Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2019

Supporting Information

Silver-catalyzed nitration/annulation of 2-alkynylanilines for tunable synthesis of nitrated indoles and indazole-2-oxides

Tian-Shu Zhang,[a] Rong Wang,[b] Pei-Jun Cai,[a,*] Wen-Juan Hao,[b] Shu-Jiang Tu,[b] Bo Jiang[b,*]

[a]School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou, 221116, P. R. China. E-mail: pjcai@cumt.edu.cn(PJC)

[b]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 (BJ) Fax: +8651683500065; Tel: +8651683500065

Context

General Information…… S2

General Procedure for the Synthesis of Product **4**…… S2-S3

General Procedure for the Synthesis of Product **5**…… S3-S4

General Procedure for the Synthesis of Products **2**……S5

Characterization Data of Compounds **2a-2ag**……S5-S13

General Procedure for the Synthesis of Products **3**……S13

Characterization Data of Compounds **3a-3k**…… S13-S16

Copies of ^{1}H NMR Spectra for Compound **1ab** …….. S17

Copies of ^{1}H and ^{13}C NMR Spectra for Products **2a-2ag**…….. S18-S84

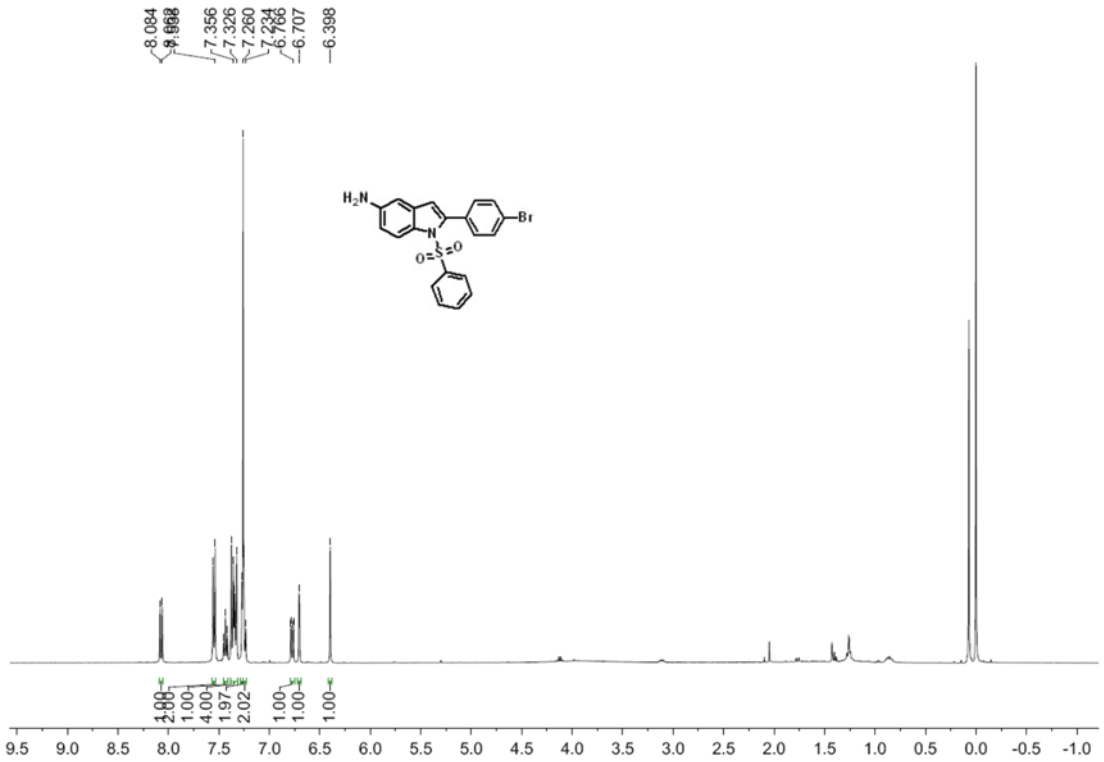
Copies of ^{1}H and ^{13}C NMR Spectra for Products **3a-3k**……S85-S108

General Information

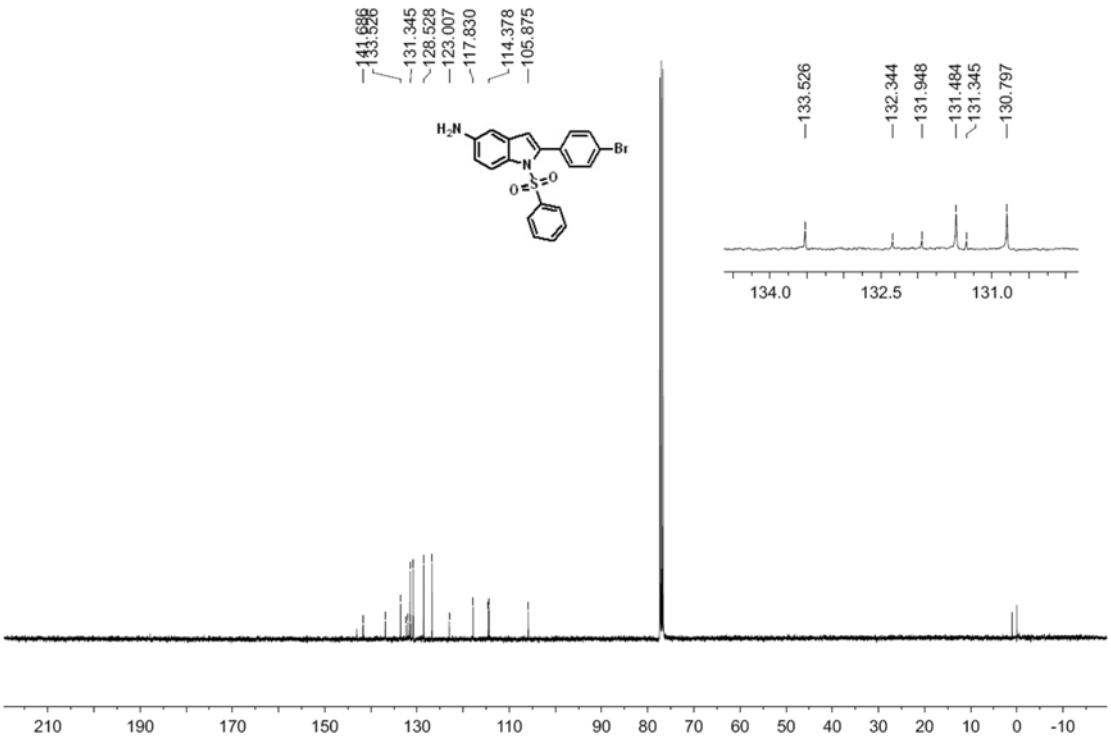
^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-*d6*) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

2-(4-bromophenyl)-1-(phenylsulfonyl)-1H-indol-5-amine (4)[1]

To a mixture of **2q** (0.24 mmol, 1 equiv) and iron powder (2.4 mmol, 10 equiv) in a round bottom flask, 2 mL of EtOH and 0.5 mL of water was added along with 45 µL of conc. HCl. The resulting mixture was allowed to reflux at 80 ºC for 2 h. After cooling at room temperature, the reaction mixture was washed with $NaHCO_3$ solution and extracted with ethyl acetate. Column chromatographic purification using 40% ethyl acetate/hexane yields **4** as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.07 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 -7.41 (m, 1H), 7.38-7.32 (m, 4H), 7.27 (s, 2H), 7.24 (d, *J* = 8.3 Hz, 5H), 6.80-6.75 (m, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 6.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 141.7, 136.9, 133.5, 132.3, 132.0, 131.5, 131.3, 130.8, 128.5, 126.7, 123.0, 117.8, 114.5, 114.4, 105.9.



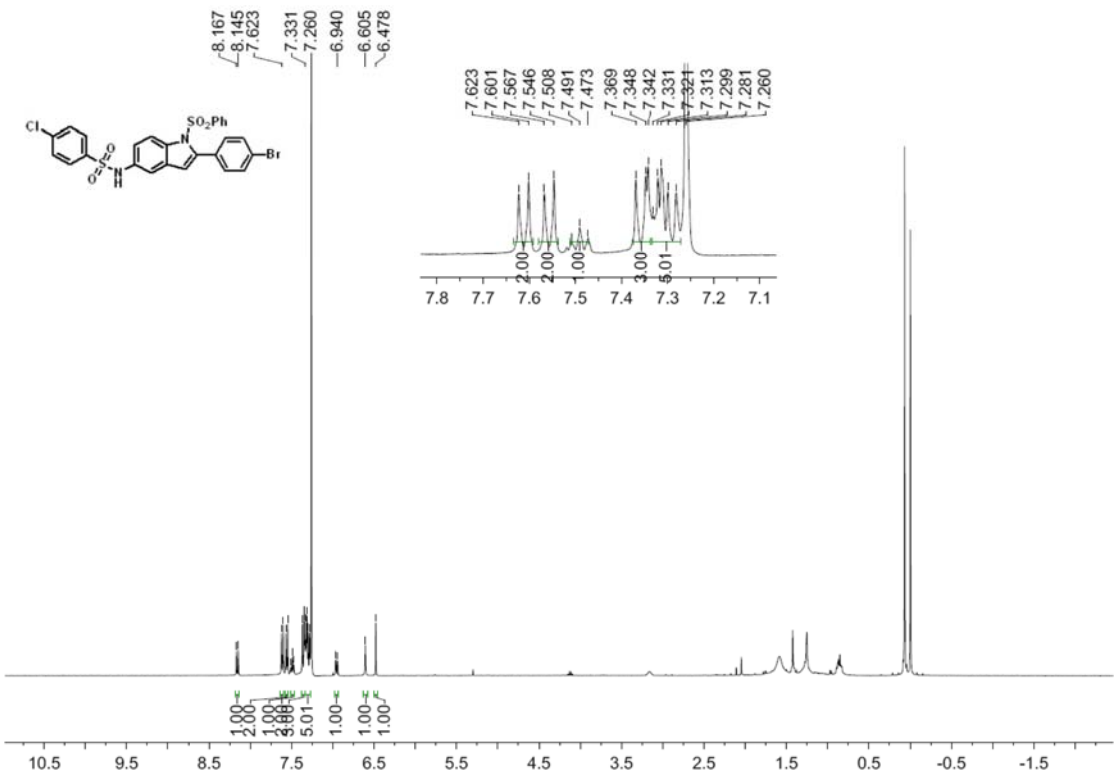
^{1}H NMR Spectrum of Compound **4**



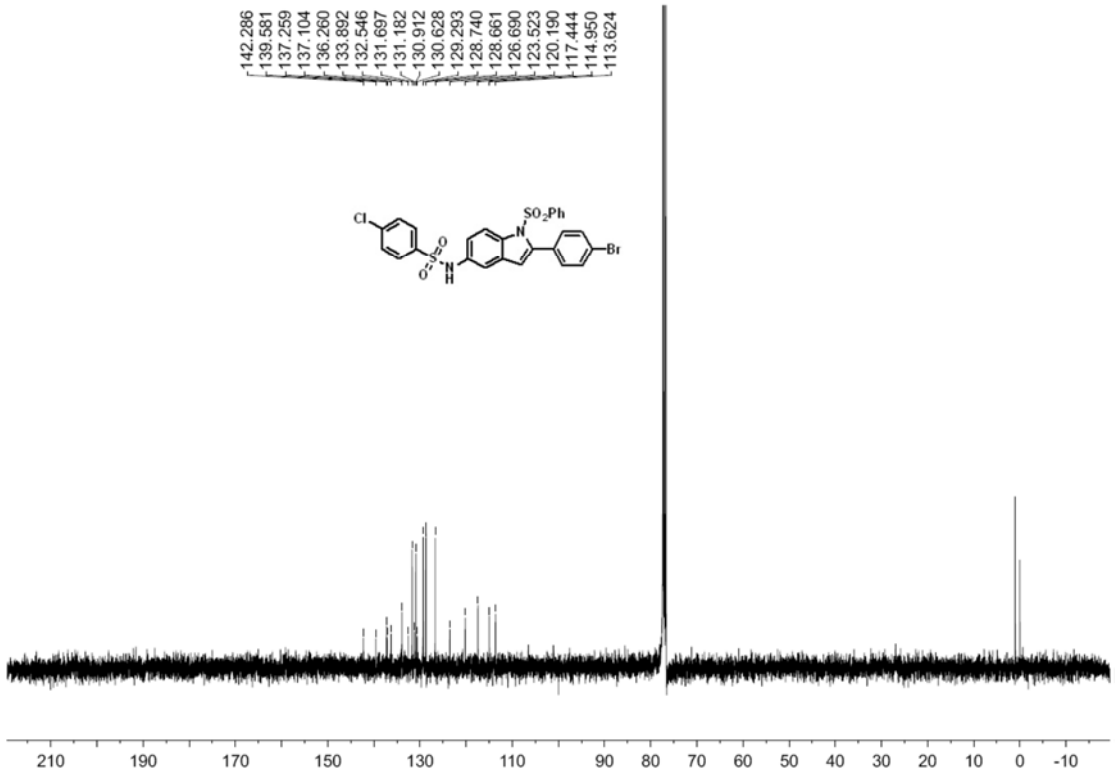
^{13}C NMR Spectrum of Compound **4**

N-(2-(4-bromophenyl)-1-(phenylsulfonyl)-1H-indol-5-yl)-4-chlorobenzenesulfonamide (5)[2]

To a stirred solution of compound **2q** (0.20 mmol) in DMSO (2 mL), $NaHSO_3$ (0.60 mmol), $FeCl_2$ (0.02 mmol), *N*,*N*-dimethyl-1,2-ethanediamine (4 μl, 0.04 mmol) and sodium 4-chlorobenzene sulfinate (0.30 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h in a sealed tube under N_2 atmosphere. After cooling to room temperature, water (8 mL) was added, the aqueous phase was extracted with DCM. The combined organic phase was washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated. The residue was purified on a silica gel column with petroleum ether/ethyl acetate (2/1) as the eluent to afford the corresponding product **5** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.16 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.51-7.47 (m, 1H), 7.38-7.34 (m, 3H), 7.33-7.27 (m, 5H), 6.98-6.93 (m, 1H), 6.61 (s, 1H), 6.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 142.3, 139.6, 137.3, 137.1, 136.3, 133. 9, 132.6, 131.7, 131.2, 130.9, 130.6, 129.3, 128.7, 128.7, 126.7, 123.5, 120.2, 117.4, 115.0, 113.6.



^{1}H NMR Spectrum of Compound **5**



^{13}C NMR Spectrum of Compound **5**

References

1 Z. Hu, J. Dong, Y. Men, Y. Li and X. Xu, *Chem. Commun.*, 2017, **53**, 1739.

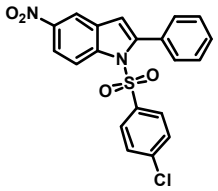
2 W. Zhang, J. Xie, B. Rao and M. Luo, *J. Org. Chem*., 2015, **80**, 3504.

General Procedure for the Synthesis of Products 2

Example for the synthesis of **2a**

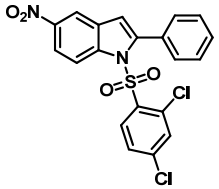
A suspension of $AgNO_3$ (0.02 mmol, 0.1 equiv.), 4-chloro-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide **1a** (0.2 mmol, 1.0 equiv.) in 2.0 mL of 1,4-dioxane was stirred at 100 °C under air conditions. The *t*-BuONO (0.4 mmol, 2.0 equiv.) were sequentially added in a 25-mL reaction vial. The mixture was sealed and stirred for 8 hours until TLC (petroleum ether: ethyl acetate = 1:8, v/v) revealed that conversion of the starting material **1a** was completed. The reaction system was evaporated under vacuum and purified by flash column chromatography (silica gel, mixtures of petroleum ether / ethyl acetate = 1:25, v/v) to afford the desired product **2a**.

1-((4-chlorophenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2a)



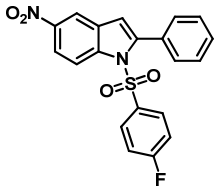
Light yellow solid, 78 mg, 95% yield; mp 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.43 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 2.4 Hz, 1H), 8.29-8.23 (m, 1H), 7.52-7.47 (m, 1H), 7.47-7.42 (m, 4H), 7.31-7.26 (m, 4H), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.91, 144.69, 141.07, 140.92, 135.72, 130.74, 130.57, 130.18, 129.63, 129.36, 128.24, 127.80, 119.96, 116.94, 116.50, 113.13. IR (KBr, v, cm^{-1}): 1580, 1520, 1447, 1385, 1344, 1185, 1054, 898, 760, 628, 577. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}ClN_2O_4S$ $[M+H]^+$ 413.0357, found 413.0345.

1-((2,4-dichlorophenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2b)



Light yellow solid, 79 mg, 88% yield; mp 152-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.49 (d, J = 2.4 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.29-8.23 (m, 1H), 7.40-7.34 (m, 2H), 7.26-7.15 (m, 4H), 6.98-6.93 (m, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.3, 143.0, 141. 7, 141.0, 134.8, 133.9, 132.7, 131.3, 130.8, 129.8, 129.5, 128.6, 127.7, 126.9, 119.8, 117.1, 116.3, 111.4. IR (KBr, v, cm^{-1}): 1577, 1514, 1458, 1413, 1375, 1150, 1031, 876, 746, 543. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{13}Cl_2N_2O_4S$ $[M+H]^+$ 446.9967, found 446.9953.

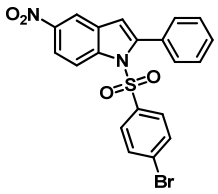
1-((4-fluorophenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2c)



Light yellow solid, 70 mg, 88% yield; mp 149-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 2.4 Hz, 1H), 8.29-8.23 (m, 1H), 7.51-7.41 (m, 5H), 7.40-7.35 (m, 2H), 7.01-6.94 (m, 2H), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 165.9 ($^1J_{CF}$ = 256.7 Hz), 144.9, 144.7, 141.0, 133.4 ($^4J_{CF}$ = 3.2 Hz), 130. 8, 130.6, 130.1, 129.8 ($^3J_{CF}$ = 9.7 Hz), 129.6, 127.8, 119.9, 116.9, 116.5, 116.4 ($^2J_{CF}$ = 22.8 Hz), 113.0. IR (KBr, v, cm^{-1}): 1590, 1519, 1491, 1445, 1382, 1346, 1233, 1186, 1156, 1087, 835, 586, 542. HRMS (APCI-TOF, m/z): calcd for

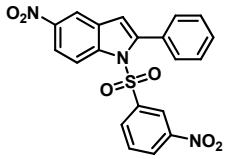
$C_{20}H_{14}FN_2O_4S$ $[M+H]^+$ 397.0652, found 397.0652.

1-((4-bromophenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2d)



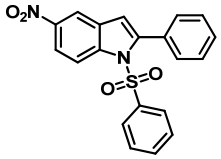
Light yellow solid, 82 mg, 90% yield; mp 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.43 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 2.4 Hz, 1H), 8.28-8.24 (m, 1H), 7.51-7.47 (m, 1H), 7.46-7.42 (m, 6H), 7.23-7.19 (m, 2H), 6.70-6.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.9, 144.7, 140.9, 136.2, 132.4, 130.7, 130.6, 130.2, 129.7, 129.6, 128.3, 127.8, 120.0, 117.0, 116.5, 113.2. IR (KBr, v, cm^{-1}): 1588, 1554, 1437, 1420, 1361, 1314, 1259, 1145, 1107, 1044, 894, 578. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}BrN_2O_4S$ $[M+H]^+$ 456.9852, found 456.9856.

5-nitro-1-((3-nitrophenyl)sulfonyl)-2-phenyl-1H-indole (2e)



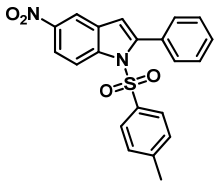
Yellow solid, 75 mg, 89% yield; mp 204-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.0 Hz, 1H), 8.37-8.32 (m, 1H), 8.31-8.26 (m, 1H), 8.14 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.59-7.51 (m, 2H), 7.49-7.41 (m, 4H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 147.9, 145.2, 144.6, 140.7, 139.0, 132.1, 130.6, 130.6, 130.3, 130.3, 130.0, 128.6, 128.0, 122.4, 120.3, 117.1, 116.5, 113.5. IR (KBr, v, cm^{-1}): 1607, 1532, 1516, 1444, 1348, 1184, 1073, 821, 764, 599. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}N_3O_6S$ $[M+H]^+$ 424.0597, found 424.0586.

5-nitro-2-phenyl-1-(phenylsulfonyl)-1H-indole (2f)



Light yellow solid, 72 mg, 95% yield; mp 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.48 (d, J = 9.2 Hz, 1H), 8.41 (d, J = 2.4 Hz, 1H), 8.30-8.25 (m, 1H), 7.56-7.49 (m, 2H), 7.46 (t, J = 4.8 Hz, 4H), 7.42-7.38 (m, 2H), 7.36-7.31 (m, 2H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.8, 144.7, 141.0, 137.4, 134.3, 130.9, 130.6, 130.1, 129.5, 129.0, 127.7, 126.8, 119.8, 116.8, 116.5, 112.8. IR (KBr, v, cm^{-1}): 3078, 1526, 1447, 1382, 1345, 1181, 1048, 764, 597. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{15}N_2O_4S$ $[M+H]^+$ 379.0747, found 379.0718.

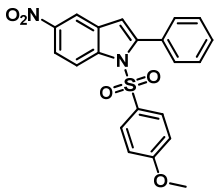
5-nitro-2-phenyl-1-tosyl-1H-indole (2g)



Light yellow solid, 72 mg, 92% yield; mp 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 2.4 Hz, 1H), 8.27-8.21 (m, 1H), 7.50-7.41 (m, 5H), 7.26 (t, J = 4.0 Hz, 3H), 7.09 (d, J = 8.0 Hz, 2H), 6.65 (s,

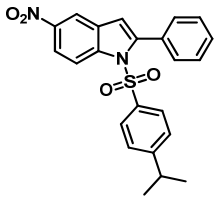
1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.5, 144. 9, 144.7, 141.0, 134.5, 131.1, 130. 6, 130.1, 129.6, 129.4, 127. 7, 126.8, 119.7, 116.8, 116.5, 112.8, 21.6. IR (KBr, v, cm^{-1}): 1597, 1519, 1447, 1379, 1343, 1188, 1178, 820, 762, 588. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{18}N_2O_4S$ $[M+H]^+$ 393.0903, found 393.0904.

1-((4-methoxyphenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2h)



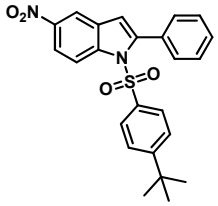
Light yellow solid, 59 mg, 72% yield; mp 173-174^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 2.4 Hz, 1H), 8.27-8.21 (m, 1H), 7.50-7.41 (m, 5H), 7.34-7.28 (m, 2H), 6.78-6.71 (m, 2H), 6.65 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 164.0, 144.9, 144.6, 141.0, 131.1, 130.6, 130.0, 129.4, 129.2, 129.0, 127.7, 119.7, 116. 8, 116.5, 114.1, 112.6, 55.7. IR (KBr, v, cm^{-1}): 1594, 1515, 1496, 1448, 1377, 1342, 1265, 1162, 1062, 727, 588. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{18}N_2O_5S$ $[M+H]^+$ 409.0852, found 409.0824.

1-((4-isopropylphenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2i)



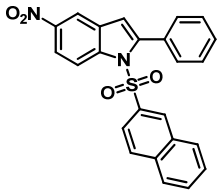
Light yellow solid, 54 mg, 64% yield; mp 103-104 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.4 Hz, 1H), 8.28-8.21 (m, 1H), 7.50-7.45 (m, 1H), 7.45-7.40 (m, 4H), 7.31-7.27 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.66 (s, 1H), 2.91-2.82 (m, 1H), 1.17 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 156.1, 144.8, 144.6, 141.0, 134.9, 131.1, 130.6, 130.0, 129.4, 127.6, 127.1, 127.0, 119.7, 116.8, 116.4, 112.6, 34.2, 23.5. IR (KBr, v, cm^{-1}): 2962, 1595, 1517, 1446, 1383, 1344, 1179, 1055, 821, 649, 592. HRMS (APCI-TOF, m/z): calcd for $C_{23}H_{21}N_2O_4S$ $[M+H]^+$ 421.1216, found 421.1187.

1-((4-(tert-butyl)phenyl)sulfonyl)-5-nitro-2-phenyl-1H-indole (2j)



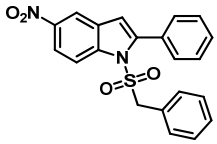
Light yellow solid, 82 mg, 95% yield; mp 109-110 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.48 (d, J = 9.2 Hz, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.30-8.25 (m, 1H), 7.52-7.47 (m, 1H), 7.47-7.41 (m, 4H), 7.33 (s, 4H), 6.68 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 158.4, 144.7, 144.6, 140.9, 134.6, 131.1, 130.6, 129.9, 129.4, 127.6, 126.8, 126.0, 119.7, 116.8, 116.4, 112.6, 35.3, 30. 9. IR (KBr, v, cm^{-1}): 2963, 1516, 1448, 1384, 1344, 1185, 1088, 821, 729, 587. HRMS (APCI-TOF, m/z): calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$ 421.1373, found 421.1349.

1-(naphthalen-2-ylsulfonyl)-5-nitro-2-phenyl-1H-indole (2k)



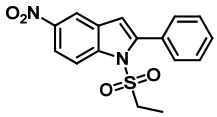
Light yellow solid, 78 mg, 91% yield; mp 166-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.54 (d, J = 9.2 Hz, 1H), 8.36 (d, J = 2.4 Hz, 1H), 8.29-8.25 (m, 1H), 7.90 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.76-7.72 (m, 2H), 7.65-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.44-7.38 (m, 4H), 7.34-7.30 (m, 1H), 6.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.7, 144.7, 141.0, 135.3, 134.3, 131.5, 131.0, 130.7, 130.0, 129.7, 129.5, 129.5, 129.5, 129.2, 127.9, 127.7, 121.0, 119.8, 116.9, 116.5, 112.7. IR (KBr, v, cm^{-1}): 3058, 1559, 1516, 1385, 1342, 1180, 1075, 904, 752, 659. HRMS (APCI-TOF, m/z): calcd for $C_{24}H_{17}N_2O_4S$ $[M+H]^+$ 429.0903, found 429.0877.

1-(benzylsulfonyl)-5-nitro-2-phenyl-1H-indole (2l)



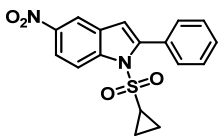
Light yellow solid, 64 mg, 81% yield; mp 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 2.4 Hz, 1H), 8.12-8.06 (m, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.48-7.43 (m, 1H), 7.41-7.35 (m, 2H), 7.28 (s, 1H), 7.26-7.23 (m, 2H), 7.11 (t, J = 7.6 Hz, 2H), 6.77 (d, J = 7.2 Hz, 2H), 6.64 (s, 1H), 4.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.1, 144.4, 140.9, 130.6, 130.5, 130.4, 129.6, 129.4, 128.9, 128.8, 127.5, 125. 9, 119.5, 116.8, 115.3, 111.4, 60.6. IR (KBr, v, cm^{-1}): 1514, 1446, 1375, 1346, 1259, 1159, 1079, 694, 611, 534. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{17}N_2O_4S$ $[M+H]^+$ 393.0903, found 393.0906.

1-ethyl-5-nitro-2-phenyl-1H-indole (2m)



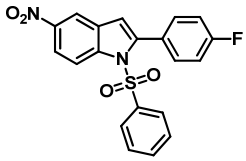
Light yellow solid, 26 mg, 40% yield; mp 188-189 °C. ^{1}H NMR (400 MHz, d_6-DMSO; δ, ppm): 12.78 (s, 1H), 8.20-8.11 (m, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.57-7.50 (m, 1H), 7.46-7.32 (m, 4H), 2.77-2.67 (m, 2H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO; δ, ppm): 146. 6, 142.4, 134.0, 130.4, 128.1, 127.5, 124.8, 124.7, 124.2, 122.1, 120.5, 113.2, 28.6, 15.9. IR (KBr, v, cm^{-1}): 3251, 1609, 1497, 1426, 1329, 1296, 1208, 1112, 1047, 845, 735, 643. HRMS (APCI-TOF, m/z): calcd for $C_{16}H_{15}N_2O_4S$ $[M+H]^+$ 331.0747, found 331.0752.

1-cyclopropyl-5-nitro-2-phenyl-1H-indole (2n)



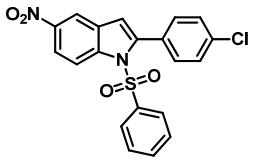
Light yellow solid, 14 mg, 21% yield; mp 194-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.51 (d, J = 2.0 Hz, 1H), 8.32-8.21 (m, 2H), 7.61-7.54 (m, 2H), 7.51-7.42 (m, 3H), 6.80 (s, 1H), 2.37-2.29 (m, 1H), 1.13-1.04 (m, 2H), 0.91-0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.8, 144.7, 141.0, 131.1, 130.5, 129.8, 129.5, 127.8, 119.7, 116.9, 115.9, 112.2, 31.6, 5.9; IR (KBr, v, cm^{-1}): 3102, 1516, 1444, 1370, 1342, 1260, 1160, 1076, 1005, 816, 717, 593; HRMS (APCI-TOF, m/z): calcd for $C_{17}H_{15}N_2O_4S$ $[M+H]^+$ 343.0747, found 343.0740.

2-(4-fluorophenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2o)



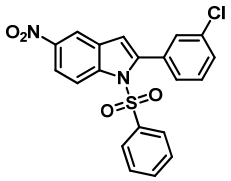
Light yellow solid, 65 mg, 82% yield; mp 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.4 Hz, 1H), 8.29-8.24 (m, 1H), 7.54-7.50 (m, 1H), 7.42-7.30 (m, 6H), 7.15-7.09 (m, 2H), 6.65 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 163.5 ($^1J_{CF}$ = 248.6 Hz), 144.79, 143.60, 140.96, 137.45, 134.37, 132.5 ($^3J_{CF}$ = 8.4 Hz), 129.90, 129.09, 126.9 ($^4J_{CF}$ = 3.5 Hz), 126.72, 119.95, 116.86, 116.48, 114.9 ($^2J_{CF}$ = 21.8 Hz), 112.90. IR (KBr, v, cm^{-1}): 1609, 1516, 1443, 1379, 1343, 1227, 1188, 1074, 845, 728, 585. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}FN_2O_4S$ $[M+H]^+$ 397.0652, found 397.0632.

2-(4-chlorophenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2p)



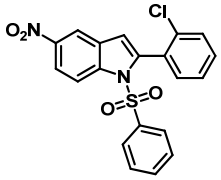
Light yellow solid, 74 mg, 90% yield; mp 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.37 (d, J = 2.4 Hz, 1H), 8.28-8.22 (m, 1H), 7.55-7.49 (m, 1H), 7.43-7.30 (m, 8H), 6.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.8, 143.5, 141.0, 137.3, 135.7, 134.4, 131.8, 130.0, 129.4, 129.1, 128.0, 126.7, 120.0, 116.9, 116.5, 113.2. IR (KBr, v, cm^{-1}): 3122, 1516, 1484, 1442, 1379, 1341, 1225, 1189, 1091, 1063, 996, 814, 724, 600. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}ClN_2O_4S$ $[M+H]^+$ 413.0357, found 413.0361.

2-(3-chlorophenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2q)



Light yellow solid, 72 mg, 87% yield; mp 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.0 Hz, 1H), 8.29-8.24 (m, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.49-7.42 (m, 1H), 7.41-7.31 (m, 7H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.8, 143.0, 141.0, 137.4, 134.5, 133.6, 132.6, 130.3, 129.8, 129.5, 129.2, 129.0, 128.9, 126.8, 120.2, 117.1, 116.5, 113.3. IR (KBr, v, cm^{-1}): 3112, 1569, 1443, 1415, 1357, 1228, 1201, 1173, 1058, 889, 761, 597. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}ClN_2O_4S$ $[M+H]^+$ 413.0357, found 413.0345.

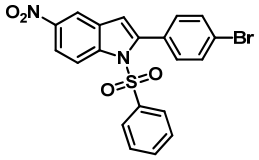
2-(2-chlorophenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2r)



Light yellow solid, 67 mg, 81% yield; mp 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 9.4 Hz, 1H), 8.30-8.24 (m, 1H), 7.57-7.52 (m, 3H), 7.48-7.42 (m, 2H), 7.41-7.35 (m, 4H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.5, 140.2, 140.0, 137. 8, 135.4, 134.5, 132.9, 131.0, 130.2, 129.5, 129.4, 129.2,

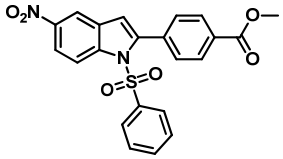
127.0, 126.08, 120.0, 117.3, 115.6, 113.3. IR (KBr, *v*, cm^{-1}): 1556, 1473, 1428, 1365, 1219, 1182, 1097, 1023, 865, 732, 588. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}ClN_2O_4S$ $[M+H]^+$ 413.0357, found 413.0368.

2-(4-bromophenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2s)



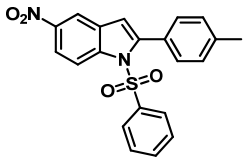
Light yellow solid, 72 mg, 79% yield; mp 179-180 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 2.4 Hz, 1H), 8.28-8.22 (m, 1H), 7.60-7.55 (m, 2H), 7.54-7.50 (m, 1H), 7.40-7.29 (m, 6H), 6.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.9, 143.5, 141.1, 137.3, 134.4, 132.0, 131.0, 123.0, 129.9, 129.1, 126.7, 124.0, 120.1, 116.9, 116.5, 113.2. IR (KBr, *v*, cm^{-1}): 1589, 1472, 1428, 1369, 1258, 1185, 1164, 1021, 862, 759, 580. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}BrN_2O_4S$ $[M+H]^+$ 456.9852, found 456.9850.

methyl 4-(5-nitro-1-(phenylsulfonyl)-1H-indol-2-yl)benzoate (2t)



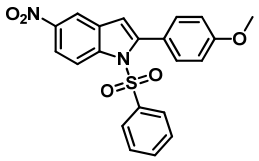
Light yellow solid, 64 mg, 73% yield; mp 191-192 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.4 Hz, 1H), 8.30-8.24 (m, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.57-7.49 (m, 3H), 7.39-7.29 (m, 4H), 6.73 (s, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 166.6, 144.9, 143.7, 141.2, 137.2, 135.4, 134.5, 130.8, 130.5, 130.0, 129.1, 128.9, 126.7, 120.2, 117.1, 116.6, 113.8, 52.4. IR (KBr, *v*, cm^{-1}): 1734, 1523, 1497, 1425, 1315, 1371, 1160, 1036, 864, 783, 583. HRMS (APCI-TOF, m/z): calcd for $C_{22}H_{17}N_2O_6S$ $[M+H]^+$ 437.0801, found 437.0809.

5-nitro-1-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (2u)



Light yellow solid, 55 mg, 70% yield; mp 200-201 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.46 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 2.4 Hz, 1H), 8.28-8.23 (m, 1H), 7.55-7.50 (m, 1H), 7.43-7.40 (m, 2H), 7.37-7.31 (m, 4H), 7.27 (d, J = 8.0 Hz, 2H), 6.65 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 145.1, 144.7, 141.0, 139.6, 137.4, 134.2, 130. 5, 130.2, 129.0, 128. 5, 128.1, 126.8, 119.7, 116.7, 116.5, 112.6, 21.5. IR (KBr, *v*, cm^{-1}): 2963, 1516, 1448, 1378, 1343, 1185, 1069, 901, 684, 565. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{17}N_2O_4S$ $[M+H]^+$ 393.0903, found 393.0892.

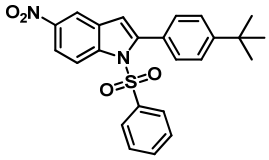
2-(4-methoxyphenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2v)



Light yellow solid, 60 mg, 73% yield; mp 180-181 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.35 (s, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.41-7.27 (m, 6H), 6.95 (d, J = 8.4 Hz, 2H), 6.60 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 160.6, 144.8, 144.7, 141.0, 137.5, 134.2, 132.0, 130.2, 129.0, 126. 8,

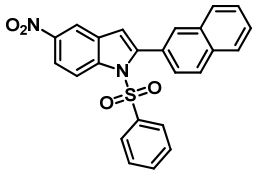
123.1, 119.6, 116.6, 116.5, 113.2, 112.2, 55.4. IR (KBr, *v*, cm^{-1}): 3120, 1613, 1518, 1441, 1413, 1342, 1253, 1188, 1072, 885, 815, 727, 588. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{17}N_2O_5S$ $[M+H]^+$ 409.0852, found 409.0873.

2-(4-(tert-butyl)phenyl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2w)



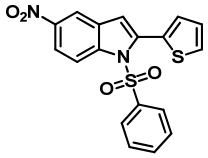
Light yellow solid, 71 mg, 82% yield; mp 212-213 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 9.2 Hz, 1H), 8.37 (d, J = 2.4 Hz, 1H), 8.26-8.21 (m, 1H), 7.52-7.47 (m, 1H), 7.45-7.42 (m, 2H), 7.39-7.33 (m, 4H), 7.32-7.27 (m, 2H), 6.63 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 152.7, 145.0, 144.7, 141.0, 137.5, 134.2, 130.3, 130.1, 128.9, 127.9, 126.9, 124.7, 119.6, 116.7, 116. 5, 112.5, 34.9, 31.3. IR (KBr, *v*, cm^{-1}): 2963, 1516, 1384, 1344, 1185, 1088, 913, 821, 729, 581. HRMS (APCI-TOF, m/z): calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$ 435.1373, found 435.1343.

2-(naphthalen-2-yl)-5-nitro-1-(phenylsulfonyl)-1H-indole (2x)



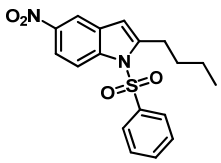
Light yellow solid, 66 mg, 77% yield; mp 126-127 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.48 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 2.4 Hz, 1H), 8.30-8.24 (m, 1H), 7.94-7.83 (m, 4H), 7.64-7.55 (m, 3H), 7.52-7.47 (m, 1H), 7.40-7.35 (m, 2H), 7.31-7.26 (m, 2H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.9, 144.8, 141.1, 137.4, 134.3, 133.5, 132.4, 130.2, 129.6, 129.0, 128.6, 128.3, 128.2, 127.9, 127.2, 127.1, 126.8, 126.7, 119.9, 116.9, 116.5, 113.3. IR (KBr, *v*, cm^{-1}): 1516, 1447, 1383, 1343, 1175, 1089, 1055, 901, 822, 729, 605. HRMS (APCI-TOF, m/z): calcd for $C_{24}H_{17}N_2O_4S$ $[M+H]^+$ 429.0903, found 429.0875.

5-nitro-2-(thiophen-2-yl)-1H-indole (2y)



Brown solid, 46 mg, 60% yield; mp 125-127 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.45 (d, J = 9.2 Hz, 1H), 8.38 (d, J = 2.2 Hz, 1H), 8.26-8.22 (m, 1H), 7.53-7.49 (m, 1H), 7.40-7.36 (m, 3H), 7.34-7.30 (m, 3H), 7.23 (d, J = 4.9 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 144.6, 140.8, 139.3, 137.6, 134.3, 130.9, 130.2, 129.7, 129.0, 127.2, 126.8, 124.8, 119.8, 116.7, 116.2, 112.5. IR (KBr, *v*, cm^{-1}): 3125, 1502, 1445, 1360, 1336, 1233, 1188, 1025, 1011, 824, 721, 587. HRMS (APCI-TOF, m/z): calcd for $C_{18}H_{13}N_2O_4S_2$ $[M+H]^+$ 385.0311, found 385.0309.

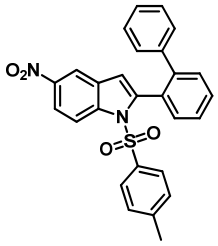
2-butyl-5-nitro-1-(phenylsulfonyl)-1H-indole (2z)



Yellow oil, 52 mg, 73% yield. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.36-8.25 (m, 2H), 8.17-8.12 (m, 1H), 7.75 (t, J =

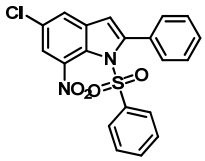
7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.52 (s, 1H), 3.00 (t, *J* = 7.6 Hz, 2H), 1.78-1.69 (m, 2H), 1.49-1.42 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 145.9, 144.3, 140.1, 138.6, 134.3, 129. 7, 129. 6, 126.3, 119.0, 116.2, 114.7, 108.5, 30.6, 28.6, 22.4, 13.9. IR (KBr, *v*, cm^{-1}): 2982, 1558, 1523, 1486, 1379, 1248, 1190, 1065, 1012, 871, 763, 620. HRMS (APCI-TOF, m/z): calcd for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$ 359.1060, found 359.1035.

2-([1,1'-biphenyl]-2-yl)-5-nitro-1-tosyl-1H-indole (2aa)



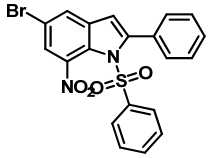
Light yellow solid, 90 mg, 96% yield; mp 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.60-7.51 (m, 6H), 7.49-7.43 (m, 5H), 7.40-7.35 (m, 1H), 7.25-7.18 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03-6.99 (m, 1H), 6.77 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 145.5, 144.4, 143.6, 143.5, 140.7, 139.8, 135.3, 130.9, 130.1, 129.9, 129.9, 129.7, 129.5, 129.1, 127.9, 127.1, 126.9, 126.4, 119.5, 116.9, 115.5, 113.2, 21.6. IR (KBr, *v*, cm^{-1}): 1594, 1519, 1447, 1377, 1345, 1179, 1076, 897, 815, 705, 670, 587. HRMS (APCI-TOF, m/z): calcd for $C_{27}H_{21}N_2O_4S$ $[M+H]^+$ 469.1216, found 469.1211.

5-chloro-7-nitro-2-phenyl-1-(phenylsulfonyl)-1H-indole (2ab)



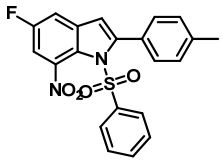
Yellow solid, 54 mg, 65% yield; mp 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 7.88 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.47-7.43 (m, 1H), 7.41-7.37 (m, 1H), 7.32-7.25 (m, 5H), 7.18-7.13 (m, 2H), 6.94-6.88 (m, 2H), 6.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 148.2, 141.4, 137.1, 135.6, 134.2, 130.4, 130.0, 129.8, 129.7, 129.7, 128.5, 128.2, 127.3, 125.3, 120.9, 111.1. IR (KBr, *v*, cm^{-1}): 3077, 1540, 1449, 1376, 1236, 1169, 1086, 998, 839, 753, 686, 594. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}ClN_2O_4S$ $[M+H]^+$ 413.0357, found 413.0364.

5-bromo-7-nitro-2-phenyl-1-(phenylsulfonyl)-1H-indole (2ac)



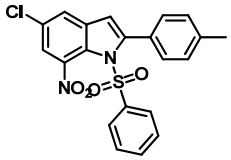
Yellow solid, 80 mg, 88% yield; mp 176-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm): 8.00 (d, *J* = 1.6 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.31-7.24 (m, 4H), 7.15 (t, *J* = 8.0 Hz, 2H), 6.94-6.85 (m, 2H), 6.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm): 148.1, 141.5, 137.1, 136.0, 134.2, 130.2, 129.9, 129.7, 129.7, 128.6, 128.4, 128.2, 127.3, 123.4, 117.4, 110.9. IR (KBr, *v*, cm^{-1}): 3075, 1459, 1448, 1366, 1238, 1169, 1087, 997, 831, 751, 686, 594. HRMS (APCI-TOF, m/z): calcd for $C_{20}H_{14}BrN_2O_4S$ $[M+H]^+$ 458.9833, found 458.9844.

5-fluoro-7-nitro-1-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (2ad)



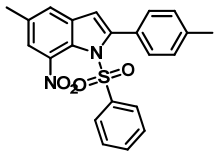
Yellow solid, 66 mg, 81% yield; mp 188-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.66-7.62 (m, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.40-7.37 (m, 1H), 7.21-7.12 (m, 6H), 6.93 (d, J = 8.0 Hz, 2H), 6.48 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 159.1 ($^1J_{CF}$ = 245.6 Hz), 148.90, 141.4 ($^1J_{CF}$ = 9.6 Hz), 140.06, 136.86, 135.8 ($^4J_{CF}$ = 9.7 Hz), 134.03, 129.60, 128.83, 128.39, 127.8 ($^7J_{CF}$ = 2.1 Hz), 127.3 ($^6J_{CF}$ = 2.3 Hz), 111.6 ($^3J_{CF}$ = 23.6 Hz), 111.4 ($^5J_{CF}$ = 3.8 Hz), 109.0 ($^2J_{CF}$ = 29.4 Hz), 21.45. IR (KBr, v, cm^{-1}): 3069, 1462, 1447, 1364, 1257, 1168, 1088, 980, 854, 750, 688. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{16}FN_2O_4S$ $[M+H]^+$ 411.0809, found 411.0815.

5-chloro-7-nitro-1-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (2ae)



Yellow solid, 67 mg, 79% yield; mp 178-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.87 (d, J = 1.6 Hz, 1H), 7.67 (d, J = 1.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.26 (s, 1H), 7.20-7.14 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 6.45 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 148.5, 141.5, 140.1, 137.1, 135.8, 134.1, 130.5, 129.7, 129.6, 128.8, 128.4, 127.3, 127.2, 125.0, 120.7, 110. 7, 21.5. IR (KBr, v, cm^{-1}): 1732, 1551, 1446, 1375, 1244, 1175, 1042, 966, 818, 752, 582. HRMS (APCI-TOF, m/z): calcd for $C_{21}H_{16}ClN_2O_4S$ $[M+H]^+$ 427.0513, found 427.0510.

5-methyl-7-nitro-1-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (2af)



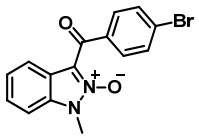
Yellow solid, 53 mg, 65% yield; mp 191-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.70 (s, 1H), 7.47 (s, 1H), 7.43 (s, 1H), 7.36 (d, J = 6.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.17-7.09 (m, 4H), 6.95 (d, J = 7.6 Hz, 2H), 6.43 (s, 1H), 2.52 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 147.2, 139.5, 137.1, 135.5, 135.1, 133.7, 129.6, 128.7, 128.2, 127.8, 127.3, 127.2, 125.7, 121.7, 111.7, 21.4, 21.1. IR (KBr, v, cm^{-1}): 1651, 1539, 1506, 1448, 1371, 1213, 1174, 1088, 820, 753, 728, 580. HRMS (APCI-TOF, m/z): calcd for $C_{22}H_{19}N_2O_4S$ $[M+H]^+$ 407.1060, found 407.1049.

General Procedure for the Synthesis of Products 3

Example for the synthesis of **3a**

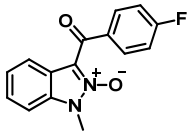
Under Ar conditions, $AgNO_3$ (0.02 mmol, 0.1 equiv.), 2-((4-bromophenyl)ethynyl)-N-methylaniline **2a** (0.2 mmol, 1.0 equiv.) in 3.0 mL of 1,4-Dioxane were added into 10-mL reaction tube. Then, *t*-BuONO (0.4 mmol, 2.0 equiv.) was added into the reaction system. The mixture was stirred for 4 hours at 60 °C. After completion of the reaction (TLC monitored), the reaction system was evaporated under vacuum and purified by flash column chromatography (silica gel, mixtures of petroleum ether / ethyl acetate = 1: 5, v/v) to afford the desired product **3a**.

3-(4-bromobenzoyl)-1-methyl-1H-indazole 2-oxide (3a)



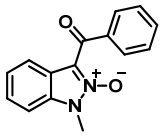
Yellow solid, 51 mg, 78% yield; mp 156-158 ºC. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.93 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.51-7.45 (m, 1H), 7.37-7.31 (m, 1H), 7.24 (d, J = 8.3 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 184.8, 135.9, 131.6, 131.0, 130.8, 128.0, 126.9, 124.4, 121.5, 120.5, 118.7, 107.3, 29.2. IR (KBr, v, cm^{-1}): 3063, 1633, 1616, 1587, 1508, 1448, 1358, 1305, 1009, 885, 748. HRMS (APCI-TOF, m/z): calcd for $C_{15}H_{12}BrN_2O_2$ $[M+H]^+$ 331.0076, found 331.0071.

3-(4-fluorobenzoyl)-1-methyl-1H-indazole 2-oxide (3b)



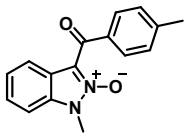
Yellow solid, 39 mg, 73% yield; mp 128-130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.95 (d, J = 5.5 Hz, 1H), 7.94-7.90 (m, 2H), 7.51-7.45 (m, 1H), 7.36-7.31 (m, 1H), 7.24 (d, J = 8.3 Hz, 1 H), 7.20-7.14 (m, J = 8.6 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 184.3, 165.7($^3J_{CF}$ = 252.9 Hz), 133.3, 132.1($^1J_{CF}$ = 9.3 Hz), 131.0, 126.9, 124.3, 121.6, 120.5, 118.8, 115.5($^2J_{CF}$ = 22.0 Hz), 107.2, 29.2. IR (KBr, v, cm^{-1}): 3085, 1633, 1600, 1501, 1436, 1359, 1306, 1236, 1158, 889, 739, 593. HRMS (APCI-TOF, m/z): calcd for $C_{15}H_{12}FN_2O_2$ $[M+H]^+$ 271.0877, found 271.0878.

3-benzoyl-1-methyl-1H-indazole 2-oxide (3c)



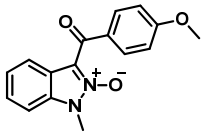
Yellow oil, 20 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.93-7.83 (m, 3H), 7.63-7.58 (m, 1H), 7.52-7.44 (m, 2H), 7.34- 7.29 (m, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.9, 137.2, 133.0, 130.9, 129.2, 128.3, 126.7, 124.1, 120.5, 118.8, 107.2, 29.1. IR (KBr, v, cm^{-1}): 3060, 1635, 1508, 1449, 1355, 1306, 1203, 1099, 1041, 880, 700, 648. HRMS (APCI-TOF, m/z): calcd for $C_{15}H_{13}N_2O_2$ $[M+H]^+$ 253.0971, found 253.0978.

1-methyl-3-(4-methylbenzoyl)-1H-indazole 2-oxide (3d)



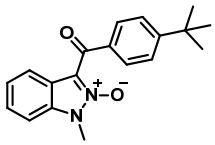
Light yellow solid, 18 mg, 34% yield; mp 150-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.85 (d, J = 8.1 Hz, 3H), 7.81 (d, J = 8.1 Hz, 1H), 7.48-7.42 (m, 1H), 7.33-7.27 (m, 3H), 7.22 (d, J = 8.3 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.5, 144.0, 134.5, 131.0, 129.5, 129.0, 126.7, 124.0, 121.8, 120. 5, 118.8, 107.1, 29.1, 21.9. IR (KBr, v, cm^{-1}): 2962, 1630, 1635, 1516, 1428, 1360, 1303, 1259, 1177, 1098, 886, 738. HRMS (APCI-TOF, m/z): calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$ 267.1128, found 267.1131.

3-(4-methoxybenzoyl)-1-methyl-1H-indazole 2-oxide (3e)



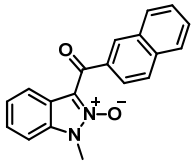
Yellow solid, 45 mg, 80% yield; mp 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.93 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.1 Hz, 1H), 7.48-7.43 (m, 1H), 7.32-7.28 (m, 1H), 7.22 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H);. ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 184.2, 163.9, 132.1, 131.0, 129.6, 126.7, 123.9, 121.9, 120.4, 118.9, 113.6, 107.1, 55.5, 29.1. IR (KBr, v, cm^{-1}): 2965, 1606, 1573, 1505, 1433, 1302, 1269, 1177, 1099, 1018, 886, 732. HRMS (APCI-TOF, m/z): calcd for $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1077, found 283.1074.

3-(4-(tert-butyl)benzoyl)-1-methyl-1H-indazole 2-oxide (3f)



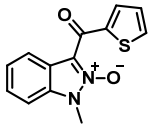
Yellow solid, 27 mg, 44% yield; mp 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.89-7.85 (m, 3H), 7.51 (d, J = 8.4 Hz, 2H), 7.48-7.44 (m, 1H), 7.33-7.29 (m, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.91 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.5, 157.0, 134.3, 131.0, 129.4, 126.7, 125.3, 124.0, 121.8, 120.5, 118.9, 107.2, 35.2, 31.1, 29.1. IR (KBr, v, cm^{-1}): 2962, 1652, 1603, 1507, 1456, 1303, 1261, 1126, 1048, 885. HRMS (APCI-TOF, m/z): calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$ 309.1597, found 309.1600.

3-(2-naphthoyl)-1-methyl-1H-indazole 2-oxide (3g)



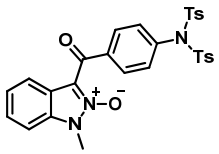
Yellow solid, 18 mg, 30% yield; mp 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (s, 1H), 7.95 (d, J = 7.7 Hz, 3H), 7.92-7.85 (m, 2H), 7.63-7.58 (m, 1H), 7.56-7.51 (m, 1H), 7.50-7.45 (m, 1H), 7.33-7.29 (m, 1H), 7.24 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.7, 135.7, 134.6, 132.5, 131.1, 131.0, 129. 7, 128.4, 128.0, 127.8, 126.7, 126.6, 125.0, 124.1, 121.9, 120.5, 118.8, 107.2, 29.1. IR (KBr, v, cm^{-1}): 2932, 1626, 1556, 1511, 1428, 1319, 1254, 1180, 1012, 885, 714. HRMS (APCI-TOF, m/z): calcd for $C_{19}H_{15}N_2O_2$ $[M+H]^+$ 303.1128, found 303.1122.

1-methyl-3-(thiophene-2-carbonyl)-1H-indazole 2-oxide (3h)



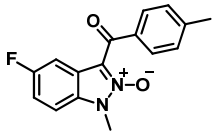
Brown solid, 18 mg, 35% yield; mp 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 8.44 (d, J = 2.7 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 5.1 Hz, 1H), 7.48-7.44 (m, 1H), 7.35-7.29 (m, 2H), 7.22 (d, J = 8.3 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 178. 6, 1406, 134.5, 131.0, 128.1, 126.8, 125.3, 124.1, 122.3, 120.7, 118. 8, 107.1, 29.1. IR (KBr, v, cm^{-1}): 3093, 1629, 1613, 1515, 1501, 1455, 1435, 1248, 849, 734. HRMS (APCI-TOF, m/z): calcd for $C_{13}H_{11}N_2O_2S$ $[M+H]^+$ 259.0535, found 259.0530.

3-benzoyl-1-methyl-1H-indazole 2-oxide (3i)



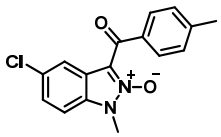
Yellow solid, 40 mg, 35% yield; mp 181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.92-7.86 (m, 3H), 7.83 (d, J = 8.3 Hz, 4H), 7.50-7.45 (m, 1H), 7.36-7.32 (m, 5H), 7.24 (d, J = 8.3 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H), 2.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 184.7, 145.2, 138.4, 138.0, 136.4, 131.5, 130.9, 130.1, 129.7, 129.6, 128.6, 126.9, 124.4, 121.5, 120.4, 118.7, 107.3, 29.2, 21.8. IR (KBr, ν, cm^{-1}): 1636, 1598, 1507, 1497, 1456, 1379, 1176, 1085, 915, 741, 659. HRMS (APCI-TOF, m/z): calcd for $C_{29}H_{26}N_3O_6S_2$ $[M+H]^+$ 576.1257, found 576.1260.

5-fluoro-1-methyl-3-(4-methylbenzoyl)-1H-indazole 2-oxide (3j)

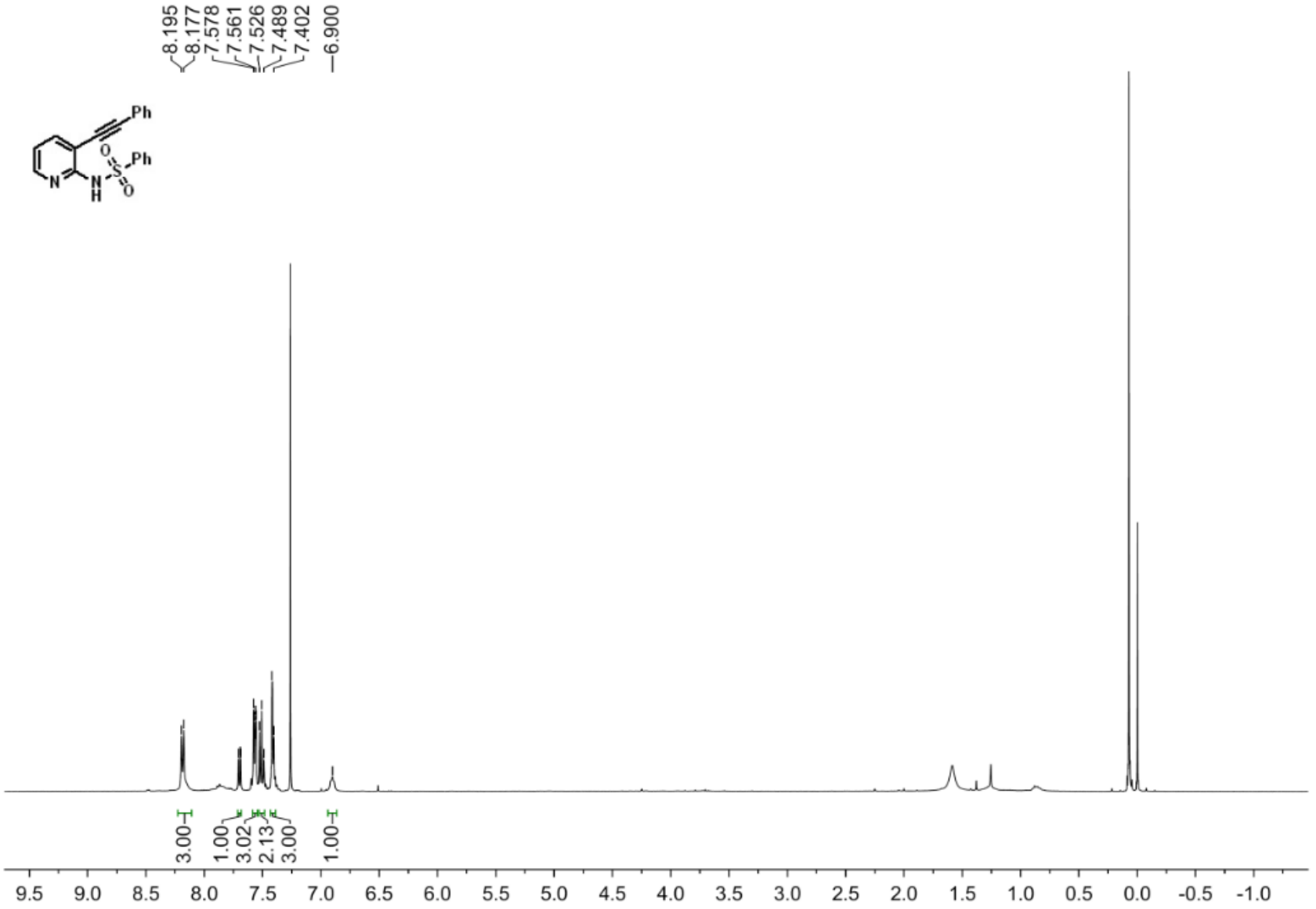


Light yellow solid, 22 mg, 38% yield; mp 159-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.79 (d, J = 8.1 Hz, 2H), 7.60-7.54 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.24-7.15 (m, 1H), 3.89 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.2, 160.0($^1J_{CF}$ = 239.6 Hz), 144.16, 134.27, 129.03, 127.41, 119.5 ($^1J_{CF}$ = 11.7 Hz), 115.5 ($^1J_{CF}$ = 26.6 Hz), 108.4 ($^1J_{CF}$ = 9.2 Hz), 106.0 ($^1J_{CF}$ = 26.4 Hz), 29.32, 21.85. IR (KBr, ν, cm^{-1}): 2966, 1606, 1517, 1503, 1424, 1361, 1266, 1179, 837, 734. HRMS (APCI-TOF, m/z): calcd for $C_{16}H_{14}FN_2O_2$ $[M+H]^+$ 285.1033, found 285.1038.

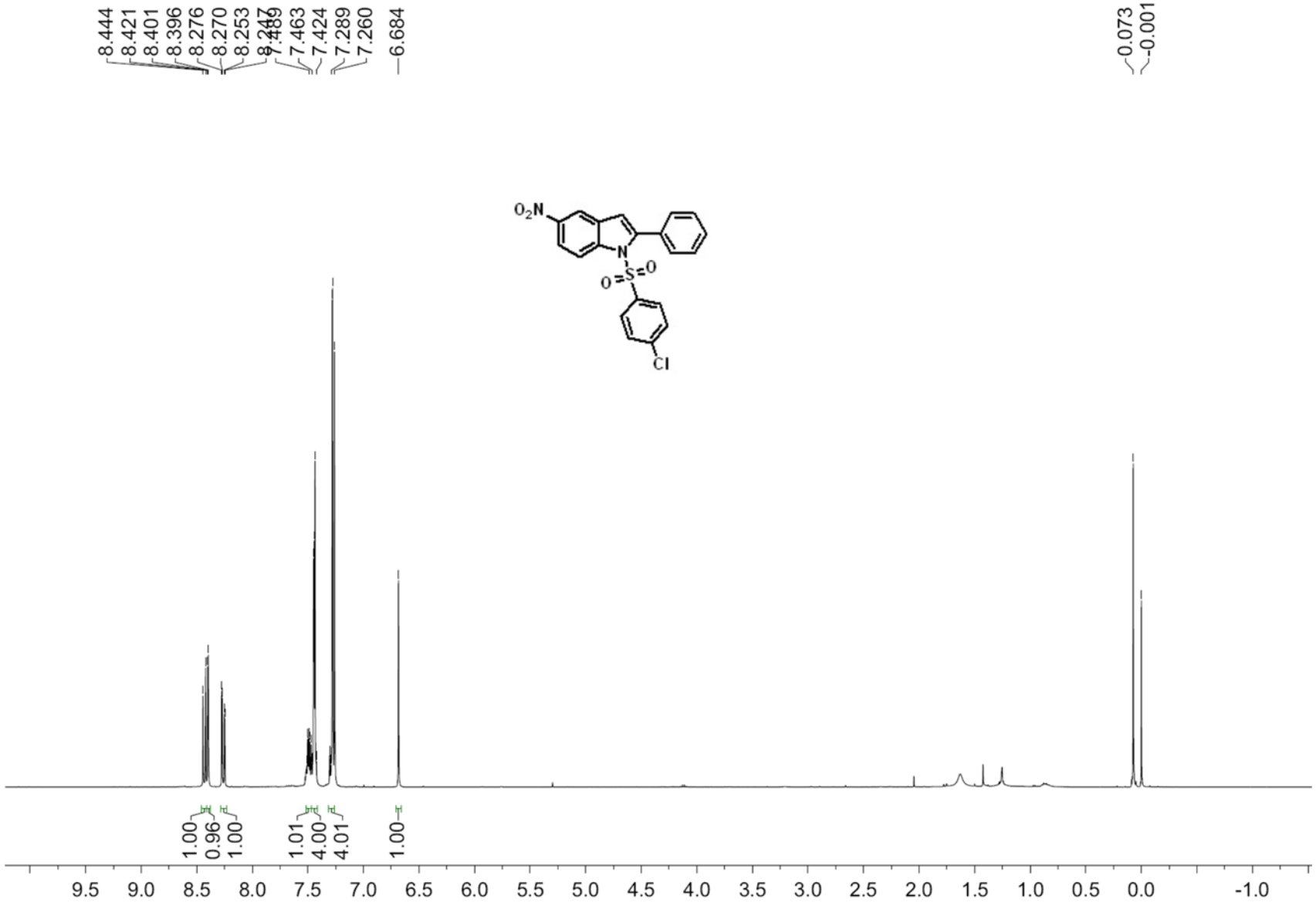
5-chloro-1-methyl-3-(4-methylbenzoyl)-1H-indazole 2-oxide (3k)



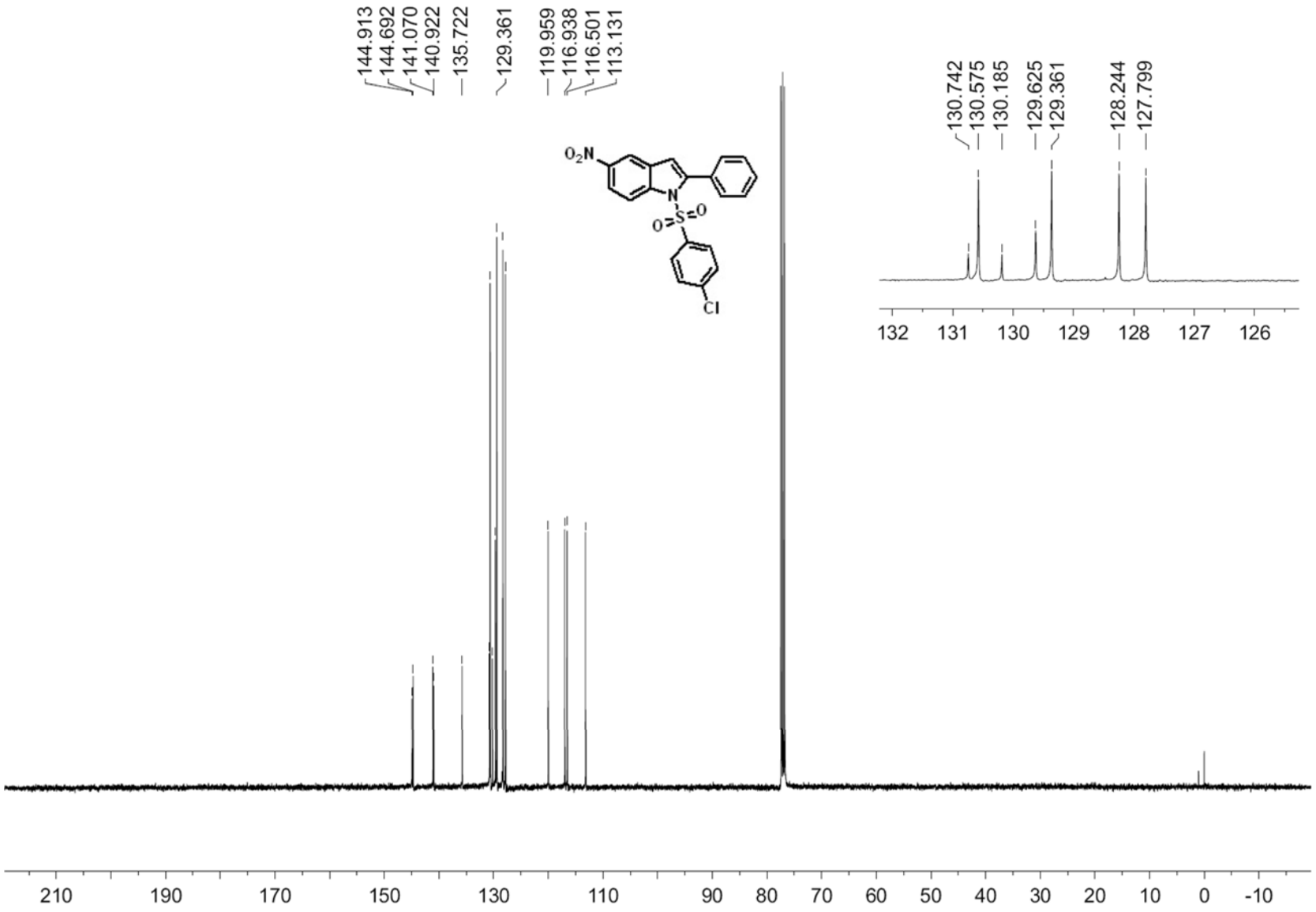
Light yellow solid, 16 mg, 27% yield; mp 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 7.90 (d, J = 1.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.44-7.40 (m, , 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.7 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 185.1, 144.3, 134.2, 130.0, 129.5, 129.2, 129.1, 127.2, 121.4, 119.9, 119.8, 108.3, 29.3, 21.9. IR (KBr, ν, cm^{-1}): 2924, 1747, 1609, 1506, 1473, 1456, 1263, 1240, 1179, 1080, 794, 745. HRMS (APCI-TOF, m/z): calcd for $C_{16}H_{14}ClN_2O_2$ $[M+H]^+$ 301.0738, found 301.0737.



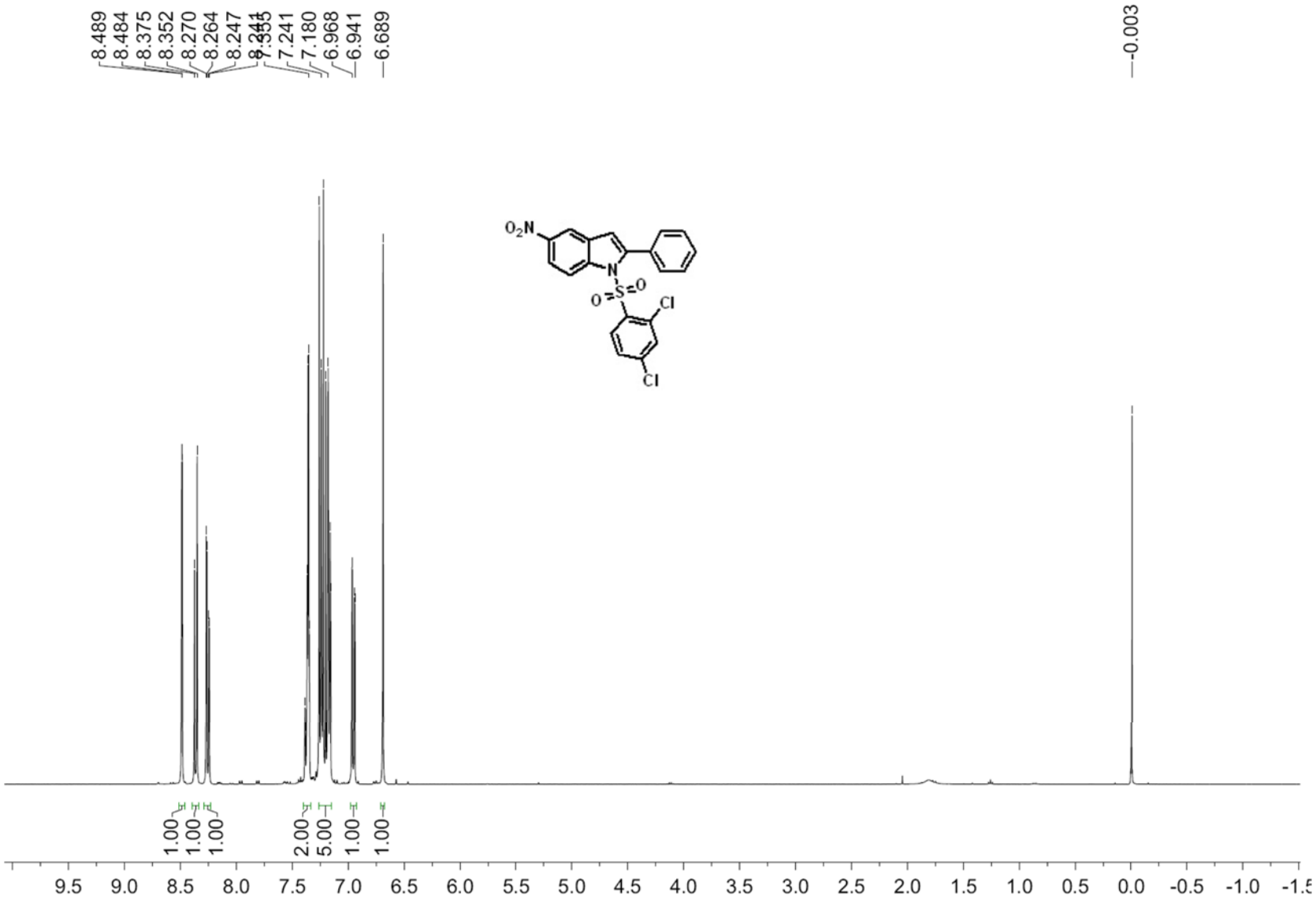
^{1}H NMR Spectrum of *N*-Tosyl 3-(Phenylethynyl)pyridin-2-amine **1ab**



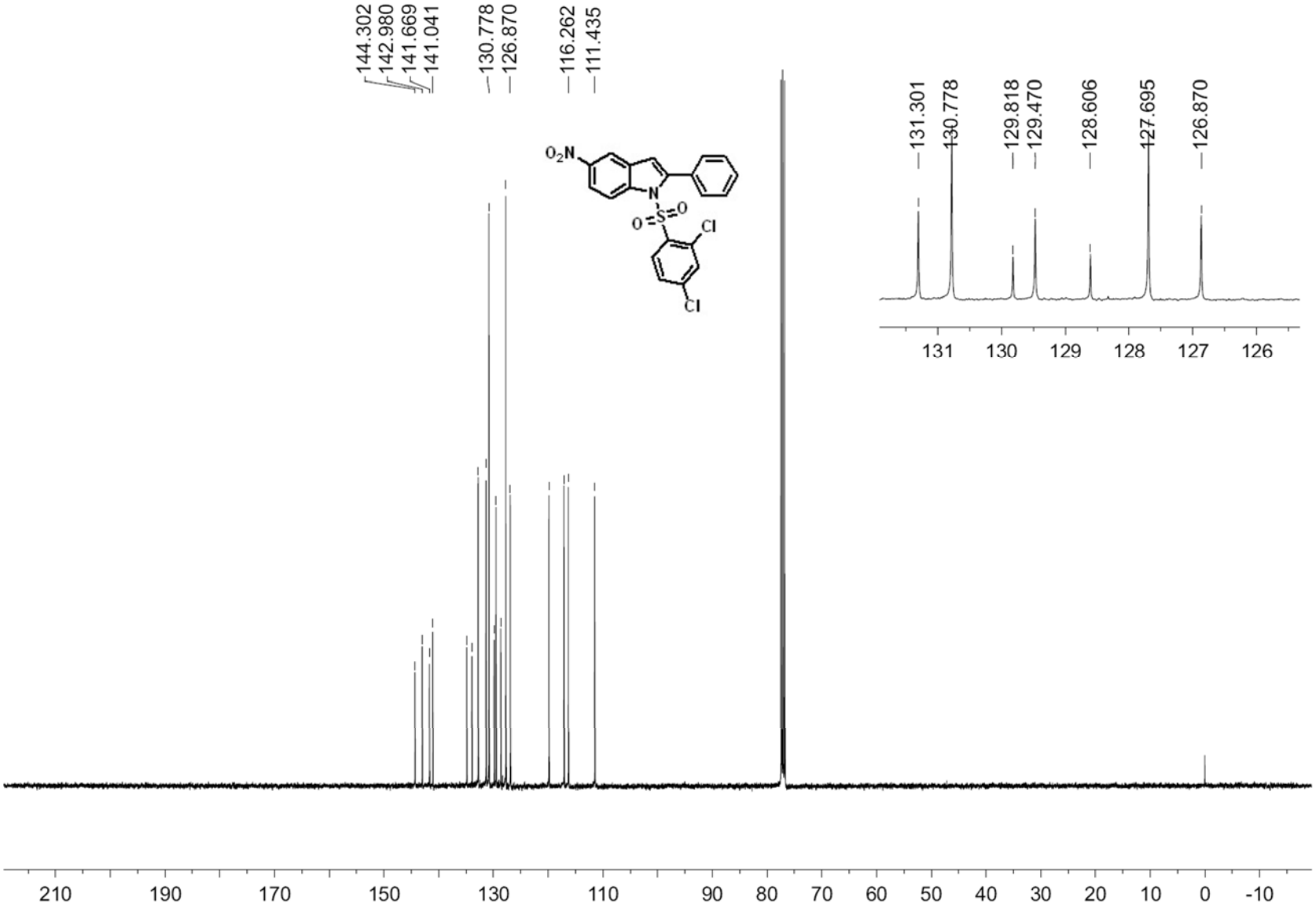
^{1}H NMR Spectrum of Compound **2a**



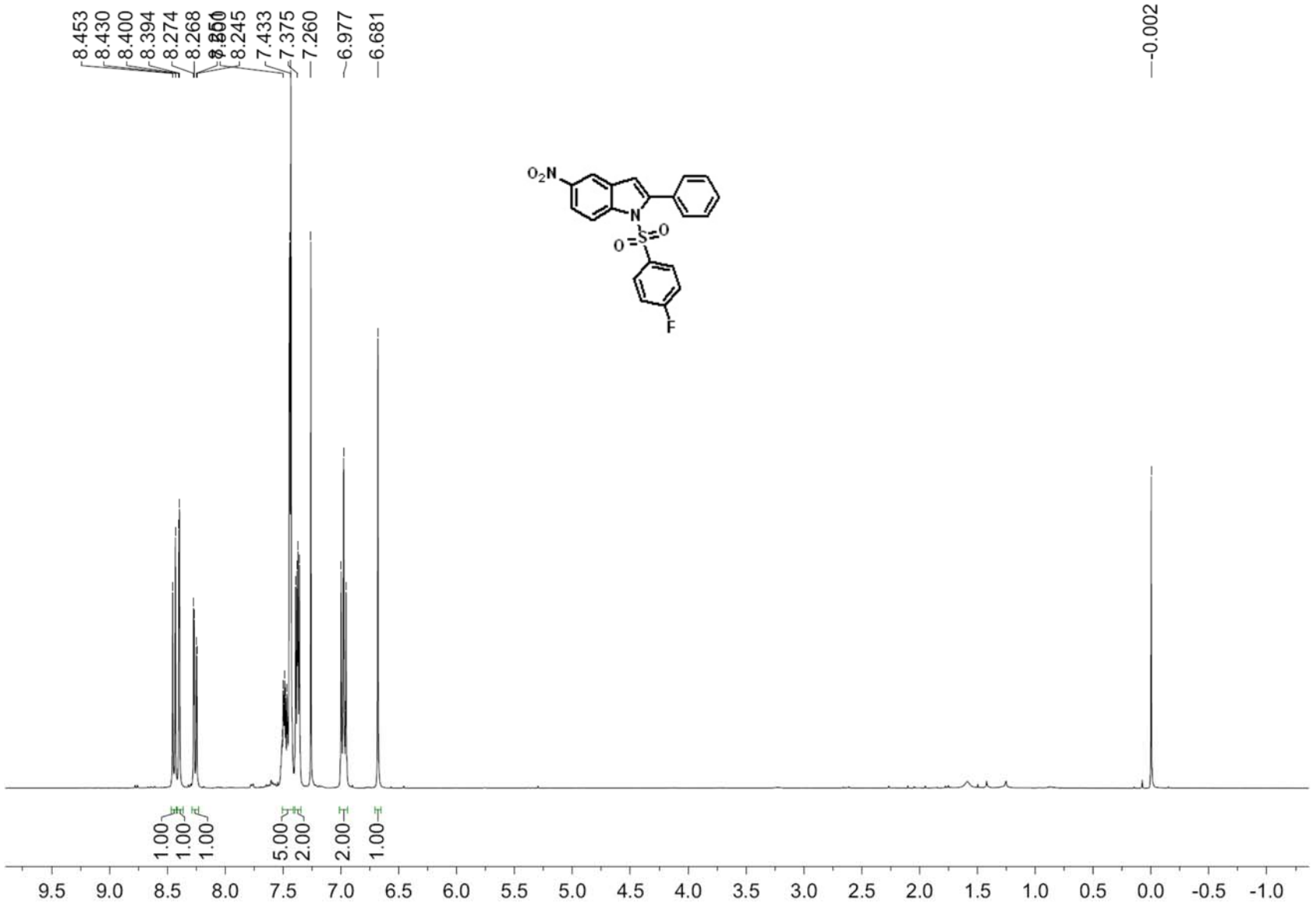
^{13}C NMR Spectrum of Compound **2a**



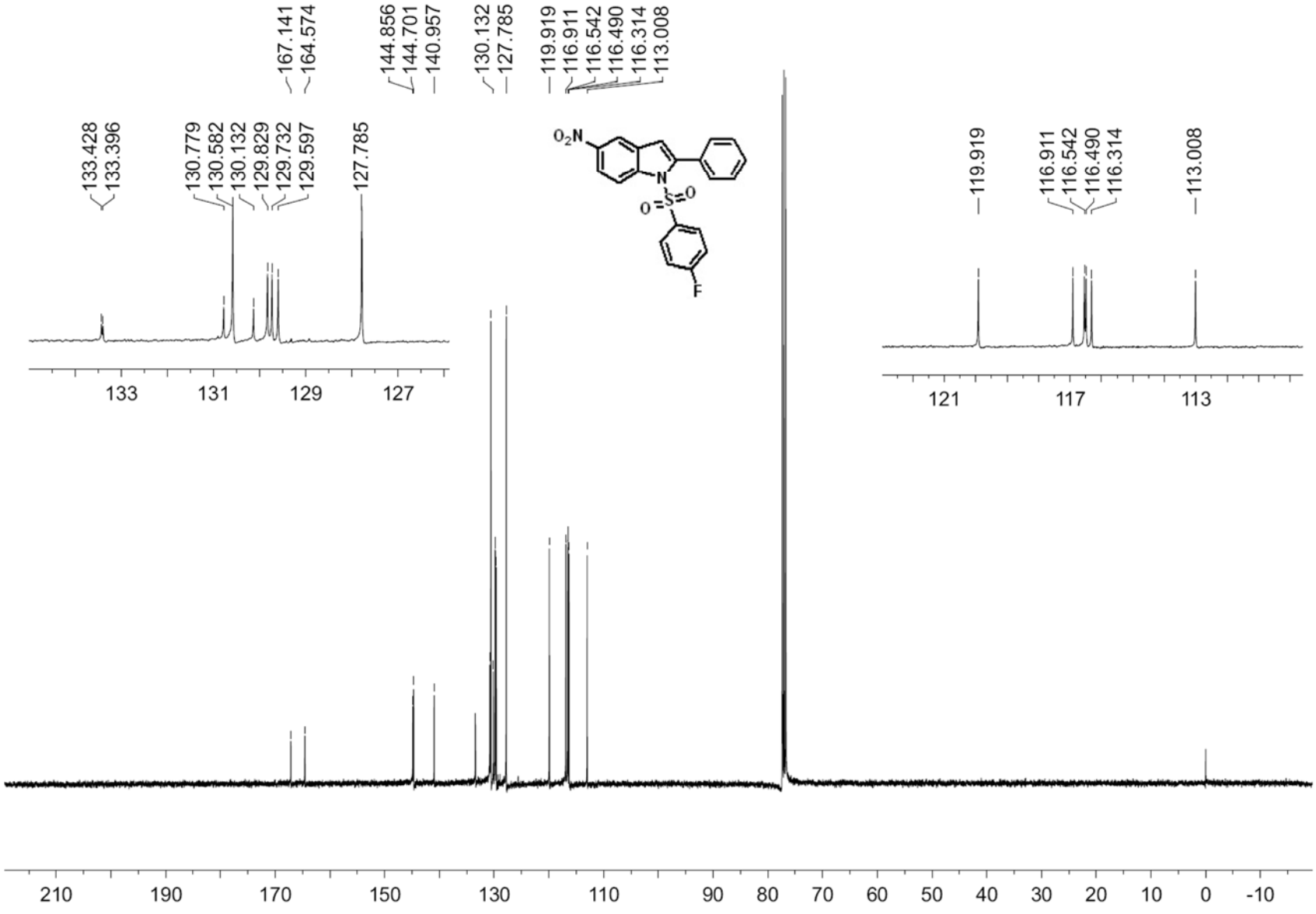
^{1}H NMR Spectrum of Compound **2b**



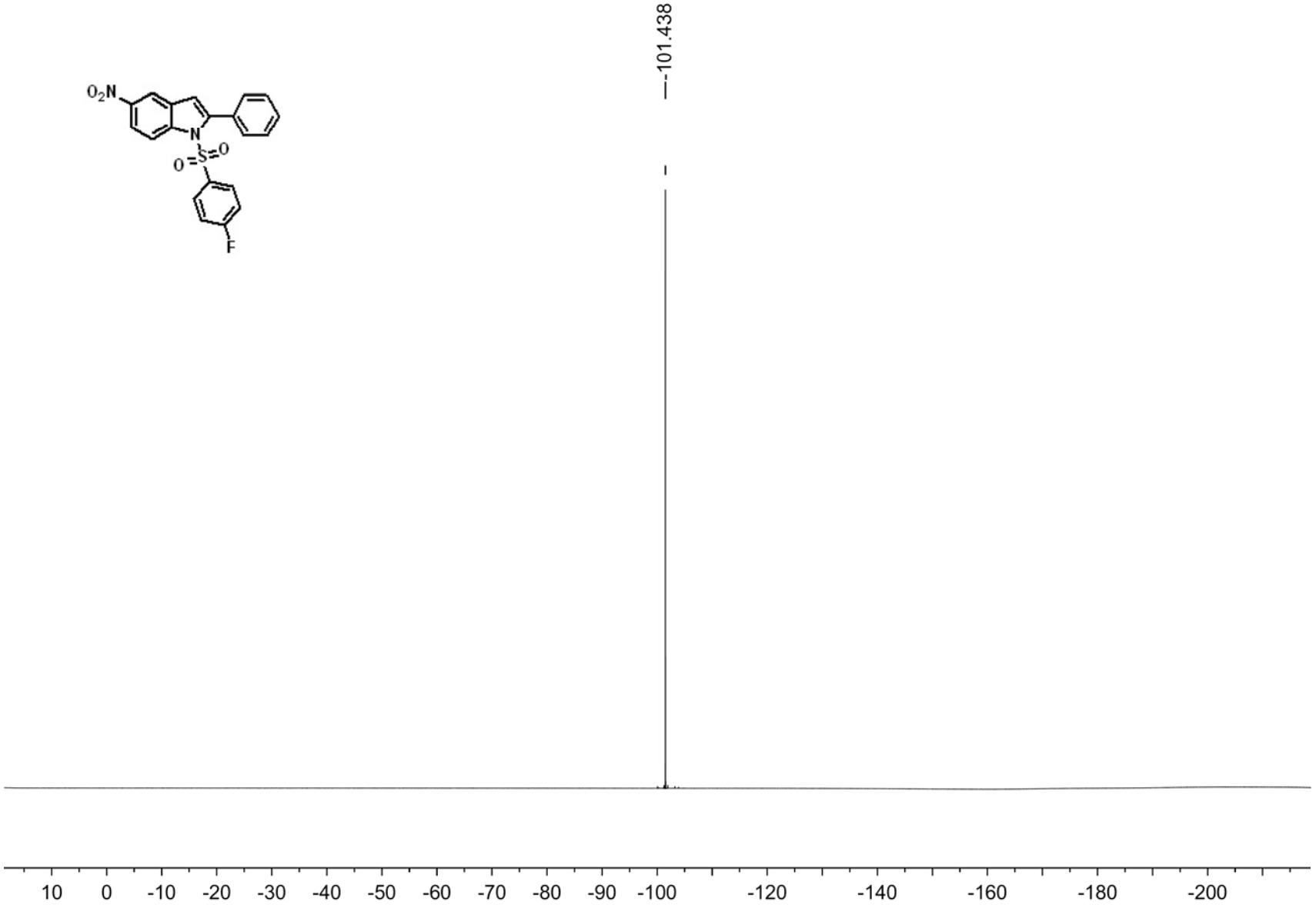
^{13}C NMR Spectrum of Compound **2b**



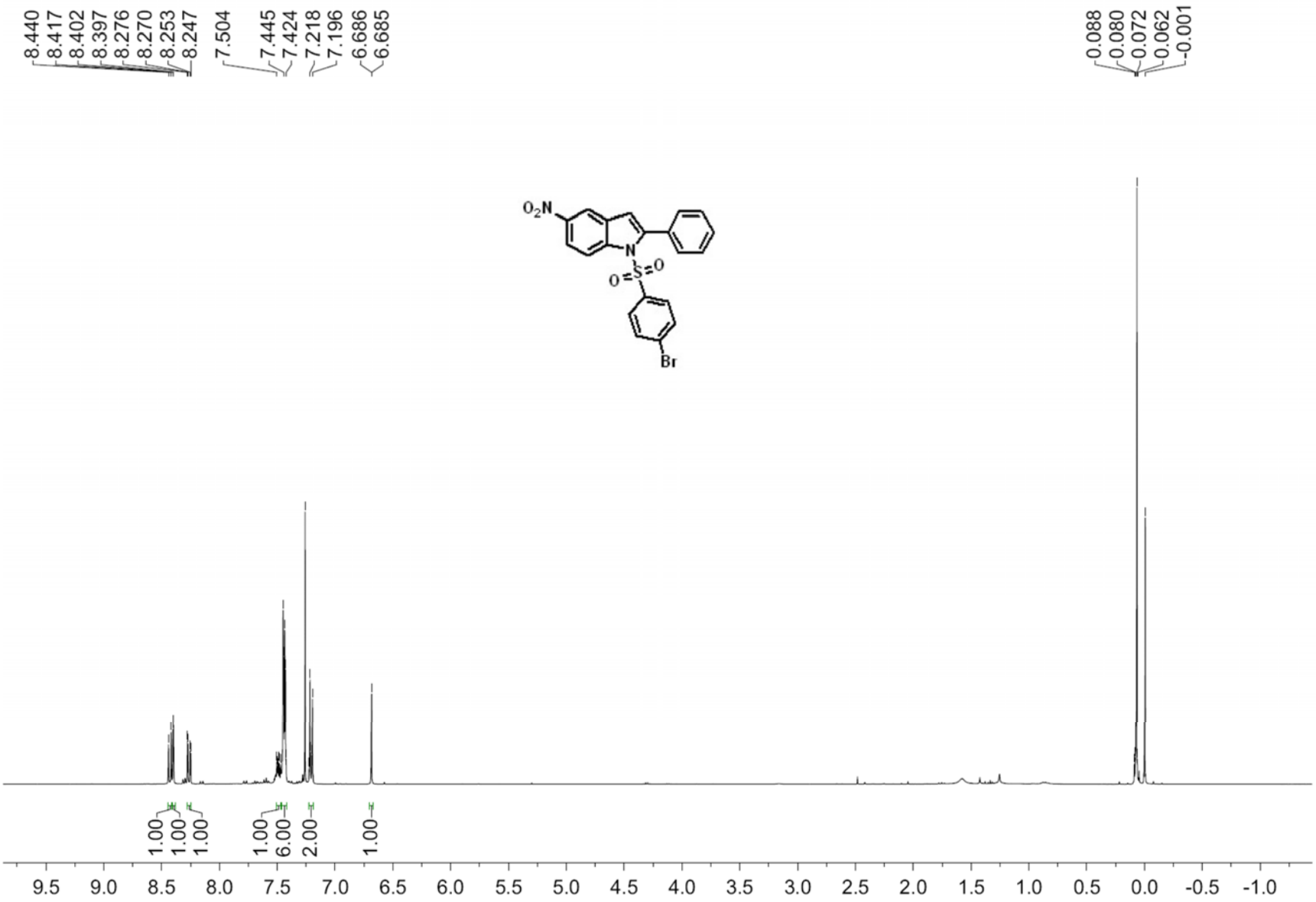
^{1}H NMR Spectrum of Compound **2c**



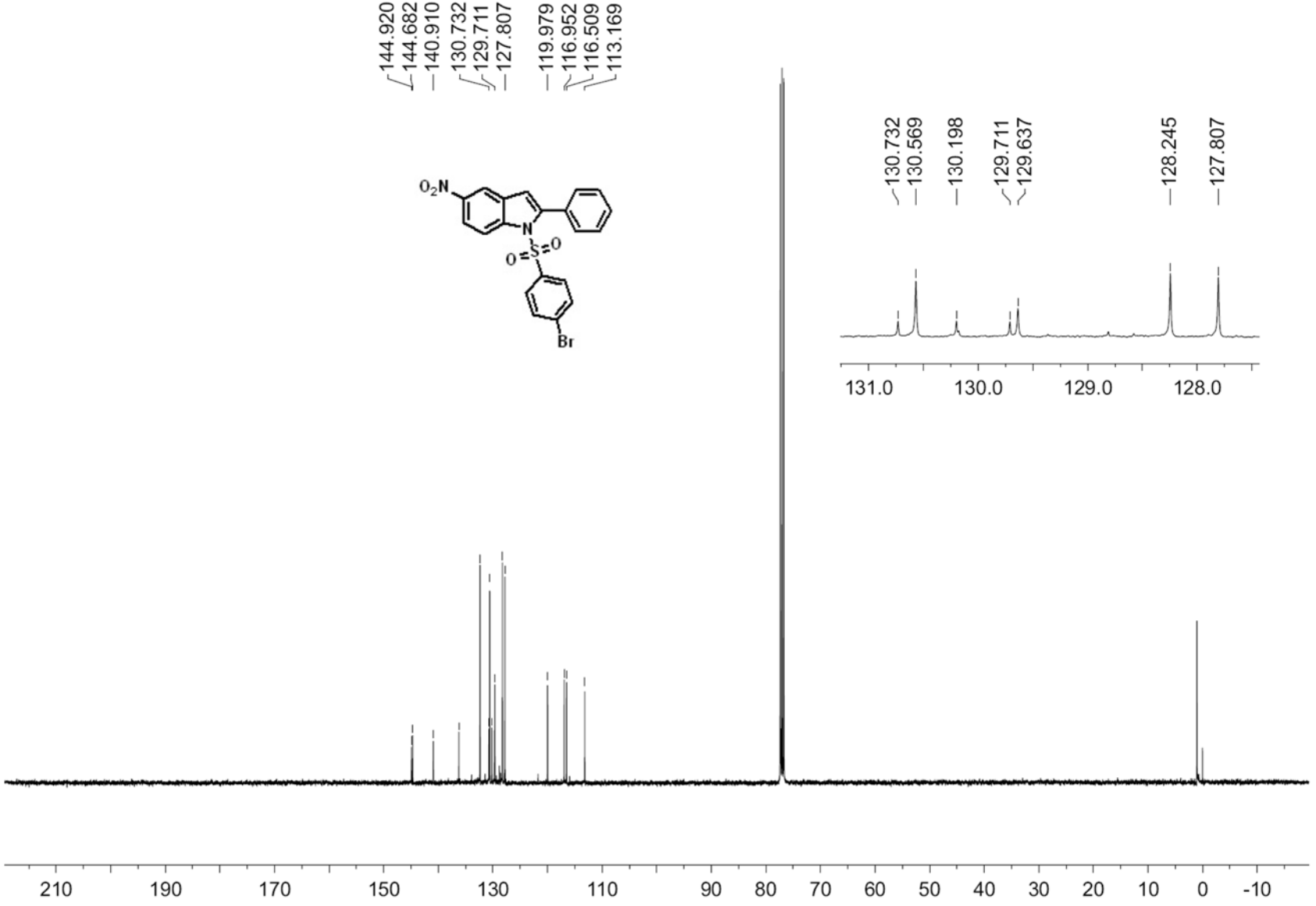
^{13}C NMR Spectrum of Compound **2c**



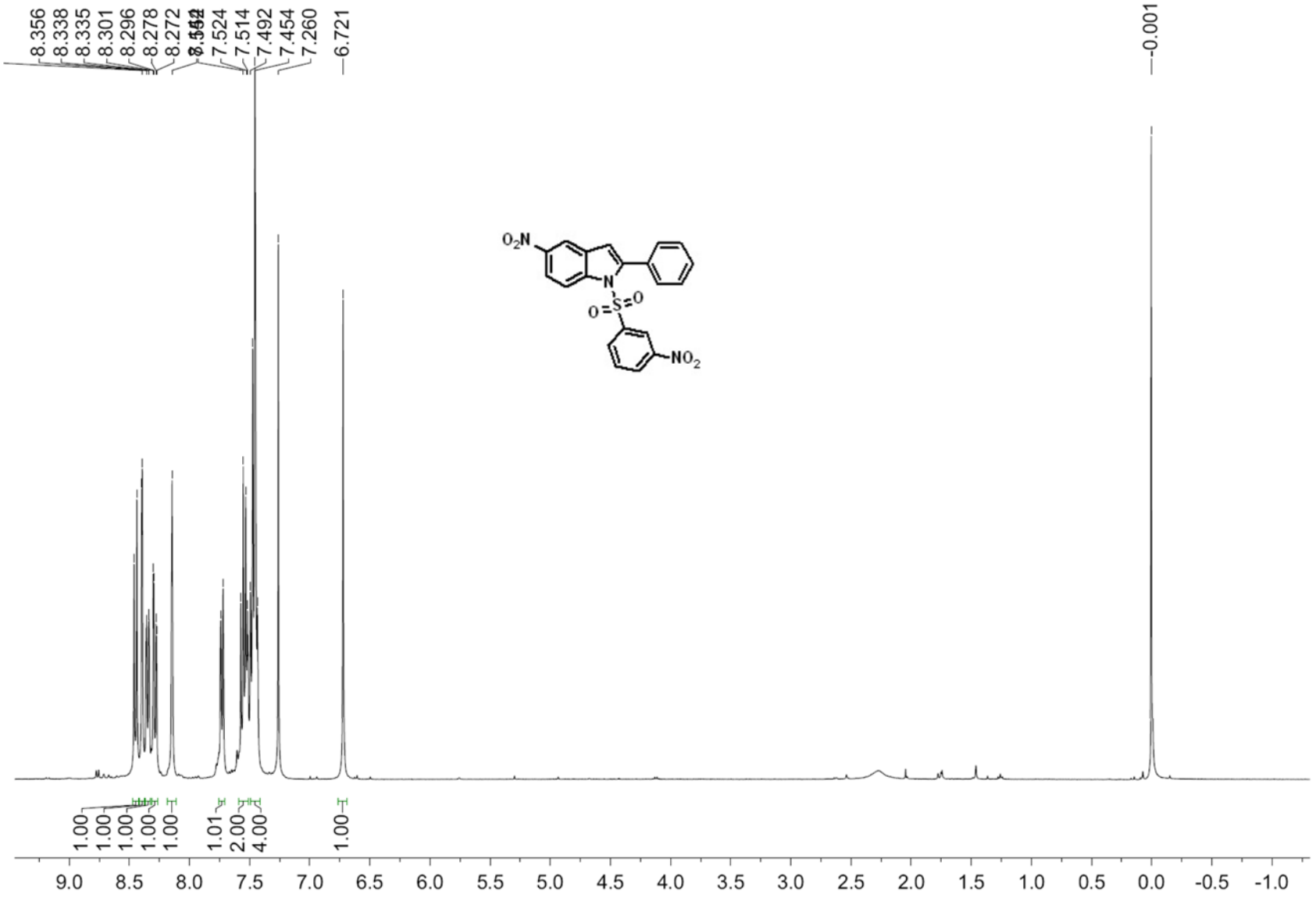
^{19}F NMR Spectrum of Compound **2c**



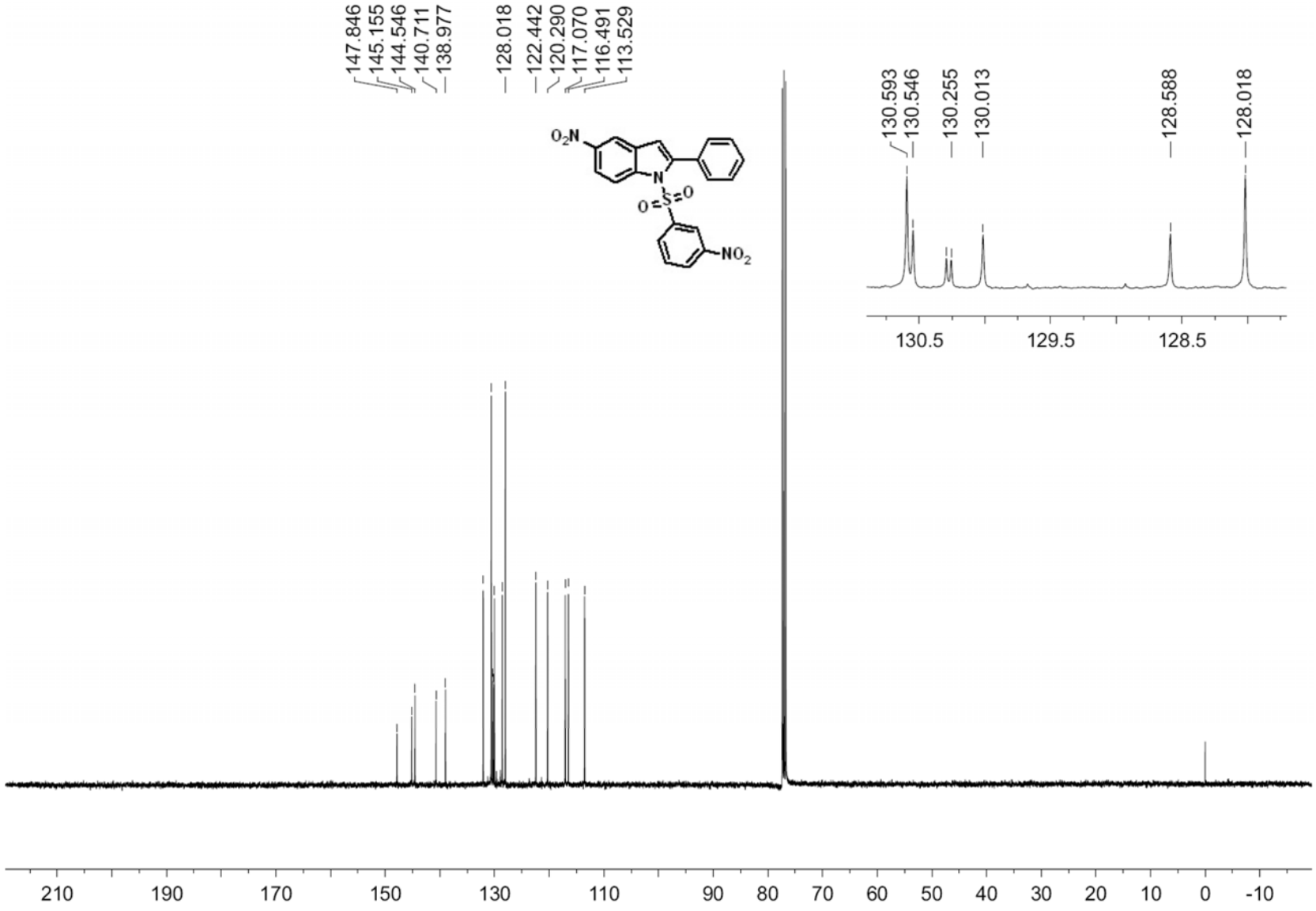
^{1}H NMR Spectrum of Compound **2d**



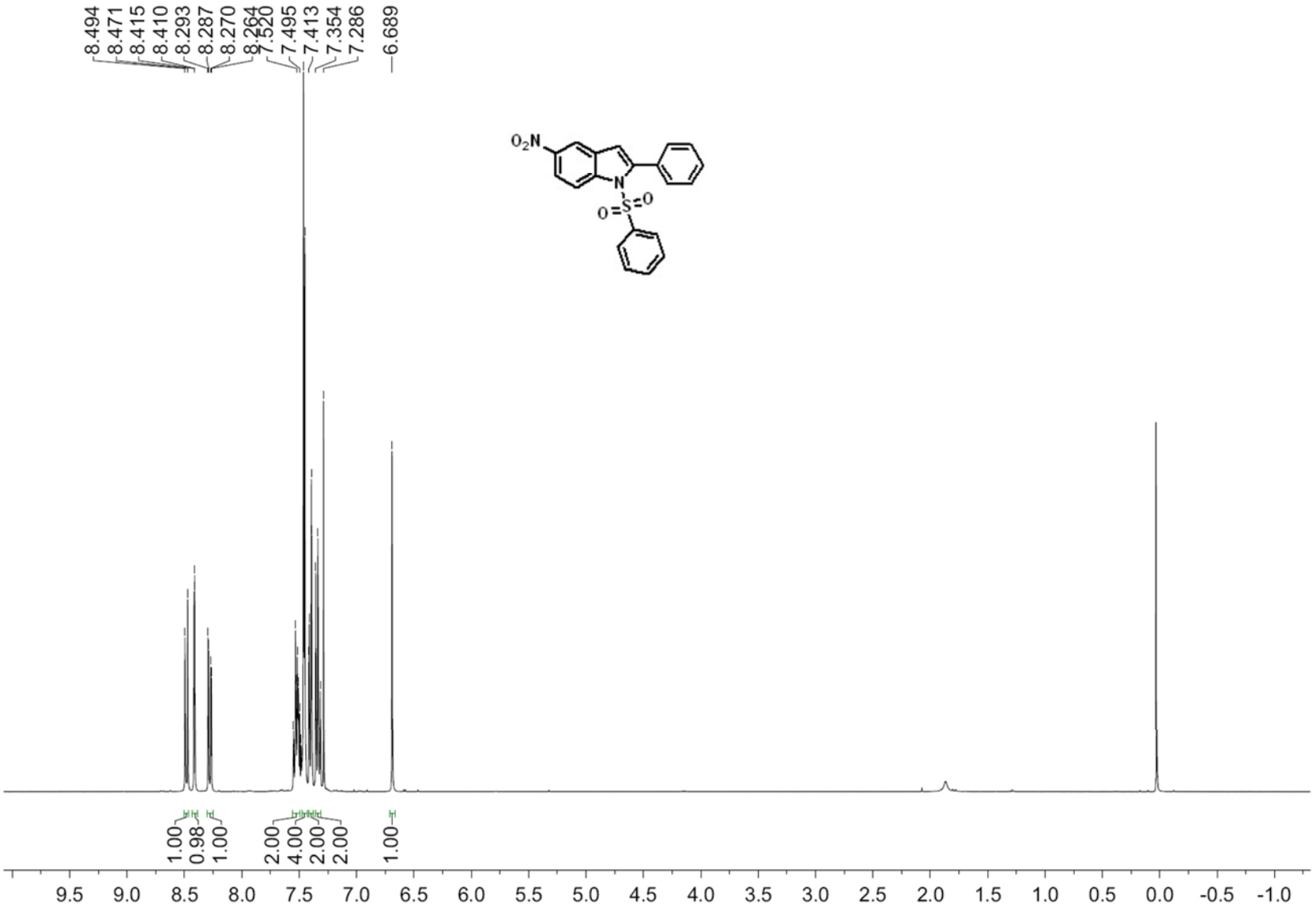
^{13}C NMR Spectrum of Compound **2d**



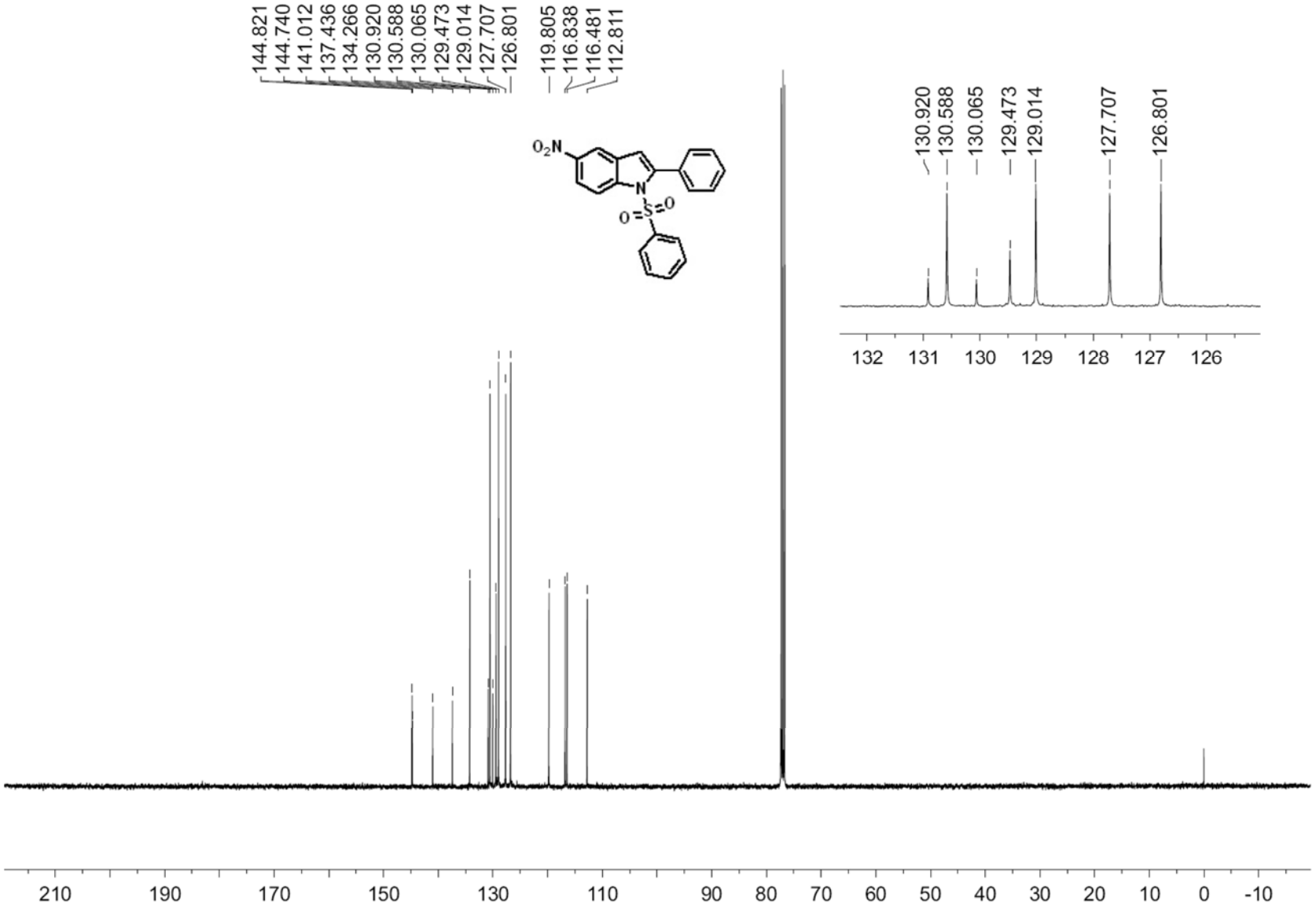
^{1}H NMR Spectrum of Compound **2e**



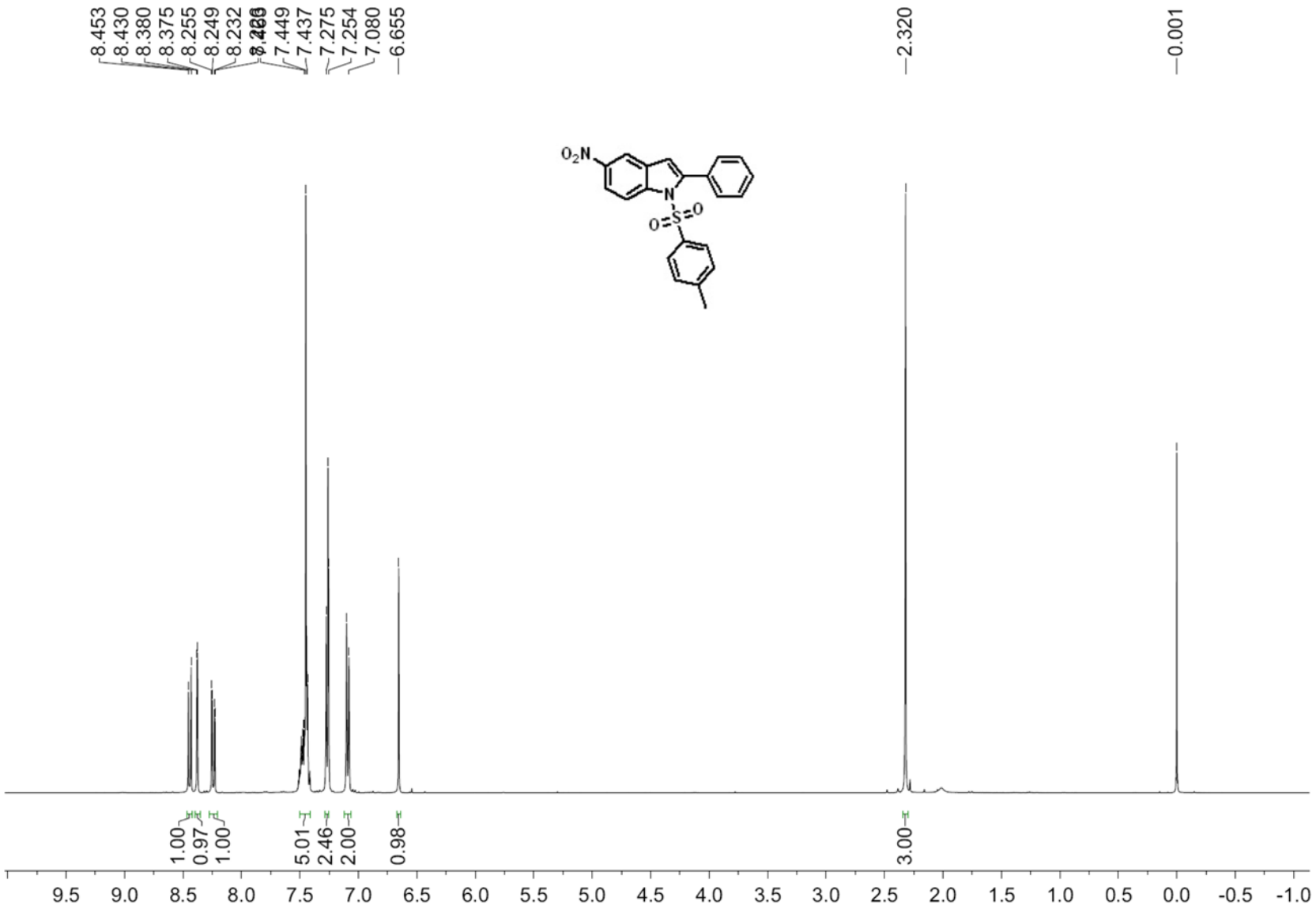
^{13}C NMR Spectrum of Compound **2e**



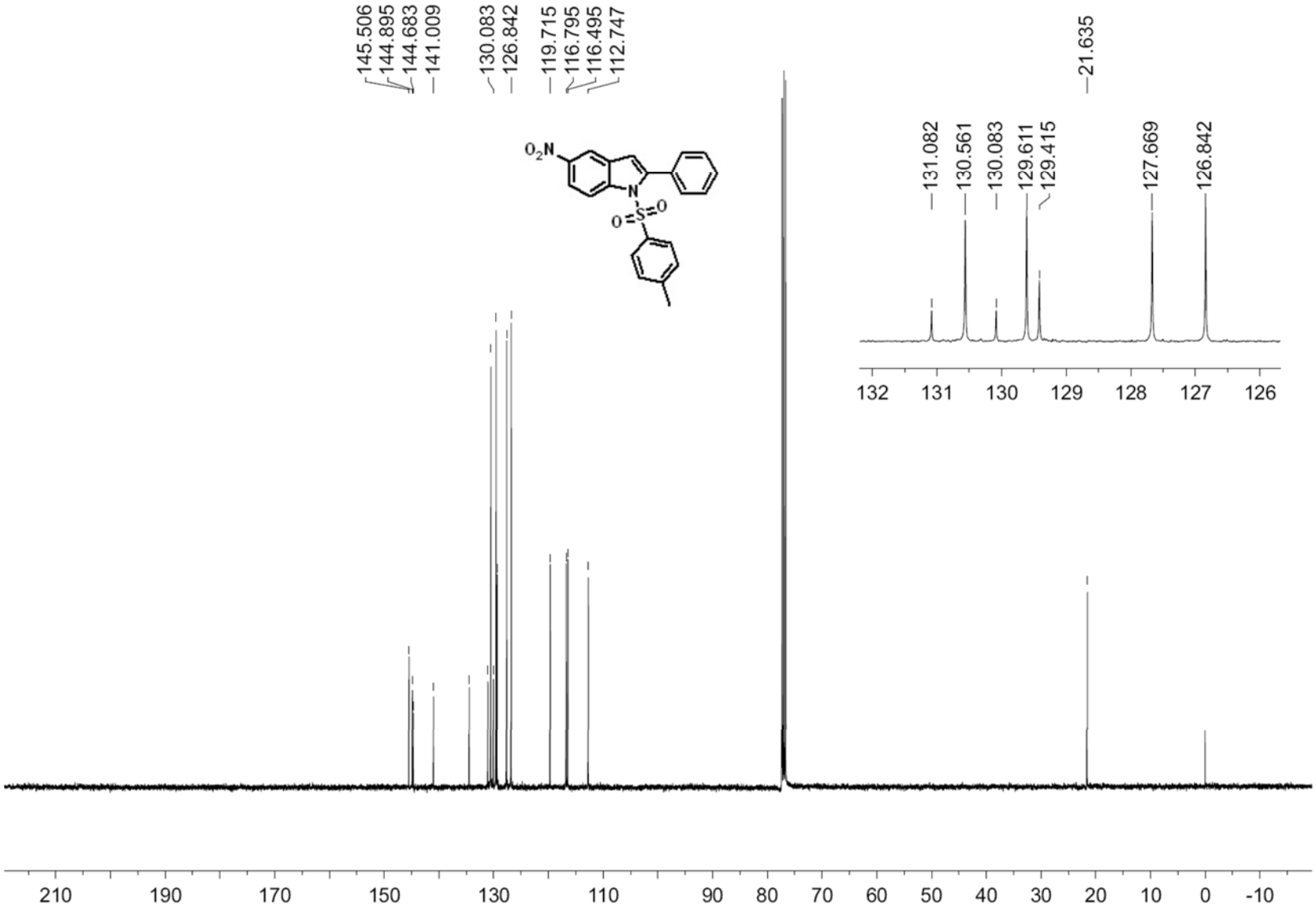
^{1}H NMR Spectrum of Compound **2f**



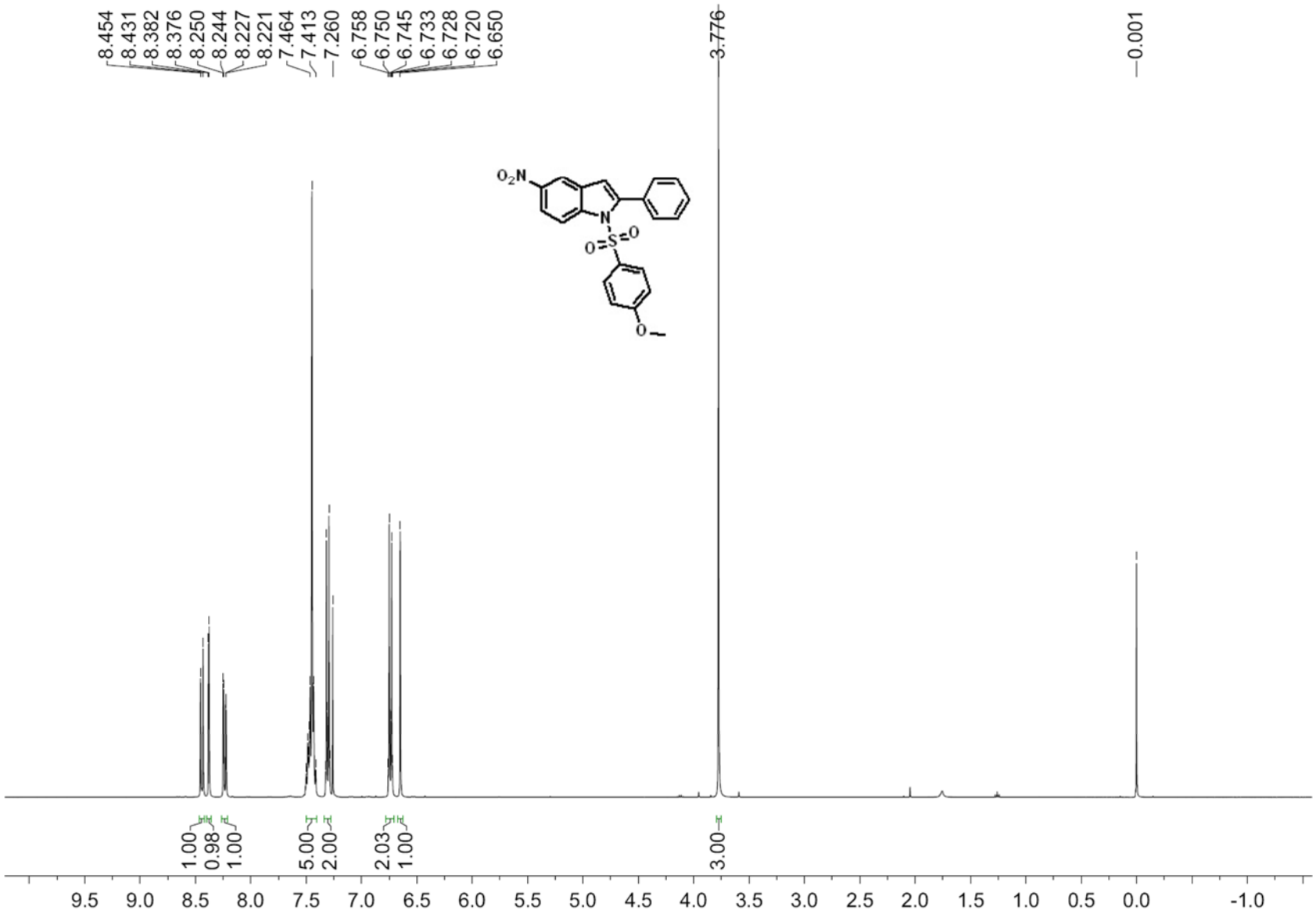
^{13}C NMR Spectrum of Compound **2f**



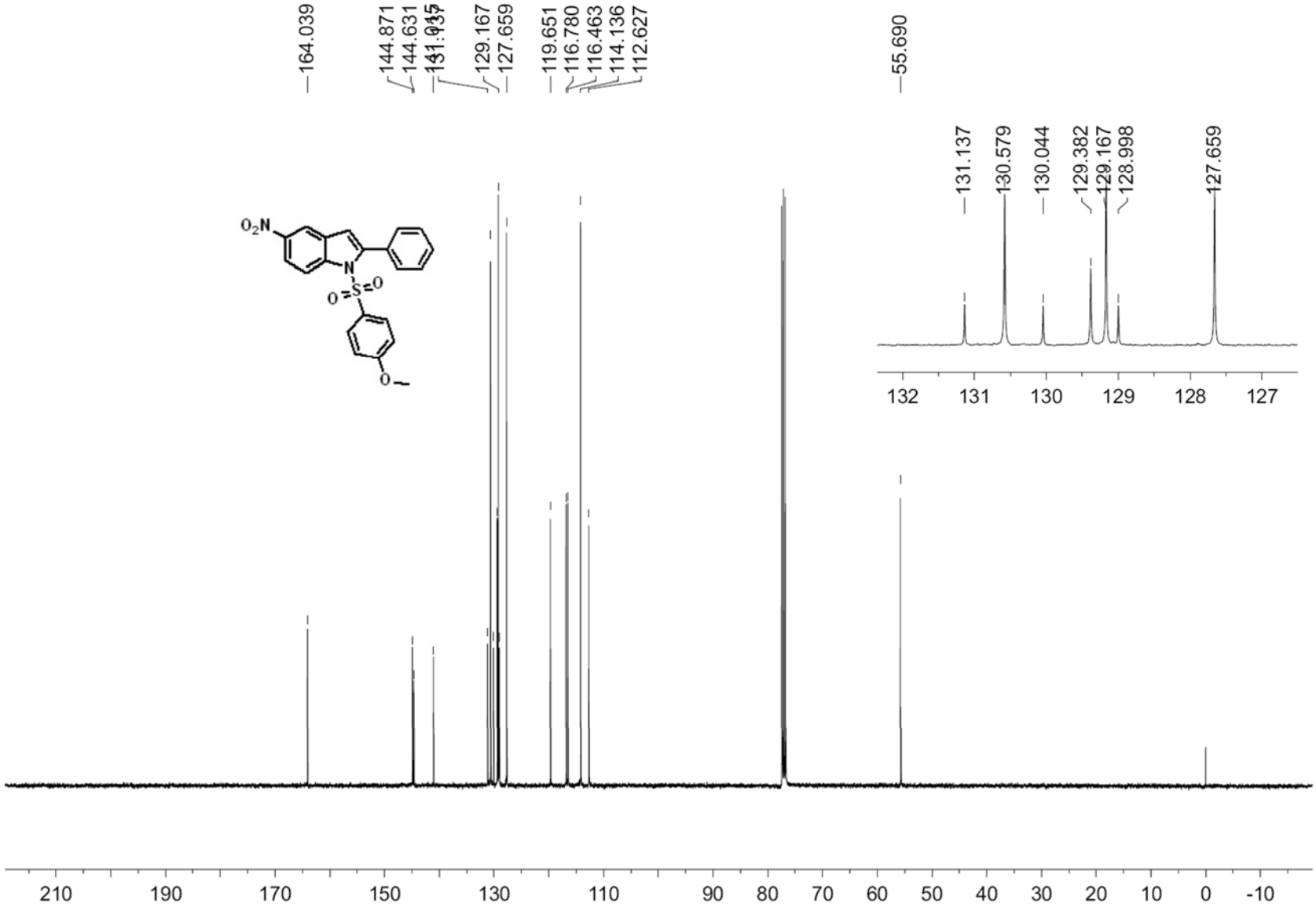
^{1}H NMR Spectrum of Compound **2g**



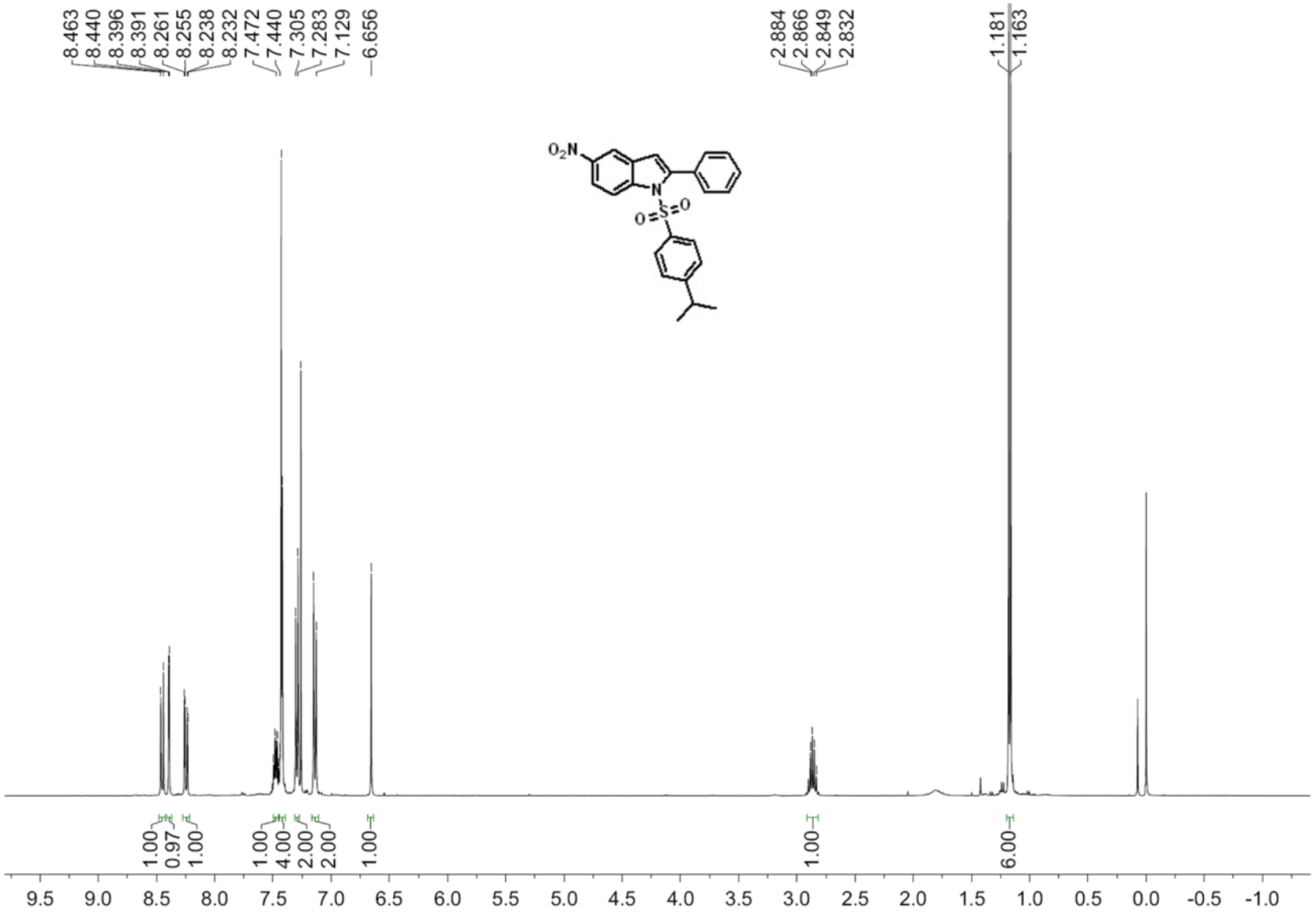
^{13}C NMR Spectrum of Compound **2g**



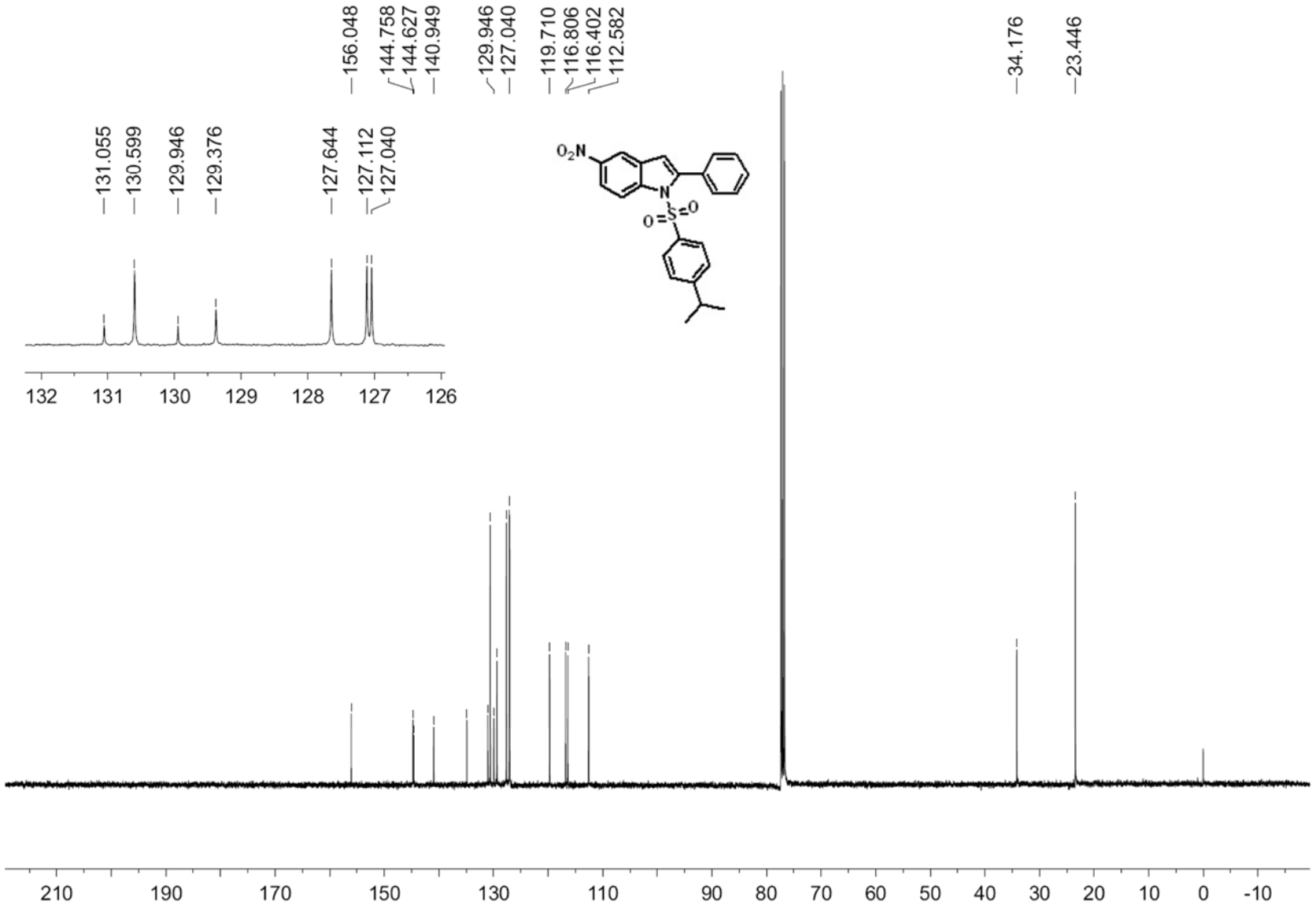
^{1}H NMR Spectrum of Compound **2h**



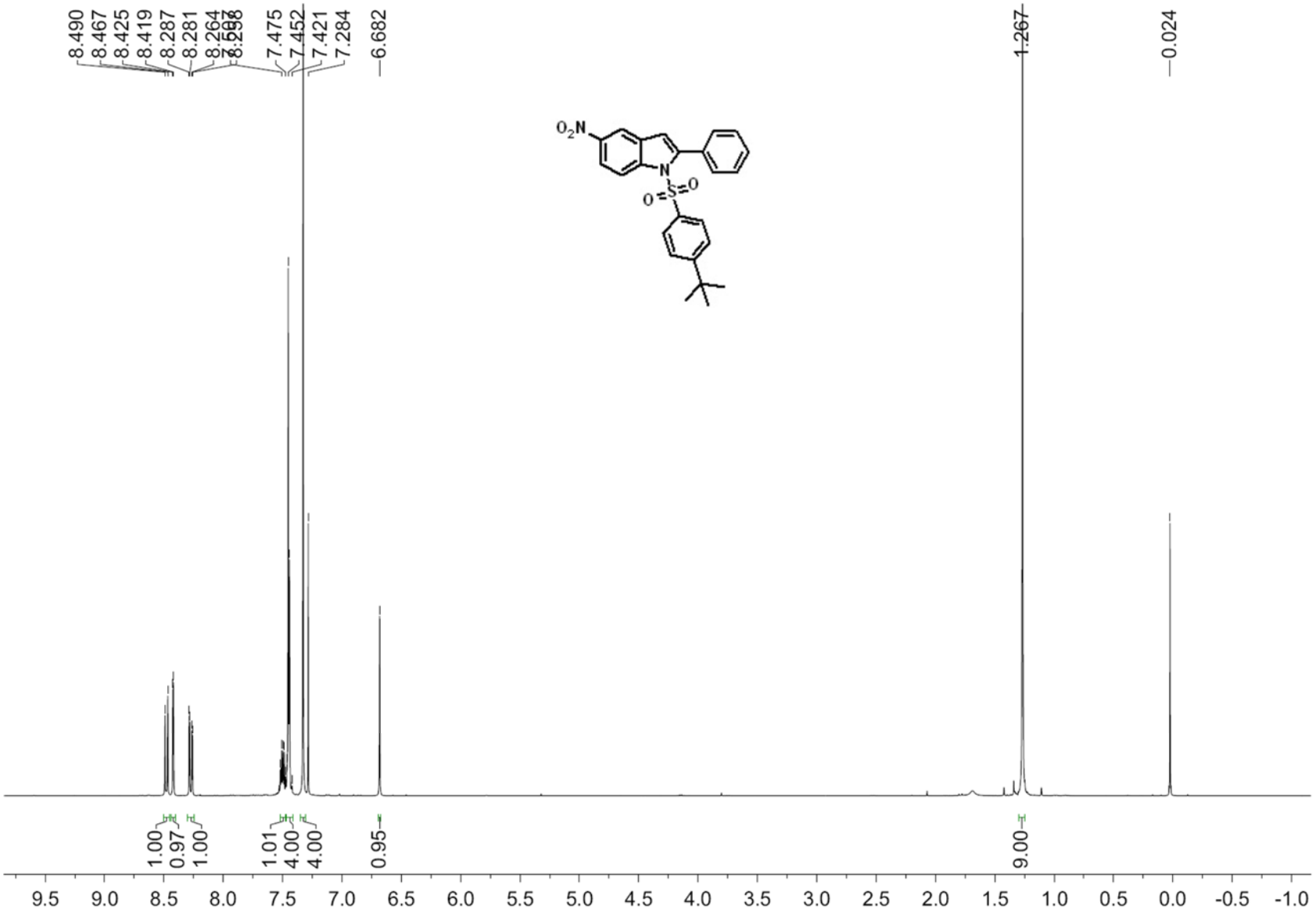
^{13}C NMR Spectrum of Compound **2h**



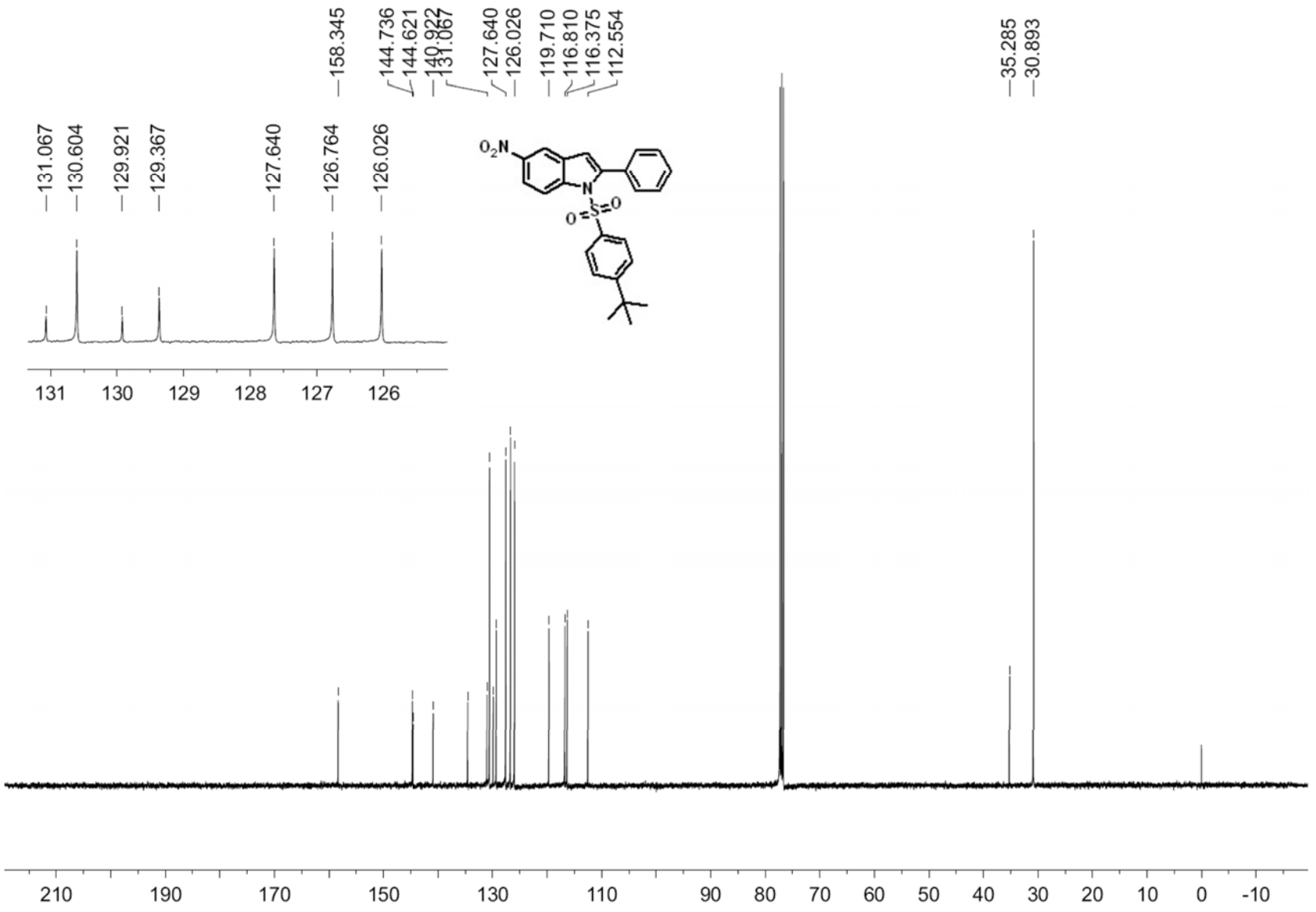
^{1}H NMR Spectrum of Compound **2i**



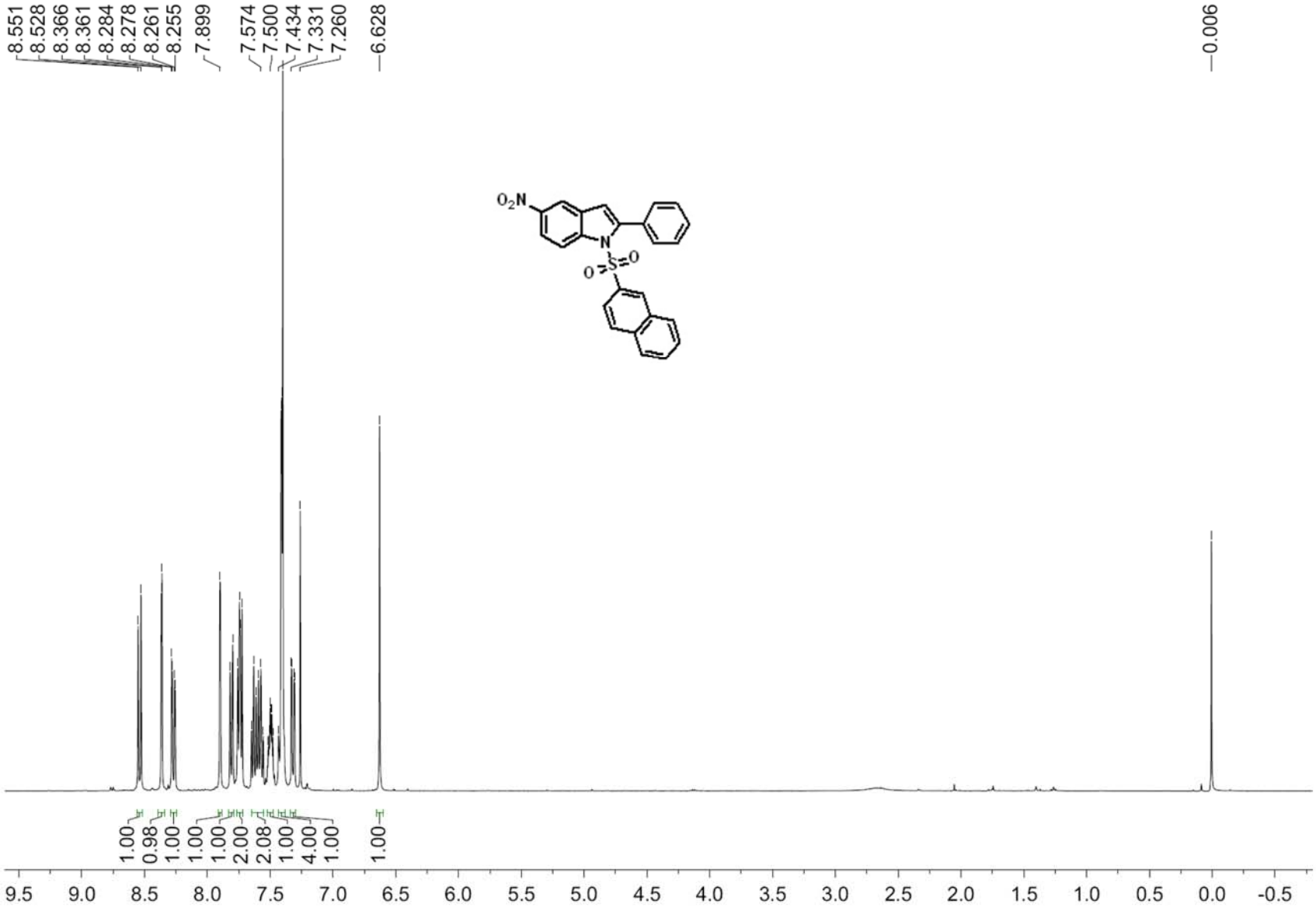
^{13}C NMR Spectrum of Compound **2i**



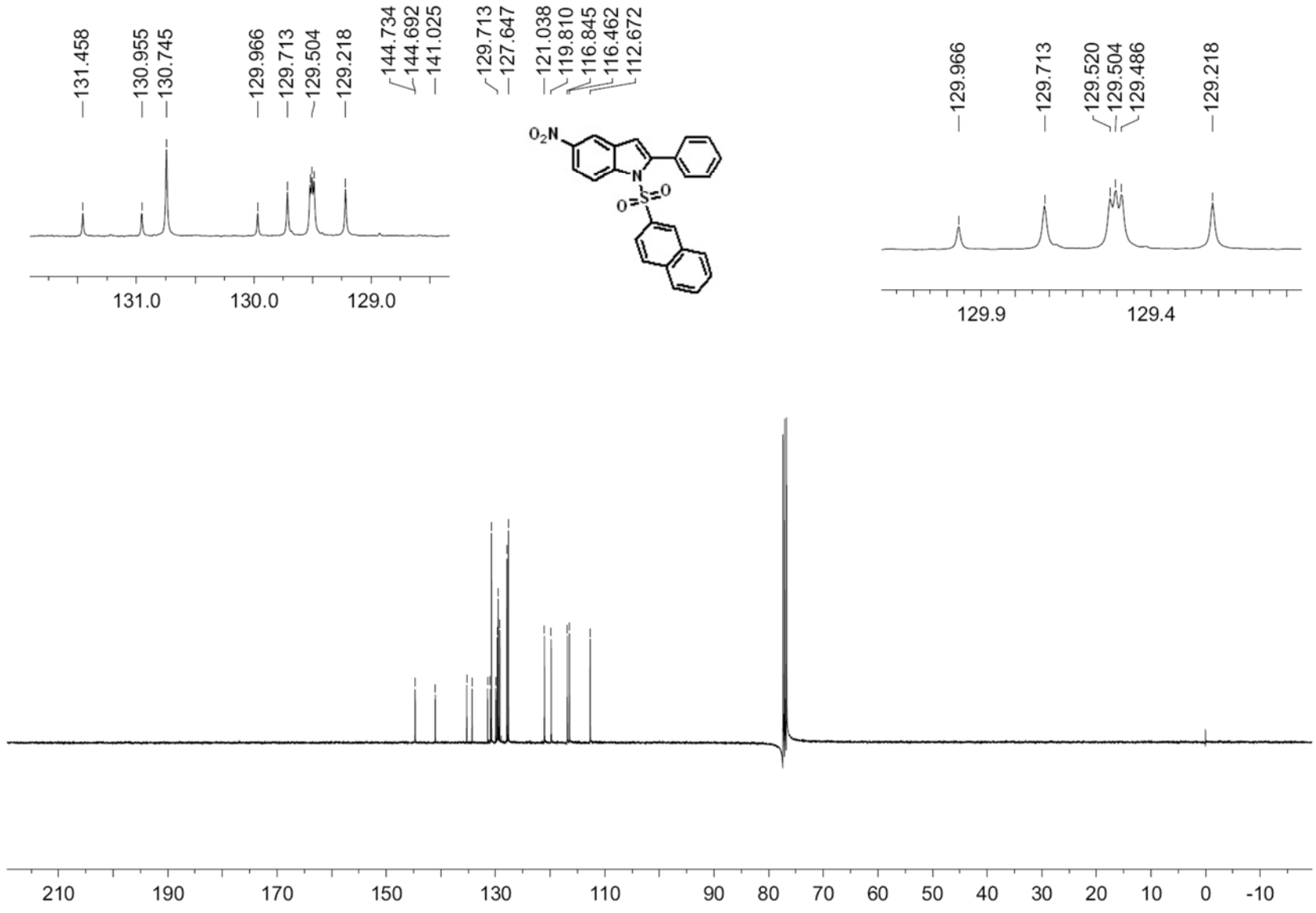
^{1}H NMR Spectrum of Compound **2j**



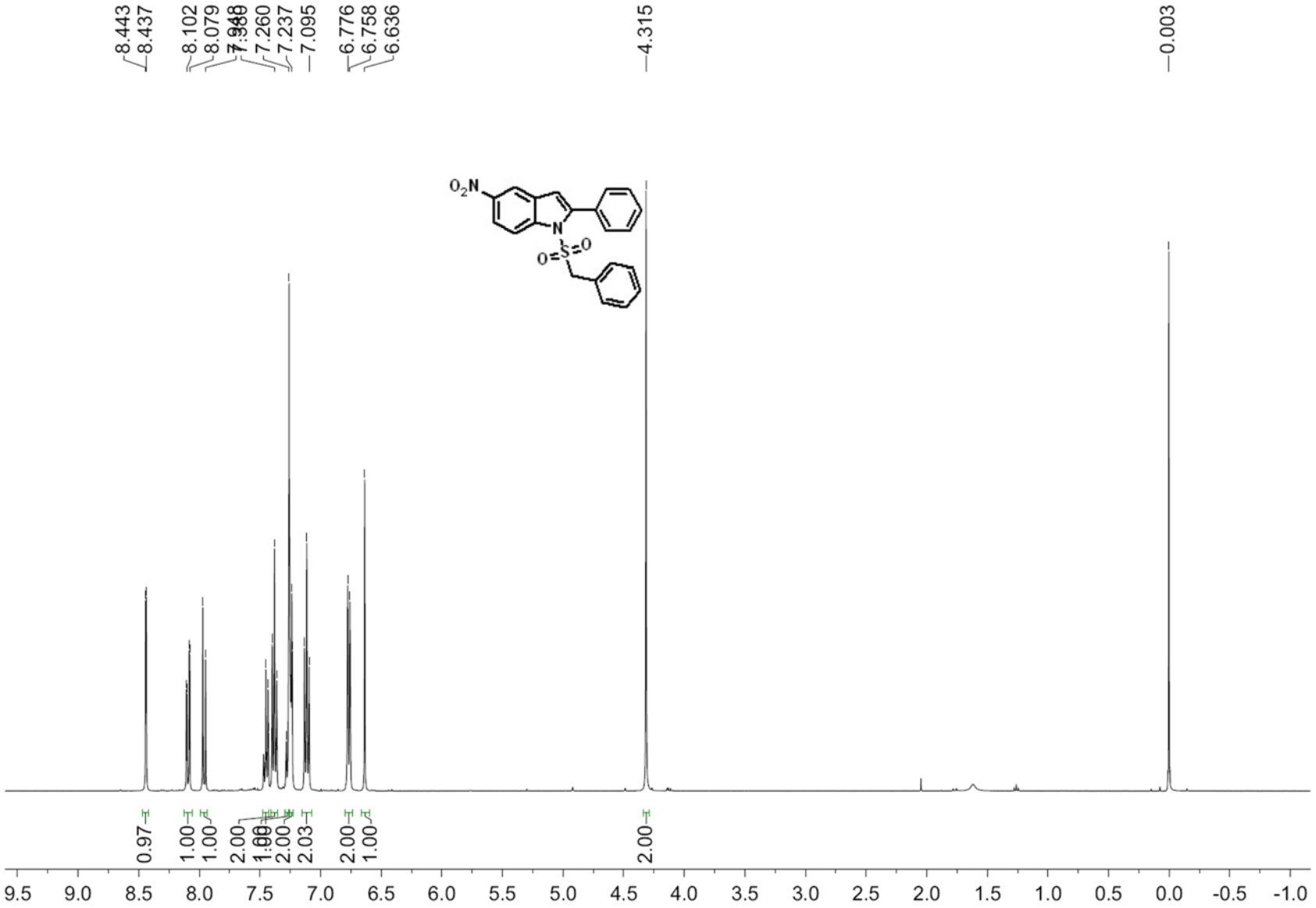
^{13}C NMR Spectrum of Compound **2j**



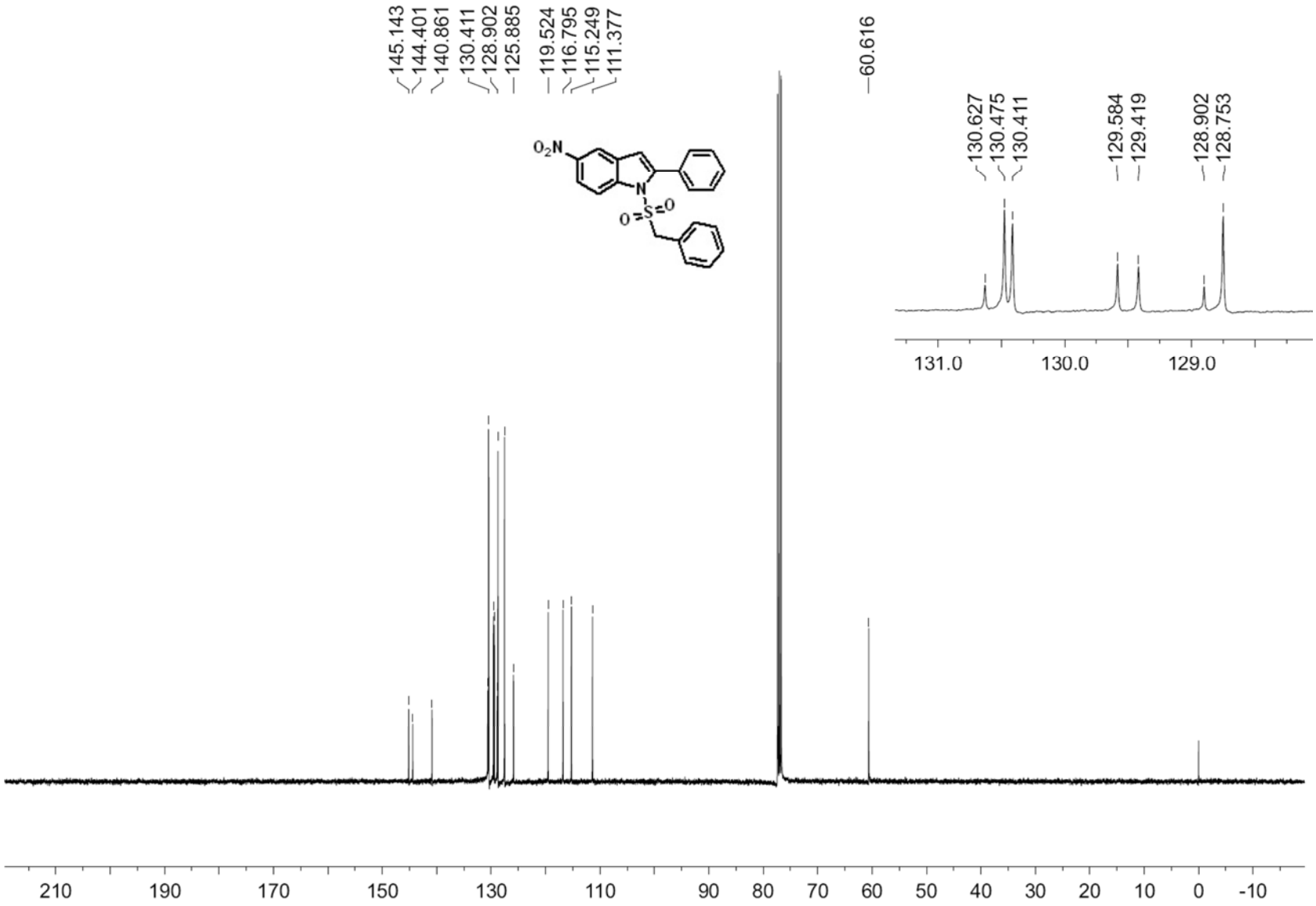
^{1}H NMR Spectrum of Compound **2k**



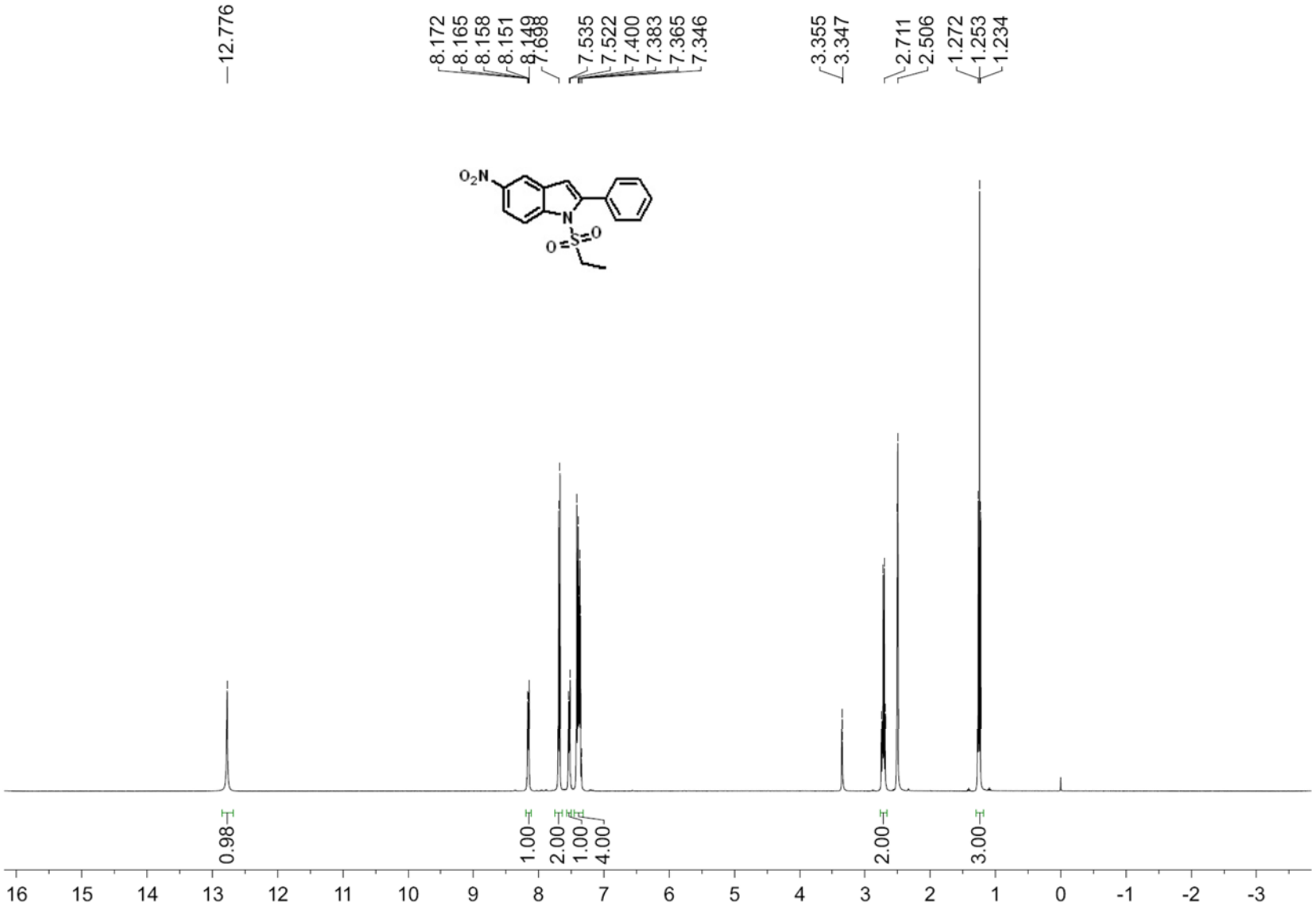
^{13}C NMR Spectrum of Compound **2k**



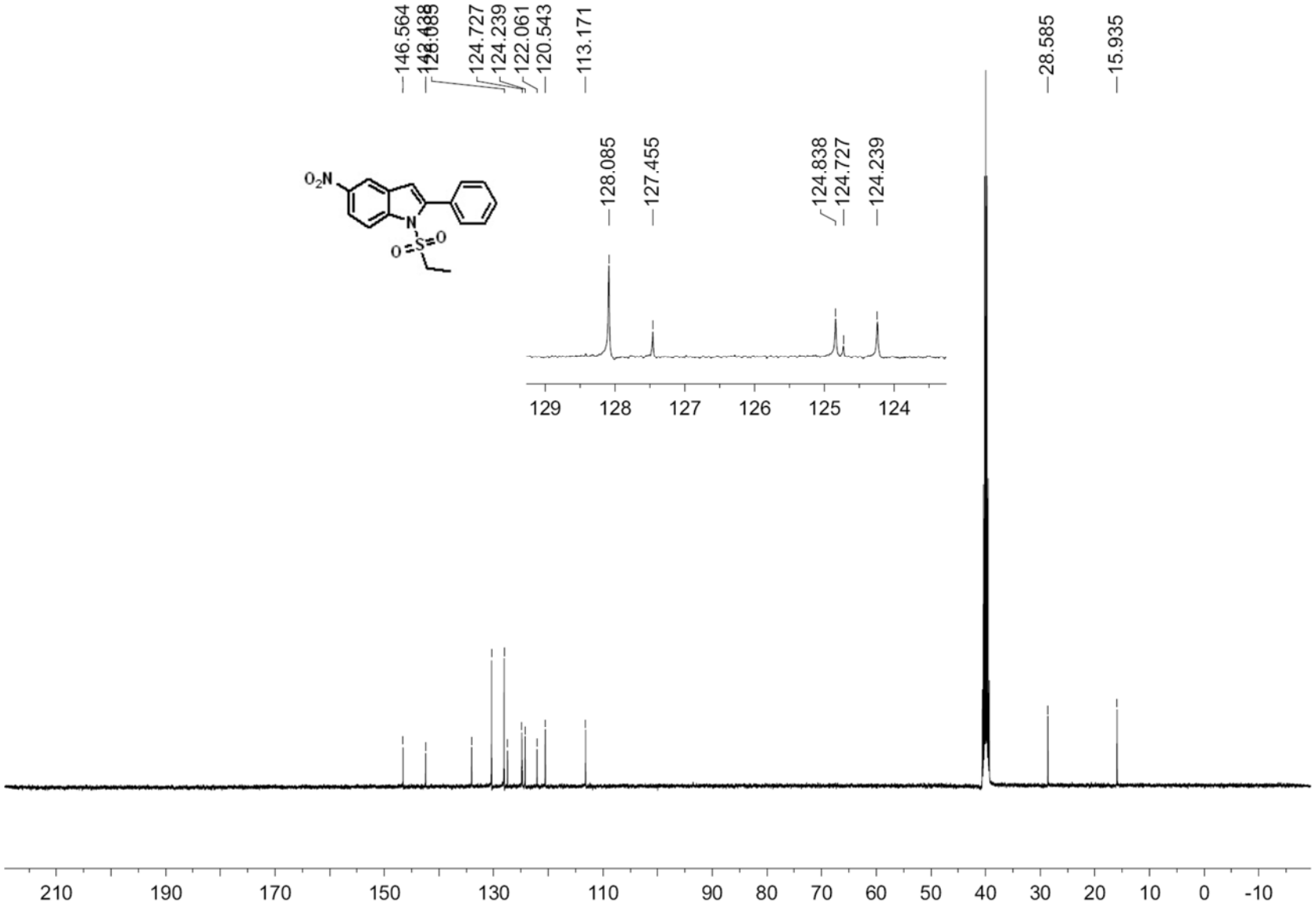
^{1}H NMR Spectrum of Compound **2l**



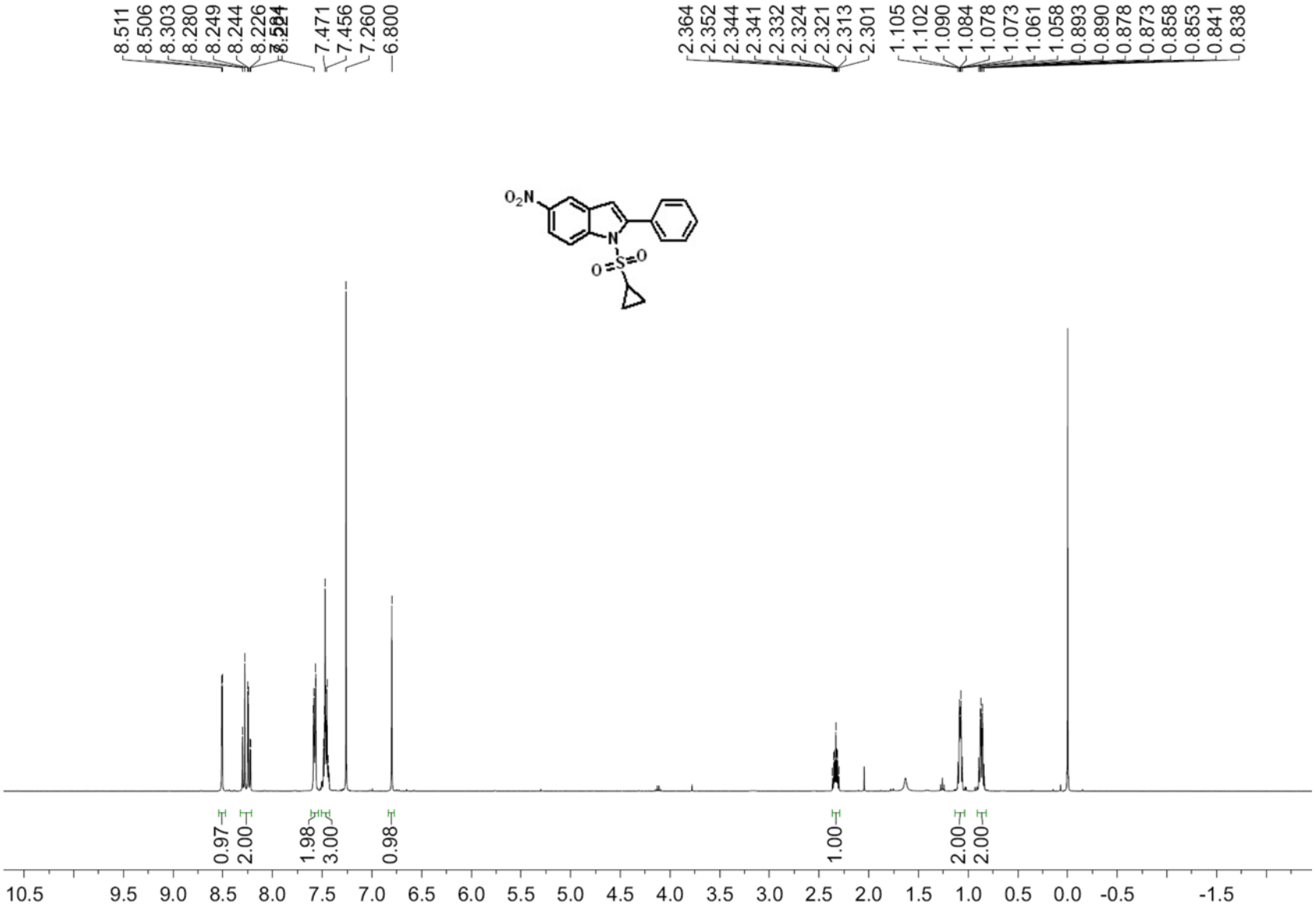
^{13}C NMR Spectrum of Compound **2l**



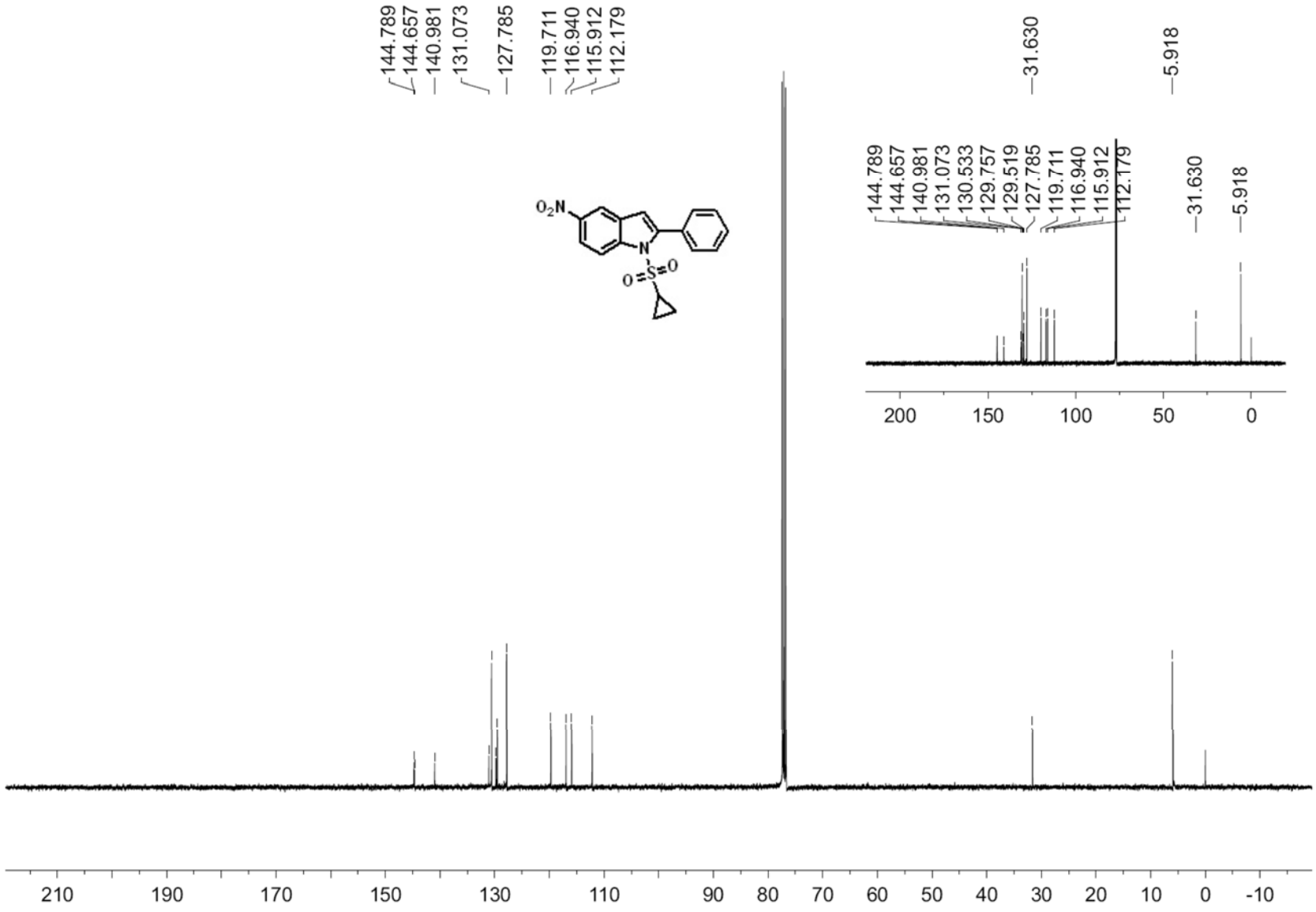
^{1}H NMR Spectrum of Compound **2m**



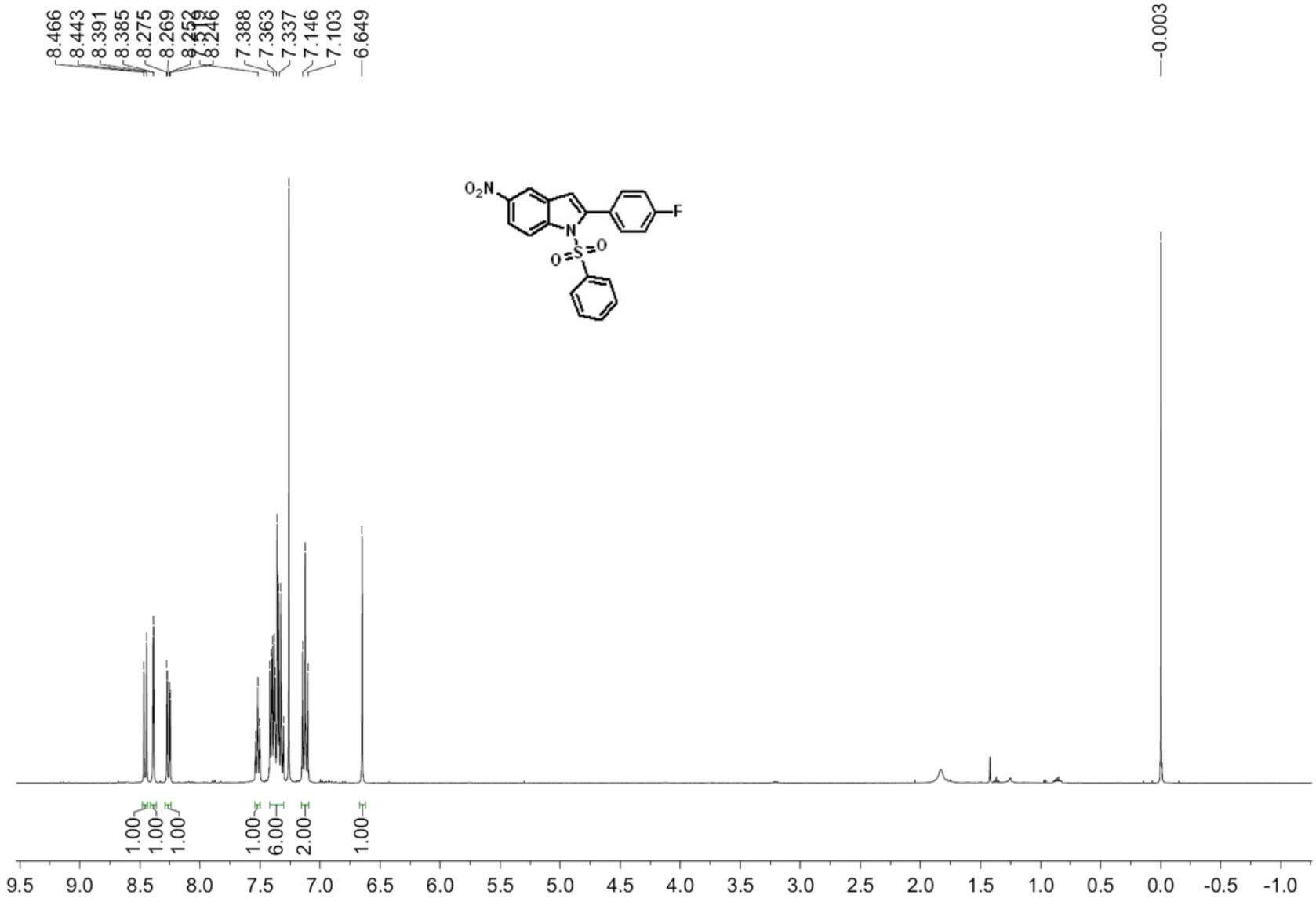
^{13}C NMR Spectrum of Compound **2m**



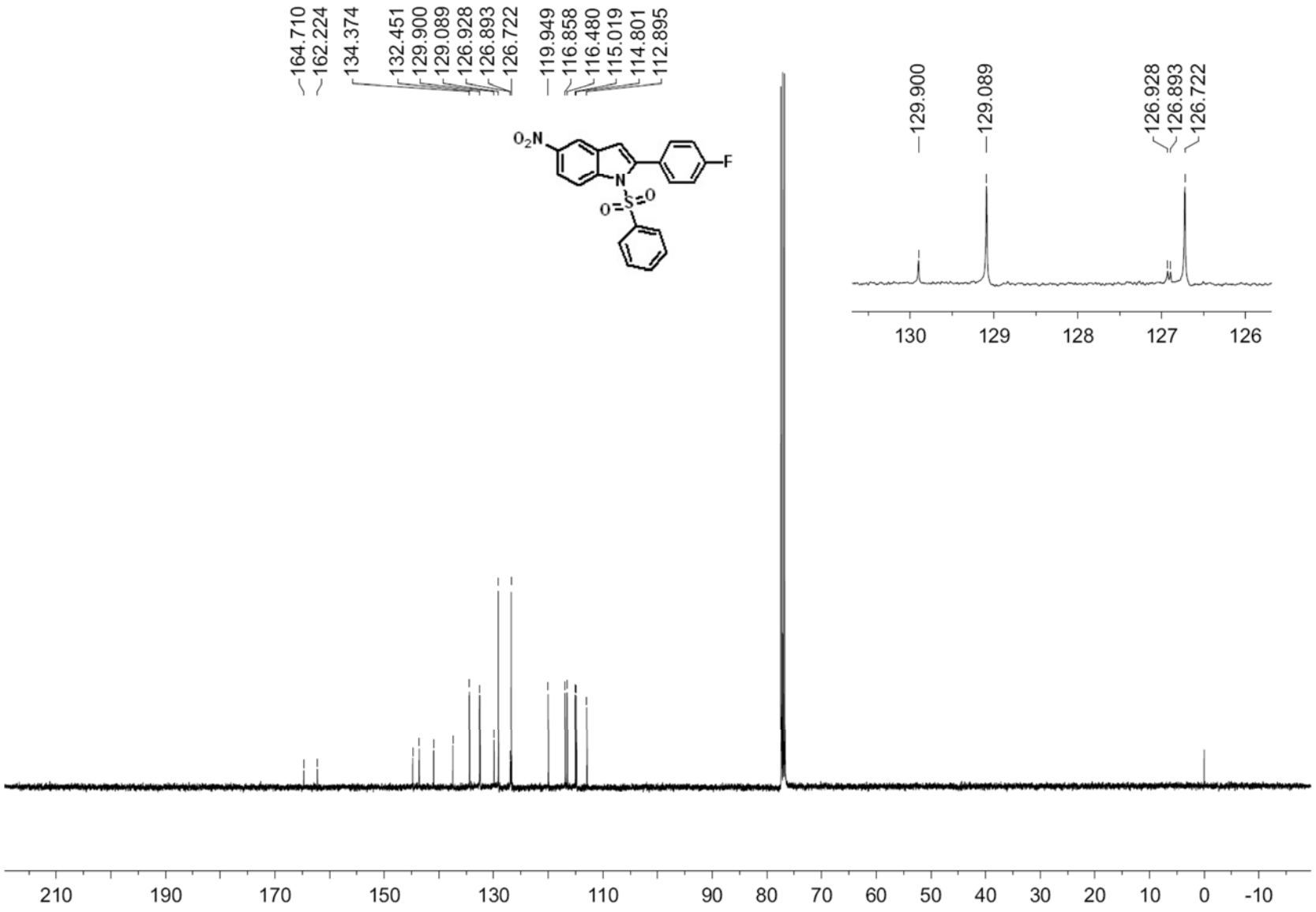
^{1}H NMR Spectrum of Compound **2n**



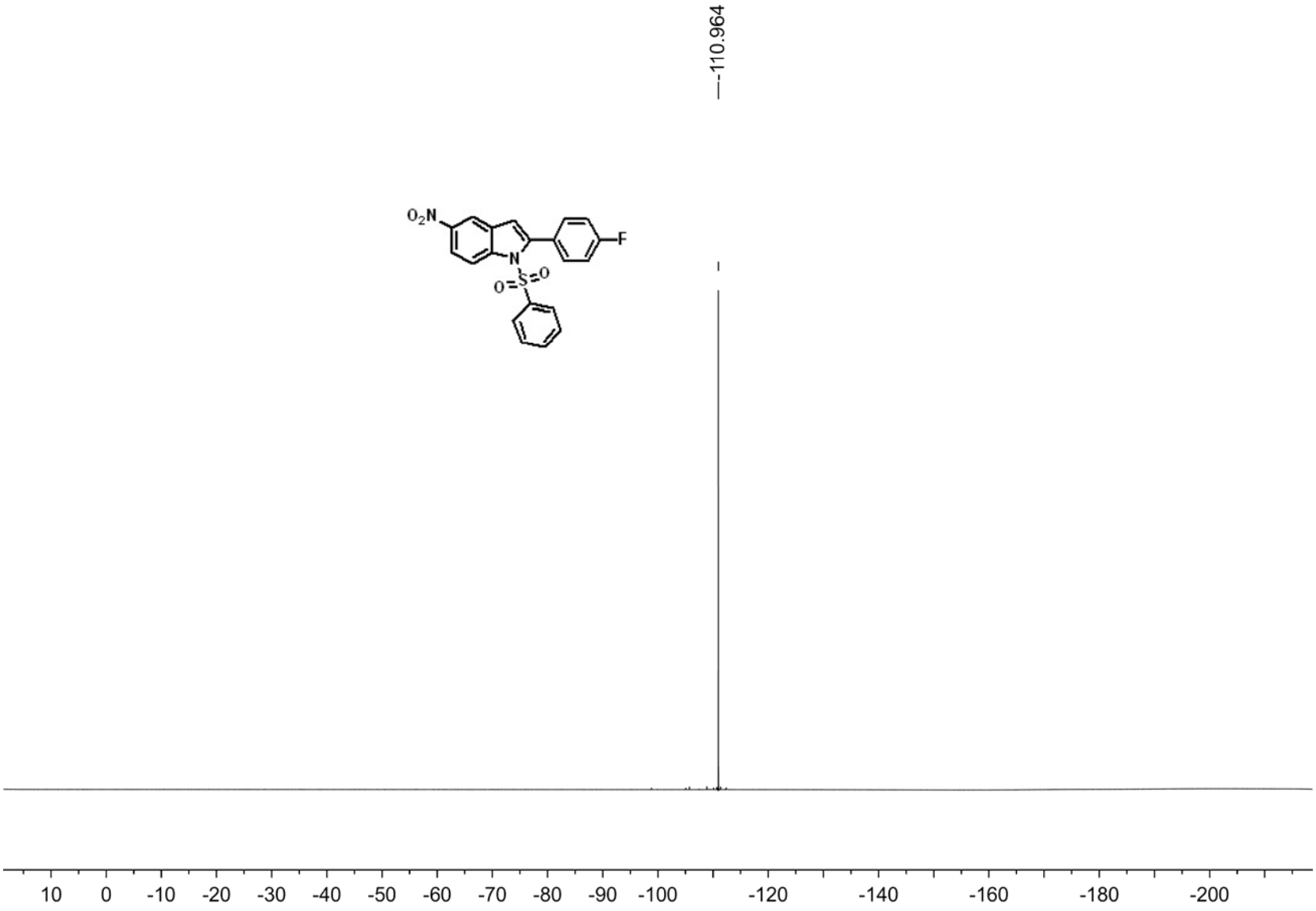
^{13}C NMR Spectrum of Compound **2n**



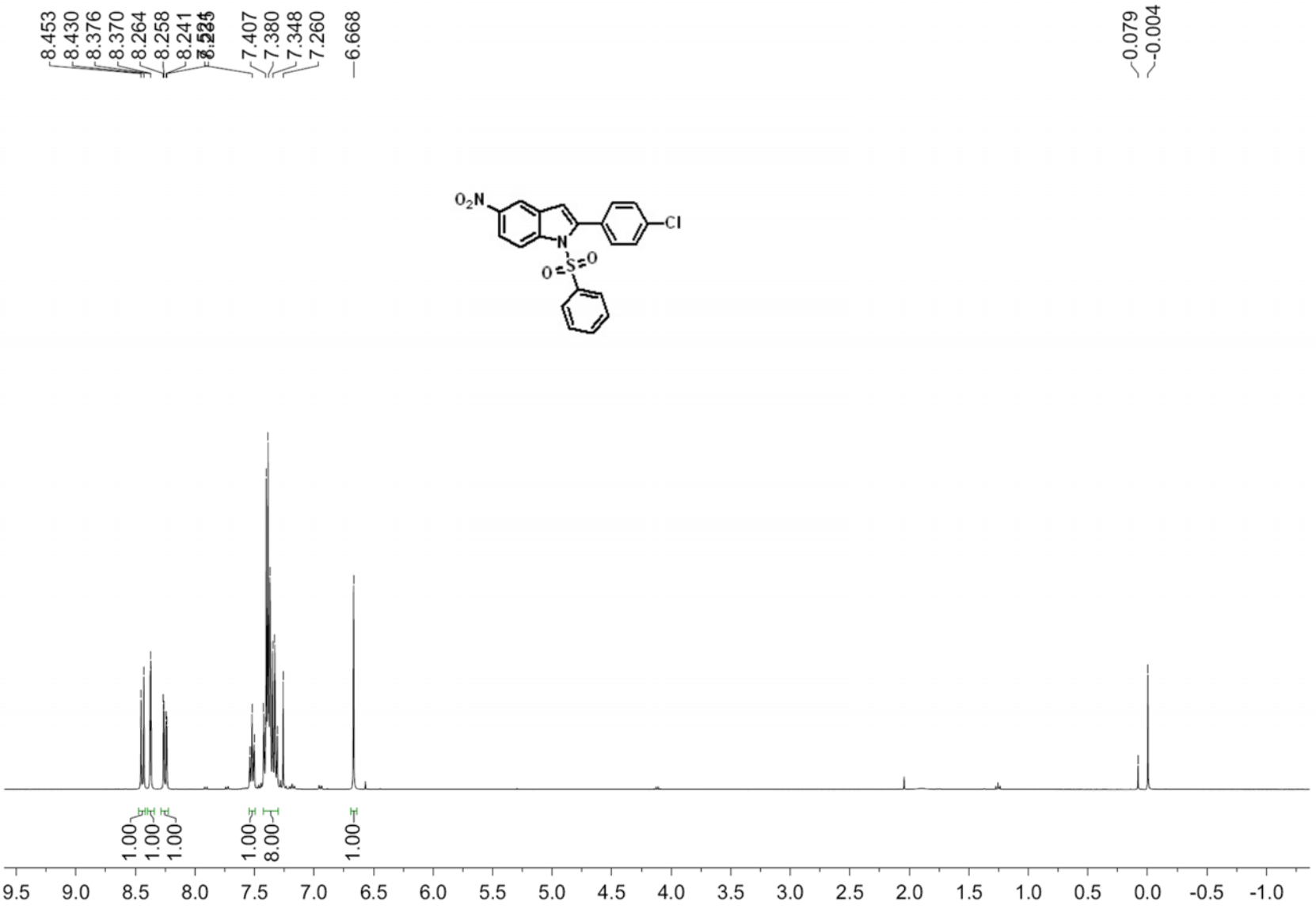
^{1}H NMR Spectrum of Compound **2o**



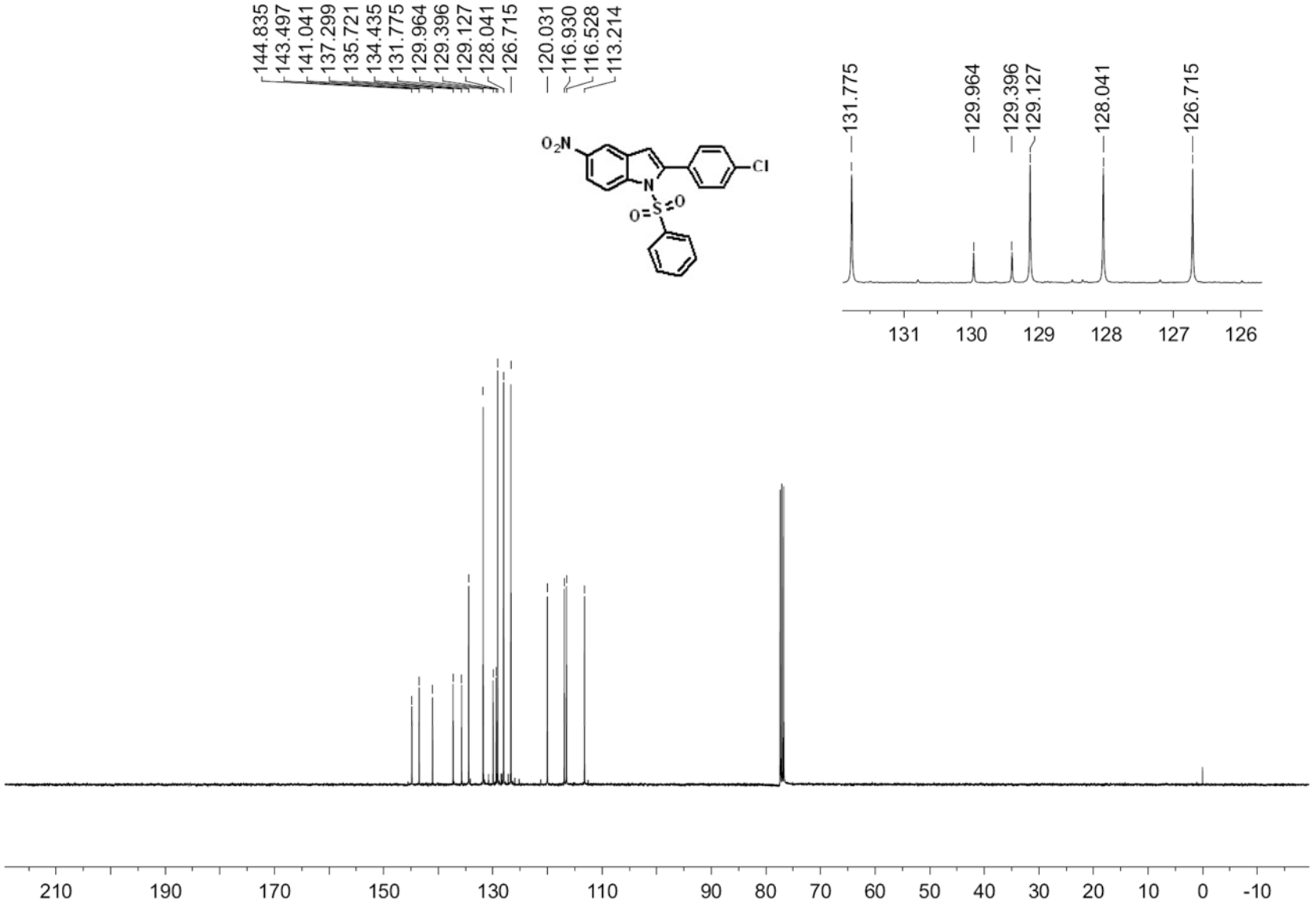
^{13}C NMR Spectrum of Compound **2o**



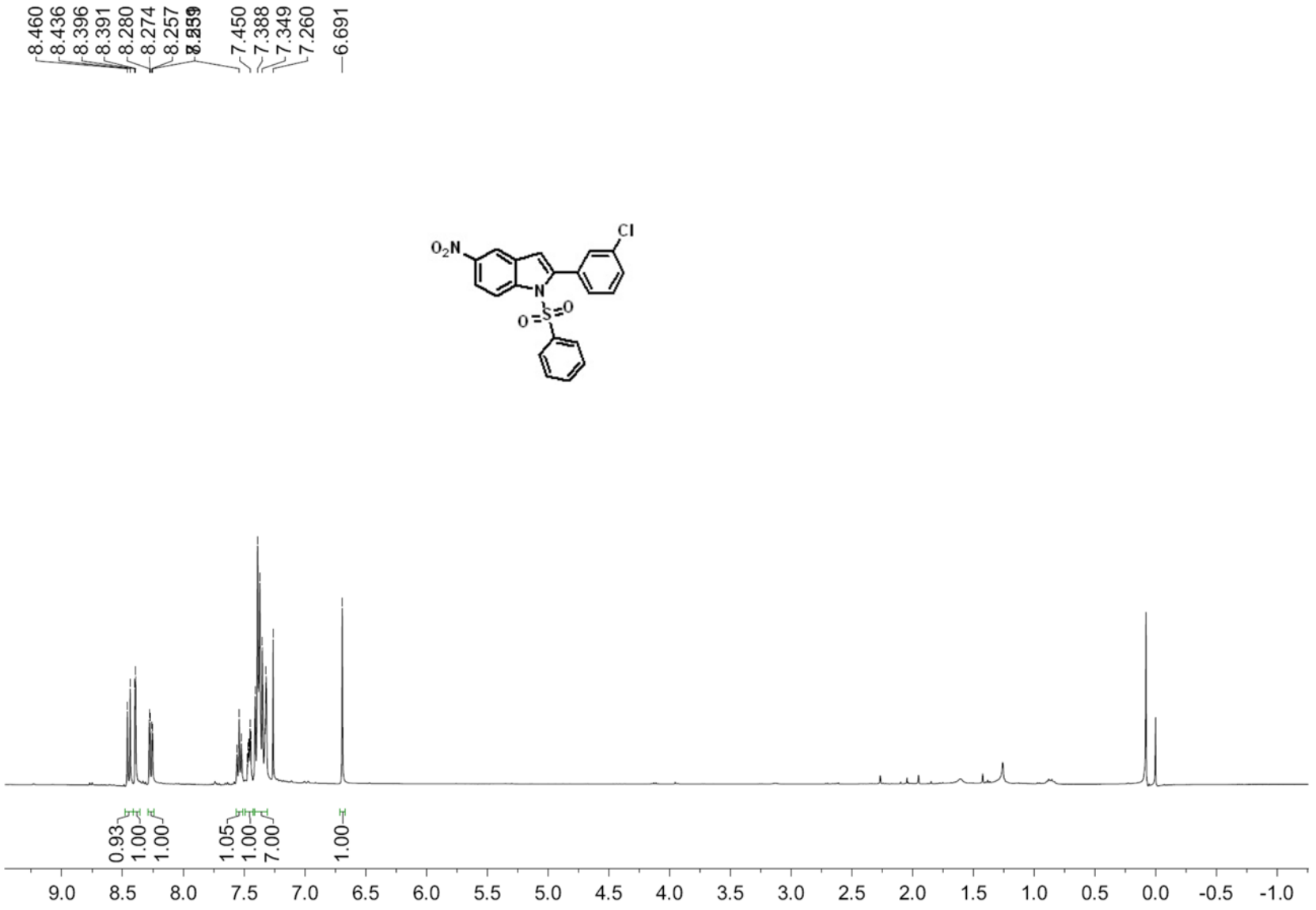
^{19}F NMR Spectrum of Compound **2o**



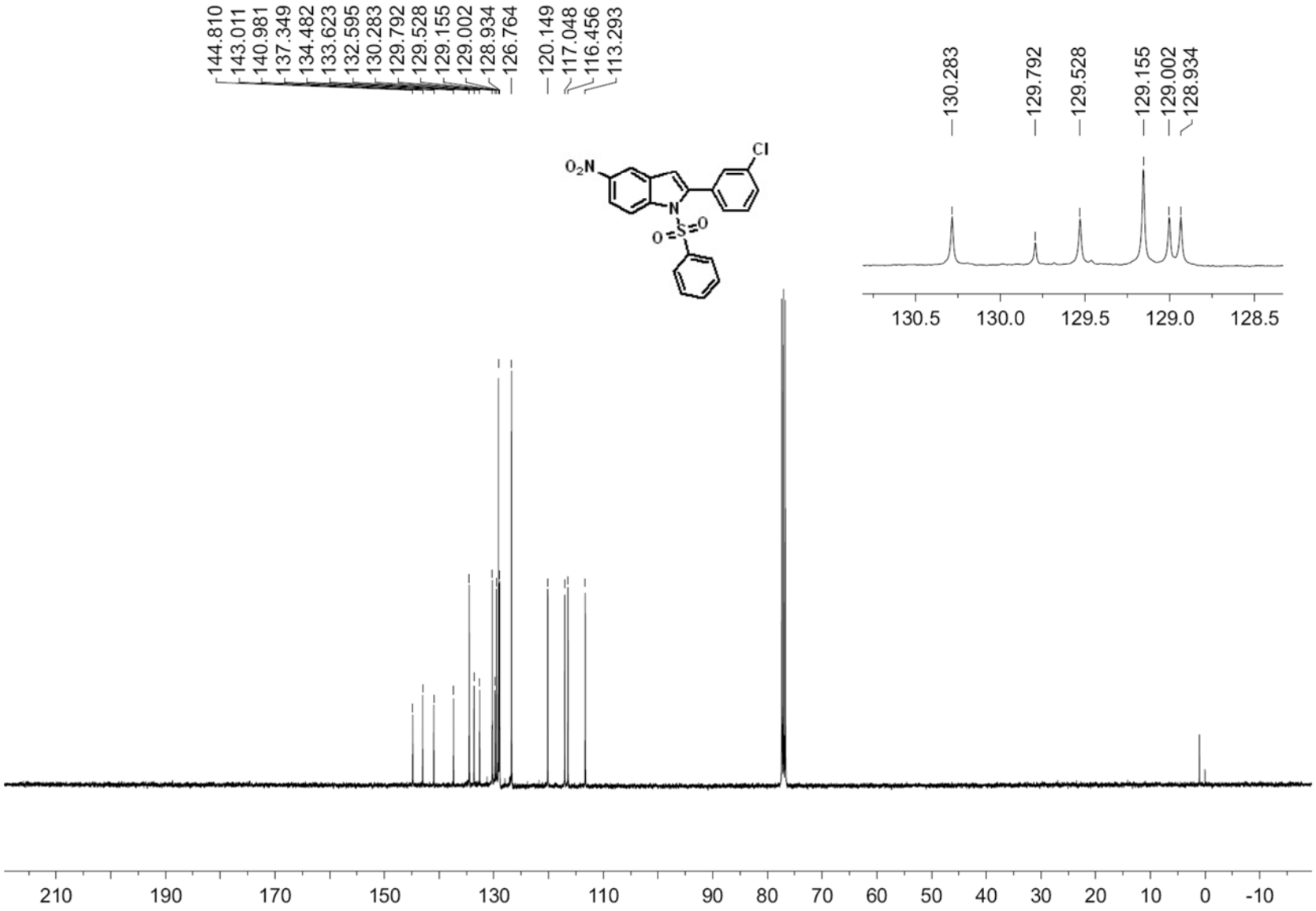
^{1}H NMR Spectrum of Compound **2p**



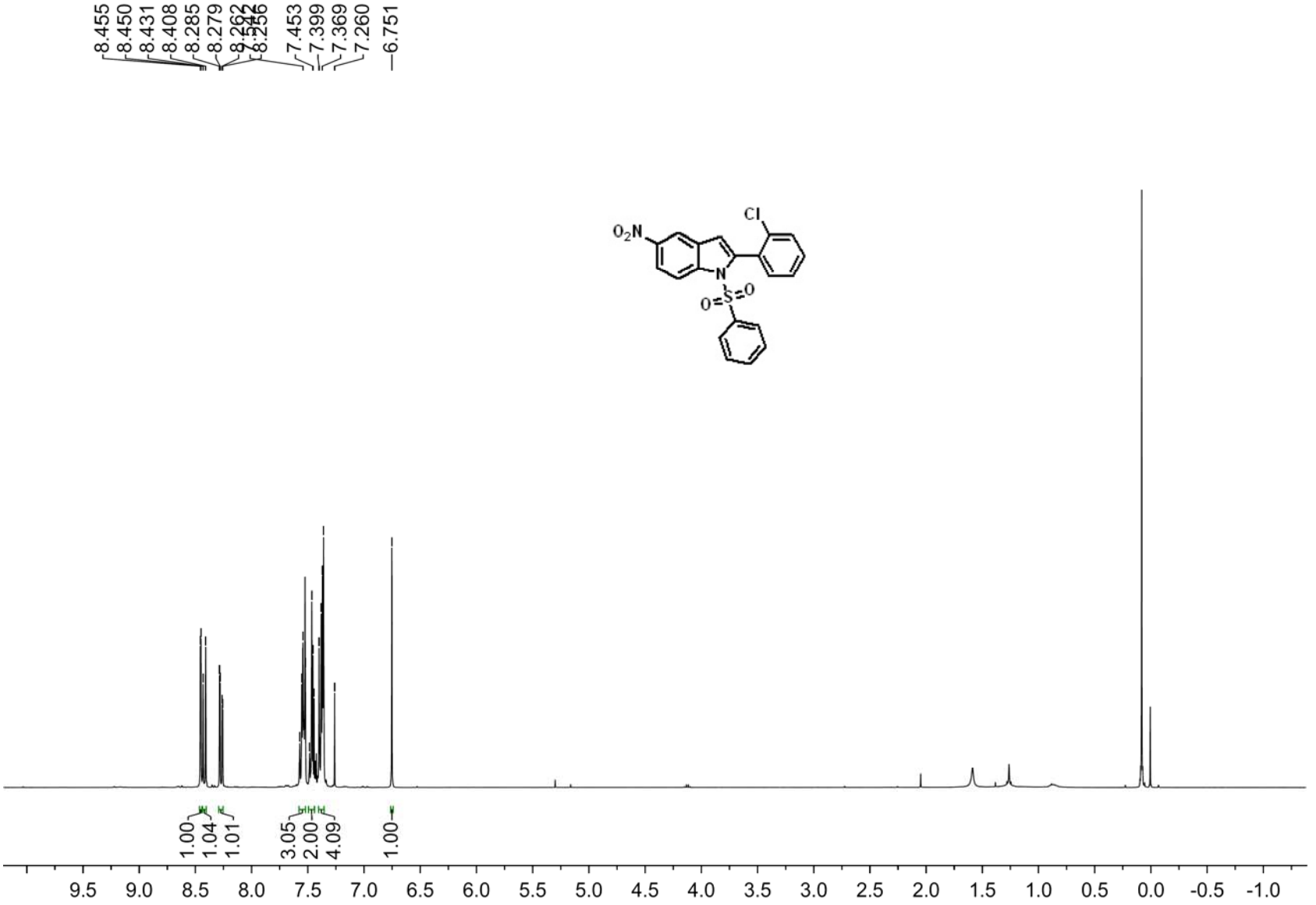
^{13}C NMR Spectrum of Compound **2p**



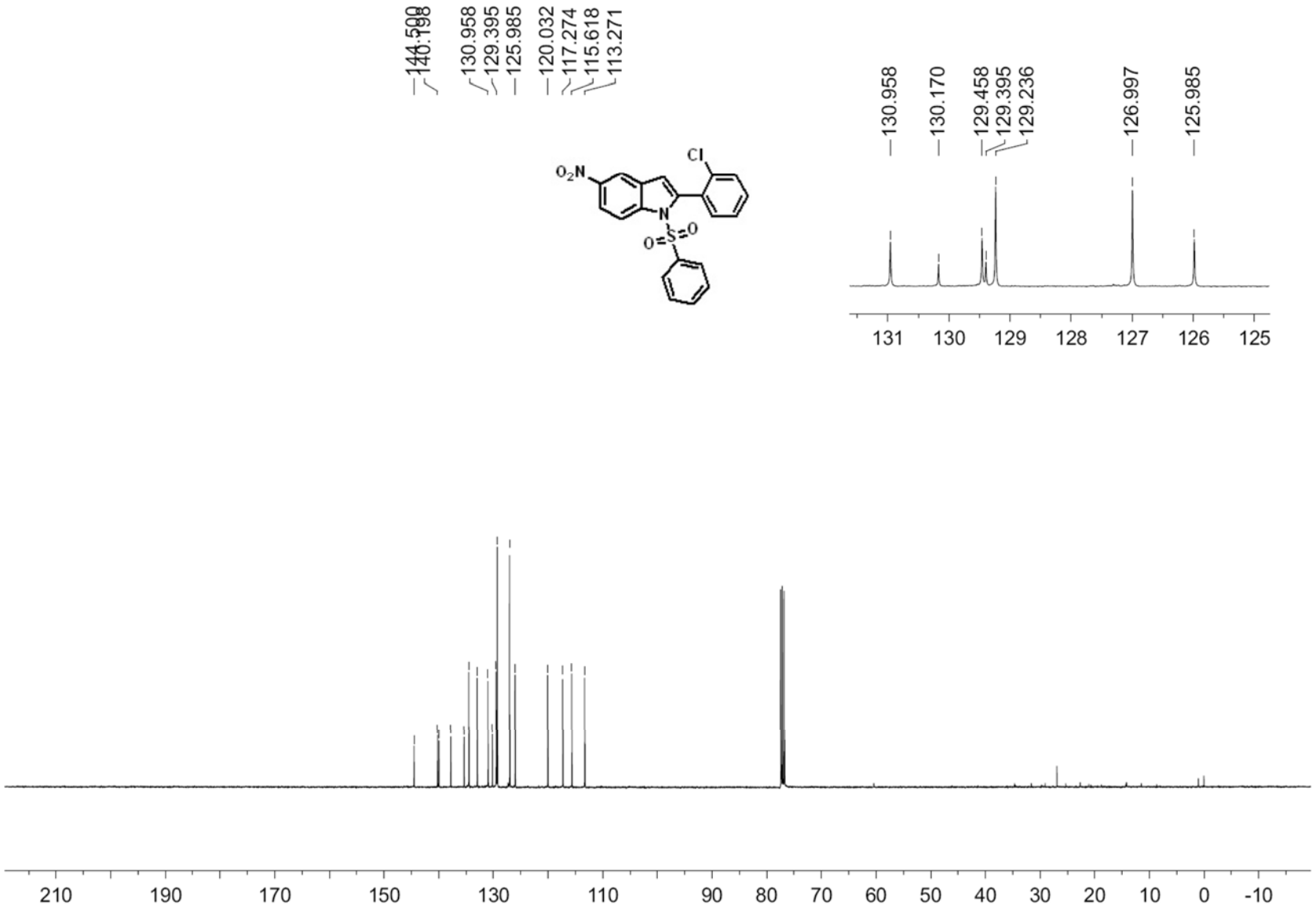
^{1}H NMR Spectrum of Compound **2q**



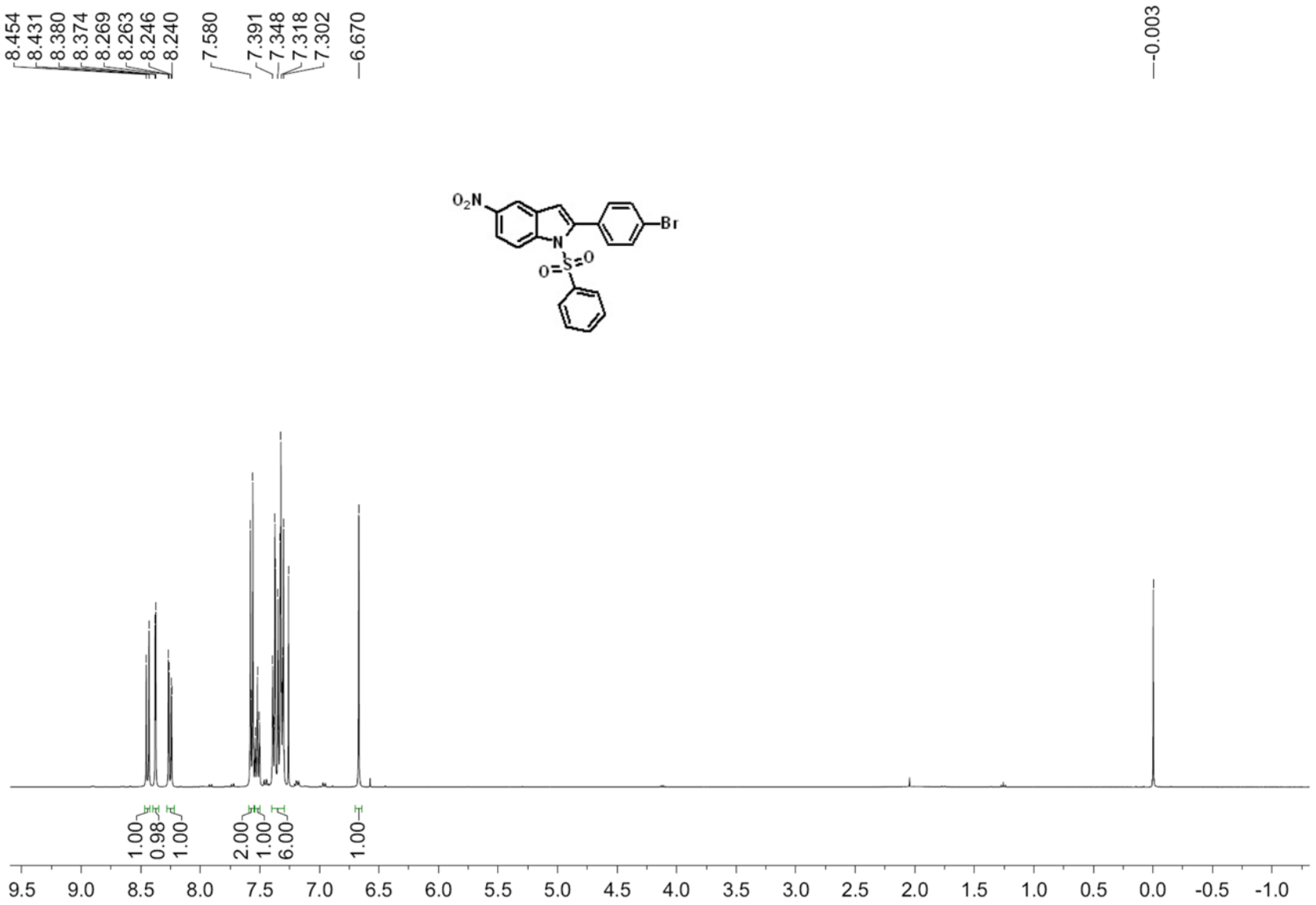
^{13}C NMR Spectrum of Compound **2q**



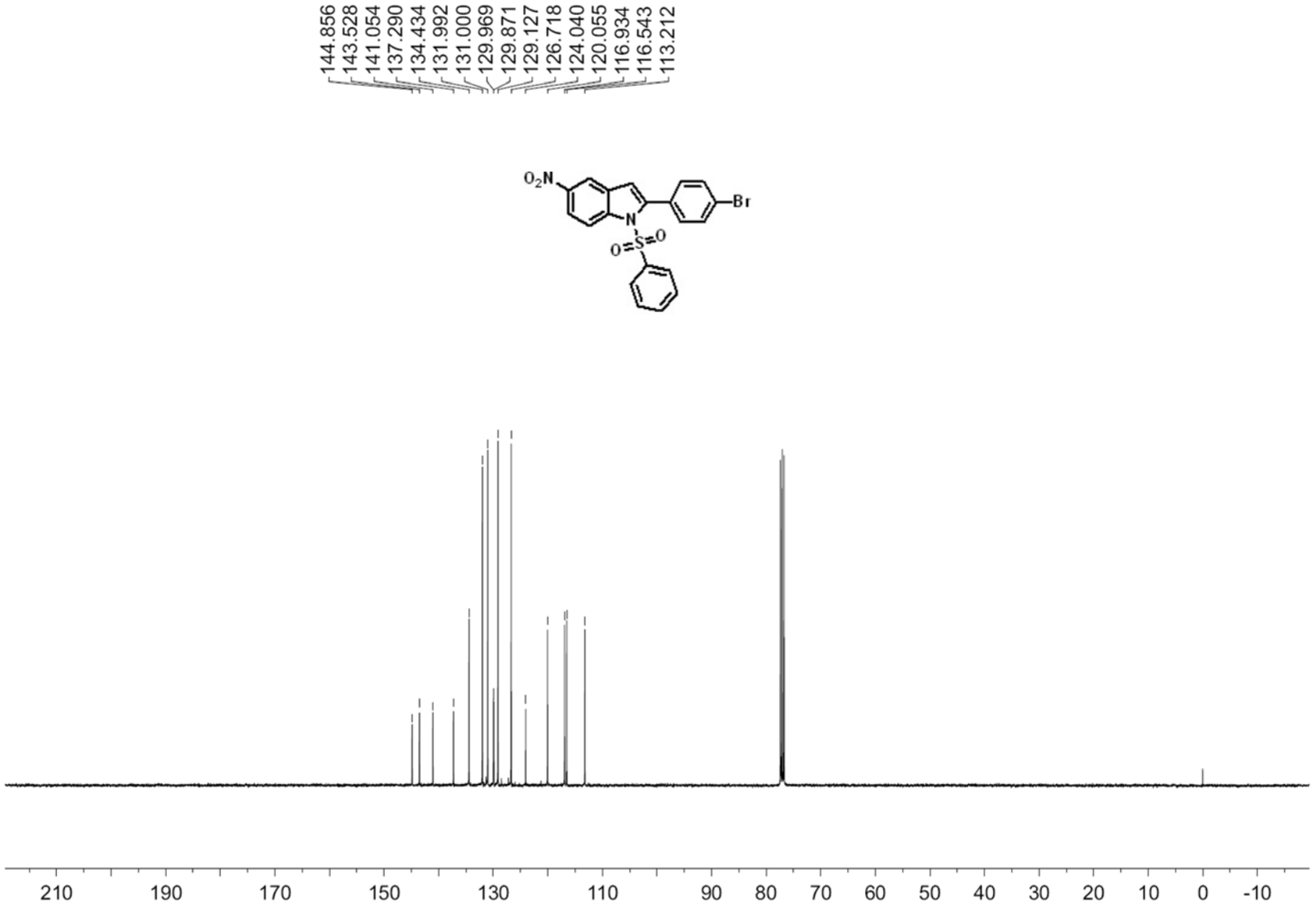
^{1}H NMR Spectrum of Compound **2r**



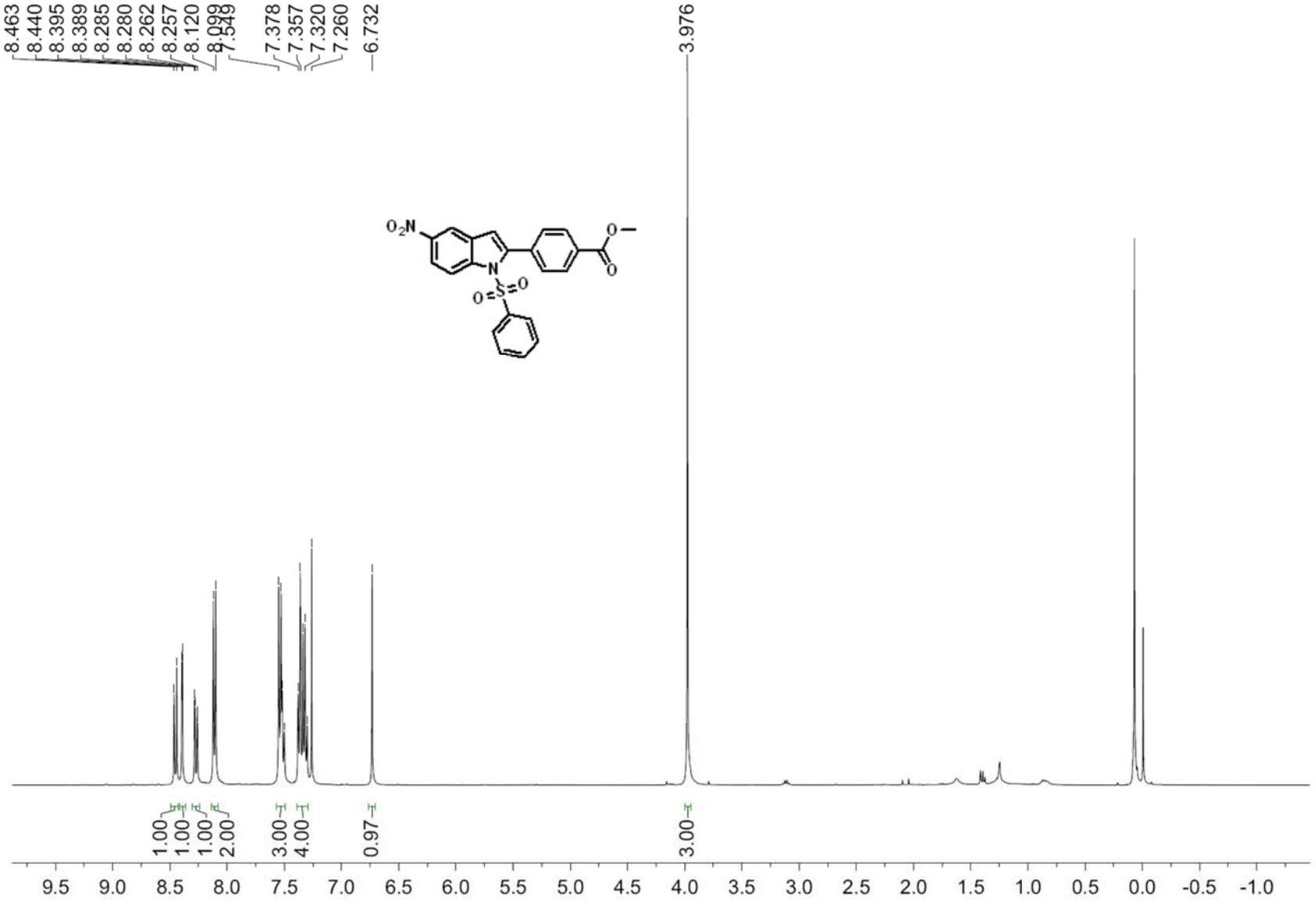
^{13}C NMR Spectrum of Compound **2r**



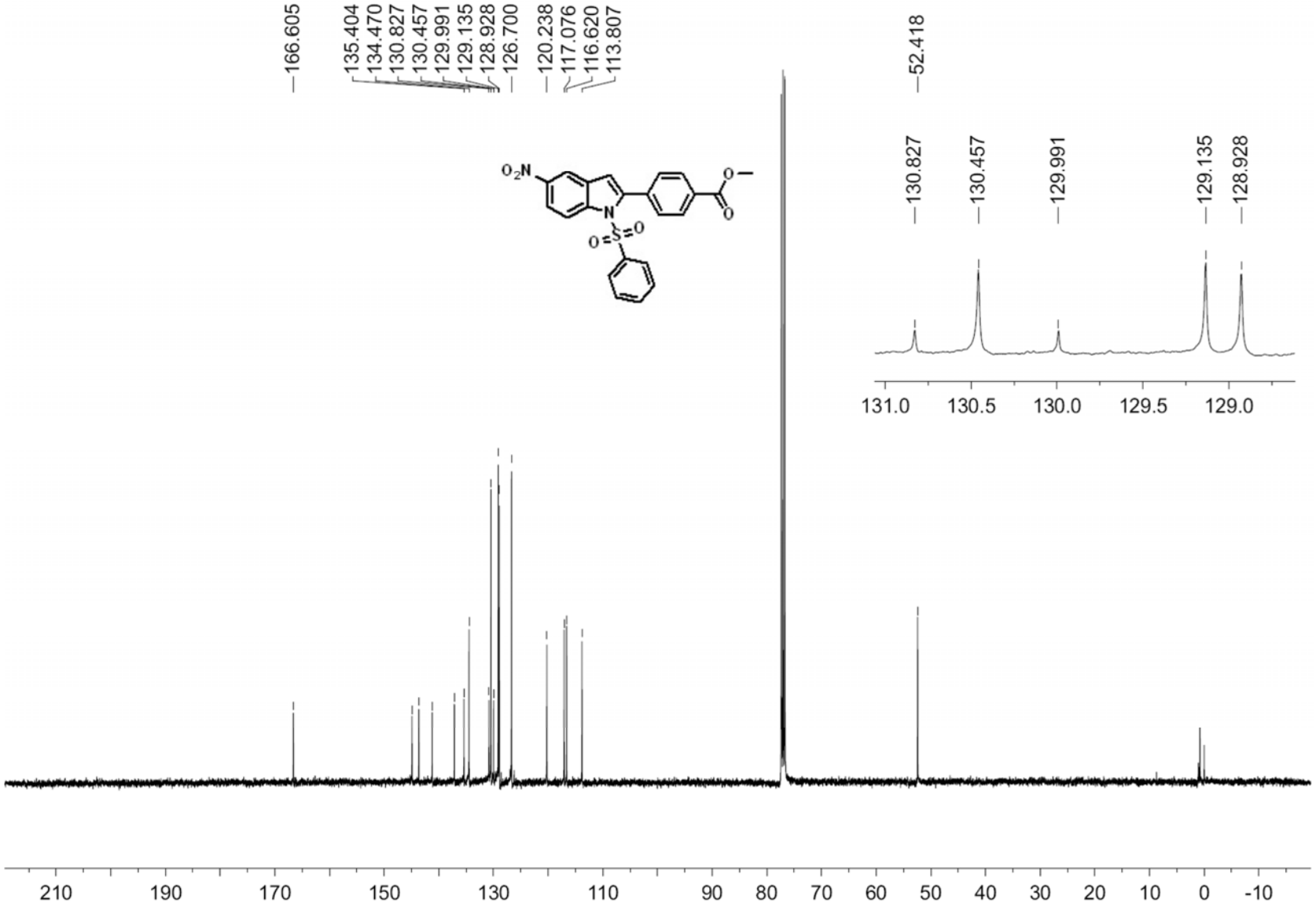
^{1}H NMR Spectrum of Compound **2s**



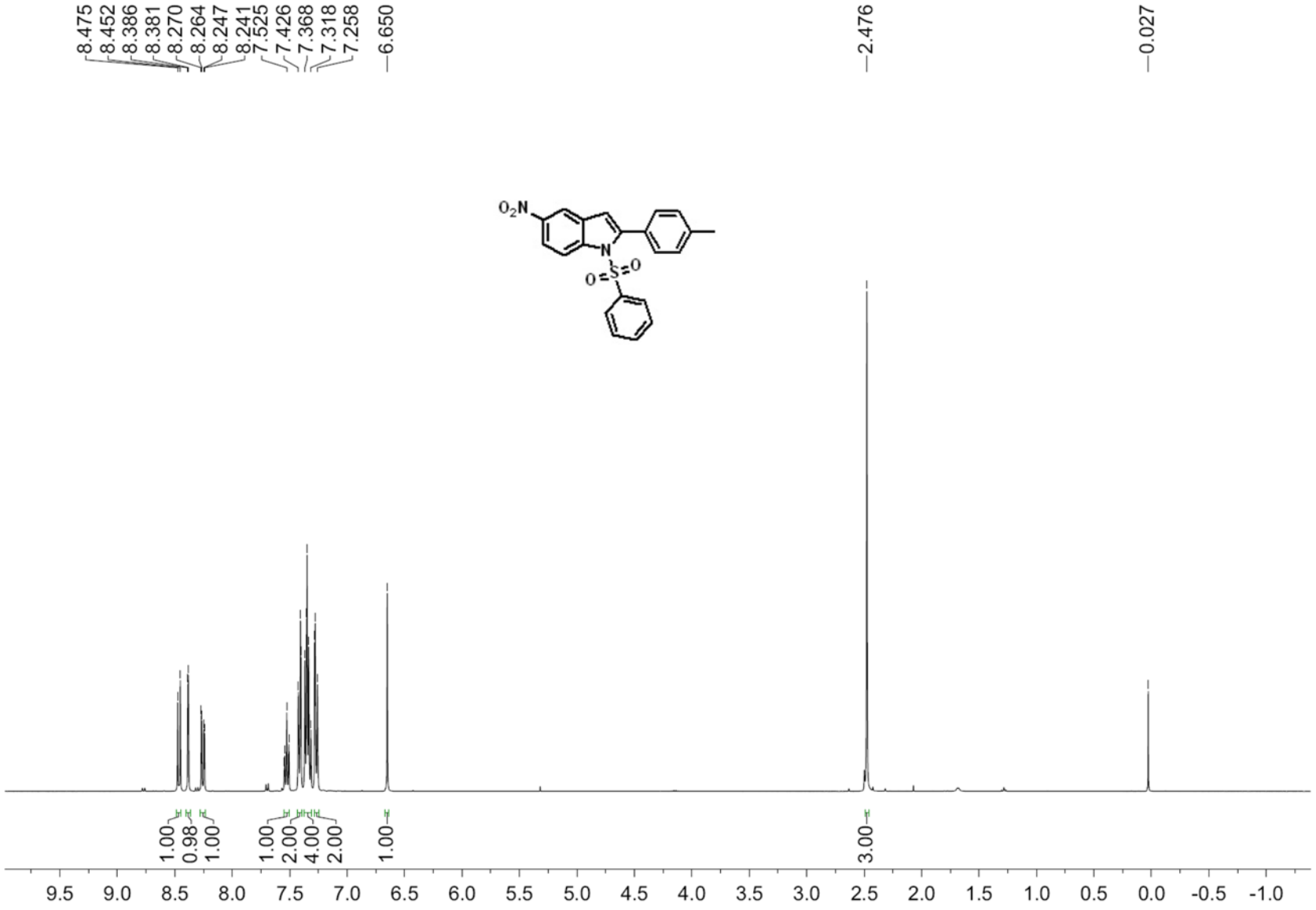
^{13}C NMR Spectrum of Compound **2s**



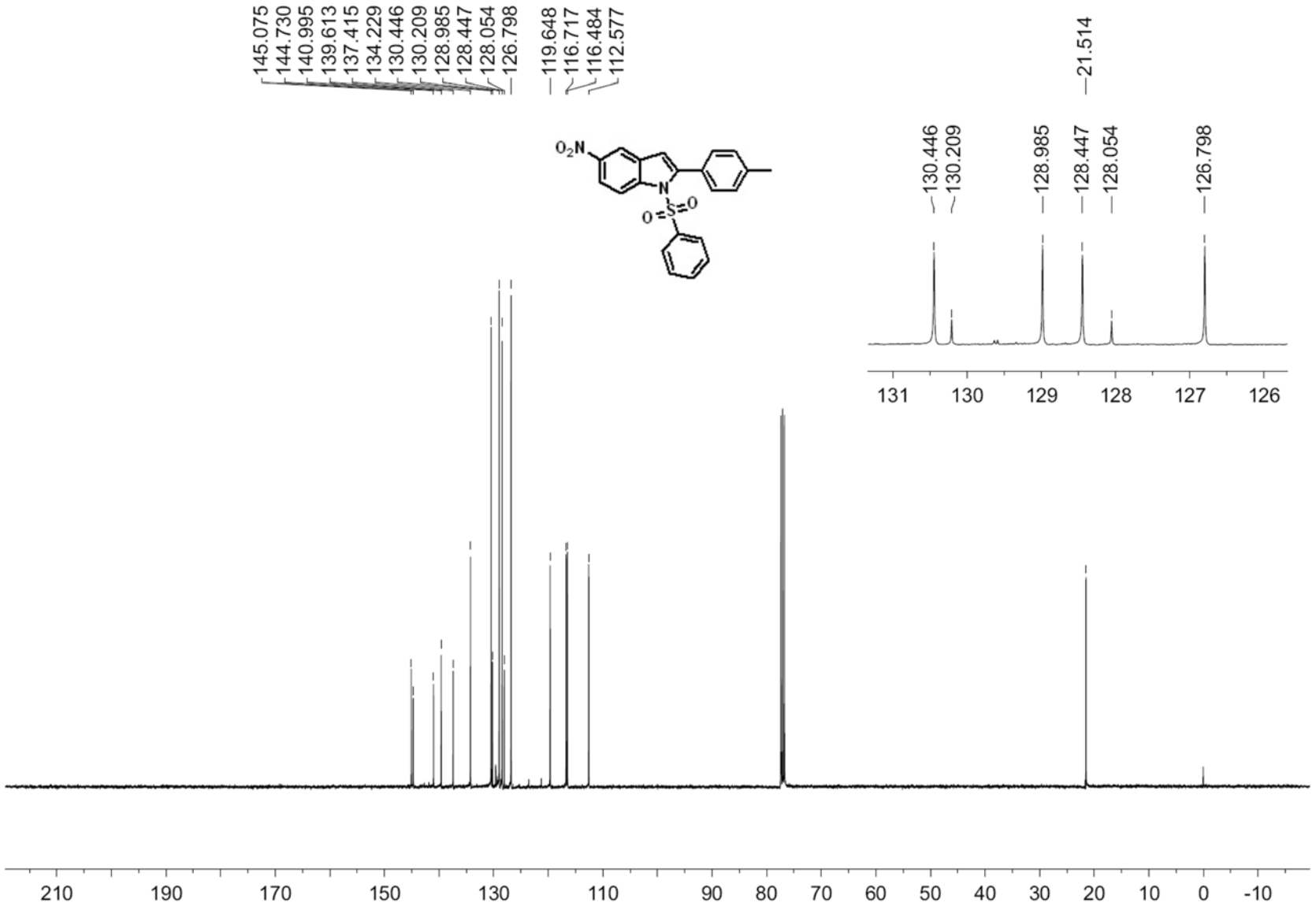
^{1}H NMR Spectrum of Compound **2t**



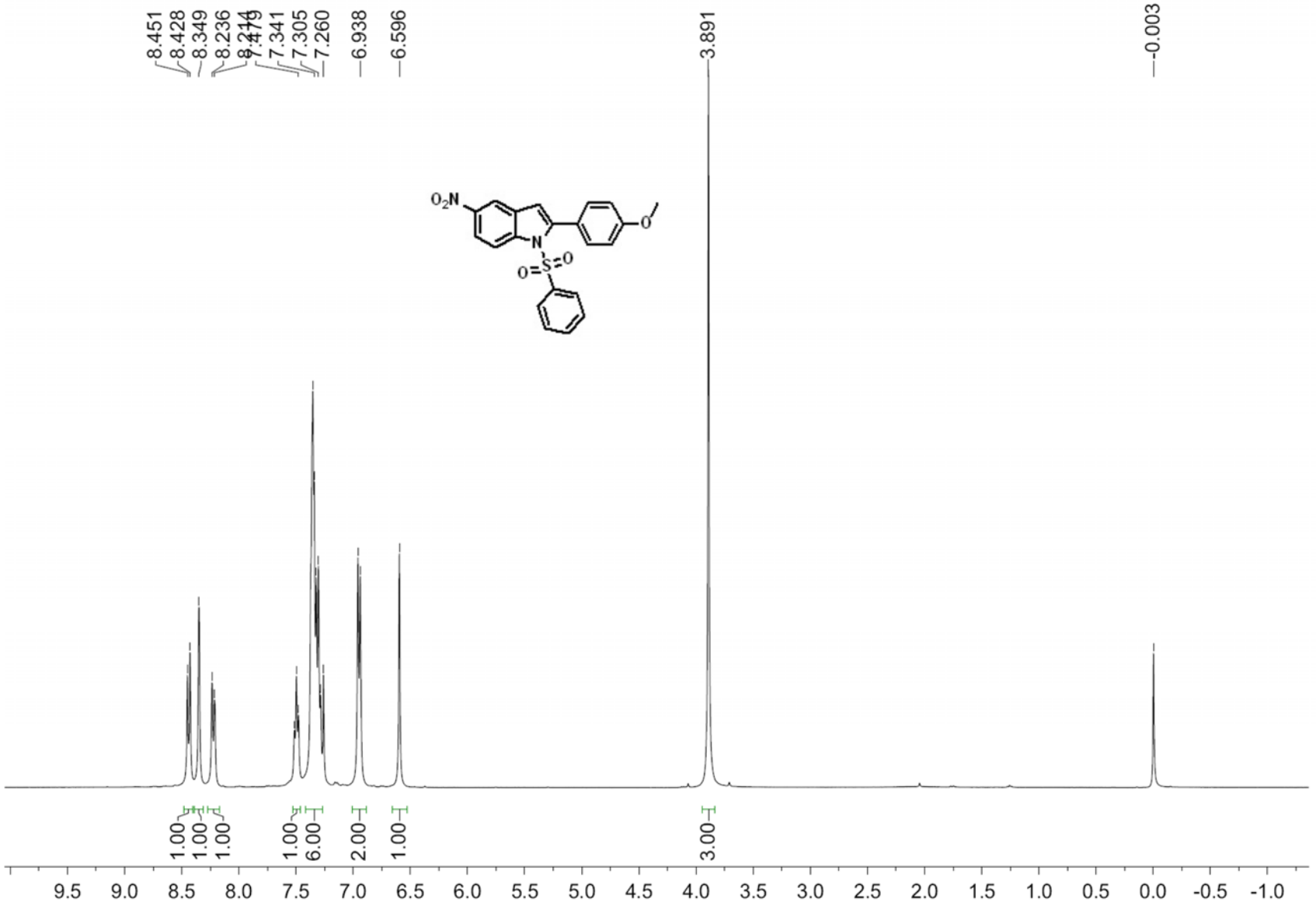
^{13}C NMR Spectrum of Compound **2t**



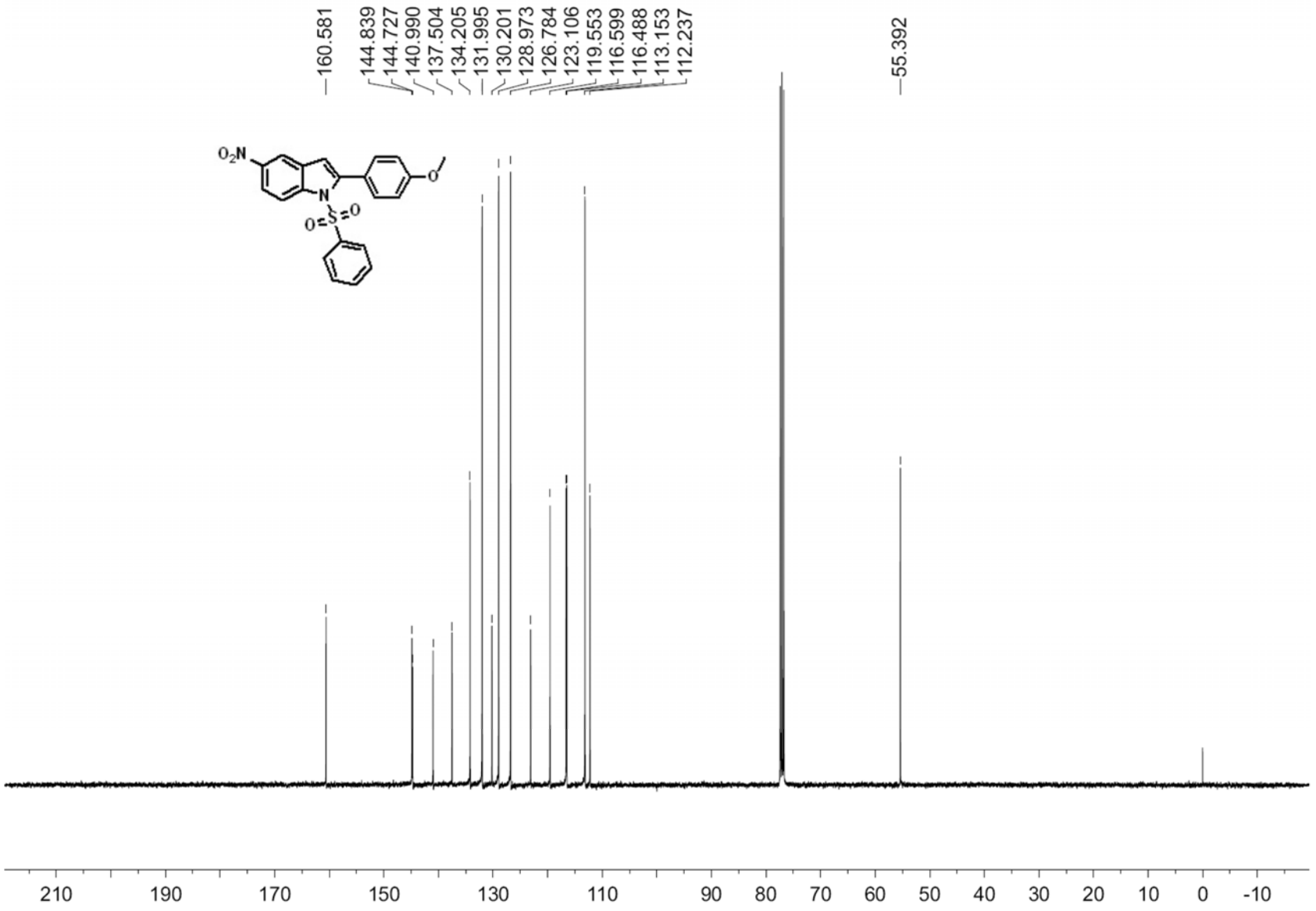
^{1}H NMR Spectrum of Compound **2u**



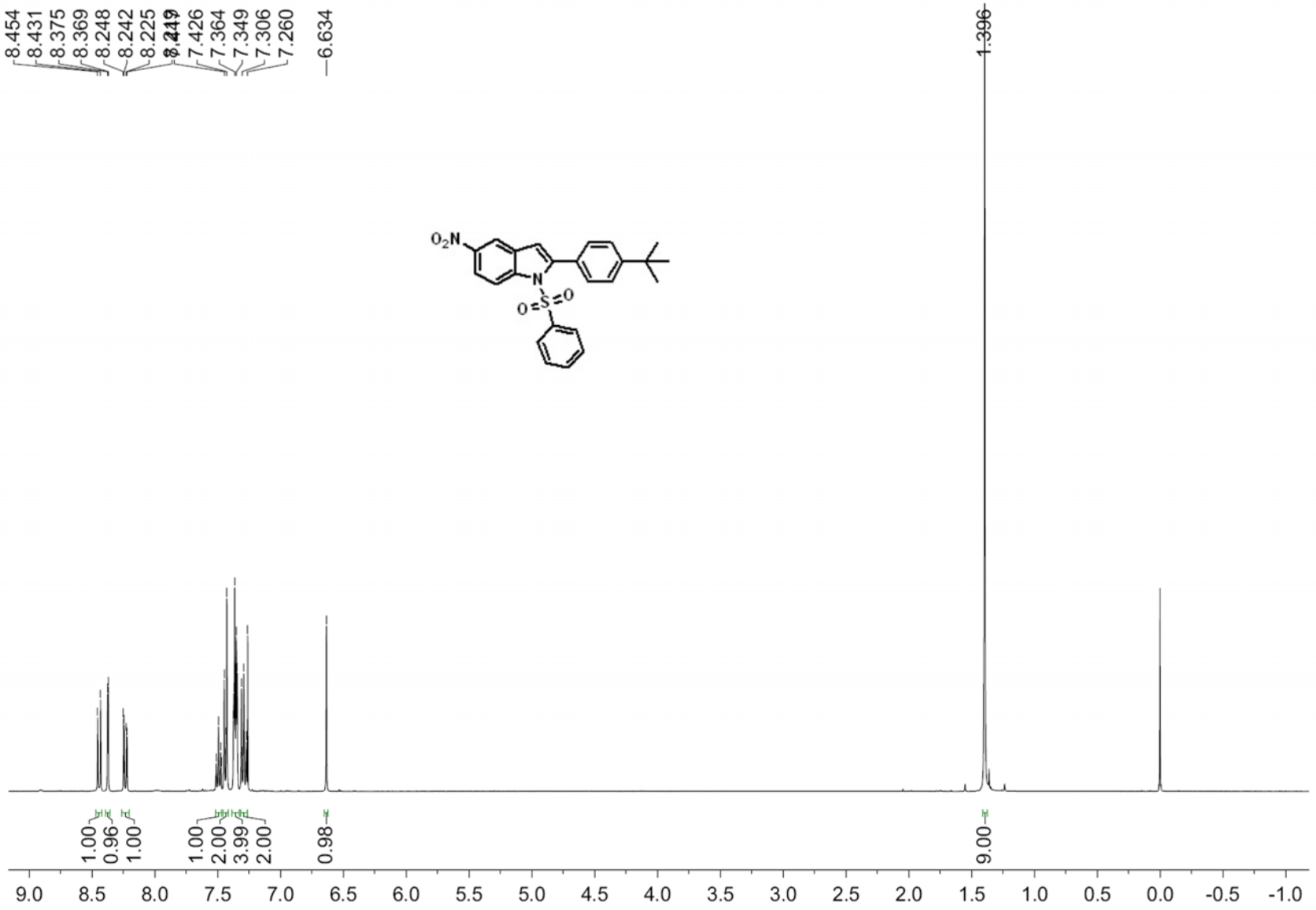
^{13}C NMR Spectrum of Compound **2u**



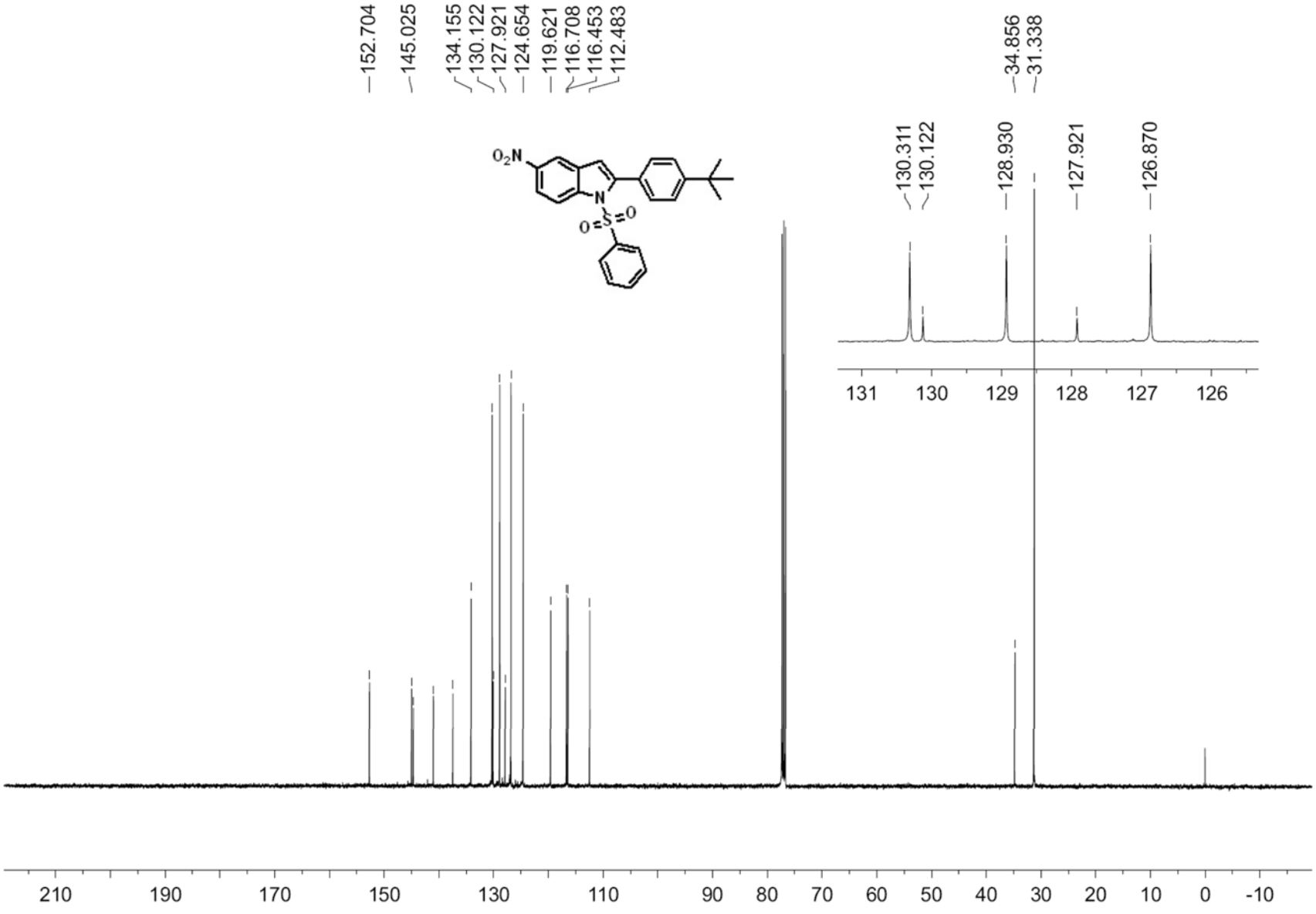
^{1}H NMR Spectrum of Compound **2v**



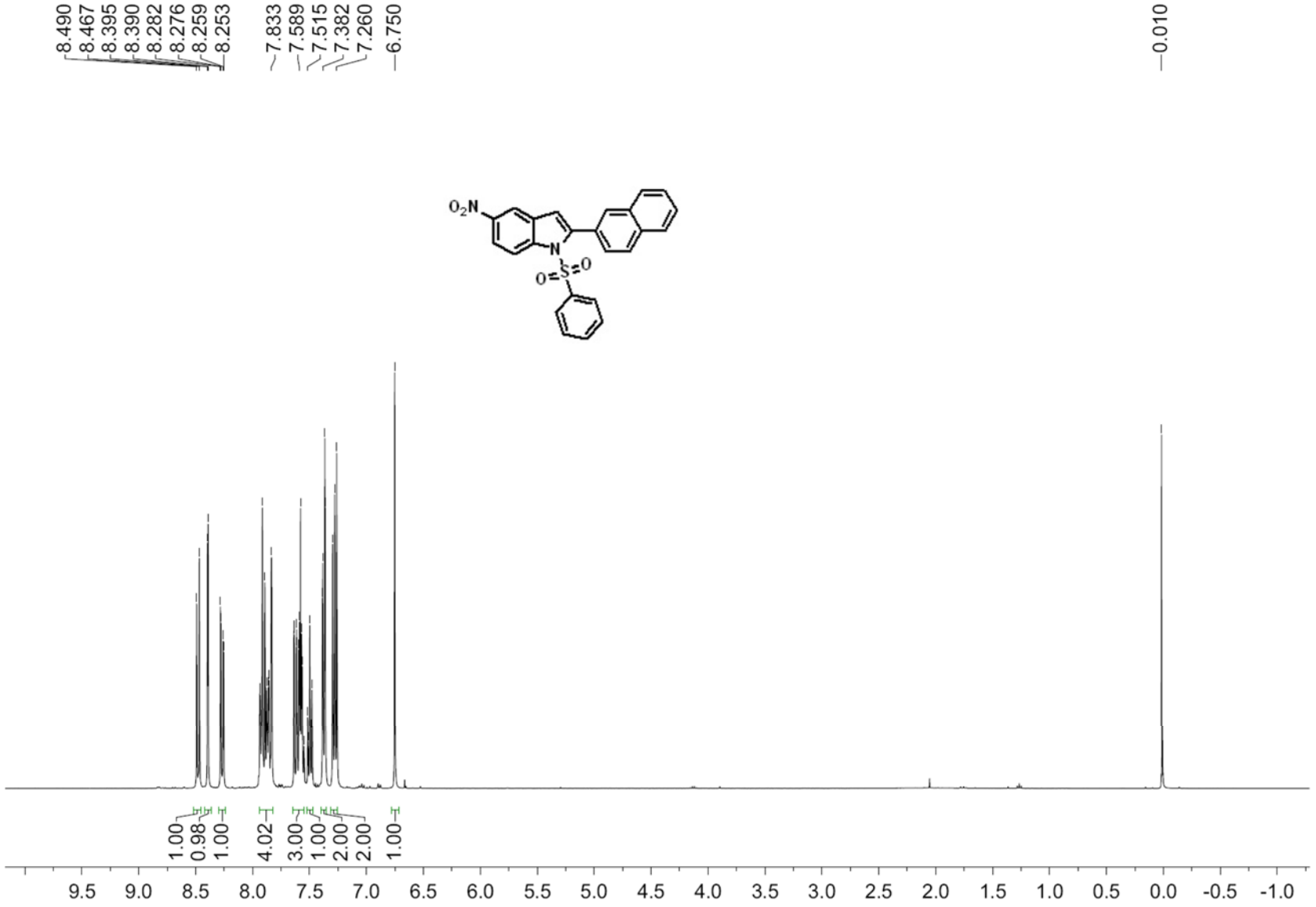
^{13}C NMR Spectrum of Compound **2v**



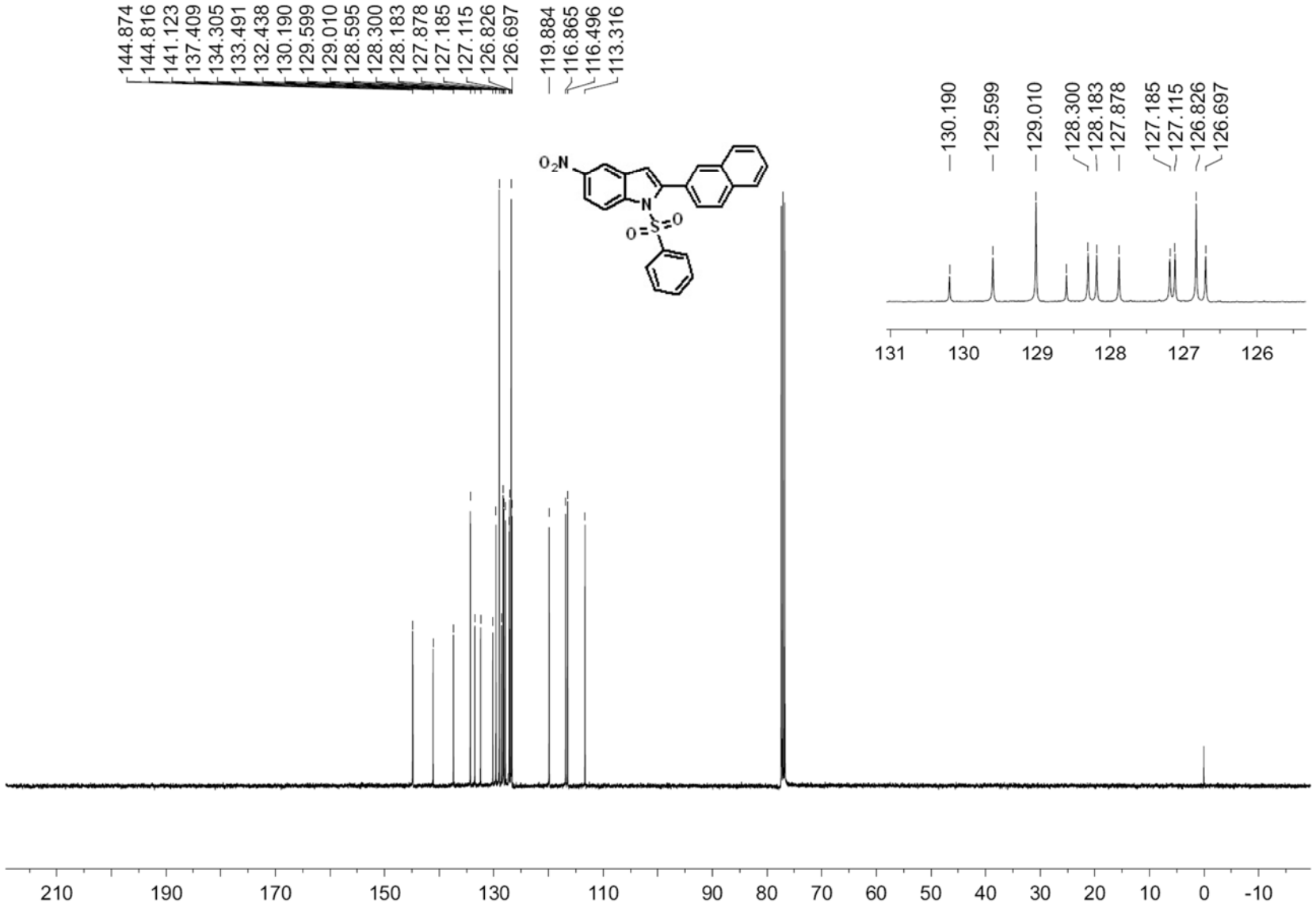
^{1}H NMR Spectrum of Compound **2w**



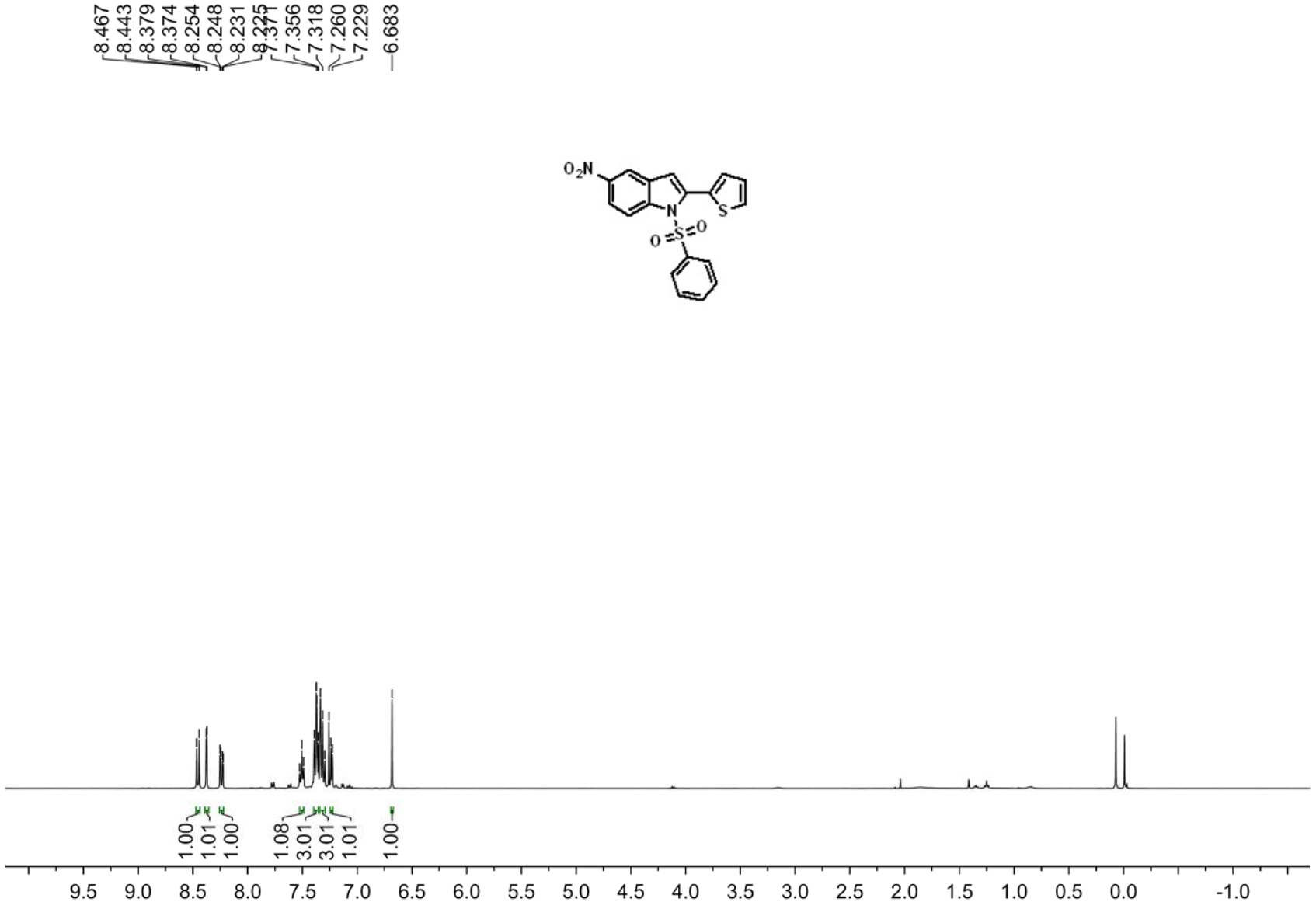
^{13}C NMR Spectrum of Compound **2w**



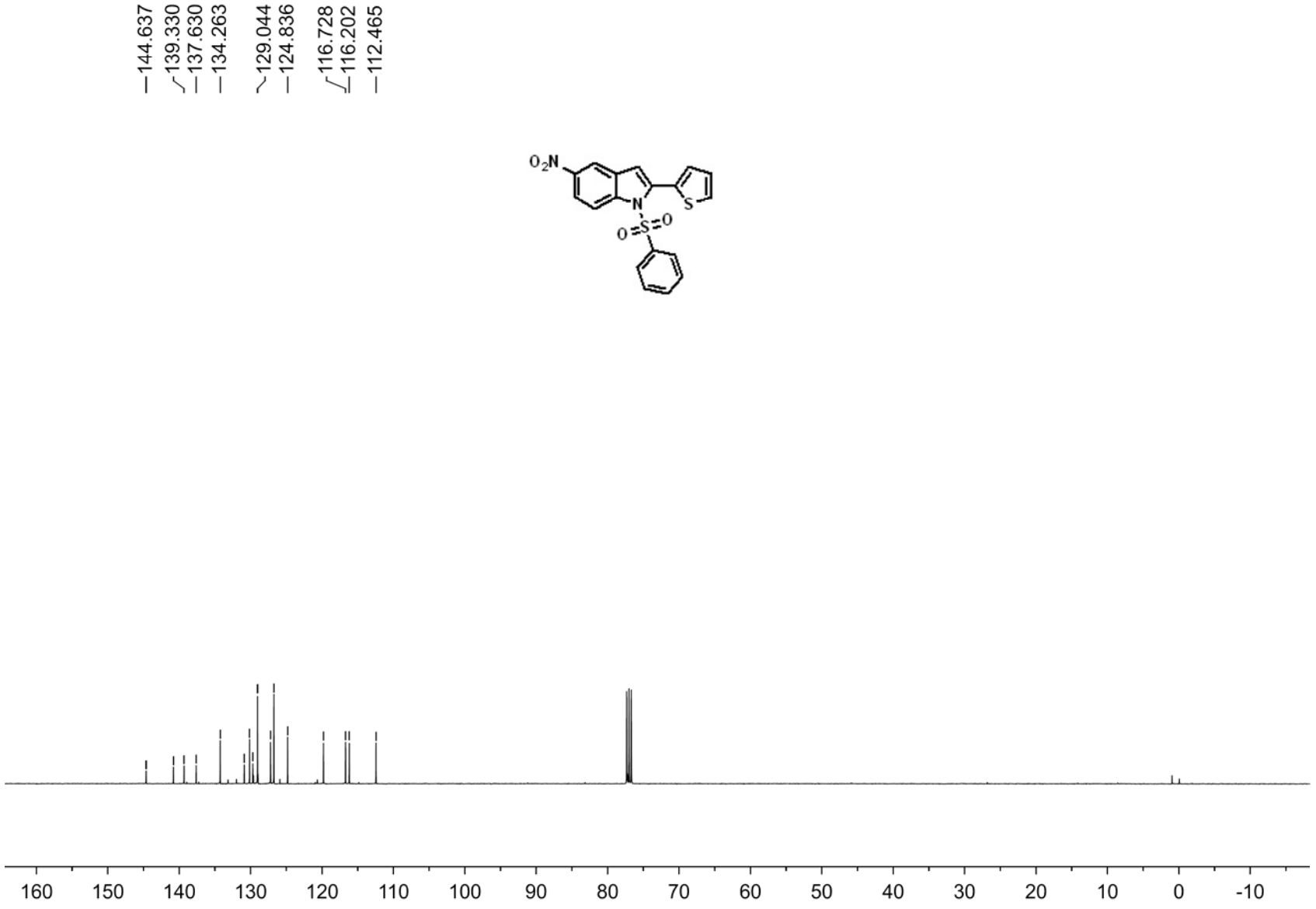
^{1}H NMR Spectrum of Compound **2x**



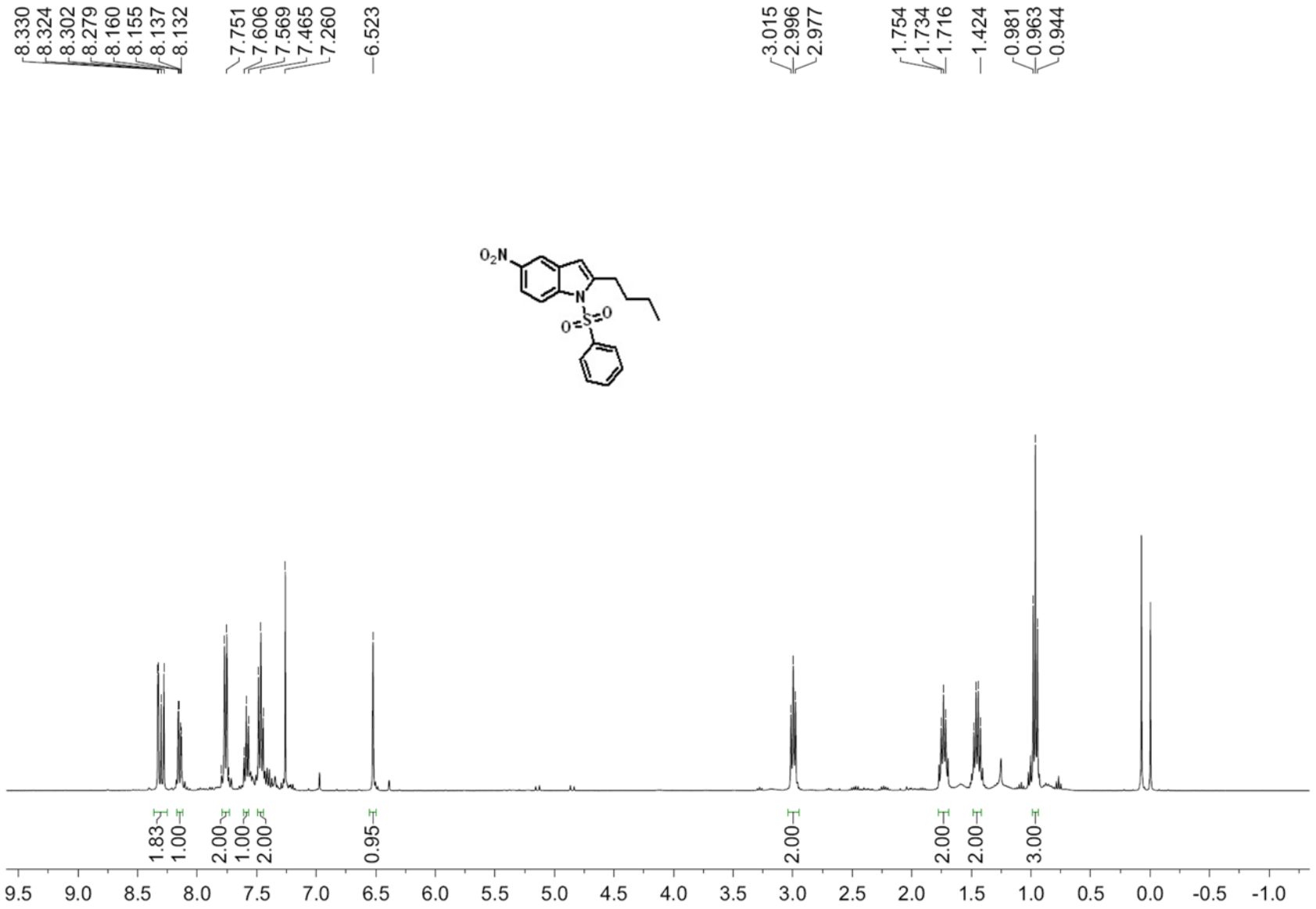
^{13}C NMR Spectrum of Compound **2x**



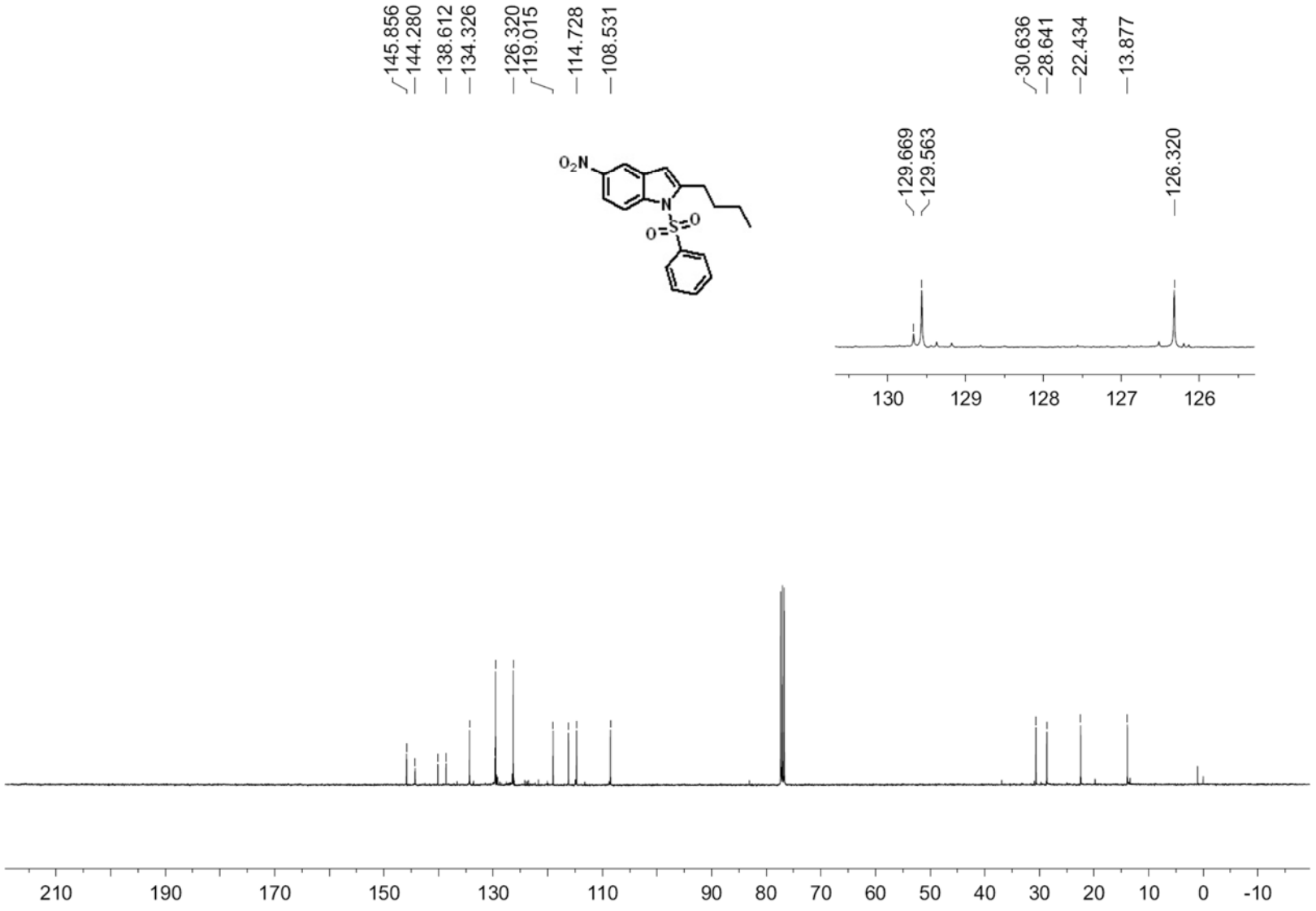
^{1}H NMR Spectrum of Compound **2y**



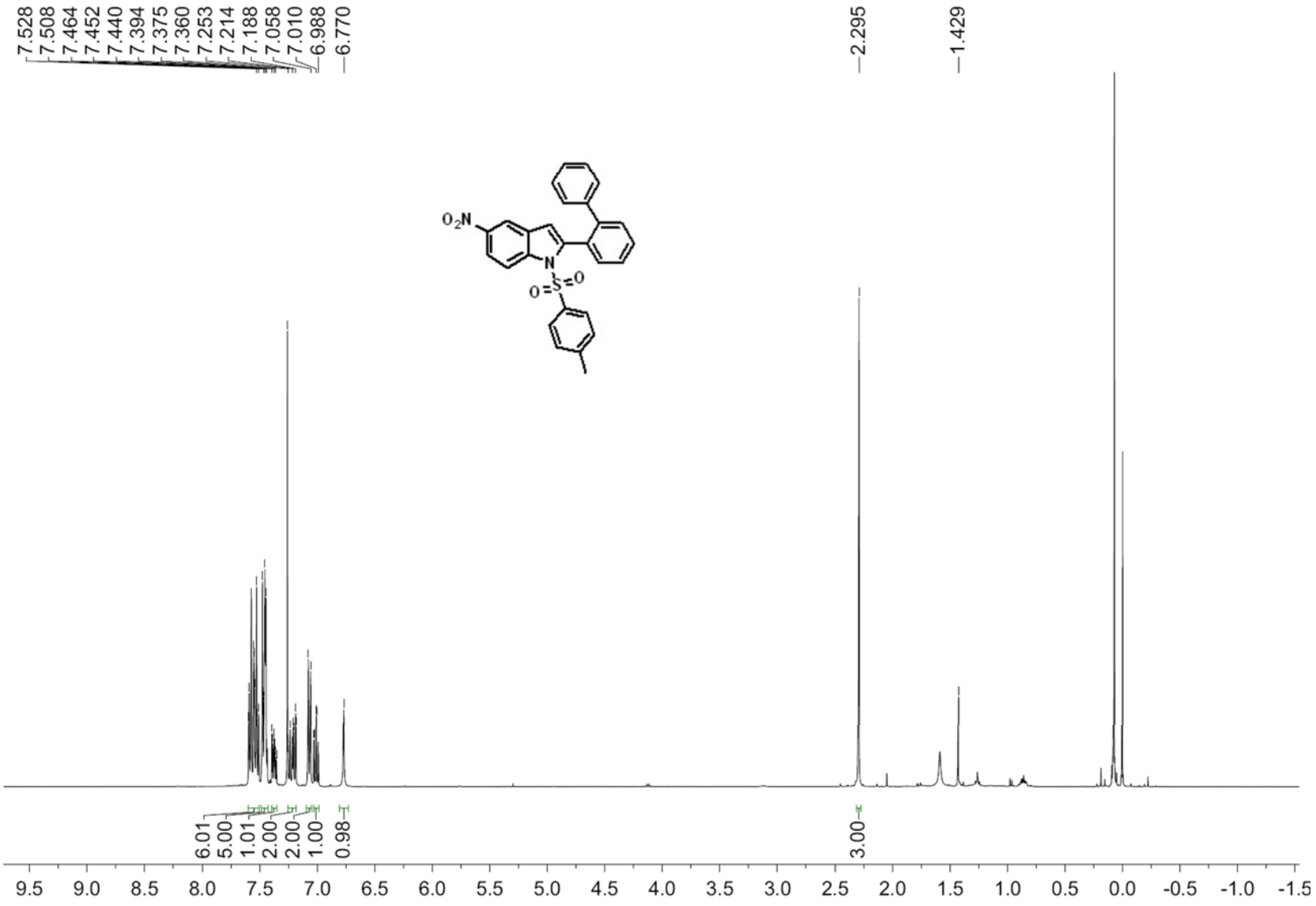
^{13}C NMR Spectrum of Compound **2y**



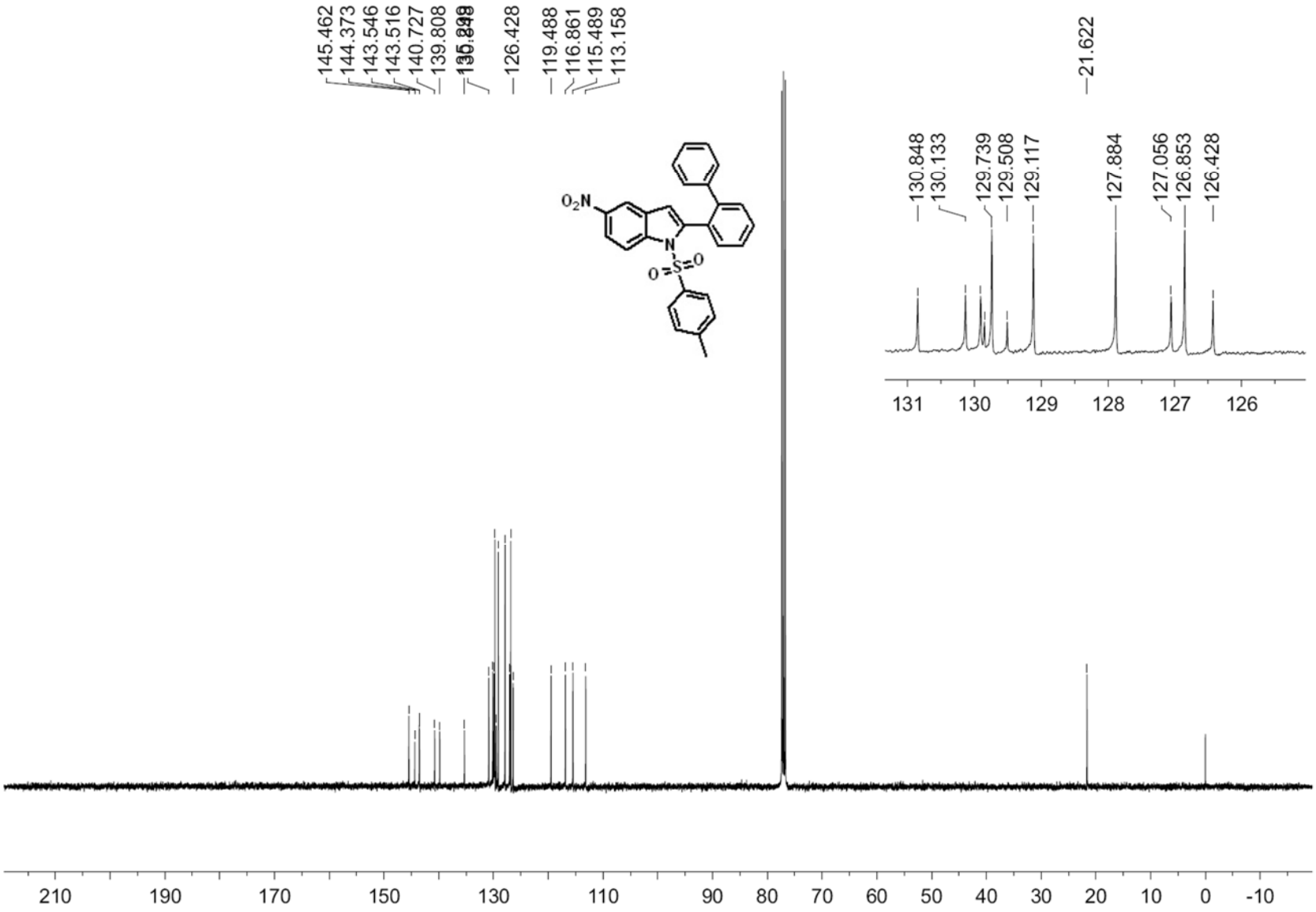
^{1}H NMR Spectrum of Compound **2z**



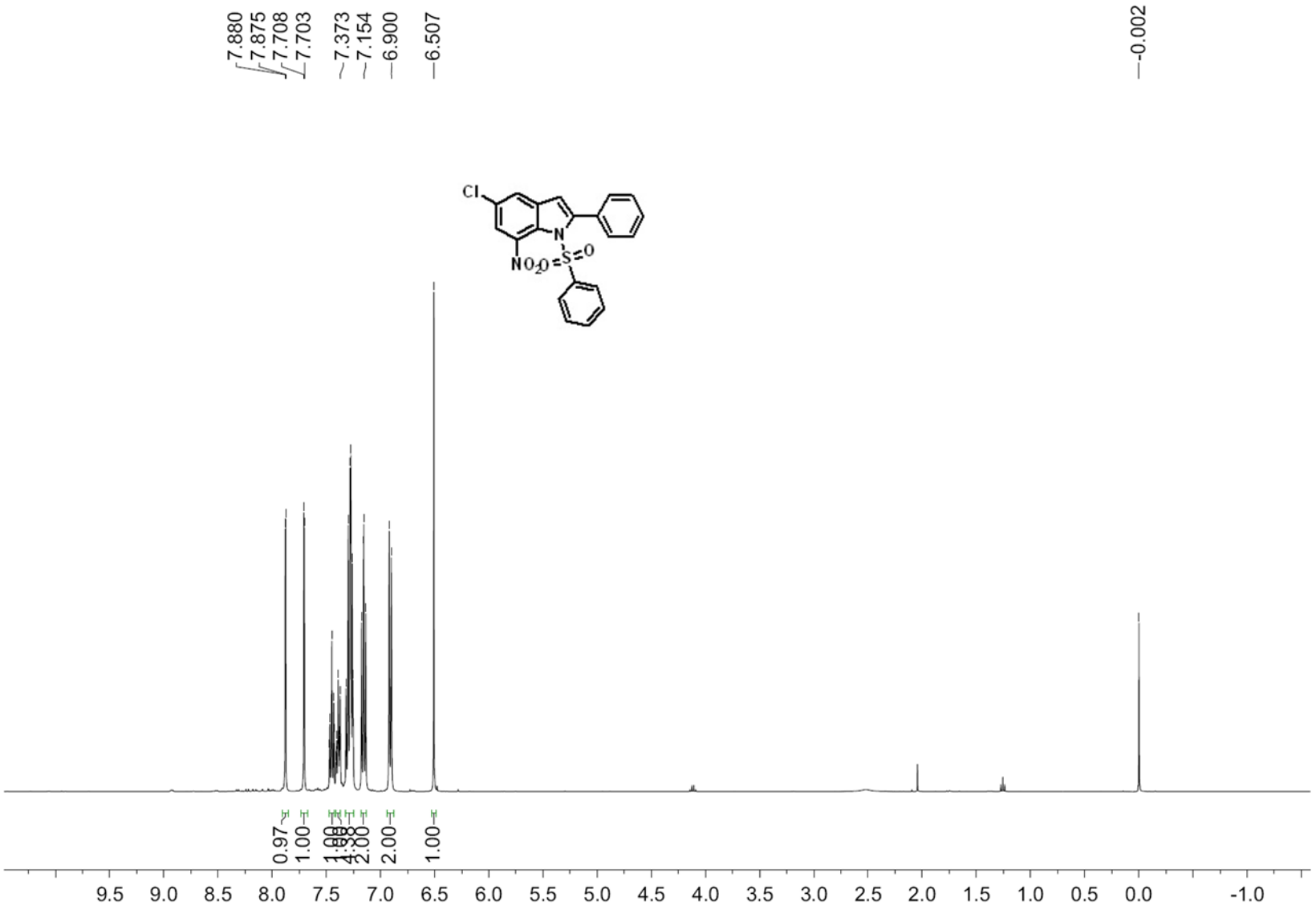
^{13}C NMR Spectrum of Compound **2z**



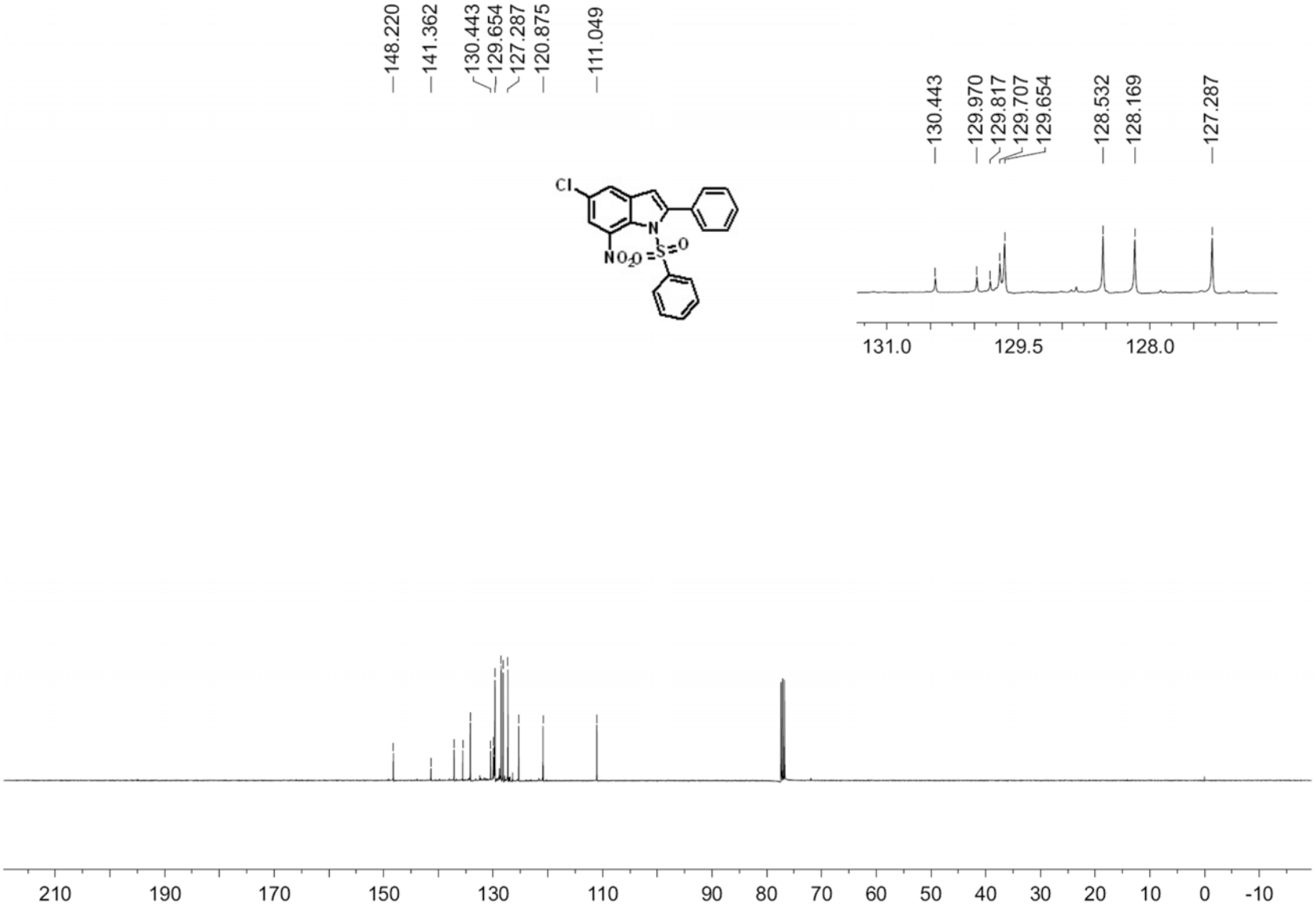
^{1}H NMR Spectrum of Compound **2aa**



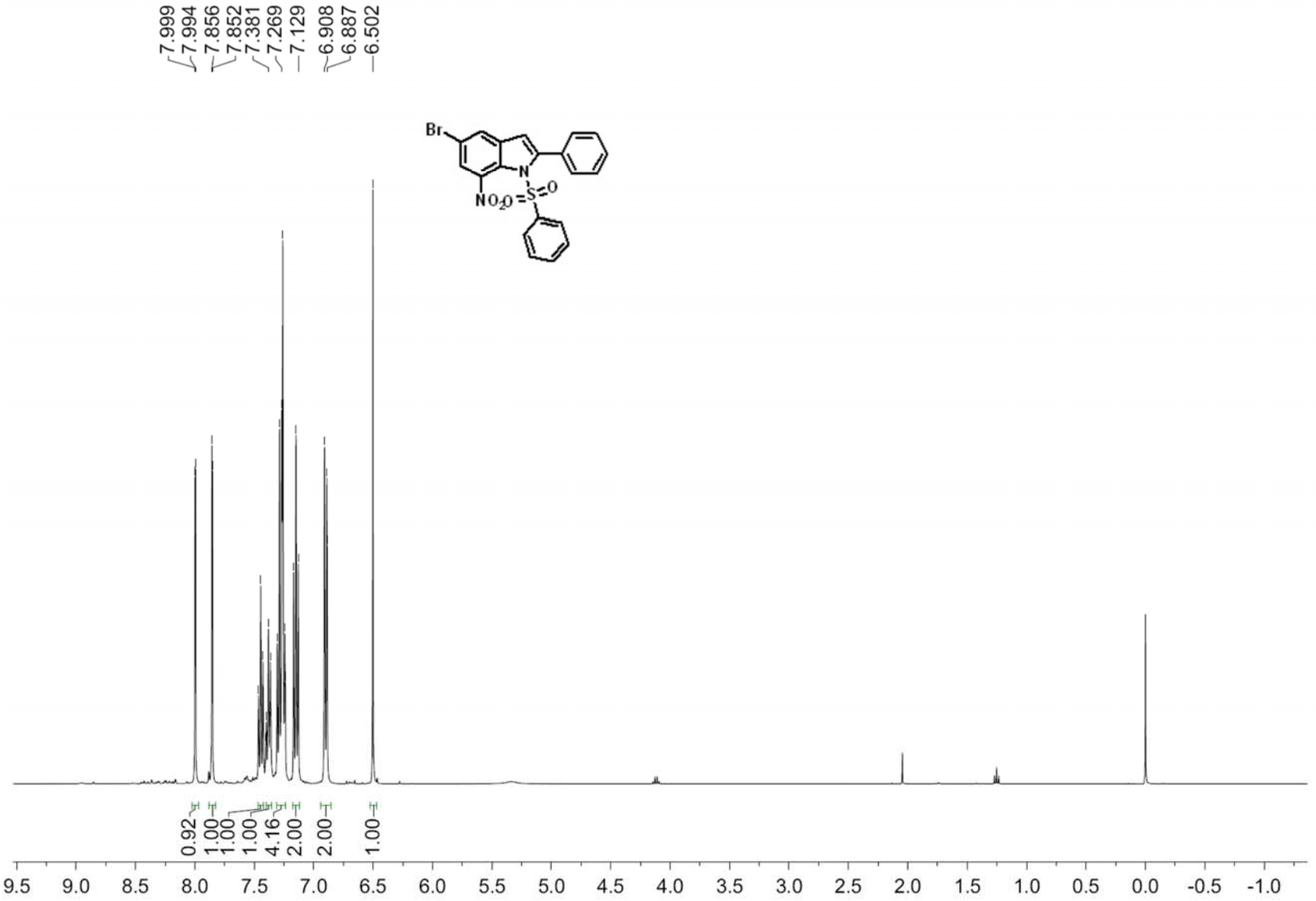
^{13}C NMR Spectrum of Compound **2aa**



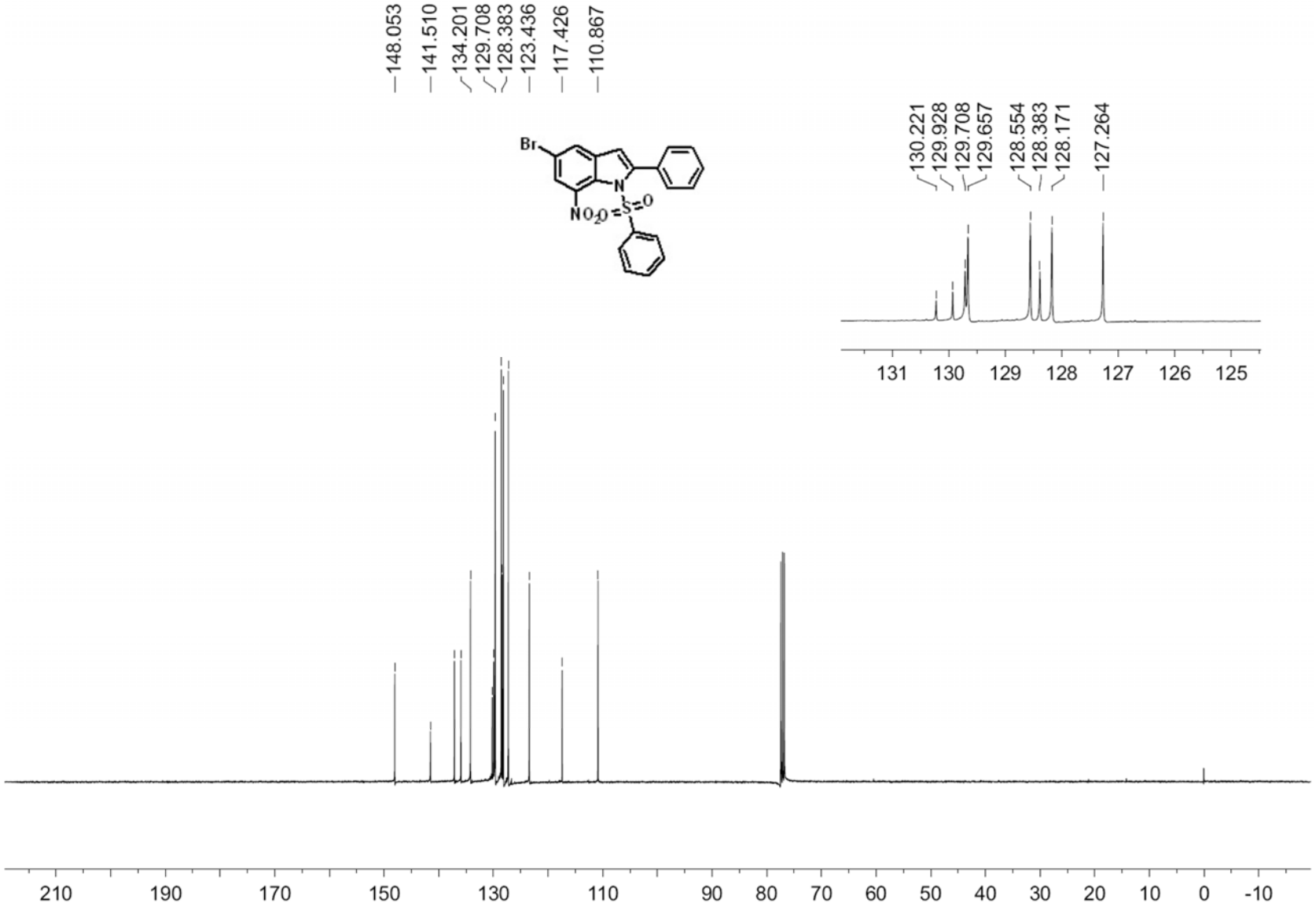
^{1}H NMR Spectrum of Compound **2ac**



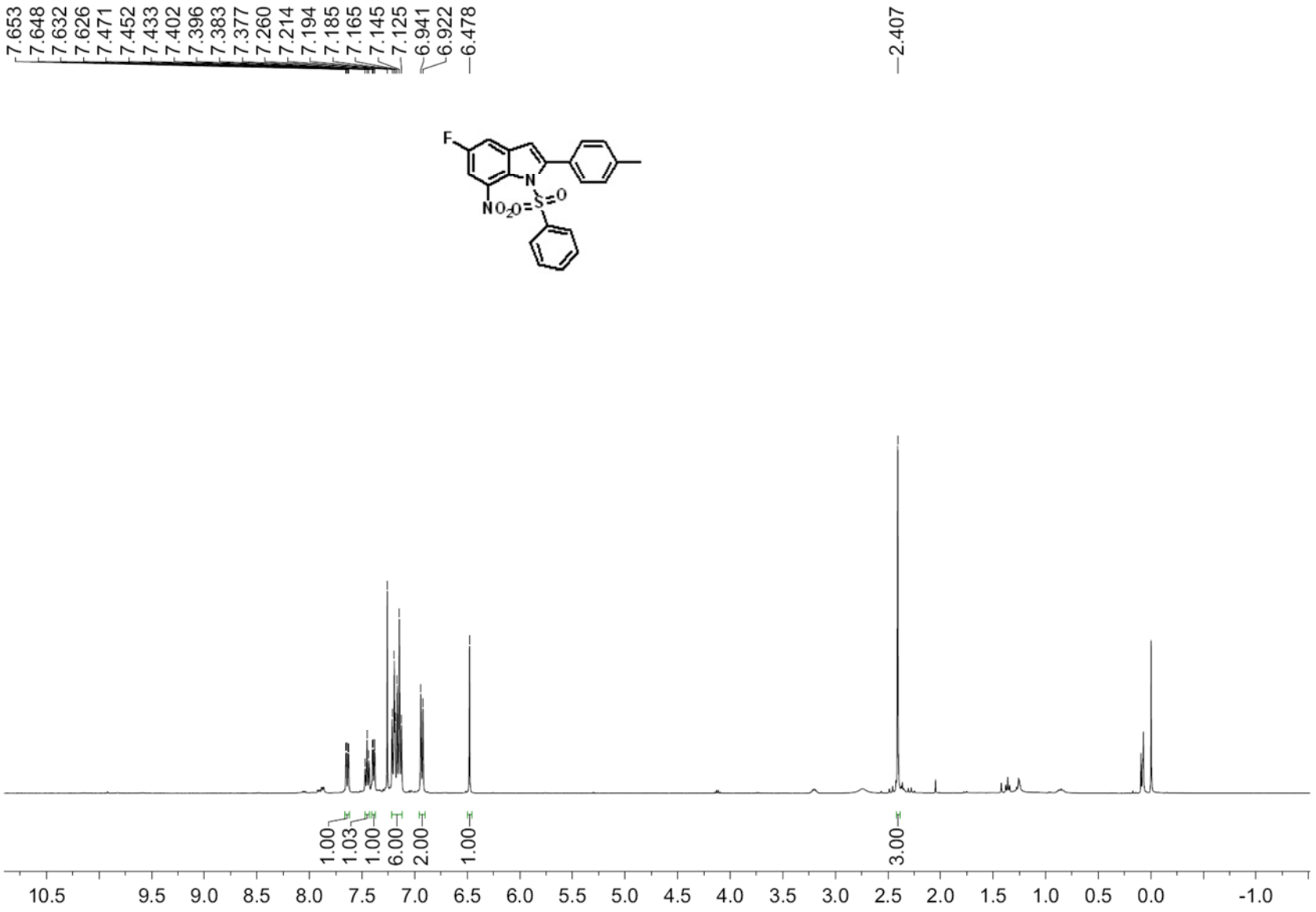
^{13}C NMR Spectrum of Compound **2ac**



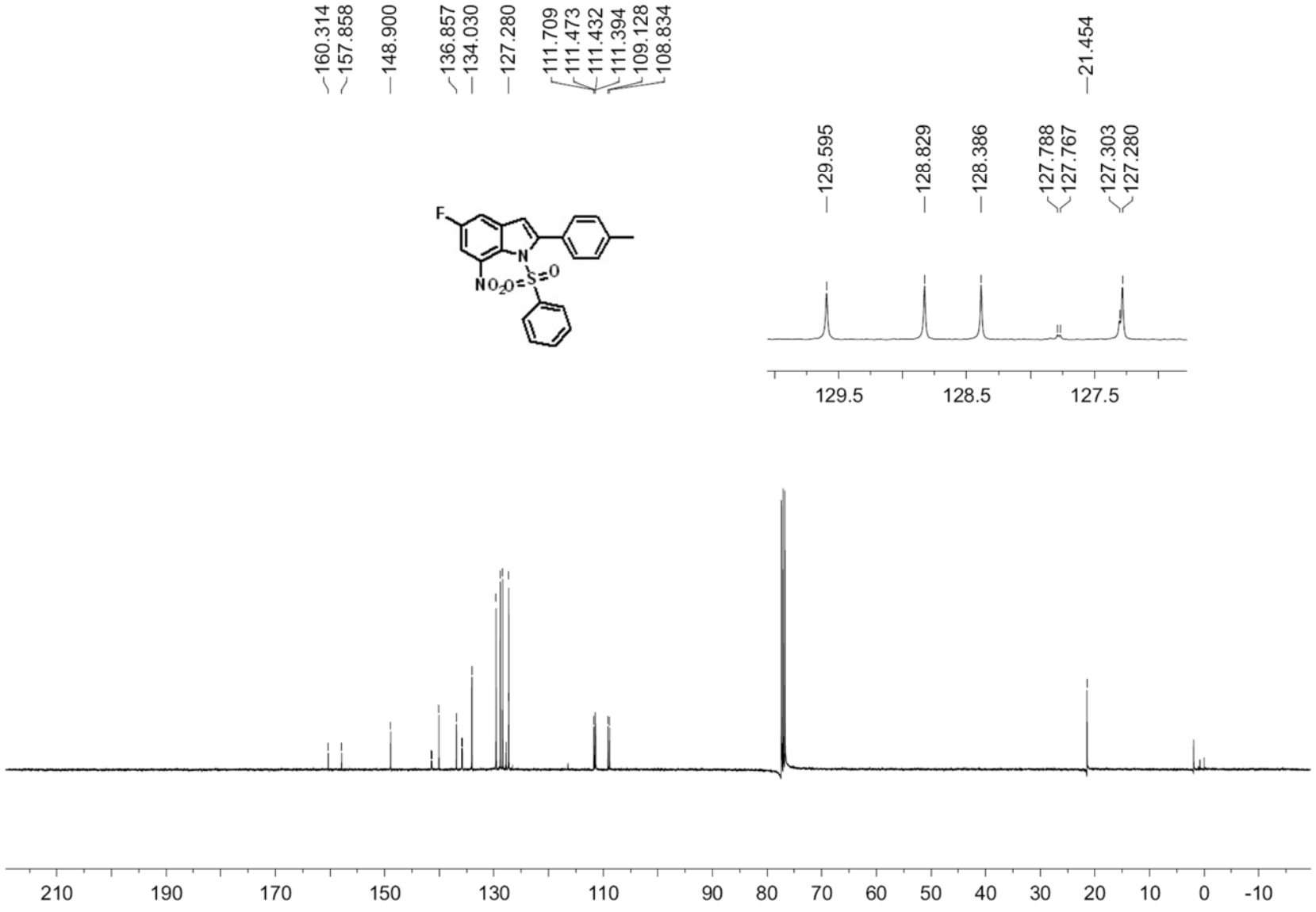
^{1}H NMR Spectrum of Compound **2ad**



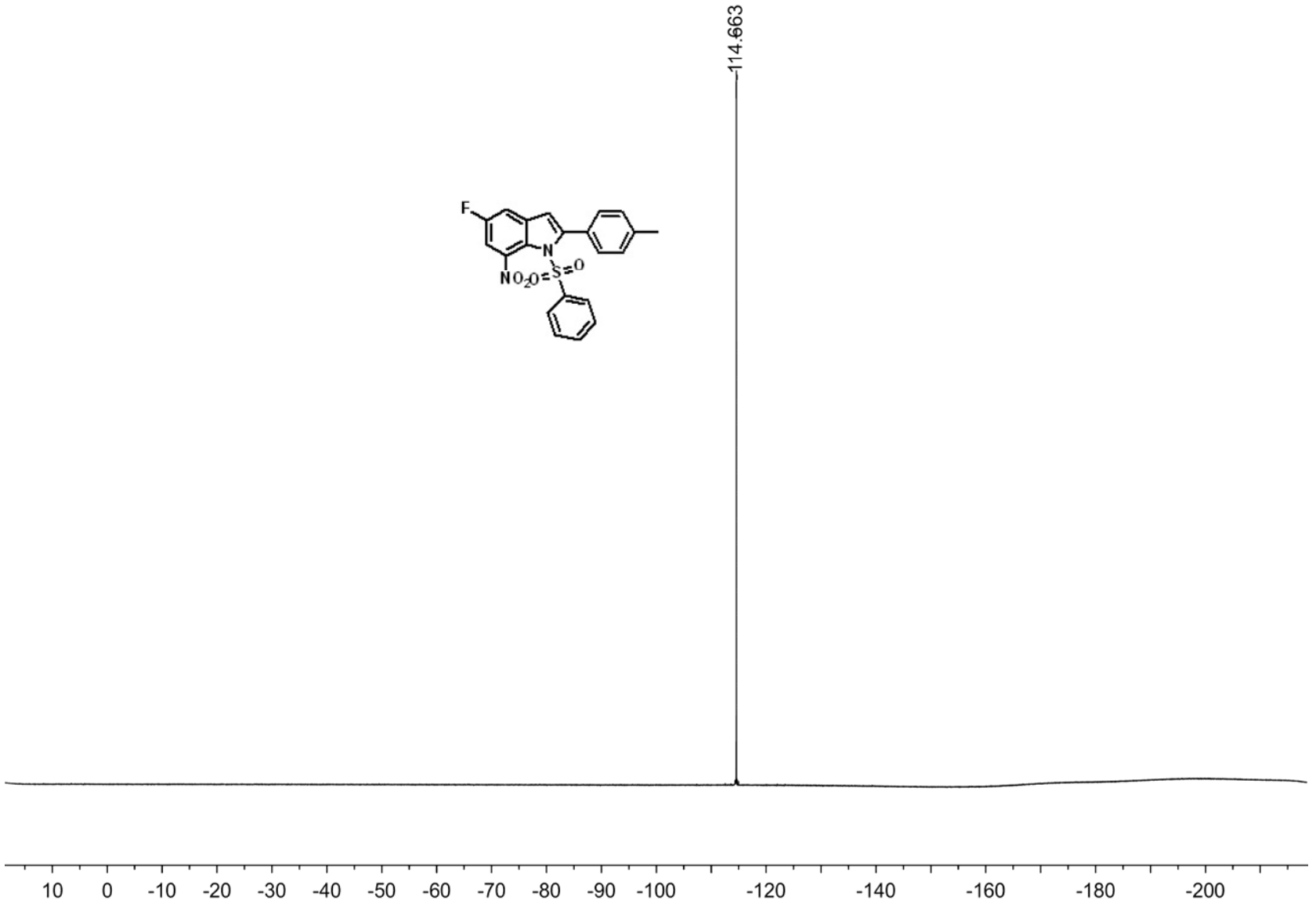
^{13}C NMR Spectrum of Compound **2ad**



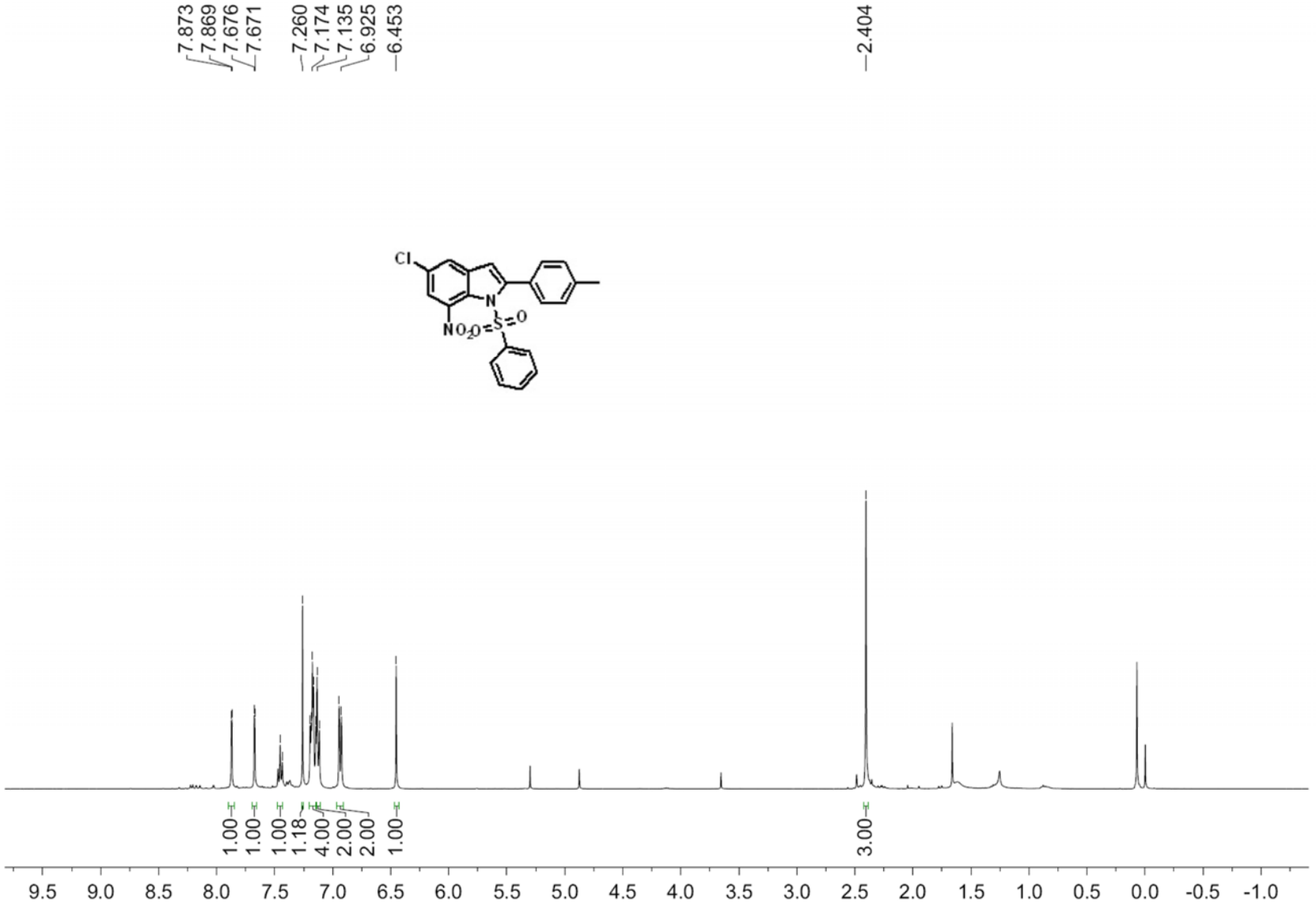
^{1}H NMR Spectrum of Compound **2ae**



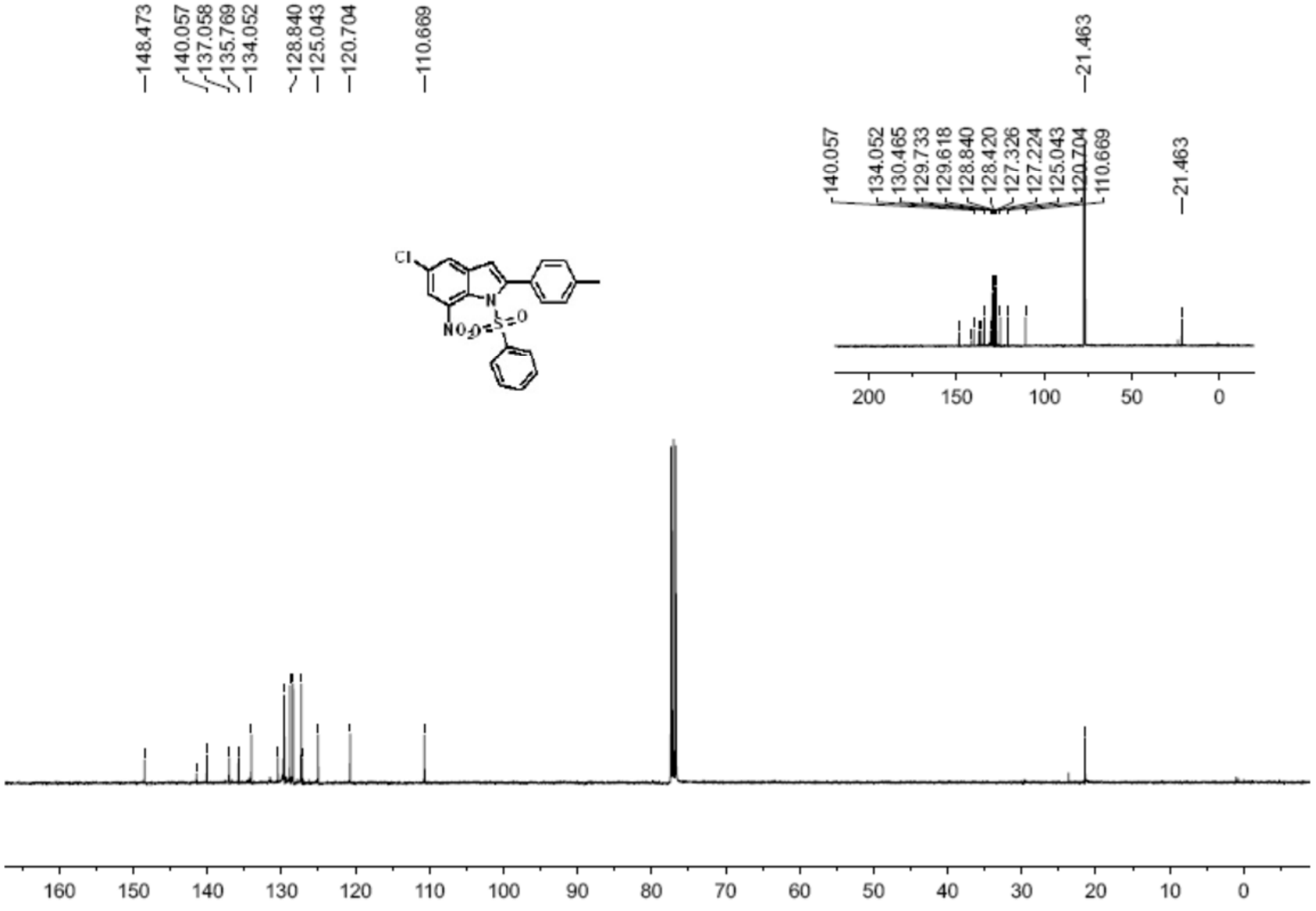
^{13}C NMR Spectrum of Compound **2ae**



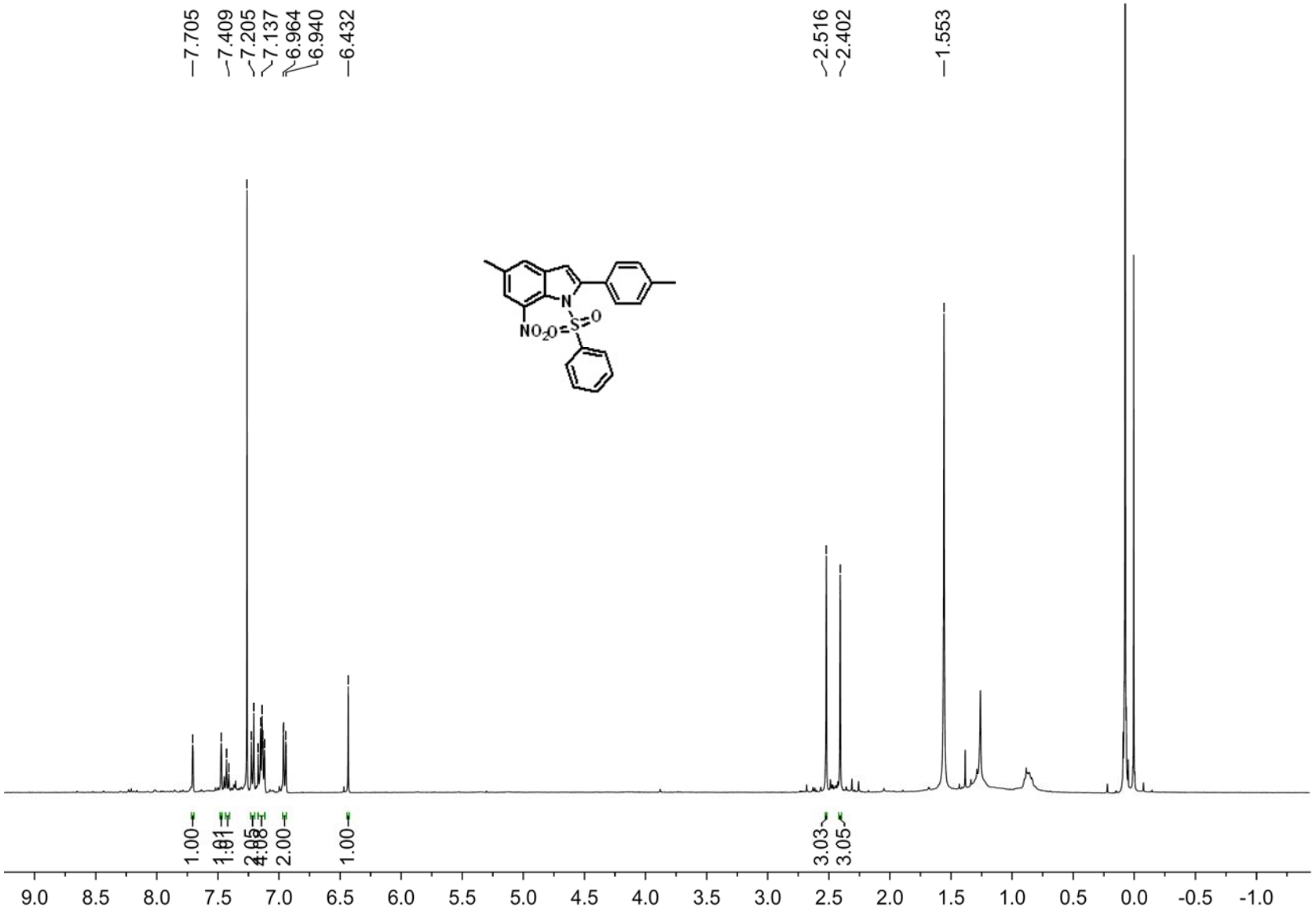
^{19}F NMR Spectrum of Compound **2ae**



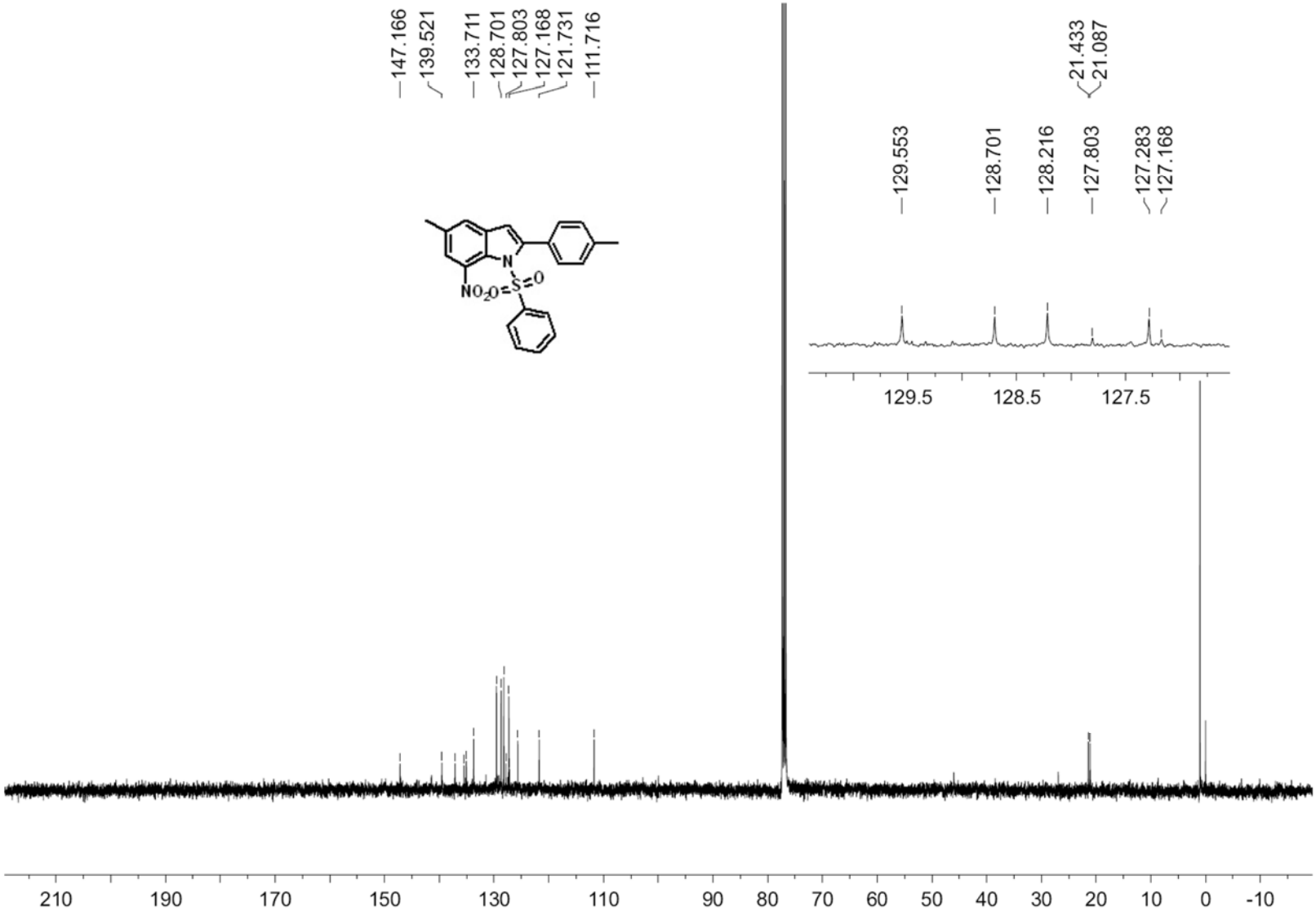
^{1}H NMR Spectrum of Compound **2af**



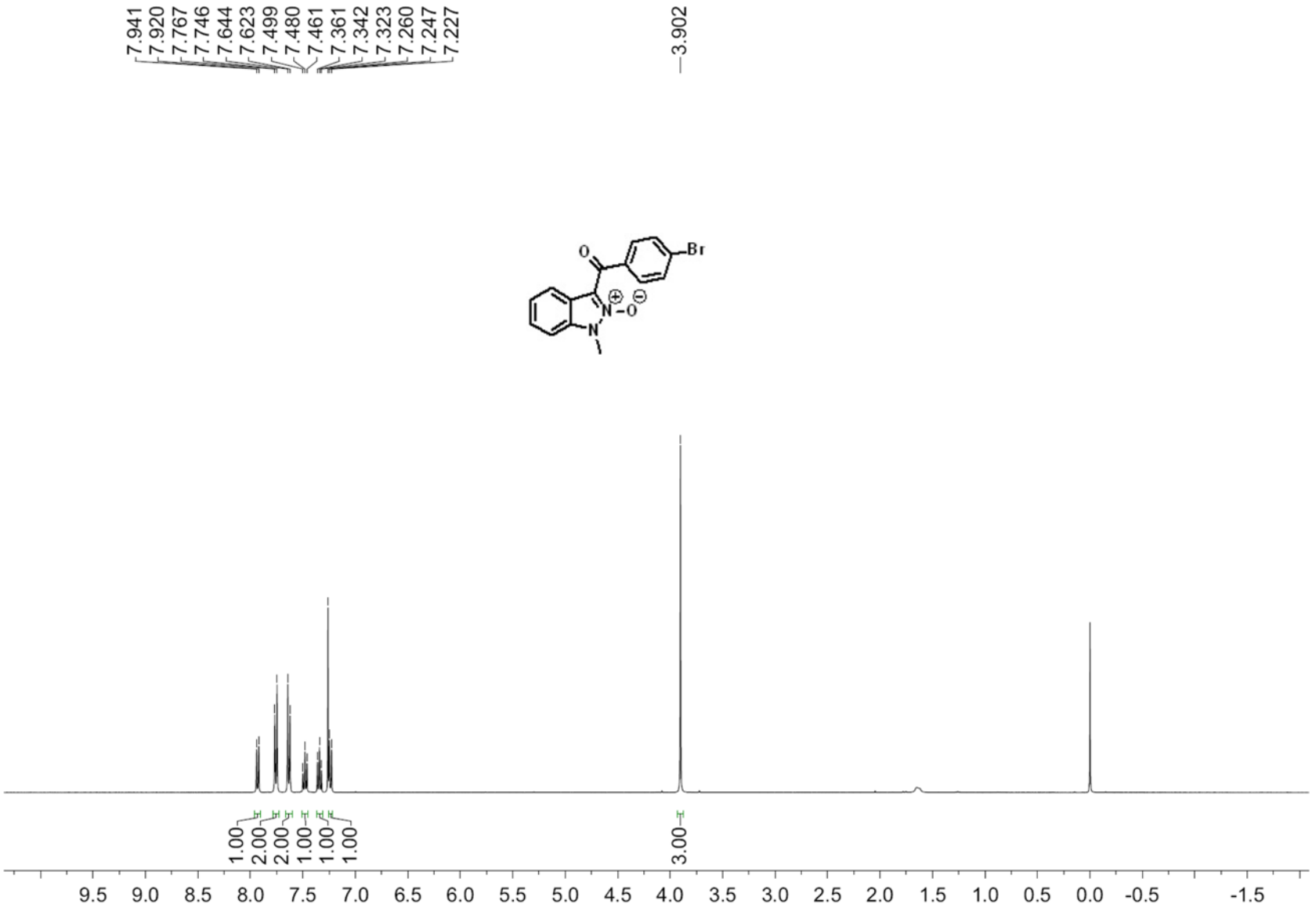
^{13}C NMR Spectrum of Compound **2af**



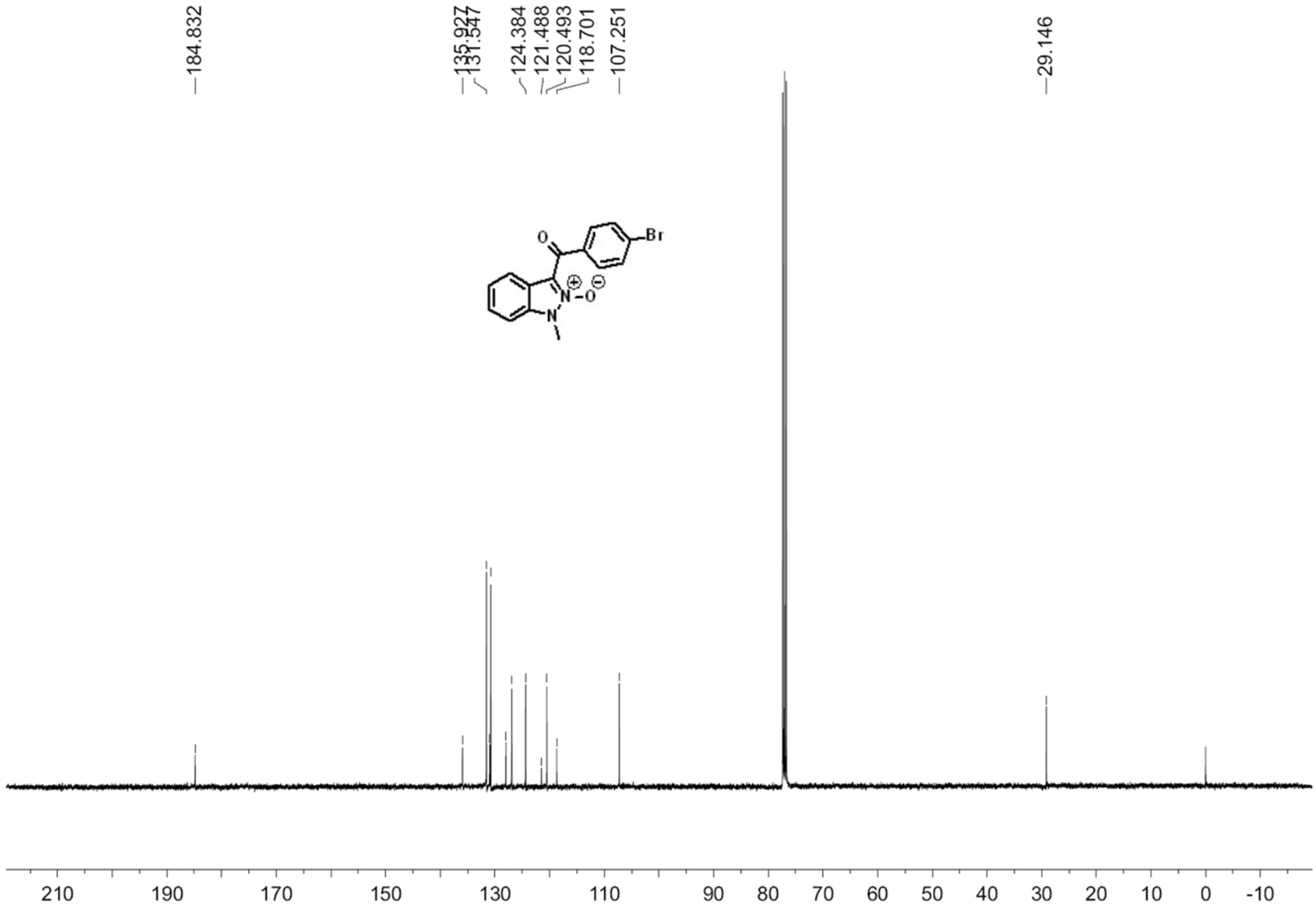
^{1}H NMR Spectrum of Compound **2ag**



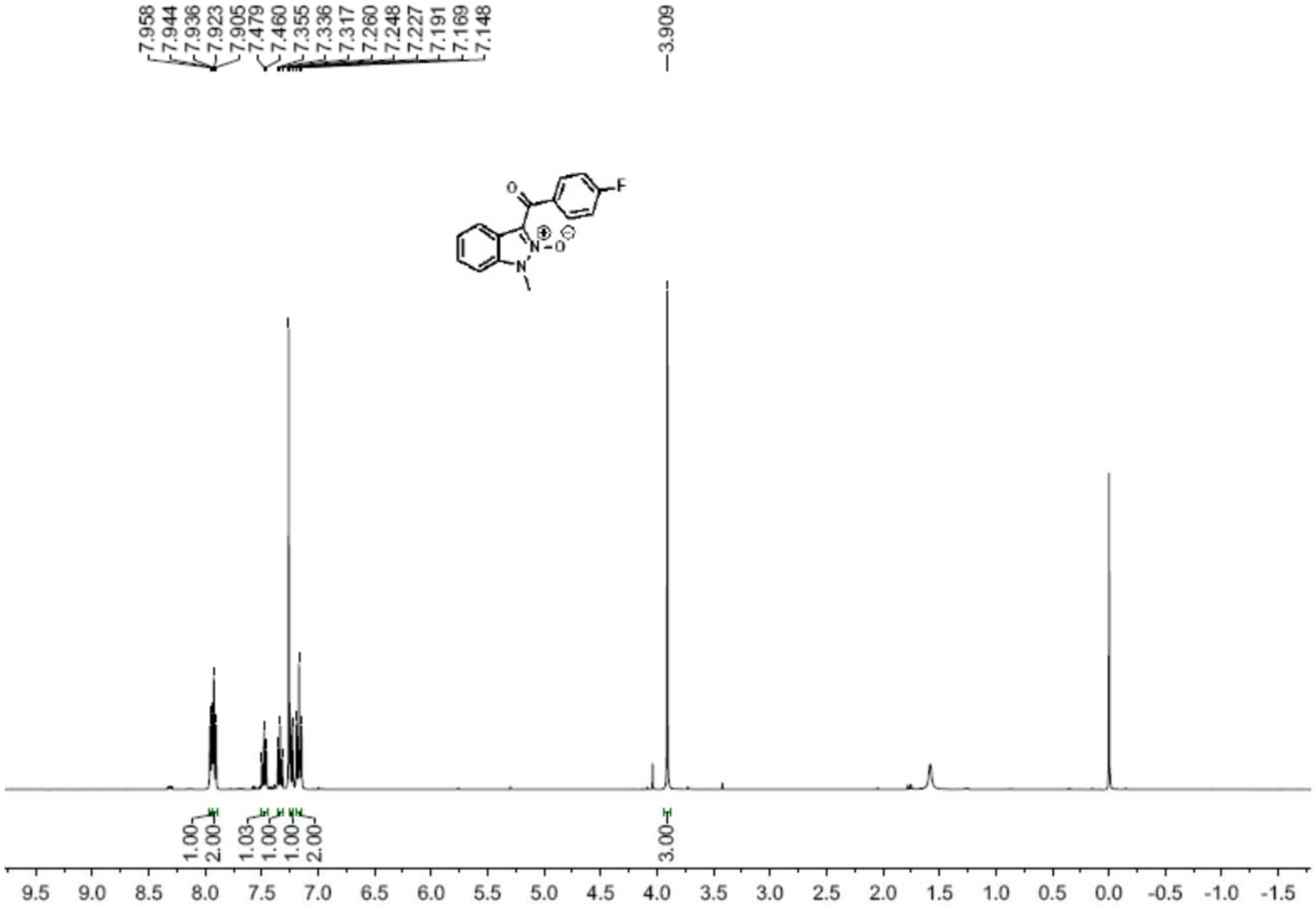
^{13}C NMR Spectrum of Compound **2ag**



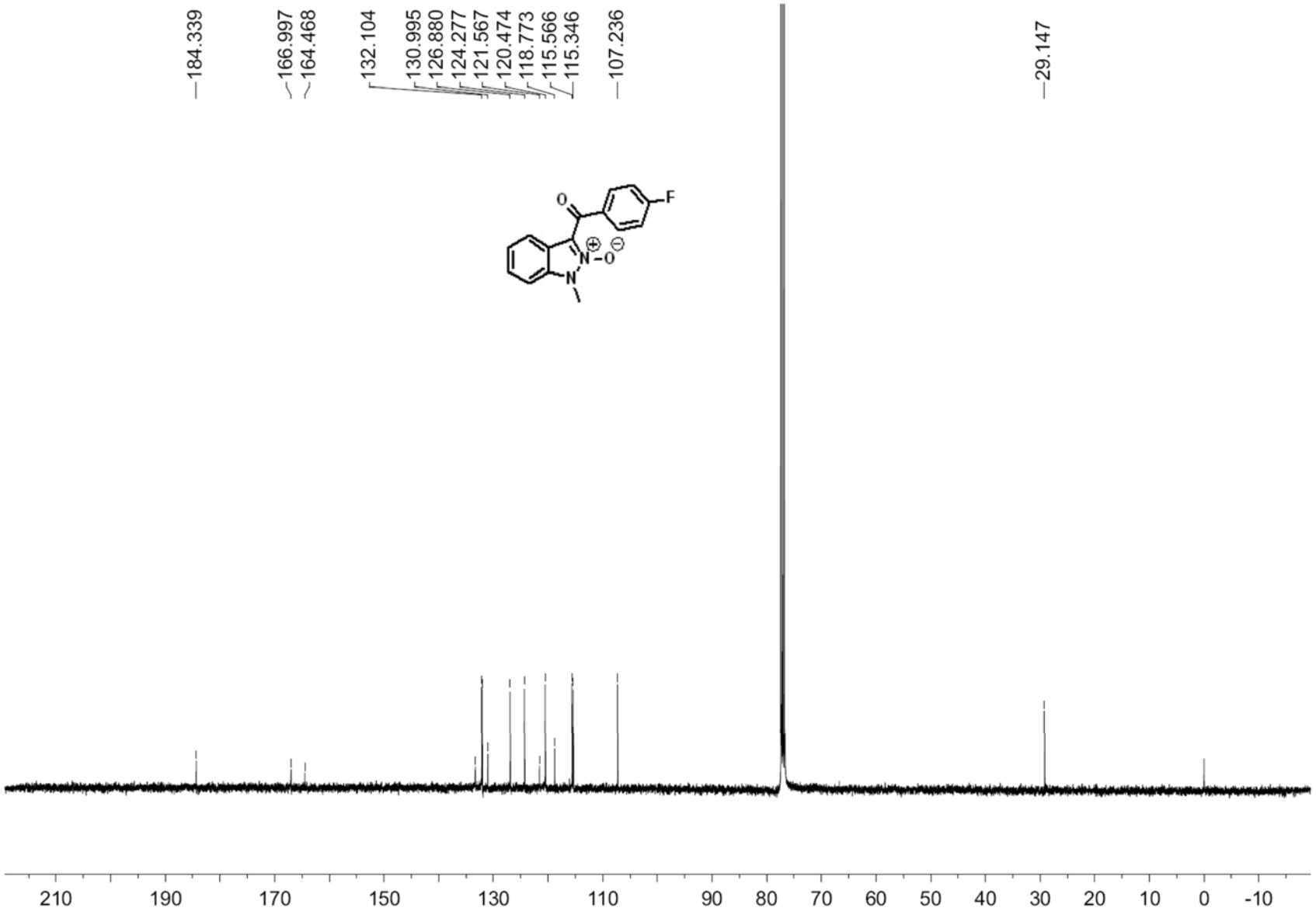
^{1}H NMR Spectrum of Compound **3a**



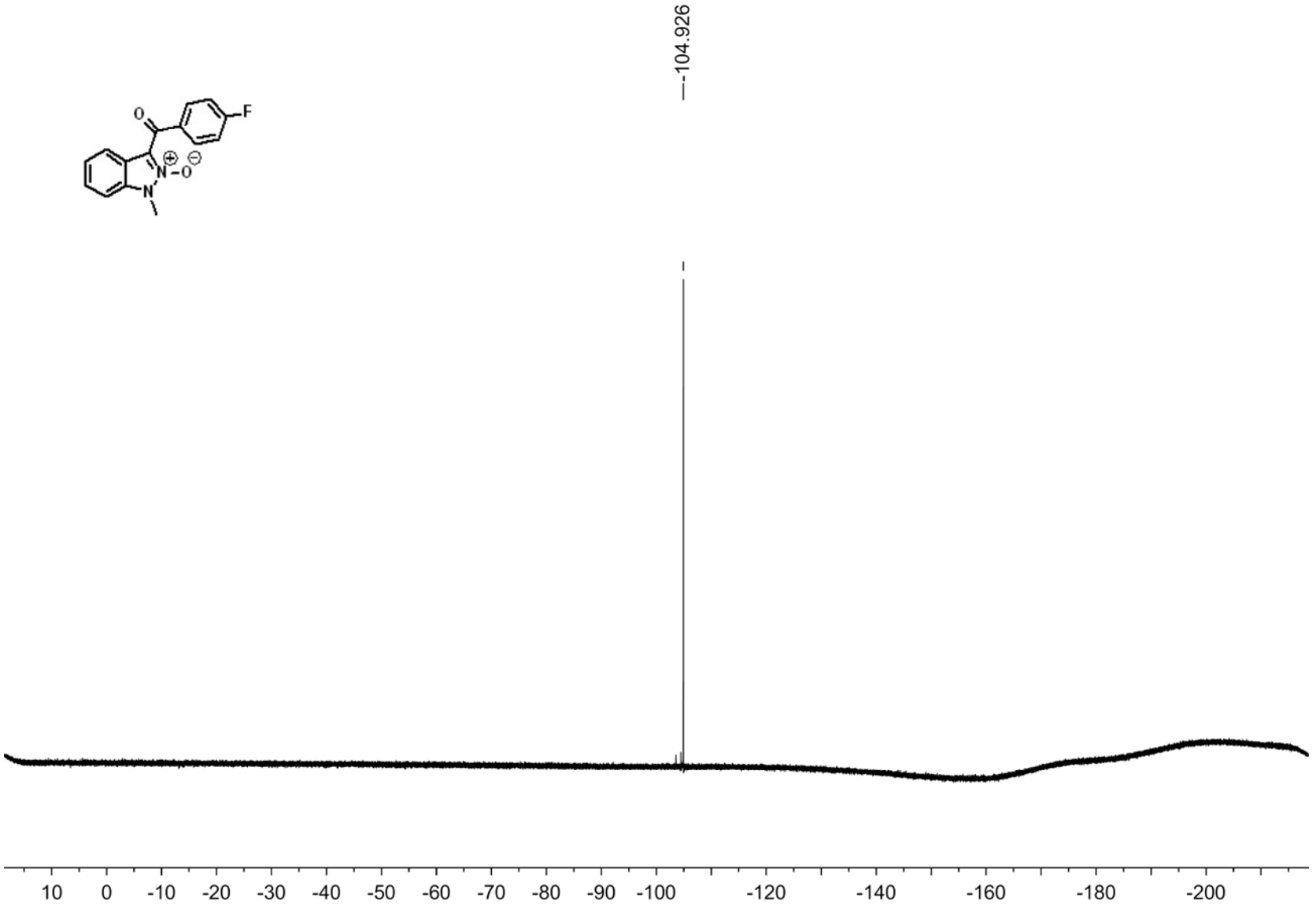
^{13}C NMR Spectrum of Compound **3a**



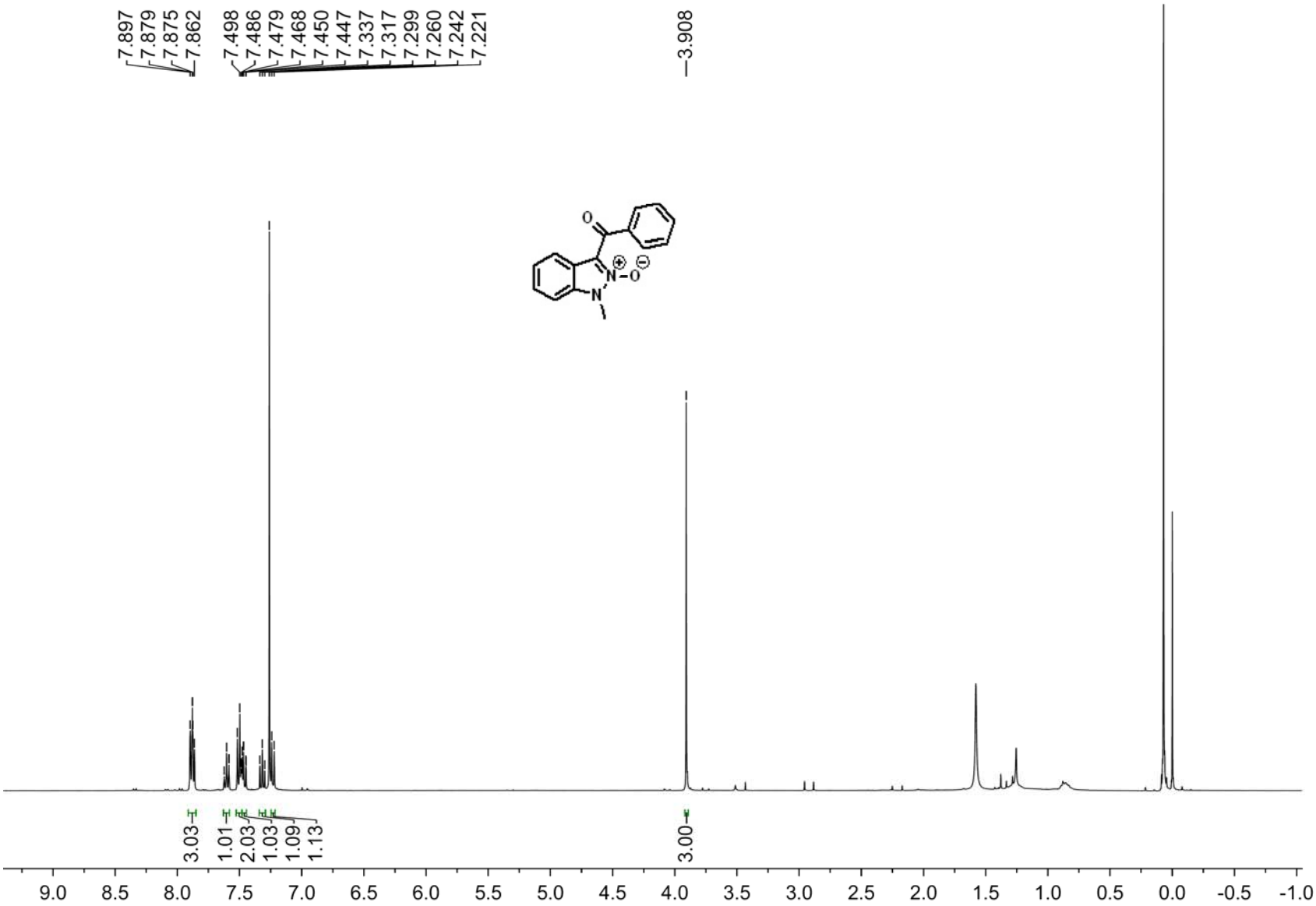
^{1}H NMR Spectrum of Compound **3b**



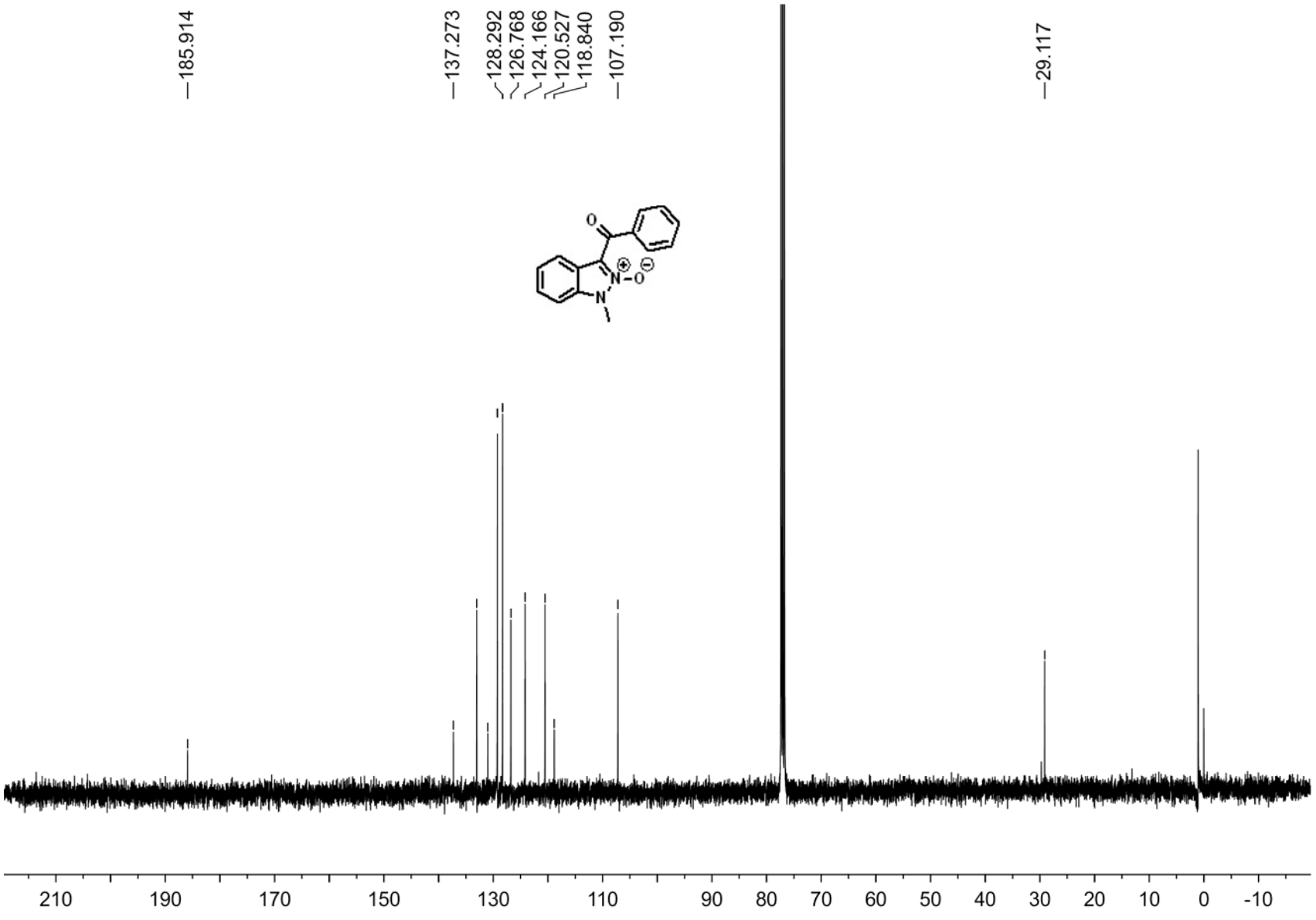
^{13}C NMR Spectrum of Compound **3b**



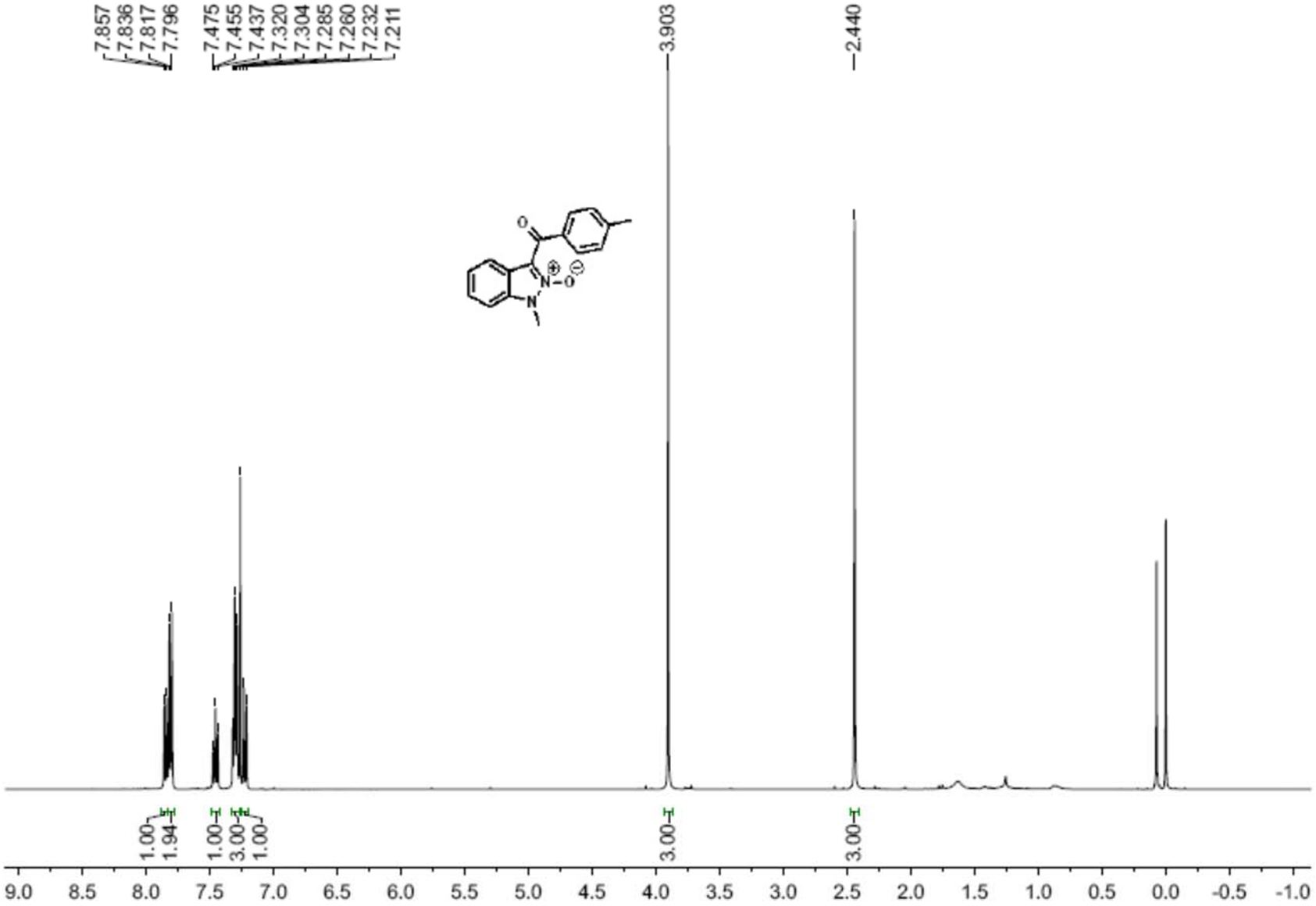
^{19}F NMR Spectrum of Compound **3b**



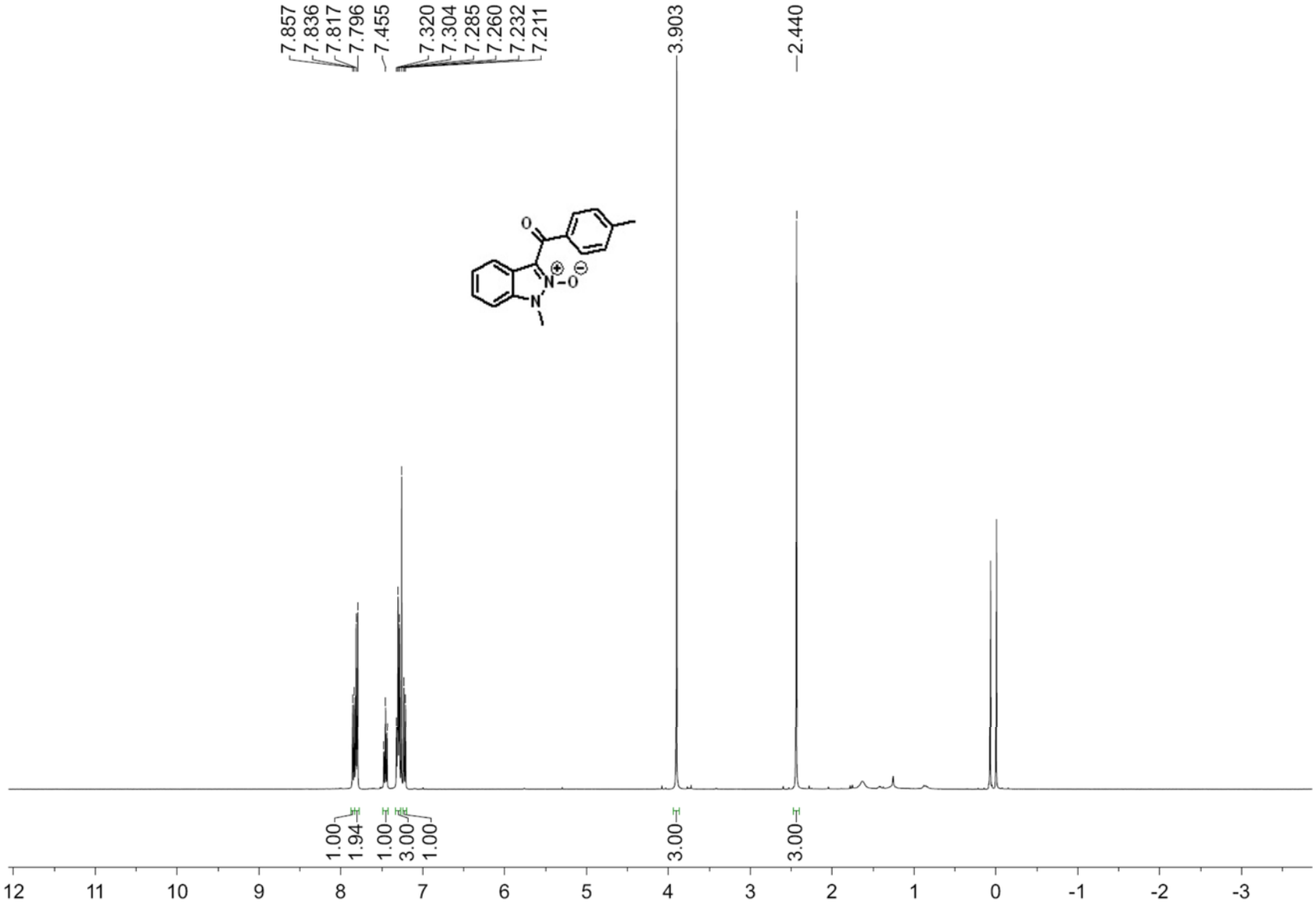
^{1}H NMR Spectrum of Compound **3c**



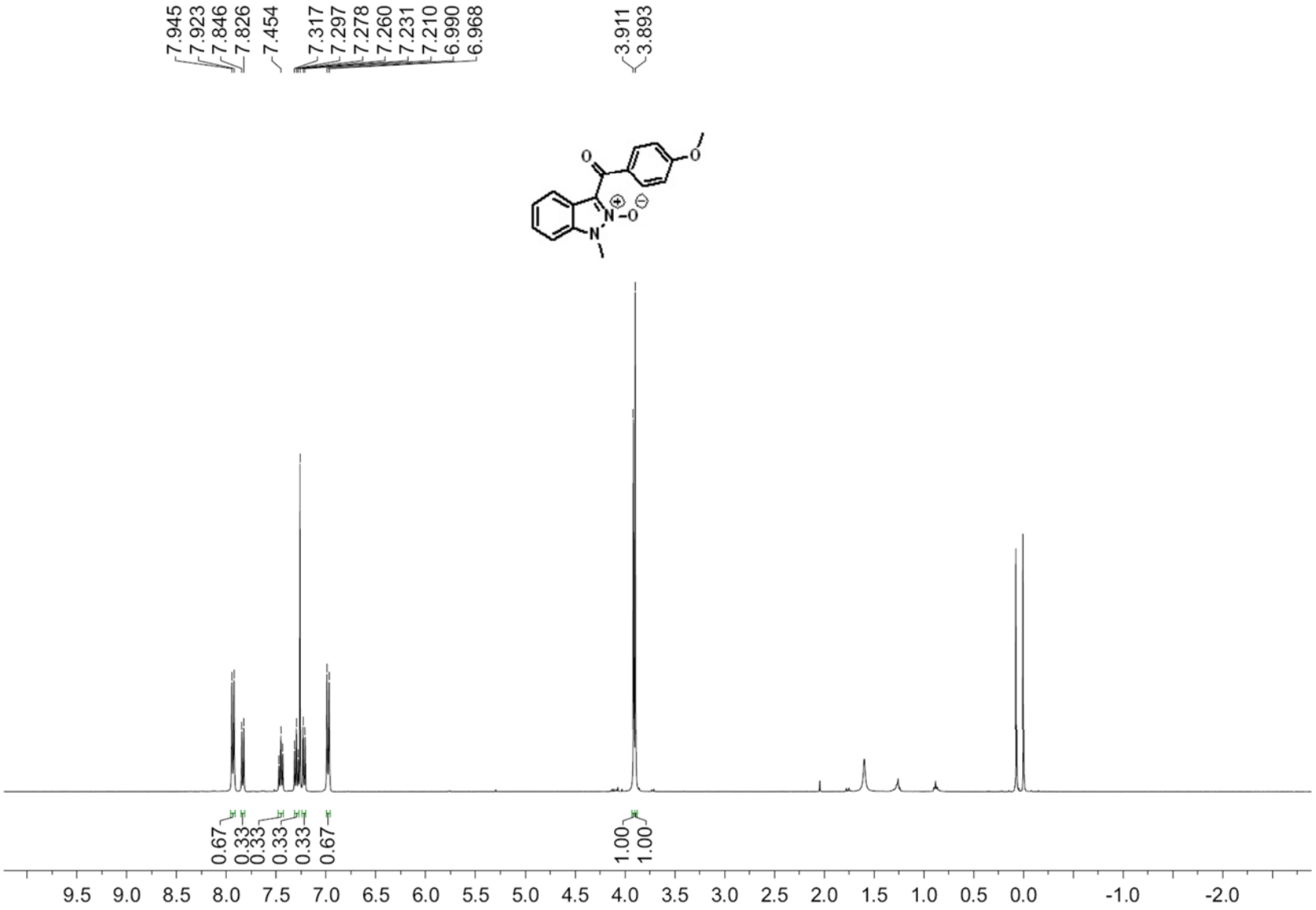
^{13}C NMR Spectrum of Compound **3c**



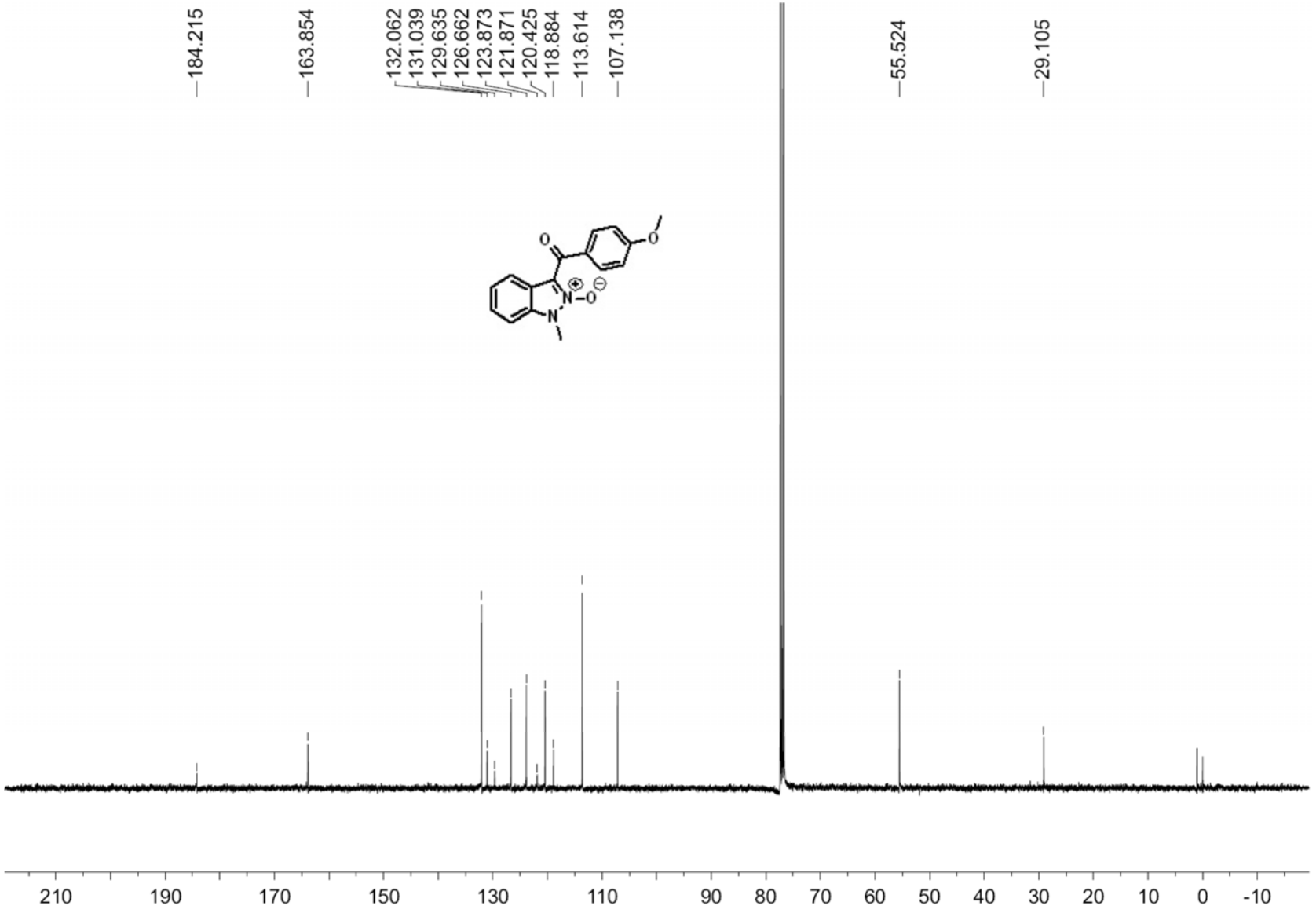
^{1}H NMR Spectrum of Compound **3d**



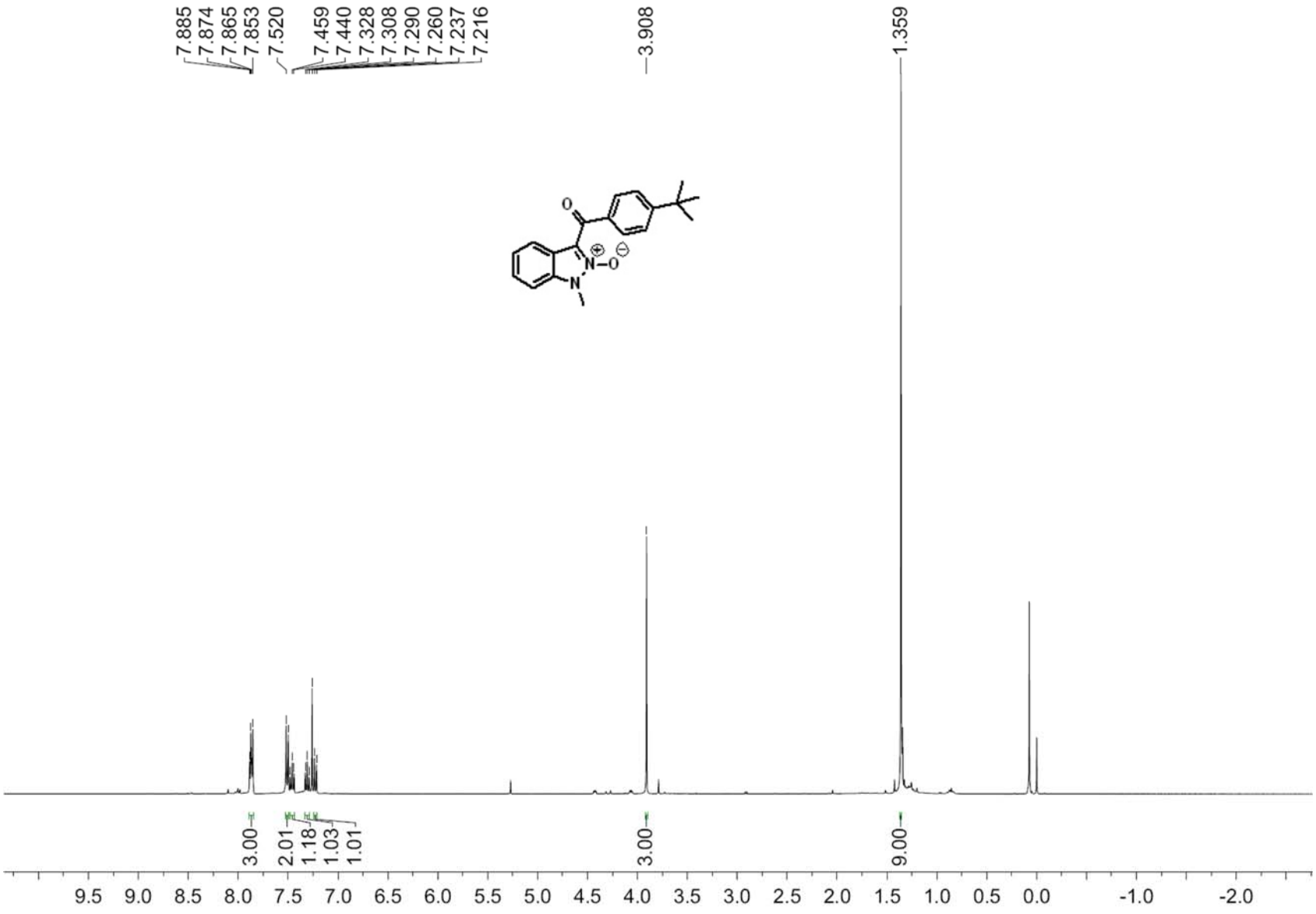
^{13}C NMR Spectrum of Compound **3d**



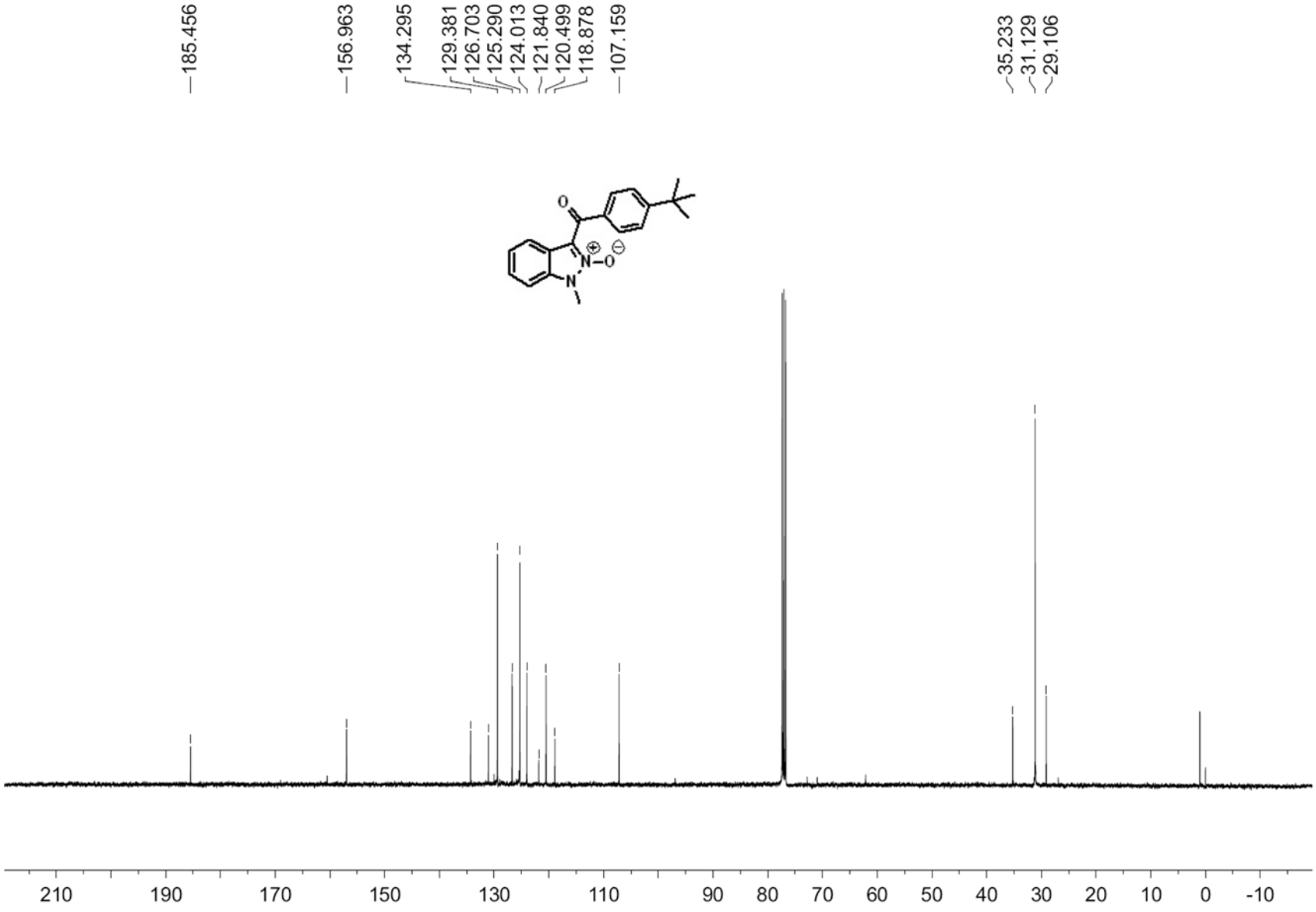
^{1}H NMR Spectrum of Compound **3e**



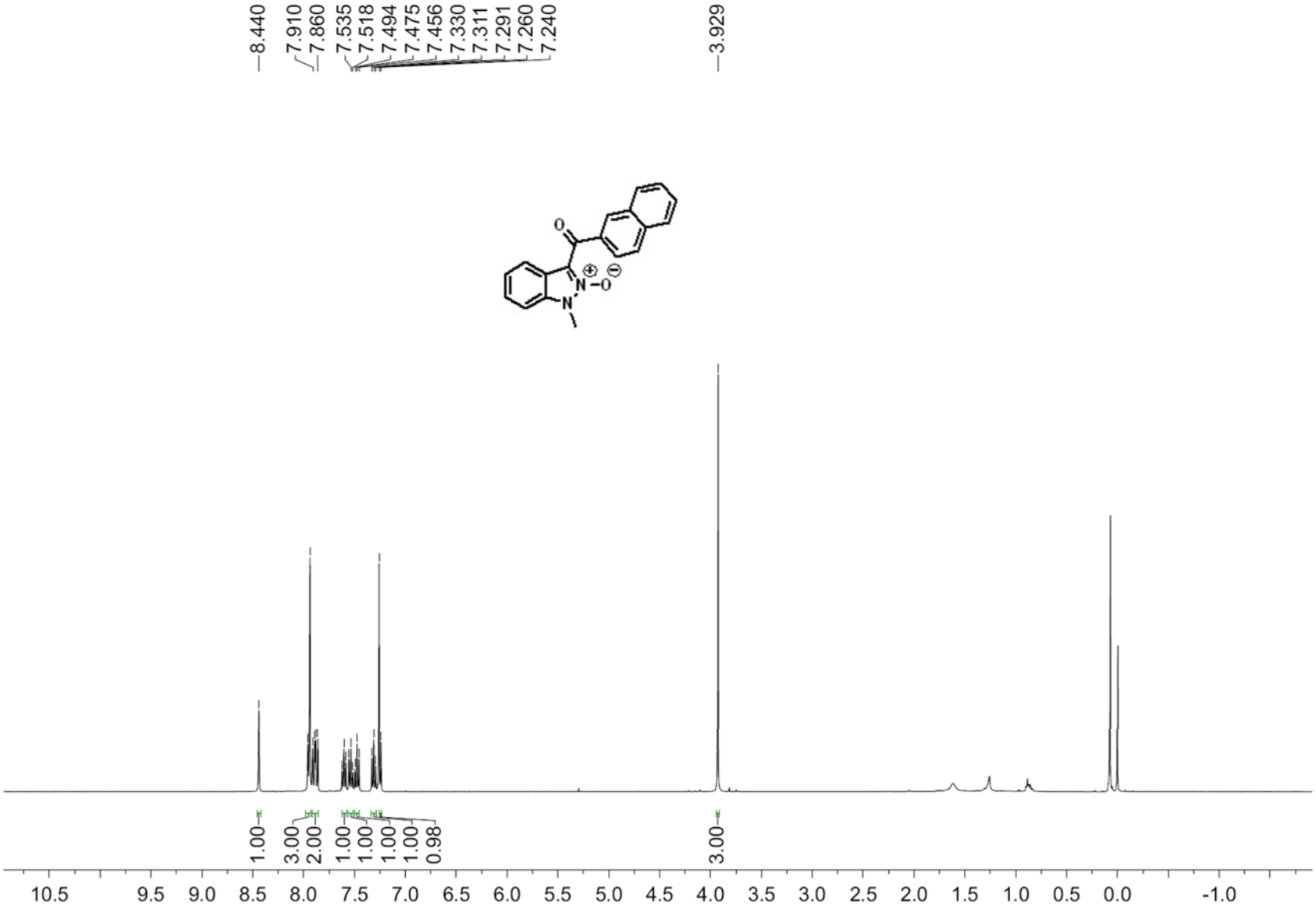
^{13}C NMR Spectrum of Compound **3e**



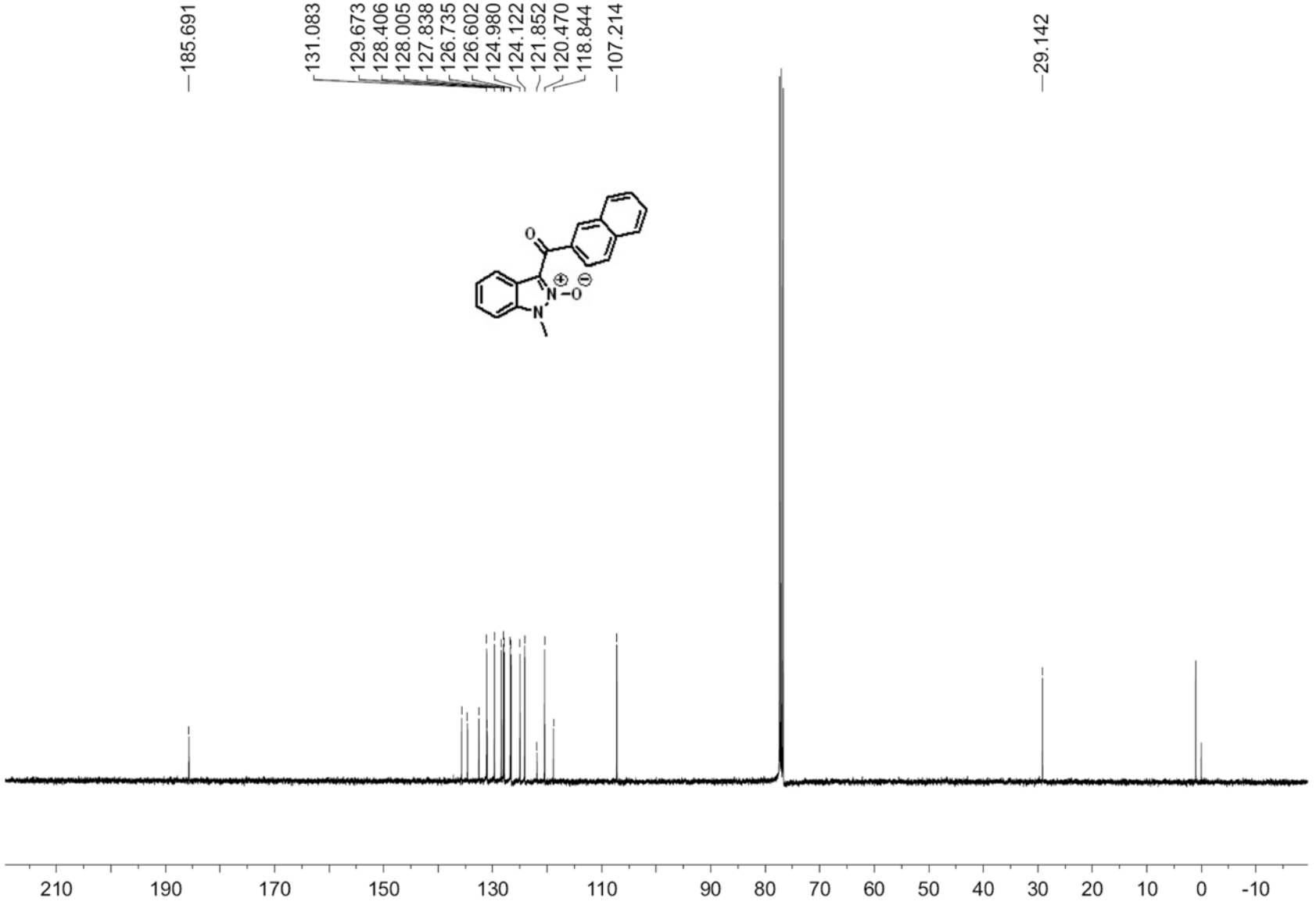
^{1}H NMR Spectrum of Compound **3f**



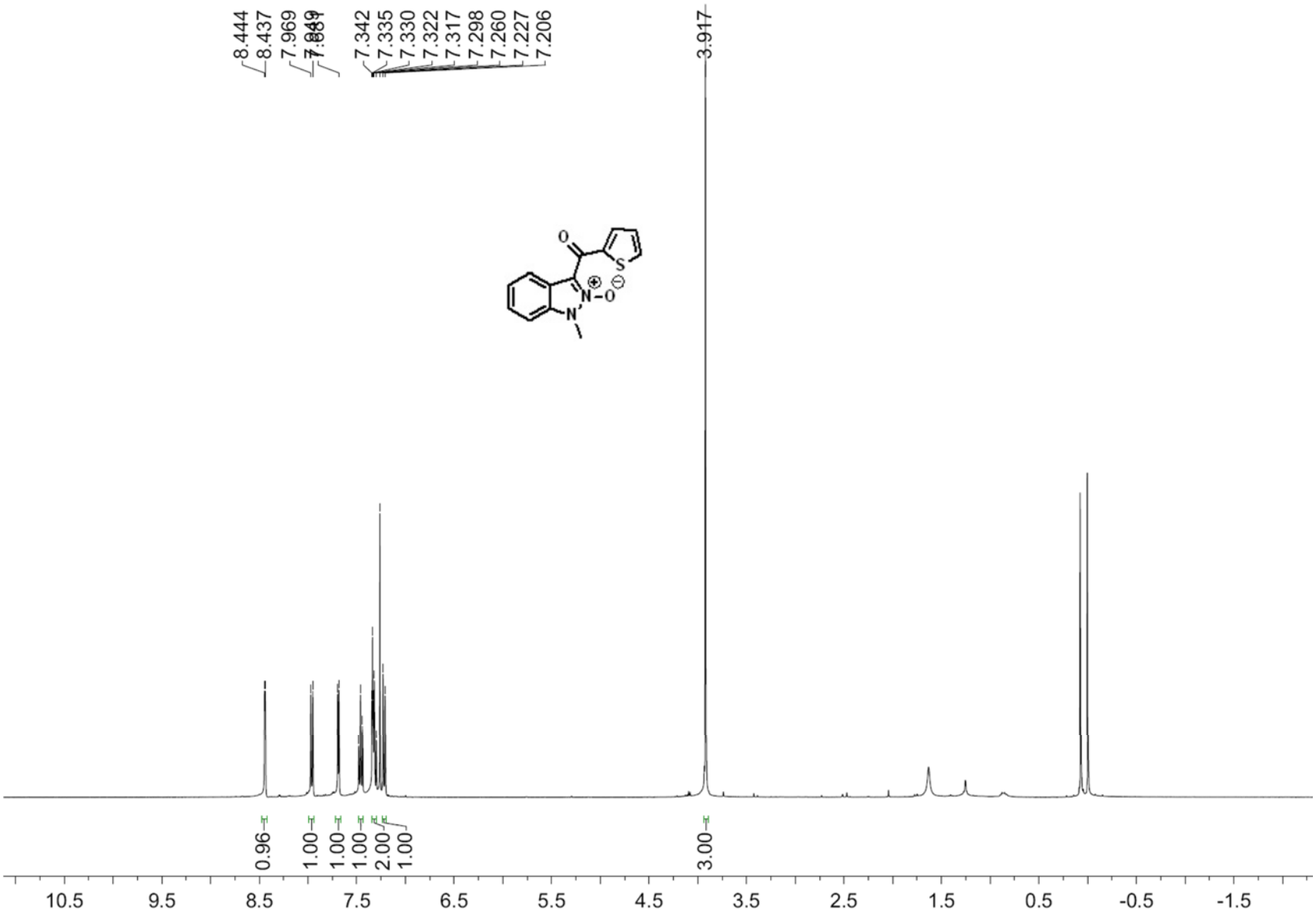
^{13}C NMR Spectrum of Compound **3f**



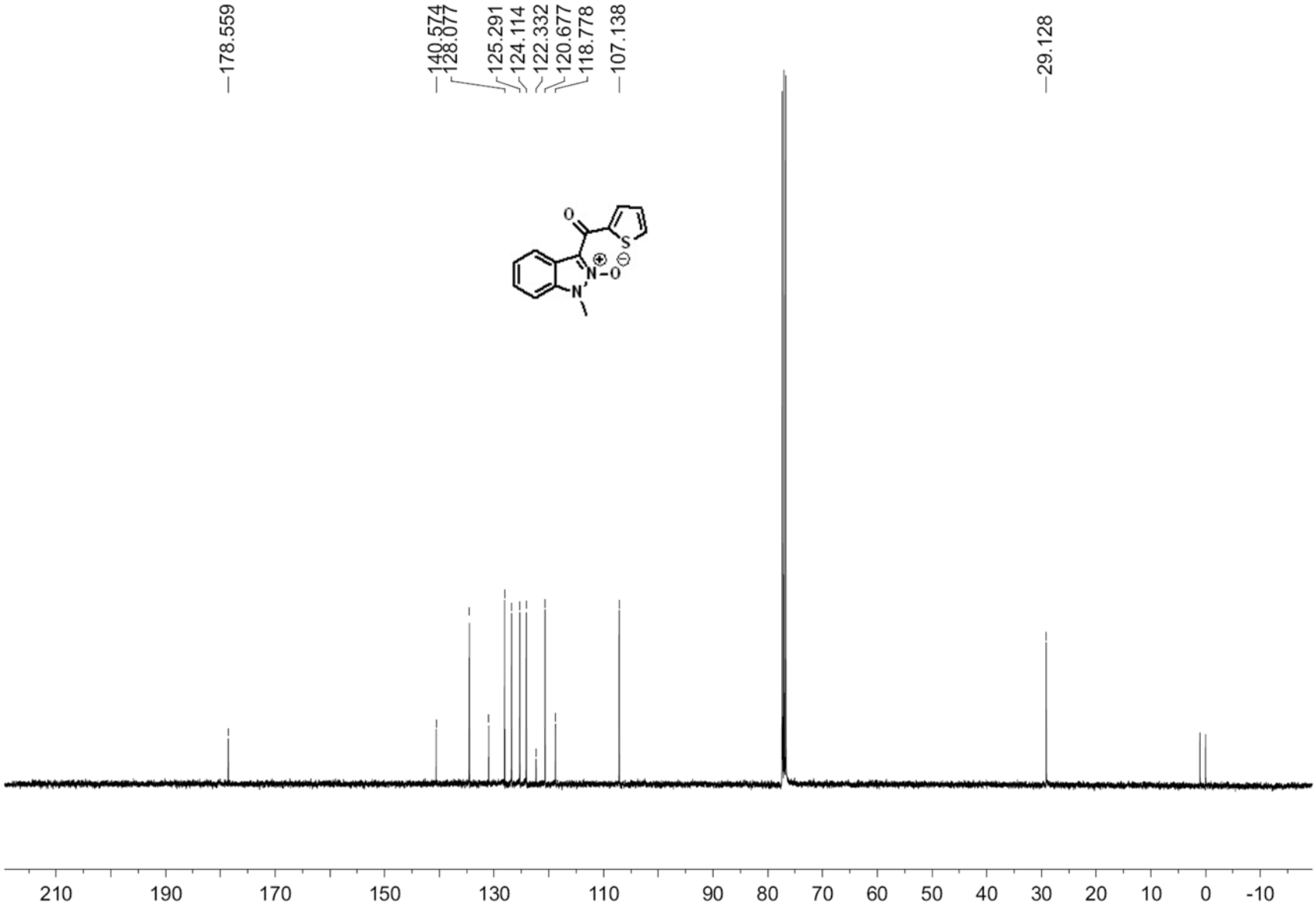
^{1}H NMR Spectrum of Compound **3g**



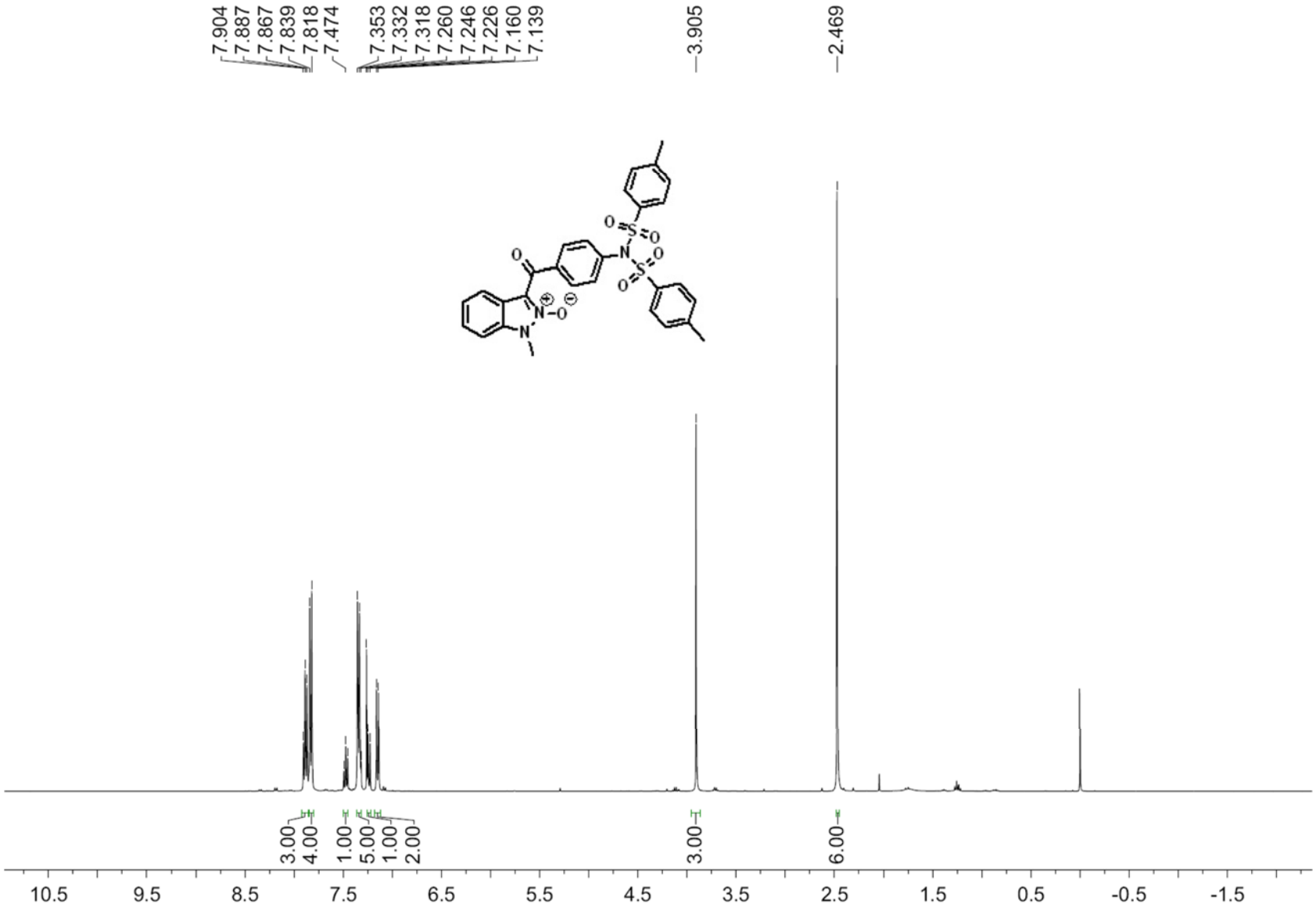
^{13}C NMR Spectrum of Compound **3g**



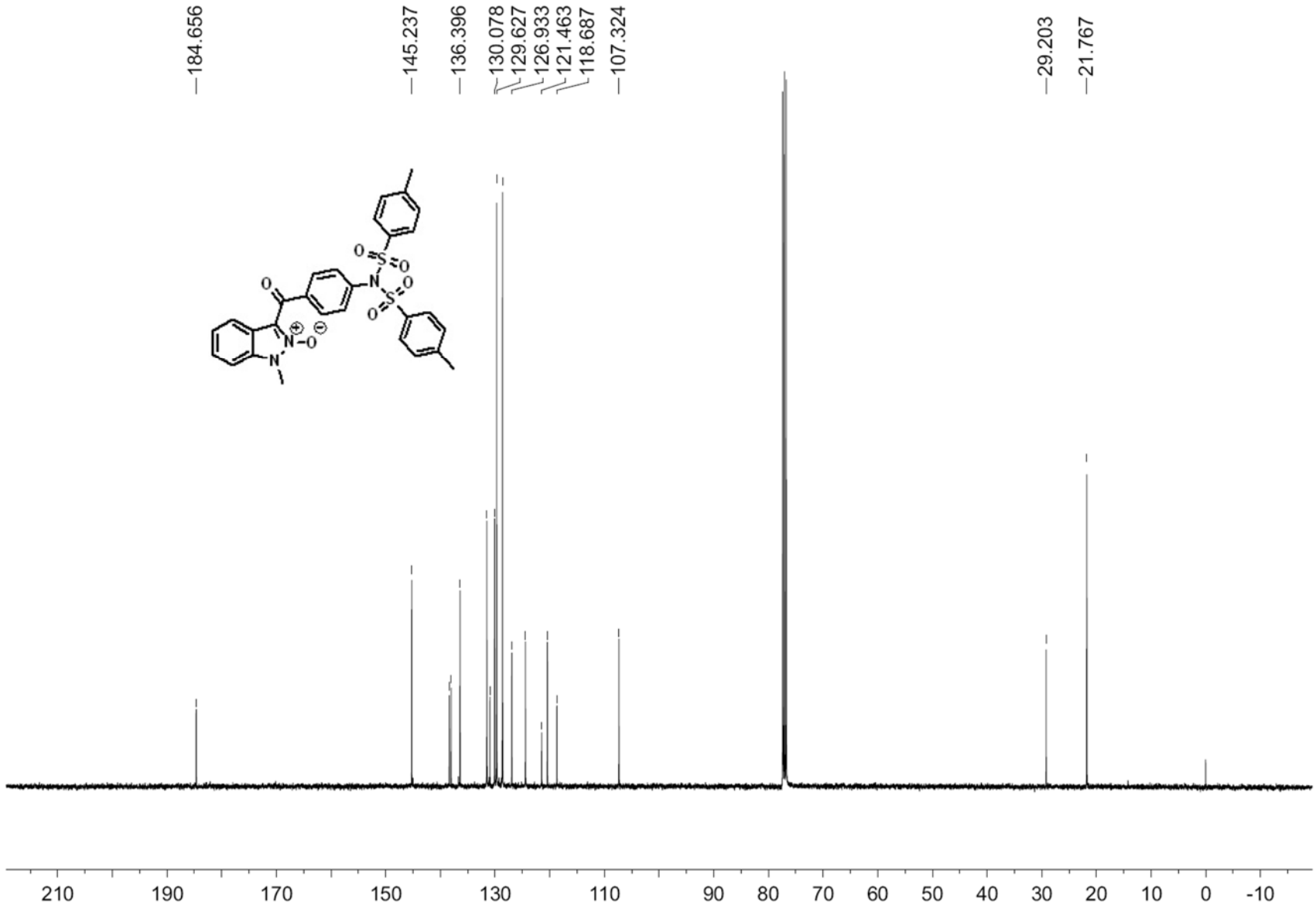
^{1}H NMR Spectrum of Compound **3h**



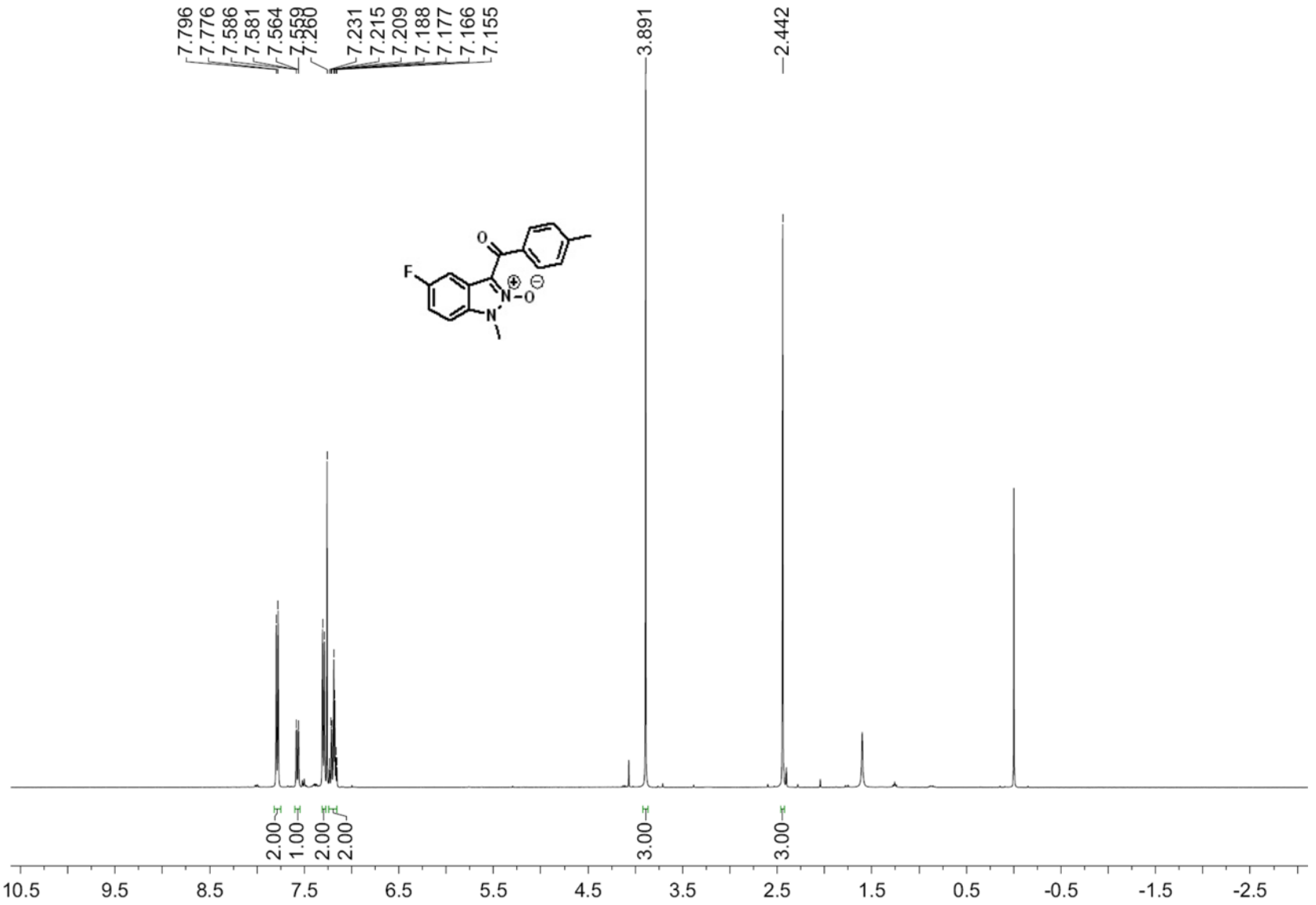
^{13}C NMR Spectrum of Compound **3h**



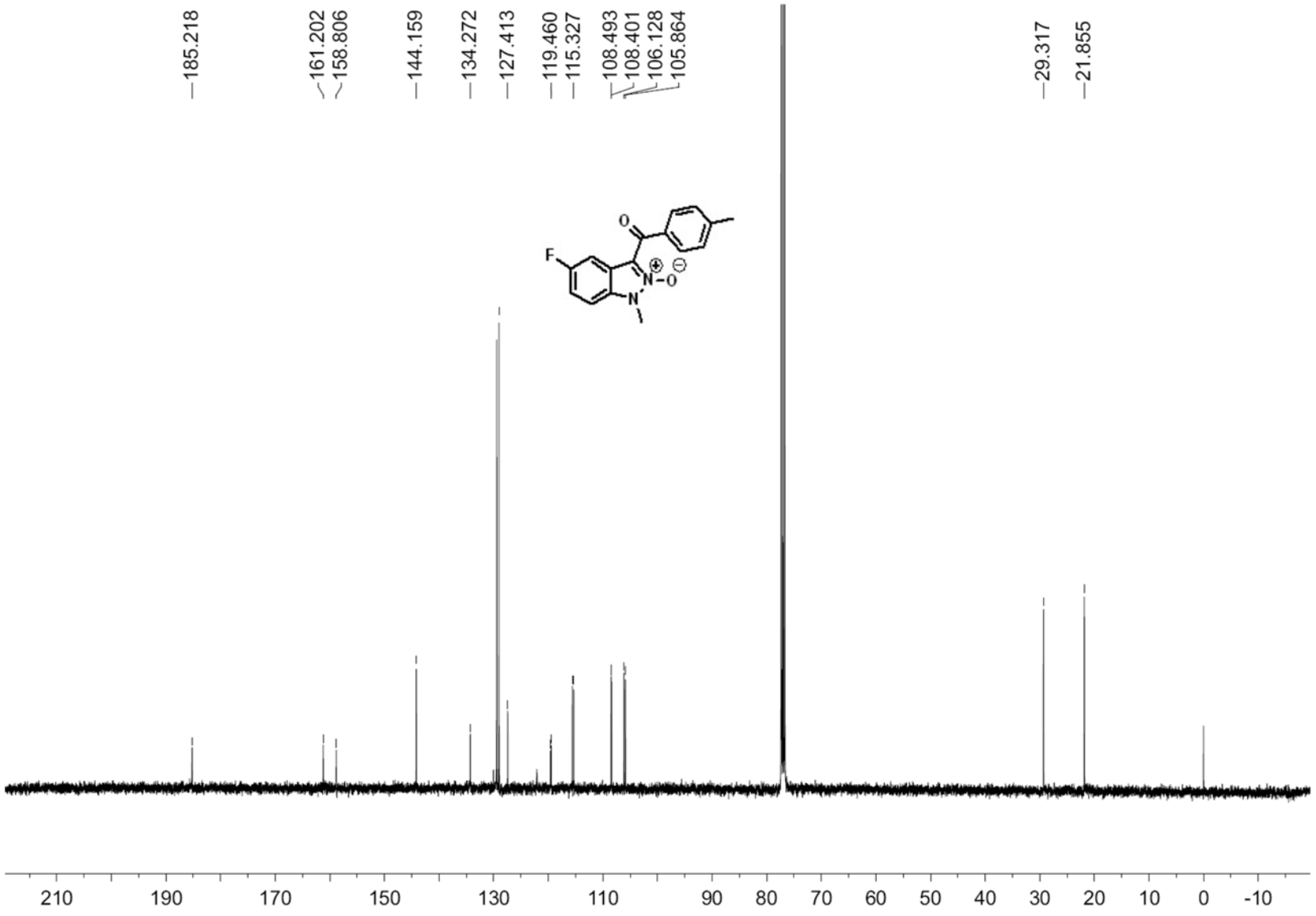
^{1}H NMR Spectrum of Compound **3i**



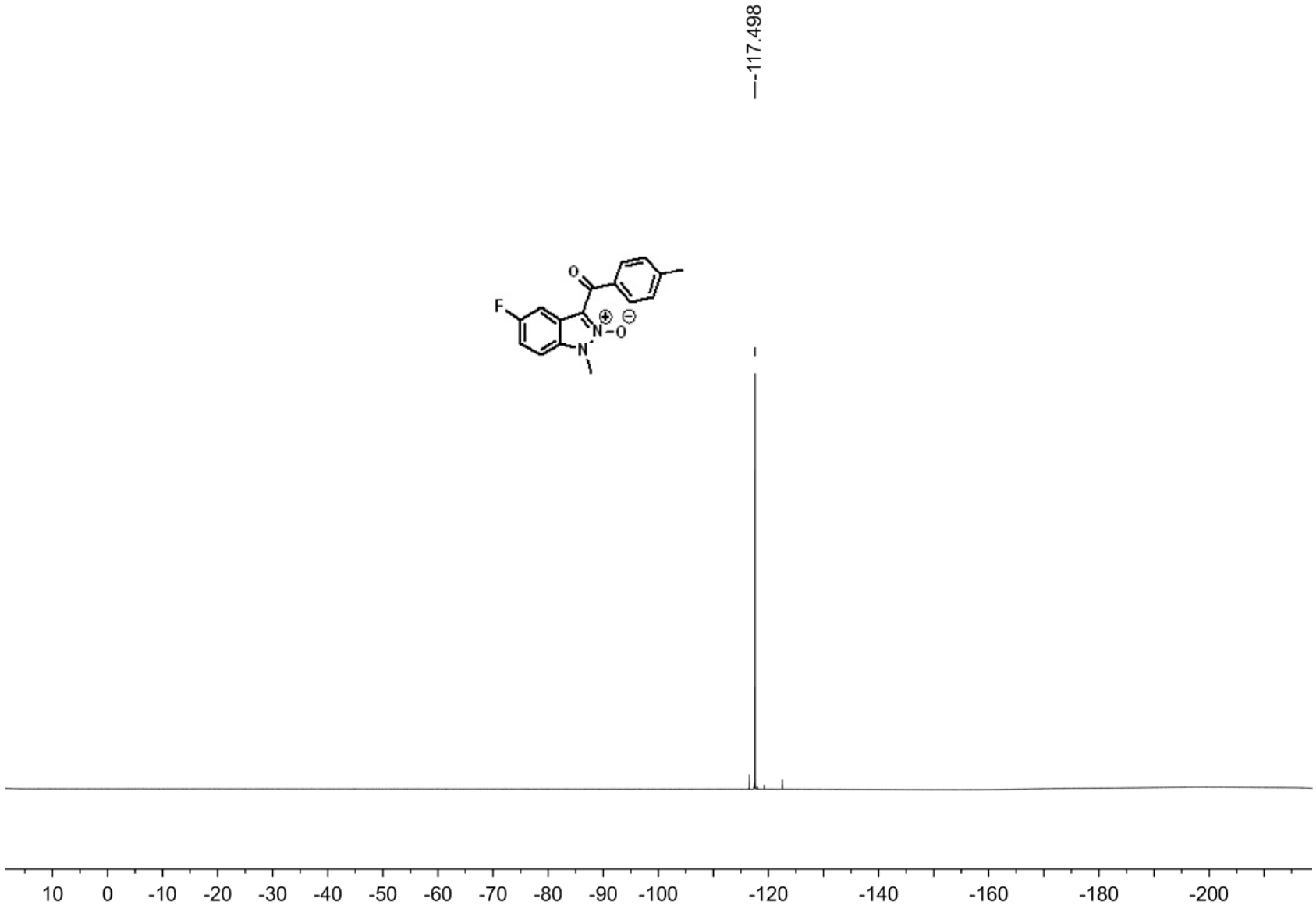
^{13}C NMR Spectrum of Compound **3i**



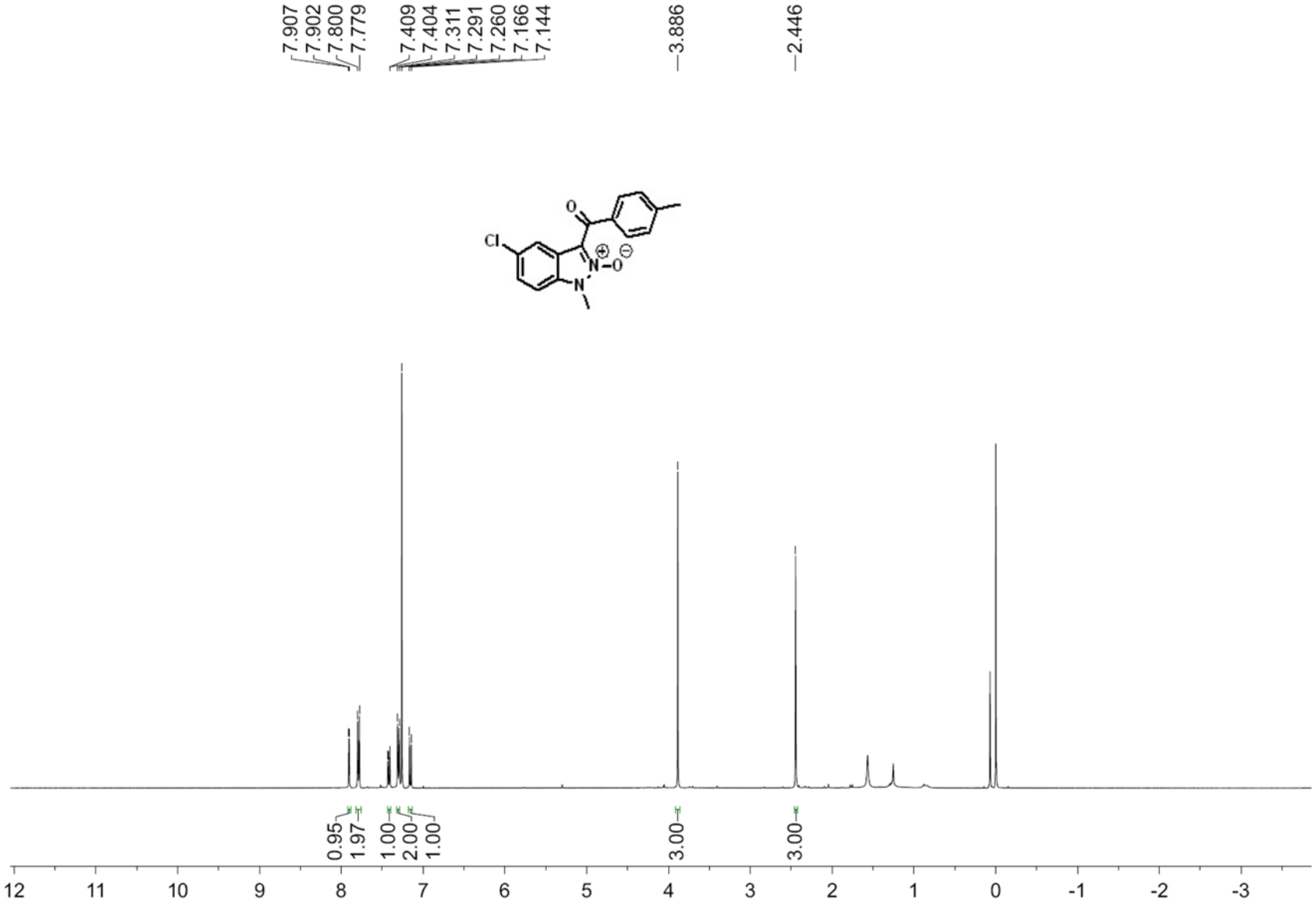
^{1}H NMR Spectrum of Compound **3j**



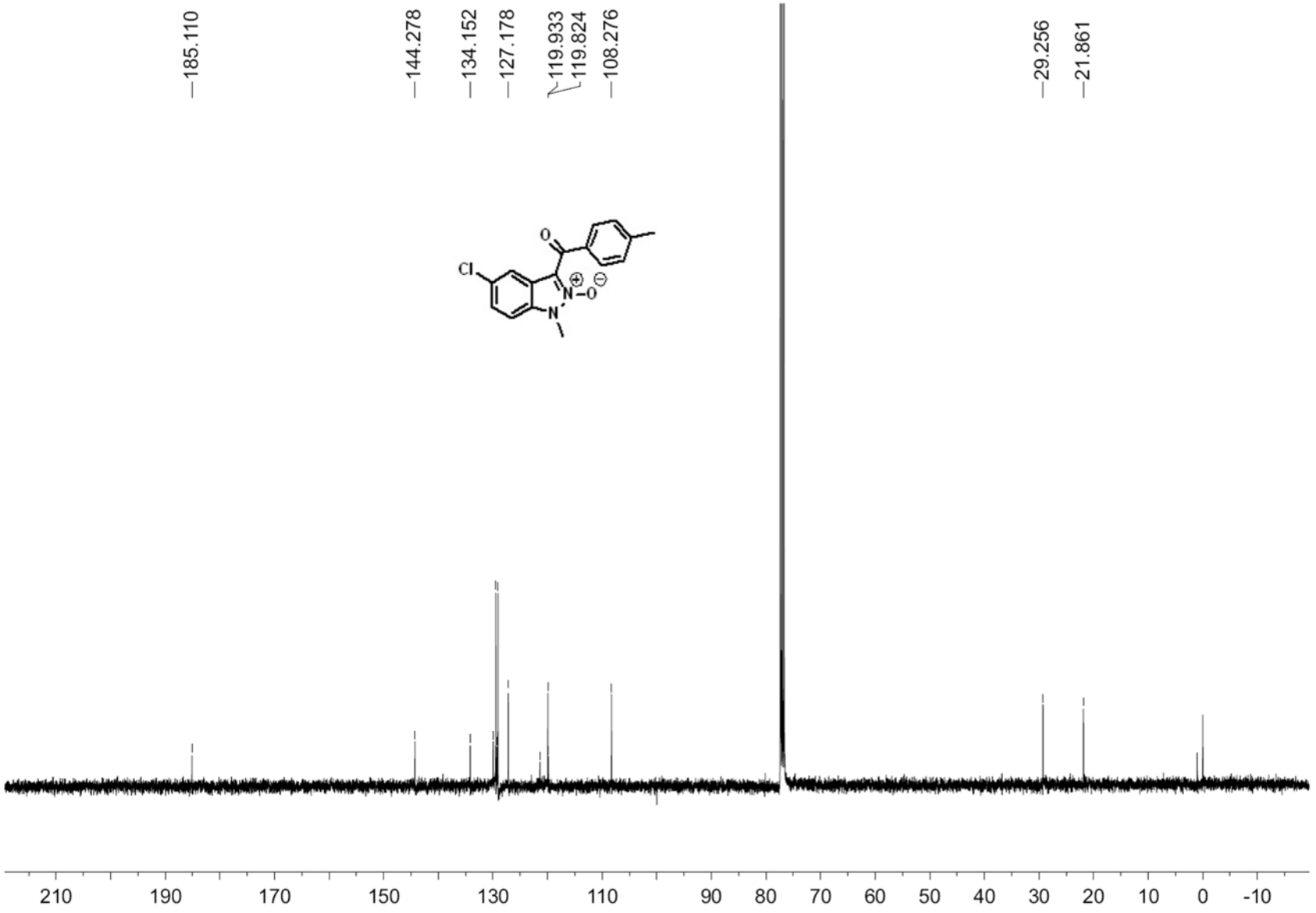
^{13}C NMR Spectrum of Compound **3j**



^{19}F NMR Spectrum of Compound **3j**



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



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