55 (s, 3H), 7.44 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 15.2, 23.5, 32.6, 123.6, 125.9, 126.3, 129.2, 129.7, 135.6, 138.5, 146.9, 152.5, 206.5; HRMS *m/z* (ESI) calcd for $C_{13}H_{13}NNaO$ $[M + Na]^+$ 222.0895 found 222.0894.

2,4-Dimethyl-quinoline-3-carboxylic acid methyl ester (**13b**)[6]: pale yellow liquid; ^{1}H NMR ($CDCl_3$): 2.53 (s, 3H), 2.63 (s, 3H), 3.92 (s, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.61 (td, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 15.7, 23.8, 52.4, 123.9, 125.6, 126.3, 127.6, 129.2, 130.0, 141.6, 147.0, 154.2, 169.6; HRMS *m/z* (ESI) calcd for $C_{13}H_{13}NNaO_2$ $[M + Na]^+$ 238.0844 found 238.0840.

2,4-Dimethyl-quinoline-3-carboxylic acid ethyl ester (**13c**)[6]: pale yellow liquid; ^{1}H NMR ($CDCl_3$): 1.36 (t, J = 7.2 Hz, 3H), 2.55 (s, 3H), 2.65 (s, 3H), 4.41 (q, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.61 (td, Ja = 0.8 Hz, Jb = 8.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H); ^{13}C

NMR ($CDCl_3$): 14.2, 15.6, 23.7, 61.6, 123.9, 125.7, 126.2, 127.9, 129.2, 129.9, 141.3, 147.0, 154.2, 169.1; HRMS *m/z* (ESI) calcd for $C_{14}H_{15}NNaO_2$ $[M + Na]^+$ 252.1000 found 252.0993.

1-(2,4-Dimethyl-quinolin-3-yl)-2,2,2-trifluoro-ethanone (**13d**)[7]: pale yellow liquid; ^1H NMR ($CDCl_3$): 2.59 (s, 3H), 2.62 (s, 3H), 7.57 (t, J = 7.6 Hz, 1H), 7.76 (t, J= 7.6 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 16.2, 23.7, 111.3, 114.2, 117.1, 120.0, 123.8, 125.2, 126.9, 127.8, 129.4, 131.0, 142.9, 147.6, 153.0, 189.1, 189.5, 189.9, 190.3; HRMS *m/z* (ESI) calcd for $C_{13}H_{10}F_3NNaO$ $[M + Na]^+$ 276.0612 found 276.0610.

2,4-Dimethyl-quinoline-3-carboxylic acid 2-methoxy-ethyl ester (**13e**)[8]: pale yellow liquid; ^1H NMR ($CDCl_3$):2.54 (s, 3H), 2.63 (s, 3H), 3.29 (s, 3H), 3.61 (t, J = 4.8 Hz, 2H), 4.47 (t, J = 4.8 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 15.6, 23.7, 58.7, 64.2, 70.2, 123.9, 125.6, 126.2, 127.6, 129.1, 130.0, 141.6, 147.0, 154.3, 169.0; HRMS *m/z* (ESI) calcd for $C_{15}H_{17}NNaO_3$ $[M + Na]^+$ 282.1106 found 282.1101.

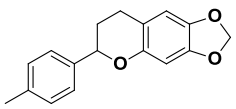
9-Methyl-3,4-dihydro-2H-acridin-1-one (**13f**)[6]: white solid, mp: 61-63 ^oC; ^1H NMR ($CDCl_3$): 2.05 (quint, J = 6.4 Hz, 2H), 2.65 (t, J = 6.4 Hz, 2H), 2.83 (s, 3H), 3.11 (t, J = 6.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 15.9, 21.2, 34.6, 40.9, 125.1, 125.3, 126.1, 127.4, 129.0, 131.3, 147.7, 149.6, 161.9, 200.3; HRMS *m/z* (ESI) calcd for $C_{14}H_{13}NNaO$ $[M + Na]^+$ 234.0895 found 234.0894.

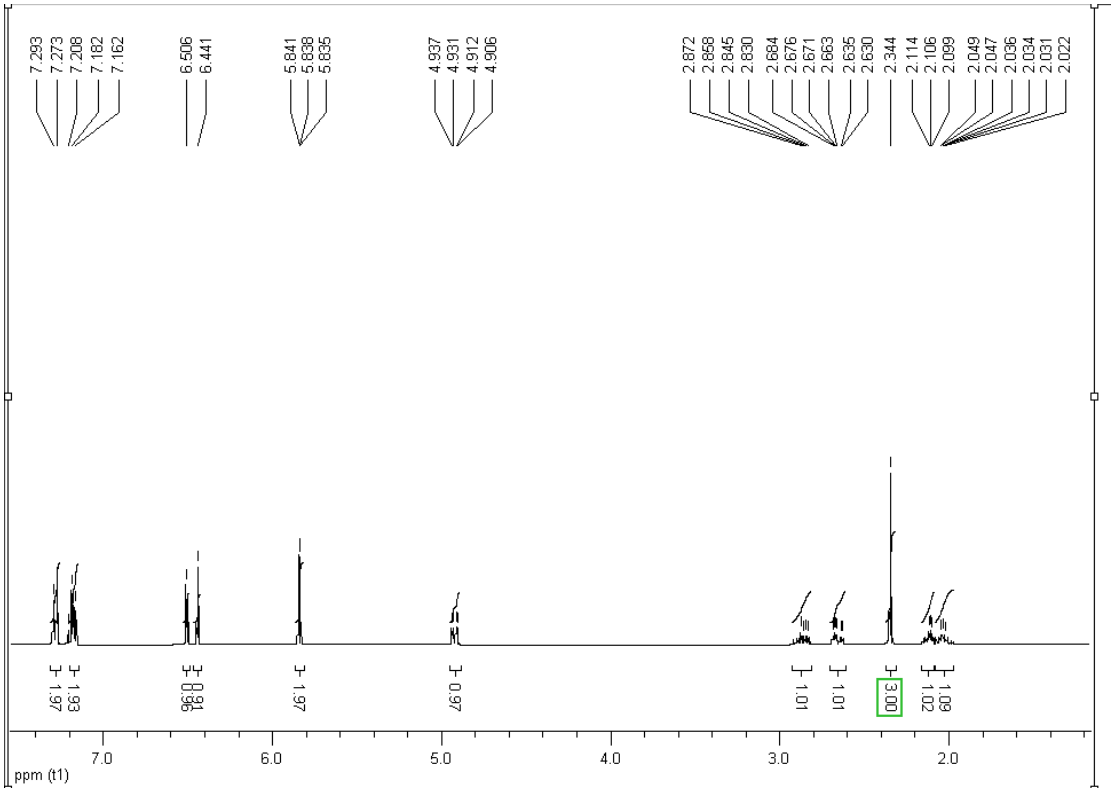
3,3,9-Trimethyl-3,4-dihydro-2H-acridin-1-one (**13h**)[6]: white solid, mp: 100-102 ^oC; ^1H NMR ($CDCl_3$): 1.06 (s, 6H), 2.57 (s, 2H), 2.96 (s, 3H), 3.09 (s, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 15.9, 28.2, 32.0, 48.5, 54.7, 124.0, 125.4, 126.3, 127.5, 129.1, 131.3, 148.2, 149.5, 161.0, 200.4; HRMS *m/z* (ESI) calcd for $C_{16}H_{17}NNaO$ $[M + Na]^+$ 262.1208 found 262.1205.

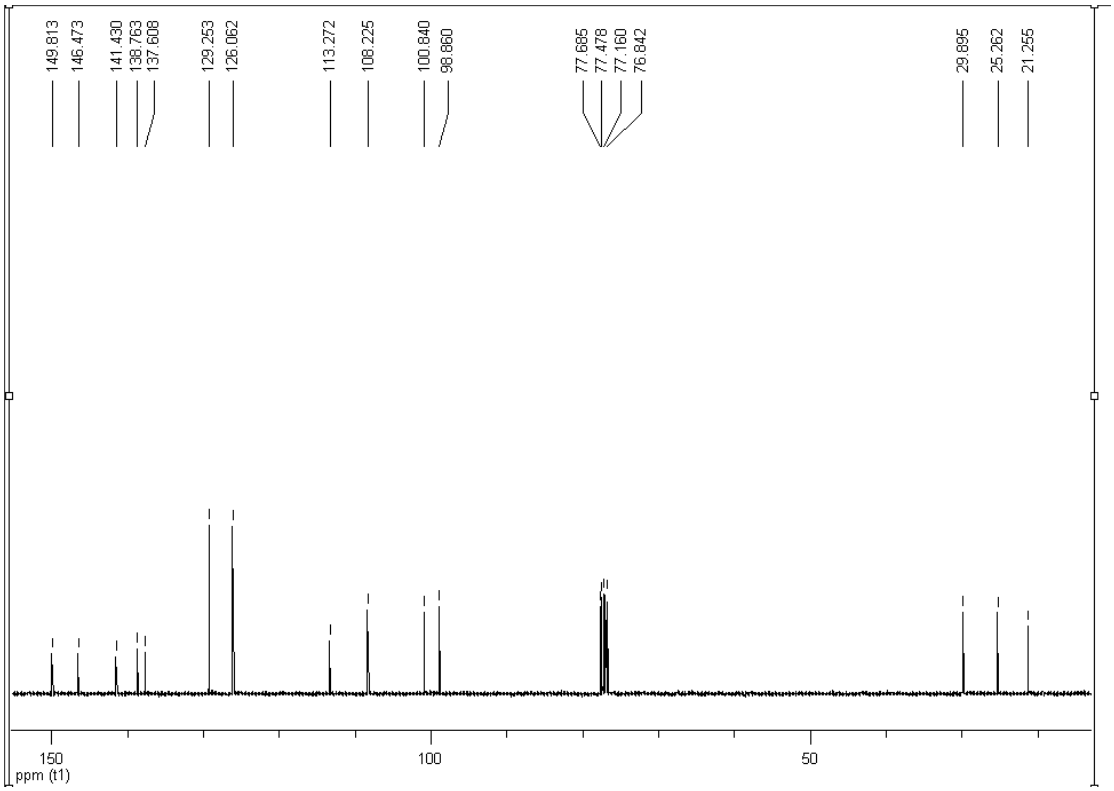
9-Methyl-3H-furo[3,4-b]quinolin-1-one (**13i**)[9]: brown solid; ^1H NMR ($CDCl_3$): 3.14 (s, 3H), 5.39 (s, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.91 (td, J_a = 1.2 Hz, J_b = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): 12.7, 69.7, 114.6, 125.3, 127.2, 127.8, 129.8, 132.5, 150.0, 150.4, 163.3, 169.6; HRMS *m/z* (ESI) calcd for $C_{12}H_9NNaO_2$ $[M + Na]^+$ 222.0531 found 222.0530.

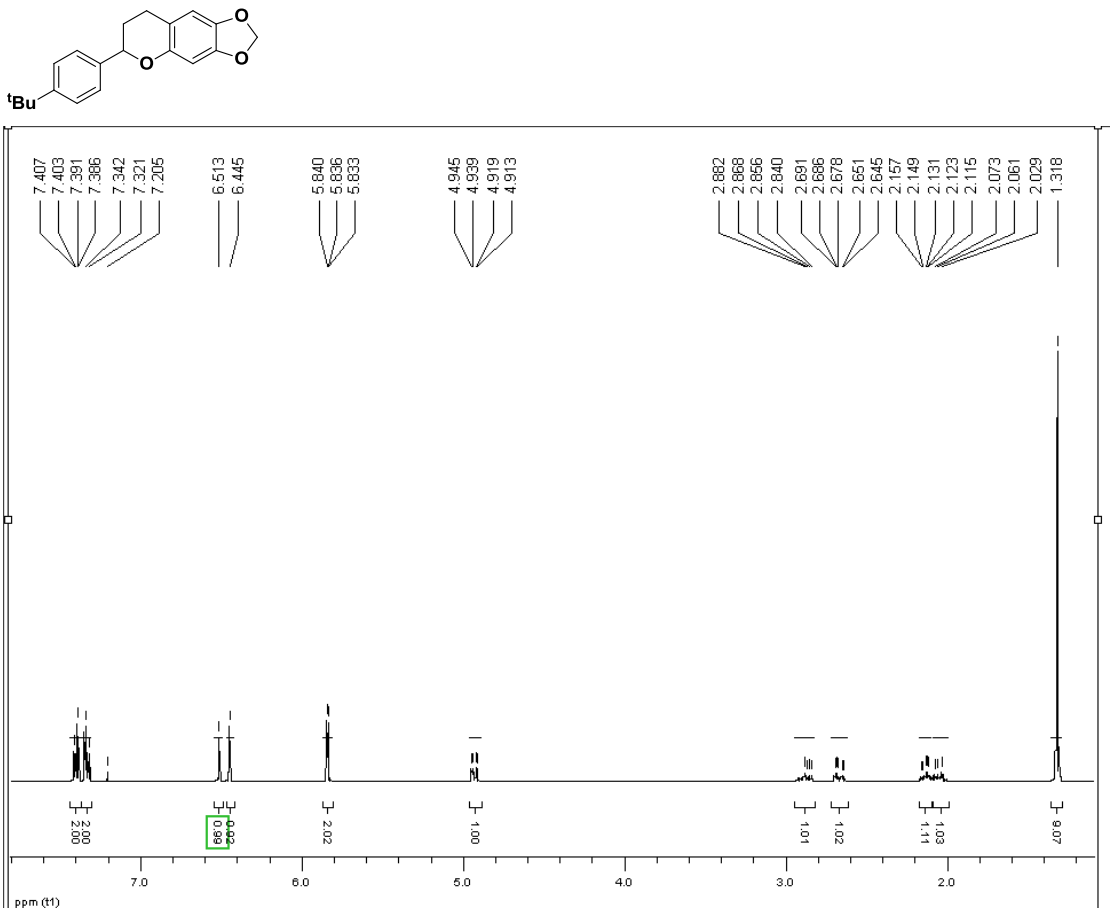
10-Methyl-indeno[1,2-b]quinolin-11-one (**13j**)[10]: green solid, mp: 166-168 ^oC; ^1H NMR ($CDCl_3$): 2.82 (s, 3H), 7.36 (q, J = 7.2 Hz, 2H), 7.50-7.59 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4

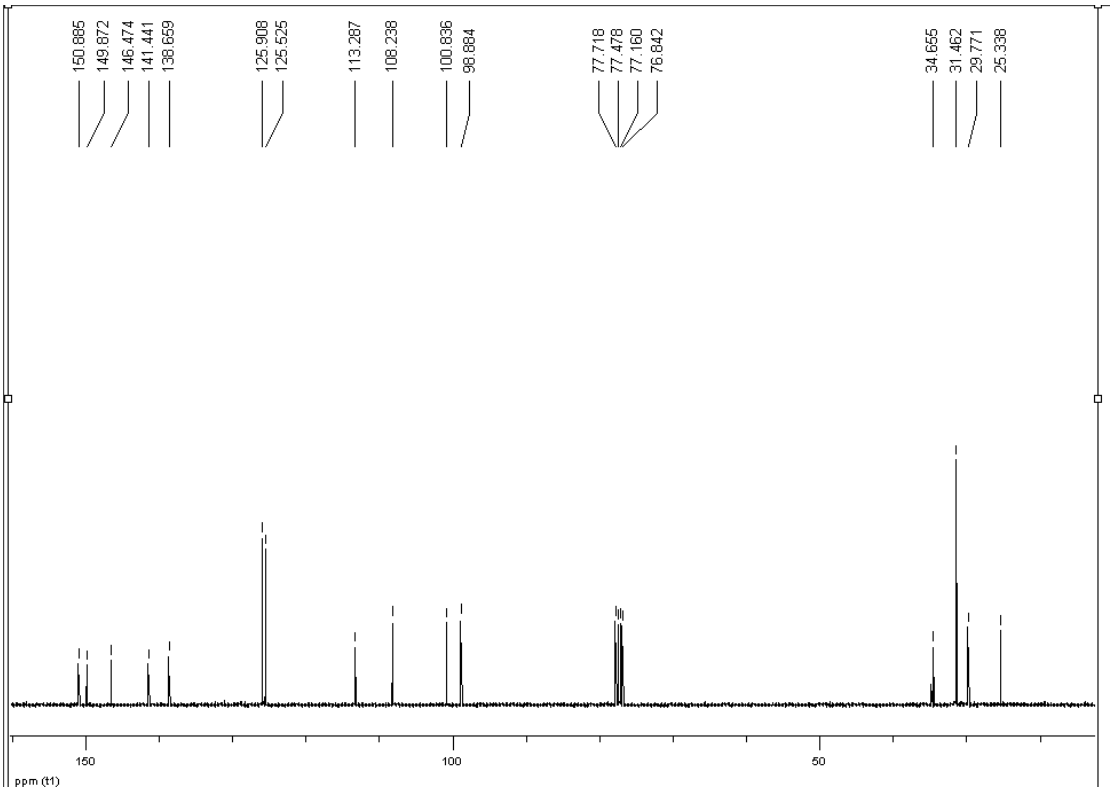
Hz, 1H), 7.87 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): 12.3, 121.5, 123.4, 123.5, 125.5, 126.7, 128.3, 130.1, 131.2, 131.3, 135.0, 137.4, 142.9, 146.3, 149.2, 161.5, 192.2; HRMS *m/z* (ESI) calcd for $C_{17}H_{11}NNaO$ $[M + Na]^+$ 268.0738 found 268.0735.

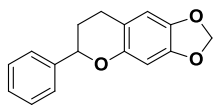


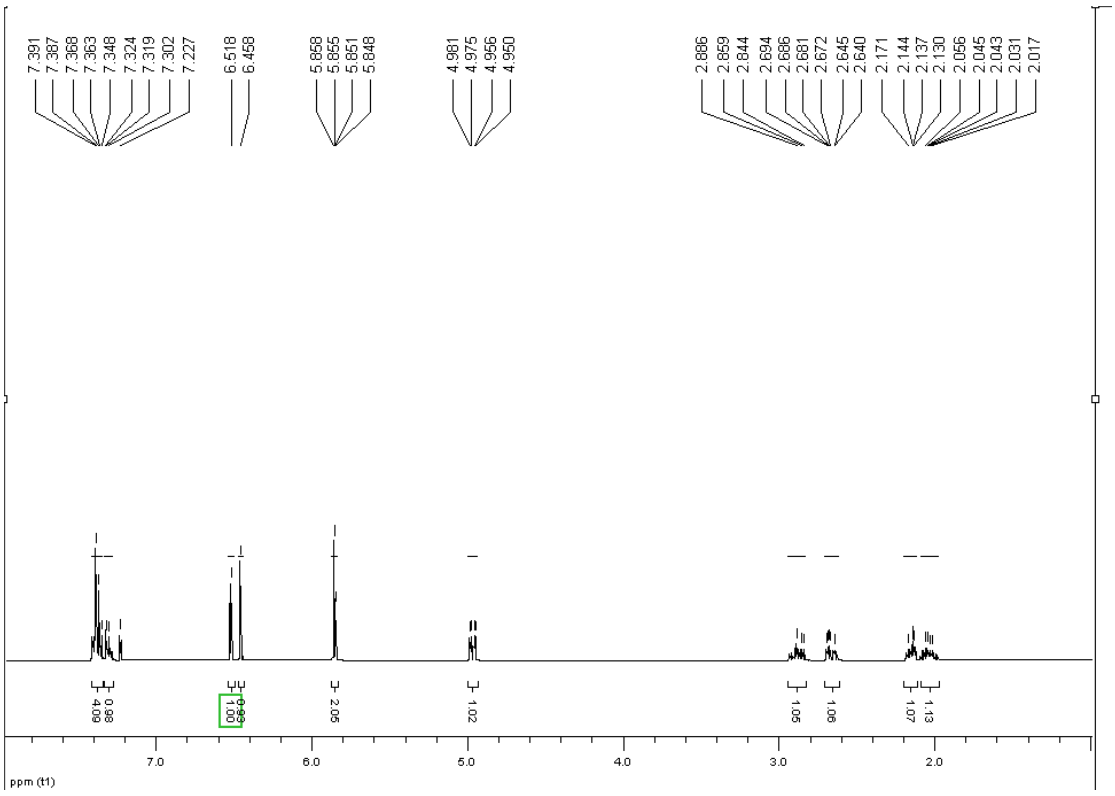


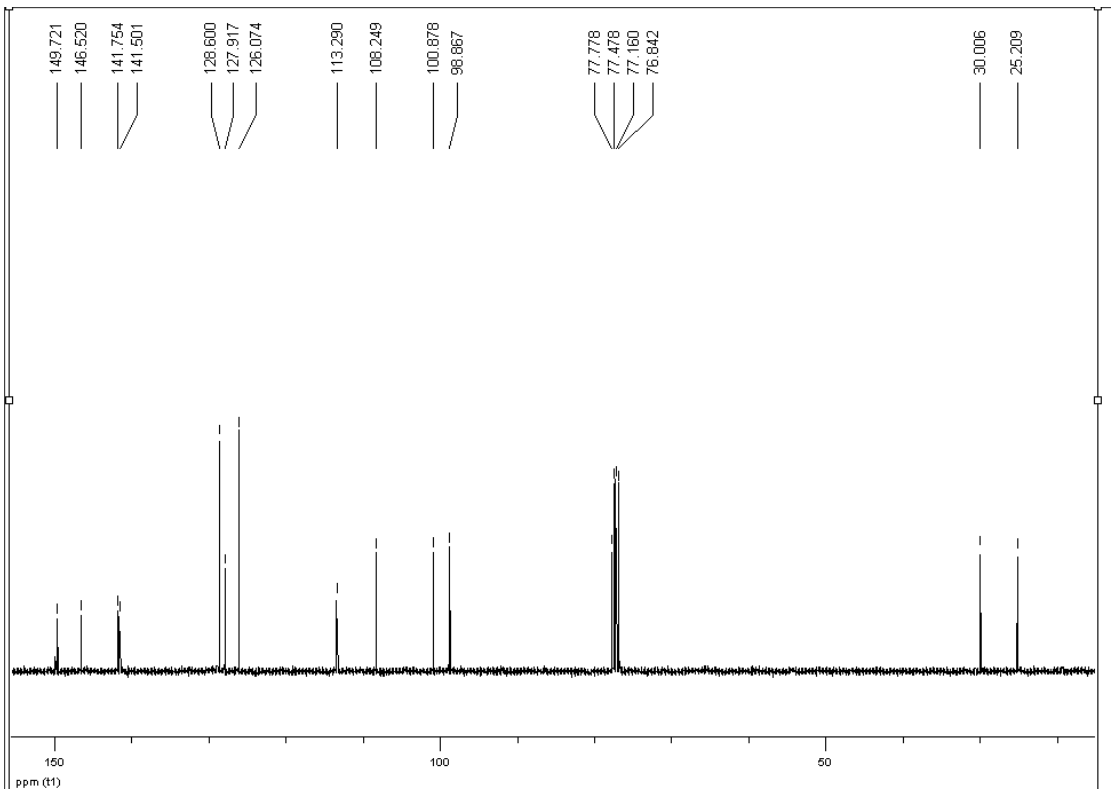


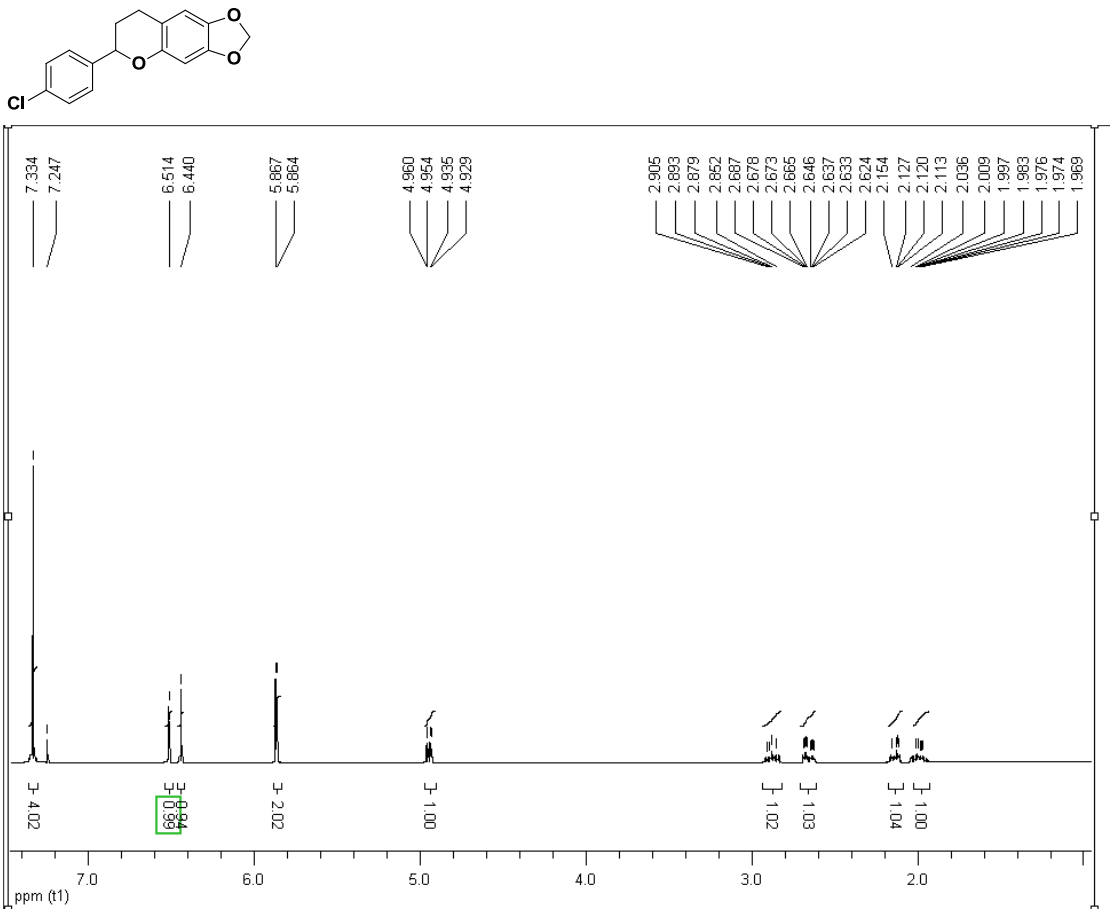

tBu
7.407
7.403
7.391
7.386
7.342
7.321
7.205
6.513
6.445
5.840
5.836
5.833
4.945
4.939
4.919
4.913
2.882
2.868
2.856
2.840
2.691
2.686
2.678
2.651
2.645
2.157
2.149
2.131
2.123
2.115
2.073
2.061
2.029
1.318
2.00
0.99
0.99
2.02
1.00
1.01
1.02
1.11
1.03
9.07
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

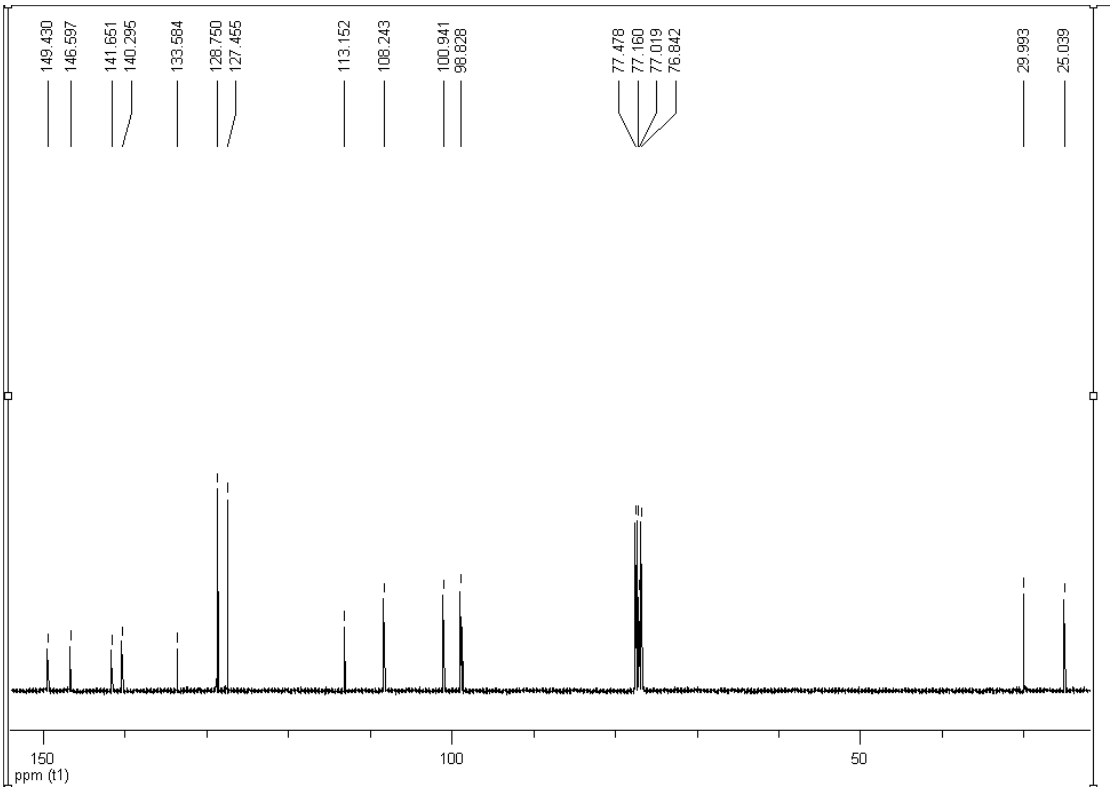

150.885
149.872
146.474
141.441
138.659
125.908
125.525
113.287
108.238
100.836
98.884
77.718
77.478
77.160
76.842
34.655
31.462
29.771
25.338
150
100
50
ppm (t1)

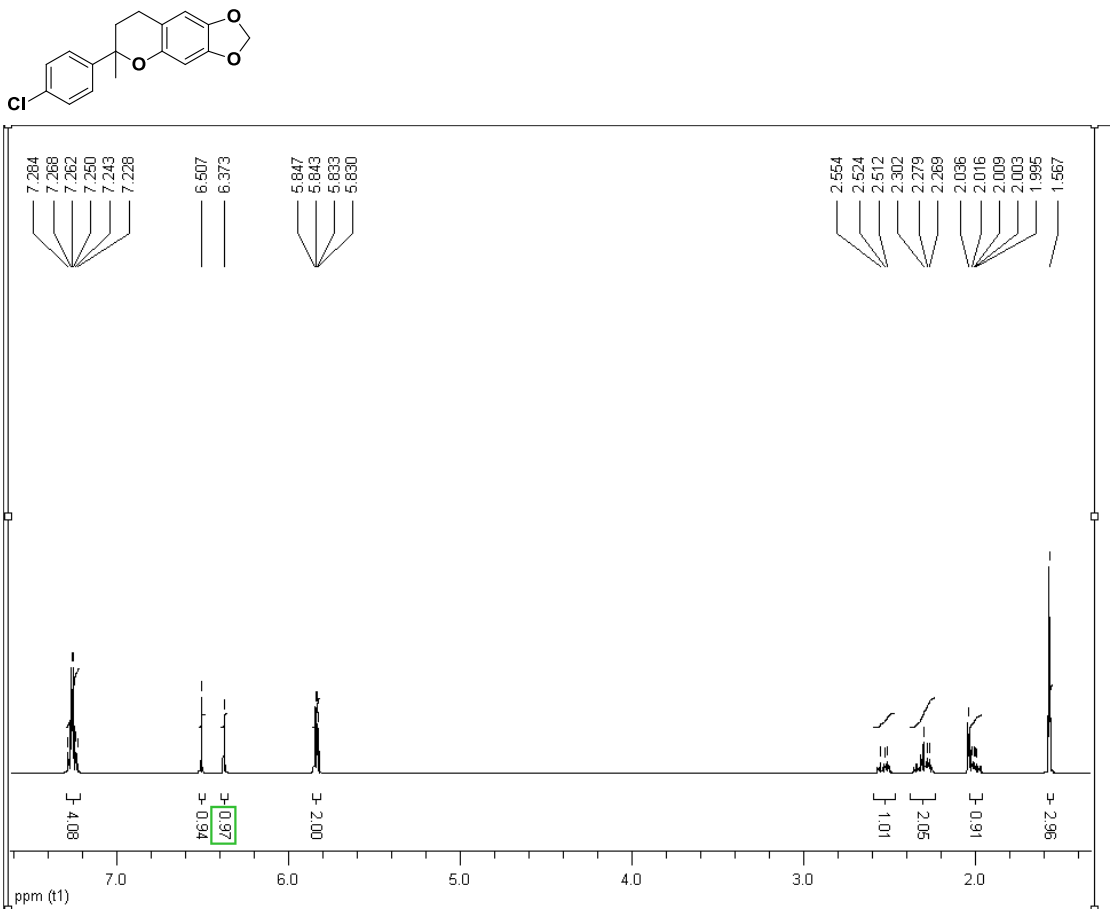


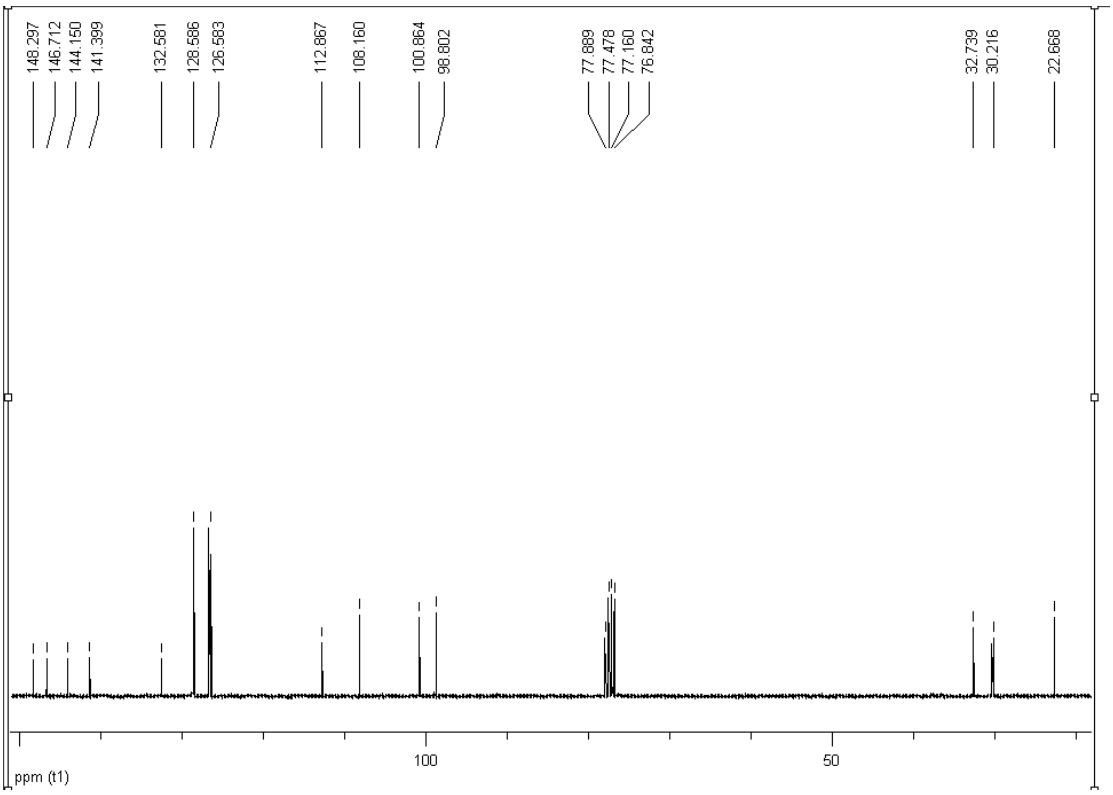

7.391
7.387
7.368
7.363
7.348
7.324
7.319
7.302
7.227
6.518
6.458
5.858
5.855
5.851
5.848
4.981
4.975
4.956
4.950
2.886
2.859
2.844
2.694
2.686
2.681
2.672
2.645
2.640
2.171
2.144
2.137
2.130
2.056
2.045
2.043
2.031
2.017
0.98
1.00
2.06
1.02
1.05
1.06
1.07
1.13
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

