Supporting Information

Redox condensation of *o*-Halonitrobenzene with 1,2,3,4-Tetrahydroisoquinoline: Involvement of an Unexpected Auto-catalyzed Redox Cascade

Thanh Binh Nguyen,* Ludmila Ermolenko, and Ali Al-Mourabit*

General information

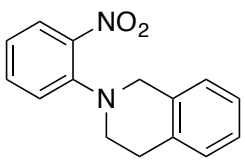
Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C; CD_3OD, δ 3.31 ppm for ^{1}H and δ 49.0 ppm for ^{13}C; DMSO-d6, δ 2.50 ppm for ^{1}H and δ 39.5 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure

A mixture of **1** (1 mmol) and **2** (2.5 mmol) was stirred at 130 °C or 150 °C (see Table 1, Schemes 4 and 5 of the manuscripts for details) for 24 h under an argon atmosphere. The cooled reaction mixture was diluted with methanol and treated with a saturated ammonia solution in methanol (0.5 mL). The resulting solution was concentrated in vacuo. The residue was purified by silica gel column chromatography (heptane: EtOAc 4:1 to EtOAc) to afford the fused benzimidazole **5**.

Characterizations of Products

2-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (3aa)[1]



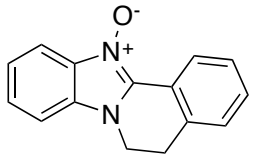
[1] Hedley, K. A.; Stanforth, S. P. *Tetrahedron* **1992**, *48*, 743.

Purification with silica gel column chromatography (EtOAc:heptane : 50:1) as an orange solid. mp. 100 °C (lit. 100-102 °C).[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 1H), 7.50-7.44 (m, 1H), 7.23-7.08 (m, 5H), 7.00-6.95 (m, 1H), 4.33 (s, 2H), 3.40 (t, J = 5.5 Hz, 2H), 3.02 (t, J = 5.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 141.8, 134.7, 133.9, 133.6, 128.9, 126.8, 126.6, 126.5, 126.3, 120.4, 120.0, 52.7, 50.3, 29.0.

5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline 12-oxide (**4aa**)

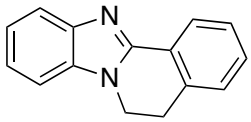


The product was obtained as a white solid by filtration of the reaction mixture in DMF diluted in CH_2Cl_2.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.38-9.33 (m, 1H), 7.79-7.74 (m, 2H), 7.49-7.43 (m, 4H), 7.37-7.31 (m, 1H), 4.43 (t, J = 6.8 Hz, 2H), 3.30 (t, J = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 134.1, 133.9, 133.6, 130.3, 128.3, 128.2, 127.1, 125.5, 124.8, 122.4, 122.0, 113.2, 111.3, 40.4, 27.6.

5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5aa)[2]

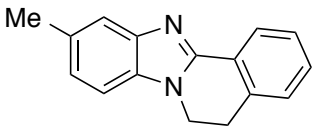


Purification of the crude mixture (Table 1, entry 2) by silica gel column chromatography (EtOAc) afforded the product as a yellow powder (30 mg, 55%), (196 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 6.5 Hz, 1H), 7.67 (m, 1H), 7.46 (m, 1H), 7.40 (m, 3H), 7.27 (m, 2H), 4.31 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 142.7, 135.3, 134.3, 130.4, 128.1, 127.3, 125.7, 124.8, 122.8, 122.5, 118.2, 109.5, 40.2, 27.7.

10-Methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ba)[3]



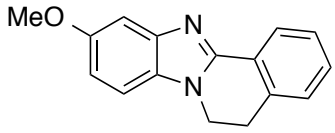
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (201 mg, 86%).

[2] Oconnell, J. M.; Moriarty, E.; Aldabbagh, F.*Synthesis* **2012**, *44*, 3371.
[3] Sun, X.; Lv, X. H.; Ye, L. M.; Hu, Y.; Chen, Y. Y.; Zhang, X. J.; Yan, M. *Org. Biomol. Chem.* **2015**, *13*, 7381.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, J = 6.3, 2.6 Hz, 1H), 7.52 (m, 1H), 7.31 (m, 2H), 7.21 (m, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.01 (dd, J = 8.1, 1.5 Hz, 1H), 4.20 (t, J = 7.0 Hz, 2H), 3.18 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 144.1, 134.2, 132.2, 130.0, 128.0, 127.7, 127.0, 125.6, 124.2, 123.5, 119.5, 108.2, 40.5, 28.3, 21.8.

10-Methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ca)



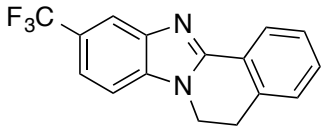
Purification of the crude mixture by silica gel column chromatography (EtOAc: heptane 1:4) afforded the product as a yellow powder (175 mg, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, J = 6.8, 2.2 Hz, 1H), 7.34 (m, 2H), 7.26 (m, 1H), 7.18 (m, 2H), 6.87 (dd, J = 8.8, 2.2 Hz, 1H), 4.25 (t, J = 7.8 Hz, 2H), 3.83 (s, 3H), 3.23 (t, J = 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 141.7, 140.1, 133.9, 130.2, 128.1, 127.8, 125.5, 113.1, 109.5, 101.8, 55.8, 40.5, 28.3.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{16}H_{15}N_2O$: 251.1184; found : 251.1173.

10-(Trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5da)



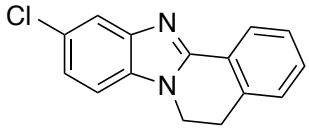
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (250 mg, 87%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (m, 1H), 8.09 (s, 1H), 7.52 (dd, J = 8.5, 1.4 Hz, 1H), 7.43 (m, 3H), 7.34 (m, 1H), 4.36 (t, J = 6.9 Hz, 2H), 3.32 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 143.3, 136.6, 134.4, 130.8, 128.2, 127.9, 126.0, 125.9, 124.9 (q, J = 270.0 Hz), 124.8 (q, J = 32.0 Hz), 119.6 (q, J = 3.5 Hz), 117.3 (q, J = 4.5 Hz), 109.4, 40.6, 28.0.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{16}H_{12}F_3N_2$: 289.0953; found : 289.0941.

10-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ea)



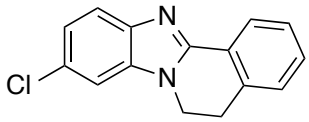
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (194 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (m, 1H), 7.78 (t, J = 1.3 Hz, 1H), 7.40 (m, 2H), 7.33 (m, 1H), 6.23 (m, 2H), 4.28 (t, J = 6.8 Hz, 2H), 3.27 (t, J = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 144.8, 134.2, 133.4, 130.6, 128.2, 128.0, 127.8, 126.2, 125.8, 123.0, 119.5, 109.7, 40.6, 28.2.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{15}H_{12}ClN_2$: 255.0689; found : 207.0681.

9-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5fa)



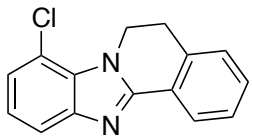
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (220 mg, 86%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.34 (m, 2H), 7.26 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5, 1.8 Hz, 1H), 4.23 (t, J = 6.9 Hz, 2H), 3.21 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 142.5, 135.4, 134.3, 130.6, 128.2, 127.9, 127.3, 125.8, 125.7, 125.2, 120.5, 109.3, 40.6, 28.2.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{15}H_{12}ClN_2$: 255.0689; found : 207.0694.

8-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ga)



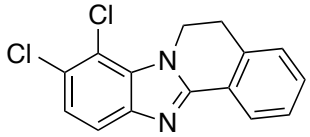
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (190 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (m, 1H), 7.70 (dd, J = 8.5 Hz, 1H), 7.44 (m, 2H), 7.35 (m, 1H), 7.23 (m, 2H), 4.85 (t, J = 6.9 Hz, 2H), 3.28 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 145.8, 134.4, 130.5, 127.9, 127.8, 126.3, 126.0, 124.1, 122.9, 118.6, 116.1, 111.2, 42.6, 28.6.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{15}H_{12}ClN_2$: 255.0689; found : 207.0678.

8,9-Dichloro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ha)



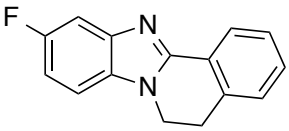
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (211 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (m, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.43 (m, 2H), 7.34 (m, 2H), 4.88 (t, J = 6.8 Hz, 2H), 3.29 (t, J = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 144.0, 134.3, 131.9, 130.7, 127.9, 127.8, 127.4, 126.0, 124.2, 118.8, 114.7, 111.7, 42.7, 28.3.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{15}H_{11}Cl_2N_2$: 289.0299; found : 289.0288.

10-Fluoro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ia)



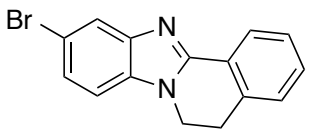
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (185 mg, 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (m, 1H), 7.47 (dd, J = 9.5, 2.4 Hz, 1H), 7.39 (m, 2H), 7.29 (m, 1H), 7.22 (2d, J = 9.0, 4.4 Hz, 1H), 7.00 (td, J = 5.0, 2.5 Hz, 1H), 4.28 (t, J = 6.9 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4 (d, J = 238 Hz), 150.4, 144.1, 134.0, 131.2, 130.4, 128.1 127.8, 126.2, 125.6, 110.9 (d, J = 27 Hz), 109.3 (d, J = 10 Hz), 105.4 (d, J = 24 Hz), 40.4, 27.9.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{15}H_{12}FN_2$: 239.0985; found : 239.0991.

10-Bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ja)



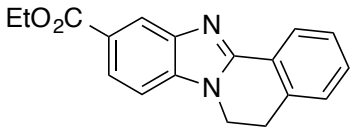
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (209 mg, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.33 (m, 2H), 7.29 (dd, J = 8.5, 1.6 Hz, 1H), 7.23 (m, 1H), 7.13 (d, J = 8.5 Hz, 1H), 4.28 (t, J = 6.9 Hz, 2H), 3.27 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 144.7, 134.2, 133.5, 130.7, 128.1, 127.8, 125.9, 125.8, 125.0, 122.3, 115.5, 110.4, 40.6, 28.0.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{15}H_{12}BrN_2$: 299.0184; found : 299.0179.

Ethyl 5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline-10-carboxylate (5ka)



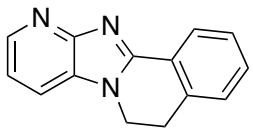
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:4) afforded the product as a yellow powder (230 mg, 79%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.31(m, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.39 (m, 4H), 4.42 (m, 4H), 3.32 (t, J = 6.8 Hz, 2H), 1.43 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 150.6, 143.1, 137.7, 134.4, 130.7, 128.1, 127.9, 126.0, 125.1, 124.4, 123.3, 121.8, 108.8, 60.9, 40.6, 28.0, 14.7.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{18}H_{17}N_2O_2$: 293.1290; found : 293.1296.

5,6-Dihydropyrido[2',3':4,5]imidazo[2,1-*a*]isoquinoline (5la)



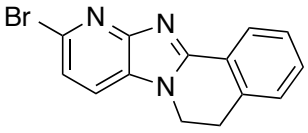
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a yellow powder (159 mg, 72%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, J = 4.7 Hz, 1H), 8.30 (m, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.45 (m, 2H), 7.37 (m, 1H), 7.25 (m, 1H), 4.53 (t, J = 6.8 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 147.5, 143.6, 136.4, 135.3, 131.1, 128.3, 127.8, 127.0, 126.2, 125.8, 118.6, 39.4, 28.0.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{14}H_{12}N_3$: 222.1031; found : 222.1042.

10-Bromo-5,6-dihydropyrido[2',3':4,5]imidazo[2,1-a]isoquinoline (5ma)



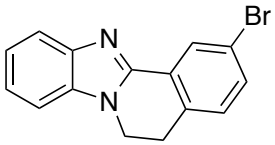
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a yellow powder (204 mg, 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 2.0 Hz, 1H), 8.09 (m, 1H), 8.00 (d, J = 2.0 Hz, 1H), 7.31 (m, 2H), 7.21 (m, 1H), 4.33 (t, J = 6.9 Hz, 2H), 3.19 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 146.1, 144.1, 137.3, 135.1, 131.2, 129.2, 128.9, 128.2, 127.7, 125.6, 113.8, 39.1, 28.0.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{14}H_{11}BrN_3$: 300.0136; found : 300.0142.

2-Bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ab)



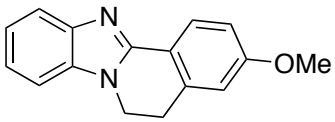
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a yellow powder (197 mg, 66%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, J = 1.7 Hz, 1H), 7.83(m, 1H), 7.50 (dd, J = 8.2, 1.7 Hz, 1H), 7.34 (m, 3H), 7.20 (d, J = 8.2 Hz, 1H), 4.34 (t, J = 6.9 Hz, 2H), 3.25 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 143.7, 134.6, 133.2, 132.9, 129.7, 128.7, 128.4, 123.1, 122.8, 121.6, 119.9, 109.3, 40.3, 27.7.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{15}H_{12}BrN_2$: 299.0184; found : 299.0199.

3-Methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ac)



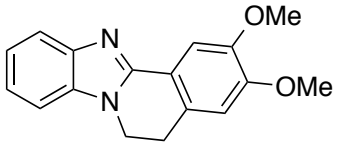
Purification of the crude mixture by silica gel column chromatography (EtOAc:CH_2Cl_2 1:1) afforded the product as a yellow powder (197 mg, 66%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7 Hz, 1H), 7.74-7.67 (m, 1H), 7.26-7.14 (m, 3H), 6.86 (dd, J = 8.7, 2.4 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 4.21(t, J = 6.9 Hz, 2H), 3.78 (s, 3H), 3.16 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 149.6, 144.1, 136.4, 134.8, 129.7, 127.6, 122.4, 119.6, 119.5, 113.8, 113.3, 109.0, 55.6, 40.5, 28.7.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{16}H_{15}N_2O$: 251.1184; found : 251.1193.

2,3-Dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ad)



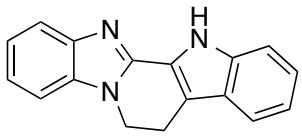
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a yellow powder (168 mg, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (m, 1H), 7.71(s, 1H), 7.27 (m, 1H), 7.19 (m, 2H), 6.72 (s, 1H), 4.23 (t, J = 6.9 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.16 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 149.3, 148.7, 143.8, 134.7, 127.5, 122.4, 122.3, 119.5, 119.2, 110.9, 109.0, 108.2, 56.4, 56.1, 40.6, 27.9.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{17}H_{17}N_2O_2$: 281.1290; found : 281.1279.

7,12-Dihydro-6*H*-benzo[4',5']imidazo[1',2':1,2]pyrido[3,4-*b*]indole (5ae)



Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a pale yellow powder (150 mg, 58%).

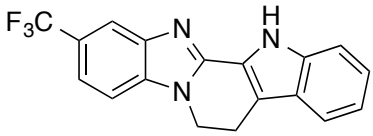
^{1}H NMR (300 MHz, $CDCl_3$) δ 12.72 (broad s, 1H), 7.89-7.86 (m, 1H), 7.76-7.73 (m, 1H), 7.56-7.23 (m, 6H),

4.60 (t, J = 6.9 Hz, 2H), 3.57 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 143.4, 138.4, 135.0, 126.2, 125.1, 124.1, 123.1, 122.7, 120.3, 119.4, 119.3, 113.9, 112.9, 109.4, 42.1, 20.9.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{17}H_{14}N_3$: 260.1188; found : 260.1193

2-(Trifluoromethyl)-7,12-dihydro-6*H*-benzo[4',5']imidazo[1',2':1,2]pyrido[3,4-*b*]indole (5af)



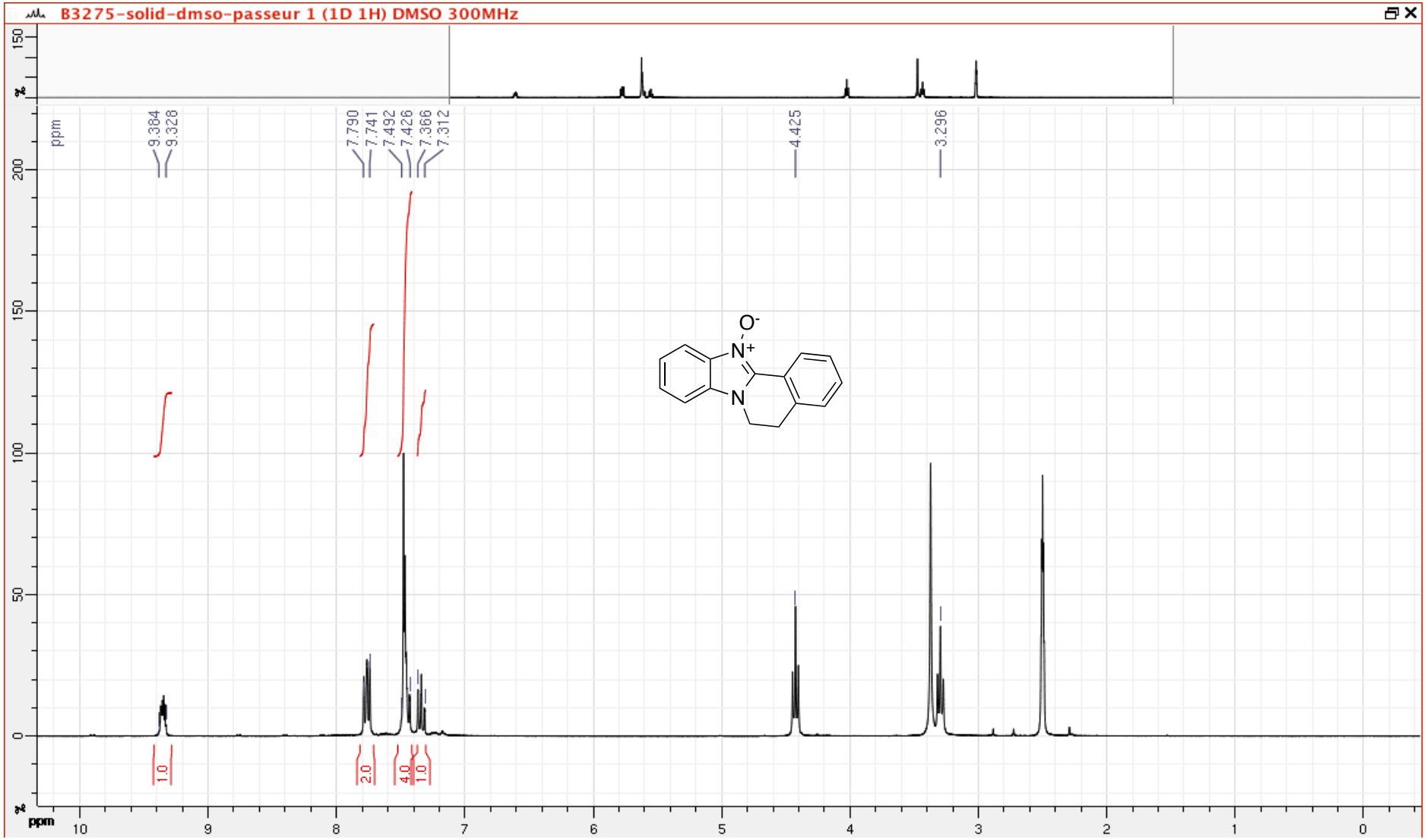
Purification of the crude mixture by silica gel column chromatography (EtOAc:heptane 1:1) afforded the product as a pale yellow powder (150 mg, 58%).

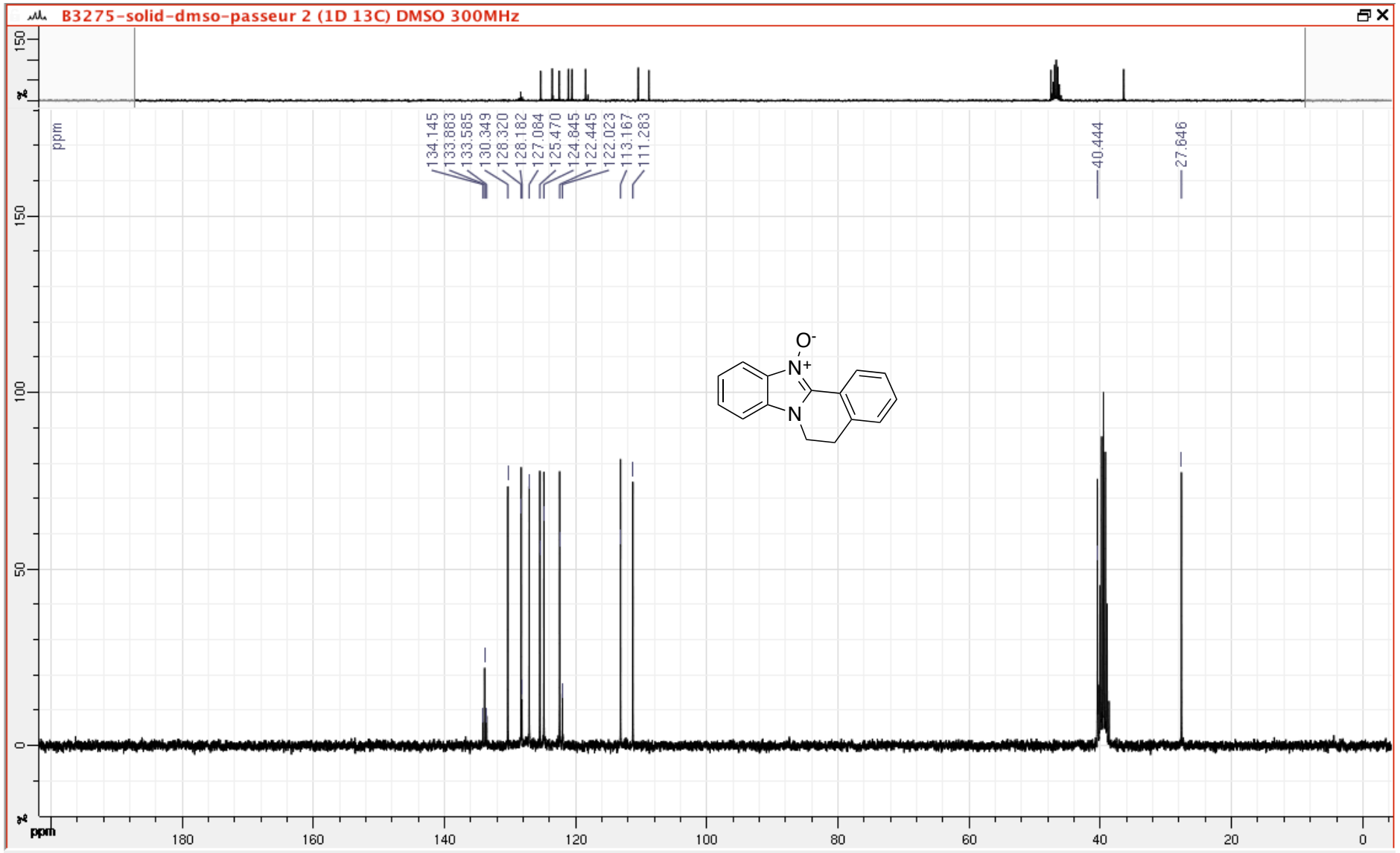
^{1}H NMR (300 MHz, $CDCl_3$) δ 12.23 (broad s, 1H), 8.03 (broad s, 1H), 7.68-7.49 (m, 3H), 7.31-7.17 (m, 3H), 4.53 (t, J = 6.9 Hz, 2H), 3.50 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 143.1, 138.5, 137.1, 126.1, 124.8, 124.7 (q, J = 273 Hz) 124.4 (q, J = 32 Hz), 120.7, 120.1 (q, J = 3.7 Hz), 119.6, 116.7 q, J = 4.0 Hz, 114.9, 112.7, 109.6, 42.4, 20.8.

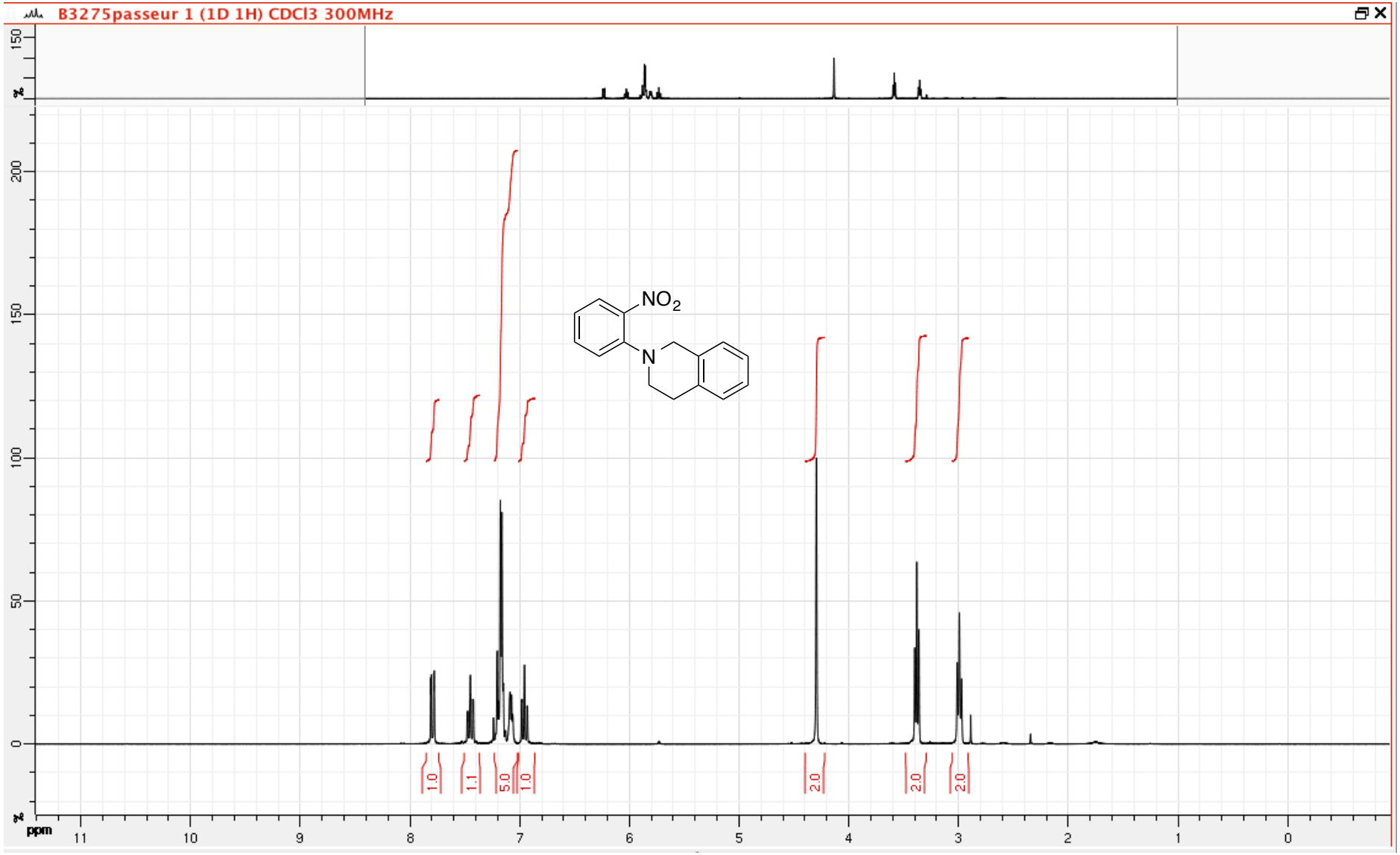
HRMS-ESI+: m/z [M + H]+ calcd for $C_{18}H_{13}F_3N_3$: 328.1062; found : 328.1073.

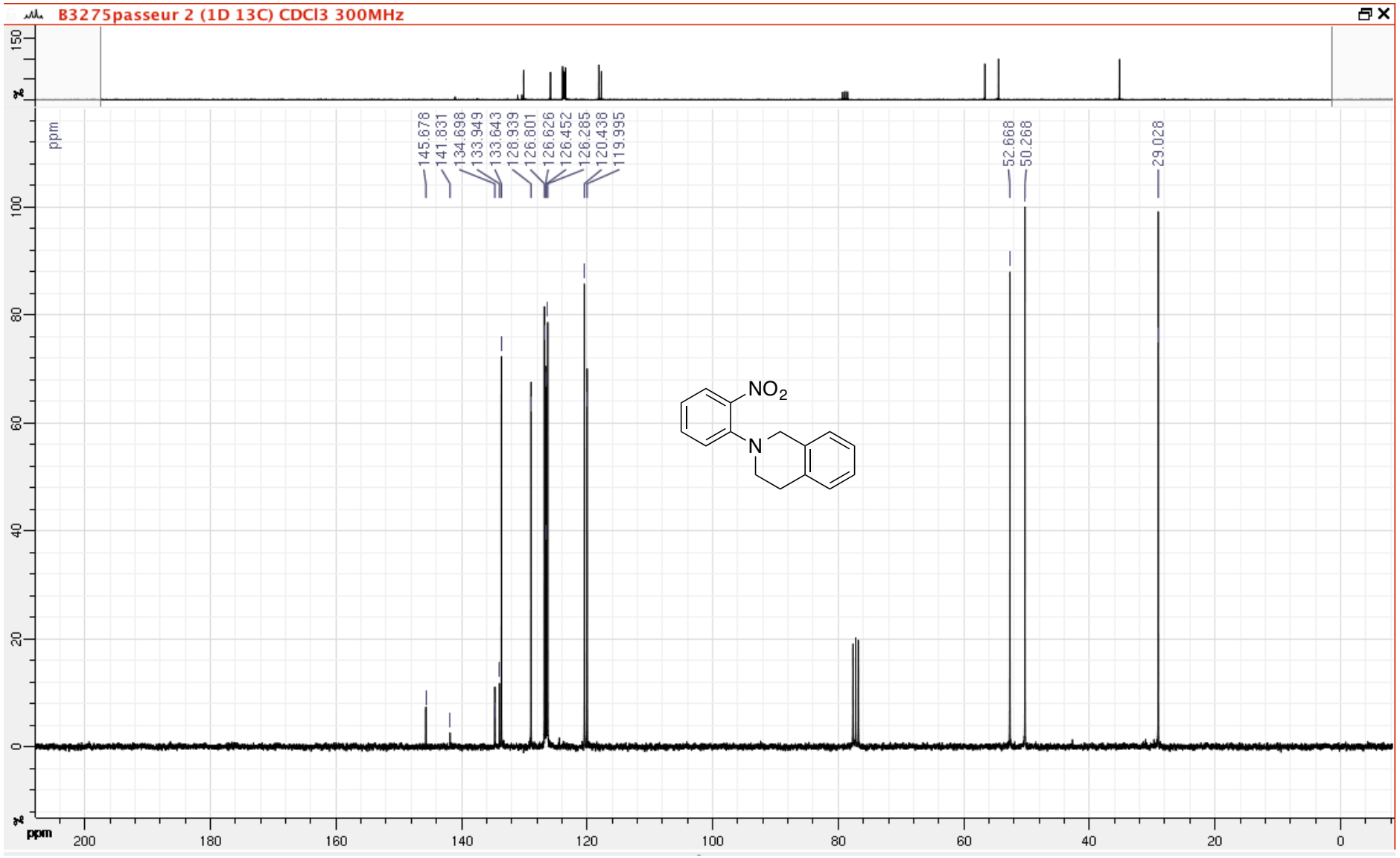
5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline 12-oxide (4aa)



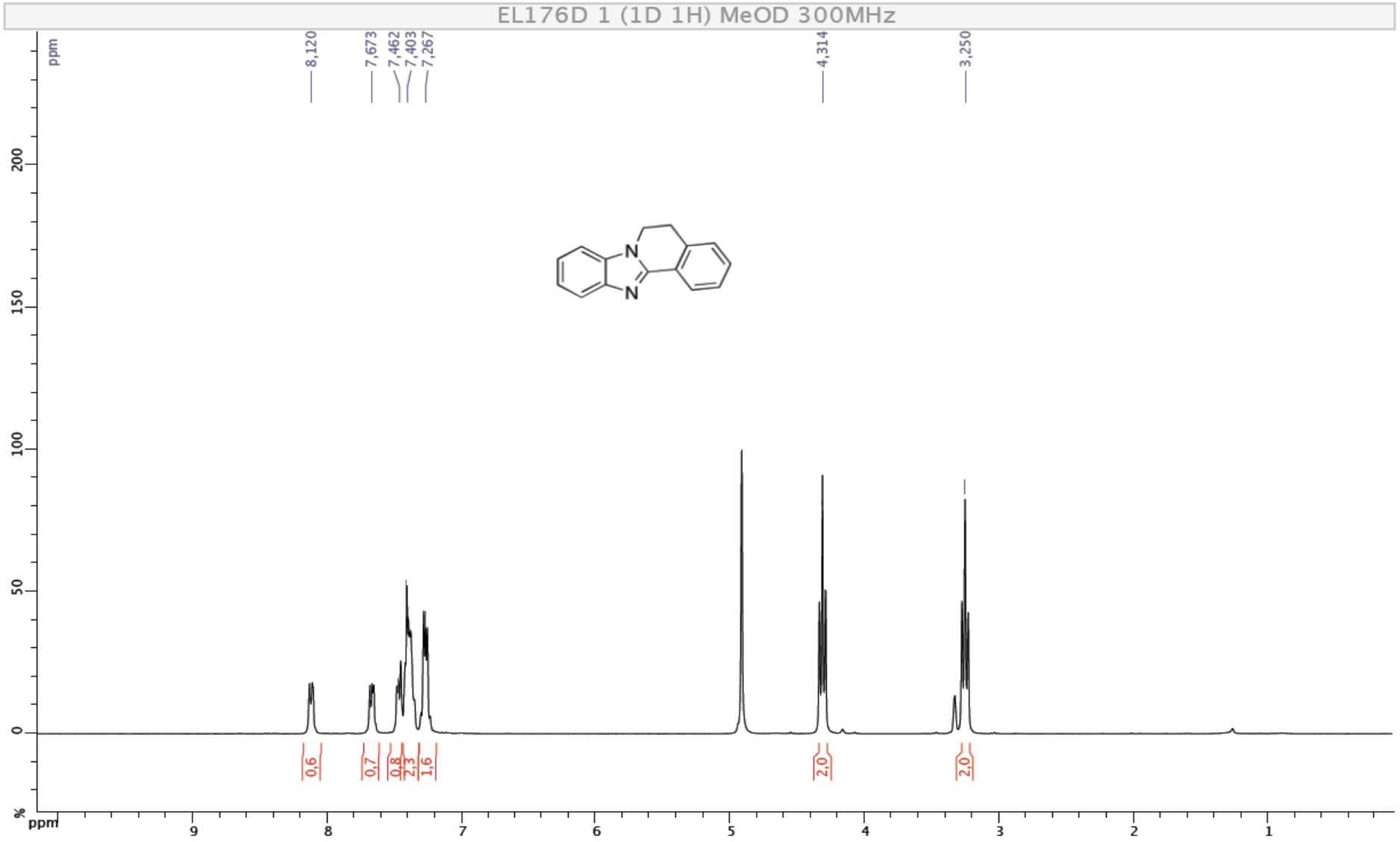

B3275-solid-dmso-passeur 2 (1D 13C) DMSO 300MHz
ppm
134.145
133.883
133.585
130.349
128.320
128.182
127.084
125.470
124.845
122.445
122.023
113.167
111.283
40.444
27.646
O-
N+
N
150
100
50
0
180
160
140
120
100
80
60
40
20
0

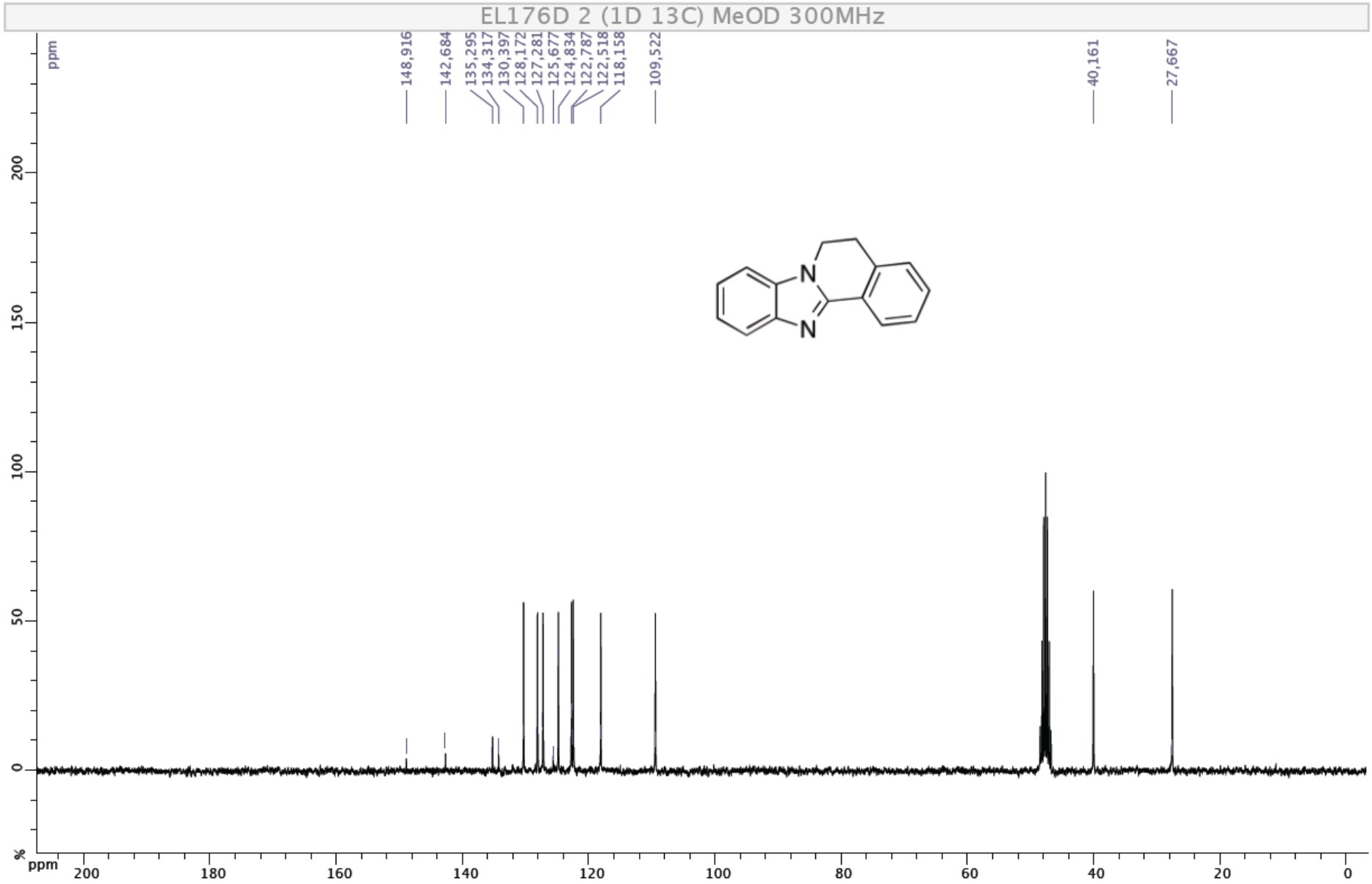
2-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (3aa)



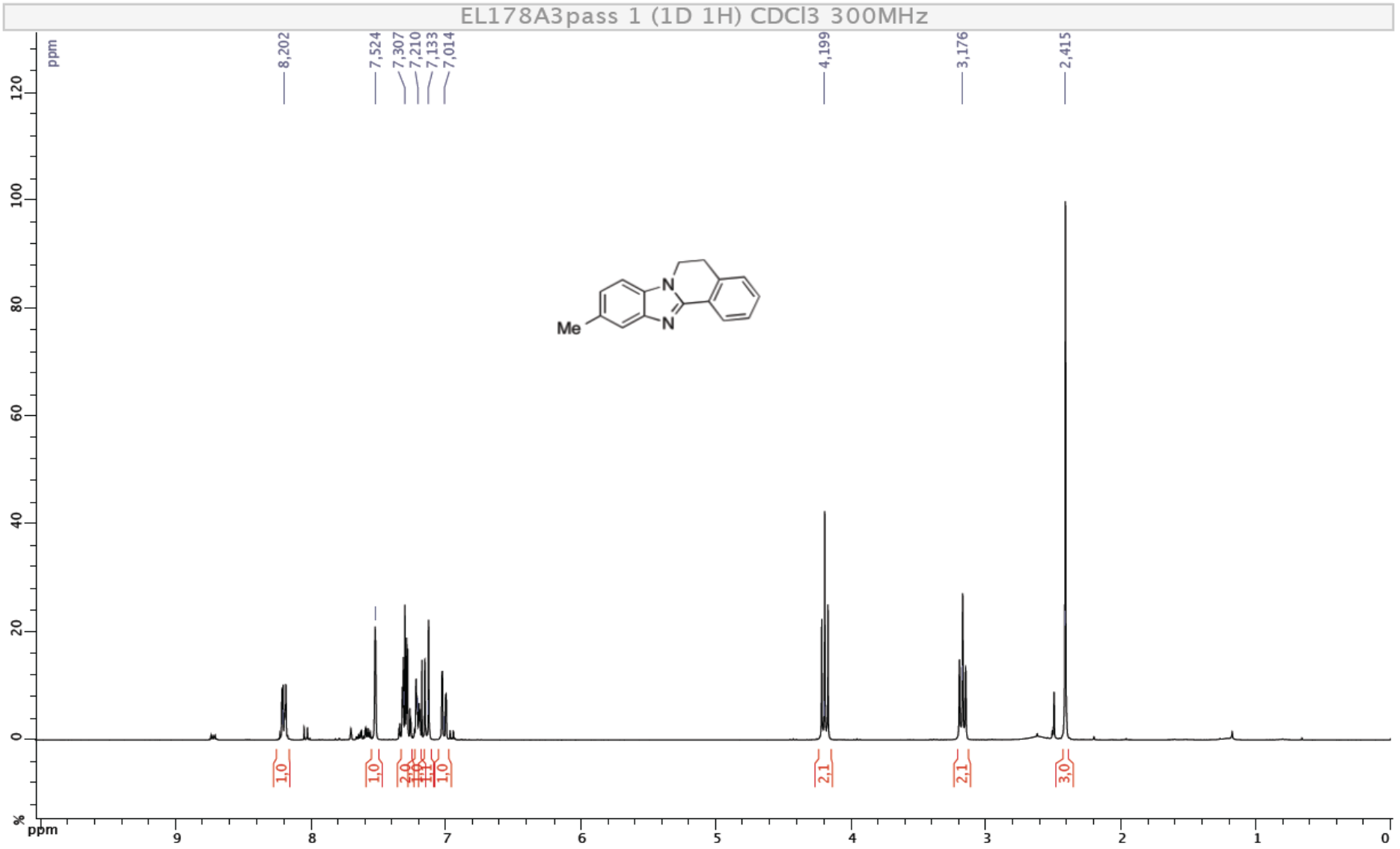

B3275passeur 2 (1D 13C) CDCl3 300MHz
ppm
145.678
141.831
134.698
133.949
133.643
128.939
126.801
126.626
126.452
126.285
120.438
119.995
52.668
50.268
29.028
NO2
N

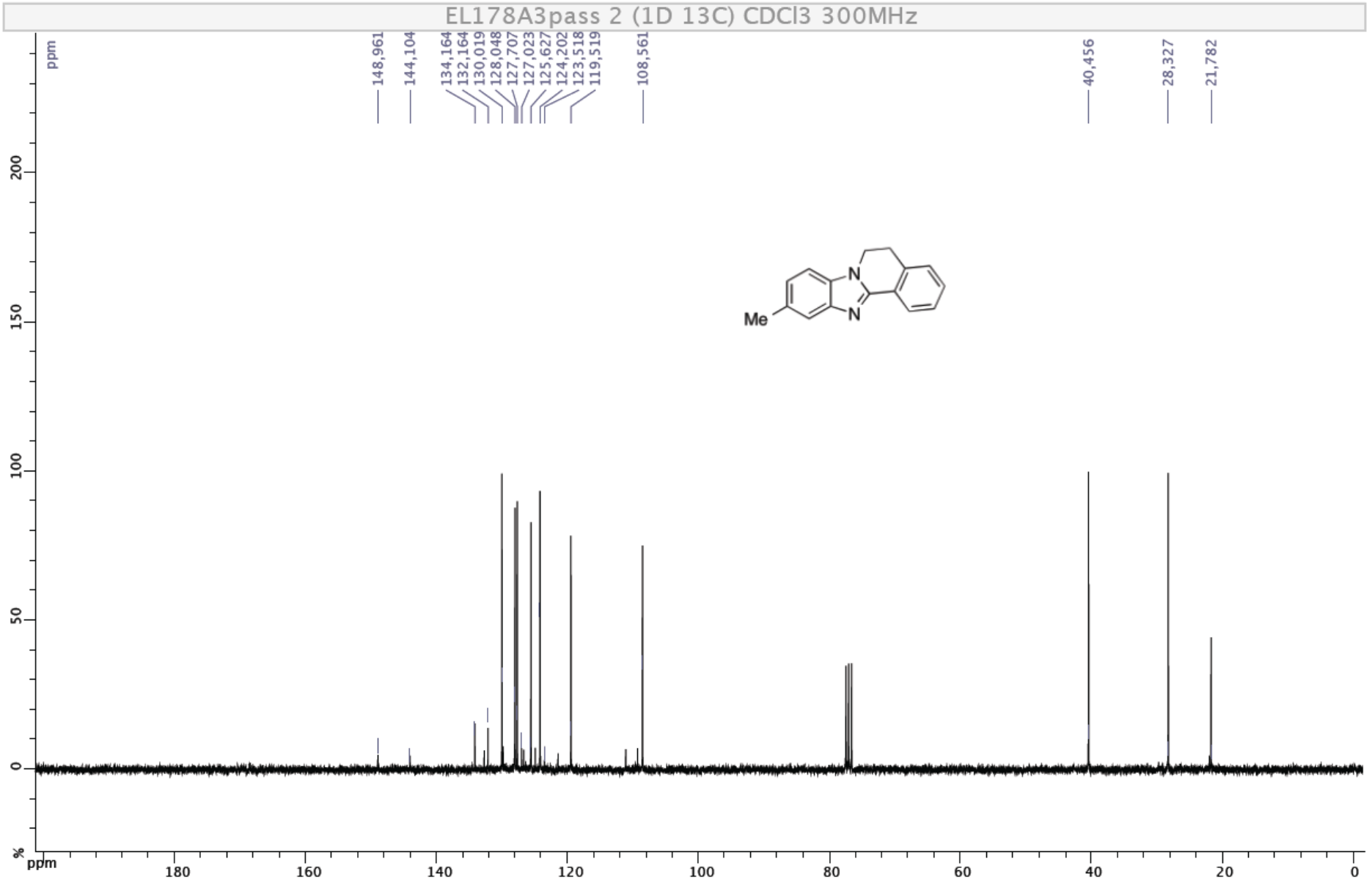
5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5aa)



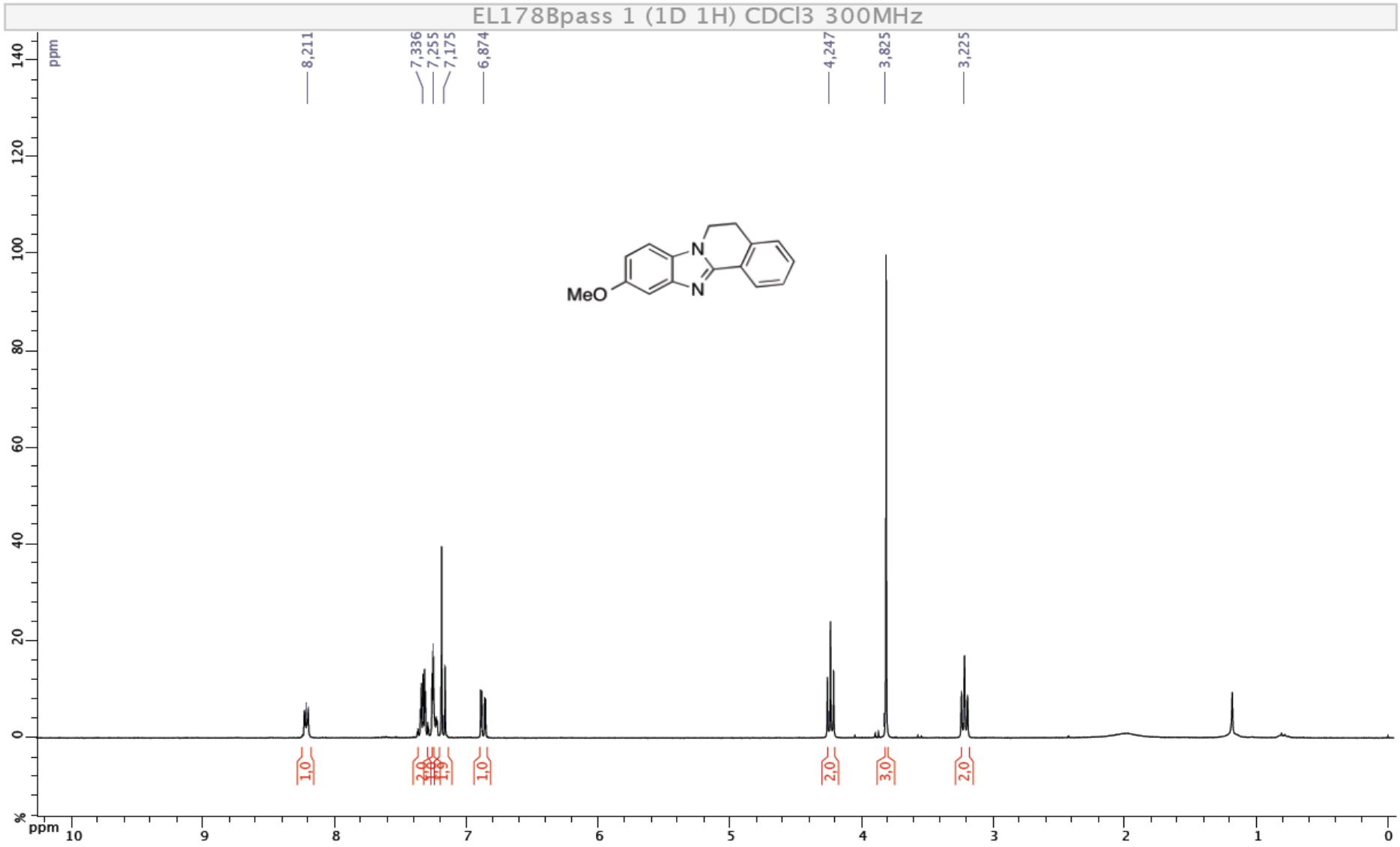

EL176D 2 (1D 13C) MeOD 300MHz
ppm
148,916
142,684
135,295
134,317
130,397
128,172
127,281
125,677
124,834
122,787
122,518
118,158
109,522
40,161
27,667
N
N
200
150
100
50
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0

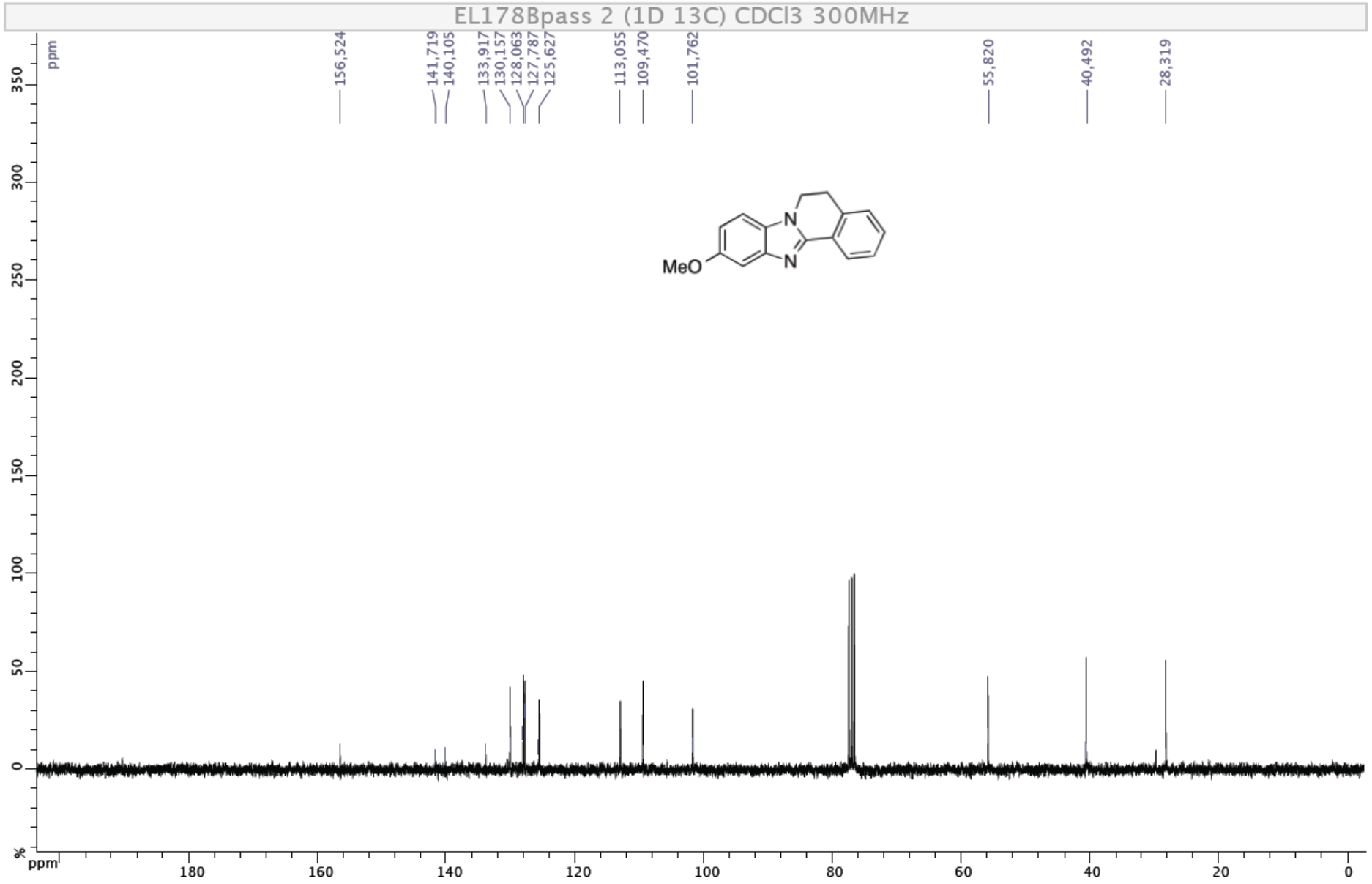
10-Methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ba)



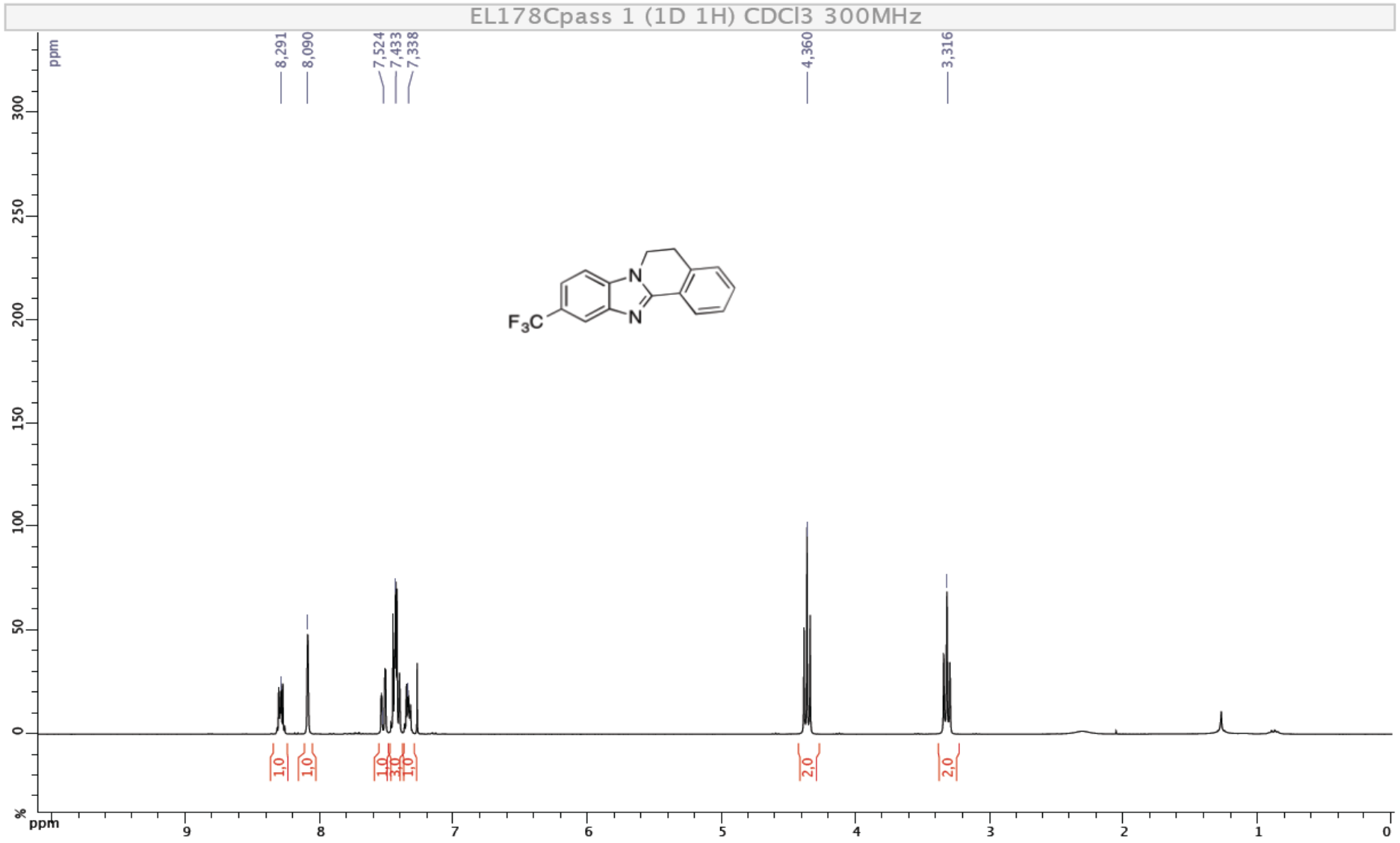

EL178A3pass 2 (1D 13C) CDCl3 300MHz
ppm
148,961
144,104
134,164
132,164
130,019
128,048
127,707
127,023
125,627
124,202
123,518
119,519
108,561
40,456
28,327
21,782
Me
N
N
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

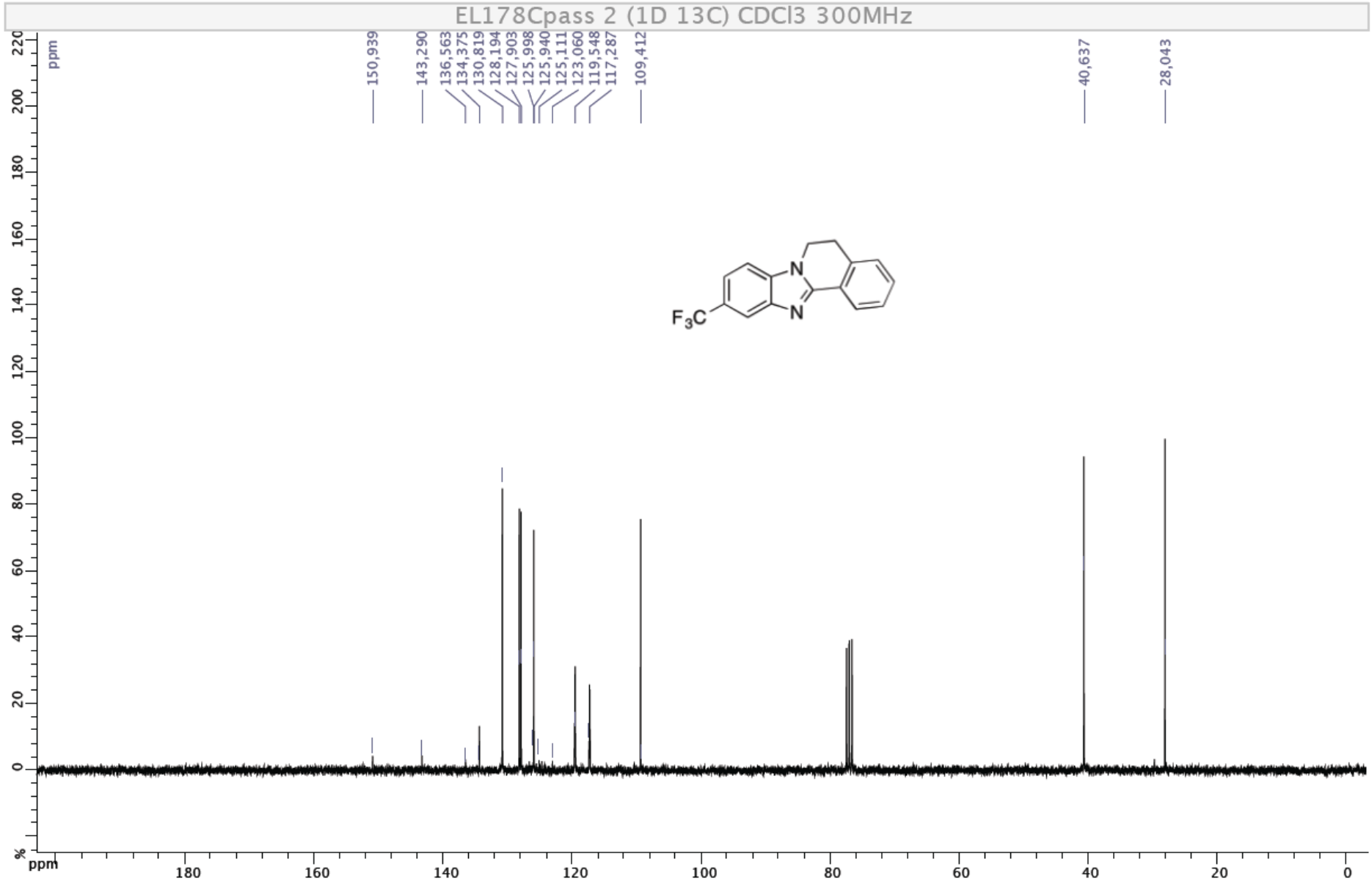
10-Methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ca)



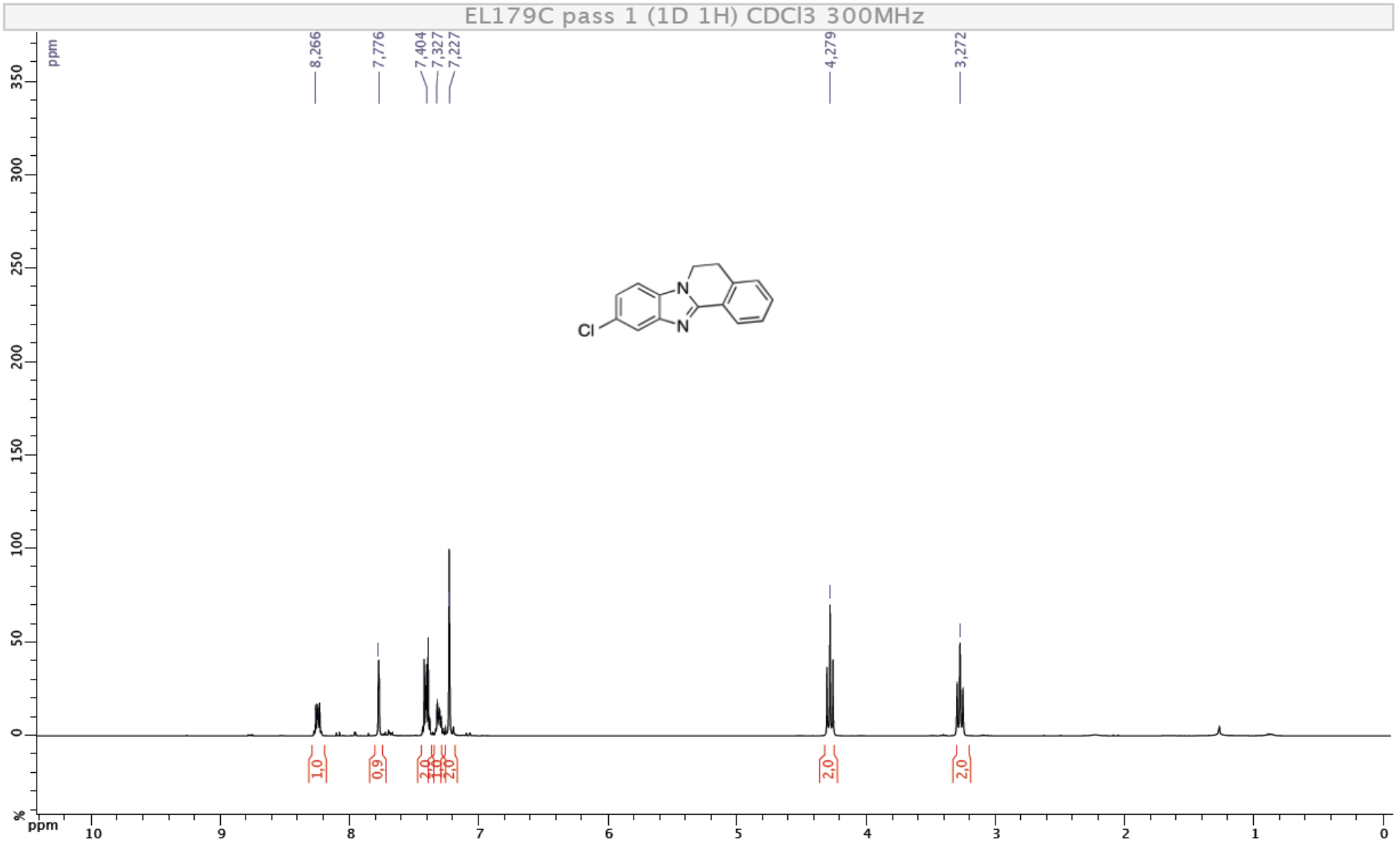

EL178Bpass 2 (1D 13C) CDCl3 300MHz
ppm
156,524
141,719
140,105
133,917
130,157
128,063
127,787
125,627
113,055
109,470
101,762
55,820
40,492
28,319
MeO
N
N
350
300
250
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

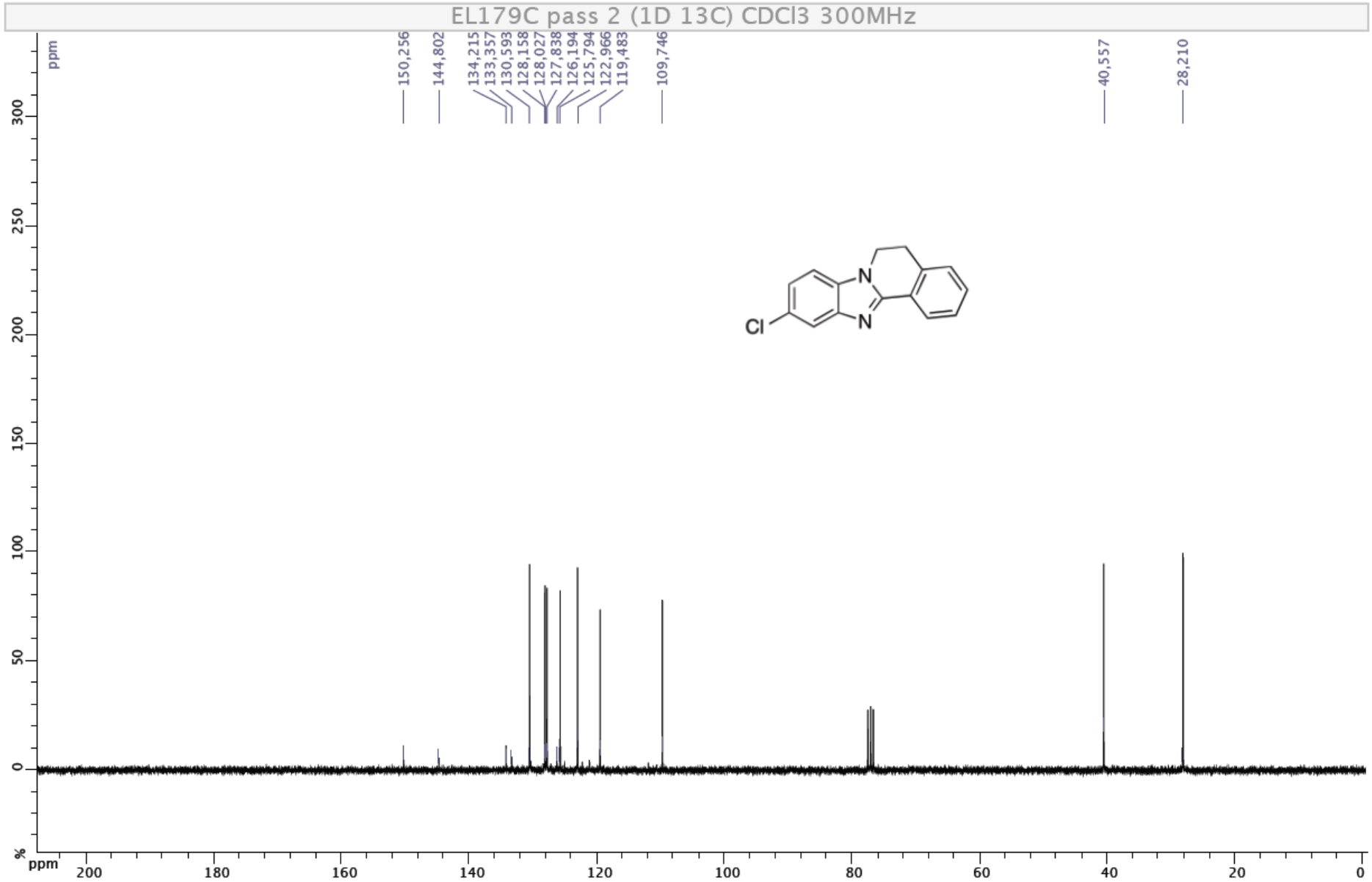
10-(Trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5da)



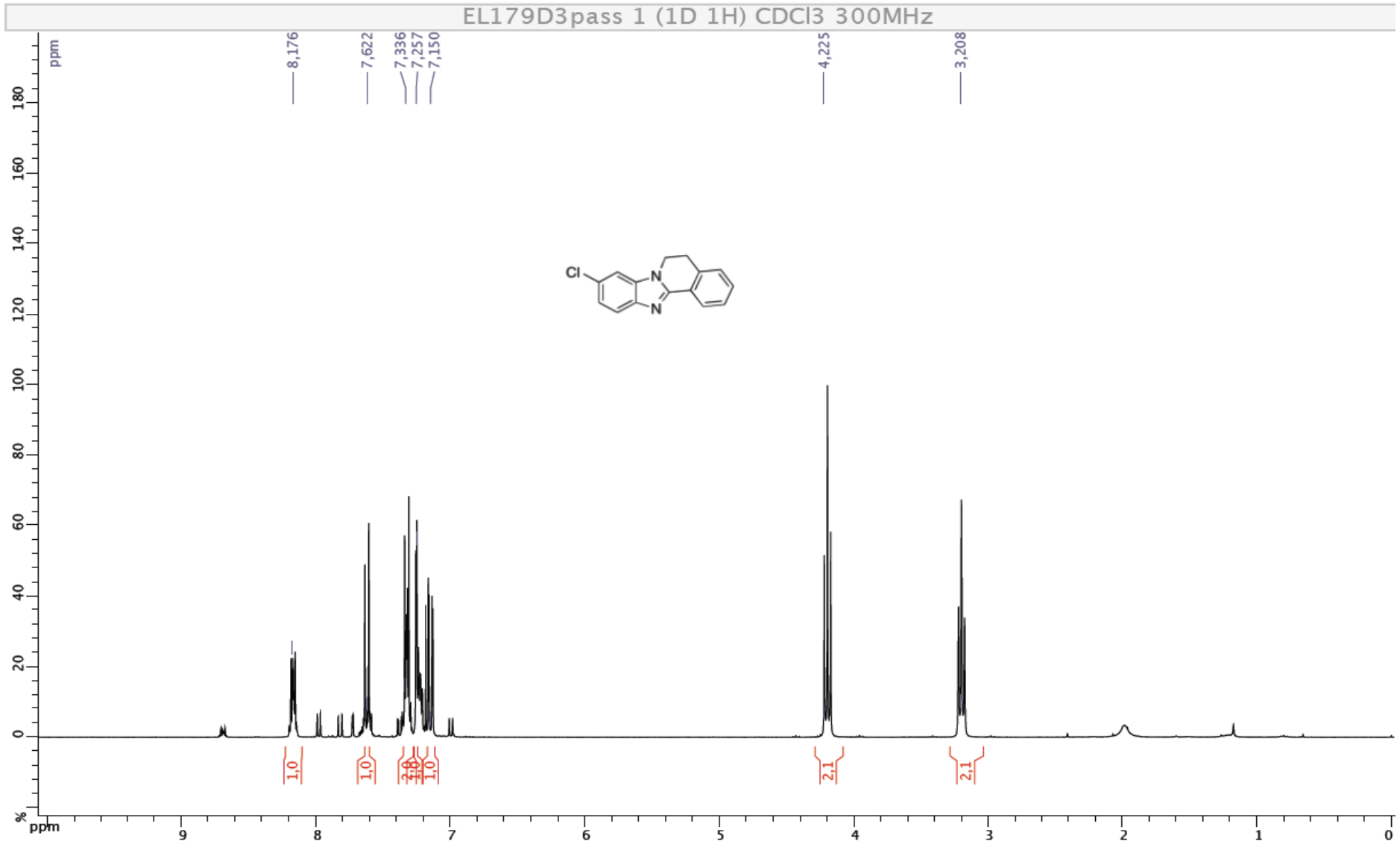

EL178Cpass 2 (1D 13C) CDCl3 300MHz
ppm
150,939
143,290
136,563
134,375
130,819
128,194
127,903
125,998
125,940
125,111
123,060
119,548
117,287
109,412
40,637
28,043
F3C
N
N
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

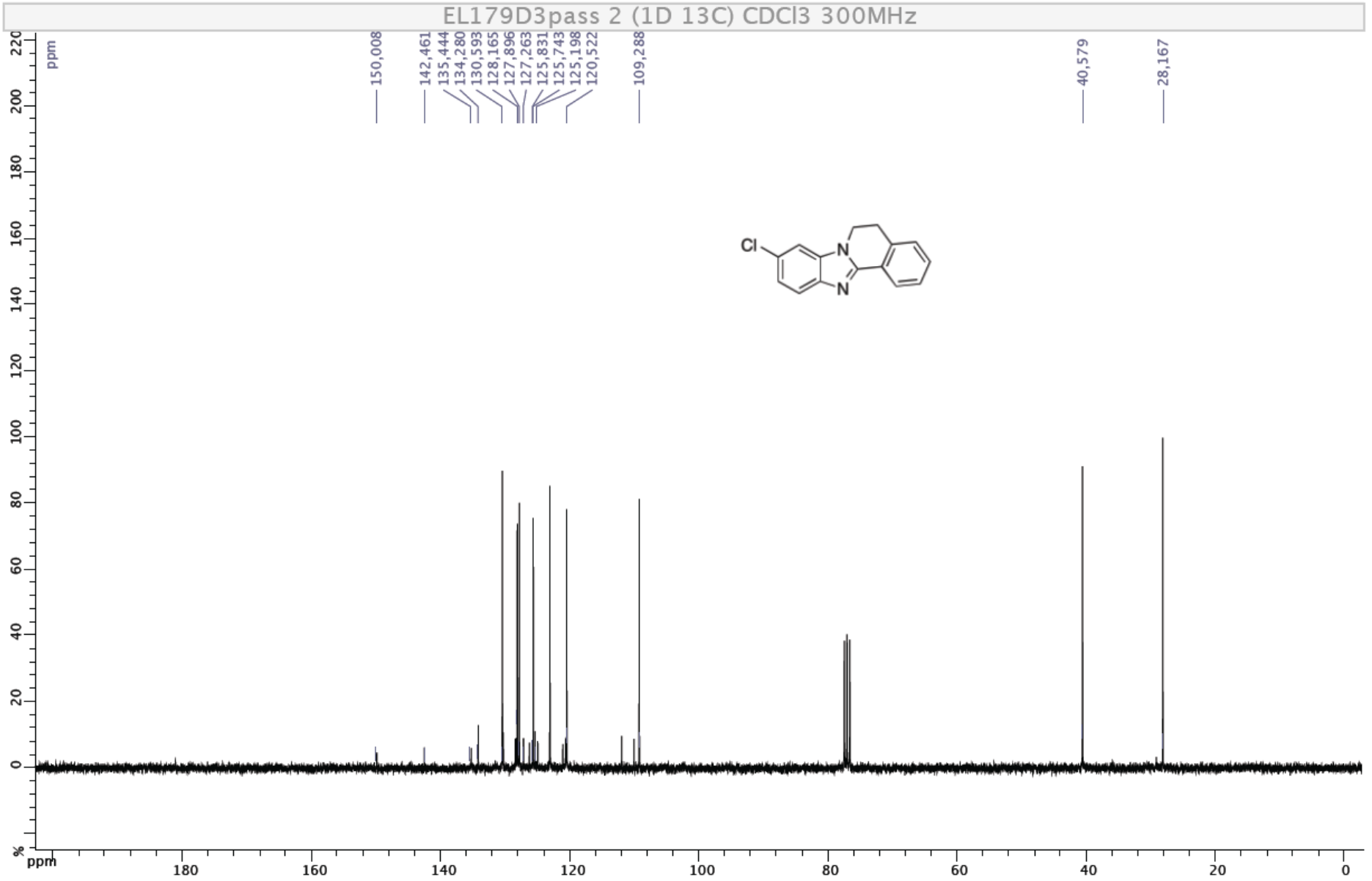
10-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ea)



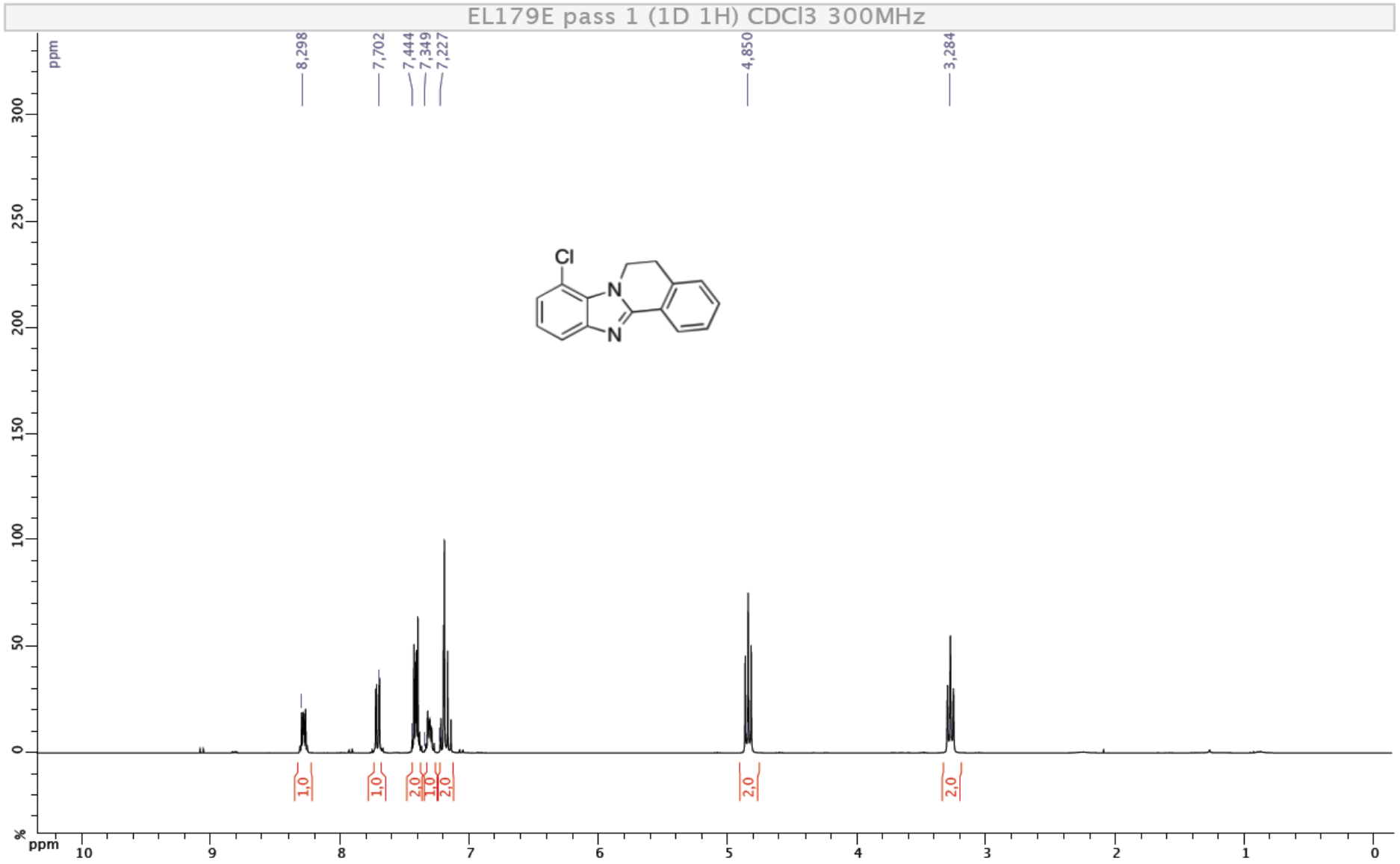

EL179C pass 2 (1D 13C) CDCl3 300MHz
ppm
150,256
144,802
134,215
133,357
130,593
128,158
128,027
127,838
126,194
125,794
122,966
119,483
109,746
40,557
28,210
Cl
N
N
300
250
200
150
100
50
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0

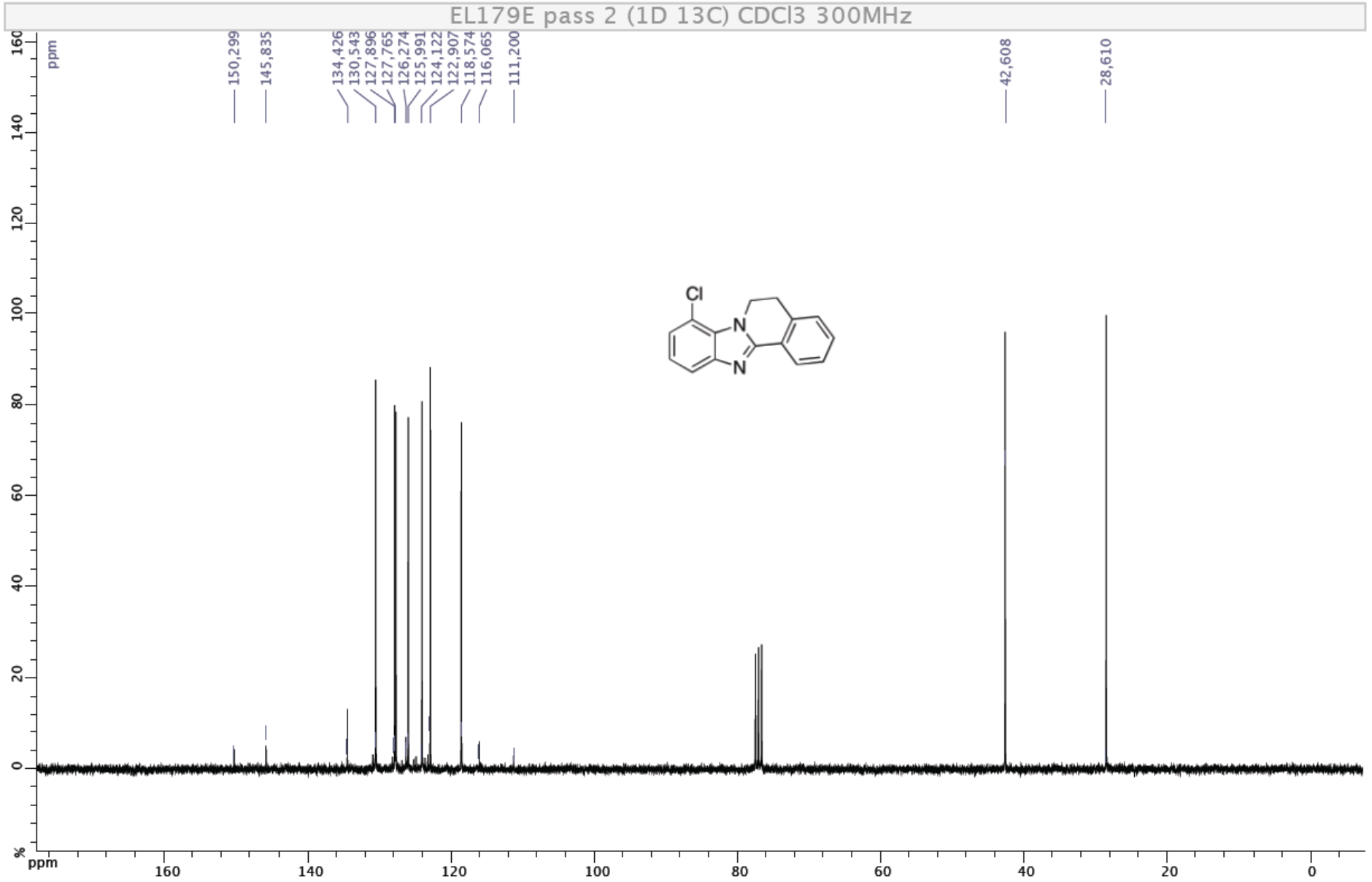
9-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5fa)



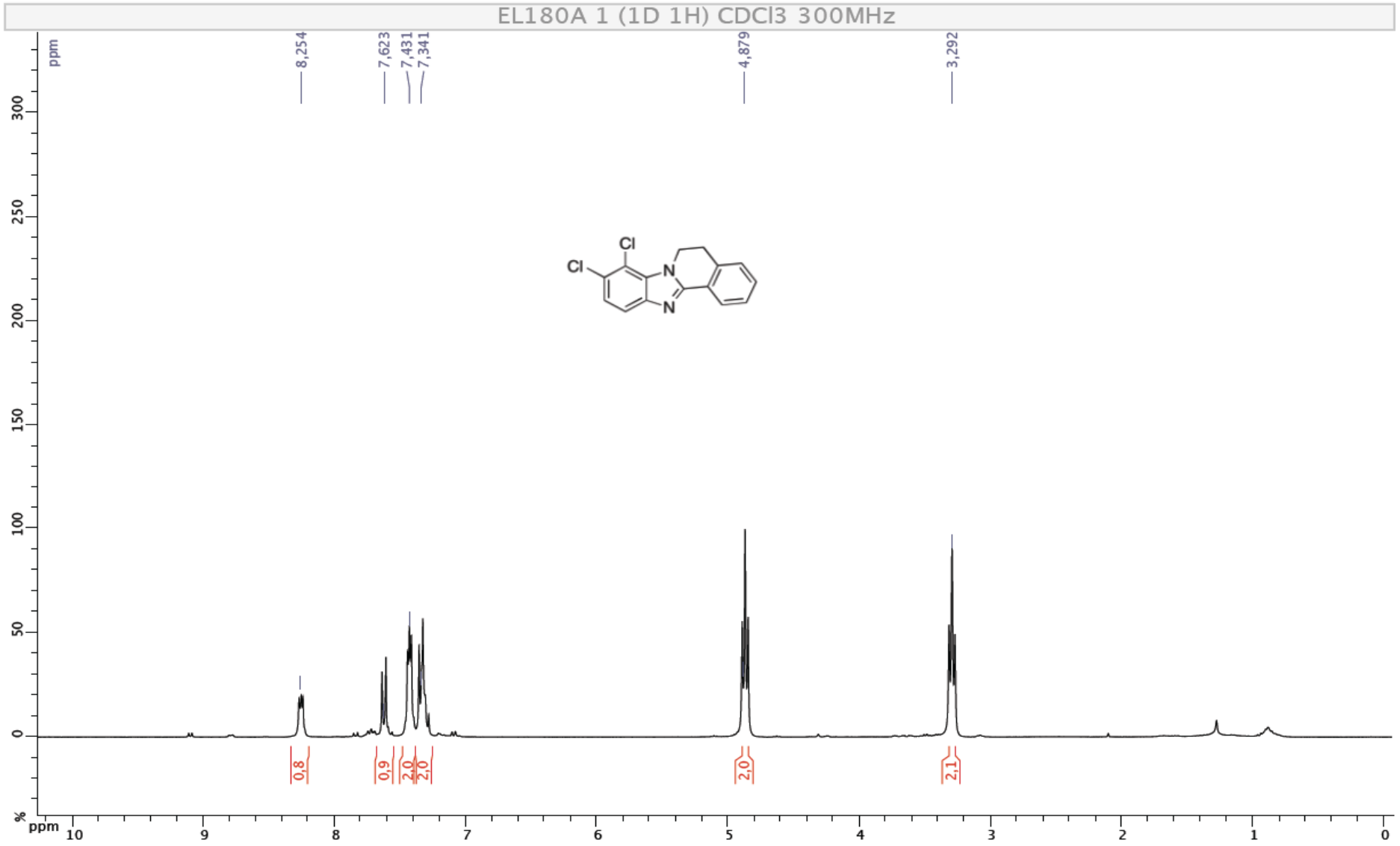

EL179D3pass 2 (1D 13C) CDCl3 300MHz
ppm
150,008
142,461
135,444
134,280
130,593
128,165
127,896
127,263
125,831
125,743
125,198
120,522
109,288
40,579
28,167
Cl
N
N
220
200
180
160
140
120
100
80
60
40
20
0
%
ppm
180
160
140
120
100
80
60
40
20
0

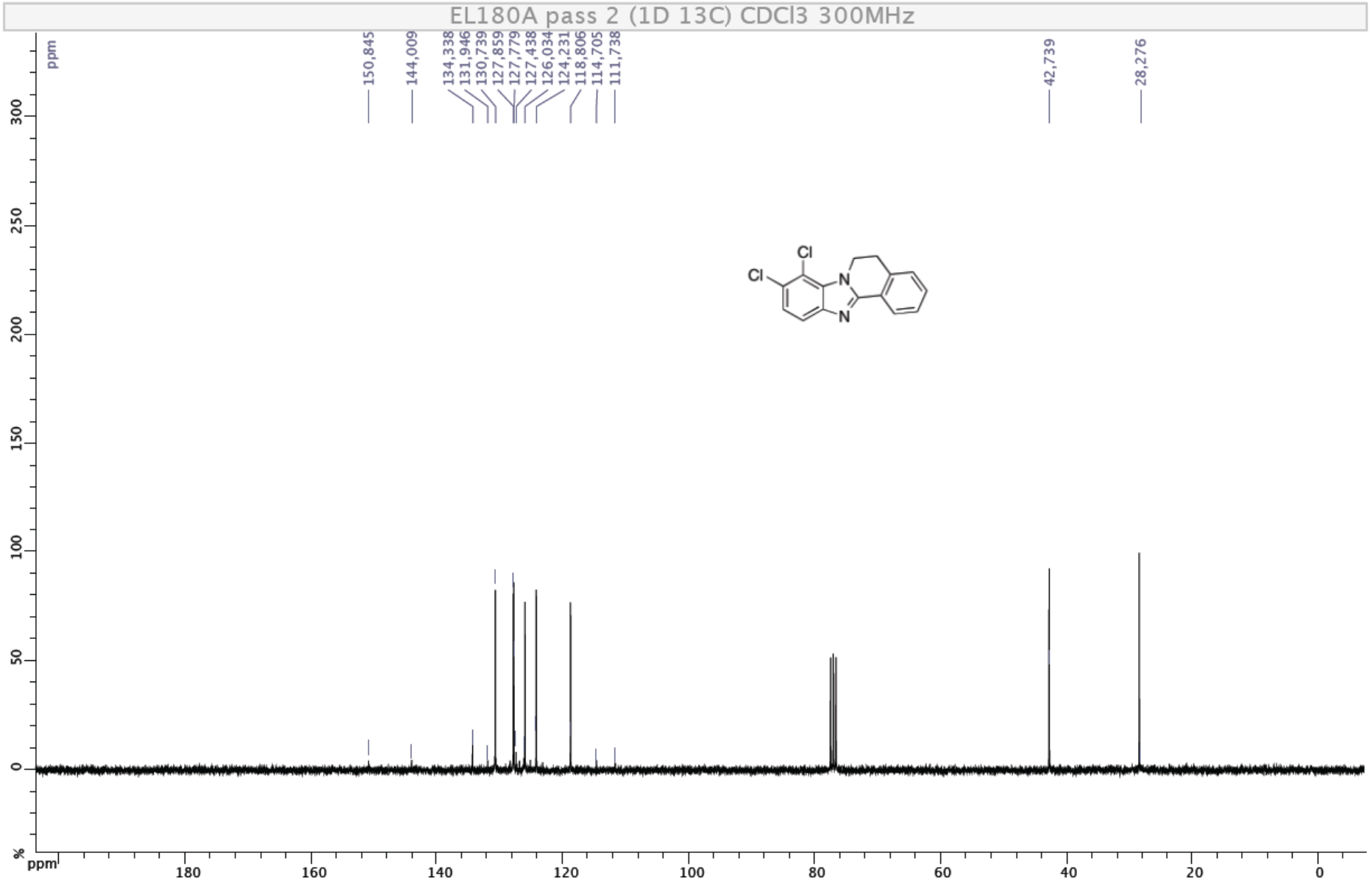
8-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ga)



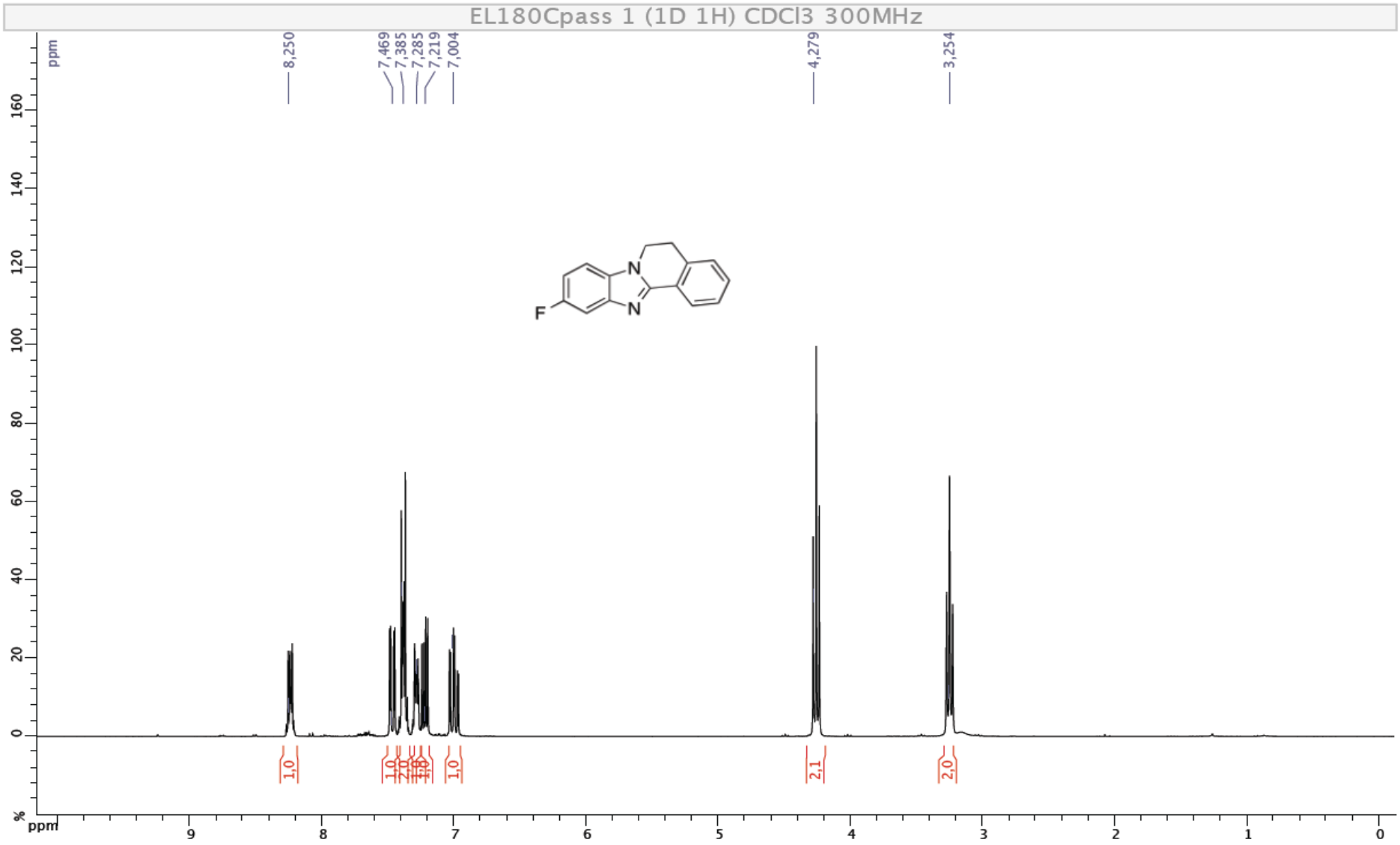

EL179E pass 2 (1D 13C) CDCl3 300MHz
ppm
150,299
145,835
134,426
130,543
127,896
127,765
126,274
125,991
124,122
122,907
118,574
116,065
111,200
42,608
28,610
Cl
N
N
%
ppm
160
140
120
100
80
60
40
20
0

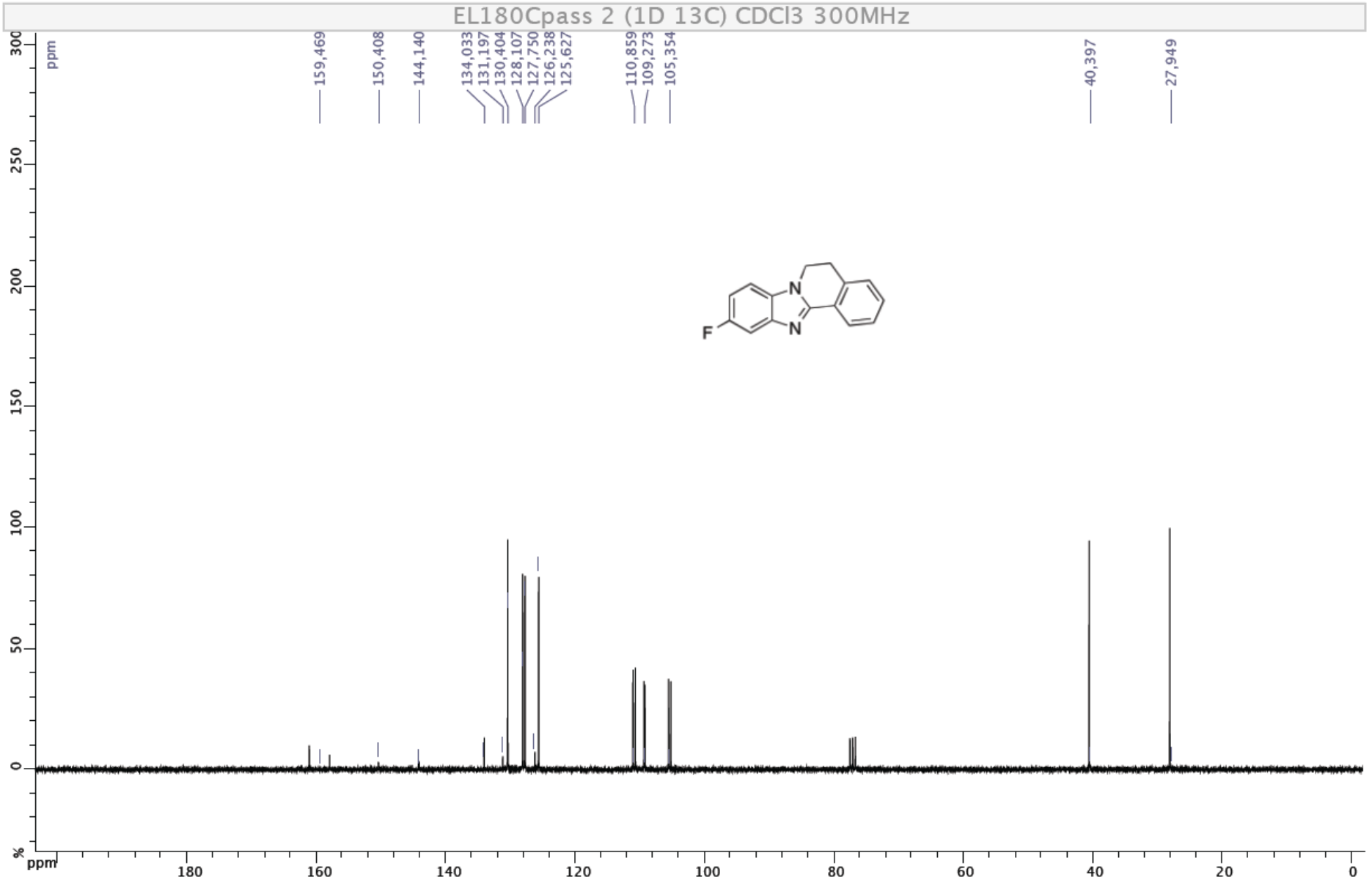
8,9-Dichloro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ha)



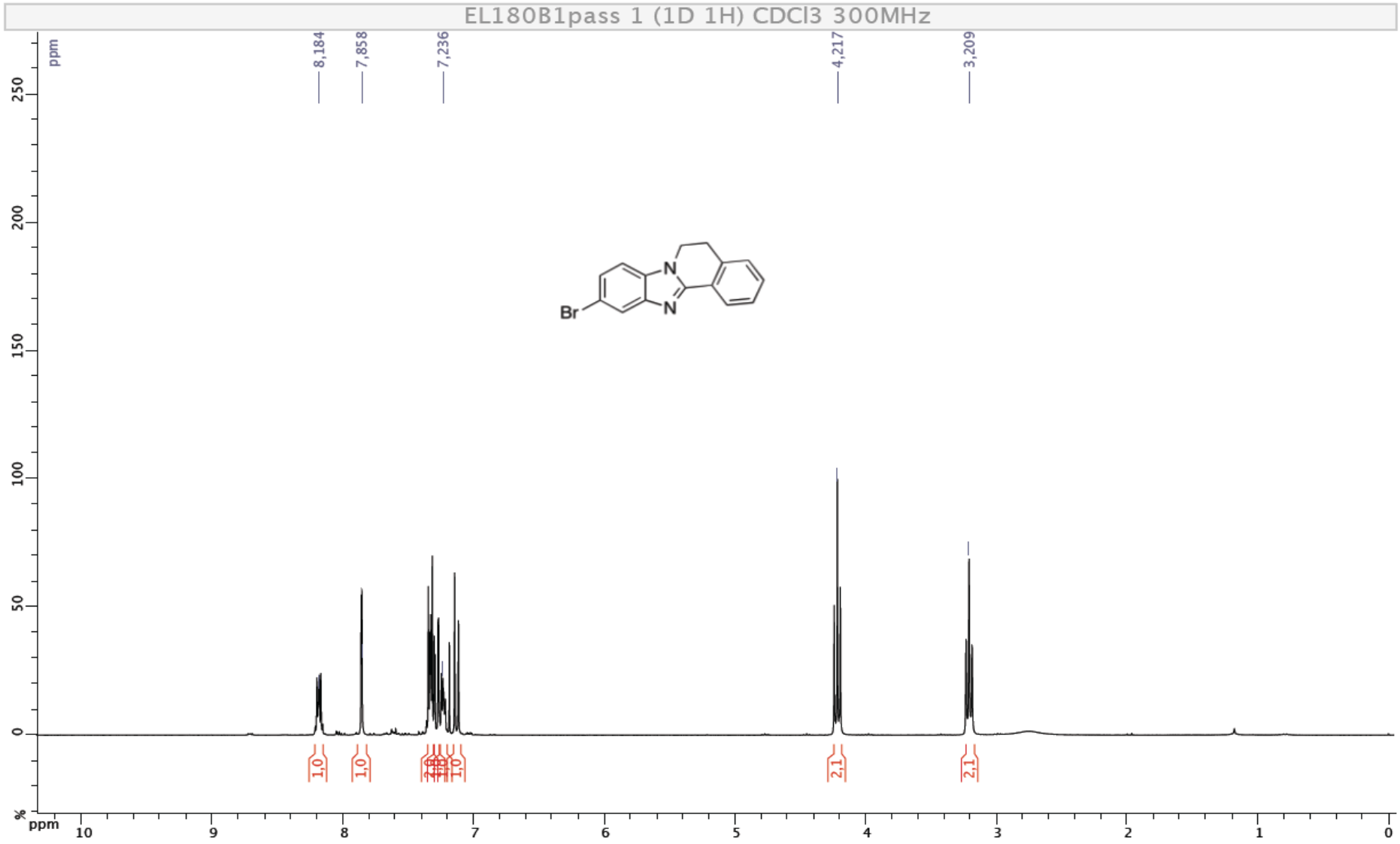

EL180A pass 2 (1D 13C) CDCl3 300MHz
ppm
150,845
144,009
134,338
131,946
130,739
127,859
127,779
127,438
126,034
124,231
118,806
114,705
111,738
42,739
28,276
Cl
Cl
N
N
300
250
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

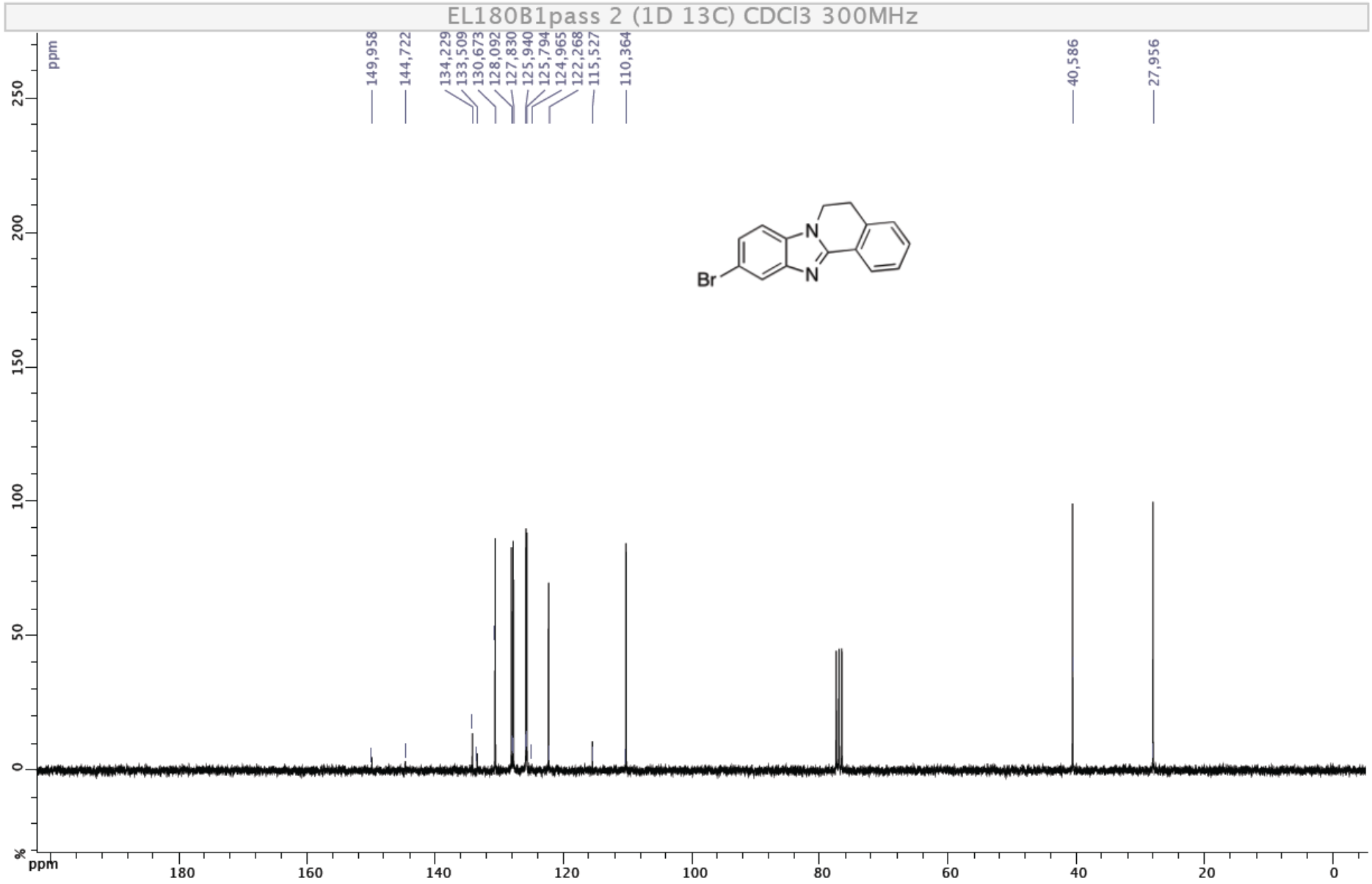
10-Fluoro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ia)



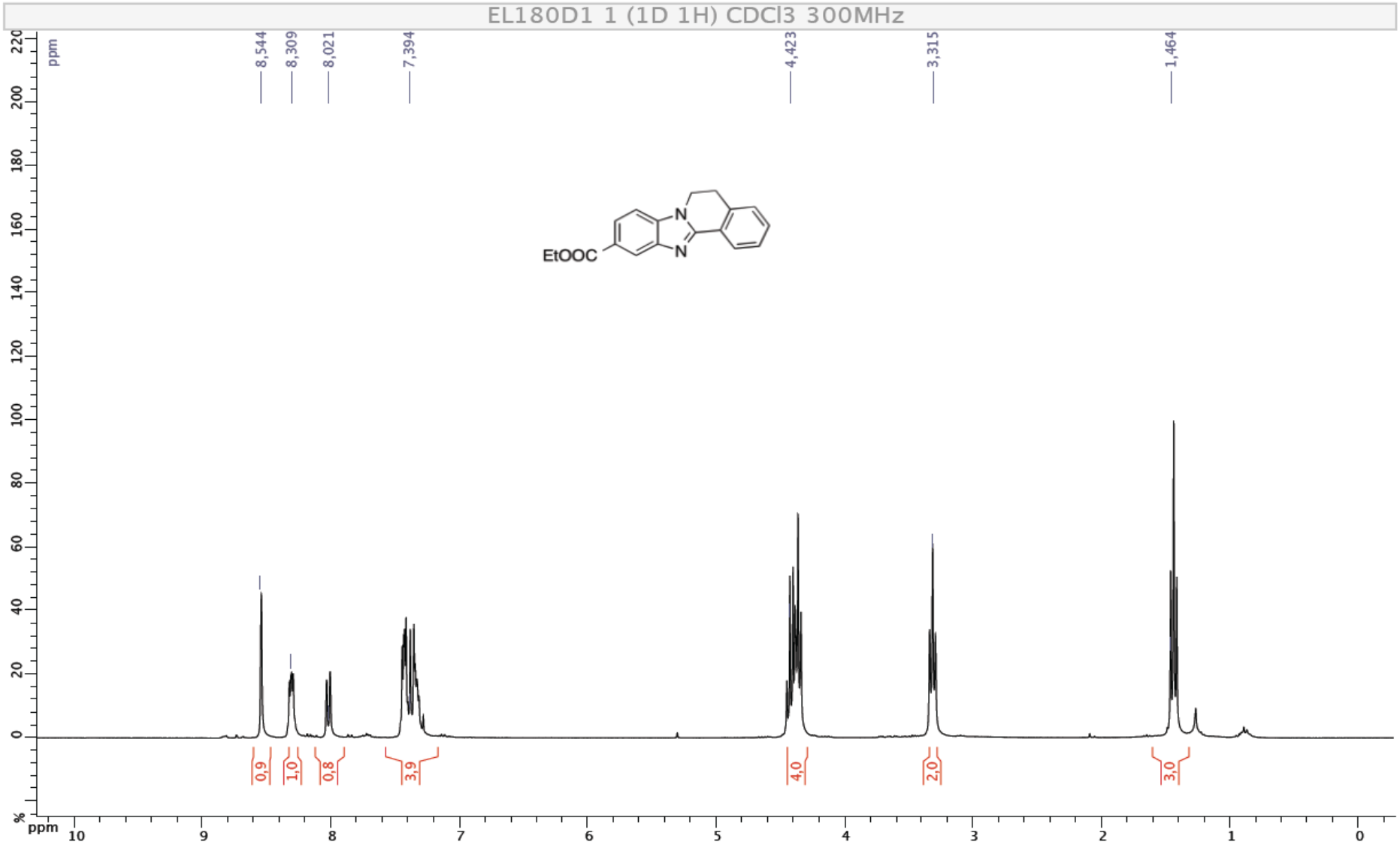

EL180Cpass 2 (1D 13C) CDCl3 300MHz
ppm
159,469
150,408
144,140
134,033
131,197
130,404
128,107
127,750
126,238
125,627
110,859
109,273
105,354
40,397
27,949
N
N
F
300
250
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

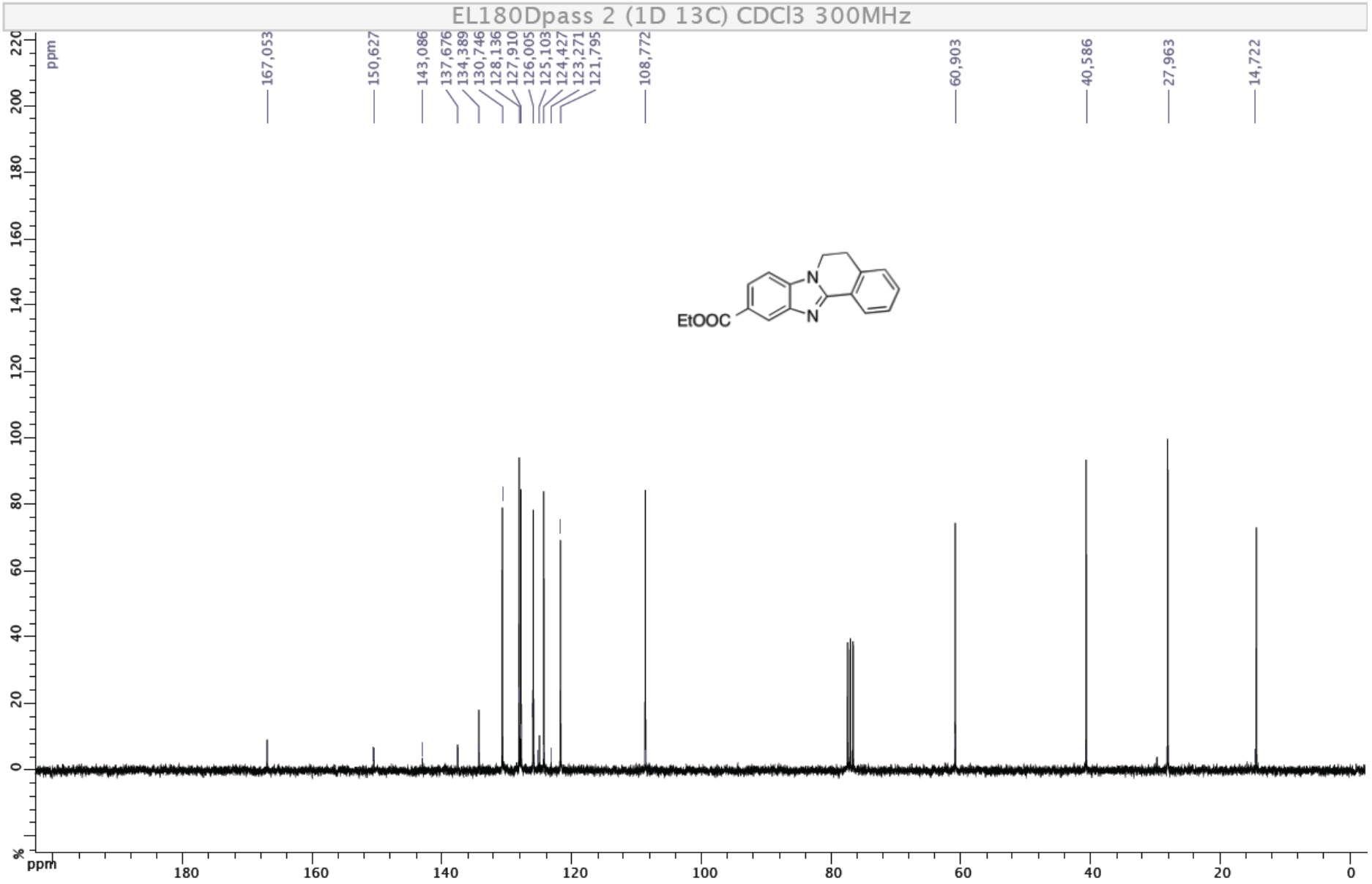
10-Bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ja)



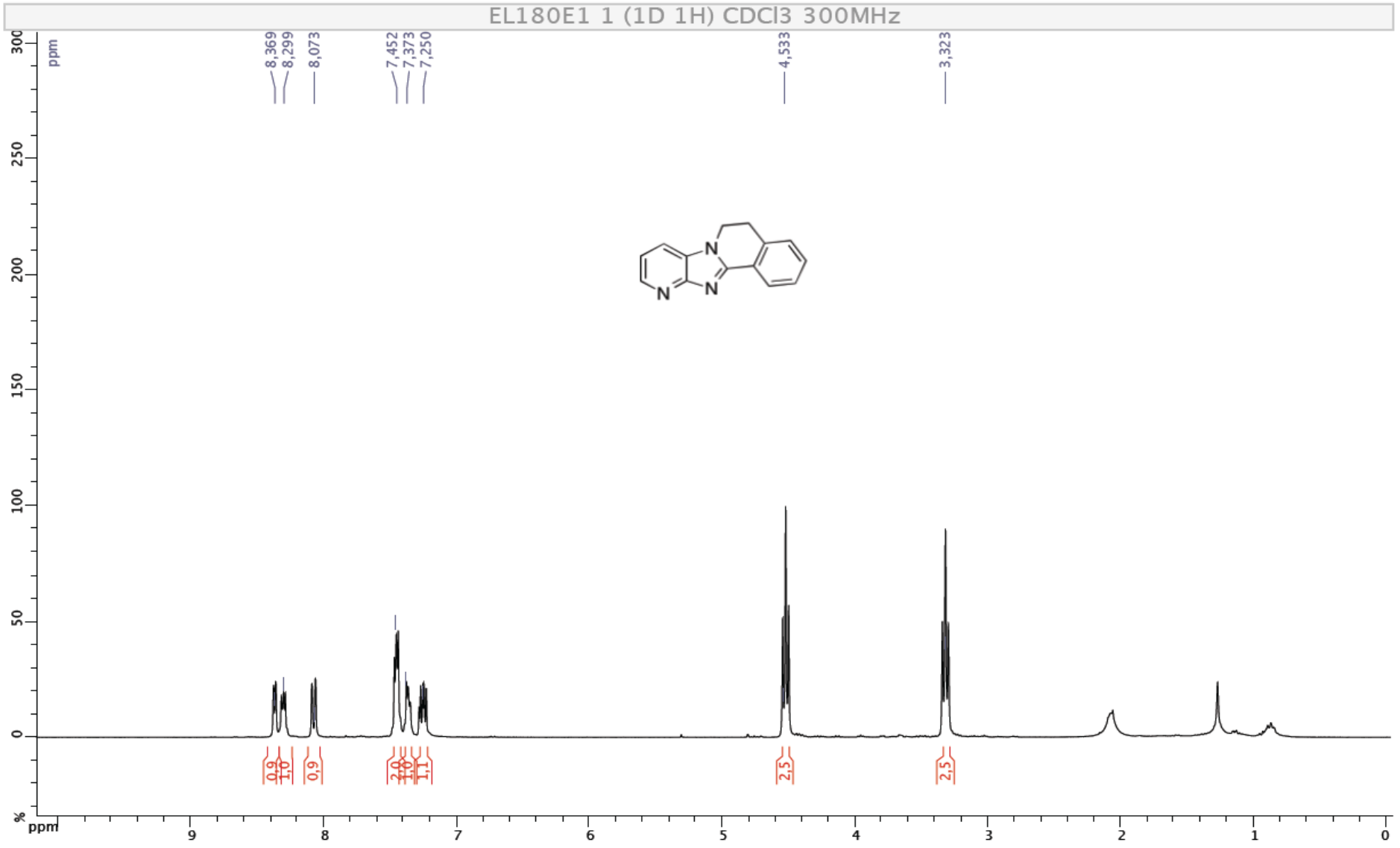

EL180B1pass 2 (1D 13C) CDCl3 300MHz
ppm
149,958
144,722
134,229
133,509
130,673
128,092
127,830
125,940
125,794
124,965
122,268
115,527
110,364
40,586
27,956
Br
N
N
250
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

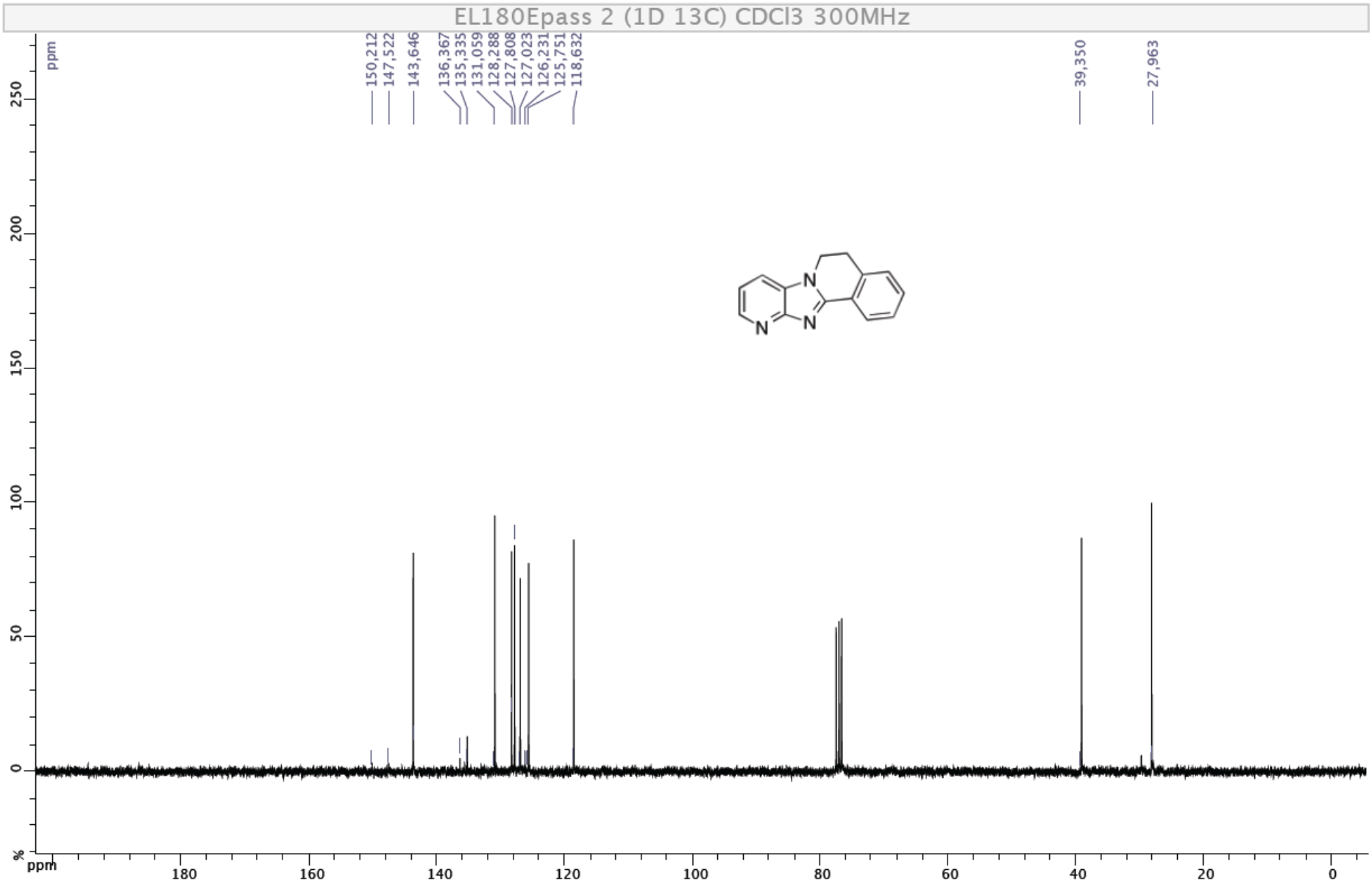
Ethyl 5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline-10-carboxylate (5ka)



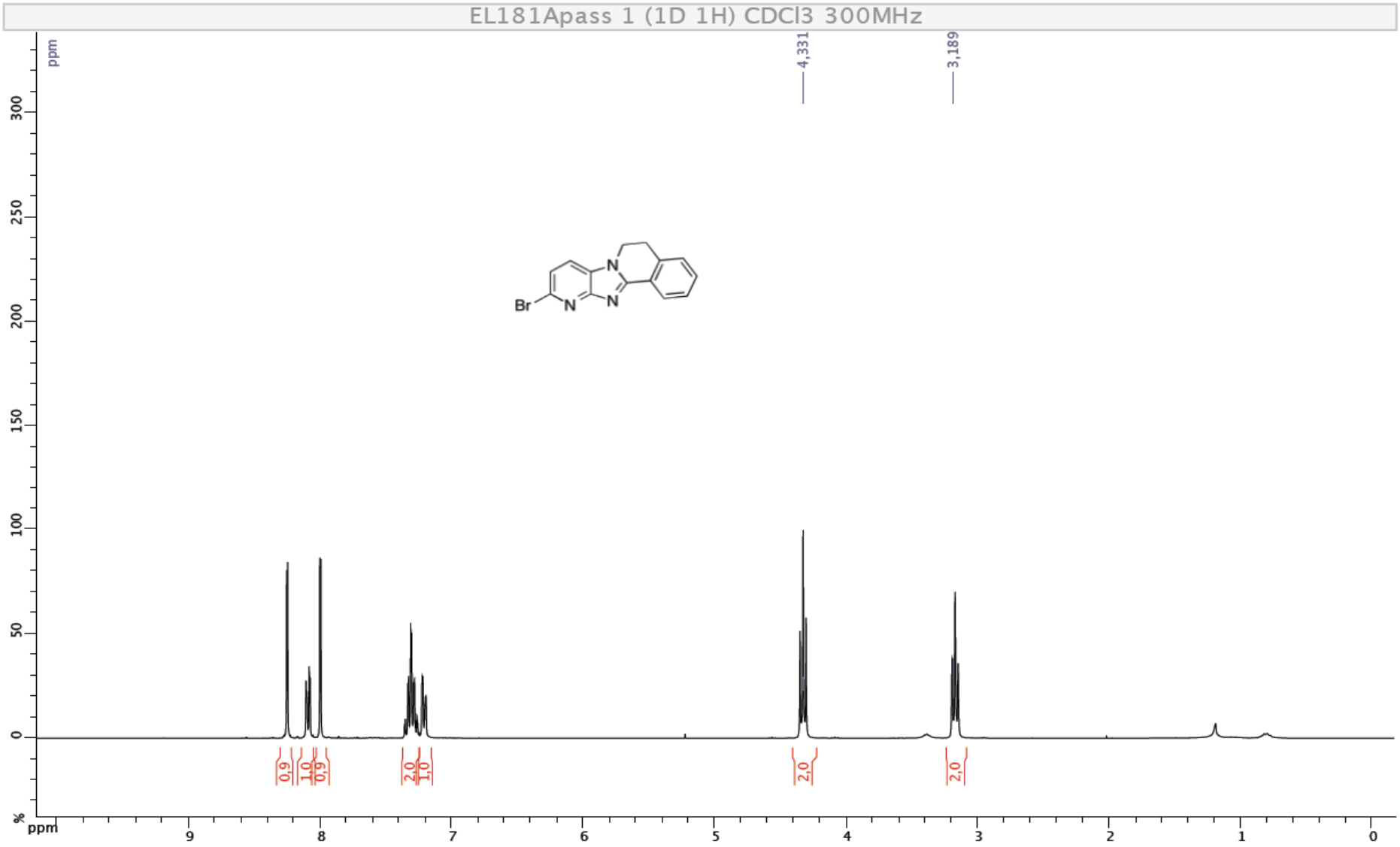

EL180Dpass 2 (1D 13C) CDCl3 300MHz
ppm
167,053
150,627
143,086
137,676
134,389
130,746
128,136
127,910
126,005
125,103
124,427
123,271
121,795
108,772
60,903
40,586
27,963
14,722
EtOOC
N
N
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

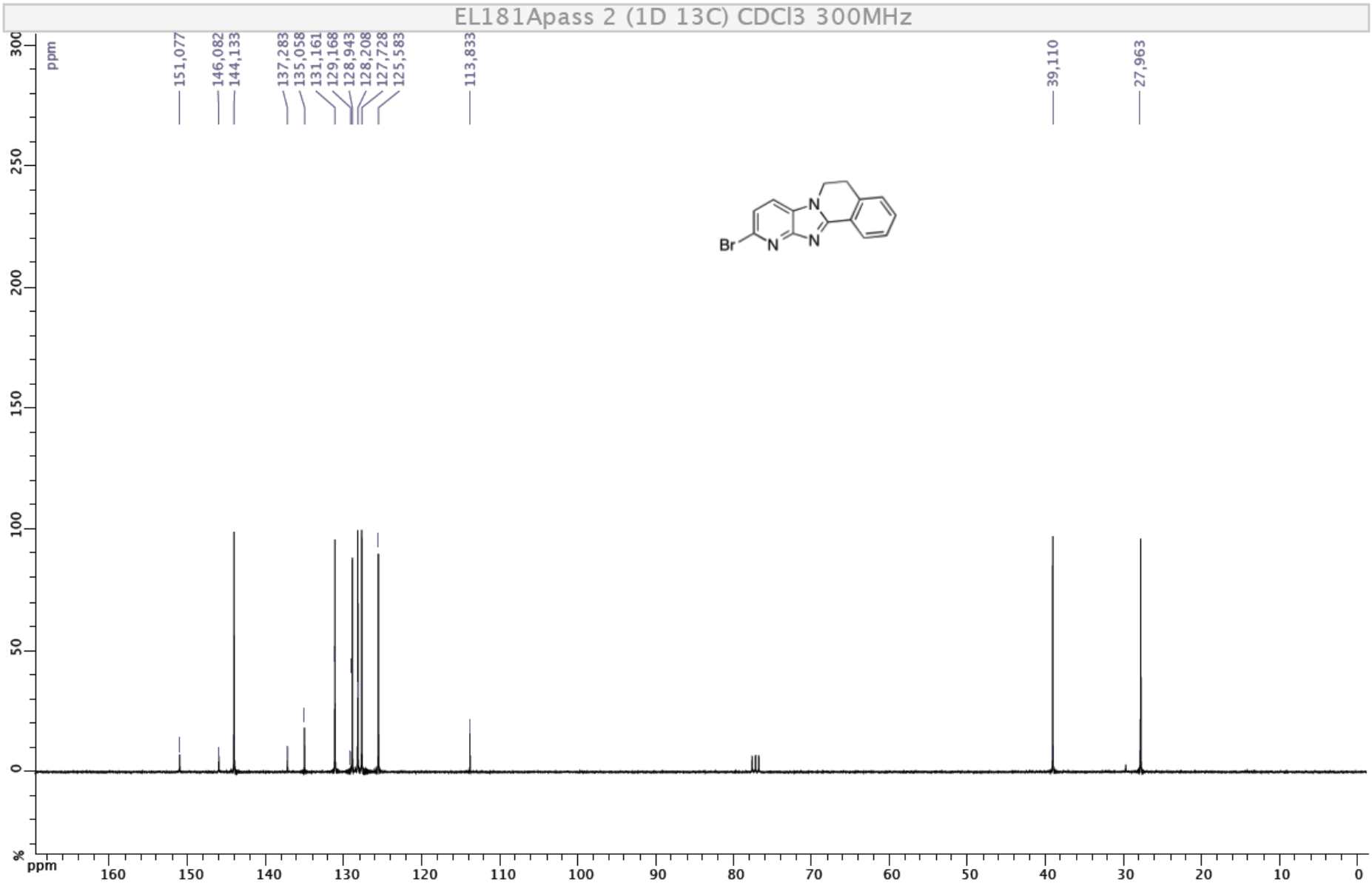
5,6-Dihydropyrido[2',3':4,5]imidazo[2,1-*a*]isoquinoline (5la)



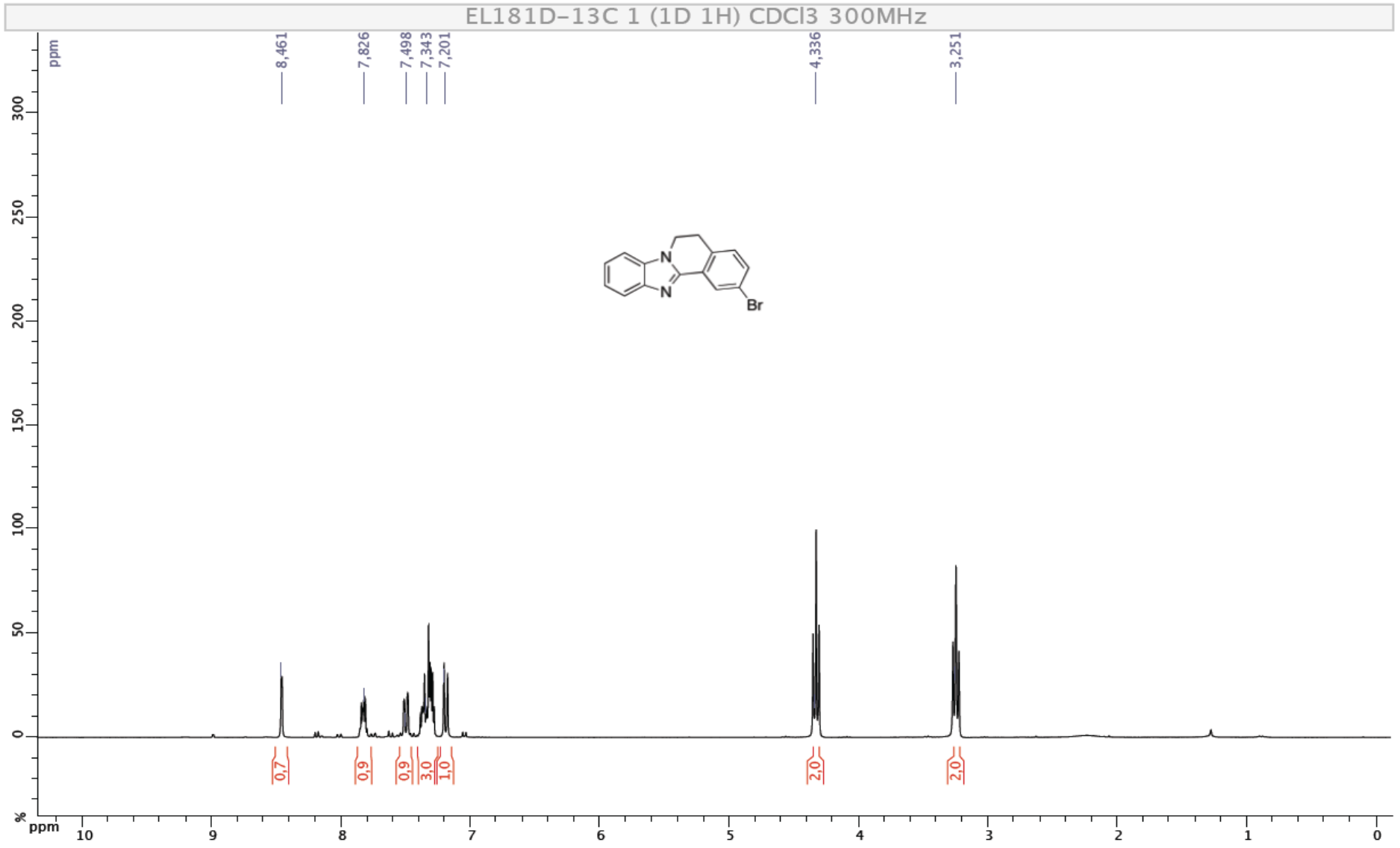

EL180Epass 2 (1D 13C) CDCl3 300MHz
ppm
150,212
147,522
143,646
136,367
135,335
131,059
128,288
127,808
127,023
126,231
125,751
118,632
39,350
27,963
N
N
N
250
200
150
100
50
0
%
ppm
180
160
140
120
100
80
60
40
20
0

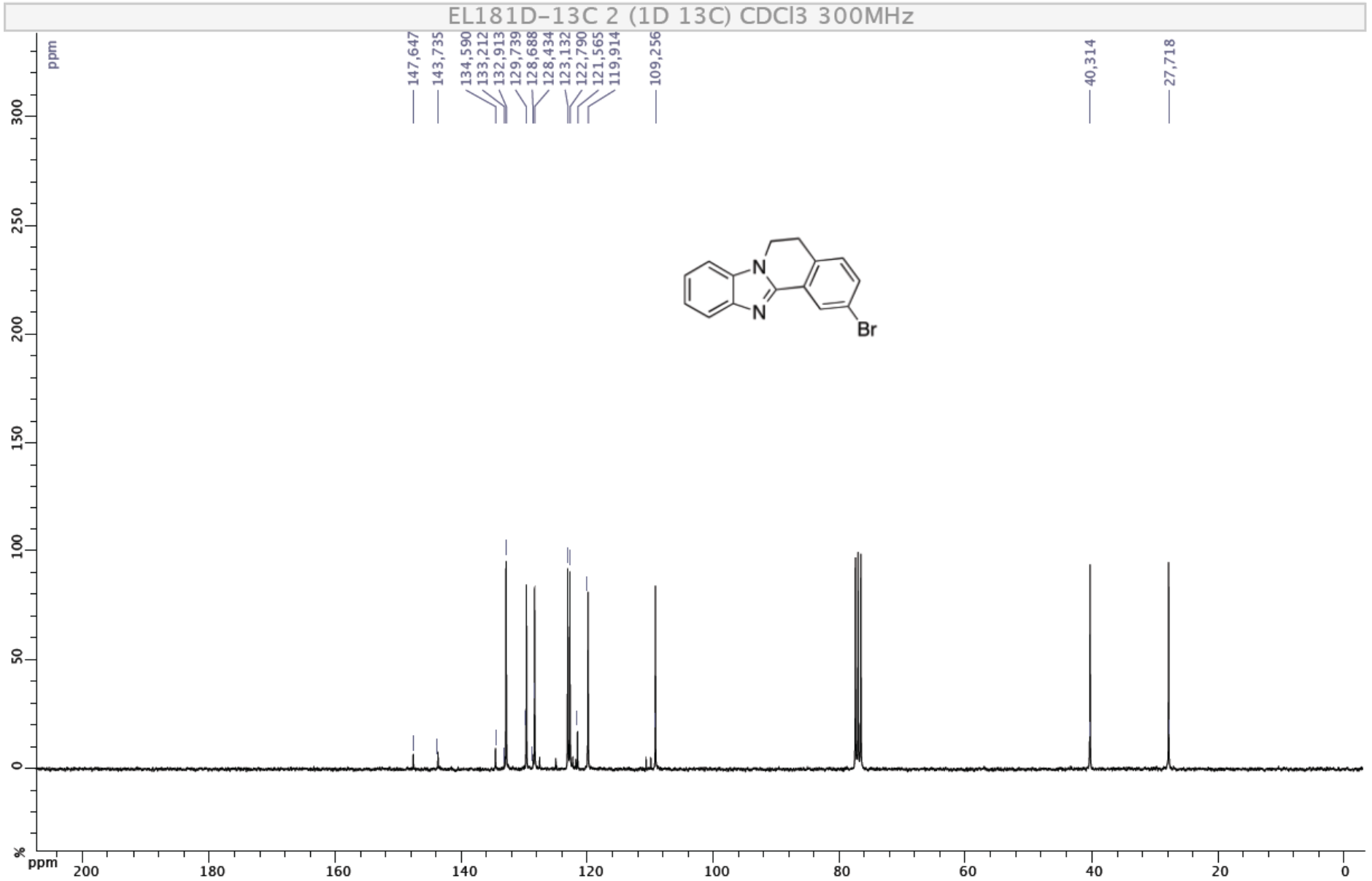
10-Bromo-5,6-dihydropyrido[2',3':4,5]imidazo[2,1-a]isoquinoline (5ma)



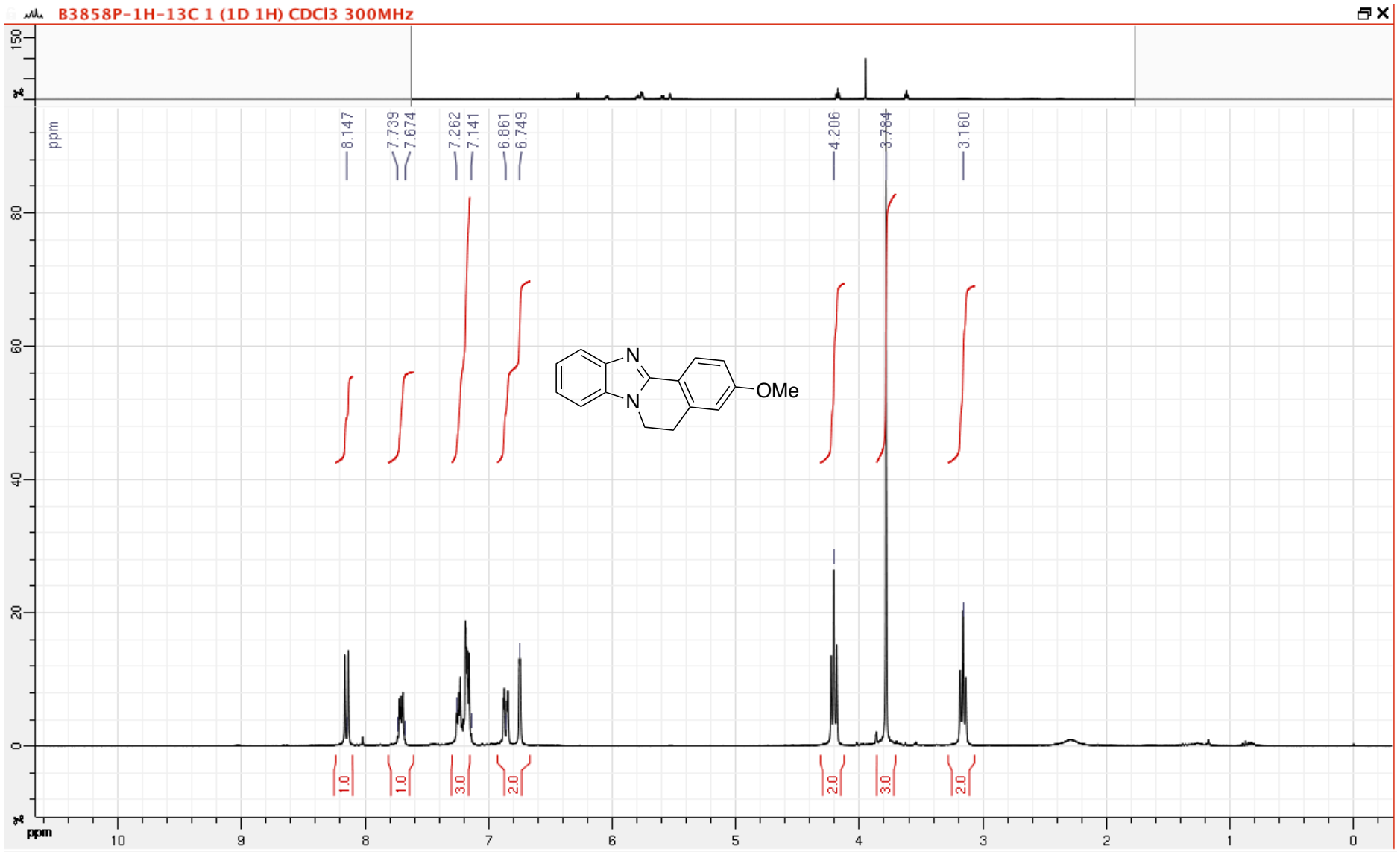

EL181Apass 2 (1D 13C) CDCl3 300MHz
ppm
151,077
146,082
144,133
137,283
135,058
131,161
129,168
128,943
128,208
127,728
125,583
113,833
39,110
27,963
Br
N
N
N
300
250
200
150
100
50
0
%
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

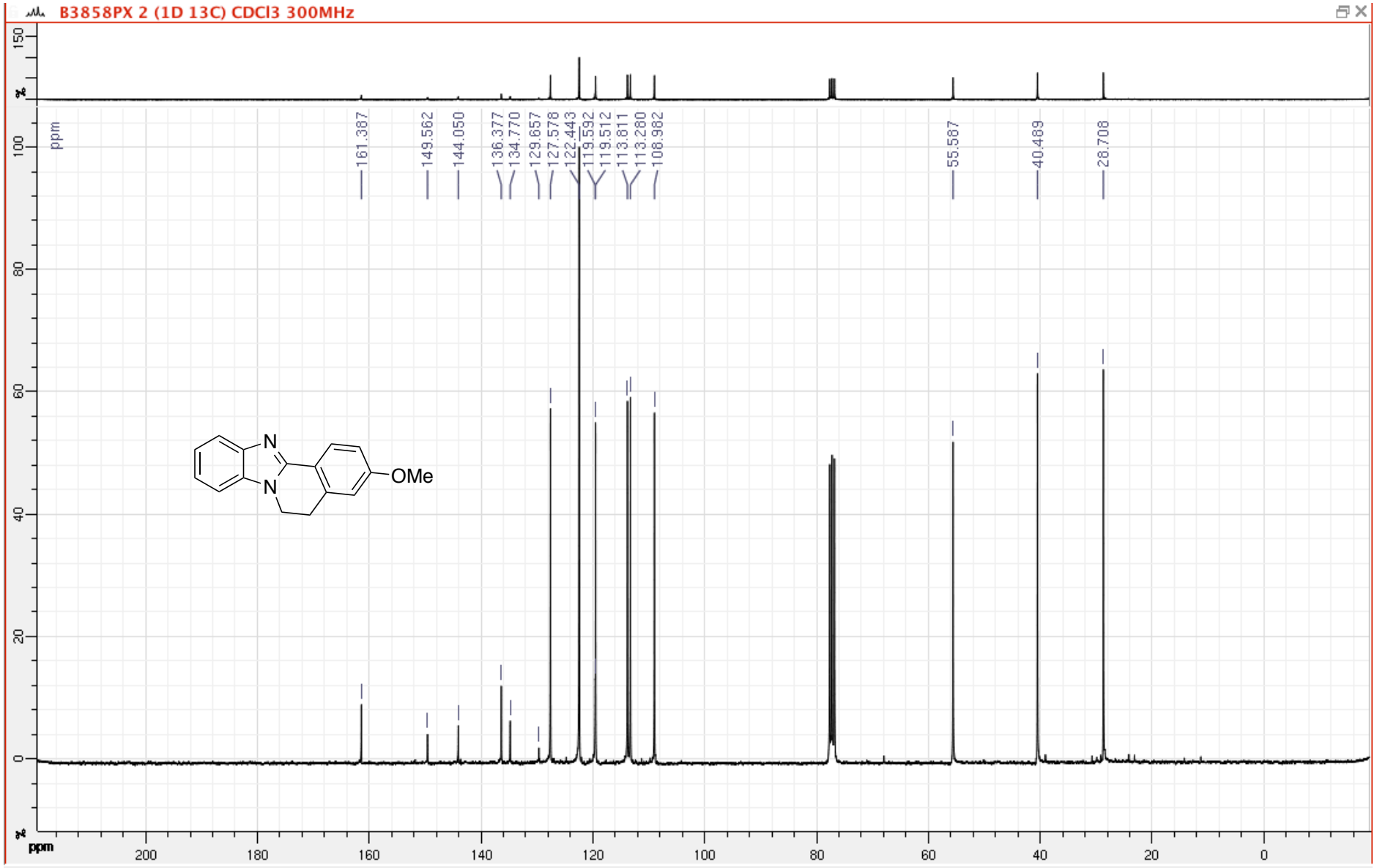
2-Bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (5ab)



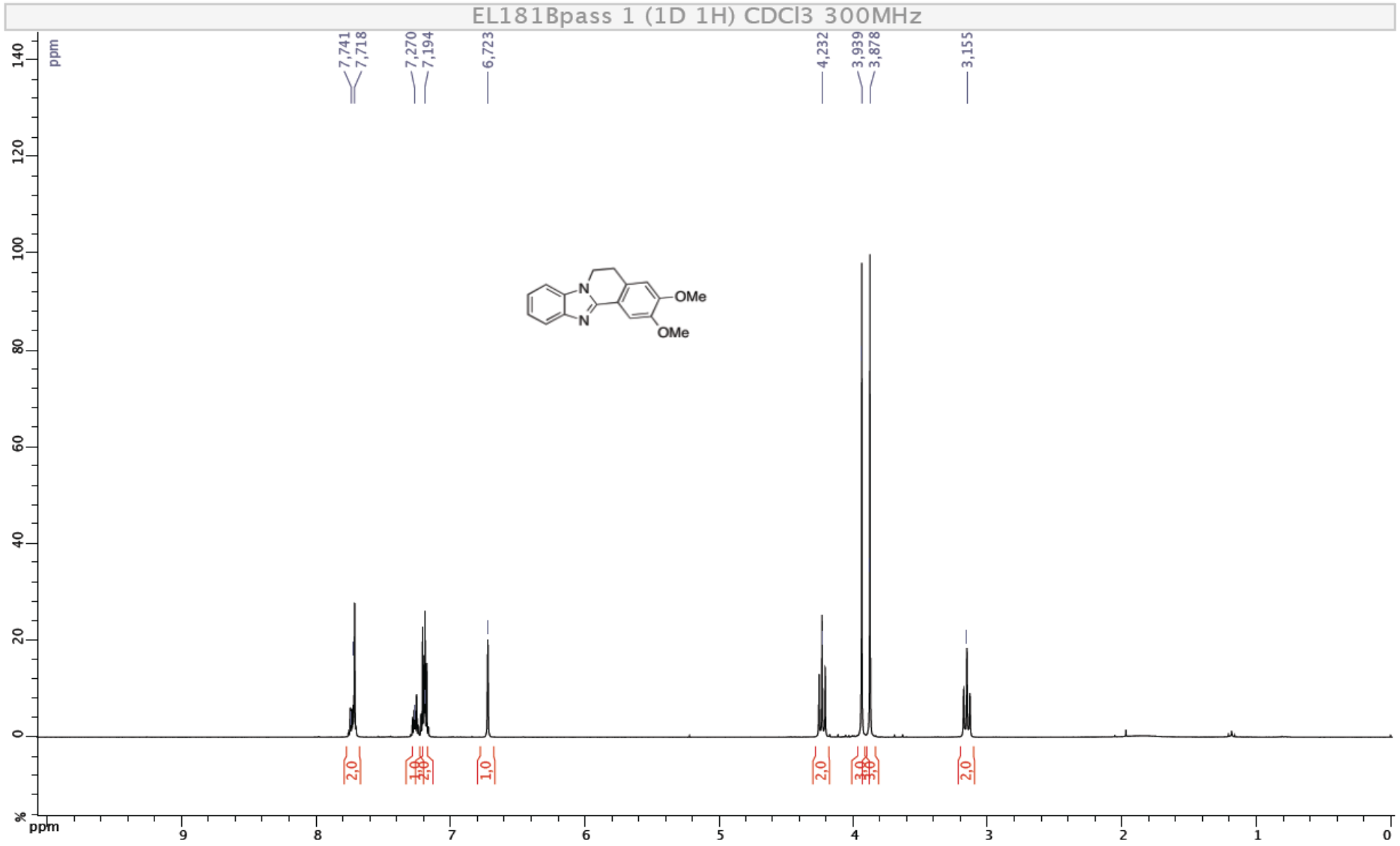

EL181D-13C 2 (1D 13C) CDCl3 300MHz
ppm
147,647
143,735
134,590
133,212
132,913
129,739
128,688
128,434
123,132
122,790
121,565
119,914
109,256
40,314
27,718
N
N
Br
300
250
200
150
100
50
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0

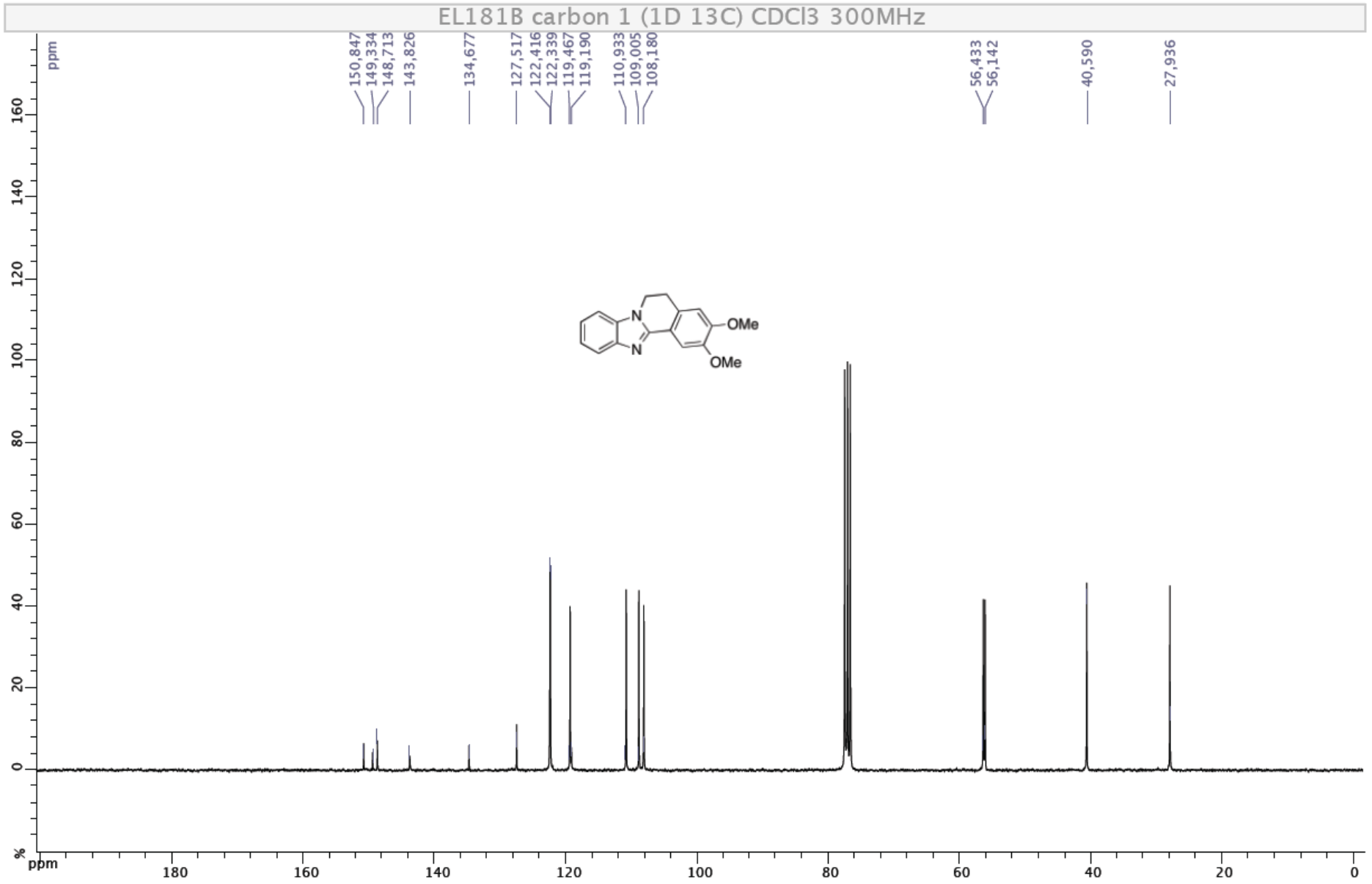
3-Methoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ac)



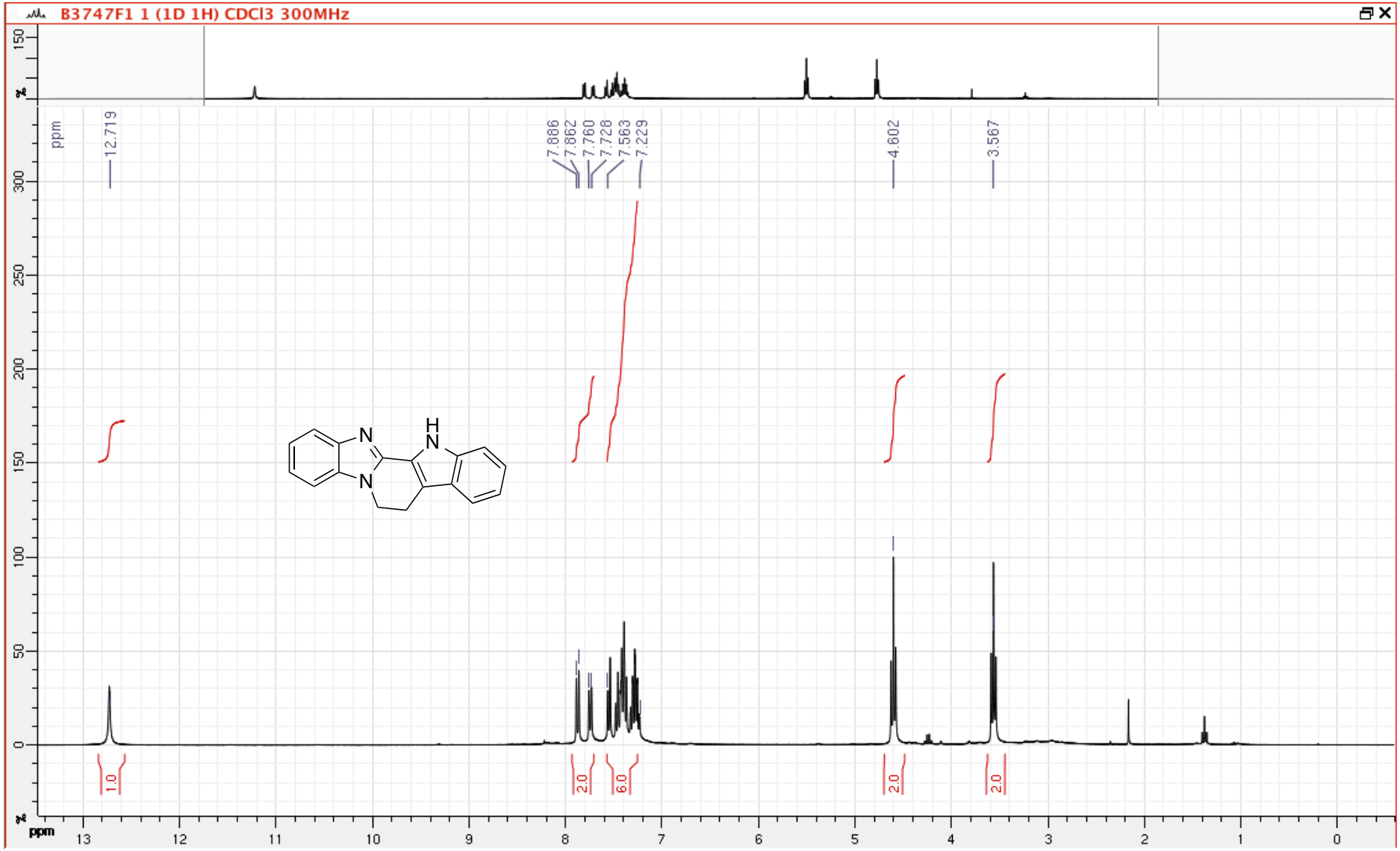

B3858PX 2 (1D 13C) CDCl3 300MHz
ppm
161.387
149.562
144.050
136.377
134.770
129.657
127.578
122.443
119.592
119.512
113.811
113.280
108.982
55.587
40.489
28.708
N
N
OMe
200
180
160
140
120
100
80
60
40
20
0

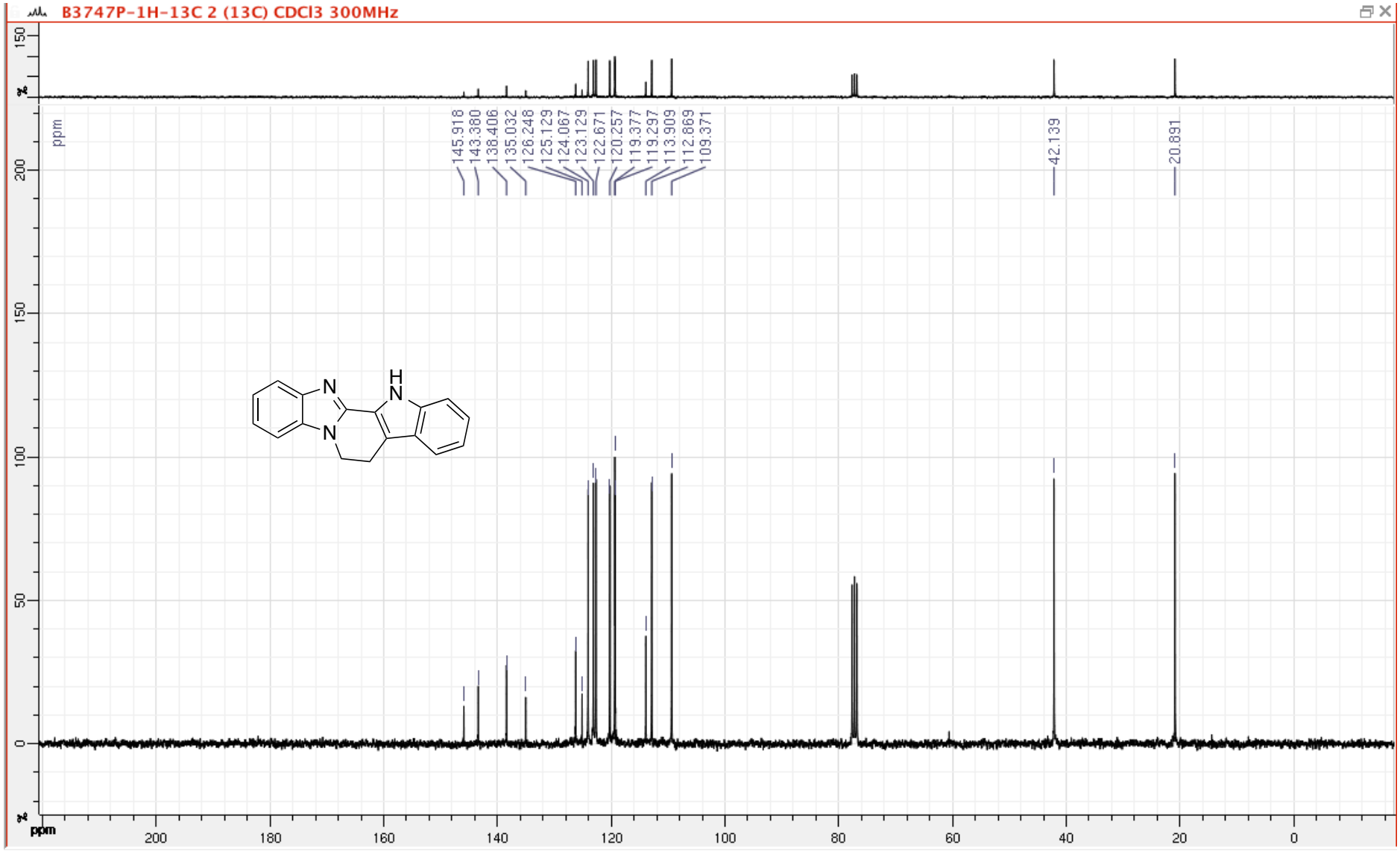
2,3-Dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (5ad)



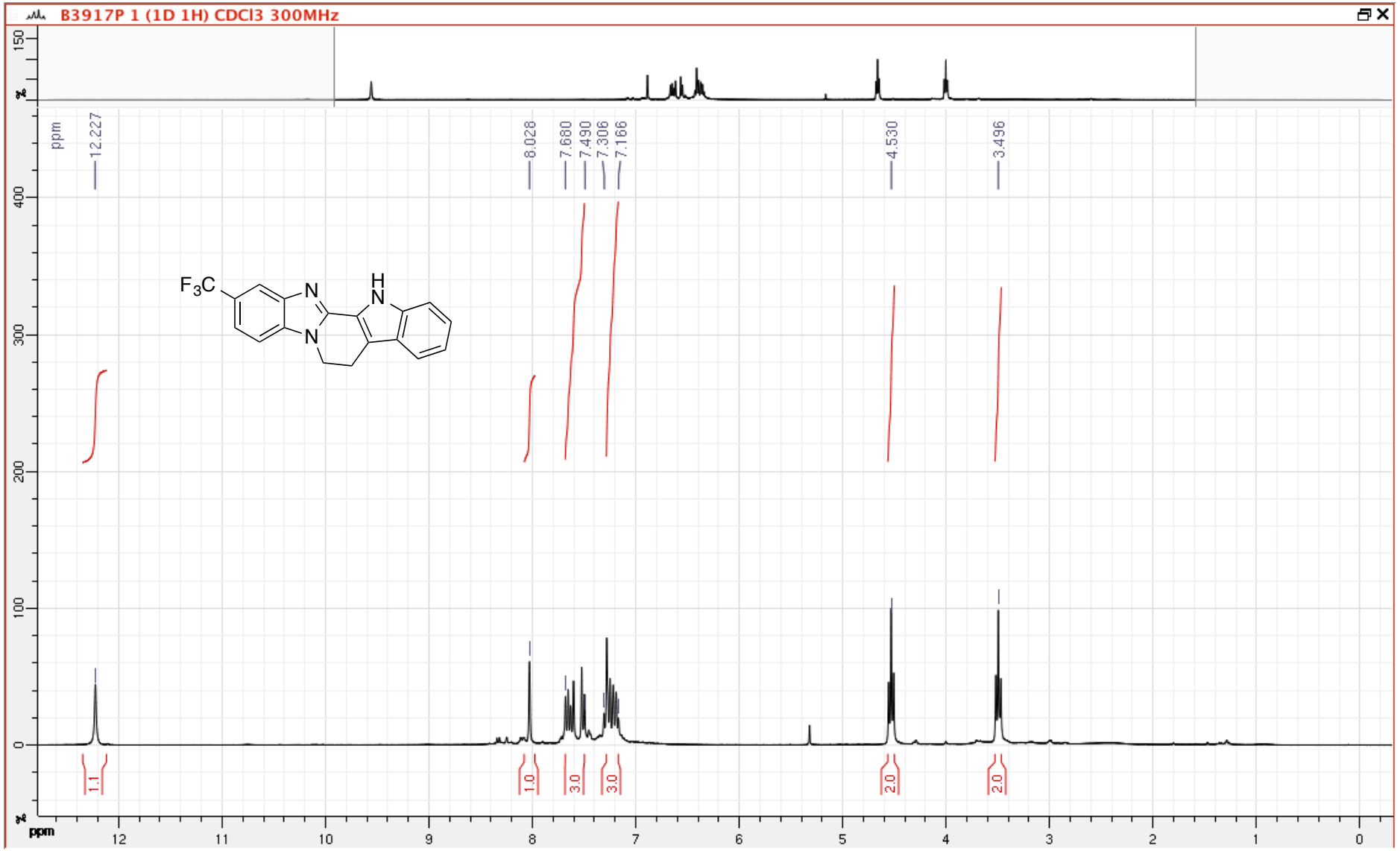

EL181B carbon 1 (1D 13C) CDCl3 300MHz
ppm
150,847
149,334
148,713
143,826
134,677
127,517
122,416
122,339
119,467
119,190
110,933
109,005
108,180
56,433
56,142
40,590
27,936
OMe
OMe
N
N
%
ppm
180
160
140
120
100
80
60
40
20
0

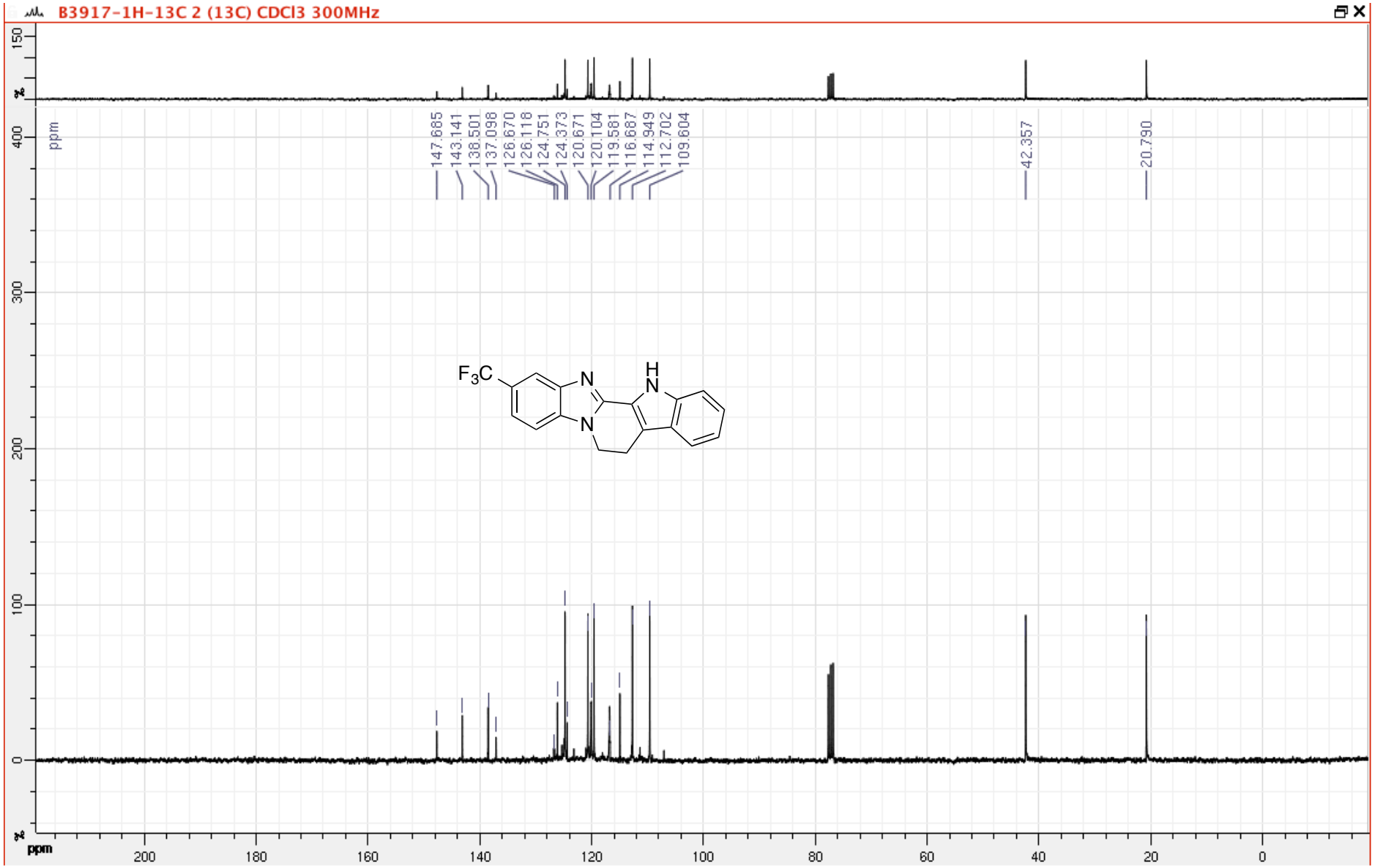
7,12-Dihydro-6*H*-benzo[4',5']imidazo[1',2':1,2]pyrido[3,4-*b*]indole (5ae)




B3747P-1H-13C 2 (13C) CDCl3 300MHz
ppm
145.918
143.380
138.406
135.032
126.248
125.129
124.067
123.129
122.671
120.257
119.377
119.297
113.909
112.869
109.371
42.139
20.891
N
H
N
N
ppm

2-(Trifluoromethyl)-7,12-dihydro-6*H*-benzo[4',5']imidazo[1',2':1,2]pyrido[3,4-*b*]indole (5af)




B3917-1H-13C 2 (13C) CDCl3 300MHz
ppm
147.685
143.141
138.501
137.098
126.670
126.118
124.751
124.373
120.671
120.104
119.581
116.687
114.949
112.702
109.604
42.357
20.790
F3C
N
H
N
N
ppm