Supplementary Information for

Three-component coupling using arynes and DMF: Straightforward access to coumarins via *ortho*-quinone methides

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Contents

General remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian 400-MR (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer or a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. KF (spray-dried) was vacuum dried at 100 °C for 12 h. DMF was distilled from calcium hydride.

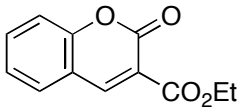
Aryne precursors.

2-(Trimethylsilyl)phenyl triflate (**1a**),[1] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1b**),[2] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1c**)[2] and 3-(trimethylsilyl)-2-naphthyl triflate (**1d**)[3] and 6-phenyl-2-(trimethylsilyl)phenyl triflate (**1e**)[4] were prepared according to literature procedures.

Three-component coupling using arynes and DMF: a general procedure.

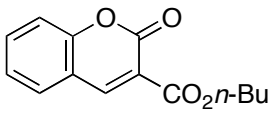
A Schlenk tube equipped with a magnetic stirring bar was charged with KF (0.80 mmol). The tube was evacuated at room temperature for 1 h with stirring before addition of DMF (4 mL), an ester (or a nitrile) (0.20 mmol), and an aryne precursor (0.40 mmol) under an argon atmosphere. The resulting mixture was stirred at 80 °C for the period as specified in Table 1, Table 2 and Scheme 2. The mixture was diluted with ethyl acetate and the organic solution was washed three times with brine. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. Silica gel-column chromatography (hexane/ethyl acetate or hexane/diethyl ether as an eluent) gave the corresponding product.

Ethyl 2-oxo-2*H*-chromene-3-carboxylate (3a)[5]



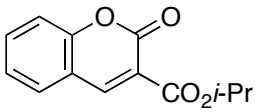
Isolated in 79% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ 1.40 (t, J = 7.0 Hz 3 H), 4.41 (q, J = 7.0 Hz 2 H), 7.31-7.36 (m, 2 H), 7.60-7.65 (m, 2 H), 8.52 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 61.9, 116.7, 117.8, 118.2, 124.8, 129.4, 134.3, 148.6, 155.1, 156.7, 163.0.

Butyl 2-oxo-2*H*-chromene-3-carboxylate (3b)[6]



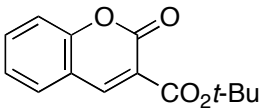
Isolated in 87% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 0.97 (t, J = 7.5 Hz 3 H), 1.45 (quint, J = 7.5 Hz, 2 H), 1.76 (q, J = 7.5 Hz, 2 H), 4.35 (q, J = 7.5 Hz, 2 H), 7.32-7.36 (m, 2 H), 7.60-7.66 (m, 2 H), 8.51 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.2, 30.6, 65.8, 116.8, 117.9, 118.5, 124.8, 129.5, 134.3, 148.5, 155.2, 156.7, 163.2.

Isopropyl 2-oxo-2*H*-chromene-3-carboxylate (3c)[7]



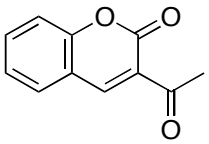
Isolated in 79% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 1.38 (d, J = 6.0 Hz, 1 H), 5.26 (sept, J = 6.0 Hz, 1 H), 7.31-7.35 (m, 2 H), 7.59-7.65 (m, 2 H), 8.46 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.8, 69.6, 116.7, 117.8, 118.7, 124.7, 129.4, 134.2, 148.0, 155.1, 156.7, 162.4.

***tert*-Butyl 2-oxo-2*H*-chromene-3-carboxylate (3d)**[8]



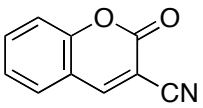
Isolated in 72% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 9 H), 7.30-7.36 (m, 2 H), 7.58-7.64 (m, 2 H), 8.40 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.6, 80.3, 114.2, 115.4, 117.2, 122.1, 126.7, 131.4, 144.9, 152.5, 154.3, 159.4.

3-Acetyl-2*H*-chromen-2-one (3e)[5]



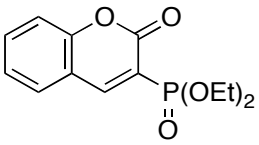
Isolated in 55% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 3 H), 7.34-7.38 (m, 2 H), 7.64-7.67 (m, 2 H), 8.51 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.3, 117.4, 118.9, 125.2, 125.7, 130.9, 135.1, 148.2, 156.0, 160.0, 196.2.

2-Oxo-2*H*-chromene-3-carbonitrile (3f)[5]



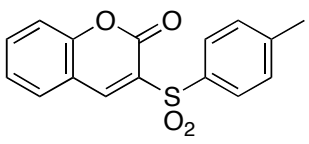
Isolated in 39% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.40-7.43 (m, 2 H), 7.62 (dd, J = 8.0, 2.0 Hz, 1 H), 7.73 (td, J = 7.2, 1.5 Hz, 1 H), 8.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 103.3, 113.5, 117.1, 117.4, 125.7, 129.3, 135.6, 151.8, 154.6, 156.4.