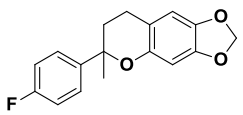

149.721
146.520
141.754
141.501
128.600
127.917
126.074
113.290
108.249
100.878
98.867
77.778
77.478
77.160
76.842
30.006
25.209
150
100
50
ppm (t1)

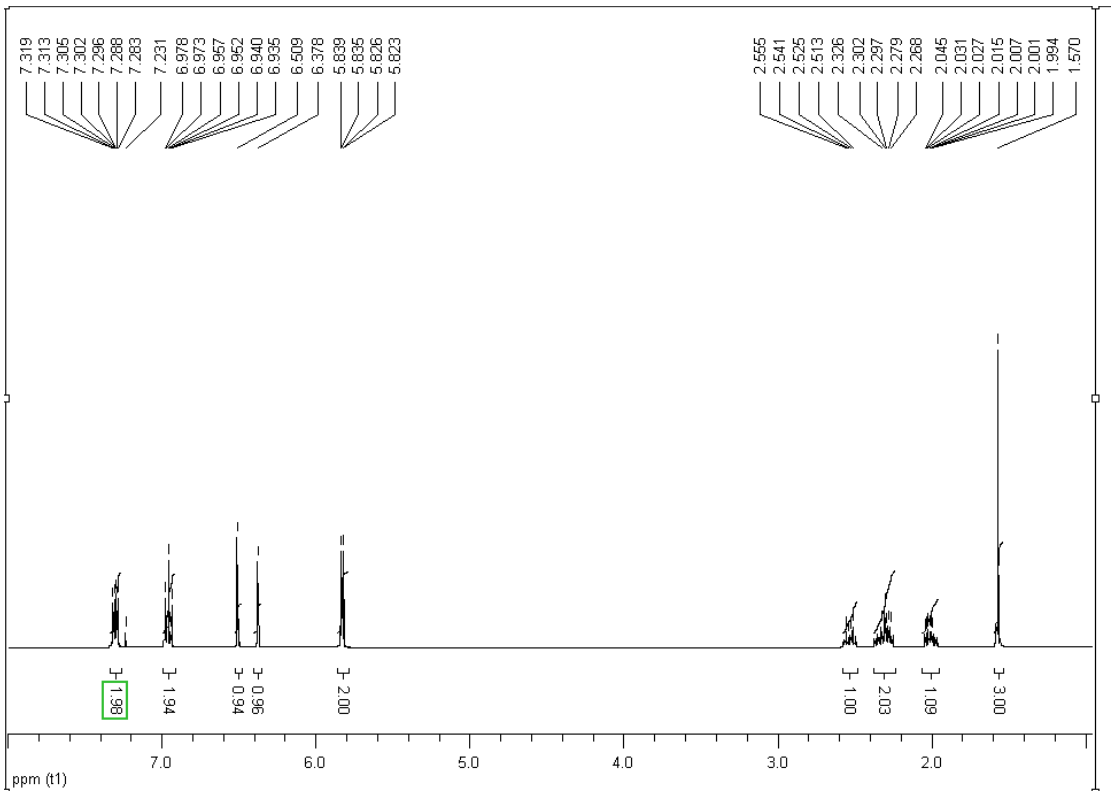

Cl
O
O
O
7.334
7.247
6.514
6.440
5.867
5.864
4.960
4.954
4.935
4.929
2.905
2.893
2.879
2.852
2.687
2.678
2.673
2.665
2.646
2.637
2.633
2.624
2.154
2.127
2.120
2.113
2.036
2.009
1.997
1.983
1.976
1.974
1.969
4.02
0.99
0.94
2.02
1.00
1.02
1.03
1.04
1.00
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

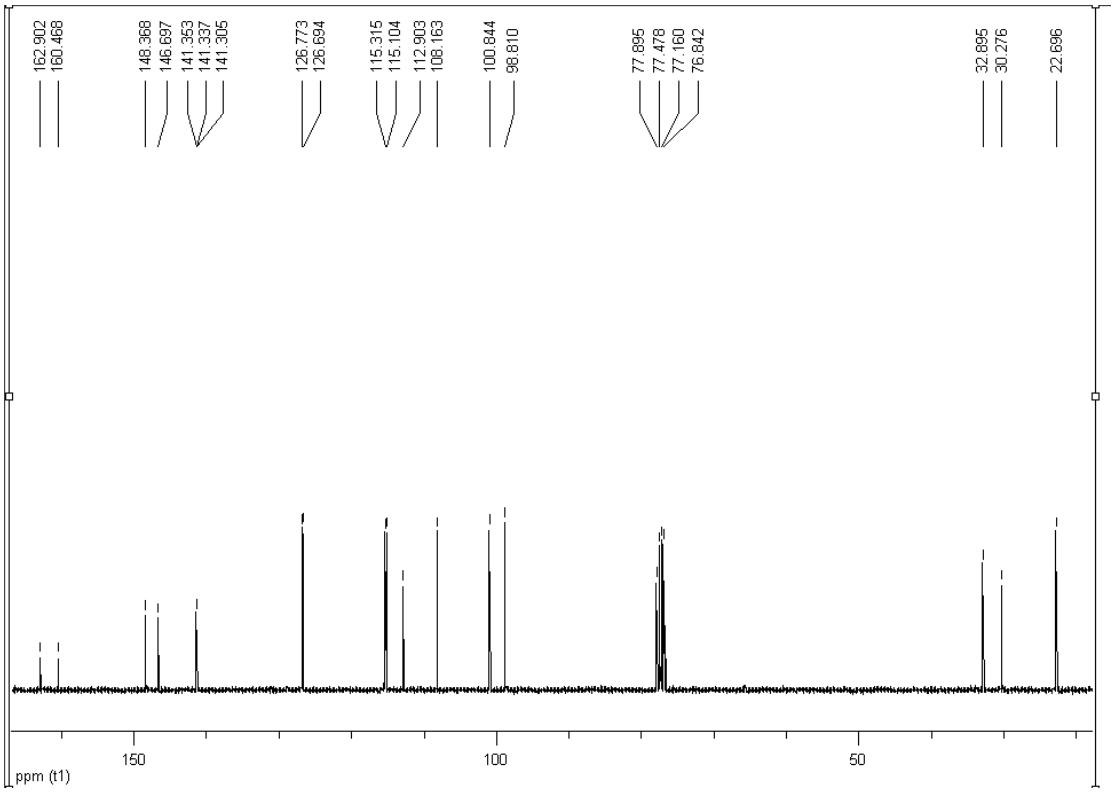

149.430
146.597
141.651
140.295
133.584
128.750
127.455
113.152
108.243
100.941
98.828
77.478
77.160
77.019
76.842
29.993
25.039
150
100
50
ppm (t1)

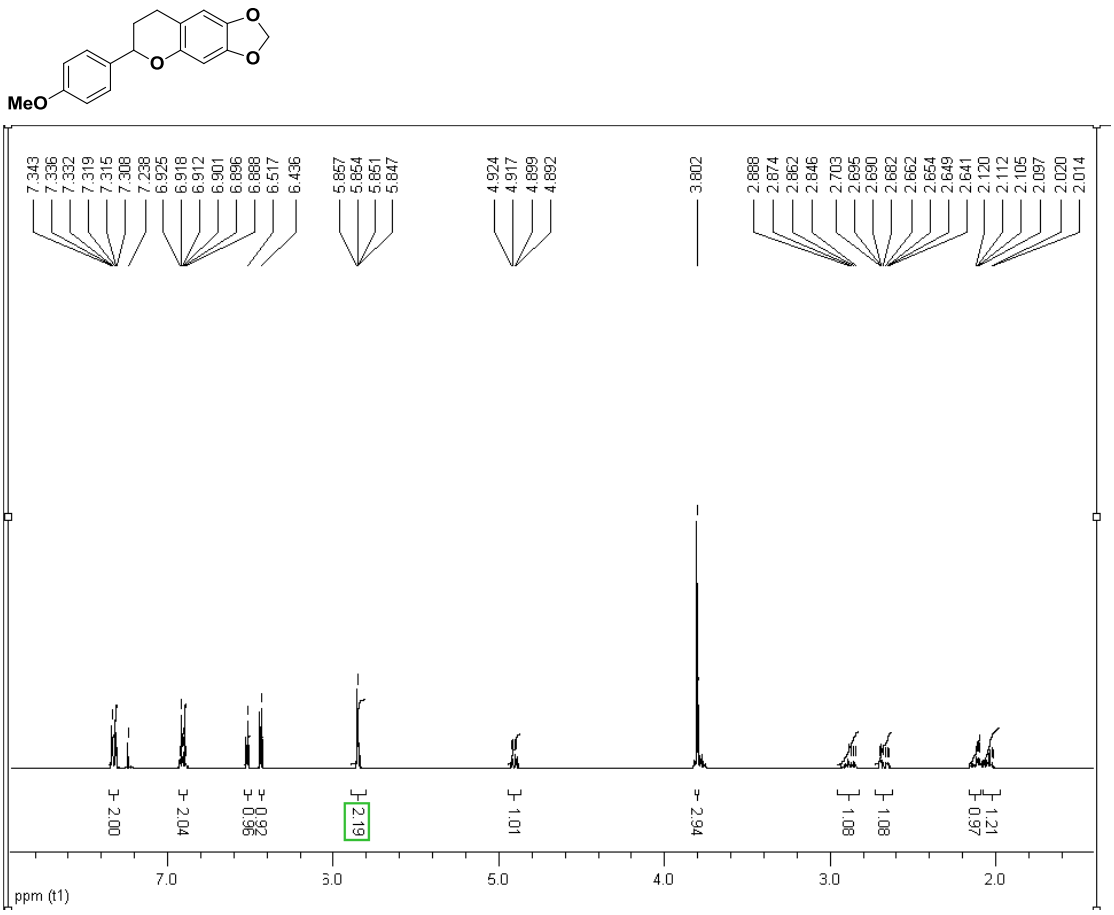


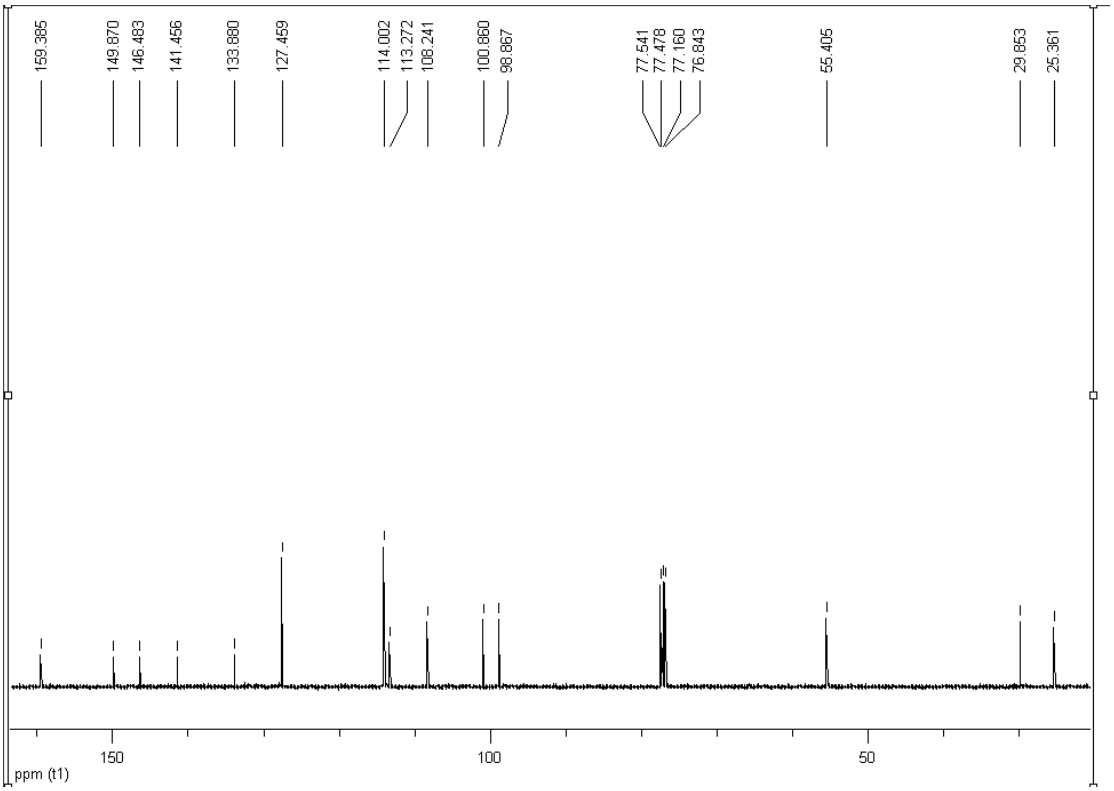


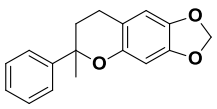


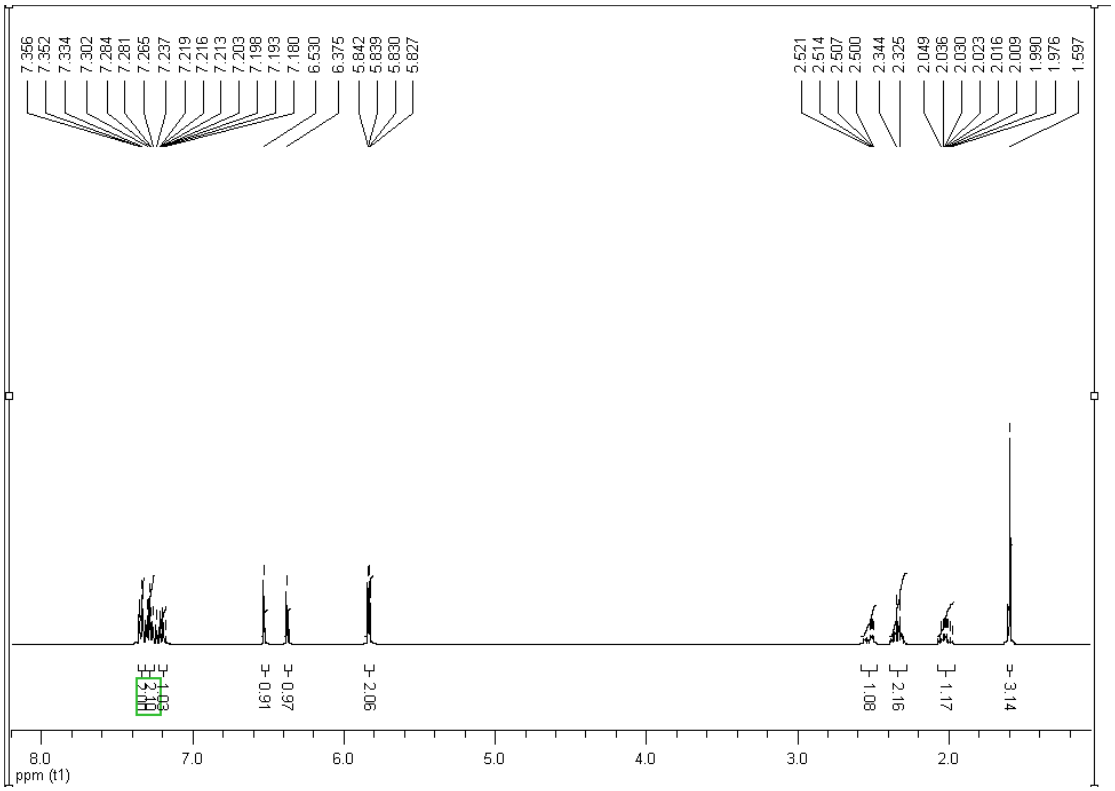


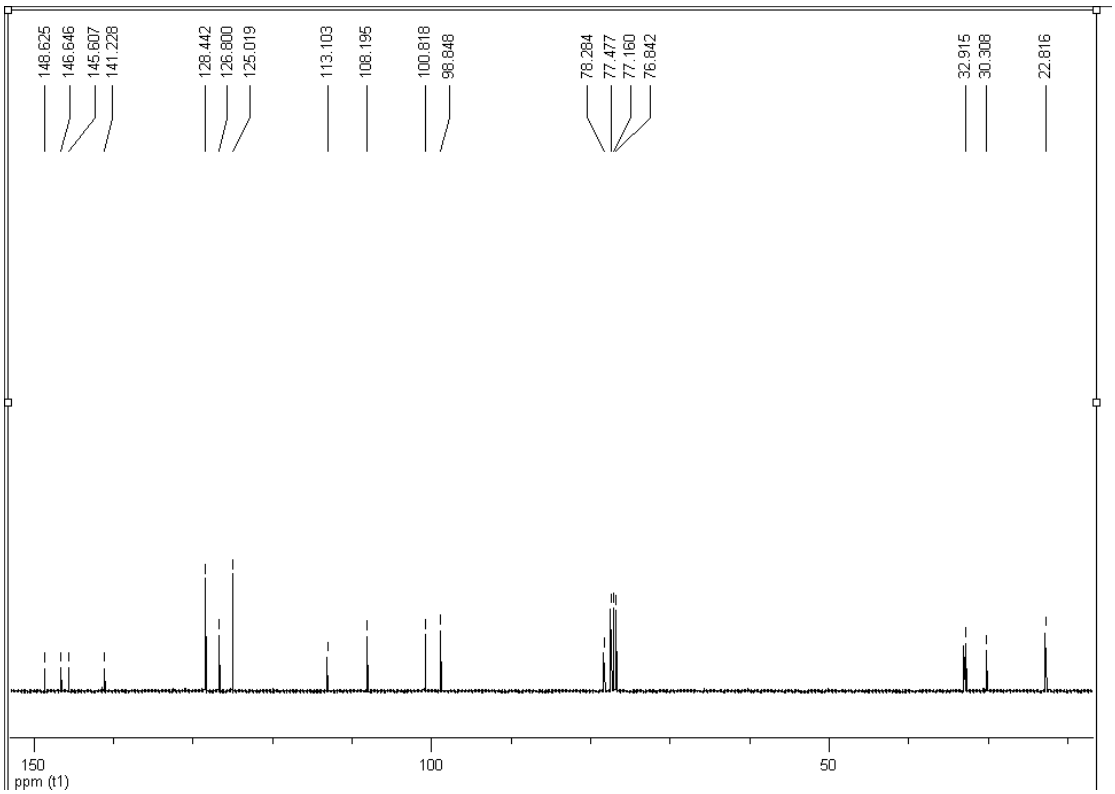


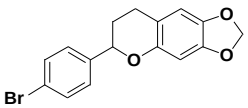

MeO
O
O
O
7.343
7.336
7.332
7.319
7.315
7.308
7.238
6.925
6.918
6.912
6.901
6.896
6.888
6.517
6.436
5.857
5.854
5.851
5.847
4.924
4.917
4.899
4.892
3.802
2.888
2.874
2.862
2.846
2.703
2.695
2.690
2.682
2.662
2.654
2.649
2.641
2.120
2.112
2.105
2.097
2.020
2.014
2.00
2.04
0.96
0.96
2.19
1.01
2.94
1.08
1.08
0.97
1.21
7.0
3.0
5.0
4.0
3.0
2.0
ppm (t1)

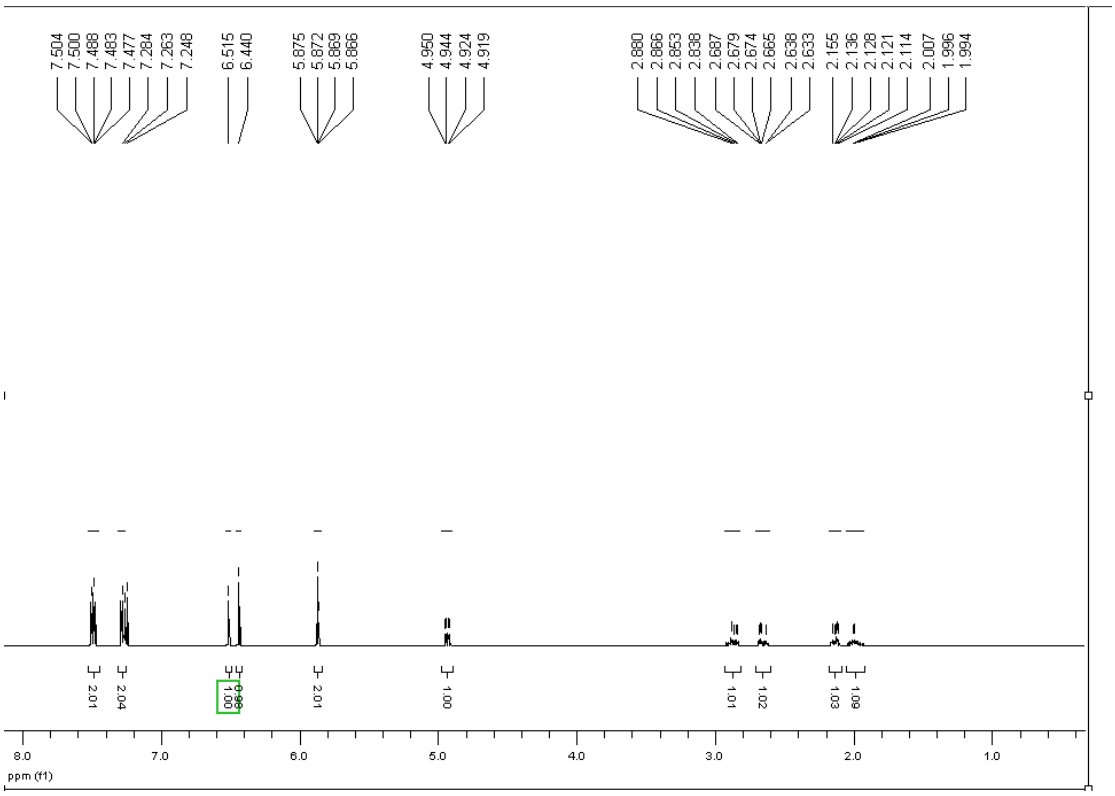

159.385
149.870
146.483
141.456
133.880
127.459
114.002
113.272
108.241
100.860
98.867
77.541
77.478
77.160
76.843
55.405
29.853
25.361
150
100
50
ppm (t1)

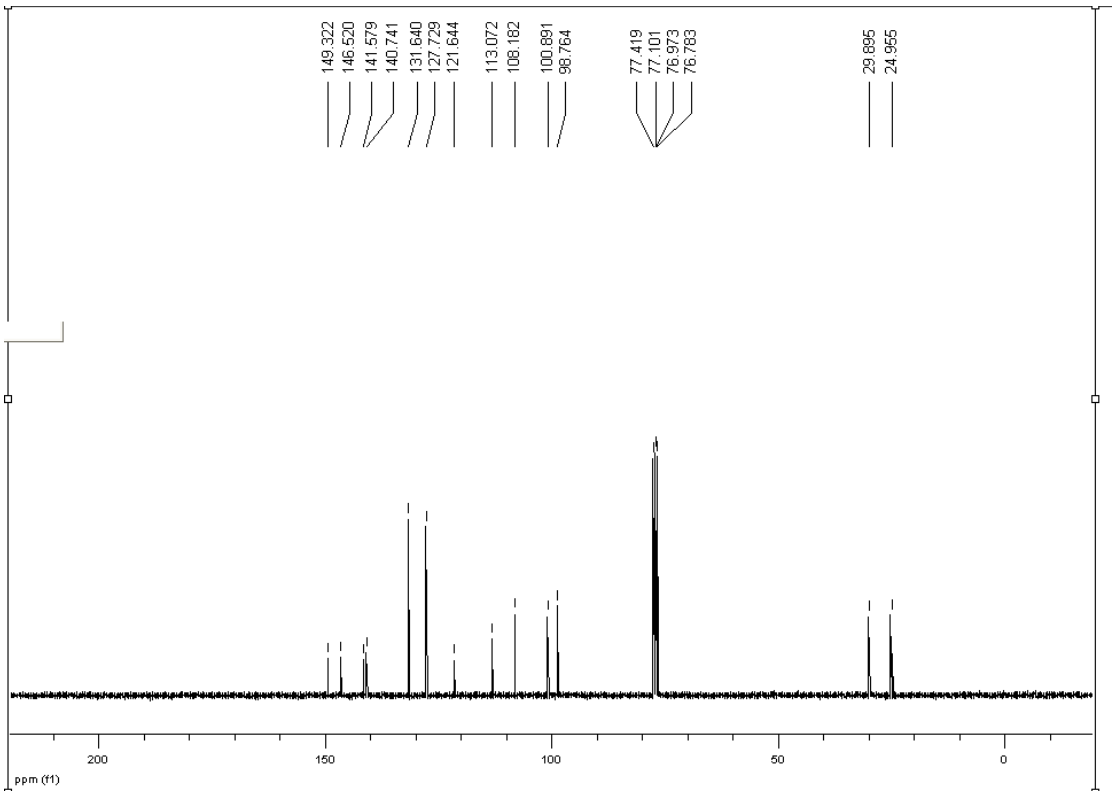


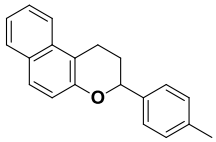


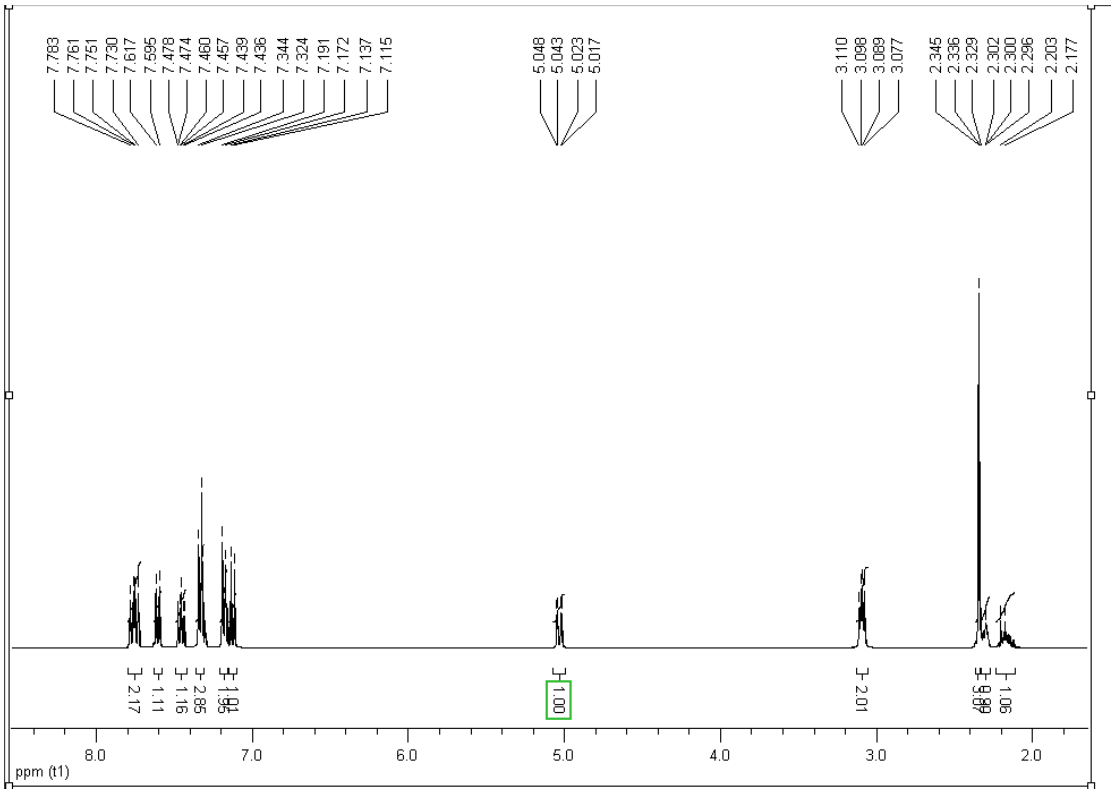


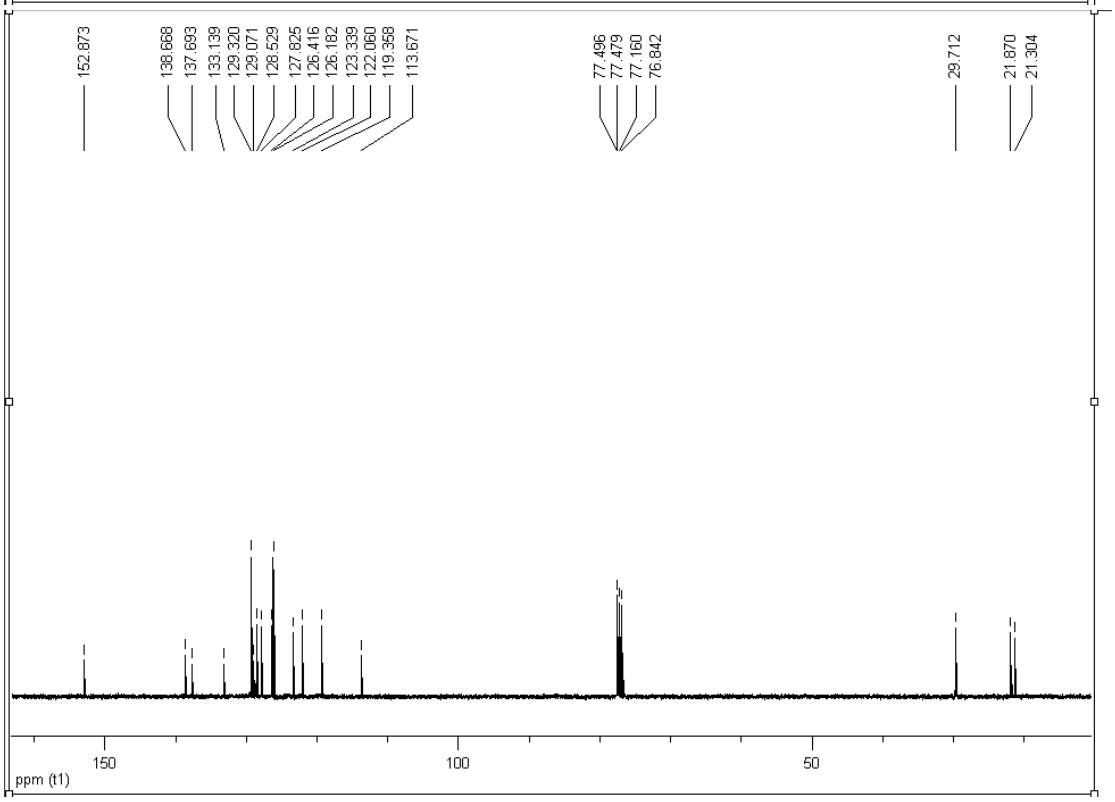

Br
O
O
O

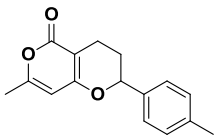

7.504
7.500
7.488
7.483
7.477
7.284
7.263
7.248
6.515
6.440
5.875
5.872
5.869
5.866
4.950
4.944
4.924
4.919
2.880
2.866
2.853
2.838
2.687
2.679
2.674
2.665
2.638
2.633
2.155
2.136
2.128
2.121
2.114
2.007
1.996
1.994
2.01
2.04
1.00
2.01
1.00
1.01
1.02
1.03
1.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

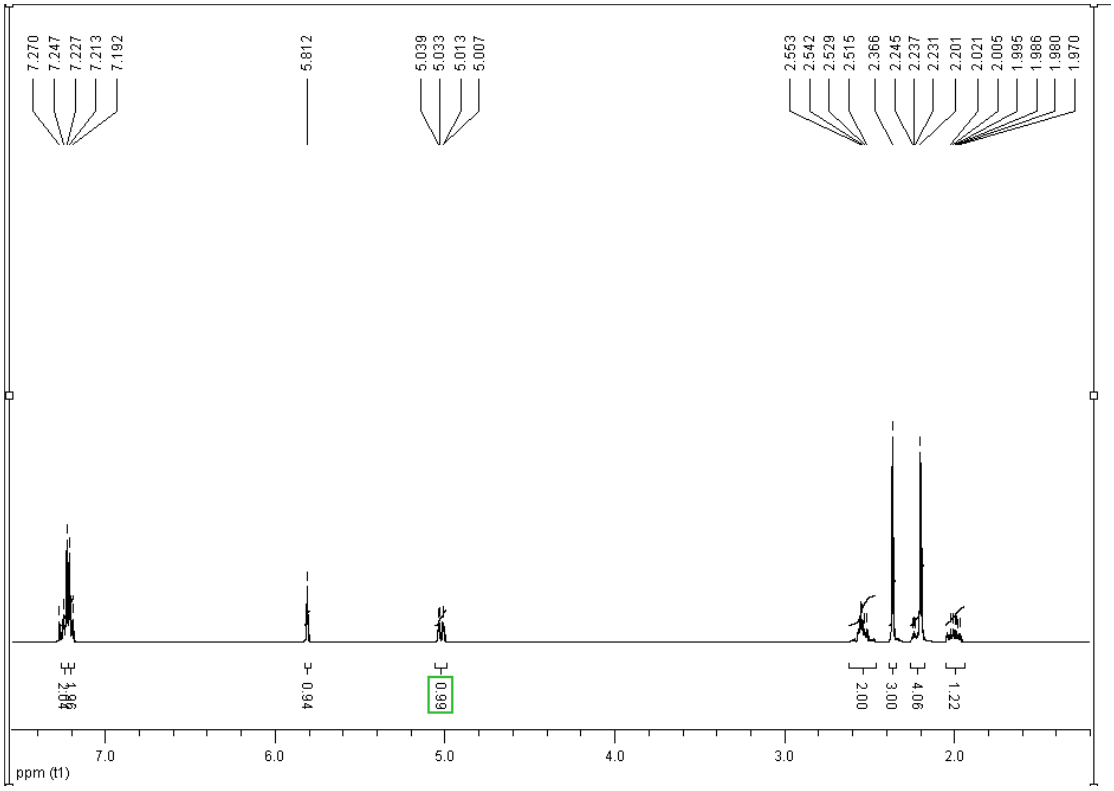

149.322
146.520
141.579
140.741
131.640
127.729
121.644
113.072
108.182
100.891
98.764
77.419
77.101
76.973
76.783
29.895
24.955
200
150
100
50
0
ppm (f1)

