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Metal-free synthesis of 4-methylthio-3,4-dihydroisocoumarins from 2-(2-arylvinyl)benzoic acids

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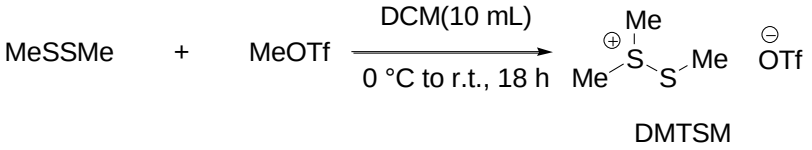
I. General Information

All reagents were purchased from Aladdin, Macklin, or Merck and directly used without further purification. Column chromatography separations were carried out on silica gel (200–300 mesh).

NMR spectra were performed on a Bruker 400MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz, ^{19}F: 376 MHz) spectrometer, using $CDCl_3$ as a solvent and TMS as the internal standard. Melting points are uncorrected. The NMR results were processed using MestReNova software. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF).

II. Experimental Procedures

General procedure for the synthesis of DMTSM:[S1]

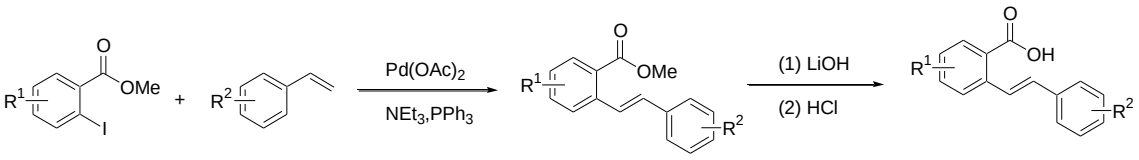


DMTSM

At 0 °C (ice bath), to a solution of methyl trifluoromethanesulfonate (12 mmol, 1.36 mL, 1.2 equiv) in CH_2Cl_2 (10 mL), Me_2S_2 (10 mmol, 0.89 mL, 1.0 equiv) was added dropwise for 30 min. The mixture was stirred for 1 h at that temperature, following by 18 h at room temperature. Upon completion, the resulting white solid was collected by filtration and washed with fresh distilled Et_2O under nitrogen atmosphere, affording dimethyl(methylthio)sulfonium trifluoromethanesulfonate (2.27 g, 88% yield) as a white solid.

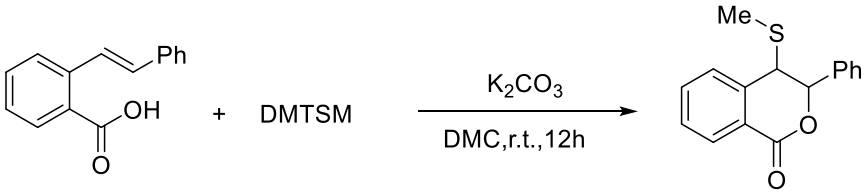
Synthesis of 2-(2-arylvinyl)benzoic acids

All of 2-(2-arylvinyl)benzoic acids were prepared according to previous procedures.[S2,S3]



A mixture of substituted methyl 2-iodobenzoate (15 mmol), substituted styrene (18 mmol, 1.2 equiv.), trimethylamine (32 mmol, 4.4 mL, 2.1 equiv.), palladium acetate (0.48 mmol, 323 mg, 3.2 mol %) and triphenylphosphine (0.96 mmol, 251 mg, 0.064 equiv.) were heated in an oil bath under reflux at 100 °C for 5 h. Solid products were isolated by diluting the reaction mixtures with 200 mL of 10% hydrochloric acid with stirring to dissolve the salts and excess amine. Finally, the residue was purified by column chromatography to give substituted methyl (*E*)-2-styrylbenzoates in good yields.

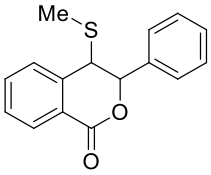
General procedure for the synthesis of 4-methylthio-3,4-dihydroisocoumarins 3:



At room temperature, to a solution of (*E*)-2-styrylbenzoic acid **1** (0.5 mmol, 1 equiv) in CH_2Cl_2 (2 mL), DMTSM (0.6 mmol, 1.2 equiv) and K_2CO_3 (0.75 mmol, 1.5 equiv) were added into the solvent. The mixture was stirred for 12 h (TLC monitored). The reaction mixture was extracted with CH_2Cl_2 after adding saturated brine. Then the organic phases were combined and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo*, the crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired products.

III. Characterization data of products

(1). 4-Methylthio-3-phenylisochroman-1-one 3a



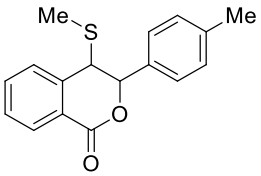
White solid (114 mg, 85%); mp =100-103 °C .

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.19 (d, J= 7.7 Hz, 1H), 7.68-7.64 (m, 2H), 7.55-7.48 (m, 1H), 7.40-7.348 (m, 5H), 5.82 (d, J= 7.6 Hz, 1H), 4.58 (d, J= 7.6 Hz,1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 136.6, 136.4, 134.9, 130.7, 129.8, 129.2, 129.1, 129.0, 127.3, 125.4, 83.2, 47.6, 26.7.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{15}O_2S^+$: 271.0787, found: 271.0791.

(2). 4-Methylthio-3-(*p*-tolyl)isochroman-1-one 3b



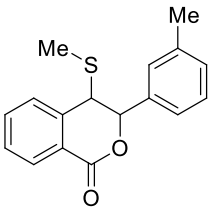
White solid (118 mg, 83%); mp =116-119 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.12 (d, J=8.0 Hz, 1H), 7.62 (d, J=8.3 Hz, 1H), 7.26 (t, J=7.5 Hz, 1H), 7.16 (t, J=7.4 Hz, 1H), 7.04 (d, J=6.4 Hz, 2H), 6.98 (d, J=6.4 Hz, 2H), 5.79 (d, J= 7.2 Hz, 1H), 4.36 (d, J= 7.2 Hz, 1H), 2.37 (s, 3H) , 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 136.4, 135.9, 134.9, 130.7, 129.8, 129.2, 129.1, 129.0, 127.0, 125.4, 83.5, 46.5, 26.3, 21.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0936.

(3). 4-Methylthio-3-(*m*-tolyl)isochroman-1-one 3c



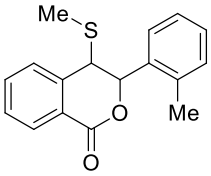
Pale yellow solid (116 mg, 81%); mp =104-107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.13 (d, J=8.0 Hz, 1H), 7.62 (d, J=8.0 Hz, 1H), 7.44 (t, J=8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.16 (t, J=8.0 Hz, 1H), 7.06-7.01 (m, 2H), 6.97 (s, 3H), 5.75 (d, J= 7.2 Hz, 1H), 4.39 (d, J= 7.2 Hz, 1H), 2.34 (s, 3H) , 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.4, 136.0, 135.3, 135.0, 132.0, 131.0, 129.7, 129.3, 128.5, 127.0, 126.9, 125.1, 83.9, 47.8, 25.8, 21.3.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0934.

(4). 4-Methylthio-3-(*o*-tolyl)isochroman-1-one 3d



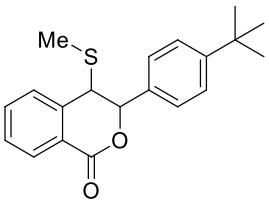
White solid (111 mg, 79%); mp =98-101 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.18 (d, J=8.0 Hz, 1H), 7.62 (d, J=7.5 Hz, 1H), 7.48-7.42 (m, 2H), 7.29-7.24 (m, 1H), 7.16 (t, J=7.5 Hz, 1H), 7.06-6.96 (m, 2H), 6.97 (s, 3H), 5.78 (d, J= 7.2 Hz, 1H), 4.33 (d, J= 7.2Hz, 1H), 2.40 (s, 3H) , 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.7, 138.6, 137.2, 134.9, 131.5, 130.9, 129.7, 129.2, 129.1, 128.0, 127.4, 126.5, 125.4, 83.5, 46.5, 25.4, 19.5.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0948.

(5). 3-(4-*tert*-Butylphenyl)-4-(methylthio)isochroman-1-one 3e



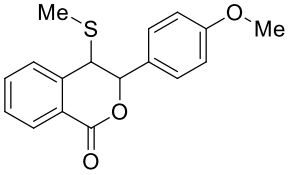
White solid (133 mg, 82%); mp =134-138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.15 (d, J=5.6 Hz, 1H), 7.66 (d, J=5.4 Hz, 1H), 7.46-7.41 (m, 2H), 7.26 (t, J=7.2 Hz, 1H), 7.16 (t, J=7.2 Hz, 1H), 5.79 (d, J= 6.4 Hz, 1H), 4.36 (d, J= 6.4 Hz, 1H), 2.24 (s, 3H) , 1.24(s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 151.2, 136.6, 134.9, 130.7, 128.2, 128.2, 127.9, 127.1, 126.9, 125.4, 84.5, 46.0, 31.1, 29.4, 26.1.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{20}H_{23}O_2S^+$: 327.1413, found: 327.1419.

(6). 3-(4-Methoxyphenyl)-4-(methylthio)isochroman-1-one 3f



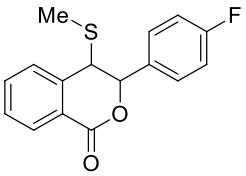
White solid (126 mg, 84%); mp =124-127 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ =8.22(d, J=6.8 Hz, 1H), 7.64 (d, J=6.4 Hz, 1H), 7.40 (t, J=7.0 Hz, 1H), 7.19-7.12 (m, 3H), 6.74 (t, J=6.6 Hz, 1H), 5.72 (d, J= 6.6 Hz, 1H), 4.36 (d, J= 6.6 Hz, 1H), 3.75 (s, 3H) , 2.27(s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ=165.0, 162.2, 139.0, 137.4, 135.5, 130.6, 129.5, 129.1, 128.1, 126.4, 114.1, 83.1, 57.7, 48.7, 28.4.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_3S^+$: 301.0893, found: 301.0898.

(7). 3-(4-Fluorophenyl)-4-(methylthio)isochroman-1-one 3g



White solid (124 mg, 85%); mp =111-116 °C.

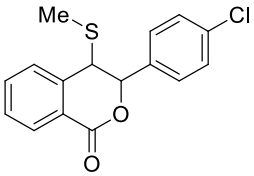
^{1}H NMR (400 MHz, $CDCl_3$): δ =8.22 (d, J= 7.7 Hz, 1H), 7.66(t, J= 7.5 Hz, 1H), 7.49(t, J= 7.5 Hz, 1H), 7.30 (d, J= 7.7 Hz, 1H), 7.18 (d, J= 8.5 Hz, 2H), 6.99 (t, J= 8.4Hz, 2H), 5.64 (d, J= 8.4 Hz, 1H), 4.43 (d, J= 8.4 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=166.3, 162.7, 137.2, 135.5(d, J= 13 Hz), 131.4, 130.6(d, J= 11 Hz), 128.5, 128.3, 128.1, 125.6, 116.4, 83.9, 48.8, 28.4.

^{19}F NMR (100 MHz, $CDCl_3$) δ=-106.7.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}FO_2S^+$: 289.0693, found: 289.0699.

(8). 3-(4-Chlorophenyl)-4-(methylthio)isochroman-1-one 3h



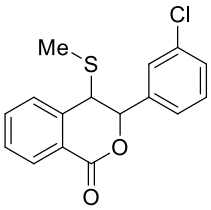
White solid (130 mg, 86%); mp =130-134 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.19 (d, J= 7.8 Hz, 1H), 7.58 (d, J= 5.8 Hz, 1H),7.43(t, J= 7.0 Hz, 1H), 7.28(t, J= 7.5 Hz, 1H), 7.12 (d, J= 8.5 Hz, 1H), 7.02 (d, J= 8.5 Hz, 1H), 5.85 (d, J= 7.4 Hz, 1H), 4.36 (d, J= 7.4 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=167.5, 163.5(d, J= 252 Hz), 137.3, 135.7, 132.0 (d, J= 3 Hz), 130.5 (d, J= 9Hz), 128.6, 128.4, 128.2, 125.8, 113.5(d, J= 22 Hz), 84.1, 48.9, 28.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}ClO_2S^+$: 305.0398, found: 305.0404.

(9). 3-(3-Chlorophenyl)-4-(methylthio)isochroman-1-one 3i



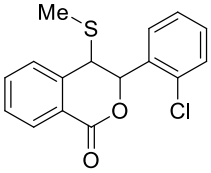
Pale yellow solid (128 mg, 81%); mp =120-124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.18 (d, J= 7.4 Hz, 1H) ,7.63(s, 1H), 7.52-7.47 (m, 3H),7.45-7.44 (m, 1H), 7.35-7.31 (m, 2H), 5.71 (d, J= 6.8Hz, 1H), 4.32 (d, J= 6.8 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=164.3, 141.2, 138.9, 137.2, 136.9, 134.4, 131.8, 129.3, 128.8, 128.0, 126.7, 126.6, 125.6, 82.7, 46.2, 25.9.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}ClO_2S^+$: 305.0398, found: 305.0399.

(10). 3-(2-Chlorophenyl)-4-(methylthio)isochroman-1-one 3j



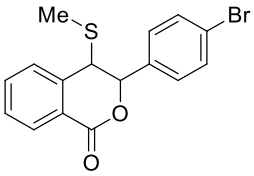
White solid (123 mg, 82%); mp =106-109 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.12 (d, J= 6.8 Hz, 1H), 7.62 (d, J= 7.2 Hz, 1H), 7.48-7.42 (m, 2H), 7.34-7.25 (m, 2H),7.16(t, J= 7.5 Hz, 1H), 7.04(t, J= 7.5 Hz, 1H), 5.81 (d, J= 7.2 Hz, 1H), 4.36 (d, J= 7.2 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=164.8, 140.7, 139.2, 136.7, 136.5 134.2, 133.3, 131.0, 130.6, 130.3 130.1, 129.8, 126.6, 83.0, 47.1, 21.5.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}ClO_2S^+$: 305.0398, found: 305.0407.

(11). 3-(4-Bromophenyl)-4-(methylthio)isochroman-1-one 3k



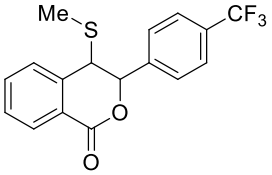
White solid (146 mg, 84%); mp =145-148 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.13 (d, J= 5.8 Hz, 1H), 7.58 (d, J= 7.4 Hz, 2H), 7.50-7.46 (m, 1H), 7.30-7.25 (m, 1H), 7.19-7.12 (m, 3H), 5.68 (d, J= 7.0 Hz, 1H), 4.32 (d, J= 7.0 Hz, 1H), 2.35(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 136.9, 136.2, 135.1, 131.2, 129.5, 129.4, 129.2, 127.2, 126.9, 125.33, 85.0, 45.7, 26.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}BrO_2S^+$: 348.9892, found: 348.9897.

(12). 4-Methylthio-3-(4-(trifluoromethyl)phenyl)isochroman-1-one 3l



Colorless solid (146 mg, 86%); mp =114-118 °C.

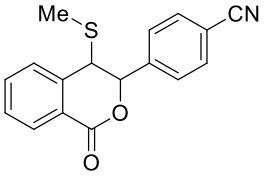
^{1}H NMR (400 MHz, DMSO-d_6): δ =8.08 (d, J= 7.0 Hz, 1H), 7.90-7.80 (m, 3H), 7.70 (d, J= 6.8 Hz,1H), 7.64-7.56 (m, 3H), 5.82 (d, J= 7.2 Hz, 1H), 4.32 (d, J= 7.2 Hz, 1H), 2.77(s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ=164.8, 141.1, 136.6, 135.2, 132.7 (q, J_{F-C} = 33.0 Hz), 130.9, 129.4, 128.1, 126.9(q, J_{F-C} = 3.5 Hz), 126.0, 125.7, 123.8 (q, J_{F-C} = 272.0 Hz), 83.4, 45.6, 25.3.

^{19}F NMR (100 MHz, $CDCl_3$) δ=-64.1.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{14}F_3O_2S^+$: 339.0661, found: 339.0666.

(13). 4-(4-Methylthio-1-oxoisochroman-3-yl)benzonitrile 3m



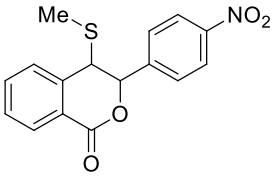
White solid (126 mg, 85%); mp =128-131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.19 (d, J= 7.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.58-7.51 (m, 3H), 7.25-7.20 (m, 3H), 5.70 (d, J= 6.6 Hz, 1H), 4.34 (d, J= 6.6 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.3, 143.0, 136.6, 135.0, 131.2, 129.6, 129.1, 127.2, 126.4, 125.1, 117.2, 116.2, 84.5, 46.9, 24.3.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{14}NO_2S^+$: 296.0740, found: 296.0744.