Diethyl 2-oxo-2*H*-chromen-3-ylphosphonate (3g)[9]



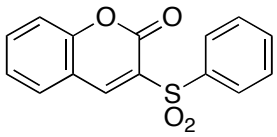
Isolated in 74% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.0 Hz, 6 H), 4.19-4.31 (m, 4 H), 7.30-7.34 (m, 2 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.62 (td, J = 8.0, 1.5 Hz, 1 H), 8.49 (d, J = 17 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, $J_{C\text{-}P}$ = 6.5 Hz), 63.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 116.8 (d, $J_{C\text{-}P}$ = 0.9 Hz), 117.4 (d, $J_{C\text{-}P}$ = 103.7 Hz), 118.2 (d, $J_{C\text{-}P}$ = 79.1 Hz), 124.8, 129.3, 134.2, 153.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 155.2 (d, $J_{C\text{-}P}$ = 0.9 Hz), 158.2 (d, $J_{C\text{-}P}$ = 14.5 Hz).

3-Tosyl-2*H*-chromen-2-one (3h)[10]



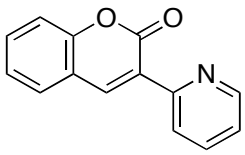
Isolated in 53% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 7.34 (d, *J* = 8.0 Hz, 3 H), 7.39 (td, *J* = 7.7, 1.0 Hz, 1 H), 7.66-7.71 (m, 2 H), 8.01 (dd, *J* = 6.5, 1.5 Hz, 2 H), 8.78 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 117.0, 117.3, 125.3, 128.8, 129.4, 129.6, 130.2, 135.1, 135.3, 145.4, 147.0, 154.9, 155.4.

3-(Phenylsulfonyl)-2*H*-chromen-2-one (3i)[10]



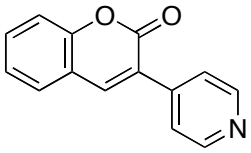
Isolated in 44% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 1 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 7.64-7.68 (m, 1 H), 7.71 (t, *J* = 7.5 Hz, 2 H), 8.14 (d, *J* = 8.5 Hz, 2 H), 8.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 117.0, 117.2, 125.4, 128.4, 129.0, 129.4, 130.3, 134.2, 135.2, 138.3, 147.4, 154.8, 155.4.

3-(Pyridin-2-yl)-2*H*-chromen-2-one (3j)[11]



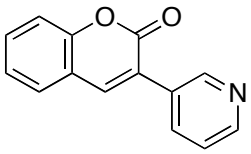
Isolated in 95% yield as a brown solid: ^{1}H NMR ($CDCl_3$) δ 7.31-7.34 (m, 2 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 7.56-7.60 (m, 1 H), 7.66 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.812 (td, J= 7.7, 1.5 Hz, 1 H), 8.43 (d, *J* = 8.0 Hz, 1 H), 8.70 (d, *J* = 5.0 Hz, 1 H), 8.80 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.3, 119.5, 123.4, 124.0, 124.6, 125.3, 128.8, 132.1, 136.6, 142.4, 149.3, 151.2, 153.8, 160.2.

3-(Pyridin-4-yl)-2*H*-chromen-2-one (3k)[12]



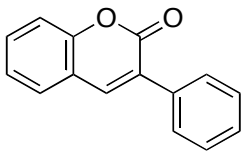
Isolated in 70% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 1 H), 7.39 (d, *J* = 9 Hz, 1 H), 7.56-7.62 (m, 2 H), 7.66 (dd, *J* = 4.5, 1.5, 2 H), 7.96 (s, 1 H), 8.70 (d, *J* = 4.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 119.1, 122.7, 124.9, 125.6, 128.4, 132.6, 141.5, 142.1, 150.1, 153.9, 159.7.

3-(Pyridin-3-yl)-2*H*-chromen-2-one (3l)[13]



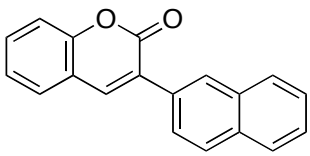
Isolated in 28% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.34 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.39-7.41 (m, 2 H), 7.57-7.60 (m, 2 H), 7.90 (s, 1 H), 8.14 (dt, *J* = 8.0, 1.7 Hz, 1 H), 8.65 (s, 1 H), 8.88 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 119.3, 123.1, 124.8, 125.3, 128.2, 132.1, 136.2, 140.5, 148.9, 149.9, 153.7, 160.2.

3-Phenyl-2*H*-chromen-2-one (3m)[14]



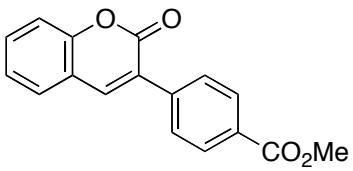
Isolated in 60% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.29-7.32 (m, 1 H), 7.37-7.46 (m, 4 H), 7.52-7.56 (m, 2 H), 7.70-7.72 (m, 2 H), 7.82 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.5, 119.7, 124.5, 127.9, 128.4, 128.5, 128.6, 128.9, 129.1, 131.4, 134.7, 139.9, 153.5, 160.6.

3-(Naphthalen-2-yl)-2*H*-chromen-2-one (3n)[15]



Isolated in 66% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 7.50-7.53 (m, 2 H), 7.56 (t, *J* = 8.0 Hz, 2 H), 7.80 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.85-7.88 (m, 1 H), 7.90-7.93 (m, 3 H), 8.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.5, 119.7, 124.5, 125.9, 126.4, 126.7, 127.6, 127.9, 128.0, 128.1, 128.2, 128.5, 131.4, 132.1, 133.1, 133.3, 140.1, 153.5, 160.7.

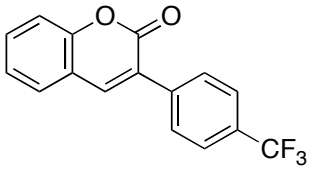
Methyl 4-(2-oxo-2*H*-chromen-3-yl)benzoate (3o)[5]



Isolated in 99% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 3.94 (s, 3 H), 7.32 (t, *J* = 7.5 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.56 (t, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 7.0 Hz, 2 H),

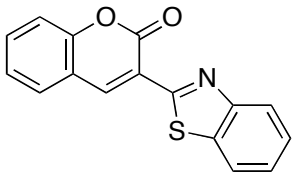
7.89 (s, 1 H), 8.11 (d, *J* = 6.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 52.2, 116.5, 119.4, 124.7, 127.2, 128.1, 128.5, 129.7, 130.2, 132.0, 139.1, 140.8, 153.6, 160.1, 166.6.

3-(4-(Trifluoromethyl)phenyl)-2*H*-chromen-2-one (3p)



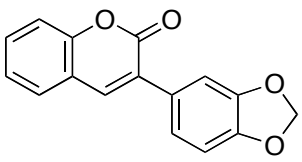
Isolated in 68% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.34 (t, *J* = 8.0 Hz, 1 H), 7.38 (d, *J* = 8.5 Hz, 1 H), 7.57 (td, J = 6.7, 2.0 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H), 7.88 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.6, 119.3, 124.0 (q, $J_{C\text{-}F}$ = 271.6 Hz), 124.7, 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.9, 128.2, 128.9, 130.7 (q, $J_{C\text{-}F}$ = 46.9 Hz), 132.1, 138.1, 140.9, 153.7, 160.2; HRMS Calcd for $C_{16}H_9F_3O_2Na$: $[M+Na]^+$, 313.0447. Found: *m/z* 313.0448.

3-(Benzo[*d*]thiazol-2-yl)-2*H*-chromen-2-one (3q)[11]



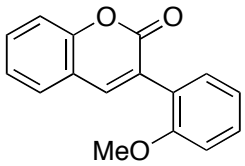
Isolated in 64% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.36-7.44 (m, 3 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 1 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 8.08 (d, *J* = 8.5 Hz, 1 H), 9.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 118.9, 120.3, 121.7, 122.9, 125.2, 125.4, 126.5, 129.3, 133.2, 136.8, 141.4, 152.4, 153.8, 159.76, 159.83.

3-(Pyridin-2-yl)-2*H*-chromen-2-one (3r)[16]



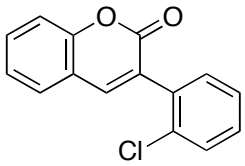
Isolated in 40% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 6.04 (s, 2 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 7.22-7.40 (m, 4 H), 7.54 (t, *J* = 7.5 Hz, 2 H), 7.78 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 101.3, 108.3, 109.1, 116.4, 119.7, 122.5, 124.5, 127.7, 127.9, 128.6, 131.2, 139.0, 147.7, 148.2, 153.3, 160.6.

3-(2-Methoxyphenyl)-2*H*-chromen-2-one (3s)[17]



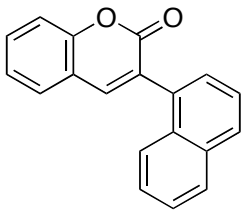
Isolated in 39% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 6.99 (d, *J* = 8.5 Hz, 1 H), 7.03 (t, *J* = 7.2 Hz, 1 H), 7.28 (t, *J* = 7.0 Hz, 1 H), 7.36-7.41 (m, 3 H), 7.50-7.54 (m, 2 H), 7.74 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.7, 111.3, 116.5, 119.5, 120.6, 124.1, 124.2, 126.6, 127.8, 130.2, 130.7, 131.1, 141.7, 153.7, 157.2, 160.3.

3-(2-Chlorophenyl)-2*H*-chromen-2-one (3t)[18]



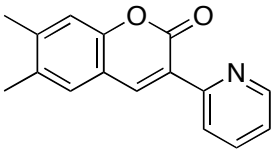
Isolated in 31% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.31-7.43 (m, 5 H), 7.45-7.51 (m, 1 H), 7.54-7.56 (m, 2 H), 7.76 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 119.0, 124.6, 126.8, 127.1, 128.1, 129.9, 130.0, 131.3, 131.9, 133.6, 133.7, 142.7, 153.9, 159.8.

3-(Naphthalen-1-yl)-2*H*-chromen-2-one (3u)[19]



Isolated in 30% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 1 H), 7.44-7.56 (m, 6 H), 7.59 (t, *J* = 7.0 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.83 (s, 1 H), 7.92 (t, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 119.3, 124.6, 125.1, 125.2, 126.1, 126.5, 127.6, 127.9, 128.4, 128.5, 129.4, 131.5, 131.7, 132.6, 133.7, 142.8, 154.0, 160.8.

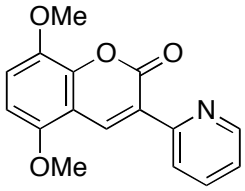
6,7-Dimethyl-3-(pyridin-2-yl)-2*H*-chromen-2-one (4a)



Isolated in 99% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 2.37 (s, 3 H), 7.15 (s, 1 H), 7.26-7.28 (m, 1 H), 7.35 (s, 1 H), 7.77 (td, *J* = 7.7, 1.5 Hz, 1 H), 8.39 (d, *J* = 7.5 Hz, 1 H), 8.66-8.67 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.2, 20.5, 116.8, 117.3, 123.1,

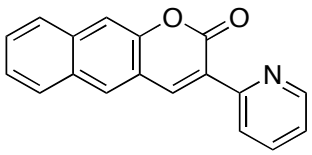
123.9, 124.0, 128.7, 133.4, 136.6, 142.5, 142.6, 149.2, 151.6, 152.4, 160.7; HRMS Calcd for $C_{16}H_{13}NO_2Na$: $[M+Na]^+$, 274.0839. Found: *m/z* 274.0844.