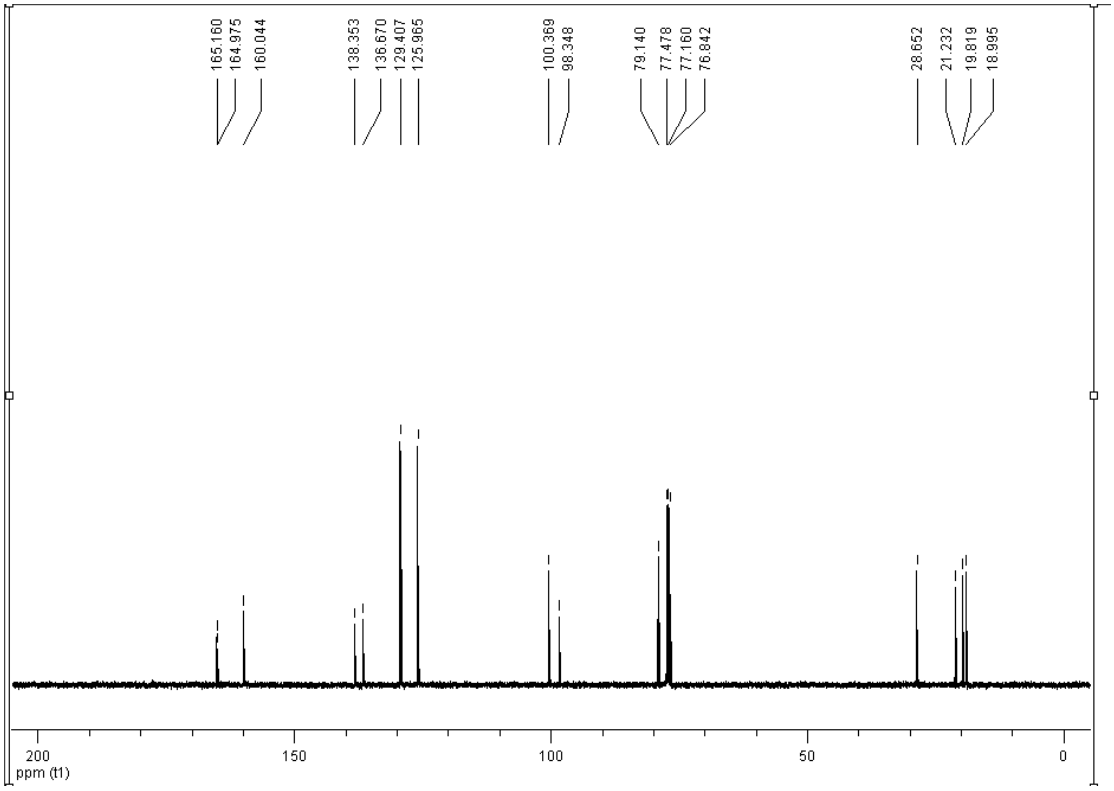


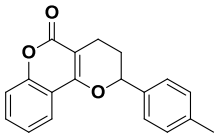


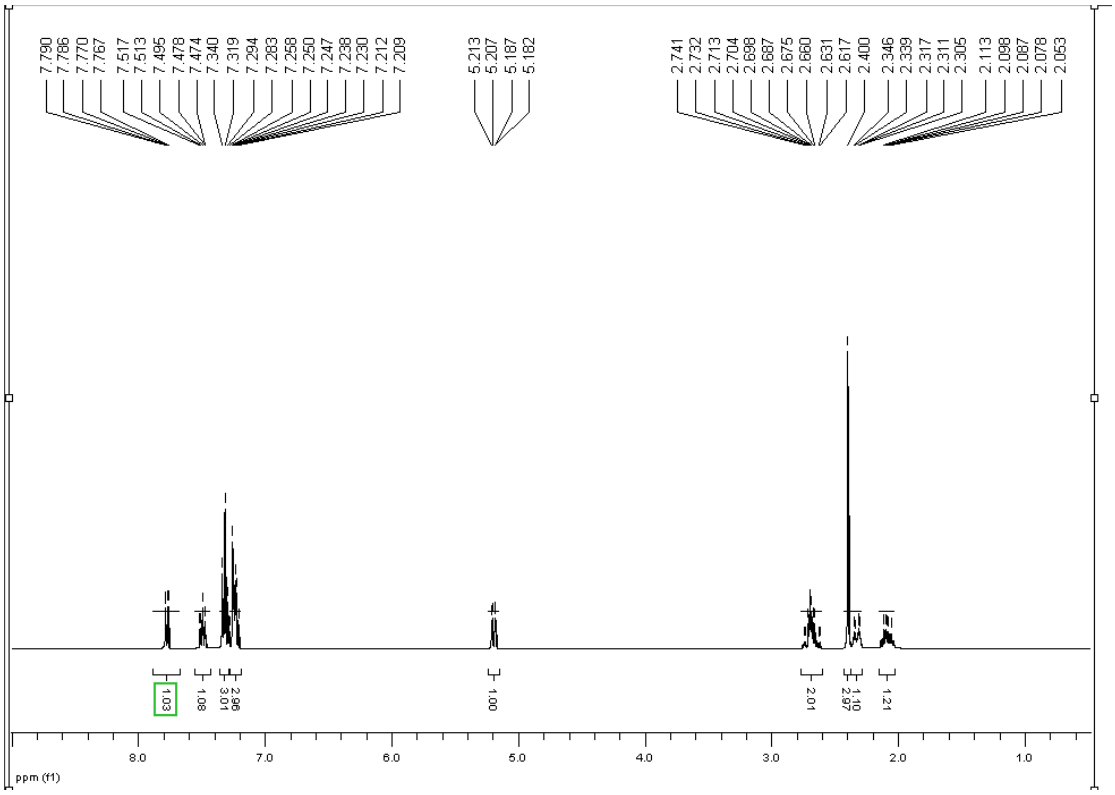


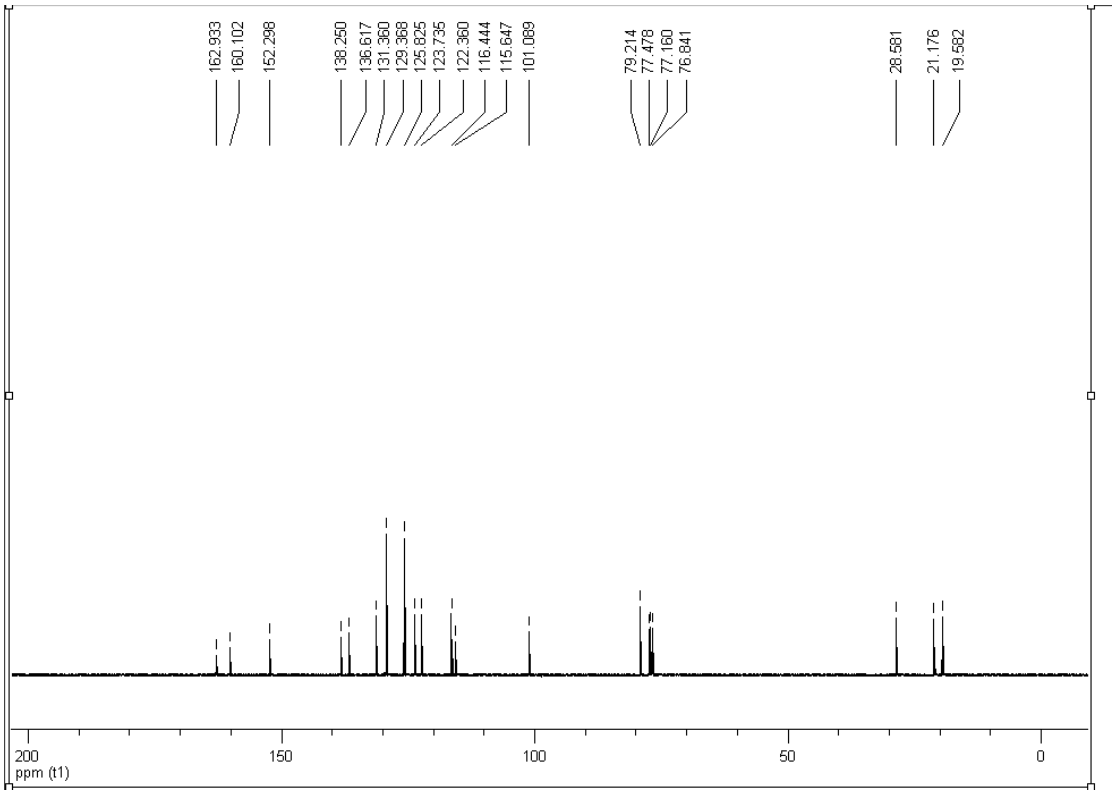


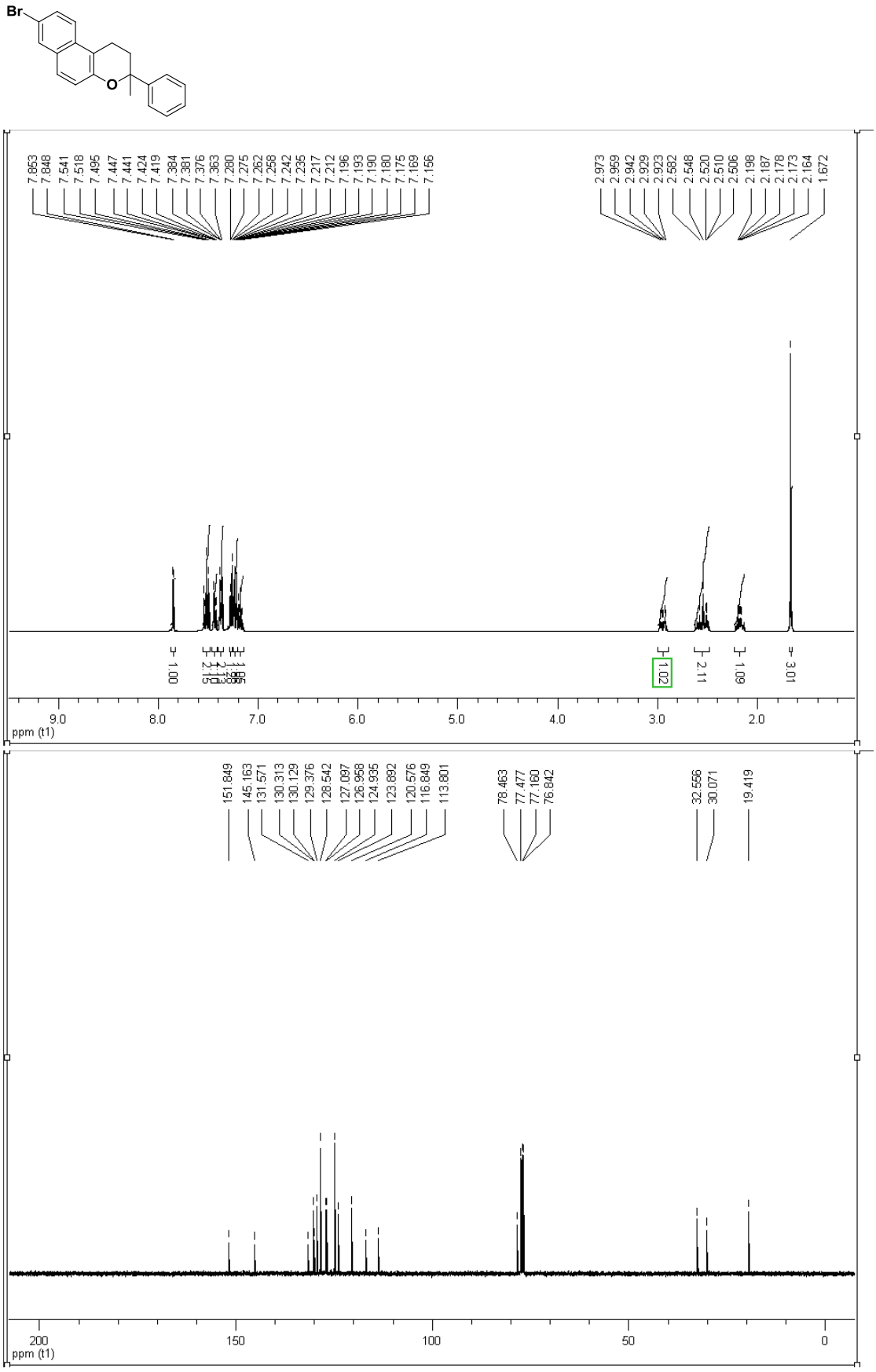


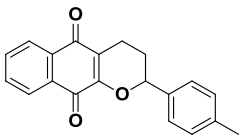


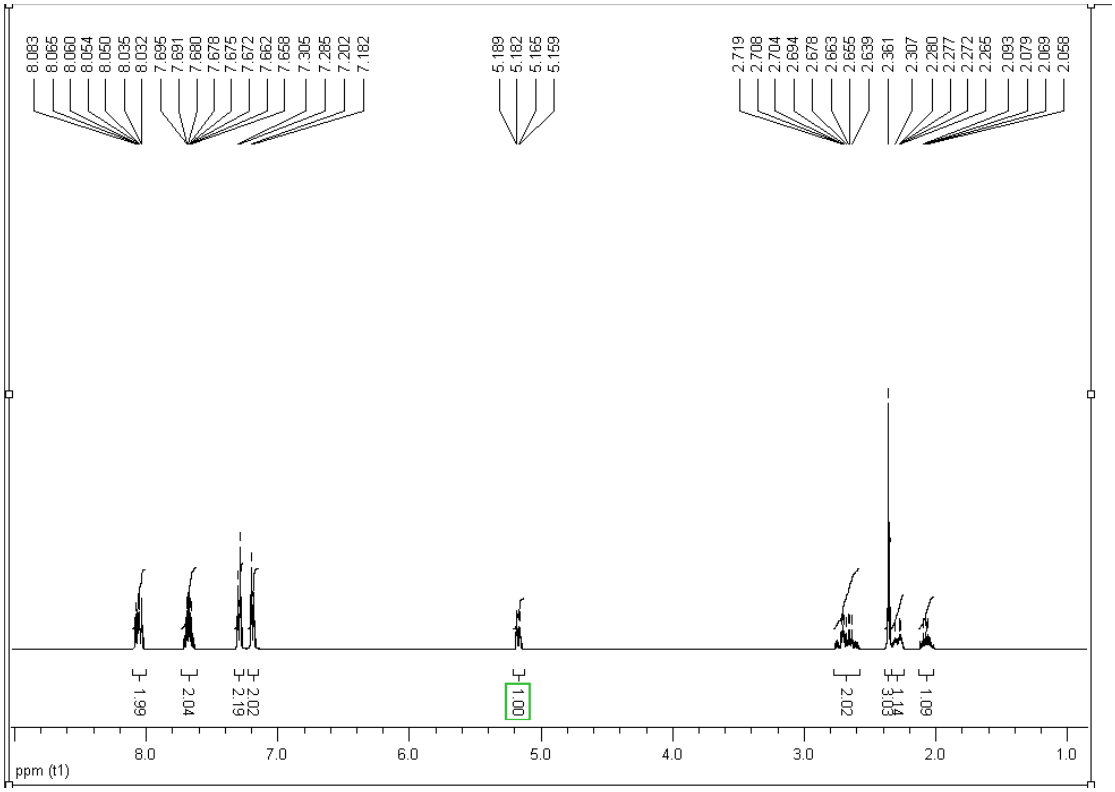


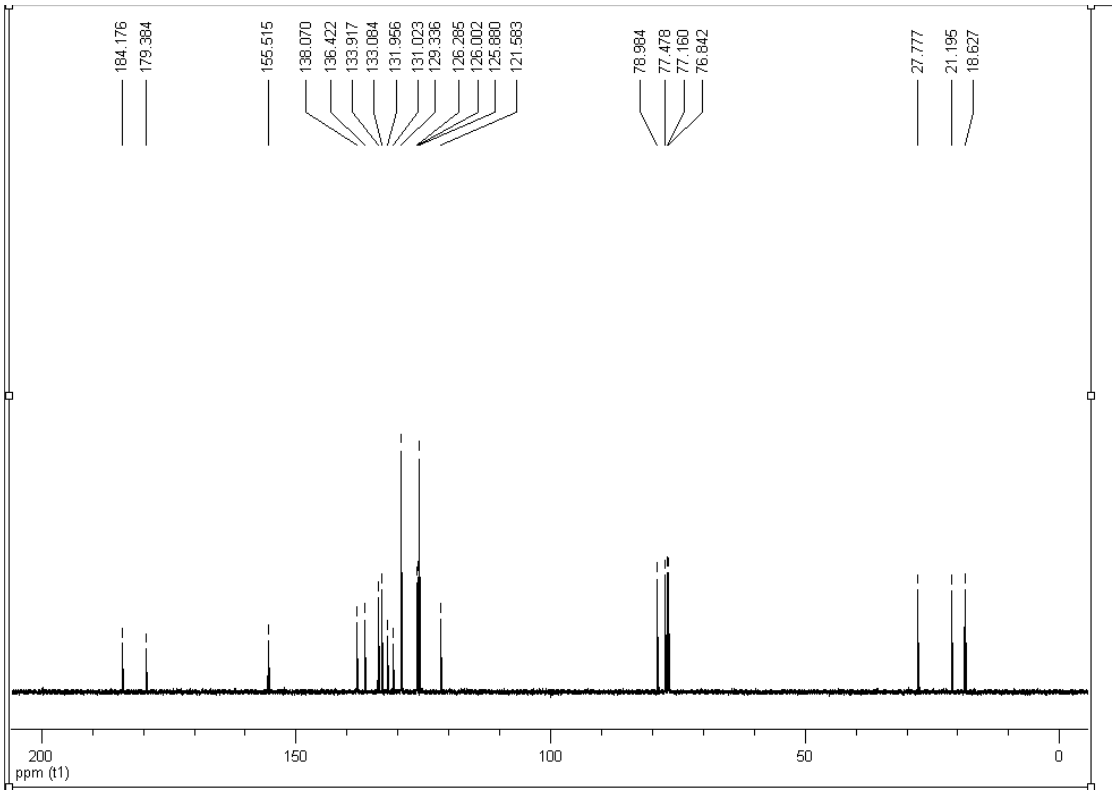

7.790
7.786
7.770
7.767
7.517
7.513
7.495
7.478
7.474
7.340
7.319
7.294
7.283
7.258
7.250
7.247
7.238
7.230
7.212
7.209
5.213
5.207
5.187
5.182
2.741
2.732
2.713
2.704
2.698
2.687
2.675
2.660
2.631
2.617
2.400
2.346
2.339
2.317
2.311
2.305
2.113
2.098
2.087
2.078
2.053
1.03
1.08
3.01
2.86
1.00
2.01
1.10
2.67
1.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

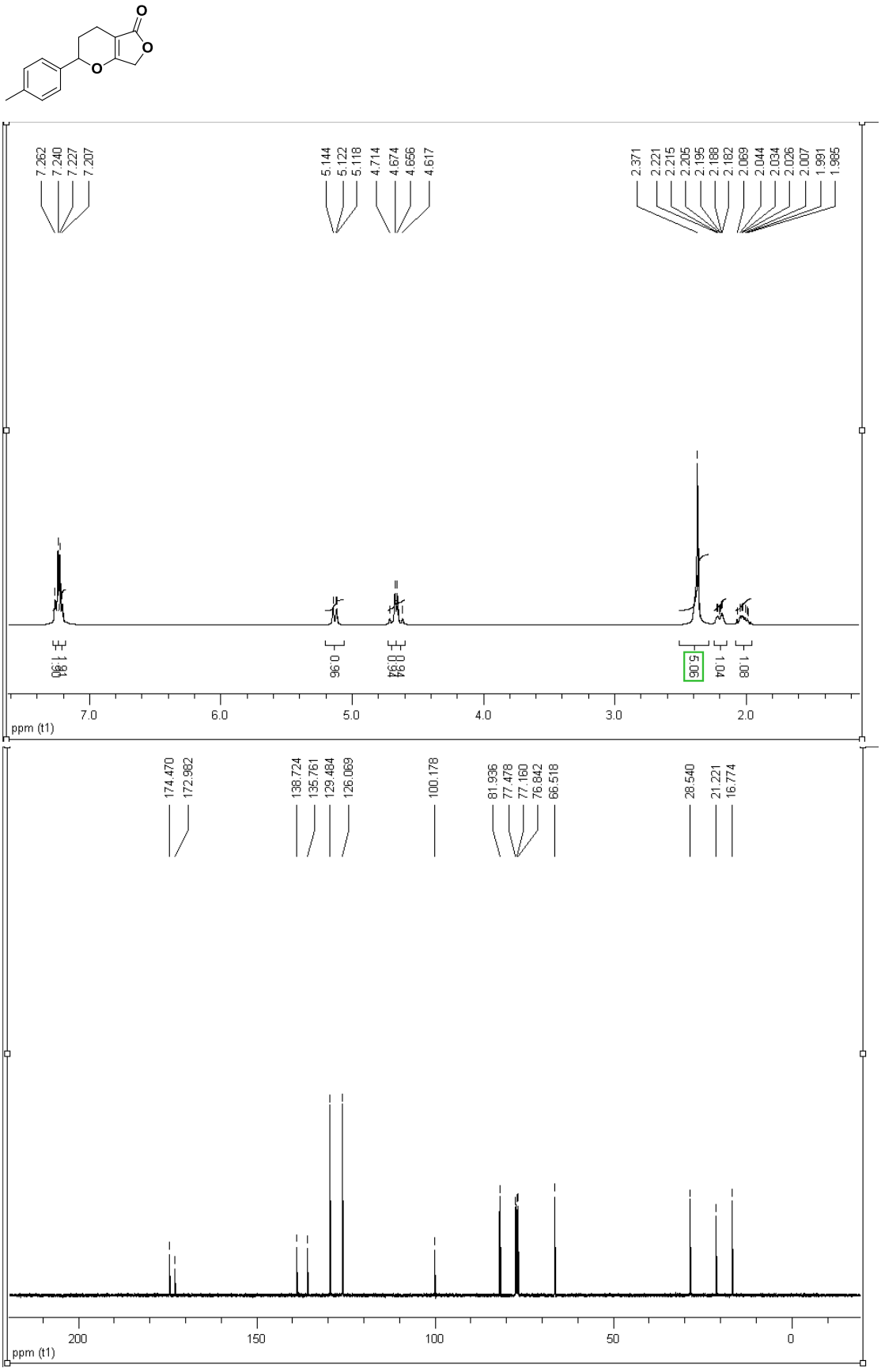

162.933
160.102
152.298
138.250
136.617
131.360
129.368
125.825
123.735
122.360
116.444
115.647
101.089
79.214
77.478
77.160
76.841
28.581
21.176
19.582
200
150
100
50
0
ppm (t1)

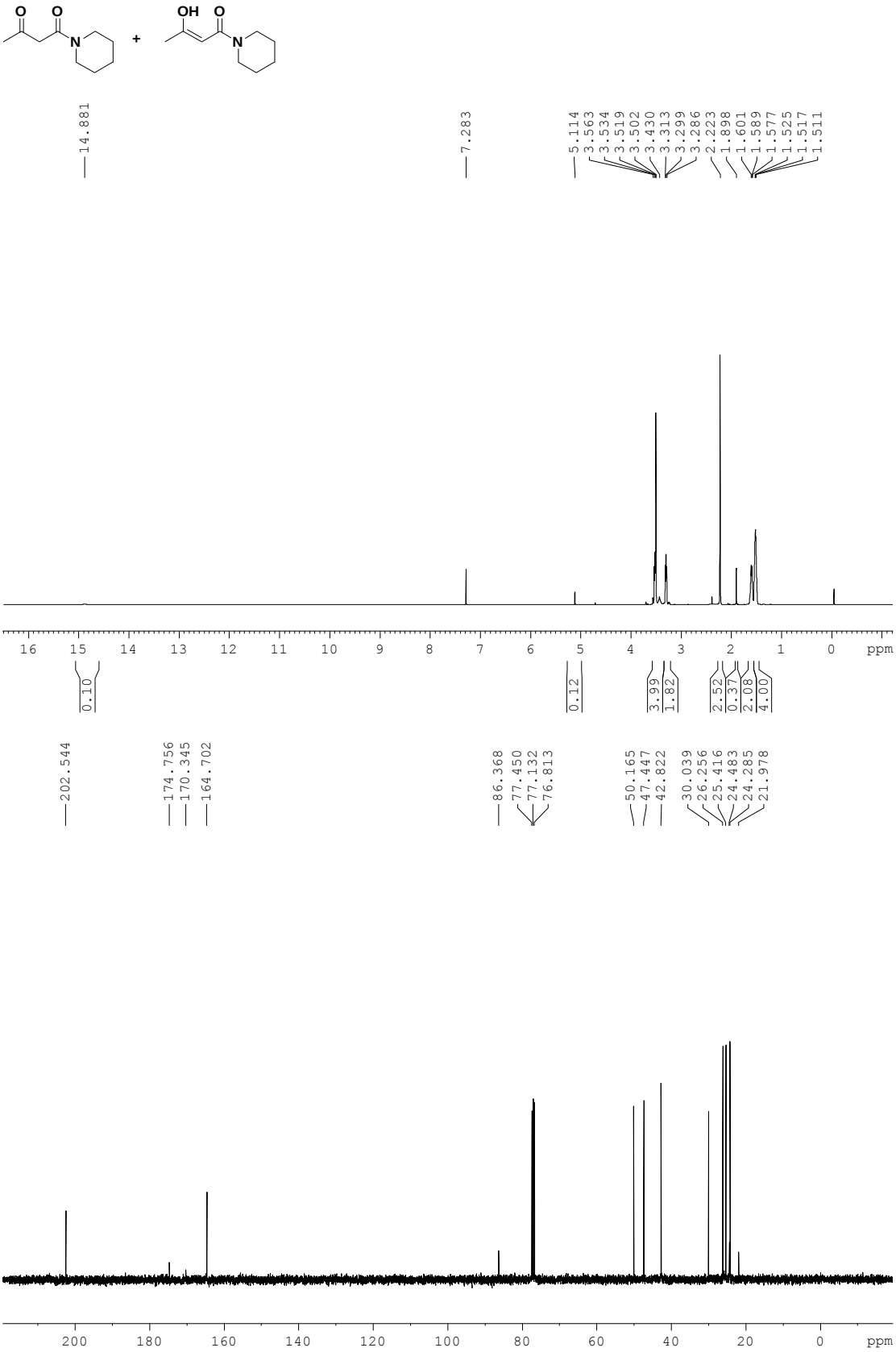

Br
O
7.853
7.848
7.541
7.518
7.495
7.447
7.441
7.424
7.419
7.384
7.381
7.376
7.363
7.280
7.275
7.262
7.258
7.242
7.235
7.217
7.212
7.196
7.193
7.190
7.180
7.175
7.169
7.156
2.973
2.959
2.942
2.929
2.923
2.582
2.548
2.520
2.510
2.506
2.198
2.187
2.178
2.173
2.164
1.672
1.00
2.15
1.02
2.11
1.09
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
151.849
145.163
131.571
130.313
130.129
129.376
128.542
127.097
126.958
124.935
123.892
120.576
116.849
113.801
78.463
77.477
77.160
76.842
32.556
30.071
19.419
200
150
100
50
0
ppm (t1)

