# Supporting Information

## A practical one-pot synthesis of coumarins in aqueous sodium bicarbonate via intramolecular Wittig reaction at room temperature

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**General Information**

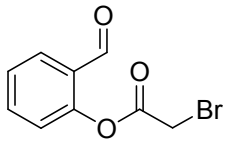
All reagents were of analytical grade and were used directly. Thin-layer chromatography (TLC) was performed on silica gel plates (60 F254; Merck). Column chromatography was performed using silica gel (60–120 mesh size; Merck). Melting points were determined in open capillaries and are uncorrected. The IR spectra were recorded on Nicolet Impact 410 FT IR spectrophotometer using KBr pellets. $^{1}H$ and $^{13}C$ NMR were recorded on Bruker 300-MHz and 400-MHz FT NMR spectrometer in $CDCl_3$ and DMSO-$d_6$ by using TMS as internal standard.

**Experimental Section:**

**General Procedure for the synthesis of 2-formylphenyl 2-bromoacetates (2a-h):**

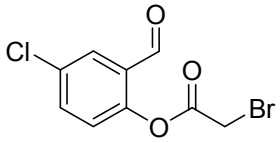
A modification of a literature method[1] was used. Salicylaldehyde (1 equiv) was added dropwise during 15 min at 0 °C to a suspension of sodium hydride (1.1 equiv) in THF (4 mL per 1 mmol of salicylaldehyde). The resulting pale yellow, viscous slurry was stirred for 2 h, and the 2-bromoacetyl bromide (1.2 equiv) was added dropwise over 10 min at 0 °C. After 25 min, the resulting white suspension of NaBr was removed by filtration; the solvent was evaporated, and the residue was quenched with saturated $NH_4Cl$ (10 mL) solution and then extracted with ethyl acetate (2 x 10mL), the combined organic extracts were washed with $H_2O$ (20 mL), brine (20 mL) and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure to afford the 2-formylphenyl 2-bromoacetates (**2a-h**) with 80-90% yield with sufficient purity for the next step reaction.

**2-formylphenyl 2-bromoacetate (2a)**



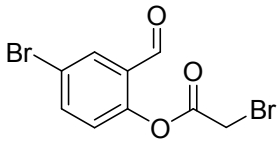

Yield: 85%; colorless oil; IR (KBr): 1765, 1702, 1276, 1254, 1196, 1118 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.65 (m, 1H), 7.44 (t, 1 H), 7.22 (d, $J$ = 8.0 Hz, 1H), 4.18 (s, 2 H); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ 188.9, 165.5, 150.6, 135.4, 131.9, 127.6, 126.9, 122.9, 25.2;

**4-chloro-2-formylphenyl 2-bromoacetate (2b)**



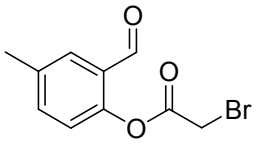

Yield: 83%; low melting solid; IR (KBr): 1767, 1705, 1278, 1257, 1200, 1119, 810 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 4.08 (s, 2 H); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ 188.9, 165.5, 150.6, 135.4, 131.8, 130.5, 123.1, 25.2;

**4-bromo-2-formylphenyl 2-bromoacetate (2c)**



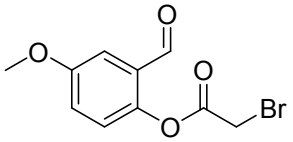

Yield: 83%; low melting solid; IR (KBr): 1763, 1696, 1278, 1257, 1200, 1119, 640 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 2H); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ 188.9, 165.5, 150.6, 139.4, 134.5, 124.2, 120.1, 25.2;

**2-formyl-4-methylphenyl 2-bromoacetate (2d)**



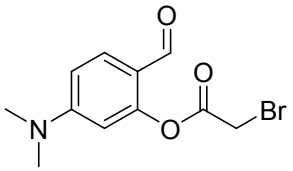

Yield: 88%; colorless oil; IR (KBr): 1761, 1698, 1278, 1257, 1200, 1119, 640 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 10.10 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 2 H), 2.4 (s, 3H); $^{13}C$ NMR (300 MHz, $CDCl_3$): δ 188.9, 165.5, 150.6, 135.4, 135.2, 134.5, 130.2, 121.3, 25.2, 24.1;

**2-formyl-4-methoxyphenyl 2-bromoacetate (2e)**



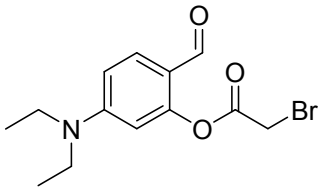
Yield: 90%; colorless oil; IR (KBr): 1760, 1696, 1278, 1257, 1200, 1119, 640 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 10.10 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.22 (dd, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 2H), 3.9 (s, 3H); $^{13}C$ NMR (300 MHz, $CDCl_3$): δ 188.9, 165.5, 159.6, 146.4, 136.2, 124.5, 121.2, 115.3, 25.2, 60.5;

**5-(dimethylamino)-2-formylphenyl 2-bromoacetate (2f)**



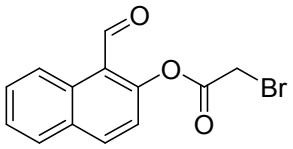
Yield: 84%; low melting solid; IR (KBr): 1660, 1690, 1278, 1257, 1200, 1119, 640 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 9.7 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 6.48 (dd, 1H), 6.22 (s, 1H), 4.10 (s, 2H), 2.9 (s, 6H); $^{13}C$ NMR (300 MHz, $CDCl_3$): δ 189.5, 166.5, 157.9, 155.4, 133.2, 125.2, 112.8, 106.1, 40.2, 25.2;

**5-(diethylamino)-2-formylphenyl 2-bromoacetate (2g)**



Yield: 85%; low melting solid; IR (KBr): 1660, 1690, 1278, 1257, 1200, 1119, 640 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 6.48 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.22 (d, J=2.4 Hz, 1H), 4.12 (s, 2H), 3.4 (q, 4H), 1.15 (t, 6H); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ 189.5, 166.5, 157.9, 155.4, 133.2, 125.2, 112.8, 106.1, 44.2, 25.2, 13.1;

**1-formylnaphthalen-2-yl 2-bromoacetate (2h)**

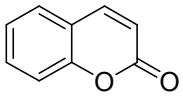



Yield: 82%; low melting solid; IR (KBr): 1775, 1702, 1278, 1257, 1200, 1119 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 10.71 (s, 1H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.22 (dd, *J* = 8.8 Hz, 3.2 Hz, 1H), 4.11 (s, 2H); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ 191.0, 167.5, 158.9, 136.4, 131.2, 130.2, 129.6, 128.2, 127.4, 126.4, 124.4, 120.4, 25.2;

**General Procedure for the Preparation of Coumarins (4a-h):**

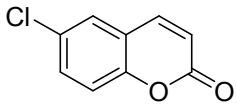
A mixture of 2-formylphenyl 2-bromoacetates (**2a-h**, 2 mmol) and triphenylphosphine (2 mmol) in ethylacetate (5 mL) was stirred at 60 $^oC$ for 2 h. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2:8). The mixture was cooled to room temperature and the seperated solid Wittig salt was filtered and washed with cold ethyl acetate (2 mL). The obtained Wittig salt (**3a-h**) was taken in saturated aqueous $NaHCO_3$ (5 mL) and stirred vigorously for 30 min at room temperature. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2:8). After completion of the reaction, the crude reaction mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layer was washed with $H_2O$ (10 mL), and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica (60–120, eluent: EtOAc–hexane, 2:8) to afford pure products **4a-h** with 65–75% yield. The physical data (mp, NMR) of all the known compounds were found to be identical with those reported in the literature.

**2H-chromen-2-one (4a)[2]**



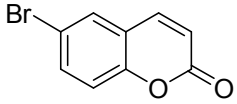
Yield: 70%; White solid; mp: 68-69 °C; IR (KBr): 1696, 1602, 1383, 1237, 1067, 985, 856, 758, 572, 525, 426 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.6 Hz, 1H), 7.56-7.48 (m, 2H), 7.35-7.26 (m, 2H), 6.42 (d, *J* = 9.6 Hz, 1H); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 161.2, 154.4, 143.9, 132.3, 128.3, 124.8, 119.2, 117.3, 117.1;

**6-chloro-2H-chromen-2-one (4b)[3]**



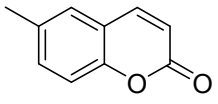
Yield: 68%; mp 152–153 °C; IR (KBr): 1699, 1602, 1383, 1237, 1067, 950, 895, 830, 820, 730, 590, 530, 500 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.6Hz, 1H), 7.41-7.43 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 159.5, 151.9, 141.7, 131.3, 129.2, 126.6, 119.3, 117.8, 117.3;

**6-bromo-2H-chromen-2-one (4c)[4]**



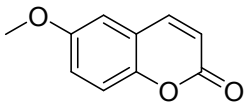
Yield: 68%; mp 162–164 °C; IR (KBr): 1690, 1600, 1383, 1237, 1067, 950, 895, 830, 730, 620, 590, 530, 500 $cm^{-1}$; 1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.57 (m, 3H), 7.15 (d, J=7.0 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 159.9, 152.9, 142.1, 134.6, 130.2, 120.3, 118.6, 117.8, 116.9;

**6-methyl-2H-chromen-2-one (4d)[5]**



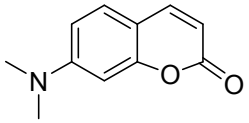
Yield: 72%; colorless solid; mp: 73-75 °C; IR (KBr): 1717, 1684, 1575, 1380, 1262, 1189, 1167, 1105, 911, 841, 820, 813 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 9.3 Hz, 1H), 7.40.7.20 (m, 3H), 6.43 (d, *J* = 9.3 Hz, 1H), 2.43 (s, 3H); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 161.0, 152.0, 143.4, 134.1, 132.8, 127.6, 118.5, 116.5, 116.4, 20.7;

**6-methoxy-2H-chromen-2-one (4e)[5]**



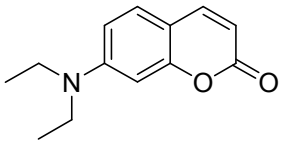
Yield: 75%; colorless solid; mp: 100-102 $^{o}$C; IR (KBr): 1705, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm$^{-1}$; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 9.6 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.07 (dd, *J* = 9.0, 2.7Hz, 1H), 6.89 (d, *J* = 2.7 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 3.82 (s, 3H,); $^{13}$C NMR (300 MHz, $CDCl_3$): δ 160.9, 155.9, 148.3, 143.2, 119.4, 119.0, 117.7, 116.9, 109.9, 55.7;

**7-(dimethylamino)-2H-chromen-2-one (4f)[6]**



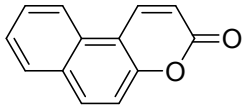
Yield: 72%; purple powder; mp: 161-162 $^{o}$C; ; IR (KBr): 1685, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm$^{-1}$; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 9.3 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 6.61 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 6.06 (d, *J* = 9.3 Hz, 1H), 3.82 (s, 3H), 2.9 (s 6H); $^{13}$C NMR (300 MHz, $CDCl_3$): δ 162.1, 156.3, 152.9, 143.7, 128.5, 109.8, 109.0, 108.8, 98.1, 40.2;

**7-(diethylamino)-2H-chromen-2-one (4g)[7]**



Yield: 72%; yellowish powder; mp: 93-95 $^{o}$C; IR (KBr): 1680, 1570, 1491, 1451, 1286, 1261,1185, 886, 808, 684 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 9.2 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.48 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 5.95 (d, *J* = 9.2 Hz, 1H), 3.33 (q, *J* = 14.2 Hz, 4H), 1.14 (t, *J* = 6.8 Hz, 6H); $^{13}$C NMR (400 MHz, $CDCl_3$): δ 162.3, 156.7, 150.7, 143.7, 128.7, 109.1, 108.6, 108.3, 97.5, 44.7, 12.4;

**3H-benzo[f]chromen-3-one (4h)[8]**



Yield: 70%; yellowish powder; mp: 117-119 $^{o}$C; IR (KBr): 1705, 1278, 1257, 1200, 1119 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 9.7 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.71-7.66 (m, 1H), 7.59-7.54 (m, 1H), 7.44 (d, *J* = 9.2 Hz, 1H), 6.56 (d, *J* = 9.8 Hz, 1H); $^{13}$C NMR (400 MHz, $CDCl_3$): δ 160.9, 153.9, 139.1, 133.1, 130.3, 129.0, 128.3, 126.1, 121.3, 117.1, 115.6, 113.0;

**References**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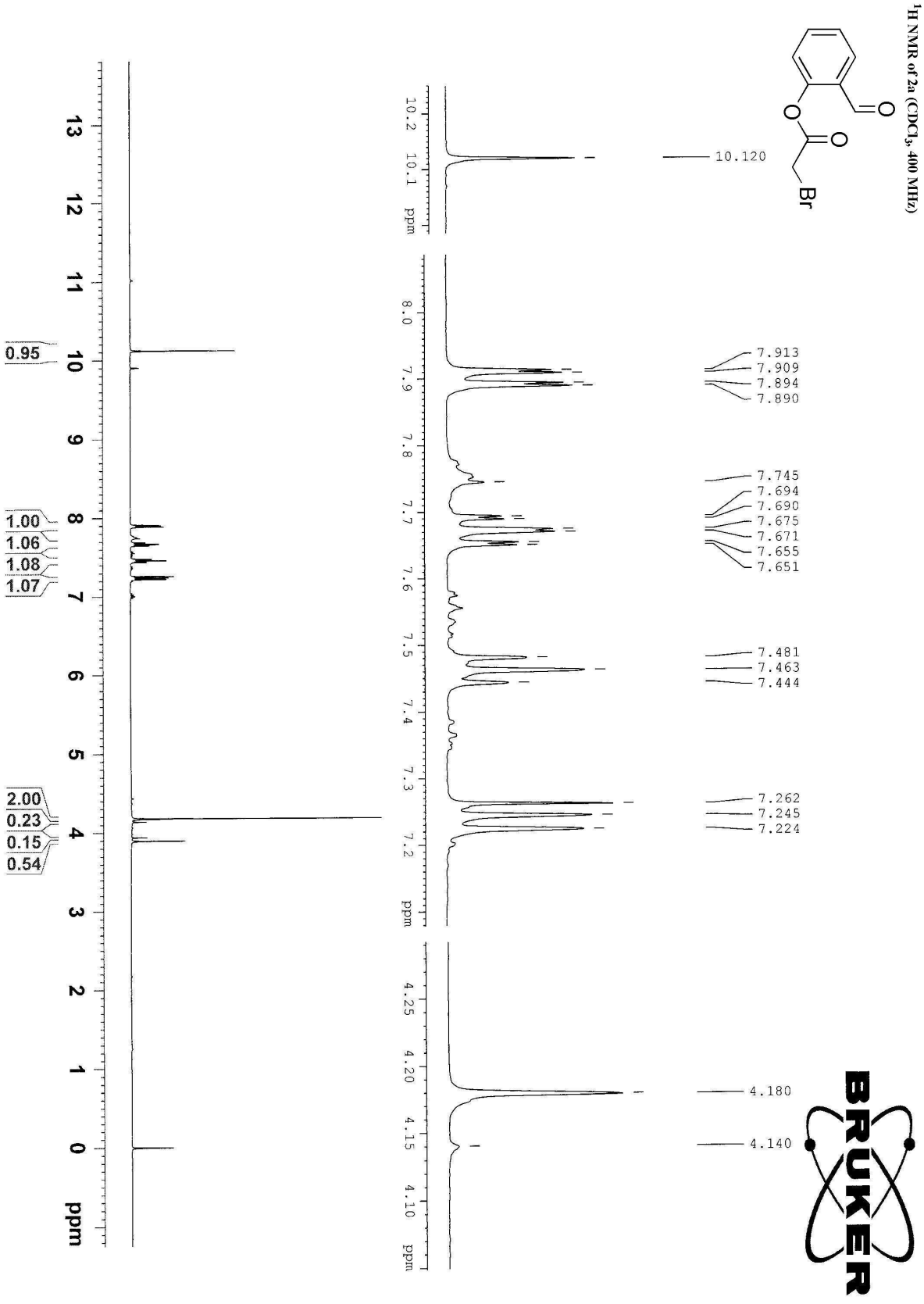
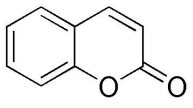
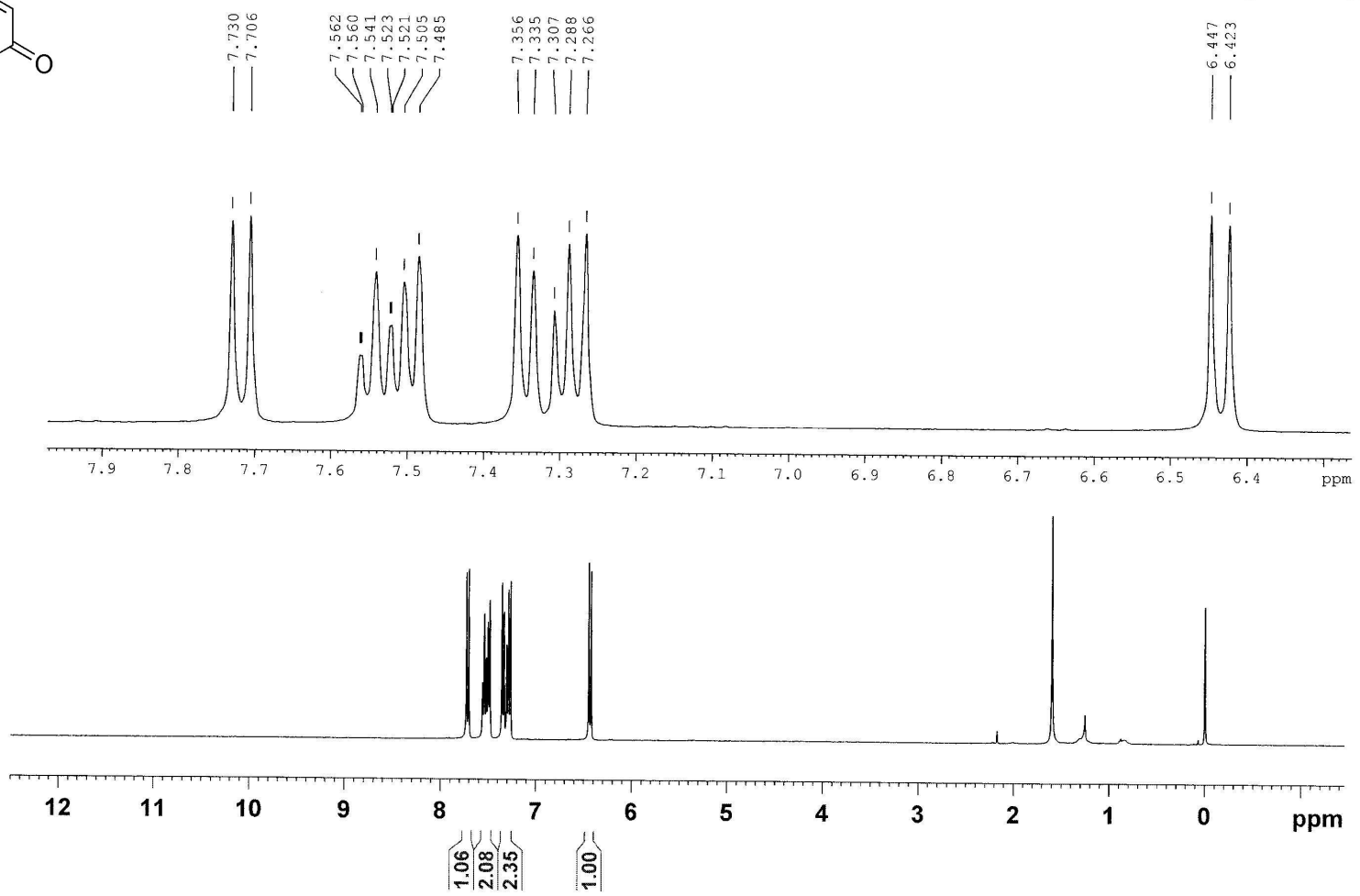
**NMR Data:**

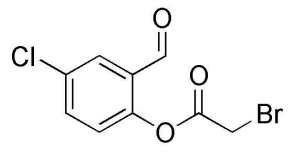

¹H NMR of 2a (CDCl₃, 400 MHz)
10.120
7.913
7.909
7.894
7.890
7.745
7.694
7.690
7.675
7.671
7.655
7.651
7.481
7.463
7.444
7.262
7.245
7.224
4.180
4.140
0.95
1.00
1.06
1.08
1.07
2.00
0.23
0.15
0.54
Br
O
ppm
BRUKER

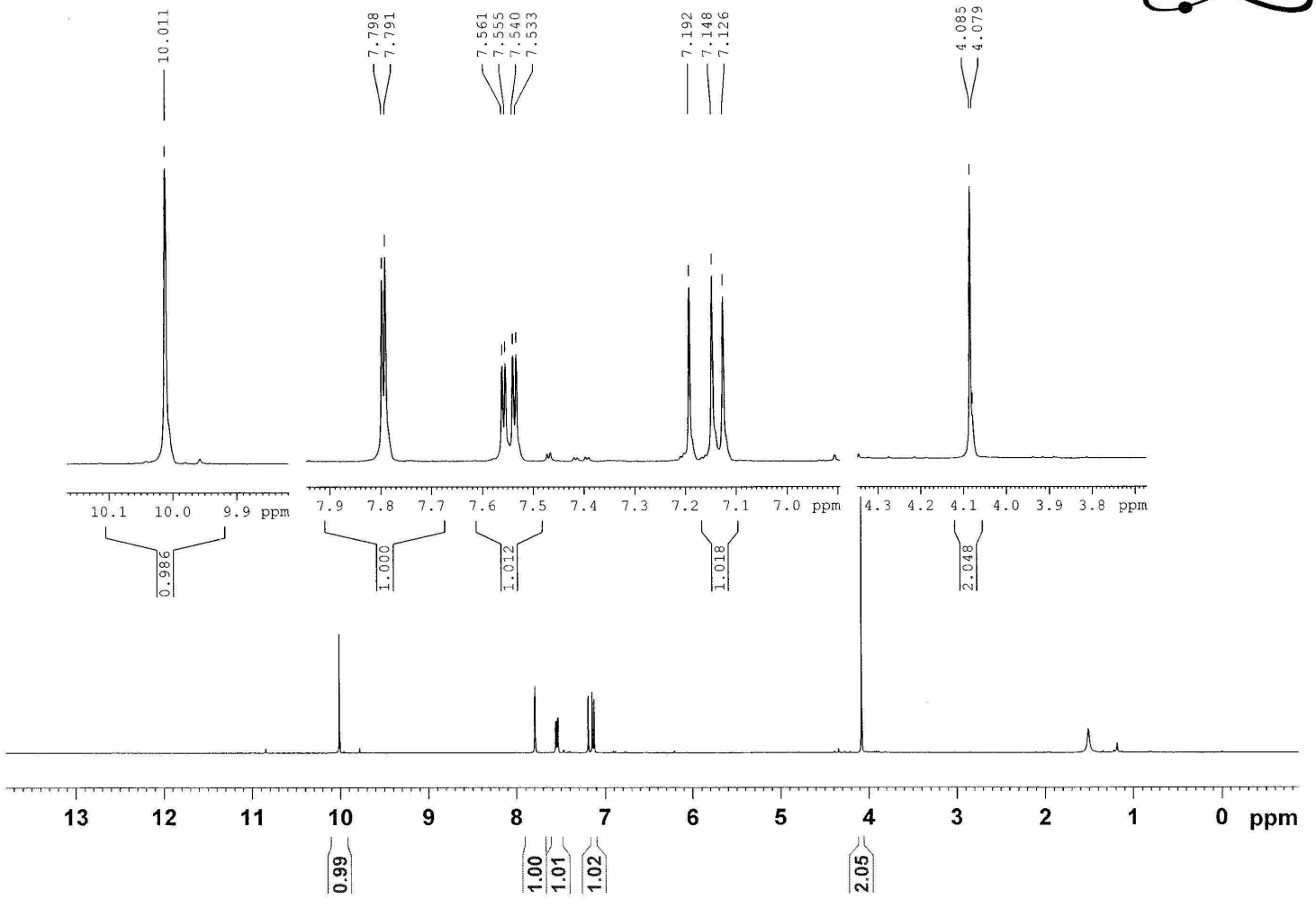
$^1$H NMR of 4a ($CDCl_3$, 400 MHz)



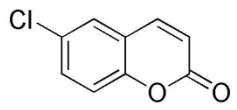


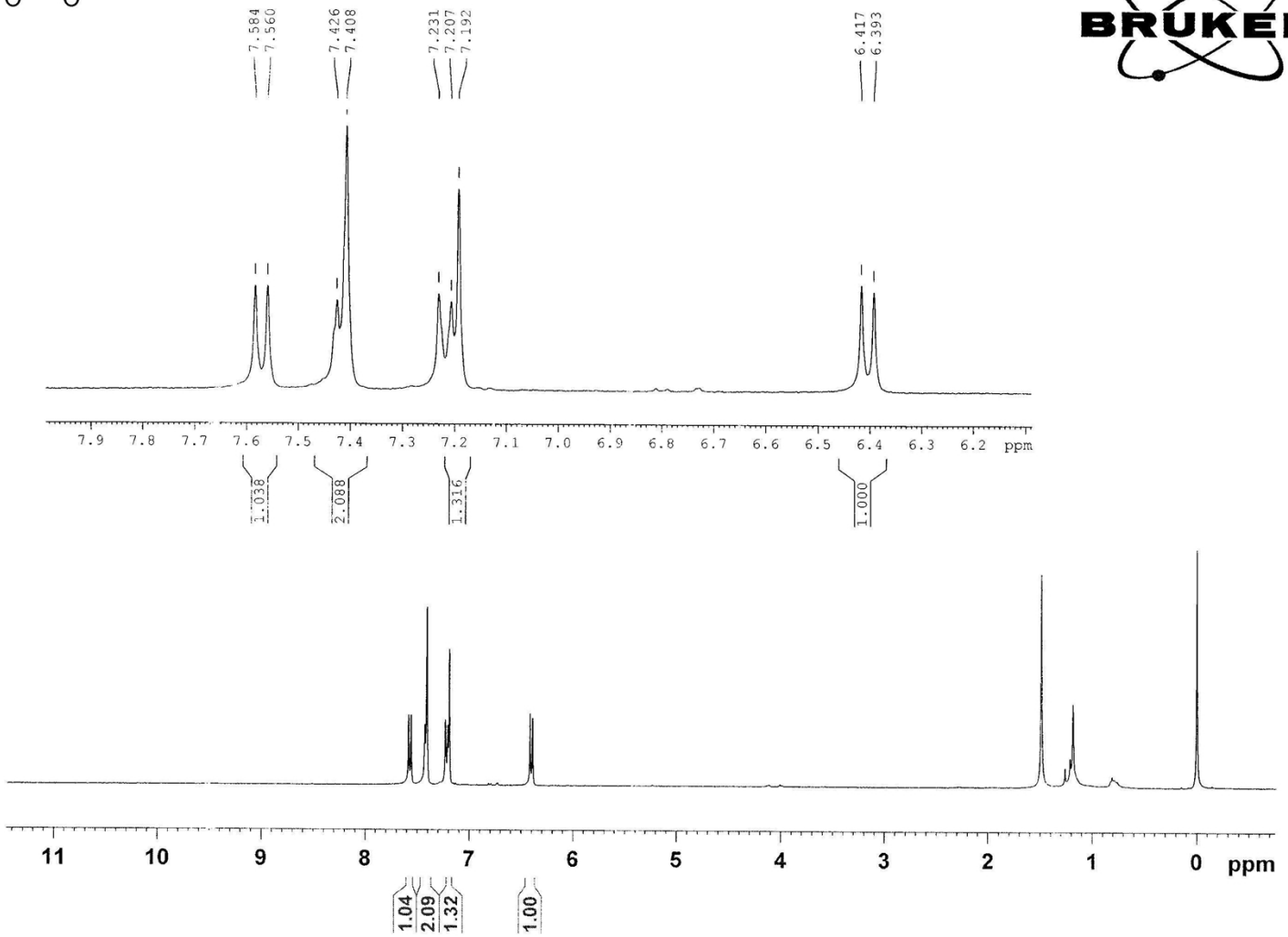
$^1$H NMR of 2b ($CDCl_3$, 400 MHz)



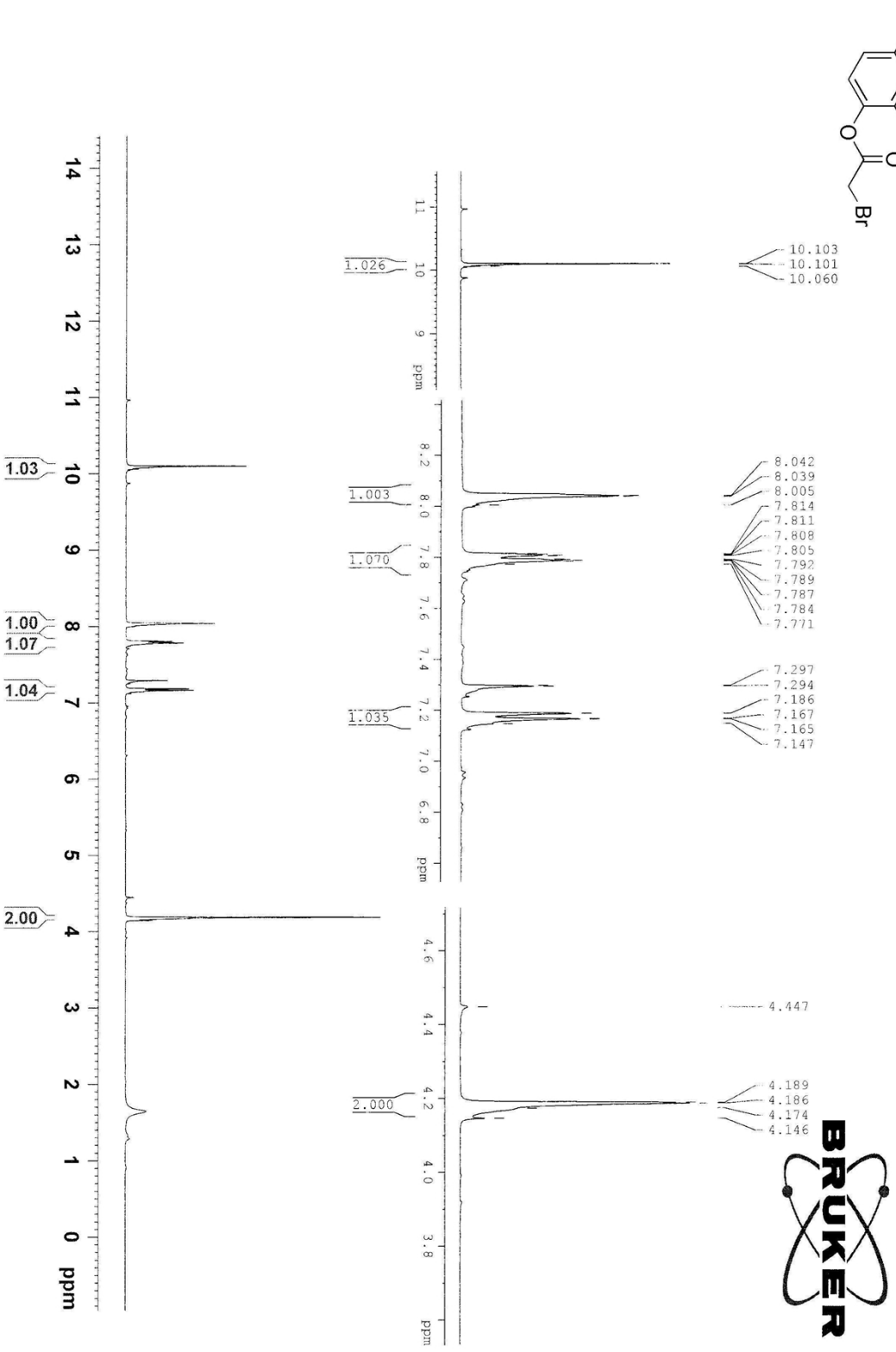



$^1$H NMR of 4b ($CDCl_3$, 400 MHz)

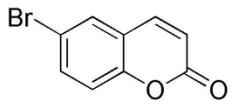


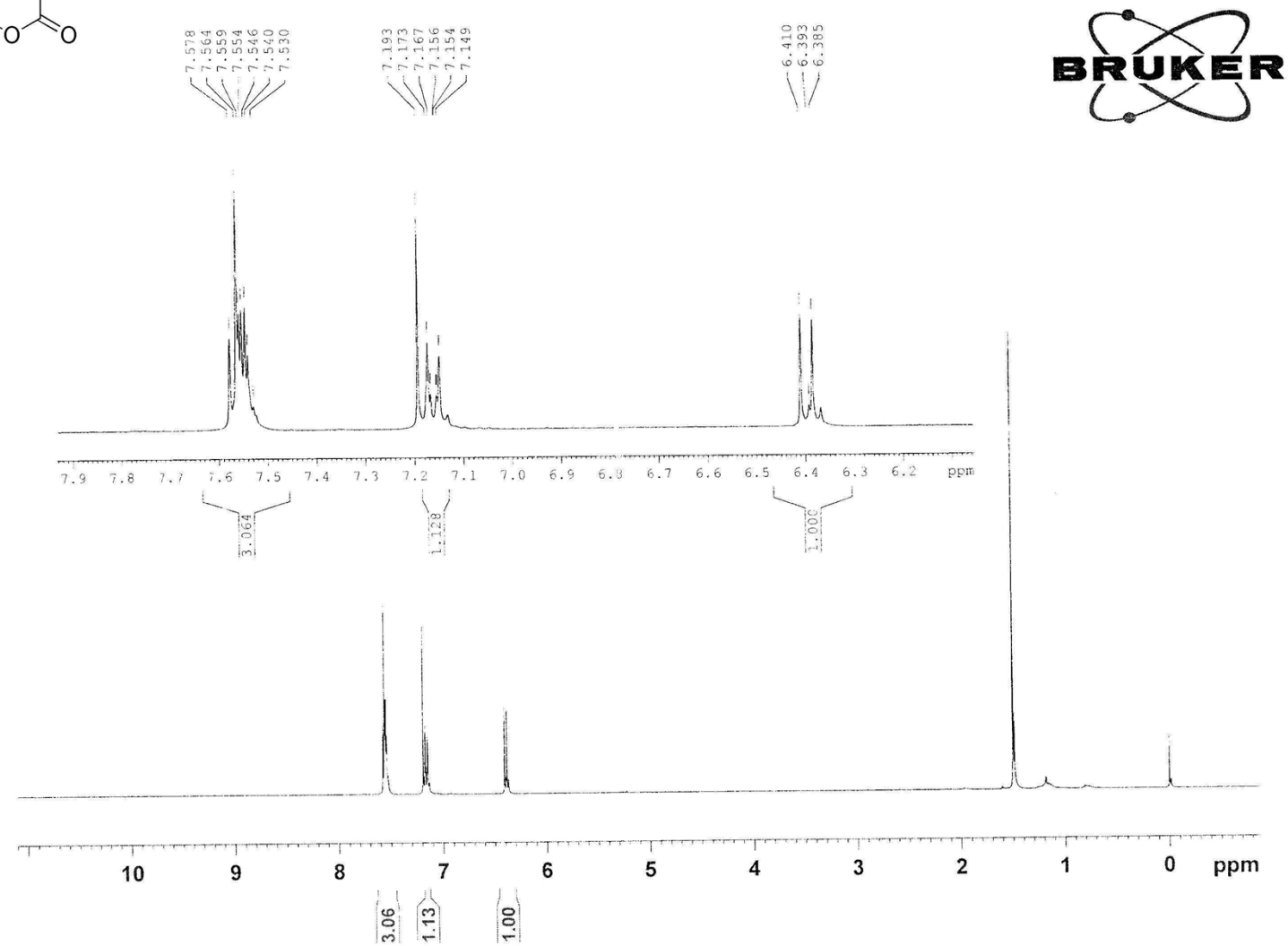



$^1$H NMR of 2c ($CDCl_3$, 400 MHz)

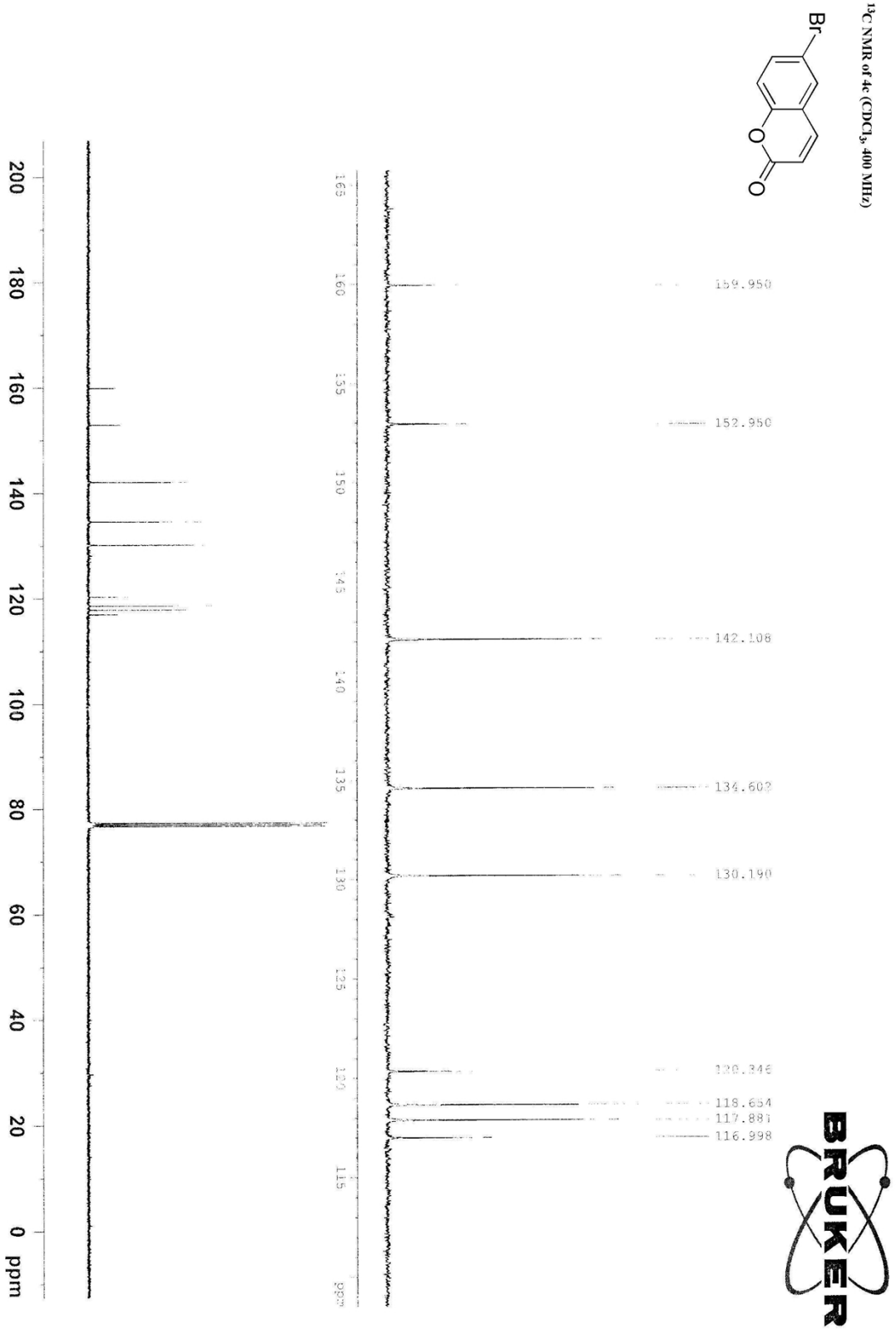


**$^1$H NMR of 4c ($CDCl_3$, 400 MHz)**

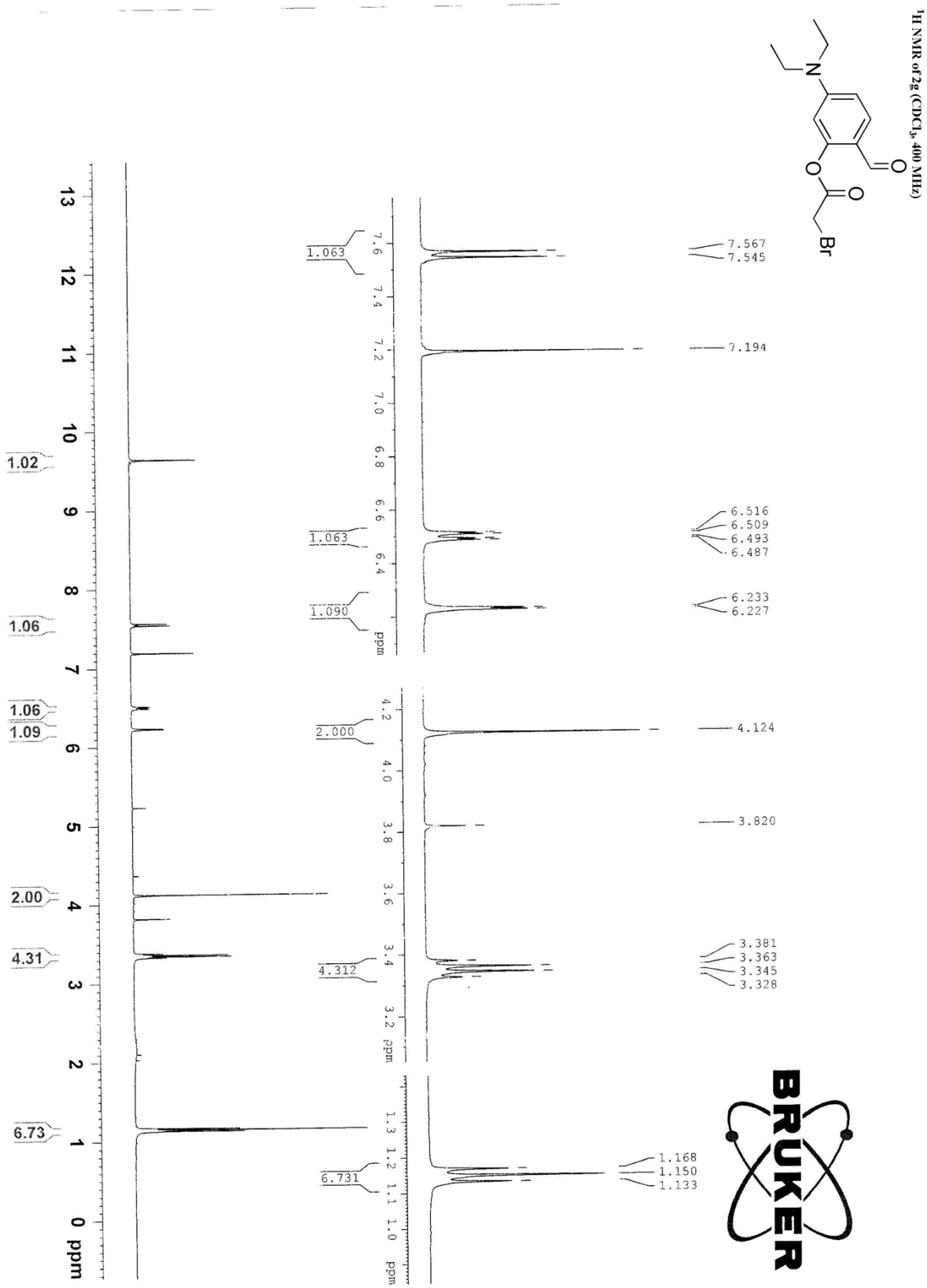


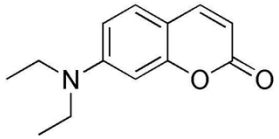
