

Supporting Information

Palladium-catalyzed C(sp³)-C(sp²) coupling: Synthesis of C(3)-arylphthalides

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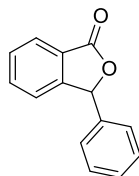
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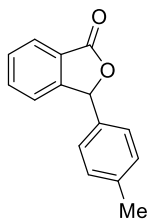
1. Experimental section

General procedure for the synthesis of 3-phenylisobenzofuran-1(3*H*)-one **8a**:



To the reaction tube with 3-bromoisobenzofuran-1(3*H*)-one (200 mg, 0.92 mmol), phenylboronic acid (114 mg, 0.92 mmol), Na₂CO₃ (100 mg, 0.92 mmol), PdCl₂(PPh₃)₂ (6.4 mg, 0.009 mmol) a solution of 20 mL of H₂O and THF (9:1, v/v). The reaction tube was kept stirring at 70 °C for 2 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated under reduced pressure. The residue was passed through a pad of silica gel with the help of EtOAc (50 mL) to give 3-phenylisobenzofuran-1(3*H*)-one **8a** as a white solid (186 mg, 94% yield); mp 113 °C; IR (KBr, cm⁻¹) 3340, 1762, 1603, 1499, 1356, 1282, 1193, 1092, 1008, 913, 749, 696, 638; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8 Hz, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.33 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.27 (dd, *J* = 7.0, 3.0 Hz, 2H), 6.41 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7 (C), 149.7 (C), 136.4 (C), 134.4 (CH), 129.49 (CH), 129.43 (CH), 129.0 (CH), 127.0 (CH), 125.7 (CH), 125.6 (CH), 122.9 (C), 82.8 (CH); HRMS (ESI) calcd for C₁₄H₁₁O₂ (M + H) 211.0759, found 211.0745.

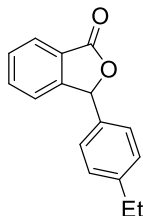
3-(*p*-Tolyl)isobenzofuran-1(3*H*)-one **8b**:



Yellow solid (180 mg, 85% yield); mp 105 °C; IR (KBr, cm⁻¹) 3023, 2916, 2852, 1760, 1493, 1274, 1057, 803, 730; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.64 (td, *J* = 7.5, 1.1 Hz,

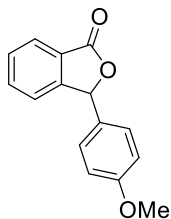
1H), 7.54 (dd, $J = 10.9, 4.1$ Hz, 1H), 7.32 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.19 – 7.13 (m, 4H), 6.38 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7 (C), 149.9 (C), 139.4 (C), 134.4 (CH), 133.4 (C), 129.7 (CH), 129.4 (CH), 127.1 (CH), 125.8 (C), 125.7 (CH), 122.9 (CH), 82.9 (CH), 21.3 (CH_3); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2$ ($\text{M} + \text{H}$) 225.0916, found 225.0908.

3-(4-Ethylphenyl)isobenzofuran-1(3H)-one 8c:



Yellow solid (158 mg, 70% yield); mp 130 °C; IR (KBr, cm^{-1}) 3058, 2971, 2932, 1756, 1606, 1512, 1461, 1288, 1209, 1063, 973, 835, 724; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.6$ Hz, 1H), 7.64 (td, $J = 7.5, 1.1$ Hz, 1H), 7.58 – 7.51 (m, 1H), 7.35 – 7.31 (m, 1H), 7.22 – 7.16 (m, 4H), 6.38 (s, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6 (C), 149.8 (C), 145.6 (C), 134.2 (CH), 133.6 (C), 129.2 (CH), 128.4 (CH), 127.1 (CH), 125.7 (C), 125.5 (CH), 122.9 (CH), 82.8 (CH), 28.6 (CH_2), 15.4 (CH_3); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2$ ($\text{M} + \text{H}$) 239.1072, found 239.1045.

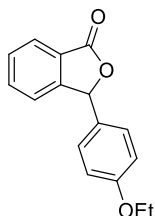
3-(4-Methoxyphenyl)isobenzofuran-1(3H)-one 8d:



White solid (188 mg, 83% yield); mp 107 °C; IR (KBr, cm^{-1}) 3062, 3007, 2953, 2838, 1761, 1611, 1512, 1458, 1346, 1292, 1247, 1173, 1067, 1026, 971, 823, 734; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.6$ Hz, 1H), 7.65 (td, $J = 7.5, 1.1$ Hz, 1H), 7.58 – 7.51 (m, 1H), 7.32 (d, $J = 0.8$ Hz,

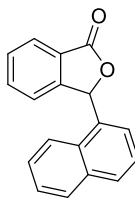
1H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.91 – 6.85 (m, 2H), 6.37 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5 (C), 160.4 (C), 149.7 (C), 134.2 (CH), 129.3 (CH), 128.8 (CH), 128.2 (C), 125.9 (C), 125.5 (CH), 122.9 (CH), 114.3 (CH), 82.7 (CH), 55.3 (CH_3); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3$ ($\text{M} + \text{H}$) 241.0865, found 241.0836.

3-(4-Ethoxyphenyl)isobenzofuran-1(3H)-one 8e:



White solid (178 mg, 75% yield); mp 78°C ; IR (KBr, cm^{-1}) 3043, 2967, 2925, 2881, 1751, 1610, 1513, 1466, 1293, 1214, 1167, 1106, 1069, 953, 836, 738; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.6$ Hz, 1H), 7.69 – 7.60 (m, 1H), 7.55 (dd, $J = 11.0, 3.9$ Hz, 1H), 7.35 – 7.27 (m, 1H), 7.19 – 7.11 (m, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 6.36 (s, 1H), 4.02 (q, $J = 7.0$ Hz, 2H), 1.40 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6 (C), 159.8 (C), 149.7 (C), 134.2 (CH), 129.3 (CH), 128.8 (CH), 128.0 (C), 125.9 (C), 125.5 (CH), 122.9 (CH), 114.8 (CH), 82.8 (CH), 63.5 (CH_2), 14.7 (CH_3); HRMS (ESI) calcd for: $\text{C}_{16}\text{H}_{15}\text{O}_3$ ($\text{M} + \text{H}$) 255.1021, found 255.1010.

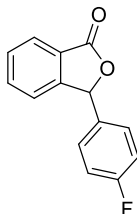
3-(Naphthalen-1-yl)isobenzofuran-1(3H)-one 8f:



White solid (216 mg, 88% yield); mp 123°C ; IR (KBr, cm^{-1}) 3056, 2928, 1754, 1603, 1516, 1467, 1290, 1065, 953, 731; ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.4$ Hz, 1H), 8.02 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.96 – 7.92 (m, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.67 – 7.62 (m, 2H), 7.60 (ddd, $J = 5.6, 2.7, 0.8$ Hz, 1H), 7.57 (ddd, $J = 3.4, 2.7, 1.5$ Hz, 1H), 7.45 – 7.42 (m, 1H), 7.42 – 7.37 (m,

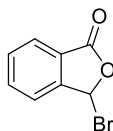
1H), 7.26 (t, $J = 5.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5 (C), 149.3 (C), 134.1 (CH), 134.0 (C), 131.9 (C), 131.3 (C), 129.9 (CH), 129.5 (CH), 129.1 (CH), 127.0 (CH), 126.2 (CH), 126.1 (C), 126.0 (CH), 125.3 (CH), 124.5 (CH), 123.2 (CH), 122.9 (CH), 79.6 (CH); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{13}\text{O}_2$ ($\text{M} + \text{H}$) 261.0916, found 261.0888.

3-(4-Fluorophenyl)isobenzofuran-1(3H)-one 8g:



White solid (176 mg, 82% yield); mp 110°C ; IR (KBr, cm^{-1}) 3065, 2935, 1758, 1604, 1510, 1464, 1288, 1222, 1155, 1059, 978, 829, 734, 581, 539; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.6$ Hz, 1H), 7.67 (dd, $J = 10.8, 4.2$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.26 – 7.23 (m, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.39 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3 (C), 149.4 (C), 134.4 (CH), 132.28 (C), 132.25 (C), 129.5 (CH), 129.1 (CH), 129.0 (CH), 125.7 (CH), 125.6 (C), 122.8 (CH), 116.1 (CH), 115.9 (CH), 82.0 (CH); HRMS (ESI) calcd for: $\text{C}_{14}\text{H}_{10}\text{FO}_2$ ($\text{M} + \text{H}$) 229.0665, found 229.0655.

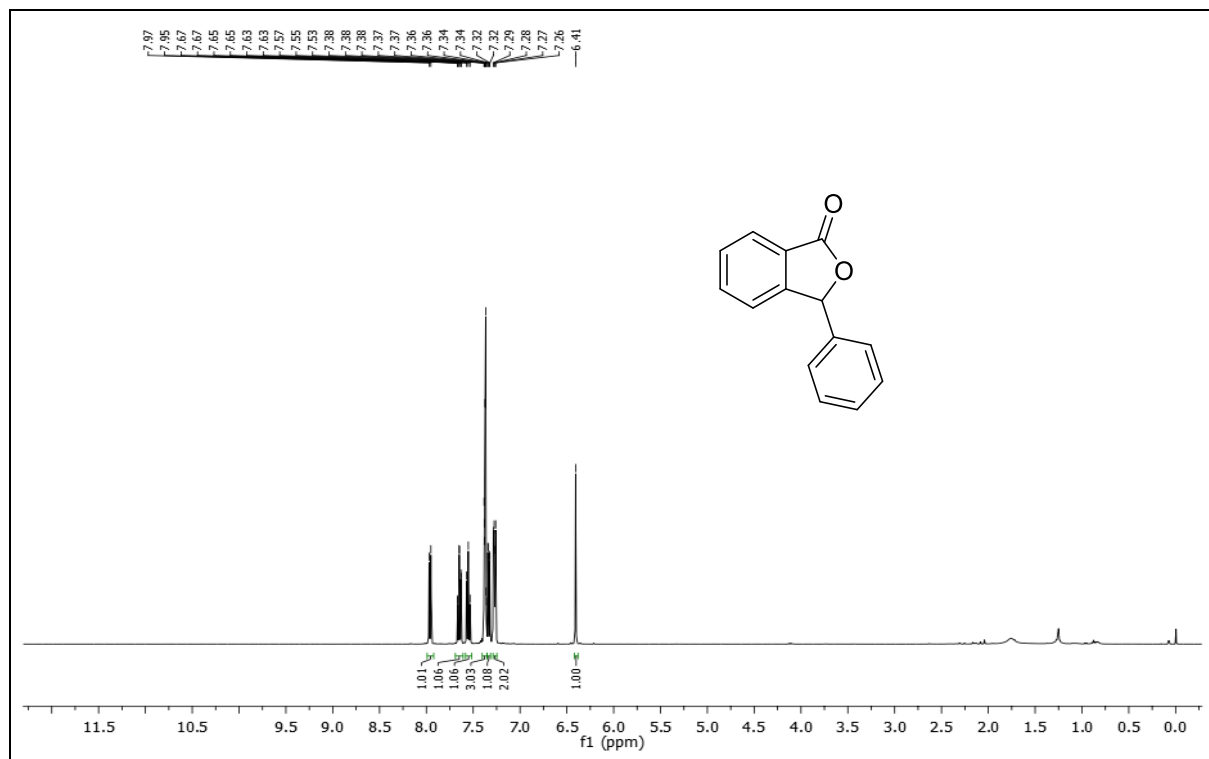
3-Bromoisobenzofuran-1(3H)-one 6:



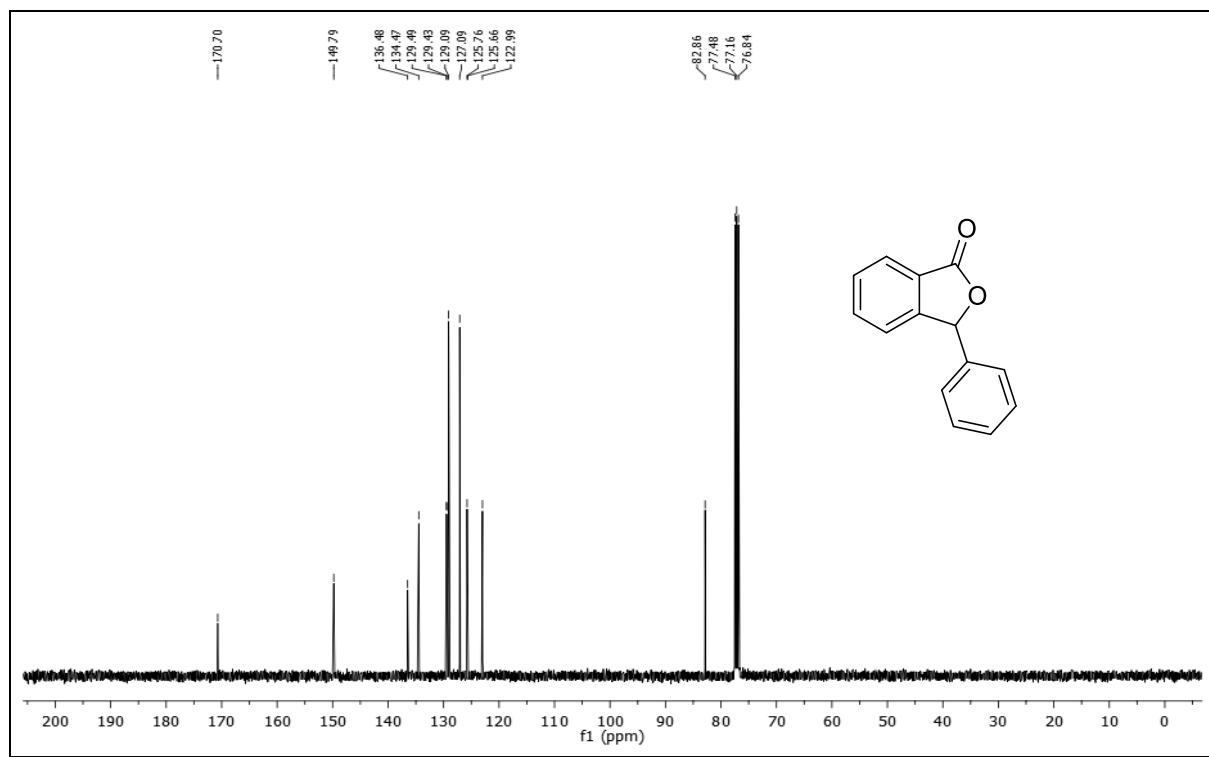
Isobenzofuran-1(3H)-one (500 mg, 3.73 mmol), NBS (611 mg, 3.72 mmol) and AIBN (41 mg, 0.23 mmol) were diluted in dry benzene and heated to 75°C for 3 h. The mixture was cooled to room temperature for overnight, filtered, and the residue was washed with benzene. The filtrate was concentrated and purified by column chromatography (hexane:ethyl acetate 9:1) as eluent to give 3-bromoisobenzofuran-1(3H)-one **6** as a white solid (786 mg, 97% yield); mp 80°C ; IR (KBr,

cm⁻¹) 3005, 2958, 1800, 1601, 1465, 1350, 1283, 1209, 1095, 1044, 982, 938, 757; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4 (C), 148.9 (C), 135.3 (CH), 131.0 (CH), 126.0 (CH), 124.1 (CH), 123.6 (C), 74.7 (CH); HRMS (ESI) calcd for: C₈H₆BrO₂ (M + H) 212.9551, found 212.9550.

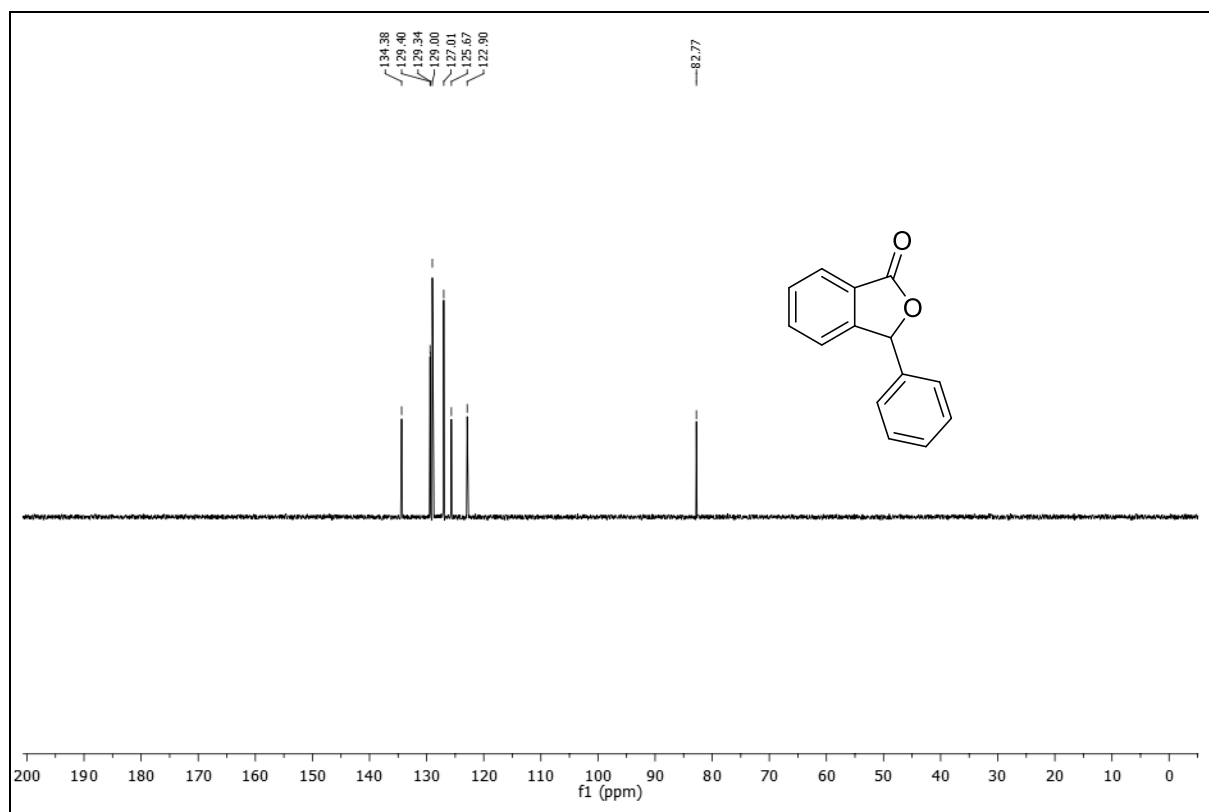
Spectral data



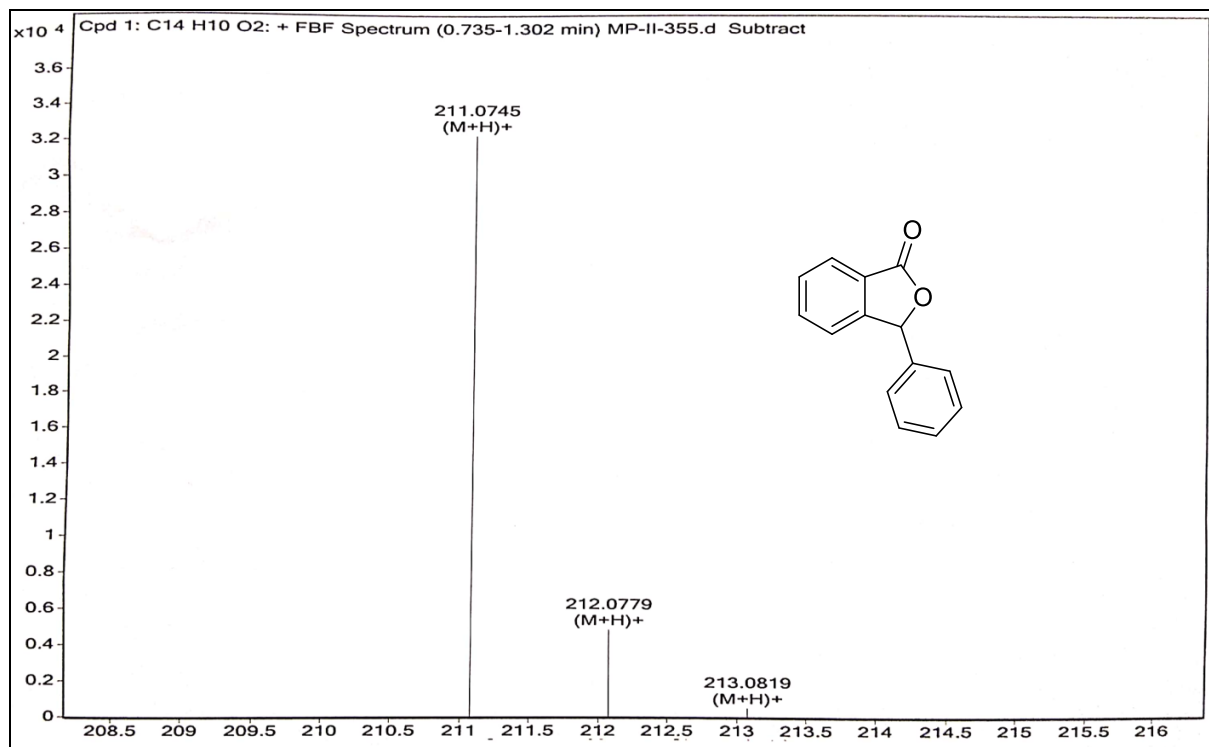
¹H NMR (400 MHz, CDCl₃) spectrum of 3-phenylisobenzofuran-1(3*H*)-one **8a**.



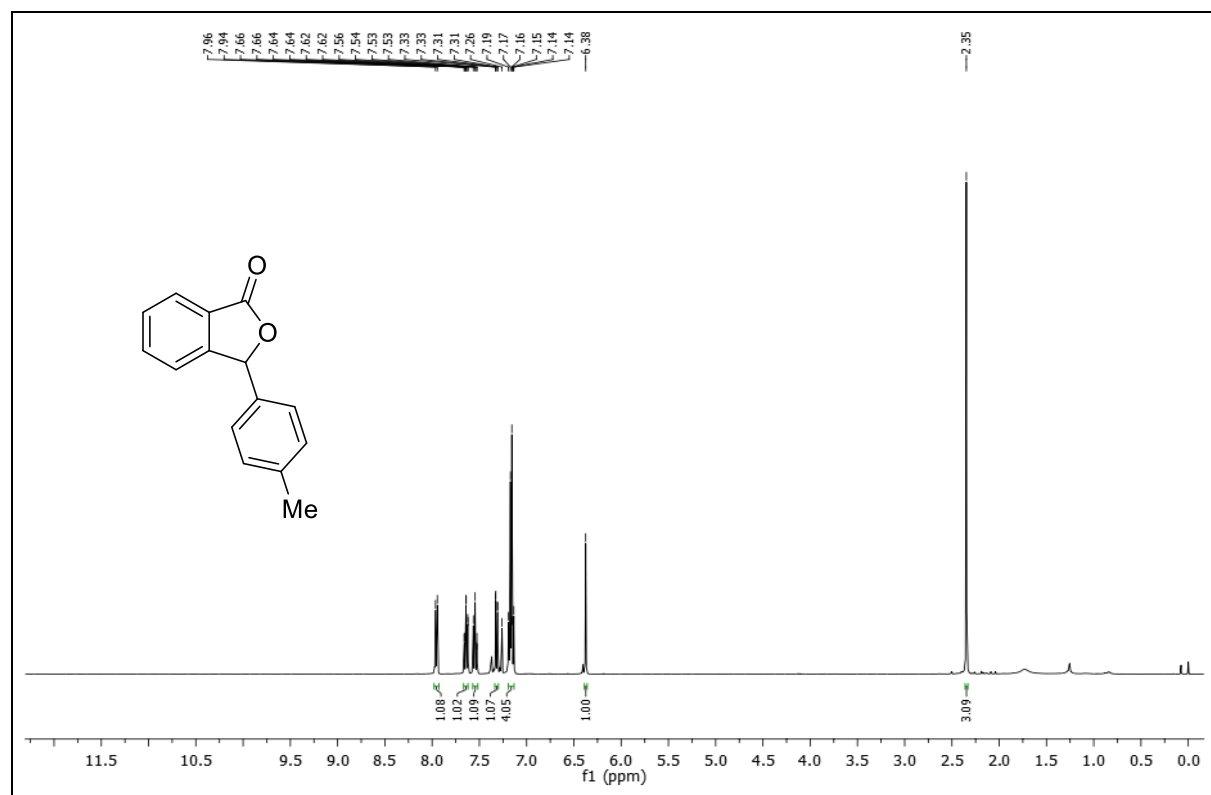
¹³C NMR (100 MHz, CDCl₃) spectrum of 3-phenylisobenzofuran-1(3*H*)-one **8a**.



