Palladium-Catalyzed Annulations of Arynes with 2-(2-Iodophenoxy)-1-substitutedethanones through α-Arylation of Ketones

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Supporting Information

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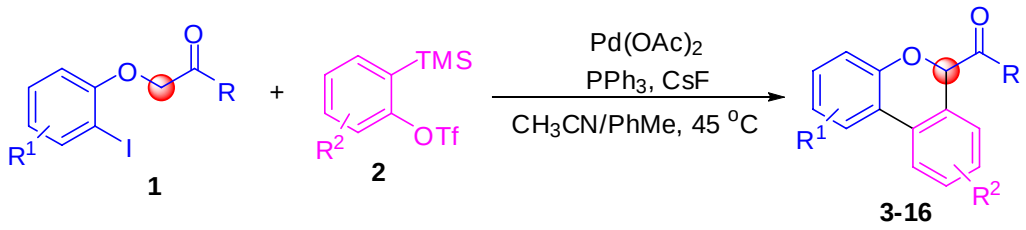
(A) Typical experimental procedure

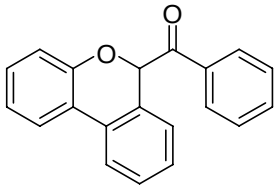
Substrates **1** were prepared according to the known procedure.[1]

(a) Typical Procedure for the Palladium-Catalyzed Annulations of 2-(2-Iodophenoxy)-1-substitutedethanones (1) with Arynes (2):



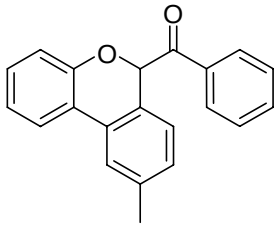
To a Schlenk tube were adde 2-(2-iodophenoxy)-1-substitutedethanones **1** (0.2 mmol), 2-(trimethylsilyl) aryltriflate **2** (0.3 mmol), $Pd(OAc)_2$ (2.4 mg, 10 mol %), triphenylphosphine (10.5 mg, 20 mol %), CsF (121 mg, 0.8 mmol), dry MeCN (1 mL) and dry toluene (1 mL). Then the tube was charged with N_2, and was stirred at 45 ^oC (oil bath temperature) for the indicated time (about 30 h) until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and filtered with a short column on silica gel. The solution was concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product.

(B) Analytical data for 3-16

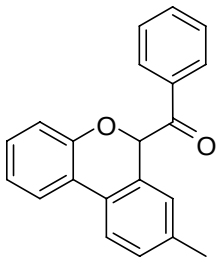


(6*H*-Benzo[*c*]chromen-6-yl)(phenyl)methanone (3):

Colorless oil; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.05 (d, *J* = 7.5 Hz, 2H), 7.78-7.73 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46-7.40 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.19-7.16 (m, 1H), 7.09-7.03 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.30 (s, 1H); ^{13}CNMR (500 Hz, $CDCl_3$) δ: 196.3, 152.7, 135.0, 133.5, 129.7, 129.6, 129.3, 129.1, 128.5, 127.8, 126.0, 123.2, 122.6, 122.4, 122.1, 117.5, 79.8; IR (KBr): 1691 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 286 (M^+, 1), 253 (1), 181 (100); HRMS (EI) for $C_{20}H_{14}O_2$ (M^+): calcd 286.0994, found 286.0990.

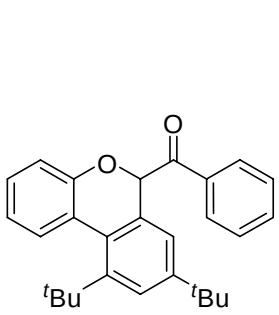


and



(9-Methyl-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (4) and (8-methyl-6*H*-benzo[c]chromen-6-yl)(phenyl)methanone (4'):

4:4' = 1.2: 1; Light yellow oil; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.06-8.03 (m, 2.07H), 7.75-7.71 (m, 1.1H), 7.69 (d, *J* = 7.5 Hz, 0.58H), 7.59-7.55 (m, 1.59H), 7.46-7.43 (m, 2.12H), 7.23 (d, *J* = 8.0 Hz, 0.64H), 7.18-7.13 (m, 1.17H), 7.07-7.02 (m, 1.59H), 6.97 (d, *J* = 7.5 Hz, 0.53H), 6.91 (m, 1.59H), 6.27 (s, 0.47H), 6.24 (s, 0.53H), 2.40 (s, 1.42H), 2.31 (s, 1.58H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 196.5, 196.4, 152.8, 152.3, 138.9, 137.8, 135.1, 135.0, 133.4 (2C), 129.9, 129.7, 129.5, 129.5, 129.4, 129.3, 129.2, 128.6, 128.5, 126.8, 126.5, 125.9, 123.2, 123.1, 123.0, 122.5 (2C), 122.4, 122.3, 122.2, 117.5, 117.4, 80.0, 79.8, 21.5, 21.3; IR (KBr): 1724 cm^{-1}; LRMS (EI 70 ev) *m*/z (%):300 (M^+, 1), 207 (0.2), 195 (100); HRMS (EI) for $C_{21}H_{16}O_2$ (M^+): calcd 300.1150, found 300.1152.



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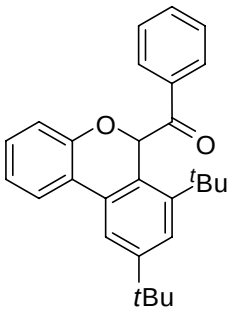
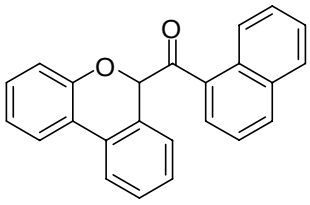


(7,9-Di-*tert*-butyl-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (5) and (8,10-Di-*tert*-butyl-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (5'):

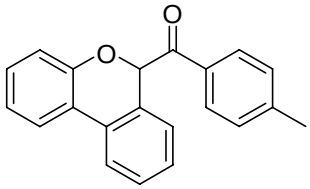
5:5' = 1.1:1; Light yellow solid, mp 127.8-129.0 ^{o}C (uncorrected); ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.14 (d, *J* = 8.0 Hz, 1.2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.77-7.76 (m, 0.6H), 7.69 (d, *J* = 1.5 Hz, 1H), 7.66 (m, 0.55H), 7.59 (m, 1.2H), 7.51 (d, *J* = 1.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1.2H), 7.45 (t, *J* = 7.5 Hz, 1.1H), 7.06 (s, 0.5H), 7.03-6.95 (m, 2.7H), 6.78-6.77 (m, 0.5H), 6.66-6.64 (m, 0.6H), 6.02 (s, 0.5H), 1.47 (s, 4.2H), 1.41 (d, *J* = 2.0 Hz, 9.7H), 1.28 (s, 4.2H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 197.2, 196.2, 153.7, 151.2, 151.0, 148.9, 148.1, 146.4, 136.6, 135.6, 135.6, 133.2 (2C), 131.1, 131.0, 129.2, 129.1, 128.7, 128.5, 128.3, 128.0, 127.7, 127.2 (2C), 125.4, 124.9, 123.6, 123.2, 122.7, 121.4, 120.4, 118.2, 117.6, 116.8, 82.4, 76.1, 37.0, 35.5, 35.0, 34.6, 33.5, 32.1, 31.4, 31.3; IR (KBr): 1687 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 398 (M^+, 0.2), 309 (0.5), 293 (100); HRMS (EI) for $C_{28}H_{30}O_2$ (M^+): calcd 398.2245, found 398.2240.



(6*H*-Benzo[*c*]chromen-6-yl)(naphthalen-1-yl)methanone (6):

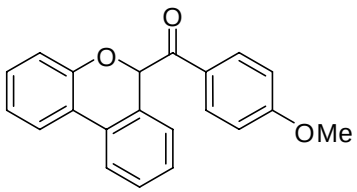
White solid, mp 144.5-145.8 ^{o}C (uncorrected); ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.67 (s, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.87-7.84 (m, 2H), 7.80-7.75

(m, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.16-7.11 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 196.2, 152.7, 135.7, 132.4, 132.3, 131.6, 129.8, 129.7, 129.5, 129.1, 128.8, 128.4, 127.8, 127.8, 126.8, 126.1, 124.9, 123.3, 122.6, 122.4, 122.2, 117.5, 79.8; IR (KBr): 1683 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 336 (M+, 5), 307 (2), 181 (100); HRMS (EI) for $C_{24}H_{16}O_2$ (M^+): calcd 336.1150, found 336.1145.



(6*H*-Benzo[*c*]chromen-6-yl)(p-tolyl)methanone (7):

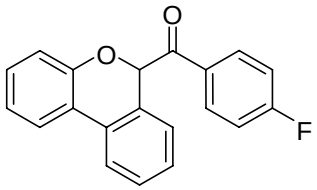
White solid, mp 103.6-104.8 ^{o}C (uncorrected); ^{1}H NMR (500 Hz, $CDCl_3$) δ: 7.97 (d, *J* = 8.5 Hz, 2H), 7.77-7.73 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 3H), 7.20-7.16 (m, 1H), 7.07-7.02 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 2.40 (s, 3H); ^{13}CNMR (500 Hz, $CDCl_3$) δ: 195.7, 152.8, 144.4, 132.4, 129.7, 129.6 (2C), 129.5, 129.2, 129.0, 127.8, 125.9, 123.2, 122.5, 122.4, 122.2, 117.5, 79.7, 21.8; IR (KBr): 1683 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 300 (M^+, 1.4), 207 (2), 181 (100); HRMS (EI) for $C_{21}H_{16}O_2$ (M^+): calcd 300.1150, found 300.1146.



(6*H*-Benzo[*c*]chromen-6-yl)(4-methoxyphenyl)methanone (8):

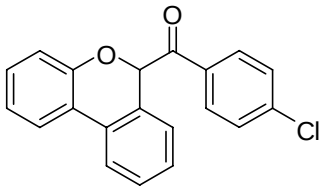
Light yellow solid, mp116.7-118.0 ^{o}C; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.09-8.07 (m,

2H), 7.79-7.74 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.27-7.23 (m, 1H), 7.21-7.18 (m, 1H), 7.08-7.04 (m, 2H), 6.99-6.92 (m, 3H), 6.25 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 194.5, 163.8, 152.7, 132.0, 129.7, 129.6, 129.5, 129.0, 127.7, 125.8, 123.2, 122.5, 122.3, 122.2, 117.4, 113.7, 79.8, 55.4; IR (KBr): 1597 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 316 (M^+, 2), 207 (2), 181 (100); HRMS (EI) for $C_{21}H_{16}O_3$ (M^+): calcd 316.1099, found 316.1097.



(6*H*-Benzo[*c*]chromen-6-yl)(4-fluorophenyl)methanone (9):

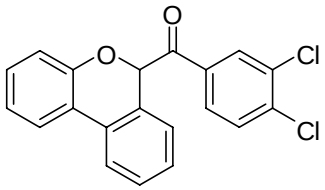
Yellow solid, mp 85.5-86.8 ^{o}C (uncorrected); ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.12-8.09 (m, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13-7.04 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H); ^{13}CNMR (500 Hz, $CDCl_3$) δ: 194.8, 165.8 (d, *J* = 254.5 Hz, 1C), 152.4, 132.4, 132.3, 131.2, 131.2, 129.6, 129.4, 129.2, 129.1, 127.8, 125.9, 123.2, 122.7, 122.4, 122.1, 117.4, 115.6 (d, *J* = 21.6 Hz, 1C), 80.0; IR (KBr): 1679 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 304 (M^+, 0.3), 275 (0.2), 181 (100); HRMS (EI) for $C_{20}H_{13}FO_2$ (M^+): calcd 304.0899, found 304.0895.



(6*H*-Benzo[*c*]chromen-6-yl)(4-chlorophenyl)methanone (10):

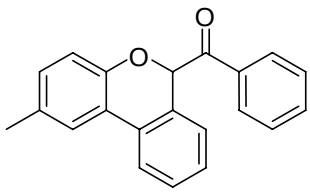
White solid, mp 113.4-114.7 ^{o}C (uncorrected); ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.01 (d, *J*

= 8.0 Hz, 2H), 7.79 (d. *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.45-7.40 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H); ^{13}CNMR (500 Hz, $CDCl_3$) δ: 195.3, 152.3, 139.9, 133.1, 131.0, 129.7, 129.4, 129.2, 129.0, 128.8, 127.8, 125.9, 123.3, 122.7, 122.5, 122.1, 117.4, 80.0; IR (KBr): 1683 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 1), 207 (2), 181 (100); HRMS (EI) for $C_{20}H_{13}ClO_2$ (M^+): calcd 320.0604, found 320.0600.



(6H-benzo[*c*]chromen-6-yl)(3,4-dichlorophenyl)methanone(11):

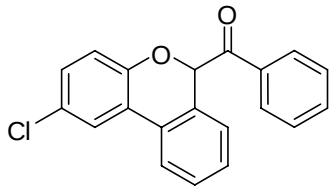
Light yellow solid, mp 129.0-130.5 ^{o}C; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.16 (d, *J* = 8.0 Hz, 1H), 7.90-7.88 (m, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.75-7.74 (m, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46-7.43 (m, 1H), 7.31-7.28 (m, 1H), 7.21-7.17 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 1H); ^{13}CNMR (500 Hz, $CDCl_3$) δ: 194.5, 152.1, 138.0, 134.4, 133.2, 131.4, 130.5, 129.7, 129.4, 128.7, 128.6, 127.9, 125.9, 123.3, 122.9, 122.5, 122.1, 117.4, 80.1; IR (KBr): 1691 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 354 (M^+, 0.2), 207 (0.4), 181 (100); HRMS (EI) for $C_{20}H_{12}Cl_2O_2$ (M^+): calcd 354.0214, found 354.0209.



(2-Methyl-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (12):

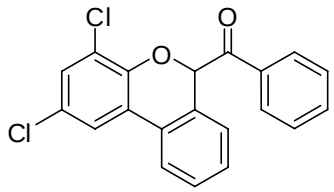
Light yellow oil; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.06 (m, 2H), 7.75 (d, *J* = 7.5 Hz, 1H),

7.63 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 1H), 7.23-7.20 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.87-6.86 (m, 1H), 6.74 (s, 1H), 6.28 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 196.2, 152.6, 140.1, 134.9, 133.4, 129.7, 129.5, 129.0, 128.8, 128.4, 127.3, 125.9, 123.4, 122.9, 122.0, 119.2, 117.8, 79.8, 21.3; IR (KBr): 1728 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 300 (M^+, 1.3), 207 (2.2), 195 (100); HRMS (EI) for $C_{21}H_{16}O_2$ (M^+): calcd 300.1150, found 300.1144.



(2-Chloro-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (13):

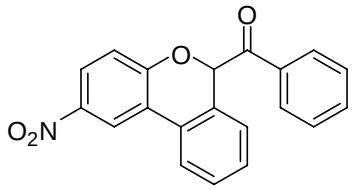
Light yellow solid, mp 126.7-128.1 ^{o}C (uncorrected), ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.03 (d, *J* = 7.5 Hz, 2H), 7.72-7.69 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47-7.40 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.13-7.09 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.33 (s, 1H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 195.8, 151.2, 134.8, 133.6, 129.4, 129.3, 129.3, 129.1, 128.5, 128.4, 127.6, 126.2, 123.5, 123.1, 122.5, 118.8, 79.5, IR (KBr): 1666 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 15), 218 (5), 215 (100); HRMS (EI) for $C_{20}H_{13}ClO_2$ (M^+): calcd 320.0604, found 320.0602.



