**Supplementary Information**

**Competitive cascade cyclization of 2'-tosyloxychalcones: An easy access to Thioflavones and Thioaurones**

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Thioaurones. S13-S32

**General information**: Reagents and solvents were analytical grade and were used without further purification. Melting points were recorded on a Mel-Temp melting point apparatus, in open capillaries and are uncorrected. 1H NMR (400 MHz), 13C NMR-DEPT (100 MHz) spectra were recorded on a Bruker AMX 400 MHz NMR spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion. In the 13C NMR spectra, the nature of the carbons (C, CH, CH2 or CH3) was determined by DEPT-135 spectra. Mass spectra were recorded on Agilent 1100 LC/MSD and HRMS were recorded on Micromass Q-TOF spectrometer using electro-spray ionization mode. 2'-Tosyloxychalcones (**1**) were prepared from the corresponding 2'-hydroxychalcones according to the literature procedure.1

The following compounds were prepared as per the general procedure described in the main text.

**2-Phenyl-4*H*-thiochromen-4-one (2a)**:



Pale yellow color solid (160 mg, 67%), mp 120–122 oC (lit.2 mp 121–122 oC). 1H NMR (400 MHz, CDCl3): δ 8.56 (1H, dd, *J* = 8.0, 0.8 Hz), 7.66–7.72 (3H, m), 7.63 (1H, td, *J* = 7.5, 1.2 Hz), 7.56 (1H, td, *J* = 7.4, 1.2 Hz), 7.48–7.53 (3H, m), 7.25 (1H, s); 13C NMR (100 MHz, CDCl3): δ 180.8, 152.9, 137.7, 136.6, 131.6, 131.0, 130.8, 129.3, 128.6, 127.7, 127.0, 126.5, 123.5; LC-MS (positive ion mode): *m/z* 239 (M+H)+.

**(*Z*)-2-Benzylidenebenzo[*b*]thiophen-3(2*H*)-one (3a)**:



Yellow color solid (35 mg, 15%), mp 124–126 oC (lit.3 mp 128–130 oC). 1H NMR (400 MHz, CDCl3): δ 7.97 (1H, s), 7.95 (1H, d, *J* = 8.0 Hz), 7.72 (2H, d, *J* = 7.6 Hz), 7.58 (1H, td, *J* = 7.4, 0.8 Hz), 7.47–7.52 (3H, m), 7.40–7.44 (1H, m), 7.30 (1H, t, *J* = 7.4 Hz); 13C NMR (100 MHz, CDCl3): δ 188.6, 146.2, 135.3, 134.4, 133.6, 131.0, 130.5, 130.3, 130.1, 129.0, 127.1, 125.6, 123.9; LC-MS (positive ion mode): *m/z* 239 (M+H)+.

**2-(4-Methoxyphenyl)-4*H*-thiochromen-4-one (2b)**:



Pale yellow color solid (165 mg, 62%), mp 118–120 oC (lit.4 mp 124–125 oC). 1H NMR (400 MHz, CDCl3): δ 8.54 (1H, dd, *J* = 8.0, 0.8 Hz), 7.64–7.68 (3H, m), 7.62 (1H, td, *J* = 7.5, 1.6 Hz), 7.54 (1H, td, *J* = 7.5, 1.2 Hz), 7.21 (1H, s), 7.02 (2H, d, *J* = 8.8 Hz), 3.88 (3H, s); 13C NMR (100 MHz, CDCl3): δ 180.9, 161.9, 152.7, 137.6, 131.5, 131.0, 128.9, 128.6, 128.3, 127.6, 126.4, 122.2, 114.7, 55.5; LC-MS (negative ion mode): *m/z* 267 (M–H)–.

**(*Z*)-2-(4-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3b)**:



Yellow color solid (32 mg, 12%), mp 148–152 oC (lit.3 mp 153–154 oC). 1H NMR (400 MHz, CDCl3): δ 7.95 (1H, s), 7.94 (1H, d, *J* = 6.0 Hz), 7.69 (2H, d, *J* = 8.8 Hz), 7.57 (1H, td, *J* = 7.5, 0.8 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.30 (1H, td, *J* = 7.5, 0.8 Hz), 7.01 (2H, d, *J* = 8.4 Hz), 3.88 (3H, s); 13C NMR (100 MHz, CDCl3): δ 188.6, 161.3, 146.0, 134.9, 133.7, 133.0, 130.8, 127.9, 127.1, 127.0, 125.5, 123.9, 114.7, 55.4; LC-MS (positive ion mode): *m/z* 269 (M+H)+.

**2-(4-Chlorophenyl)-4*H*-thiochromen-4-one (2c)**:



Pale yellow color solid (170 mg, 63%), mp 162–164 oC (lit.4 mp 161–165 oC). 1H NMR (400 MHz, CDCl3): δ 8.55 (1H, d, *J* = 8.0 Hz), 7.62–7.67 (4H, m), 7.56 (1H, td, *J* = 7.5, 1.8 Hz), 7.48 (2H, d, *J* = 8.4 Hz), 7.20 (1H, s); 13C NMR (100 MHz, CDCl3): δ 180.7, 151.5, 137.4, 137.1, 135.0, 131.7, 130.9, 129.6, 128.7, 128.2, 127.9, 126.5, 123.6; LC-MS (positive ion mode): *m/z* 273, 275 (M+H)+.

**(Z)-2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3c)**:



Yellow color solid (35 mg, 13%), mp 160–162 oC (lit.5 mp 162–165 oC). 1H NMR (400 MHz, CDCl3): δ 7.95 (1H, d, *J* = 7.6 Hz), 7.90 (1H, s), 7.64 (2H, d, *J* = 8.4 Hz), 7.60 (1H, td, *J* = 8.0, 1.2 Hz), 7.51 (1H, d, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 8.4 Hz), 7.32 (1H, t, *J* = 7.4 Hz); 13C NMR (100 MHz, CDCl3): δ 188.5, 145.8, 136.2, 135.4, 132.9, 132.0, 131.9, 130.9, 130.3, 129.4, 127.2, 125.8, 124.0; LC-MS (positive ion mode): *m/z* 273, 275 (M+H)+.

**2-(p-Tolyl)-4*H*-thiochromen-4-one (2d)**:



Pale yellow color solid (165 mg, 66%), mp 110–112 oC (lit.4 118–119 oC). 1H NMR (400 MHz, CDCl3): δ 8.55 (1H, d, *J* = 8.0 Hz), 7.59–7.67 (4H, m), 7.55 (1H, t, *J* = 7.4 Hz), 7.31 (2H, d, *J* = 8.0 Hz), 7.24 (1H, s), 2.43 (3H, s); 13C NMR (100 MHz, CDCl3): δ 180.9, 153.1, 141.3, 137.7, 133.8, 131.5, 131.0, 130.0, 128.6, 127.7, 126.8, 126.4, 122.9, 21.4; LC-MS (positive ion mode): *m/z* 253 (M+H)+.

**(*Z*)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3d)**:



Yellow color solid (42 mg, 17%), mp 126–128 oC (lit.3 mp 134–136 oC). 1H NMR (400 MHz, CDCl3): δ 7.95 (1H, s), 7.94 (1H, d, *J* = 8.8 Hz), 7.62 (2H, d, *J* = 8.0 Hz), 7.57 (1H, td, *J* = 7.5, 1.2 Hz), 7.51 (1H, d, *J* = 8.0 Hz), 7.28–7.31 (3H, m), 2.41 (3H, s); 13C NMR (100 MHz, CDCl3): δ 188.7, 146.1, 140.9, 135.1, 133.8, 131.6, 131.1, 130.7, 129.8, 129.3, 127.0, 125.5, 123.9, 21.6; LC-MS (positive ion mode): *m/z* 253 (M+H)+.

**2-(3-Nitrophenyl)-4*H*-thiochromen-4-one (2e)**:



Pale yellow color solid (180 mg, 64%), mp 178–180 oC (lit.6 mp 176 oC). 1H NMR (400 MHz, CDCl3): δ 8.55–8.58 (2H, m), 8.39 (1H, dd, *J* = 8.4, 2.0 Hz), 8.03 (1H, d, *J* = 8.0 Hz), 7.73 (1H, t, *J* = 8.0 Hz), 7.66–7.70 (2H, m), 7.58–7.63 (1H, m), 7.28 (1H, s); 13C NMR (100 MHz, CDCl3): δ 180.5, 149.8, 148.8, 138.3, 136.9, 132.7, 132.0, 130.8, 130.5, 128.8, 128.3, 126.6, 125.2, 124.7, 122.1; LC-MS (positive ion mode): *m/z* 284 (M+H)+.

**(*Z*)-2-(3-Nitrobenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3e)**:



Yellow color solid (32 mg, 11%), mp 238–240 oC (lit.7 mp 229 oC). 1H NMR (400 MHz, DMSO-d6): δ 8.63 (1H, s), 8.33 (1H, dd, *J* = 7.8, 1.0 Hz), 8.23 (1H, d, *J* = 8.0 Hz), 8.08 (1H, s), 7.92 (1H, d, *J* = 7.6 Hz), 7.84–7.89 (2H, m), 7.78 (1H, t, *J* = 7.4 Hz), 7.45 (1H, t, *J* =7.4 Hz); 13C NMR (100 MHz, DMSO-d6): δ 187.5, 148.3, 144.7, 136.7, 136.5, 135.4, 132.3, 130.8, 130.4, 129.2, 126.8, 126.6, 124.8, 124.5, 124.4; LC-MS (positive ion mode): *m/z* 284 (M+H)+.

**2-(4-(Dimethylamino)phenyl)-4*H*-thiochromen-4-one (2f)**:



Yellow color solid (191 mg, 68%), mp 168–170 oC. 1H NMR (400 MHz, CDCl3): δ 8.52 (1H, d, *J* = 8.0 Hz), 7.55–7.63 (4H, m), 7.50 (1H, t, *J* = 7.4 Hz), 7.20 (1H, s), 6.74 (2H, d, *J* = 8.8 Hz), 3.04 (6H, s); 13C NMR (100 MHz, CDCl3): δ 180.9, 153.3, 152.2, 137.7, 131.2, 131.1, 128.4, 127.8, 127.3, 126.3, 123.3, 120.1, 112.0, 40.1; LC-MS (positive ion mode): *m/z* 282 (M+H)+; HRMS-(EI) (*m/z*): (M+Na)+ calcd for C17H15NOSNa 304.0772, found 304.0769.

**(Z)-2-(4-(Dimethylamino)benzylidene)benzo[b]thiophen-3(2H)-one (3f):**



Red color solid (64 mg, 23%), mp 158–160 oC (lit.8 mp 170 oC). 1H NMR (400 MHz, CDCl3): δ 7.96 (1H, s), 7.94 (1H, d, *J* = 8.8 Hz), 7.64 (2H, d, *J* = 8.8 Hz), 7.50–7.56 (2H, m), 7.28–7.30 (1H, m), 6.76 (2H, d, *J* = 8.8 Hz), 3.08 (6H, s); 13C NMR (100 MHz, CDCl3): δ 188.3, 151.6, 145.9, 135.2, 134.0, 133.4, 131.4, 126.7, 125.1, 124.8, 123.8, 122.1, 112.0, 40.0; LC-MS (positive ion mode): *m/z* 282 (M+H)+.

**7-Methoxy-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one (2g)**:



Pale yellow color solid (200 mg, 67%), mp 126–128 oC (lit.9 mp 136-138 oC). 1H NMR (400 MHz, CDCl3): δ 8.46 (1H, d, *J* = 8.8 Hz), 7.64 (2H, d, *J* = 8.8 Hz), 7.13 (1H, s), 7.09 (1H, dd, *J* = 8.8, 2.4 Hz), 7.04 (1H, d, *J* = 2.4 Hz), 7.00 (2H, d, *J* = 8.8 Hz), 3.92 (3H, s), 3.87 (3H, s); 13C NMR (100 MHz, CDCl3): δ 180.4, 161.9, 161.8, 151.6, 139.8, 130.5, 128.9, 128.3, 124.8, 122.3, 116.3, 114.7, 108.6, 55.7, 55.5; LC-MS (positive ion mode): *m/z* 299 (M+H)+.

**(*Z*)-6-Methoxy-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3g)**:



Yellow color solid (48 mg, 16%), mp 122–124 oC. 1H NMR (400 MHz, CDCl3): δ 7.88 (1H, s), 7.87 (1H, d, *J* = 8.8 Hz), 7.66 (2H, d, *J* = 8.8 Hz), 7.00 (2H, d, *J* = 8.8 Hz), 6.96 (1H, d, *J* = 2.0 Hz), 6.82 (1H, dd, *J* = 8.4, 2.0 Hz), 3.91 (3H, s), 3.88 (3H, s); 13C NMR (100 MHz, CDCl3): δ 187.1, 165.5, 161.1, 148.8, 132.8, 132.6, 128.5, 128.4, 127.2, 124.3, 114.6, 113.3, 107.6, 55.8, 55.4; LC-MS (positive ion mode): *m/z* 299 (M+H)+; HRMS-(EI) (*m/z*): (M+Na)+ calcd for C17H14O3SNa 321.0561, found 321.0566.

**2-(4-Bromophenyl)-7-methoxy-4*H*-thiochromen-4-one (2h)**:



Pale yellow color solid (200 mg, 58%), mp 144–146 oC. 1H NMR (400 MHz, CDCl3): δ 8.45 (1H, d, *J* = 8.8 Hz), 7.63 (2H, d, *J* = 8.4 Hz), 7.53 (2H, d, *J* = 8.8 Hz), 7.12 (1H, s), 7.10 (1H, dd, *J* = 8.8, 2.4 Hz), 7.04 (1H, d, *J* = 2.4 Hz), 3.92 (3H, s); 13C NMR (100 MHz, CDCl3): δ 180.1, 162.1, 150.5, 139.5, 135.5, 132.5, 130.6, 128.4, 125.2, 124.7, 123.6, 116.6, 108.6, 55.7; LC-MS (positive ion mode): *m/z* 347, 349 (M+H)+; HRMS-(EI) (*m/z*): (M+Na)+ calcd for C16H11BrO2SNa 368.9561, 370.9541 found 368.9559, 370.9533.

**(*Z*)-2-(4-Bromobenzylidene)-6-methoxybenzo[*b*]thiophen-3(2*H*)-one (3h)**:



Yellow color solid (45 mg, 13%), mp 196–198 oC. 1H NMR (400 MHz, CDCl3): δ 7.87 (1H, d, *J* = 8.8 Hz), 7.81 (1H, s), 7.60 (2H, d, *J* = 8.8 Hz), 7.53 (2H, d, *J* = 8.4 Hz), 6.94 (1H, d, *J* = 2.0 Hz), 6.83 (1H, dd, *J* = 8.6, 2.0 Hz), 3.92 (3H, s); 13C NMR (100 MHz, CDCl3): δ 186.8, 165.9, 148.6, 133.4, 132.3, 132.0, 131.6, 130.9, 128.7, 124.2, 123.8, 113.5, 107.8, 55.9; LC-MS (positive ion mode): *m/z* 347, 349 (M+H)+; HRMS-(EI) (*m/z*): (M+H)+ calcd for C16H12BrO2S 346.9741, 348.9721 found 346.9738, 348.9715.

**6-Chloro-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one (2i)**:



Pale yellow color solid (200 mg, 66%), mp 182–184 oC (lit.9 mp 190-192 oC). 1H NMR (400 MHz, CDCl3): δ 8.50 (1H, s), 7.64 (2H, d, *J* = 8.4 Hz), 7.54–7.59 (2H, m), 7.19 (1H, s), 7.01 (2H, d, *J* = 8.8 Hz), 3.88 (3H, s); 13C NMR (100 MHz, CDCl3): δ 179.6, 162.1, 152.8, 135.7, 134.2, 132.1, 131.8, 128.5, 128.3, 128.2, 127.8, 122.0, 114.8, 55.5; LC-MS (positive ion mode): *m/z* 303, 305 (M+H)+.

**(*Z*)-5-Chloro-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (3i)**:



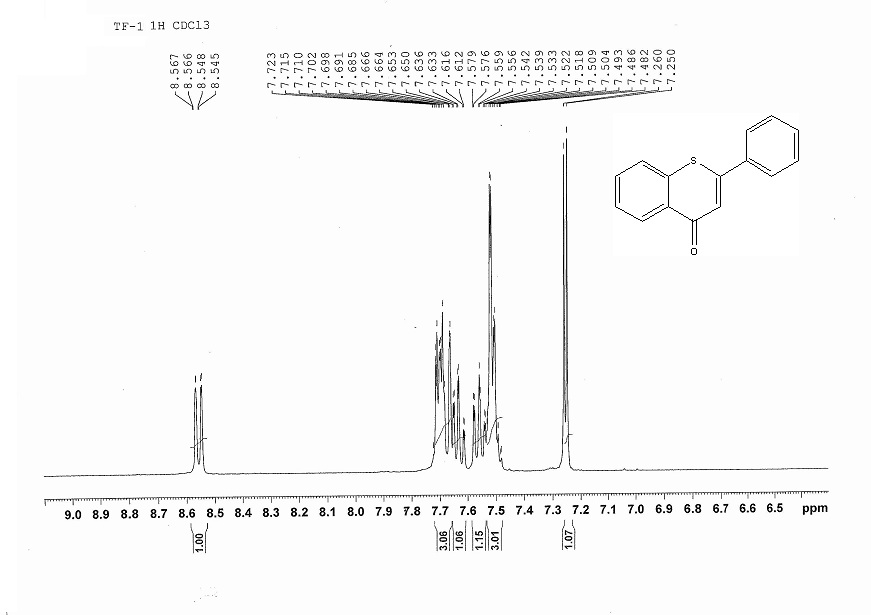
Yellow color solid (40 mg, 13%), mp 188–190 oC. 1H NMR (400 MHz, CDCl3): δ 7.95 (1H, s), 7.90 (1H, d, *J* = 2.4 Hz), 7.66 (2H, d, *J* = 8.4 Hz), 7.52 (1H, dd, *J* = 8.4, 2.0 Hz), 7.44 (1H, d, *J* = 8.4 Hz), 7.01 (2H, d, *J* = 8.8 Hz), 3.88 (3H, s); 13C NMR (100 MHz, CDCl3): δ 187.3, 161.6, 144.1, 134.8, 134.7, 133.1, 132.3, 131.9, 127.8, 126.8, 126.7, 124.8, 114.8, 55.5; LC-MS (positive ion mode): *m/z* 303, 305 (M+H)+; HRMS-(EI) (*m/z*): (M+Na)+ calcd for C16H11ClO2SNa 325.0066, 327.0036 found 325.0068, 327.0040.

**Procedure for cyclization in presence of metal catalyst**: To a solution of 2'-tosyloxychalcone (**1**, 1 mmol) in dry DMSO (5 mL) was added sulphur powder (160 mg, 5 mmol), Cu(OAc)2 (181.6 mg 1 mmol), and triethylamine (0.69 mL, 5 mmol) successively at rt. The mixture was stirred at 80oC for 2 h and poured into ice cold water (40 mL). The mixture was stirred for 15 min and extracted with ethyl acetate (3 × 50 mL). The combined EtOAc layer was washed with water (50 mL), brine (50 mL), and dried over sodium sulfate. The solution was filtered and evaporated the solvent. The residue was chromatographed over silica gel column using hexane: ethyl acetate mixture as eluents to give thioaurone (**3a),** as ayellow color solid (24 mg, 10%), mp 126–128 oC (lit.3 mp 128–130oC). Further elution of the column with the same solvent system gave thioflavone (**2a**), as a pale yellow color solid (167 mg, 70%), mp 120–122 oC (lit.2 mp 121–122 oC).

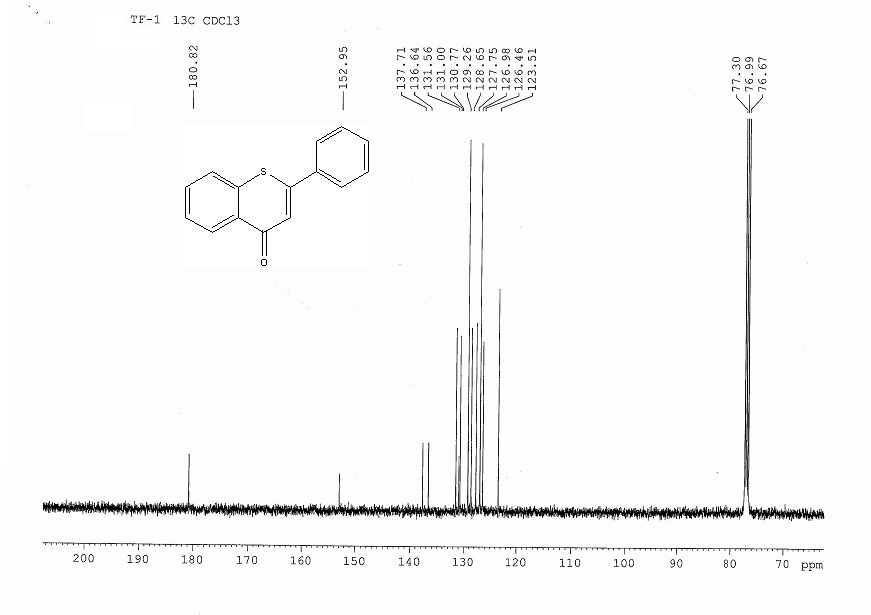
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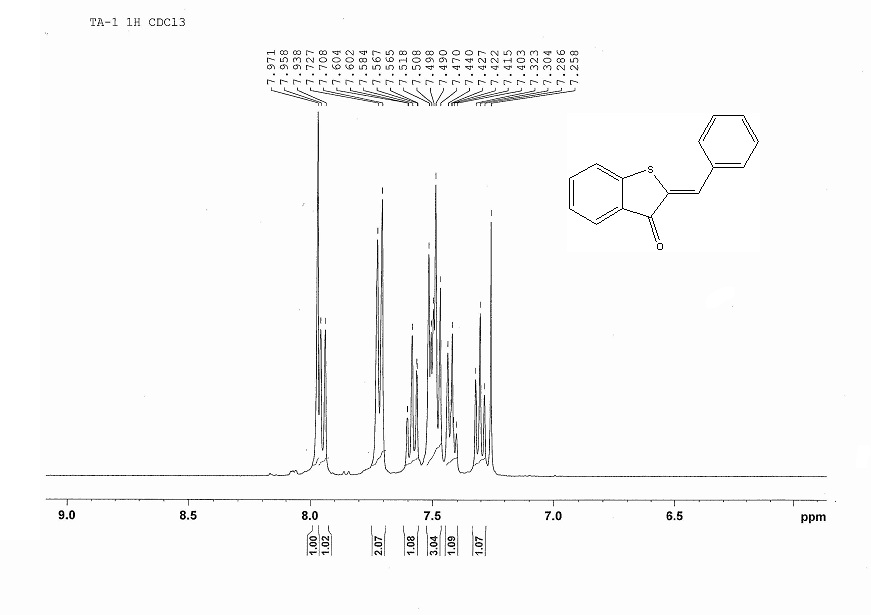
1H-spectrum of 2-Phenyl-4*H*-thiochromen-4-one.



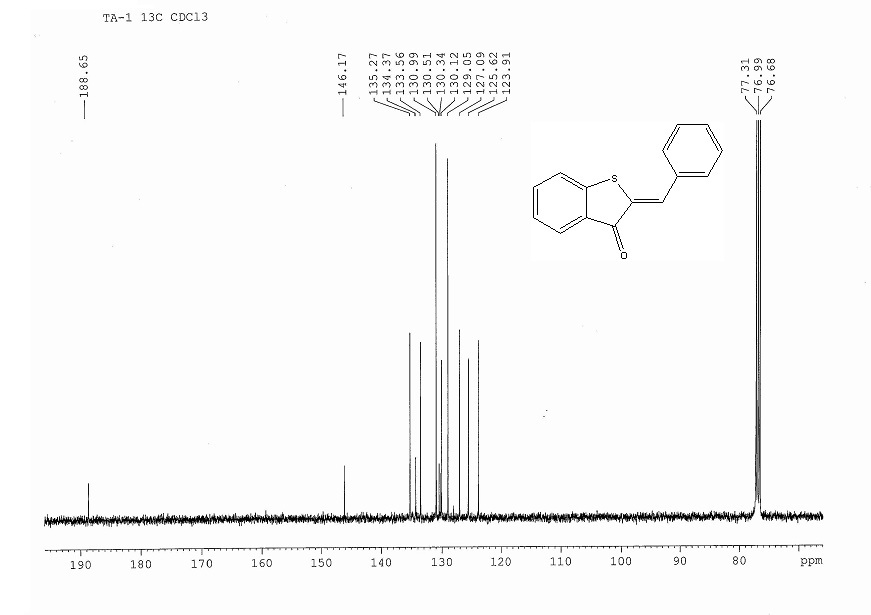
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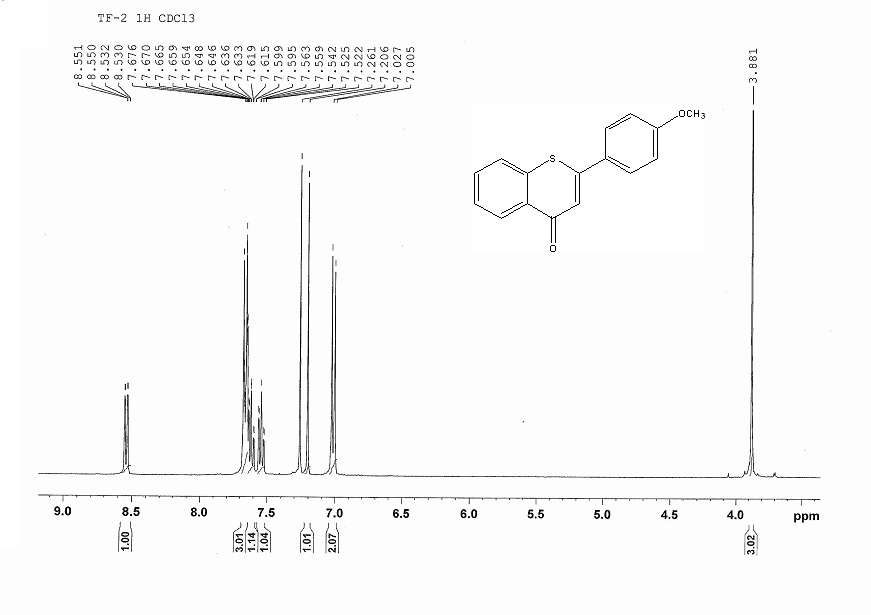
1H-spectrum (*Z*)-2-Benzylidenebenzo[*b*]thiophen-3(2*H*)-one.



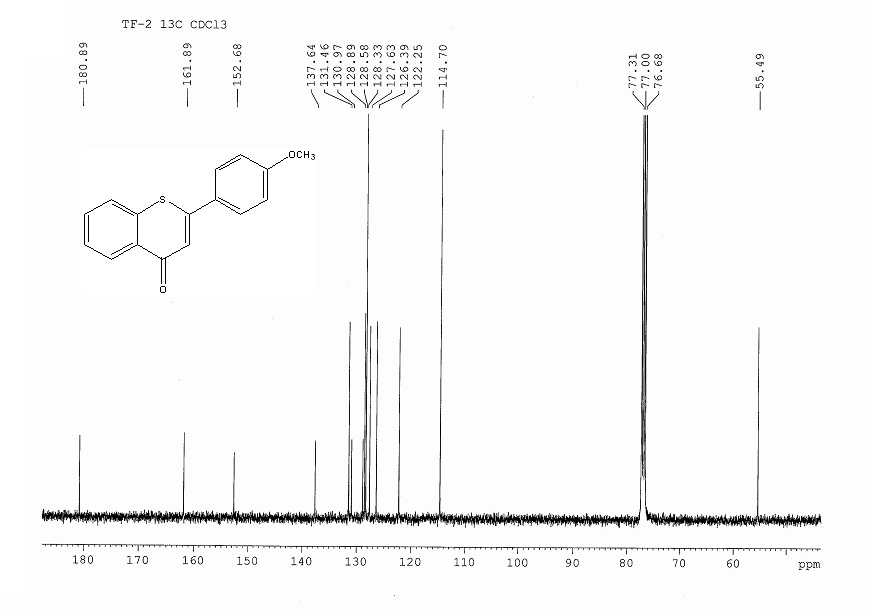
13C-spectrum (*Z*)-2-Benzylidenebenzo[*b*]thiophen-3(2*H*)-one.



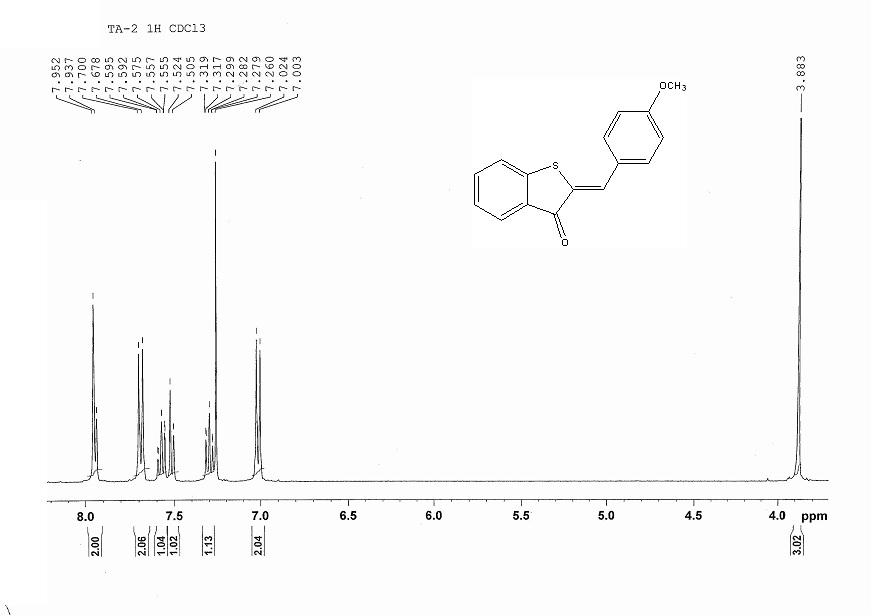
1H-NMR spectrum of 2-(4-Methoxyphenyl)-4*H*-thiochromen-4-one.



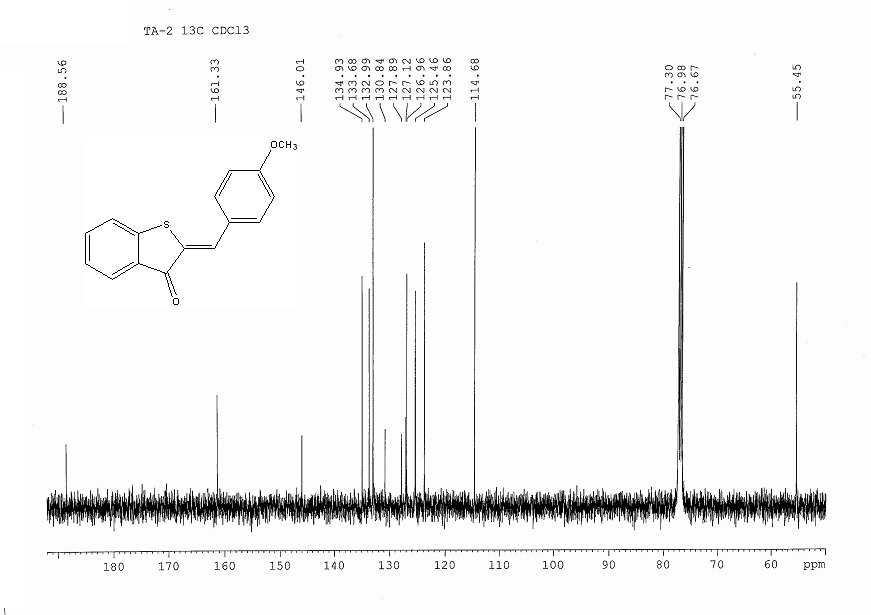
13C-NMR spectrum of 2-(4-Methoxyphenyl)-4*H*-thiochromen-4-one.



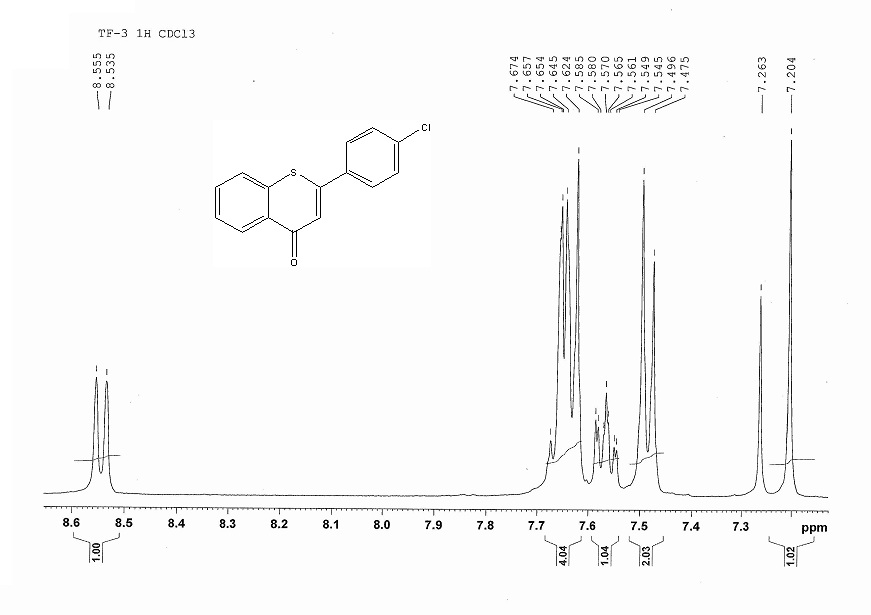
1H-NMR spectrum (*Z*)-2-(4-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



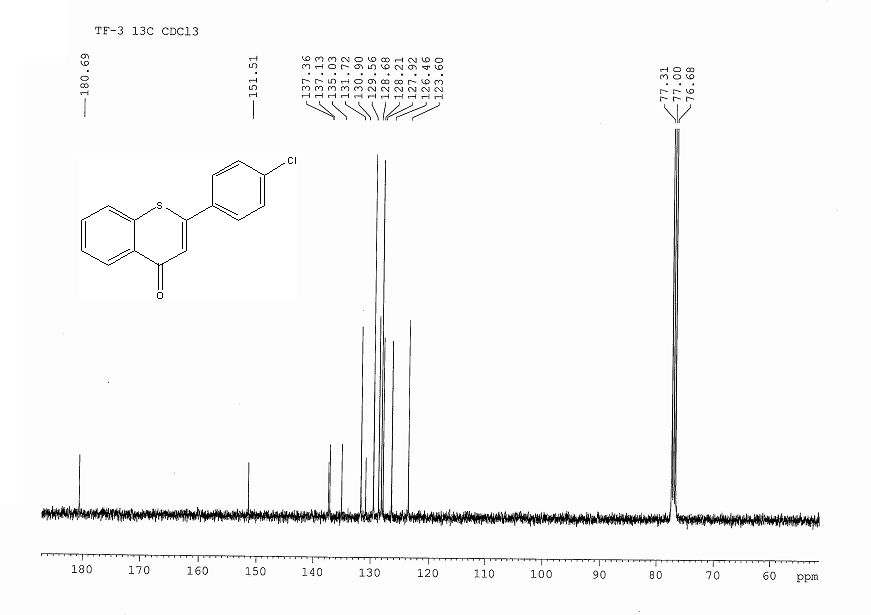
13C-NMR spectrum (*Z*)-2-(4-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



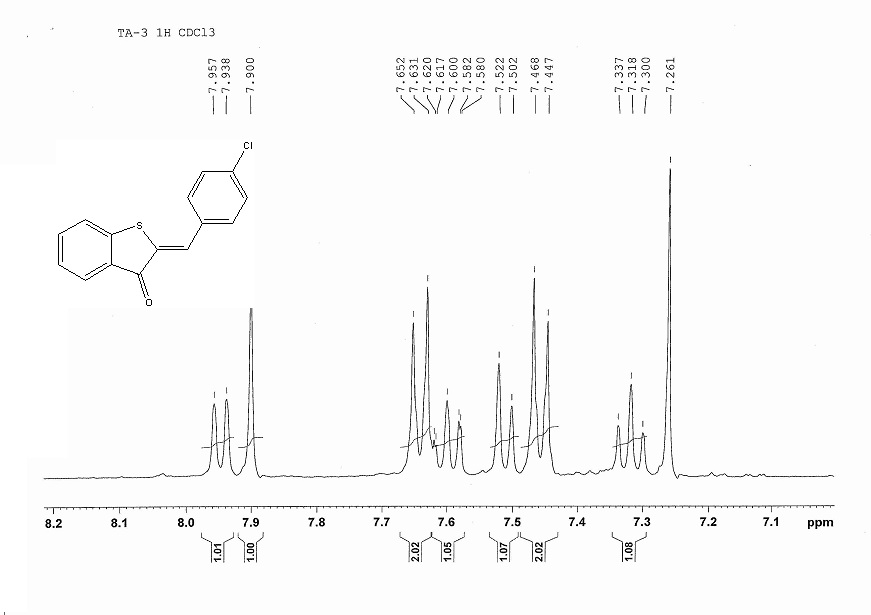
1H-NMR spectrum 2-(4-Chlorophenyl)-4*H*-thiochromen-4-one.



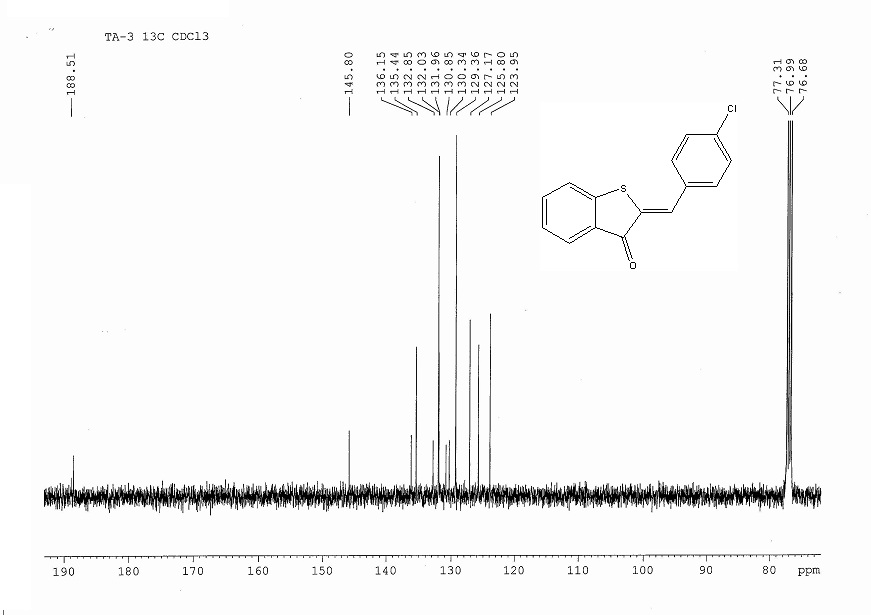
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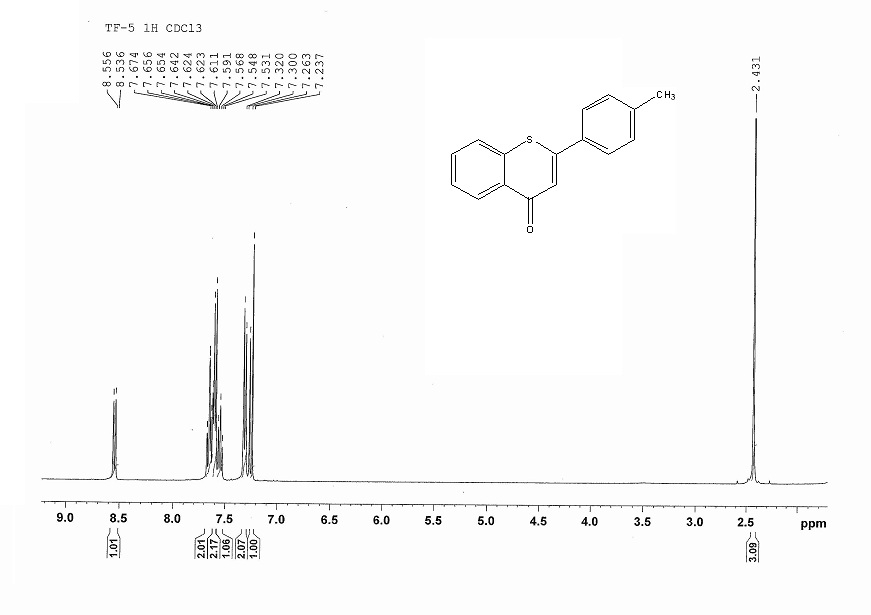
1H-NMR spectrum (Z)-2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



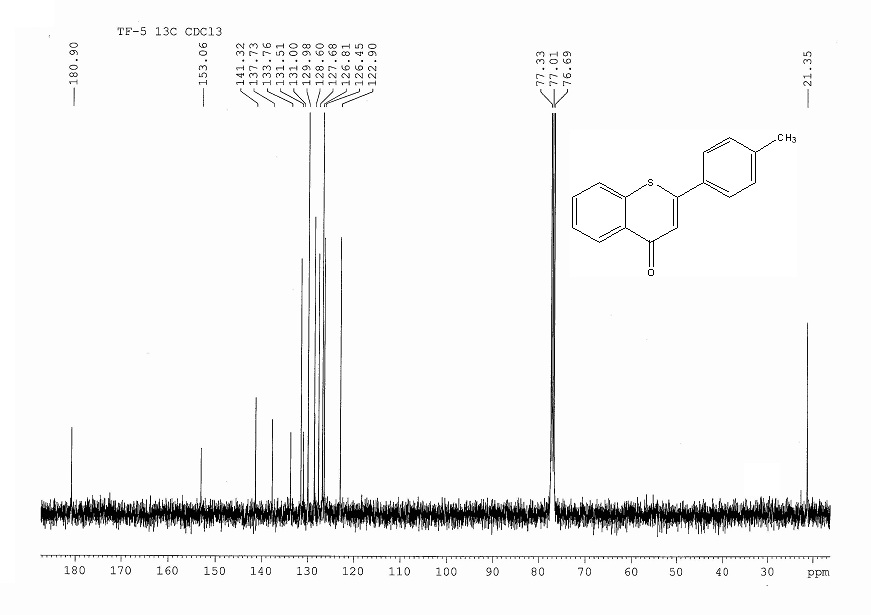
13C-NMR spectrum (Z)-2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



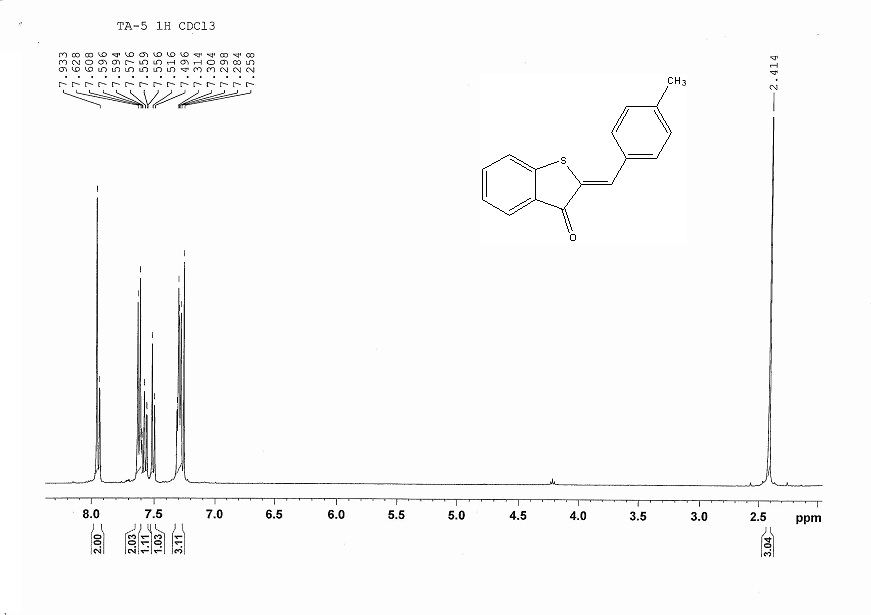
1H-NMR spectrum of 2-(p-Tolyl)-4*H*-thiochromen-4-one.



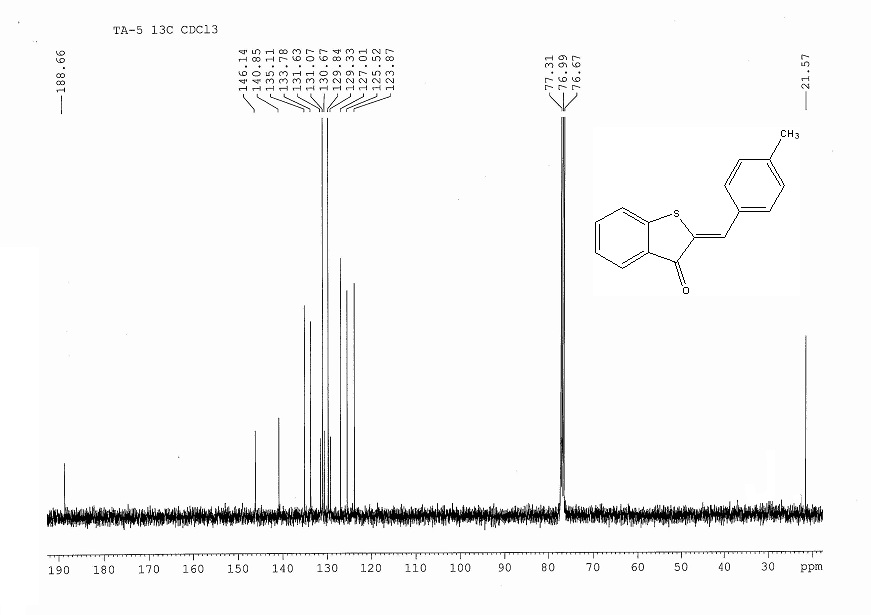
13C-NMR spectrum of 2-(p-Tolyl)-4*H*-thiochromen-4-one.



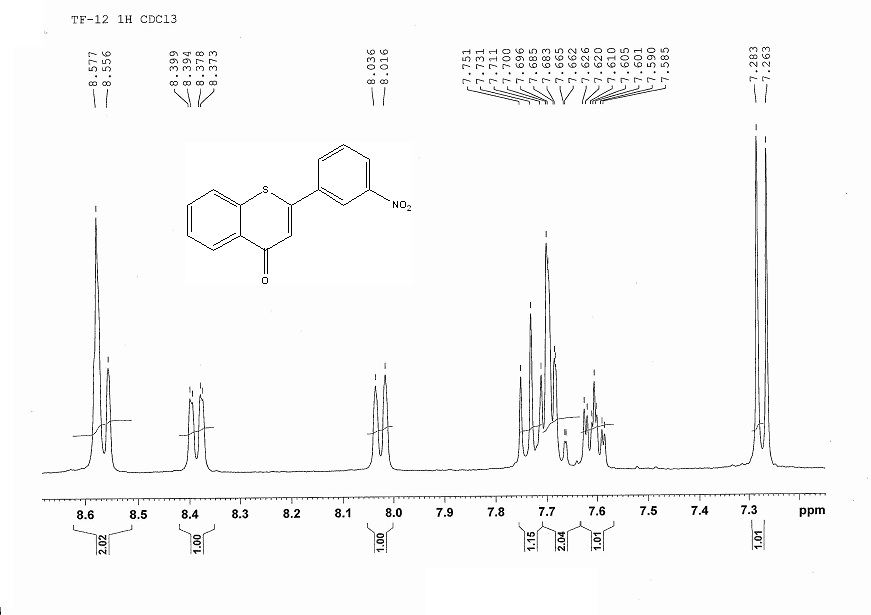
1H-NMR spectrum of (Z)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



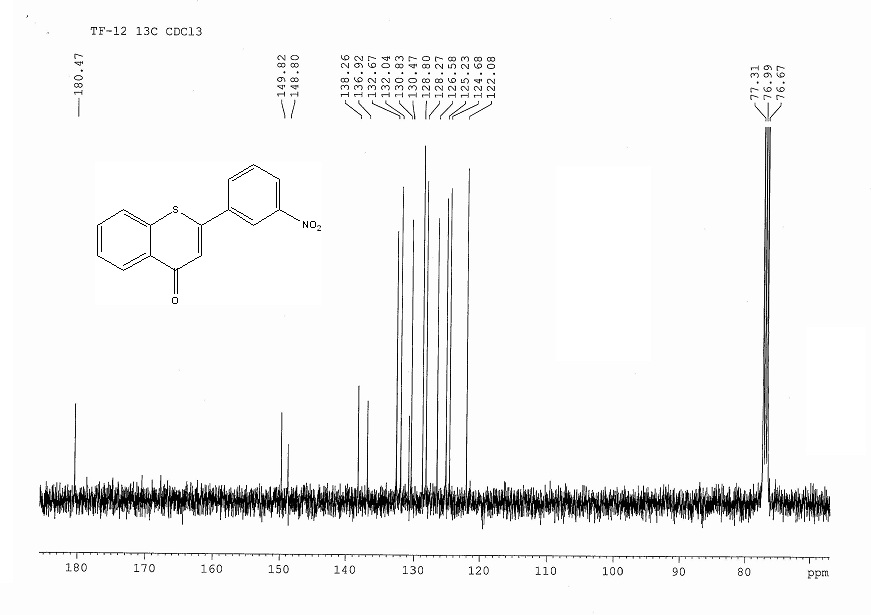
13C-NMR spectrum of (Z)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



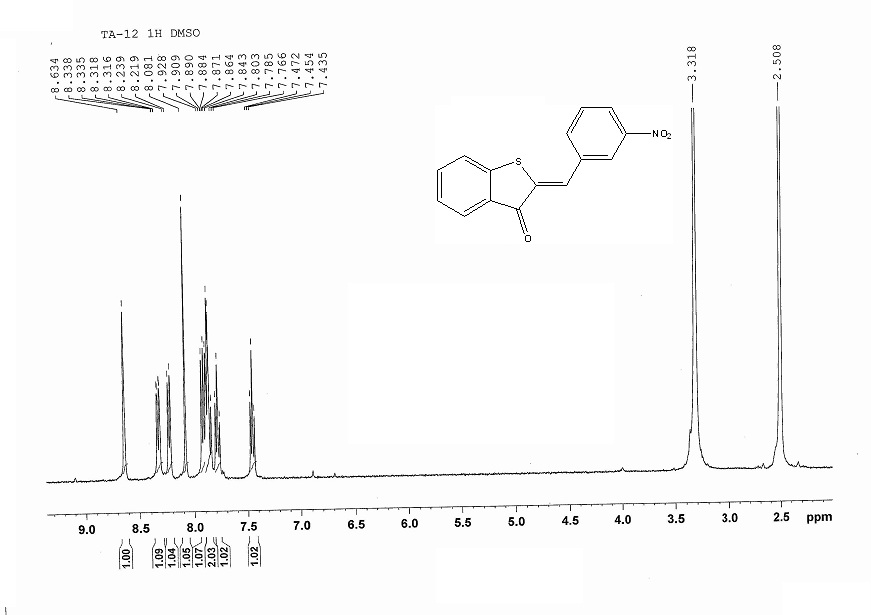
1H-NMR spectrum of 2-(3-Nitrophenyl)-4*H*-thiochromen-4-one.



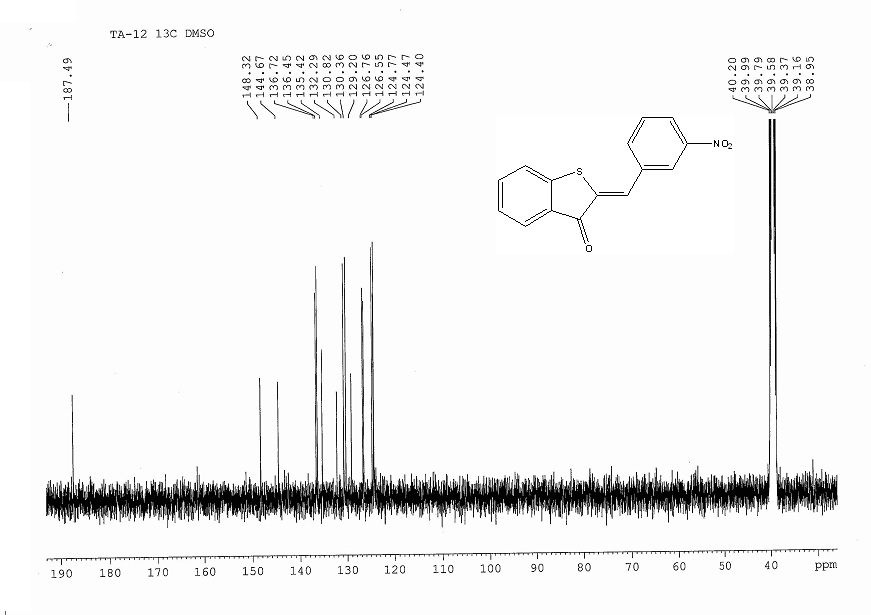
13C-NMR spectrum of 2-(3-Nitrophenyl)-4*H*-thiochromen-4-one.