(14). 4-Methylthio-3-(4-nitrophenyl)isochroman-1-one 3n



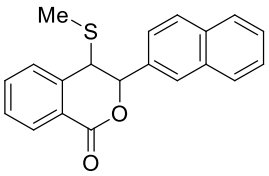
Pale yellow solid (132 mg, 84%); mp =160-163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.16 (d, J= 7.0 Hz, 1H), 7.99 (d, J= 7.6 Hz, 2H), 7.52-7.48 (m, 2H), 7.34-7.30 (m, 1H), 7.19 (d, J= 7.6 Hz, 2H), 6.07 (d, J= 6.8 Hz, 1H), 4.78 (d, J= 6.8 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 146.5, 146.2, 138.43, 130.7, 129.2, 129.2, 128.6, 127.4, 127.4, 125.4, 82.2, 46.7, 28.8.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}NO_4S^+$: 316.0638, found: 316.0646.

(15). 4-Methylthio-3-(naphthalen-2-yl)isochroman-1-one 3o



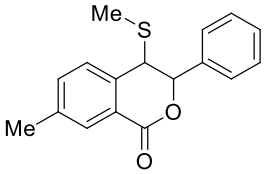
Pale yellow solid (124 mg, 78%); mp =150-153 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.05 (d, J= 7.8 Hz, 1H), 7.72 (d, J= 7.3 Hz, 1H), 7.66-7.61 (m, 2H), 7.56 (d, J= 7.4 Hz, 1H), 7.53 (d, J= 3.8 Hz, 1H), 7.39-7.31 (m, 2H), 7.30-7.25 (m, 3H), 5.68 (d, J=7.2 Hz, 1H), 4.28 (d, J= 7.2 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.9, 140.6, 137.1, 134.0, 133.6, 133.0, 130.3, 128.9, 128.6, 128.4, 128.00, 127.9, 127.3, 126.9, 125.7, 123.4, 122.3, 82.6, 46.6, 21.4.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{20}H_{17}O_2S^+$: 321.0944, found: 321.0951.

(16). 7-Methyl-4-methylthio-3-phenylisochroman-1-one 3p



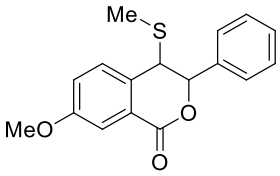
White solid (109 mg, 76%); mp =110-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.20(s, 1H), 7.38-7.29 (m, 7H), 5.81 (d, J = 6.4 Hz, 1H), 4.31 (d, J = 6.4 Hz, 1H), 2.59 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=164.7, 140.6, 137.0, 134.0, 130.6, 130.2, 129.8, 128.9, 128.8, 123.3, 122.3, 85.1, 47.7, 24.2.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0949.

(17). 7-Methoxy-4-(methylthio)-3-phenylisochroman-1-one 3q



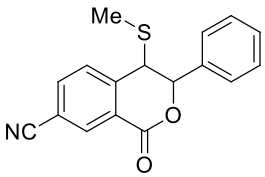
White solid (118 mg, 78%); mp =130-133 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.92 (d, J= 7.6 Hz, 1H), 7.59-7.51 (m, 3H), 7.47-7.43 (m, 2H),7.37 (d, J= 3.6 Hz, 1H), 7.37 (d, J= 7.6 Hz, 1H), 5.71 (d, J = 6.8 Hz, 1H), 4.22 (d, J = 6.8 Hz, 1H), 3.91 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=167.4, 163.6, 136.7, 135.9, 133.0, 129.1, 129.0, 127.4, 117.8, 116.1, 111.3, 83.9, 54.6, 49.6, 21.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_3S^+$: 301.0893, found: 301.0901.

(18). 4-Methylthio-1-oxo-3-phenylisochromane-7-carbonitrile 3r



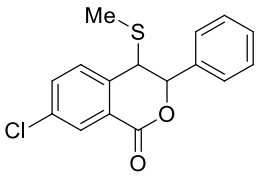
Pale yellow solid (111 mg, 75%); mp =144-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.03 (d, J = 8.0 Hz, 1H), 8.03 (dd, J = 8.0, 2.1 Hz, 1H), 7.40-7.29 (m, 6H), 5.72 (d, J = 7.4 Hz, 1H), 4.40 (d, J = 7.4 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.4, 144.2, 139.2, 135.4, 133.1, 130.79, 130.1, 127.0, 126.4, 125.3, 121.9, 112.0, 84.8, 45.7, 21.8.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{14}NO_2S^+$: 296.0740, found: 296.0743.

(19). 7-Chloro-4-methylthio-3-phenylisochroman-1-one 3s



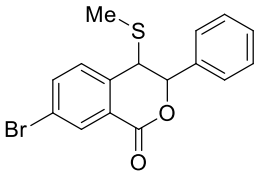
White solid (106 mg, 70%); mp =126-129 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.15 (d, J = 2.0 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.40-7.29 (m, 6H), 5.78 (d, J = 7.6 Hz, 1H), 4.31 (d, J = 7.6 Hz, 1H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=162.6, 140.2, 136.1, 135.1, 135.0, 130.6, 129.4, 129.2, 129.1, 127.0, 127.0, 84.0, 49.0, 23.1.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}ClO_2S^+$: 305.0398, found: 305.0402.

(20). 7-Bromo-4-methylthio-3-phenylisochroman-1-one 3t



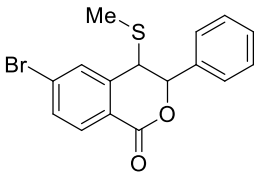
White solid (126 mg, 72%); mp =138-141 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.22(s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.42-7.29 (m, 3H), 7.28-7.23(m, 3H), 5.76 (d, J = 6.4 Hz, 1H), 4.20 (d, J = 6.4 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=162.4, 144.0, 138.0, 136.1, 133.5, 129.4, 129.4, 129.1, 127.1, 127.0, 123.4, 85.5, 48.1, 27.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}BrO_2S^+$: 348.9892, found: 348.9898.

(21). 6-Bromo-4-methylthio-3-phenylisochroman-1-one 3u



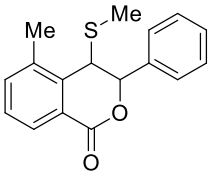
White solid (130 mg, 75%); mp =140-143 °C.

^{1}H NMR (400 MHz, $CDCl_3$):δ =7.91 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.26-7.19 (m, 6H), 5.62 (d, J = 7.6 Hz, 1H), 4.24 (d, J = 7.8 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=163.1, 138.1, 136.1, 132.9, 132.3, 130.6, 130.3, 129.4, 129.1, 126.9, 124.4, 84.2, 47.5, 24.6.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{14}BrO_2S^+$: 348.9892, found: 348.9901.

(22). 5-Methyl-4-methylthio-3-phenylisochroman-1-one 3v



White solid (40 mg, 28%); mp =108-111 °C.

^{1}H NMR (400 MHz, DMSO-d_6):δ =8.45 (d, J = 6.6 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.56-7.46 (m, 4H), 7.43-7.36 (m, 2H), 6.28 (d, J = 7.4 Hz, 1H), 4.82 (d, J = 7.4 Hz, 1H), 2.41 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ=163.9, 139.9, 137.5, 136.7, 133.1, 129.9, 129.5, 128.7, 127.5, 127.2, 125.9, 84.8, 47.5, 21.6, 17.5.

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0941.

IV. References

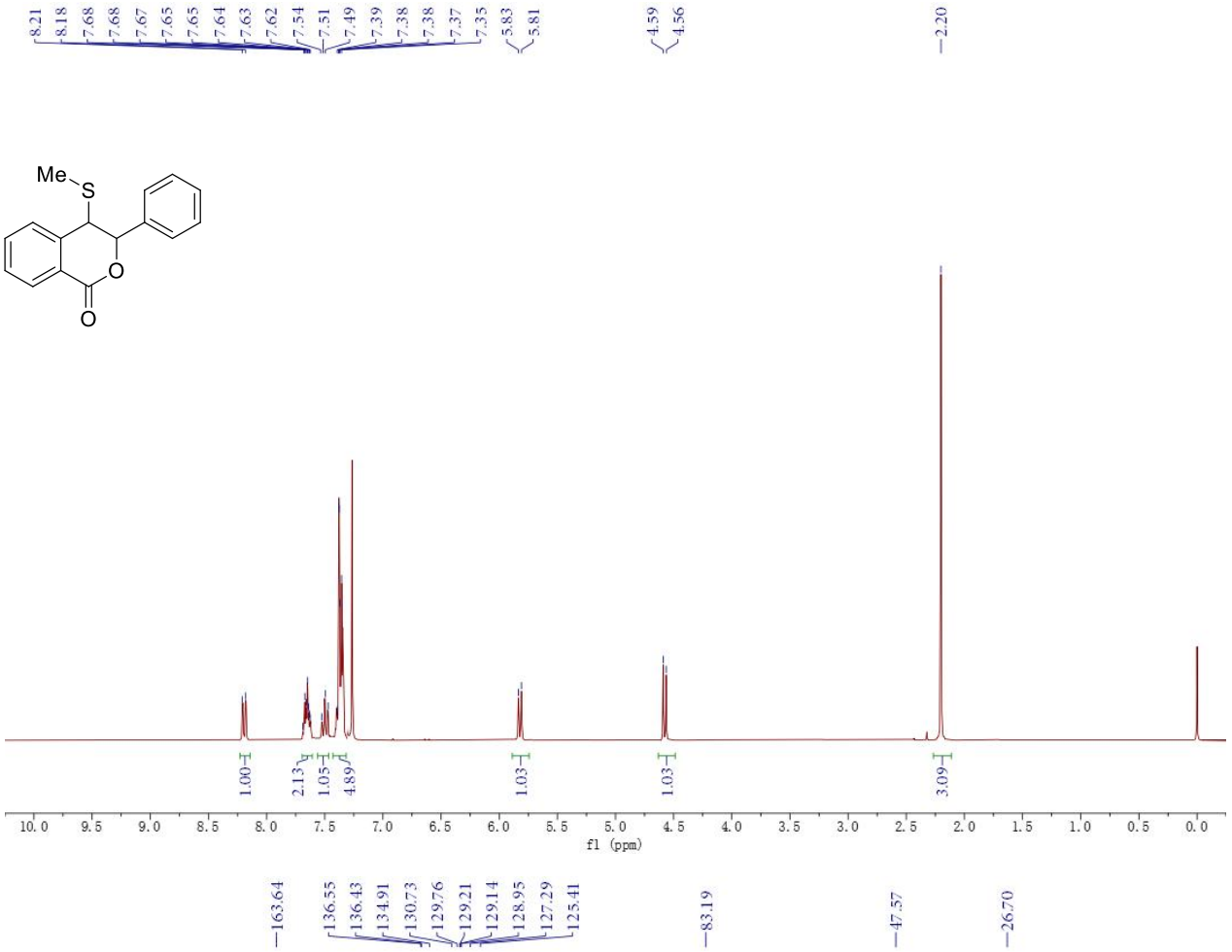
S1. M. Tang, Y. Wei, S. Huang and L.-G. Xie, *Org. Lett.*, 2022, **24**, 7026; https://doi.org/10.1021/acs.orglett.2c02880.

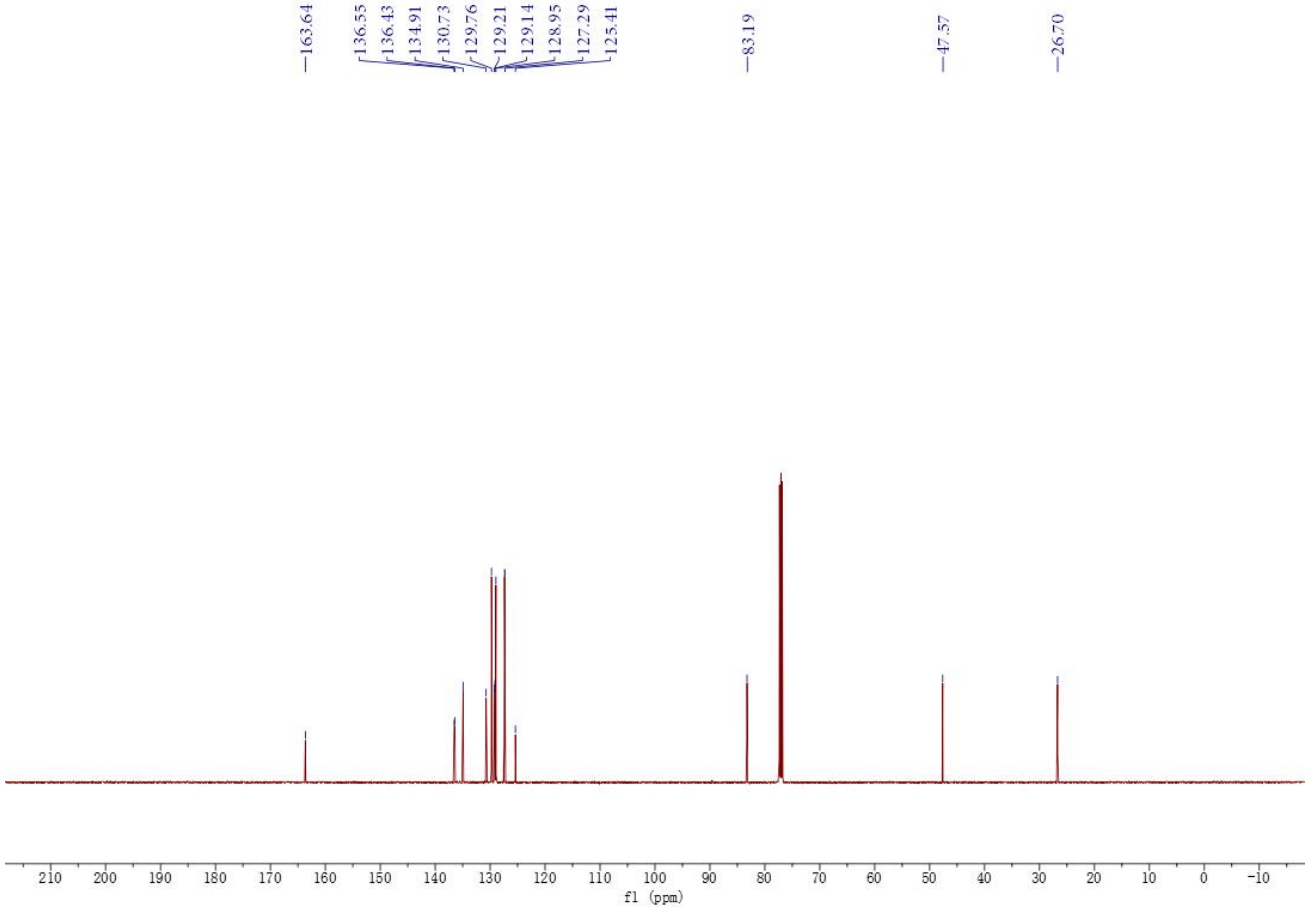
S2. J. Yuan, F. Zeng, W. Mai, L. Yang, Y. Xiao, P. Mao and D. Wei, *Org. Biomol. Chem.*, 2019, **17**, 5038; https://doi.org/10.1039/C9OB00509A.

S3. S. A. Shahzad and T. Wirth, *Angew. Chem., Int. Ed.*, 2009, **48**, 2588; https://doi.org/10.1002/anie.200806148.

