Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Metal-free cascade reaction of β-halo-α,β-unsaturated aldehyde and 1,4-dithiane-2,5-diol: synthesis of polycyclic 2-formylthiophenes

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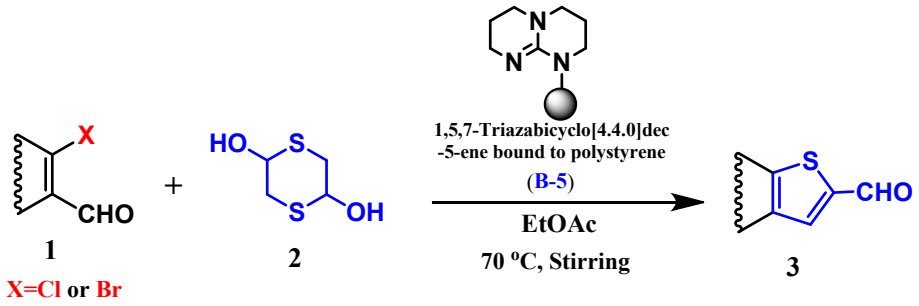
Experimental data and copies of ^{1}H , ^{13}C NMR and HRMS spectra of all products

EXPERIMENTAL SECTION

General Information. All reactions involving oxygen- or moisture-sensitive compounds were carried out under argon atmosphere using oven-dried or flame-dried glassware. Reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized first with ultraviolet light (254 nm) and then by immersion in solutions of *p*-anisaldehyde followed by heating. Flash column chromatography was performed with silica gel 60 (100-200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 500 MHz NMR spectrometer (125 MHz for ^{13}C). IR spectra were recorded on a spectrophotometer using $CHCl_3$. HRMS data were recorded by electronspray ionization with a Q-TOF mass analyzer.

General experimental procedure for the synthesis of 2-formylthiophenes from β-halo-α,β-unsaturated aldehyde and 1,4-dithiane-2,5-diol



1,5,7-Triazabicyclo[4.4.0]dec-5-ene bound to polystyrene **B-5** (1 g; ~3 mmol/g loading) was added to a 50 mL round-bottom flask containing β-halo-α,β-unsaturated aldehyde (1 mmol, 1 equiv), 1,5-dithiane-1,4-dithiol (0.5 mmol; 0.5 equiv), EtOAc (7 mL). The resultant mixture was stirred at 70 °C for 4 hrs and monitored by thin-layer chromatography (TLC). The reaction was terminated by filtering the supported base from the reaction mixture. The recovered base was washed with aq. NaOH solution (0.5 N; 10 mL) followed by ethanol (10 mL) and dried at 80 °C for 6 hrs. Then, the filtrate was concentrated in *vacuo* and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent.

Characterization data of polycyclic 2-formylthiophenes:

4,5-Dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3a

Flash column chromatography on silica gel (3% ethyl acetate in hexanes) gave **3a** (0.190 g, 89% yield) as brown gummy solid; R_f = 0.48 % (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.74 (s, 1H), 7.45 (s, 1H), 7.37-7.40 (m, 1H), 7.10-7.18 (m, 3H), 2.74-2.94 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.6, 146.3, 140.4, 138.1, 136.6, 135.7, 130.2, 129.0, 128.3, 127.2, 124.1, 29.6, 28.6; **IR ($CHCl_3$):** 1659, 1494, 1460, 1218, 1122, 772, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{11}OS$ $[M+H]^+$** : 215.0531 found: 215.0759

6-Methoxy-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3b

Flash column chromatography on silica gel (6% ethyl acetate in hexanes) gave **3b** (0.227 g, 93% yield) as yellow solid, R_f = 0.4 (10% ethyl acetate in hexanes), mp 110-114 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.85 (s, 1H), 7.56 (s, 1H), 7.23 (t, *J*=7.7 Hz, 1H), 7.14 (d, *J*=7.6 Hz, 1H), 6.87 (d, *J*=8.1 Hz, 1H), 3.87 (s, 3H), 2.98 (t, *J*= 7.7 Hz, 2H), 2.85 (t, *J*= 6.9 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.8, 156.7, 146.3, 140.5, 138.2, 136.7, 131.1, 127.6, 123.9, 116.7, 111.1, 55.6, 23.1, 20.8; **IR ($CHCl_3$):** 3583, 2929, 1660, 1582, 1539, 1432, 1361, 1258, 1218, 1020, 772, 666cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{13}O_2S$ $[M+H]^+$** : 245.0636; found: 245.0697.

7-Methoxy-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3c

Flash column chromatography on silica gel (6% ethyl acetate in hexanes) gave **3c** (0.212 g, 87% yield) as greenish yellow solid, R_f = 0.4 (10% ethyl acetate in hexanes), mp 67-72 °C ; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.78 (s, 1H), 7.51 (s, 1H), 7.38 (d, *J*=8.1 Hz, 1H), 6.72-6.87 (m, 2H), 3.81 (s, 3H), 2.78-3.01 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.4, 160.3, 146.7, 139.2, 137.7, 136.9, 136.4, 125.5, 123.2, 113.9, 112.3, 55.3, 29.1, 23.4; **IR ($CHCl_3$):** 3583, 2922, 1656, 1604, 1575, 1418, 1308, 1284, 1220, 1141, 1109, 1036, 772 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{13}O_2S$ $[M+H]^+$** :245.0636; found: 245.0697.

8-Methoxy-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3d

Flash column chromatography on silica gel (6% ethyl acetate in hexanes) gave **3d** (0.198 g, 81% yield) as brown solid, R_f = 0.4 (10% ethyl acetate in hexanes), mp 73-77 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.85 (s, 1H), 7.57 (s, 1H), 7.16 (d, *J*=8.2 Hz, 1H), 7.01 (d, *J*=2.2 Hz, 1H), 6.82 (dd, J_1=2.4 Hz, J_2=8.3 Hz, 1H), 3.84 (s, 3H), 2.80-2.95 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.7, 158.7, 146.3, 140.4, 138.5, 136.7, 131.1, 129.2, 127.9, 114.6, 109.3, 55.4, 29.6, 27.8 **; IR ($CHCl_3$):** 3583, 2922, 1656, 1605, 1574, 1450, 1418, 1285, 1236, 1142, 1039, 865 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{13}O_4S$ $[M+H]^+$** : 245.0636; found: 245.0729.

8-Fluoro-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3e

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3e** (0.209 g, 90% yield) as yellow solid, R_f = 0.42 (10% ethyl acetate in hexanes), mp 126-131 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.87 (s, 1H), 7.58 (s, 1H), 7.21 (dd, J_1=5.6 Hz, J_2=8.3 Hz, 1H), 7.17 (dd, J_1=2.6 Hz, J_2=9.0 Hz, 1H), 6.95 (dt, J_1=2.6 Hz, J_2=8.4 Hz, 1H), 2.83-3.01 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.7, 161.8 (d, *J*=244.8 Hz), 145.0 (d, *J* =2.7 Hz), 141.1, 138.8, 136.5, 131.8 (d, *J* =8.3 Hz), 131.3 (d, *J* =2.9 Hz), 129.7 (d, *J* =7.9 Hz), 115.0 (d, *J* =21.4 Hz), 110.9 (d, *J* =23.0 Hz), 28.0, 23.8**; IR ($CHCl_3$):** 3583, 2946, 1651, 1610, 1586, 1489, 1463, 1403, 1358, 1290, 1241, 1220, 1112, 867 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{10}FOS$ $[M+H]^+$**: 233.0436; found: 233.0470.

6,8-Dimethoxy-4,5-dihydronaphtho[1,2-b]thiophene-2-carbaldehyde; 3f

Flash column chromatography on silica gel (9% ethyl acetate in hexanes) gave **3f** (0.258g, 94% yield) as brown solid, R_f = 0.36 (10% ethyl acetate in hexanes), mp 135-141 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.79 (s, 1H), 7.53 (s, 1H), 6.95 (s, 1H), 6.75 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.76-2.94 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.5, 149.7, 148.0, 146.9, 139.2, 136.9, 136.6, 129.0, 122.8, 111.3, 107.2, 56.1, 55.9, 28.5, 23.7**; IR ($CHCl_3$):** 3583, 2928, 1655, 1607, 1512, 1458, 1436, 1393, 1343, 1245, 1214, 1146, 1015 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{15}O_3S$ $[M+H]^+$** : 275.0742; found: 275.0746.

6,8-Dimethyl-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3g

Flash column chromatography on silica gel (3% ethyl acetate in hexanes) gave **3g** (0.211 g, 87% yield) as brown solid, R_f = 0.47 (10% ethyl acetate in hexanes), mp 121-127 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.84 (s, 1H), 7.55 (s, 1H), 7.18 (s, 1H), 6.98 (s, 1H), 2.78-2.97 (m, 4H), 2.32 (s, 3H), 2.30 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.6, 147.2, 140.3, 137.7, 136.6, 136.2, 135.8, 132.0, 131.1, 129.9, 122.7, 24.3, 23.5, 20.9, 19.8; **IR ($CHCl_3$):** 3583, 2919, 1657, 1425, 1361, 1249, 1175, 1133, 873, 844 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{15}OS$ $[M+H]^+$** : 243.0844; found: 243.0841.

5-Methyl-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbaldehyde; 3h

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3h** (0.207 g, 91% yield) as brown solid; R_f = 0.46 % (10% ethyl acetate in hexanes); mp 69-75 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.76 (s, 1H), 7.48 (s, 1H), 7.40 (d, J=7.3 H_Z, 1H), 7.15-7.24 (m, 3H), 3.00-3.11 (m, 1H), 2.91 (dd, J_1= 6.3 H_Z, J_2=15.5 H_Z, 1H), 2.60 (dd, J_1= 6.4 H_Z, J_2= 15.5 H_Z, 1H), 1.16 (d, J=6.9 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.7, 145.7, 140.7, 140.4, 137.2, 136.8, 129.4, 129.2, 127.1, 127.0, 124.3, 33.1, 31.2, 20.4; **IR ($CHCl_3$):** 3583, 2922, 1661, 1464, 1425, 1284, 1235, 1144, 1116 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{13}OS$ $[M+H]^+$**: 229.0687 found: 229.0756.

5,6-Dihydro-4H-benzo[6,7]cyclohepta[1,2-*b*]thiophene-2-carbaldehyde; 3i

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3i** (0.176 g, 77% yield) as yellow sticky solid, R_f = 0.46 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.85 (s, 1H), 7.61 (s, 1H), 7.42-7.52 (m, 1H), 7.27-7.35 (m, 3H), 2.57-2.70 (m, 4H), 2.17-2.34 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.7, 149.1, 140.9, 140.7, 140.4, 138.5, 133.8, 129.7, 128.9, 128.5, 126.9, 32.6, 32.5, 26.6; **IR ($CHCl_3$):** 3584, 2929, 1664, 1427, 1248, 1220, 1138 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{13}OS$ $[M+H]^+$**: 229.0687; found: 229.0725.

5,6,7,8-Tetrahydro-4H-cyclohepta[*b*]thiophene-2-carbaldehyde; 3j

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3j** (0.117 g, 65% yield) as brown liquid; R_f= 0.48 % (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.57 (s, 1H), 7.28 (s, 1H), 2.50-2.83 (m, 4H), 1.45-1.83 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.5, 152.7, 142.8, 139.5, 138.0, 32.2, 30.9, 30.5, 27.7, 27.5; **IR ($CHCl_3$):** 3583, 2923, 2850,

1665, 1453, 1241, 1159 cm^{-1}; **HRMS (+ESI) Calcd for $C_{10}H_{13}OS$ $[M+H]^+$**: 181.0687 found: 181.0738

4,5,6,7,8,9-Hexahydrocycloocta[*b*]thiophene-2-carbaldehyde; 3k

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3k** (0.140 g, 72% yield) as brown liquid; R_f = 0.47 % (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.67 (s, 1H), 7.37 (s, 1H), 2.28-2.96 (m, 4H), 1.04-1.68 (m, 8H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.3, 151.1, 140.6, 139.3, 138.4, 31.7, 30.7, 27.4, 26.7, 25.4, 25.2; **IR ($CHCl_3$):** 2926, 2852, 1661, 1455, 1405, 1239, 1214, 1149, 1074, 853 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_{15}OS$ $[M+H]^+$**: 195.0844 found: 195.0926

4*H*-Thieno[3,2-*c*]chromene-2-carbaldehyde; 3l[1]

Flash column chromatography on silica gel (6% ethyl acetate in hexanes) gave **3l** (0.168 g, 78% yield) as yellow solid, R_f = 0.42 (10% ethyl acetate in hexane); mp 103-105 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.86 (s, 1H), 7.49 (s, 1H), 7.40 (d, *J*=7.6 Hz, 1H), 7.23-7.30 (m, 1H), 7.00 (t, *J*=7.5 Hz, 1H), 6.91 (d, *J*=8.2 Hz, 1H), 5.29 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.4, 153.1, 142.5, 141.8, 132.9, 132.0, 131.3, 124.1, 122.4, 119.1, 117.1, 65.6; **IR ($CHCl_3$):** 2922, 1660, 1467, 1440, 1233, 1147, 1112, 1032 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_9O_2S$ $[M+H]^+$** : 217.0323; found: 217.0397.

4H-Thieno[3,2-c]thiochromene-2-carbaldehyde; 3m

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3m** (0.137 g, 59% yield) as yellow sticky solid, R_f = 0.46 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.86 (s, 1H), 7.52-7.58 (m, 2H), 7.38 (d, *J*=7.7 Hz, 1H), 7.17-7.28 (m, 2H), 3.97 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.5, 146.1, 140.9, 135.4, 132.3, 129.4, 129.3, 127.8, 126.5, 125.7, 25.9 one peak is missing due to overlap; **IR ($CHCl_3$):** 3583, 1663, 1453, 1220, 1034 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_9OS_2$ $[M+H]^+$**: 233.0095; found: 233.0095.

5-Phenylthiophene-2-carbaldehyde; 3n[2]

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3n** (0.135 g, 72% yield) as brown solid, R_f = 0.47 (10% ethyl acetate in hexane); mp 75-78 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.87 (s, 1H), 7.73 (d, *J* =3.9 Hz, 1H), 7.62-7.70 (m, 2H), 7.29-7.50 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.9, 154.3, 142.3, 137.5, 132.9, 129.4, 129.1, 126.3, 124.1; **IR ($CHCl_3$):** 1655, 1454, 1441, 1222, 1062, 807, 772, 755, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_9OS$ $[M+H]^+$** : 189.0374; found: 189.0473.

5-(*p*-Tolyl)thiophene-2-carbaldehyde; 3o[3]

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3o** (0.139 g, 69% yield) as brown solid, R_f = 0.42 (10% ethyl acetate in hexane); mp 81-84 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.87 (s, 1H), 7.72 (d, *J*=3.9 Hz,1H), 7.56 (d, *J*=8.2 Hz, 2H), 7.35 (d, *J*=3.9 Hz, 1H), 7.23 (d, *J*=7.9 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.8, 154.6, 141.8, 139.7, 137.6, 130.2, 129.8, 126.3, 123.5, 21.3; **IR ($CHCl_3$):** 2923, 1655, 1452, 1225, 1054, 803 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{11}OS$ $[M+H]^+$** : 203.0531; found: 203.0607.

5-(4-Fluorophenyl)thiophene-2-carbaldehyde; 3p[4]

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3p** (0.111g, 54% yield) as brown solid, R_f = 0.44 (10% ethyl acetate in hexanes), mp: 100-103 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.88 (s, 1H), 7.74 (d, *J*= 3.9 H_Z, 1H), 7.60-7.68 (m, 2H), 7.34 (d, *J*= 3.9 H_Z, 1H), 7.07-7.18 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.8, 163.4 (d, *J*=250.3 Hz), 153.0, 142.4, 137.5, 129.3 (d, *J*=3.5 Hz), 128.3 (d, *J*=8.3 Hz), 124.1, 116.3 (d, *J*=21.9 Hz); **IR ($CHCl_3$):** 2922, 1646, 1447, 1234, 1162, 1063, 811 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_8FOS$ $[M+H]^+$** : 207.0280; found: 207.0333.

5-(4-Nitrophenyl)thiophene-2-carbaldehyde; 3q[5]

Flash column chromatography on silica gel (30% ethyl acetate/hexanes) gave **3q** (0.119g, 51% yield) as yellow solid, R_f = 0.5 (in 40% ethyl acetate/ hexane), mp 164-168 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.95 (s, 1H), 8.30 (d, *J*=8.7 Hz, 2H), 7.83 (d, *J*=8.7 Hz, 2H), 7.80 (d, *J*=3.9 Hz, 1H), 7.55 (d, *J*=3.9 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.8, 150.4, 147.8, 144.5, 139.0,

137.1, 126.9, 126.3, 124.6; **IR ($CHCl_3$):** 1674, 1512, 1342, 1220 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_8NO_3S$ $[M+H]^+$** : 234.0225; found: 234.0226.

5-(Benzo[d][1,3]dioxol-5-yl)thiophene-2-carbaldehyde; 3r[6]

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3r** (0.172 g, 74% yield) as yellow solid, R_f = 0.43 (10% ethyl acetate in hexane); mp 125-129 ^oC; **^1H NMR (500 MHz, $CDCl_3$):** δ 9.86 (s, 1H), 7.71 (d, *J*=3.9 Hz, 1H), 7.27 (d, *J*=3.9 Hz, 1H), 7.19 (dd, J_1=1.8 Hz, J_2=8.1 Hz, 1H), 7.13 (d, *J*=1.8 Hz, 1H), 6.87 (d, *J*=8.1 Hz, 1H), 6.04 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.6, 154.2, 148.7, 148.3, 141.5, 137.5, 127.2, 123.3, 120.7, 108.8, 106.6, 101.5; **IR ($CHCl_3$):** 1651, 1454, 1220, 1056 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_9O_3S$ $[M+H]^+$** : 233.0272; found: 233.0314.

5-(4-Cyclohexylphenyl)thiophene-2-carbaldehyde; 3s

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3s** (0.184 g, 68% yield) as yellow solid, R_f = 0.45 (10% ethyl acetate in hexane); mp 116-118 ^oC; **^1H NMR (500 MHz, $CDCl_3$):** δ 9.78 (s, 1H), 7.64 (d, *J*=3.9 Hz, 1H), 7.51 (d, *J*=8.2 Hz, 2H), 7.27 (d, *J*=3.9 Hz, 1H), 7.18 (d, *J*=8.1 Hz, 2H), 2.45 (m, 1H), 1.55-1.89 (m, 6H), 1.24-1.42 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.8, 154.6, 149.8, 141.9, 137.6, 130.5, 127.6, 126.4, 123.6, 44.3, 34.2, 26.7, 25.9; **IR ($CHCl_3$):** 2850, 1664, 1454, 1220, 1061, 803 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{19}OS$ $[M+H]^+$** : 271.1157; found: 271.1227.

5-(Naphthalen-2-yl)thiophene-2-carbaldehyde; 3t[7]

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3t** (0.145 g, 61% yield) as brown solid, R_f = 0.43 (10% ethyl acetate in hexane); mp 44-49 ^oC; **^1H NMR (500 MHz, $CDCl_3$):** δ 9.96 (s, 1H), 8.05-8.24 (m, 1H), 7.87-7.96 (m, 2H), 7.84 (d, *J*=3.8 Hz, 1H), 7.59 (dd, J_1=1.0 Hz, J_2=7.1 Hz, 1H), 7.49-7.56 (m, 3H), 7.36 (d, *J*=3.8 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 182.9, 152.3, 143.4, 136.6, 133.7, 131.0, 130.9, 129.7, 128.6, 128.5, 128.3, 126.9, 126.3, 125.2, 124.9; **IR ($CHCl_3$):** 1662, 1450, 1220, 772 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{11}OS$ $[M+H]^+$** : 239.0531; found: 239.0537.

(6βS,8αS,12αS,12βR)-4-Methoxy-8α-methyl-2,6β,7,8,8α,12,12α,12β-octahydro-1H-naphtho[2',1':4,5]indeno[1,2-b]thiophene-10-carbaldehyde; 3u

Flash column chromatography on silica gel (5% ethyl acetate in hexanes) gave **3u** (0.232 g, 66% yield) as brown solid; mp 172-176 ^{o}C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.78 (s, 1H), 7.54 (s, 1H), 7.22 (d, *J*=8.6 Hz, 1H), 6.74 (dd, J_1=2.7 Hz, J_2=8.5 Hz, 1H), 6.67 (d, *J*=2.6 Hz, 1H), 3.79 (s, 3H), 2.87-3.01 (m, 2H), 2.78 (dd, J_1=6.4 Hz, J_1=14.1 Hz, 1H), 2.29-2.56 (m, 3H); 2.13-2.27 (m, 2H), 1.92-2.03 (m, 1H), 1.67-1.90 (m, 3H), 1.45-1.57 (m, 1H), 1.05 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 182.7, 166.1, 157.5, 144.9, 144.5, 137.6, 132.7, 132.0, 126.0, 113.8, 111.5, 60.1, 55.1, 45.9, 43.9, 37.6, 35.1, 29.5, 28.5, 27.5, 26.2, 19.2; **IR ($CHCl_3$):** 2929, 2853, 1664, 1609, 1499, 1461, 1425, 1252, 1154, 1129 cm^{-1}; **HRMS (+ESI) Calcd for $C_{22}H_{25}O_2S$ $[M+H]^+$** : 353.1575 found: 353.1577

References

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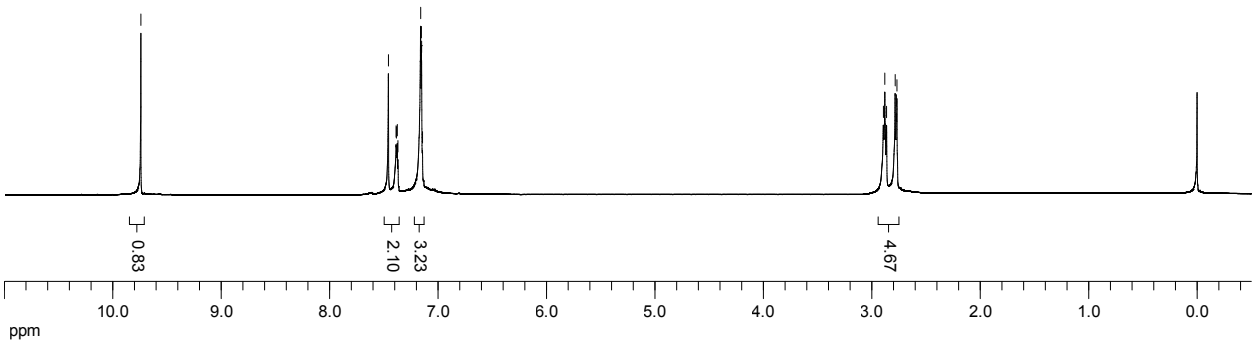
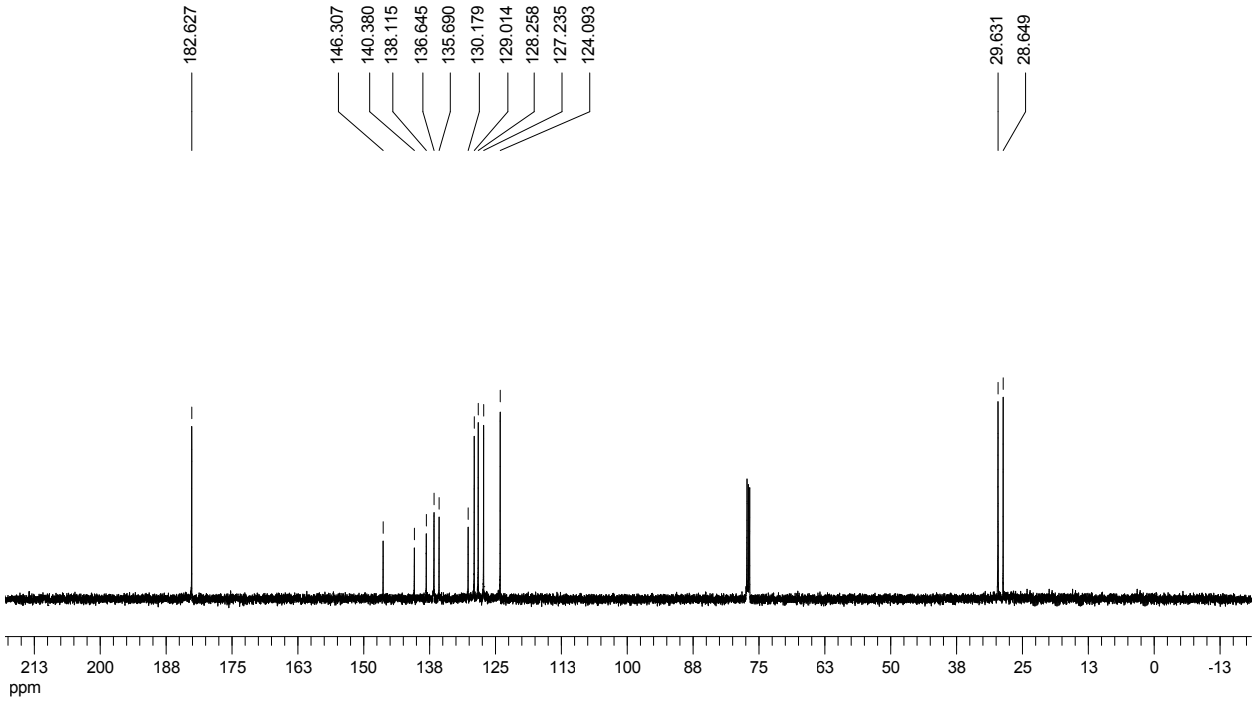
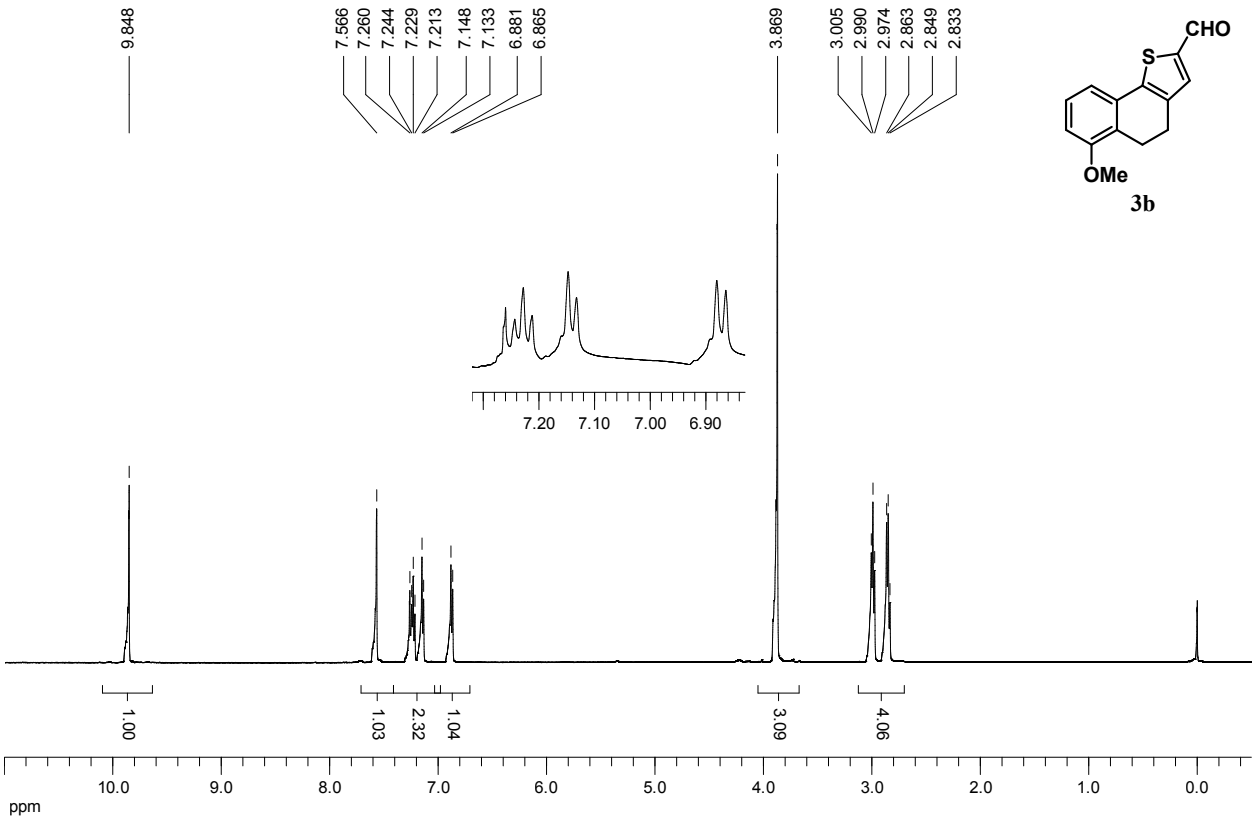
Copies of ^{1}H and ^{13}C NMR spectra of all thiophene products