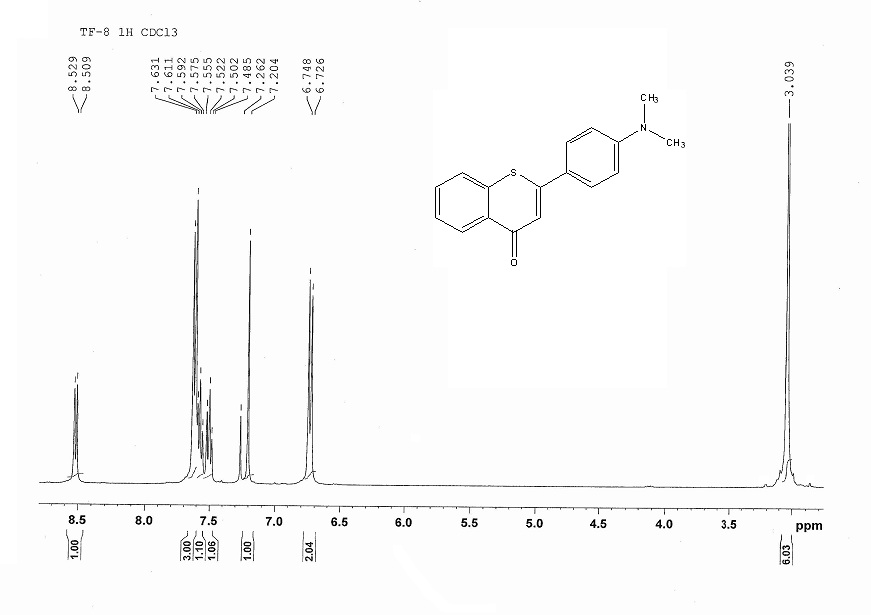
1H-NMR spectrum of (*Z*)-2-(3-Nitrobenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



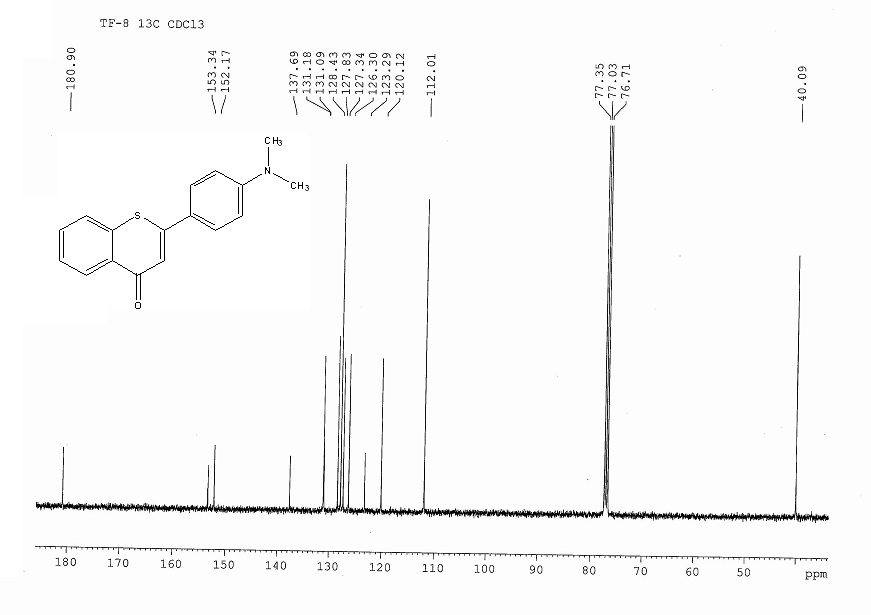
13C-NMR spectrum of (*Z*)-2-(3-Nitrobenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



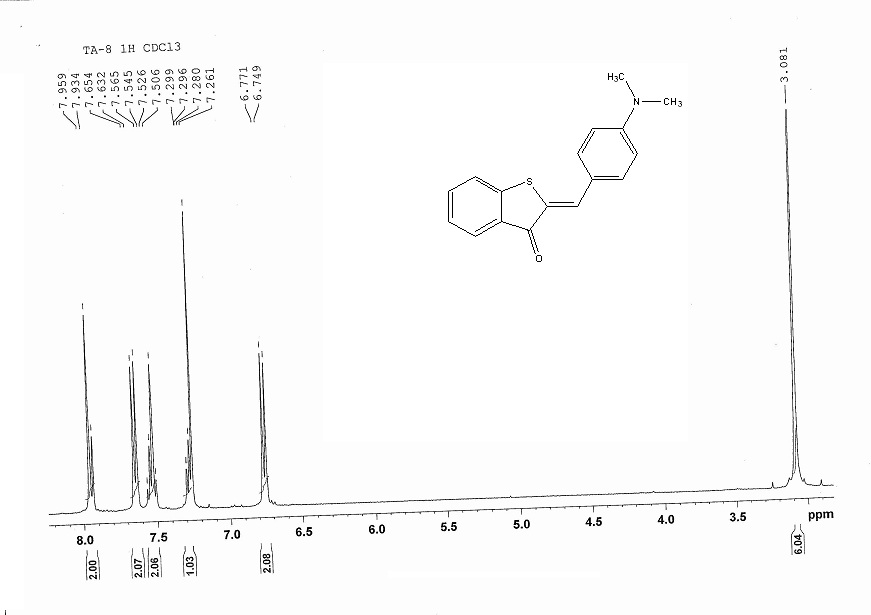
1H-NMR spectrum of 2-(4-(Dimethylamino)phenyl-4*H*-thiochromen-4-one.



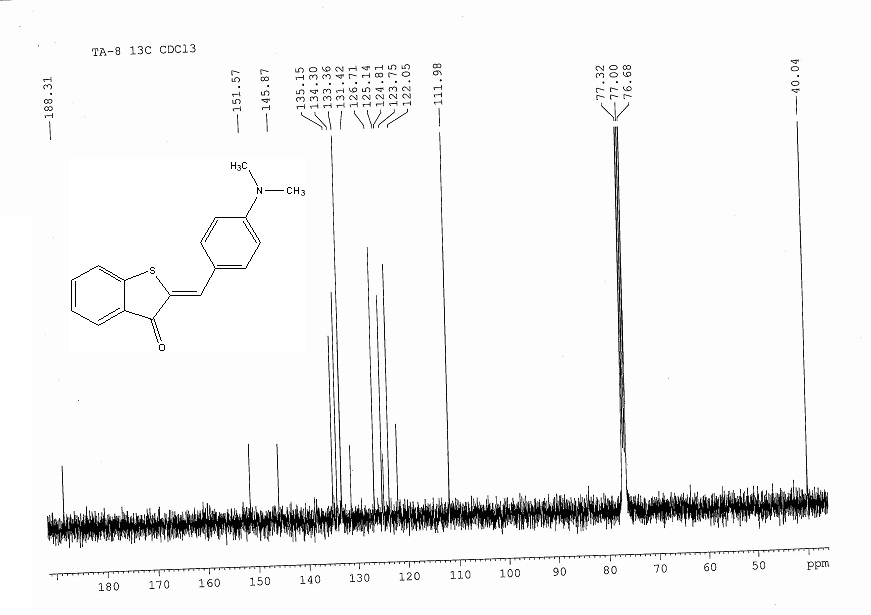
13C-NMR spectrum of 2-(4-(Dimethylamino)phenyl-4*H*-thiochromen-4-one.



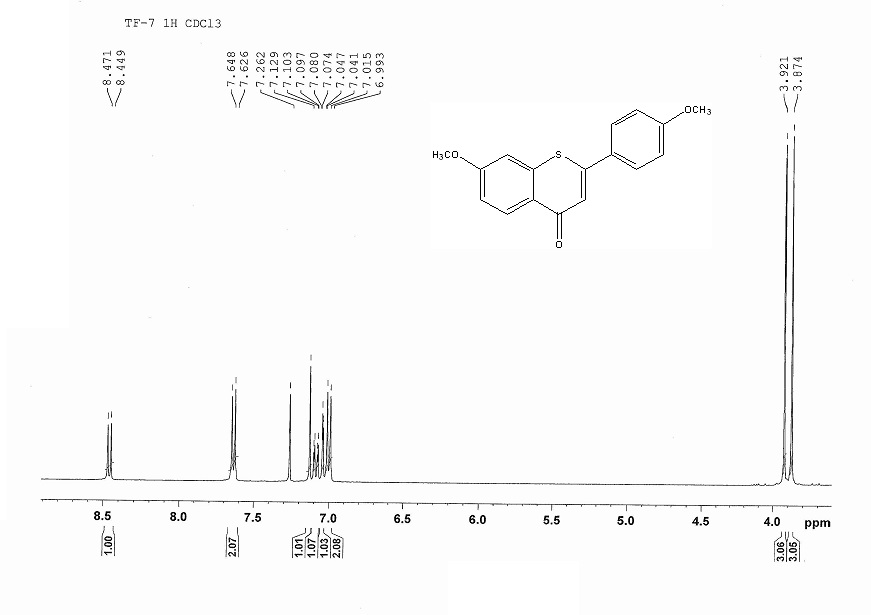
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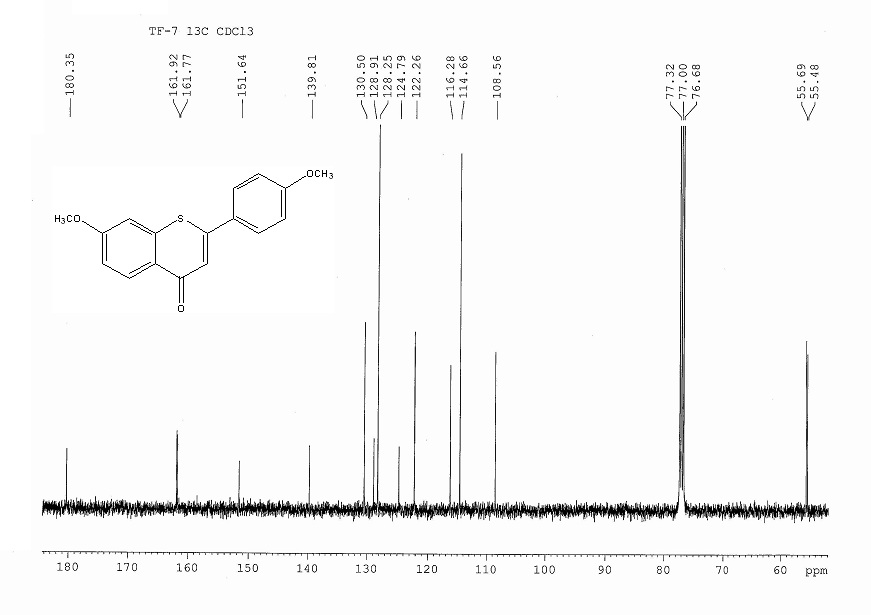
13C-NMR spectrum of (*Z*)-2-(4-Dimethylamino)benzylidene)benzo[*b*]thiophen-3(2*H*)-one.



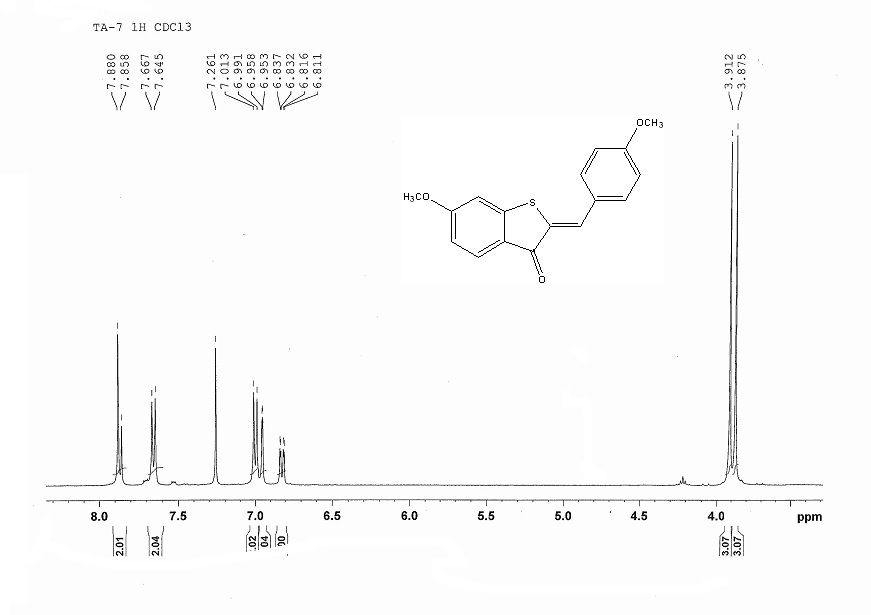
1H-NMR spectrum of 7-Methoxy-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one.