5,8-Dimethoxy-3-(pyridin-2-yl)-2*H*-chromen-2-one (4b)



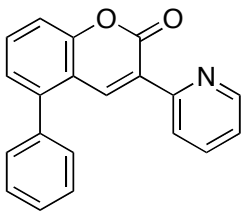
Isolated in 91% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3 H), 3.94 (s, 3 H), 6.63 (d, *J* = 9.0 Hz, 1 H), 7.03 (d, *J* = 8.5 Hz, 1 H), 7.26-7.29 (m, 1 H), 7.76 (td, J = 7.5, 2.0 Hz, 1 H), 8.69 (d, *J* = 4.0 Hz, 1 H), 8.40 (d, *J* = 8.0 Hz, 1 H), 9.09 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.9, 56.8, 104.0, 111.2, 114.9, 123.2, 123.7, 124.0, 136.6, 138.0, 140.9, 144.3, 149.3, 150.4, 151.6, 159.6; HRMS Calcd for $C_{16}H_{13}NO_4Na$: $[M+Na]^+$, 306.0737. Found: *m/z* 306.0739.

3-(Pyridin-2-yl)-2*H*-benzo[*g*]chromen-2-one (4c)



Isolated in 39% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.32 (qd, *J* = 4.5, 1.0 Hz, 1 H), 7.49 (td, *J* = 7.0, 1.0 Hz, 1 H), 7.58 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.74 (s, 1 H), 7.80 (td, J = 8.0, 1.5 Hz, 1 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 8.15 (s, 1 H), 8.41 (d, *J* = 8.0 Hz, 1 H), 8.71 (d, *J* = 4.2 Hz, 1 H), 8.87 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.2, 119.6, 123.5, 124.2, 125.8, 125.9, 127.6, 128.4, 128.6, 129.4, 130.3, 134.8, 136.7, 142.3, 149.4, 150.2, 151.3, 160.3; HRMS Calcd for $C_{18}H_{11}NO_2Na$: $[M+Na]^+$, 296.0682. Found: *m/z* 296.0686.

5-Phenyl-3-(pyridin-2-yl)-2*H*-chromen-2-one (4d)



Isolated in 88% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.22-7.27 (m, 1 H), 7.30 (dd, *J* = 7.5, 0.5 Hz, 1 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 7.43-7.55 (m, 5 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.75 (td, *J* = 7.5, 2.0 Hz, 1 H), 8.32 (d, *J* = 8.0 Hz, 1 H), 8.58 (dq, *J* = 5.0, 1.0 Hz, 1

H), 8.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 115.5, 117.5, 123.3, 124.1, 125.9, 128.2, 128.7, 129.9, 131.6, 136.5, 138.1, 141.0, 142.5, 149.4, 151.6, 154.5, 160.2; HRMS Calcd for $C_{20}H_{13}NO_2Na$: $[M+Na]^+$, 322.0839. Found: *m/z* 322.0843.

