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

$BF_3.OEt_2$-Catalyzed synthesis of 2,2'-spirobi-2*H*-1-benzopyrans from 2*H*-chromenes

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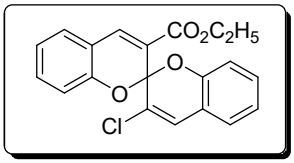
1. General information: Salicylaldehydes, β-ketoesters, 4 Å molecular sieves and Boron trifluoride diethyl etherate were procured from Sigma-Aldrich. General chemicals and solvents were obtained from local suppliers. All the reactions were carried at -78 ^{0}C to room temperature, monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F254 (mesh) and spots were visualized under UV light. Merck silica gel (60-120, 100-200 mesh) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Avance 300, 400, 500 MHz spectrometers in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on Nicollet Nexus 670 FT spectrometer. ESI-MS obtained on quarto micro spectrometer. HRMS were measured on Agilent Technologies 6510, Q-TOFLC/MS ESI-Technique. Melting points were determined in open glass capillary tubes on a Stuart melting point apparatus and are uncorrected.

2. Typical procedure for the synthesis of 2,2'-spirobi-2*H*-1-benzopyran (3a): Boron trifluoride diethyl etherate (0.25 mL, 2.0 mmol) was added dropwise to a stirred solution of ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate (**1a**, 0.268 g, 1.0 mmol) in dry CH_2Cl_2 (4 mL) at -78 ^{o}C under nitrogen atmosphere in presence of 4 Å molecular sieves. The reaction mixture was turned to lemon yellow colour was observed from colourless. Then, salicylaldehyde (**2a**, 0.122 g, 1.0 mmol) in dry CH_2Cl_2 (2 mL) was added slowly at the same temperature and stirring was continued for 30 minutes. The contents were slowly brought to room temperature and monitored by TLC. After completion of the reaction (8h, TLC), the reaction mixture was quenched with cold water and extracted with diethyl ether (3 x 10 mL). The layers were separated, the organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was subjected to column chromatography purification afforded ethyl 3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (**3a**, 0.26 g, 74% yield) as colourless solid.

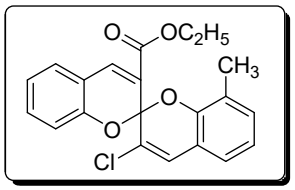
Ethyl 3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (3a):



Yield: 74%, Colourless solid, m.p. 144-146 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.34 (dd, J = 12.7, 4.6 Hz, 2H,), 7.2-7.15 (m, 2H), 7.09-6.99 (m, 2H), 6.96 (s, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 4.35-4.17 (m, 2H), 1.28-1.24 (m, 3H) ppm. ^{13}C NMR

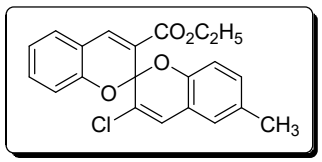
(125 MHz, $CDCl_3$): δ 163.78, 151.10, 148.77, 136.17, 132.77, 129.61, 128.91, 126.31, 126.26, 123.78, 122.42, 122.34, 121.30, 119.52, 117.92, 116.71, 116.34, 99.21, 61.14, 13.97 ppm. FT-IR (KBr): 3087, 2977, 2925, 1709, 1635, 1604, 1482, 1380, 1233, 1210, 1033, 930, 761 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{16}O_4Cl$ $[M+H]^+$: 355.0732; found: 355.0742.

Ethyl 3'-chloro-8'-methyl-2,2'-spirobi[chromene]-3-carboxylate (3b):



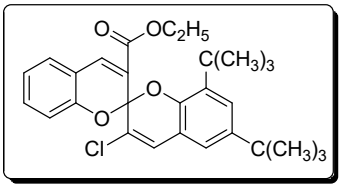
Yield: 65%, Colourless solid. m.p.: 104-106 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.38-7.31 (m, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 2H), 7.03-7.00 (m, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.94-6.87 (m, 2H), 4.27 (dd, *J* = 17.1, 7.1 Hz, 2H), 1.99 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.90, 151.16, 146.80, 136.21, 132.64, 131.12, 128.82, 126.04, 125.80, 124.15, 124.04, 122.34, 121.89, 121.66, 119.25, 118.10, 116.74, 99.25, 61.11, 15.25, 13.99 ppm. FT-IR (KBr): 2901, 1706, 1639, 1608, 1487. 1375, 1292, 1209, 1124, 1038, 926, 806 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_4Cl$ $[M+H]^+$: 369.0888; found: 369.0879.

Ethyl 3'-chloro-6'-methyl-2,2'-spirobi[chromene]-3-carboxylate (3c):



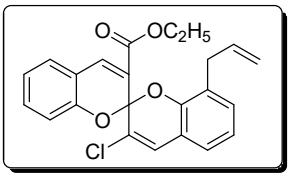
Yield: 70%, Colourless solid. m.p.: 148-150 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H,), 7.38-7.31 (m, 2H,), 7.06 (td, *J* = 7.5, 0.8 Hz, 1H), 7.00 (dd, *J* = 11.8, 3.6 Hz, 2H), 6.89 (d, *J* = 10.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 4.34-4.18 (m, 2H), 2.31 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.81, 151.16, 146.67, 136.13, 132.71, 131.68, 130.22, 128.89, 126.55, 126.26, 123.83, 122.35, 121.40, 119.28, 117.96, 116.71, 116.05, 99.24, 61.11, 20.57, 13.97ppm. FT-IR (KBr): 2922, 1705, 1639, 1607, 1487, 1374, 1293, 1209, 1123, 1037, 926, 804 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_4Cl$ $[M+H]^+$: 369.0888; found: 369.0906.

Ethyl 6',8'-*di-tert*-butyl-3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (3d):



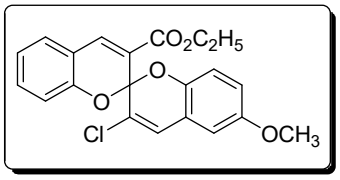
Yield: 65%, Colourless solid. m.p.: 156-158 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.37 (dd, J = 7.6, 1.4 Hz, 1H), 7.32-7.27 (m, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.05-7.01 (m, 2H), 6.94 (s, 1H), 6.86 (d, J = 8.2 Hz, 1H), 4.33-4.20 (m, 2H), 1.31 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H), 1.09 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.91, 151.53, 144.86, 144.22, 136.85, 136.00, 132.65, 128.76, 125.11, 125.00, 124.56, 122.26, 121.89, 121.62, 121.62, 119.39, 118.22, 116.75, 99.05, 61.05, 34.63, 34.43, 31.54, 29.62, 14.07 ppm. FT-IR (KBr): 3060, 2958, 1712, 1637, 1609, 1377, 1294, 1212, 1123, 1038, 932, 759 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{31}O_4ClNa$ $[M+Na]^+$: 489.1803; found: 489.1793.

Ethyl 8'-allyl-3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (3e):



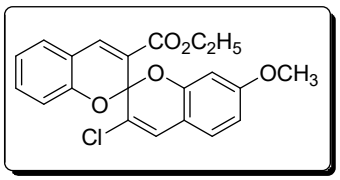
Yield: 58%, Colourless solid. m.p.: 112-114 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.38-7.30 (m, 2H), 7.08-7.03 (m, 3H), 6.99-6.93 (m, 2H), 6.86 (d, J = 8.2 Hz, 1H), 5.64-5.54 (m, 1H), 4.73 (ddd, J = 17.0, 3.3, 1.6 Hz, 1H), 4.63 (dd, J = 10.0, 1.7 Hz, 1H), 4.34-4.19 (m, 2H), 3.23 (dd, J = 15.0, 6.9 Hz, 1H), 3.06 (dd, J = 15.0, 6.5 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.90, 151.24, 146.46, 136.30, 135.84, 132.63, 130.33, 128.82, 128.00, 126.22, 124.63, 124.18, 122.42, 122.20, 121.65, 119.61, 118.17, 116.91, 115.43, 99.22, 61.15, 34.01, 14.04 ppm. FT-IR (KBr): 2925, 1709, 1635, 1606, 1453, 1377, 1293, 1211, 1125, 1029, 918, 775 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{23}H_{19}O_4ClNa$ $[M+Na]^+$: 417.0864; found: 417.0848.

Ethyl 3'-chloro-6'-methoxy-2,2'-spirobi[chromene]-3-carboxylate (3f):



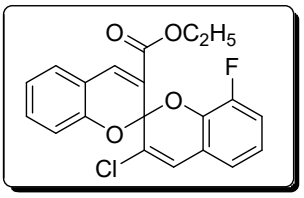
Yield: 72%, Colourless solid. m.p.: 116-118 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.38-7.31 (m, 2H), 7.06 (td, J = 7.5, 0.8 Hz, 1H), 6.93-6.87 (m, 2H), 6.77 (t, J = 5.0 Hz, 2H), 6.71 (d, J = 1.0 Hz, 1H), 4.34-4.19 (m, 2H), 3.78 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 163.81, 154.77, 151.18, 142.83, 136.17, 132.73, 128.92, 127.17, 123.76, 122.38, 121.38, 120.03, 117.99, 117.08, 116.75, 115.42, 110.69, 99.25, 61.14, 55.79, 14.00 ppm. FT-IR (KBr): 3057, 2928, 1708, 1635, 1607, 1490, 1374, 1289, 1212, 1124, 1041, 927, 757 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_5Cl$ $[M+H]^+$: 385.0837; found: 385.0813.

Ethyl 3'-chloro-7'-methoxy-2,2'-spirobi[chromene]-3-carboxylate (3g):



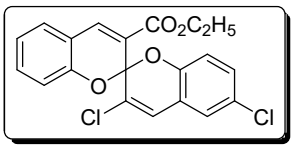
Yield: 52%, Colourless solid. m.p.: 124-126 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.07 (t, J = 7.4 Hz, 2H), 6.94-6.88 (m, 2H), 6.59 (dd, J = 8.4, 1.9 Hz, 1H), 6.41 (s, 1H), 4.34-4.20 (m, 2H), 3.73 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 163.83, 161.08, 151.15, 150.04, 136.12, 132.75, 128.91, 127.04, 123.52, 123.29, 122.41, 121.47, 117.96, 116.79, 112.84, 109.08, 101.62, 89.34, 61.14, 55.41, 13.99. FT-IR (KBr): 3054, 2985, 2929, 1707, 1635, 1607, 1491, 1374, 1258, 1211, 1044, 931, 755 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{17}O_5ClNa$ $[M+Na]^+$: 407.0657; found: 407.0643.

Ethyl 3'-chloro-8'-fluoro-2,2'-spirobi[chromene]-3-carboxylate (3h):



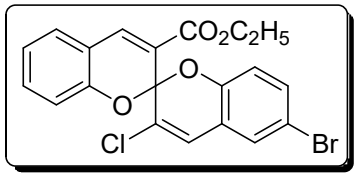
Yield: 69%, Colourless solid. m.p.: 140-142 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 7.03-6.96 (m, 2H), 6.97-6.92 (m, 3H), 6.91 (d, J = 8.4 Hz, 1H), 4.34-4.21 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.66, 152.12, 150.93, 149.67, 136.76, 132.99, 129.13, 127.57, 123.19, 122.71, 122.18, 122.11, 121.86, 121.49, 120.66, 117.76, 116.68, 99.16, 61.24, 14.04 ppm. FT-IR (KBr): 3068, 2982, 1707, 1640, 1609, 1475, 1377, 1295, 1234, 1209, 1125, 1031, 915, 773 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{14}O_4ClFNa$ $[M+Na]^+$: 395.0457; found: 395.0456.

Ethyl 3',6'-dichloro-2,2'-spirobi[chromene]-3-carboxylate (3i):



Yield: 68%, Colourless solid. m.p.: 190-192 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.17-7.13 (m, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.6 Hz, 1H), 4.33-4.20 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 163.65, 150.95, 147.28, 136.35, 132.92, 129.28, 128.99, 127.84, 127.27, 125.69, 122.73, 122.62, 120.99, 120.86, 117.82, 117.74, 116.67, 99.25, 61.23, 14.00 ppm. FT-IR (KBr): 2926, 1702, 1642, 1606, 1479, 1377, 1294, 1212, 1124, 1039, 930, 753 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{14}O_4Cl_2Na$ $[M+Na]^+$: 411.0161; found: 411.0130.

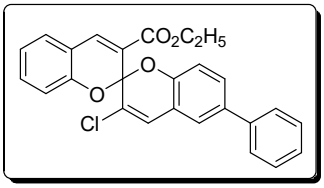
Ethyl 6'-bromo-3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (3k):



Yield: 70%, Colourless solid. m.p.: 196-198 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.36 (dd, J = 11.6, 4.5 Hz, 2H), 7.30-7.27 (m, 2H), 7.10-7.05 (m, 1H), 6.89 (d, J = 10.8 Hz,

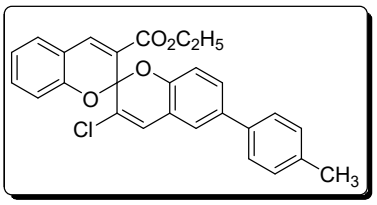
2H), 6.73 (d, J = 8.2 Hz, 1H), 4.33-4.20 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.63, 150.92, 147.79, 136.35, 132.92, 132.18, 128.98, 128.60, 127.78, 122.62, 121.37, 120.97, 118.16, 117.80, 116.66, 114.51, 99.24, 61.22, 13.99 ppm. FT-IR (KBr): 3068, 2926, 1701, 1642, 1604, 1477, 1375, 1293, 1210, 1122, 1038, 930, 7754 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{14}O_4ClBrNa$ $[M+Na]^+$: 454.9656; found: 454.9641.

Ethyl 3'-chloro-6'-phenyl-2,2'-spirobi[chromene]-3-carboxylate (3m):



Yield: 76%, Colourless solid. m.p.: 156-158 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.54 (d, J = 7.3 Hz, 2H), 7.46-7.40 (m, 3H), 7.40-7.31 (m, 4H), 7.07 (t, J = 7.4 Hz, 1H), 7.02 (s, 1H), 6.94-6.88 (m, 2H), 4.32-4.22 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.82, 151.17, 148.39, 140.40, 136.27, 135.74, 132.89, 129.02, 128.85, 128.49, 127.14, 126.91, 126.79, 124.95, 123.88, 122.55, 121.34, 119.82, 117.98, 116.79, 116.74, 99.44, 61.24, 14.07 ppm. FT-IR (KBr): 3061, 2982, 1712, 1635, 1606, 1478, 1377, 1209, 1121, 1038, 927, 757 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{19}O_4ClNa$ $[M+Na]^+$: 453.0864; found: 453.0840.

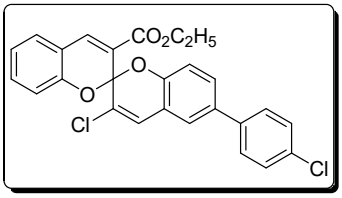
Ethyl 3'-chloro-6'-*p*-tolyl-2,2'-spirobi[chromene]-3-carboxylate (3n):



Yield: 74%, Colourless solid. m.p.: 180-182 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.42-7.39 (m, 1H), 7.38-7.33 (m, 3H), 7.25 (d, J = 3.5 Hz, 2H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 7.01 (s, 1H), 6.91 (dd, J = 12.4, 8.3 Hz, 2H), 4.34-4.21 (m, 2H), 2.39 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.78, 151.13, 148.12, 137.47, 136.84, 136.20, 135.63, 132.81, 129.50, 128.94, 128.24, 126.68, 124.67, 123.87, 122.46, 121.30, 119.72, 117.93, 116.74, 116.62, 99.37, 61.17, 21.07, 14.01 ppm. FT-

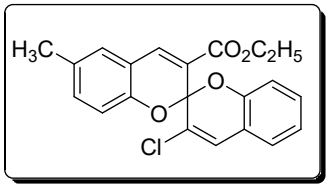
IR (KBr): 3055, 2981, 2920, 1713, 1639, 1608, 1483, 1377, 1234, 1213, 1126, 1003, 926, 760 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{21}O_4ClNa$ $[M+Na]^+$: 467.1021; found: 467.1011.

Ethyl 3'-chloro-6'-(4-chlorophenyl)-2,2'-spirobi[chromene]-3-carboxylate (3o):



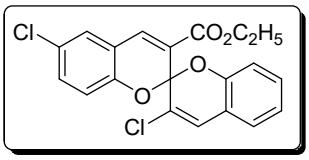
Yield: 72%, Colourless solid. m.p.: 194-196 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.49-7.44 (m, 2H), 7.41-7.36 (m, 5H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.08 (td, *J* = 7.5, 0.7 Hz, 1H), 7.01 (s, 1H), 6.91 (dd, *J* = 8.2, 3.3 Hz, 2H), 4.34-4.21 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.77, 151.11, 148.58, 138.84, 136.29, 134.47, 133.21, 132.90, 128.98, 128.28, 128.12, 127.03, 124.75, 123.68, 122.58, 121.24, 119.93, 117.94, 116.88, 116.75, 99.41, 61.24, 14.07 ppm. FT-IR (KBr): 3054, 2983, 1709, 1638, 1608, 1478, 1376, 1233, 1213, 1127, 1002, 925, 751 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{18}O_4Cl_2Na$ $[M+Na]^+$: 487.0474; found: 487.0455.

Ethyl 3'-chloro-6-methyl-2,2'-spirobi[chromene]-3-carboxylate (3p):



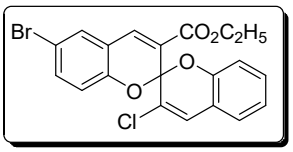
Yield: 62%, Colourless solid. m.p.: 130-132 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.21-7.13 (m, 4H), 7.02 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.94 (s, 1H), 6.81 (dd, *J* = 17.3, 8.0 Hz, 2H), 4.31-4.19 (m, 2H), 2.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.93, 149.09, 148.90, 136.38, 133.59, 131.87, 129.61, 129.03, 126.46, 126.34, 123.77, 122.31, 121.31, 119.63, 117.74, 116.50, 116.40, 99.28, 61.14, 20.56, 14.02 ppm. FT-IR (KBr): 3081, 2976, 1710, 1637, 1483, 1377, 1243, 1215, 1036, 932, 764 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_4Cl$ $[M+H]^+$: 369.0888; found: 369.0857.

Ethyl 3',6-dichloro-2,2'-spirobi[chromene]-3-carboxylate (3s):



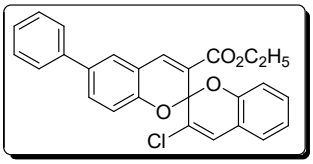
Yield: 64%, Colourless solid. m.p.: 126-128 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.35 (s, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.23-7.15 (m, 2H), 7.03 (s, 1H), 6.96 (s, 1H), 6.84 (d, J = 8.3 Hz, 2H), 4.33-4.20 (m, 2H), 1.27 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.42, 149.53, 148.62, 134.84, 132.34, 129.75, 128.06, 127.32, 126.38, 125.82, 124.01, 122.52, 119.41, 119.20, 118.17, 116.30, 99.33, 61.34, 13.94 ppm. FT-IR (KBr): 3083, 2930, 1718, 1635, 1641, 1479, 1374, 1224, 1205, 1039, 921, 761 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{14}O_4Cl_2Na$ $[M+Na]^+$: 411.0161; found: 411.0132.

Ethyl 6-bromo-3'-chloro-2,2'-spirobi[chromene]-3-carboxylate (3t):



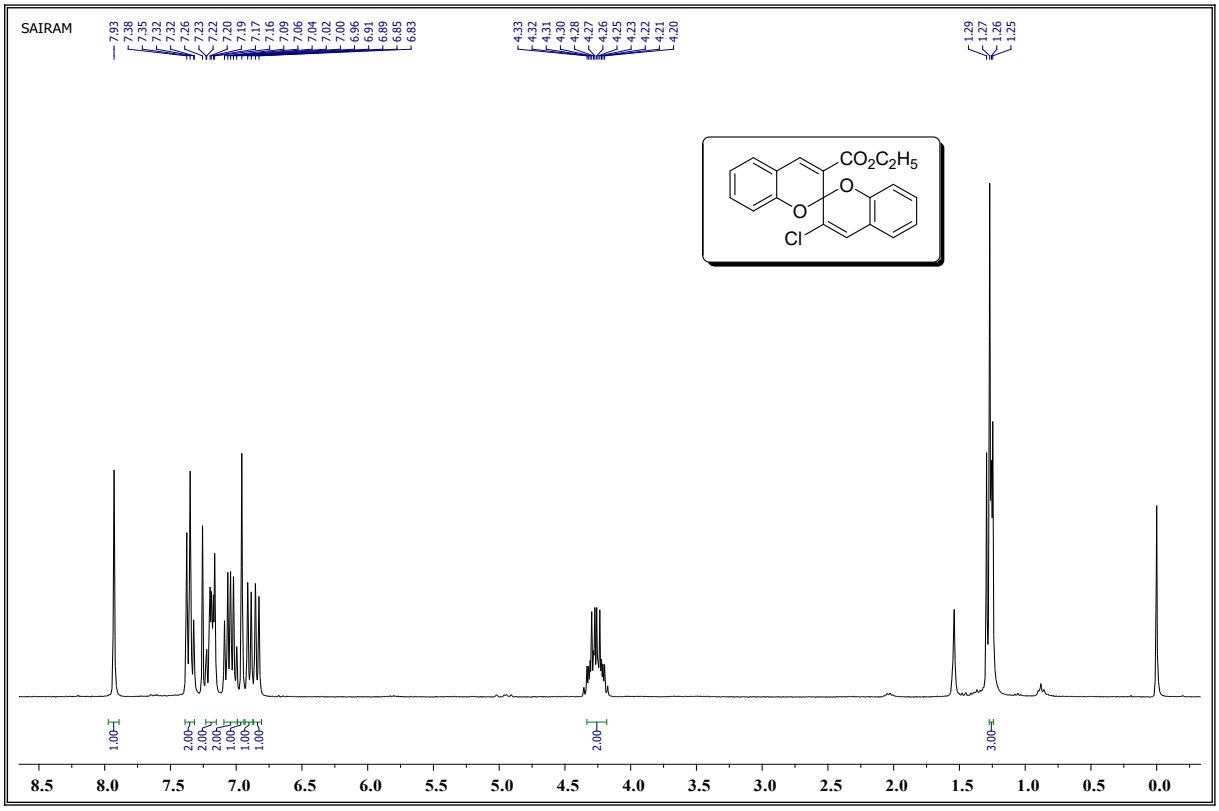
Yield: 68%, Colourless solid. m.p.: 120-122 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.50 (d, J = 2.2 Hz, 1H), 7.43 (dd, J = 8.7, 2.3 Hz, 1H), 7.23-7.16 (m, 2H), 7.03 (t, J = 7.3 Hz, 1H), 6.96 (s, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.79 (d, J = 8.7 Hz, 1H), 4.33-4.20 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.45, 150.10, 148.66, 135.26, 134.77, 131.07, 129.81, 126.43, 125.85, 124.07, 122.58, 119.80, 119.45, 118.62, 116.35, 114.52, 99.35, 61.40, 13.99 ppm. FT-IR (KBr): 3080, 2978, 1720, 1640, 1479, 1373, 1223, 1204, 1107, 1039, 004, 923, 761 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{14}O_4ClBrNa$ $[M+Na]^+$: 454.9656; found: 454.9630.

Ethyl 3'-chloro-6-phenyl-2,2'-spirobi[chromene]-3-carboxylate (3u):

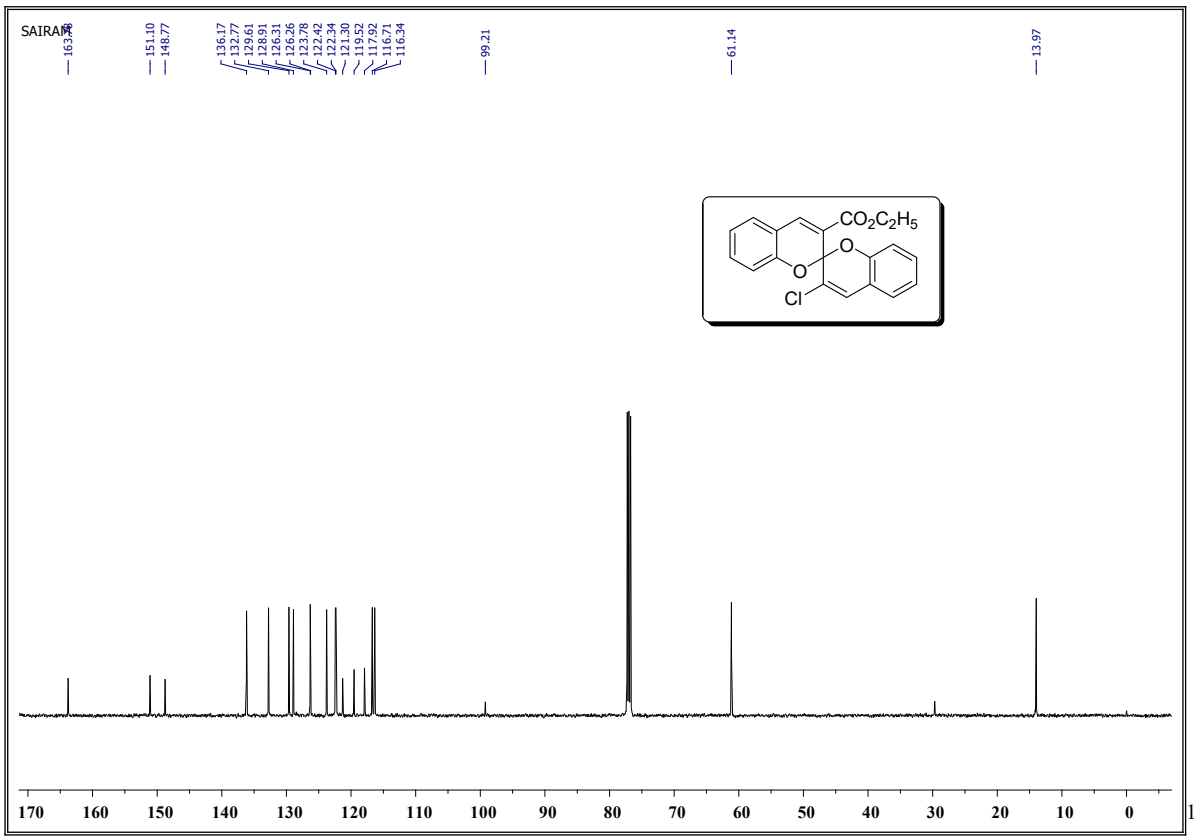


Yield: 70%, Colourless solid. m.p.: 132-134 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.60-7.52 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 16.0, 7.7 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 4.2 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.34-4.21 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.79, 150.65, 148.83, 139.98, 136.25, 135.85, 131.62, 129.72, 128.92, 127.36, 126.86, 126.40, 126.27, 123.89, 122.44, 121.74, 119.58, 118.20, 117.12, 116.42, 99.40, 61.25, 14.03 ppm. FT-IR (KBr): 3032, 2985, 1710, 1638, 1481, 1254, 1223, 1036, 923, 695 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{19}O_4ClNa$ $[M+Na]^+$: 453.0864; found: 453.0858.