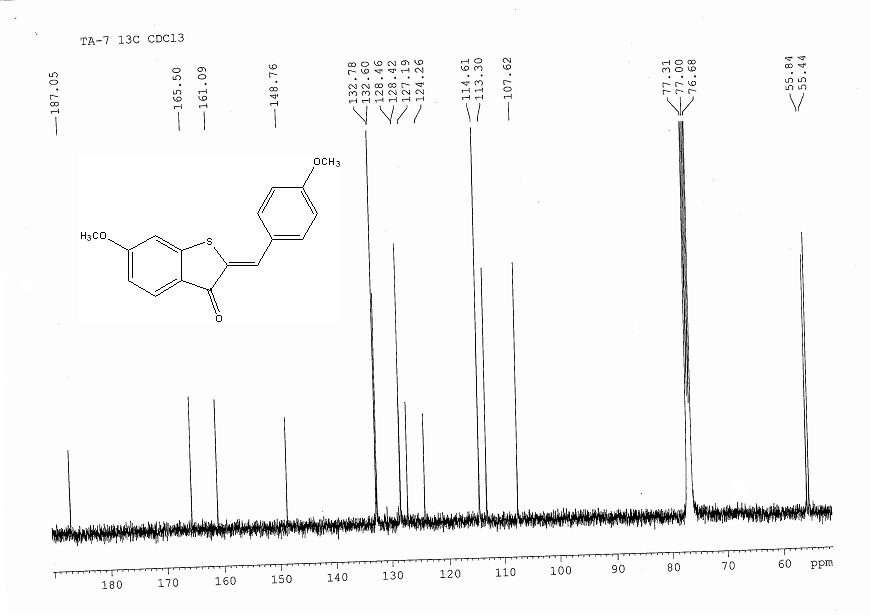
13C-NMR spectrum of 7-Methoxy-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one.



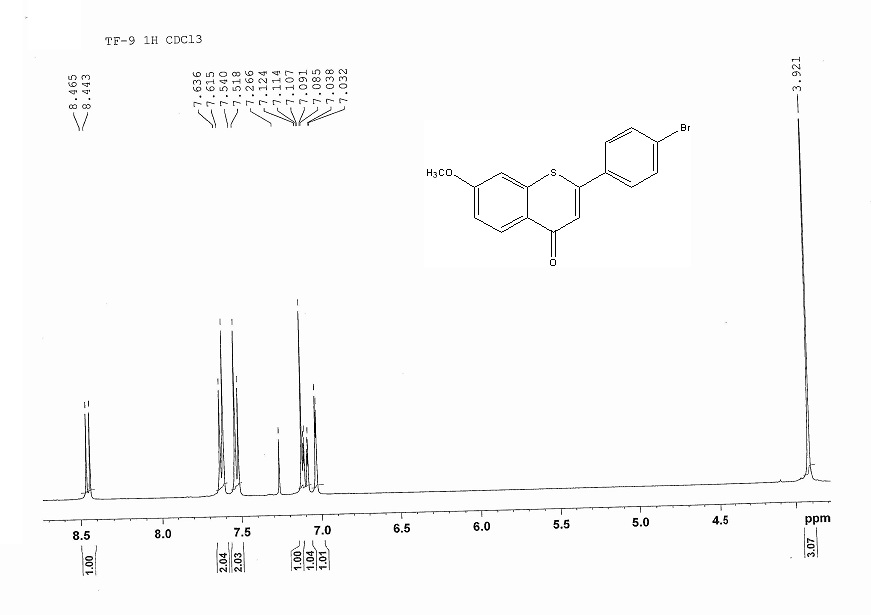
1H-NMR spectrum of (*Z*)-6-Methoxy-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



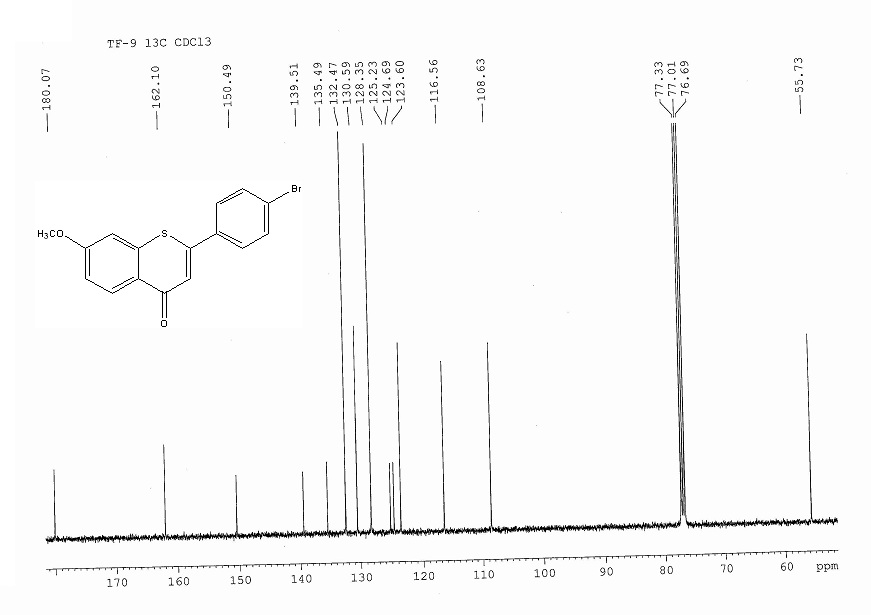
13C-NMR spectrum of (*Z*)-6-Methoxy-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



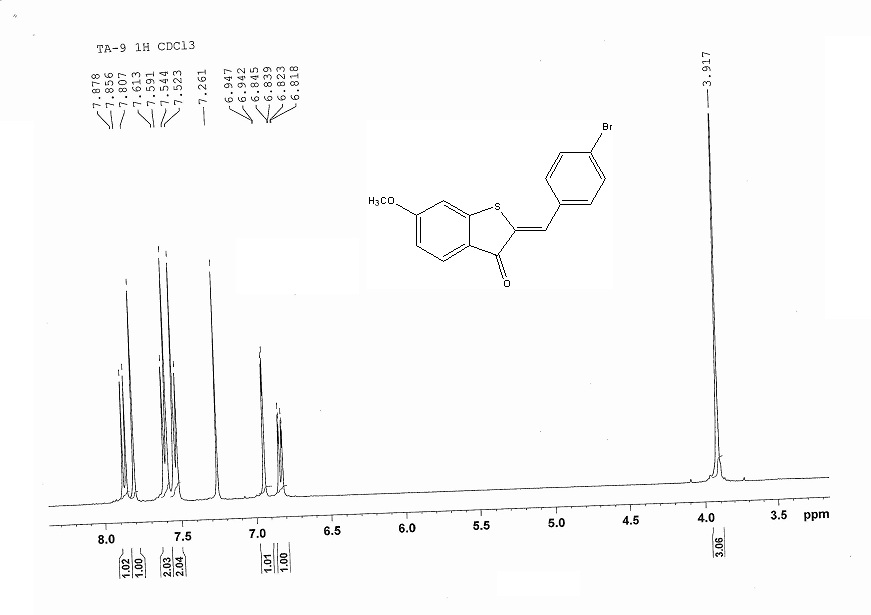
1H-NMR spectrum of 2-(4-Bromophenyl)-7-methoxy-4*H*-thiochromen-4-one.



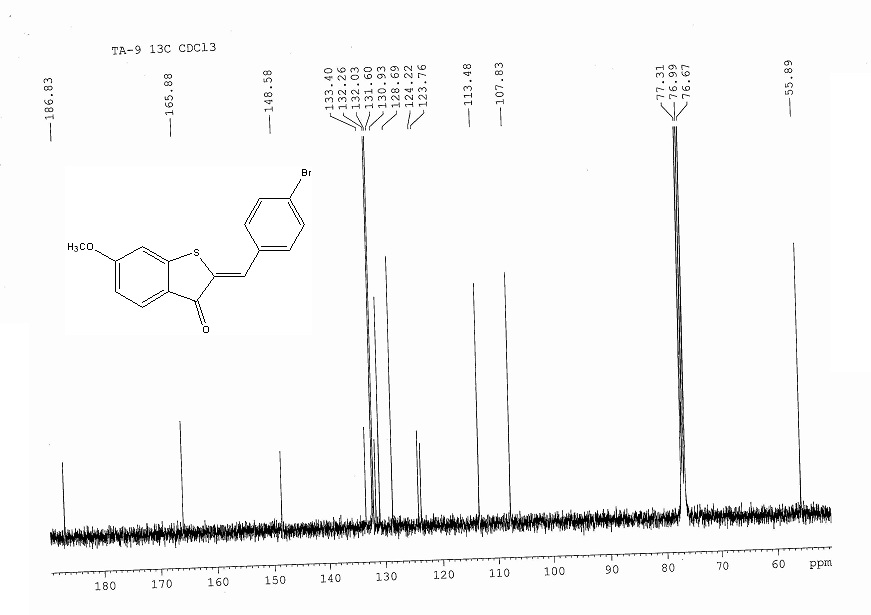
13C-NMR spectrum of 2-(4-Bromophenyl)-7-methoxy-4*H*-thiochromen-4-one.



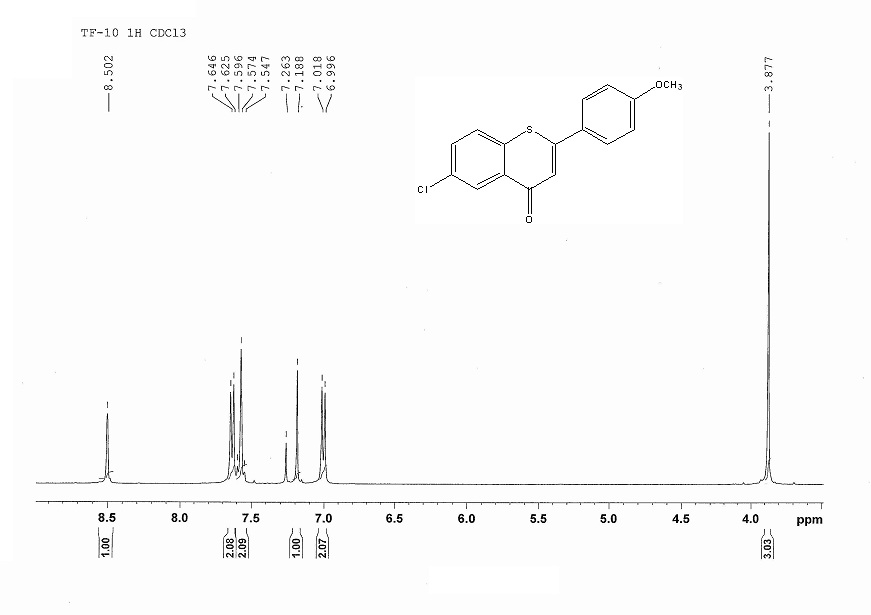
1H-NMR spectrum of (*Z*)-2-(4-Bromobenzylidene)-6-methoxybenzo[*b*]thiophen-3(2*H*)-one.