3a



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OMe
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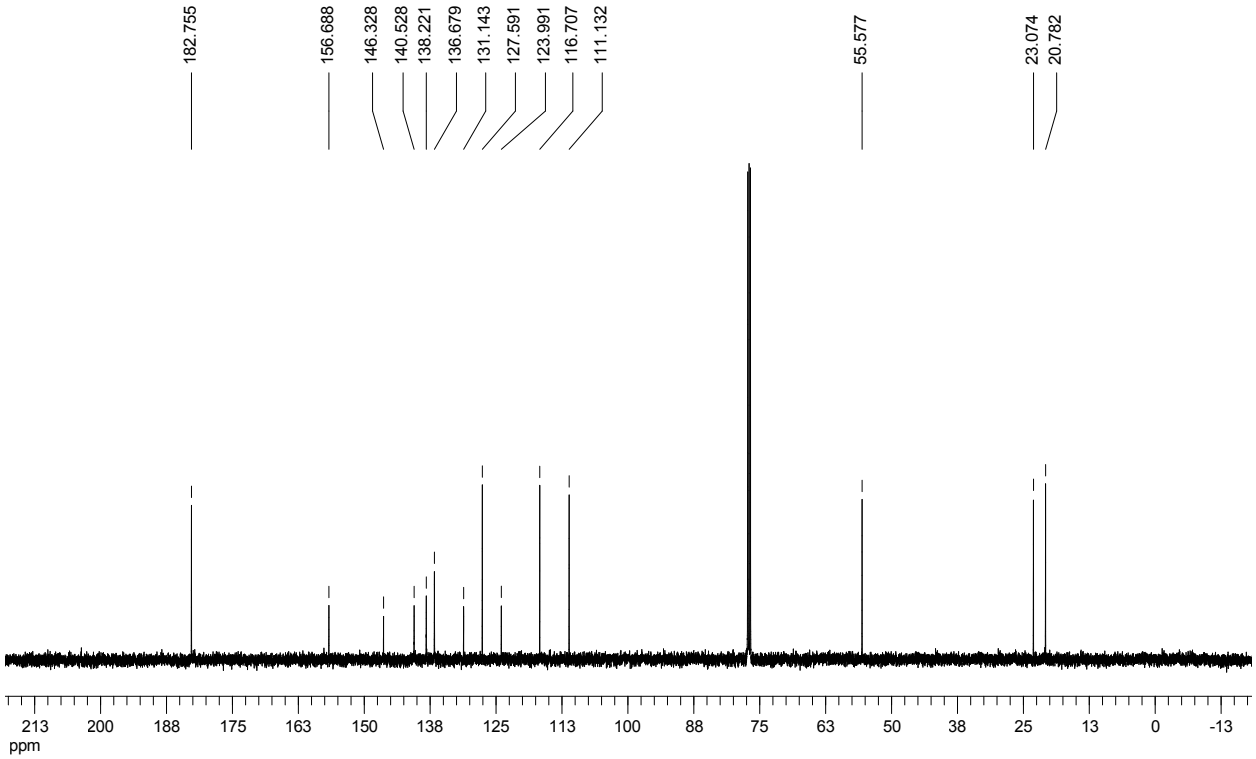
3b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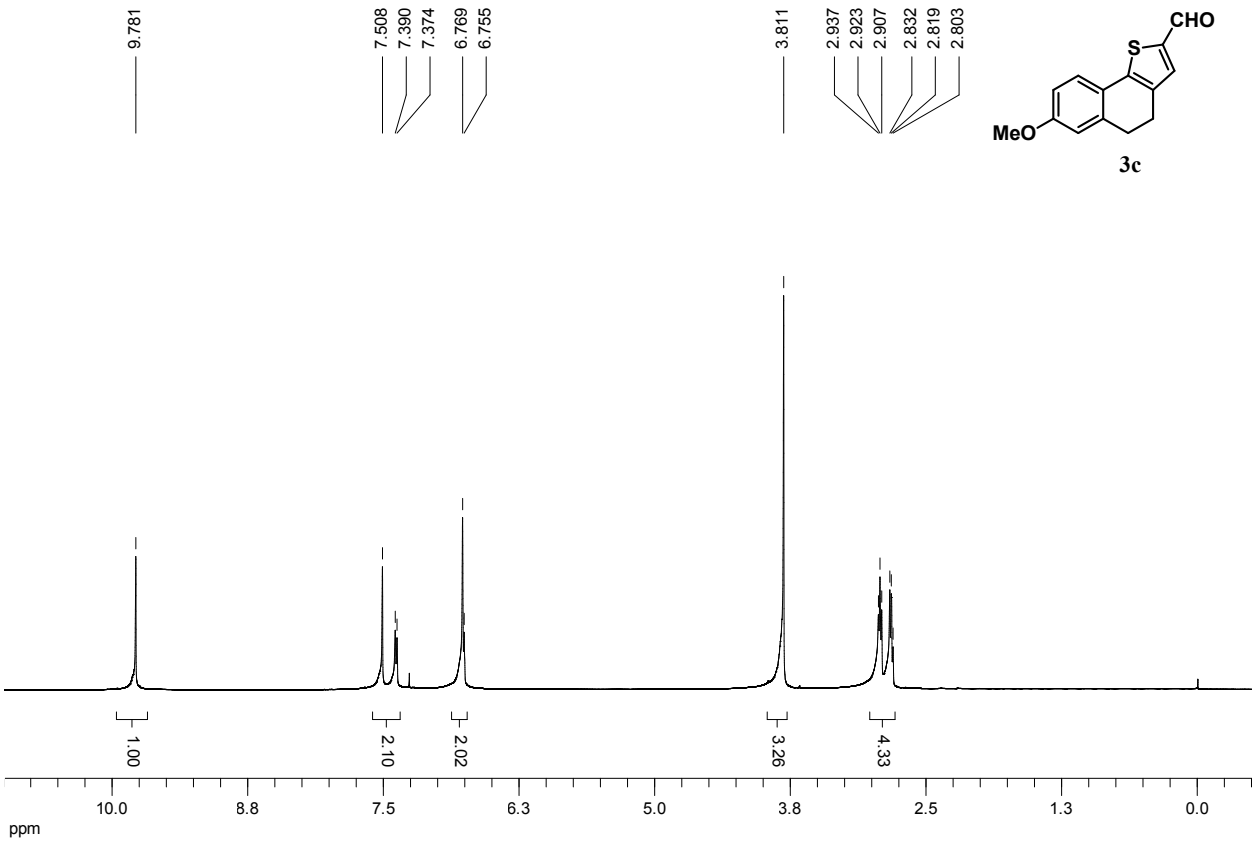
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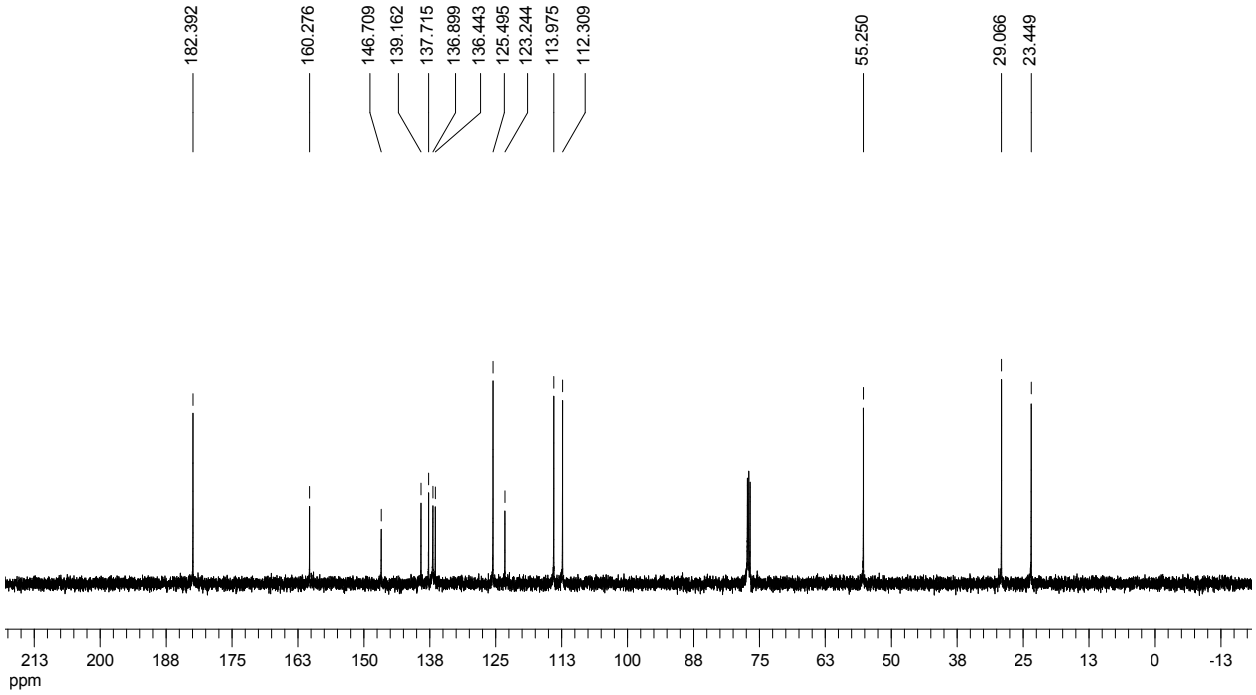
3c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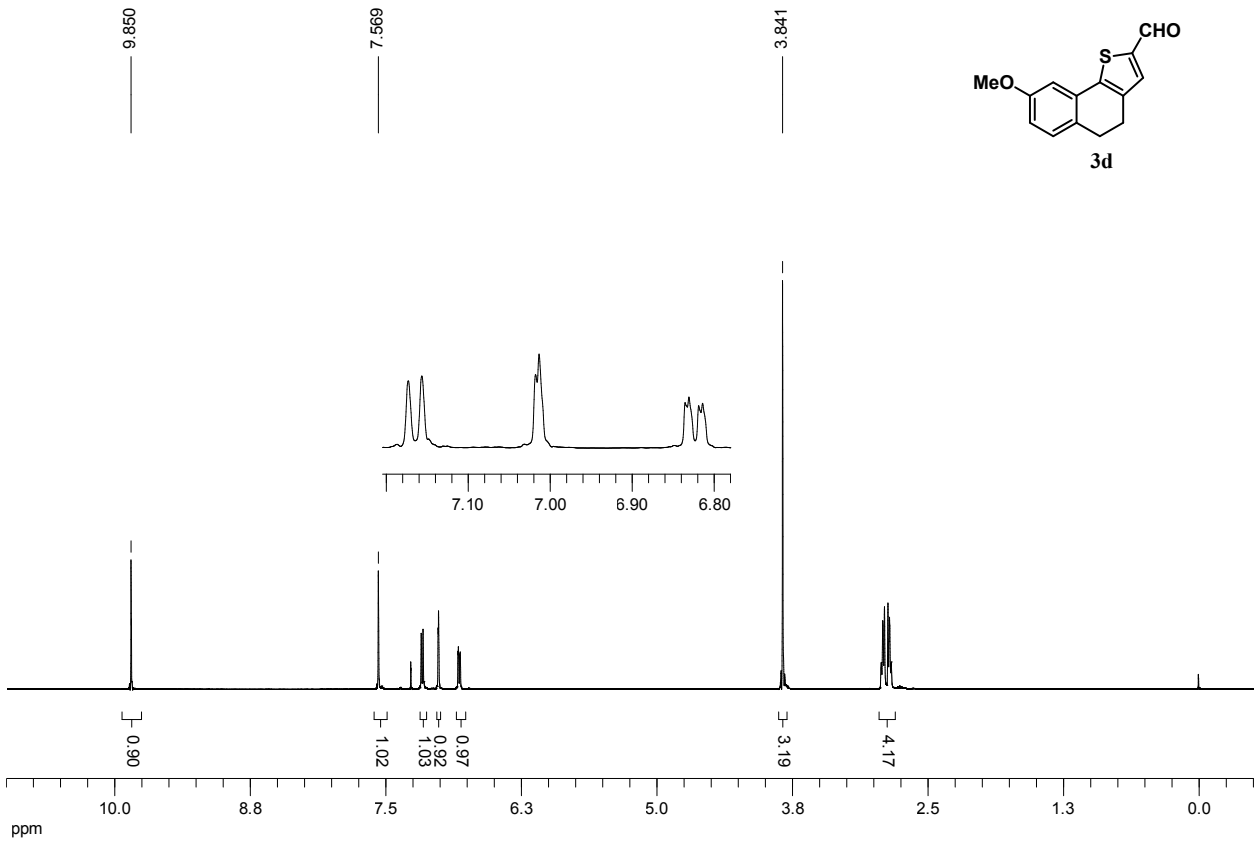
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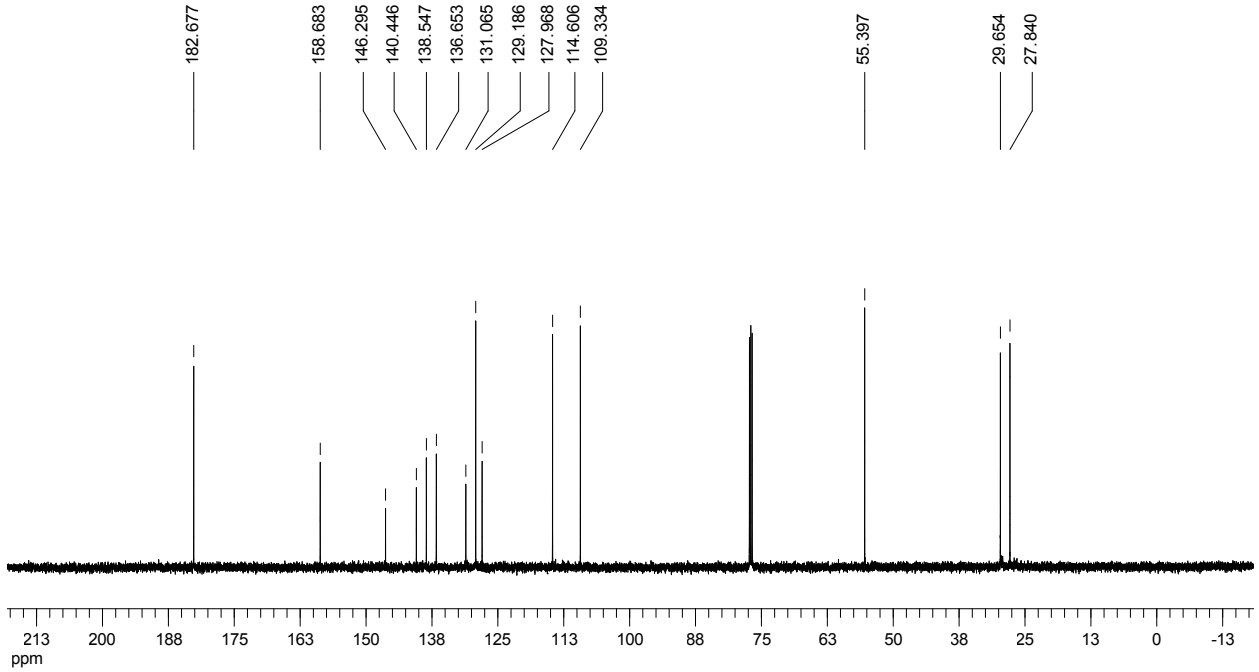
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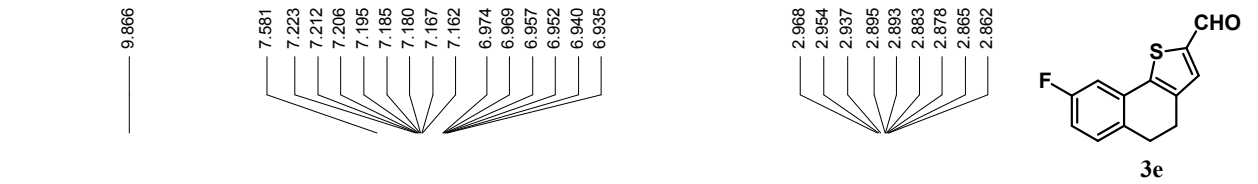
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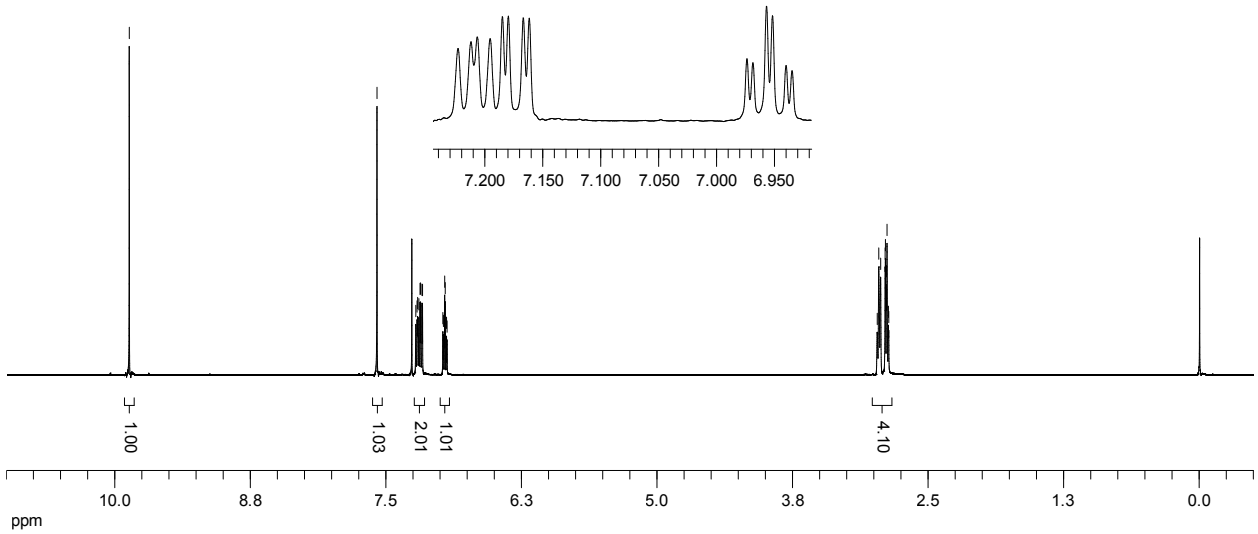
3e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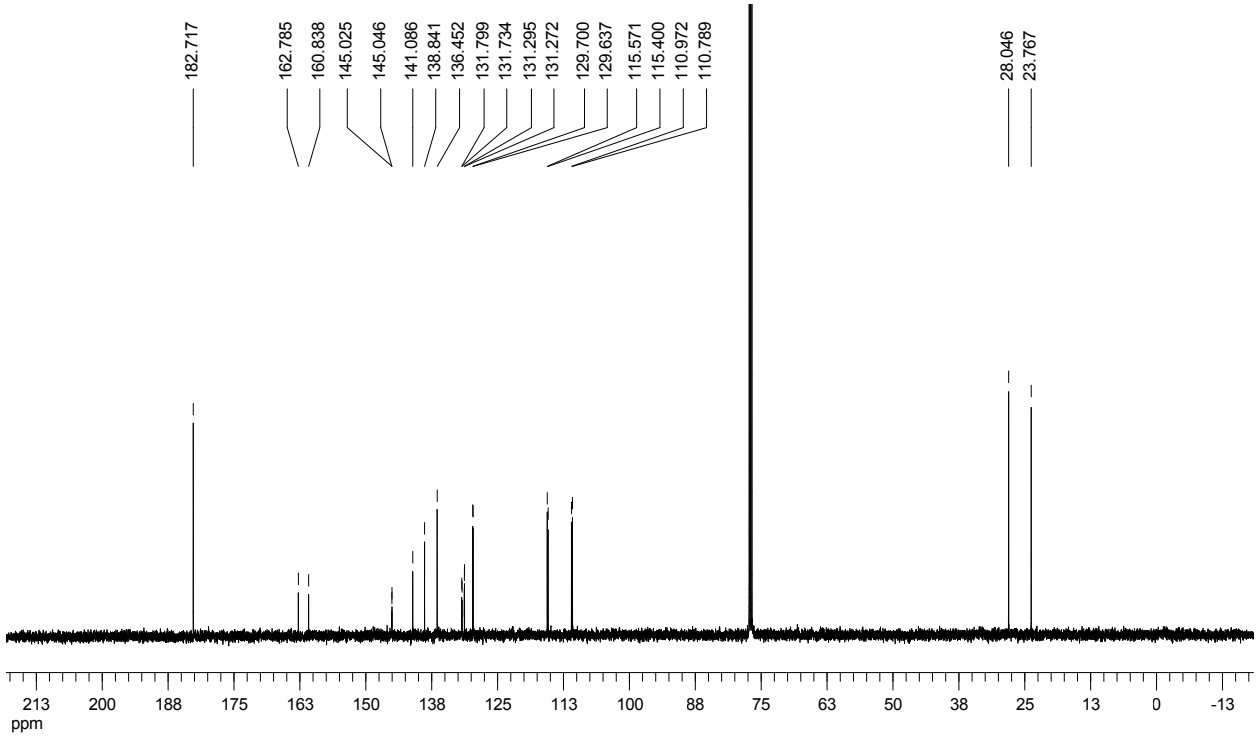
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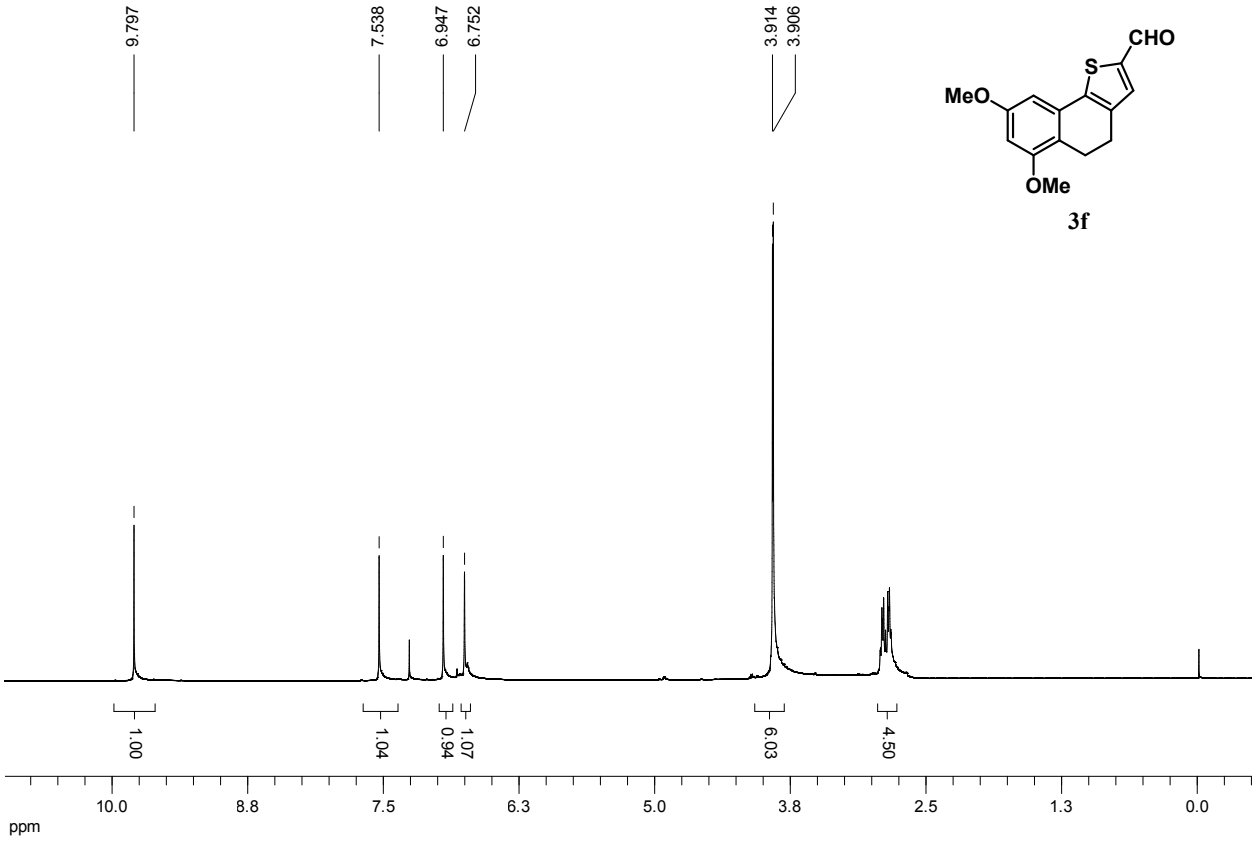
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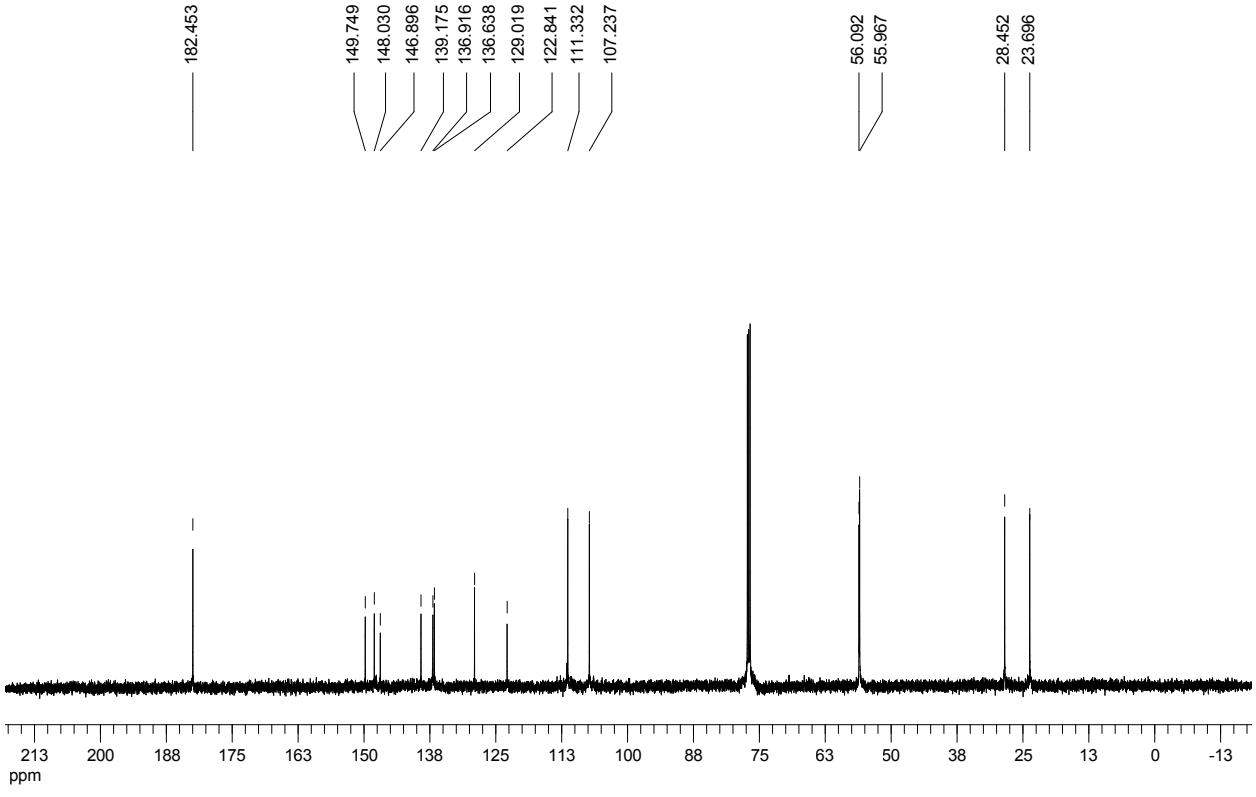
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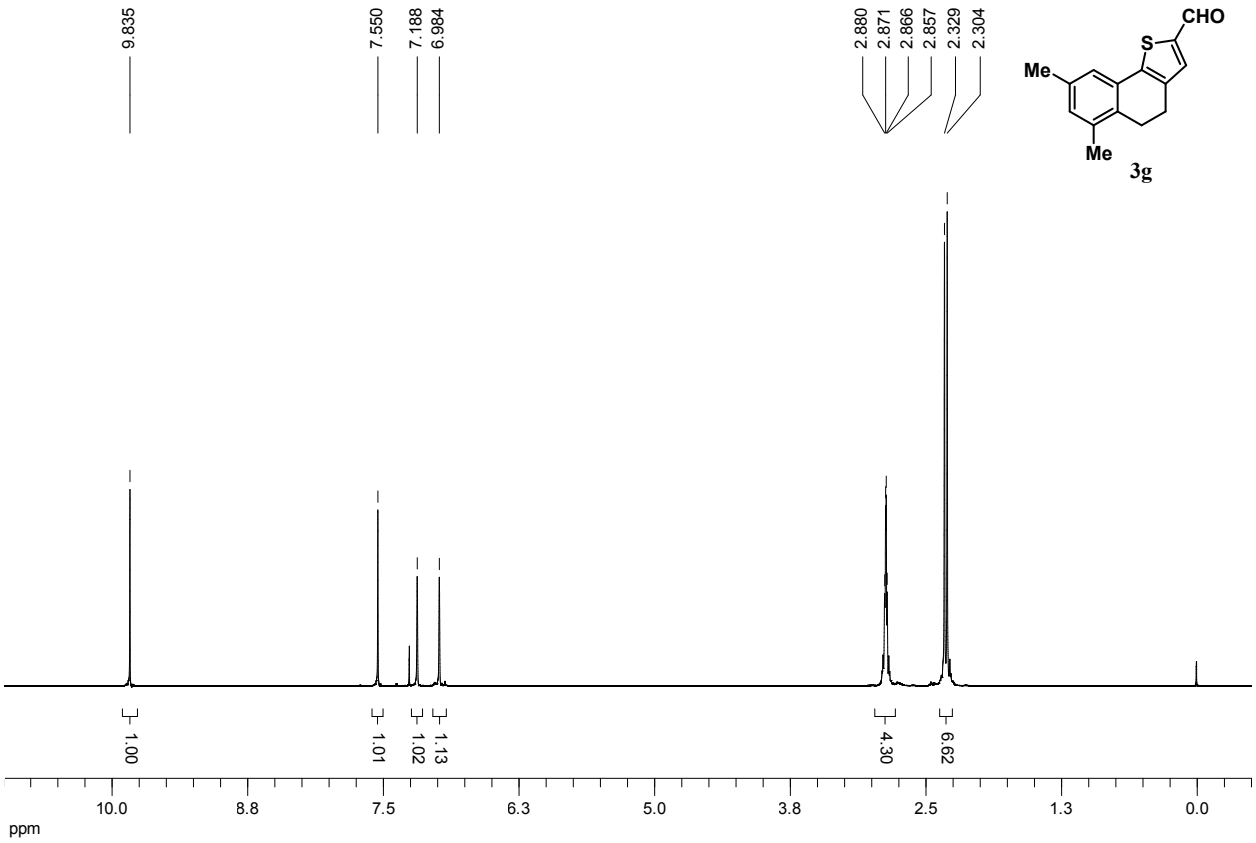
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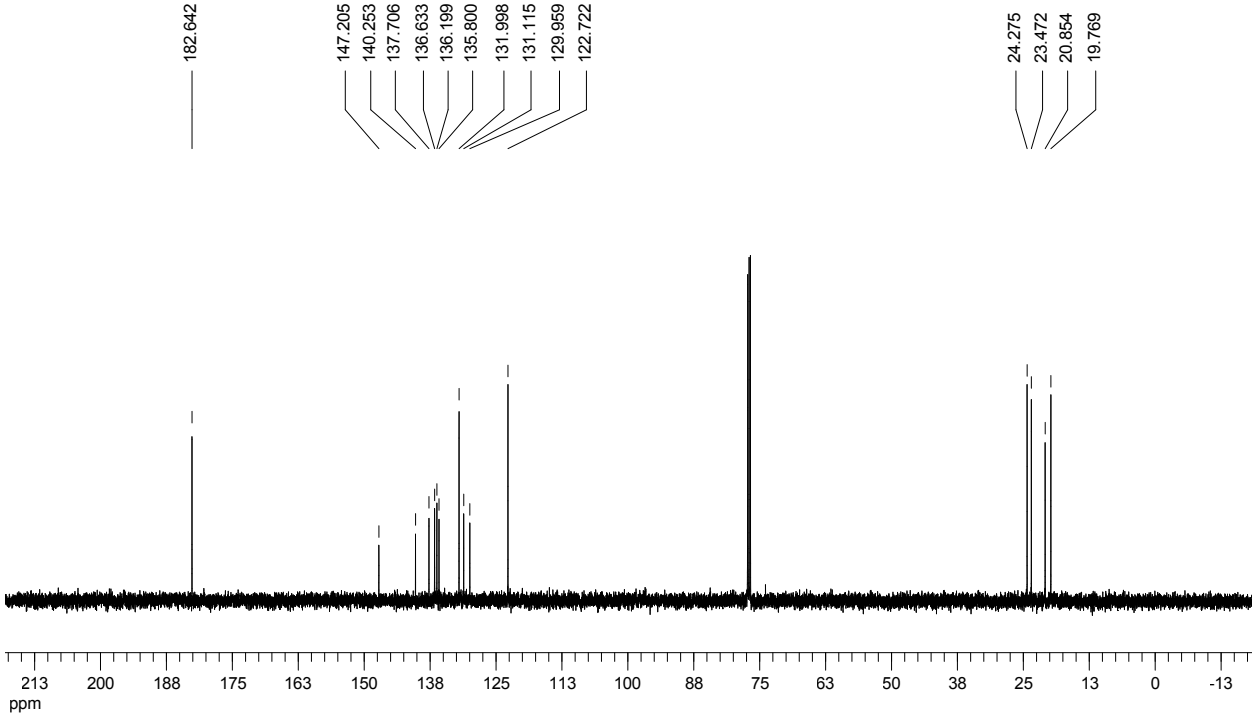
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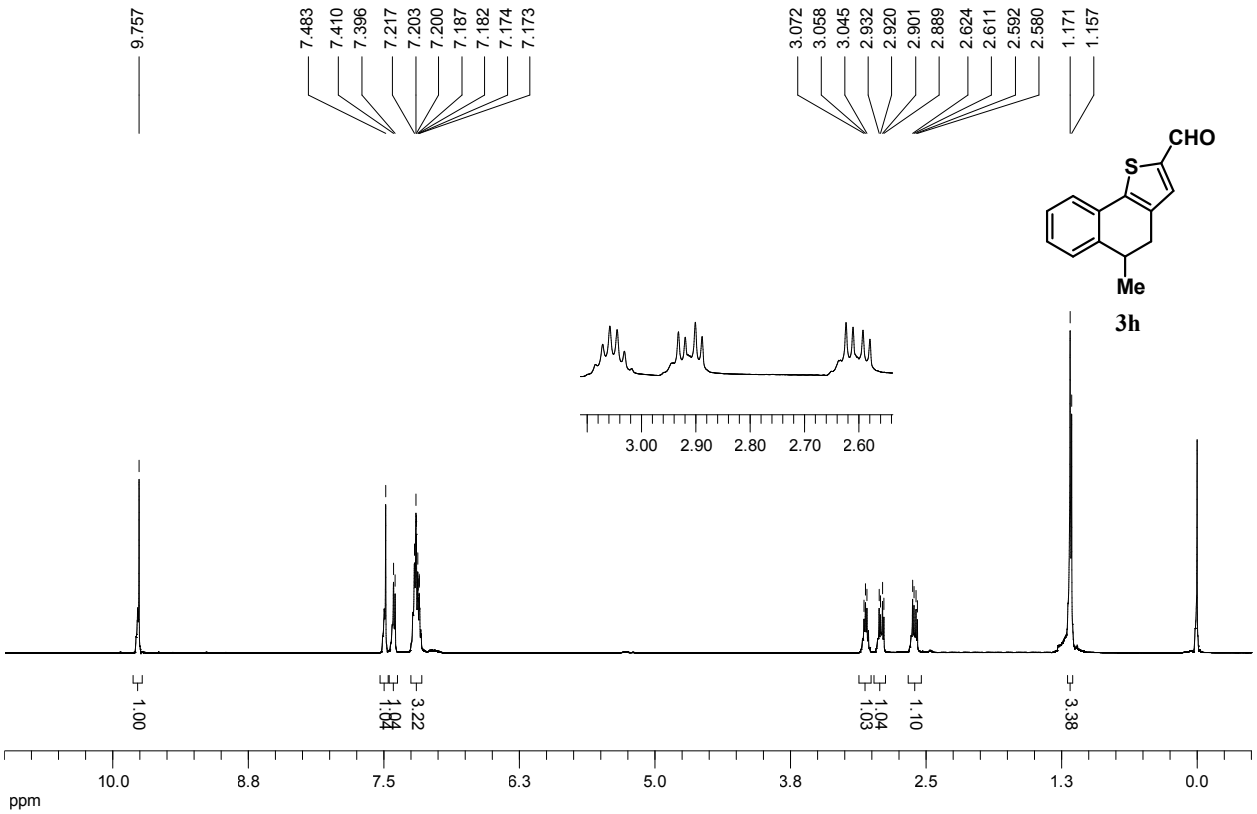
