Electronic Supplementary Information for

Regioselective, Cascade [3+2] Annulation of β-Naphthols(Resorcinols) with *Z*-enoate Propargylic alcohols: A Novel entry into Complex Naphtho(*benzo*)furans

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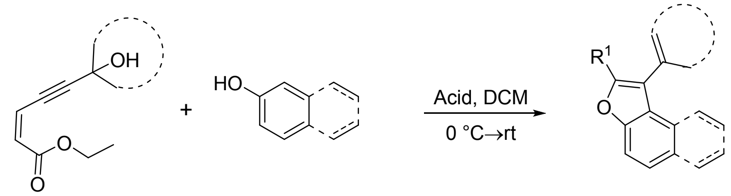
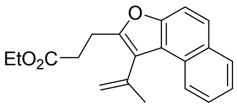
General procedure for the synthesis of naphtho(benzo)furans *via Z*-enoate assisted M-S rearrangement strategy:



To a solution of the enynoate-propargylic alcohol (1equi.) and naphthalene-2-ol or resorcinol (5 equi.) in dichloromethane (DCM) (5 mL/0.2 mmol, 0.04 *M*) under nitrogen atmosphere was added an acid (MsOH, 1.3 equi.). The reaction tube was stirred at 0 °C to RT for 1-8 h. After completion of the reaction (by TLC analysis), saturated $NaHCO_3$, and DCM were added to reaction mixture and extracted with DCM. The combined organic layer was washed with the brine, dried ($MgSO_4$) and solvent was evaporated under reduced pressure. The crude material was purified by flash column chromatography using hexane-ethyl acetate mixture as eluent to yield the corresponding naphtho(benzo)furan derivatives.

Ethyl 3-[1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (5)



The hydroxyl-ester[1] (30 mg, 0.16 mmol), naphthalen-2-ol (115 mg, 0.82 mmol), in DCM (3 mL) and MsOH (19.2 mg, 0.2 mmol, 0.14 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave napthofuran **5** (45 mg, 0.15 mmol, 96%) as a red color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (1 H, d, *J* = 8.3 Hz), 7.94 (1 H, d, *J* = 8.3 Hz), 7.69 (1 H, d, *J* = 8.8 Hz), 7.69-7.52 (2 H, m), 7.49-7.52 (1 H, m), 5.51 (1 H, q, *J* = 1.5 Hz), 5.21 (1 H, q, *J* = 1.2 Hz), 4.18 (2 H, q, *J* = 7.1 Hz), 3.19 (2 H, t, *J* = 7.2 Hz), 2.79 (2 H, t, *J* = 7.1 Hz), 2.23 (3 H, s) and 1.27 (3 H, t, *J* = 7.1 Hz) ppm.

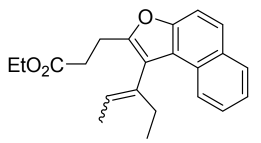
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 151.5, 151.3, 138.1, 130.7, 128.9, 128.0, 126.2, 124.8, 124.2, 123.4, 121.9, 120.8, 118.1, 112.3, 33.3, 24.6, 22.1 and 14.3 ppm.

IR (neat): 3059, 2976, 2926, 2854, 1736 (OC=O), 1579, 1525, 1444, 1374, 1283, 1181, 1062, 1006, 908, 805 and 783 cm^{-1}.

HR ESI-MS: $[C_{20}H_{21}O_3]^+$ = $[M+H]^+$ requires 309.1485; found 309.1482

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-(pent-2-en-3-yl)naphtho[2,1-b]furan-2-yl]propanoate (7)



The hydroxyl-ester[1] (50 mg, 0.24 mmol), naphthalen-2-ol (173 mg, 1.2 mmol), in DCM (5 mL) and MsOH (30 mg, 0.31 mmol, 0.2 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **7** (72 mg, 0.22 mmol, 90%) as a red color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (1 H, d, *J* = 8.5 Hz), 7.92 (1 H, d, *J* = 8.3 Hz), 7.68-7.65 (1 H, m), 7.58 (1 H, d, *J* = 8.7 Hz), 7.52-7.41 (2 H, m), 5.66 (1 H, q, *J* = 7.0 Hz), 4.20 (2 H, q, *J* = 7.1 Hz), 3.15 (2 H, t, *J* = 8.2 Hz), 2.78 (2 H, t, *J* = 7.8 Hz), 1.93 (3 H, d, *J* = 6.9 Hz), 1.30 (2 H, q, *J* = 7.3 Hz), 1.27 (3 H, t, *J* = 7.1 Hz) and 0.96 (3 H, t, *J* = 7.5 Hz) ppm.

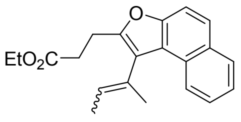
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 152.3, 151.4, 134.6, 130.7, 128.8, 128.1, 126.2, 126.0, 124.6, 124.1, 123.7, 122.5, 120.8, 112.3, 60.7, 33.4, 29.8, 24.8, 22.2, 14.4, 13.8 and 12.8 ppm.

IR (neat): 2965, 2929, 1734 (OC=O), 1618, 1590, 1451, 1379, 1267, 1181, 1014, 805 and 782 cm^{-1}.

HR ESI-MS: $[C_{22}H_{25}O_3]^+$ = $[M+H]^+$ requires 333.1804; found 333.1791

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-(but-2-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (8)



The hydroxyl-ester[1] (30 mg, 0.17 mmol), naphthalen-2-ol (122 mg, 0.85 mmol), in DCM (3 mL) and MsOH (21.2 mg, 0.22 mmol, 0.16 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **8** (50 mg, 0.16 mmol, 91%) as a red color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (1 H, d, *J* = 8.2 Hz), 7.92 (1 H, d, *J* = 8.0 Hz), 7.66 (1 H, d, *J* = 8.8 Hz), 7.57 (1 H, d, *J* = 8.8 Hz), 7.51 (1 H, t, *J* = 7.2 Hz), 7.44 (1 H, t, *J* = 7.0 Hz), 5.70 (1 H, q, *J* = 7.0 Hz), 4.17 (2 H, q, *J* = 7.1 Hz), 3.17-3.06 (2 H, m), 2.76 (2 H, t, *J* = 7.8 Hz), 2.07 (3 H, s), 1.91 (3 H, d, *J* = 6.8 Hz) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

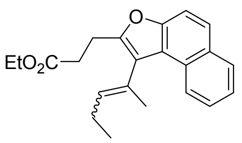
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 151.5, 151.4, 130.7, 128.9, 128.3, 128.1, 126.8, 126.1, 124.6, 124.1, 123.5, 122.6, 122.3, 112.3, 60.7, 33.4, 29.8, 22.1, 18.1, 14.4 and 14.3 ppm.

IR (neat): 2975, 2924, 2855, 1736 (OC=O), 1654, 1623, 1580, 1443, 1392, 1348, 1183, 1040, 804 and 739 cm^{-1}.

HR ESI-MS: $[C_{21}H_{23}O_3]^+$ = $[M+H]^+$ requires 323.1642; found 323.1639

LC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-(pent-2-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (9)



The hydroxyl-ester[1] (45 mg, 0.21 mmol), naphthalen-2-ol (151 mg, 1.05 mmol), in DCM (4 mL) and MsOH (26.7 mg, 0.28 mmol, 0.2 ml of 1.4 *M* in DCM) were stirred for 1.5 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **9** (59 mg, 0.19 mmol, 91%) as a red color oil.

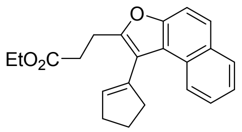
^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.21 (1 H, d, *J* = 8.3 Hz), 7.93 (1 H, d, *J* = 8.3 Hz), 7.67 (1 H, d, *J* = 8.9 Hz), 7.58 (1 H, d, *J* = 8.9 Hz), 7.52 (1 H, t, *J* = 8.2 Hz), 7.45 (1 H, t, *J* = 7.1 Hz), 5.64 (1 H, t, *J* = 7.2 Hz), 4.17 (2 H, q, *J* = 7.1 Hz), 3.18-3.12 (2 H, m), 2.78 (2 H, t, *J* = 8.0 Hz), 2.40-2.32 (2 H, m), 2.08 (3 H, s), 1.26 (3 H, t, *J* = 7.1 Hz) and 1.15 (3 H, t, *J* = 7.5 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.6, 151.4, 151.2, 134.3, 130.6, 128.8, 128.0, 126.8, 125.9, 124.5, 124.0, 123.4, 122.4, 122.1, 112.2, 60.6, 33.3, 22.0, 21.8, 18.1, 14.2 and 14.0 ppm.

IR (neat): 2965, 2925, 2861, 1736 (OC=O), 1627, 1587, 1449, 1383, 1271, 1182, 1013, 805 and 737 cm^{-1}.

TLC: R$_f$ = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-cyclopentenylnaphtho[2,1-b]furan-2-yl]propanoate (10)



The hydroxyl-ester[2] (45 mg, 0.22 mmol), naphthalen-2-ol (158.4 mg, 1.1 mmol), in DCM (4 mL) and MsOH (27.5 mg, 0.29 mmol, 0.2 ml of 1.4 *M* in DCM) were stirred for 1.5 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **10** (69 mg, 0.21 mmol, 94%) as a red color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.16 (1 H, d, *J* = 8.3 Hz), 7.91 (1 H, d, *J* = 8.3 Hz), 7.67 (1 H, d, *J* = 8.9 Hz), 7.57 (1 H, d, *J* = 8.9 Hz), 7.53-7.49 (1 H, m),7.46-7.42 (1 H, m), 5.90 (1 H, t, *J* = 2.1 Hz), 4.16 (2 H, q, *J* = 7.1 Hz), 3.12 (2 H, t, *J* = 8.0 Hz), 2.76 (2 H, t, *J* = 8.0 Hz), 2.73-2.63 (4 H, m), 2.33-2.15 (2 H, m) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

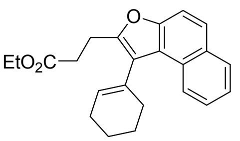
^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.7, 151.8, 151.6, 135.9, 132.0, 130.7, 128.9, 128.2, 126.1, 124.7, 124.2, 123.4, 122.6, 116.1, 112.3, 60.7, 37.5, 33.5, 33.4, 24.2, 22.4 and 14.3 ppm.

IR (neat): 2975, 2925, 2854, 1734 (OC=O), 1657, 1621, 1602, 1569, 1443, 1373, 1249, 1182, 1019, 935, 813 and 767 cm^{-1}.

HR ESI-MS: $[C_{22}H_{23}O_3]^+ = [M+H]^+$ requires 335.1642; found 335.1641

TLC: R$_f$ = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-cyclohexenylnaphtho[2,1-b]furan-2-yl]propanoate (11)



The hydroxyl-ester[2] (40 mg, 0.18 mmol), naphthalen-2-ol (130 mg, 0.9 mmol), in DCM (4 mL) and MsOH (22.5 mg, 0.24 mmol, 0.17 ml of 1.4 *M* in DCM) were stirred for 4 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **11** (58 mg, 0.17 mmol, 93%) as a red color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (1 H, d, J = 8.2 Hz), 7.92 (1 H, d, J = 8.2 Hz), 7.66 (1 H, d, J = 8.8 Hz), 7.58 (1 H, d, J = 8.8 Hz), 7.55-7.51 (1 H, m),7.46-7.42 (1 H, m), 5.90 (1 H, t, J = 2.1 Hz), 4.17 (2 H, q, J = 7.1 Hz), 3.14 (2 H, t, J = 7.8 Hz), 2.78 (2 H, t, J = 7.8 Hz), 2.53-2.50 (1 H, m), 2.37-2.30 (2 H, m), 2.23-2.15 (1 H, m), 1.96-1.90 (4 H, m) and 1.26 (3 H, t, J = 7.1 Hz) ppm.

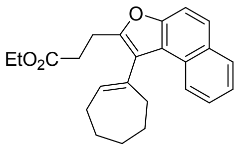
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 151.6, 151.4, 130.8, 130.7, 129.1, 128.9, 128.1, 126.1, 124.6, 124.1, 123.4, 121.3, 112.3, 60.7, 33.4, 30.4, 25.8, 23.3, 22.3, 22.1 and 14.3 ppm.

IR (neat): **IR** (neat): 2958, 2927, 2854, 1731 (OC=O), 1586, 1419, 1373, 1238, 1118, 1029, 923, 879 and 736 cm^{-1}.

HR ESI-MS: $[C_{23}H_{25}O_3]^+ = [M+H]^+$ requires 349.1803; found 349.1804

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-cycloheptenylnaphtho[2,1-b]furan-2-yl]propanoate (12)



The hydroxyl-ester[4] (30 mg, 0.13 mmol), naphthalen-2-ol (92 mg, 0.64 mmol), in DCM (3 mL) and MsOH (16.2 mg, 0.17 mmol, 0.12 ml of 1.4 *M* in DCM) were stirred for 1.5 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **12** (45 mg, 0.124 mmol, 98%) as a red color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (1 H, d, J = 8.3 Hz), 7.92 (1 H, d, J = 8.3 Hz), 7.67 (1 H, d, J = 8.9 Hz), 7.58-7.51 (2 H, m), 7.48-7.42 (1 H, m), 6.05 (1 H, t, J = 6.4 Hz), 4.18 (2 H, q, J = 7.1 Hz), 3.18 (2 H, t, J = 7.6 Hz), 2.81-2.76 (3 H, m), 2.51-2.33 (2 H, m), 2.06-2.01 (1 H, m), 1.89-2.85 (2 H, m), 1.67-1.56 (2 H, m) and 1.31-1.25 (5 H, m) ppm.

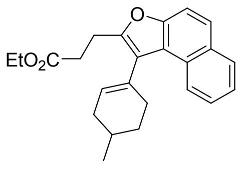
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 151.5, 151.4, 136.6, 134.1, 130.7, 128.8, 128.1, 128.0, 125.9, 124.6, 124.1, 123.7, 122.8, 122.0, 112.3, 60.7, 35.0, 33.6, 32.4, 29.1, 27.4, 26.8, 22.4 and 14.3 ppm.

IR (neat): 2974, 2922, 2850, 1736 (OC=O), 1654, 1622, 1601, 1579, 1444, 1393, 1241, 1181, 1009, 803 and 757 cm^{-1}.

HR ESI-MS: $[C_{24}H_{27}O_3]^+$ = $[M+H]^+$ requires 363.1955; found 363.1950

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-(4-methylcyclohex-1-enyl)naphtho[2,1-b]furan-2-yl]propanoate (13)



The hydroxyl-ester[2] (55 mg, 0.23 mmol), naphthalen-2-ol (166 mg, 1.15 mmol), in DCM (5 mL) and MsOH (28.7 mg, 0.3 mmol, 0.21 ml of 1.4 *M* in DCM) were stirred for 4.5 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **13** (68 mg, 0.19 mmol, 89%) as a red color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8. 18 (1 H, d, *J* = 8.2 Hz), 7.89 (1 H, d, *J* = 8.3 Hz), 7.64 (1 H, d, *J* = 9.1 Hz), 7.55 (1 H, d, *J* = 9.1 Hz), 7.52-7.48 (1 H, m),7.44-7.39 (1 H, m), 5.84 (1 H, t, *J* = 2.3 Hz), 4.15 (2 H, q, *J* = 7.1 Hz), 3.11 (2 H, br s), 2.75 (2 H, t, *J* = 7.5 Hz), 2.58-2.19 (3 H, m), 2.09-1.85 (2 H, m), 1.70-1.53 (2 H, m), (3 H, t, *J* = 7.1 Hz) and 1.11 (3 H, d, *J* = 5.9 Hz) ppm.

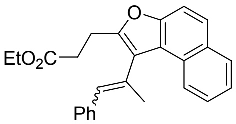
^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.7, 151.6, 151.4, 130.7, 130.4, 128.9, 128.7, 128.1, 127.2, 126.2, 124.6, 124.1, 123.4, 122.5, 112.3, 60.7, 34.5, 33.4, 31.8, 30.5, 29.8, 27.6, 22.2 and 14.3 ppm.

IR (neat): 2959, 2925, 2856, 1735 (OC=O), 1585, 1414, 1372, 1248, 1128, 1059, 943, 819 and 767 cm^{-1}.

HR ESI-MS: $[C_{24}H_{27}O_3]^+$ = $[M+H]^+$ requires 363.1973; found 363.1965

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[1-(1-phenylprop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (14)



The hydroxyl-ester[3] (40 mg, 0.16 mmol), naphthalen-2-ol (111 mg, 0.8 mmol), in DCM (4 mL) and MsOH (19.4 mg, 0.2 mmol, 0.14 ml of 1.4 *M* in DCM) were stirred for 5 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **14** (54 mg, 0.141 mmol, 92%) as a red color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.11 (1 H, d, *J* = 7.7 Hz), 7.85 (1 H, d, *J* = 8.1 Hz), 7.61 (1 H, d, *J* = 8.6 Hz), 7.53-7.48 (1 H, m), 7.42-7.35 (5 H, m), 7.25-7.21(1 H, m), 7.01-6.95 (1 H, m), 6.62 (1 H, s), 4.05 (2 H, q, *J* = 7.1 Hz), 3.13 (2 H, br s), 2.73 (2 H, t, *J* = 7.1 Hz), 2.28 (3 H, s) and 1.15 (3 H, t, *J* = 7.1 Hz) ppm.

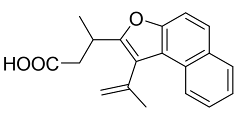
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 151.6, 151.5, 137.7, 131.8, 130.8, 130.7, 129.5, 129.2, 129.0, 128.5, 127.1, 126.5, 126.3, 124.9, 124.2, 123.6, 122.8, 112.3, 60.8, 33.3, 22.3, 20.3 and 14.3 ppm.

IR (neat): 2967, 2926, 2857, 1733 (OC=O), 1628, 1588, 1448, 1381, 1271, 1181, 1013, 804 and 747 cm^{-1}.

HR ESI-MS: $[C_{26}H_{24}O_3Na]^+$ = $[M+Na]^+$ requires 407.1623; found 407.1632

TLC: R_f = 0.4 (9:1, hex/EtOAc).

3-[1-(Prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]butanoic acid (15)



The hydroxyl-ester[1] (60 mg, 0.3 mmol), naphthalen-2-ol (230 mg, 1.6 mmol), in DCM (5 mL) and MsOH (38 mg, 0.4 mmol, 0.28 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan ester. Since it was not very clean, it a hydrolysis was performed on the mixture. Reaction of the mixture with aq. LiOH (11 mg, 0.45 mmol) in MeOH (6 mL) for 4 h at RT gave the corresponding acid. Purification by flash column chromatography (1:1 hexanes:EtOAc) gave naptho-furan acid **15** (58 mg, 0.2 mmol, 65% over 2 steps) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (1 H, d, J = 8.2 Hz), 7.92 (1 H, d, J = 8.2 Hz), 7.67 (1 H, d, J = 8.9 Hz), 7.57 (1 H, d, J = 8.9 Hz), 7.52 (1 H, t, J = 6.9 Hz), 7.44 (1 H, t, J =6.9 Hz), 5.46 (1 H, s), 5.17 (1 H, s), 3.63 (H, q, J = 7.2 Hz), 2.89 (1 H, q, J = 7.3 Hz), 2.72 (1 H, q, J = 7.4 Hz) 2.18 (3 H, s) and 1.40 (3 H, d, J = 7.0 Hz) ppm.

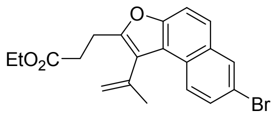
^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.7, 154.6, 151.3, 130.7, 129.4, 128.9, 128.1, 126.2, 125.7, 124.8, 124.2, 123.5, 123.2, 121.9, 112.4, 39.7, 29.8 and 28.5 ppm.

IR (neat): 2984, 2918, 2364, 2340, 1711 (OC=O), 1671, 1586, 1513, 1372, 1237, 1151, 1047, 1024, 1004 and 767 cm^{-1}.

TLC: R_f = 0.4 (1:1, hex/EtOAc).

Ethyl 3-[7-bromo-1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (16)

The hydroxyl-ester[1] (30 mg, 0.16 mmol), 6-bromonaphthalen-2-ol (178 mg, 0.8 mmol), in DCM (3 mL) and MsOH (19.2 mg, 0.2 mmol, 0.2 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **16** (56 mg, 0.15 mmol, 90%) as a red color oil.



^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.13 (1 H, d, *J* = 8.8 Hz), 8.07 (1 H, d, *J* = 1.3 Hz), 7.61-7.55 (3 H, m), 5.49 (1 H, s), 5.81 (1 H, s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.16 (2 H, t, *J* = 7.3 Hz), 2.78 (2 H, t, *J* = 7.7 Hz), 2.18 (3 H, s) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

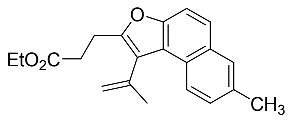
^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.5, 151.9, 151.4, 137.7, 132.0, 130.8, 129.3, 126.4, 125.1, 123.7, 122.0, 120.6, 118.5, 117.9, 113.3, 60.8, 33.2, 24.5, 22.1 and 14.3 ppm.

IR (neat): 2964, 2924, 2853, 1736 (OC=O), 1646, 1572, 1438, 1427, 1393, 1373, 1183, 1036, 905, 876, 817 and 795 cm^{-1}.

HR ESI-MS: $[C_{20}H_{20}BrO_3]^+$ = $[M+H]^+$ requires 387.0590; found 387.0587

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-(7-methyl-1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl)propanoate (17)



The hydroxyl-ester[1] (50 mg, 0.274 mmol), 6-methylnaphthalen-2-ol (216 mg, 1.37 mmol), in DCM (5 mL) and MsOH (34.3 mg, 0.38 mmol, 0.25 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **17** (78 mg, 0.242 mmol, 88%) as a red color oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.18 (1 H, d, *J* = 8.6 Hz), 7.71 (1 H, s), 7.61-7.55 (2 H, m), 7.38 (1 H, d, *J* = 8.6 Hz), 5.49 (1 H, s), 5.19 (1 H, s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.18 (2 H, t, *J* = 7.9 Hz), 2.79 (2 H, t, *J* = 7.6 Hz), 2.53 (3 H, s), 2.22 (3 H, s) and 1.27 (3 H, t, *J* = 7.1 Hz) ppm.

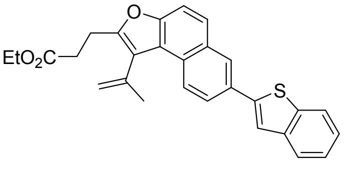
^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.6, 151.3, 151.1, 138.2, 133.6, 131.0, 128.3, 128.1, 126.0, 124.2, 123.2, 121.8, 120.7, 118.0, 112.2, 60.7, 33.3, 24.6, 22.1, 21.6 and 14.3 ppm.

IR (neat): 2966, 2924, 2858, 1735 (OC=O), 1646, 1588, 1449, 1430, 1376, 1273, 1256, 1183, 1018, 810 and 789 cm^{-1}.

HR ESI-MS: $[C_{21}H_{22}O_3Na]^+$ = $[M+Na]^+$ requires 345.1467; found 345.1455

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-(7-(benzo[b]thiophen-2-yl)-1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl)propanoate (18)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), 6-Phenylnaphthalen-2-ol[5] (345 mg, 1.23 mmol), in DCM (5 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 7 h at 0 °C to

RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **18** (75 mg, 0.17 mmol, 68%) as a red color oil.

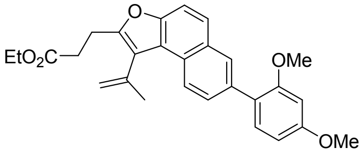
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (1 H, d, *J* = 8.6 Hz), 8.13 (1 H, s), 8.01-7.98 (H, m), 7.95-7.92 (1 H, m), 7.76 (1 H, d, *J* = 8.6 Hz), 7.72 (1 H, d, *J* = 9.0 Hz), 7.62 (1 H, d, *J* = 8.9 Hz), 7.48 (1 H, s), 7.41-7.39 (2 H, m), 5.52 (1 H, s), 5.22 (1 H, s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.18 (2 H, t, *J* = 7.6 Hz), 2.79 (2 H, t, *J* = 7.5 Hz), 2.25 (3 H, s) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 151.7, 151.6, 140.9, 138.3, 138.0, 131.9, 130.9, 128.5, 127.2, 124.9, 124.6, 124.5, 123.8, 123.6, 123.2, 123.1, 122.0, 120.8, 118.3, 112.8, 60.8, 33.3, 24.7, 22.2 and 14.4 ppm.

IR (neat): 2971, 2923, 2855, 1734 (OC=O), 1640, 1587, 1427, 1377, 1265, 1181, 1018, 905, 797 and 730 cm^{-1}.

TLC: R_f = 0.4 (9:1, hex/EtOAc).

Ethyl 3-[7-(2,4-dimethoxyphenyl)-1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (19)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), 6-phenylnaphthalen-2-ol (271 mg, 1.23 mmol), in DCM (5 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (6:1 hexanes:EtOAc) gave naptho-furan **19** (87 mg, 0.2 mmol, 79%) as a red color oil.

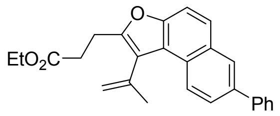
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (1 H, d, *J* = 8.5 Hz), 8.06 (1 H, s), 7.76-7.70 (2 H, m), 7.59 (1 H, d, *J* = 8.9 Hz), 7.03 (1 H, d, *J* = 3.0 Hz), 6.97 (1 H, d, *J* = 8.9 Hz), 6.89 (1 H, dd, *J* = 8.9 & 3.0 Hz), 5.51 (1 H, s), 5.20 (1 H, s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.84 (3 H, s), 3.78 (3 H, s), 3.18 (2 H, t, *J* = 8.5 Hz), 2.79 (2 H, t, *J* = 7.6 Hz), 2.24 (3 H, s) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 153.9, 151.5, 151.2, 151.1, 138.0, 134.3, 131.8, 130.6, 129.1, 128.0, 126.9, 125.0, 122.8, 121.8, 120.8, 118.0, 117.0, 113.2, 112.9, 112.2, 60.6, 56.5, 55.9, 33.3, 24.6, 22.1 and 14.3 ppm.

IR (neat): 2925, 2842, 2371, 1733 (OC=O), 1646, 1628, 1587, 1500, 1457, 1429, 1219, 1180, 1024, 906 and 797 cm^{-1}.

TLC: R_f = 0.4 (6:1, hex/EtOAc).

Ethyl 3-[7-phenyl-1-(prop-1-en-2-yl)naphtho[2,1-b]furan-2-yl]propanoate (20)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), 6-phenylnaphthalen-2-ol (271 mg, 1.23 mmol), in DCM (5 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave naptho-furan **20** (89 mg, 0.23 mmol, 94%) as a red color solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (1 H, d, *J* = 8.6 Hz), 7.14 (1 H, d, *J* = 1.5 Hz), 7.81 (1 H, dd, *J* = 8.6 & 1.6 Hz), 7.76-7.73 (3 H. m), 7.61 (1 H, d, *J* = 8.7 Hz), 7.52-7.48 (2 H, m), 7.38 (1 H, t, *J* = 7.4 Hz), 5.52 (1 H, s), 5.22 (1 H, s), 4.18 (2 H, q, *J* = 7.1 Hz), 3.19 (2 H, t, *J* = 8.2 Hz), 2.80 (2 H, t, *J* = 7.5 Hz), 2.25 (3 H, s) and 1.27 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 151.6, 151.5, 141.4, 138.0, 137.0, 131.0, 129.0, 127.5, 127.3, 127.1, 126.9, 125.8, 125.1, 123.9, 121.9, 120.8, 118.2, 112.7, 60.7, 33.3, 24.6, 22.1 and 14.4 ppm.

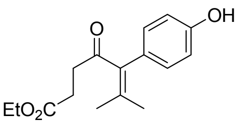
IR (neat): 2974, 2925, 2854, 1734 (OC=O), 1645, 1584, 1494, 1443, 1373, 1280, 1257, 1183, 1018, 904, 830 and 796 cm^{-1}.

HR ESI-MS: $[C_{26}H_{24}O_3Na]^+ = [M+Na]^+$ requires 407.1623; found 407.1631

TLC: $R_f = 0.4$ (9:1, hex/EtOAc).

M.P.: 92 °C.

Ethyl 5-(4-hydroxyphenyl)-6-methyl-4-oxohept-5-enoate (21)



The hydroxyl-ester[1] (40 mg, 0.22 mmol), phenol (77 mg, 0.82 mmol), in DCM (4 mL) and MsOH (27.4 mg, 0.02 mmol, 0.29 ml of 1.4 *M* in DCM) were stirred for 24 h at 0 °C to RT. Purification by flash column chromatography (8:1 hexanes:EtOAc) gave the α-arylenone **21** (18 mg, 0.065 mmol, 30%) as a pale yellow oil. Further elution with (6:1 hexanes:EtOAc) gave the α-OMs-enone **6c**[4] (22 mg, 0.08 mmol, 36%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.37 (2 H, m), 7.00 (1 H, t, *J* = 7.3 Hz), 6.89 (1 H, d, *J* = 7.8 Hz), 4.09 (2 H, q, *J* = 7.1 Hz), 2.75 (2 H, t, *J* = 6.6 Hz), 2.49 (2 H, t, *J* = 6.6 Hz), 2.22 (3 H, s), 1.781 (3 H, s) and 1.22 (3 H, t, *J* = 7.1 Hz) ppm.

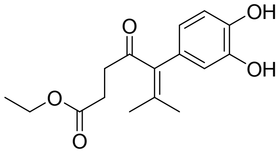
^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 173.0, 157.5, 143.0, 139.6, 130.1, 122.1, 114.7, 60.6, 35.1, 28.0, 20.7, 20.1 and 14.3 ppm.

IR (neat): 2952, 2854, 2361, 2354, 1734 (OC=O), 1699 (C=O), 1611, 1548, 1514, 1442, 1364, 1312, 1281, 1155, 1105, 1054, 954 and 817 cm^{-1}.

HR ESI-MS: $[C_{16}H_{20}O_4Na]^+ = [M+Na]^+$ requires 299.1254; found 299.1258

TLC: $R_f = 0.4$ (8:1, hex/EtOAc).

Ethyl 5-(3,4-dihydroxyphenyl)-6-methyl-4-oxohept-5-enoate (22)



The hydroxyl-ester**[1]** (30 mg, 0.16 mmol), catechol (82 mg, 0.82 mmol), in DCM (3 mL) and MsOH (19.2 mg, 0.02 mmol, 0.14 ml of 1.4 *M* in DCM) were stirred for 6 h at 0 °C to RT. Purification by flash column chromatography (3:1 hexanes:EtOAc) gave 1,4-keto-ester **22** (33 mg, 0.11 mmol, 71%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (1 H, d, *J* = 7.9 Hz), 6.77 (1 H, br s), 6.64 (1 H, s), 4.10 (2 H, q, *J* = 7.1 Hz), 2.62 (2 H, t, *J* = 6.2 Hz), 2.50 (2 H, t, *J* = 6.2 Hz), 1.99 (3 H, s), 1.65 (3 H, s), 1.65 (3 H, s) and 1.23 (3 H, t, *J* = 7.1 Hz) ppm.

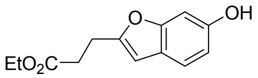
^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.3, 173.9, 144.1, 143.9, 143.7, 137.6, 130.7, 122.5, 116.6, 115.5, 61.1, 37.4, 28.5, 23.6, 22.5 and 14.2 ppm.

IR (neat): 3444, 2980, 2921, 2853, 1734 (OC=O), 1689 (C=O), 1598, 1456, 1426, 1372, 1344, 1261, 1205, 1178, 1150, 1014 and 764 cm^{-1}.

HR ESI-MS: $[C_{16}H_{21}O_5]^+ = [M+H]^+$ requires 293.1384; found 293.1392

TLC: $R_f = 0.4$ (3:1, hex/EtOAc)

Ethyl 3-(6-hydroxybenzofuran-2-yl)propanoate (23)



The hydroxyl-ester[1] (30 mg, 0.16 mmol), resorcinol (88 mg, 0.8 mmol), in DCM (4 mL) and MsOH (20 mg, 0.21 mmol, 0.15 ml of 1.4 *M* in DCM) were stirred for 3.5 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **23** (26 mg, 0.11 mmol, 70%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (1 H, d, *J* = 4.3 Hz), 6.87 (1 H, d, *J* = 1.9 Hz), 6.69 (1 H, dd, *J* = 8.4 & 2.3 Hz), 6.30 (1 H, s), 5.23 (1 H, br s), 4.13 (2 H, q, *J* = 7.1 Hz), 3.04 (2 H, t, *J* = 7.3 Hz), 2.70 (2 H, t, *J* = 7.3 Hz) and 1.22 (3 H, t, *J* = 7.1 Hz) ppm.

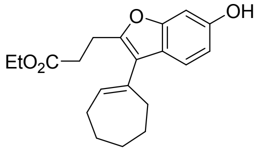
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 156.5, 155.7, 153.2, 122.3, 120.6, 111.6, 102.3, 98.3, 60.9, 32.6, 24.0 and 14.3 ppm.

IR (neat): 3403, 2923, 2856, 2368, 1719 (OC=O), 1626, 1617, 1499, 1455, 1140, 1020, 828 and 732 cm^{-1}.

HR ESI-MS: $[C_{13}H_{15}O_4]^+ = [M+H]^+$ requires 235.0965; found 235.0958

TLC: $R_f = 0.4$ (4:1, hex/EtOAc).

Ethyl 3-(3-cycloheptenyl-6-hydroxybenzofuran-2-yl)propanoate (25a)



The hydroxyl-ester[4] (60 mg, 0.25 mmol), resorcinol (180 mg, 1.25 mmol), in DCM (5.5 mL), and MsOH (32 mg, 0.33 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **25a** (49 mg, 0.15 mmol, 60%) as a pale yellow color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.28 (1 H, d, *J* = 8.4 Hz), 6.89 (1 H, d, *J* = 2.0 Hz), 6.75 (1 H, dd, *J* = 8.4 & 2.0 Hz), 5.96 (1 H, t, *J* = 6.6 Hz), 4.17 (2 H, q, *J* = 7.1 Hz), 3.11 (2 H, t, *J* = 8.2 Hz), 2.73 (2 H, t, *J* = 7.4 Hz), 2.34-2.29 (2 H, m), 1.89-1.85 (2 H, m), 1.72-1.66 (2 H, m), 1.64-1.59 (2 H, m) and 1.27 (3 H, t, *J* = 7.1 Hz) ppm.

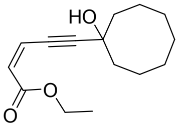
^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.2, 154.8, 153.5, 150.2, 136.3, 132.9, 122.3, 121.0, 120.3, 111.3, 98.1, 60.8, 33.7, 33.3, 32.9, 29.1, 27.2, 22.6 and 14.3 ppm.

IR (neat): 3412, 2925, 2854, 1727 (OC=O), 1618, 1482, 1451, 1372, 1299, 1159, 1024, 845, 806 and 734 cm^{-1}.

HR ESI-MS: $[C_{20}H_{24}O_4K]^+ = [M+K]^+$ requires 367.1312; found 367.1303

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

(*Z*)-Ethyl 5-(1-hydroxycyclooctyl)pent-2-en-4-ynoate (24e)



The (*Z*)-2-iodo-acrylate[4] (562 mg, 2.5 mmol) and propargylic alcohol[7] (418 mg, 2.7 mmol) were taken into a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous THF (15 ml) and diisopropyl amine (DIPA) (5 ml) were added under nitrogen atmosphere and cooled the flask to 0 °C. Subsequently, CuI (71.3 mg, 0.38 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (17.6 mg, 0.025 mmol) were added to the reaction flask, and stirred the reaction mixture 30 min at 0 °C. The reaction mixture was allowed to warm to room temperature (RT) and continued the stirring for 14 h. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the alcohol, reaction was quenched with saturated NH$_4$Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried (MgSO$_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (4:1 hexanes:EtOAc) gave (*Z*)-enynoate-propargylic alcohol **24e** (510 mg, 2.04 mmol, 82%) as a pale yellow color oil.

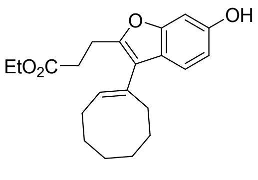
^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.15 (1 H, *J* = 11.6 Hz), 6.05 (1 H, *J* = 11.6 Hz), 4.21 (2 H, q, *J* = 7.1 Hz), 2.46 (1 H, br s), 2.05-1.95 (4 H, m), 1.73-1.58 (8 H, m), 1.53-1.45 (2 H, m) and 1.30 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 164.8, 128.6, 122.9, 106.6, 80.1, 60.6, 37.9, 28.0, 24.6, 22.1 and 14.4 ppm.

IR (neat): 3451 (OH), 3024, 2929, 2854, 1727 (OC=O), 1607, 1494, 1452, 1409, 1350, 1230, 1186, 1033, 818 and 700 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

(*E*)-Ethyl 3-(3-cyclooctenyl-6-hydroxybenzofuran-2-yl)propanoate (25b)



The hydroxyl-ester **24e** (45 mg, 0.18 mmol), resorcinol (99 mg, 0.9 mmol), in DCM (5 mL) and MsOH (22.5 mg, 0.24 mmol, 0.17 ml of 1.4 *M* in DCM) were stirred for 80 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **25b** (50 mg, 0.15 mmol, 81%) as a pale yellow color oil.

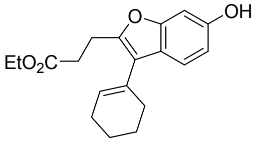
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25 (1 H, d, *J* = 8.4 Hz), 6.87 (1 H, d, *J* = 2.2 Hz), 6.72 (1 H, dd, *J* = 8.4 & 2.2 Hz), 5.91 (1 H, br s), 5.71 (1 H, t, *J* = 8.2 Hz), 4.16 (2 H, q, *J* = 7.1 Hz), 3.08 (2 H, t, *J* = 8.3 Hz), 2.70 (2 H, t, *J* = 7.9 Hz), 2.54-2.51 (2 H, m), 2.30-2.25 (2 H, m), 1.62-1.55 (6 H, m), 1.50-1.46 (2 H, m) and 1.23 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.2, 154.9, 153.5, 151.2, 132.8, 130.9, 122.5, 120.3, 119.5, 111.3, 98.2, 60.9, 33.5, 30.0, 29.6, 29.0, 26.9, 26.8, 26.5, 22.7 and 14.3 ppm.

IR (neat): 3402, 2930, 2860, 1729 (OC=O), 1617, 1482, 1454, 1272, 1173, 1154, 1106, 1023, 840, 817 and 735 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(3-cyclohexenyl-6-hydroxybenzofuran-2-yl)propanoate (26)



The hydroxyl-ester^2 (40 mg, 0.18 mmol), resorcinol (99 mg, 0.9 mmol), in DCM (4 mL) and MsOH (22.5 mg, 0.23 mmol, 0.17 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **26** (38 mg, 0.12 mmol, 67%) as a pale yellow oil. Further elution with same solvent mixture yielded the benzofuran **23** (8 mg, 0.03 mmol, 19%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (1 H, d, *J* = 8.4 Hz), 6.87 (1 H, d, *J* = 2.2 Hz), 6.72 (1 H, dd, *J* = 8.4 & 2.2 Hz), 5.48 (1 H, br s), 5.79 (1 H, t, *J* = 2.0 Hz), 4.16 (2 H, q, *J* = 7.1 Hz), 3.08 (2 H, t, *J* = 8.1 Hz), 2.72 (2 H, t, *J* = 7.4 Hz), 2.33-2.19 (2 H, m), 1.80-1.75 (2 H, m), 1.73-1.68 (2 H, m) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

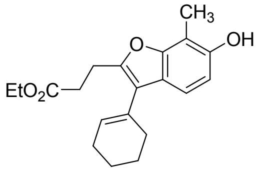
^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 158.4, 153.3, 150.6, 129.6, 127.7, 122.5, 120.4, 119.4, 111.2, 98.1, 60.8, 33.2, 29.4, 25.7, 23.1, 22.8, 22.3 and 14.3 ppm.

IR (neat): 3402, 2930, 2860, 1727 (OC=O), 1617, 1482, 1450, 1272, 1183, 1154, 1116, 1023, 840, 807 and 732 cm^{-1}.

HR ESI-MS: $[C_{19}H_{22}O_4Na]^+ = [M+Na]^+$ requires 337.1416; found 337.1424

TLC: $R_f = 0.4$ (4:1, hex/EtOAc).

Ethyl 3-(3-cyclohexenyl-6-hydroxy-7-methylbenzofuran-2-yl)propanoate (27a)



The hydroxyl-ester[2] (50 mg, 0.23 mmol), 2-methylbenzene-1,3-diol (140 mg, 1.2 mmol), in DCM (4.5 mL) and MsOH (28 mg, 0.29 mmol, 0.2 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **27a** (52 mg, 0.16 mmol, 70%) as a pale yellow color oil.

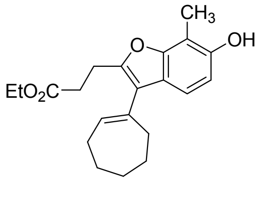
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (1 H, d, *J* = 8.4 Hz), 6.70 (1 H, d, *J* = 8.2 Hz), 5.78-5.76 (1 H, m), 5.02 (1 H, br s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.10 (2 H, t, *J* = 7.4 Hz), 2.74 (2 H, t, *J* = 7.4 Hz), 2.35 (3 H, s), 2.34-2.30 (2 H, m), 2.22-2.19 (2 H, m), 1.79-1.68 (4 H, m) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 153.8, 150.9, 150.6, 129.7, 127.5, 122.0, 119.7, 117.1, 111.0, 107.3, 60.8, 33.3, 29.4, 25.7, 23.1, 22.8, 22.3, 14.3 and 8.4 ppm.

IR (neat): 3417, 2930, 2860, 1725 (OC=O), 1608, 1449, 1374, 1293, 1259, 1183, 1079, 1023, 803 and 737 cm^{-1}.

TLC: $R_f = 0.4$ (4:1, hex/EtOAc).

Ethyl 3-(3-cycloheptenyl-6-hydroxy-7-methylbenzofuran-2-yl)propanoate (27b)



The hydroxyl-ester[4] (45 mg, 0.19 mmol), 2-methylbenzene-1,3-diol (118 mg, 0.95 mmol), in DCM (5 mL), and MsOH (24 mg, 0.25 mmol, 0.18 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **27b** (45 mg, 0.13 mmol, 70%) as a pale yellow color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.09 (1 H, d, *J* = 8.3 Hz), 6.71 (1 H, d, *J* = 8.3 Hz), 5.92 (1 H, t, *J* = 6.6 Hz), 5.32 (1 H, br s), 4.17 (2 H, q, *J* = 7.1 Hz), 3.11 (2 H, t, *J* = 8.2 Hz), 2.75 (2 H, t, *J* = 8.2 Hz), 2.52-2.49 (2 H, m), 2.35 (3 H, s), 2.32-2.27 (2 H, m), 1.89-1.83 (2 H, m), 1.69-1,65 (2 H, m), 1.63-1.58 (2 H, m) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

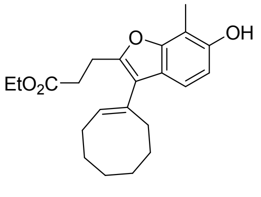
^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.1, 153.8, 151.0, 150.3, 136.5, 132.8, 121.9, 121.3, 117.0, 111.1, 107.3, 60.8, 33.7, 33.3, 33.0, 29.1, 27.3, 27.2, 22.7, 14.3 and 8.4 ppm.

IR (neat): 3417, 2930, 2858, 1726 (OC=O), 1608, 1447, 1375, 1293, 1219, 1185, 1079, 1023, 813 and 739 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

HR ESI-MS: [$C_{21}H_{26}O_4Na$]$^+$ = [M+Na]$^+$ requires 365.1729; found 365.1719

(*E*)-Ethyl 3-(3-cyclooctenyl-6-hydroxy-7-methylbenzofuran-2-yl)propanoate (27c)



The hydroxyl-ester **24e** (45 mg, 0.18 mmol), 2-methylbenzene-1,3-diol (112 mg, 0.9 mmol), in DCM (5 mL), and MsOH (23 mg, 0.24 mmol, 0.17 ml of 1.4 *M* in DCM) were stirred for 90 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **27c** (48 mg, 0.14 mmol, 75%) as a pale yellow color oil.

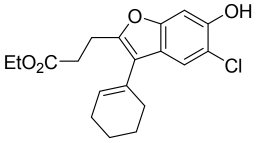
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.13 (1 H, d, *J* = 8.2 Hz), 6.70 (1 H, d, *J* = 8.2 Hz), 5.73 (1 H, t, *J* = 8.3 Hz), 5.23 (1 H, br s), 4.18 (2 H, q, *J* = 7.1 Hz), 3.13 (2 H, t, *J* = 8.0 Hz), 2.74 (2 H, t, *J* = 7.9 Hz), 2.57-2.53 (2 H, m), 2.36 (3 H, s), 2.33-2.28 (2 H, m), 1.65-1.57 (6 H, m), 1.53-1.48 (2 H, m) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.0, 153.9, 151.2, 151.0, 132.9, 130.7, 122.2, 119.7, 111.1, 107.4, 60.8, 33.5, 30.1, 29.6, 29.0, 26.9, 26.8, 26.5, 22.8, 14.3 and 8.4 ppm.

IR (neat): 3412, 2932, 2857, 1730 (OC=O), 1621, 1452, 1275, 1173, 1155, 1114, 1083, 937, 843, 804 and 737 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(5-chloro-3-cyclohexenyl-6-hydroxybenzofuran-2-yl)propanoate (28a)



The hydroxyl-ester[2] (40 mg, 0.18 mmol), 4-chlorobenzene-1,3-diol (130 mg, 0.9 mmol), in DCM (4 mL) and MsOH (22.5 mg, 0.24 mmol, 0.16 ml of 1.4 *M* in DCM) were stirred for 3 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **28a** (43 mg, 0.12 mmol, 70%) as a pale yellow color oil.

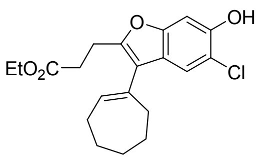
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (1 H, s), 7.04 (1 H, s), 5.79-5.77 (1 H, m), 5.64 (1 H, br s), 4.15 (2 H, q, *J* = 7.1 Hz), 3.07 (2 H, t, *J* = 8.0 Hz), 2.71 (2 H, t, *J* = 8.0 Hz), 2.31-2.27 (2 H, m), 2.23-2.19 (2 H, m), 1.81-1.75 (2 H, m), 1.74-1.68 (2 H, m) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 153.5, 151.9, 148.3, 129.0, 128.3, 123.2, 119.3, 119.0, 115.6, 98.7, 60.8, 33.0, 29.4, 25.7, 23.1, 22.8, 22.2 and 14.3 ppm.

IR (neat): 3416, 2928, 2857, 1721 (OC=O), 1614, 1464, 1298, 1261, 1184, 1023, 860 and 779 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(5-chloro-3-cycloheptenyl-6-hydroxybenzofuran-2-yl)propanoate (28b)



The hydroxyl-ester[4] (45 mg, 0.19 mmol), 4-chlorobenzene-1,3-diol (137 mg, 0.95 mmol), in DCM (5 mL), and MsOH (24 mg, 0.25 mmol, 0.18 ml of 1.4 *M* in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **28b** (49 mg, 0.14 mmol, 71%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (1 H, s), 7.04 (1 H, s), 5.94 (1 H, t, *J* = 6.6 Hz), 4.15 (2 H, q, *J* = 7.1 Hz), 3.08 (2 H, t, *J* = 7.9 Hz), 2.71 (2 H, t, *J* = 7.9 Hz), 2.50-2.46 (2 H, m), 2.32-2.27 (2 H, m), 1.89-1.84 (2 H, m), 1.70-1.66 (2 H, m), 1.64-1.59 (2 H, m) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

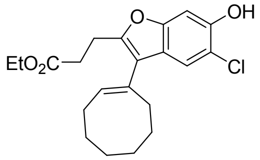
^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 153.4, 151.6, 148.3, 135.7, 133.6, 131.1, 129.0, 119.3, 115.6, 98.7, 60.8, 33.7, 33.0, 32.9, 29.1, 27.2, 22.6, 19.3 and 14.3 ppm.

IR (neat): 3413, 2927, 2854, 1728 (OC=O), 1618, 1482, 1451, 1372, 1299, 1157, 1034, 845, 806 and 734 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

HR ESI-MS: $[C_{20}H_{23}O_4NaCl]^+$ = $[M+Na]^+$ requires 385.1183; found 385.1202

(E)-Ethyl 3-(5-chloro-3-cyclooctenyl-6-hydroxybenzofuran-2-yl)propanoate (28c)



The hydroxyl-ester **24e** (45 mg, 0.18 mmol), 4-chlorobenzene-1,3-diol (130 mg, 0.9 mmol), in DCM (5 mL), and MsOH (23 mg, 0.24 mmol, 0.17 ml of 1.4 *M* in DCM) were stirred for 90 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **28c** (46 mg, 0.12 mmol, 68%) as a pale yellow color oil.

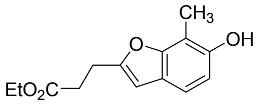
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (1 H, s), 7.05 (1 H, s), 5.74 (1 H, t, *J* = 8.0 Hz), 5.64 (1 H, br s), 4.15 (2 H, q, *J* = 7.1 Hz), 3.10 (2 H, t, *J* = 8.1 Hz), 2.71 (2 H, t, *J* = 8.1 Hz), 2.54-2.49 (2 H, m), 2.32-2.28 (2 H, m), 1.65-1.58 (6 H, m), 1.53-1.48 (2 H, m) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.6, 153.5, 152.5, 148.4, 132.2, 131.5, 123.3, 119.3, 119.0, 115.6, 98.8, 60.8, 33.2, 30.0, 29.8, 29.6, 29.0, 26.9, 26.8, 26.5, 22.7 and 14.3 ppm.

IR (neat): 3409, 2935, 2861, 1726 (OC=O), 1617, 1472, 1447, 1356, 1272, 1183, 1144, 1106, 1023, 837 and 749 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(6-hydroxy-7-methylbenzofuran-2-yl)propanoate (29)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), 2-methylbenzene-1,3-diol (155 mg, 1.25 mmol), in DCM (4 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 6 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **29** (44 mg, 0.18 mmol, 71%) as a pale yellow color oil.