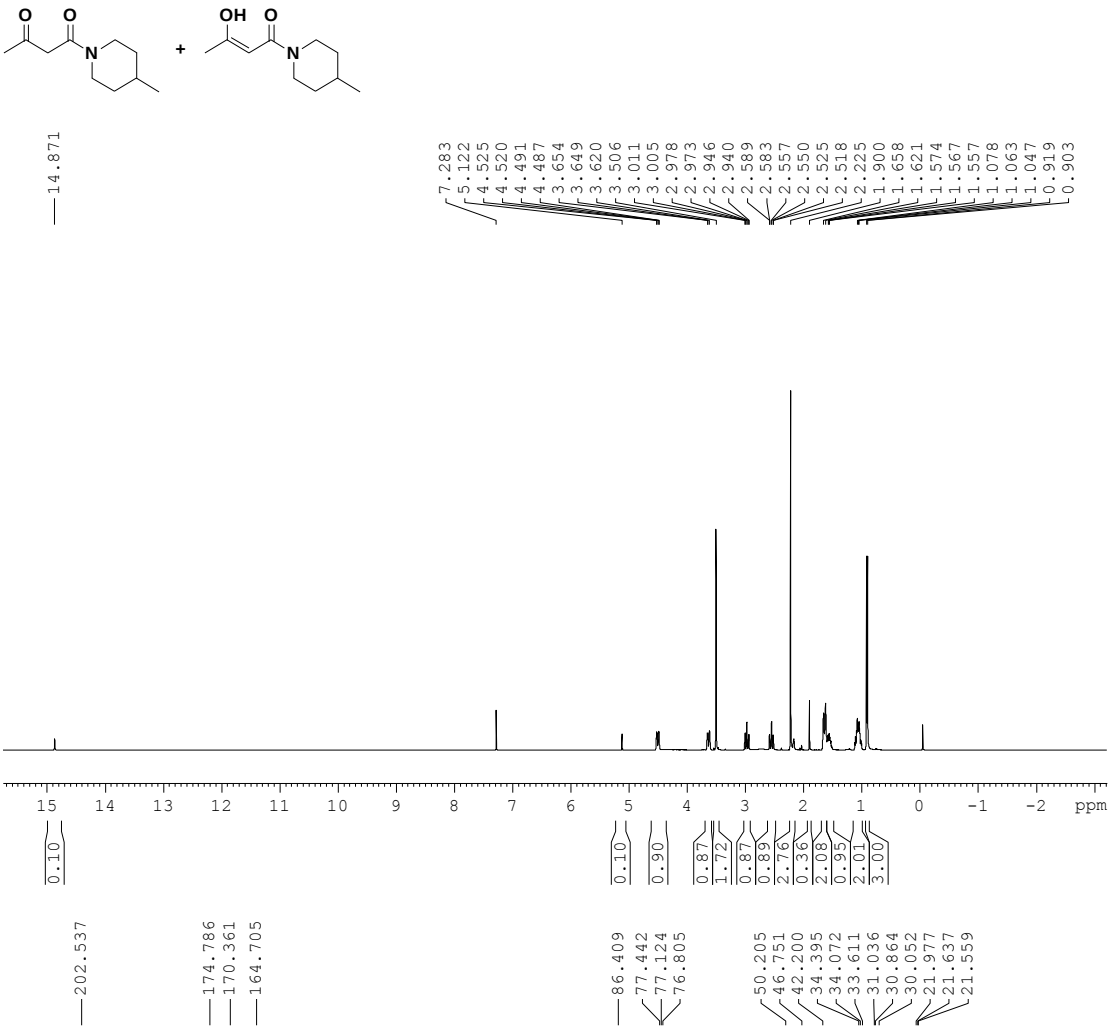


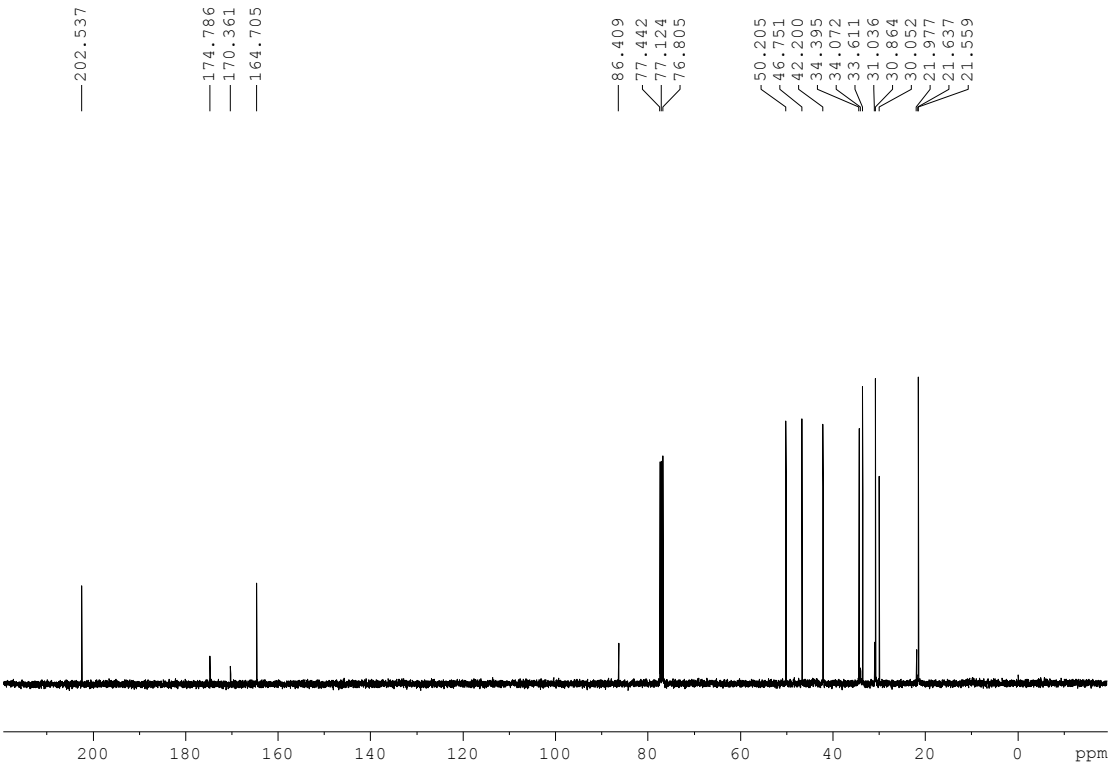


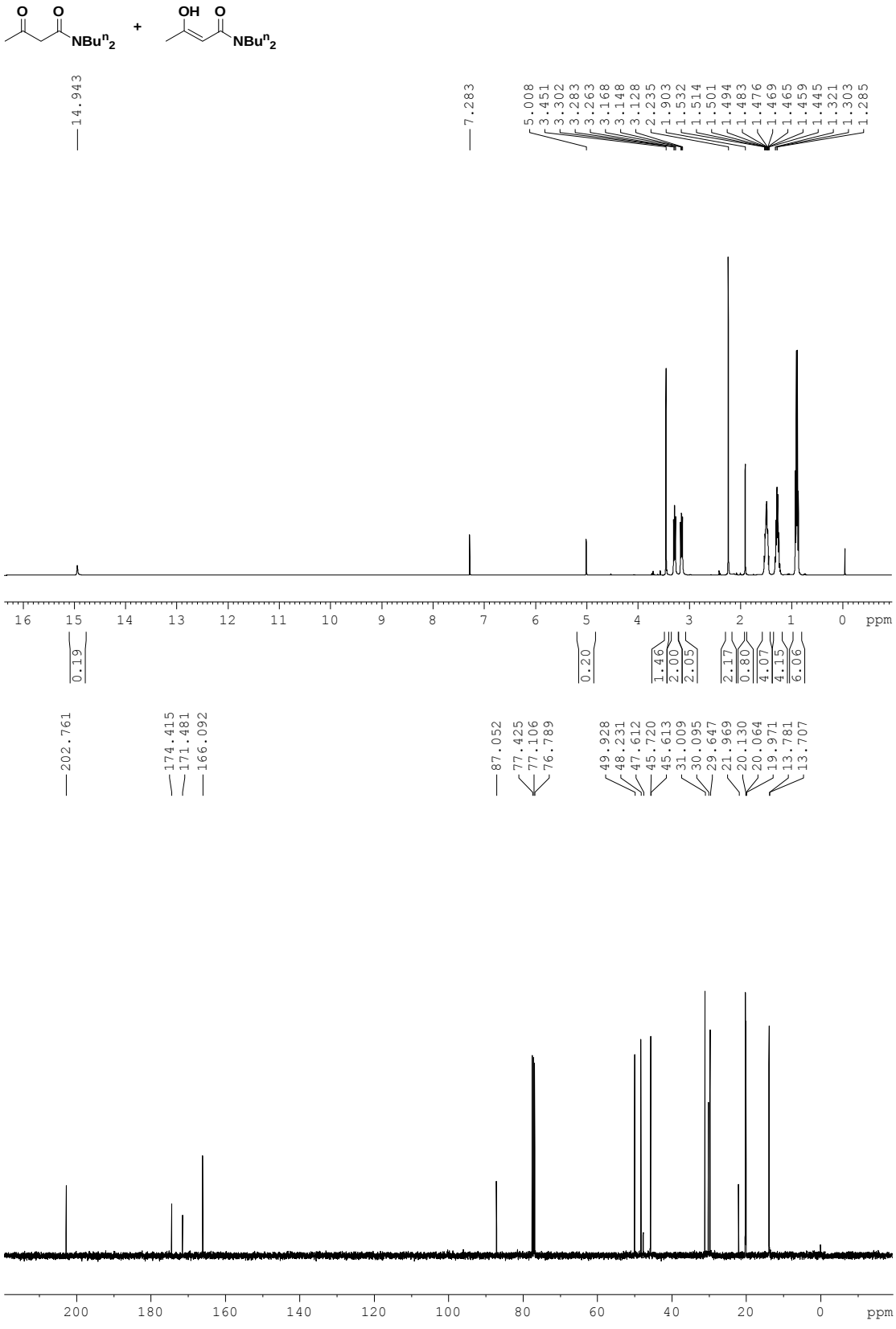


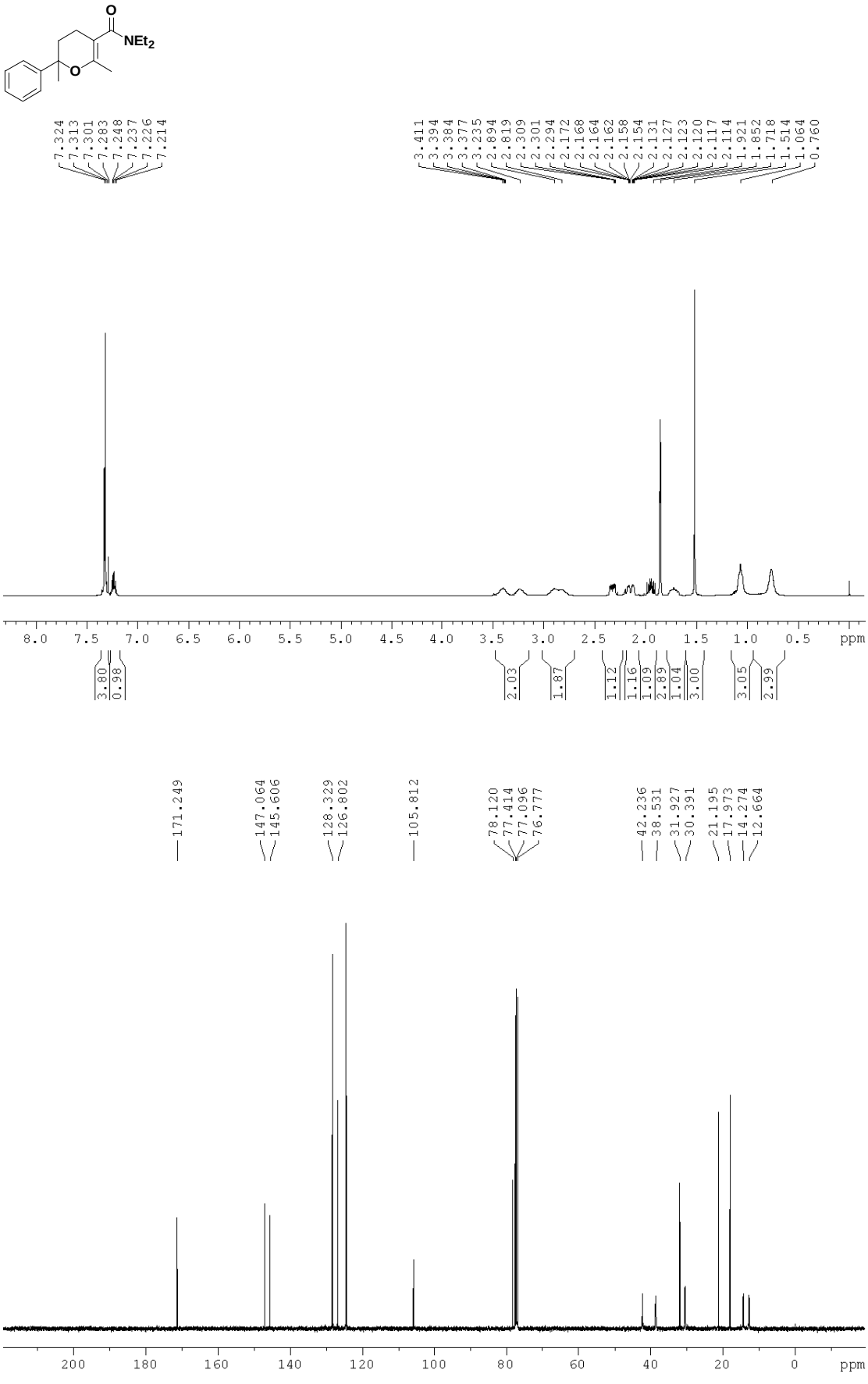


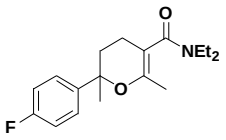


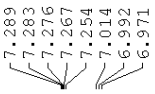

O
O
N
+
OH
O
N
14.871
7.283
5.122
4.525
4.520
4.491
4.487
3.654
3.649
3.620
3.506
3.011
3.005
2.978
2.973
2.946
2.940
2.589
2.583
2.557
2.550
2.525
2.518
2.225
1.900
1.658
1.621
1.574
1.567
1.557
1.078
1.063
1.047
0.919
0.903
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
0.10
0.10
0.90
0.87
1.72
0.87
0.89
2.76
0.36
2.08
0.95
2.01
3.00

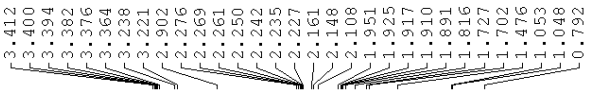

202.537
174.786
170.361
164.705
86.409
77.442
77.124
76.805
50.205
46.751
42.200
34.395
34.072
33.611
31.036
30.864
30.052
21.977
21.637
21.559
200 180 160 140 120 100 80 60 40 20 0 ppm

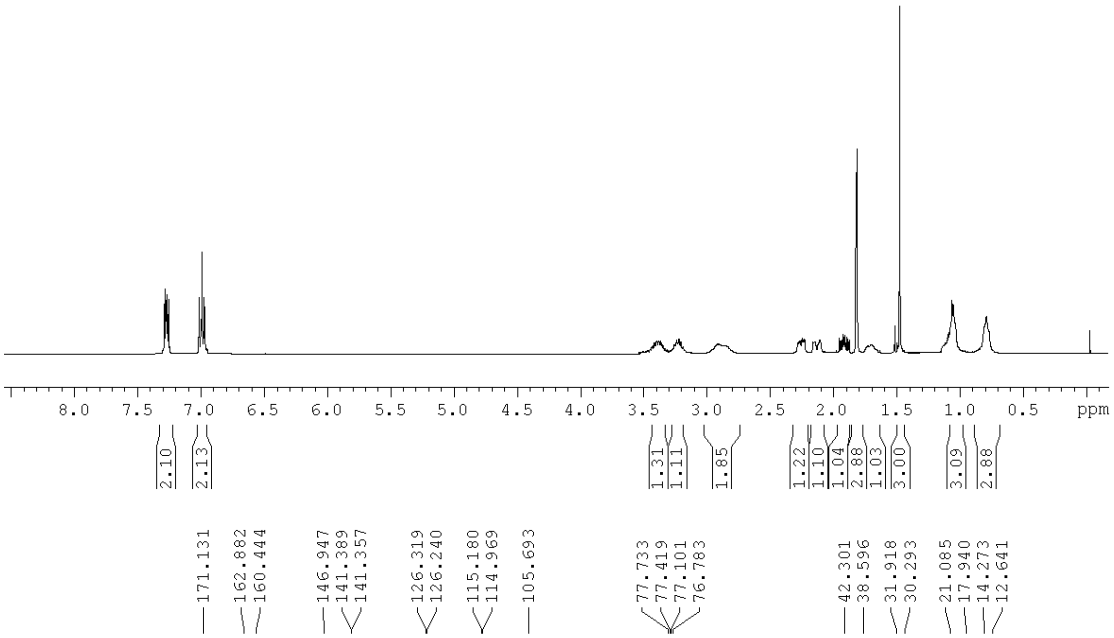

O
O
NBu$^n_2$
+
OH
O
NBu$^n_2$
14.943
7.283
5.008
3.451
3.302
3.283
3.263
3.168
3.148
3.128
2.235
1.903
1.532
1.514
1.501
1.494
1.483
1.476
1.469
1.465
1.459
1.445
1.321
1.303
1.285
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.19
0.20
1.46
2.00
2.05
2.17
0.80
4.07
4.15
6.06
202.761
174.415
171.481
166.092
87.052
77.425
77.106
76.789
49.928
48.231
47.612
45.720
45.613
31.009
30.095
29.647
21.969
20.130
20.064
19.971
13.781
13.707
200 180 160 140 120 100 80 60 40 20 0 ppm

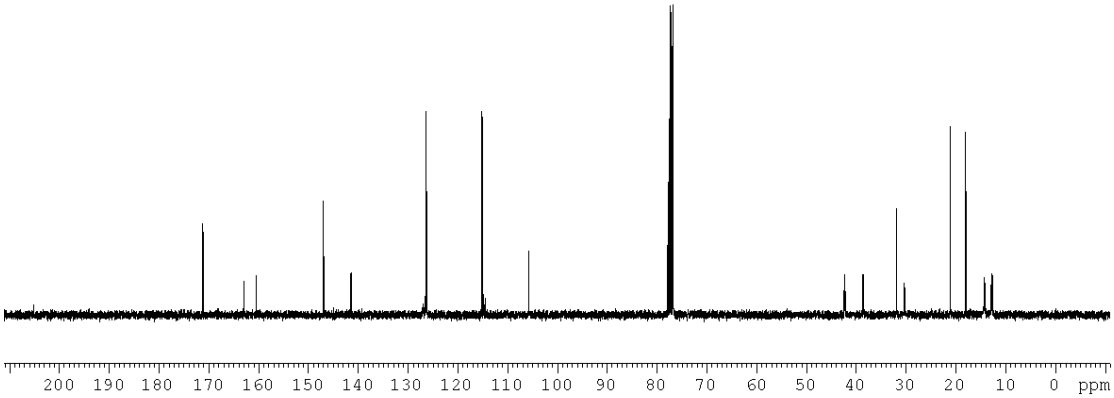

O
NEt2
O
7.324
7.313
7.301
7.283
7.248
7.237
7.226
7.214
3.411
3.394
3.384
3.377
3.235
2.894
2.819
2.309
2.301
2.294
2.172
2.168
2.164
2.162
2.158
2.154
2.131
2.127
2.123
2.120
2.117
2.114
1.921
1.852
1.718
1.514
1.064
0.760
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.80
0.98
2.03
1.87
1.12
1.16
1.09
2.89
1.04
3.00
3.05
2.99
171.249
147.064
145.606
128.329
126.802
105.812
78.120
77.414
77.096
76.777
42.236
38.531
31.927
30.391
21.195
17.973
14.274
12.664
200
180
160
140
120
100
80
60
40
20
0
ppm

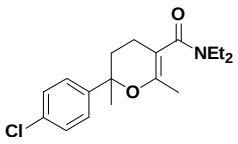






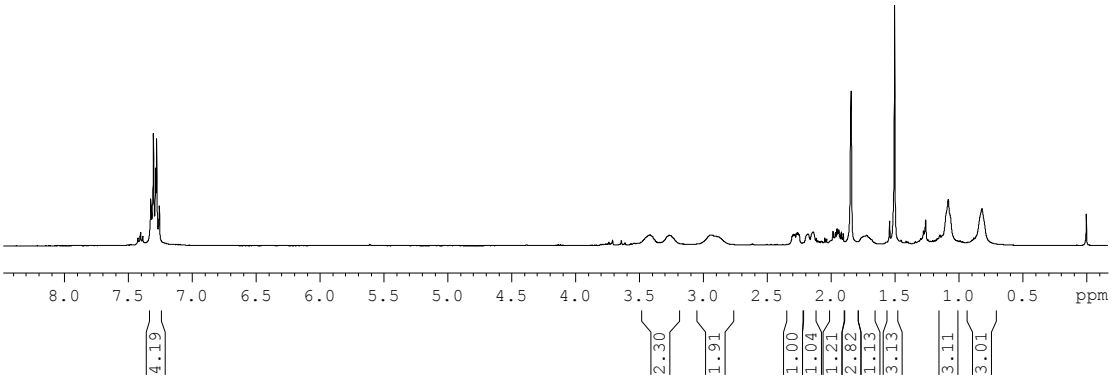




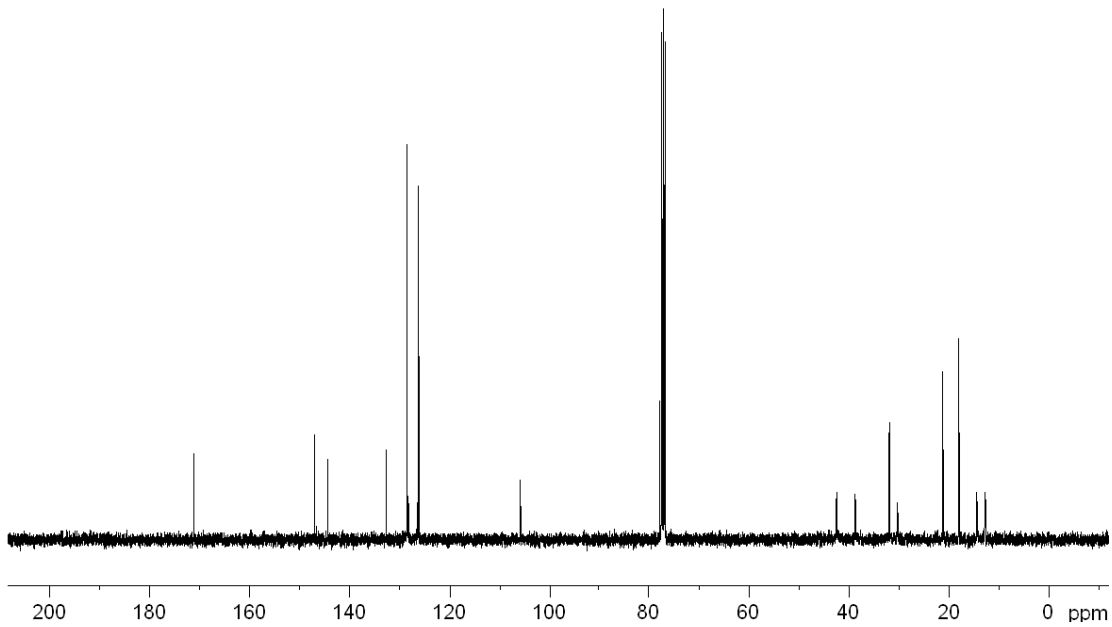


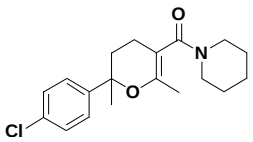
7.321
7.316
7.299
7.283
7.274
7.257
7.253

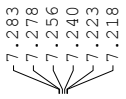
3.413
3.261
2.942
2.301
2.294
2.287
2.279
2.268
2.260
2.253
2.245
2.179
2.137
1.980
1.954
1.946
1.940
1.843
1.722
1.503
1.260
1.084
0.820

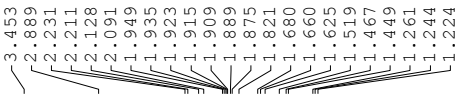


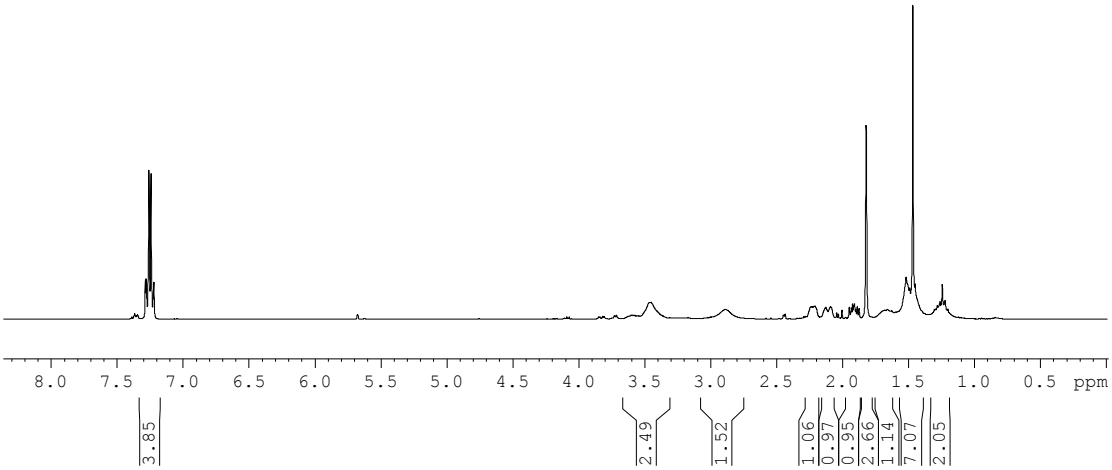
171.102
147.021
144.274
132.628
128.478
126.141
105.775
77.761
77.372
77.054
76.736
42.356
38.634
31.826
30.159
21.091
17.966
14.296
12.675

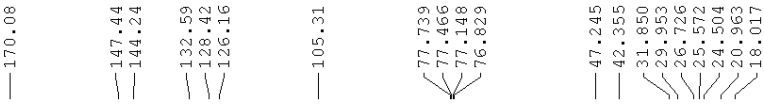


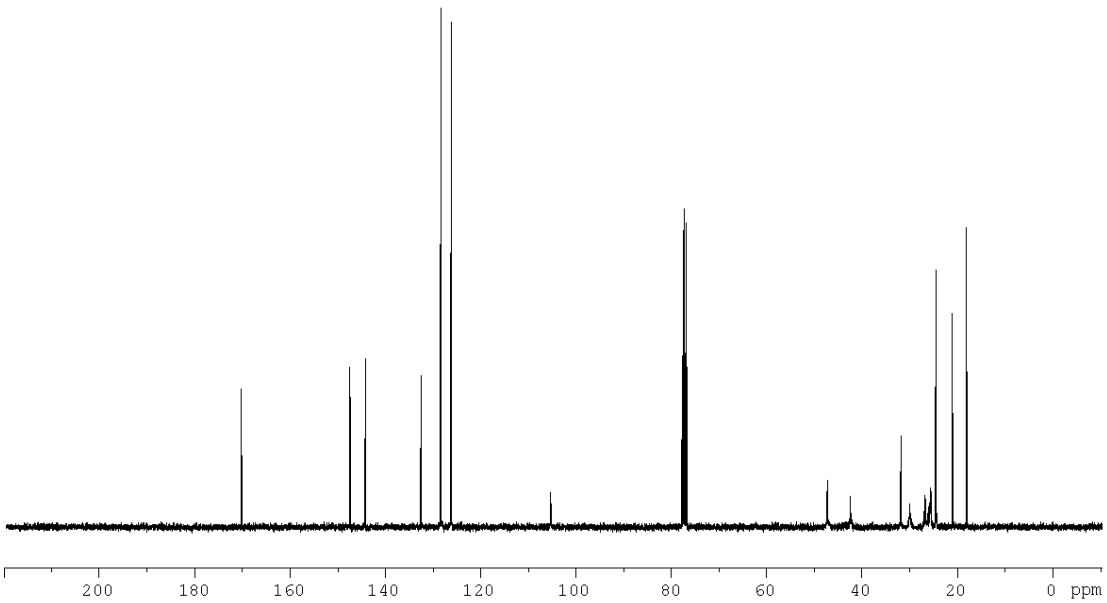


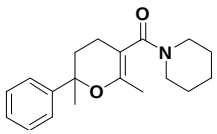


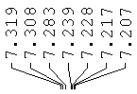


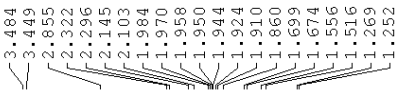


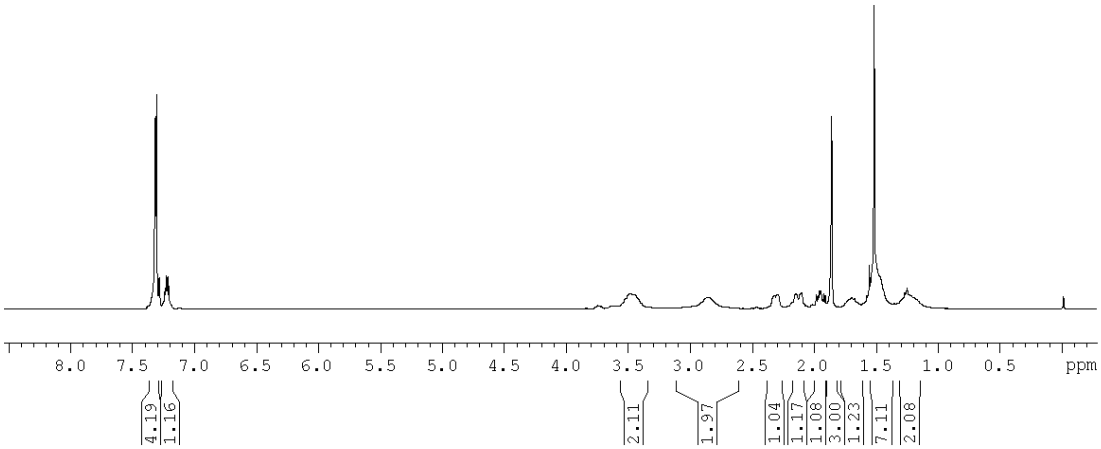


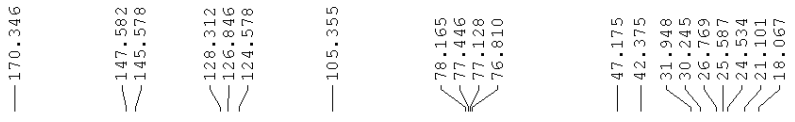


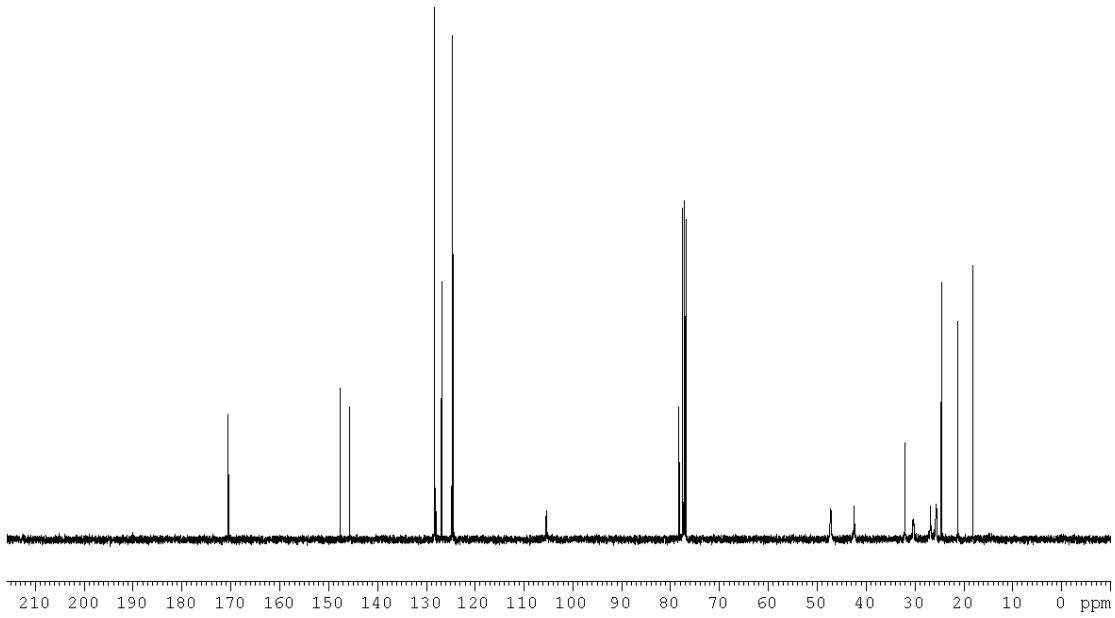


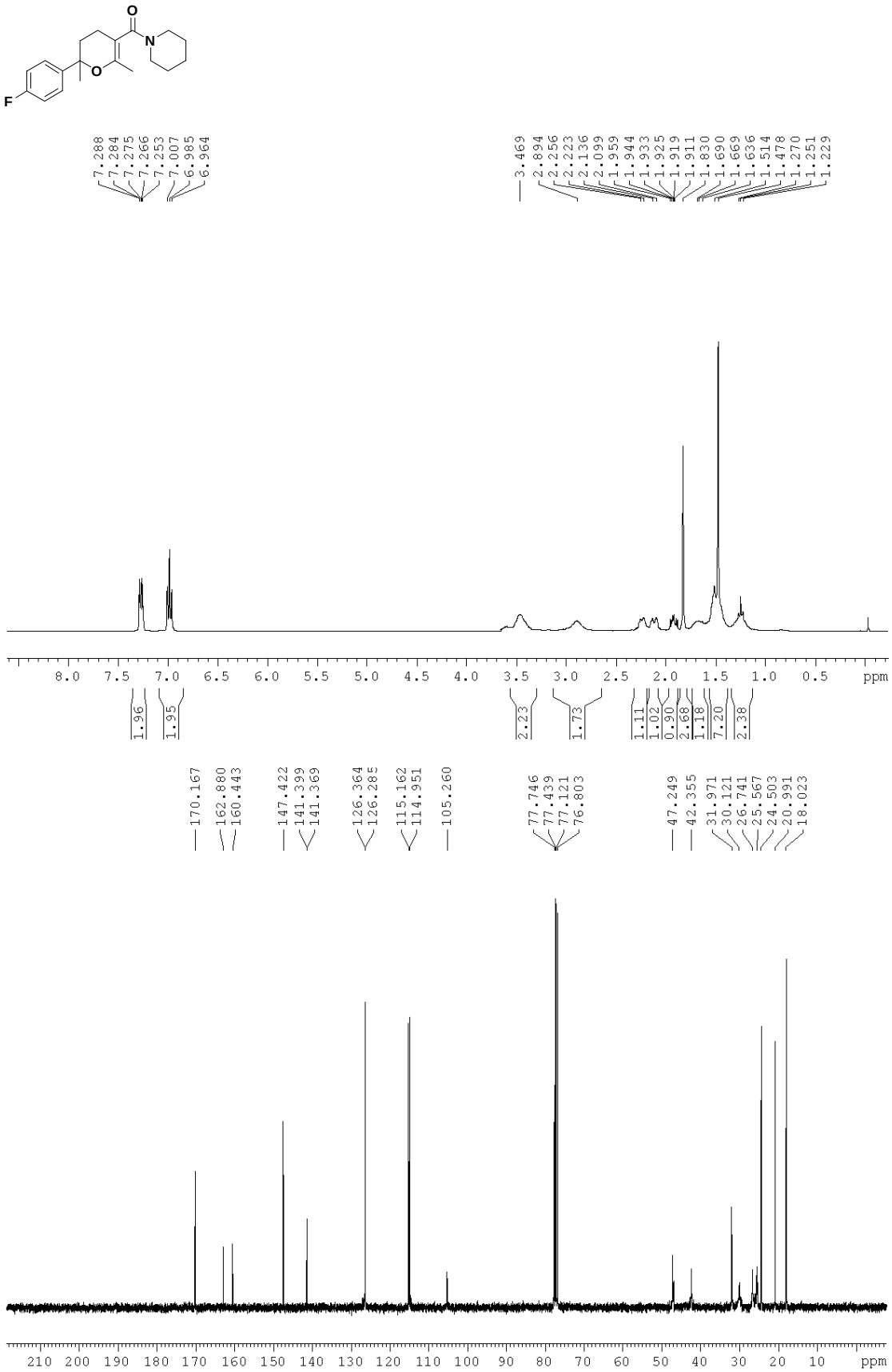


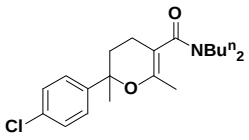


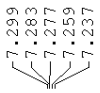


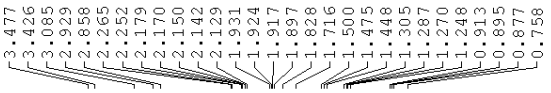


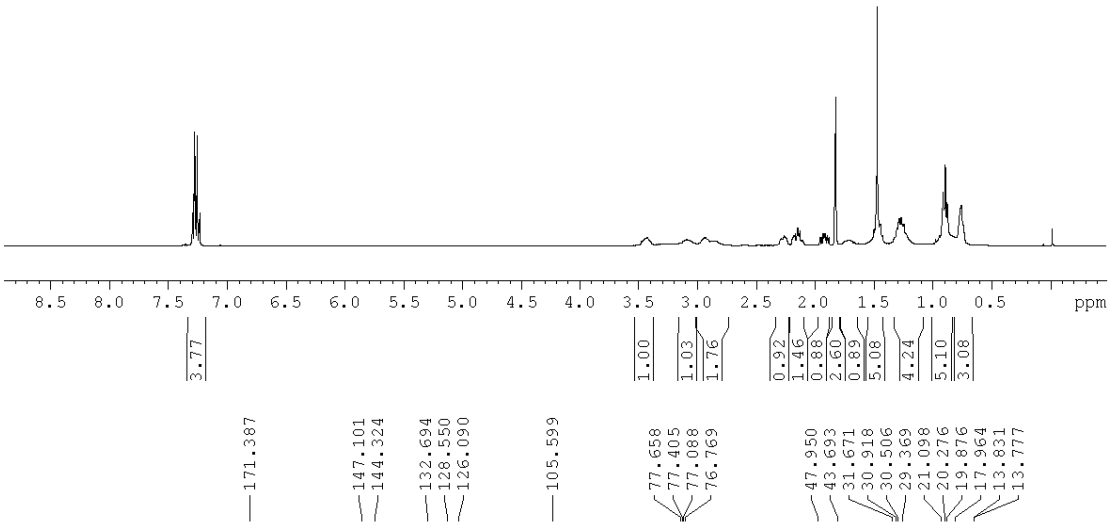


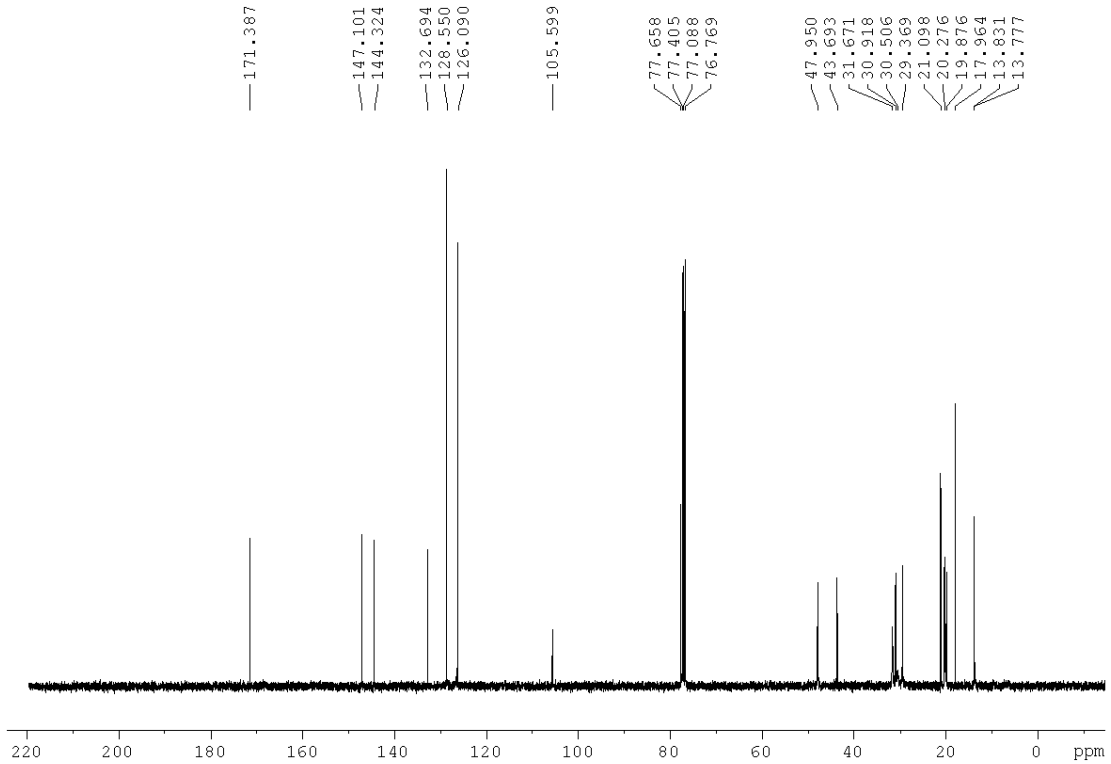

O
N
O
F
7.288
7.284
7.275
7.266
7.253
7.007
6.985
6.964
3.469
2.894
2.256
2.223
2.136
2.099
1.959
1.944
1.933
1.925
1.919
1.911
1.830
1.690
1.669
1.636
1.514
1.478
1.270
1.251
1.229
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.96
1.95
2.23
1.73
1.11
1.02
0.90
2.68
1.18
7.20
2.38
170.167
162.880
160.443
147.422
141.399
141.369
126.364
126.285
115.162
114.951
105.260
77.746
77.439
77.121
76.803
47.249
42.355
31.971
30.121
26.741
25.567
24.503
20.991
18.023
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