$^{13}$C NMR of 4c ($CDCl_3$, 400 MHz)

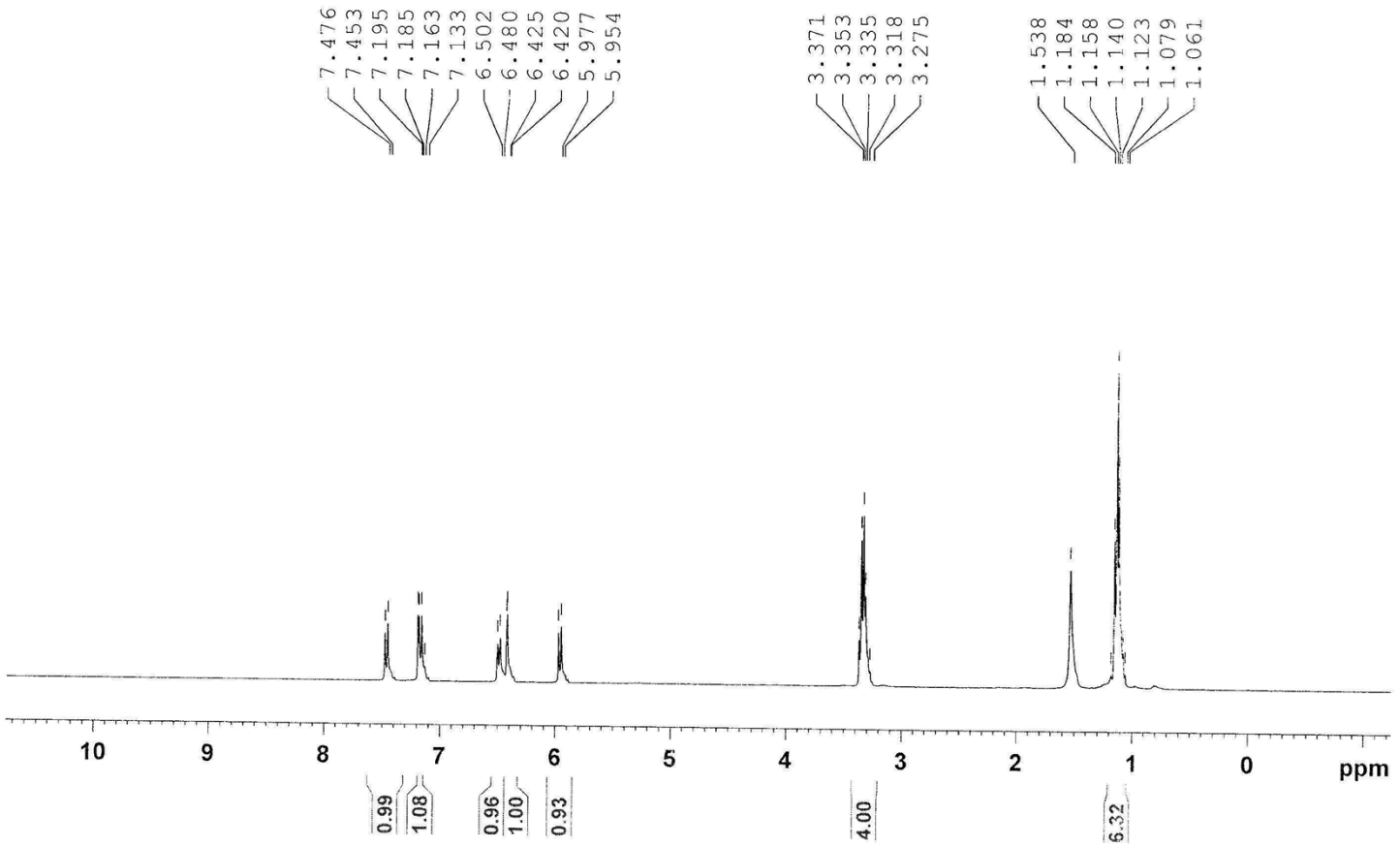


$^1$H NMR of 2g ($CDCl_3$, 400 MHz)



**$^1$H NMR of 4g ($CDCl_3$, 400 MHz)**



$^{13}$C NMR of 4g ($CDCl_3$, 400 MHz)