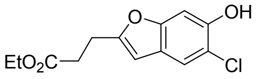
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.12 (1 H, d, *J* = 8.6 Hz), 6.71 (1 H, d, *J* = 8.2 Hz), 6.31 (1 H, s), 5.45 (1 H, br s), 4.18 (2 H, q, *J* = 7.1 Hz), 3.09 (2 H, t, *J* = 7.7 Hz), 2.76 (2 H, t, *J* = 7.6 Hz), 2.37 (3 H, s) and 1.27 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.0, 156.2, 154.8, 151.0, 128.7, 123.1, 117.3, 111.4, 102.5, 60.9, 32.7, 24.1, 14.3 and 8.5 ppm.

IR (neat): 3406, 2960, 2925, 2859, 1732 (OC=O), 1588, 1456, 1417, 1378, 1205, 1155, 1023, 833, 804 and 698 cm^{-1}.

TLC: R$_f$ = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(5-chloro-6-hydroxybenzofuran-2-yl)propanoate (30)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), 4-chlorobenzene-1,3-diol (180 mg, 1.25 mmol), in DCM (5 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 1.5 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **30** (38 mg, 0.14 mmol, 57%) as a pale yellow color oil.

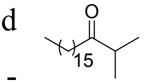
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39 (1 H, s), 7.08 (1 H, s), 6.29 (1 H, s), 4.15 (2 H, q, *J* = 7.1 Hz), 3.07 (2 H, t, *J* = 7.4 Hz), 2.73 (2 H, t, *J* = 7.4 Hz) and 1.23 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4, 157.8, 154.3, 154.3, 148.4, 122.9, 119.6, 115.9, 101.8, 98.8, 60.9, 32.4, 24.0 and 14.3 ppm.

IR (neat): 3409, 2978, 2924, 2860, 1722 (OC=O), 1598, 1473, 1440, 1340, 1297, 1187, 1137, 1020, 863 and 784 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

2-Methylnonadecan-3-one (31a)



To a solution of isobutyraldehyde (288 mg, 4 mmol) in THF at 0 °C, was added the hexadecanylmagnesium bromide [2.0 mmol, freshly prepared from 1-bromohexadecane (610 mg, 2 mmol) and Mg (72 mg, 3 mmol) in THF (5 mL)] under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature for 2 hours. After completion of the reaction (TLC analysis), quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with EtOAc (2 x 15 mL). The combined organic layer was washed with brine (10 mL) and dried (Na_2SO_4). Solvent was removed under reduced pressure. To the solution of the crude mixture of the corresponding alcohol in DCM (5 mL), at 0 °C were added PCC (1350 mg, 6 mmol) and silica gel (1350 mg) and stirred for 5 h. After complete consumption of the alcohol, reaction mixture was filtered through a small plug of silica gel using DCM. Evaporation fo the solvent and purification of the crude reaction mixture by flash column chromatography (44:1 hexanes:EtOAc) afforded the ketone **31a** (428 mg, 1.45 mmol, 72%) as a colorless oil.

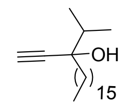
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60-2.56 (1 H, m), 2.43 (2 H, t, *J* = 7.5 Hz), 1.60-1.52 (2 H, m), 1.33-1.19 (26 H, m), 1.08 (6 H, d, *J* = 6.8 Hz) and 0.88 (3 H, t, *J* = 6.8 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.1, 40.9, 40.5, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 24.0, 22.8, 18.4 and 14.2 ppm.

IR (neat): 2958, 2923, 2854, 1698 (C=O), 1612, 1476, 1407, 1371, 1255, 1175, 1053, 935, 835, and 732 cm^{-1}.

TLC: R_f = 0.4 (44:1, hex/EtOAc).

3-Isopropylnonadec-1-yn-3-ol (31b)



To an ice cold solution of the ketone **31a** (400 mg, 1.35 mmol) in anhydrous THF (5 mL) under nitrogen atmosphere, was added ethynylmegnesium bromide (2.7 mmol, 5.4 ml of 0.5 *M* in THF) and stirred the reaction mixture 2 h at 0 °C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the carbonyl compound, reaction was quenched with saturated aq.

NH_4Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (19:1 hexanes:EtOAc) to give propargylic alcohol **31b** (296 mg, 0.92 mmol, 67%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (1 H, s), 1.85-1.79 (1 H, m), 1.67-1.56 (2 H, m), 1.30-1.22 (28 H, m), 1.03 (3 H, d, *J* = 5.4 Hz) and 0.88 (3 H, t, *J* = 6.9 Hz) ppm.

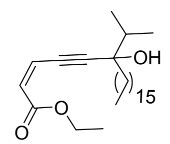
^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.1, 74.7, 72.9, 39.3, 37.3, 30.0, 29.9, 29.8, 29.7, 29.5, 24.1, 22.8, 17.9, 16.9 and 14.3 ppm.

IR (neat): 3458, 3298, 3068, 3028, 2936, 2854, 1608, 1458, 1090, 920 and 700 cm^{-1}.

TLC: R_f = 0.4 (19:1, hex/EtOAc).

(*Z*)-Ethyl 6-hydroxy-6-isopropyldocos-2-en-4-ynoate (31c)

The (*Z*)-2-iodo-acrylate[4] (168 mg, 0.75 mmol) and propargylic alcohol **31b** (185 mg, 0.6 mmol) were taken into a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous THF and diisopropyl amine (DIPA) were added under nitrogen atmosphere and cooled the flask to 0 °C. Subsequently, CuI (17.1 mg, 0.1 mmol), and $Pd(PPh_3)_2Cl_2$ (4.2 mg, 0.006 mmol) were added to the reaction flask, and stirred the reaction mixture 30 min at 0 °C. The reaction mixture was allowed to warm to room temperature (RT) and continued the stirring for 14 h. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the alcohol, reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (5:1 hexanes:EtOAc) gave (*Z*)-enynoate-propargylic alcohol **31c** (197 mg, 0.47 mmol, 78%) as a pale yellow color oil.



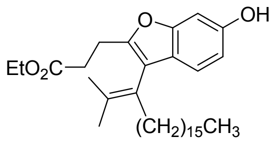
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.17 (1 H, *J* = 11.4 Hz), 6.07 (1 H, *J* = 11.4 Hz), 4.22 (2 H, q, *J* = 7.1 Hz), 2.30 (1 H, br s), 1.93-1.86 (1 H, m), 1.73-1.60 (4 H, m), 1.55-1.49 (2 H, m), 1.31-1.24 (27 H, m), 1.06 (3 H, d, *J* = 2.9 Hz) 1.04 (3 H, d, *J* = 2.9 Hz) and 0.88 (3 H, t, *J* = 7.0 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 128.6, 122.7, 104.4, 81.9, 75.4, 60.5, 39.1, 37.4, 32.0, 30.0, 29.8, 29.7, 29.5, 24.1, 22.8, 17.9, 17.1, 14.4 and 14.2 ppm.

IR (neat): 3450 (OH), 3026, 2929, 2854, 2361, 1728 (OC=O), 1607, 1494, 1452, 1409, 13850, 1230, 1186, 1033, 818 and 700 cm^{-1}.

TLC: $R_f = 0.4$ (5:1, hex/EtOAc).

Benzofuran-ester (31)



The hydroxyl-ester **31c** (70 mg, 0.17 mmol), resorcinol (94 mg, 0.22 mmol), in DCM (8 mL) and MsOH (21.2 mg, 0.22 mmol, 0.16 ml of 1.4 *M* in DCM) were stirred for 45 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **31** (62 mg, 0.12 mmol, 71%) as a pale yellow oil.

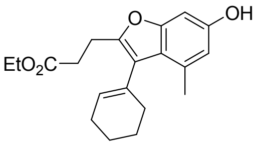
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (1 H, d, *J* = 8.4 Hz), 6.89 (1 H, d, *J* = 2.1 Hz), 6.71 (1 H, dd, *J* = 8.4 & 2.1 Hz), 5.21 (1 H, br s), 4.17 (2 H, q, *J* = 7.1 Hz), 2.90 (2 H, t, *J* = 7.7 Hz), 2.70 (2 H, t, *J* = 7.8 Hz), 2.29 (2 H, t, *J* = 5.5 Hz), 1.85 (3 H, s), 1.52 (3 H, m), 1.30-1.22 (31 H, m) and 0.88 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 155.0, 153.2, 151.0, 131.5, 124.9, 123.4, 120.3, 117.8, 111.1, 98.2, 60.8, 33.4, 32.6, 32.1, 29.9, 29.8, 29.7, 29.5, 28.9, 22.8, 22.7, 22.4, 20.1, 14.3 and 14.2 ppm.

IR (neat): 3405, 2958, 2926, 2857, 1731 (OC=O), 1610, 1456, 1412, 1372, 1235, 1212, 1157, 1023, 838, 805 and 697 cm^{-1}.

TLC: $R_f = 0.4$ (4:1, hex/EtOAc).

Ethyl 3-(3-cyclohexenyl-6-hydroxy-4-methylbenzofuran-2-yl)propanoate (32)



The hydroxyl-ester[2] (45 mg, 0.2 mmol), orcinol (126 mg, 1.02 mmol), in DCM (5 mL) and MsOH (25 mg, 0.26 mmol, 0.19 ml of 1.4 *M* in DCM) were stirred for 1 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **32** (52 mg, 0.16 mmol, 78%) as a pale yellow color oil.

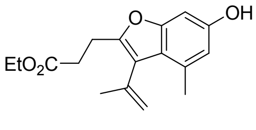
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (1 H, d, *J* = 1.9 Hz), 6.49 (1 H, d, *J* = 1.9 Hz), 5.66 (1 H, t, *J* = 1.8 Hz), 5.11 (1 H, br s), 4.15 (2 H, q, *J* = 7.1 Hz), 2.96 (2 H, t, *J* = 8.4 Hz), 2.67 (2 H, t, *J* = 7.8 Hz), 2.41 (3 H, s), 2.19-2.14 (4 H, m), 1.79-1.74 (2 H, m), 1.72-1.67 (2 H, m) and 1.25 (3 H, t, *J* = 7.2 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 154.9, 153.1, 150.6, 131.7, 130.6, 128.8, 121.3, 120.1, 112.7, 95.6, 60.8, 33.4, 31.5, 25.7, 23.1, 22.2, 22.0, 18.3 and 14.3 ppm.

IR (neat): 3409, 2932, 2861, 1728 (OC=O), 1607, 1532, 1481, 1447, 1282, 1193, 1163, 1113, 1013, 942, 817 and 737 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(6-hydroxy-4-methyl-3-(prop-1-en-2-yl)benzofuran-2-yl)propanoate (33)



The hydroxyl-ester[1] (45 mg, 0.25 mmol), orcinol (155 mg, 1.25 mmol), in DCM (5 mL) and MsOH (31 mg, 0.32 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 45 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **33** (54 mg, 0.19 mmol, 75%) as a pale yellow color oil.

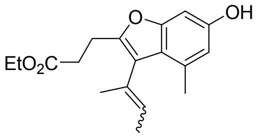
^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.71 (1 H, d, *J* = 1.9 Hz), 6.51 (1 H, d, *J* = 1.9 Hz), 5.30 (1 H, d, *J* = 1.3 Hz), 4.98 (1 H, d, *J* = 1.3 Hz), 4.87 (1 H, br s), 4.14 (2 H, q, *J* = 7.1 Hz), 2.99 (2 H, t, *J* = 7.5 Hz), 2.68 (2 H, t, *J* = 7.5 Hz), 2.44 (3 H, s), 2.05 (3 H, s) and 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.2, 155.0, 153.3, 150.3, 138.0, 131.7, 120.8, 119.5, 117.9, 112.9, 95.6, 60.9, 33.4, 25.5, 22.0, 18.4 and 14.3 ppm.

IR (neat): 3403, 2927, 2854, 1731 (OC=O), 1638, 1472, 1441, 1273, 1173, 1144, 1106, 1023, 817 and 742 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(3-(but-2-en-2-yl)-6-hydroxy-4-methylbenzofuran-2-yl)propanoate (34)



The hydroxyl-ester[1] (45 mg, 0.23 mmol), orcinol (142 mg, 1.15 mmol), in DCM (5 mL) and MsOH (29 mg, 0.3 mmol, 0.21 ml of 1.4 *M* in DCM) were stirred for 45 min at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran **34** (47 mg, 0.16 mmol, 67%) as a pale yellow color oil.

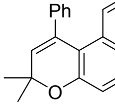
^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.70 (1 H, d, *J* = 1.8 Hz), 6.50 (1 H, d, *J* = 1.8 Hz), 5.49 (1 H, q, *J* = 6.6 Hz), 4.15 (2 H, q, *J* = 7.2 Hz), 2.96 (2 H, t, *J* = 8.4 Hz), 2.66 (2 H, t, *J* = 7.9 Hz), 2.38 (3 H, s), 1.90 (3 H, s), 1.76 (3 H, d, *J* = 6.7 Hz) and 1.25 (3 H, t, *J* = 7.2 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 173.2, 154.9, 153.1, 150.5, 131.7, 128.2, 126.4, 121.2, 121.1, 112.7, 95.6, 60.8, 33.4, 22.0, 18.9, 18.4, 14.3 and 14.1 ppm.

IR (neat): 3411, 2932, 2858, 1729 (OC=O), 1614, 1471, 1440, 1357, 1275, 1173, 1153, 1104, 1013, 846 and 735 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

3,3-Dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (37)



The 2-methyl-4-phenylbut-3-yn-2-ol[6] (40 mg, 0.25 mmol), naphthalen-2-ol (180 mg, 1.25 mmol), in DCM (4 mL) and MsOH (31.2 mg, 0.33 mmol, 0.23 ml of 1.4 *M* in DCM) were stirred for 4 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave benzo-chromene **37** (66 mg, 0.23 mmol, 92%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (2 H, d, *J* = 8.5 Hz), 7.31-7.27 (3 H, m), 7.20-7.16 (4 H, m), 7.09 (1 H, d, *J* = 8.5 Hz), 7.03-6.99 (1 H, m), 5.69 (1 H, s) and 1.49 (6 H, s) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 141.7, 135.6, 130.6, 130.5, 130.3, 130.0, 128.5, 127.9, 127.4, 126.5, 125.1, 123.1, 118.9, 116.2, 75.4 and 26.5 ppm.

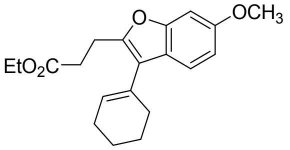
IR (neat): 3052, 2979, 2928, 2861, 1625, 1591, 1510, 1445, 1372, 1345, 1265, 1247, 1222, 1146, 1069, 989, 897, 819, 806, 757 and 750 cm^{-1}.

HR ESI-MS: $[C_{21}H_{19}O]^+$ = $[M+H]^+$ requires 287.1430; found 287.1442

TLC: R_f = 0.4 (4:1, Hex/EtOAc).

M.P.: 108 °C

Ethyl 3-(3-cyclohexenyl-6-methoxybenzofuran-2-yl)propanoate (39a)



The benzofuran **23** (280 mg, 0.89 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous acetone, K_2CO_3 (160 mg, 1.16 mmol) and dimethyl sulfate (146 mg, 1.16 mmol) were added under nitrogen atmosphere stirred the reaction mixture 3 h at 70 ^{0}C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the benzofura **23**, reaction was quenched with H_2O and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (19:1 hexanes:EtOAc) gave anisole-ester **39a** (262 mg, 0.8 mmol, 90%) as a pale yellow color oil.

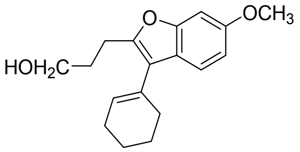
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (1 H, d, *J* = 8.5 Hz), 6.93 (1 H, d, *J* = 2.1 Hz), 6.81 (1 H, dd, *J* = 8.5 & 2.1 Hz), 5.81-5.78 (1 H, m), 4.16 (2 H, q, *J* = 7.1 Hz), 3.83 (3 H, s), 3.09 (2 H, t, *J* = 8.1 Hz), 2.72 (2 H, t, *J* = 7.5 Hz), 2.35-2.31 (2 H, m), 2.24-2.21 (2 H, m), 1.82-1.76 (2 H, m), 1.75-1.69 (2 H, m) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 157.5, 154.9, 150.7, 129.6, 127.7, 122.3, 120.3, 119.4, 111.0, 95.9, 60.7, 55.9, 33.2, 29.4, 25.7, 23.1, 22.8, 22.3 and 14.3 ppm.

IR (neat): 2926, 2855, 2366, 1724 (OC=O), 1612, 1474, 1442, 1283, 1146, 1114, 1021, 972, 837 and 735 cm^{-1}.

TLC: R$_f$ = 0.4 (19:1, hex/EtOAc).

3-(3-Cyclohexenyl-6-methoxybenzofuran-2-yl)propan-1-ol (39b)



The ansole-ester **39a** (255 mg, 0.78 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous DCM was added under nitrogen atmosphere and cooled the flask to 0 °C. Then DIBAL-H (1.6 mmol, 1.6 ml of 1 *M* in toulene) was added to the reaction flask, and stirred the reaction mixture 3 h at 0 °C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the anisole-ester, reaction was quenched with H_2O (4-6 droups) and ethyl acetate (EtOAc). Reaction solution filtered through short colum chromatography. The crude material was typically purified by flash column chromatography (3:1 hexanes:EtOAc) gave anisole-alcohol **39b** (174 mg, 0.61 mmol, 78%) as a pale yellow color oil.

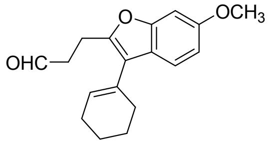
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.30 (1 H, d, *J* = 8.4 Hz), 6.86 (1 H, d, *J* = 2.0 Hz), 6.86 (1 H, dd, *J* = 8.4 & 2.0 Hz), 5.77-5.76 (1 H, m), 3.76 (3 H, s), 3.32 (2 H, t, *J* = 6.2 Hz), 2.78 (2 H, t, *J* = 6.9 Hz), 2.26 (2 H, br s), 2.13 (2 H, br s), 1.89 (2 H, t, *J* = 6.9 Hz), 1.74-1.66 (2 H, m) and 1.67-1.68 (2 H, m) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.4, 154.8, 152.2, 129.8, 127.5, 127.1, 122.4, 110.9, 95.9, 62.3, 55.9, 31.6, 29.8, 25.7, 23.4, 23.2 and 22.4 ppm.

IR (neat): 3443, 2925, 2857, 2363, 1614, 1414, 1447, 1298, 1197, 1134, 1069, 1016, 837 and 738 cm^{-1}.

TLC: R$_f$ = 0.4 (3:1, hex/EtOAc).

3-(3-Cyclohexenyl-6-methoxybenzofuran-2-yl)propanal (39)



The Benzofuran-alcohol **39b** (200 mg, 0.7 mmol), in EtOAc (14 mL), and IBX (360 mg, 1.25 mmol) were stirred for 3 h at 70 °C. Reaction mixture was filtered through a small plug of silica gel. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran-aldehyde **39** (160 mg, 0.56 mmol, 80%) as a pale yellow color oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (1 H, t , *J* = 1.3 Hz), 7.35 (1 H, d, *J* = 8.6 Hz), 6.92 (1 H, d, *J* = 2.3 Hz), 6.82 (1 H, dd, *J* = 8.6 & 2.3 Hz), 5.79-5.77 (1 H, m), 3.83 (3 H, s), 3.09 (2 H, d, *J* = 7.9 Hz), 2.88-2.84 (2 H, m), 2.34-2.30 (2 H, m), 2.24-2.18 (2 H, m) and 1.82-1.68 (4 H, t, *J* = 7.1 Hz) ppm.

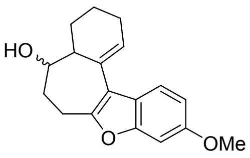
^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 157.6, 154.9, 150.4, 129.6, 127.8, 122.2, 120.3, 119.5, 111.1, 95.8, 55.9, 42.5, 29.4, 25.7, 23.1, 22.3 and 20.1 ppm.

IR (neat): 2928, 2844, 2368, 1716 (C=O), 1618, 1491, 1440, 1286, 1196, 1151, 1114, 1024, 942, 826 and 815 cm^{-1}.

HR ESI-MS: $[C_{18}H_{20}O_3Na]^+$ = $[M+Na]^+$ requires 307.1305; found 307.1310

TLC: R_f = 0.4 (4:1, hex/EtOAc).

10-Methoxy-3,4,4*a*,5,6,7-hexahydro-2*H*-benzo[3,4]cyclohepta[1,2-*b*]benzofuran-5-ol (38)



The benzofuran-aldehyde **39** (70 mg, 0.25 mmol) in DCM (9 mL), and BF_3Et_2O (17.5 mg, 0.12 mmol, 0.02 ml) were stirred for 1.5 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexanes:EtOAc) gave benzofuran-alcohol **38** (52 mg, 0.18 mmol, 74%) as a pale yellow color solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (1 H, d, *J* = 8.6 Hz), 6.92 (1 H, d, *J* = 2.2 Hz), 6.83 (1 H, dd, *J* = 8.6 & 2.2 Hz), 4.09 (1 H, d, *J* = 6.0 Hz), 3.83 (3 H, s), 3.16-3.08 (1 H, m), 2.86-2.79 (1 H, m), 2.50-2.45 (1 H, m), 2.31-2.14 (2 H, m), 1.95-1.82 (4 H, m) and 1.72-1.62 (2 H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 154.7, 153.6, 131.9, 127.0, 122.0, 120.3, 117.8, 111.0, 95.7, 74.6, 55.8, 44.2, 33.5, 30.4, 25.9, 22.1 and 20.7 ppm.

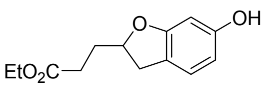
IR (neat): 3438, 2927, 2857, 2367, 1619, 1497, 1448, 1277, 1197, 1154, 1079, 1025, 822 and 733 cm^{-1}.

HR ESI-MS: $[C_{18}H_{20}NaO_3]^+$ = $[M+Na]^+$ requires 307.1305; found 307.1313

TLC: R_f = 0.4 (4:1, hex/EtOAc).

M.P.: 141 °C.

Ethyl 3-(6-hydroxy-2,3-dihydrobenzofuran-2-yl)propanoate (23a)



The benzofuran-ester **23** (200 mg, 0.85 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous EtOH and Pd/c (40 mg, 20 wt%) were added under hydrogen atmosphere stirred the reaction mixture 1.5h at RT. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the benzofuran-ester, reaction was filtered through short column by washing with ethyl acetate (EtOAc). The combined organic layer was dried with ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (4:1 hexanes:EtOAc) gave phenol-ester **23a** (167 mg, 0.71 mmol, 82%) as a colorless oil.

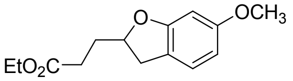
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (1 H, d, *J* = 8.0 Hz), 6.44-6.38 (2 H, m), 4.83-4.76 (1 H, m), 4.14 (2 H, q, *J* = 7.2 Hz), 3.21 (1 H, dd, *J* = 9.0 & 15.0 Hz), 2.75 (1 H, dd, *J* = 7.1 & 15.0 Hz), 2.55-2.47 (2 H, m), 2.08-2.01 (2 H, m) and 1.26 (3 H, t, *J* = 7.2 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 160.5, 156.5, 125.1, 118.2, 107.3, 97.7, 83.1, 60.7, 34.7, 31.2, 30.5 and 14.3 ppm.

IR (neat): 3404, 2924, 2854, 2358, 1721 (OC=O), 1614, 1499, 1455, 1325, 1219, 1141, 1020, 828 and 732 cm^{-1}.

TLC: R_f = 0.4 (4:1, hex/EtOAc).

Ethyl 3-(6-methoxy-2,3-dihydrobenzofuran-2-yl)propanoate (23b)



The phenol-ester **23a** (250 mg, 1.06 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous acetone, K_2CO_3 (190 mg, 1.38 mmol) and dimethyl sulfate (174 mg, 1.38 mmol) were added under nitrogen atmosphere stirred the reaction mixture 3 h at 60 ^{0}C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the phenol-ester, reaction was quenched with H_2O and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (9:1 hexanes:EtOAc) gave anisole-ester **23b** (247 mg, 0.99 mmol, 93%) as a pale yellow color oil.

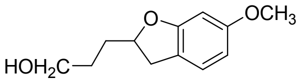
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (1 H, d, *J* = 8.1 Hz), 6.40-6.35 (2 H, m), 4.86-4.78 (1 H, m), 4.14 (2 H, q, *J* = 7.1 Hz), 3.76 (3 H, s), 3.24 (1 H, dd, *J* = 9.0 & 15.0 Hz), 2.79 (1 H, dd, *J* = 7.2 & 15.0 Hz), 2.53-2.48 (2 H, m), 2.07-2.02 (2 H, m) and 1.26 (3 H, t, *J* = 7.1 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 160.7, 160.5, 125.0, 105.9, 96.3, 83.1, 60.6, 55.6, 34.8, 31.3, 30.5 and 14.4 ppm.

IR (neat): 2925, 2854, 2364, 1723 (OC=O), 1614, 1471, 1441, 1285, 1192, 1156, 1124, 1021, 954, 837 and 793 cm^{-1}.

TLC: R$_f$ = 0.4 (9:1, hex/EtOAc).

3-(6-Methoxy-2,3-dihydrobenzofuran-2-yl)propan-1-ol (23c)



The ansole-ester **23b** (265 mg, 1.06 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous DCM was added under nitrogen atmosphere and cooled the flask to 0 °C. Then DIBAL-H (1.6 mmol, 1.6 ml of 1 *M* in toulene) was added to the reaction flask, and stirred the reaction mixture 4 h at 0 °C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the anisole-ester, reaction was quenched with H_2O (4-6 droups) and ethyl acetate (EtOAc). Reaction solution filtered through short colum chromatography. The crude material was typically purified by flash column chromatography (3:1 hexanes:EtOAc) gave anisole-alcohol **23c** (170 mg, 0.82 mmol, 77%) as a pale yellow color oil.

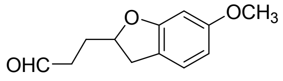
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.02 (1 H, d, *J* = 8.1 Hz), 6.40-6.36 (2 H, m), 4.86-4.79 (1 H, m), 3.76 (3 H, s), 3.71 (2 H, t, *J* = 5.8 Hz), 3.22 (1 H, dd, *J* = 9.0 & 15.1 Hz), 2.79 (1 H, dd, *J* = 7.7 & 15.1 Hz) and 1.85-1.71 (4 H, m) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.7, 160.4, 125.0, 118.8, 105.9, 96.2, 84.3, 62.7, 55.6, 35.0, 32.7 and 28.9 ppm.

IR (neat): 3441, 2924, 2857, 2364, 1614, 1494, 1441, 1278, 1197, 1144, 1069, 1015, 832 and 739 cm^{-1}.

TLC: R$_f$ = 0.4 (3:1, hex/EtOAc).

3-(6-Methoxy-2,3-dihydrobenzofuran-2-yl)propanal (23d)



The anisole-alcohol **23c** (160 mg, 0.76 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous EtOAc, IBX (319 mg, 1.14 mmol) were added under hydrogen atmosphere stirred the reaction mixture 3.5 h at 80 ^{0}C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the anisole-alcohol, reaction was filtered through short column by washing with ethyl acetate (EtOAc). The crude material was typically purified by flash column chromatography (5:1 hexanes:EtOAc) gave ansole-aldehyde **23d** (143 mg, 0.7 mmol, 91%) as a pale yellow color oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.82 (1 H, t, *J* = 1.26 Hz), 7.01 (1 H, d, *J* = 8.1 Hz), 6.40-6.35 (2 H, m), 4.86-4.78 (1 H, m), 3.76 (3 H, s), 3.25 (1 H, dd, *J* = 9.0 & 15.1 Hz), 2.79 (1 H, dd, *J* = 7.1 & 15.1 Hz), 2.69-2.64 (2 H, m) and 2.07-2.01 (2 H, m) ppm.

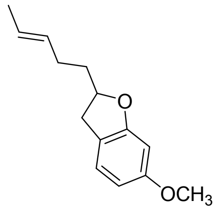
^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 160.6, 160.5, 125.1, 118.5, 106.1, 96.3, 83.0, 55.6, 40.1, 34.9 and 28.5 ppm.

IR (neat): 2957, 2925, 2856, 1679 (C=O), 1591, 1409, 1324, 1221, 1118, 1017, 918, 853 and 724 cm^{-1}

TLC: R_f = 0.4 (5:1, hex/EtOAc).

HR ESI-MS: $[C_{12}H_{14}O_3Na]^+$ = $[M+Na]^+$ requires 229.0841; found 229.0854

(E)-6-Methoxy-2-(pent-3-enyl)-2,3-dihydrobenzofuran (40)



The ethyl wittig reagent (196 mg, 0.68 mmol) was taken in to a clean, anhydrous round bottom flask equipped with stir bar. Then anhydrous THF was added under hydrogen atmosphere and cooled the flask to 0 °C. Then n-BuLi (0.62 mmol, 0.4 ml of 1.6 *M* in hexane) was added to the reaction flask, and stirred the reaction mixture 30 min at 0 °C. Then anisole-aldehyde **23d** (100 mg, 0.48 mmol), anhydrous THF solution was added to the reaction flask at 0 ^{0}C and stirred the reaction mixture 2 h at 0 °C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the anisole-aldehyde, reaction was quenched with saturated NH_4Cl, extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was typically purified by flash column chromatography (49:1 hexanes:EtOAc) gave ansole-olefine **40** (77 mg, 0.35 mmol, 77%) as a pale yellow color oil.

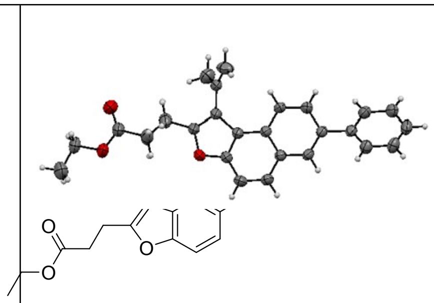
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (1 H, d, *J* = 8.7 Hz), 6.40-6.36 (2 H, m), 5.52-5.39 (2 H, m), 4.83-4.73 (1 H, m), 3.76 (3 H, s), 3.21 (1 H, dd, *J* = 8.8 & 15.0 Hz), 2.79 (1 H, dd, *J* = 8.6 & 15.0 Hz), 2.25-2.14 (2 H, m), 1.94-1.85 (1 H, m), 1.75-1.67 (1 H, m) and 1.64 (3 H, d, *J* = 6.5 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 160.4, 129.5, 125.0, 124.9, 119.0, 105.8, 96.2, 84.0, 55.6, 36.0, 35.0, 29.8 and 23.1 ppm.

IR (neat): 2925, 2854, 2351, 1617, 1499, 1455, 1320, 1255, 1210, 1140, 1020, 935, 828 and 732 cm^{-1}.

TLC: R_f = 0.4 (49:1, hex/EtOAc).

HR ESI-MS: $[C_{14}H_{18}O_2Na]^+$ = $[M+Na]^+$ requires 241.1199; found 241.1190

Crystallographic Data and Structure Refinements Summary for Compound **20**	
Molecular Structure (ORTEP Diagram) For compound **20**	
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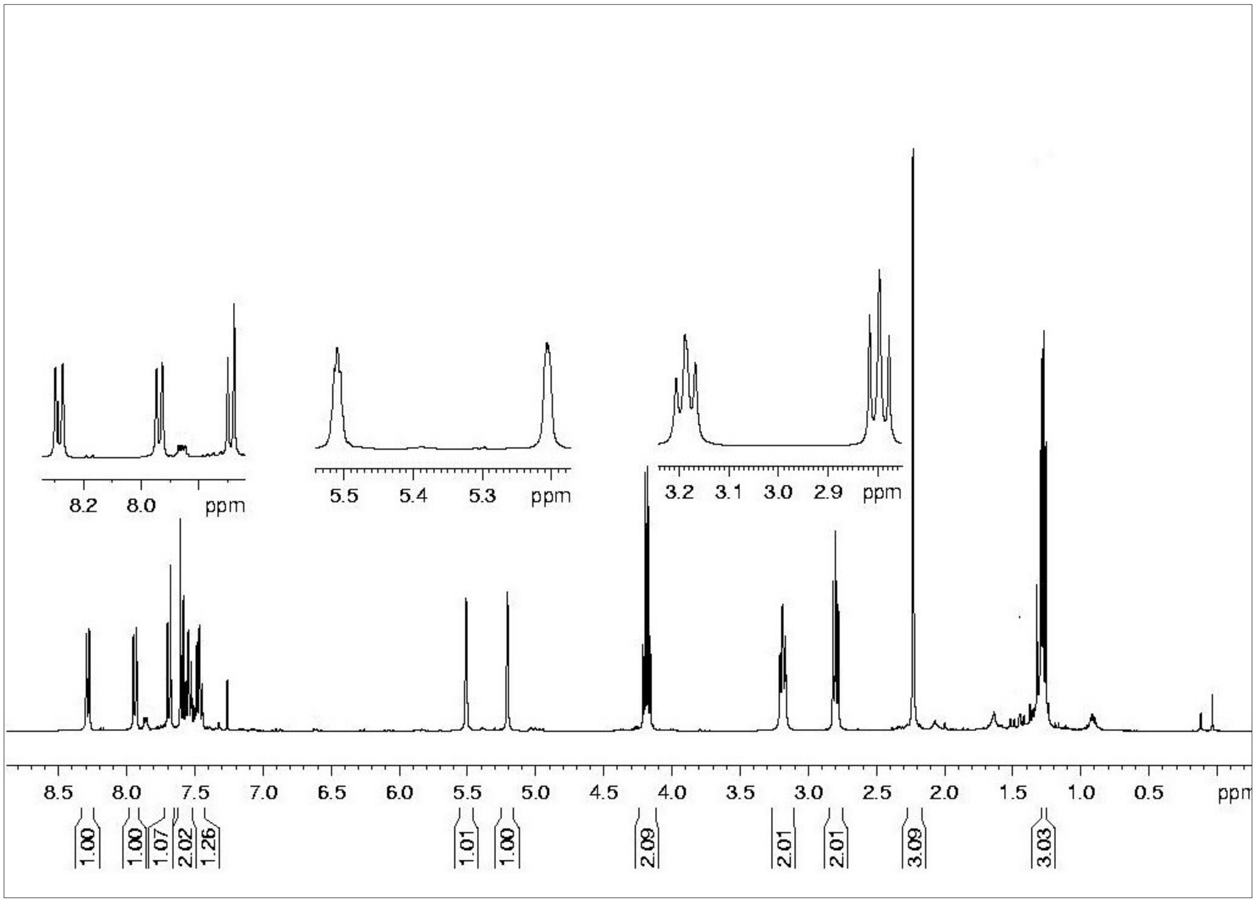
Formula	$C_{24}H_{24}O_3$
Formula weight	384
	light yellow
Crystal morphology	clear light less Rectangular
Temperature/K	296(2)
Radiation	Mo k/a
Wavelength/Å	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
a (Å)	8.9587(7) Å
b (Å)	8.4815(5) Å
c (Å)	27.445(2) Å
α (°)	90°
β (°)	92.802(4)°
γ (°)	90°
Volume(Å3)	2082.9(3) Å3
Z	4
Density (g/ml)	1.220 g/cm3

μ (1/mm)	0.079 mm-1
F (000)	808
θ (min, max)	0.9920 and 0.9830
No. of unique reflns	14082
No. of parameters	265
R_obs, wR2_obs	0.0847, 0.1835
Δρmin, Δρmax (eÅ-3)	-0.347, 0.691
Goodness-of-fit on F^2	1.021

References:

1) Trost, B. M.; Papillon, J. P. N. and Nussbaumer, T. *J. Am. Chem. Soc.* **2005**,*127*, 17921.
2) Thomas, M.; Jens, F.; Stefan, L.; Doering, K. V.; Pascal; Ines, H.; Hugh, R.C.; Hahn, H.; Isolde; Jeffrey, H. M. *Eur. Pat. Appl.* **2012** EP 2511255 A1 20121017.
3) Tharra, P.; Baire, B. *Chem. Commun.* **2016**, *52*, 12147.
4) Tharra, P.; Baire, B. *Communicated elsewhere.*
5) Carter; Michael D. *PCT Int. Appl*., **2006**, 2006125324.
6) Hussain, K. M.; Ansari, I. M.; Kant, R.; Hajela, K. *Org. Lett.*, **2014**, *16*, 560.
7) Fukumoto, Y.; Tamura, Y.; Iyori, Y.; Chatani, N. *J. Org. Chem.* **2016**, *81*, 3161.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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
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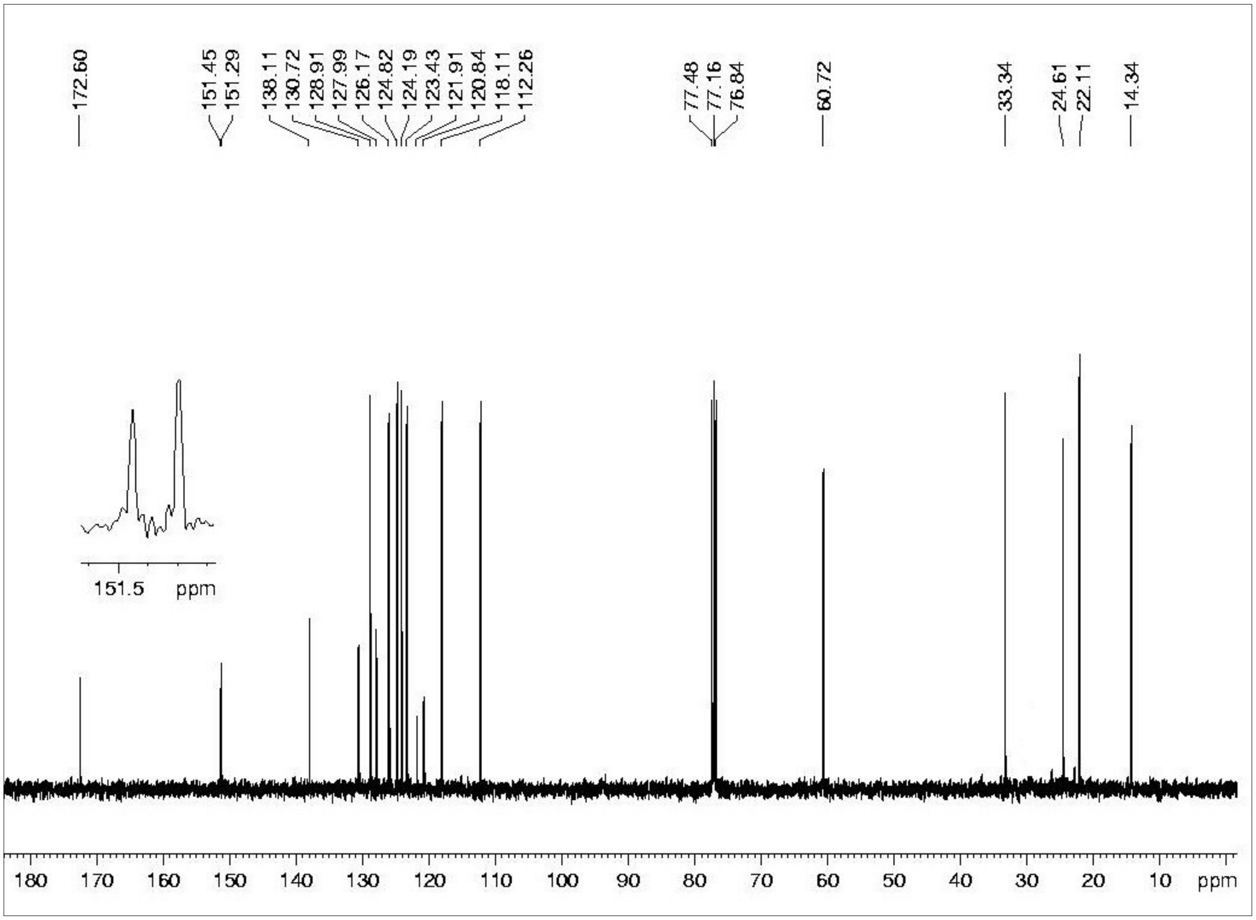
1.00
2.09
2.01
2.01
3.09
3.03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118.11
112.26
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77.16
76.84
60.72
33.34
24.61
22.11
14.34
151.5
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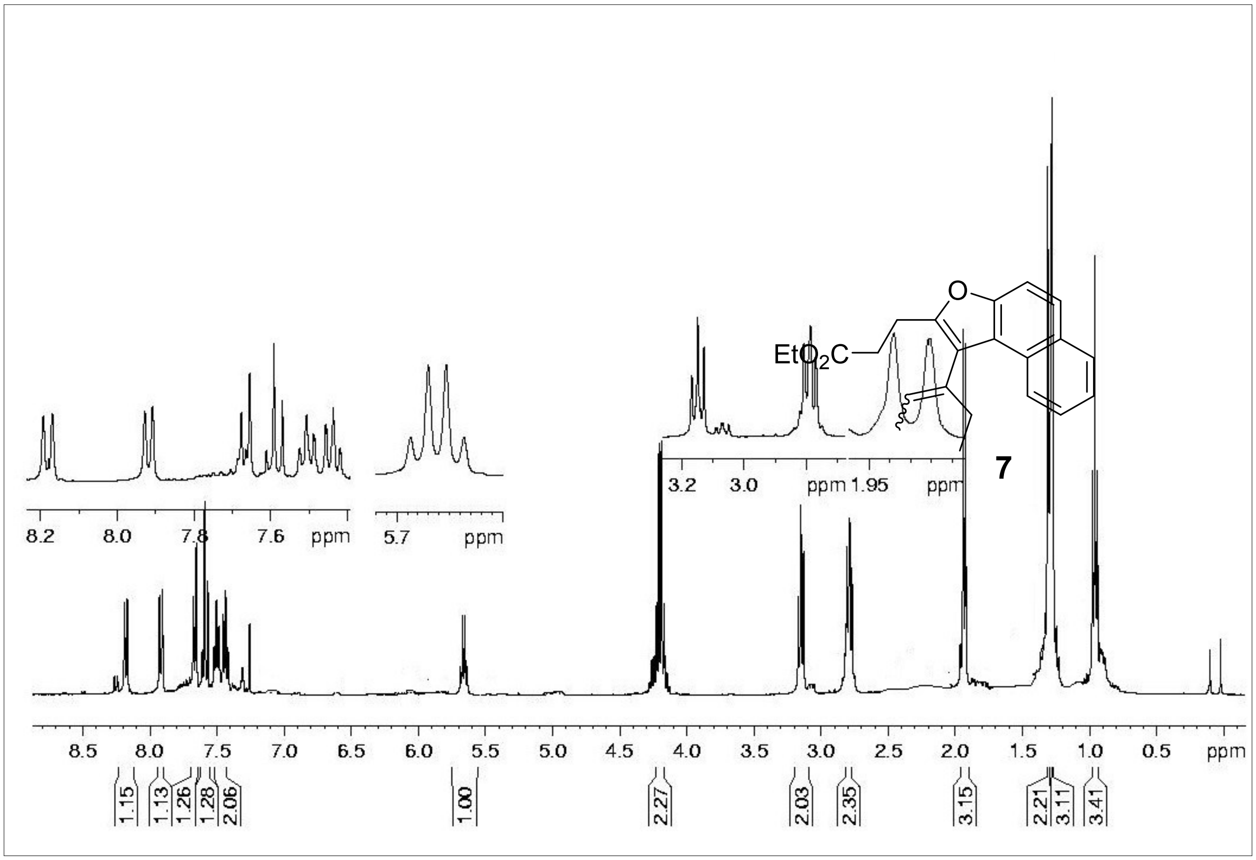
20
10
ppm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5.7 ppm
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1.15
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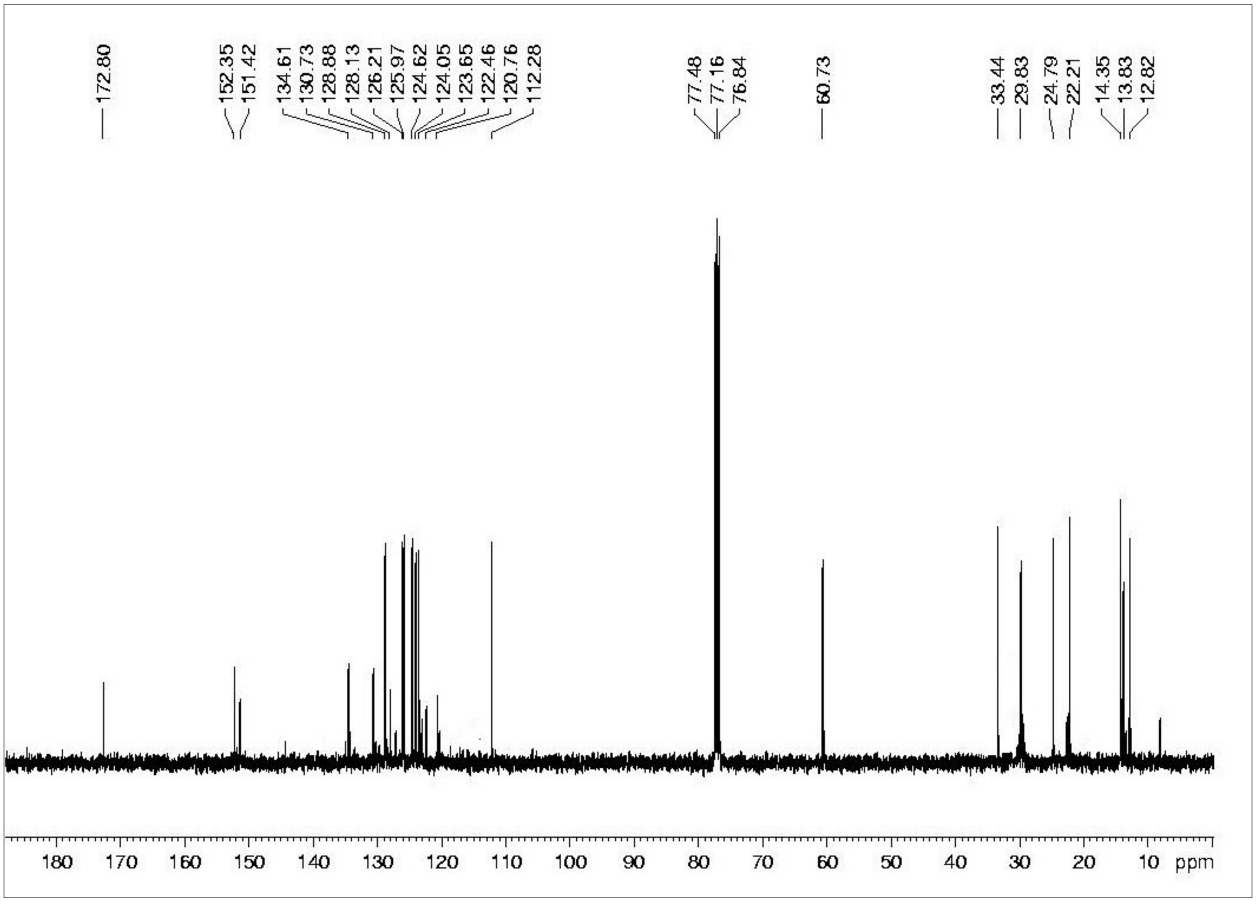
3.11
3.41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77.16
76.84
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12.82
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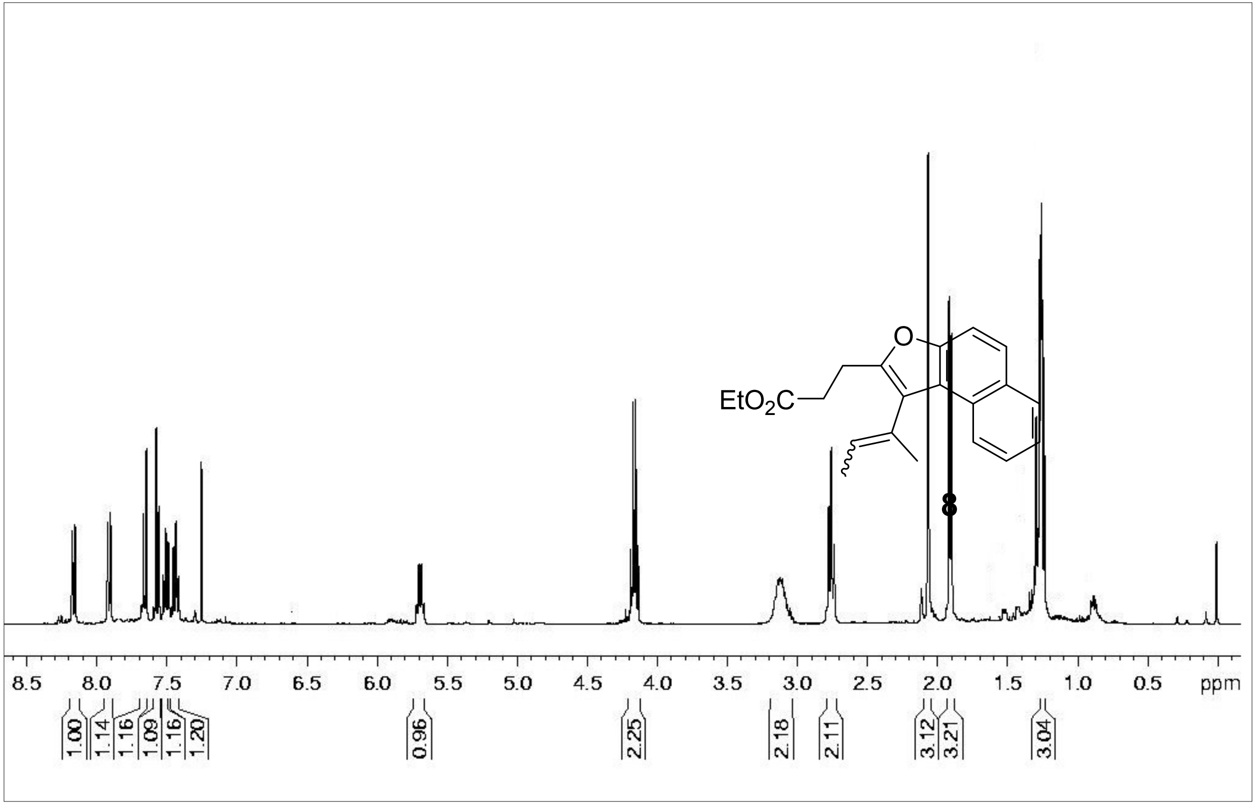
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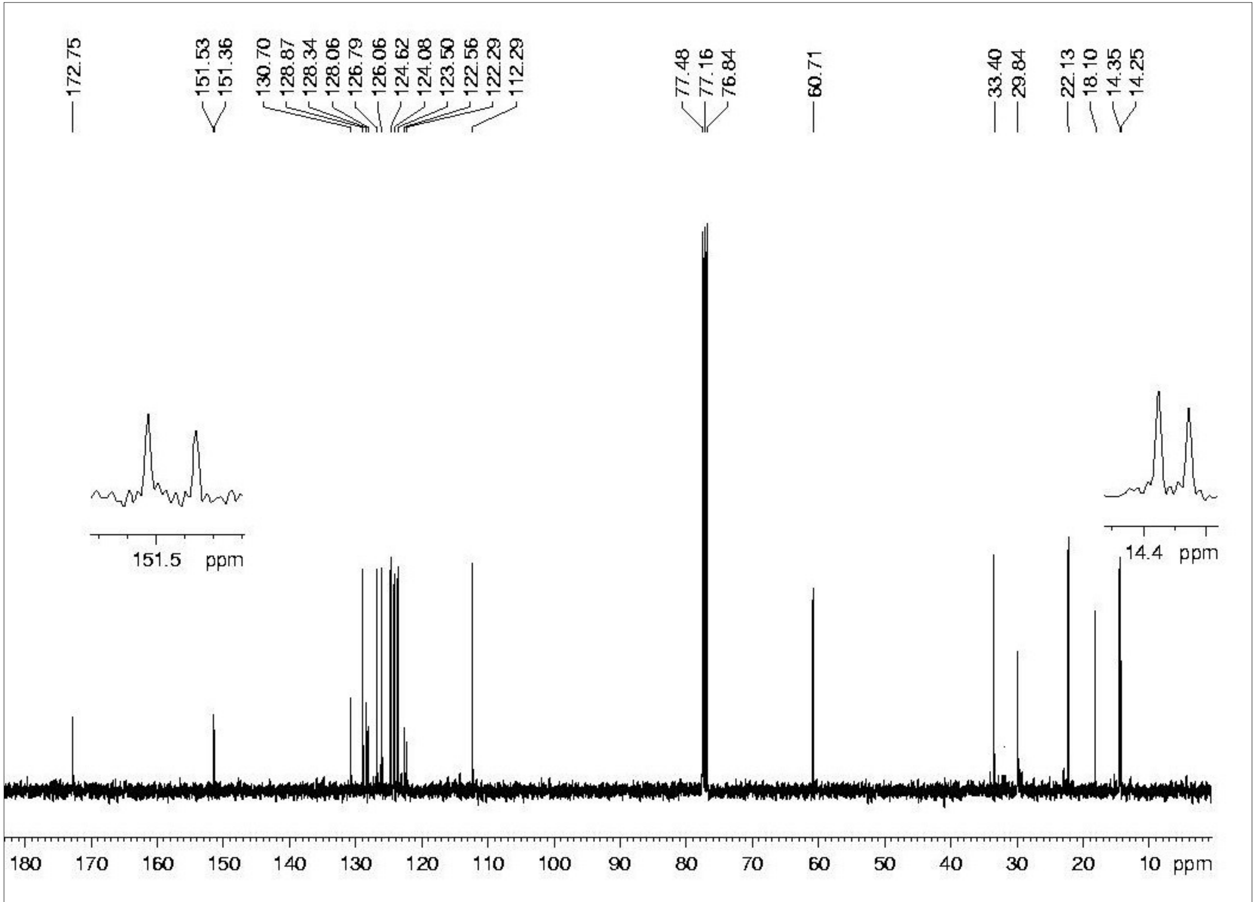
3.21
3.04