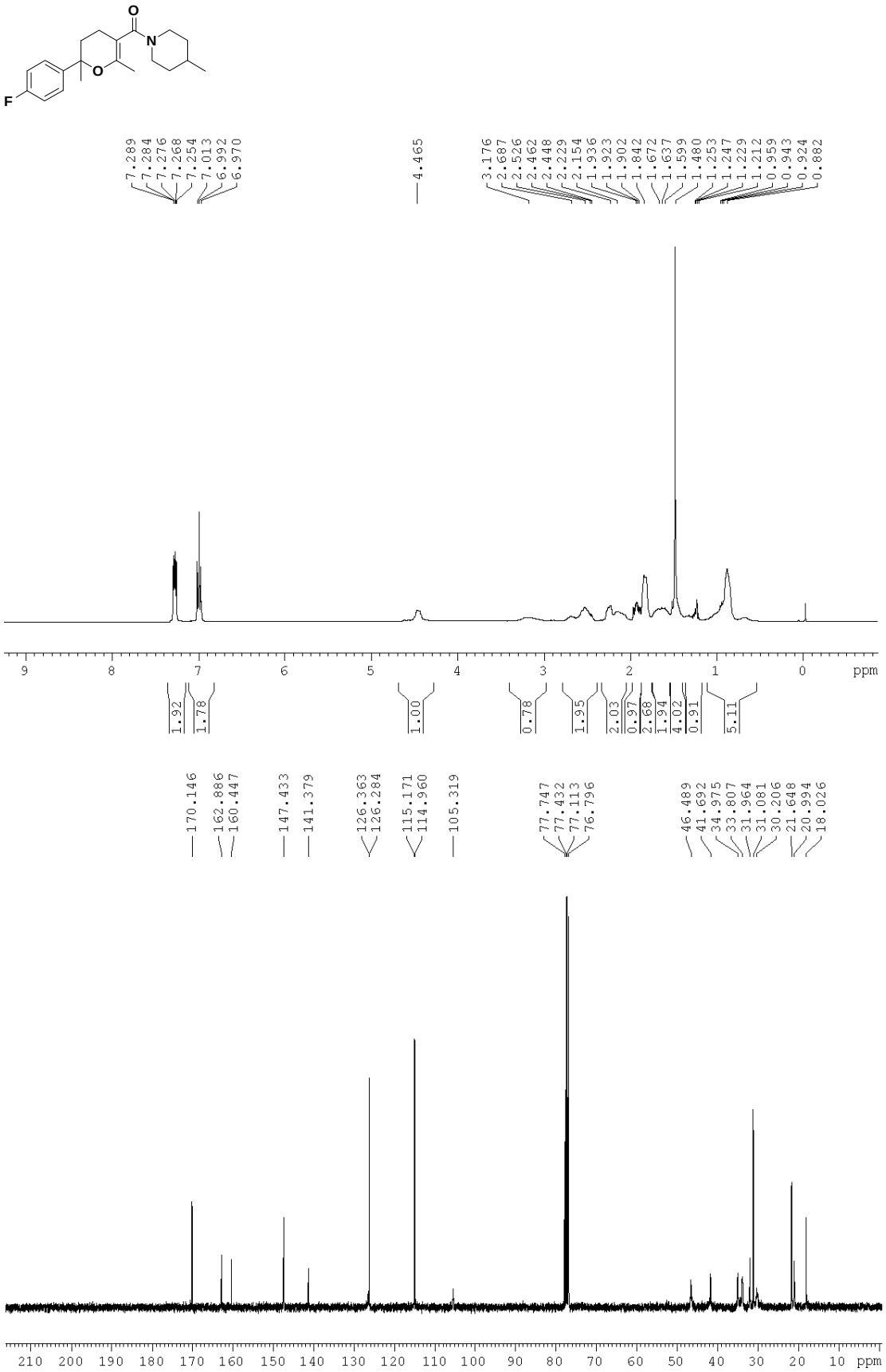


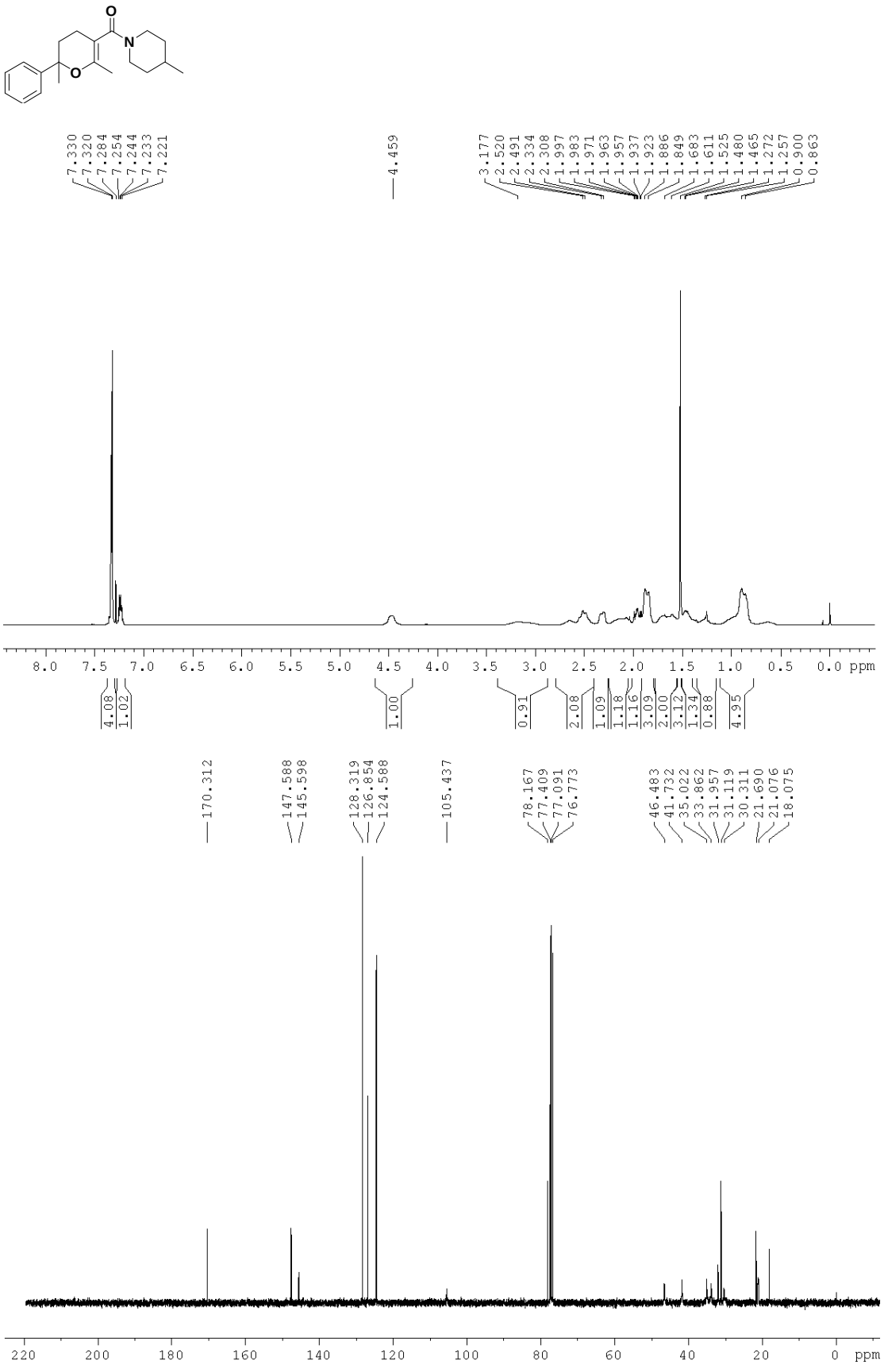


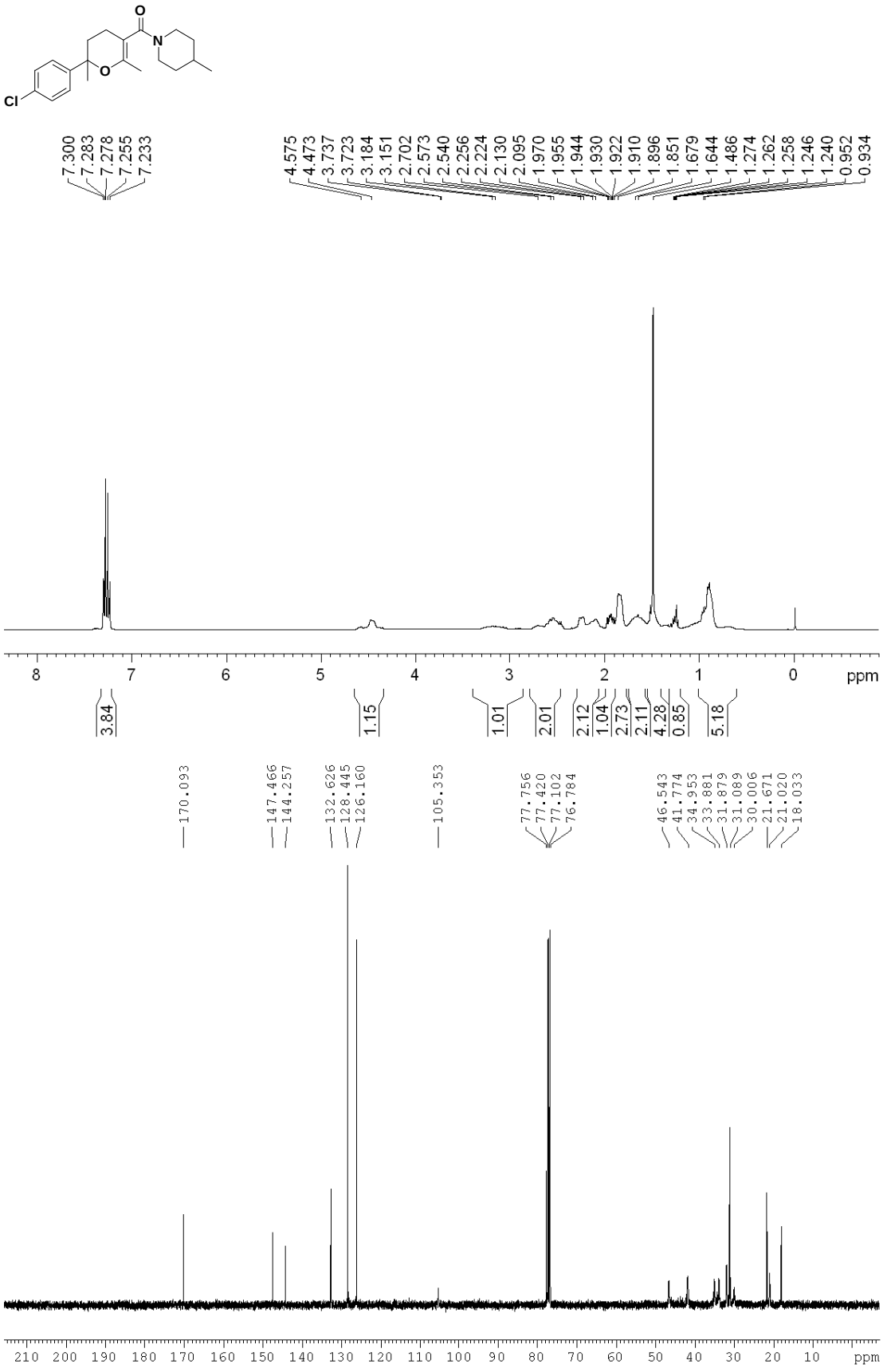


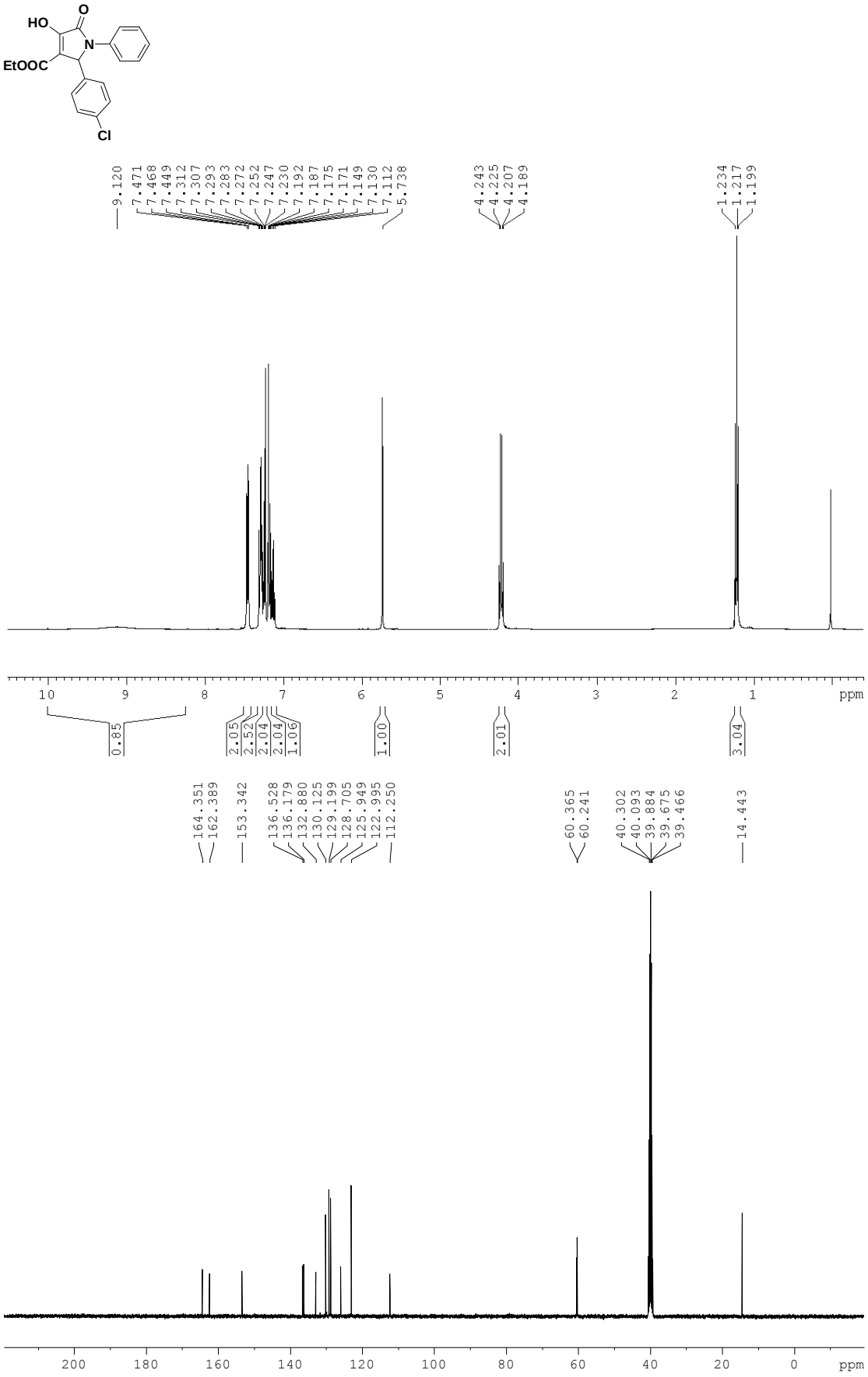


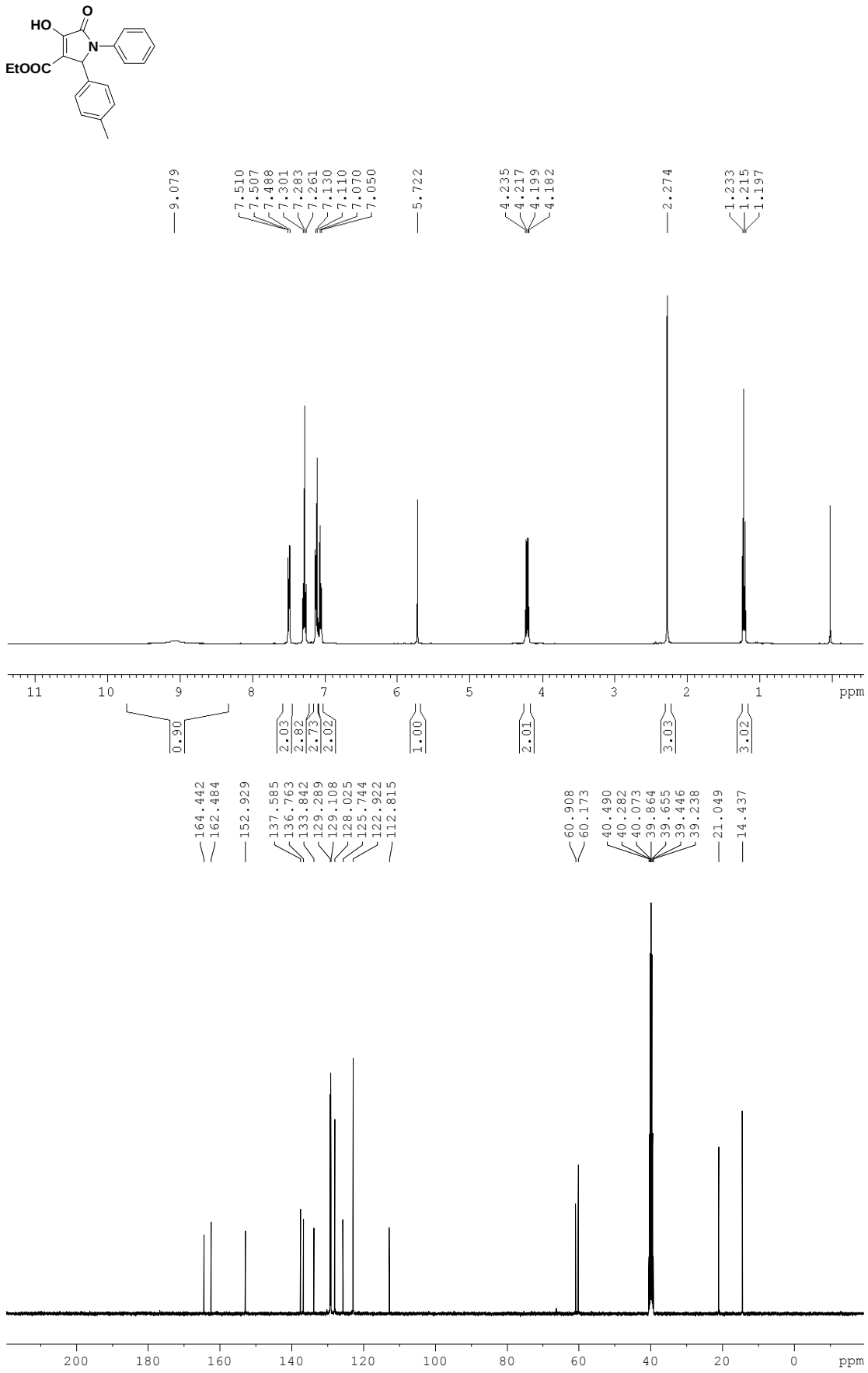


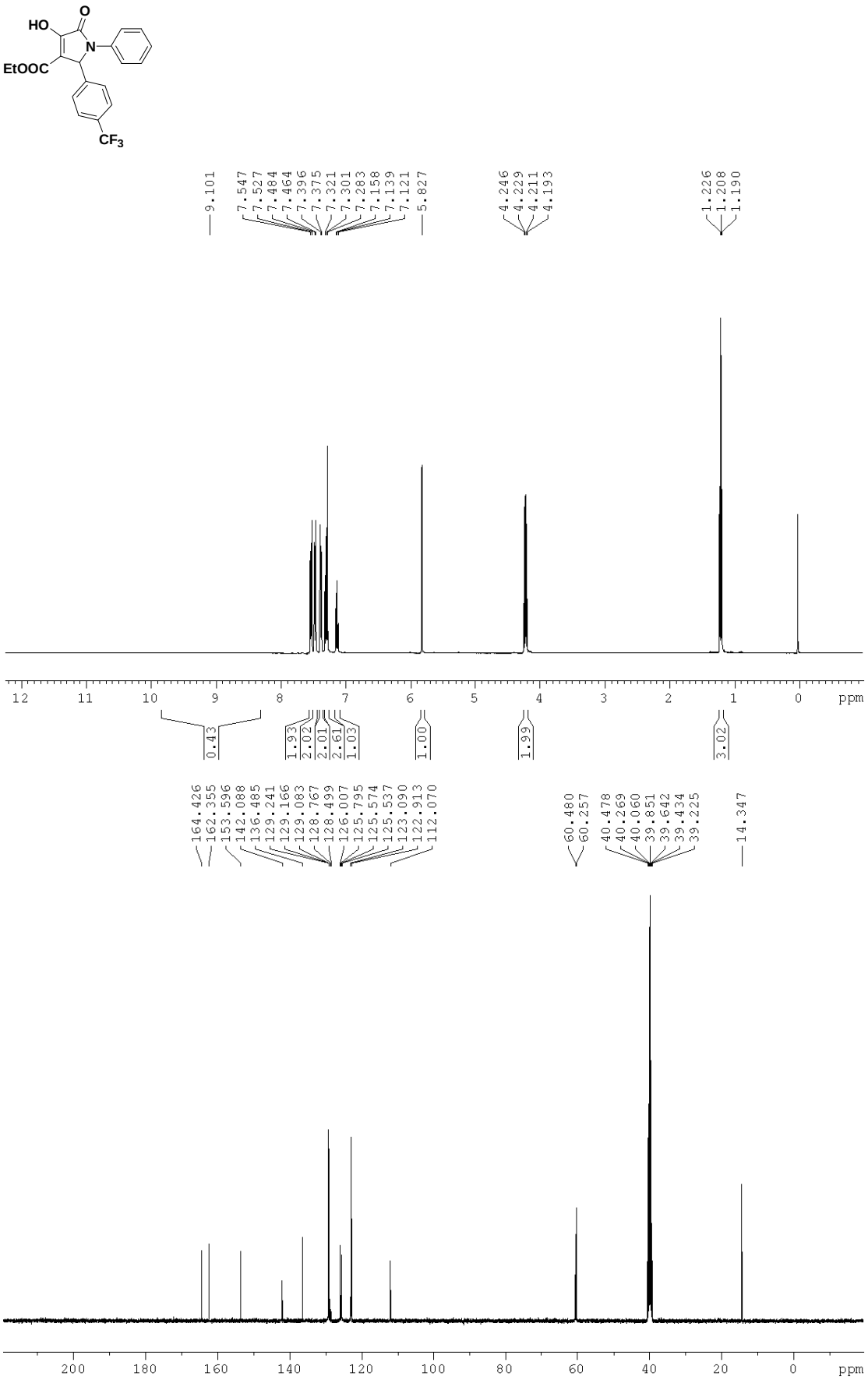


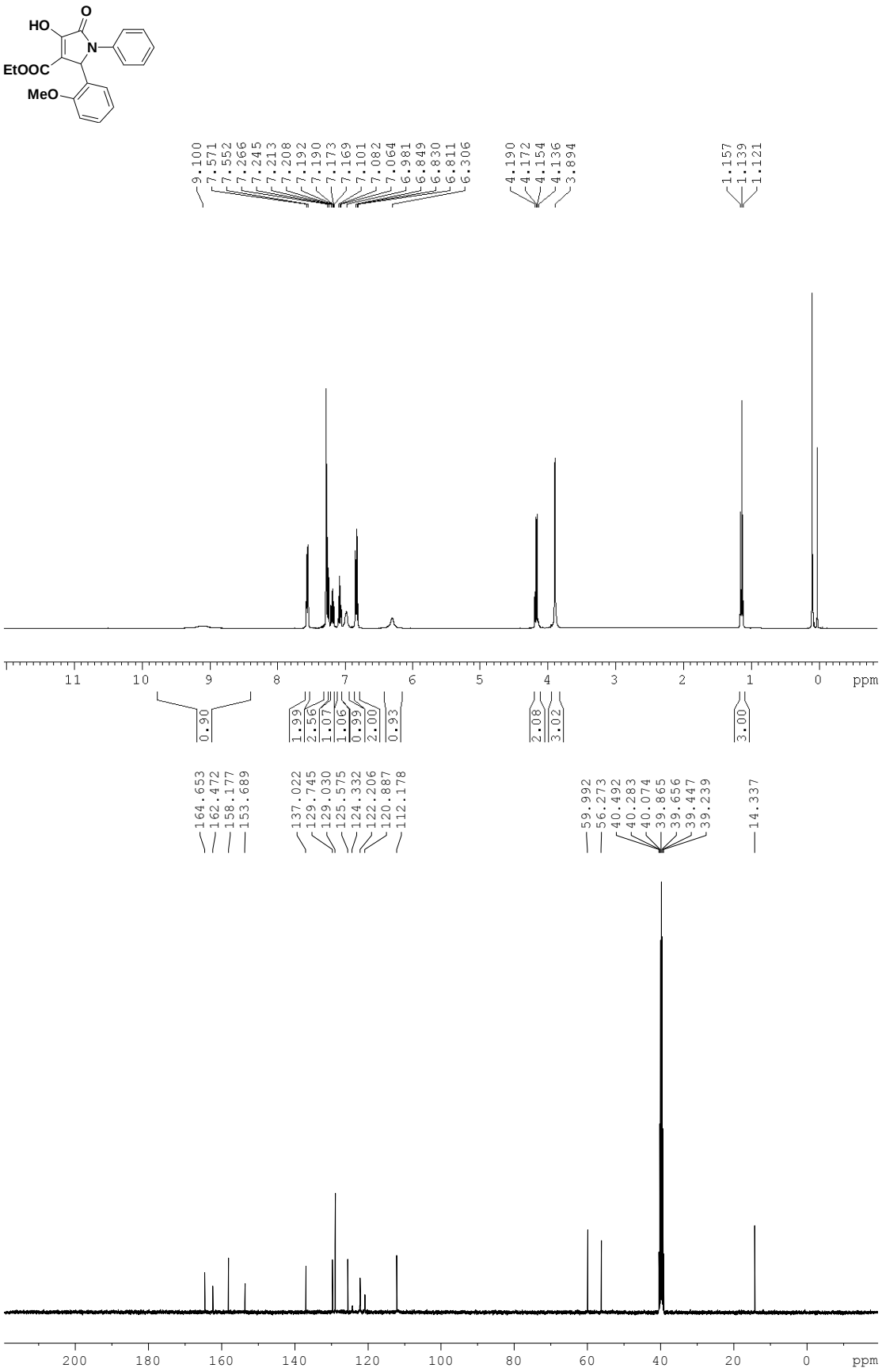


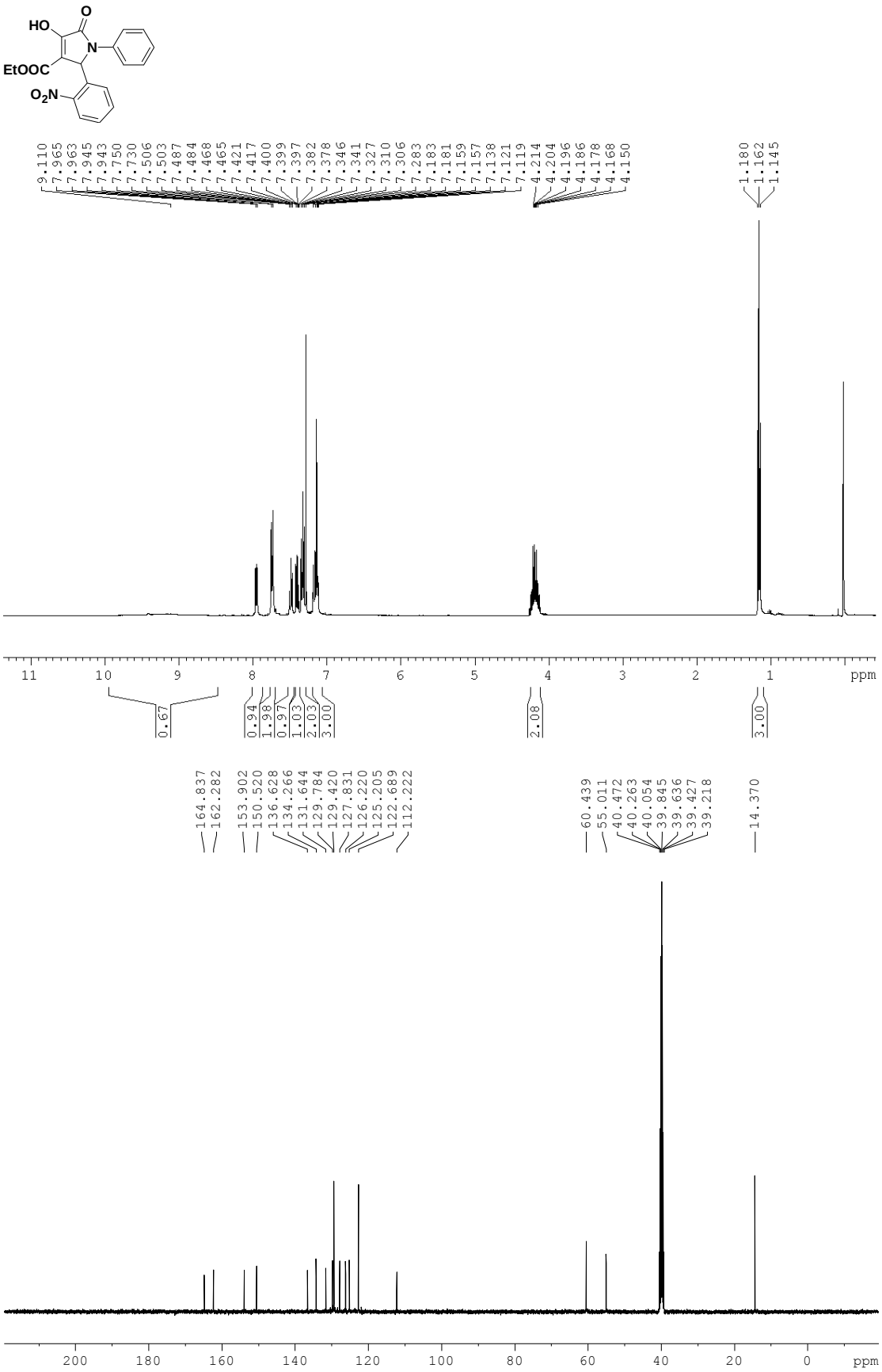


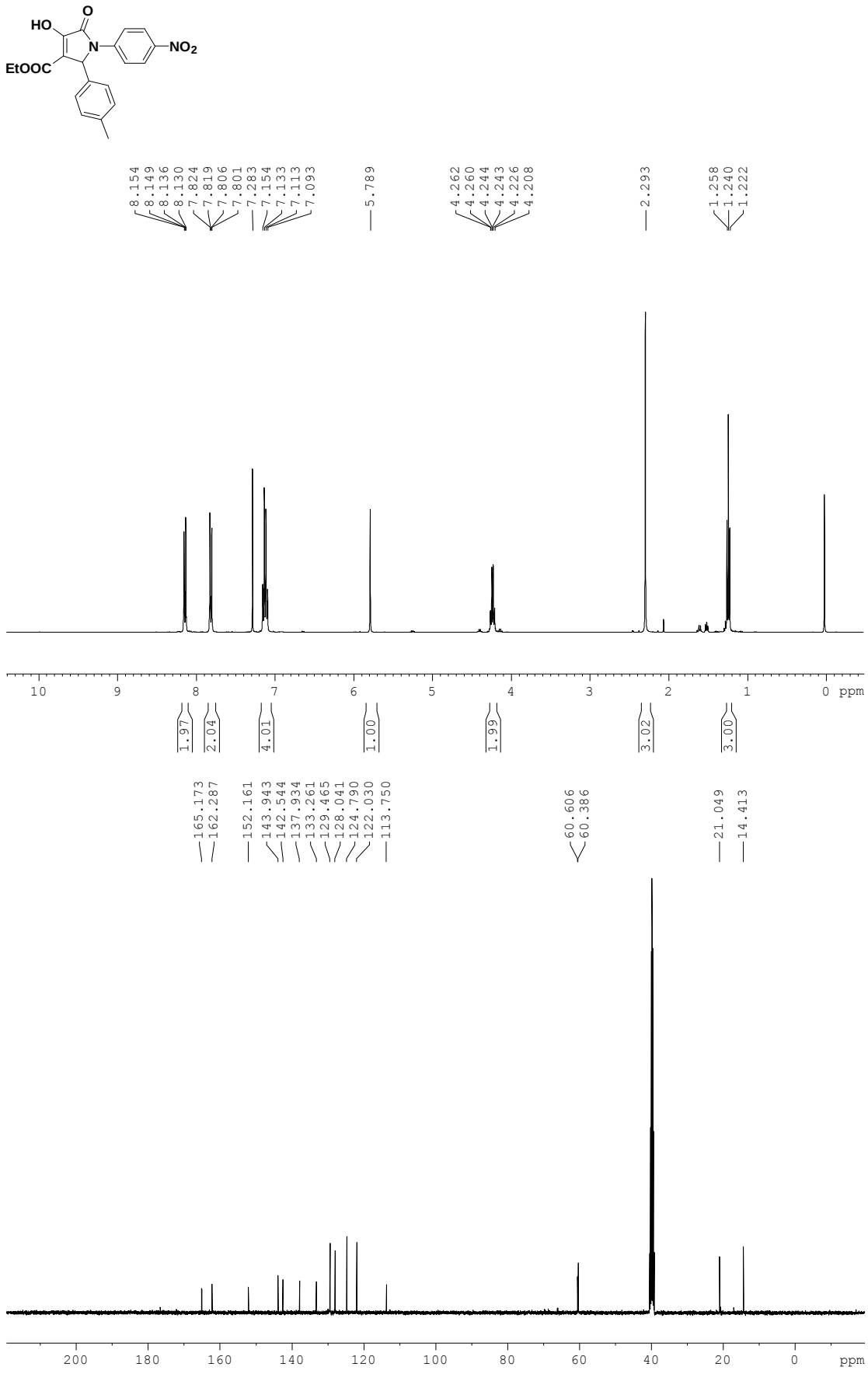


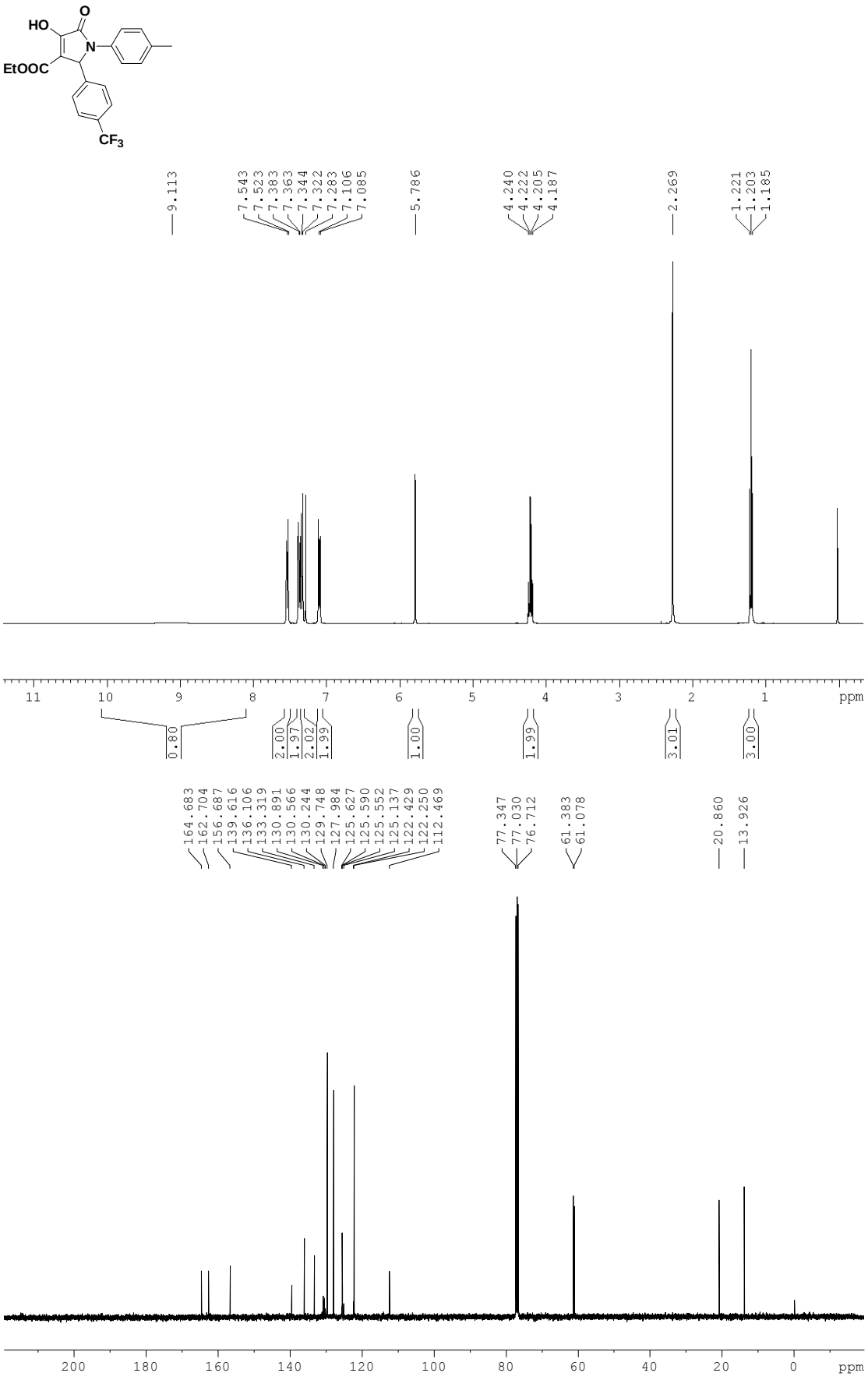


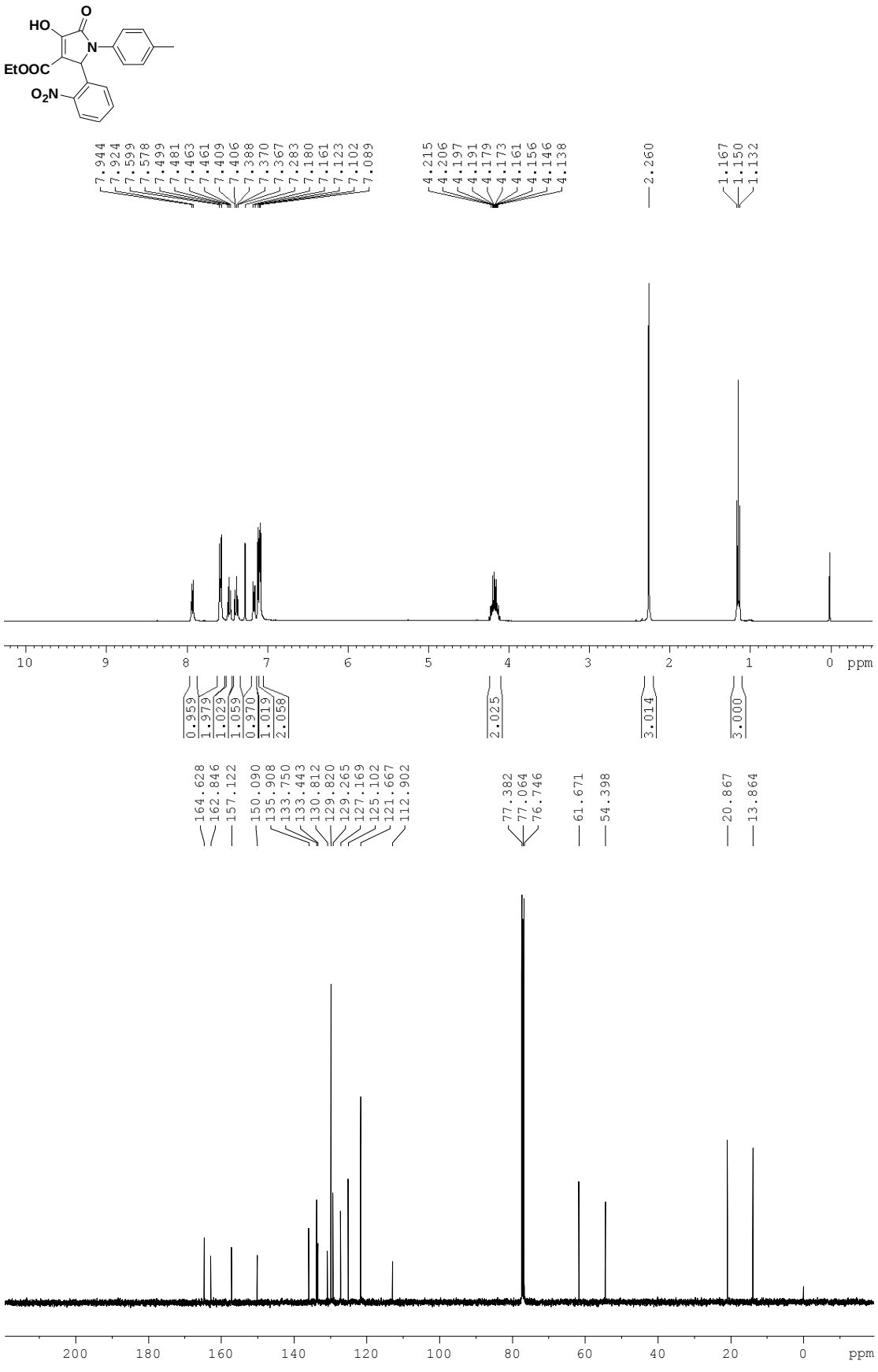


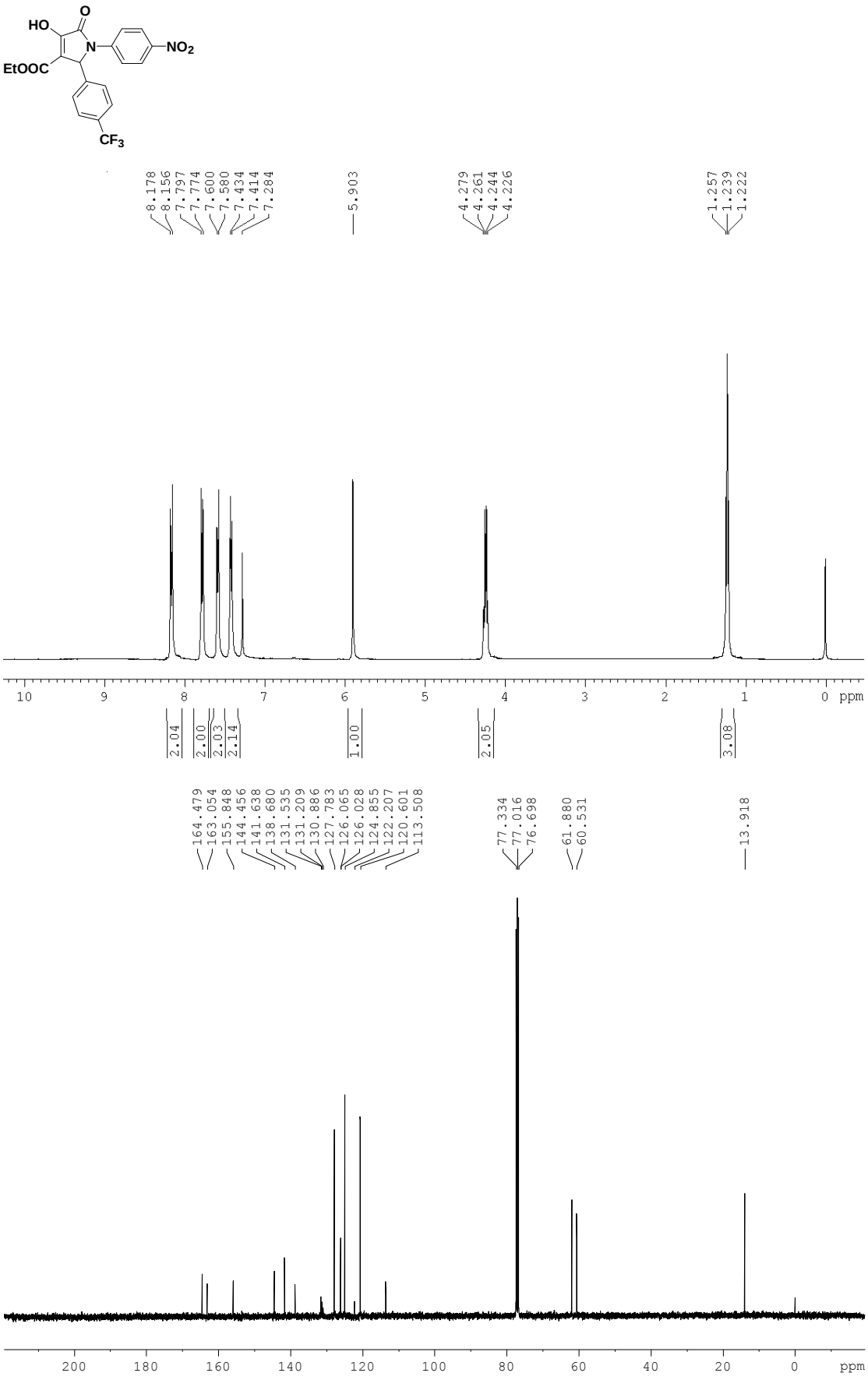


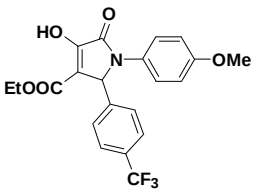