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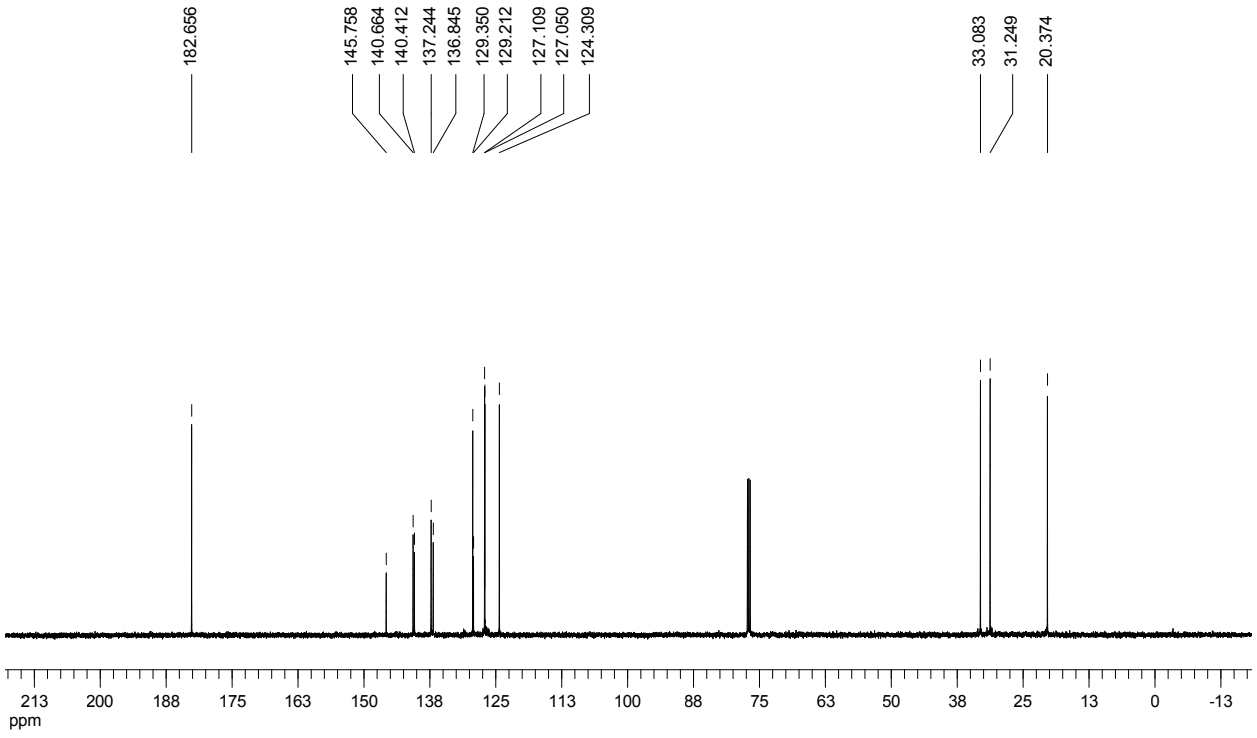
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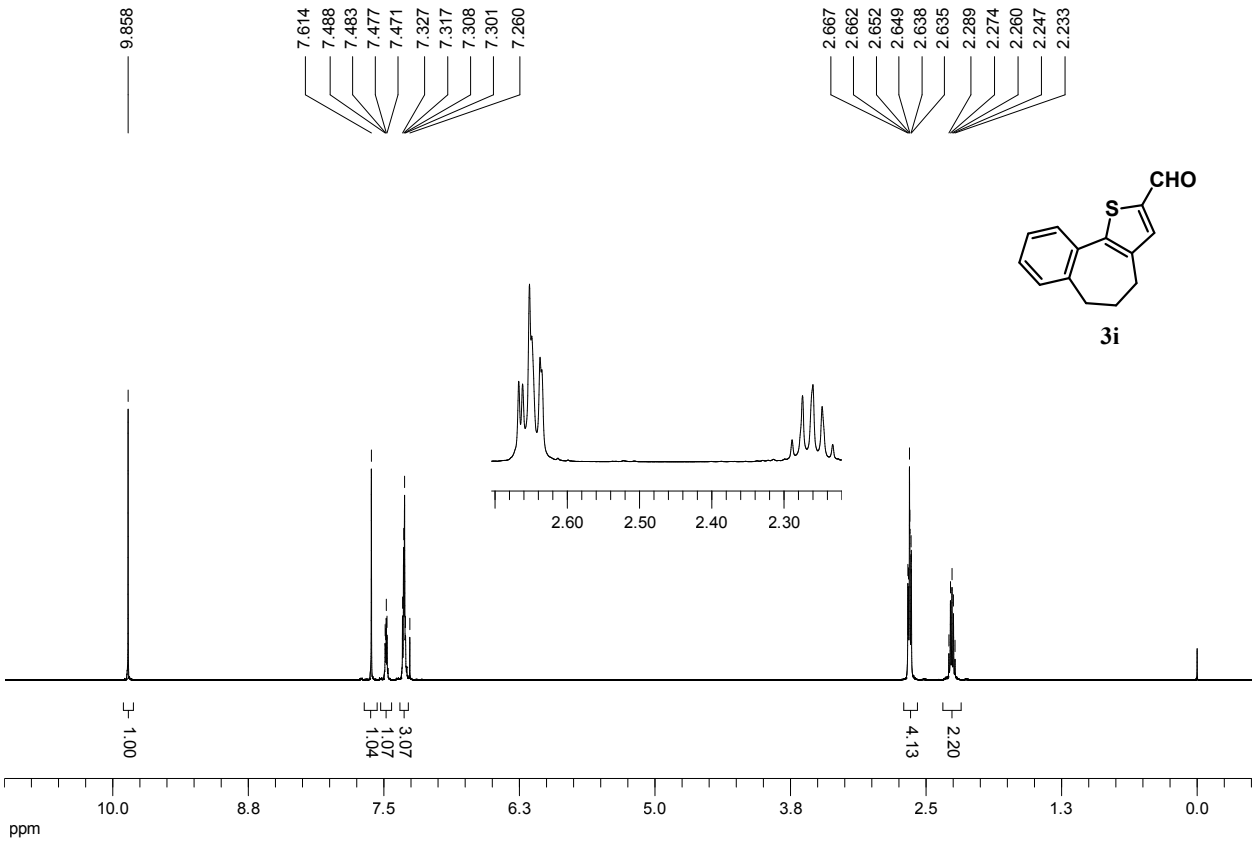
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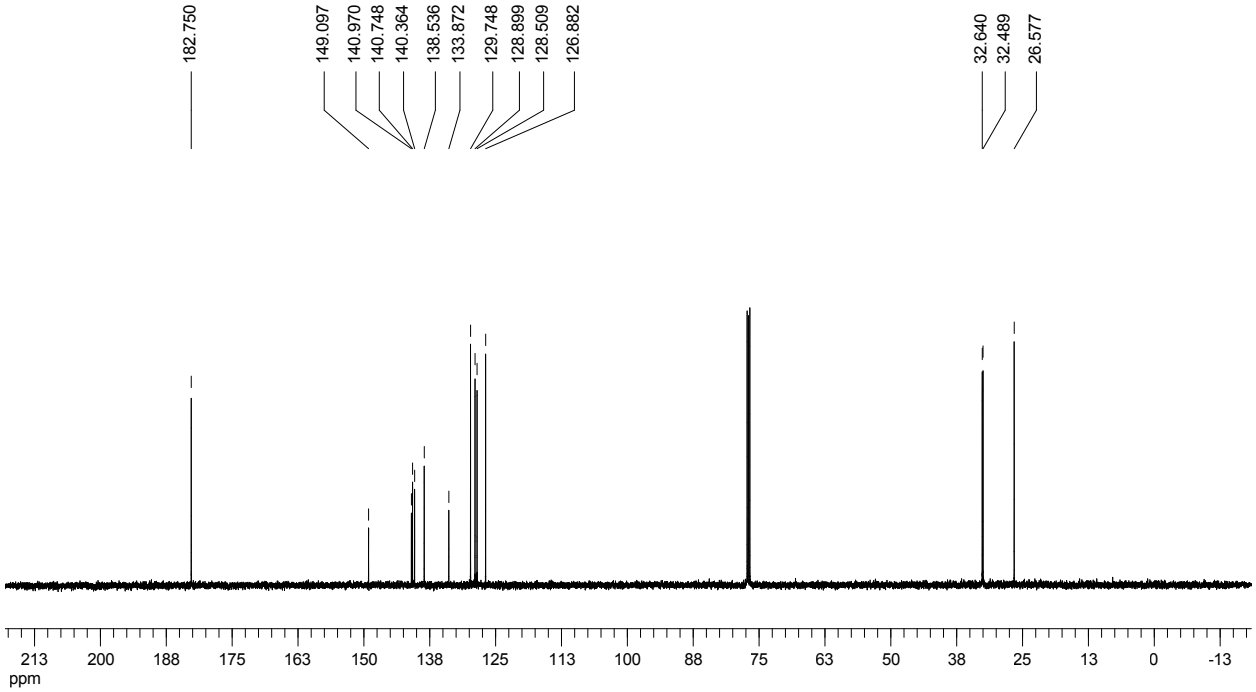
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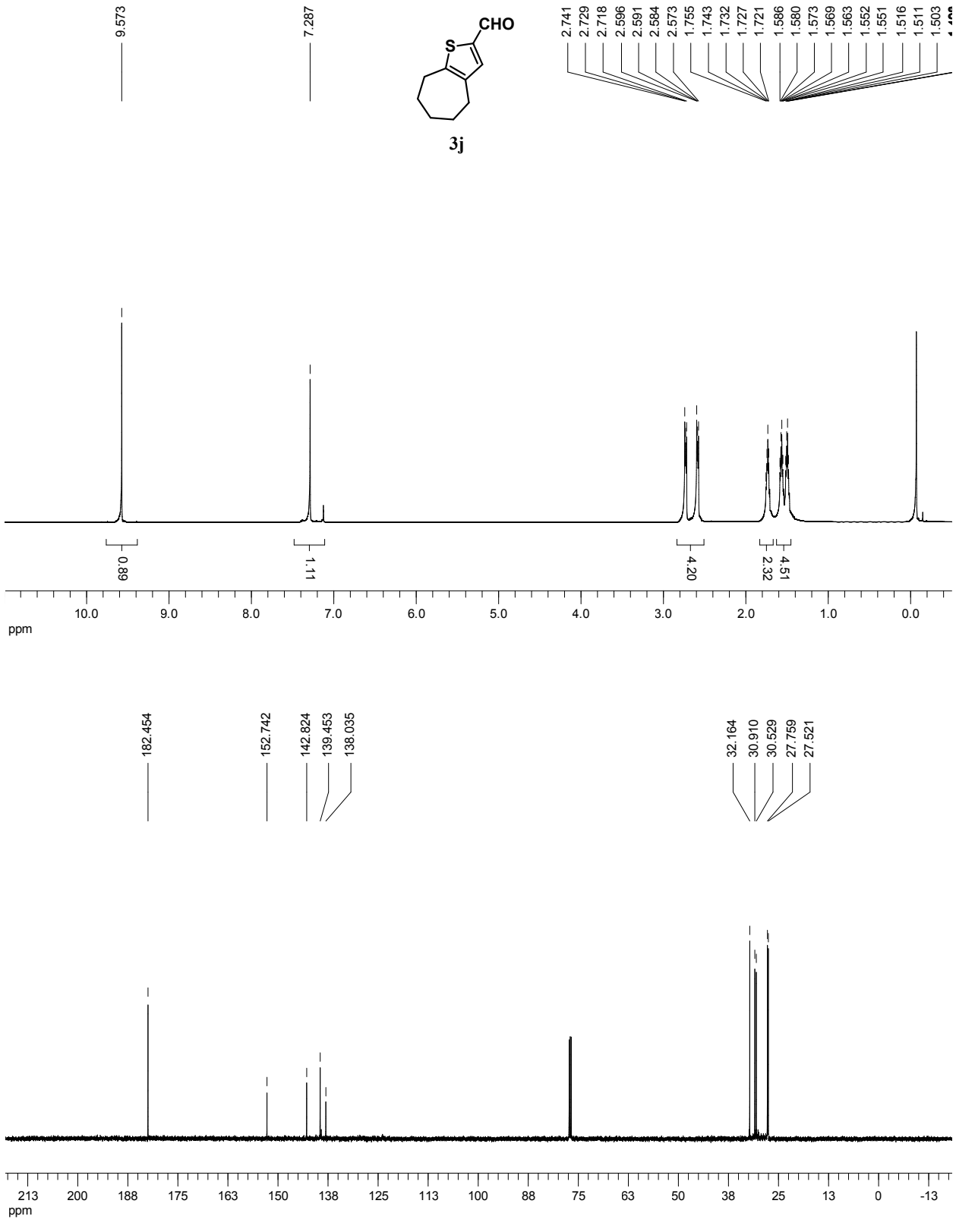
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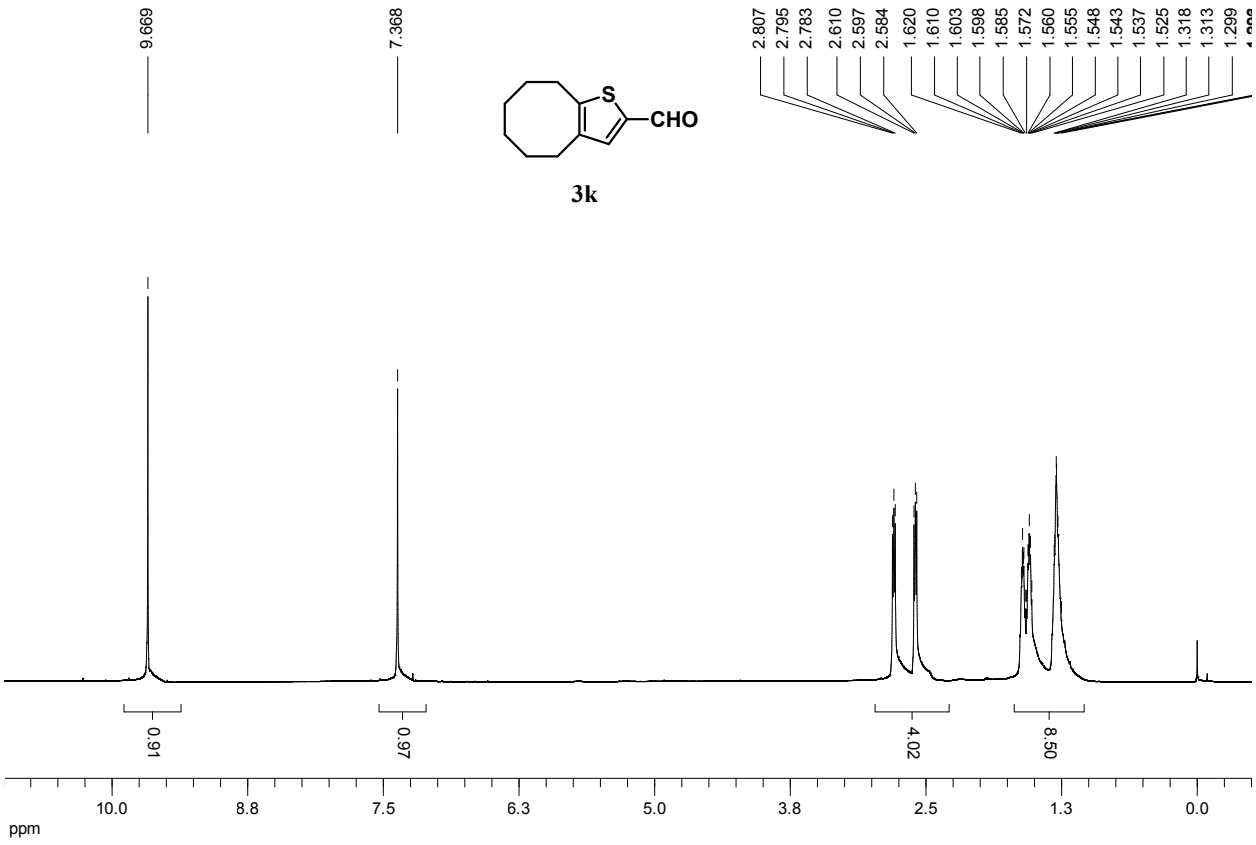
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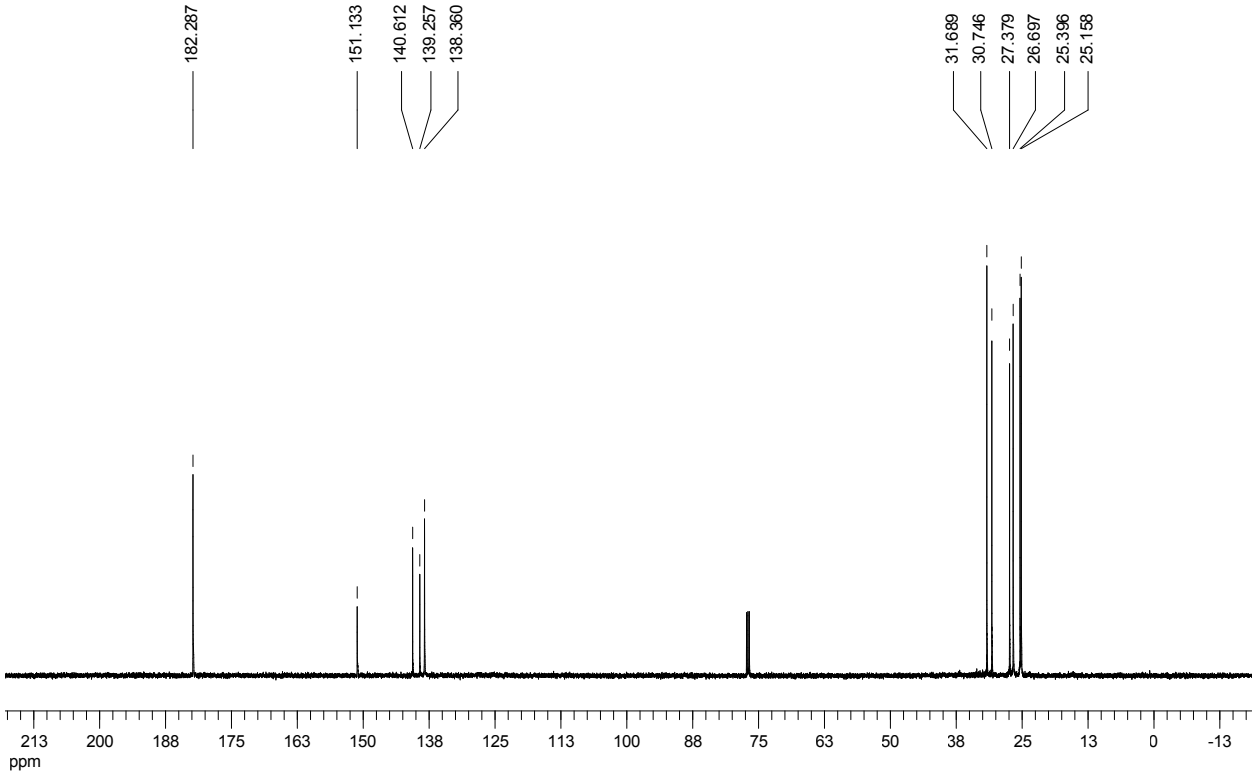
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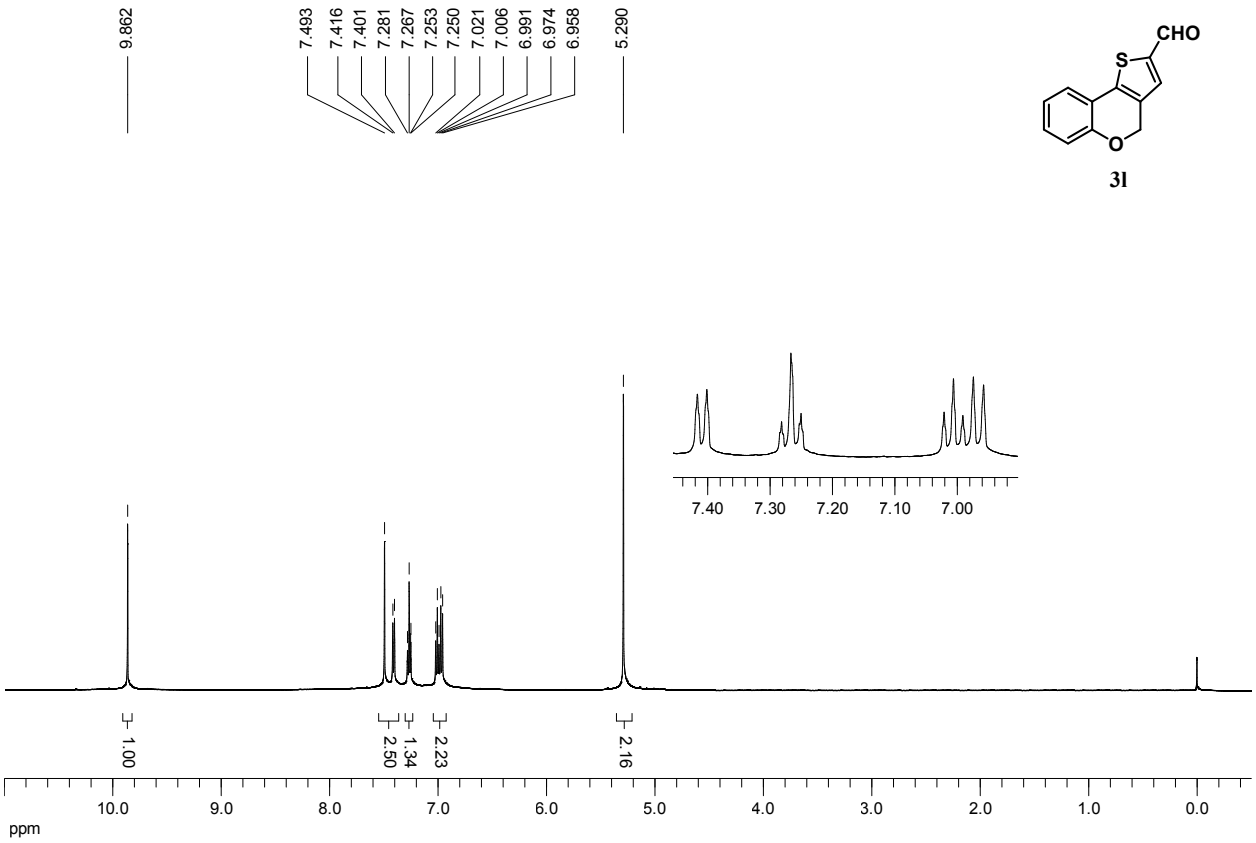
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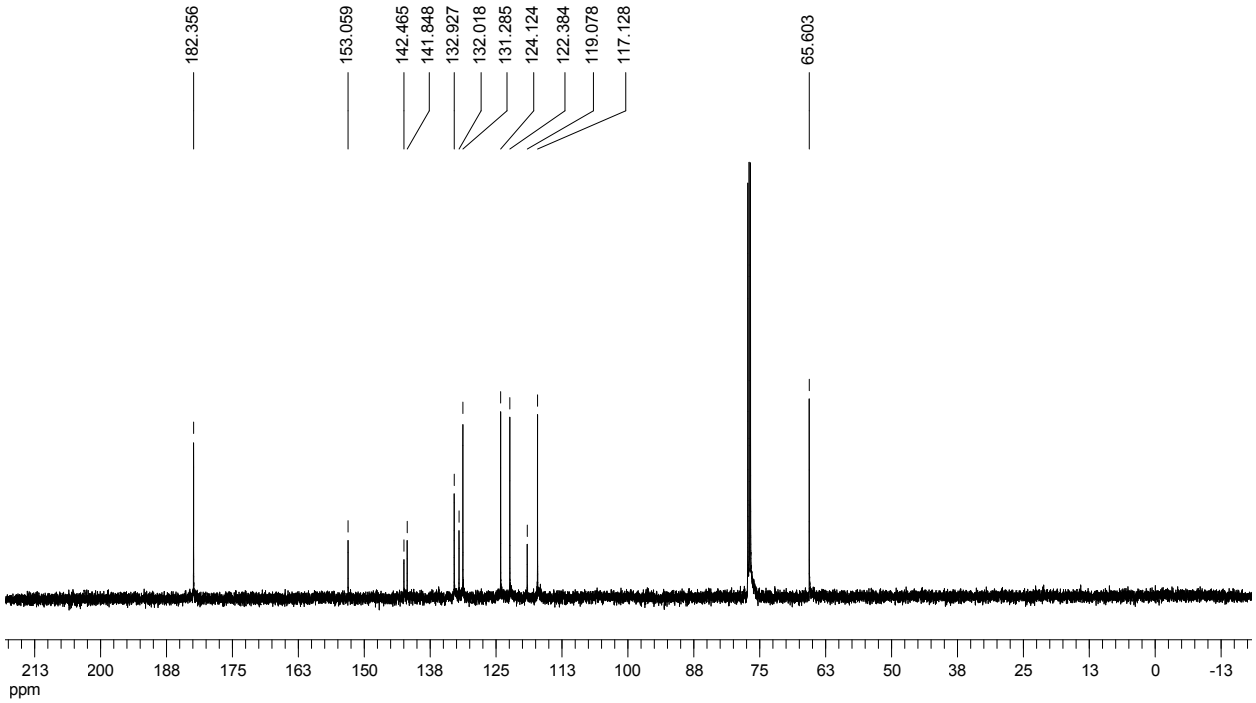
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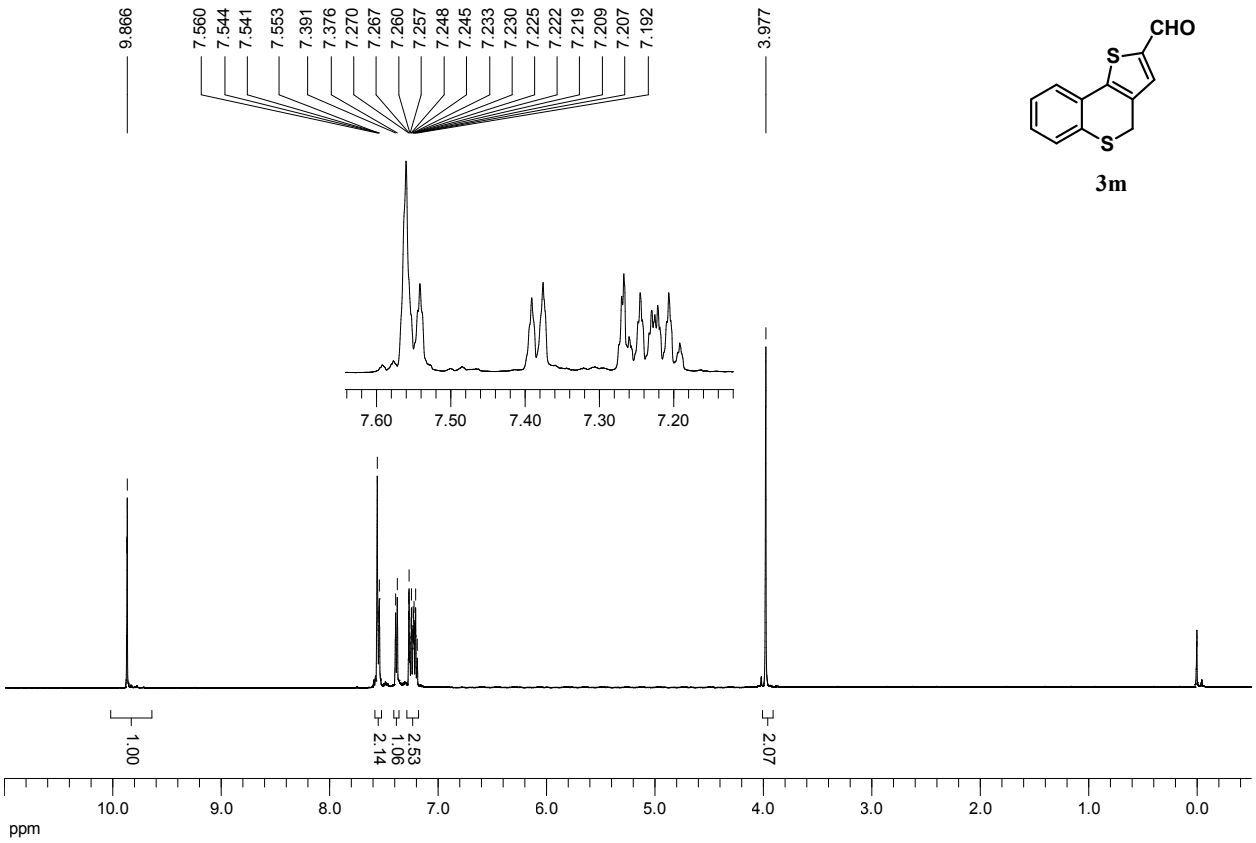
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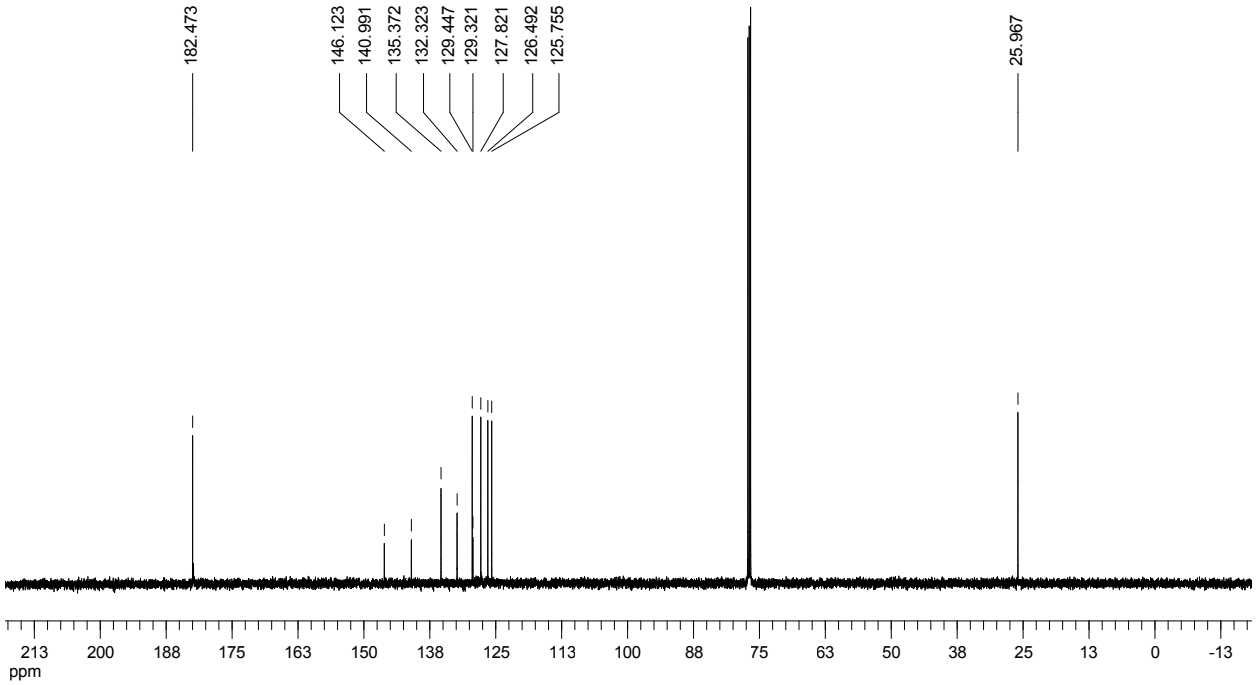
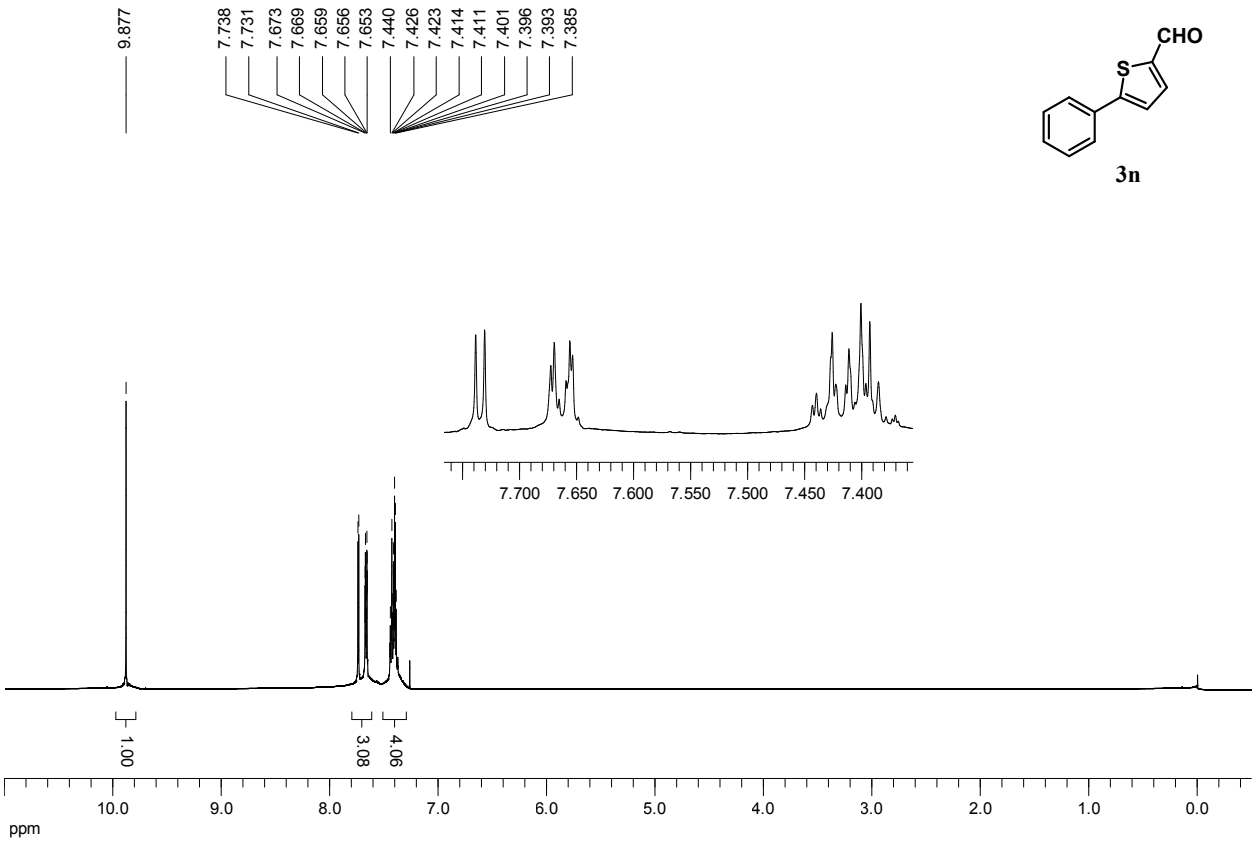
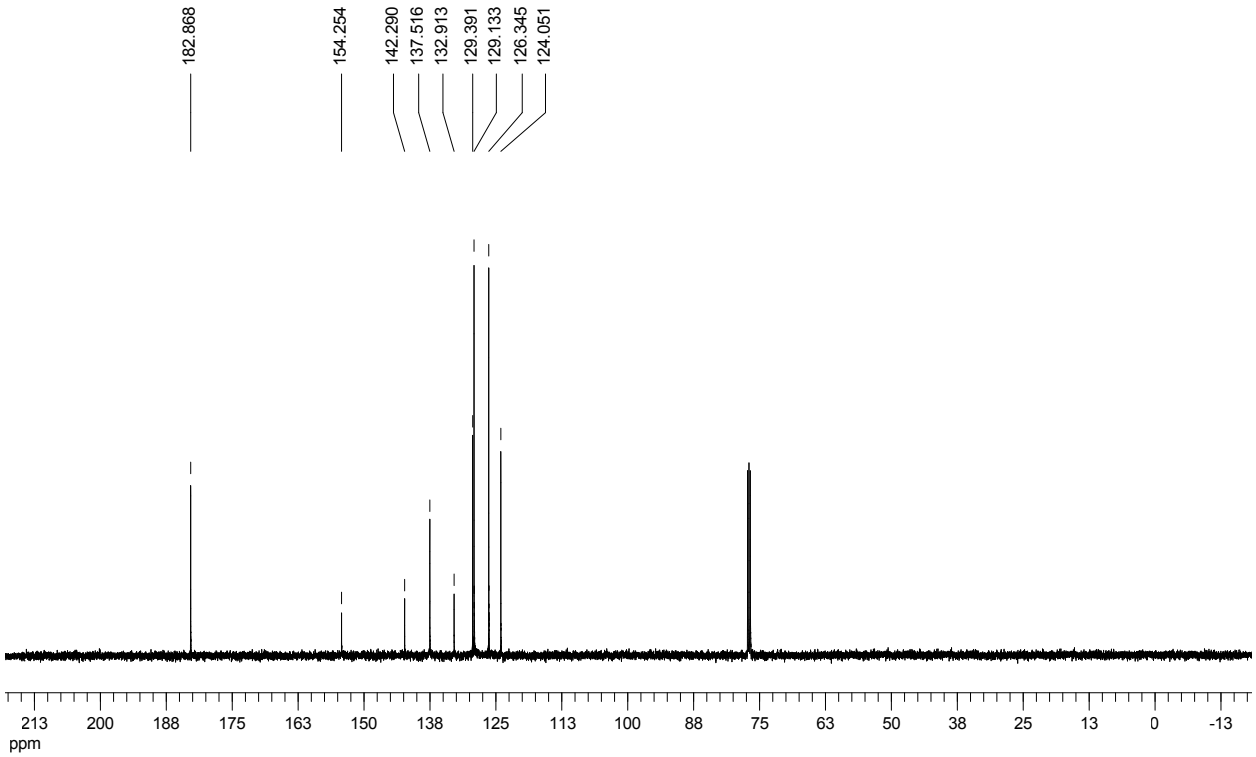
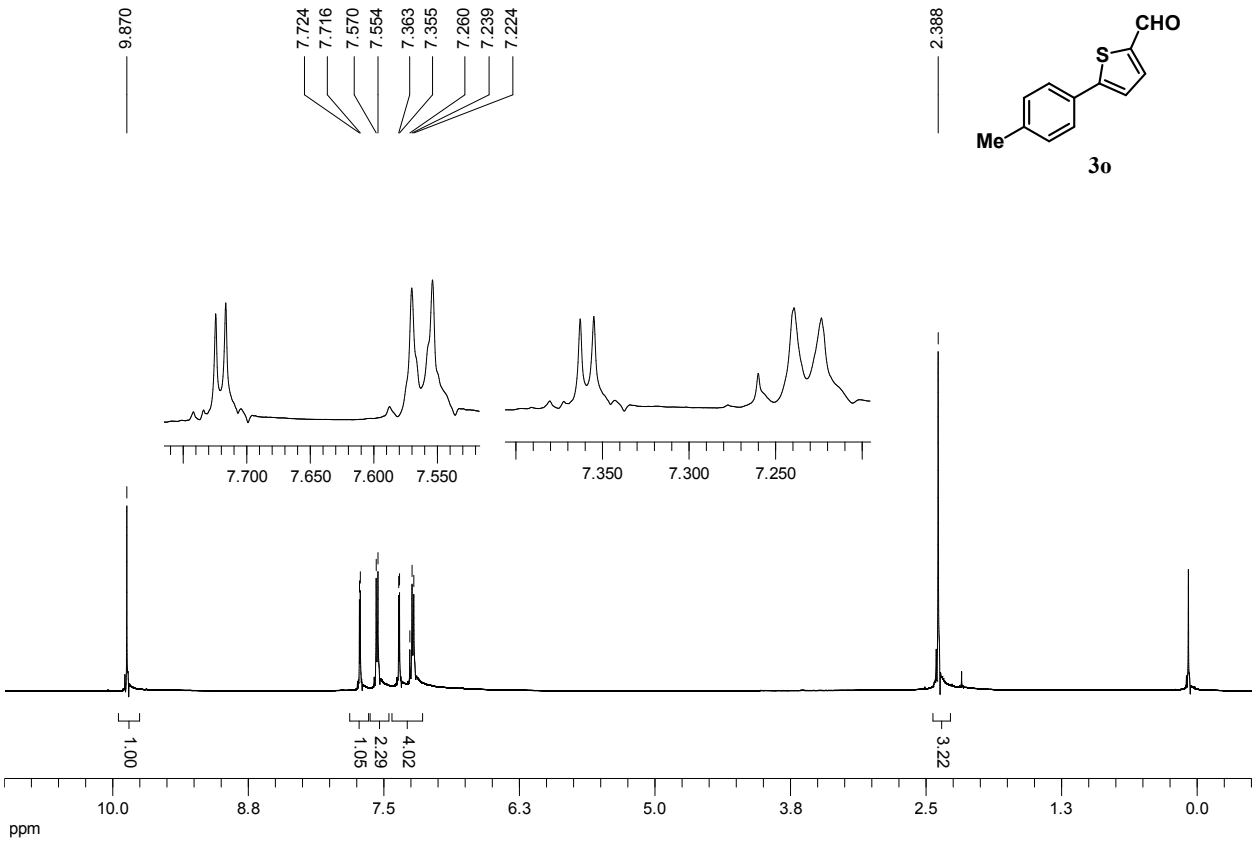
7.260
7.257
7.248
7.245
7.233
7.230
7.225
7.222
7.219
7.209
7.207
7.192
3.977
CHO
S
S
7.60
7.50
7.40
7.30
7.20
1.00
2.14
1.06
2.53
2.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