8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76.84
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33.40
29.84
22.13
18.10
14.35
14.25
151.5 ppm
14.4 ppm
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80
70
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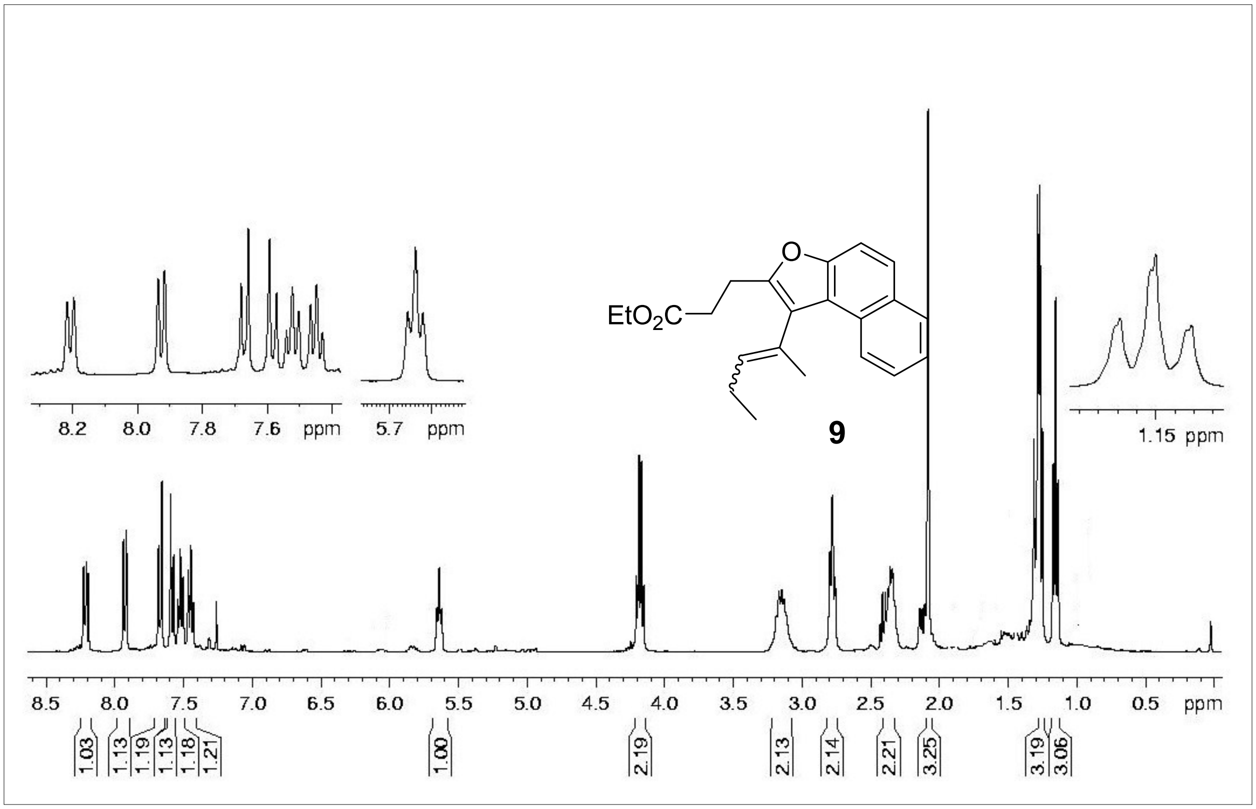
40
30
20
10 ppm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1.15 ppm
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1.03
1.13
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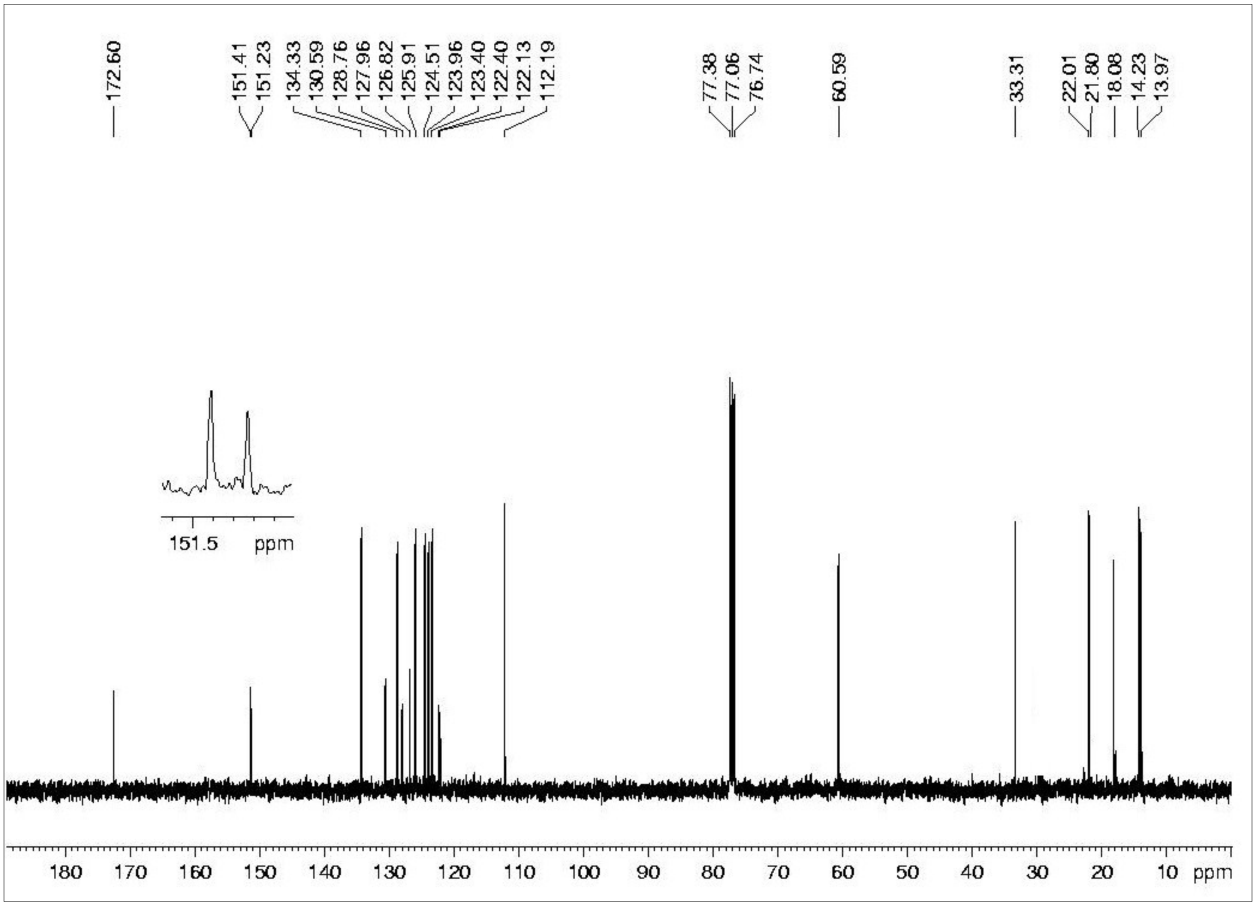
3.19
3.06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77.06
76.74
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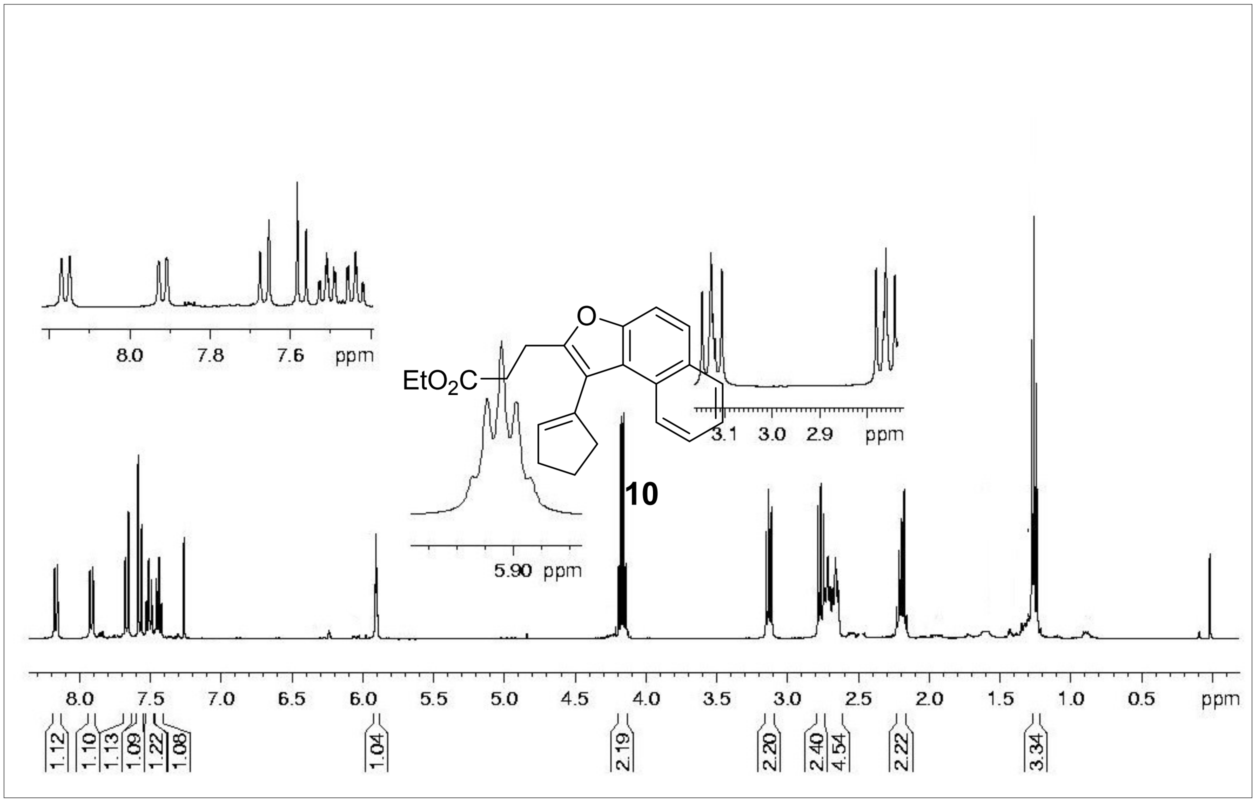
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4.0
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3.0
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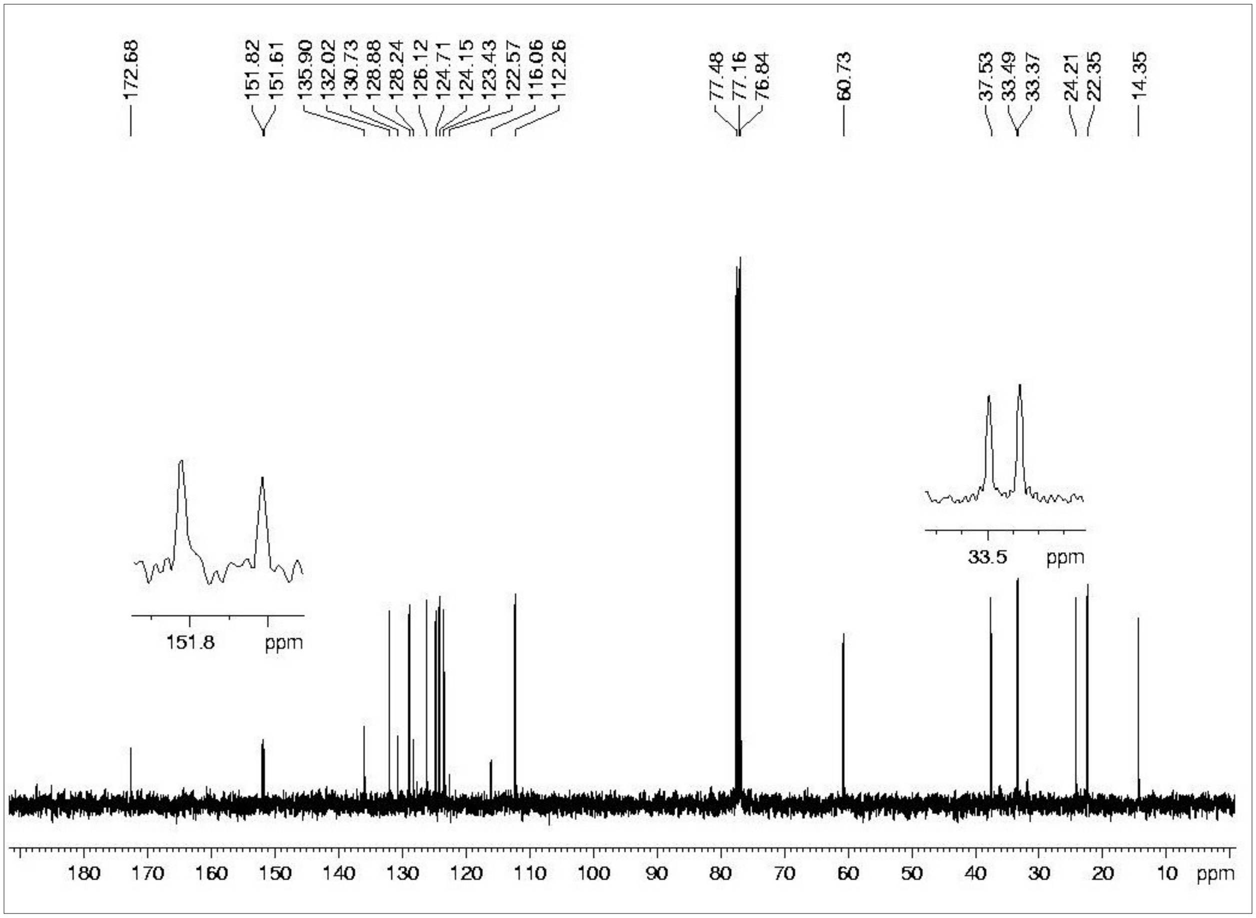
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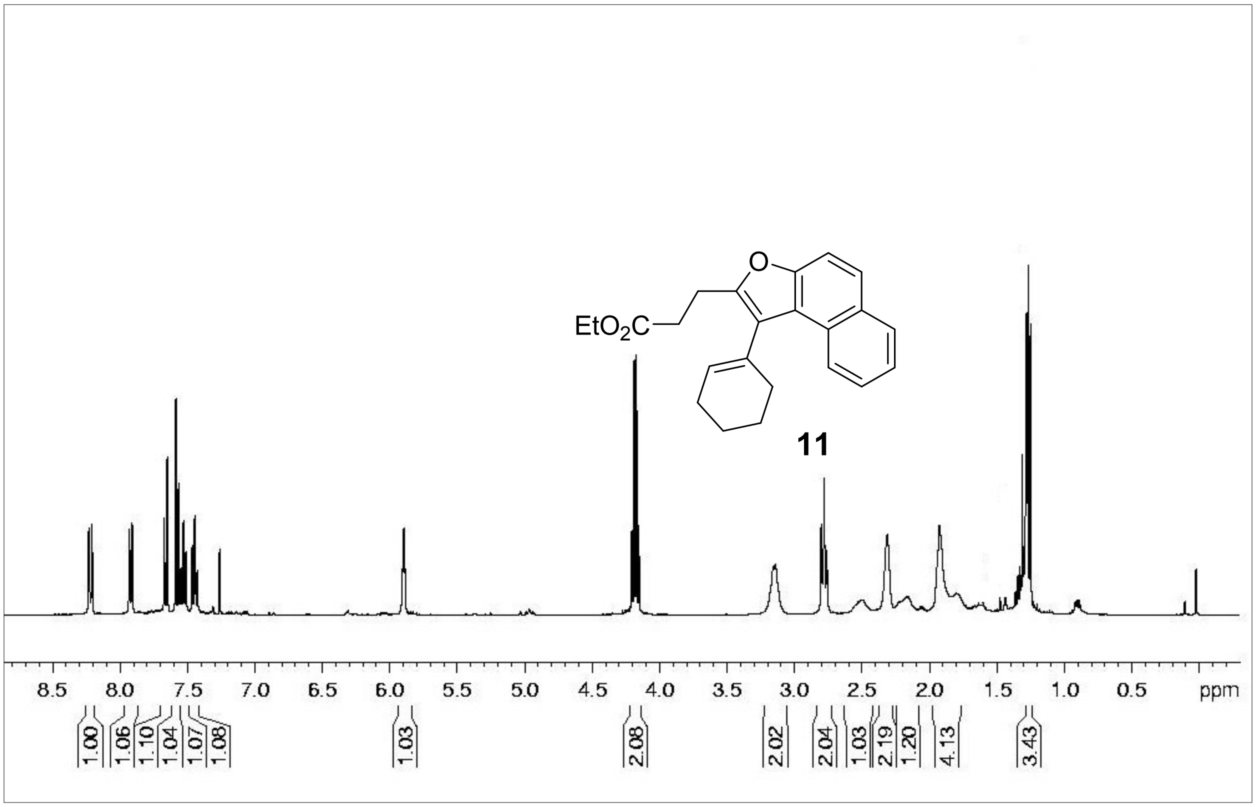
ppm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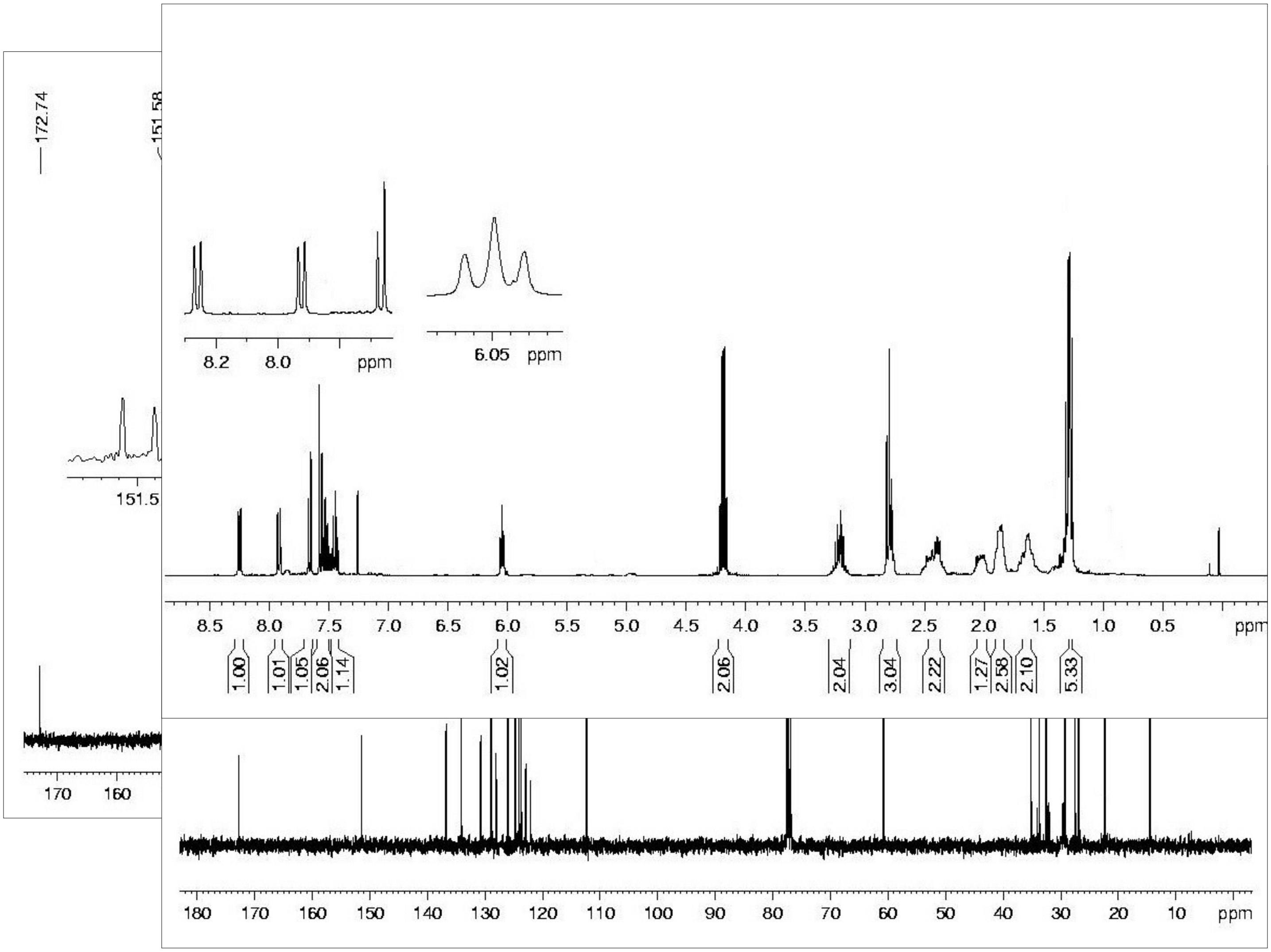
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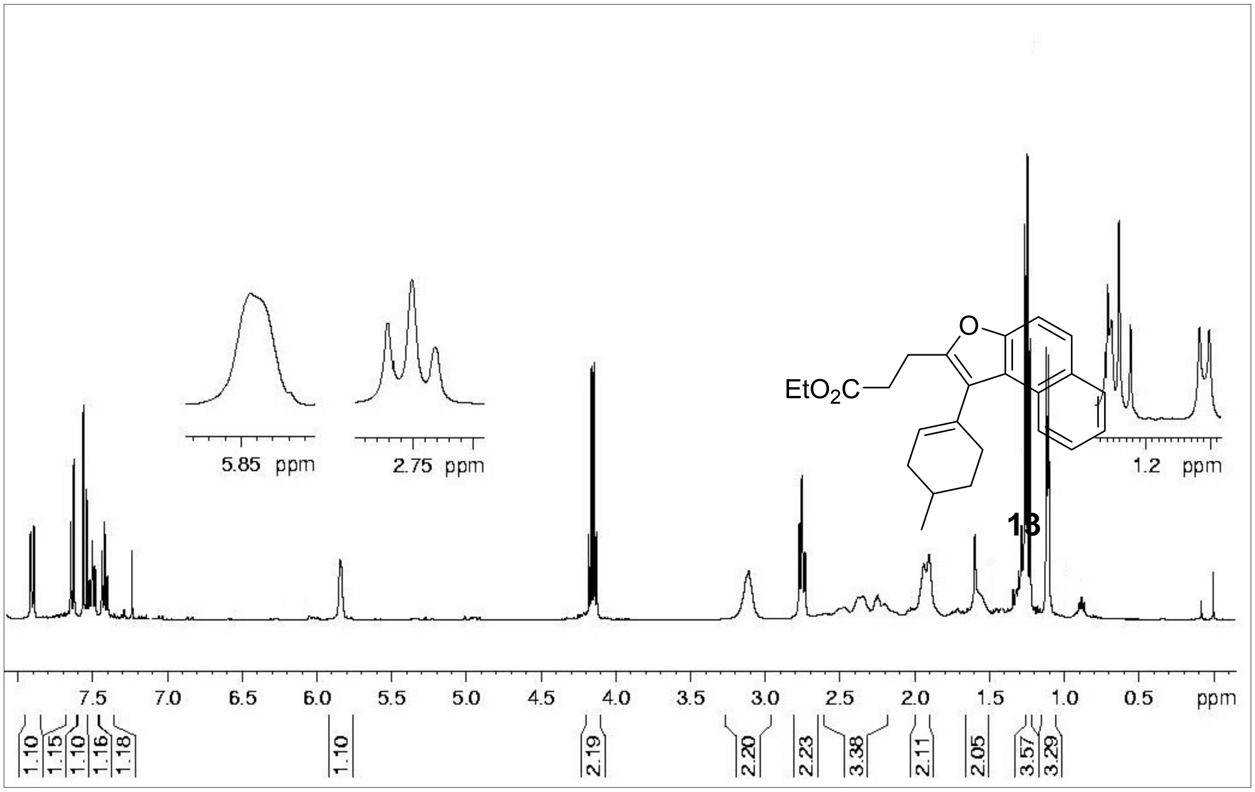
10
ppm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1.15
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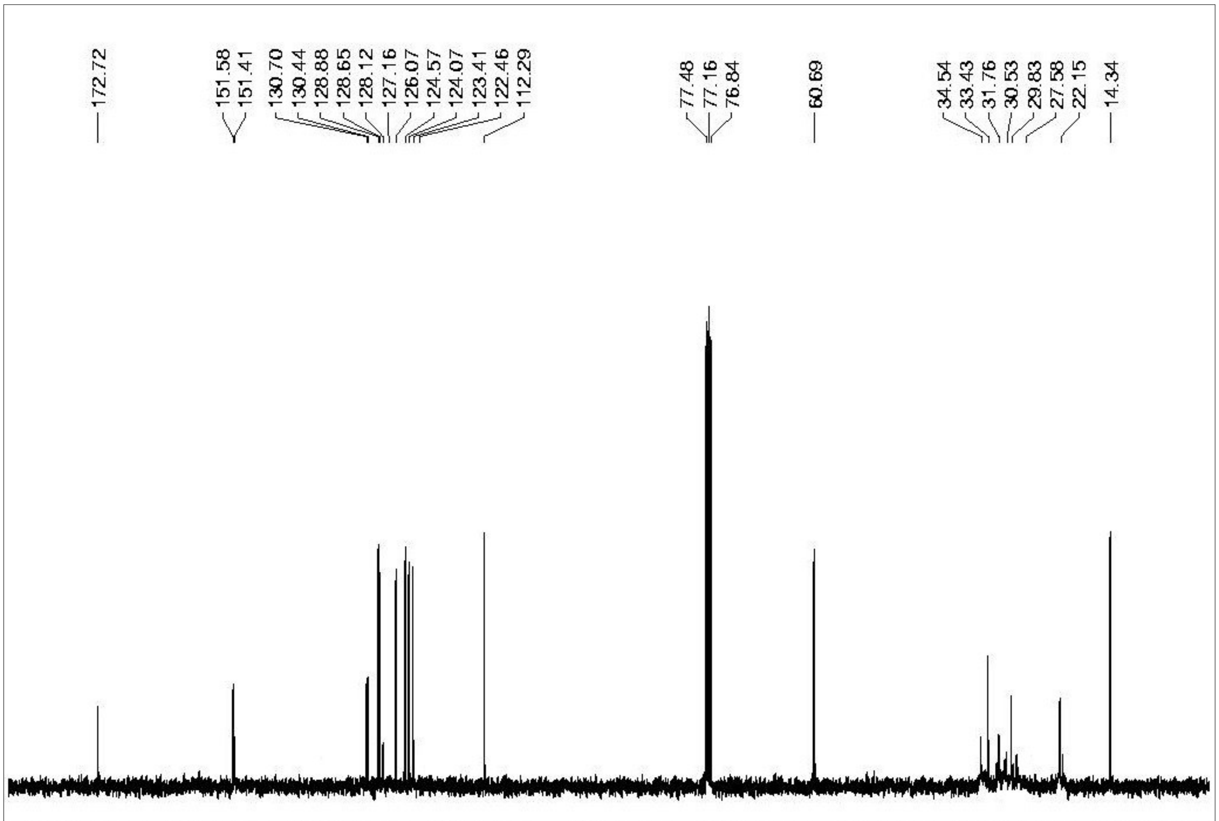
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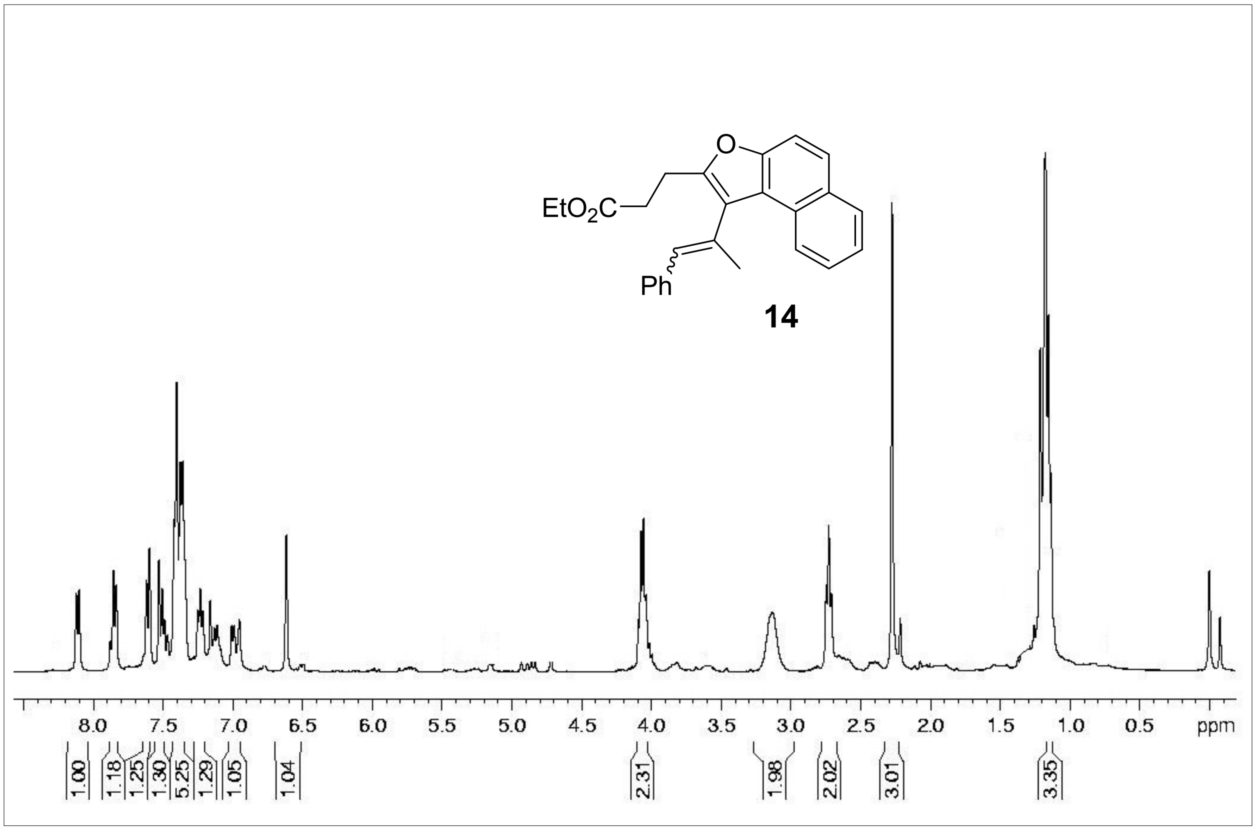
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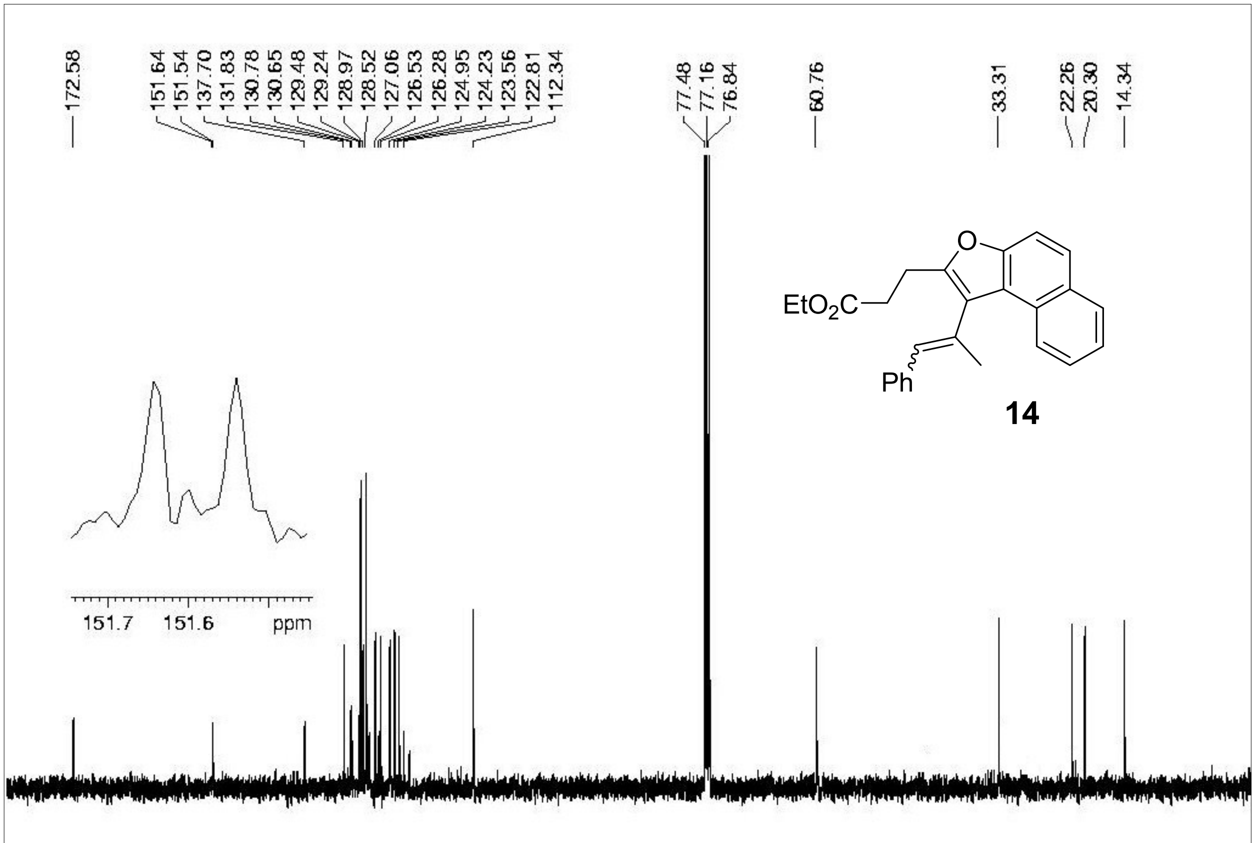
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O
Ph
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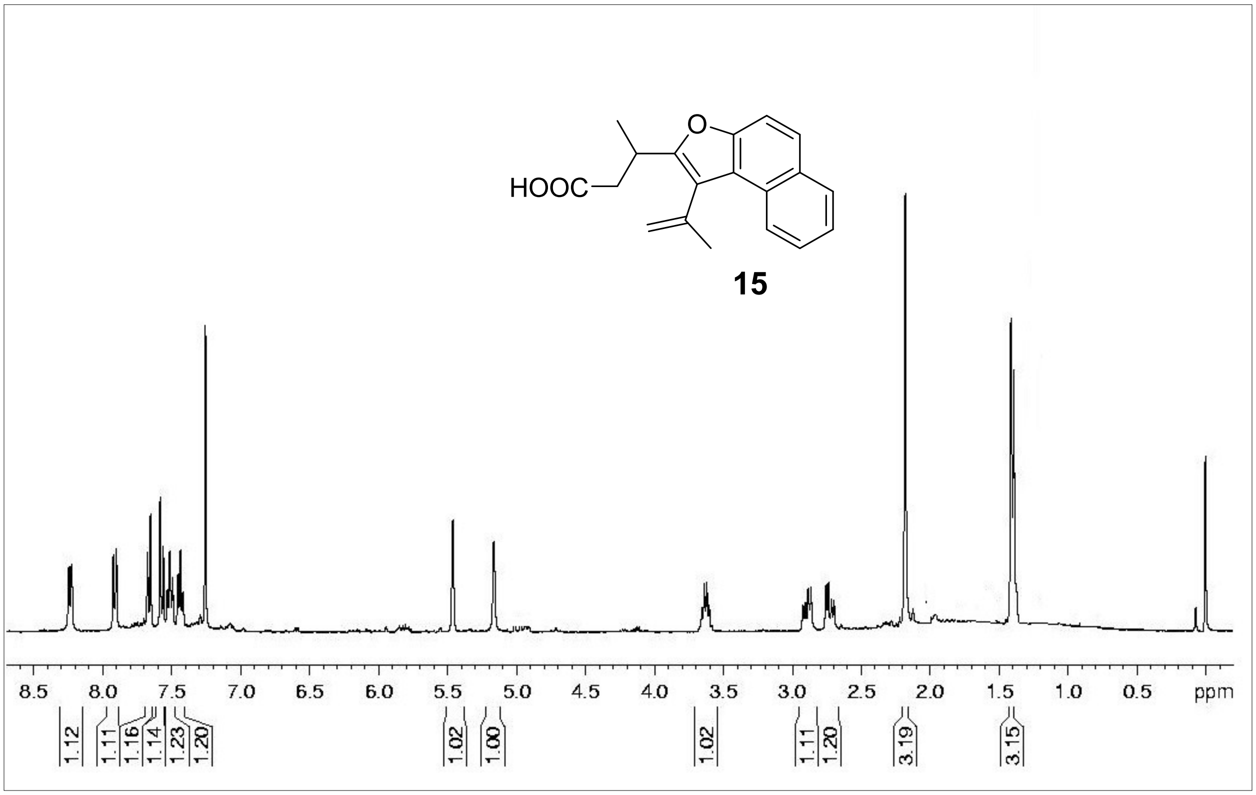
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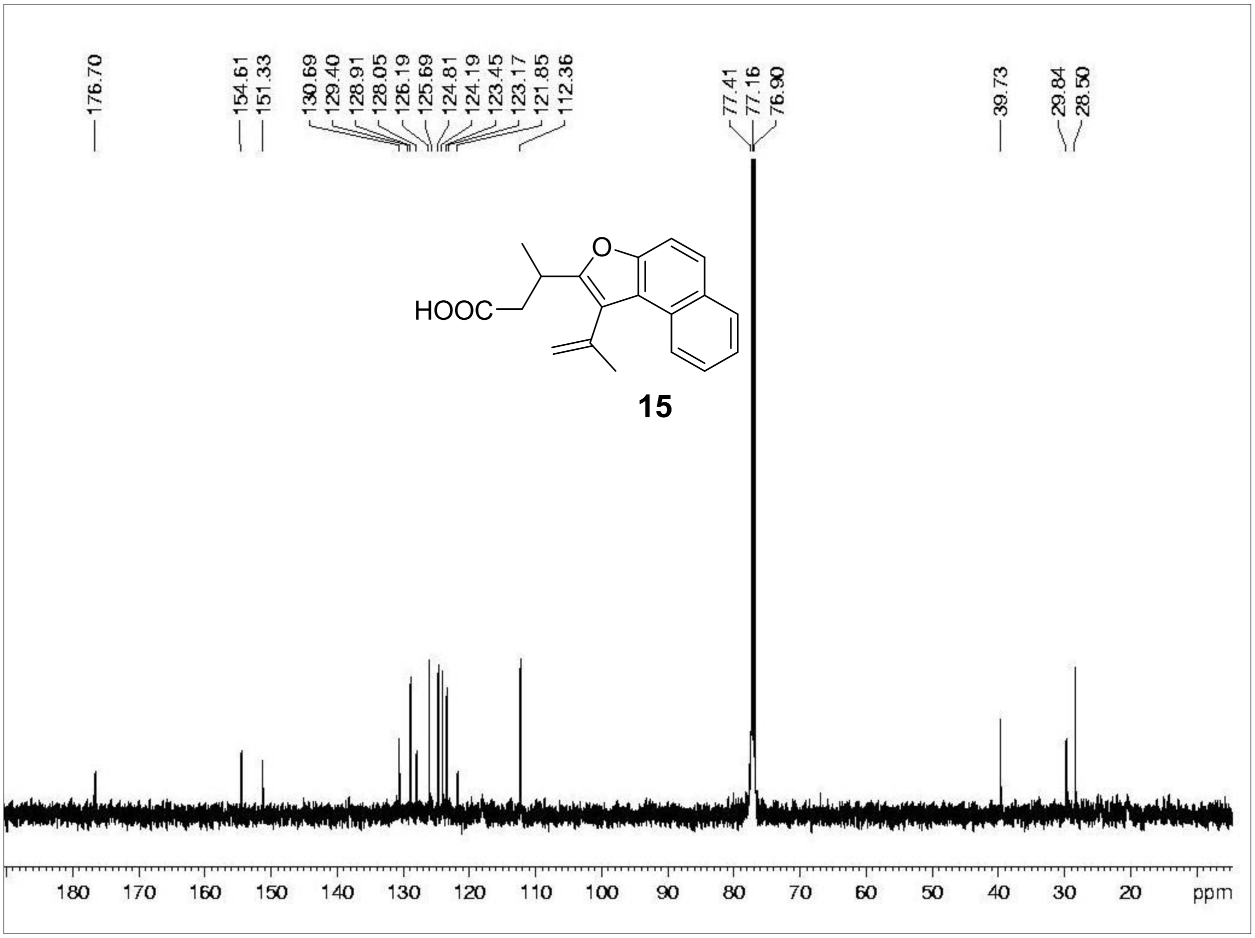
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28.50
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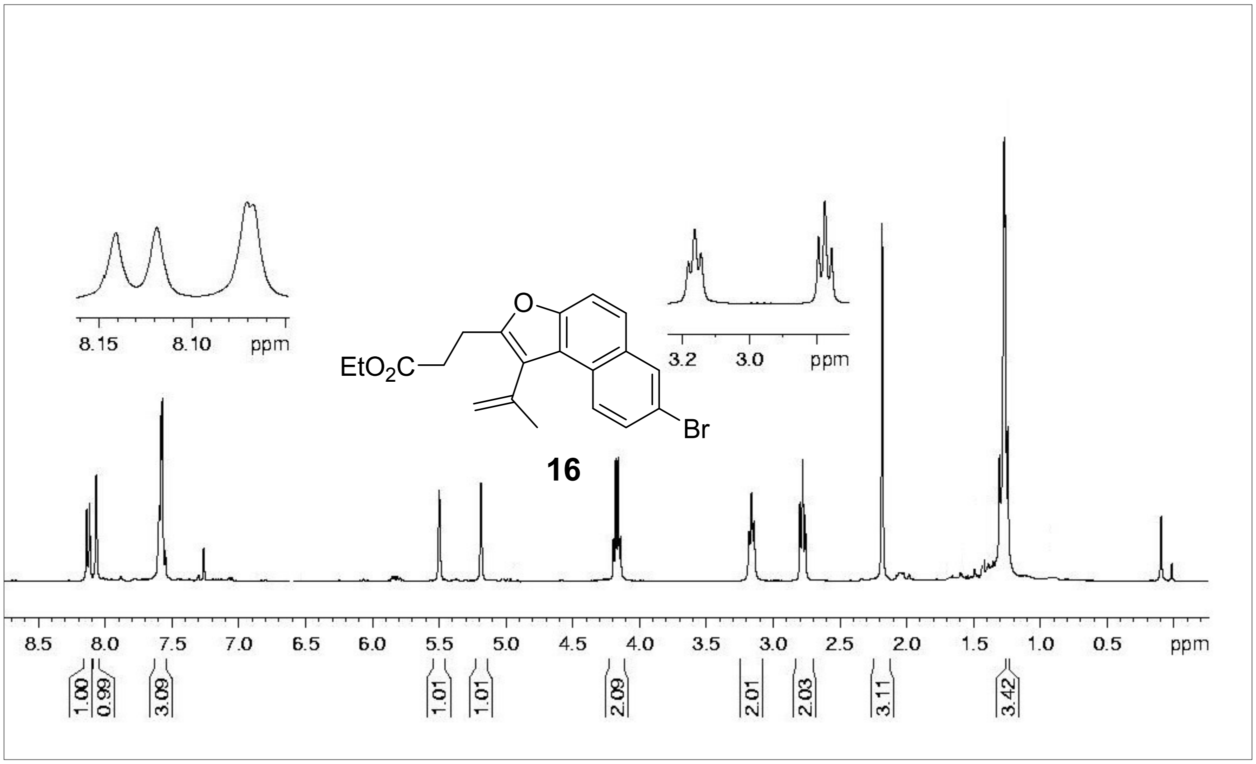
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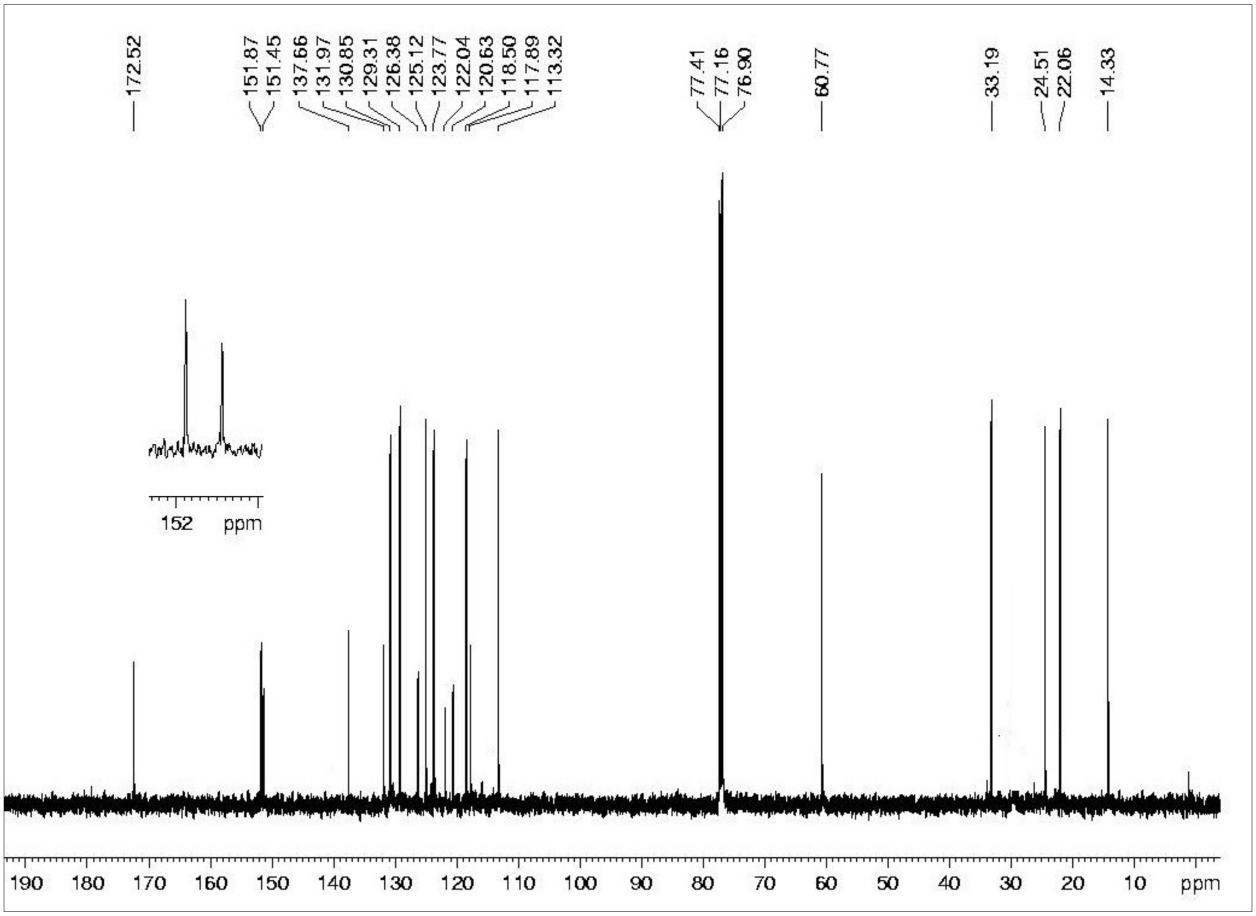
3.42