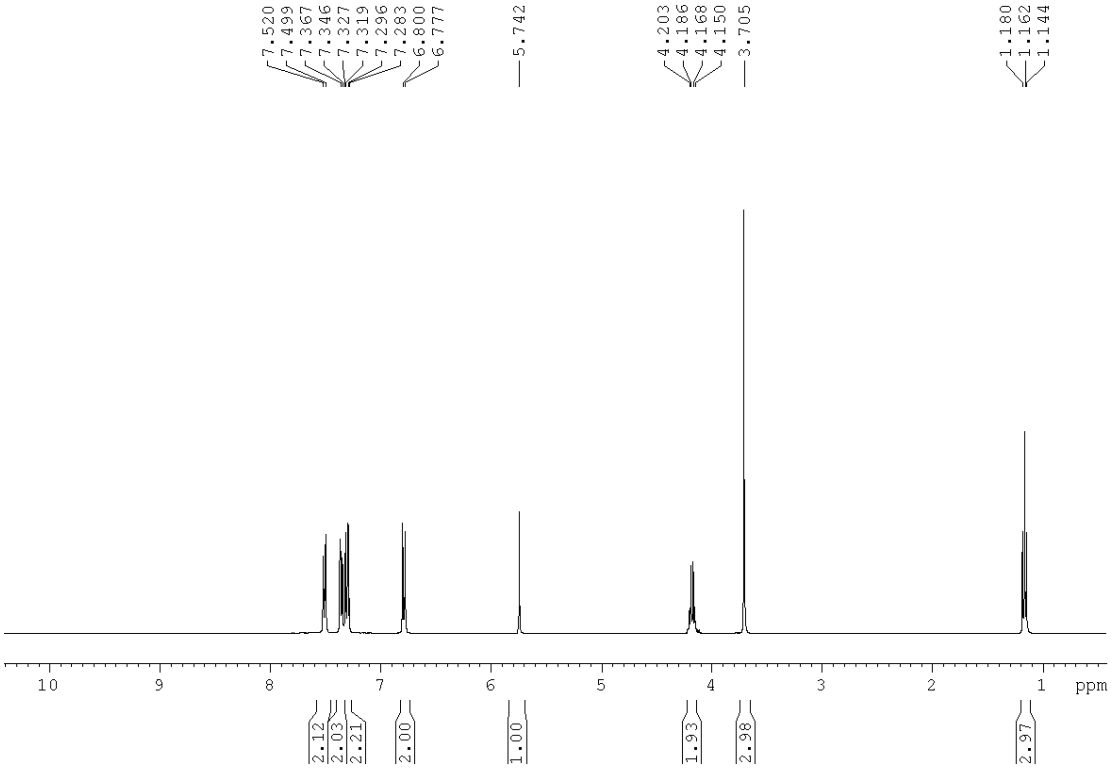


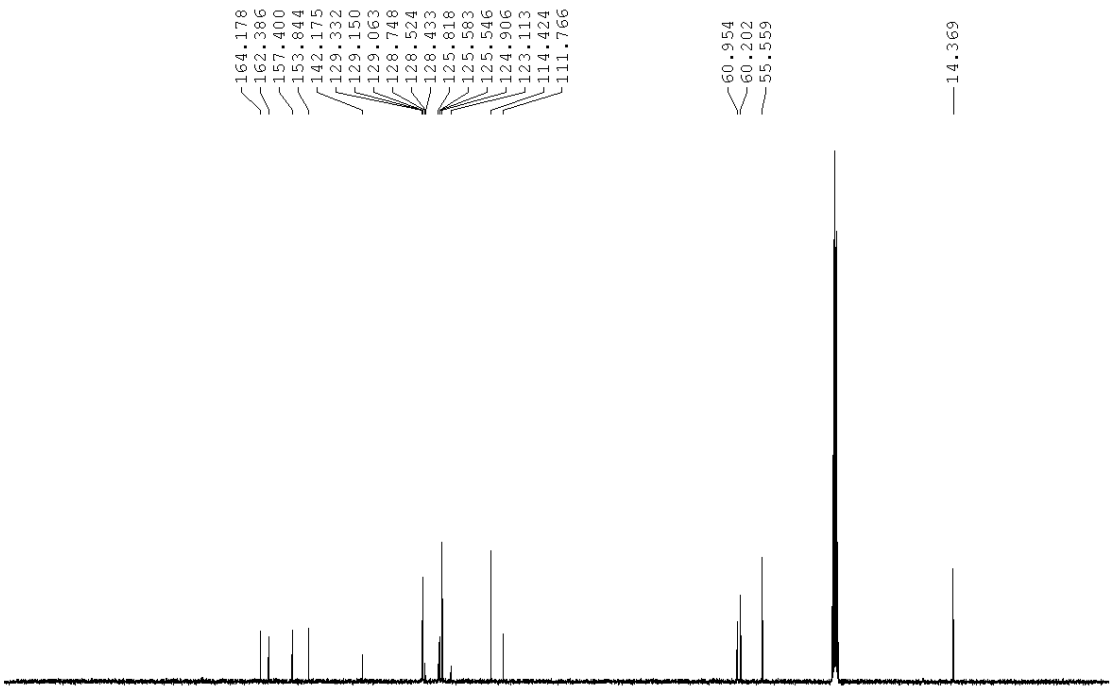


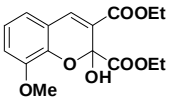

HO
O
N
EtOOC
O2N
7.944
7.924
7.599
7.578
7.499
7.481
7.463
7.461
7.409
7.406
7.388
7.370
7.367
7.283
7.180
7.161
7.123
7.102
7.089
4.215
4.206
4.197
4.191
4.179
4.173
4.161
4.156
4.146
4.138
2.260
1.167
1.150
1.132
ppm
0.959
1.979
1.029
1.059
0.970
1.019
2.058
2.025
3.014
3.000
164.628
162.846
157.122
150.090
135.908
133.750
133.443
130.812
129.820
129.265
127.169
125.102
121.667
112.902
77.382
77.064
76.746
61.671
54.398
20.867
13.864
ppm