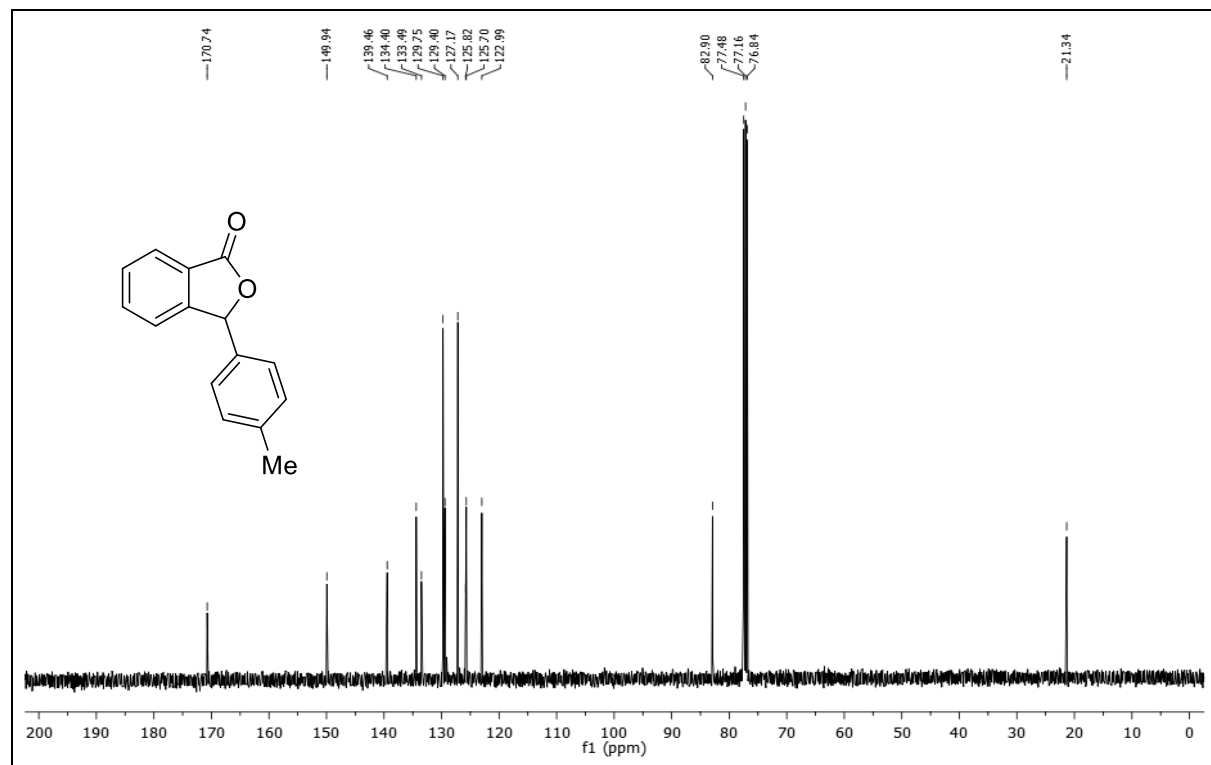
DEPT-135 spectrum of 3-phenylisobenzofuran-1(3H)-one **8a**.



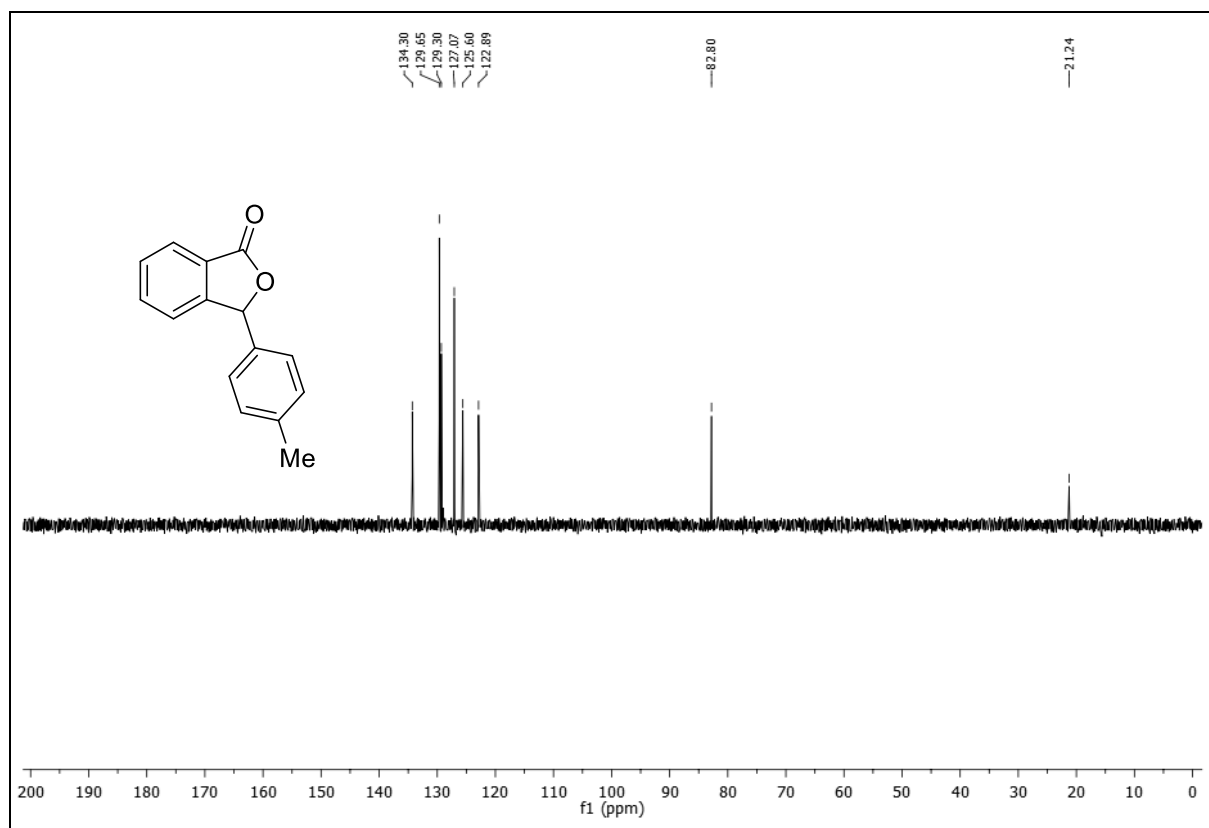
HRMS spectrum of 3-phenylisobenzofuran-1(3H)-one **8a**.



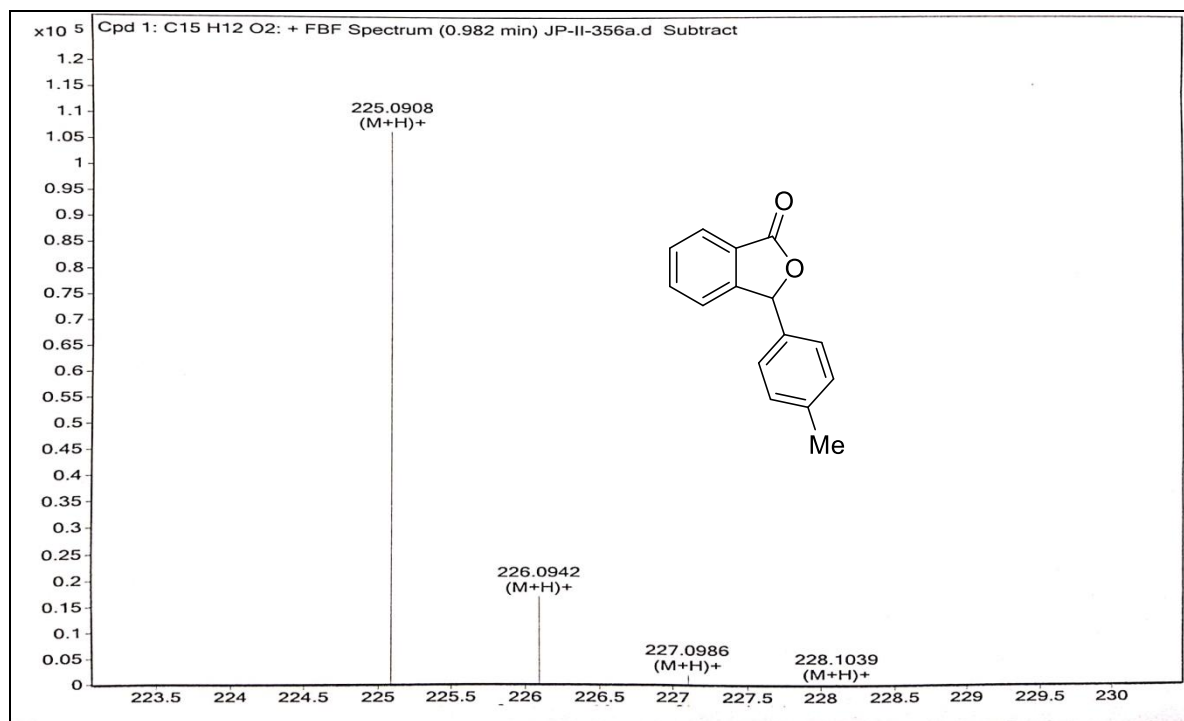
¹H NMR (400 MHz, CDCl₃) spectrum of 3-(*p*-tolyl)isobenzofuran-1(3*H*)-one **8b**.



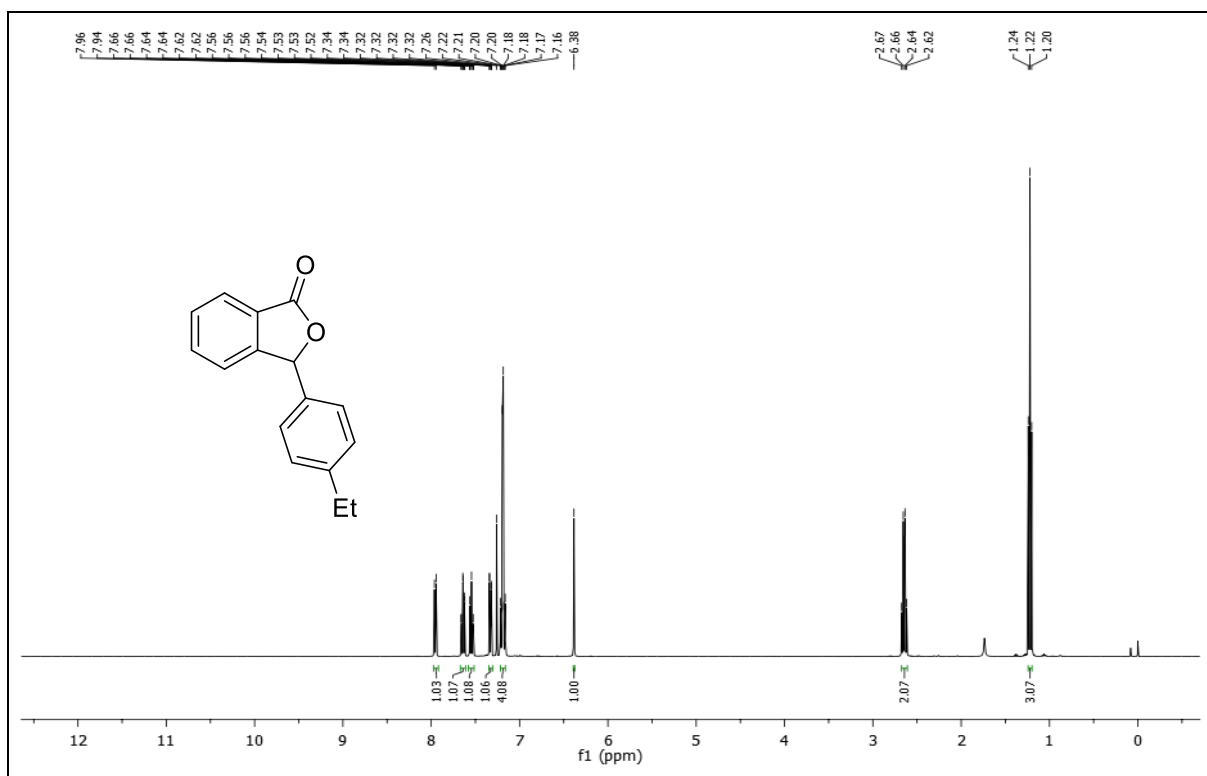
¹³C NMR (100 MHz, CDCl₃) spectrum of 3-(*p*-tolyl)isobenzofuran-1(3*H*)-one **8b**.



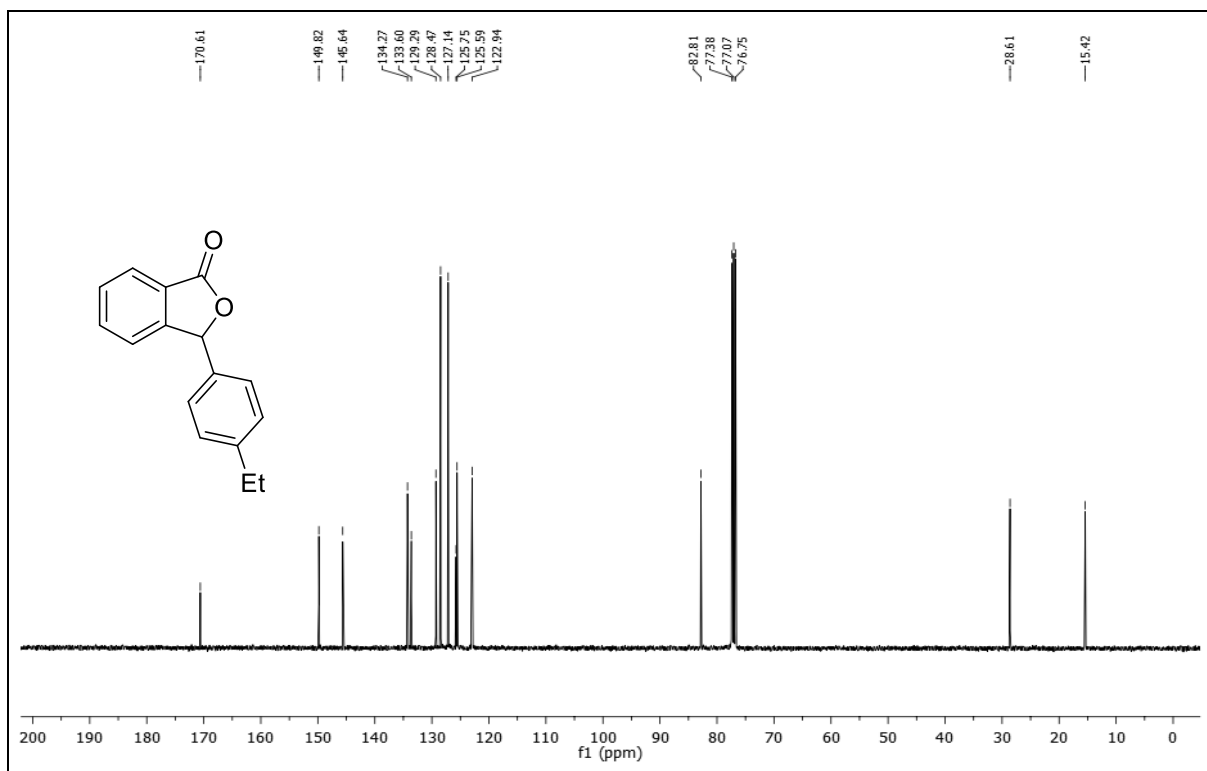
DEPT-135 spectrum of 3-(*p*-tolyl)isobenzofuran-1(3*H*)-one **8b**.