16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117.89
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77.16
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14.33
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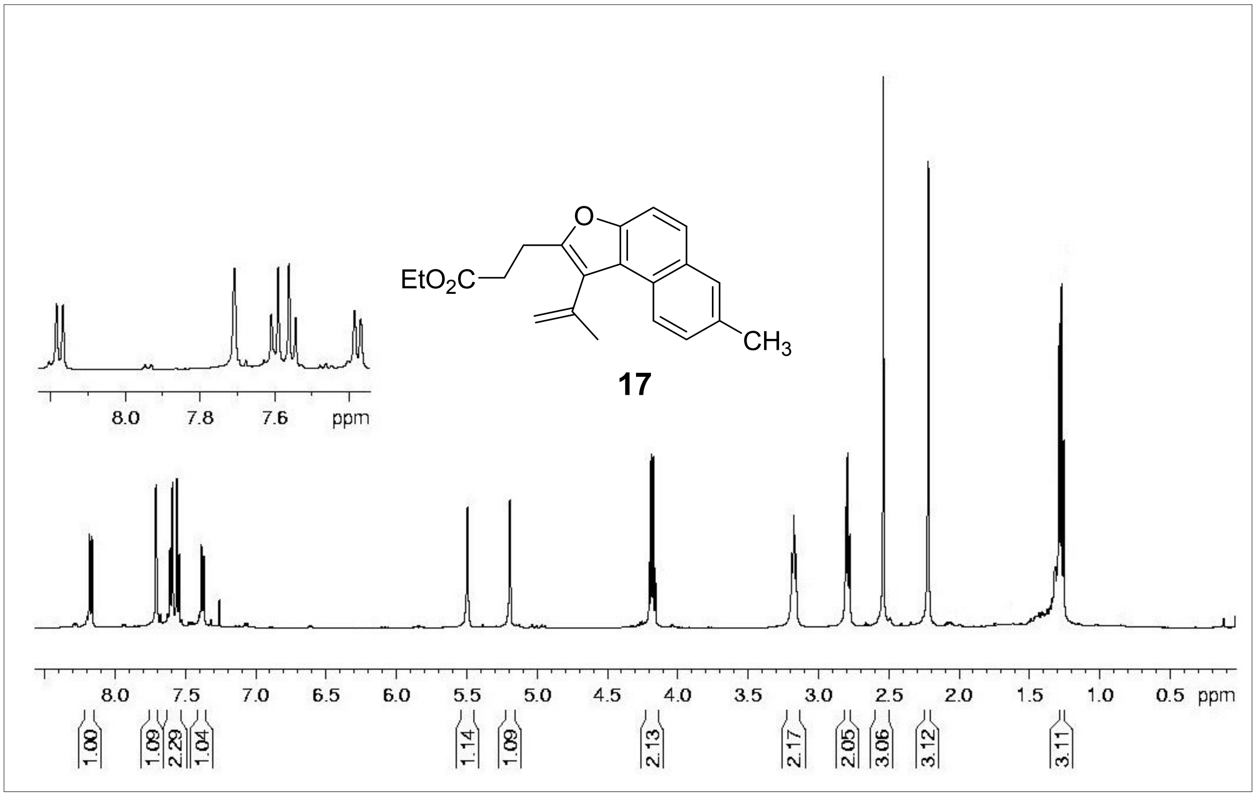
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4.0
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ppm
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1.09
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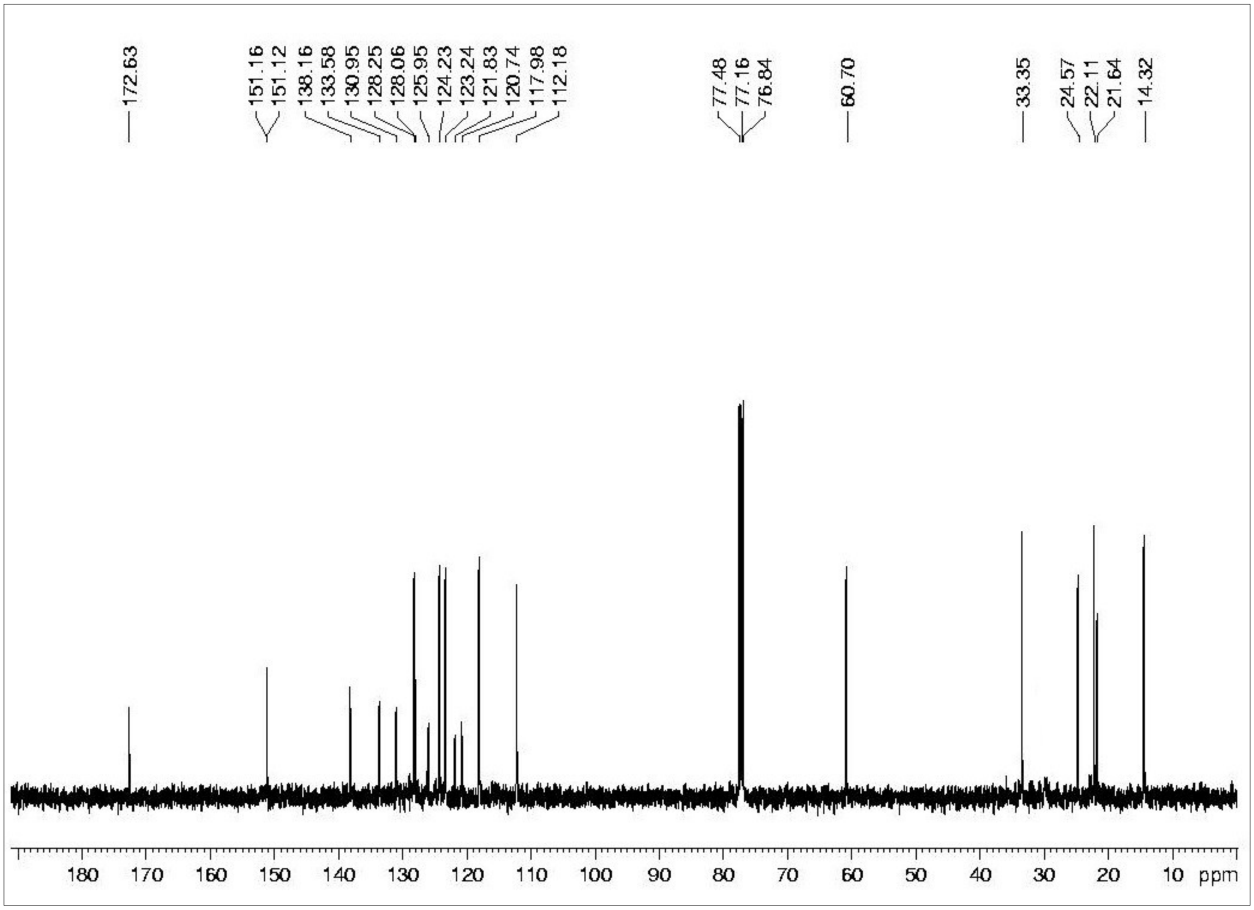
2.17
2.05
3.06
3.12
3.11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151.12
138.16
133.58
130.95
128.25
128.06
125.95
124.23
123.24
121.83
120.74
117.98
112.18
77.48
77.16
76.84
60.70
33.35
24.57
22.11
21.64
14.32
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140
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110
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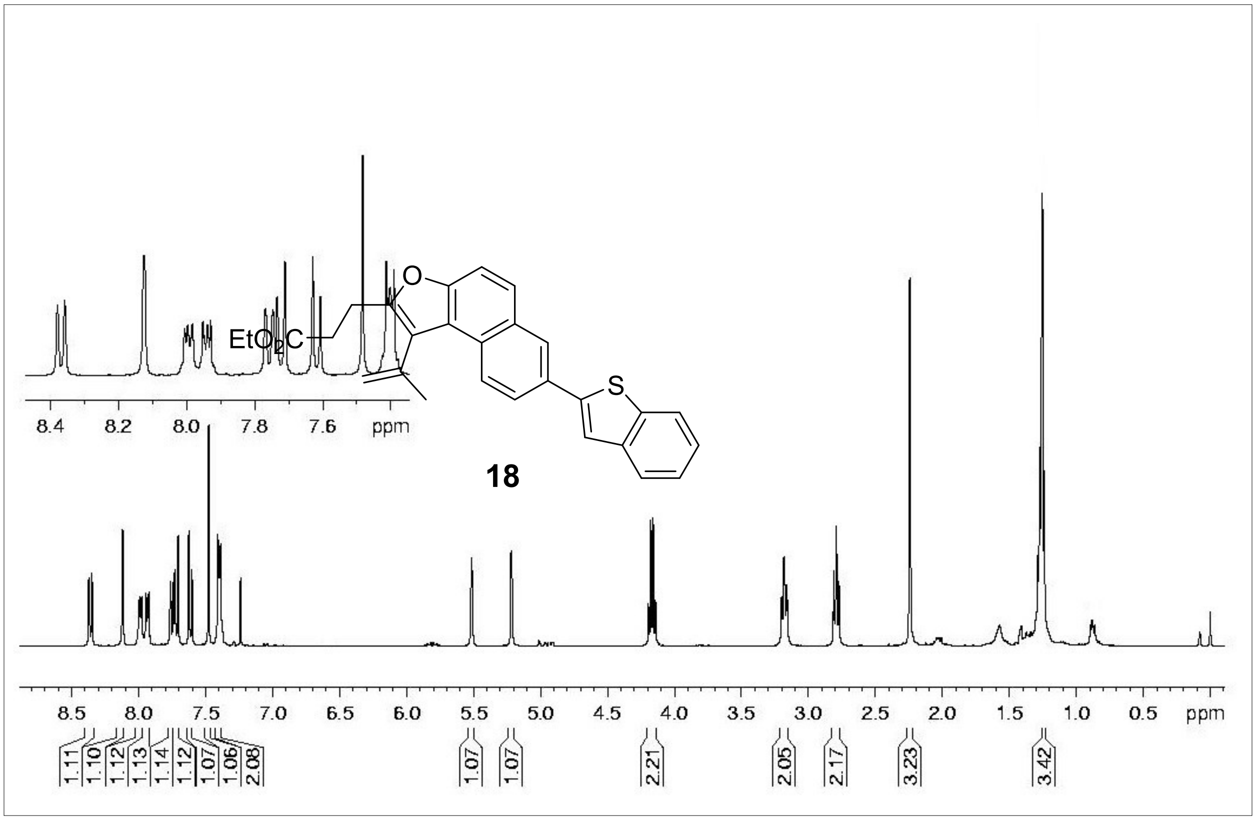
ppm


EtO2C
O
S
8.4
8.2
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7.6
ppm
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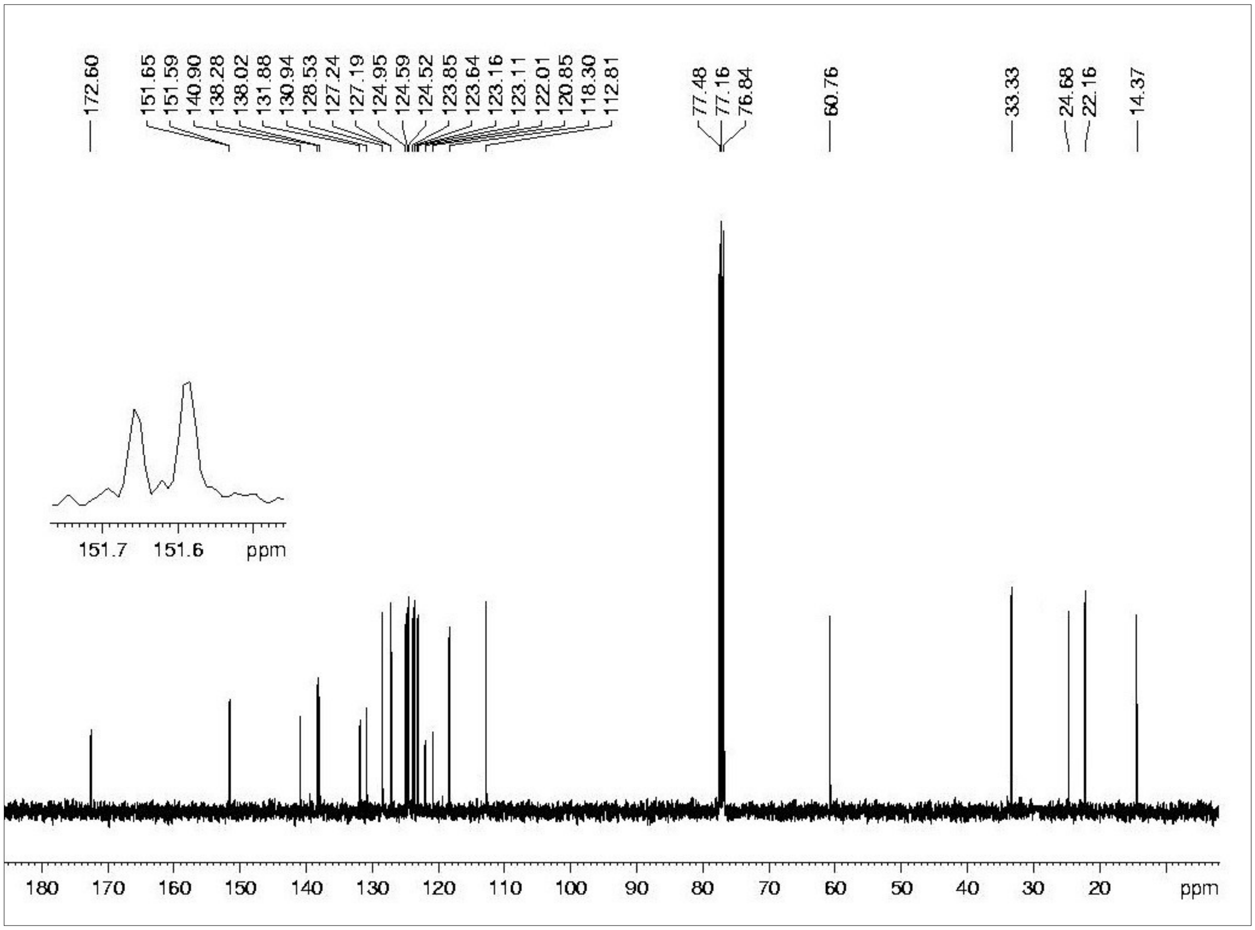
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.11
1.10
1.12
1.13
1.14
1.12
1.07
1.06
2.08
1.07
1.07
2.21
2.05
2.17
3.23
3.42

18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131.88
130.94
128.53
127.24
127.19
124.95
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124.52
123.85
123.64
123.16
123.11
122.01
120.85
118.30
112.81
77.48
77.16
76.84
60.76
33.33
24.68
22.16
14.37
151.7
151.6
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160
150
140
130
120
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80
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40
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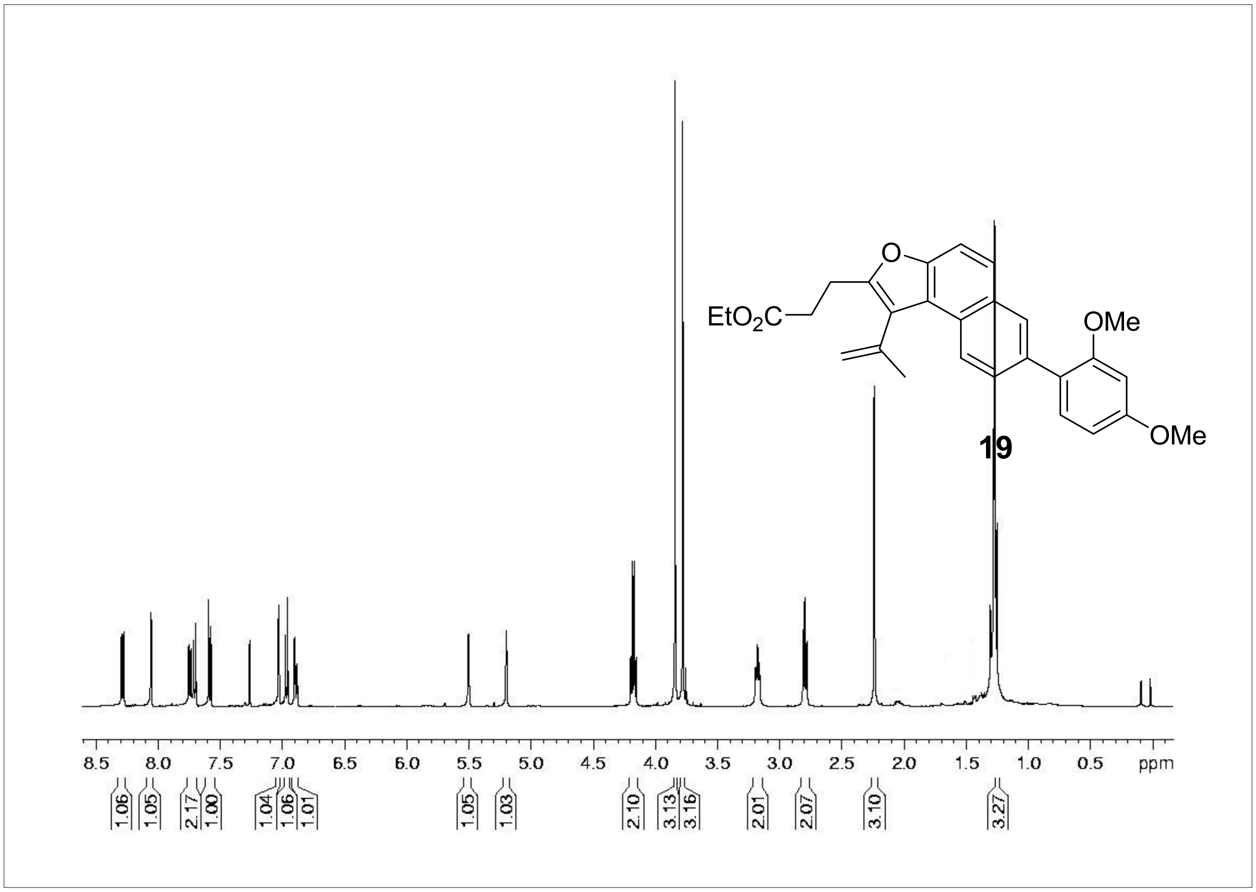
20
ppm


EtO$_2$C
OMe
OMe
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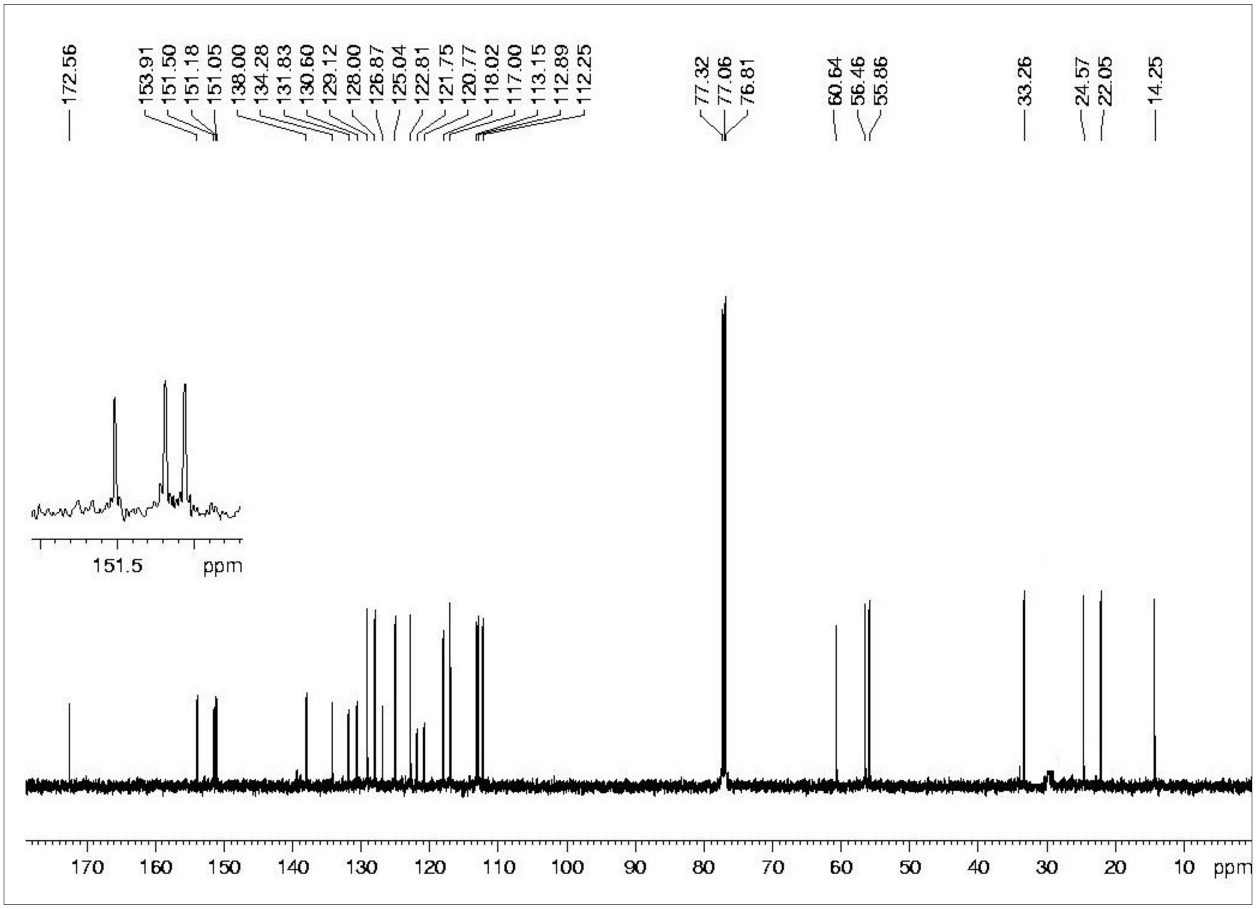
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.06
1.05
2.17
1.00
1.04
1.06
1.01
1.05
1.03
2.10
3.13
3.16
2.01
2.07
3.10
3.27

19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134.28
131.83
130.60
129.12
128.00
126.87
125.04
122.81
121.75
120.77
118.02
117.00
113.15
112.89
112.25
77.32
77.06
76.81
60.64
56.46
55.86
33.26
24.57
22.05
14.25
151.5
ppm
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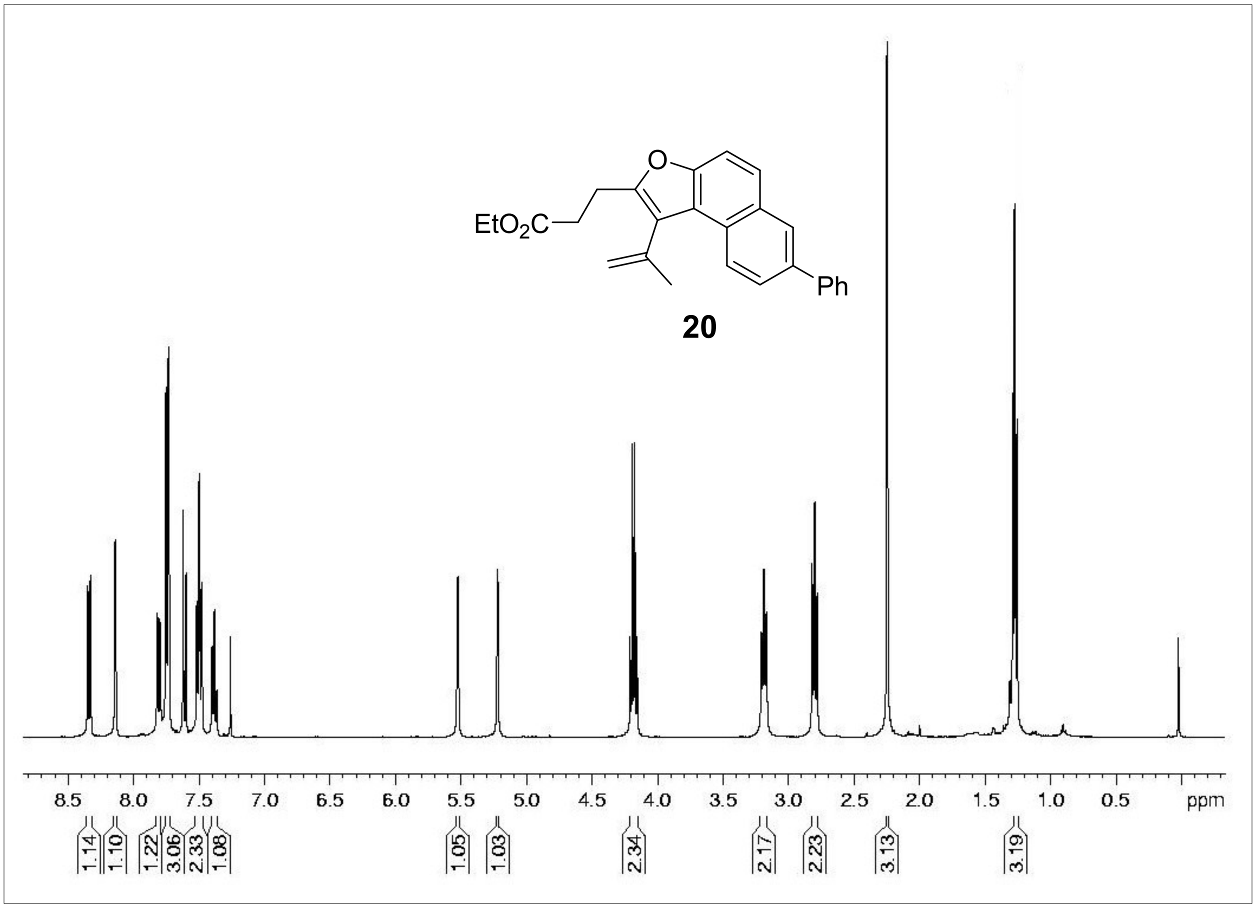
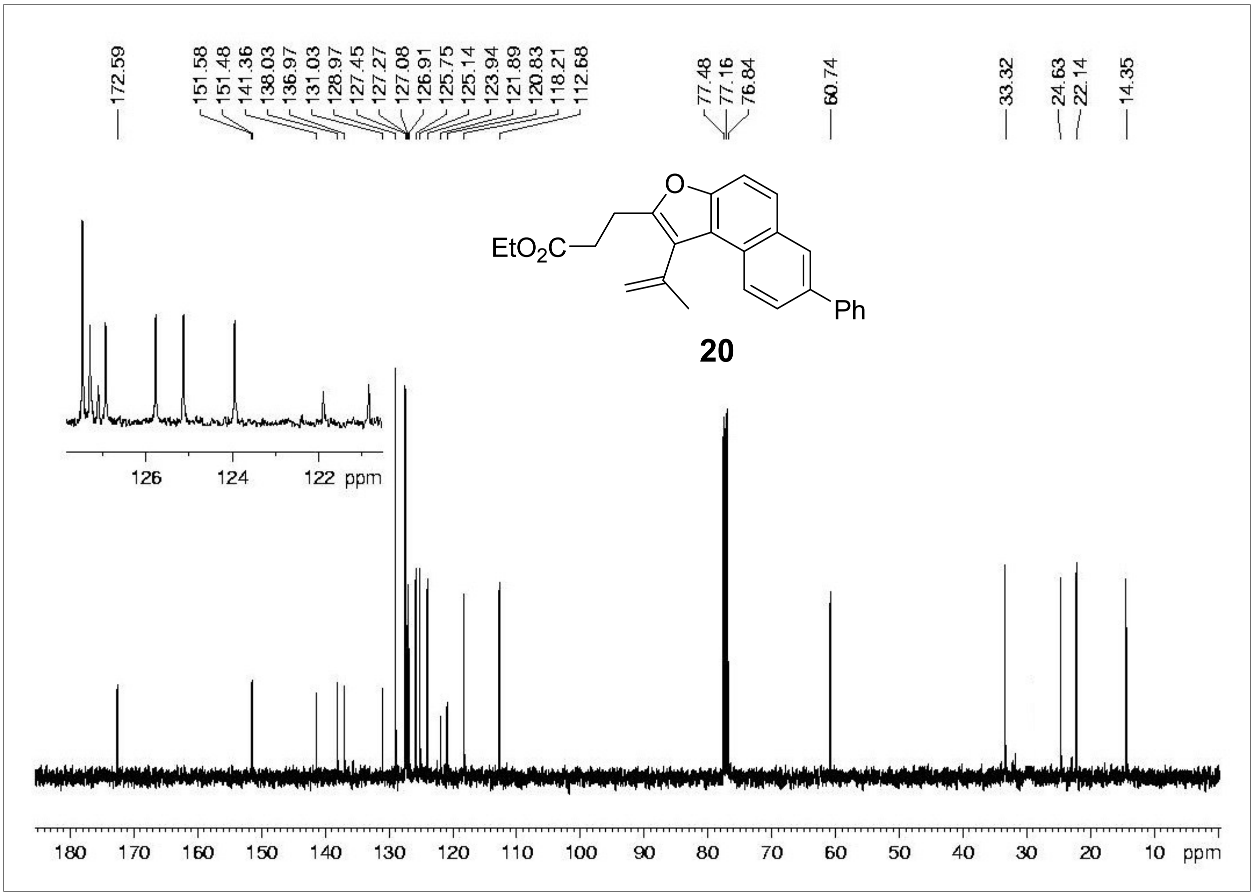
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
EtO2C
Ph
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
1.14
1.10
1.22
3.06
2.33
1.08
1.05
1.03
2.34
2.17
2.23
3.13
3.19

20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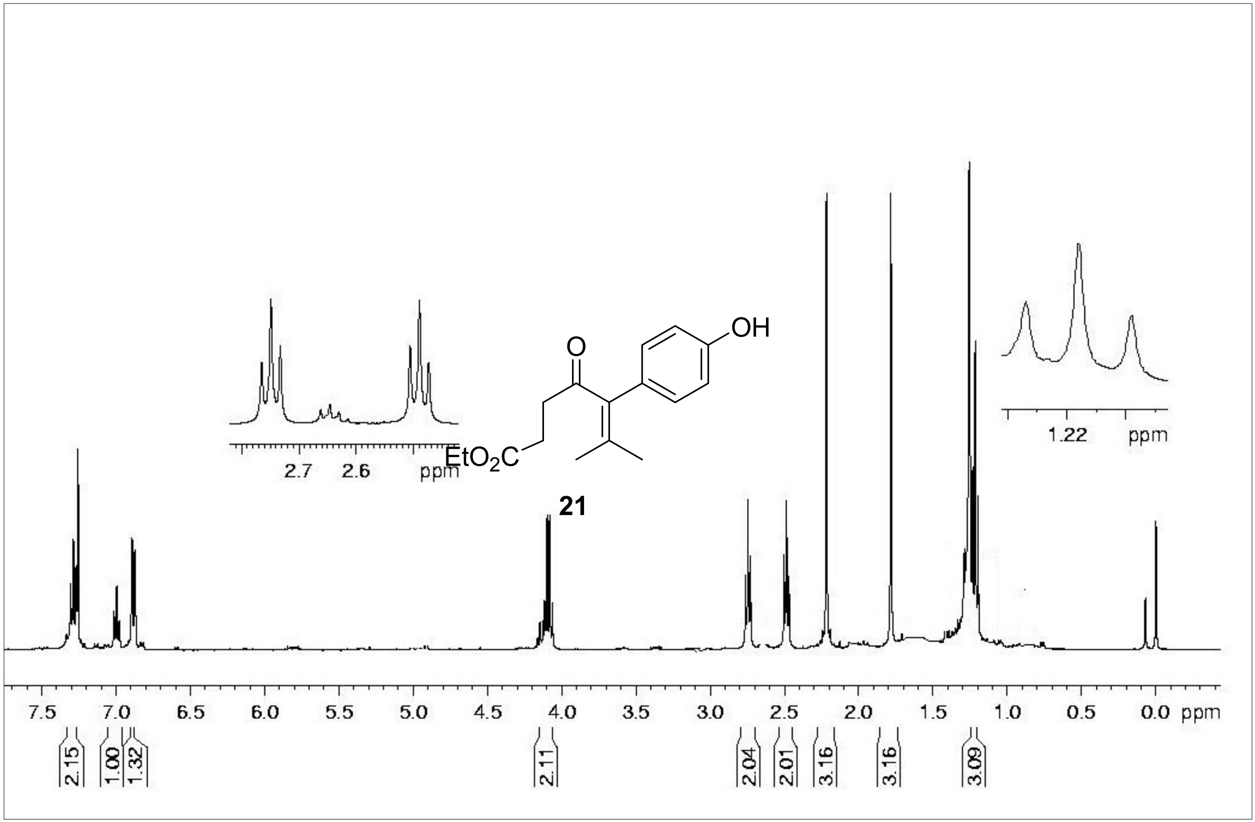
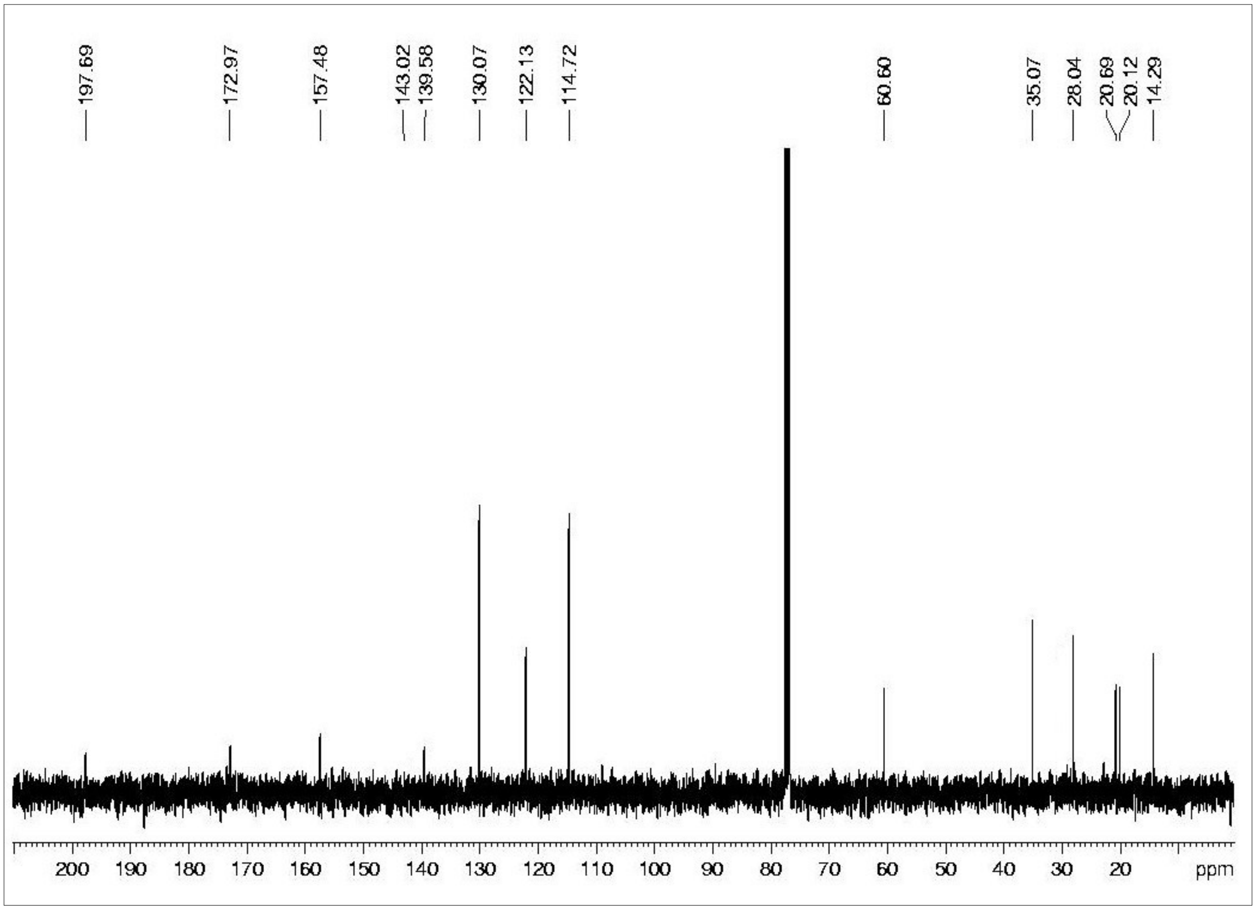
136.97
131.03
128.97
127.45
127.27
127.08
126.91
125.75
125.14
123.94
121.89
120.83
118.21
112.68
77.48
77.16
76.84
60.74
33.32
24.63
22.14
14.35
O
EtO2C
Ph
126
124
122 ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

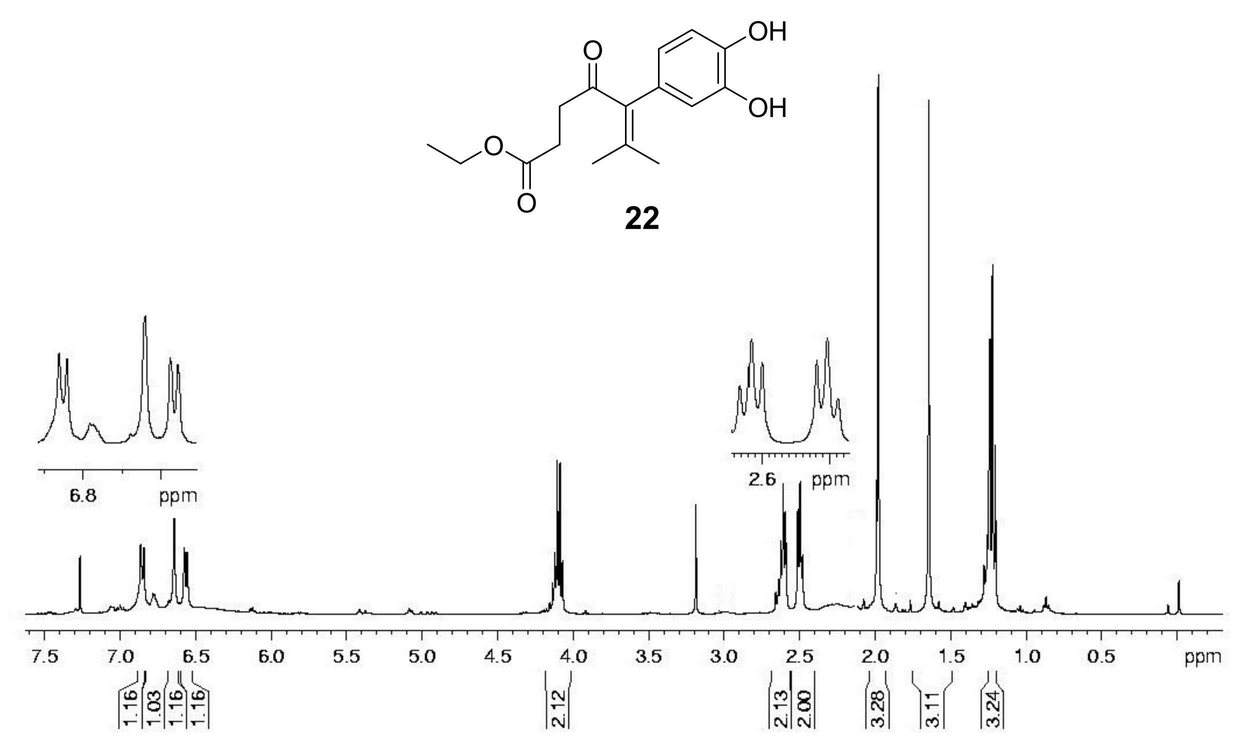
20



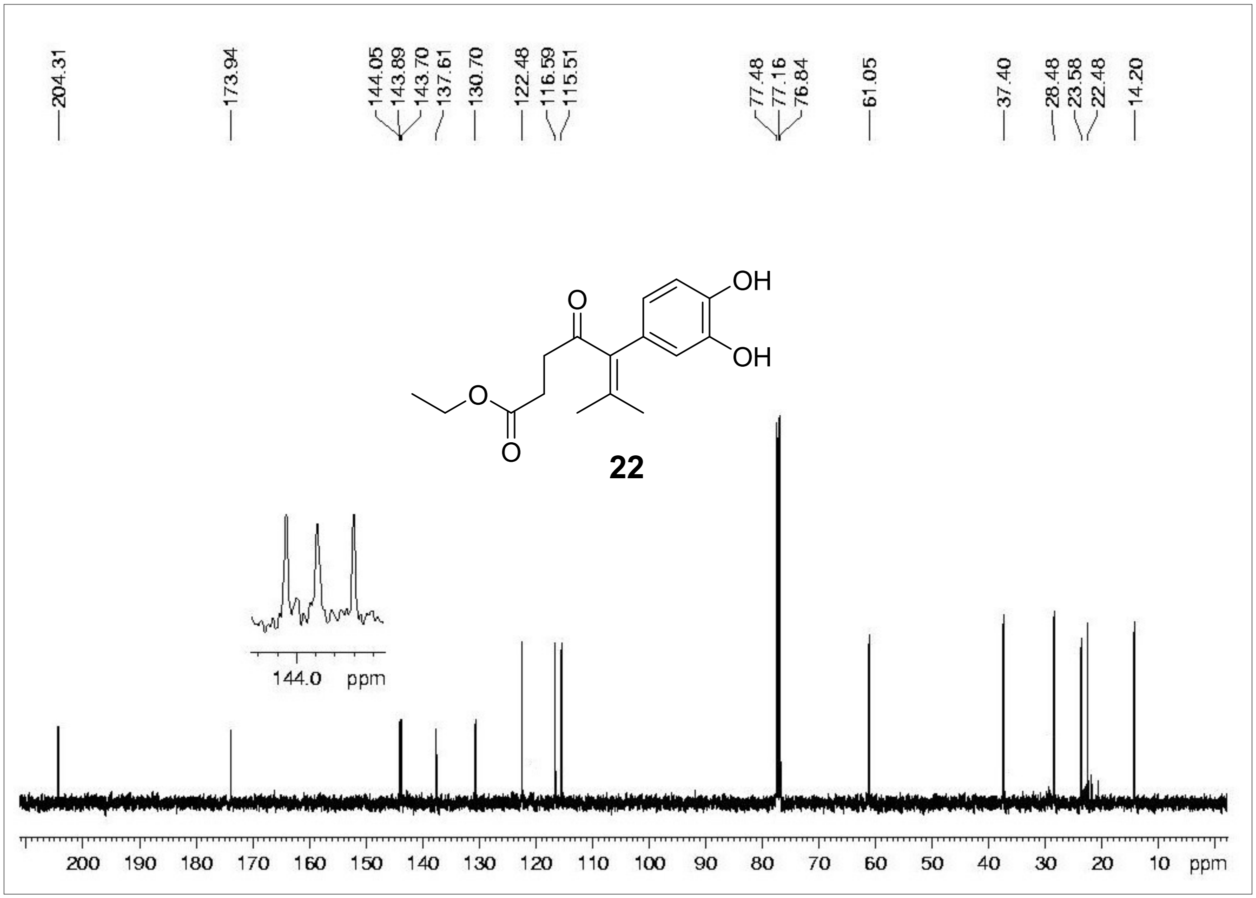
OH
O
EtO2C
21
2.7
2.6
ppm
1.22
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.15
1.00
1.32
2.11
2.04
2.01
3.16
3.16
3.09



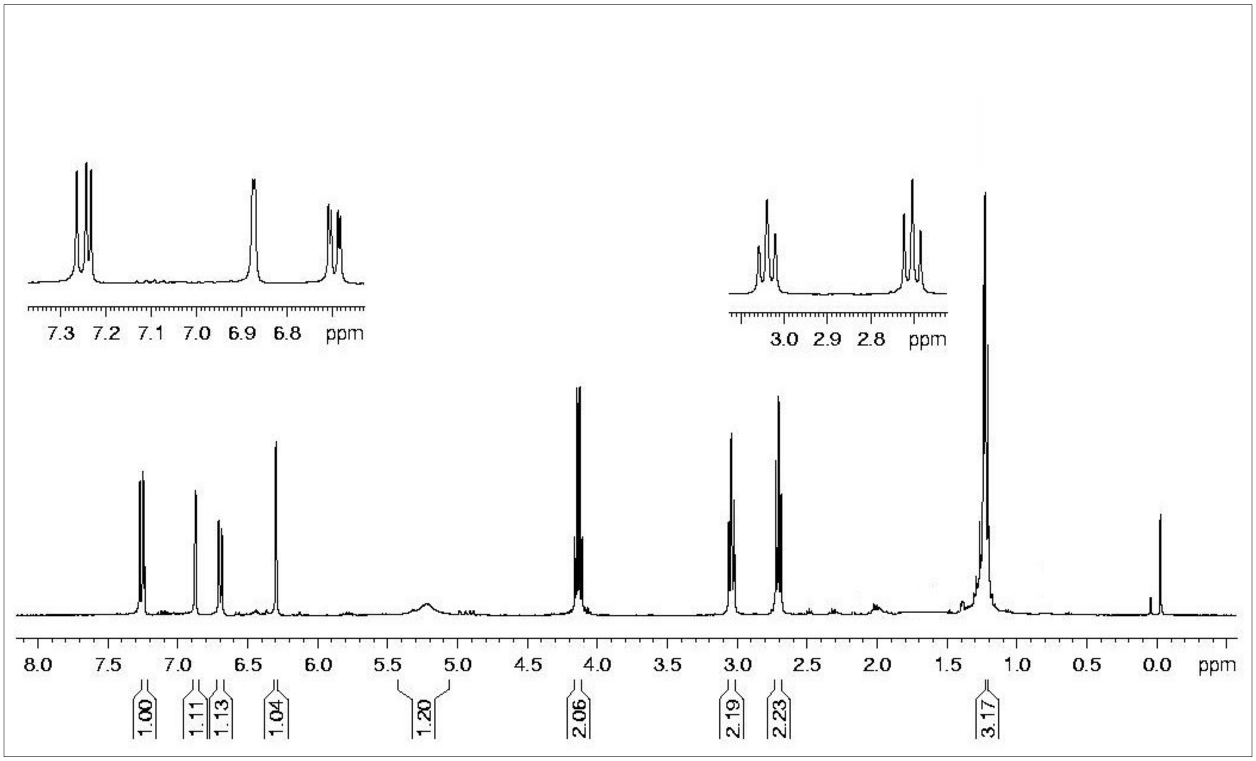
197.69
172.97
157.48
143.02
139.58
130.07
122.13
114.72
60.60
35.07
28.04
20.69
20.12
14.29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

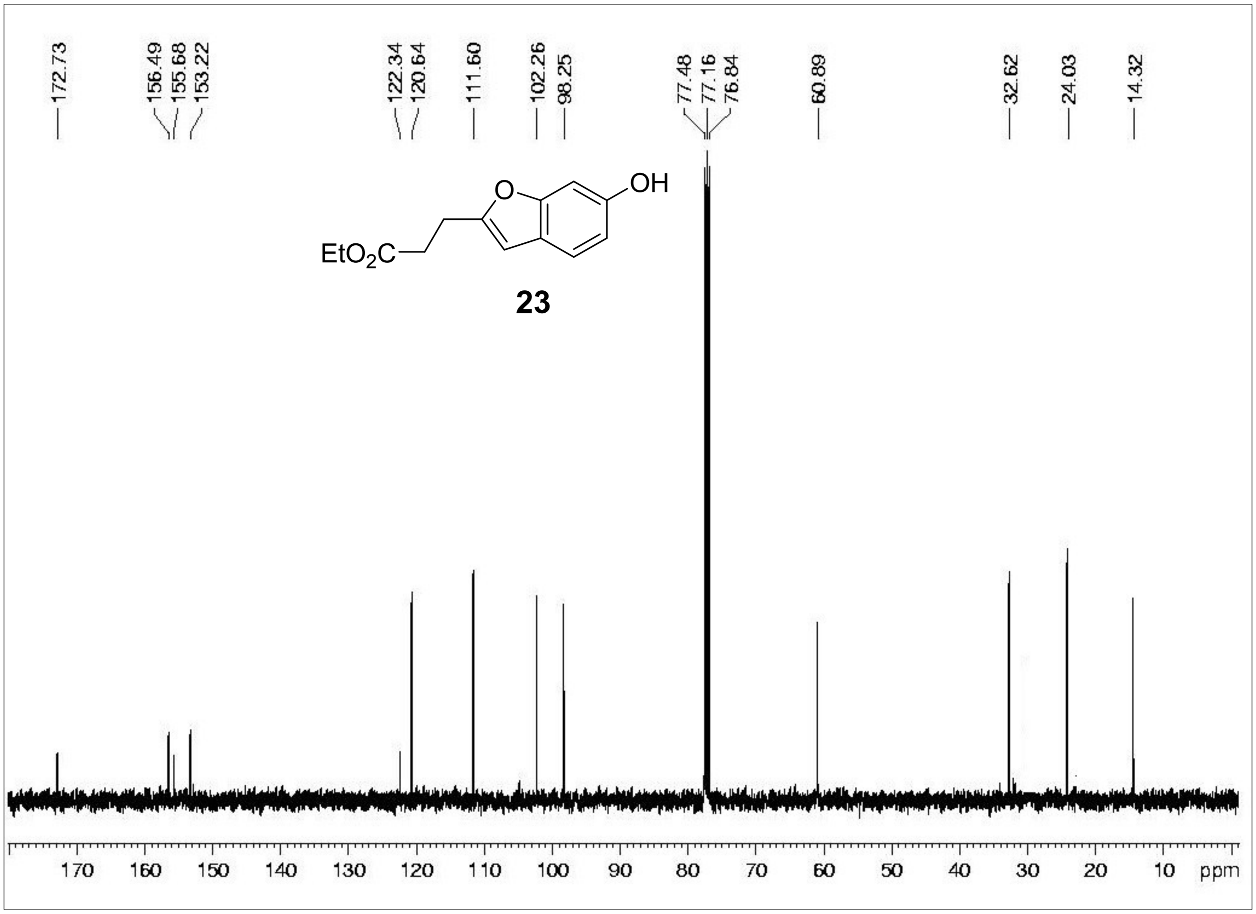

OH
OH
O
O
O
6.8
ppm
2.6
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.16
1.03
1.16
1.16
2.12
2.13
2.00
3.28
3.11
3.24