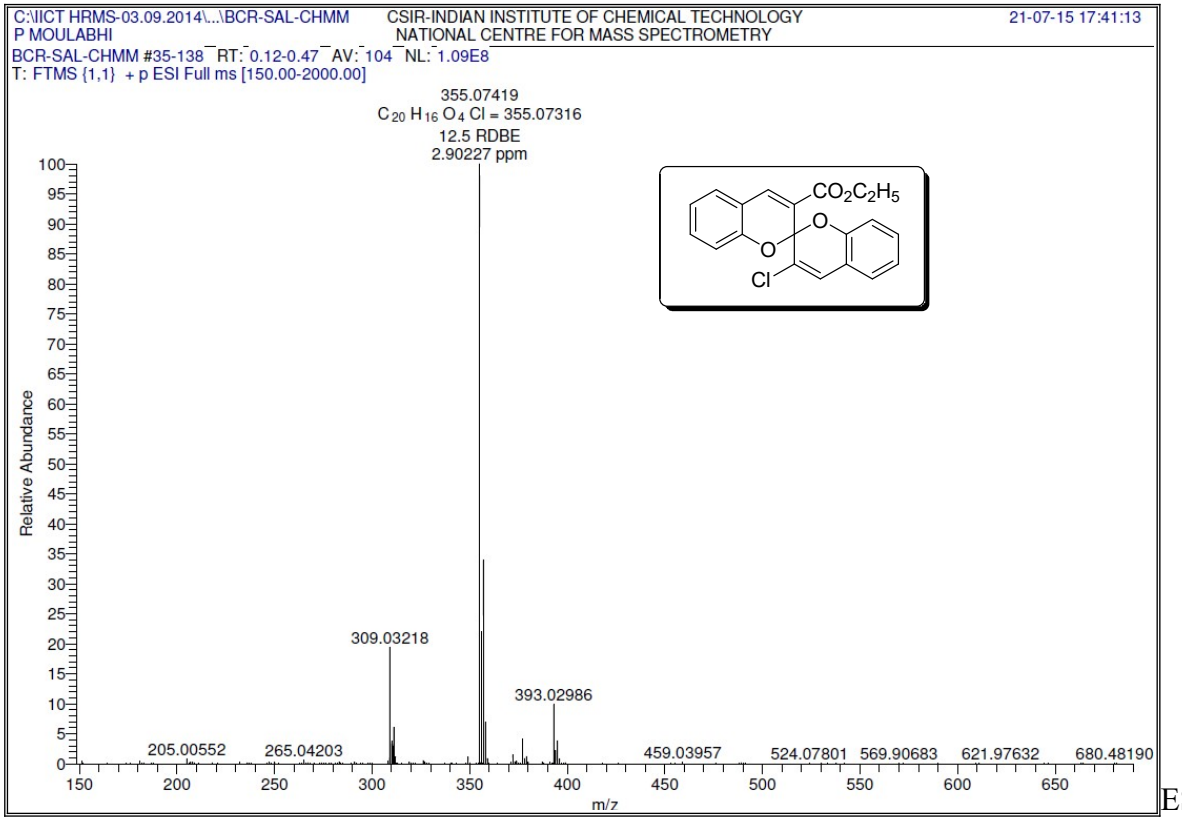
3. Copies of ^{1}H-NMR, ^{13}C-NMR and HRMS Spectrums of compounds **3a-i, 3k, 3m-p, 3s-u**:



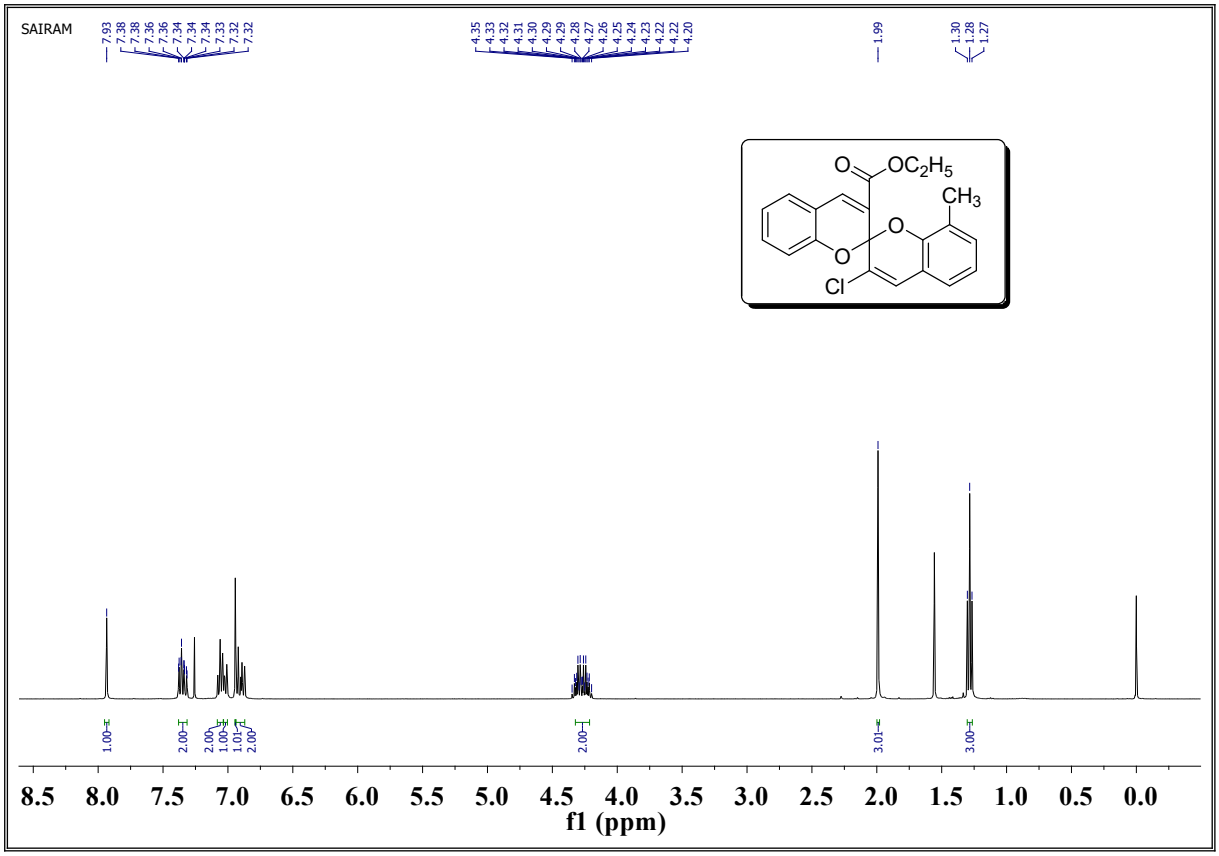
^{1}H NMR spectrum of compound **3a**



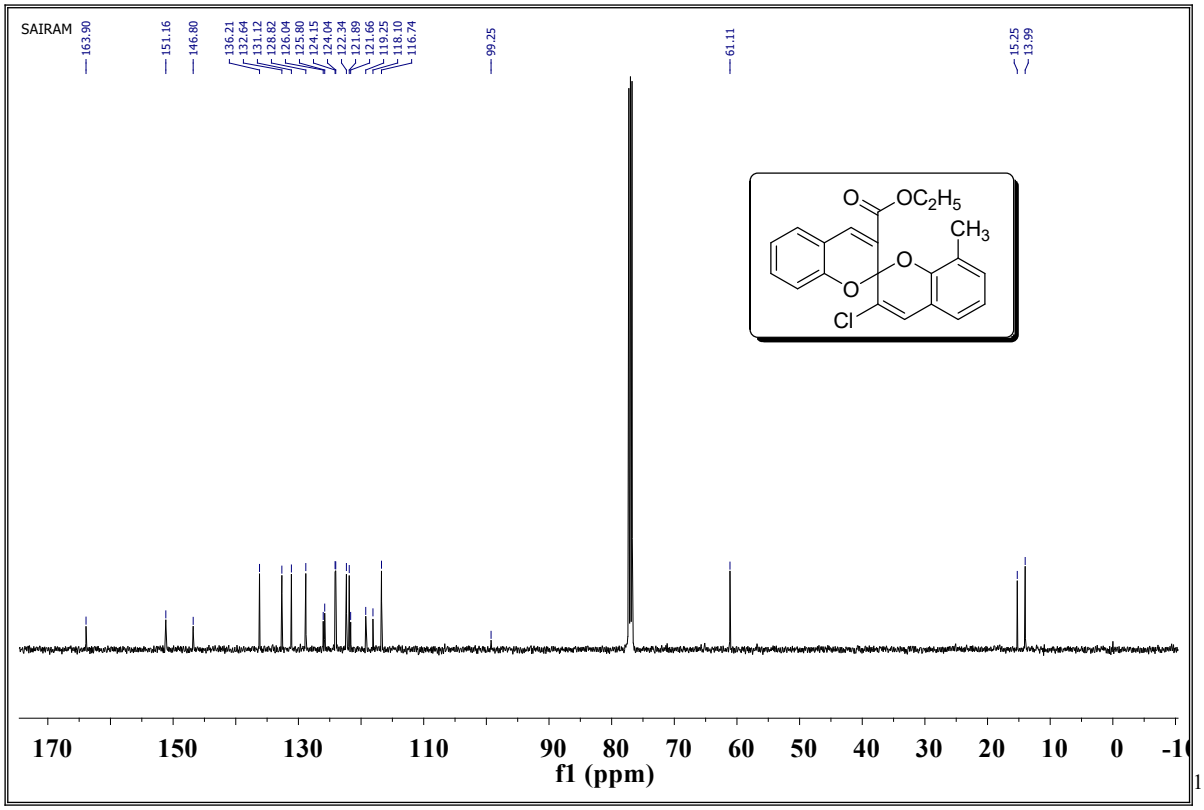
13 C NMR spectrum of compound **3a**



ES I-HRMS of compound **3a**



^{1}H NMR spectrum of compound **3b**

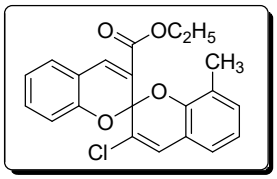


^{3}C NMR spectrum of compound **3b**

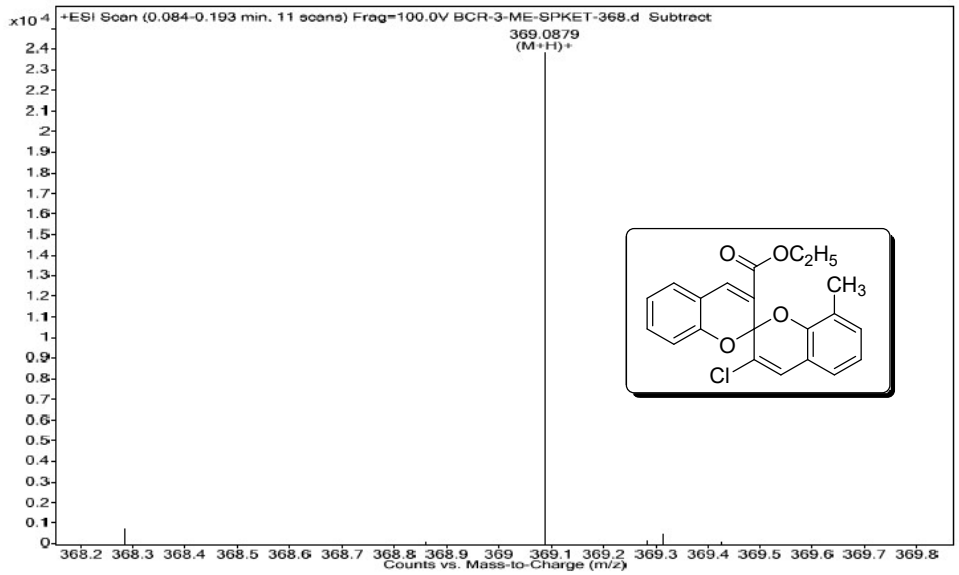
MS Formula Results: + Scan (0.084-0.193 min) Sub - BCR-3-ME-SPKET-368.d (BCR-3-ME-SPKET-368.d)

m/z	Ion	Formula	Abundance
369.0879	(M+H)+	C21 H18 Cl O4	23832.1

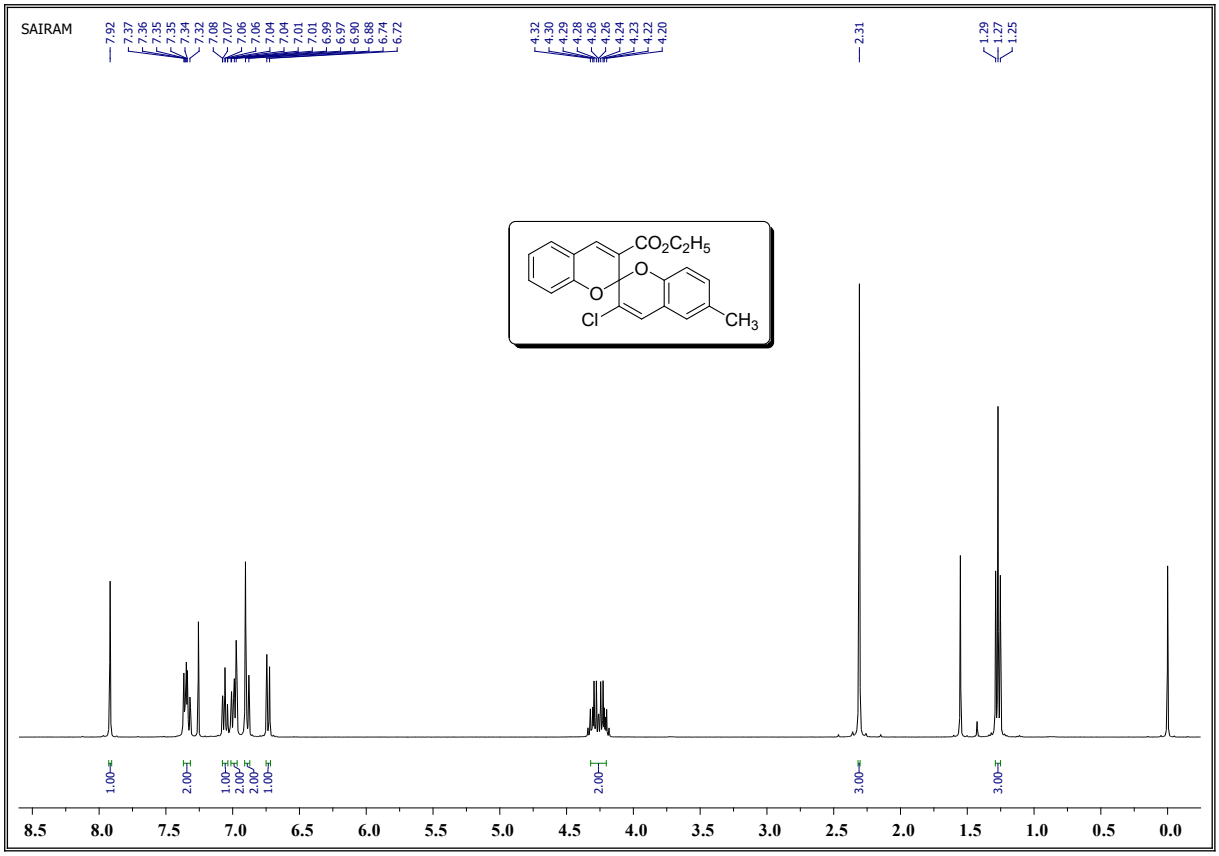
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C21 H17 Cl O4	C21 H18 Cl O4	369.0888	97.47		368.0807	368.0815	2.29	2.29	99.72	98.14	95.79	369.0879	13



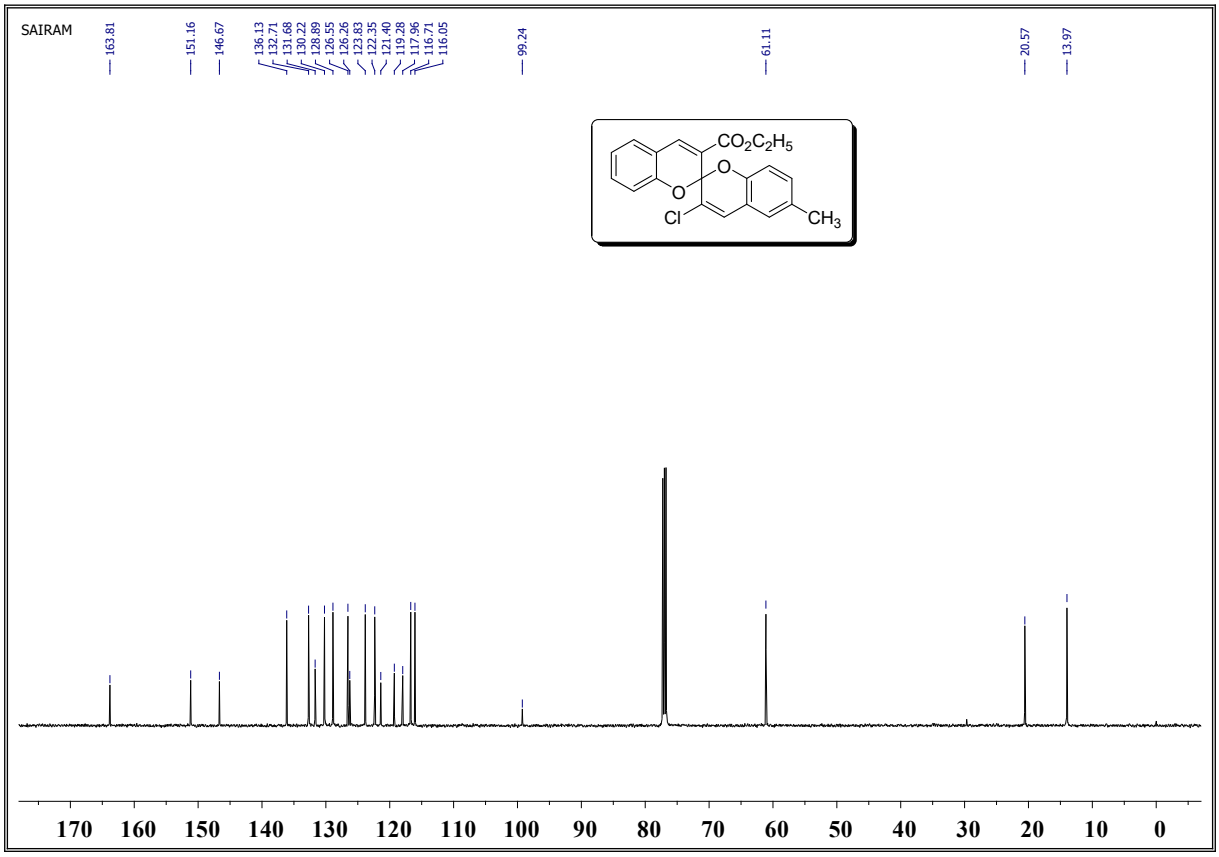
Sample Name	BCR-3-ME-SPKET-368	**Position**	Vial 33	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-3-ME-SPKET-368.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	5/11/2016 12:00:40 PM