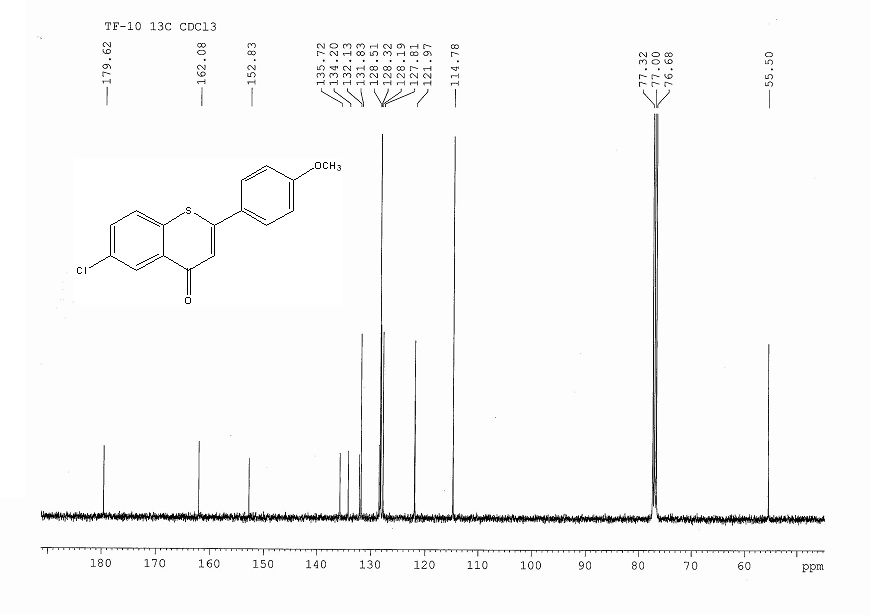
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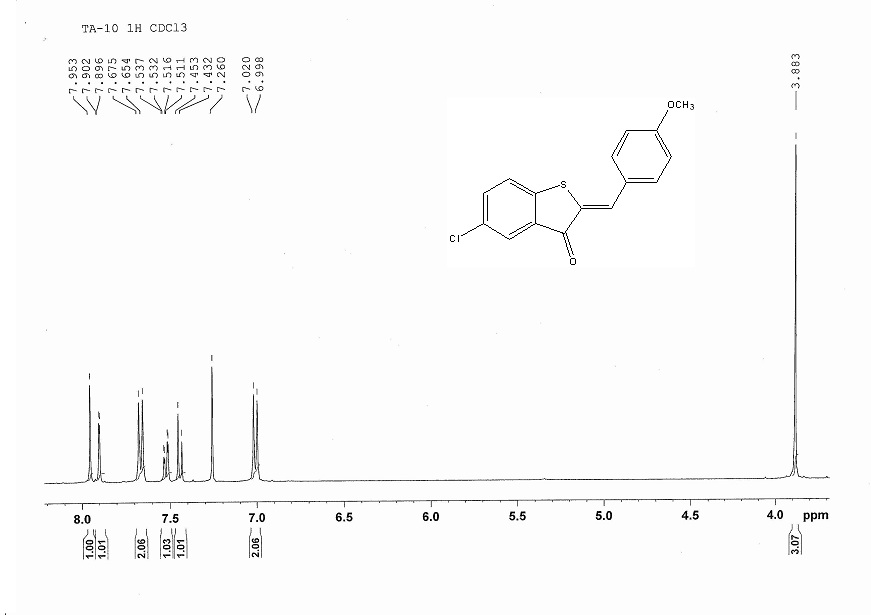
1H-NMR spectrum of 6-Chloro-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one.



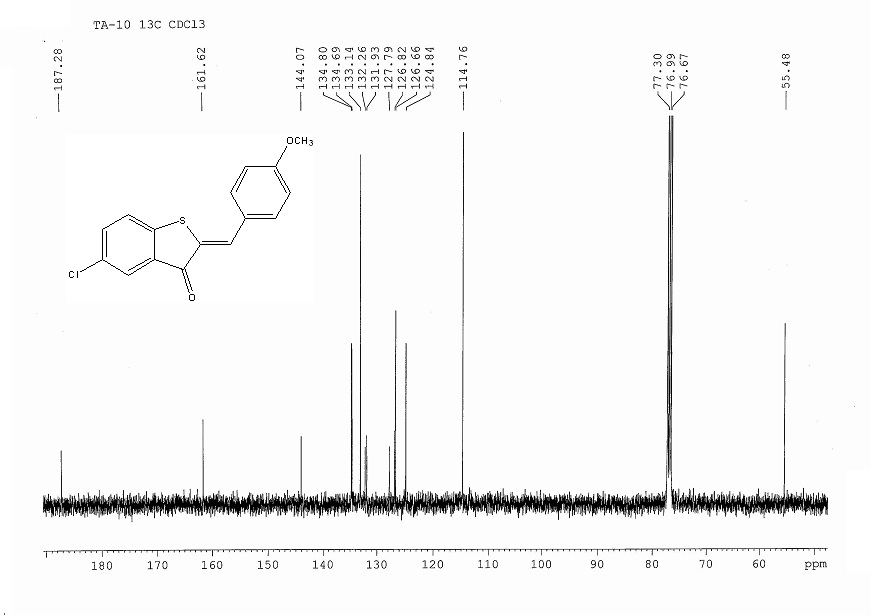
13C-NMR spectrum of 6-Chloro-2-(4-methoxyphenyl)-4*H*-thiochromen-4-one.



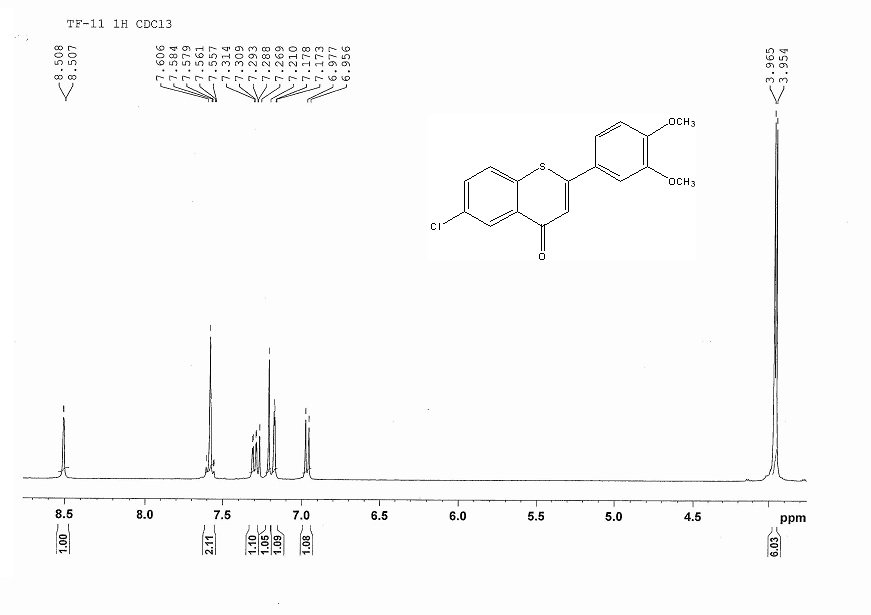
1H-NMR spectrum of (*Z*)-5-Chloro-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



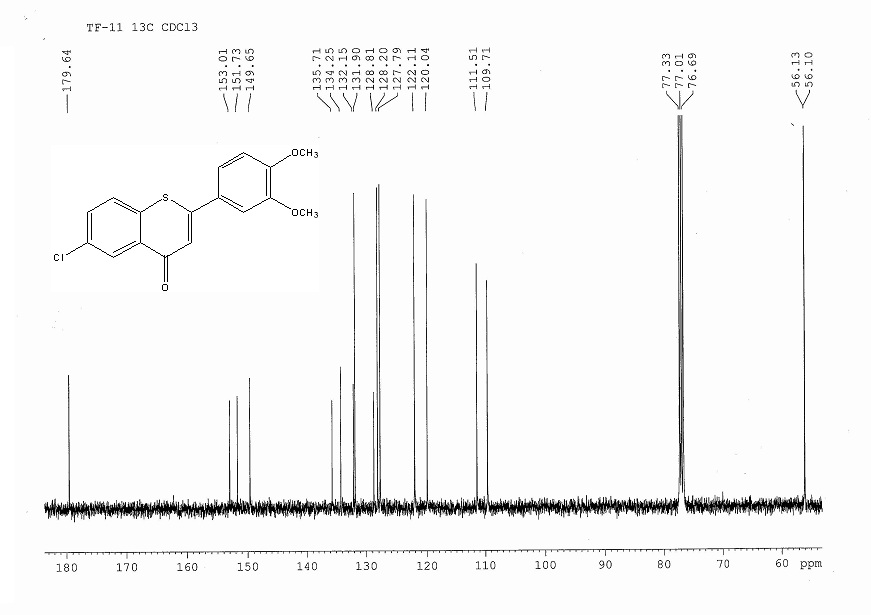
13C-NMR spectrum of (*Z*)-5-Chloro-2-(4-methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



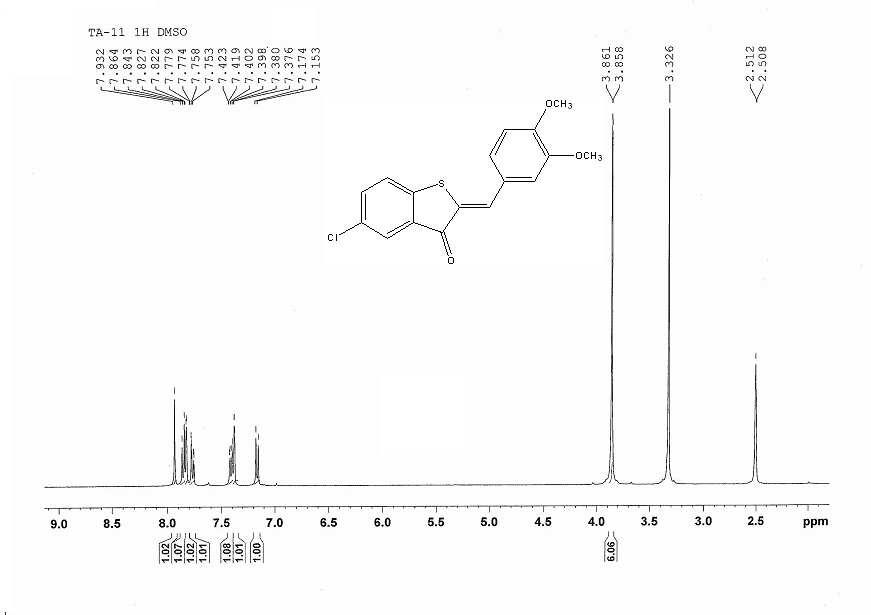
1H-NMR spectrum of 6-Chloro-2-(3,4-dimethoxyphenyl)-4*H*-thiochromen-4-one.



13C-NMR spectrum of 6-Chloro-2-(3,4-dimethoxyphenyl)-4*H*-thiochromen-4-one.



1H-NMR spectrum of (*Z*)-5-Chloro-2-(3,4-dimethoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.



13C-NMR spectrum of (*Z*)-5-Chloro-2-(3,4-dimethoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one.