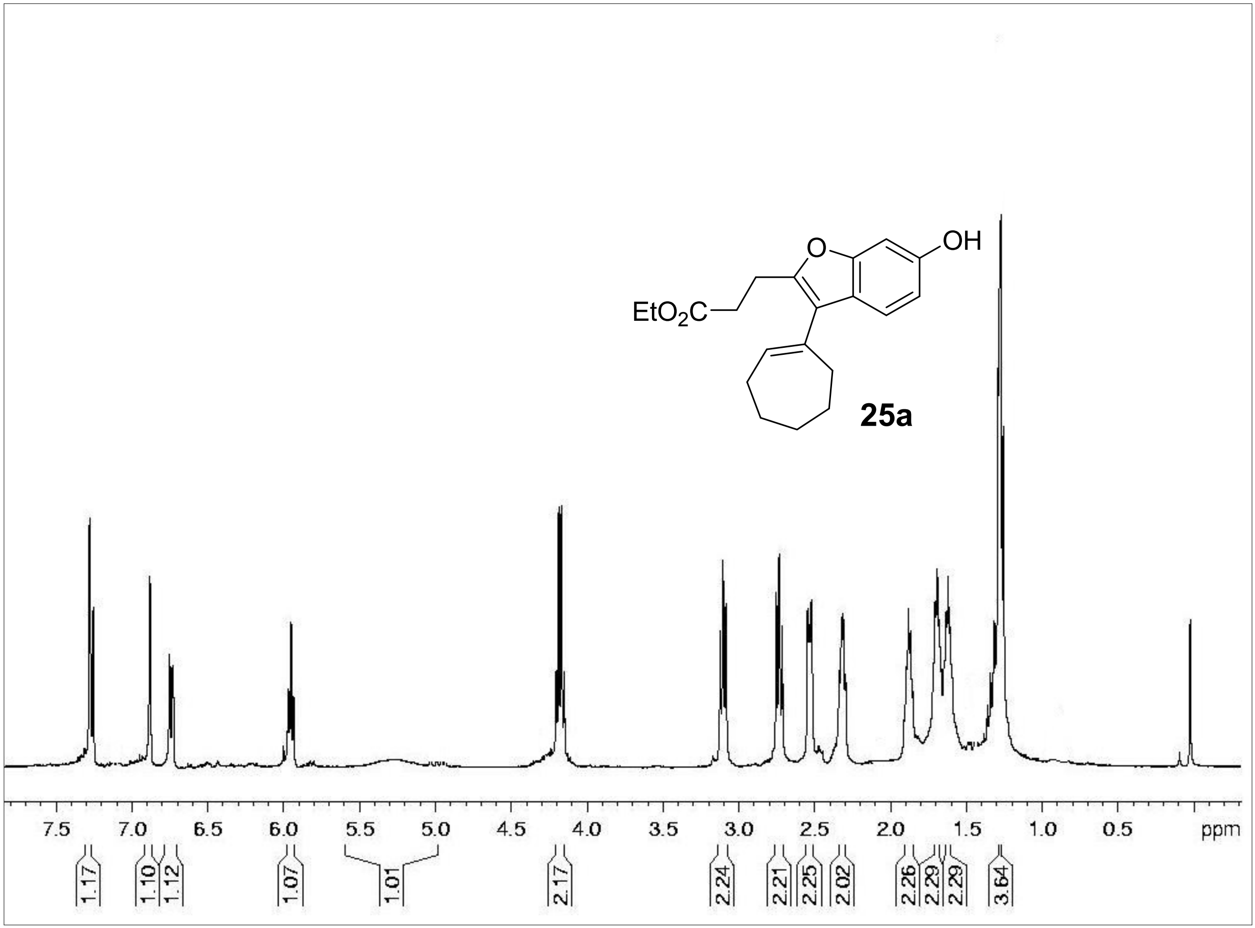
22

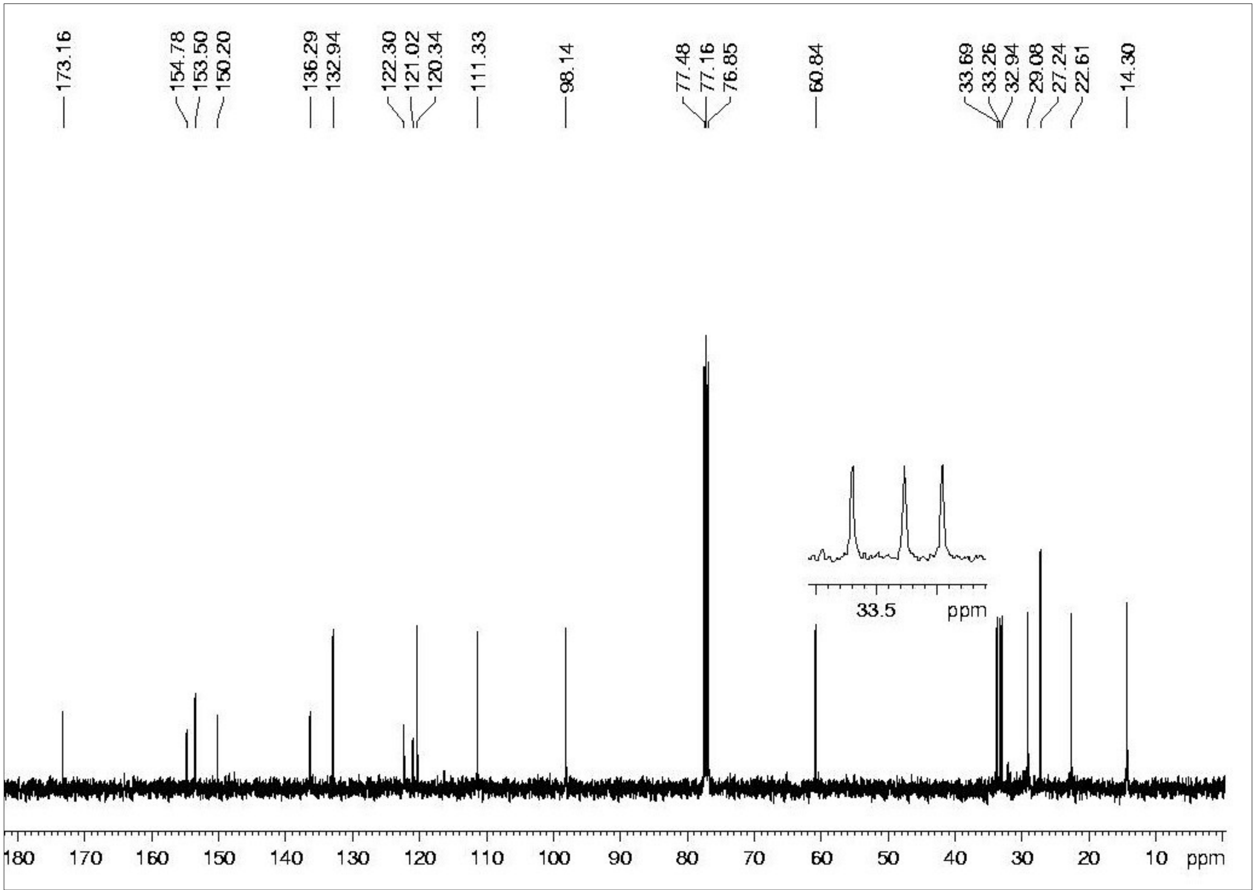

204.31
173.94
144.05
143.89
143.70
137.61
130.70
122.48
116.59
115.51
77.48
77.16
76.84
61.05
37.40
28.48
23.58
22.48
14.20
OH
OH
O
O
O
144.0
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

22


7.3 7.2 7.1 7.0 6.9 6.8 ppm
3.0 2.9 2.8 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.11
1.13
1.04
1.20
2.06
2.19
2.23
3.17


172.73
156.49
155.68
153.22
122.34
120.64
111.60
102.26
98.25
77.48
77.16
76.84
60.89
32.62
24.03
14.32
OH
O
EtO2C
23
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OH
O
EtO_2C
25a
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
1.17
1.10
1.12
1.07
1.01
2.17
2.24
2.21
2.25
2.02
2.26
2.29
2.29
3.64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154.78
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150.20
136.29
132.94
122.30
121.02
120.34
111.33
98.14
77.48
77.16
76.85
60.84
33.69
33.26
32.94
29.08
27.24
22.61
14.30
33.5
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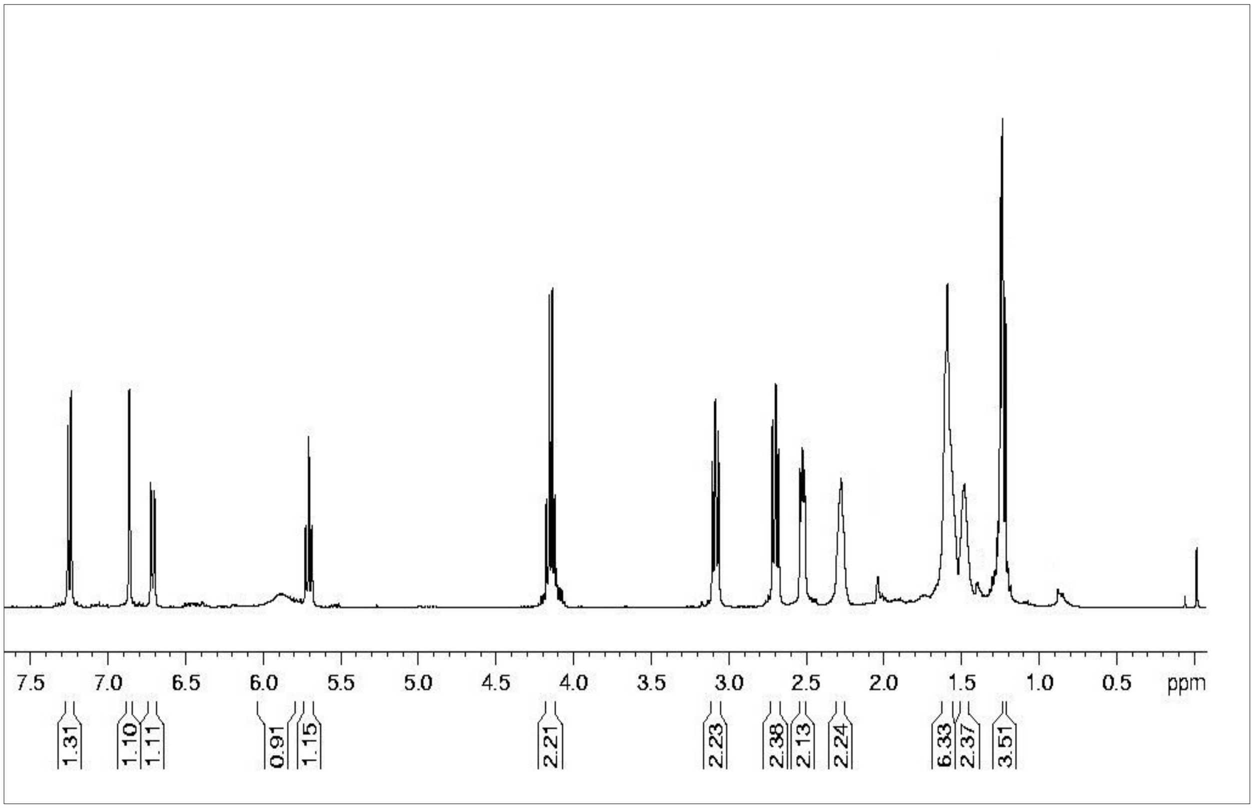
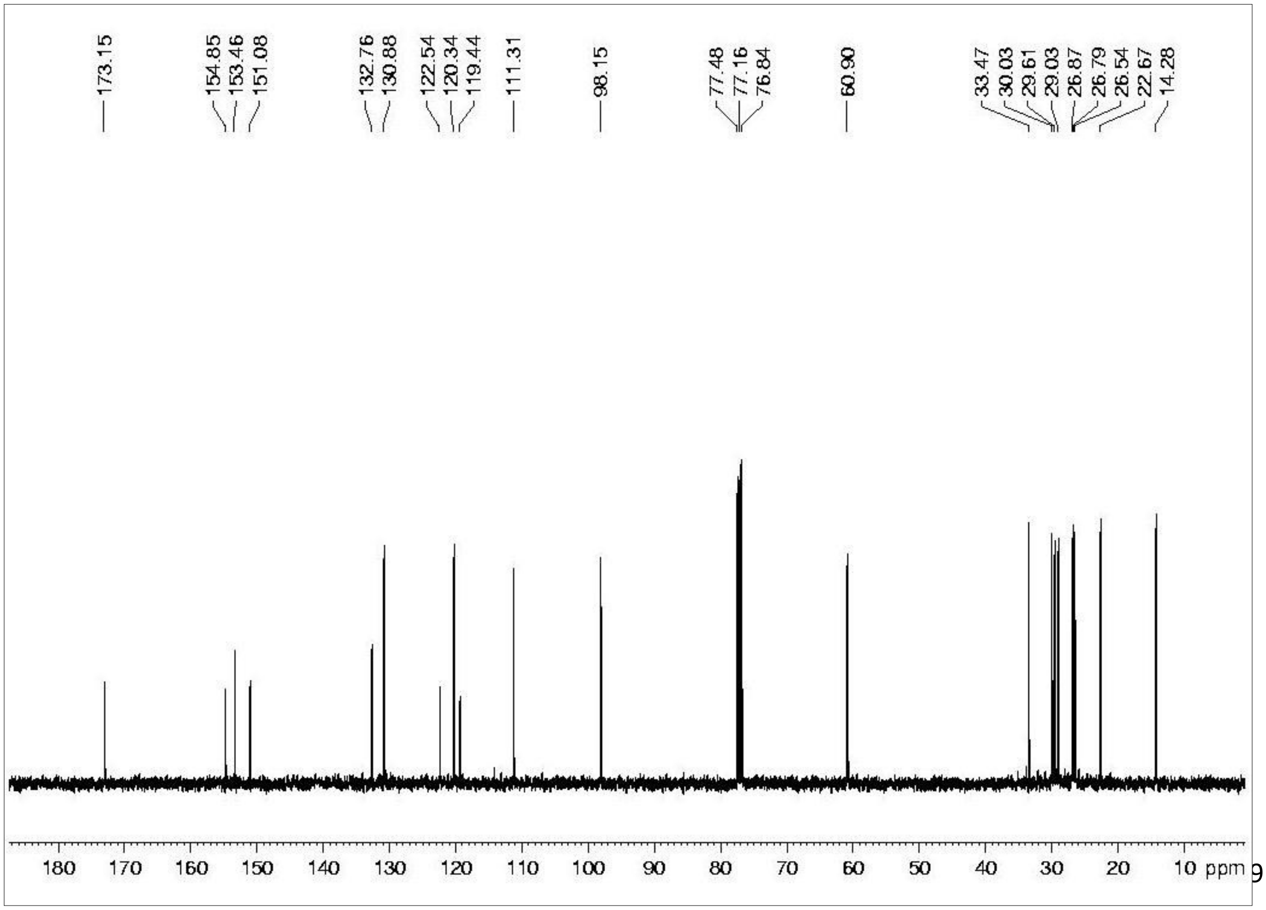
50
40
30
20
10
ppm


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
1.31
1.10
1.11
0.91
1.15
2.21
2.23
2.38
2.13
2.24
6.33
2.37
3.51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130.88
122.54
120.34
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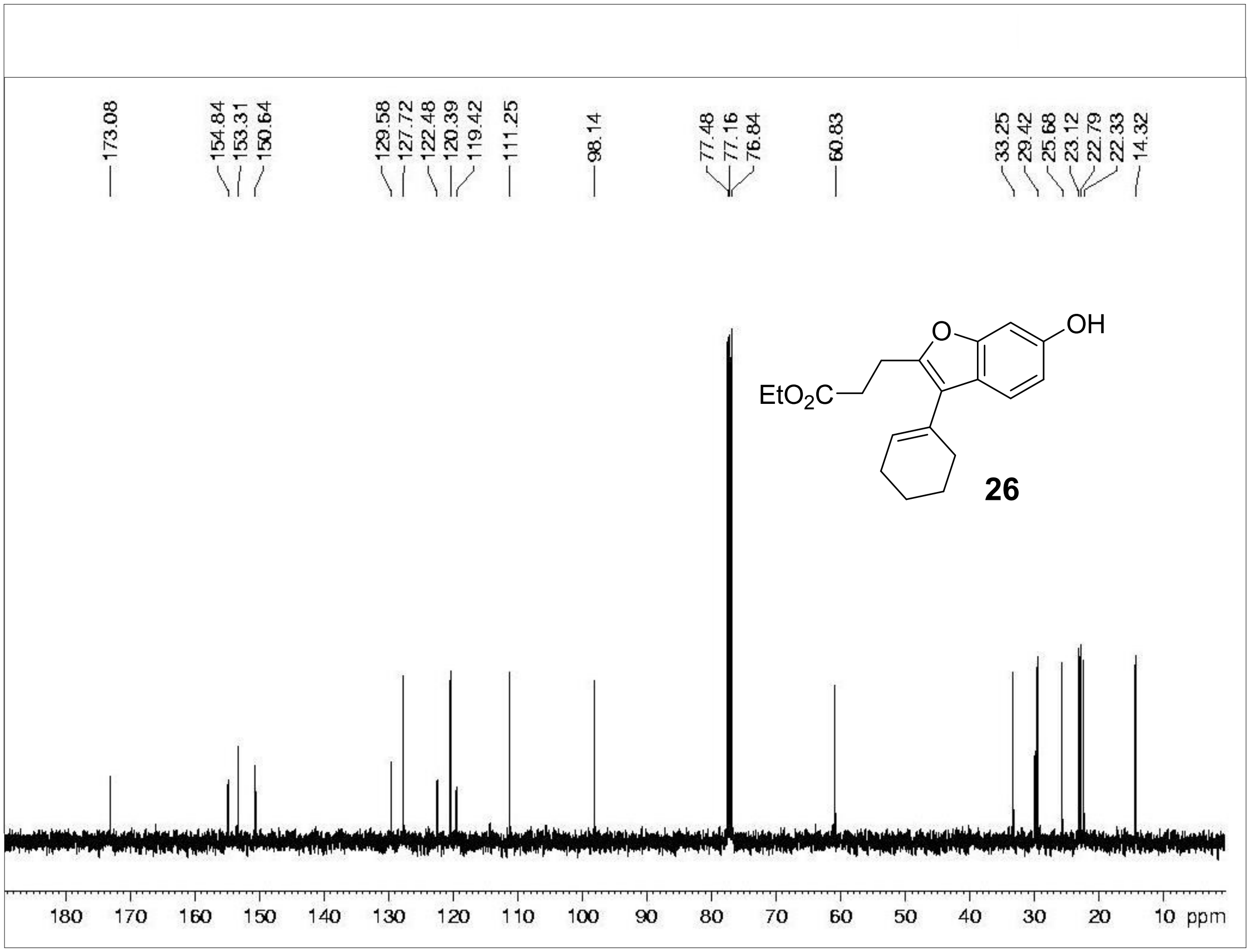
111.31
98.15
77.48
77.16
76.84
60.90
33.47
30.03
29.61
29.03
26.87
26.79
26.54
22.67
14.28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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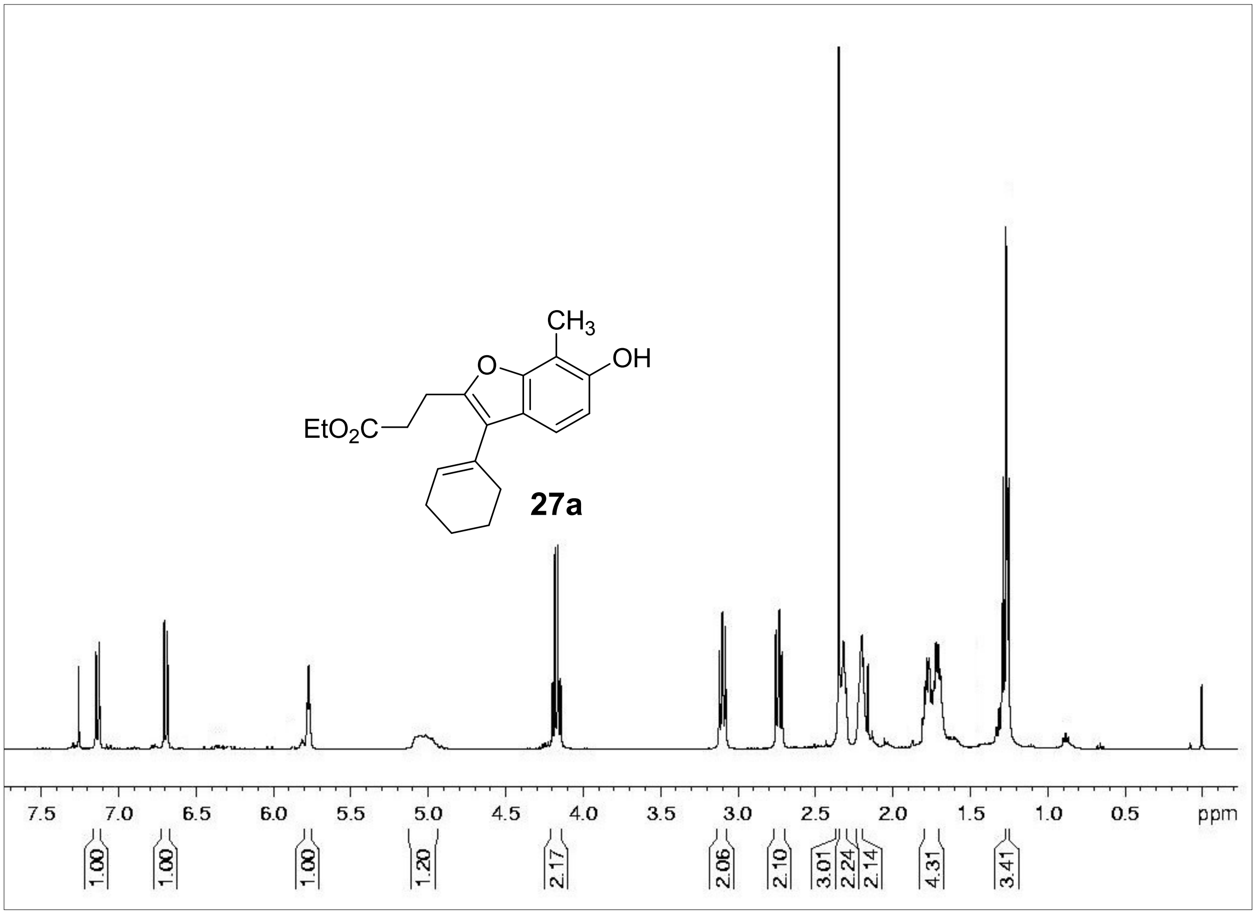
154.84
153.31
150.64
129.58
127.72
122.48
120.39
119.42
111.25
98.14
77.48
77.16
76.84
60.83
33.25
29.42
25.68
23.12
22.79
22.33
14.32
EtO2C
O
OH
26
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CH3
OH
O
EtO2C
27a
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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
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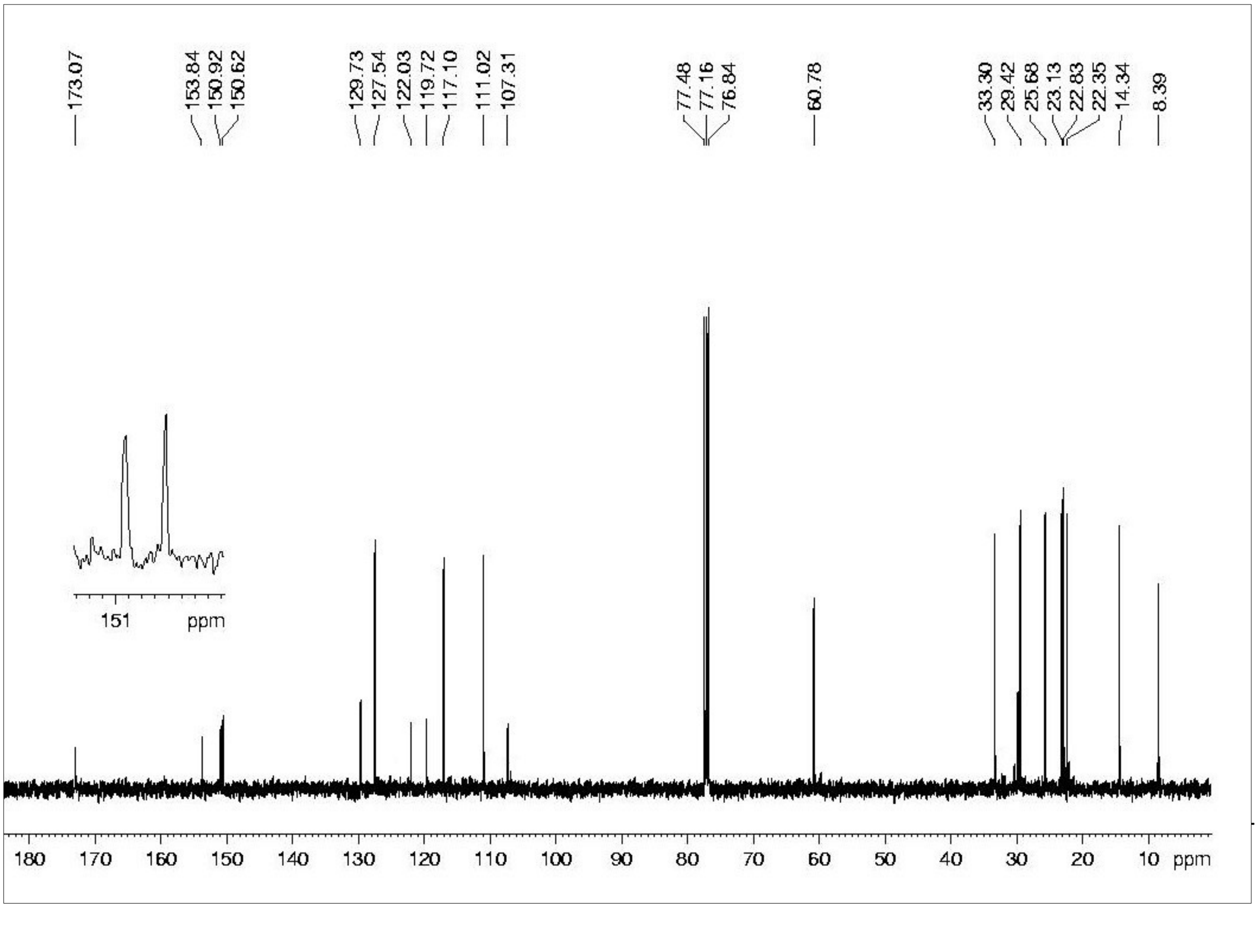
1.00
1.00
1.20
2.17
2.06
2.10
3.01
2.24
2.14
4.31
3.41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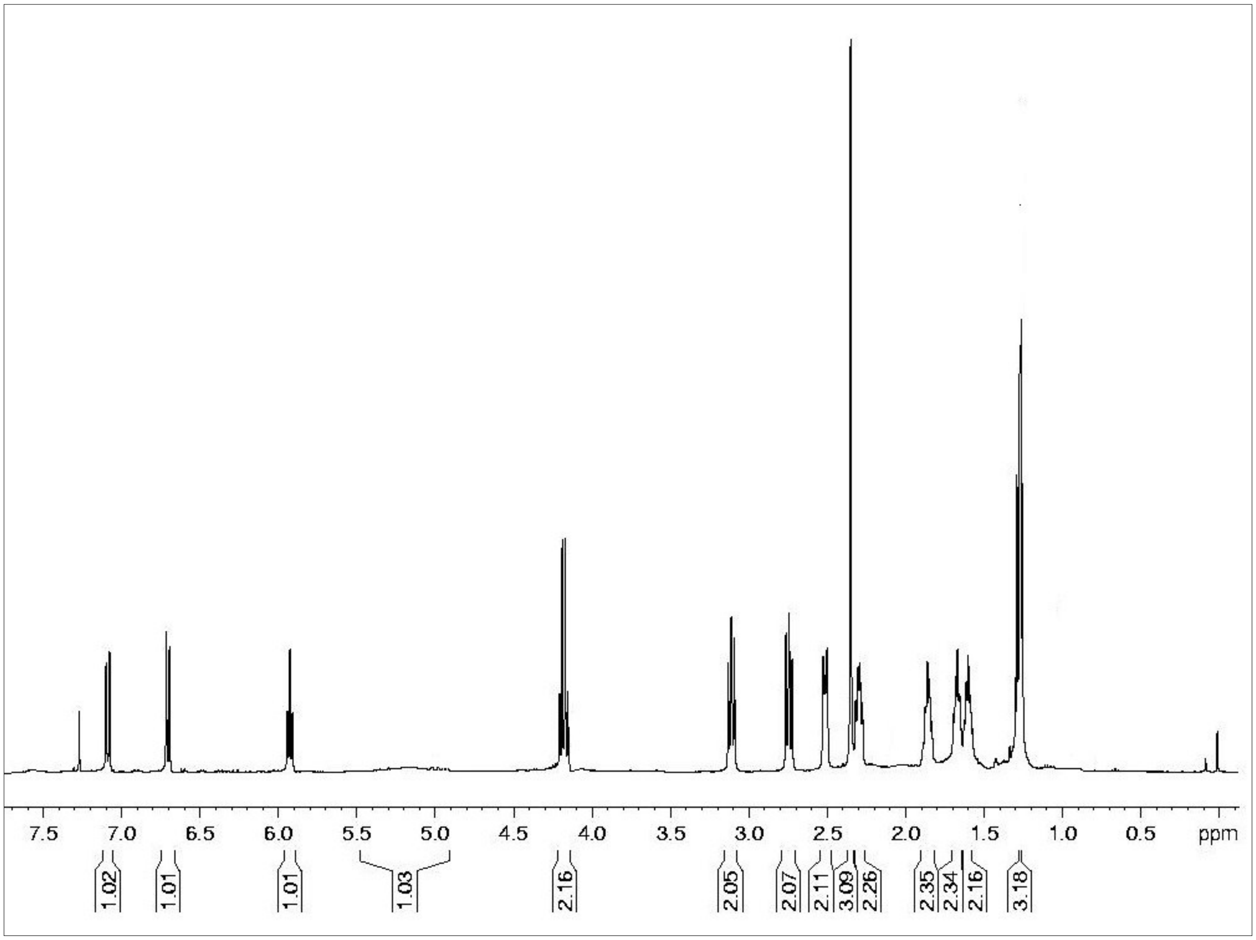
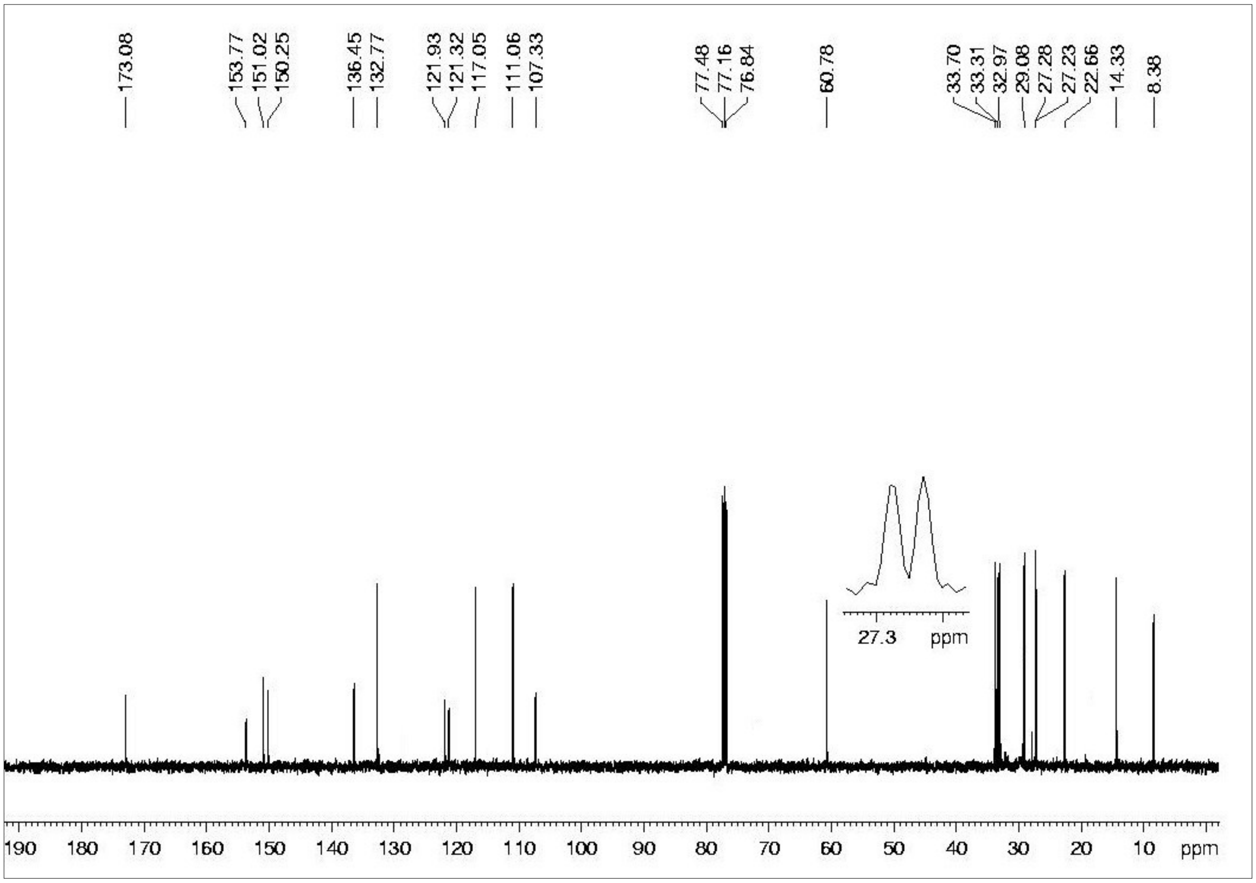
150.92
150.62
129.73
127.54
122.03
119.72
117.10
111.02
107.31
77.48
77.16
76.84
60.78
33.30
29.42
25.68
23.13
22.83
22.35
14.34
8.39
151
ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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
1.02
1.01
1.01
1.03
2.16
2.05
2.07
2.11
3.09
2.26
2.35
2.34
2.16
3.18



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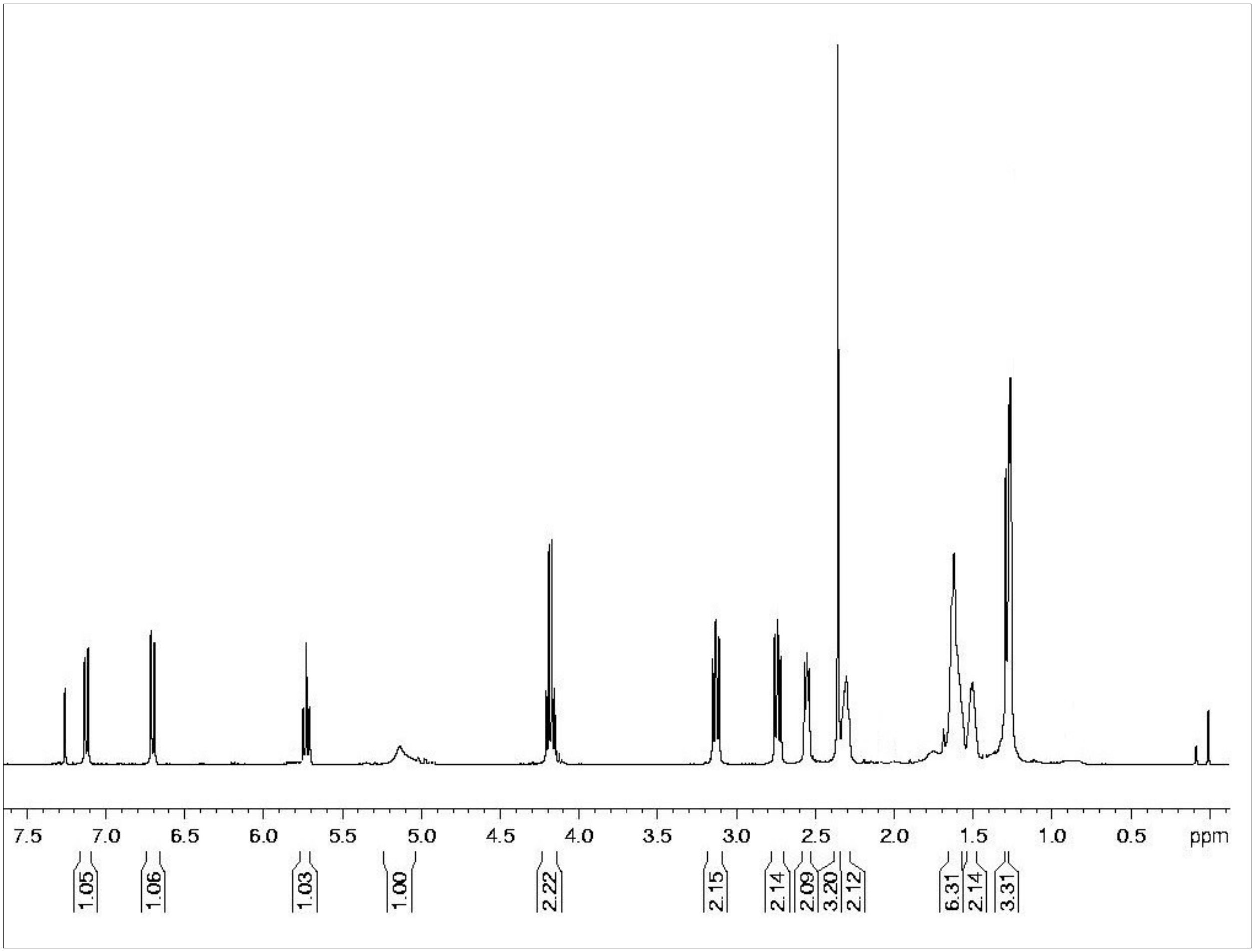
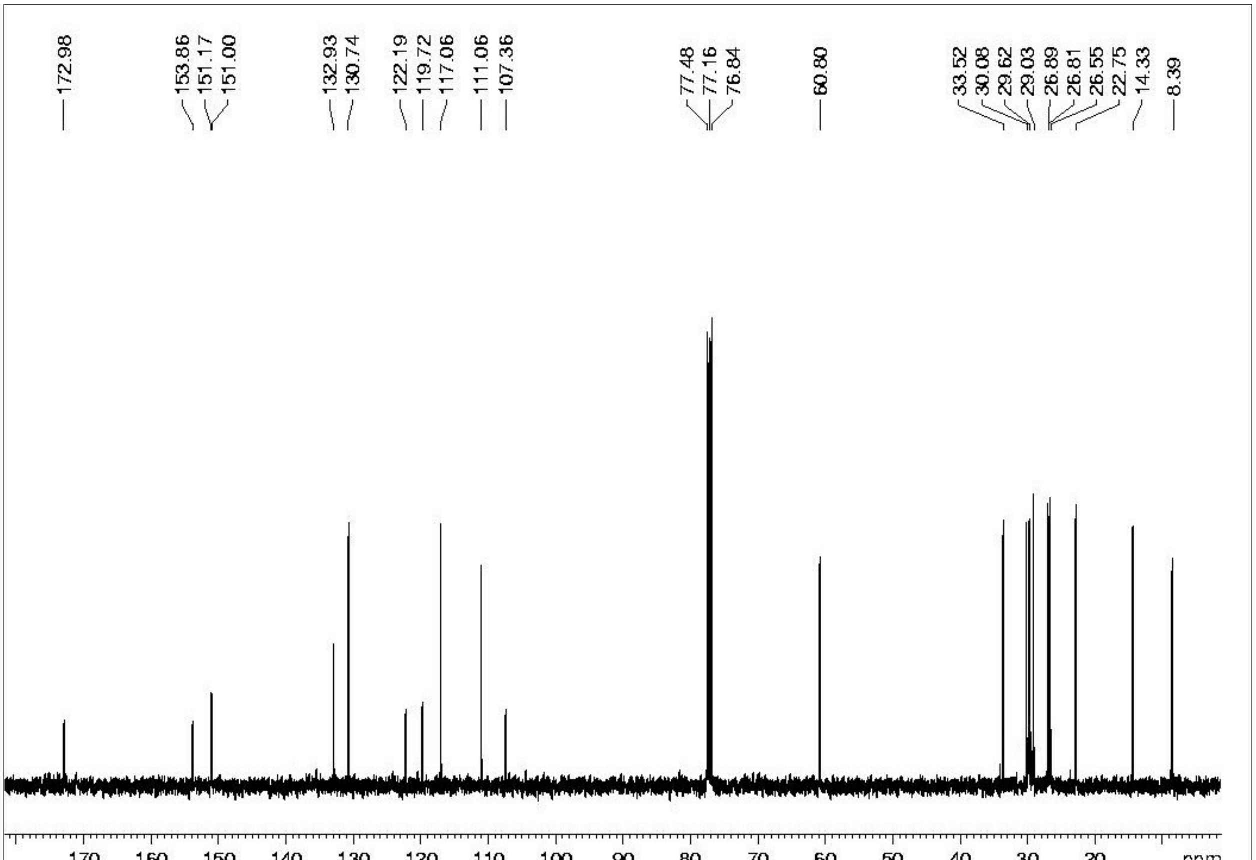
151.02
150.25
136.45
132.77
121.93
121.32
117.05
111.06
107.33
77.48
77.16
76.84
60.78
33.70
33.31
32.97
29.08
27.28
27.23
22.66
14.33
8.38
27.3
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


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
1.05
1.06
1.03
1.00
2.22
2.15
2.14
2.09
3.20
2.12
6.31
2.14
3.31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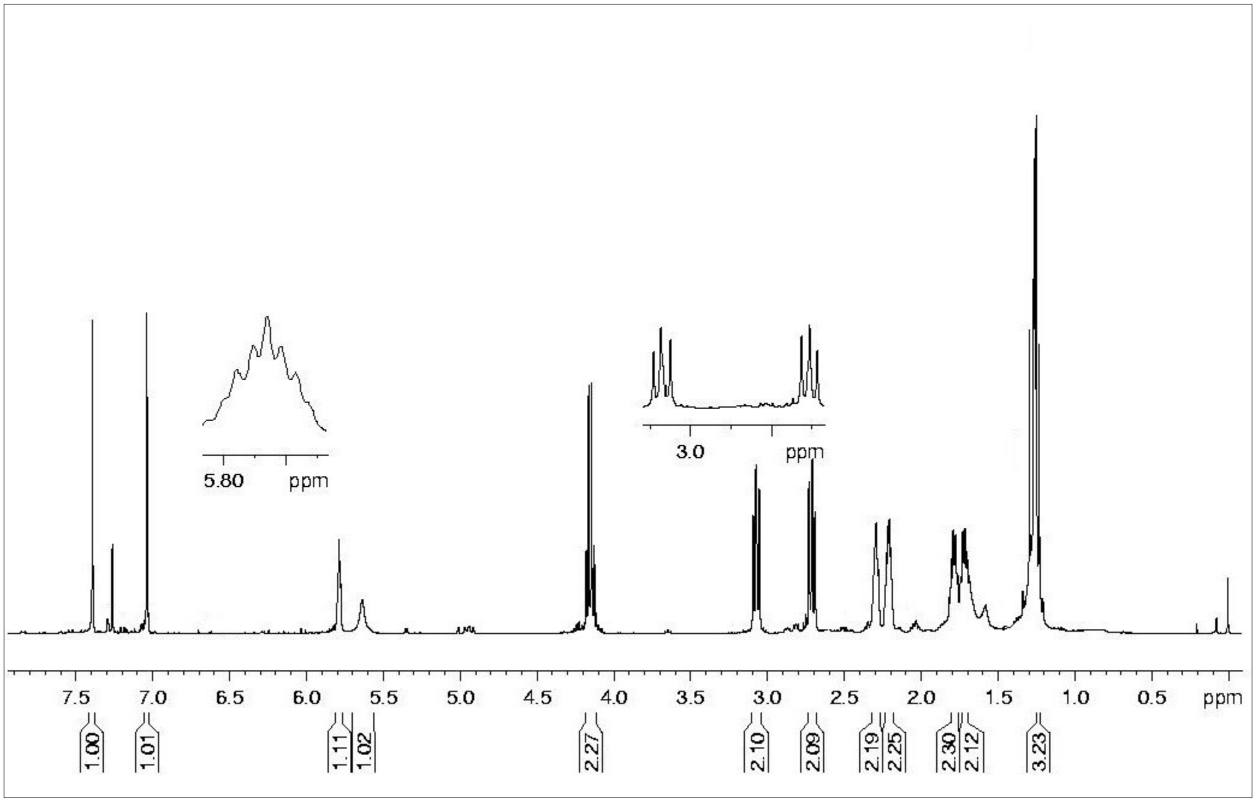
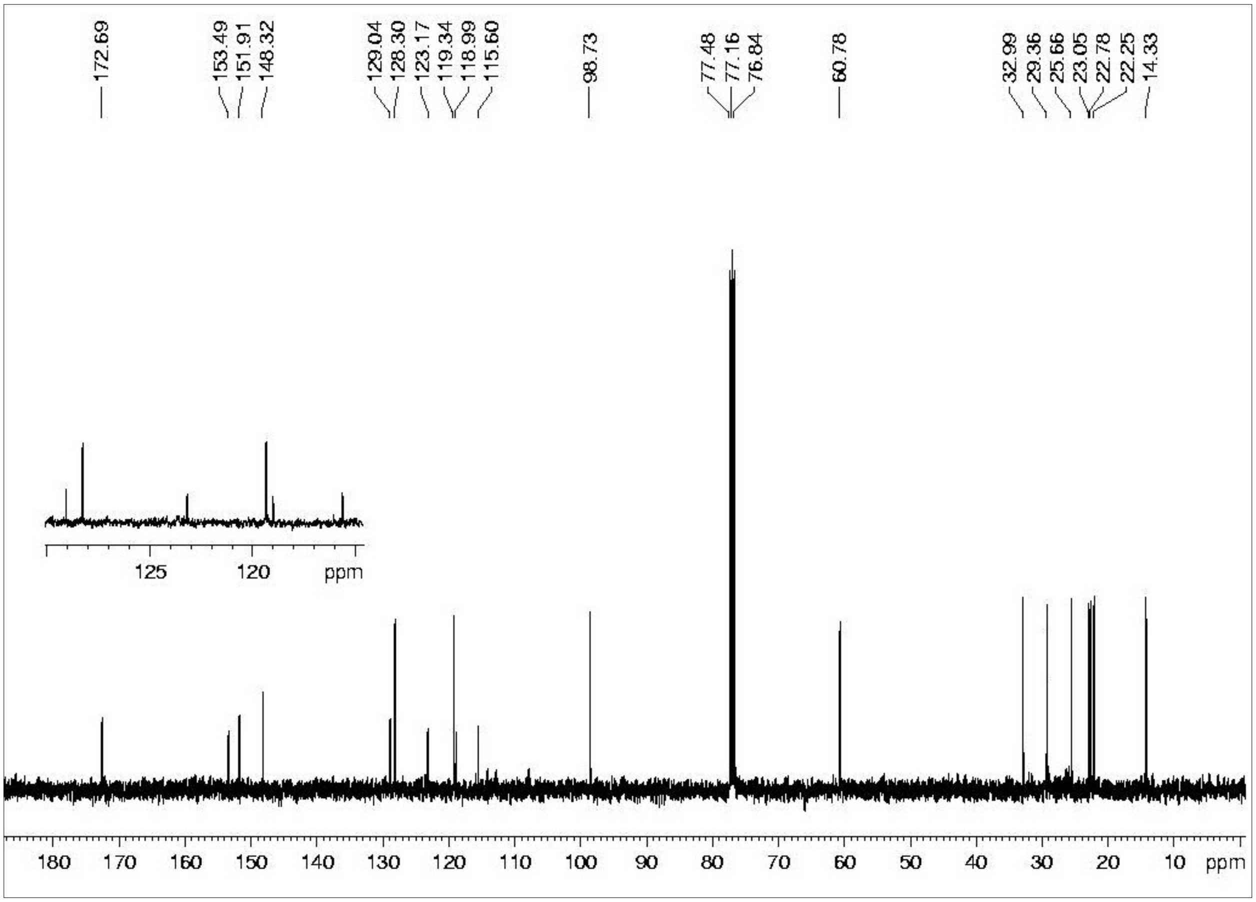
122.19
119.72
117.06
111.06
107.36
77.48
77.16
76.84
60.80
33.52
30.08
29.62
29.03
26.89
26.81
26.55
22.75
14.33
8.39
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.80
ppm
3.0
ppm
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
1.00
1.01
1.11
1.02
2.27
2.10
2.09
2.19
2.25
2.30
2.12
3.23