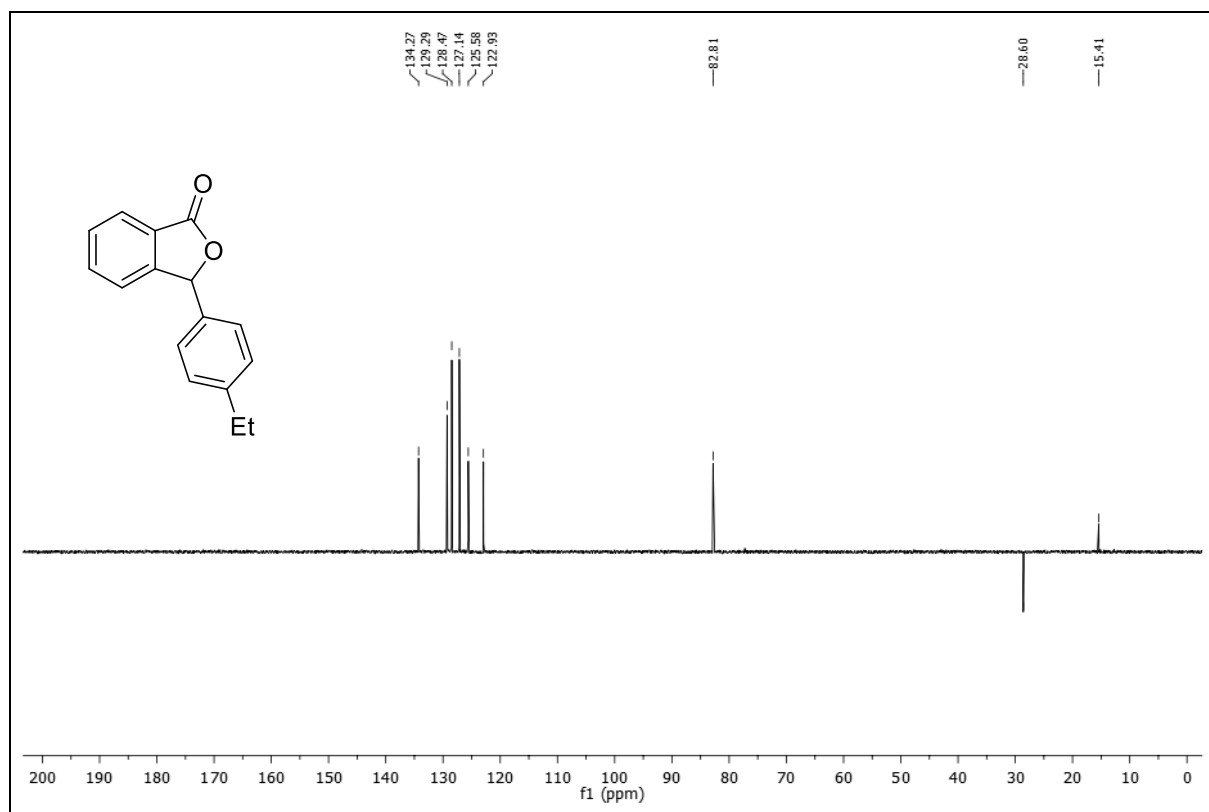
HRMS spectrum of 3-(*p*-tolyl)isobenzofuran-1(3*H*)-one **8b**.



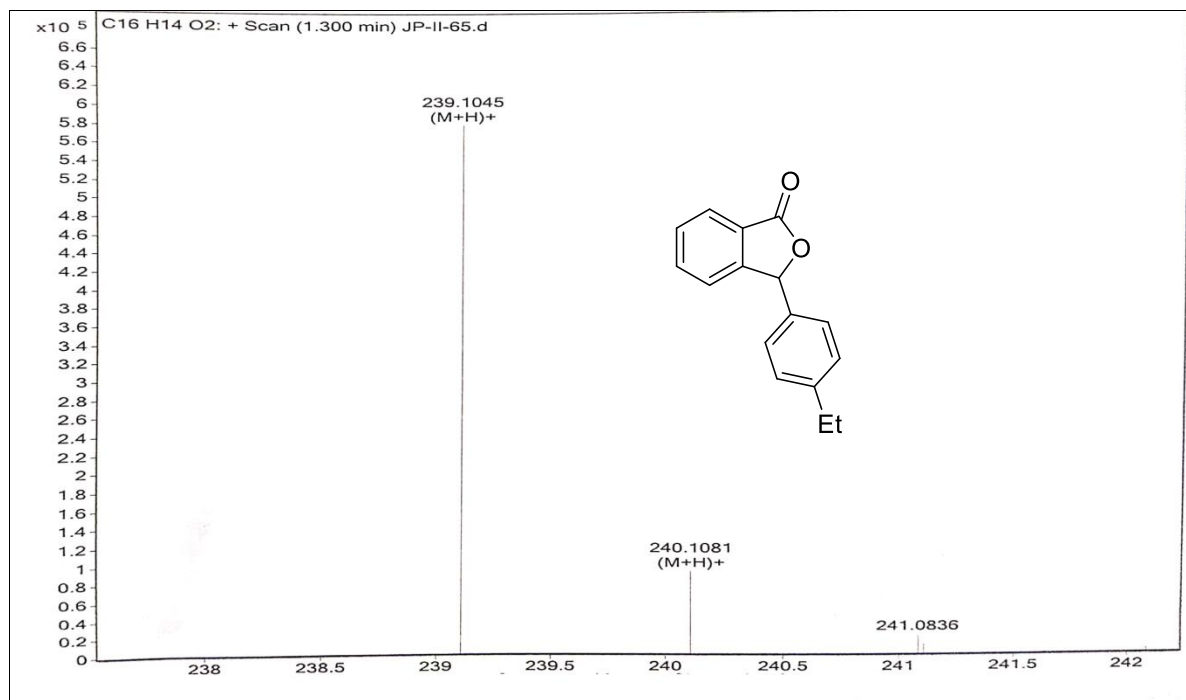
¹H NMR (400 MHz, CDCl₃) spectrum of 3-(4-ethylphenyl)isobenzofuran-1(3H)-one **8c**.



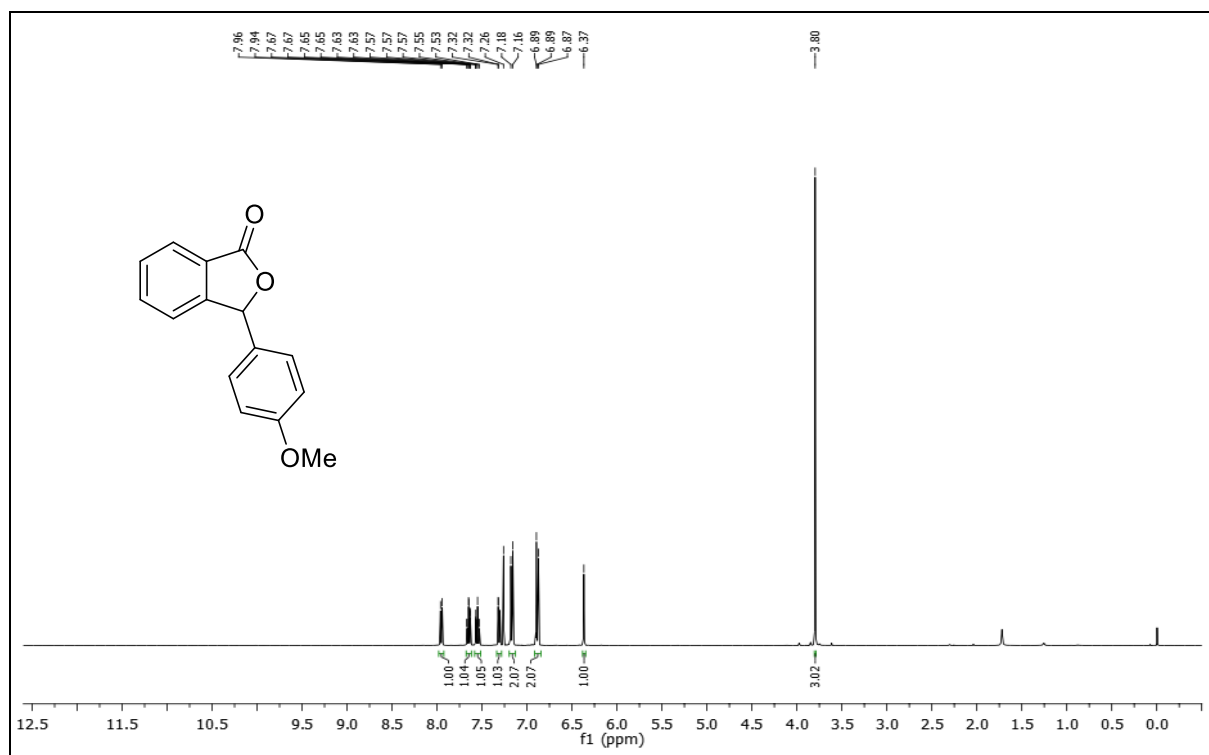
¹³C NMR (100 MHz, CDCl₃) spectrum of 3-(4-ethylphenyl)isobenzofuran-1(3H)-one **8c**.



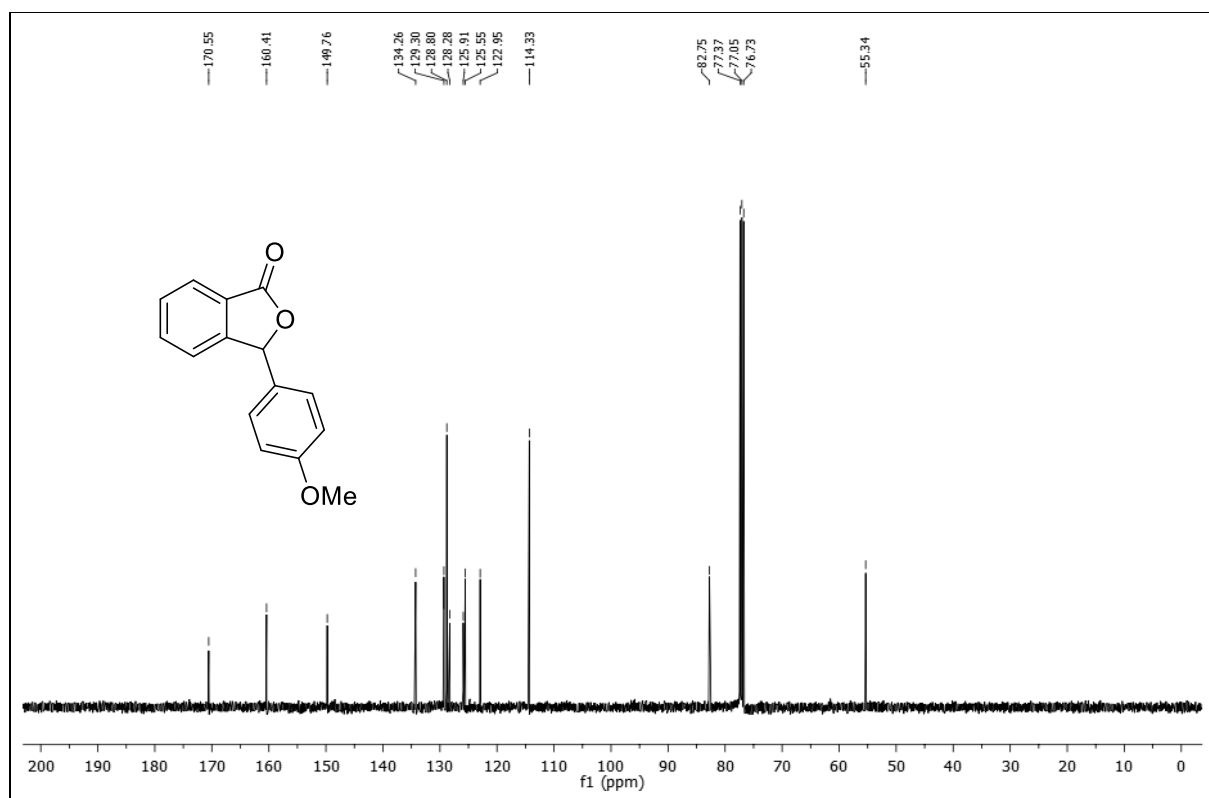
DEPT-135 spectrum of 3-(4-ethylphenyl)isobenzofuran-1(3*H*)-one **8c**.



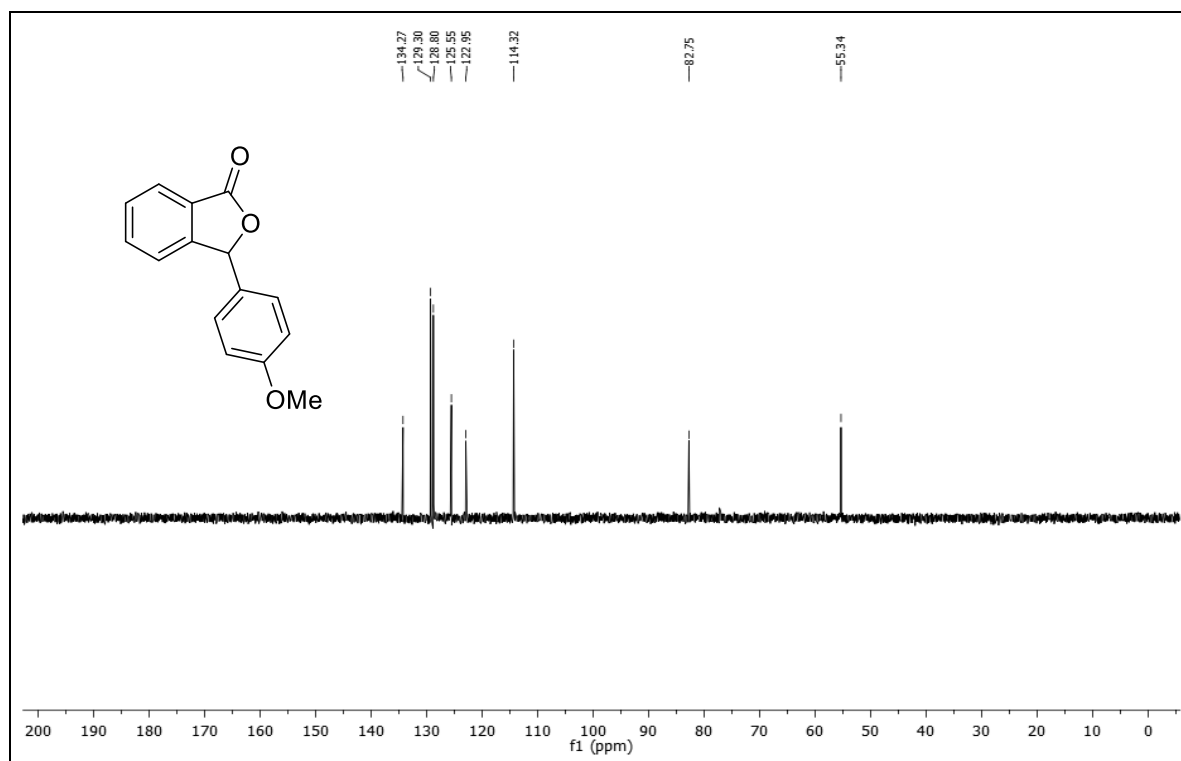
HRMS spectrum of 3-(4-ethylphenyl)isobenzofuran-1(3*H*)-one **8c**.



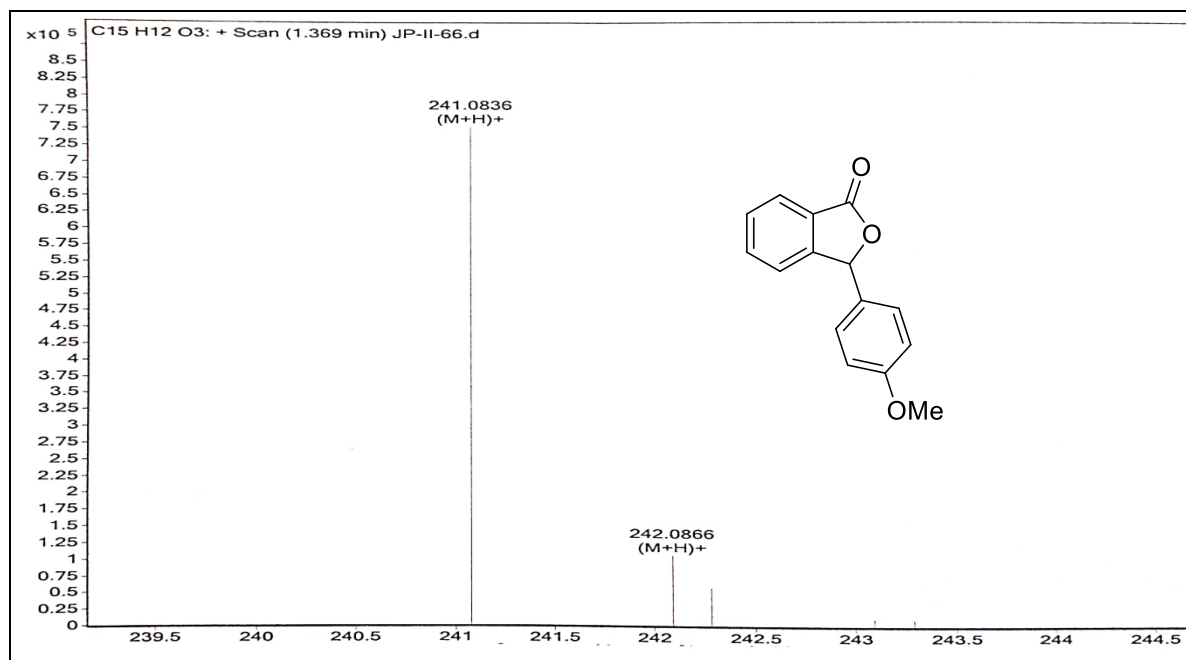
¹H NMR (400 MHz, CDCl₃) spectrum of 3-(4-methoxyphenyl)isobenzofuran-1(3H)-one **8d**.



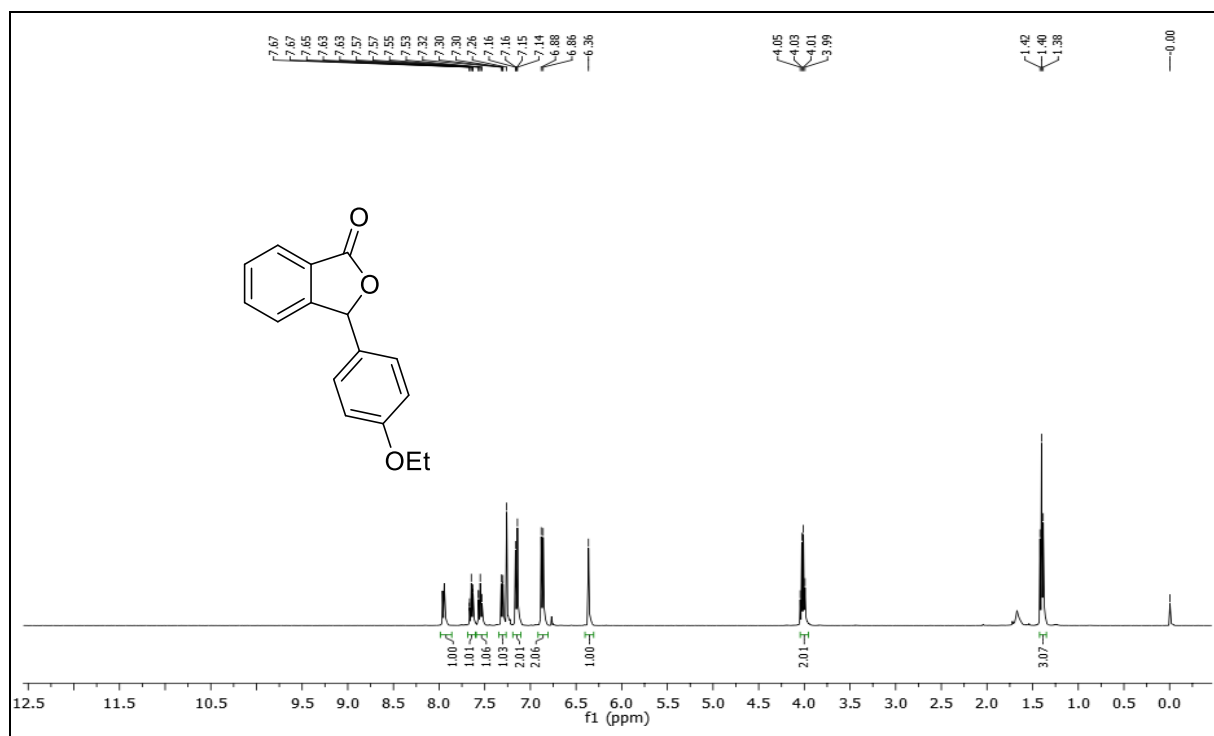
¹³C NMR (100 MHz, CDCl₃) spectrum of 3-(4-methoxyphenyl)isobenzofuran-1(3H)-one **8d**.



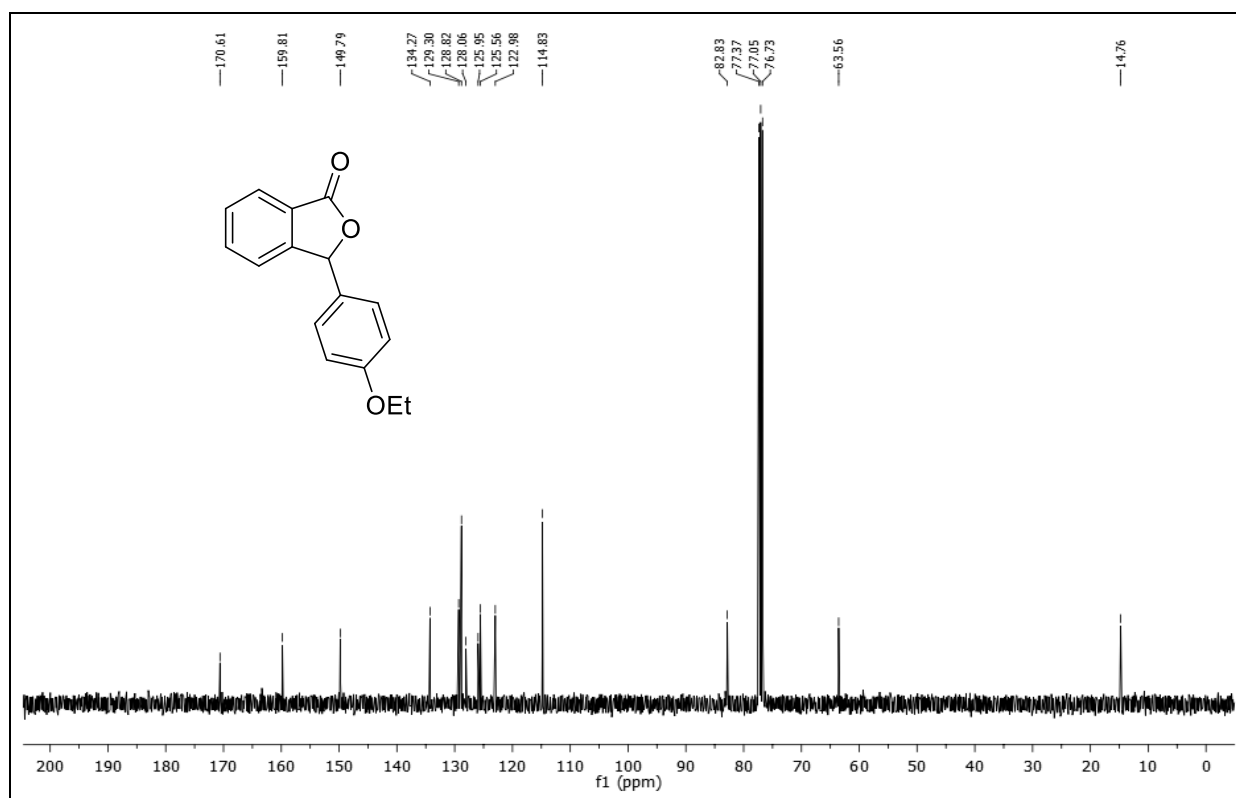
DEPT-135 spectrum of 3-(4-methoxyphenyl)isobenzofuran-1(3H)-one **8d**.



