Supplementary Information

One Pot Synthesis of Bioactive Benzopyranones through Palladium-Catalyzed C−H Activation and CO Insertion to 2-Arylphenols

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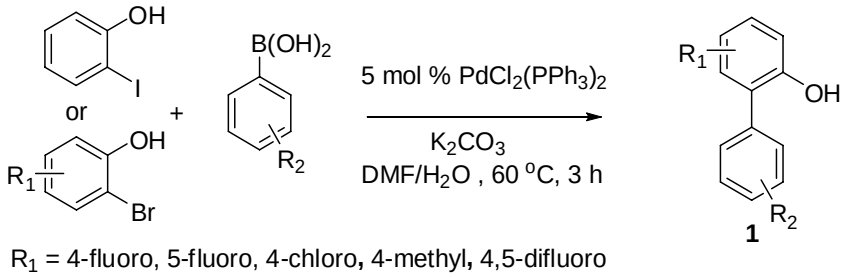
Content **Page**

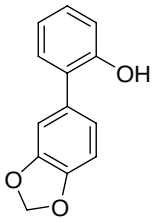
General procedure for the synthesis of 2-arylphenols (1)



R_1 = 4-fluoro, 5-fluoro, 4-chloro, 4-methyl, 4,5-difluoro

To a flame-dried round-bottom flask containing substituted 2-iodophenol or 2-bromophenol (1.0 g), arylboronic acids (1.5 equiv), K_2CO_3 (3 equiv) and 5 mol% of $PdCl_2(PPh_3)_2$was added DMF/H_2O (23 mL/26 mL). The resulting mixture was stirred at 60°C for 3 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and extracted with EtOAc for several times. The combined organic layer was washed with saturated $NaCl_{(aq)}$ for two times and dried over anhydrous $MgSO_{4(s)}$. The organic layer was then concentrated under vacuum, and the crude residue was purified by silica gel column chromatography (hexanes/EtOAc) to afford the coupling product 2-arylphenols (**1**).

Spectroscopic and physical data of 2-arylphenol derivatives (1a-y):compound 1a, is commercial available and used as received; 1b,[1a] 1c, [1a] 1d,[1a] 1e,[1b] 1f,[1c] 1g,[1c] 1m,[1d] 1r,[1e] 1t,[1f] 1w[1g] were known compounds.



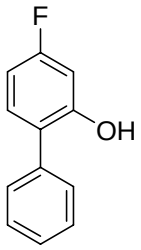
2-(benzo[d][1,3]dioxol-5-yl) phenol (1h)

White solid; Yield: 83% (808 mg); R_f= 0.48 (hexanes/EtOAc = 2:1); m.p. 88–90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (br, 1H), 6.02 (s, 2H), 6.92–6.97 (m, 5H), 7.19–7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.9, 108.4, 109.5, 115.7, 120.5, 122.2, 127.7, 128.5, 130.1,

[1](a) Wei, Y.; Yoshikai, N.*Org. Lett.* **2011**, 5504–5507; (b) Ishikawa, S.; Manabe, K. *Tetrahedron.***2010**, 297–303; (c) Ohe, K.; Yokoi, T.; Miki, K.; Nishino, F.; Uemura, S. *J. Am. Chem. Soc.*, **2002**, 526–527; (d) Gao, Z.; Lim, Y.–H.; Tredwell, M.; Li, L.; Verhoog, S.; Hopkinson, M.; Kaluza, W.; Collier, T. L.; Passchier, J.; Huiban, M.; Gouverneur, V. *Angew. Chem. Int. Ed.***2012**, 6733–6737; (e) Lin, N.–H.; Wang, L.; Cohen, J.; Gu, W.–Z.; Frost, D.; Zhang, H.–Y.; Rosenberg, S.; Sham, H. *Bioorg. Med. Chem. Lett.* **2003**, 1293–1296; (f) Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C.; Berta, G. *Tetrahedron* **1990**, *46*, 7977–7990. (g) Wawrzyniak, P.; Heinicke, J. *Tetrahedron Lett.* **2006**, 8921–8924.

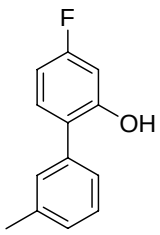
130.9, 146.7, 147.2, 152.3; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1})1579, 1608, 3513; HRMS (EI^+): calcd for $C_{13}H_{10}O_3$ (M^+) 214.0630, found 214.0629.

4-fluoro-[1,1'-biphenyl]-2-ol(1i)



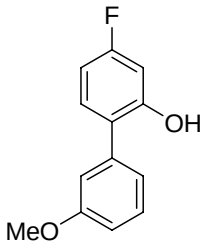
Yellow liquid; Yield: 88% (867 mg); R_f = 0.58 (hexanes/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (br, 1H), 6.75 (d, J = 2.3 Hz, 2H), 7.22 (t, J_{HH} = 6.6 Hz, $^3J_{HF}$ = 13.2 Hz, 1H), 7.44–7.50 (m, 3H), 7.51–7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.3 (d, $^2J_{FC}$= 24.7 Hz), 107.7 (d, $^2J_{FC}$= 21.2 Hz), 124.3, 127.9, 129.0, 129.2, 131.0 (d, $^3J_{FC}$= 9.5 Hz), 136.2, 153.4 (d, $^3J_{FC}$= 12.1 Hz), 163.0 (d, $^1J_{FC}$= 244.4 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1603, 3541; HRMS (EI^+): calcd for $C_{12}H_9FO$ (M^+) 188.0637 found 188.0632.

4-fluoro-3'-methyl-[1,1'-biphenyl]-2-ol (1j)



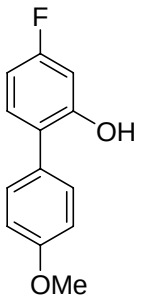
Yellow liquid; Yield: 86% (911 mg); R_f = 0.60 (hexanes/EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.51 (s, 3H), 5.74 (br, 1H), 6.77 (d, J = 1.2 Hz, 1H), 6.78–6.83 (m, 1H), 7.25 (dd, J_{HH} = 1.2 Hz, $^3J_{HF}$ = 10.8 Hz, 1H), 7.29 (s, 1H), 7.32 (d, J = 4.5 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 103.1 (d, $^2J_{FC}$= 24.7 Hz), 107.6 (d, $^2J_{FC}$= 21.2 Hz), 124.3, 125.9, 128.6, 129.1, 129.7, 130.9 (d, $^3J_{FC}$=9.8 Hz), 136.1, 139.0, 152.4 (d, $^3J_{FC}$= 12.0 Hz), 162.9 (d, $^1J_{FC}$= 244.0 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1601, 3539; HRMS (EI^+): calcd for $C_{13}H_{11}FO$ (M^+) 202.0794 found 202.0792.

4-fluoro-3'-methoxy-[1,1'-biphenyl]-2-ol(1k)



Yellow liquid; Yield: 90% (1028 mg); R_f = 0.53 (hexanes/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.80 (br, 1H), 6.72–6.76 (m, 2H), 6.96 (d, J = 8.0 Hz, 1H), 7.00–7.06 (m, 2H),7.20–7.25 (m, 1H), 7.41 (t, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 103.2 (d, $^2J_{FC}$= 24.7 Hz), 107.6 (d, $^2J_{FC}$= 21.3 Hz), 113.4, 114.6, 121.1, 124.1, 130.3, 130.9 (d, $^3J_{FC}$= 9.4 Hz), 137.6, 153.5 (d, $^3J_{FC}$= 11.8 Hz), 160.1, 163.0 (d, $^1J_{FC}$= 244.4 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1615, 3529; HRMS (EI^+): calcd for $C_{13}H_{11}FO_2$ (M^+) 218.0743 found 218.0742.

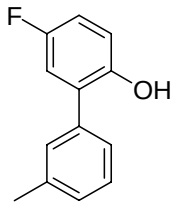
4-fluoro-4'-methoxy-[1,1'-biphenyl]-2-ol(1l)



White solid; Yield: 91% (1040 mg); R_f = 0.55 (hexanes/EtOAc = 3:1); m.p. 63–65℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 5.65 (br, 1H), 6.69–6.74 (m, 2H), 7.02 (d, J = 8.7 Hz, 2H), 7.17 (dd, J = 2.7 Hz, $^3J_{HF}$ = 15.9 Hz, 1H), 7.36 (d, J = 8.7 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$) δ 55.2, 103.1 (d, $^2J_{FC}$= 24.8 Hz), 107.6 (d, $^2J_{FC}$= 21.3 Hz), 114.7, 124.0 (d, $^4J_{FC}$= 2.9 Hz), 128.4, 130.2, 131.0 (d, $^3J_{FC}$= 9.7 Hz), 153.6 (d, $^3J_{FC}$= 11.9 Hz), 159.2, 162.8 (d, $^1J_{FC}$= 243.8 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1606, 3441,

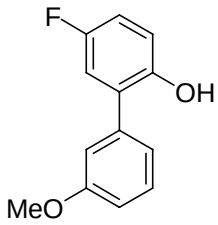
3532; HRMS (EI^+): calcd for $C_{13}H_{11}FO_2$ (M^+) 218.0743 found 218.0744.

5-fluoro-3'-methyl-[1,1'-biphenyl]-2-ol (1n)



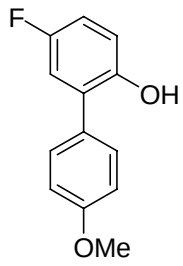
Yellow liquid; Yield: 72% (762 mg); R_f = 0.60(hexanes/EtOAc = 3:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 5.30 (br, 1H), 6.92–7.00 (m, 3H), 7.24–7.29 (m, 3H), 7.40 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 115.2 (d, $^2J_{FC}$= 22.8 Hz), 116.2 (d, $^2J_{FC}$= 23.1 Hz), 116.6 (d, $^3J_{FC}$= 7.3 Hz), 125.8, 129.0 (2C), 129.2, 129.5, 136.1 (d, $^3J_{FC}$= 6.1 Hz), 139.1 (d, $^4J_{FC}$= 3.0 Hz), 148.4, 156.9 (d, $^1J_{FC}$= 237.2 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1583, 1605, 3545; HRMS (EI^+): calcd for $C_{13}H_{11}FO$ (M^+) 202.0794 found 202.0790.

5-fluoro-3'-methoxy-[1,1'-biphenyl]-2-ol (1o)



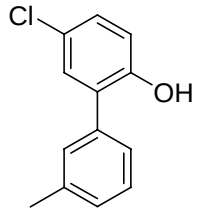
White solid; Yield: 70% (800 mg); R_f = 0.48 (hexanes/EtOAc = 3:1); m.p. 86–88 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.92 (d, J = 4.8 Hz, 1H), 6.95 (d, J = 2.8, 1H), 6.97 (d, J = 2.8 Hz, 1H), 7.00 (d, J = 2.8, 1H), 7.03 (t, J = 3.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 113.6, 114.4, 115.2 (d, $^2J_{FC}$= 22.8 Hz), 116.2 (d, $^2J_{FC}$= 23.6 Hz), 116.7 (d, $^3J_{FC}$= 7.9 Hz), 121.0, 128.8 (d, $^3J_{FC}$= 7.6 Hz), 130.2, 137.6 (d, $^4J_{FC}$= 1.5 Hz), 148.4 (d, $^4J_{FC}$= 2.2 Hz), 156.8 (d, $^1J_{FC}$= 237.2 Hz), 159.9; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1579, 1603, 3442, 3543; HRMS (EI^+): calcd for $C_{13}H_{11}FO_2$ (M^+) 218.0743, found 218.0742.

5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-ol (1p)



Yellow liquid; Yield: 77% (880 mg); R_f = 0.43 (hexanes/EtOAc = 3:1); ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.45 (br, 1H), 6.89 (dd, J = 3.9 Hz, $^3J_{HF}$ = 10.5 Hz, 1H), 6.95 (dd, J= 2.4 Hz, $^3J_{HF}$ = 10.6 Hz,1H),6.99 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 114.5, 114.7 (d, $^2J_{FC}$= 22.7 Hz), 116.2 (d, $^2J_{FC}$= 23.1 Hz), 116.5 (d, $^3J_{FC}$=8.4 Hz), 128.4, 128.8 (d, $^3J_{FC}$= 7.6 Hz), 130.0, 148.4 (d, $^4J_{FC}$= 2.3 Hz), 156.9 (d, $^1J_{FC}$= 236.8 Hz), 159.2; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1609, 3439, 3541; HRMS (EI^+): calcd for $C_{13}H_{11}FO_2$ (M^+) 218.0743, found 218.0745.

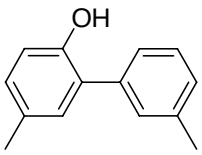
5-chloro-3'-methyl-[1,1'-biphenyl]-2-ol(1q)



Yellow liquid; Yield:74% (780 mg); R_f = 0.58 (hexanes/EtOAc =3:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 5.41 (br, 1H), 6.92 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 2.7 Hz, 1H), 7.24–7.26(m, 4H), 7.39 (t, J = 7.8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 117.0, 125.3, 125.8, 128.6, 129.0, 129.2, 129.5, 129.55, 129.61, 135.7, 139.2, 151.0; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1604, 3539; HRMS (EI^+): calcd for

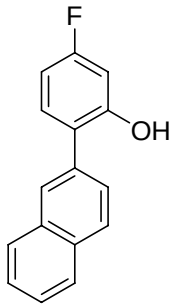
$C_{13}H_{11}ClO(M^+)$ 218.0498 found 218.0505.

3',5-dimethylbiphenyl-2-ol (1s)



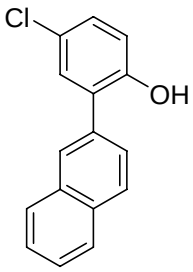
Yellow liquid; Yield: 86% (916 mg); R_f = 0.48 (hexanes/EtOAc = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H),2.55 (s, 3H), 5.52 (br, 1H), 7.02(d, J = 7.8 Hz, 1H),7.18–7.21(m, 2H), 7.32(d, J = 7.5 Hz, 1H),7.39–7.51(m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.3, 21.3, 115.5, 125.9, 127.9, 128.3, 128.9, 129.3, 129.7 (2C), 130.5, 137.2, 138.7, 150.1; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1590, 1625, 3442, 3542; HRMS (EI^+): calcd for $C_{14}H_{14}O$ (M^+) 198.1045, found198.1046.

5-fluoro-2-(naphthalen-2-yl)phenol(1u)



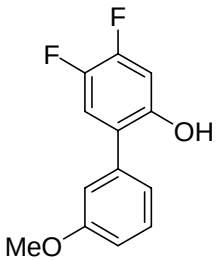
White solid; Yield: 80% (998 mg); R_f = 0.55 (hexanes/EtOAc = 3:1); m.p. 102–104℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (br, 1H), 6.75–6.81 (m, 2H), 7.30 (dd, J_{HH} = 2.7 Hz, $^3J_{HF}$ = 14.6 Hz, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.56–7.58 (m, 2H), 7.87–7.93 (m, 3H), 7.97 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.3 (d, $^2J_{FC}$= 24.8 Hz), 107.8 (d, $^2J_{FC}$= 21.4 Hz), 124.2 (d, $^4J_{FC}$= 2.6 Hz), 126.5 , 126.7, 127.0, 127.7, 127.8, 127.9, 129.2, 131.2 (d, $^3J_{FC}$= 9.7 Hz), 132.6, 133.49, 133.52, 153.7 (d, $^3J_{FC}$= 12.1 Hz), 163.1 (d, $^1J_{FC}$= 244.4 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1597, 1615, 3530; HRMS (EI^+): calcd for $C_{16}H_{11}FO$ (M^+) 238.0794 found 238.0793.

4-chloro-2-(naphthalen-2-yl)phenol(1v)



Yellow liquid; Yield: 82% (1007 mg); R_f = 0.63 (hexanes/EtOAc =3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (br, 1H), 6.96 (dd, J = 5.7, 9.5 Hz, 1H), 7.28 (dd, J = 2.7, 8.4 Hz, 1H), 7.38 (d, J = 2.7 Hz, 1H), 7.55–7.62 (m, 3H), 7.89–7.94 (m, 3H), 7.98 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ117.2, 125.6, 126.59, 126.64, 126.7, 127.7, 127.9, 128.0, 128.9, 129.2, 129.5, 129.9, 132.8, 133.2, 133.4, 151.2; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1595, 1631, 3458, 3540; HRMS (EI^+): calcd for $C_{16}H_{11}ClO$ (M^+) 254.0498 found 254.0499.

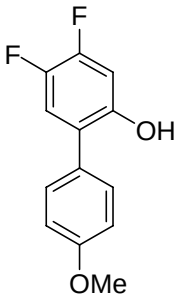
4,5-difluoro-3'-methoxy-[1,1'-biphenyl]-2-ol(1x)



Yellow solid; Yield: 85% (961 mg); R_f = 0.48 (hexanes/EtOAc =3:1); m.p. 98–100℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H),6.83 (dd, $^3J_{HF}$ = 7.2 Hz, $^2J_{HF}$ = 18.4 Hz, 1H), 6.93 (dd, J = 2.4, 8.4 Hz, 1H), 7.06–7.10 (m, 2H), 7.17 (dd, $^3J_{HF}$ = 6.8 Hz, $^2J_{HF}$ = 18.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 105.5 (d, $^2J_{FC}$= 28.8 Hz), 113.2, 114.5, 116.4 (d, $^2J_{FC}$= 20.5), 121.0 (d, $^3J_{FC}$= 9.9 Hz), 121.3, 129.5, 136.1, 143.6 (t, $^3J_{FC}$= 14.4 Hz), 147.5 (d, $^1J_{FC}$= 233.0 Hz), 155.7 (d, $^1J_{FC}$= 244.4 Hz), 159.5; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1})

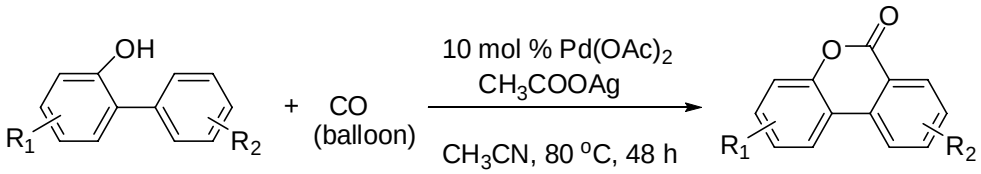
1595, 1633, 3404; HRMS (EI^+): calcd for $C_{13}H_{10}F_2O_2$ (M^+) 236.0649, found 236.0646.

4,5-difluoro-4'-methoxy-[1,1'-biphenyl]-2-ol(1y)



White solid; Yield: 88% (995 mg); R_f = 0.48 (hexanes/EtOAc =3:1);m.p. 126–129℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.80 (dd, $^3J_{HF}$ = 7.6 Hz, $^2J_{HF}$ = 18.4 Hz, 1H), 6.96 (dd, J = 2.4, 6.6 Hz, 2H), 7.11 (dd, $^3J_{HF}$= 7.2 Hz, $^2J_{HF}$ = 18.4 Hz, 1H), 7.41 (dd, J = 1.6, 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 105.3 (d, $^2J_{FC}$= 28.9), 114.0, 116.1 (dd, $^3J_{FC}$= 20.5, $^4J_{FC}$= 5.4 Hz), 127.1, 127.7, 129.8, 142.9 (dd, $^2J_{FC}$= 28.8, $^3J_{FC}$= 16.3 Hz), 147.4 (d, $^1J_{FC}$= 232.3 Hz), 155.6 (d, $^1J_{FC}$= 242.3 Hz), 159.1; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1609, 1645, 3366; HRMS (EI^+): calcd for $C_{13}H_{10}F_2O_2$ (M^+) 236.0649, found 236.0648.

General procedure for the synthesis of benzopyranone derivatives (2a-y)



To a dried reaction tube containing 2-arylphenols **1** (50 mg), $Pd(OAc)_2$ (10mol %), CH_3COOAg (3 equiv) and a stir bar was sealed with septum and purged with CO gas. Anhydrous acetonitrile (4 mL) was then injected into the tube followed by insertion of a CO balloon to the reaction system. The reaction tube was placed in an oil bath with vigorous stirring at 80℃ for 48 h. Upon completion of the reaction, the reaction mixture was added to hot ethyl acetate followed by filtration through a thin pad of silica gel. The filtrate was concentrated by vacuum and crude residue was purified by silica gel column chromatography (hexanes/EtOAc) to afford benzopyranone derivatives **2**.

Spectroscopic and physical data of benzopyranone derivatives:2a,[2a,b] 2b,[2a,b] 2c,[2b] 2d,[2a,b] 2e,[2a,b] 2m,[2a,b] 2f,[2c] 2h[2d] and 2w[2e] were known compounds.

9-methoxy-6H-benzo[c]chromen-6-one (2c)

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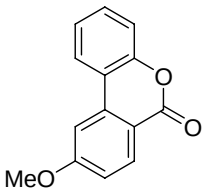
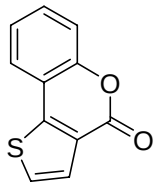
[2] (a) Vishnumurthy, K.; Makriyannis, A. *J. Comb. Chem.* **2010**, 664–669; (b) Inamoto, K.; Kadokawa, J.; Kondo, Y. *Org. Lett.* **2013**, 3962–3965; (c) Majumdar, K. C.; Bhattacharyya, T. *J. Chem. Research (S)* **1997**, 244–245; (d) Håkansson, A. E.; Palmelund, A.; Holm, H.; Madsen, R. *Chem. Eur. J.* **2006**, 3243–3253; (e) He, Y.; Zhang, X.–Y.; Cui, L.–Y.; Wang, J.–J.; Fan, X.–S. *Green Chem.* **2012**, 3429–3435.



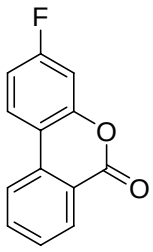
Pale yellow solid; Yield: 85% (48 mg); R_f= 0.50 (hexanes/EtOAc =2:1); m.p. 173–175℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.07 (dd, *J* = 2.1, 9.0 Hz, 1H), 7.26–7.33 (m, 2H), 7.43–7.48 (m, 2H), 7.95 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.7, 105.0, 114.2, 116.1, 117.7, 117.9, 122.7, 124.3, 130.4, 132.8, 136.8, 151.6, 160.9, 164.8; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718; HRMS (EI^+): calcd for $C_{14}H_{10}O_3$ (M^+) 226.0630, found 226.0629.

4H-thieno[3,2-c]chromen-4-one(2g)



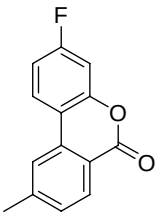
White solid; Yield: 62% (36 mg); R_f= 0.49 (hexanes/EtOAc =3:1); m.p. 198–200℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.36 (m, 2H), 7.41–7.52 (m, 2H), 7.67 (d, *J* = 5.4 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.1, 117.5, 123.4, 124.6, 125.9, 126.9, 128.3, 130.4, 148.5, 151.2, 157.2; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1739; HRMS (EI^+): calcd for $C_{11}H_6O_2S$ (M^+) 202.0089, found 202.0087.

3-fluoro-6H-benzo[c]chromen-6-one(2i)



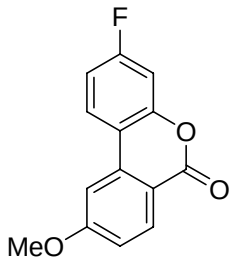
White solid; Yield:65% (37 mg); R_f= 0.55(hexanes/EtOAc =3:1); m.p. 149–150 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05–7.10 (m, 2H), 7.58 (td, *J* = 0.9, 7.4Hz, 1H),7.83 (td, *J* = 1.2, 7.2Hz, 1H), 8.00–8.06 (m, 2H), 8.38 (dd, *J* = 1.2, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.1 (d, $^2J_{FC}$= 25.0 Hz), 112.4 (d, $^2J_{FC}$= 22.0 Hz), 114.6 (d, $^4J_{FC}$= 3.0 Hz), 120.4, 121.5, 124.3 (d, $^3J_{FC}$= 9.9 Hz), 128.7, 130.7, 134.2, 135.1, 152.1 (d, $^3J_{FC}$= 12.6 Hz), 160.8, 163.4 (d, $^1J_{FC}$= 250.1 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1})1752; HRMS (EI^+): calcd for $C_{13}H_7FO_2$ (M^+) 214.0430, found 214.0427.

3-fluoro-9-methyl-6H-benzo[c]chromen-6-one(2j)



White solid; Yield:72% (41 mg); R_f= 0.53 (hexanes/EtOAc =5:1);m.p.143–145 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 6.92 (dd, J_{HH}= 2.7 Hz, $^3J_{HF}$ = 14.7 Hz, 1H), 6.98 (dd, *J* = 2.4, 8.3 Hz, 1H), 7.26(d, *J* = 8.1 Hz, 1H), 7.65(s, 1H), 7.86 (dd, J_{HH}= 5.7 Hz,$^3J_{HF}$ = 14.7 Hz, 1H), 8.09(d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 104.8 (d,$^2J_{FC}$= 25.0 Hz), 112.1 (d,$^2J_{FC}$= 22.0 Hz), 114.5 (d,$^4J_{FC}$= 3.0 Hz), 117.7, 121.5, 124.2 (d,$^3J_{FC}$= 9.9 Hz), 129.9, 130.4, 133.9, 146.2, 152.1 (d,$^3J_{FC}$= 12.2 Hz), 160.7, 163.2 (d,$^1J_{FC}$= 249.7Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1729; HRMS (EI^+): calcd for $C_{14}H_9FO_2$ (M^+) 228.0587, found 228.0591.

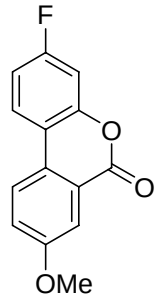
3-fluoro-9-methoxy-6H-benzo[c]chromen-6-one(2k)



White solid; Yield: 87% (49 mg); R_f= 0.33 (hexanes/EtOAc = 3:1); m.p. 230–232 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.99 (s, 3H), 7.03–7.10 (m, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.98 (dd, J_{HH}= 7.2 Hz, $^3J_{HF}$ = 15.0 Hz, 1H), 8.32 (d, *J* =

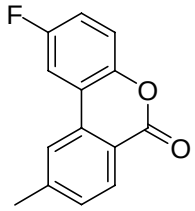
8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 105.09, 105.12 (d, $^2J_{FC}$= 25.1 Hz) 112.2 (d, $^2J_{FC}$= 22.3 Hz), 113.5, 114.6, 115.9, 124.3 (d, $^3J_{FC}$= 9.9 Hz), 133.1, 136.4, 152.6 (d, $^3J_{FC}$= 12.1 Hz), 160.6, 163.6 (d, $^1J_{FC}$= 249.7 Hz), 165.0; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718; HRMS (EI^+): calcd for $C_{14}H_9FO_3$ (M^+) 244.0536, found 244.0539.

3-fluoro-8-methoxy-6H-benzo[c]chromen-6-one(2l)



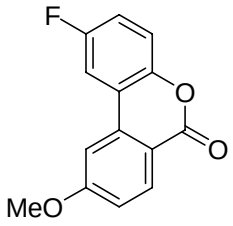
White solid; Yield:74% (41 mg); R_f= 0.48 (hexanes/EtOAc =3:1); m.p. 147–150℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.08 (d, J = 8.4 Hz, 2H), 7.40 (dd, J_{HH} = 3.0 Hz, $^3J_{HF}$ = 11.7 Hz, 1H), 7.78 (d, J = 2.7 Hz, 1H), 7.96 (d, J = 8.7Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 104.9 (d, $^2J_{FC}$= 25.5 Hz), 111.2, 112.3 (d, $^2J_{FC}$= 22.4 Hz), 114.7 (d, $^4J_{FC}$= 3.0 Hz), 121.5, 123.2, 123.6 (d, $^3J_{FC}$= 9.9 Hz), 124.5, 127.6, 151.1 (d, $^3J_{FC}$= 12.1 Hz), 159.9, 160.9, 162.7 (d,$^1J_{FC}$= 248.6 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1733; HRMS (EI^+): calcd for $C_{14}H_9FO_3$ (M^+) 244.0536, found 244.0539.

2-fluoro-9-methyl-6H-benzo[c]chromen-6-one (2n)

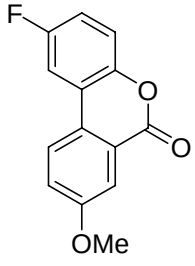


White solid; Yield:75% (42 mg); R_f= 0.55 (hexanes/EtOAc =5:1); m.p. 144–147 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.19 (dd, J = 3.0, 7.8 Hz, 1H), 7.34 (dd, J_{HH}= 4.2 Hz, $^3J_{HF}$ = 13.8 Hz, 1H), 7.43 (d, $^3J_{HF}$ = 13.5 Hz, 1H), 7.71 (dd, J = 2.7, 9.2 Hz, 1H), 7.82 (s, 1H), 8.30 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 108.7 (d, $^2J_{FC}$= 24.7 Hz), 117.5 (d,$^2J_{FC}$= 24.3 Hz), 118.8 (d, $^3J_{FC}$= 9.1 Hz), 119.3 (d, $^3J_{FC}$= 8.7 Hz), 122.1, 130.5, 130.7, 130.8, 133.9, 146.2, 147.6, 159.3 (d, $^1J_{FC}$= 241.7 Hz), 160.9; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1})1730; HRMS (EI^+): calcd for $C_{14}H_9FO_2$ (M^+) 228.0587, found 228.0585.

2-fluoro-9-methoxy-6H-benzo[c]chromen-6-one (2o)



Pale yellow solid; Yield: 81% (45 mg); R_f= 0.48 (hexanes/EtOAc =3:1); m.p. 140–143℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 3H), 7.16 (dd, J = 2.1, 8.9 Hz, 1H), 7.21 (dd, J_{HH} = 4.8 Hz, $^3J_{HF}$ = 10.5 Hz, 1H), 7.34 (dd, J_{HH} = 4.2 Hz, $^3J_{HF}$ = 13.8 Hz,1H), 7.39 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 2.7, 9.2 Hz, 1H), 8.35 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 105.4, 108.8 (d, $^2J_{FC}$= 24.7 Hz), 114.3, 116.8, 117.8 (d, $^2J_{FC}$= 23.9 Hz), 119.4 (d, $^3J_{FC}$= 8.3 Hz), 129.1, 133.1, 136.1, 147.8, 159.2 (d, $^1J_{FC}$= 241.8 Hz), 160.7, 164.9; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1714; HRMS (EI^+): calcd for $C_{14}H_9FO_3$ (M^+) 244.0536, found 244.0537.

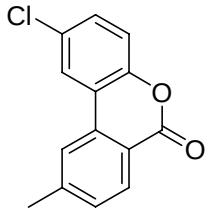


2-fluoro-8-methoxy-6H-benzo[c]chromen-6-one (2p)

Pale yellow solid; Yield: 86% (48 mg); R_f= 0.45 (hexanes/EtOAc =3:1); m.p. 145–147℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (s, 3H),

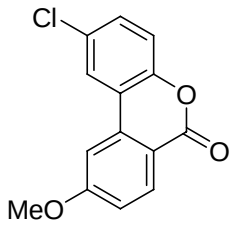
7.11–7.18 (m, 1H), 7.35 (dd, J_{HH}= 4.8 Hz, $^{3}J_{HF}$ = 13.8 Hz, 1H), 7.43 (dd, J = 2.7, 8.9 Hz, 1H), 7.65 (dd, J = 3.0, 9.3 Hz, 1H), 7.84 (d, J = 2.7 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 108.2(d, $^{2}J_{FC}$= 24.6 Hz), 111.4, 116.5 (d, $^{2}J_{FC}$= 24.3 Hz), 119.1 (d, $^{3}J_{FC}$= 8.4 Hz), 119.4 (d, $^{3}J_{FC}$= 8.0 Hz), 122.5, 123.7, 124.3, 127.2, 128.3, 146.5, 159.4 (d, $^{1}J_{FC}$= 238.7Hz), 160.9; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718; HRMS (EI^{+}): calcd for $C_{14}H_9FO_3$ (M^{+}) 244.0536, found 244.0535.

2-chloro-9-methyl-6H-benzo[c]chromen-6-one(2q)



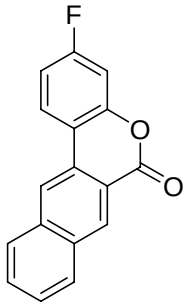
White solid; Yield:75% (42 mg); R_f= 0.53 (hexanes/EtOAc =5:1); m.p. 146–148℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.27 (d, J = 6.6Hz, 1H), 7.41(dd, J = 2.4, 8.7 Hz, 1H), 7.45 (s, 1H), 7.84 (s, 1H), 8.00(d, J = 2.1 Hz, 1H), 8.28(d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 118.8, 119.1, 119.4, 121.9, 122.5, 129.9, 130.2, 130.7, 130.8, 133.5, 146.2, 149.8, 160.7; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1730; HRMS (EI^{+}): calcd for $C_{14}H_9ClO_2$ (M^{+}) 244.0291, found 244.0288.

2-chloro-9-methoxy-6H-benzo[c]chromen-6-one(2r)



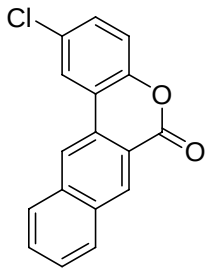
White solid; Yield: 85% (47 mg); R_f= 0.43 (hexanes/EtOAc =3:1); m.p. 219–221℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.15 (dd, J = 2.4, 8.7 Hz, 1H), 7.29 (t, J = 8.7 Hz, 1H), 7.41–7.45 (m, 2H), 7.95 (d, J = 2.1 Hz, 1H), 8.34 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 105.2, 114.3, 117.0, 119.3, 119.4, 122.6, 129.8, 130.5, 133.1, 135.8, 150.1, 160.5, 165.0; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1713; HRMS (EI^{+}): calcd for $C_{14}H_9ClO_3$ (M^{+}) 260.0240, found 260.0249.

3-fluoro-6H-naphtho[2,3-c]chromen-6-one (2u)



White solid; Yield: 72% (40 mg); R_f= 0.43 (hexanes/EtOAc =5:1); m.p. 198–190℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00–7.10 (m, 2H), 7.54–7.59 (m, 1H), 7.64–7.69 (m, 1H), 7.97 (t, J = 7.5 Hz, 2H), 8.12 (dd, J_{HH} = 6.0 Hz, $^{3}J_{HF}$ = 14.7 Hz, 1H), 8.36 (s, 1H), 8.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 105.2 (d, $^{2}J_{FC}$= 25.4 Hz), 112.4 (d, $^{2}J_{FC}$= 22.2 Hz), 114.8, 118.4, 118.5, 120.3, 124.3 (d, $^{3}J_{FC}$= 9.5 Hz), 127.2, 128.0, 129.5, 129.7, 132.2, 133.0, 136.2, 151.6 (d, $^{3}J_{FC}$= 12.0 Hz),161.0, 163.2 (d, $^{1}J_{FC}$= 249.1 Hz); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1})1731; HRMS (ESI^{+}): calcd for $C_{17}H_{10}FO_2$ (M^{+}) 265.0665, found 265.0668.

2-chloro-6H-naphtho[2,3-c]chromen-6-one(2v)



White solid; Yield: 74% (41 mg); R_f= 0.60 (hexanes/EtOAc =3:1); m.p. 210–212℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7Hz, 1H),7.43 (dd, J = 2.4, 8.7Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 7.72 (td, J = 1.5, 7.7 Hz, 1H), 8.06 (t, J = 9.0 Hz, 2H), 8.19 (d, J = 2.4Hz,

1H), 8.51 (s, 1H), 9.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 118.9, 119.4, 119.8, 121.1, 122.7, 127.6, 128.2, 128.5, 129.6, 129.9, 130.0, 130.2, 132.8, 133.1, 136.2, 149.3, 160.9; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1730; HRMS (EI^+): calcd for $C_{17}H_9ClO_2$ (M^+) 280.0291, found 280.0293.

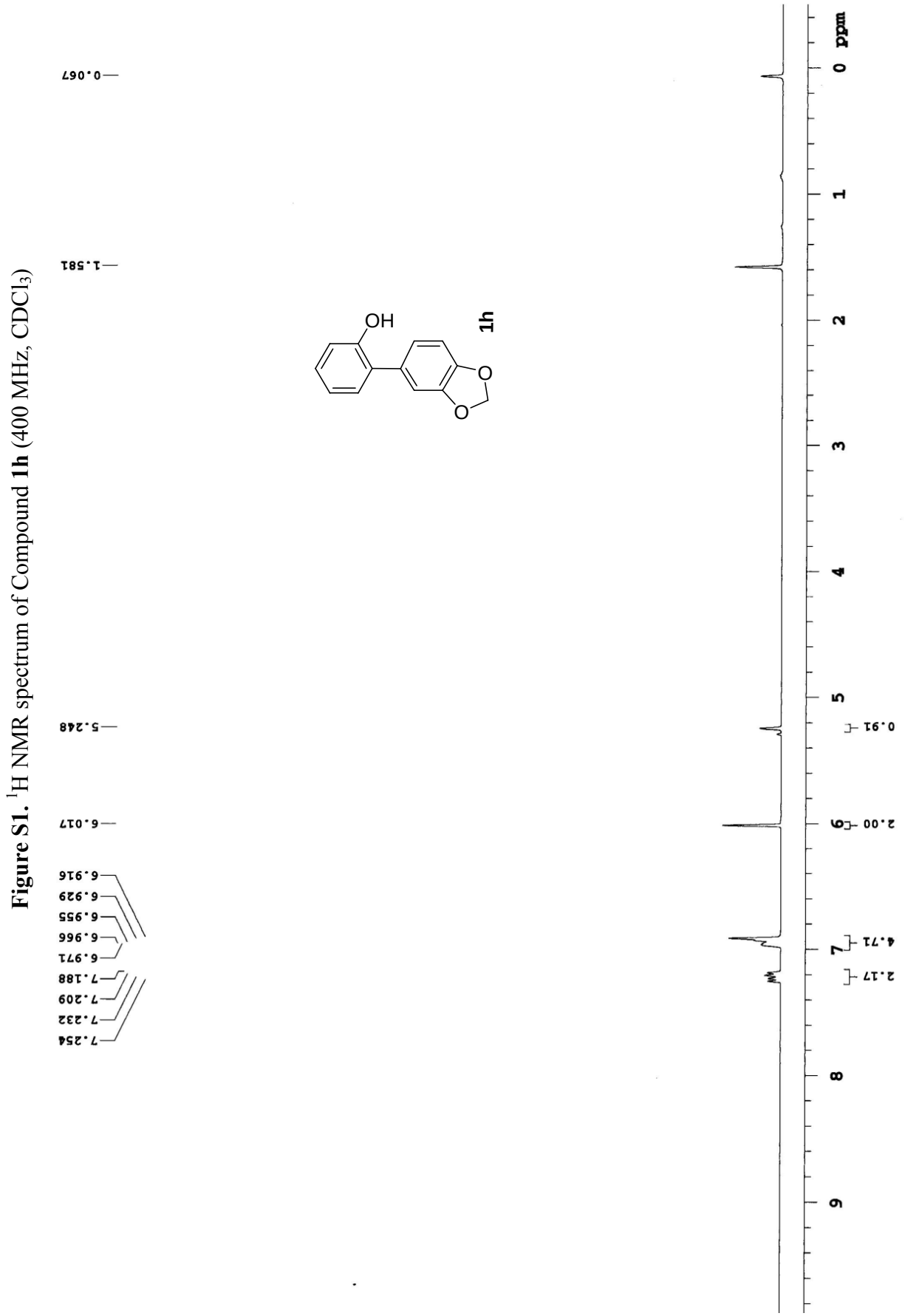
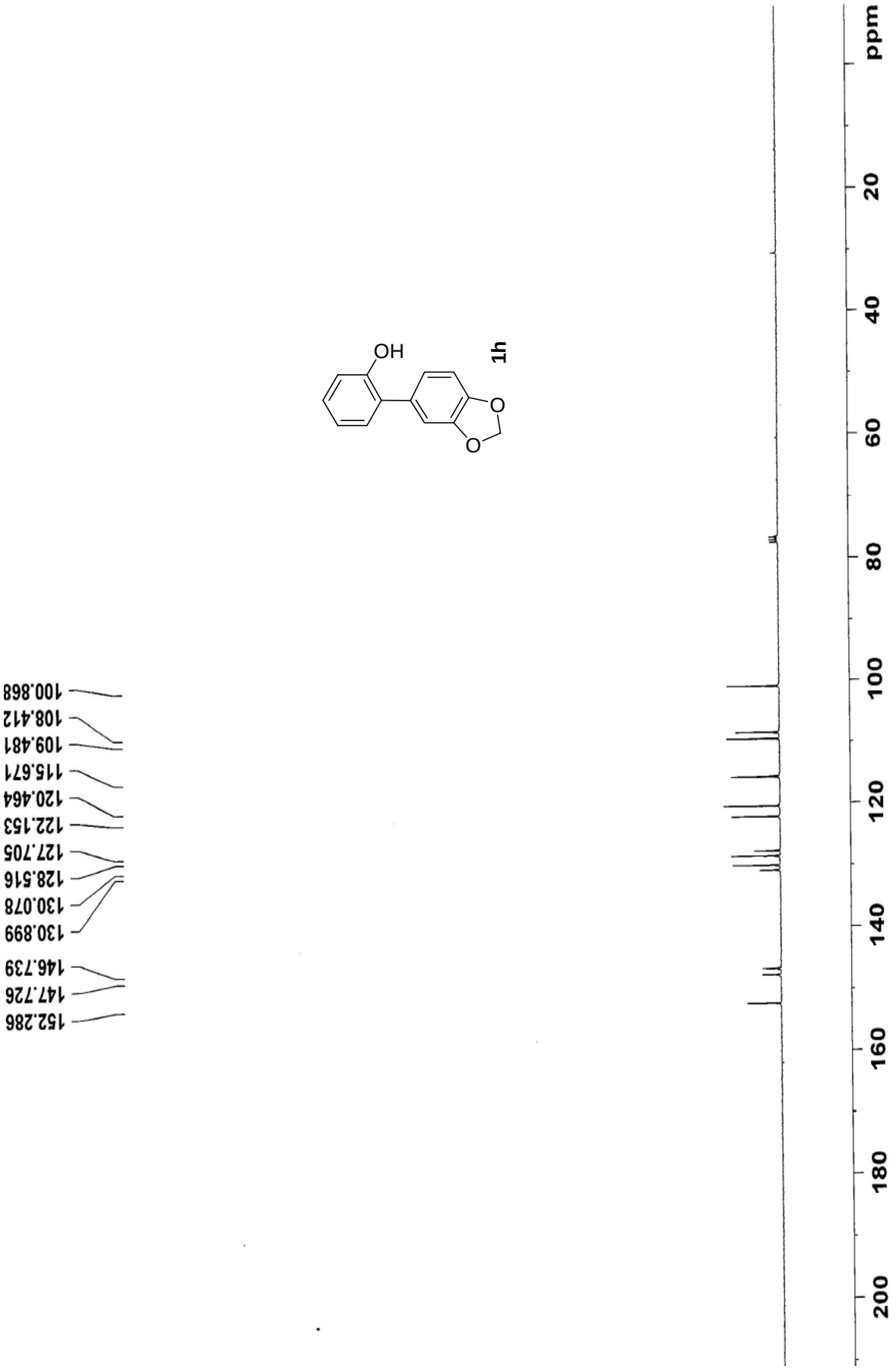


Figure S1. ^{1}H NMR spectrum of Compound **1h** (400 MHz, $CDCl_3$)

Figure S2. ^{13}C NMR spectrum of Compound **1h** (100 MHz, $CDCl_3$)



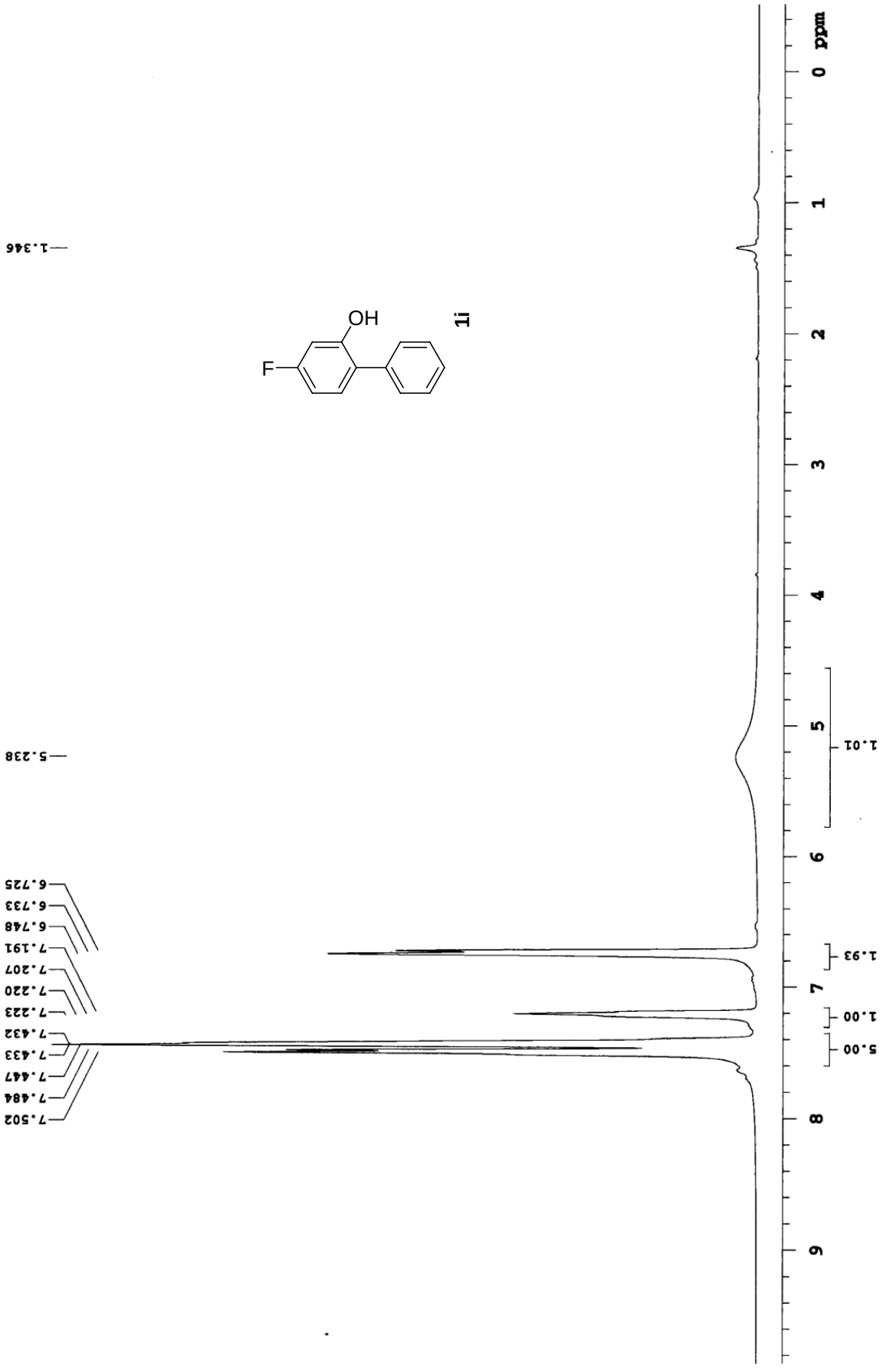


Figure S3. ^{1}H NMR spectrum of Compound **1i** (400 MHz, $CDCl_3$)

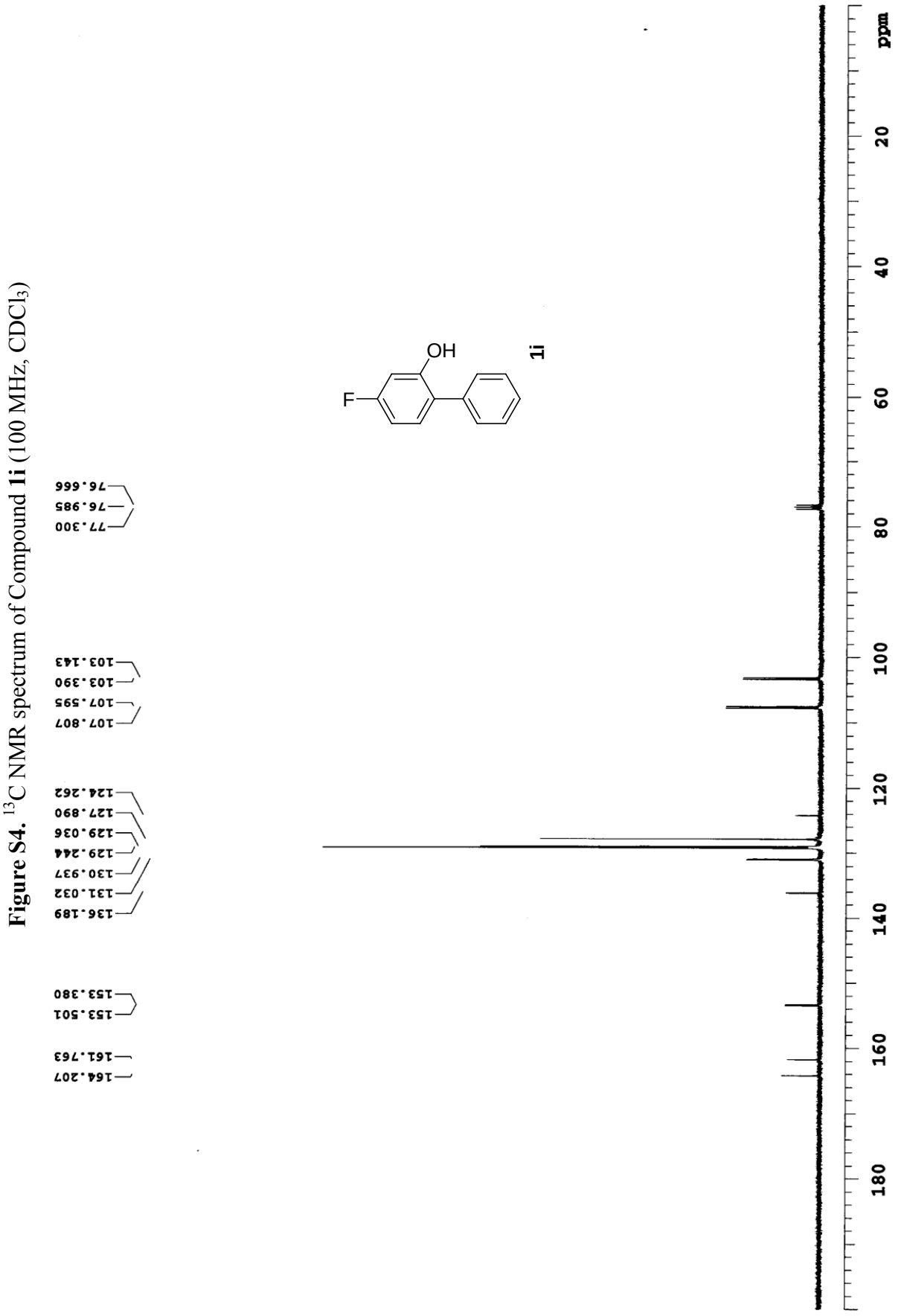


Figure S4. ^{13}C NMR spectrum of Compound **1i** (100 MHz, $CDCl_3$)

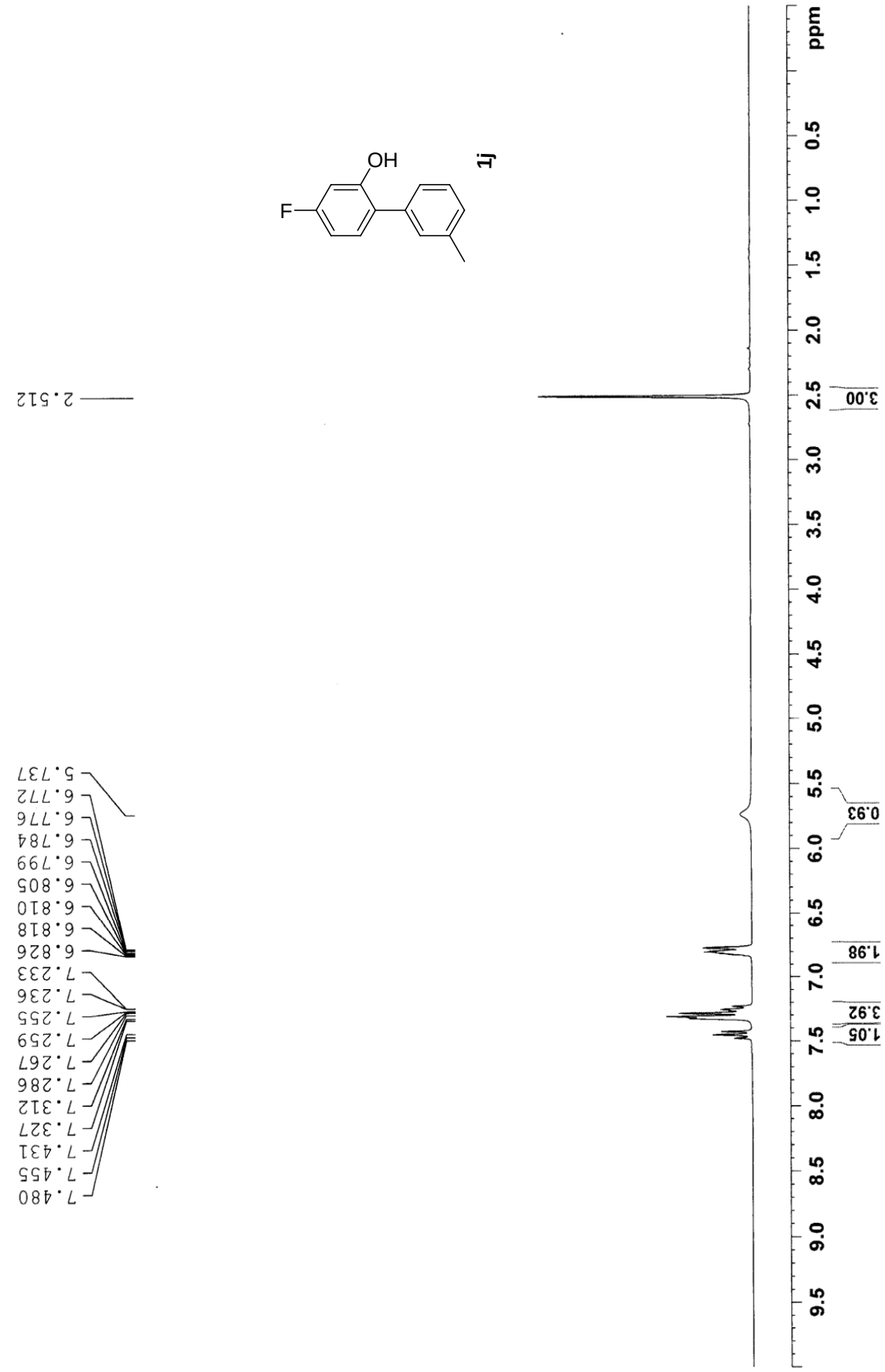


Figure S5. ^{1}H NMR spectrum of Compound **1j** (300 MHz, $CDCl_3$)

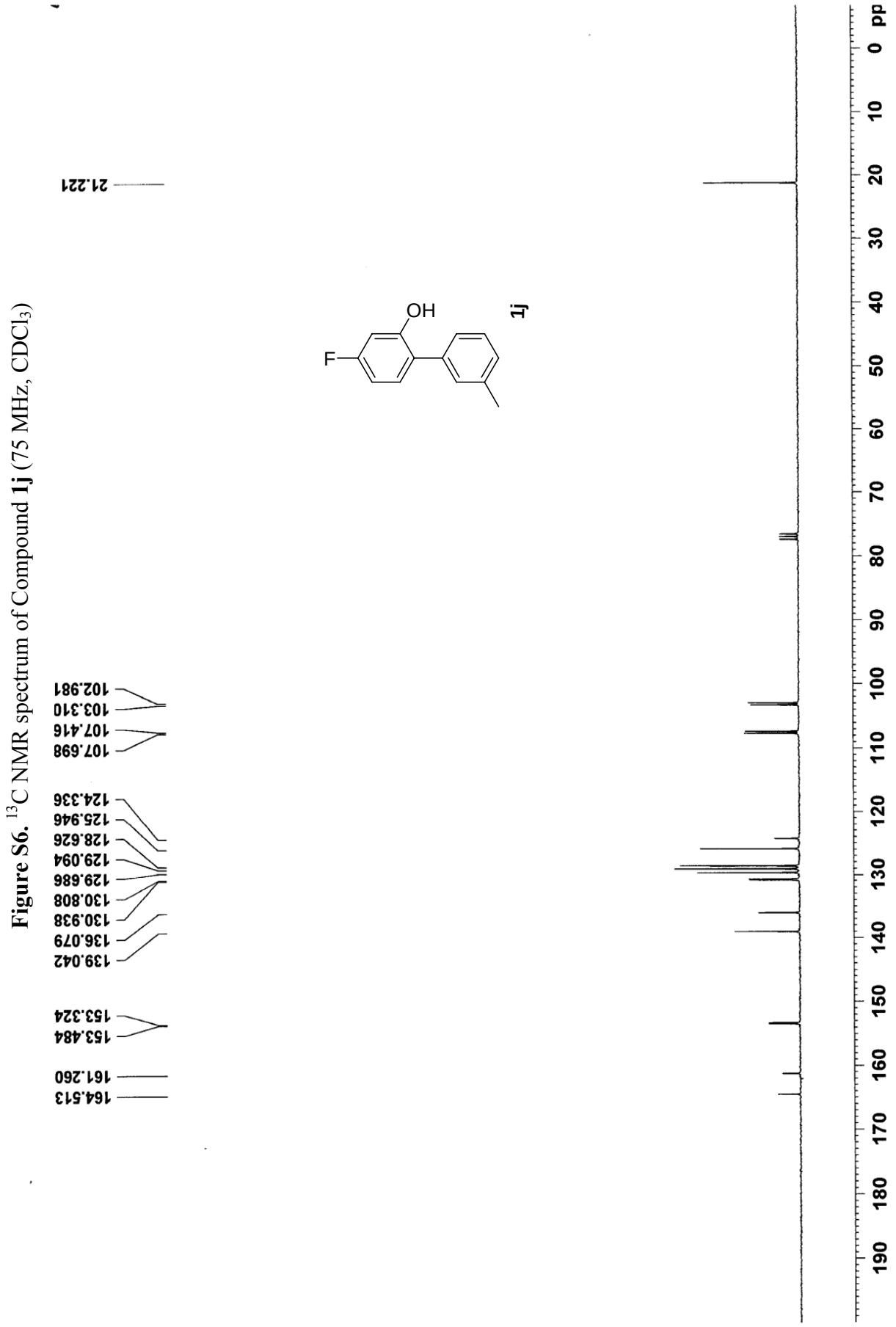


Figure S6. ^{13}C NMR spectrum of Compound **1j** (75 MHz, $CDCl_3$)

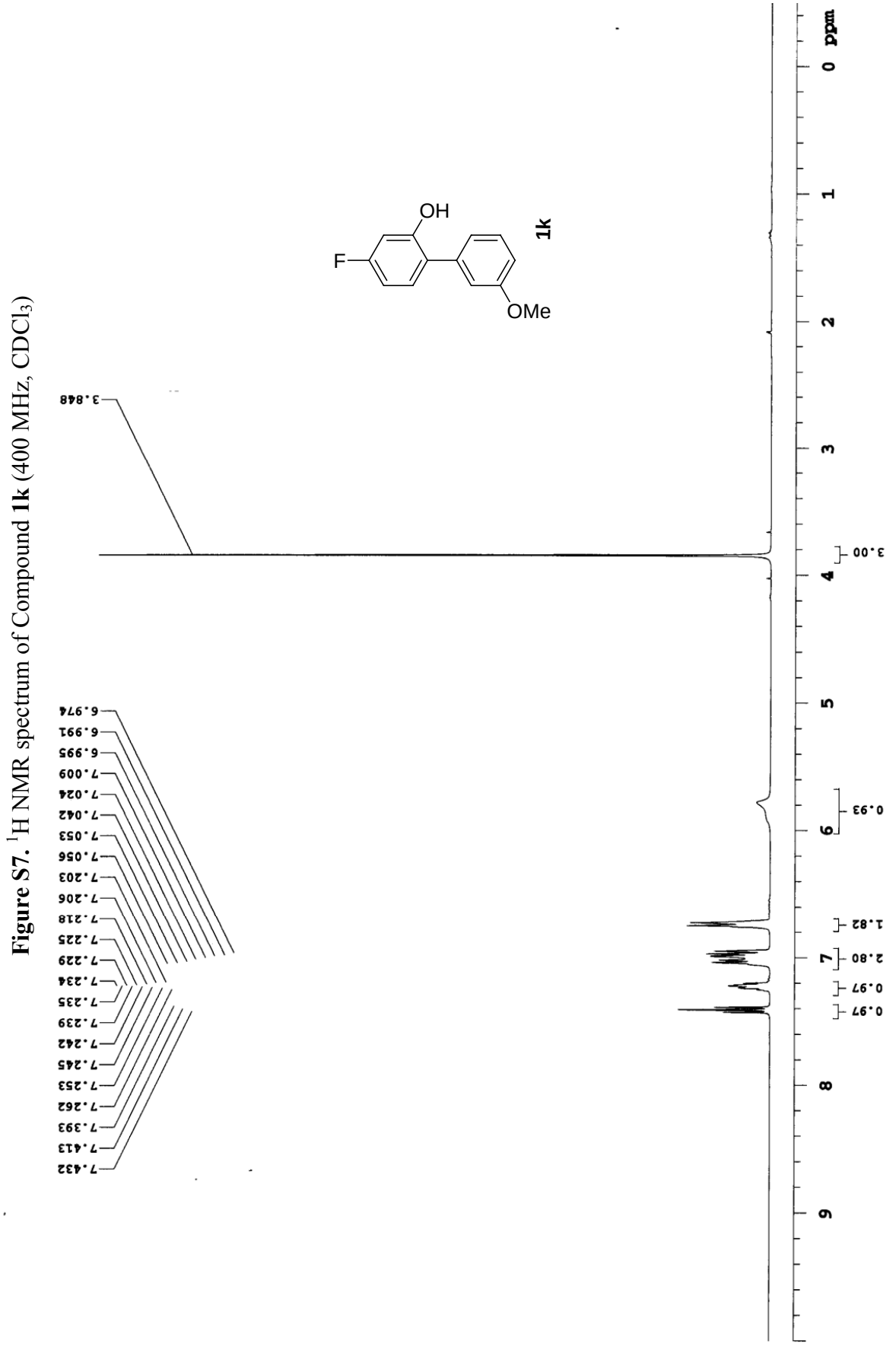


Figure S7. ^{1}H NMR spectrum of Compound **1k** (400 MHz, $CDCl_3$)

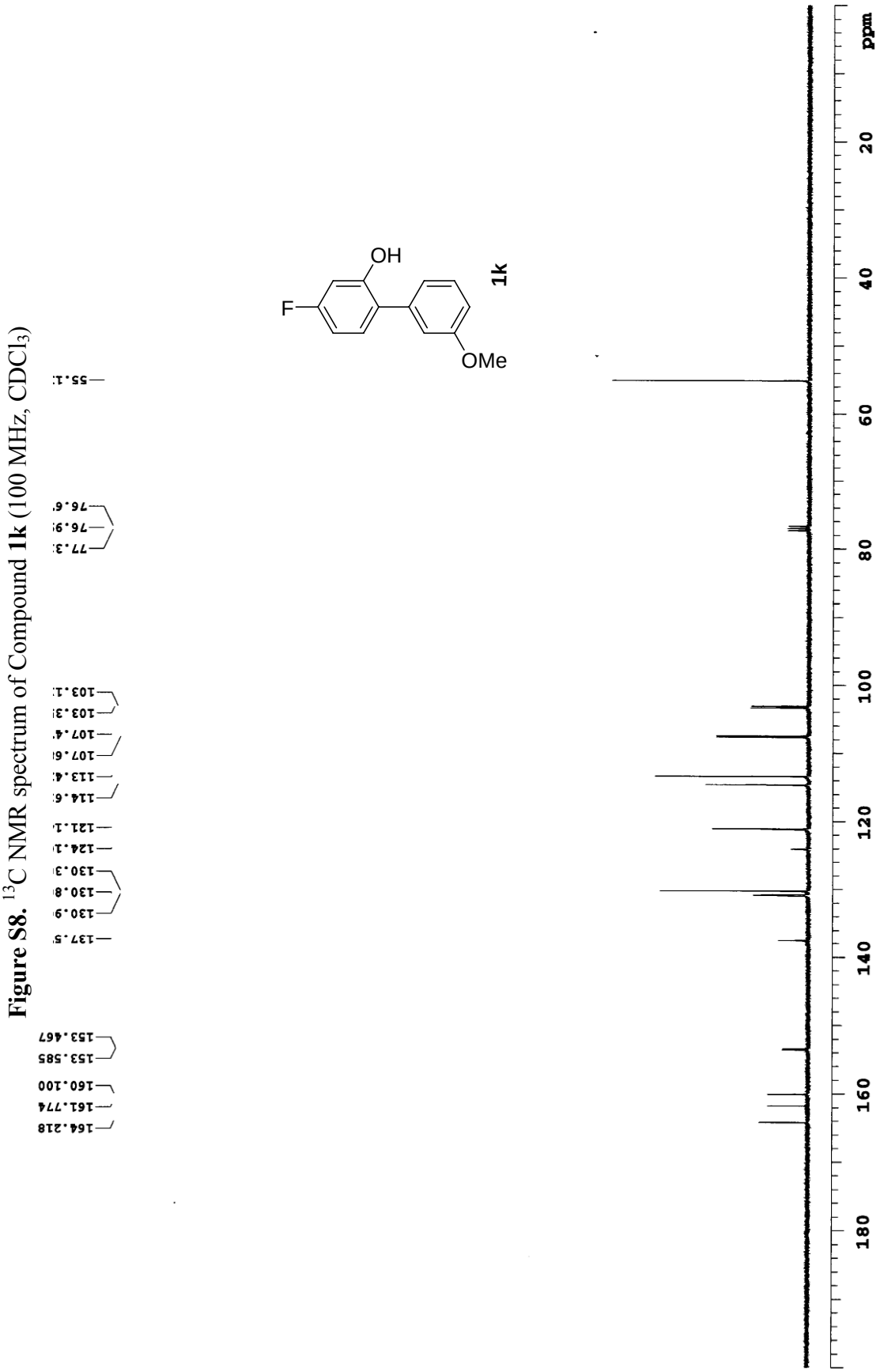


Figure S8. ^{13}C NMR spectrum of Compound **1k** (100 MHz, $CDCl_3$)

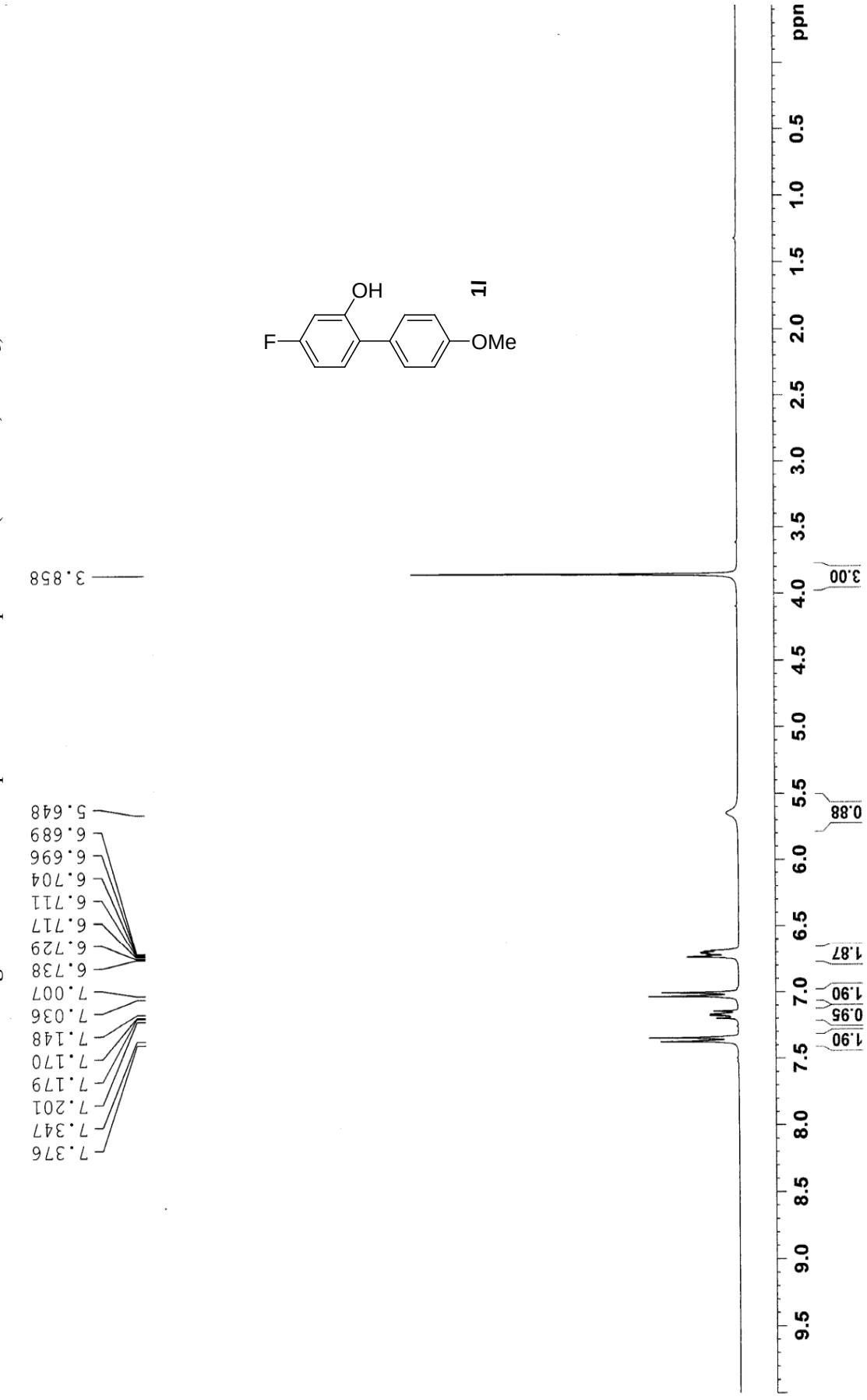


Figure S9. ^{1}H NMR spectrum of Compound **1l** (300 MHz, $CDCl_3$)

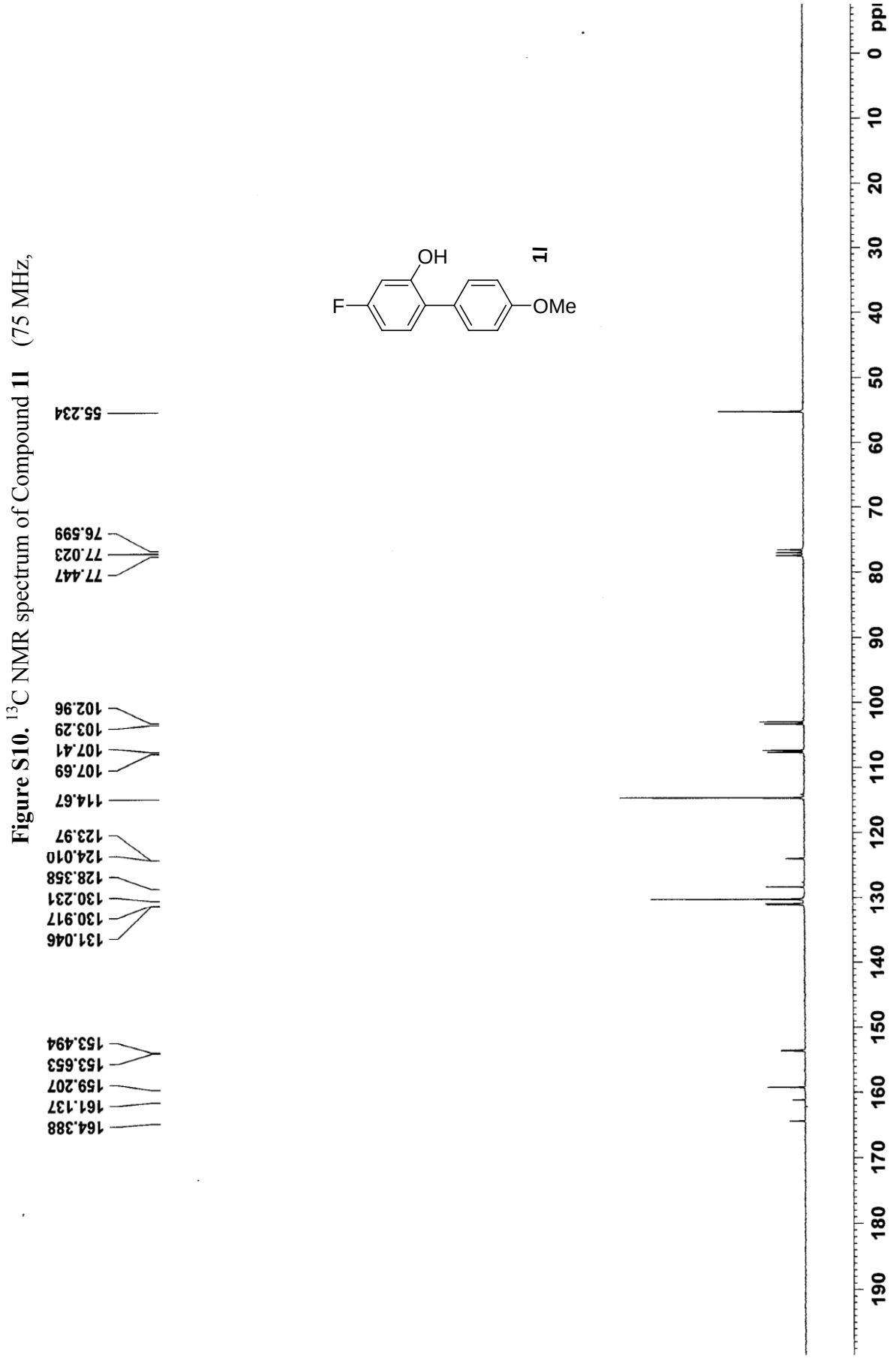


Figure S10. ^{13}C NMR spectrum of Compound **1l** (75 MHz,

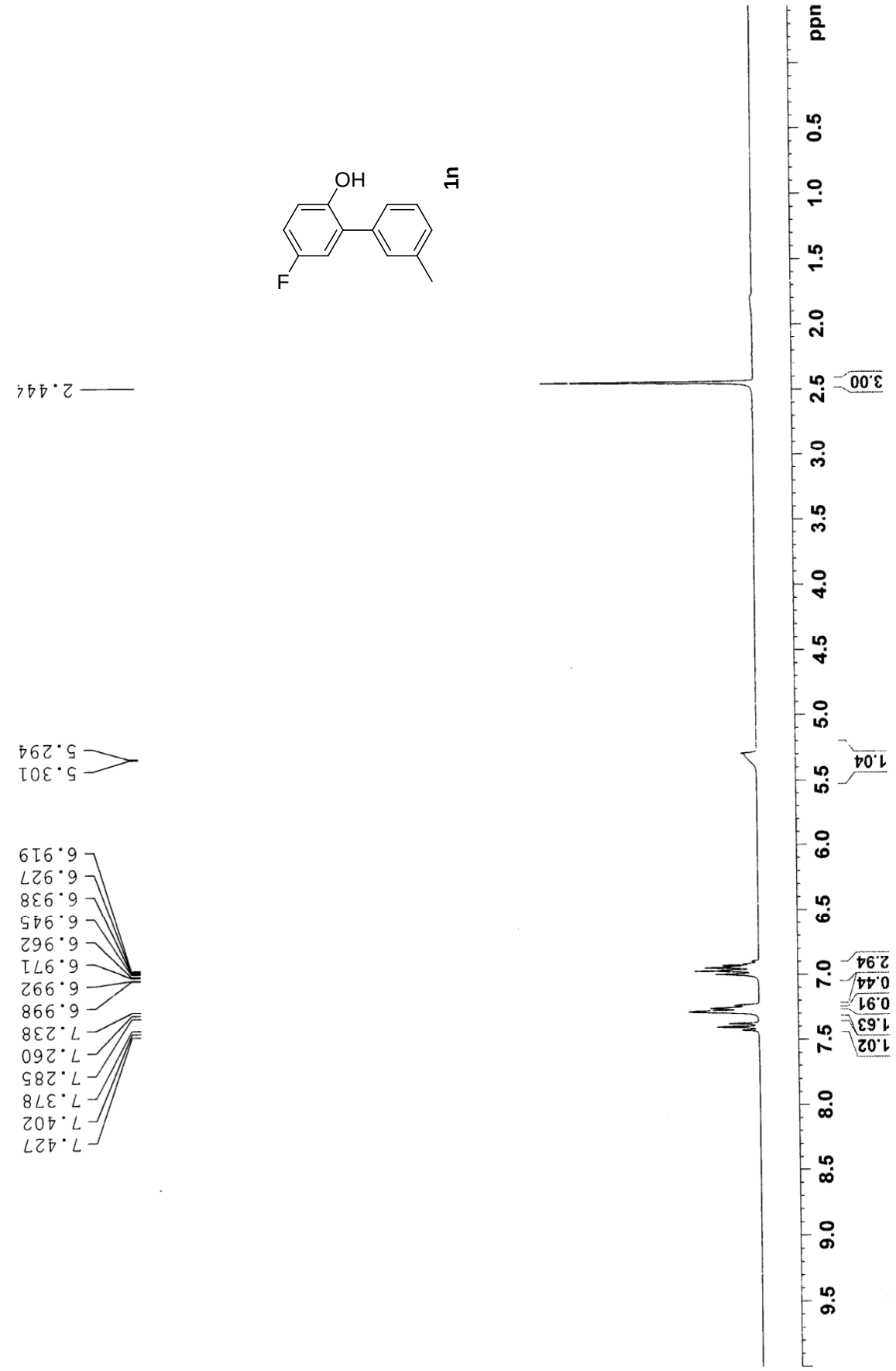


Figure S11. ^{1}H NMR spectrum of Compound **1n** (300 MHz, $CDCl_3$)

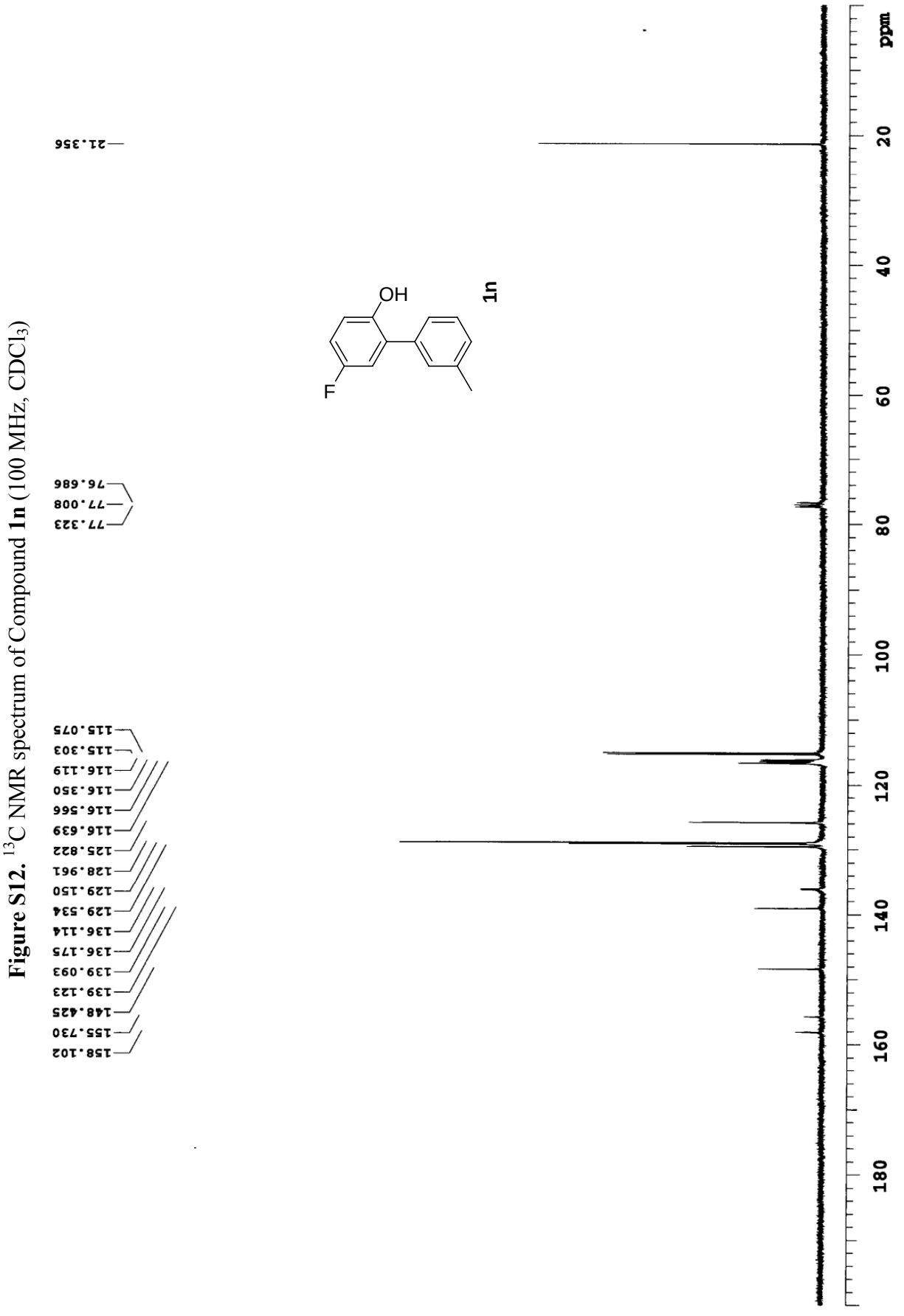


Figure S12. ^{13}C NMR spectrum of Compound **1n** (100 MHz, $CDCl_3$)

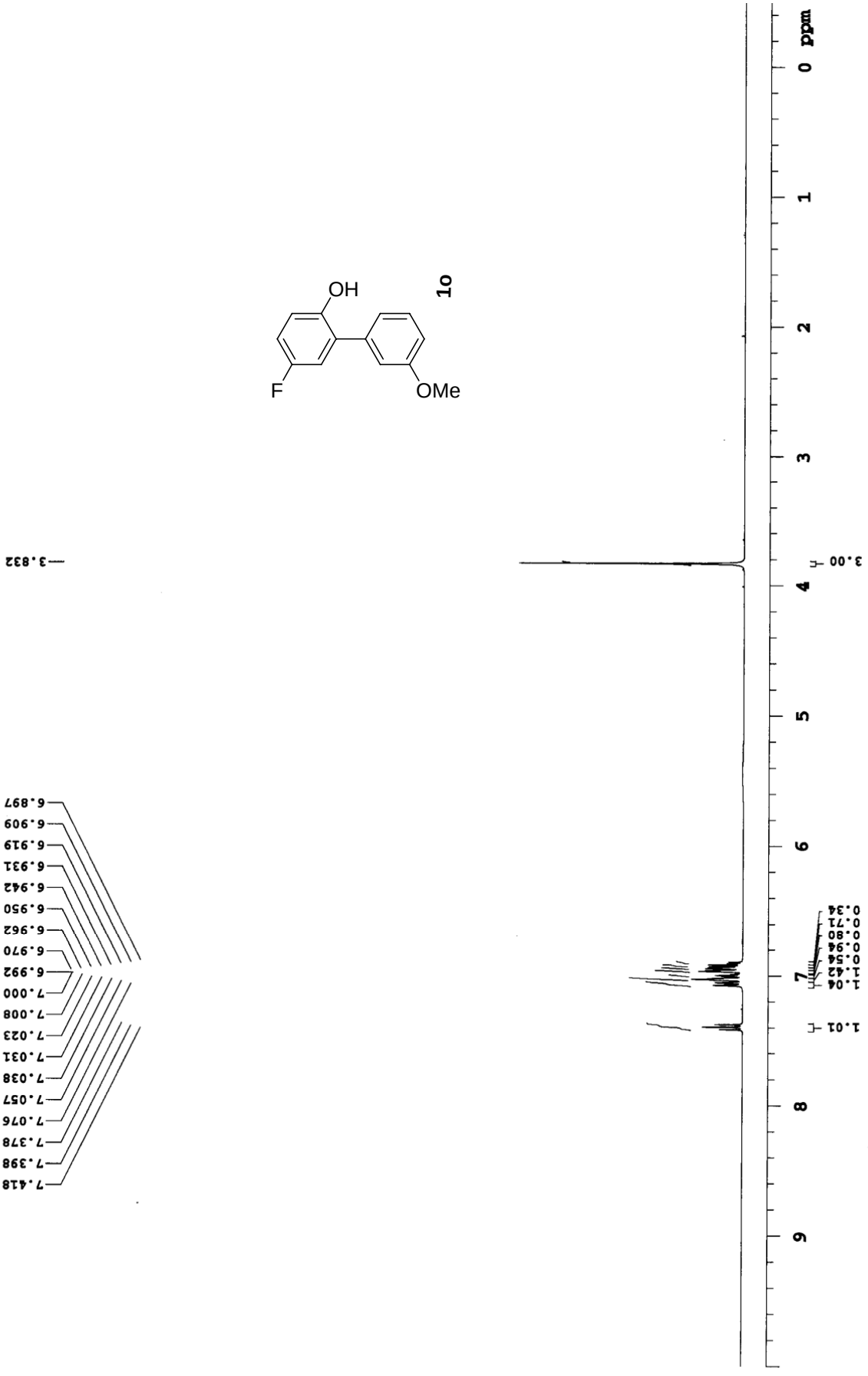


Figure S13. ^{1}H NMR spectrum of Compound **1o** (400 MHz, $CDCl_3$)

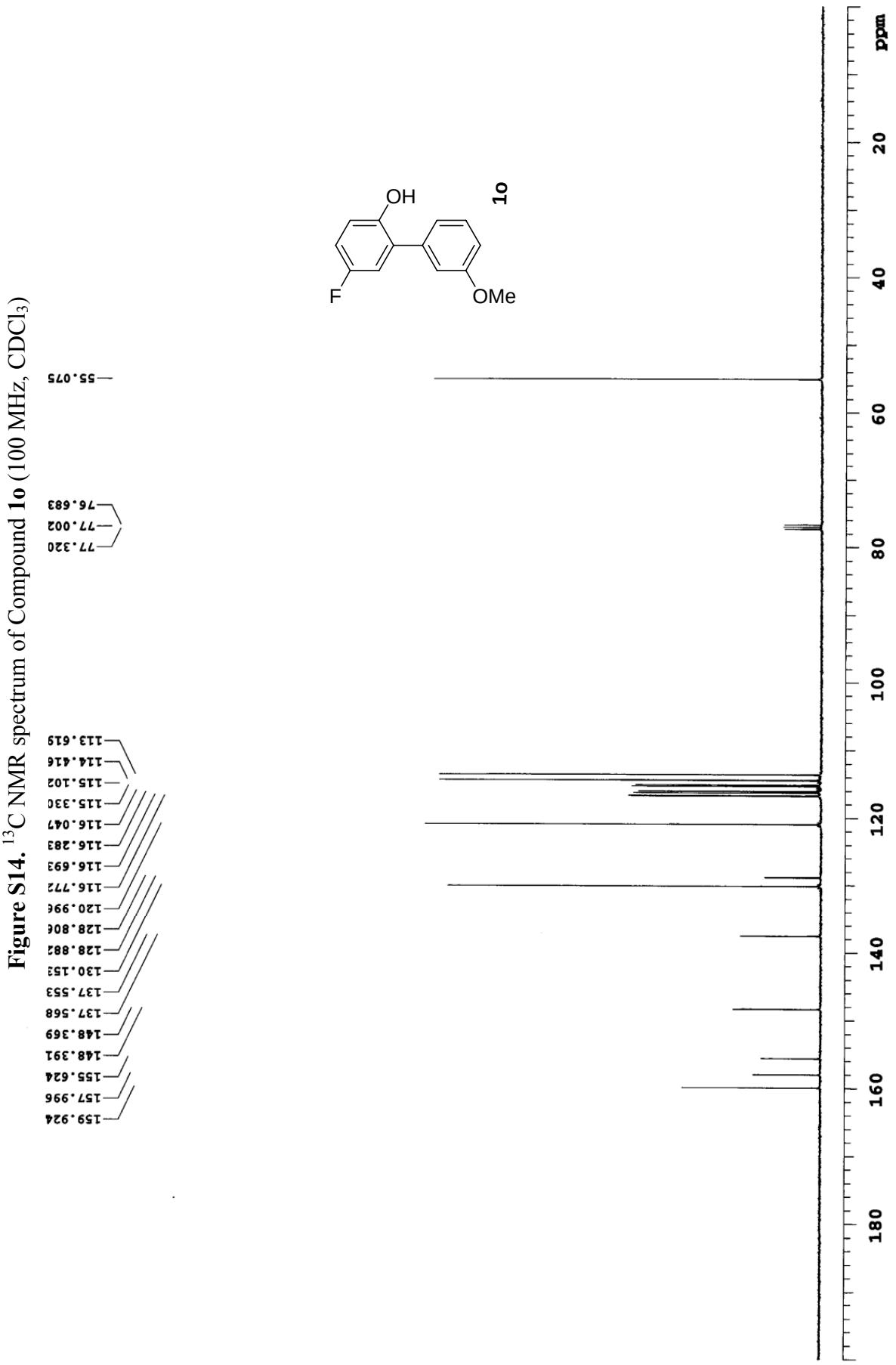


Figure S14. ^{13}C NMR spectrum of Compound **1o** (100 MHz, $CDCl_3$)

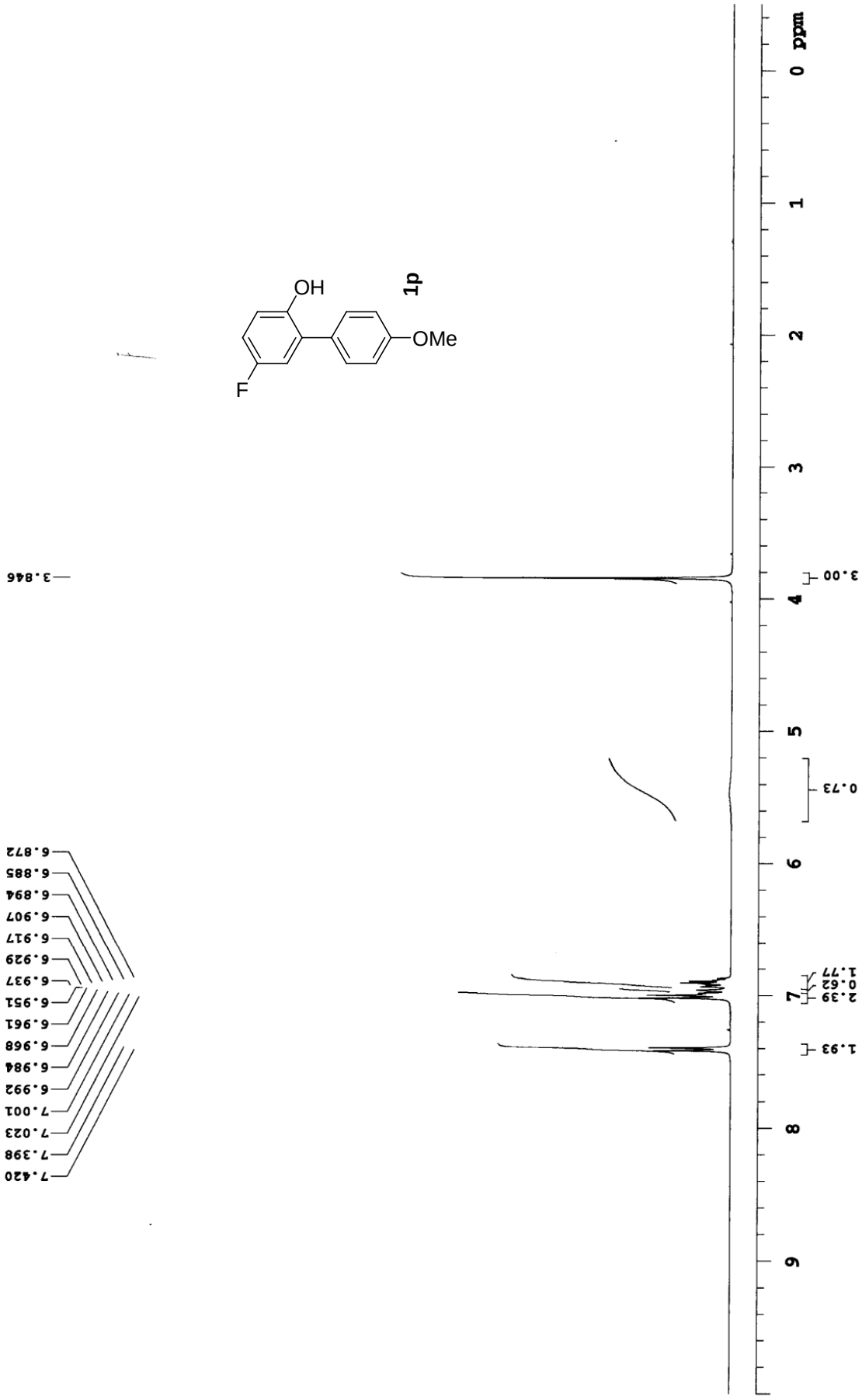


Figure S15. ^{1}H NMR spectrum of Compound **1p** (400 MHz, $CDCl_3$)

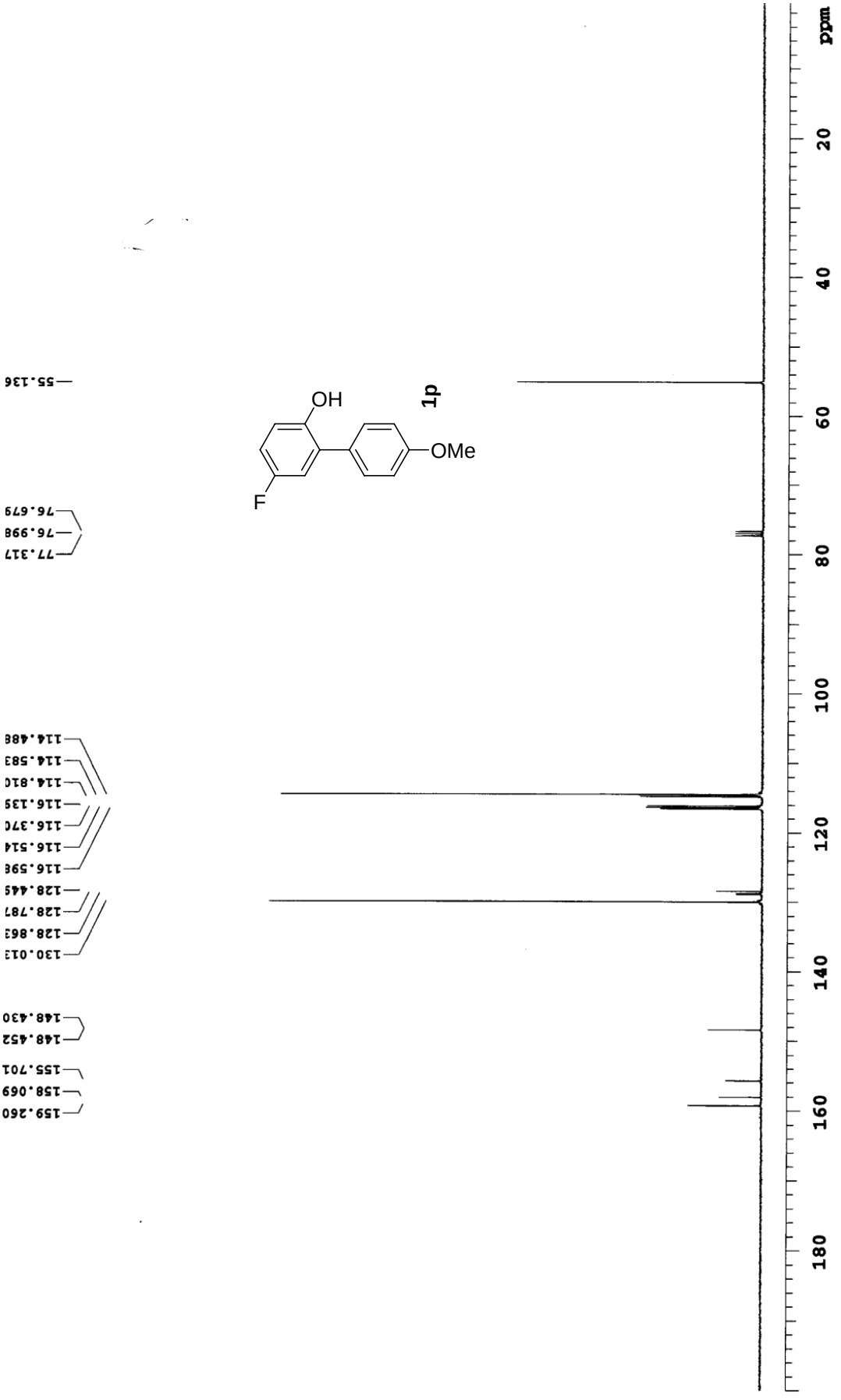


Figure S16. ^{13}C NMR spectrum of Compound **1p** (100 MHz, $CDCl_3$)

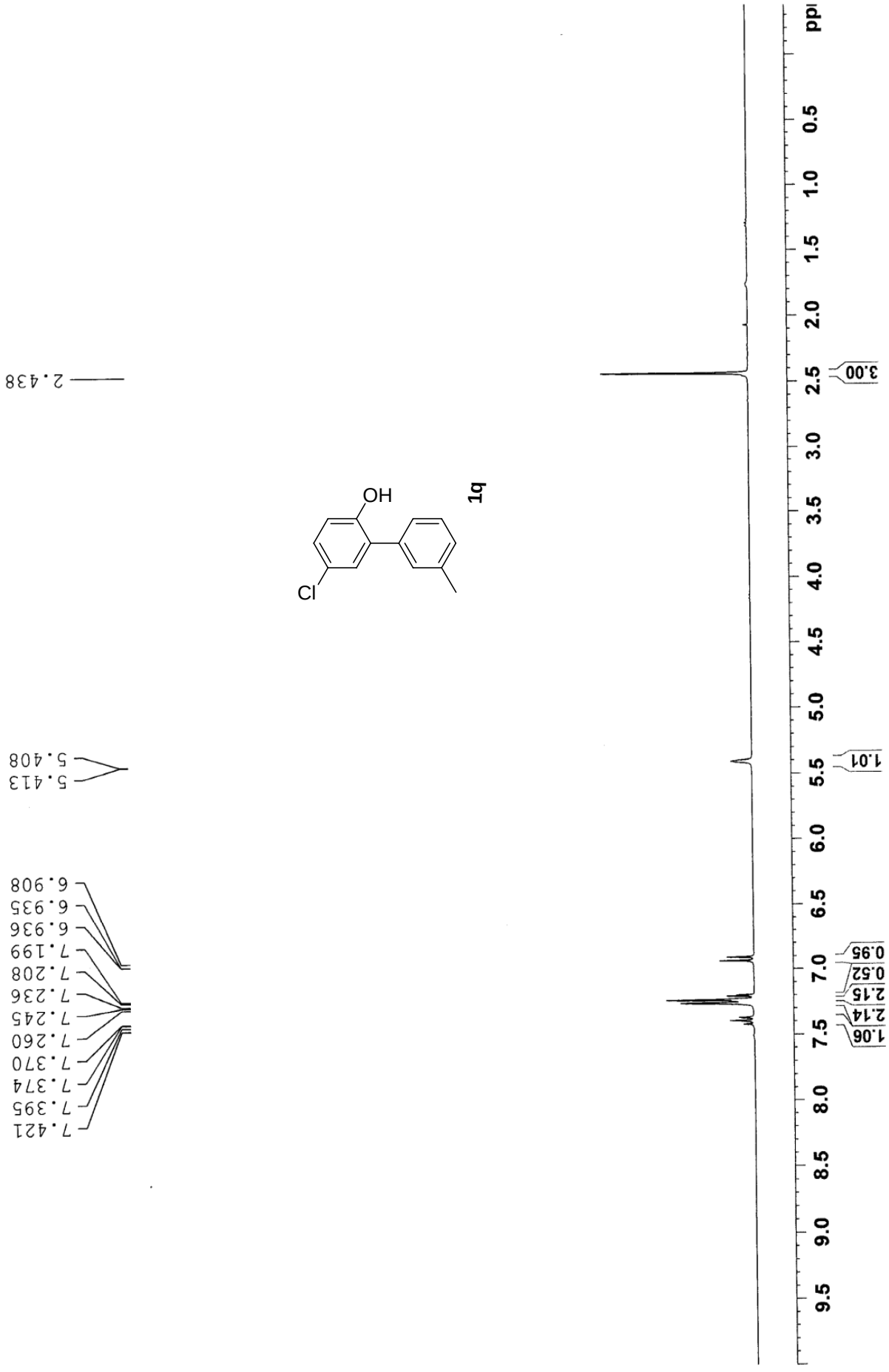


Figure S17. ^{1}H NMR spectrum of Compound **1q** (300 MHz, $CDCl_3$)

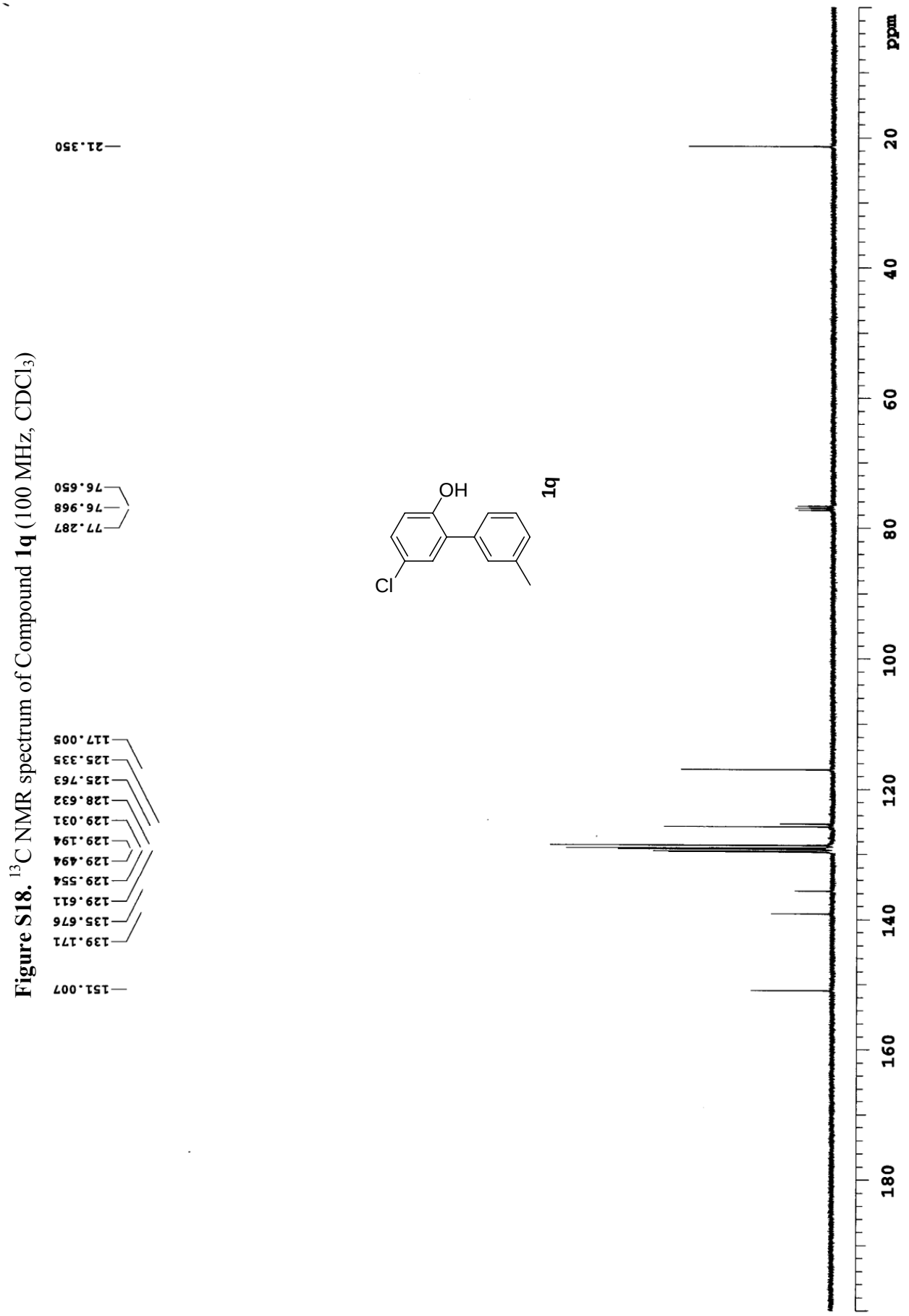


Figure S18. ^{13}C NMR spectrum of Compound **1q** (100 MHz, $CDCl_3$)

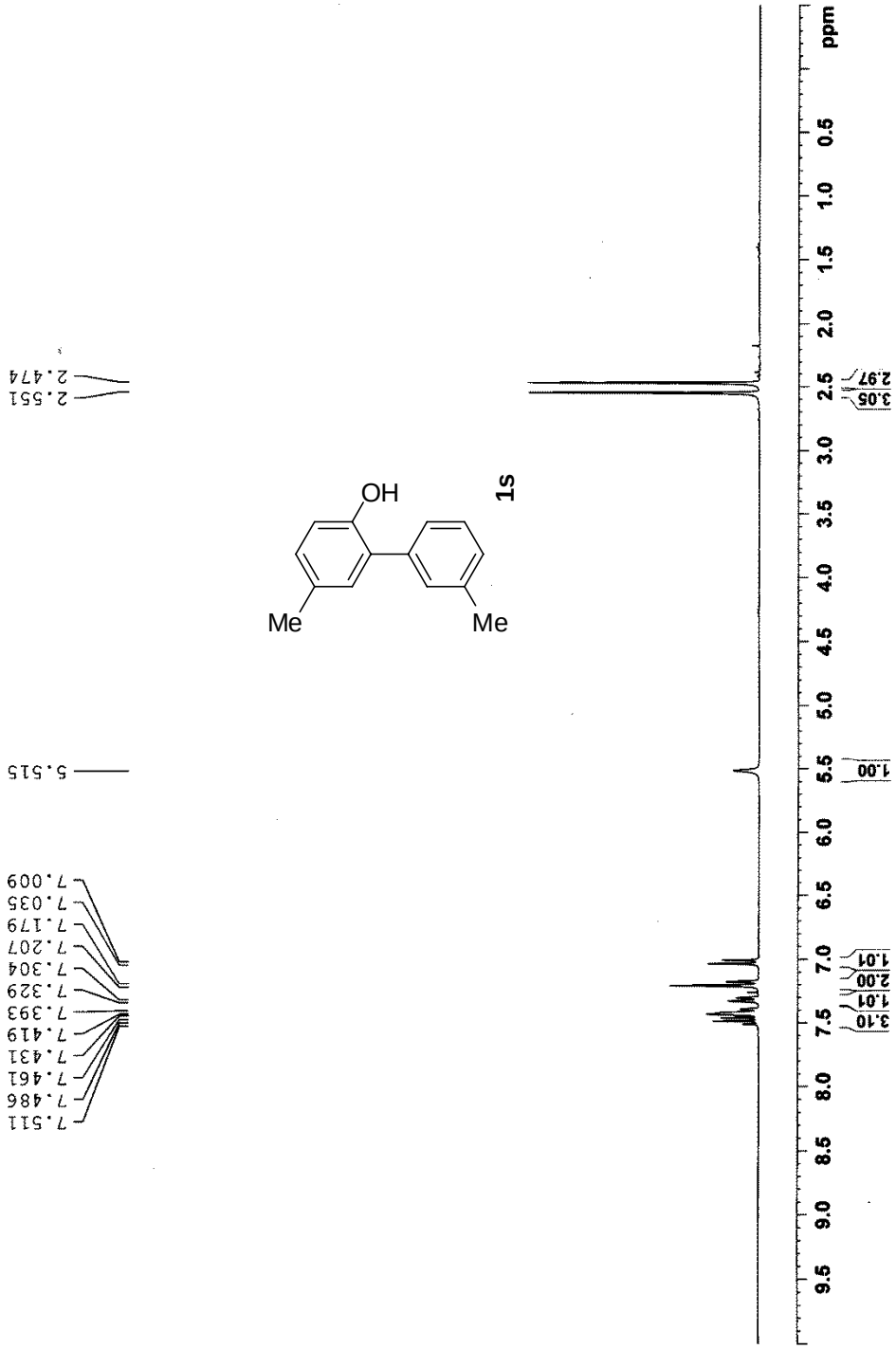


Figure S19. ^{1}H NMR spectrum of Compound **1s** (300 MHz, $CDCl_3$)

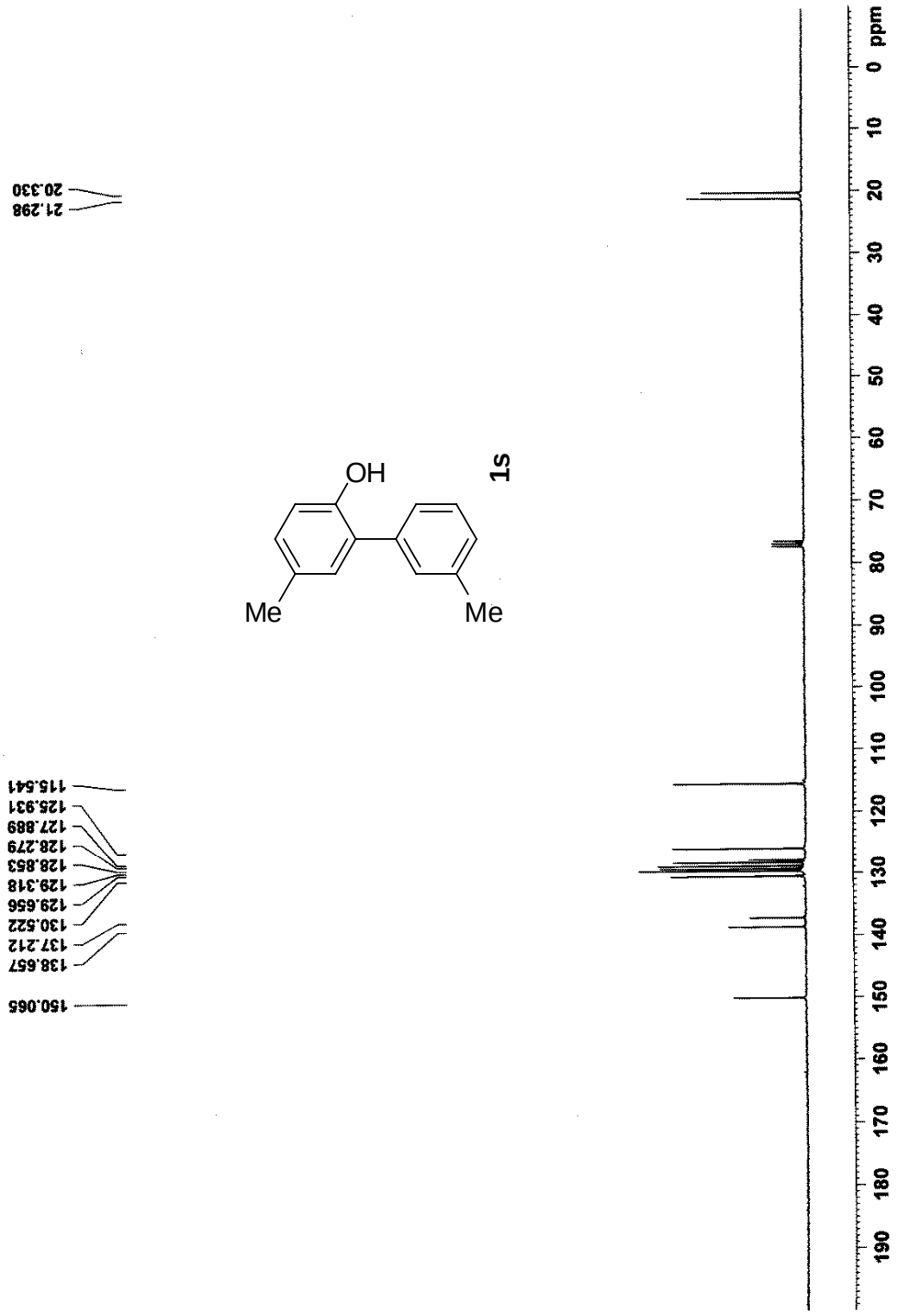
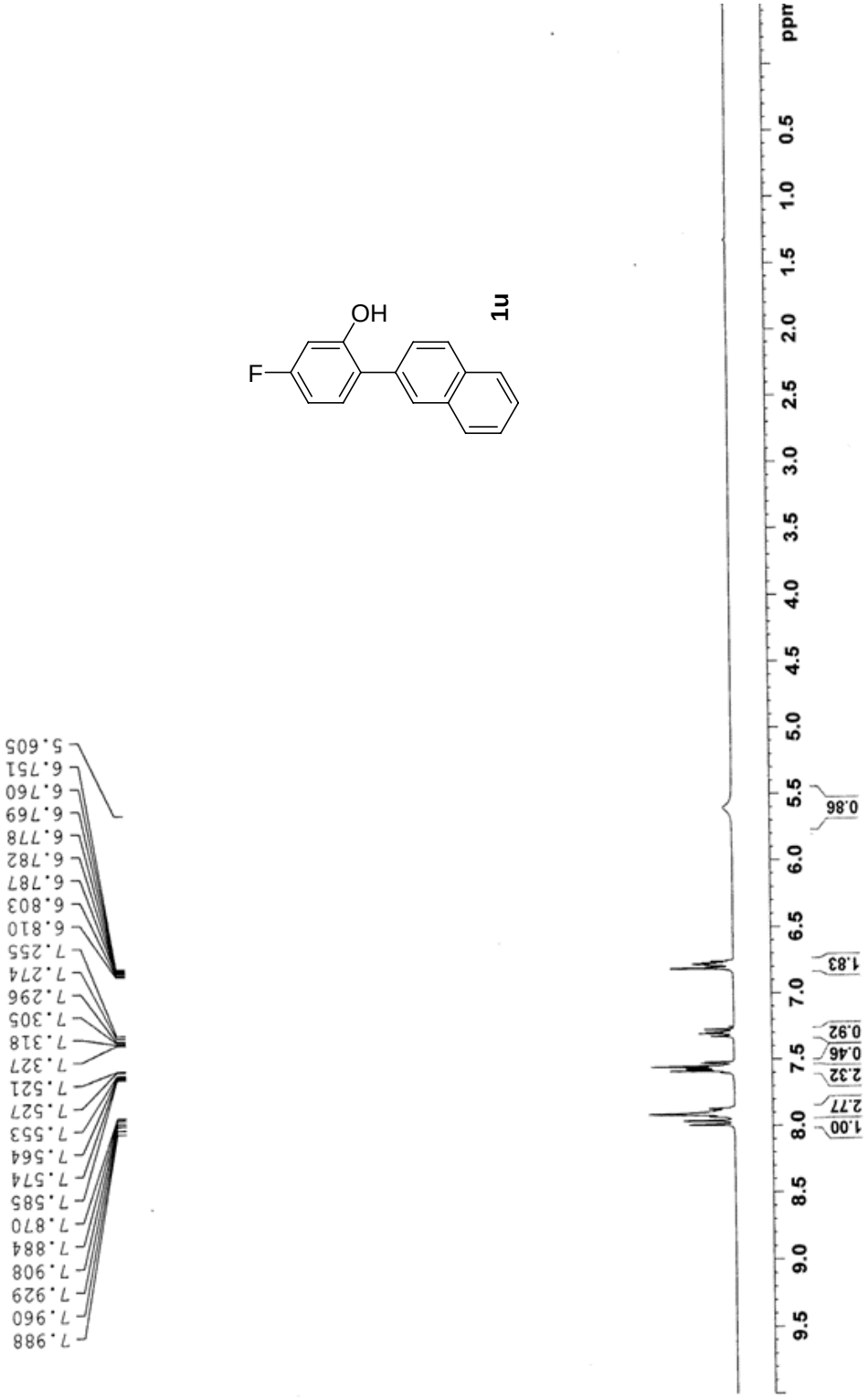


Figure S20. ^{13}C NMR spectrum of Compound **1s** (100 MHz, $CDCl_3$)

Figure S21. ^{1}H NMR spectrum of Compound **1u** (300 MHz, $CDCl_3$)



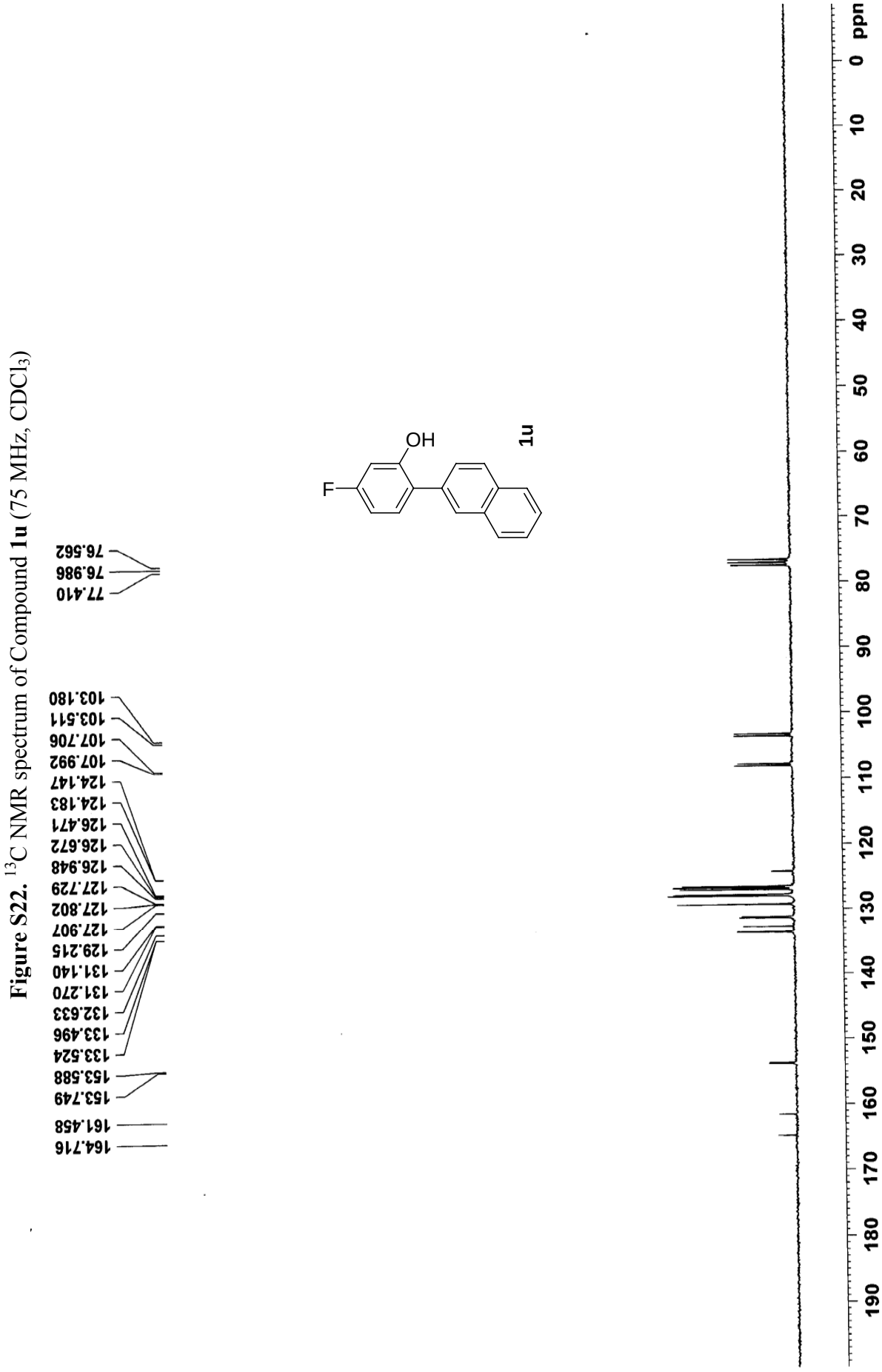


Figure S22. ^{13}C NMR spectrum of Compound **1u** (75 MHz, $CDCl_3$)

Figure S23. ^{1}H NMR spectrum of Compound **1v** (300 MHz, $CDCl_3$)

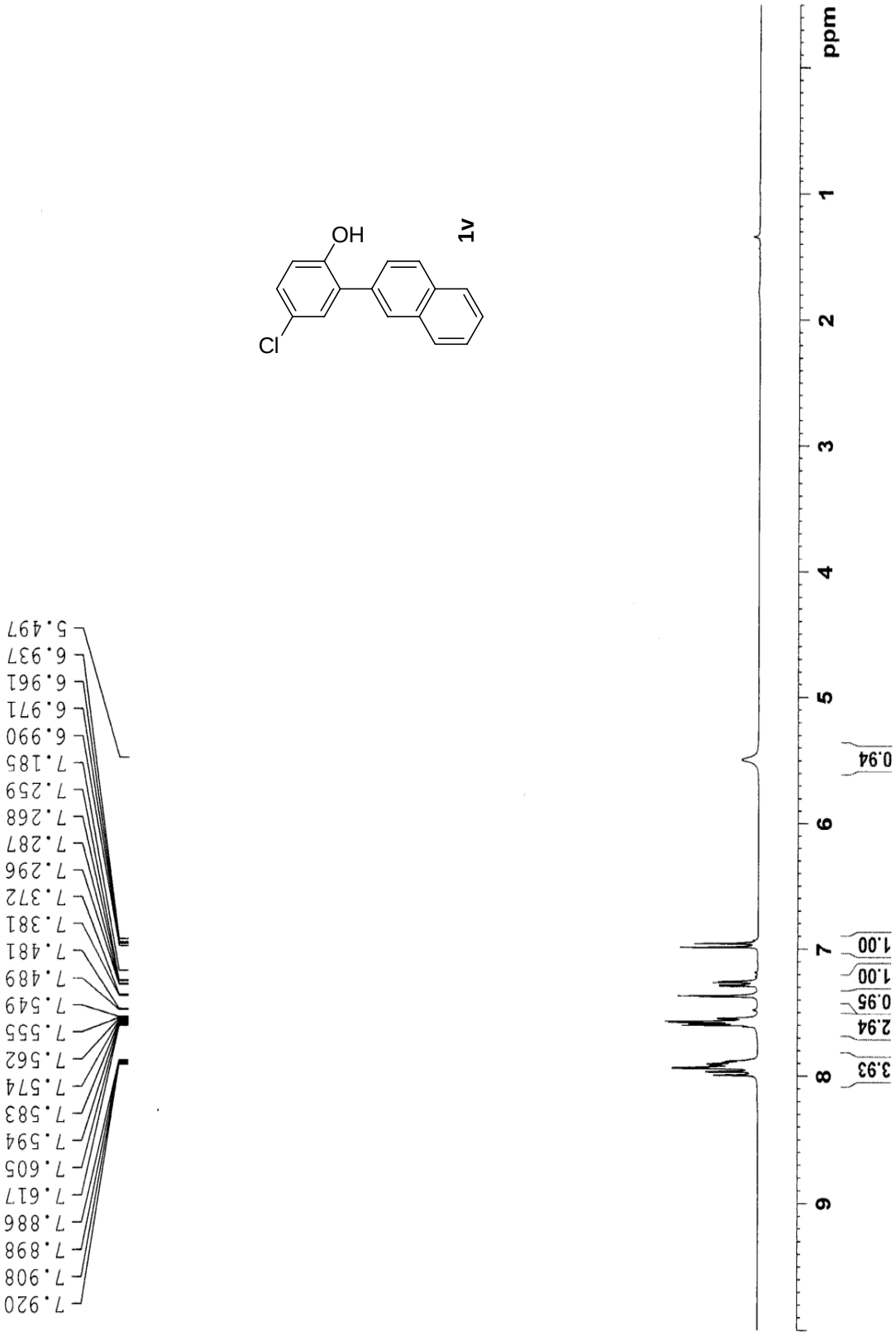
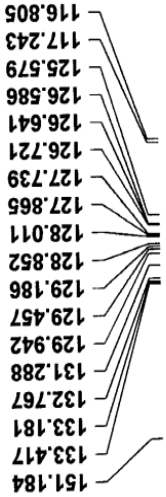
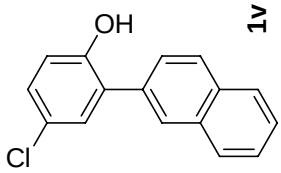
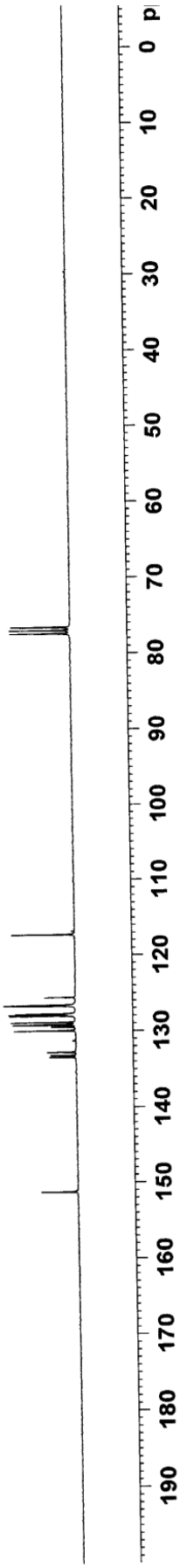


Figure S24. ^{13}C NMR spectrum of Compound **1v** (75 MHz, $CDCl_3$)





1v



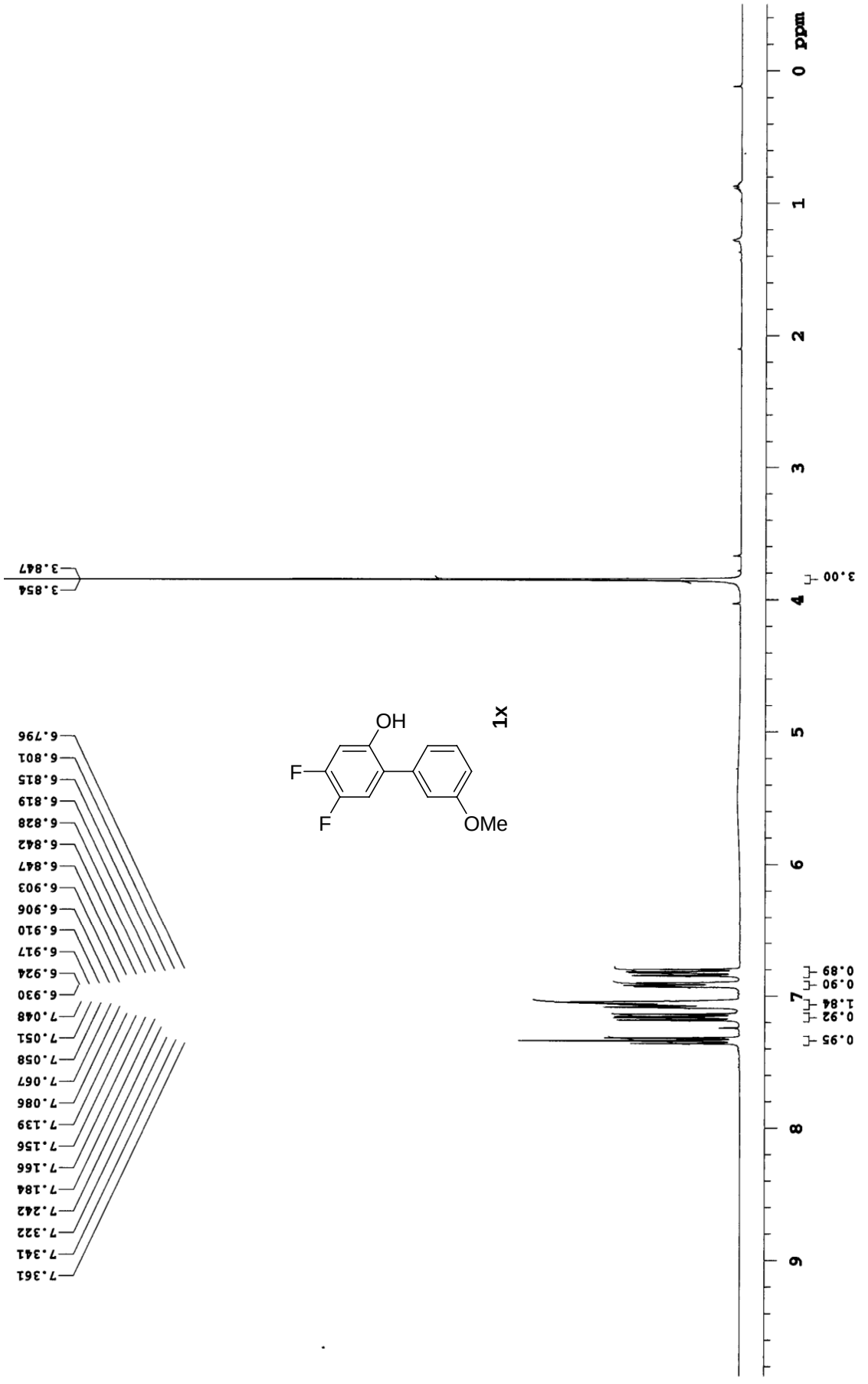


Figure S25. ^{1}H NMR spectrum of Compound **1x** (400 MHz, $CDCl_3$)

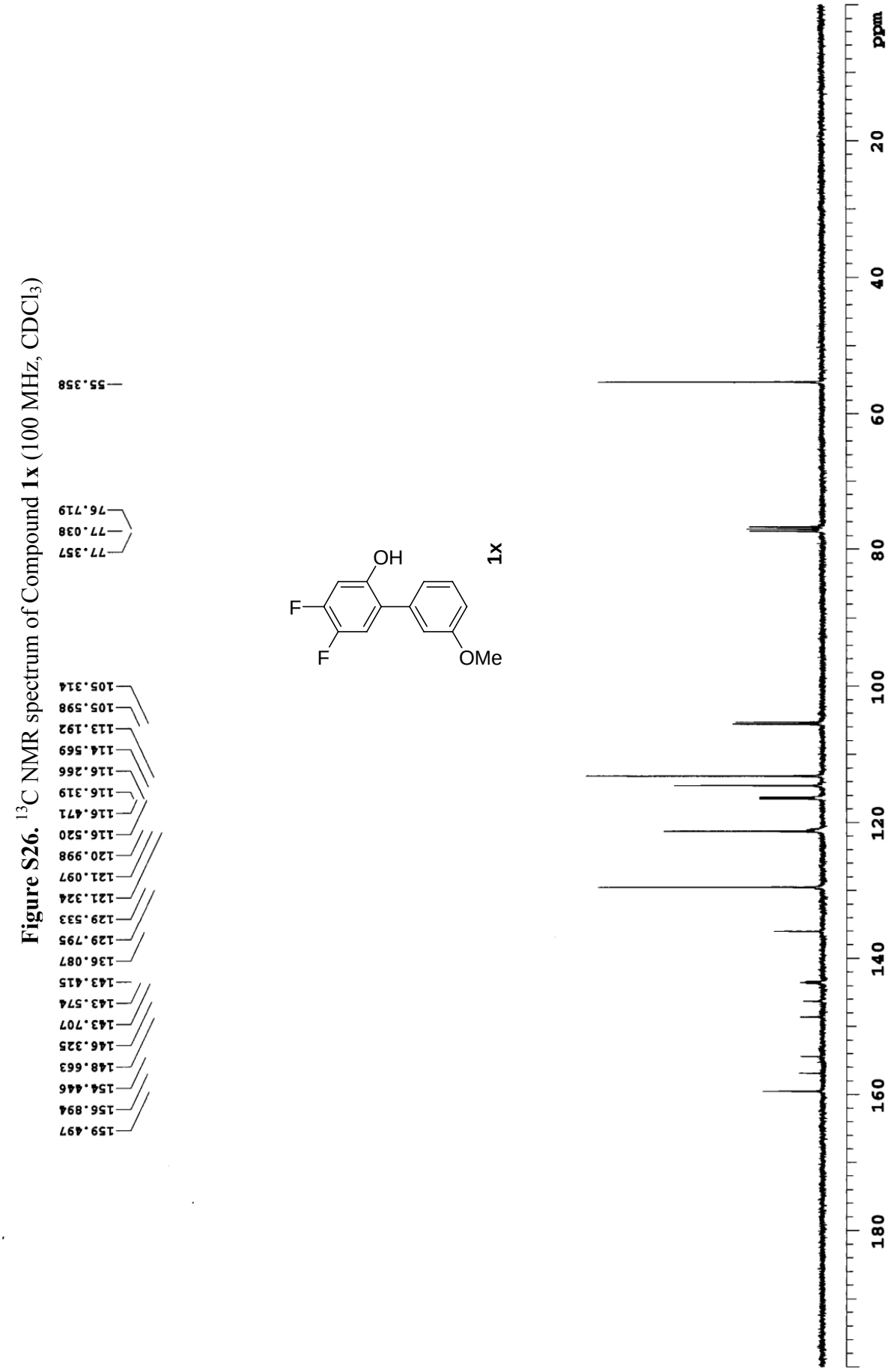


Figure S26. ^{13}C NMR spectrum of Compound **1x** (100 MHz, $CDCl_3$)

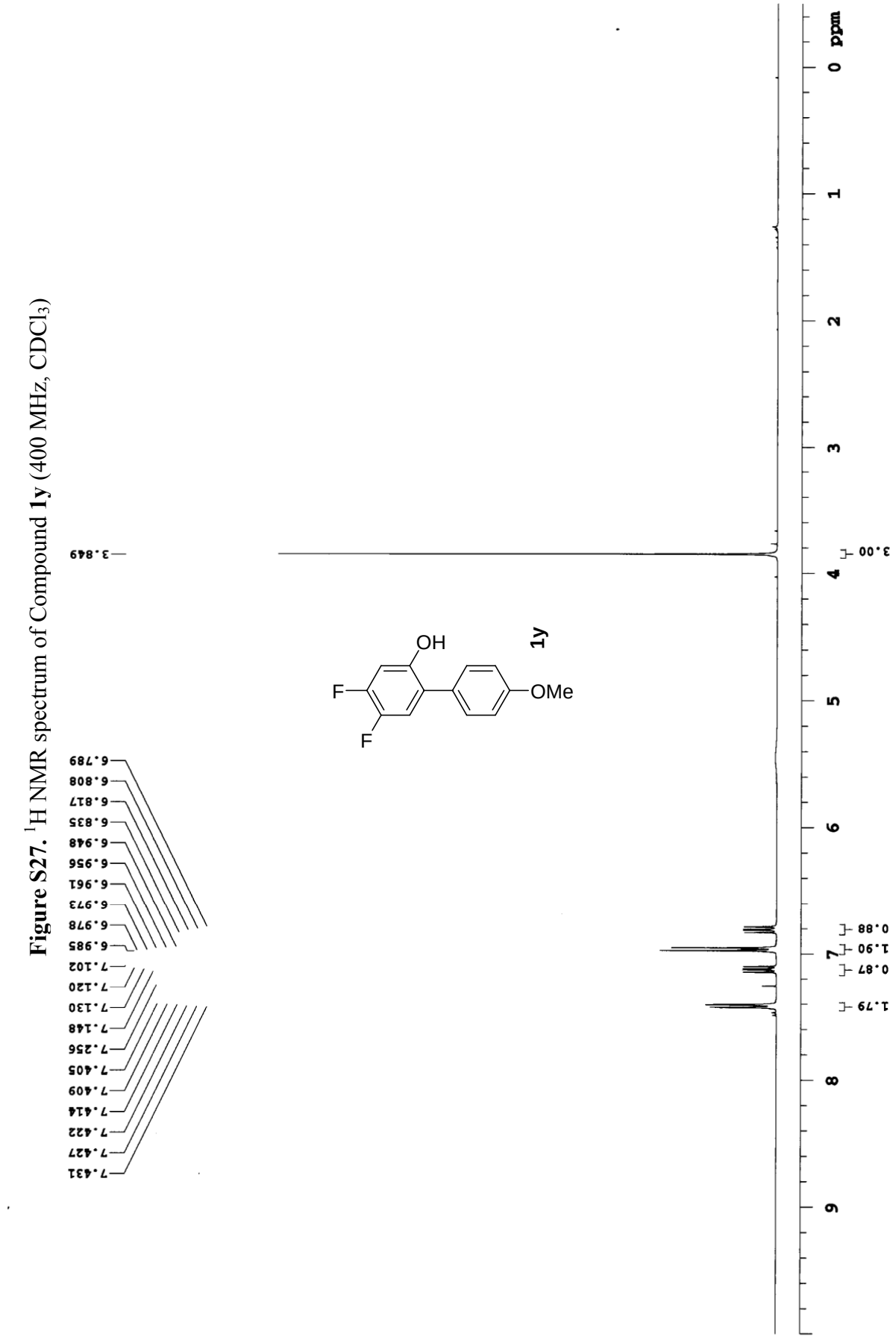


Figure S27. ^{1}H NMR spectrum of Compound **1y** (400 MHz, $CDCl_3$)

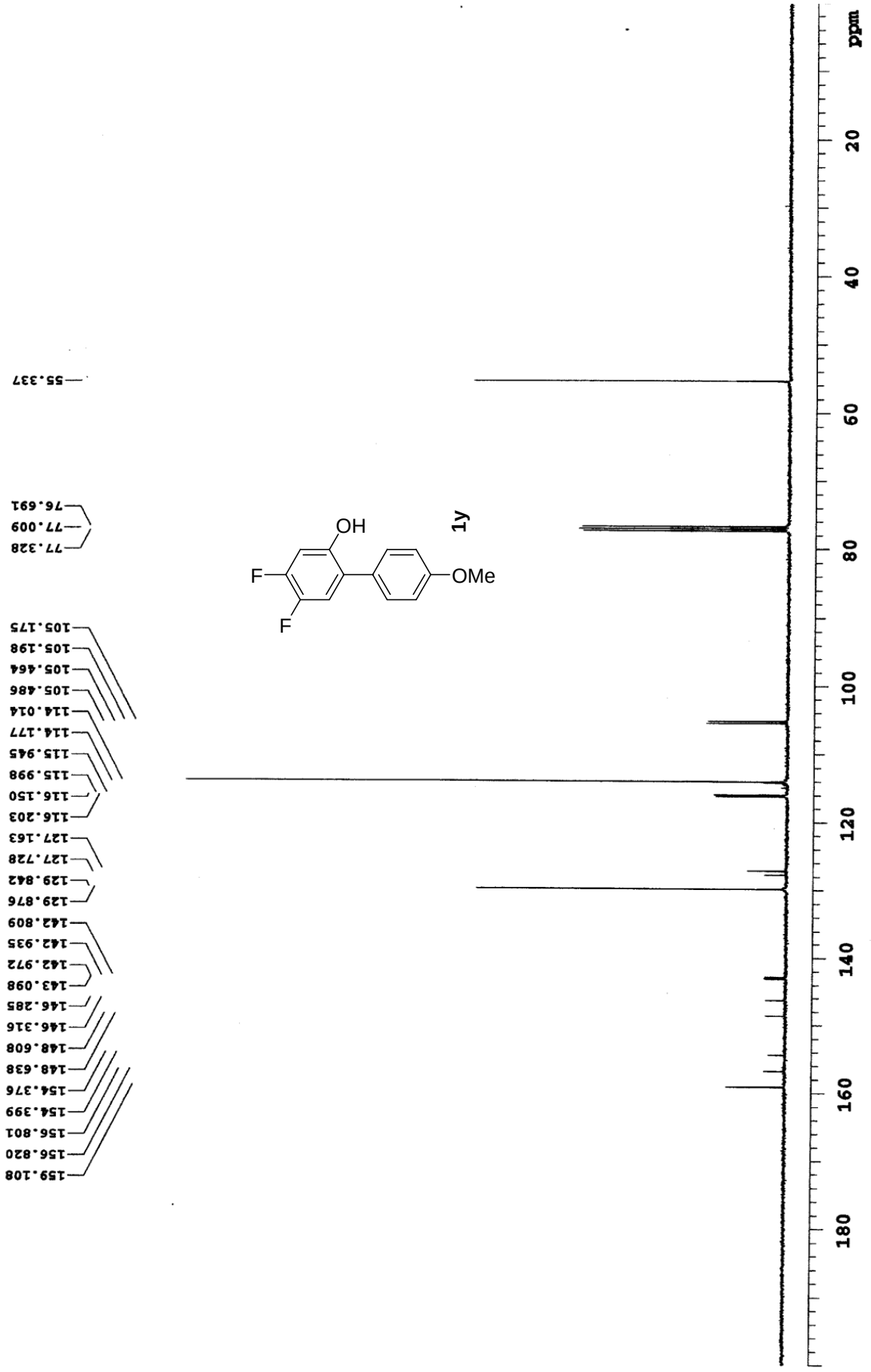


Figure S28. ^{13}C NMR spectrum of Compound **1y** (100 MHz, $CDCl_3$)

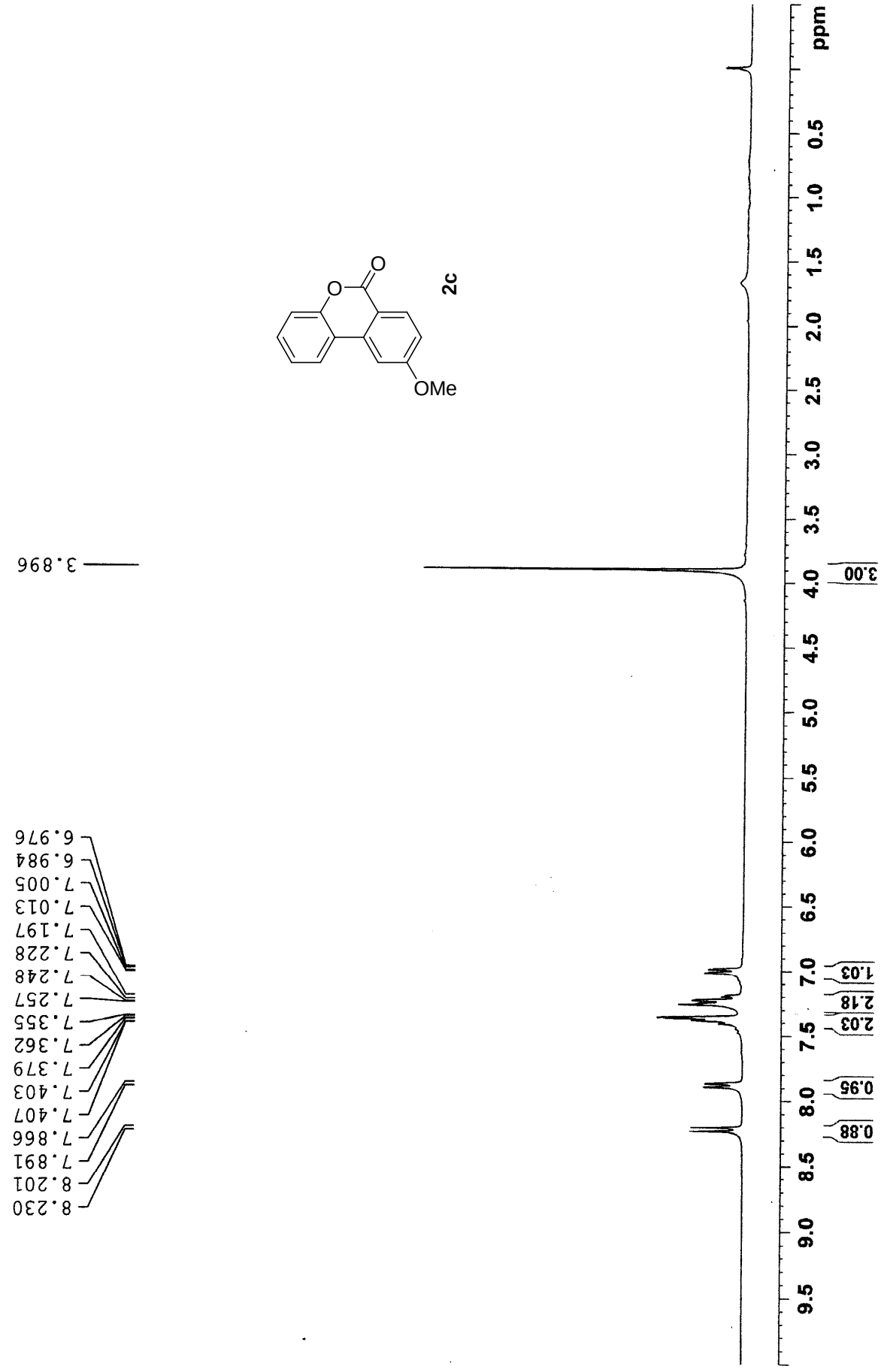


Figure S29. ^{1}H NMR spectrum of Compound **2c** (300 MHz, $CDCl_3$)

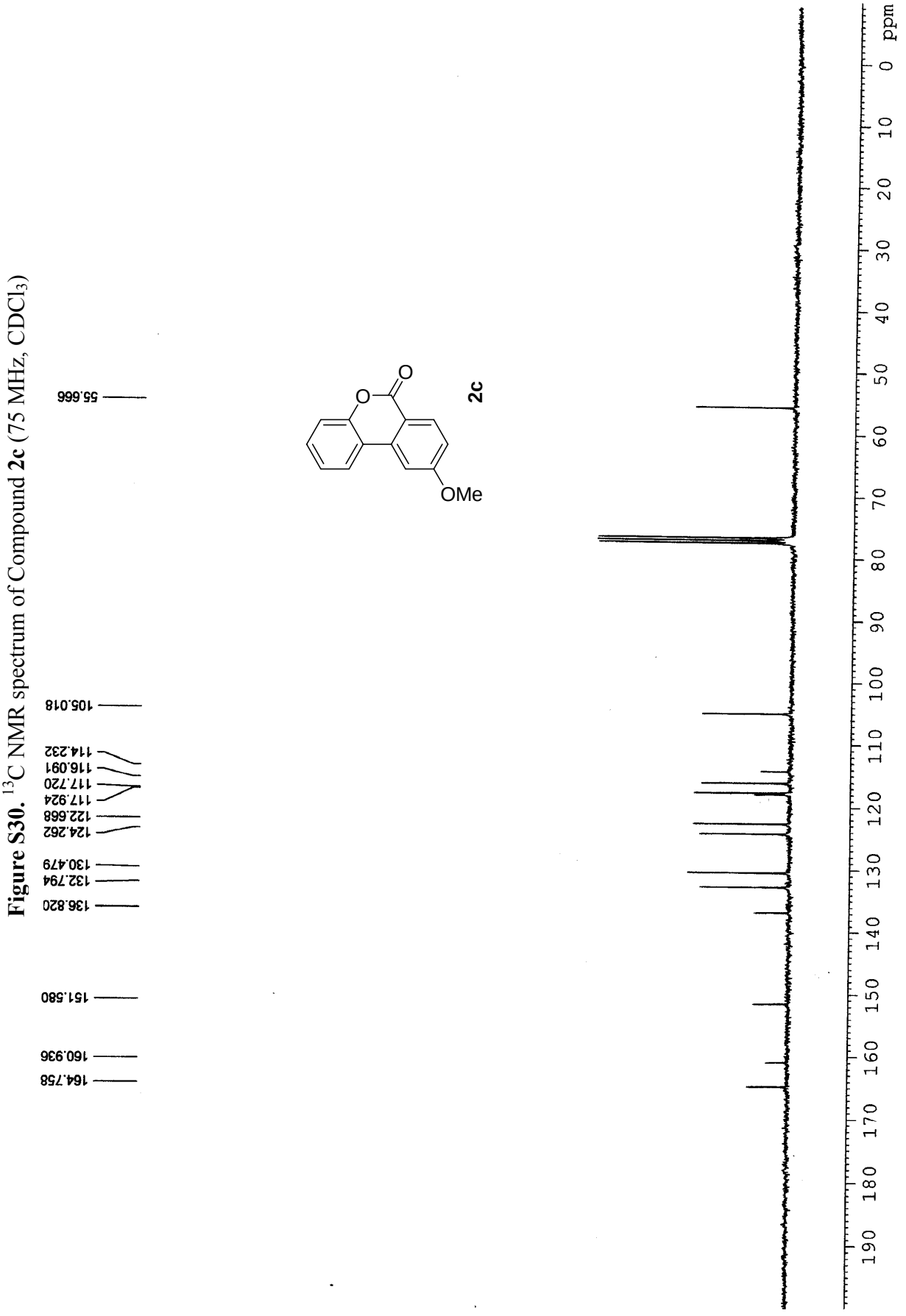
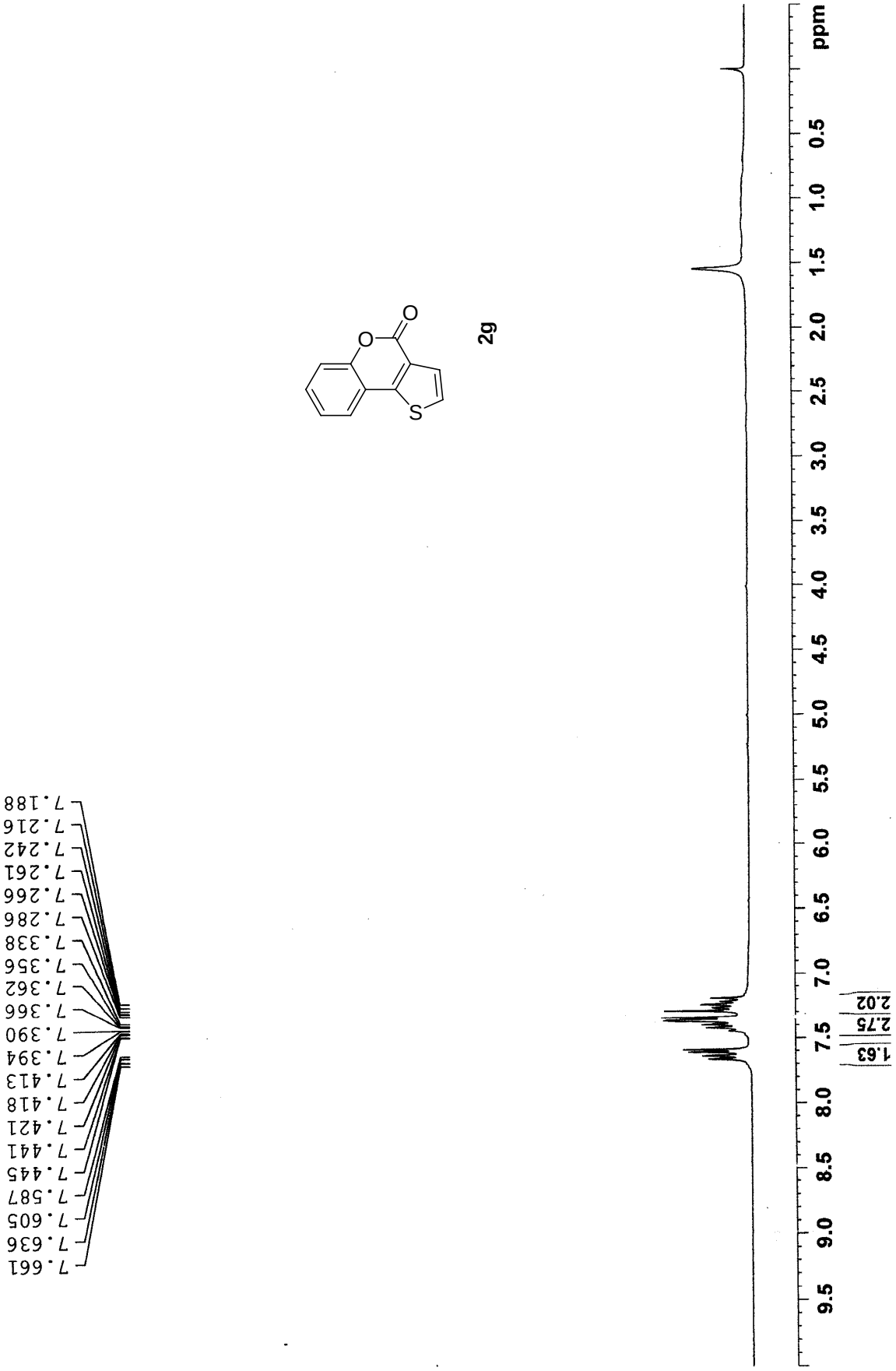


Figure S30. ^{13}C NMR spectrum of Compound **2c** (75 MHz, $CDCl_3$)

Figure S31. ^{1}H NMR spectrum of Compound **2g** (300 MHz, $CDCl_3$)



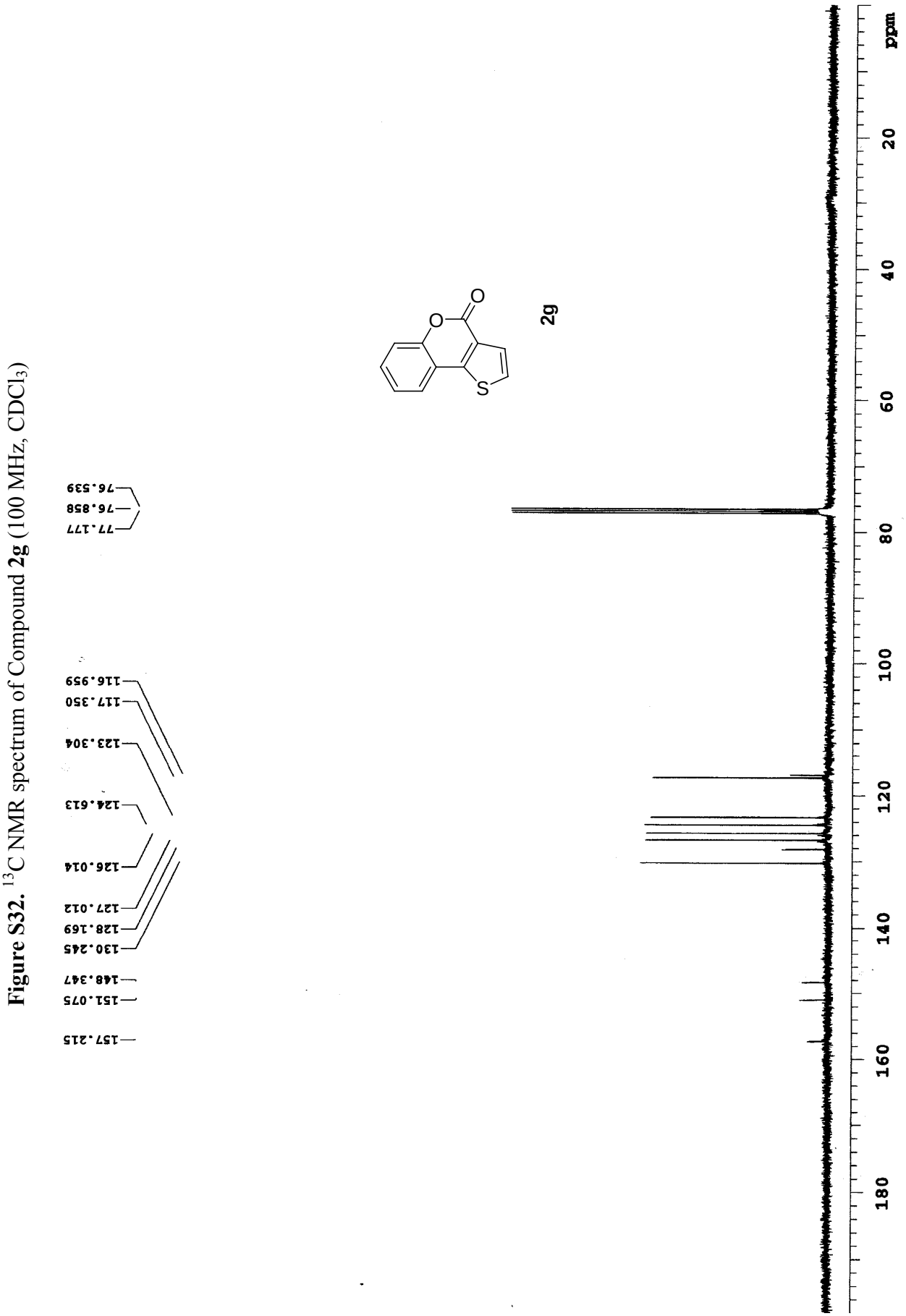


Figure S32. ^{13}C NMR spectrum of Compound **2g** (100 MHz, $CDCl_3$)

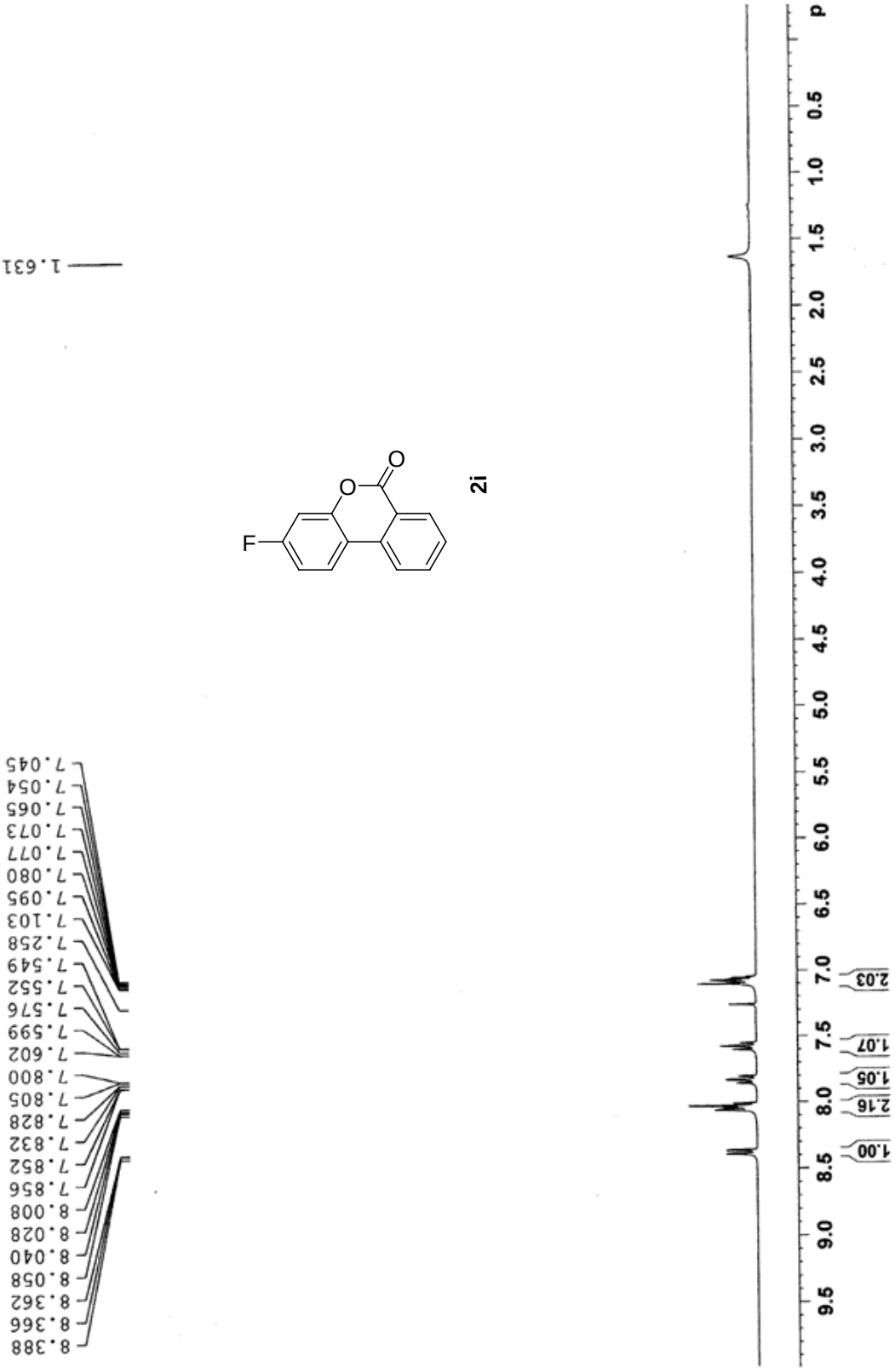


Figure S33. ^{1}H NMR spectrum of Compound **2i** (300 MHz, $CDCl_3$)

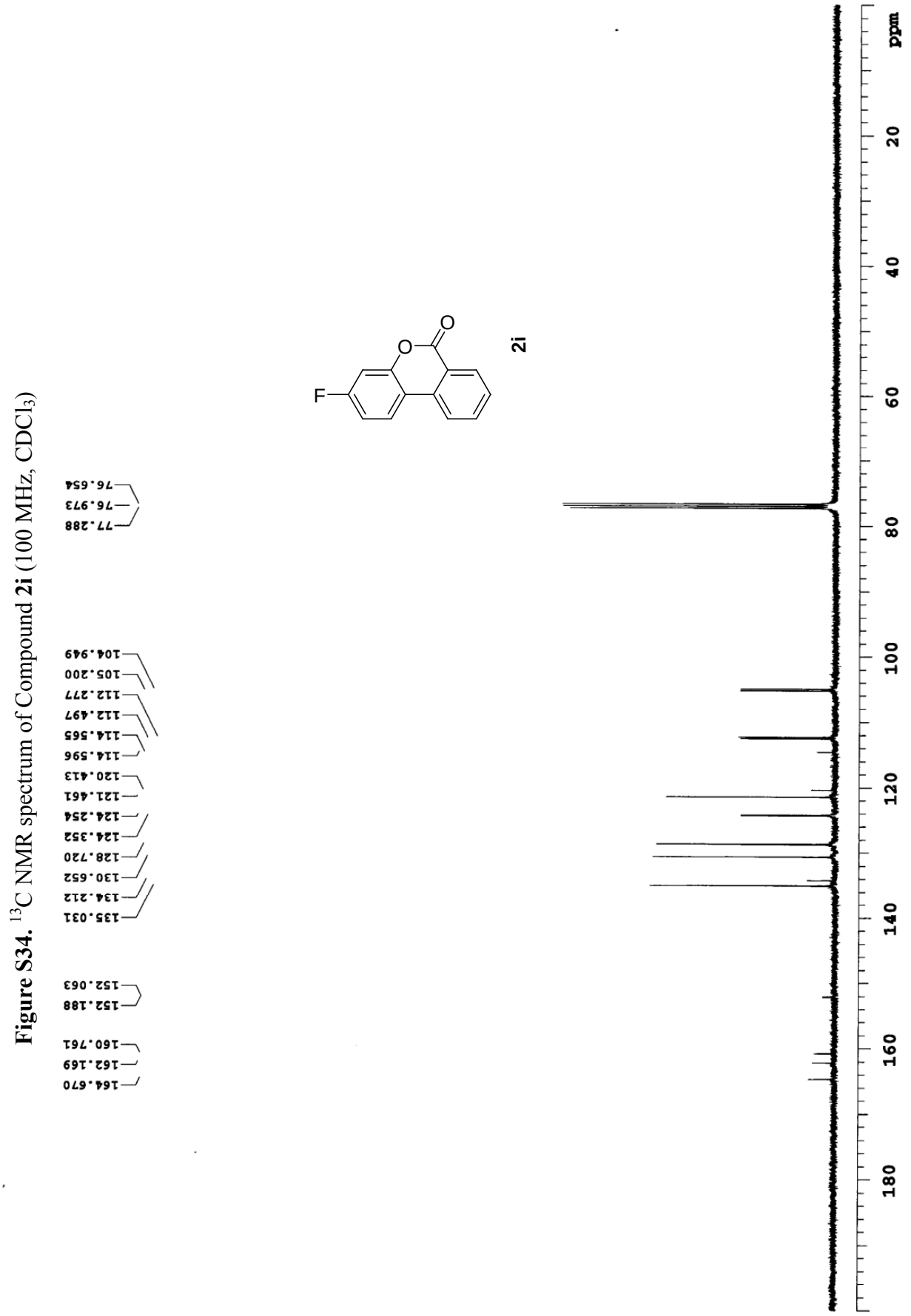


Figure S34. ^{13}C NMR spectrum of Compound **2i** (100 MHz, $CDCl_3$)

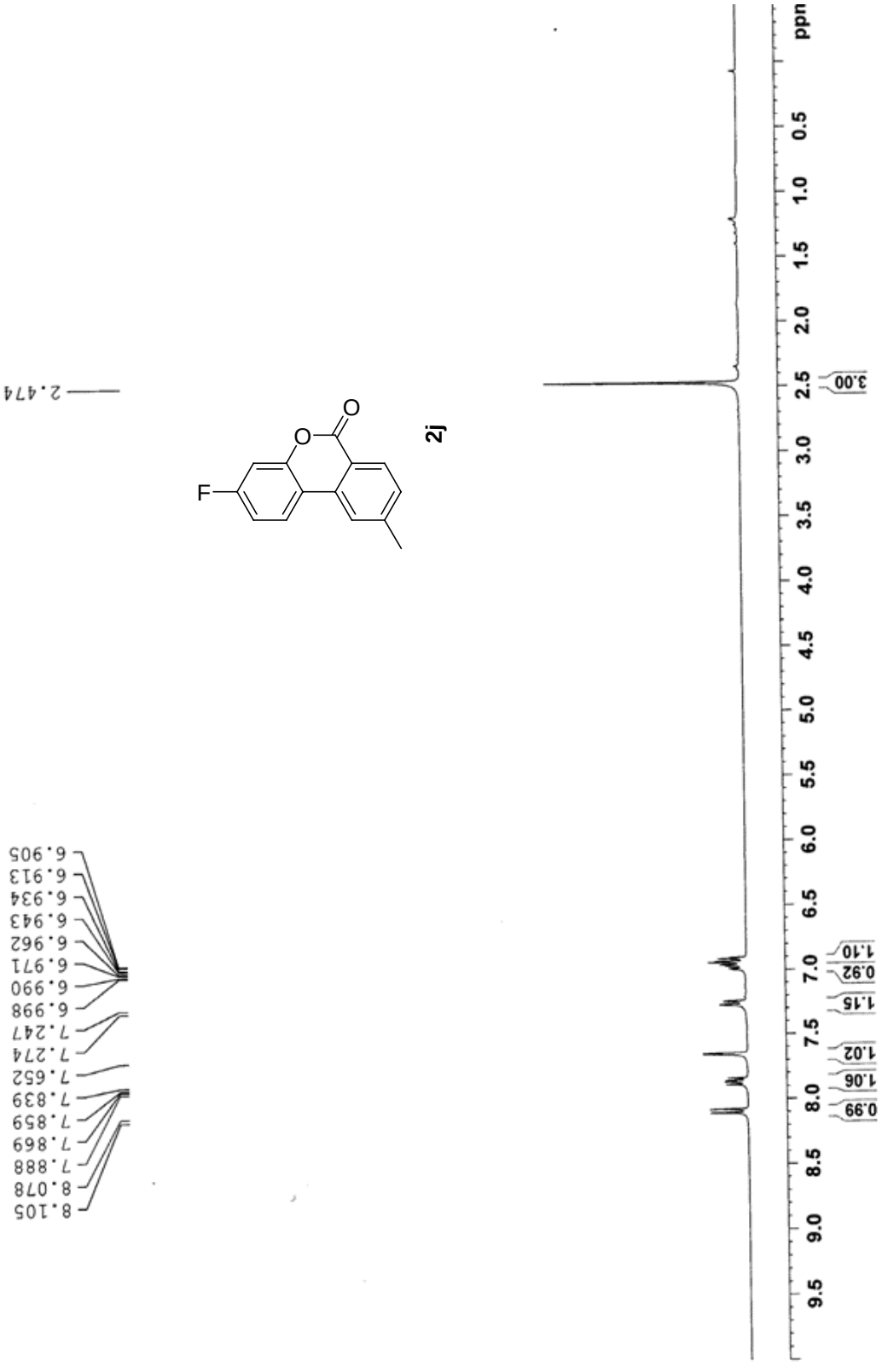


Figure S35. ^{1}H NMR spectrum of Compound **2j** (300 MHz, $CDCl_3$)

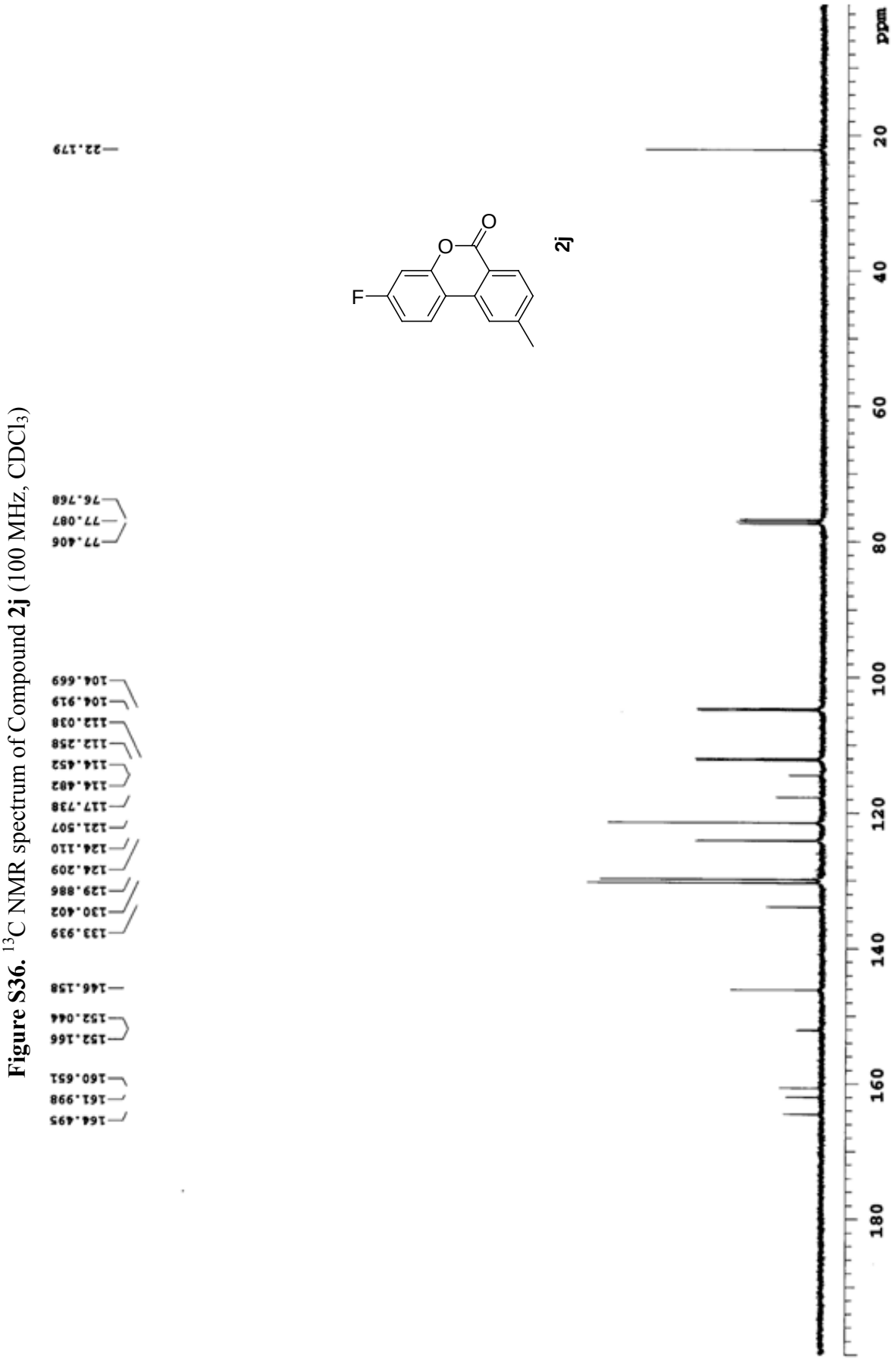


Figure S36. ^{13}C NMR spectrum of Compound **2j** (100 MHz, $CDCl_3$)

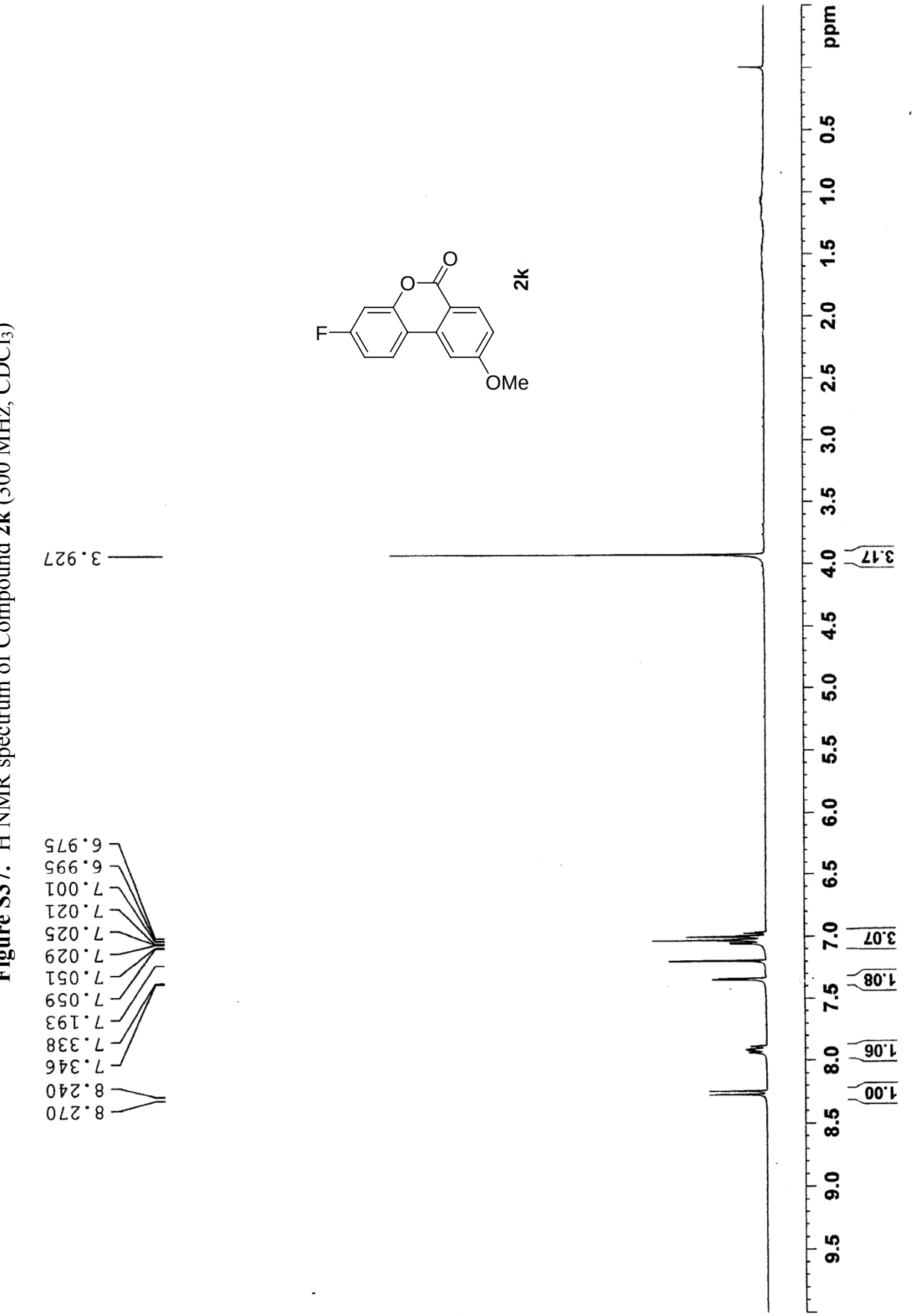


Figure S37. ^{1}H NMR spectrum of Compound **2k** (300 MHz, $CDCl_3$)

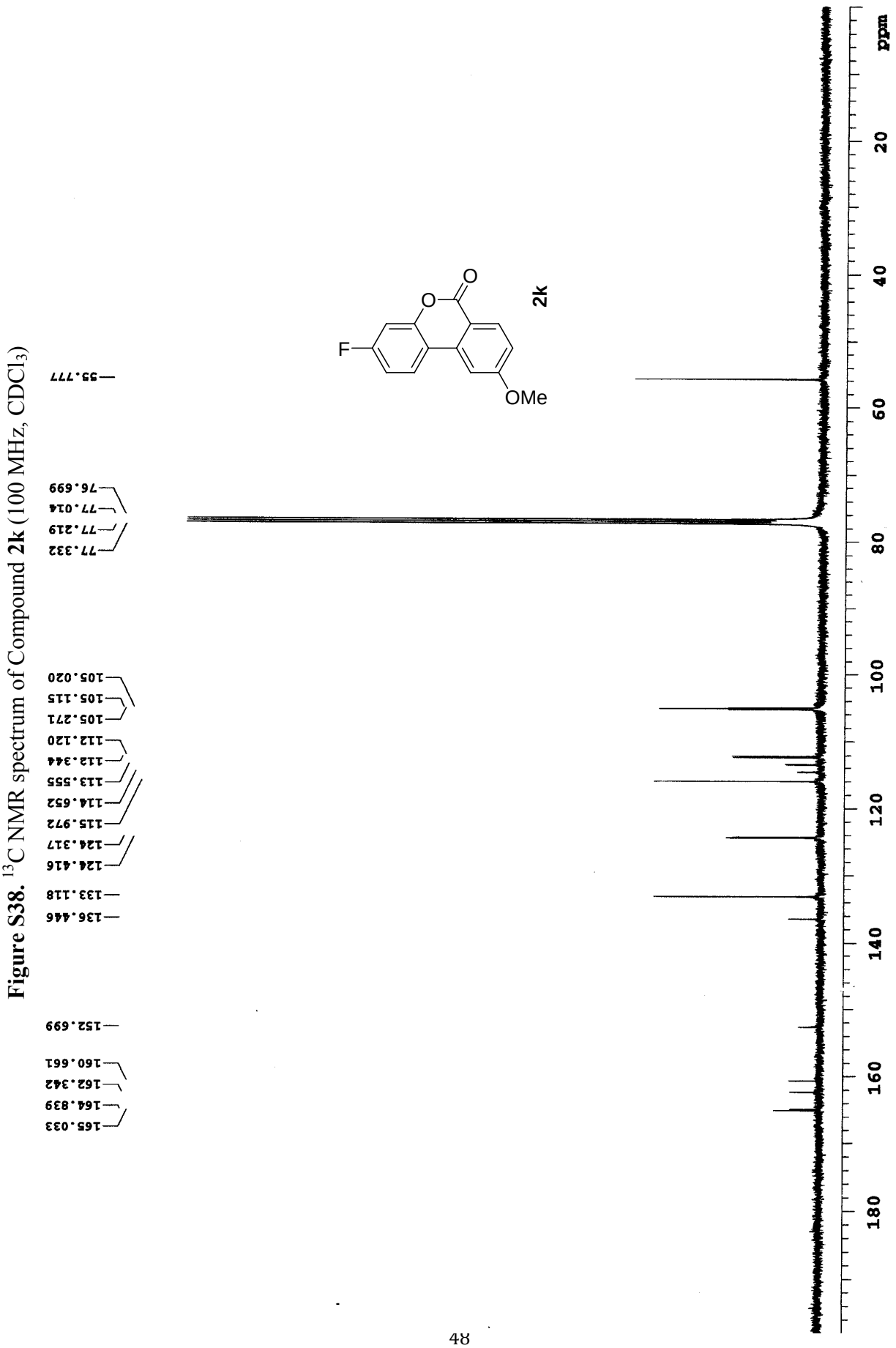


Figure S38. ^{13}C NMR spectrum of Compound **2k** (100 MHz, $CDCl_3$)

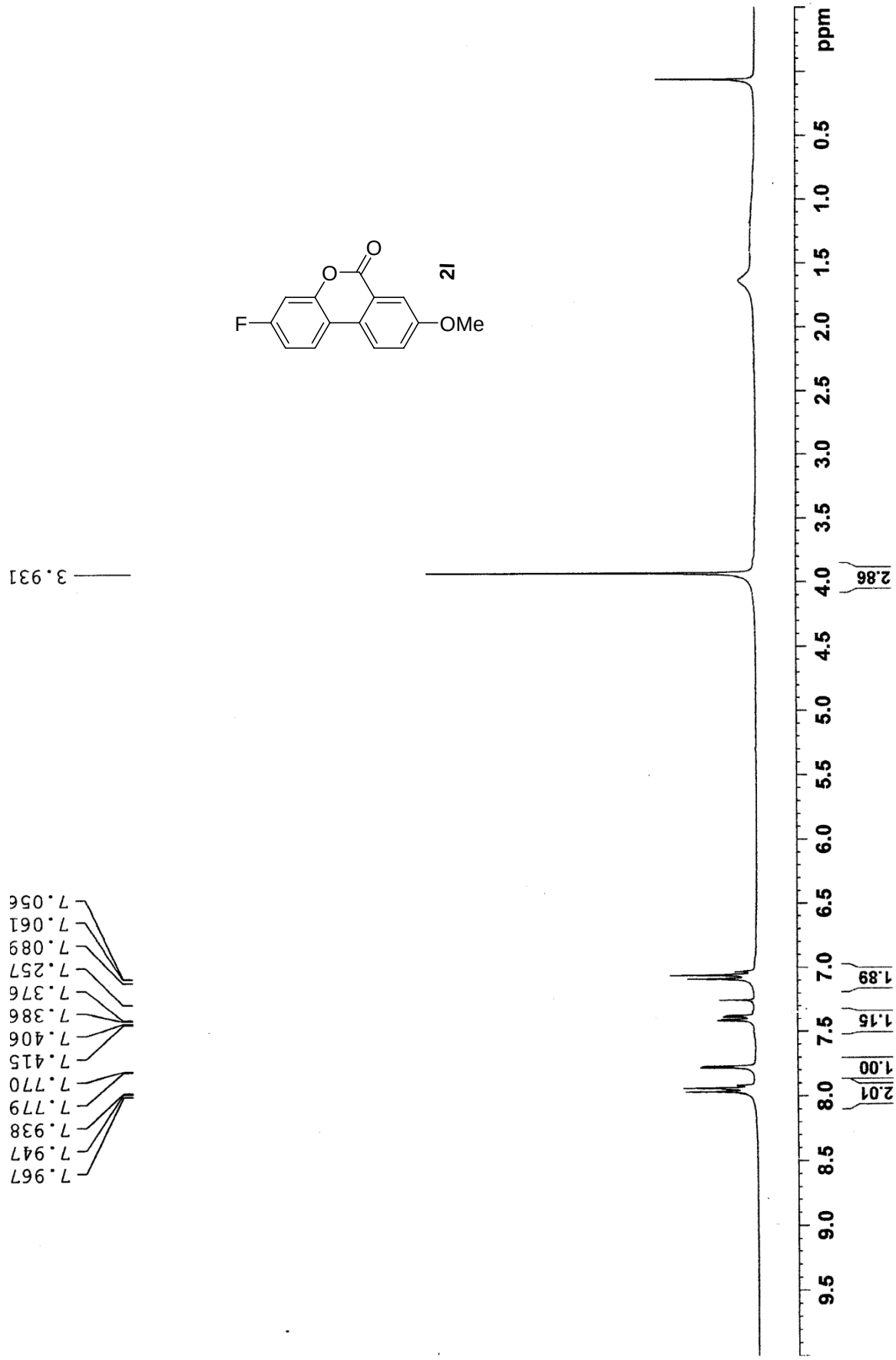


Figure S39. ^{1}H NMR spectrum of Compound **2l** (300 MHz, $CDCl_3$)

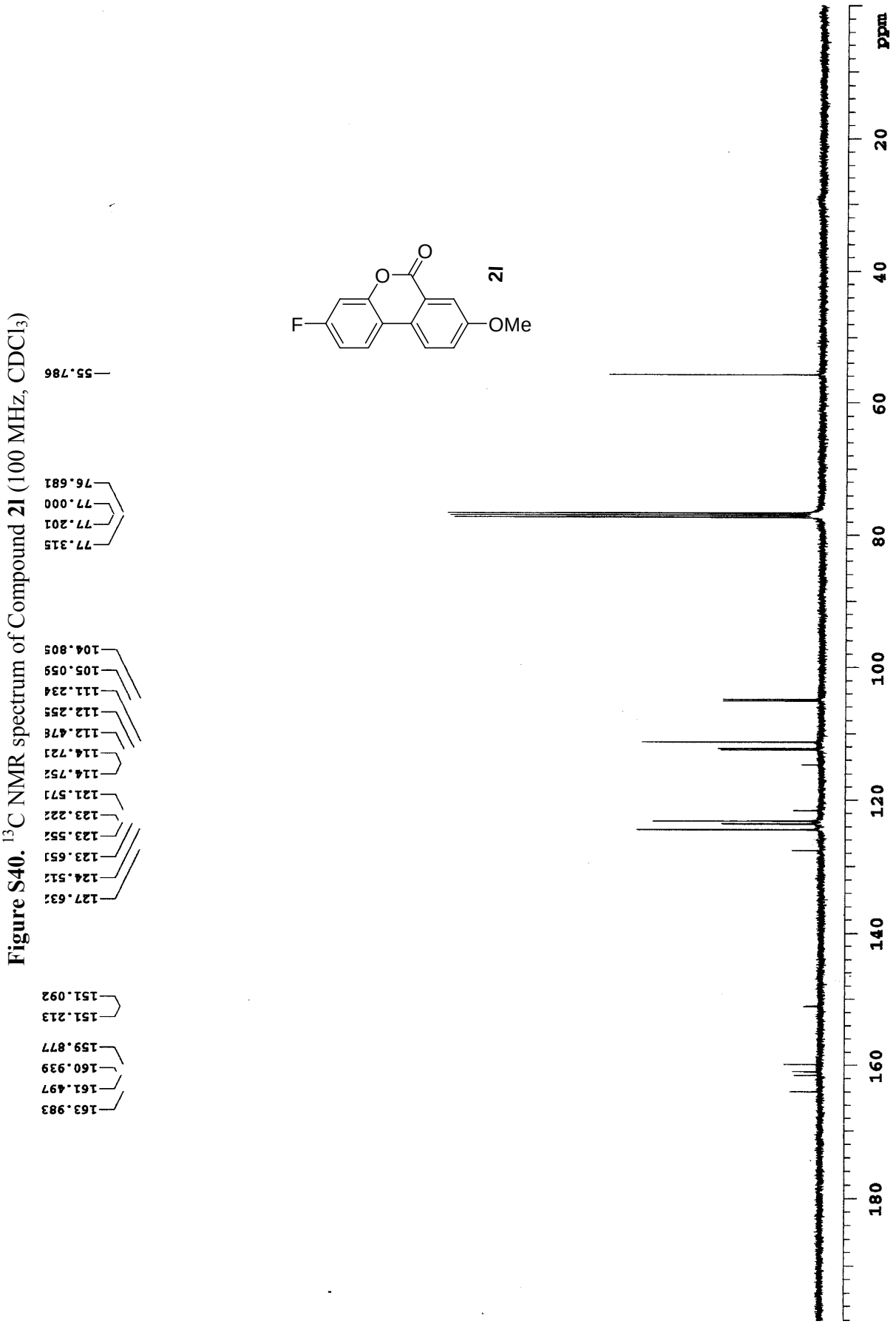
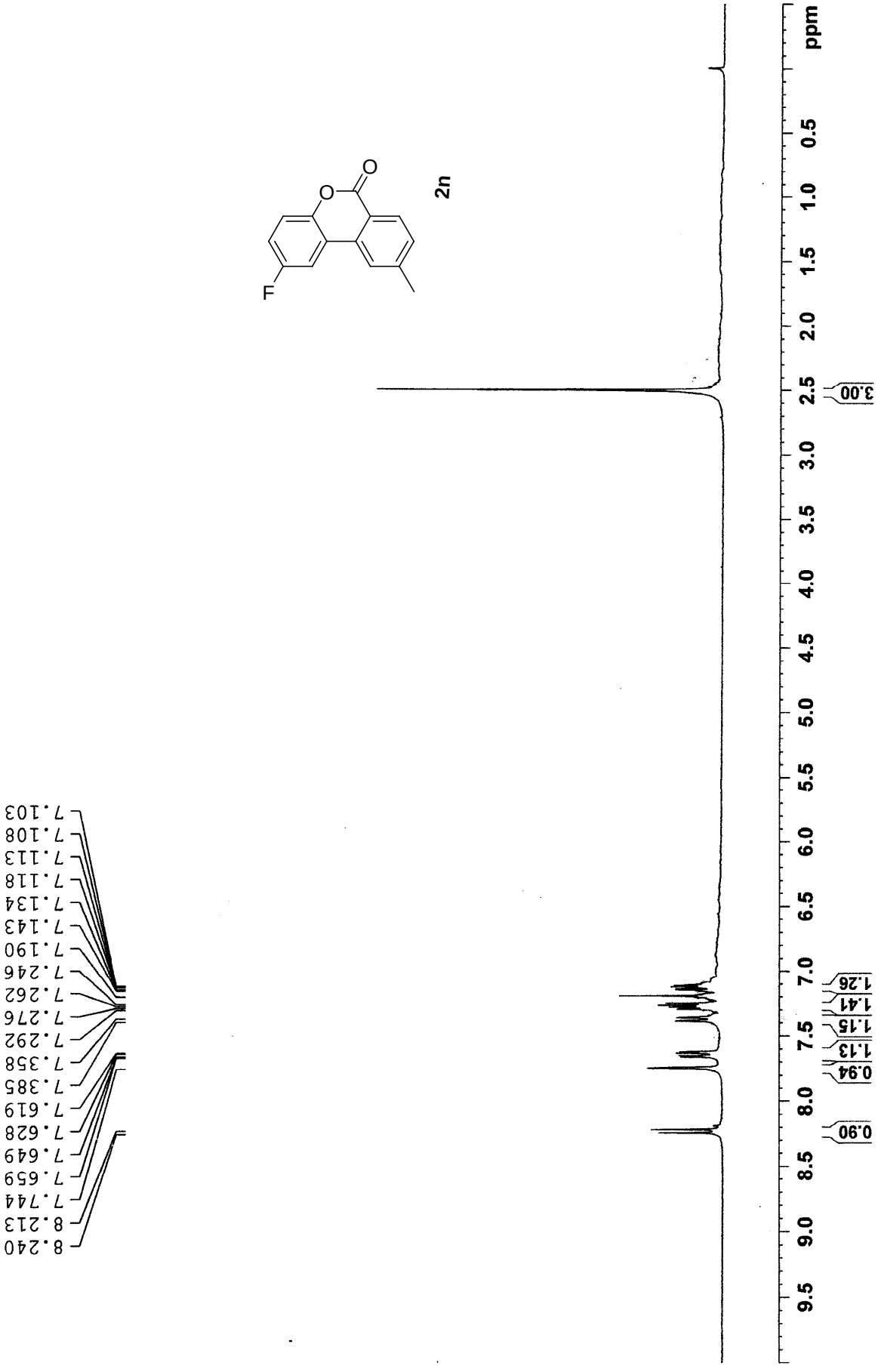


Figure S40. ^{13}C NMR spectrum of Compound **2l** (100 MHz, $CDCl_3$)

Figure S41. ^{1}H NMR spectrum of Compound **2n** (300 MHz, $CDCl_3$)



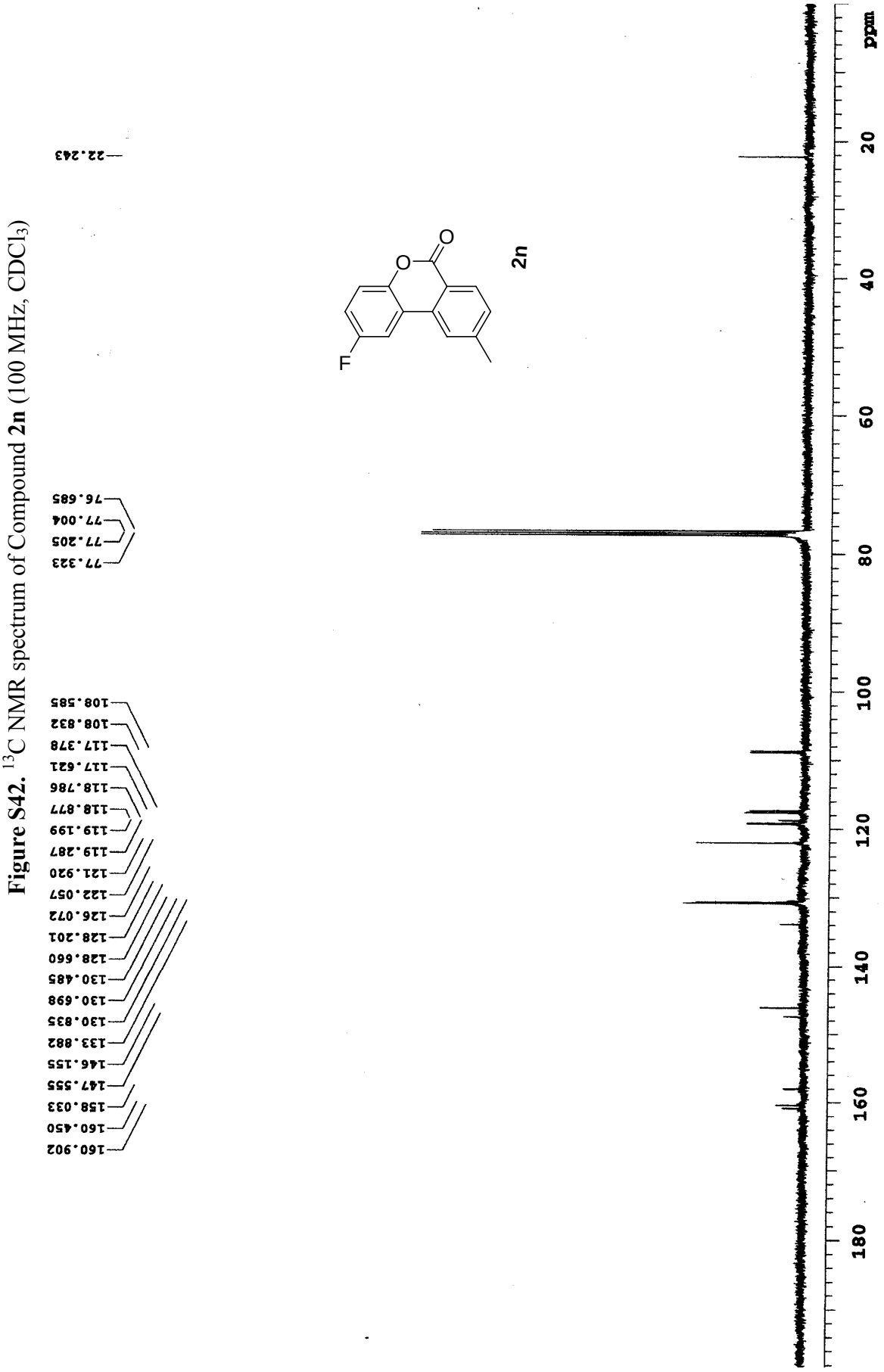


Figure S42. ^{13}C NMR spectrum of Compound **2n** (100 MHz, $CDCl_3$)

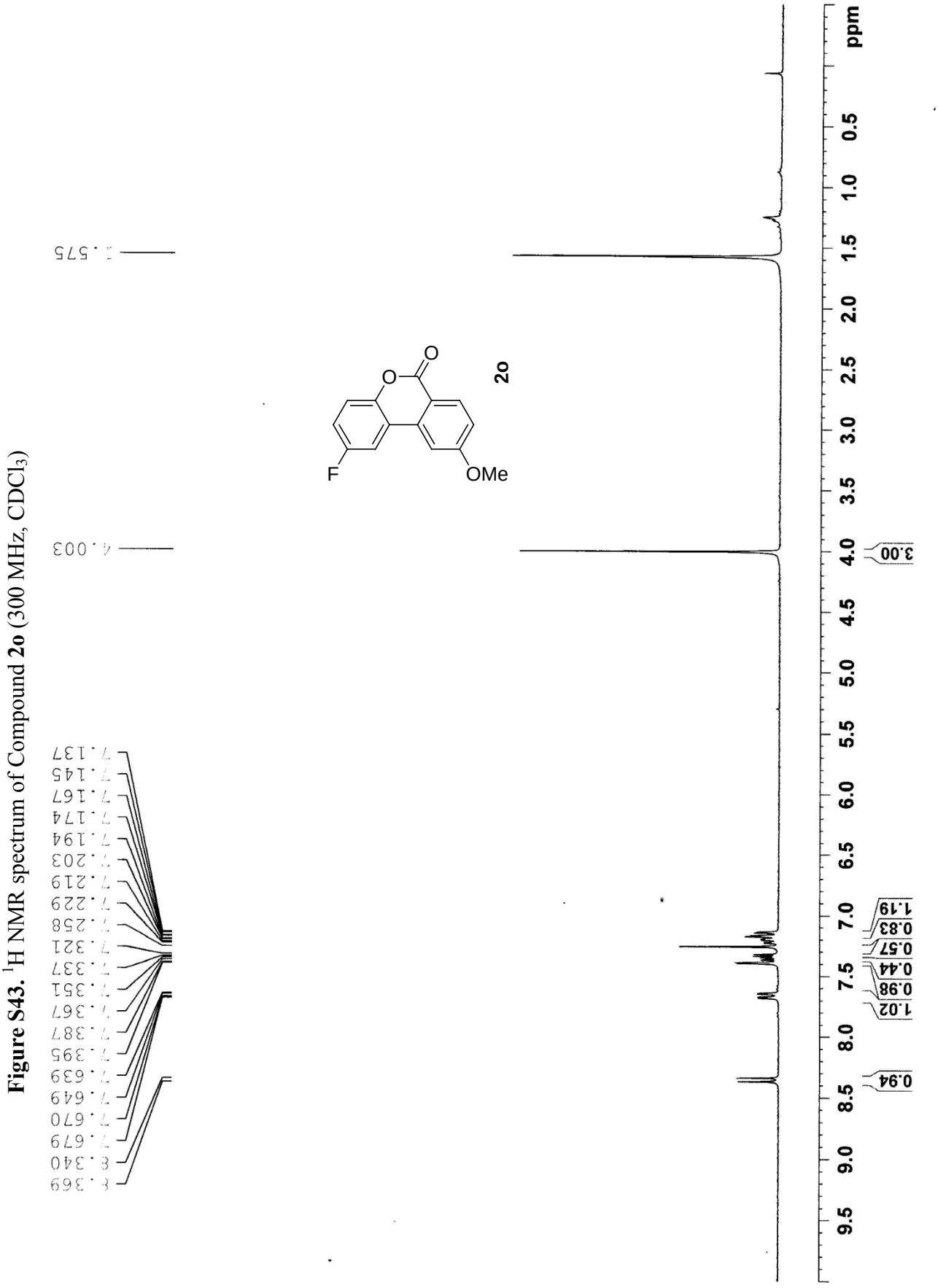


Figure S43. ^{1}H NMR spectrum of Compound **2o** (300 MHz, $CDCl_3$)

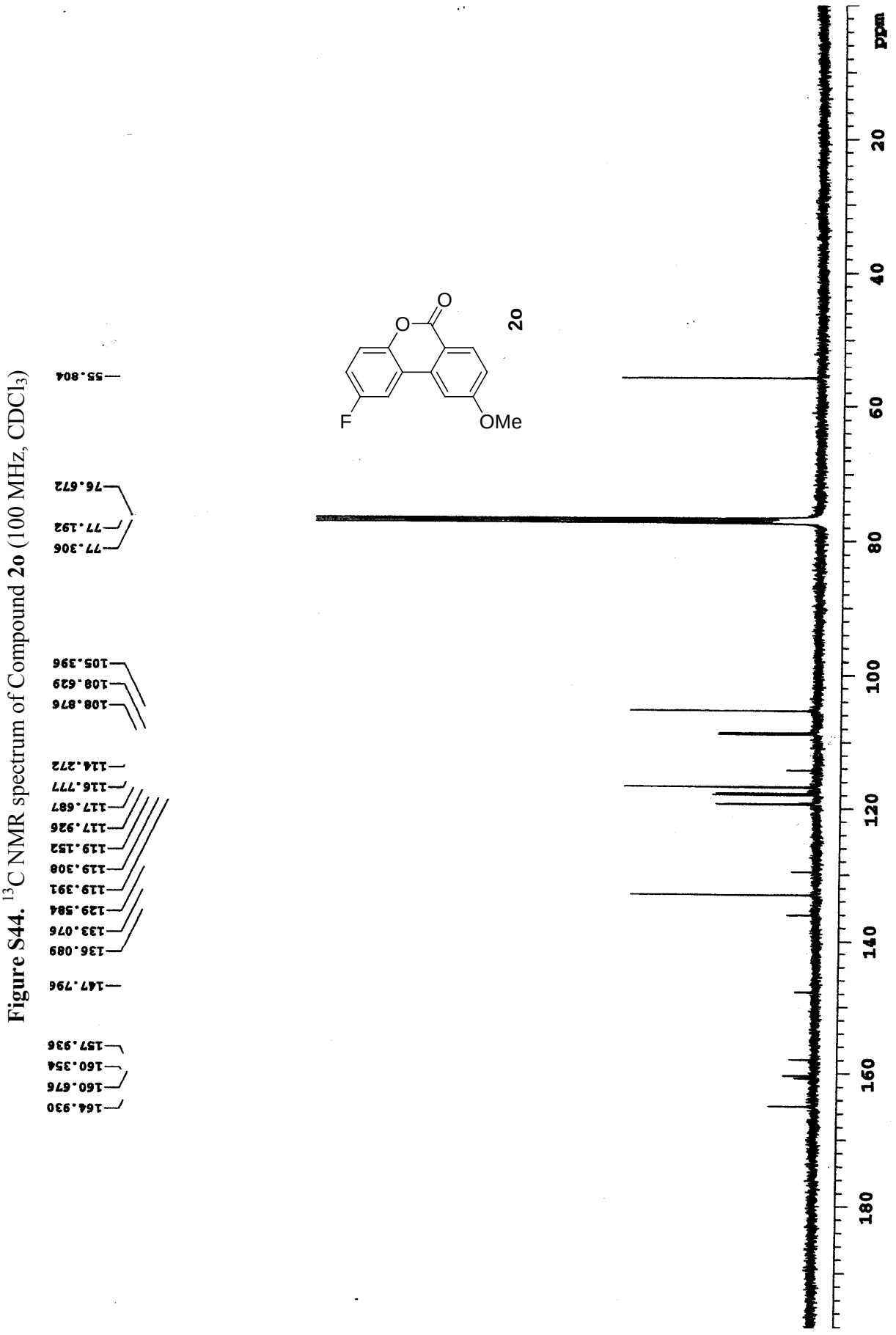


Figure S44. ^{13}C NMR spectrum of Compound **2o** (100 MHz, $CDCl_3$)

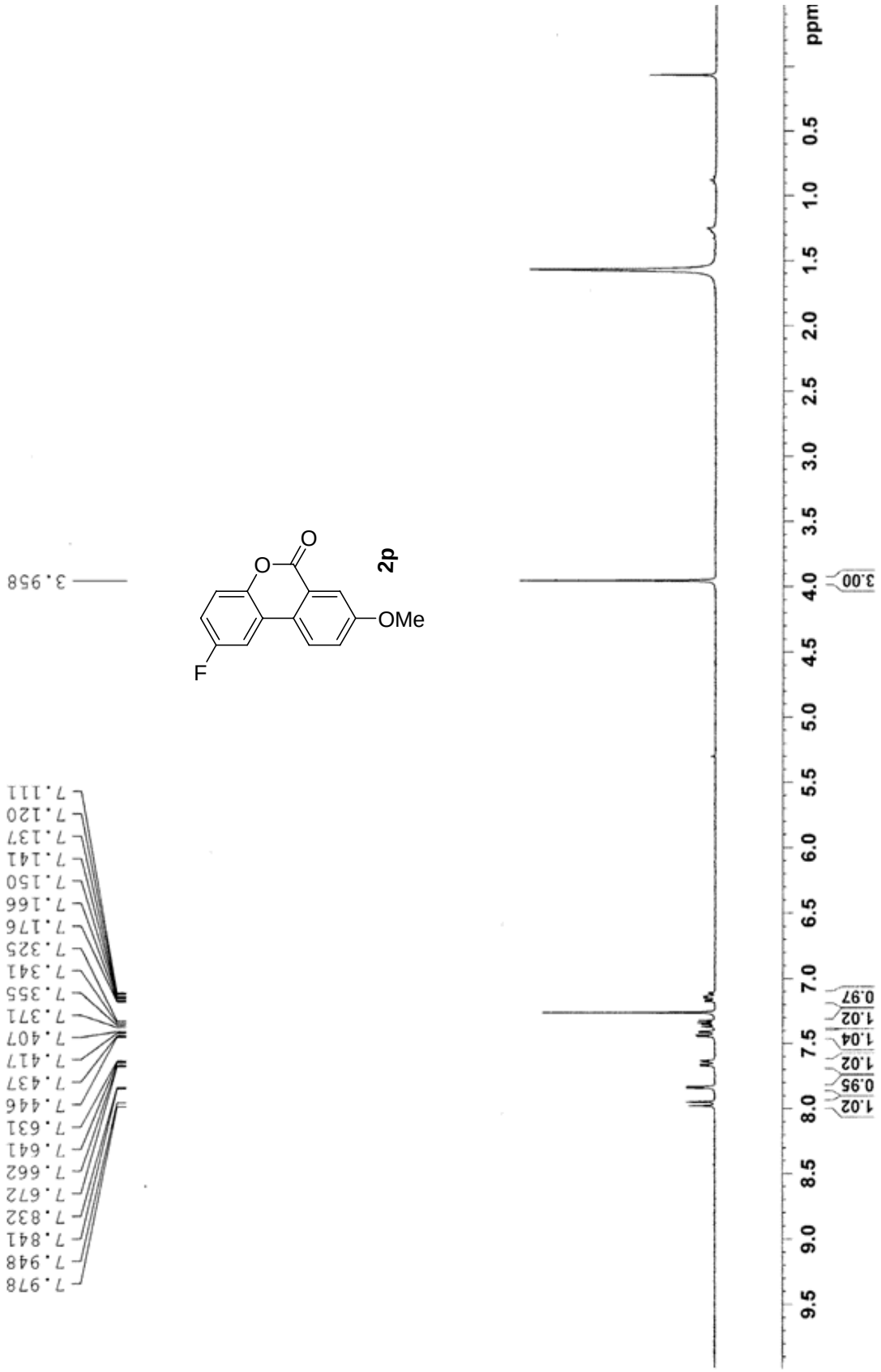


Figure S45. ^{1}H NMR spectrum of Compound **2p** (300 MHz, $CDCl_3$)

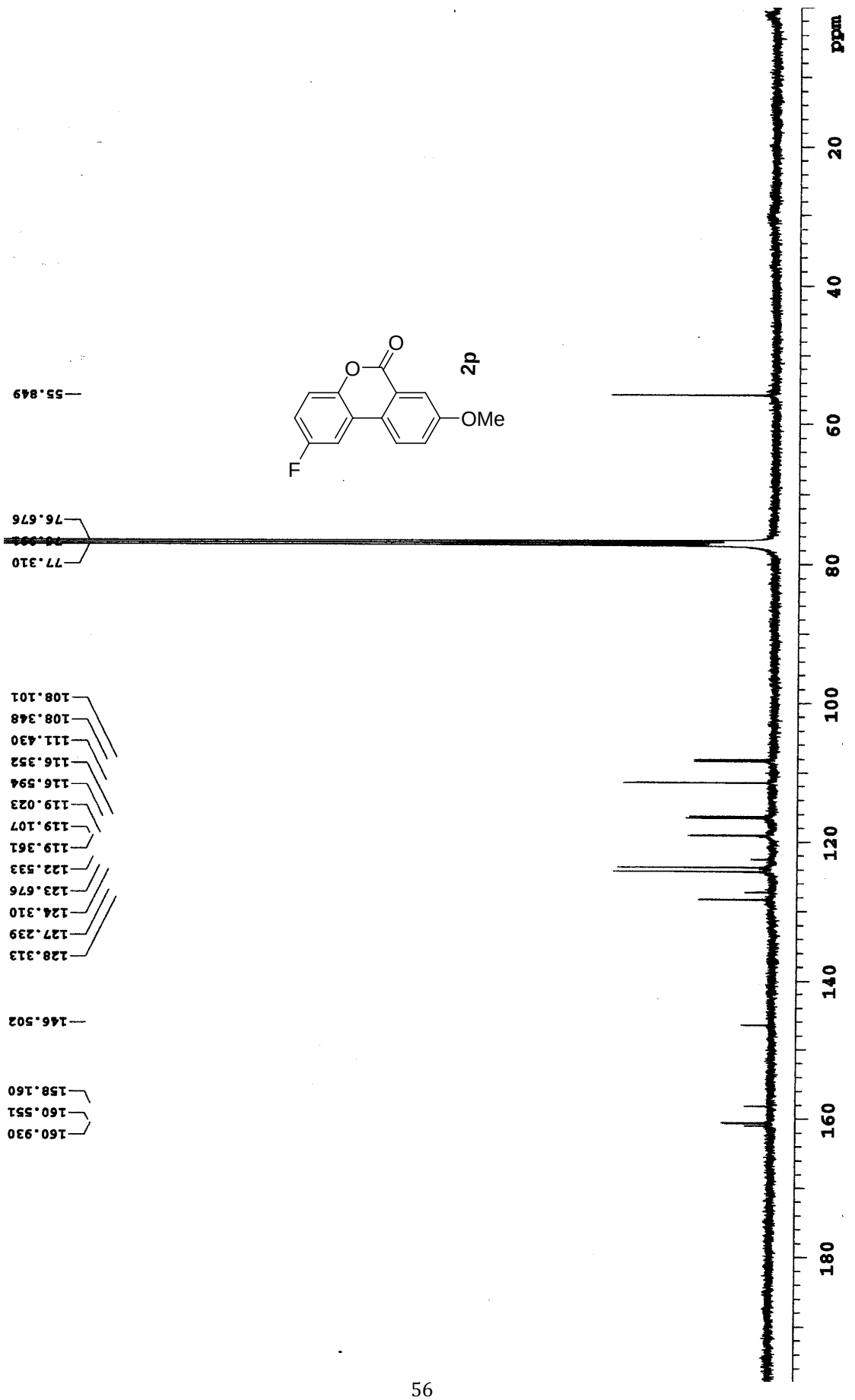


Figure S46. ^{13}C NMR spectrum of Compound **2p** (100 MHz, $CDCl_3$)

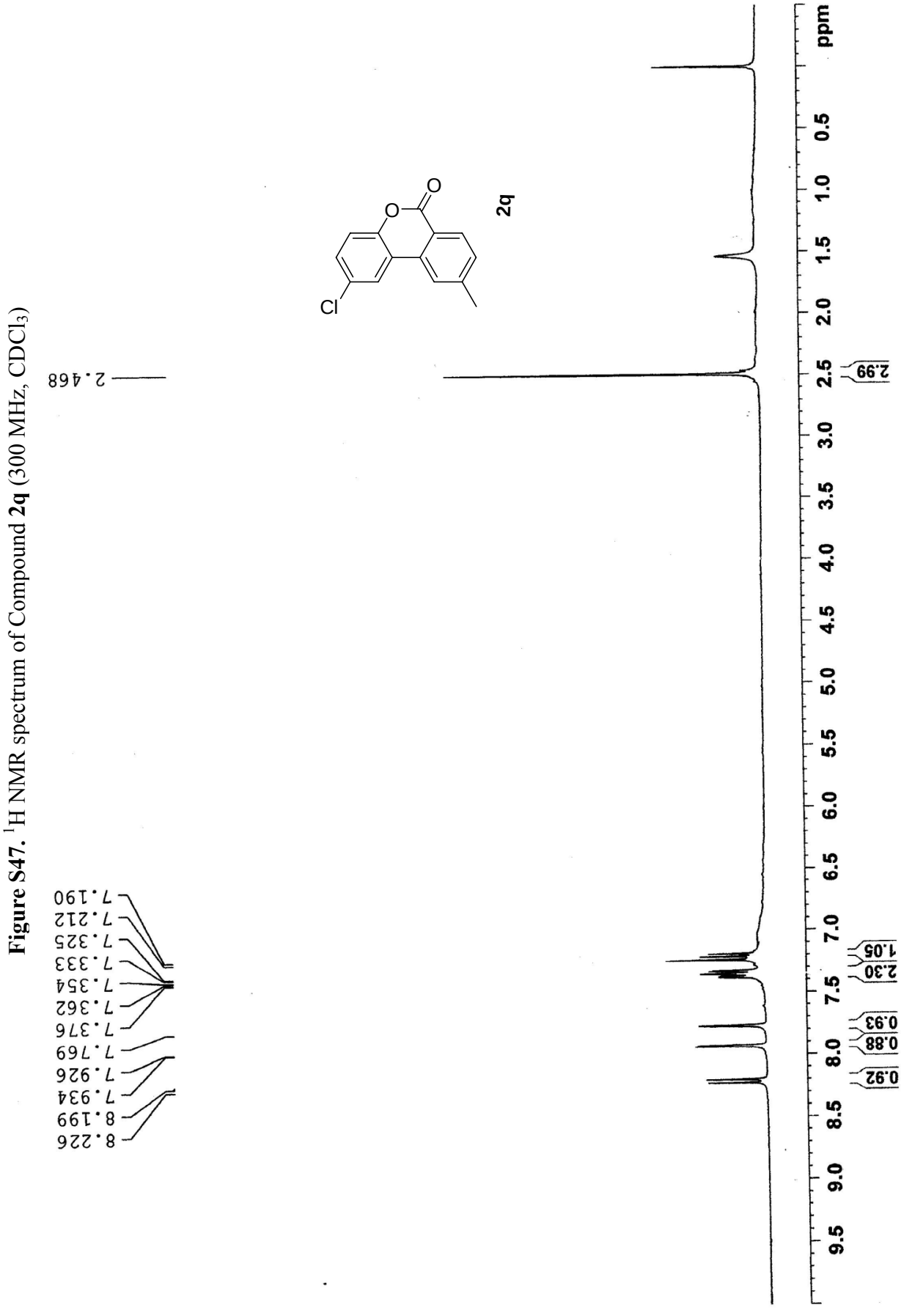


Figure S47. ^{1}H NMR spectrum of Compound **2q** (300 MHz, $CDCl_3$)

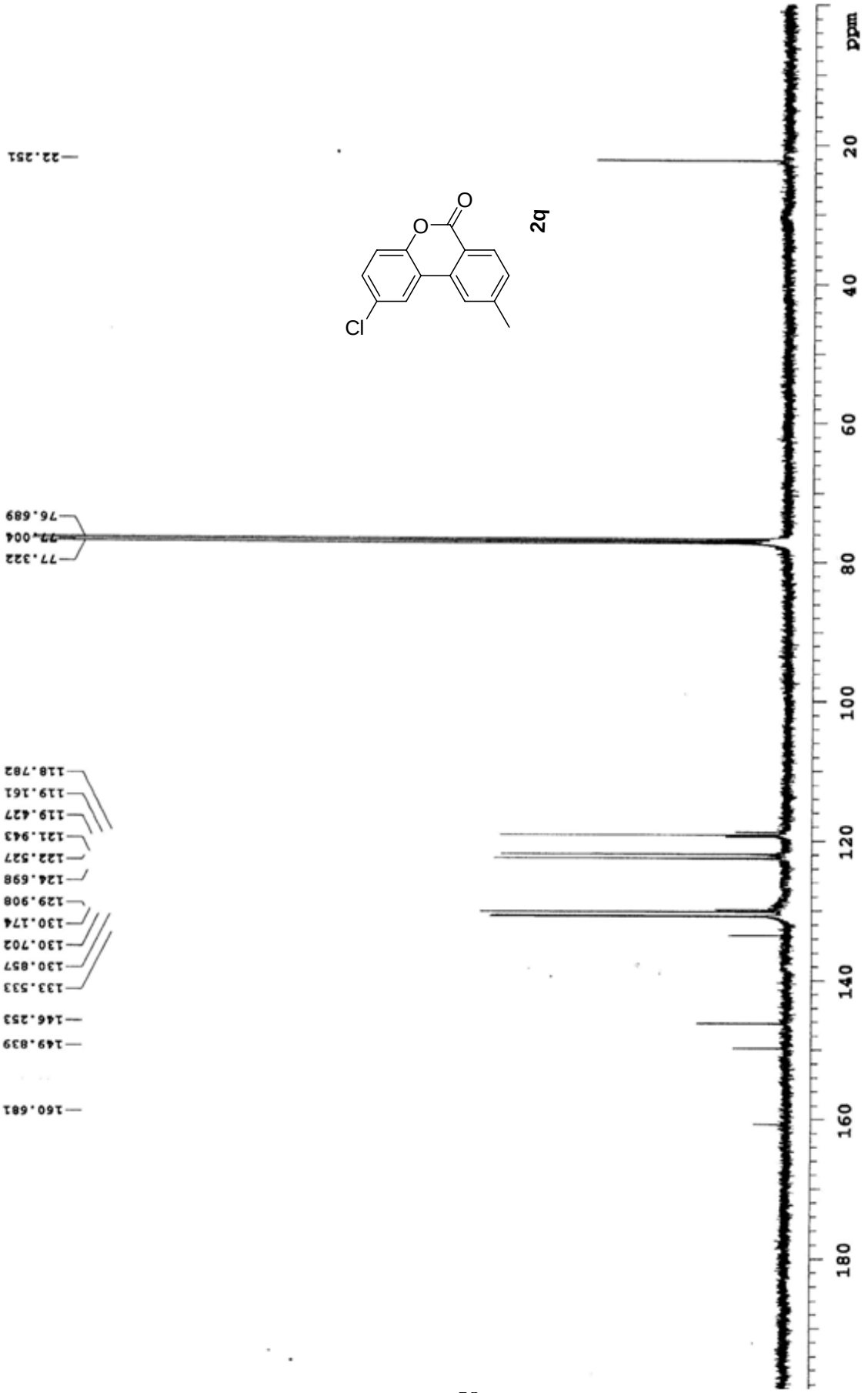


Figure S48. ^{1}H NMR spectrum of Compound **2q** (100 MHz, $CDCl_3$)

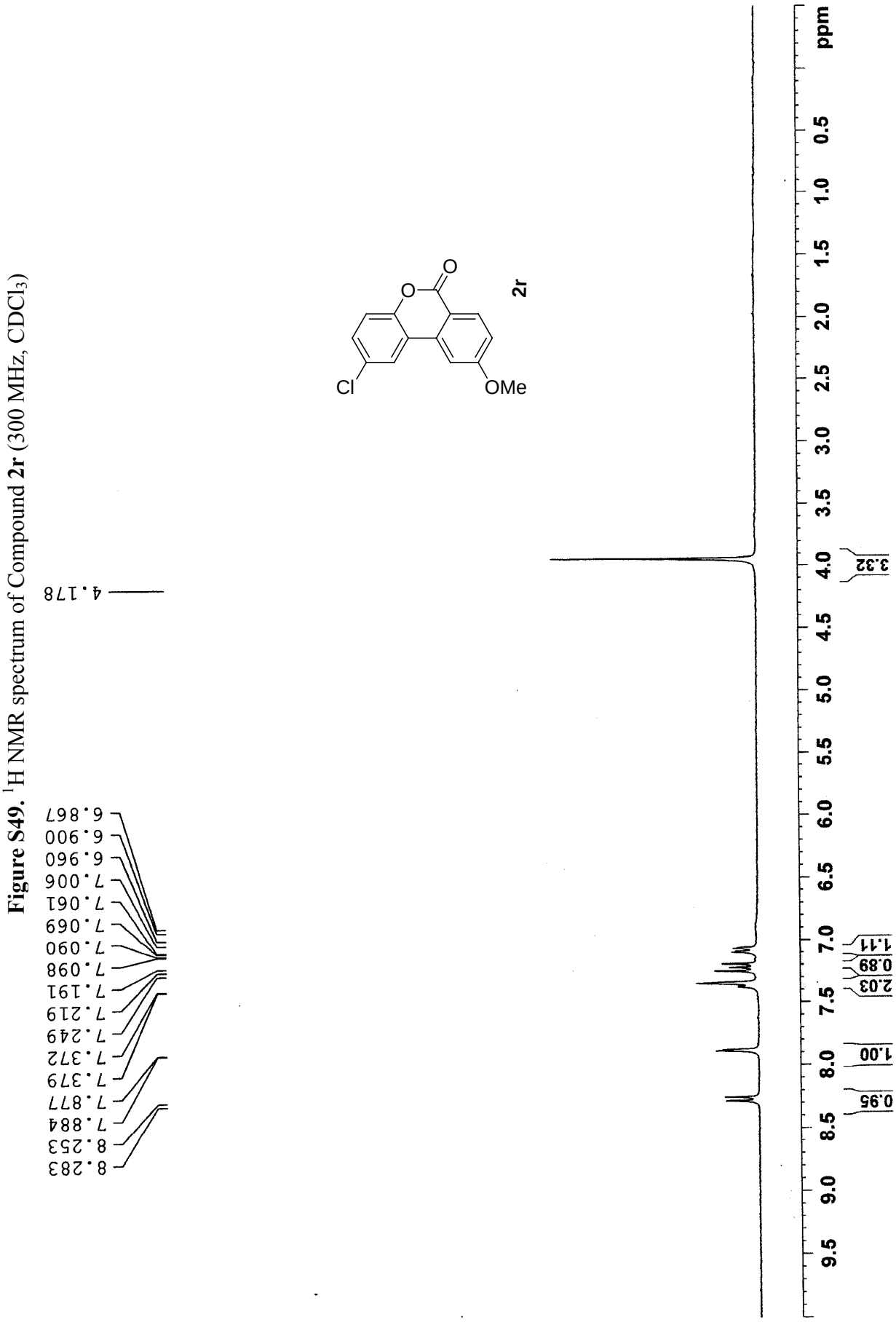


Figure S49. ^{1}H NMR spectrum of Compound **2r** (300 MHz, $CDCl_3$)

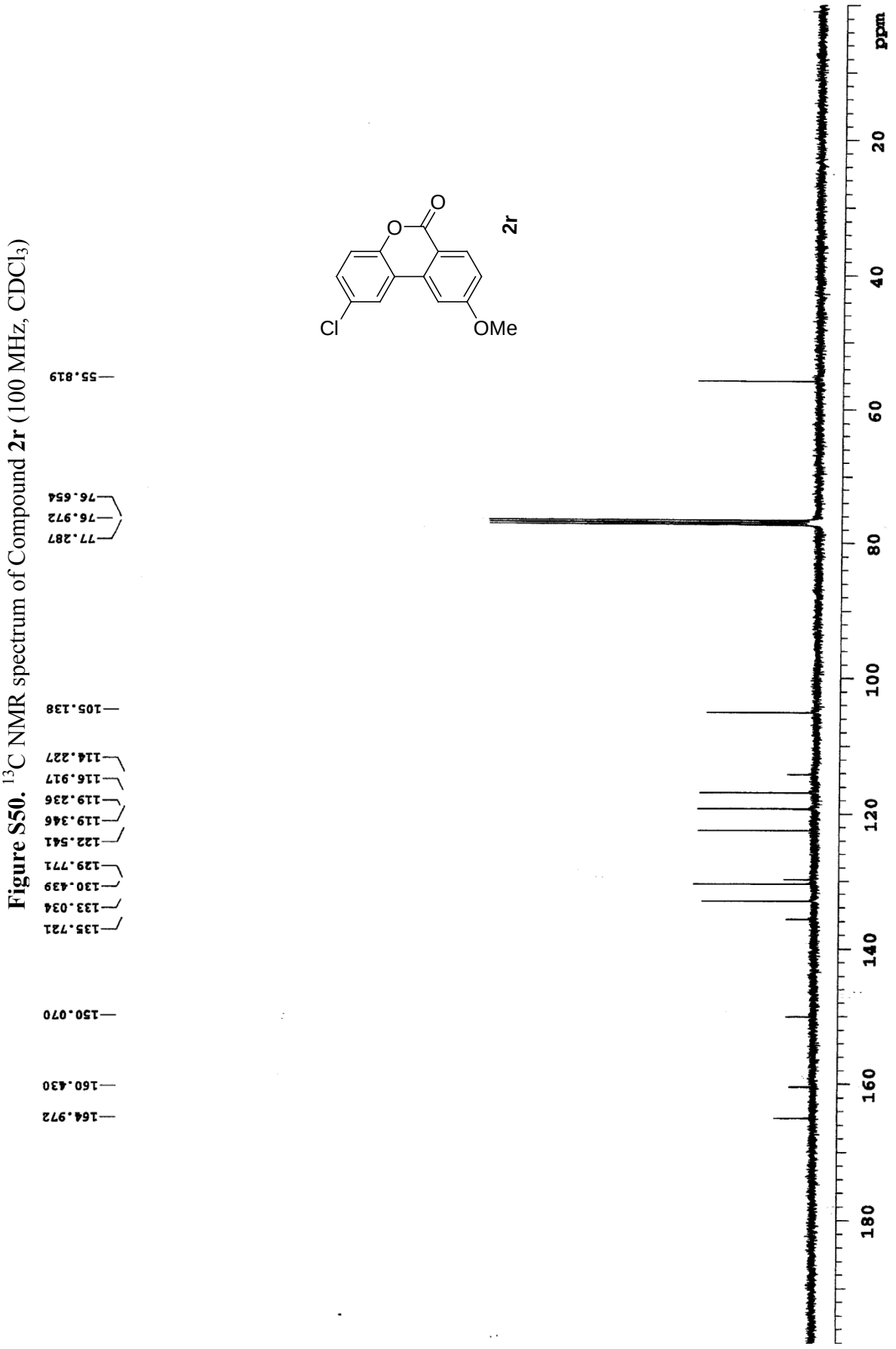
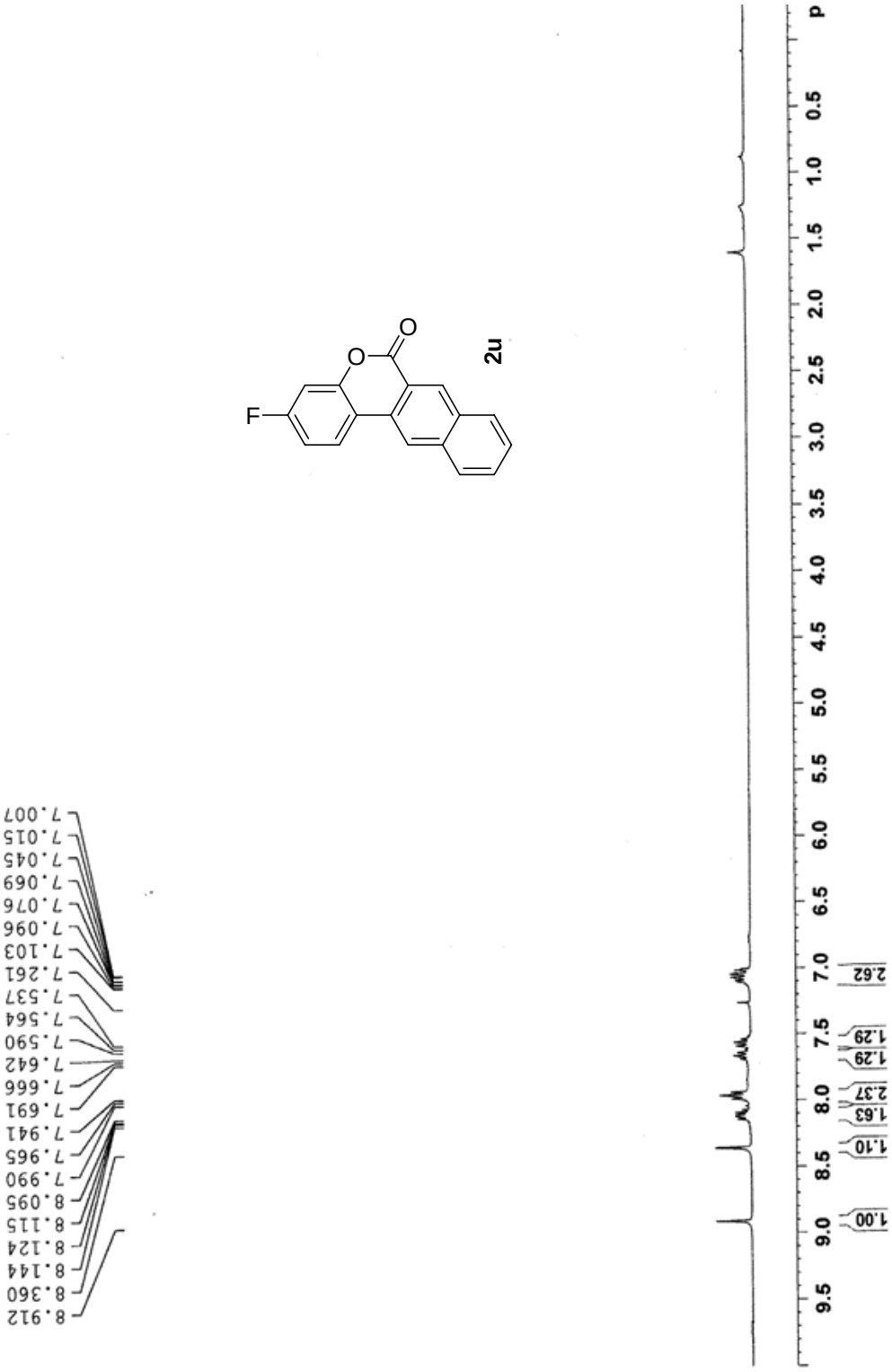


Figure S50. ^{13}C NMR spectrum of Compound **2r** (100 MHz, $CDCl_3$)

Figure S51. ^{1}H NMR spectrum of Compound **2u** (300 MHz, $CDCl_3$)



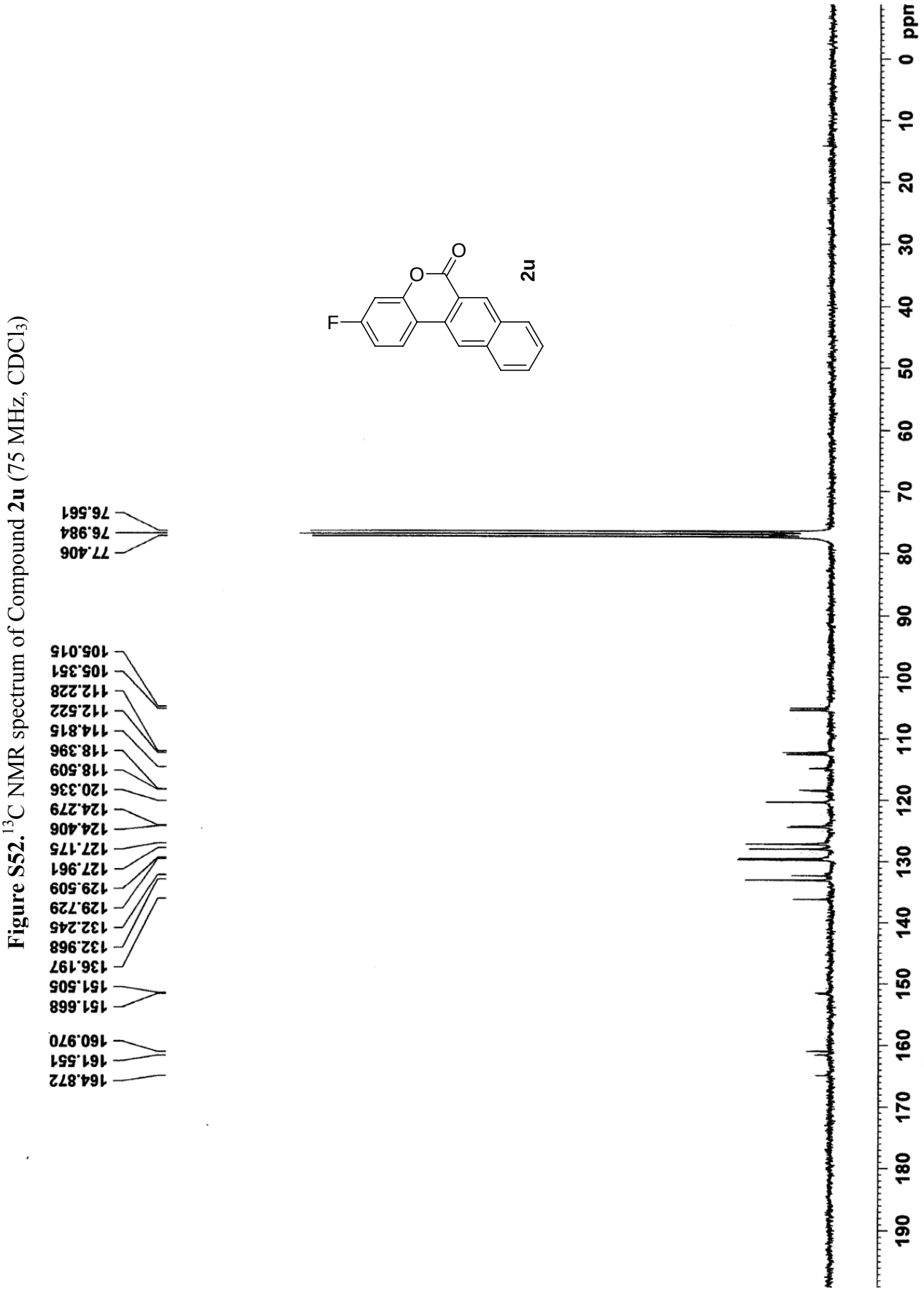
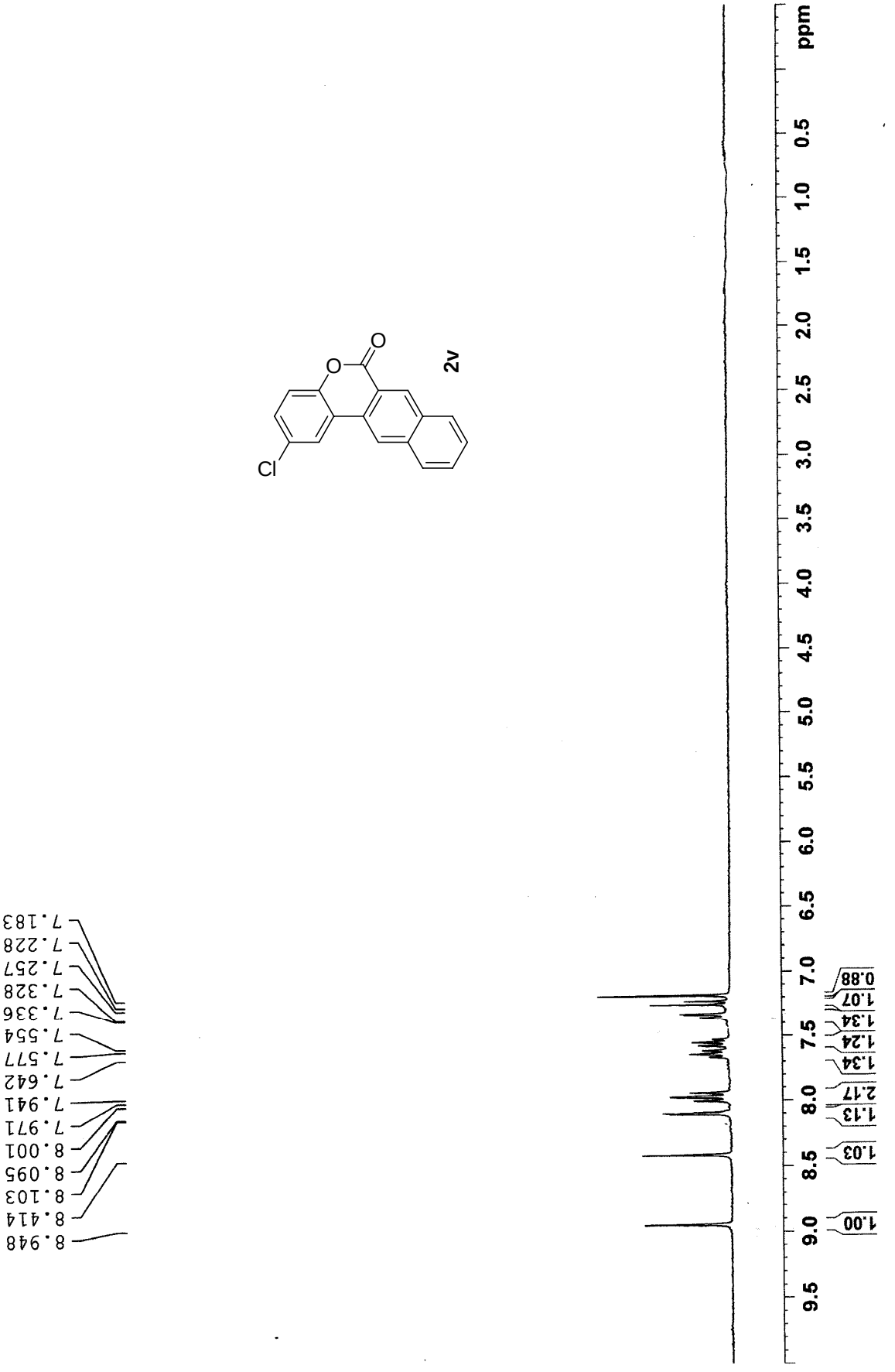


Figure S52. ^{13}C NMR spectrum of Compound **2u** (75 MHz, $CDCl_3$)

Figure S53. ^{1}H NMR spectrum of Compound **2v** (300 MHz, $CDCl_3$)



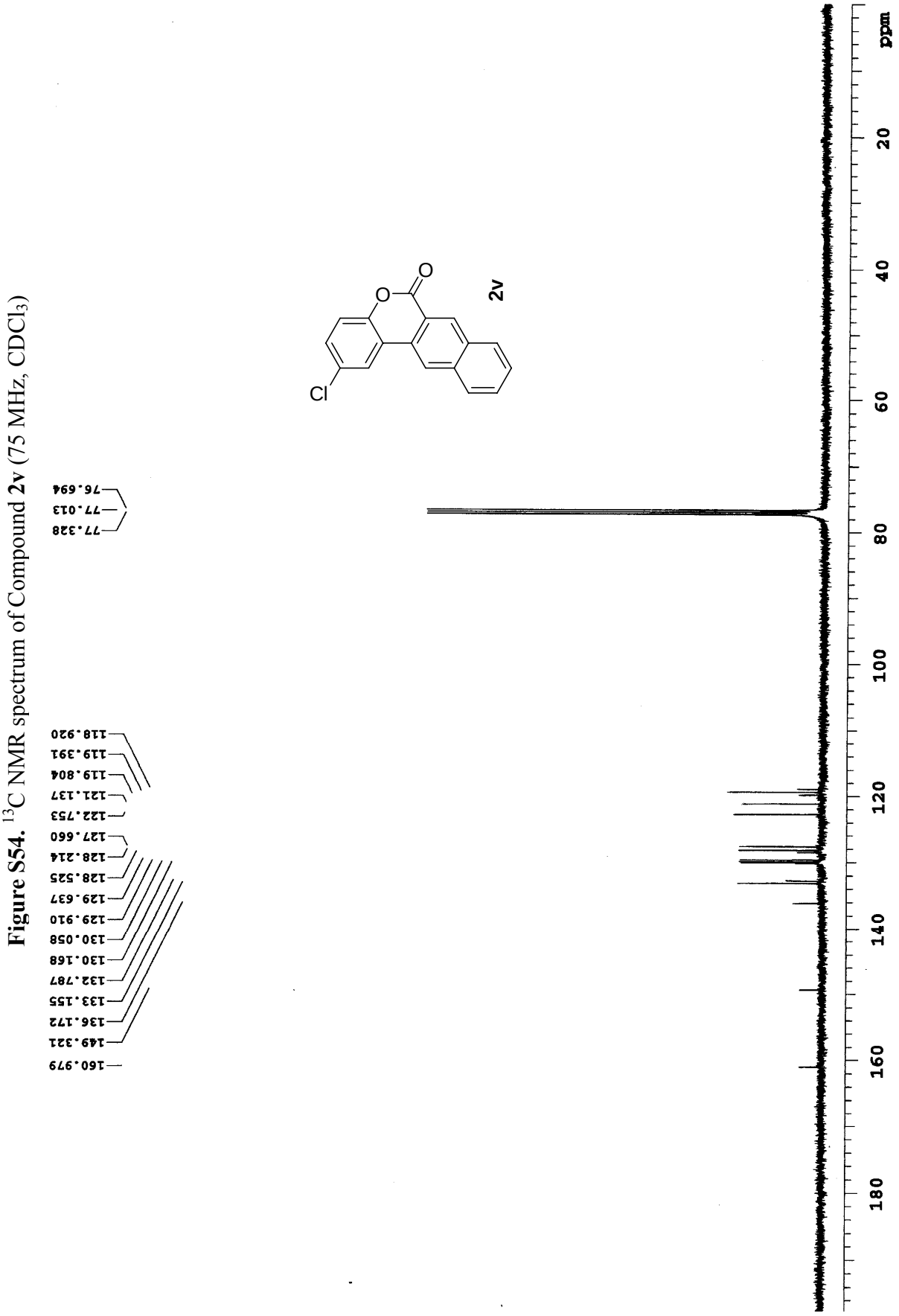


Figure S54. ^{13}C NMR spectrum of Compound **2v** (75 MHz, $CDCl_3$)

Table S1. Crystallographic data for 2o.[3]

Empirical formula	$C_{14}H_9FO_3$	
Formula weight	244.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 13.897(8) Å	α= 90°.
	b = 19.944(11) Å	β= 90°.
	c = 3.7595(19) Å	γ = 90°.
Volume	1042.0(10) $Å^3$	
Z	4	
Density (calculated)	1.557 Mg/m^3	
Absorption coefficient	0.121 mm^{-1}	
F(000)	504	
Crystal size	0.30 x 0.02 x 0.02 mm^3	
Theta range for data collection	1.79 to 26.29°.	
Index ranges	-17<=h<=17, -24<=k<=22, -3<=l<=4	
Reflections collected	8476	
Independent reflections	1849 [R(int) = 0.0518]	
Completeness to theta = 26.29°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9486 and 0.7291	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1849 / 1 / 164	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1243	
R indices (all data)	R1 = 0.0591, wR2 = 0.1735	
Absolute structure parameter	0.0(15)	
Largest diff. peak and hole	0.446 and -0.431 $e.Å^{-3}$	

[3] CCDC-949418 and CCDC-951032 contain the supplementary crystallographic data for compounds **2o** and **2r** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

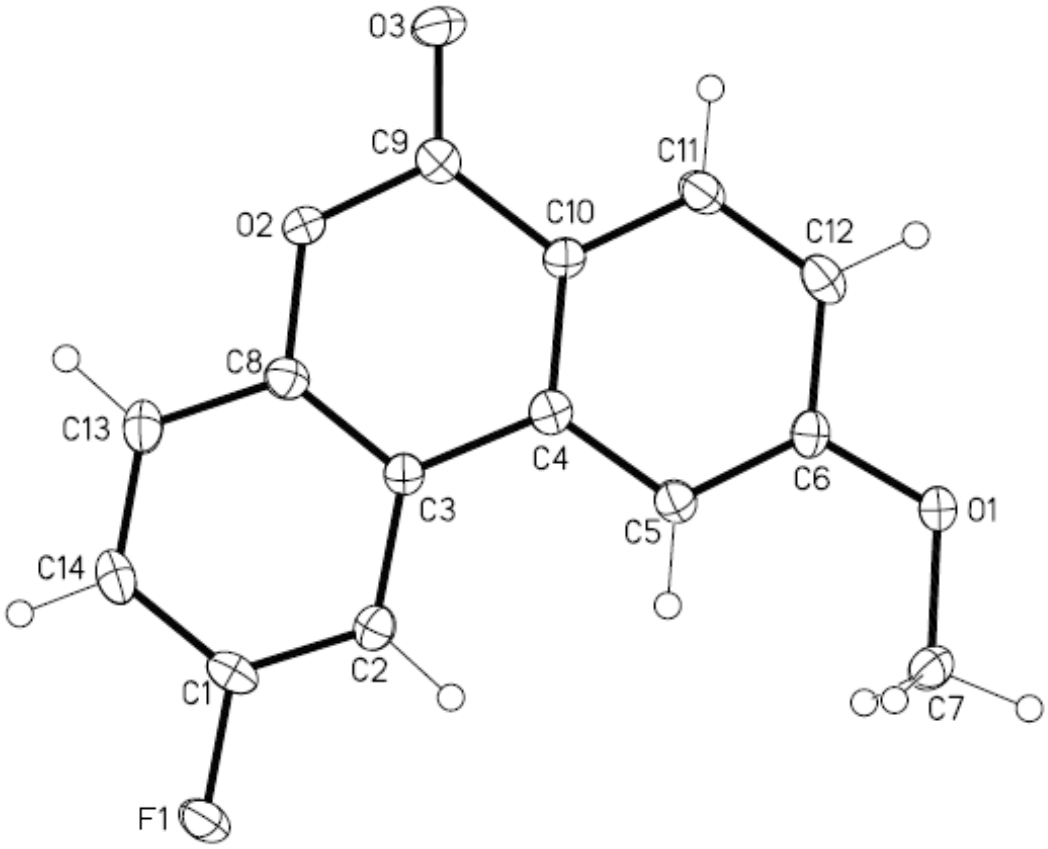


Figure S55. X-ray crystal structure of compound **2o.**

Table S2. Crystallographic data for 2r.

Empirical formula	$C_{14}H_9ClO_3$	
Formula weight	260.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 3.7732(3) Å	α= 90°.
	b = 20.6380(19) Å	β= 90.389(2)°.
	c = 13.9764(13) Å	γ = 90°.
Volume	1088.34(17) $Å^3$	
Z	4	
Density (calculated)	1.591 Mg/m^3	
Absorption coefficient	0.346 mm^{-1}	
F(000)	536	
Crystal size	0.25 x 0.03 x 0.02 mm^3	
Theta range for data collection	1.76 to 26.45°.	
Index ranges	-4<=h<=4, -25<=k<=25, -17<=l<=17	
Reflections collected	9738	
Independent reflections	2235 [R(int) = 0.0397]	
Completeness to theta = 26.45°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9486 and 0.8714	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2235 / 0 / 164	
Goodness-of-fit on F^2	1.269	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1925	
R indices (all data)	R1 = 0.0718, wR2 = 0.2333	
Largest diff. peak and hole	0.693 and -0.538 $e.Å^{-3}$	

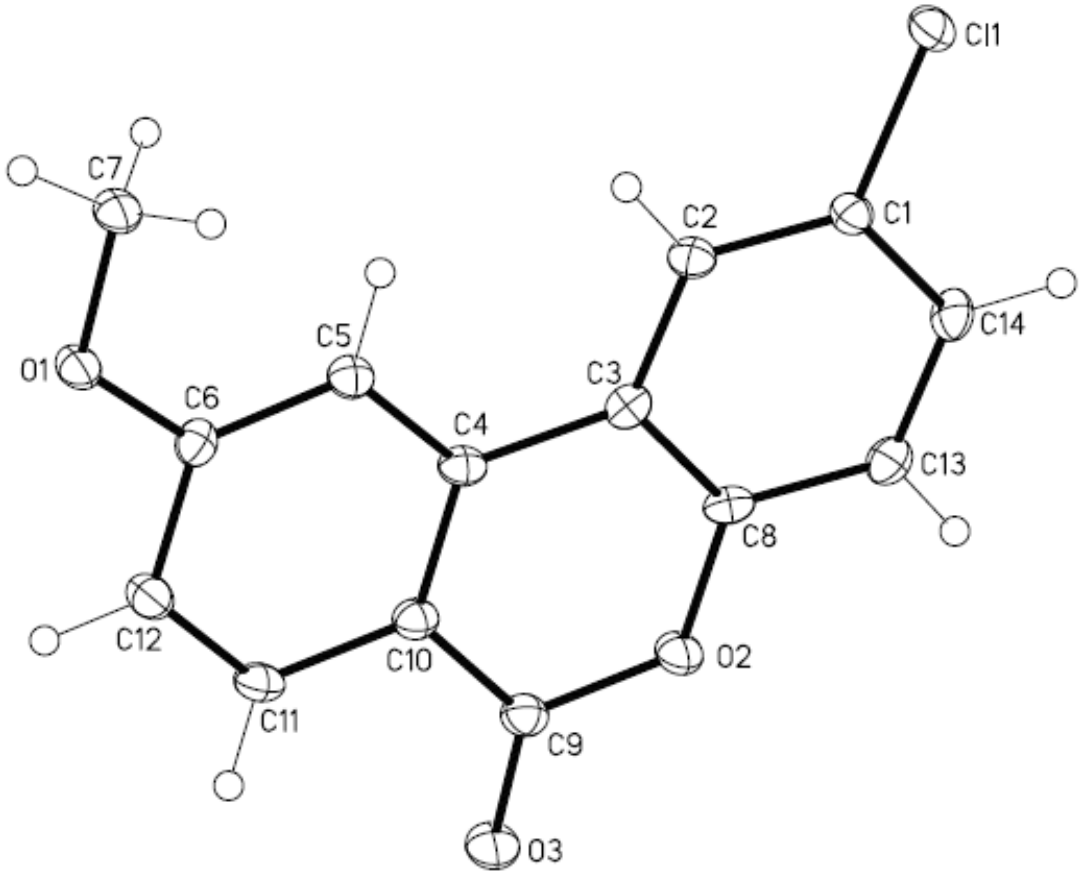
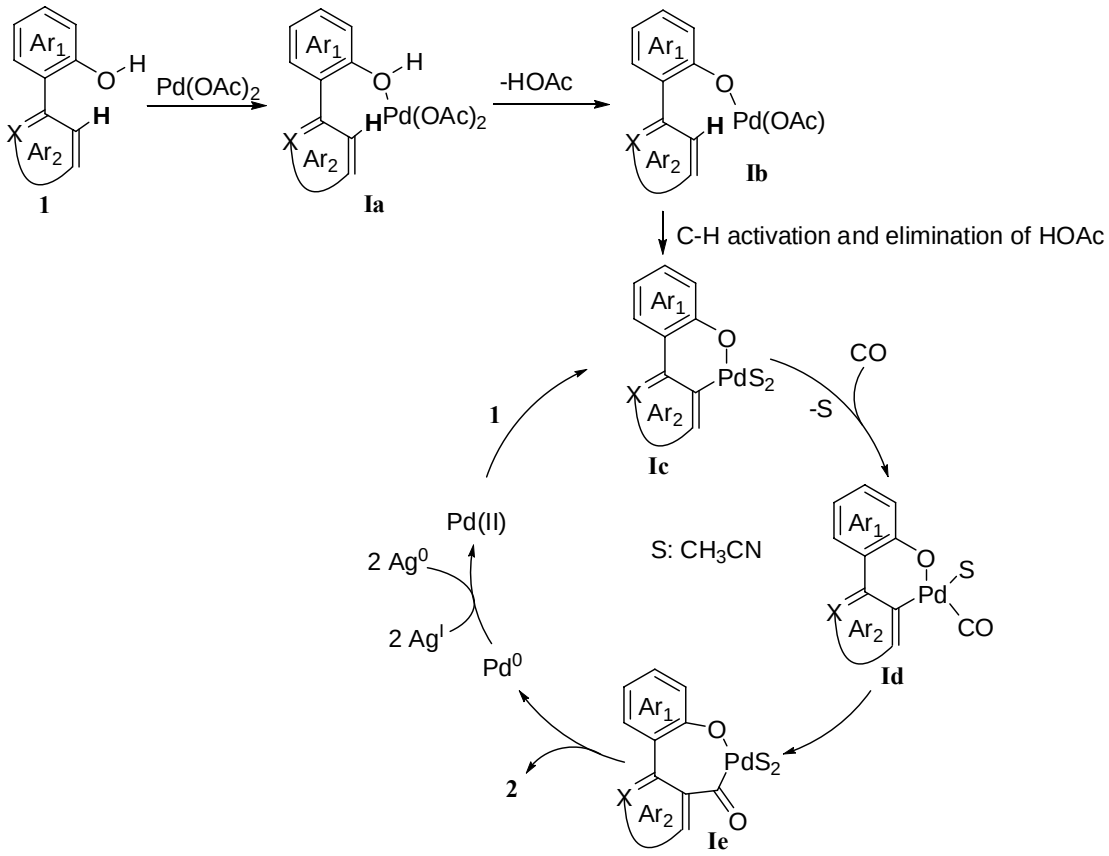


Figure S56. X-ray crystal structure of compound **2r.**

Scheme S1. Proposed reaction mechanism.



Initially, coordination of substrates **1** with $Pd(OAc)_2$ takes place, followed by activation of *ortho* C−H bond in aryl ring Ar_2, to form a six-membered palladacycle intermediate **Ic**. The detail process from **1** to **Ic** may go through initial formation of a σ-complex **Ia** followed by elimination of an acetic acid to give **Ib**. Next, C-H bond activation and elimination of an acetic acid proceed to form a pallacycle **Ic**. Intermediate **Ic** can be stabilized by the solvent (S: acetonitrile). Subsequent dissociation of solvent and association of CO on intermediate **Ic** give **Id**. Then insertion of CO between Pd−C bond produces a seven-membered palladacycle **Ie**. Finally, reductive elimination occurs to give benzopyranone derivatives **2** and Pd(0). The Pd(0) species are oxidized to Pd(II) by silver acetate to perform the next cycle. Silver mirror can be observed clearly around the reaction tube during the reaction.