3m

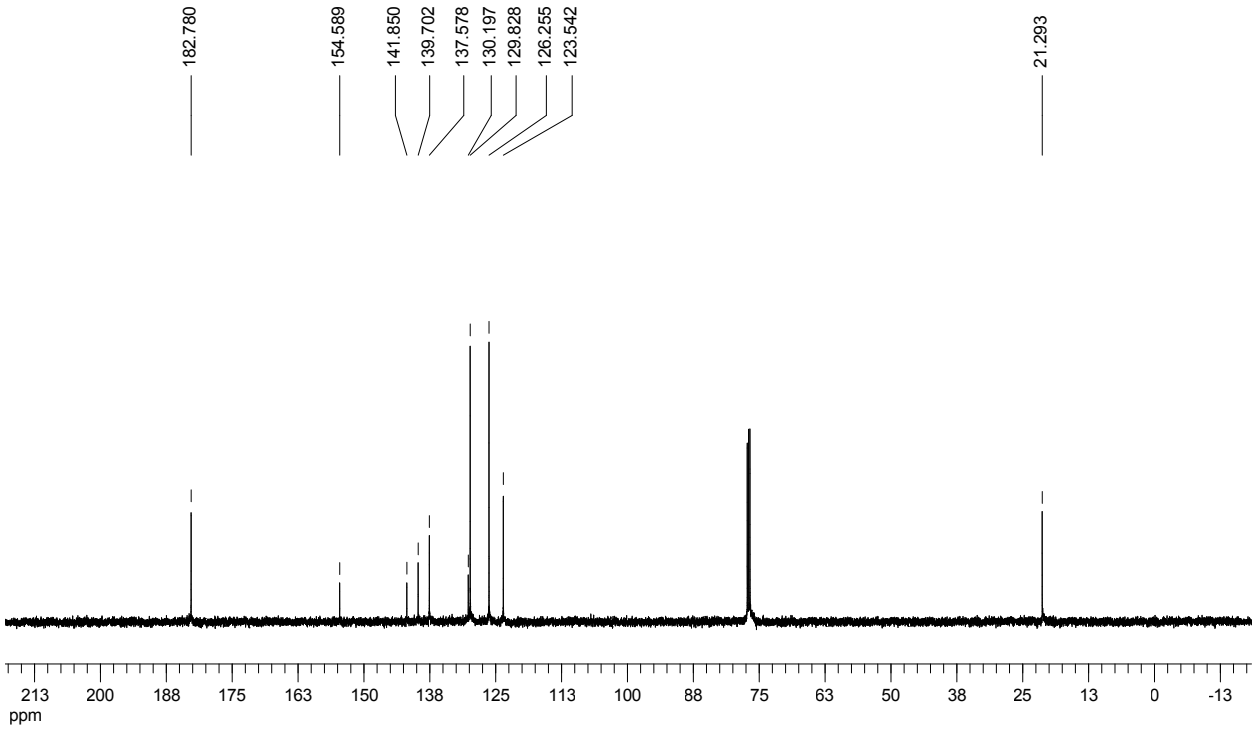

182.473
146.123
140.991
135.372
132.323
129.447
129.321
127.821
126.492
125.755
25.967
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm

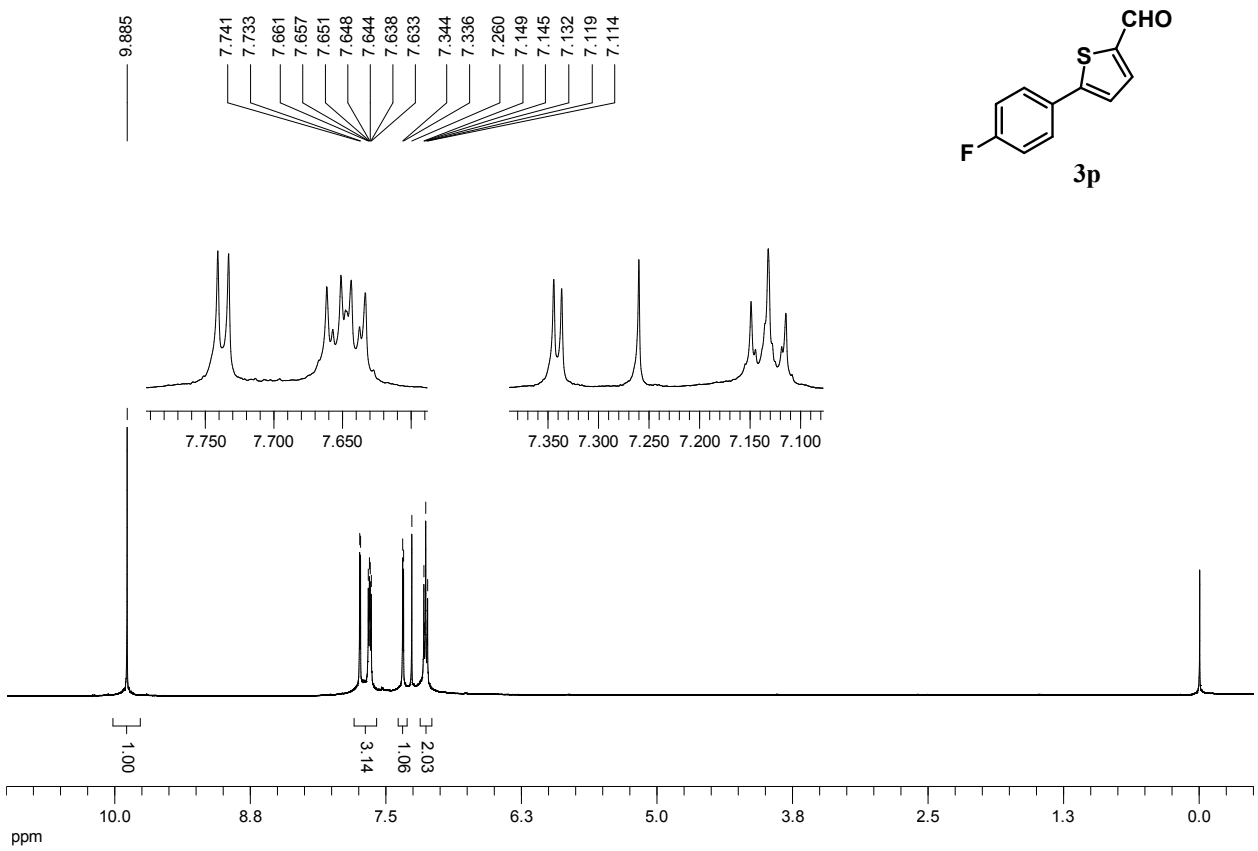

9.877
7.738
7.731
7.673
7.669
7.659
7.656
7.653
7.440
7.426
7.423
7.414
7.411
7.401
7.396
7.393
7.385
CHO
S
3n
7.700 7.650 7.600 7.550 7.500 7.450 7.400
1.00
3.08
4.06
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm

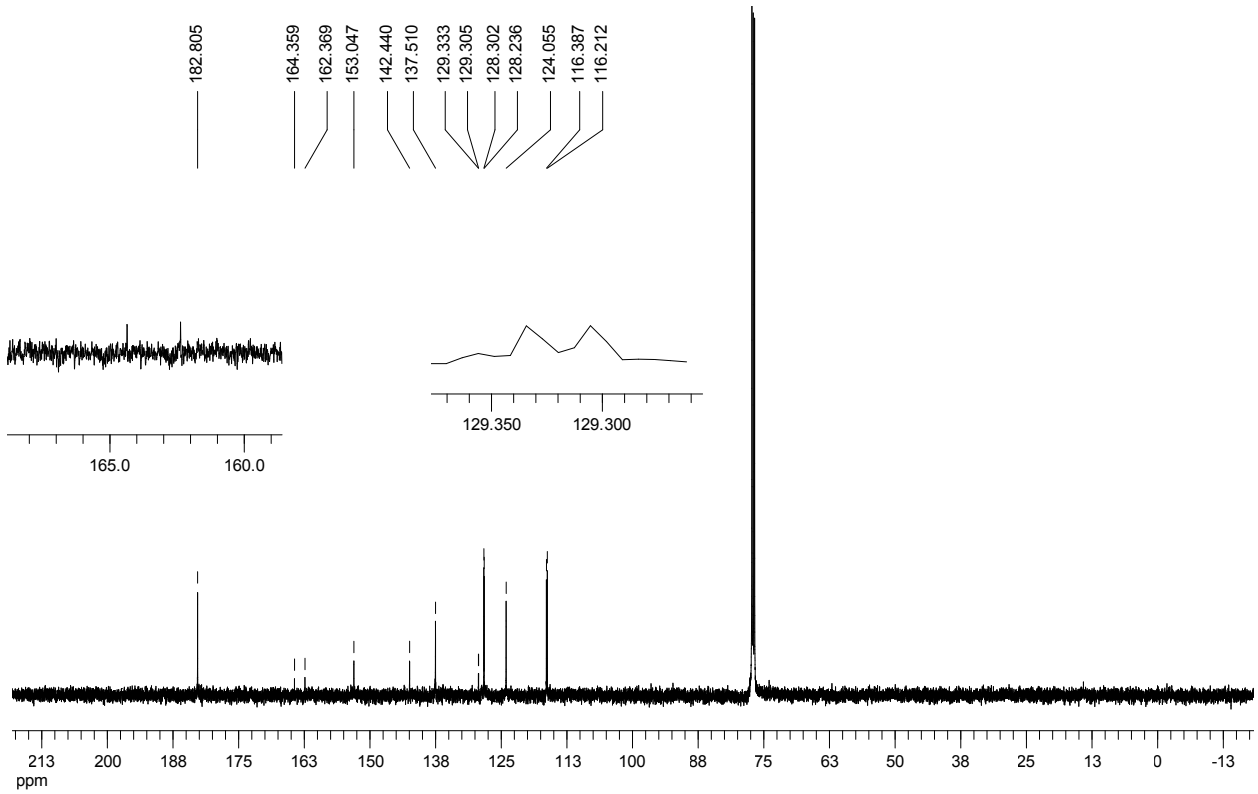

182.868
154.254
142.290
137.516
132.913
129.391
129.133
126.345
124.051
213 200 188 175 163 150 138 125 113 100 88 75 63 50 38 25 13 0 -13
ppm

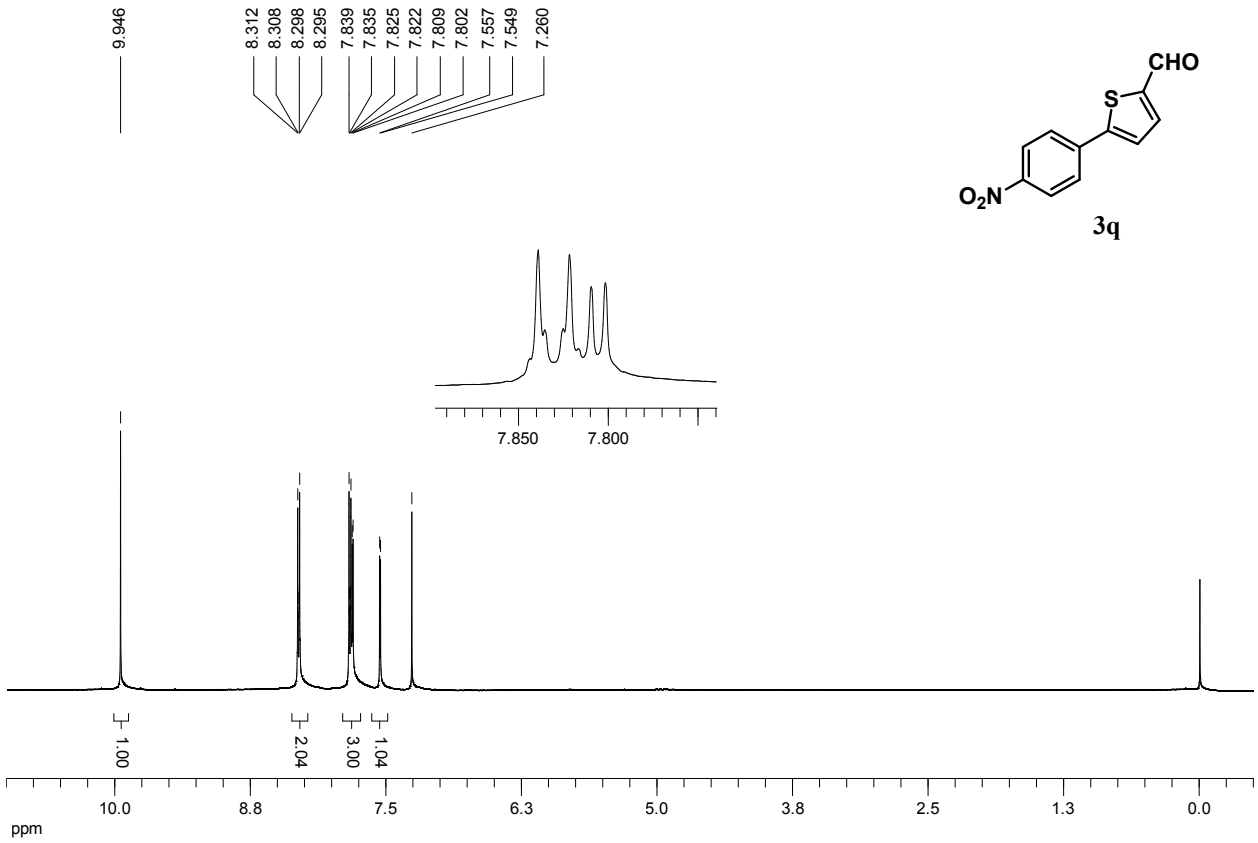

9.870
7.724
7.716
7.570
7.554
7.363
7.355
7.260
7.239
7.224
2.388
CHO
S
Me
7.700
7.650
7.600
7.550
7.350
7.300
7.250
1.00
1.05
2.29
4.02
3.22
10.0
8.8
7.5
6.3
5.0
3.8
2.5
1.3
0.0
ppm

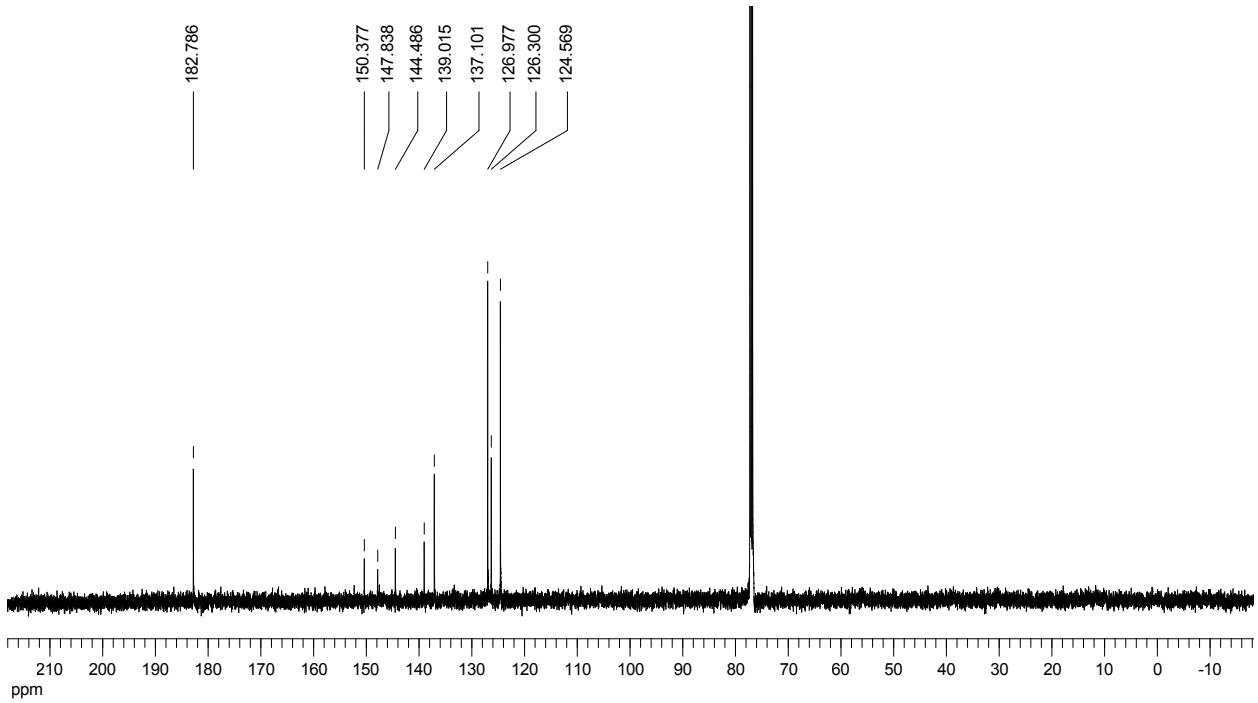
3o

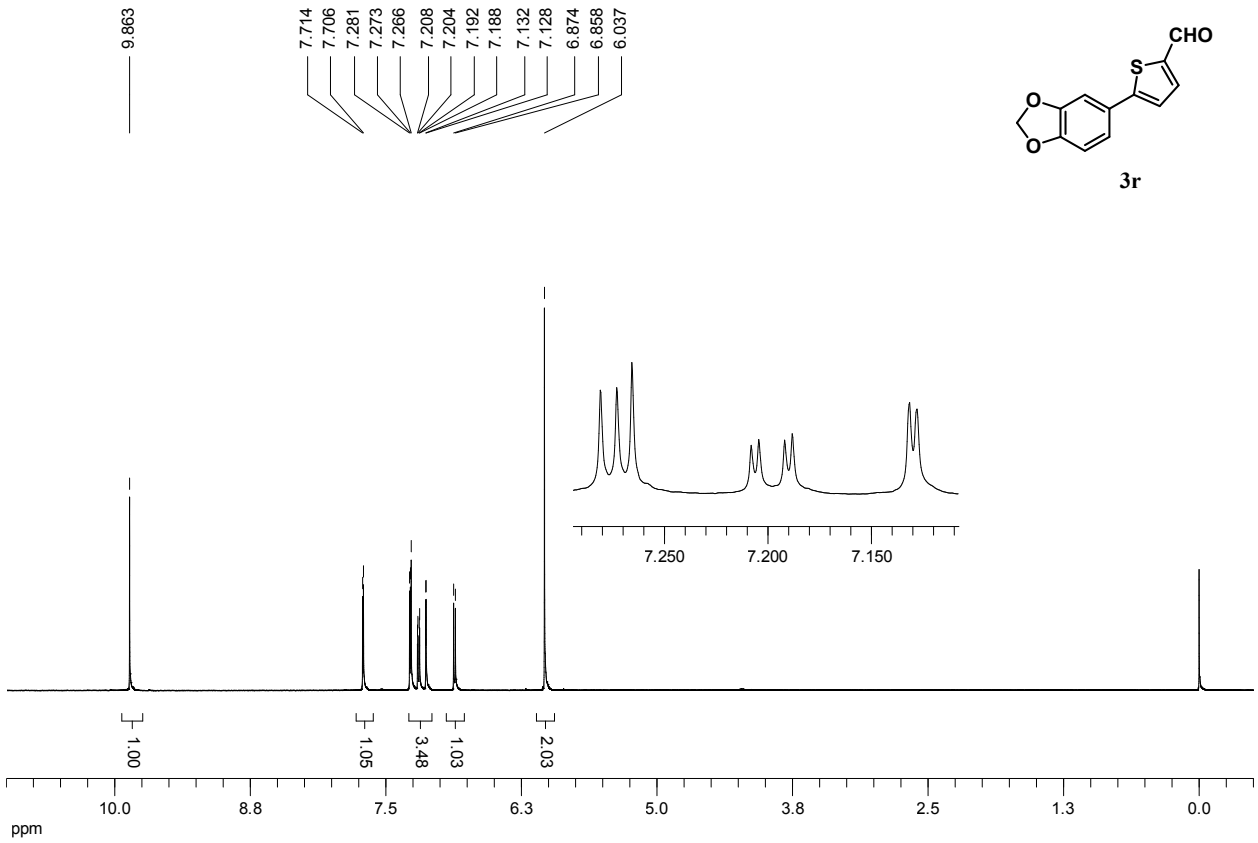

182.780
154.589
141.850
139.702
137.578
130.197
129.828
126.255
123.542
21.293
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm


9.885
7.741
7.733
7.661
7.657
7.651
7.648
7.644
7.638
7.633
7.344
7.336
7.260
7.149
7.145
7.132
7.119
7.114
CHO
S
F
3p
7.750
7.700
7.650
7.350
7.300
7.250
7.200
7.150
7.100
1.00
3.14
1.06
2.03
10.0
8.8
7.5
6.3
5.0
3.8
2.5
1.3
0.0
ppm

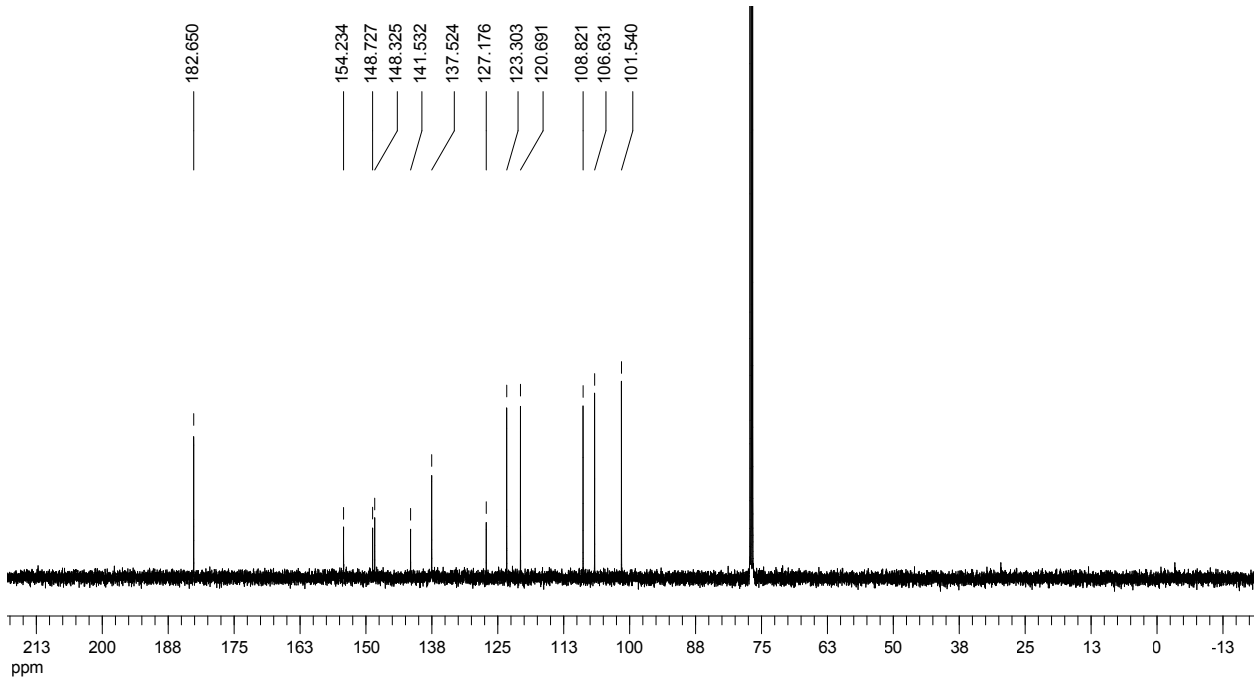

182.805
164.359
162.369
153.047
142.440
137.510
129.333
129.305
128.302
128.236
124.055
116.387
116.212
165.0
160.0
129.350
129.300
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm

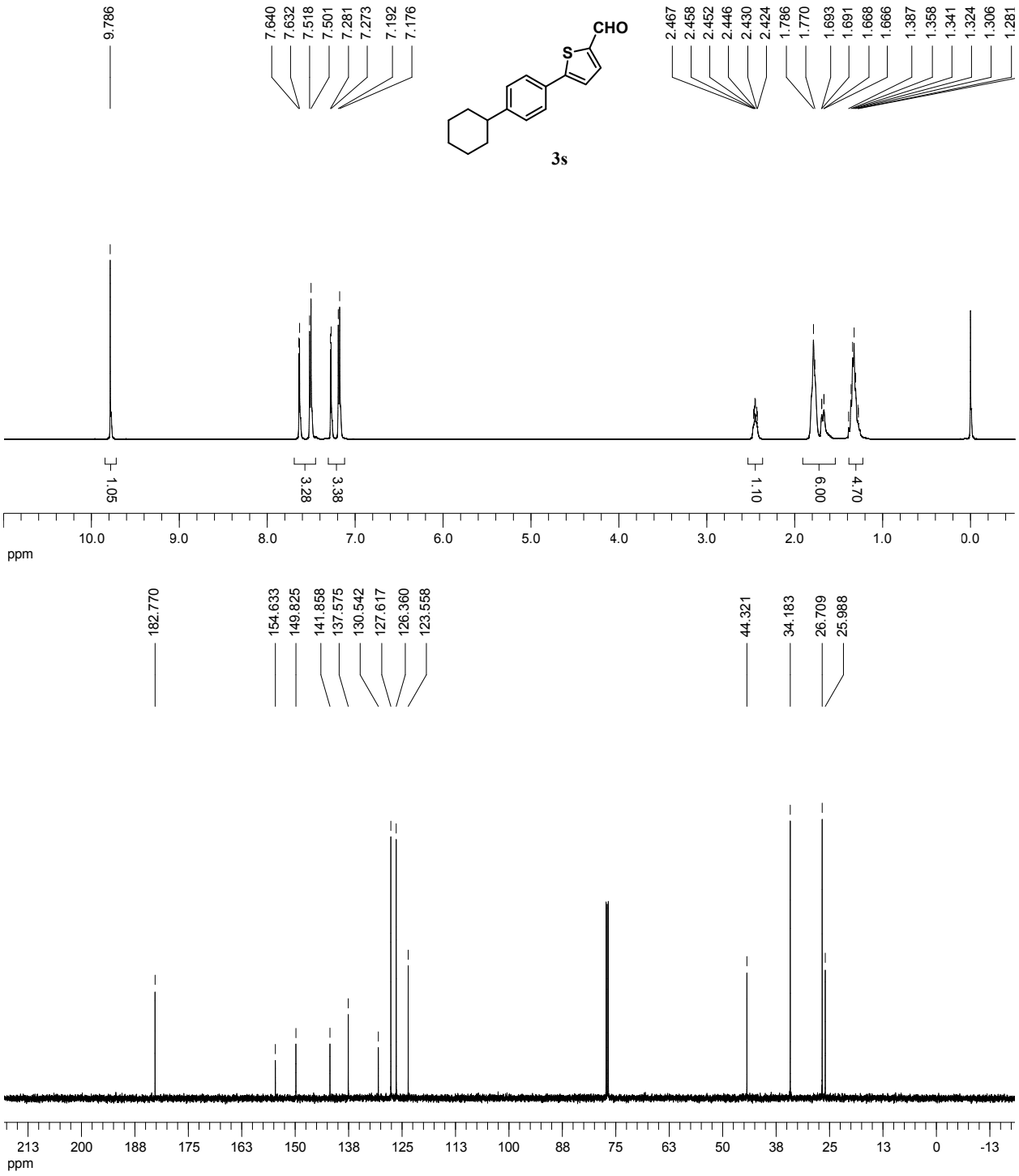

9.946
8.312
8.308
8.298
8.295
7.839
7.835
7.825
7.822
7.809
7.802
7.557
7.549
7.260
CHO
S
O2N
3q
7.850
7.800
1.00
2.04
3.00
1.04
10.0
8.8
7.5
6.3
5.0
3.8
2.5
1.3
0.0
ppm

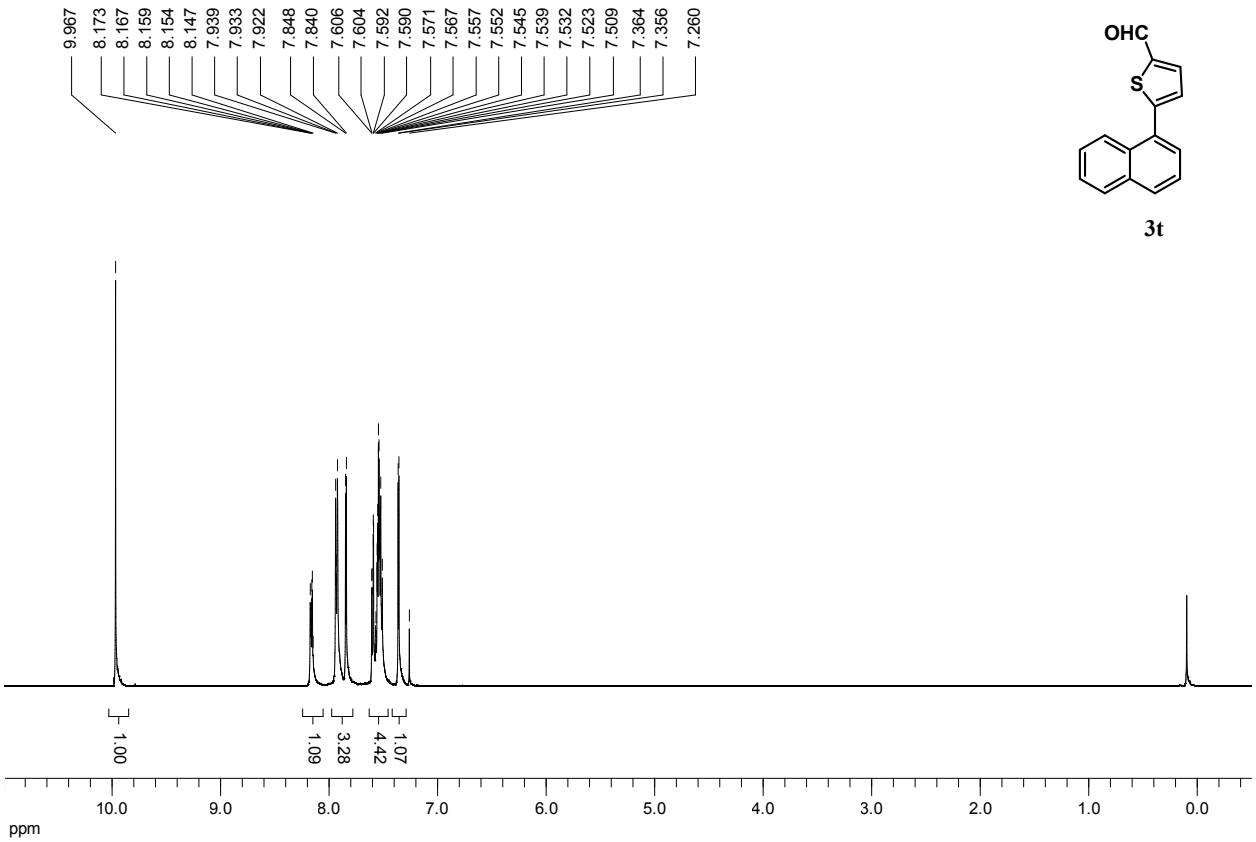

182.786
150.377
147.838
144.486
139.015
137.101
126.977
126.300
124.569
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


9.863
7.714
7.706
7.281
7.273
7.266
7.208
7.204
7.192
7.188
7.132
7.128
6.874
6.858
6.037
CHO
S
O
O
7.250
7.200
7.150
1.00
1.05
3.48
1.03
2.03
10.0
8.8
7.5
6.3
5.0
3.8
2.5
1.3
0.0
ppm

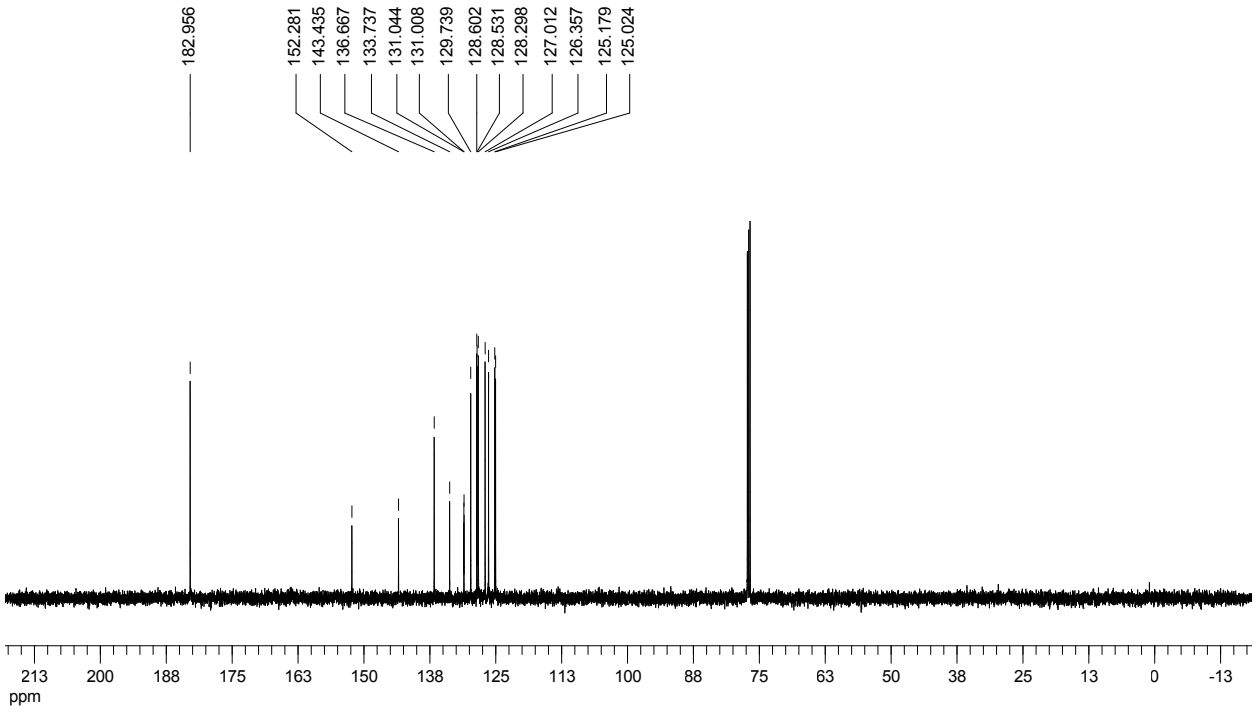
3r

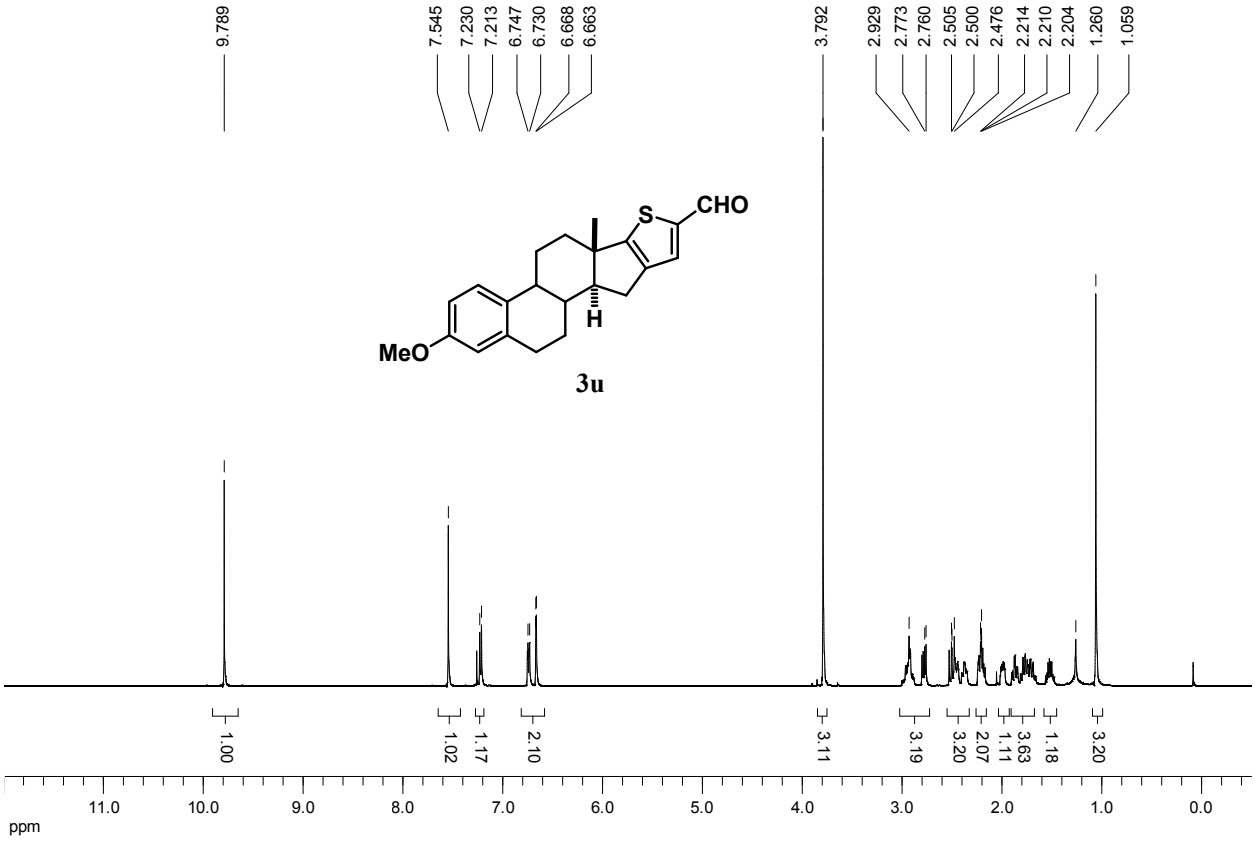

182.650
154.234
148.727
148.325
141.532
137.524
127.176
123.303
120.691
108.821
106.631
101.540
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm


9.786
7.640
7.632
7.518
7.501
7.281
7.273
7.192
7.176
CHO
S
2.467
2.458
2.452
2.446
2.430
2.424
1.786
1.770
1.693
1.691
1.668
1.666
1.387
1.358
1.341
1.324
1.306
1.281
3s
1.05
3.28
3.38
1.10
6.00
4.70
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm
182.770
154.633
149.825
141.858
137.575
130.542
127.617
126.360
123.558
44.321
34.183
26.709
25.988
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm

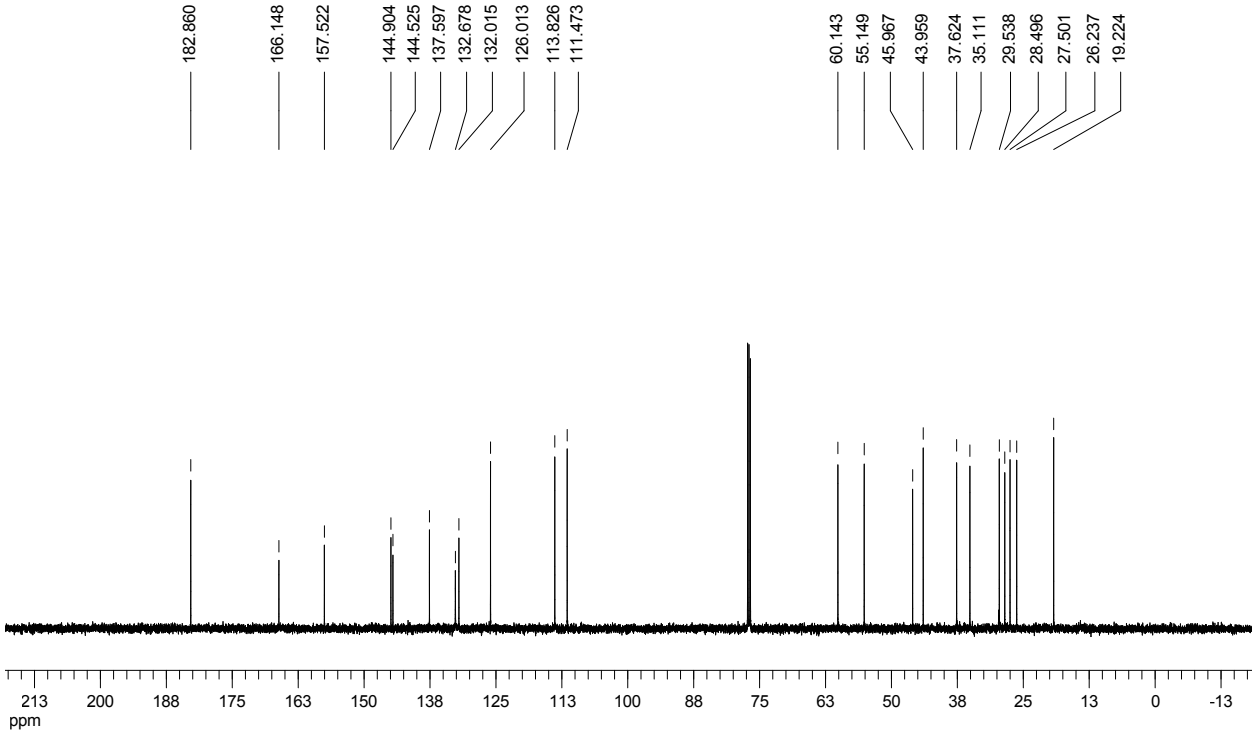

9.967
8.173
8.167
8.159
8.154
8.147
7.939
7.933
7.922
7.848
7.840
7.606
7.604
7.592
7.590
7.571
7.567
7.557
7.552
7.545
7.539
7.532
7.523
7.509
7.364
7.356
7.260
OHC
S
1.00
1.09
3.28
4.42
1.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

3t

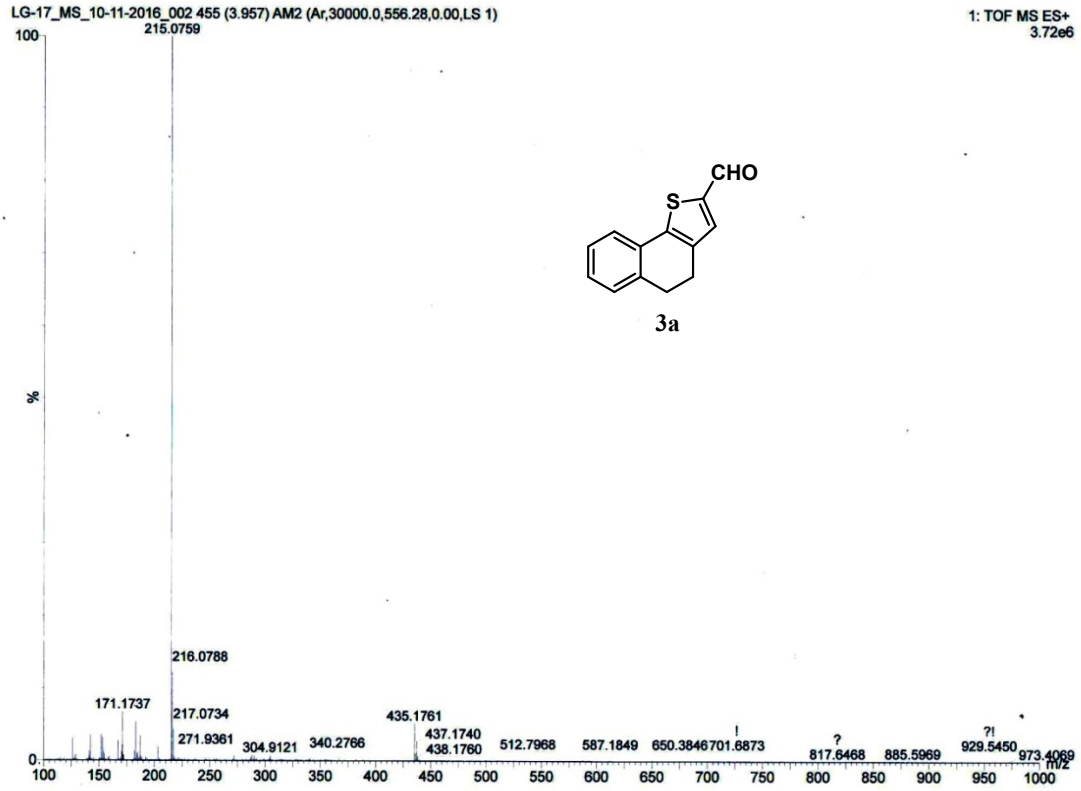

182.956
152.281
143.435
136.667
133.737
131.044
131.008
129.739
128.602
128.531
128.298
127.012
126.357
125.179
125.024
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm


9.789
7.545
7.230
7.213
6.747
6.730
6.668
6.663
3.792
2.929
2.773
2.760
2.505
2.500
2.476
2.214
2.210
2.204
1.260
1.059
S
CHO
H
MeO
1.00
1.02
1.17
2.10
3.11
3.19
3.20
2.07
1.11
3.63
1.18
3.20
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

3u

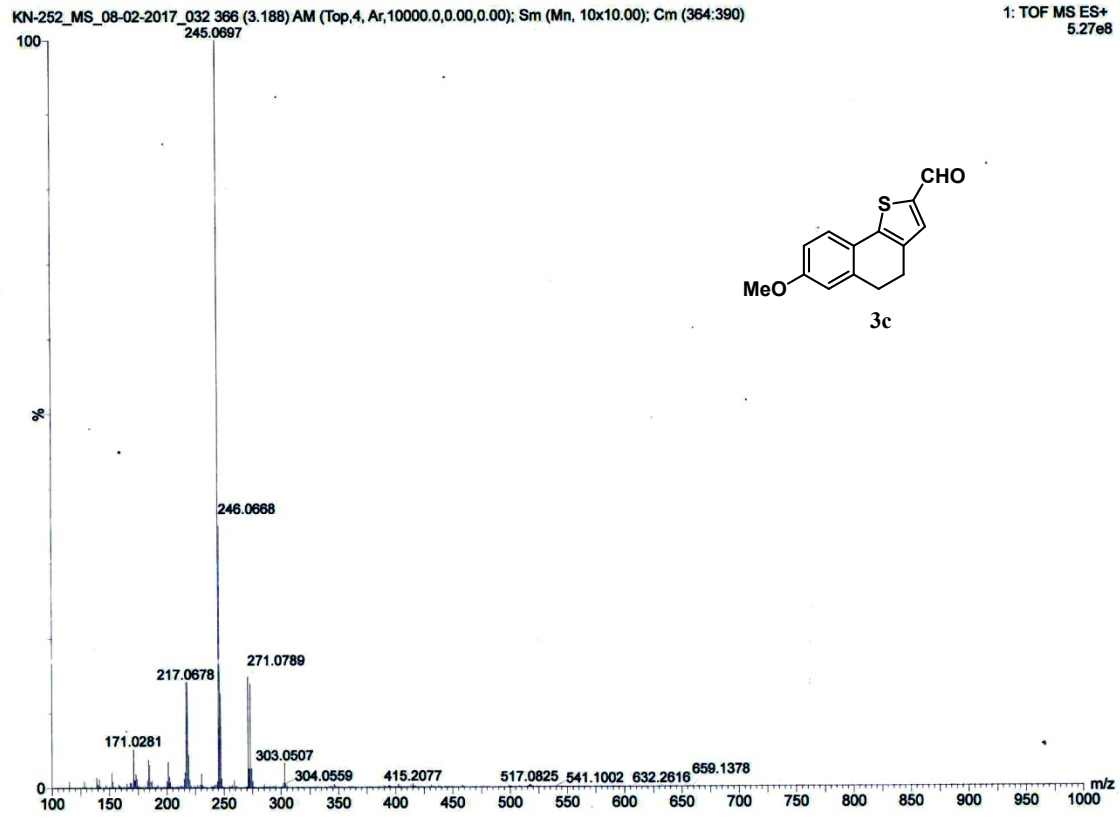

182.860
166.148
157.522
144.904
144.525
137.597
132.678
132.015
126.013
113.826
111.473
60.143
55.149
45.967
43.959
37.624
35.111
29.538
28.496
27.501
26.237
19.224
213
200
188
175
163
150
138
125
113
100
88
75
63
50
38
25
13
0
-13
ppm

Copies of HRMS spectra of all thiophene products

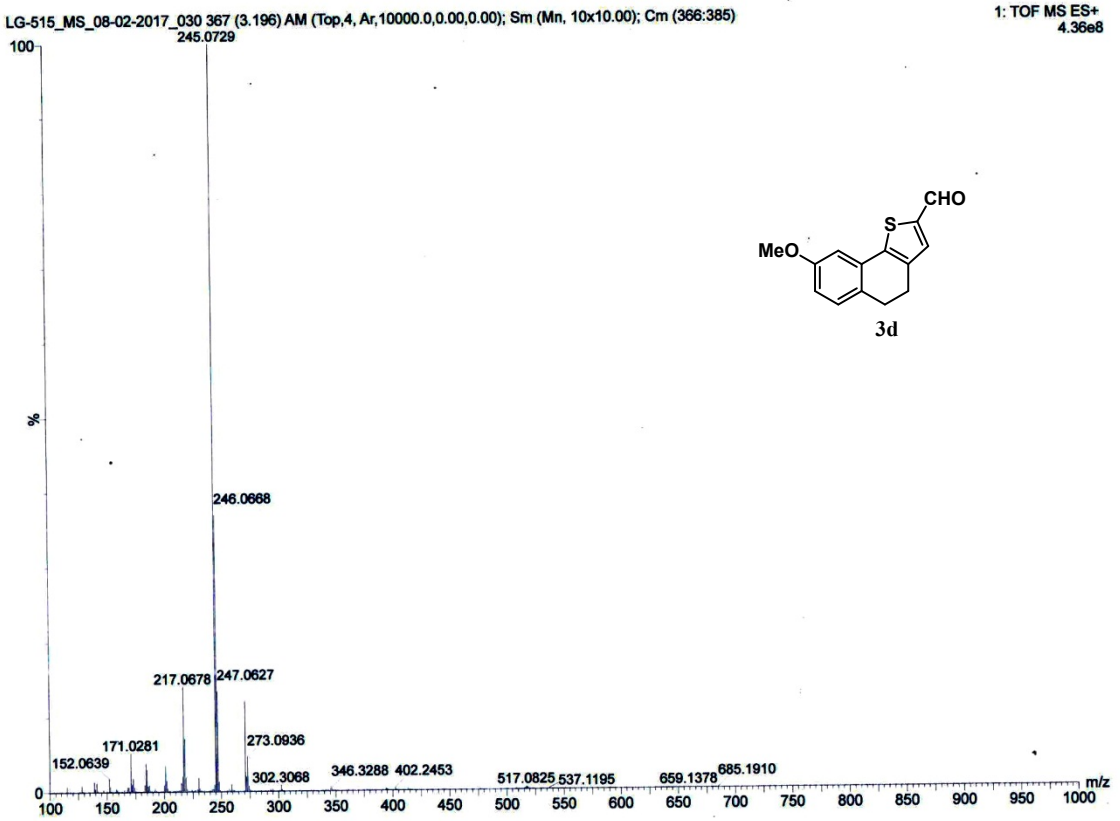


3a

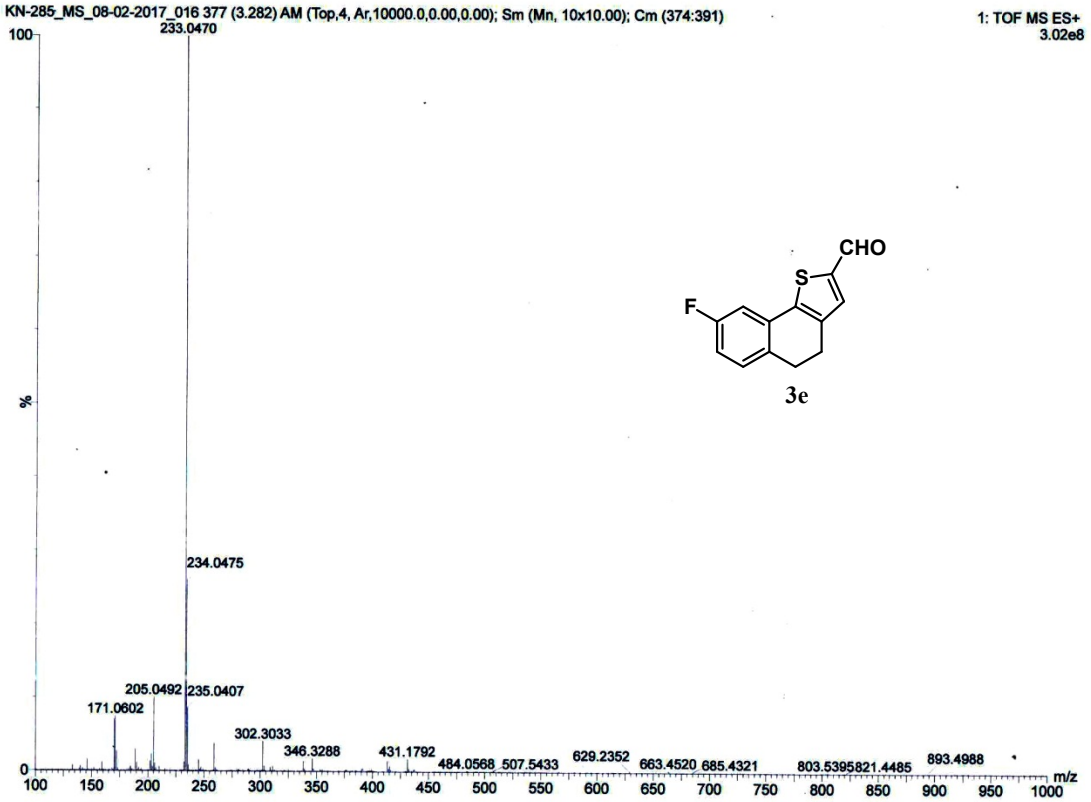
3b


KN-252_MS_08-02-2017_032 366 (3.188) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (364:390)
1: TOF MS ES+
5.27e8
245.0697
246.0668
217.0678
271.0789
171.0281
303.0507
304.0559
415.2077
517.0825
541.1002
632.2616
659.1378
CHO
S
MeO
%
m/z