(2,4-Dichloro-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (14):

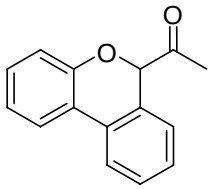
White solid, mp 131.5-130.0 ^{o}C; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.06 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61-7.58 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.43-7.40

(m, 1H), 7.32-7.29 (m, 1H), 7.24-7.23 (m, 1H), 7.15 (d, J = 8.0, 1H), 6.49 (s, 1H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 195.2, 147.5, 134.3, 133.7, 129.4 (2C), 128.9, 128.7, 128.6, 127.9, 127.2, 126.6, 124.5, 123.4, 122.8, 121.6, 79.2; IR (KBr): 1695 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 354 (M^+, 2), 325 (0.2), 249 (100); HRMS (EI) for $C_{20}H_{12}Cl_2O_2$ (M^+): calcd 354.0214, found 354.0211.



(2-Nitro-6*H*-benzo[*c*]chromen-6-yl)(phenyl)methanone (15):

Light yellow oil; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 8.66 (d, J = 8.0 Hz, 1H), 8.12-8.10 (m, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.51-7.45 (m, 3H), 7.35-7.30 (m, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H), 6.59 (s, 1H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 194.7, 158.2, 142.9, 134.3, 134.0, 129.7, 129.3, 129.2, 128.8, 128.2, 127.4, 126.4, 125.3, 122.9, 122.1, 119.2, 117.9, 79.2; IR (KBr): 1687 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 331 (M^+, 1), 242 (3), 226 (100); HRMS (EI) for $C_{20}H_{13}NO_4$ (M^+): calcd 331.0844, found 331.0842.



1-(6*H*-Benzo[*c*]chromen-6-yl)ethanone (16):

Colorless oil; ^{1}H NMR (500 Hz, $CDCl_3$) δ: 7.73 (m, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.33-7.28 (m, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.08-7.04 (m, 2H), 5.51 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (500 Hz, $CDCl_3$) δ: 206.4, 152.6, 129.9, 129.1, 128.8, 128.3, 127.9,

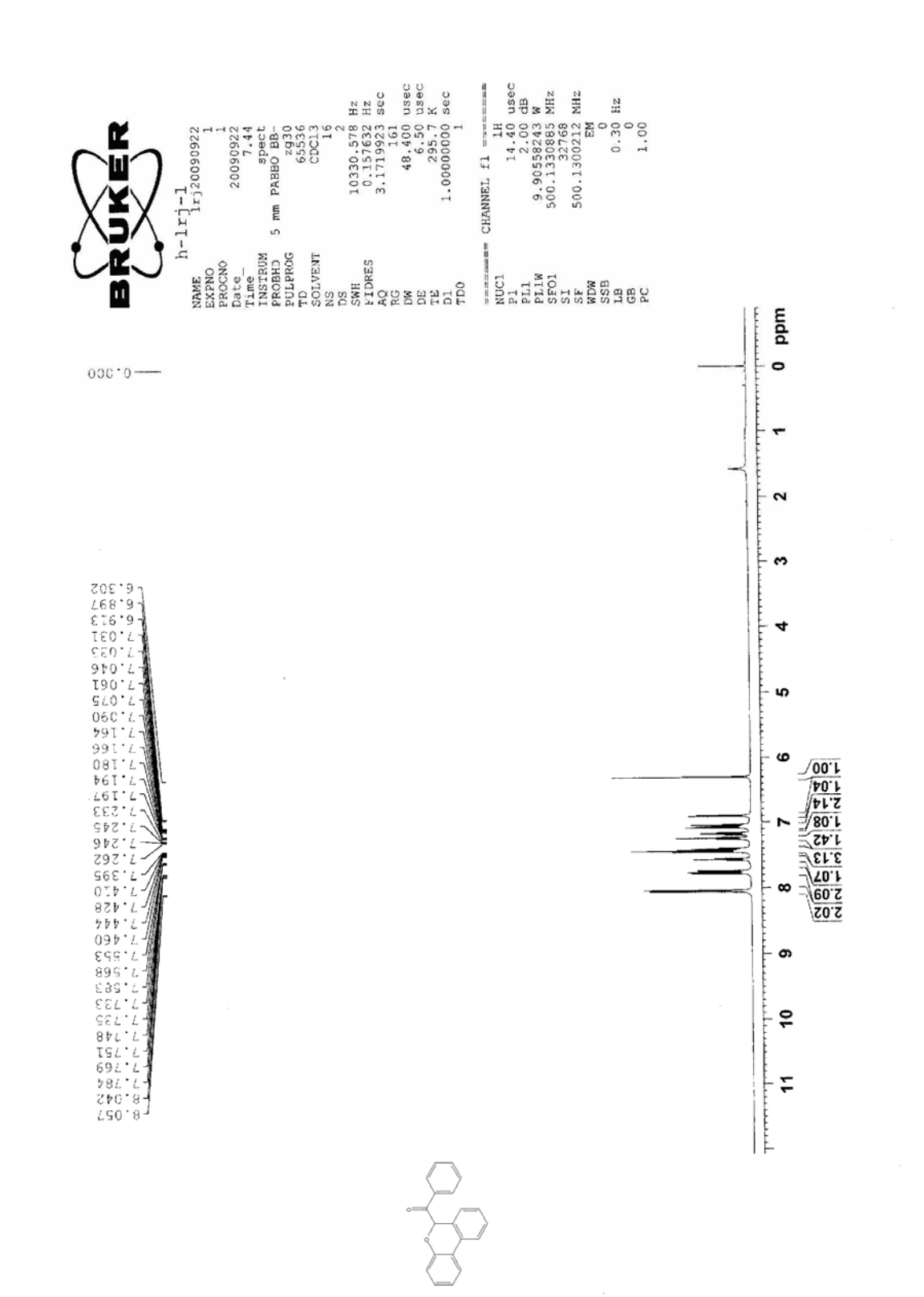
126.4, 123.2, 122.4, 122.1, 121.3, 117.4, 82.6, 26.8; IR (KBr): 1728 cm^{-1}; LRMS (EI 70 ev) *m*/z (%): 224 (M^+, 0.3), 207 (1), 181 (100); HRMS (EI) for $C_{15}H_{12}O_2$ (M^+): calcd 224.0837, found 224.0832.

(C) References

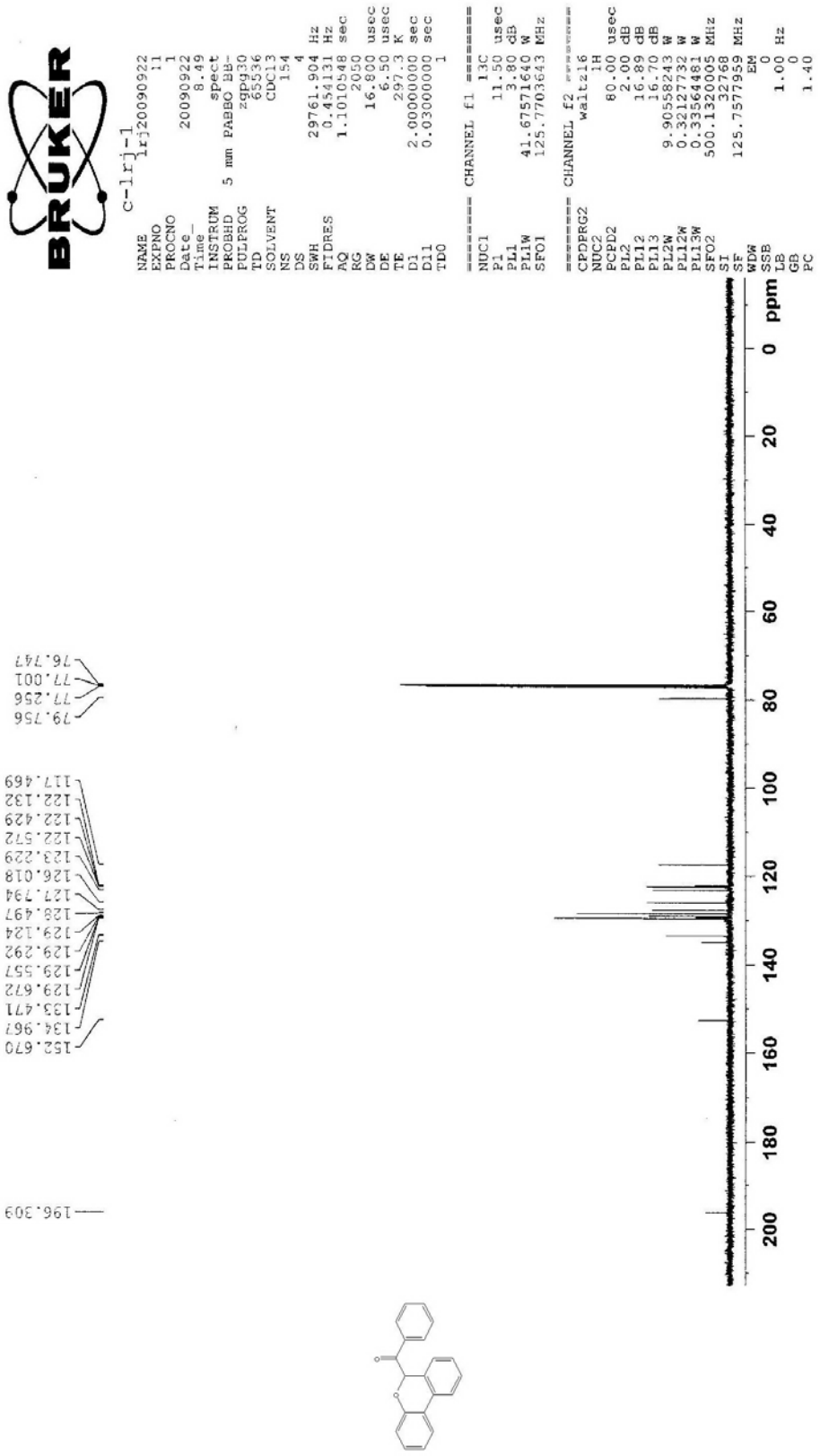
(1) Jacob, G. A.; Schroeder, D. *Synlett* **2005**, *16*, 2504.

(D) Spectra

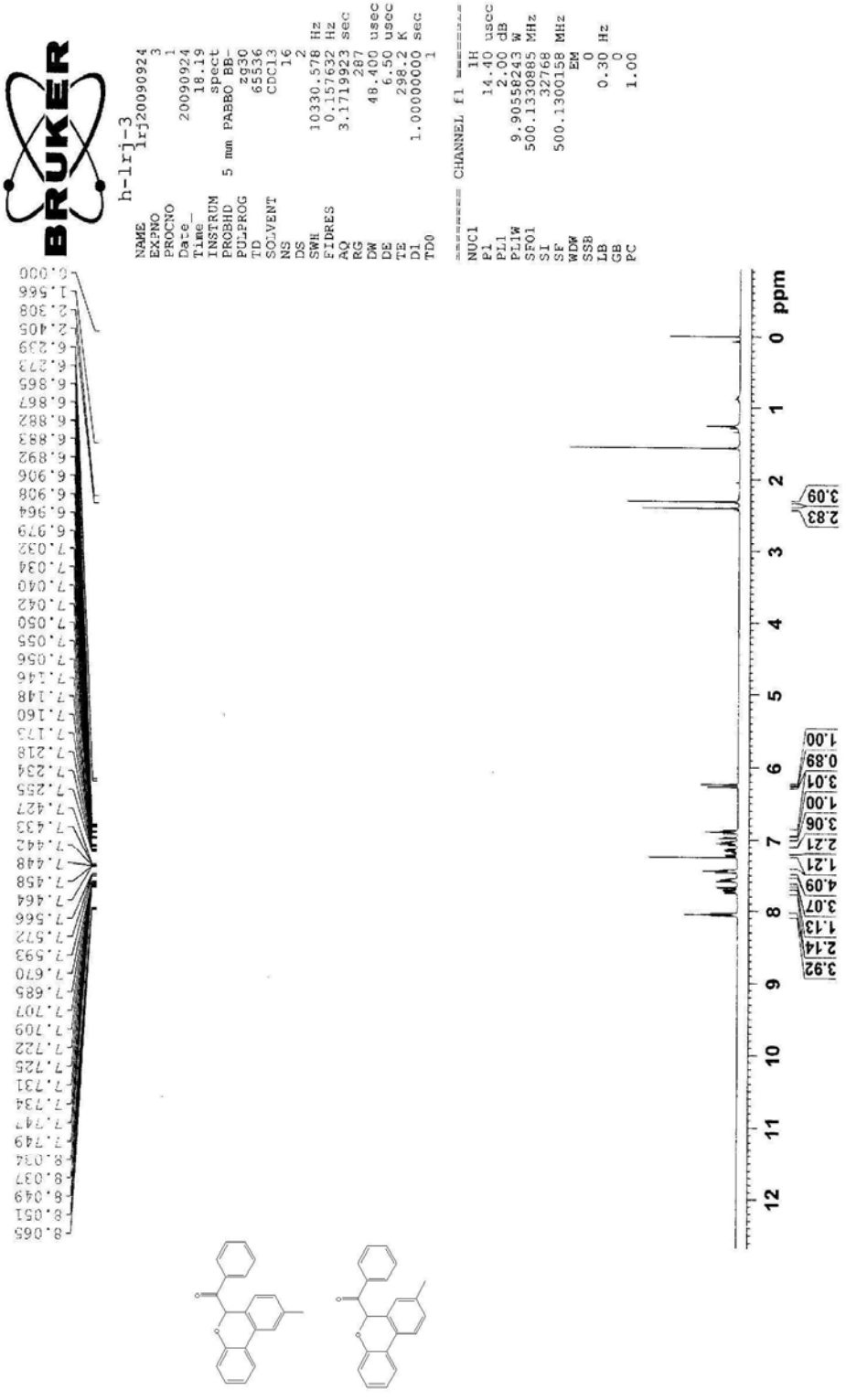
(6H-benzo[c]chromen-6-yl)(phenyl)methanone (3)



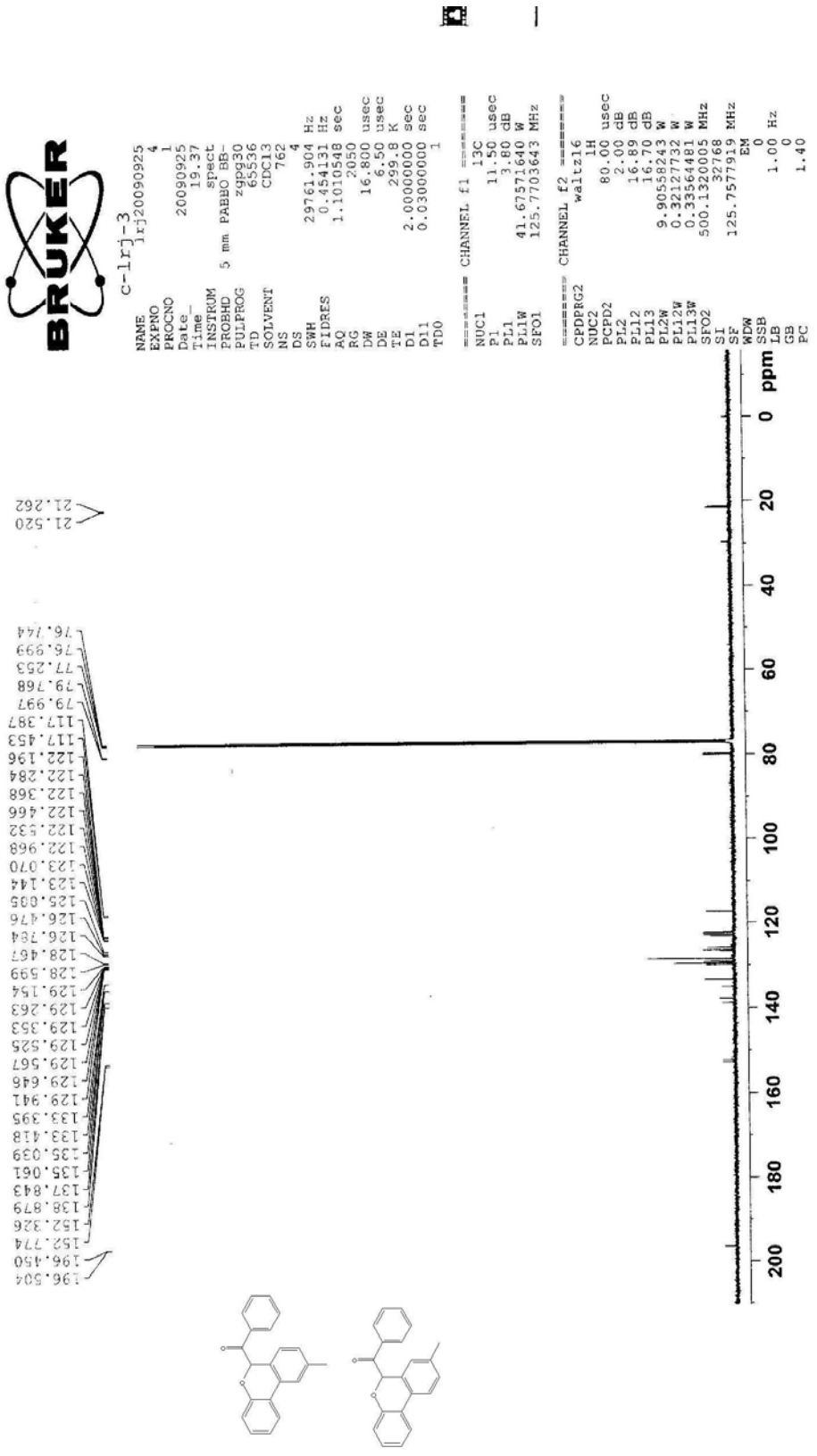
(6H-benzo[c]chromen-6-yl)(phenyl)methanone (3)



(9-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (4) and (8-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (4')

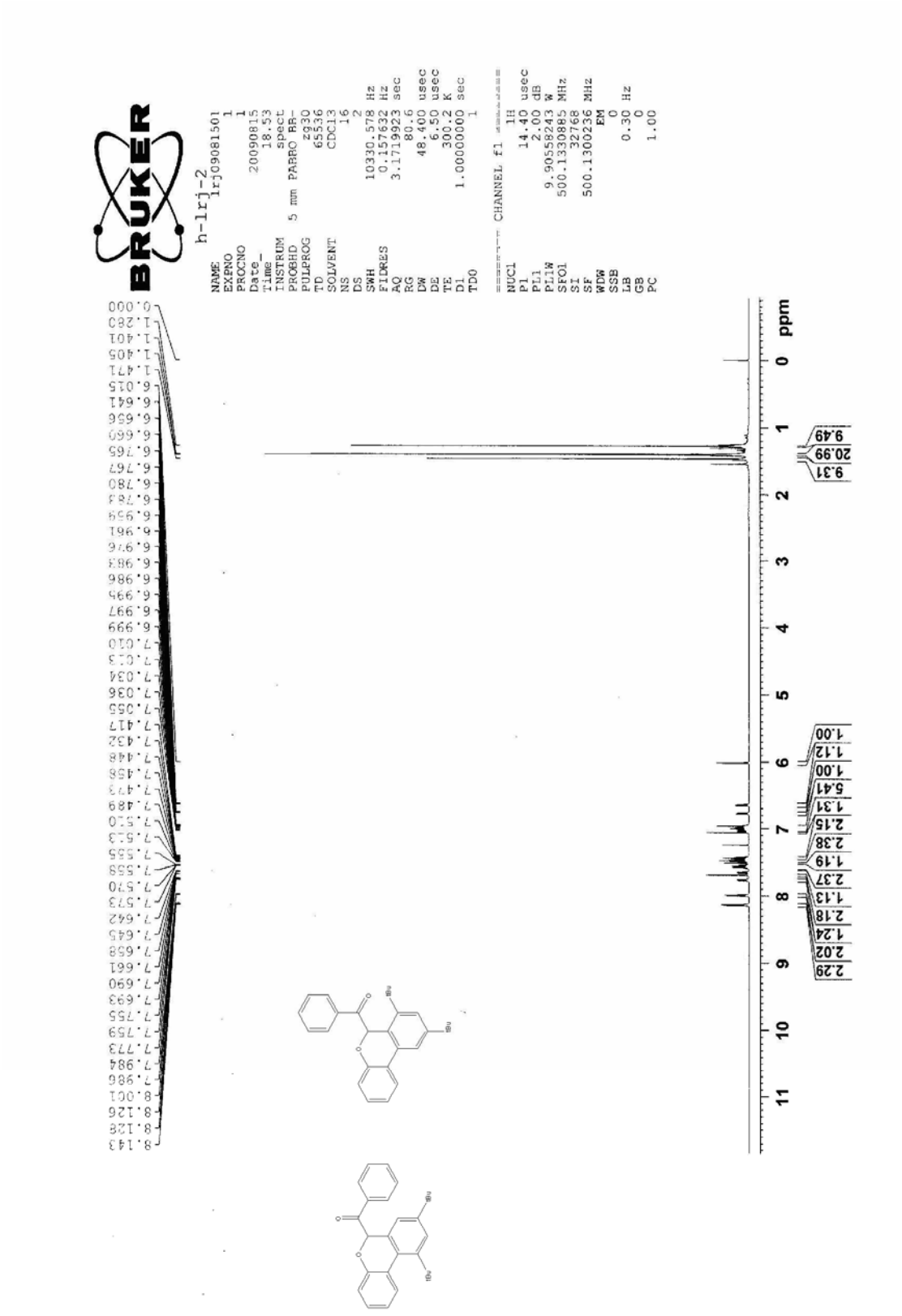


(9-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (4) and (8-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (4')



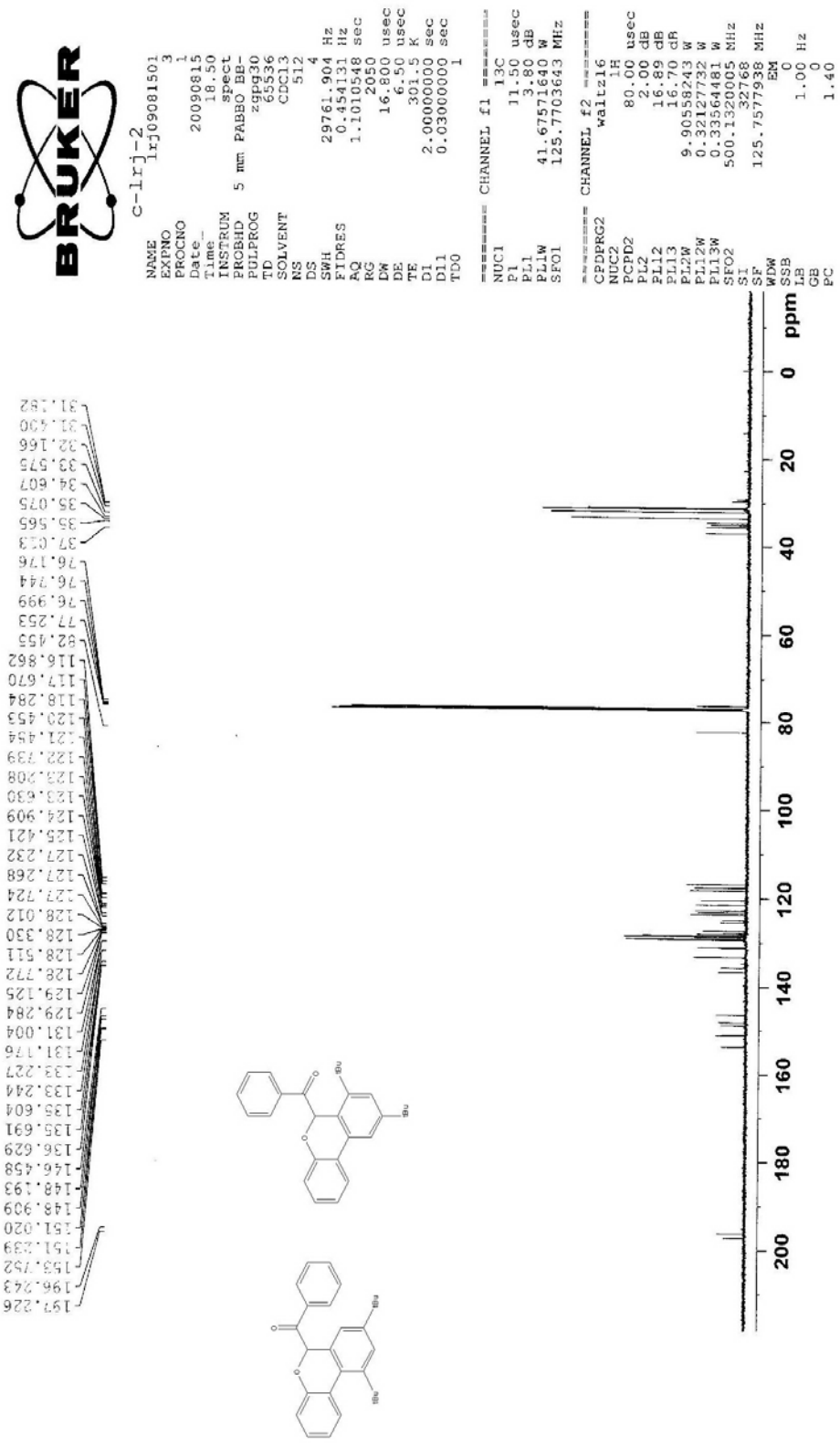
(8,10-di-tert-butyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (5)

and (7,9-di-tert-butyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (5')

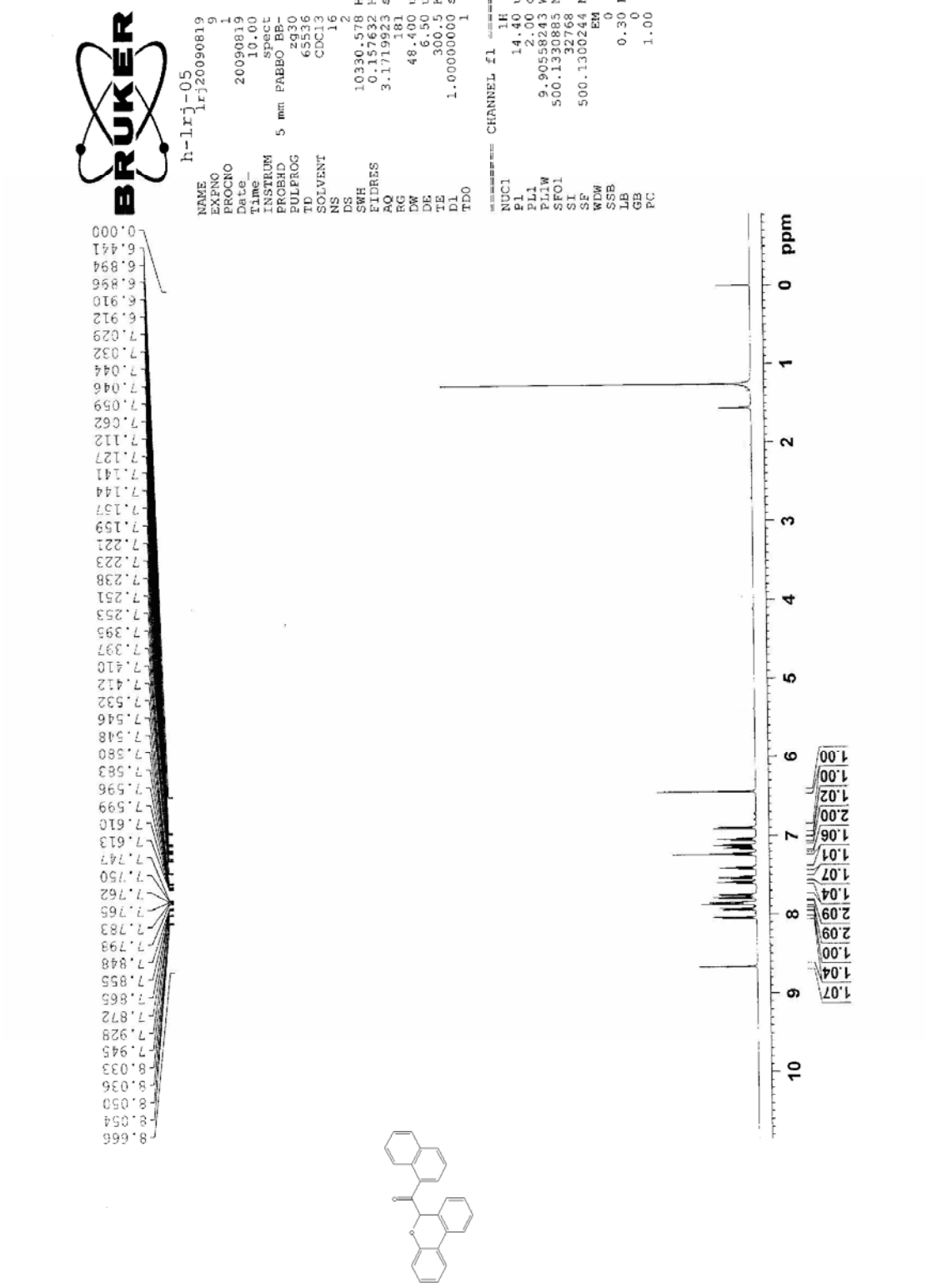


(8,10-di-tert-butyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (5)

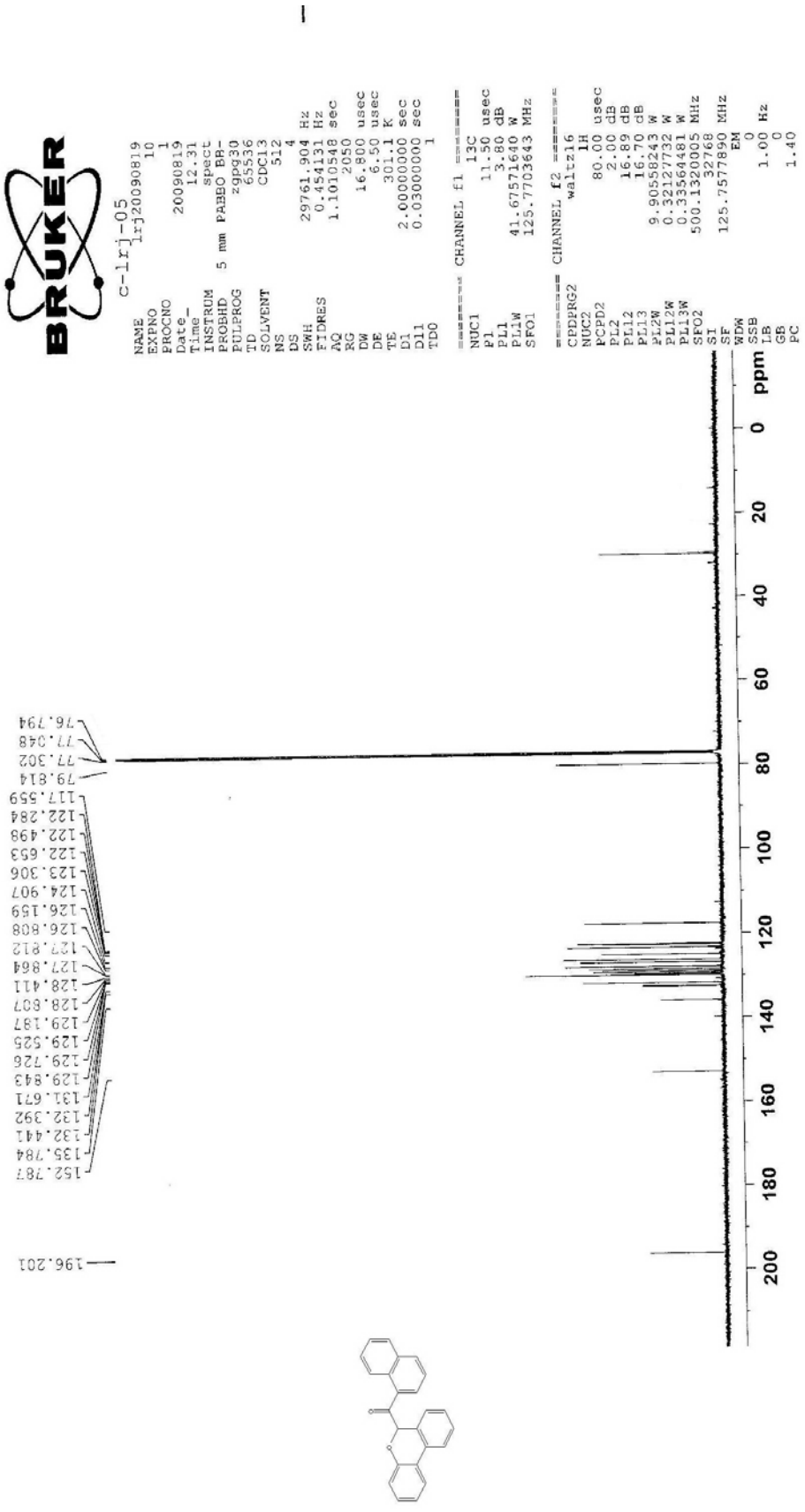
and (7,9-di-tert-butyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (5')



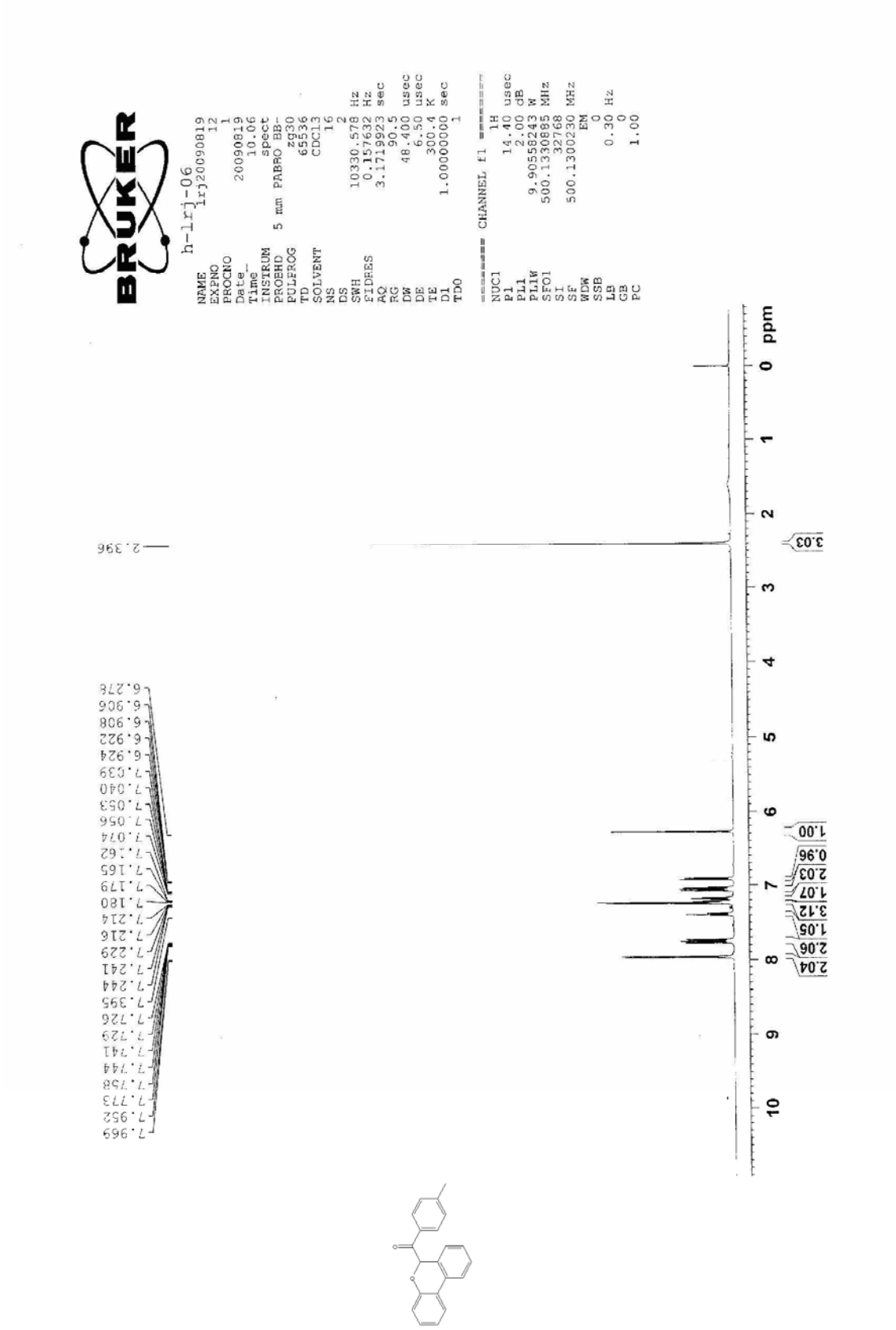
(6H-benzo[c]chromen-6-yl)(naphthalen-1-yl)methanone (6)



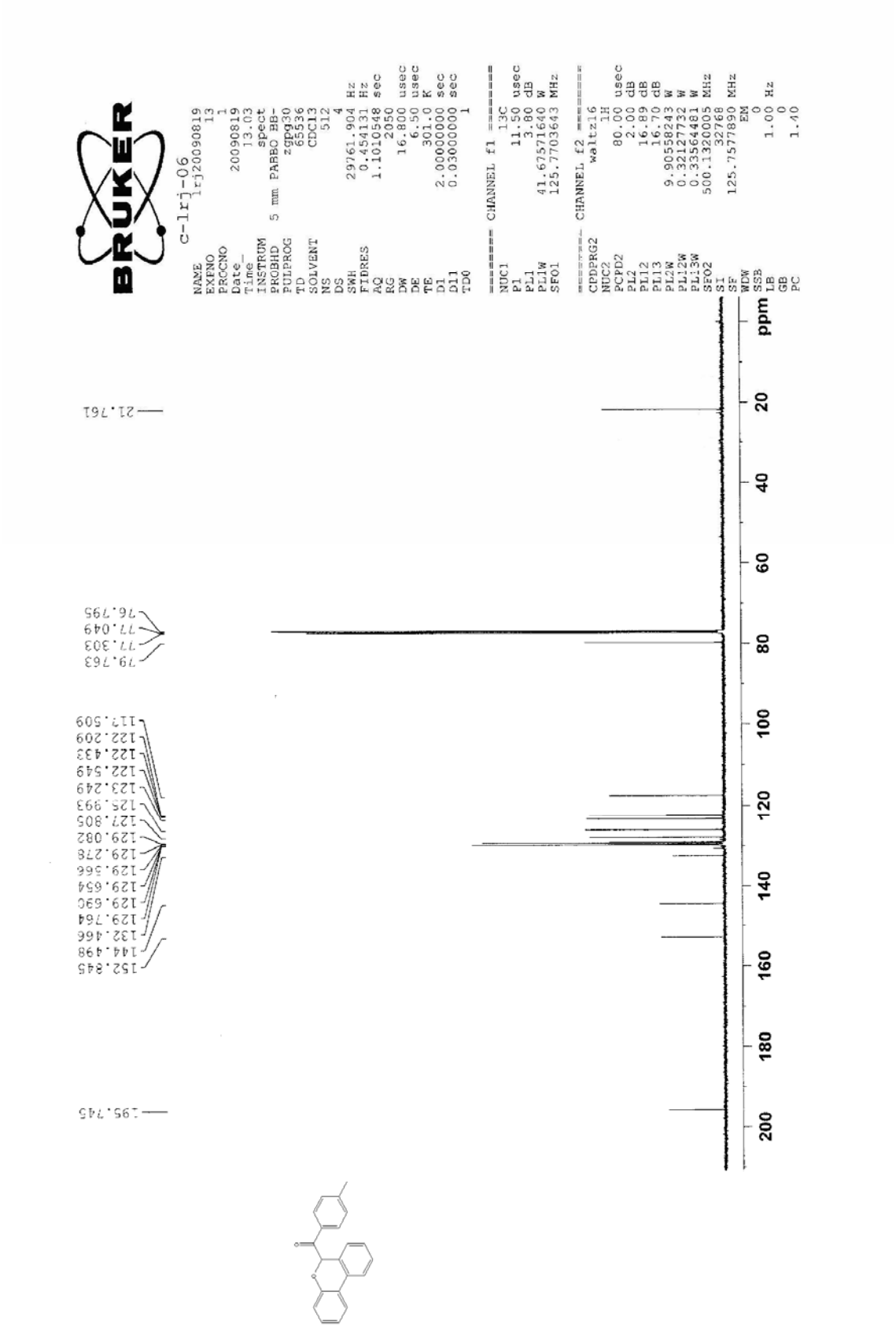
(6H-benzo[c]chromen-6-yl)(naphthalen-1-yl)methanone (6)



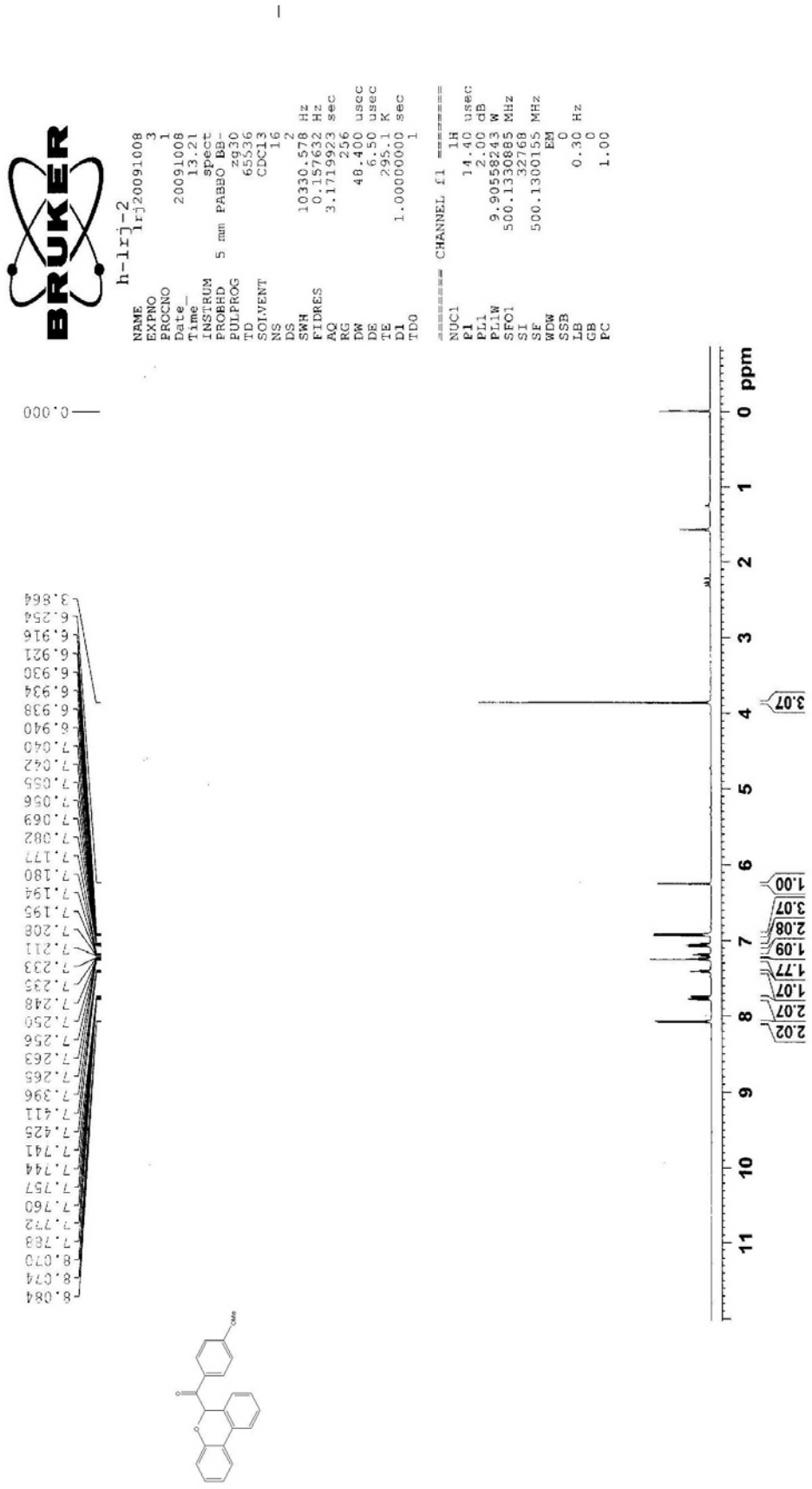
(6H-benzo[c]chromen-6-yl)(p-tolyl)methanone (7)



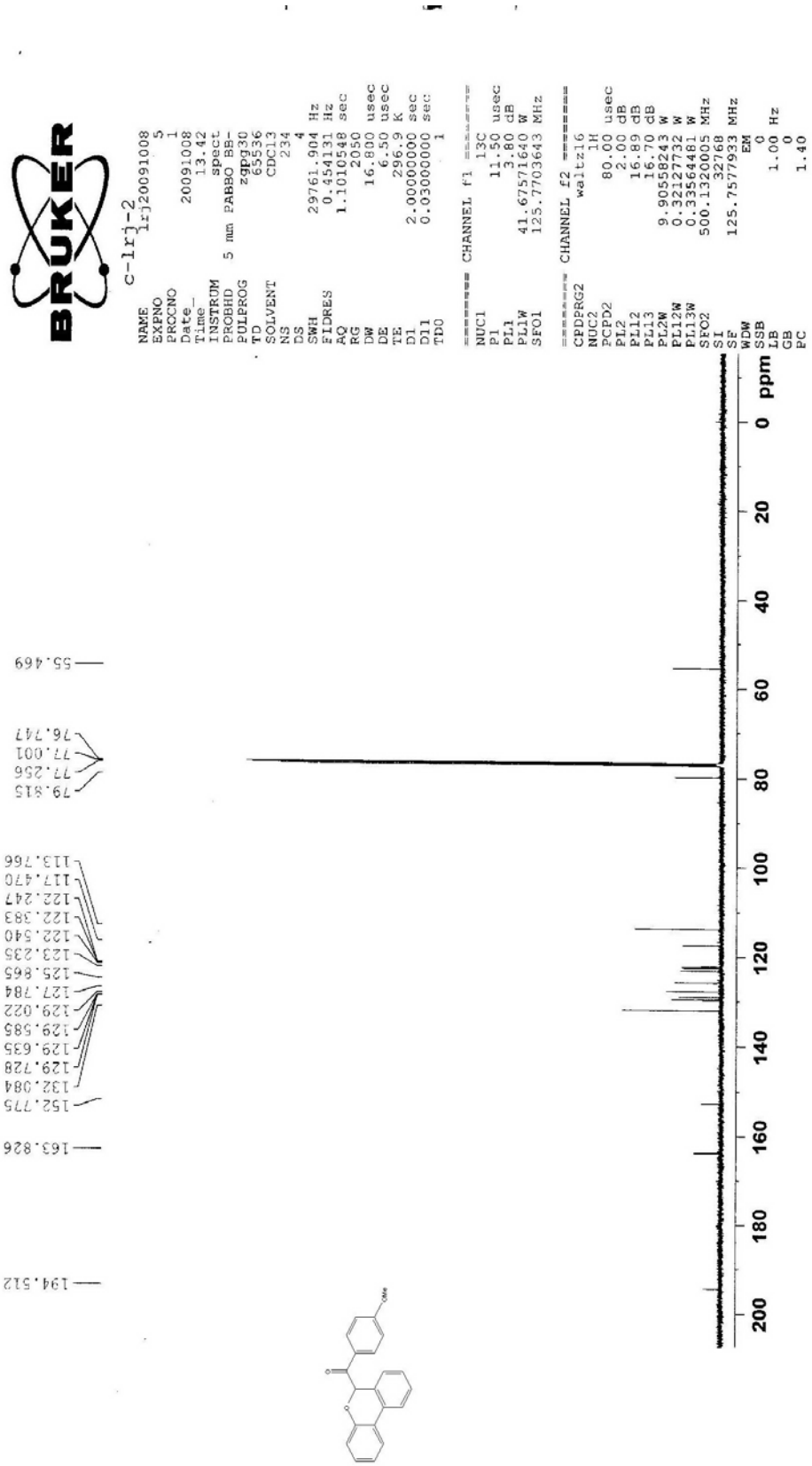
(6H-benzo[c]chromen-6-yl)(p-tolyl)methanone (7)



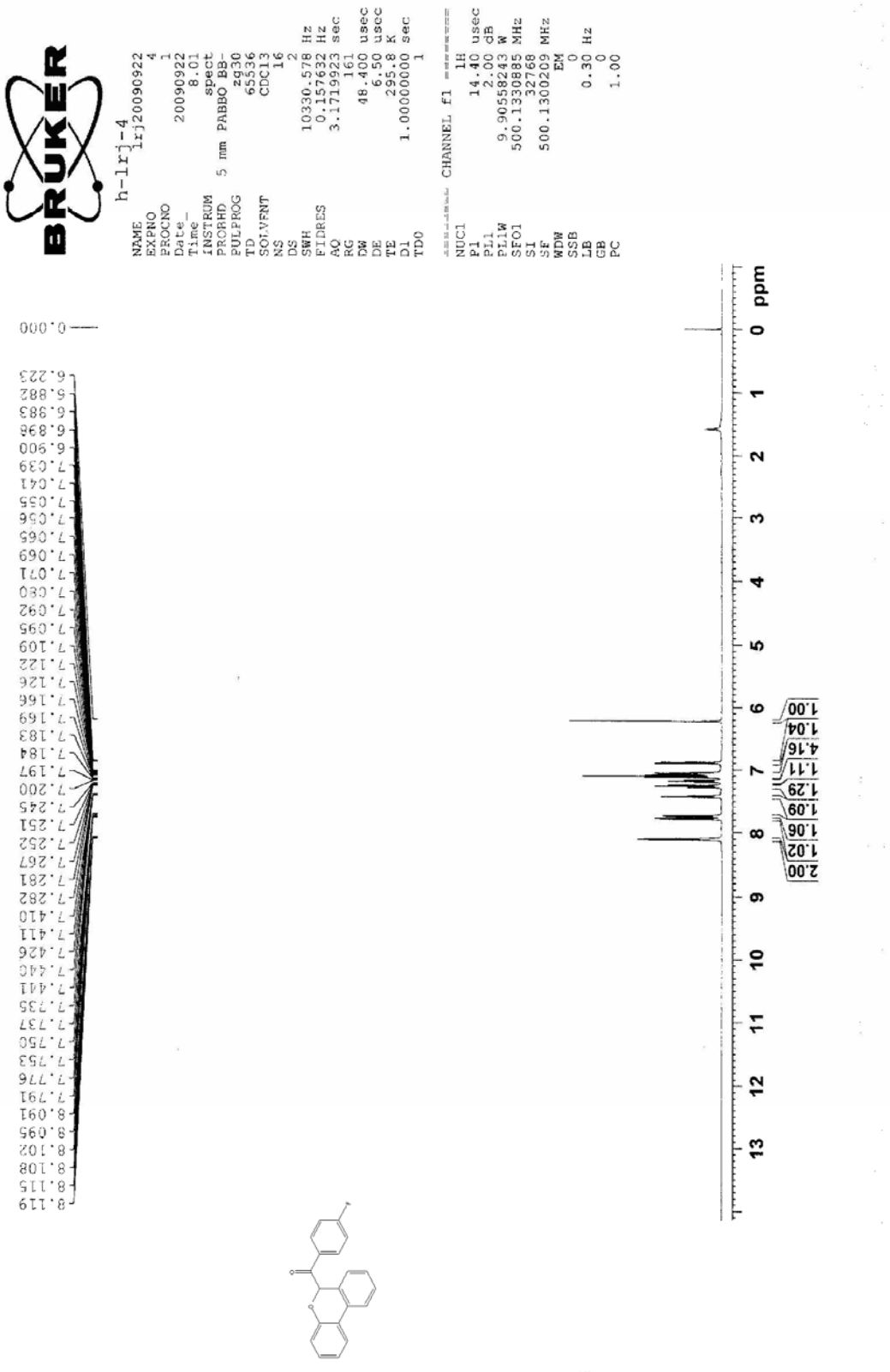
(6H-benzo[c]chromen-6-yl)(4-methoxyphenyl)methanone (8)



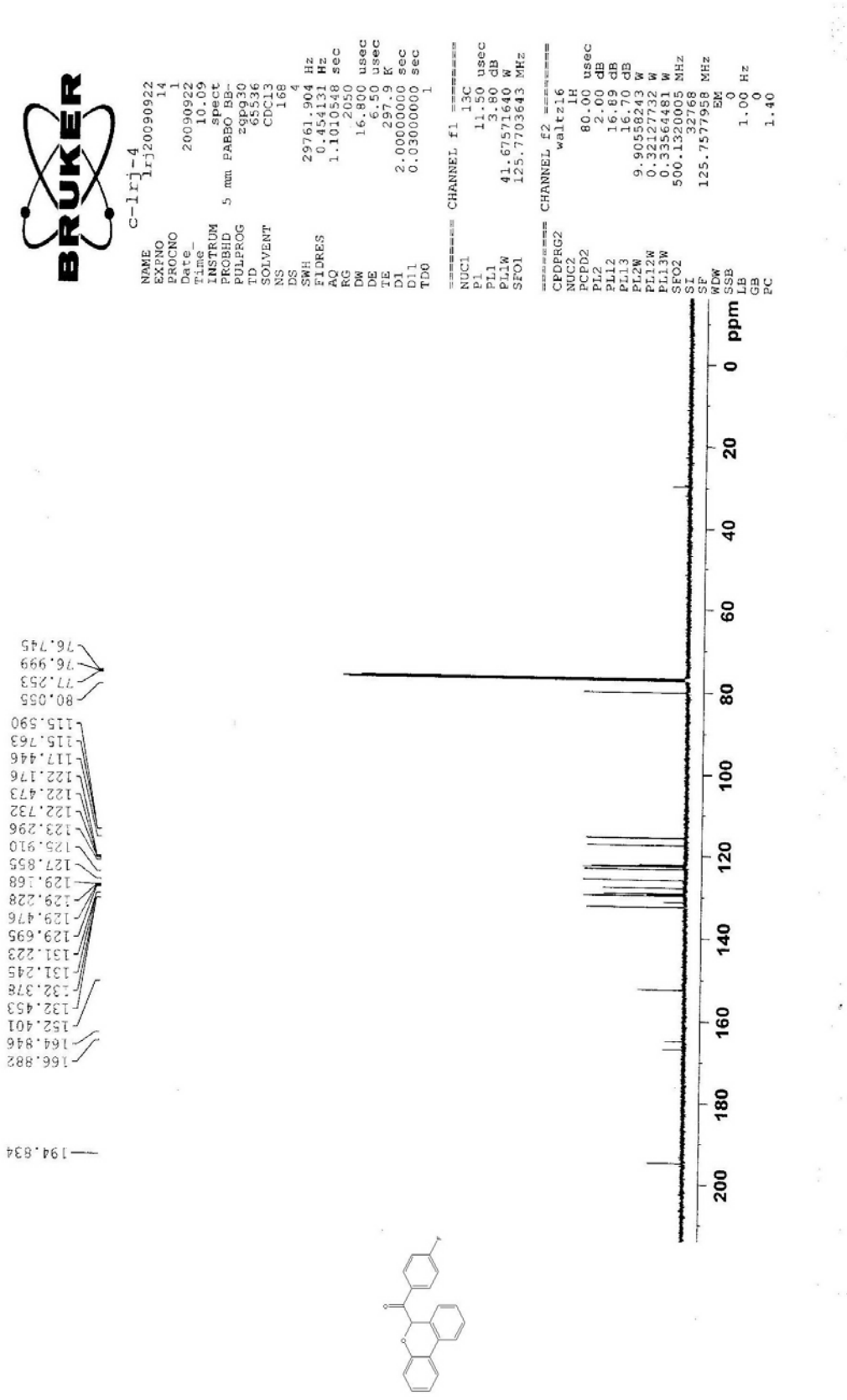
(6H-benzo[c]chromen-6-yl)(4-methoxyphenyl)methanone (8)



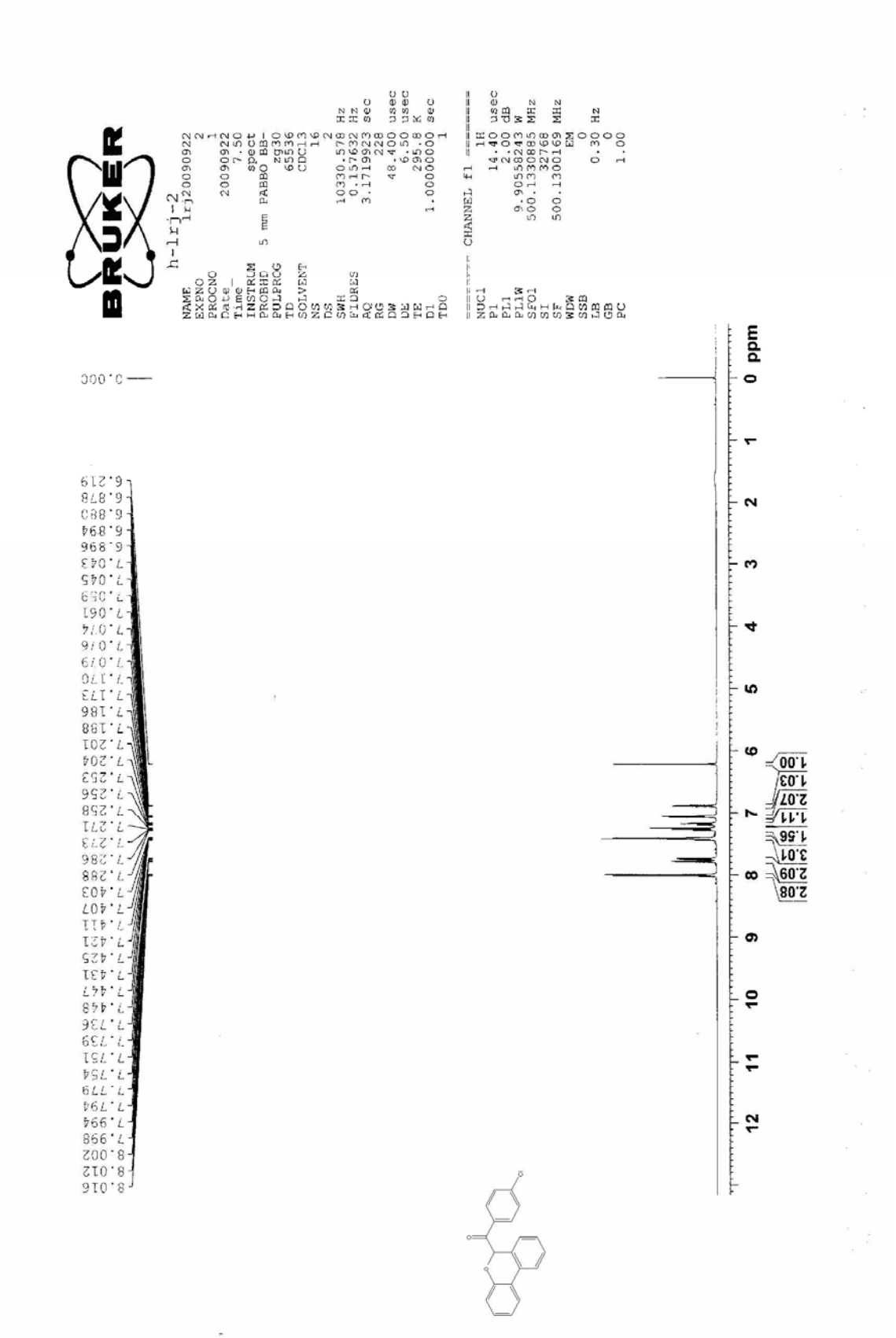
(6H-benzo[c]chromen-6-yl)(4-fluorophenyl)methanone (9)



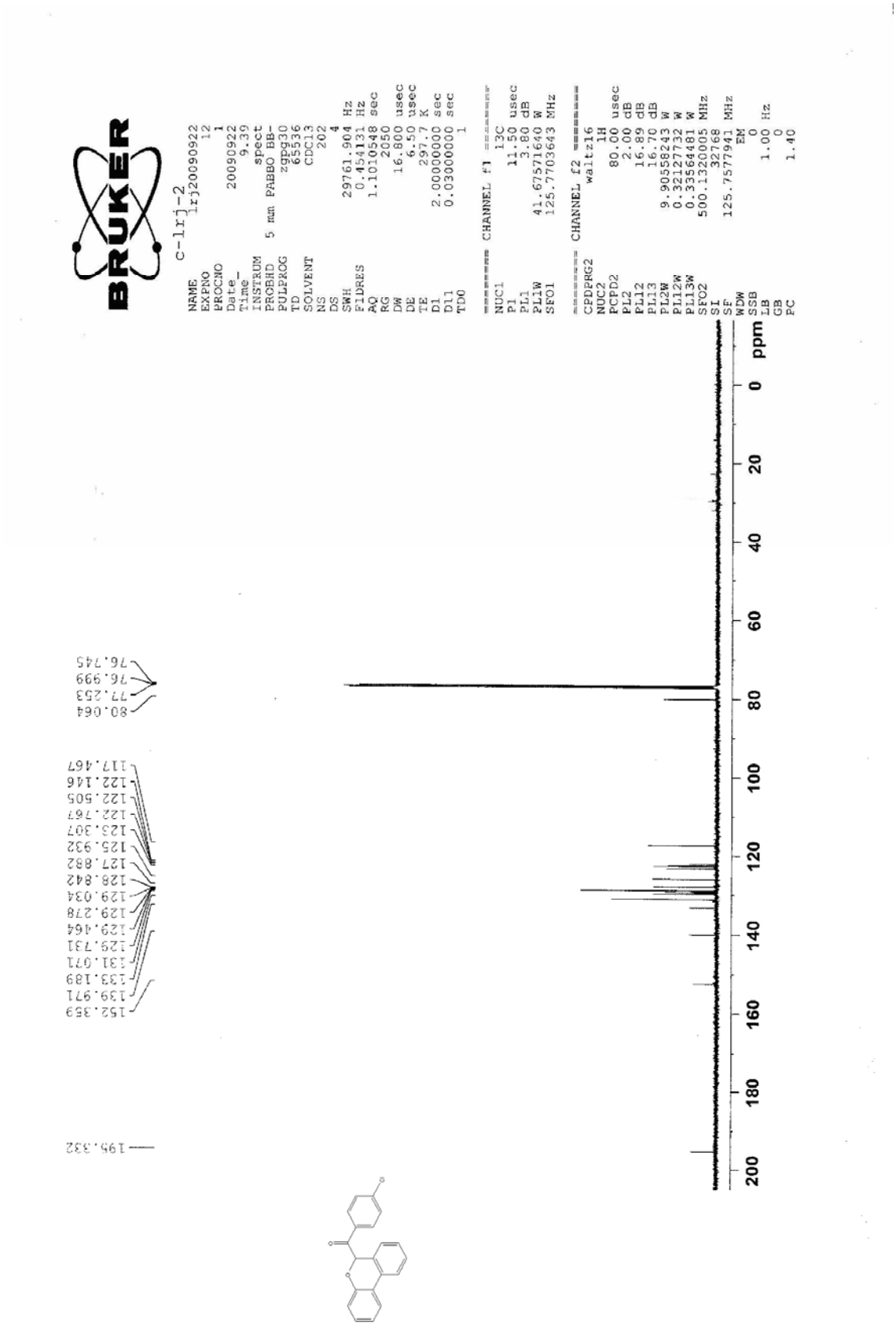
(6H-benzo[c]chromen-6-yl)(4-fluorophenyl)methanone (9)



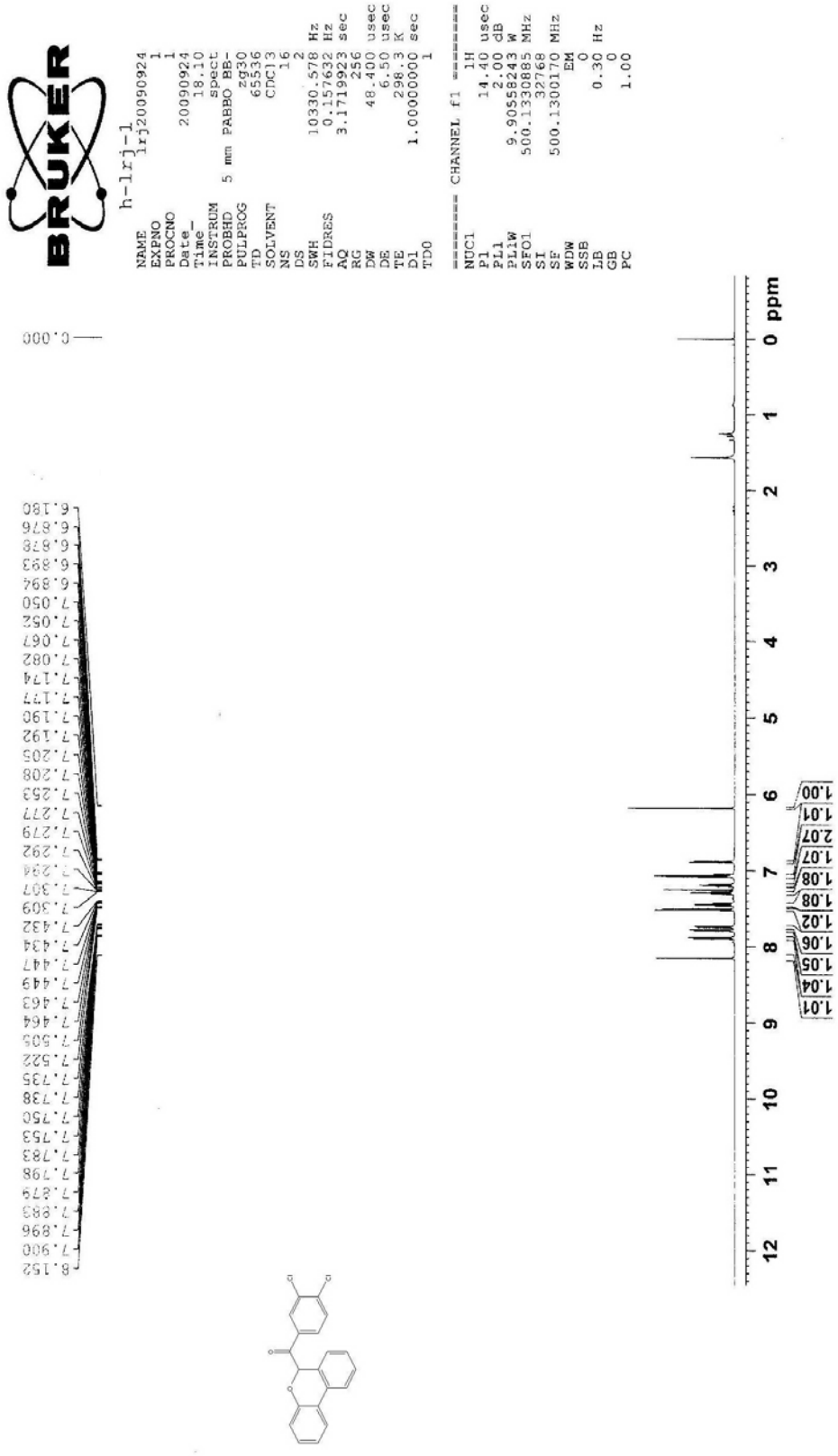
(6H-benzo[c]chromen-6-yl)(4-chlorophenyl)methanone (10)



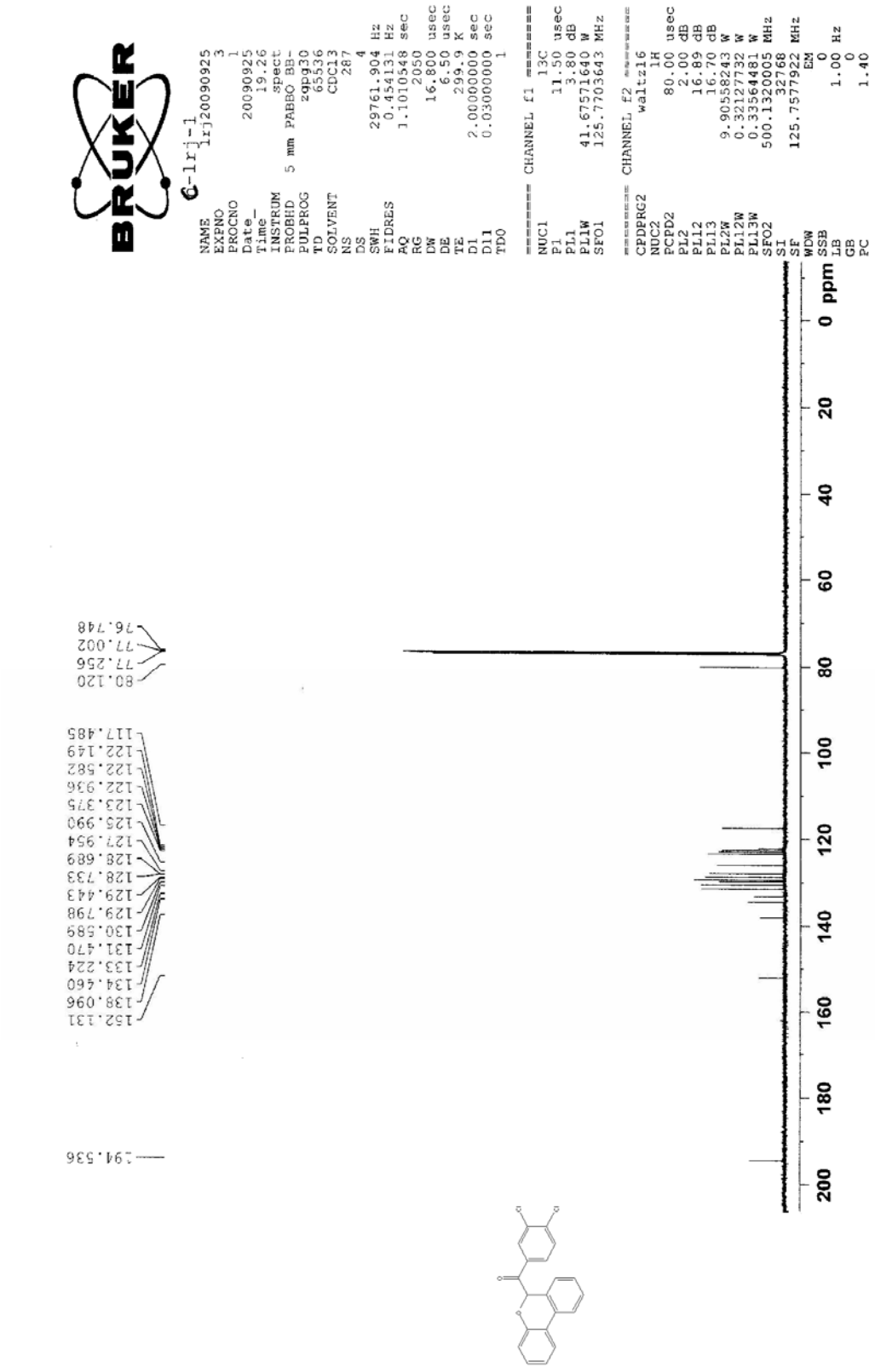
(6H-benzo[c]chromen-6-yl)(4-chlorophenyl)methanone (10)



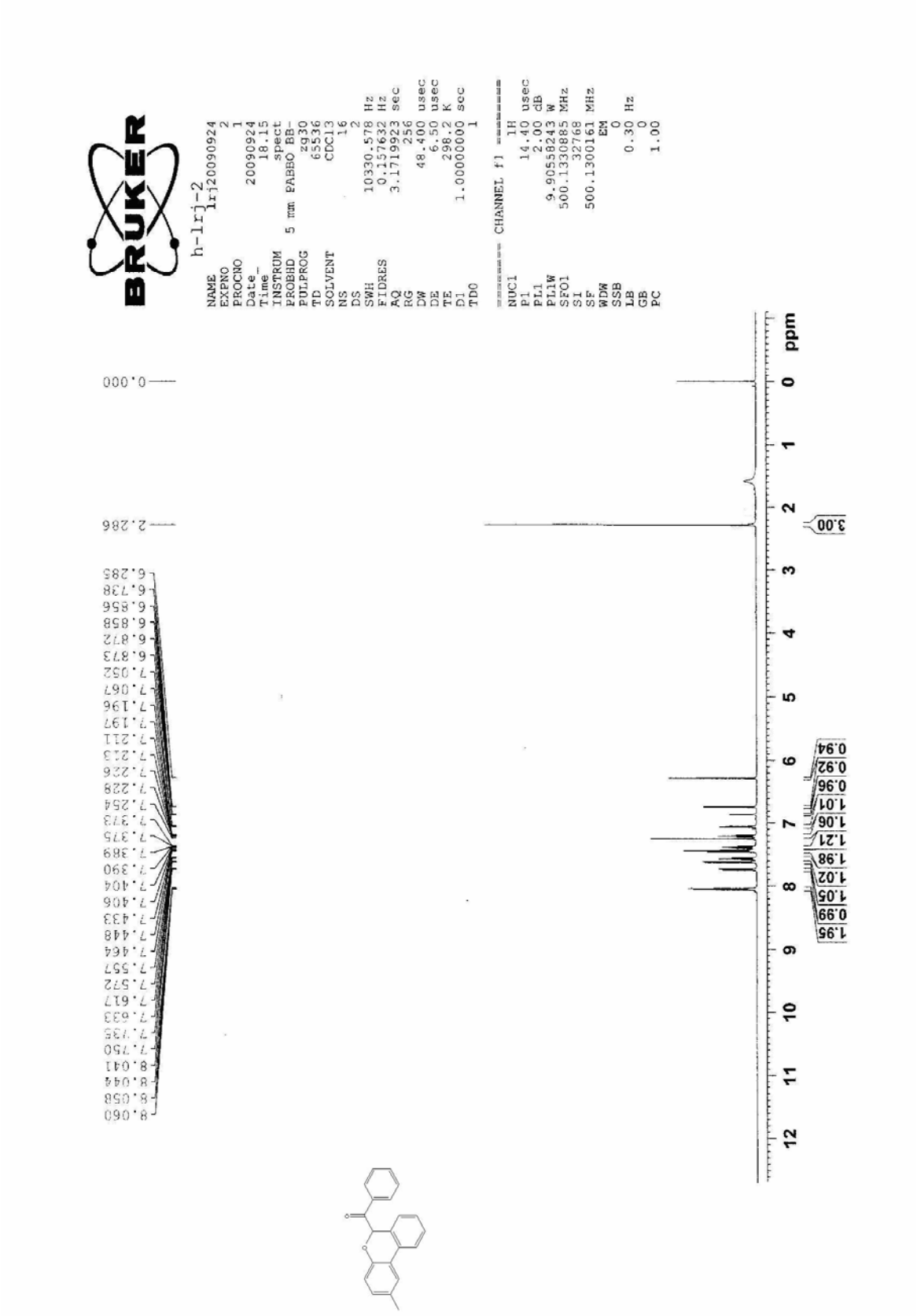
(6H-benzo[c]chromen-6-yl)(3,4-dichlorophenyl)methanone (11)



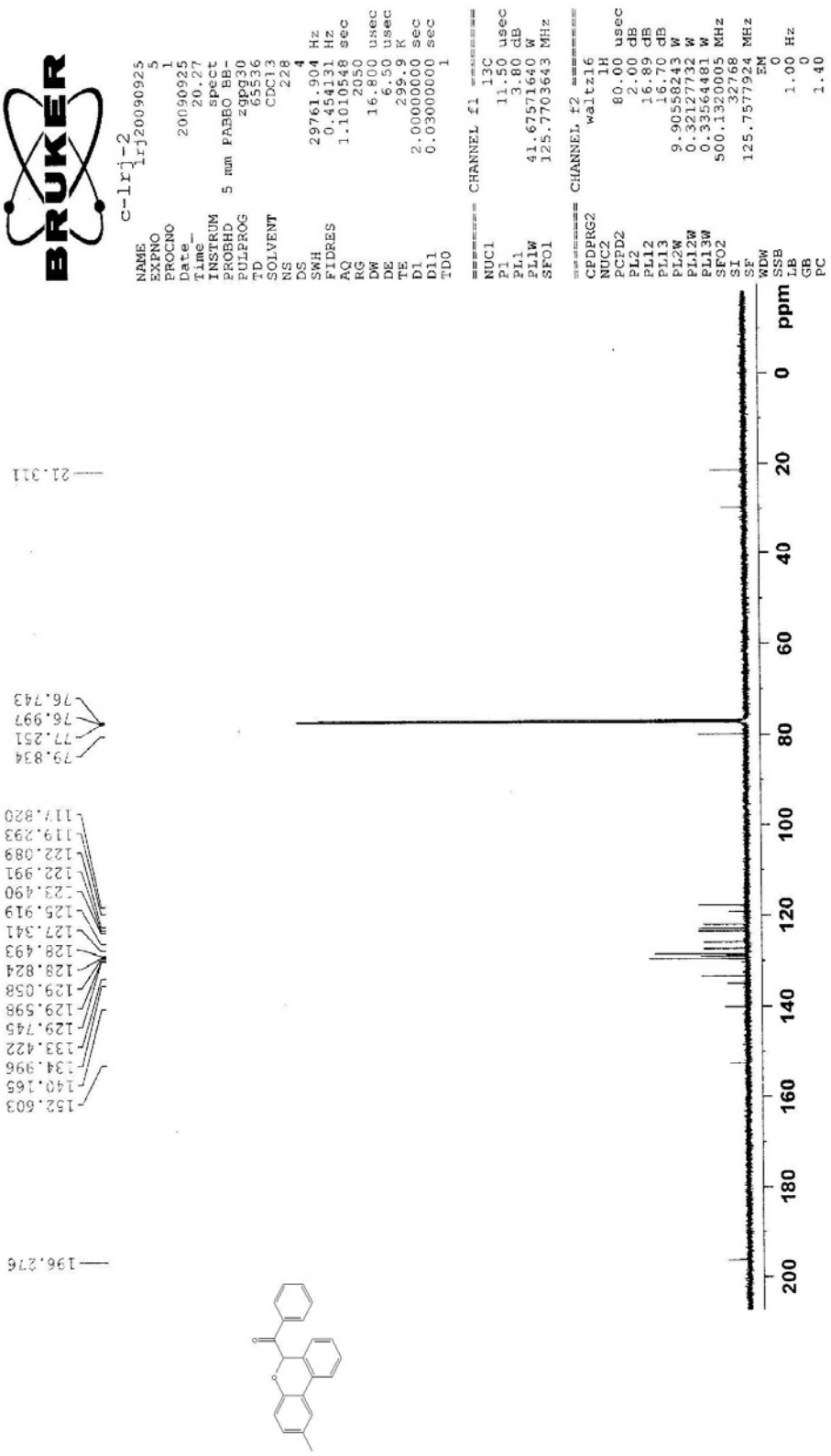
(6H-benzo[c]chromen-6-yl)(3,4-dichlorophenyl)methanone (11)



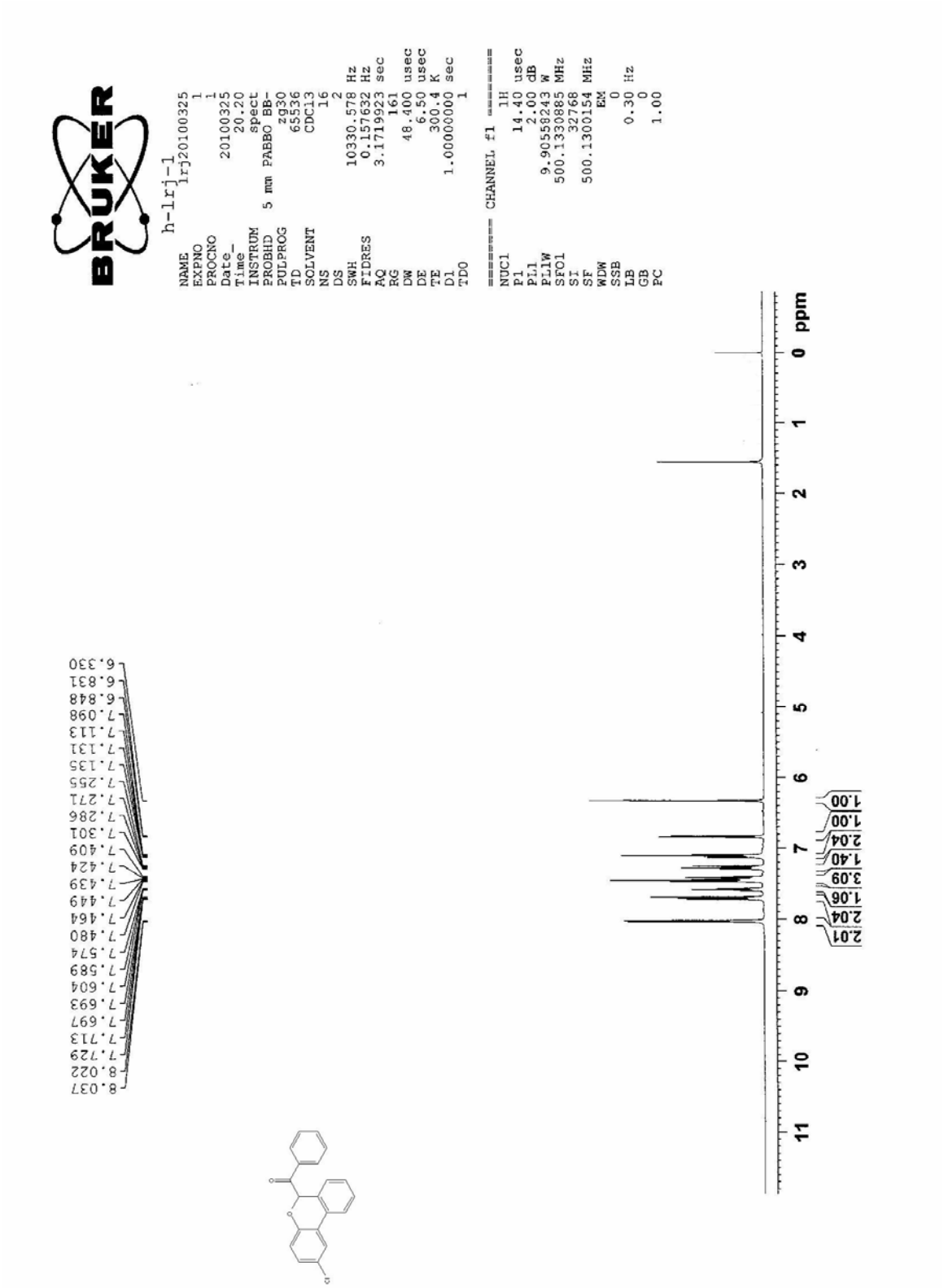
(2-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (12)



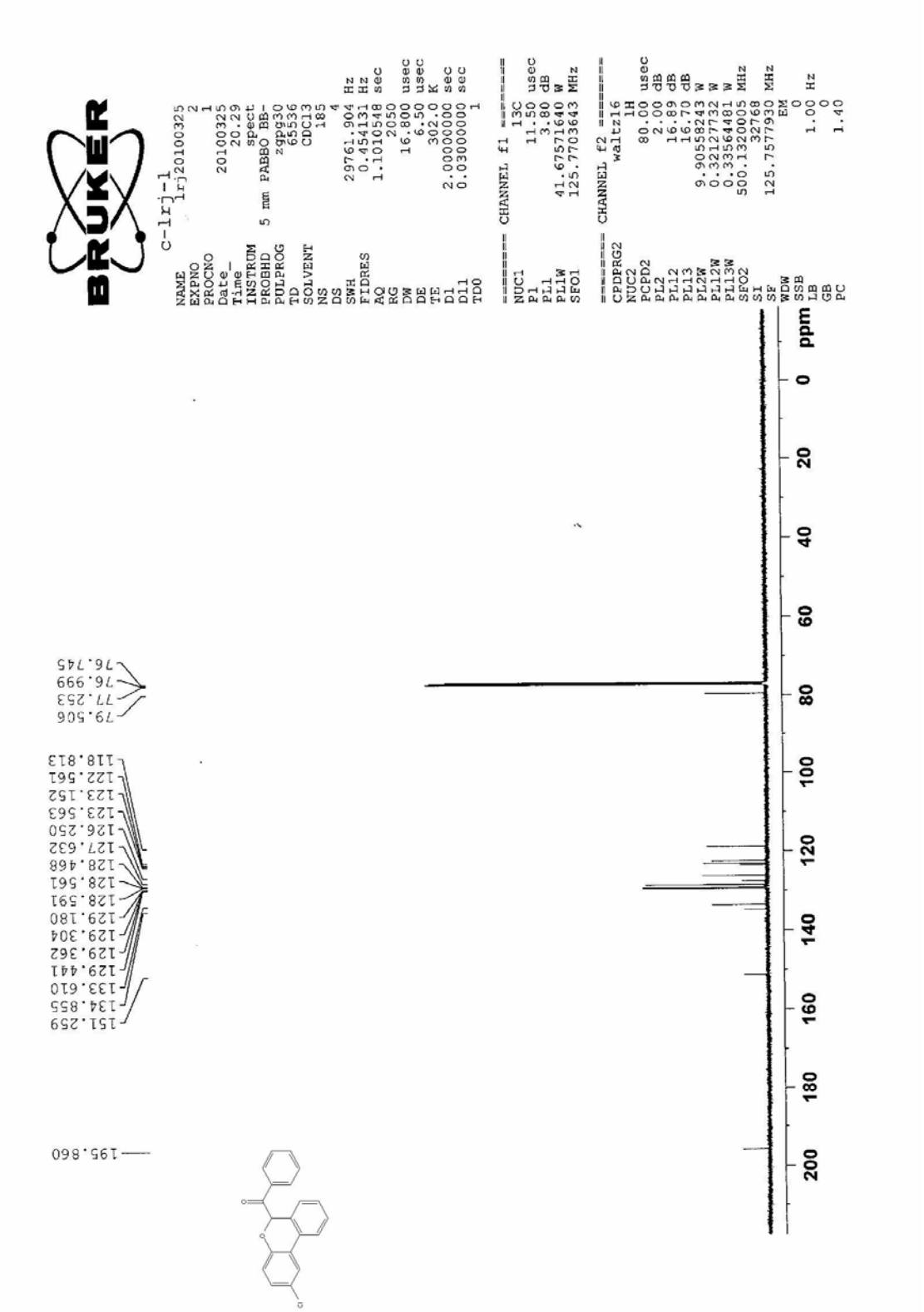
(2-methyl-6H-benzo[c]chromen-6-yl)(phenyl)methanone (12)



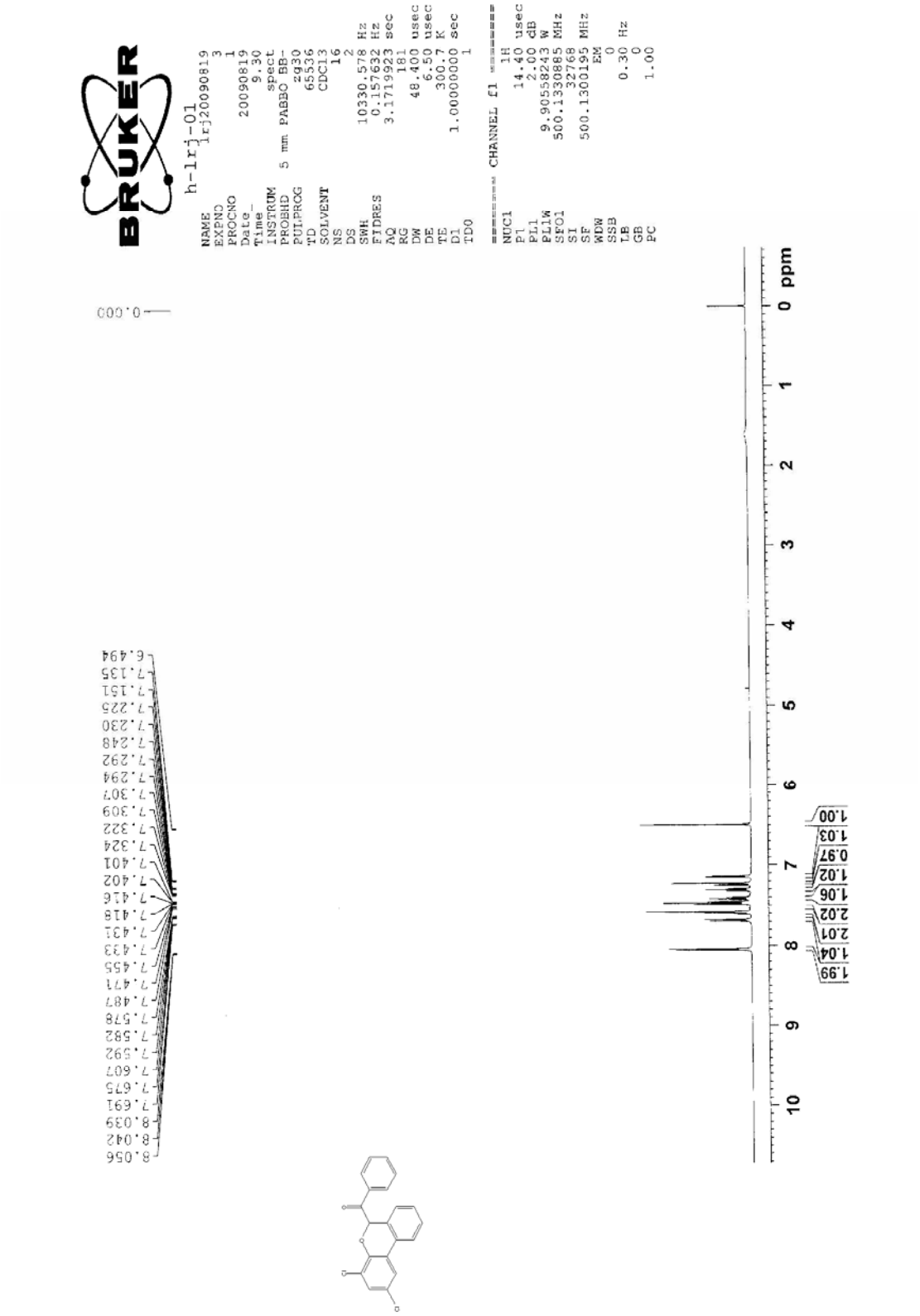
(2-chloro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (13)



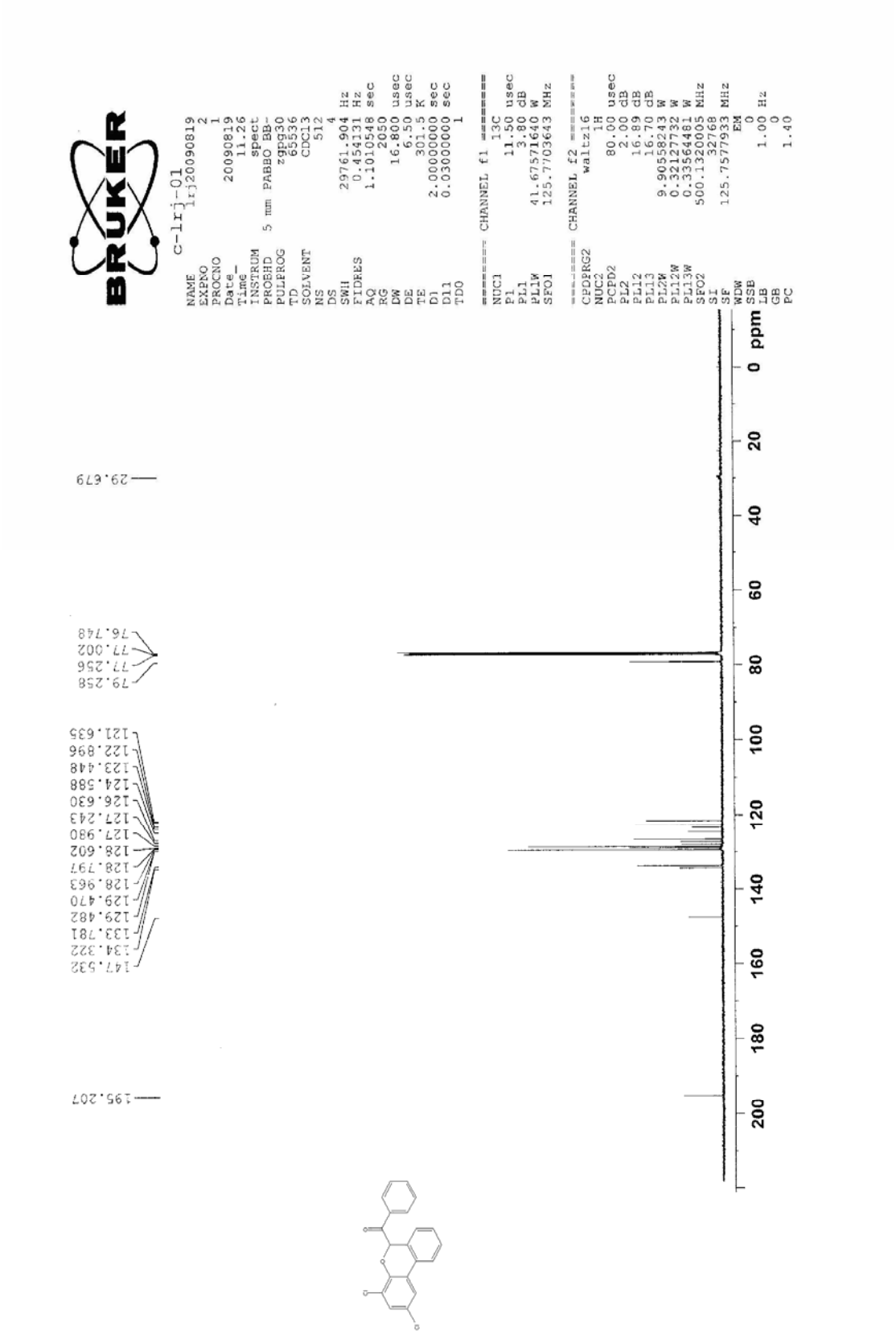
(2-chloro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (13)



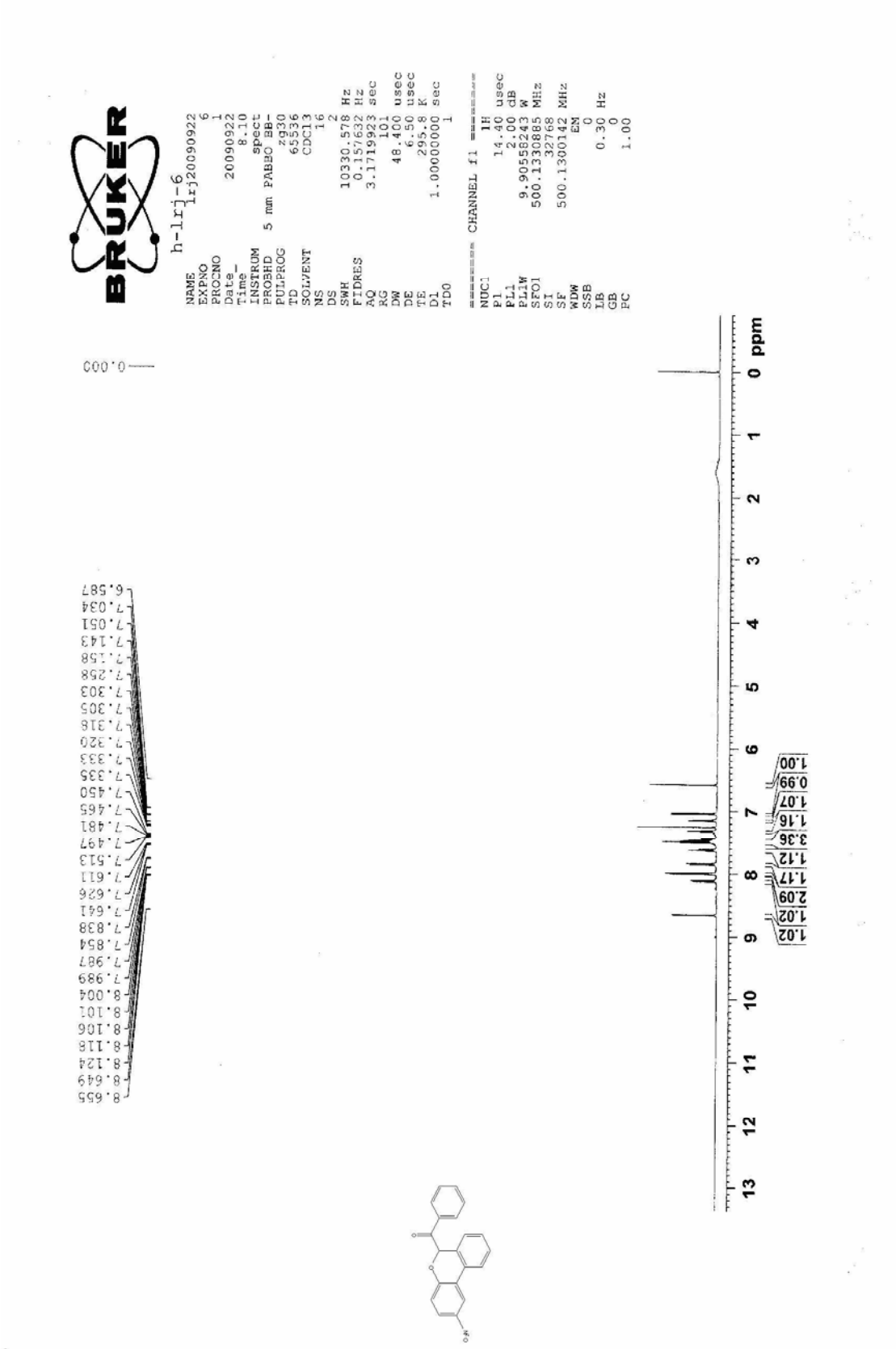
(2,4-dichloro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (14)



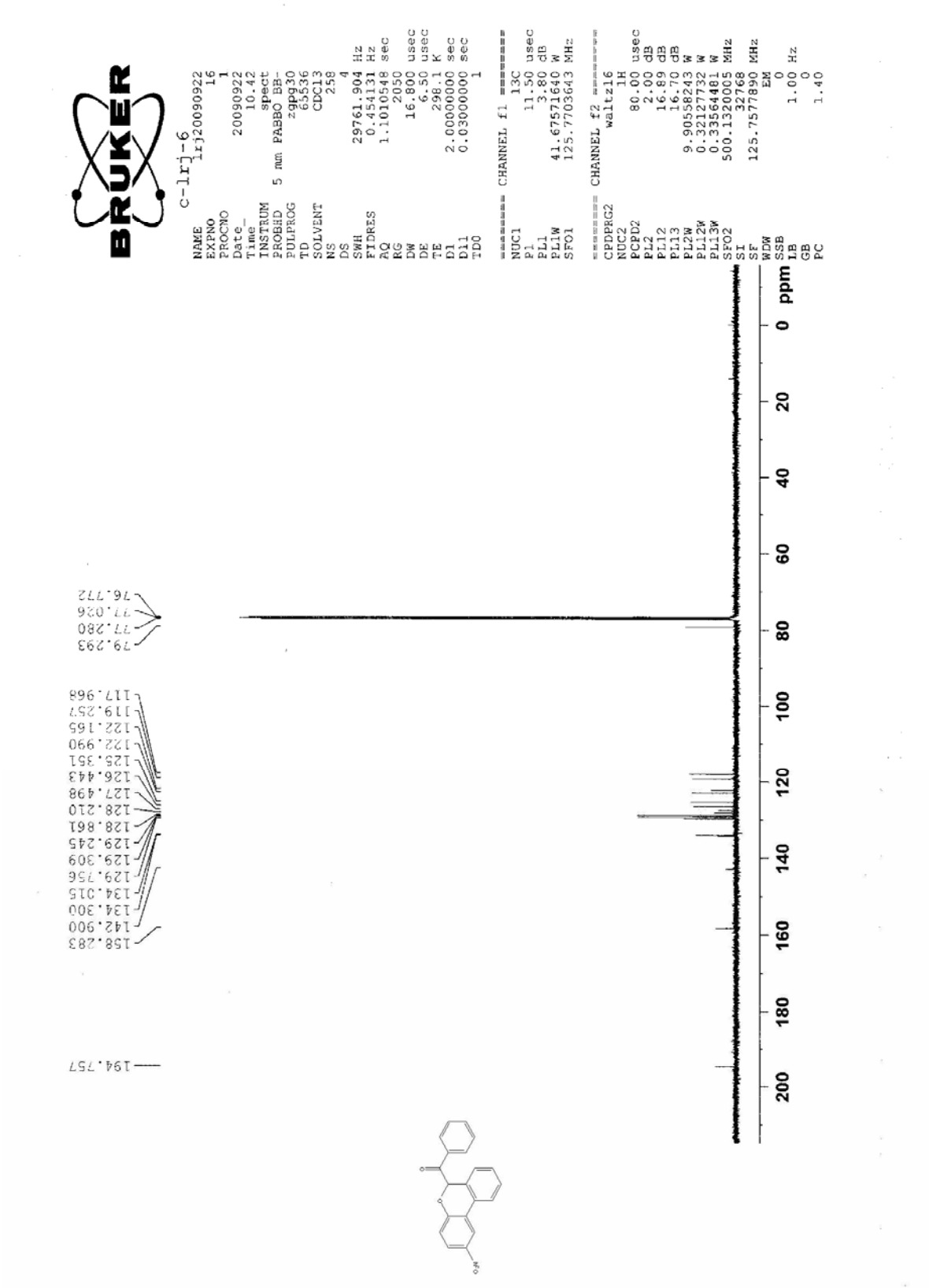
(2,4-dichloro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (14)



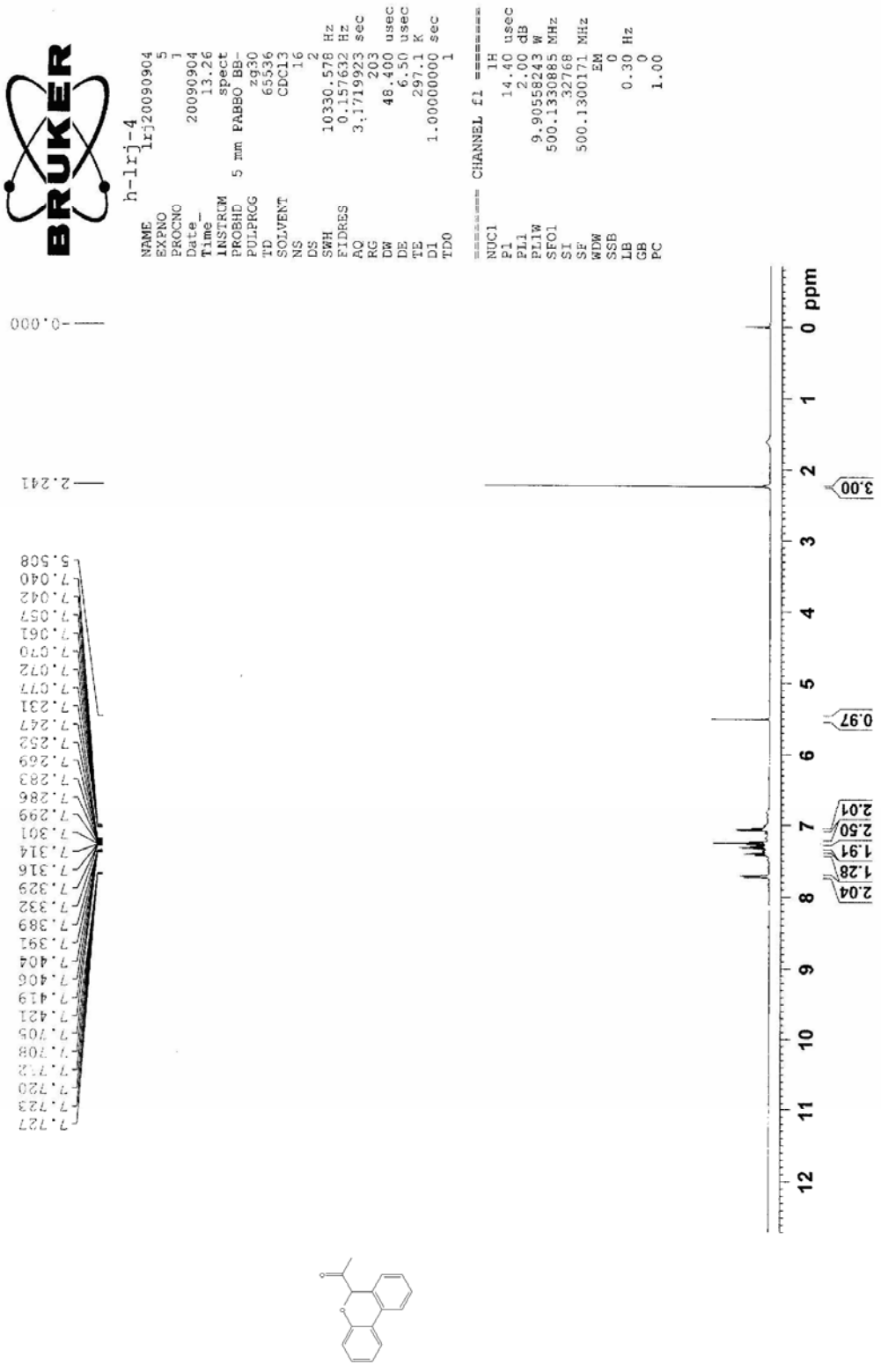
(2-nitro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (15)



(2-nitro-6H-benzo[c]chromen-6-yl)(phenyl)methanone (15)



1-(6H-benzo[c]chromen-6-yl)ethanone (16)



1-(6H-benzo[c]chromen-6-yl)ethanone (16)