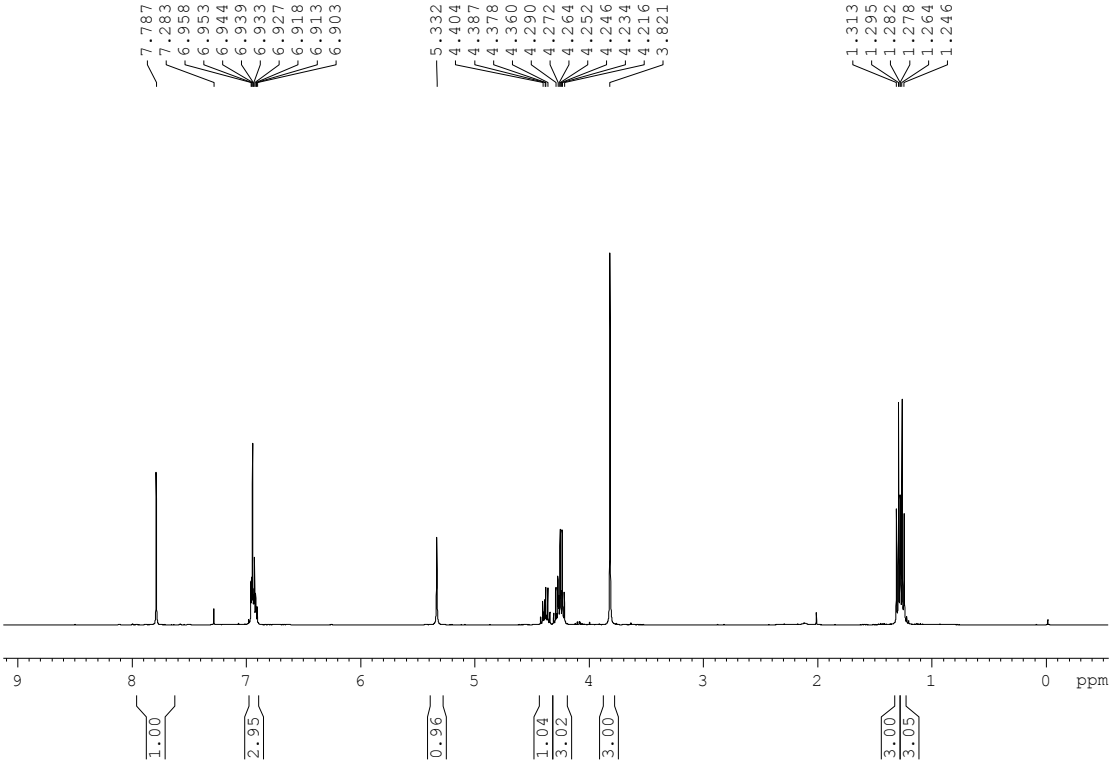


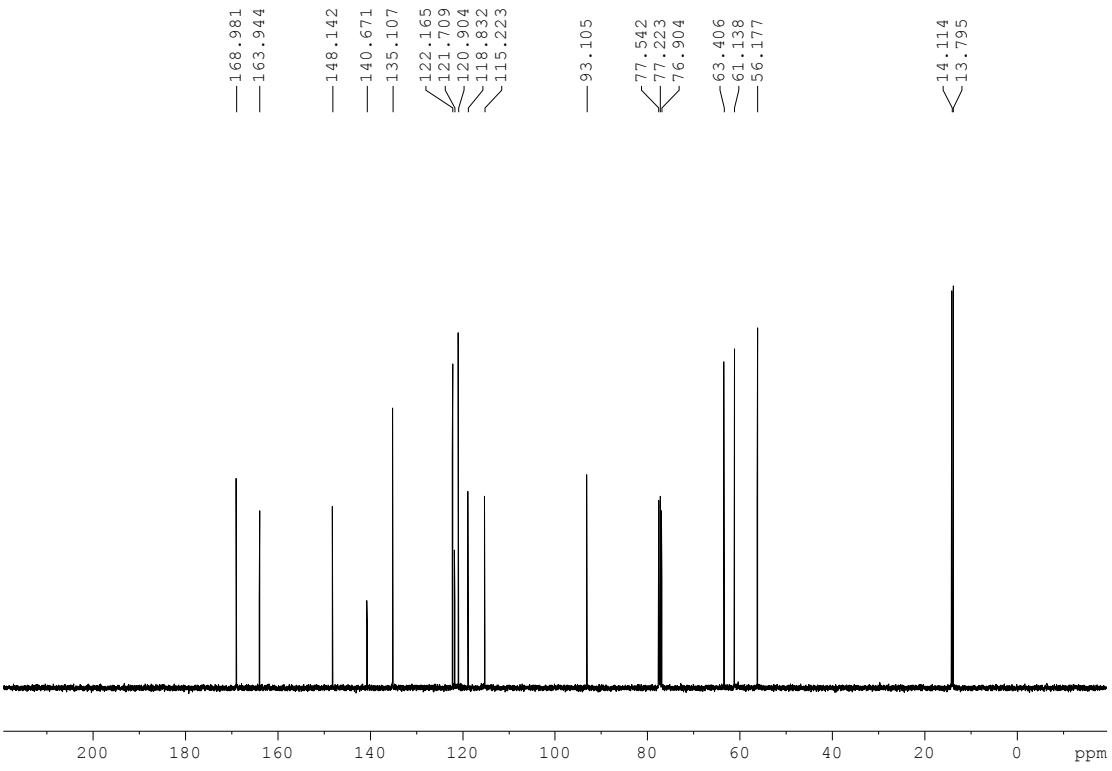


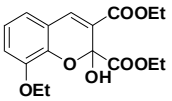


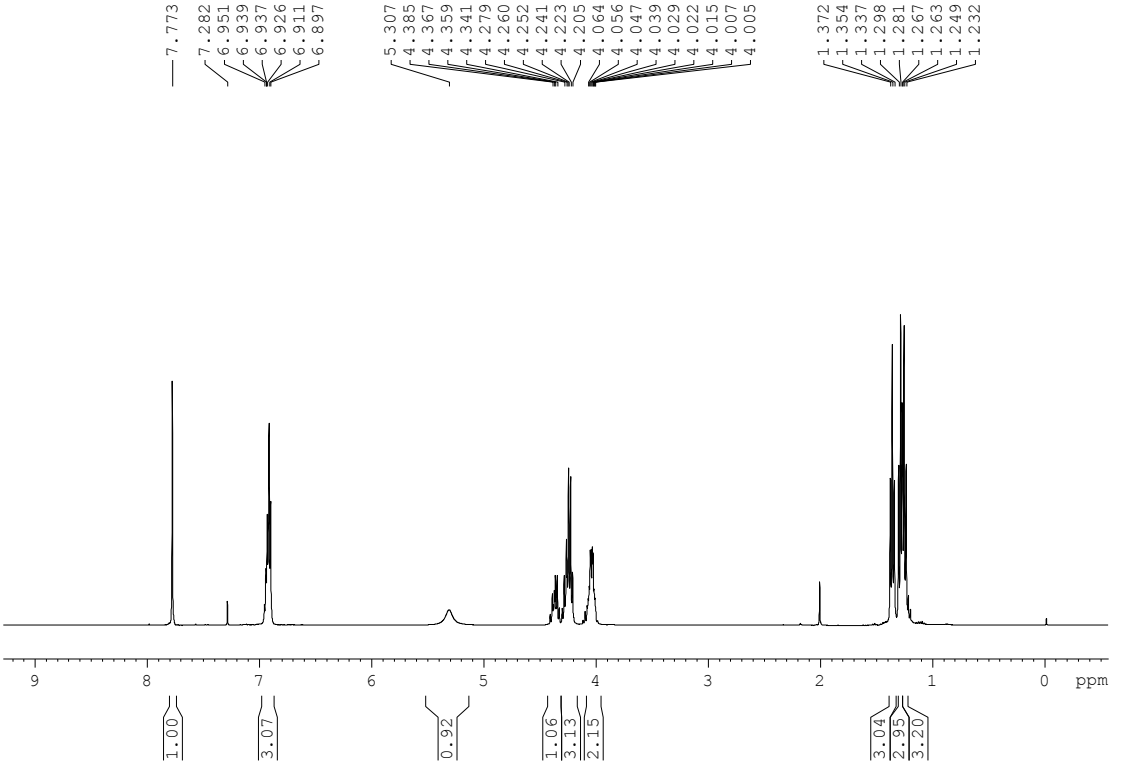


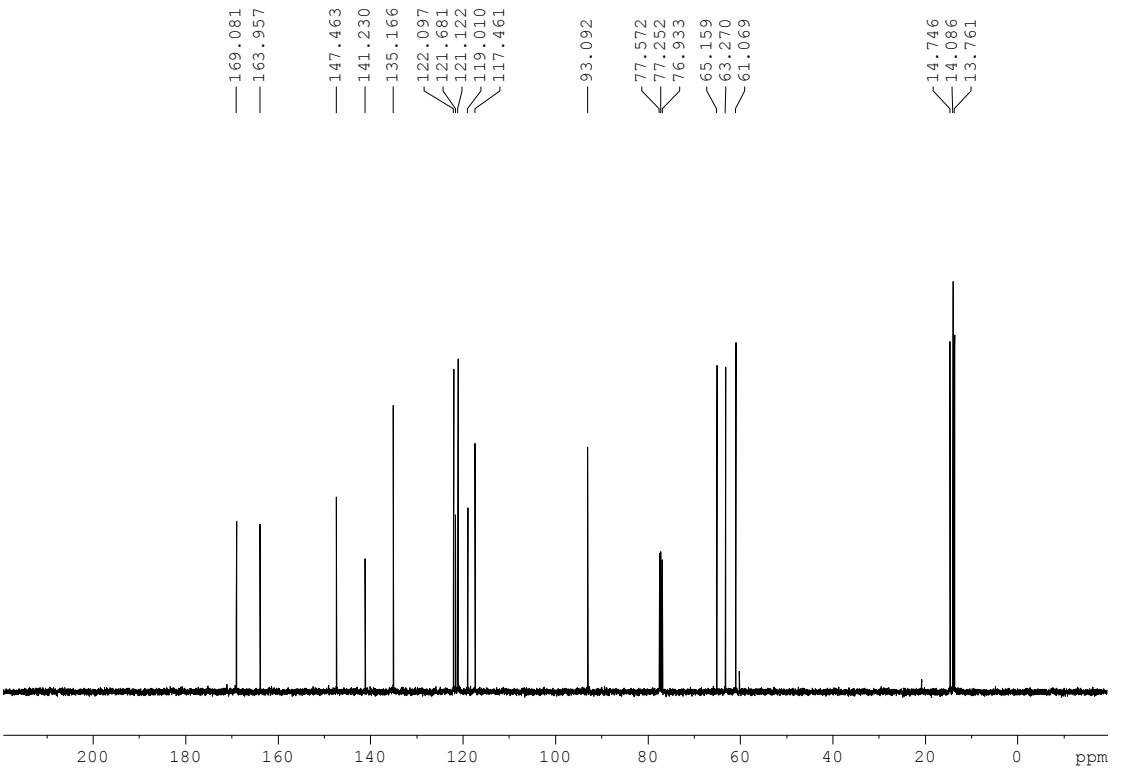


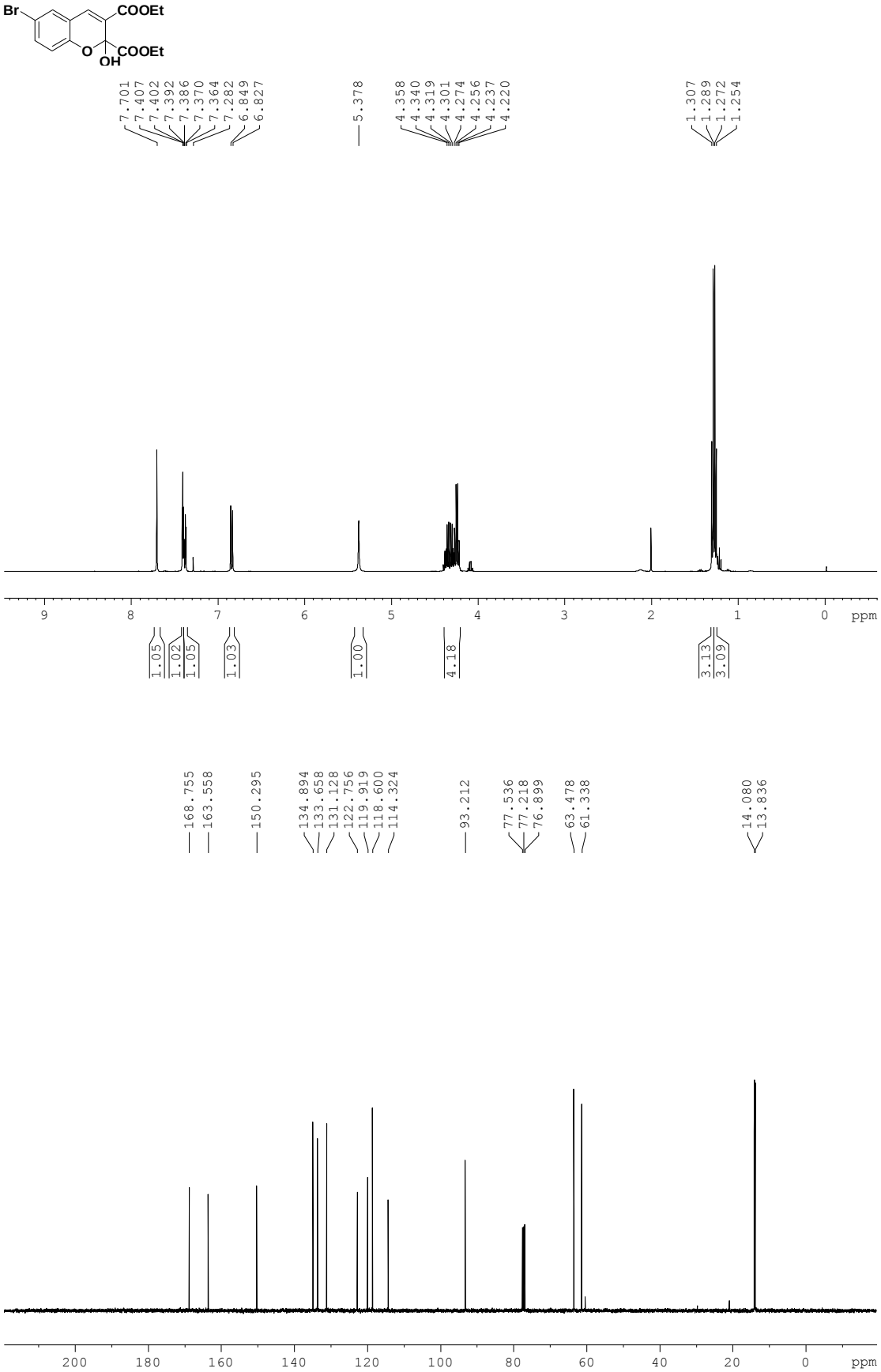


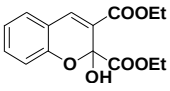


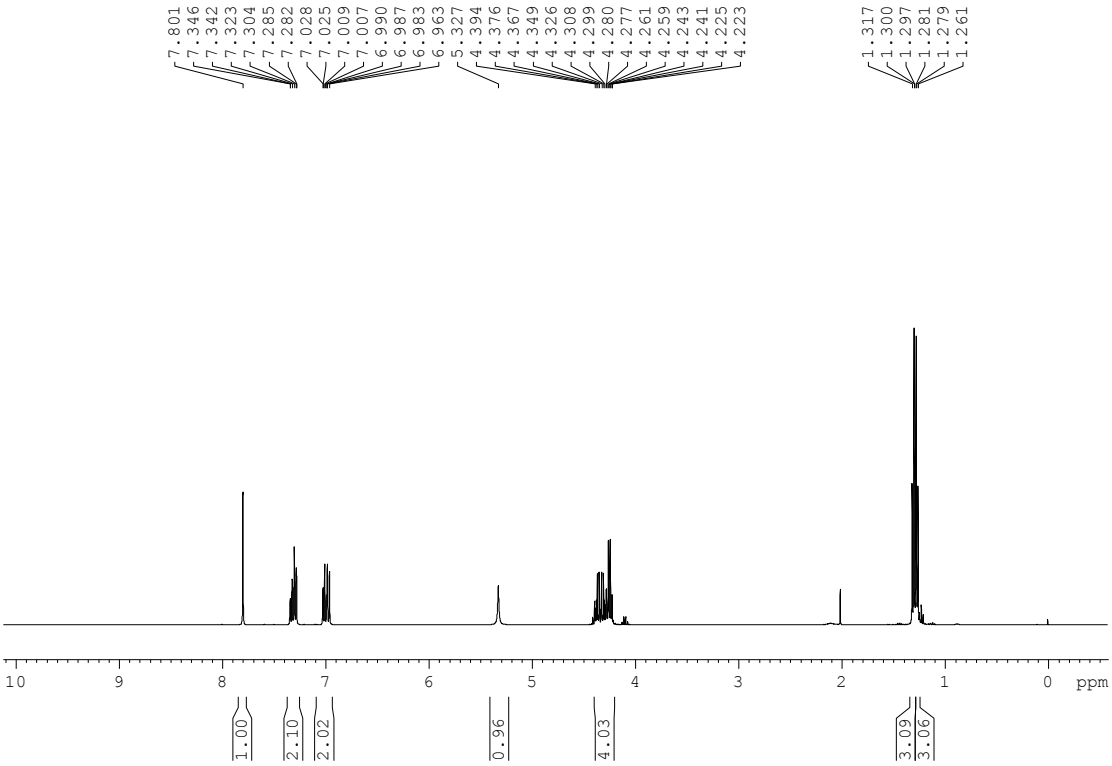

COOEt
O
COOEt
OH
OEt

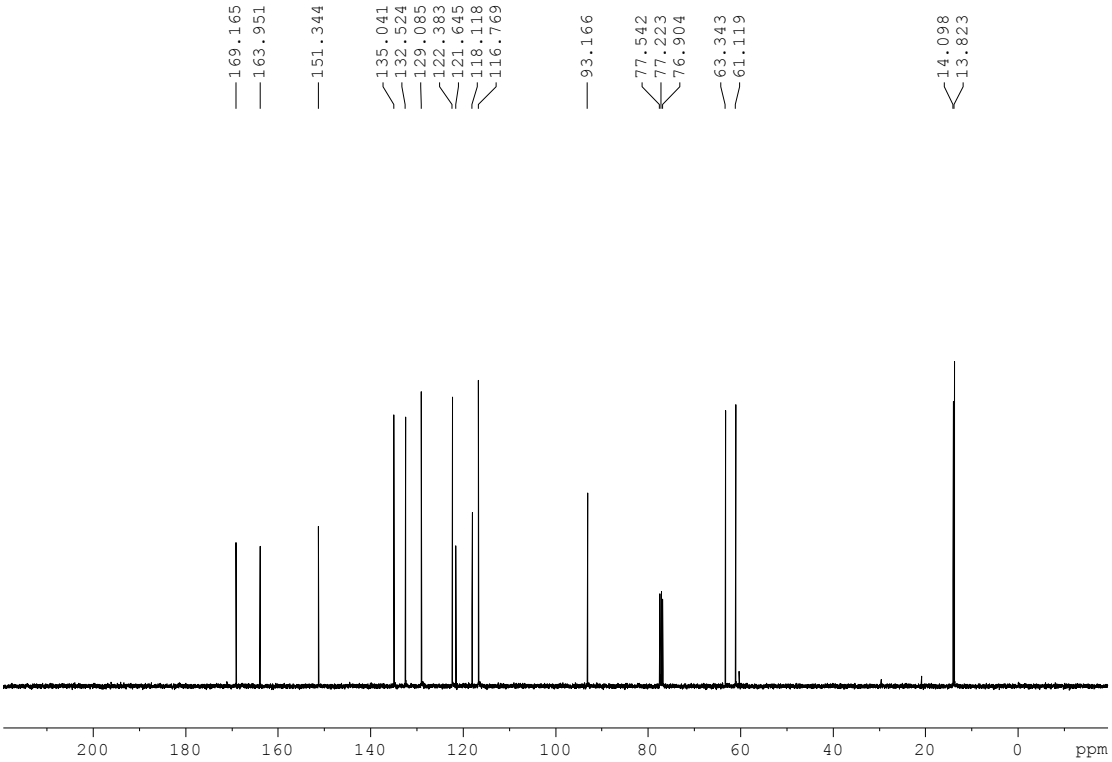

7.773
7.282
6.951
6.939
6.937
6.926
6.911
6.897
5.307
4.385
4.367
4.359
4.341
4.279
4.260
4.252
4.241
4.223
4.205
4.064
4.056
4.047
4.039
4.029
4.022
4.015
4.007
4.005
1.372
1.354
1.337
1.298
1.281
1.267
1.263
1.249
1.232
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.07
0.92
1.06
3.13
2.15
3.04
2.95
3.20

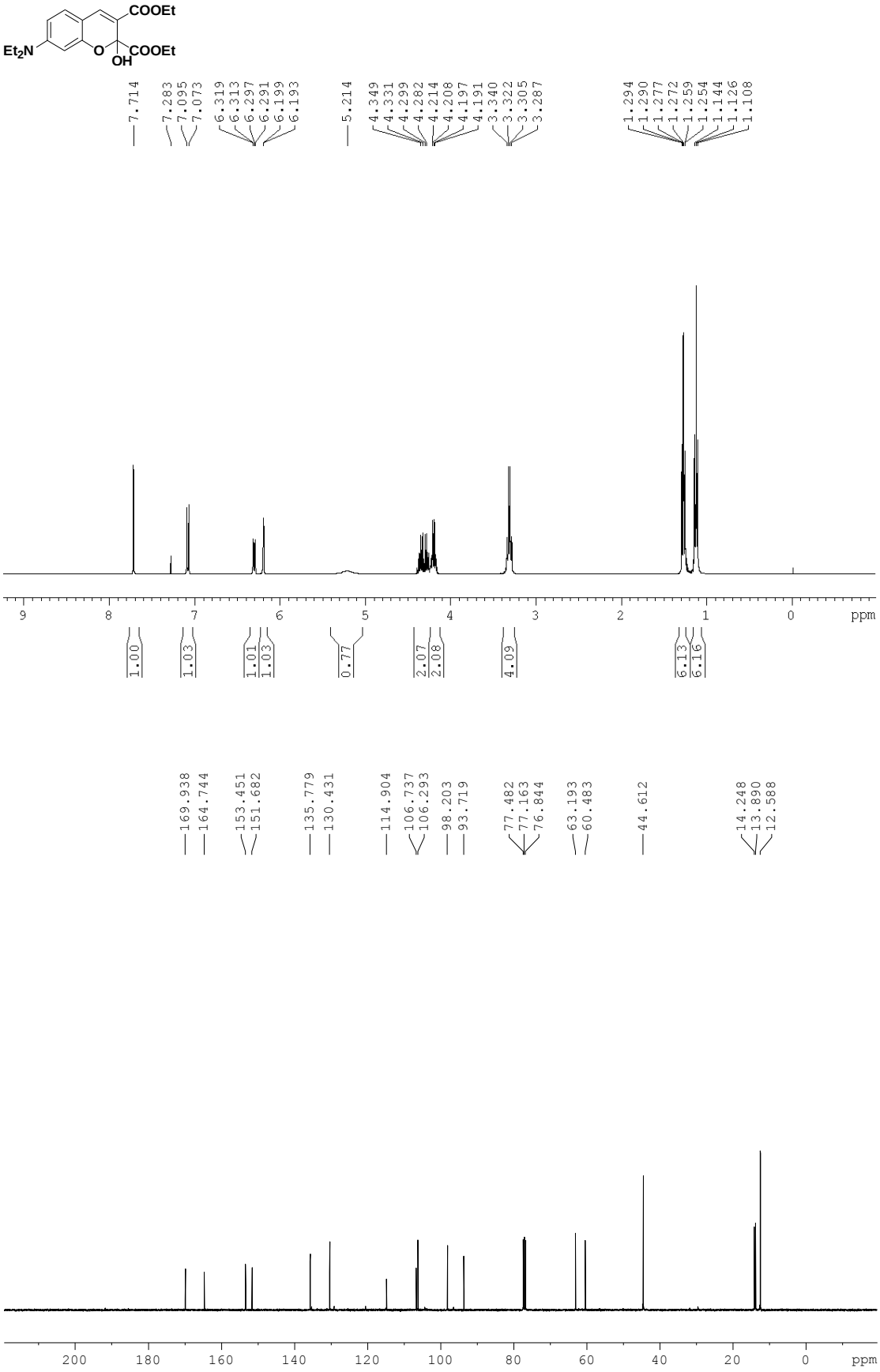

169.081
163.957
147.463
141.230
135.166
122.097
121.681
121.122
119.010
117.461
93.092
77.572
77.252
76.933
65.159
63.270
61.069
14.746
14.086
13.761
200
180
160
140
120
100
80
60
40
20
0
ppm

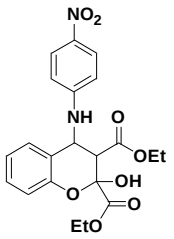


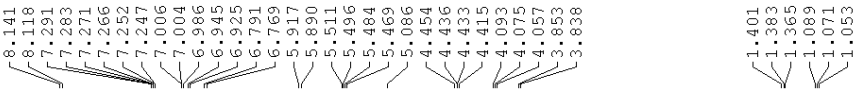


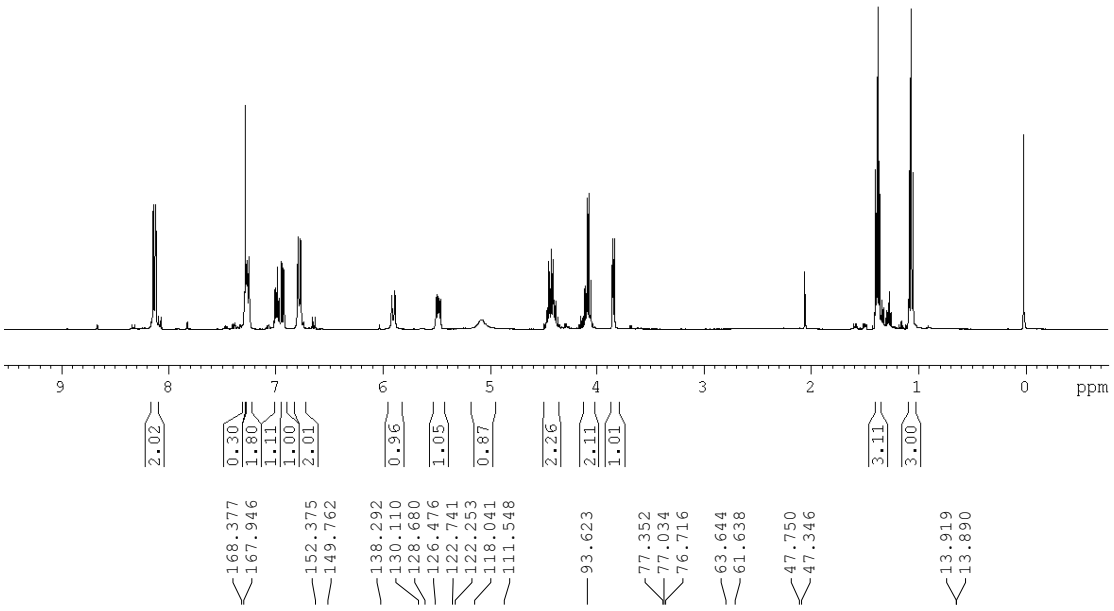


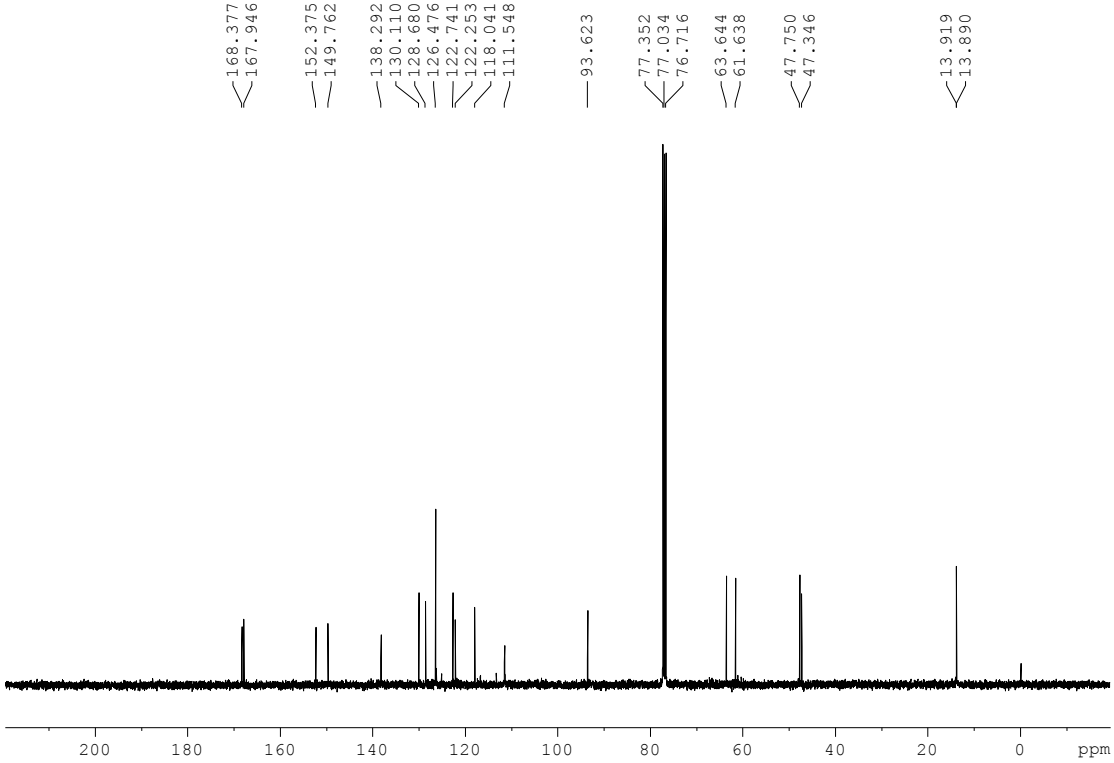


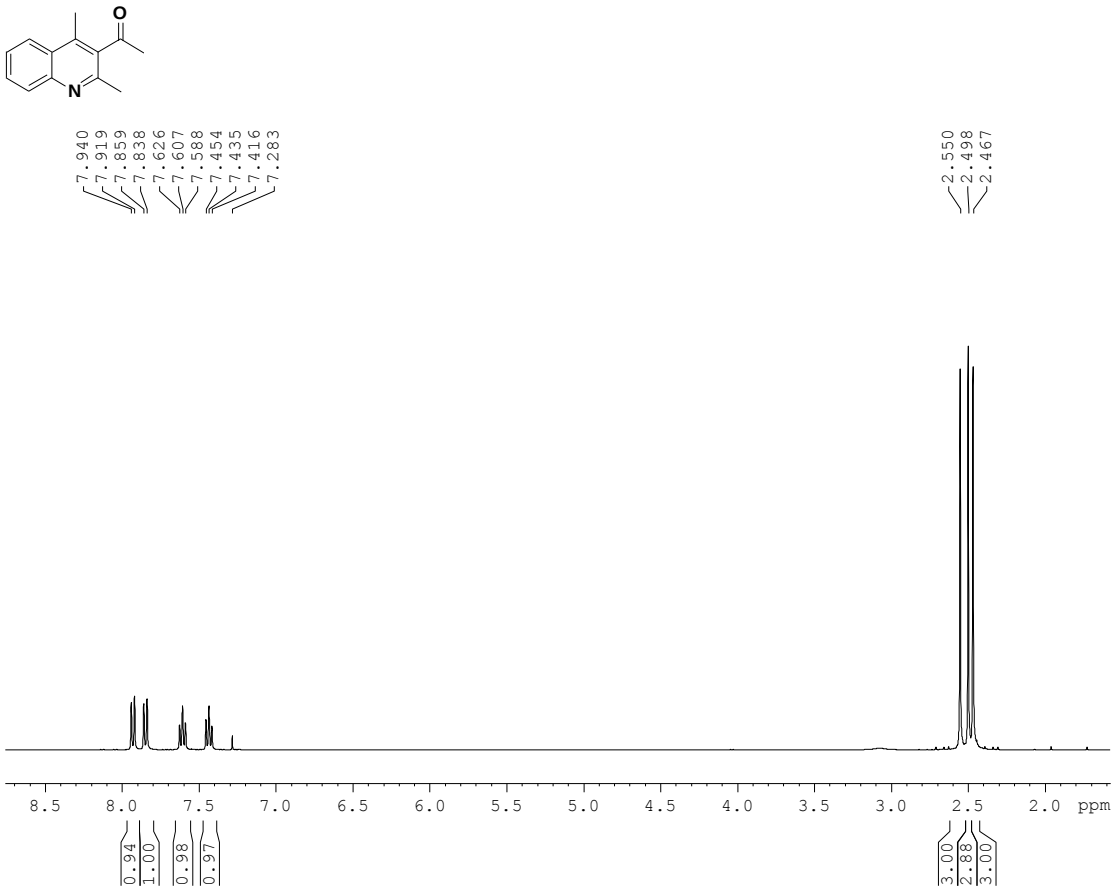

COOEt
Et2N
O
COOEt
OH
7.714
7.283
7.095
7.073
6.319
6.313
6.297
6.291
6.199
6.193
5.214
4.349
4.331
4.299
4.282
4.214
4.208
4.197
4.191
3.340
3.322
3.305
3.287
1.294
1.290
1.277
1.272
1.259
1.254
1.144
1.126
1.108
ppm
1.00
1.03
1.01
1.03
0.77
2.07
2.08
4.09
6.13
6.16
169.938
164.744
153.451
151.682
135.779
130.431
114.904
106.737
106.293
98.203
93.719
77.482
77.163
76.844
63.193
60.483
44.612
14.248
13.890
12.588
ppm