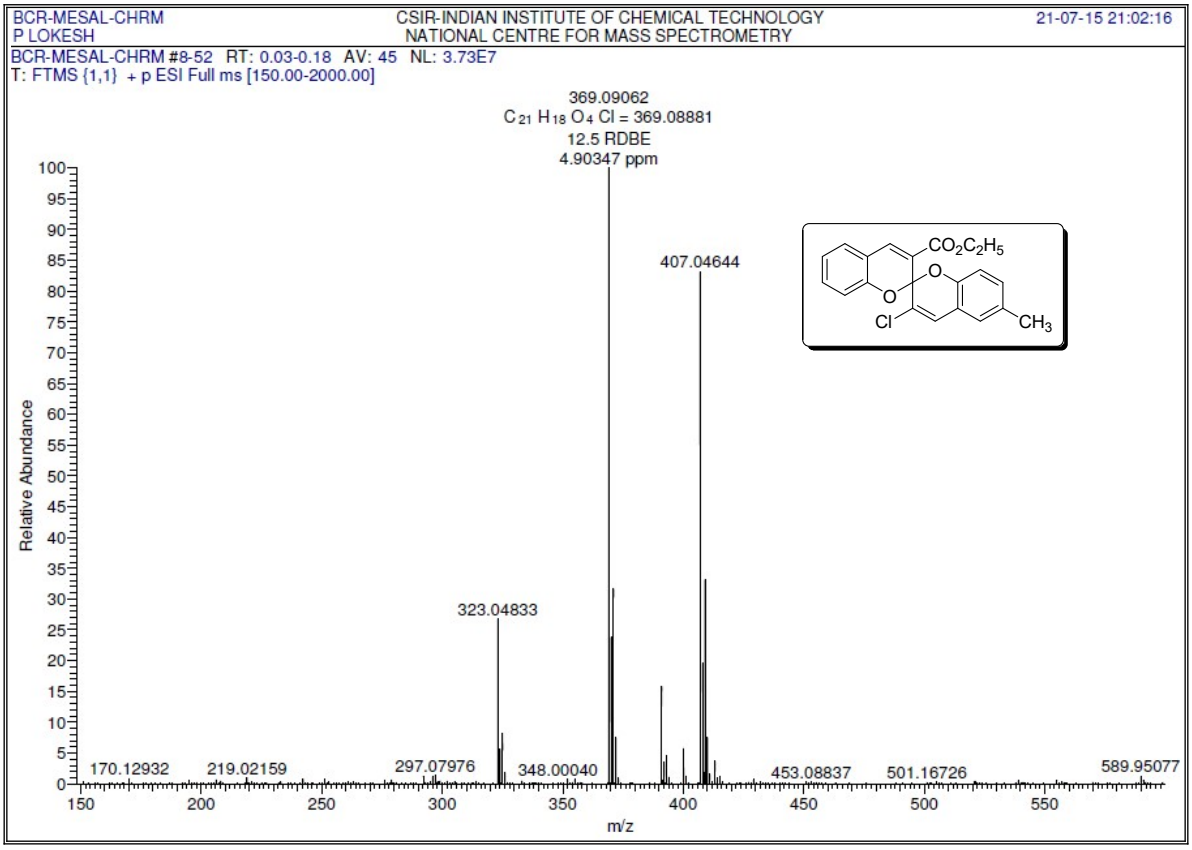
ESI-HRMS of compound **3b**



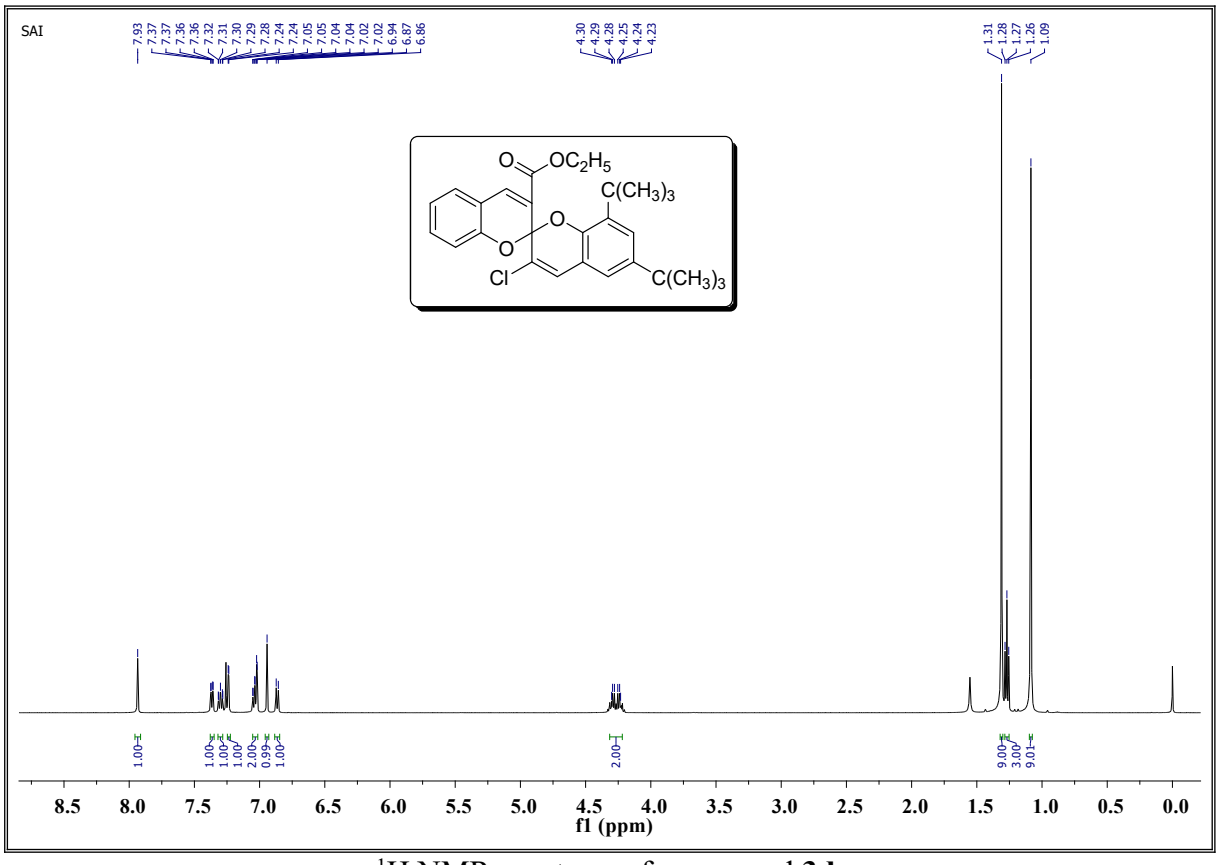
^{1}H NMR spectrum of compound **3c**



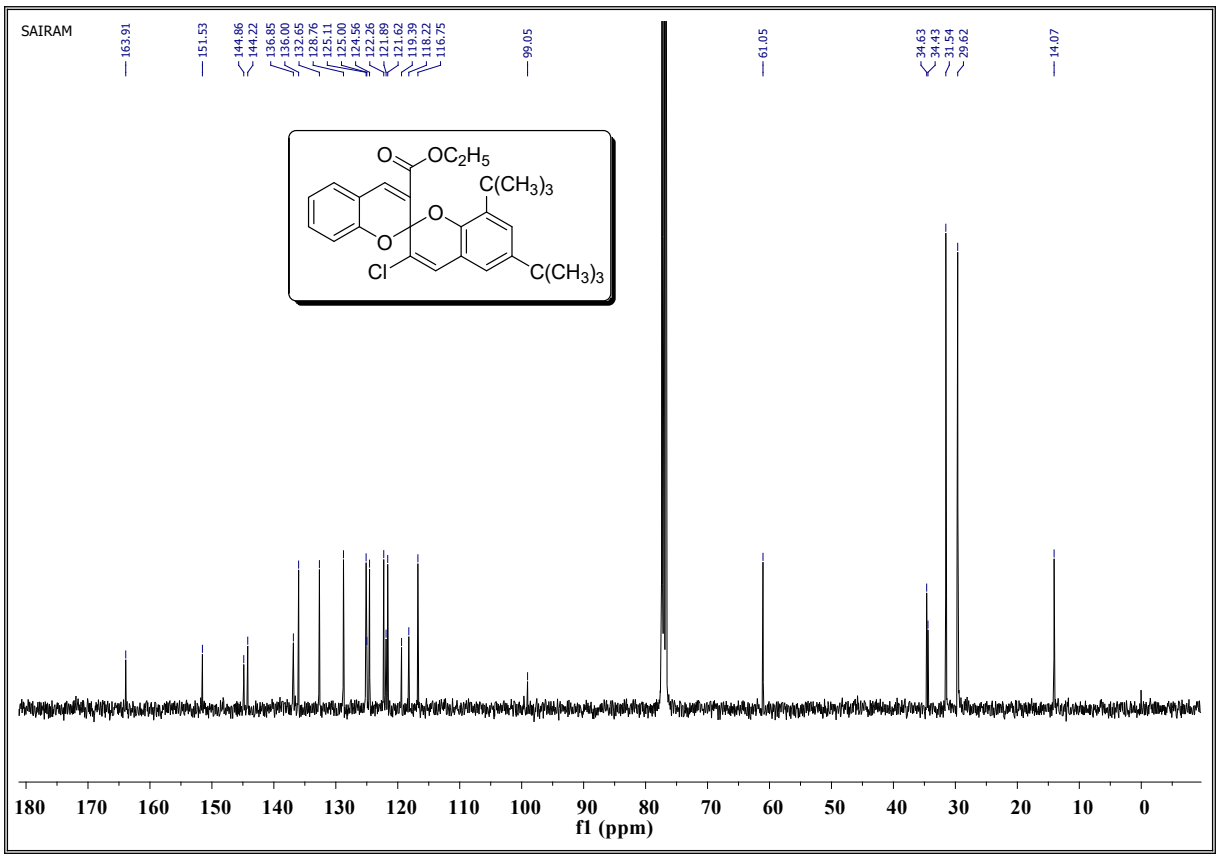
^{13}C NMR spectrum of compound **3c**



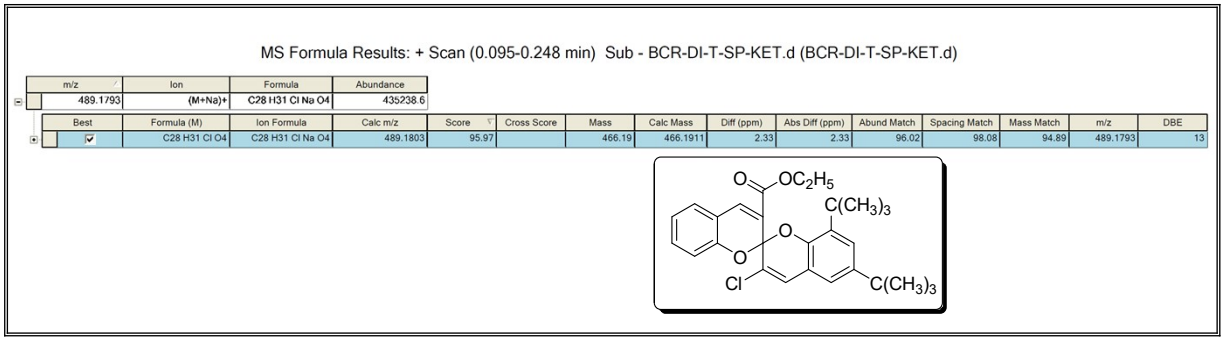
ESI-HRMS of compound **3c**

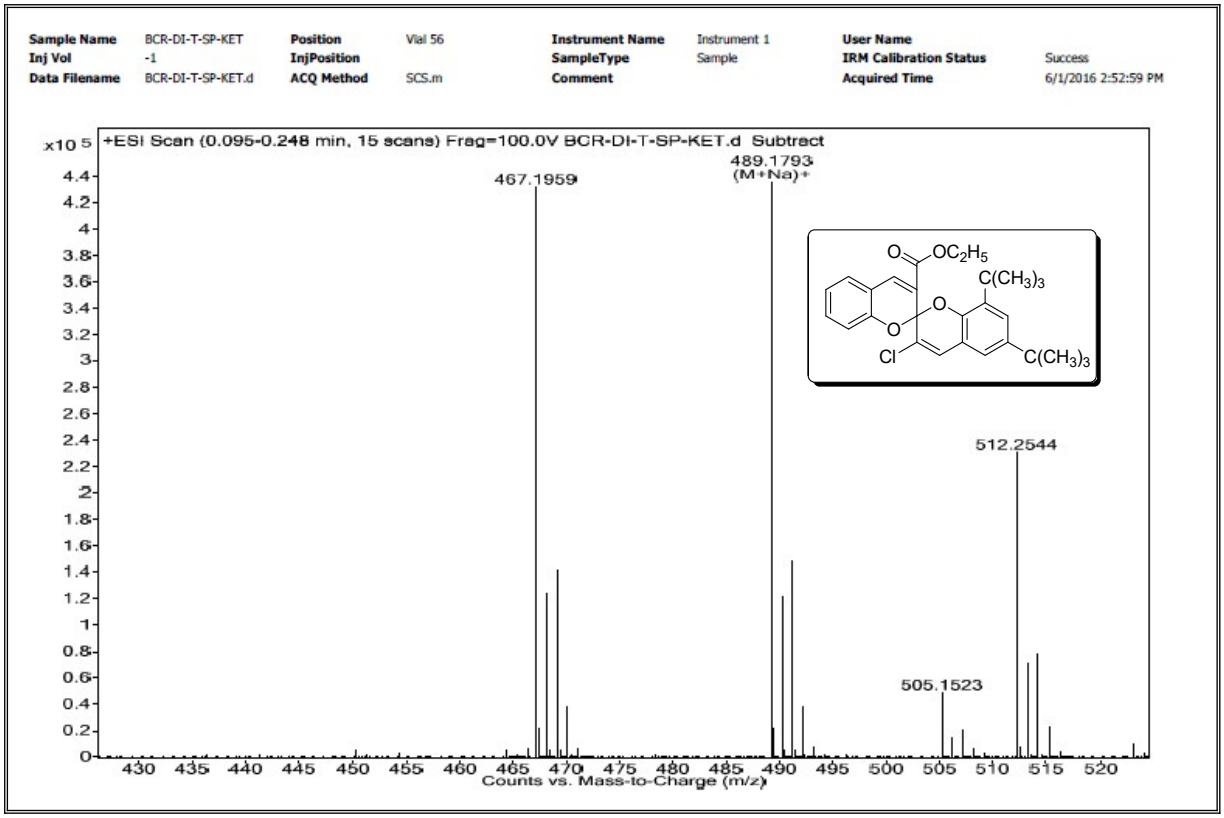


^{1}H NMR spectrum of compound **3d**

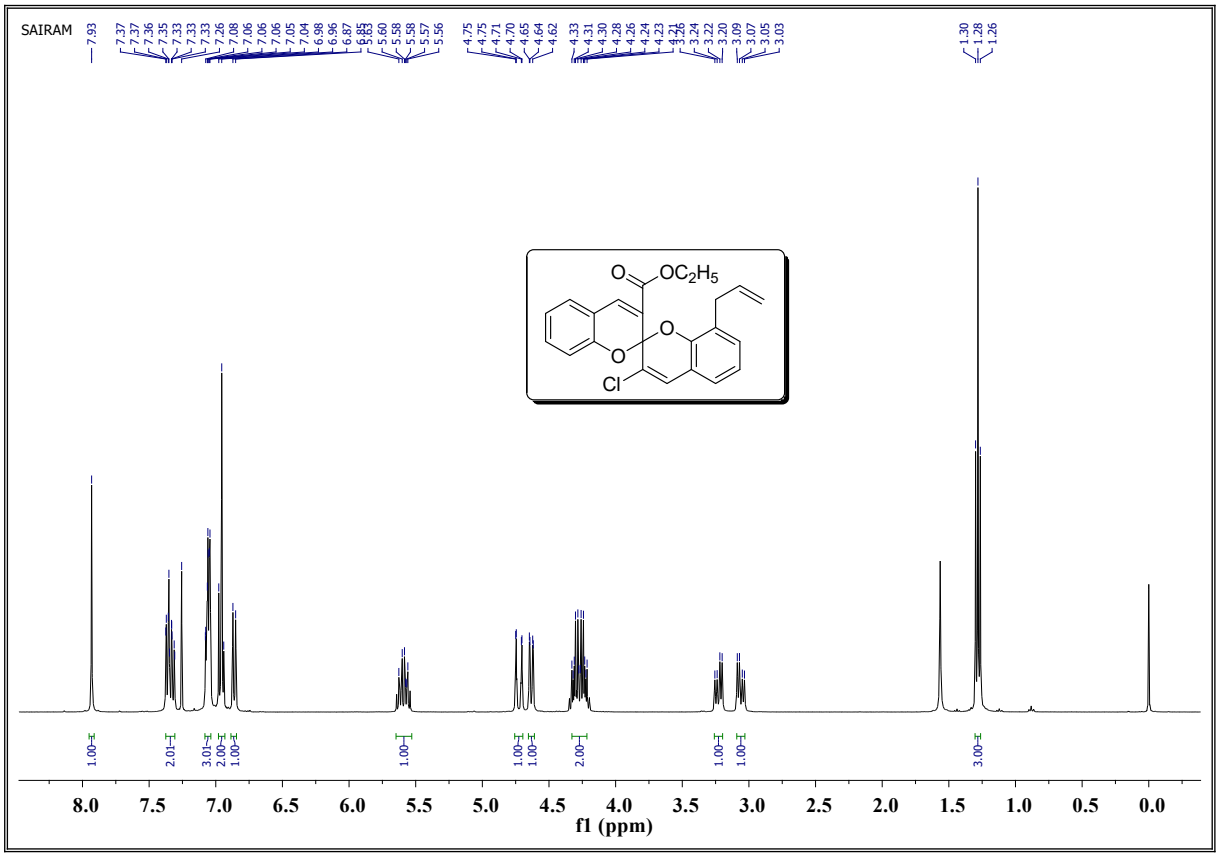


^{13}C NMR spectrum of compound **3d**

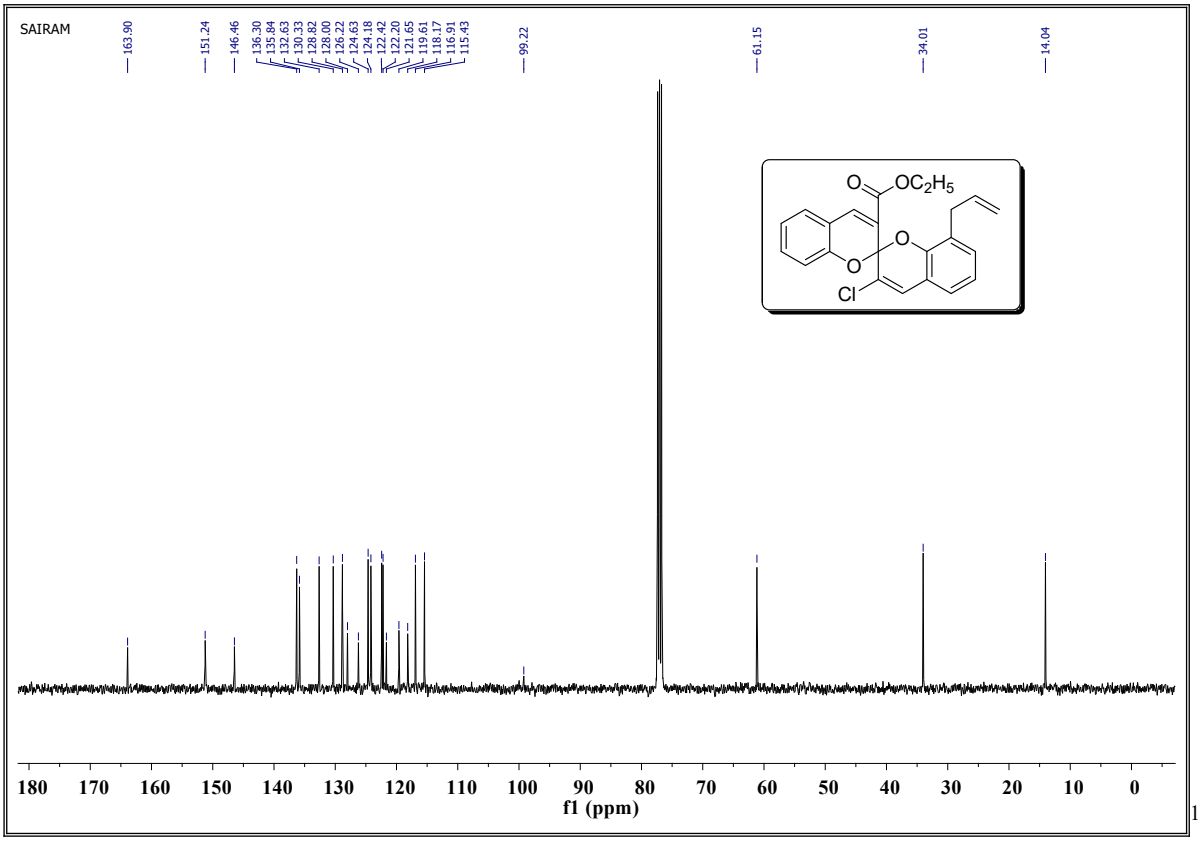




ESI-HRMS of compound **3d**



^{1}H NMR spectrum of compound **3e**

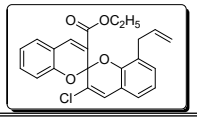


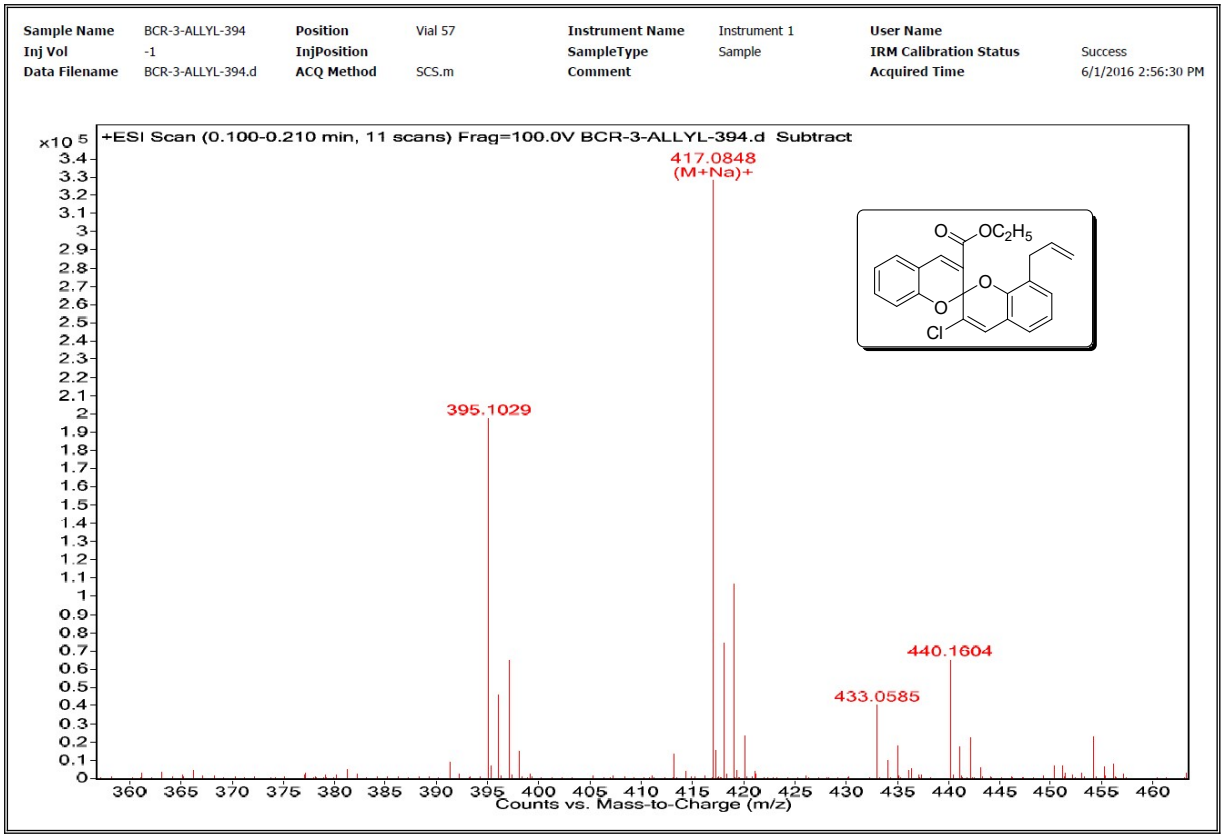
^{3}C NMR spectrum of compound **3e**

MS Formula Results: + Scan (0.100-0.210 min) Sub - BCR-3-ALLYL-394.d (BCR-3-ALLYL-394.d)

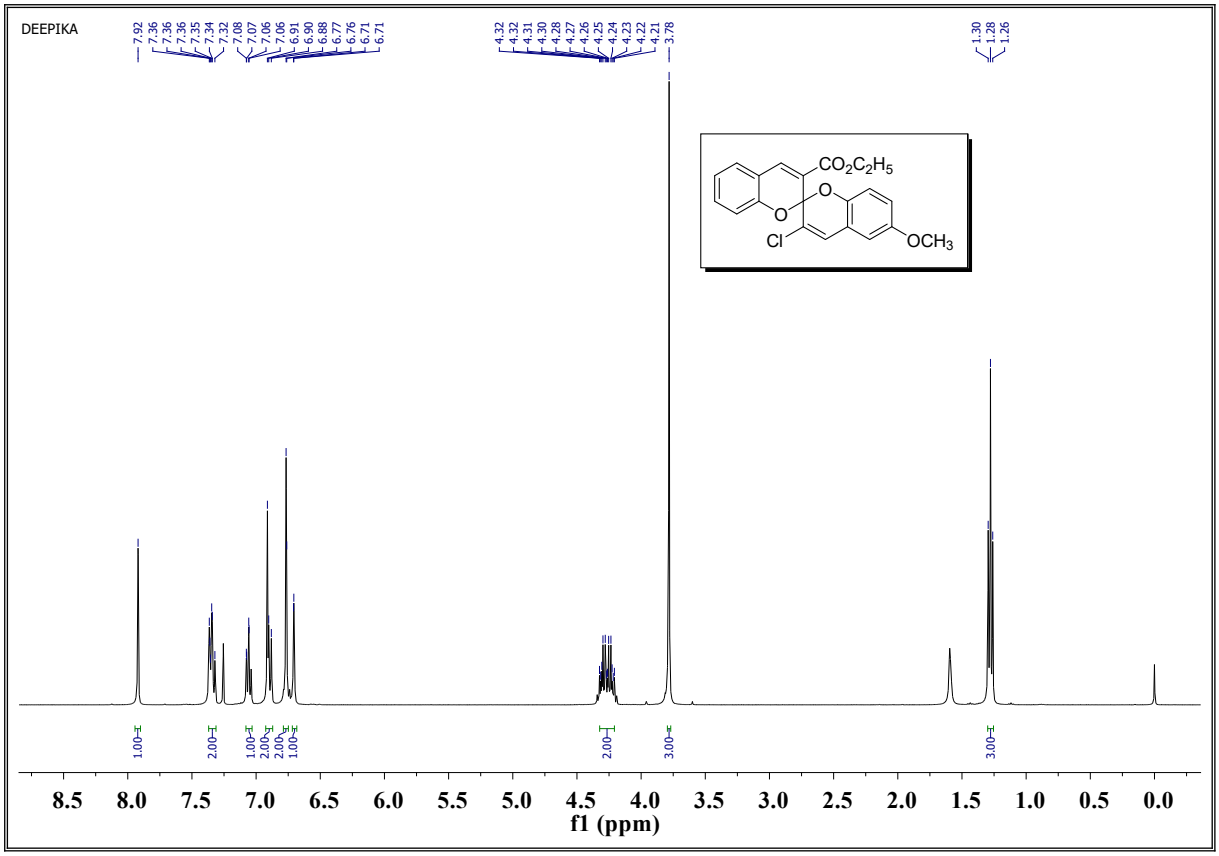
m/z	Ion	Formula	Abundance
417.0848	(M+Na)+	C23 H19 Cl Na O4	327875

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C23 H19 Cl O4	C23 H19 Cl Na O4	417.0864	92.56		394.0956	394.0972	4.02	4.02	95.91	98.67	87.49	417.0848	14