3c

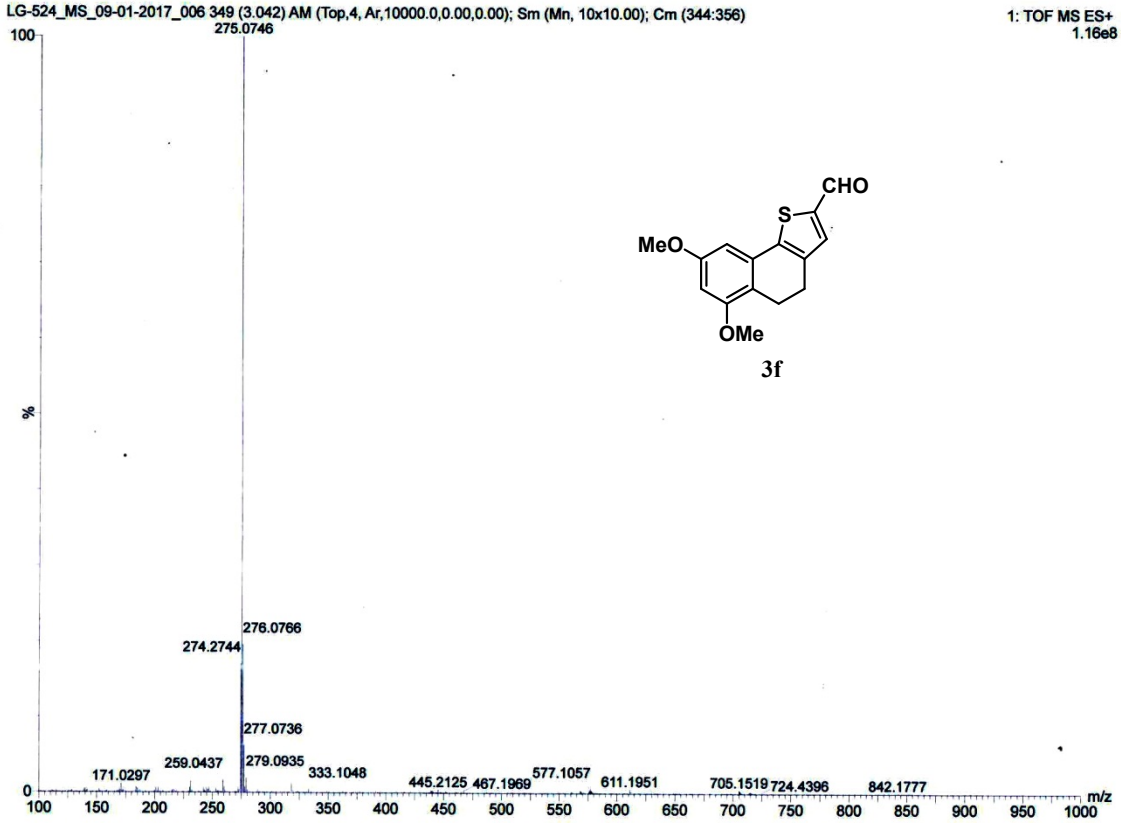

LG-515_MS_08-02-2017_030 367 (3.196) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (366:385)
1: TOF MS ES+
4.36e8
245.0729
246.0668
217.0678
247.0627
171.0281
273.0936
152.0639
302.3068
346.3288
402.2453
517.0825
537.1195
659.1378
685.1910
CHO
S
MeO
%
m/z

3d


KN-285_MS_08-02-2017_016 377 (3.282) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (374:391)
1: TOF MS ES+
3.02e8
233.0470
234.0475
205.0492
235.0407
171.0602
302.3033
346.3288
431.1792
484.0568
507.5433
629.2352
663.4520
685.4321
803.5395
821.4485
893.4988
%
m/z

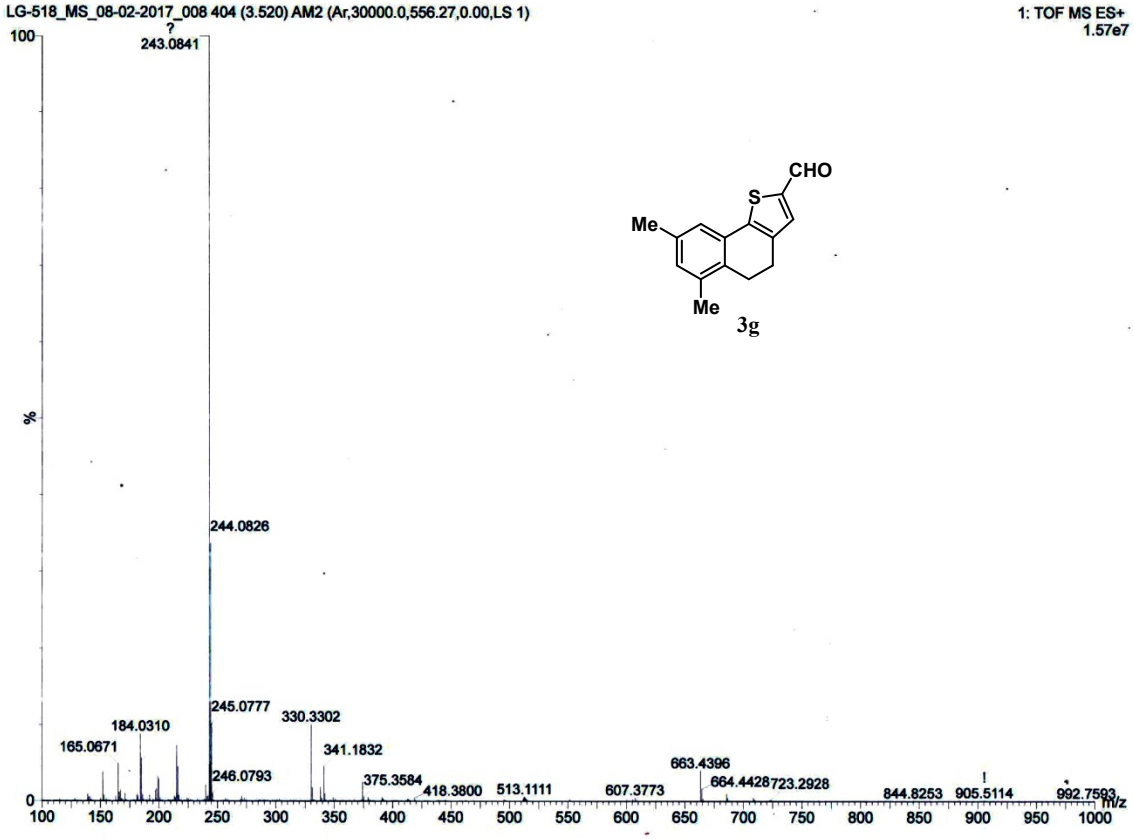
CHO
S
F

3e


LG-524_MS_09-01-2017_006 349 (3.042) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (344:356)
1: TOF MS ES+
1.16e8
275.0746
276.0766
274.2744
277.0736
279.0935
259.0437
171.0297
333.1048
445.2125
467.1969
577.1057
611.1951
705.1519
724.4396
842.1777
%
m/z

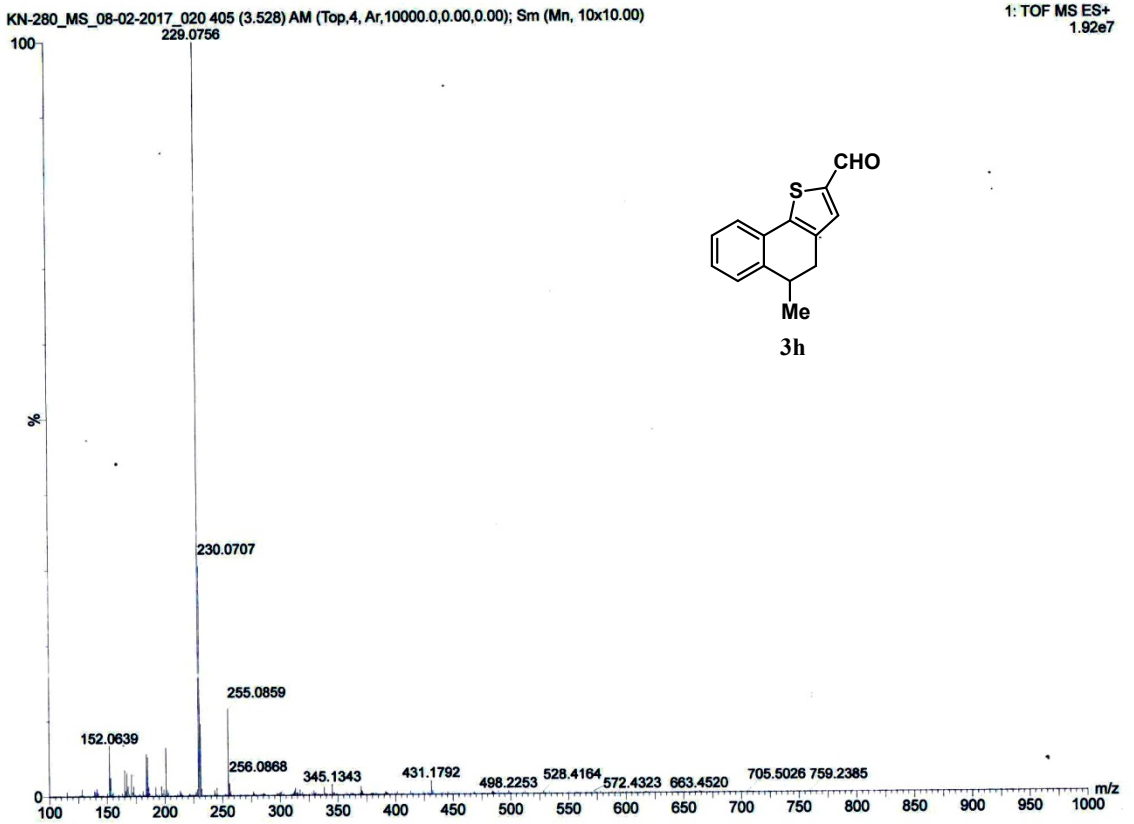
CHO
S
MeO
OMe

3f


LG-518_MS_08-02-2017_008 404 (3.520) AM2 (Ar,30000.0,556.27,0.00,LS 1)
1: TOF MS ES+
1.57e7
243.0841
244.0826
245.0777
330.3302
184.0310
165.0671
341.1832
246.0793
375.3584
663.4396
664.4428
723.2928
418.3800
513.1111
607.3773
844.8253
905.5114
992.7593
%
m/z

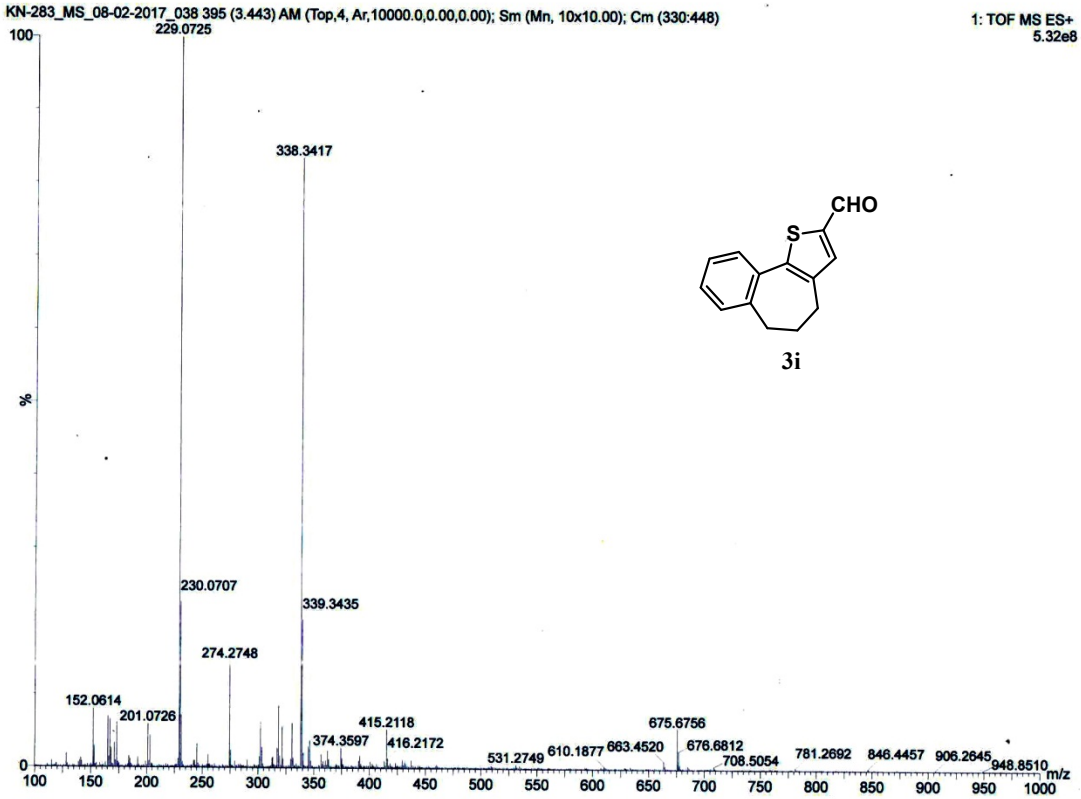
CHO
S
Me
Me

3g


KN-280_MS_08-02-2017_020 405 (3.528) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00)
1: TOF MS ES+
1.92e7
229.0756
230.0707
255.0859
152.0639
256.0868
345.1343
431.1792
498.2253
528.4164
572.4323
663.4520
705.5026
759.2385
%
m/z

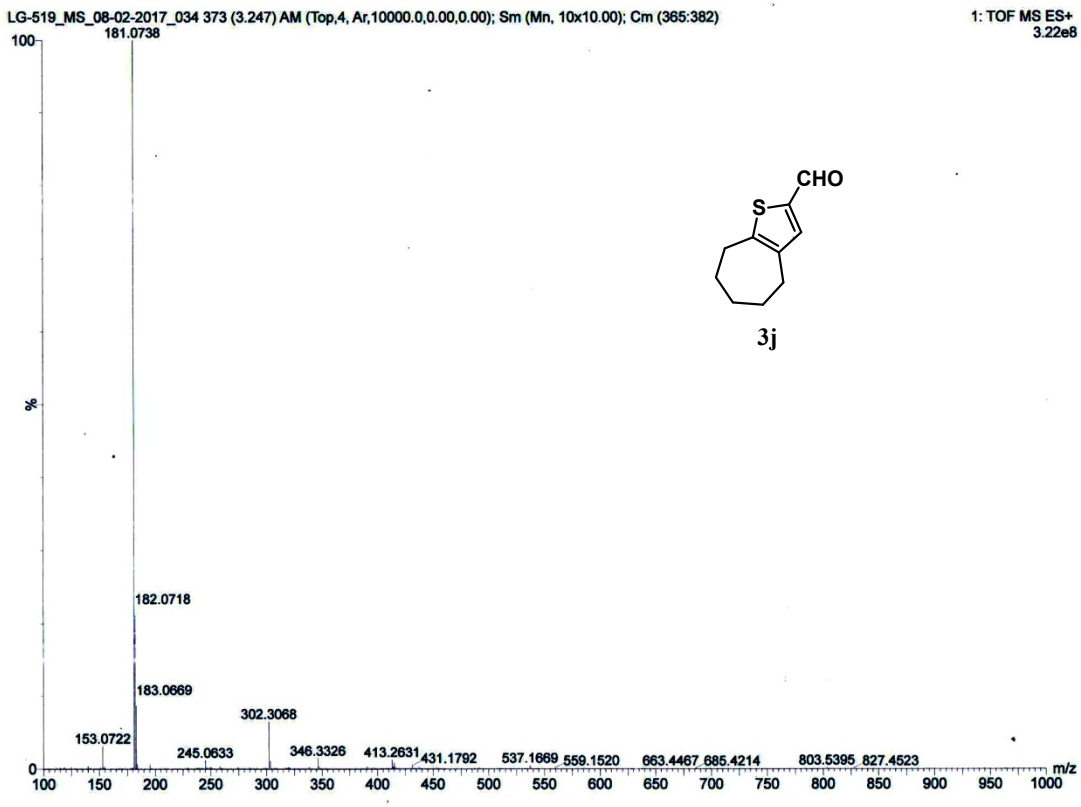
CHO
S
Me

3h


KN-283_MS_08-02-2017_038 395 (3.443) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (330:448)
1: TOF MS ES+
5.32e8
229.0725
338.3417
230.0707
339.3435
274.2748
152.0614
201.0726
415.2118
374.3597
416.2172
675.6756
676.6812
531.2749
610.1877
663.4520
708.5054
781.2692
846.4457
906.2645
948.8510
%
m/z

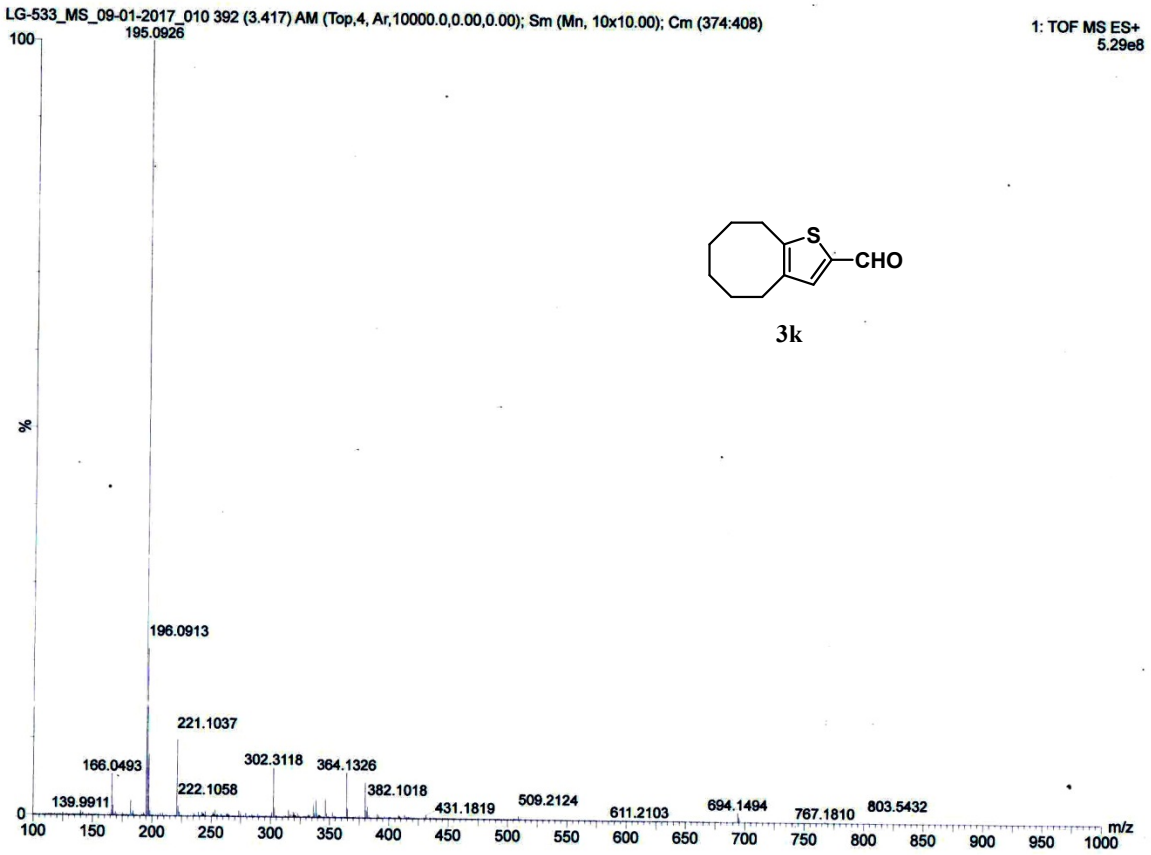
CHO
S

3i


LG-519_MS_08-02-2017_034 373 (3.247) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (365:382)
1: TOF MS ES+
3.22e8
181.0738
182.0718
183.0669
302.3068
153.0722
245.0633
346.3326
413.2631
431.1792
537.1669
559.1520
663.4467
685.4214
803.5395
827.4523
%
m/z

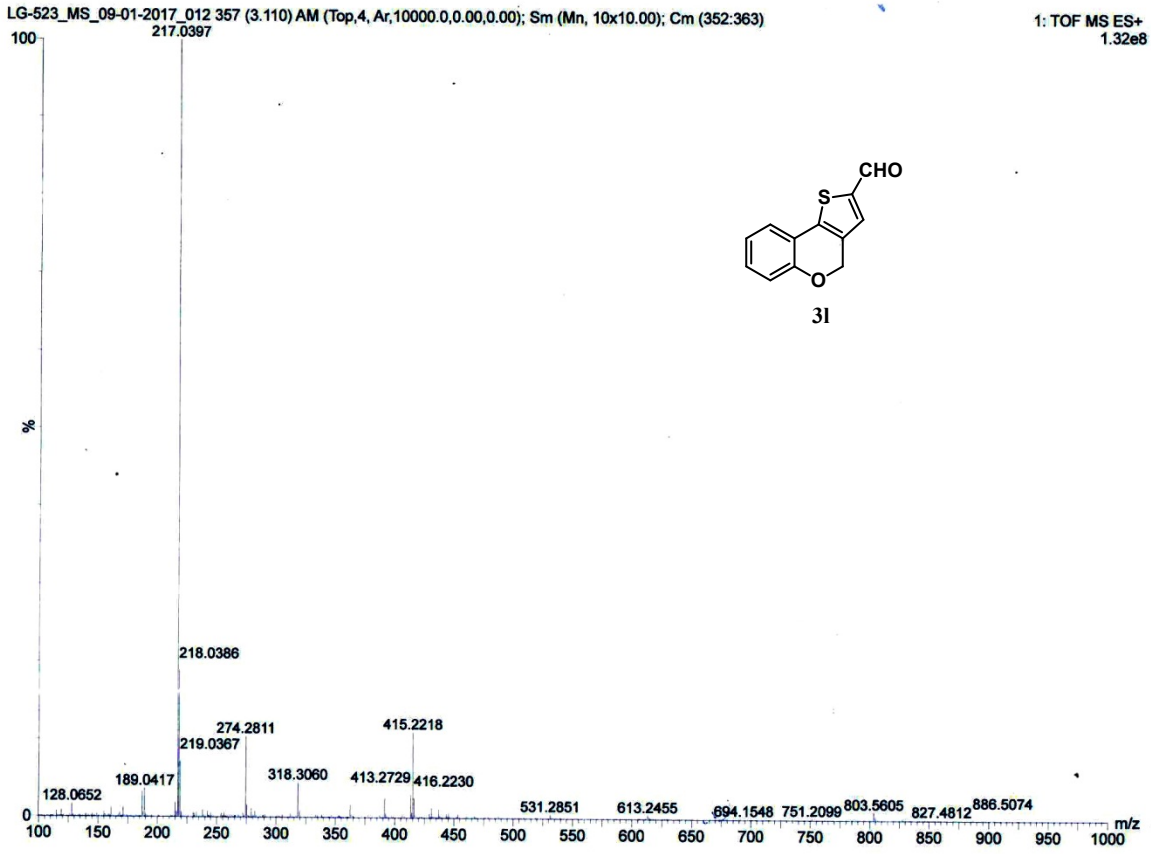
CHO
S

3j


LG-533_MS_09-01-2017_010 392 (3.417) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (374:408)
1: TOF MS ES+
5.29e8
195.0926
196.0913
221.1037
166.0493
302.3118
364.1326
222.1058
382.1018
139.9911
431.1819
509.2124
611.2103
694.1494
767.1810
803.5432
%
m/z

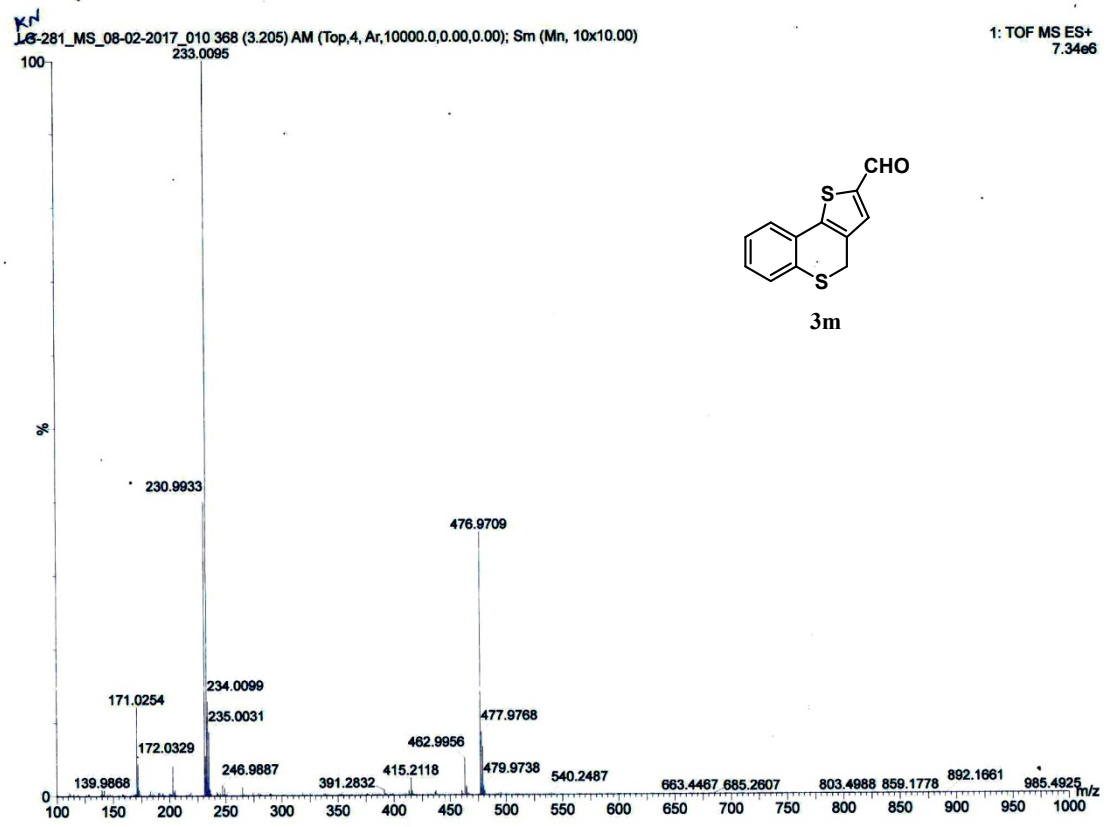
S
CHO

3k


LG-523_MS_09-01-2017_012 357 (3.110) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (352:363)
1: TOF MS ES+
1.32e8
217.0397
218.0386
274.2811
219.0367
415.2218
189.0417
318.3060
413.2729
416.2230
128.0652
531.2851
613.2455
694.1548
751.2099
803.5605
827.4812
886.5074
%
m/z

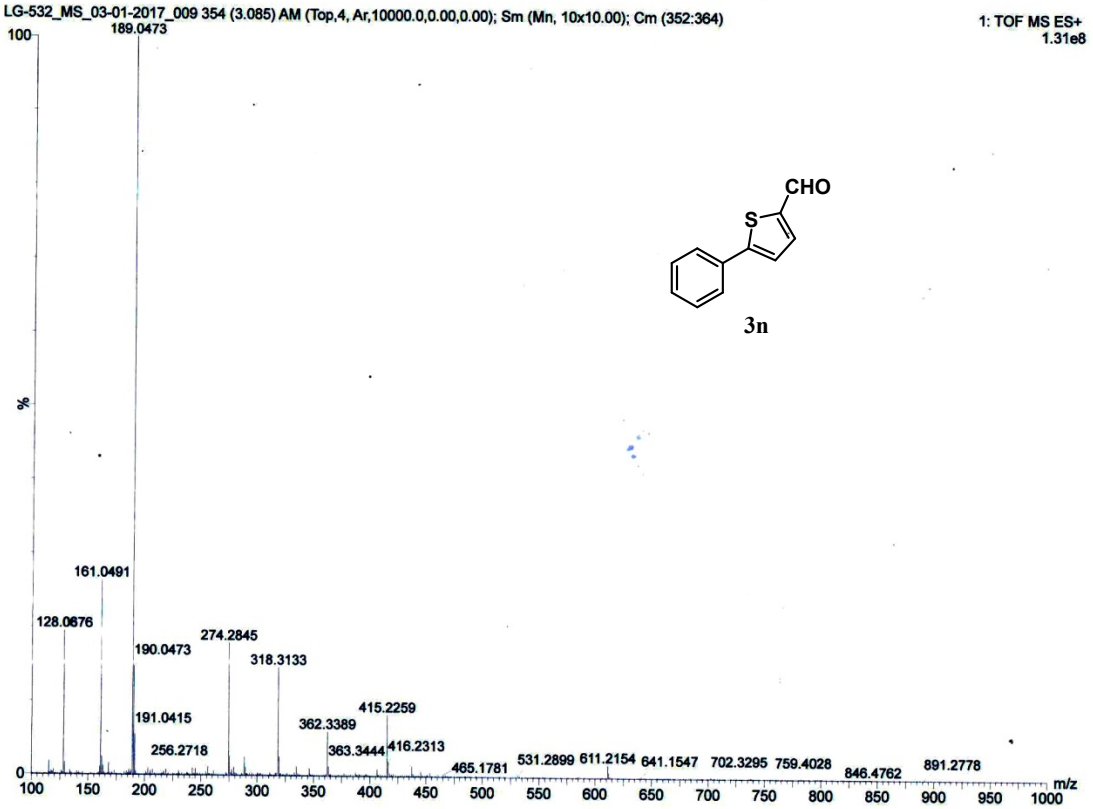
CHO
S
O

3l


LG-281_MS_08-02-2017_010 368 (3.205) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00)
1: TOF MS ES+
7.34e6
233.0095
230.9933
476.9709
234.0099
171.0254
235.0031
477.9768
462.9956
172.0329
246.9887
479.9738
139.9868
391.2832
415.2118
540.2487
663.4467 685.2607
803.4988 859.1778
892.1661
985.4925
%
m/z

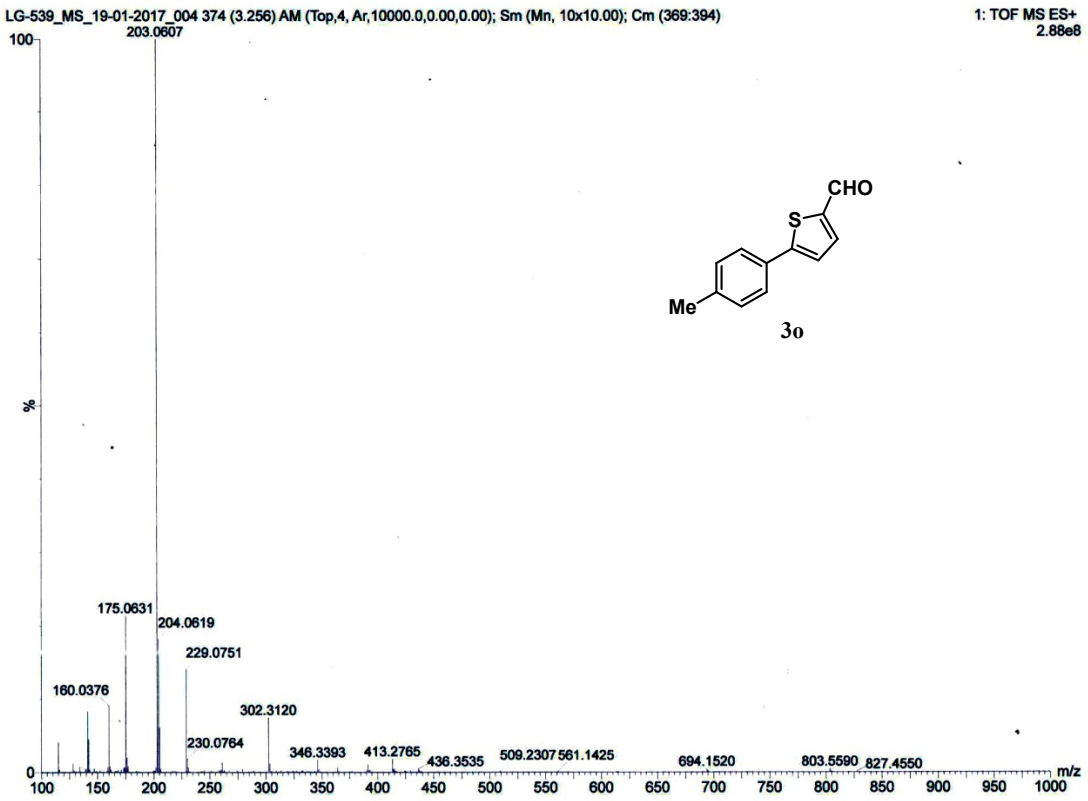
CHO
S
S

3m


LG-532_MS_03-01-2017_009 354 (3.085) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (352:364)
1: TOF MS ES+
1.31e8
189.0473
161.0491
128.0676
274.2845
190.0473
318.3133
415.2259
191.0415
362.3389
256.2718
363.3444
416.2313
465.1781
531.2899
611.2154
641.1547
702.3295
759.4028
846.4762
891.2778
%
m/z

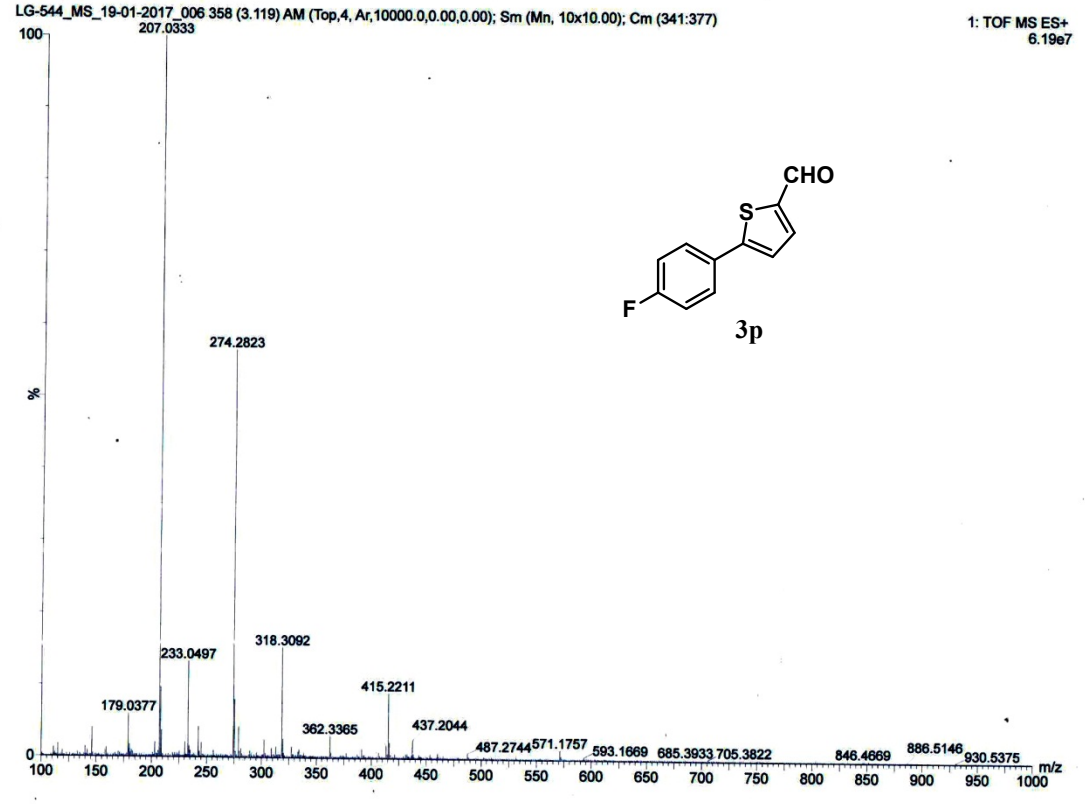
CHO
S

3n


LG-539_MS_19-01-2017_004 374 (3.256) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (369:394)
1: TOF MS ES+
2.88e8
203.0607
175.0631
204.0619
229.0751
160.0376
302.3120
230.0764
346.3393
413.2765
436.3535
509.2307
561.1425
694.1520
803.5590
827.4550
m/z
%

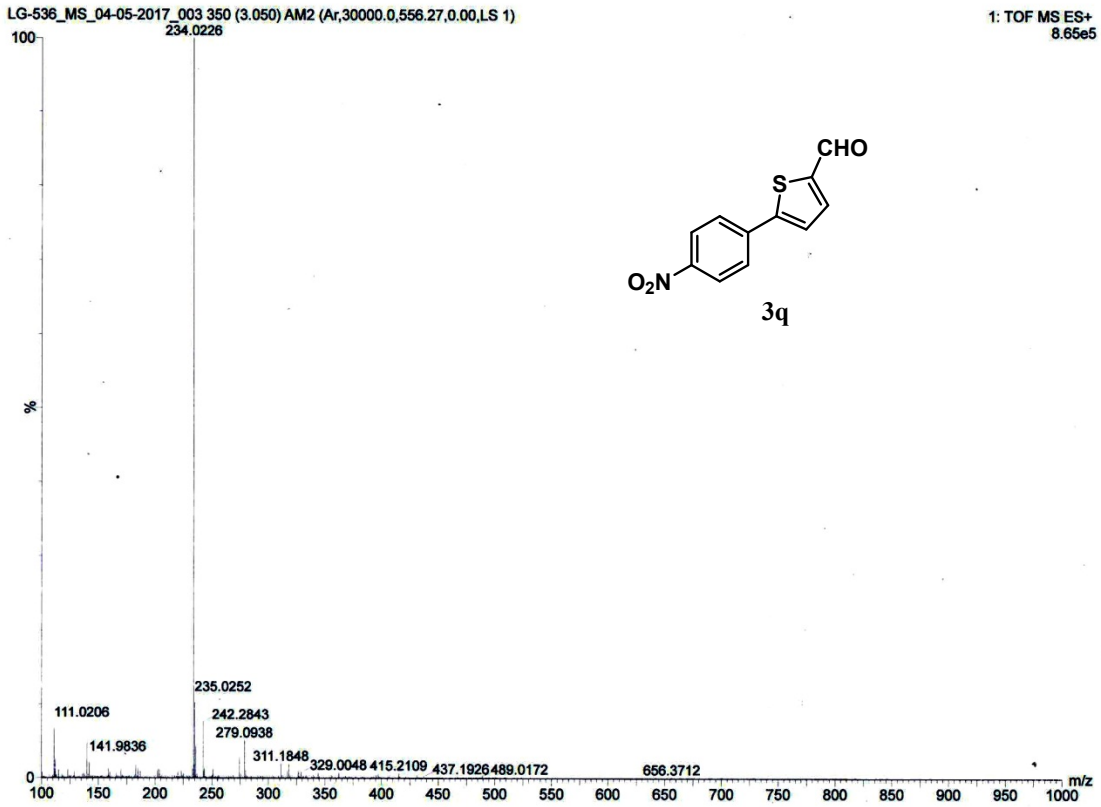
CHO
S
Me

3o


LG-544_MS_19-01-2017_006 358 (3.119) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (341:377)
1: TOF MS ES+
6.19e7
207.0333
274.2823
233.0497
318.3092
179.0377
415.2211
362.3365
437.2044
487.2744
571.1757
593.1669
685.3933
705.3822
846.4669
886.5146
930.5375
m/z
%

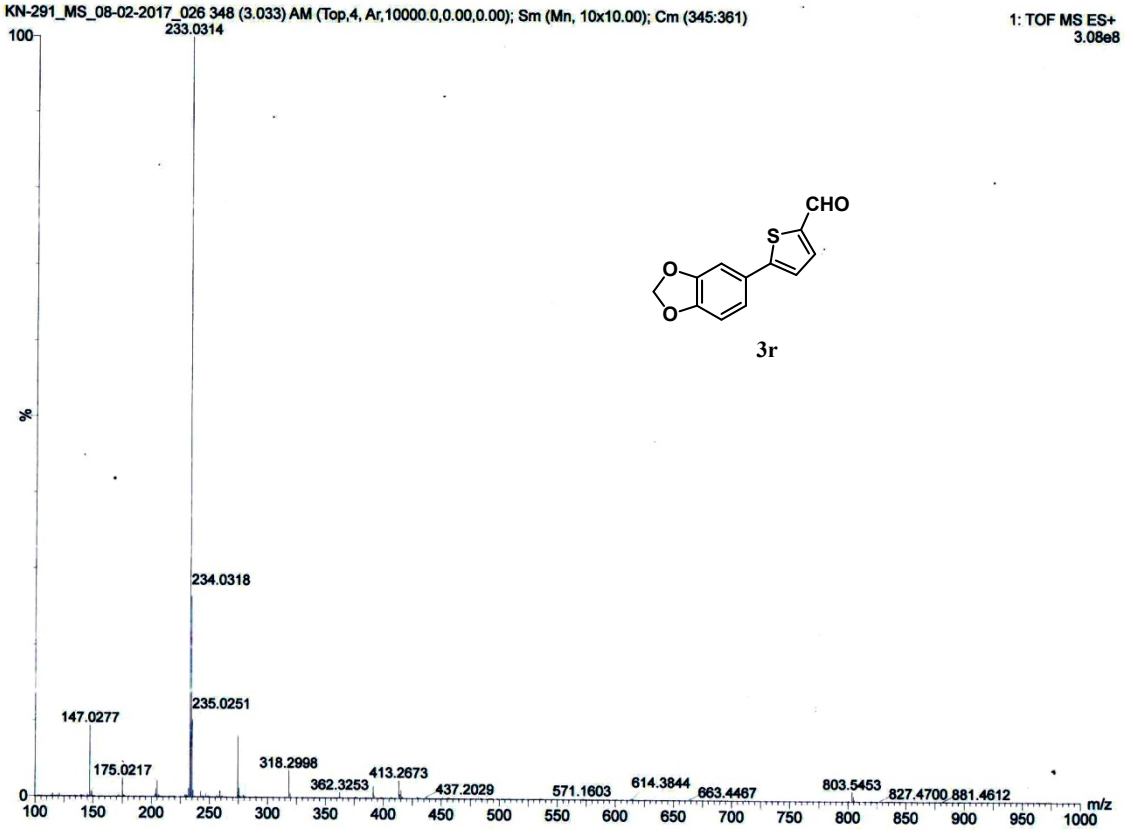
CHO
S
F

3p


LG-536_MS_04-05-2017_003 350 (3.050) AM2 (Ar,30000.0,556.27,0.00,LS 1)
1: TOF MS ES+
8.65e5
234.0226
235.0252
111.0206
242.2843
279.0938
141.9836
311.1848
329.0048 415.2109 437.1926 489.0172
656.3712
%
m/z

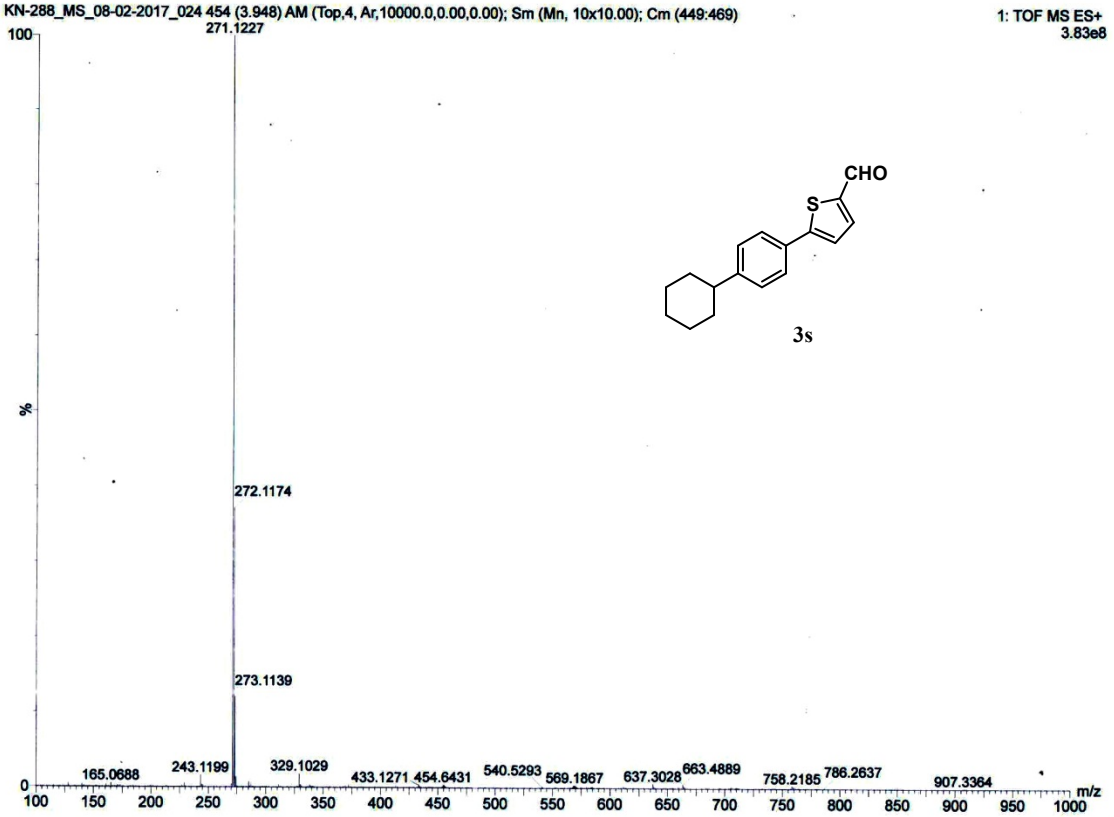
CHO
S
O2N

3q

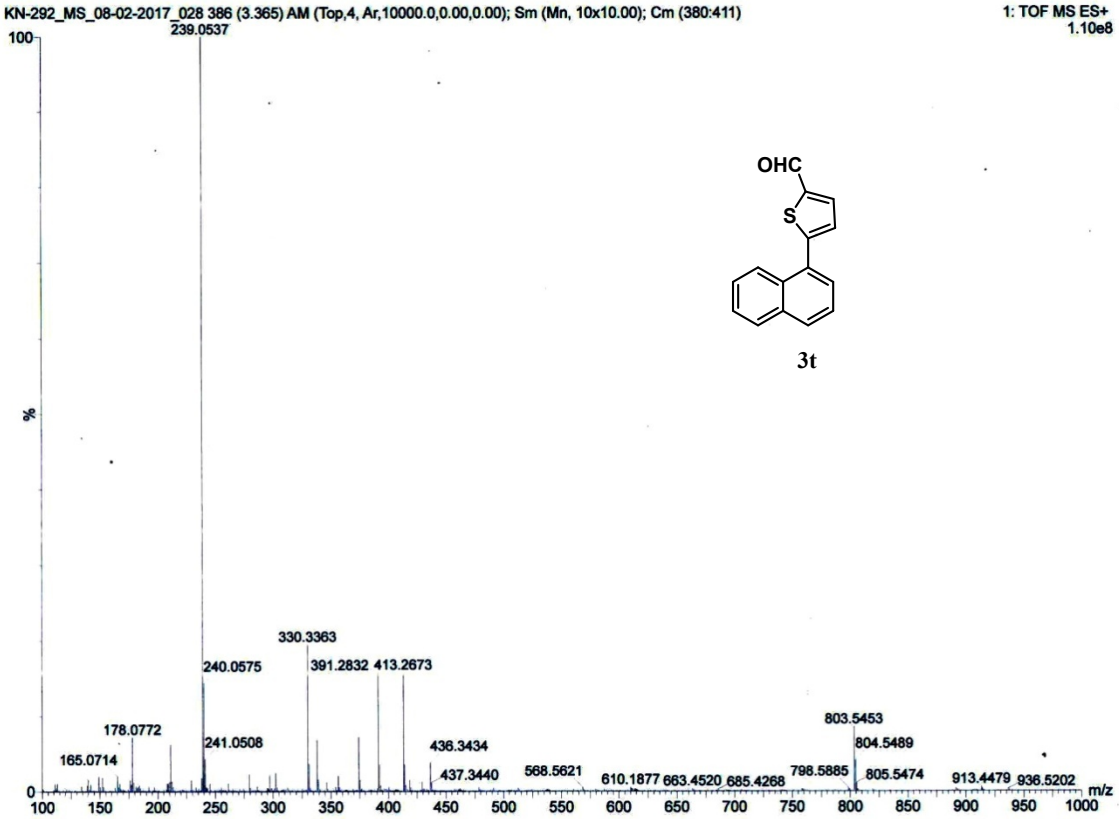

KN-291_MS_08-02-2017_026 348 (3.033) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (345:361)
1: TOF MS ES+
3.08e8
233.0314
234.0318
235.0251
147.0277
175.0217
318.2998
362.3253
413.2673
437.2029
571.1603
614.3844
663.4467
803.5453
827.4700 881.4612
%
m/z

CHO
S
O
O

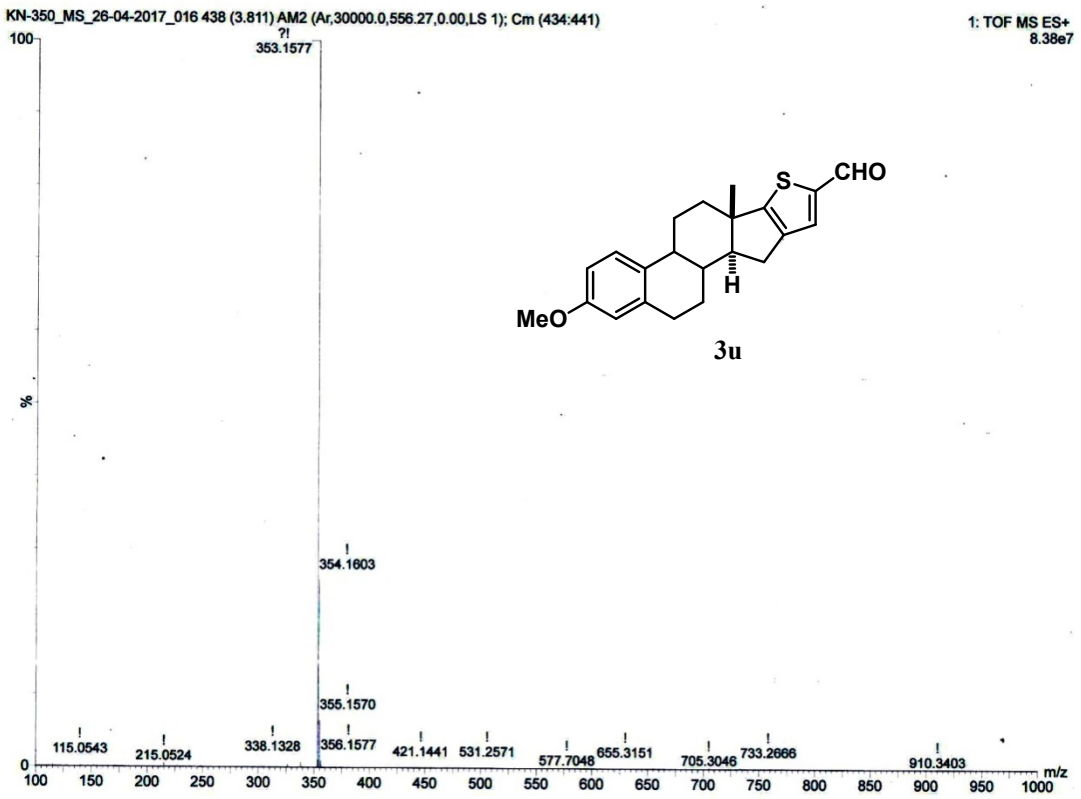
3r


KN-288_MS_08-02-2017_024 454 (3.948) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (449:469)
1: TOF MS ES+
3.83e8
271.1227
272.1174
273.1139
165.0688
243.1199
329.1029
433.1271
454.6431
540.5293
569.1867
637.3028
663.4889
758.2185
786.2637
907.3364
%
m/z
CHO
S

3s


KN-292_MS_08-02-2017_028 386 (3.365) AM (Top,4, Ar,10000.0,0.00,0.00); Sm (Mn, 10x10.00); Cm (380:411)
1: TOF MS ES+
1.10e8
239.0537
330.3363
240.0575
391.2832
413.2673
178.0772
241.0508
165.0714
436.3434
437.3440
568.5621
610.1877
663.4520
685.4268
798.5885
803.5453
804.5489
805.5474
913.4479
936.5202
%
m/z
OHC
S

3t


KN-350_MS_26-04-2017_016 438 (3.811) AM2 (Ar,30000.0,556.27,0.00,LS 1); Cm (434:441)
1: TOF MS ES+
8.38e7
353.1577
354.1603
355.1570
115.0543
215.0524
338.1328
356.1577
421.1441
531.2571
577.7048
655.3151
705.3046
733.2666
910.3403
%
m/z
S
CHO
H
MeO

3u