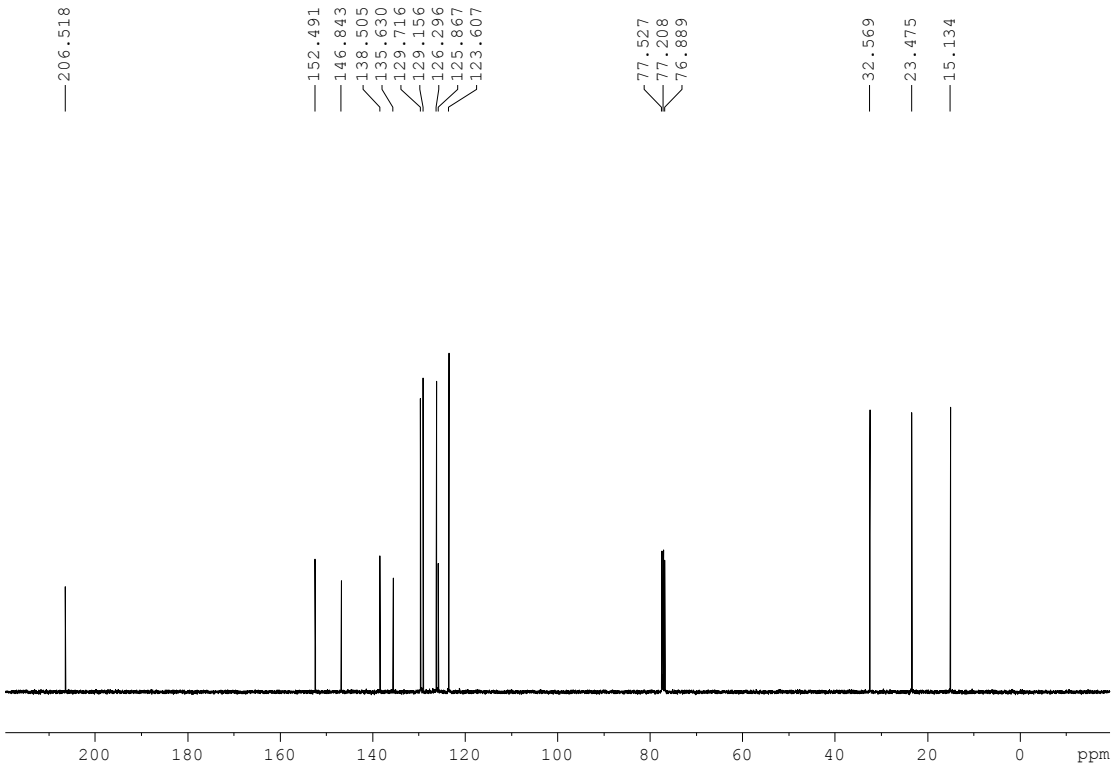


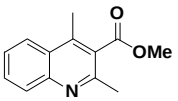


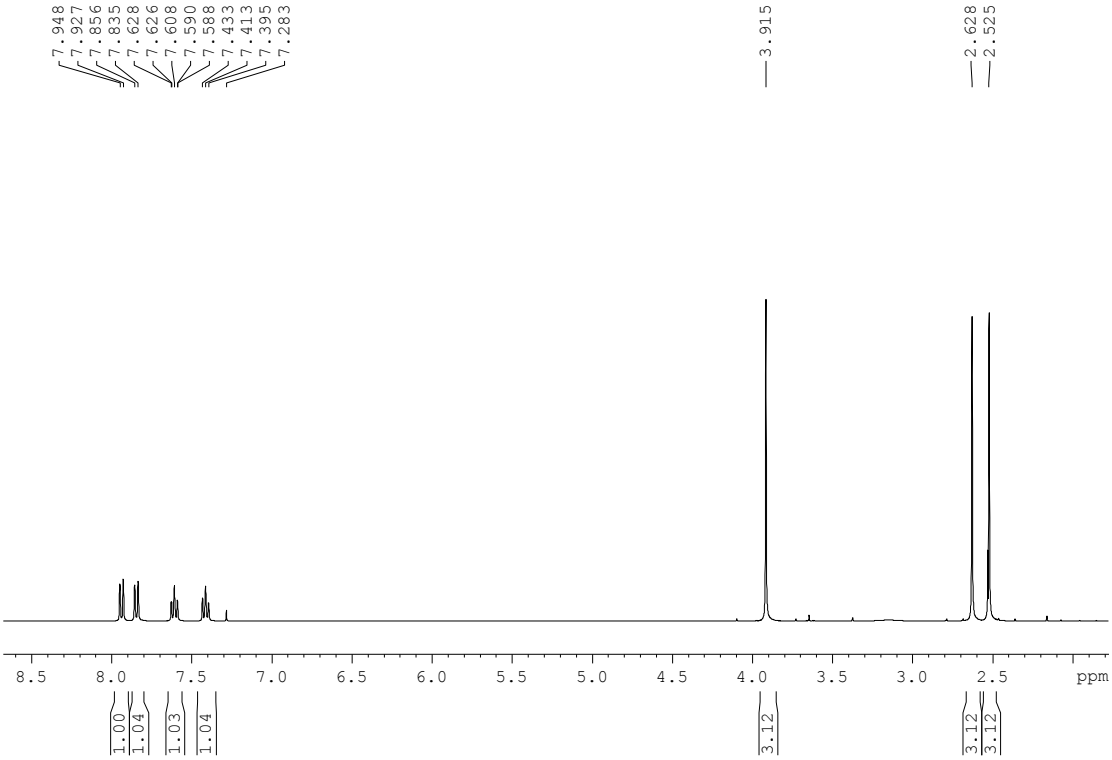


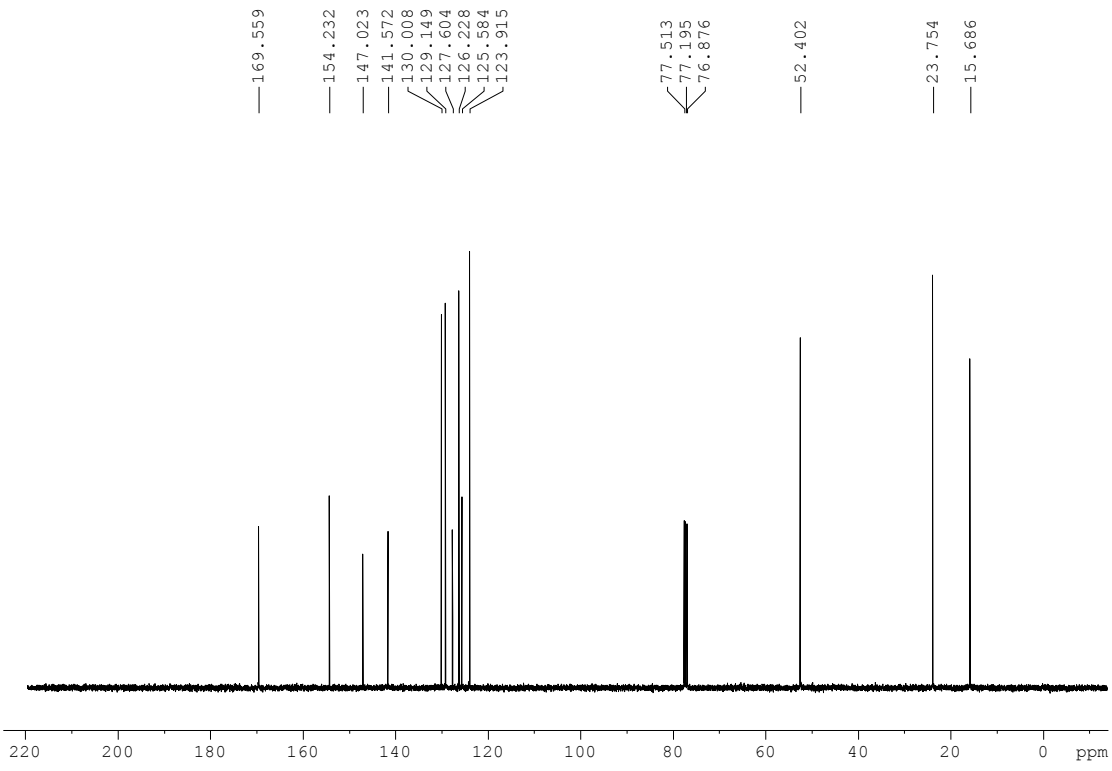


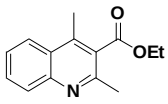


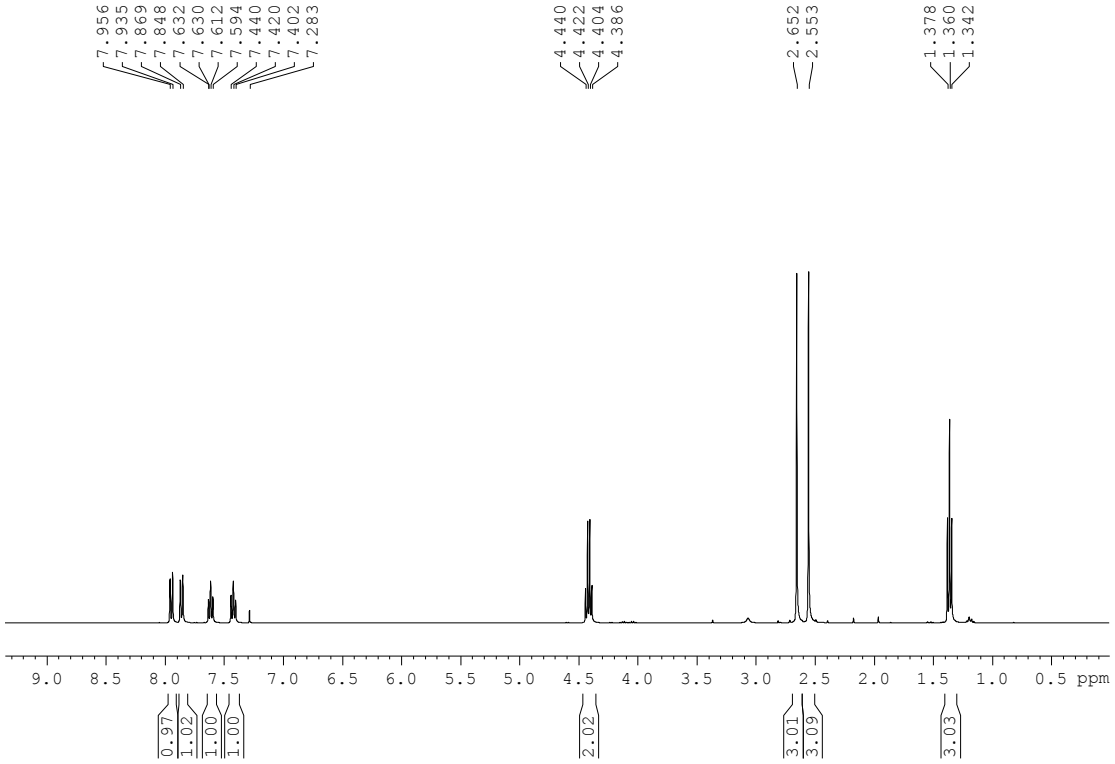


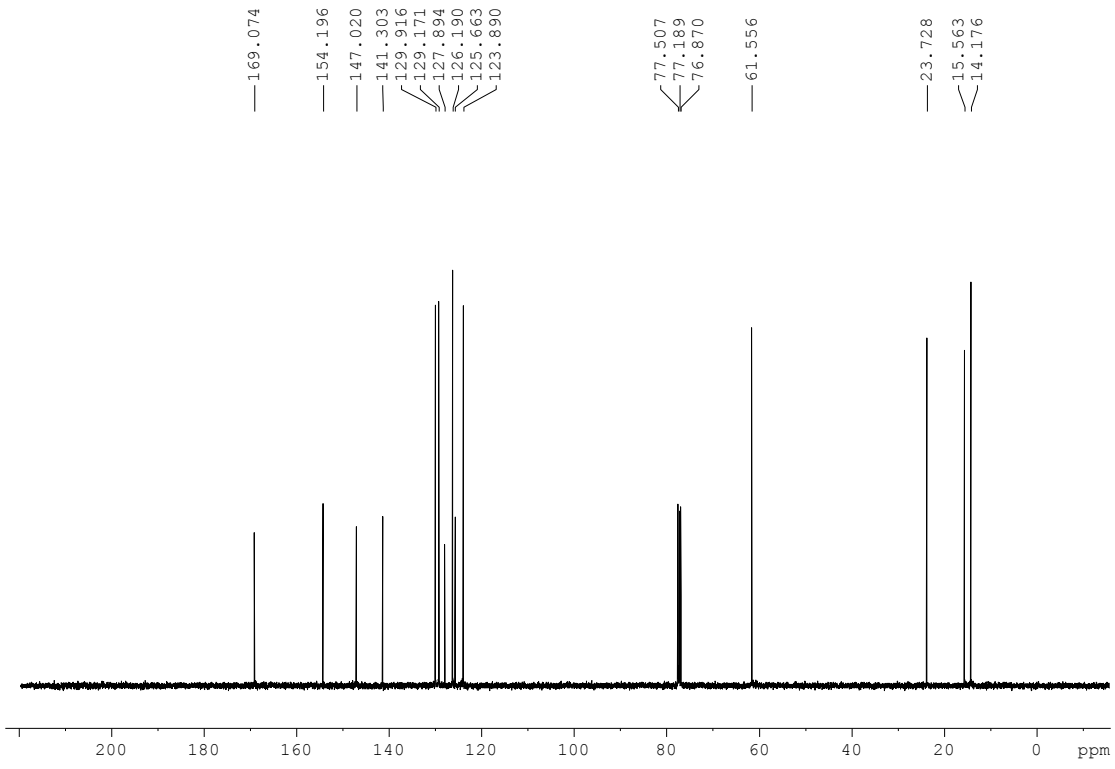


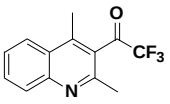


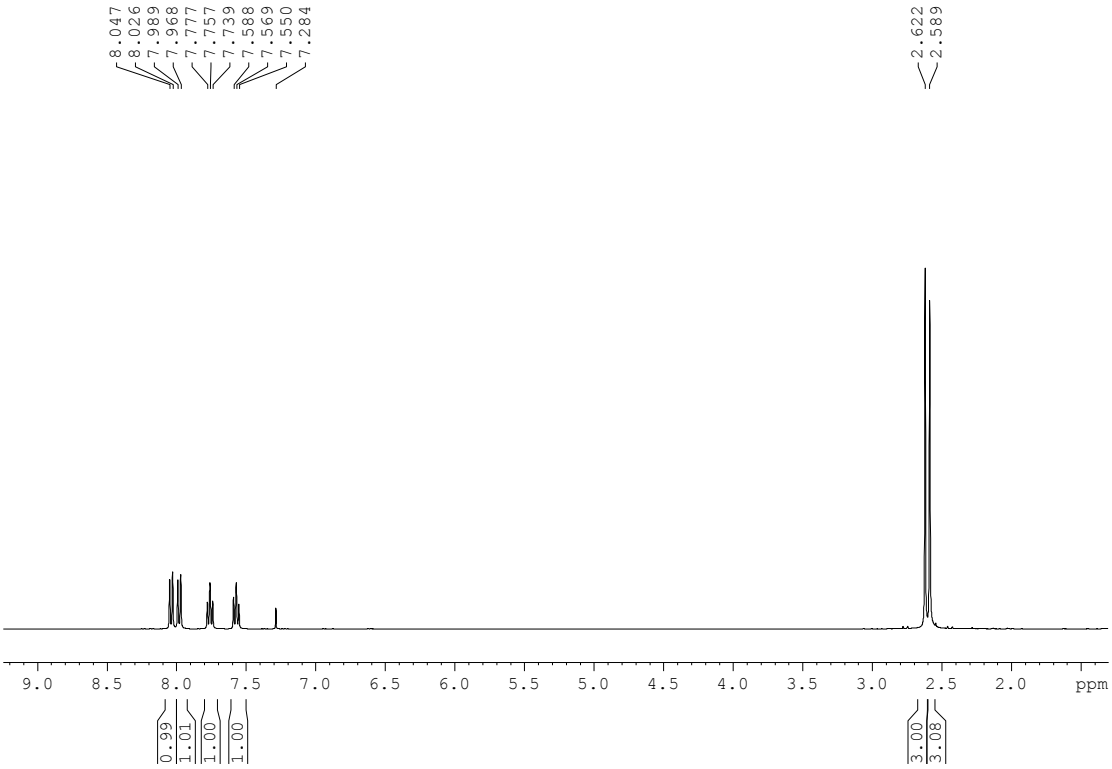


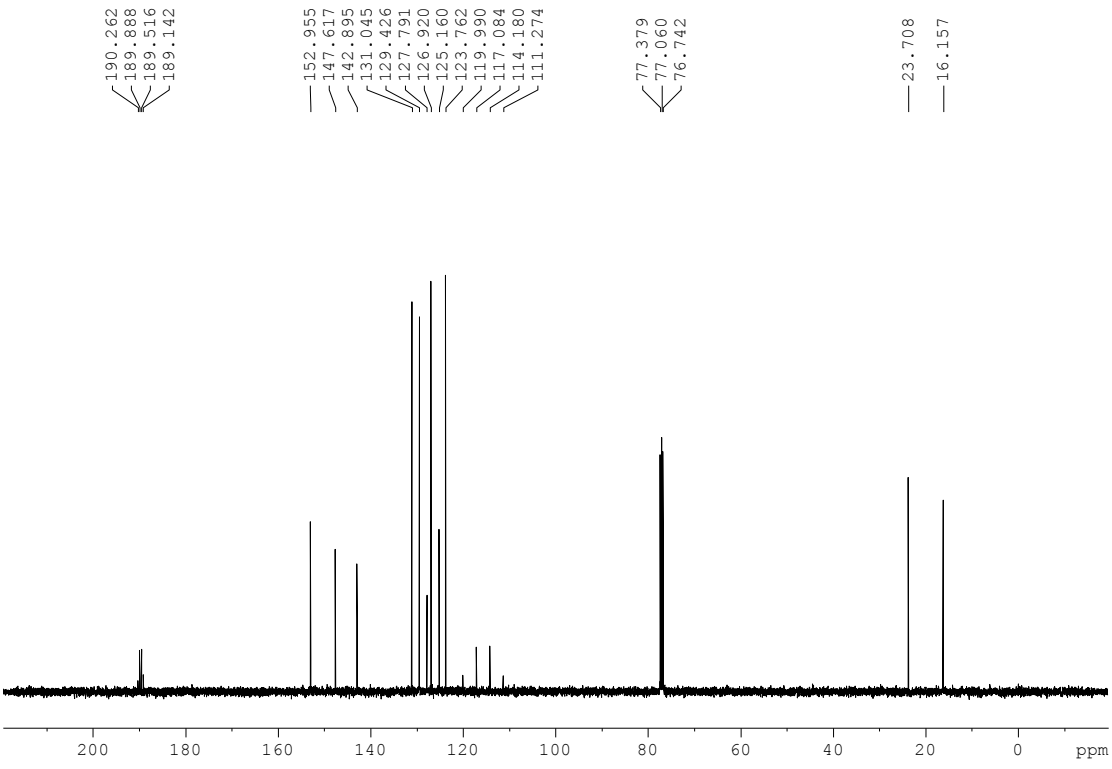

O
OEt
N

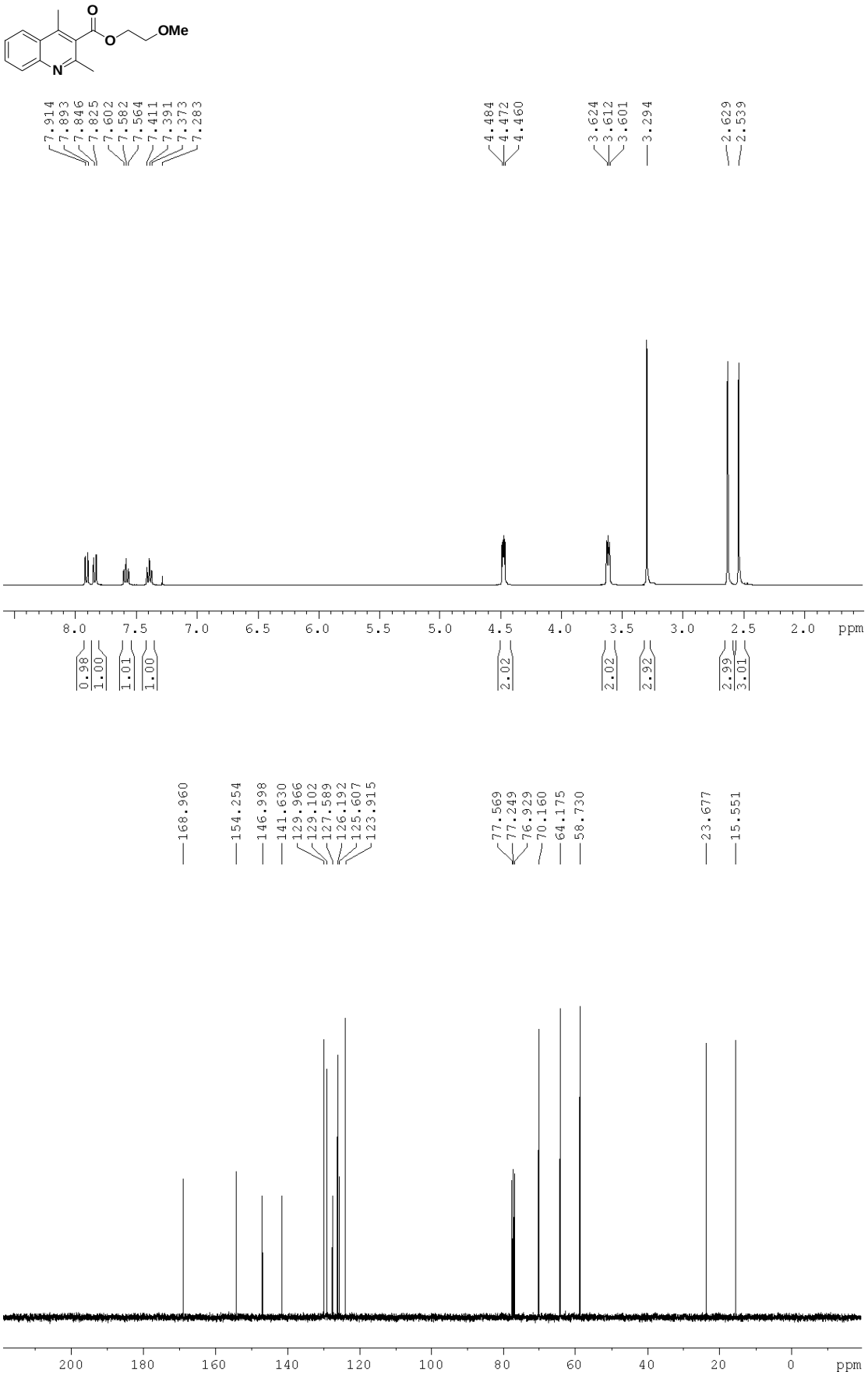

7.956
7.935
7.869
7.848
7.632
7.630
7.612
7.594
7.440
7.420
7.402
7.283
4.440
4.422
4.404
4.386
2.652
2.553
1.378
1.360
1.342
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.02
1.00
1.00
2.02
3.01
3.09
3.03

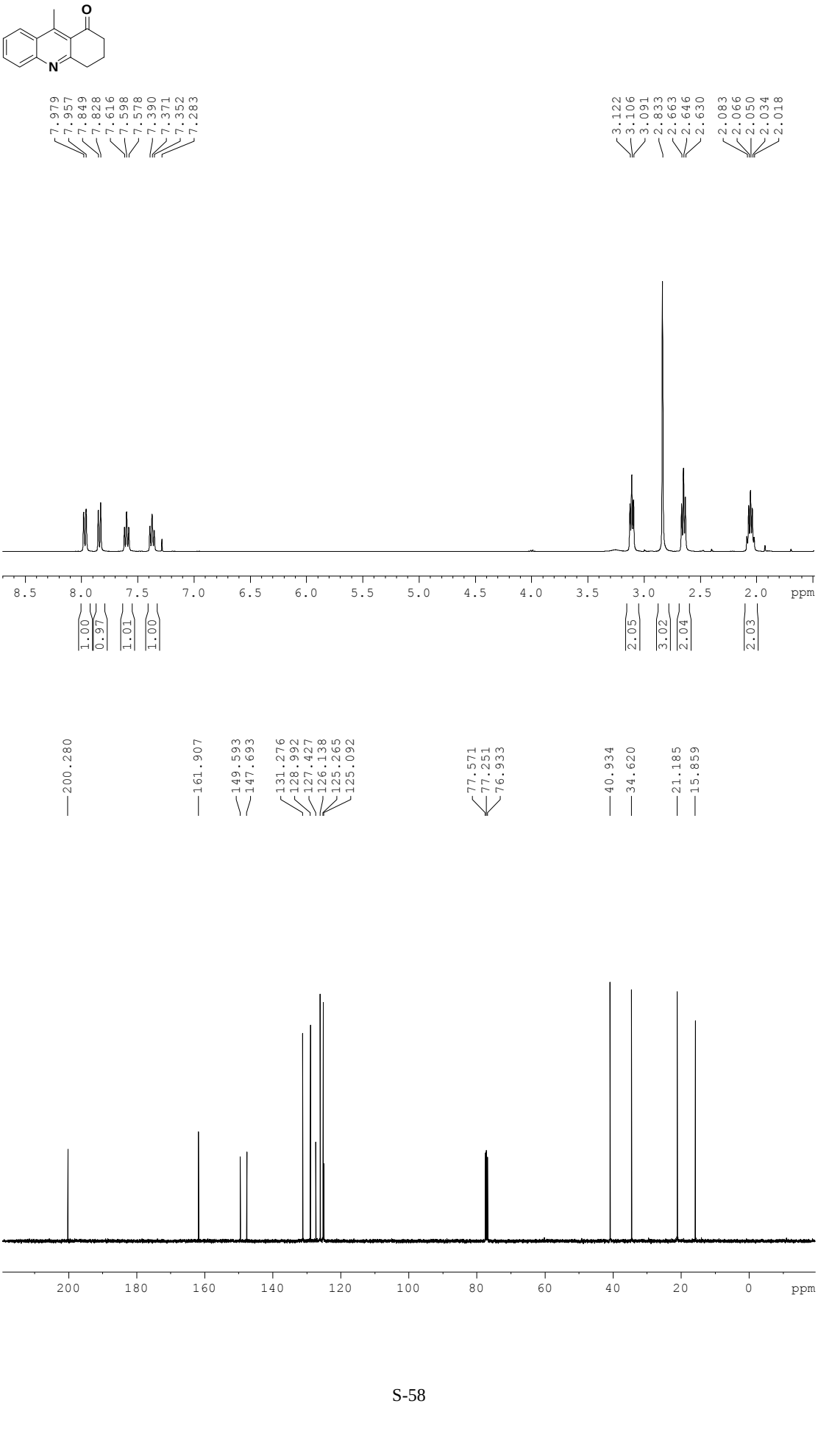

169.074
154.196
147.020
141.303
129.916
129.171
127.894
126.190
125.663
123.890
77.507
77.189
76.870
61.556
23.728
15.563
14.176
200 180 160 140 120 100 80 60 40 20 0 ppm

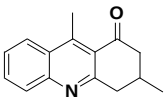

O
CF3
N


8.047
8.026
7.989
7.968
7.777
7.757
7.739
7.588
7.569
7.550
7.284
2.622
2.589
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
ppm
0.99
1.01
1.00
1.00
3.00
3.08


190.262
189.888
189.516
189.142
152.955
147.617
142.895
131.045
129.426
127.791
126.920
125.160
123.762
119.990
117.084
114.180
111.274
77.379
77.060
76.742
23.708
16.157
200
180
160
140
120
100
80
60
40
20
0
ppm

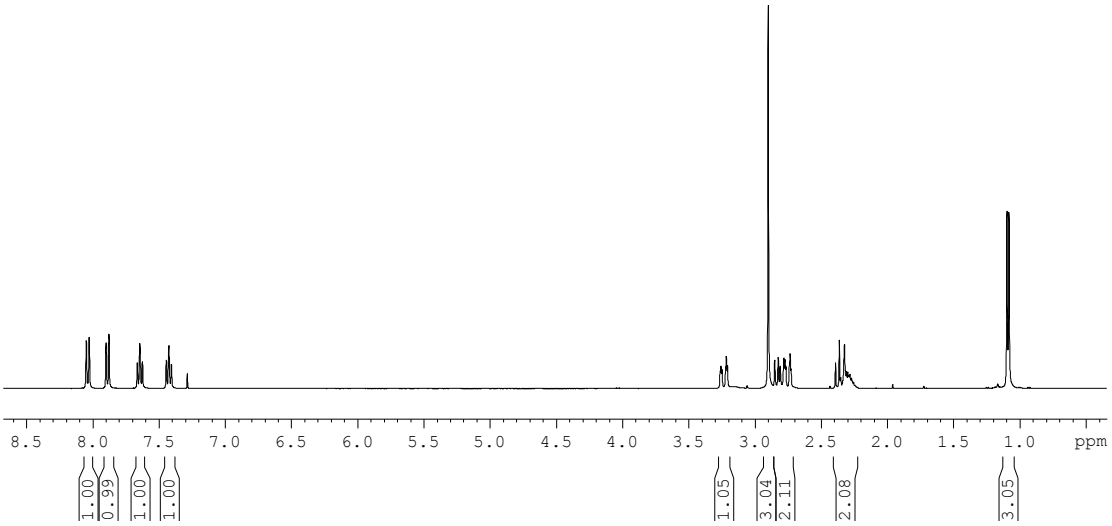




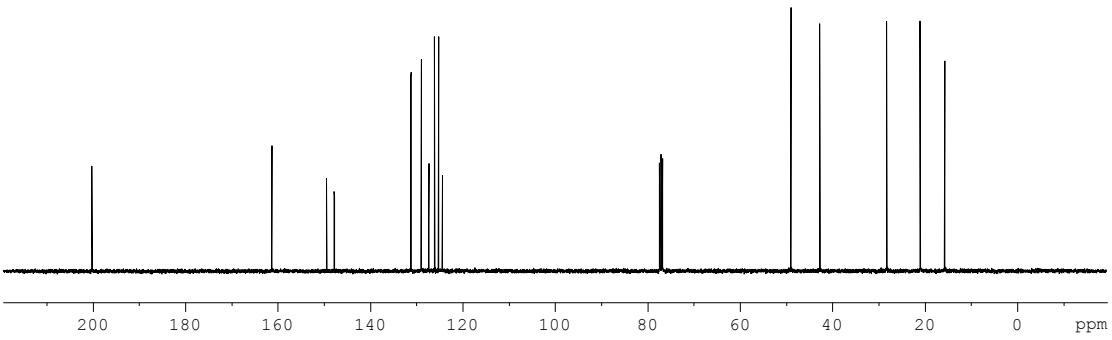


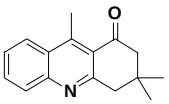
8.046
8.025
7.896
7.876
7.661
7.659
7.641
7.623
7.442
7.422
7.404
7.283

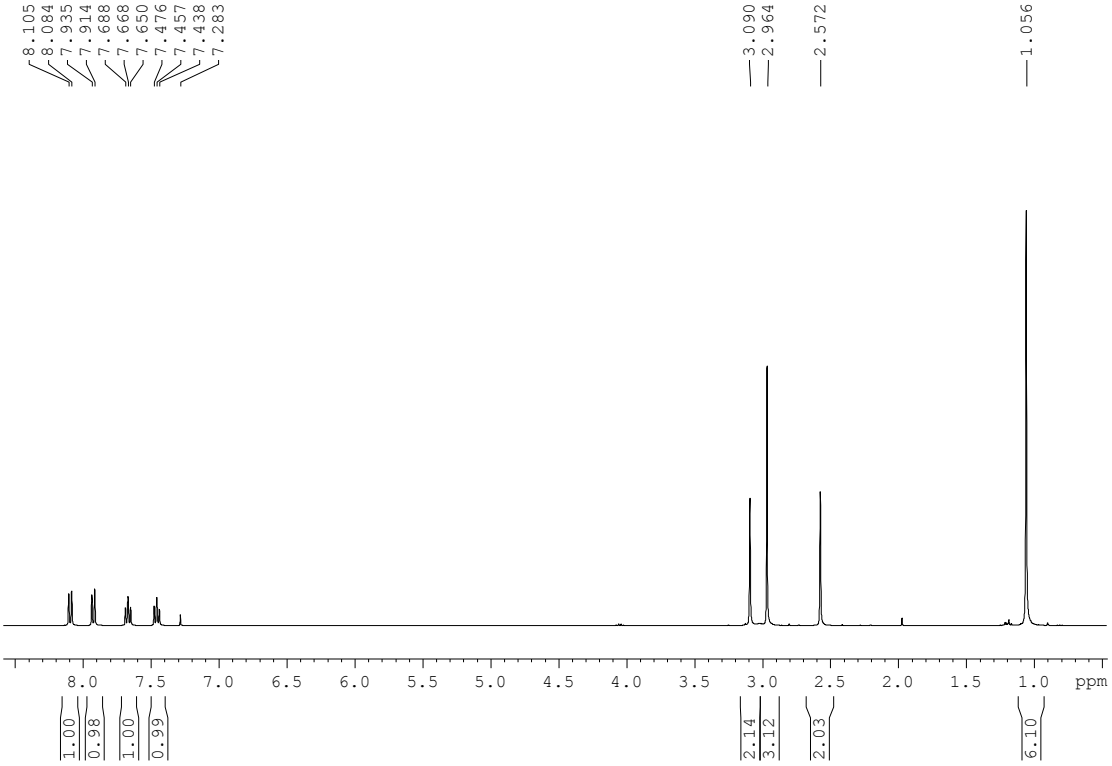
3.260
3.255
3.252
3.246
3.214
3.205
2.897
2.848
2.822
2.807
2.780
2.770
2.764
2.738
2.732
2.725
2.389
2.360
2.321
2.314
2.305
2.296
2.280
1.099
1.083

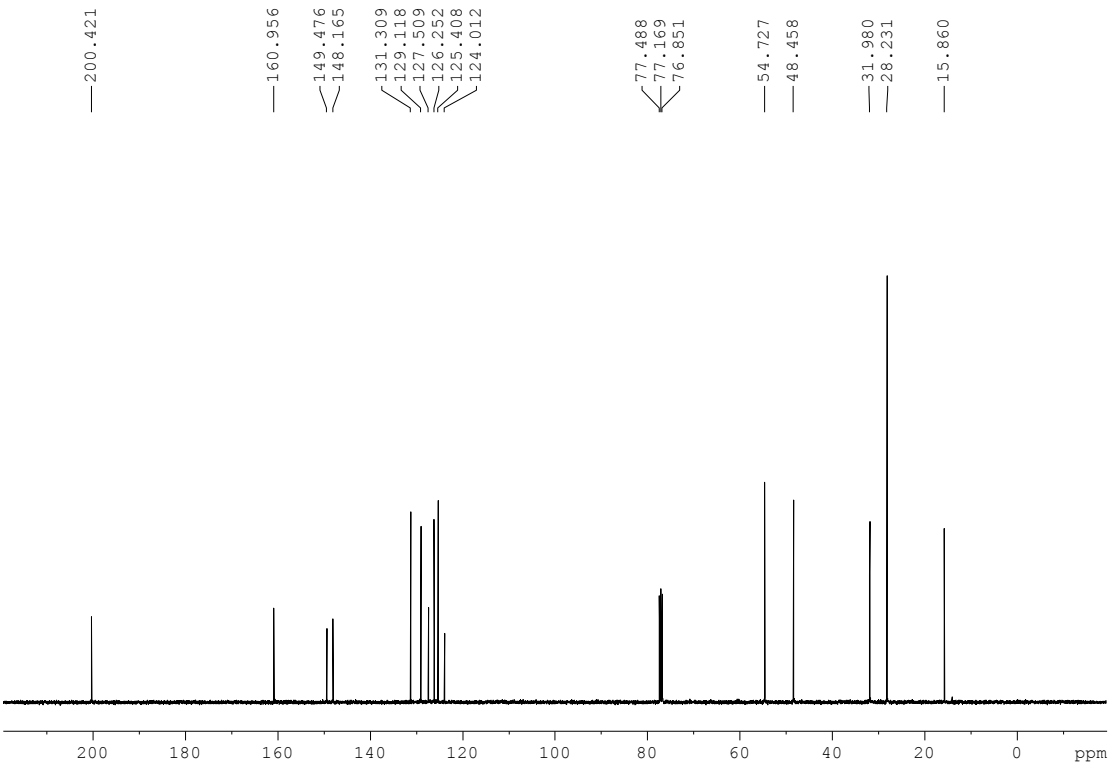


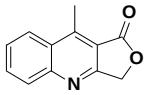
200.328
161.392
149.559
147.892
131.318
129.075
127.465
126.205
125.330
124.497
77.517
77.198
76.879
49.083
42.850
28.379
21.144
15.816

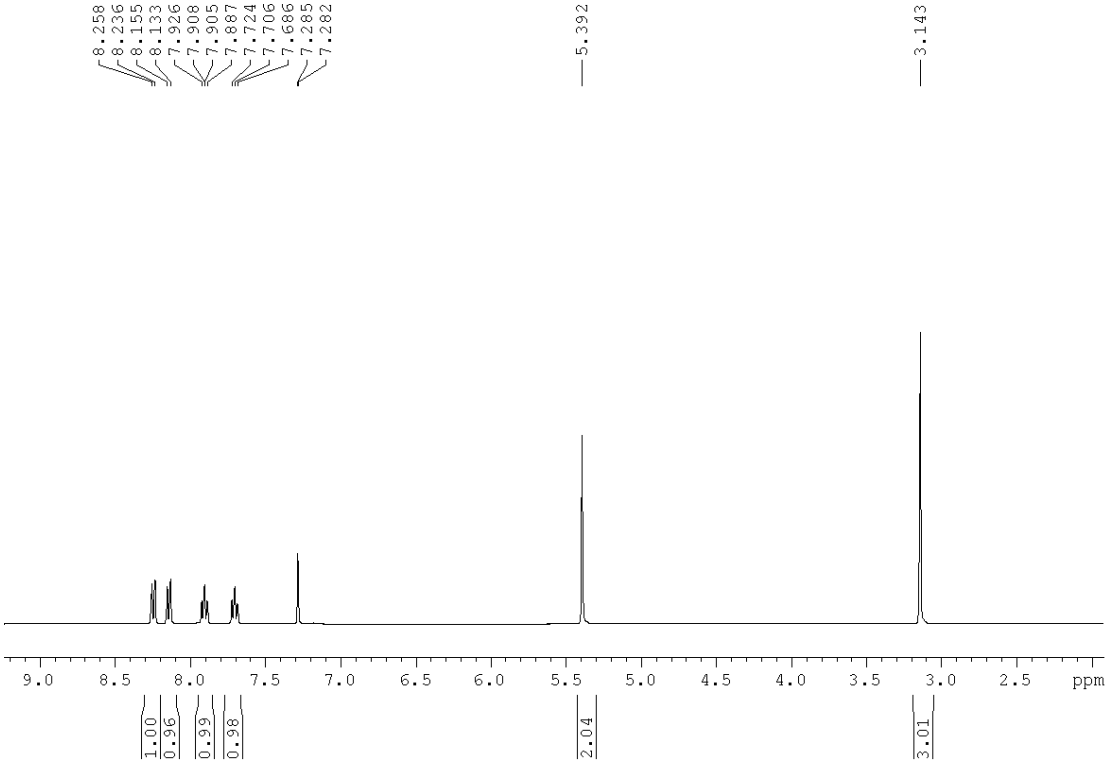


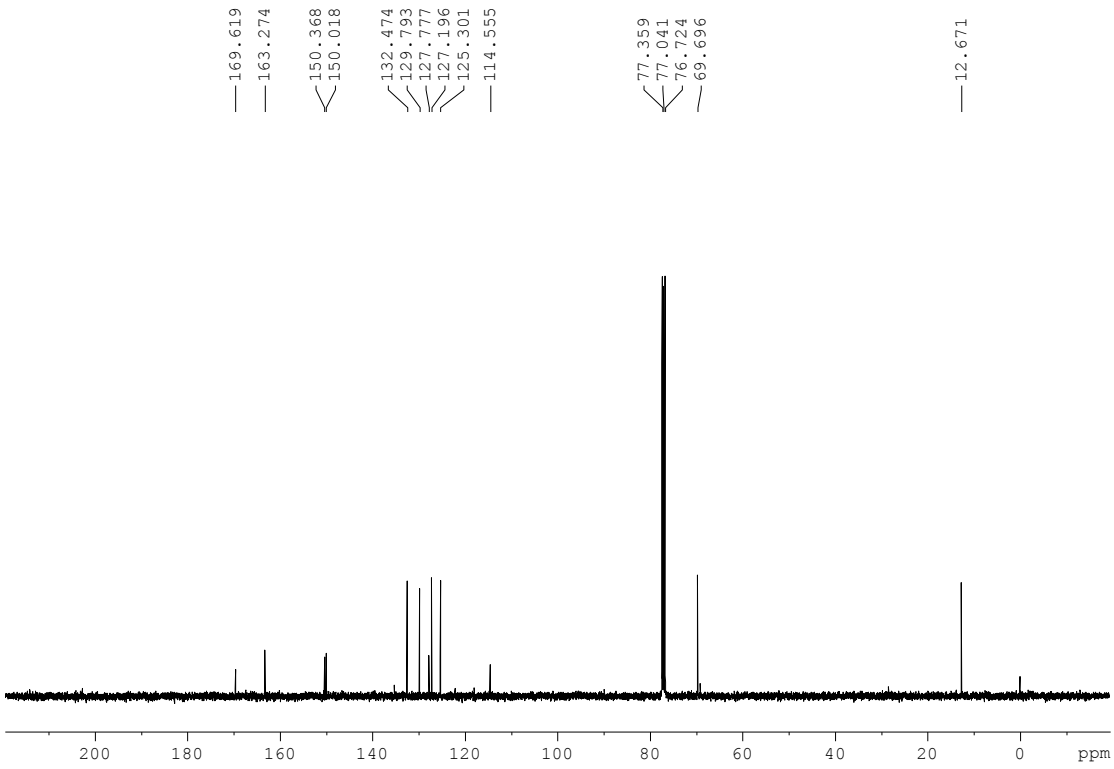


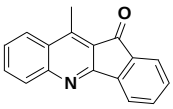


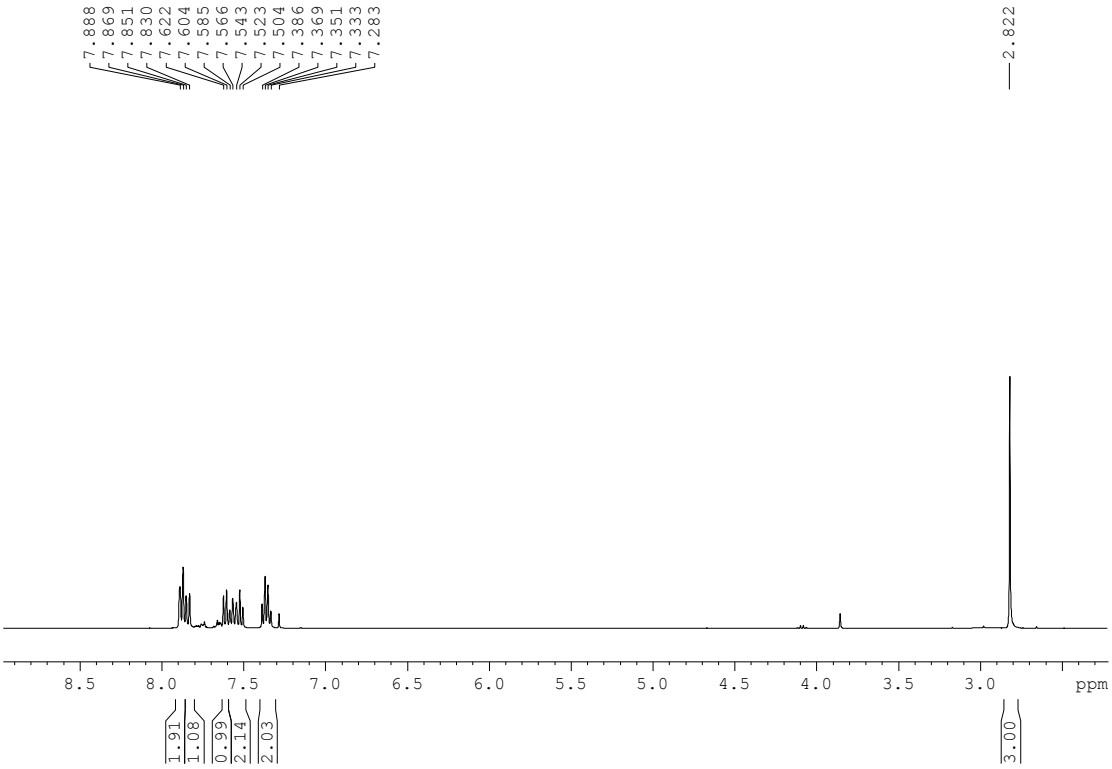


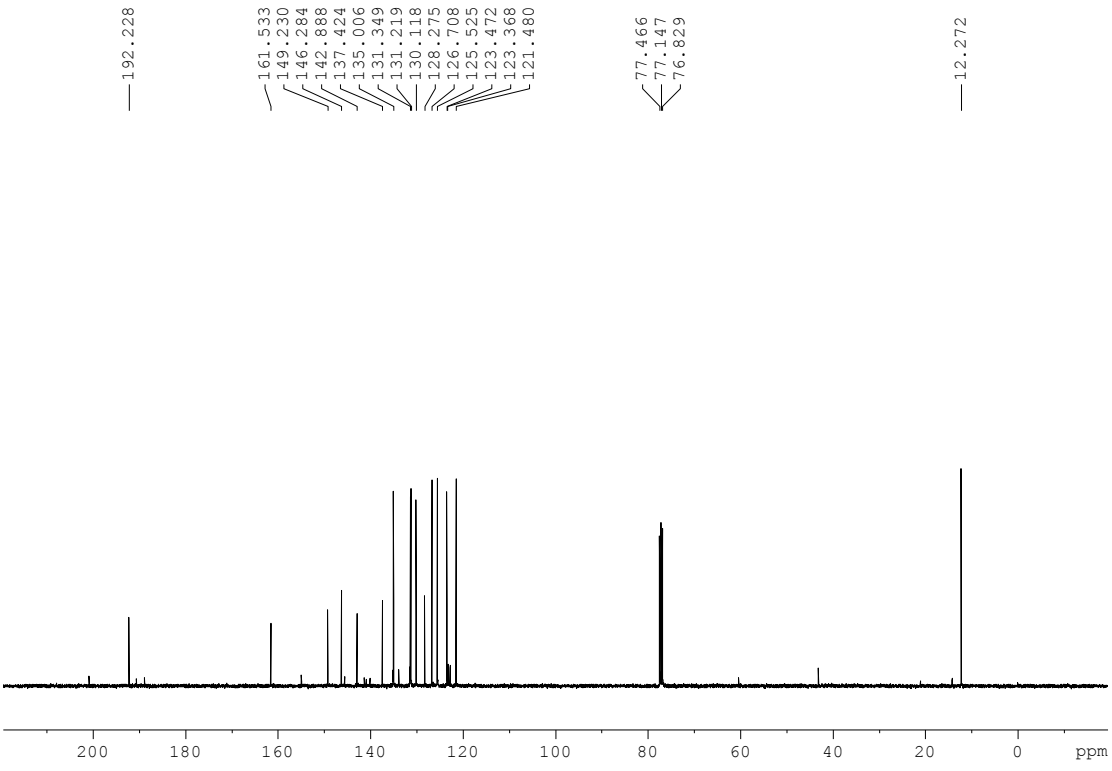







O
N


7.888
7.869
7.851
7.830
7.622
7.604
7.585
7.566
7.543
7.523
7.504
7.386
7.369
7.351
7.333
7.283
2.822
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.91
1.08
0.99
2.14
2.03
3.00


192.228
161.533
149.230
146.284
142.888
137.424
135.006
131.349
131.219
130.118
128.275
126.708
125.525
123.472
123.368
121.480
77.466
77.147
76.829
12.272
200
180
160
140
120
100
80
60
40
20
0
ppm

References

[1] Y. Gu, J. Barrault and F. Jérôme, *Adv. Synth. Catal.*, **2009**, *351*, 3269-3278

[2] J. S. Witzeman and W. D. Nottingham, *J. Org. Chem.*, **1991**, *56*, 1713-1718.

[3] G. O. Torosyan, *Zhurmal Organicheskoi Khimii*, **1982**, *18*, 1413-1416

[4] N. Noshiranzadeh and A. Ramazani, *Synth. Commun.*, **2007**, *37*, 3181-3189

[5] J. K. Augustine, A. bombrun, and S. Venkatachaliah, *Tetrahedron lett.*, **2011**, *52*, 6814-6818

[6] X. Zhang, Q. Wang, and S. Sheng, *Synth. Commun.*, **2009**, *39*, 3293-3304

[7] M. Hosseni-Sarvai, *J. Iran. Chem. Soc.*, **2011**, *8*, 119-128

[8] F. Ma, G. Cheng, Z. He and Z. Zhang, *Aust. J. Chem.*, **2012**, *65*, 409-416

[9] E. A. Fehnel, J. A. Deyrup, and M. B. Davidson, *J. Org. Chem.*, **1958**, *23*, 1996-2001

[10] T. H. Tong and H. N. C. Wong, *Synth. Commun.*, **1992**, *22*, 1773-1782