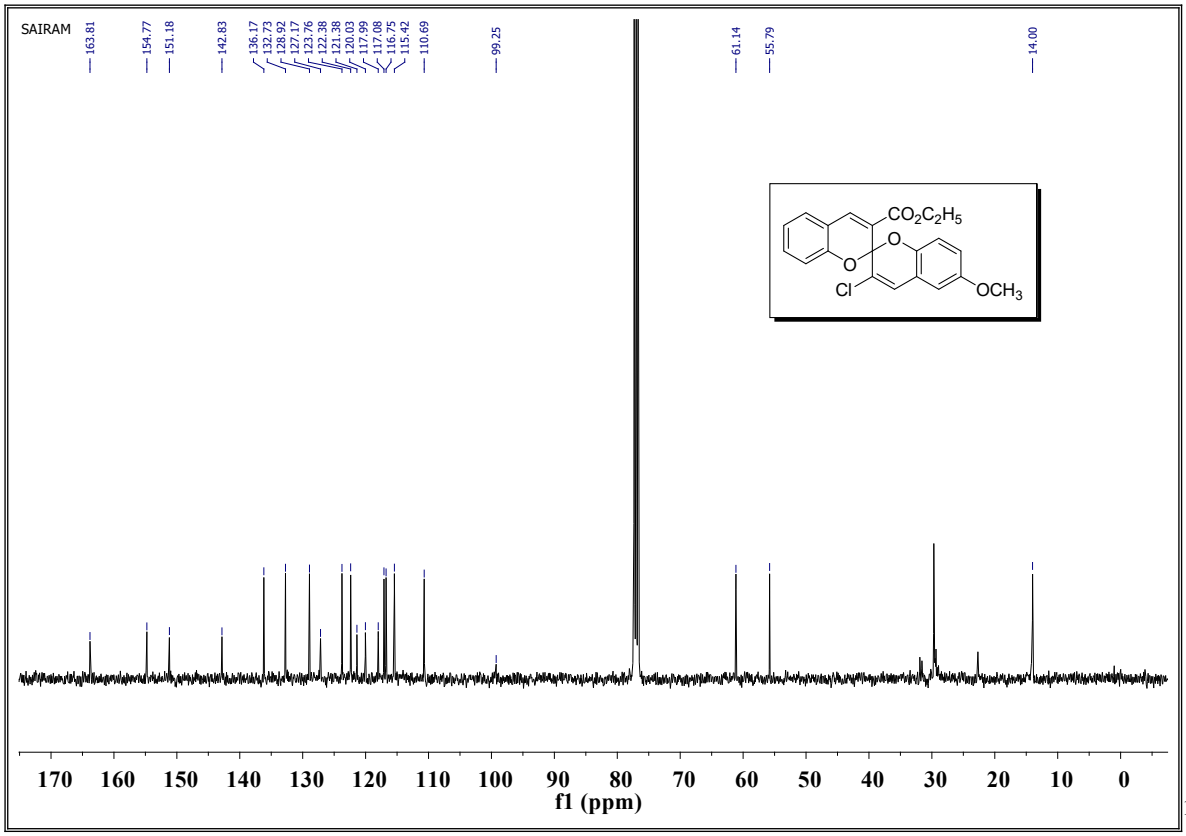




ESI-HRMS of compound **3e**



^{1}H NMR spectrum of compound **3f**



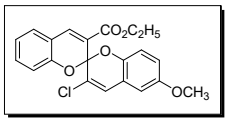
13

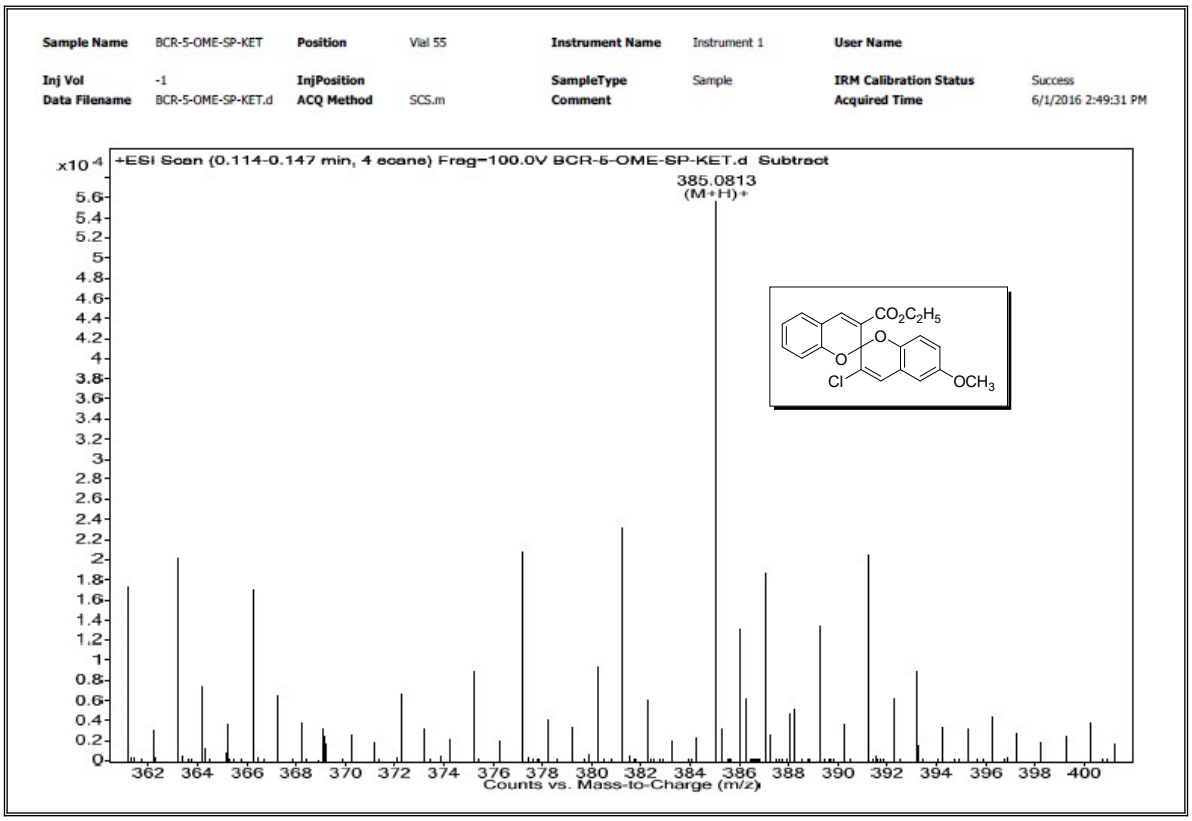
C NMR spectrum of compound **3f**

MS Formula Results: + Scan (0.114-0.147 min) Sub - BCR-5-OME-SP-KET.d (BCR-5-OME-SP-KET.d)

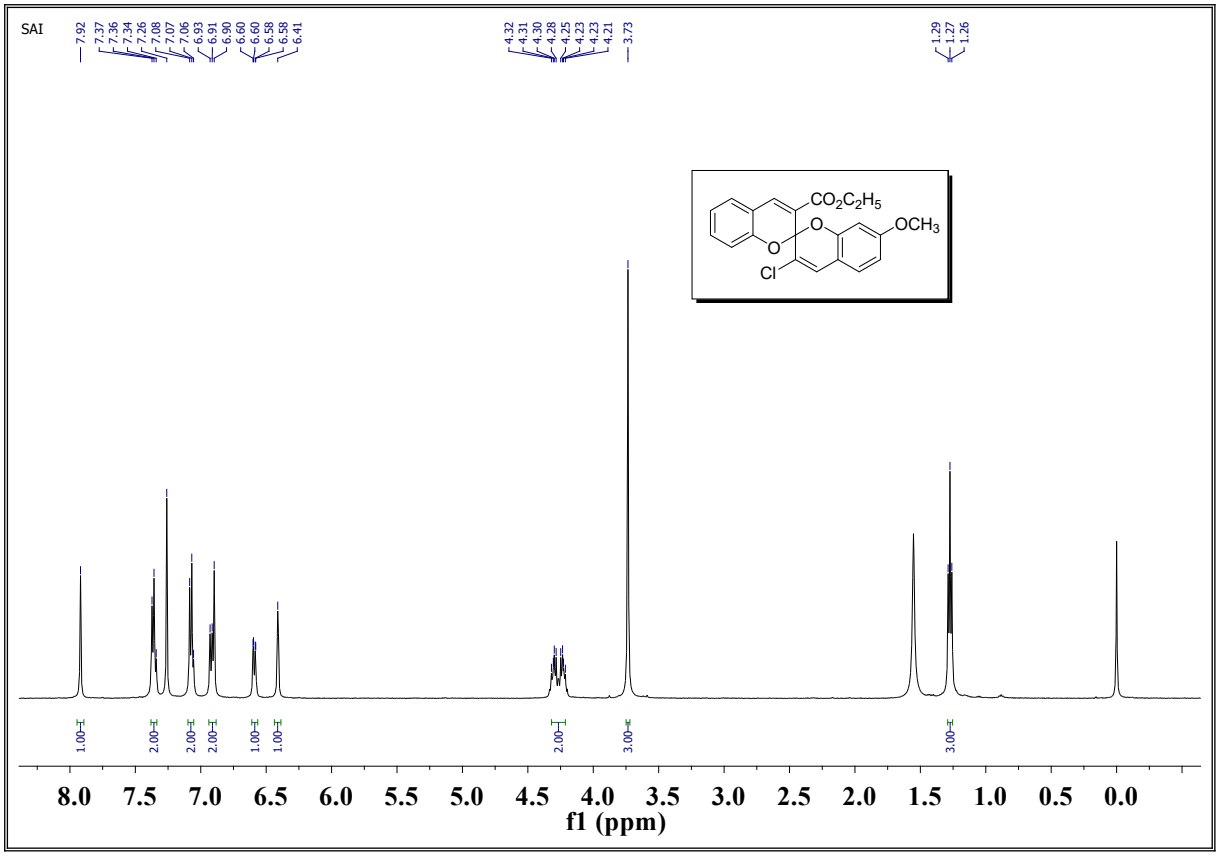
m/z	Ion	Formula	Abundance
385.0813	(M+H)+	C21 H18 Cl O5	55647.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C21 H17 Cl O5	C21 H18 Cl O5	385.0837	85.4		384.074	384.0765	6.28	6.28	96.91	99.54	71.42	385.0813	13

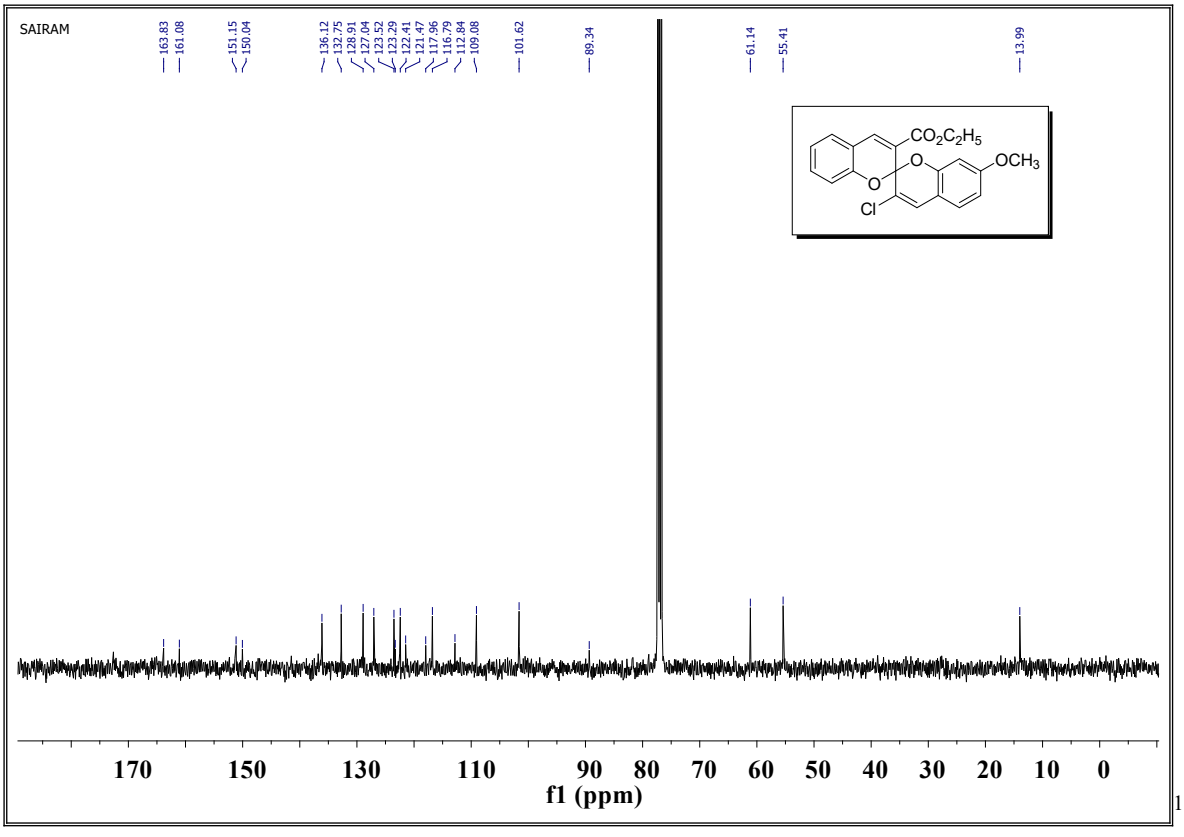




ESI-HRMS of compound **3f**



^{1}H NMR spectrum of compound **3g**

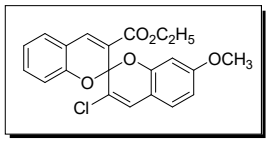


^{13}C NMR spectrum of compound **3g**

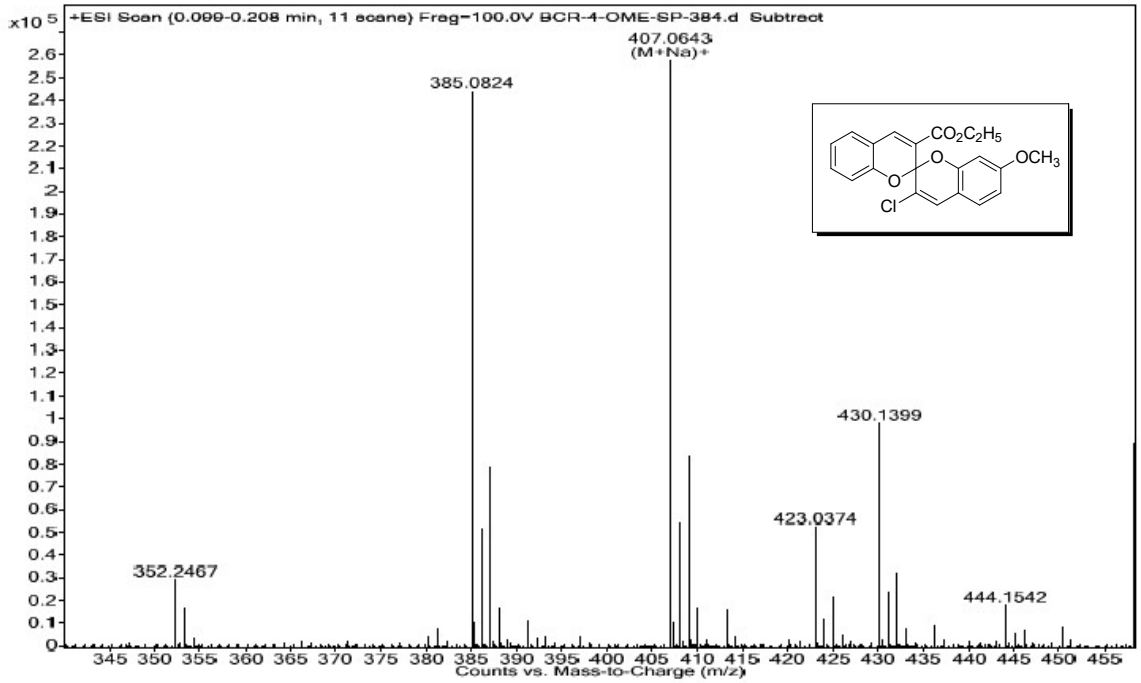
MS Formula Results: + Scan (0.099-0.208 min) Sub - BCR-4-OME-SP-384.d (BCR-4-OME-SP-384.d)

m/z	Ion	Formula	Abundance
407.0643	(M+Na)+	C21 H17 Cl Na O5	257590.8

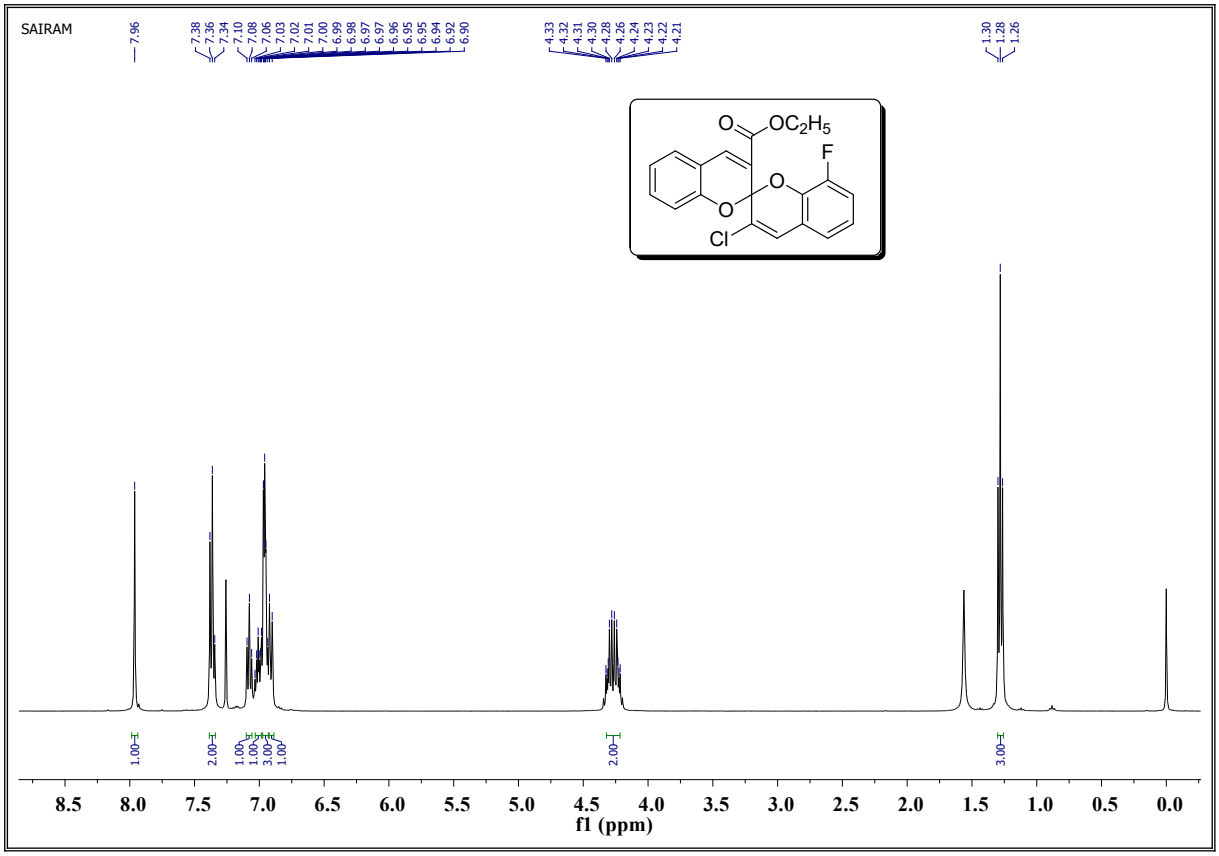
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C21 H17 Cl O5	C21 H17 Cl Na O5	407.0657	93.89		384.0751	384.0765	3.54	3.54	96.41	97.85	90.39	407.0643	13



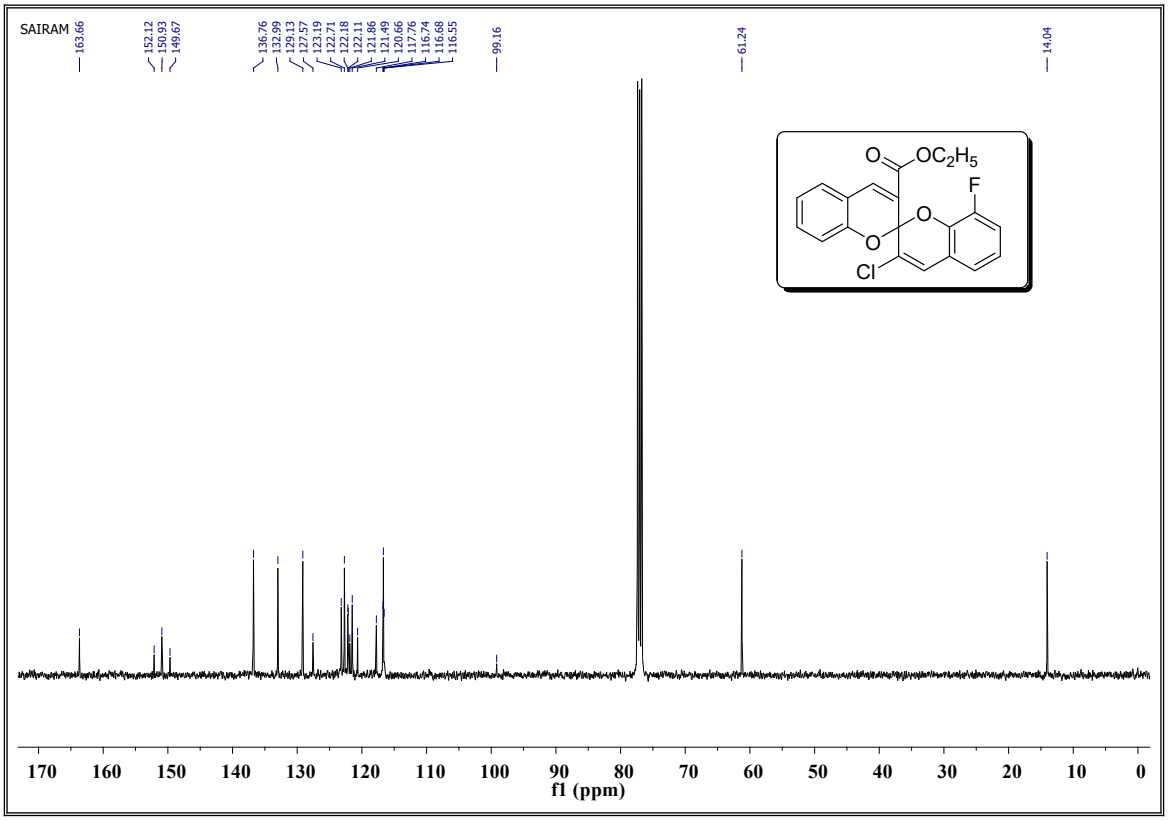
Sample Name	BCR-4-OME-SP-384	**Position**	Vial 70	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-4-OME-SP-384.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	6/1/2016 3:42:14 PM



