

4-Chloro-3-nitrocoumarin as a Precursor for Synthesis of 2-Arylchromeno[3,4-*b*]pyrrol-4(3*H*)-ones: A case of Nitro Group Directed Reductive Coupling

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Supporting Information

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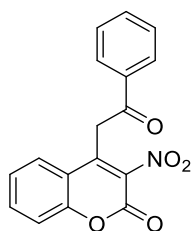
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1. Instrumentation

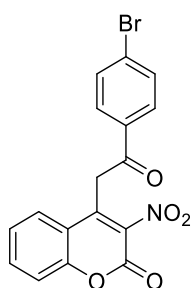
Melting points were determined on a Mel-Temp melting point apparatus in open capillaries and are uncorrected. MS were performed on JEOL JMS-SX/SX 102A spectrometer. IR spectra were obtained using a 1725XFT-IR spectrophotometer. Single crystal structures were determined by a Bruker AXS SMART-1000 X-ray single-crystal diffractometer. ^1H and ^{13}C NMR spectra were recorded at 400 and 150 MHz on a Bruker 400/600 spectrometer. Chemical shifts were reported in parts per million on the δ scale relative to an internal standard (tetramethylsilane, or appropriate solvent peaks) with coupling constants given in hertz. ^1H NMR multiplicity data are denoted by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60G-254 plates (25 mm) and developed with the solvents mentioned. Flash chromatography was performed in columns of various diameters with Merck silica gel (230-400 mesh ASTM 9385 kieselgel 60H) by elution with the solvent systems.

2. Characterization data of prepared compounds

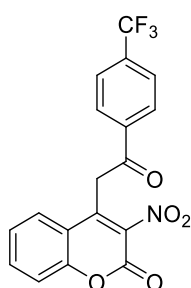
5a. 3-nitro-4-(2-oxo-2-phenylethyl)-2H-chromen-2-one. Pale yellow solid; yield 42%; R_f = 0.42 (30% EtOAc/hexanes); mp 182–184 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.03 (d, J = 7.2 Hz, 2H), 7.70 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 8.0 Hz, 2H), 7.51 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 4.63 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 191.7, 152.8, 152.5, 143.2, 138.3, 135.2, 134.5, 134.3, 129.1, 128.4, 126.6, 125.7, 117.7, 117.5, 37.8; IR ν_{max} (KBr) 3233, 2426, 1715, 1683, 1607, 1566, 1379, 1215, 1072, 763 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{11}\text{NO}_5$ [M^+] 309.0637, found 309.0634.



5b. 4-(2-(4-bromophenyl)-2-oxoethyl)-3-nitro-2H-chromen-2-one. White solid; yield 40%; R_f = 0.40 (30% EtOAc/hexanes); mp 220–222 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.88 (d, J = 8.0 Hz, 2H), 7.72–7.67 (m, 3H), 7.48 (tt, J = 9.2, 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 4.58 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, 150 MHz) δ 192.9, 152.9, 151.9, 145.3, 137.3, 134.8, 134.3, 131.9, 130.6, 128.4, 128.3, 125.7, 117.6, 117.1, 38.1; IR ν_{max} (KBr) 3413, 2273, 1712, 1683, 1565, 1530, 1452, 1314, 984, 763 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{BrNO}_5$ [M^+] 386.9742, found 386.9751.

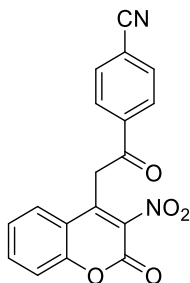


5c. 3-nitro-4-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-2H-chromen-2-one. Pale yellow solid; yield 47%; R_f = 0.40 (30% EtOAc/hexanes); mp 212–214 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.14 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 8.8 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 4.63 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 191.0, 152.7, 152.6, 142.4, 138.3, 137.9, 135.8 (q, $^2J_{\text{CF}}$ = 33.0 Hz), 134.5, 128.8, 126.5, 126.2 (d, $^3J_{\text{CF}}$ = 3.0 Hz), 123.3 (q, $^1J_{\text{CF}}$ = 270.0

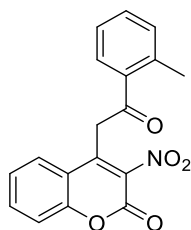


Hz), 117.9, 117.4, 38.0; IR ν_{max} (KBr) 3444, 2272, 1736, 1684, 1610, 1540, 1316, 1128, 831, 757 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{10}\text{F}_3\text{NO}_5$ [M^+] 377.0511, found 377.0520.

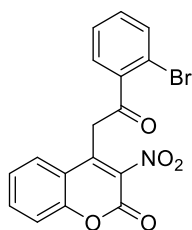
5d. 4-(2-(3-nitro-2-oxo-2*H*-chromen-4-yl)acetyl)benzonitrile. Light yellow solid; yield 48%; R_f = 0.38 (40% EtOAc/hexanes); mp 200–202 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.12 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 4.62 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 190.7, 152.7, 152.5, 142.2, 138.1, 134.6, 133.0, 132.6, 128.8, 126.4, 125.8, 117.9, 117.4, 117.3, 37.9; IR ν_{max} (KBr) 2975, 2232, 1726, 1694, 1607, 1532, 1370, 1213, 985, 765 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_5$ [M^+] 334.0590, found 334.0594.



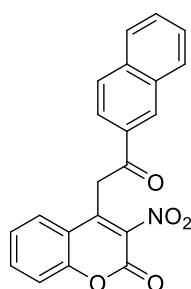
5e. 3-nitro-4-(2-oxo-2-(*o*-tolyl)ethyl)-2*H*-chromen-2-one. White solid; yield 49%; R_f = 0.42 (30% EtOAc/hexanes); mp 164–166 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.82 (d, J = 7.6 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.52–7.45 (m, 2H), 7.42–7.38 (m, 2H), 7.36–7.33 (m, 1H), 4.57 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 194.6, 152.8, 152.6, 143.3, 139.9, 134.3, 132.9, 132.7, 128.8, 126.6, 126.2, 125.7, 117.8, 117.6, 40.2, 21.6; IR ν_{max} (KBr) 3438, 2273, 1728, 1606, 1533, 1450, 1288, 986, 774, 659 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_5$ [M^+] 323.0794, found 323.0800.



5f. 4-(2-(2-bromophenyl)-2-oxoethyl)-3-nitro-2*H*-chromen-2-one. Off-white solid; yield 52%; R_f = 0.45 (30% EtOAc/hexanes); mp 142–144 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.73 (t, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.55 (dd, J = 7.6, 1.6 Hz, 1H), 7.49–7.47 (m, 1H), 7.46–7.45 (m, 1H), 7.43–7.39 (m, 2H), 4.62 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 195.3, 152.7, 152.6, 142.4, 134.5, 133.9, 132.9, 129.2, 128.0, 127.0, 125.8, 118.6, 117.7, 117.4, 41.7; IR ν_{max} (KBr) 3454, 2971, 1732, 1709, 1532, 1371, 1212, 1054, 976, 754 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{BrNO}_5$ [M^+] 386.9742, found 386.9749.

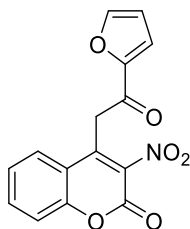


5g. 4-(2-(naphthalen-1-yl)-2-oxoethyl)-3-nitro-2*H*-chromen-2-one. Pale yellow solid; yield 46%; R_f = 0.43 (30% EtOAc/hexanes); mp 200–202 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.57 (s, 1H), 8.03 (t, J = 8.4 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.71–7.67 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 4.77 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, 150 MHz) δ 193.5, 152.9, 151.9, 145.5, 137.4, 135.4, 134.7, 132.6, 132.1, 131.2, 129.7, 129.1, 128.4, 128.3, 127.7, 127.2, 125.7, 123.5, 117.6, 117.1, 38.2;



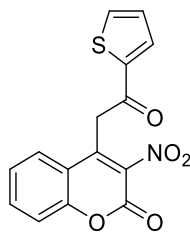
IR ν_{max} (KBr) 3439, 3036, 2106, 1675, 1609, 1527, 1451, 1309, 820, 761 cm^{-1} ;
HRMS (EI) calcd for $\text{C}_{21}\text{H}_{13}\text{NO}_5$ [M^+] 359.0794, found 359.0802.

5h. 4-(2-(furan-2-yl)-2-oxoethyl)-3-nitro-2H-chromen-2-one. White solid; yield 47%; $R_f = 0.37$



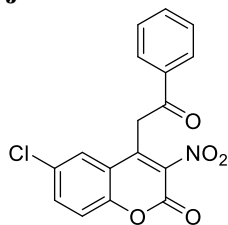
(40% EtOAc/hexanes); mp 176–178 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.70 (t, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 6.68–6.63 (m, 1H), 4.51 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 180.5, 152.8, 152.6, 151.3, 147.4, 141.9, 138.5, 134.3, 127.0, 125.7, 118.7, 117.7, 117.5, 113.2, 37.5; IR ν_{max} (KBr) 3447, 2273, 1812, 1731, 1675, 1567, 1377, 1022, 766, 674 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_6$ [M^+] 299.0430, found 299.0424.

5i. 3-nitro-4-(2-oxo-2-(thiophen-2-yl)ethyl)-2H-chromen-2-one. White solid; yield 50%; $R_f = 0.42$



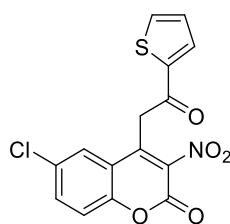
(30% EtOAc/hexanes); mp 182–184 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 4.4$ Hz, 1H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 1H), 4.56 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 184.2, 152.8, 152.5, 142.2, 141.9, 138.3, 135.7, 134.4, 133.2, 128.7, 126.8, 125.7, 117.7, 117.4, 38.1; IR ν_{max} (KBr) 3438, 2273, 1664, 1529, 1413, 1356, 1224, 1063, 928, 728 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_5\text{S}$ [M^+] 315.0201, found 315.0206.

5j. 6-chloro-3-nitro-4-(2-oxo-2-phenylethyl)-2H-chromen-2-one. Light grey solid; yield 49%; $R_f =$



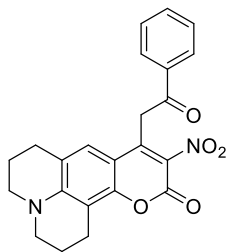
0.45 (30% EtOAc/hexanes); mp 210–212 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.71 (t, $J = 7.2$ Hz, 1H), 7.64 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.46 (d, $J = 2.0$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 1H), 4.58 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, 150 MHz) δ 194.6, 153.5, 151.2, 145.7, 138.3, 135.7, 135.24, 135.20, 130.9, 129.8, 129.3, 127.9, 119.8, 38.9; IR ν_{max} (KBr) 3438, 2273, 1664, 1529, 1413, 1356, 1224, 1063, 928, 728 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{ClNO}_5$ [M^+] 343.0248, found 343.0242.

5k. 6-chloro-3-nitro-4-(2-oxo-2-(thiophen-2-yl)ethyl)-2H-chromen-2-one. White solid; yield 59%;

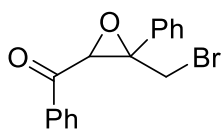


$R_f = 0.49$ (40% EtOAc/hexanes); mp 186–188 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.87 (d, $J = 3.6$ Hz, 1H), 7.82 (d, $J = 4.2$ Hz, 1H), 7.65 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.56 (d, $J = 2.0$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 7.25 (d, $J = 8.8$ Hz, 1H), 4.51 (s, 2H); ^{13}C NMR (Acetone- d_6 , 150 MHz) δ 186.4, 153.4, 152.0, 143.7, 143.3, 139.5, 136.5, 135.3, 135.0, 131.3, 129.6, 128.1, 120.4, 119.9, 38.8; IR ν_{max} (KBr) 3438, 2273, 1664, 1529, 1413, 1356, 1224, 1063, 928, 728 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_8\text{ClNO}_5\text{S}$ [M^+] 348.9812, found 348.9806.

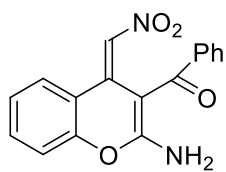
5l. 7,8,11,12-tetrahydro-6*H*,10*H*-pyrido[3,2,1-*ij*]3-nitro-4-(2'-oxo-2'-phenylethyl)-2*H*-chromen-2-one. Orange solid; yield 55%; $R_f = 0.55$ (50% EtOAc/hexanes); mp 212–214 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.66 (t, $J = 7.2$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 6.90 (s, 1H), 4.59 (s, 2H), 3.34 (t, $J = 5.2$ Hz, 4H), 2.90–2.89 (m, 2H), 2.71 (t, $J = 6.0$ Hz, 2H), 1.99–1.93 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz) δ 193.1, 154.7, 151.1, 148.8, 145.8, 135.9, 134.4, 134.1, 129.6, 129.1, 128.5, 124.2, 120.5, 106.5, 50.3, 49.9, 38.2, 29.8, 27.8, 20.3, 20.2; IR ν_{max} (KBr) 3224, 3148, 1726, 1683, 1518, 1285, 1210, 1174, 1082, 974 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_5$ [M^+] 404.1372, found 404.1381.



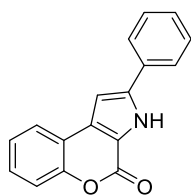
7l. White solid; yield 55%; $R_f = 0.48$ (30%) EtOAc/hexanes); mp 154–156 °C (lit. 120–122 °C); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.90 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.34 (dd, $J = 2.4, 6.0$ Hz, 2H), 7.22–7.20 (m, 3H), 4.62 (s, 1H), 3.92 (ABq, $J = 11.2$ Hz, 1H each).



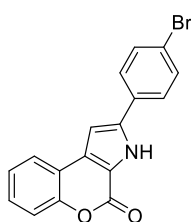
13. (*Z*)-(2-amino-4-(nitromethylene)-4*H*-chromen-3-yl)(phenyl)methanone. Orange solid; yield; 70%; $R_f = 0.45$ (30% EtOAc/hexanes); mp 178–180 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.69 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.61–7.56 (m, 3H), 7.43–7.38 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 7.2$ Hz, 1H), 7.16 (s, 1H); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$, 150 MHz) δ 191.8, 162.1, 149.2, 139.2, 139.1, 132.3, 131.2, 128.0, 127.8, 125.9, 124.2, 120.9, 119.2, 116.9, 88.2.; IR ν_{max} (KBr) 3438, 2273, 1664, 1529, 1413, 1356, 1224, 1063, 928, 728 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_4$ [M^+] 308.0797, found 308.0804.



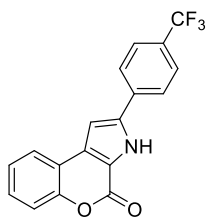
18a^{2,3}. 2-phenylchromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 96%; $R_f = 0.42$ (20% EtOAc/hexanes); mp 182–184 °C; $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 400 MHz) δ 12.94 (s, 1H), 7.97 (d, $J = 7.6$ Hz, 3H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.40–7.34 (m, 5H).



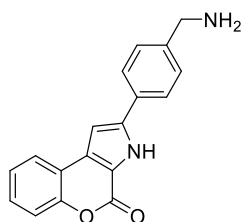
18b. 2-(4-bromophenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 88%; $R_f = 0.40$ (20% EtOAc/hexanes); mp 220–224 °C; $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 400 MHz) δ 13.05 (s, 1H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.44 (s, 1H), 7.39–7.37 (m, 1H); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$, 150 MHz) δ 155.2, 151.5, 142.2, 137.9, 132.8, 130.1, 129.2, 128.5, 125.5, 124.3, 122.8, 120.3, 117.9, 117.5, 102.0; IR ν_{max} (KBr) 3240, 3093, 2807, 1738, 1433, 1288, 1179, 1113, 816, 729 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{BrNO}_2$ [M^+] 338.9895, found 338.9893.



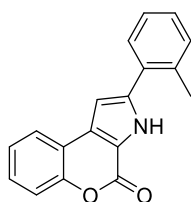
18c. 2-(4-(trifluoromethyl)phenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 95%; $R_f = 0.43$ (40% EtOAc/hexanes); mp 212–214 °C; $^1\text{H NMR}$ (DMSO-*d*₆, 400 MHz) δ 13.22 (s, 1H), 8.22–8.18 (m, 2H), 8.00–7.97 (m, 1H), 7.87–7.82 (m, 2H), 7.60–7.57 (m, 1H), 7.46–7.38 (m, 3H); $^{13}\text{C NMR}$ (DMSO-*d*₆, 150 MHz) δ 154.2, 151.0, 140.5, 134.5, 130.0, 128.6 (q, $^2J_{\text{CF}} = 33.0$ Hz) 128.4, 126.5, 126.0 (d, $^3J_{\text{CF}} = 3.0$ Hz), 124.8 (q, $^1J_{\text{CF}} = 189.0$ Hz), 124.6, 123.7, 123.4, 118.2, 117.5, 117.0; IR ν_{max} (KBr) 3463, 2979, 1738, 1673, 1538, 1375, 1219, 1040, 882, 760 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{10}\text{F}_3\text{NO}_2$ [M^+] 329.0664, found 329.0659.



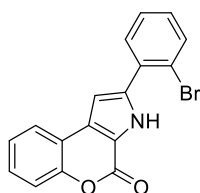
18d. 2-(4-(aminomethyl)phenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 90%; $R_f = 0.38$ (50% EtOAc/hexanes); mp 200–202 °C; $^1\text{H NMR}$ (DMSO-*d*₆, 400 MHz) δ 12.94 (s, 1H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.43–7.41 (m, 6H), 7.39–7.35 (m, 1H), 5.26 (t, $J = 7.6$ Hz, 1H), 4.55 (d, $J = 5.2$ Hz, 2H); $^{13}\text{C NMR}$ (DMSO-*d*₆, 150 MHz) δ 155.0, 151.5, 143.5, 143.4, 130.9, 129.6, 129.0, 127.9, 126.4, 125.3, 124.3, 118.0, 117.8, 117.47, 117.45, 101.3, 63.3; IR ν_{max} (KBr) 3213, 3147, 1699, 1483, 1286, 1114, 1084, 976, 745, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ [M^+] 290.1055, found 290.200.



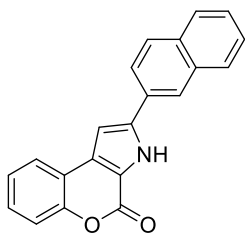
18e.² 2-(2-tolyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. Grey solid; yield 95%; $R_f = 0.42$ (20% EtOAc/hexanes); mp 164–166 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.57 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.49–7.39 (m, 3H), 7.35–7.31 (m, 4H), 6.82 (s, 1H), 2.52 (s, 3H).



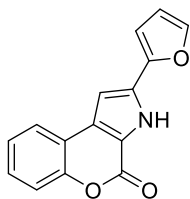
18f. 2-(2-bromophenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 92%; $R_f = 0.45$ (30% EtOAc/hexanes); mp 142–144 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.95 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.46–7.40 (m, 3H), 7.35–7.28 (m, 2H), 7.03 (d, $J = 2.4$ Hz, 1H); $^{13}\text{C NMR}$ (DMSO-*d*₆, 150 MHz) δ 155.1, 151.4, 141.9, 134.1, 132.7, 132.4, 131.5, 129.9, 129.0, 128.7, 125.4, 124.3, 122.4, 117.9, 117.4, 117.1, 104.9; IR ν_{max} (KBr) 3226, 3116, 1699, 1569, 1483, 1284, 1174, 1083, 975, 738.3 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{BrNO}_2$ [M^+] 338.9895, found 338.9897.



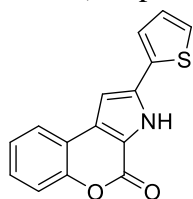
18g. 2-(naphthalen-2-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. Off yellow solid; yield 81%; $R_f=0.42$ (30% EtOAc/hexanes); mp 200–202 °C; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ 13.13 (s, 1H), 8.62 (s, 1H), 8.13 (d, $J = 7.6$ Hz, 1H), 8.03 (d, $J = 7.6$ Hz, 2H), 7.95 (d, $J = 6.4$ Hz, 2H), 7.59 (brs, 3H), 7.45–7.40 (m, 3H); $^{13}\text{C NMR}$ (DMSO- d_6 , 150 MHz) δ 154.0, 150.9, 142.2, 133.0, 132.7, 129.9, 128.5, 128.2, 128.04, 127.96, 127.7, 126.9, 126.7, 124.6, 124.4, 123.8, 123.5, 117.5, 117.4, 116.8, 101.5; IR ν_{max} (KBr) 3275, 3052, 2882, 1703, 1605, 1499, 1272, 1180, 796 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{13}\text{NO}_2$ [M^+] 311.0946, found 311.0938.



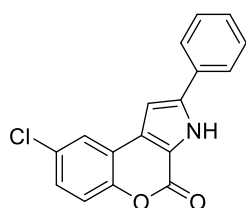
18h. 2-(furan-2-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 88%; $R_f = 0.37$ (20% EtOAc/hexanes); mp 176–178 °C; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ 13.06 (s, 1H), 8.03 (d, $J = 7.2$ Hz, 1H), 7.84 (s, 1H), 7.43–7.35 (m, 3H), 7.17 (d, $J = 12.0$ Hz, 2H), 6.67 (s, 1H); $^{13}\text{C NMR}$ (DMSO- d_6 , 150 MHz) δ 154.0, 150.9, 146.1, 143.7, 133.5, 129.7, 128.1, 124.3, 123.7, 117.4, 116.7, 112.1, 108.1, 99.6; IR ν_{max} (KBr) 309, 3146, 1698, 1508, 1286, 1113, 1080, 977, 803, 740 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_3$ [M^+] 251.0582, found 251.0586.



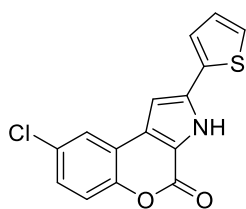
18i. 2-(thiophen-2-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 91%; $R_f = 0.43$ (30% EtOAc/hexanes); mp 182–184 °C; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ 13.09 (s, 1H), 8.03 (d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 3.2$ Hz, 1H), 7.65 (d, $J = 4.8$ Hz, 1H), 7.47–7.42 (m, 2H), 7.38–7.35 (m, 1H), 7.19–7.17 (m, 2H); $^{13}\text{C NMR}$ (DMSO- d_6 , 150 MHz) δ 153.8, 150.9, 136.6, 133.4, 129.9, 128.3, 128.0, 126.9, 125.6, 124.3, 123.7, 117.3, 116.7, 100.9; IR ν_{max} (KBr) 3225, 3116, 1695, 1482, 1282, 1174, 1082, 973, 735 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_2\text{S}$ [M^+] 267.0354, found 267.0348.



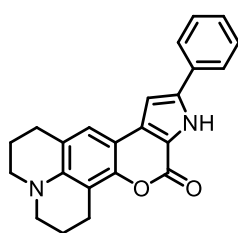
18j. 8-chloro-2-phenylchromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 94%; $R_f = 0.43$ (30% EtOAc/hexanes); mp 182–184 °C; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ 13.09 (s, 1H), 8.12 (d, $J = 7.6$ Hz, 1H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.51–7.46 (m, 5H), 7.41 (d, $J = 7.2$ Hz, 1H); $^{13}\text{C NMR}$ (DMSO- d_6 , 150 MHz) δ 153.5, 149.5, 142.4, 130.4, 129.0, 128.8, 128.7, 128.3, 127.6, 125.8, 122.9, 119.1, 118.6, 117.3, 101.4; IR ν_{max} (KBr) 3248, 3109, 1738, 1672, 1537, 1375, 1218, 1040, 760, 691 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{10}\text{ClNO}_2$ [M^+] 295.0400, found 295.0392.



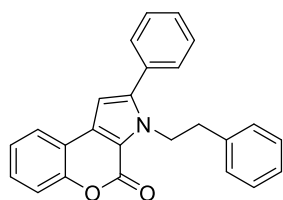
18k. 8-chloro-2-(thiophen-2-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one. Light yellow; yield 86%; $R_f = 0.35$ (40% EtOAc/hexanes); mp 230–232 °C; $^1\text{H NMR}$ (Acetone- d_6 , 400 MHz), δ 12.08 (bs, 1H), 8.05 (s, 1H), 7.75–7.73 (m, 1H), 7.55 (d, $J = 4.0$ Hz, 1H), 7.43–7.38 (m, 2H), 7.43–7.38 (m, 2H); $^{13}\text{C NMR}$ (Acetone- d_6 , 150 MHz) δ 154.2, 151.0, 137.7, 134.3, 130.0, 129.8, 129.1, 128.6, 127.5, 126.3, 123.9, 120.2, 119.4, 118.3, 101.9; IR ν_{max} (KBr) 3275, 3052, 1703, 1605, 1272, 1180, 1088, 1033, 898, 797 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_8\text{ClNO}_2\text{S}$ [M^+] 300.9964, found 300.9961.



18l. 7,8,11,12-tetrahydro-6*H*,10*H*-pyrido[3,2,1-*ij*]-2'-phenylchromeno[3',4'-*b*]pyrrol-4'(3'*H*)-one. Grey solid; yield 95%; $R_f = 0.43$ (30% EtOAc/hexanes); mp 200–202 °C; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ 12.57 (s, 1H), 7.95 (d, $J = 7.6$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.33 (s, $J = 8.0$ Hz, 1H), 7.16 (s, 1H), 3.17 (d, $J = 4.4$ Hz, 4H), 2.79 (d, $J = 4.4$ Hz, 4H), 1.92–1.92 (brs, 4H); $^{13}\text{C NMR}$ (Acetone- d_6 , 150 MHz) δ 156.3, 150.4, 144.8, 143.6, 133.7, 132.9, 130.6, 130.0, 127.2, 122.1, 119.9, 117.5, 109.5, 107.7, 100.8, 51.3, 50.9, 29.0, 23.4, 22.7, 22.6; IR ν_{max} (KBr) 3062, 2882, 2826, 1614, 1525, 1368, 1307, 1151, 953, 761 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2$ [M^+] 356.1525, found 356.1528.



20. 3-phenethyl-2-phenylchromeno[3,4-*b*]pyrrol-4(3*H*)-one. White solid; yield 86%; $R_f = 0.45$ (10% EtOAc/hexanes); mp 142–144 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.44–7.41 (m, 4H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.25–7.22 (m, 2H), 7.16–7.15 (m, 3H), 6.93 (d, $J = 2.8$ Hz, 2H), 6.62 (s, 1H), 4.65 (t, $J = 7.6$ Hz, 2H), 3.01 (t, $J = 7.6$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz) δ 155.2, 151.5, 145.9, 137.9, 131.2, 130.4, 129.5, 129.02, 128.99, 128.7, 128.5, 128.0, 126.6, 124.2, 123.1, 117.9, 117.2, 116.5, 102.9, 47.6, 38.2; IR ν_{max} (KBr) 3065, 1703, 1467, 1427, 1199, 1037, 1018, 954, 759, 695 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{19}\text{NO}_2$ [M^+] 365.1416, found 365.1418.



3. References

1. P. R. Huddleston and J. M. Barker, *Synth. Commun.* 1979, **9**, 171–178.
2. L. Chen and M. -H. Xu, *Adv. Synth. Catal.* 2009, **351**, 2005–2012.

4.1 X-ray crystallographic analysis of 5a

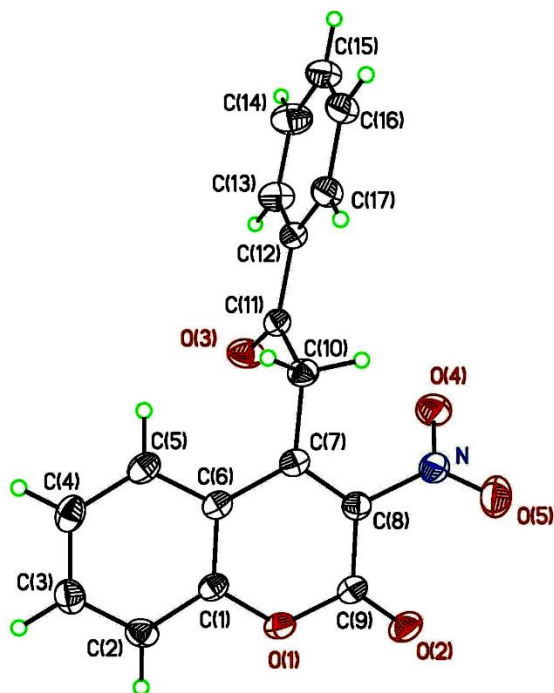


Figure S1: ORTEP diagram of compound **5a**. The ellipsoid contour probability levels: 50%.

Table S1. Crystal data and structure refinement for **5a**

Identification code	BSK020_1	
Empirical formula	C ₁₇ H ₁₁ N O ₅	
Formula weight	309.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 14.3346(9) Å	a = 90°.
	b = 12.1876(8) Å	b = 92.995(3)°.
	c = 7.9189(5) Å	g = 90°.
Volume	1381.58(15) Å ³	
Z	4	
Density (calculated)	1.487 Mg/m ³	
Absorption coefficient	0.111 mm ⁻¹	
F(000)	640	
Crystal size	0.480 x 0.290 x 0.070 mm ³	
Theta range for data collection	3.071 to 27.971°.	
Index ranges	-18 ≤ h ≤ 18, -15 ≤ k ≤ 16, -9 ≤ l ≤ 10	
Reflections collected	21696	
Independent reflections	3314 [R(int) = 0.0380]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6299	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3314 / 0 / 208	

Goodness-of-fit on F^2	1.071
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0452, wR2 = 0.1229
R indices (all data)	R1 = 0.0605, wR2 = 0.1353
Extinction coefficient	n/a
Largest diff. peak and hole	0.268 and -0.199 e. \AA^{-3}

4.2 X-ray crystallographic analysis of 7

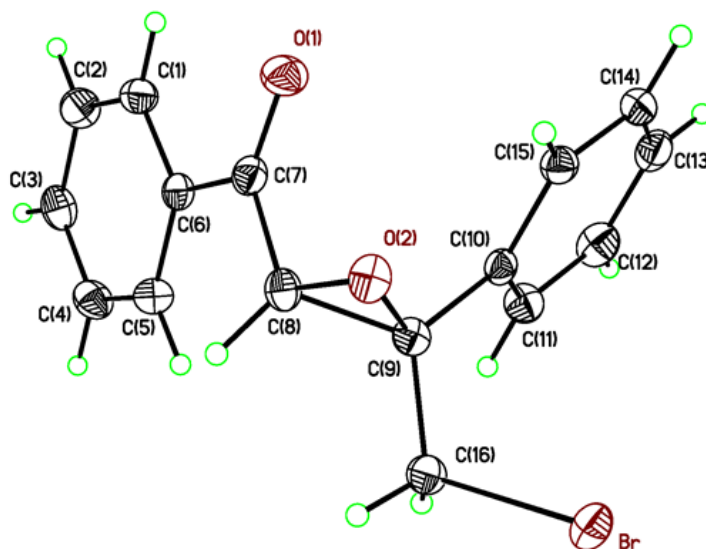


Figure S2: ORTEP diagram of compound **7**. The ellipsoid contour probability levels: 50%.