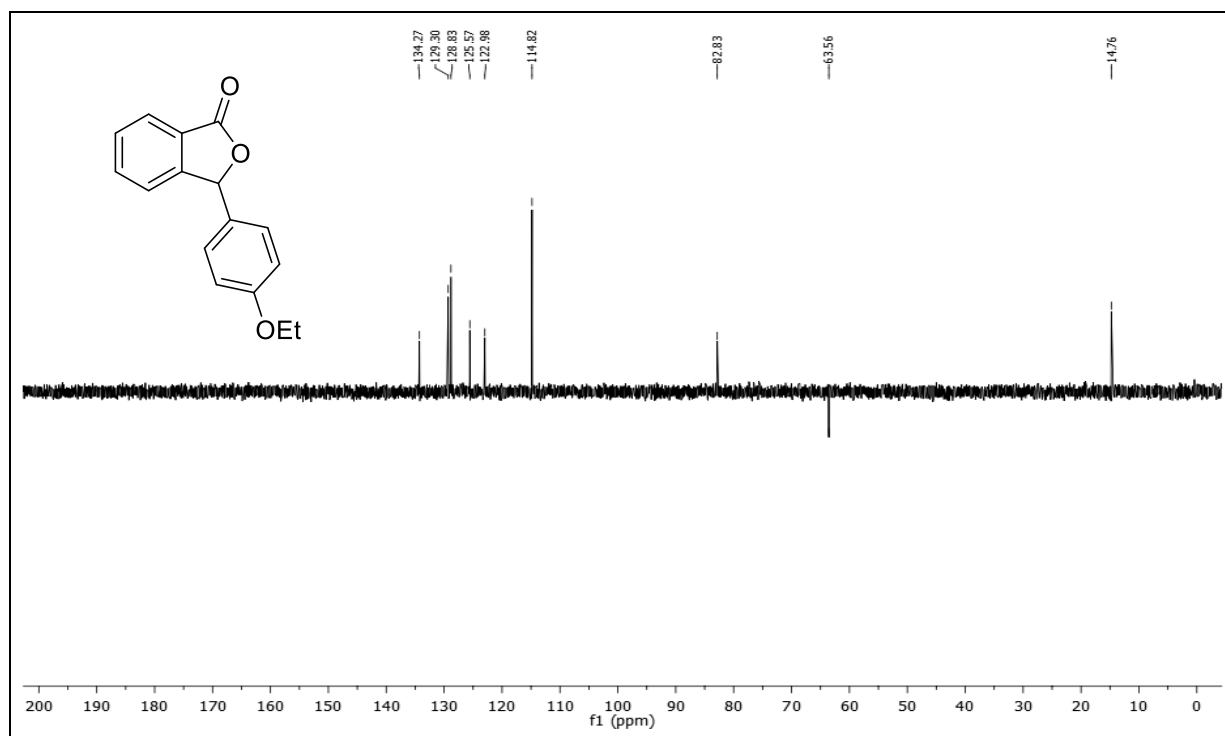
HRMS spectrum of 3-(4-methoxyphenyl)isobenzofuran-1(3H)-one **8d**.



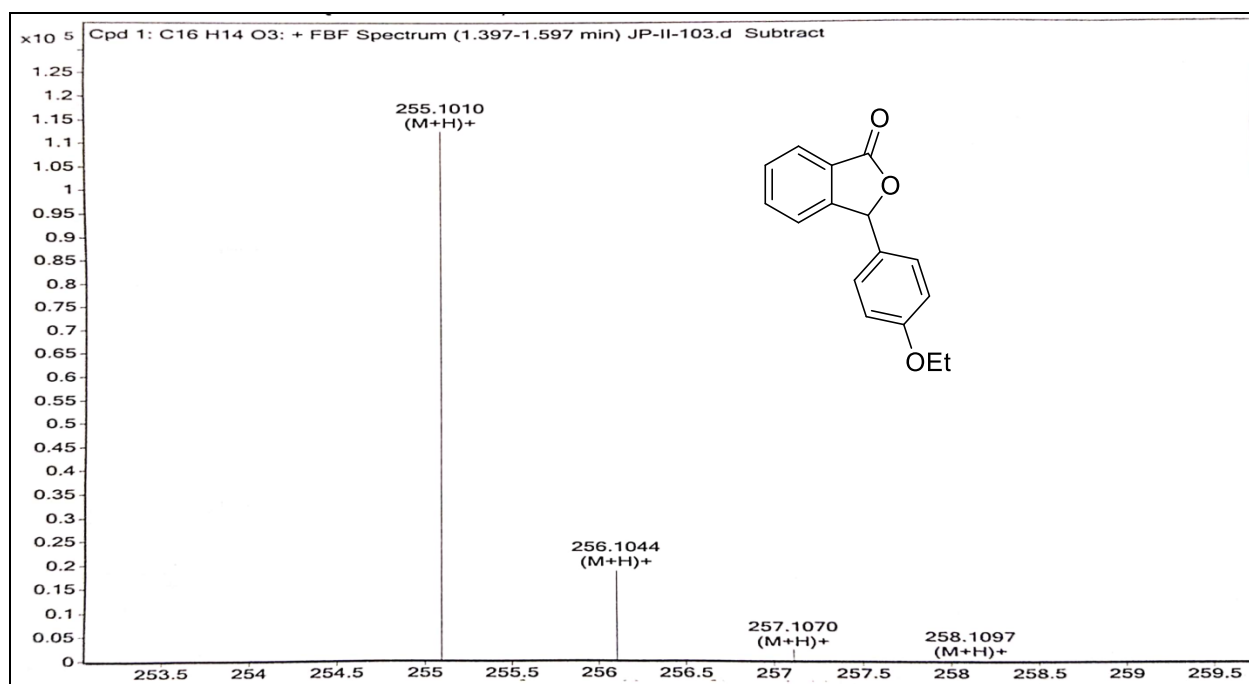
^1H NMR (400 MHz, CDCl_3) spectrum of 3-(4-ethoxyphenyl)isobenzofuran-1(3H)-one **8e**.



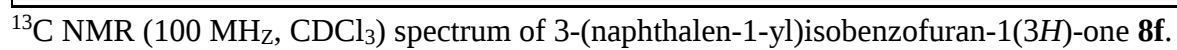
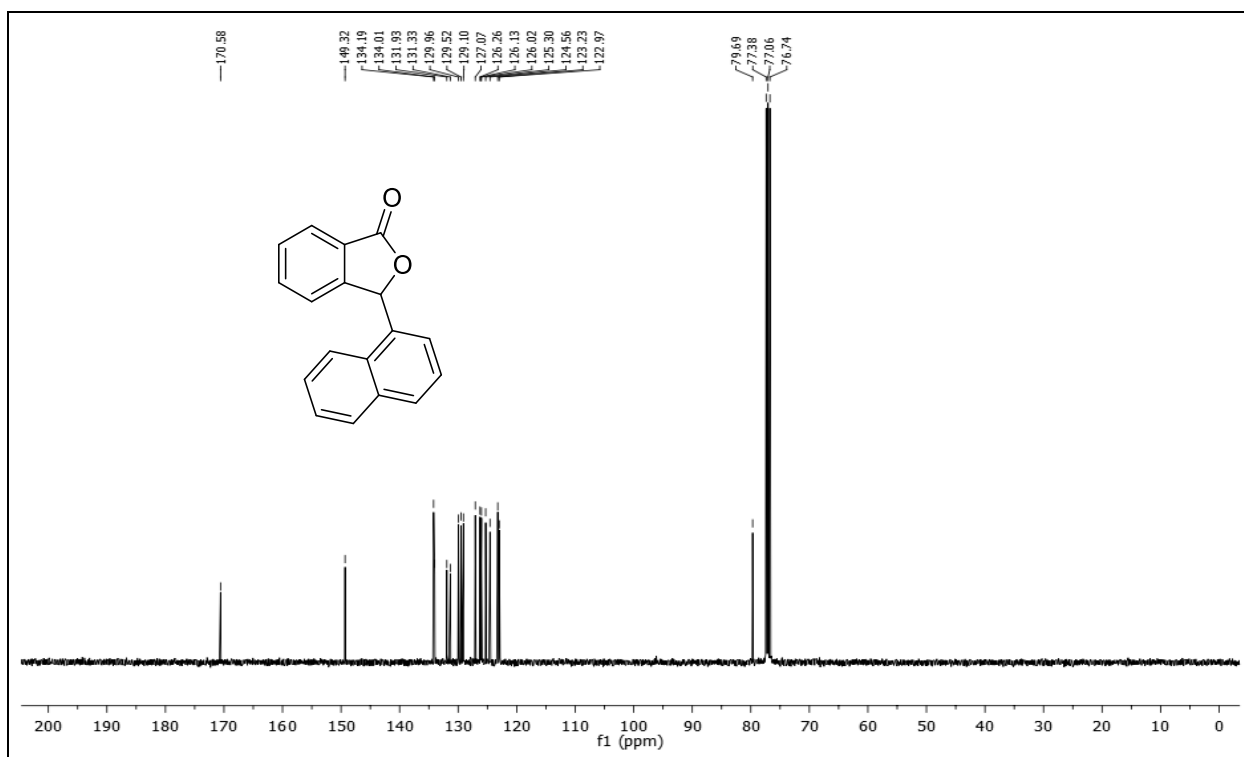
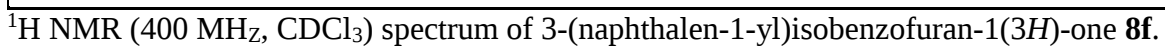
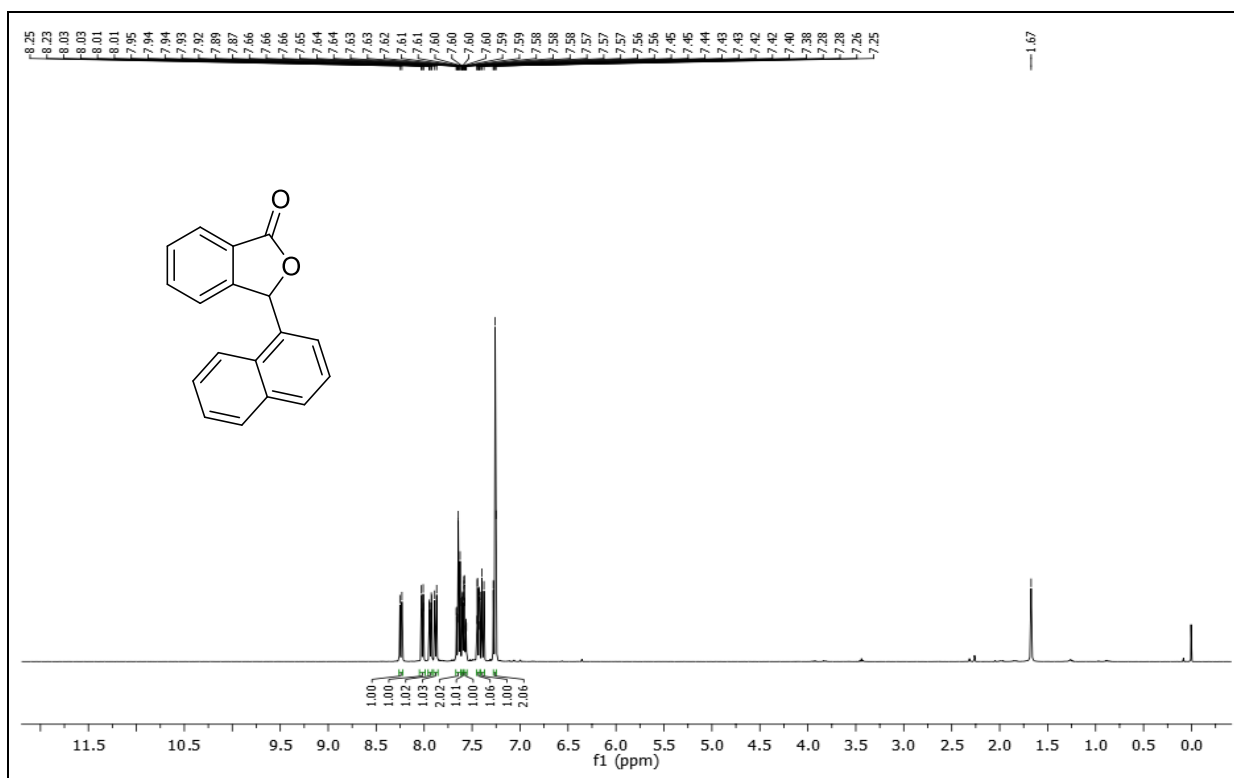
^{13}C NMR (100 MHz, CDCl_3) spectrum of 3-(4-ethoxyphenyl)isobenzofuran-1(3H)-one **8e**.