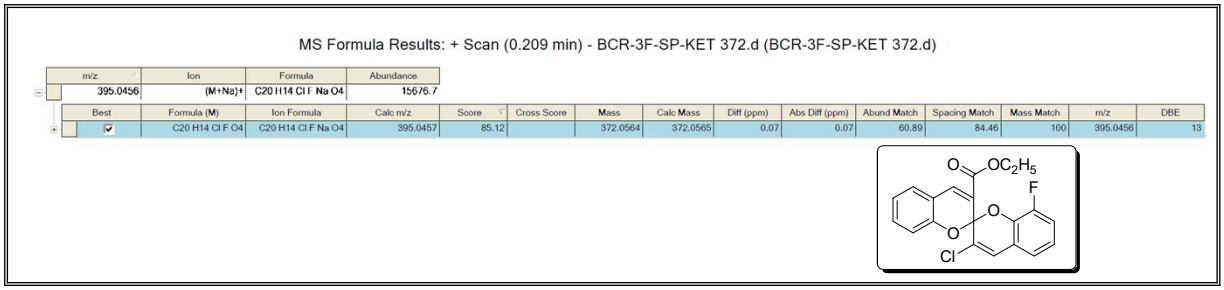
ESI-HRMS of compound **3g**

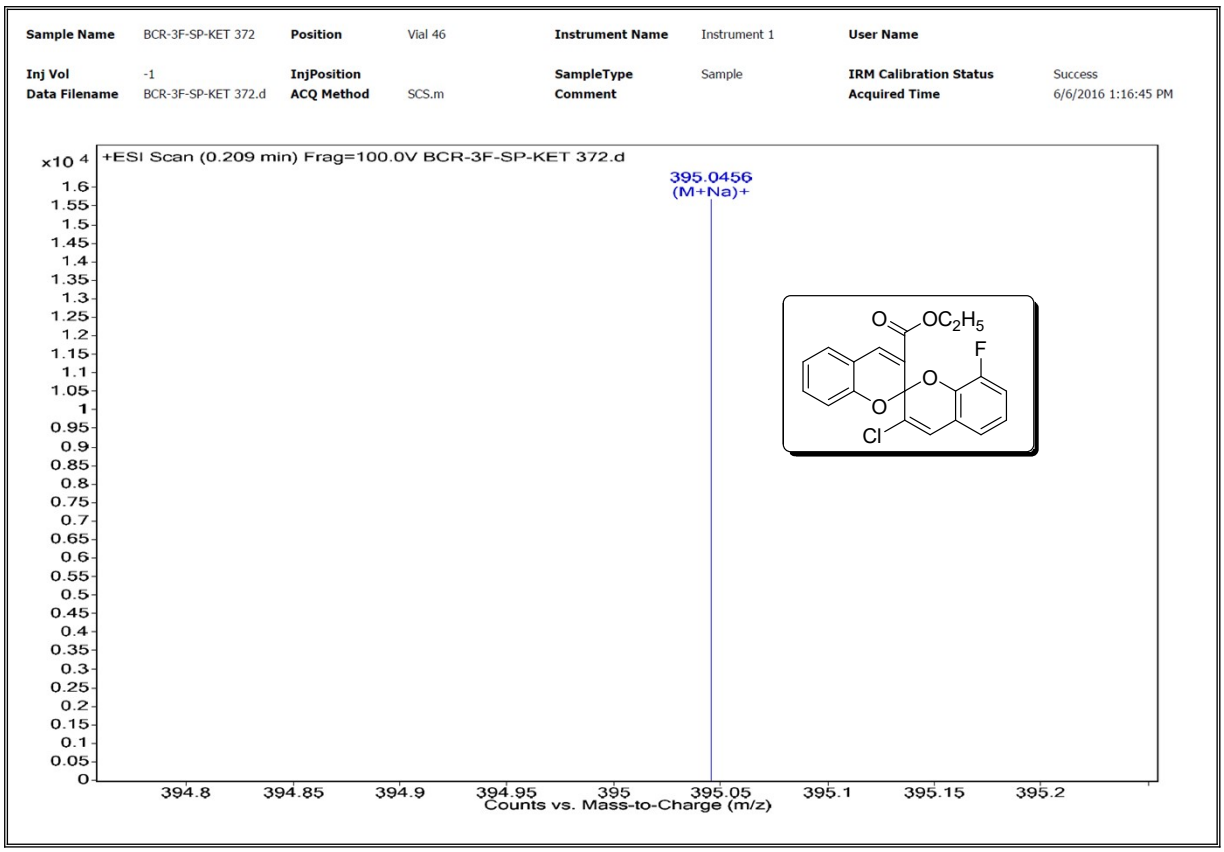


^{1}H NMR spectrum of compound **3h**

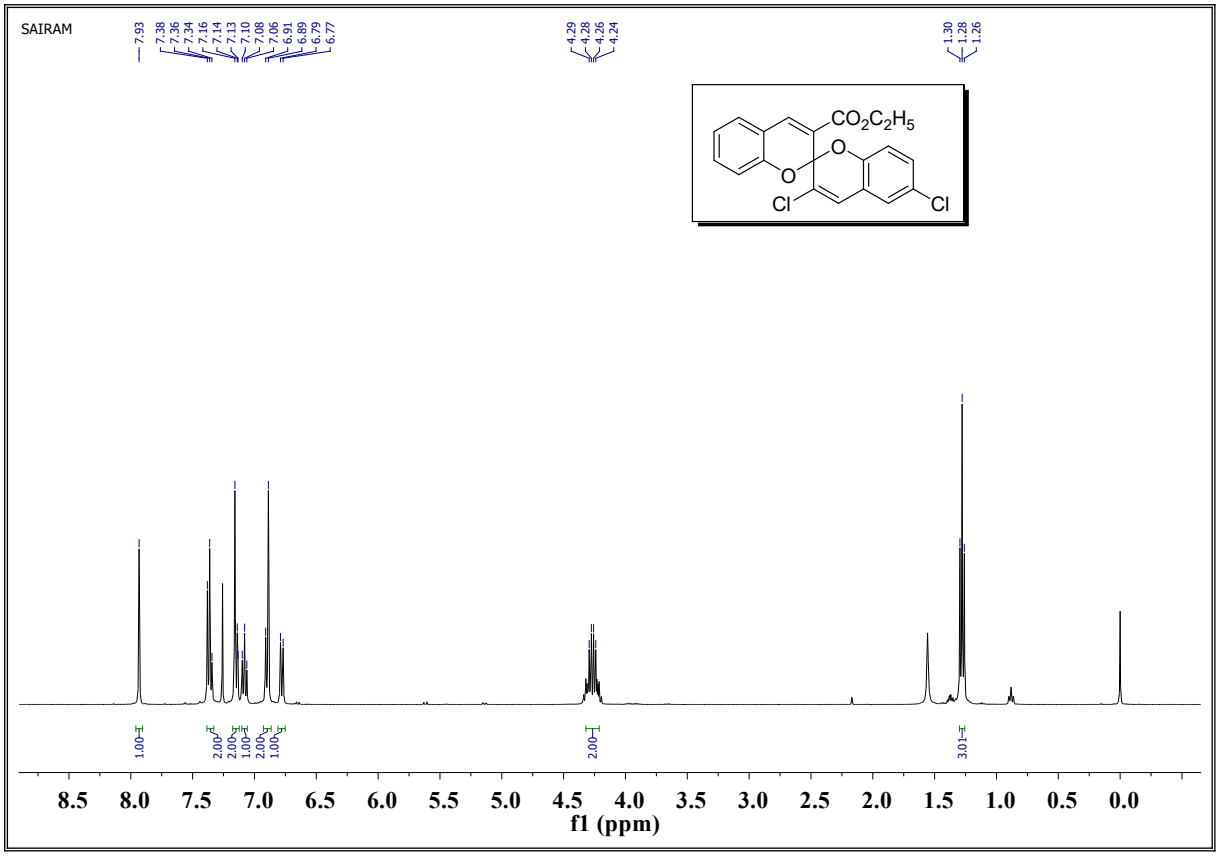


^{13}C NMR spectrum of compound **3h**

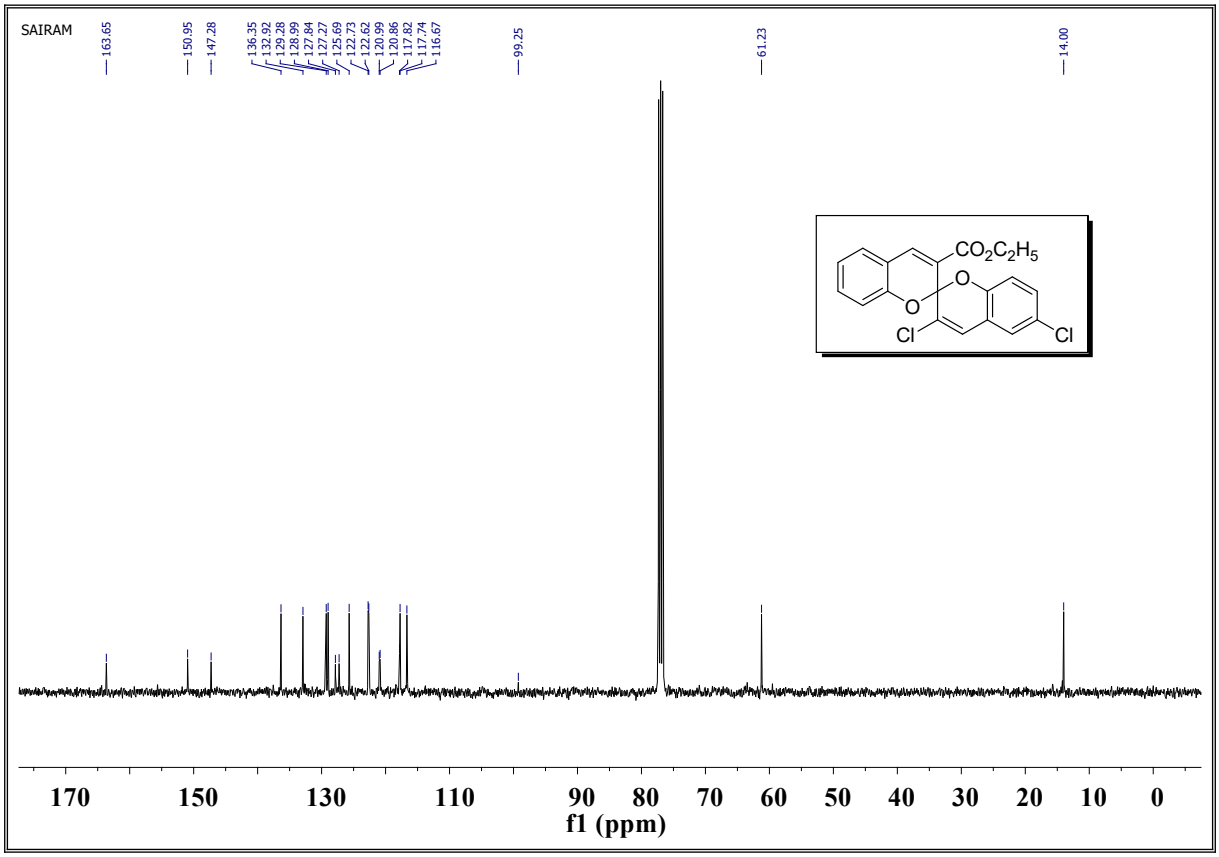




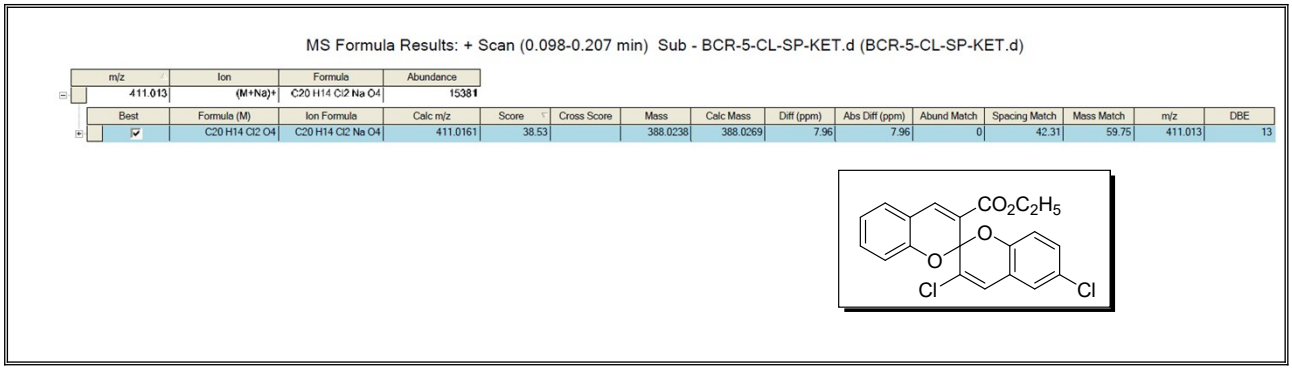
ESI-HRMS of compound **3h**

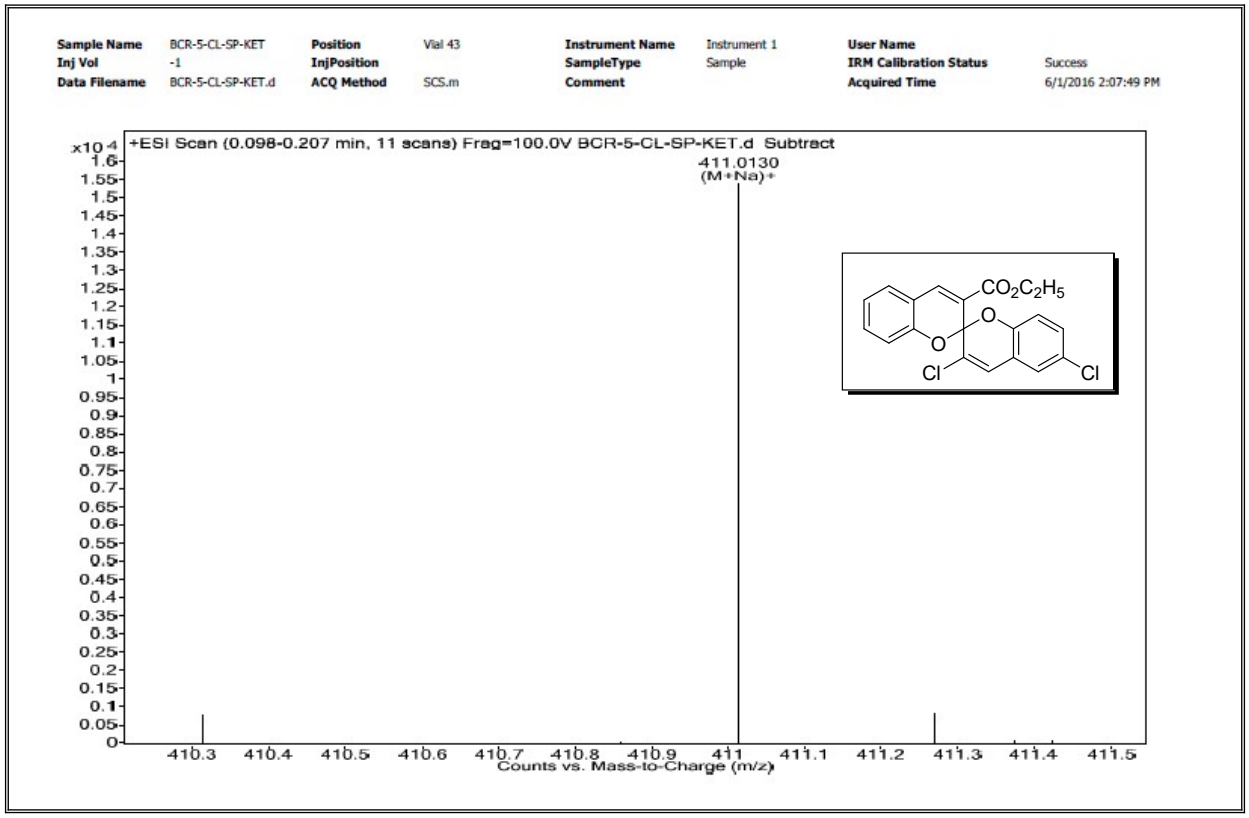


^{1}H NMR spectrum of compound **3i**

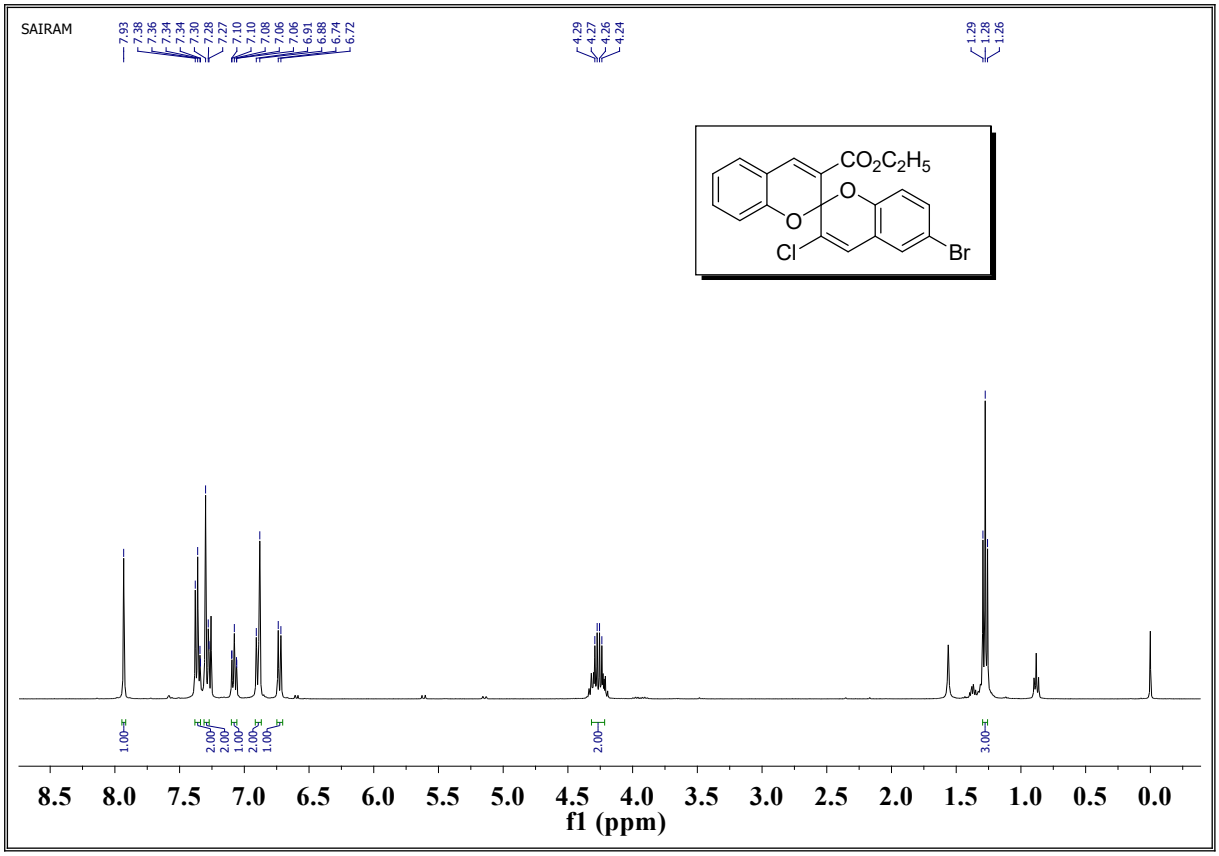


^{13}C NMR spectrum of compound **3i**

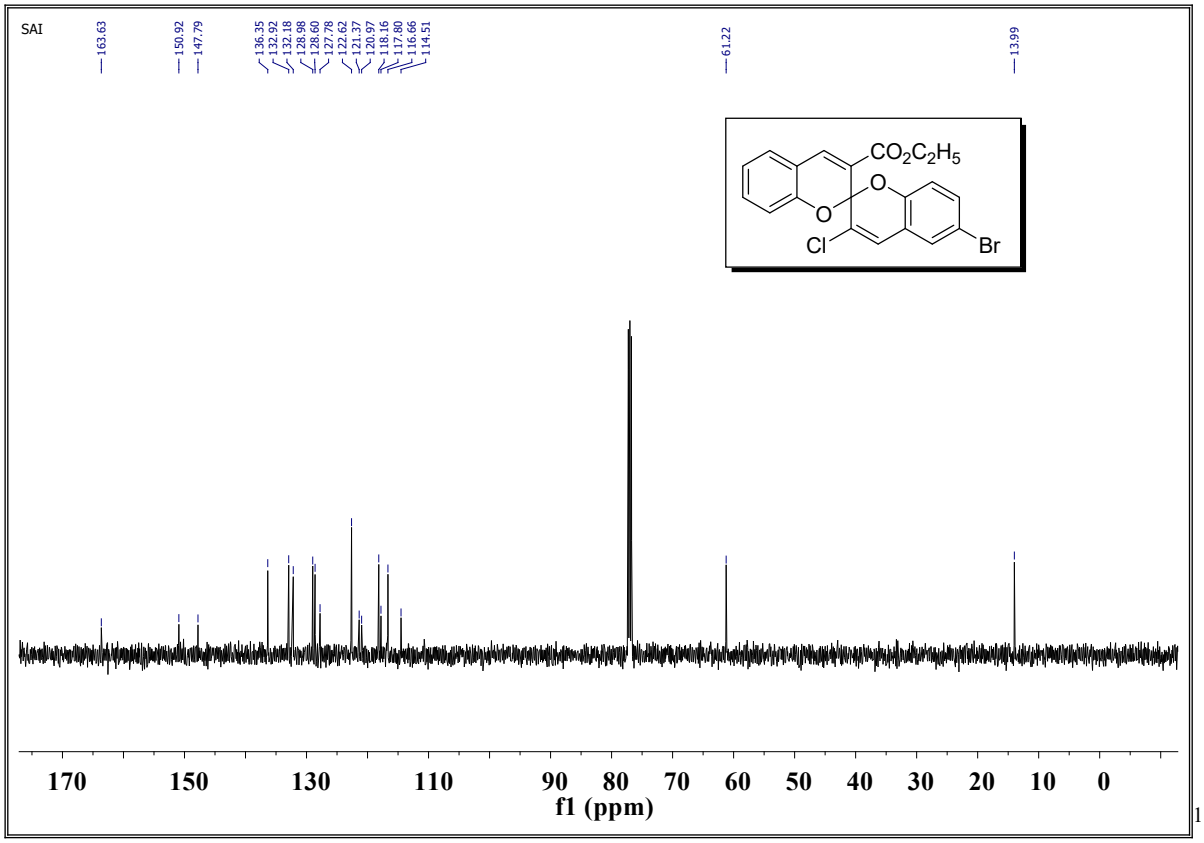




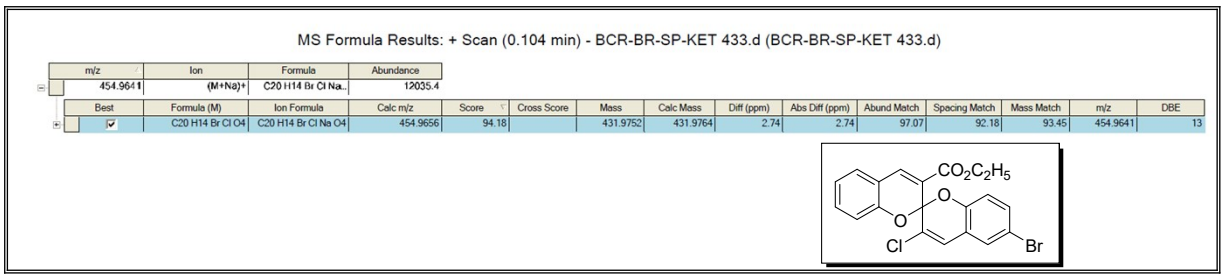
ESI-HRMS of compound **3i**

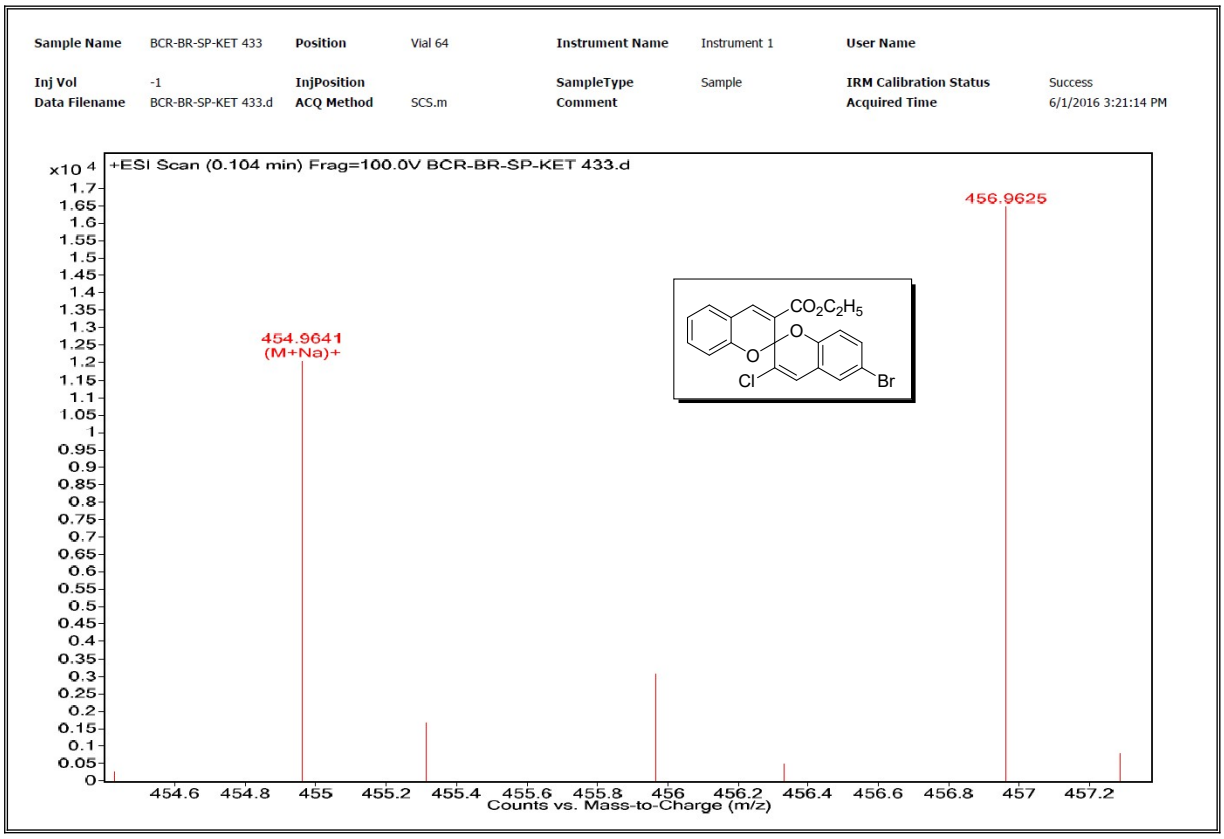


^{1}H NMR spectrum of compound **3k**

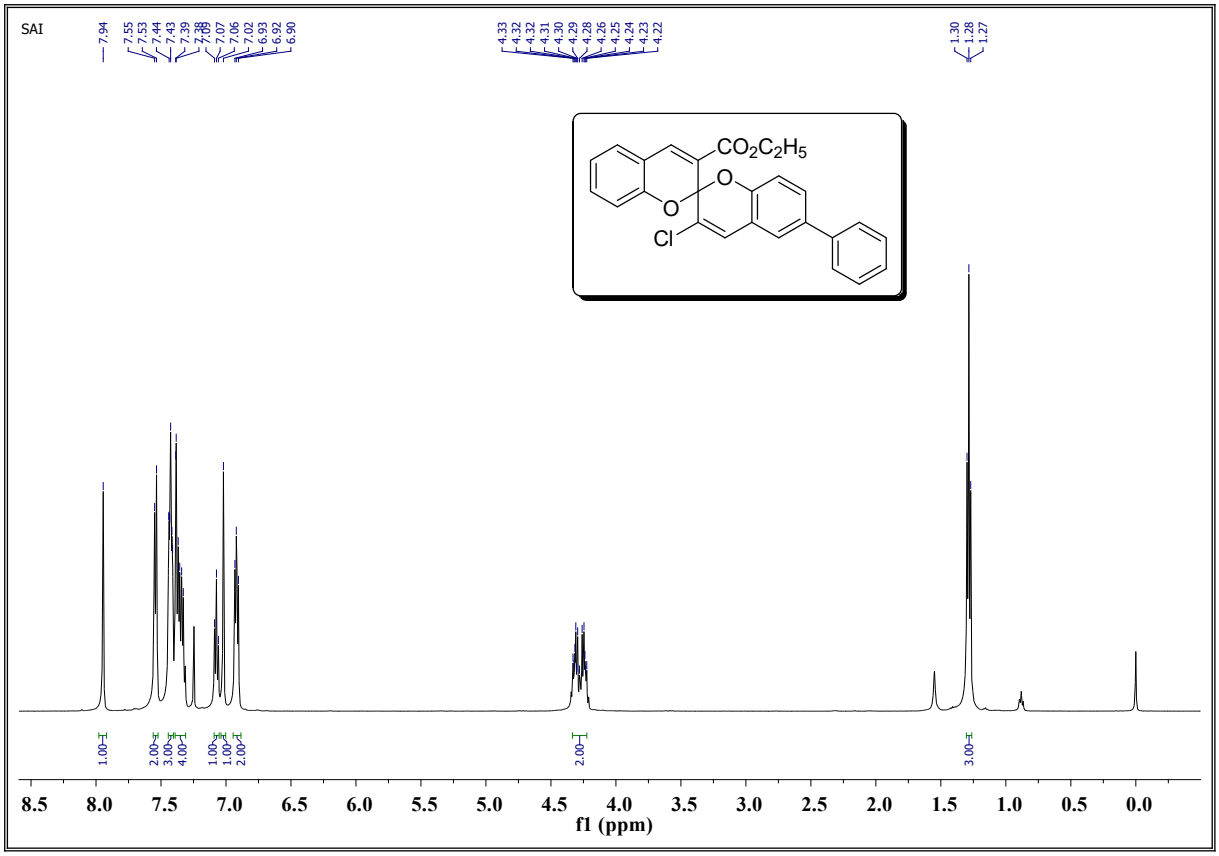


^{3}C NMR spectrum of compound **3k**

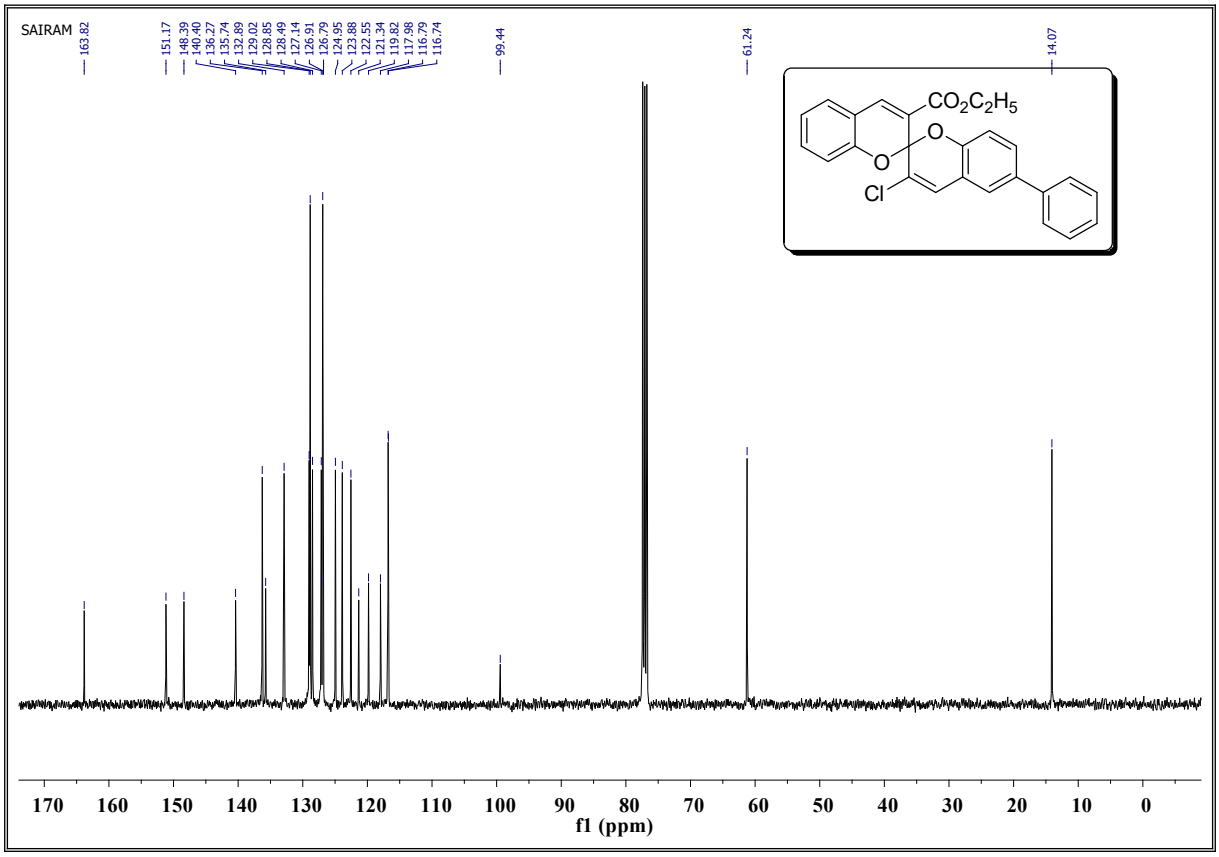




ESI-HRMS of compound **3k**



^{1}H NMR spectrum of compound **3m**

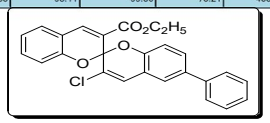


^{13}C NMR spectrum of compound **3m**

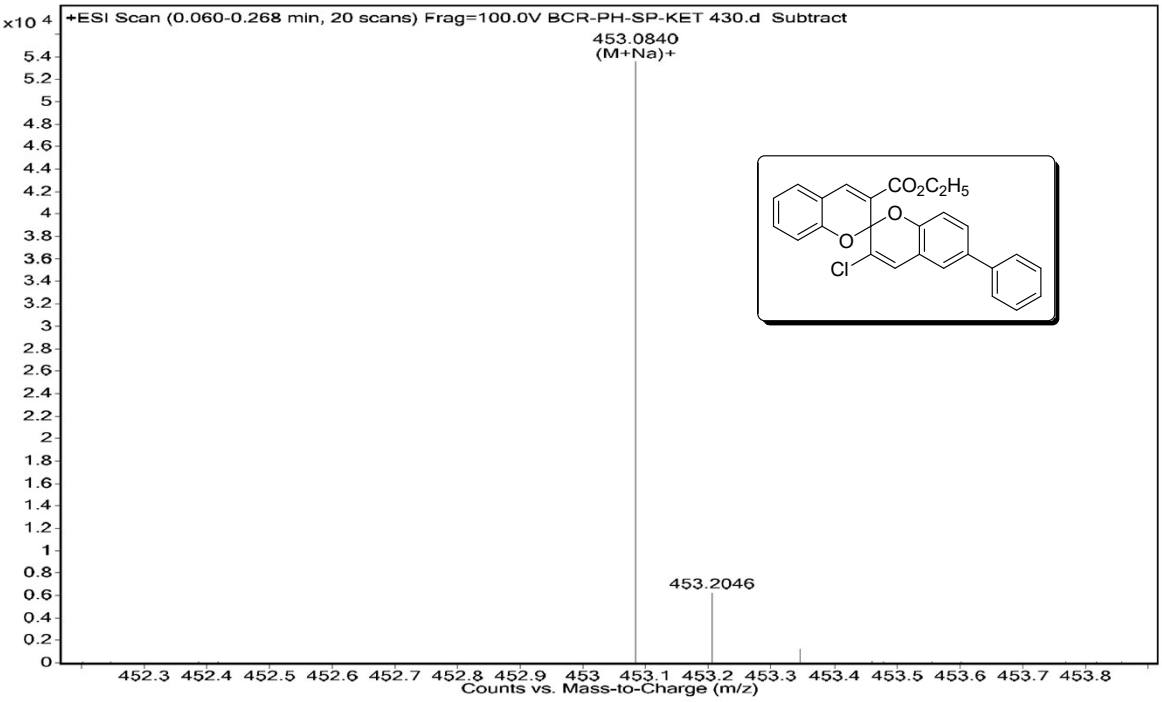
MS Formula Results: + Scan (0.060-0.268 min) Sub - BCR-PH-SP-KET 430.d (BCR-PH-SP-KET 430.d)