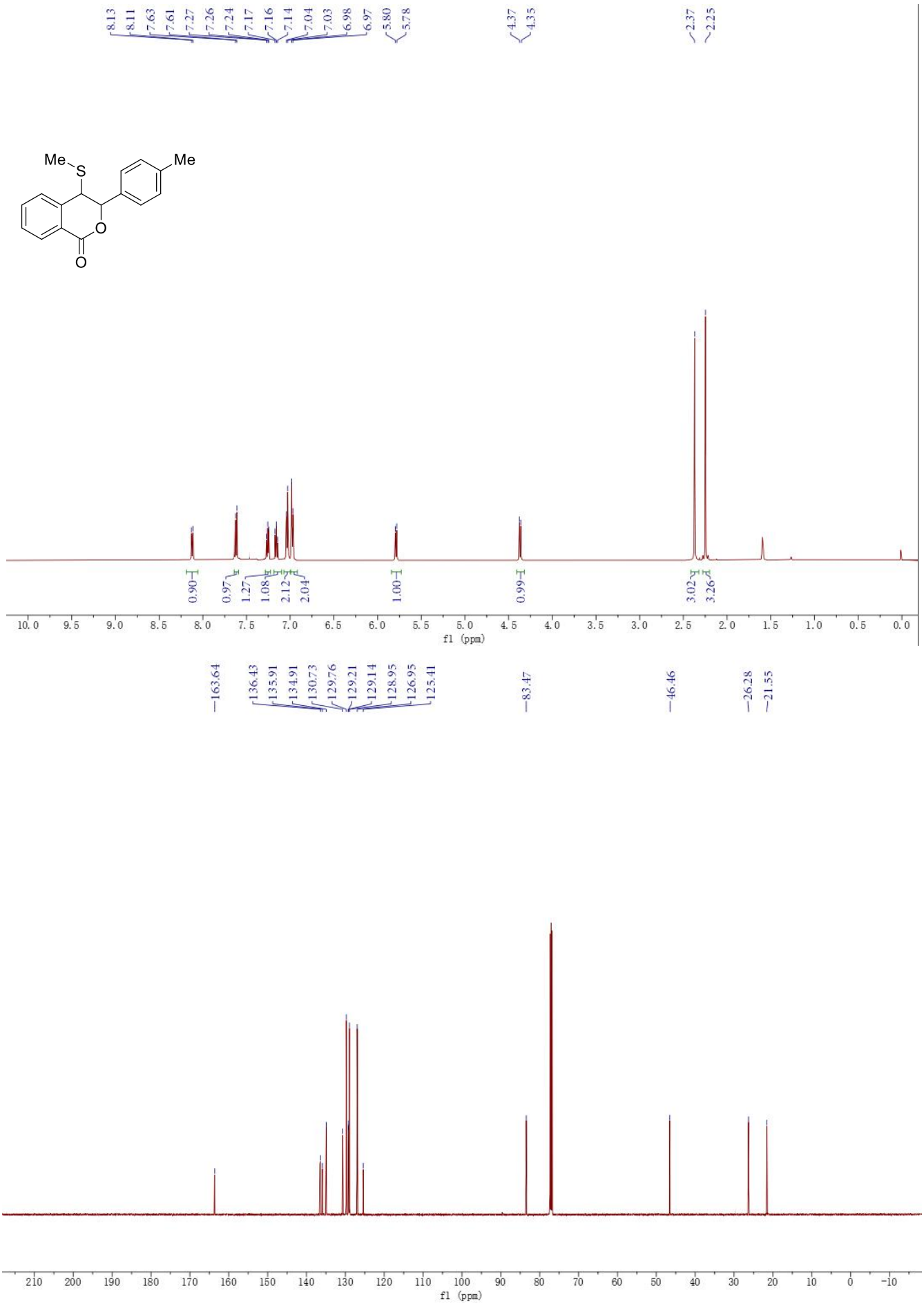
V. NMR spectra

(1). 4-(methylthio)-3-phenylisochroman-1-one 3a

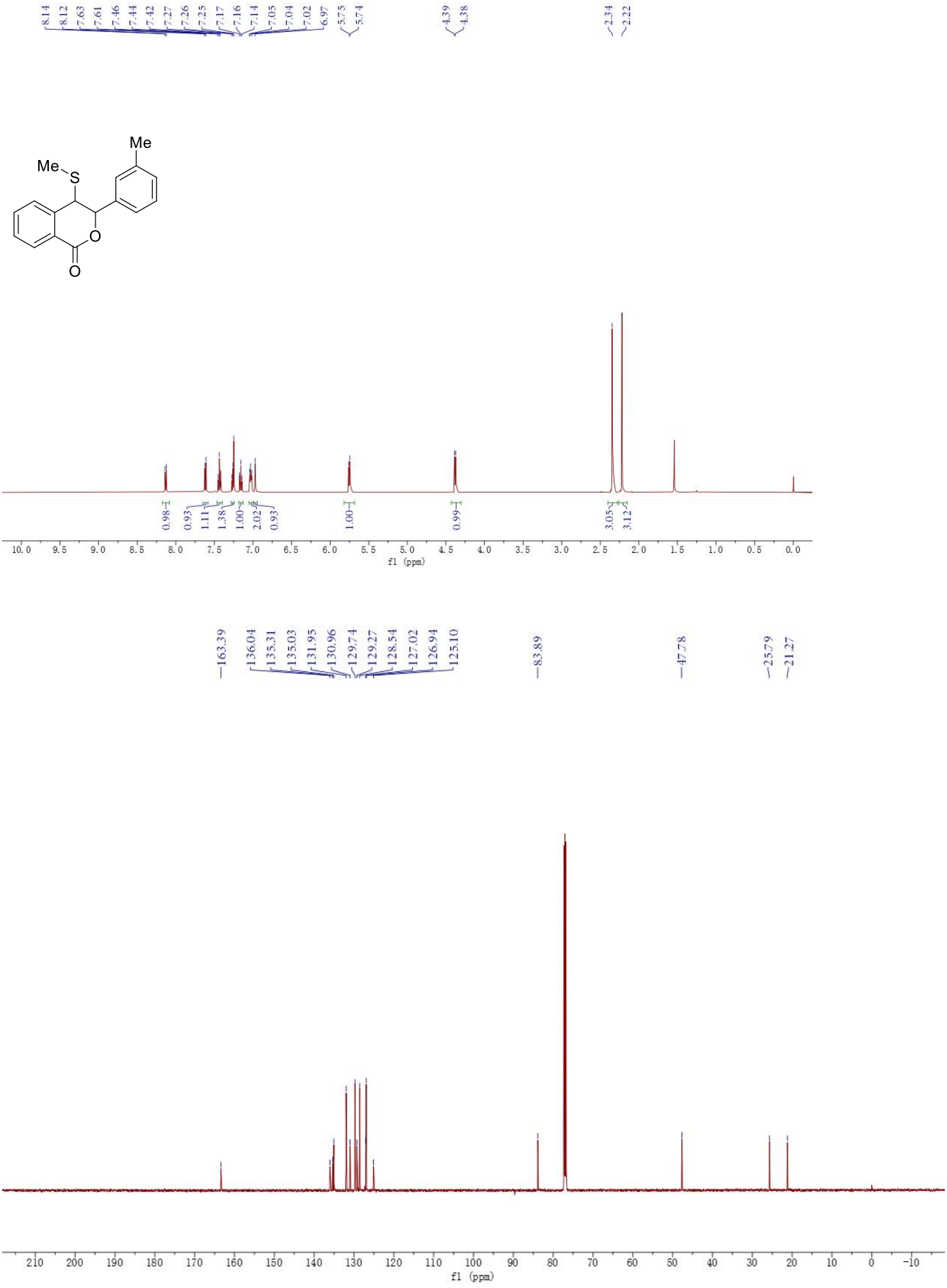




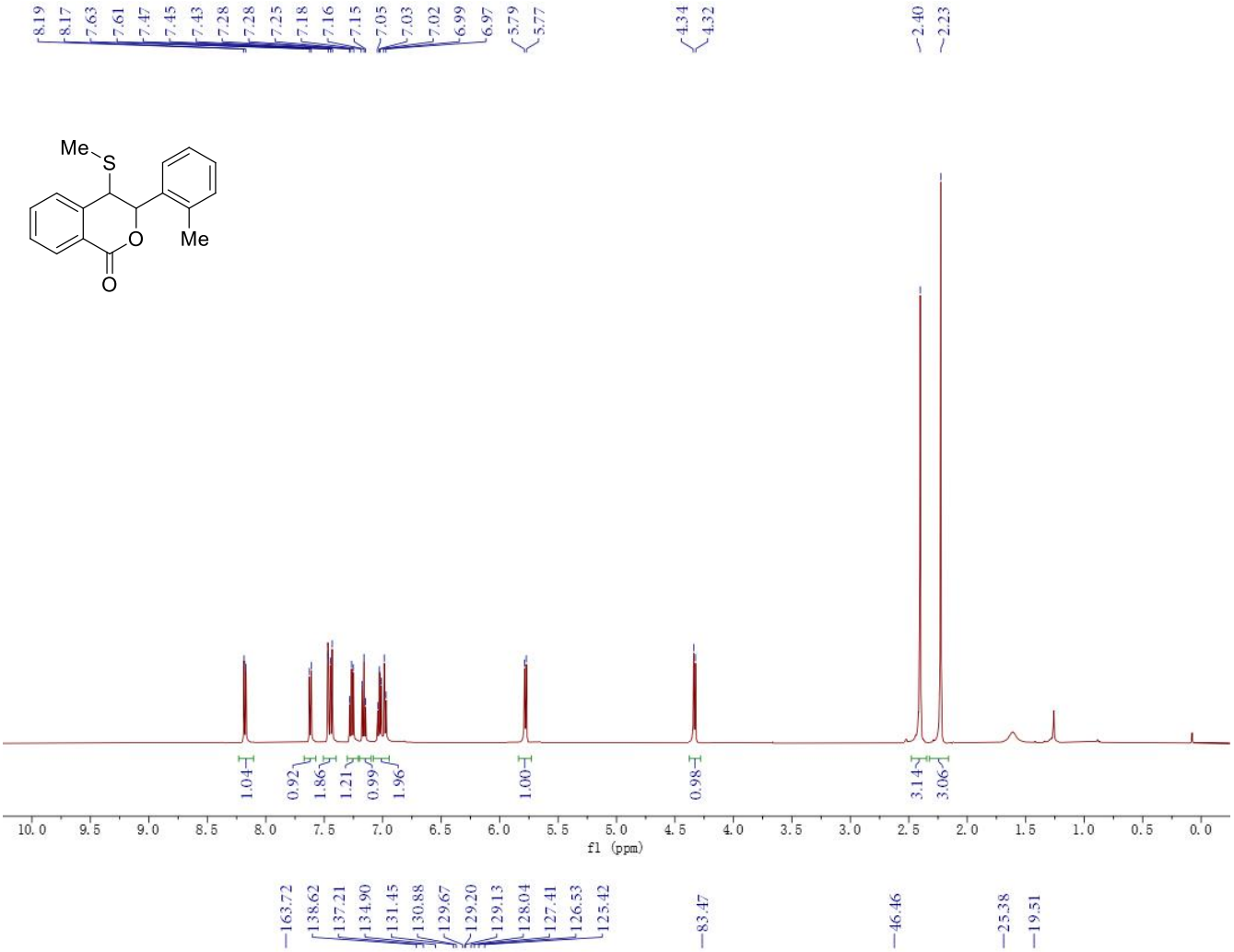
(2). 4-(methylthio)-3-(*p*-tolyl)isochroman-1-one 3b

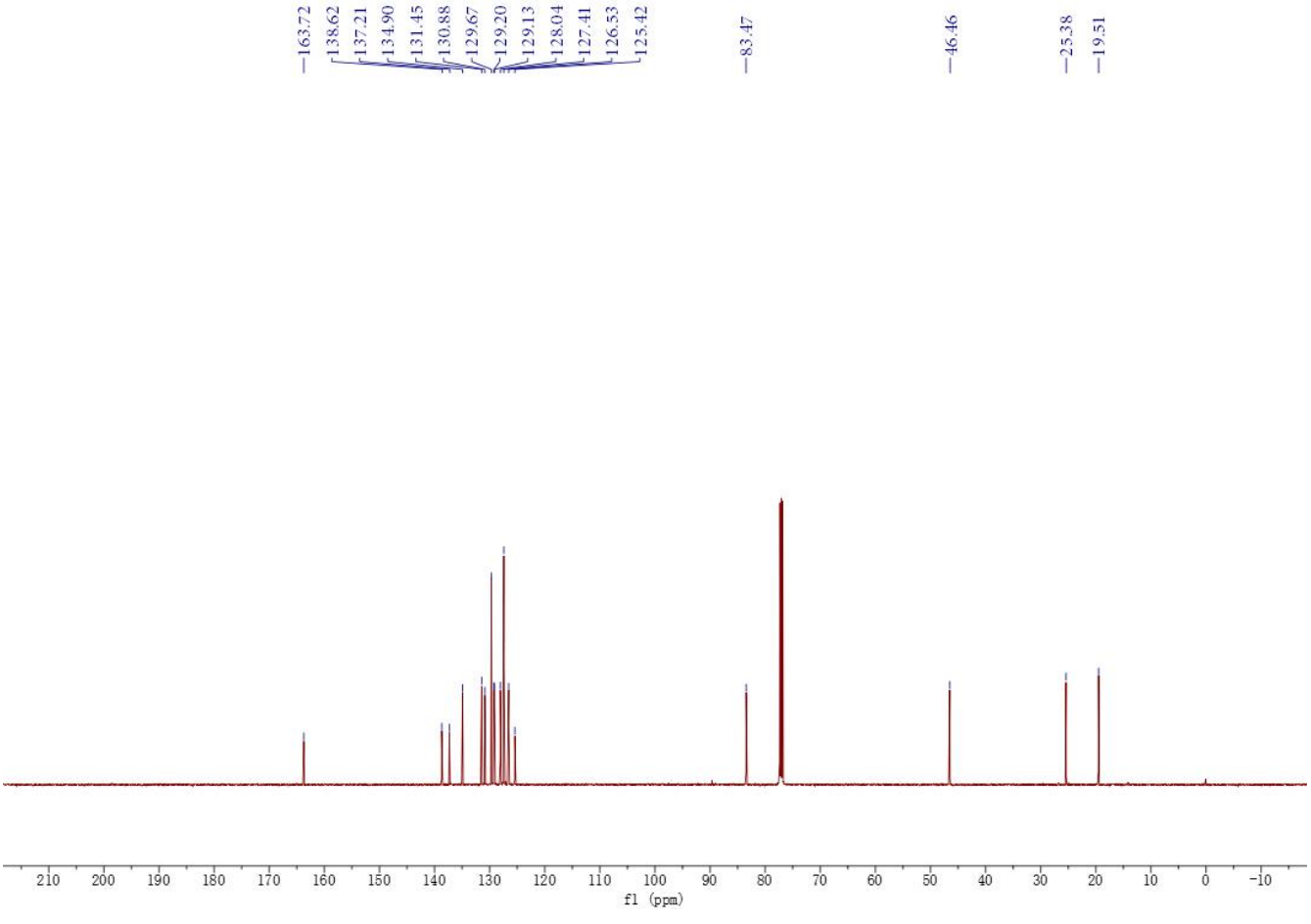


(3). 4-(methylthio)-3-(*m*-tolyl)isochroman-1-one 3c

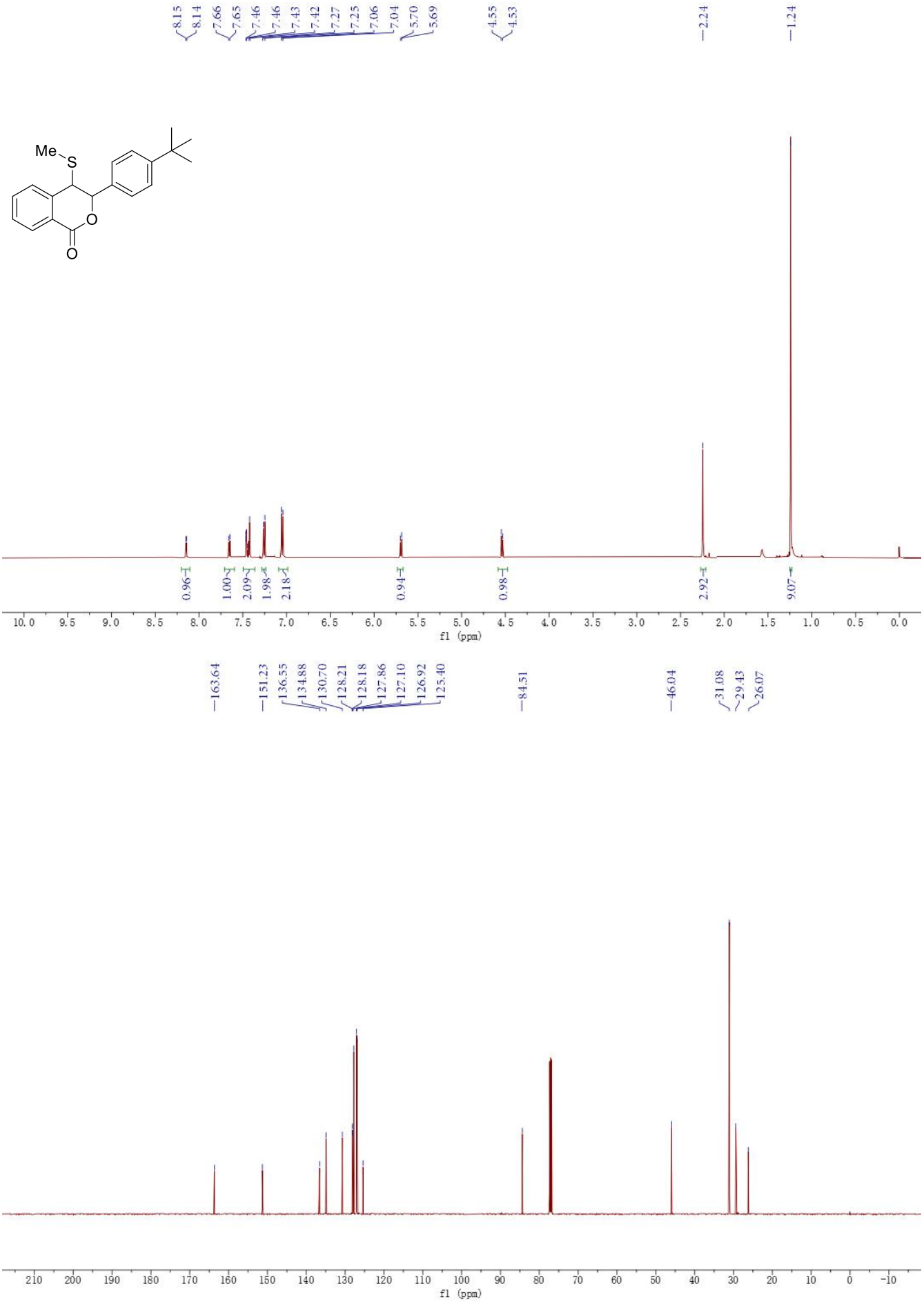


(4). 4-(methylthio)-3-(*o*-tolyl)isochroman-1-one 3d

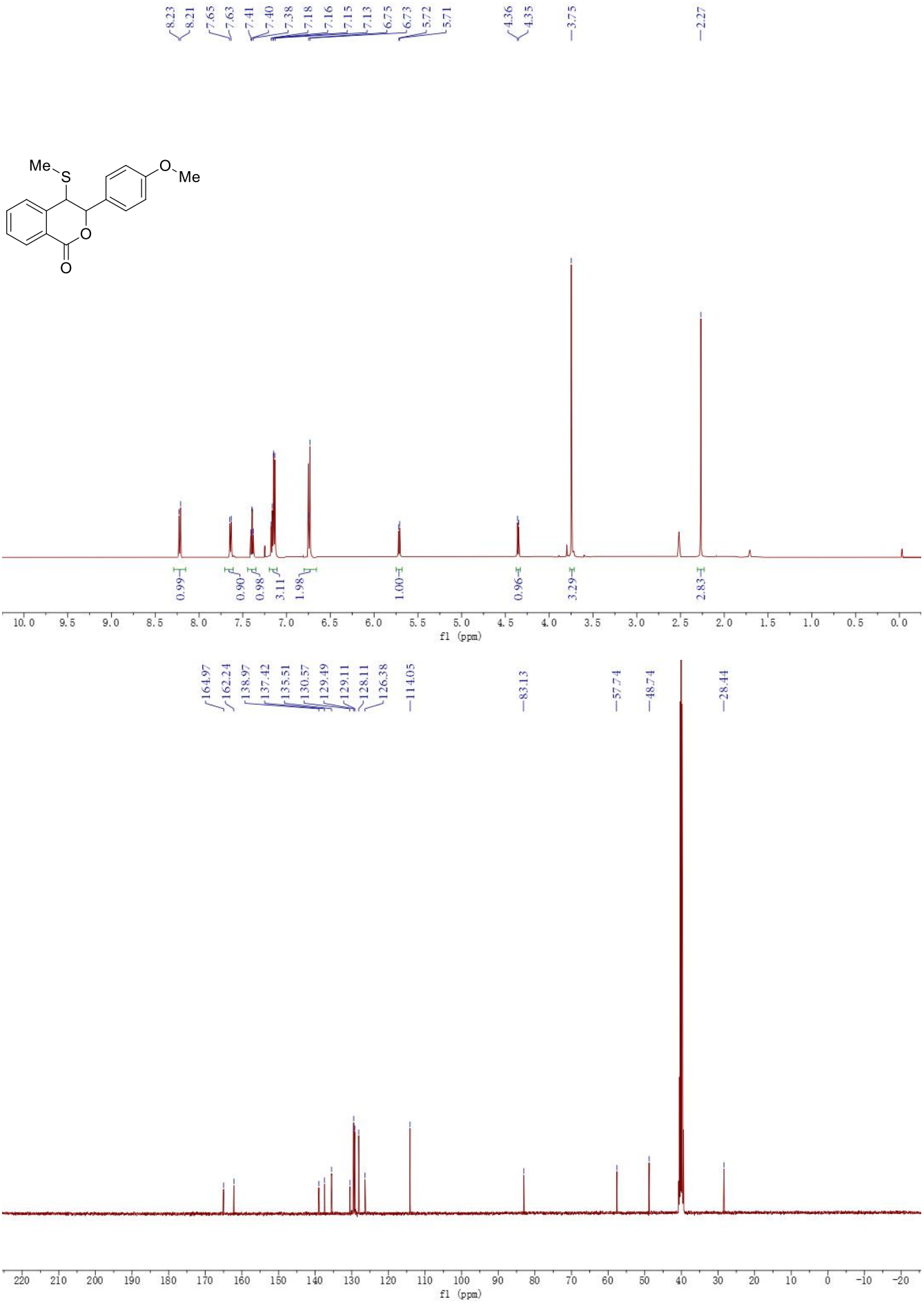




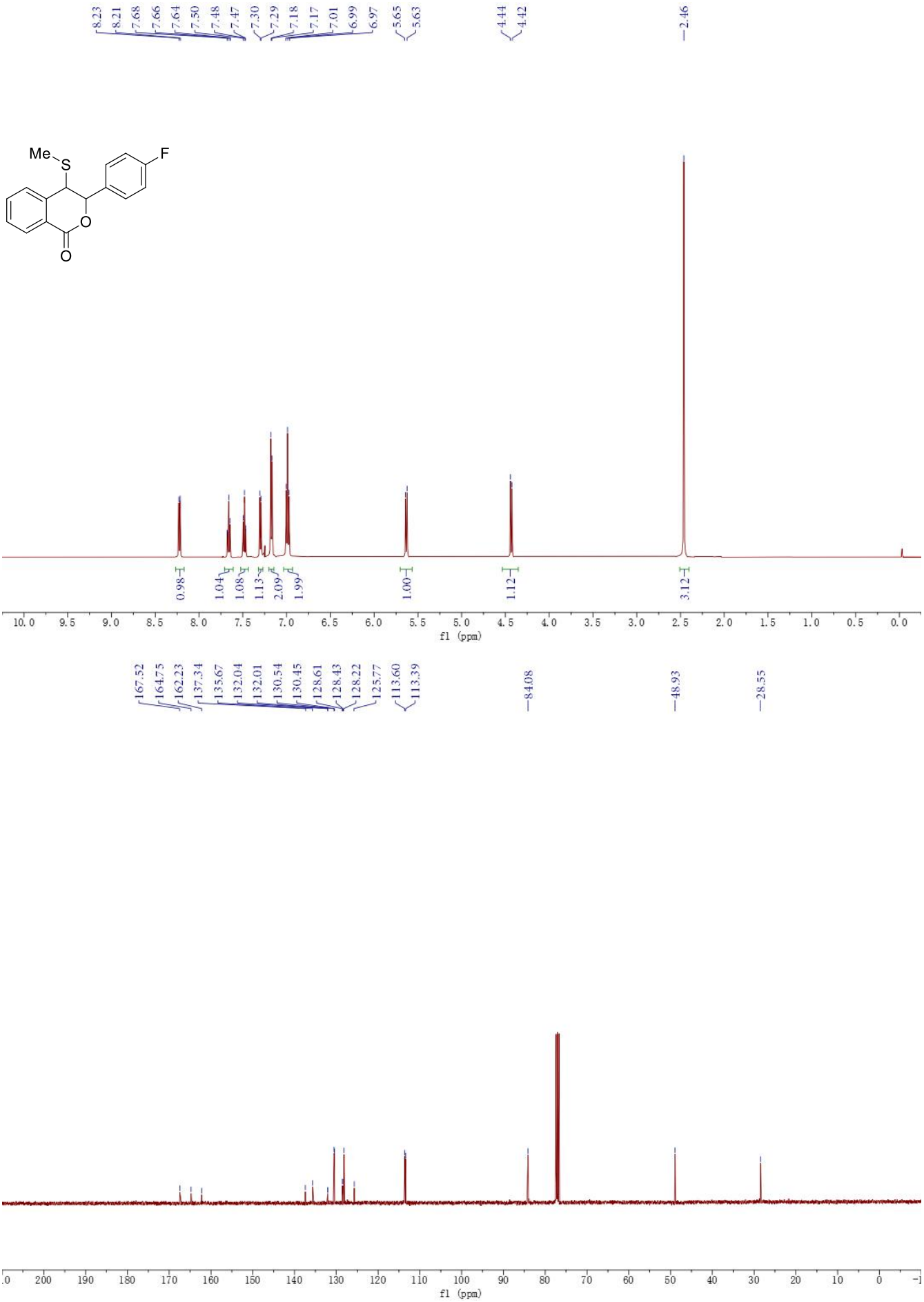
(5). 3-(4-*tert*-butylphenyl)-4-(methylthio)isochroman-1-one 3e

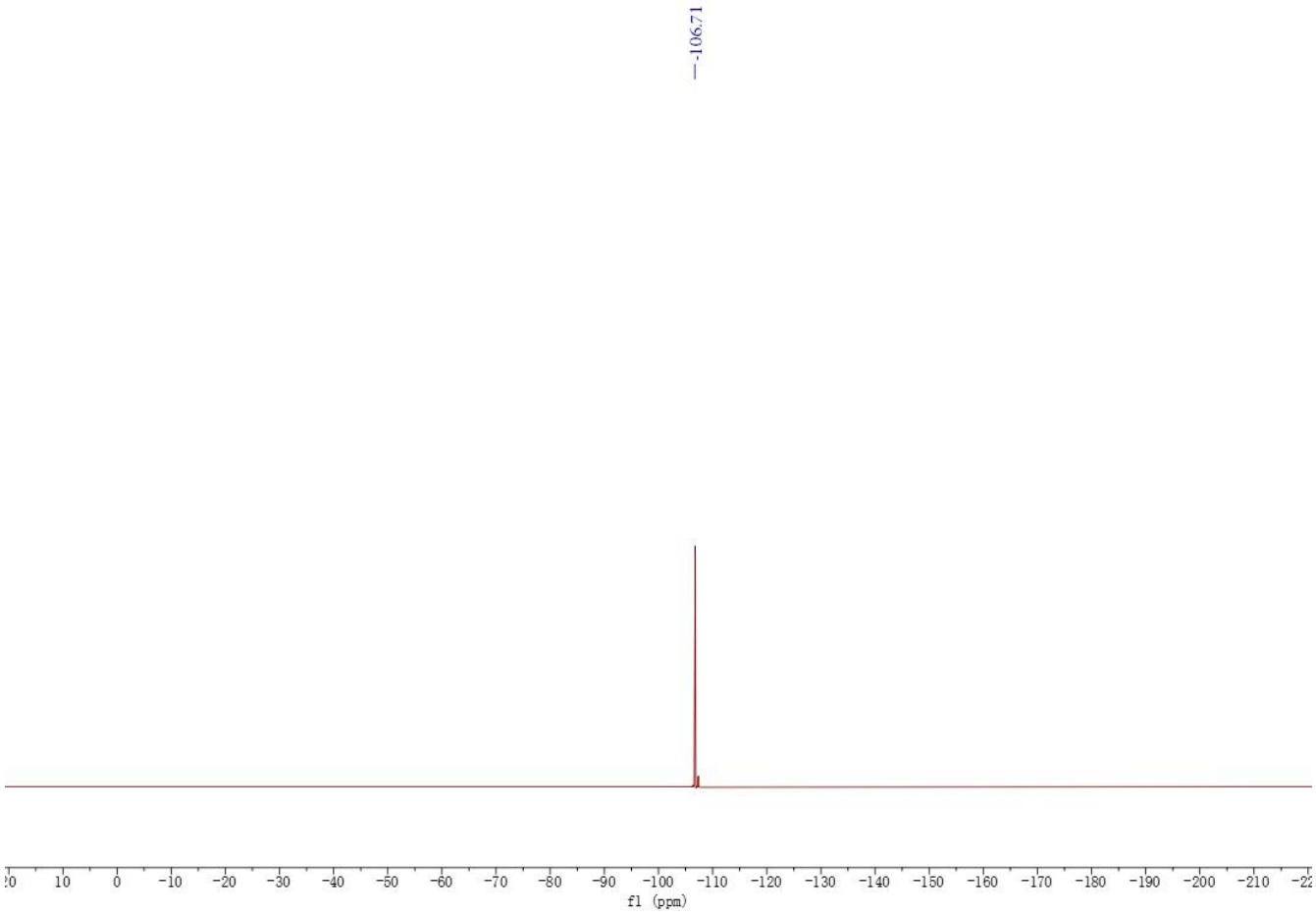


(6). 3-(4-methoxyphenyl)-4-(methylthio)isochroman-1-one 3f



(7). 3-(4-fluorophenyl)-4-(methylthio)isochroman-1-one 3g

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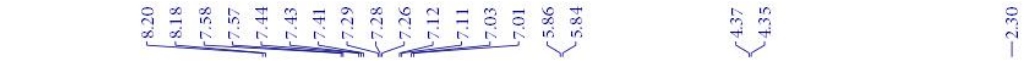
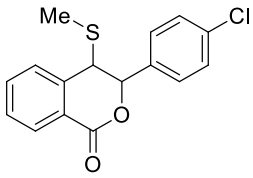
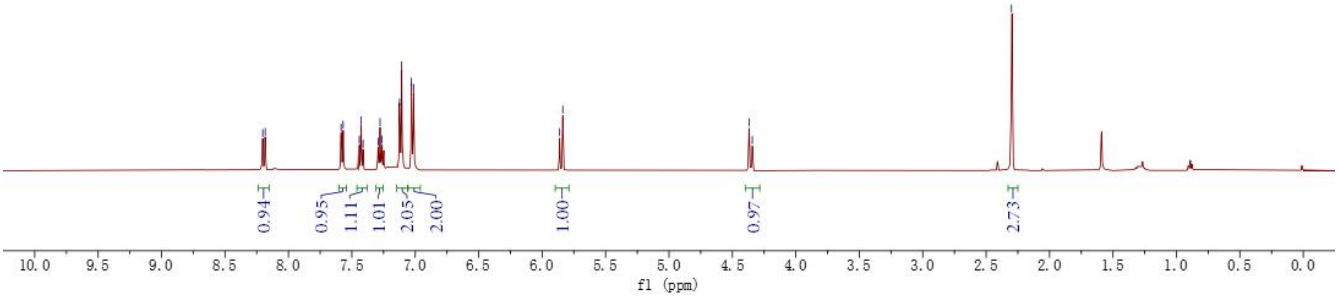
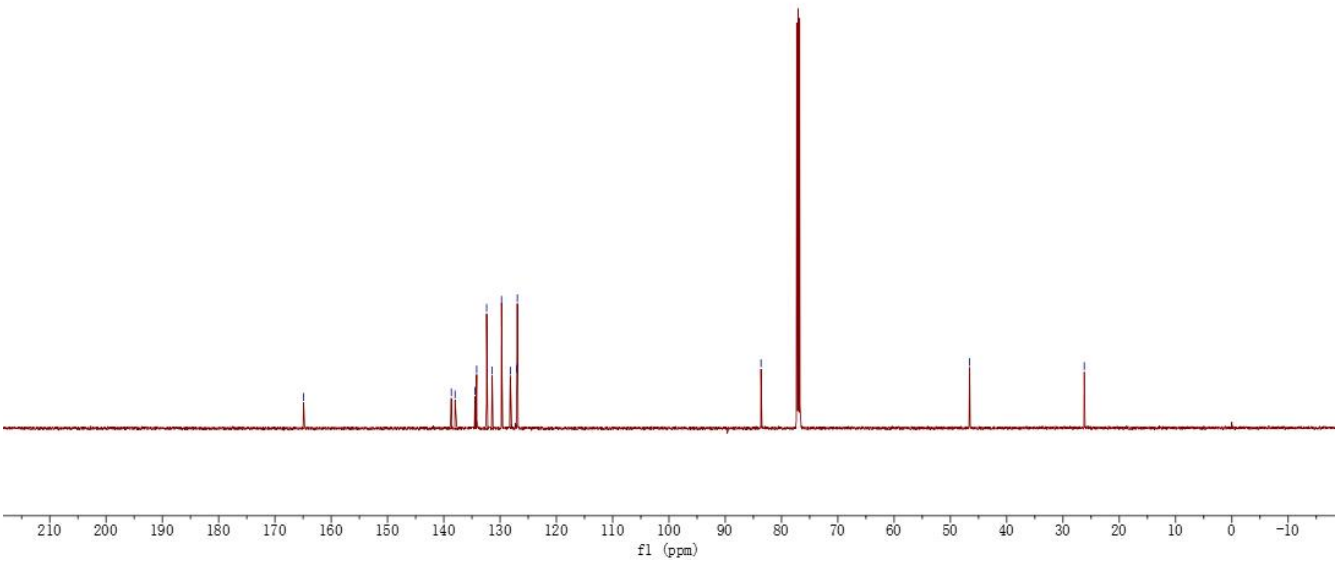
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(8). 3-(4-chlorophenyl)-4-(methylthio)isochroman-1-one 3h

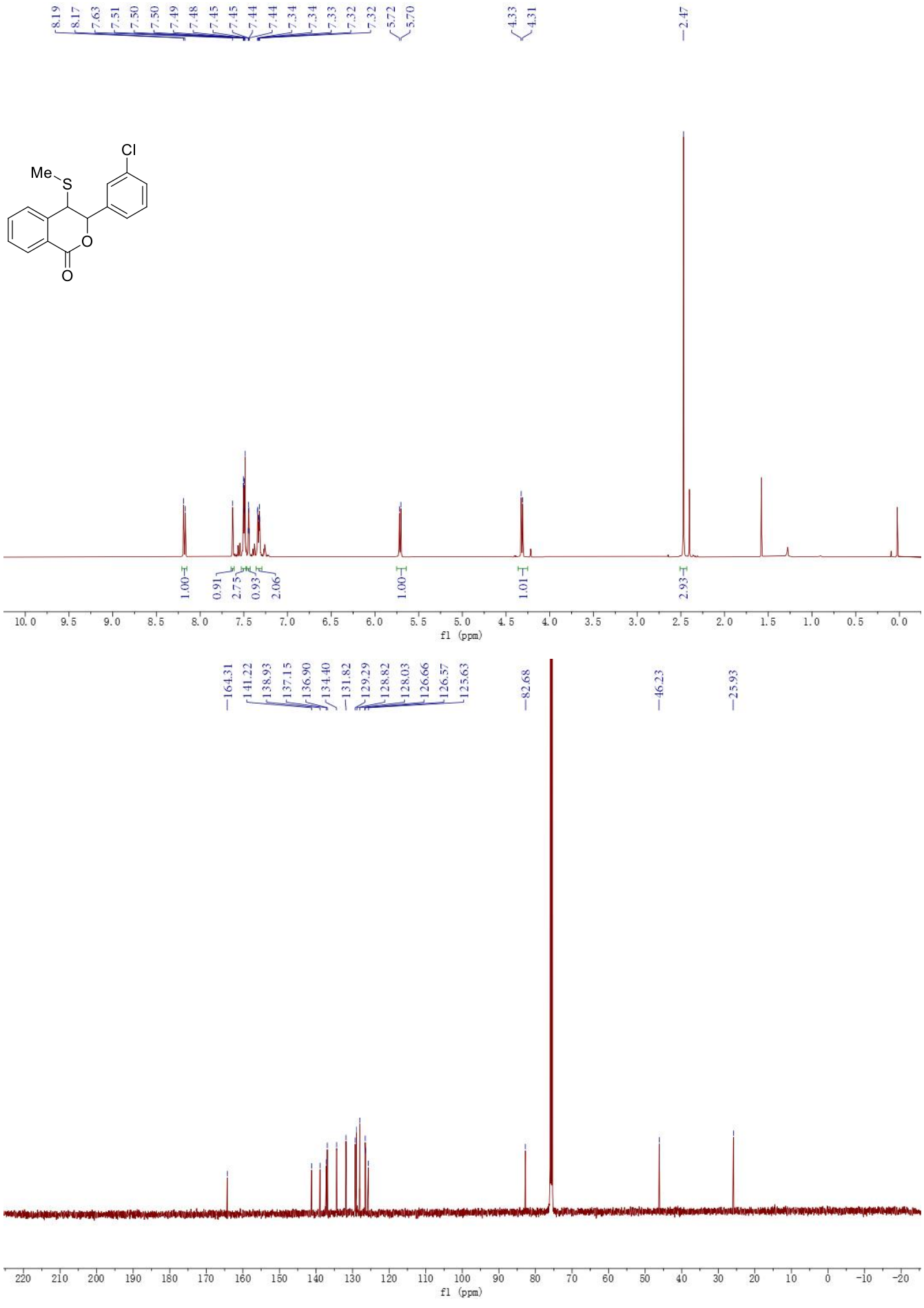




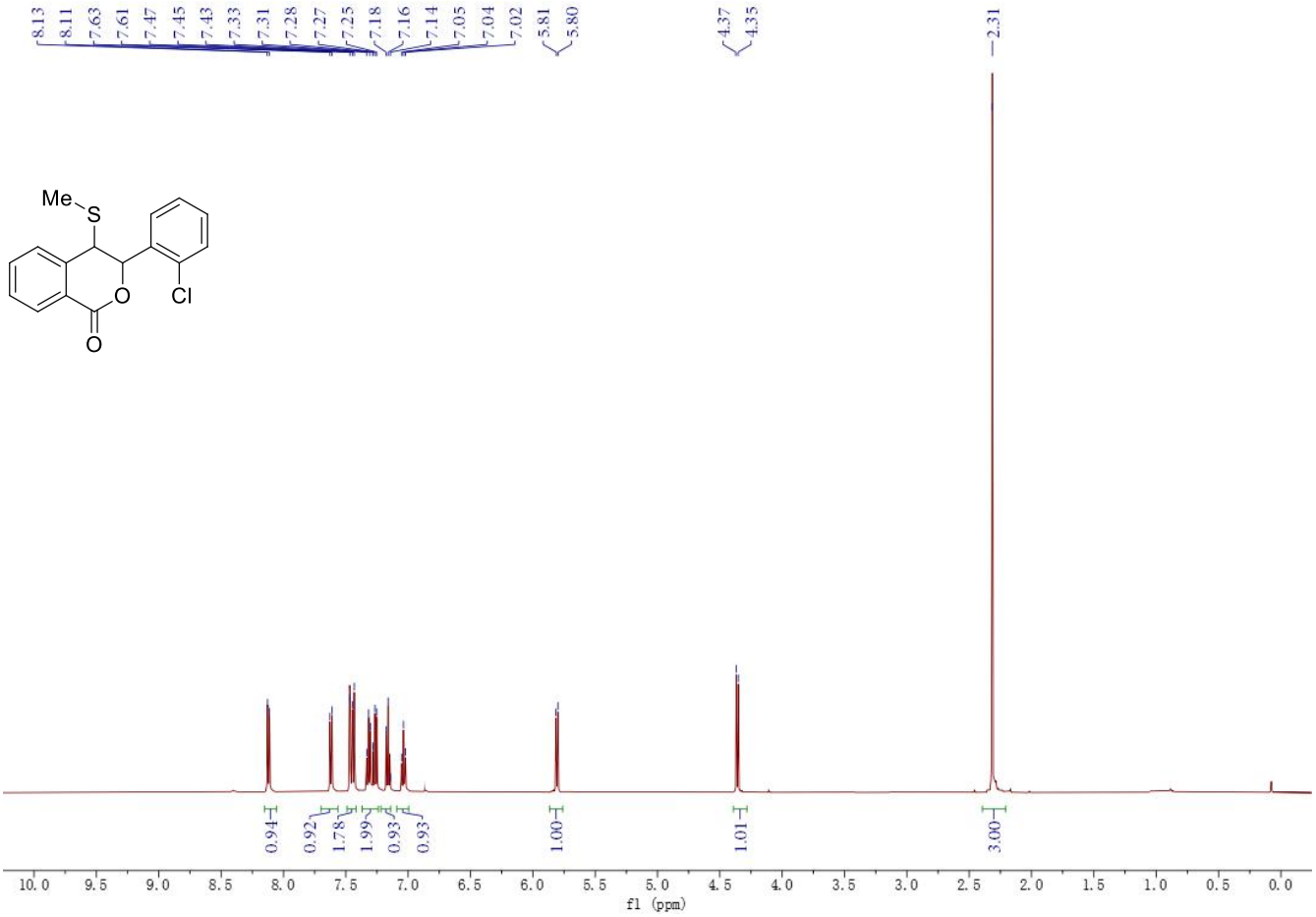


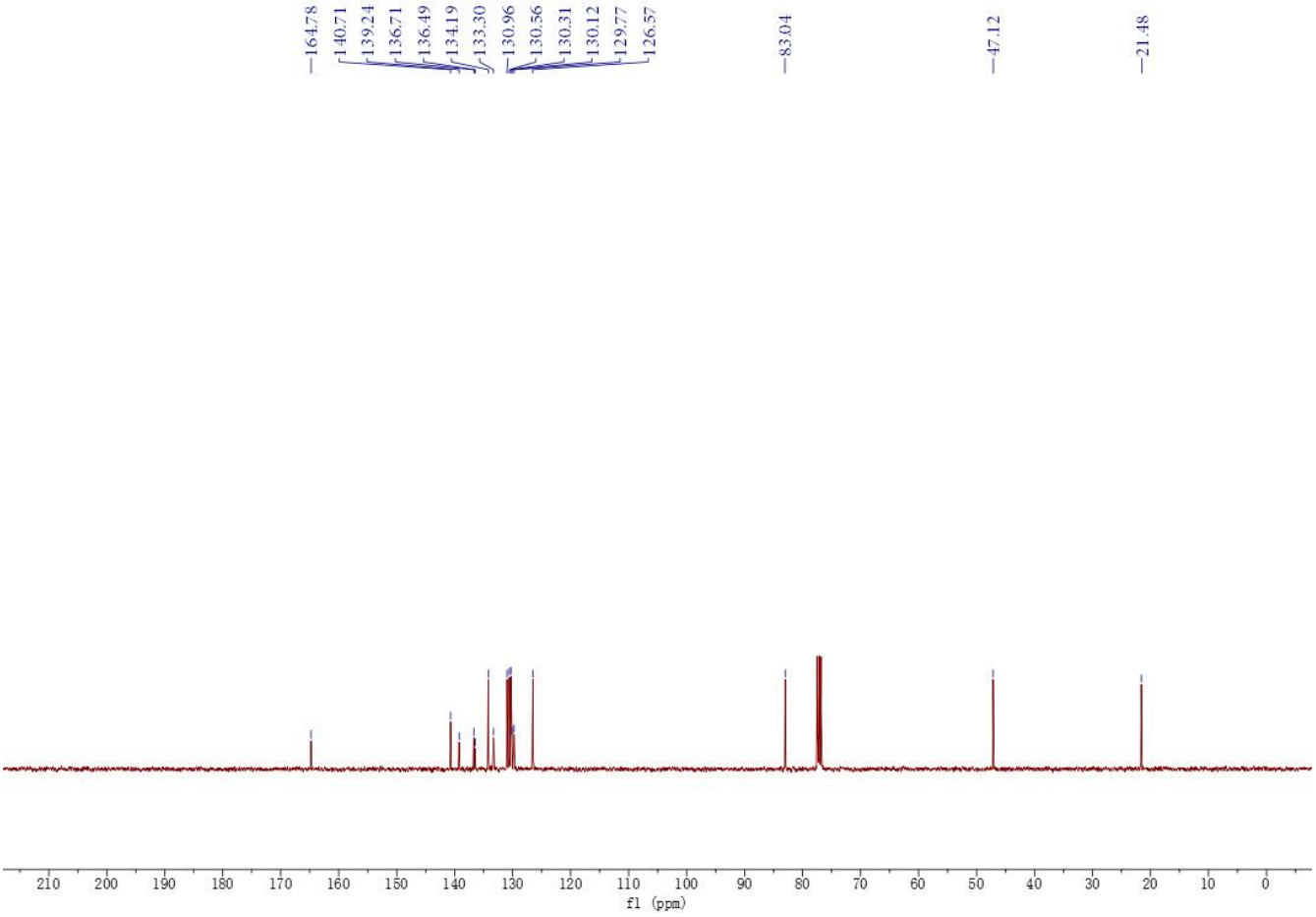


(9). 3-(3-chlorophenyl)-4-(methylthio)isochroman-1-one 3i

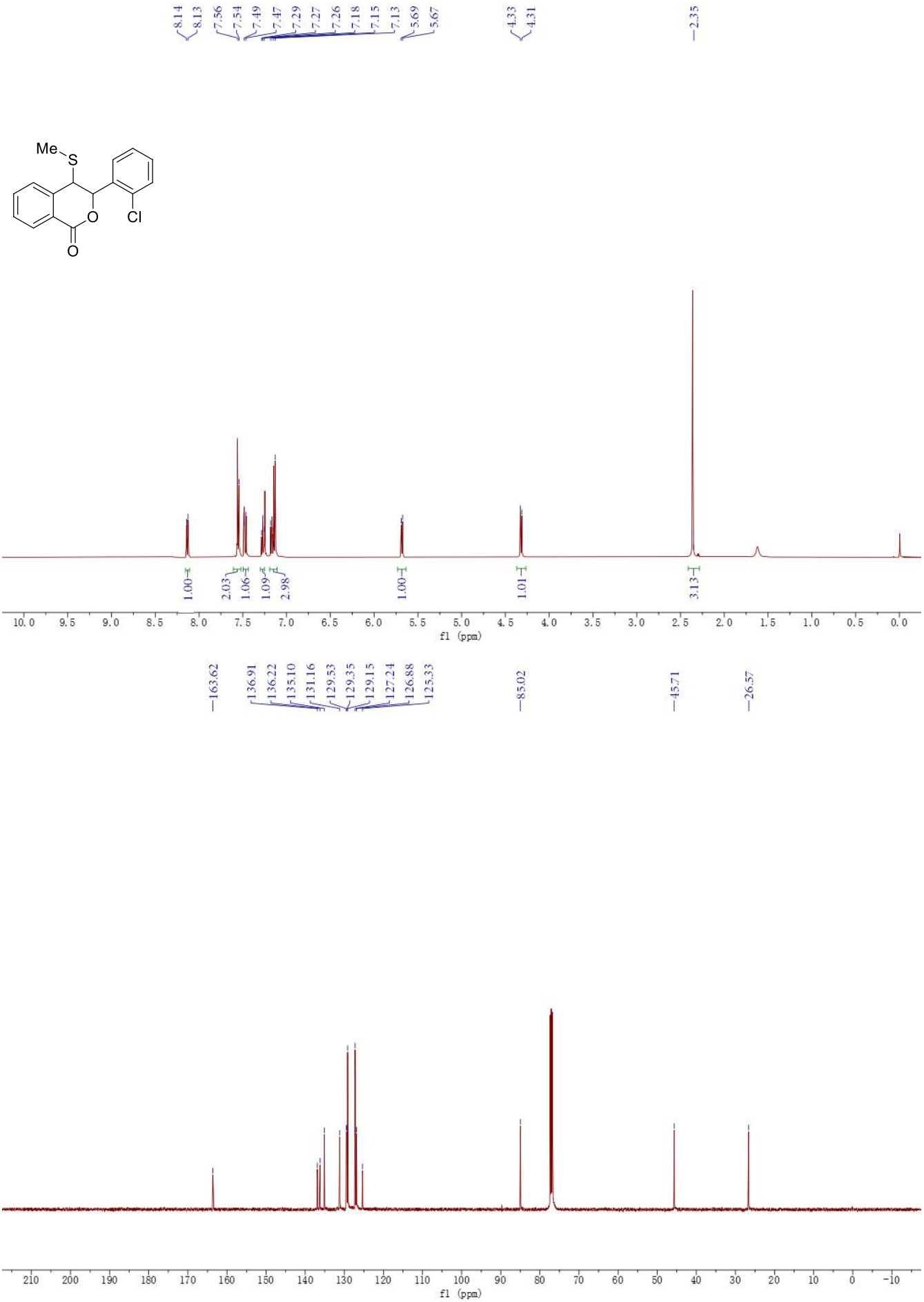


(10). 3-(2-chlorophenyl)-4-(methylthio)isochroman-1-one 3j

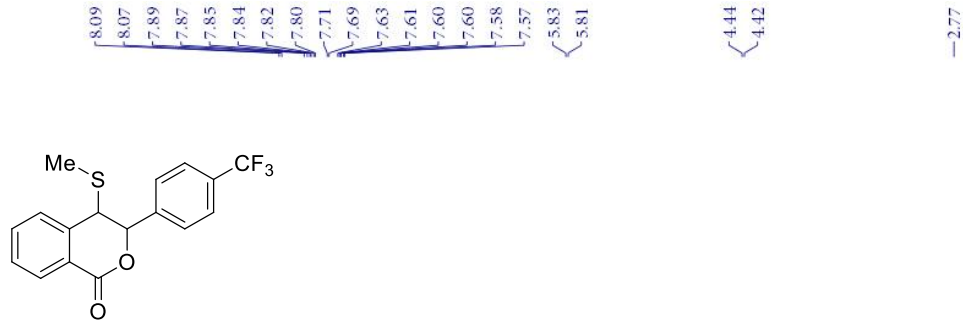


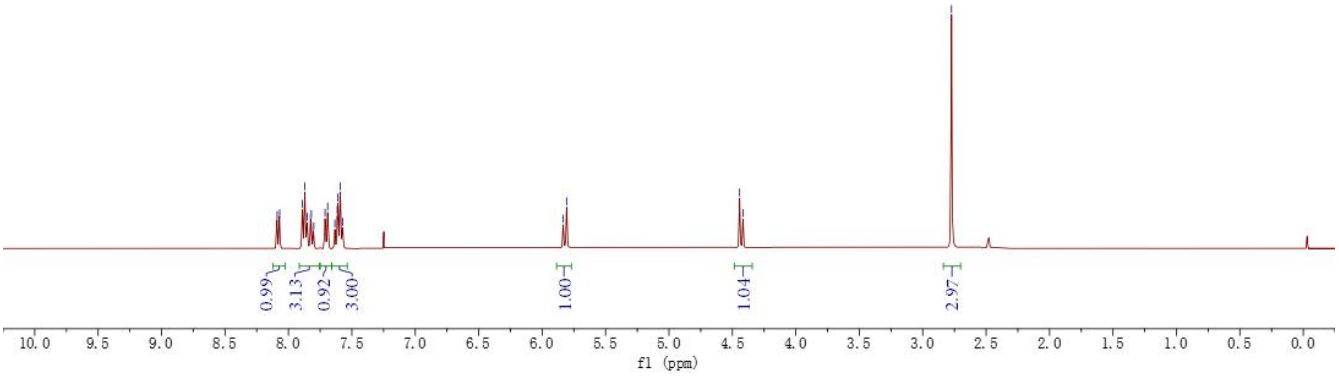


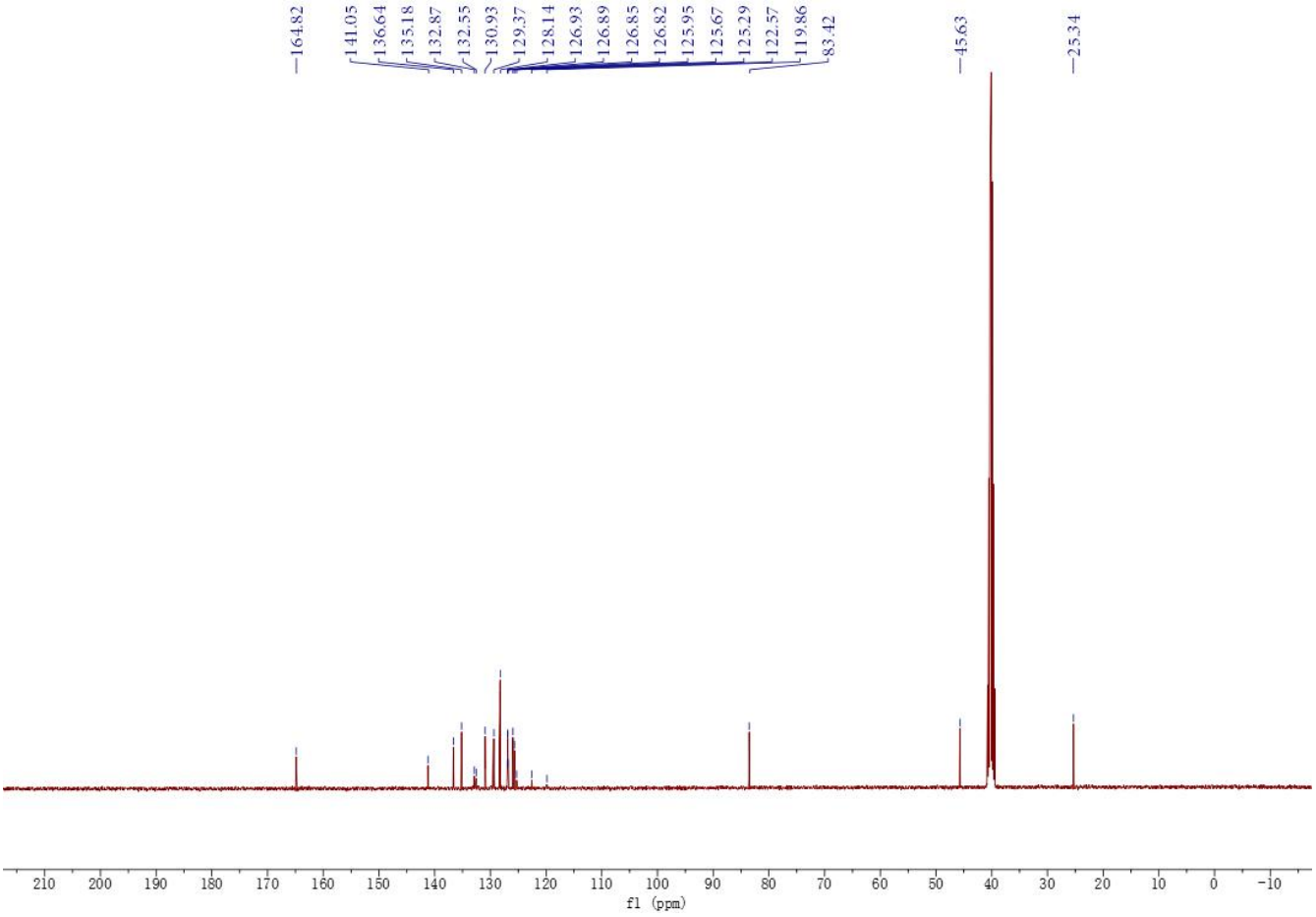
(11). 3-(4-bromophenyl)-4-(methylthio)isochroman-1-one 3k

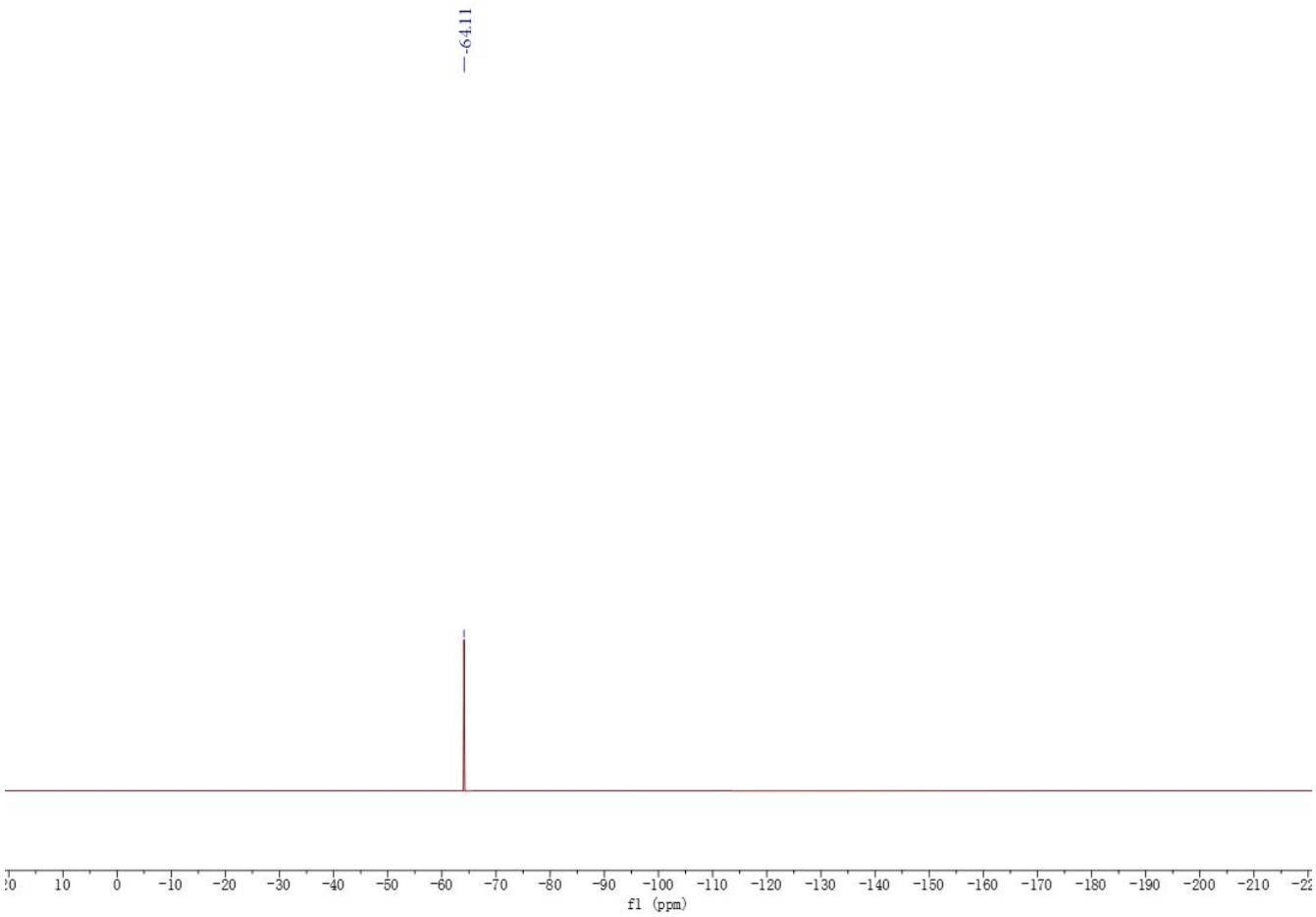


(12). 4-(methylthio)-3-(4-(trifluoromethyl)phenyl)isochroman-1-one 3l





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-140
-150
-160
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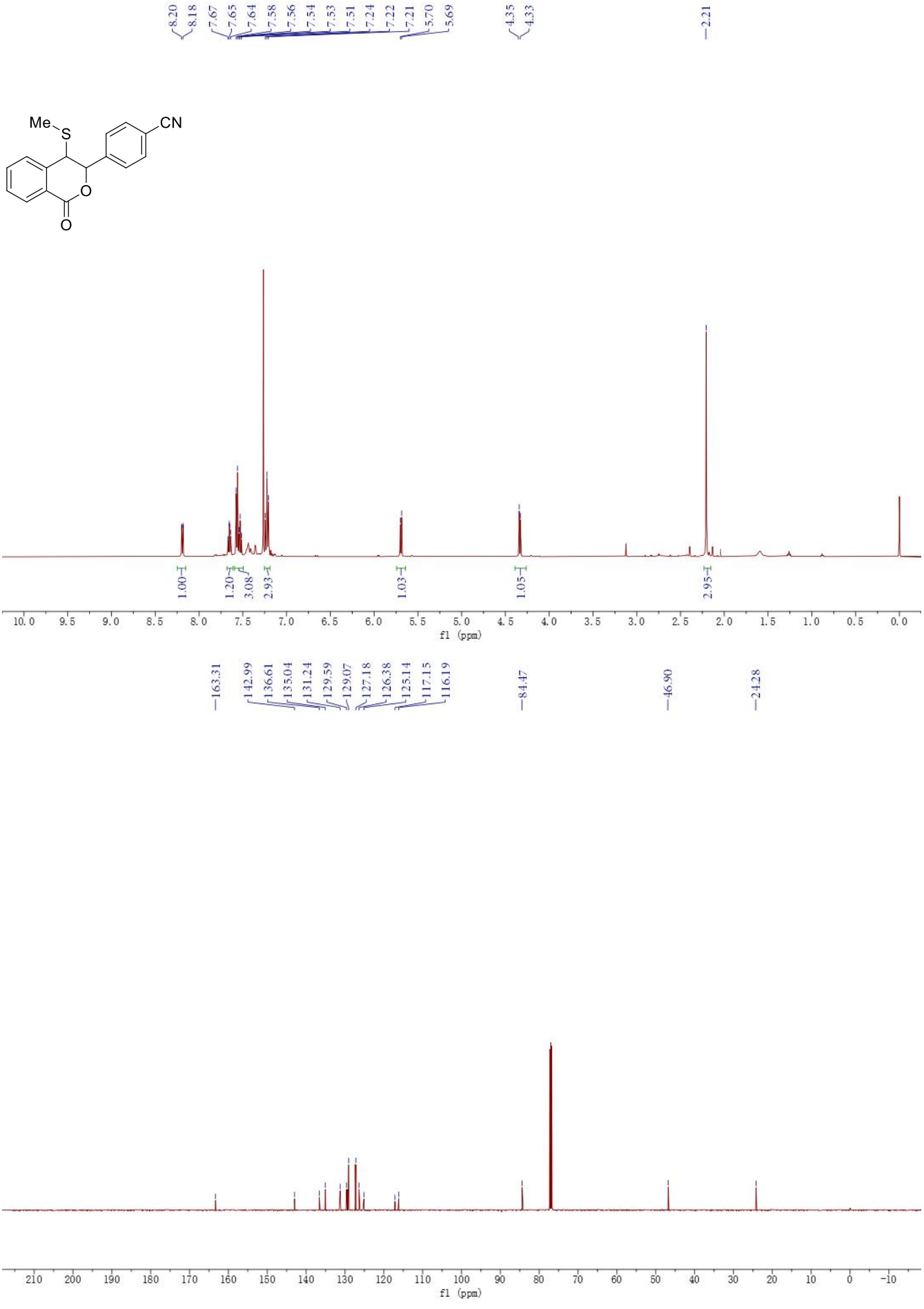
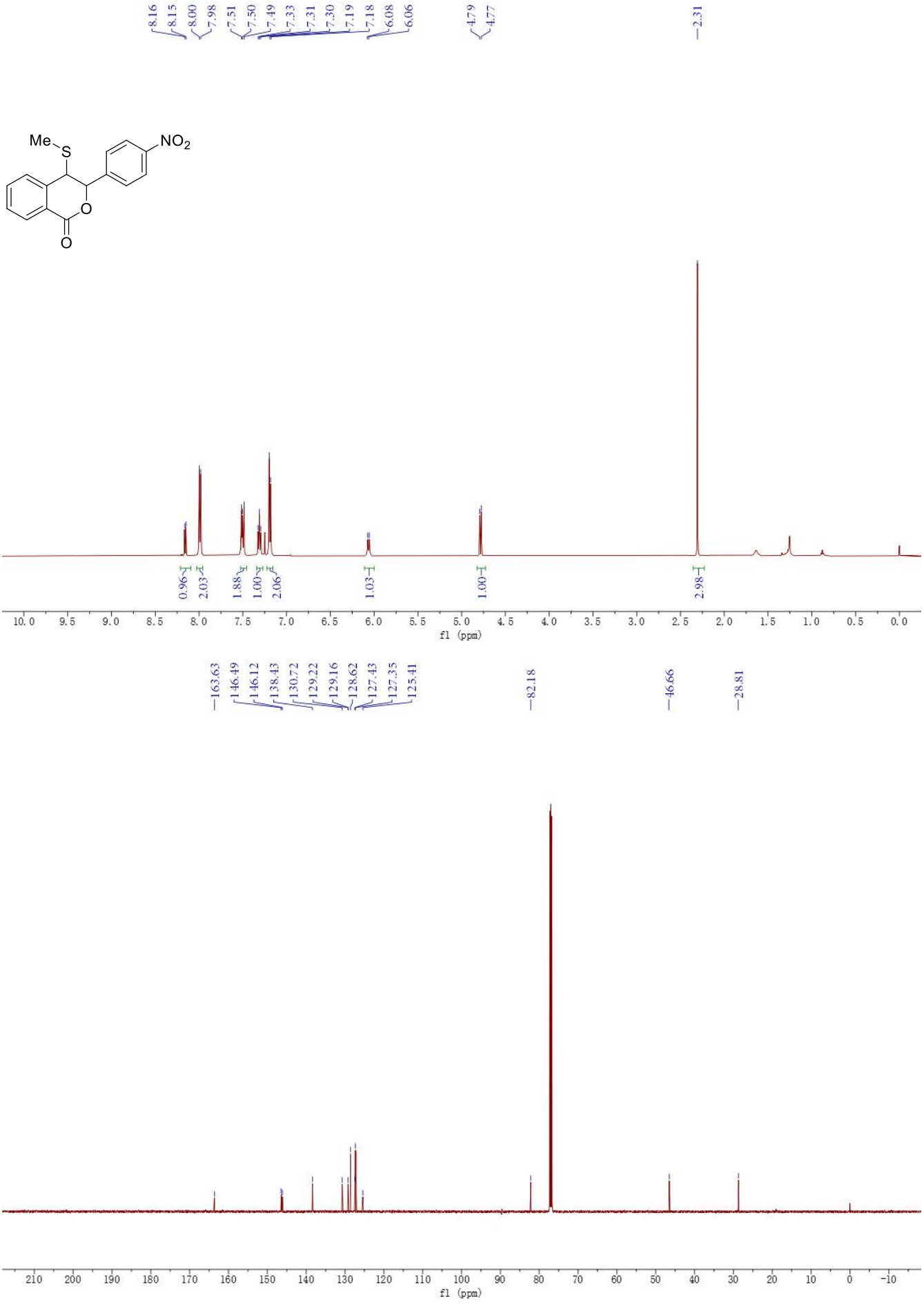
-180
-190
-200
-210
f1 (ppm)

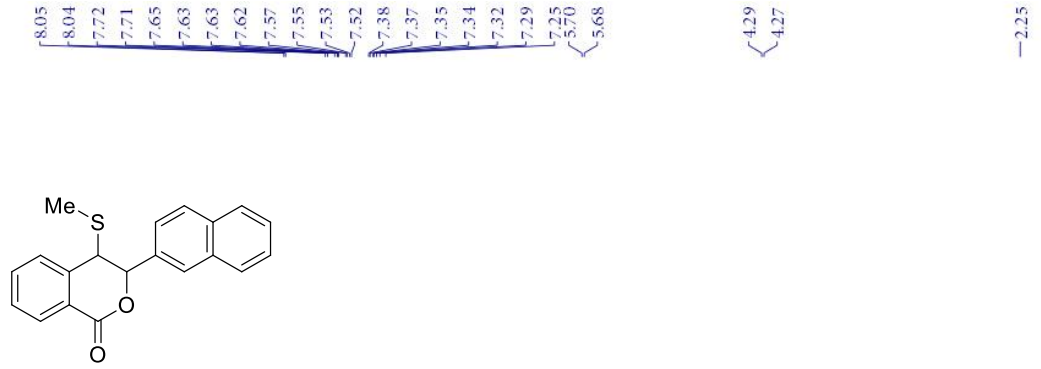
(13). 4-(4-(methylthio)-1-oxoisochroman-3-yl)benzonitrile 3m

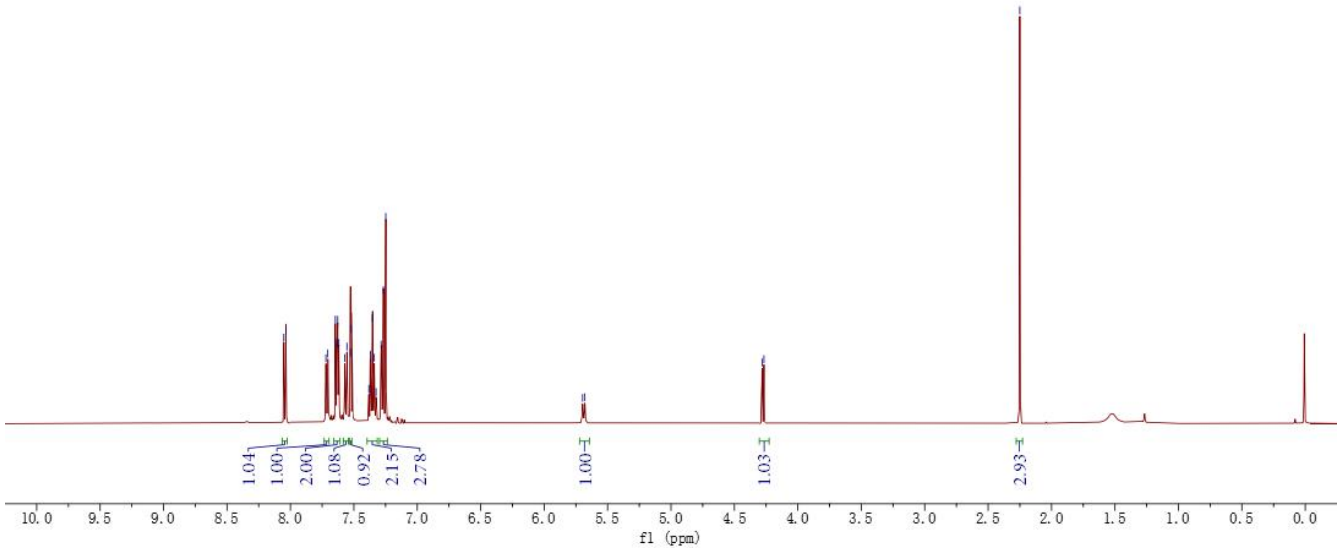


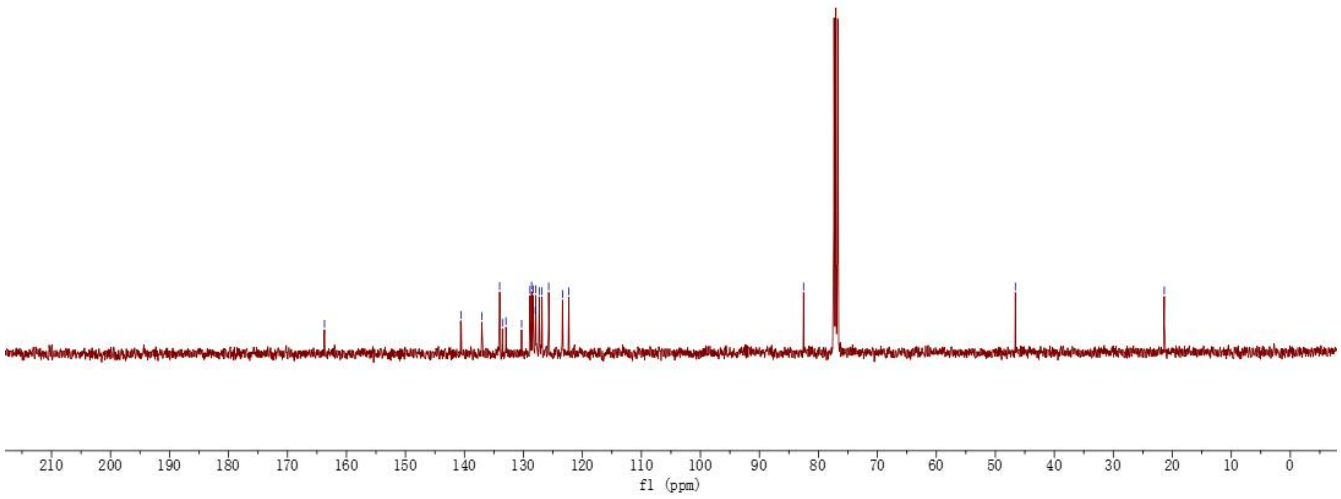
(14). 4-(methylthio)-3-(4-nitrophenyl)isochroman-1-one 3n



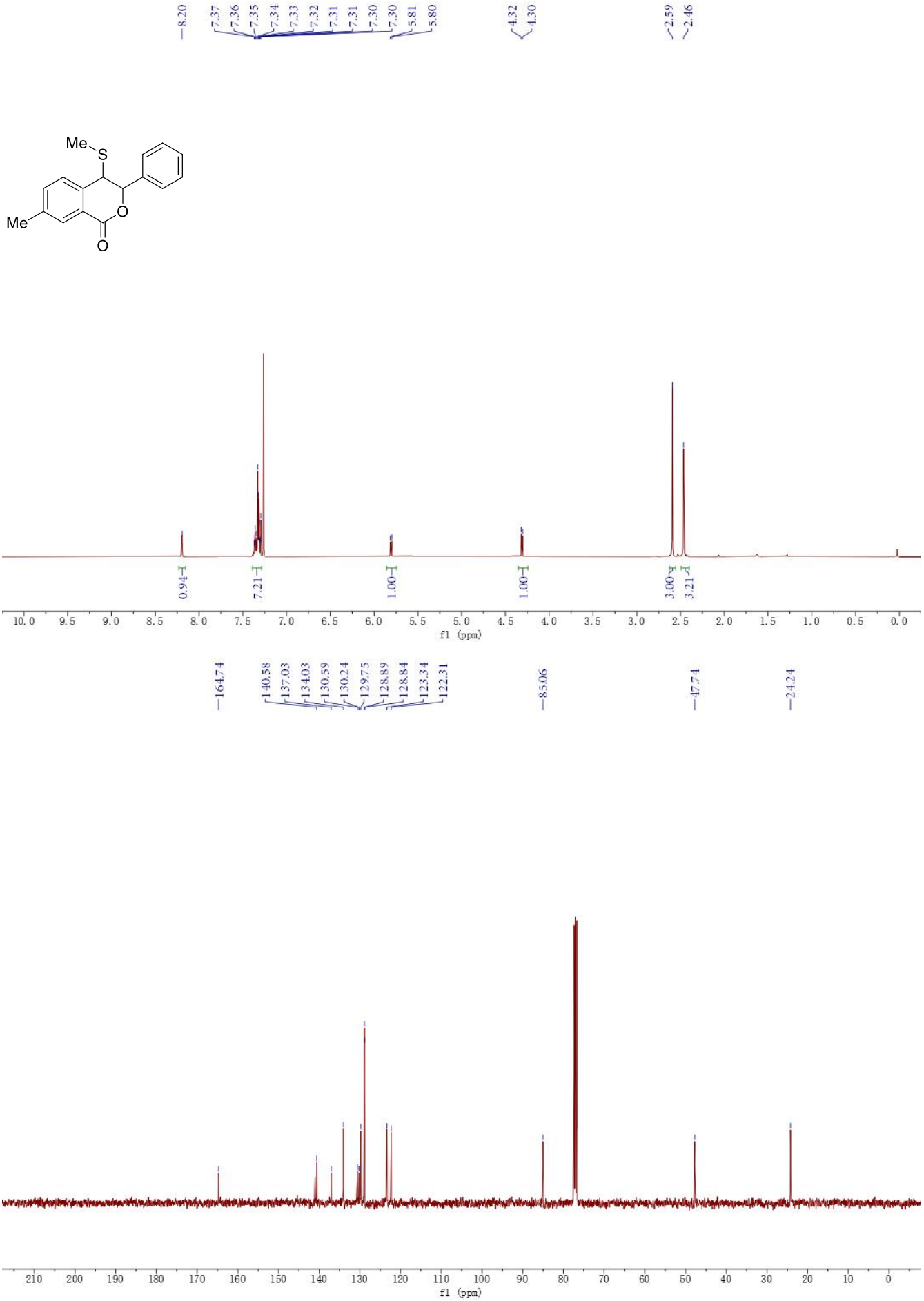
(15). 4-(methylthio)-3-(naphthalen-2-yl)isochroman-1-one 3o



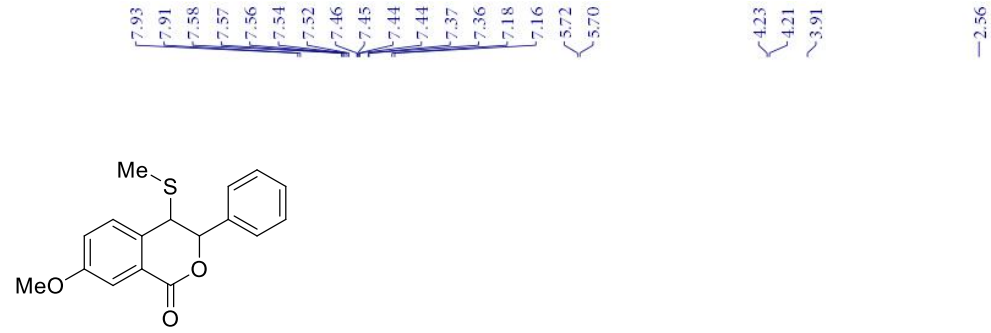


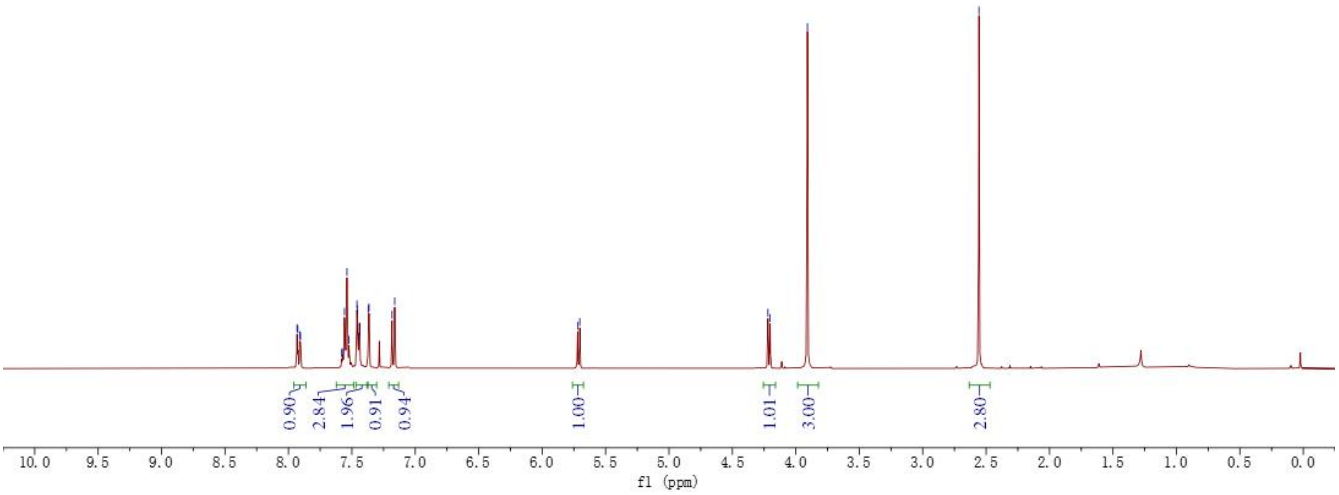


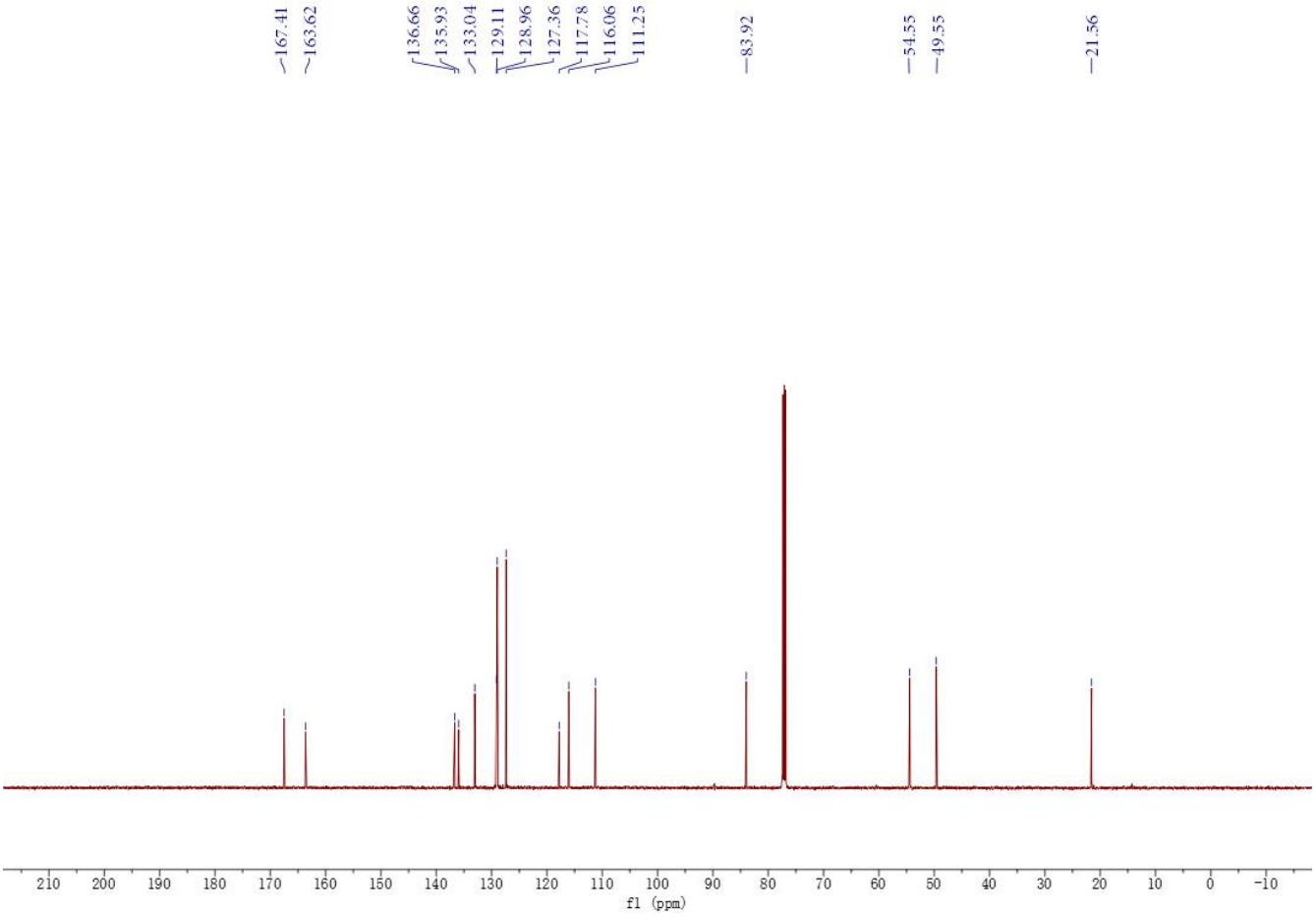
(16). 7-methyl-4-(methylthio)-3-phenylisochroman-1-one 3p



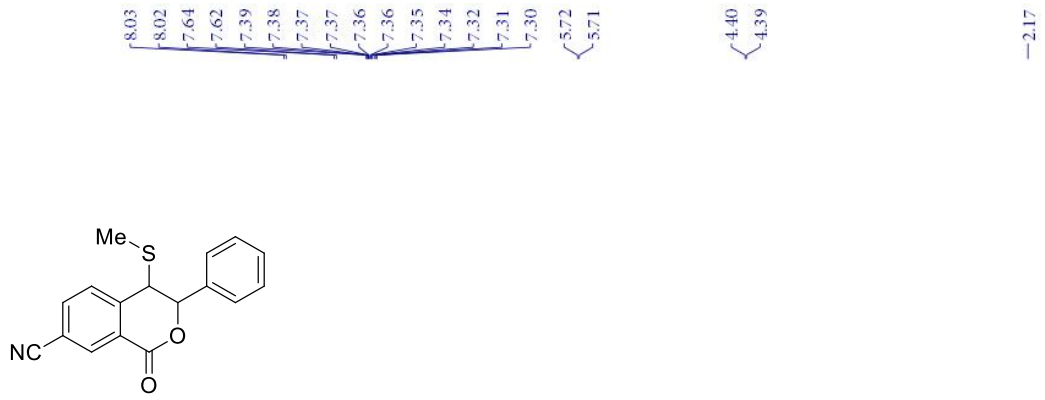
(17). 7-methoxy-4-(methylthio)-3-phenylisochroman-1-one 3q

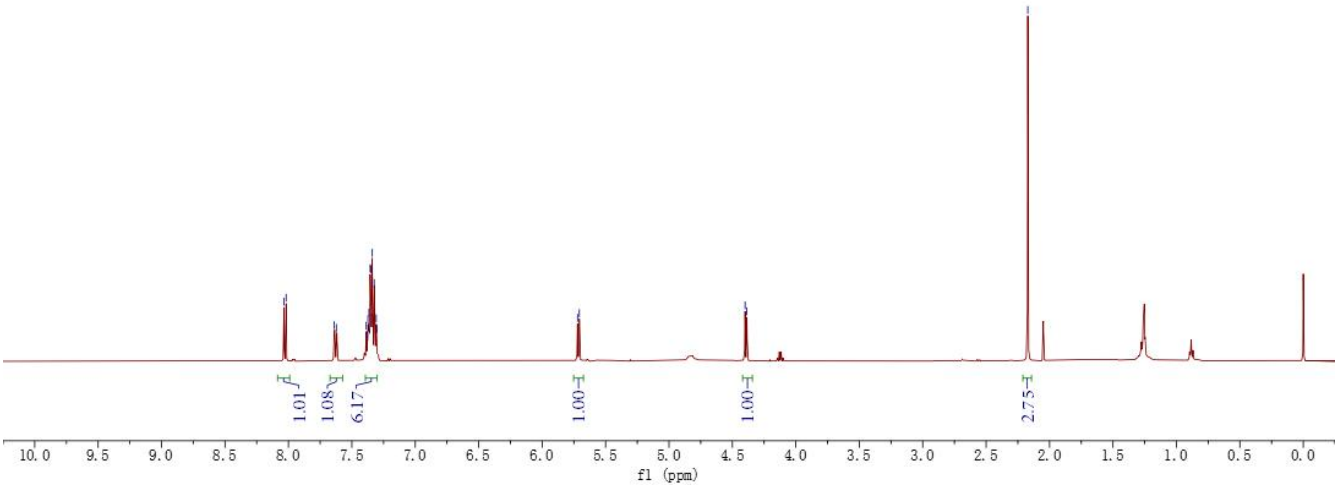


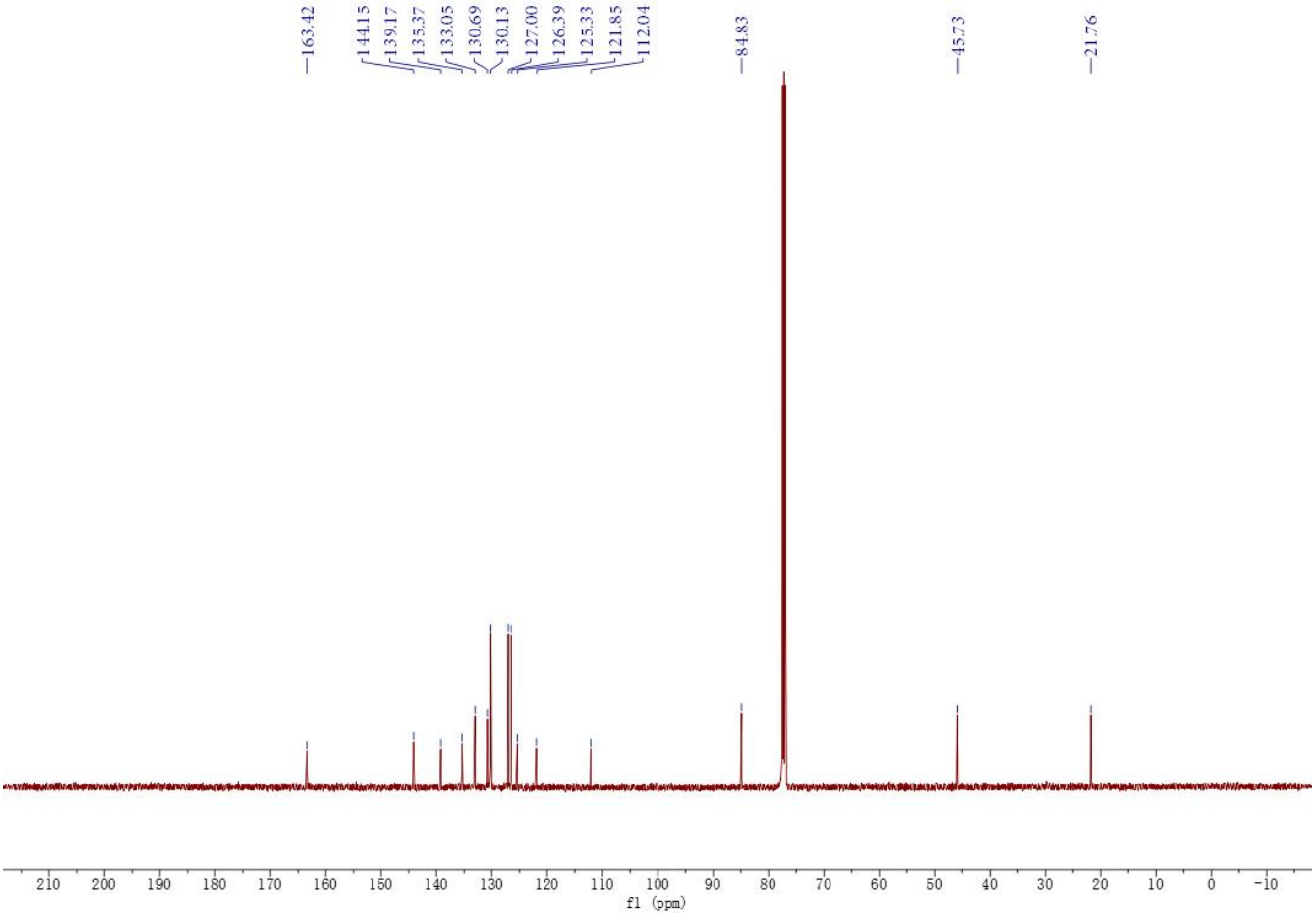




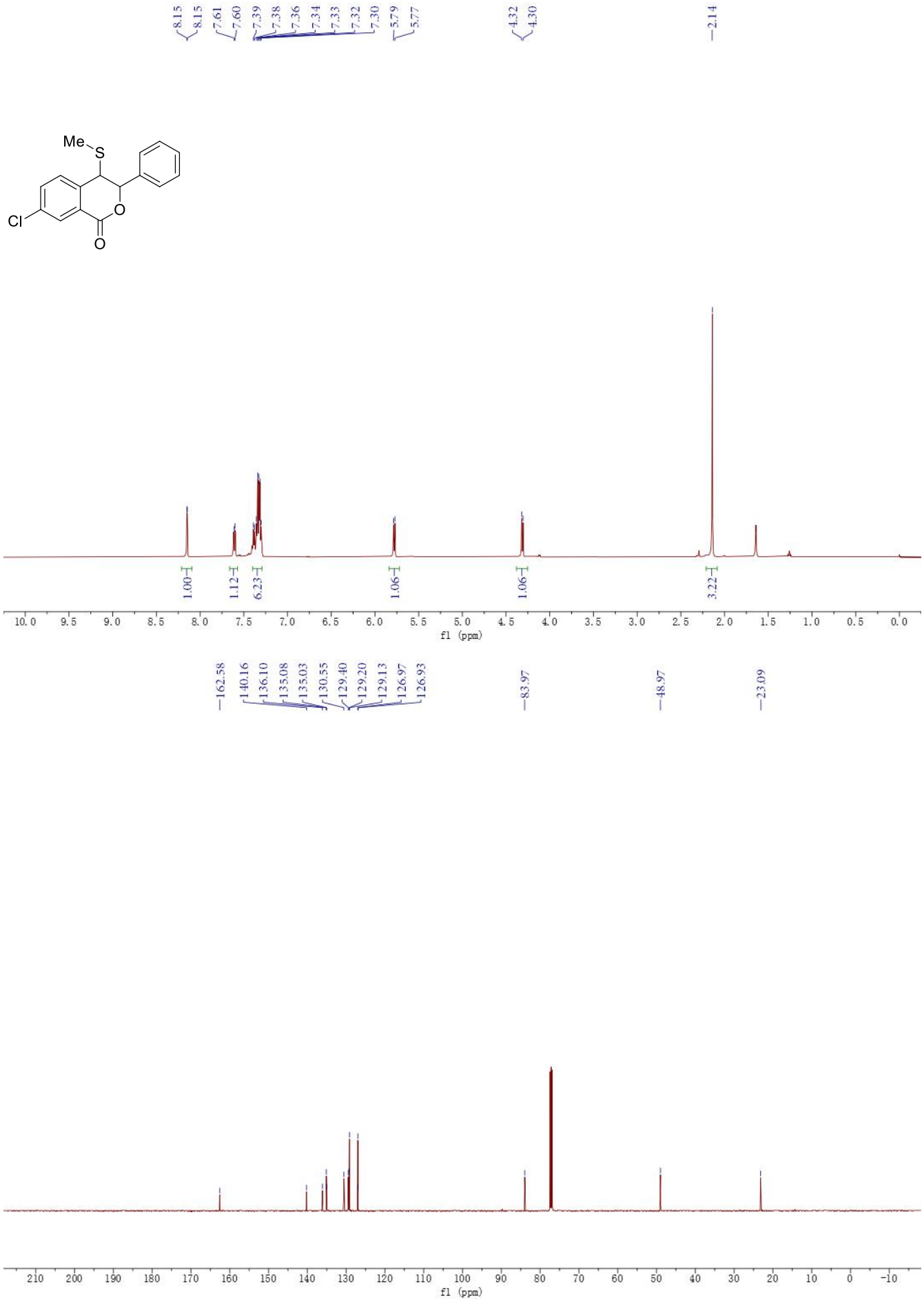
(18). 4-(methylthio)-1-oxo-3-phenylisochromane-7-carbonitrile 3r



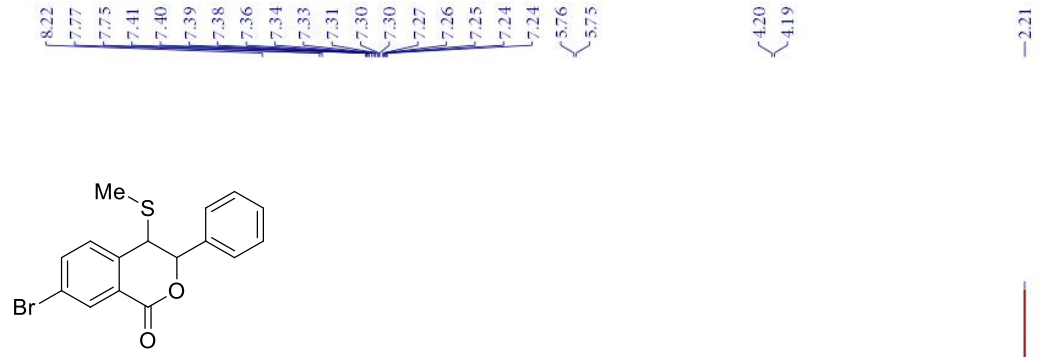


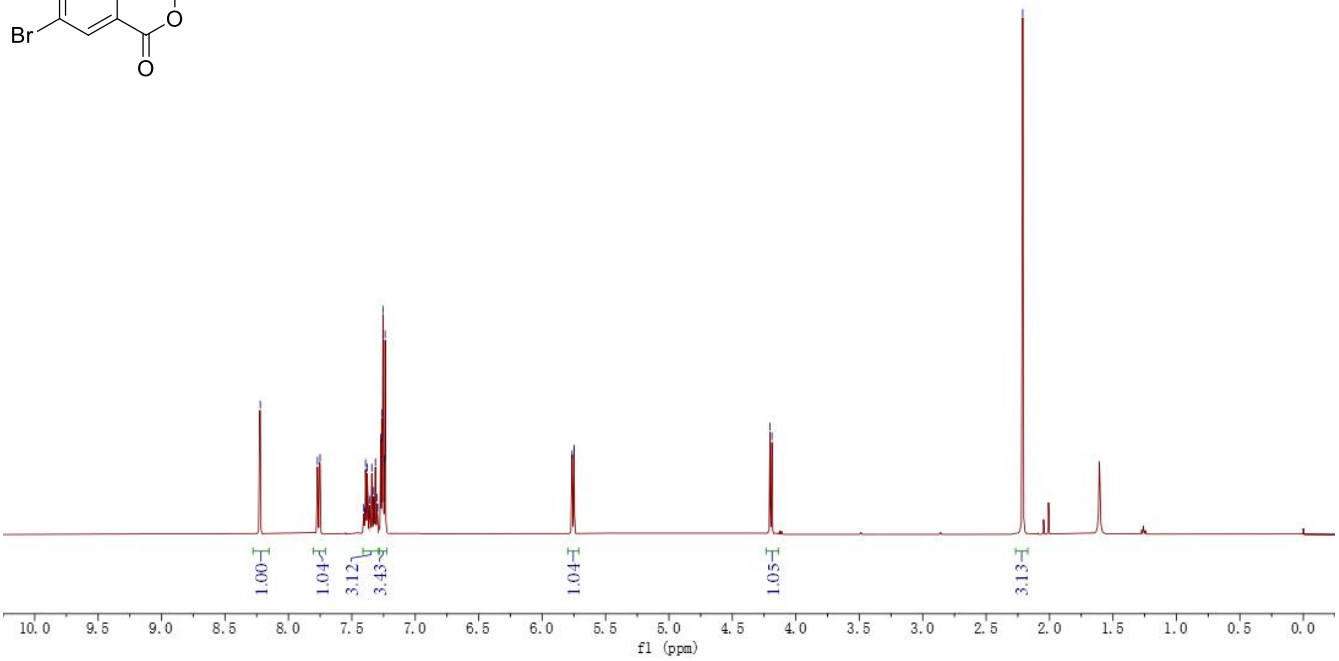


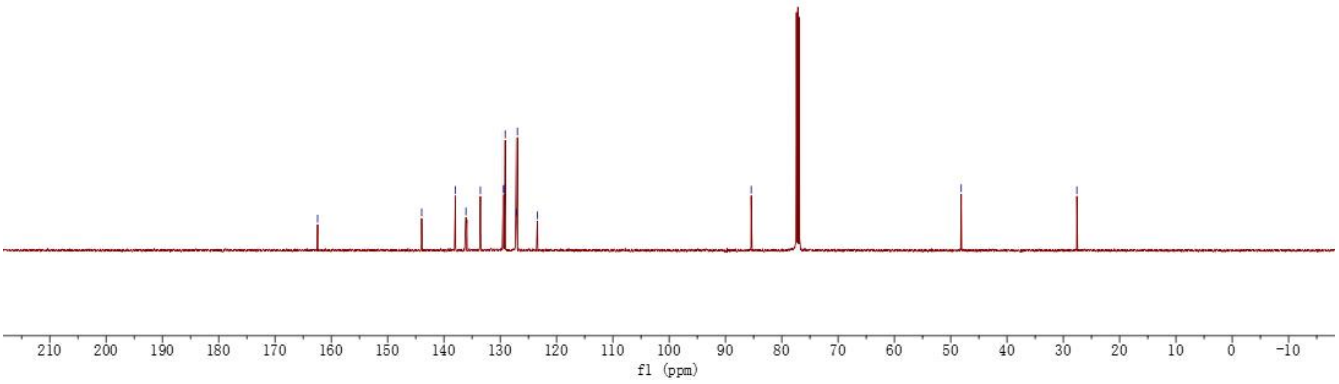
(19). 7-chloro-4-(methylthio)-3-phenylisochroman-1-one 3s



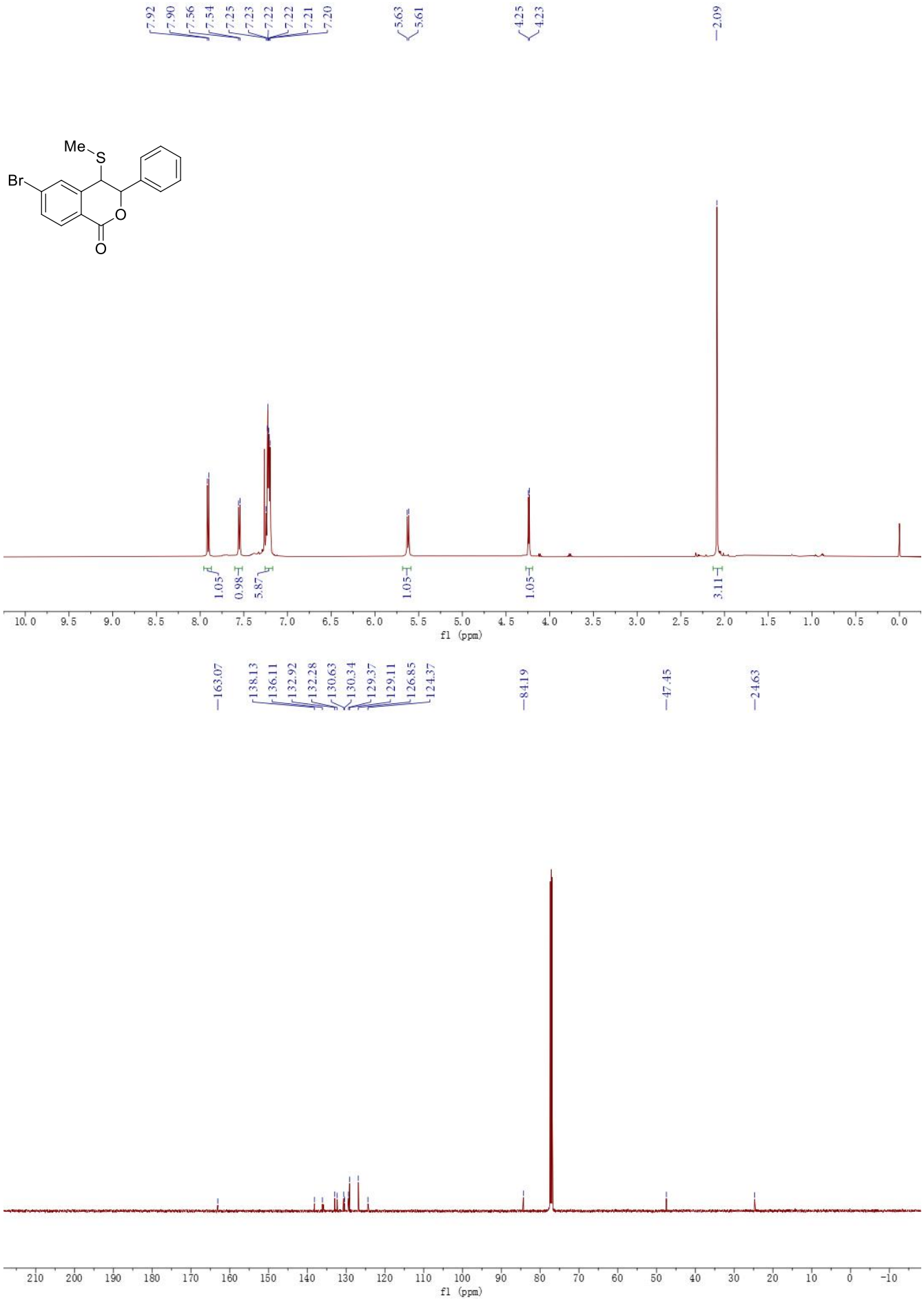
(20). 7-bromo-4-(methylthio)-3-phenylisochroman-1-one 3t







(21). 6-bromo-4-(methylthio)-3-phenylisochroman-1-one 3u



(22). 5-methyl-4-(methylthio)-3-phenylisochroman-1-one 3v