Table S2. Crystal data and structure refinement for **7**

Identification code	BSK061	
Empirical formula	C ₁₆ H ₁₃ Br O ₂	
Formula weight	317.17	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 10.1139(5) Å	a = 90°.
	b = 11.6747(7) Å	b = 108.9428(18)°.
	c = 11.8454(6) Å	g = 90°.
Volume	1322.92(12) Å ³	
Z	4	
Density (calculated)	1.592 Mg/m ³	
Absorption coefficient	3.101 mm ⁻¹	
F(000)	640	
Crystal size	0.400 x 0.330 x 0.220 mm ³	
Theta range for data collection	2.893 to 27.889°.	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	
Reflections collected	35462	
Independent reflections	3156 [R(int) = 0.0389]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7456 and 0.5911
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3156 / 0 / 172
Goodness-of-fit on F ²	0.942
Final R indices [I>2sigma(I)]	R1 = 0.0193, wR2 = 0.0506
R indices (all data)	R1 = 0.0227, wR2 = 0.0527
Extinction coefficient	n/a
Largest diff. peak and hole	0.322 and -0.444 e.Å ⁻³

4.3 X-ray crystallographic analysis of 13

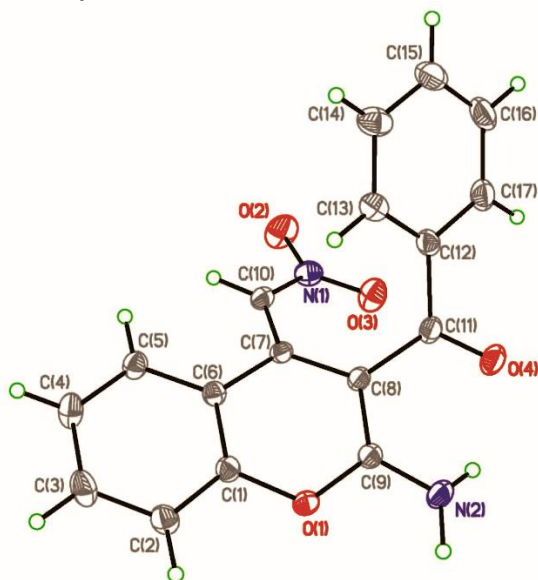


Figure S3: ORTEP diagram of compound **13**. The ellipsoid contour probability levels: 50%.

Table S3. Crystal data and structure refinement for **13**

Identification code	wc367	
Empirical formula	C ₁₇ H ₁₂ N ₂ O ₄	
Formula weight	308.29	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9701(6) Å	a = 95.001(2)°.
	b = 13.2908(8) Å	b = 105.659(2)°.
	c = 15.0201(8) Å	g = 110.163(2)°.
Volume	1762.88(18) Å ³	
Z	4	
Density (calculated)	1.162 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	640	
Crystal size	0.57 x 0.48 x 0.37 mm ³	
Theta range for data collection	3.05 to 26.44°.	
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -18 ≤ l ≤ 17	
Reflections collected	29560	
Independent reflections	7212 [R(int) = 0.0340]	
Completeness to theta = 26.44°	99.3 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9694 and 0.9534
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7212 / 0 / 419
Goodness-of-fit on F ²	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0869, wR2 = 0.2620
R indices (all data)	R1 = 0.1087, wR2 = 0.2894
Largest diff. peak and hole	0.467 and -0.457 e.Å ⁻³

4.4 X-ray crystallographic analysis of 18a

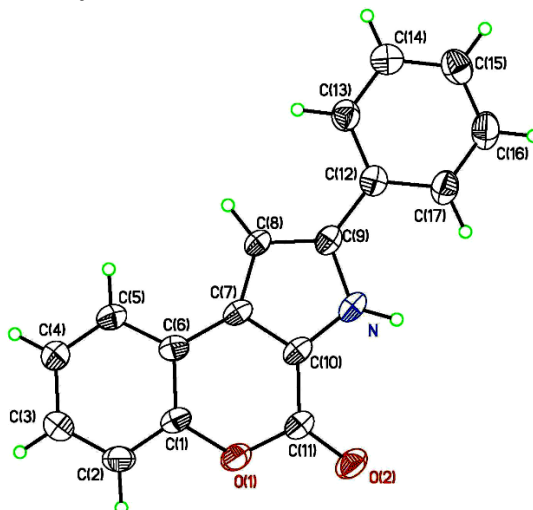


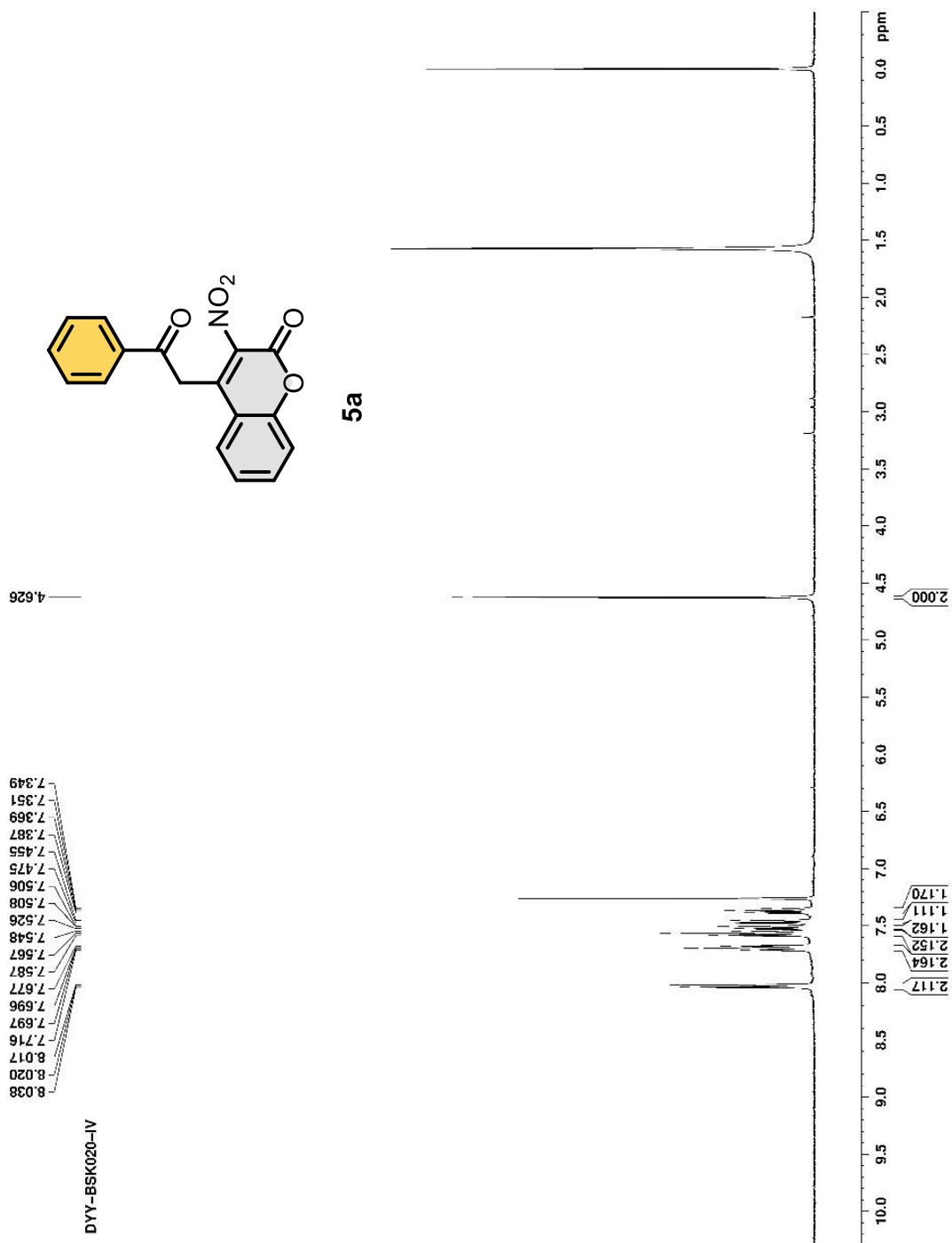
Figure S4: ORTEP diagram of compound **18a**. The ellipsoid contour probability levels: 50%.

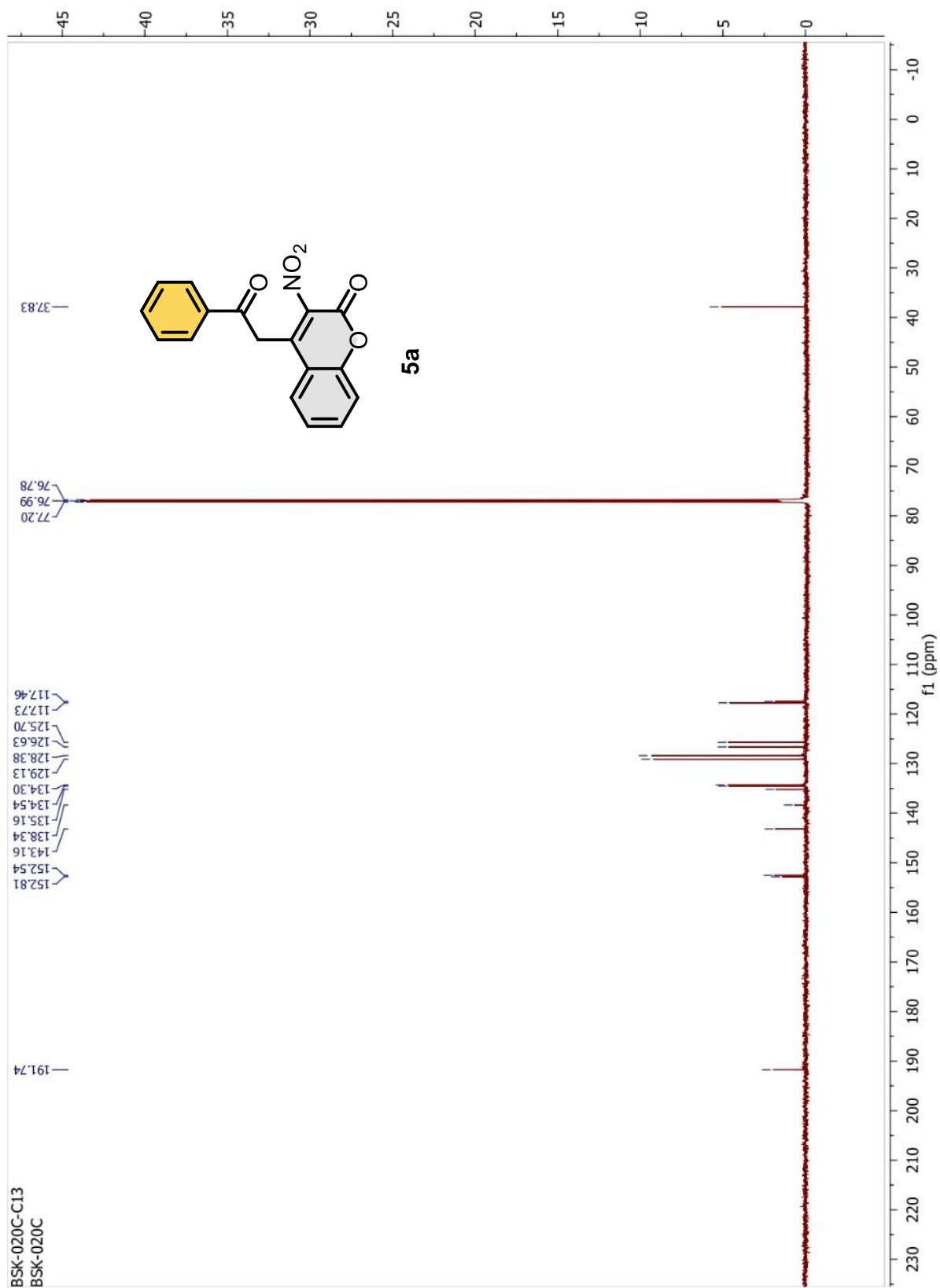
Table S4. Crystal data and structure refinement for **18a**.

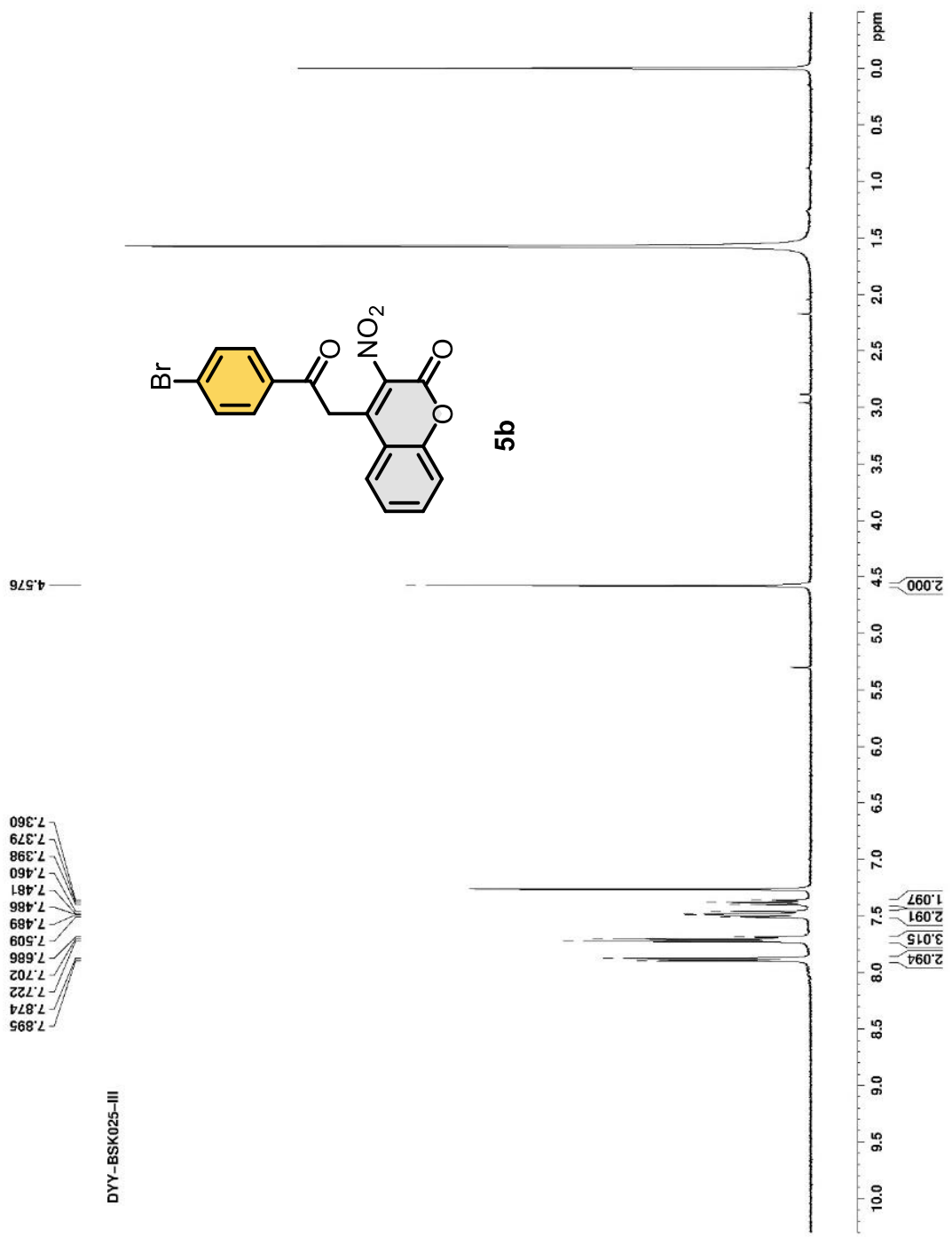
Identification code	BSK054	
Empirical formula	C ₁₇ H ₁₁ N O ₂	
Formula weight	261.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 13.1240(5) Å	a = 90°.
	b = 7.1357(3) Å	b = 97.3102(15)°.
	c = 13.3340(6) Å	g = 90°.
Volume	1238.56(9) Å ³	
Z	4	
Density (calculated)	1.401 Mg/m ³	
Absorption coefficient	0.093 mm ⁻¹	
F(000)	544	
Crystal size	0.380 x 0.260 x 0.070 mm ³	
Theta range for data collection	3.130 to 27.906°.	
Index ranges	-16 ≤ h ≤ 17, -9 ≤ k ≤ 9, -17 ≤ l ≤ 17	
Reflections collected	43722	
Independent reflections	2969 [R(int) = 0.0803]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7047	

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2969 / 0 / 182
Goodness-of-fit on F ²	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1403
R indices (all data)	R1 = 0.0763, wR2 = 0.1576
Extinction coefficient	n/a
Largest diff. peak and hole	0.619 and -0.247 e.Å ⁻³

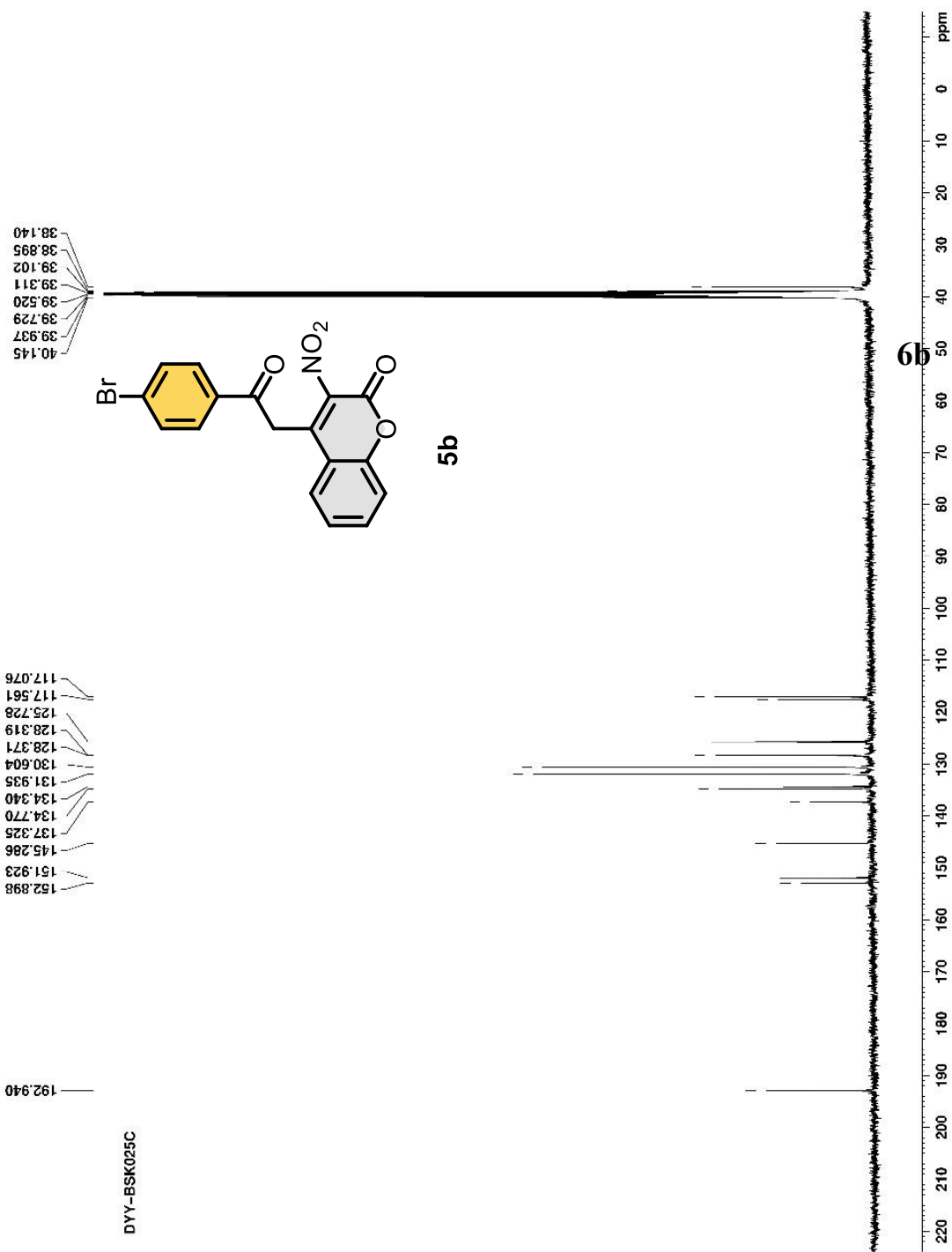
5. Copies of ^1H and ^{13}C NMR spectra of synthesized compounds

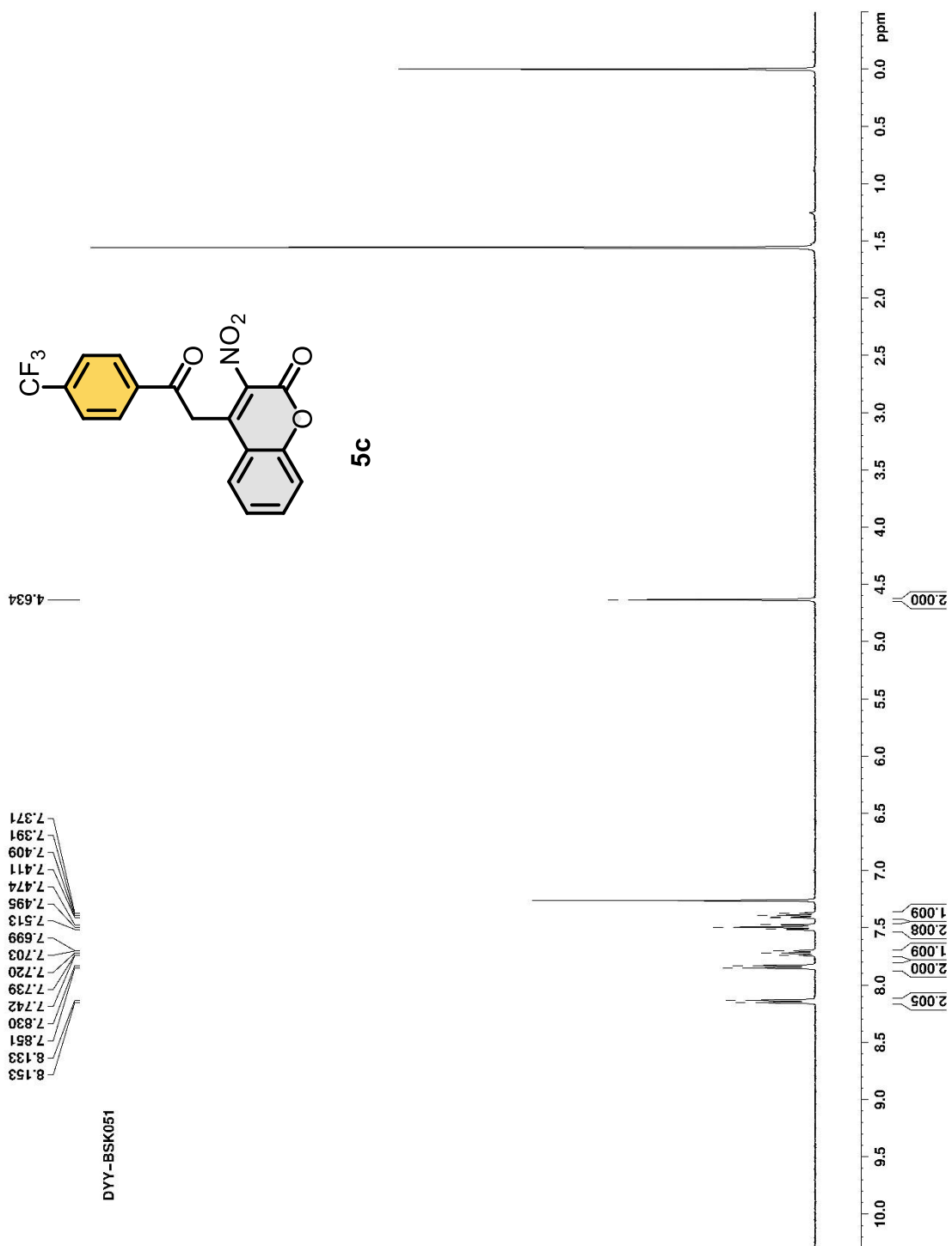


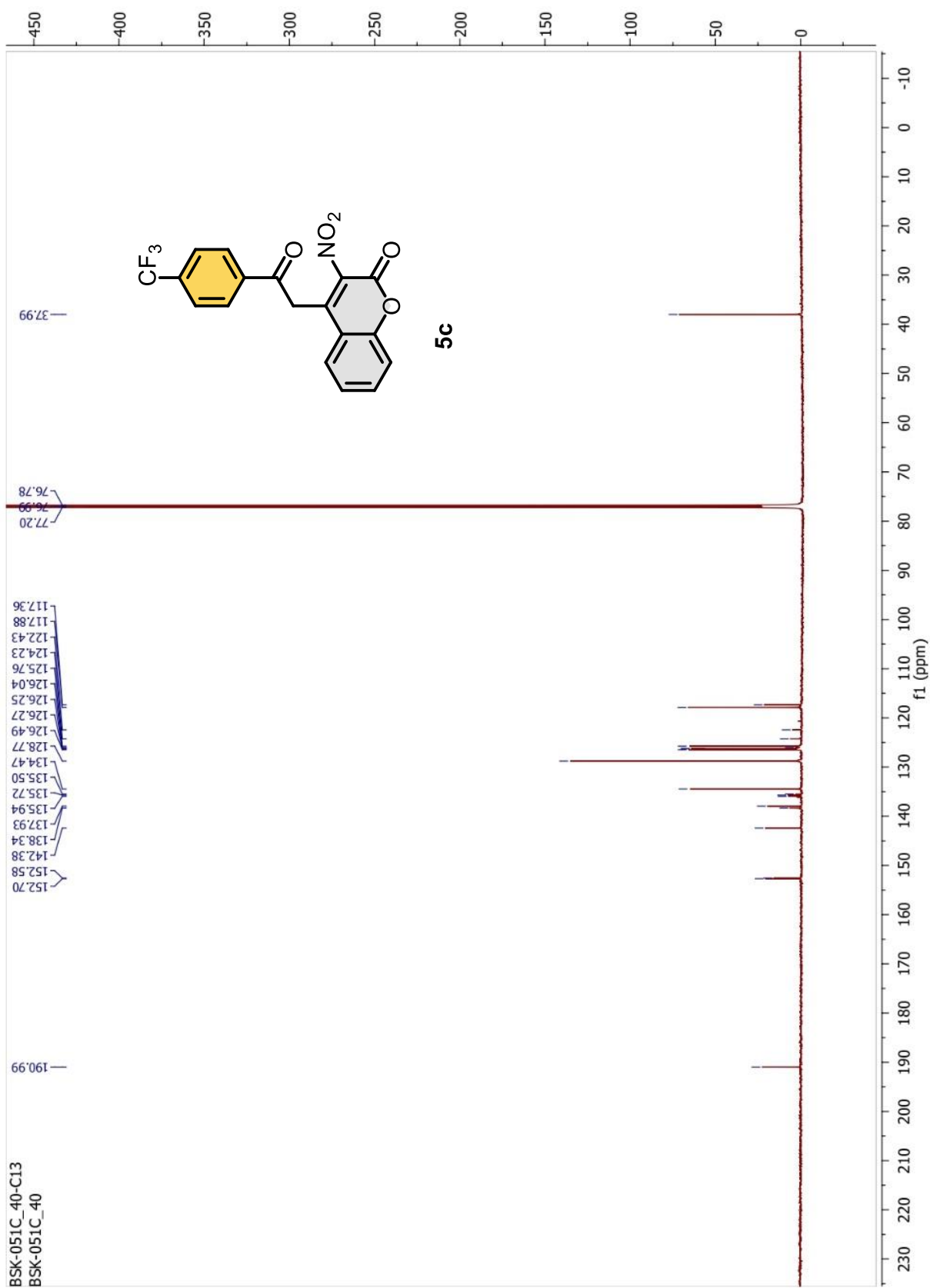


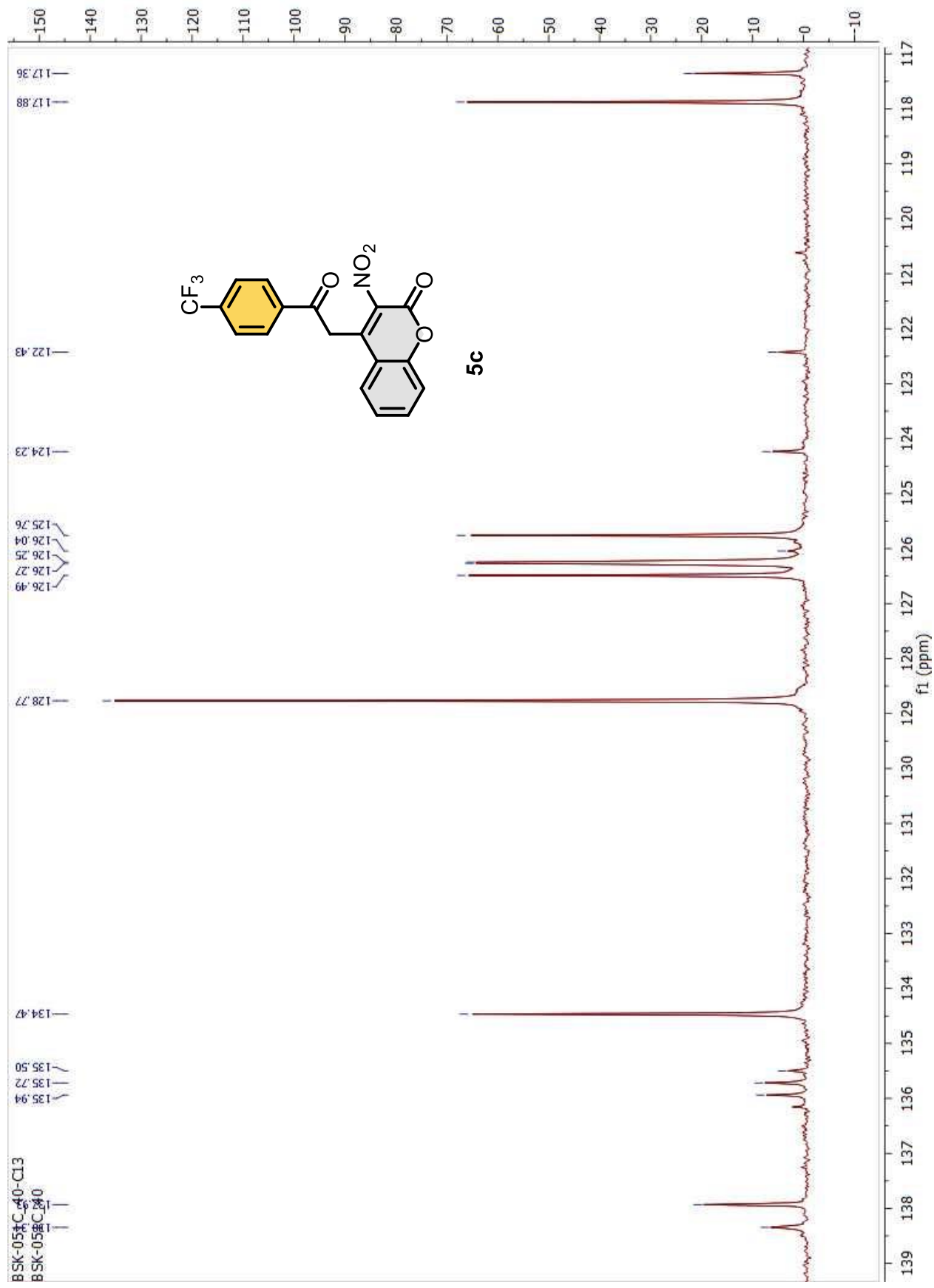


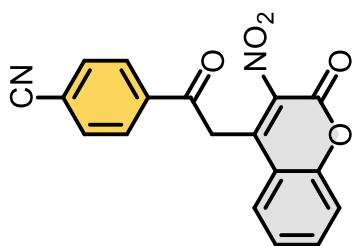
DYY-BSK025-III









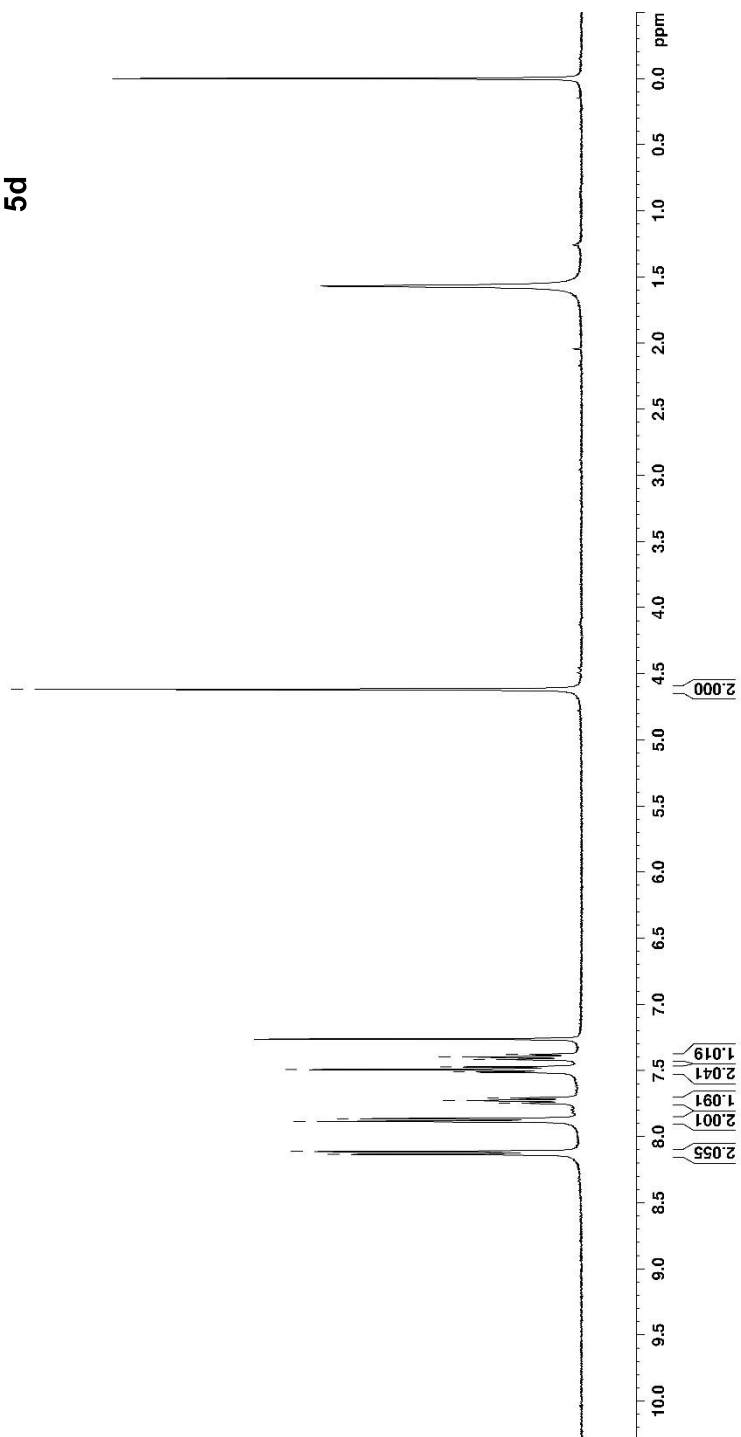


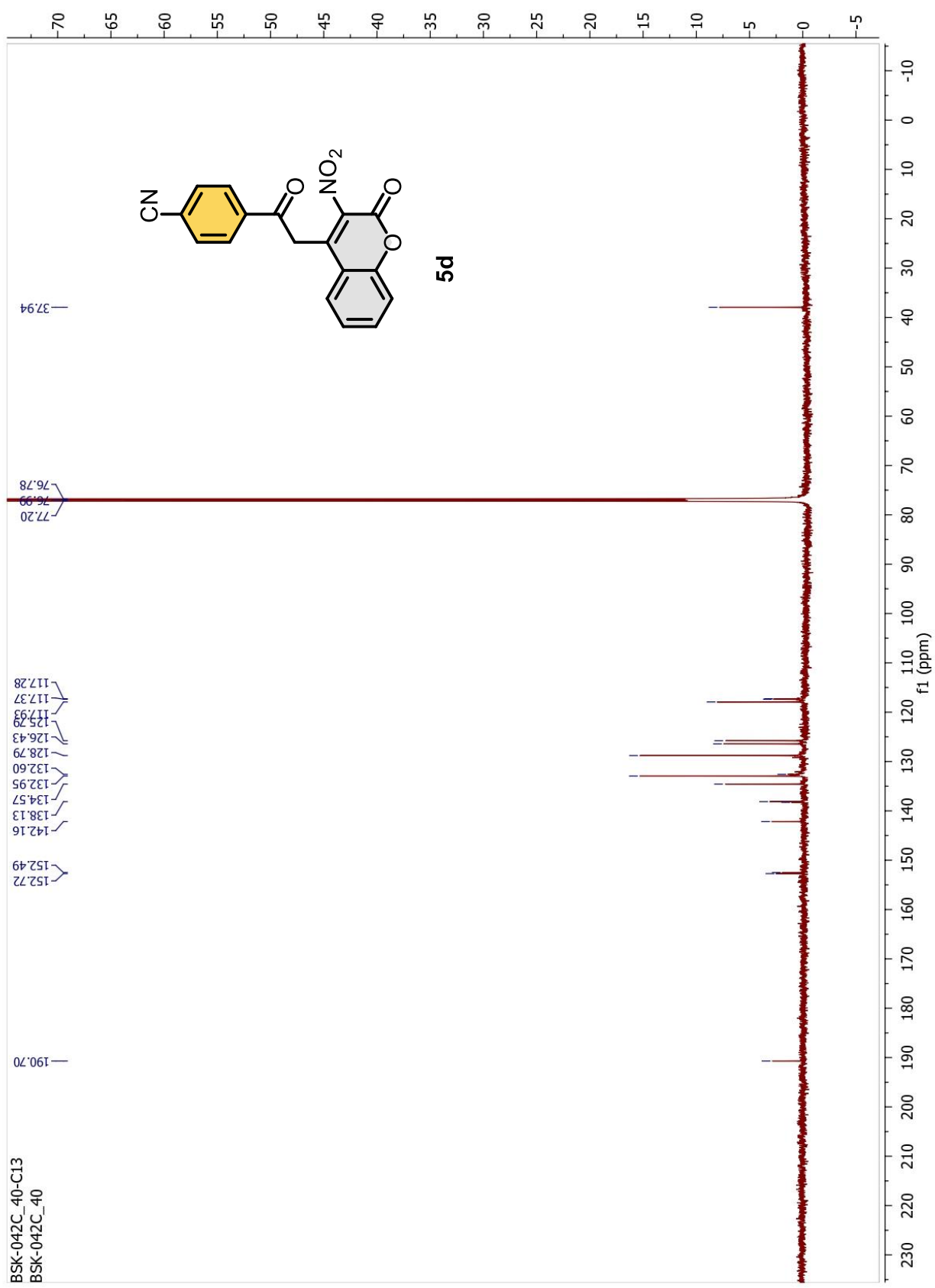
5d

4.619

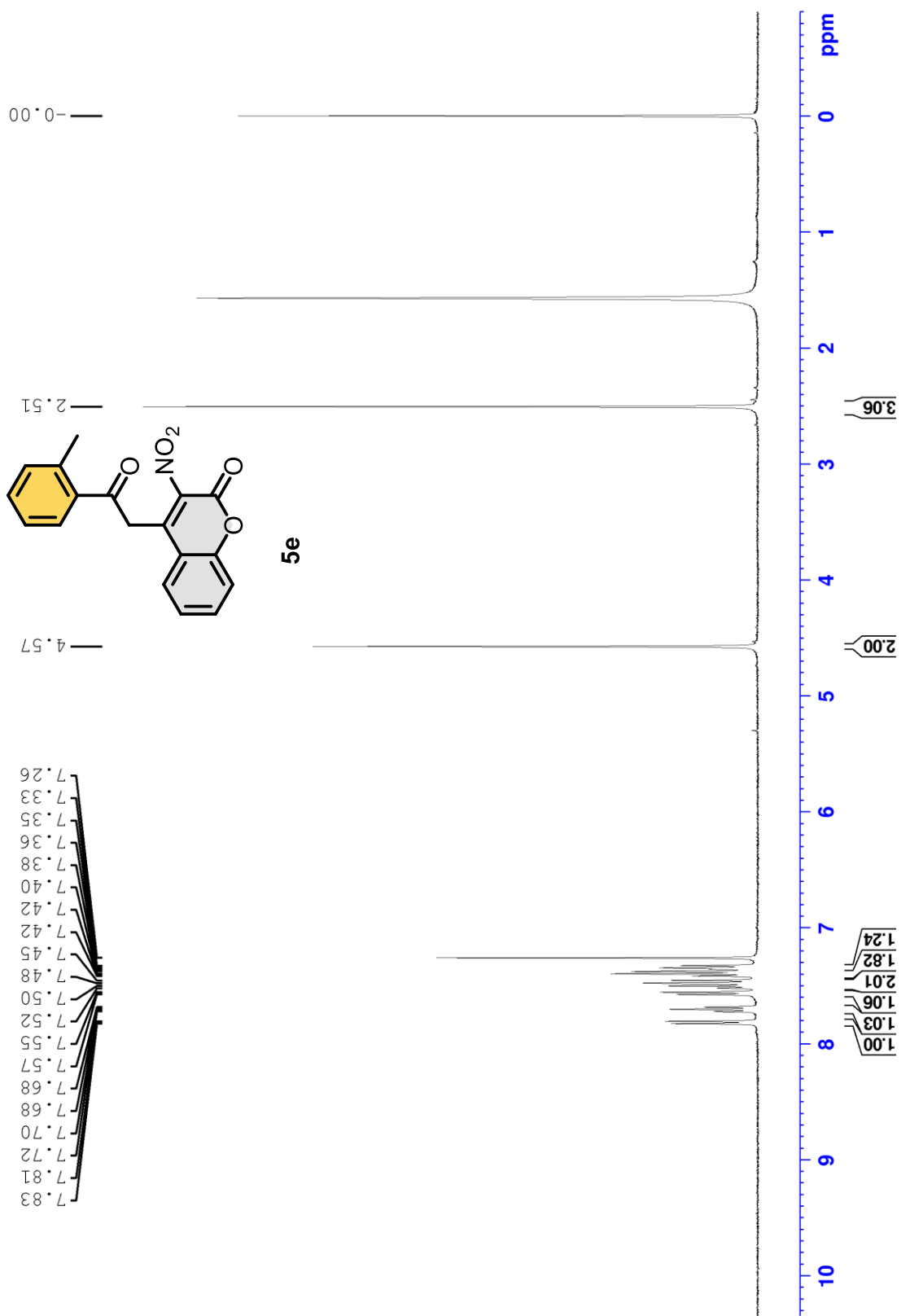
8.134
8.114
7.885
7.865
7.747
7.728
7.708
7.512
7.494
7.474
7.418
7.398
7.379

DYY-BSK042-IV

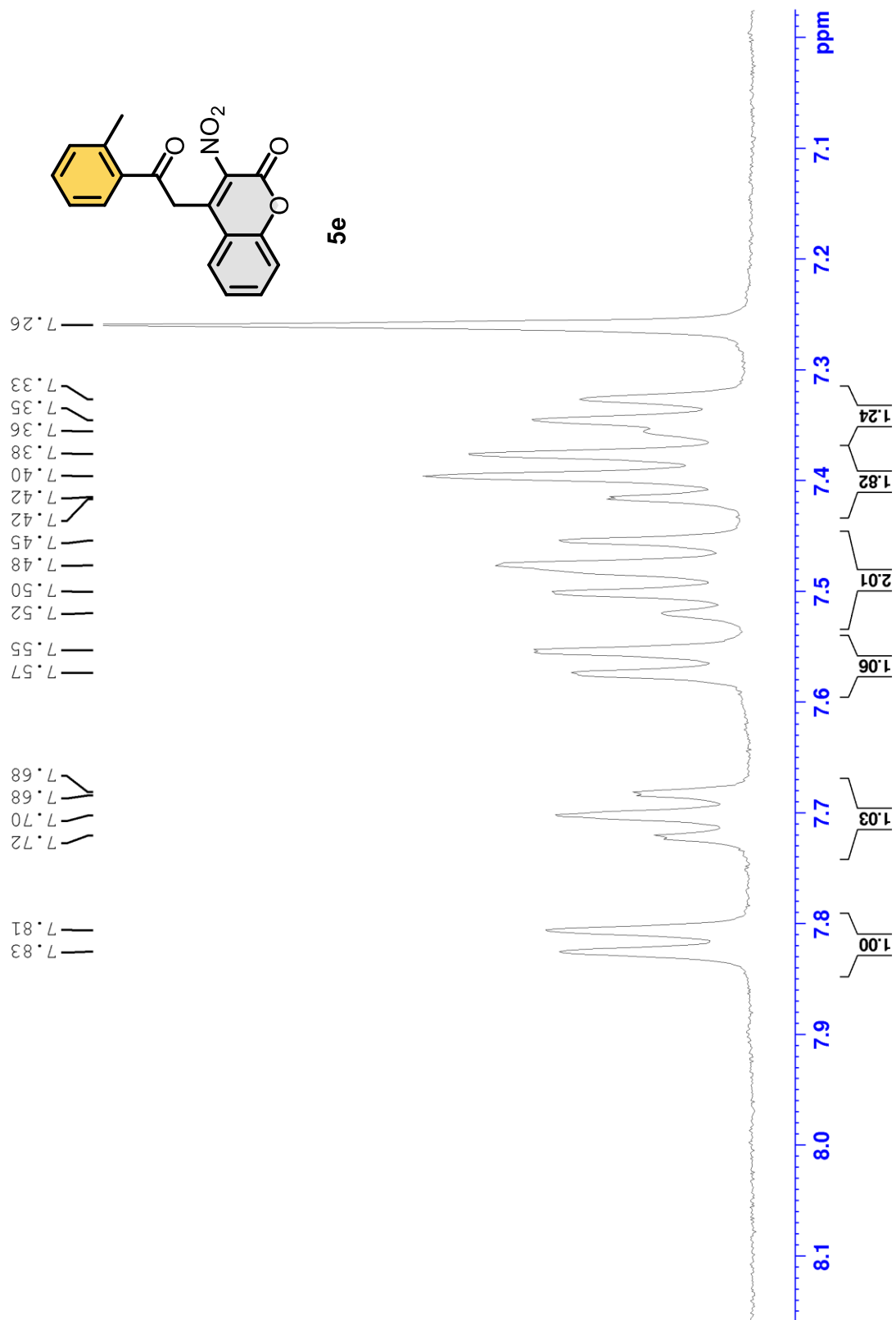


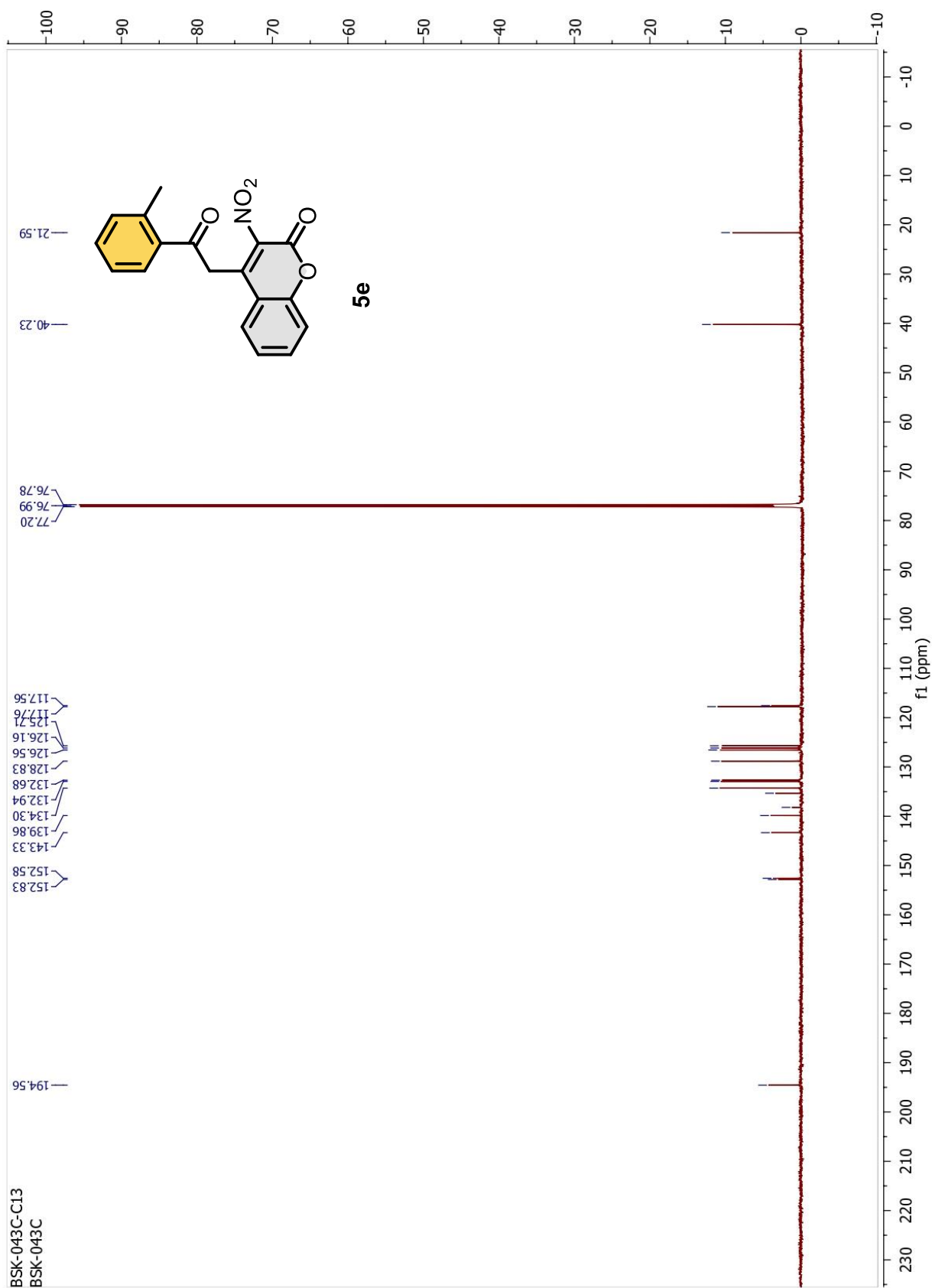


DYY-BSK043

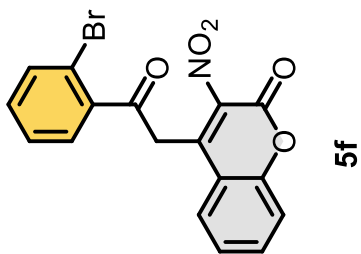


DYY-BSK043



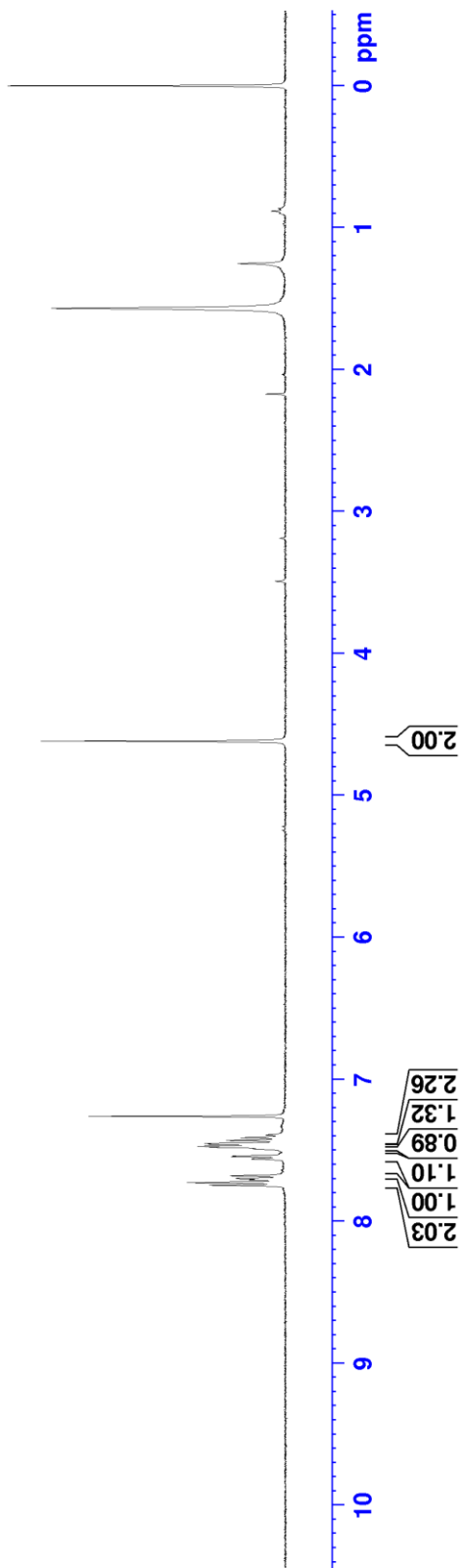


DYY-BSK050

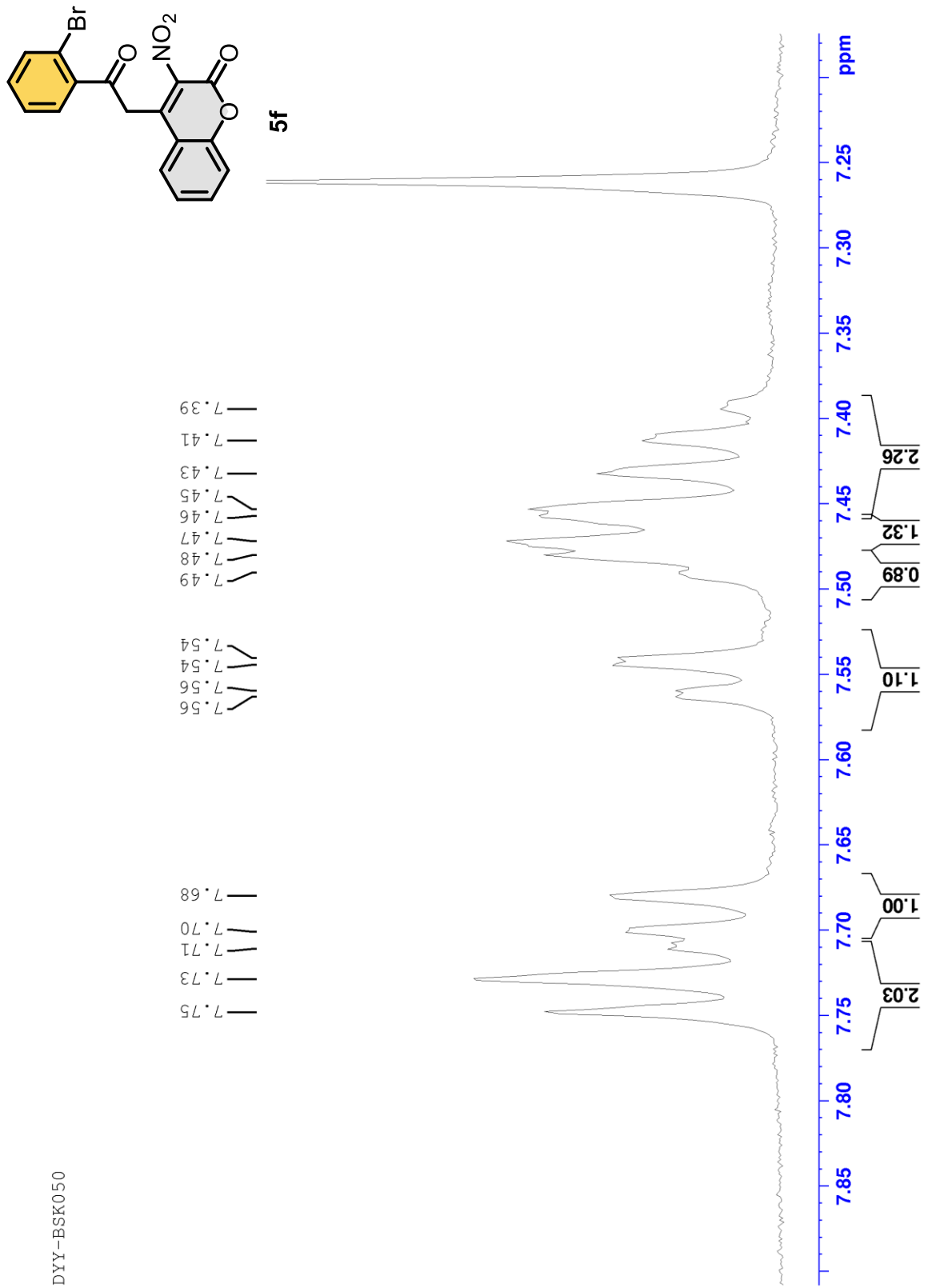


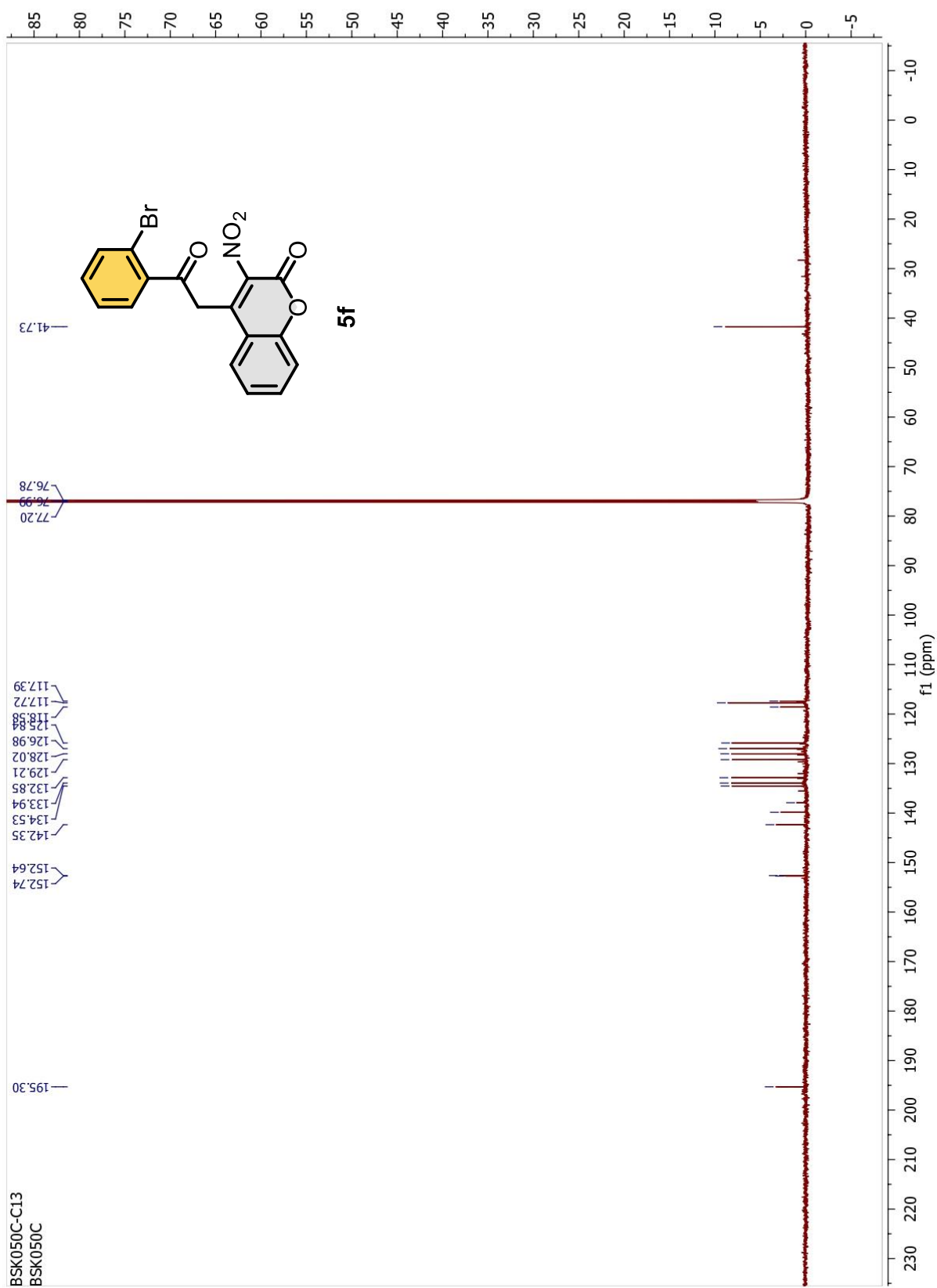
4.62

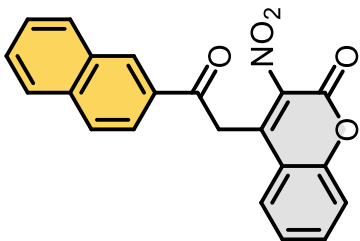
7.39
7.41
7.43
7.45
7.46
7.47
7.48
7.49
7.54
7.54
7.56
7.56
7.68
7.70
7.71
7.73
7.75



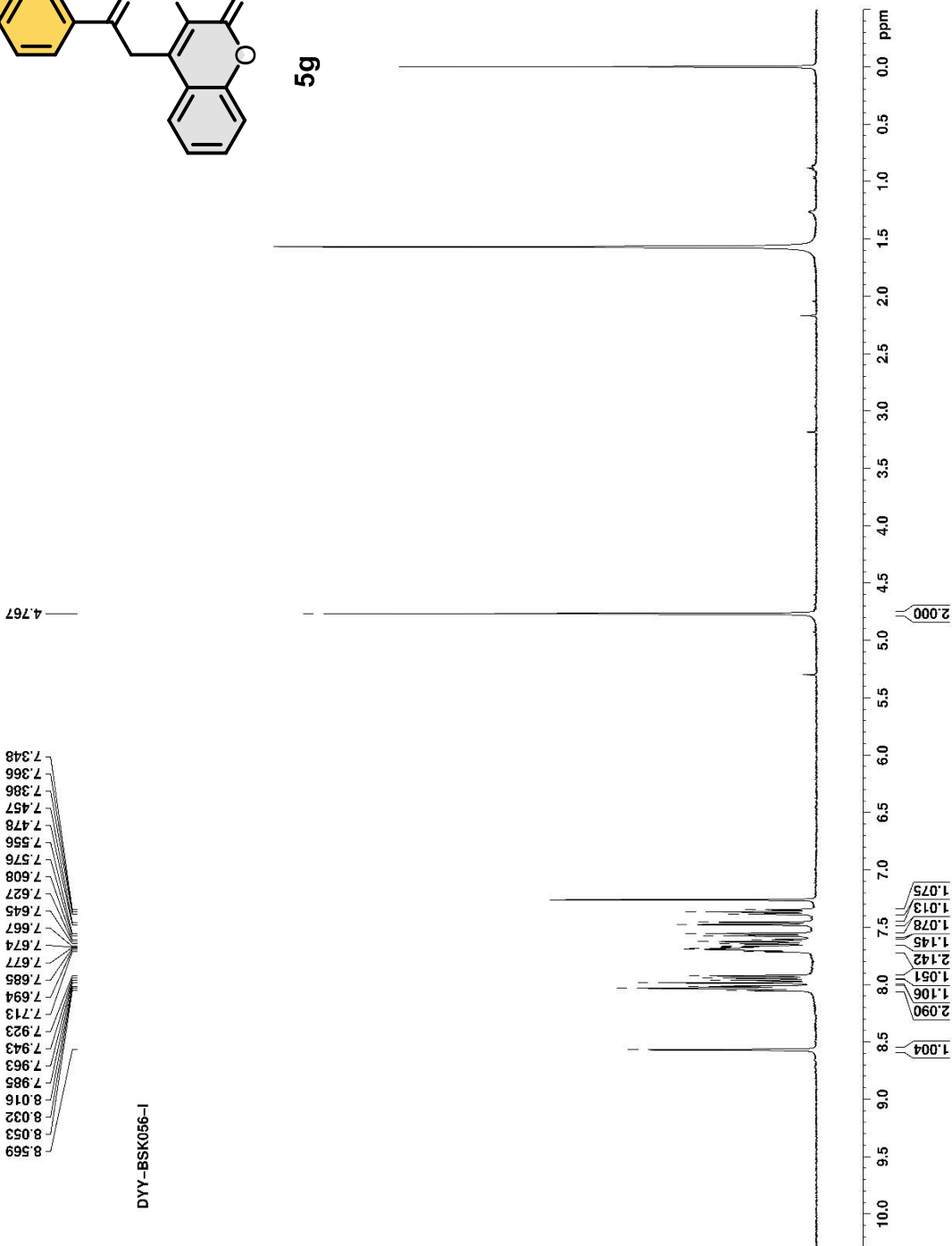
DYY-BSK050



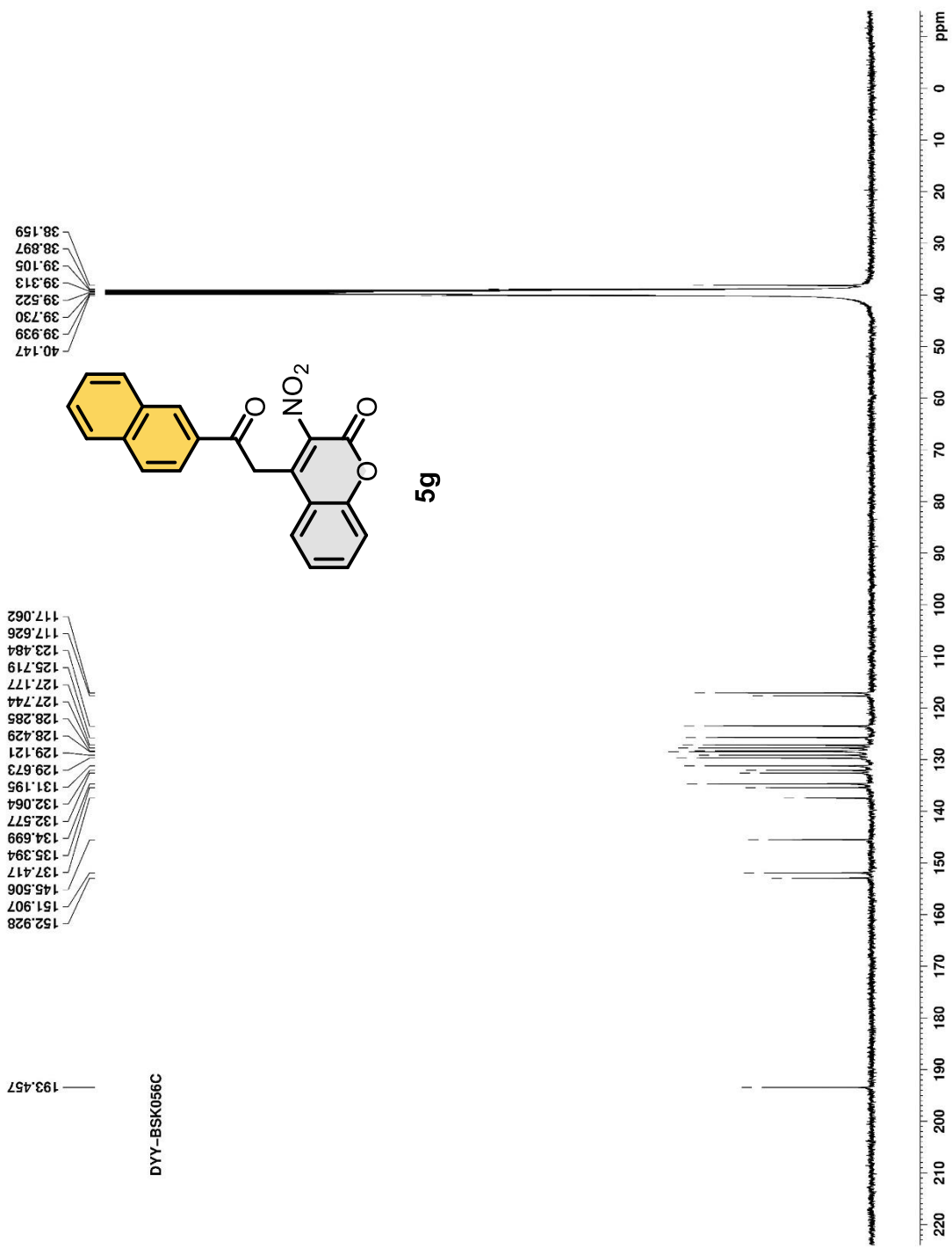


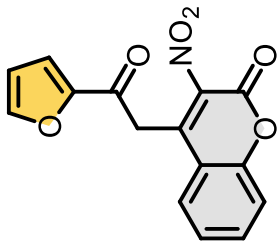


5g

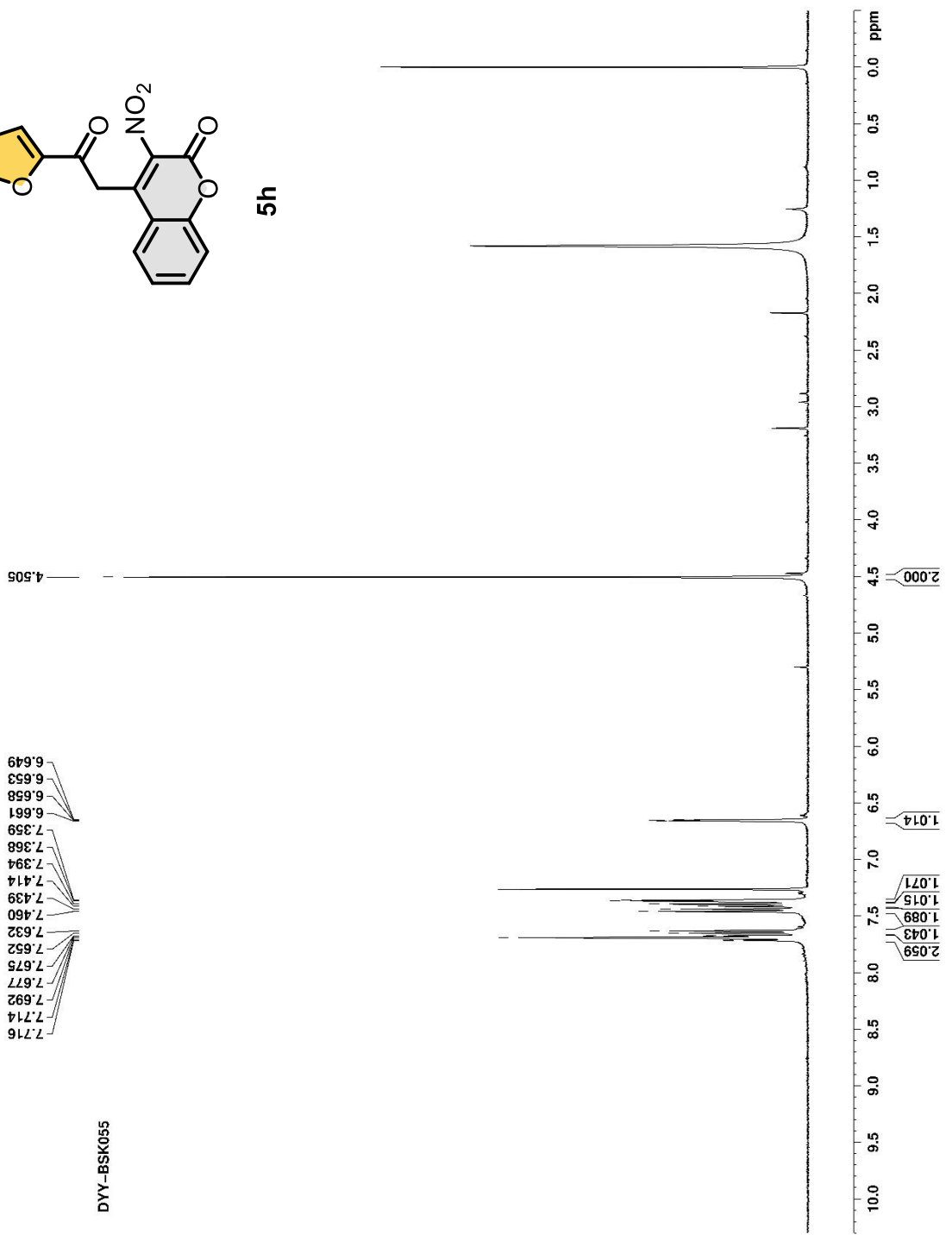


DYY-BSK056-I

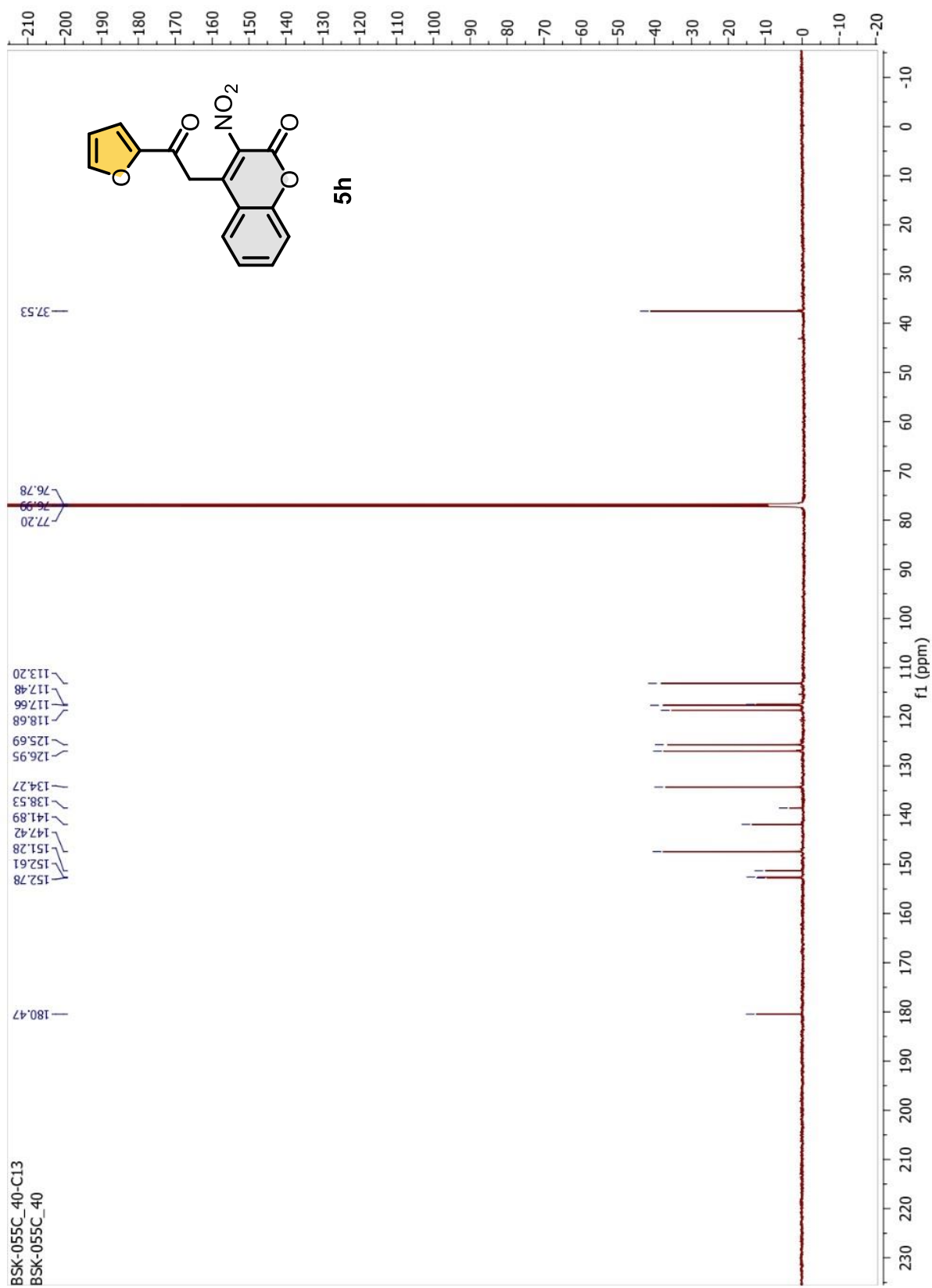


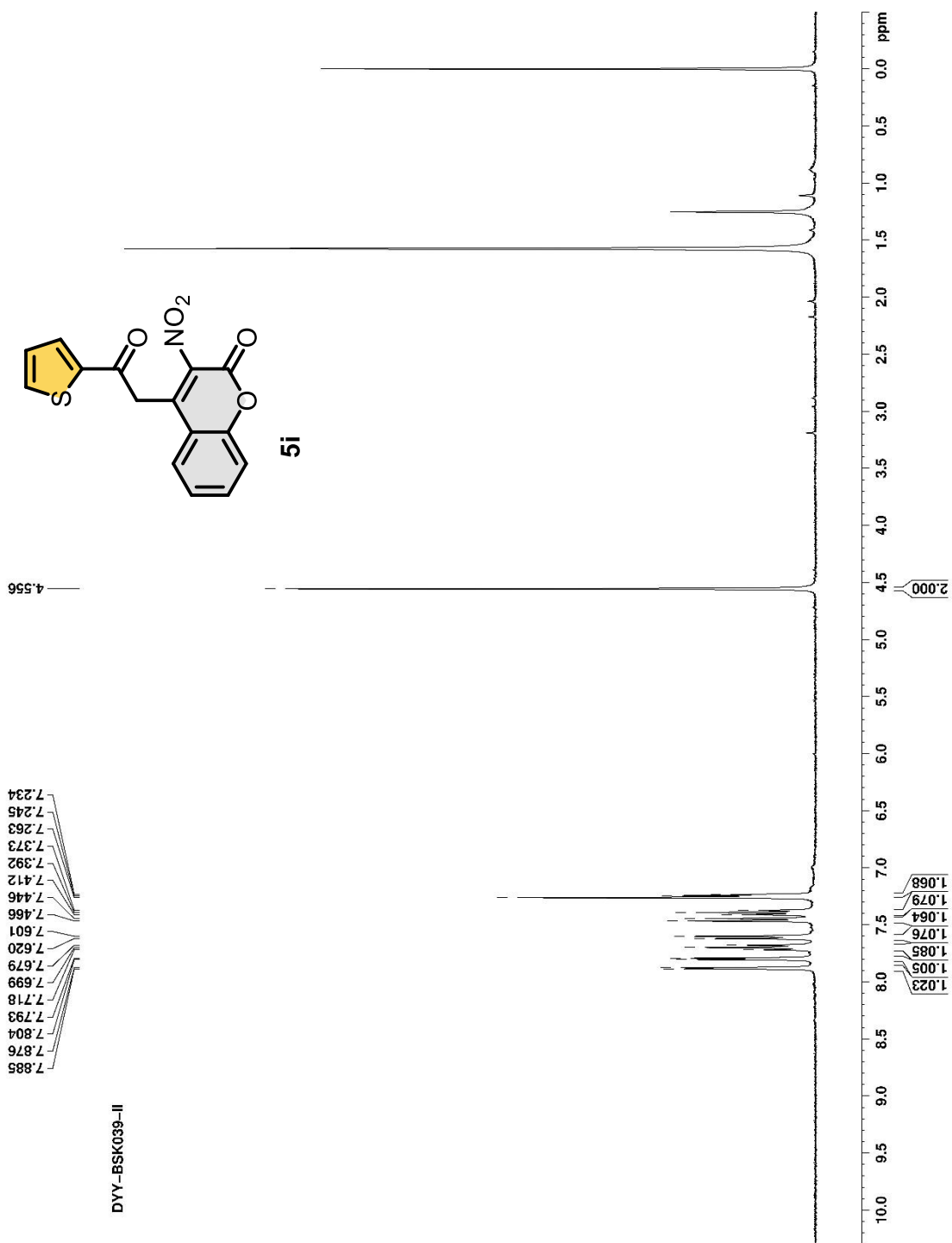


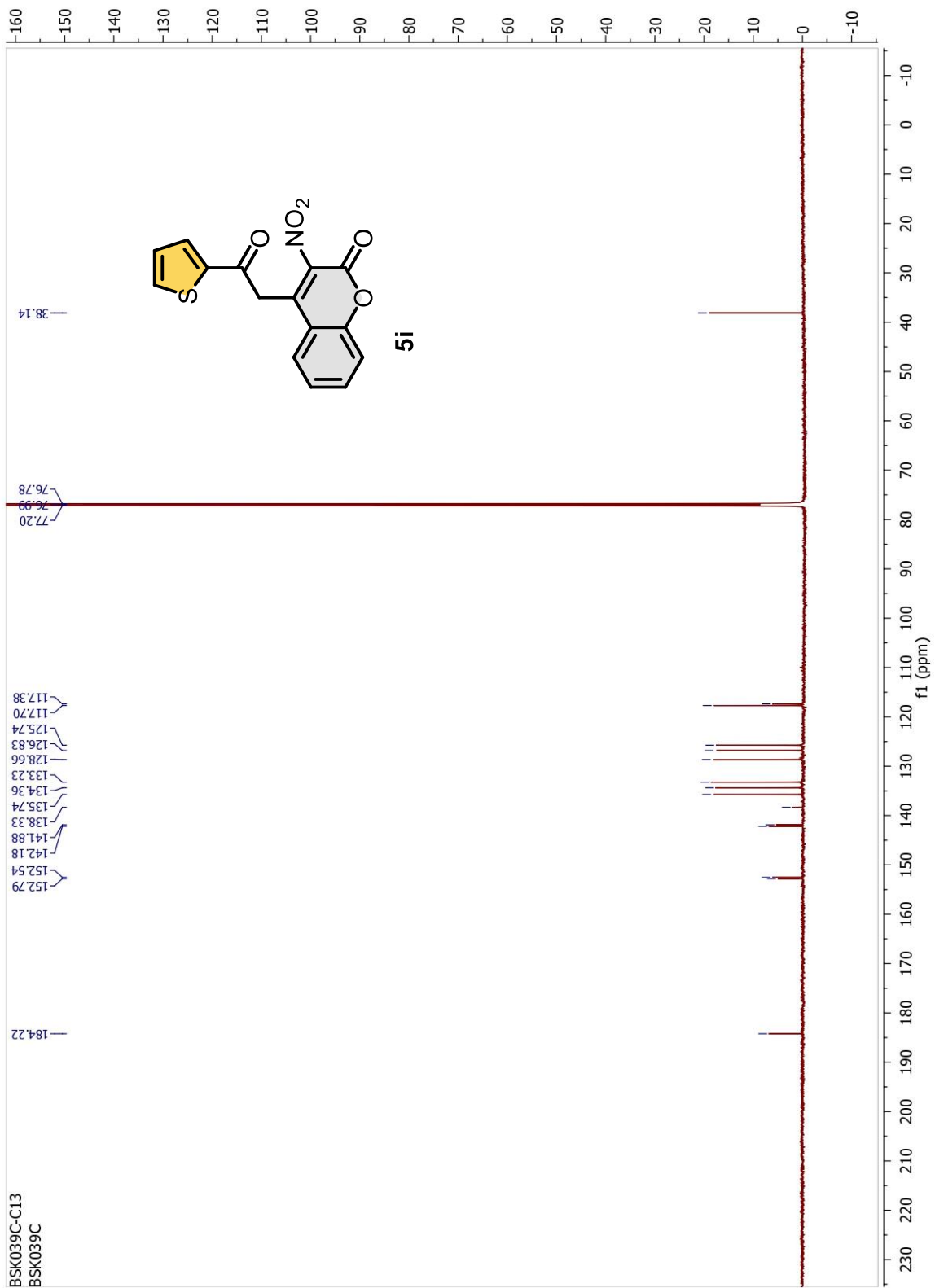
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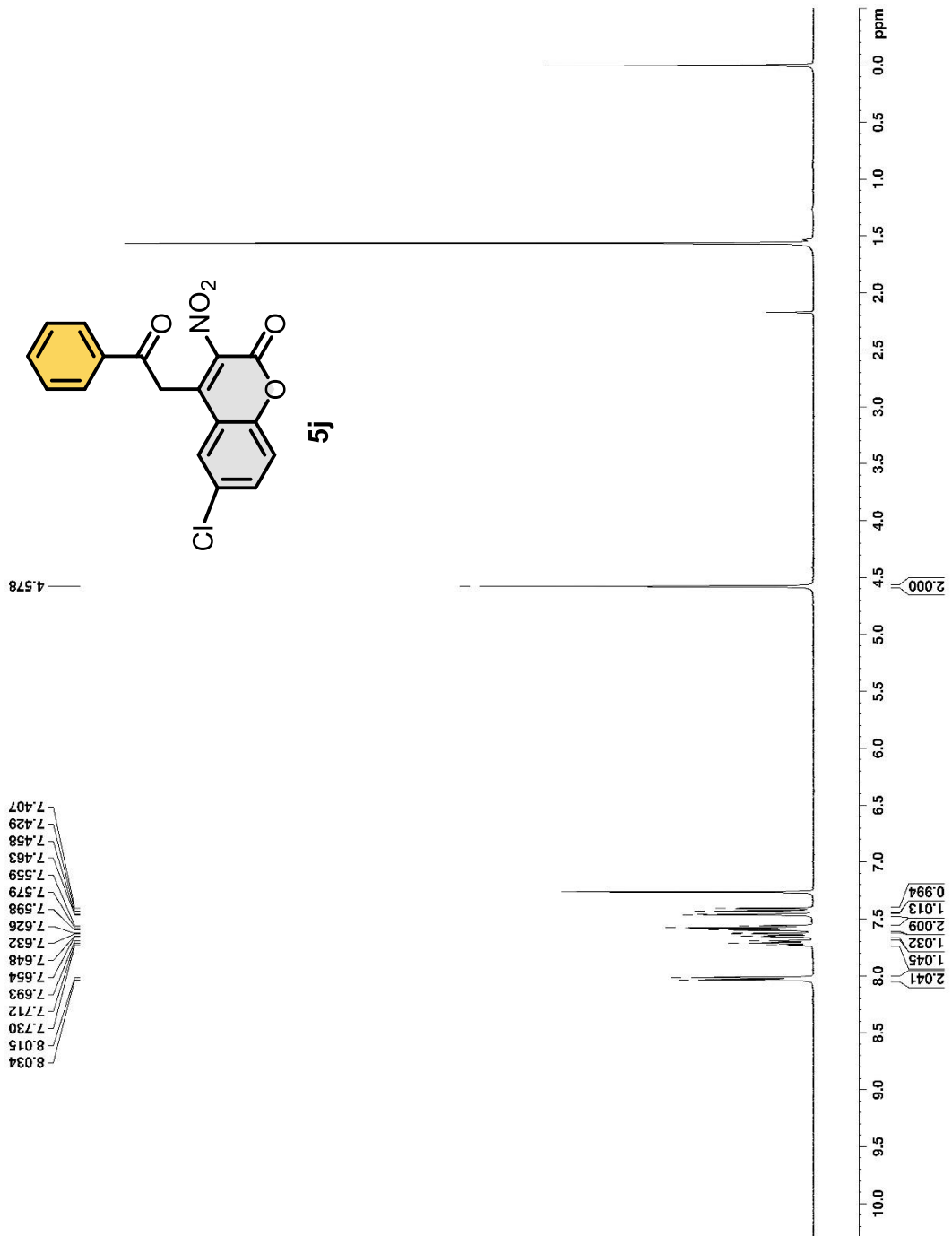


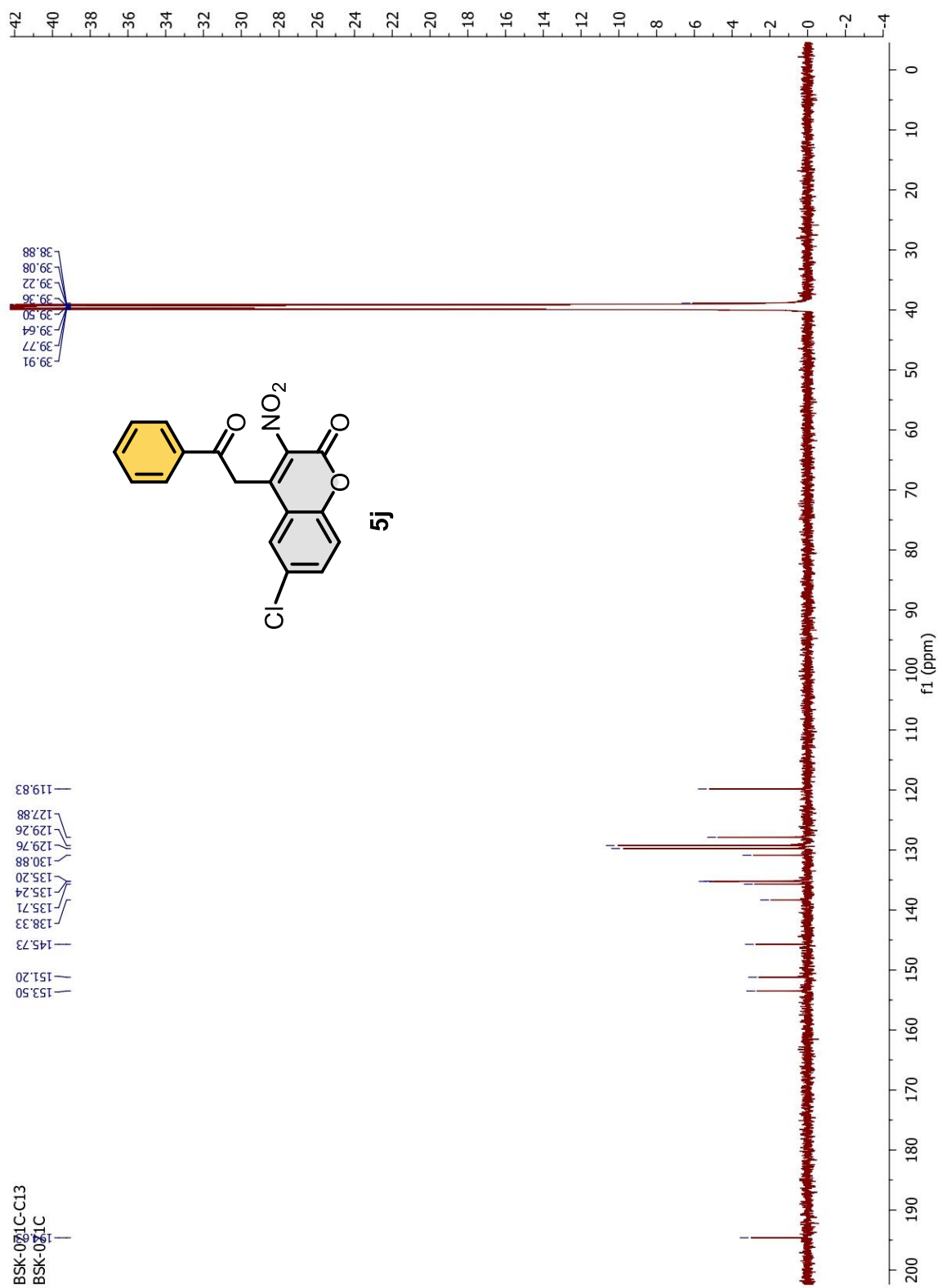
DYY-BSK055

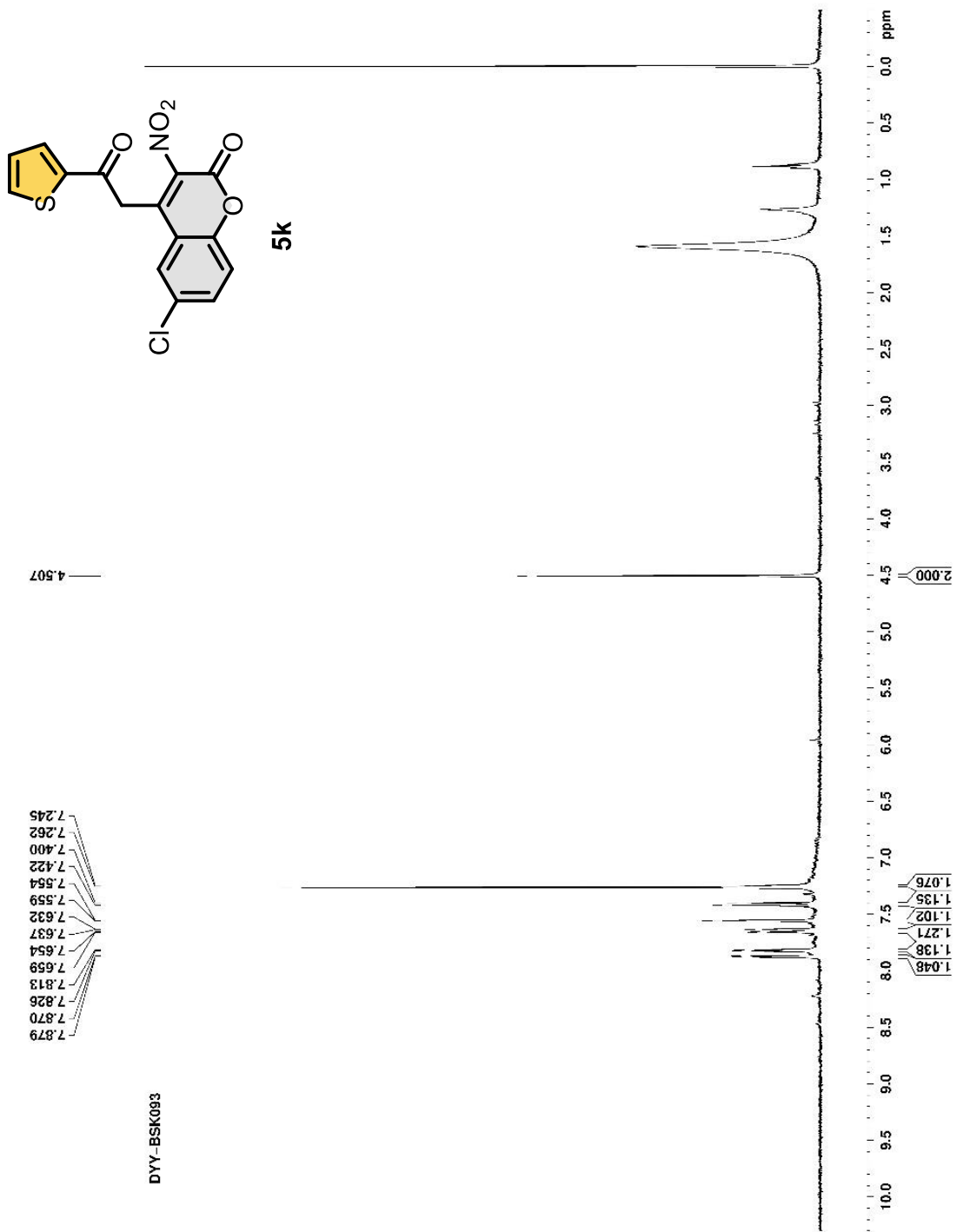


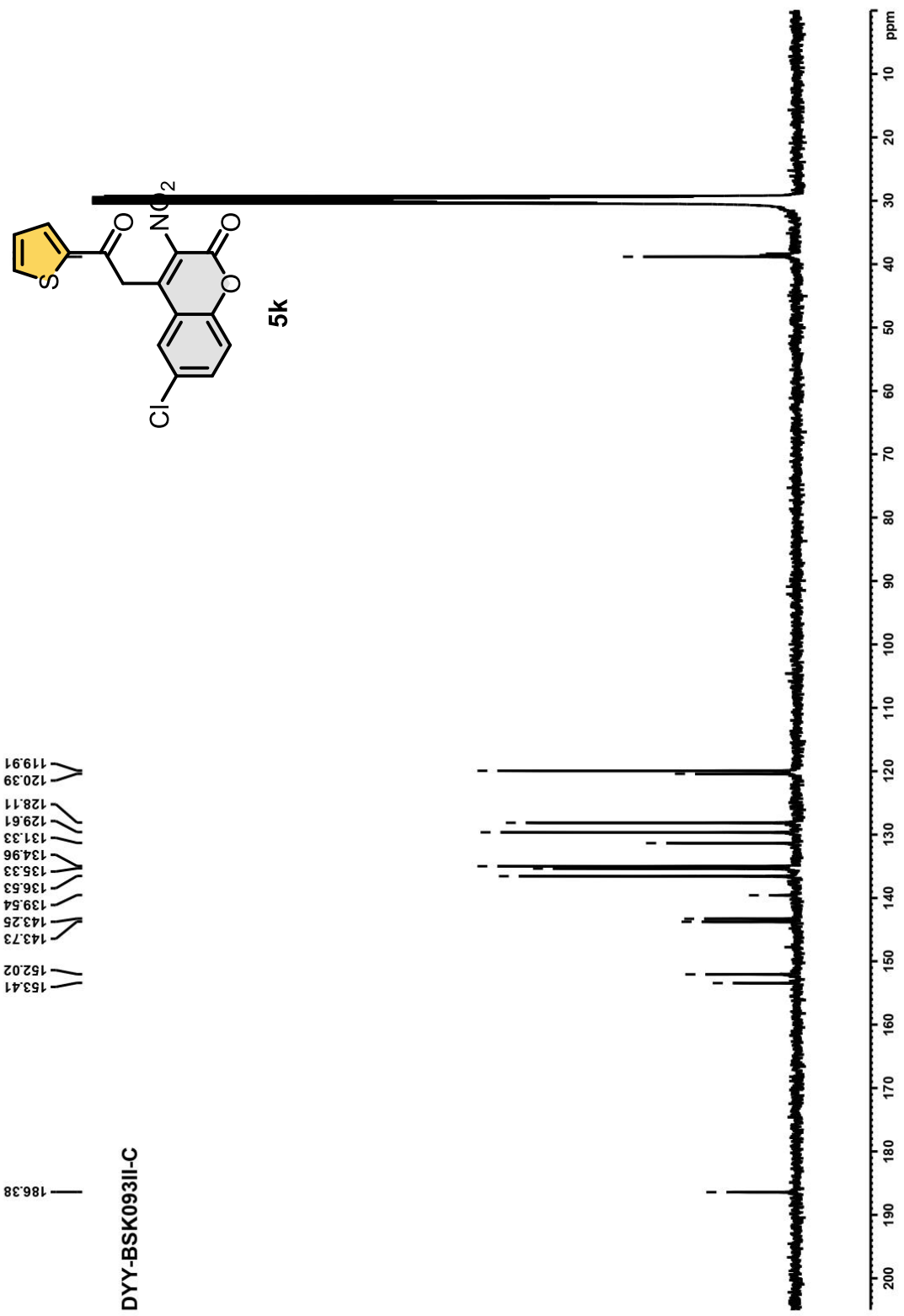


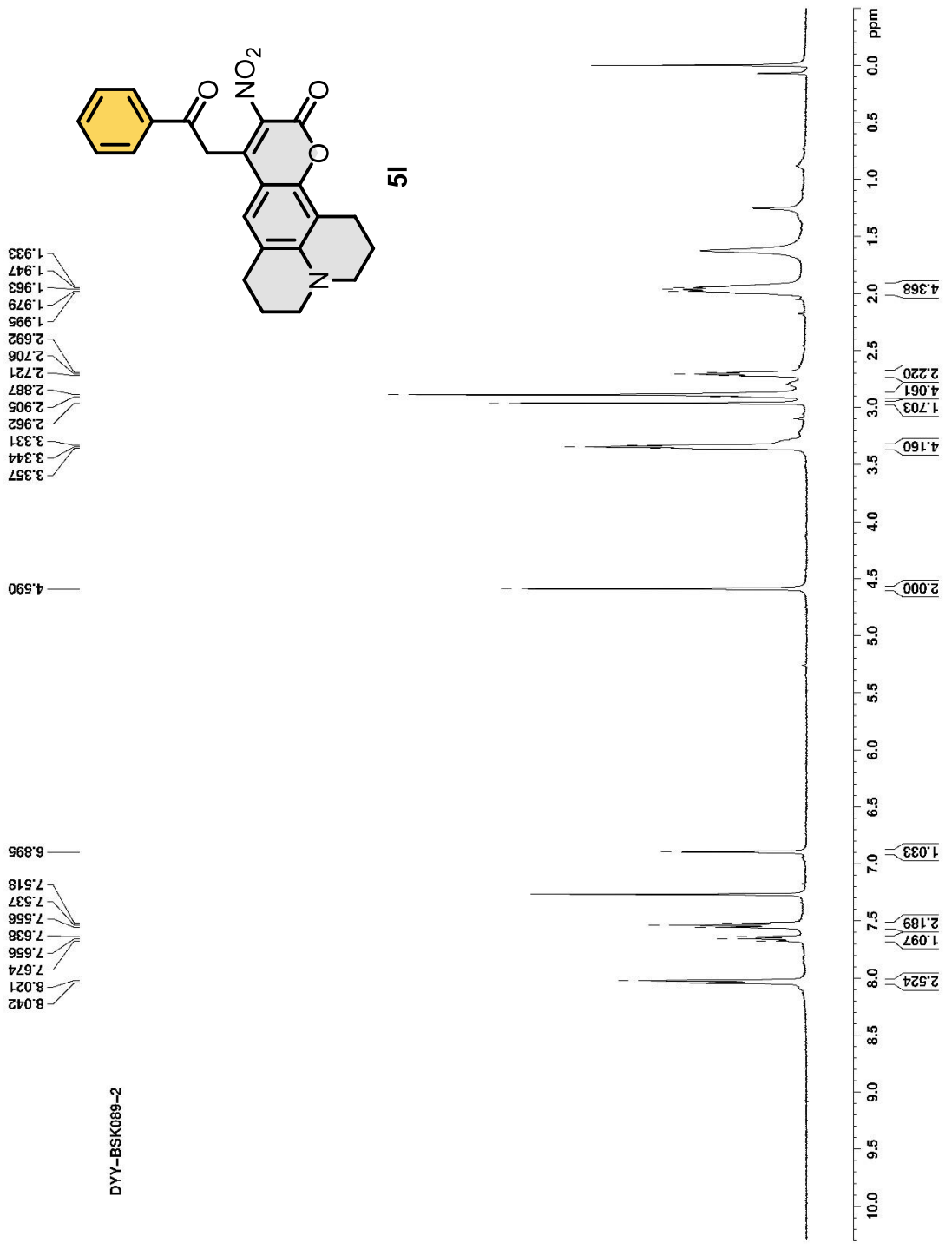


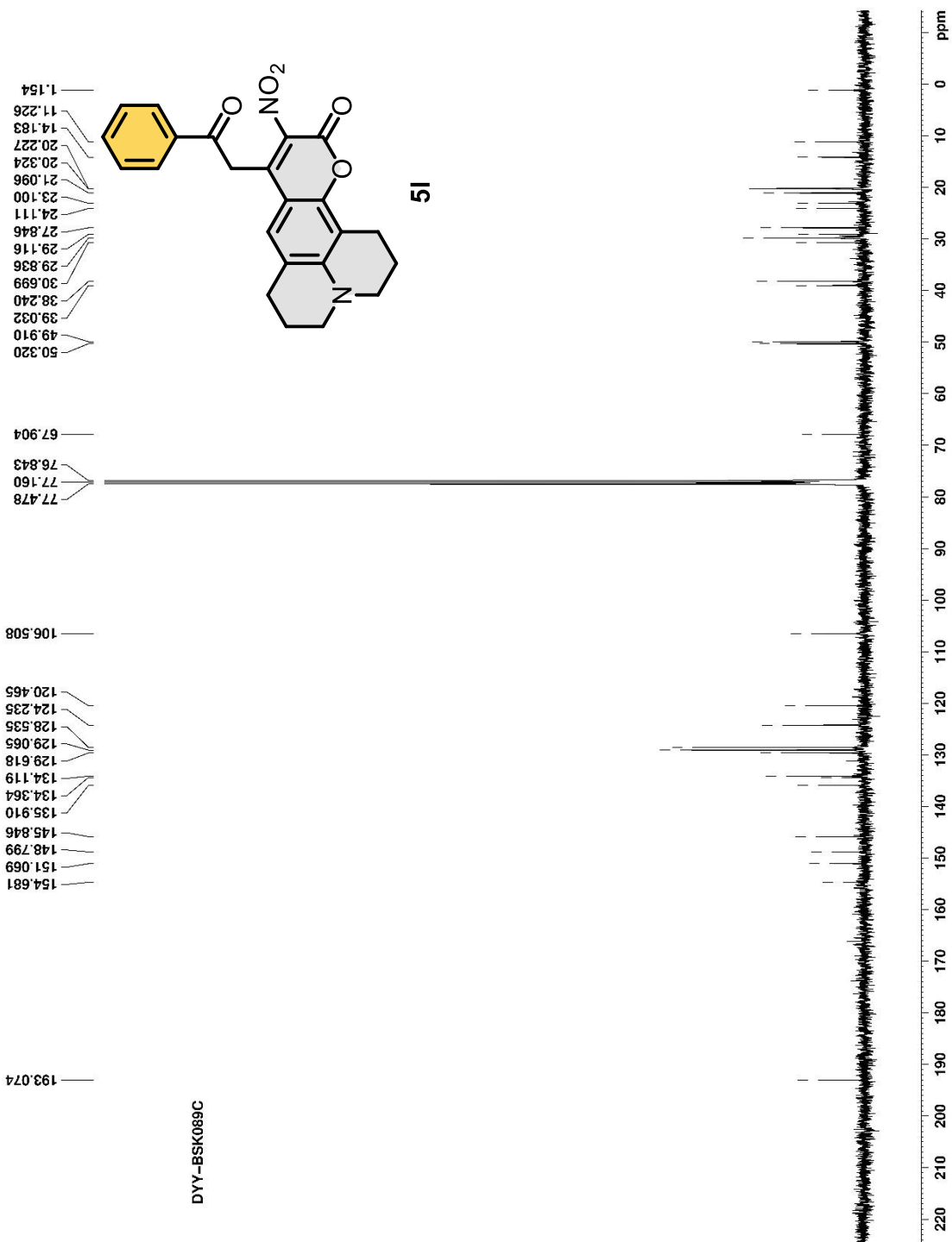


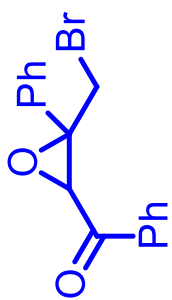












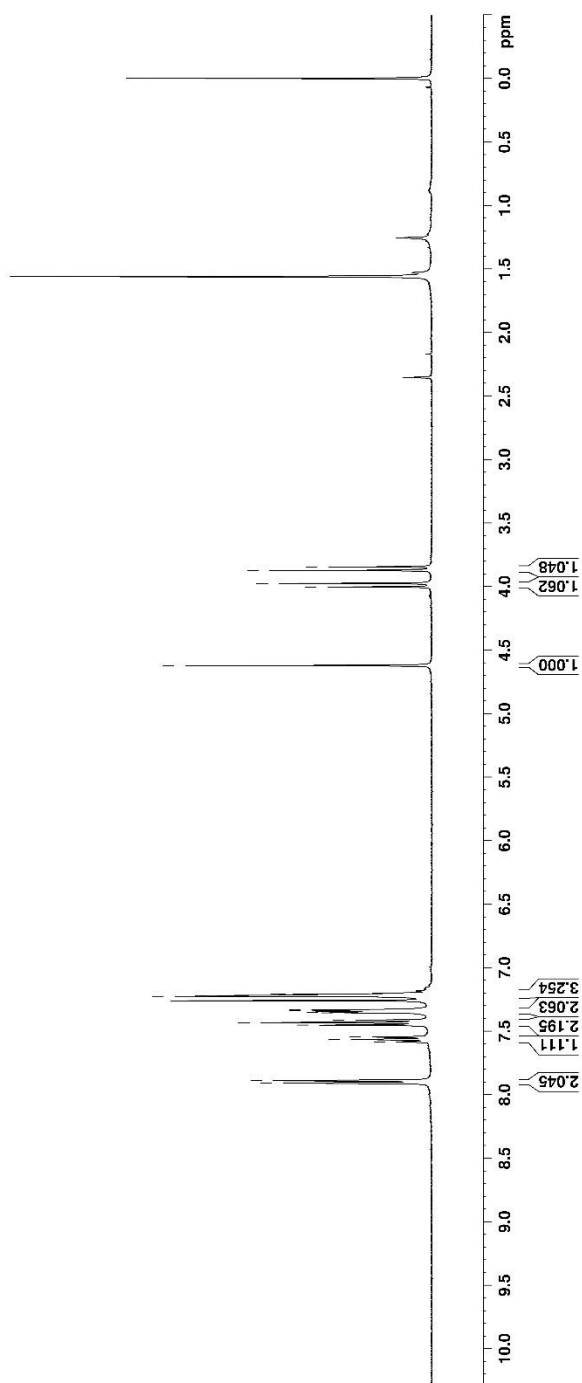
7

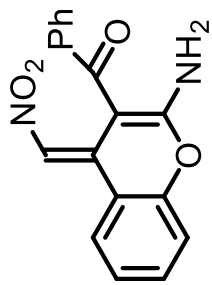
4.003
3.975
3.873
3.845

4.622

7.908
7.890
7.584
7.565
7.547
7.452
7.433
7.413
7.366
7.350
7.341
7.331
7.225
7.219
7.211
7.208
7.199

DYY-BSK061-1-II

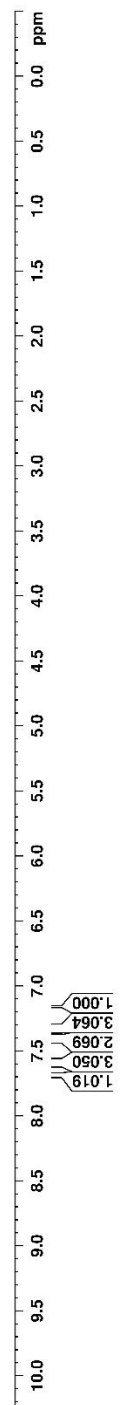


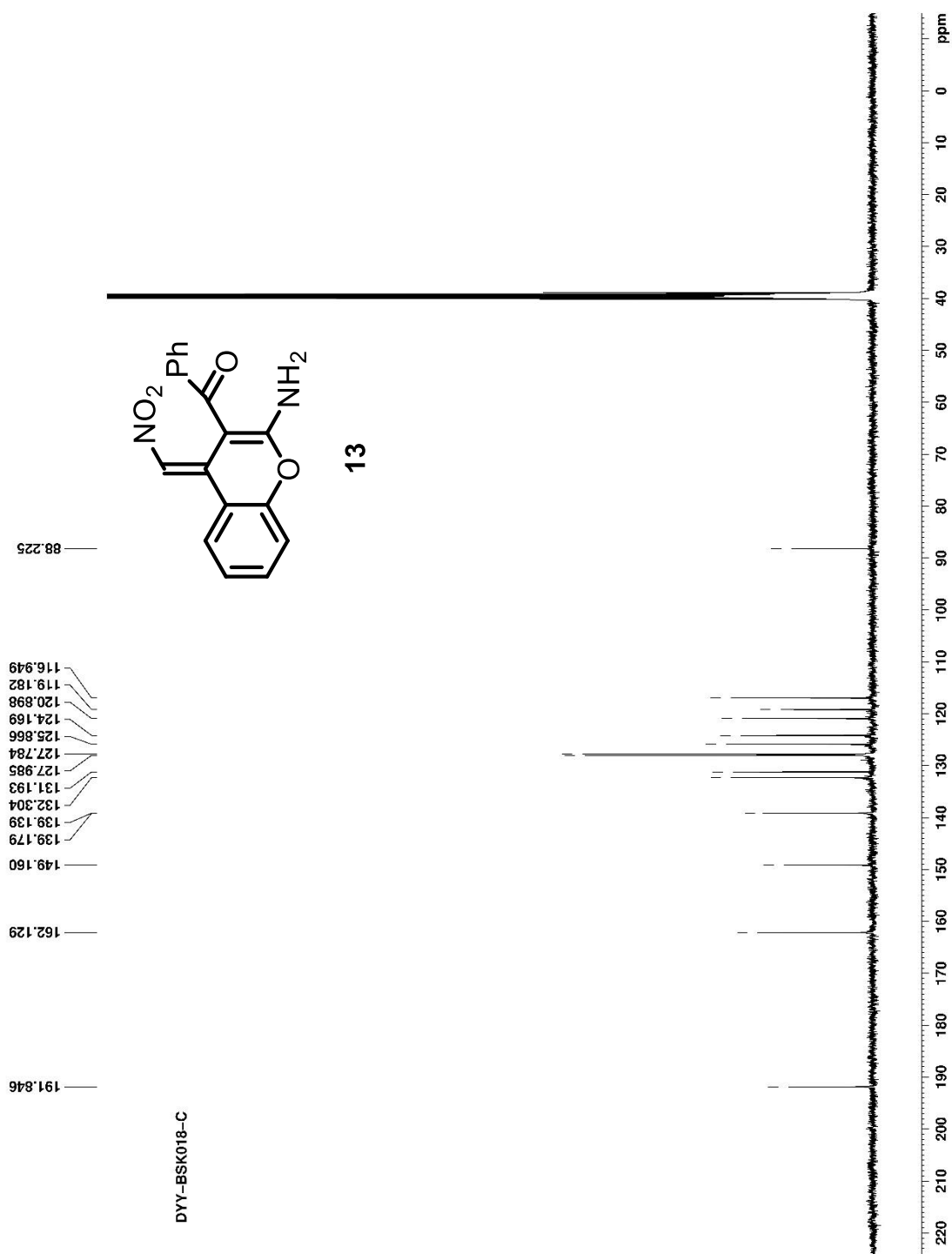


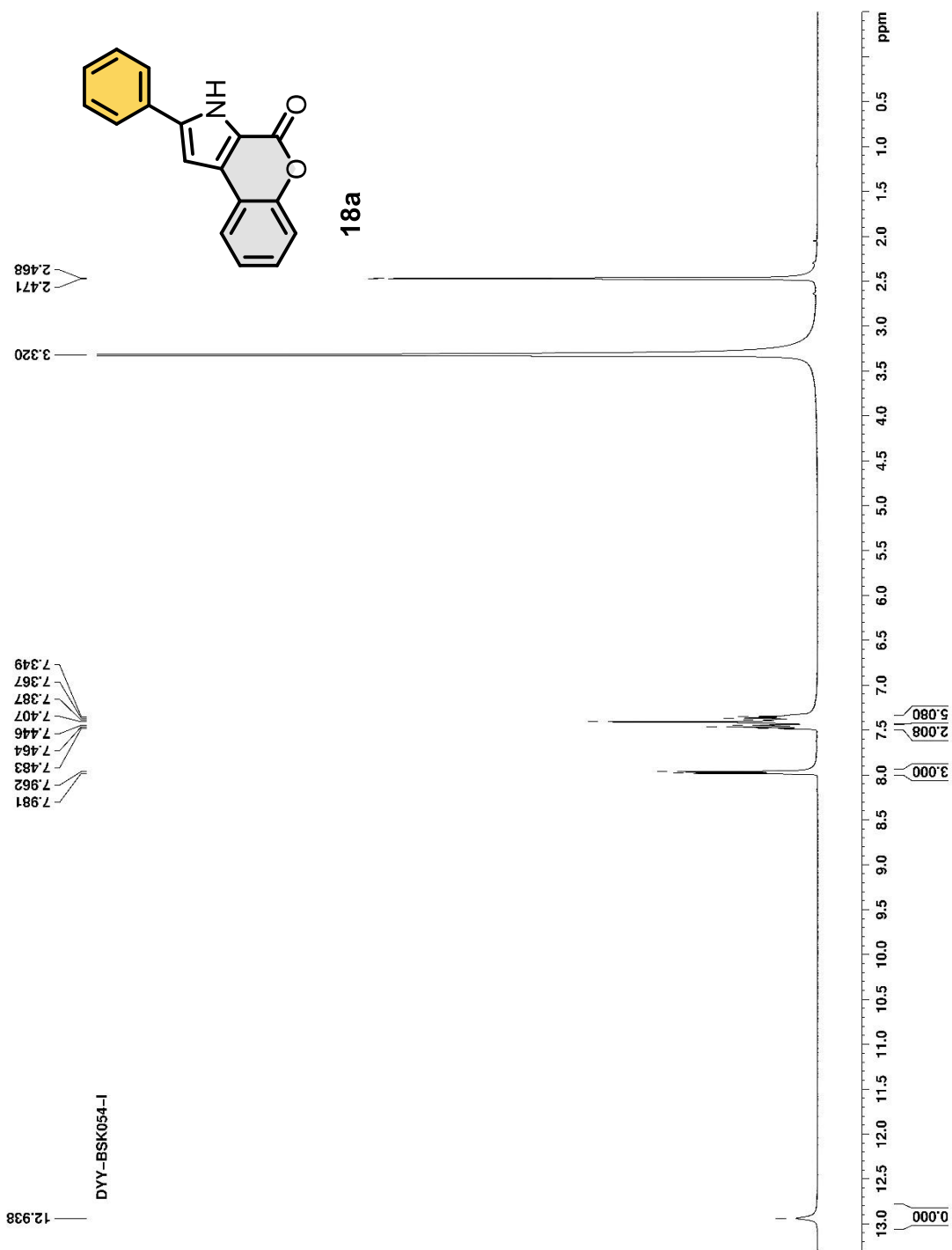
13

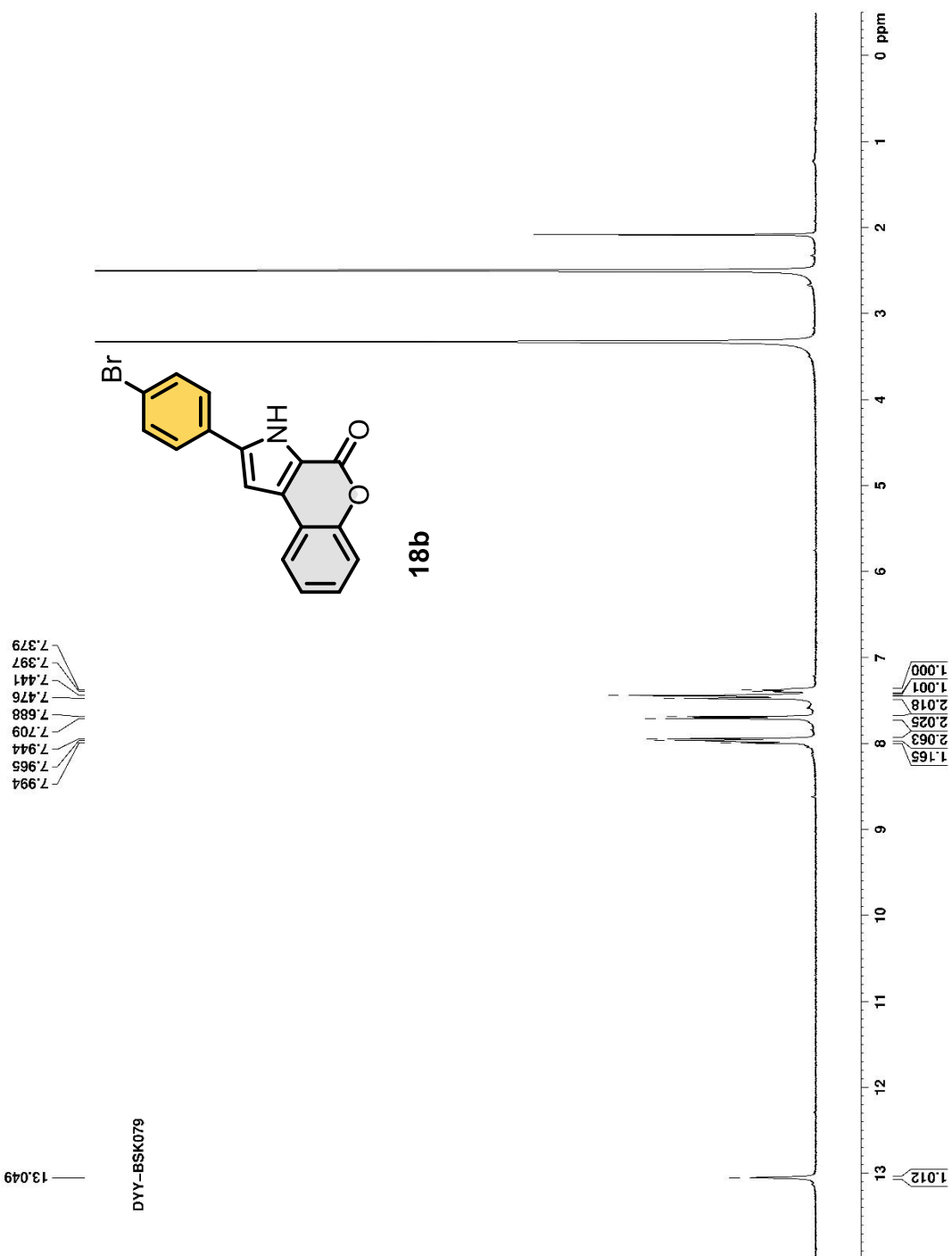
7.699
7.696
7.678
7.675
7.612
7.594
7.590
7.568
7.565
7.437
7.434
7.418
7.400
7.382
7.380
7.357
7.355
7.338
7.319
7.301
7.159

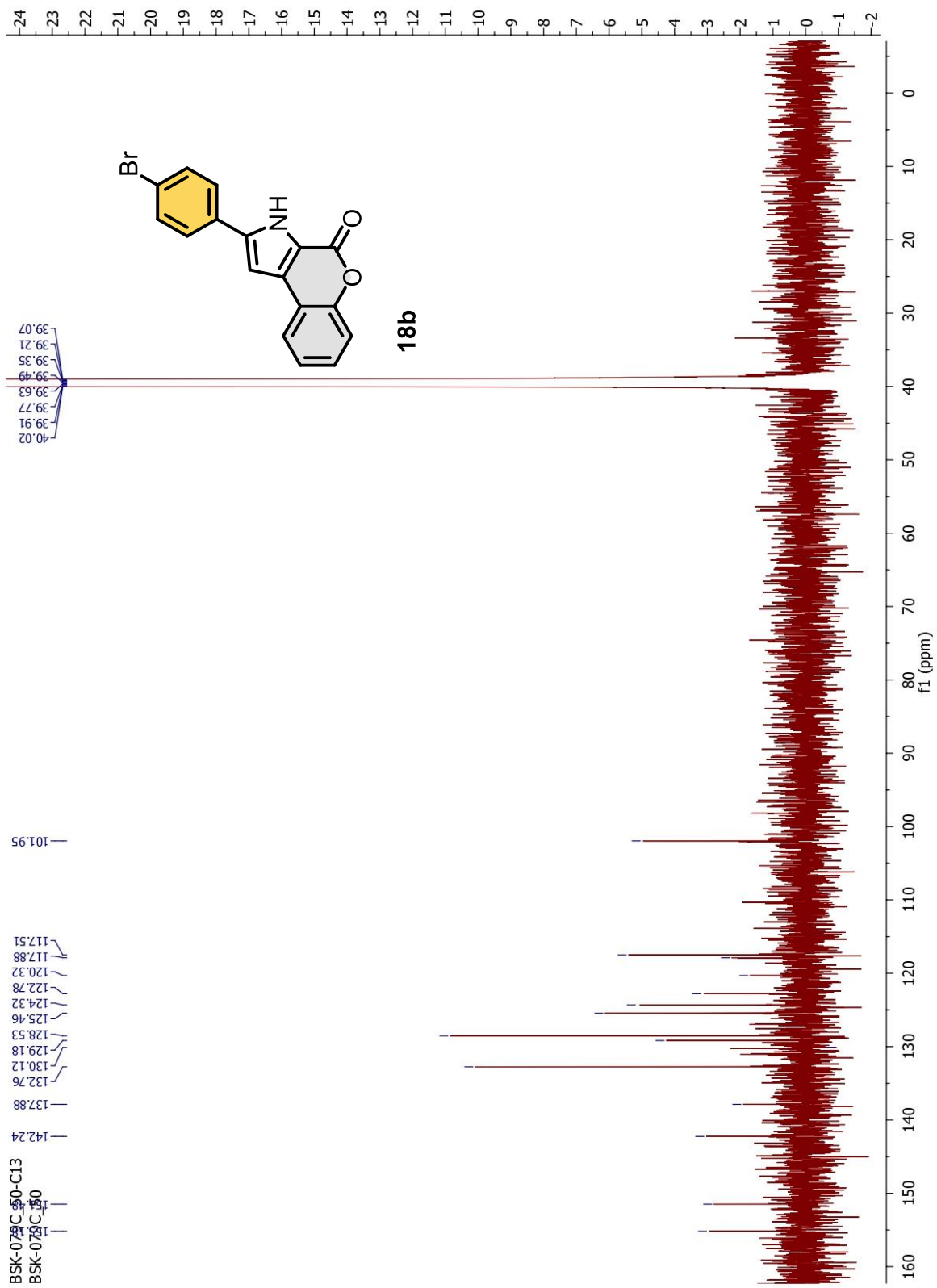
DYY-BSK018-II

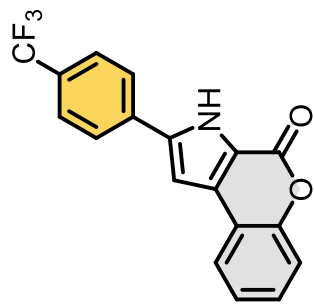




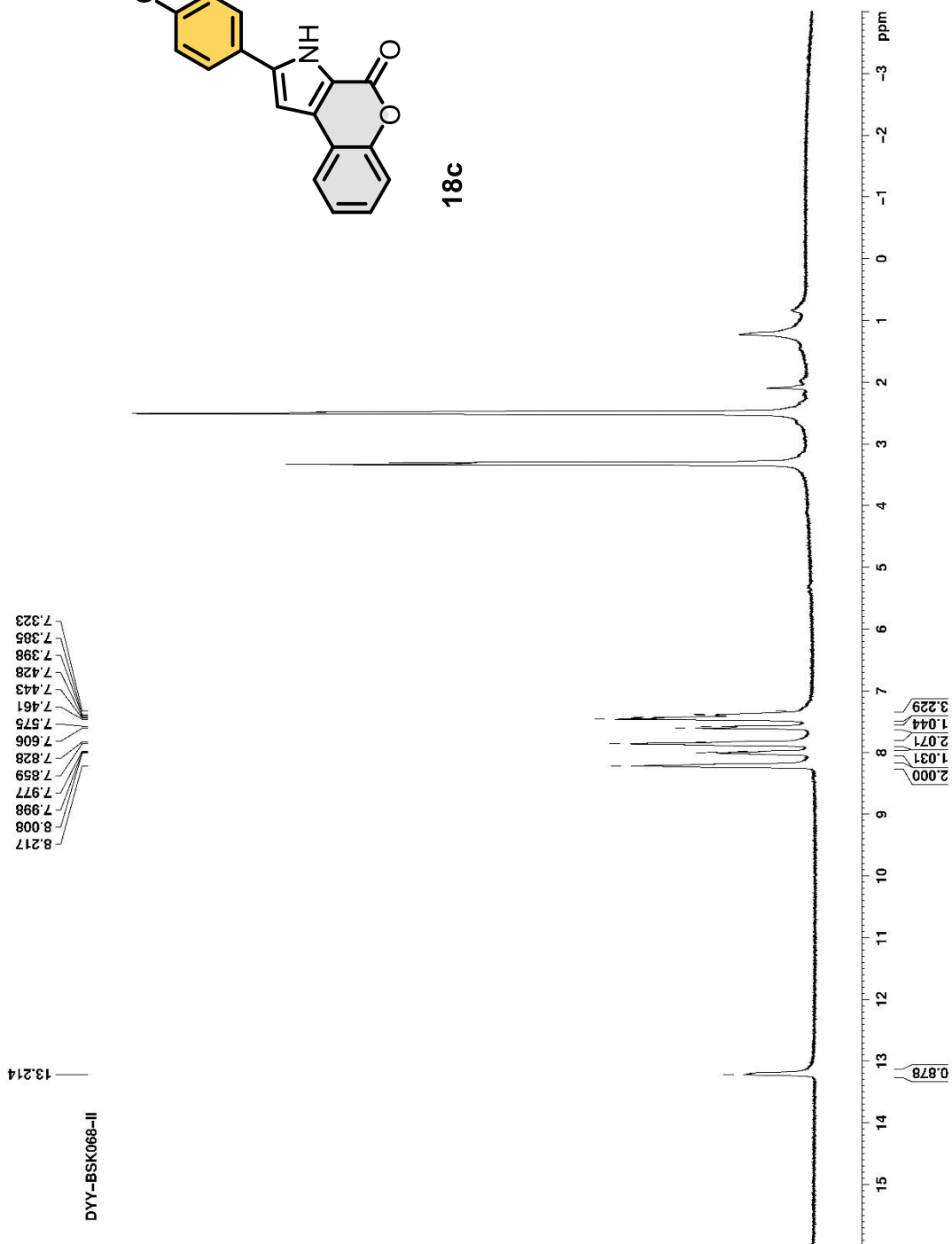


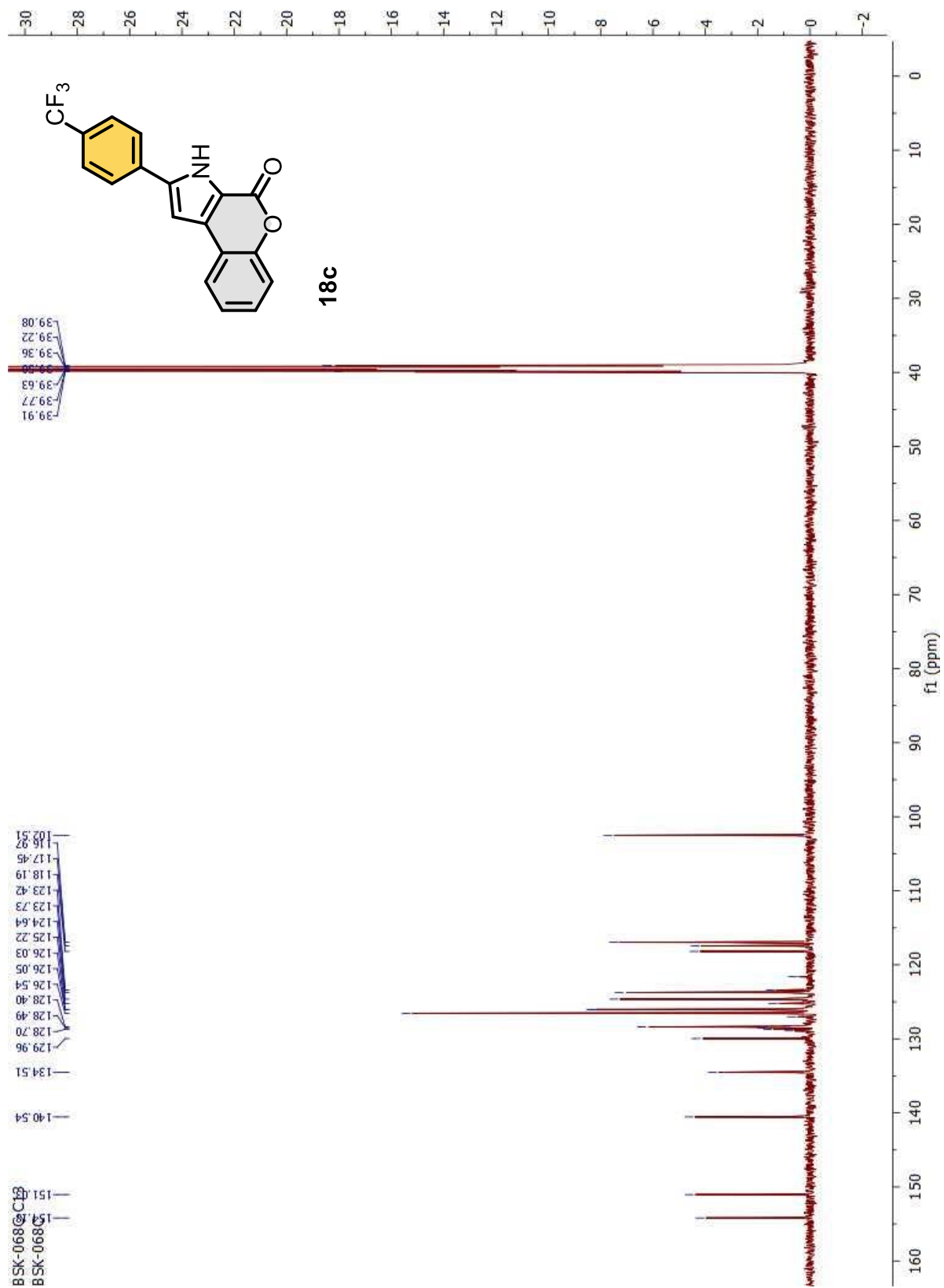


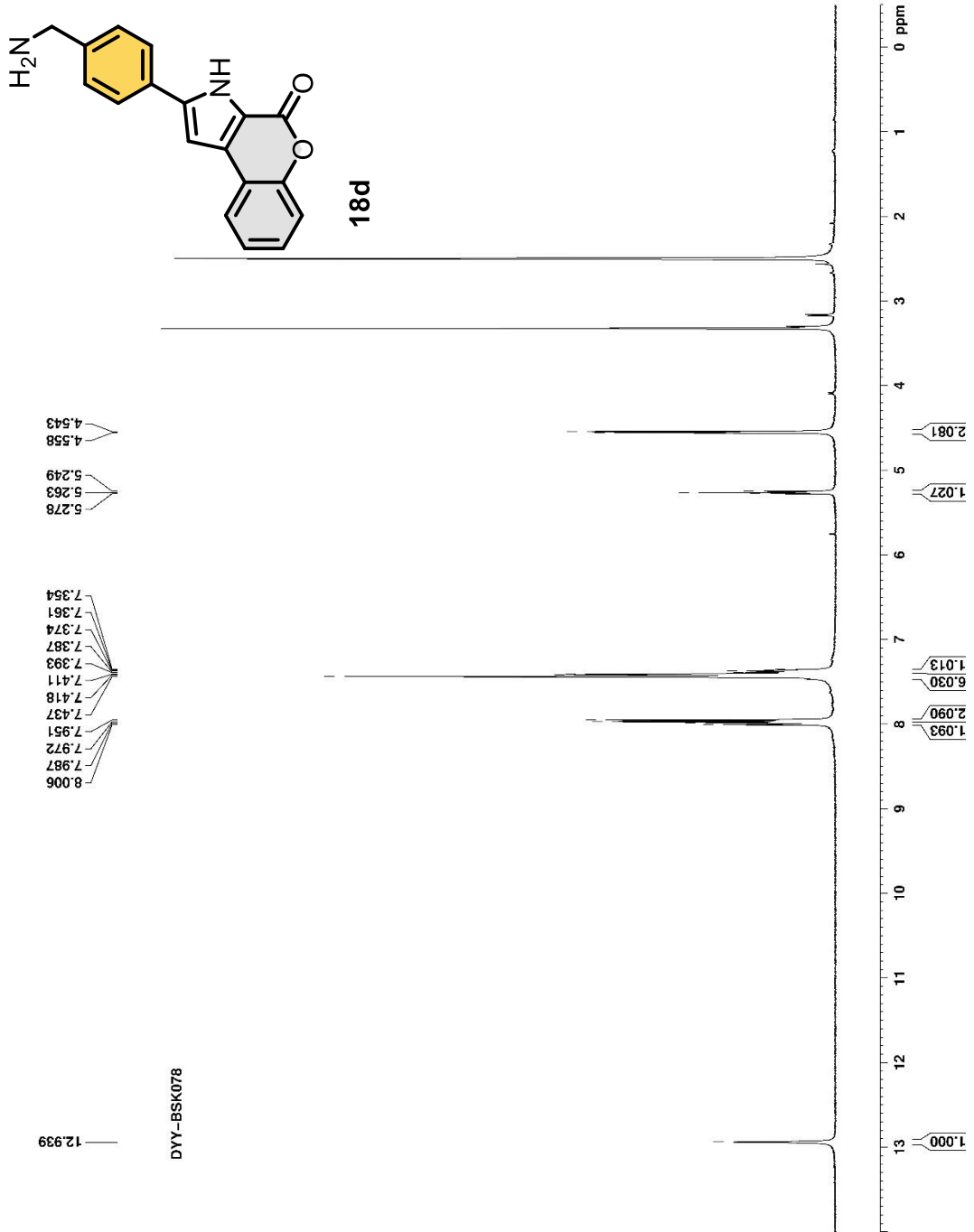


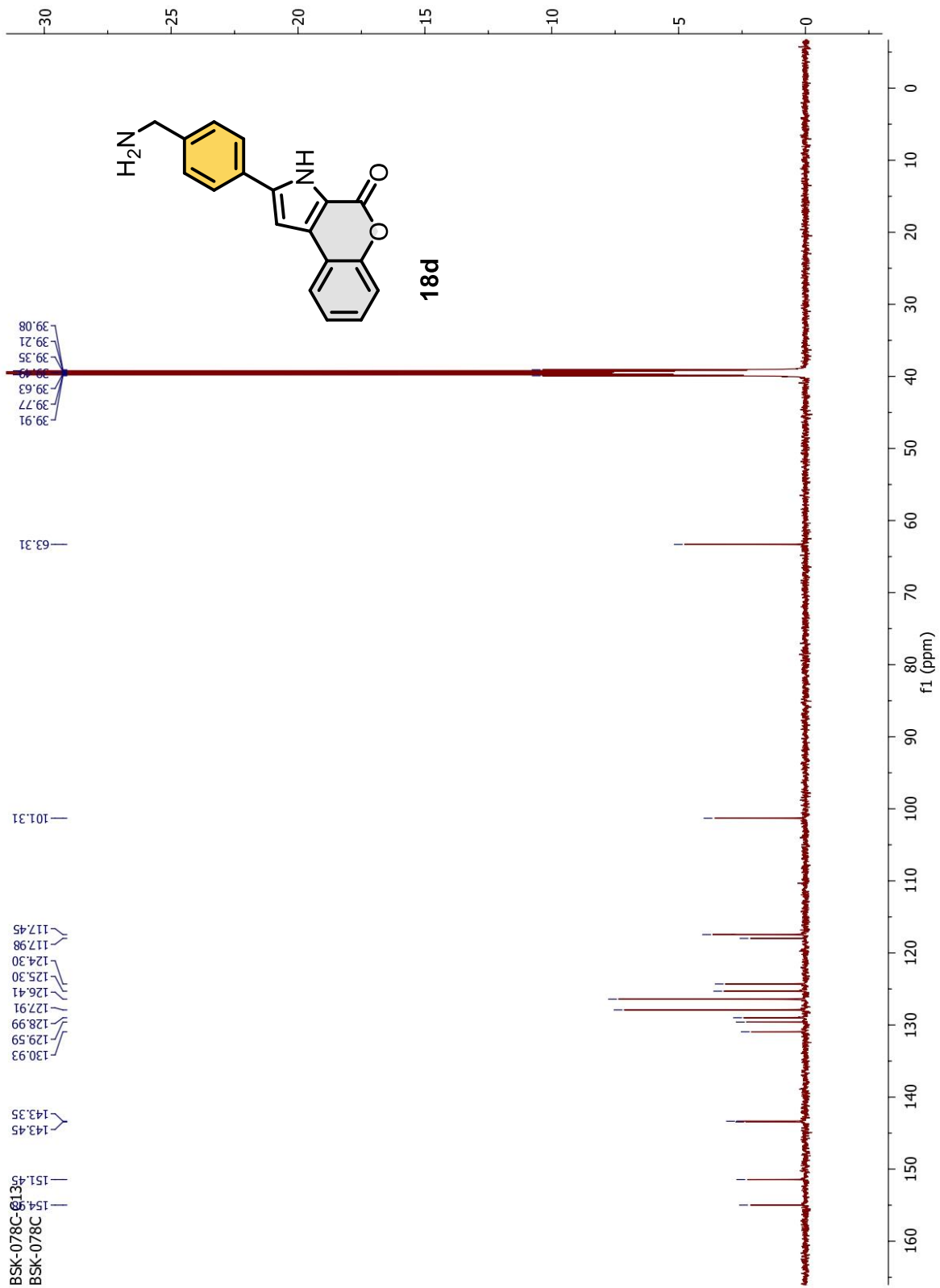


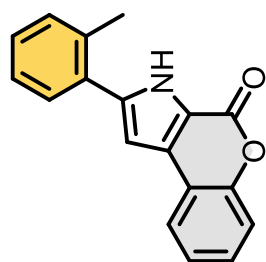
18c



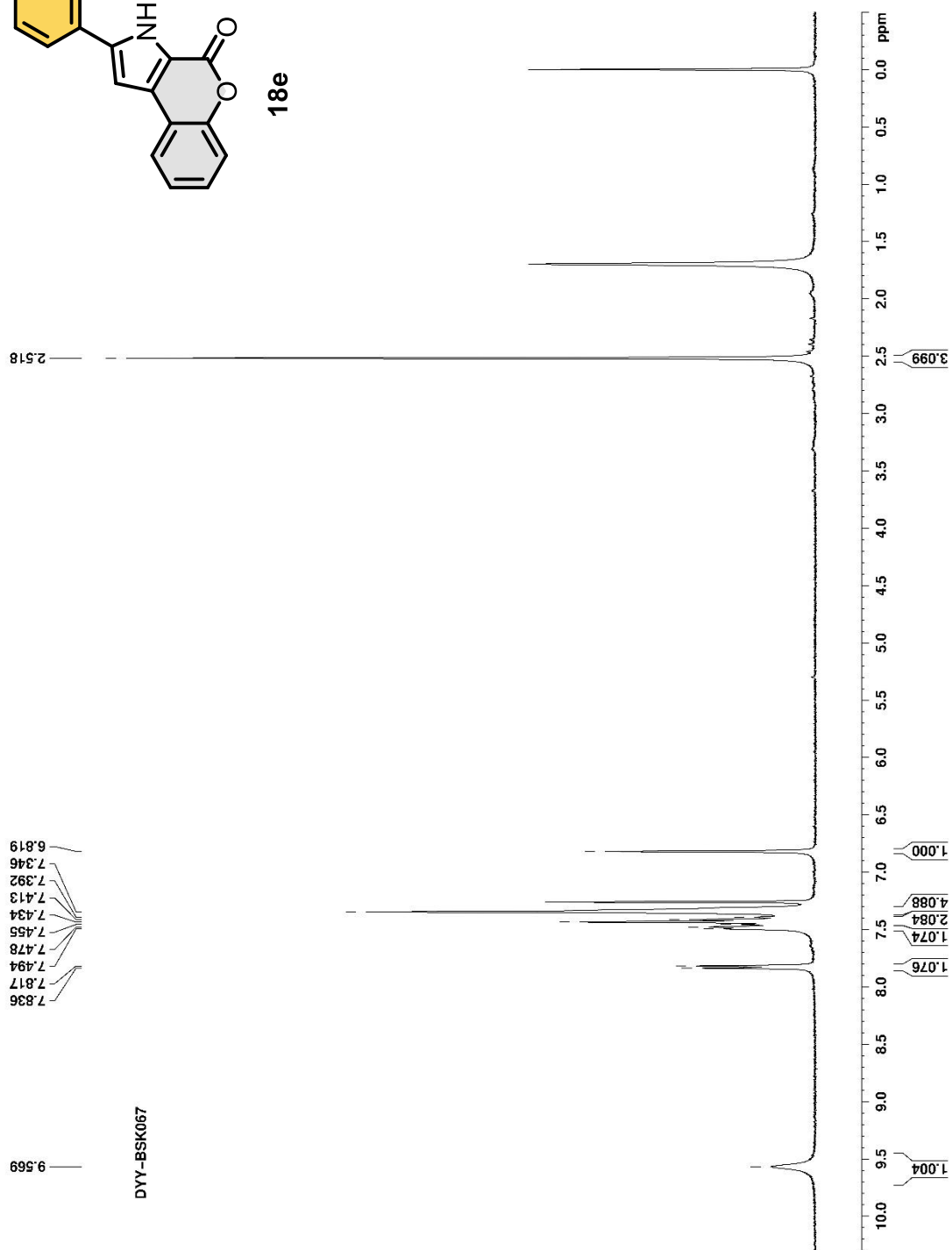


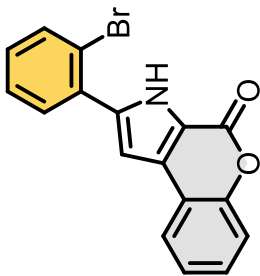






18e



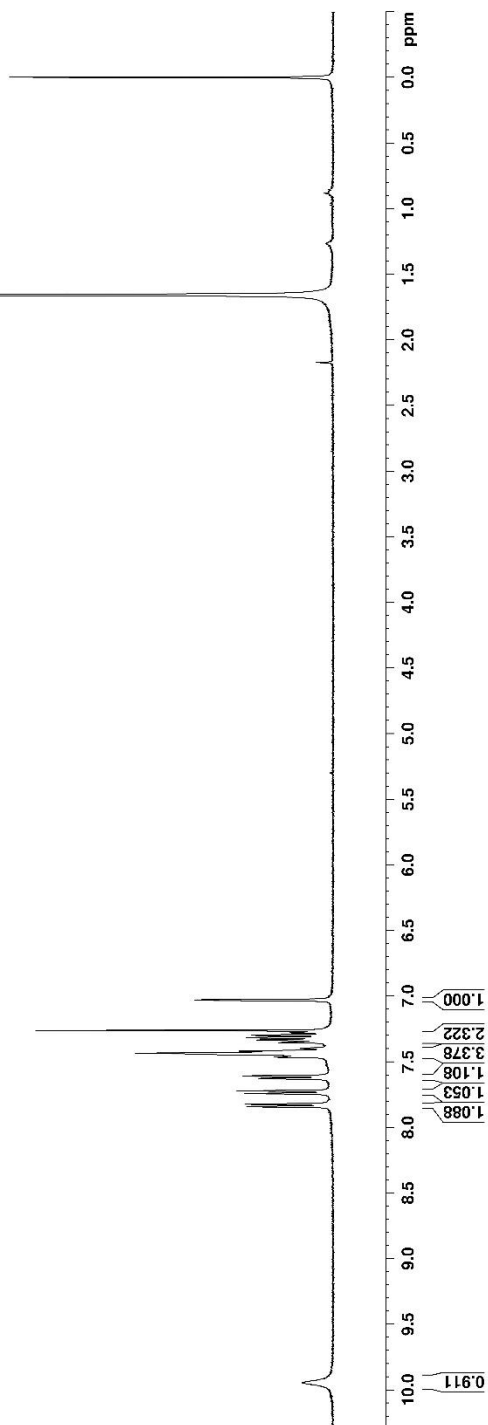


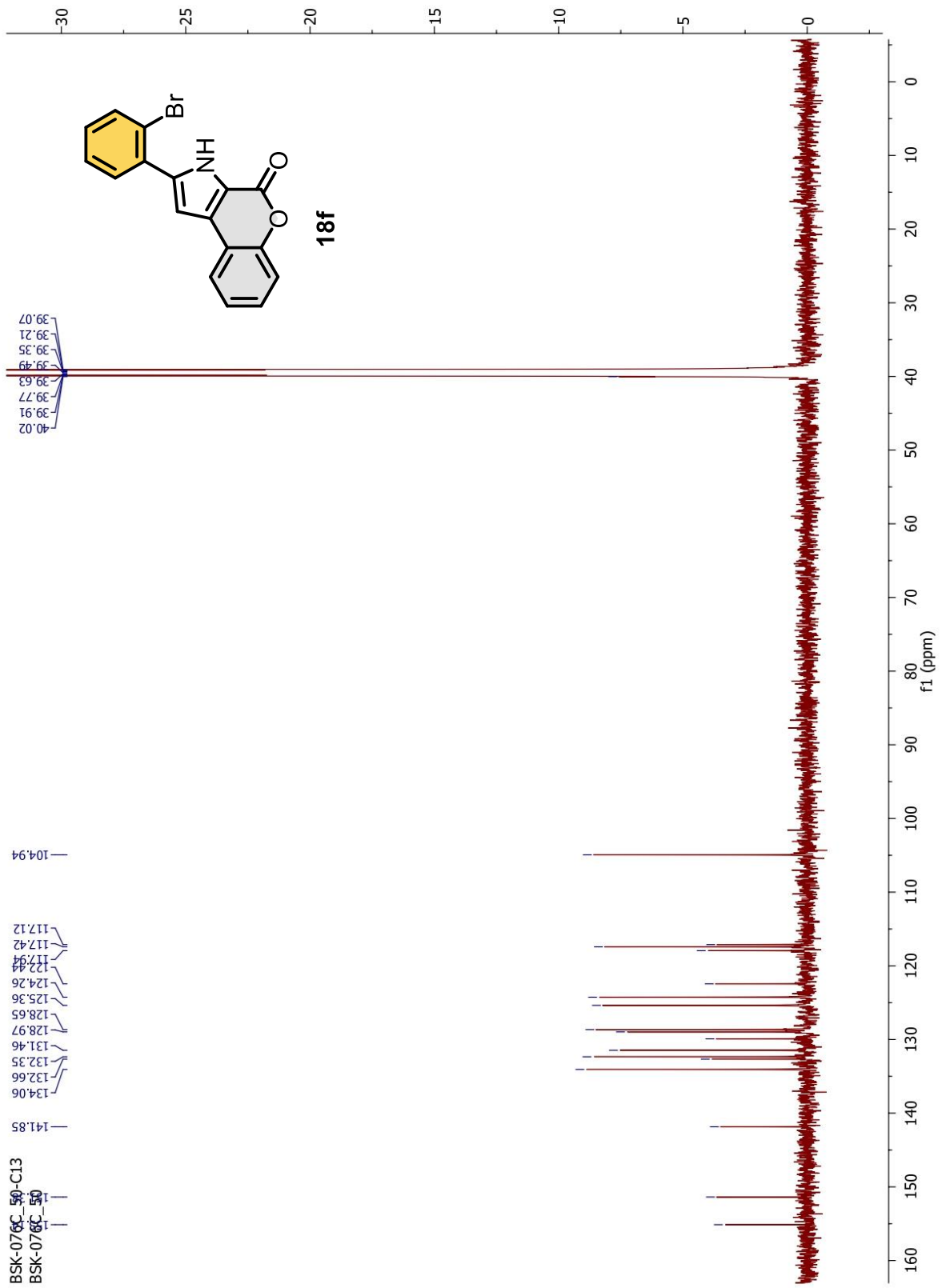
18f

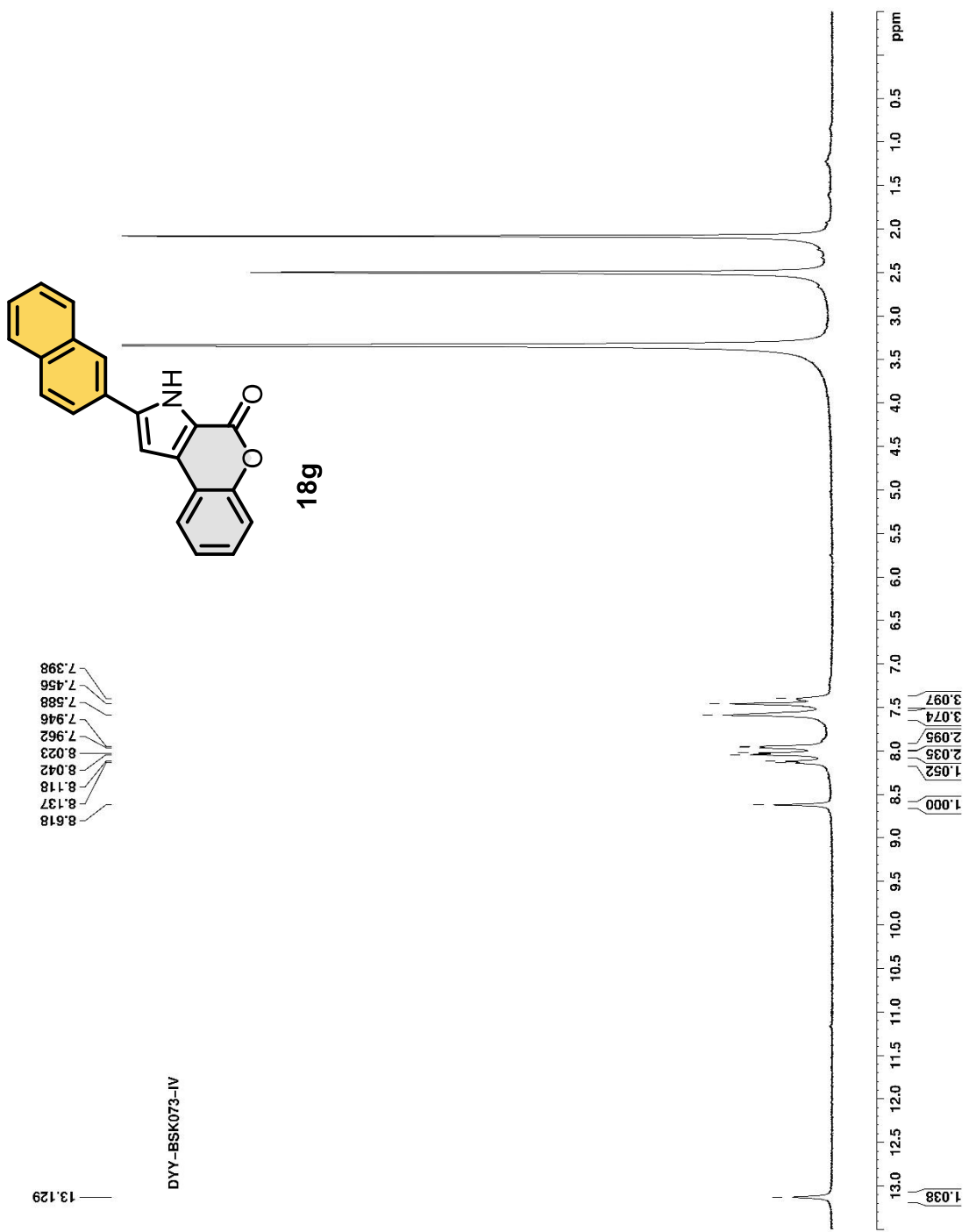
7.843
7.824
7.743
7.723
7.629
7.610
7.463
7.455
7.444
7.435
7.420
7.399
7.354
7.350
7.335
7.319
7.299
7.279
7.033
7.027

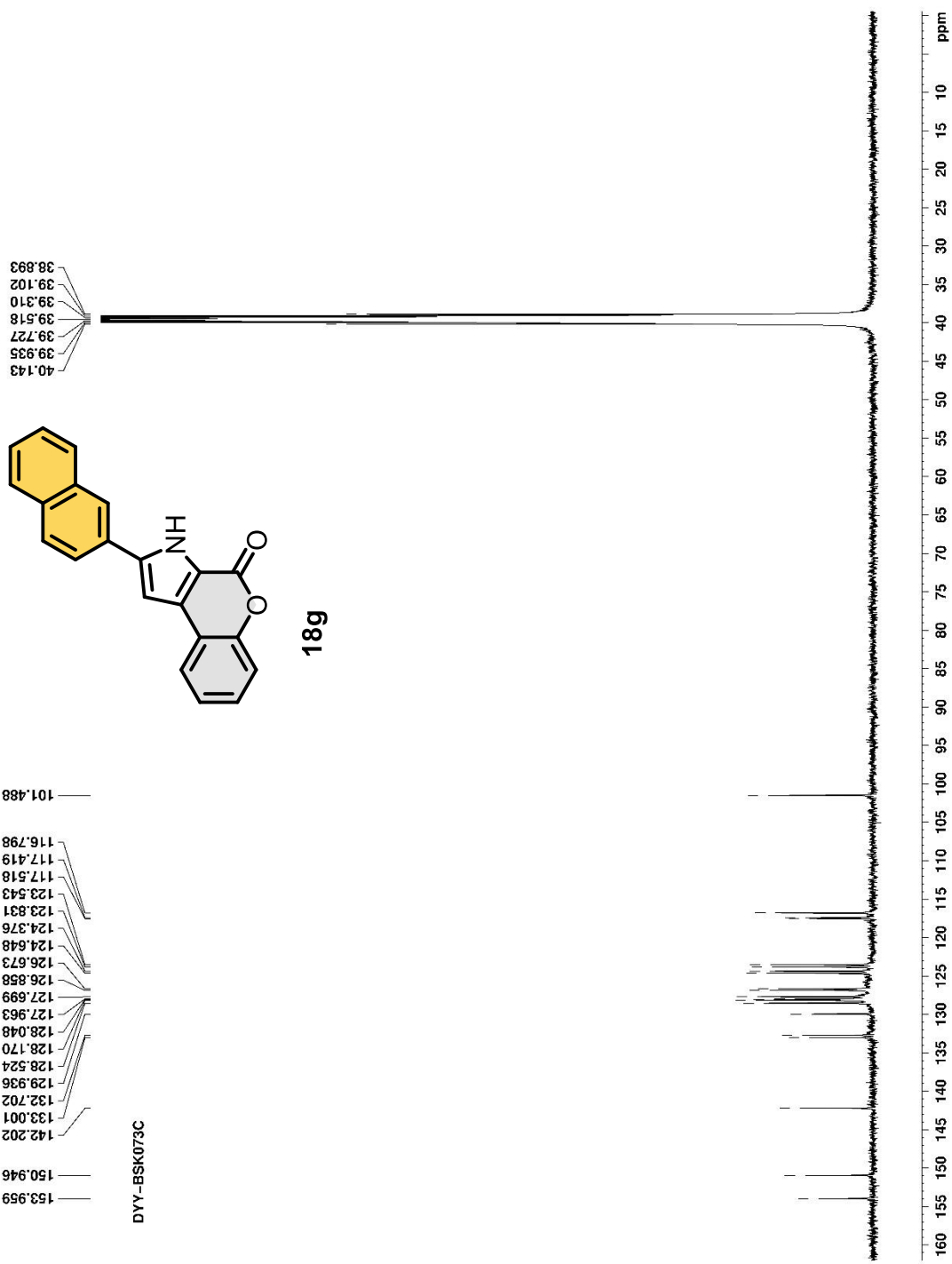
9.945

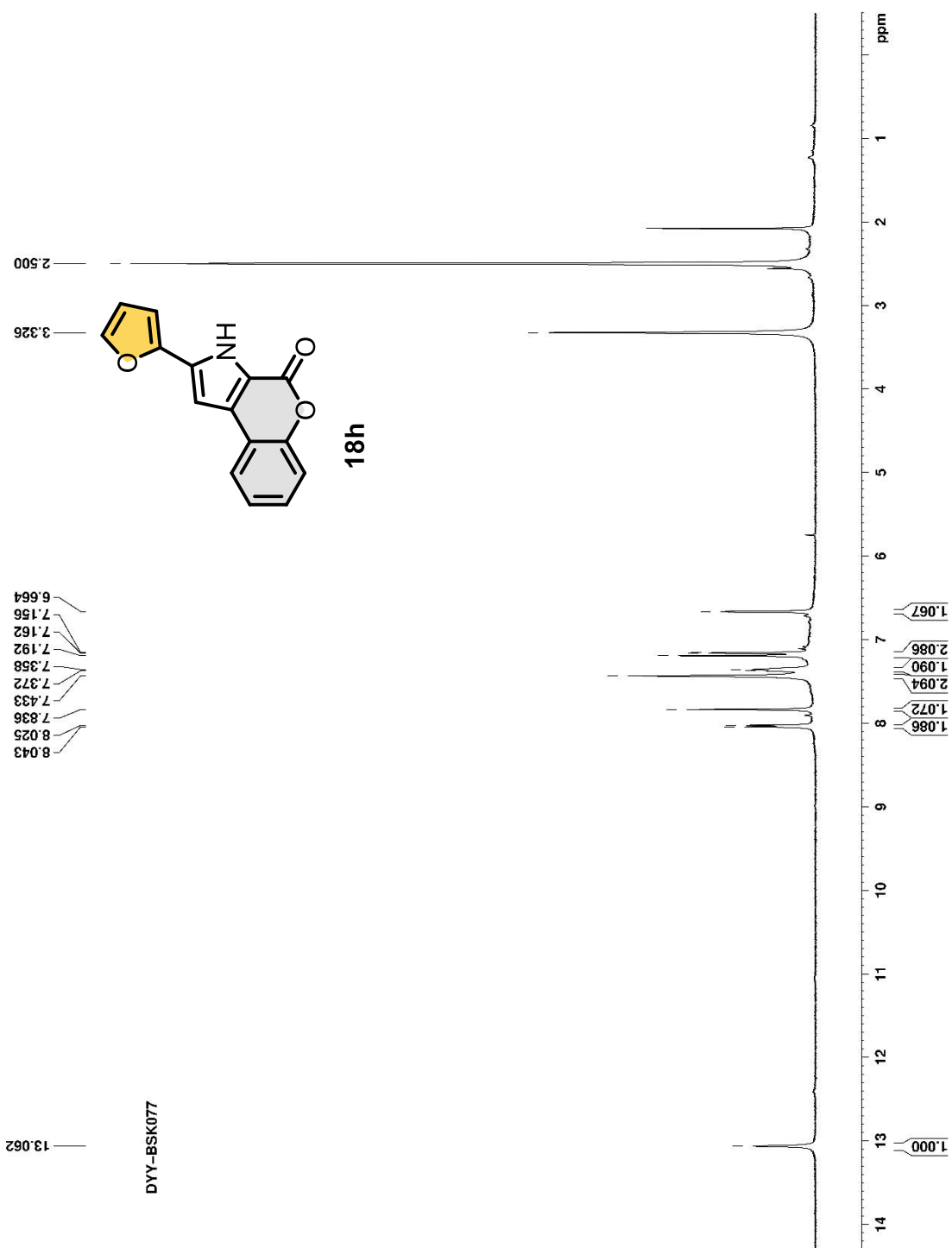
BSK076

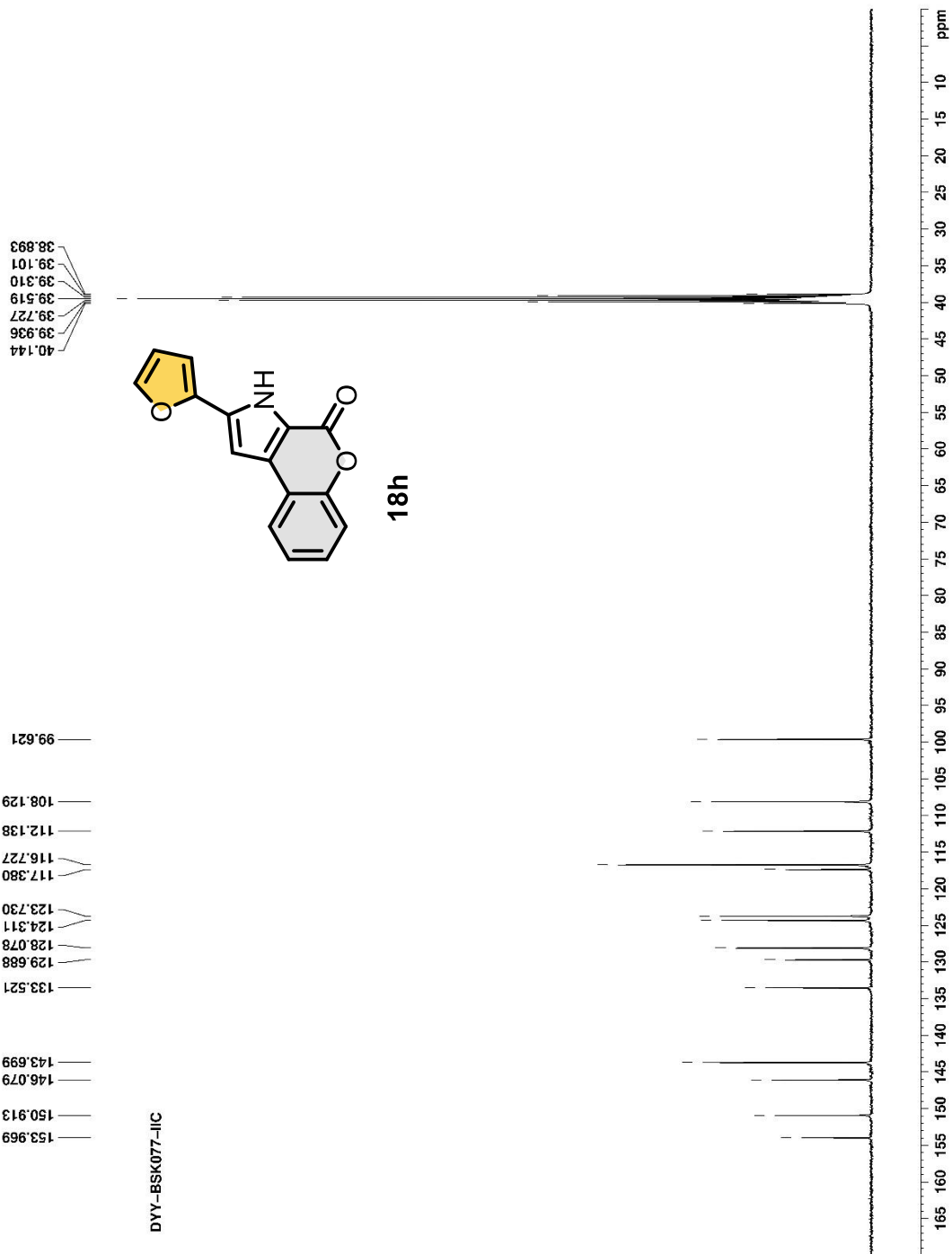


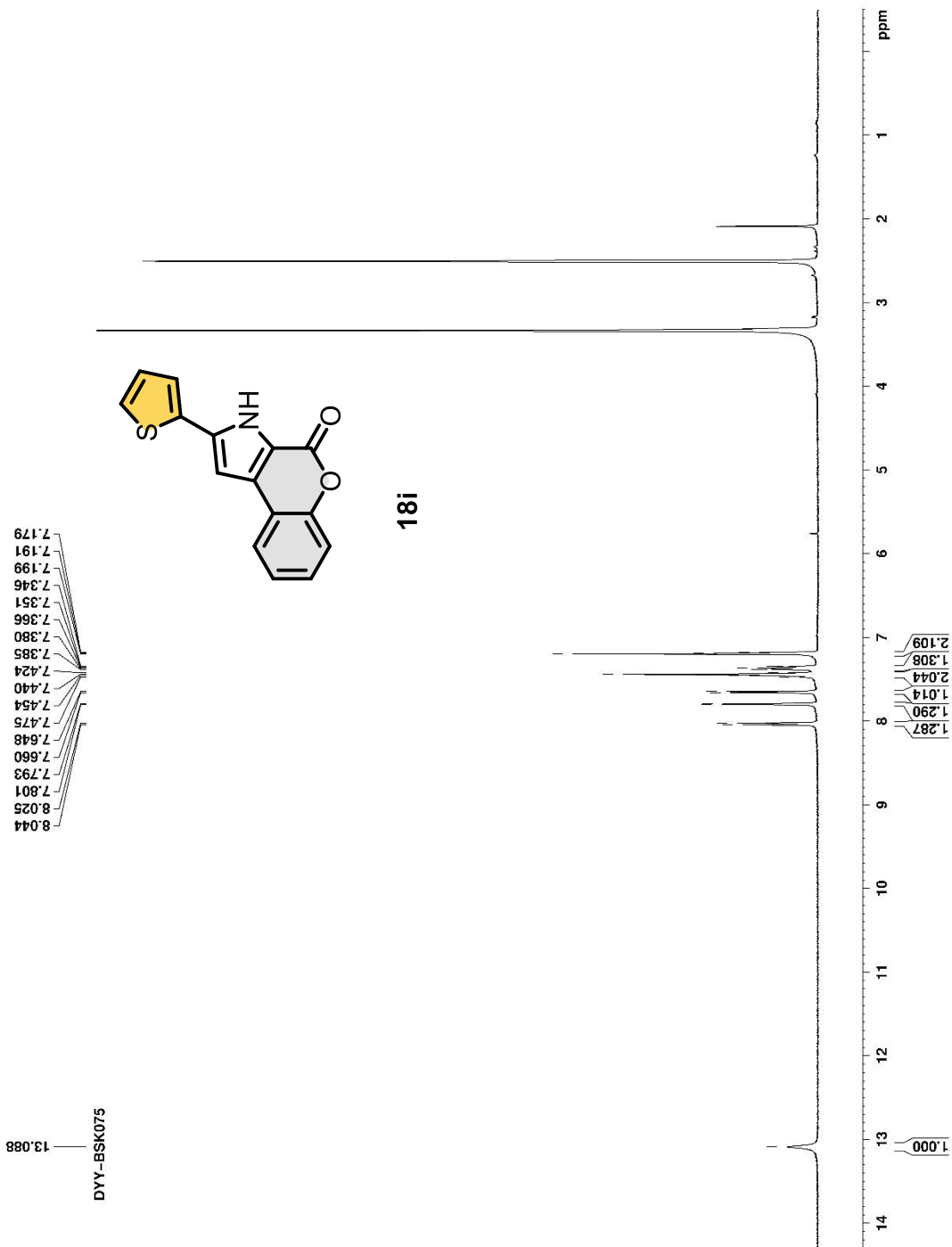


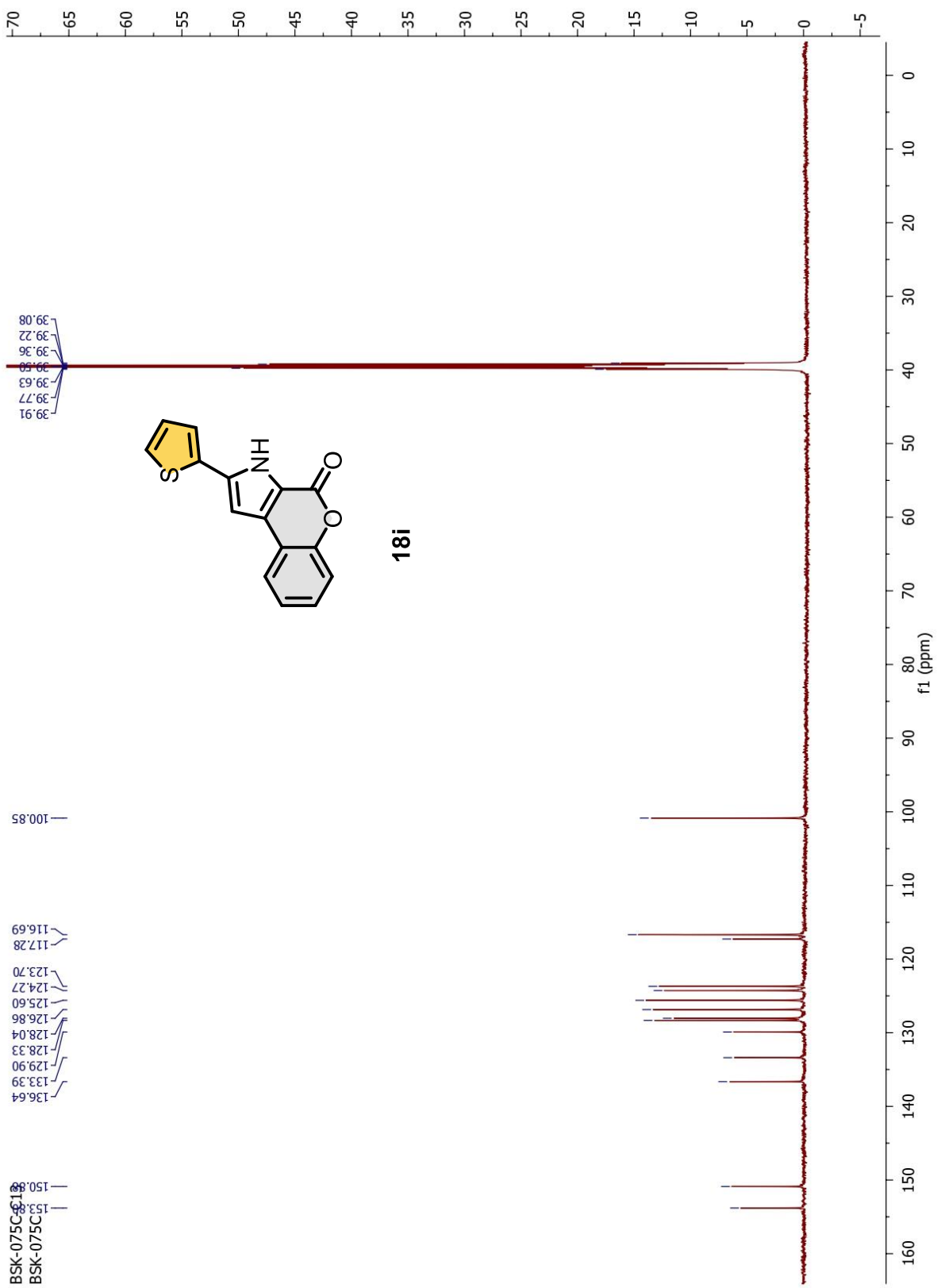


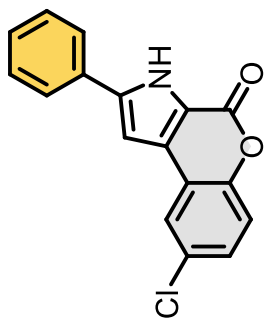




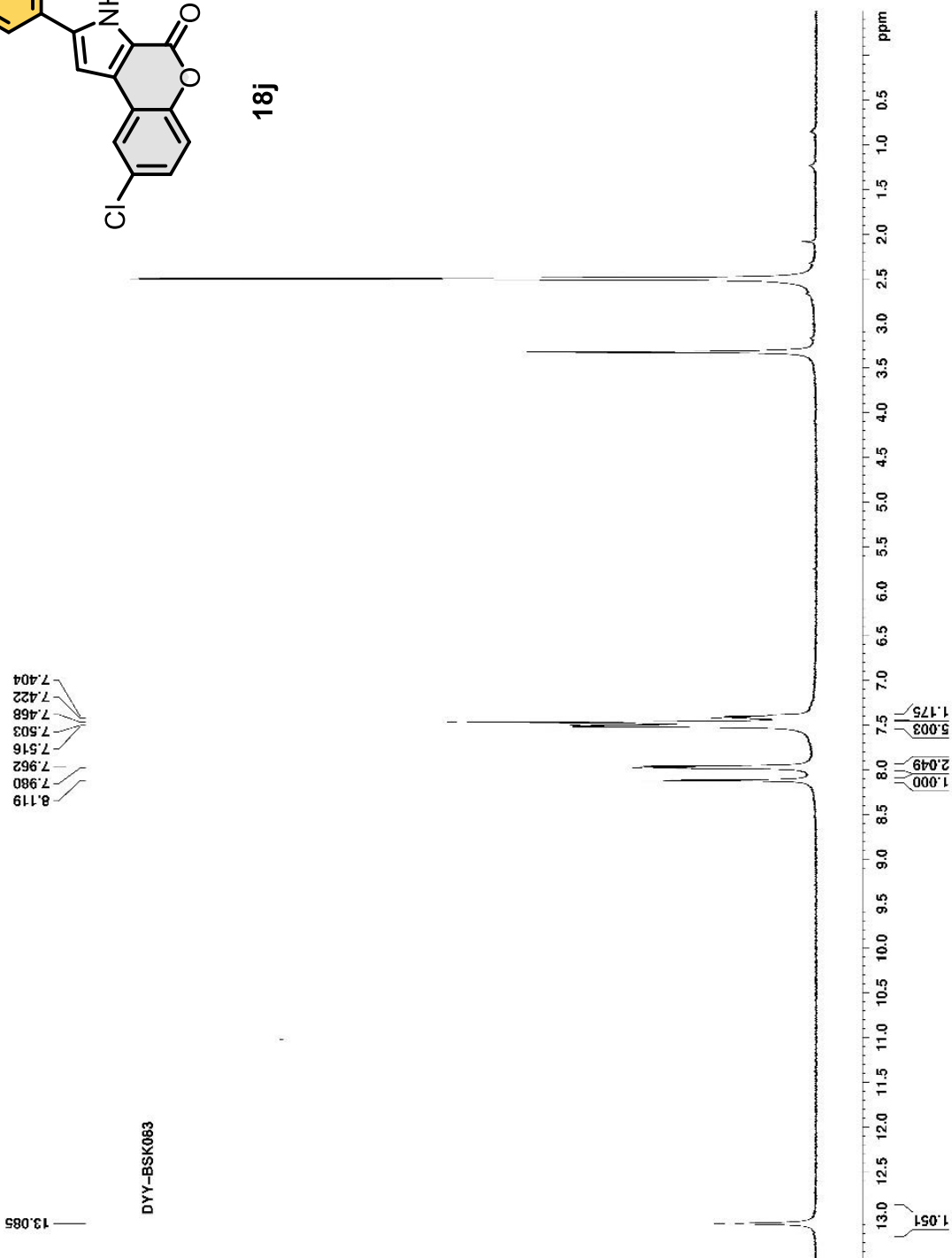


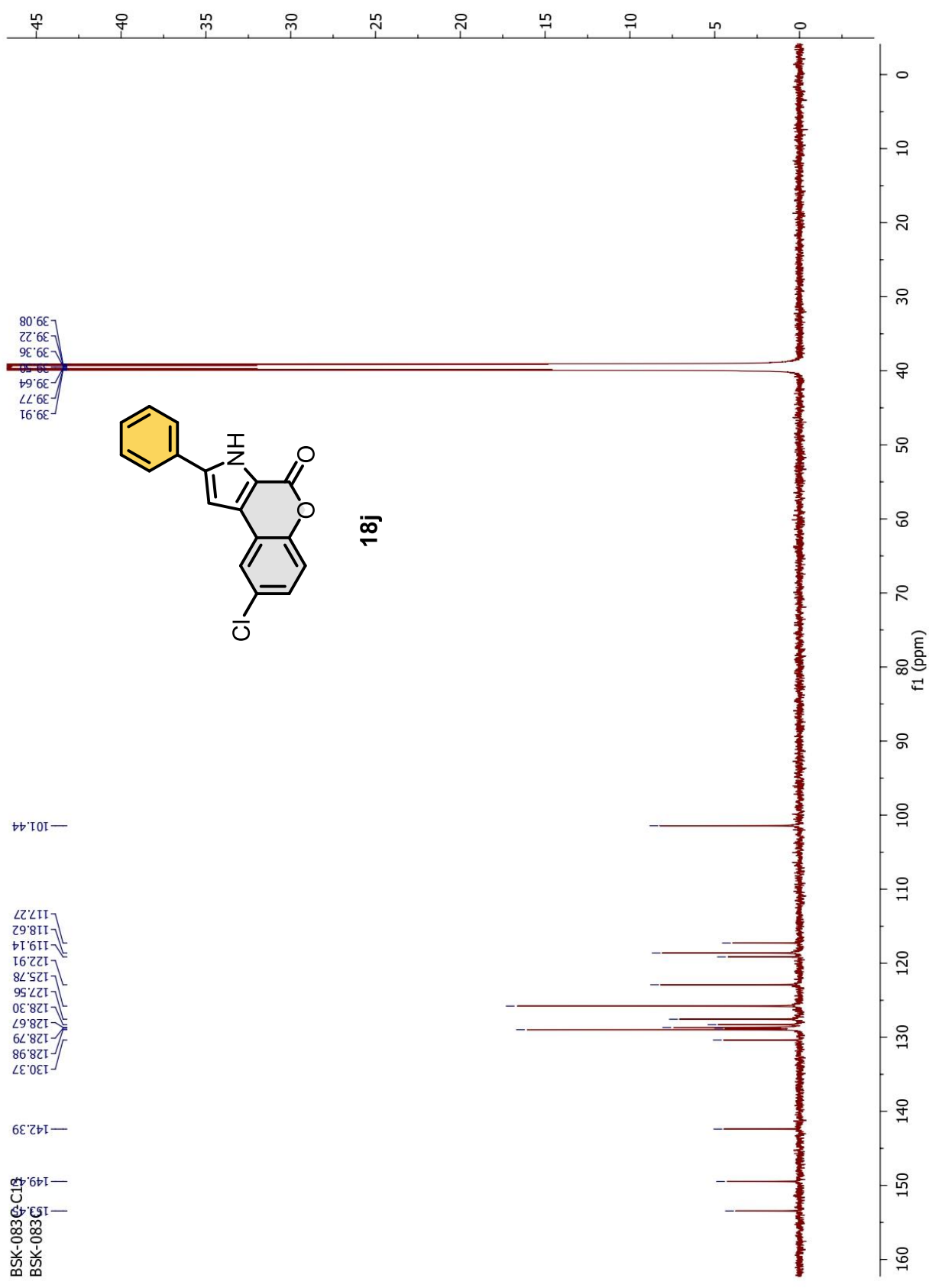


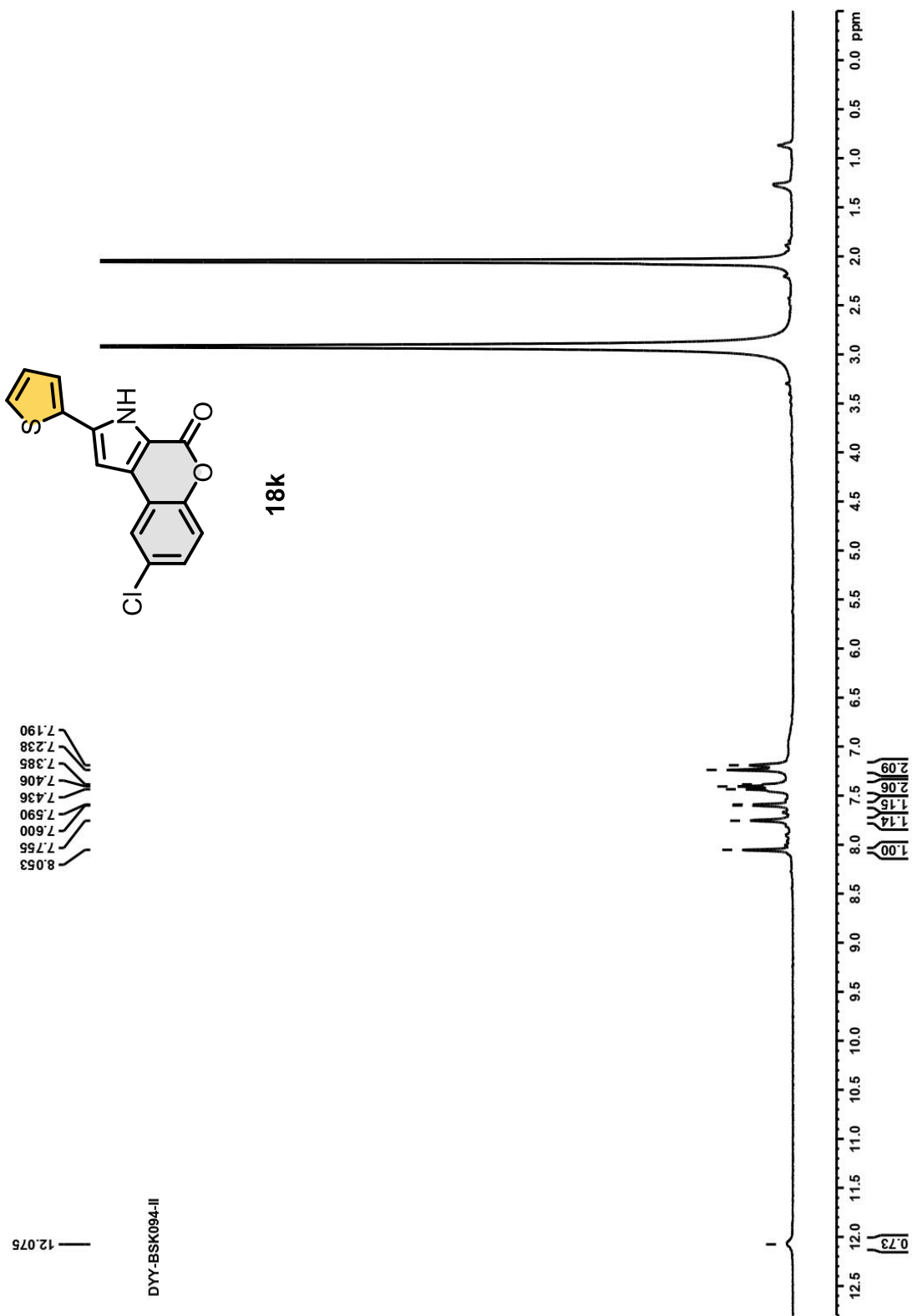


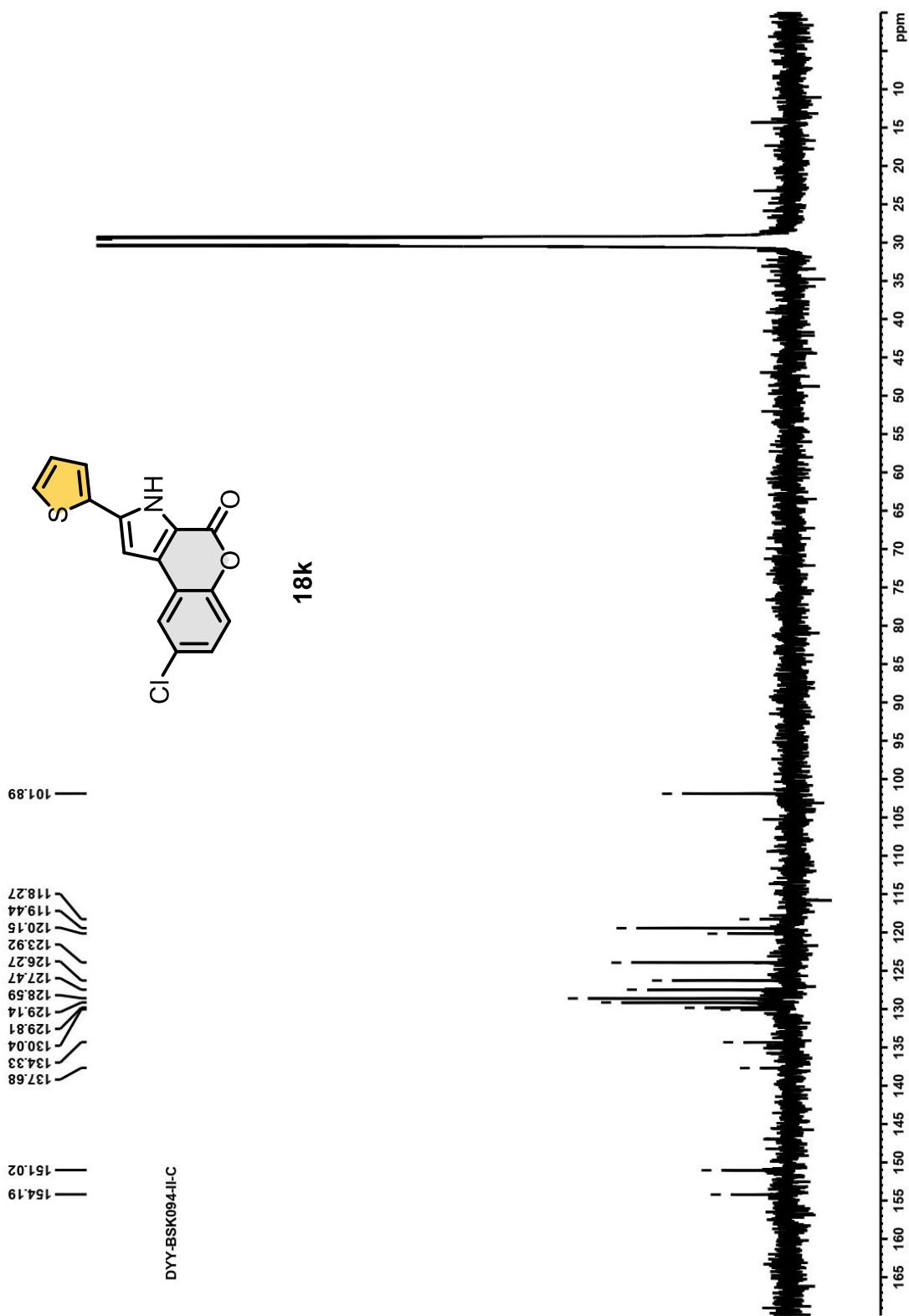


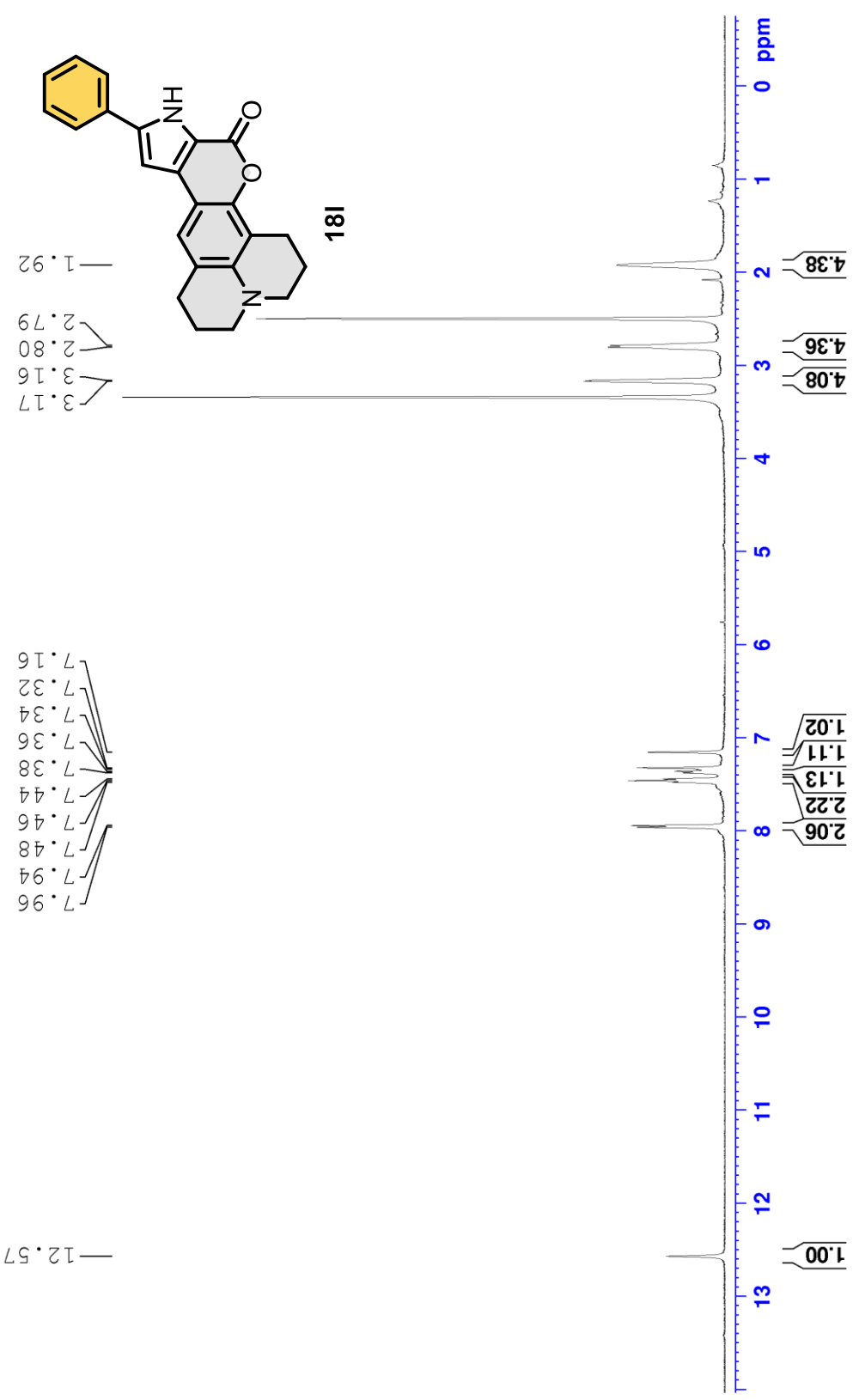
18j









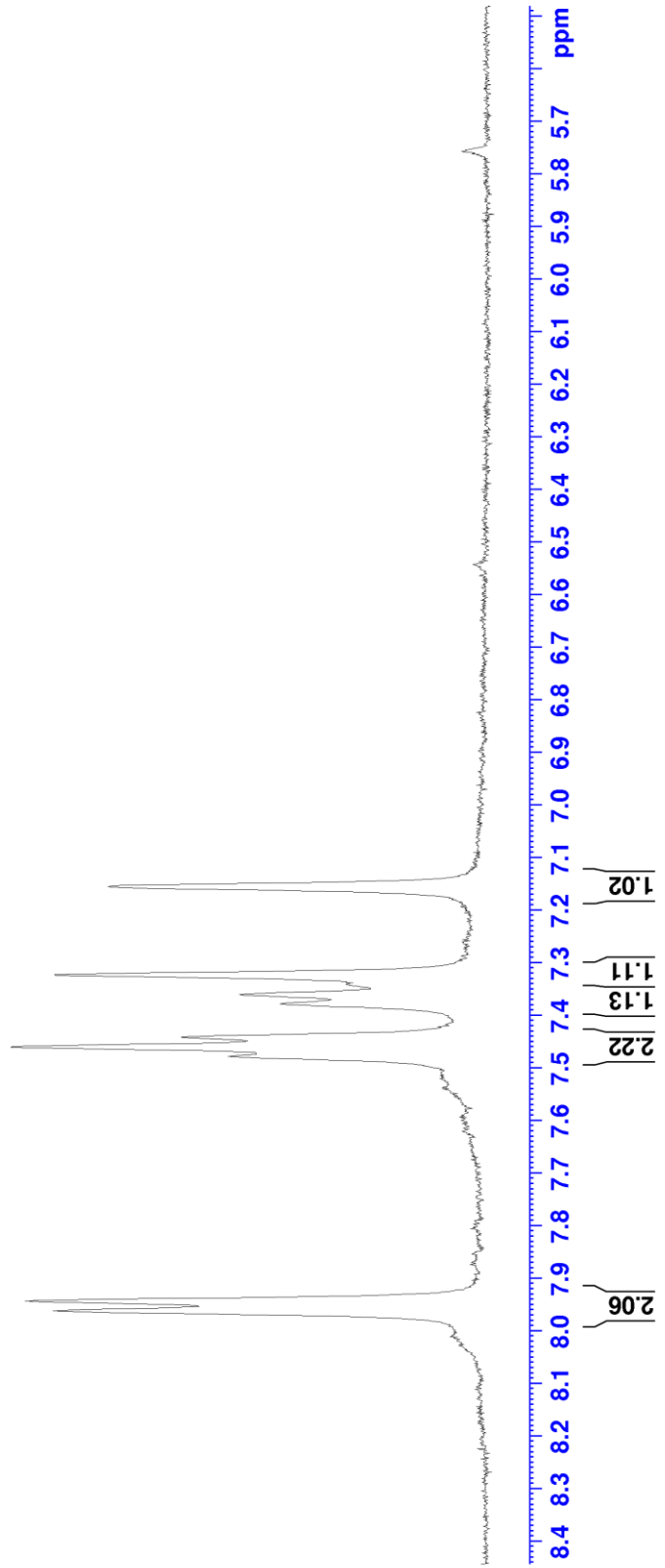


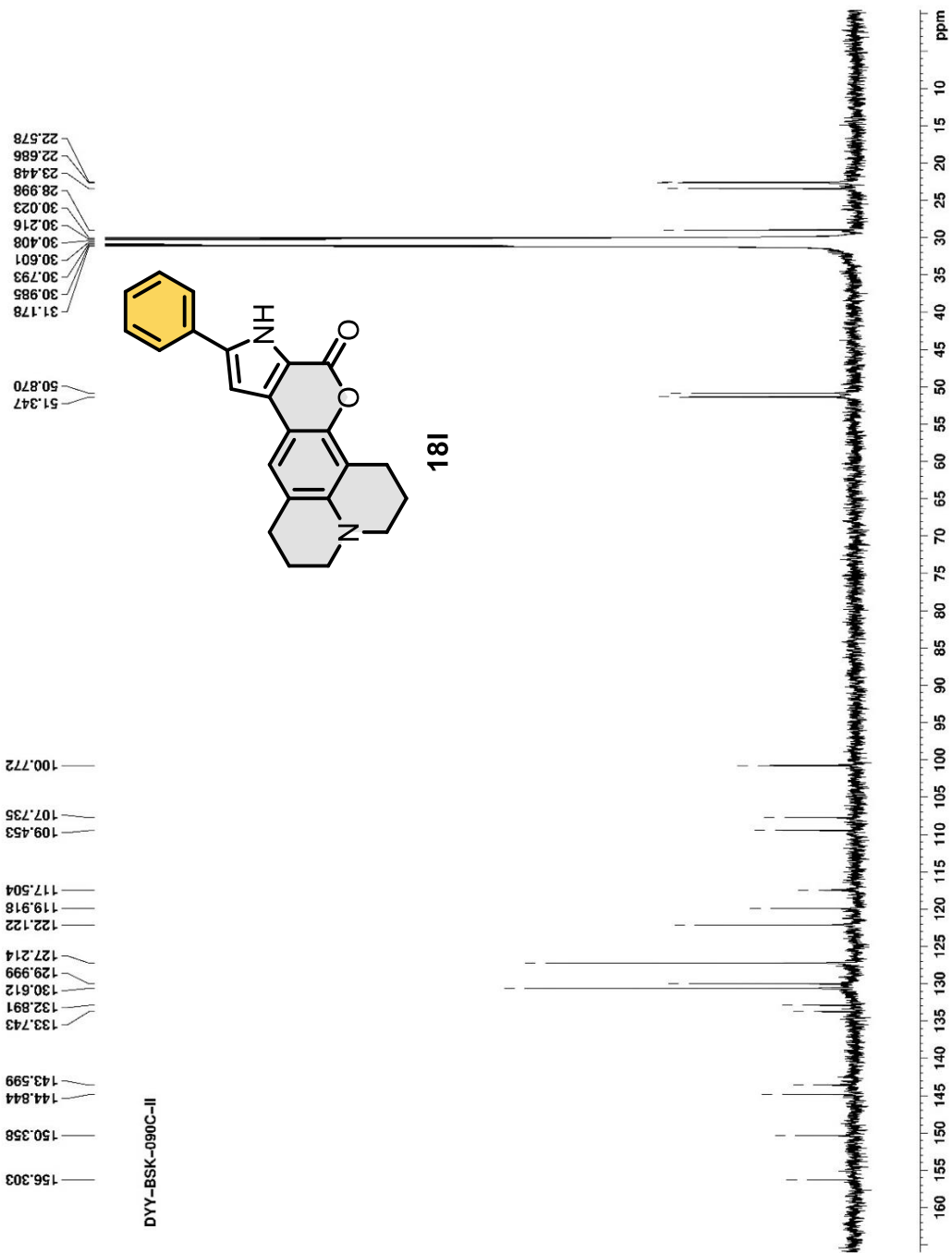
DYY-BSK090

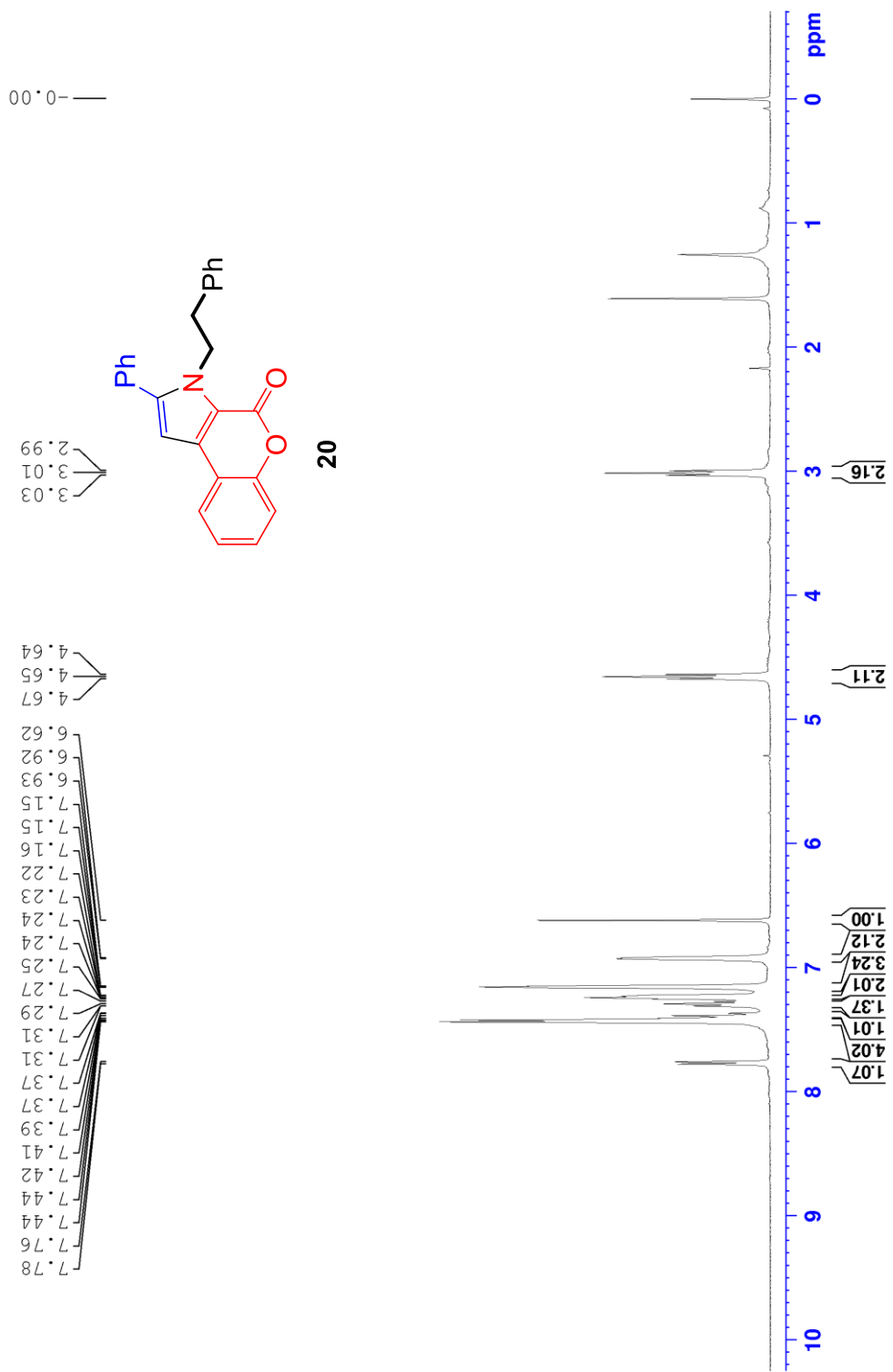
DYY-BSK090

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7.36
7.38
7.44
7.46
7.48

7.94
7.96

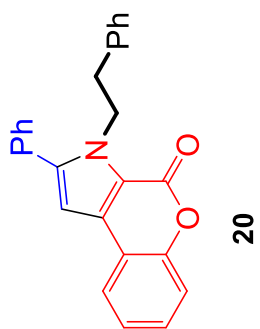




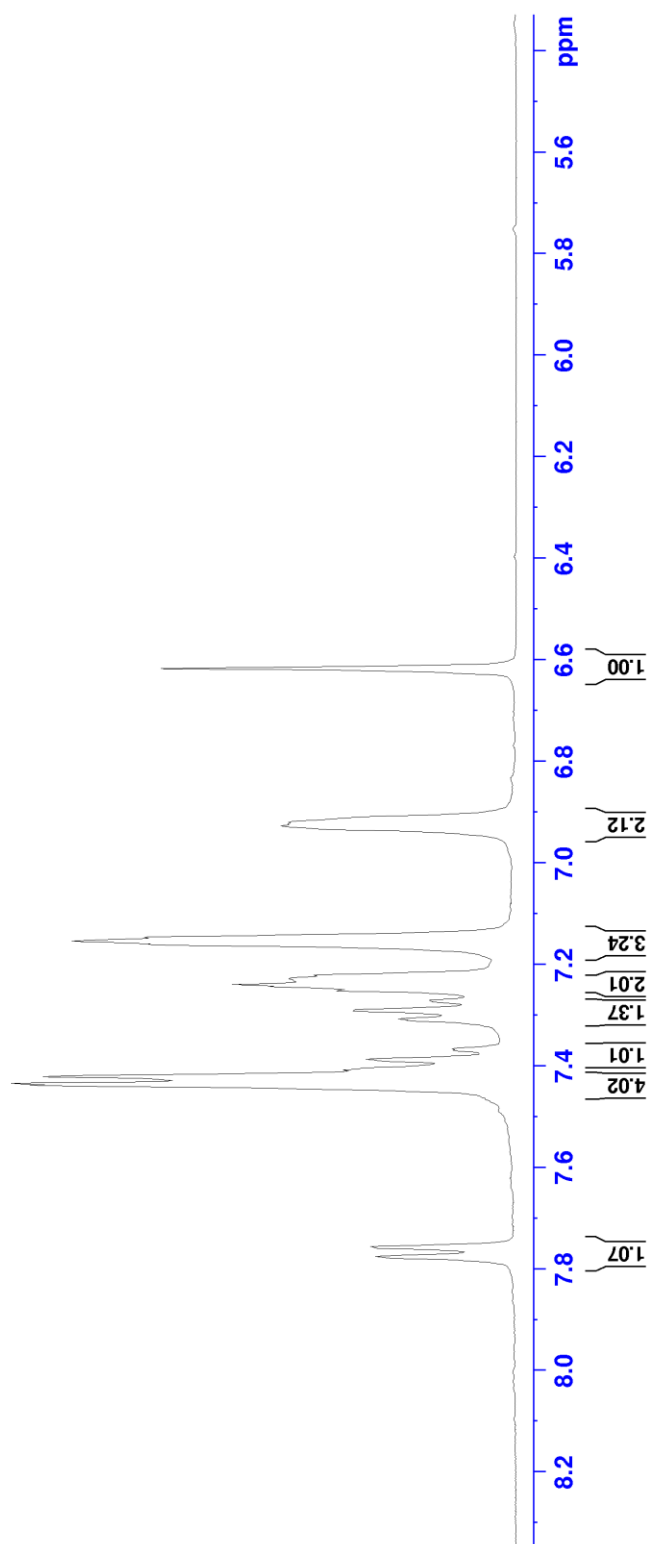


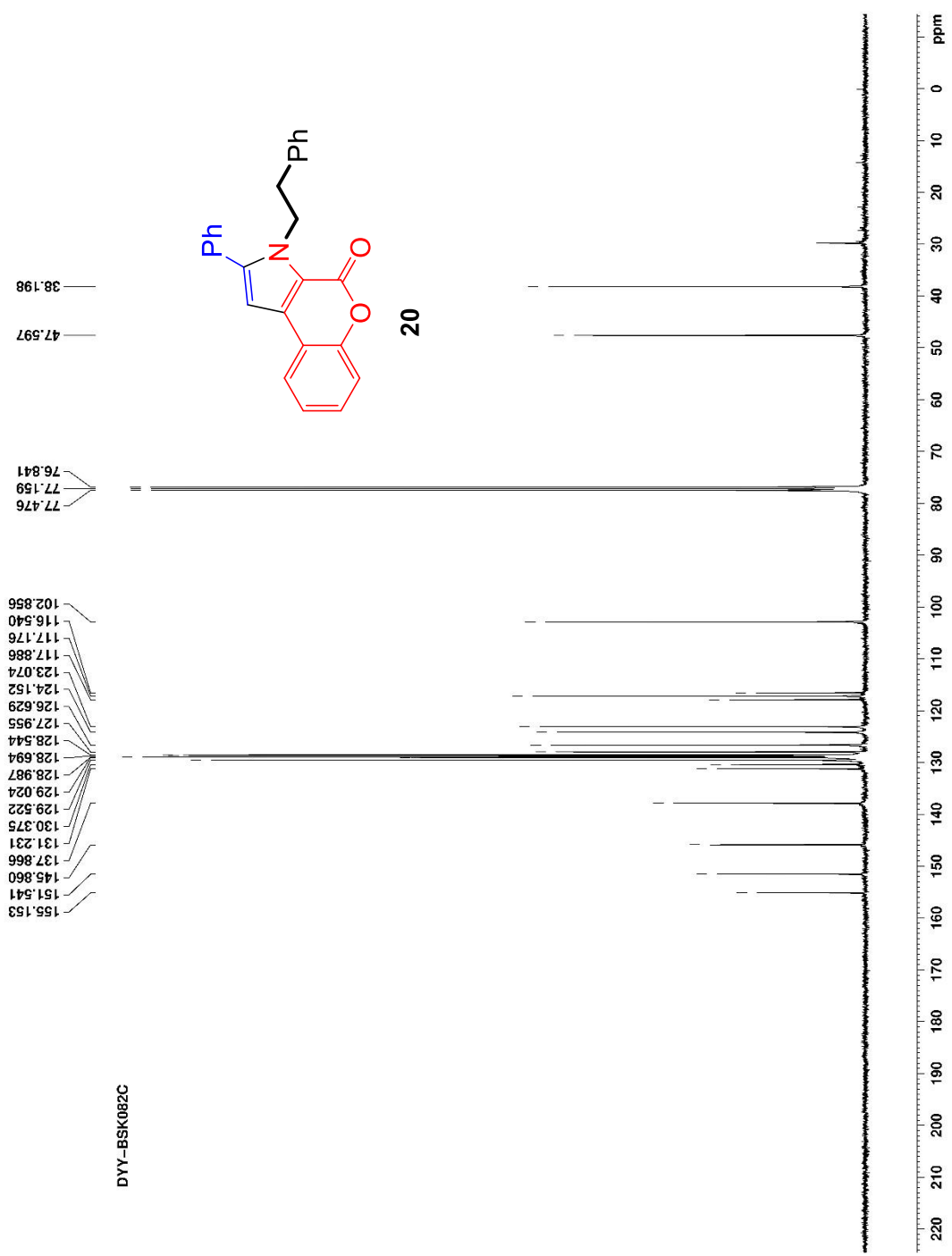
DYY-BSK082-II

DYY-BSK082-II



6.62
6.92
6.93
7.15
7.15
7.16
7.22
7.23
7.24
7.24
7.25
7.27
7.29
7.31
7.31
7.37
7.37
7.37
7.39
7.41
7.42
7.44
7.44
7.76
7.78





DYY-BSK082C