m/z	Ion	Formula	Abundance
453.084	(M+Na)+	C26 H19 Cl Na O4	53567.3

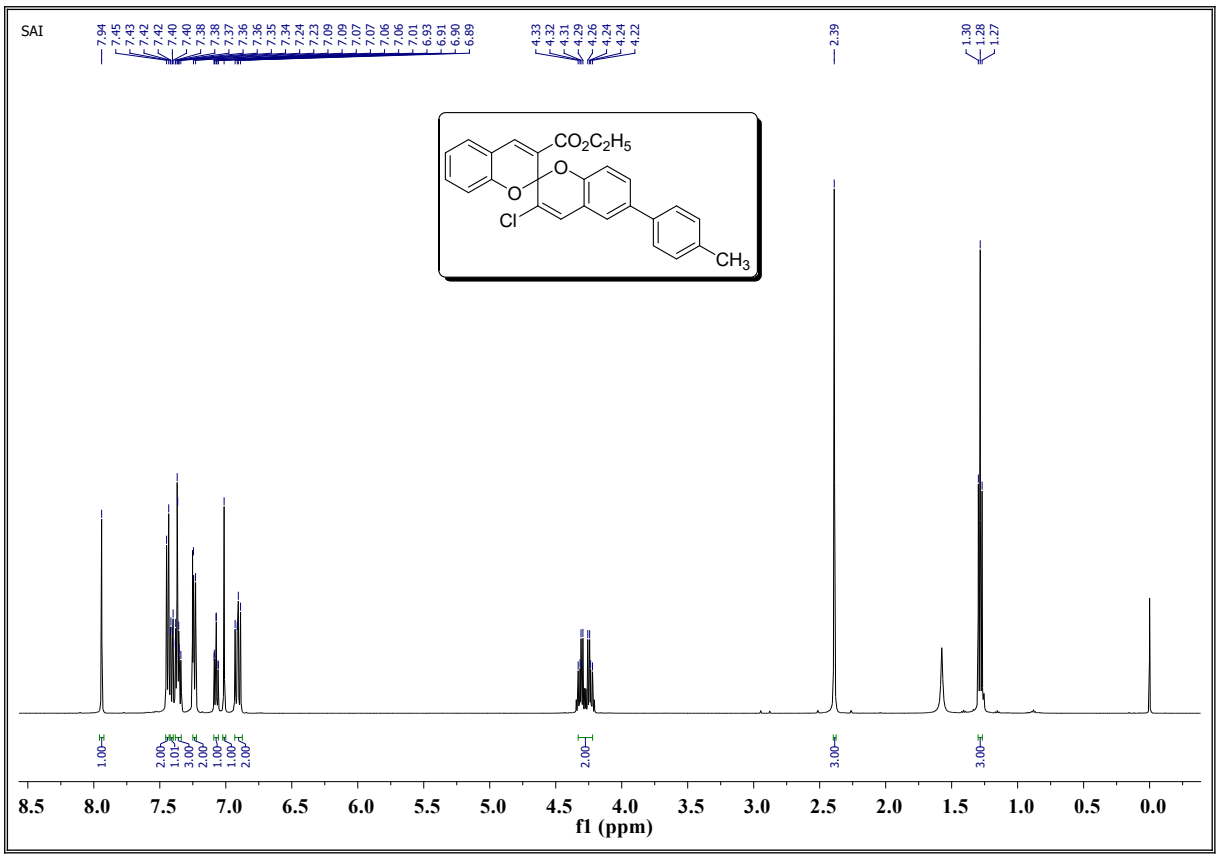
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C26 H19 Cl O4	C26 H19 Cl Na O4	453.0864	87.62		430.0948	430.0972	5.63	5.63	98.11	99.86	75.21	453.084	17



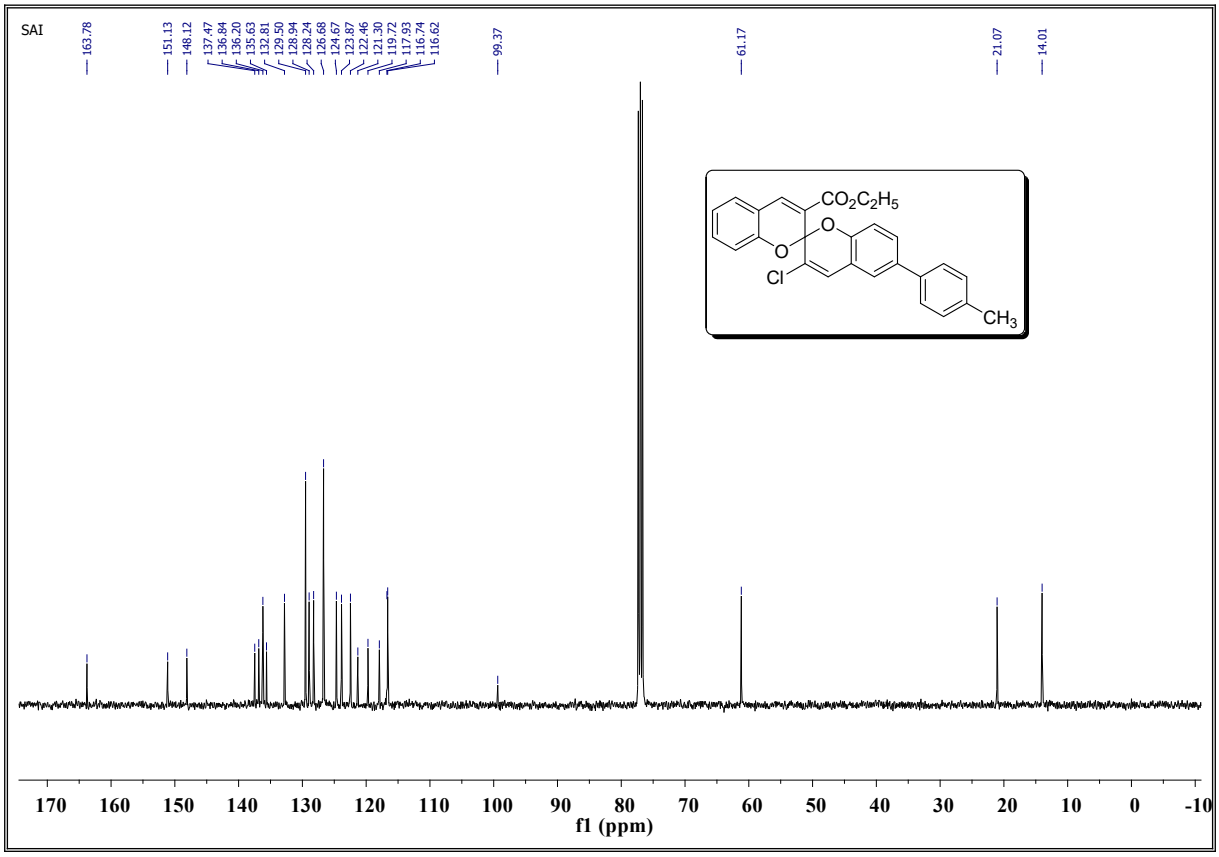
Sample Name	BCR-PH-SP-KET 430	**Position**	Vial 26	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-PH-SP-KET 430.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	5/11/2016 11:36:41 A



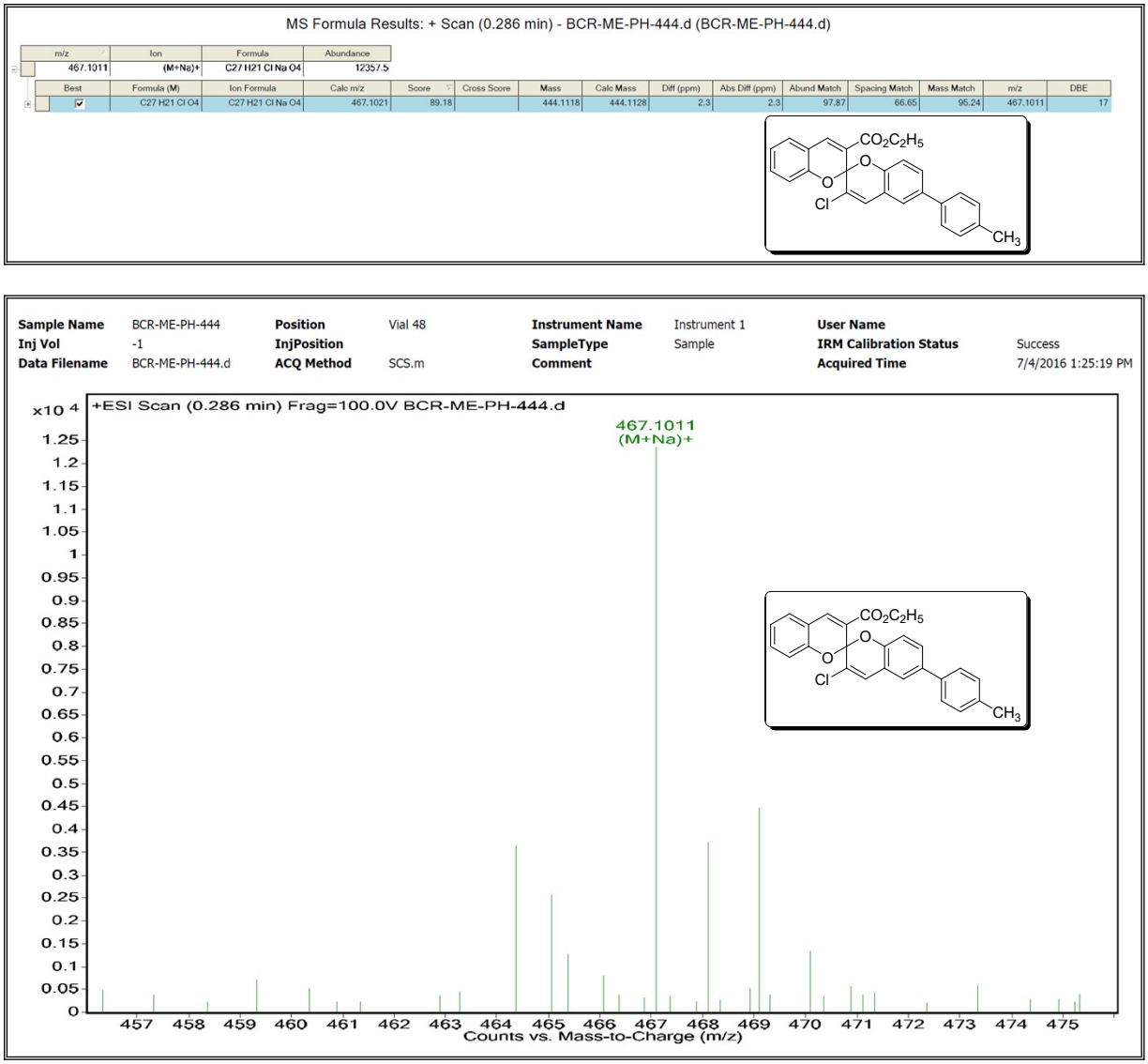
ESI-HRMS of compound **3m**



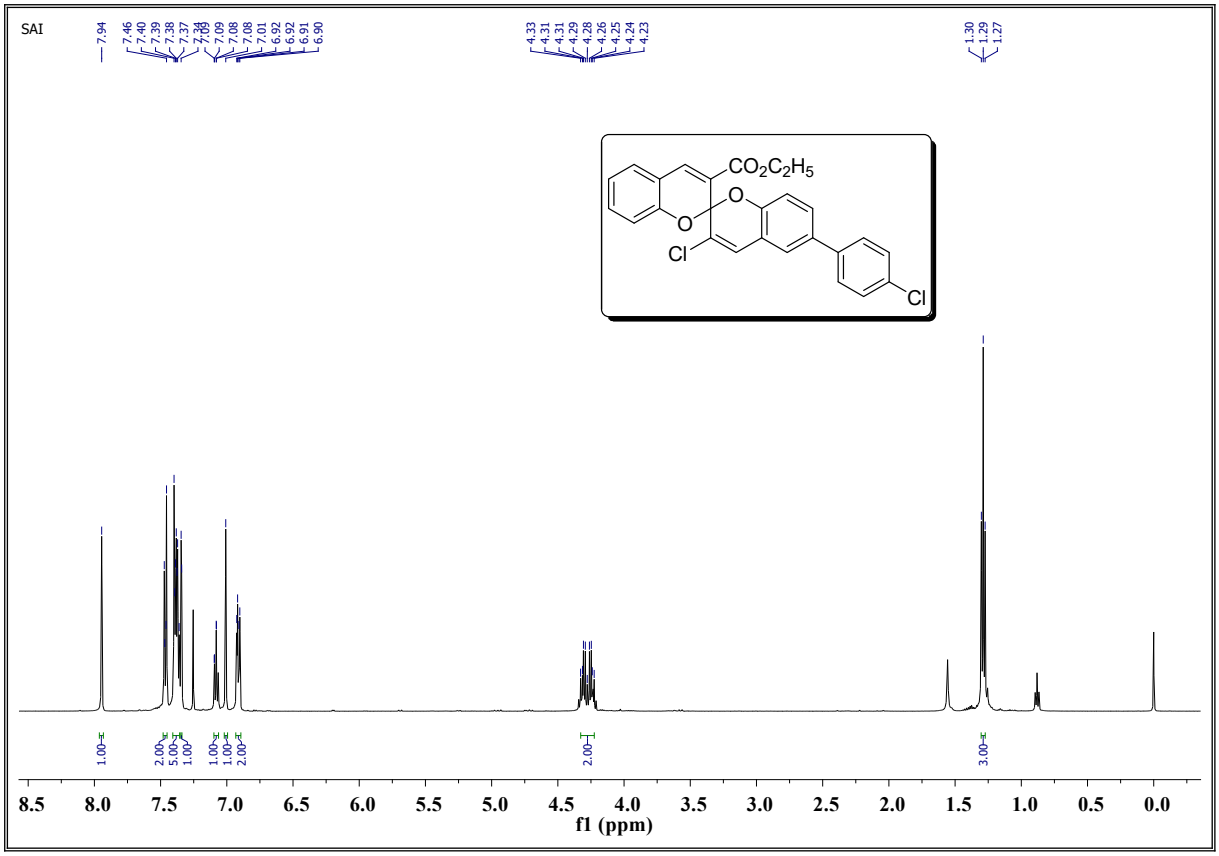
^{1}H NMR spectrum of compound **3n**



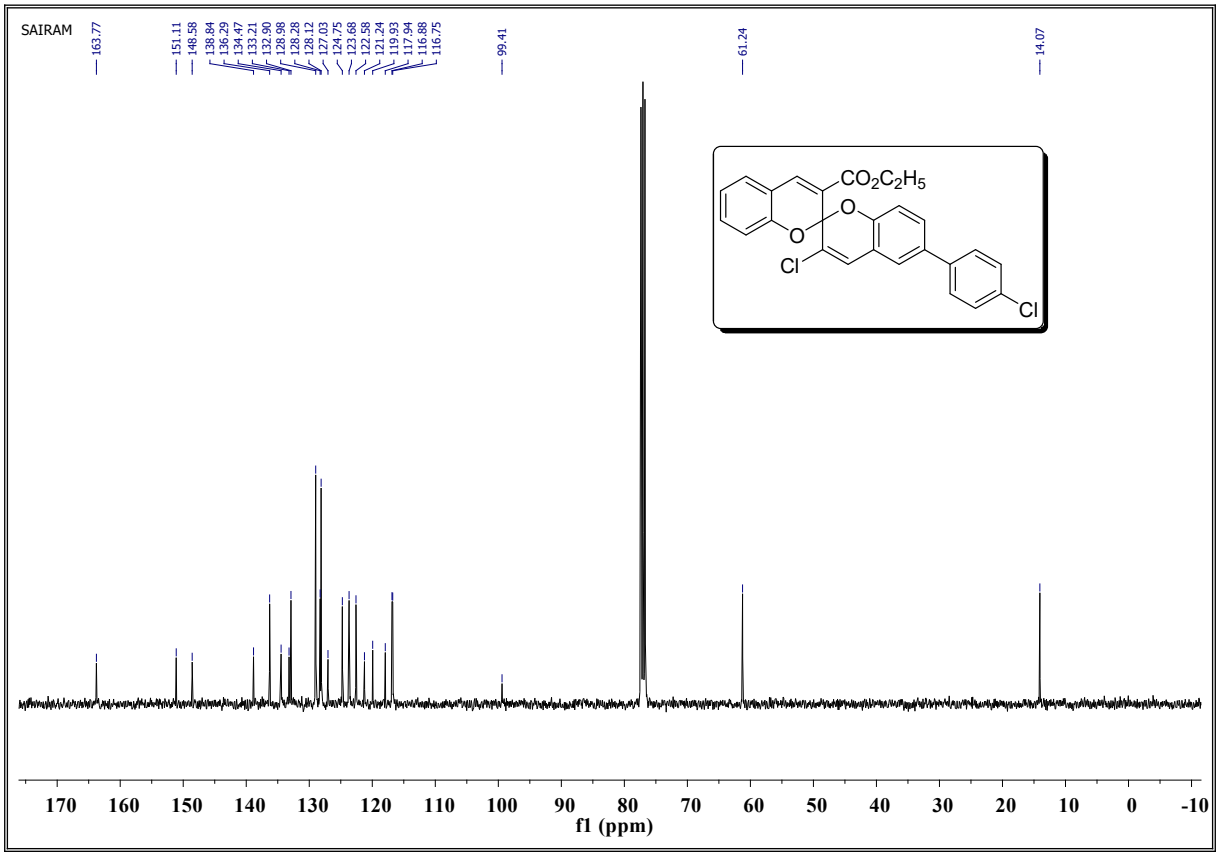
^{13}C NMR spectrum of compound **3n**



ESI-HRMS of compound **3n**



^{1}H NMR spectrum of compound **3o**

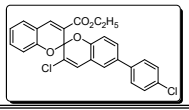


^{13}C NMR spectrum of compound **3o**

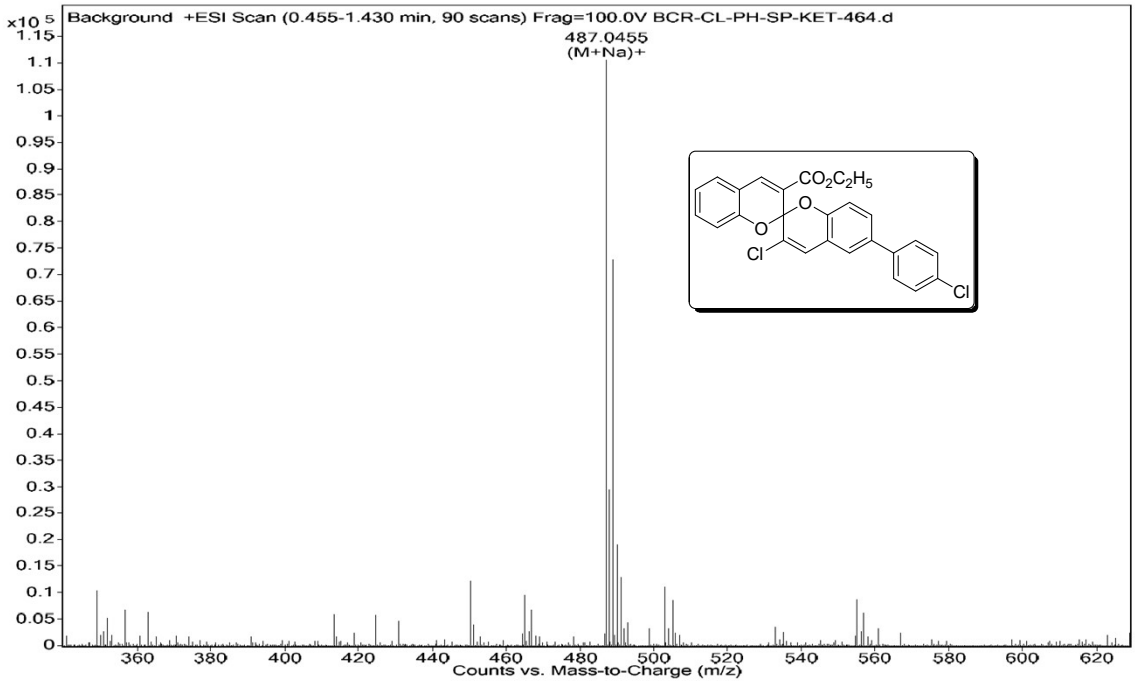
MS Formula Results: + Scan (0.455-1.430 min) - BCR-CL-PH-SP-KET-464.d (BCR-CL-PH-SP-KET-464.d)