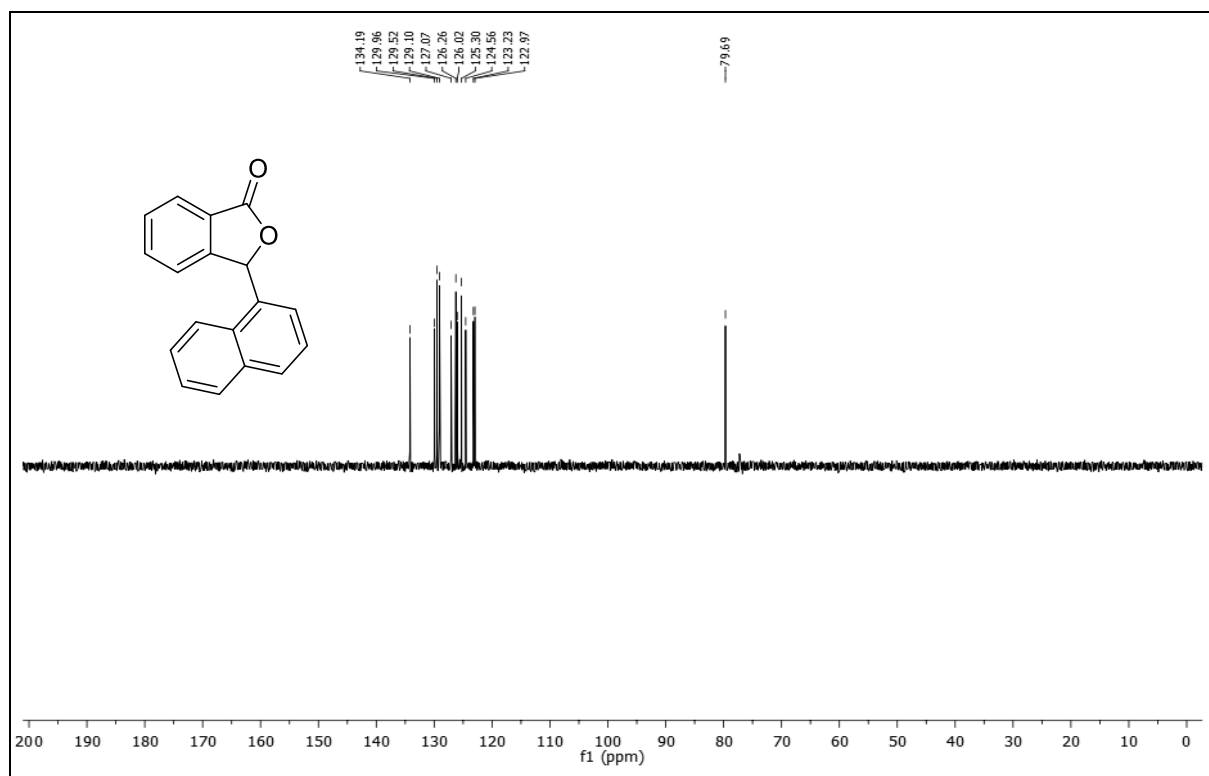


DEPT-135 spectrum of 3-(4-ethoxyphenyl)isobenzofuran-1(3H)-one **8e**.

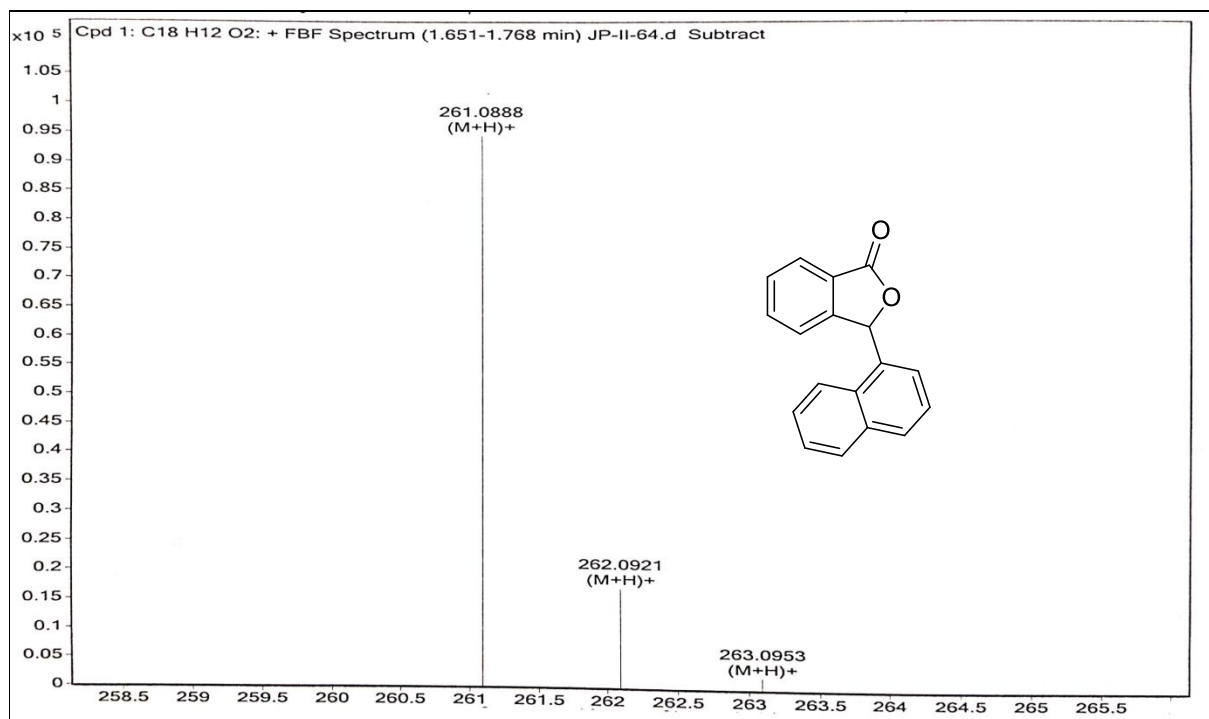


HRMS spectrum of 3-(4-ethoxyphenyl)isobenzofuran-1(3H)-one **8e**.

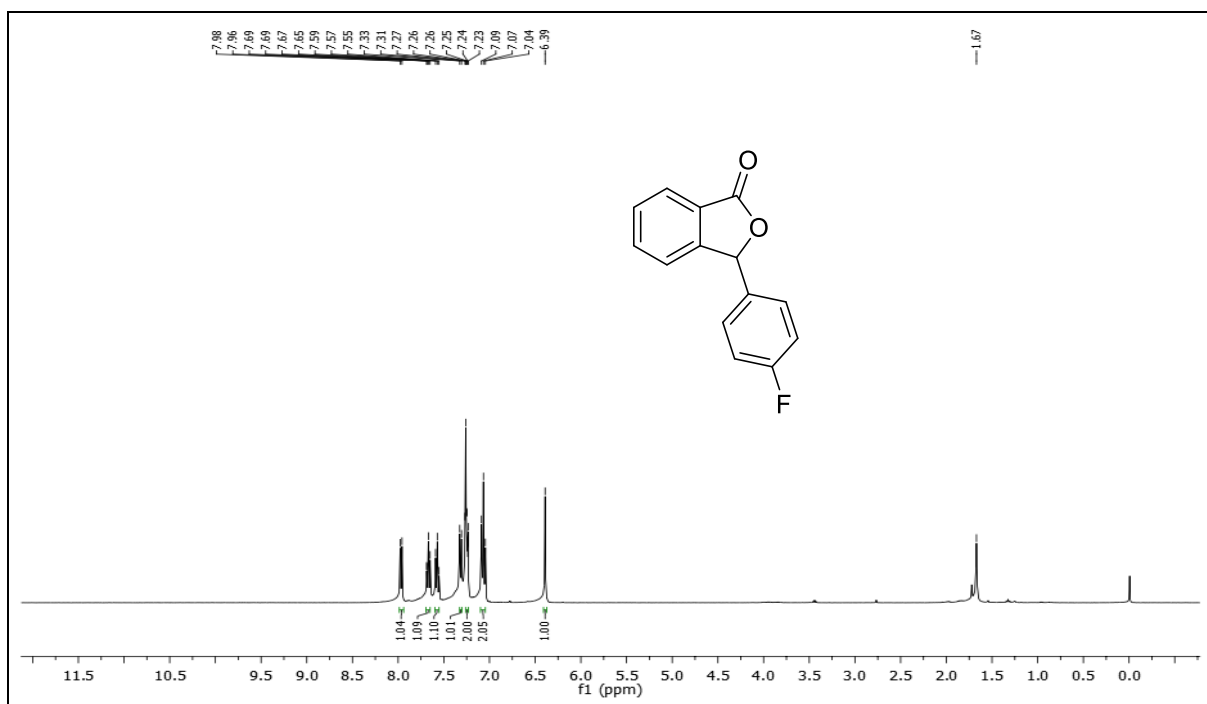




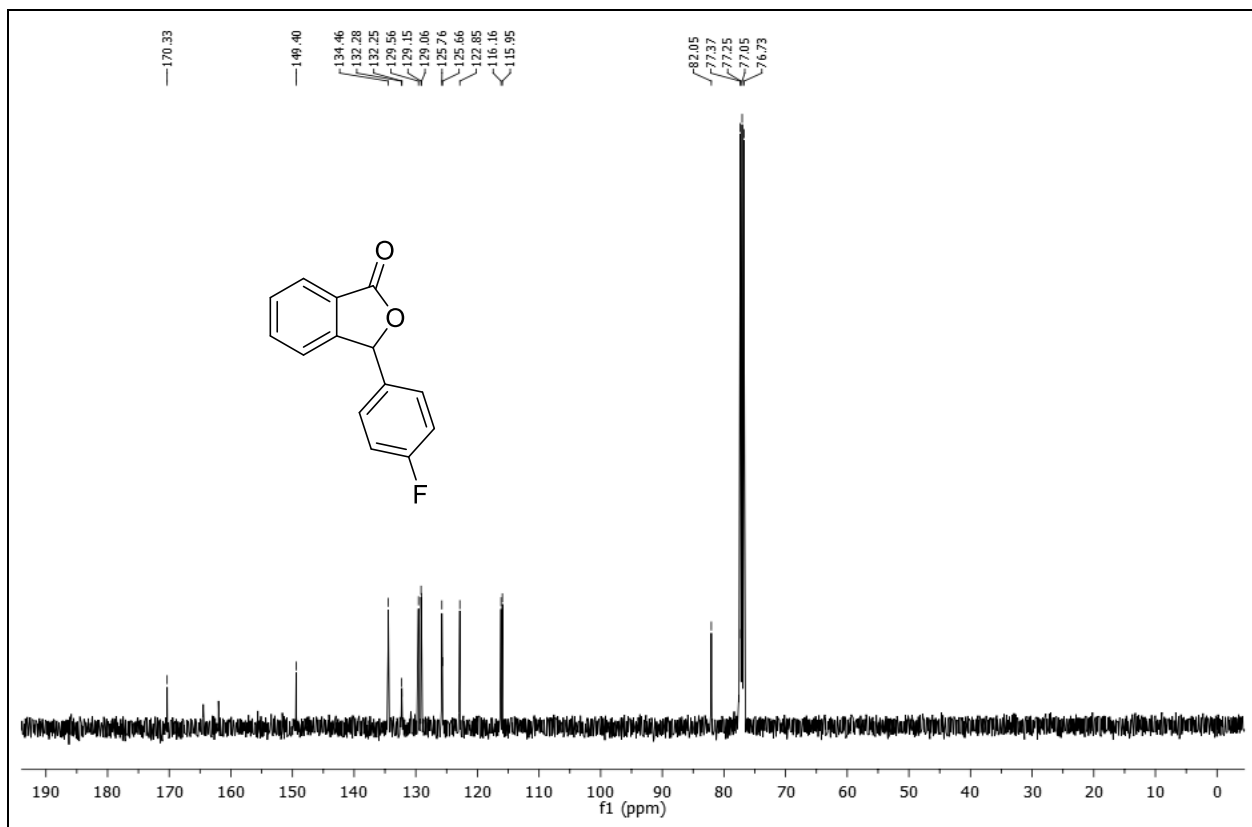
DEPT-135 spectrum of 3-(naphthalen-1-yl)isobenzofuran-1(3H)-one **8f**.



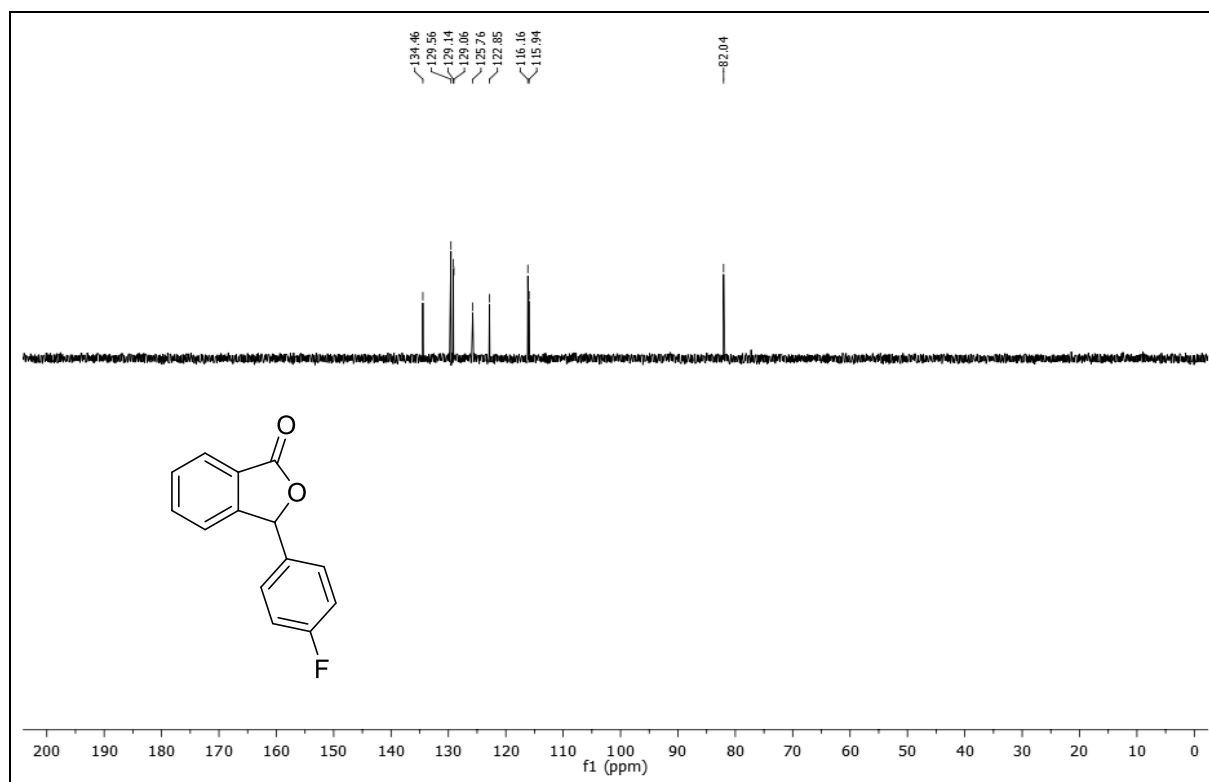
HRMS spectrum of 3-(naphthalen-1-yl)isobenzofuran-1(3H)-one **8f**.



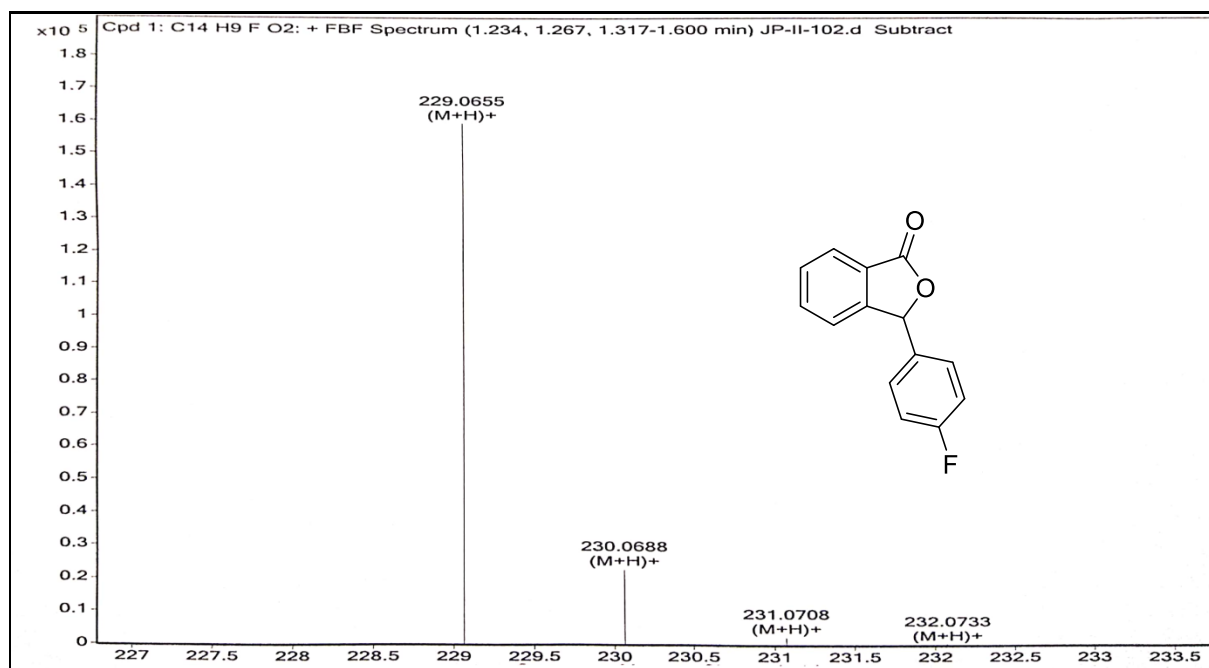
¹H NMR (400 MHz, CDCl₃) spectrum of 3-(4-fluorophenyl)isobenzofuran-1(3H)-one **8g**.



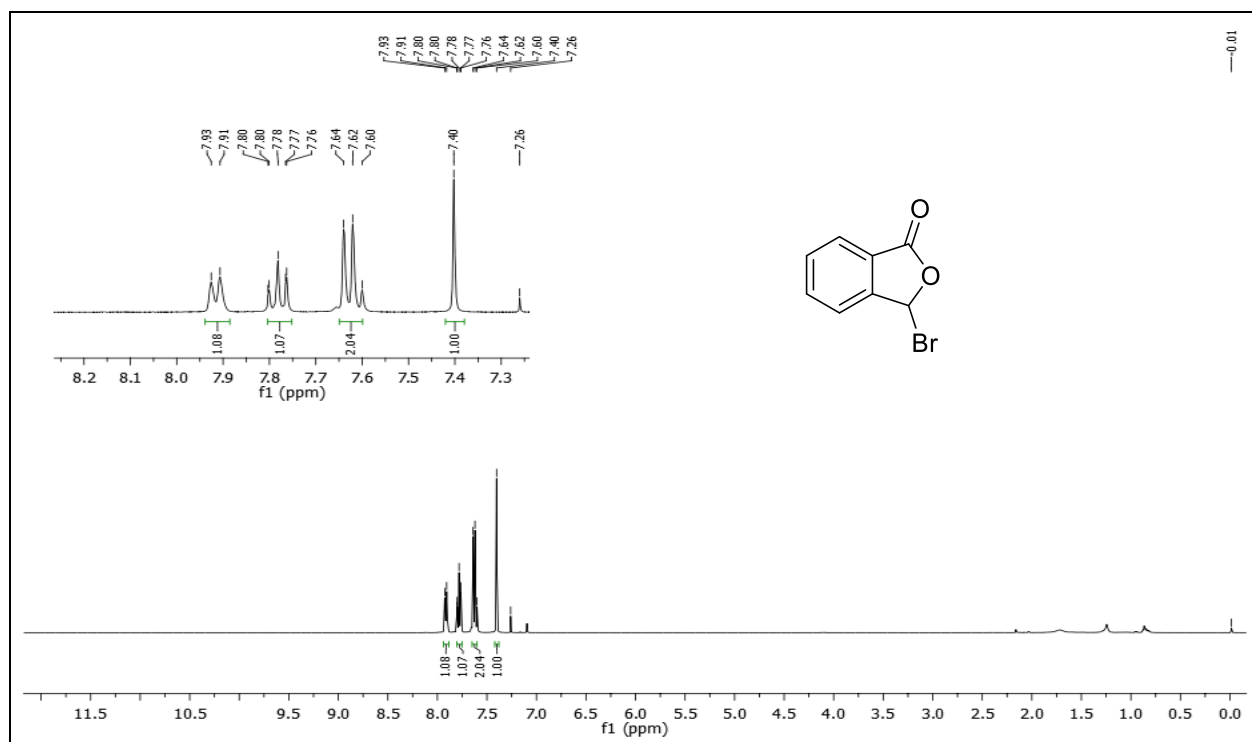
¹³C NMR (100 MHz, CDCl₃) spectrum of 3-(4-fluorophenyl)isobenzofuran-1(3H)-one **8g**.



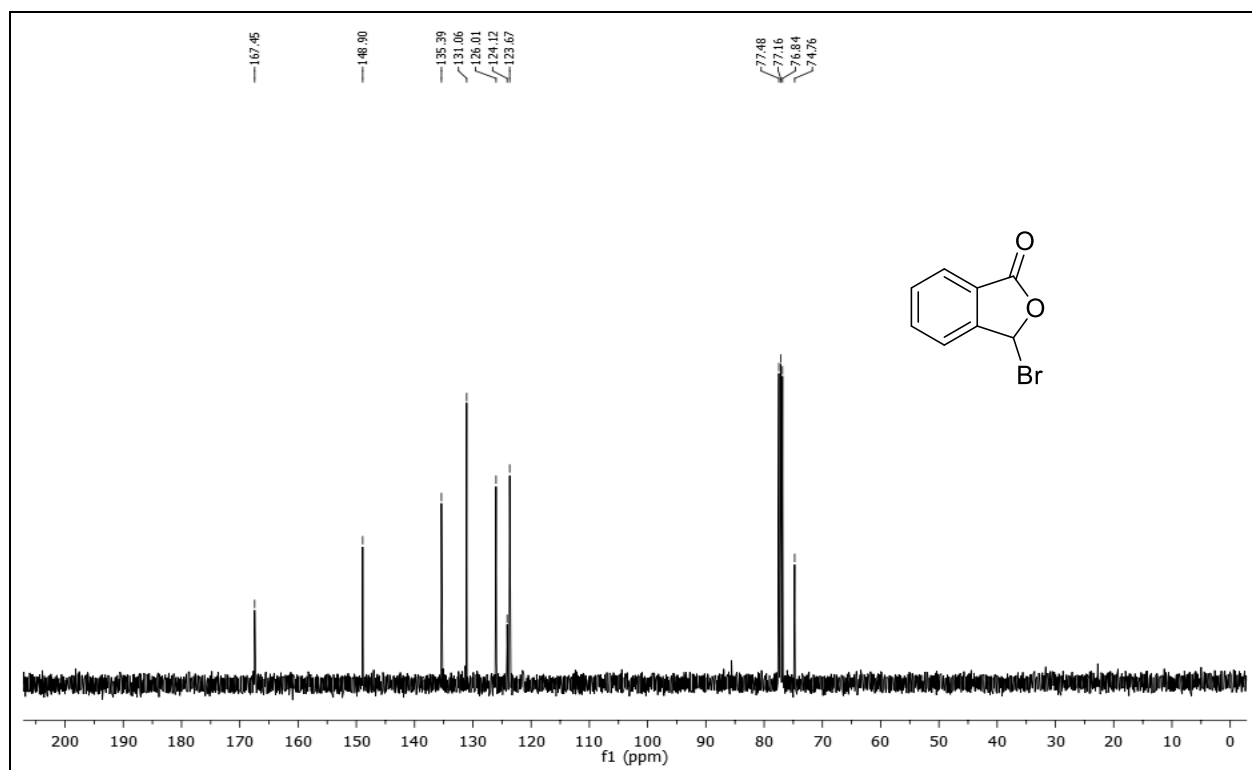
DEPT-135 spectrum of 3-(4-fluorophenyl)isobenzofuran-1(3H)-one **8g**.



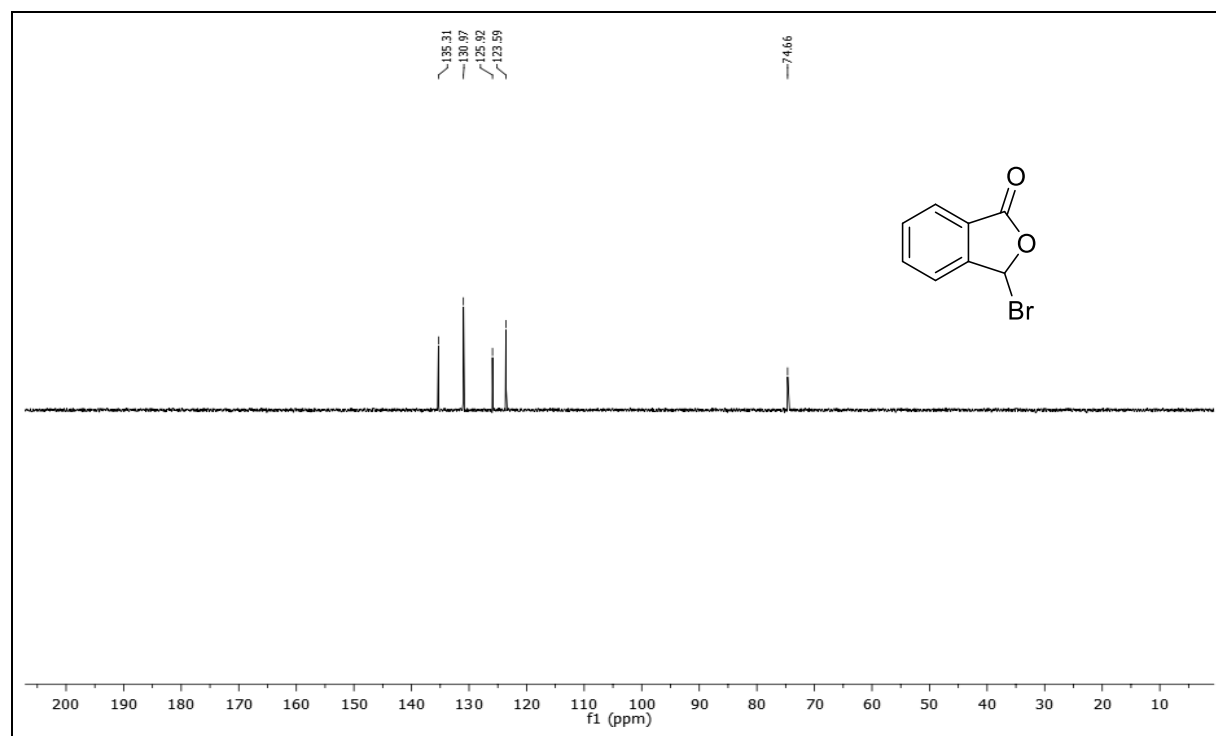
HRMS spectrum of 3-(4-fluorophenyl)isobenzofuran-1(3H)-one **8g**.



¹H NMR (400 MHz, CDCl₃) spectrum of 3-bromoisobenzofuran-1(3H)-one **6**.



¹³C NMR (100 MHz, CDCl₃) spectrum of 3-bromoisobenzofuran-1(3H)-one **6**.



DEPT-135 spectrum of 3-bromoisobenzofuran-1(3H)-one **6**.