172.69
153.49
151.91
148.32
129.04
128.30
123.17
119.34
118.99
115.60
98.73
77.48
77.16
76.84
60.78
32.99
29.36
25.66
23.05
22.78
22.25
14.33
125
120
ppm
180
170
160
150
140
130
120
110
100
90
80
70
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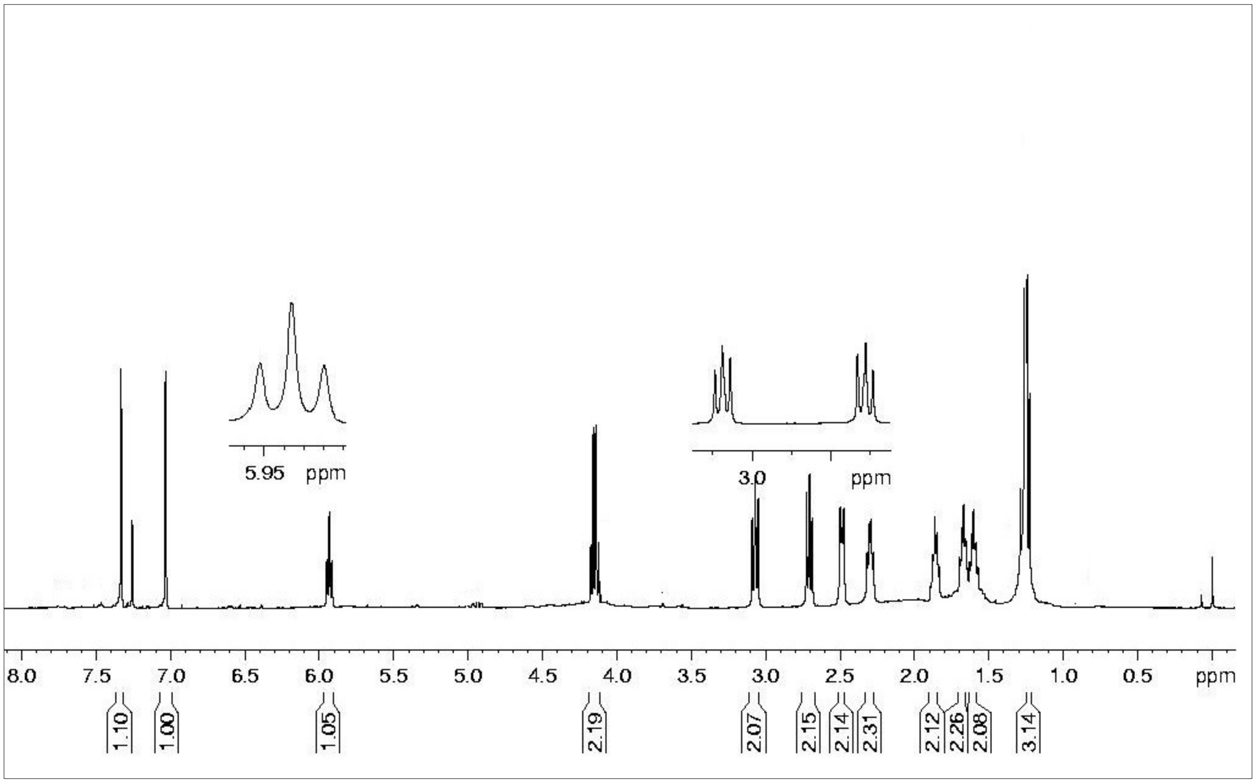
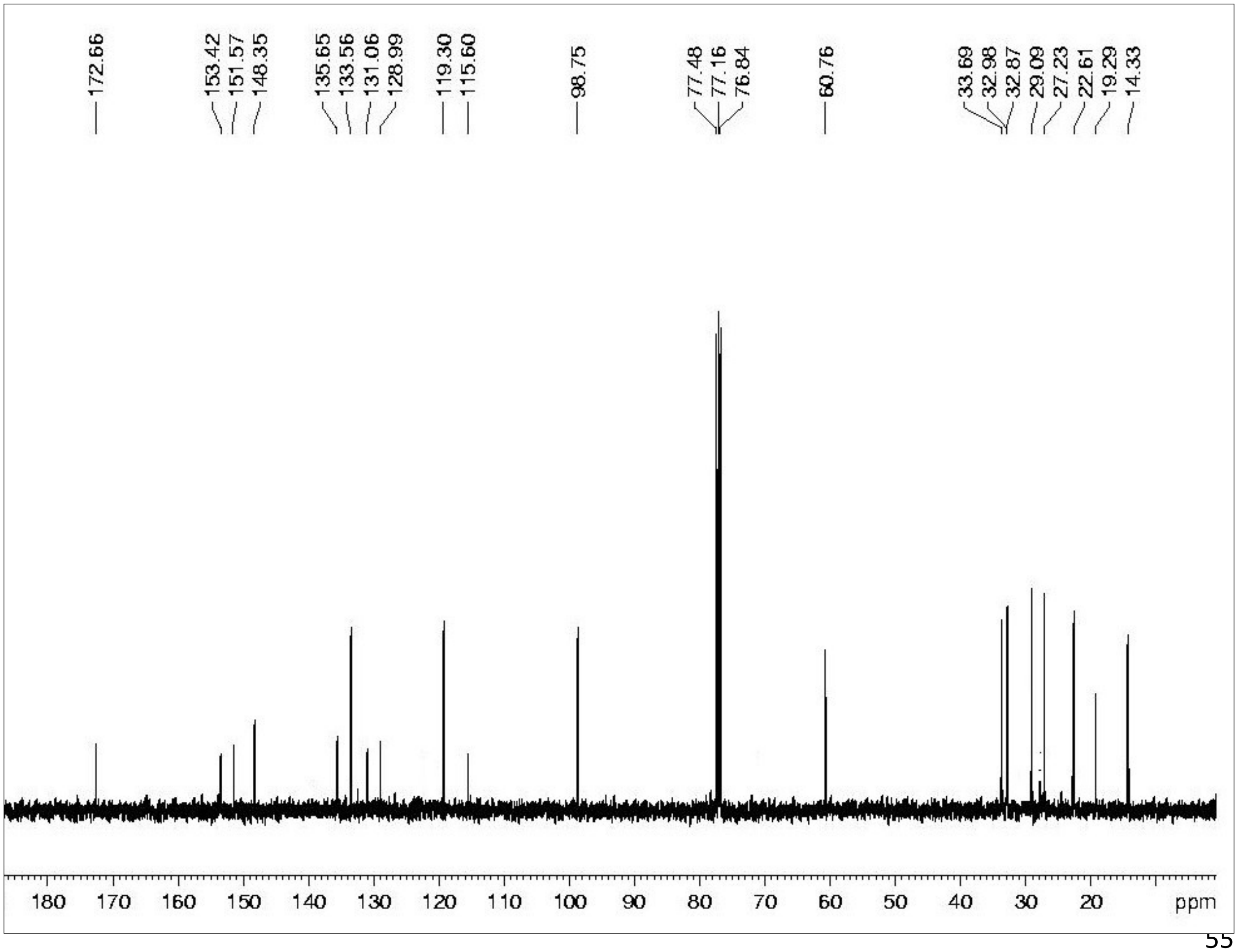
50
40
30
20
10
ppm


5.95 ppm
3.0 ppm
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
1.10
1.00
1.05
2.19
2.07
2.15
2.14
2.31
2.12
2.26
2.08
3.14


172.66
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135.65
133.56
131.06
128.99
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115.60
98.75
77.48
77.16
76.84
60.76
33.69
32.98
32.87
29.09
27.23
22.61
19.29
14.33
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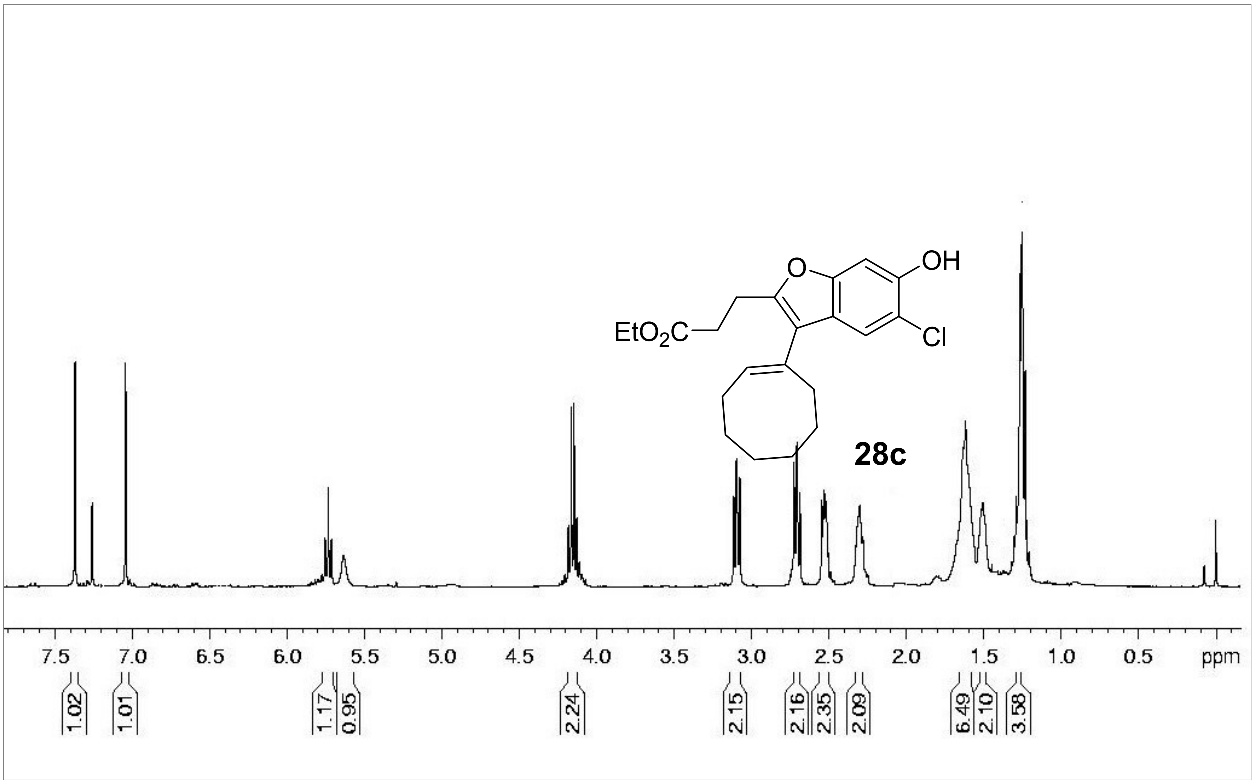
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
OH
EtO2C
Cl
28c
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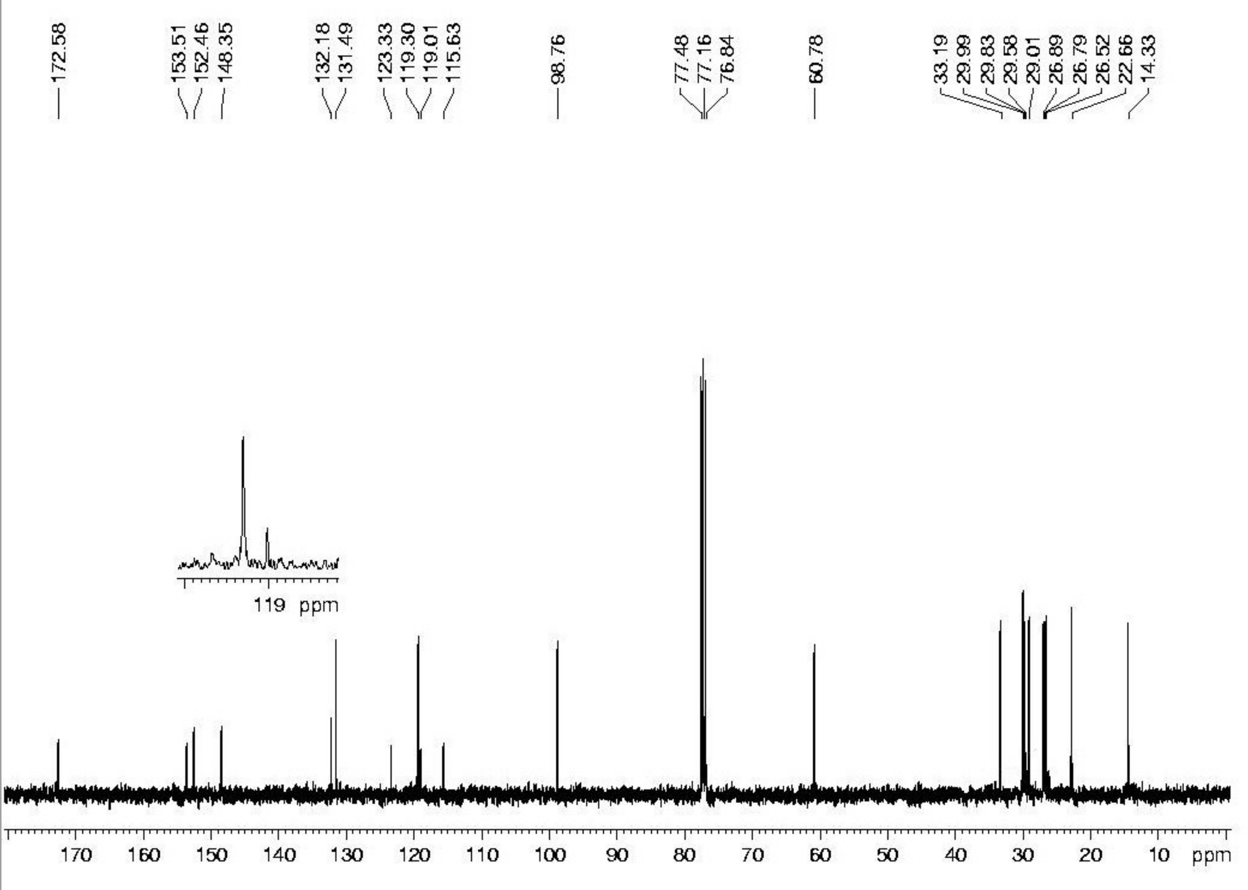
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
1.01
1.17
0.95
2.24
2.15
2.16
2.35
2.09
6.49
2.10
3.58


172.58
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131.49
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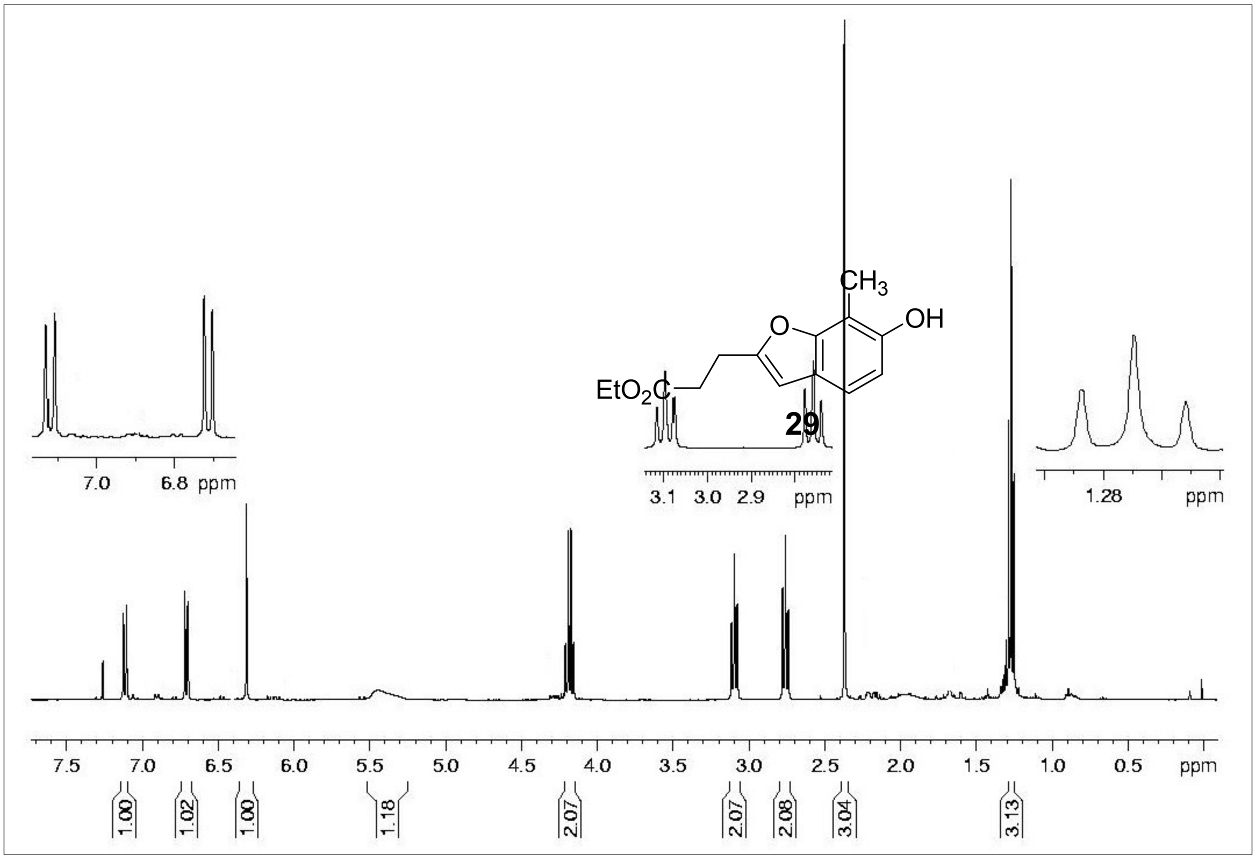
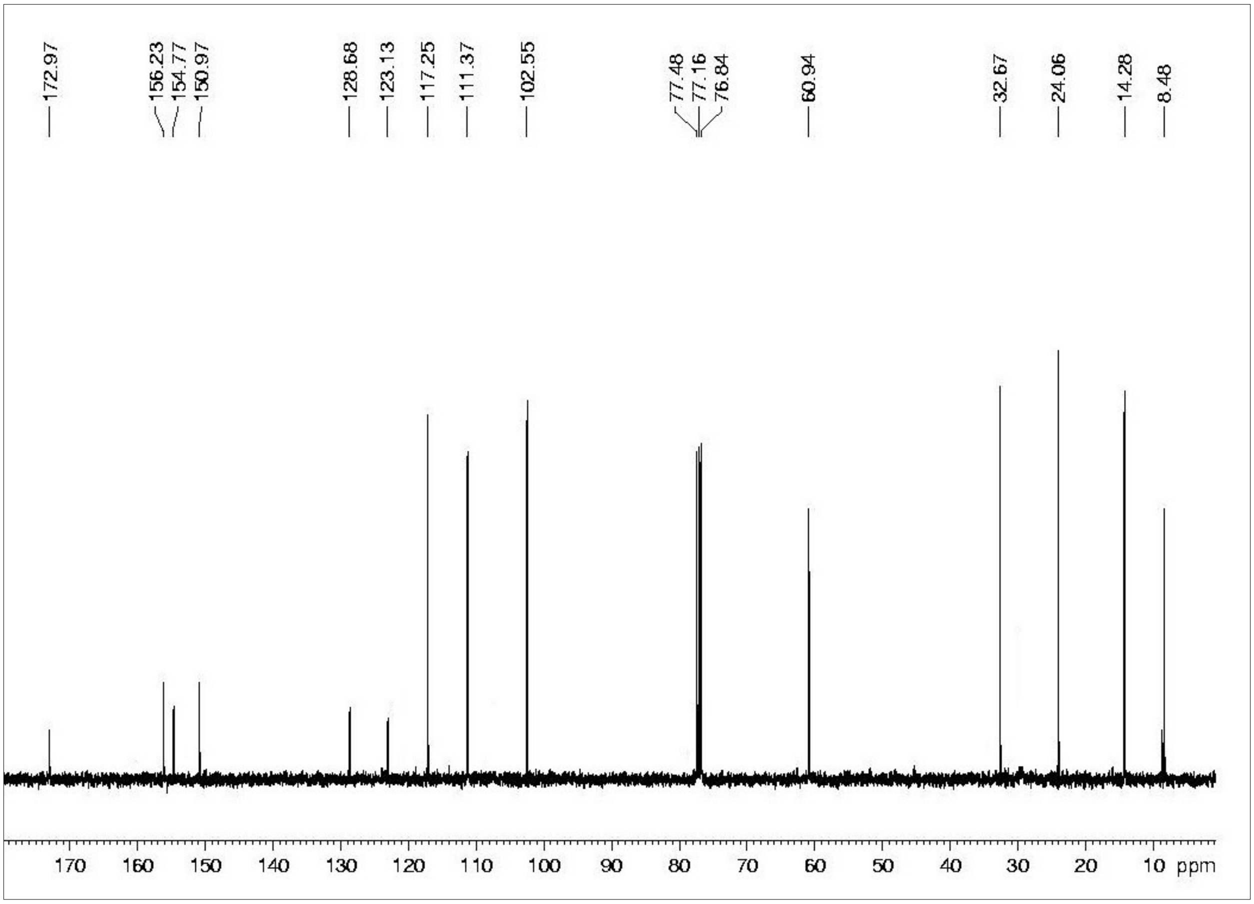
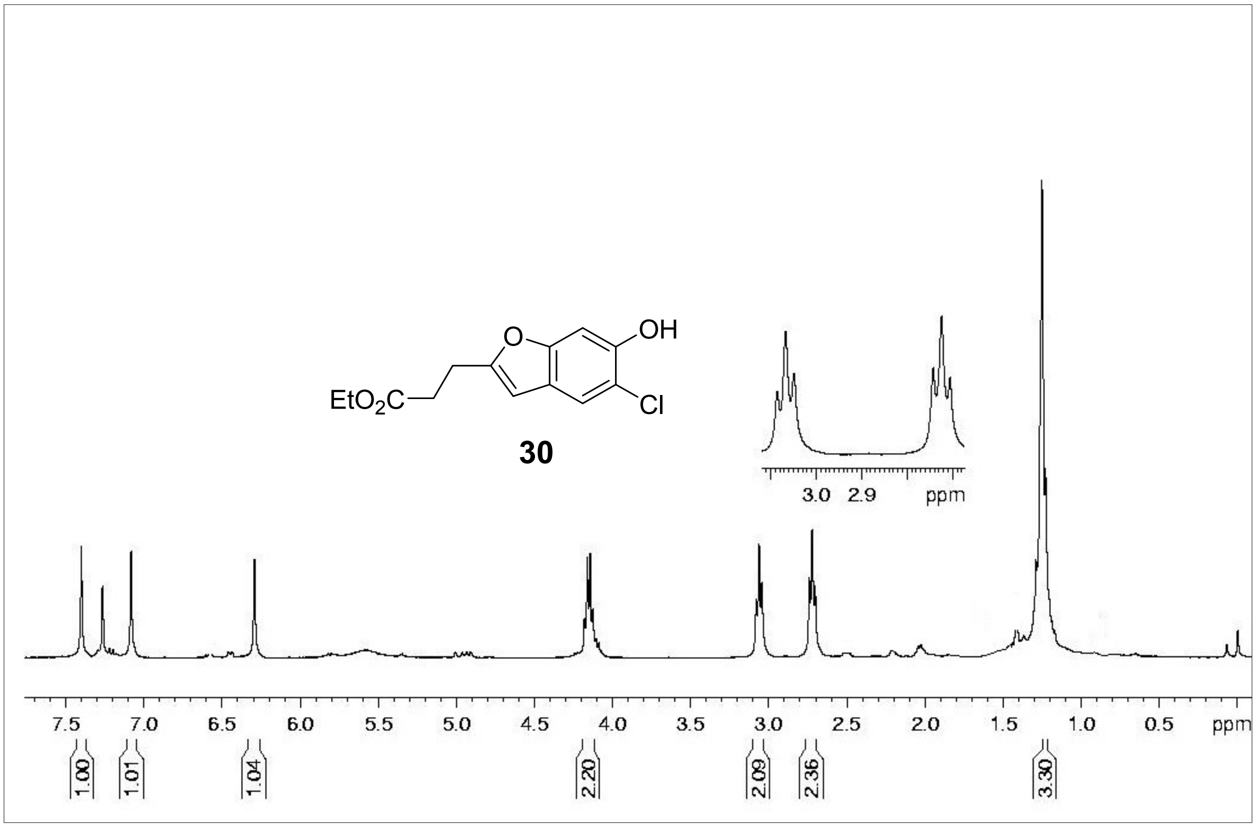
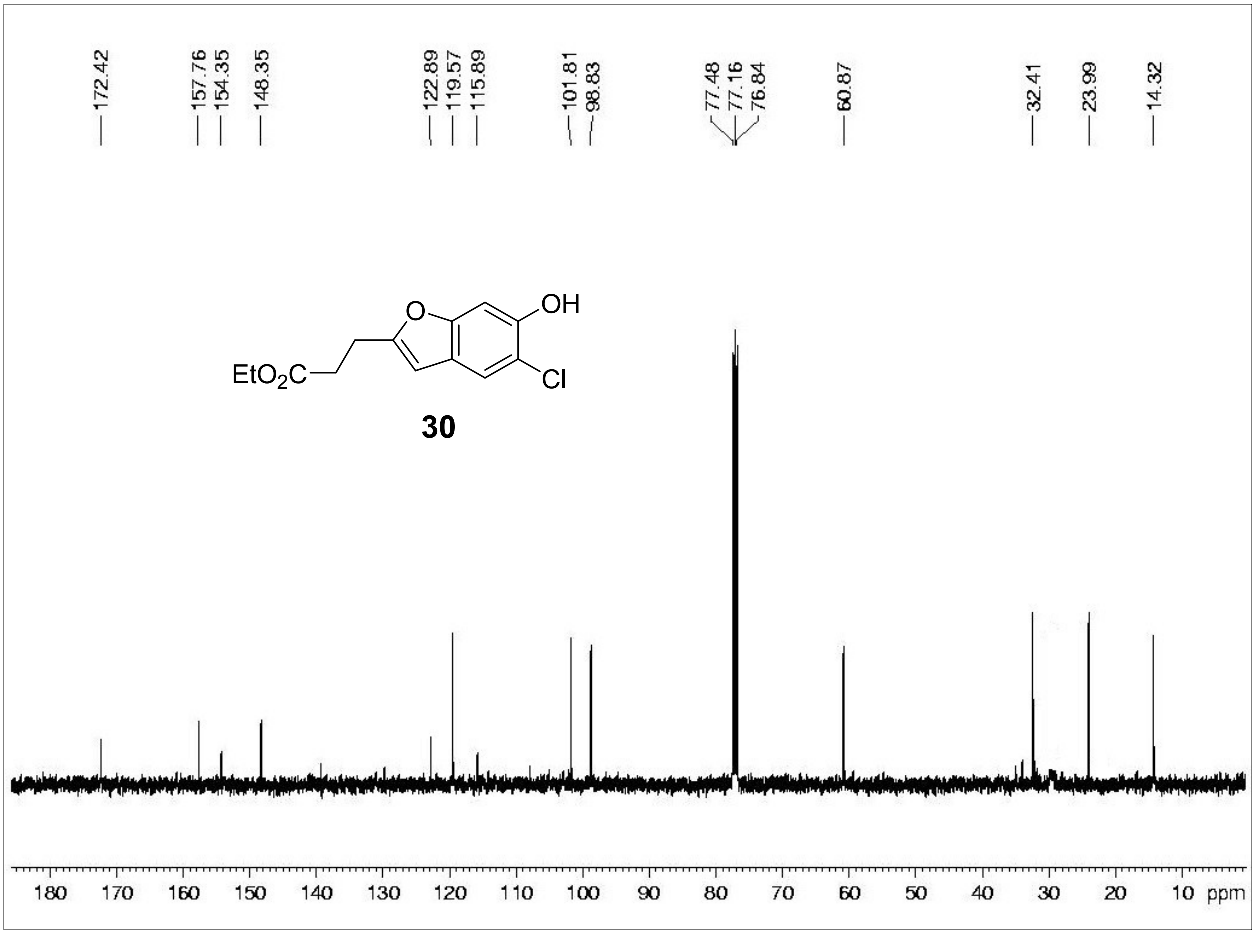
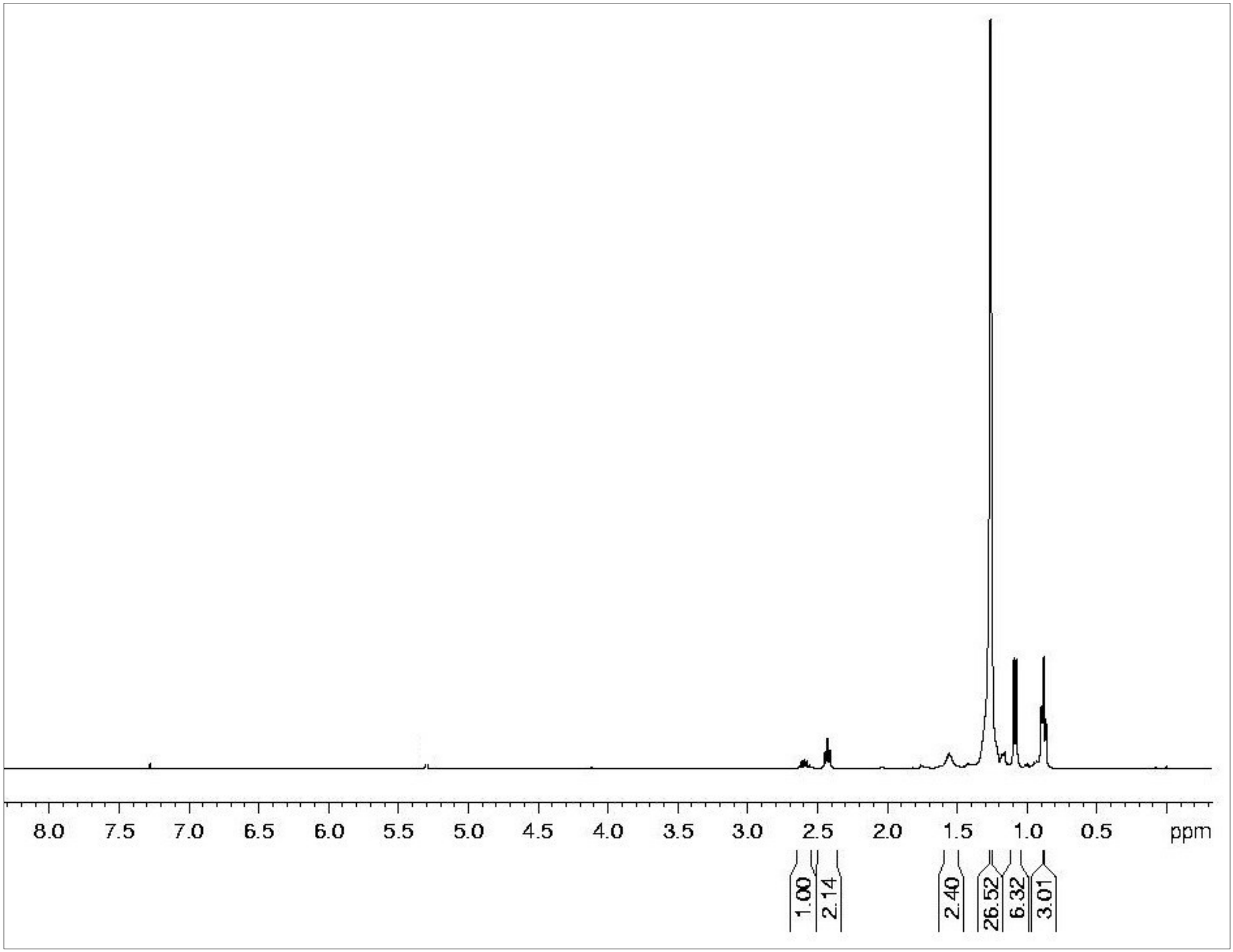
77.16
76.84
60.78
33.19
29.99
29.83
29.58
29.01
26.89
26.79
26.52
22.66
14.33
119 ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

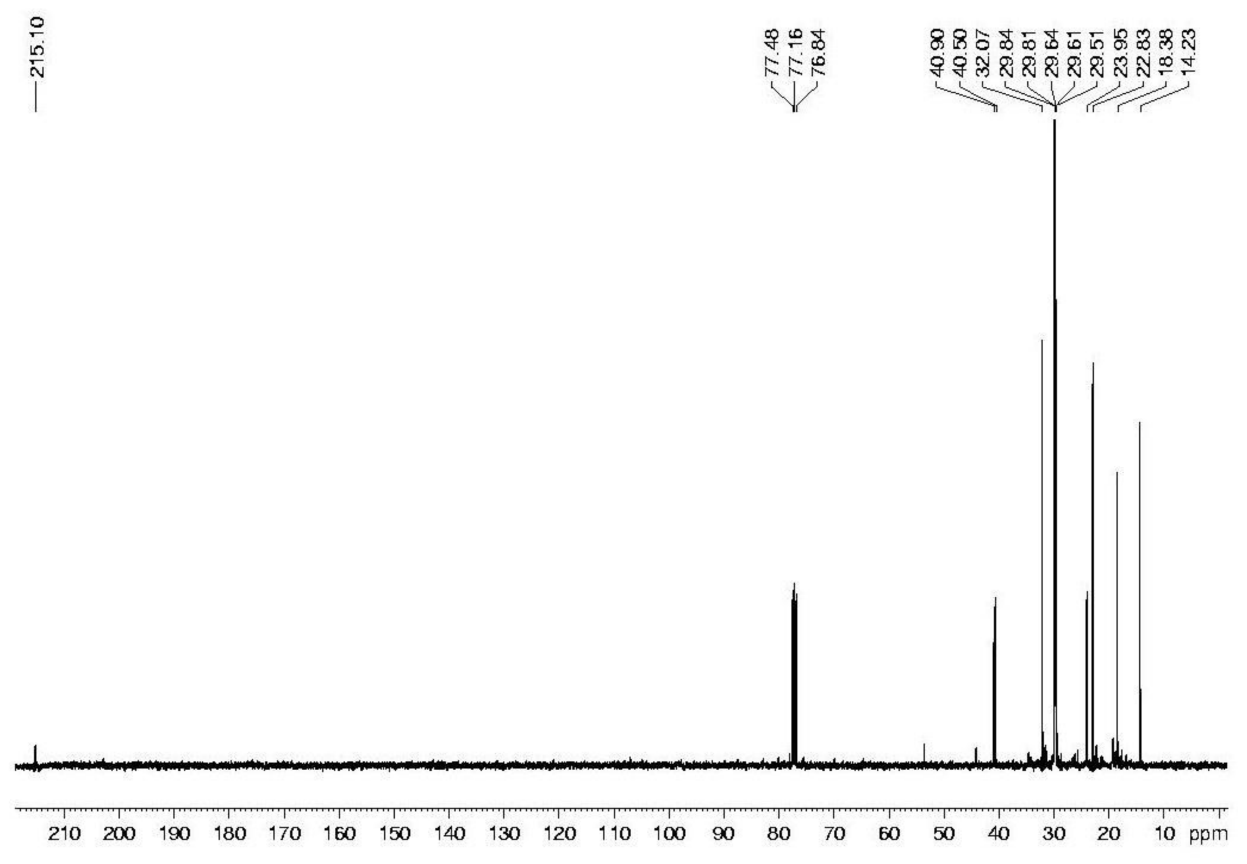

CH3
OH
O
EtO2C
29
7.0
6.8 ppm
3.1 3.0 2.9 ppm
1.28 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.02
1.00
1.18
2.07
2.07
2.08
3.04
3.13

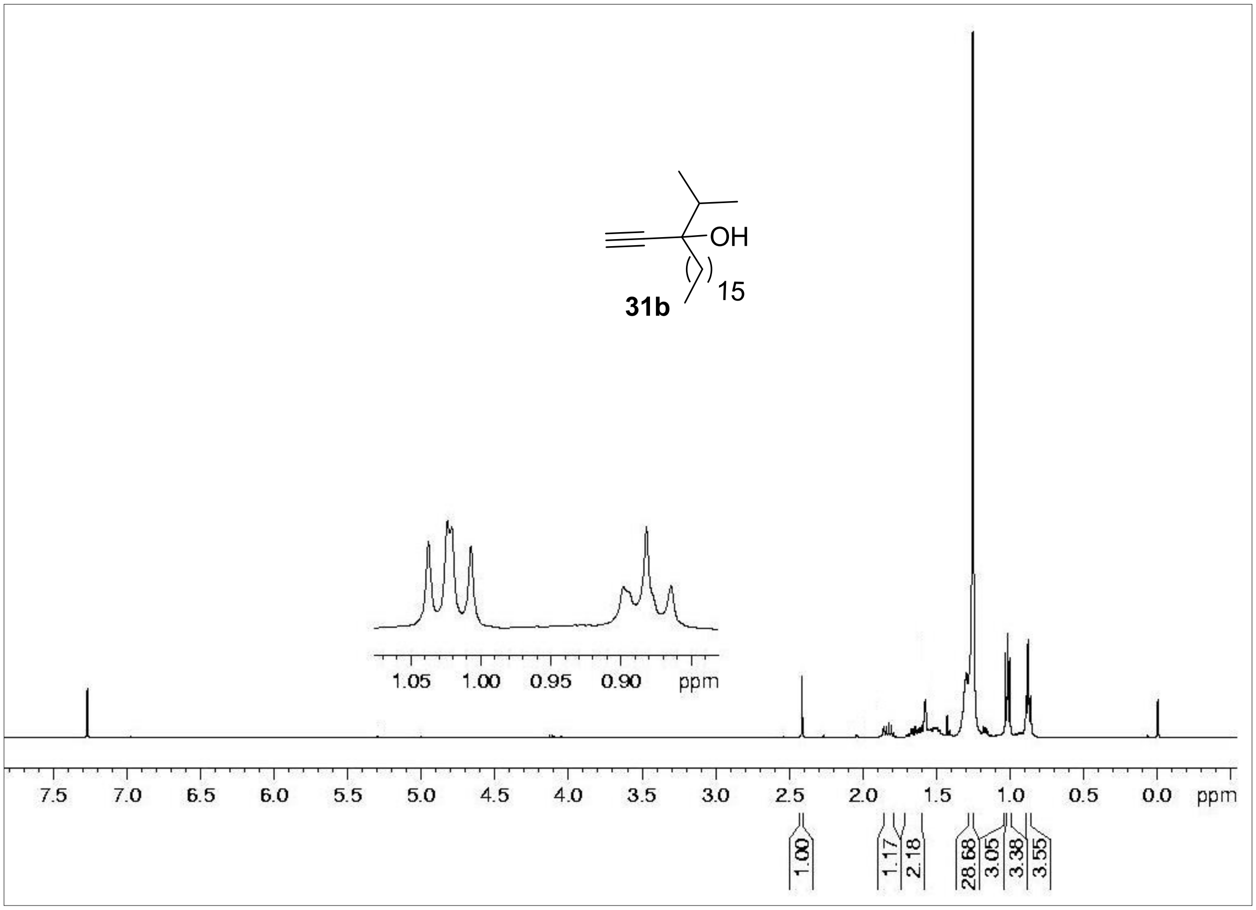

172.97
156.23
154.77
150.97
128.68
123.13
117.25
111.37
102.55
77.48
77.16
76.84
60.94
32.67
24.06
14.28
8.48
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

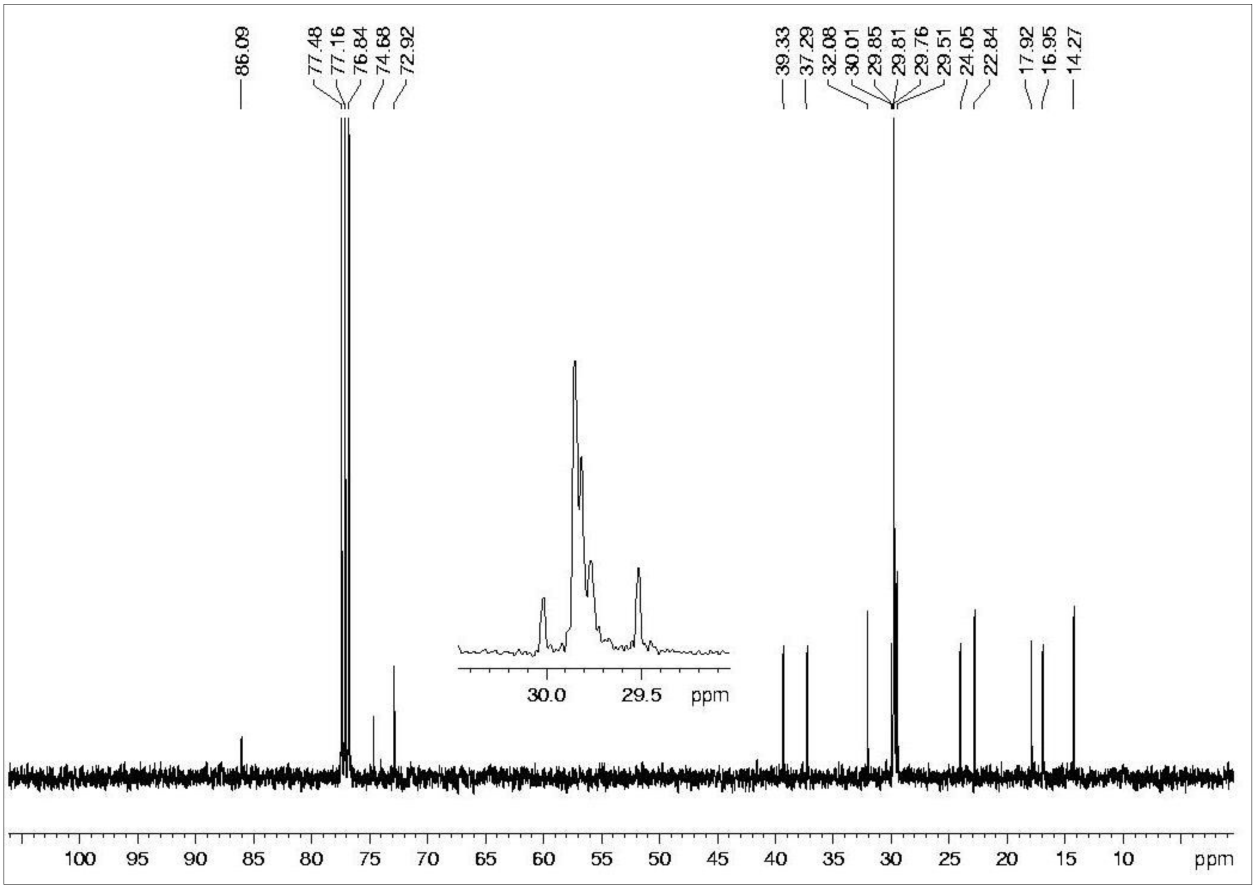

O
OH
EtO2C
Cl
30
3.0 2.9 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
1.04
2.20
2.09
2.36
3.30

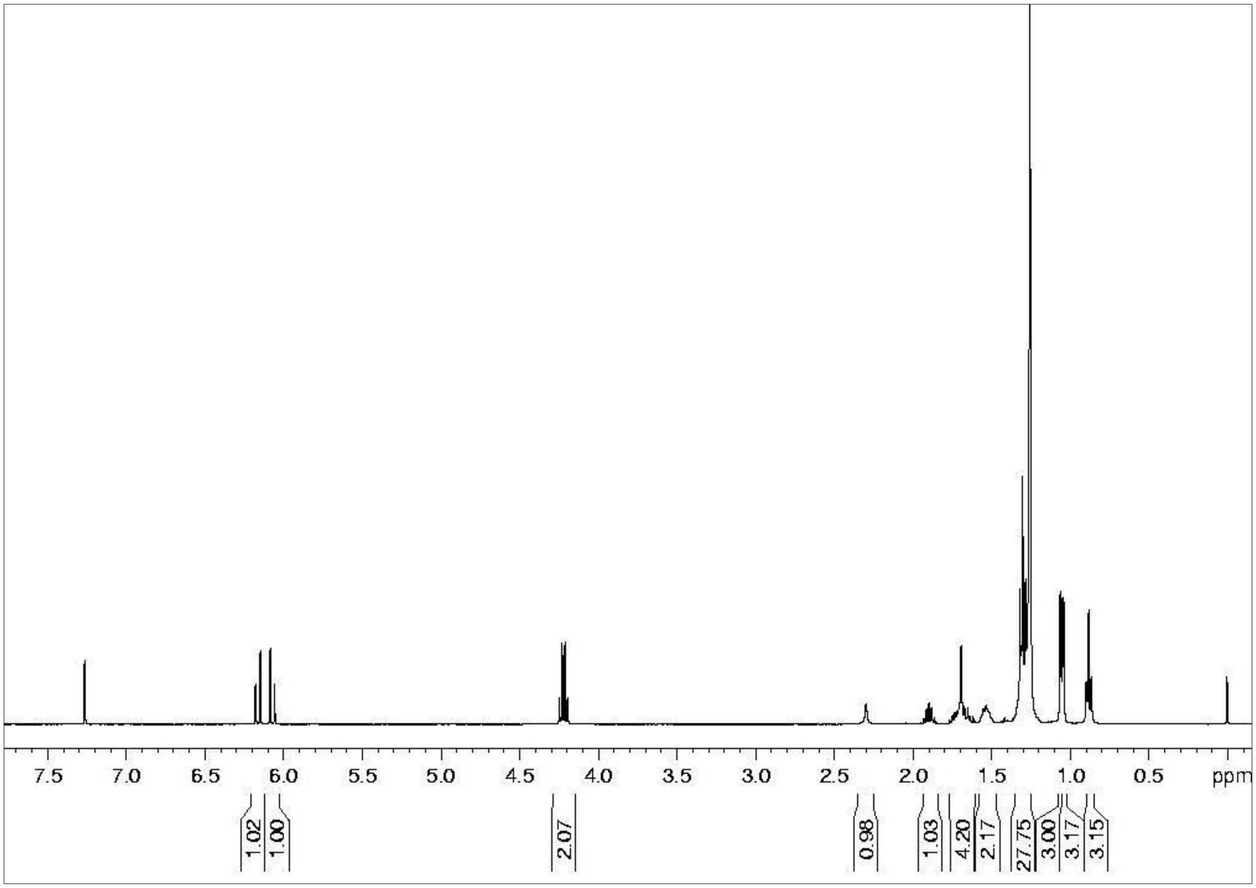

172.42
157.76
154.35
148.35
122.89
119.57
115.89
101.81
98.83
77.48
77.16
76.84
60.87
32.41
23.99
14.32
O
OH
EtO2C
Cl
30
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

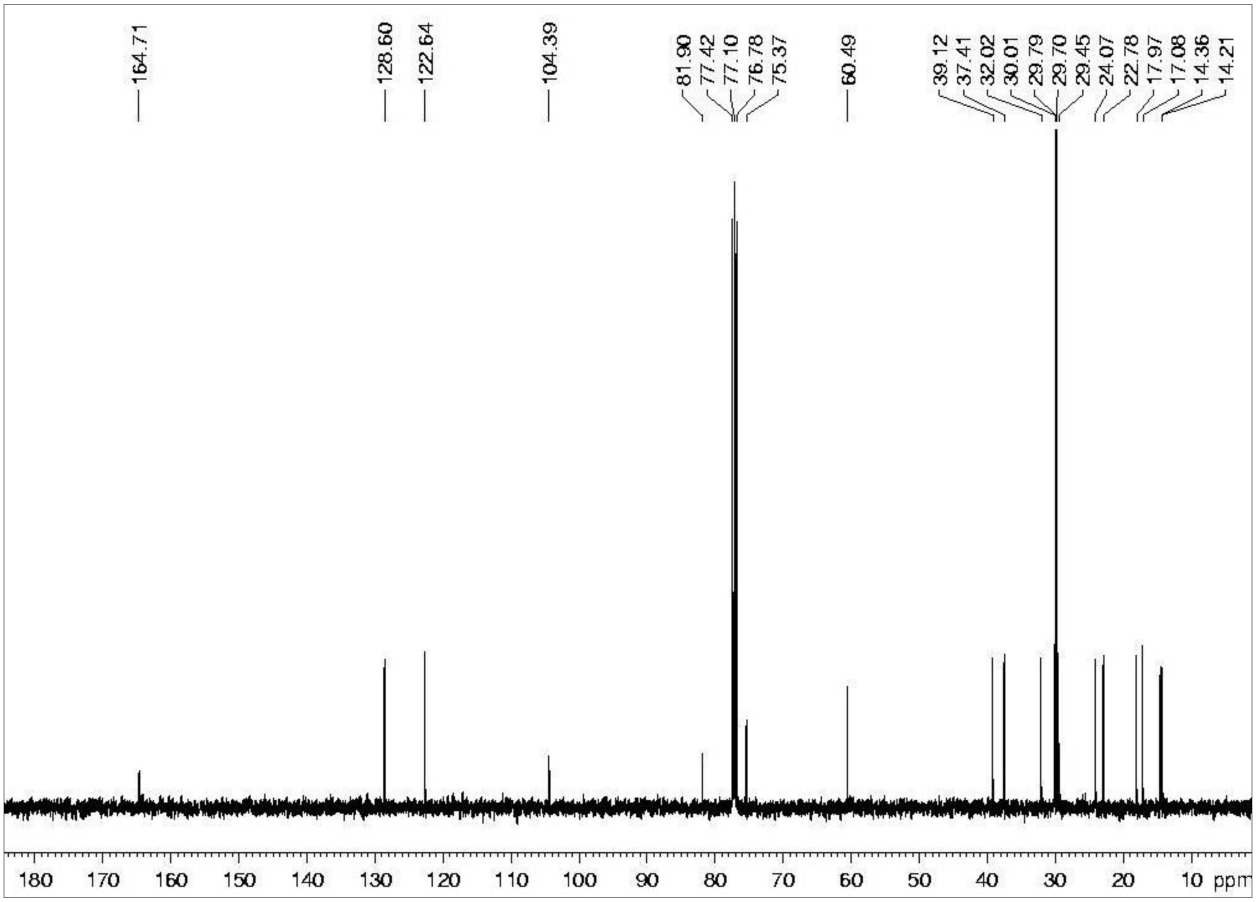

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.14
2.40
26.52
6.32
3.01

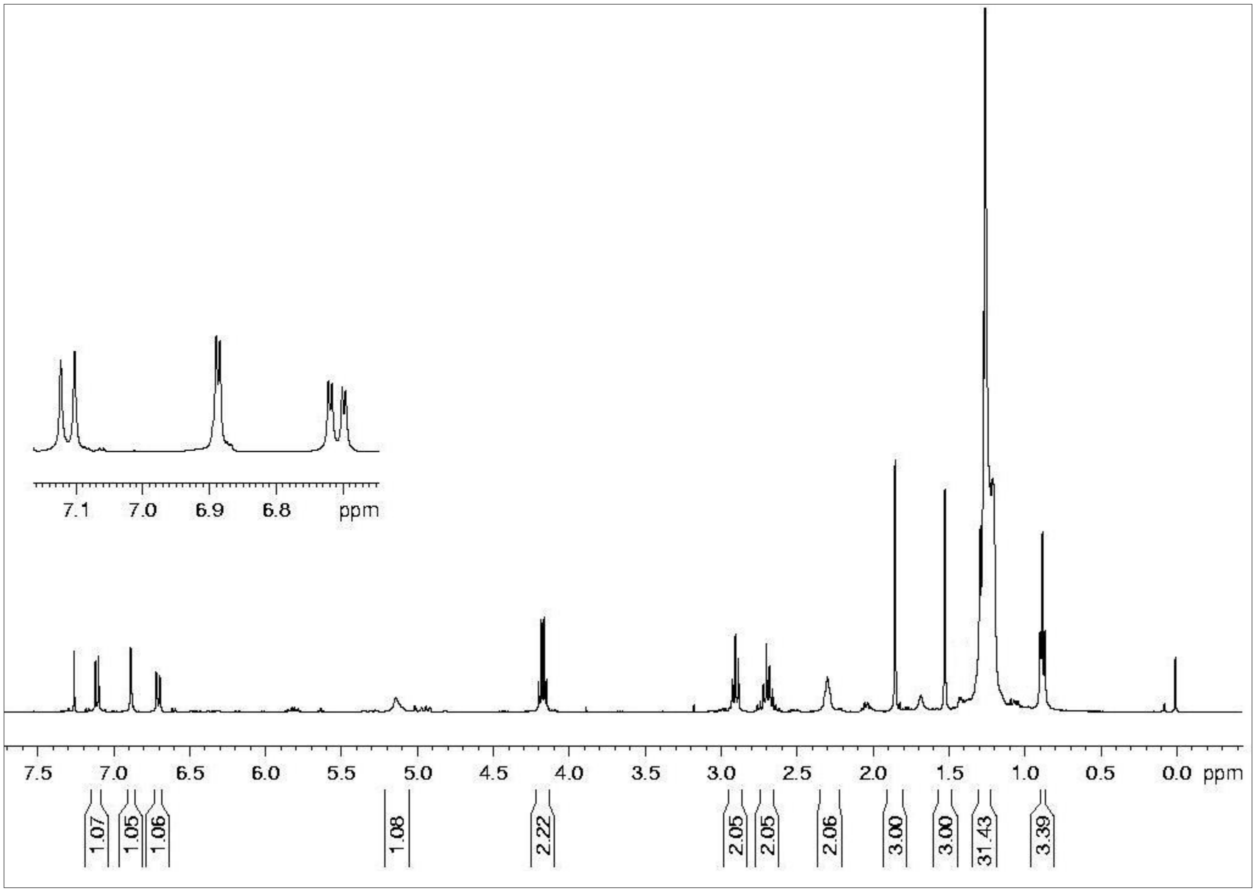

215.10
77.48
77.16
76.84
40.90
40.50
32.07
29.84
29.81
29.64
29.61
29.51
23.95
22.83
18.38
14.23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