m/z	Ion	Formula	Abundance
487.0455	(M+Na)+	C26 H18 Cl2 Na O4	110466.7

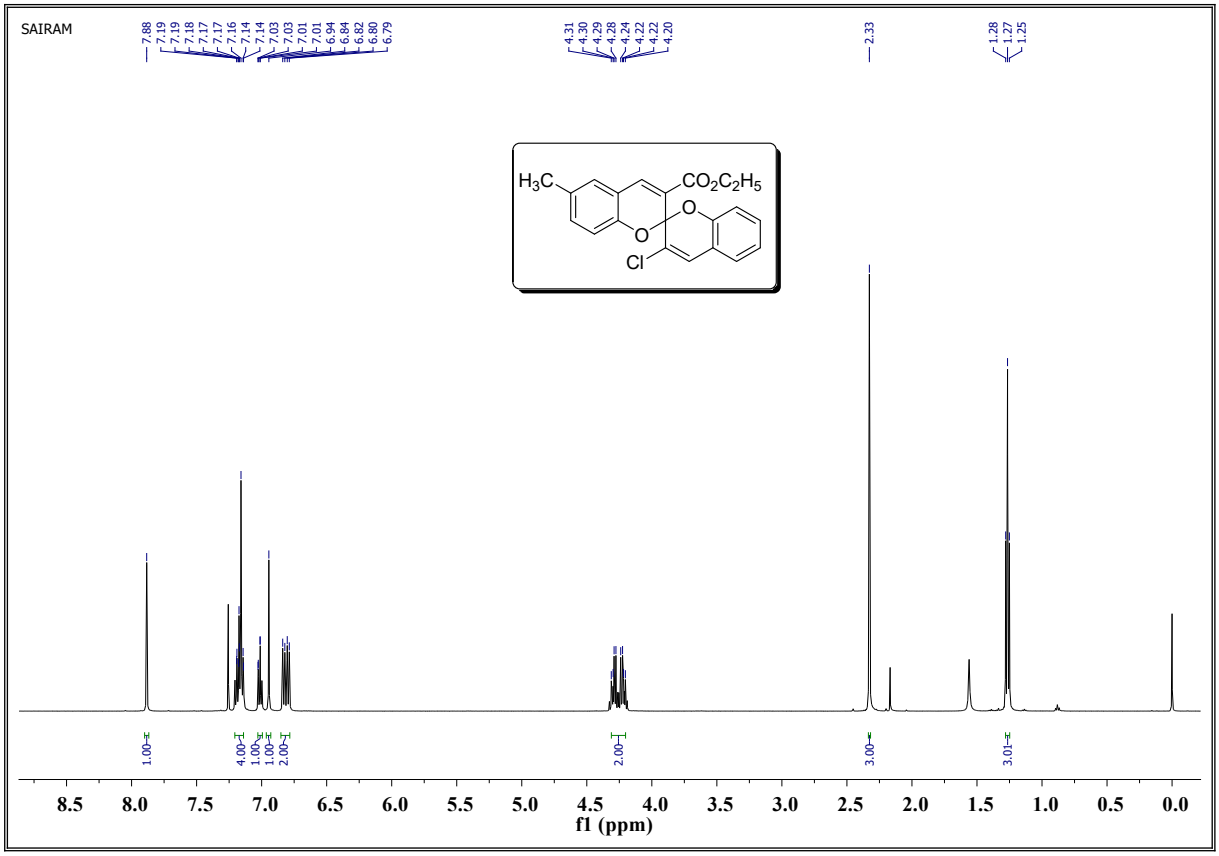
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C26 H18 Cl2 O4	C26 H18 Cl2 Na O4	487.0474	91.74		464.0562	464.0582	4.34	4.34	98.89	99.88	83.39	487.0455	17



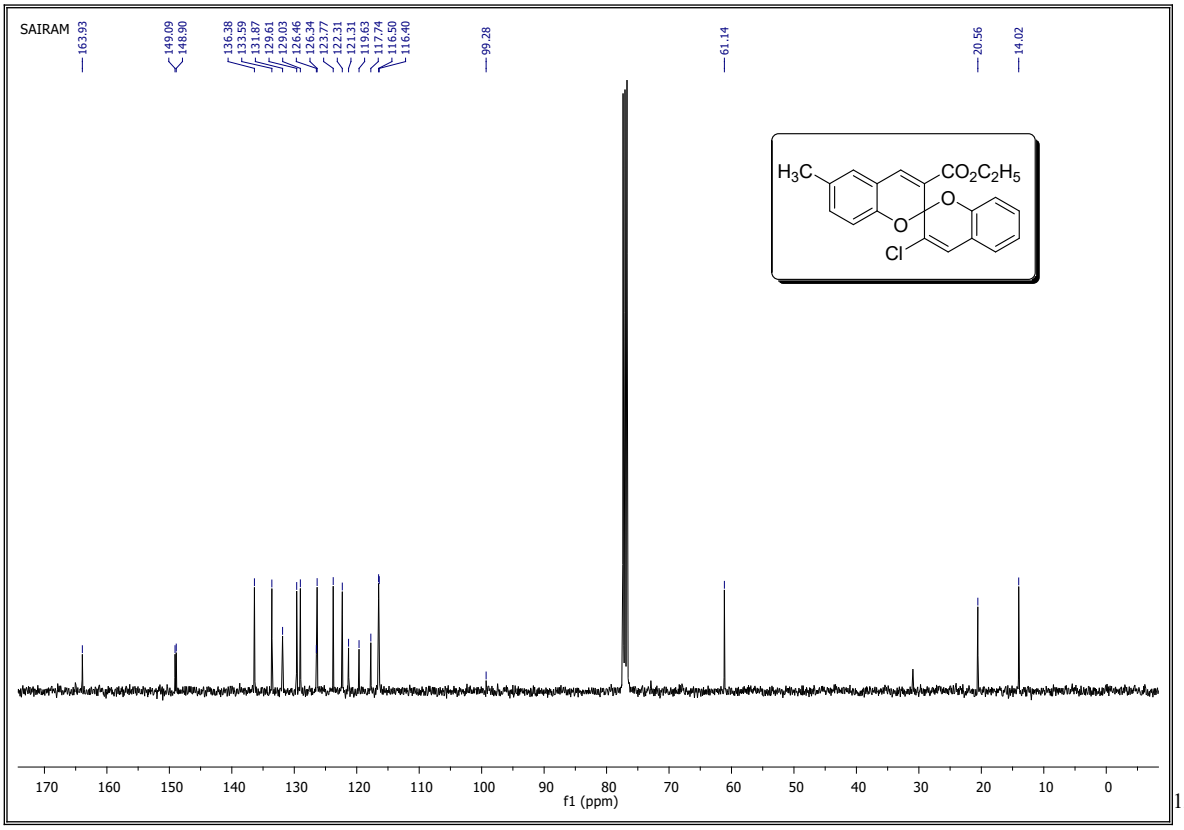
Sample Name	BCR-CL-PH-SP-KET-464	**Position**	Vial 37	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-CL-PH-SP-KET-464	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	7/4/2016 12:47:14 PM



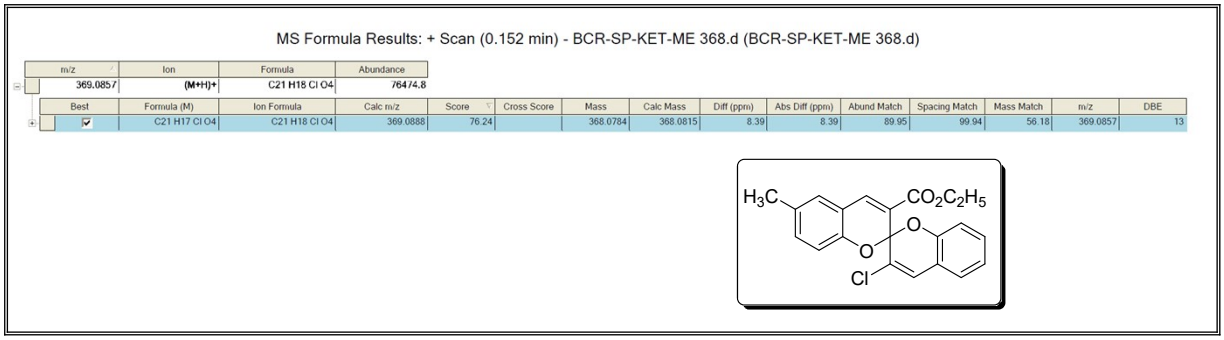
ESI-HRMS of compound **3o**

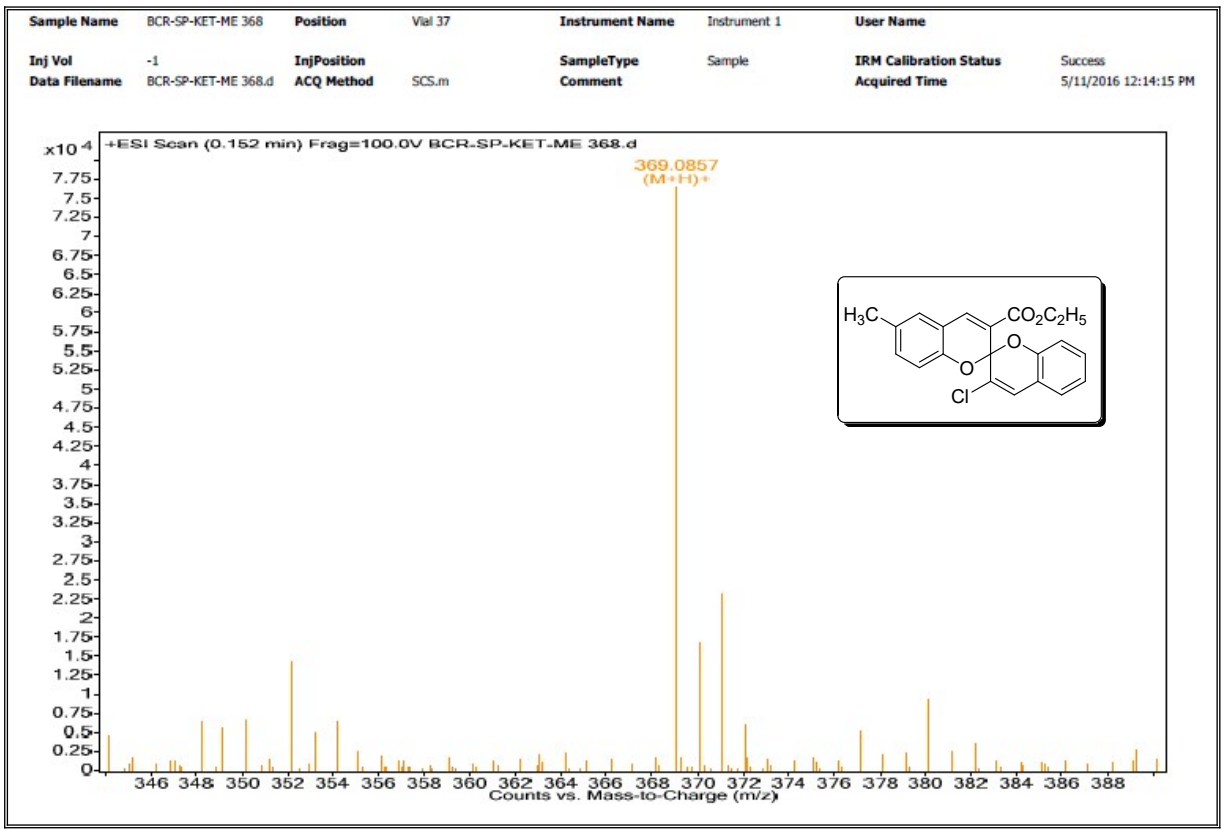


^{1}H NMR spectrum of compound **3p**

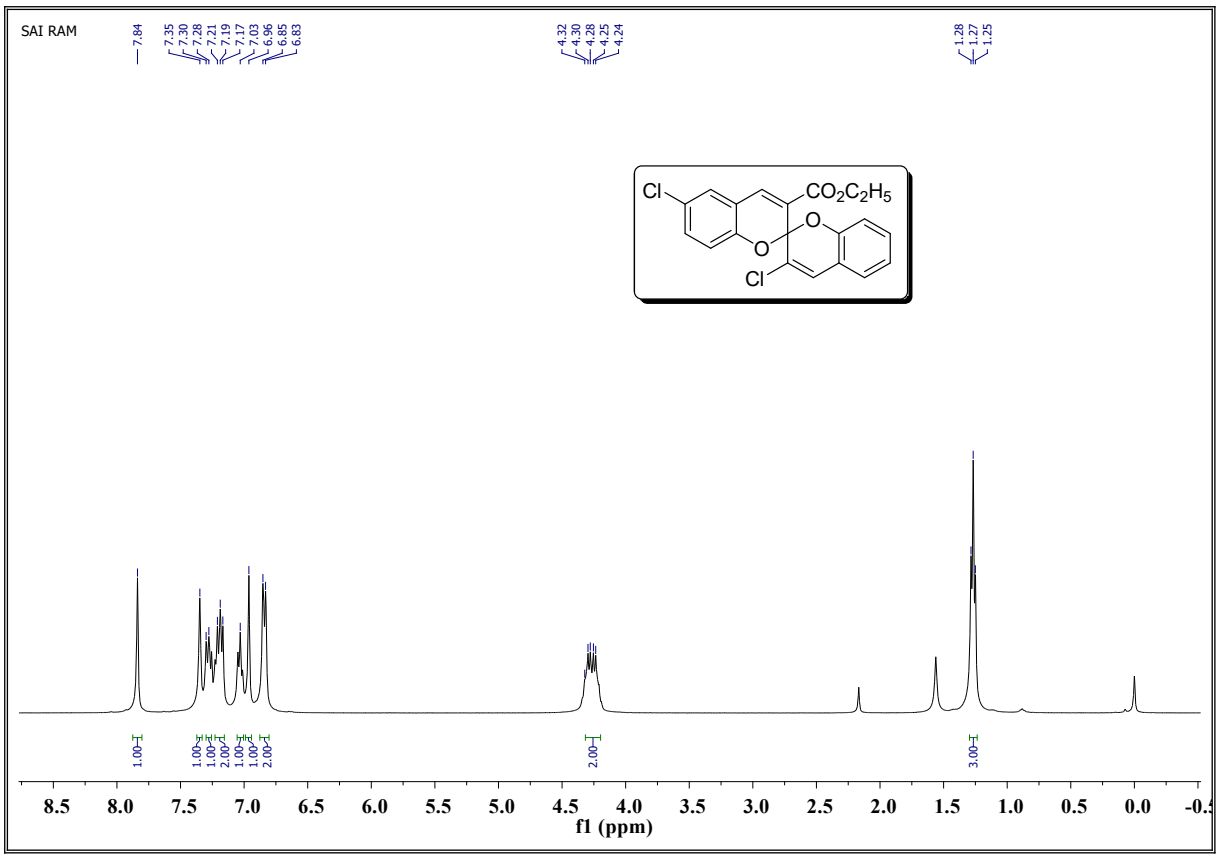


^{13}C NMR spectrum of compound **3p**

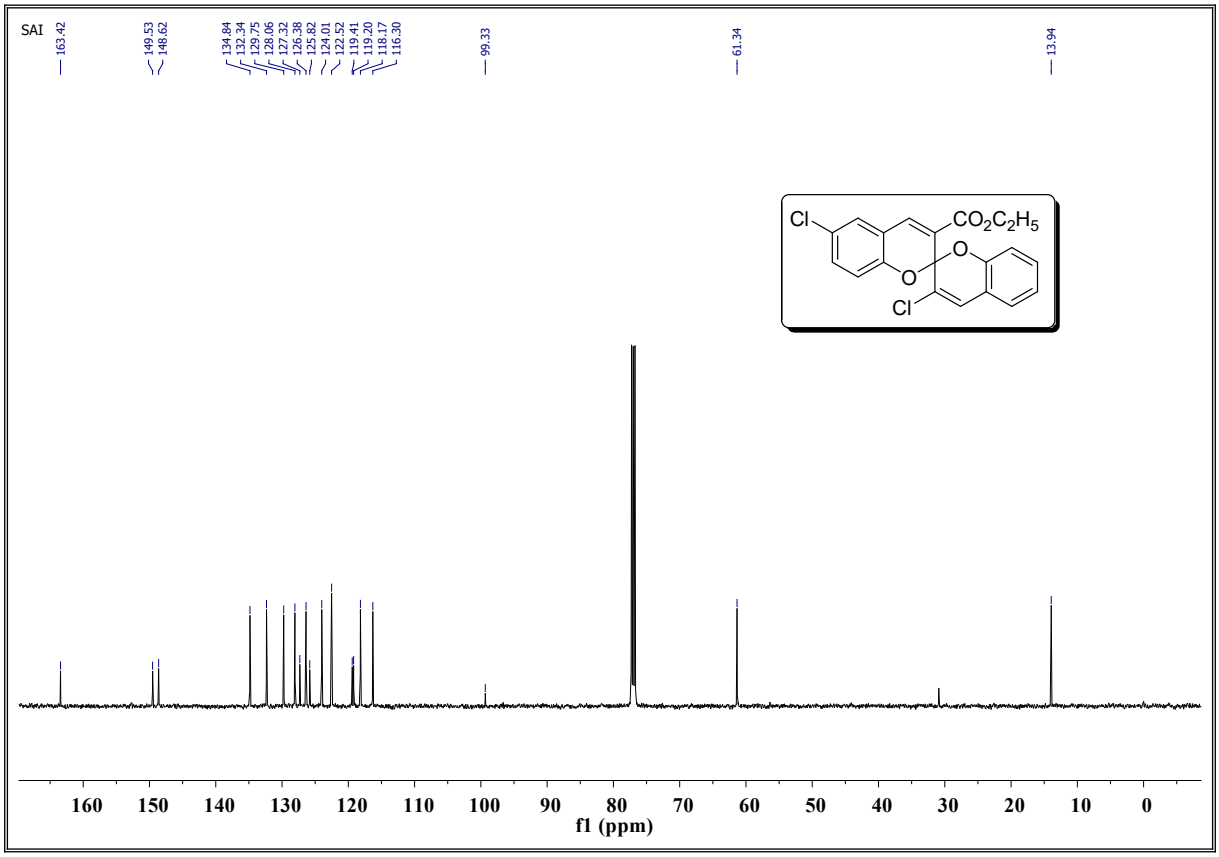




ESI-HRMS of compound **3p**



^{1}H NMR spectrum of compound **3s**

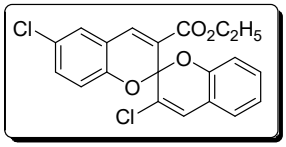


^{13}C NMR spectrum of compound **3s**

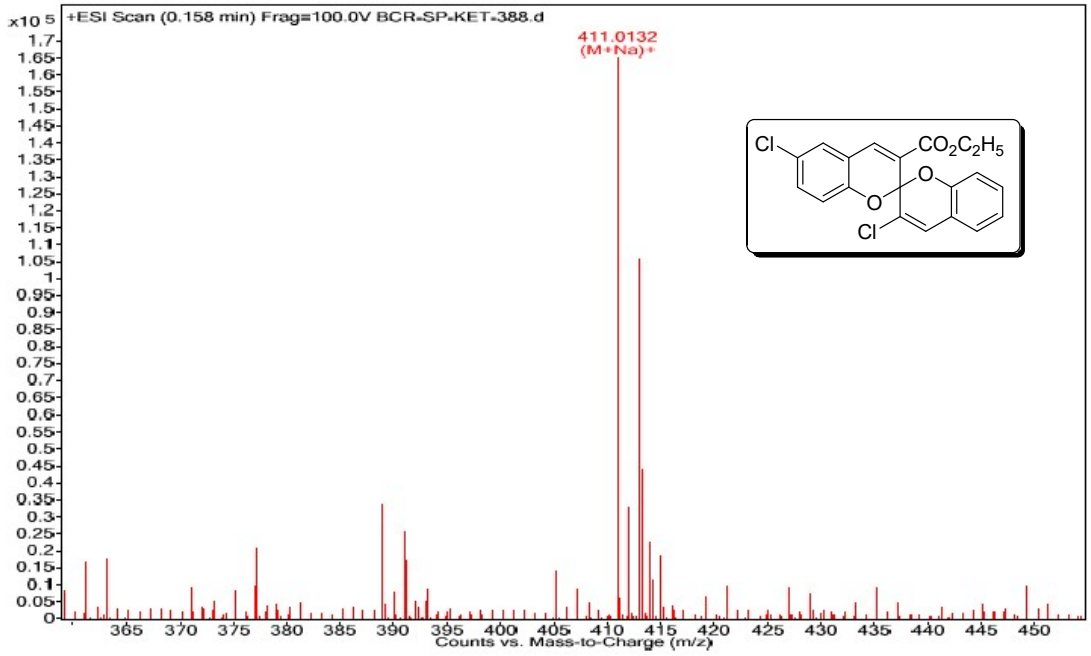
MS Formula Results: + Scan (0.158 min) - BCR-SP-KET-388.d (BCR-SP-KET-388.d)

m/z	Ion	Formula	Abundance
411.0132	(M+Na)+	C20 H14 Cl2 Na O4	164896.5

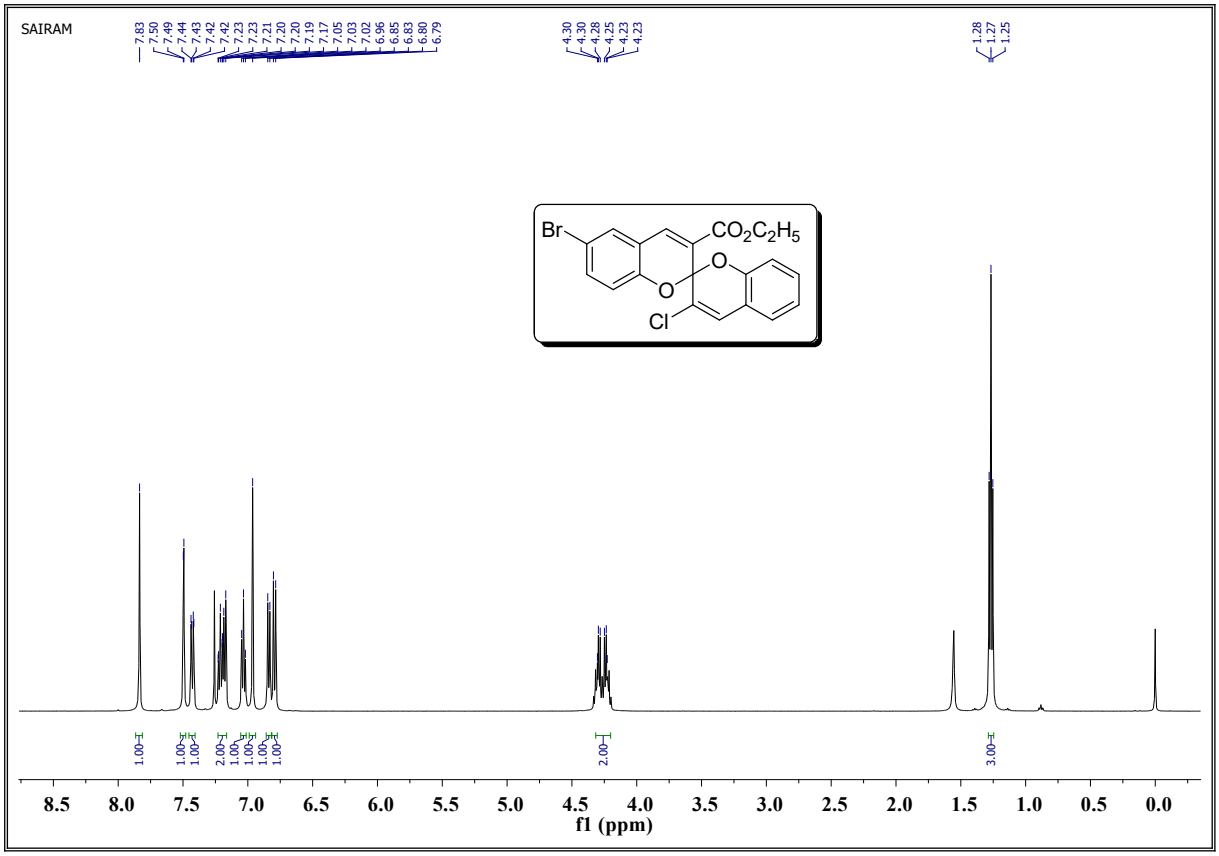
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C20 H14 Cl2 O4	C20 H14 Cl2 Na O4	411.0161	79.9		388.0238	388.0269	7.96	7.96	98.79	97.6	59.72	411.0132	13



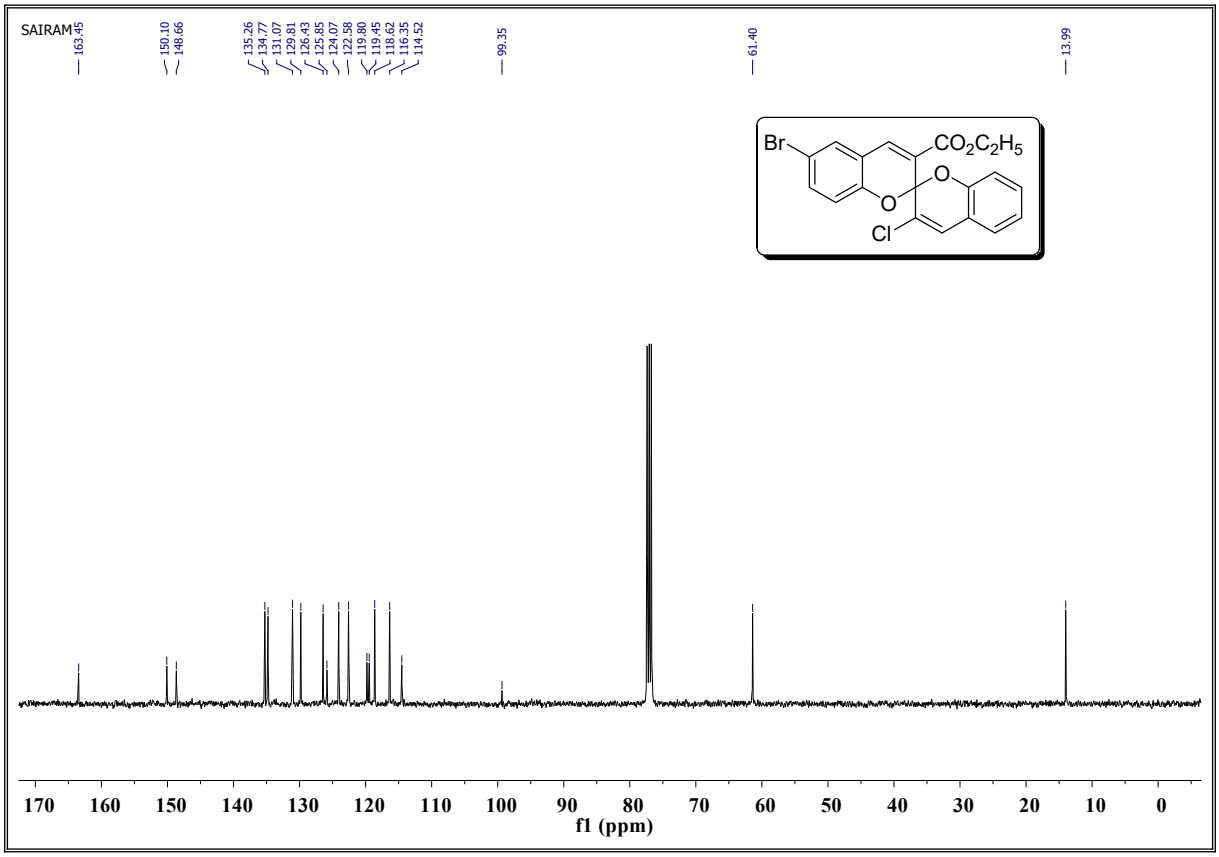
Sample Name	BCR-SP-KET-388	**Position**	Vial 52	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-SP-KET-388.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	6/6/2016 1:37:49 PM



ESI-HRMS of compound **3s**



^{1}H NMR spectrum of compound **3t**

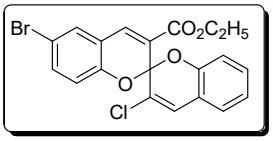


^{13}C NMR spectrum of compound **3t**

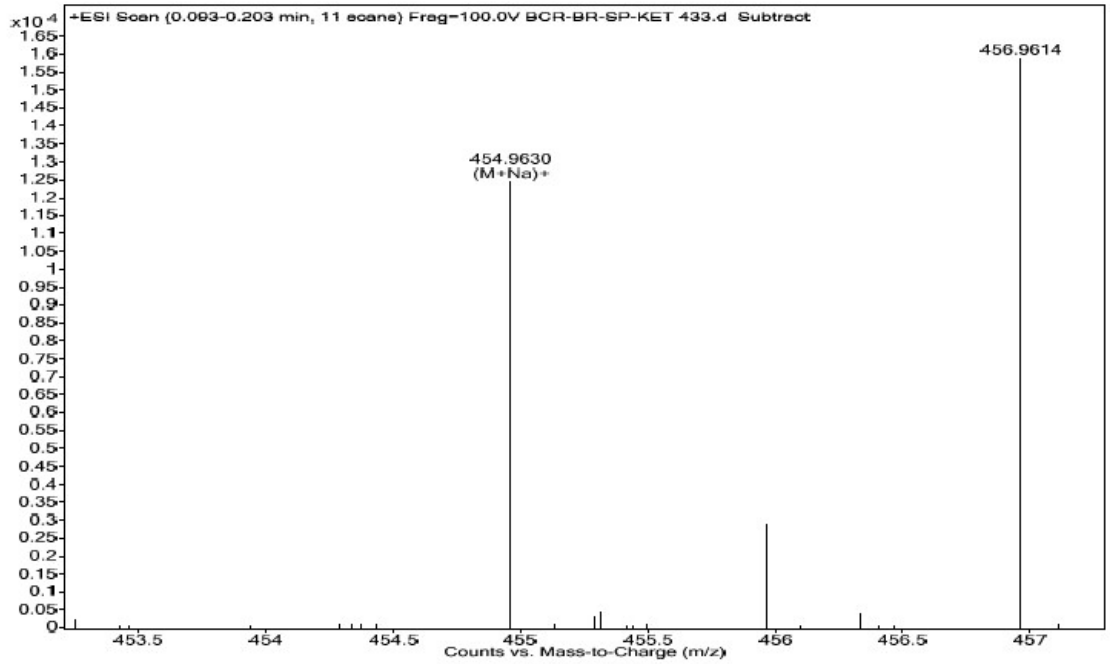
MS Formula Results: + Scan (0.093-0.203 min) Sub - BCR-BR-SP-KET 433.d (BCR-BR-SP-KET 433.d)

m/z	Ion	Formula	Abundance
454.963	(M+Na)+	C20 H14 Br Cl Na...	12441

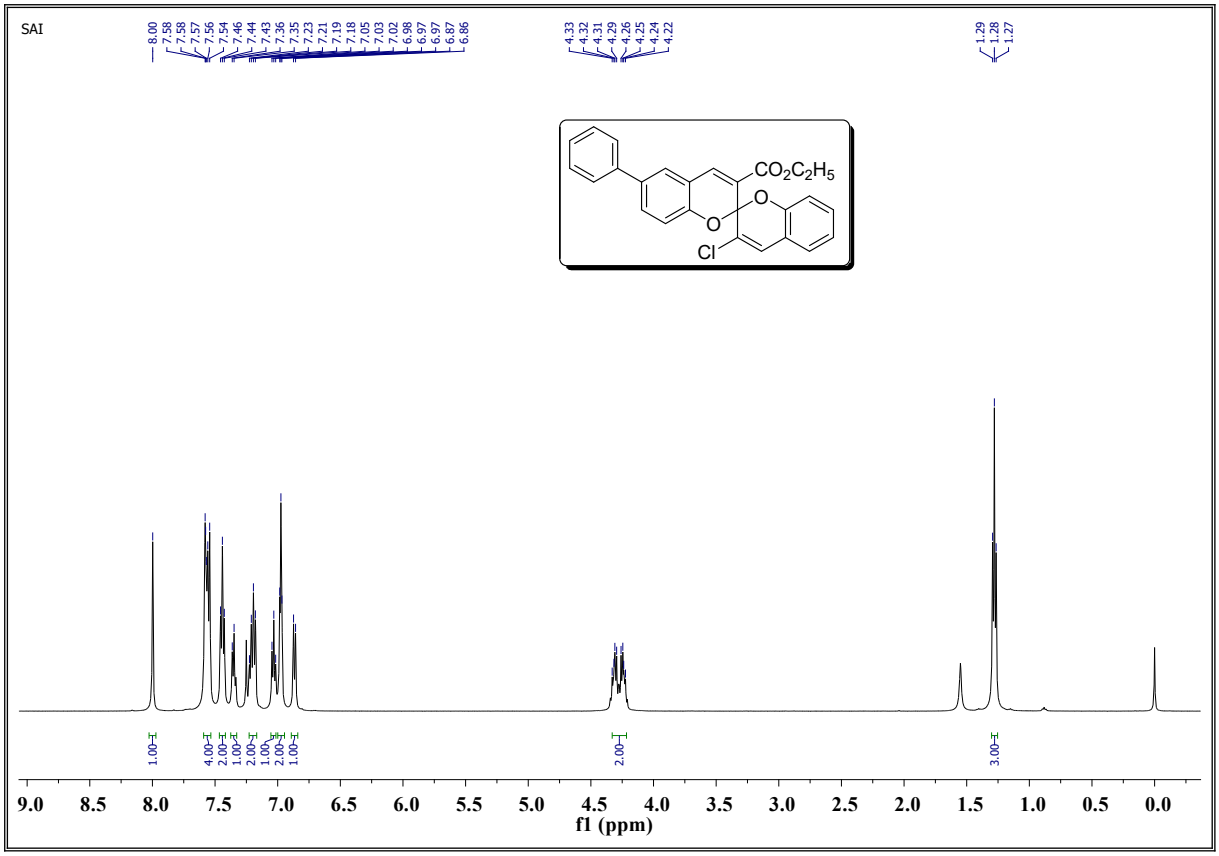
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C20 H14 Br Cl O4	C20 H14 Br Cl Na O4	454.9656	88.88		431.9741	431.9764	5.32	5.32	98.96	99.64	77.46	454.963	13



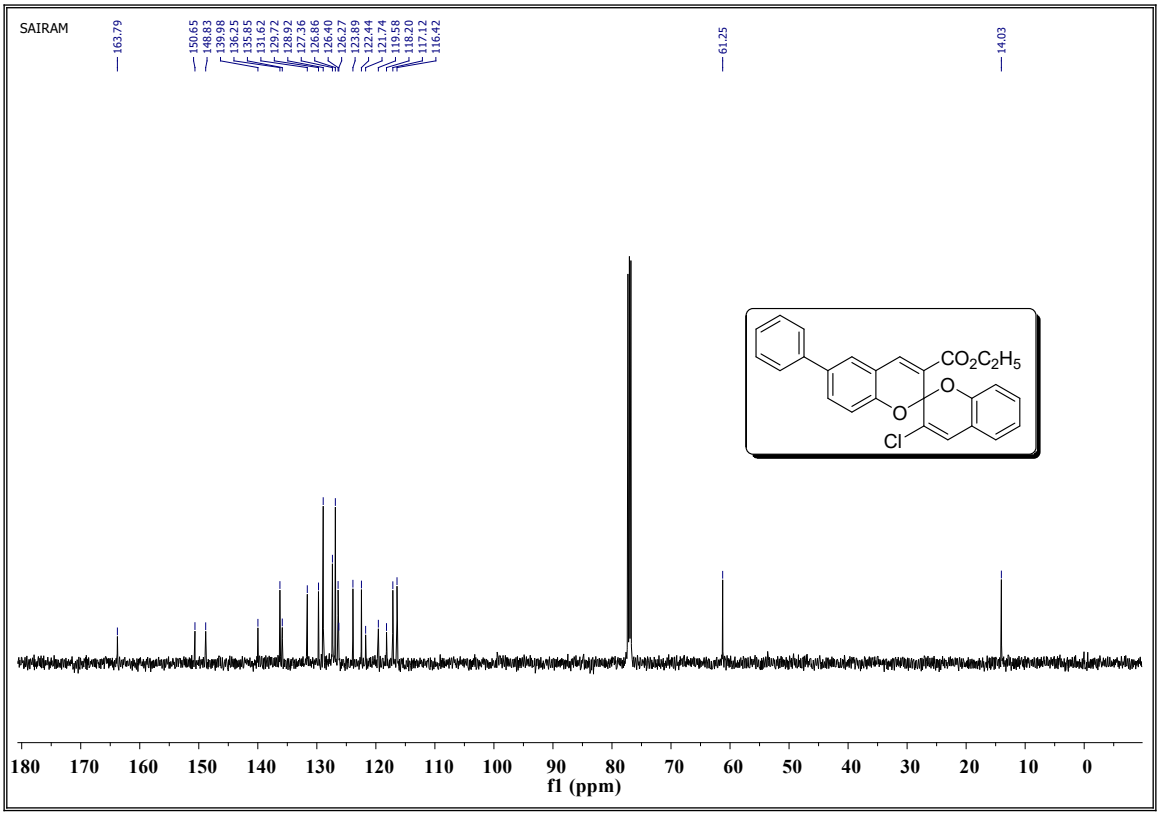
Sample Name	BCR-BR-SP-KET 433	**Position**	Vial 64	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-BR-SP-KET 433.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	6/1/2016 3:21:14 PM



ESI-HRMS of compound **3t**



^{1}H NMR spectrum of compound **3u**

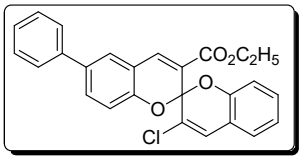


^{13}C NMR spectrum of compound **3u**

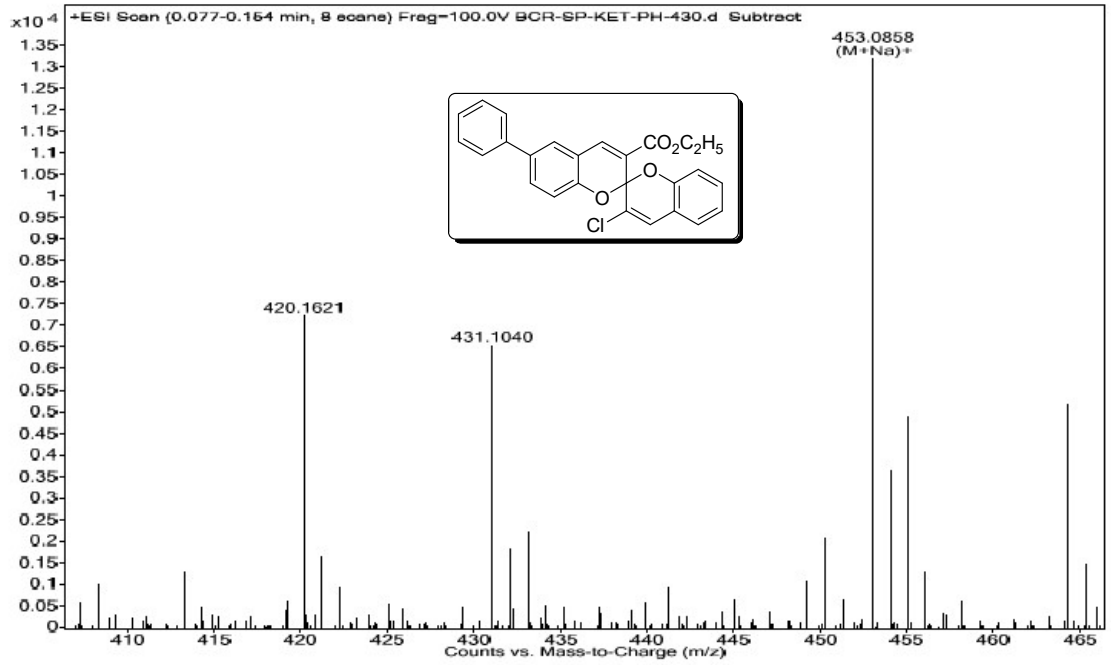
MS Formula Results: + Scan (0.077-0.154 min) Sub - BCR-SP-KET-PH-430.d (BCR-SP-KET-PH-430.d)

m/z	Ion	Formula	Abundance
453.0858	(M+Na)+	C26 H19 Cl Na O4	13196.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross Score	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☑	C26 H19 Cl O4	C26 H19 Cl Na O4	453.0864	98.61		430.0966	430.0972	1.42	1.42	98.92	99.04	98.2	453.0858	17



Sample Name	BCR-SP-KET-PH-430	**Position**	Vial 72	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BCR-SP-KET-PH-430.d	**ACQ Method**	SCS.m	**Comment**		**Acquired Time**	6/1/2016 3:49:12 PM



ESI-HRMS of compound **3u**

4. X-ray Crystallography: X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS97 [2] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(c) for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for 3c: $C_{21}H_{17}O_4Cl$ (M =368.82): triclinic, space group P-1 (no. 2), a = 8.7937(7) Å, b = 10.0005(8) Å, c = 11.2448(9) Å, α = 92.850(1)°, β = 111.870(1)°, γ = 95.702(1)°, V = 909.14(13) Å^3, Z = 2, T = 294.15 K, μ(MoKα) = 0.233 mm^{-1}, *Dcalc* = 1.3472 g/mm^3, 10400 reflections measured (3.92 ≤ 2Θ ≤ 56.76), 4239 unique (R_{int} = 0.0180) which were used in all calculations. The final R_1 was 0.0443 (I>=2u(I)) and wR_2 was 0.1369 (all data).CCDC 1502138 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

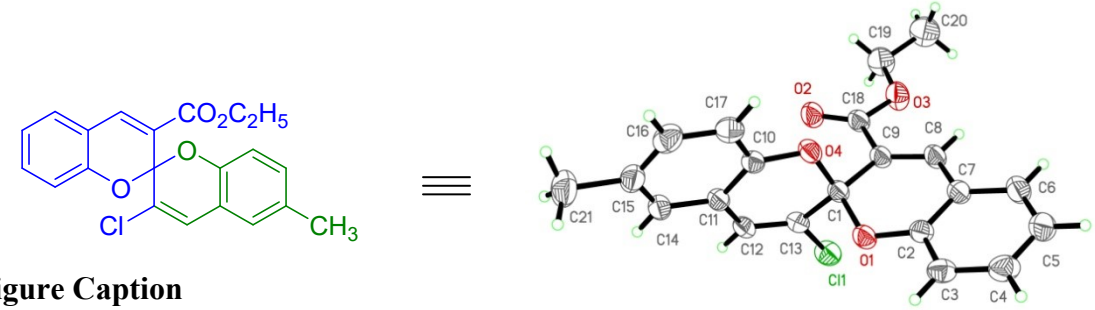


Figure Caption

A view of compound **3c**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

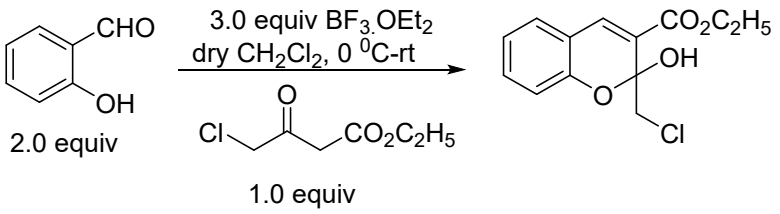
1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.

Response to the Reviewers about suggested experiments

Is it possible to obtain the described compounds (with the same substituents in the aromatic cores) in one step from 2 equivalents of the corresponding salicylaldehyde and ethyl 4-chloroacetoacetate under the conditions? I believe that such an experiment will make the manuscript interesting not only for those who work with 2*H*-chromenes, that is, it will expand the scope of possible readers.

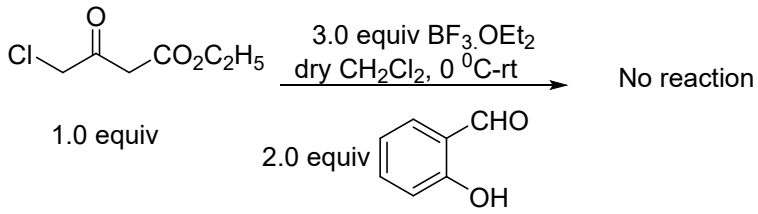
Reaction between salicylaldehyde and ethyl 4-chloroacetoacetate: Couple of one-pot reactions have been carried out as per the suggestions of Reviewer and described below.

A) $BF_3.OEt_2$ (3.0 equiv) was added to a stirred solution of salicylaldehyde (2.0 equiv) in dry CH_2Cl_2 at 0 ^oC under nitrogen atmosphere in presence of 4 Å molecular sieves and reaction was continued for 30 minutes. The reaction mixture was turned to lemon yellow color from colorless after addition of $BF_3.OEt_2$. The ethyl 4-chloroacetoacetate (1.0 equiv) in dry CH_2Cl_2 was added slowly to the reaction mixture at the same temperature and continued for 24 hours. The reaction upon workup, 2*H*-chromene was obtained in 10% only and starting materials were recovered (**Scheme-1**). Since the formation of 2*H*-chromene was only 10% and no further reaction was observed to form the spiro compound.



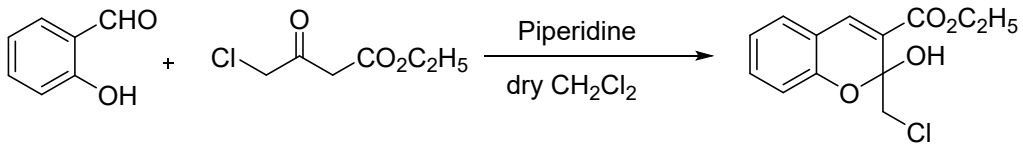
Scheme-1

B) $BF_3.OEt_2$ (3.0 equiv) was added to a stirred solution of ethyl 4-chloroacetoacetate (1.0 equiv) in dry CH_2Cl_2 at 0 ^oC under nitrogen atmosphere in presence of 4 Å molecular sieves and reaction was continued for 30 minutes. No colour change was observed in the reaction mixture. The salicylaldehyde (2.0 equiv) in dry CH_2Cl_2 was added slowly to the reaction mixture at the same temperature. The reaction was monitored by TLC and found no reaction was occurred even after 24 hours. All the starting materials were recovered (**Scheme-2**).



Scheme-2

C) The ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylates were reported by the reaction of salicyladehydes with ethyl 4-chloroacetoacetate in presence of piperidine in dry DCM solvent (**Scheme-3**, *Helv. Chim. Acta.*, 2011, **94**, 248-253**)**.



Scheme-3

Based on the above reactions, the one-pot reaction between saliylaldehyde and ethyl 4-chloroacetoacetate could not provide the ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate in presence of $BF_3.OEt_2$. The reaction is base catalyzed as depicted in Scheme-3 to provide ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate.