Supporting information

Synthesis of polycyclic indoles via an organocatalytic bicyclization of α-alkynylnaphthalen-2-ols with nitrones

Ting Xu, Na Lin, Wen-Juan Hao,* Jie Zhang, Meng-Fan Li, Shu-Jiang Tu,* and Bo Jiang*

[a]School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China; email jiangchem@jsnu.edu.cn (B.J.); wjhao@jsnu.edu.cn (W.J.H.), laotu@jsnu.edu.cn (S.J.T.)

Context

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-d_6) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI and ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

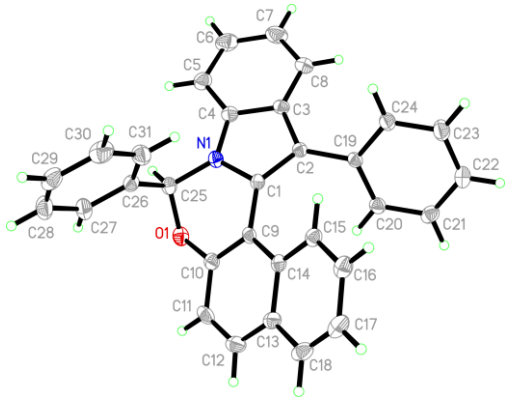
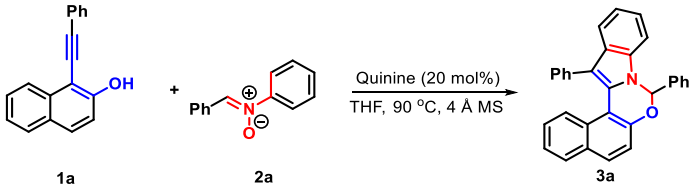


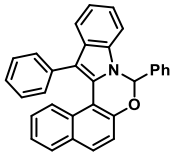
Figure S1 X-Ray structure of product **3a** (CCDC 2018309)

General Procedure for the Synthesis of Products 3



Under air conditions, 1-(phenylethynyl)naphthalen-2-ol (**1a**, 0.2 mmol, 48.8 mg), nitrone (**2a**, 0.2 mmol, 39.4 mg), Quinine (20 mol %, 13 mg), 4Å molecular sieves (100 mg) were added in the 25-mL Schlenk tube. Then, THF (3 mL) was added into this reaction system. The reaction vial was sealed and heated in metal bath at 90 °C until TLC (petroleum ether: ethyl acetate= 5:1) revealed that conversion of the starting material **1a** was completed. Then the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ ethyl acetate = 100:1) to afford the desired product **3a** as yellow solid.

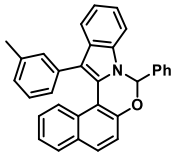
8,14-diphenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3a)



Yellow solid, 64 mg, 75% yield; mp 226-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.42-7.36 (m, 3H), 7.34-7.26 (m, 6H), 7.26-7.20 (m, 5H), 7.19-7.15 (m, 2H), 6.87-6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.0, 136.9, 135.7, 135.1, 130.5(9), 130.5(6), 129.9(8), 129.9(2), 128.9, 128.7, 128.5, 128.0, 127.7, 127.1, 126.7, 126.3, 126.0, 125.3, 124.3, 123.2, 120.8,

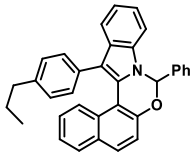
120.1, 118.8, 114.7, 114.3, 108.9, 83.2, IR (KBr, *v*, cm^{-1}) 1491, 1363, 1248, 1019, 926, 746, 699. HRMS (ESI) m/z calcd for $C_{31}H_{21}NNaO$, 446.1521, $[M+Na]^+$, Found 446.1516

8-phenyl-14-(m-tolyl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3b)



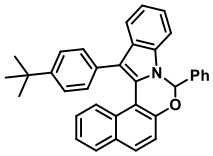
Yellow solid, 63 mg, 72% yield; mp 199-201 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.39-7.36 (m, 3H), 7.32-7.27 (m, 2H), 7.25-7.21 (m, 4H), 7.20-7.15 (m, 3H), 7.13 (d, J = 6.0 Hz, 2H), 7.03 (d, J = 6.8 Hz, 1H), 6.86-6.82 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.9, 138.0, 136.9, 135.5, 135.1, 130.5(5), 130.5(4), 130.4, 129.2, 128.9, 128.7, 128.4, 128.0, 127.6, 127.1, 127.0(4), 127.0(9), 126.9, 126.0, 125.2, 124.2, 123.2, 120.7, 120.2, 118.7, 114.8, 114.4, 108.8, 83.1, 21.4. IR (KBr, *v*, cm^{-1}) 1507, 1473, 1420, 1220, 820, 736. HRMS (ESI) m/z calcd for $C_{32}H_{23}NNaO$, 460.1677, $[M+Na]^+$, Found 460.1656

8-phenyl-14-(4-propylphenyl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3c)



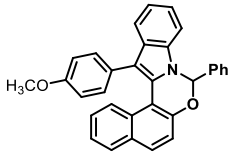
Yellow solid, 65 mg, 70% yield; mp 189-190 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 7.6 Hz, 1H), 7.71-7.63 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.40-7.34 (m, 3H), 7.32-7.26 (m, 2H), 7.26-7.23 (m, 4H), 7.21 (d, J = 6.0 Hz, 2H), 7.18-7.14 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.85-6.79 (m, 1H), 2.64-2.52 (m, 2H), 1.70-1.60 (m, 2H), 0.98-0.91 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.9, 140.7, 136.9, 135.1, 132.9, 130.5, 130.4, 129.7, 129.2, 129.0, 128.7, 128.0, 127.6, 127.1, 126.9, 125.9, 125.2, 124.2, 123.1, 120.7, 120.2, 118.8, 114.8, 114.5, 108.8, 83.2, 37.8, 24.7, 13.7. IR (KBr, *v*, cm^{-1}) 1508, 1363, 1300, 1206, 1044, 816, 740. HRMS (ESI) m/z calcd for $C_{34}H_{28}NO$, 466.2171, $[M+H]^+$ Found 466.2151

14-(4-(tert-butyl)phenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3d)



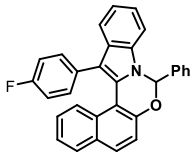
Yellow solid, 62 mg, 65% yield; mp 182-183 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89 (d, J = 8.0 Hz, 1H), 7.70-7.63 (m, 2H), 7.48 (d, J = 8.8 Hz, 1H), 7.40-7.35 (m, 3H), 7.29 (d, J = 8.8 Hz, 4H), 7.26-7.23 (m, 5H), 7.20 (d, J = 6.8 Hz, 1H), 7.17-7.12 (m, 2H), 6.78-6.73 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 145.0, 149.3, 137.0, 135.1, 132.7, 130.5, 130.4, 129.6, 129.2, 129.0, 128.7, 128.1, 127.6, 127.2, 126.9, 126.1, 125.4, 125.1, 124.2, 123.2, 120.7, 120.3, 118.8, 114.8, 114.5, 108.8, 83.2, 34.6, 31.4. IR (KBr, *v*, cm^{-1}) 1557, 1456, 1378, 1231, 1155, 1006, 742, 702. HRMS (ESI) m/z calcd for $C_{35}H_{29}NNaO$, 502.2147, $[M+Na]^+$, Found 502.2144

14-(4-methoxyphenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3e)



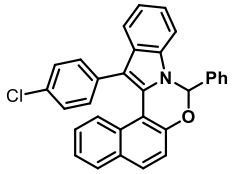
Yellow solid, 65 mg, 72% yield; mp 213-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.84 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.39-7.34 (m, 3H), 7.31-7.26 (m, 2H), 7.26-7.22 (m, 5H), 7.22-7.15 (m, 3H), 6.91-6.87 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 158.2, 149.9, 137.0, 135.1, 130.9, 130.5, 130.4, 129.2, 129.1, 128.7, 128.1, 128.0, 127.7, 127.1, 126.8, 125.8, 125.5, 124.3, 123.2, 120.7, 120.1, 118.8, 114.5, 114.4, 114.0, 108.8, 83.2, 55.3. IR (KBr, v, cm^{-1}) 1559, 1465, 1361, 1243, 1045, 826, 734. HRMS (ESI) m/z calcd for $C_{32}H_{24}NO_2$, 454.1807, $[M+H]^+$, Found 454.1782

14-(4-fluorophenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3f)



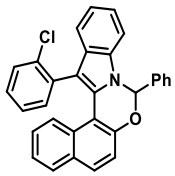
Yellow solid, 73 mg, 83% yield; mp 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.81 (d, J = 7.6 Hz, 1H), 7.72-7.65 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.39-7.34 (m, 3H), 7.33-7.26 (m, 4H), 7.24 (d, J = 2.8 Hz, 3H), 7.23-7.15 (m, 3H), 7.00-6.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 162.8, 161.5 ($^1J_{CF}$ = 243.7 Hz), 150.1, 136.8, 135.1, 131.4, 131.3, 130.6 ($^3J_{CF}$ = 7.5 Hz), 129.2, 128.7, 127.9, 127.8 ($^4J_{CF}$ = 1.6 Hz), 127.1, 126.6, 125.5, 124.4, 123.3, 120.9, 119.8, 118.8, 115.4 ($^2J_{CF}$ = 21.2 Hz) 114.1, 113.5, 109.0, 83.2. IR (KBr, v, cm^{-1}) 1589, 1543, 1505, 1363, 1219, 1040, 924, 808. HRMS (ESI) m/z calcd for $C_{31}H_{21}FNO$, 442.1607, $[M+H]^+$, Found 442.1623

14-(4-chlorophenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3g)



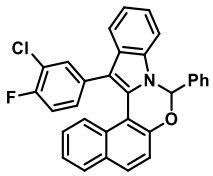
Yellow solid, 52 mg, 57% yield; mp 192-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.82 (d, J = 7.6 Hz, 1H), 7.73-7.66 (m, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.39-7.34 (m, 3H), 7.32-7.26 (m, 3H), 7.24 (d, J = 4.0 Hz, 5H), 7.24-7.16 (m, 4H), 6.95-6.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 136.7, 135.1, 134.3, 132.1, 131.1, 130.7, 130.5, 129.3, 128.7(1), 128.7(5), 127.9, 127.8, 127.1, 126.6, 126.2, 125.6, 124.5, 123.4, 121.0, 119.7, 118.8, 114.0, 113.3, 109.0, 83.2. IR (KBr, v, cm^{-1}) 1503, 1245, 1042, 813, 746, 697. HRMS (ESI) m/z calcd for $C_{31}H_{21}ClNO$, 458.1312, $[M+H]^+$, Found 458.1334

14-(2-chlorophenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3h)



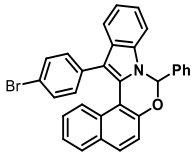
Yellow solid, 46 mg, 50% yield; mp 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.40-7.36 (m, 3H), 7.34-7.27 (m, 4H), 7.24 (d, J = 2.0 Hz, 4H), 7.23-7.19 (m, 2H), 7.18 (d, J = 7.2 Hz, 2H), 6.86-6.81 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.2, 137.7, 136.7, 135.1, 134.3, 130.9, 130.6, 129.7, 129.6, 129.3, 128.8(0), 128.8(6), 128.6, 128.2, 127.9(4), 127.9(7), 127.1, 126.6, 126.4, 125.6, 124.5, 123.5, 121.1, 119.7, 118.8, 113.9, 113.1, 109.0, 83.2. IR (KBr, v, cm^{-1}) 1559, 1490, 1363, 1211, 1017, 943, 740. HRMS (ESI) m/z calcd for $C_{31}H_{21}ClNO$, 458.1312, $[M+H]^+$, Found 458.1332

14-(3-chloro-4-fluorophenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3i)



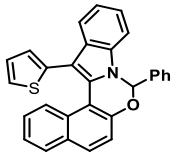
Yellow solid, 67 mg, 70 % yield; mp 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.82 (d, J = 8.0 Hz, 1H), 7.76-7.68 (m, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 6.4 Hz, 1H), 7.39-7.35 (m, 3H), 7.33-7.26 (m, 4H), 7.26-7.16 (m, 4H), 7.09 (s, 1H), 7.02-6.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 157.4, 156.2 ($^1J_{CF}$ = 247 Hz), 149.7, 136.1, 134.5(2), 134.5(9), 132.5(1), 132.5(7), 130.5 ($^3J_{CF}$ = 8.2 Hz), 128.8, 128.2, 127.5, 126.6(0), 126.6(9), 126.5, 125.8, 125.2, 124.0, 123.0, 120.4 ($^4J_{CF}$ = 17.7 Hz), 118.9, 118.2, 116.1, 115.6 ($^2J_{CF}$ = 20.7 Hz), 113.1, 111.6, 108.5, 82.7. IR (KBr, v, cm^{-1}) 1508, 1465, 1352, 1253, 1212, 1014, 920, 741, 700. HRMS (ESI) m/z calcd for $C_{31}H_{19}ClFNNaO$, 498.1037, $[M+Na]^+$, Found 498.1025

14-(4-bromophenyl)-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3j)



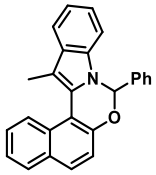
Yellow solid, 58 mg, 58% yield; mp 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.81 (d, J = 7.6 Hz, 1H), 7.73-7.66 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.39-7.34 (m, 4H), 7.31-7.27 (m, 2H), 7.26-7.23 (m, 5H), 7.23-7.16 (m, 4H), 6.95-6.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 136.7, 135.1, 134.8, 131.6, 131.4, 131.0, 130.7, 130.5, 129.3, 128.7(0), 128.7(5), 127.9, 127.1, 126.6, 125.6, 124.5, 123.4, 121.0, 119.7, 118.8, 113.9, 113.3, 109.0, 83.2. IR (KBr, v, cm^{-1}) 1559, 1465, 1355, 1252, 1048, 825, 743. HRMS (ESI) m/z calcd for $C_{31}H_{21}BrNO$, 502.0807, $[M+H]^+$, Found 502.0836

8-phenyl-14-(thiophen-2-yl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3k)



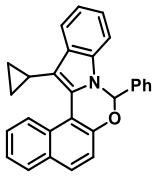
Yellow solid, 57 mg, 66% yield; mp 184-1845 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99-7.96 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.39-7.35 (m, 3H), 7.32-7.27 (m, 3H), 7.26-7.22 (m, 5H), 7.16-7.13 (m, 1H), 7.06-6.96 (m, 2H), 6.85 (d, J = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.5, 136.1, 135.5, 135.0, 131.9, 131.8, 130.6, 129.85, 128.7(2), 128.7(0), 128.6, 128.5, 127.8, 125.5, 124.5, 123.4(2), 123.4(8), 121.0, 120.2, 118.6, 115.0, 114.3, 108.6, 82.4. IR (KBr, v, cm^{-1}) 1508, 1457, 1420, 1296, 1138, 1001, 809, 741, 668. HRMS (ESI) m/z calcd for $C_{29}H_{20}NOS$, 430.1266, $[M+H]^+$, Found 430.1284

14-methyl-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3l)



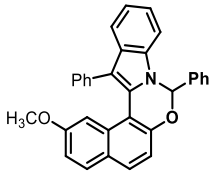
Yellow solid, 27 mg, 38% yield; mp 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.18 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.75-7.71 (m, 2H), 7.62-7.48 (m, 2H), 7.43-7.36 (m, 3H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 4H), 7.09-7.05 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.5, 137.2, 135.5, 130.9, 130.7, 129.7, 129.3, 128.9, 128.8, 128.6, 127.2, 126.6(4), 126.6(6), 125.9, 124.6, 122.9, 122.4, 120.0, 119.3, 118.6, 115.3, 108.8, 108.6, 83.5, 12.6. IR (KBr, v, cm^{-1}) 1491, 1363, 1248, 1019, 926, 746, 699. HRMS (ESI) m/z calcd for $C_{26}H_{19}NNaO$, 384.1364, $[M+Na]^+$, Found 384.1375

14-cyclopropyl-8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3m)



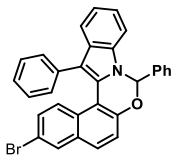
Yellow solid, 35 mg, 45% yield; mp 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.53 (d, J = 8.8 Hz, 1H), 7.94-7.89 (m, 1H), 7.79-7.72 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.28 (d, J = 9.2 Hz, 2H), 7.25-7.21 (m, 5H), 7.11-7.06 (m, 1H), 2.25-2.18 (m, 1H), 1.01-0.94 (m, 1H), 0.52-0.39 (m, 2H), 0.12-0.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.3, 137.2, 135.1, 130.7, 130.5, 129.9(0), 129.9(7), 129.1, 128.6, 127.9, 127.1, 125.4, 124.5, 122.8, 120.4, 120.1, 118.5, 115.1, 114.5, 108.8, 94.2, 83.3, 8.8, 8.0, 7.5. IR (KBr, v, cm^{-1}) 1489, 1356, 1250, 1212, 1143, 1012, 937, 740. HRMS (ESI) m/z calcd for $C_{28}H_{21}NNaO$, 410.1521, $[M+Na]^+$, Found 410.1504

2-methoxy-8,14-diphenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (30)



Yellow solid, 59 mg, 65% yield; mp 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.40-7.36 (m, 4H), 7.31-7.26 (m, 3H), 7.26-7.23 (m, 5H), 7.22-7.15 (m, 3H), 6.87-6.82 (m, 2H), 3.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 157.9, 150.8, 136.9, 135.8, 135.4, 130.3, 129.7, 129.6, 129.4, 129.1, 128.7(2), 128.7(8), 128.5, 127.0, 126.3, 125.9, 123.2, 120.9, 120.0, 117.5, 116.2, 113.8, 113.7, 108.9, 105.7, 83.0, 54.8. IR (KBr, v, cm^{-1}) 1516, 1465, 1438, 1376, 1252, 1230, 1207, 1048, 832, 745. HRMS (ESI) m/z calcd for $C_{32}H_{23}NNaO_2$, 476.1626, $[M+Na]^+$, Found 476.1652

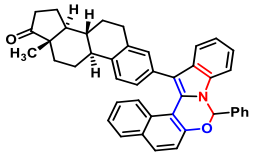
3-bromo-8,14-diphenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3p)



Yellow solid, 71 mg, 71% yield; mp 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89-7.85 (m, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.54-7.50 (m, 3H), 7.38-7.36 (m, 3H), 7.35-7.33 (m, 4H), 7.31-7.27 (m, 4H), 7.22 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.97-6.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 136.2, 135.0, 134.6, 131.1, 130.8, 129.7, 129.3, 128.8, 128.4, 128.2(3), 128.2(6), 127.9, 127.8, 127.4 127.0, 126.6, 126.3, 126.1, 125.2, 122.9, 120.4, 119.7, 119.0, 118.5, 114.5, 114.0, 108.4, 89.2, 88.9, 82.8. IR (KBr, v, cm^{-1}) 1559, 1521, 1363, 1212, 1018, 886, 748. HRMS (ESI) m/z calcd for $C_{31}H_{21}BrNO$, 502.0807, $[M+H]^+$, Found 502.0833

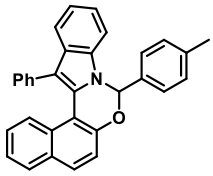
(8R,9S,13S,14S)-13-methyl-3-(8-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indol-14-yl)-

6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3q)



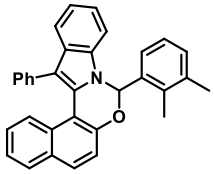
Yellow solid, 66 mg, 55% yield; mp 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93-7.88 (m, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.37 (d, J = 4.8 Hz, 3H), 7.30 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 3.2 Hz, 4H), 7.22-7.05 (m, 4H), 6.95 (d, J = 57.6 Hz, 1H), 6.84-6.79 (m, 1H), 2.79-2.66 (m, 1H), 2.56-2.49 (m, 1H), 2.43 (d, J = 10.4 Hz, 1H), 2.33 (d, J = 9.2 Hz, 1H), 2.20-1.92 (m, 4H), 1.68-1.33 (m, 7H), 0.95 (d, J = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 220.6, 149.4, 137.2, 136.5, 136.0, 134.6, 132.4, 129.9, 128.2, 127.1, 126.6(2), 126.6(8), 125.5, 125.0, 124.9, 124.5, 123.7, 123.6, 122.7, 122.6, 120.2, 114.0, 108.3, 108.3, 82.7, 82.6, 50.1, 47.6, 47.6, 44.0, 37.8, 35.4, 31.2, 28.6, 26.0, 25.3, 21.2, 21.2, 13.4. IR (KBr, v, cm^{-1}) 1720, 1515, 1496, 1466, 1364, 1255, 1211, 1057, 942, 822, 750. HRMS (ESI) m/z calcd for $C_{43}H_{37}NNaO_2$, 622.2722, $[M+Na]^+$, Found 622.2734

14-phenyl-8-(p-tolyl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3r)



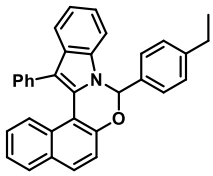
Yellow solid, 59 mg, 68% yield; mp 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89 (d, J = 7.6 Hz, 1H), 7.73-7.65 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.35-7.32 (m, 3H), 7.31-7.26 (m, 5H), 7.26-7.15 (m, 5H), 7.06 (d, J = 8.0 Hz, 2H), 6.87-6.83 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 139.1, 135.8, 135.0, 133.9, 130.5, 130.4, 129.9, 129.4, 128.9, 128.5, 128.0, 127.7, 127.1, 126.8, 126.3, 126.1, 125.3, 124.3, 123.2, 120.7, 120.0, 118.8, 114.6, 114.3, 109.0, 83.3, 21.2. IR (KBr, v, cm^{-1}) 1489, 1356, 1251, 1212, 1141, 1012, 937, 740. HRMS (ESI) m/z calcd for $C_{32}H_{23}NNaO$ $[M+Na]^+$ 460.1677, Found 460.1674

8-(2,3-dimethylphenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3s)



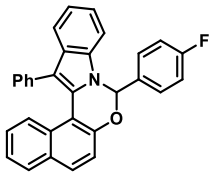
Yellow solid, 48 mg, 53% yield; mp 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.86 (d, J = 7.6 Hz, 1H), 7.71-7.66 (m, 4H), 7.35 (d, J = 6.8 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.24-7.16 (m, 5H), 7.07 (d, J = 7.6 Hz, 1H), 6.93-6.84 (m, 2H), 6.76-6.71 (m, 1H), 6.52 (d, J = 7.8 Hz, 1H), 4.15 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.9, 152.8, 150.0, 147.5, 142.6, 141.3, 135.8, 130.5, 129.9, 129.5, 128.9, 128.8, 128.0, 127.8, 126.7, 126.3, 125.6, 124.2, 124.0, 123.2, 120.7, 119.9, 118.6, 116.4, 114.5, 113.8, 110.6, 109.1, 98.4, 79.2, 61.7, 55.9. IR (KBr, v, cm^{-1}) 1588, 1483, 1313, 1211, 1036, 822, 747, 698. HRMS (ESI) m/z calcd for $C_{33}H_{25}NNaO$, 474.1834, $[M+Na]^+$, Found 474.1827

8-(4-ethylphenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3t)



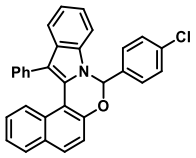
Yellow solid, 70 mg, 77% yield; mp 107-108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.87 (d, J = 8.0 Hz, 1H), 7.72-7.64 (m, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.36-7.29 (m, 5H), 7.27 (d, J = 4.4 Hz, 3H), 7.25-7.13 (m, 5H), 7.08 (d, J = 8.0 Hz, 2H), 6.87-6.82 (m, 1H), 2.59-2.52 (m, 2H), 1.18-1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 145.4, 135.8, 135.0, 134.1, 130.5, 130.4, 129.9, 128.9, 128.5, 128.2, 128.0, 127.7, 127.1, 126.8, 126.3, 126.1, 125.3, 124.2, 123.1, 120.7, 120.0, 118.8, 114.6, 114.3, 109.0, 83.3, 28.5, 15.3. IR (KBr, v, cm^{-1}) 1507, 1473, 1297, 1250, 1209, 1007, 810, 740. HRMS (ESI) m/z calcd for $C_{33}H_{25}NNaO$, 474.1834, $[M+Na]^+$, Found 474.1833

8-(4-fluorophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3u)



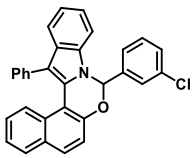
Yellow solid, 51 mg, 58% yield; mp 190-191 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.43-7.37 (m, 4H), 7.36-7.32 (m, 4H), 7.31-7.21 (m, 5H), 7.01-6.94 (m, 2H), 6.92-6.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 164.1 ($^1J_{CF}$ = 247 Hz), 161.9, 149.7, 135.6, 135.0, 132.8, 132.8, 130.6 ($^3J_{CF}$ = 4.8 Hz), 129.9, 129.0, 128.9 ($^4J_{CF}$ = 8.2 Hz), 128.5, 127.9, 127.8, 126.7, 126.4, 125.8, 125.5, 124.4, 123.3, 120.9, 120.2, 118.7, 115.7 ($^2J_{CF}$ = 21.7 Hz), 115.6, 114.9, 114.3, 108.7, 82.5. IR (KBr, v, cm^{-1}) 1534, 1339, 1249, 1210, 1003, 802, 765, 701. HRMS (ESI) m/z calcd for $C_{31}H_{21}FNO$, 442.1607, $[M+H]^+$, Found 442.1614

8-(4-chlorophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3v)



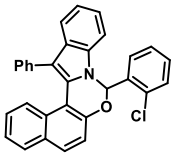
Yellow solid, 63 mg, 69% yield; mp 204-206 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89-7.86 (m, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.37 (s, 1H), 7.35-7.27 (m, 6H), 7.26-7.21 (m, 5H), 7.20-7.15 (m, 3H), 6.86-6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.6, 135.6, 135.5, 135.1, 135.0, 130.6(1), 130.6(5), 129.8, 129.0, 128.9, 128.5, 128.4, 127.9, 127.8, 126.7, 126.5, 125.7, 125.5, 124.4, 123.4, 121.0, 120.2, 118.7, 115.0, 114.3, 108.6, 82.4. IR (KBr, v, cm^{-1}) 1489, 1464, 1363, 1301, 1252, 1089, 1013, 817, 747, 713. HRMS (ESI) m/z calcd for $C_{31}H_{21}ClNO$, 458.1312, $[M+H]^+$, Found 458.1332

8-(3-chlorophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3w)



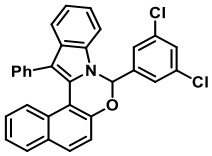
Yellow solid, 61 mg, 67% yield; mp 178-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89 (d, J = 7.6 Hz, 1H), 7.74-7.62 (m, 3H), 7.56-7.46 (m, 1H), 7.40-7.35 (m, 2H), 7.33-7.26 (m, 5H), 7.25-7.18 (m, 5H), 7.16-7.08 (m, 1H), 7.00-6.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.0, 136.9, 135.7, 135.1, 130.5, 130.5, 129.9, 129.2, 128.9, 128.7, 128.5, 128.0, 127.7, 127.1, 126.8, 126.4, 126.0, 125.3, 124.3, 123.2, 120.8, 120.1, 118.8, 114.7, 114.3, 108.9, 83.2. HRMS (ESI) m/z calcd for $C_{31}H_{21}ClNO$, 458.1312, $[M+H]^+$, Found 458.1324

8-(2-chlorophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3x)



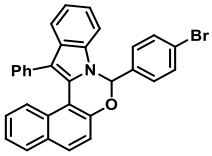
Yellow solid, 48 mg, 52% yield; mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.87 (d, J = 7.6 Hz, 1H), 7.70-7.62 (m, 4H), 7.46 (d, J = 8.0 Hz, 1H), 7.37-7.26 (m, 4H), 7.25-7.16 (m, 6H), 7.08 (d, J = 7.6 Hz, 1H), 6.98-6.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.6, 135.6, 134.5, 133.8, 133.4, 130.9, 130.7, 130.2, 129.9, 129.2, 129.0, 128.6, 127.8, 126.9, 126.6, 126.5, 125.5, 124.4, 123.3, 121.0, 120.1, 118.6, 115.0, 114.2, 108.9, 80.8. IR (KBr, v, cm^{-1}) 1498, 1458, 1304, 1249, 1012, 813, 743, 701. HRMS (ESI) m/z calcd for 458.1312 $[M+H]^+$ $C_{31}H_{21}ClNO$, Found 458.1334

8-(3,5-dichlorophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3y)



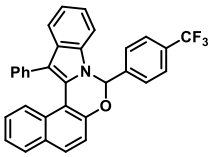
Yellow solid, 57 mg, 58% yield; mp 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.39-7.32 (m, 3H), 7.31-7.26 (m, 5H), 7.26-7.21 (m, 4H), 7.21-7.17 (m, 2H), 6.88-6.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.1, 140.9, 135.5, 135.3, 135.2, 130.8, 130.6, 129.8, 129.4, 129.1, 128.5, 127.9, 127.8, 126.8, 126.6, 125.6, 125.5, 125.3, 124.6, 123.7, 121.2, 120.4, 118.5, 115. 4, 114.3, 108.4, 81.4. IR (KBr, v, cm^{-1}) 1589, 1570, 1464, 1359, 1304, 1250, 1140, 1051, 851, 813, 740. HRMS (ESI) m/z calcd for $C_{31}H_{20}Cl_2NO$, 492.0922, $[M+H]^+$, Found 492.0932

8-(4-bromophenyl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3z)



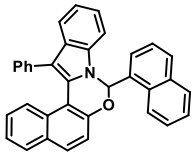
Yellow solid, 53 mg, 53% yield; mp 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89 (d, J = 7.6 Hz, 1H), 7.73-7.65 (m, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.38-7.31 (m, 5H), 7.29 (d, J = 8.8 Hz, 4H), 7.26-7.16 (m, 6H), 6.88-6.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.1, 140.9, 135.5, 135.3, 135.2, 130.8, 130.6, 129.8, 129.4, 129.1, 128.5, 127.9, 127.8, 126.8, 126.6, 125.6, 125.5, 125.3, 124.6, 123.7, 121.2, 120.4, 118.5, 115.4, 114.3, 108.4, 81.4. IR (KBr, v, cm^{-1}) 1482, 1362, 1302, 1252, 1211, 1175, 1054, 1010, 855, 816, 795. HRMS (ESI) m/z calcd for $C_{31}H_{21}BrNO$, 502.0807, $[M+H]^+$, Found 502.0824

14-phenyl-8-(4-(trifluoromethyl)phenyl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3aa)



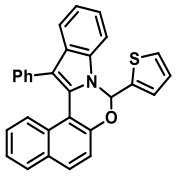
Yellow solid, 51 mg, 52% yield; mp 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 12.0 Hz, 5H), 7.36-7.31 (m, 3H), 7.30-7.26 (m, 4H), 7.24 (d, J = 6.8 Hz, 2H), 7.21-7.16 (m, 1H), 6.87-6.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 148.9, 140.6, 140.6, 135.0, 134.6, 130.7 ($^1J_{CF}$ = 323 Hz), 130.2 ($^2J_{CF}$ = 130 Hz), 129.4, 128.5, 128.1, 127.3 ($^4J_{CF}$ = 92 Hz), 126.9, 126.2, 126.0, 125.2 ($^5J_{CF}$ = 4.0 Hz), 125.0 ($^3J_{CF}$ = 4.0 Hz) 124.0, 123.1, 120.6, 119.8, 118.1, 114.7, 113.8, 107.9, 81.6. IR (KBr, v, cm^{-1}) 1508, 1456, 1423, 1232, 1167, 1125, 1066, 1010, 853, 741. HRMS (ESI) m/z calcd for $C_{32}H_{21}F_3NO$, 492.1575, $[M+H]^+$, Found 492.1558

8-(naphthalen-1-yl)-14-phenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3bb)



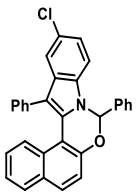
Yellow solid, 62 mg 65% yield; mp 238-240 °C ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.79 (d, J = 8.4 Hz, 1H), 8.08 (s, 1H), 7.99-7.95 (m, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.81-7.76 (m, 2H), 7.71 (d, J = 8.4 Hz, 1H), 7.67-7.59 (m, 3H), 7.45 (d, J = 6.4 Hz, 2H), 7.38-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.10 (m, 4H), 7.04 (d, J = 7.2 Hz, 1H), 6.96-6.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.4, 135.8, 134.7, 133.9, 131.1, 131.0, 130.6, 130.4, 130.3, 129.9, 129.0, 128.9, 128.6, 127.9, 127.8, 126.9, 126.6, 126.4, 126.1, 126.0, 125.4, 124.9, 124.2, 123.2, 120.9, 120.1, 118.6, 114.8, 114.3, 108.9, 81.9. IR (KBr, v, cm^{-1}) 1507, 1249, 1003, 787, 746, 701. HRMS (ESI) m/z calcd for $C_{35}H_{24}NO$, 474.1858, $[M+H]^+$, Found 474.1888

14-phenyl-8-(thiophen-2-yl)-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3cc)



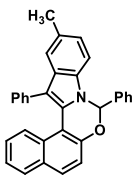
Yellow solid, 66 mg, 77% yield; mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.92 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.67-7.61 (m, 2H), 7.40-7.34 (m, 5H), 7.33 – 7.31 (m, 2H), 7.30-7.22 (m, 4H), 7.02-6.97 (m, 1H), 6.95-6.89 (m, 1H), 6.87-6.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.4, 140.3, 135.6, 134.6, 130.7, 130.6, 129.9, 128.9, 128.5, 128.0, 127.8, 127.5, 127.3, 126.8, 126.4, 125.5, 124.4, 123.4, 130.0, 120.2, 118.9, 114., 114.3, 108.6, 79.9. IR (KBr, v, cm^{-1}) 1508, 1253, 1045, 818, 732. HRMS (ESI) m/z calcd for $C_{29}H_{19}NNaOS$, 452.1085, $[M+Na]^+$, Found 452.1064

12-chloro-8,14-diphenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3ee)

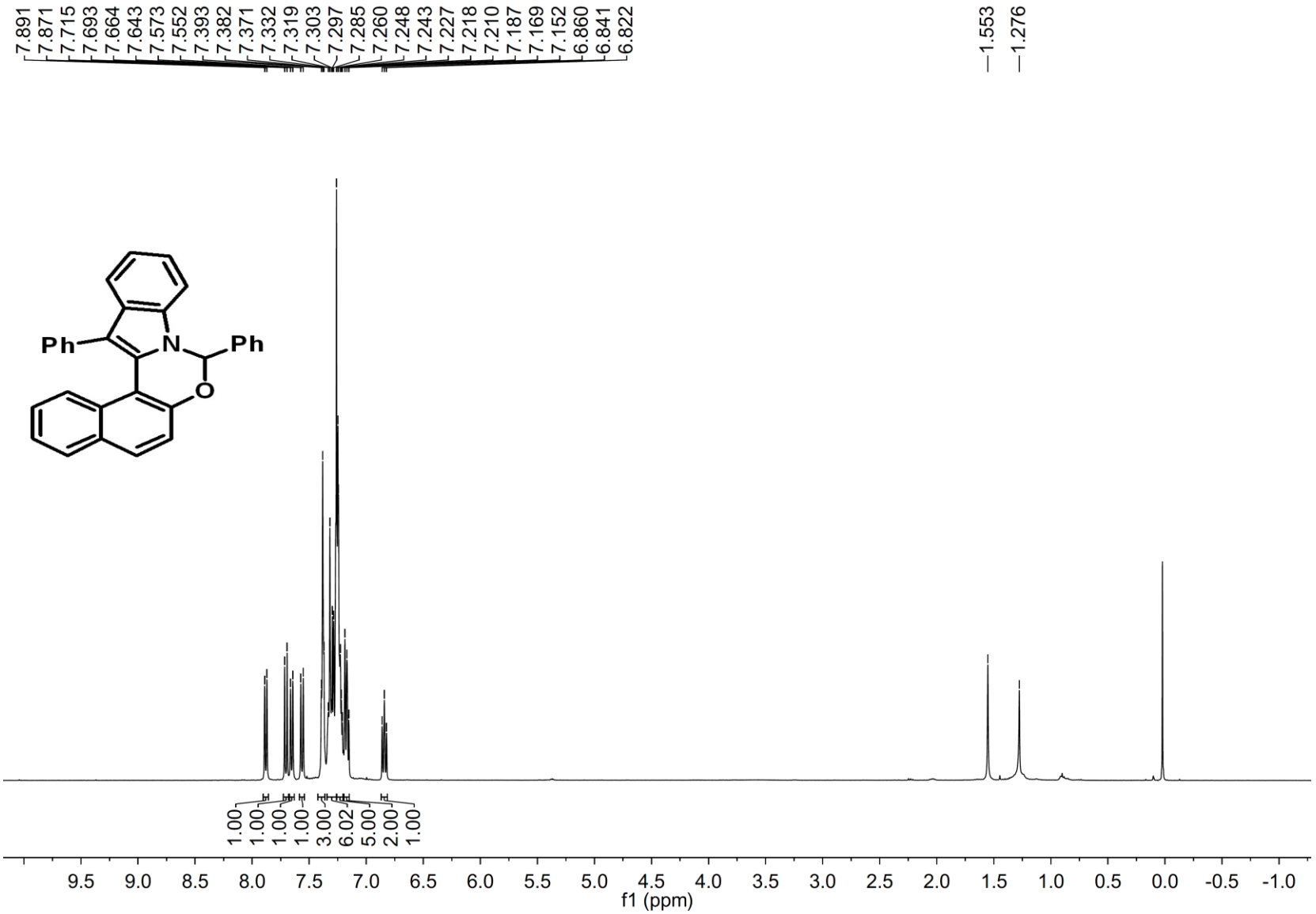


Yellow solid, 48 mg, 52% yield; mp 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.80 (d, J = 1.6 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.38-7.34 (m, 2H), 7.31-7.27 (m, 6H), 7.26-7.22 (m, 4H), 7.20-7.15 (m, 2H), 6.99 (d, J = 8.8 Hz, 1H), 6.86-6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.2, 136.3, 135.1, 133.4, 130.9, 130.5, 130.0, 129.7, 129.5, 128.8, 128.6, 127.8, 127.1, 126.6(4), 126.6(7), 126.6(5), 125.5, 124.4, 123.3, 119.4, 118.6, 110.0, 83.4. IR (KBr, v, cm^{-1}) 1507, 1089, 1363, 1252, 924, 808, 740, 696. HRMS (ESI) m/z calcd for $C_{31}H_{21}ClNO$, 458.1312, $[M+H]^+$, Found 458.1328

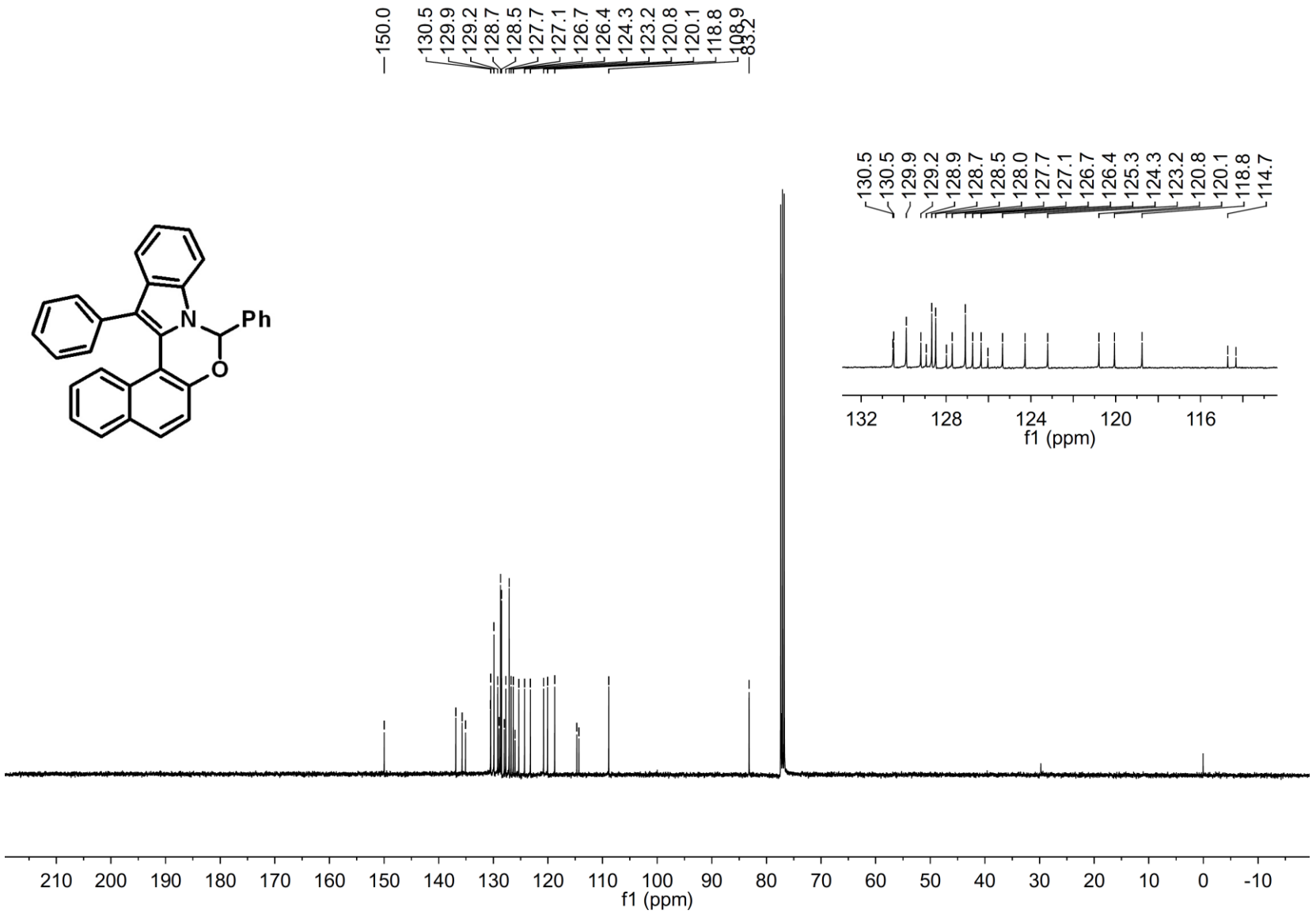
12-methyl-8,14-diphenyl-8H-naphtho[1',2':5,6][1,3]oxazino[3,4-a]indole (3ff)



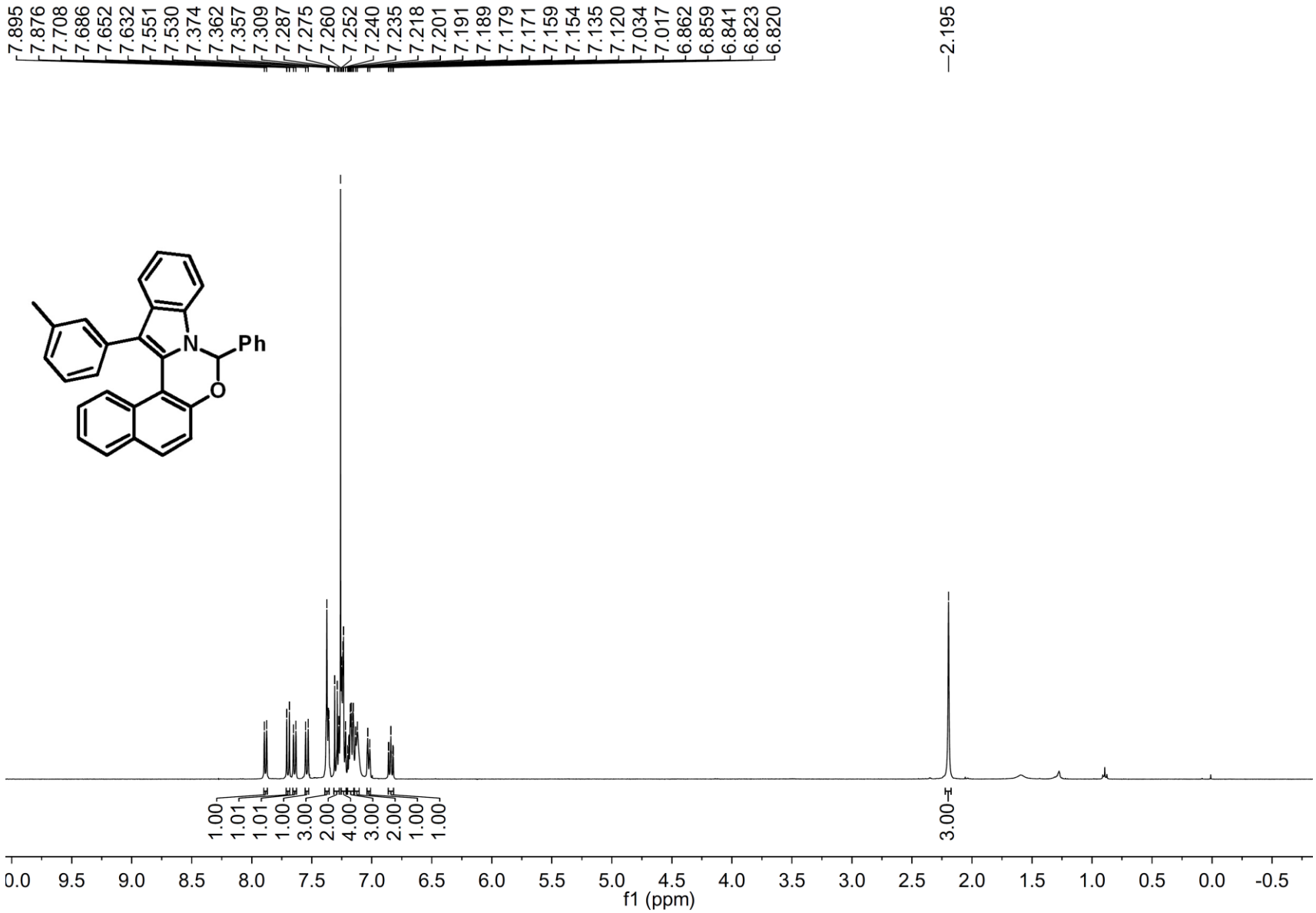
Yellow solid, 63 mg, 72%; mp 192-193 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 4.8 Hz, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.38-7.35 (m, 2H), 7.34-7.27 (m, 5H), 7.26-7.23 (m, 4H), 7.22-7.13 (m, 2H), 7.10 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.85-6.80 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 149.9, 137.0, 135.9, 133.5, 130.5, 130.3, 130.2, 129.9, 129.2, 129.1, 128.6, 128.5, 128.0, 127.7, 127.1, 126.8, 126.3, 126.1, 125.3, 124.7, 124.2, 119.6, 118.7, 114.4, 114.3, 108.6, 100.0, 83.2, 21.8 IR (KBr, v, cm^{-1}) 1507, 1089, 1362, 1252, 924, 805, 740, 696. HRMS (ESI) m/z calcd for $C_{32}H_{23}NNaO$, 460.1677, $[M+Na]^+$, Found 460.1677



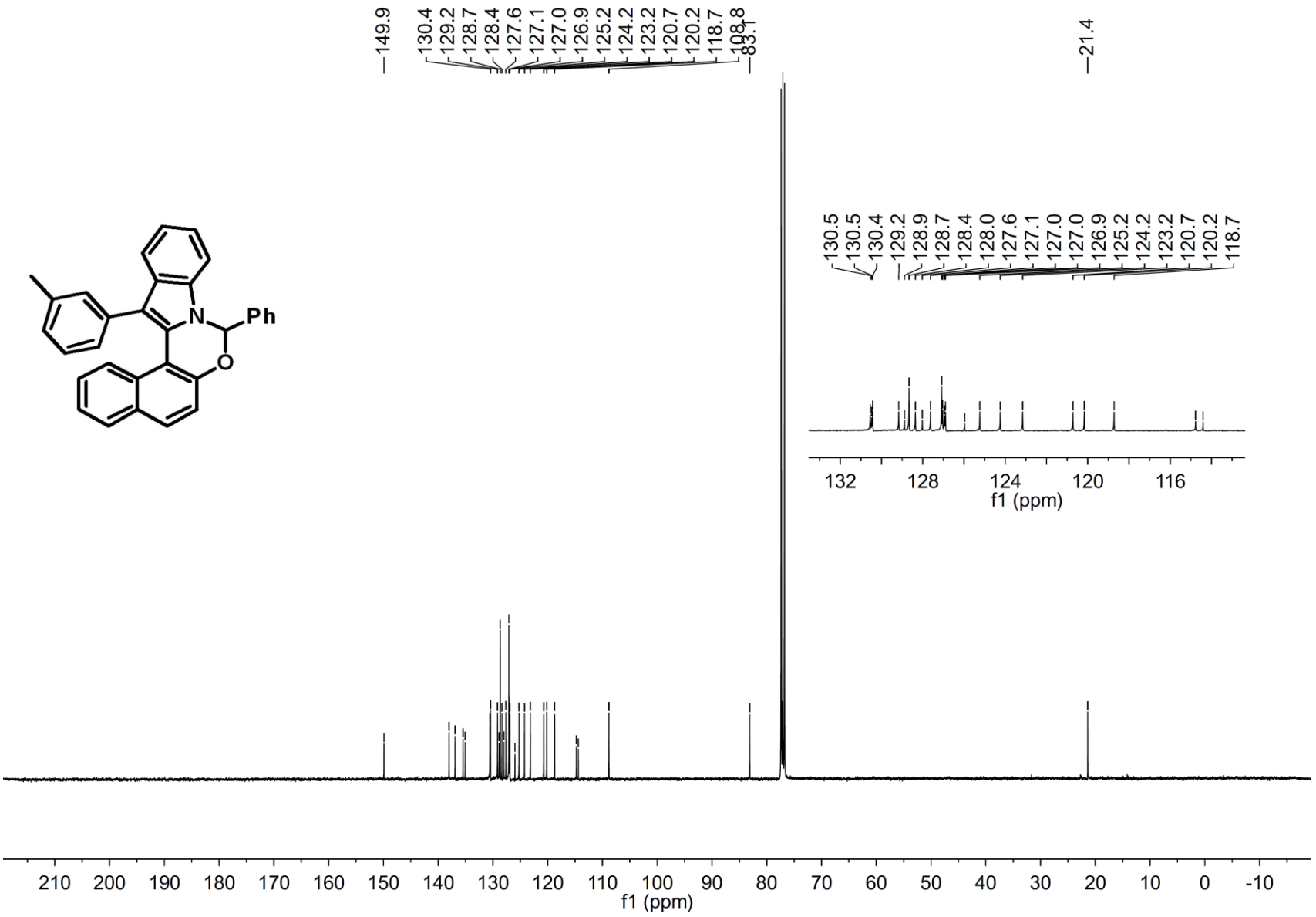
^{1}H NMR Spectrum of Compound **3a**



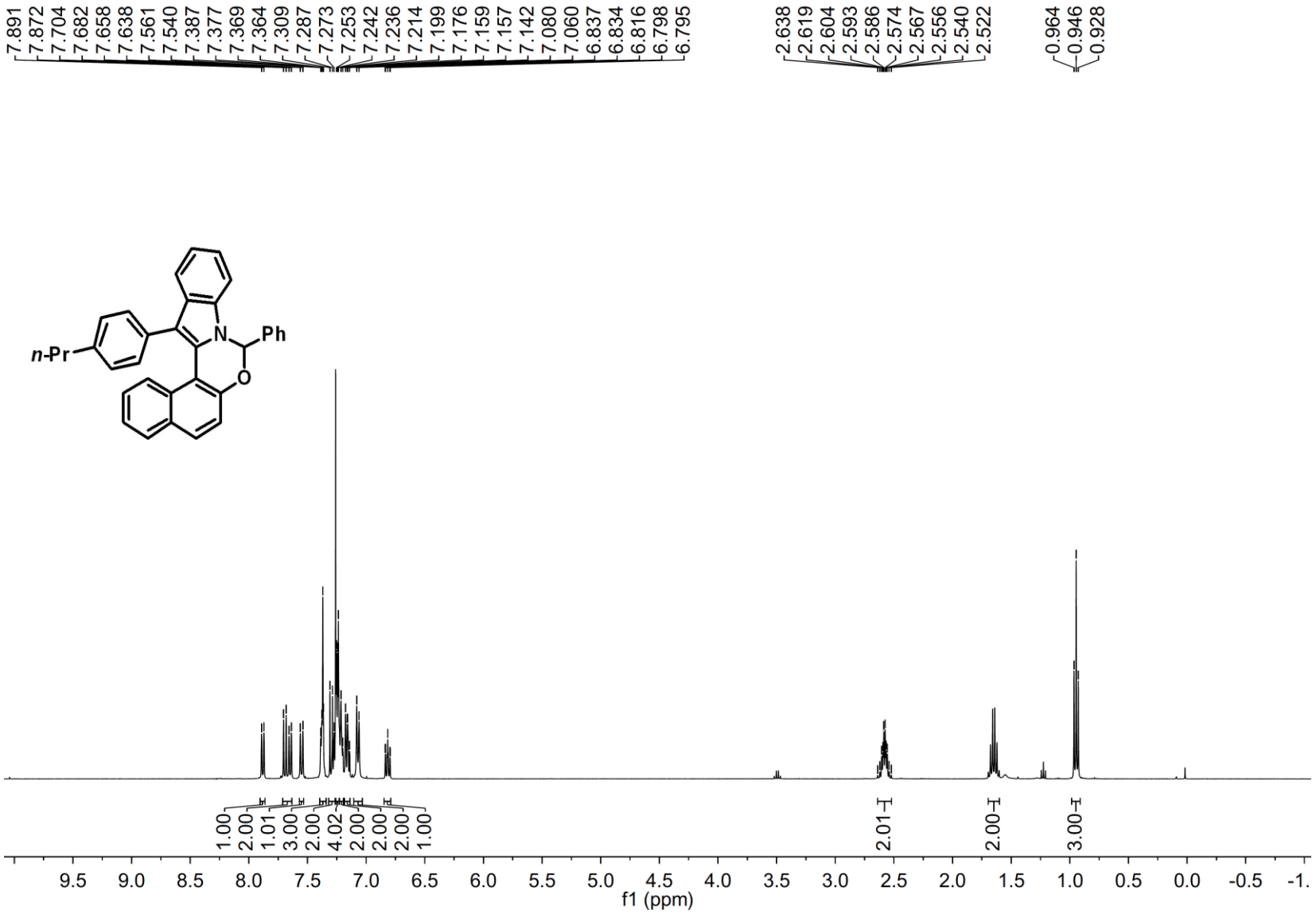
^{13}C NMR Spectrum of Compound **3a**



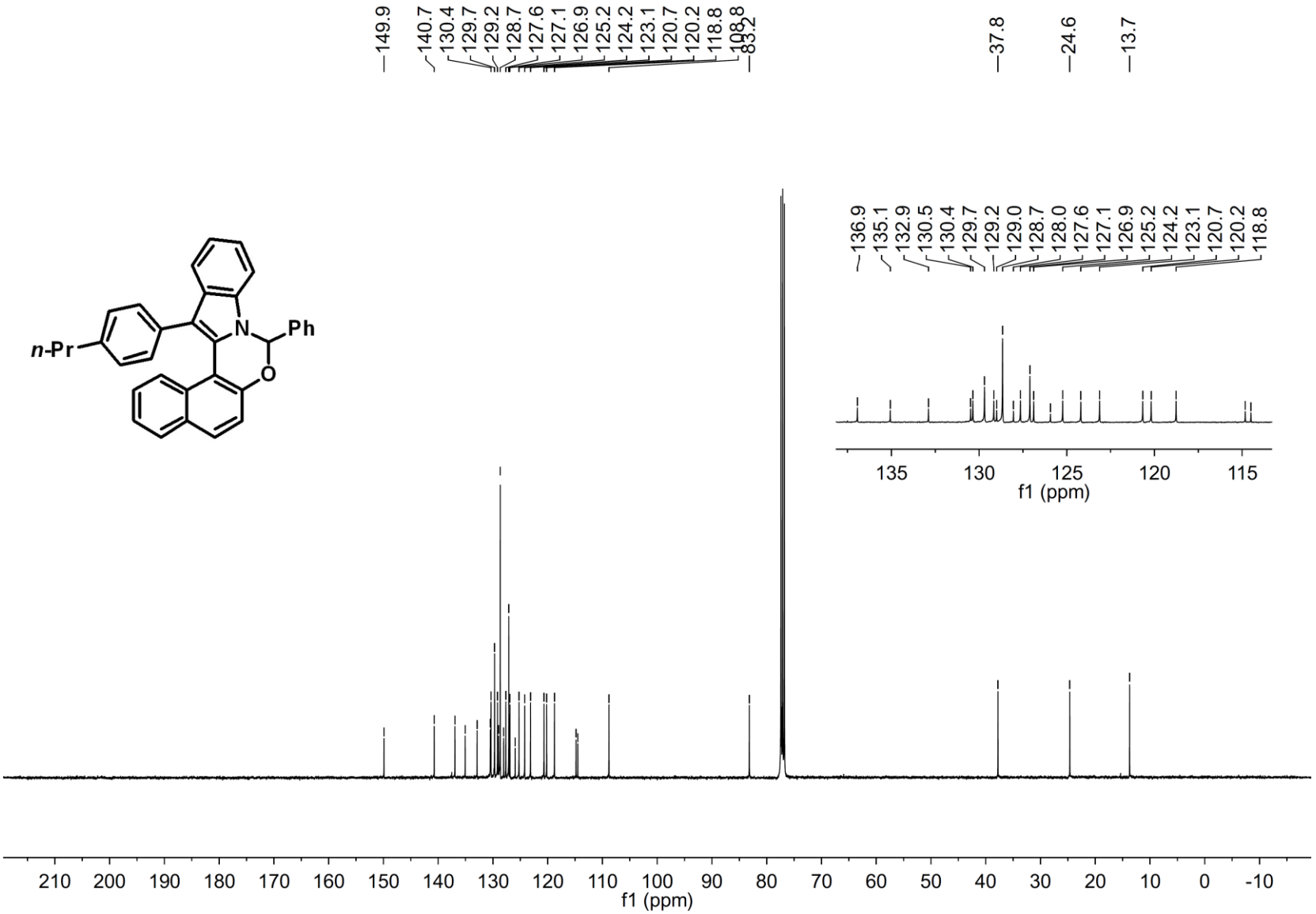
^{1}H NMR Spectrum of Compound **3b**



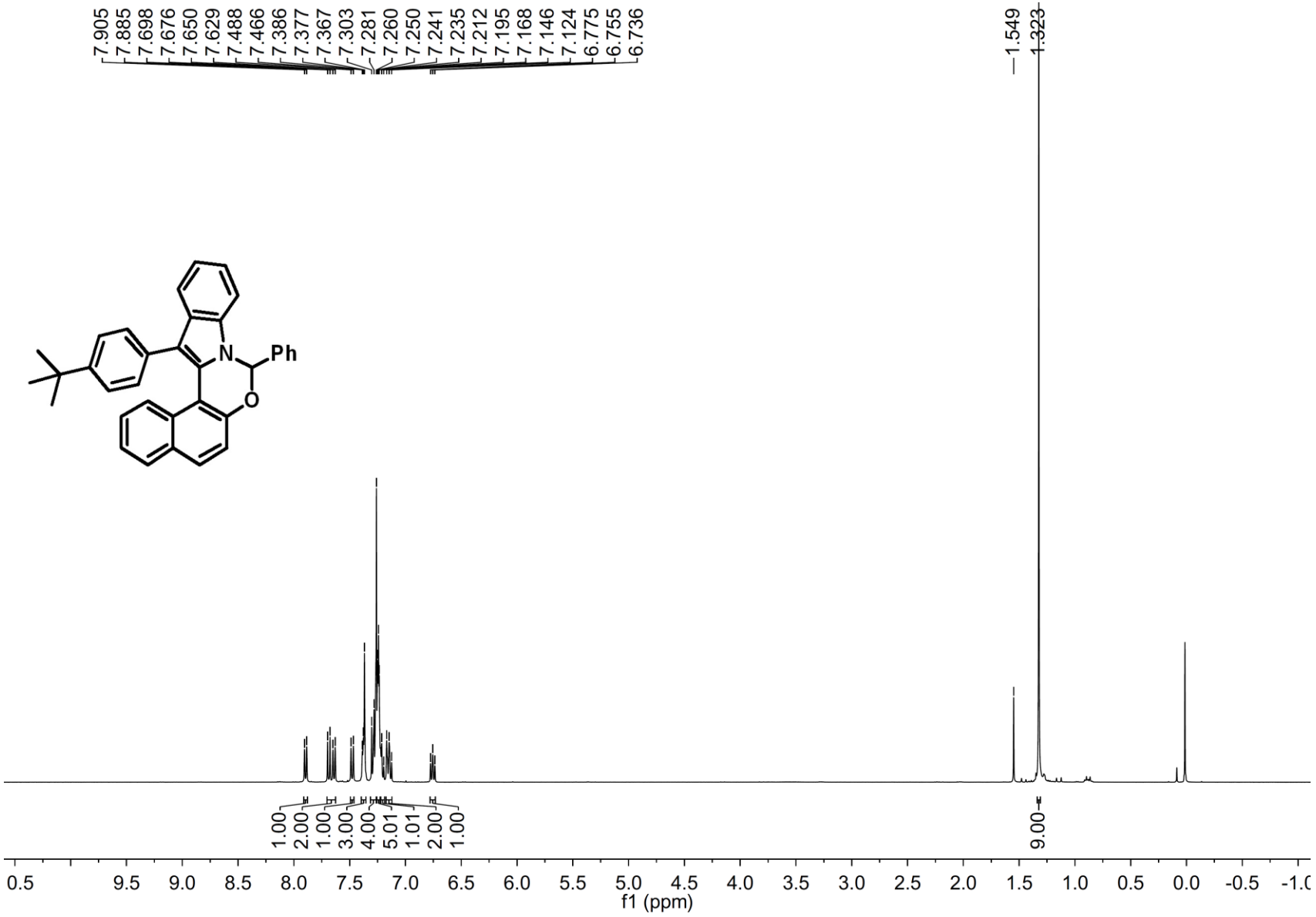
^{13}C NMR Spectrum of Compound **3b**



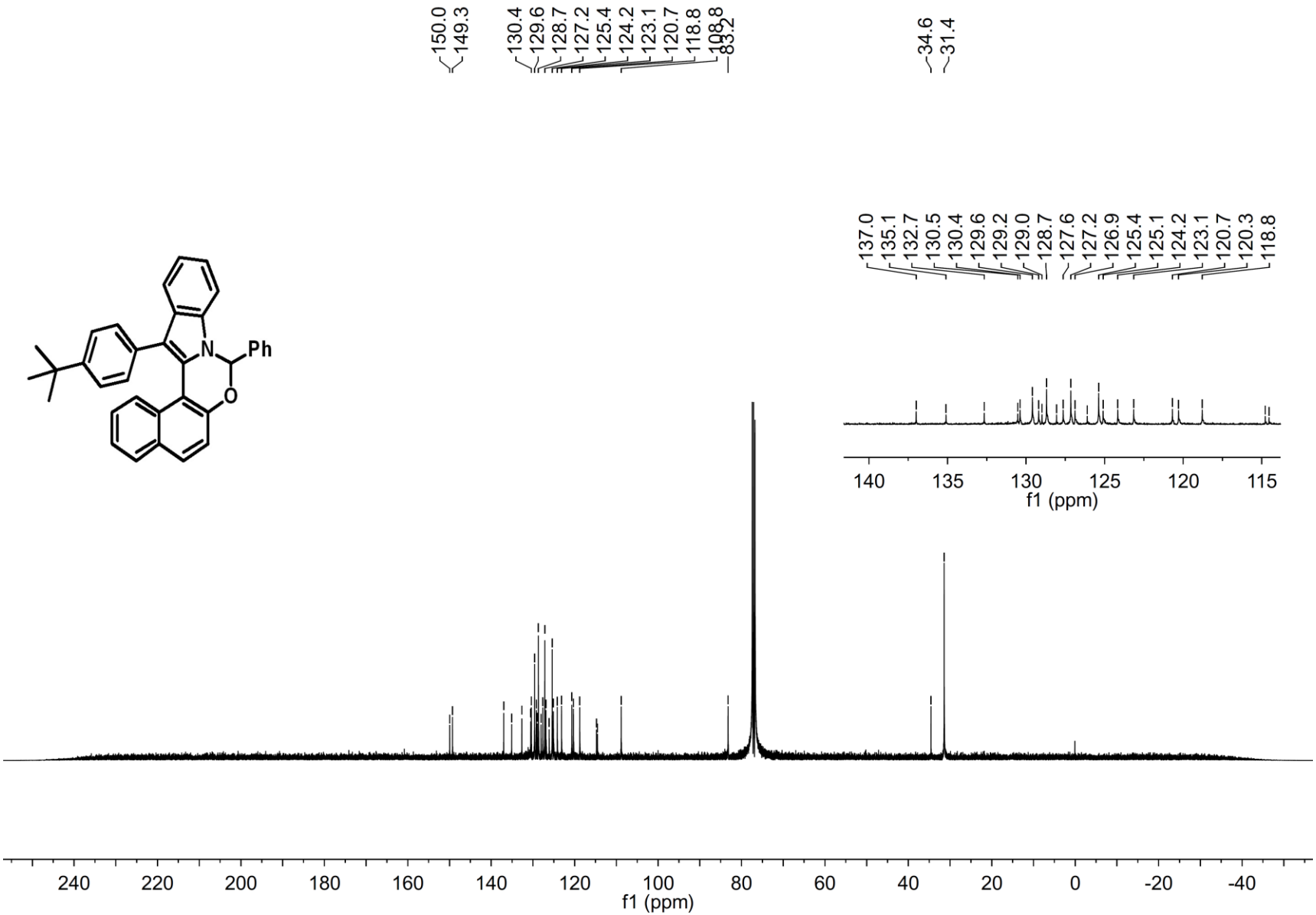
^{1}H NMR Spectrum of Compound **3c**



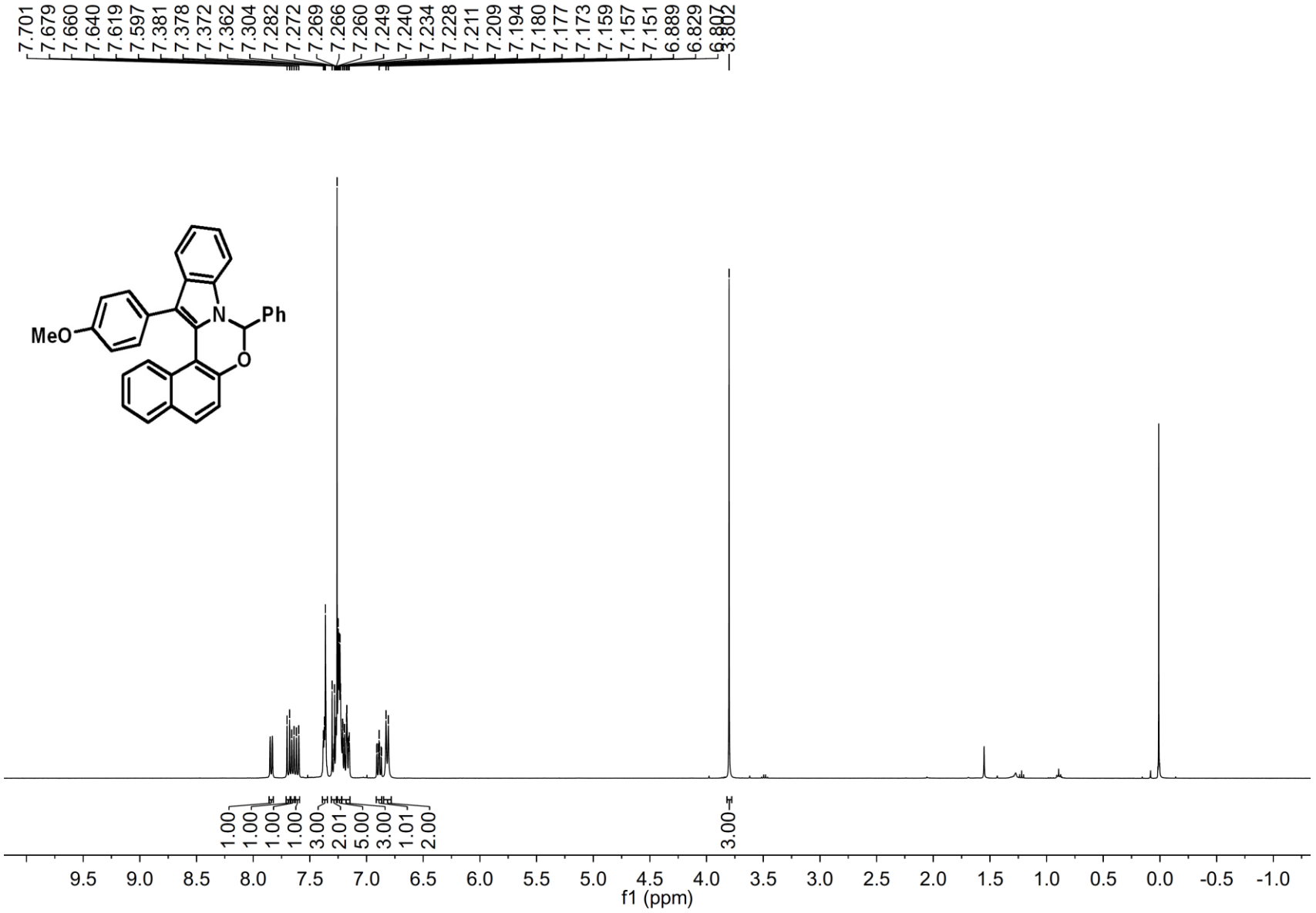
^{13}C NMR Spectrum of Compound **3d**



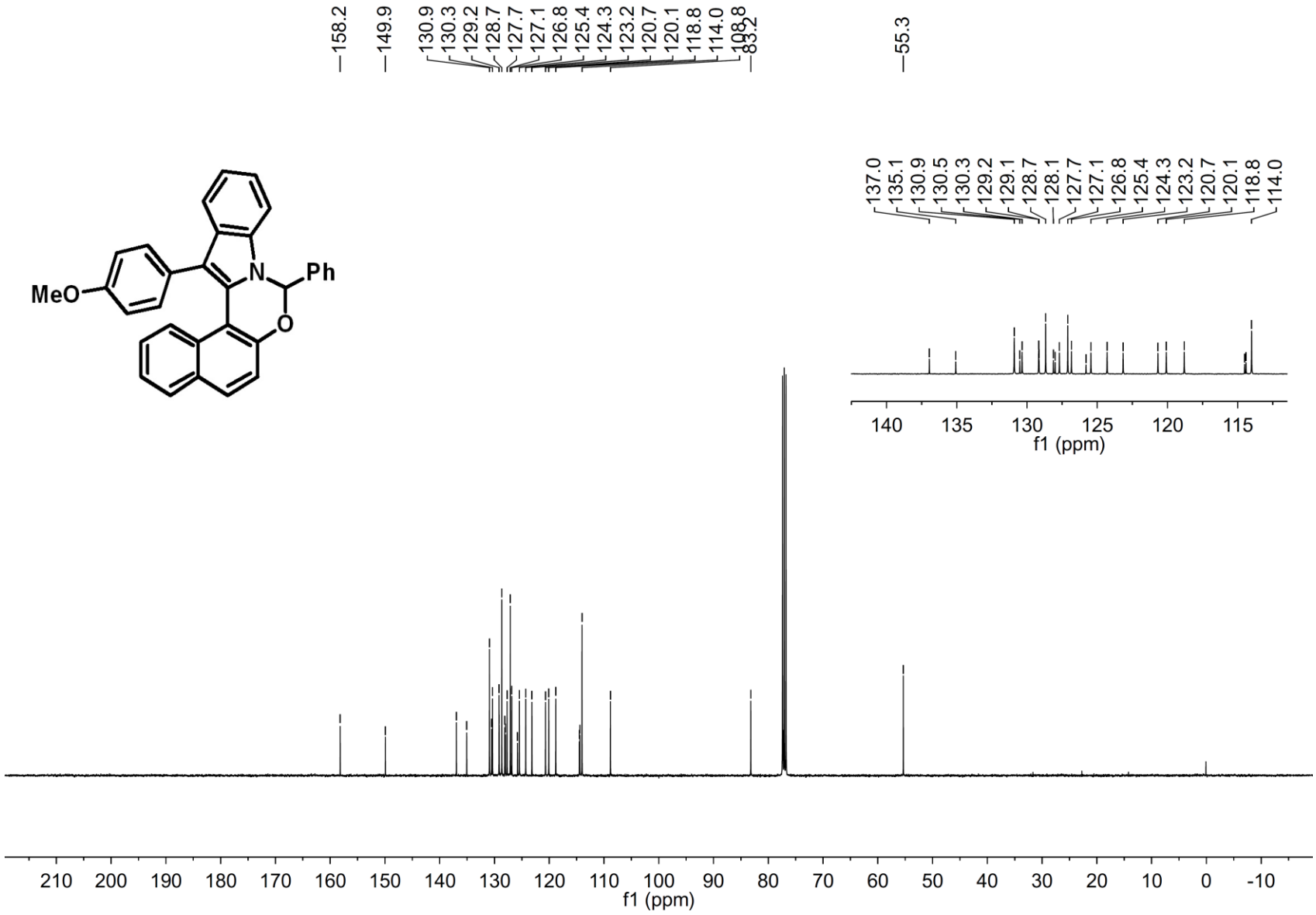
^{1}H NMR Spectrum of Compound **3d**



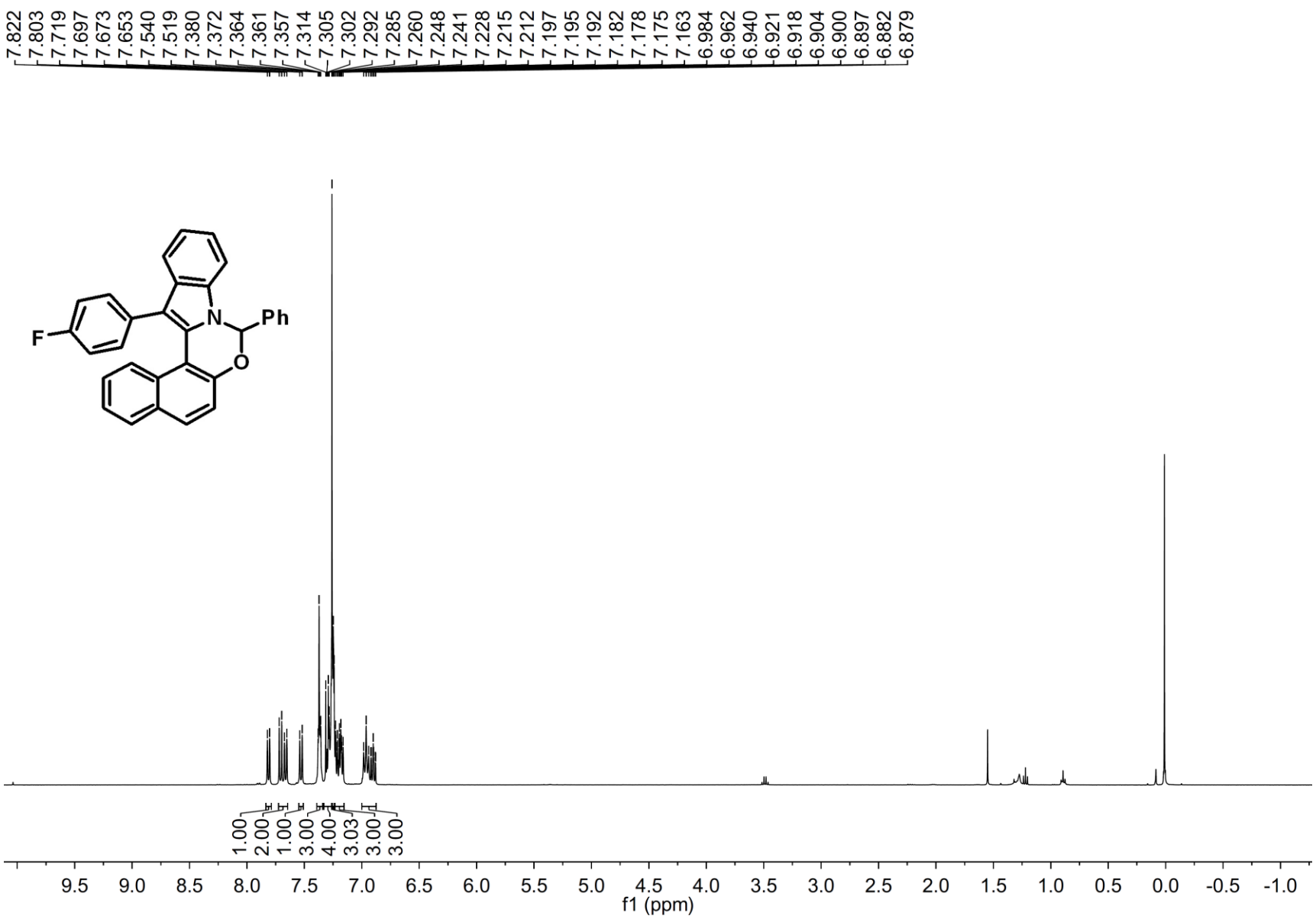
^{13}C NMR Spectrum of Compound **3d**



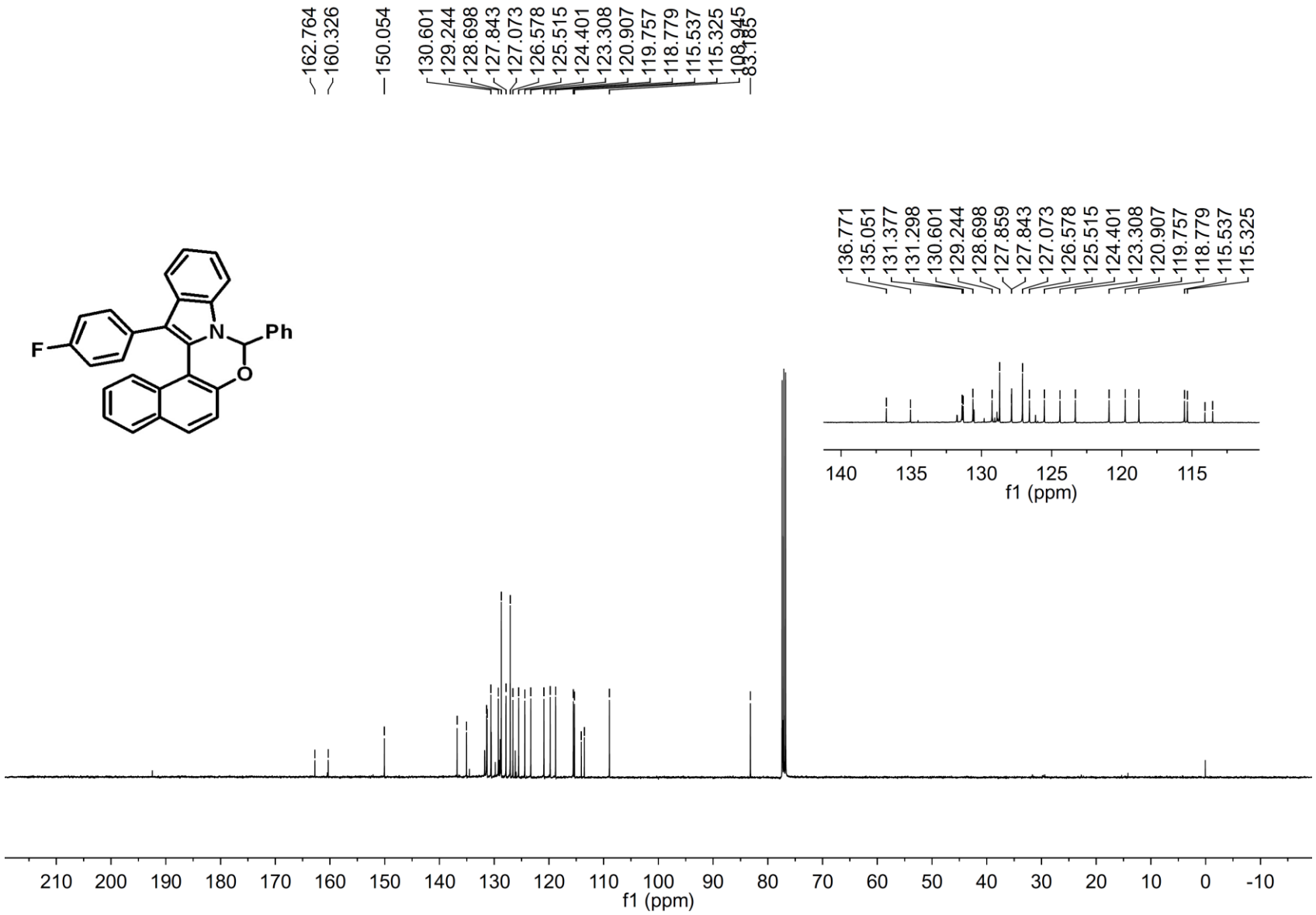
^{1}H NMR Spectrum of Compound **3e**



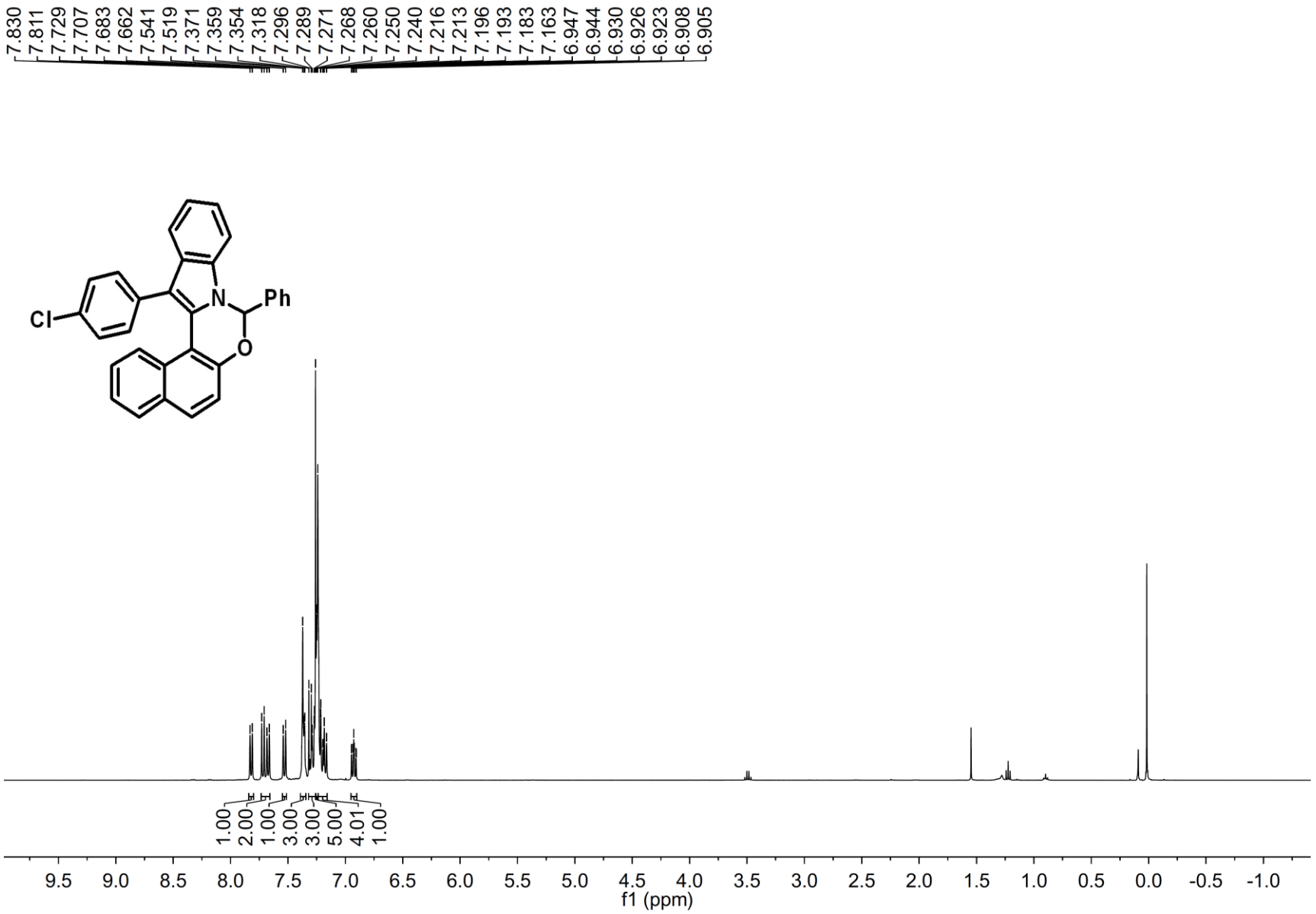
^{13}C NMR Spectrum of Compound **3e**



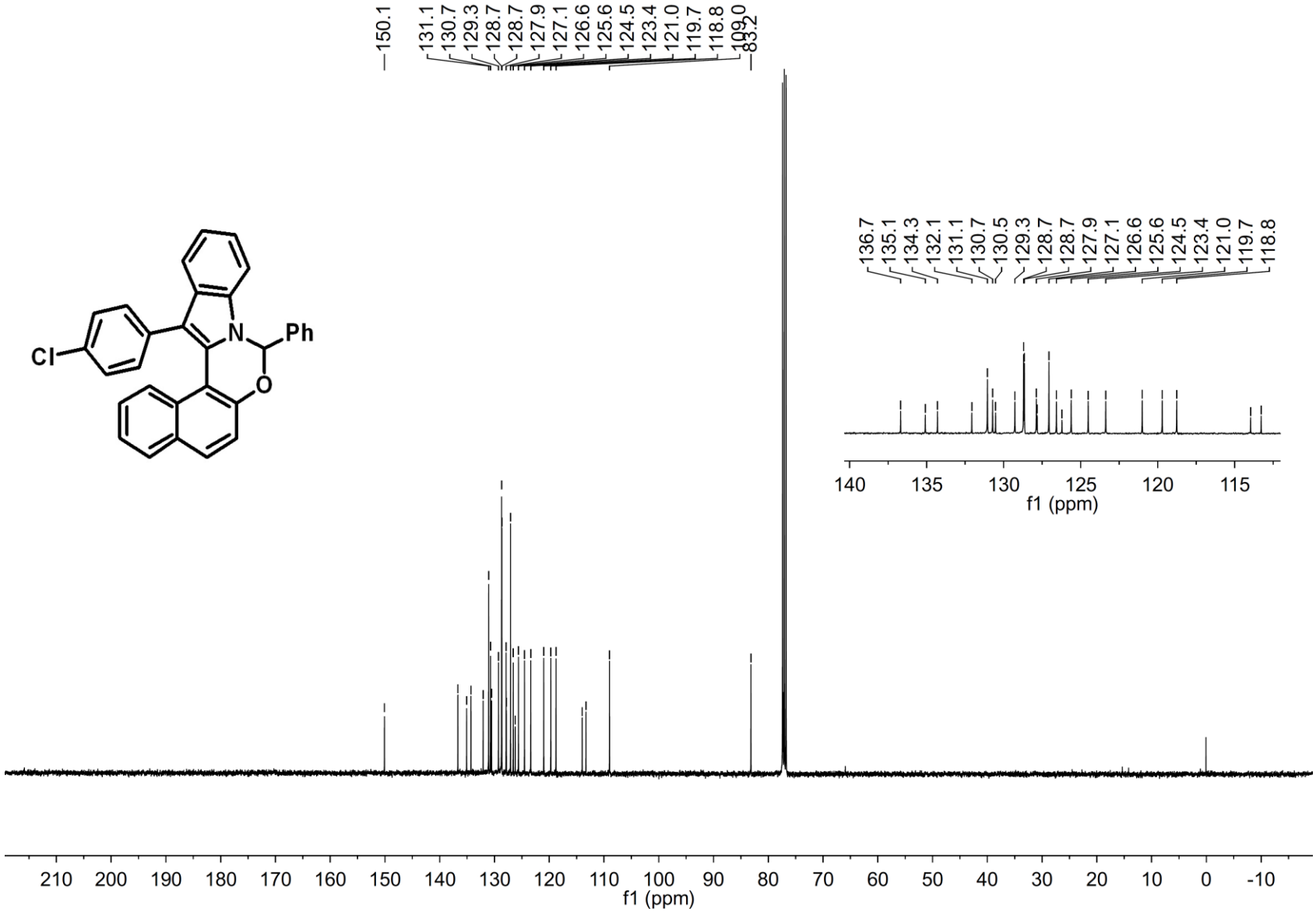
^{1}H NMR Spectrum of Compound **3f**



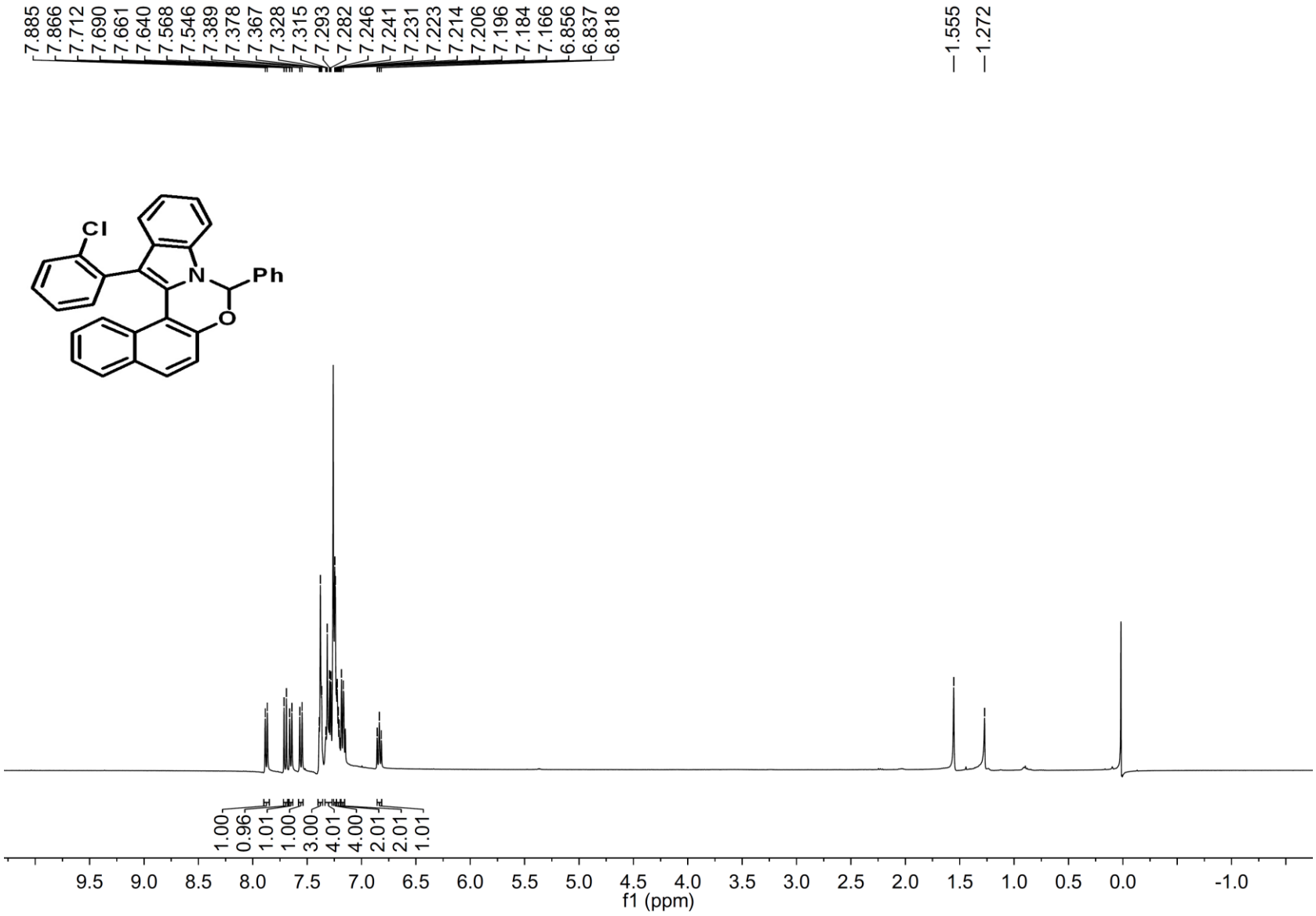
^{13}C NMR Spectrum of Compound **3f**



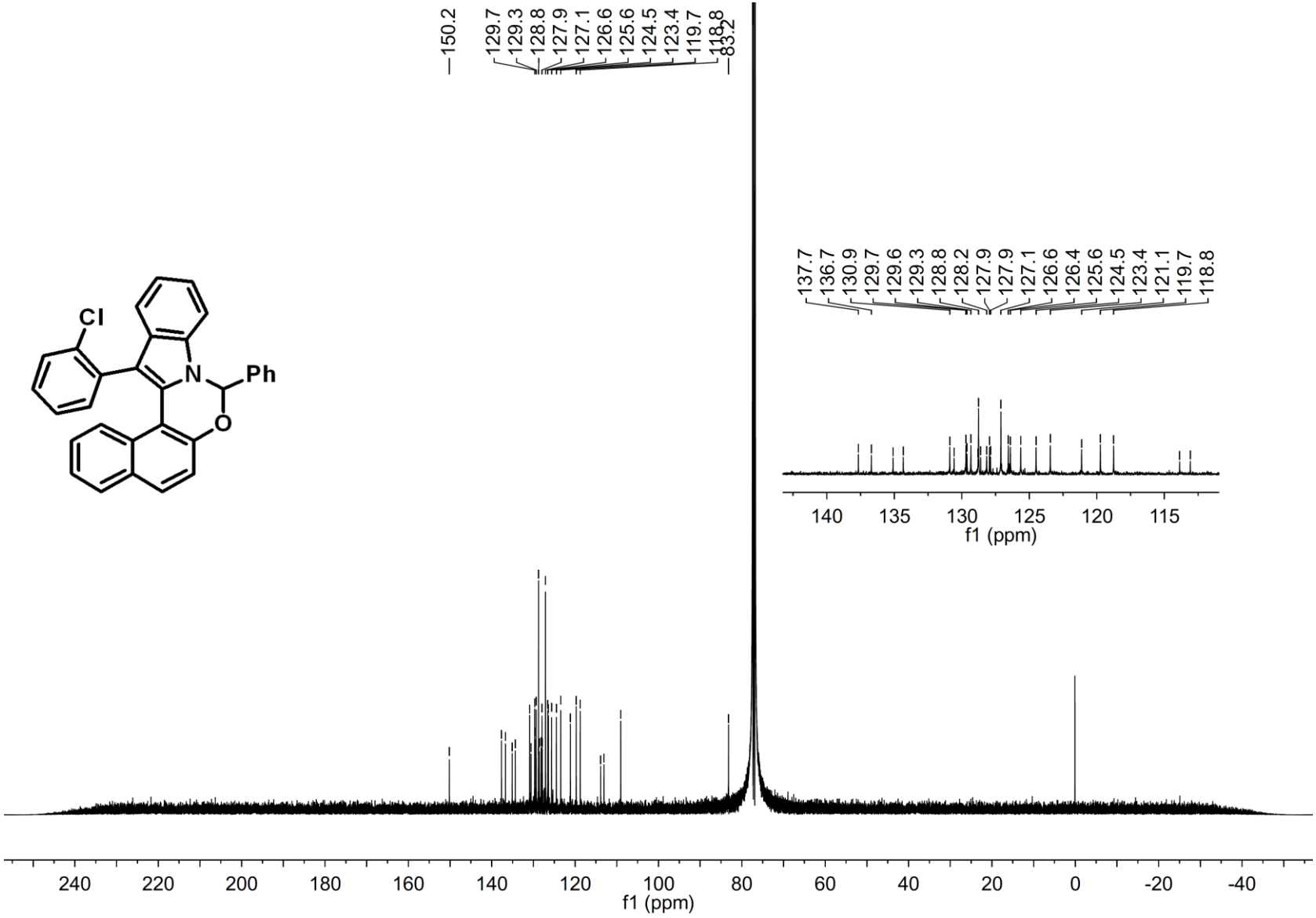
^{1}H NMR Spectrum of Compound **3g**



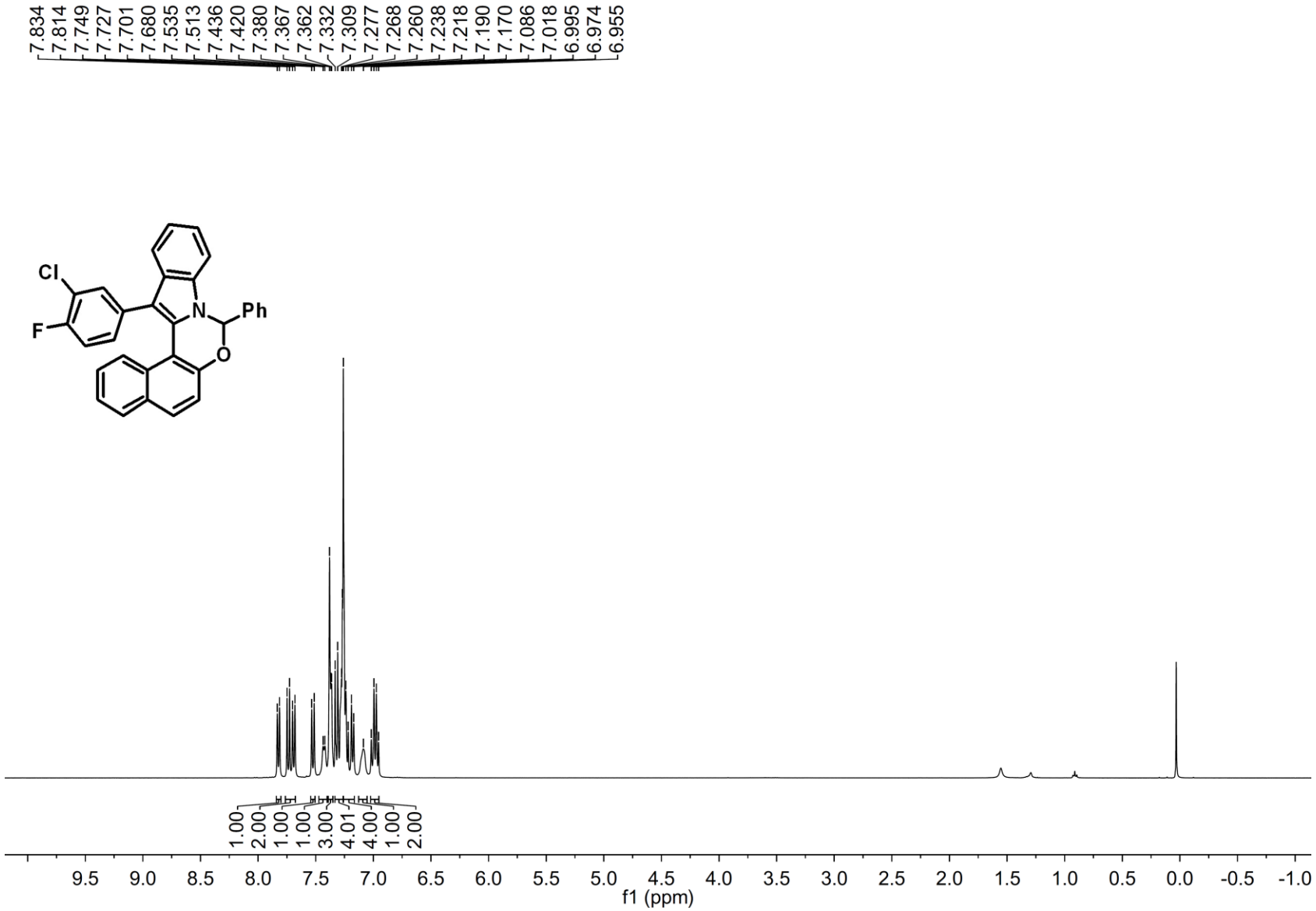
^{13}C NMR Spectrum of Compound **3g**



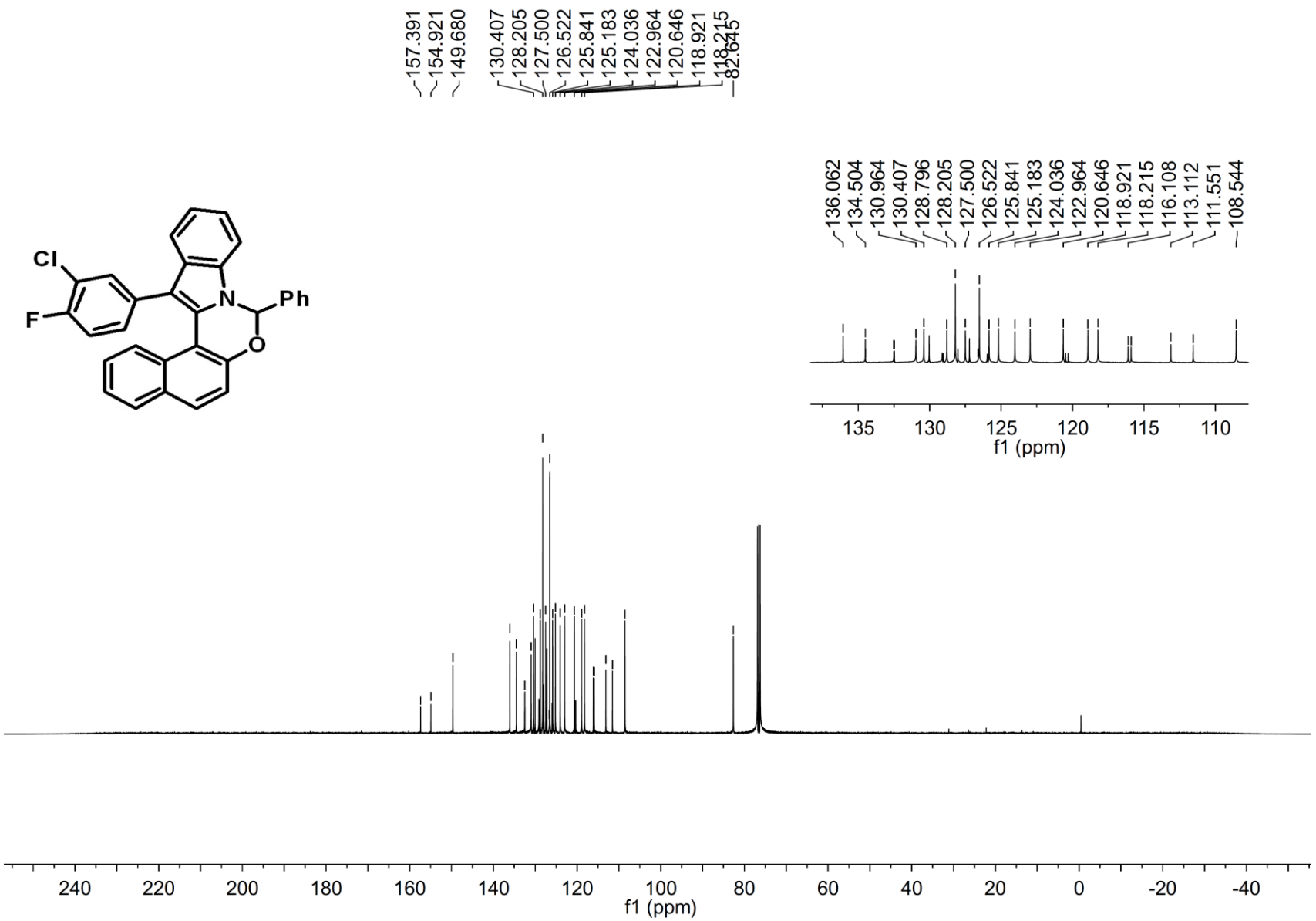
^{1}H NMR Spectrum of Compound **3h**



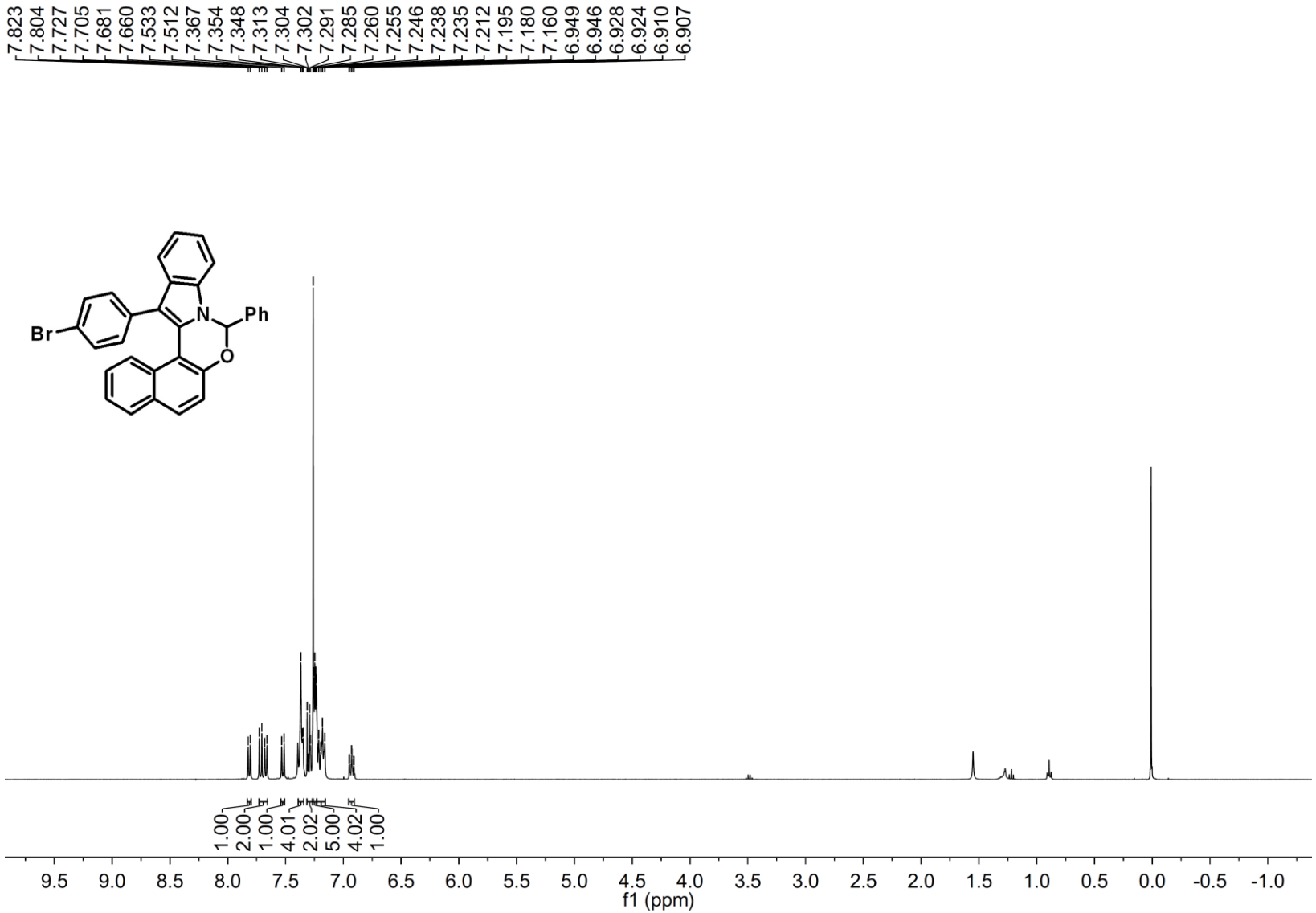
^{13}C NMR Spectrum of Compound **3h**



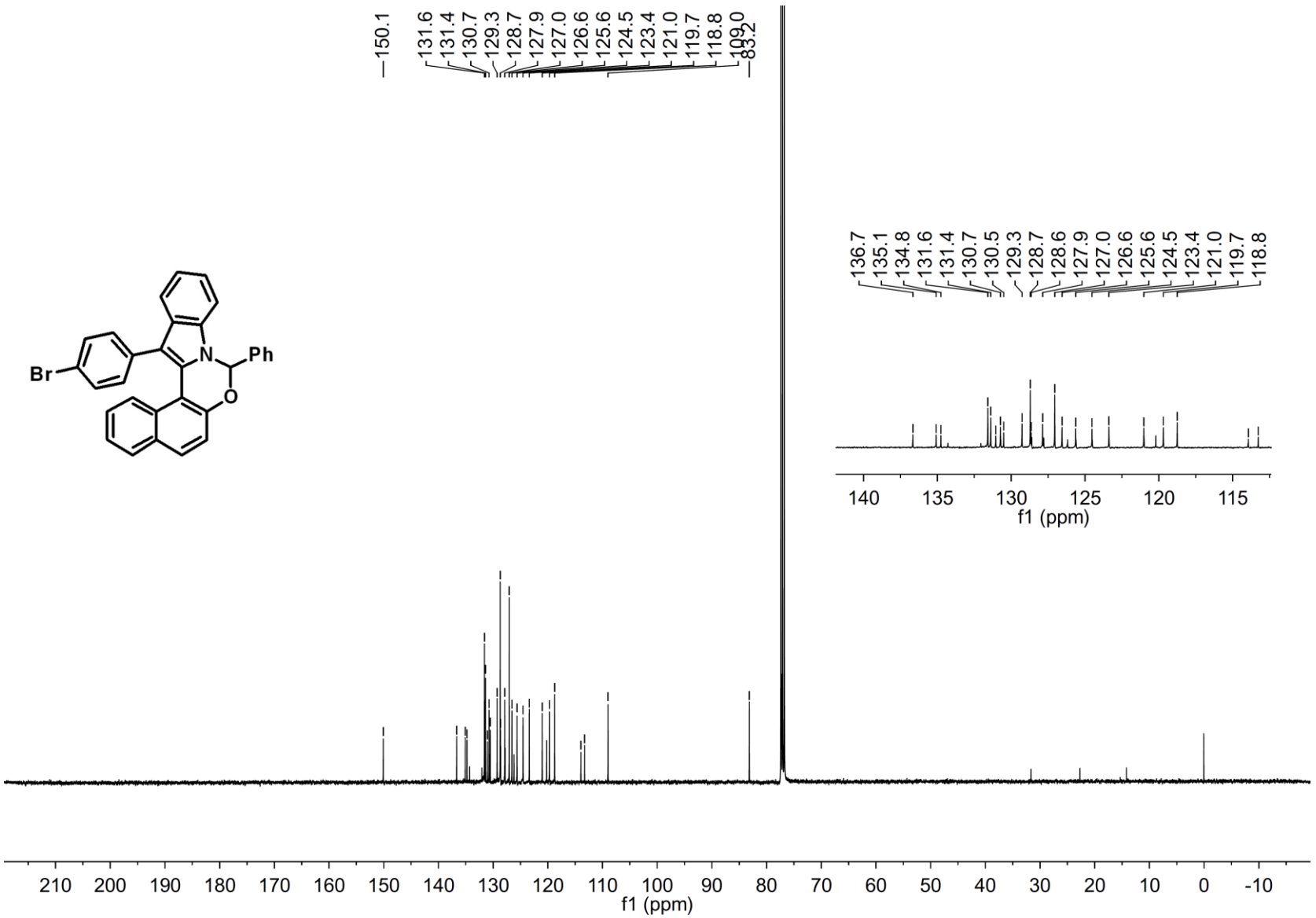
^{1}H NMR Spectrum of Compound **3i**



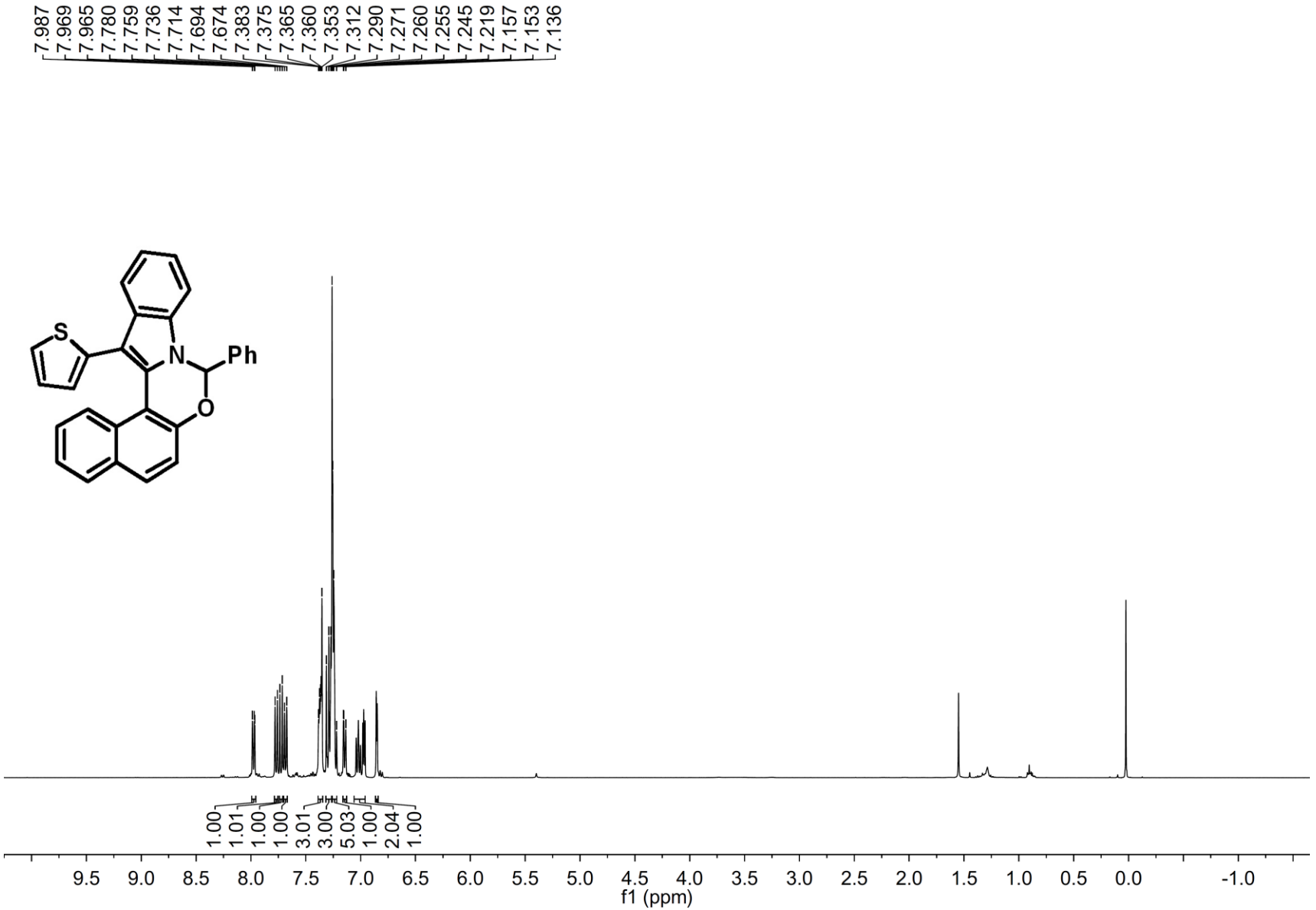
^{13}C NMR Spectrum of Compound **3i**



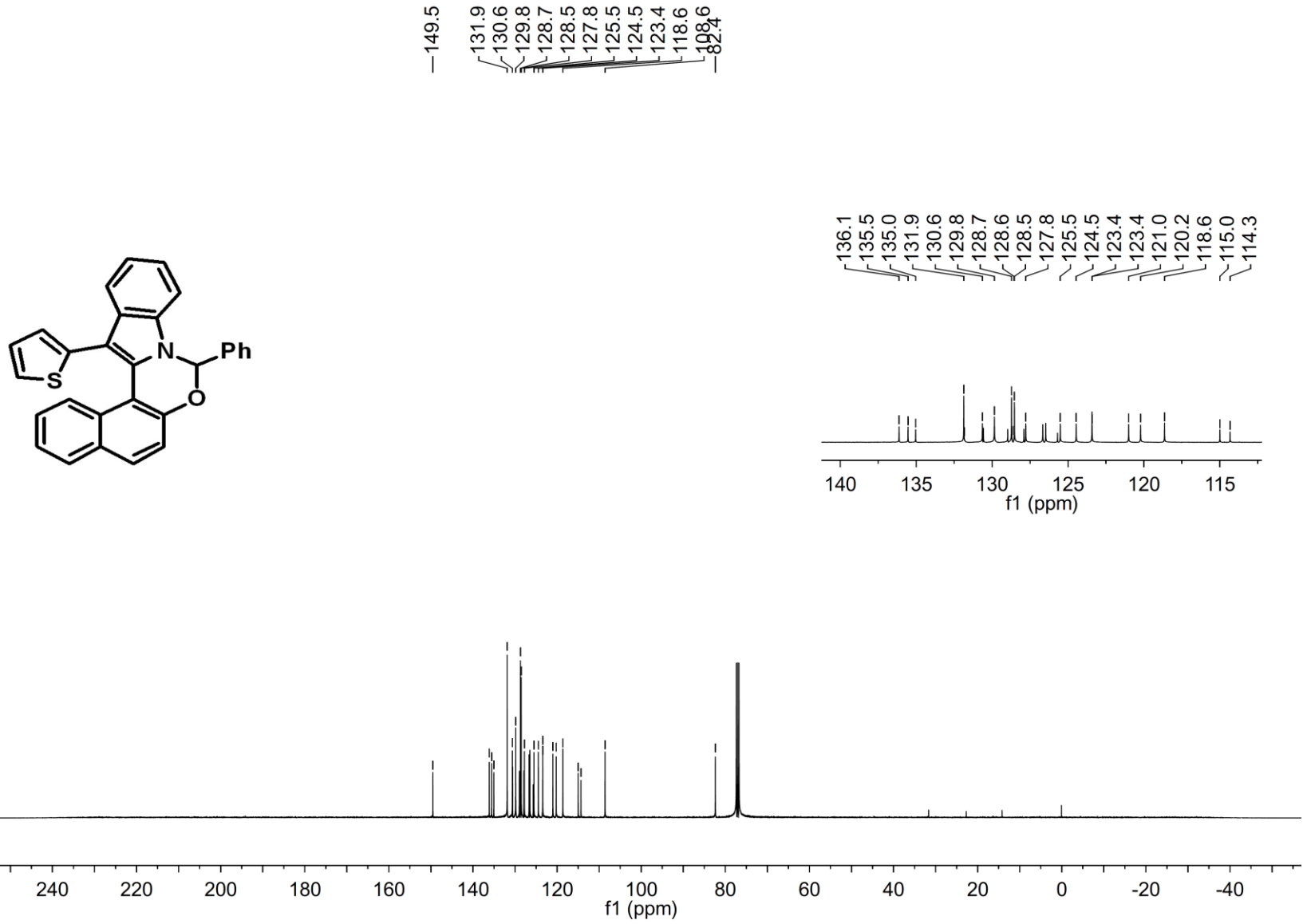
^{1}H NMR Spectrum of Compound **3j**



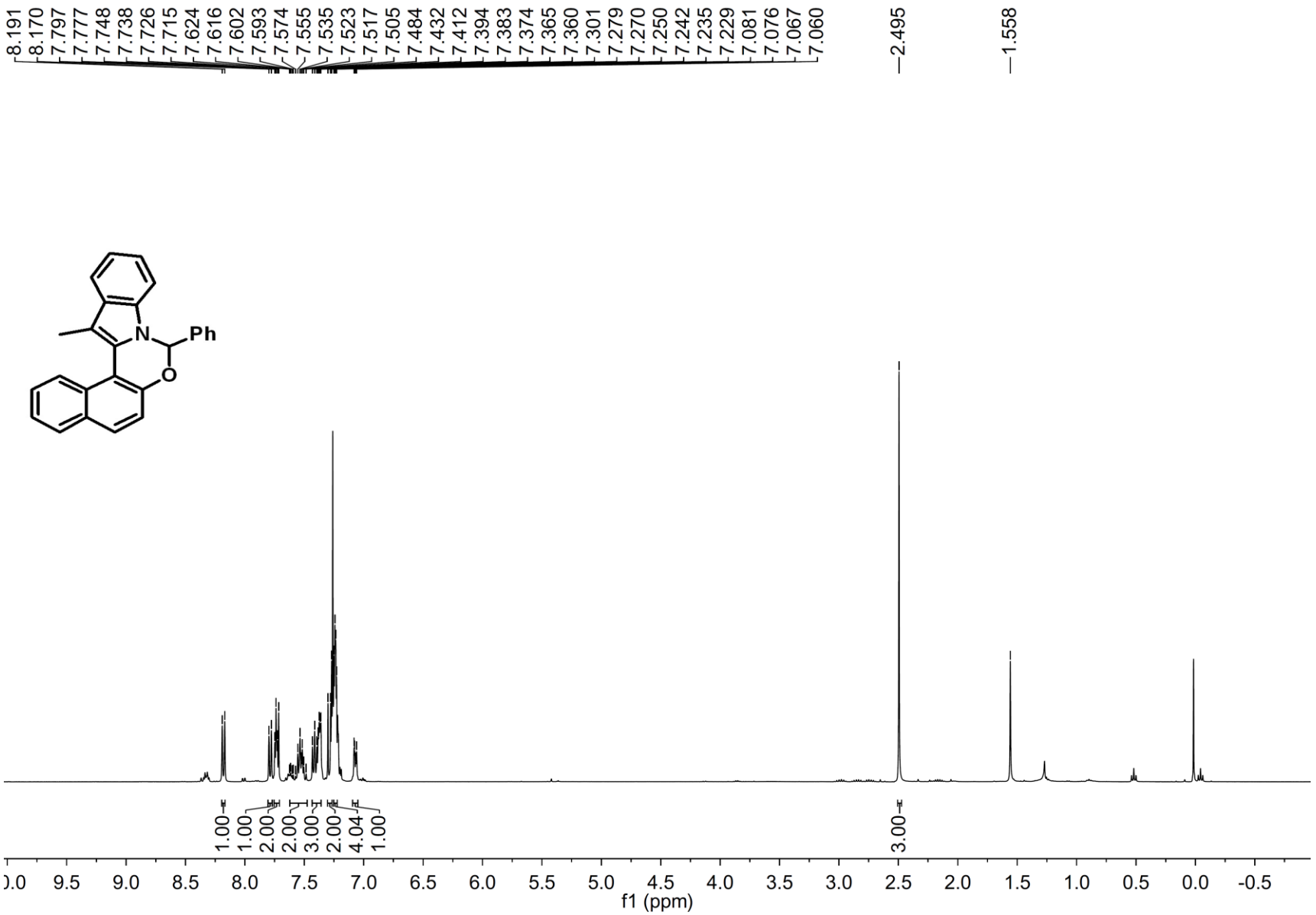
^{13}C NMR Spectrum of Compound **3j**



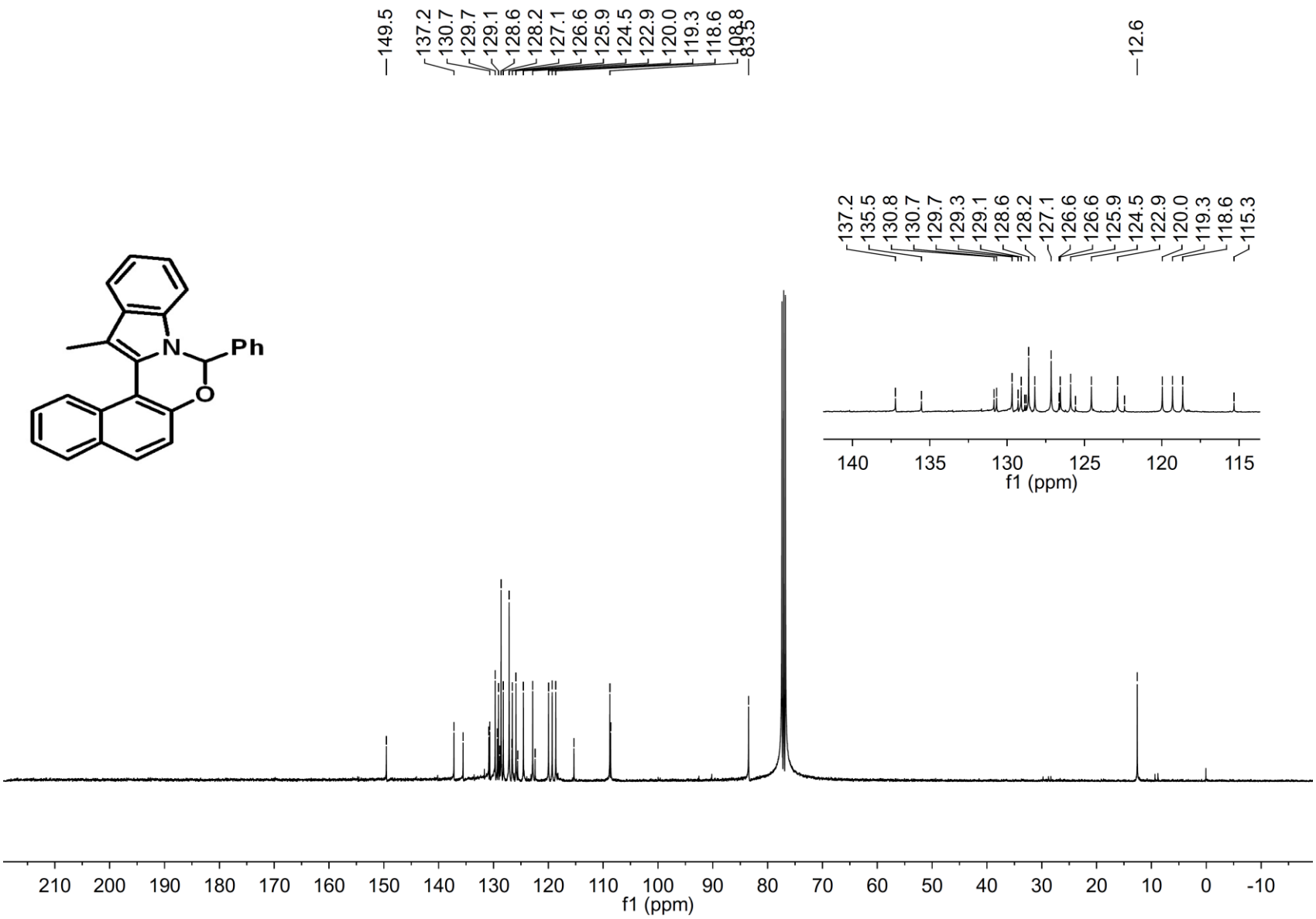
^{1}H NMR Spectrum of Compound **3k**



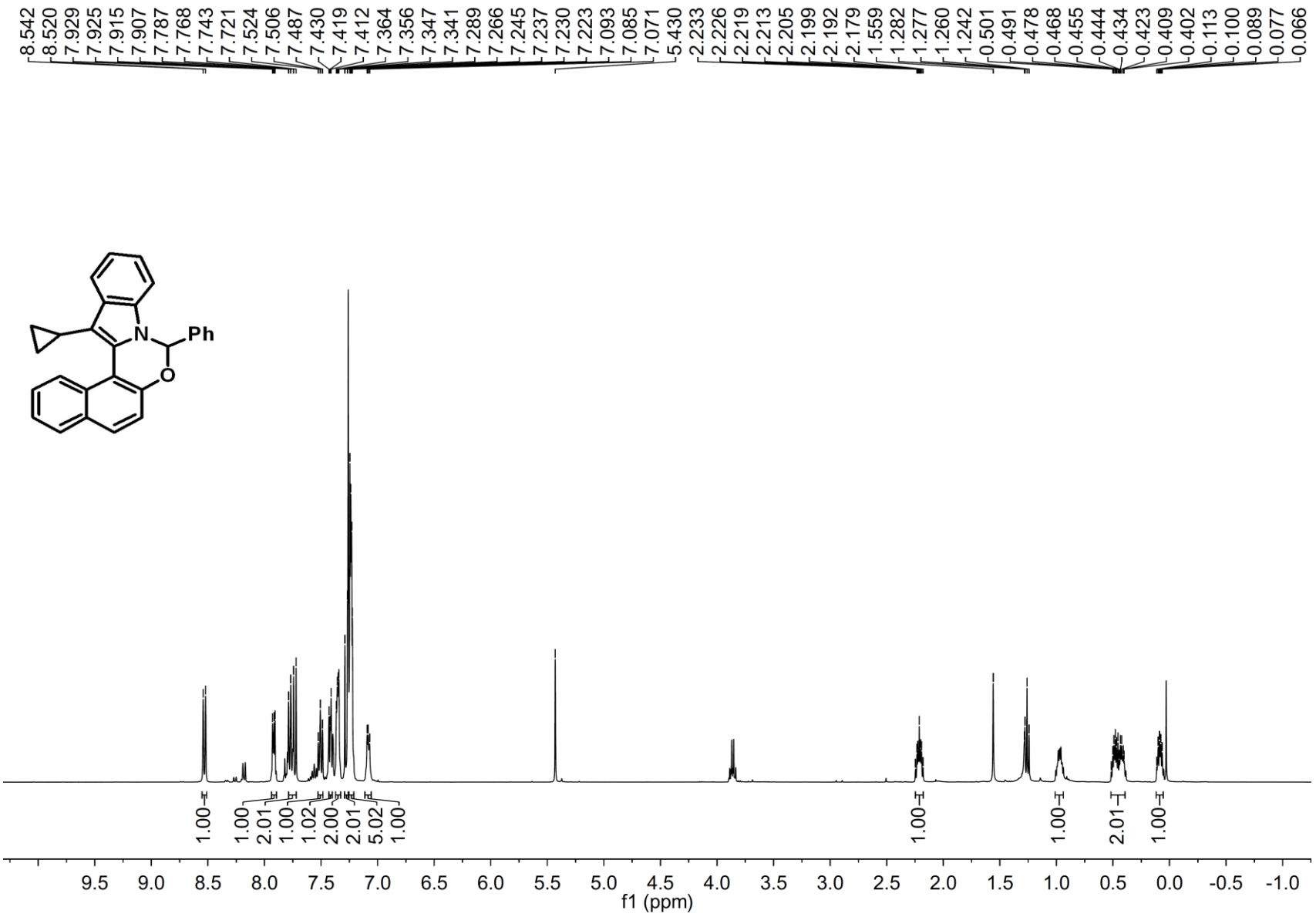
^{13}C NMR Spectrum of Compound **3k**



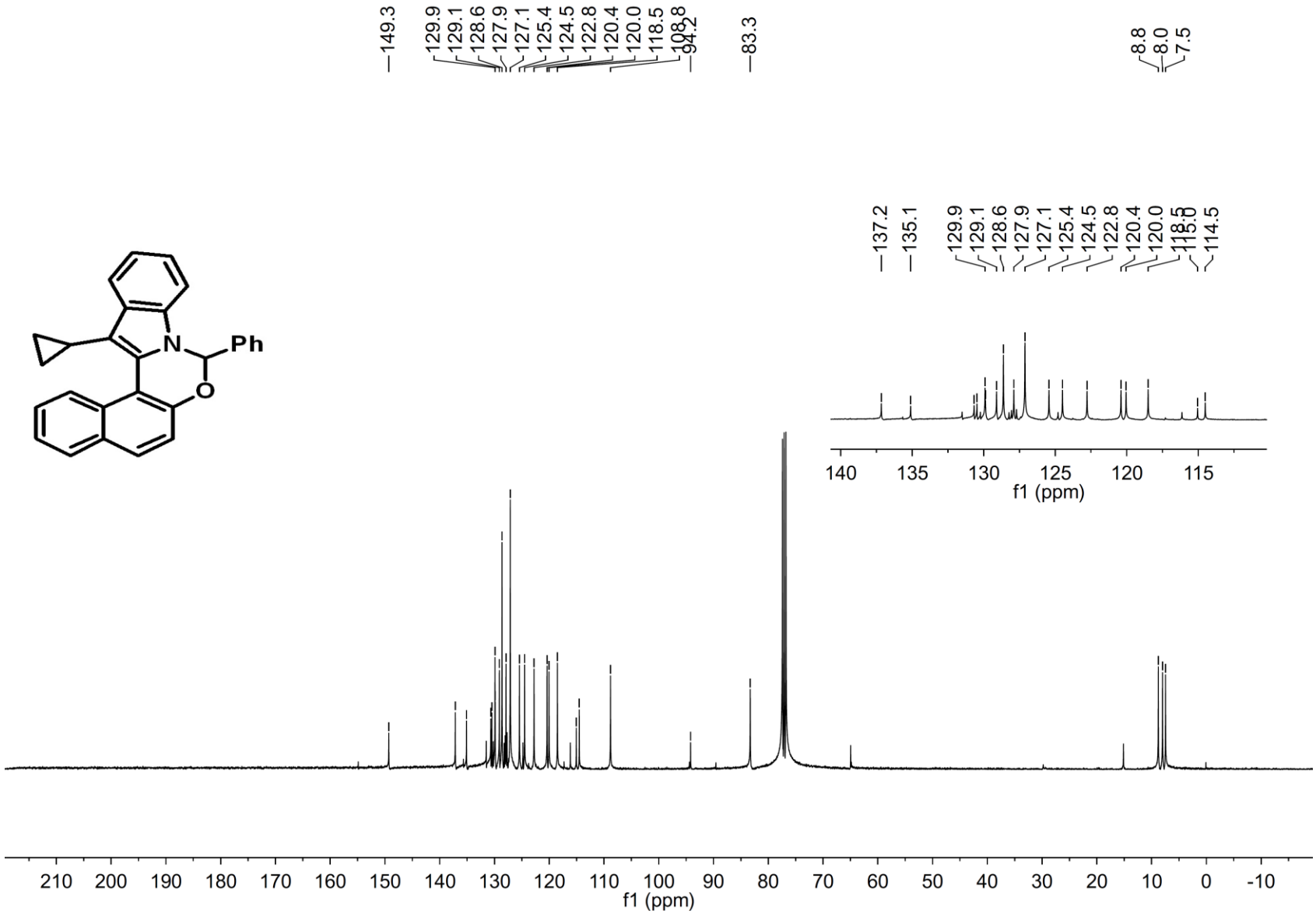
^{1}H NMR Spectrum of Compound **3l**



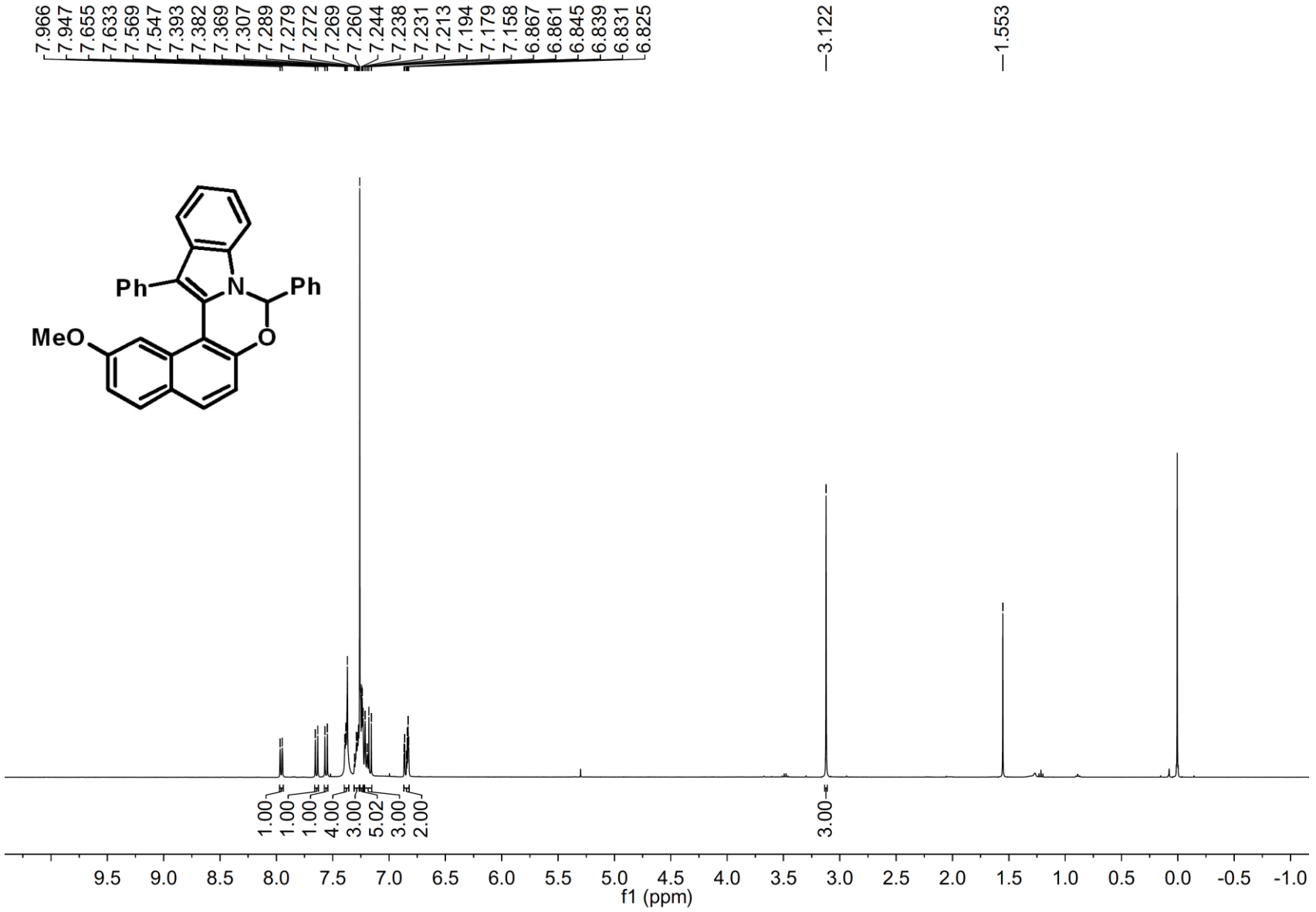
^{13}C NMR Spectrum of Compound **3l**



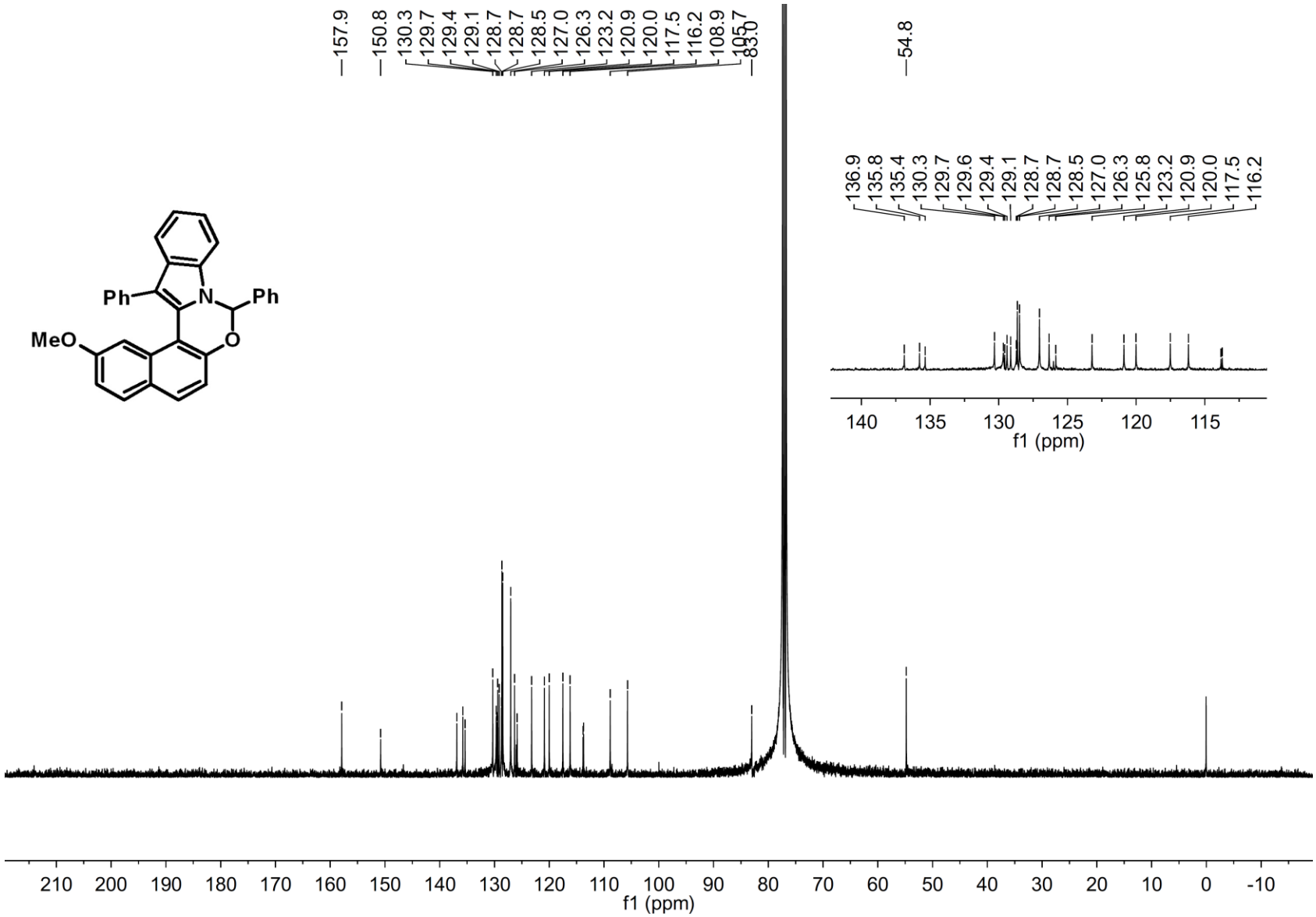
^{1}H NMR Spectrum of Compound **3m**



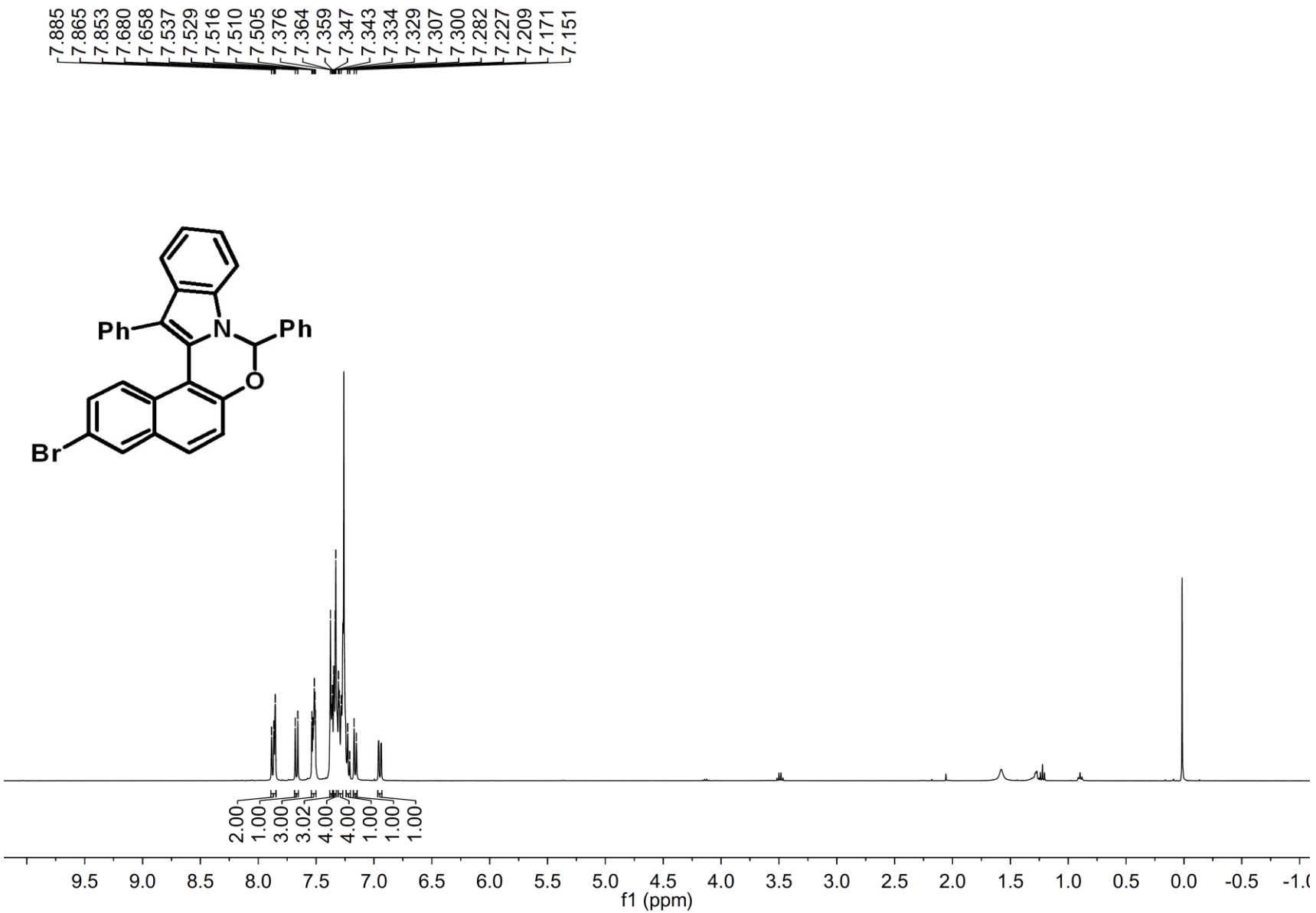
^{13}C NMR Spectrum of Compound **3m**



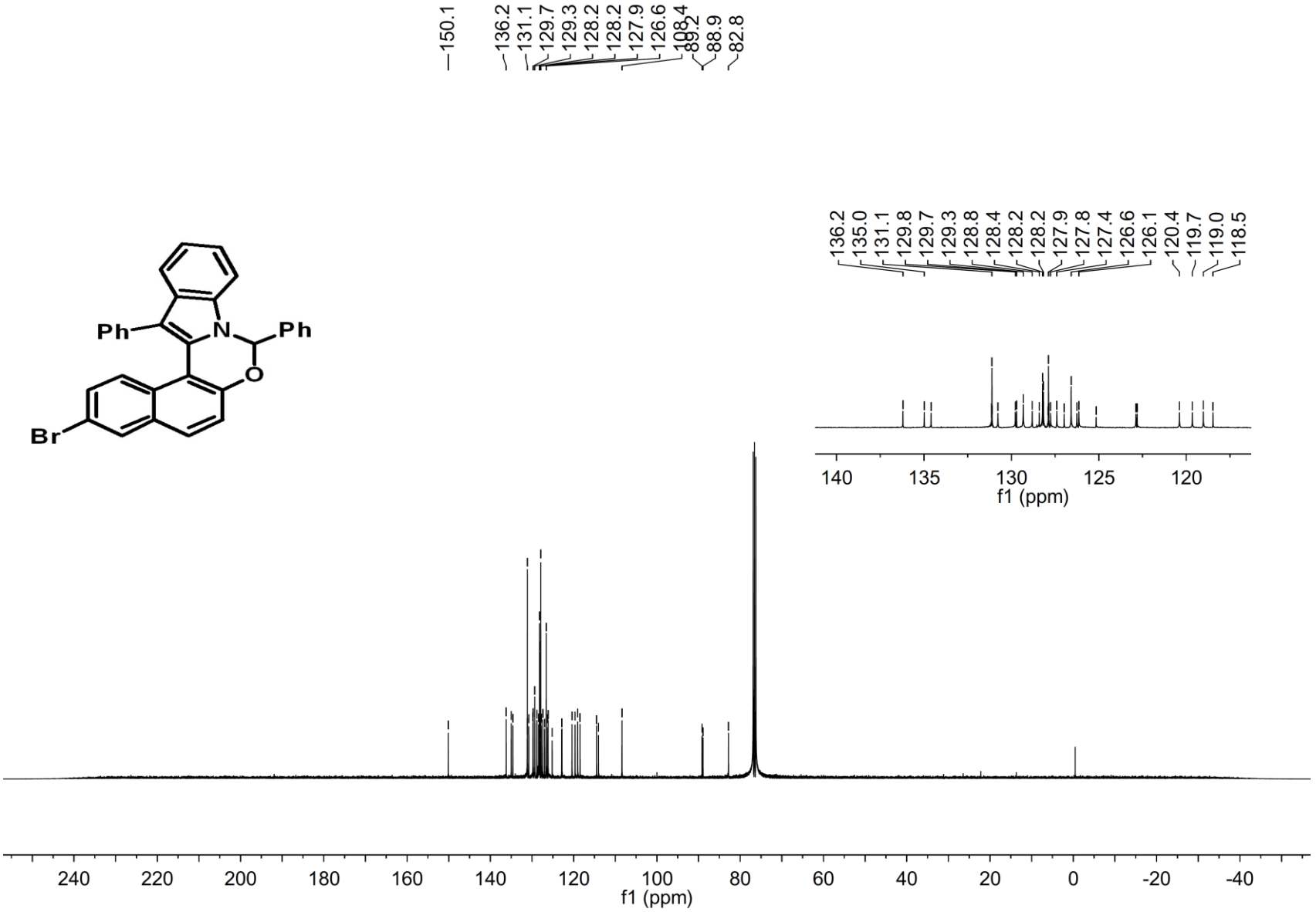
^{1}H NMR Spectrum of Compound **3o**



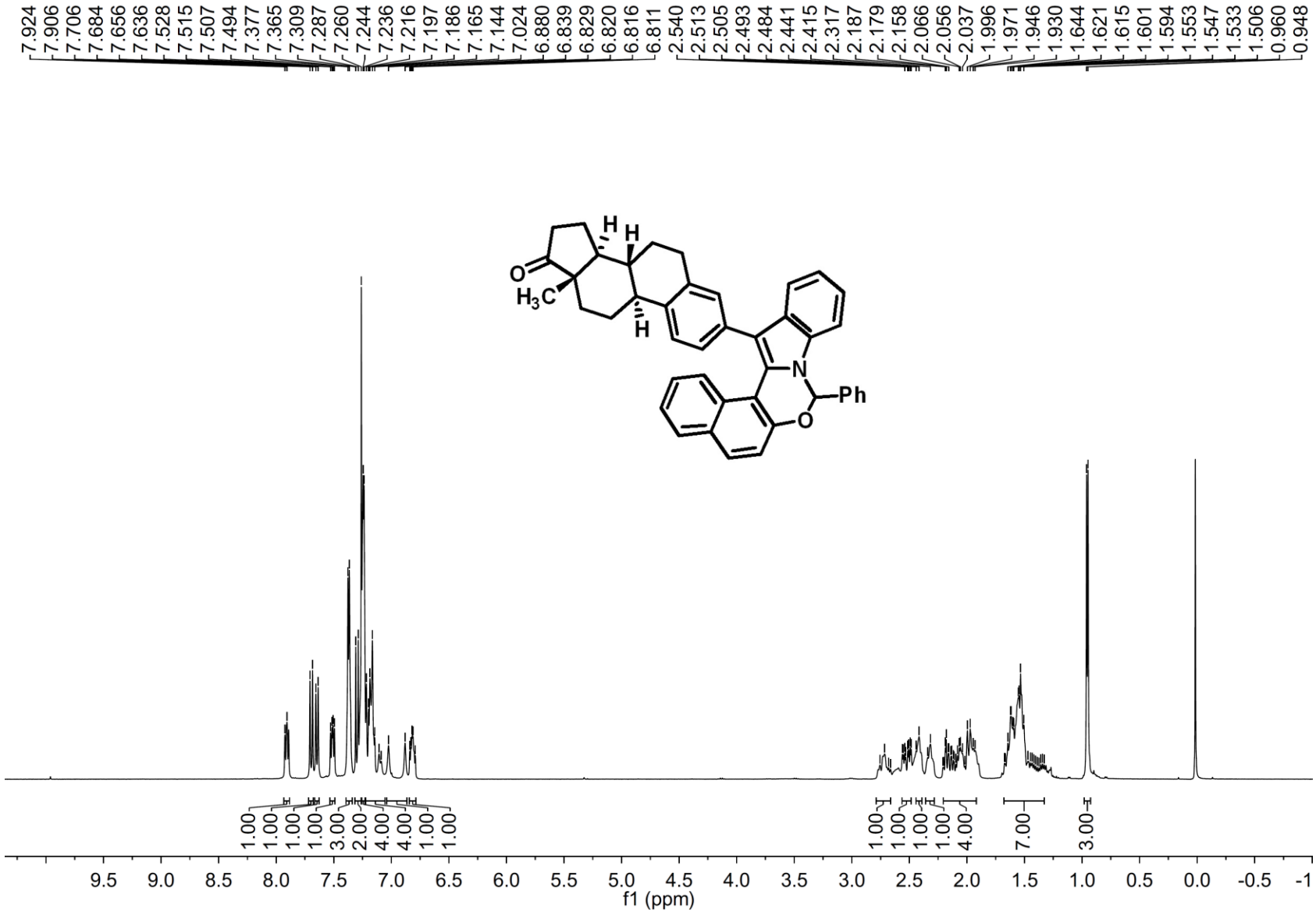
^{13}C NMR Spectrum of Compound **3o**



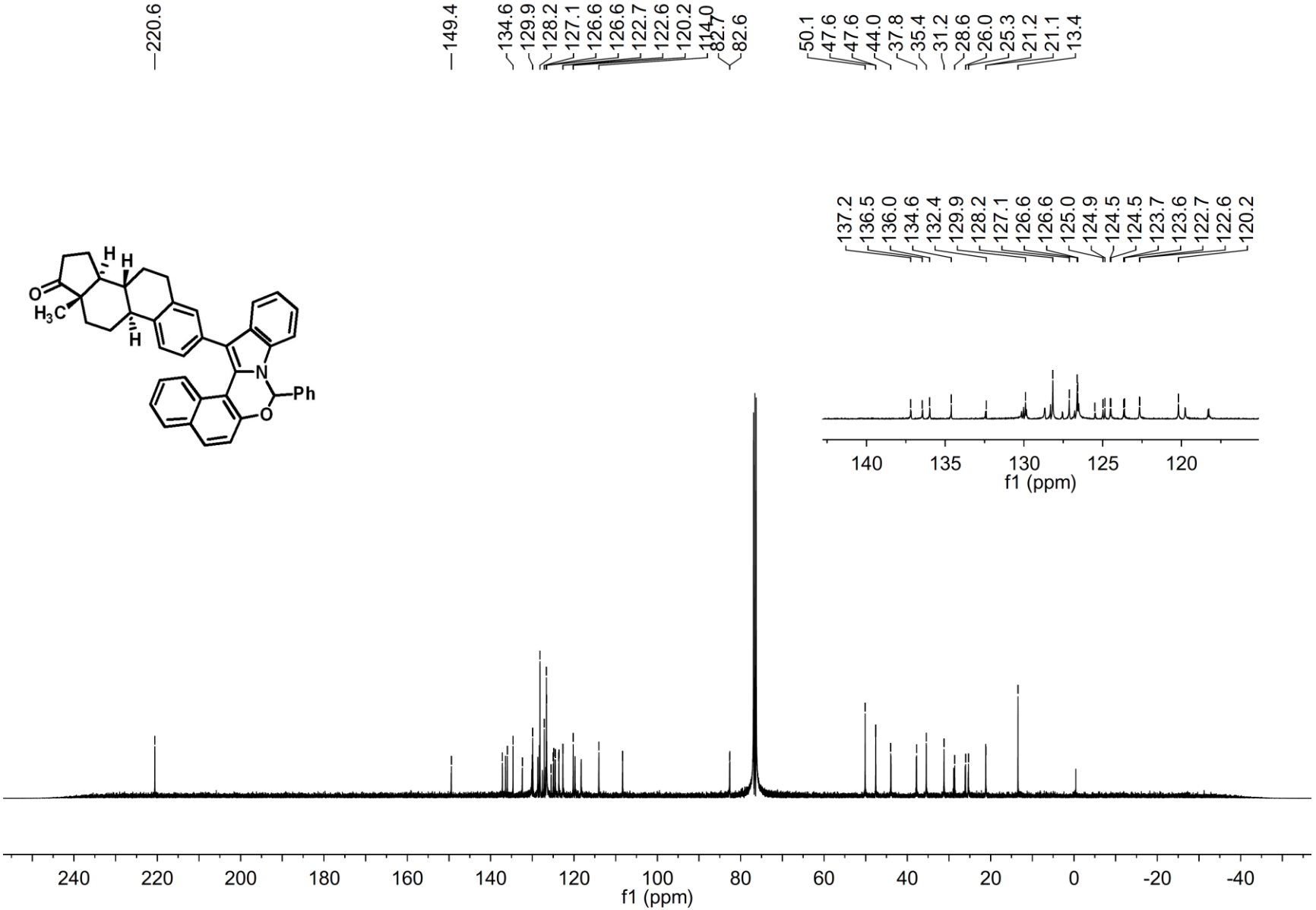
^{1}H NMR Spectrum of Compound **3p**



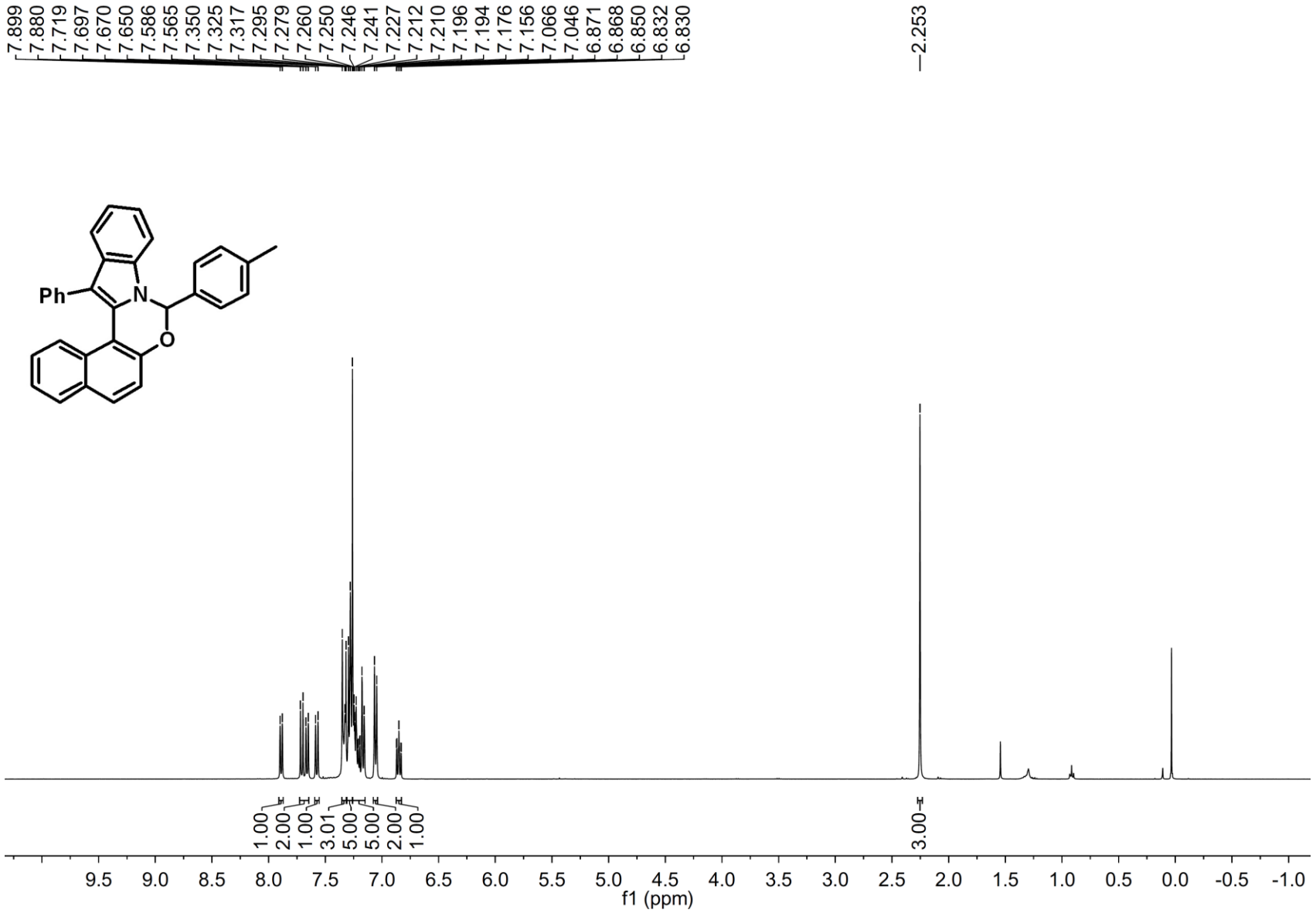
^{13}C NMR Spectrum of Compound **3p**



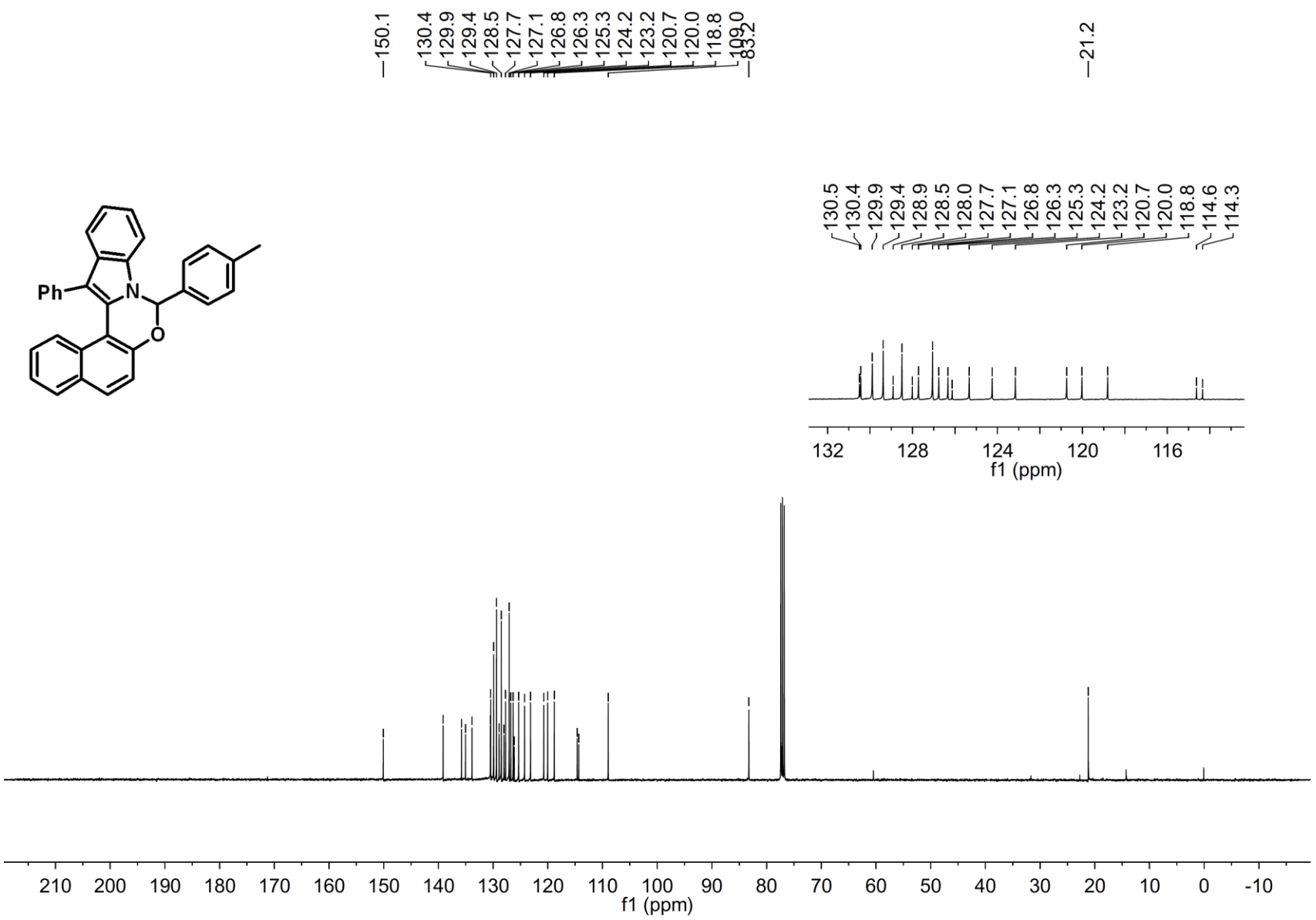
^{1}H NMR Spectrum of Compound **3q**



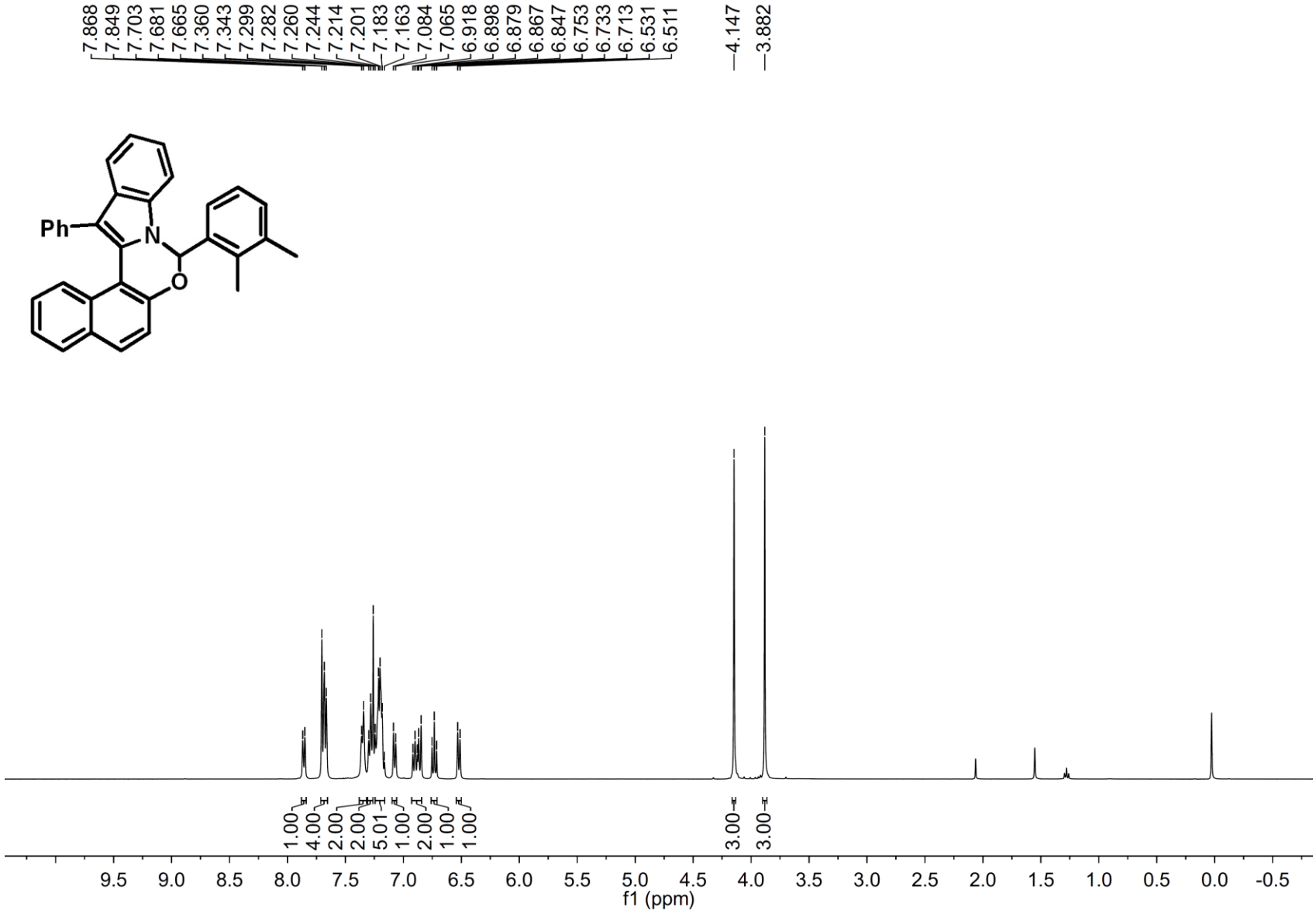
^{13}C NMR Spectrum of Compound **3q**



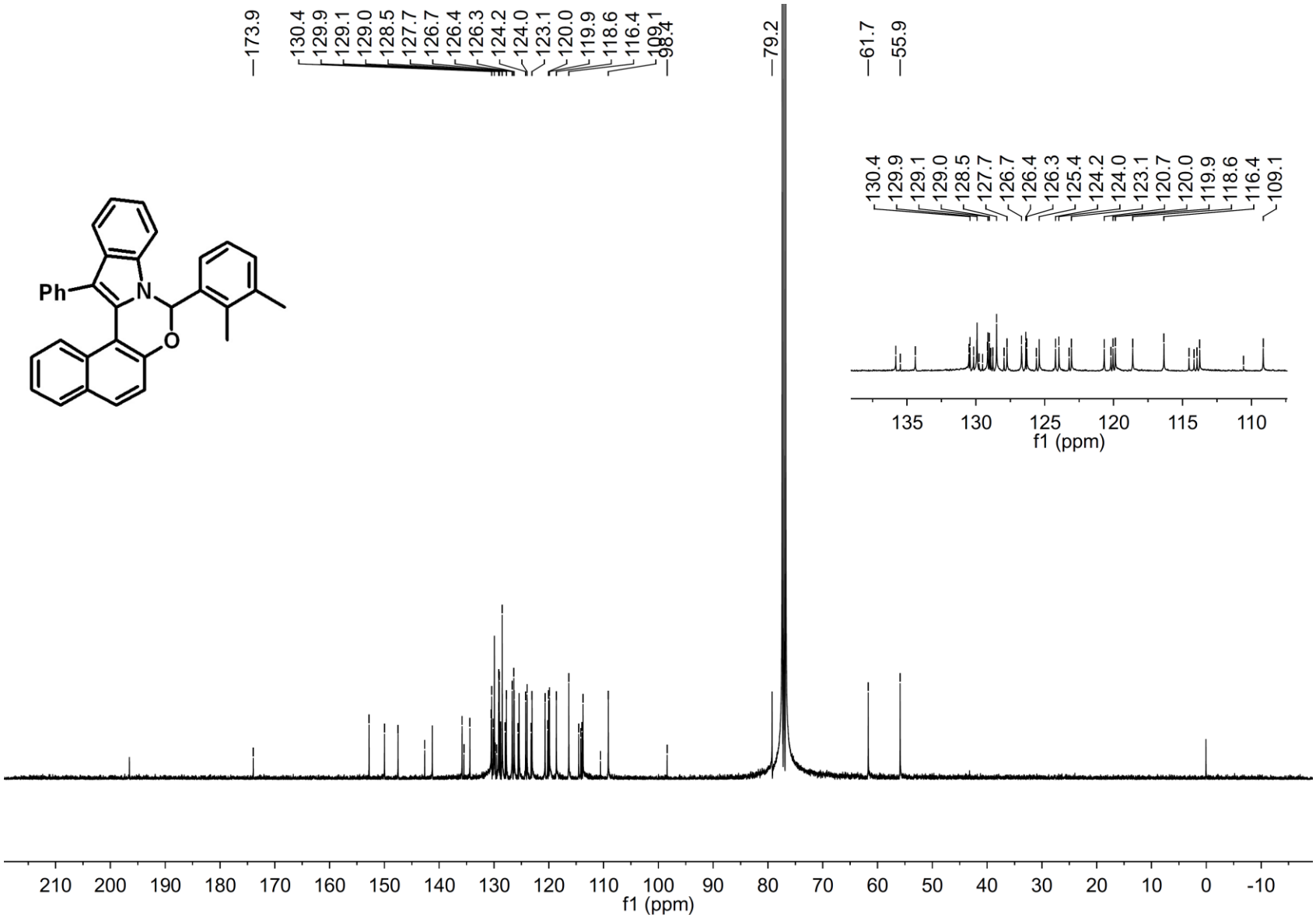
^{1}H NMR Spectrum of Compound **3r**



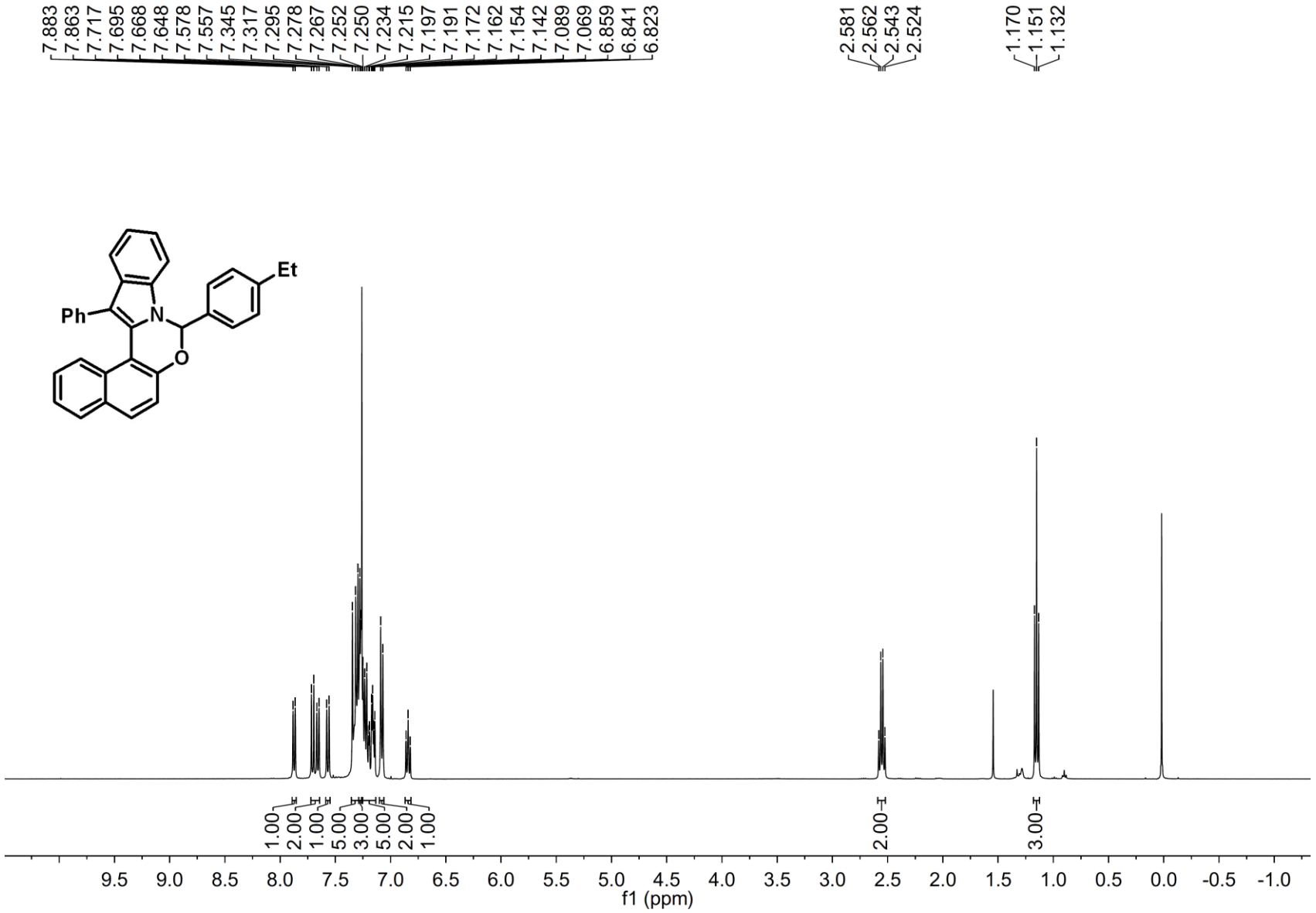
^{13}C NMR Spectrum of Compound **3r**



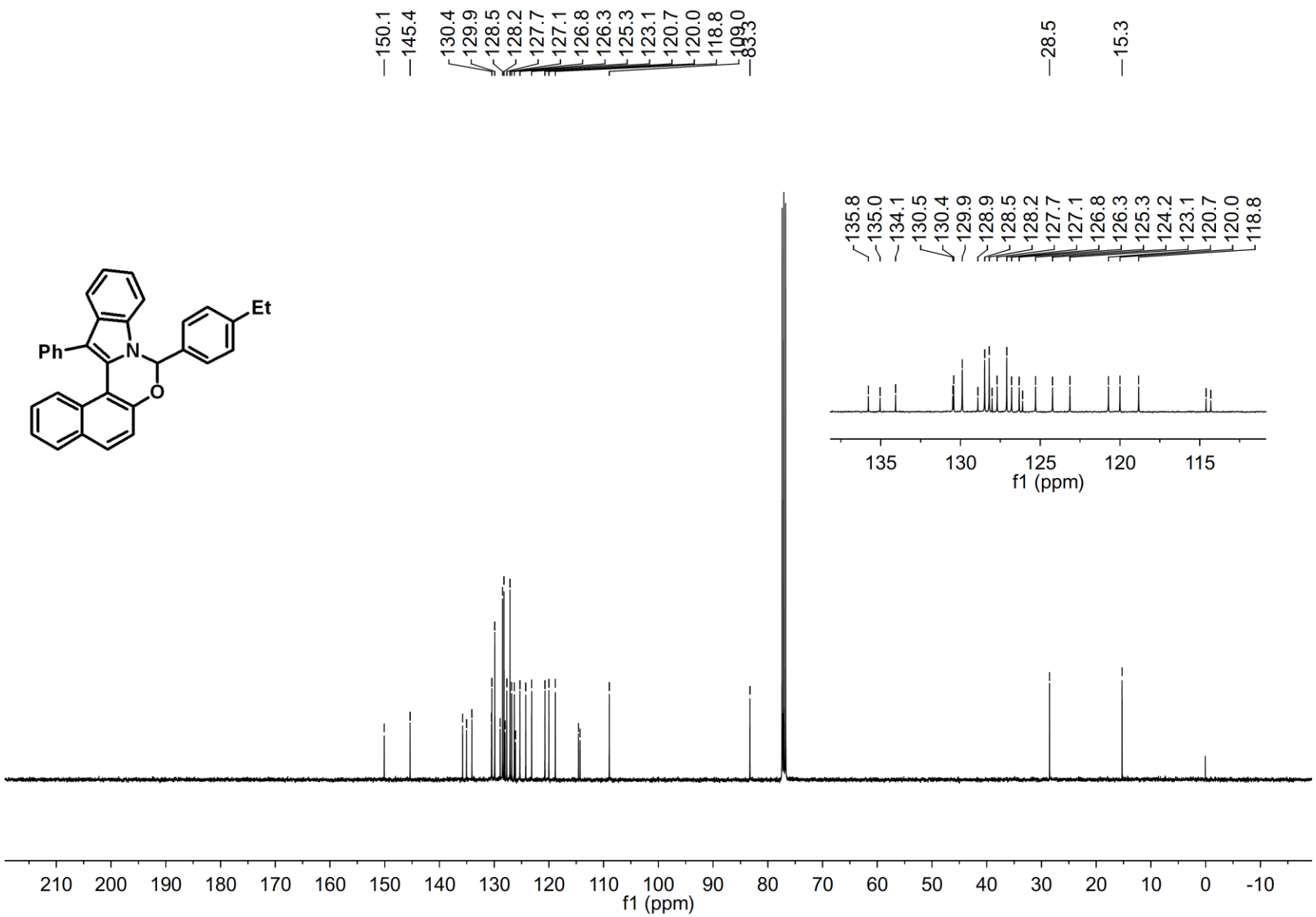
^{1}H NMR Spectrum of Compound **3s**



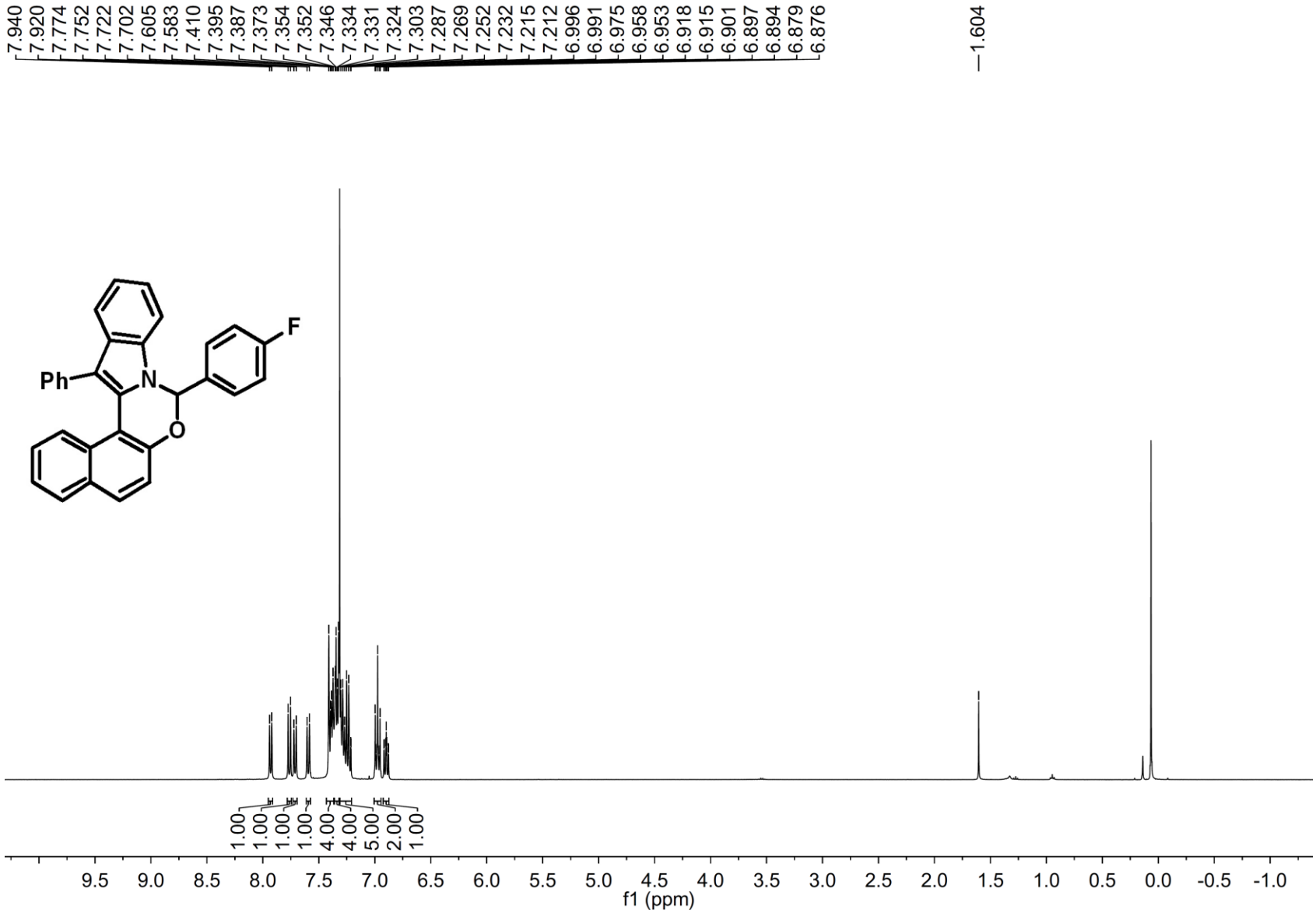
^{13}C NMR Spectrum of Compound **3s**



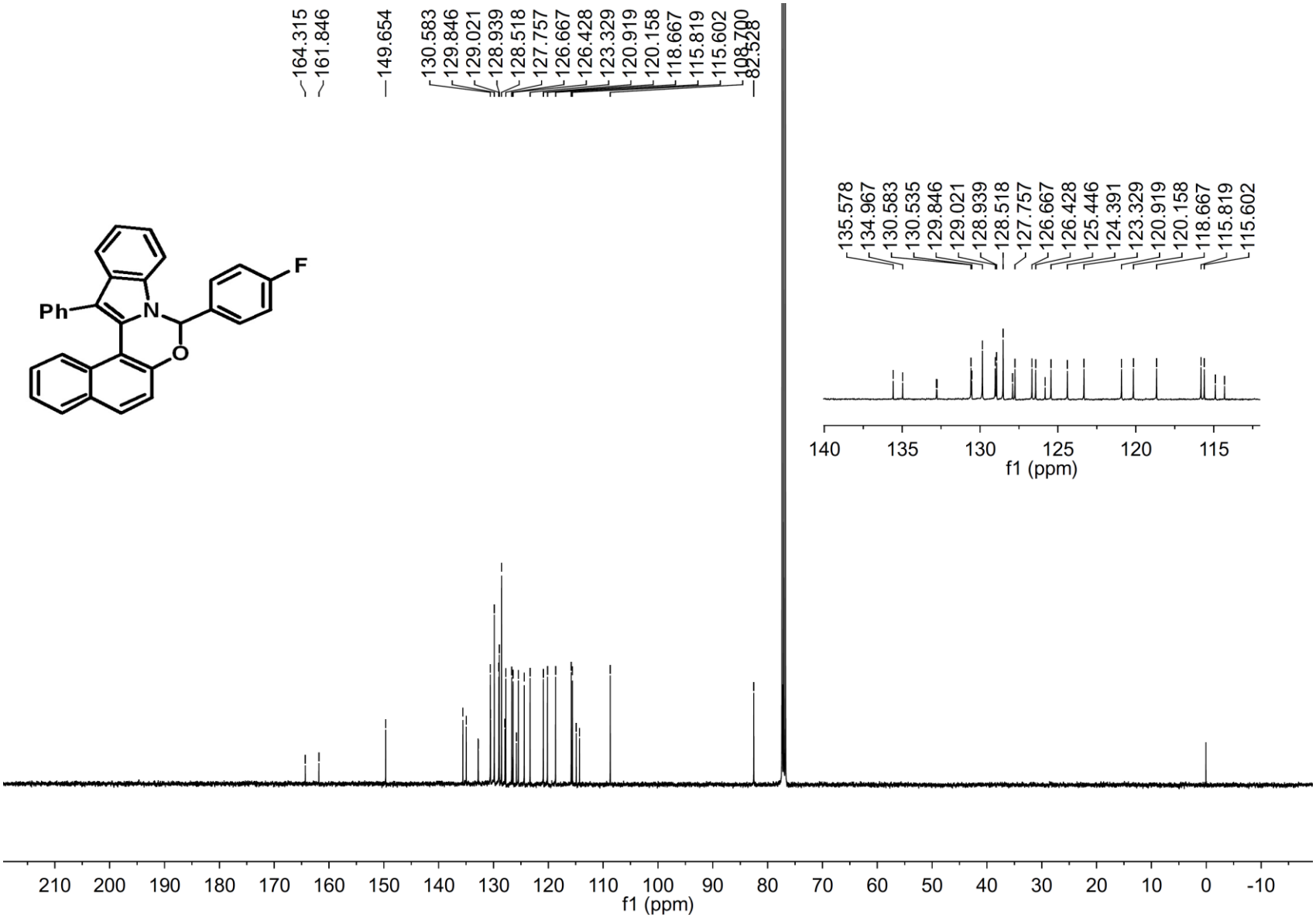
^{1}H NMR Spectrum of Compound **3t**



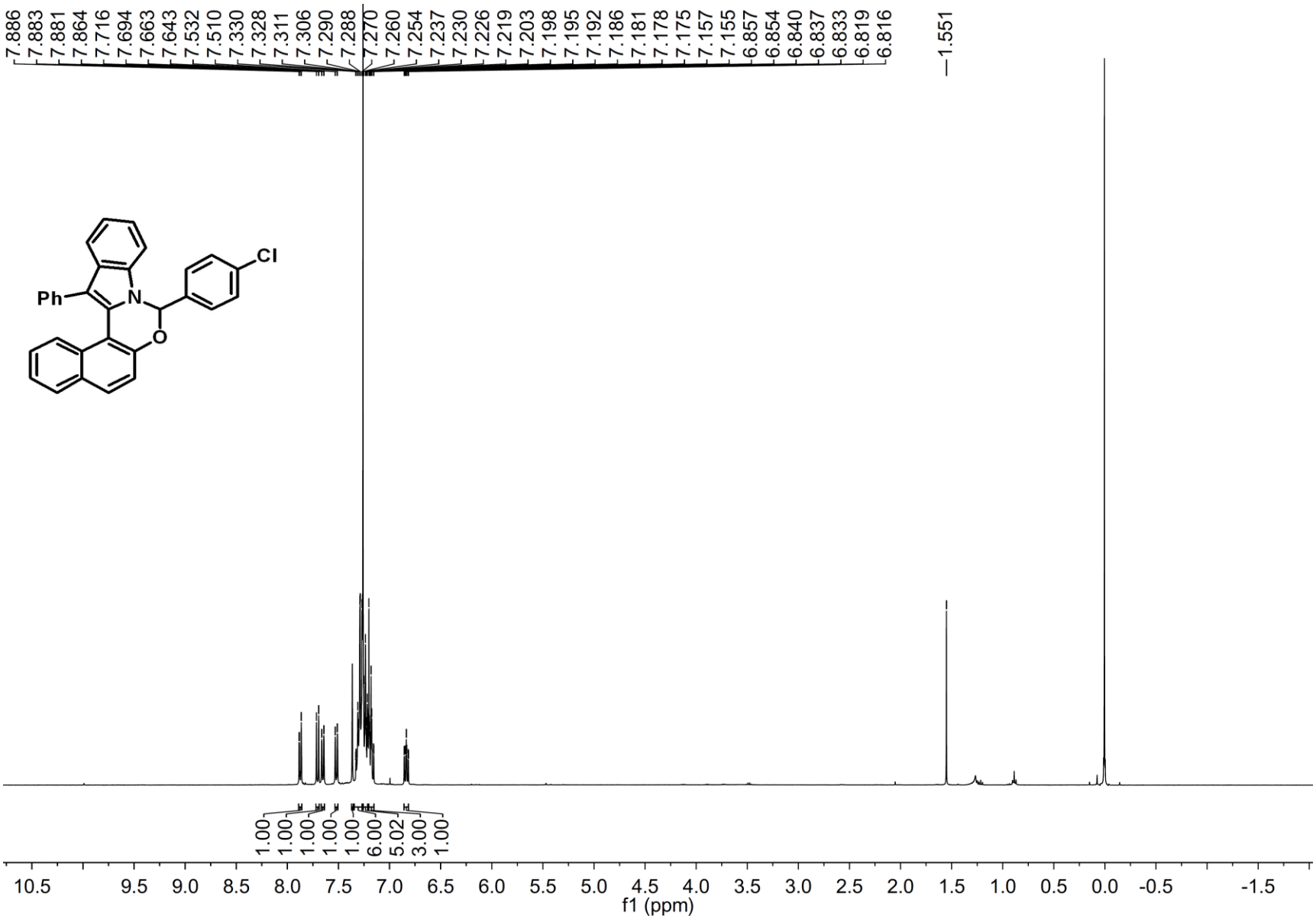
^{13}C NMR Spectrum of Compound **3t**



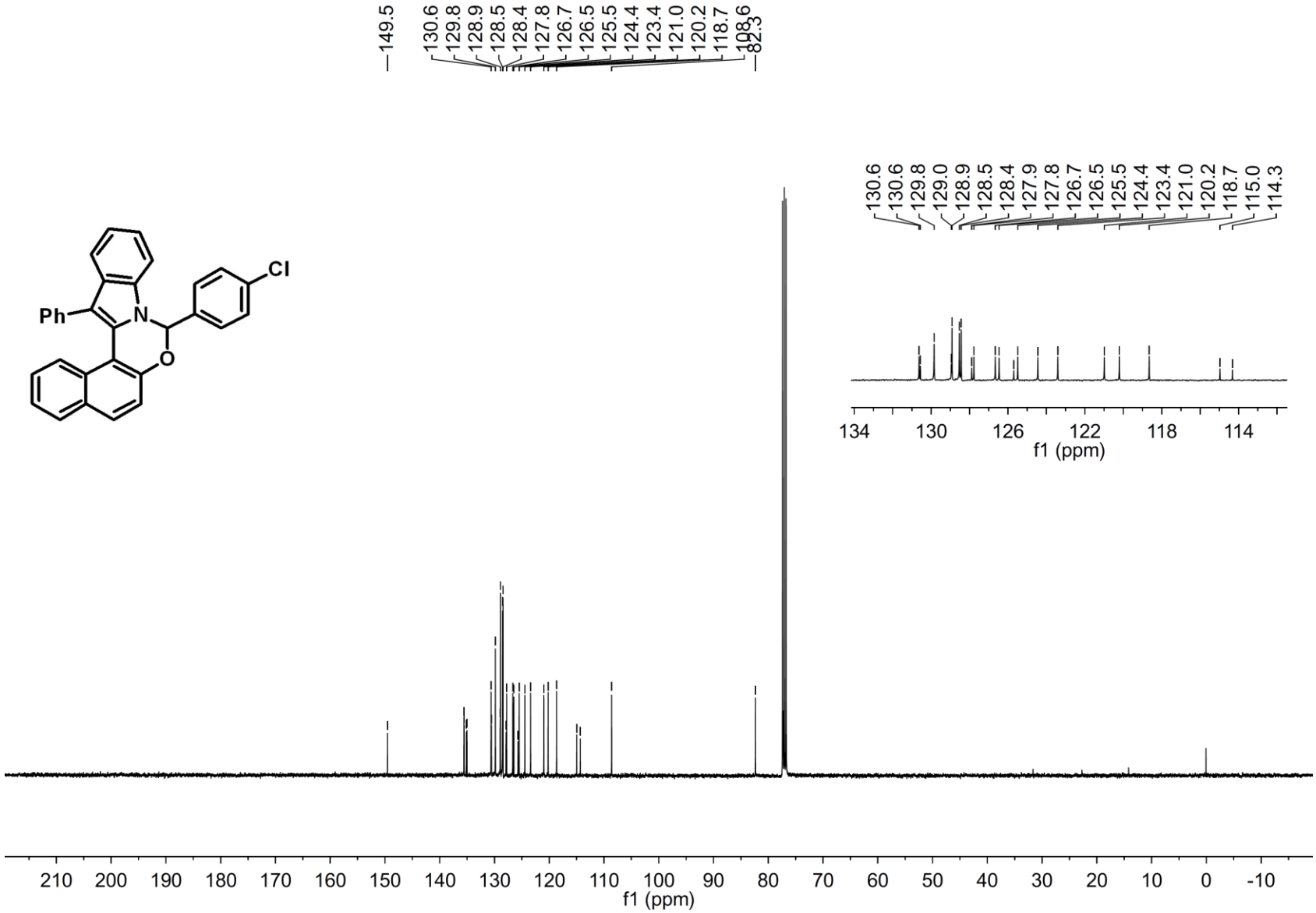
^{1}H NMR Spectrum of Compound **3u**



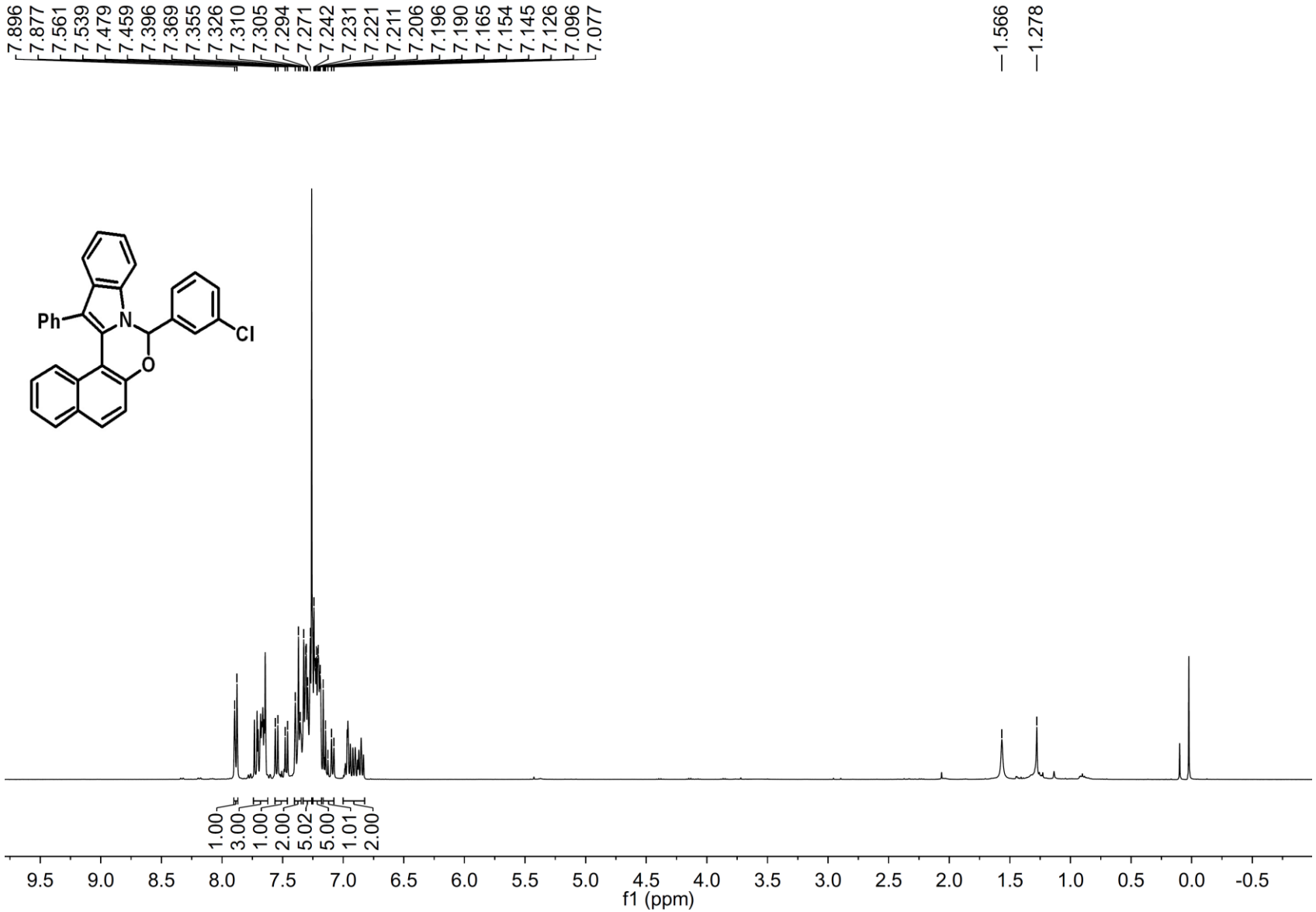
^{13}C NMR Spectrum of Compound **3u**



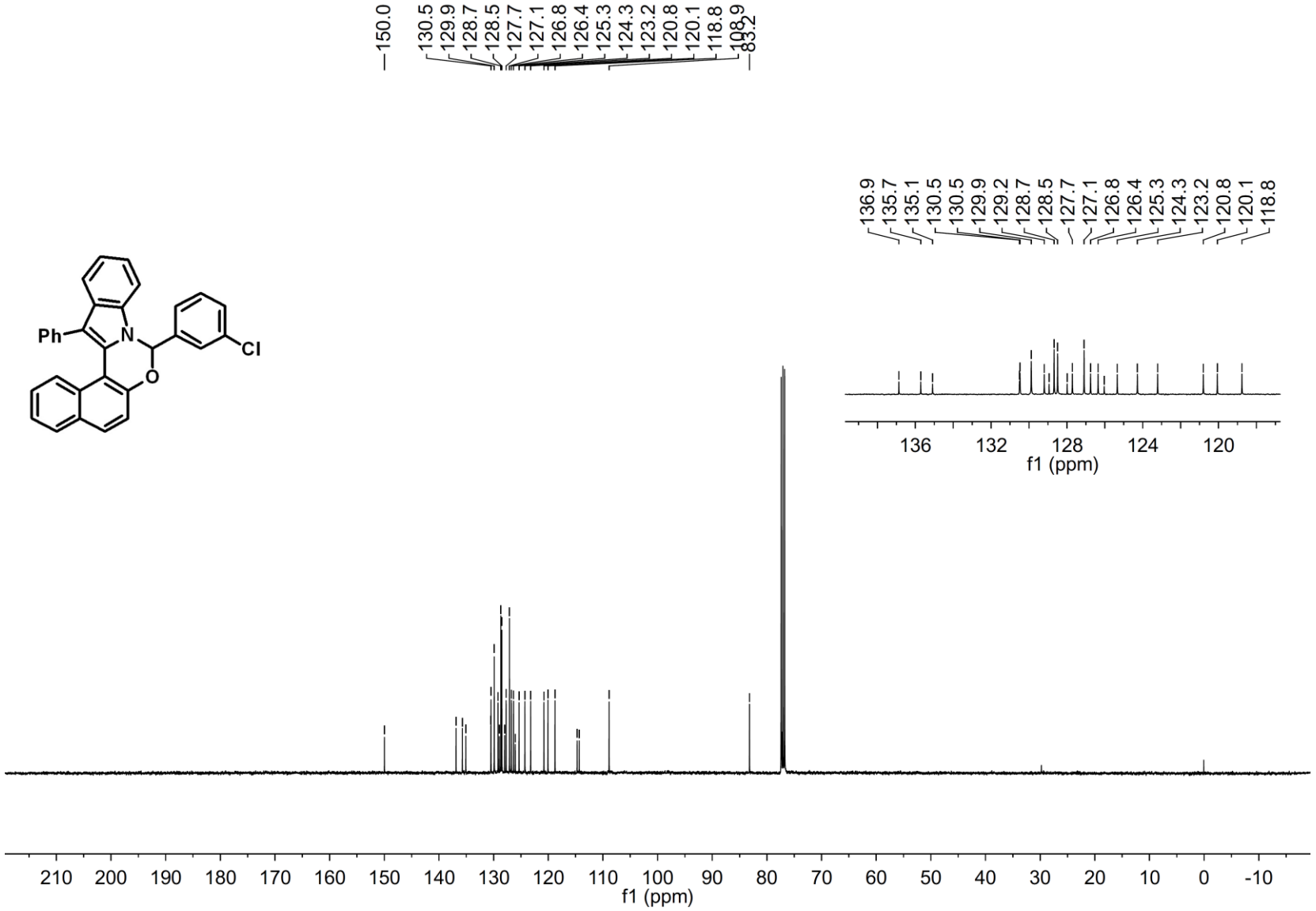
^{1}H NMR Spectrum of Compound **3v**



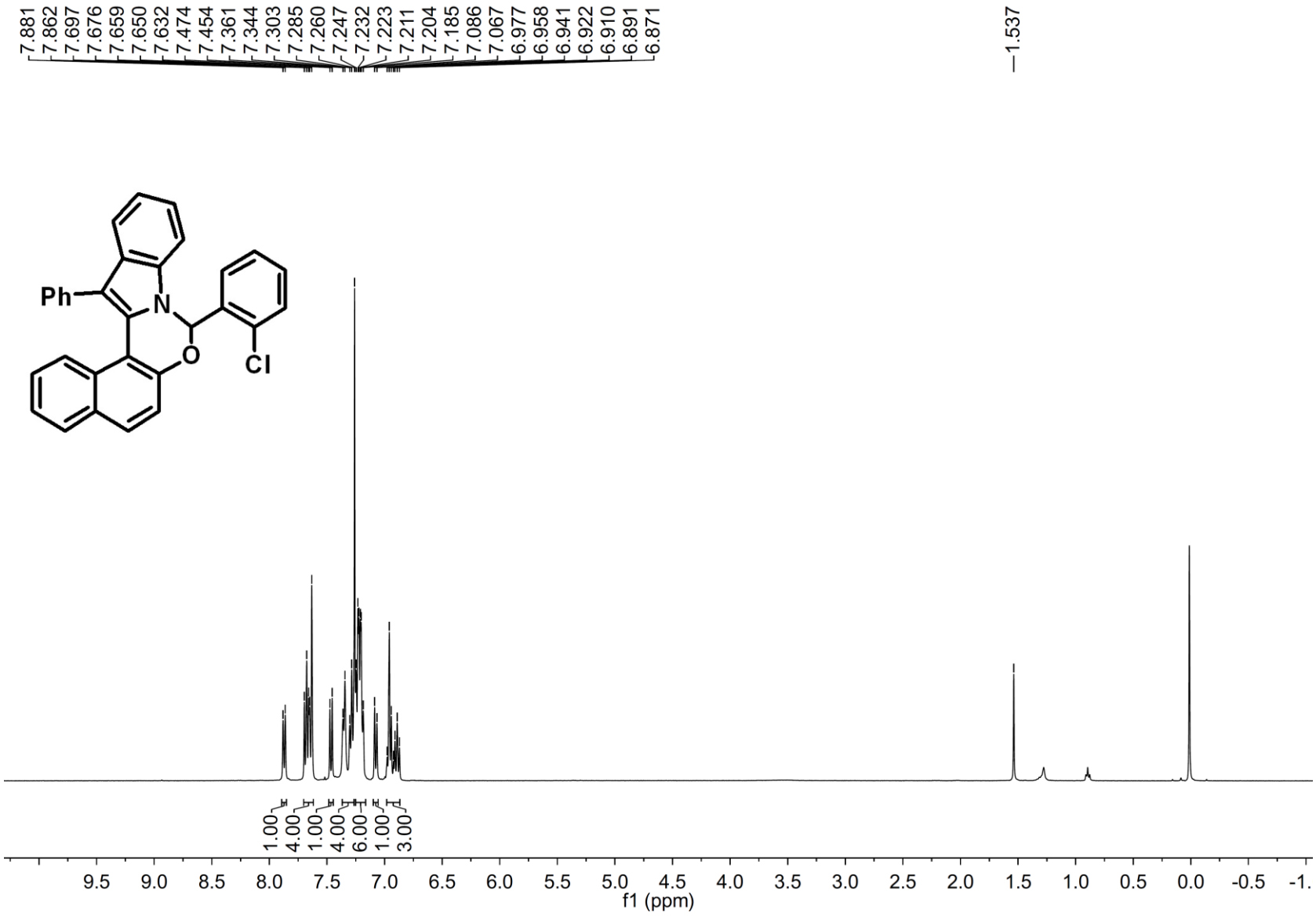
^{13}C NMR Spectrum of Compound **3v**



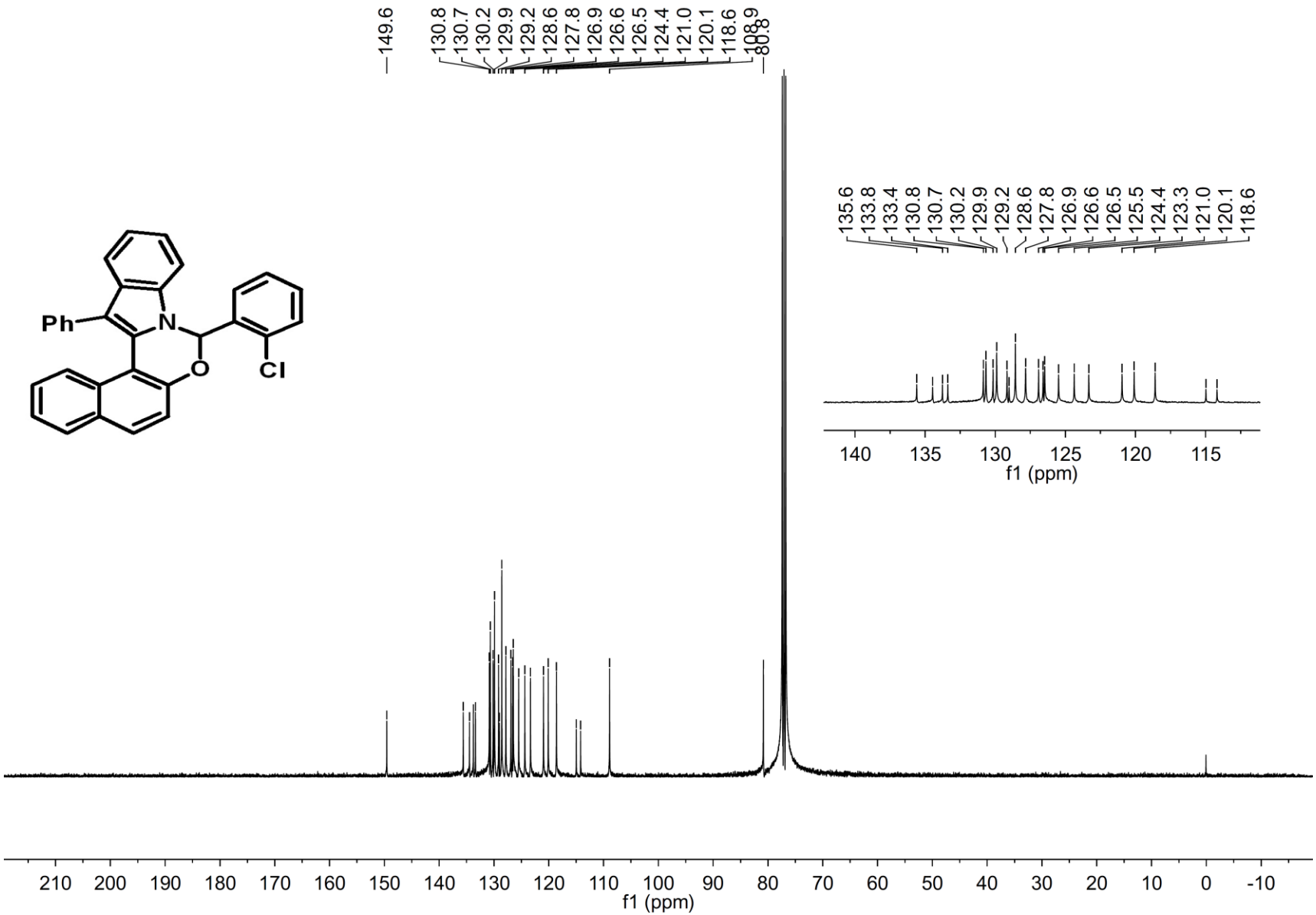
^{1}H NMR Spectrum of Compound **3w**



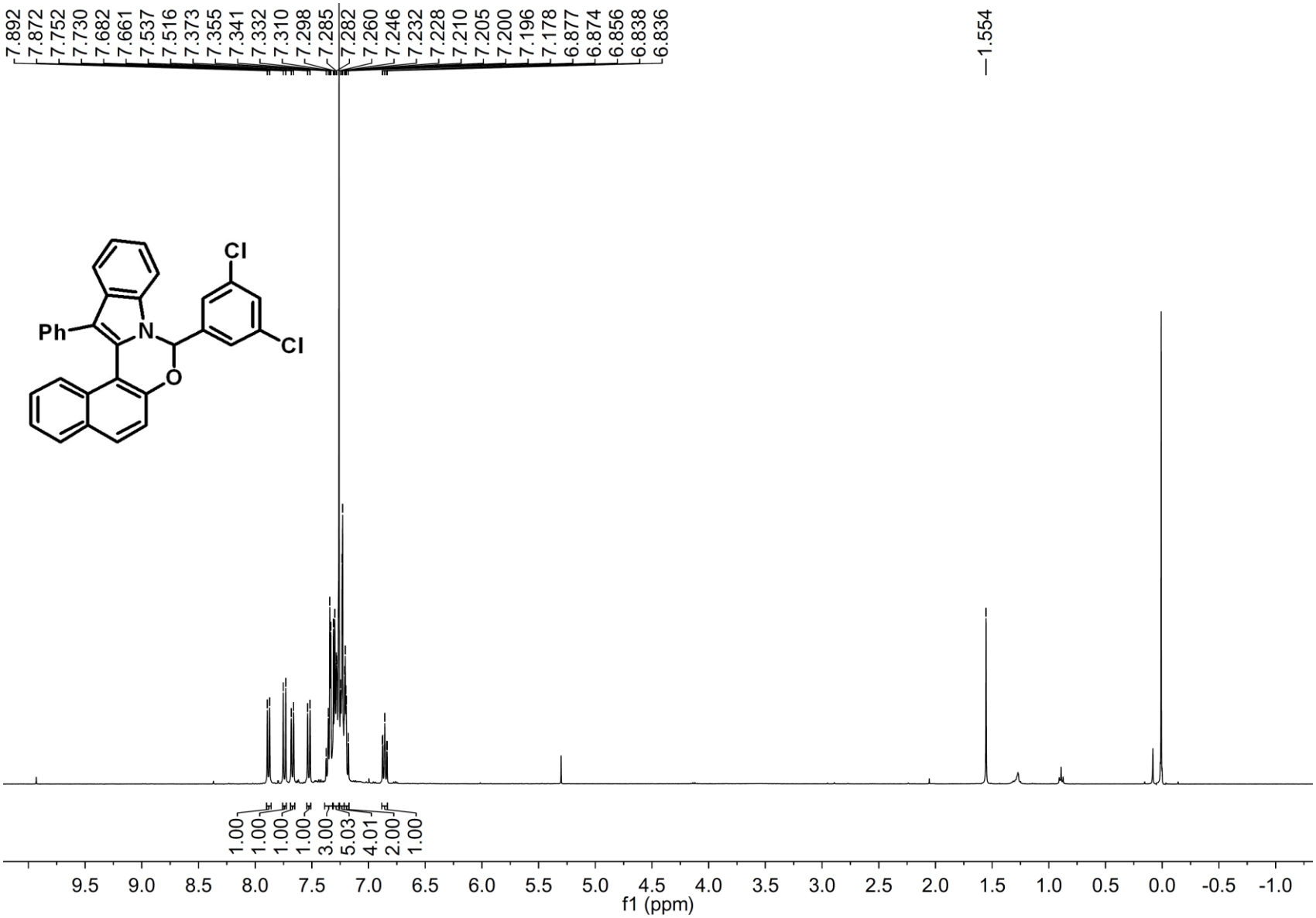
^{13}C NMR Spectrum of Compound **3w**



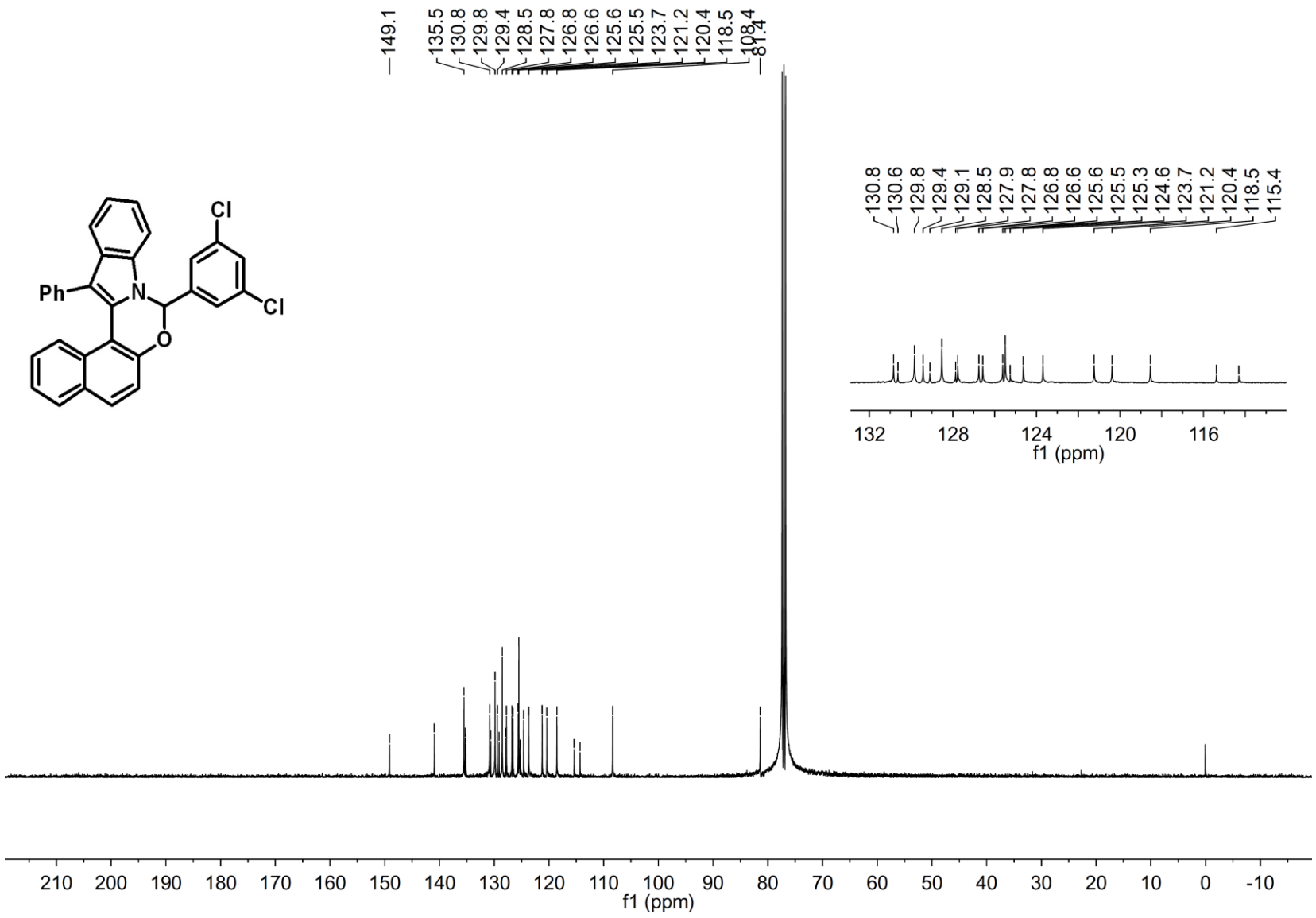
^{1}H NMR Spectrum of Compound **3x**



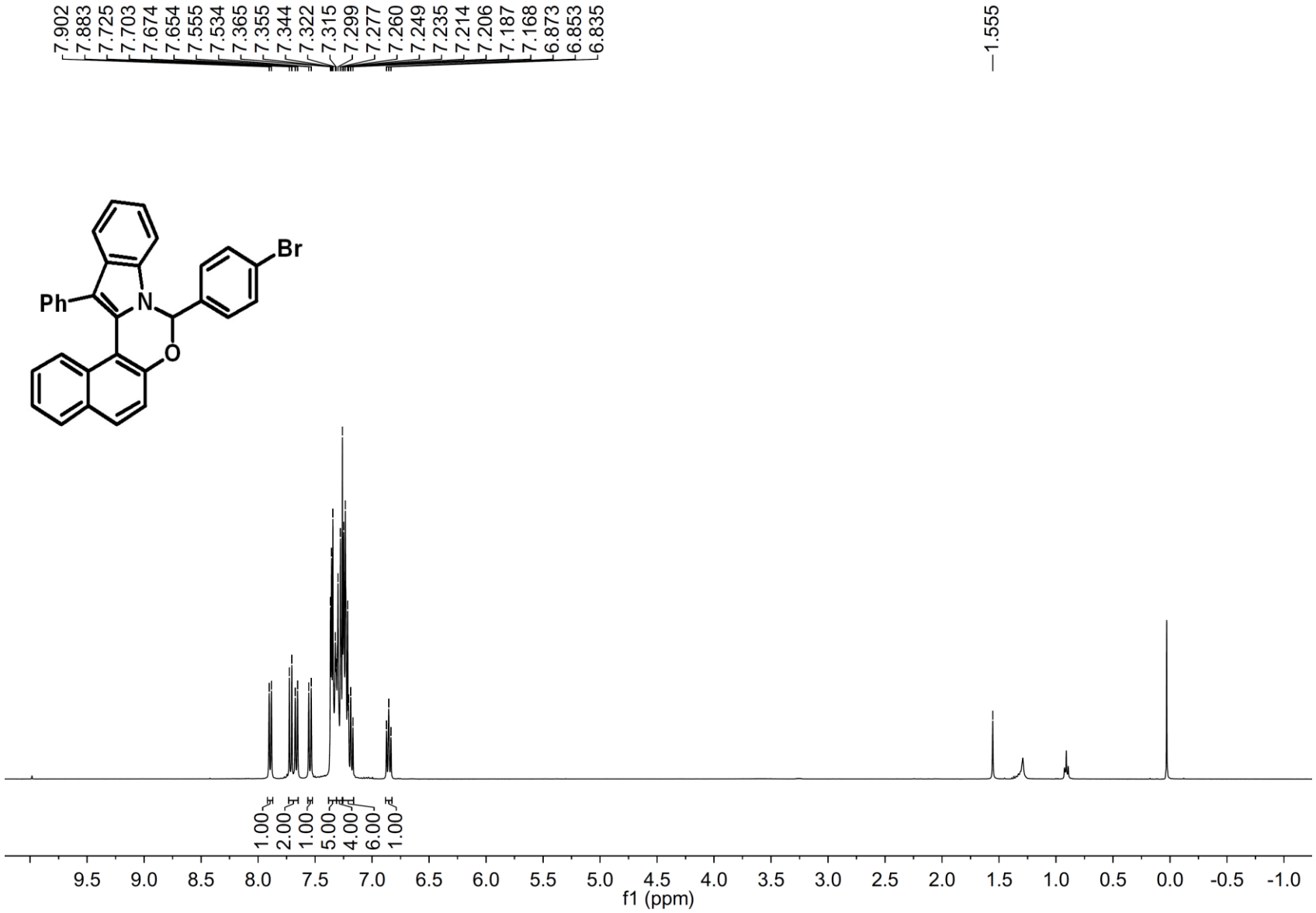
^{13}C NMR Spectrum of Compound **3x**



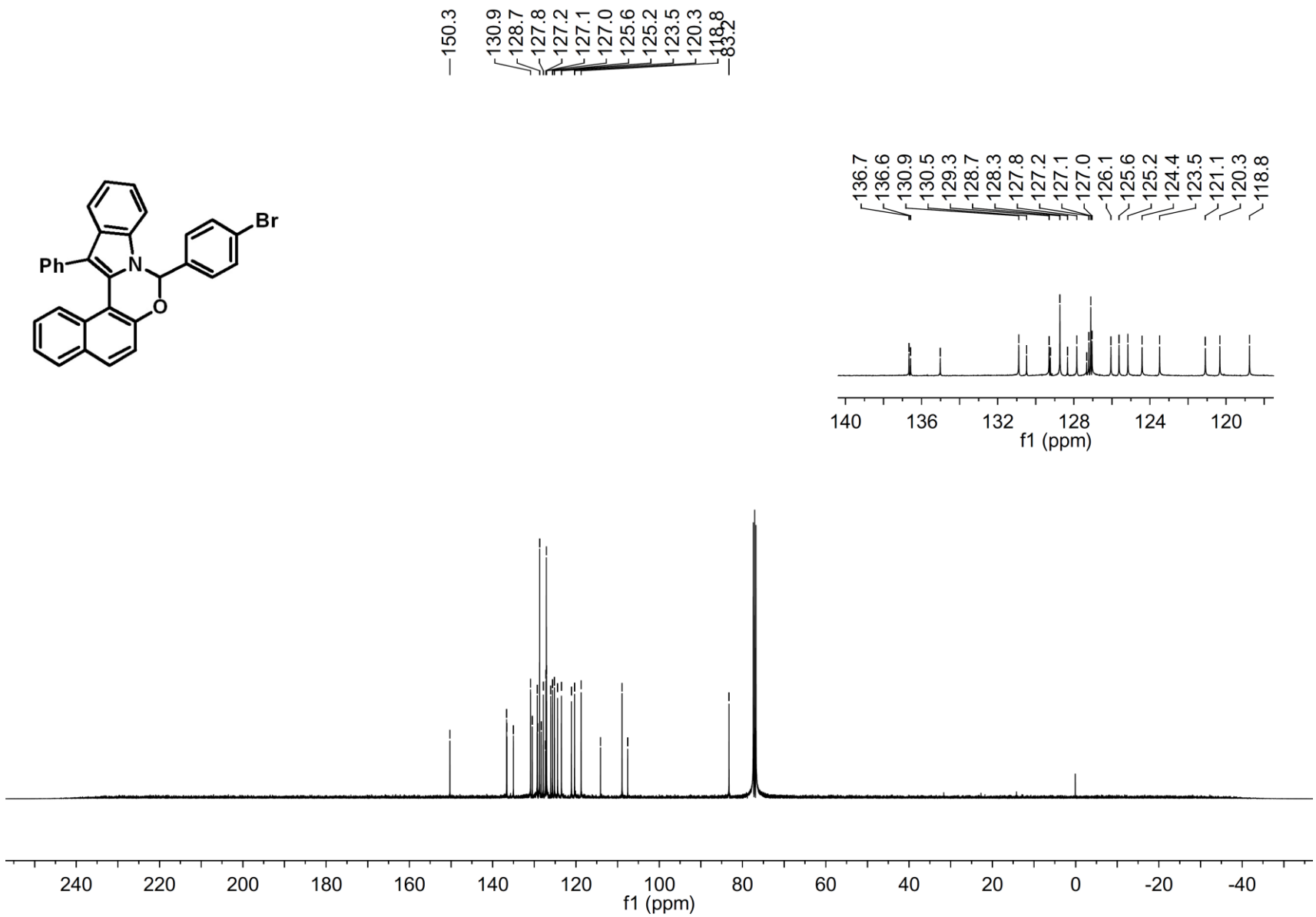
^{1}H NMR Spectrum of Compound **3y**



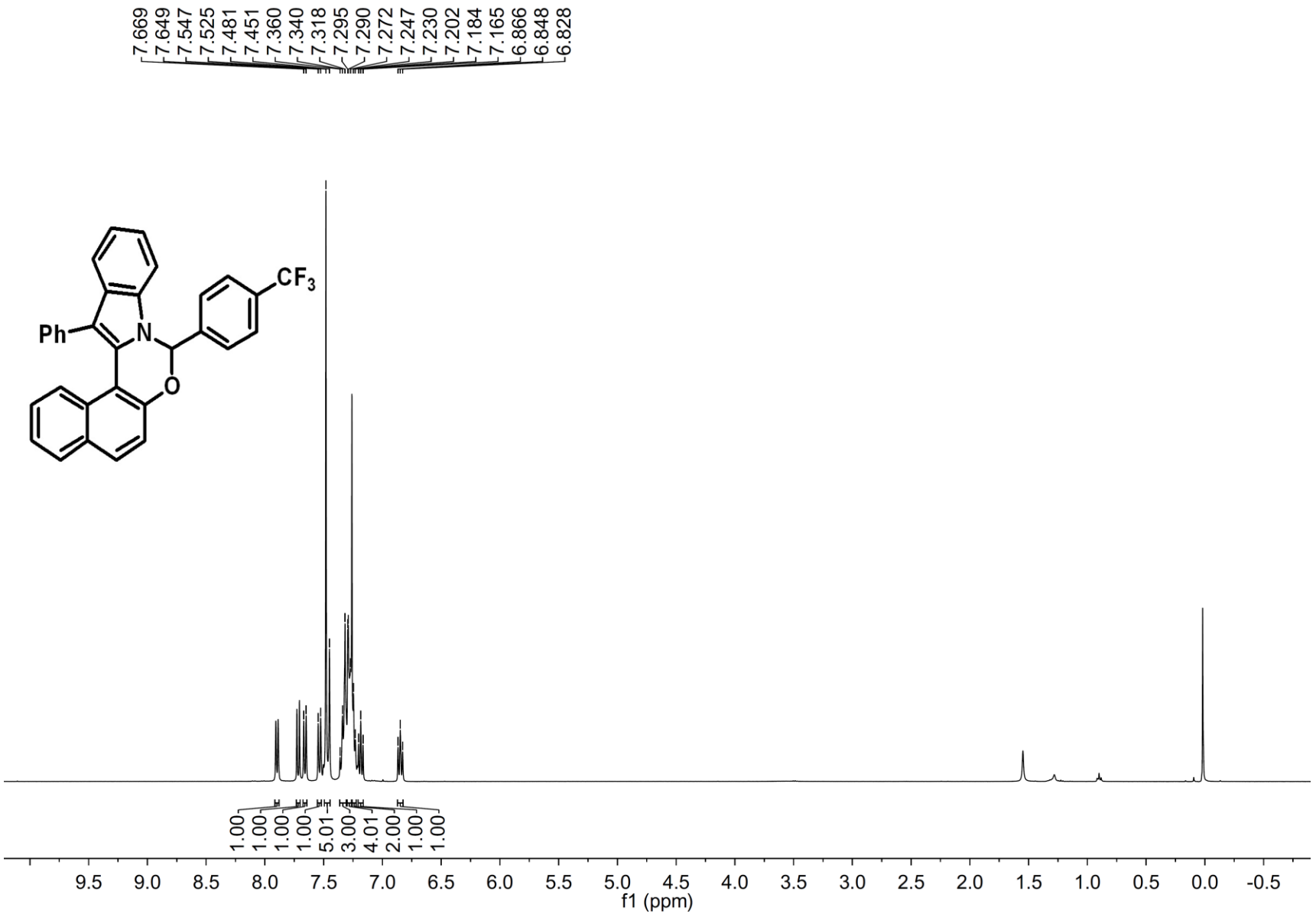
^{13}C NMR Spectrum of Compound **3y**



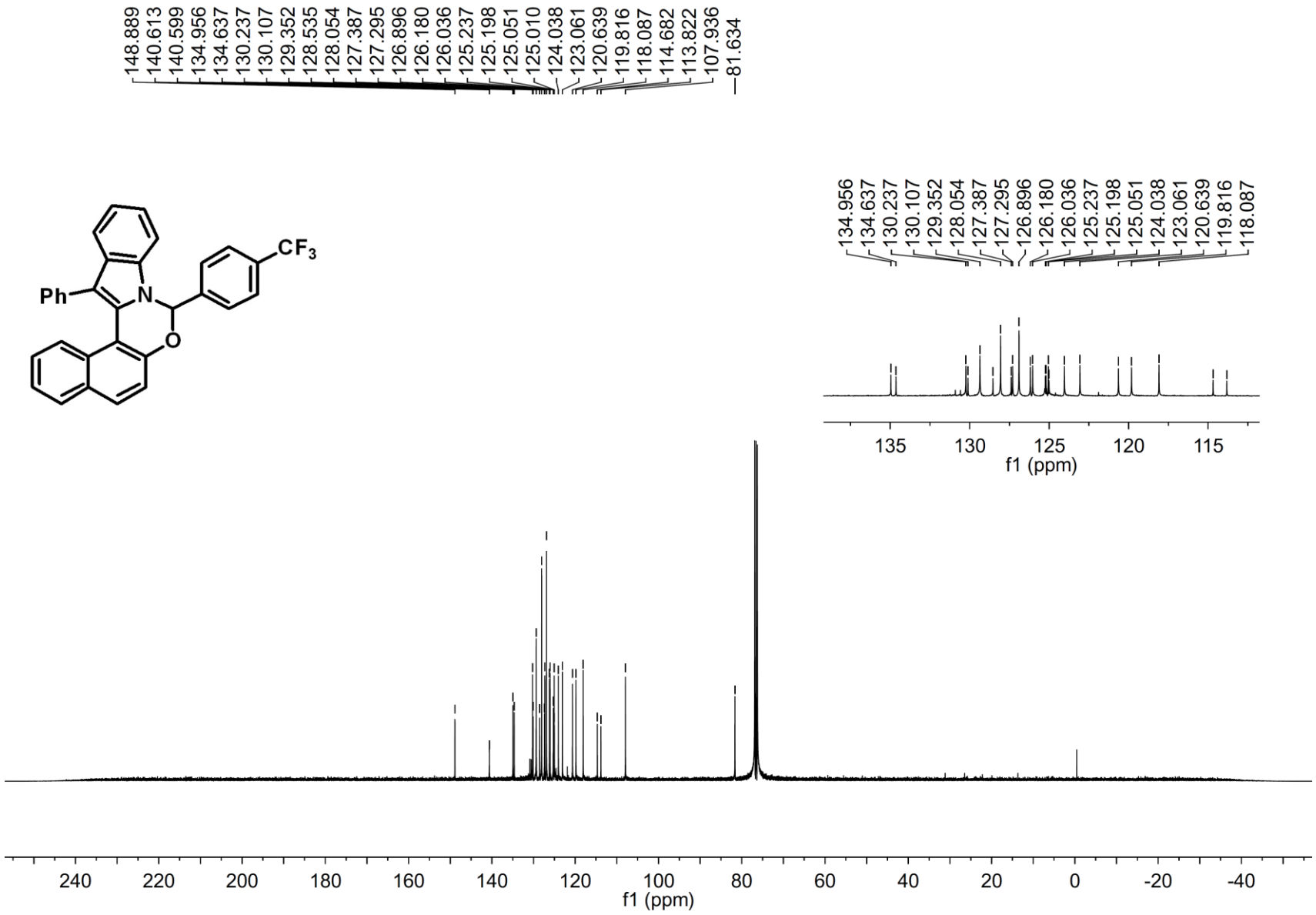
^{1}H NMR Spectrum of Compound **3z**



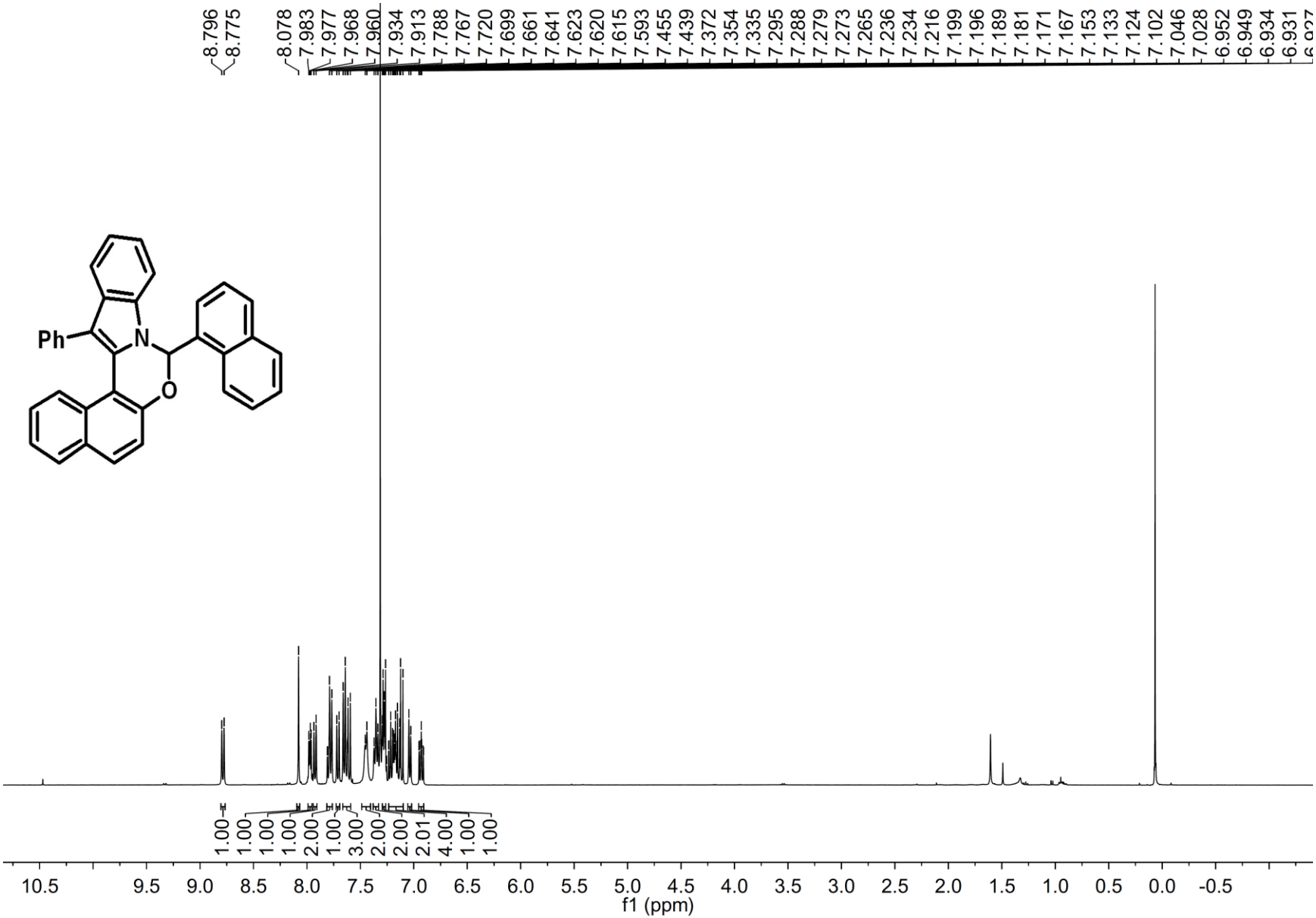
^{13}C NMR Spectrum of Compound **3z**



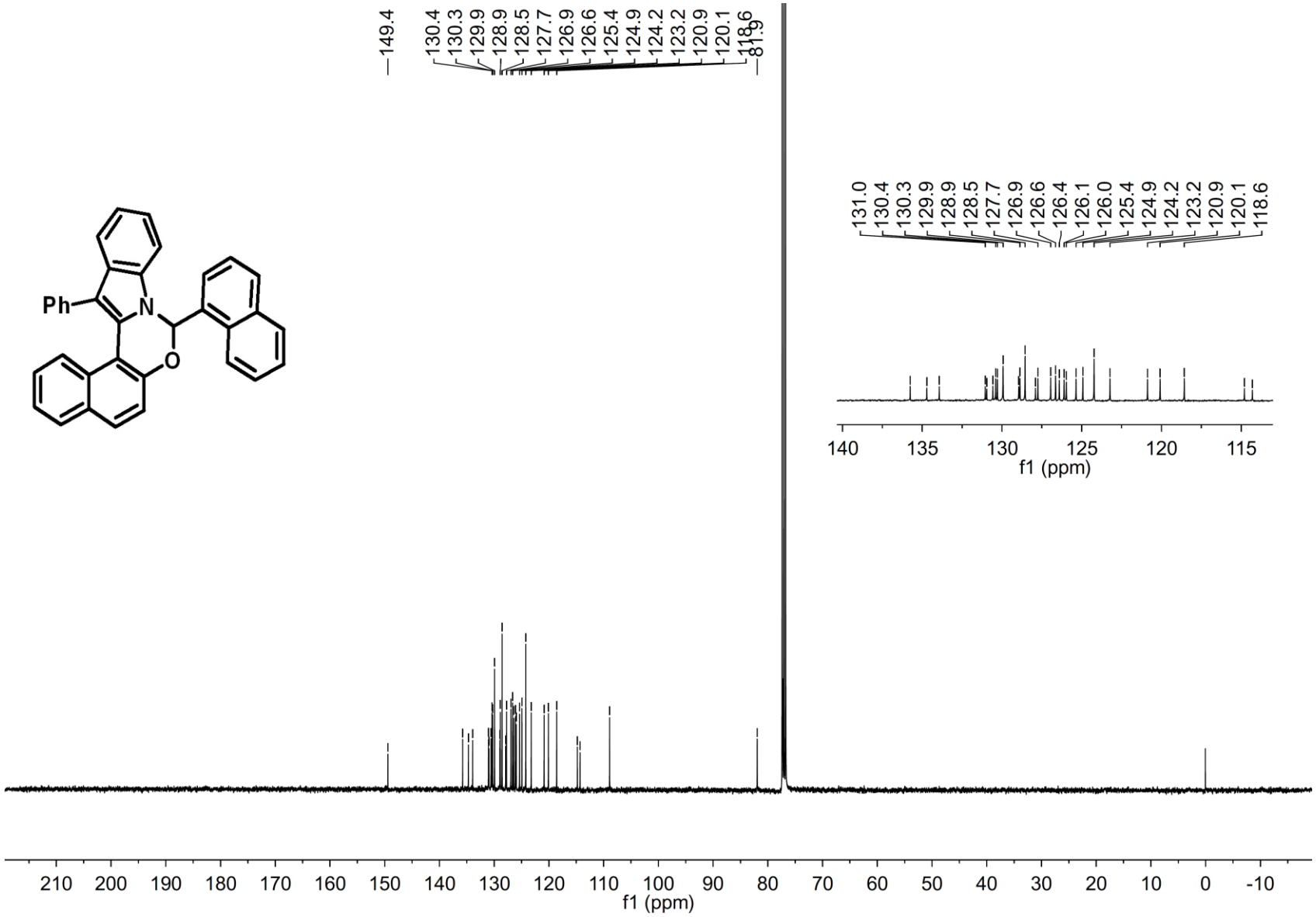
^{1}H NMR Spectrum of Compound **3aa**



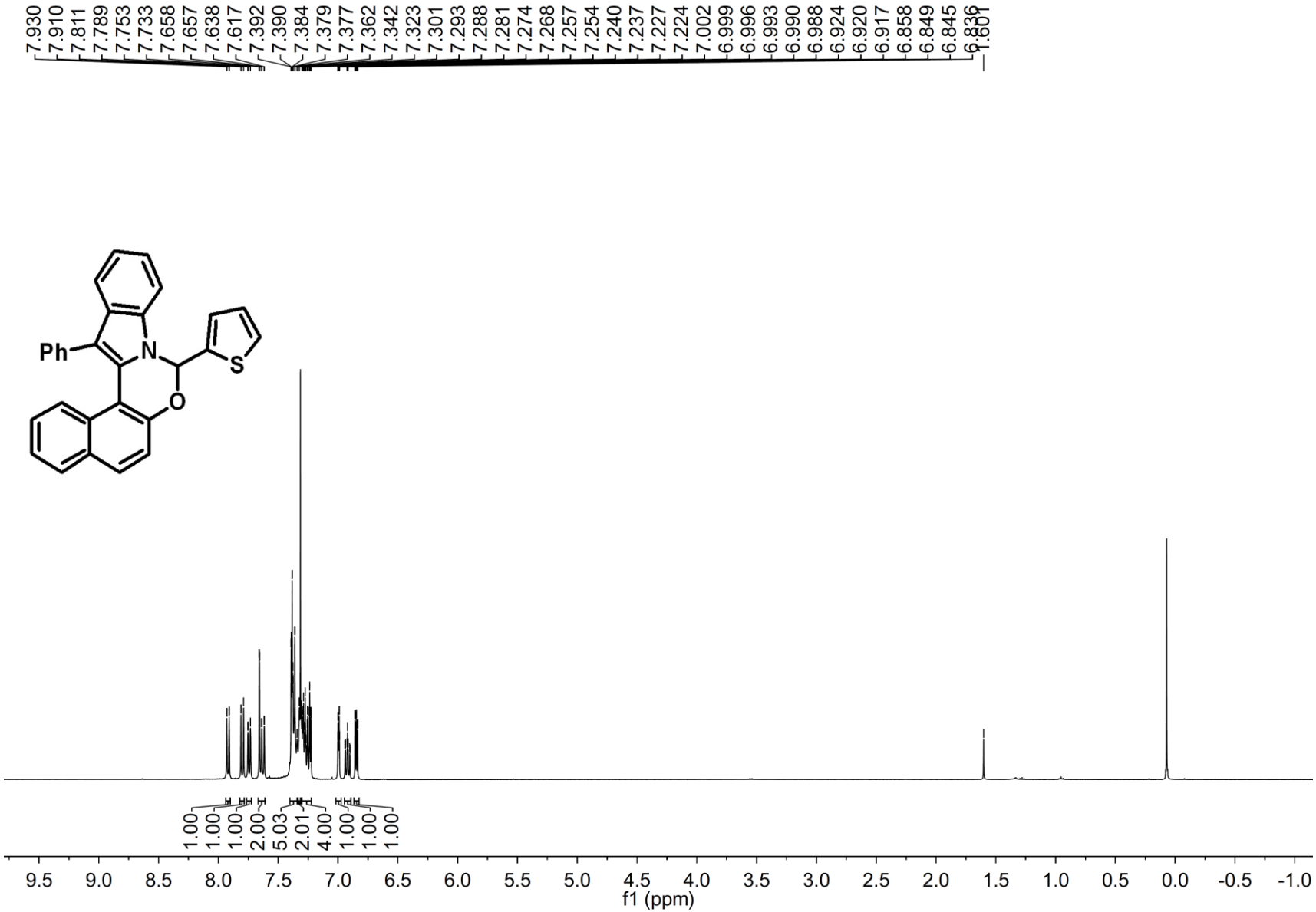
^{13}C NMR Spectrum of Compound **3aa**



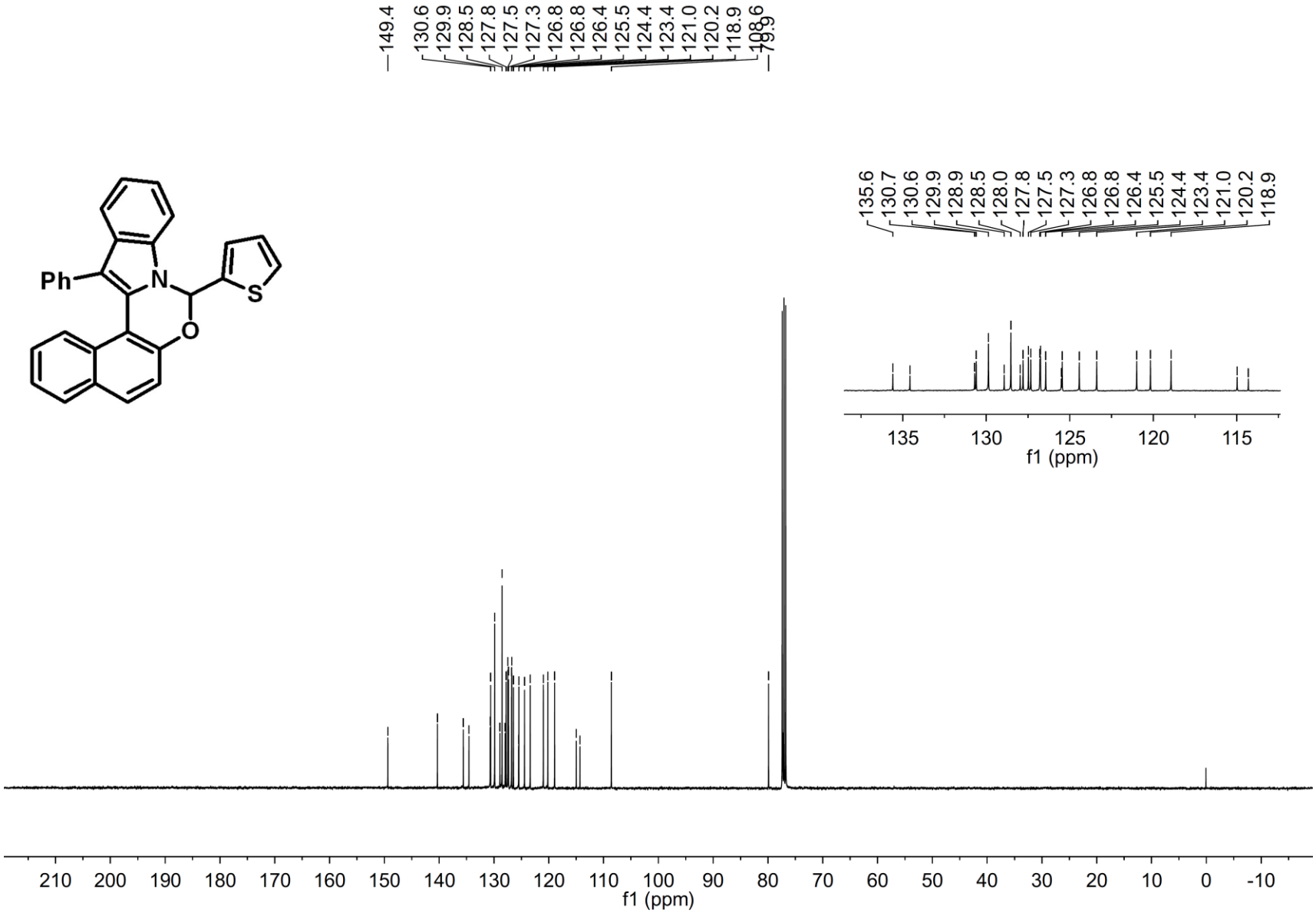
^{1}H NMR Spectrum of Compound **3bb**



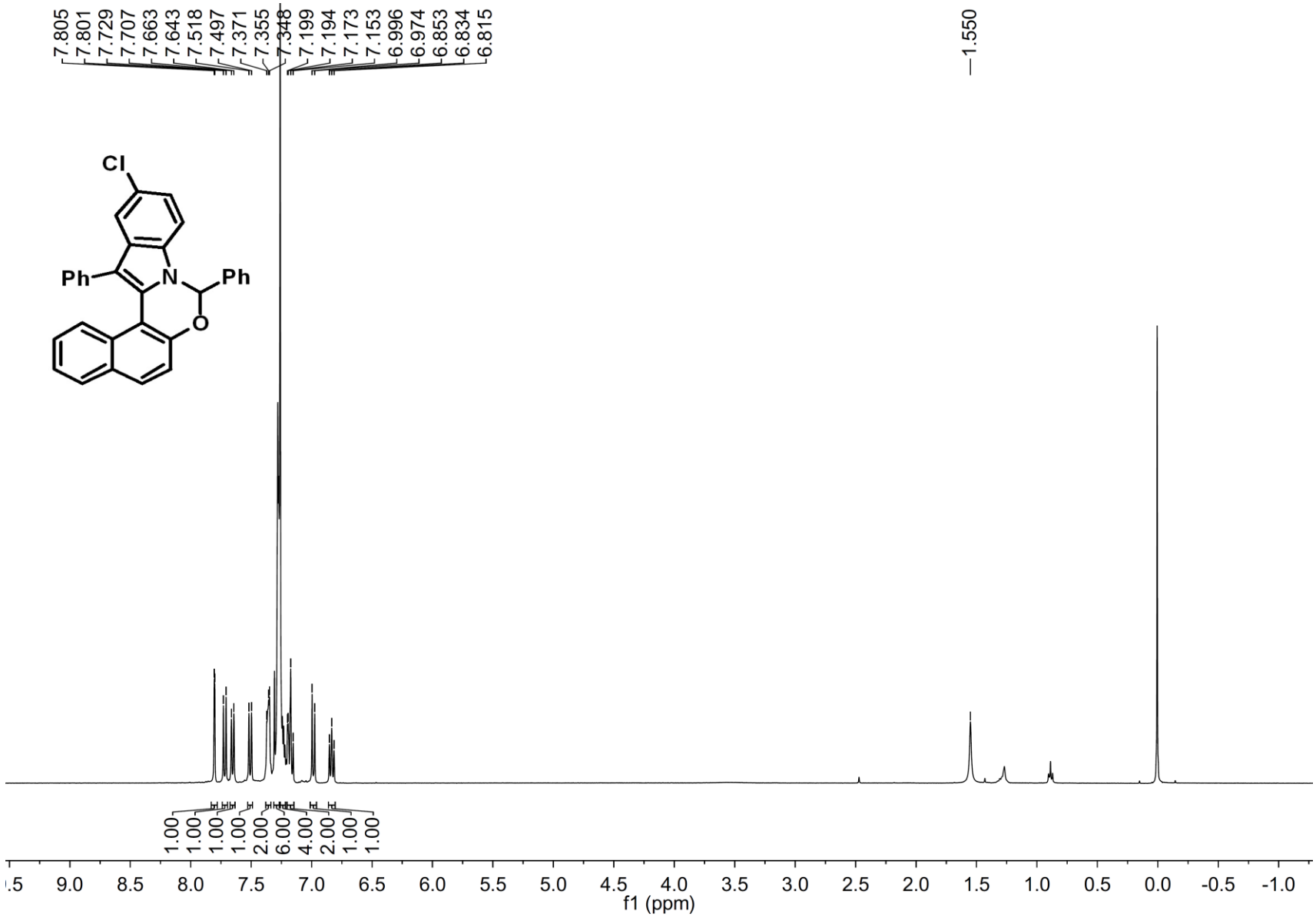
^{13}C NMR Spectrum of Compound **3bb**



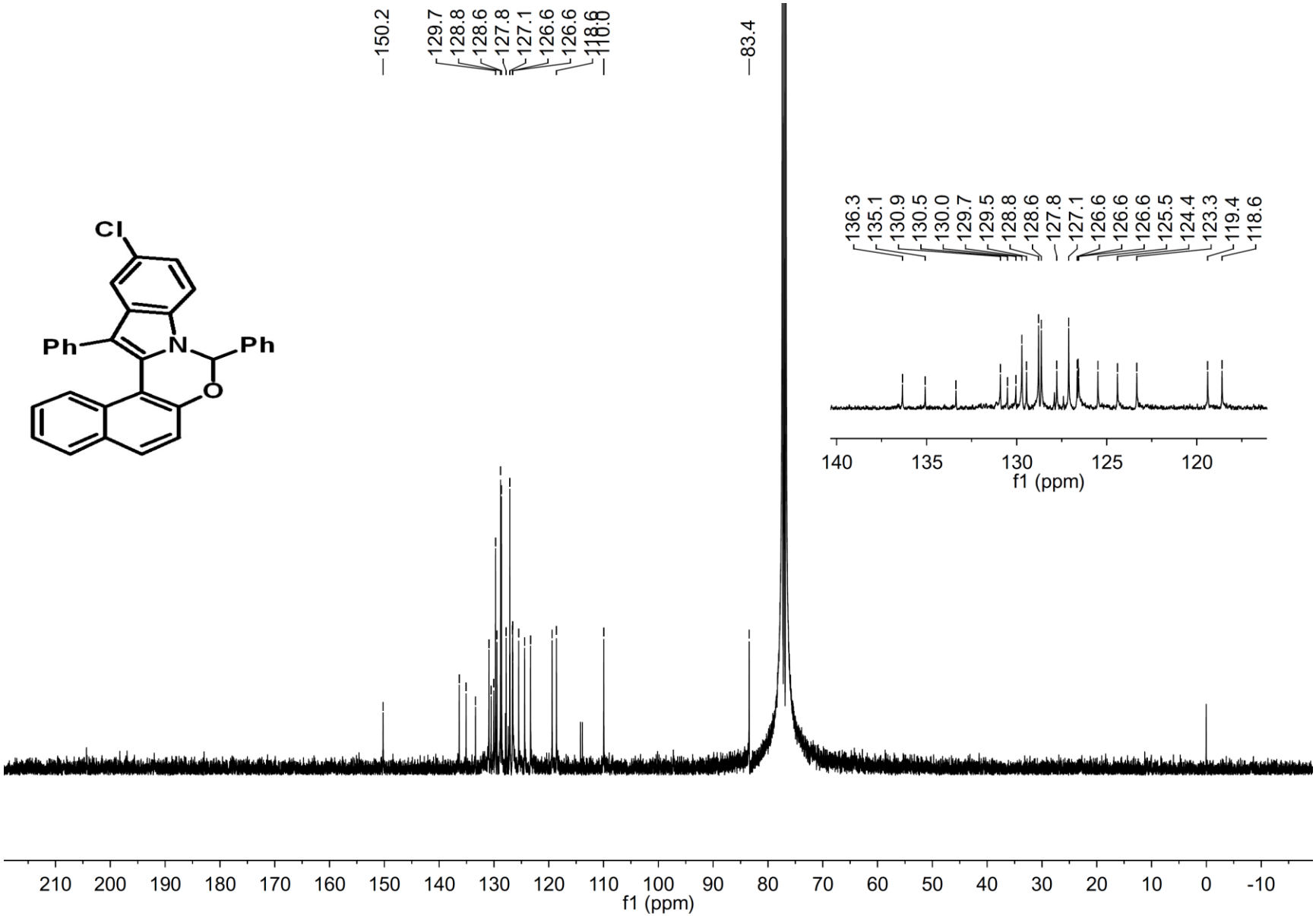
^{1}H NMR Spectrum of Compound **3cc**



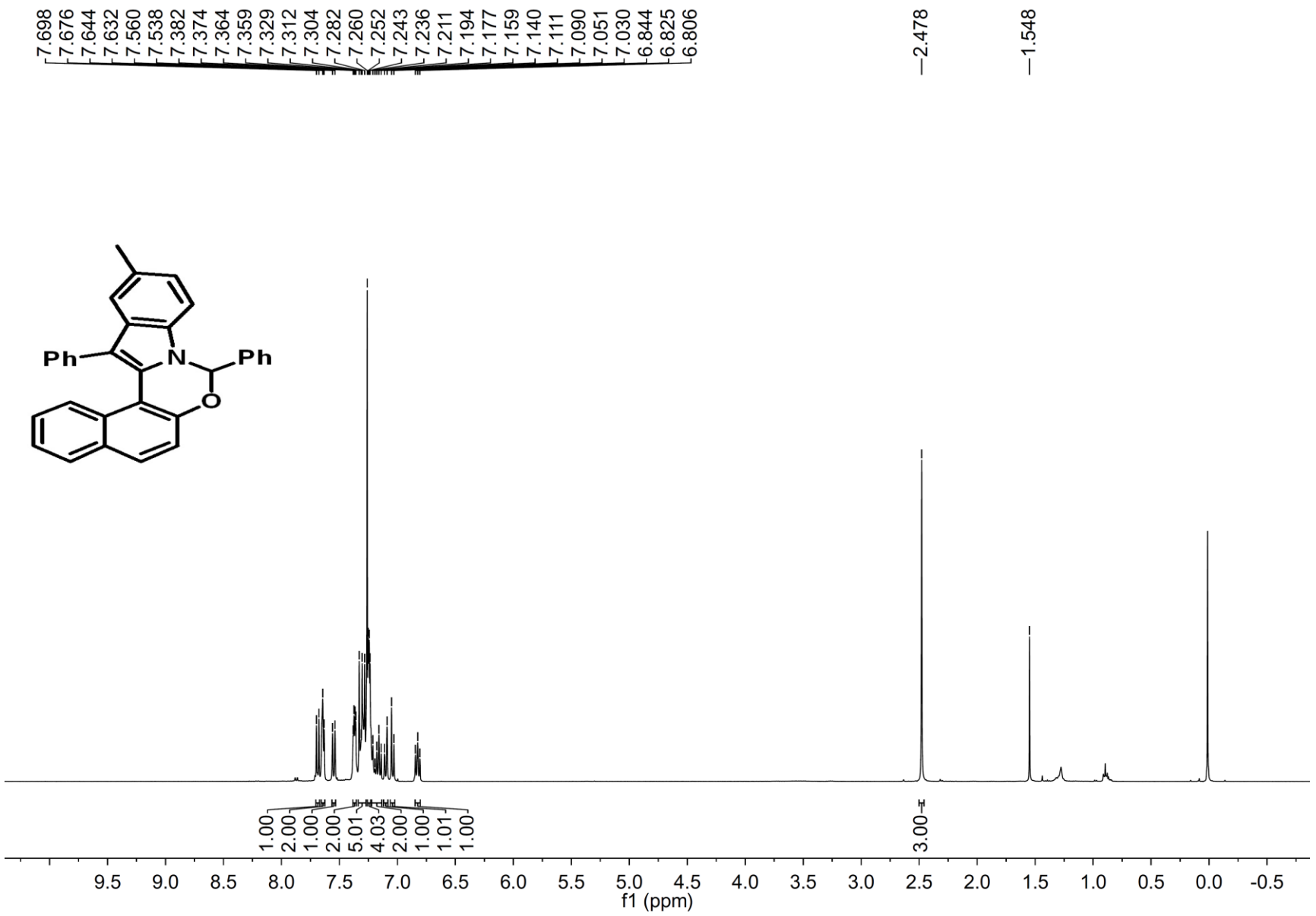
^{13}C NMR Spectrum of Compound **3cc**



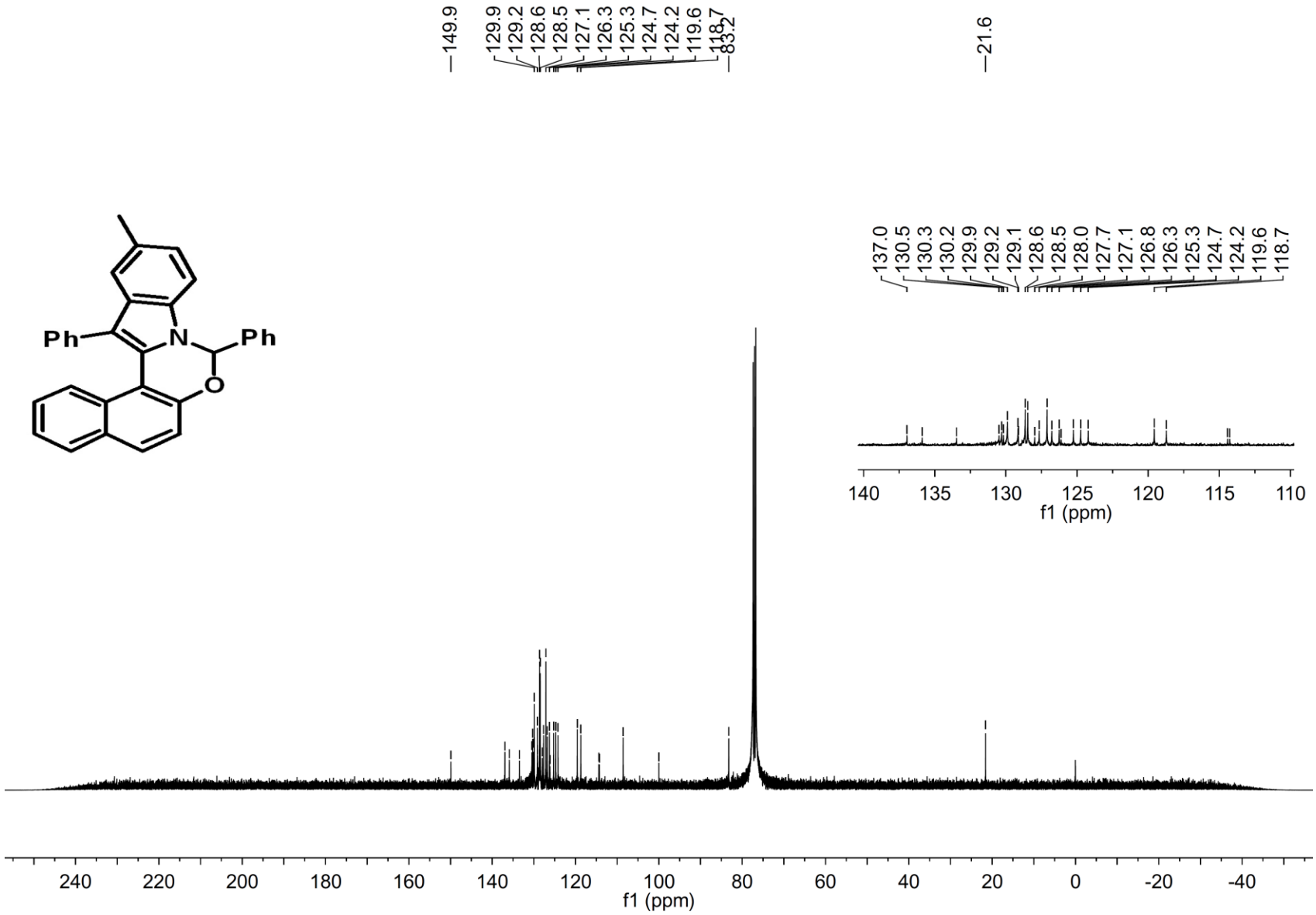
^{1}H NMR Spectrum of Compound **3ee**



^{13}C NMR Spectrum of Compound **3ee**



^{1}H NMR Spectrum of Compound **3ff**



^{13}C NMR Spectrum of Compound **3ff**