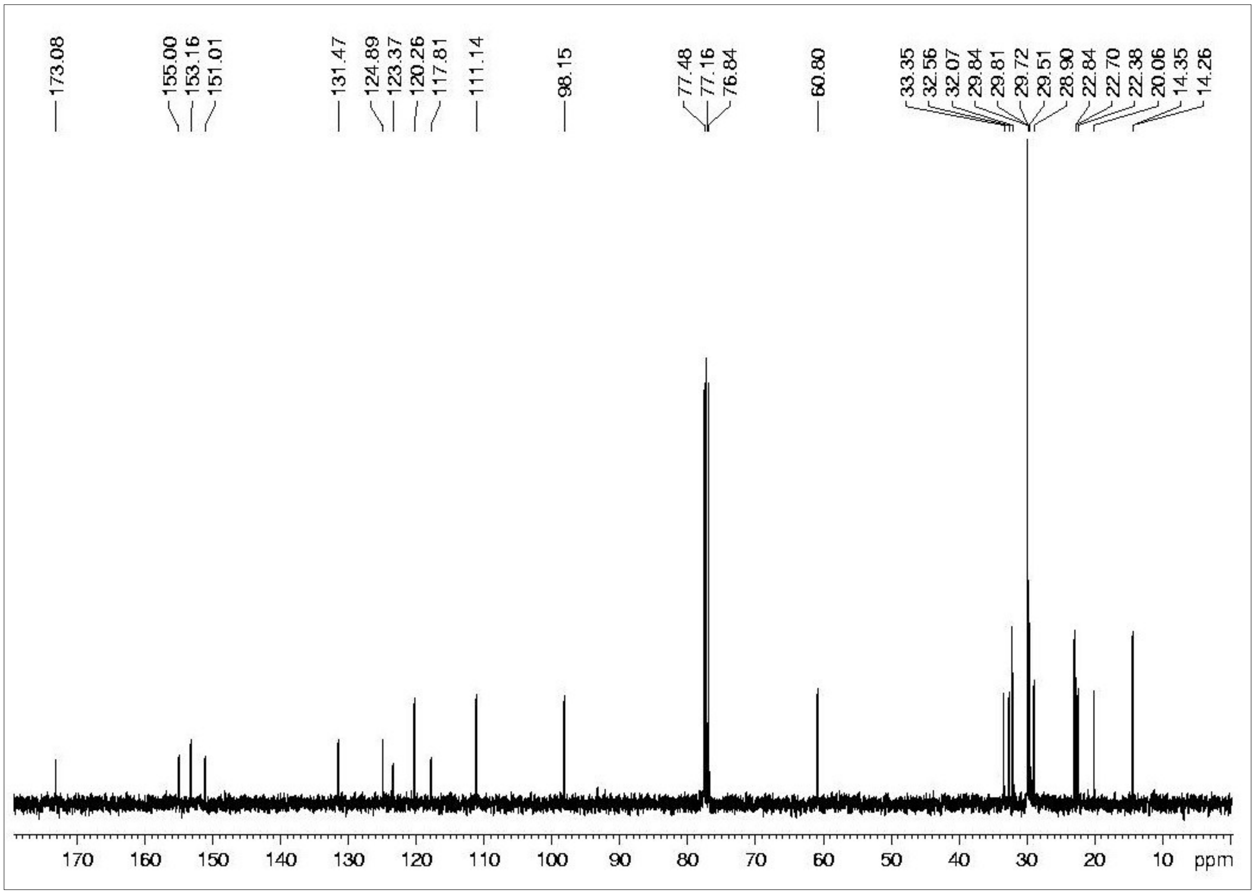

OH
15
31b
1.05
1.00
0.95
0.90
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.17
2.18
28.68
3.05
3.38
3.55

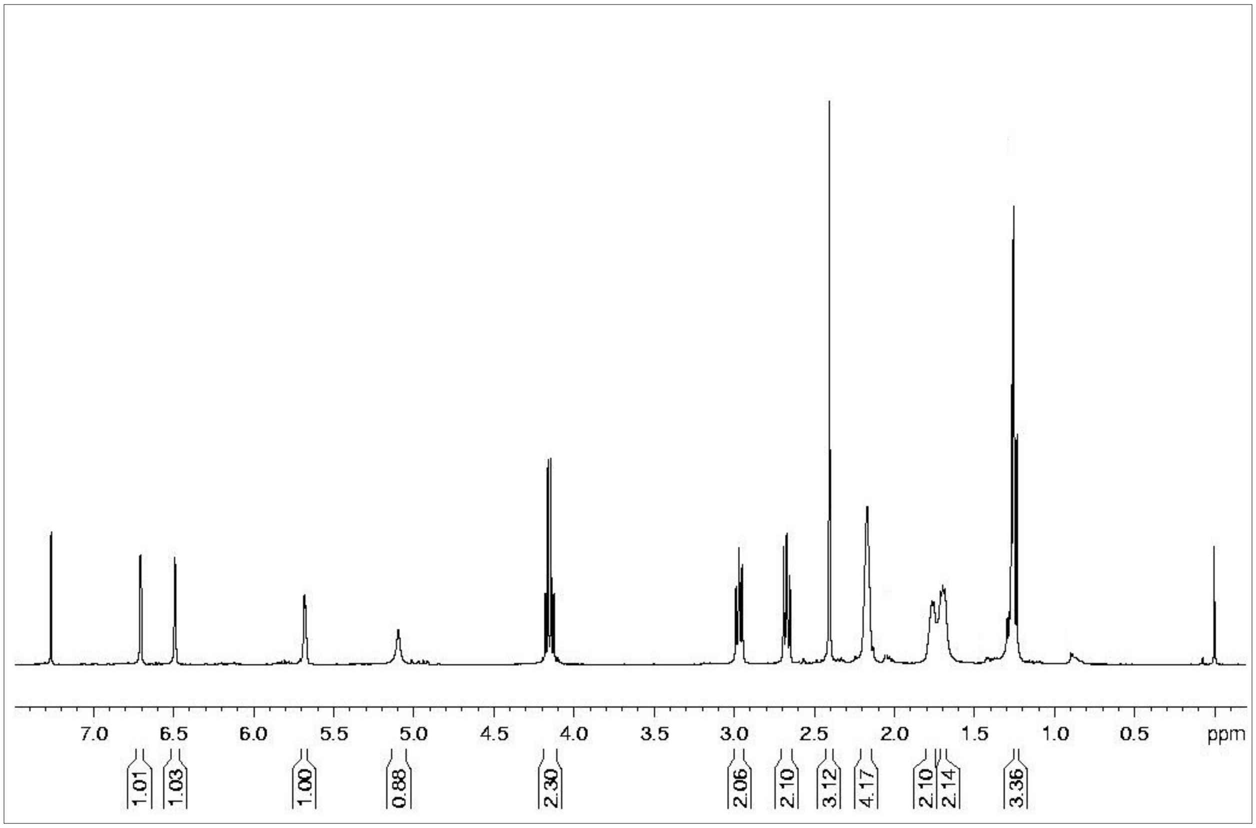

86.09
77.48
77.16
76.84
74.68
72.92
39.33
37.29
32.08
30.01
29.85
29.81
29.76
29.51
24.05
22.84
17.92
16.95
14.27
30.0
29.5
ppm
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
ppm

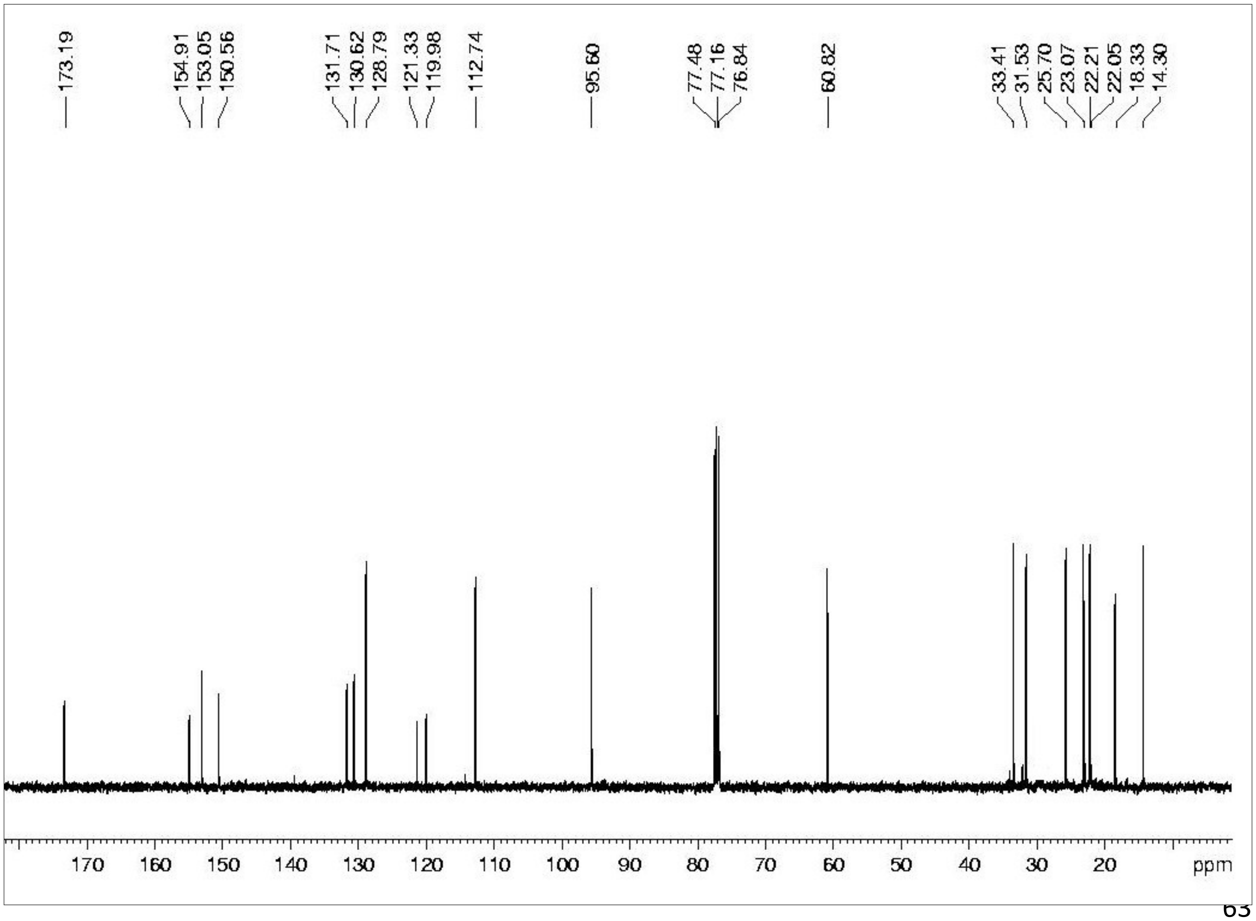

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
1.00
2.07
0.98
1.03
4.20
2.17
27.75
3.00
3.17
3.15

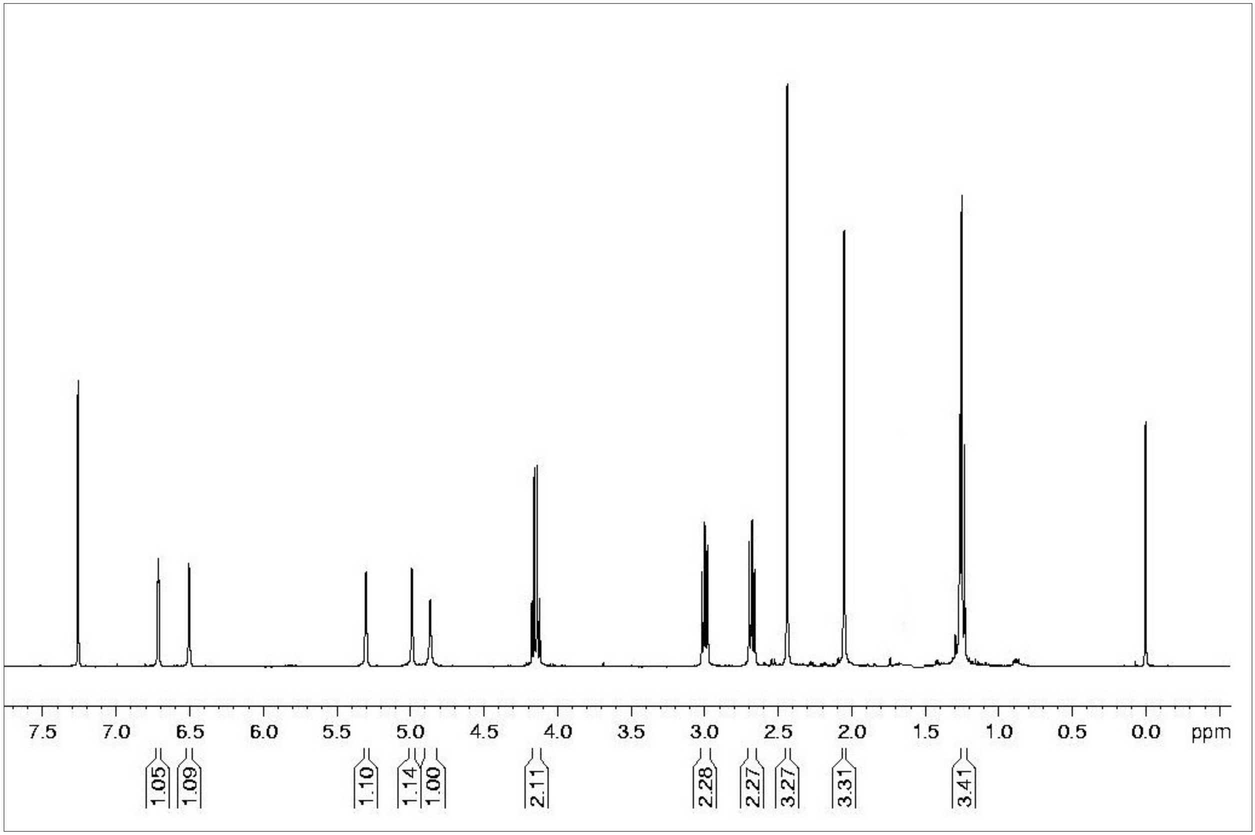

164.71
128.60
122.64
104.39
81.90
77.42
77.10
76.78
75.37
60.49
39.12
37.41
32.02
30.01
29.79
29.70
29.45
24.07
22.78
17.97
17.08
14.36
14.21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

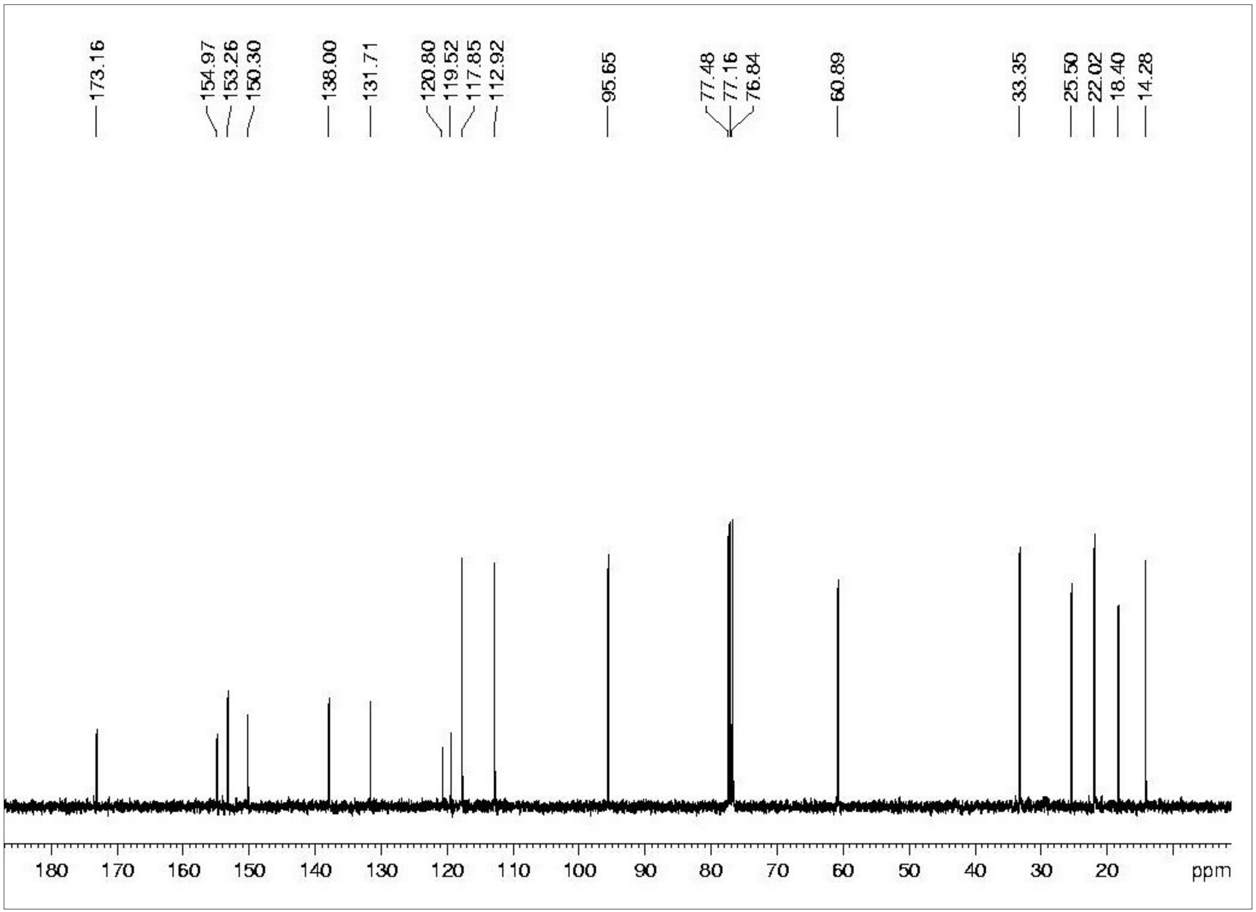

7.1
7.0
6.9
6.8
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.07
1.05
1.06
1.08
2.22
2.05
2.05
2.06
3.00
3.00
31.43
3.39

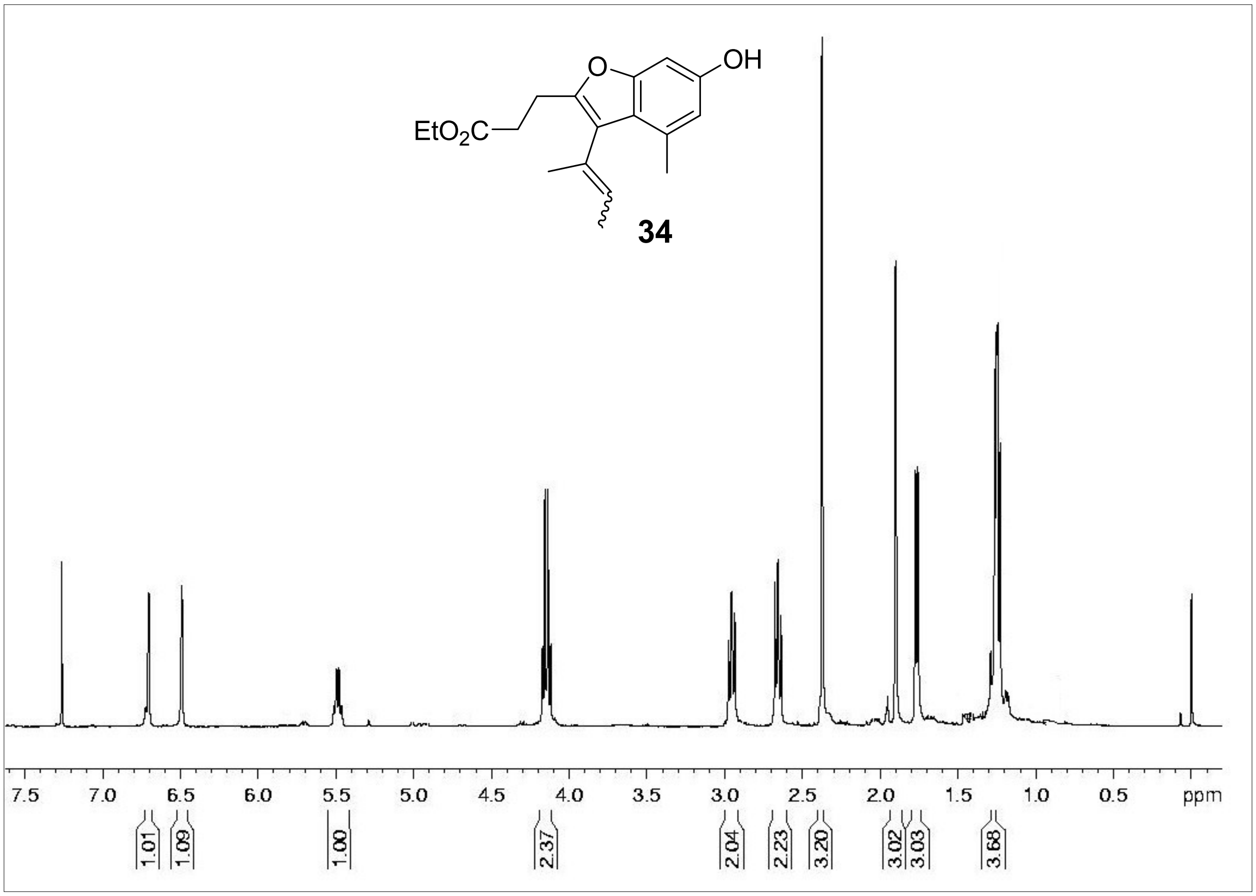

173.08
155.00
153.16
151.01
131.47
124.89
123.37
120.26
117.81
111.14
98.15
77.48
77.16
76.84
60.80
33.35
32.56
32.07
29.84
29.81
29.72
29.51
28.90
22.84
22.70
22.38
20.06
14.35
14.26
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

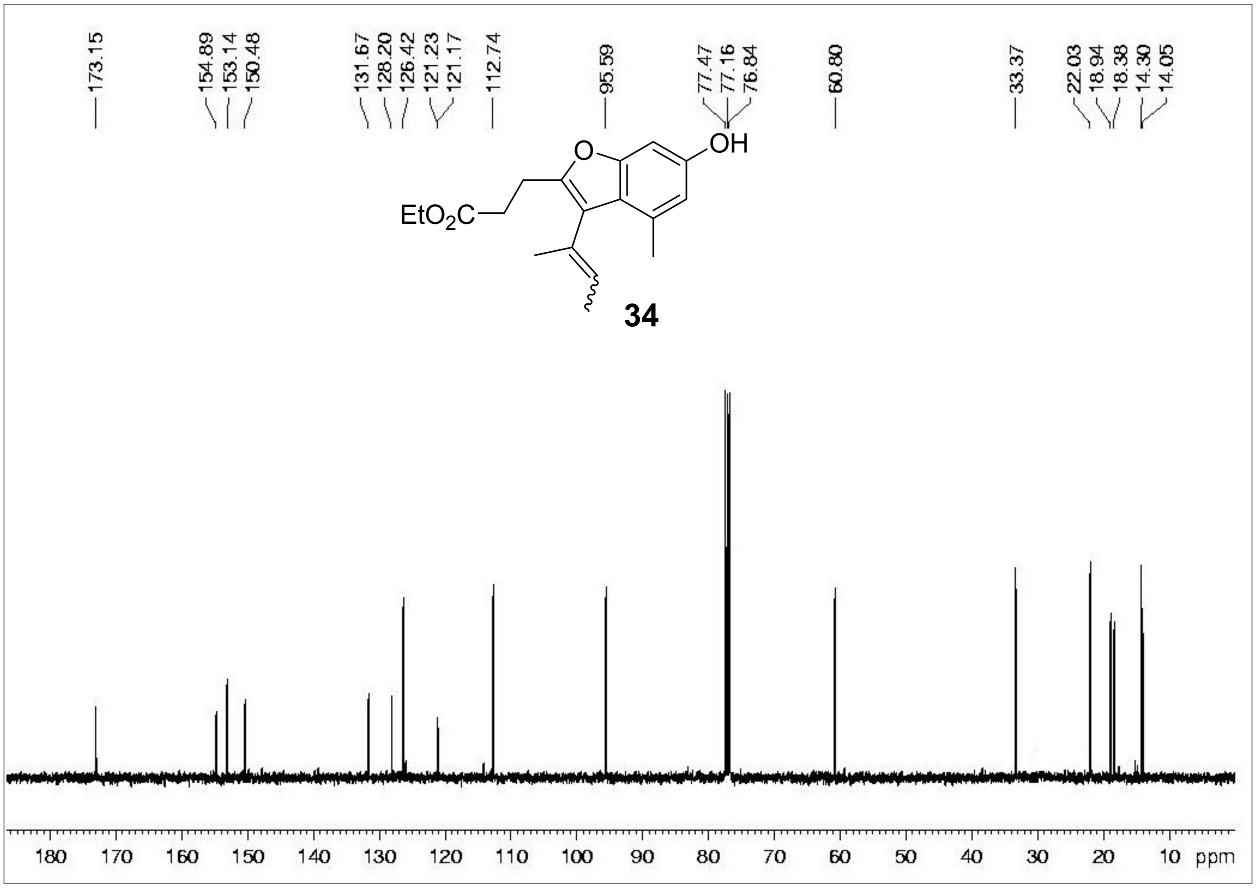

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.03
1.00
0.88
2.30
2.06
2.10
3.12
4.17
2.10
2.14
3.36

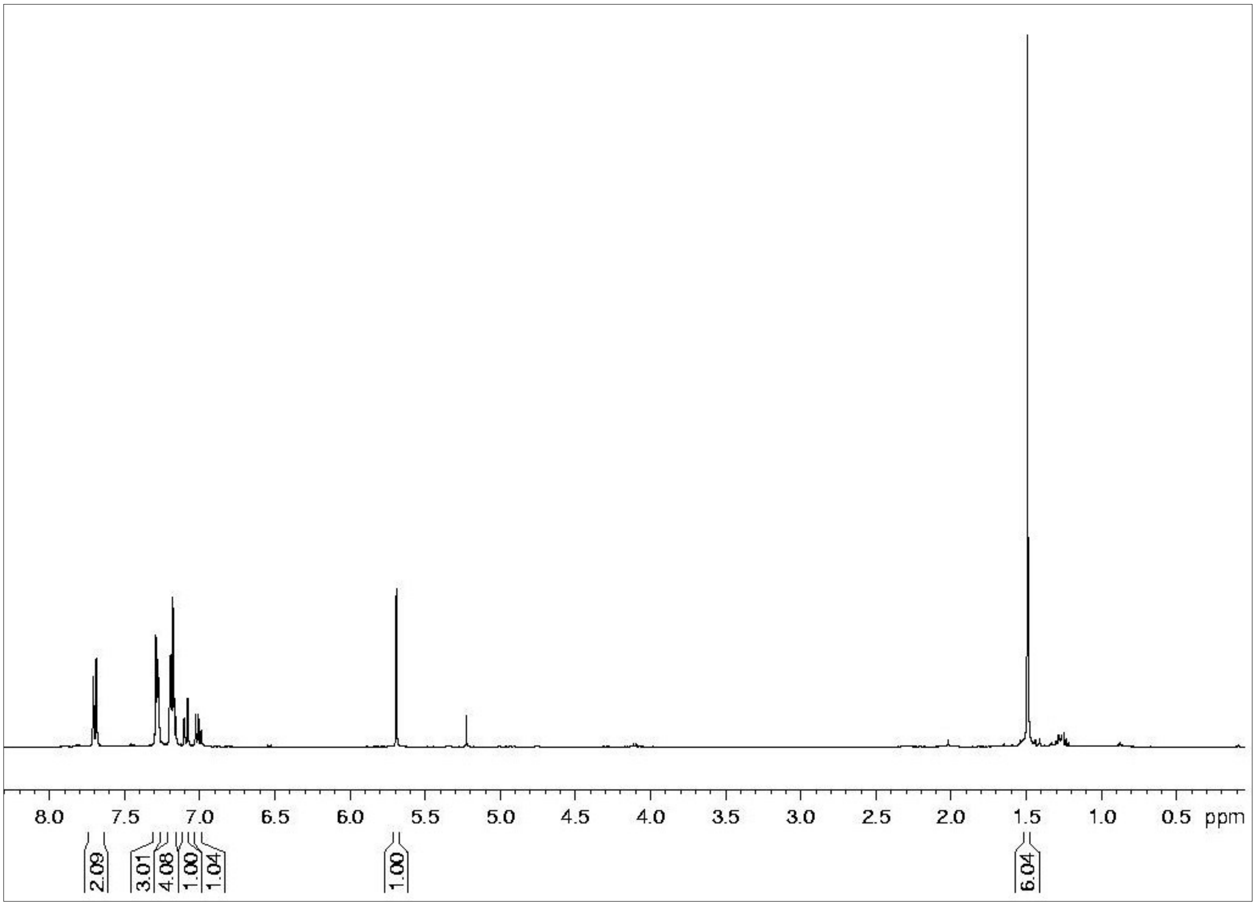

173.19
154.91
153.05
150.56
131.71
130.62
128.79
121.33
119.98
112.74
95.60
77.48
77.16
76.84
60.82
33.41
31.53
25.70
23.07
22.21
22.05
18.33
14.30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

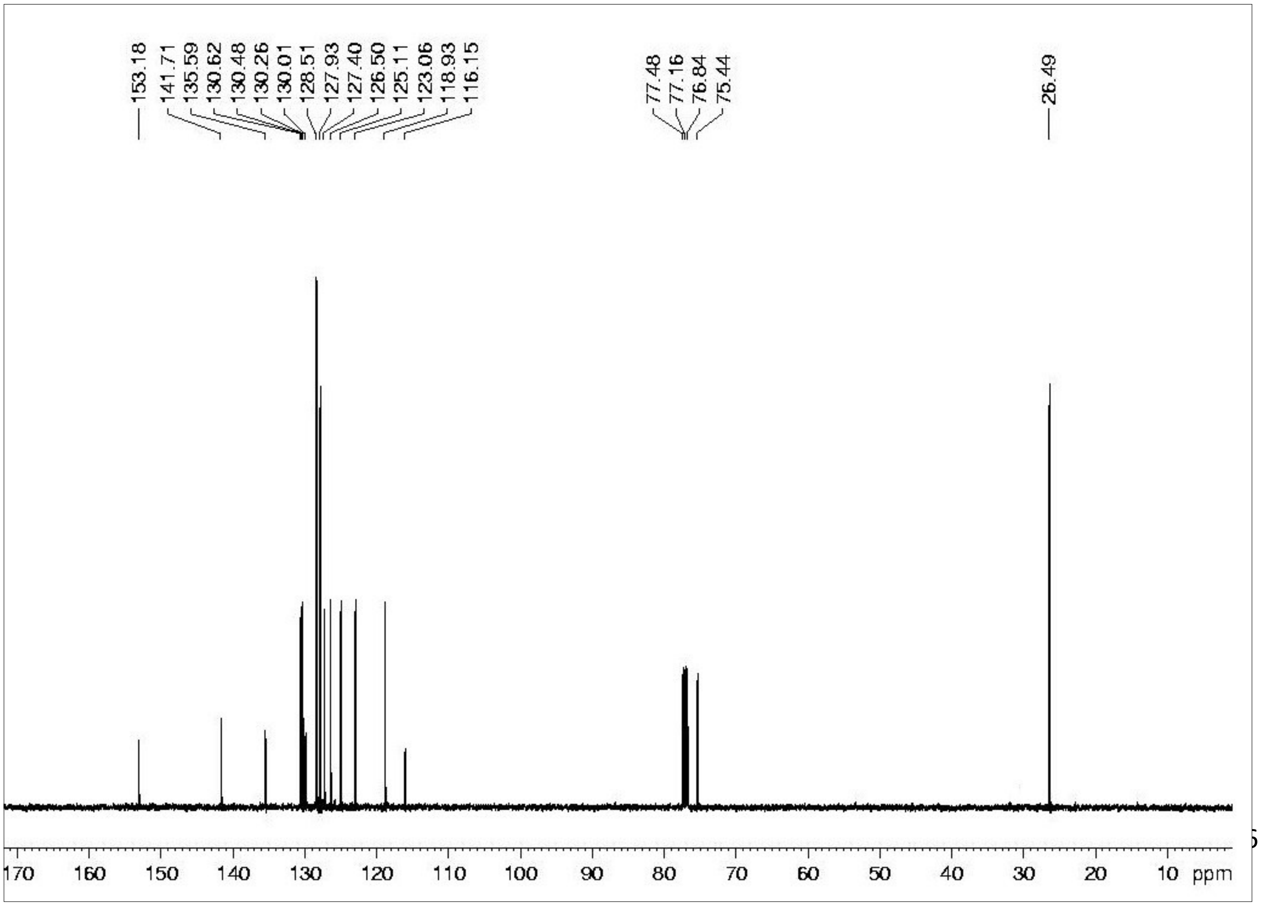

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
1.09
1.10
1.14
1.00
2.11
2.28
2.27
3.27
3.31
3.41

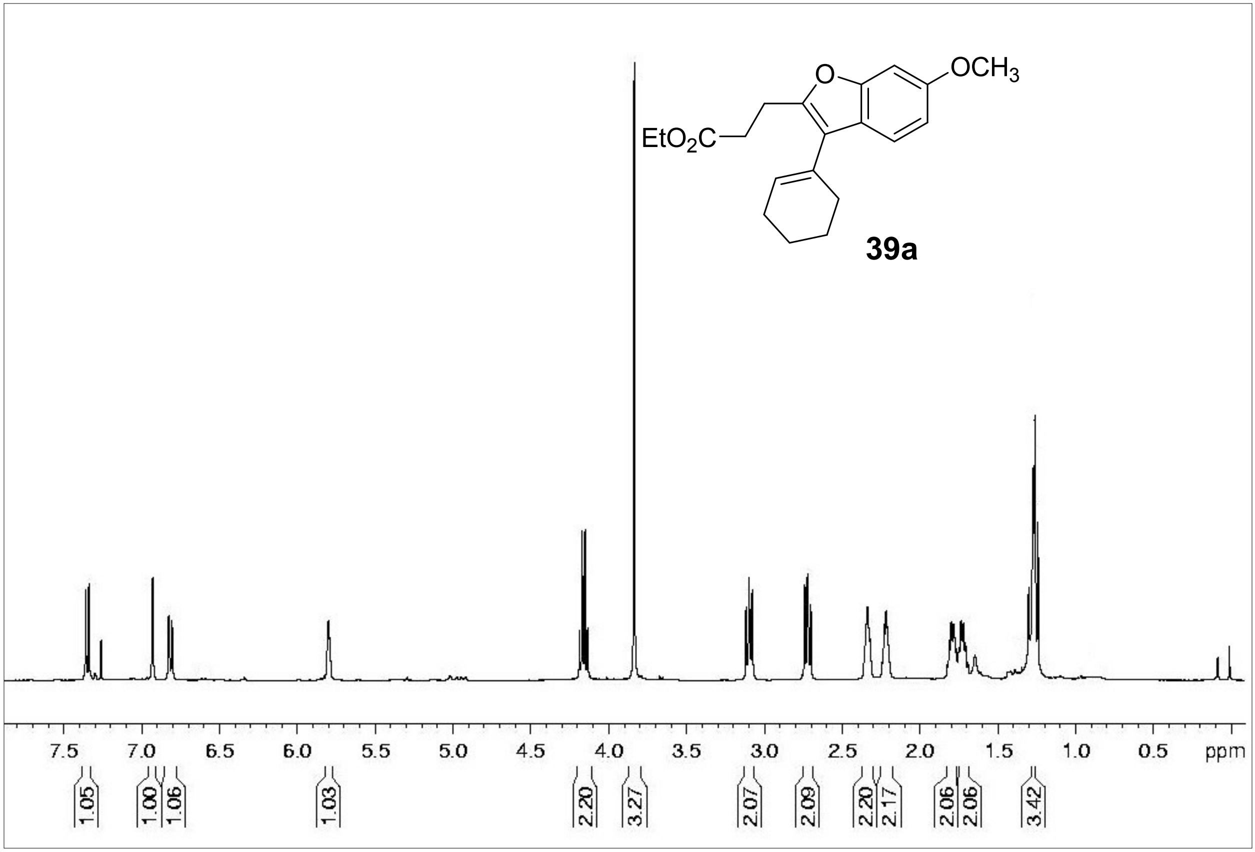

173.16
154.97
153.26
150.30
138.00
131.71
120.80
119.52
117.85
112.92
95.65
77.48
77.16
76.84
60.89
33.35
25.50
22.02
18.40
14.28
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

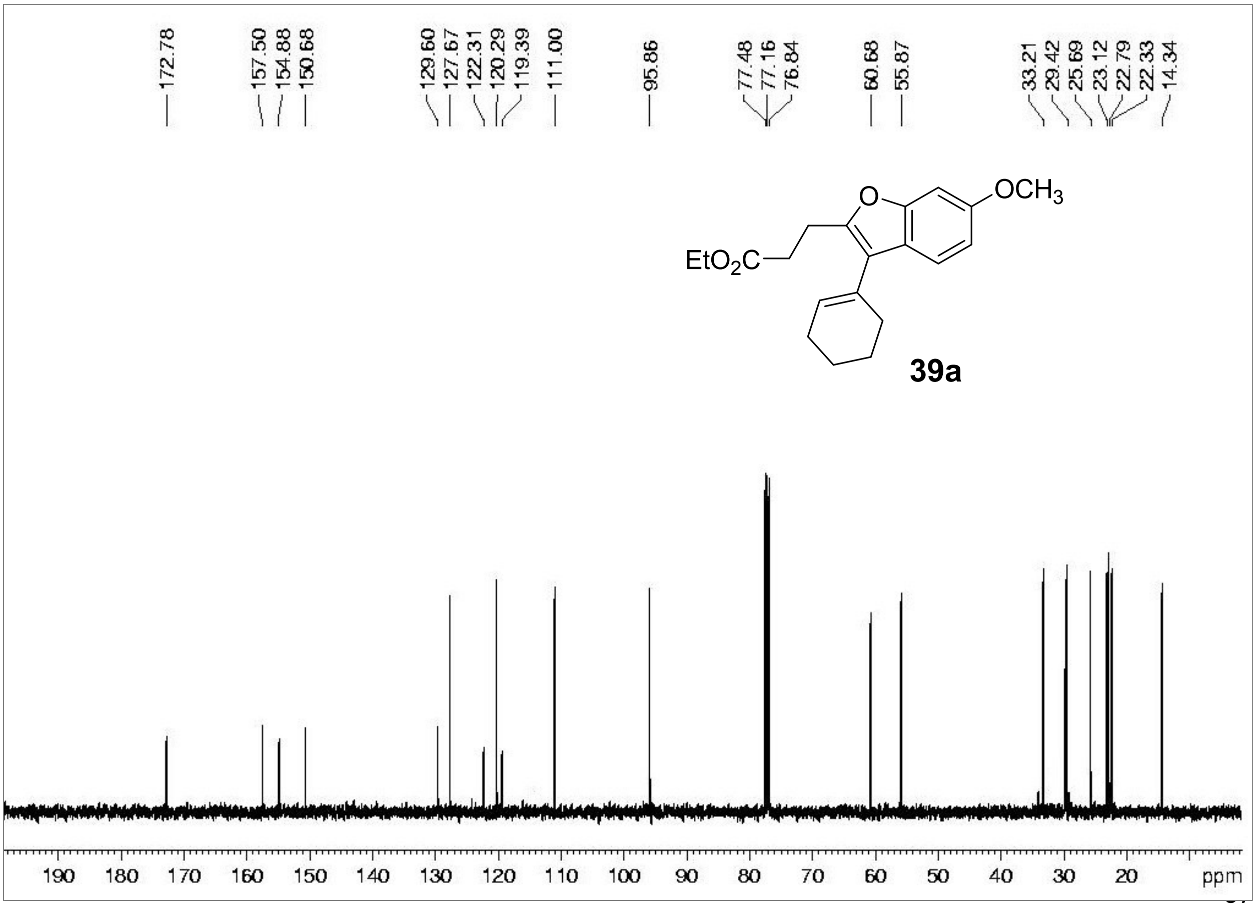

OH
EtO2C
34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.09
1.00
2.37
2.04
2.23
3.20
3.02
3.03
3.68

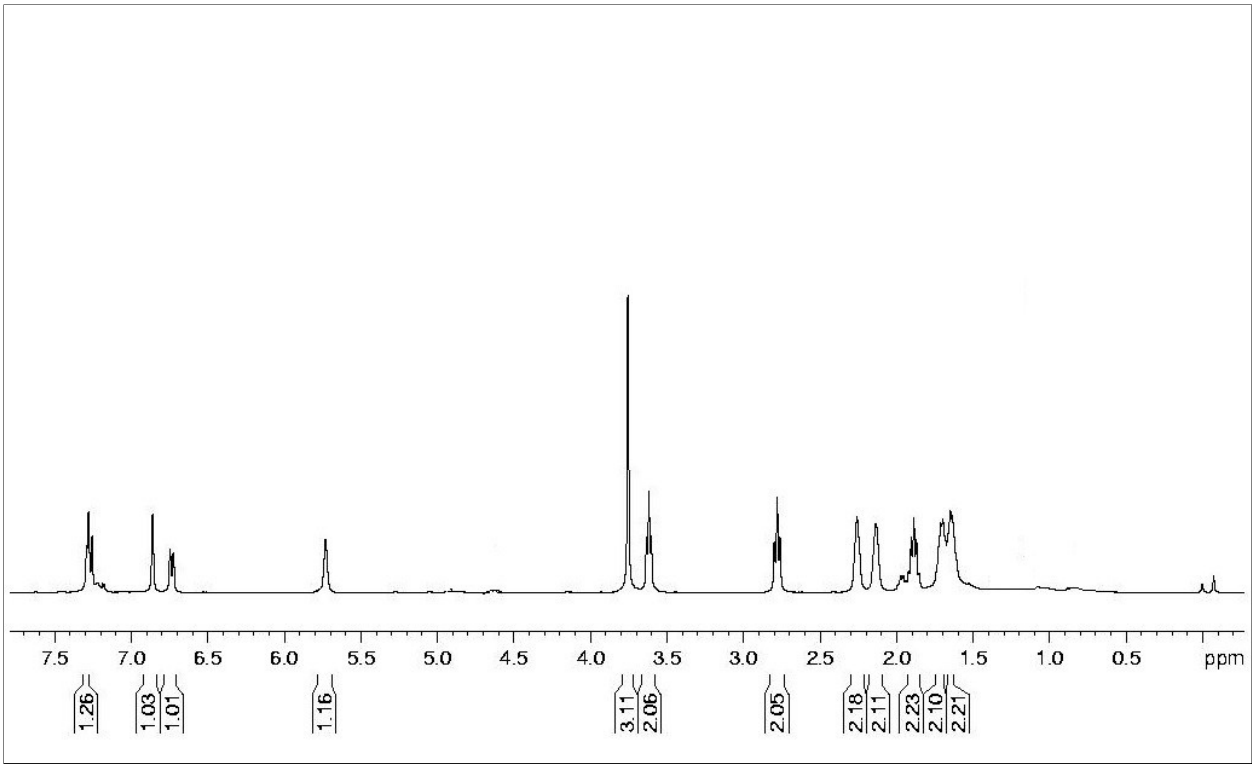

173.15
154.89
153.14
150.48
131.67
128.20
126.42
121.23
121.17
112.74
95.59
77.47
77.16
76.84
60.80
33.37
22.03
18.94
18.38
14.30
14.05
OH
EtO2C
34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


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
2.09
3.01
4.08
1.00
1.00
1.04
1.00
6.04

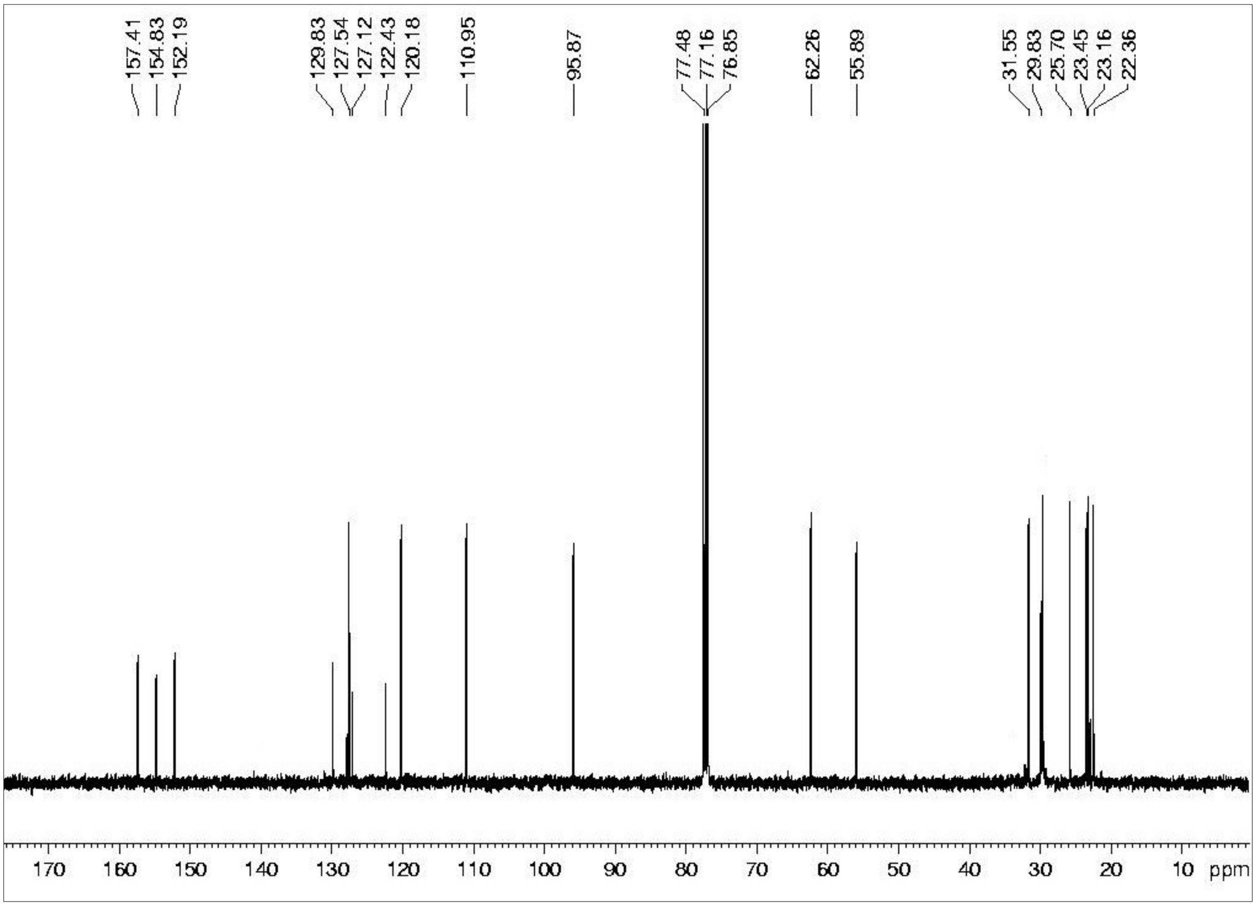

153.18
141.71
135.59
130.62
130.48
130.26
130.01
128.51
127.93
127.40
126.50
125.11
123.06
118.93
116.15
77.48
77.16
76.84
75.44
26.49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OCH3
O
EtO2C
39a
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
1.05
1.00
1.06
1.03
2.20
3.27
2.07
2.09
2.20
2.17
2.06
2.06
3.42