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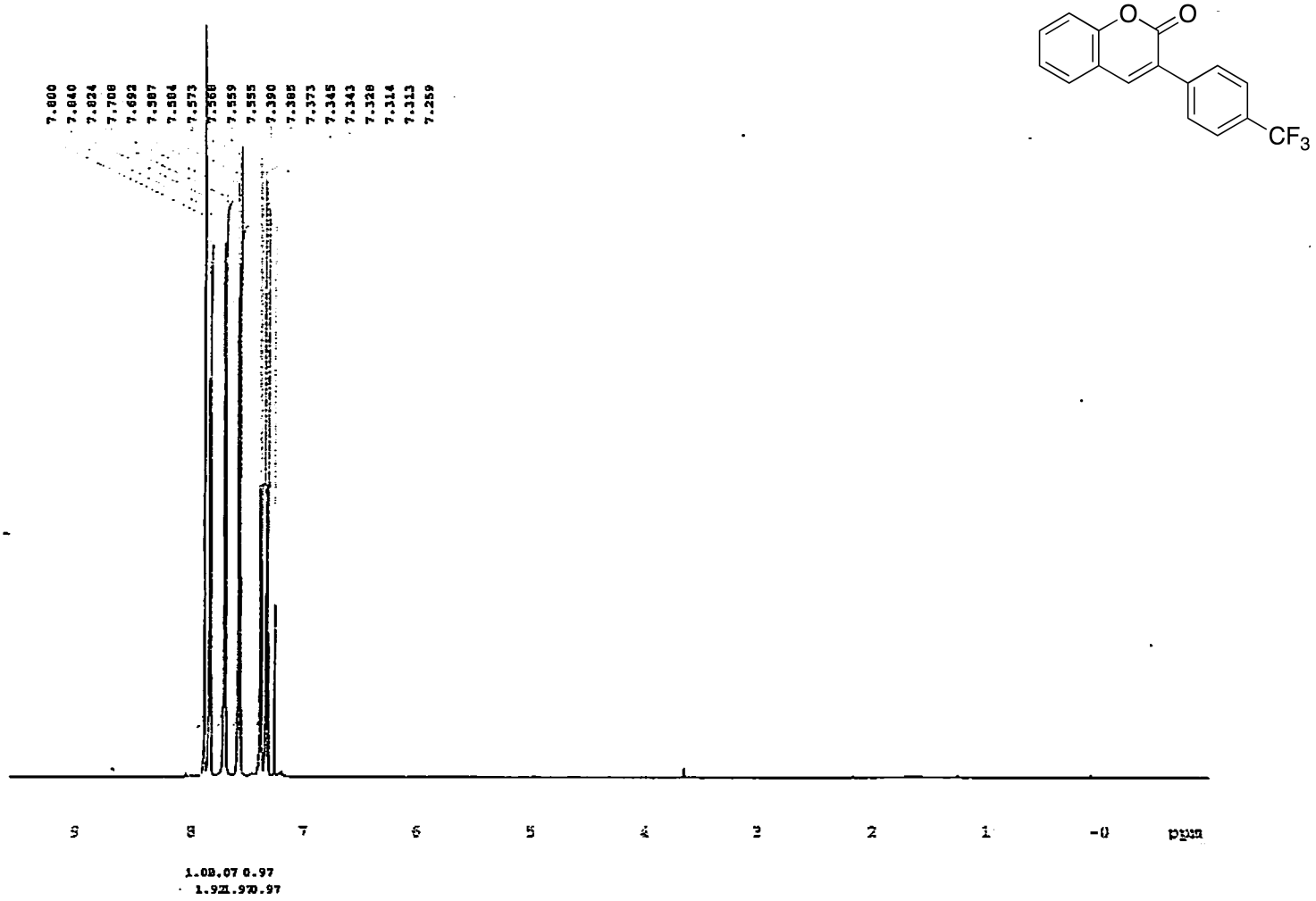
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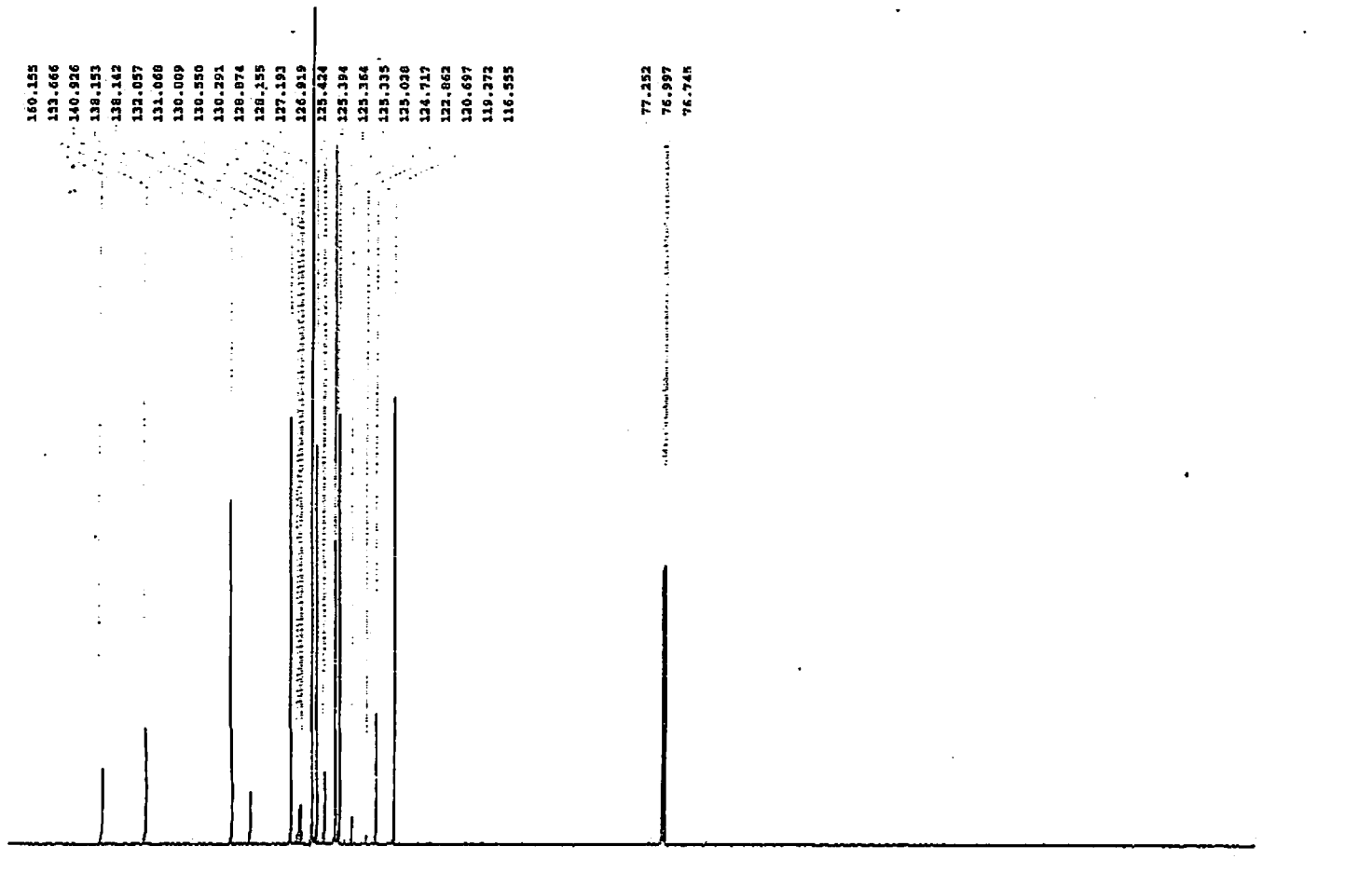
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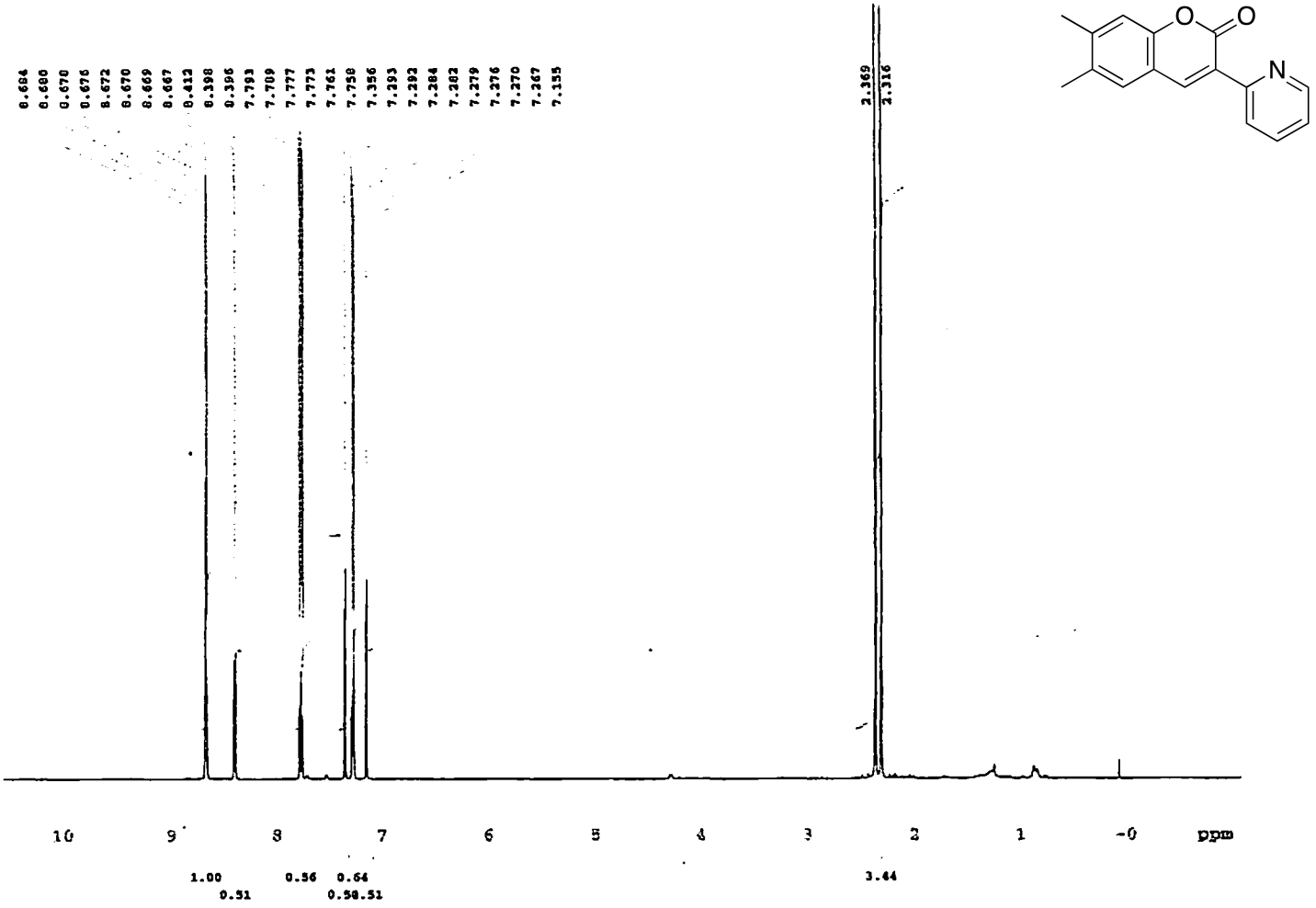
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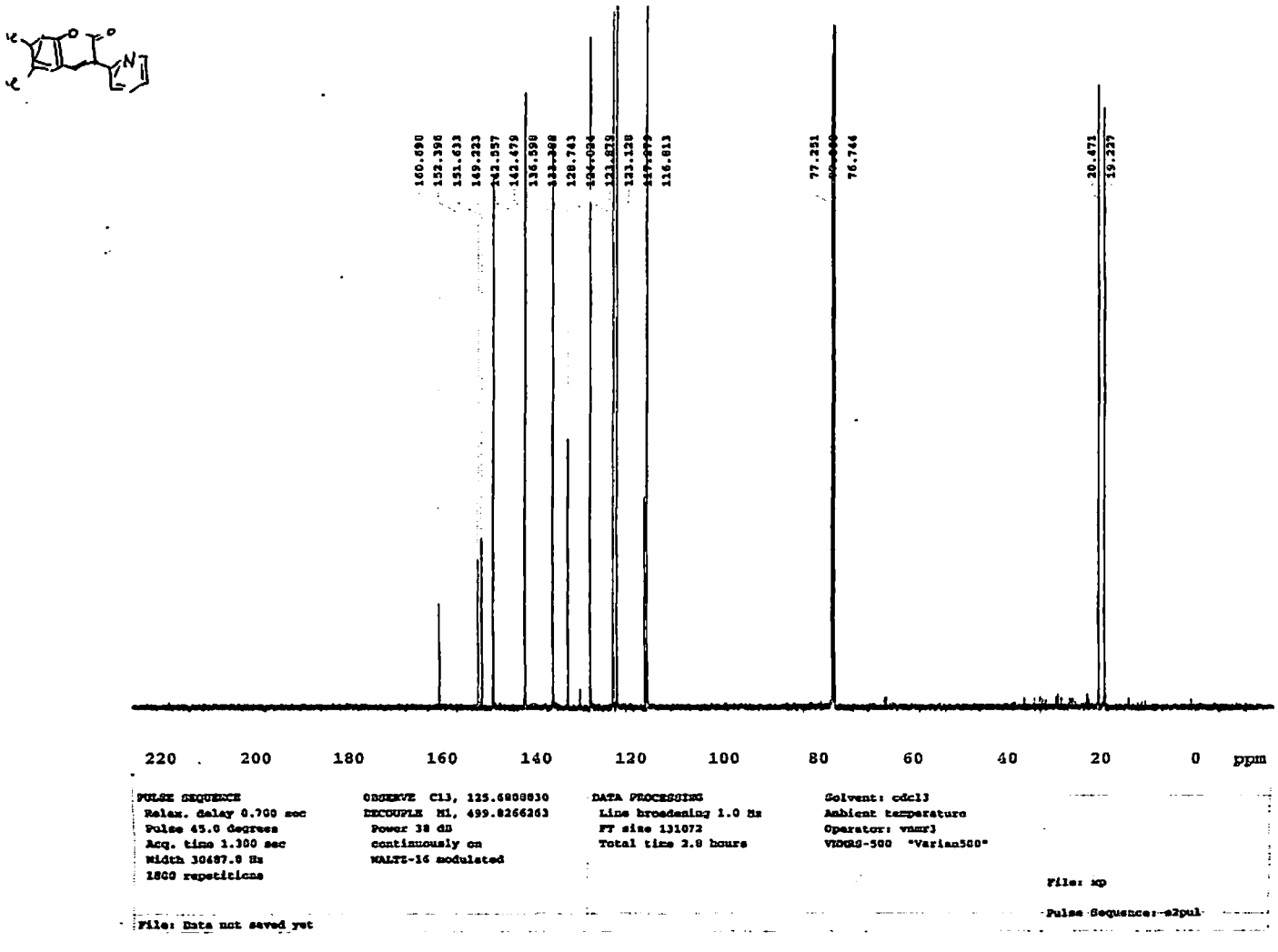
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100
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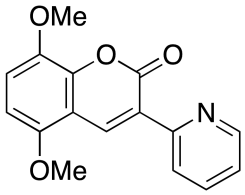
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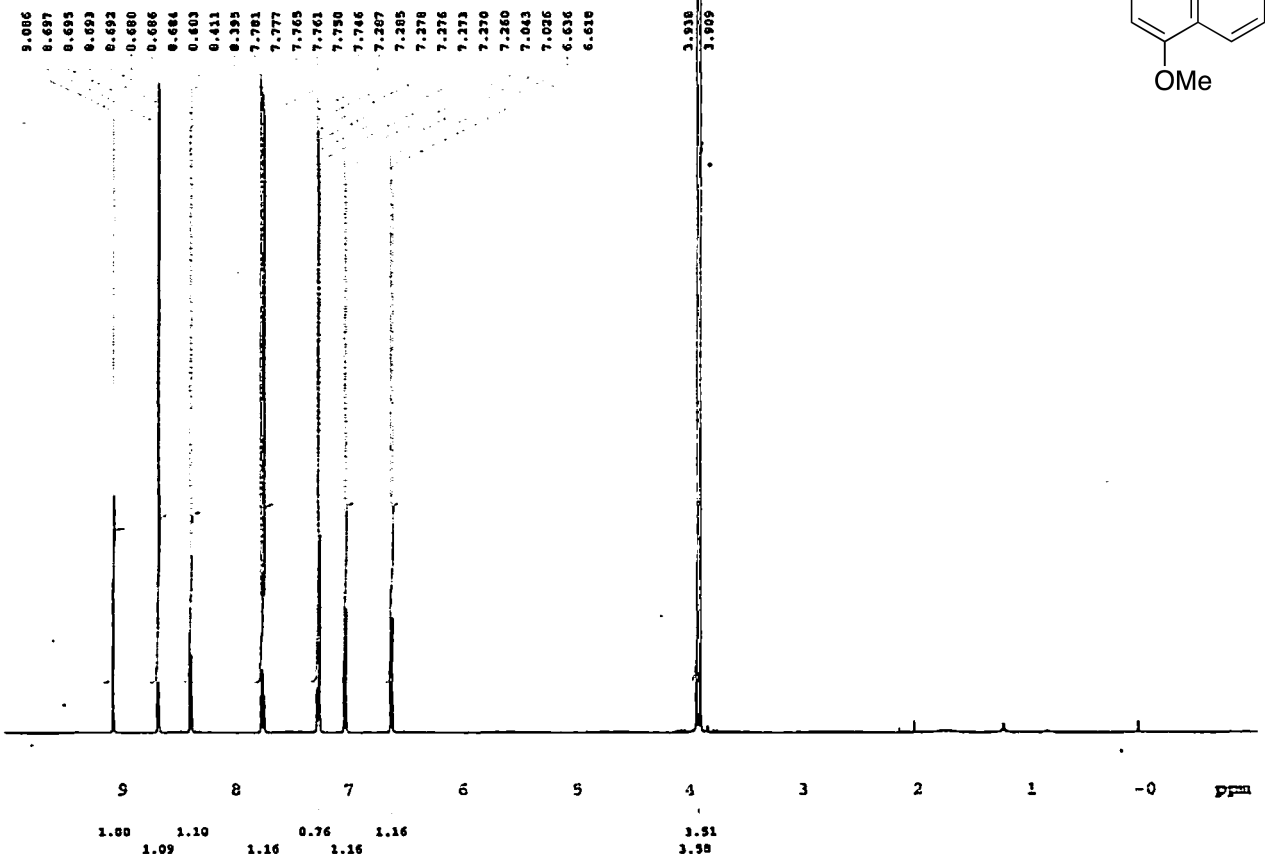
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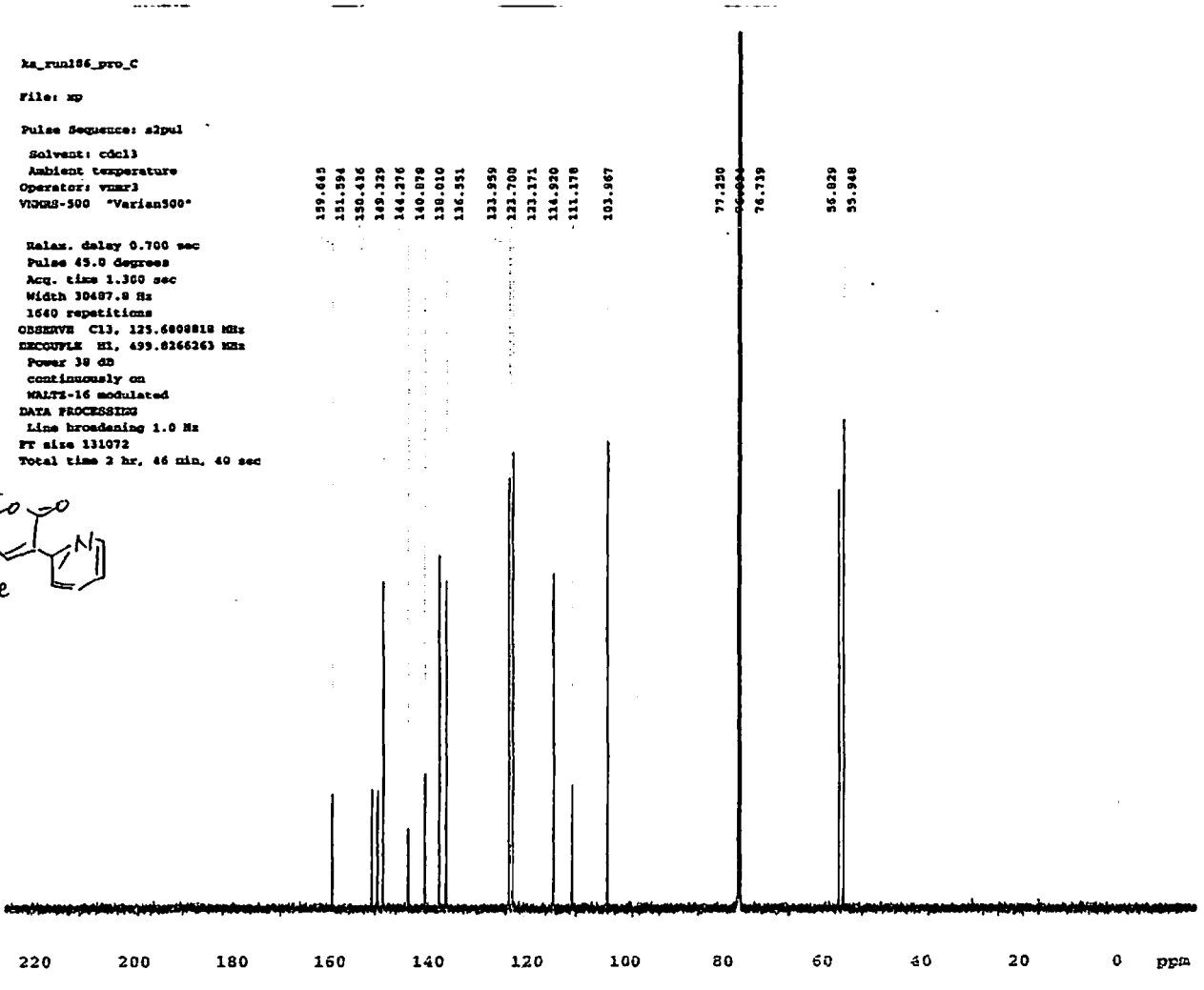
44 (3)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Pulse 45.0 degrees
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DECOUPLE H1, 499.8266263 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
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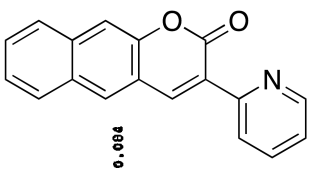
OMe



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