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Supporting Information

Divergent Reactivity of α-azidochalcones with Metal β-Diketonates: Tunable Synthesis of Substituted Pyrroles and Indoles

Kandasamy Rajaguru,[a] Arumugam Mariappan,[a] Shanmugam Muthusubramanian,*[a] and Nattamai Bhuvanesh[b]

[a] *Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University,*

Madurai - 625 021, India

[b] *X-ray Diffraction Laboratory, Department of Chemistry, Texas A & M University,*

College Station, Texas 77842, USA

e-mail: muthumanian2001@yahoo.com

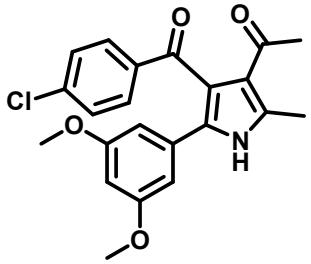
Table of contents	**Page No**

Characterization of compounds **2** and **3**	S4
^{1}H &^{13}C NMR spectra of compound **2a**	S15
^{1}H &^{13}C NMR spectra of compound **2b**	S17
^{1}H &^{13}C NMR spectra of compound **2c**	S19
^{1}H &^{13}C NMR spectra of compound **2d**	S21
^{1}H &^{13}C NMR spectra of compound **2e**	S23
^{1}H &^{13}C NMR spectra of compound **2f**	S25
^{1}H & ^{13}C NMR spectra of compound **2g**	S27
^{1}H & ^{13}C NMR spectra of compound **2h**	S29
^{1}H & ^{13}C NMR spectra of compound **2i**	S31
^{1}H & ^{13}C NMR spectra of compound **2j**	S33
^{1}H &^{13}C NMR spectra of compound **2k**	S35
^{1}H &^{13}C NMR spectra of compound **2l**	S37
^{1}H & ^{13}C NMR spectra of compound **2m**	S39
^{1}H & ^{13}C NMR spectra of compound **2n**	S41
^{1}H &^{13}C NMR spectra of compound **2o**	S43
^{1}H & ^{13}C NMR spectra of compound **3a**	S45
^{1}H & ^{13}C NMR spectra of compound **3b**	S47
^{1}H &^{13}C NMR spectra of compound **3c**	S49
^{1}H &^{13}C NMR spectra of compound **3d**	S51
^{1}H & ^{13}C NMR spectra of compound **3e**	S53
^{1}H &^{13}C NMR spectra of compound **3f**	S55

^{1}H &^{13}C NMR spectra of compound **3g** S57
^{1}H &^{13}C NMR spectra of compound **3h** S59
^{1}H &^{13}C NMR spectra of compound **3i** S61
^{1}H &^{13}C NMR spectra of compound **3j** S63
^{1}H &^{13}C NMR spectra of compound **3k** S65
^{1}H &^{13}C NMR spectra of compound **3l** S67
^{1}H &^{13}C NMR spectra of compound **3m** S69
^{1}H &^{13}C NMR spectra of compound **3n** S71
^{1}H &^{13}C NMR spectra of compound **3o** S73
^{1}H &^{13}C NMR spectra of compound **3p** S75

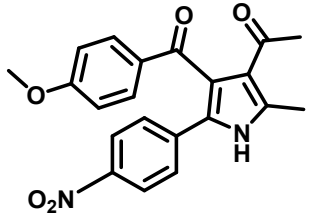
Characterisation data for compounds 2 and 3

1-(4-(4-Chlorobenzoyl)-5-(3,5-dimethoxyphenyl)-2-methyl-1*H*-pyrrol-3-yl)ethan-1-one (2a):



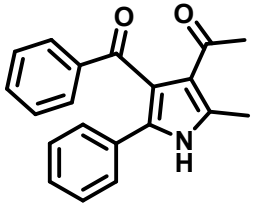
Isolated as white solid; mp: 201−202 °C; IR (KBr): 3195, 2842, 1689, 1644, 1421, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.99 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.51 (s, 1H), 7.33 – 7.23 (m, 2H), 6.87 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 2.54 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 192.9, 162.4, 151.8, 148.2, 140.2, 137.1, 135.4, 130.2, 128.1, 122.4, 120.1, 115.2, 107.4, 56.1, 55.9, 31.1, 13.8. ESI-MS *m/z* calcd for $C_{22}H_{20}ClNO_4$: $[M]^+$ 397.85; Found: $[M+H]^+$ 398.44. Anal. Calcd for $C_{22}H_{20}ClNO_4$: C, 66.42; H, 5.07; N, 3.52 %. Found: C, 66.45; H, 5.11; N, 3.56 %.

1-(4-(4-Methoxybenzoyl)-2-methyl-5-(4-nitrophenyl)-1*H*-pyrrol-3-yl)ethan-1-one (2b):



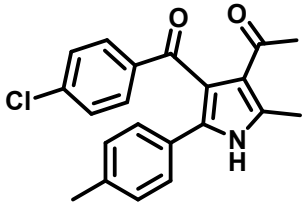
Isolated as pale yellow solid; mp: 168−170 °C; IR (KBr): 3192, 2837, 1695, 1638, 1428, 1593, 1384 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.50 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.63 (s, 3H), 2.43 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 192.8, 163.1, 145.2, 137.0, 136.8, 131.0, 130.6, 125.9,* 123.6, 123.2, 113.2, 54.8, 29.3, 13.5. ESI-MS *m/z* calcd for $C_{21}H_{18}N_2O_5$: $[M]^+$ 378.38; Found: $[M+H]^+$ 379.12. Anal. Calcd for $C_{21}H_{18}N_2O_5$: C, 66.66; H, 4.80; N, 7.40%. Found: C, 66.69; H, 4.86; N, 7.42%. (*Two carbons are merged); (One quarnery carbon not picked up).

1-(4-Benzoyl-2-methyl-5-phenyl-1*H*-pyrrol-3-yl)ethan-1-one (2c):[1]



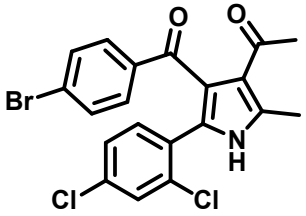
Isolated as white solid; mp: 176−177 °C; IR (KBr): 3221, 1677, 1628, 1582, 1431 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.36 – 7.31 (m, 2H), 7.28 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 2.52 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 193.0, 138.1, 134.9, 131.9, 130.6, 129.7, 128.6, 127.7, 127.6, 126.6, 126.5, 122.8, 120.5, 29.2, 13.3. ESI-MS *m/z* calcd for $C_{20}H_{17}NO_2$: $[M]^+$ 303.36; Found: $[M+H]^+$ 304.25.

1-(4-(4-Chlorobenzoyl)-2-methyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethan-1-one (2d):[1]



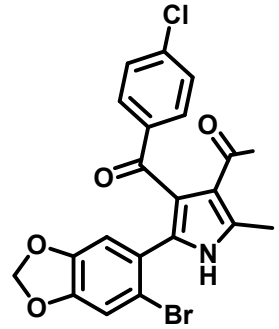
Isolated as white solid; mp: 218−220 °C; IR (KBr): 3192, 1688, 1624, 1595, 1426, 1074 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 193.9, 139.1, 137.5, 136.9, 135.0, 130.7, 129.3, 128.6, 127.6, 126.6, 123.5, 120.3, 29.7, 21.1, 13.9. One quartnary carbon not picked up.

1-(4-(4-Bromobenzoyl)-5-(2,4-dichlorophenyl)-2-methyl-1*H*-pyrrol-3-yl)ethan-1-one (2e):



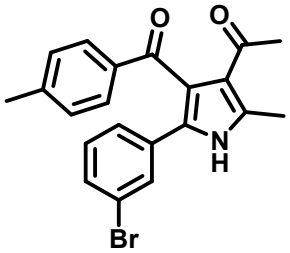
Isolated as white solid; mp: 238−240 °C; IR (KBr): 3204, 1678, 1635, 1432, 1082, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 2.59 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 192.6, 137.1, 135.3, 134.2, 133.7, 132.8, 130.8, 130.2, 128.7, 128.4, 127.7, 126.9, 126.3, 122.5, 29.5, 13.2. ESI-MS *m/z* calcd for $C_{20}H_{14}BrCl_2NO_2$: $[M]^+$ 451.14; Found: $[M+H]^+$ 452.12. Anal. Calcd for $C_{20}H_{14}BrCl_2NO_2$: C, 53.25; H, 3.13; N, 3.10; %. Found: C, 53.28; H, 3.18; N, 3.07%. One quartnary carbon not picked up.

1-(5-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-4-(4-chlorobenzoyl)-2-methyl-1*H*-pyrrol-3-yl)ethan-1-one (2f):



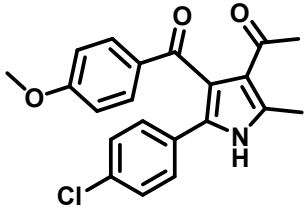
Isolated as white solid; mp: 208−210 °C; IR (KBr): 3022, 1669, 1631, 1421, 1078, 921 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.04 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 1H), 6.74 (s, 1H), 5.95 (s, 2H), 2.55 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 192.5, *162.2, 148.3, 146.5, 138.1, 137.1, 134.7, 130.4, 127.9, 125.1, 122.1, 114.7, 112.2, 112.1, 101.7, 31.1, 13.3. ESI-MS *m/z* calcd for $C_{21}H_{15}BrClNO_4$: $[M]^+$ 460.71; Found: $[M+H]^+$ 461.02. Anal. Calcd for $C_{21}H_{15}BrClNO_4$: C, 54.75; H, 3.28; N, 3.04%. Found: C, 54.78; H, 3.32; N, 3.07%. (*Two carbons are merged).

1-(5-(3-Bromophenyl)-2-methyl-4-(4-methylbenzoyl)-1*H*-pyrrol-3-yl)ethan-1-one (2g):



Isolated as white solid; mp: 190−192 °C; IR (KBr): 3213, 1685, 1623, 1436, 628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.43 (s, 1H), 7.28 – 7.13 (m, 4H), 7.04 (t, *J* = 7.4 Hz, 1H), 2.55 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 192.9, 142.9, 135.4, 132.7, 129.3, 129.2, 128.7,* 128.4, 127.4, 125.0, 122.8, 121.5, 29.2, 20.9, 13.3. ESI-MS *m/z* calcd for $C_{21}H_{18}BrNO_2$: $[M]^+$ 396.28; Found: $[M+H]^+$ 397.41. Anal. Calcd for $C_{21}H_{18}BrNO_2$: C, 63.65; H, 4.58; N, 3.53%. Found: C, 63.69; H, 4.54; N, 3.58%. (*Three carbons are merged); One quartnarey carbon is not picked up.

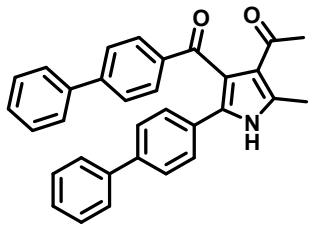
1-(5-(4-Chlorophenyl)-4-(4-methoxybenzoyl)-2-methyl-1*H*-pyrrol-3-yl)ethan-1-one (2h):



Isolated as white solid; mp: 162−163 °C; IR (KBr): 3193, 2841, 1684, 1642, 1433, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.18 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.57 (s, 3H), 2.34 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 193.1, 162.8, 135.4, 132.0, 131.0, 129.2, 127.9, 127.8, 127.5, 122.6, 121.1,

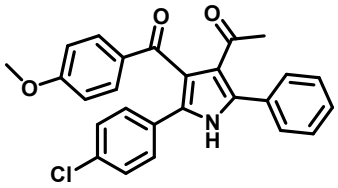
113.0, 54.8, 29.3, 13.4. ESI-MS *m/z* calcd for $C_{21}H_{18}ClNO_3$: $[M]^+$ 367.83; Found: $[M+H]^+$ 368.92. Anal. Calcd for $C_{21}H_{18}ClNO_3$: C, 68.57; H, 4.93; N, 3.81%. Found: C, 68.61; H, 4.96; N, 3.84%. One quatrnery carbon is not picked up.

1-(4-([1,1'-Biphenyl]-4-carbonyl)-5-([1,1'-biphenyl]-4-yl)-2-methyl-1*H*-pyrrol-3-yl)ethan-1-one (2i):



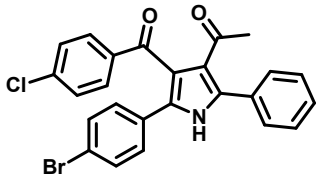
Isolated as white solid; mp: 182−184 °C; IR (KBr): 3199, 3023, 1691, 1652, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.53 (m, 4H), 7.48 – 7.30 (m, 12H), 2.49 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 193.4, 144.9, 139.8, 139.6, 139.3, 137.2, 135.4, 129.8, 129.6, 129.5, 128.6, 128.5, 128.4, 127.7, 127.0, 126.9, 126.7, 126.6, 126.4, 123.3, 121.1, 29.6, 13.7. ESI-MS *m/z* calcd for $C_{32}H_{25}NO_2$: $[M]^+$ 455.56; Found: $[M+H]^+$ 456.48. Anal. Calcd for $C_{32}H_{25}NO_2$: C, 84.37; H, 5.53; N, 3.07% Found: C, 84.41; H, 5.55; N, 3.03%.

1-(5-(4-Chlorophenyl)-4-(4-methoxybenzoyl)-2-phenyl-1*H*-pyrrol-3-yl)ethan-1-one (2j):



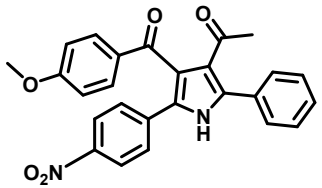
Isolated as white solid; mp: 212−214 °C; IR (KBr): 3197, 3011, 2836, 1688, 1652, 1427, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.53 – 7.44 (m, 5H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 193.9, 163.4, 131.6, 131.4, 130.0, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9,* 128.6, 128.1, 128.0, 124.6, 113.6, 55.4, 29.6. ESI-MS *m/z* calcd for $C_{26}H_{20}ClNO_3$: $[M]^+$ 429.90; Found: $[M+H]^+$ 430.25. Anal. Calcd for $C_{26}H_{20}ClNO_3$: C, 72.64; H, 4.69; N, 3.26%. Found: C, 72.68; H, 4.72; N, 3.23%. (*Two carbons are merged).

1-(5-(4-Bromophenyl)-4-(4-chlorobenzoyl)-2-phenyl-1*H*-pyrrol-3-yl)ethan-1-one (2k):



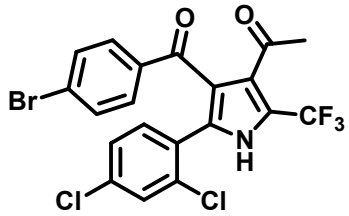
Isolated as white solid; mp: 198−199 °C; IR (KBr): 3182, 3054, 1688, 1652, 1432, 1071, 633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)) δ 9.65 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.15 – 7.55 (m, 11H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 193.9, 145.6, 139.9, 137.3, 130.0, 129.9, 129.6, 128.9, 128.8, 128.7, 128.0, 127.3, 127.2, 127.1, 126.9, 126.6, 121.3, 29.8. ESI-MS *m/z* calcd for $C_{25}H_{17}BrClNO_2$: $[M]^+$ 478.77; Found: $[M+H]^+$ 479.31. Anal. Calcd for $C_{25}H_{17}BrClNO_2$: C, 62.72; H, 3.58; N, 2.93%. Found: C, 62.76; H, 3.63; N, 2.91 %.

1-(4-(4-Methoxybenzoyl)-5-(4-nitrophenyl)-2-phenyl-1*H*-pyrrol-3-yl)ethan-1-one (2l):



Isolated as white solid; mp: 205−207 °C; IR (KBr): 3177, 3062, 2829, 1672, 1636, 1378, 1449, 1071 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.49 (m, 5H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 191.9, 162.7, 145.9, 139.8, 137.5, 136.2, 131.9, 131.2, 130.8, 129.7, 129.0, 128.2, 128.0, 127.6, 127.5, 123.1, 112.9, 53.1, 12.3. ESI-MS *m/z* calcd for $C_{26}H_{20}N_2O_5$: $[M]^+$ 440.46; Found: $[M+H]^+$ 441.28. Anal. Calcd for $C_{26}H_{20}N_2O_5$: C, 70.90; H, 4.58; N, 6.36%. Found: C, 70.94; H, 4.52; N, 6.38%.

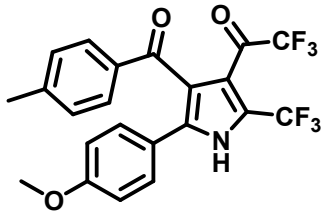
1-(4-(4-Bromobenzoyl)-5-(2,4-dichlorophenyl)-2-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethan-1-one (2m):



Isolated as white solid; mp: 178−180 °C; IR (KBr): 3201, 1686, 1658, 1454, 1085, 769, 654 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.35-7.33 (m, 2H), 7.27 (s, 1H), 7.14 – 7.05 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 185.0, 139.2, 136.6, 135.2, 134.1, 133.2, 131.2 ($^2J_{C\text{-}F}$ = 32.1 Hz), 131.0, 130.3, 129.2, 129.0, 128.1, 127.3, 126.6, 123.8

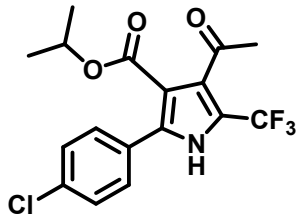
($^{1}J_{C\text{-}F}$ = 270 Hz), 115.3, 29.3. ESI-MS *m/z* calcd for $C_{20}H_{11}BrCl_2F_3NO_2$: $[M]^+$ 505.11; Found: $[M+H]^+$ 506.22. Anal. Calcd for $C_{20}H_{11}BrCl_2F_3NO_2$: C, 47.56; H, 2.20; N, 2.77%. Found: C, 47.52; H, 2.24; N, 2.75%.

2,2,2-Trifluoro-1-(5-(4-methoxyphenyl)-4-(4-methylbenzoyl)-2-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethan-1-one (2n):



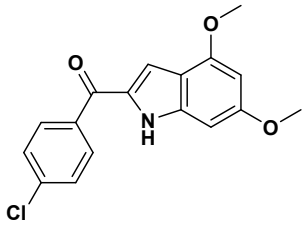
Isolated as white solid; mp: 152−153 °C; IR (KBr): 3173, 2832, 1677, 1664, 1438, 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 3.82 (s, 2H), 2.35 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 186.2, 160.6, 144.9, 138.7 ($^{1}J_{C\text{-}F}$ = 256.8 Hz), 130.9, 130.8, 130.5, 129.2, 129.1,* 123.9 ($^{1}J_{C\text{-}F}$ = 272.2 Hz), 121.2, 118.0, 114.1, 113.0, 55.3, 21.7. ESI-MS *m/z* calcd for $C_{22}H_{15}F_6NO_3$: $[M]^+$ 455.36; Found: $[M+H]^+$ 456.12. Anal. Calcd for $C_{22}H_{15}F_6NO_3$: C, 58.03; H, 3.32; N, 3.08%. Found: C, 58.05; H, 3.37; N, 3.11%. (*Two carbons are merged).

Isopropyl 4-acetyl-2-(4-chlorophenyl)-5-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate (2o):



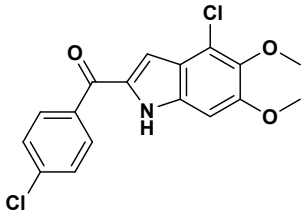
Isolated as white solid; mp: 133−134 °C; IR (KBr): 3167, 3034 2813, 1671, 1648, 1078, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.48 – 7.26 (m, 4H), 5.16 – 5.08 (m, 1H), 2.39 (s, 3H), 1.22 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 166.4, 134.5 ($^{2}J_{C\text{-}F}$ = 33.5 Hz), 133.5, 130.9, 129.5, 128.9, 128.7, 128.2, 122.4 ($^{1}J_{C\text{-}F}$ = 255 Hz), 113.9, 68.5, 30.1, 21.4. ESI-MS *m/z* calcd for $C_{17}H_{15}ClF_3NO_3$: $[M]^+$ 373.76; Found: $[M+H]^+$ 374.38. Anal. Calcd for $C_{17}H_{15}ClF_3NO_3$: C, 54.63; H, 4.05; N, 3.75%. Found: C, 54.66; H, 4.09; N, 3.71%.

(4-Chlorophenyl)(4,6-dimethoxy-1*H*-indol-2-yl)methanone (3a):



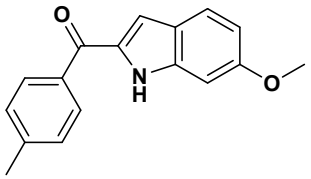
Isolated as white solid; mp: 131−133 °C; IR (KBr): 3317, 2846, 1687, 1115, 1072, 714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.17 (s, 1H), 6.46 (s, 1H), 6.20 (s, 1H), 3.92 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.5, 161.6, 155.7, 139.8, 136.6, 132.3, 130.4, 128.7, 125.4, 114.6, 111.2, 93.1, 86.1, 55.6, 55.4. ESI-MS *m/z* calcd for $C_{17}H_{14}ClNO_3$: $[M]^+$ 315.75; Found: $[M+H]^+$ 316.12. Anal. Calcd for $C_{17}H_{14}ClNO_3$: C, 64.67; H, 4.47; N, 4.44%. Found: C, 64.69; H, 4.43; N, 4.46%.

(4-Chloro-5,6-dimethoxy-1*H*-indol-2-yl)(4-chlorophenyl)methanone (3b):



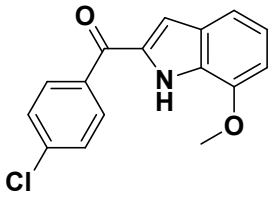
Isolated as white solid; mp: 148−149 °C; IR (KBr): 3304, 2853, 1679, 1115, 1086, 828 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.12 (s, 1H), 6.82 (s, 1H), 3.93 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1, 154.6, 136.6, 134.7, 132.6, 131.8, 130.6, 128.4, 127.4, 125.3, 120.9, 111.9, 92.8, 61.1, 56.2. ESI-MS *m/z* calcd for $C_{17}H_{13}Cl_2NO_3$: $[M]^+$ 350.19; Found: $[M+H]^+$ 351.52. Anal. Calcd for $C_{17}H_{13}Cl_2NO_3$: C, 58.31; H, 3.74; N, 4.00%. Found: C, 58.34; H, 3.79; N, 4.02%.

(6-Methoxy-1*H*-indol-2-yl)(p-tolyl)methanone (3c):



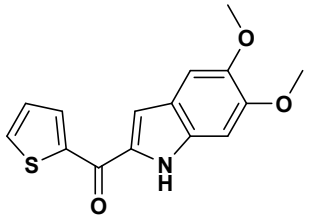
Isolated as white solid; mp: 102−103 °C; IR (KBr): 3312, 2850, 1683, 1102, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.10 (s, 1H), 6.90 – 6.80 (m, 2H), 3.88 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 191.9, 160.6, 143.2, 134.2, 132.4, 131.7, 129.7, 129.6, 129.1, 126.0, 124.6, 113.9, 97.2, 55.3, 21.6. ESI-MS *m/z* calcd for $C_{17}H_{15}NO_2$: $[M]^+$ 265.31; Found: $[M+H]^+$ 266.12. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%. Found: C, 76.98; H, 5.66; N, 5.25%.

(4-Chlorophenyl)(7-methoxy-1*H*-indol-2-yl)methanone (3d):



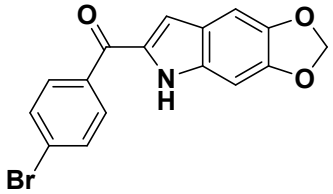
Isolated as white solid; mp: 112−114 °C; IR (KBr): 3319, 3012, 1678, 1109, 1077, 811 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.49 – 7.28 (m, 6H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 159.4, 139.1, 134.9, 134.1, 133.5, 130.9, 129.6, 129.4, 128.8, 123.4, 115.8, 115.4, 55.2. ESI-MS *m/z* calcd for $C_{16}H_{12}ClNO_2$: $[M]^+$ 285.73; Found: $[M+H]^+$ 286.12. Anal. Calcd for $C_{16}H_{12}ClNO_2$: C, 67.26; H, 4.23; N, 4.90%. Found: C, 67.29; H, 4.25; N, 4.95%.

(5,6-Dimethoxy-1*H*-indol-2-yl)(thiophen-2-yl)methanone (3e):



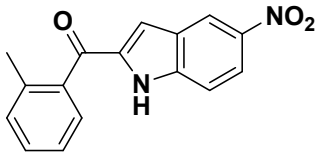
Isolated as pale orange solid; mp: 98−99 °C; IR (KBr): 3318, 2867, 1688, 1418, 1123, 827 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.01 (d, *J* = 3.7 Hz, 1H), 7.70 (d, *J* = 4.9 Hz, 1H), 7.36 (s, 1H), 7.24 – 7.20 (m, 1H), 7.08 (s, 1H), 6.94 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 151.1, 146.4, 142.8, 133.5, 132.9, 132.5, 132.3, 127.9, 120.8, 111.2, 102.5, 93.8, 56.1, 56.0. ESI-MS *m/z* calcd for $C_{15}H_{13}NO_3S$: $[M]^+$ 287.33; Found: $[M+H]^+$ 288.62. Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87; S, 11.16%. Found: C, 62.74; H, 4.60; N, 4.83; S, 11.18%.

(5*H*-[1,3]dioxolo[4,5-*f*]indol-6-yl)(4-bromophenyl)methanone (3f):



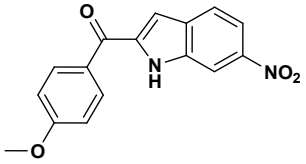
Isolated as white solid; mp: 157−159 °C; IR (KBr): 3296, 3012, 1691, 1099, 911, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.89 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.07 (s, 1H), 6.79 (s, 1H), 6.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 149.3, 147.2, 139.3, 133.2, 131.1, 129.7, 128.8, 127.9, 126.0, 118.3, 112.9, 110.1, 102.3. ESI-MS *m/z* calcd for $C_{16}H_{10}BrNO_3$: $[M]^+$ 344.16; Found: $[M+H]^+$ 345.38. Anal. Calcd for $C_{16}H_{10}BrNO_3$: C, 55.84; H, 2.93; N, 4.07 %. Found: C, 55.88; H, 2.99; N, 4.03 %.

(5-Nitro-1*H*-indol-2-yl)(o-tolyl)methanone (3g):



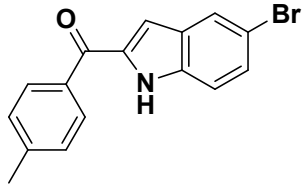
Isolated as pale white solid; mp: 143−144 °C; IR (KBr): 3328, 2918, 1687, 1373, 1117, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.48 (s, 1H), 8.01-7-96 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 – 7.30 (m, 2H), 7.21 – 7.14 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 148.1, 137.1, 136.8, 135.9, 134.6, 131.3, 131.0, 129.3, 128.3, 125.4, 124.9, 123.7, 119.2, 105.9, 19.6. ESI-MS *m/z* calcd for $C_{16}H_{12}N_2O_3$: $[M]^+$ 280.28; Found: $[M+H]^+$ 281.38. Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 9.99%. Found: C, 68.53; H, 4.35; N, 10.03%.

(4-Methoxyphenyl)(6-nitro-1*H*-indol-2-yl)methanone (3h):



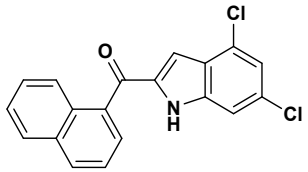
Isolated as white solid; mp: 163−164 °C; IR (KBr): 3323, 2838, 1686, 1376, 1116, 733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.91(s, 1H), 7.63 – 7.54 (m, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.04 (s, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.5, 164.6, 147.6, 139.7, 135.4, 132.9, 132.2, 129.9, 127.2, 123.8, 119.4, 113.9, 106.2, 55.6. ESI-MS *m/z* calcd for $C_{16}H_{12}N_2O_4$: $[M]^+$ 296.28 ; Found: $[M+H]^+$ 297.12. Anal. Calcd for: C, 64.86; H, 4.08; N, 9.46%. Found: C, 64.89; H, 4.03; N, 9.48%.

(5-bromo-1H-indol-2-yl)(p-tolyl)methanone (3i):



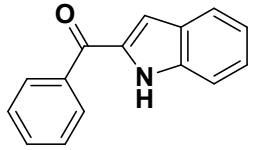
Isolated as white solid; mp: 101−102 °C; IR (KBr): 3325, 3011, 1693, 1077, 782, 651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.98 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.24 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 143.8, 135.1, 133.4, 132.8, 132.1, 129.7, 129.2, 128.9, 128.3, 122.4, 115.4, 101.5, 21.6. ESI-MS *m/z* calcd for $C_{16}H_{12}BrNO$: $[M]^+$ 314.18; Found: $[M+H]^+$ 315.12. Anal. Calcd for $C_{16}H_{12}BrNO$: C, 61.17; H, 3.85; N, 4.46%. Found: C, 61.21; H, 3.83; N, 4.42%.

(4,6-Dichloro-1*H*-indol-2-yl)(naphthalen-1-yl)methanone (3j):



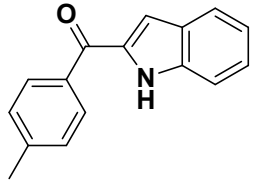
Isolated as white solid; mp: 121−122 °C; IR (KBr): 3326, 3018, 1688, 1117, 812 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.40 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.41 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.7, 136.7, 135.3, 134.8, 134.2, 132.9, 132.8, 131.2, 131.1, 130.7, 129.2, 128.6, 128.4, 127.8, 127.4, 126.7, 126.6, 124.8, 123.9. ESI-MS *m/z* calcd for $C_{19}H_{11}Cl_2NO$: $[M]^+$ 340.20; Found: $[M+H]^+$ 341.22. Anal. Calcd for $C_{19}H_{11}Cl_2NO$: C, 67.08; H, 3.26; N, 4.12%. Found: C, 67.11; H, 3.28; N, 4.09%.

(1*H*-indol-2-yl)(phenyl)methanone (3k):[2]



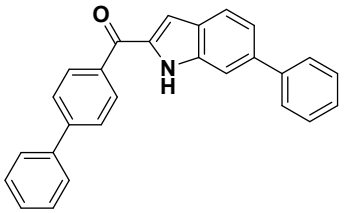
Isolated as pale yellow solid; mp: 145−146 °C; IR (KBr): 3302, 3031, 1678, 1108 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.35 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.9, 134.2, 133.5, 130.4, 129.5, 129.4, *129.1, 128.9, 128.8, 128.1, 116.5, 107.3. ESI-MS *m/z* calcd for $C_{15}H_{11}NO$: $[M]^+$ 221.26; Found: $[M+H]^+$ 222.12. (*Two carbons are merged).

(1*H*-Indol-2-yl)(p-tolyl)methanone (3l):[2]



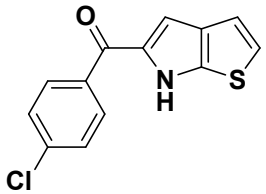
Isolated as pale yellow solid; mp: 186−187 °C; IR (KBr): 3310, 3022, 1693, 1107, 792 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.74 – 7.69 (m, 5H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 140.4, 138.8, 135.1, 132.5, 130.8, 130.6, 130.2, 130.1, 129.2, 128.7, 115.4, 106.4, 21.4. ESI-MS *m/z* calcd for $C_{16}H_{13}NO$: $[M]^+$ 235.29; Found: $[M+H]^+$ 236.42.

[1,1'-Biphenyl]-4-yl(6-phenyl-1*H*-indol-2-yl)methanone (3m):



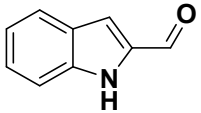
Isolated as white solid; mp: 169−170 °C; IR (KBr): 3308, 3023, 1692, 1125, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.97 – 7.35 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 145.3, 142.1, 139.9, 139.5, 135.2, 133.5, 132.1, 131.1, 130.2, 129.0, 128.9, 128.8, 128.2, 127.7, 127.1, *127.0, 126.9, 117.3, 108.6. ESI-MS *m/z* calcd for $C_{27}H_{19}NO$: $[M]^+$ 373.45; Found: $[M+H]^+$ 374.22. Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75%. Found: C, 86.87; H, 5.17; N, 3.78%. (*Two carbons are merged).

(4-Chlorophenyl)(6*H*-thieno[2,3-*b*]pyrrol-5-yl)methanone (3n):



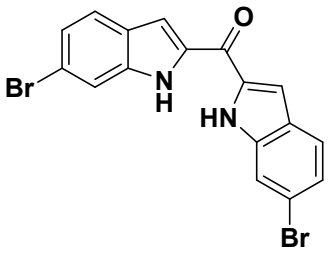
Isolated as yellow solid; mp: 97−99 °C; IR (KBr): 3316, 2878, 1691, 1127, 822 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.66 (d, J = 6.4 Hz, 2H), 7.41 (d, J = 3.3 Hz, 1H), 7.26 (d, J = 6.4 Hz, 2H), 7.05 (s, 1H), 6.52 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.0, 142.6, 135.4, 134.6, 133.3, 131.7, 131.1, 128.7, 125.5, 123.9, 111.3. ESI-MS *m/z* calcd for $C_{13}H_8ClNOS$: $[M]^+$ 261.72; Found: $[M+H]^+$ 262.28. Anal. Calcd for $C_{13}H_8ClNOS$: C, 59.66; H, 3.08; N, 5.35; S, 12.25%. Found: C, 59.69; H, 3.05; N, 5.38; S, 12.30%.

1*H*-indole-2-carbaldehyde (3o):[3]



Isolated as white solid; mp: 139−141 °C; IR (KBr): 3313, 2824, 1702, 1102 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.22 (s, 1H), 8.36 – 8.30 (m, 1H), 7.87 (s, 1H), 7.48 – 7.45 (m, 1H), 7.34 – 7.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 136.6, 136.5, 123.7, 123.0, 121.7, 120.7, 118.0, 111.6. ESI-MS *m/z* calcd for C_9H_7NO: $[M]^+$ 145.16; Found: $[M+H]^+$ 146.22.

Bis(6-bromo-1*H*-indol-2-yl)methanone (3p)



Isolated as white solid; mp: 171−172 ^{o}C; IR (KBr): 3331, 3016, 1698, 1121, 813, 649cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 2H), 7.33 (s, 2H), 7.29 (s, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.62 (d, J = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 136.4, 134.0, 130.4, 127.8, 127.4, 124.5, 120.4, 110.6. ESI-MS *m/z* calcd for $C_{17}H_{10}Br_2N_2O$: $[M]^+$ 418.09; Found: $[M+2H]^+$ 420.44. Anal. Calcd for $C_{17}H_{10}Br_2N_2O$: C, 48.84; H, 2.41; N, 6.70%. Found: C, 48.89; H, 2.44; N, 6.76%.

Reference:

1. R. Suresh, S. Muthusubramanian, M. Nagaraj and G. Manickam, *Tetrahedron Lett.* 2013, **54**, 1779.
2. Q. –Q. Yang, C. Xiao, L. –Q. Lu, J.An, F. Tan, B. –J. Li and W. –J. Xiao, 2012, **51**, 9137.
3. CAS Number: 19005-93-7

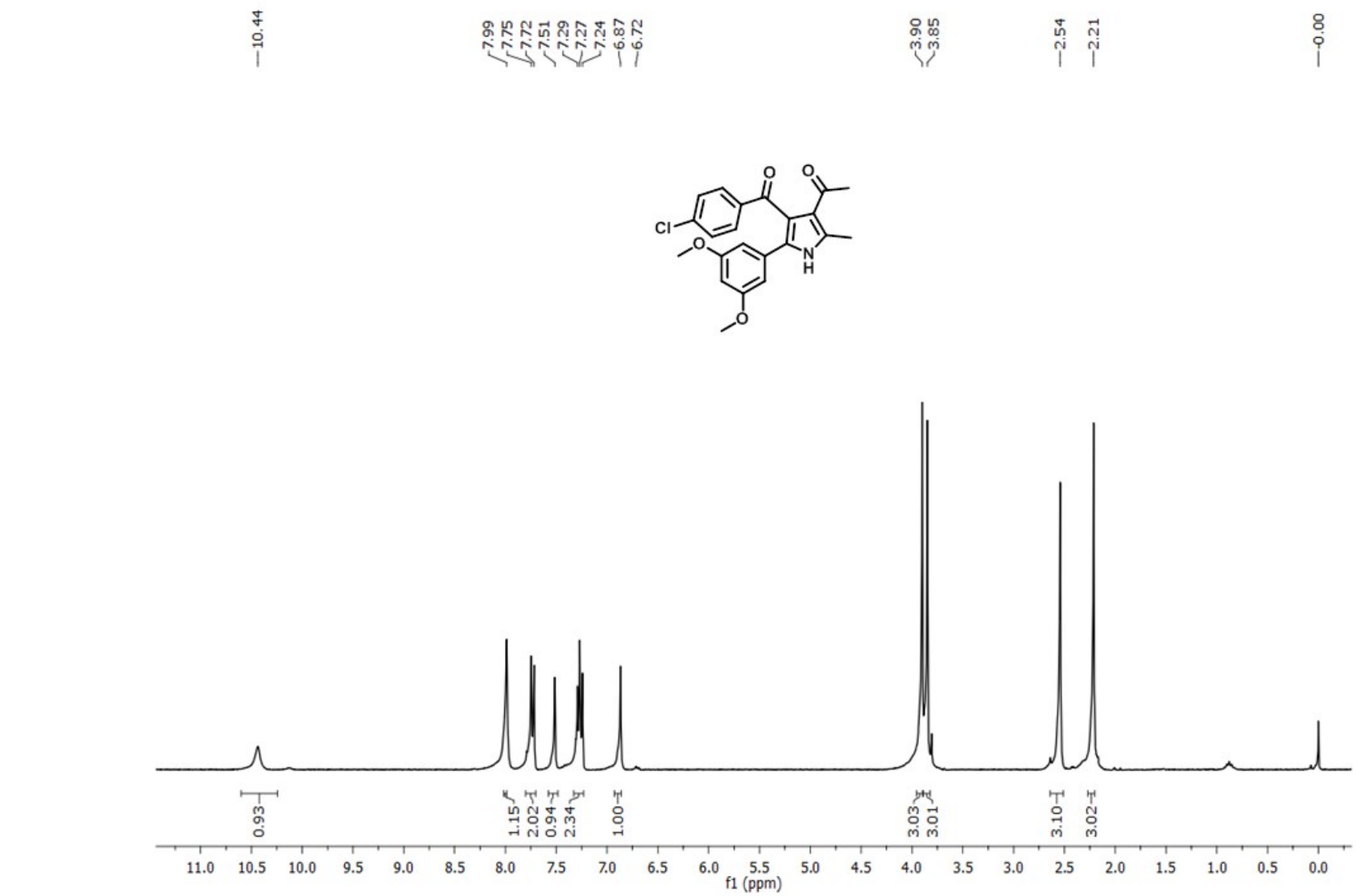


Figure 1. ^{1}H NMR spectrum of compound **2a**

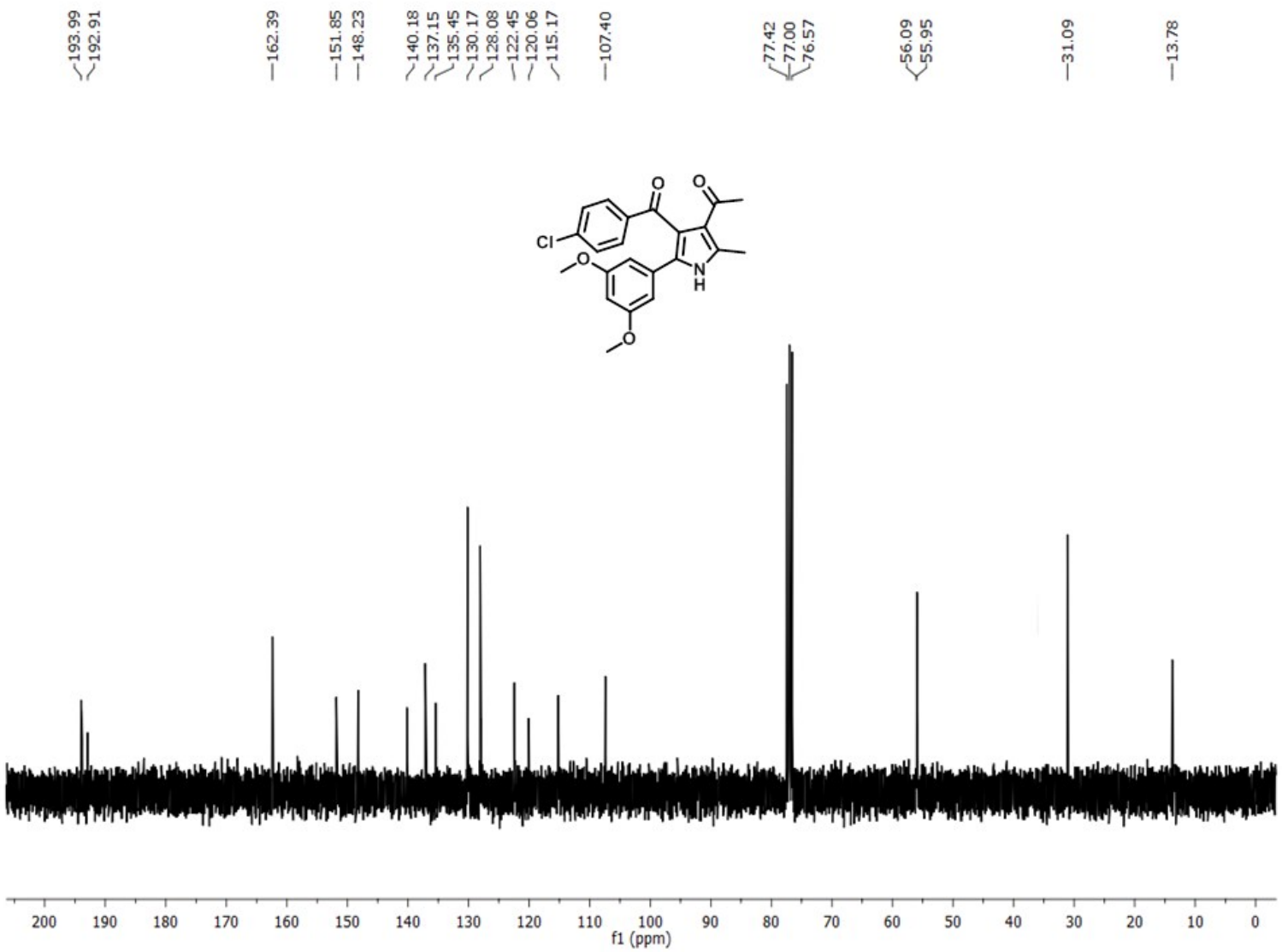


Figure 2. ^{13}C NMR spectrum of compound **2a**

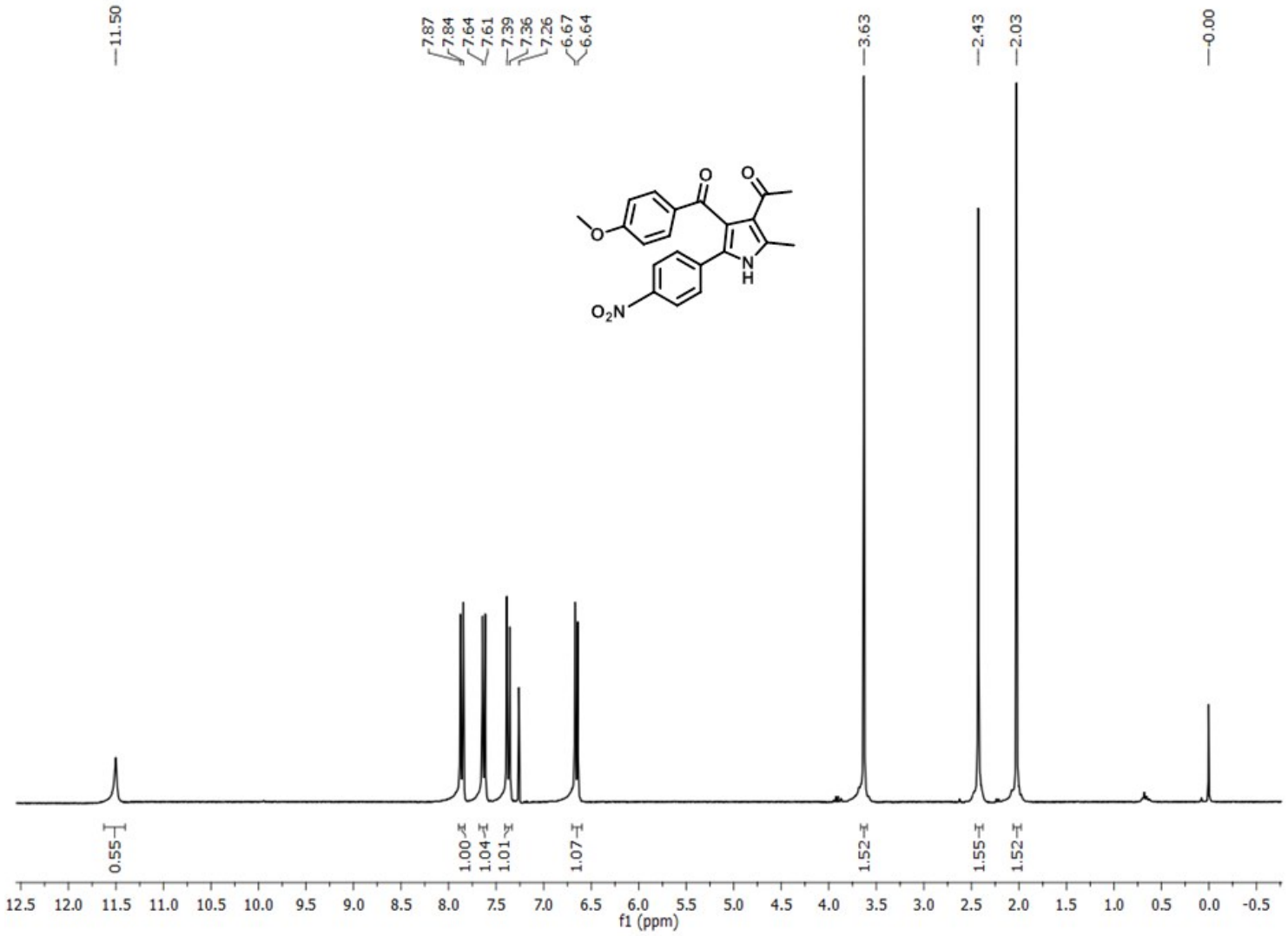


Figure 3. ^{1}H NMR spectrum of compound **2b**

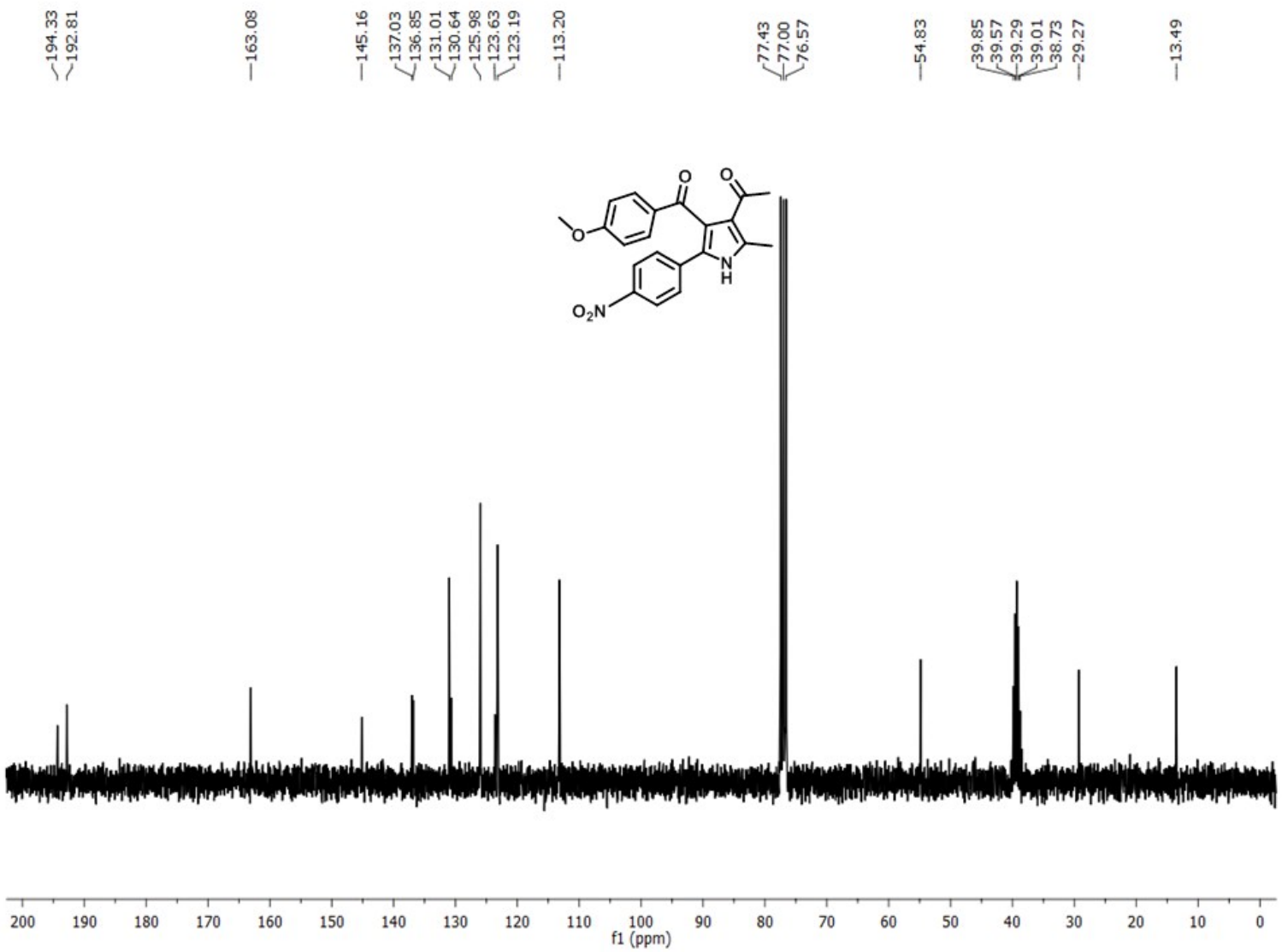


Figure 4. ^{13}C NMR spectrum of compound **2b**

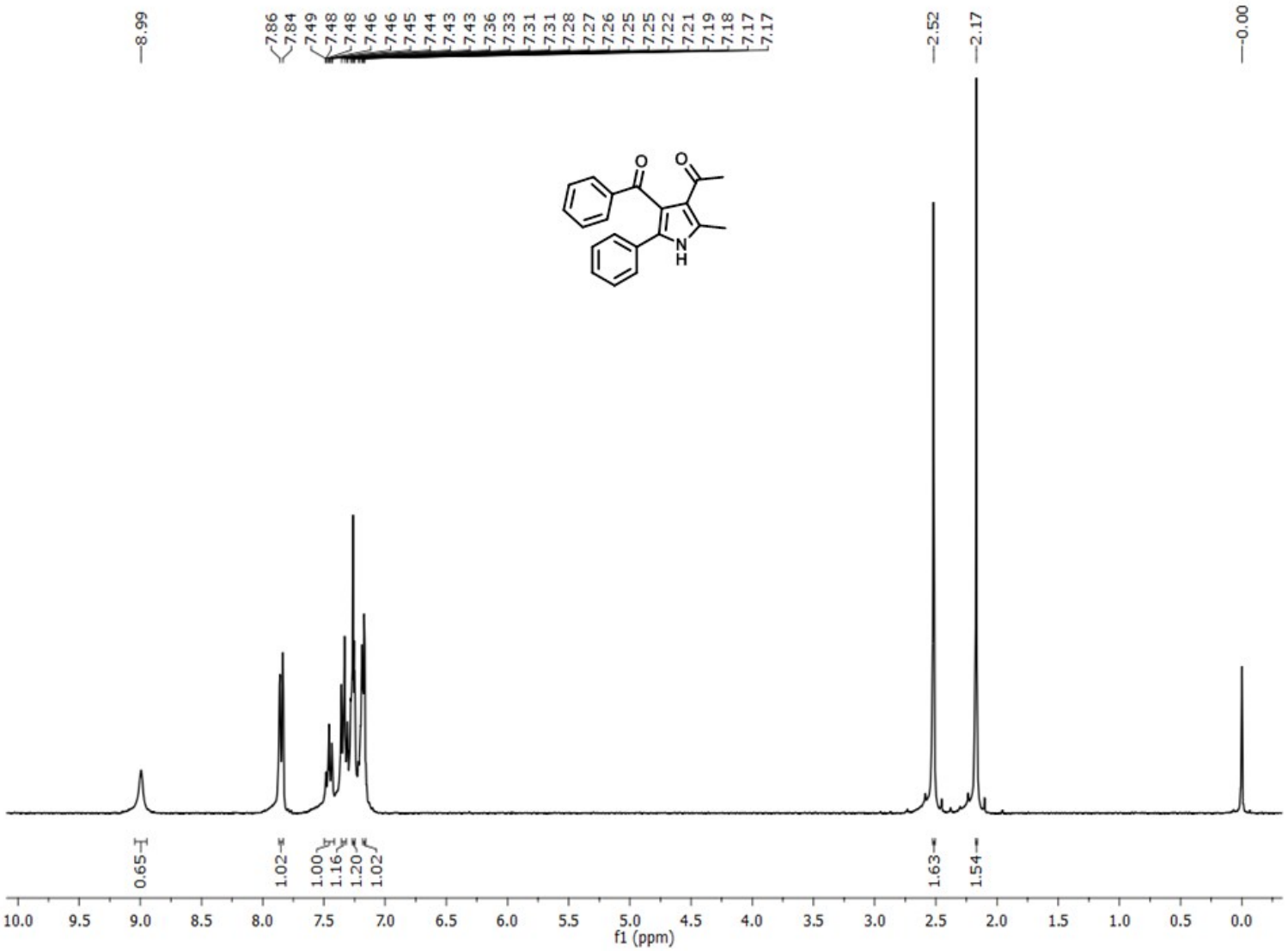


Figure 5. ^{1}H NMR spectrum of compound **2c**

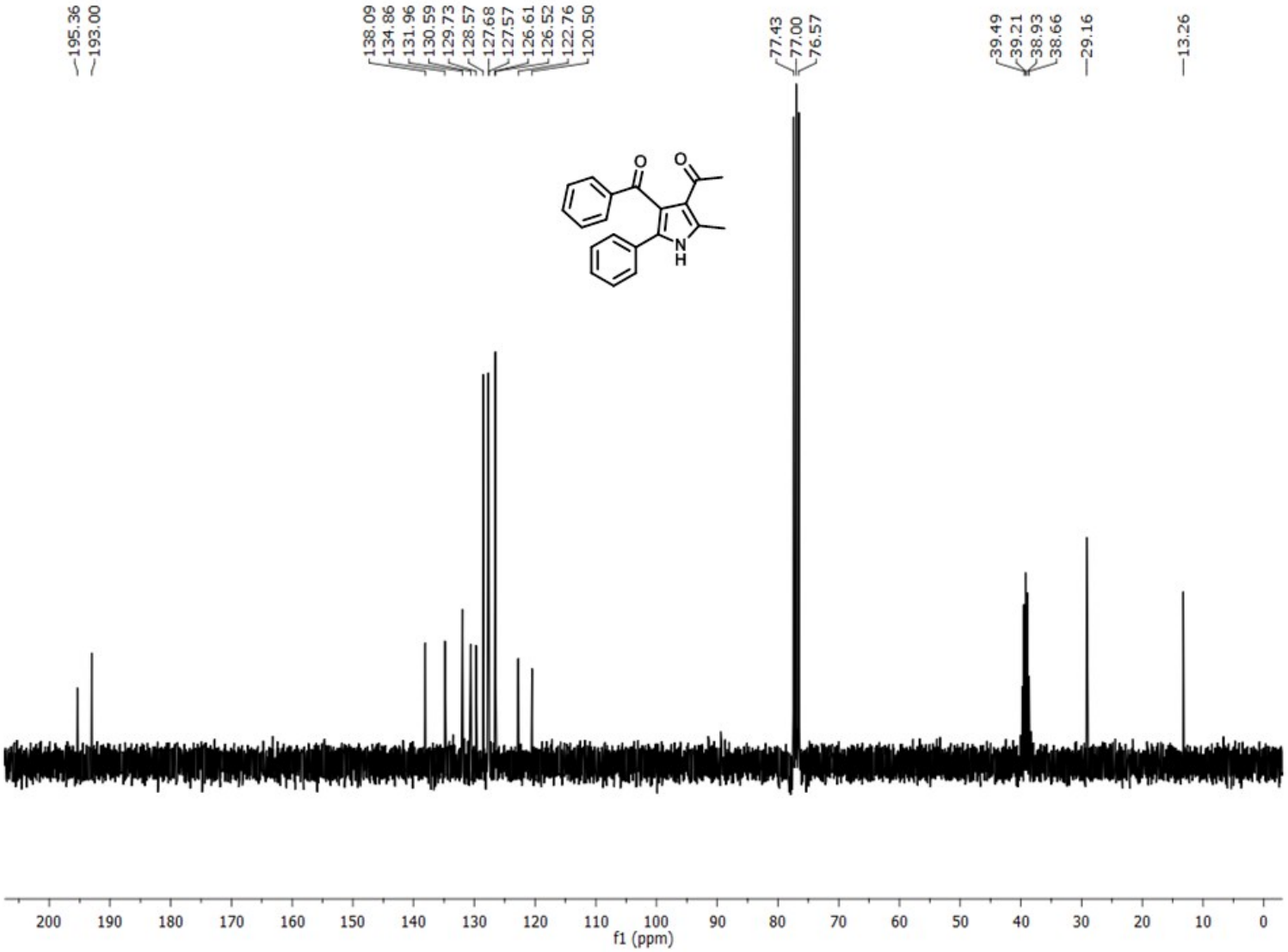


Figure 6. ^{13}C NMR spectrum of compound **2c**

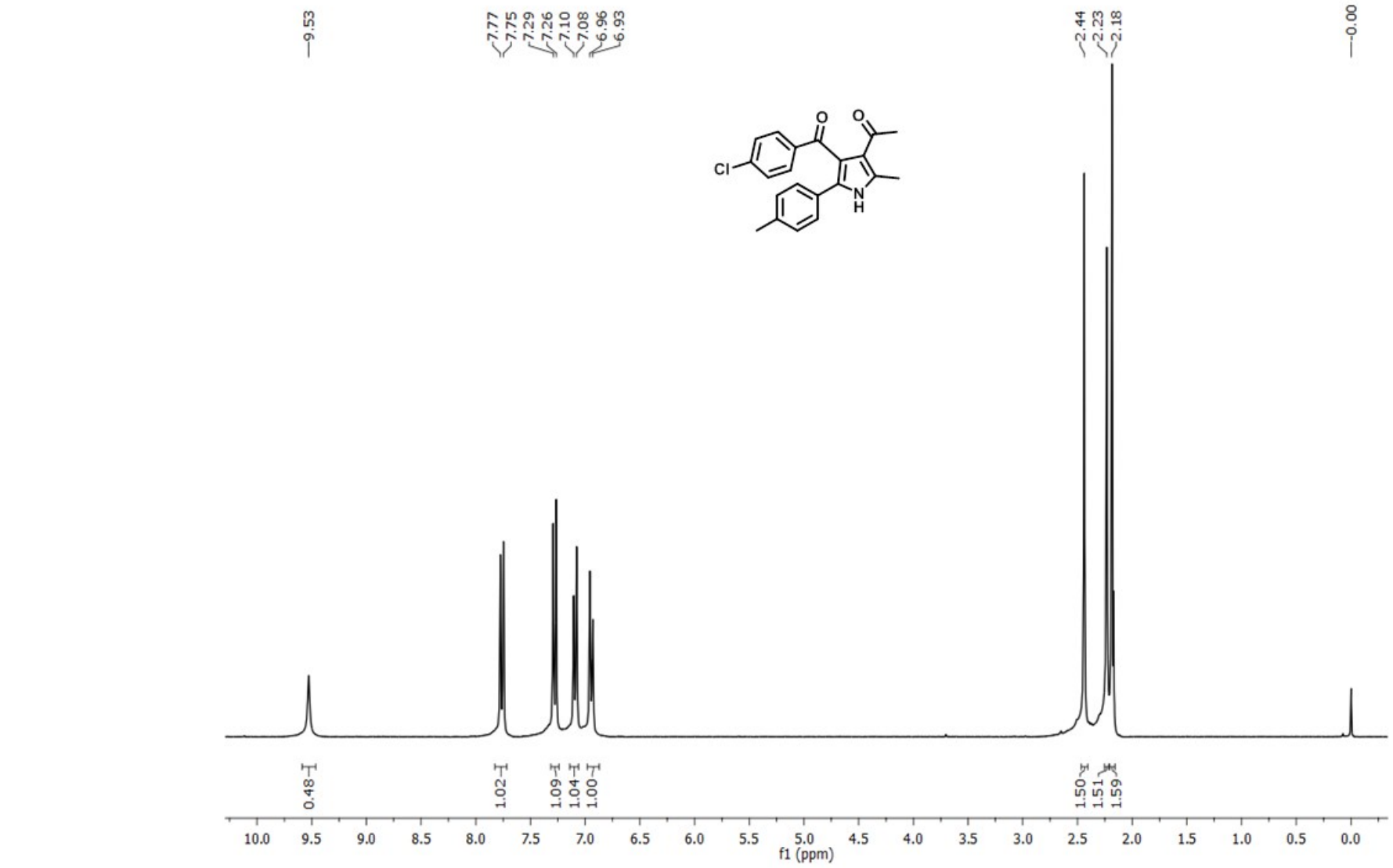


Figure 7. ^{1}H NMR spectrum of compound **2d**

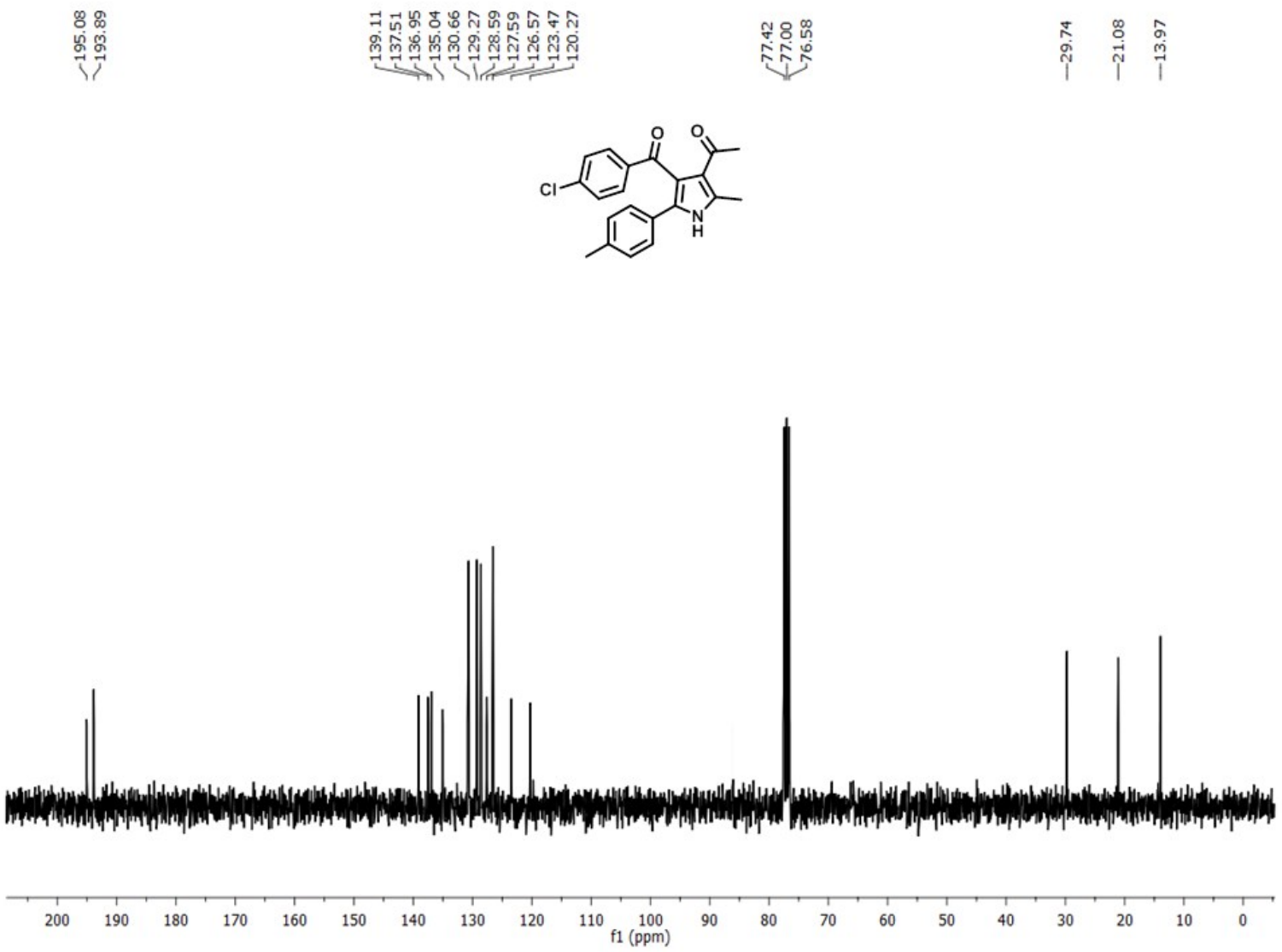


Figure 8. ^{13}C NMR spectrum of compound **2d**

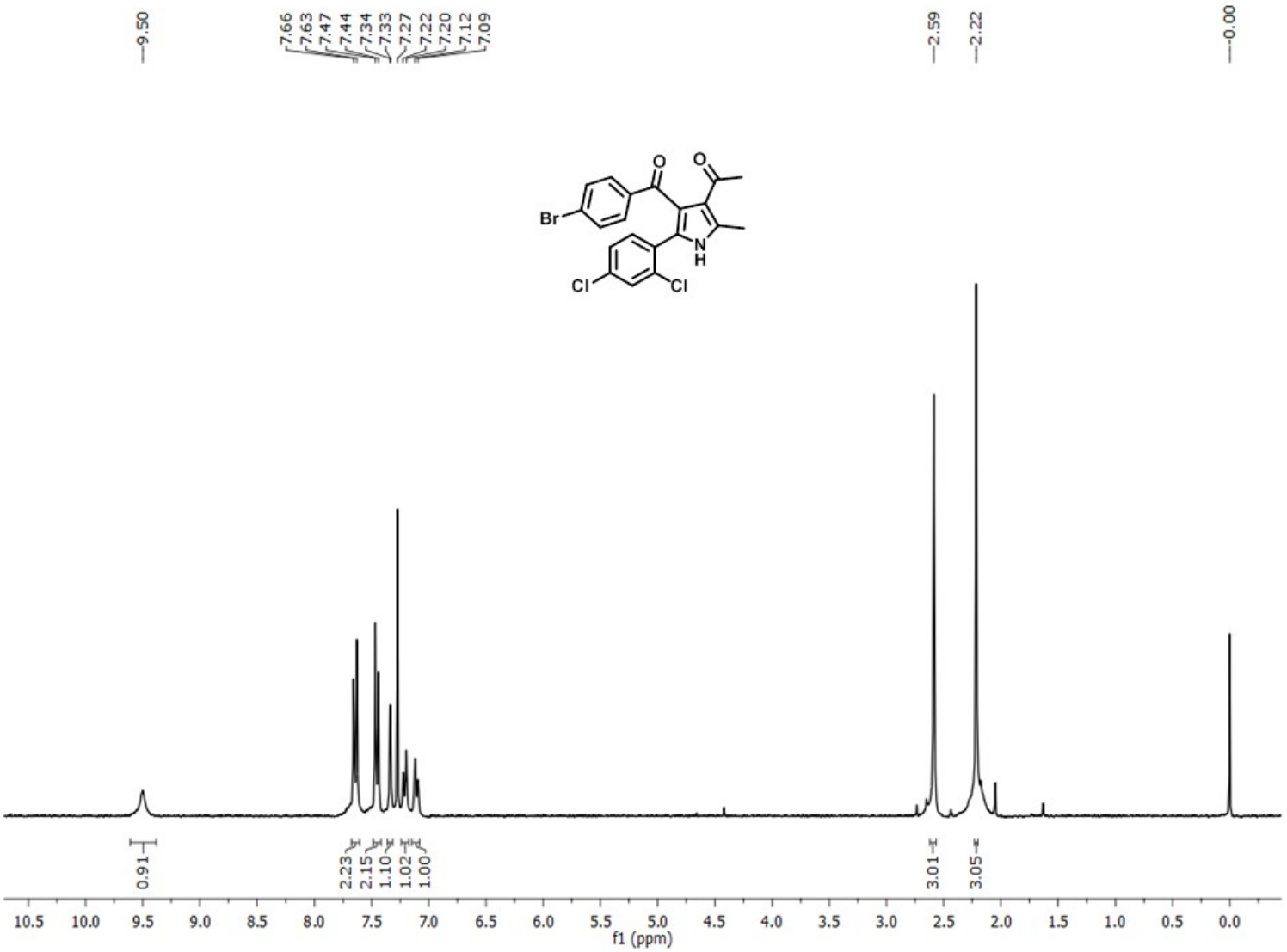


Figure 9. ^{1}H NMR spectrum of compound **2e**

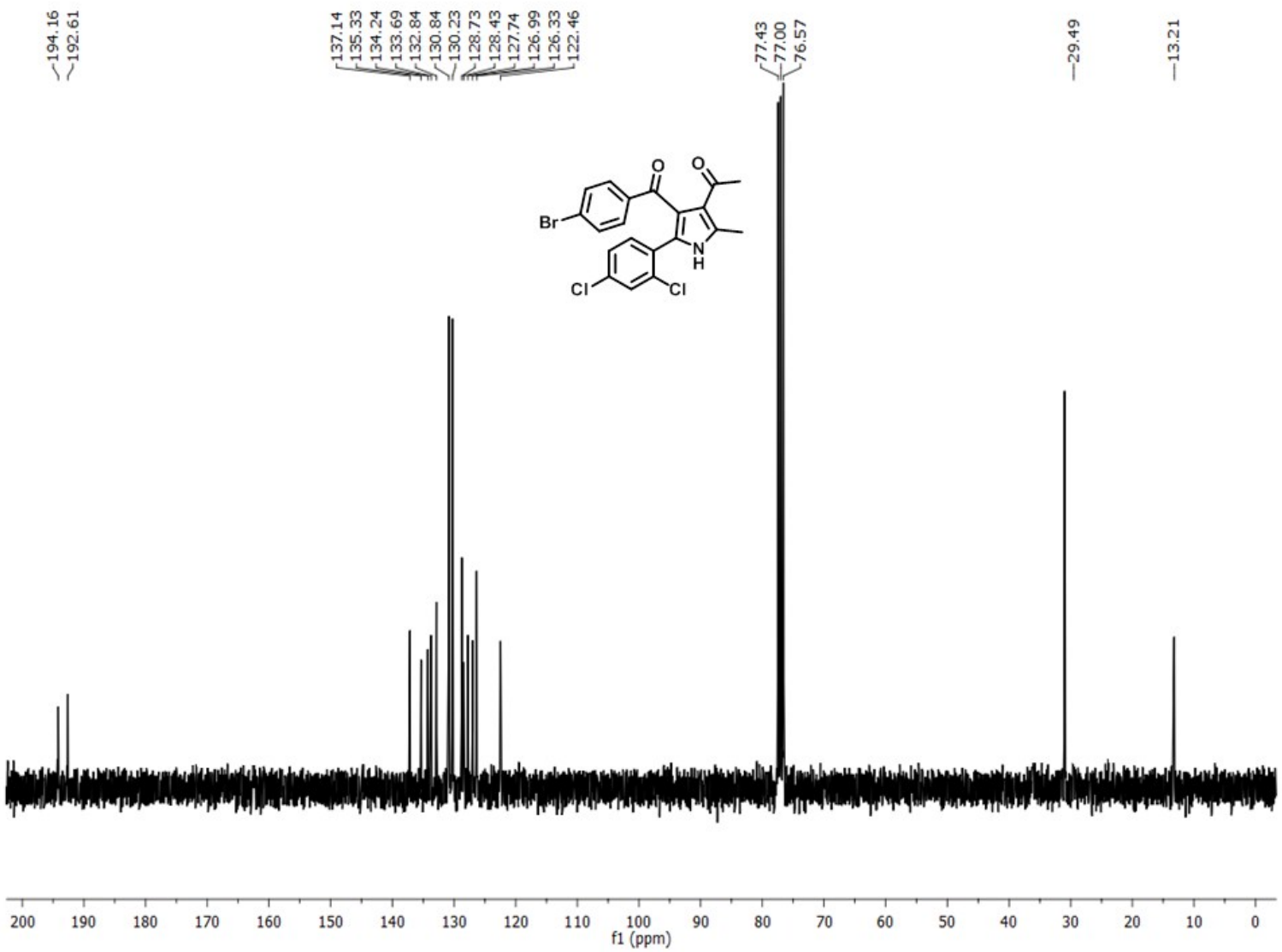


Figure 10. ^{13}C NMR spectrum of compound **2e**

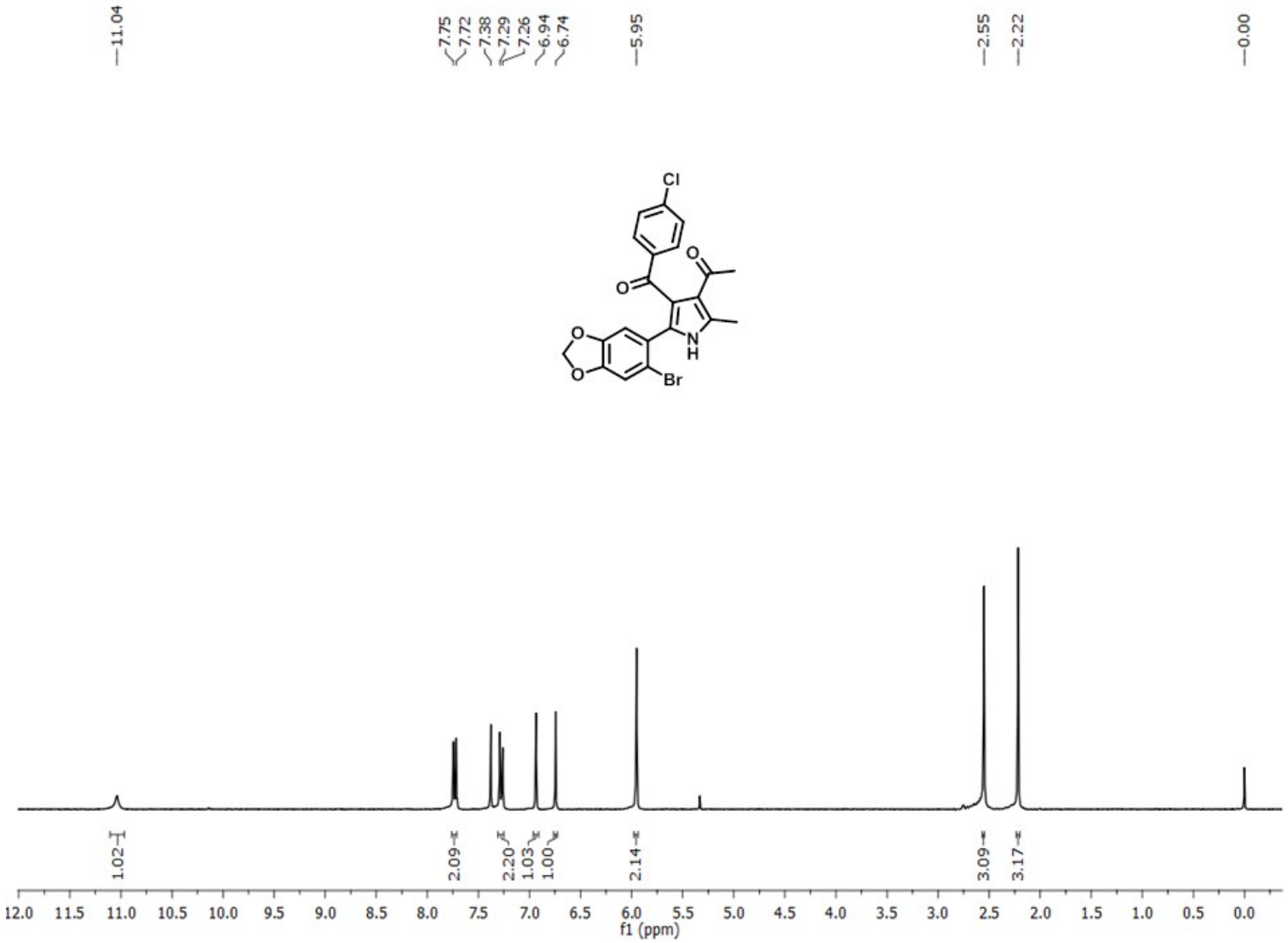


Figure 11. ^{1}H NMR spectrum of compound **2f**

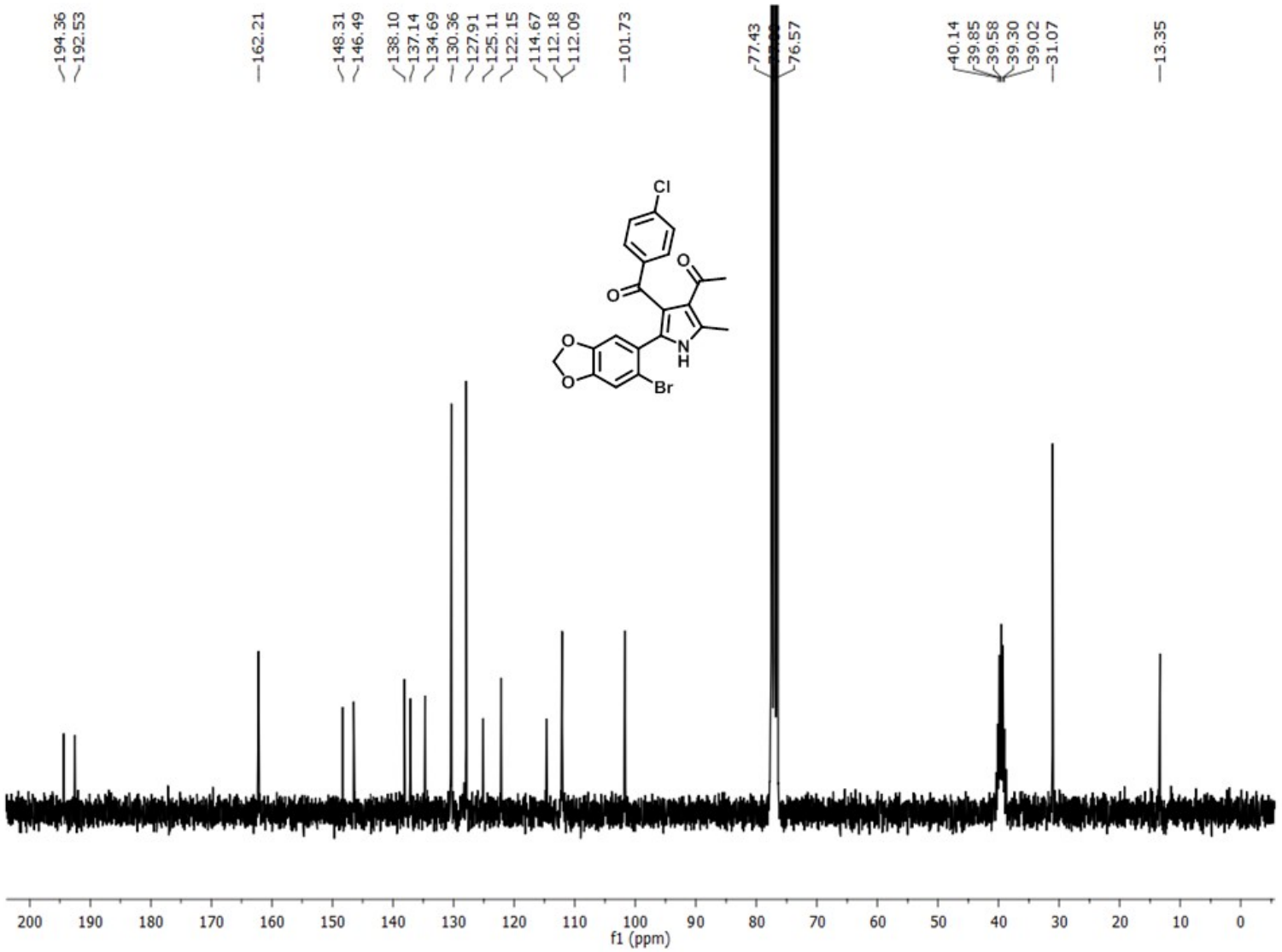


Figure 12. ^{13}C NMR spectrum of compound **2f**

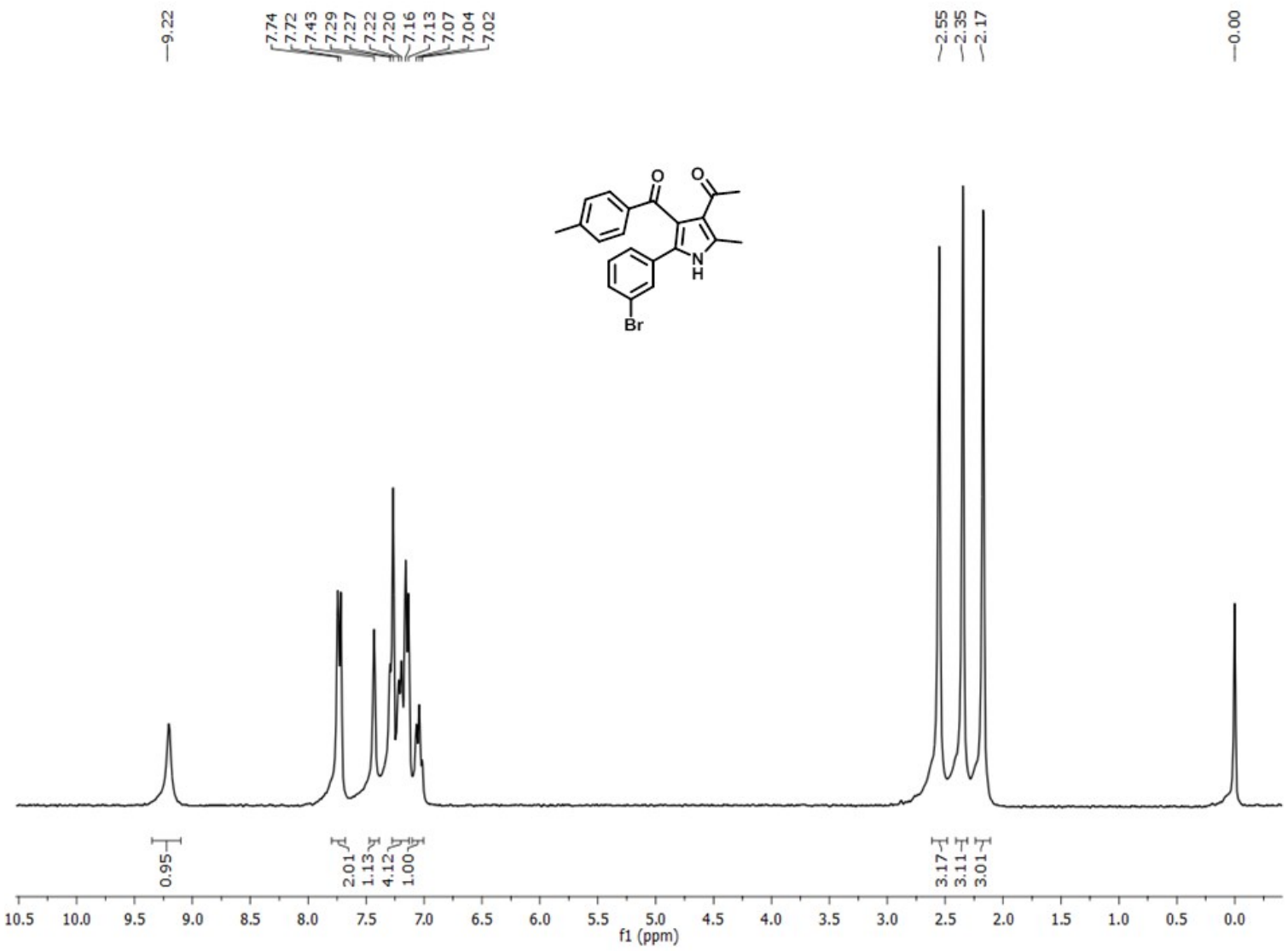


Figure 13. ^{1}H NMR spectrum of compound **2g**

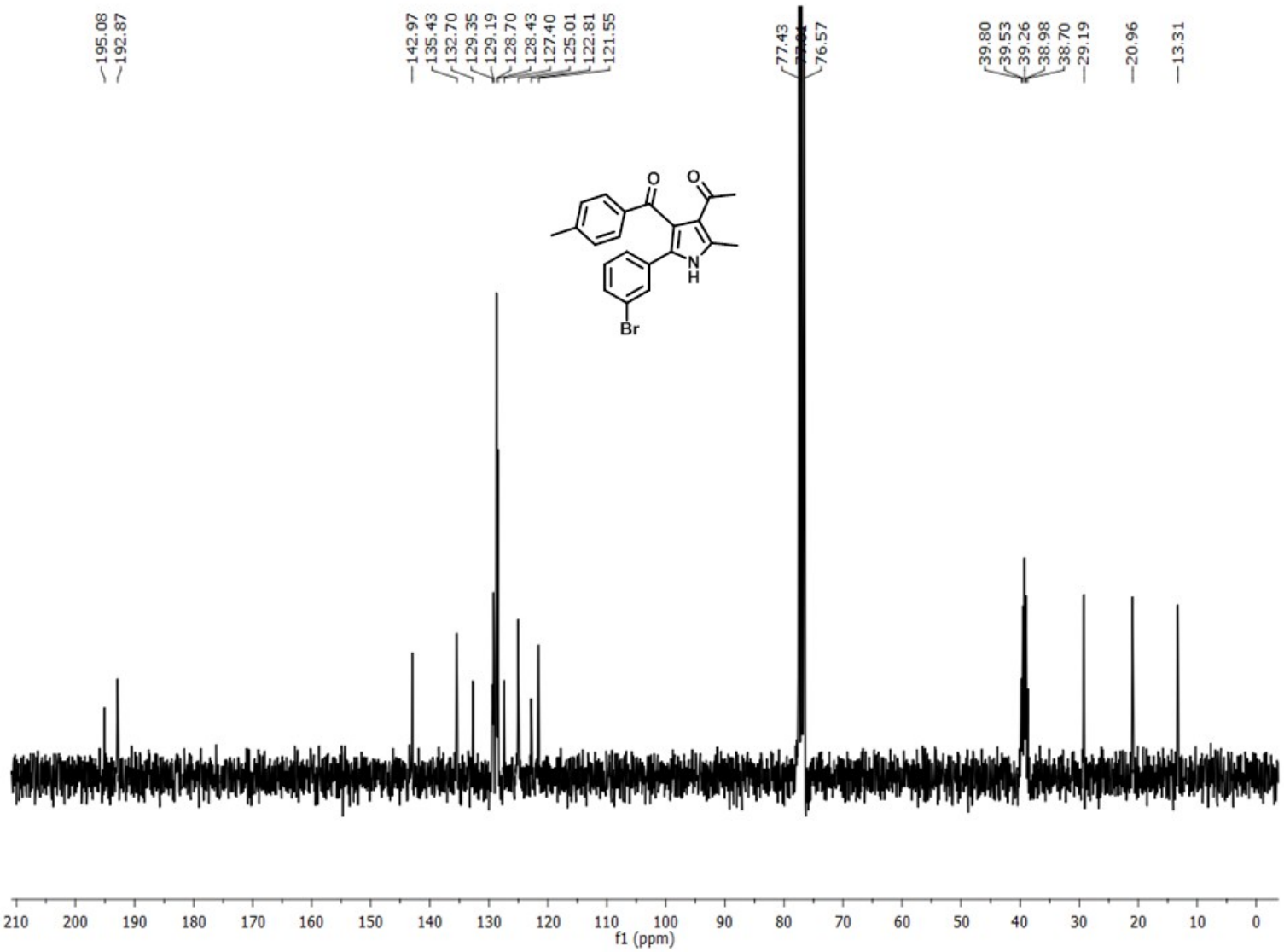


Figure 14. ^{13}C NMR spectrum of compound **2g**

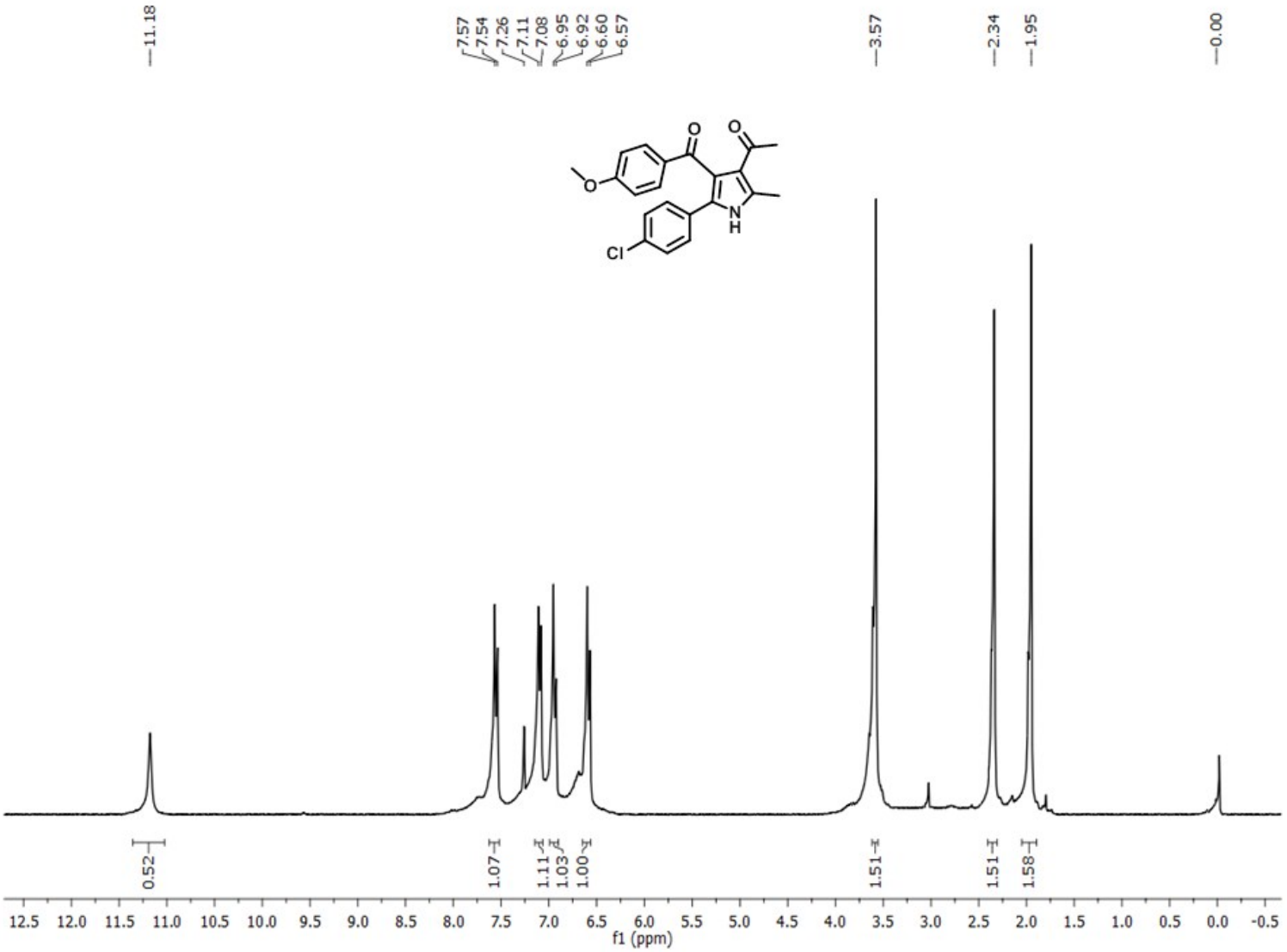


Figure 15. ^{1}H NMR spectrum of compound **2h**

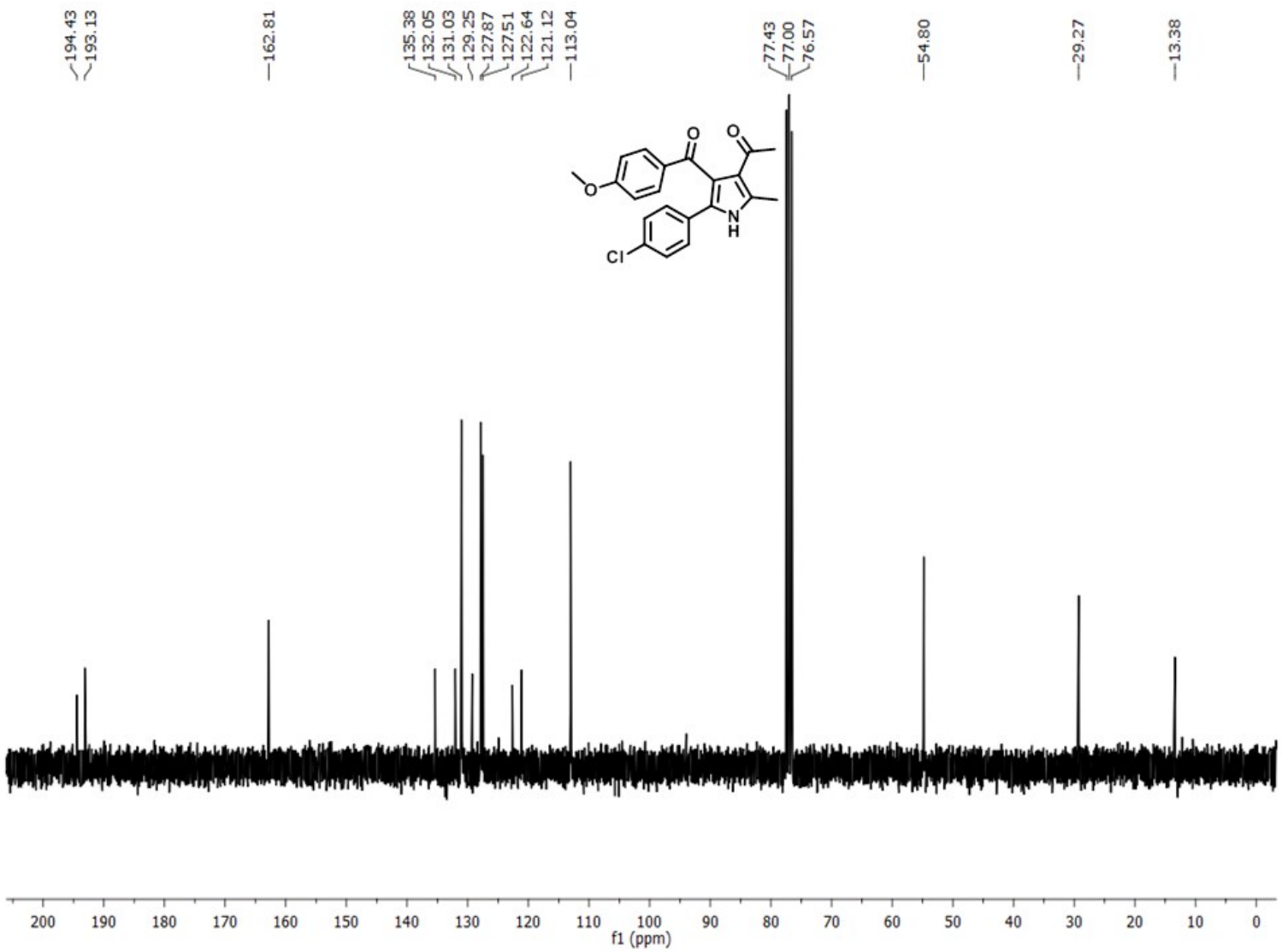


Figure 16. ^{13}C NMR spectrum of compound **2h**

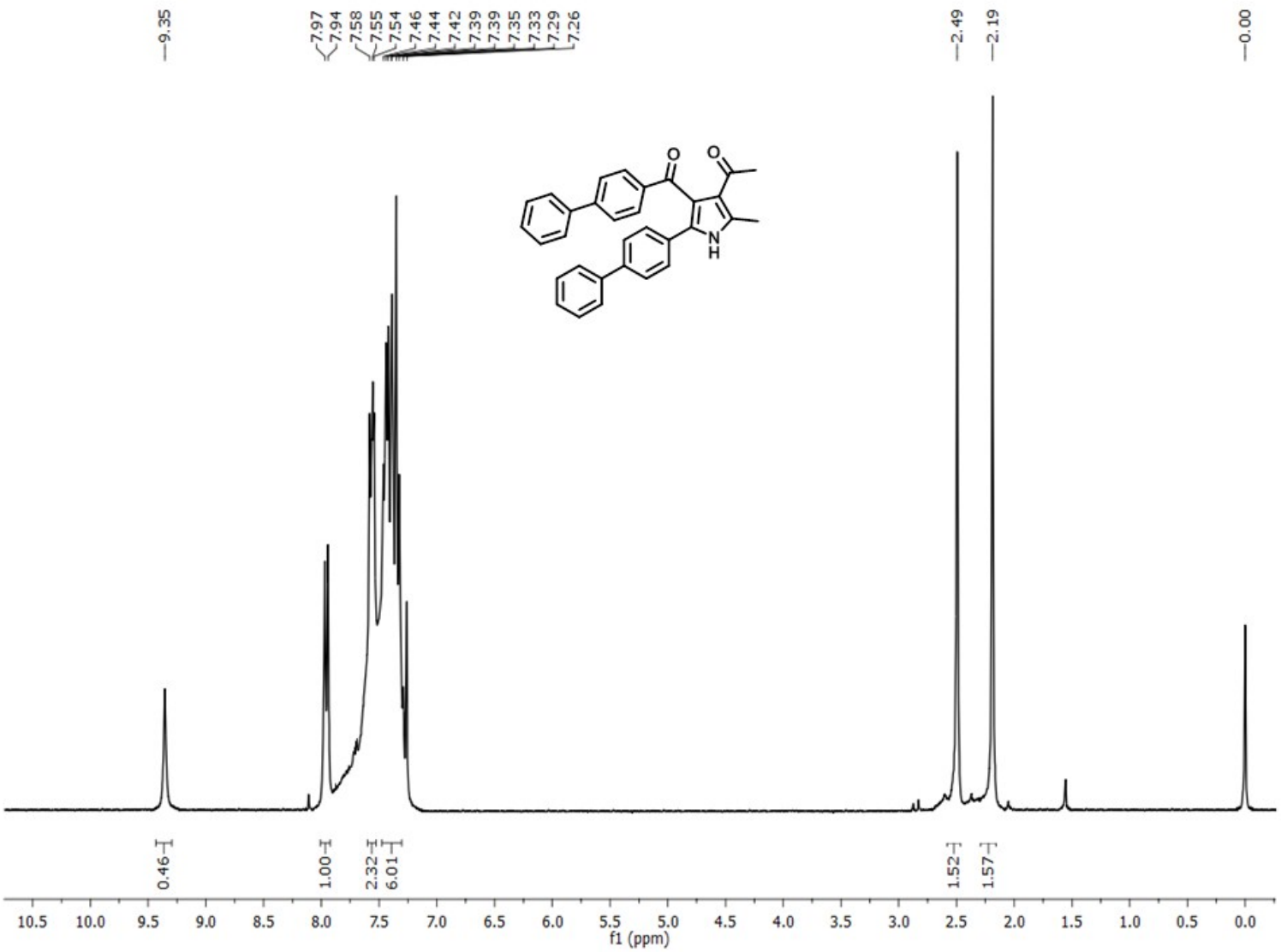


Figure 17. ^{1}H NMR spectrum of compound **2i**

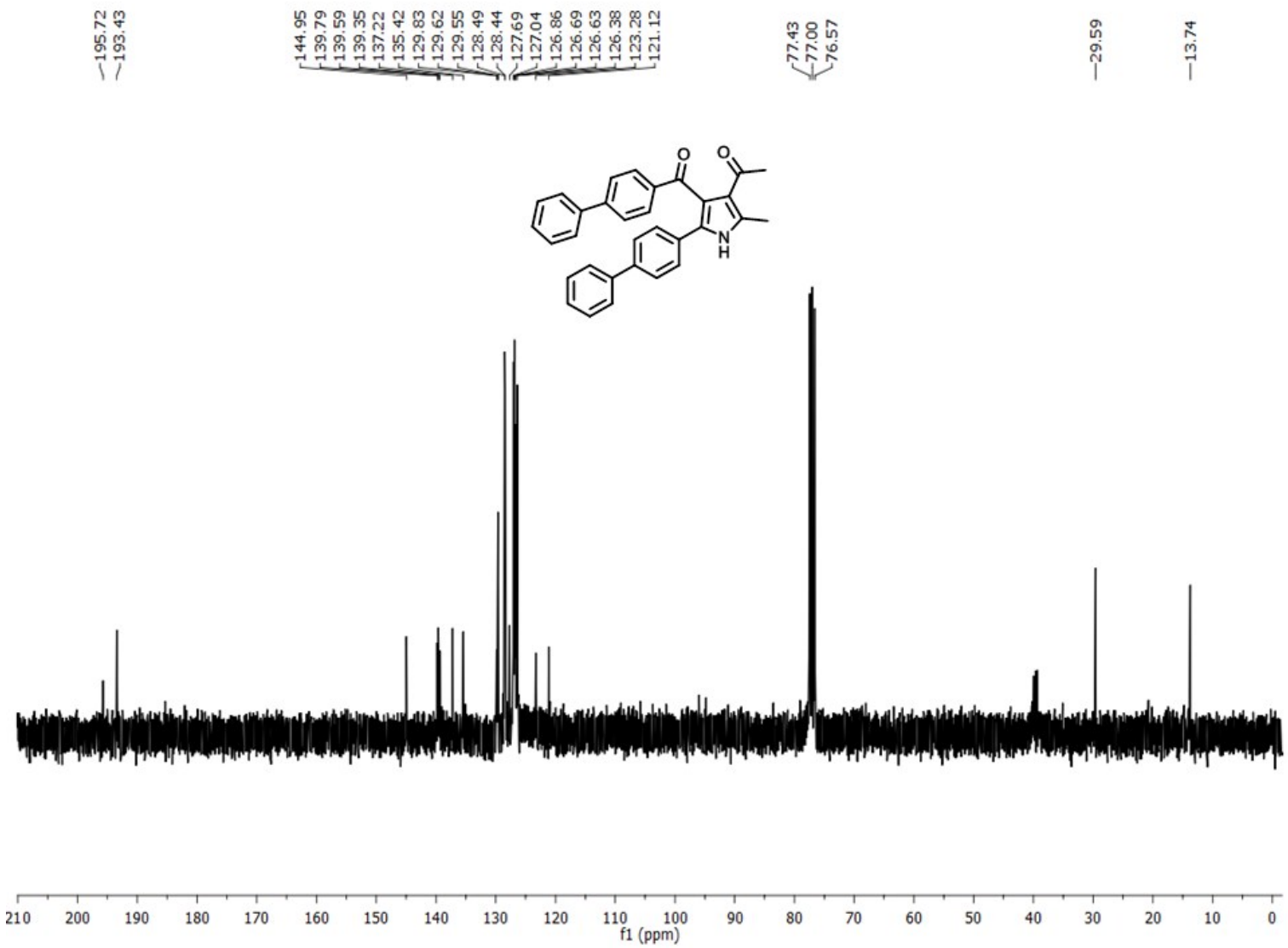


Figure 18. ^{13}C NMR spectrum of compound **2i**

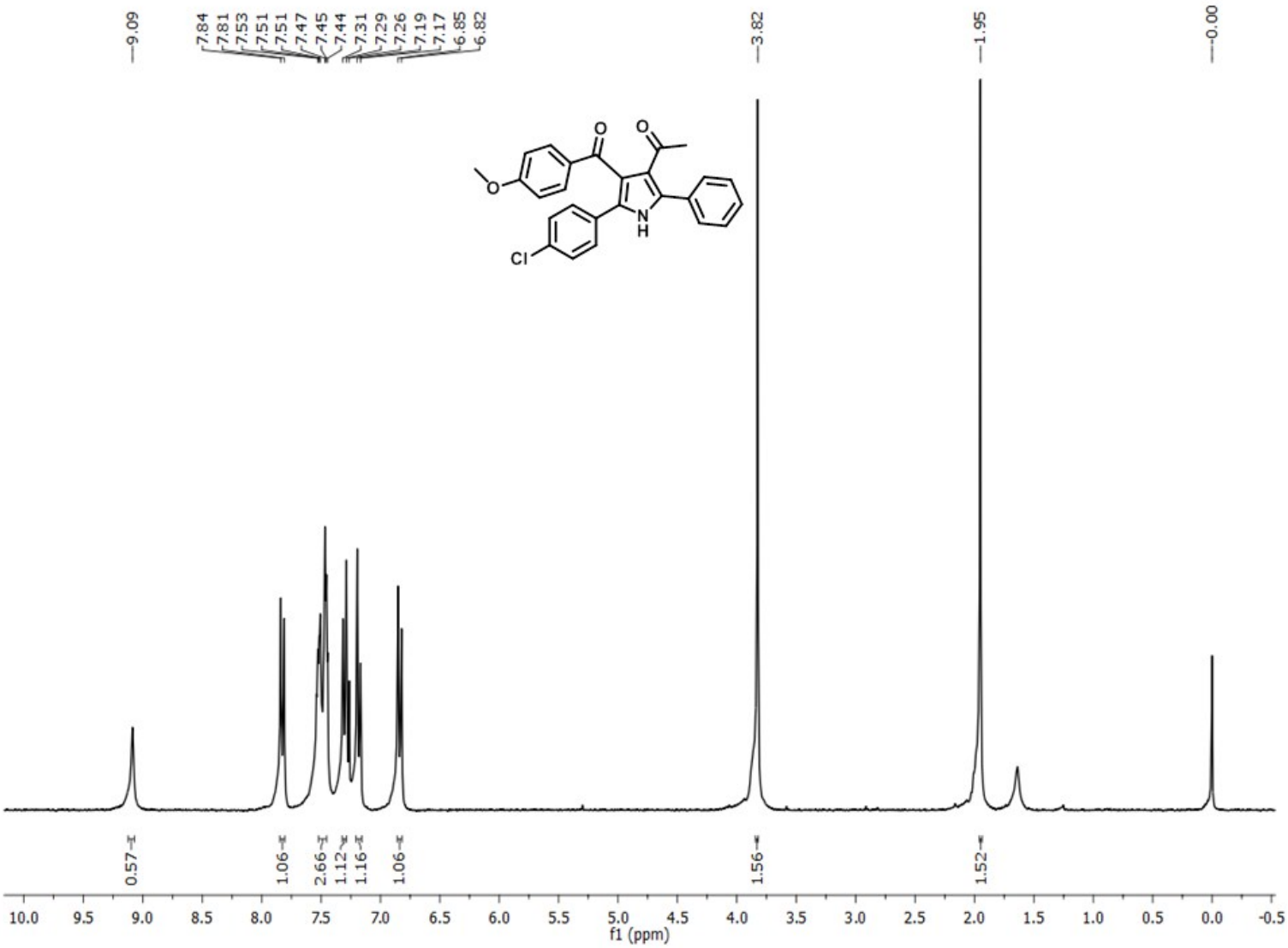


Figure 19. ^{1}H NMR spectrum of compound **2j**

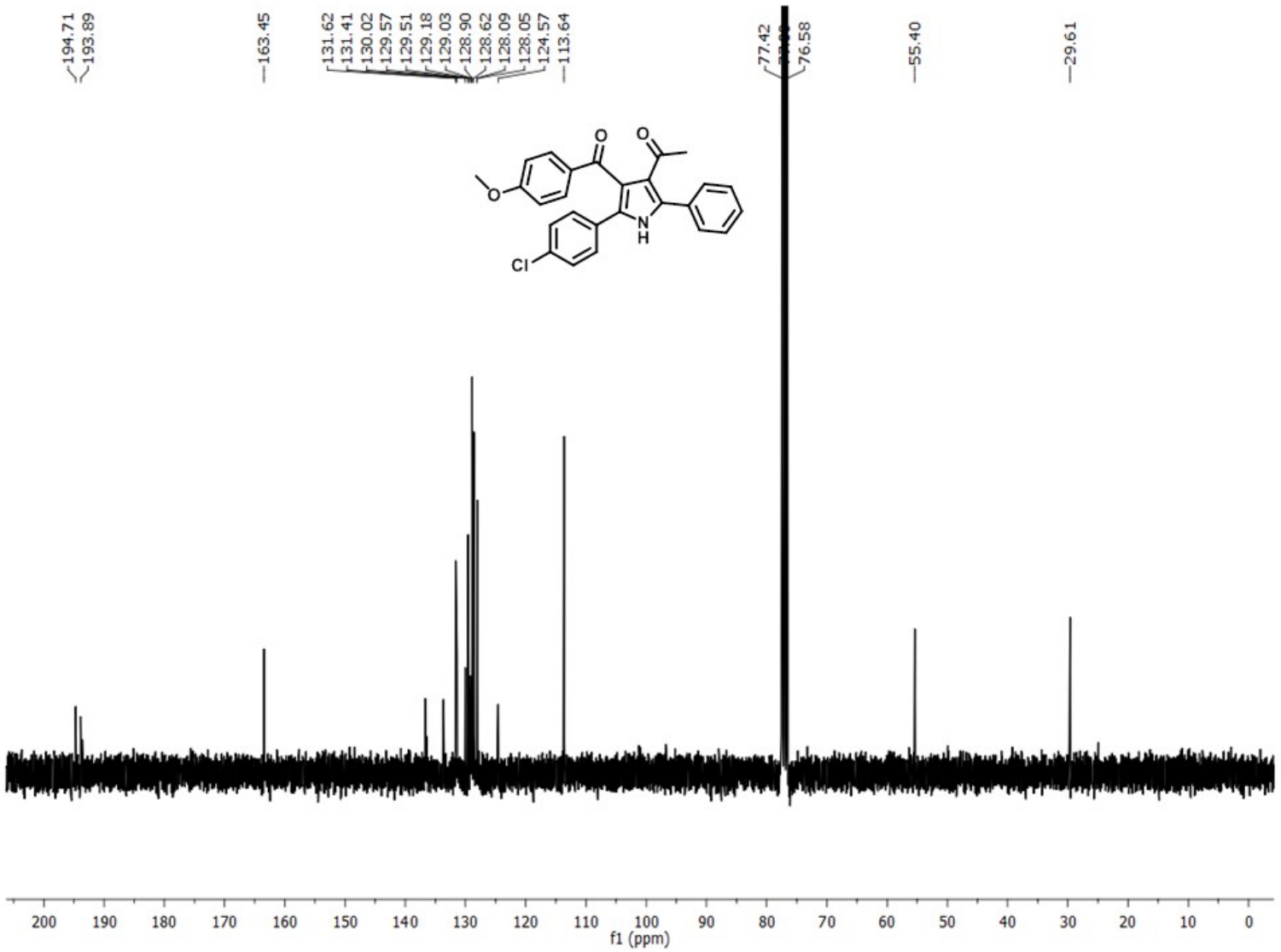


Figure 20. ^{13}C NMR spectrum of compound **2j**

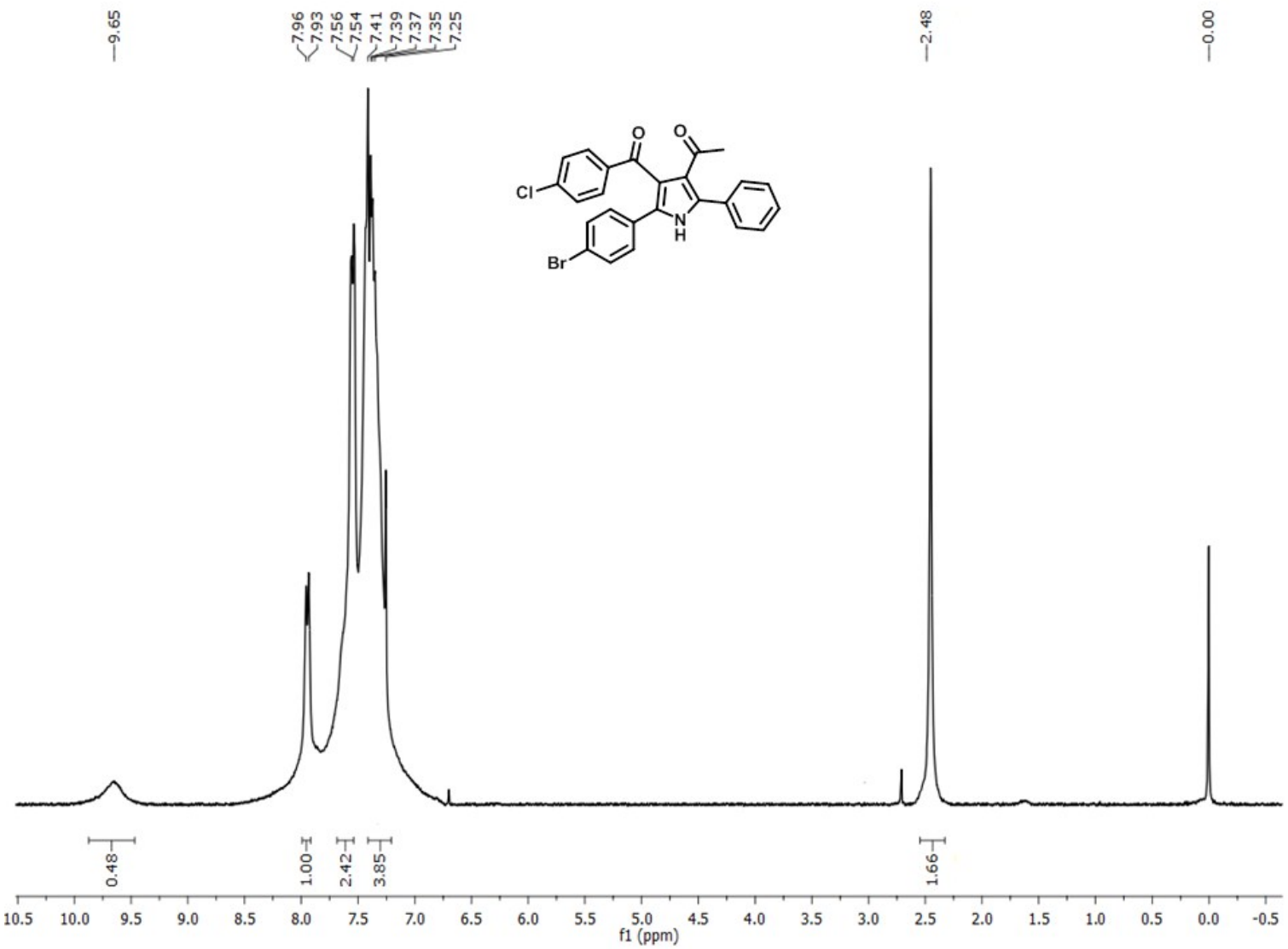


Figure 21. ^{1}H NMR spectrum of compound **2k**

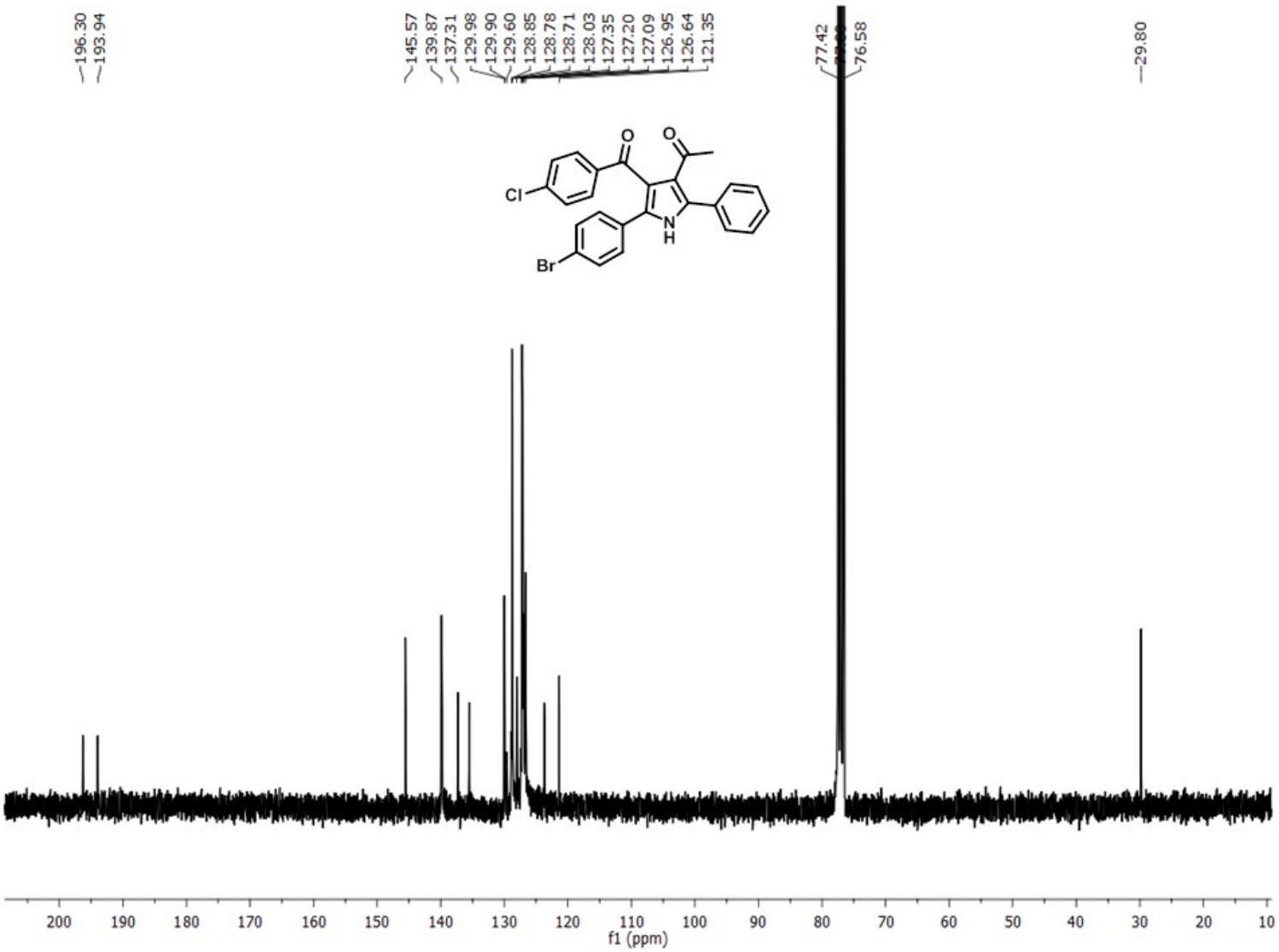


Figure 22. ^{13}C NMR spectrum of compound **2k**

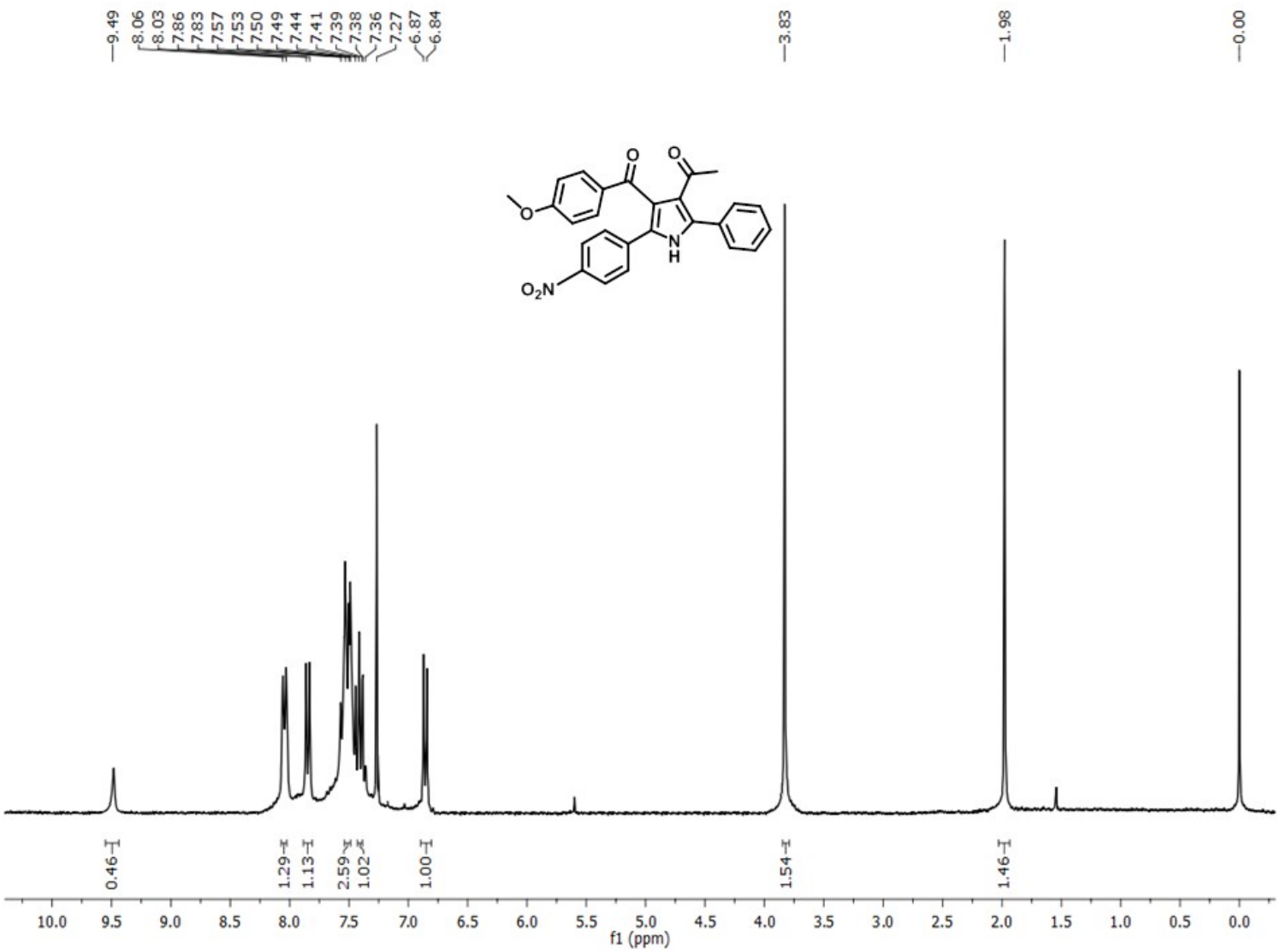


Figure 23. ^{1}H NMR spectrum of compound **2l**

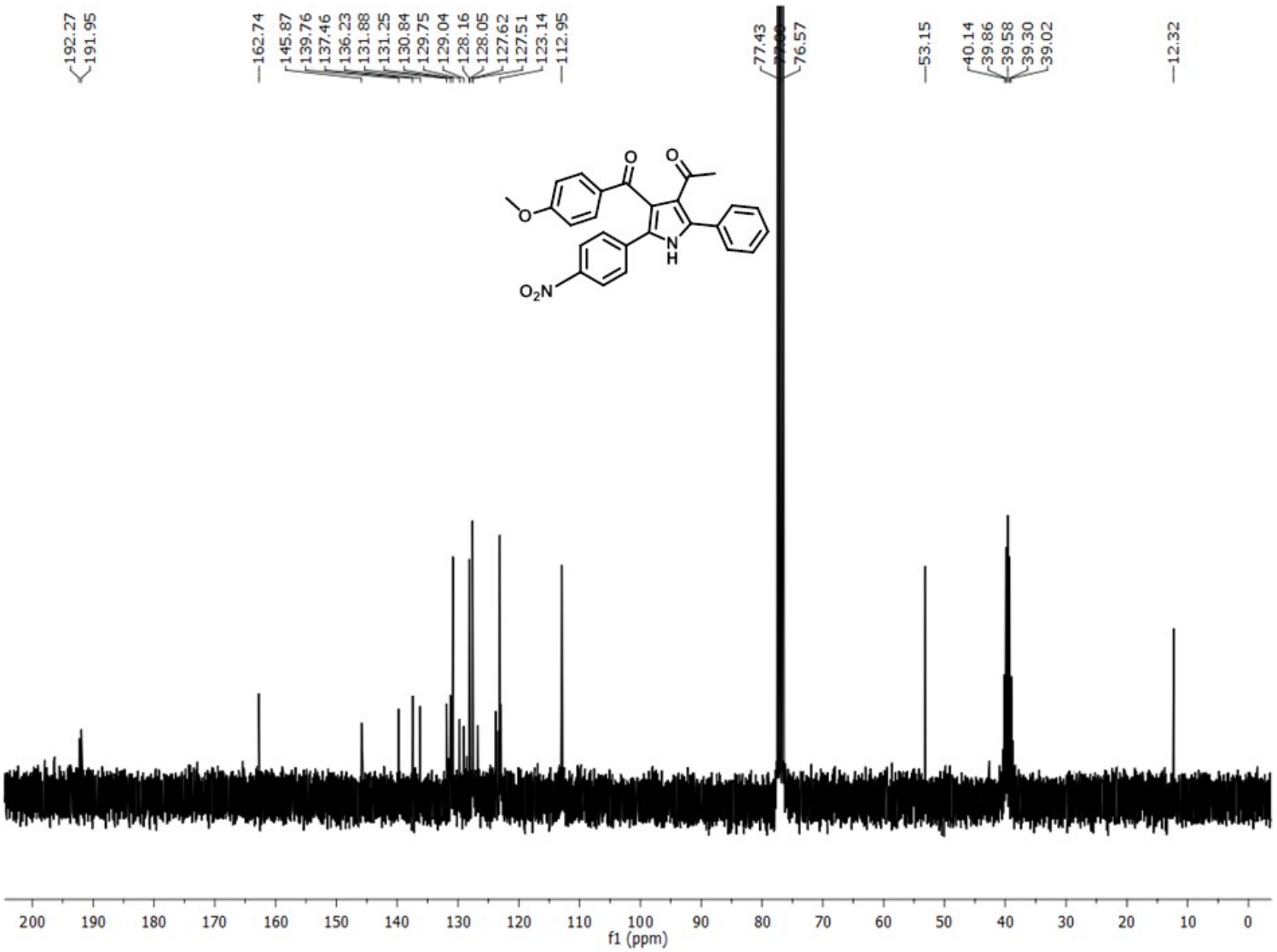


Figure 24. ^{13}C NMR spectrum of compound **2l**

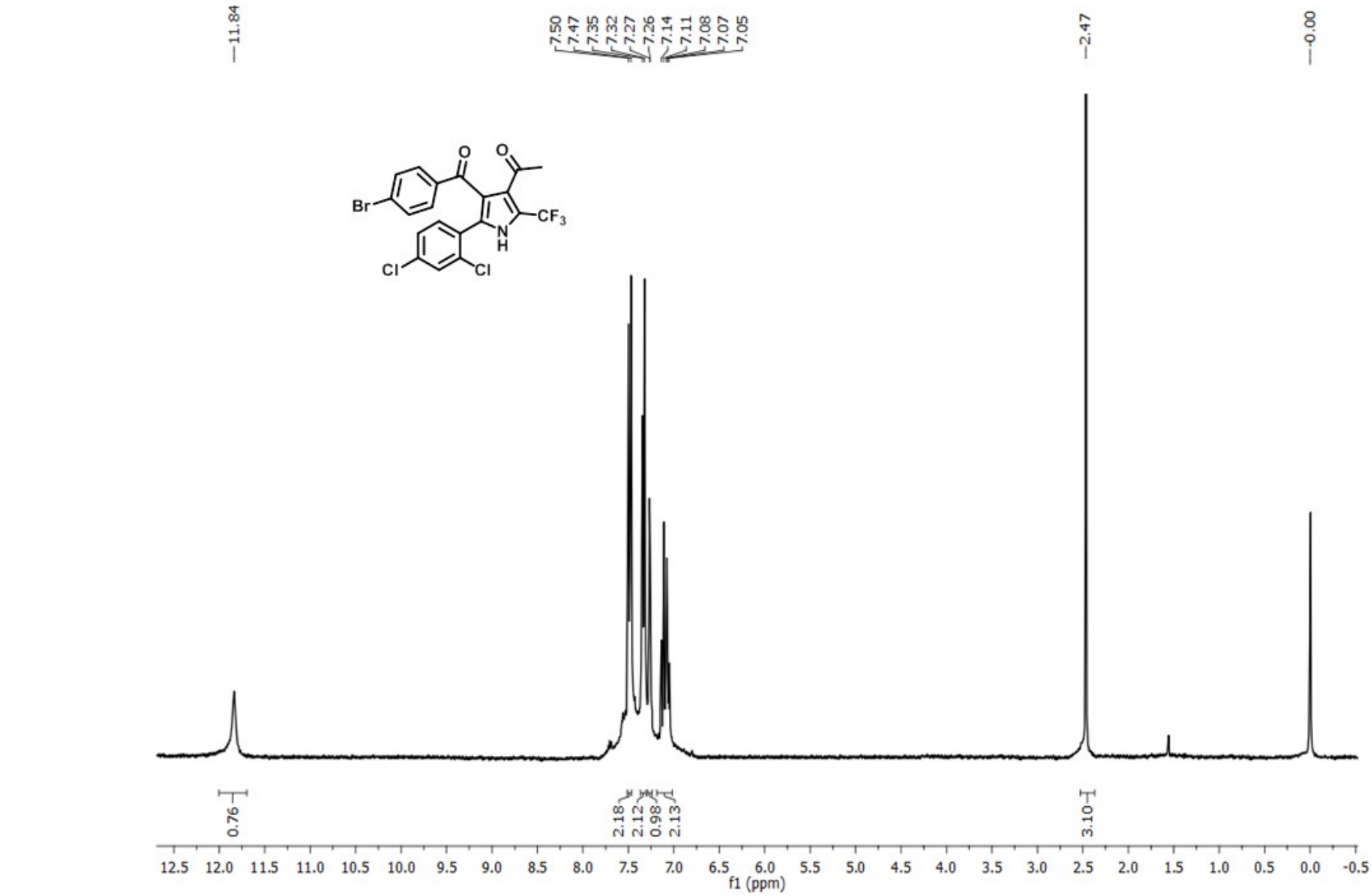


Figure 25. ^{1}H NMR spectrum of compound **2m**

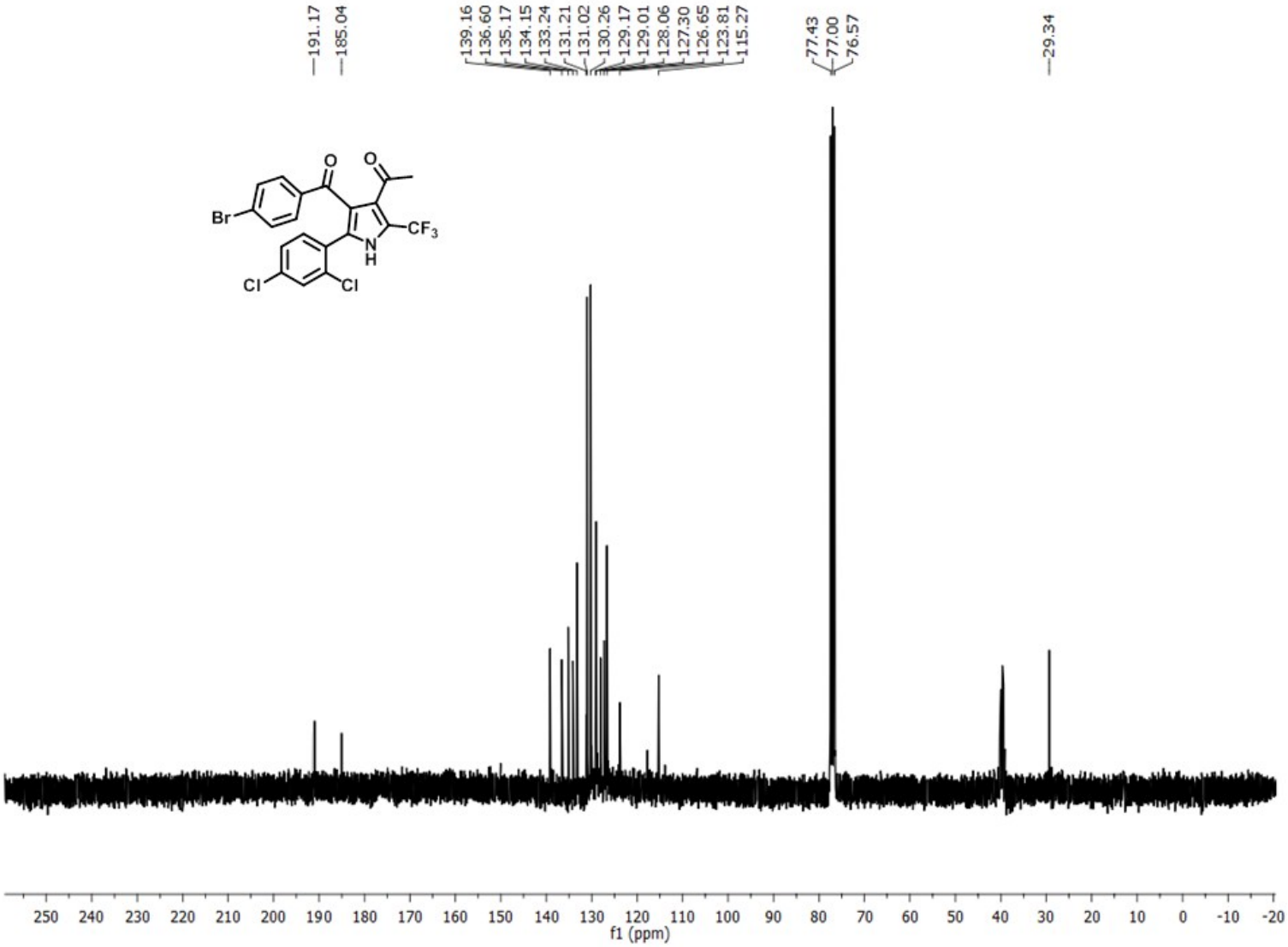


Figure 26. ^{13}C NMR spectrum of compound **2m**

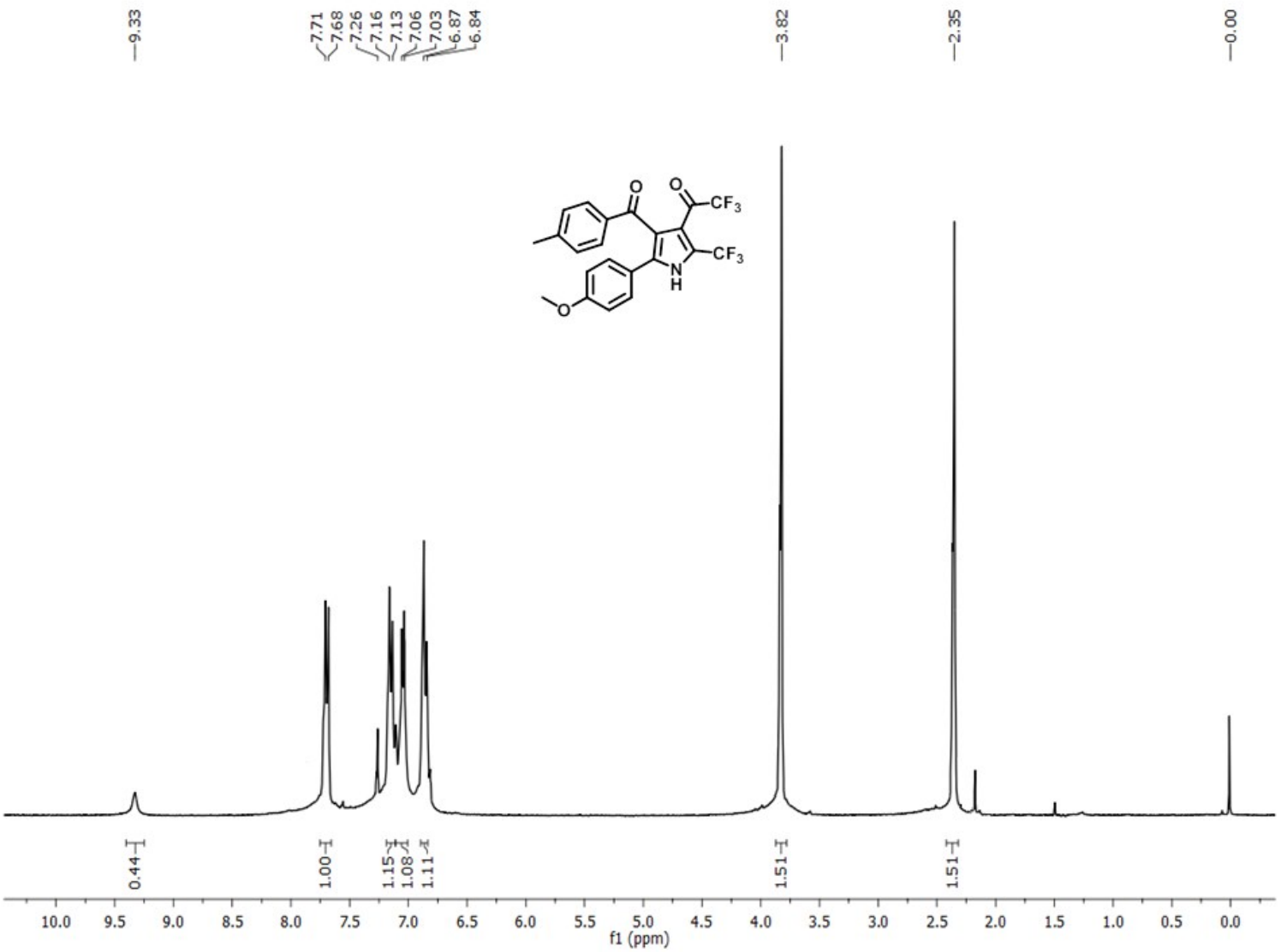


Figure 27. ^{1}H NMR spectrum of compound **2n**

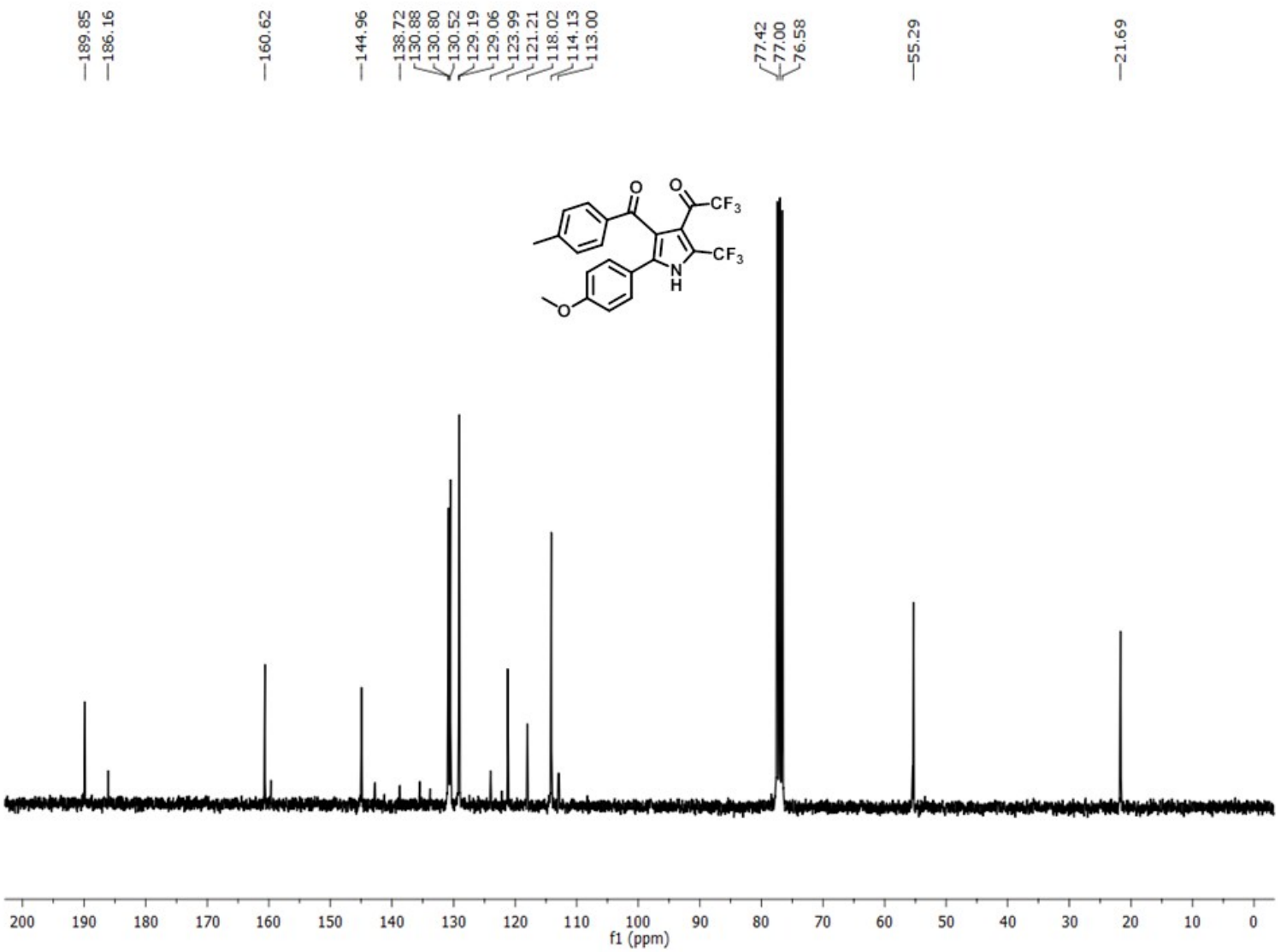


Figure 28. ^{13}C NMR spectrum of compound **2n**

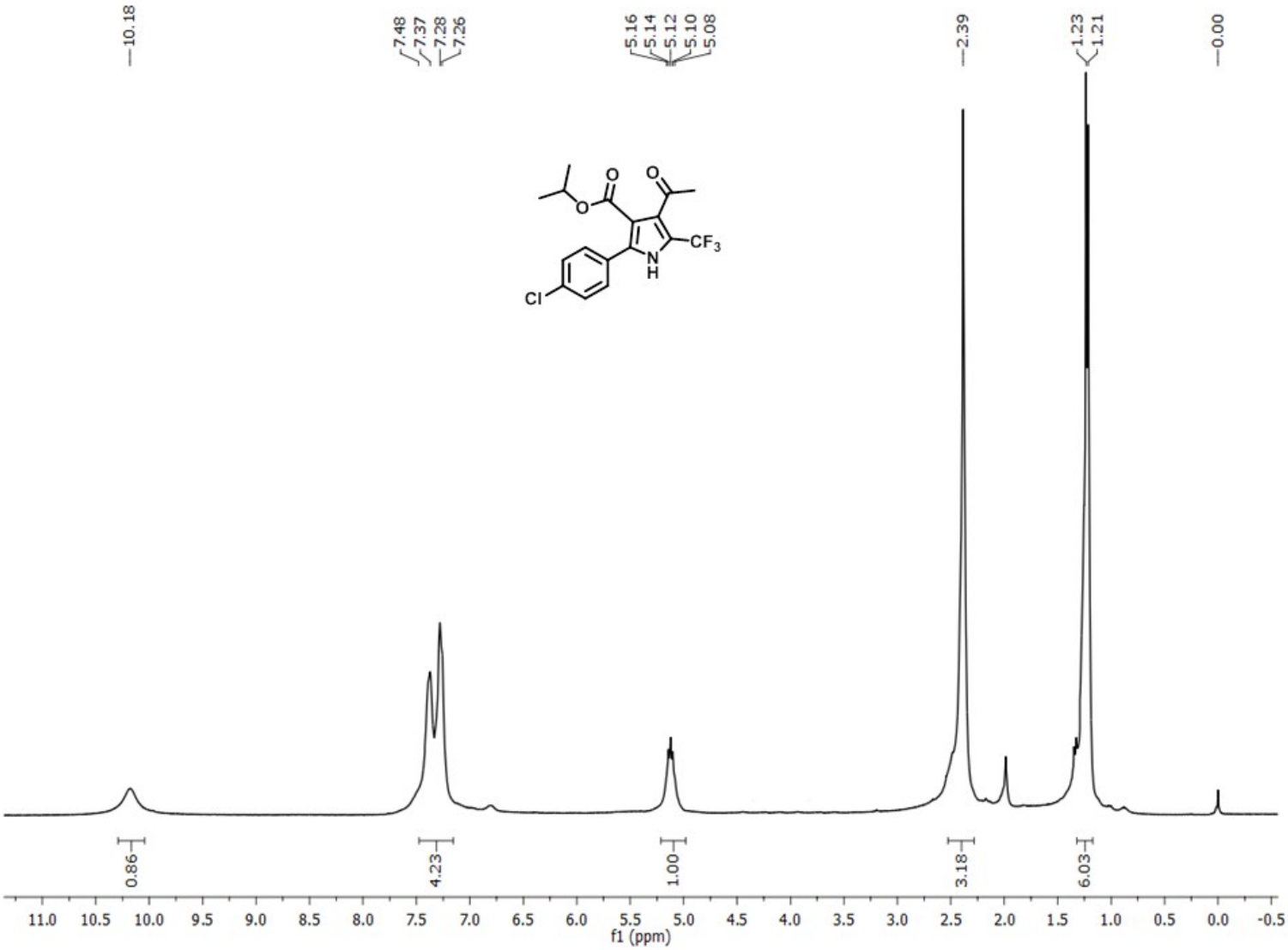


Figure 29. ^{1}H NMR spectrum of compound **2o**

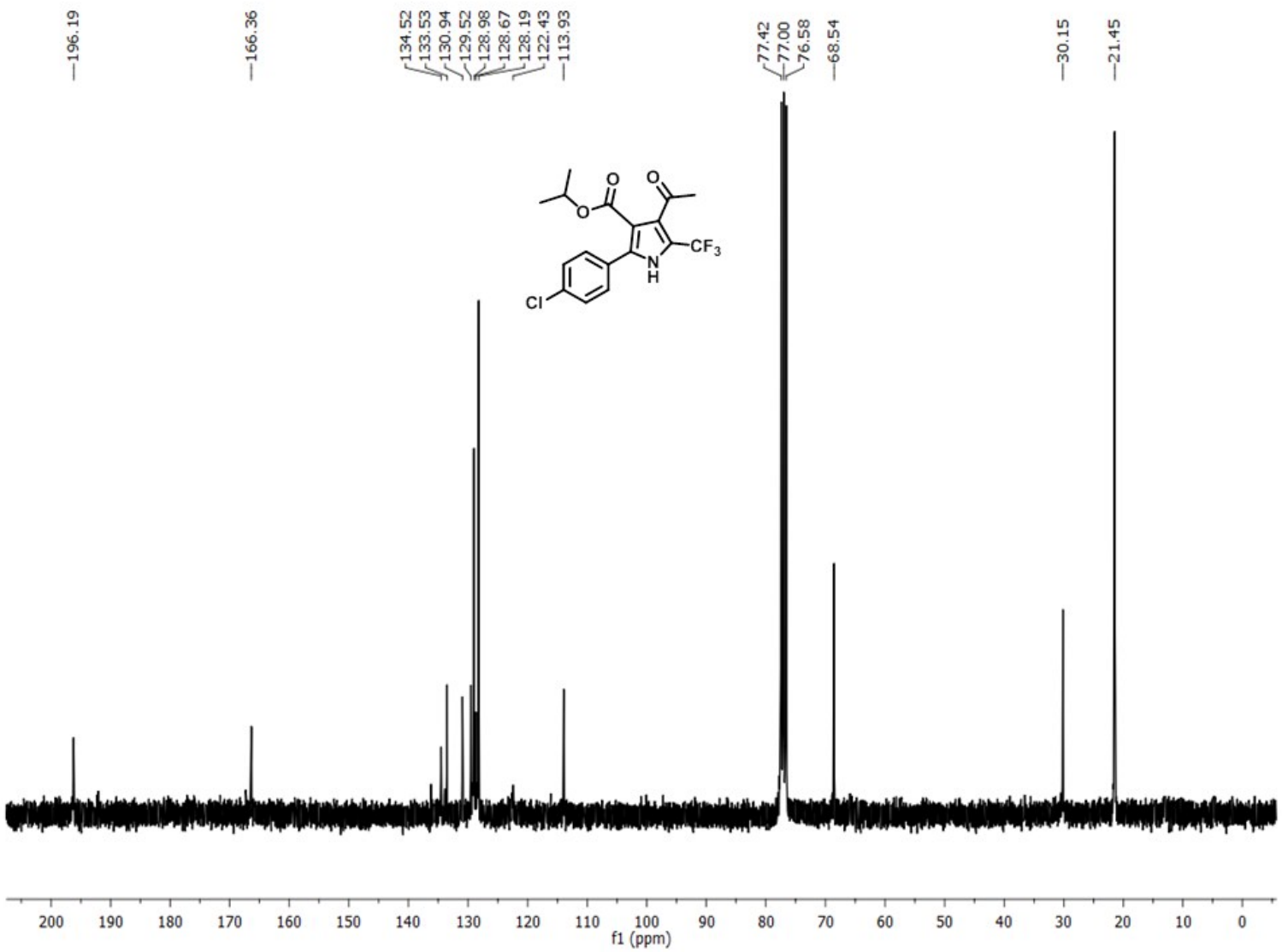


Figure 30. ^{13}C NMR spectrum of compound **2o**

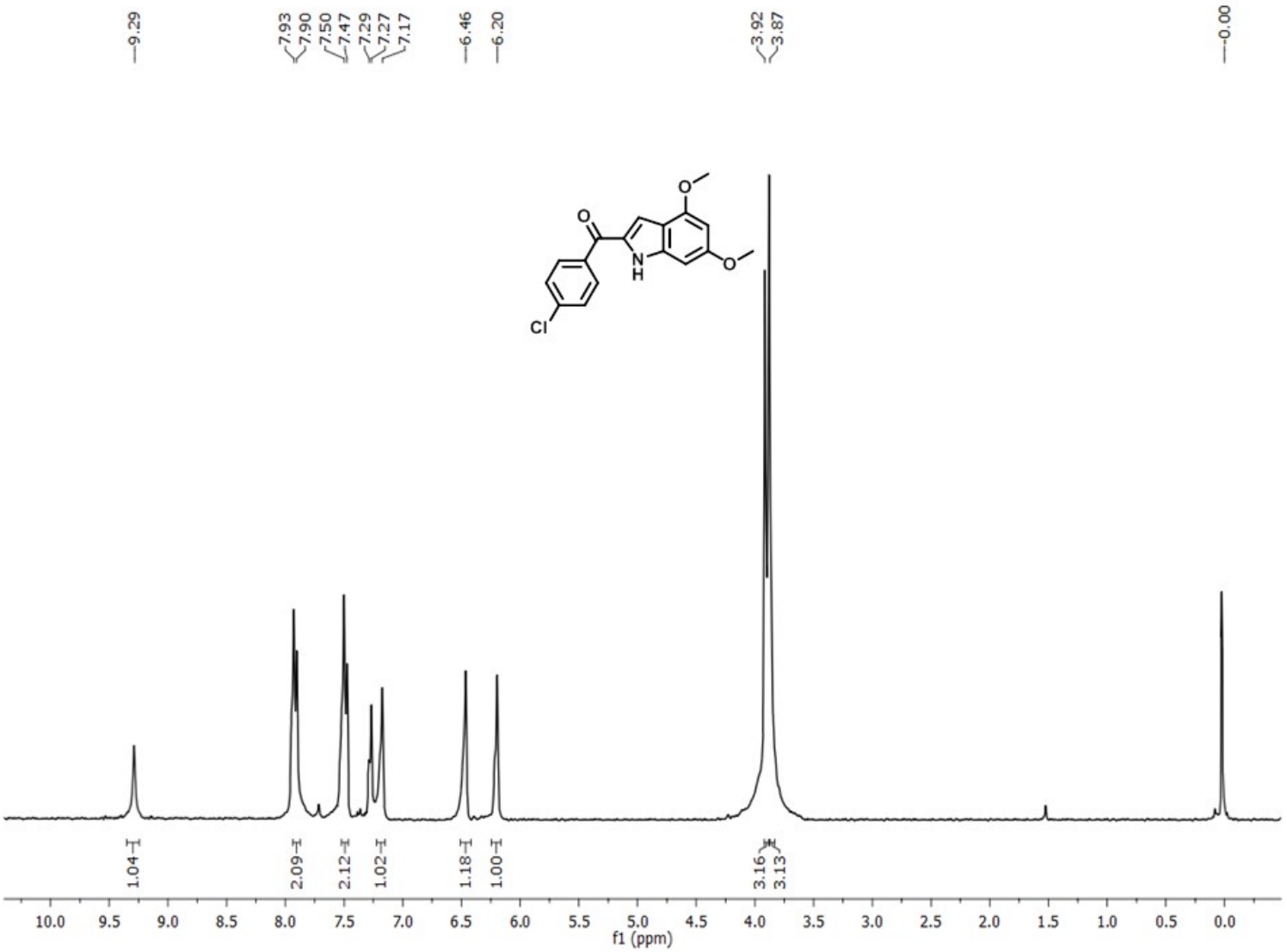


Figure 31. ^{1}H NMR spectrum of compound **3a**

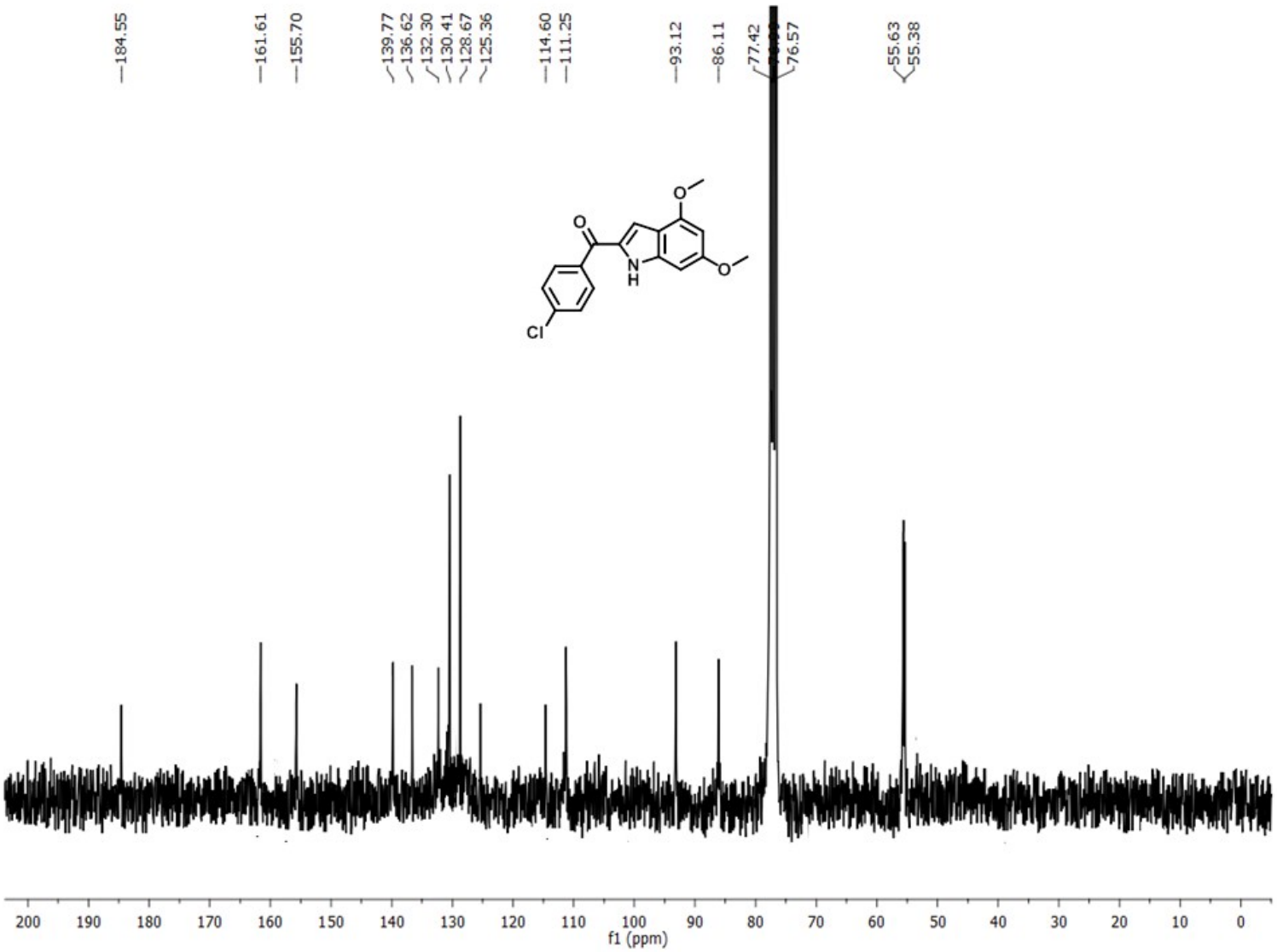


Figure 32. ^{13}C NMR spectrum of compound **3a**

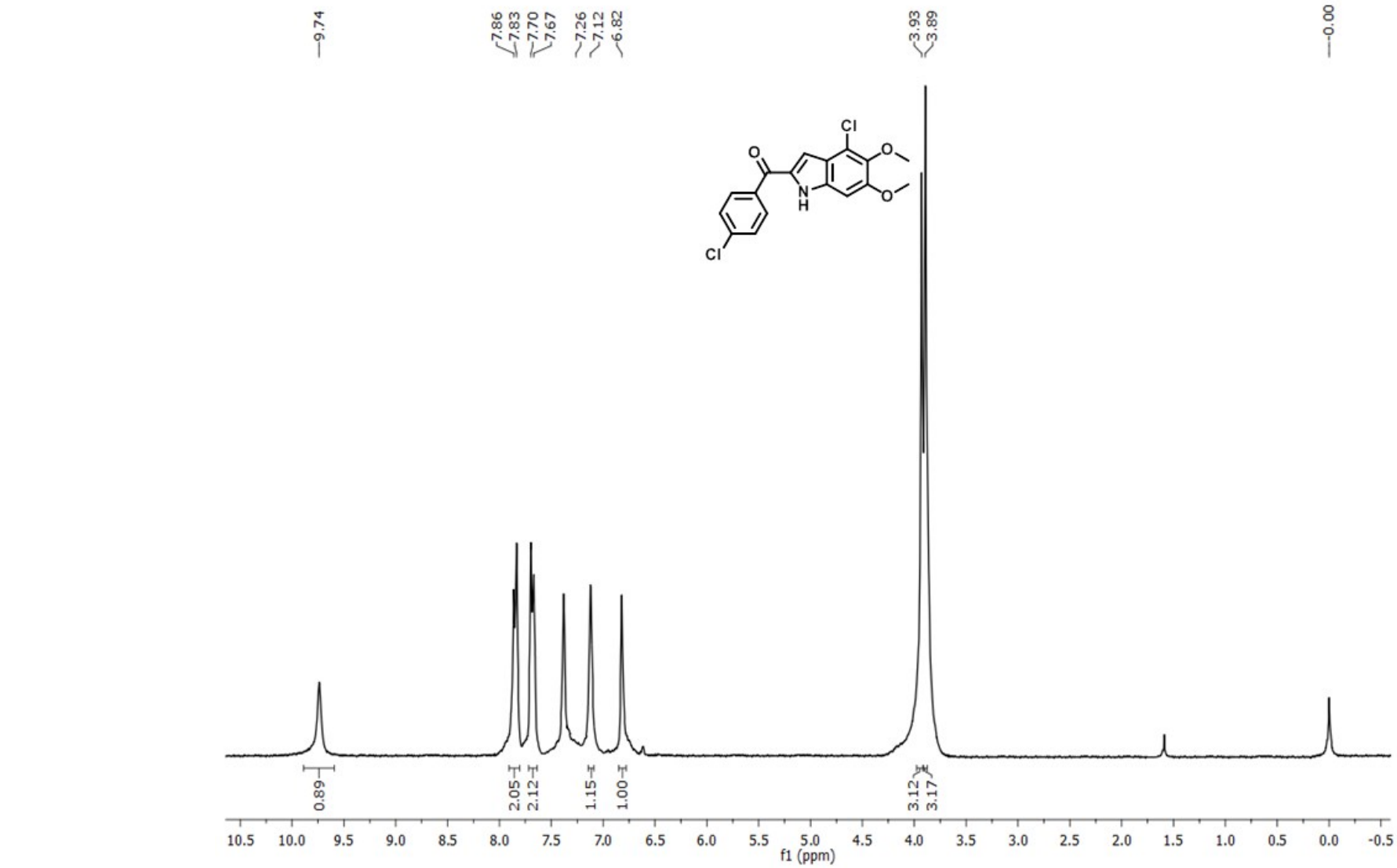


Figure 33. ^{1}H NMR spectrum of compound **3b**

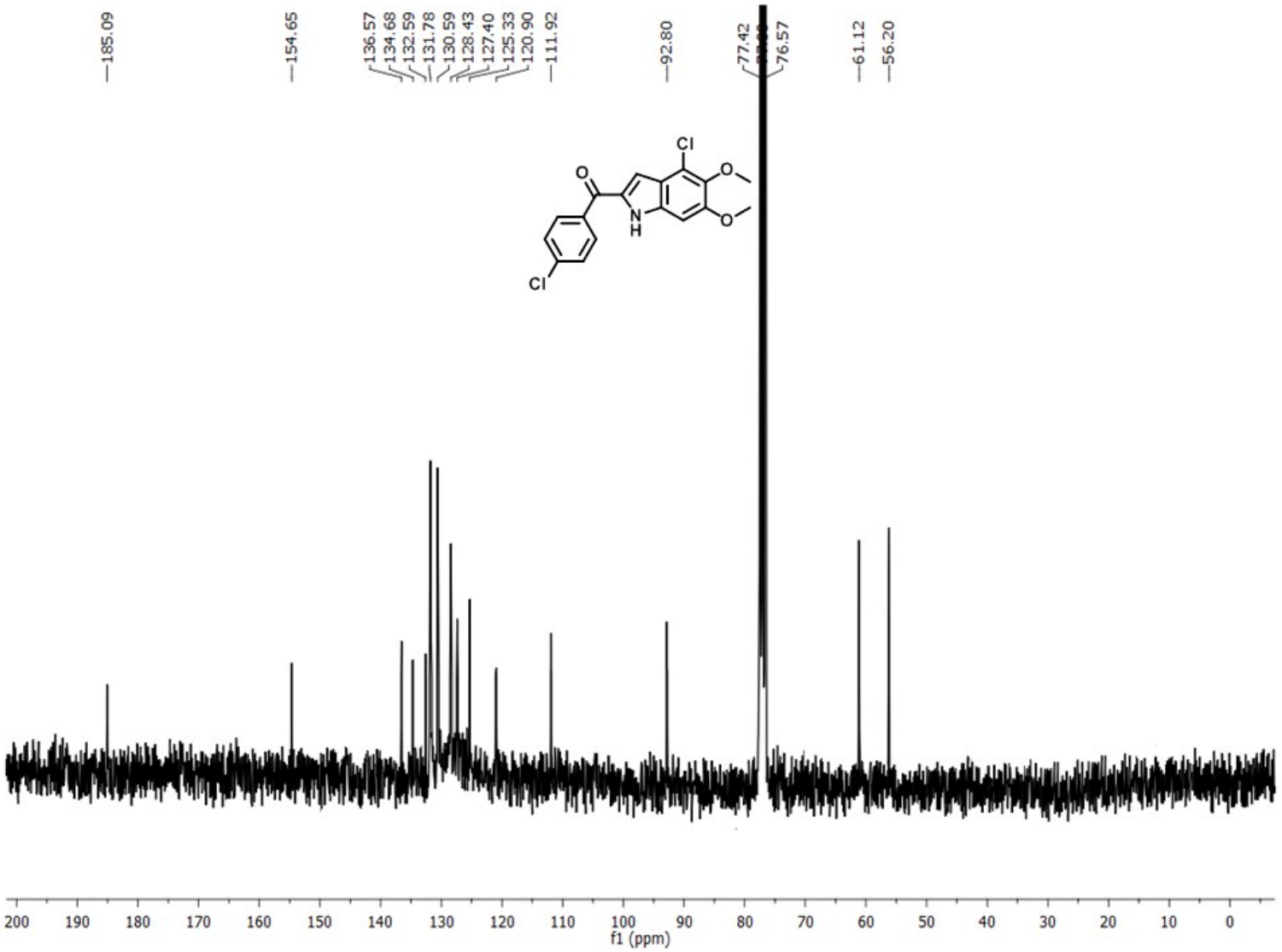


Figure 34. ^{13}C NMR spectrum of compound **3b**

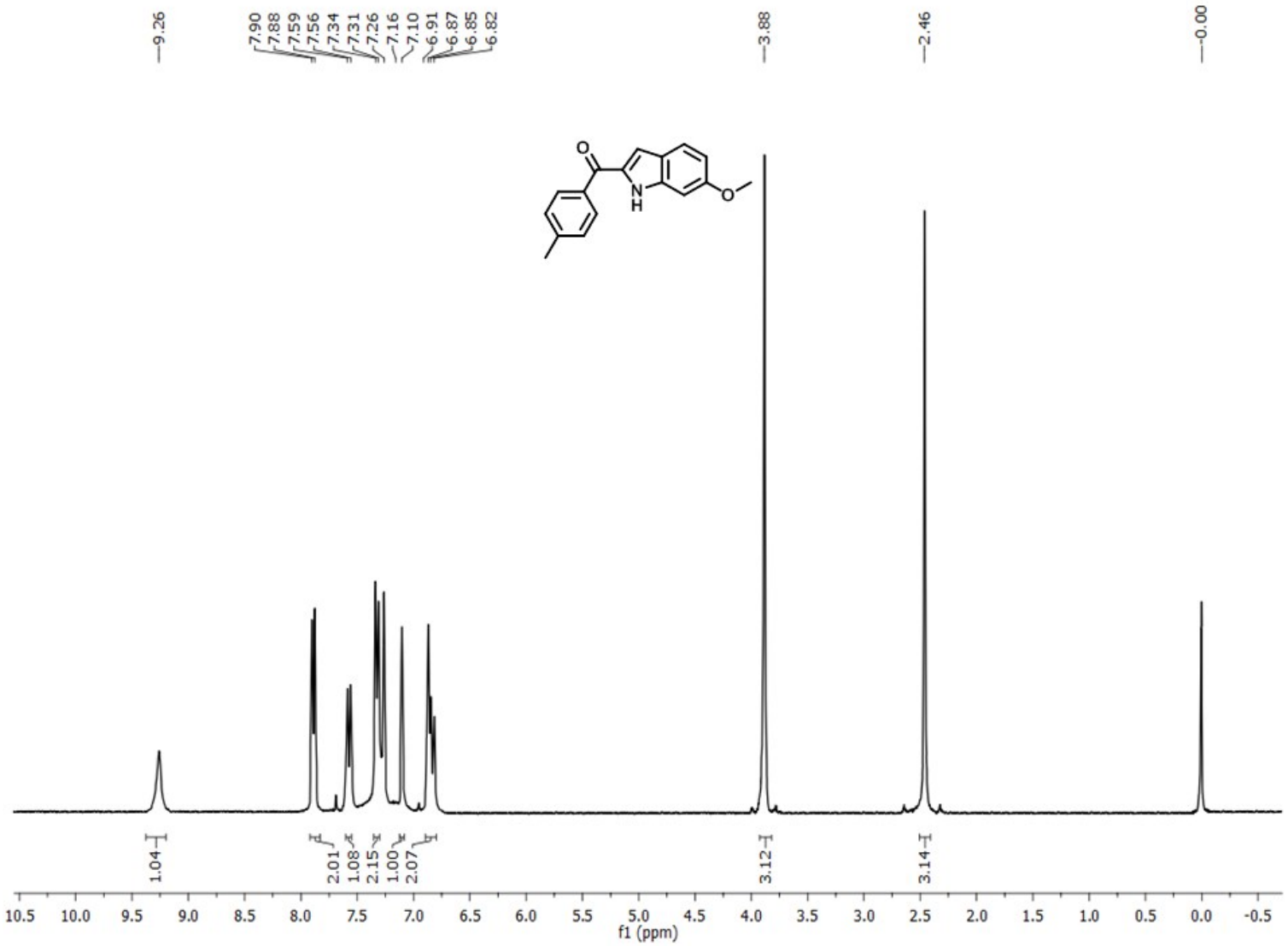


Figure 35. ^{1}H NMR spectrum of compound **3c**

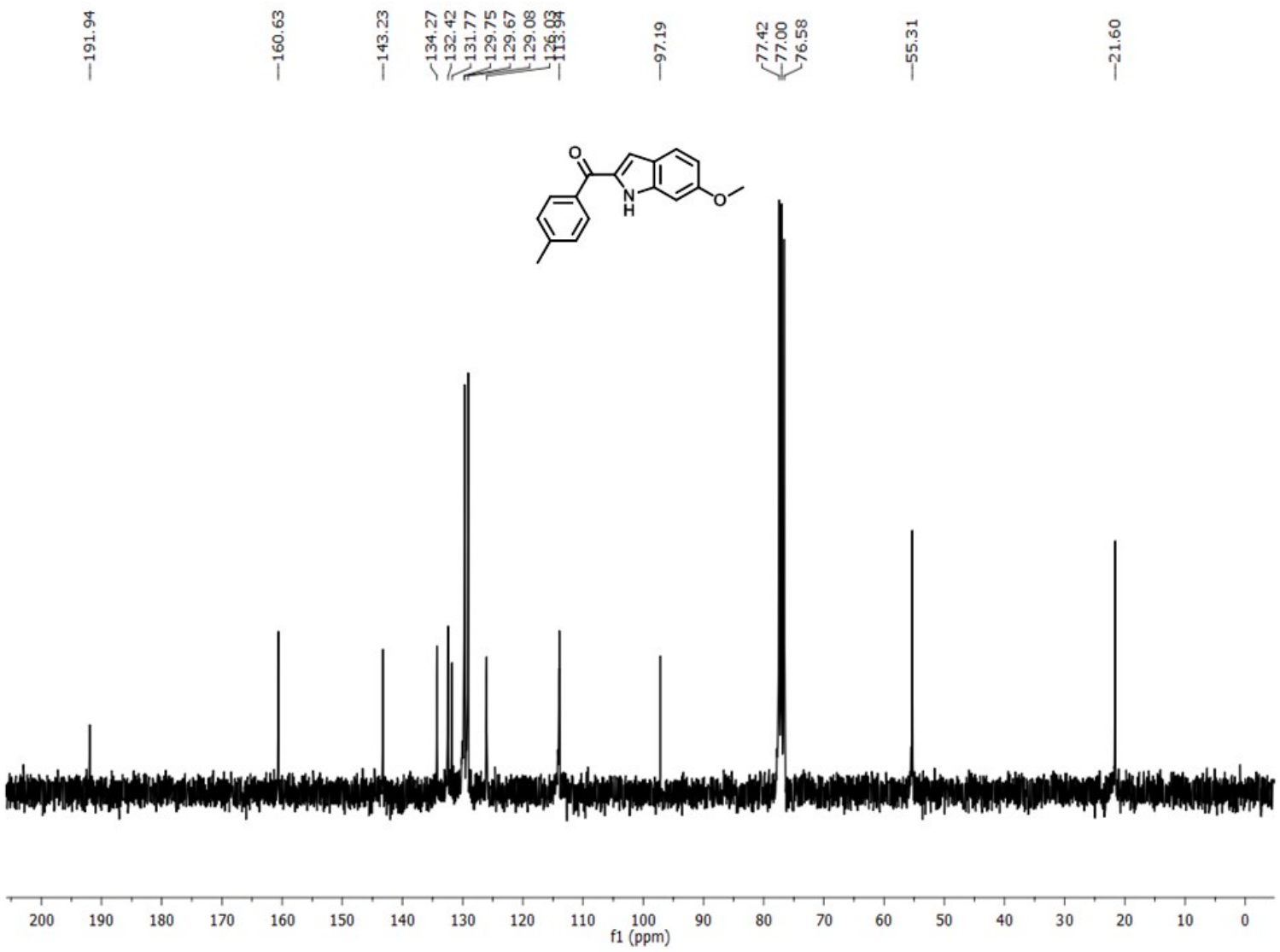


Figure 36. ^{13}C NMR spectrum of compound **3c**

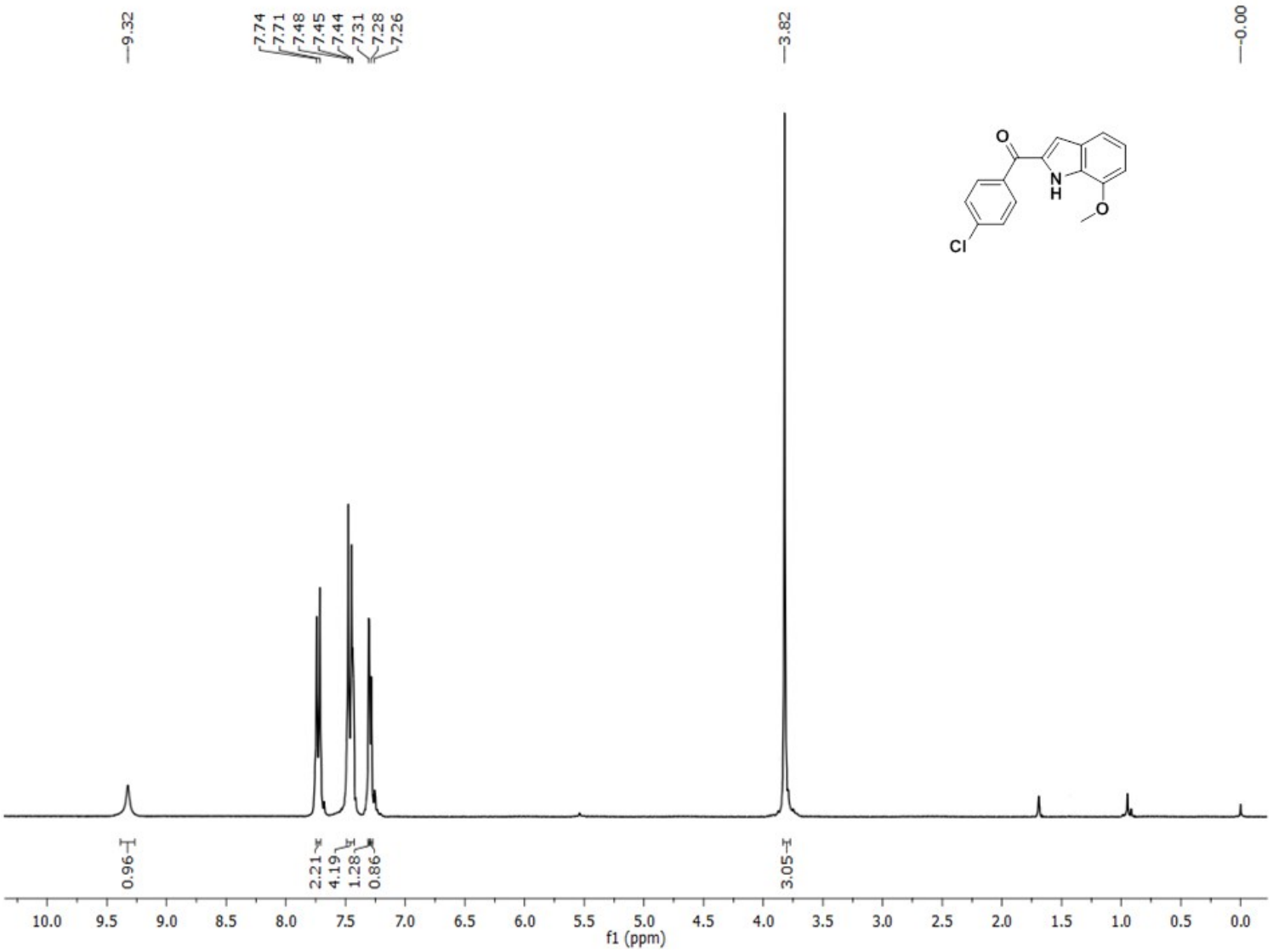


Figure 37. ^{1}H NMR spectrum of compound **3d**

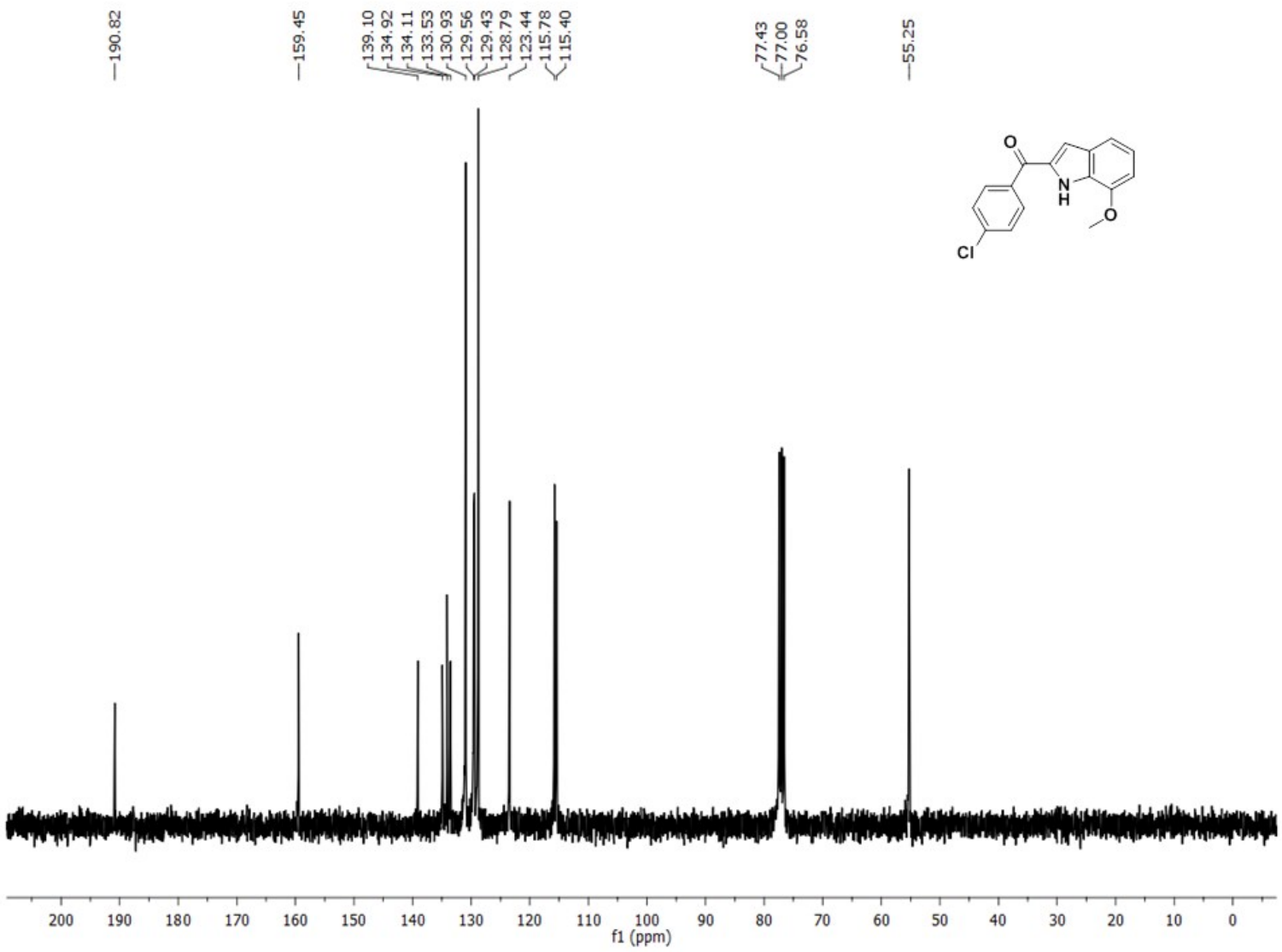


Figure 38. ^{13}C NMR spectrum of compound **3d**

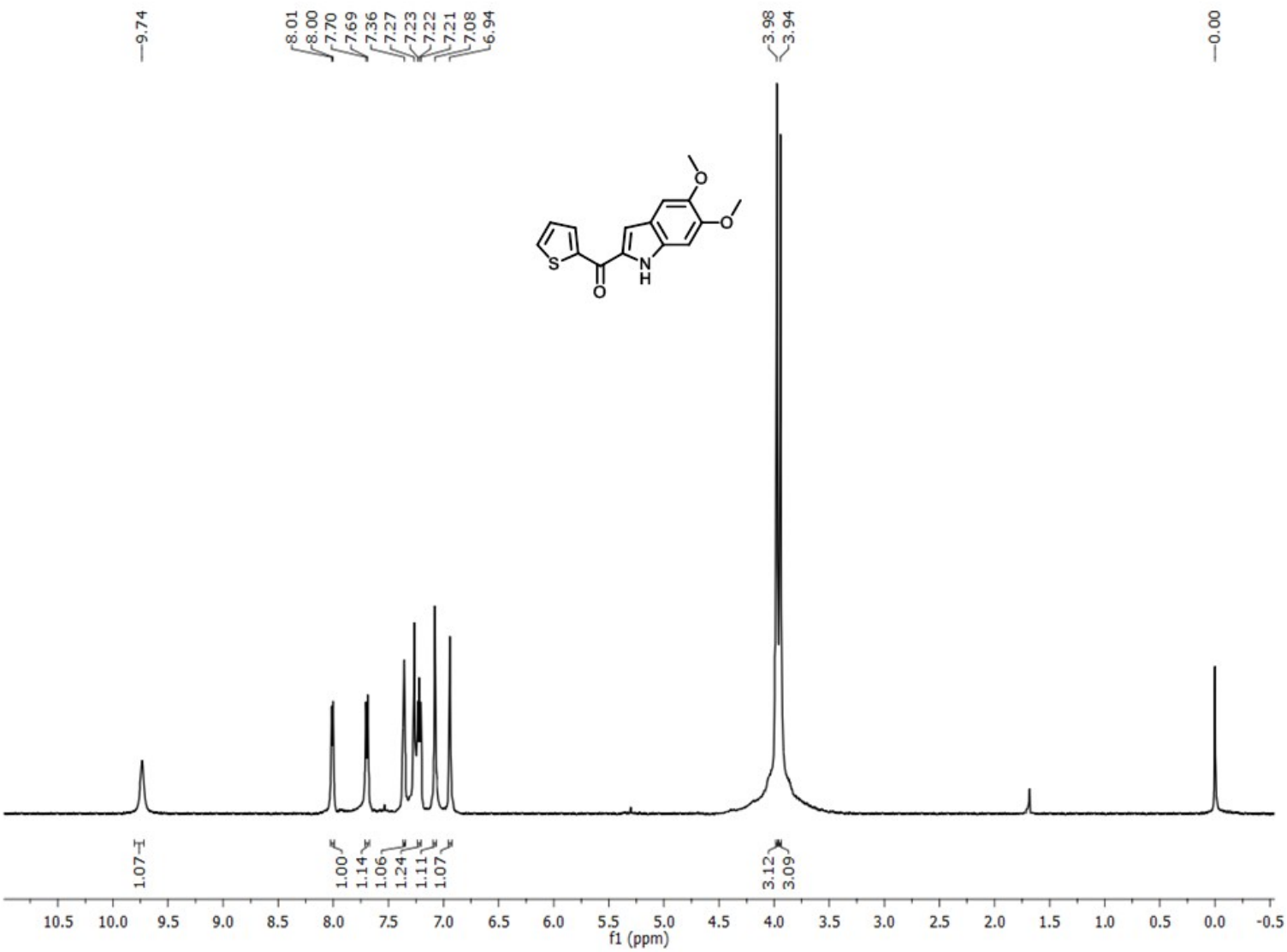


Figure 39. ^{1}H NMR spectrum of compound **3e**

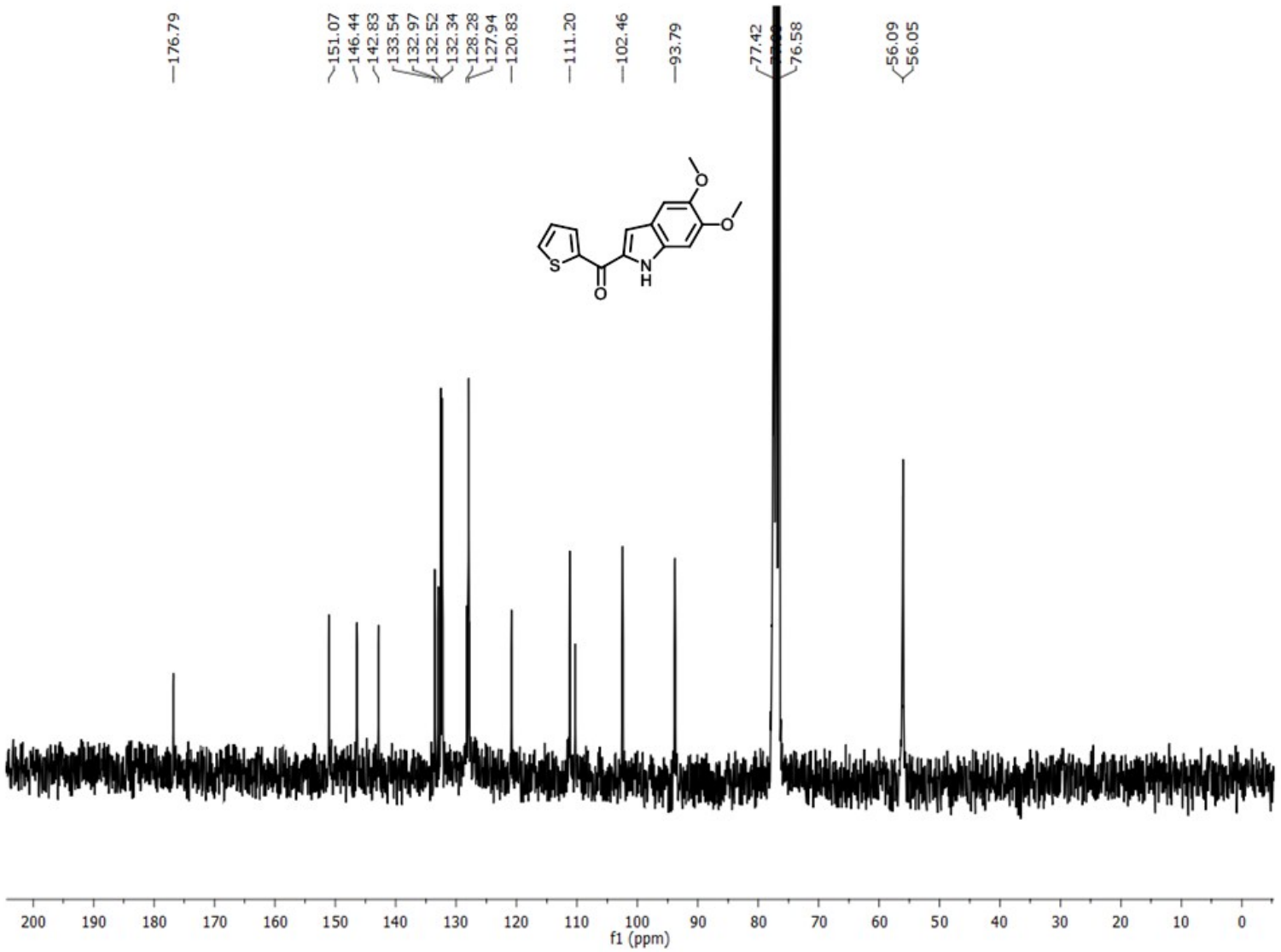


Figure 40. ^{13}C NMR spectrum of compound **3e**

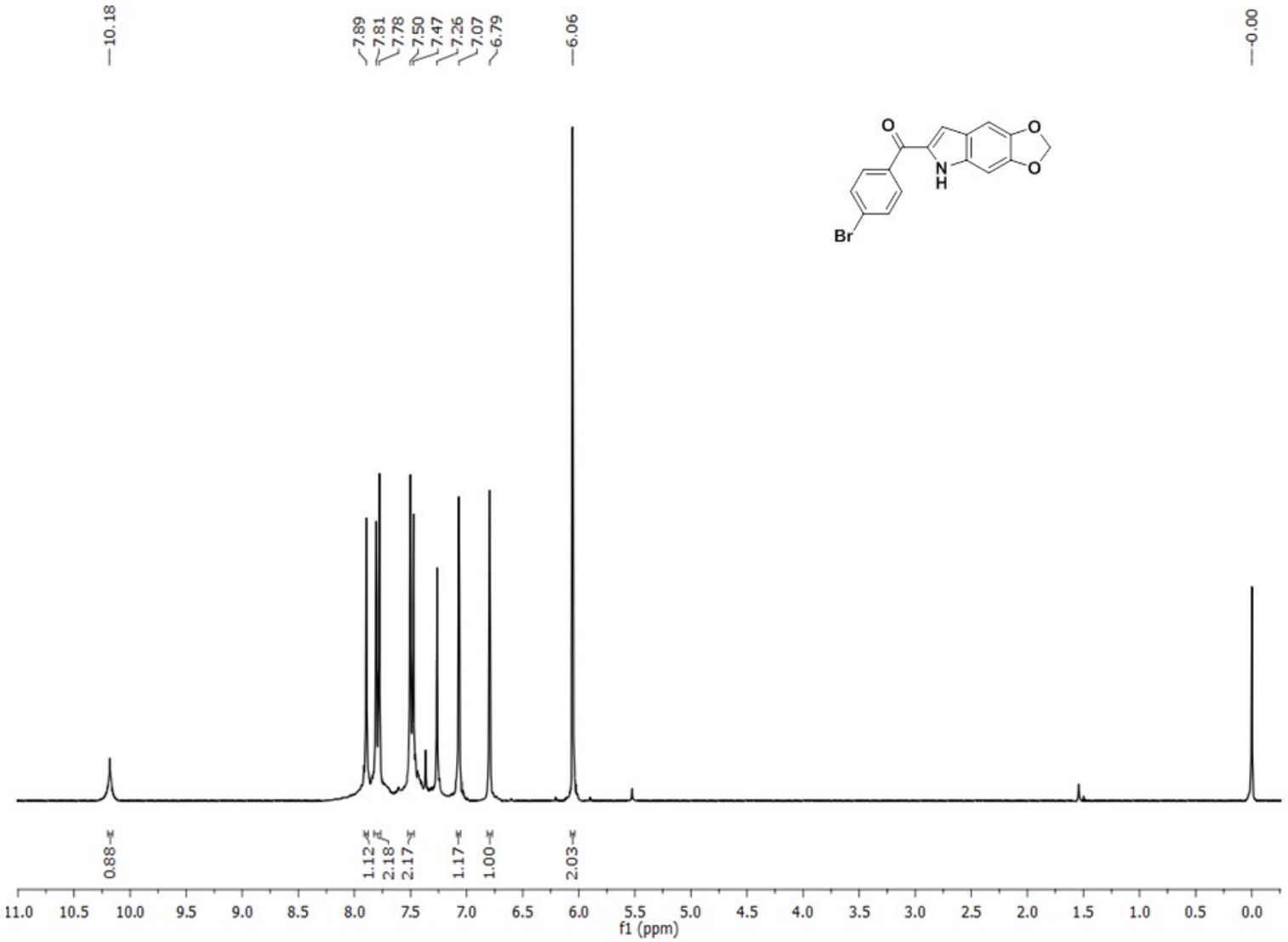


Figure 41. ^{1}H NMR spectrum of compound **3f**

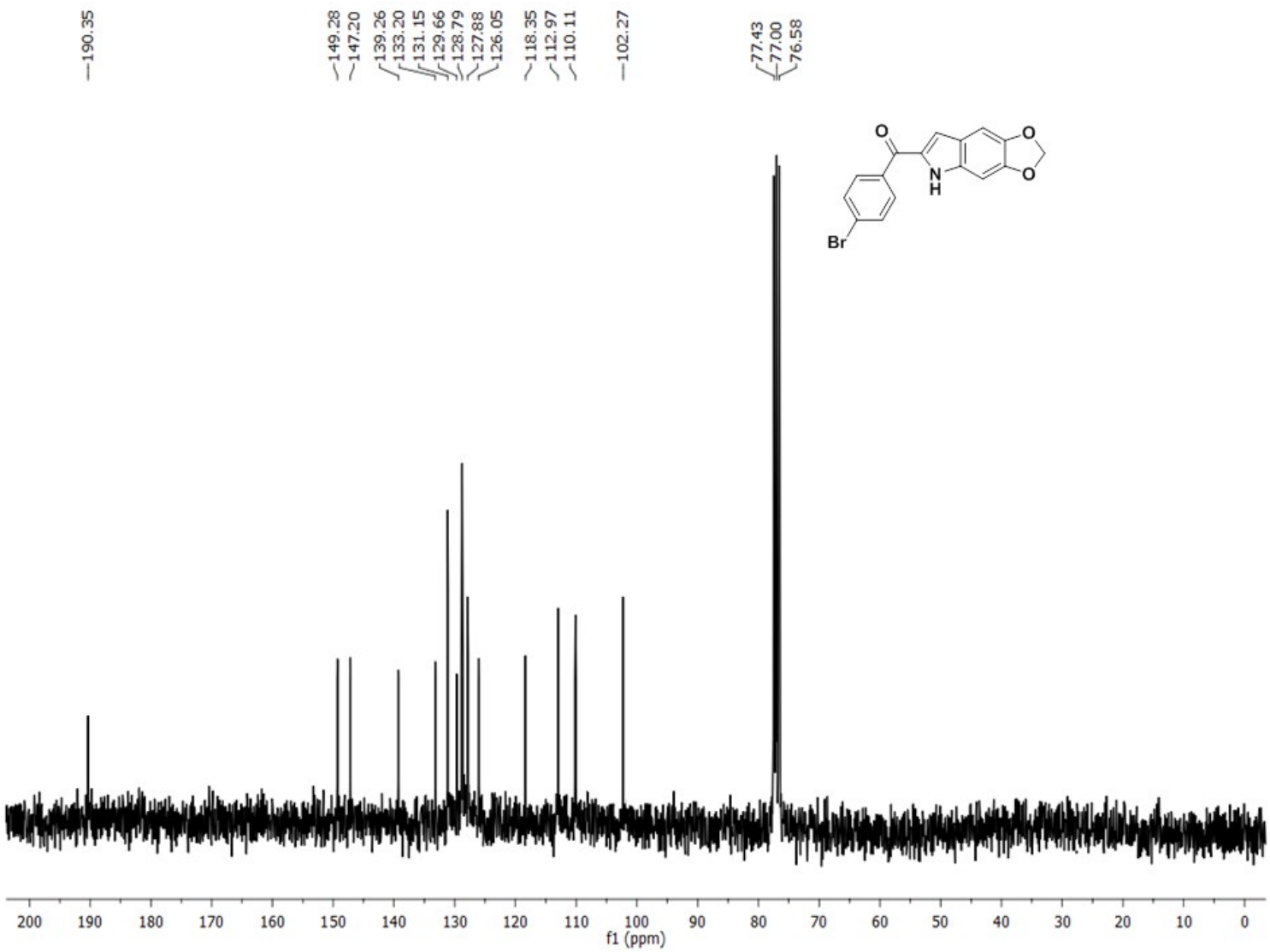


Figure 42. ^{13}C NMR spectrum of compound **3f**

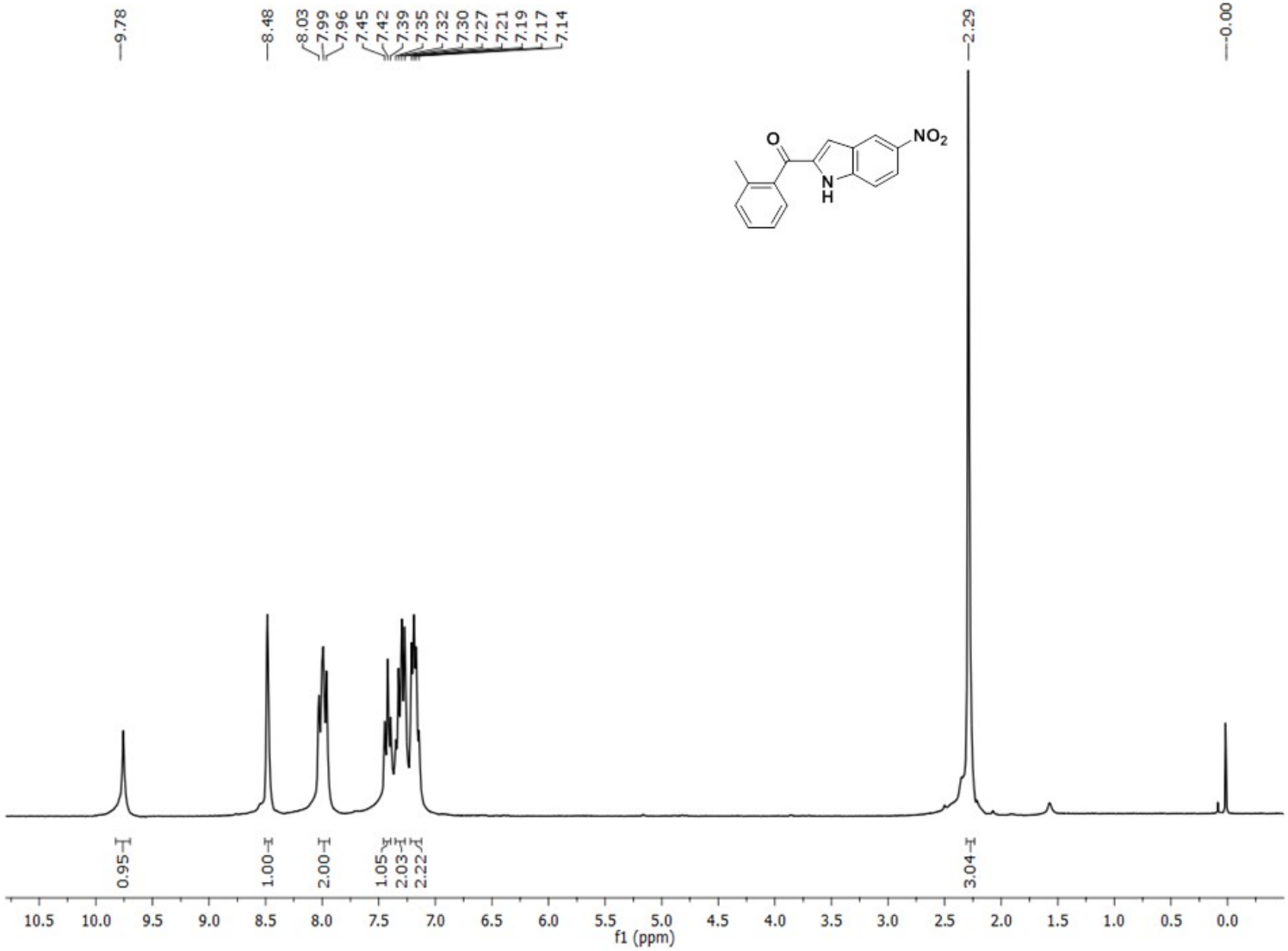


Figure 43. ^{1}H NMR spectrum of compound **3g**

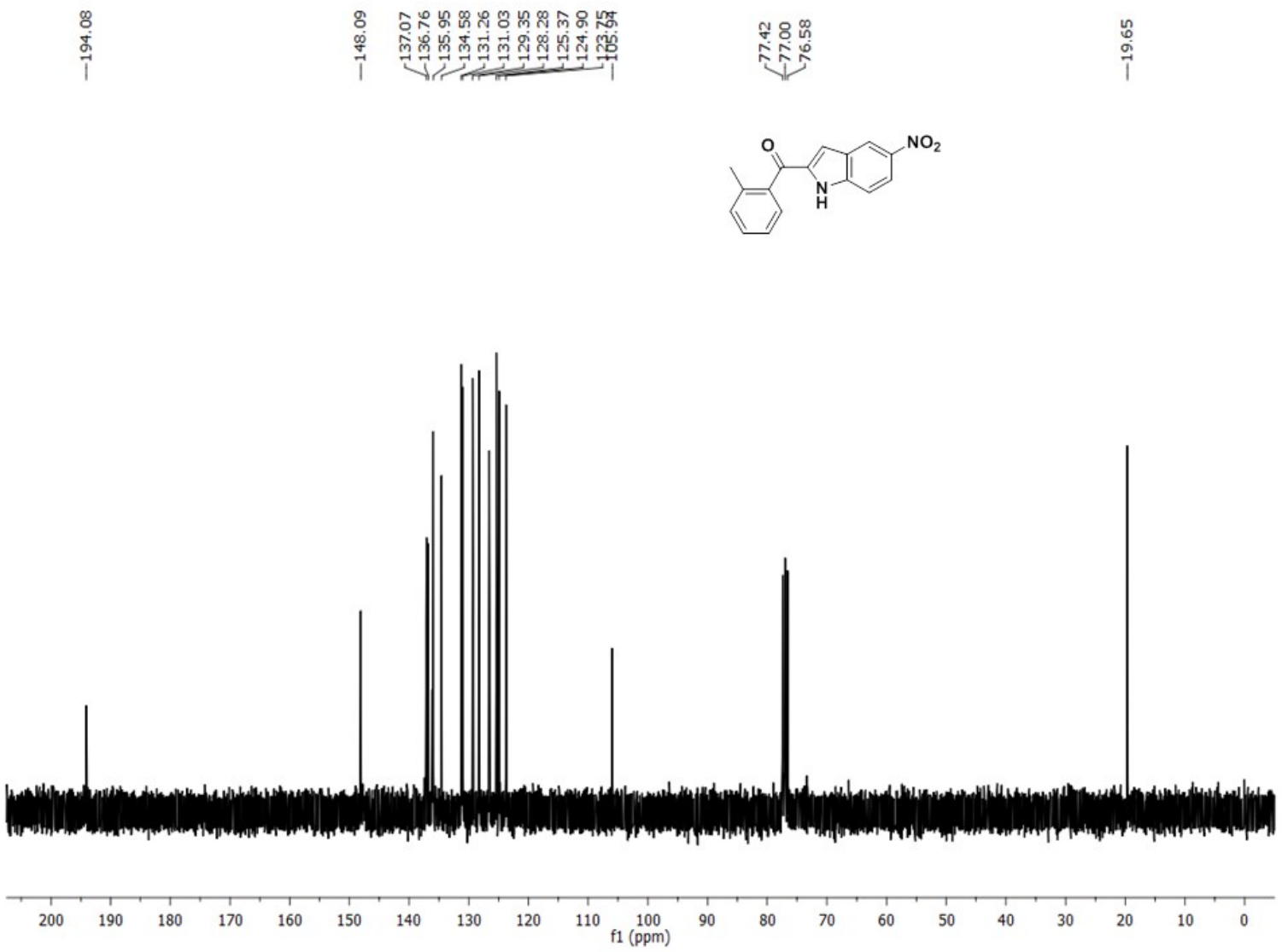


Figure 44. ^{13}C NMR spectrum of compound **3g**

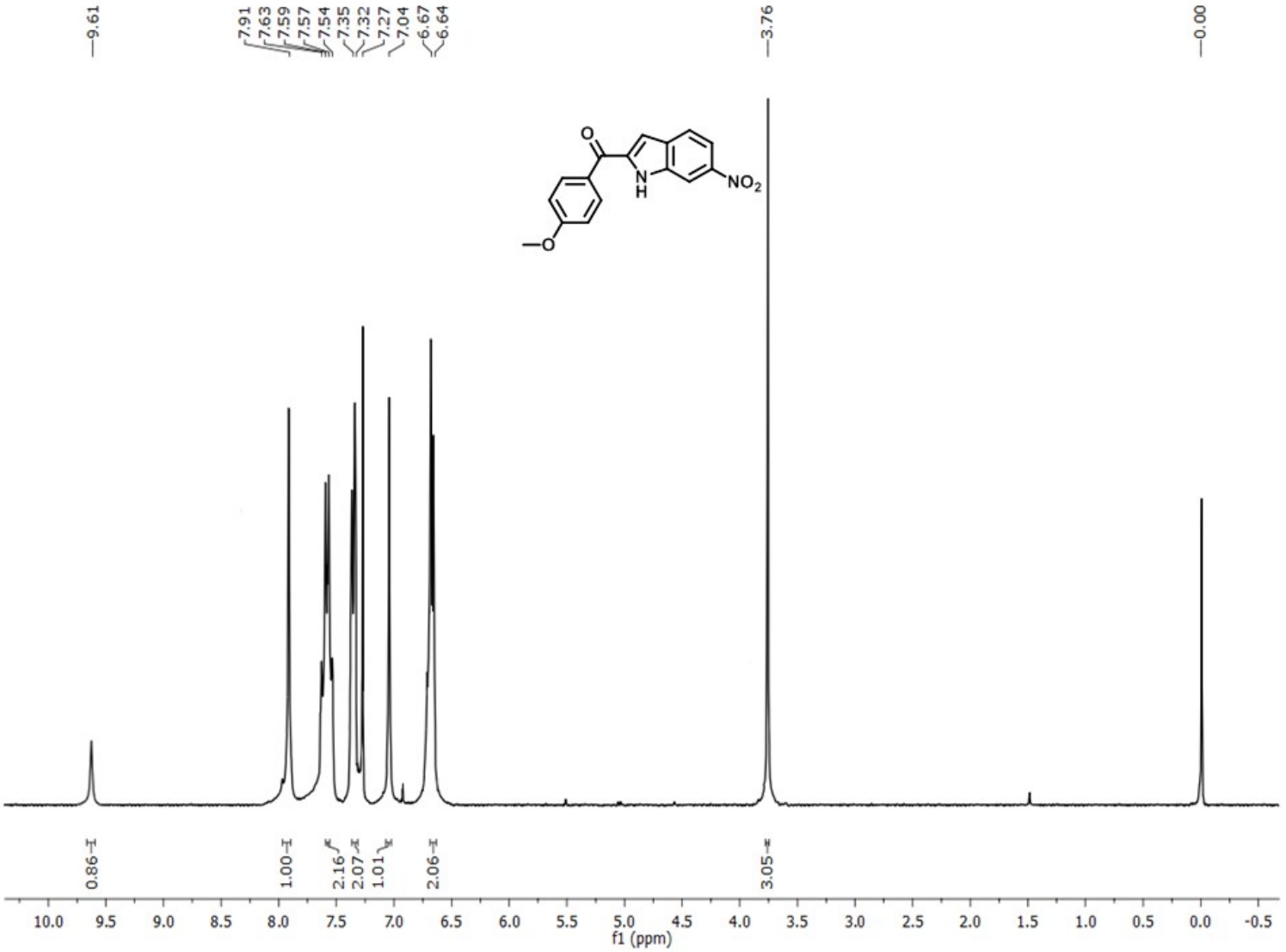


Figure 45. ^{1}H NMR spectrum of compound **3h**

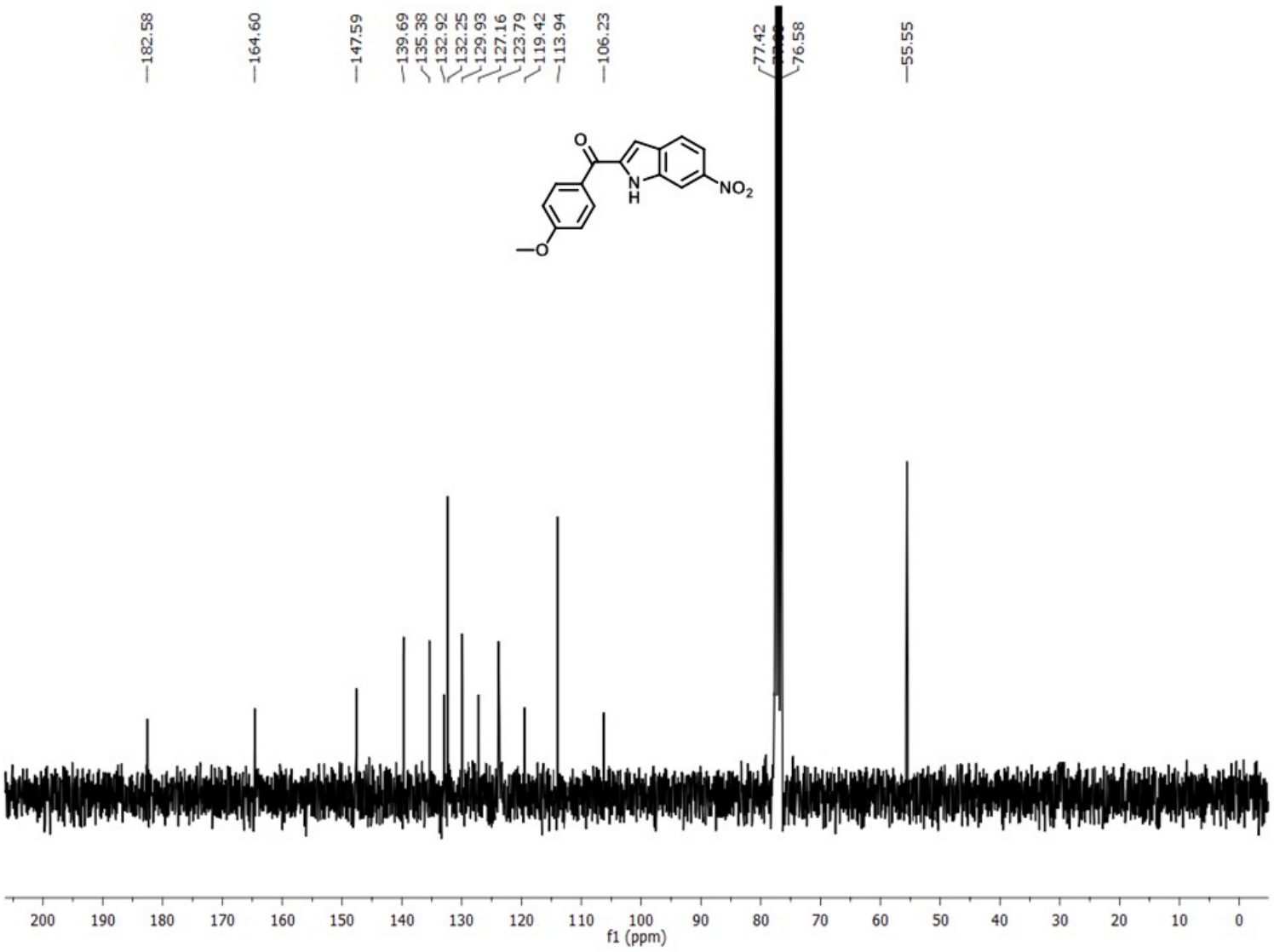


Figure 46. ^{13}C NMR spectrum of compound **3h**

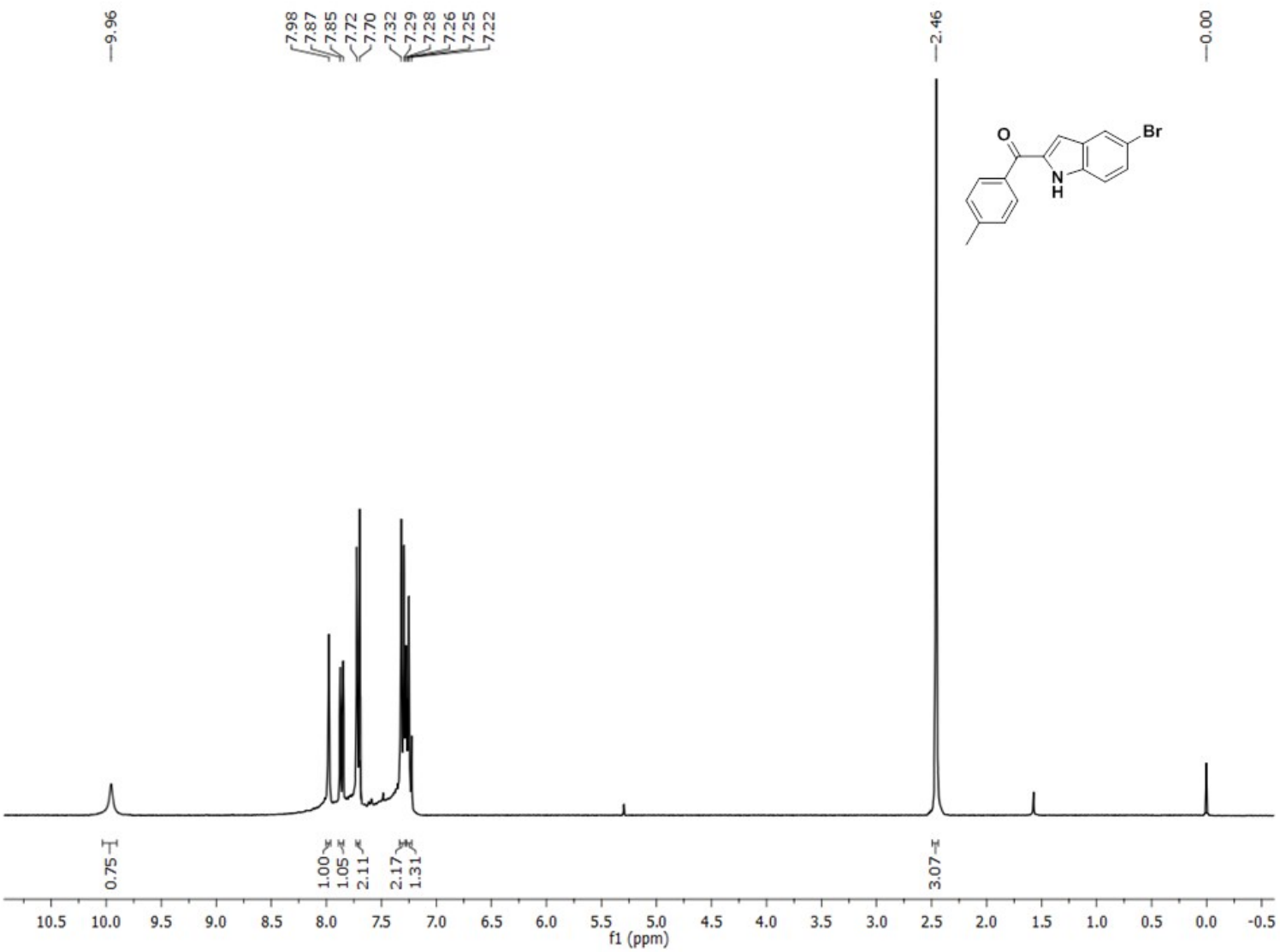


Figure 47. ^{1}H NMR spectrum of compound **3i**

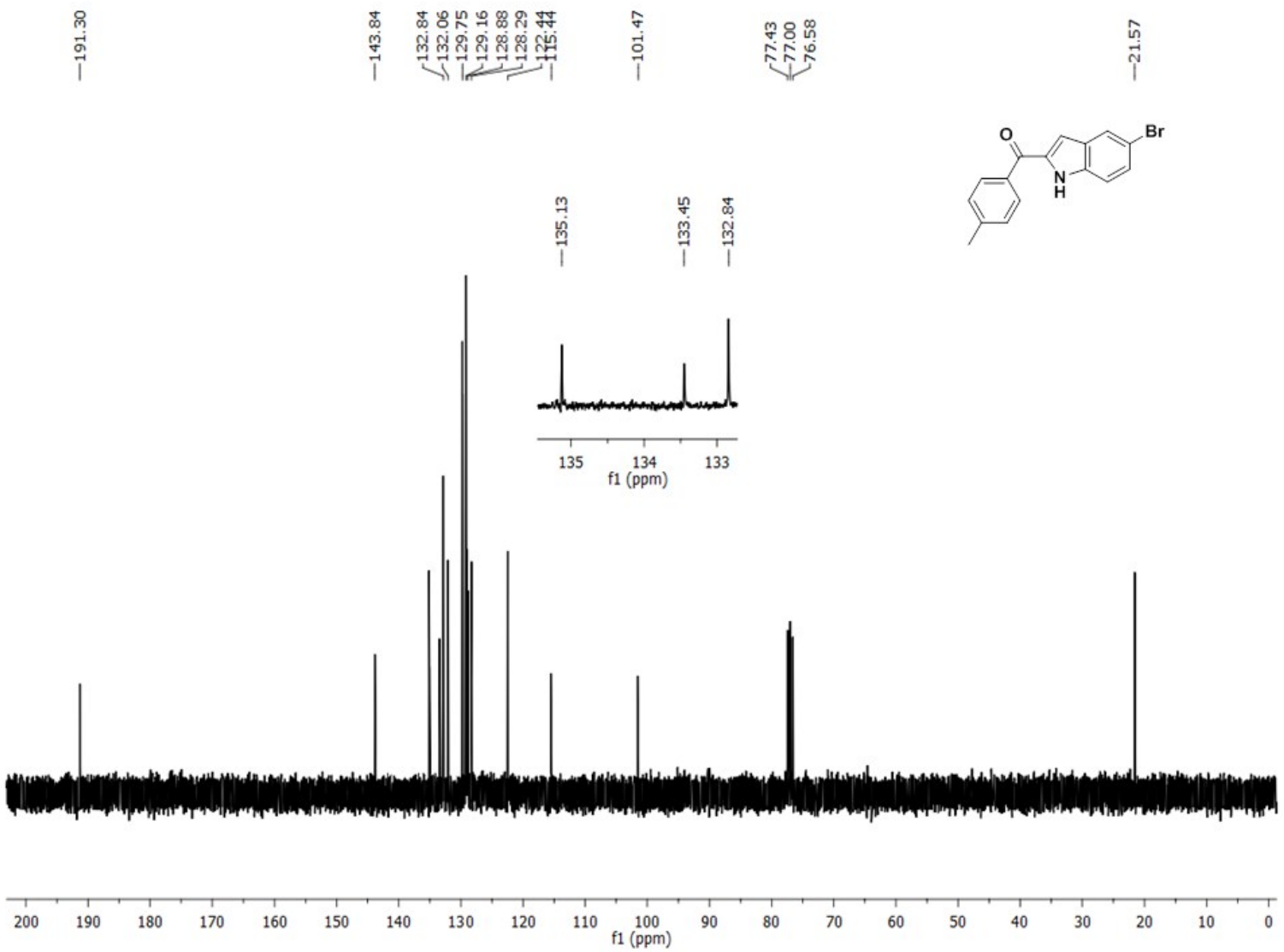


Figure 48. ^{13}C NMR spectrum of compound **3i**

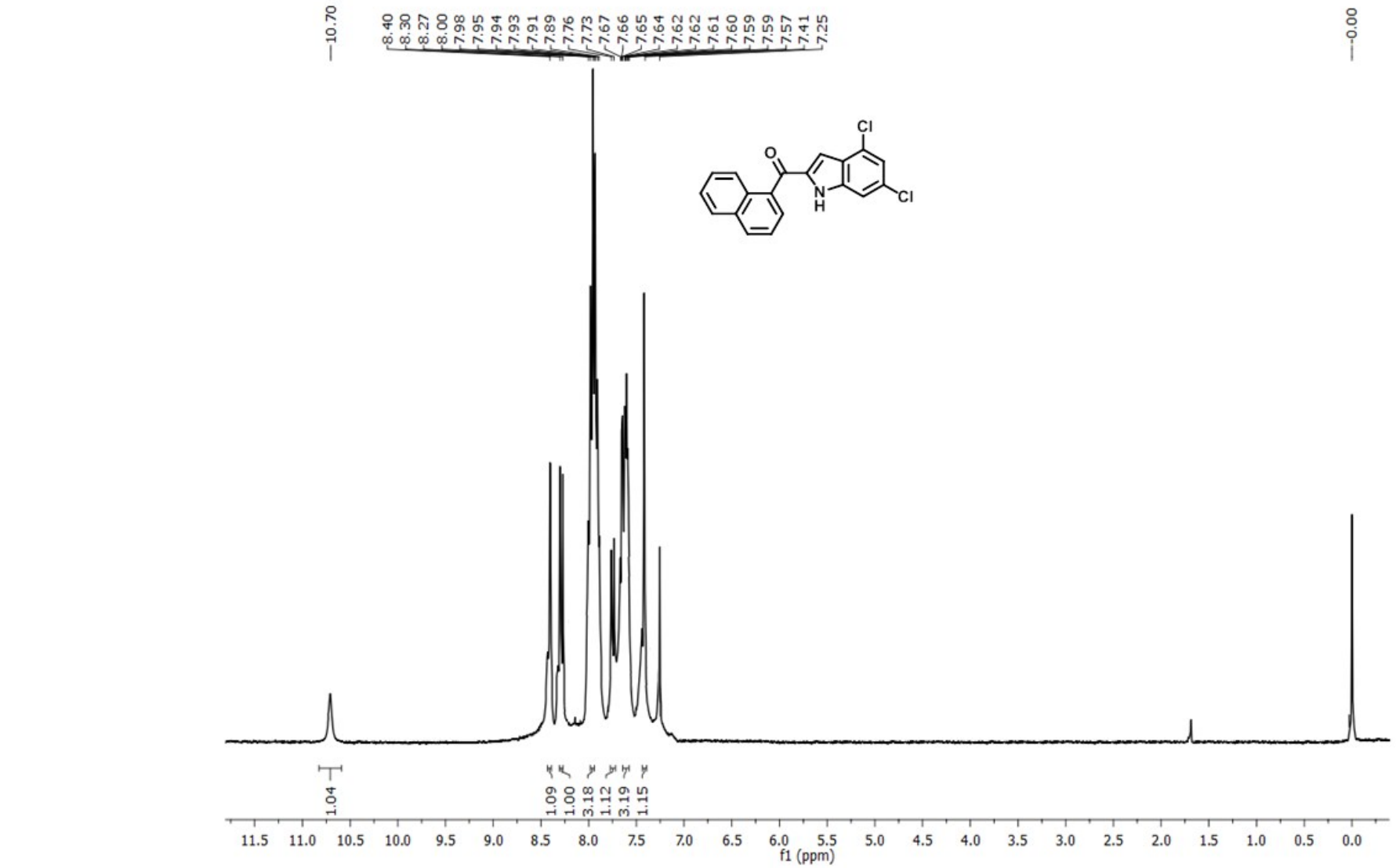


Figure 49. ^{1}H NMR spectrum of compound **3j**

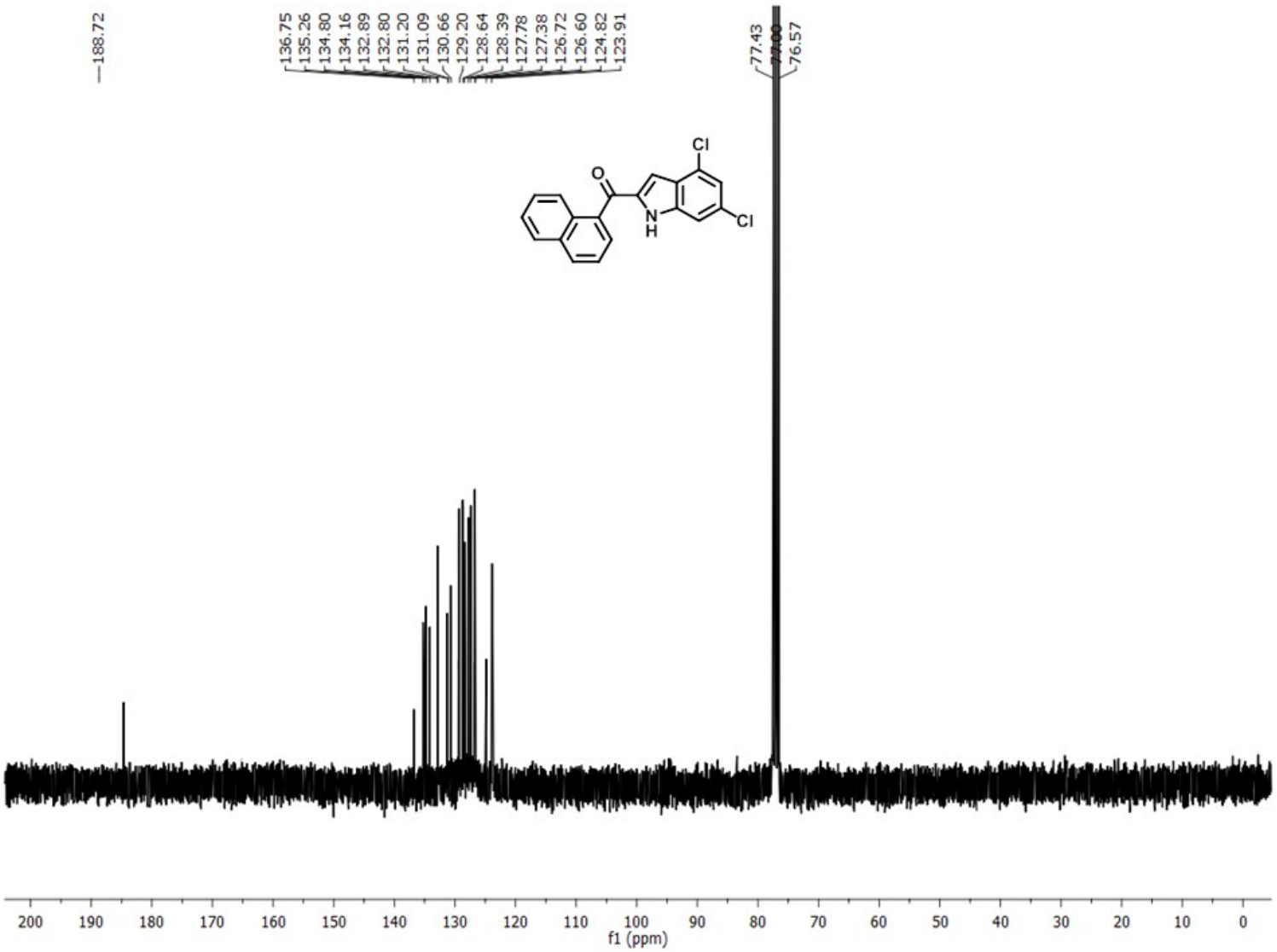


Figure 50. ^{13}C NMR spectrum of compound **3j**

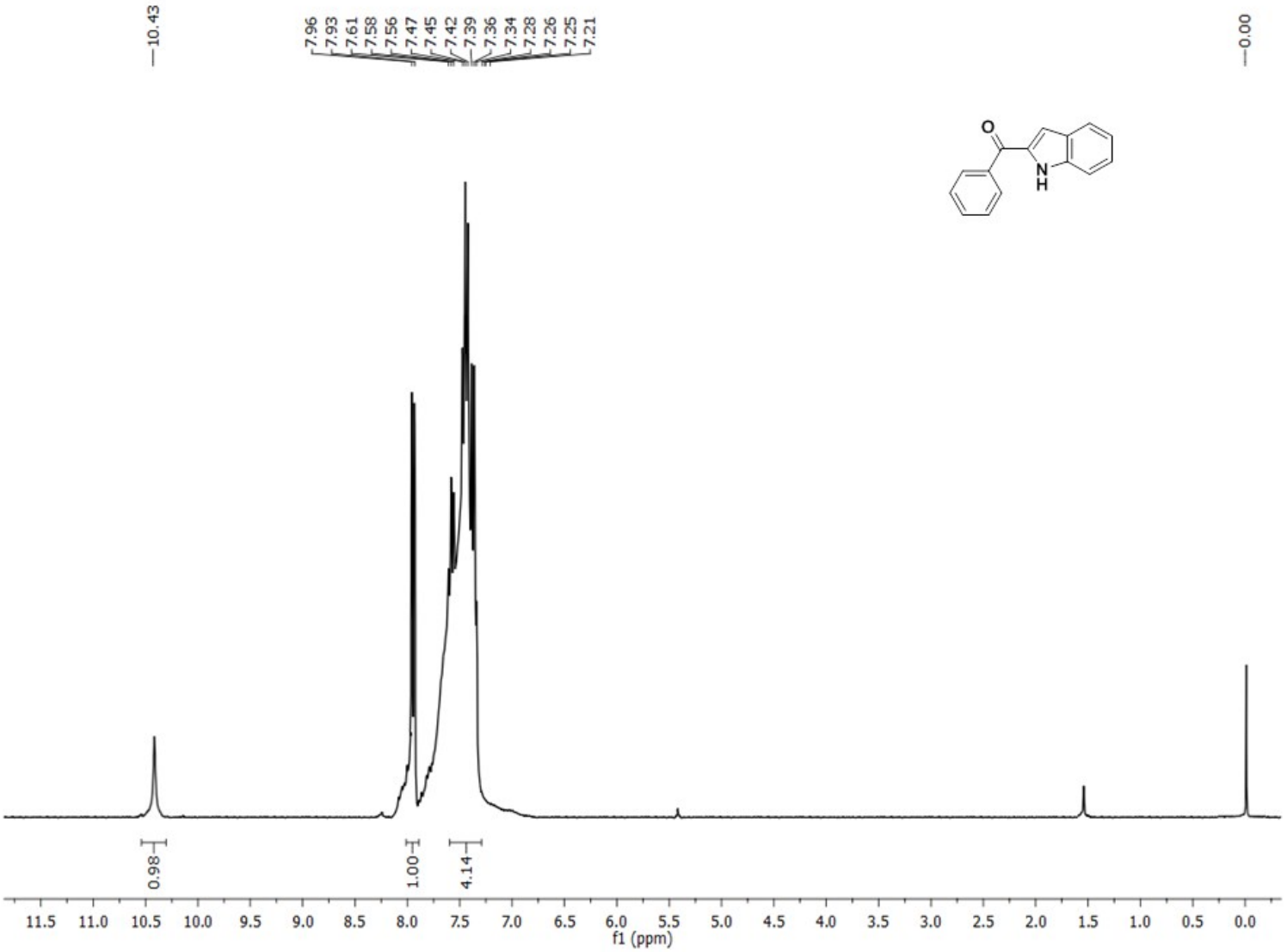


Figure 51. ^{1}H NMR spectrum of compound **3k**

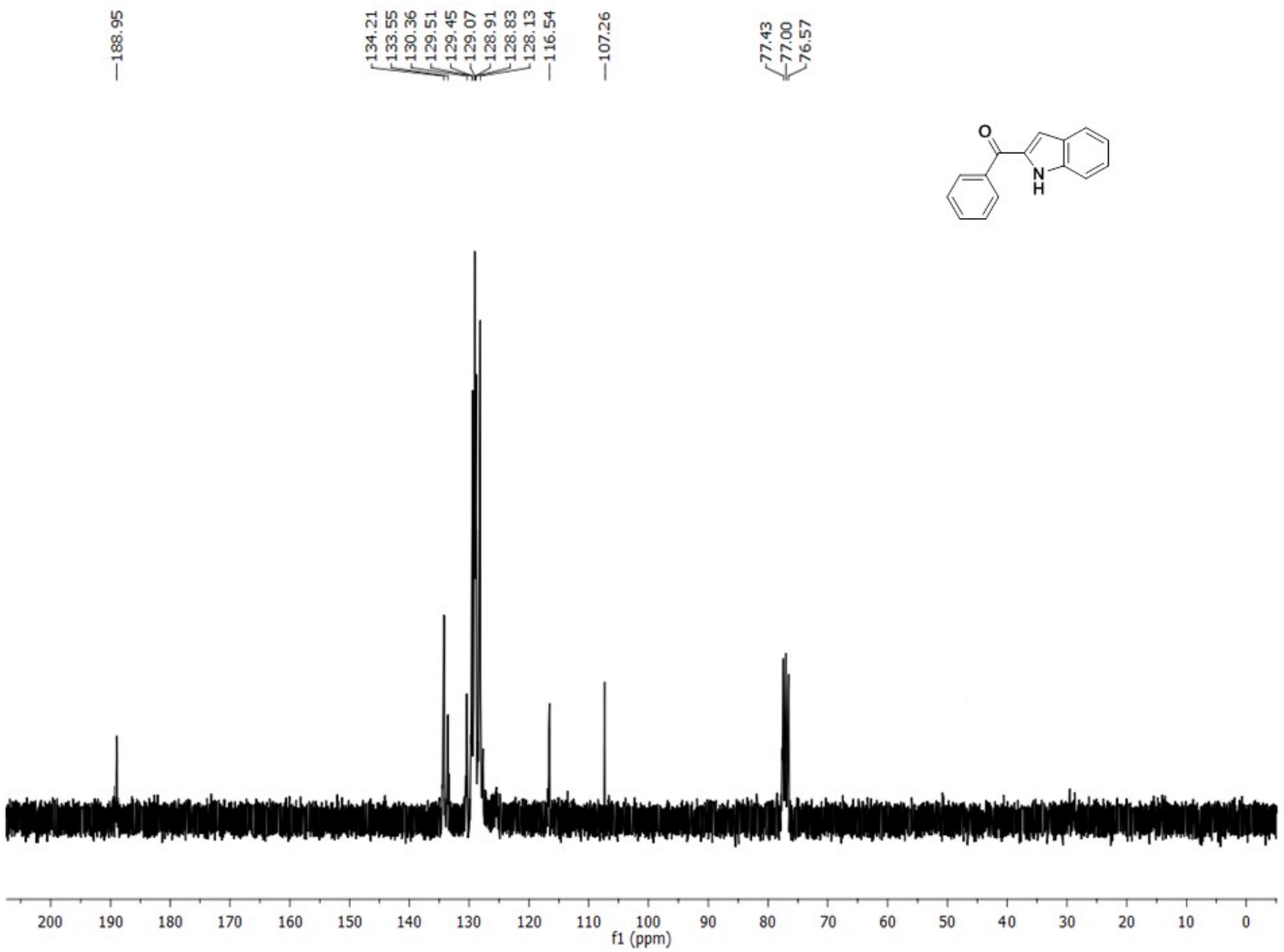


Figure 52. ^{13}C NMR spectrum of compound **3k**

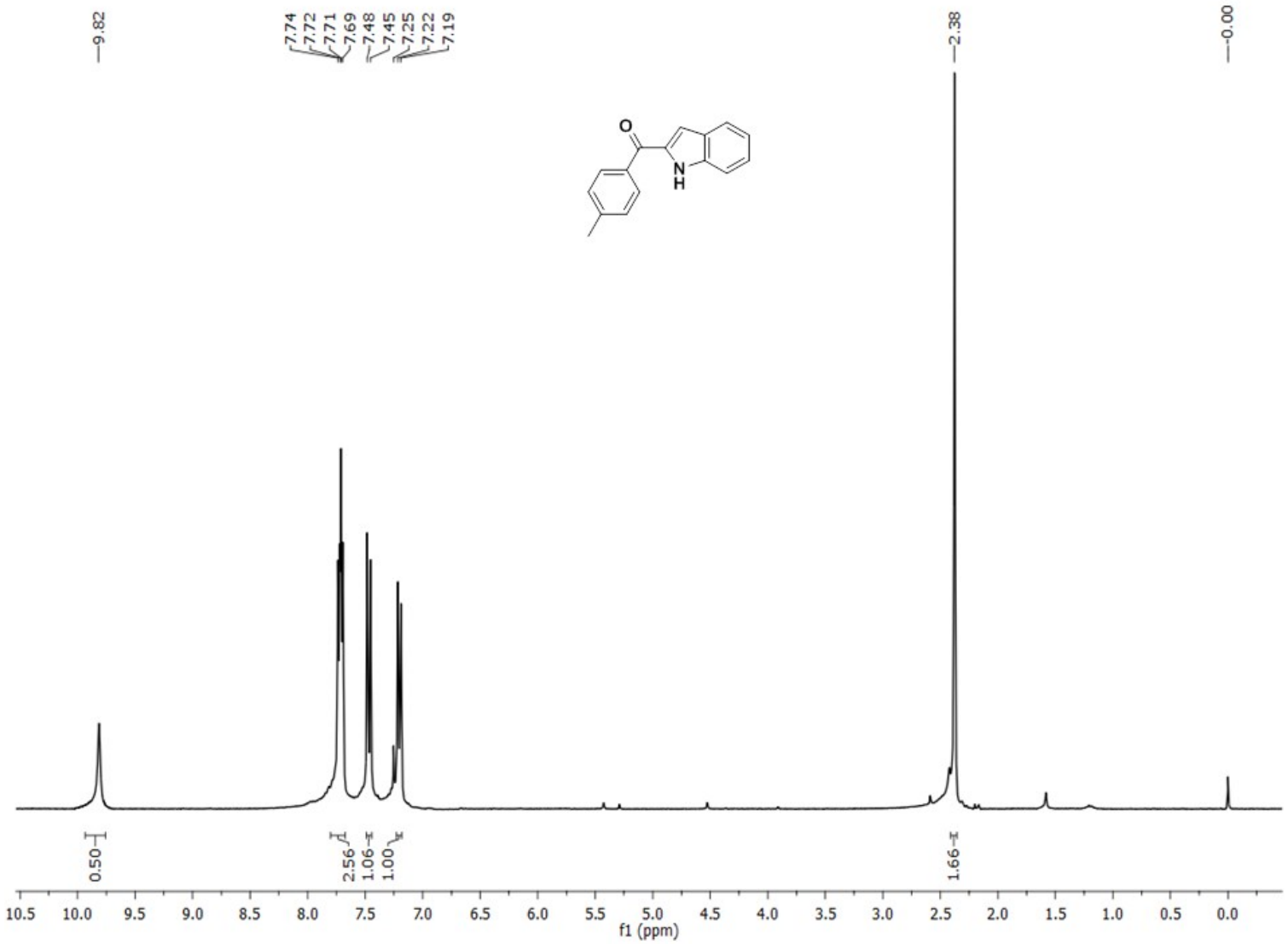


Figure 53. ^{1}H NMR spectrum of compound **3l**

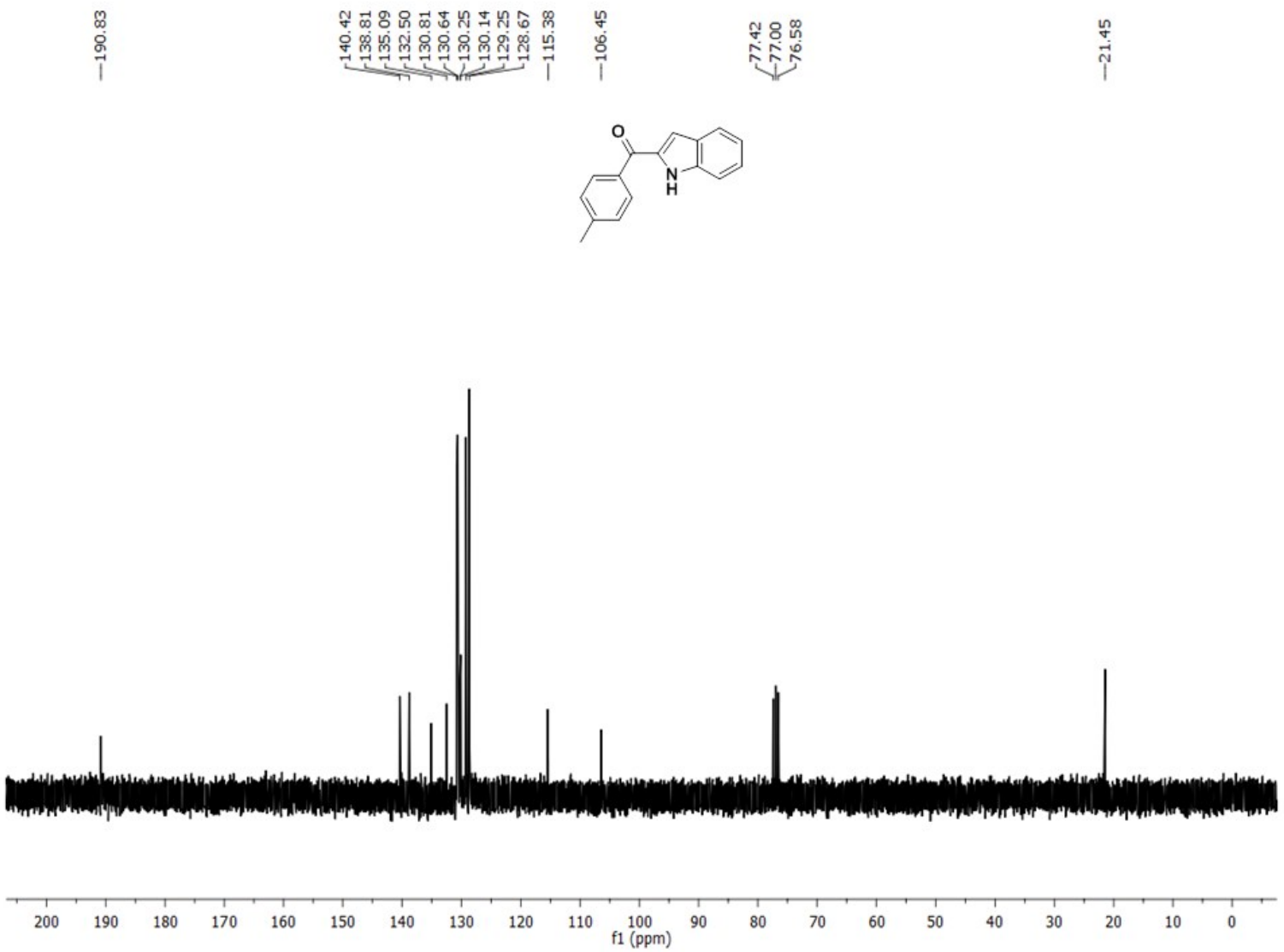


Figure 54. ^{13}C NMR spectrum of compound **3l**

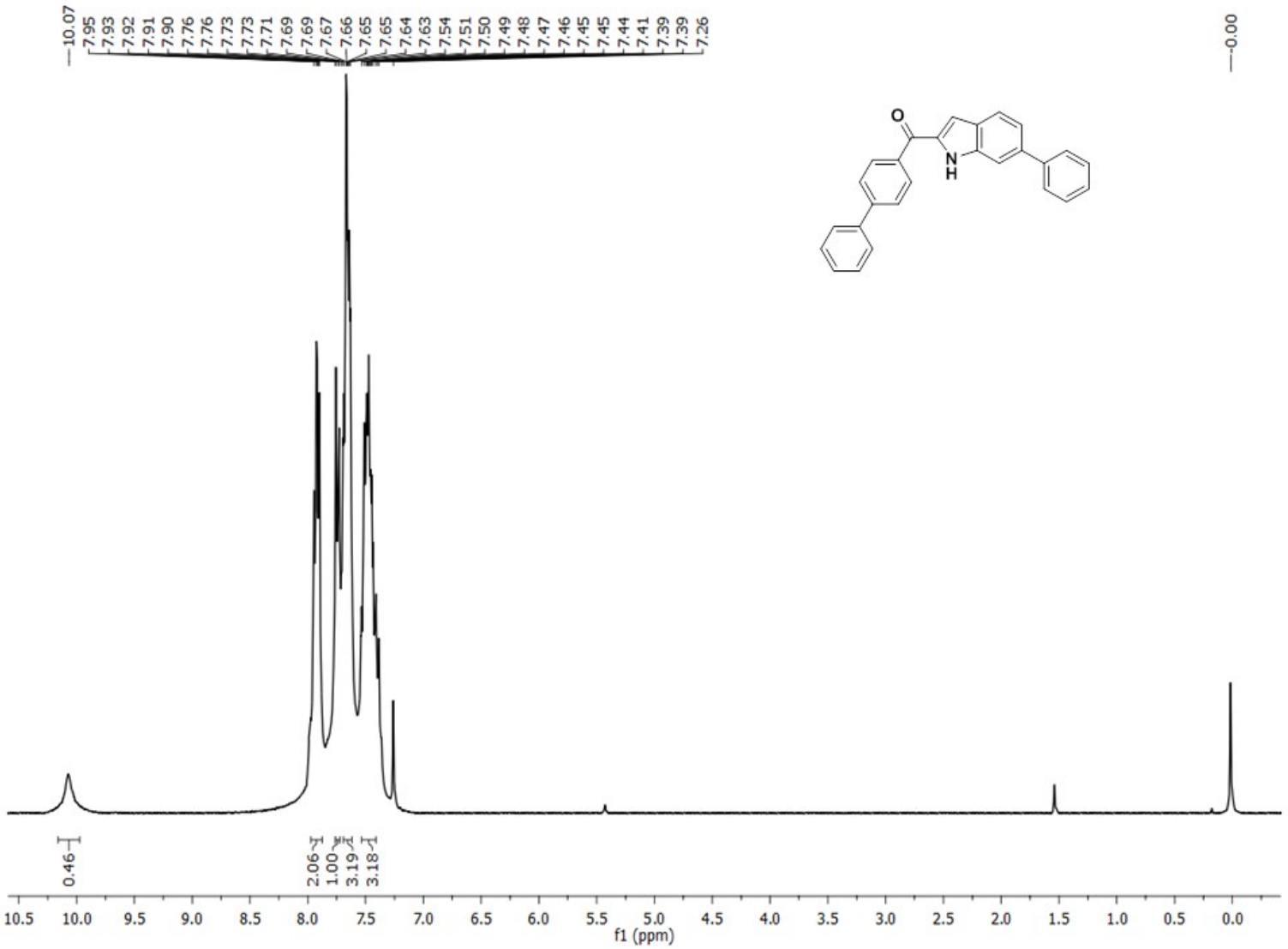


Figure 55. ^{1}H NMR spectrum of compound **3m**

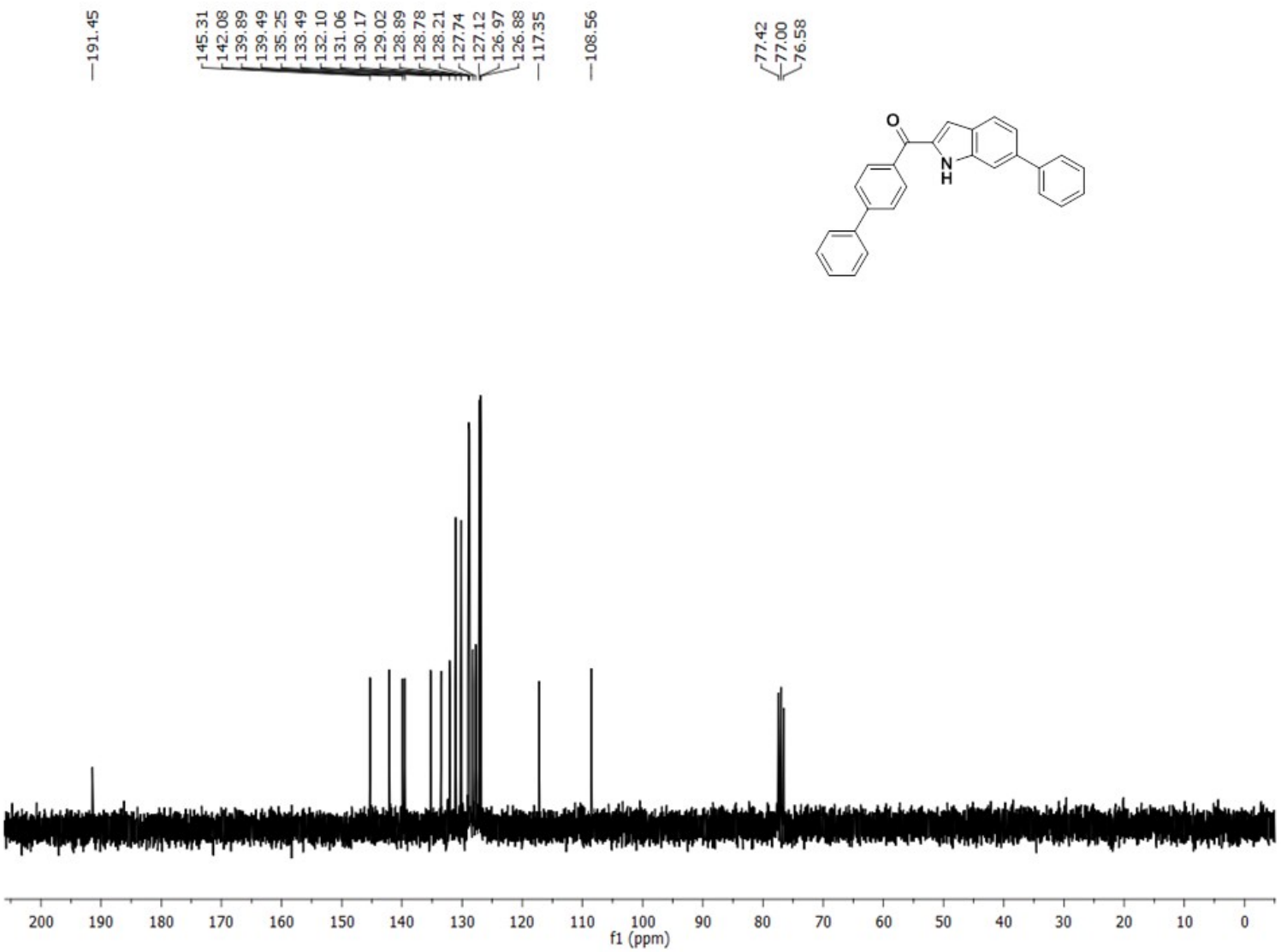


Figure 56. ^{13}C NMR spectrum of compound **3m**

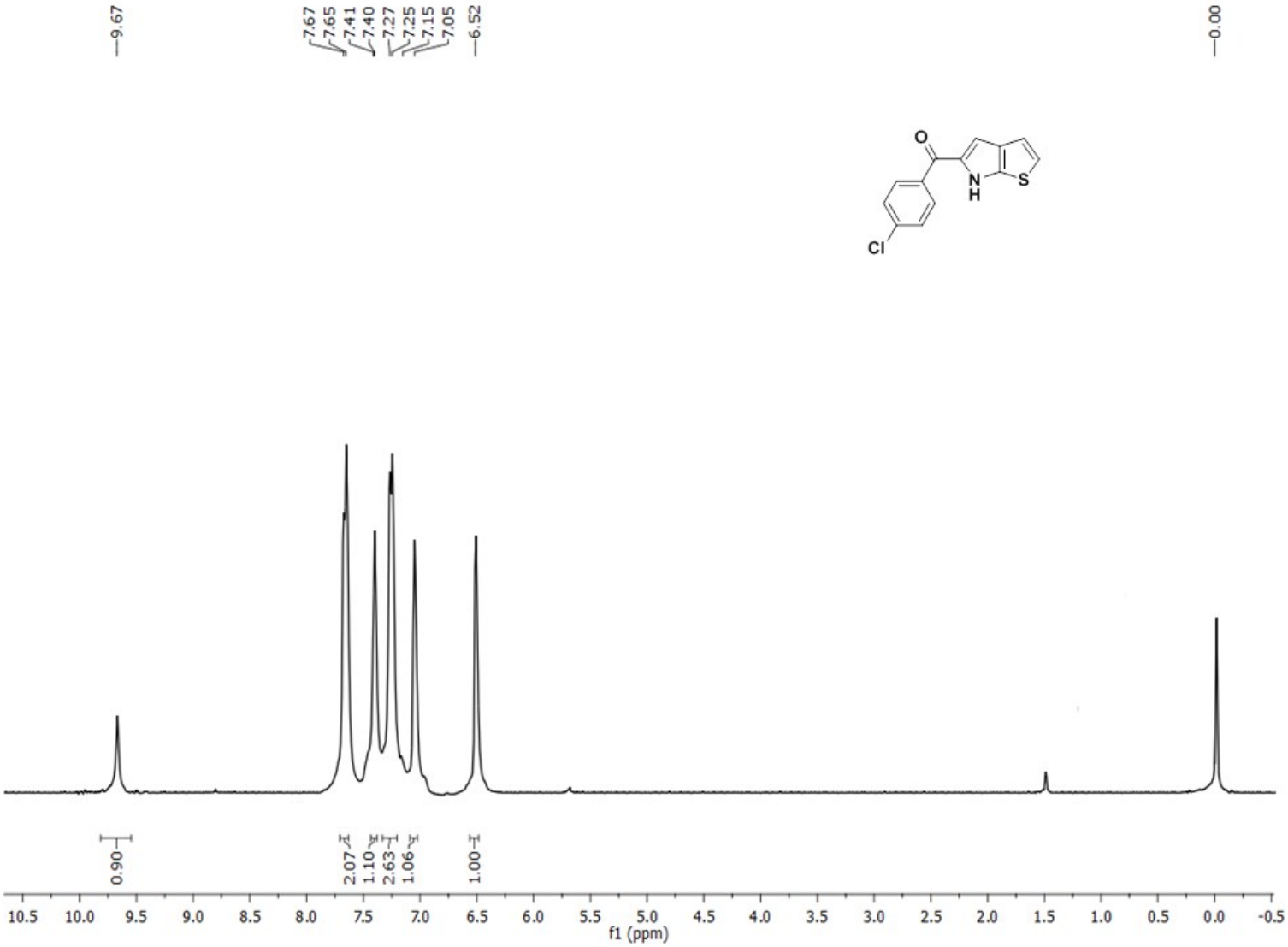


Figure 57. ^{1}H NMR spectrum of compound **3n**

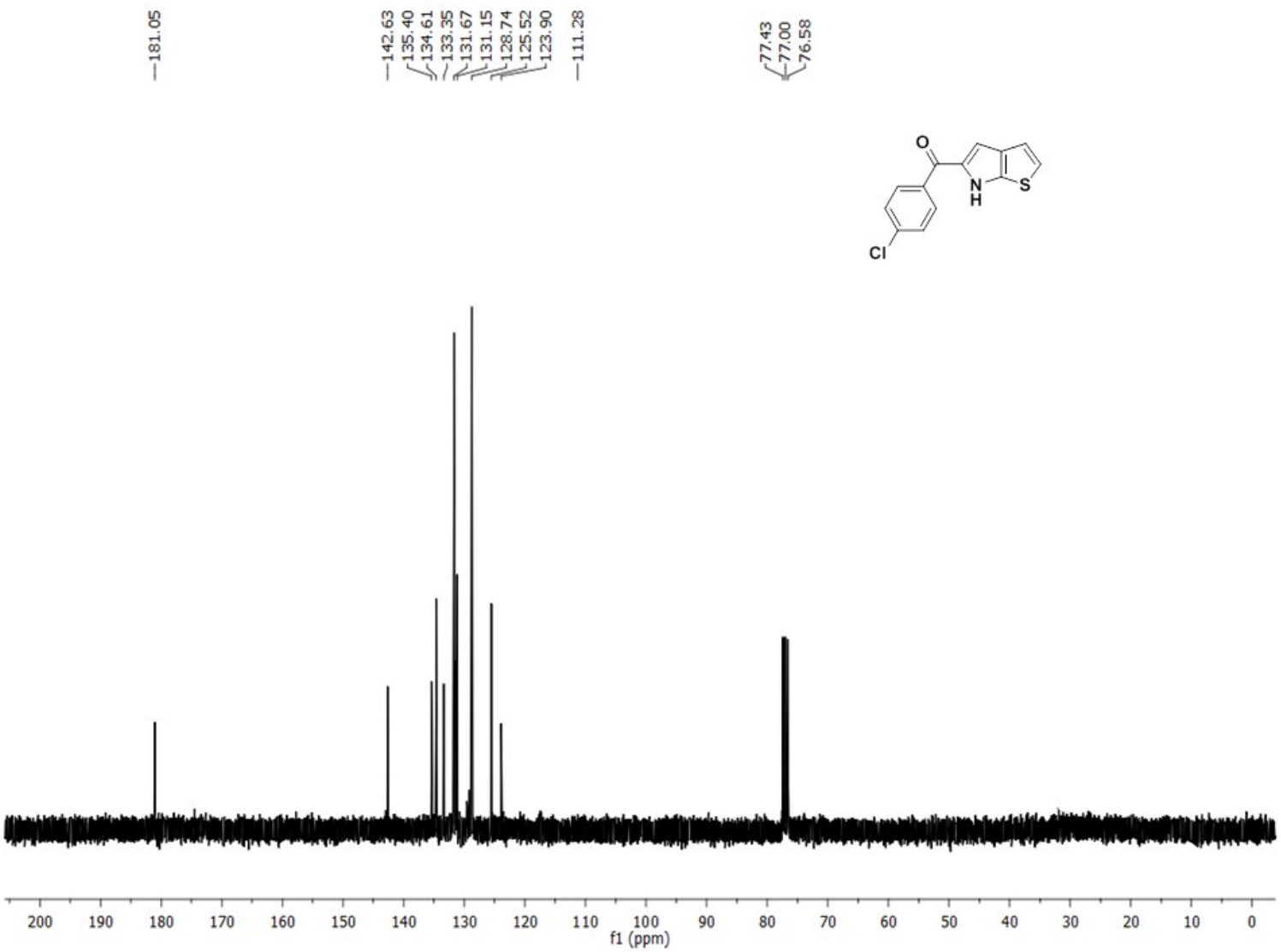


Figure 58. ^{13}C NMR spectrum of compound **3n**

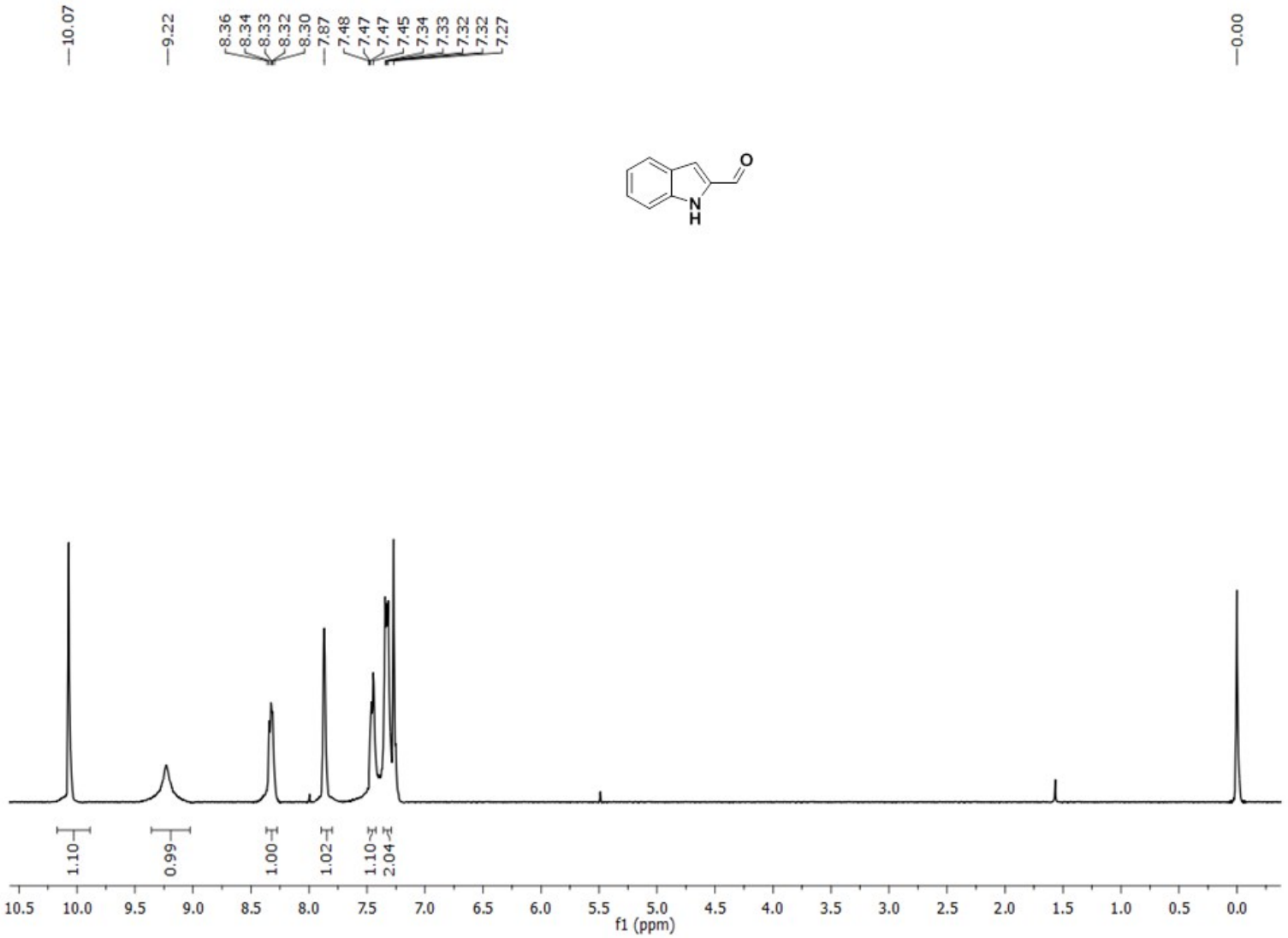


Figure 59. ^{1}H NMR spectrum of compound **3o**

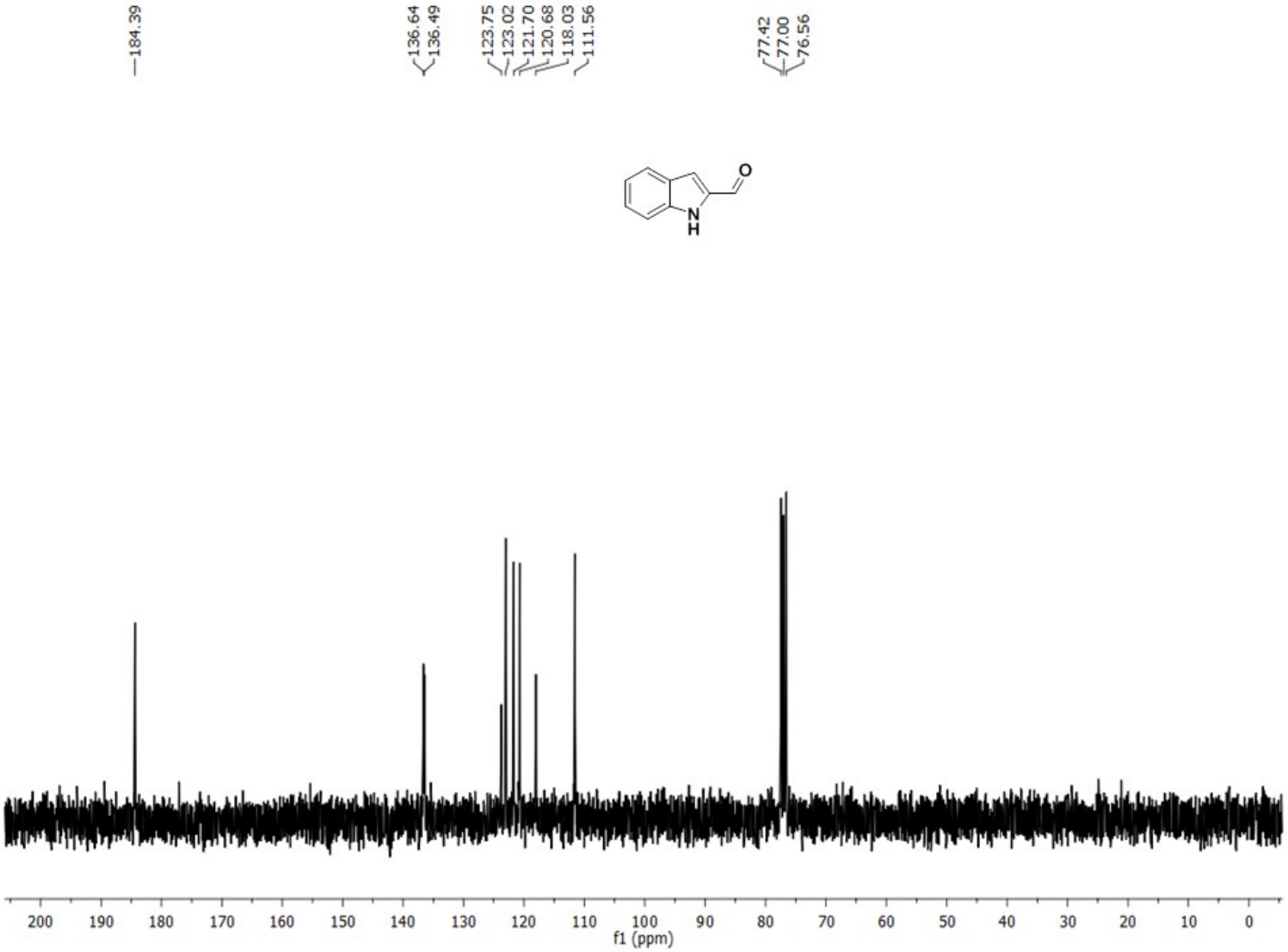


Figure 60. ^{13}C NMR spectrum of compound **3o**

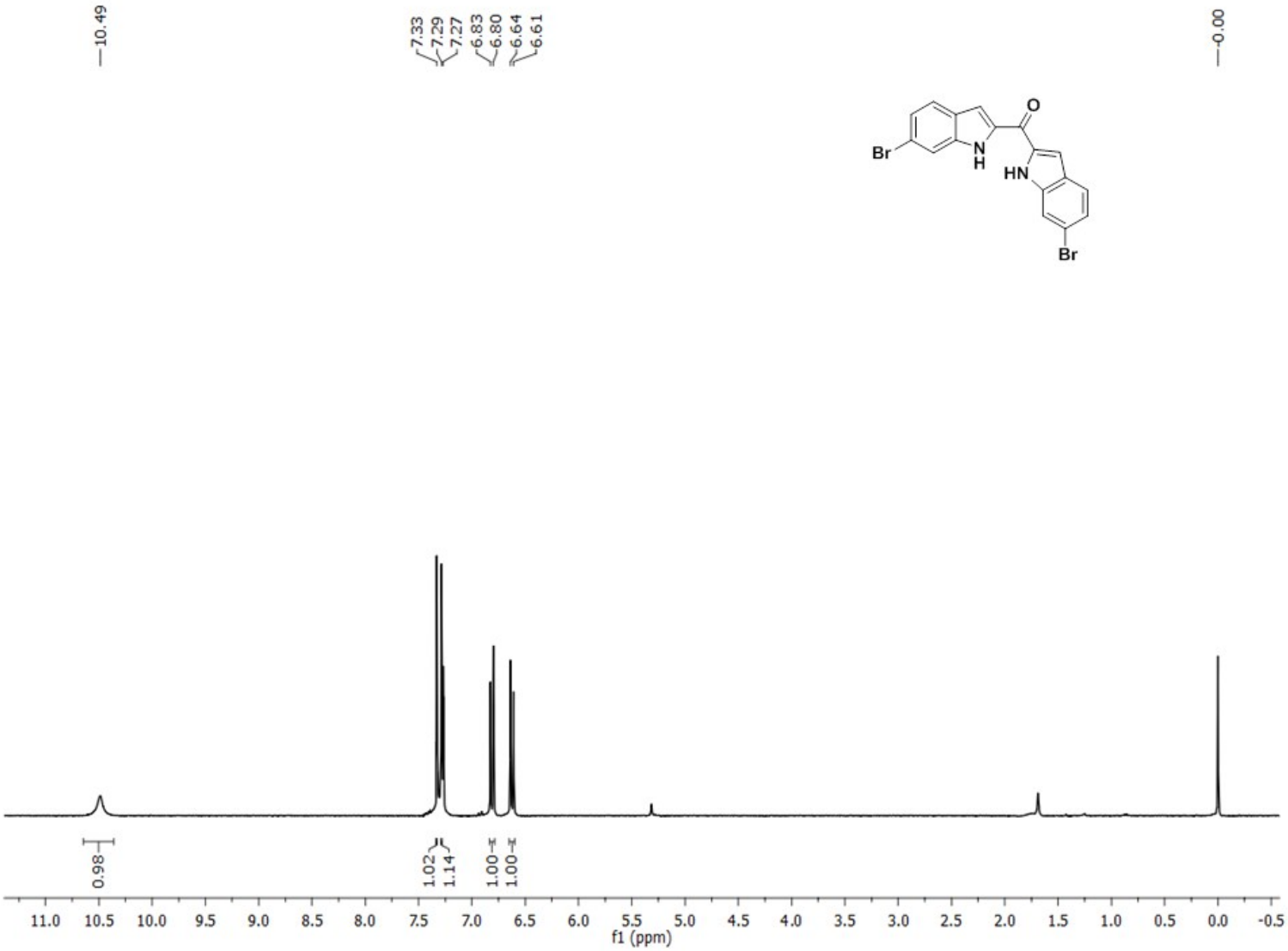


Figure 61. ^{1}H NMR spectrum of compound **3p**

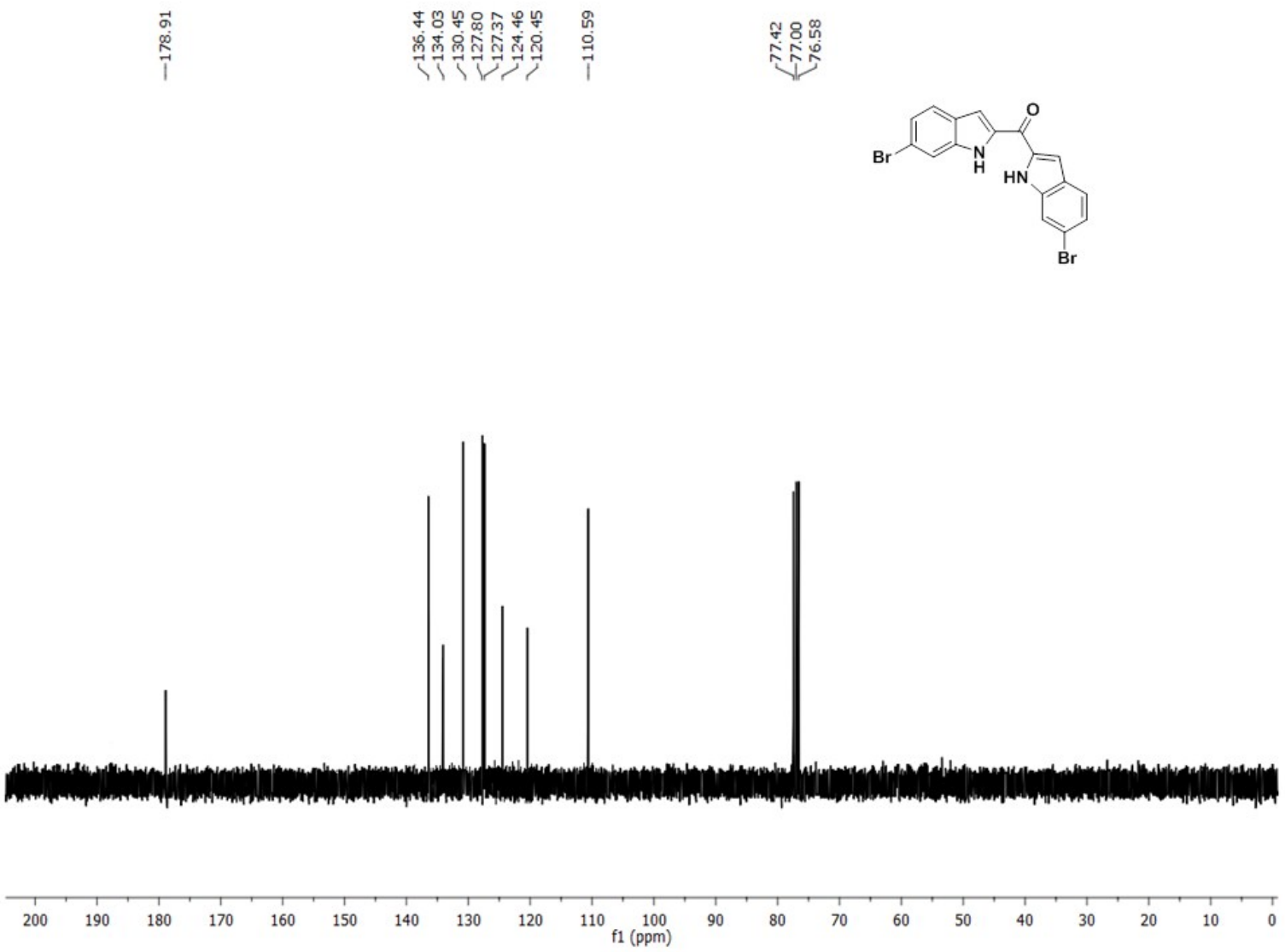


Figure 62. ^{13}C NMR spectrum of compound **3p**