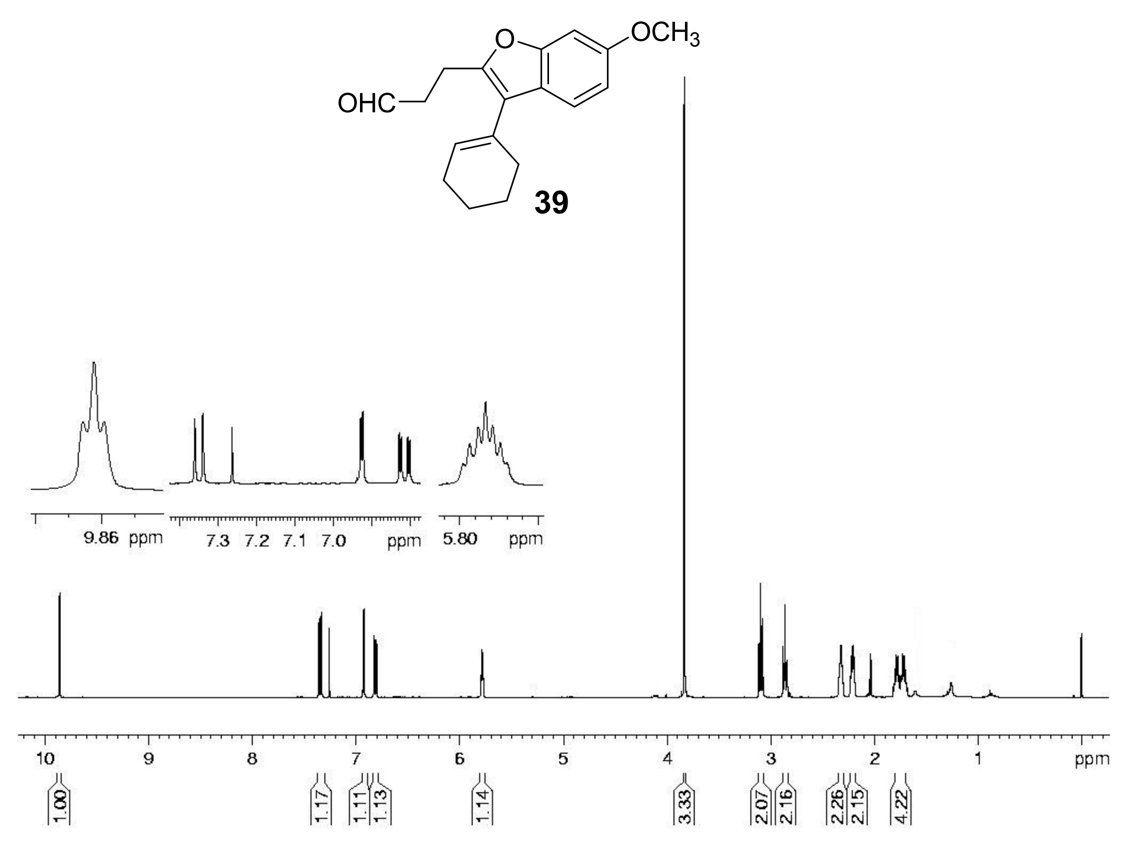

172.78
157.50
154.88
150.68
129.60
127.67
122.31
120.29
119.39
111.00
95.86
77.48
77.16
76.84
60.68
55.87
33.21
29.42
25.69
23.12
22.79
22.33
14.34
OCH3
O
EtO2C
39a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

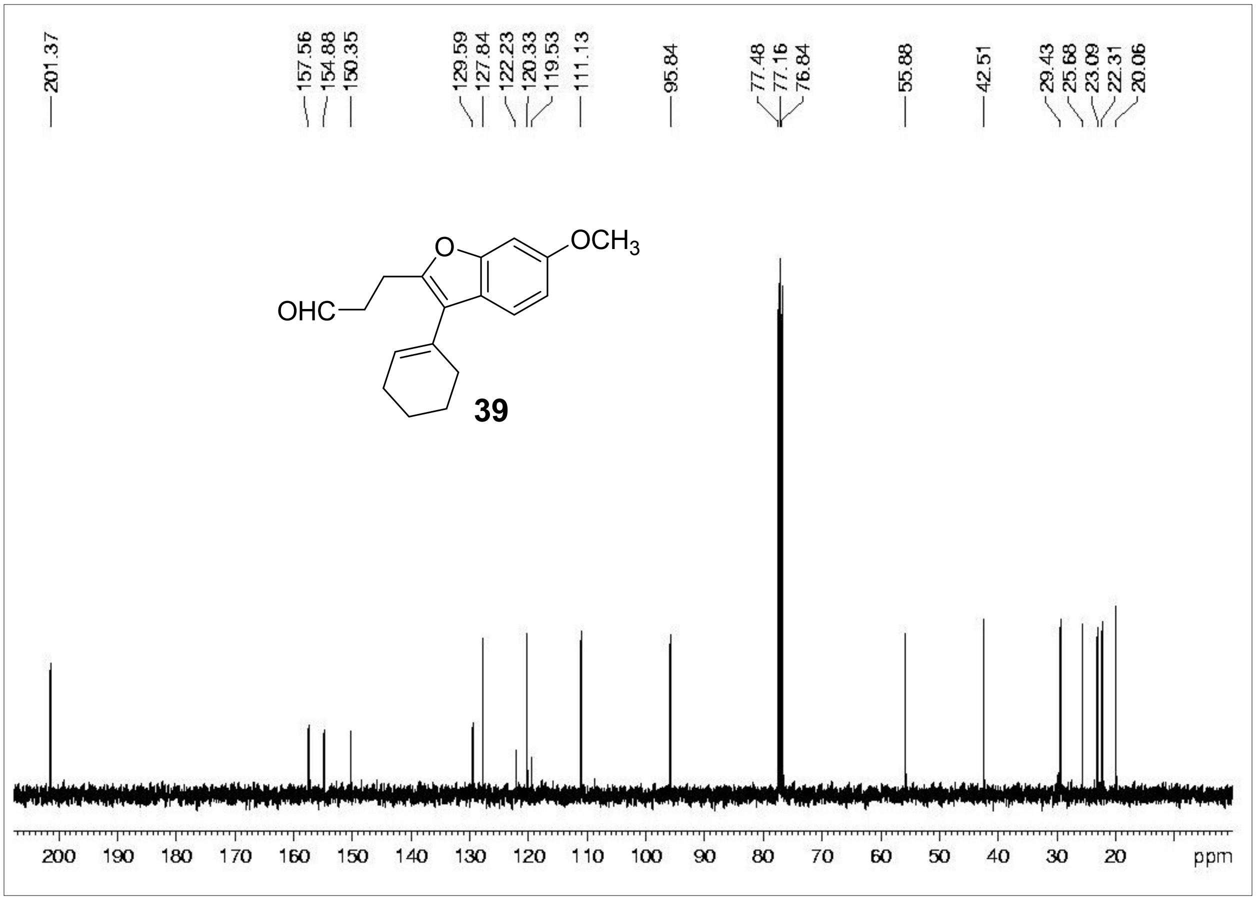


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.26
1.03
1.01
1.16
3.11
2.06
2.05
2.18
2.11
2.23
2.10
2.21



157.41
154.83
152.19
129.83
127.54
127.12
122.43
120.18
110.95
95.87
77.48
77.16
76.85
62.26
55.89
31.55
29.83
25.70
23.45
23.16
22.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OCH3
OHC
39
9.86 ppm
7.3 7.2 7.1 7.0 ppm
5.80 ppm
10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.17
1.11
1.13
1.14
3.33
2.07
2.16
2.26
2.15
4.22


201.37
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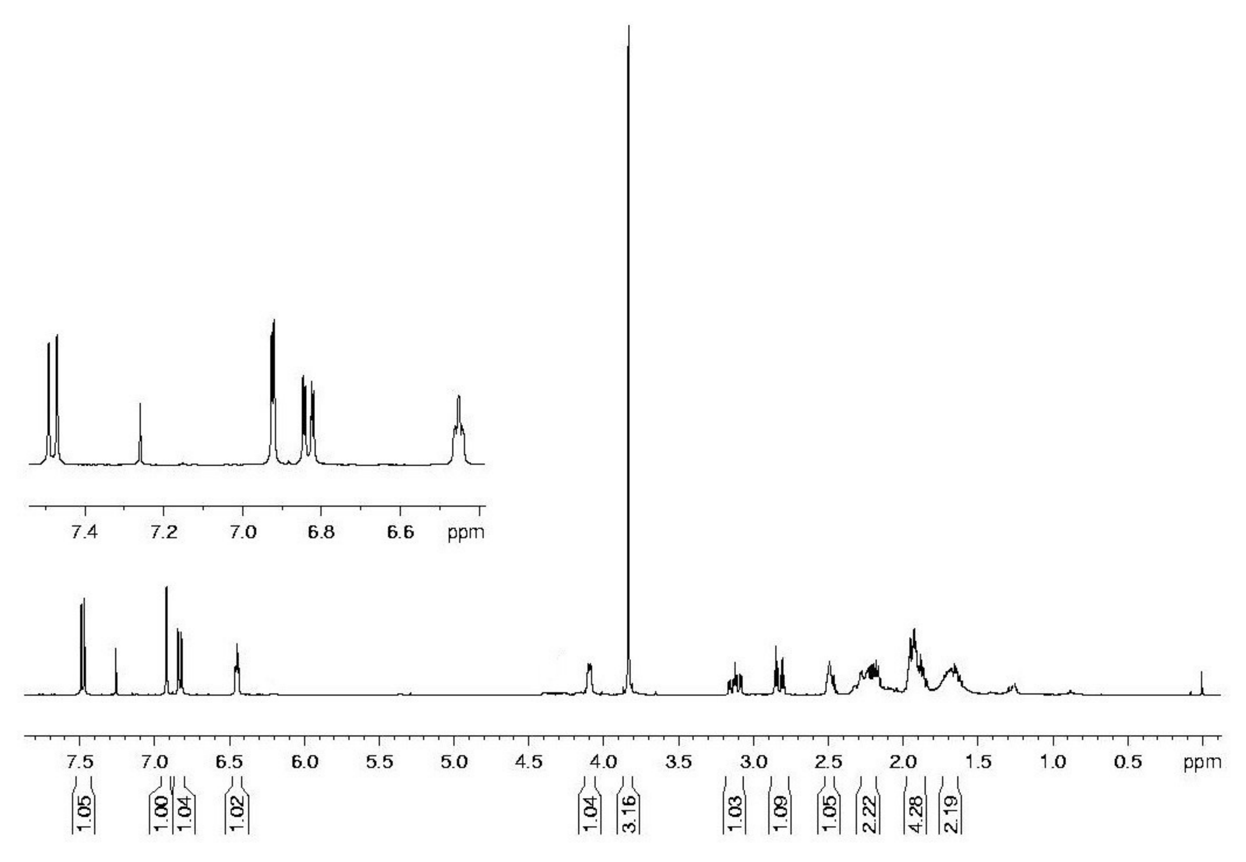
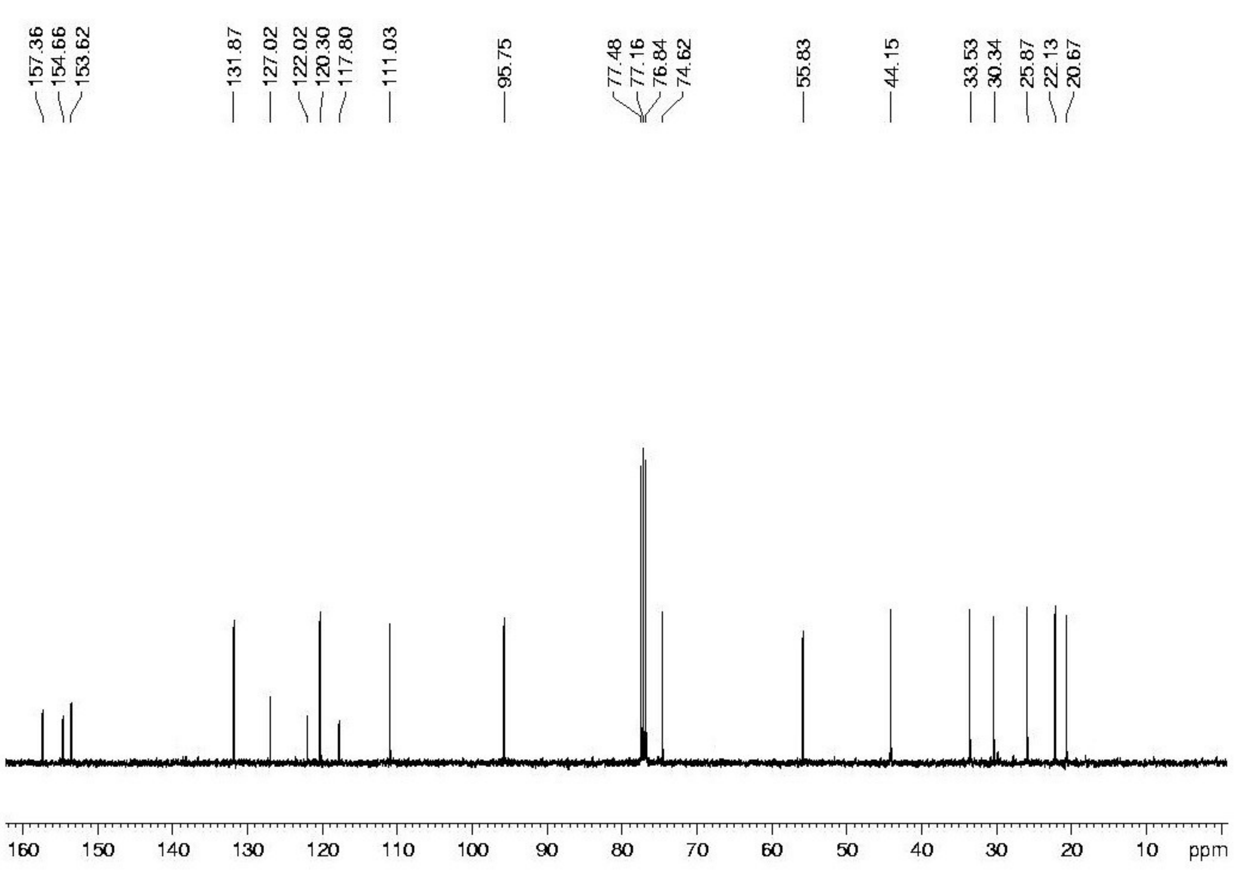
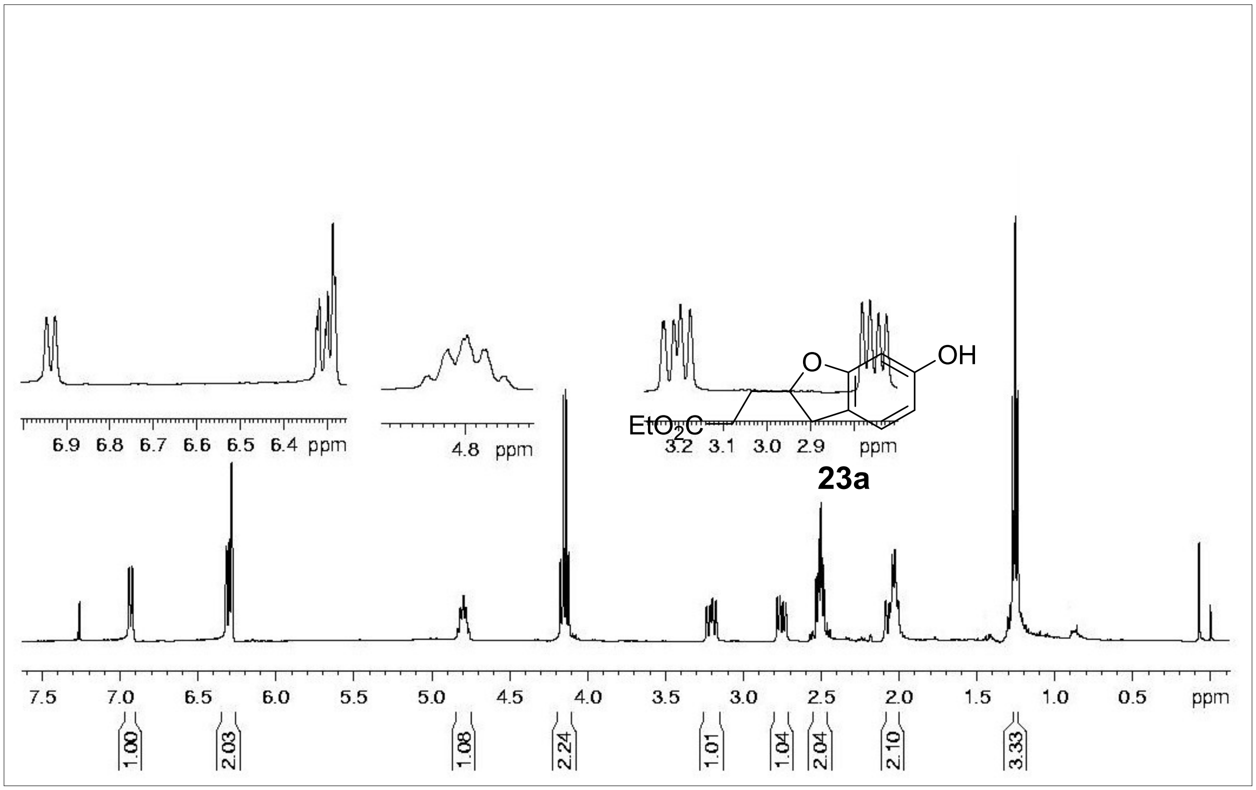
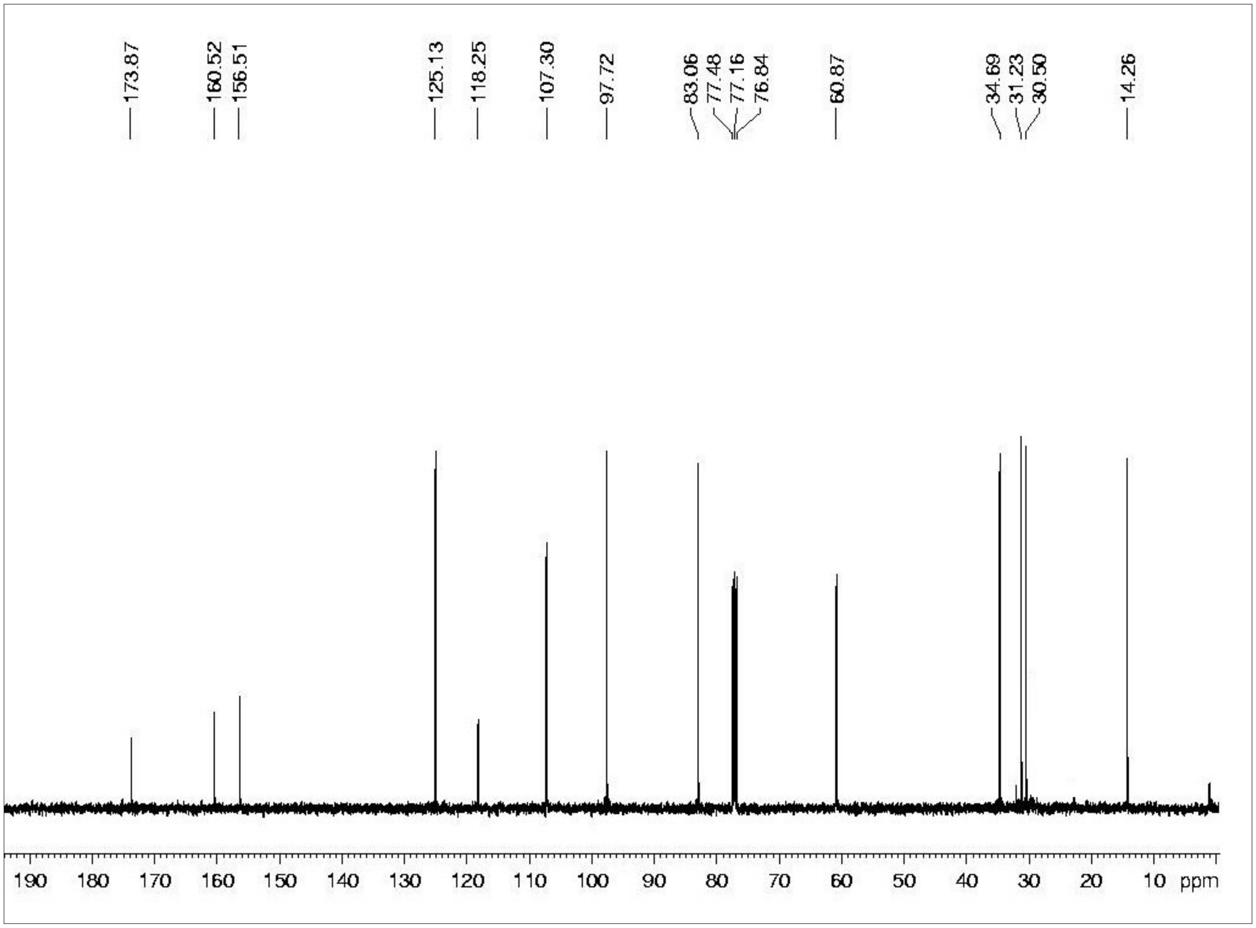
150.35
129.59
127.84
122.23
120.33
119.53
111.13
95.84
77.48
77.16
76.84
55.88
42.51
29.43
25.68
23.09
22.31
20.06
OCH3
OHC
39
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

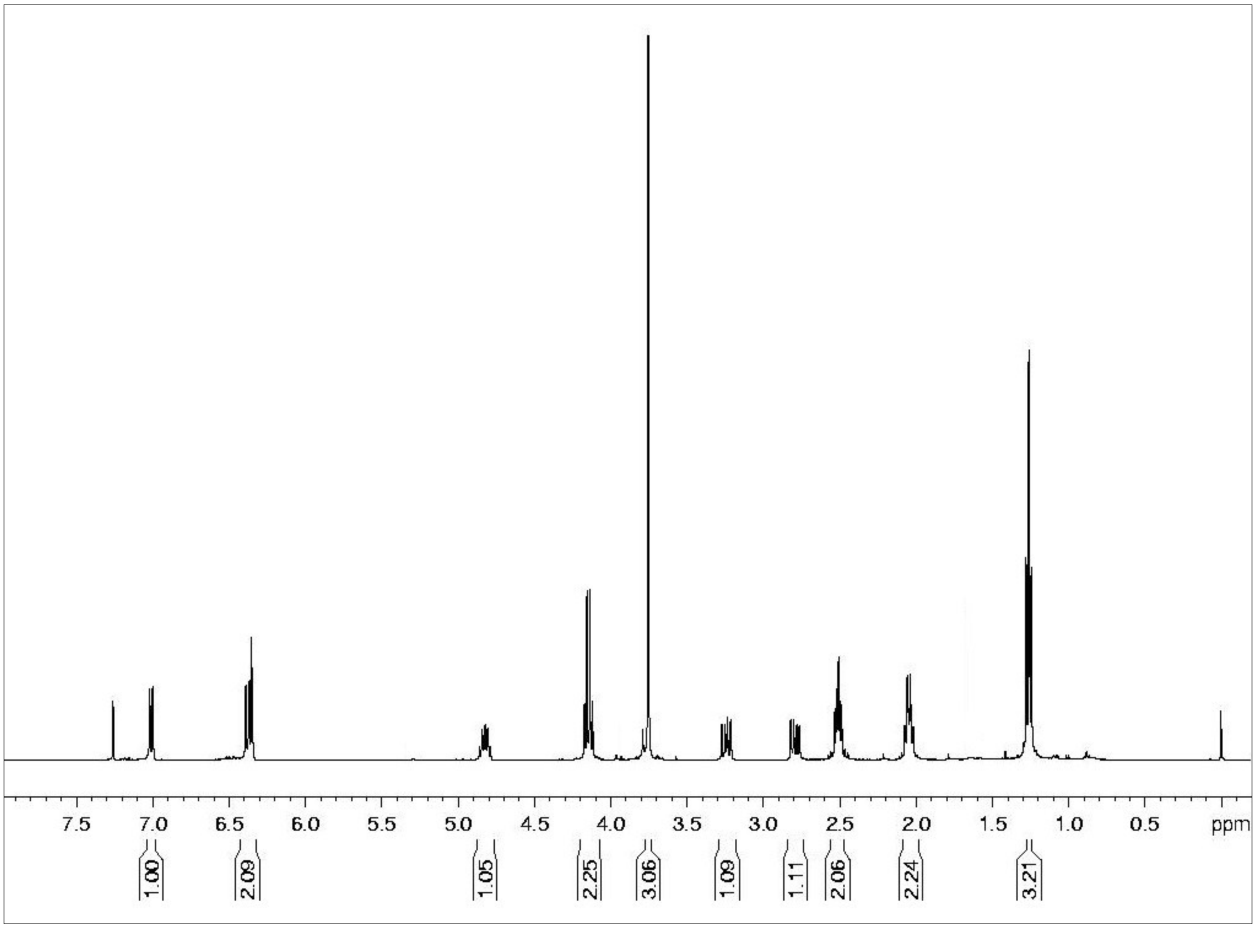

7.4
7.2
7.0
6.8
6.6
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.05
1.00
1.04
1.02
1.04
3.16
1.03
1.09
1.05
2.22
4.28
2.19

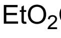

157.36
154.66
153.62
131.87
127.02
122.02
120.30
117.80
111.03
95.75
77.48
77.16
76.84
74.62
55.83
44.15
33.53
30.34
25.87
22.13
20.67
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

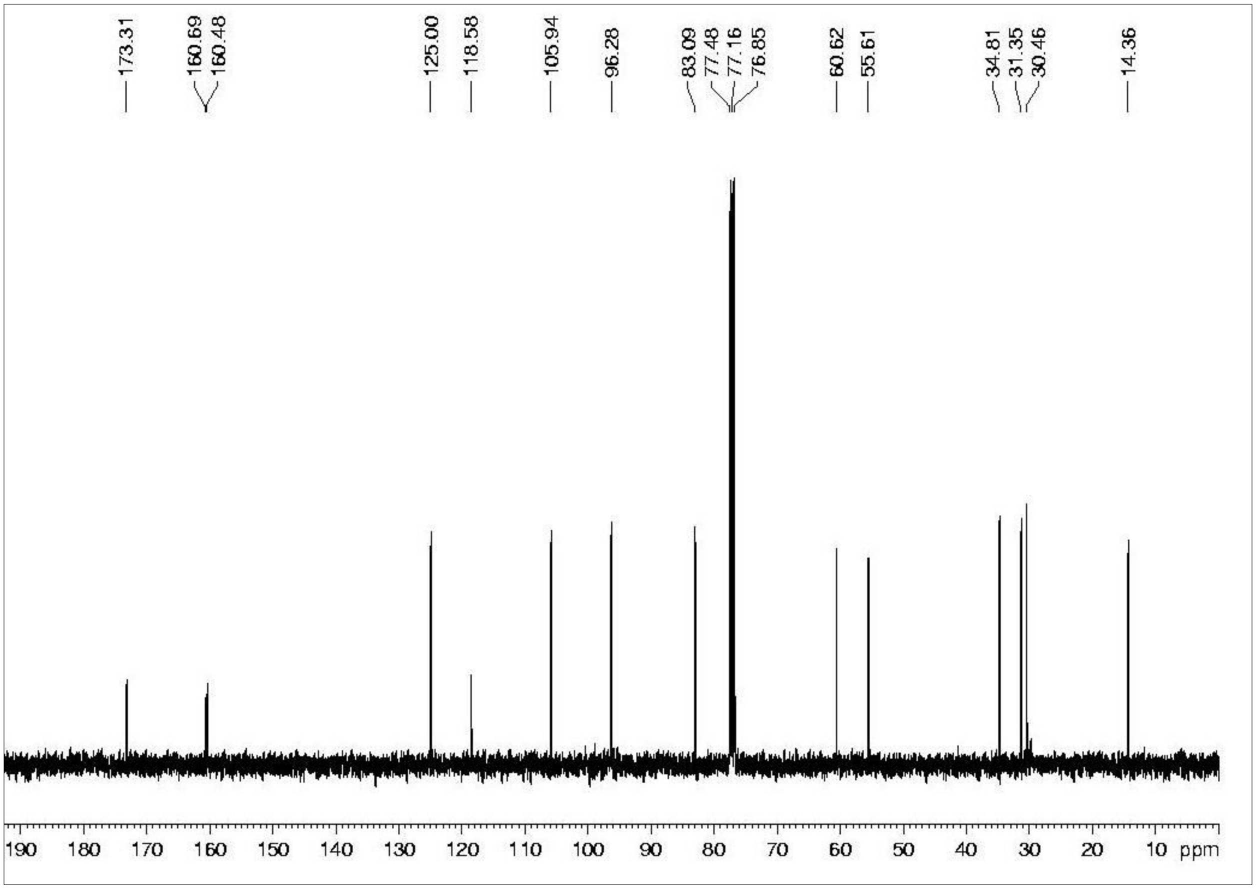

6.9 6.8 6.7 6.6 6.5 6.4 ppm
4.8 ppm
3.2 3.1 3.0 2.9 ppm
OH
O
EtO2C
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.03
1.08
2.24
1.01
1.04
2.04
2.10
3.33

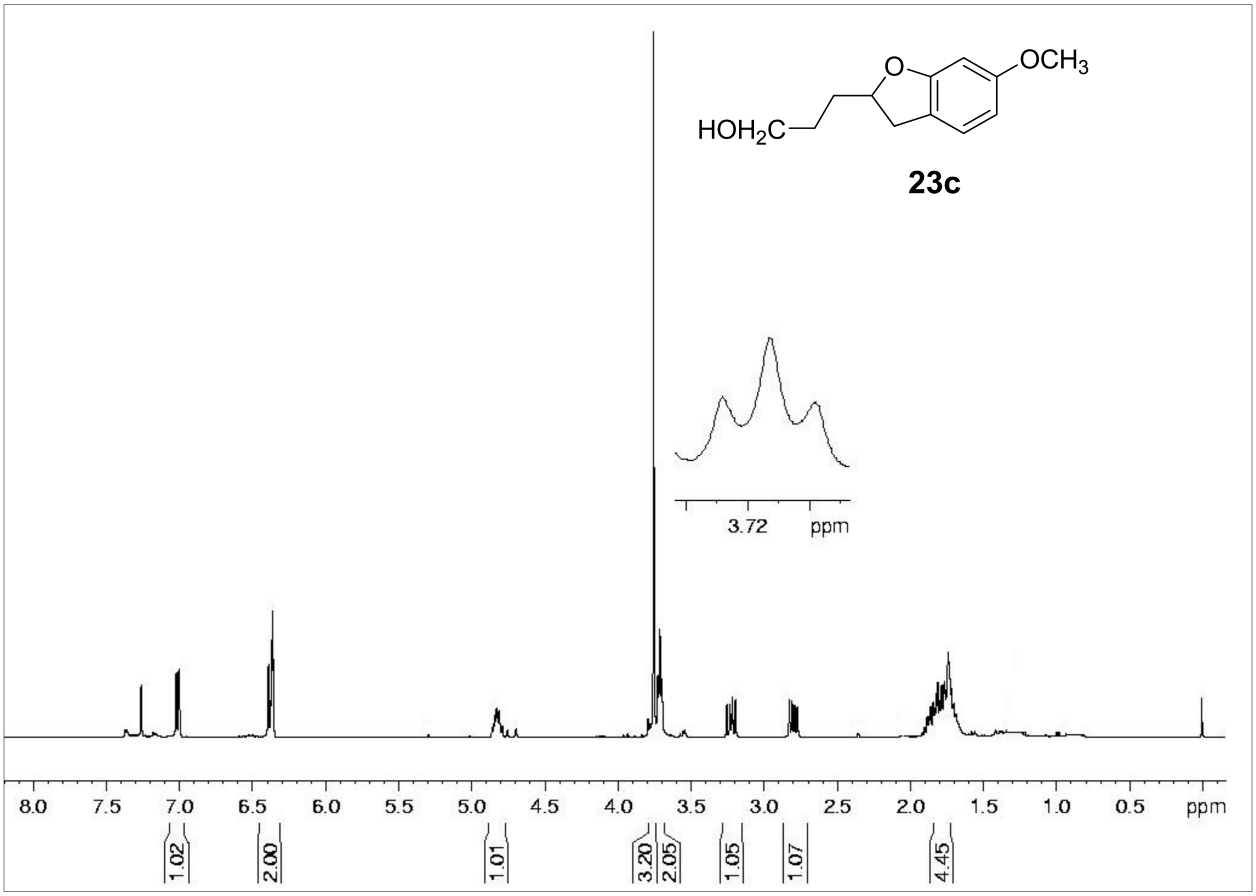
23a

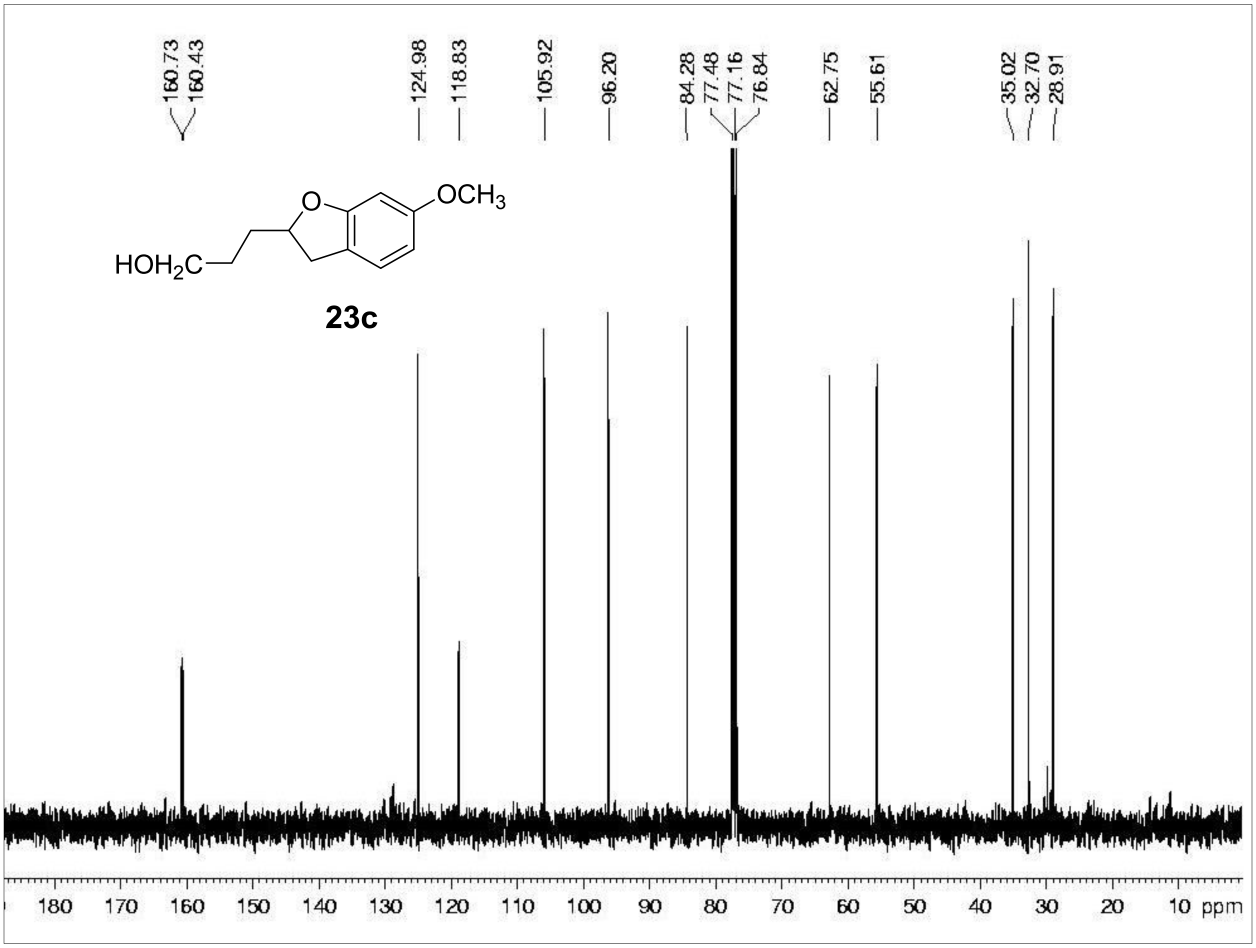

173.87
160.52
156.51
125.13
118.25
107.30
97.72
83.06
77.48
77.16
76.84
60.87
34.69
31.23
30.50
14.26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

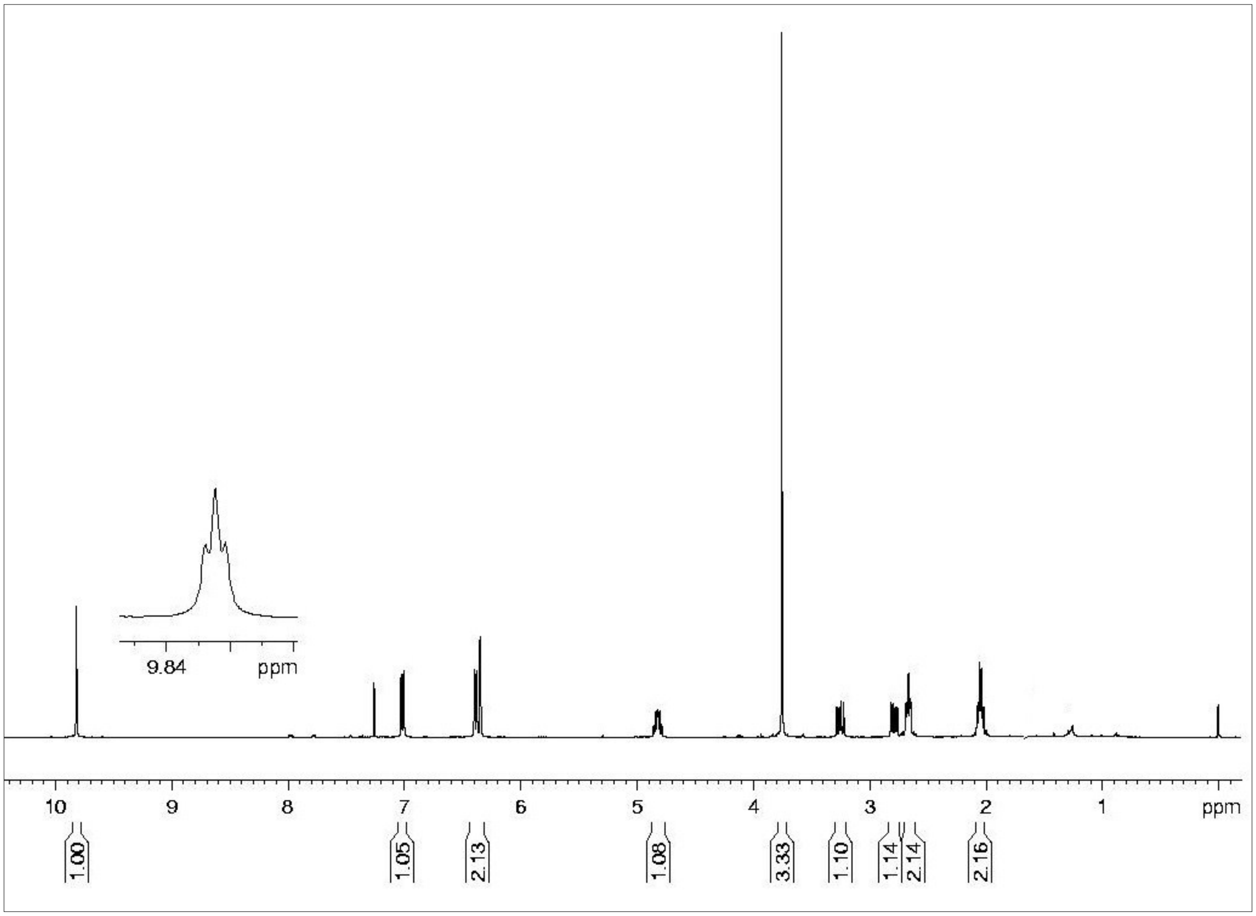

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.09
1.05
2.25
3.06
1.09
1.11
2.06
2.24
3.21

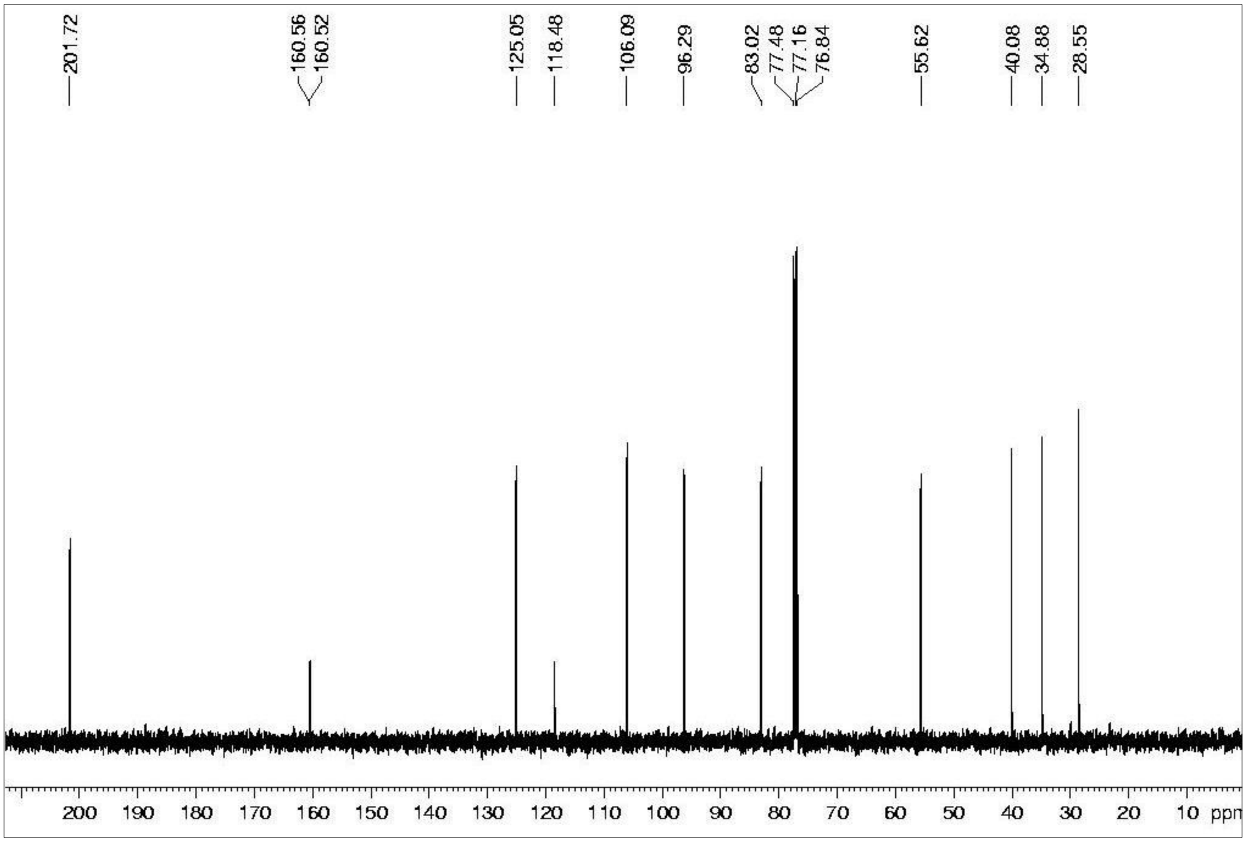

EtO$_2$

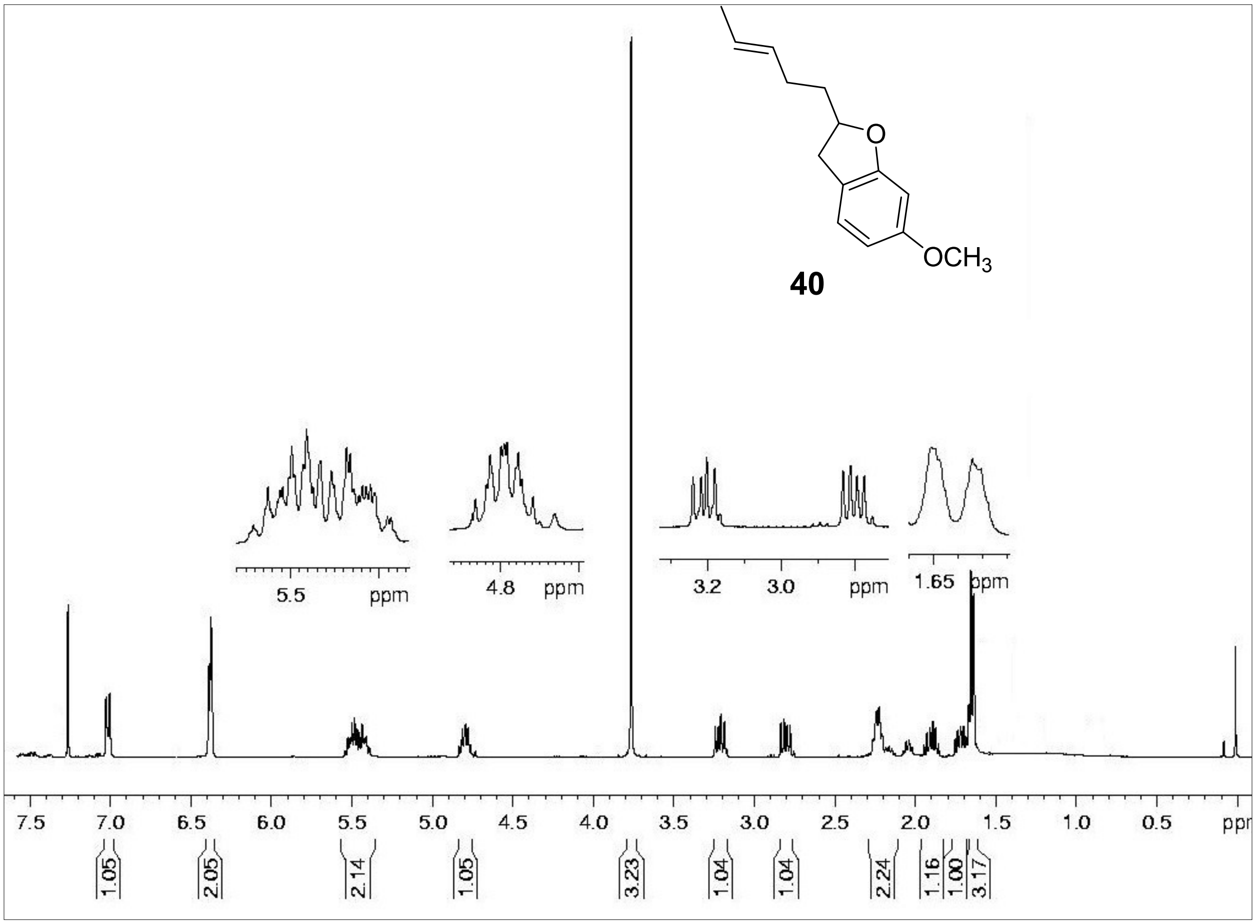

173.31
160.69
160.48
125.00
118.58
105.94
96.28
83.09
77.48
77.16
76.85
60.62
55.61
34.81
31.35
30.46
14.36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OCH3
HOH2C
O
23c
3.72
ppm
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
1.02
2.00
1.01
3.20
2.05
1.05
1.07
4.45

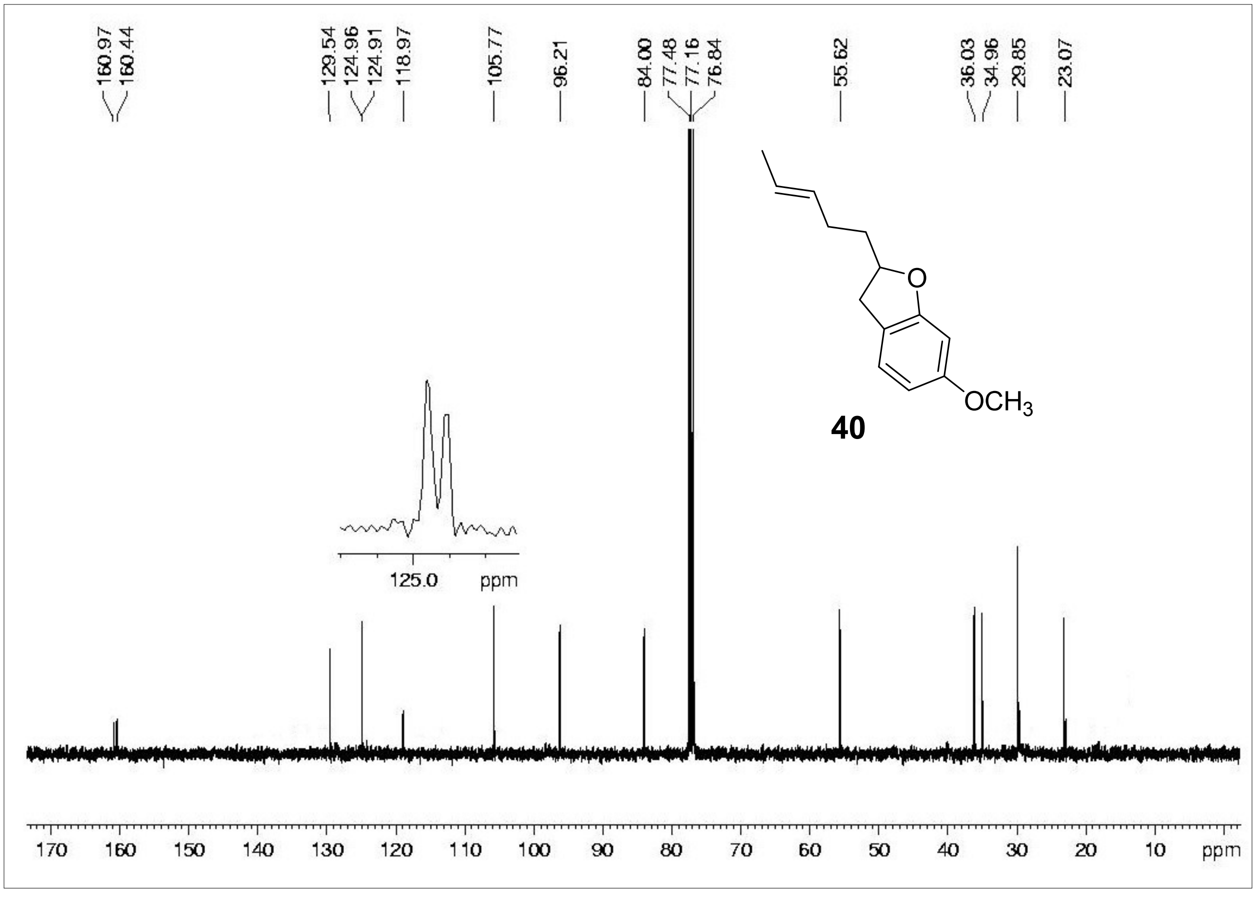

160.73
160.43
124.98
118.83
105.92
96.20
84.28
77.48
77.16
76.84
62.75
55.61
35.02
32.70
28.91
OCH3
HOH2C
O
23c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.84
ppm
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
2.13
1.08
3.33
1.10
1.14
2.14
2.16


201.72
160.56
160.52
125.05
118.48
106.09
96.29
83.02
77.48
77.16
76.84
55.62
40.08
34.88
28.55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



40
OCH3
O
5.5 ppm
4.8 ppm
3.2 3.0 ppm
1.65 ppm
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
1.05
2.05
2.14
1.05
3.23
1.04
1.04
2.24
1.16
1.00
3.17



160.97
160.44
129.54
124.96
124.91
118.97
105.77
96.21
84.00
77.48
77.16
76.84
55.62
36.03
34.96
29.85
23.07
40
OCH3
O
125.0 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm