Supplementary Information

An Umpolung Strategy for Intermolecular [2+2+1] Cycloaddition of Aryl Aldehydes and Nitriles: A Facile Access to 2,4,5-Trisubstituted Oxazoles

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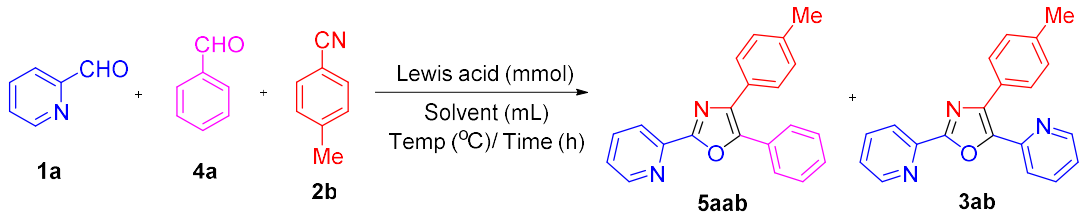
1. **Table S1: Optimization of reaction between pyridine-2-carboxaldehyde (1a), benzaldehyde (4a) and *p*-tolunitrile (2b): Preparation of 5-phenyl-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5aab):**



Entry	Aldehyde (**1a**) (mmol)	Aldehyde (**4a**) (mmol	Nitrile (**2b**) (mmol)	Lewis acid (mmol)	Solvent (mL)	Temp (°C)[b]/ Time (h)	Yield (%)[c] (**5aab**)	Yield (%)[c] (**3ab**)
1	1	1	2	TMSOTf (1.5)	*n*-PrOAc (2)	120 °C/ 4 h	37	12
2	1	1	3	TMSOTf (1.5)	*n*-PrOAc (2)	120 °C /3 h	46	16
3[d]	1	1	3	TMSOTf (3)	*n*-PrOAc (2)	120 °C /3 h	45	-
4	**1**	**2**	**3**	**TMSOTf** (1.5)	*n*-PrOAc (2)	**120 °C /3 h**	**56**	**8**
5	1	3	3	TMSOTf (1.5)	*n*-PrOAc (2)	120 °C /3 h	50	7
6	1	3	3	TMSOTf (2)	*n*-PrOAc (2)	120 °C /3 h	52	7

[a]All reactions were performed with 1 mmol of pyridine-2-carboxaldehyde (**1a**) (limiting reagent). [b]Oil bath temperature. [c]Isolated yields (based on pyridine-2-carboxaldehyde). [d]Trace amount of oxazole (**3ab**) formed.

2. General information

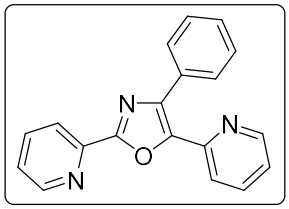
All solvents were obtained from commercial sources and purified and dried according to standard procedures. All required reagents and chemicals were procured from Aldrich or local manufacturers and used as purchased without further purification (all liquid carboxaldehydes were distilled prior to use). All reactions were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tubes on a Bruker-Ultrashield (400 and 500 MHz) and Bruker-Ascend (500 MHz) NMR spectrometers [field strengths: 400/100 or 500/125 MHz respectively] in $CDCl_3$ solution, with chemical shifts referenced to tetramethylsilane (TMS, $\delta = 0$) for ^{1}H NMR spectra and chloroform-d middle peak of the triplet ($\delta = 77.10$ ppm) for ^{13}C NMR spectra. For fluorinated compounds ^{19}F NMR spectra were recorded on a 400 MHz Bruker-Ultrashield NMR spectrometer (field strength: 400/376 MHz) in $CDCl_3$ solution using trifluoro toluene ($\delta = -62.71$ ppm) as a reference. The ^{1}H NMR spectra were presented as follows: chemical shifts (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublets of doublets), coupling constant (*J*) in Hz and integration. HRMS spectra were recorded on Bruker-maXis (ESI-TOF) spectrometer. Melting points were determined on MR-Vis^{+} visual melting point range apparatus of LABINDIA private limited or on Bio-Tech (India) capillary melting point apparatus and were uncorrected. Crystallographic data were collected at 293 K on Rigaku Oxford Diffraction XtaLAB Synergy diffractometer and Bruker D8 Quest CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) radiation. Structures were solved and refined using standard methods. Infrared spectra were recorded using ATR technique on a Thermo-Fisher Scientific FT-IR spectrophotometer. Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh), for column elution process hexane-EtOAc mixture was used as the eluent unless otherwise stated.

3. General synthetic procedure for oxazoles (3)

An oven-dried 10 mL round-bottomed flask was charged with pyridine-2-carboxaldehydes/quinoline-2-carboxaldehyde (**1**) (1 mmol), nitrile (**2)** (2 mmol), and *n*-PrOAc (2 mL) under nitrogen. The contents were cooled to 0 ºC (ice bath) and then TMSOTf (1.5 mmol) was added. The reaction mixture was allowed to stir at room temperature for 5-10 min and then heated under reflux (oil bath temperature 120 ºC). After completion of the reaction (monitored by TLC) (2-24 h), the reaction mixture was cooled to room temperature and quenched with saturated K_2CO_3 solution (4 mL). Then reaction mixture was diluted with ethyl acetate (7-10 mL). The organic layer was washed with saturated $NaHCO_3$ solution (2X5 mL) followed by brine (1X5 mL). Organic layer was dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure. The residue obtained was purified by column chromatography using silica gel (100-200 mesh)

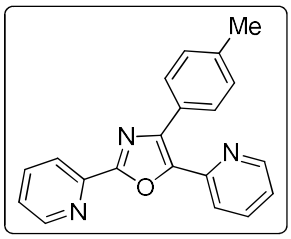
(hexanes:ethyl acetate 60:40 to 50:50 (v/v)) to provide the desired products **3** as crystalline solids. (except **3ad** which was obtained as a viscous liquid).

4-Phenyl-2,5-di(pyridin-2-yl)oxazole (3aa):



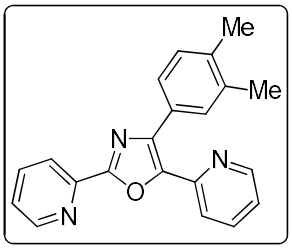
Yield: 89% (134 mg); white solid; mp:104-106 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 4.8 Hz, 1H), 8.69 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.06-7.99 (m, 2H), 7.86 (td, *J* = 7.6, 1.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.8, 1.6 Hz, 1H), 7.48-7.36 (m, 4H), 7.30-7.23 (m, 1H)*; (*This multiplet also contains $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 150.1, 149.7, 148.1, 145.8, 145.7, 139.9,136.9, 136.5, 131.7, 128.8, 128.7, 128.2, 124.8, 123.1, 122.5, 122.1; IR (neat): 3049, 1578, 1544, 1419, 1111, 989, 968, 754, 715 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{13}N_3O$+H, 300.1137; found, 300.1139.

2,5-Di(pyridin-2-yl)-4-(*p*-tolyl)oxazole (3ab):



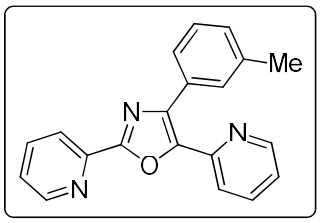
Yield: 90% (142 mg); white solid; mp: 110-112 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.22; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 8.80-8.76 (m, 1H), 8.70-8.66 (m, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.94-7.90 (m, 2H), 7.86-7.81 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 1H), 7.26-7.21 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 150.2, 149.7, 148.3, 145.9, 145.4, 140.0, 138.6, 136.9, 136.5, 128.9, 128.8, 128.7, 124.8, 123.0, 122.5, 122.1, 21.4; IR (neat): 3052, 1579, 1510, 1469, 1454, 1421, 1115, 990, 968, 826, 781, 730 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{15}N_3O$+H, 314.1293; found, 314.1293.

4-(3,4-Dimethylphenyl)-2,5-di(pyridin-2-yl)oxazole (3ac):



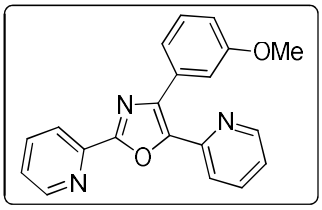
Yield: 92% (152 mg); white solid; mp: 141-143 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.0 Hz, 1H), 8.68 (d, *J* = 4.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.87-7.76 (m, 3H)*, 7.74-7.67 (m, 2H), 7.42-7.35 (m, 1H), 7.25-7.21 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 6H); (*This multiplet contains a td (*J* = 8.0, 1.5 Hz) (1H) and a multiplet (2H)); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 150.2, 149.7, 148.4, 146.0, 145.4, 140.2,137.3, 136.9, 136.5, 136.4, 130.0, 129.5, 129.2, 126.3, 124.8, 123.0, 122.6, 122.2, 19.8, 19.7; IR (neat): 2971, 1588, 1550, 1457, 1439, 1425, 1116, 788, 726 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{21}H_{17}N_3O$+H, 328.1450; found, 328.1450.

2,5-Di(pyridin-2-yl)-4-(*m*-tolyl)oxazole (3ad):



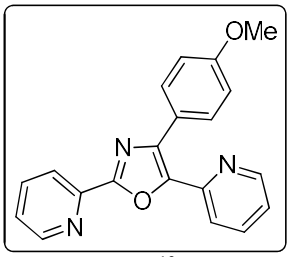
Yield: 68% (108 mg); viscous liquid; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.29; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.66 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.27 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.86 (s, 1H), 7.84-7.76 (m, 3H), 7.69 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (ddd, *J* = 7.5, 5.0, 1.5 Hz, 1H), 7.32-7.26 (m, 1H)*, 7.22 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.21-7.17 (m, 1H), 2.39 (s, 3H) (*It has a triplet *J* = 7.5 Hz and $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 150.1, 149.6, 148.1, 145.8, 145.6, 140.0, 137.8, 136.8, 136.4, 131.5, 129.42, 129.39, 128.0, 125.9, 124.8, 123.0, 122.5, 122.1, 21.4; IR (neat): 3051, 2919, 1584, 1458, 1426, 1152, 1113, 993, 784, 725 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{15}N_3O$+H, 314.1293; found, 314.1296.

4-(3-Methoxyphenyl)-2,5-di(pyridin-2-yl)oxazole (3ae):



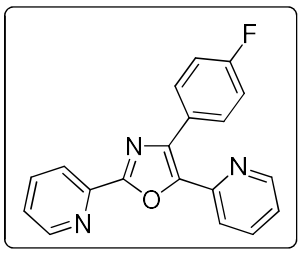
Yield: 62% (104 mg); pale yellow solid; mp: 100-102 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.22; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (dd, *J* = 4.0, 0.5 Hz, 1H), 8.69 (dd, *J* = 4.0, 1.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.88-7.80 (m, 2H), 7.76-7.70 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.42-7.37 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 6.97-6.92 (m, 1H), 3.85 (s, 3H) ($CHCl_3$ peak appeared at δ 7.28); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 159.2, 150.2, 149.6, 148.2, 145.9, 139.8, 136.9, 136.6, 132.9, 129.2, 124.9, 123.2, 122.6, 122.4, 121.3, 115.1, 113.9, 55.4; IR (neat): 3051, 2998, 2922, 2826, 1585, 1471, 1451, 1422, 1291, 1243, 1154, 1110, 1042, 992, 776, 726 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{15}N_3O_2$+H, 330.1242; found, 330.1243.

4-(4-Methoxyphenyl)-2,5-di(pyridin-2-yl)oxazole (3af):



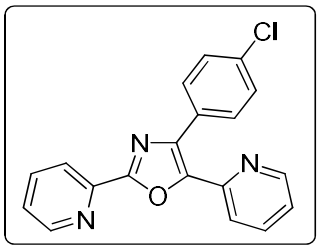
Yield: 83% (139 mg); white solid; mp: 112-114 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.18; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.68 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.28 (dt, *J* = 7.5, 1.0 Hz, 1H), 8.05-8.00 (m, 2H), 7.87-7.79 (m, 2H), 7.73 (td, *J* = 7.5, 2.0 Hz, 1H), 7.39 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.24 (ddd, *J* =7.5, 5.0, 1.0 Hz, 1H), 6.99-6.94 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 159.2, 150.2, 149.7, 148.5, 146.0, 145.1, 139.9, 137.0, 136.6, 130.4, 124.9, 124.2, 122.9, 122.6, 122.1, 113.7, 55.4; IR (neat): 3052, 2998, 1613, 1582, 1551, 1506, 1459, 1437, 1419, 1249, 1175, 1114, 1025, 967, 836, 781, 734 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{15}N_3O_2$+H, 330.1242; found, 330.1241.

4-(4-Fluorophenyl)-2,5-di(pyridin-2-yl)oxazole (3ag):



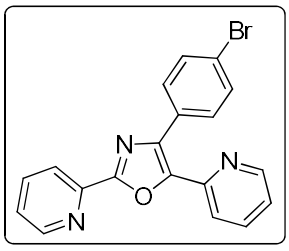
Yield: 80% (127 mg); white solid; mp: 138-140 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 8.66 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 8.27 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.15-8.09 (m, 2H), 7.89-7.82 (m, 2H), 7.76 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 7.29-7.24 (m, 1H)*, 7.15-7.09 (m, 2H); (*It also contains $CHCl_3$ peak);^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (d, *J* = 246.3 Hz), 159.1, 150.2, 149.5, 148.1, 145.7, 145.5, 139.0, 137.0, 136.6, 130.9 (d, *J* = 7.5 Hz), 127.8 (d, *J* = 3.8 Hz), 124.9, 123.2, 122.5, 122.0, 115.1 (d, *J* = 21.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.7; IR (neat): 3058, 2928, 1602, 1580, 1505, 1471, 1426, 1222, 1157, 1116, 970, 764 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{19}H_{12}FN_3O$+H, 318.1042; found, 318.1044.

4-(4-Chlorophenyl)-2,5-di(pyridin-2-yl)oxazole (3ah):



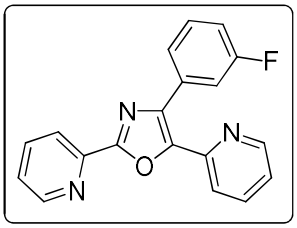
Yield: 75% (125 mg); white solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81-8.76 (m, 1H), 8.67-8.63 (m, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.12-8.06 (m, 2H), 7.87-7.80 (m, 2H), 7.78-7.71 (m, 1H), 7.43-7.36 (m, 3H), 7.28-7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 150.2, 149.5, 148.0, 145.9, 145.7, 138.9, 136.9, 136.7, 134.5, 130.4, 130.2, 128.3, 124.9, 123.3, 122.6, 122.1; IR (neat): 3058, 1589, 1491, 1473, 1457, 1439, 1426, 1116, 1089, 994, 787, 727 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{12}ClN_3O$+H, 334.0747; found, 334.0743.

4-(4-Bromophenyl)-2,5-di(pyridin-2-yl)oxazole (3ai):



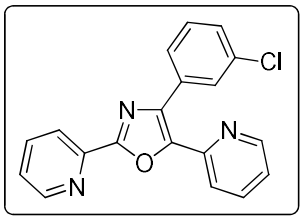
Yield: 53% (101 mg); white solid; mp: 118-120 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.14; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 8.83-8.78 (m, 1H), 8.67 (d, *J* = 4.8 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.05-8.00 (m, 2H), 7.90-7.83 (m, 2H), 7.77 (td, *J* = 7.6, 2.0 Hz, 1H), 7.59-7.53 (m, 2H), 7.41 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 7.31-7.25 (m, 1H)*; (*It contains a ddd *J* = 7.6, 4.8. 0.8 Hz and $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 150.3, 149.7, 148.2, 146.1, 145.9, 139.0, 137.1, 136.8, 131.3, 130.8, 130.7, 125.0, 123.4, 122.9, 122.7, 122.2; IR (neat): 3050, 1587, 1488, 1457, 1424, 1276, 1114, 1072, 967, 833, 788, 741 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{12}BrN_3O$+H, 378.0242; found, 378.0246.

4-(3-Fluorophenyl)-2,5-di(pyridin-2-yl)oxazole (3aj):



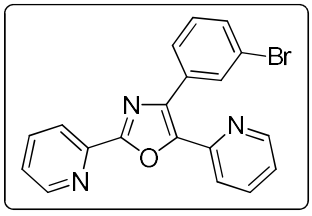
Yield: 54% (86 mg); white solid; mp: 118-120 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.25; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.70 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.89-7.84 (m, 2H), 7.80-7.75 (m, 1H), 7.43-7.36 (m, 2H), 7.31-7.27 (m, 1H), 7.11-7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 242.0 Hz), 159.2, 150.3, 149.6, 148.0, 146.3, 145.8, 138.7, 137.0, 136.8, 133.8 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 8.0 Hz), 125.0, 124.6, 123.4, 122.7, 122.4, 116.0 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 21.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.5; IR (neat): 3049, 1583, 1466, 1214, 1141, 1110, 992, 858, 782, 728 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{19}H_{12}FN_3O$+H, 318.1042; found, 318.1040.

4-(3-Chlorophenyl)-2,5-di(pyridin-2-yl)oxazole (3ak):



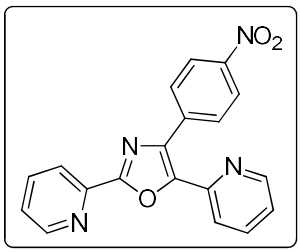
Yield: 49% (82 mg); white solid; mp: 128-130 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83-8.79 (m, 1H), 8.71-8.67 (m, 1H), 8.31-8.27 (m, 1H), 8.22-8.18 (m, 1H), 8.05-8.00 (m, 1H), 7.90-7.84 (m, 2H), 7.78 (td, *J* = 7.5, 2.0 Hz, 1H), 7.42 (ddd, *J* = 7.5, 5.0, 1.5 Hz, 1H), 7.38-7.34 (m, 2H), 7.29 (ddd, *J* =7.5, 5.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 150.3, 149.7, 148.0, 146.3, 145.8, 138.6, 137.0, 136.8, 134.1, 133.6, 129.4, 129.1, 128.7, 127.1, 125.1, 123.5, 122.7, 122.3; IR (neat): 3056, 1583, 1460, 1426, 1250, 1116, 996, 783, 724 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{12}ClN_3O$+H, 334.0747; found, 334.0746.

4-(3-Bromophenyl)-2,5-di(pyridin-2-yl)oxazole (3al):



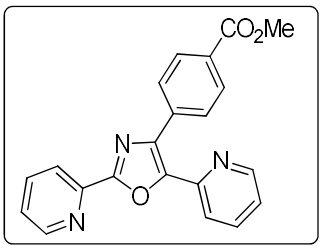
Yield: 51% (96 mg); white solid; mp: 133-135 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82-8.78 (m, 1H), 8.70-8.66 (m, 1H), 8.36 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.06 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.89-7.84 (m, 2H),7.78 (td, *J* = 7.5, 1.0 Hz, 1H), 7.51 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.44-7.39 (m, 1H), 7.32-7.26 (m, 2H)* (* It also contains $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 150.3, 149.7, 148.0, 146.3, 145.8, 138.5, 137.1, 136.8, 133.8, 132.0, 131.7, 129.6, 127.6, 125.1, 123.5, 122.7, 122.30, 122.27; IR (neat): 3051, 1584, 1549, 1481, 1455, 1424, 1168, 1117, 1073, 995, 775, 737 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{12}BrN_3O$+H, 378.0242; found, 378.0245.

4-(4-Nitrophenyl)-2,5-di(pyridin-2-yl)oxazole (3am):



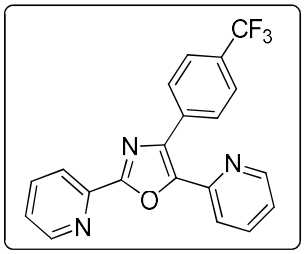
Yield: 21% (36 mg); pale yellow solid; mp: 201-203 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 4.4 Hz, 1H), 8.67 (d, *J* = 4.4 Hz, 1H), 8.44 (d, *J* = 8.8 Hz, 2H), 8.30-8.24 (m, 3H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.92-7.80 (m, 2H), 7.44 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.33 (dd, *J* = 7.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 150.4, 149.5, 147.7, 147.6, 147.5, 145.5, 138.2, 137.8, 137.1, 137.0, 129.9, 125.3, 123.9, 123.2, 122.7, 122.5; IR (neat): 3051, 3005, 1584, 1511, 1458, 1341, 1289, 1107, 994, 970, 784, 737 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{19}H_{12}N_4O_3$+H, 345.0987; found, 345.1002.

Methyl 4-(2,5-di(pyridin-2-yl)oxazol-4-yl)benzoate (3an):



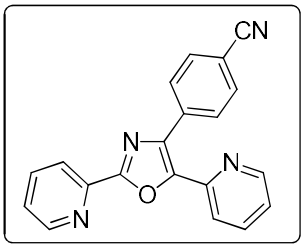
Yield: 50% (91 mg); white solid; mp: 153-155 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.21; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (ddd, *J* = 4.5, 2.0, 1.0 Hz, 1H), 8.68 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.30 (dt, *J* = 7.5, 1.0 Hz, 1H), 8.22-8.18 (m, 2H), 8.12-8.08 (m, 2H), 7.90-7.85 (m, 2H), 7.78 (td, *J* = 7.5, 2.0 Hz, 1H), 7.43 (ddd, *J* =7.5, 5.0, 1.5 Hz, 1H), 7.30 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.4, 150.3, 149.7, 148.0, 146.7, 145.7, 138.9, 137.1, 136.8, 136.2, 130.0, 129.4, 128.9, 125.1, 123.6, 122.7, 122.4, 52.2; IR (neat): 3050, 2999, 1714, 1585, 1459, 1440, 1292 1115, 968, 861, 774, 739 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{21}H_{15}N_3O_3$+H, 358.1191; found, 358.1192.

2,5-Di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)oxazole (3ao):



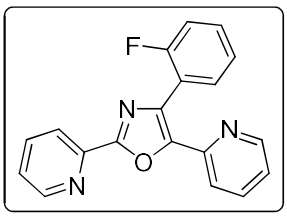
Yield: 57% (107 mg); white solid; mp: 119-121°C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84-8.79 (m, 1H), 8.69-8.66 (m, 1H), 8.31-8.25 (m, 3H), 7.92-7.86 (m, 2H), 7.80 (td, *J* = 7.5, 2.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.43 (ddd, *J* = 7.5,5.0,1.0 Hz, 1H), 7.31 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 150.2, 149.5, 147.9, 146.6, 145.6, 138.5, 137.0, 136.8, 135.3, 130.3 (q, *J* = 32.0 Hz), 129.3, 125.04, 124.96, 124.3 (q, *J* = 271.0 Hz), 123.5, 122.6, 122.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6; IR (neat): 3056, 1581, 1459, 1326, 1153, 1104, 1065, 969, 841, 781, 735 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{12}F_3N_3O$+H, 368.1010; found, 368.1019.

4-(2,5-Di(pyridin-2-yl)oxazol-4-yl)benzonitrile (3ap):



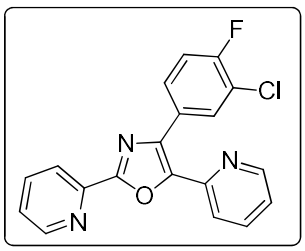
Yield: 26% (42 mg); white solid; mp: 174-176 °C; TLC (Hexane:EtOAc, 50:50 (v/v): R_f = 0.22; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (ddd, *J* = 4.5, 1.5, 1.0 Hz, 1H), 8.67 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.38-8.34 (m, 2H), 8.28 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.93 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.88 (td, *J* = 8.0, 2.0 Hz, 1H), 7.82 (td, *J* = 8.0, 2.0 Hz, 1H), 7.73-7.69 (m, 2H), 7.44 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 7.32 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 150.4, 149.6, 147.8, 147.2, 145.6, 138.1, 137.1, 137.0, 136.3, 131.8, 129.6, 125.2, 123.8, 122.7, 122.4, 119.1, 111.9; IR (neat): 2920, 2850, 2222, 1580, 1458, 1425, 1251, 1113, 992, 971, 785, 734 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{20}H_{12}N_4O$+H, 325.1089; found, 325.1086.

4-(2-Fluorophenyl)-2,5-di(pyridin-2-yl)oxazole (3aq):



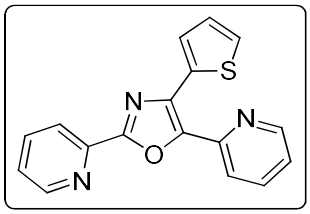
Yield: 33% (53 mg); white solid; mp:130-132 °C; TLC (Hexane:EtOAc, 55:45 (v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82-8.77 (m, 1H), 8.62-8.57 (m, 1H), 8.30-8.25 (m, 1H), 7.88-7.77 (m, 2H), 7.73-7.67 (m, 2H), 7.45-7.36 (m, 2H), 7.31-7.18 (m, 2H)*, 7.16-7.09 (m, 1H) (*It has also $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, *J* = 250.0 Hz), 159.7, 150.3, 149.8, 147.8, 147.5, 145.8, 137.0, 136.3, 134.0, 131.7, 130.5 (d, *J* = 8.0 Hz), 125.0, 124.2 (d, *J* = 4.0 Hz), 123.0, 122.6,121.4, 120.5 (d, *J* = 15.0 Hz), 115.8 (d, *J* = 22.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.1; IR (neat): 2918, 2849, 1579, 1453, 1423, 1221, 1110, 991, 765, 735 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{19}H_{12}FN_3O$+H, 318.1042; found, 318.1046.

4-(3-Chloro-4-fluorophenyl)-2,5-di(pyridin-2-yl)oxazole (3ar):



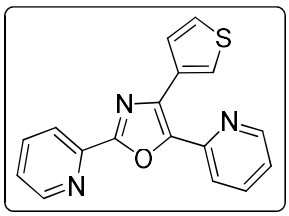
Yield: 52% (93 mg); white solid; mp: 182-184 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (d, *J* = 4.5 Hz, 1H), 8.67 (d, *J* = 4.5 Hz, 1H), 8.38 (dd, *J* = 7.5, 2.5 Hz, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.12 (ddd, *J* = 7.5, 5.0, 2.5 Hz, 1H), 7.93-7.85 (m, 2H)*, 7.80 (td, *J* = 8.0, 2.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.32-7.27 (m, 1H), 7.19 (t, *J* = 8.8 Hz, 1H),(*It contains a doublet at δ 7.91 (*J* = 8.5 Hz, 1H); and at td at δ 7.87 (*J* = 7.5, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 158.2 (d, *J* = 249.4, Hz), 150.3, 149.5, 148.0, 146.1, 145.7, 138.0, 137.1, 136.9, 131.5, 129.1 (d, *J* = 7.3 Hz), 129.0 (d, *J* = 3.8 Hz), 125.1, 123.5, 122.7, 122.1, 120.7 (d, *J* = 17.5 Hz), 116.1 (d, *J* = 21.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.4; IR (neat): 3051, 2923, 1579, 1552, 1499, 1457, 1423, 1244, 1113, 1060, 994, 814, 740 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{11}ClFN_3O$+H, 352.0653; found, 352.0651.

2,5-Di(pyridin-2-yl)-4-(thiophen-2-yl)oxazole (3as):



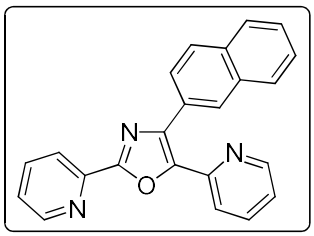
Yield: 50% (78 mg); pale yellow solid; mp: 132-134 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.21; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.77 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.44 (dd, *J* = 4.0, 1.0 Hz, 1H), 8.31 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.98 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.87 (td, *J* = 7.5, 2.0 Hz, 1H), 7.80 (td, *J* = 7.5, 2.0 Hz, 1H), 7.43-7.39 (m, 2H), 7.30-7.25 (m, 1H)*, 7.15 (dd, *J* = 5.0, 4.0 Hz, 1H); (*It contains a ddd at δ 7.28 (*J* = 7.5, 5.0, 1.0 Hz, 1H) merged with $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 150.2, 149.0, 148.0, 145.7, 144.3, 137.0, 136.7, 135.2, 134.6, 128.9, 127.4, 127.3, 125.0, 122.9, 122.8, 121.4; IR (neat): 3084, 2920, 2850, 1583, 1453, 1438, 1412, 1241, 1148, 1042, 963, 842, 783 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{11}N_3OS$+H, 306.0701; found, 306.0703.

2,5-Di(pyridin-2-yl)-4-(thiophen-3-yl)oxazole (3at):



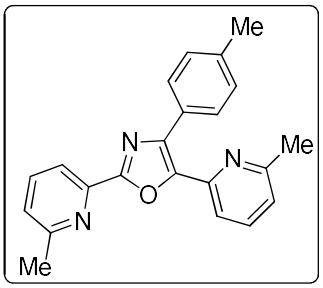
Yield: 62% (96 mg); pale yellow solid; mp: 136-138 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.28; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.73 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.60 (dd, *J* = 3.5, 1.5 Hz, 1H), 8.29 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.99 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.95 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.86 (td, *J* = 8.0, 2.0 Hz, 1H), 7.79 (td, *J* = 8.0, 2.0 Hz, 1H), 7.40 (ddd, *J* = 8.0, 5.0, 1.5 Hz, 1H), 7.36 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.27 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H).* (*It also contains $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 150.2, 149.3, 148.3, 145.9, 145.1, 137.0, 136.7, 136.0, 132.8, 128.7, 126.2, 124.9, 124.8, 122.9, 122.7, 121.9; IR (neat): 3113, 3078, 1582, 1460, 1429, 1153, 1116, 1085, 992, 853, 721 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{17}H_{11}N_3OS$+H, 306.0701; found, 306.0708.

4-(Naphthalen-2-yl)-2,5-di(pyridin-2-yl)oxazole (3au):



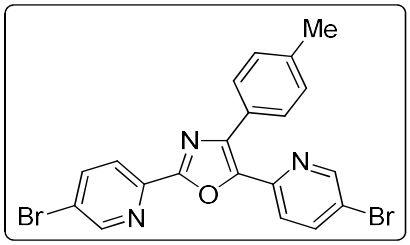
Yield: 58% (102 mg); brown solid; mp: 140-142 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.23; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83-8.79 (m, 1H), 8.72-8.67 (m, 1H), 8.63 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.92-7.80 (m, 5H), 7.72 (td, *J* = 8.0, 1.5 Hz, 1H), 7.52-7.46 (m, 2H), 7.39 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.28-7.23 (m, 1H).* (* It has a ddd, *J* = 7.5, 5.0, 1.5 Hz and $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 150.2, 149.6, 148.2, 146.0, 145.8, 139.9, 136.8, 136.5, 133.4, 133.2, 129.1, 128.5, 128.4, 127.6, 127.5, 126.5, 126.3, 126.0, 124.8, 123.1, 122.5, 122.2; IR (neat): 3045, 2919, 2849, 1580, 1457, 1425, 1256, 1114, 1093, 994, 787, 740 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{23}H_{15}N_3O$+H, 350.1293; found, 350.1291.

2,5-Bis(6-methylpyridin-2-yl)-4-(*p*-tolyl)oxazole (3bb):



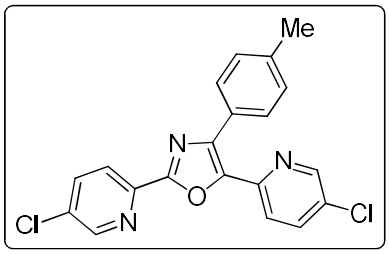
Yield: 32% (56 mg); pale yellow solid; mp: 109-110 °C; TLC (Hexane:EtOAc, 85:15 (v/v): R_f = 0.32; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.96-7.92 (m, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.61-7.53 (m, 2H), 7.27-7.20 (m, 3H)*, 7.12-7.09 (m, 1H), 2.70 (s, 3H), 2.61 (s, 3H), 2.40 (s, 3H); (*It contains a doublet at δ 7.25, *J* = 7.5 Hz, 1H and another doublet at δ 7.22, *J* = 8.5 Hz, 2H and also $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 159.3, 158.6, 147.6, 145.6, 145.4, 139.9, 138.5, 137.1, 136.7, 129.0, 128.93, 128.86, 124.7, 122.7, 119.9, 119.3, 24.7, 24.4, 21.5; IR (neat): 2918, 1591, 1573, 1443, 1256, 1157, 1087, 989, 965, 825, 787 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{22}H_{19}N_3O$+H, 342.1606; found, 342.1609.

2,5-Bis(5-bromopyridin-2-yl)-4-(*p*-tolyl)oxazole (3cb):



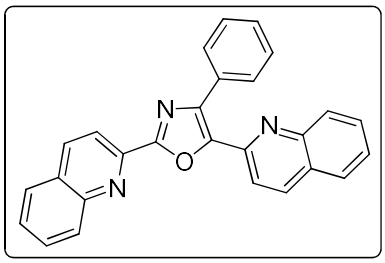
Yield: 49% (115 mg); white solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (d, *J* = 2.5 Hz, 1H), 8.72 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.98 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.84 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 151.4, 150.9, 146.5, 144.9, 144.2, 140.9, 139.7, 139.2, 139.1, 129.1, 128.8, 128.4, 123.7, 123.0, 122.5, 120.1, 21.5; IR (neat): 2912, 1567, 1462, 1446, 1362, 1233, 1107, 1086, 1004, 969, 824, 753 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{20}H_{13}Br_2N_3O$+H, 469.9503; found, 469.9501.

2,5-Bis(5-chloropyridin-2-yl)-4-(*p*-tolyl)oxazole (3db):



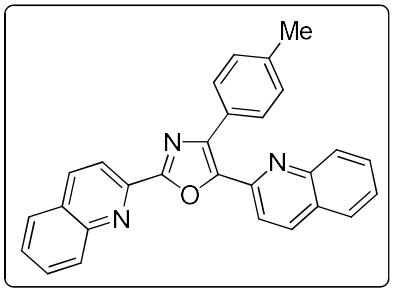
Yield: 45% (87 mg); pale yellow solid; mp: 139-141 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.31; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74-8.71 (m, 1H), 8.61 (dd, *J* = 2.5, 0.5 Hz, 1H), 8.22 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.74 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 149.2, 148.7, 146.2, 144.8, 143.9, 140.7, 139.1, 136.8, 136.4, 133.6, 131.3, 129.1, 128.8, 128.4, 123.4, 122.6, 21.5; IR (neat): 3043, 2916, 1573, 1508, 1466, 1453, 1362, 1110, 1010, 970, 818, 753, 725 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{20}H_{13}Cl_2N_3O$+H, 382.0514; found, 382.0514.

4-Phenyl-2,5-di(quinolin-2-yl)oxazole (3ea):



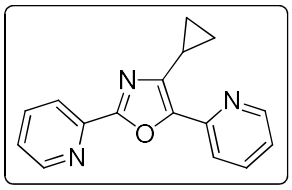
Yield: 30% (62 mg); pale yellow solid; mp: 203-205 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.31; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.33 (t, *J* = 8.5 Hz, 2H), 8.23-8.18 (m, 3H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.84-7.77 (m, 2H), 7.77-7.72 (m, 1H), 7.64-7.59 (m, 1H), 7.59-7.54 (m, 1H), 7.52-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 148.1, 148.0, 147.9, 146.5, 145.6, 141.4, 137.2, 136.6, 131.8, 130.34, 130.25, 130.1, 129.7, 129.3, 129.1, 128.5, 128.3, 127.8, 127.7, 127.6, 127.5, 127.2, 120.0; IR (neat): 3039, 2921, 2851, 1594, 1500, 1421, 1129, 1104, 973, 824, 765 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{27}H_{17}N_3O$+H, 400.1450; found, 400.1453.

2,5-Di(quinolin-2-yl)-4-(*p*-tolyl)oxazole (3eb):



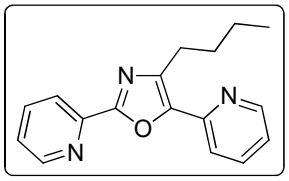
Yield: 61% (126 mg); white solid; mp: 200-202 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.23; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.5 Hz, 1H), 8.33 (t, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.84-7.72 (m, 3H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 148.1, 148.0, 146.2, 145.7, 141.5, 139.0, 137.2, 136.5, 130.3, 130.0, 129.7, 129.2, 129.0, 128.9, 128.5, 127.8, 127.7, 127.6, 127.5, 127.1, 120.04, 120.0, 21.6; IR (neat): 3042, 1595, 1501, 1422, 1130, 1103, 974, 938, 821, 766, 748 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{28}H_{19}N_3O$+H, 414.1606; found, 414.1609.

4-Cyclopropyl-2,5-di(pyridin-2-yl)oxazole (3av):



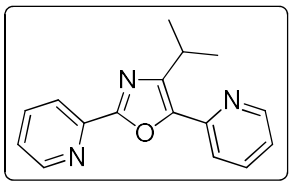
Yield: 93% (124 mg); white solid; mp: 112-114 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.31; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.5 Hz, 1H), 8.65 (d, *J* = 4.0 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80 (td, *J* = 7.5, 1.5 Hz, 1H), 7.75 (td, *J* = 8.0, 1.5 Hz, 1H), 7.37-7.32 (m, 1H), 7.21-7.16 (m, 1H), 3.10-3.02 (m, 1H),1.23-1.18 (m, 2H), 1.08-1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 150.2, 149.5, 149.1, 146.0, 145.7, 144.0, 136.9, 136.5, 124.6, 122.4, 121.9, 120.1, 8.1; IR (neat): 3051, 3002, 1603, 1582, 1477, 1456, 1428, 1391, 1149, 1114, 1042, 1014, 991, 960, 884, 786, 739, 694 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{13}N_3O$+H, 264.1137; found, 264.1137.

4-Butyl-2,5-di(pyridin-2-yl)oxazole (3aw):



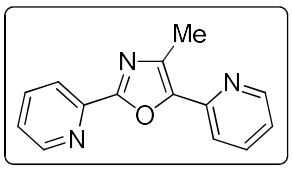
Yield: 46% (65 mg); white solid; mp: 84-86 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.27; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79-8.74 (m, 1H), 8.68-8.64 (m, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.86-7.80 (m, 2H), 7.75 (td, *J* = 8.0, 2.0 Hz, 1H), 7.39-7.35 (m, 1H), 7.19 (ddd, *J* = 7.0, 5.0, 0.5 Hz, 1H), 3.17 (t, *J* = 8.0 Hz, 2H), 1.85-1.76 (m, 2H), 1.52-1.41 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 150.2, 149.6, 148.9, 146.1, 145.6, 142.8, 136.9, 136.5, 124.6, 122.3, 122.0, 120.3, 30.9, 27.0, 22.6, 14.0; IR (neat): 3054, 2955, 2928, 2859, 1613,1582, 1474, 1456, 1438, 1428, 1284, 1151, 1115, 1023, 993, 792, 741, 704 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}N_3O$+H, 280.1450; found, 280.1451.

4-Isopropyl-2,5-di(pyridin-2-yl)oxazole (3ax):



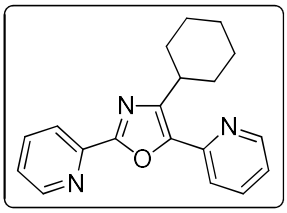
Yield: 54% (72 mg); white solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.32; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.66 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.21 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.85-7.81 (m, 2H), 7.76 (td, *J* = 7.5, 2.0 Hz, 1H), 7.37 (ddd, *J* = 7.5, 5.0, 1.5 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 4.03 (septet, *J* = 7.0 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 150.2, 149.6, 149.1, 147.9, 146.2, 144.2, 136.9, 136.5, 124.5, 122.4, 122.0, 120.5, 25.9, 21.7; IR (neat): 2969, 2928, 1582, 1474, 1458, 1439, 1427, 1215, 1114, 1016, 791, 753, 704 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{16}H_{15}N_3O$+H, 266.1293; found, 266.1295.

4-Methyl-2,5-di(pyridin-2-yl)oxazole (3ay):



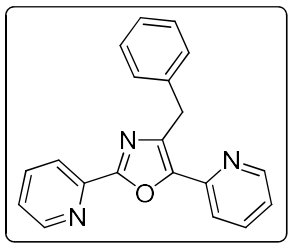
Yield: 39% (47 mg, using *n*-ProAc as solvent), 26% (32 mg, using acetonitrile as solvent); white solid; mp: 110-112 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.21; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 4.5, 1.5, 0.5 Hz, 1H), 8.67 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.88-7.81 (m, 2H), 7.77 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.20 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 150.2, 149.7, 148.9, 146.0, 145.8, 138.3, 137.0, 136.6, 124.7, 122.3, 122.1, 120.3, 13.8; IR (neat): 3044, 2919, 2851,1618, 1581, 1477, 1452, 1437, 1425, 1383, 1243, 1151, 1113, 1038, 990, 961, 795, 782, 735, 710, 673 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{14}H_{11}N_3O$+H, 238.0980; found, 238.0980.

4-Cyclohexyl-2,5-di(pyridin-2-yl)oxazole (3az):



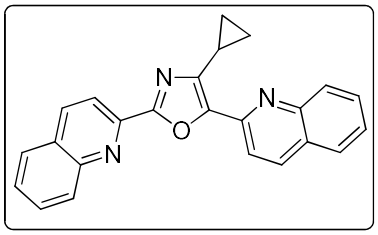
Yield: 51% (78 mg); white solid; mp: 162-164 ºC; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 8.67 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.19 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.84-7.80 (m, 2H), 7.75 (td, *J* = 7.5, 2.0 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 3.68-3.61 (m, 1H), 1.94-1.73 (m, 7H)*, 1.51-1.32 (m, 3H) (*It also contains moisture peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 150.2, 149.8, 149.1, 147.2, 146.3, 144.6, 136.9, 136.5, 124.5, 122.4, 122.0, 120.5, 35.6, 31.6, 26.5, 26.1; IR (neat): 2926, 2849, 1580, 1473, 1455, 1438, 1427, 1113, 1045, 996, 789, 738, 703 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{19}H_{19}N_3O$+H, 306.1606; found, 306.1607.

4-Benzyl-2,5-di(pyridin-2-yl)oxazole (3az'):



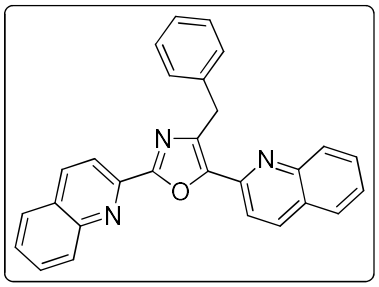
Yield: 58% (92 mg); pale yellow solid; mp: 129-131 ºC; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77-8.74 (m, 1H), 8.67 (d, *J* = 4.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.90-7.86 (m, 1H), 7.81 (td, *J* = 8.0, 2.0 Hz, 1H), 7.75 (td, *J* = 8.0, 2.0 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.36 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 2H)*, 7.21 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.60 (s, 2H) (*It also contains $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 150.1, 149.6, 148.6, 146.12, 146.05, 140.9, 139.5, 136.9, 136.6, 129.1, 128.4, 126.2, 124.7, 122.5, 122.4, 120.3, 33.2; IR (neat): 3055, 1581, 1493, 1474, 1455, 1427, 1264, 1152, 1111, 1026, 991, 961, 792, 737, 704 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{20}H_{15}N_3O$+H, 314.1293; found, 314.1293.

4-Cyclopropyl-2,5-di(quinolin-2-yl)oxazole (3ev):



Yield: 52% (96 mg); white solid; mp: 166-168 ºC; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.6; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30-8.19 (m, 4H), 8.11 (d, *J* = 8.5 Hz,1H), 8.08 (d, *J* = 8.5 Hz,1H), 7.84 -7.68 (m, 4H), 7.59-7.54 (m, 1H), 7.53 -7.47 (m, 1H), 3.32-3.22 (m, 1H), 1.32-1.25 (m, 2H), 1.19-1.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 148.8, 148.0, 146.5, 145.8, 145.6, 137.0, 136.6, 130.2, 130.1, 129.9, 129.4, 128.4, 127.6, 127.1, 126.5, 119.9, 118.7, 8.6; IR (neat): 3053, 3011, 1595, 1500, 1427, 1303, 1131, 1028, 834, 754 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{24}H_{17}N_3O$+H, 364.1450; found, 364.1449.

4-Benzyl-2,5-di(quinolin-2-yl)oxazole (3ez'):

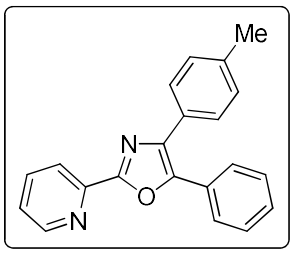


Yield: 87% (182 mg); white solid; mp: 219-221 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36-8.25 (m, 4H), 8.16-8.12 (m, 2H),7.86 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.63-7.58 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 148.4, 148.1, 146.8, 145.7, 142.4, 139.6, 137.1, 136.7, 130.3, 130.2, 130.0, 129.6, 129.2, 128.5, 127.7, 127.2, 126.7, 126.3, 119.9, 118.6, 33.6; IR (neat): 3022, 1593, 1495, 1424, 1343, 1125, 1095, 1033, 829, 762, 734, 700 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{28}H_{19}N_3O$+H, 414.1606; found, 414.1605.

4. General synthetic procedure for mixed oxazoles 5

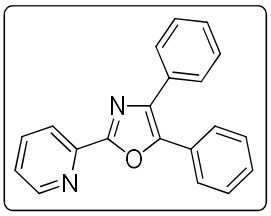
An oven-dried 10 mL round-bottomed flask was charged with pyridine-2-carboxaldehydes/ quinoline-2-carboxaldehye (**1**) (1 mmol), aryl aldehyde (**4**) (2 mmol), nitrile (**2**) (3 mmol), and *n*-PrOAc (2 mL) under nitrogen. The contents were cooled to 0 °C (ice bath) and then TMSOTf (1.5 mmol) was added. The reaction mixture was allowed to stir at room temperature for 5-10 min and then heated under reflux (oil bath temperature 120 °C). After completion of the reaction (monitored by TLC) (2-6 h), the reaction mixture was cooled to room temperature and quenched with saturated K_2CO_3 solution (4 mL). Then reaction mixture was diluted with ethyl acetate (7-10 mL). The organic layer was washed with saturated $NaHCO_3$ solution (2X5 mL) followed by brine (1X5 mL). Organic layer was dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure. The residue obtained was purified by column chromatography using silica gel (100-200 mesh) hexanes:ethyl acetate 60:40 (v/v)] to afford the desired oxazoles **5** as crystalline solids.

5-Phenyl-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5aab):



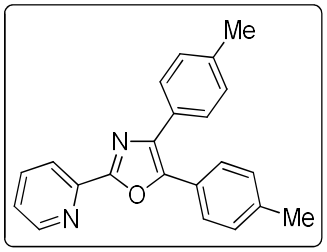
Yield: 56% (177 mg); white solid; mp:110-112 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.48; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 8.22 (dt, *J* = 8.0, 1.0 Hz, 1H),7.82 (td, *J* = 8.0,1.5 Hz, 1H), 7.75-7.71 (m, 2H), 7.67-7.62 (m, 2H), 7.41-7.33 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 150.2, 146.6, 146.3, 138.2, 137.3, 136.9, 129.4, 129.3, 128.9, 128.7, 128.1, 127.1, 124.5, 122.3, 21.4; IR (neat): 2919, 2852, 1586, 1513, 1459, 1435, 1104, 964, 826, 764 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{16}N_2O$+H, 313.1341; found, 313.1343.

4,5-Diphenyl-2-(pyridin-2-yl)oxazole (5aaa):



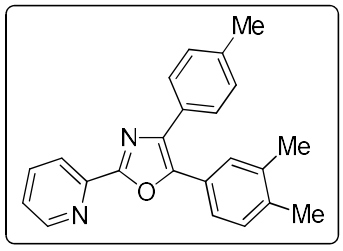
Yield: 40% (120 mg); white solid; mp: 124-126 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 8.23 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.83 (td, *J* = 8.0, 1.5 Hz, 1H), 7.78-7.70 (m, 4H), 7.43-7.34 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 150.2, 147.0, 146.2, 137.2, 136.9, 132.3 129.0, 128.7, 128.6, 128.4, 128.2, 127.2, 124.6, 122.3; IR (neat): 3035, 1584, 1435, 1102, 963, 759, 737 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{20}H_{14}N_2O$+H, 299.1184; found, 299.1184.

2-(Pyridin-2-yl)-4,5-di-*p*-tolyloxazole (5abb):



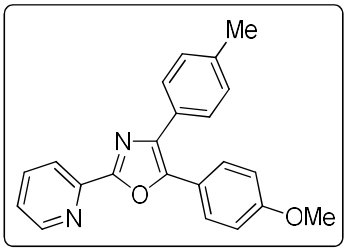
Yield: 46% (151 mg); white solid; mp: 114-116 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.51; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 4.5, 0.5 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.81 (td, *J* = 8.0, 2.0 Hz, 1H), 7.67-7.58 (m, 4H), 7.35 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.23-7.15 (m, 4H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 150.1, 146.8, 146.3, 138.9, 138.1, 136.9, 136.7, 129.44, 129.36, 129.3, 128.0, 127.0, 126.0, 124.4, 122.2, 21.5, 21.4; IR (neat): 3025, 2915, 1587, 1496, 1458, 1436, 1328, 1096, 967, 816, 792 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{18}N_2O$+H, 327.1497; found, 327.1495.

5-(3,4-Dimethylphenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5acb):



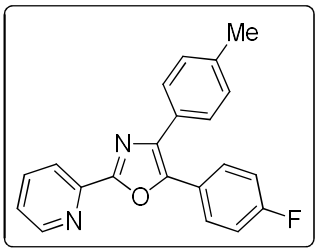
Yield: 48% (165 mg); white solid; mp: 148-150 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.65; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (ddd, *J* = 4.5, 1.5, 1.0 Hz, 1H), 8.22 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.83 (td, *J* = 8.0, 2.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.42 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 150.1, 147.0, 146.4, 138.0, 137.7, 137.0, 136.9, 136.6, 129.9, 129.5, 129.2, 128.2, 128.0, 126.3, 124.7, 124.4, 122.2, 21.4, 19.78, 19.76; IR (neat): 3050, 1588, 1514, 1492, 1457, 1439, 1264, 1106, 999, 976, 821, 732 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{23}H_{20}N_2O$+H, 341.1654; found, 341.1655.

5-(4-Methoxyphenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5adb):



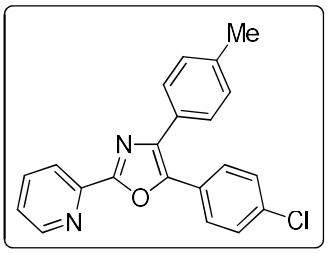
Yield: 30% (103 mg); white solid; mp: 116-118 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 8.0, 2.0 Hz, 1H), 7.68-7.61 (m, 4H), 7.35 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.94-6.91 (m, 2H), 3.85 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 158.5, 150.0, 146.7, 146.3, 137.9, 136.8, 136.0, 129.5, 129.2, 128.6, 127.9, 124.3, 122.1, 121.3, 114.1, 55.3, 21.3; IR (neat): 3041, 2994, 2919, 2848, 1588, 1516, 1495, 1457, 1439, 1246, 1179, 1101, 1025, 966, 829, 819, 792, cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{22}H_{18}N_2O_2$+H, 343.1446; found, 343.1448.

5-(4-Fluorophenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5aeb):



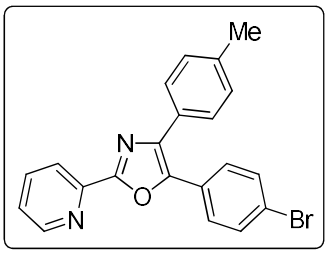
Yield: 42% (139 mg); white solid; mp: 130-132 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.47; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.22 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.83 (td, *J* = 7.5, 1.5 Hz, 1H), 7.73-7.67 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.37 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.11-7.05 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (d, *J* = 247.5 Hz), 158.9, 150.2, 146.2, 145.8, 138.4, 137.1, 136.9, 129.4, 129.14, 129.13 (d, *J* = 8.8 Hz), 128.0, 125.1 (d, *J* = 3.8 Hz), 124.6, 122.3, 115.9 (d, *J* = 22.5 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.5; IR (neat): 3058, 2918, 1589, 1516, 1494, 1461, 1434, 1222, 1156, 1093, 967, 839, 817, 791 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{15}FN_2O$+H, 331.1246; found, 331.1247.

5-(4-Chlorophenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5afb):



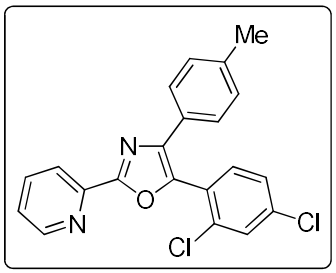
Yield: 40% (140 mg); white solid; mp: 128-130 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.48; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 4.5, 1.5 1.0 Hz, 1H), 8.22 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.83 (td, *J* = 8.0, 1.5 Hz, 1H), 7.68-7.64 (m, 2H), 7.63-7.59 (m, 2H), 7.39-7.32 (m, 3H), 7.24-7.20 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 150.2, 146.1, 145.5, 138.5, 137.7, 136.9, 134.7, 129.4, 129.1, 129.0, 128.2, 128.1, 127.3, 124.7, 122.4, 21.4; IR (neat): 3057, 1585, 1482, 1453, 1437, 1109, 1091, 965, 845, 815, 734 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{15}ClN_2O$+H, 347.0951; found, 347.0950.

5-(4-Bromophenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5agb):



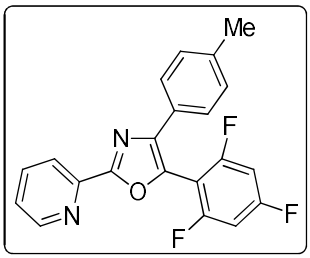
Yield: 39% (154 mg); white solid; mp: 131-133 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.54; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 4.5, 1.5, 1.0 Hz, 1H), 8.23 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.83 (td, *J* = 8.0, 2.0 Hz, 1H), 7.63-7.57 (m, 4H), 7.53-7.48 (m, 2H), 7.38 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 150.2, 146.1, 145.6, 138.6, 137.8, 137.0, 132.0, 129.5, 129.1, 128.5, 128.1, 127.8, 124.7, 122.9, 122.4, 21.4; IR (neat): 3056, 1585, 1479, 1454, 1436, 1110, 1072, 964, 815, 788, 734 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{15}BrN_2O$+H, 391.0446; found, 391.0448.

5-(2,4-Dichlorophenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5ahb):



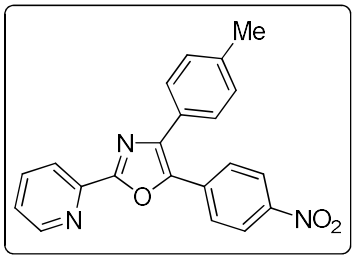
Yield: 40% (152 mg); white solid; mp:148-150 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78-8.73 (m, 1H), 8.27-8.21 (m, 1H), 7.85 (td, *J* = 8.0, 2.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.54-7.48 (m, 3H), 7.39 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 150.2, 146.0, 142.4, 139.3, 138.3, 137.0, 136.5, 135.6, 133.2, 130.3, 129.3, 128.3, 127.5, 127.2, 126.8, 124.8, 122.4, 21.3; IR (neat): 3006, 1588, 1512, 1468, 1436, 1328, 1275, 1098, 1038, 967, 818, 748 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{14}Cl_2N_2O$+H, 381.0561; found, 381.0564.

2-(Pyridin-2-yl)-4-(*p*-tolyl)-5-(2,4,6-trifluorophenyl)oxazole (5aib):



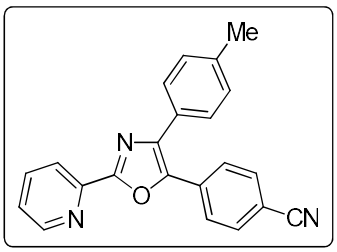
Yield: 38% (140 mg); white solid; mp: 165-167 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.26 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.85 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.39 (ddd, *J* = 8.0, 5.0, 1.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.85-6.78 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1 (dt, *J* = 251.3, 15.0 Hz,), 161.5 (ddd, *J* = 253.8, 15.0, 8.8 Hz), 160.8, 150.2, 146.0, 141.4, 138.5, 137.0, 133.6, 129.4, 128.2, 126.5, 124.9, 122.5, 104.2 (td, *J* = 18.8, 5.0 Hz), 101.3-100.9 (m), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.5 (d, *J* = 3.8 Hz), -104.6; IR (neat): 3053, 1650, 1591, 1460, 1438, 1331, 1182, 1128, 1096, 1027, 998, 967, 818, 796 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{21}H_{13}F_3N_2O$+H, 367.1058; found, 367.1058.

5-(4-Nitrophenyl)-2-(pyridin-2-yl)-4-(*p*-tolyl)oxazole (5ajb):



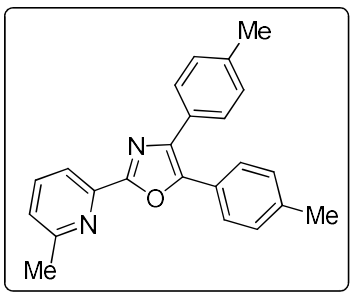
Yield: 37% (132 mg); white solid; mp: 206-208 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.49; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (ddd, *J* = 4.5, 1.5, 1.0 Hz, 1H), 8.27 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.24-8.20 (m, 2H), 7.93-7.91 (m, 2H), 7.87 (td, *J* = 8.0, 2.0 Hz, 1H), 7.62-7.58 (m, 2H), 7.43 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H)*, 2.43 (s, 3H) (*One of the peaks of doublet merges with $CHCl_3$ peak); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 150.3, 147.3, 145.7, 144.3, 140.6, 139.4, 137.1, 134.8, 129.7, 128.6, 128.4, 126.9, 125.2, 124.2, 122.8, 21.5; IR (neat): 2924, 1600, 1585, 1514, 1333, 1107, 968, 852, 824, 755 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{15}N_3O_3$+H, 358.1191; found, 358.1190.

4-(2-(Pyridin-2-yl)-4-(*p*-tolyl)oxazol-5-yl)benzonitrile (5akb):



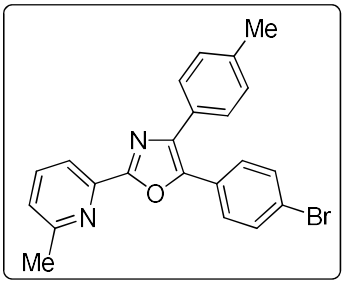
Yield: 37% (126 mg); white solid; mp: 208-210 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.34; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81-8.77 (m, 1H), 8.27-8.23 (m, 1H), 7.88-7.82 (m, 3H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (ddd, *J* = 7.5, 5.0, 1.0 Hz,1H), 7.25 (d, *J* = 8.0 Hz, 2H)*, 2.42 (s, 3H) (*It also contains $CHCl_3$ peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 150.3, 145.8, 144.5, 139.9, 139.2, 137.0, 132.9, 132.5, 129.6, 128.7, 128.3, 126.8, 125.0, 122.6, 118.6, 111.8, 21.5; IR (neat): 3049, 2222, 1608, 1583, 1454, 1437, 1109, 966, 843, 822, 739 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{15}N_3O$+H, 338.1293; found, 338.1295.

2-(6-Methylpyridin-2-yl)-4,5-di-*p*-tolyloxazole (5bbb):



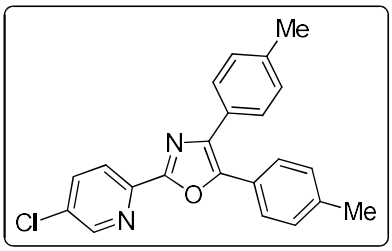
Yield: 62% (215 mg); white solid; mp: 142-144 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.61; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.23-7.16 (m, 5H), 2.68 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 158.9, 146.7, 145.7, 138.8, 138.0, 137.0, 136.7, 129.5, 129.3, 129.2, 128.1, 127.0, 126.1, 124.3, 119.4, 24.7, 21.4; IR (neat): 3028, 2920, 1595, 1574, 1520, 1497, 1457, 1158, 1118, 967, 820, 741 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{23}H_{20}N_2O$+H, 341.1654; found, 341.1652.

5-(4-Bromophenyl)-2-(6-methylpyridin-2-yl)-4-(*p*-tolyl)oxazole (5bgb):



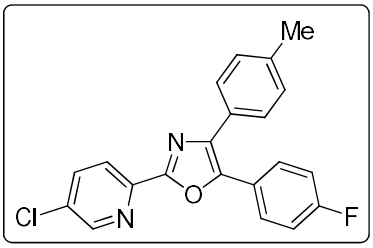
Yield: 58% (236 mg); white solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.75; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 4H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.24-7.18 (m, 3H), 2.67 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 159.2, 145.4, 145.3, 138.4, 137.7, 137.0, 131.8, 129.3, 129.1, 128.3, 128.1, 127.8, 124.5, 122.7, 119.6, 24.7, 21.4; IR (neat): 3025, 1589, 1574, 1509, 1480, 1456, 1256, 1158, 1085, 1008, 964, 821, 801, 737 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{17}BrN_2O$+H, 405.0602; found, 405.0603.

2-(5-Chloropyridin-2-yl)-4,5-di-*p*-tolyloxazole (5dbb):



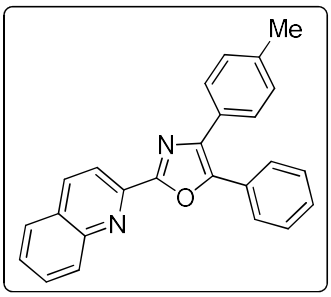
Yield: 88% (318 mg); white solid; mp: 156-158 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.63; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 8.70 (dd, *J* = 2.5, 0.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.78 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.64-7.58 (m, 4H), 7.21-7.17 (m, 4H), 2.384 (s, 3H), 2.379 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 149.1, 147.1, 144.3, 139.1, 138.2, 136.9, 136.7, 132.9, 129.7, 129.4, 129.3, 128.0, 127.0, 125.7, 122.8, 21.5, 21.4; IR (neat): 3035, 1575, 1519, 1495, 1452, 1363, 1234, 1110, 1010, 966, 821 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{17}ClN_2O$+H, 361.1107; found, 361.1106.

2-(5-Chloropyridin-2-yl)-5-(4-fluorophenyl)-4-(*p*-tolyl)oxazole (5deb):



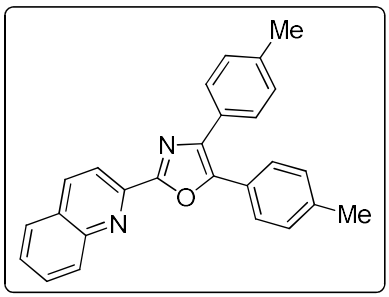
Yield: 78% (285 mg); white solid; mp: 143-145 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.74; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (dd, *J* = 2.5, 0.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.70-7.65 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 248.0 Hz), 158.0, 149.0, 145.9, 144.0, 138.4, 137.1, 136.7, 133.1, 129.4, 129.0 (d, *J* = 8.0 Hz), 128.8, 127.9, 124.7, 122.9, 115.8 (d, *J* = 22.0 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.2; IR (neat): 3041, 1517, 1494, 1454, 1365, 1231, 1159, 1109, 1009, 968, 836, 819 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{21}H_{14}ClFN_2O$+H, 365.0857; found, 365.0859.

5-Phenyl-2-(quinolin-2-yl)-4-(*p*-tolyl) oxazole (5eab):



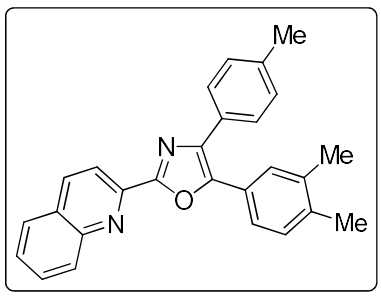
Yield: 68% (251 mg); white solid; mp: 178-180 °C; TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.77; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.31-8.27 (m, 2H), 7.86 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.80-7.75 (m, 3H), 7.69-7.65 (m, 2H), 7.62-7.57 (m, 1H), 7.44-7.35 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 148.1, 147.2, 146.0, 138.3, 137.6, 137.1, 130.22, 130.16, 129.4, 129.0, 128.8, 128.7, 128.3, 128.2, 127.7, 127.5, 127.2, 119.7, 21.4; IR (neat): 1599, 1508, 1429, 1343, 1125, 1094, 962, 823, 761, 701 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{25}H_{18}N_2O$+H, 363.1497; found, 363.1499.

2-(Quinolin-2-yl)-4,5-di-*p*-tolyloxazole (5ebb):



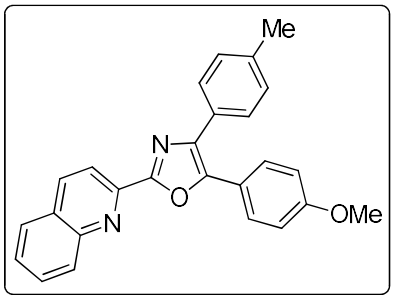
Yield: 71% (274 mg); white solid; mp: 194-196 °C; TLC (Hexane:EtOAc, 60:40 (v/v): R_f = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.5 Hz, 1H), 8.28 (t, *J* = 9.5 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.61-7.56 (m, 1H), 7.25-7.19 (m, 4H), 2.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 148.1, 147.4, 146.1, 139.1, 138.2, 137.1, 137.0, 130.2, 130.1, 129.5, 129.4, 129.3, 128.3, 128.1, 127.7, 127.5, 127.2, 126.0, 119.7, 21.5, 21.4; IR (neat): 3004, 1593, 1495, 1424, 1276, 1088, 963, 816, 764 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{26}H_{20}N_2O$+H, 377.1654; found, 377.1660.

5-(3,4-Dimethylphenyl)-2-(quinolin-2-yl)-4-(*p*-tolyl)oxazole (5ecb):



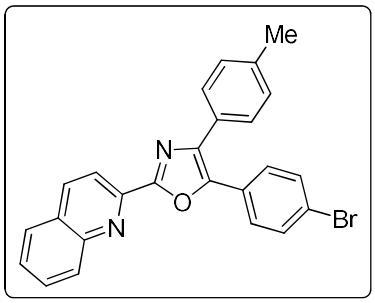
Yield: 73% (286 mg); white solid; mp: 206-208 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.68; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32-8.27 (m, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.73-7.67 (m, 3H), 7.58 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 148.0, 147.4, 146.0, 138.0, 137.7, 136.9, 136.84, 136.82, 130.1, 130.0, 129.8, 129.5, 129.2, 128.20, 128.17, 128.0, 127.6, 127.3, 126.2, 124.6, 119.6, 21.3, 19.7; IR (neat): 2917, 1593, 1546, 1495, 1426, 1097, 1000, 977, 843, 819, 767 cm^{-1}; HRMS (ESI,m/z): $[M+H]^+$ calcd. for $C_{27}H_{22}N_2O$+H, 391.1810; found, 391.1808.

5-(4-Methoxyphenyl)-2-(quinolin-2-yl)-4-(*p*-tolyl)oxazole (5edb):



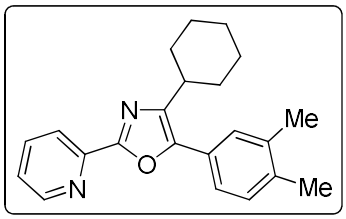
Yield: 61% (241 mg); white solid; mp: 173-175 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.72; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.28 (t, *J* = 8.5 Hz, 2H), 7.85 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.79-7.74 (m, 1H), 7.71 (dt, *J* = 8.5, 3.0 Hz, 2H), 7.68-7.64 (m, 2H), 7.61-7.56 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.94 (dt, *J* = 8.5, 3.0 Hz, 2H), 3.86 (s, 3H), 2.40 (s, 3H): ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, 158.8, 148.1, 147.3, 146.1, 138.1, 137.0, 136.4, 130.2, 130.1, 129.5, 129.3, 128.8, 128.3, 128.0, 127.7, 127.4, 121.4, 119.7, 114.2, 55.4, 21.4; IR (neat): 2916, 1598, 1518, 1496, 1344, 1289, 1244, 1176, 1090, 1026, 837, 818, 760 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{26}H_{20}N_2O_2$+H, 393.1603; found, 393.1601.

5-(4-Bromophenyl)-2-(quinolin-2-yl)-4-(*p*-tolyl)oxazole (5egb):



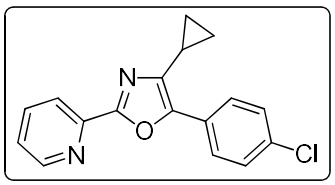
Yield: 43% (194 mg); white solid; mp:194-196 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.76; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.30-8.26 (m, 2H), 7.85 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.80-7.75 (m, 1H), 7.67-7.57 (m, 5H), 7.53 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.24 (dd, *J* = 8.0, 0.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 148.1, 146.0, 145.7, 138.6, 138.0, 137.1, 131.9, 130.2, 130.1, 129.5, 129.0, 128.5, 128.3, 128.1, 127.7, 127.6, 123.0, 119.7, 21.4; IR (neat): 3023, 1594, 1479, 1425, 1099, 1072, 1009, 963, 821, 763 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{25}H_{17}BrN_2O$+H, 441.0602; found, 441.0601.

4-Cyclohexyl-5-(3,4-dimethylphenyl)-2-(pyridin-2-yl)oxazole (5acz):



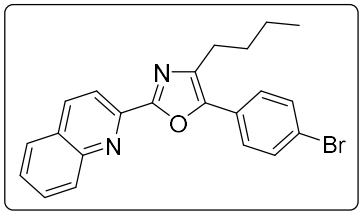
Yield: 38% (126 mg); white solid; mp: 128-130 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.39; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (ddd, *J* = 4.5, 1.0, 0.5 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.79 (td, *J* = 7.5, 1.5 Hz, 1H), 7.48 (s, 1H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.32 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 2.93-2.85 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.92-1.83 (m, 6H), 1.78-1.71 (m, 1H)*, 1.44-1.32 (m, 3H); (*It also contains moisture peak); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 150.2, 146.6, 146.0, 142.7, 137.1, 137.0, 136.8, 130.1, 127.7, 126.6, 124.1, 124.0, 122.0, 36.1, 32.1, 26.6, 26.0, 20.0, 19.7; IR (neat): 2926, 2852, 1589, 1499, 1451, 1215, 1119, 989, 886, 791, 749 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{24}N_2O$+H, 333.1967; found, 333.1968.

5-(4-Chlorophenyl)-4-cyclopropyl-2-(pyridin-2-yl)oxazole (5afv):



Yield: 35% (105 mg); white solid; mp: 160-162 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.0 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.83-7.75 (m, 3H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.36-7.29 (m, 1H), 2.09-2.01 (m, 1H), 1.15-1.09 (m, 2H), 1.06-0.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 150.1, 146.13, 146.07, 139.7, 136.8, 133.7, 129.0, 127.4, 127.1, 124.4, 122.1, 8.2, 7.4; IR (neat): 3003, 1584, 1490, 1462, 1437, 1248, 1125, 1087, 1042, 1024, 998, 831, 796, 743, 713 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{17}H_{13}ClN_2O$+H, 297.0794; found, 297.0795.

5-(4-Bromophenyl)-4-butyl-2-(quinolin-2-yl)oxazole (5egw):



Yield: 21% (89 mg); white solid; mp: 149-151 °C; TLC (Hexane:EtOAc, 80:20 (v/v): R_f = 0.64; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31-8.24 (m, 3H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.80-7.75 (m, 1H), 7.68-7.56 (m, 5H), 2.87 (t, *J* = 8.0 Hz, 2H), 1.82 (quintet, *J* = 8.0 Hz, 2H), 1.48 (sextet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.2, 146.1, 145.8, 139.5, 137.1, 132.1, 130.2, 128.3, 127.8, 127.5, 122.2, 119.5, 31.0, 27.3, 22.7, 14.0; IR (neat): 2953, 2927, 2859, 1597, 1501, 1484, 1428, 1334, 1136, 1098, 1072, 1003, 829, 763 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{22}H_{19}BrN_2O$+H, 407.0759; found, 407.0757.

5. Crystallographic Information

A suitable single crystal was mounted on a glass fiber (for **3aa**, **3bb**, **3ea**, **5aab**, **5aib**, and **5afv**) and X-ray data were collected at 293 K on Rigaku Oxford Diffraction XtaLAB Synergy diffractometer and Bruker D8 Quest CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods. All non-hydrogen atoms were refined anisotropically. Crystal data with molecular structures are summarized below. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

5. (i) Crystal data and molecular structure of compound 3aa

Crystal data for **3aa** (CCDC deposition number 2108509): Empirical formula, $C_{19}H_{13}N_3O$; Formula weight, 299.32; crystal color, colorless, crystal description, block; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Triclinic; lattice type, primitive; lattice parameters, a = 6.1025(3) Å, b = 8.5817(5) Å, c = 14.6868(9) Å, α = 86.201(5), β = 80.086(5), γ = 76.138(5); V = 735.34(7) Å^3 ; space group, P -1; Z = 2; Dcald = 1.352g/cm^3; F(000) = 312; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.092; R1[I≥2σ(I)] = 0.0483 (2035), wR2 = 0.1458 (2583).

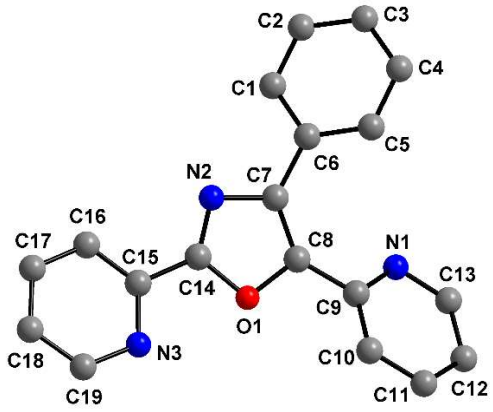


Fig. S1. Molecular structure of compound **3aa** (CCDC deposition number 2108509). Hydrogen atoms are omitted for clarity.

5. (ii) Crystal data and molecular structure of compound 3bb

Crystal data for **3bb** (CCDC deposition number 2108510): Empirical formula, $C_{22}H_{19}N_3O$; Formula weight, 341.40; crystal color, white; crystal description, plate; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Monoclinic; lattice type, primitive; lattice parameters, a = 21.1606(10) Å, b = 7.1694(3) Å, c = 25.5604(14) Å, α = 90, β = 110.862(6), γ = 90; V = 3623.5(3) $Å^3$; space group, I2/a; Z = 8; Dcald = 1.252 g/cm^3 ; F(000) = 1440; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.086; R1[I≥2σ(I)] = 0.0548 (2137), wR2 = 0.1725 (3210).

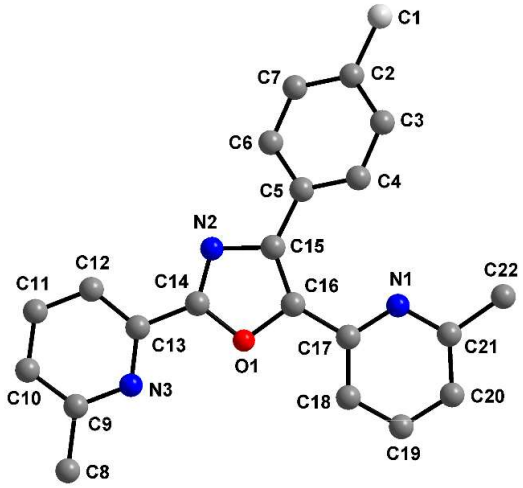


Fig. S2. Molecular structure of compound **3bb** (CCDC deposition number 2108510). Hydrogen atoms are omitted for clarity.

5. (iii) Crystal data and molecular structure of compound 3ea

Crystal data for **3ea** (CCDC deposition number 2108511): Empirical formula, $C_{27}H_{17}N_3O$; Formula weight, 399.44; crystal color, yellow; crystal description, plate; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Monoclinic; lattice type, primitive; lattice parameters, a = 11.3712(5) Å, b = 9.2050(4) Å, c = 19.1767(9) Å, α = 90, β = 104.402(5), γ = 90; V = 1944.18(15) $Å^3$; space group, $P2_1/n$; Z = 4; Dcald = 1.365 g/cm^3; F(000) = 832; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.088; R1[I≥2σ(I)] = 0.0428 (2570), wR2 = 0.1236 (3423).

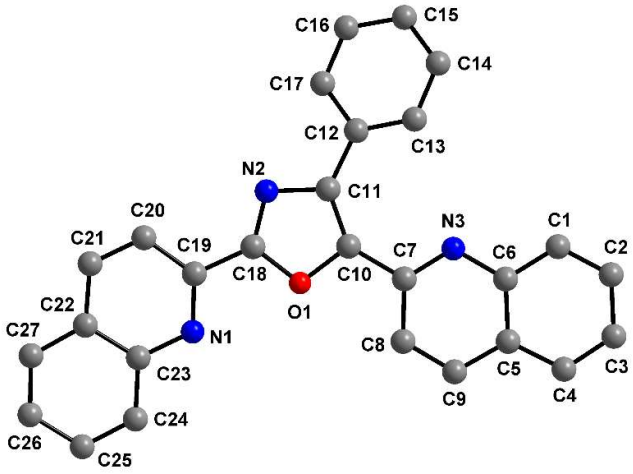


Fig. S3. Molecular structure of compound **3ea** (CCDC deposition number 2108511). Hydrogen atoms are omitted for clarity.

5. (iv) Crystal data and molecular structure of compound 5aab

Crystal data for **5aab** (CCDC deposition number 2110001): Empirical formula, $C_{21}H_{16}N_2O$; Formula weight, 312.36; crystal color, white; crystal description, needle; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Orthorhombic; lattice type, primitive; lattice parameters, a = 7.4535(11) Å, b = 11.5915(16) Å, c = 18.893(3) Å, α = 90, β = 90, γ = 90; V = 1632.3(4) $Å^3$; space group, $P2_12_12_1$; Z = 4; Dcald = 1.271 g/cm^3 ; F(000) = 656; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.067; R1[I≥2σ(I)] = 0.0574 (2086), wR2 = 0.1461 (2816).

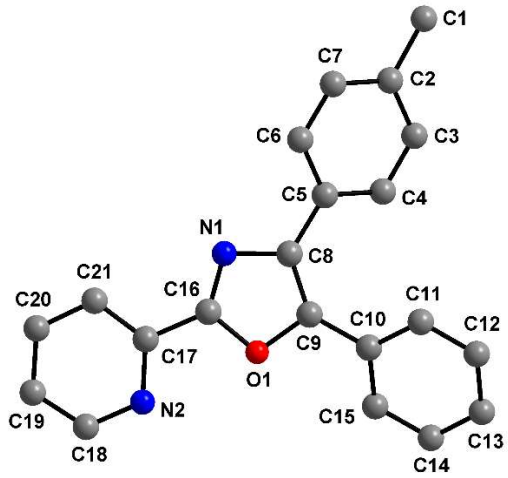


Fig. S4. Molecular structure of compound **5aab** (CCDC deposition number 2110001). Hydrogen atoms are omitted for clarity.

5. (v) Crystal data and molecular structure of compound 5aib

Crystal data for **5aib** (CCDC deposition number 2110003): Empirical formula, $C_{21}H_{13}F_3N_2O$; Formula weight, 366.33; crystal color, white; crystal description, block; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Monoclinic; lattice type, primitive; lattice parameters, a = 12.0851(4) Å, b = 7.7428(3) Å, c = 19.0267(8) Å, α = 90, β = 102.465(4), γ = 90; V = 1738.41(11) $Å^3$; space group, $P2_1/c$; Z = 4; Dcald = 1.400 g/cm^3; F(000) = 752; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.082; R1[I≥2σ(I)] = 0.0404 (2276), wR2 = 0.1166 (3059).

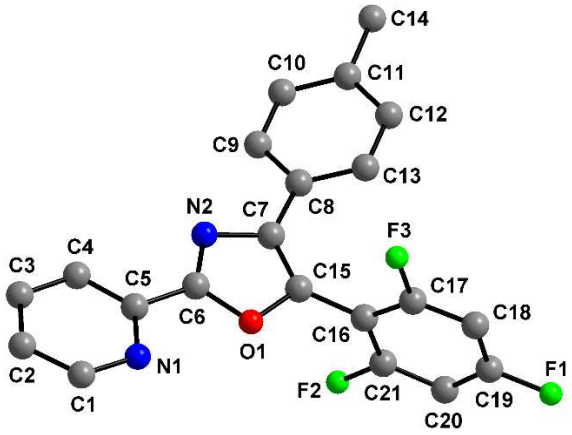


Fig. S5. Molecular structure of compound **5aib** (CCDC deposition number 2110003). Hydrogen atoms are omitted for clarity

5. (vi) Crystal data and molecular structure of compound 5afv

Crystal data for **5afv** (CCDC deposition number 2110002): Empirical formula, $C_{17}H_{13}ClN_2O$; Formula weight, 296.74; crystal color, white; crystal description, block; crystal dimensions, 0.20 x 0.15 x 0.10 mm^3; Crystal system, Monoclinic; lattice type, primitive; lattice parameters, a = 5.7112(16) Å, b = 23.177(8) Å, c = 10.865(4) Å, α = 90, β = 90.891(13), γ = 90; V = 1438.1(8) $Å^3$; space group, Cc; Z = 4; Dcald = 1.371 g/cm^3 ; F(000) = 616; λ (Mo-Kα) = 0.71073 Å; goodness of fit, 1.094; R1[I≥2σ(I)] = 0.0471 (2173), wR2 = 0.1183 (2422).

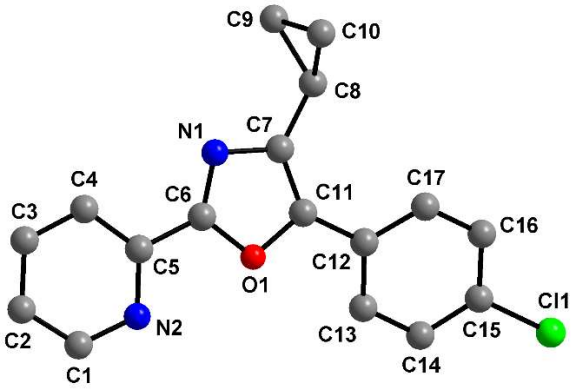


Fig. S6. Molecular structure of compound **5afv** (CCDC deposition number 2110002). Hydrogen atoms are omitted for clarity.

6. Notes:

Compounds **5aaa** and **5abb** are reported in the literature (ref: H. Meng, Y. Zi, X.-P. Xu and S.-J. Ji, *Tetrahedron,* 2015, **71**, 3819-3826).

7. ^{13}C NMR spectral studies: Chemical shifts of carbonyl carbon of 1a, 1e, pyridine-4-carboxaldehyde and benzaldehyde and their salts/complex with TMSOTf

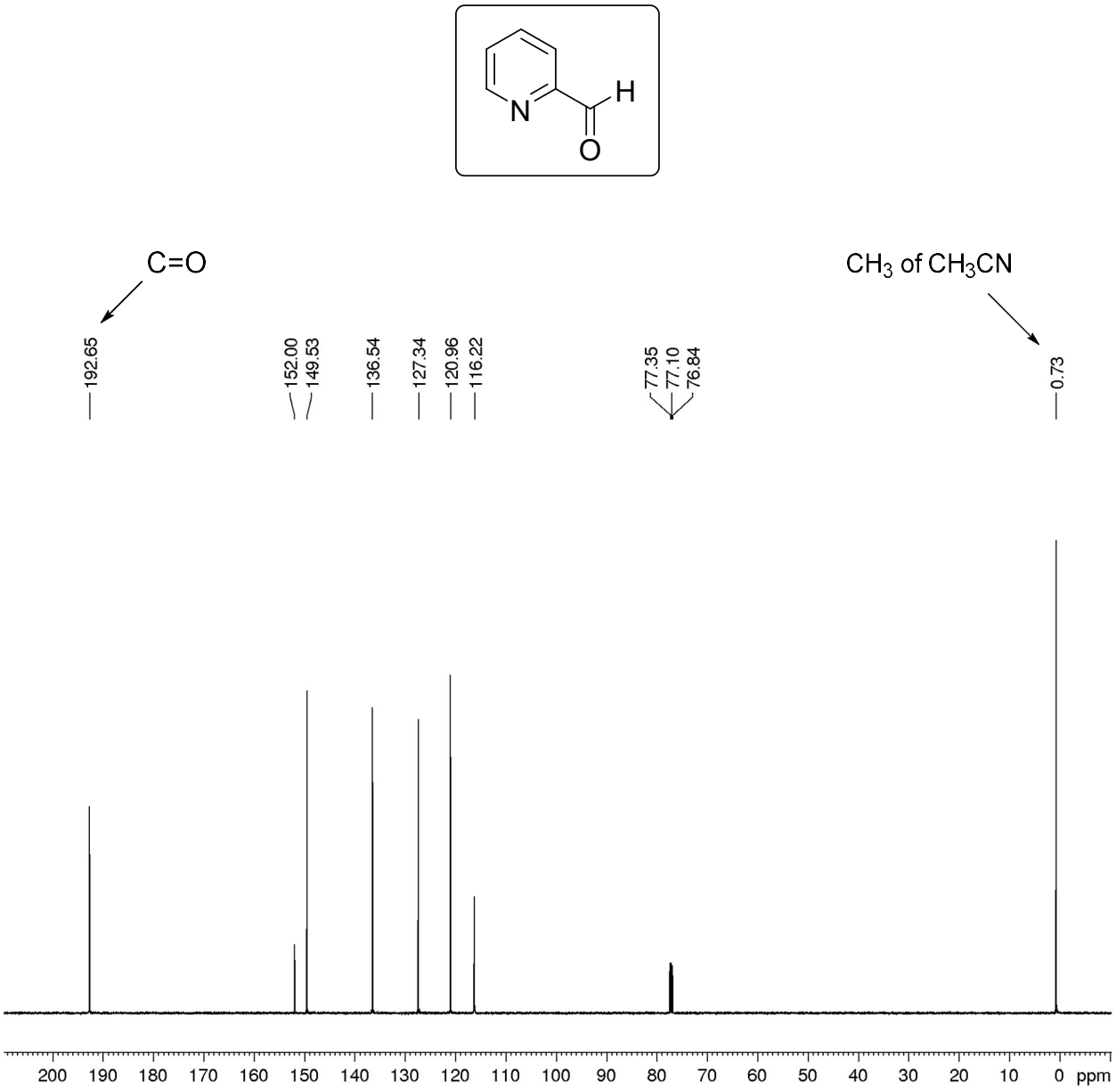
To a solution of aldehyde (except benzaldehyde) (1.0 mmol) in *n*-propyl acetate (2 mL), TMSOTf (1.0 mmol) was added at 0 ºC and stirred at 25 ºC for 5-10 minutes. Solid obtained was filtered, washed with ether and dried under vacuum. ^{13}C NMR spectrum of salt thus obtained was recorded in a mixture of $CDCl_3$ and CH_3CN (2:1). Acetonitrile was added for solubility purpose.

To have uniformity we have also recorded ^{13}C NMR spectra for **1a, 1e** and pyridine-4-carboxaldehyde in a mixture of $CDCl_3$ and CH_3CN (2:1).

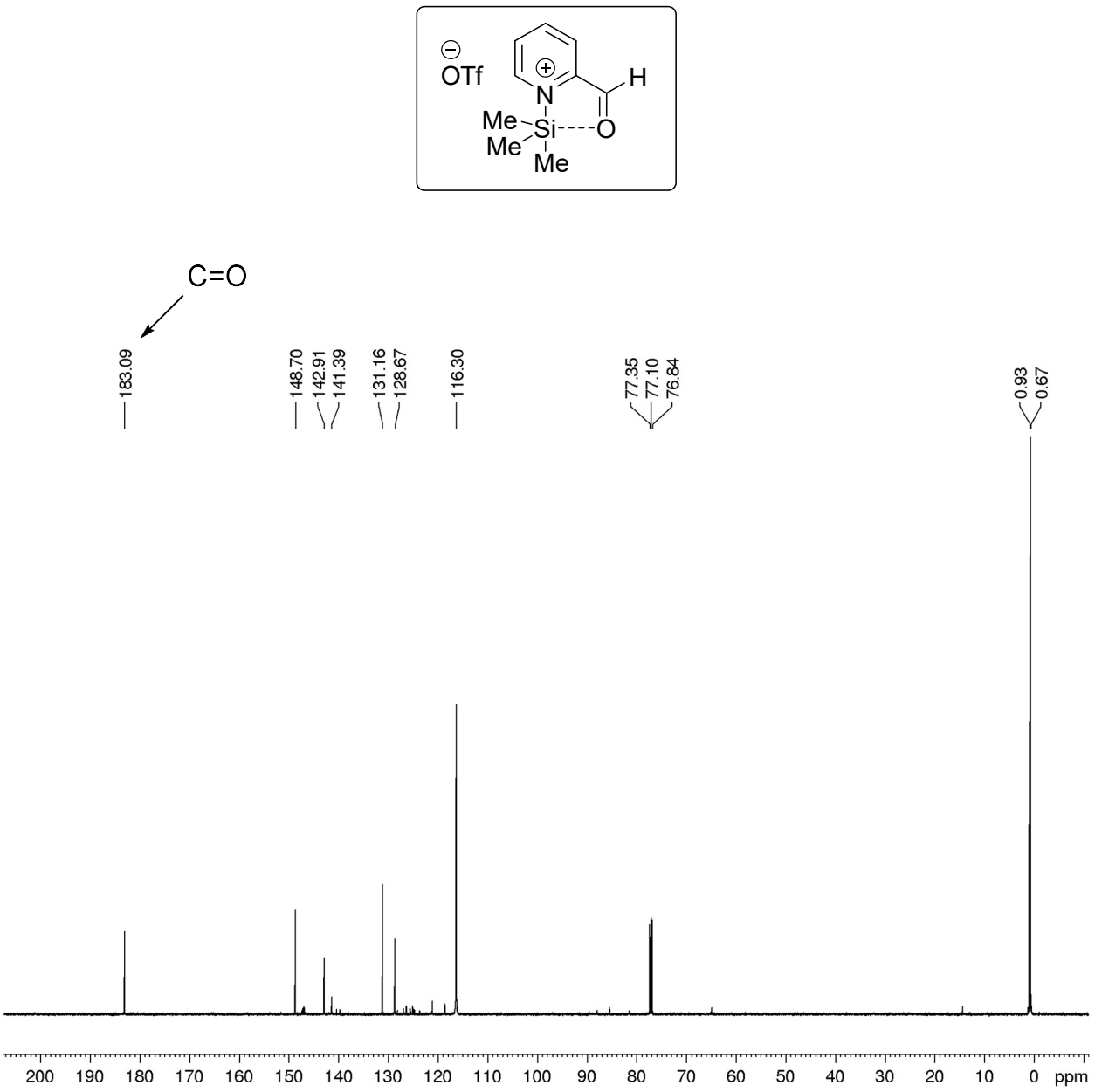
For benzaldehyde:

To benzaldehyde (1.0 mmol) TMSOTf (1.0 mmol) was added at 0 ºC and stirred at 25 ºC for 5-10 minutes. ^{13}C NMR spectrum of complex thus obtained was recorded in a mixture of $CDCl_3$ and CH_3CN (2:1). Similarly we have also recorded ^{13}C NMR spectrum of benzaldehyde. These spectra are attached below.

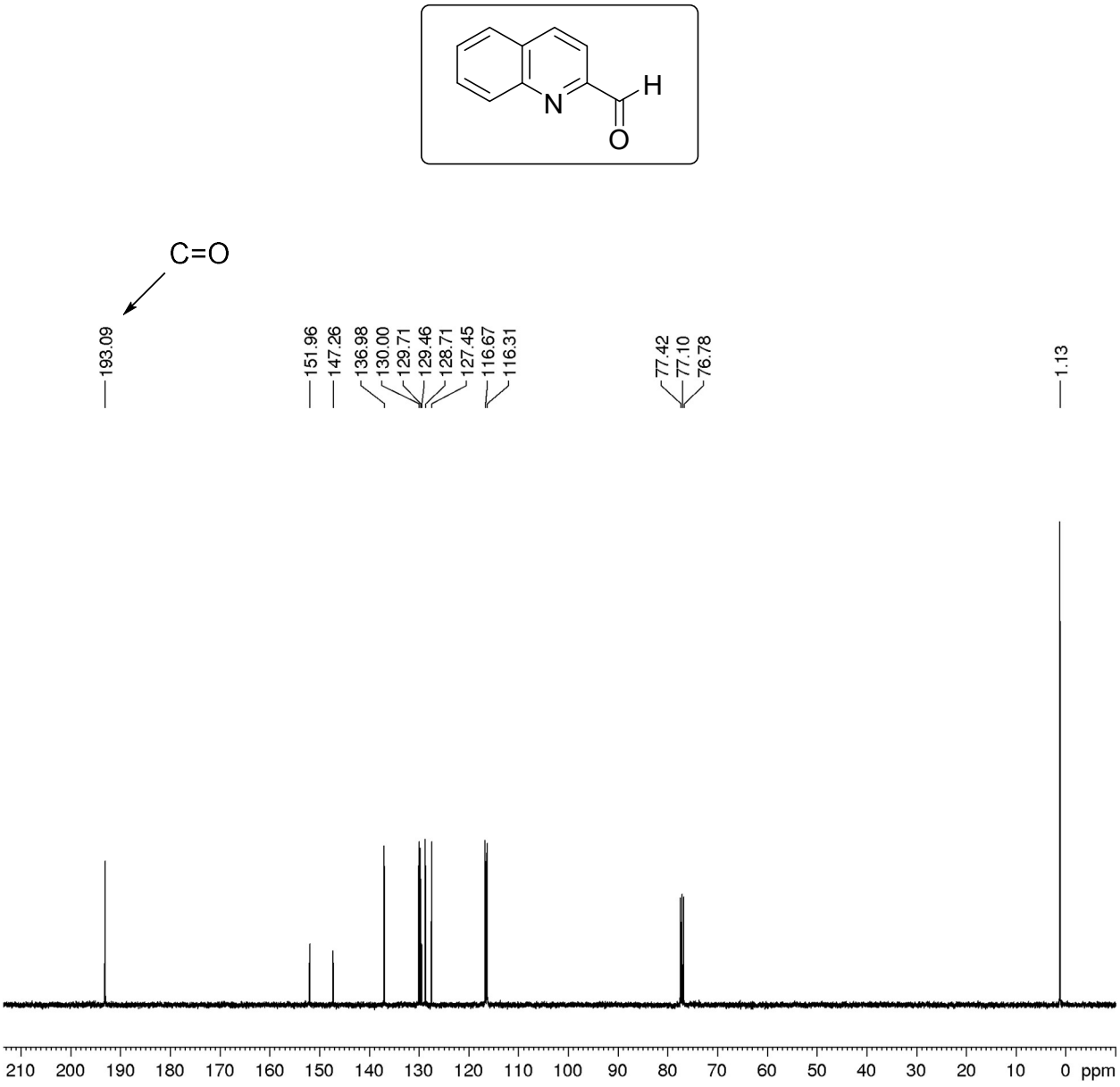
^{13}C NMR Spectrum of pyridine-2-carboxaldehyde (1a) in $CDCl_3$:CH_3CN (2:1)



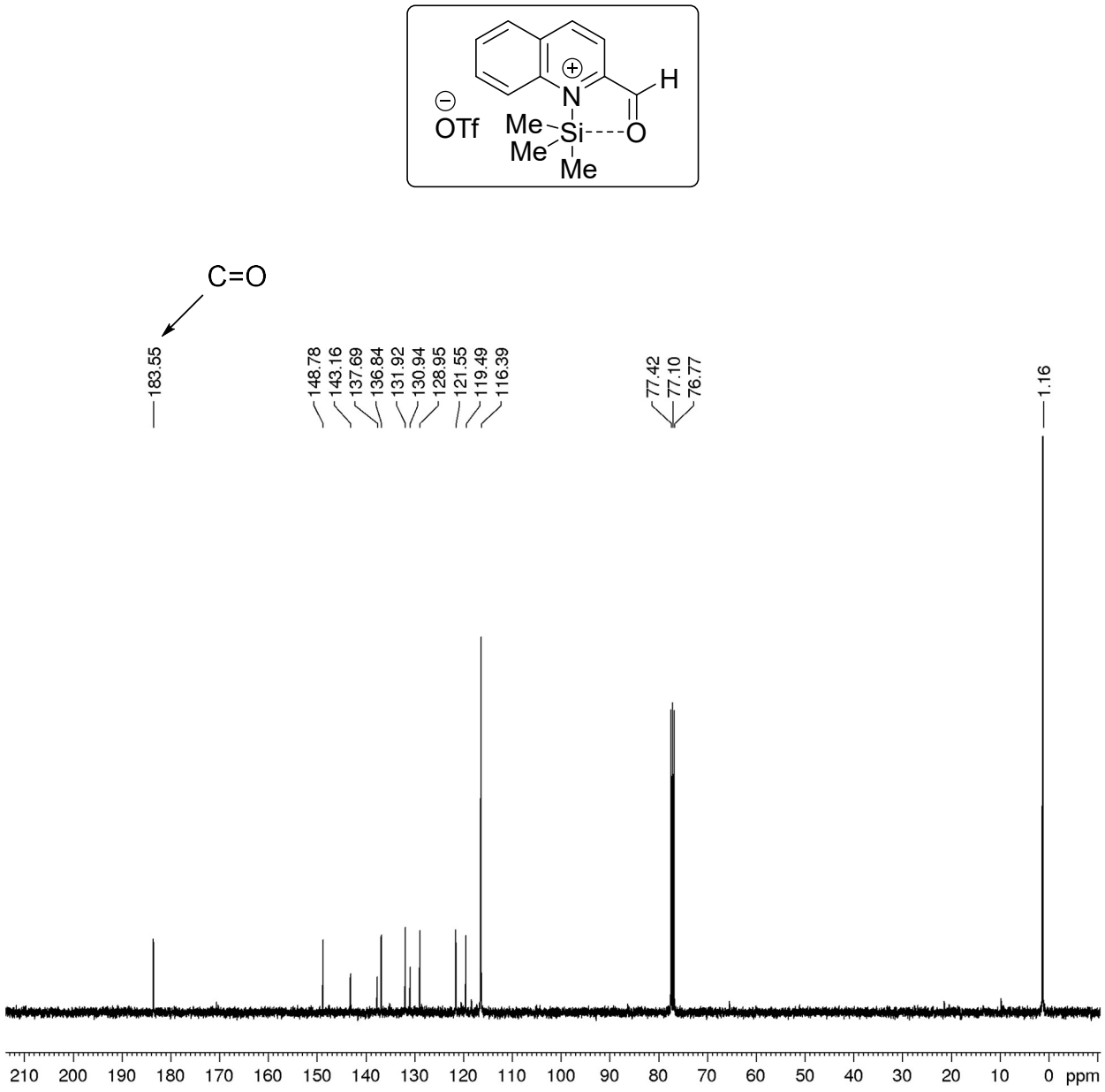
^{13}C NMR Spectrum of salt of pyridine-2-carboxaldehyde (1a) and TMSOTf in $CDCl_3$:CH_3CN (2:1)



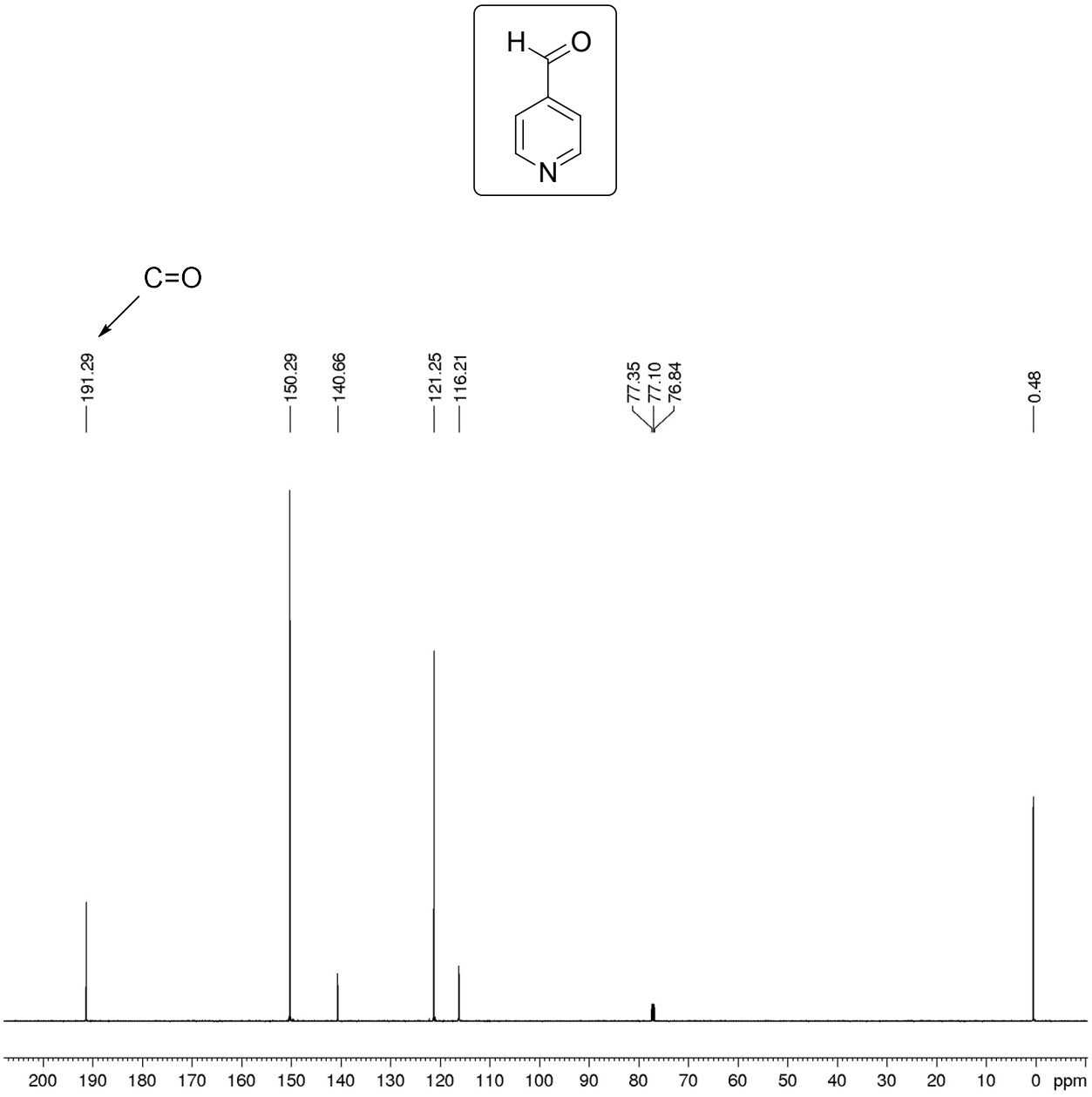
^{13}C NMR Spectrum of quinoline-2-carboxaldehyde (1e) in $CDCl_3$:CH_3CN (2:1)



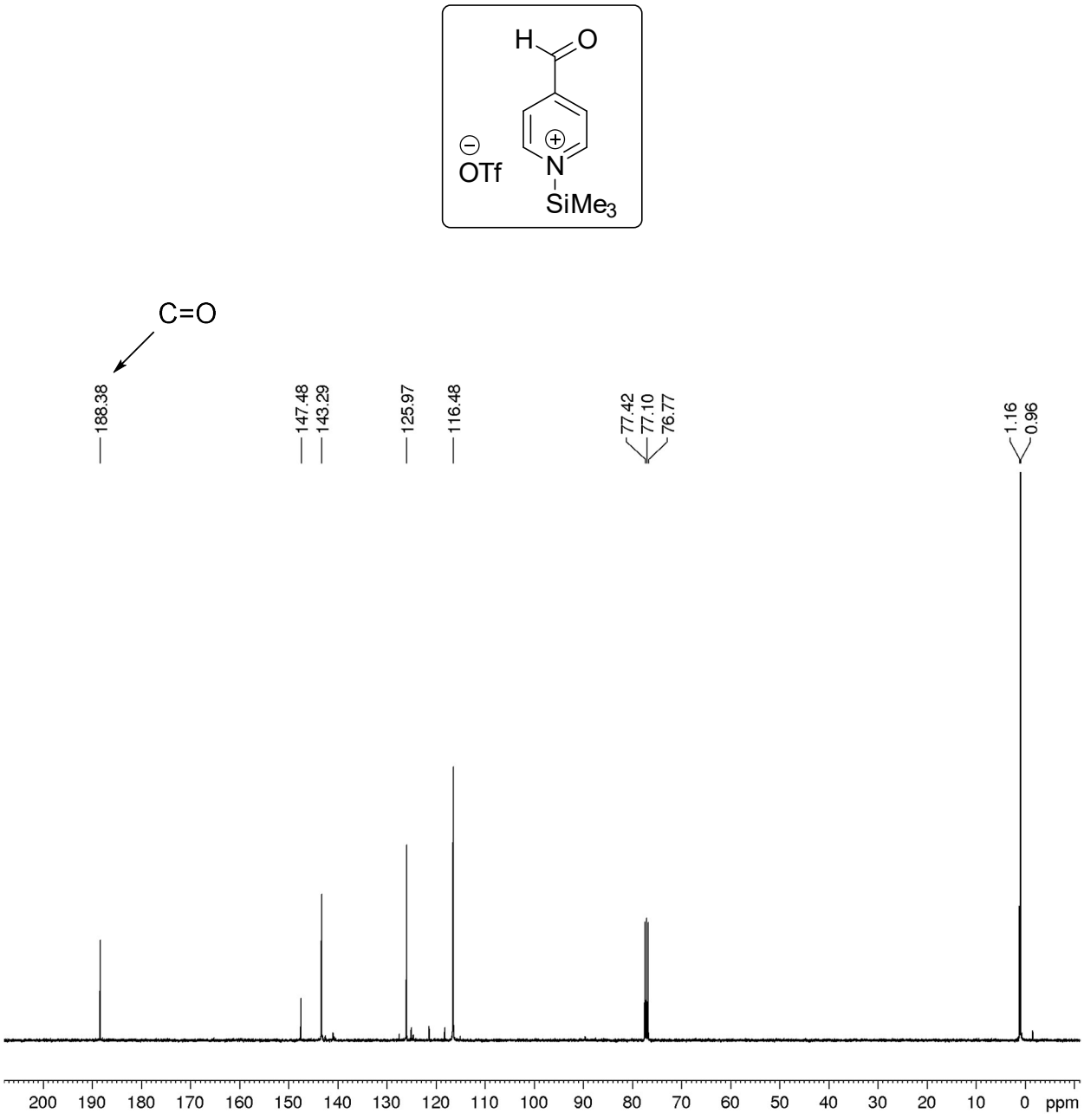
^{13}C NMR Spectrum of salt of quinoline-2-carboxaldehyde (1e) and TMSOTf in $CDCl_3$:CH_3CN (2:1)



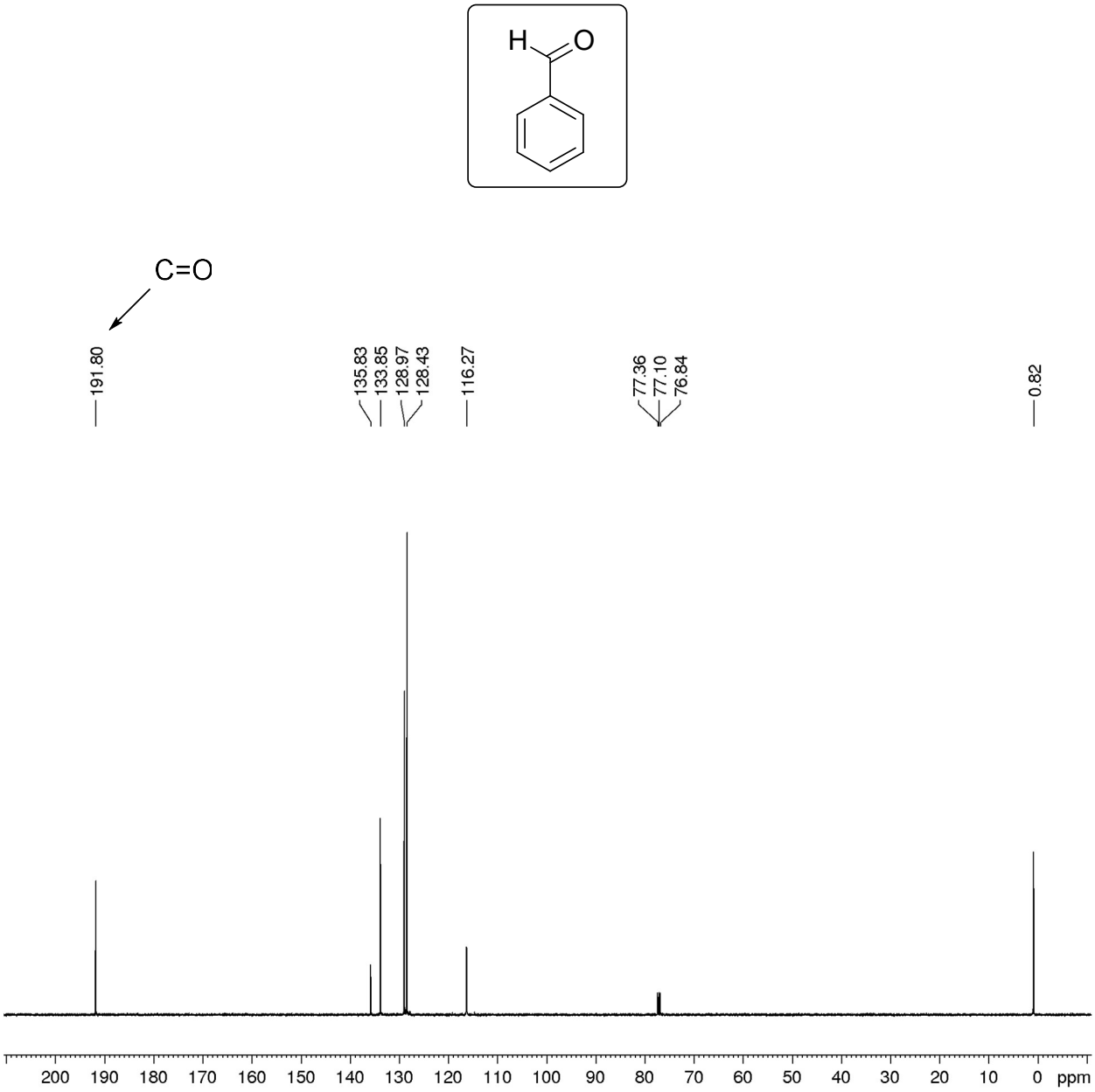
^{13}C NMR Spectrum of pyridine-4-carboxaldehyde in $CDCl_3$:CH_3CN (2:1)



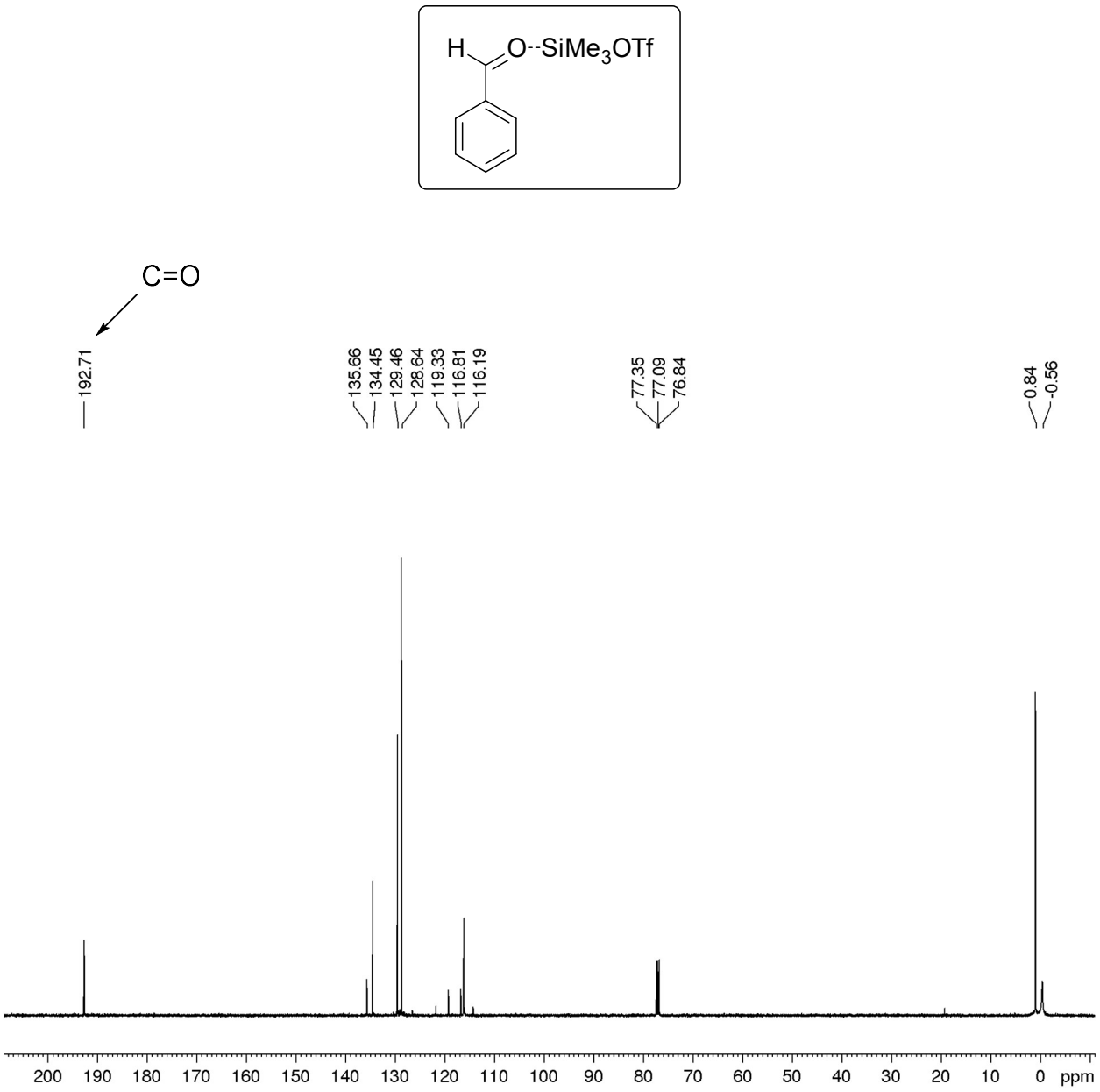
^{13}C NMR Spectrum of salt of pyridine-4-carboxaldehyde and TMSOTf in $CDCl_3$:CH_3CN (2:1)



^{13}C NMR Spectrum of benzaldehyde in $CDCl_3$:CH_3CN (2:1)



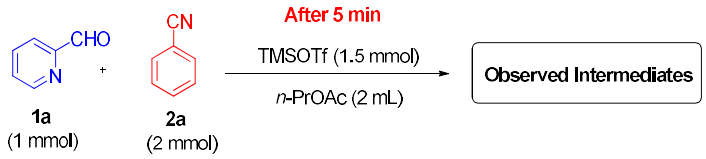
^{13}C NMR Spectrum of complex of benzaldehyde and TMSOTf in $CDCl_3$:CH_3CN (2:1)

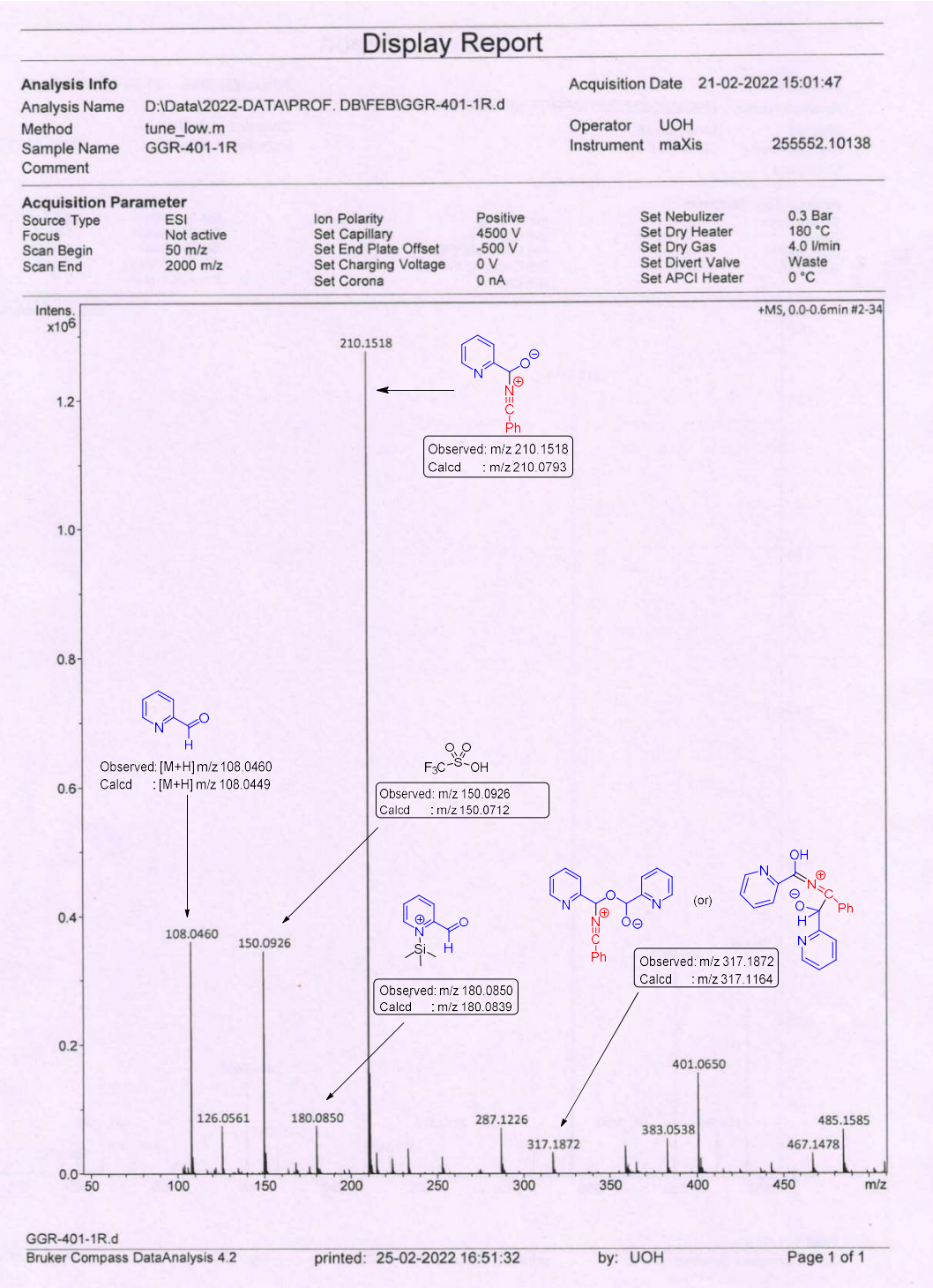


8. Mechanistic Studies: Reaction monitored by HRMS (ESI-MS)

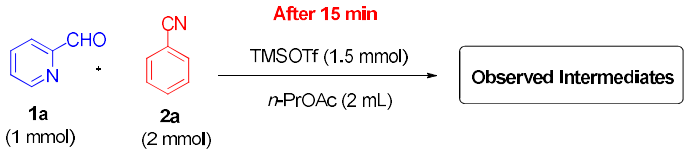
An oven-dried 10 mL round-bottomed flask was charged with pyridine-2-carboxaldehyde (**1a**) (1 mmol, 0.108 g), benzonitrile (**2a)** (2 mmol, 0.208 g), and *n*-PrOAc (2 mL) under nitrogen. The contents were cooled to 0 ^{o}C (ice bath) and then TMSOTf (1.5 mmol, 0.336 g) was added. The reaction mixture was allowed to stir at room temperature for 5-10 min and then heated under reflux (oil bath temperature 120 ^{o}C). The reaction was monitored by HRMS at different intervals (after 5, 15, 30, 60, 120, 180, and 240 minutes). Results are presented in the Mass Spectra 1-7.

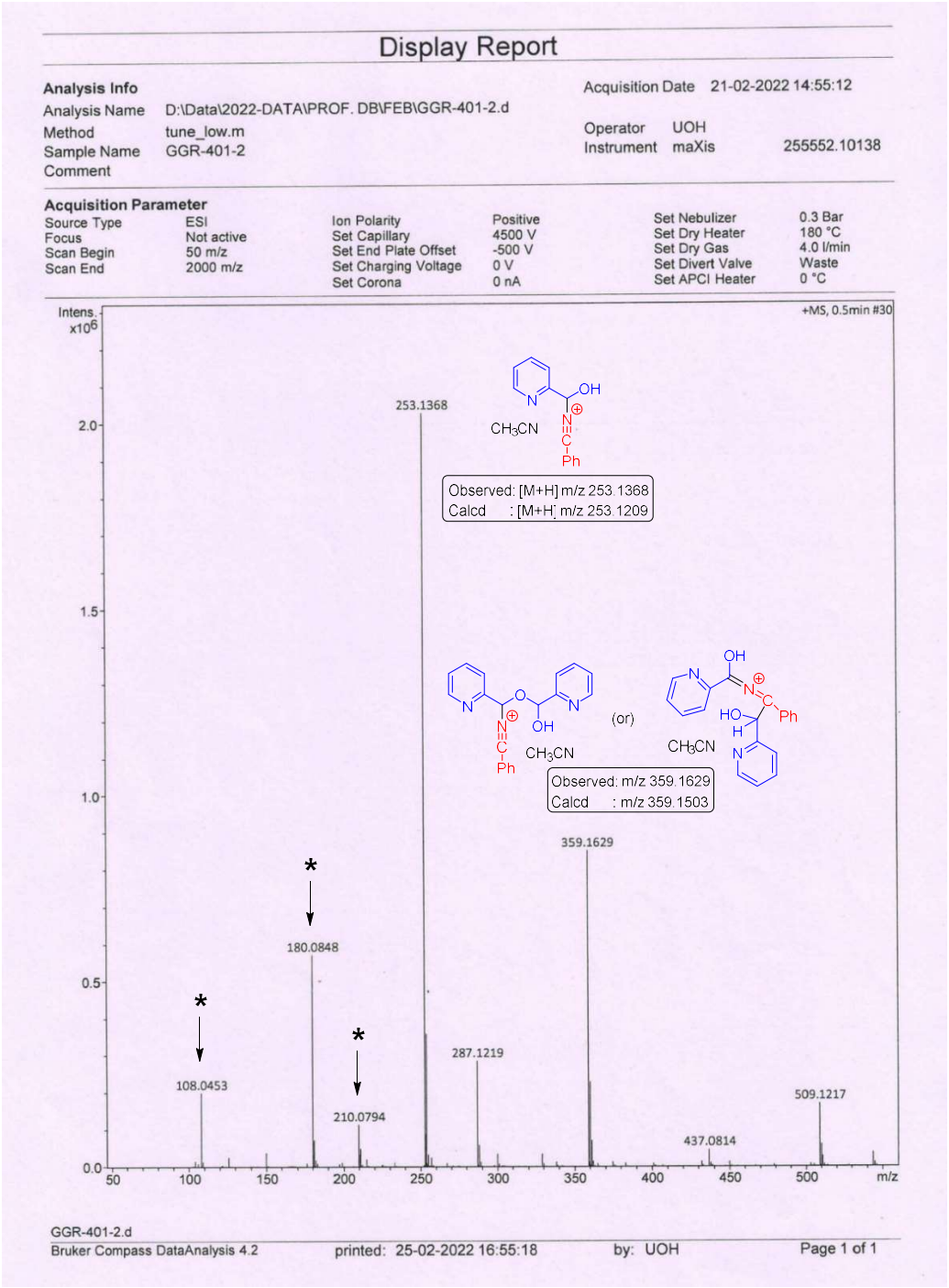
Mass Spectrum-1





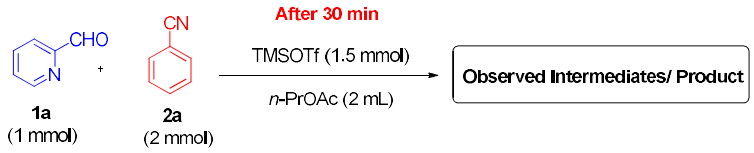
Mass Spectrum-2

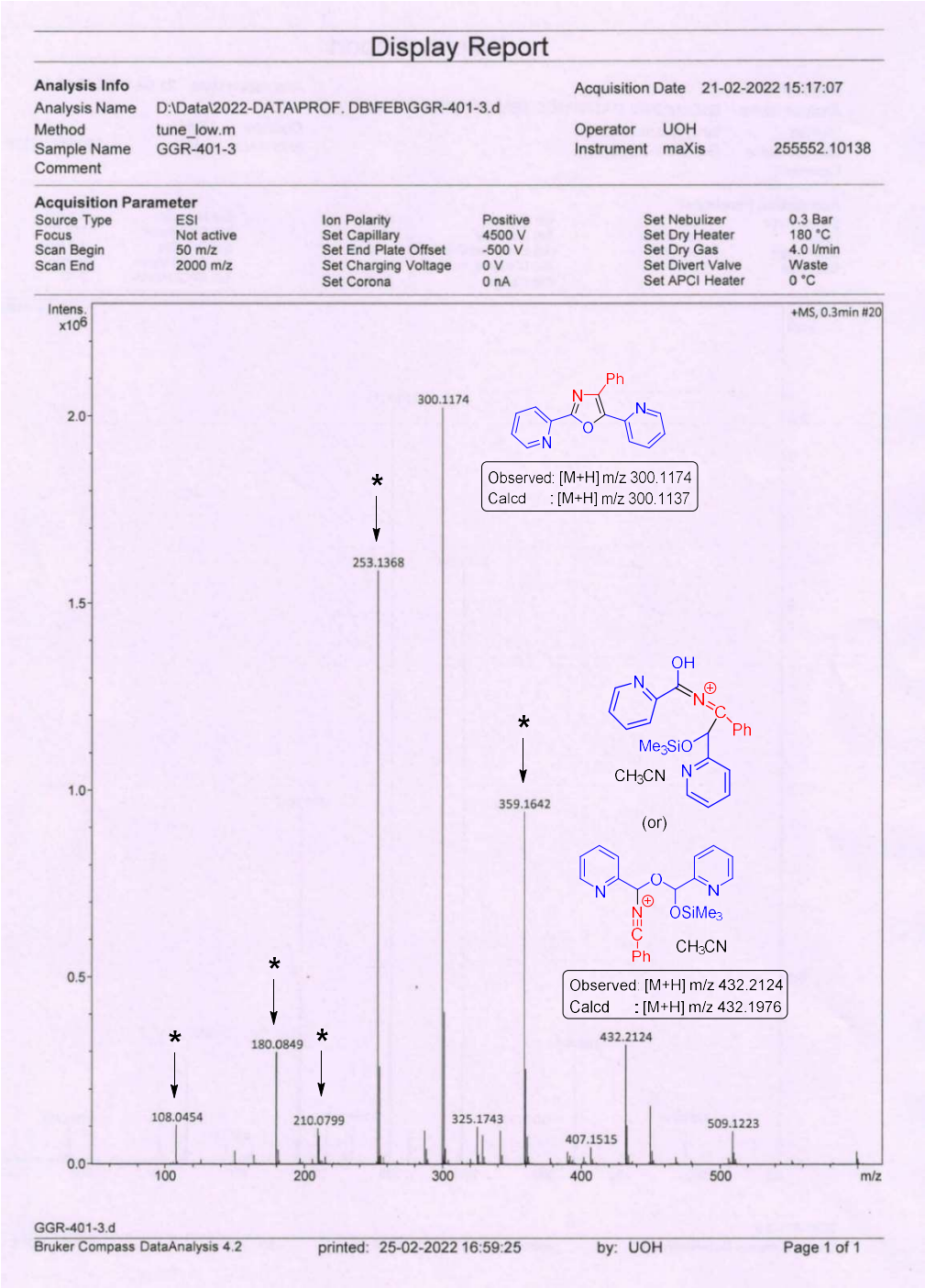




* All these intermediates are assigned in the Mass Spectrum-1

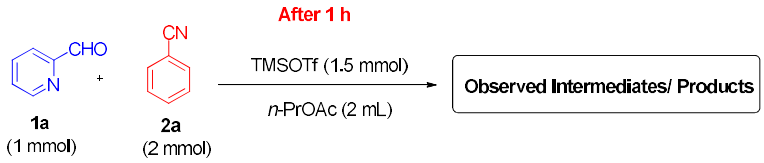
Mass Spectrum-3

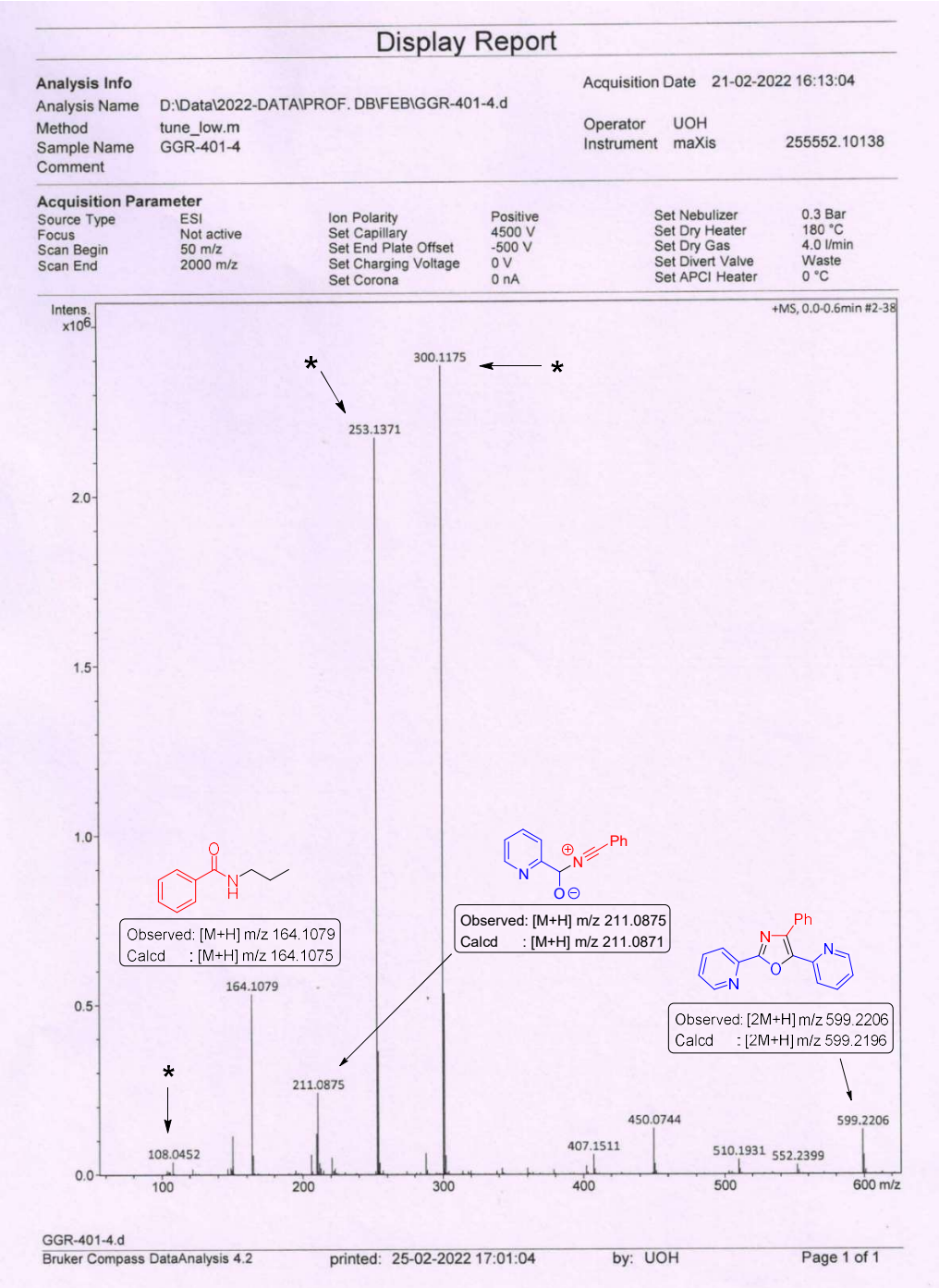




* All these intermediates are assigned in the Mass Spectra-1 and 2

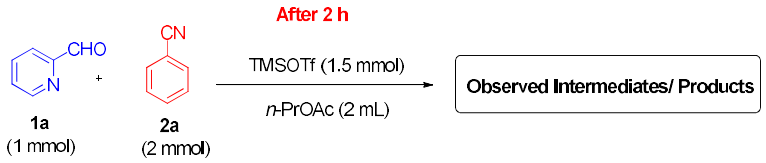
Mass Spectrum-4

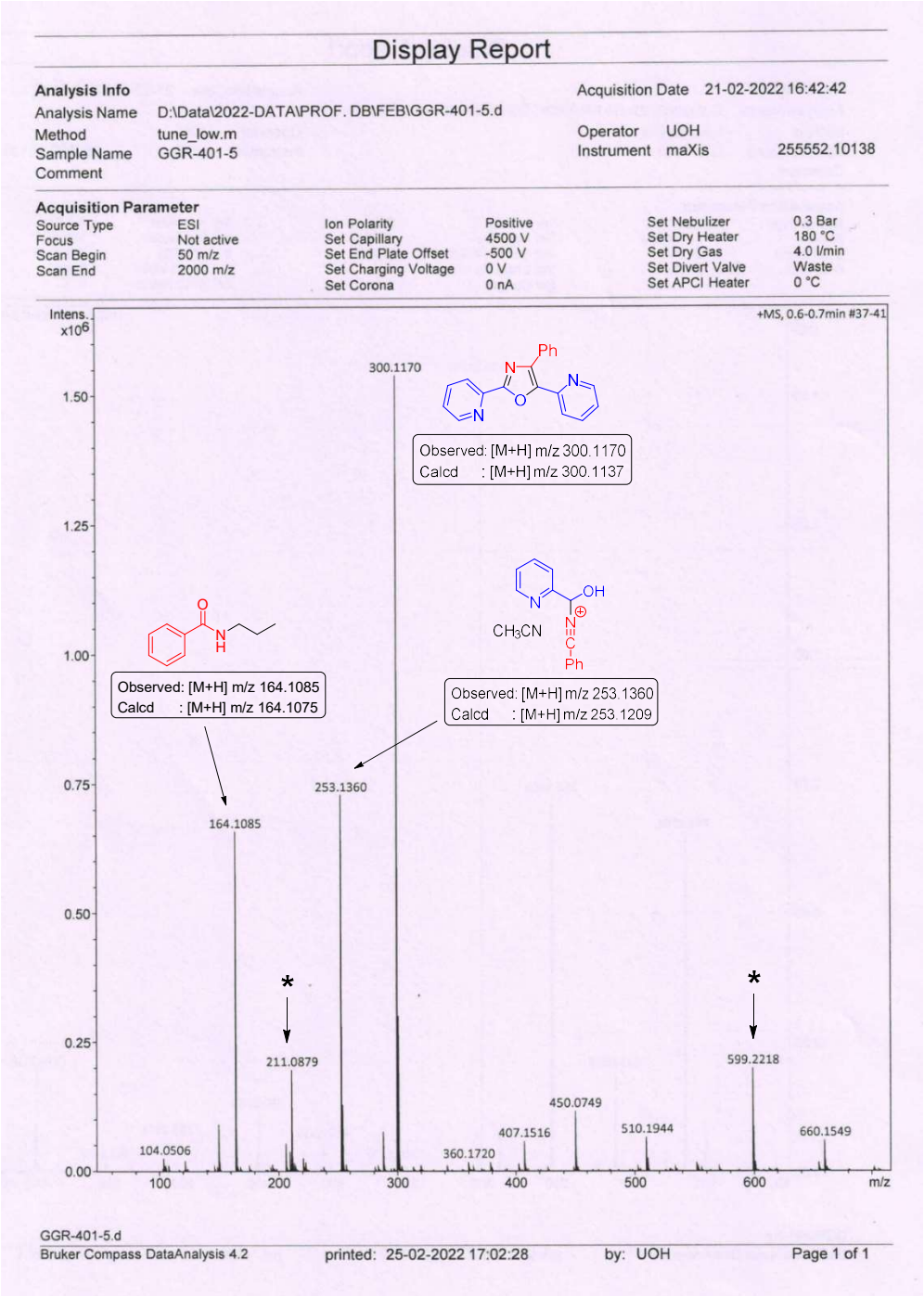




* All these intermediates are assigned in the Mass Spectra-1, 2 and 3

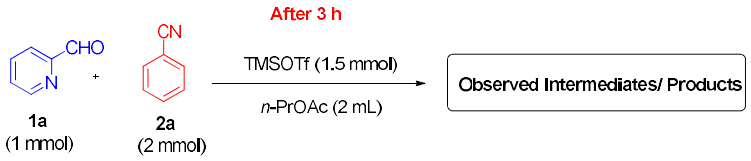
Mass Spectrum-5

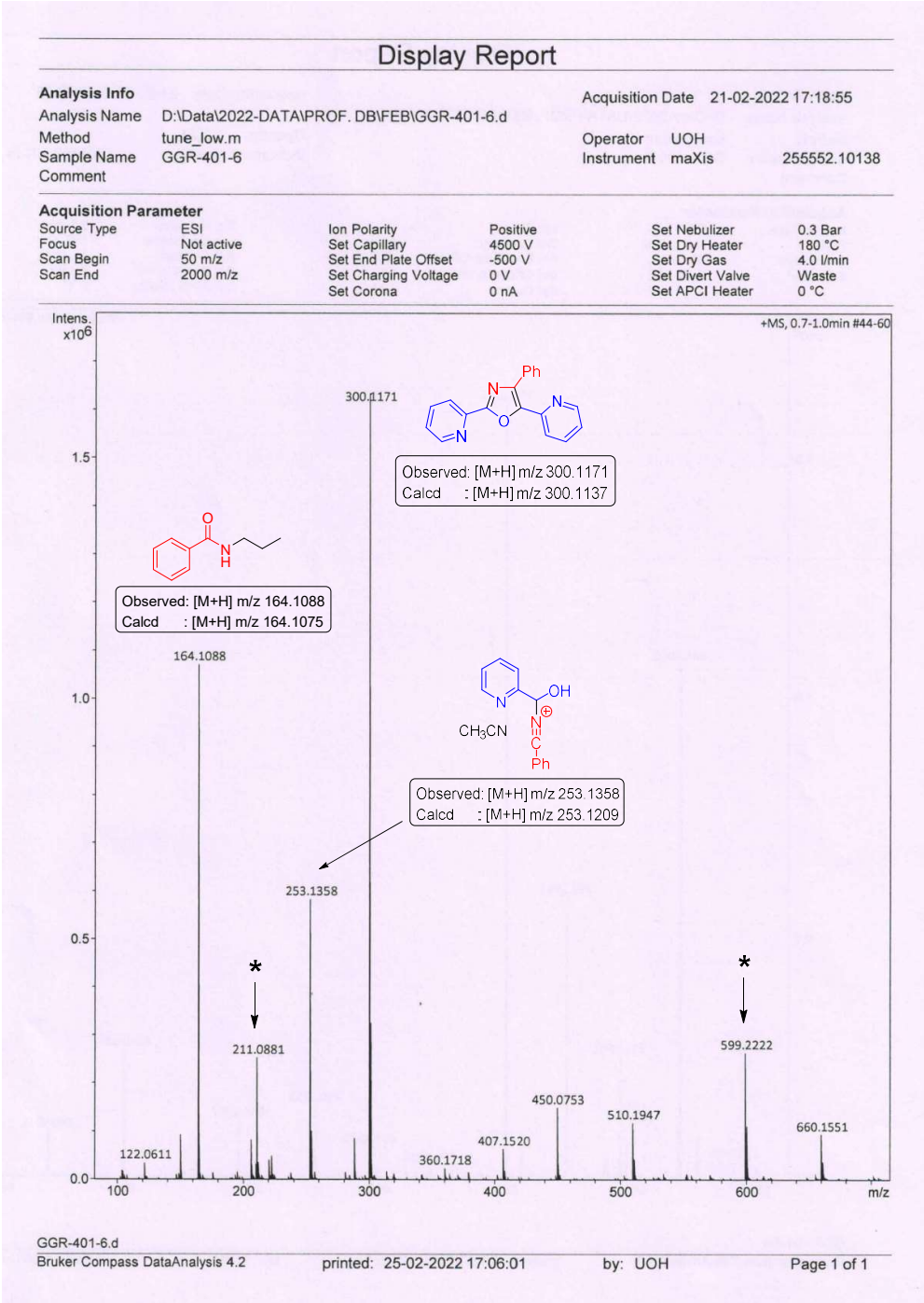




* All these intermediates are assigned in the Mass Spectra-1, 2, 3 and 4

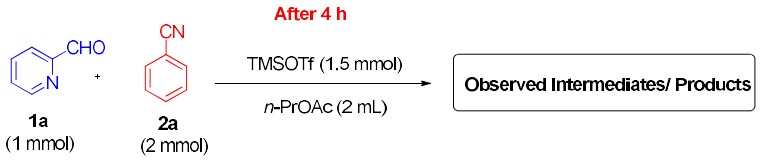
Mass Spectrum-6

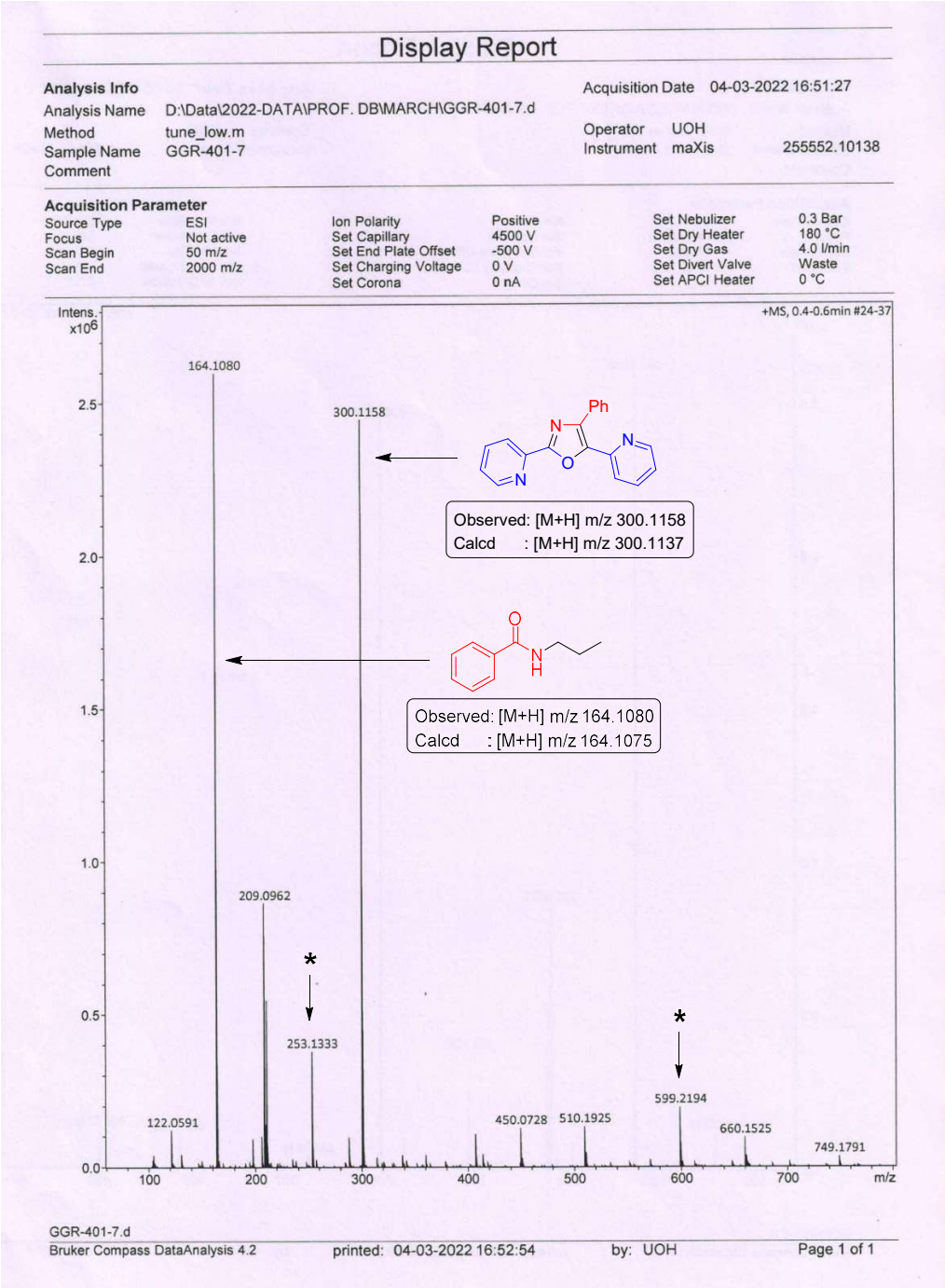




* All these intermediates are assigned in the Mass Spectra-1, 2, 3, 4 and 5

Mass Spectrum-7





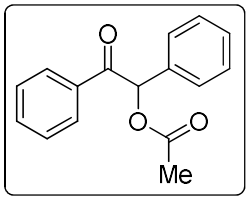
* All these intermediates are assigned in the Mass Spectra-1, 2, 3, 4, 5 and 6

9. Reactions of benzoin and α-pyridoin with benzonitrile

Reaction of benzoin with benzonitrile:

An oven-dried 10 mL round-bottomed flask was charged with benzoin (1 mmol, 0.213 g), benzonitrile (2 mmol, 0.208 g) and *n*-PrOAc (2 mL) under nitrogen. The contents were cooled to 0 °C (ice bath) and then TMSOTf (1.5 mmol, 0.336 g) was added. The reaction mixture was allowed to stir at room temperature for 5-10 min and then heated under reflux (oil bath temperature 120 °C). After 4 h reaction mixture was cooled to room temperature and quenched with saturated K_2CO_3 solution (4 mL). TLC examination of the reaction mixture shows multiple spots indicating that this reaction is not clean. Usual work-up (as described for compound **3aa)** followed by careful chromatographic separation [silica gel (100-200 mesh) (hexanes:ethyl acetate 85:15 (v/v))] provided 2-acetoxy-1,2-diphenylethanone (26 mg, 10%). This compound is known and spectral data is reported and our data matches with known data.[1]

2-Acetoxy-1,2-diphenylethanone:



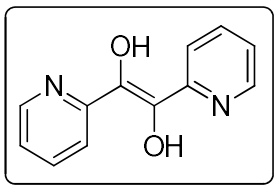
Yield: 10% (26 mg); TLC (Hexane:EtOAc, 85:15 (v/v): R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.51-7.44 (m, 3H), 7.41-7.33 (m, 5H), 6.86 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 170.5, 134.7, 133.7, 133.5, 129.4, 129.2, 128.8, 128.7, 128.68, 77.7, 20.8; IR (neat): 1736, 1693, cm^{-1}; HRMS (ESI, m/z):[M+Na] calcd. for $C_{16}H_{14}O_3$ +Na, 277.0841; found, 277.0840.

Preparation of *α*-pyridoin:

This was prepared following the literature procedure.[2,3]

To a stirred solution of pyridine-2-carboxaldehyde (2 g, 18.51 mmol) in methanol (10 mL) was added a solution of sodium cyanide (0.5 g, 10.2 mmol) in water (5 mL) at room temperature under nitrogen. The reaction mixture was heated at 80 °C for 8-10 min. Then the reaction mixture was cooled to room temperature and diluted with water. The resulting orange solid was filtered, washed with water and then dried under reduced pressure to afford (1.83 g, 92 %,) as an orange solid.

(*E*)-1,2-Di(pyridin-2-yl)ethene-1,2-diol (*α*-pyridoin):

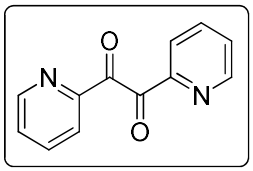


Yield: 92% (1.83 g); orange solid; mp. 153-155 °C [lit.[3] mp. 141–143 °C], TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.43; ^{1}H NMR (500 MHz, Acetone-d6): δ 13.0 (s, 2H), 8.58 (ddd, *J* = 4.5 Hz, 1.5 Hz, 0.5 Hz, 2H), 7.99 (td, *J* = 8.0 Hz, 2.0 Hz, 2H), 7.89 (dt, *J* = 8.0 Hz, 1.0 Hz, 2H), 7.35 (ddd, *J* = 7.5 Hz, 5.0 Hz, 1.5 Hz, 2H); ^{13}C NMR (125 MHz, Acetone-d6): δ 157.5, 147.0, 138.9, 136.5, 122.6, 120.2; IR (neat): 1587, 1559, 1459, 1400 cm^{-1}; HRMS (ESI, m/z):[M+H] calcd. for $C_{12}H_{10}N_2O_2$ +H, 215.0820; found, 215.0821.

Reaction of *α*-pyridoin with benzonitrile:

Reaction of *α*-pyridoin (0.46 mmol, 0.1g) with benzonitrile (0.92 mmol, 0.096g) in the presence of TMSOTf in *n*-propyl acetae was performed as in the case of compound **3aa.** After 4 h reaction mixture was worked-up as usual. ^{1}H and ^{13}C NMR spectral data of the reaction mixture showed the presence of unreacted *α*-pyridoin (~ 40%) and oxidized *α*-pyridoin (*2,2'*-pyridil) (~60%). Column chromatography of the crude mixture [silica gel (100-200 mesh) (hexanes:ethyl acetate 70:30 (v/v))] provided 2,2'-pyridil as a white crystalline solid. It looks that *α*-pyridoin underwent oxidation during column chromatography indicating that it very sensitive towards air-oxidation.

1,2-Di(pyridin-2-yl)ethane-1,2-dione:



Yield: 96% (94 mg); white solid; mp. 152-154 ^{o}C [lit.[4] mp. 151-153 ^{o}C],TLC (Hexane:EtOAc, 70:30 (v/v): R_f = 0.43; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (ddd, *J* = 5.0 Hz, 2.0 Hz, 1.0 Hz, 2H), 8.22 (dt, *J* = 8.0 Hz, 1.0 Hz, 2H), 7.93 (td, *J* = 8.0 Hz, 1.5 Hz, 2H), 7.49 (ddd, *J* = 7.5 Hz, 5.0 Hz, 1.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.0, 151.9, 149.6, 137.2, 127.9, 122.4; IR (neat): 1708, 1688, 1581 cm^{-1}; HRMS(ESI, m/z):[M+H] calcd. for $C_{12}H_8N_2O_2$+H, 213.0664; found, 213.0686.

References

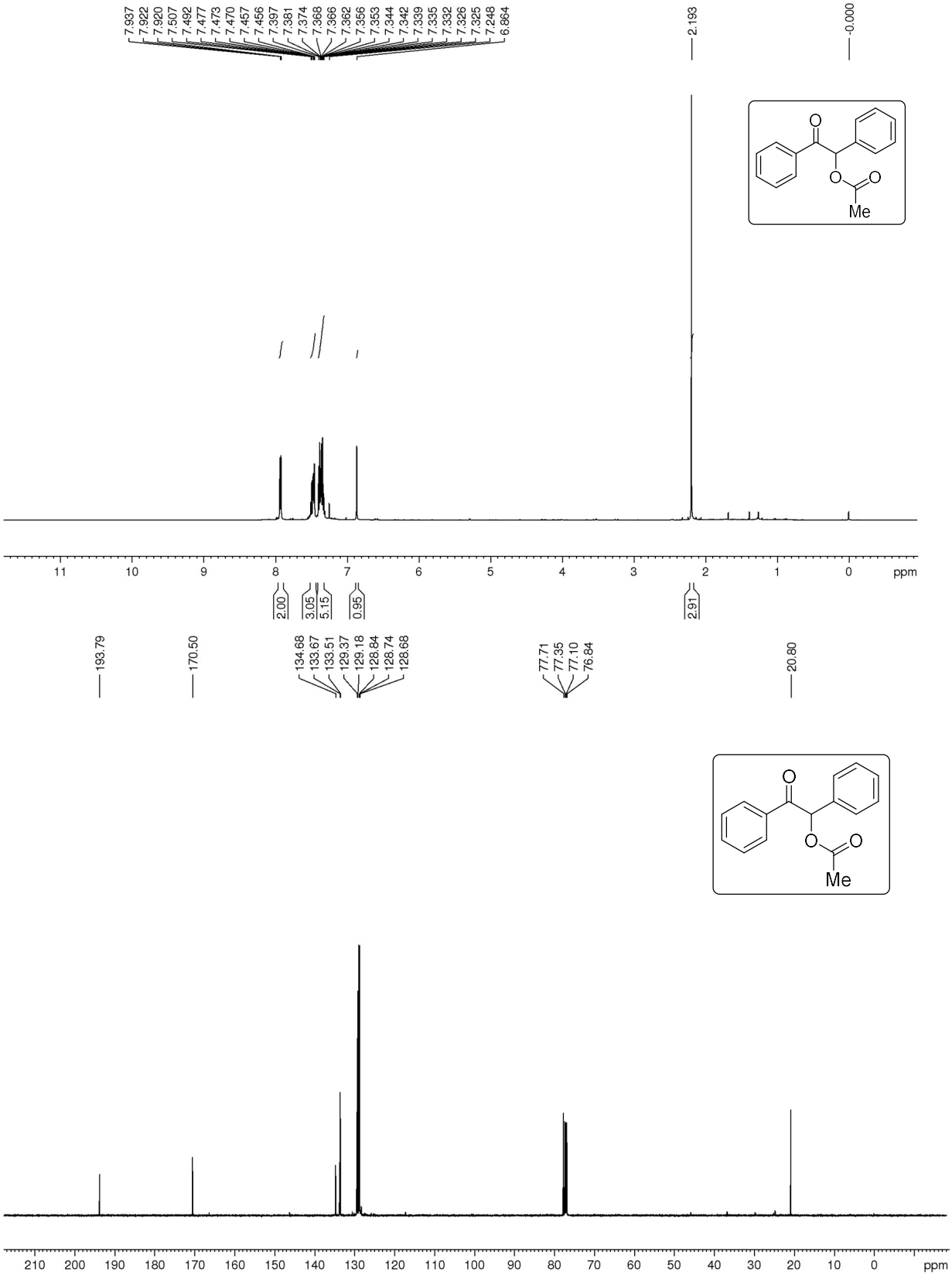
1 J. Zhang, J.-D. Yang, and J.-P. Cheng, *Chem. Sci*., 2020, **11**, 8476-8481.

2. M. Hatanaka, K. Takahashi, S. Nakamura, and T. Mashino, *Bioorg. Med. Chem.,* 2005*,* **13**, 6763-6770.

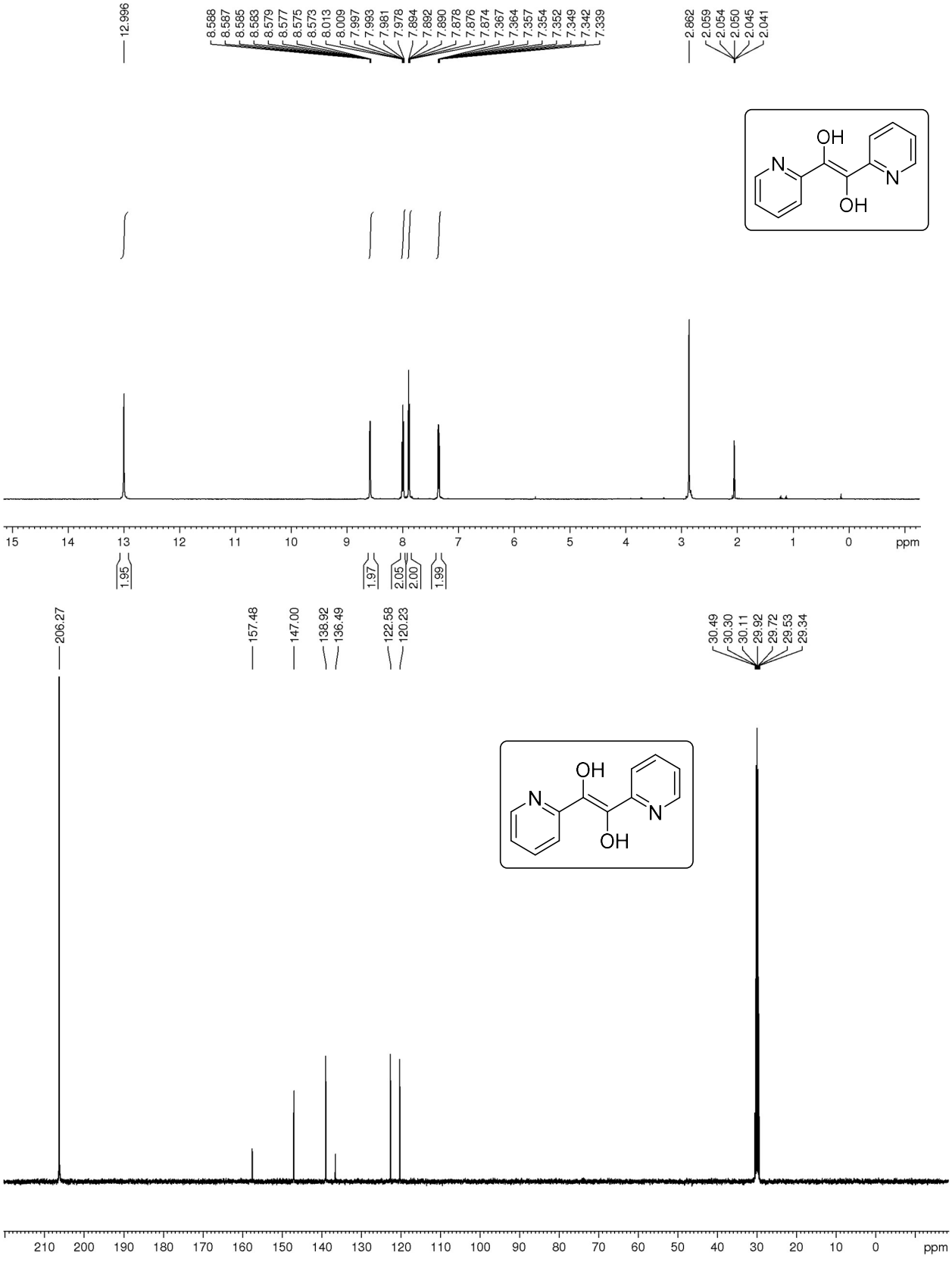
3. L.-X. Cheng, X. L. Jin, Q.-F. Teng, J. Chang, X.-J. Yao, F. Dai, Y.-P. Qian, J.-J. Tang, X.-Z. Li and B. Zhou, *Org. Biomol. Chem.*, 2010, **8**, 1058-1063.

4. M. Okimoto,Y.Takahashi, Y.Nagata, G. Sasaki and K. Numata, *Synthesis,* 2005*,* 705-707.

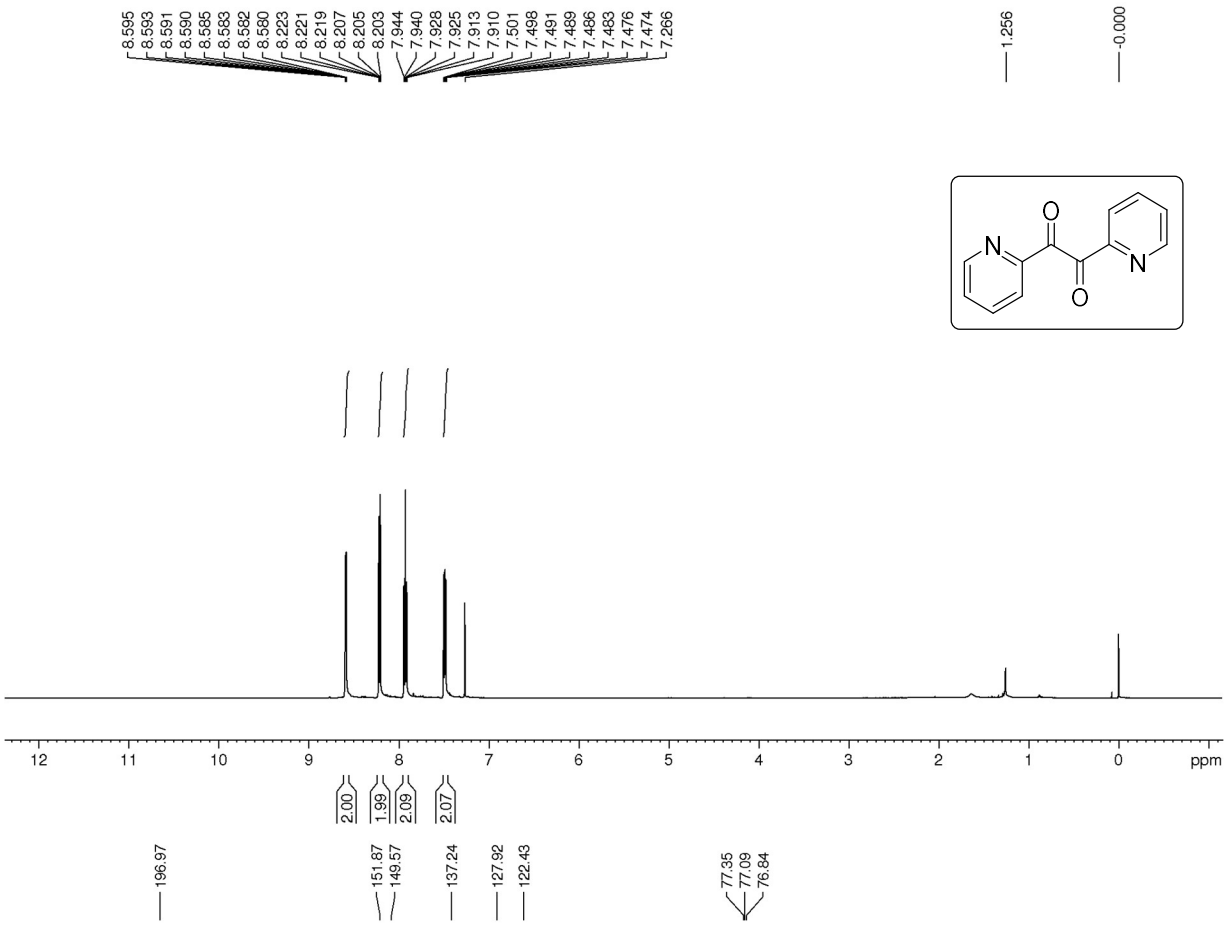
^{1}H and ^{13}C NMR Spectra of 2-acetoxy-1,2-diphenylethanone

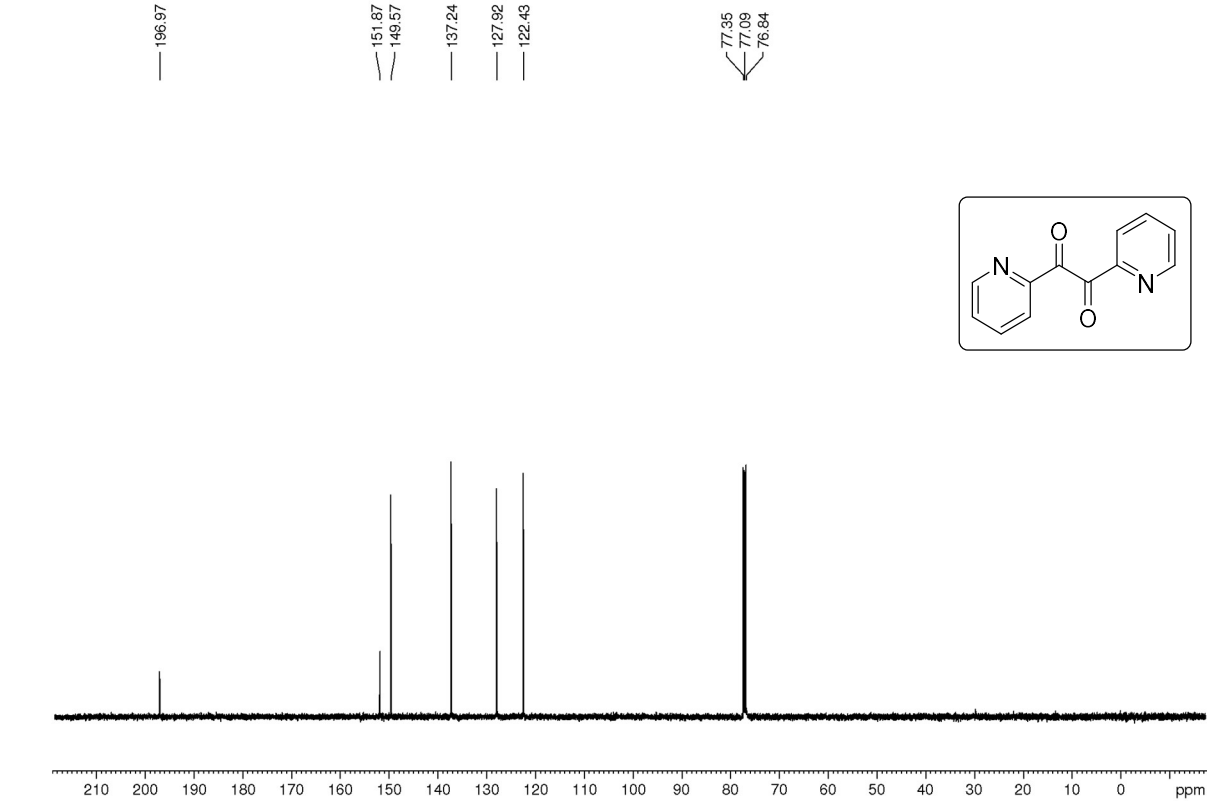


^{1}H and ^{13}C NMR Spectra of *α*-pyridoin



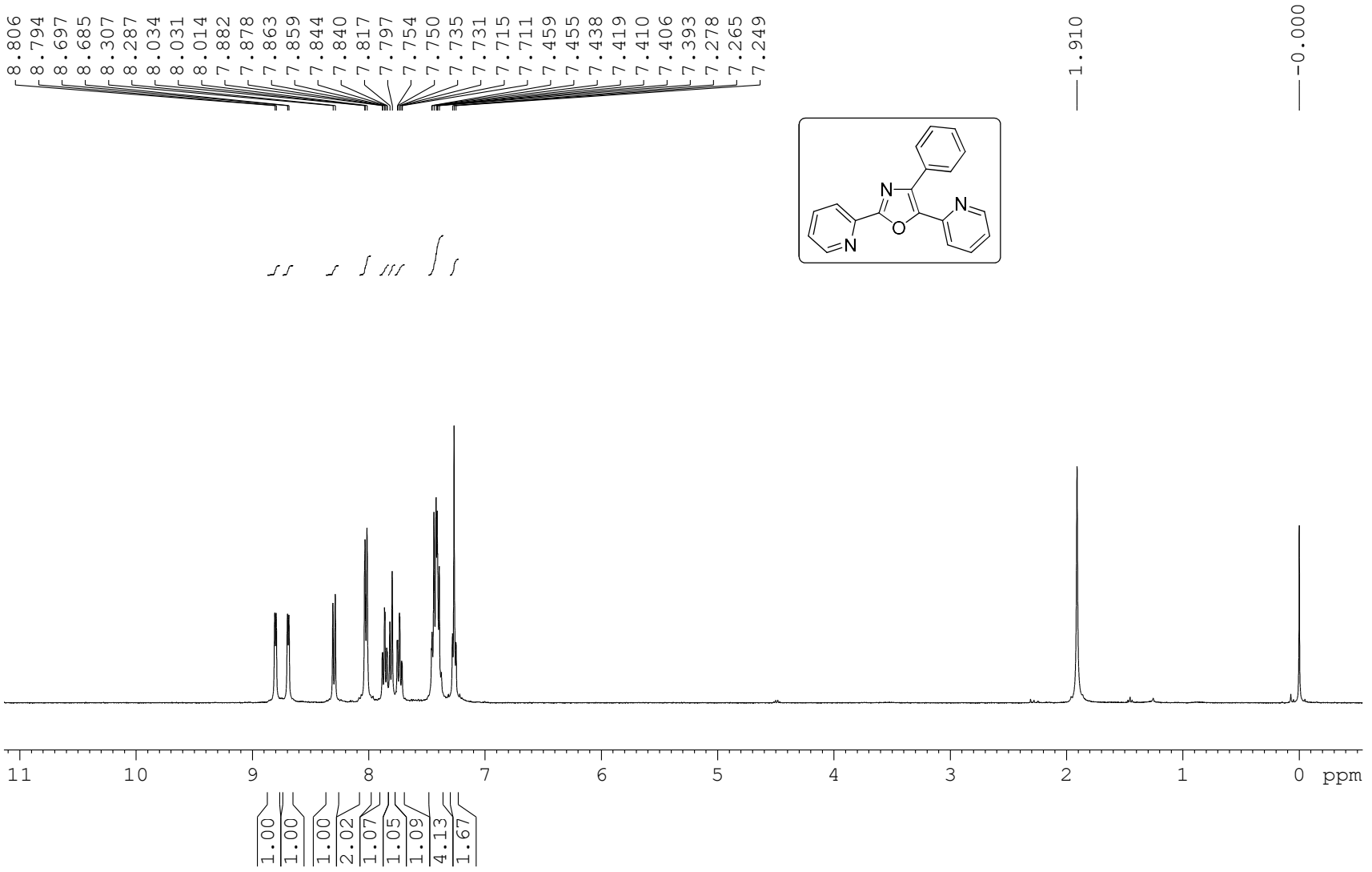
^{1}H and ^{13}C NMR Spectra of 2,2'-pyridil



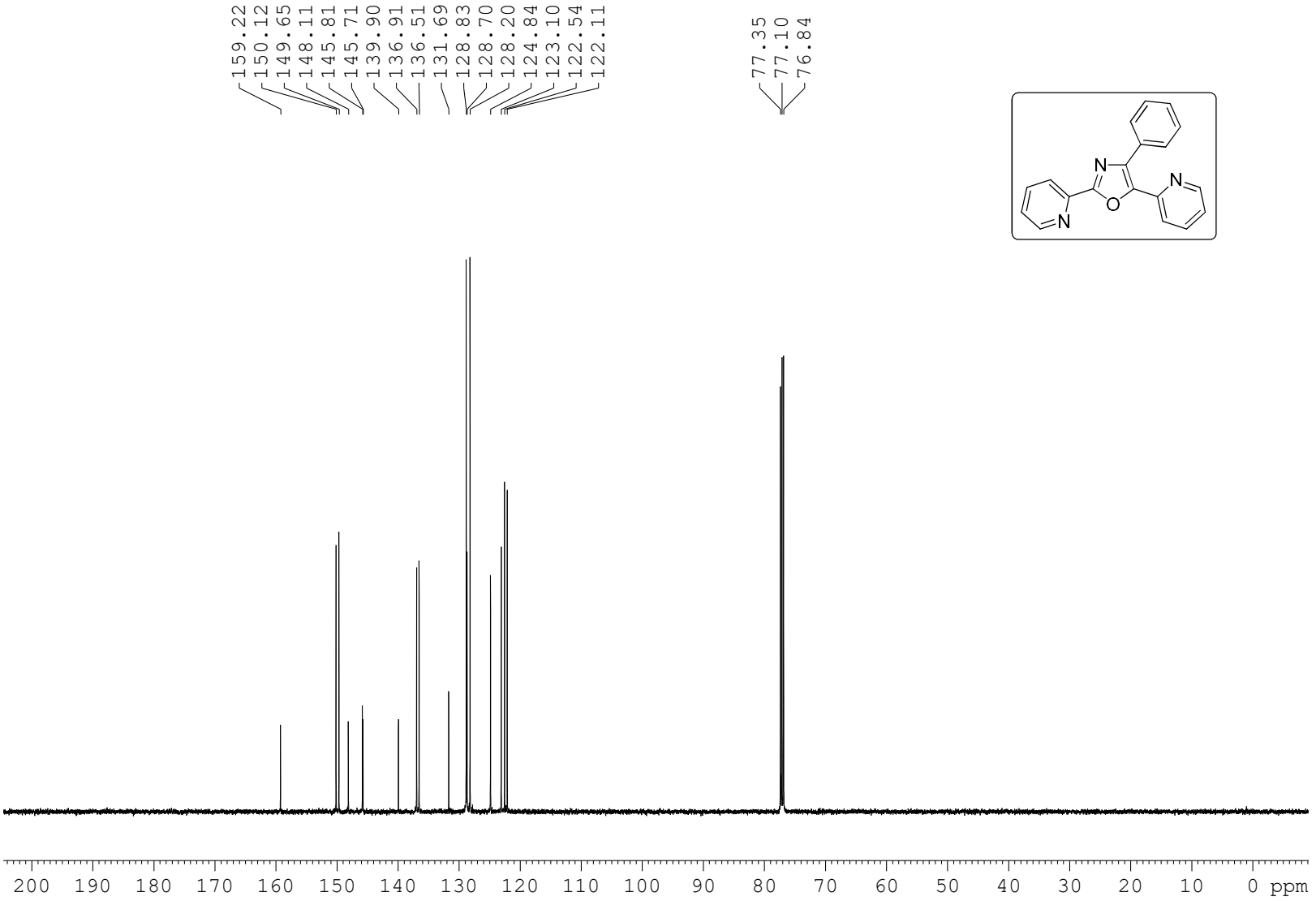


9. ^{1}H, ^{13}C and ^{19}F NMR spectra of oxazoles (3) and mixed oxazoles (5)

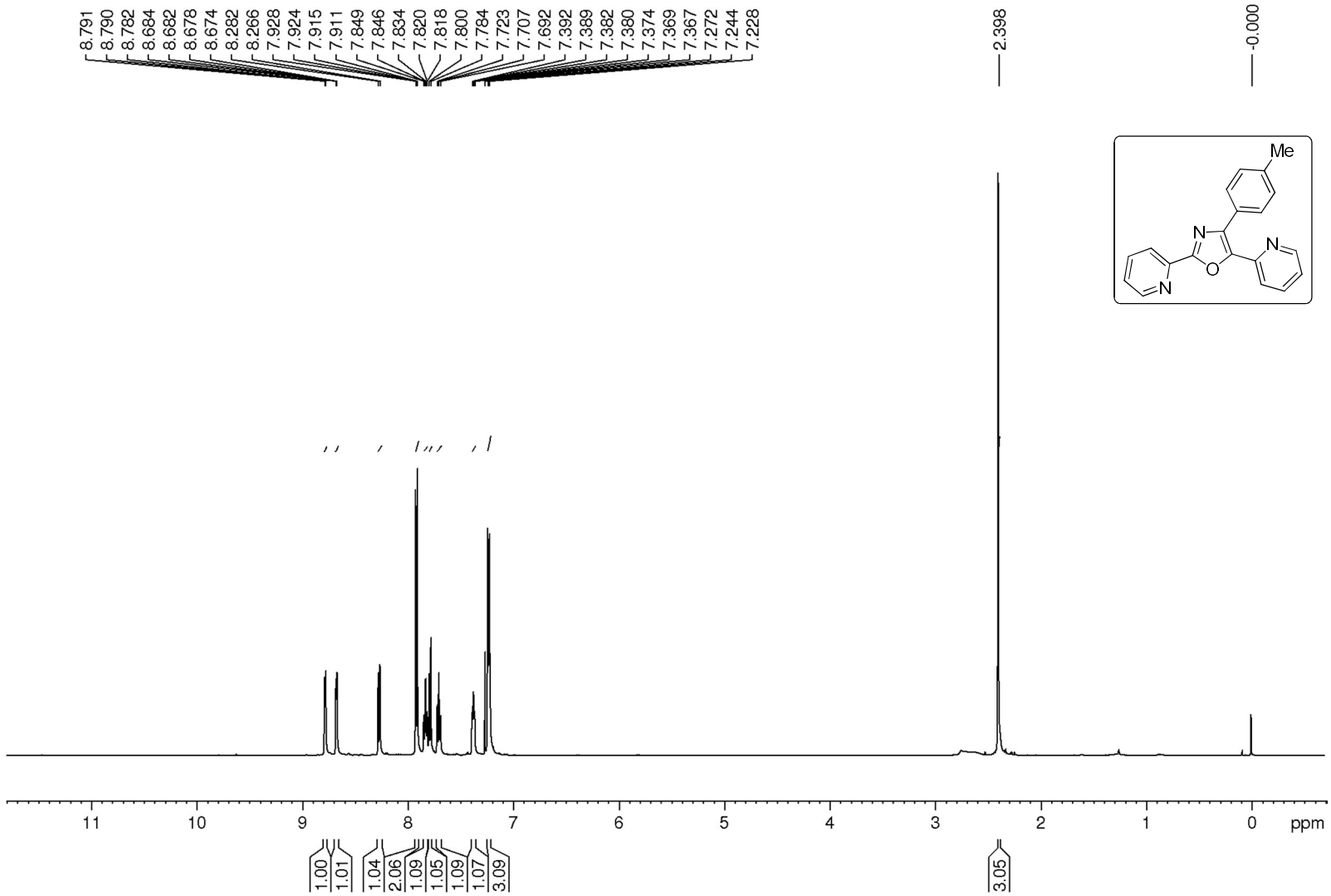
^{1}H NMR Spectrum of 3aa



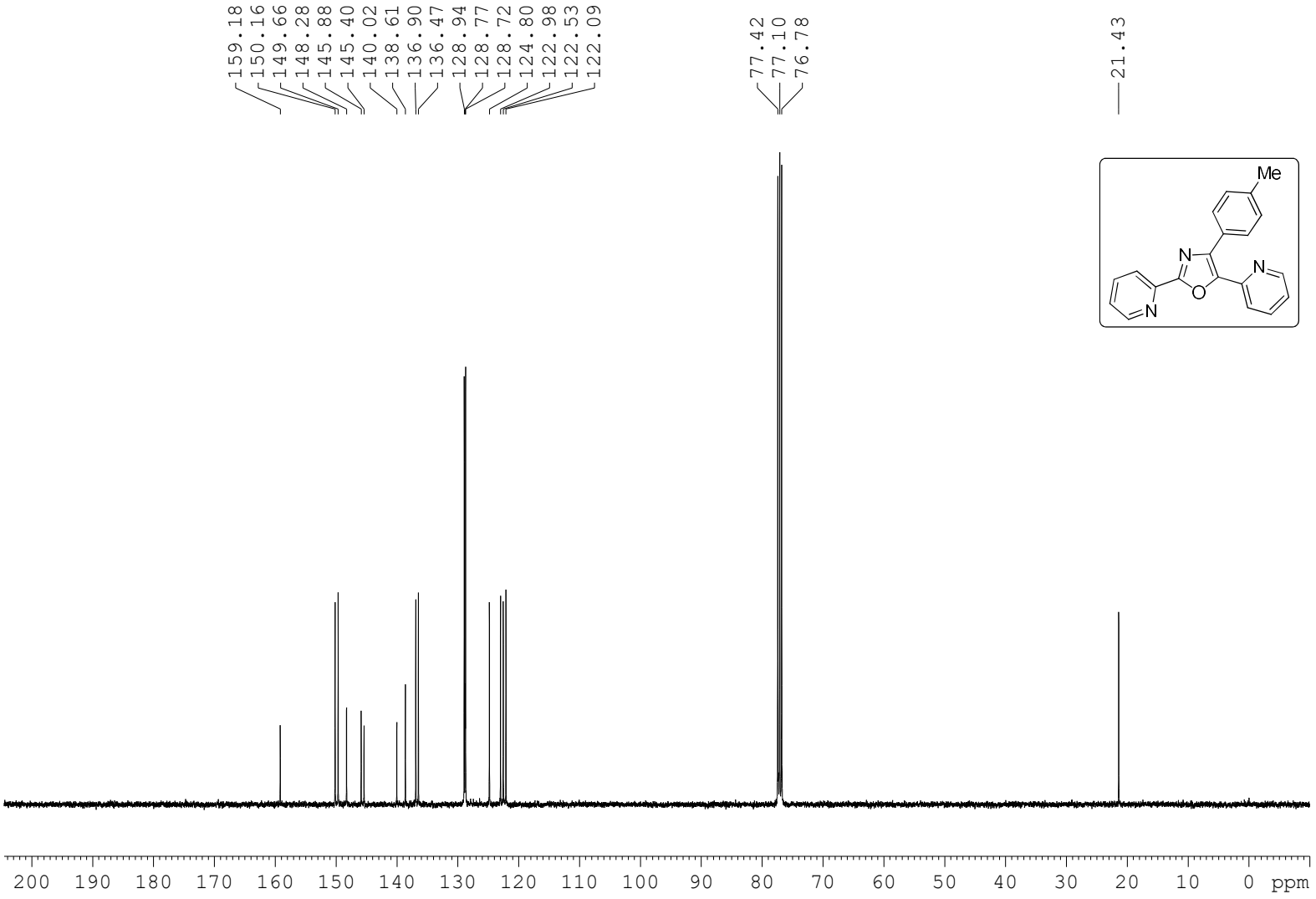
^{13}C NMR Spectrum of 3aa



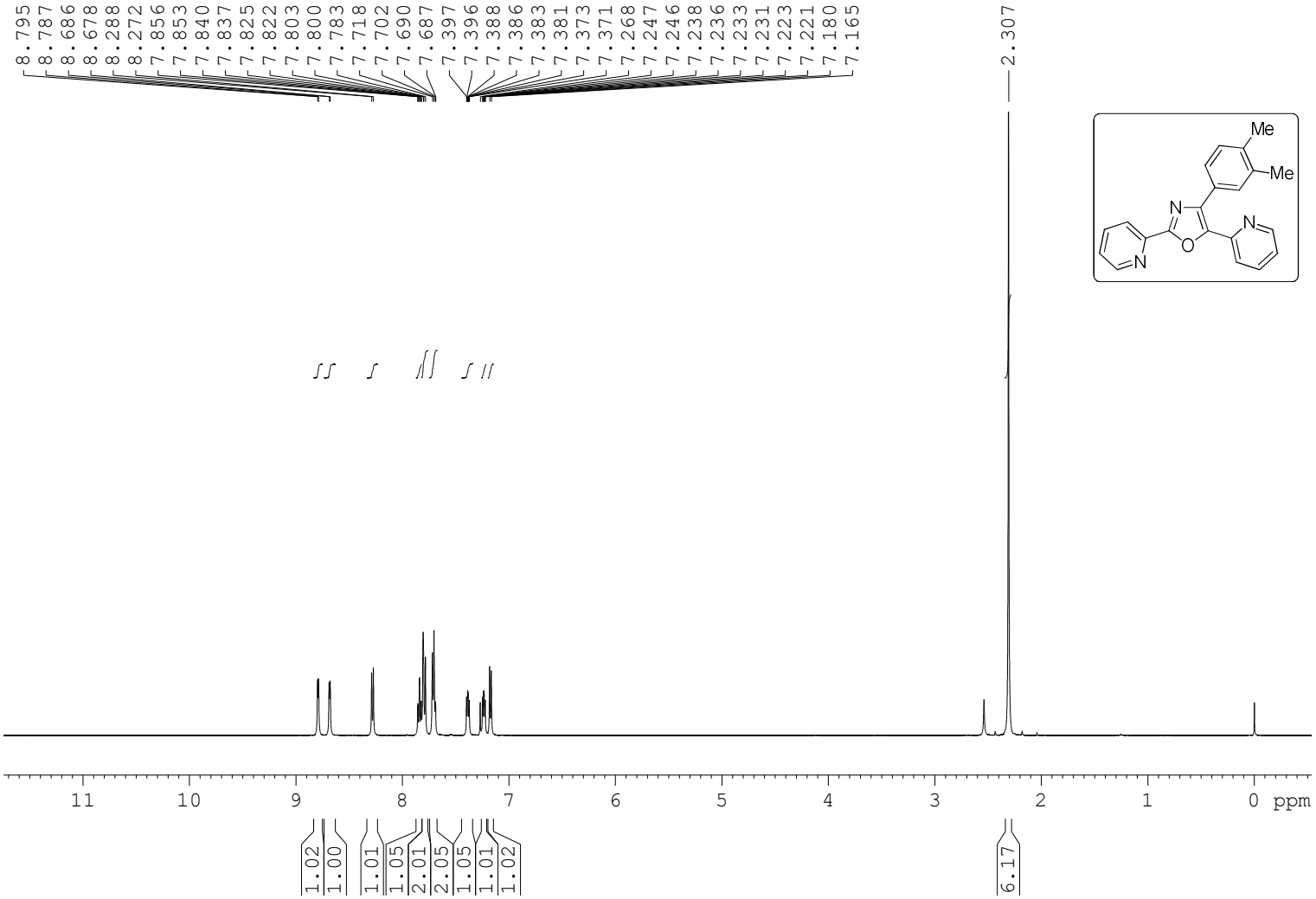
^{1}H NMR Spectrum of 3ab



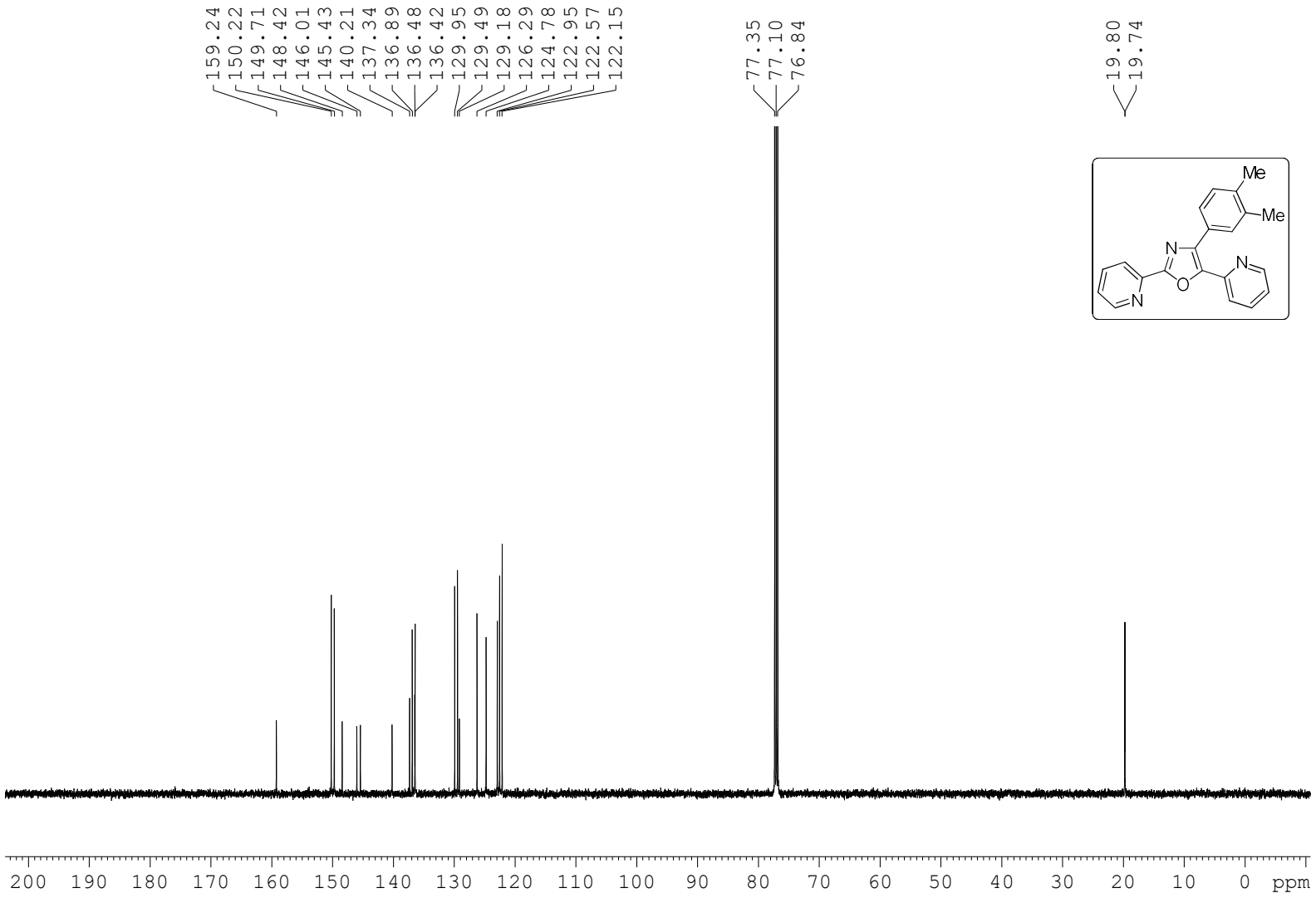
^{13}C NMR Spectrum of 3ab



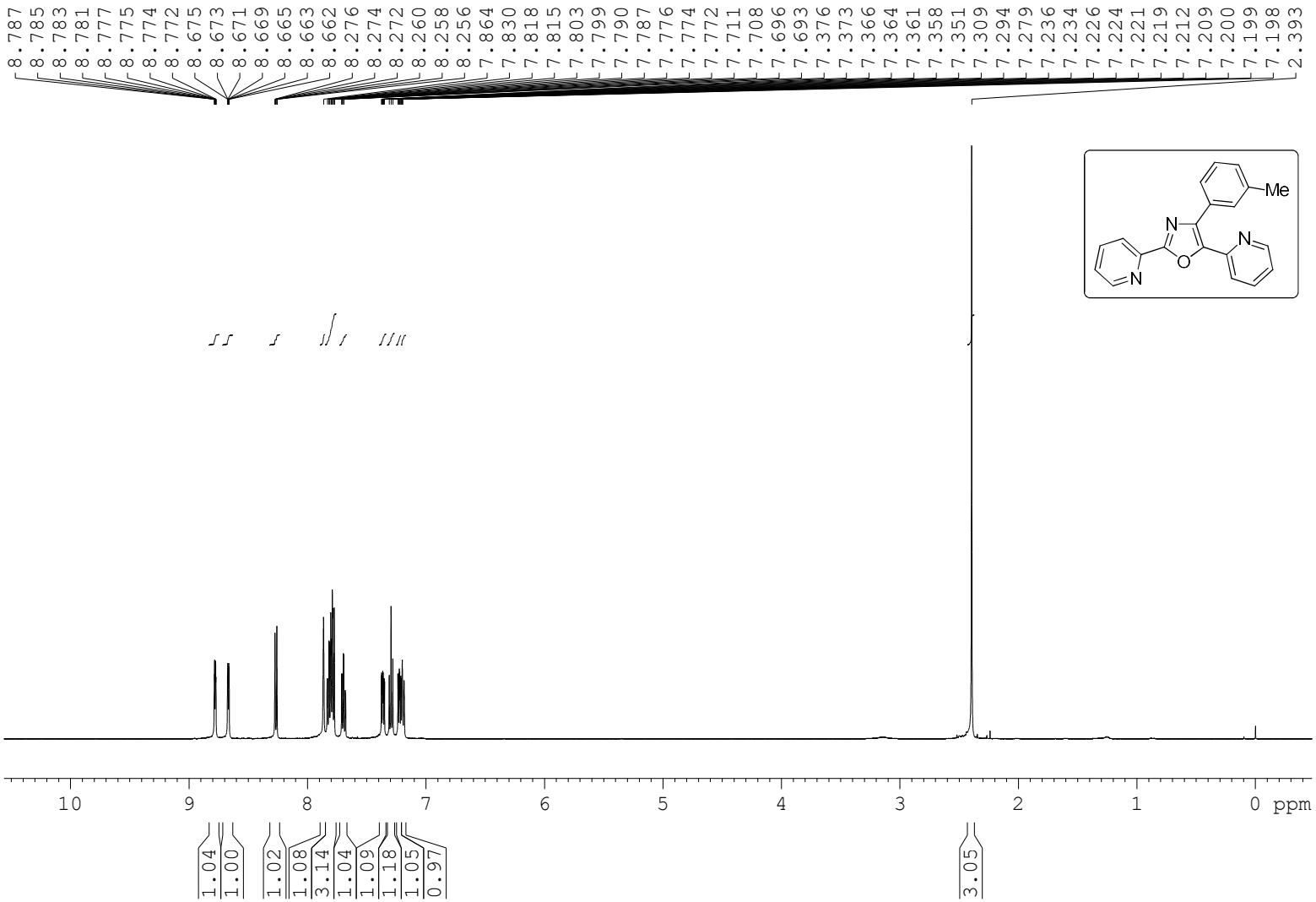
[1]H NMR Spectrum of 3ac



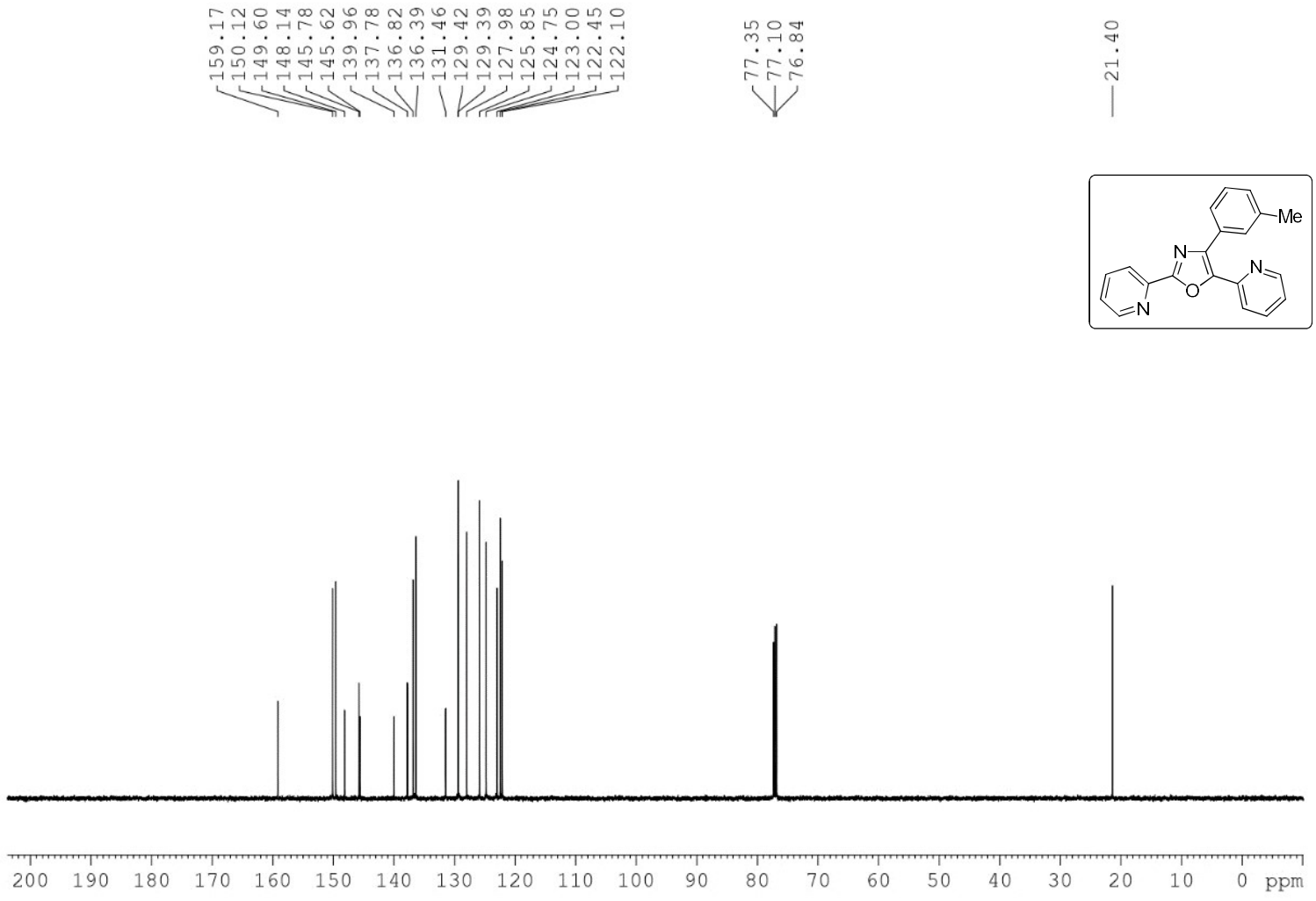
^{13}C NMR Spectrum of 3ac



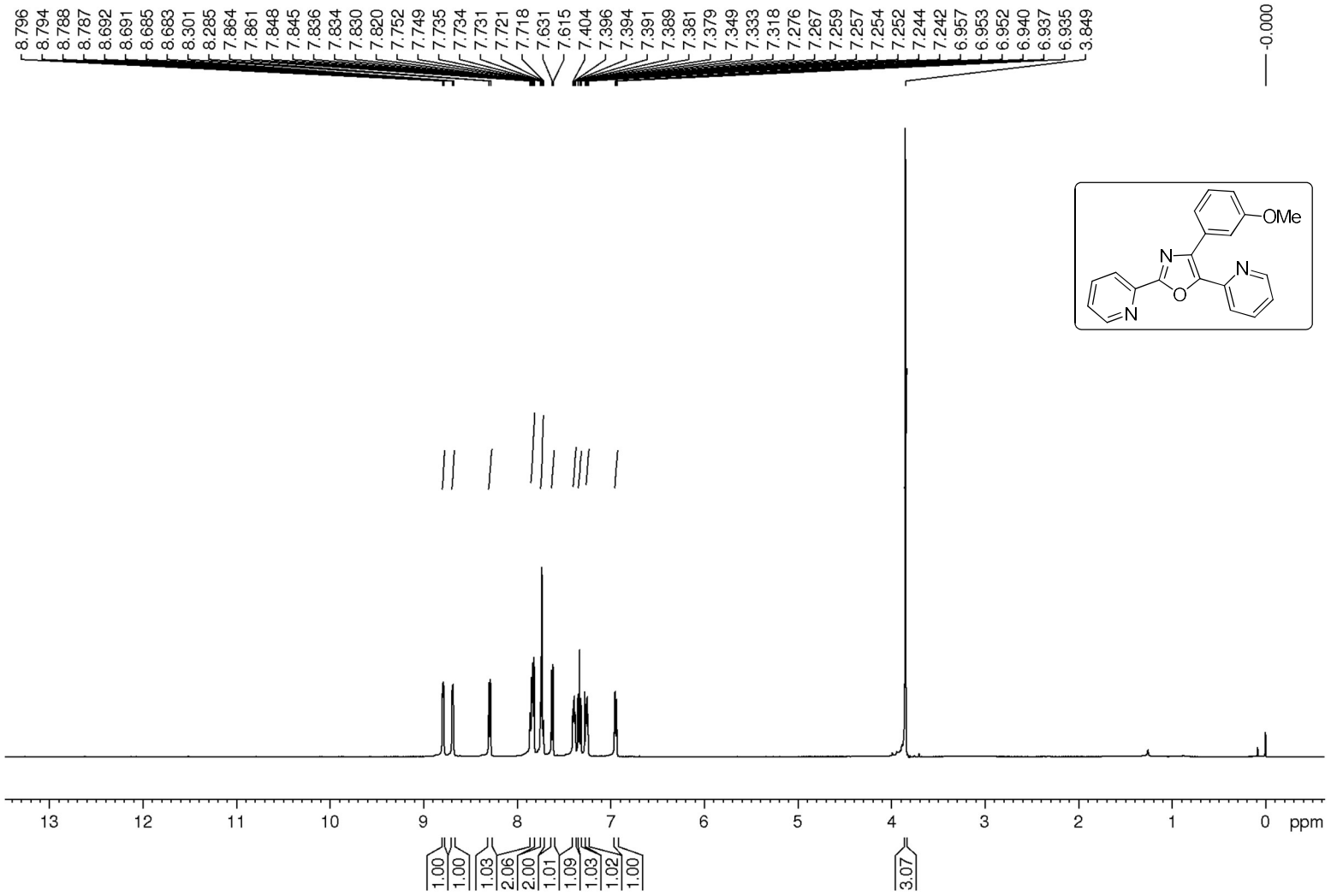
^{1}H NMR Spectrum of 3ad



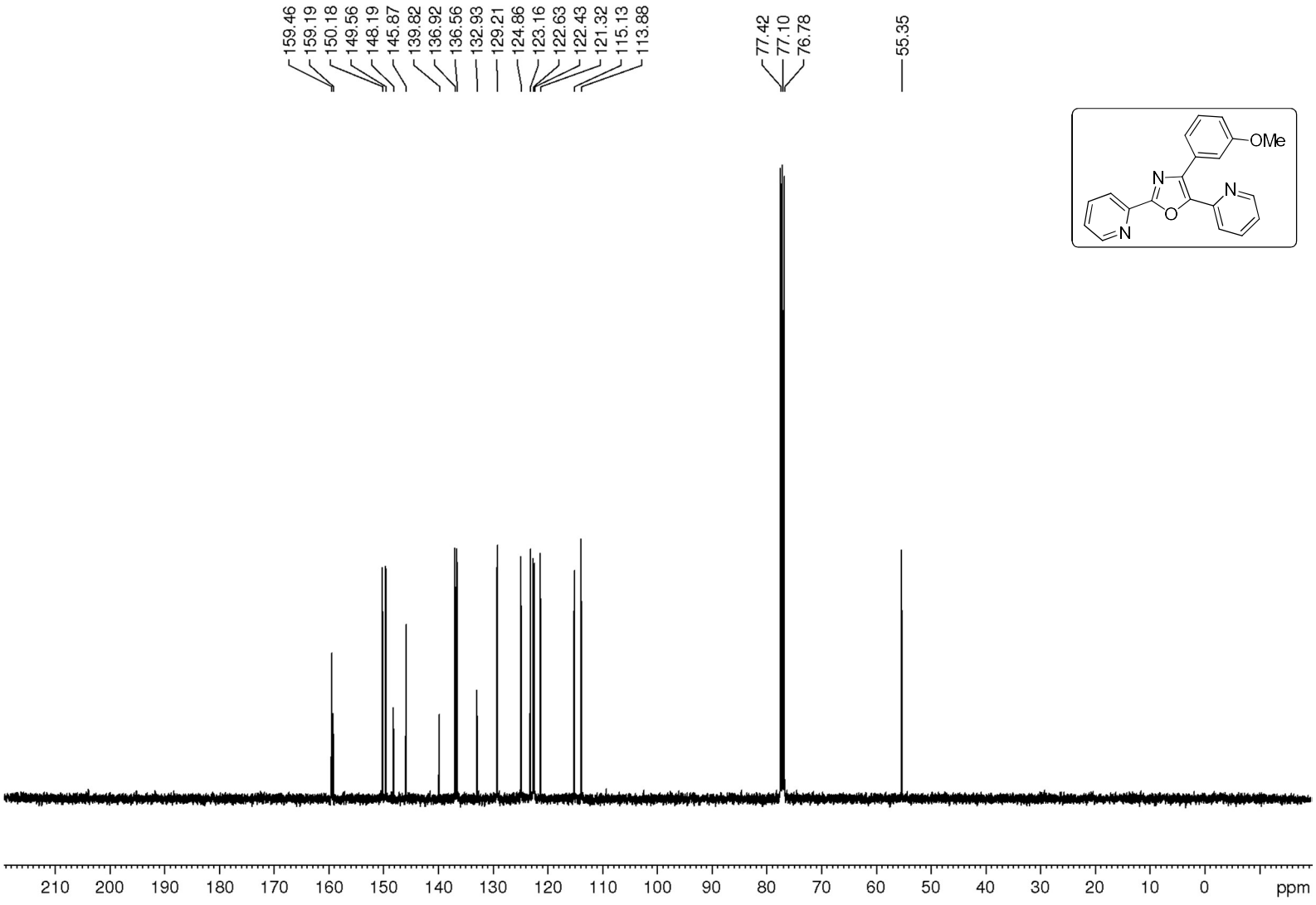
^{13}C NMR Spectrum of 3ad



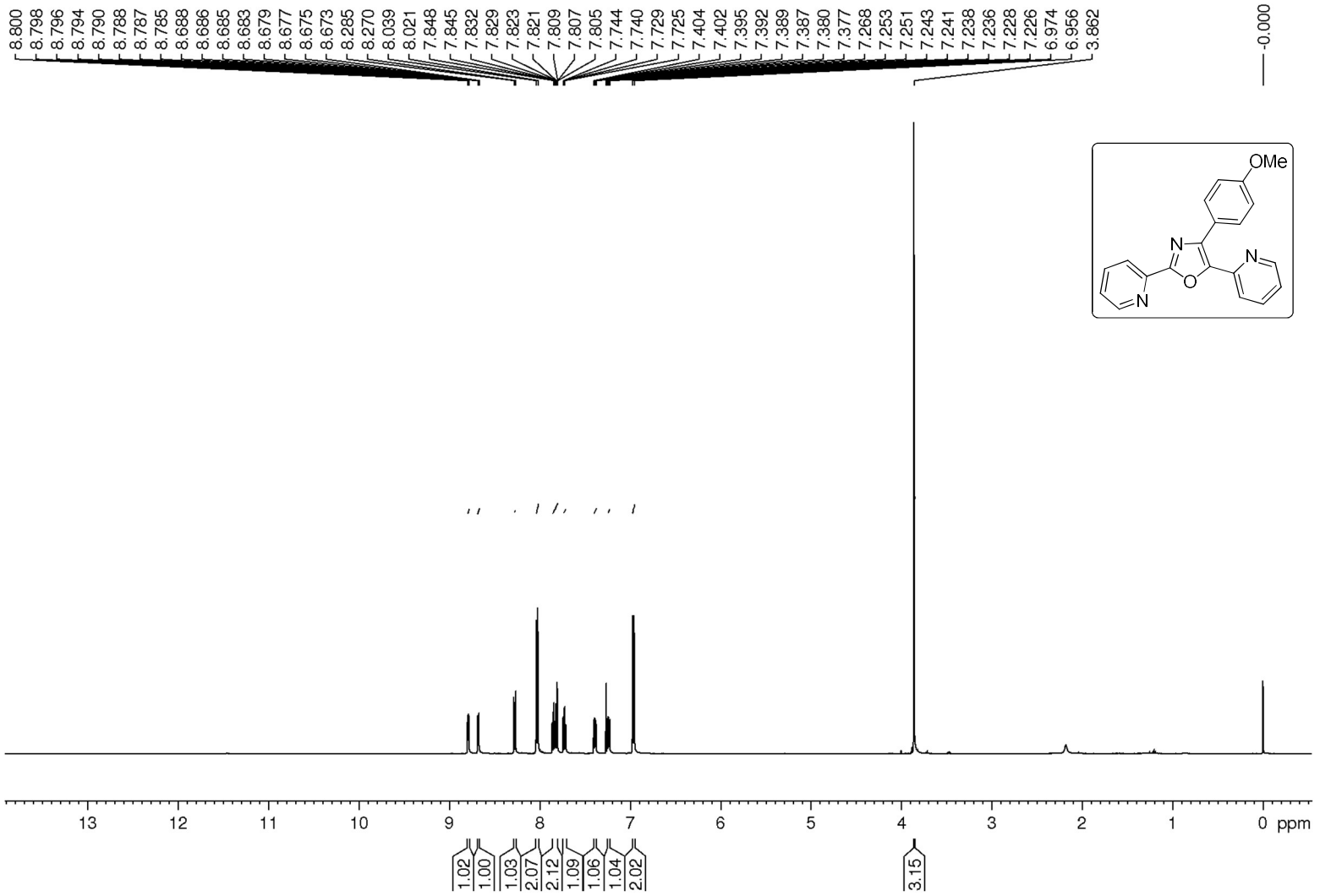
[1]H NMR Spectrum of 3ae



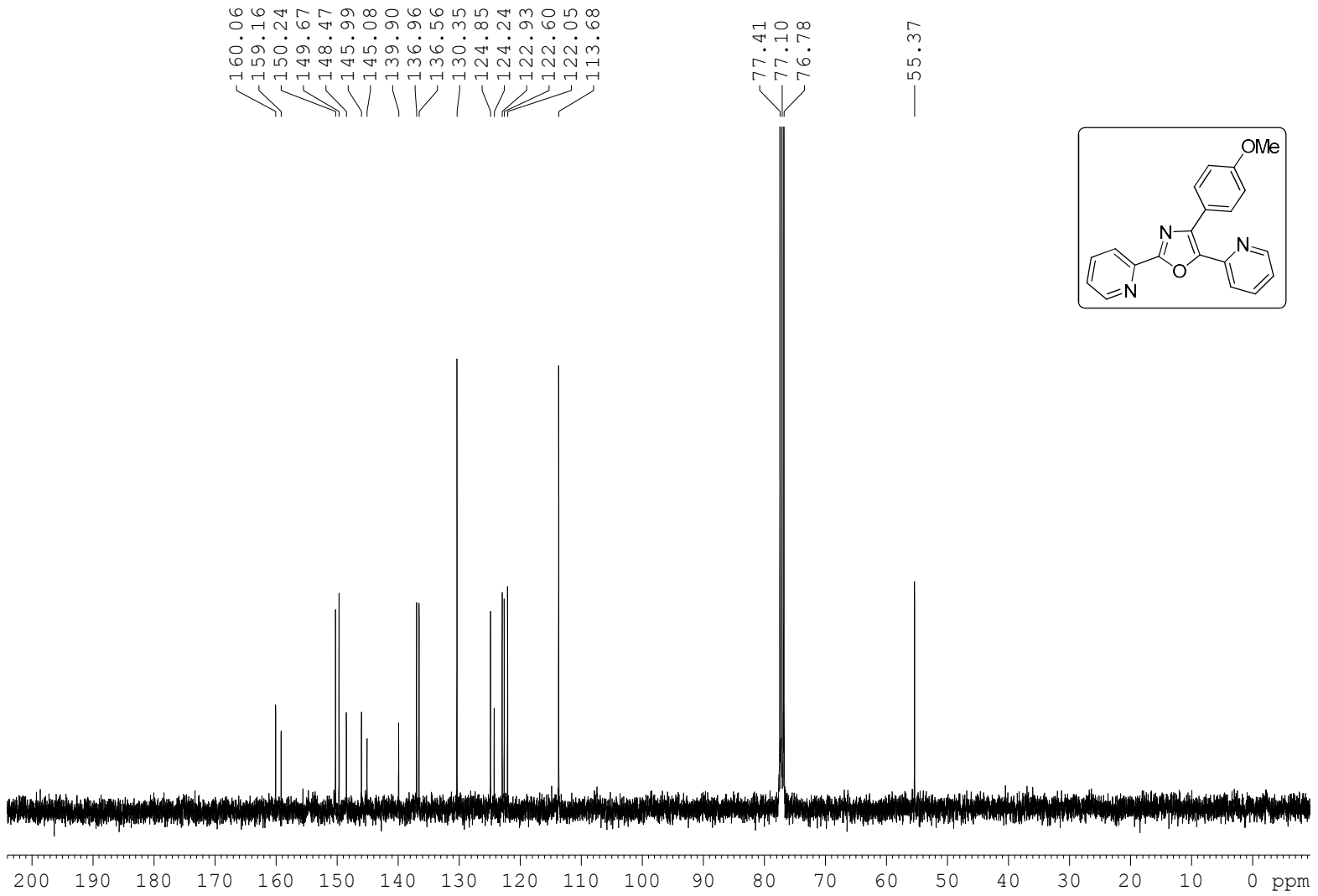
^{13}C NMR Spectrum of 3ae



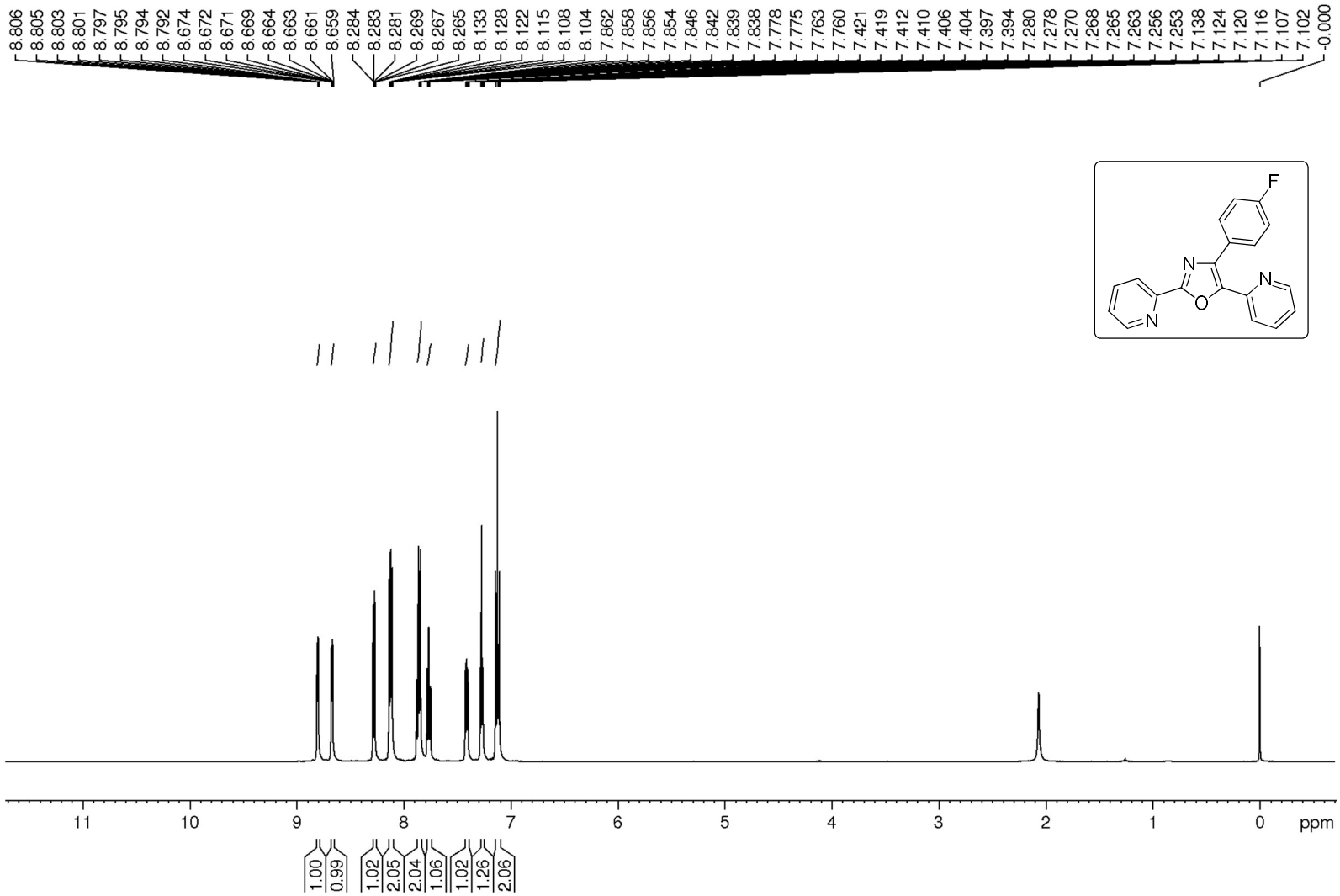
^{1}H NMR Spectrum of 3af



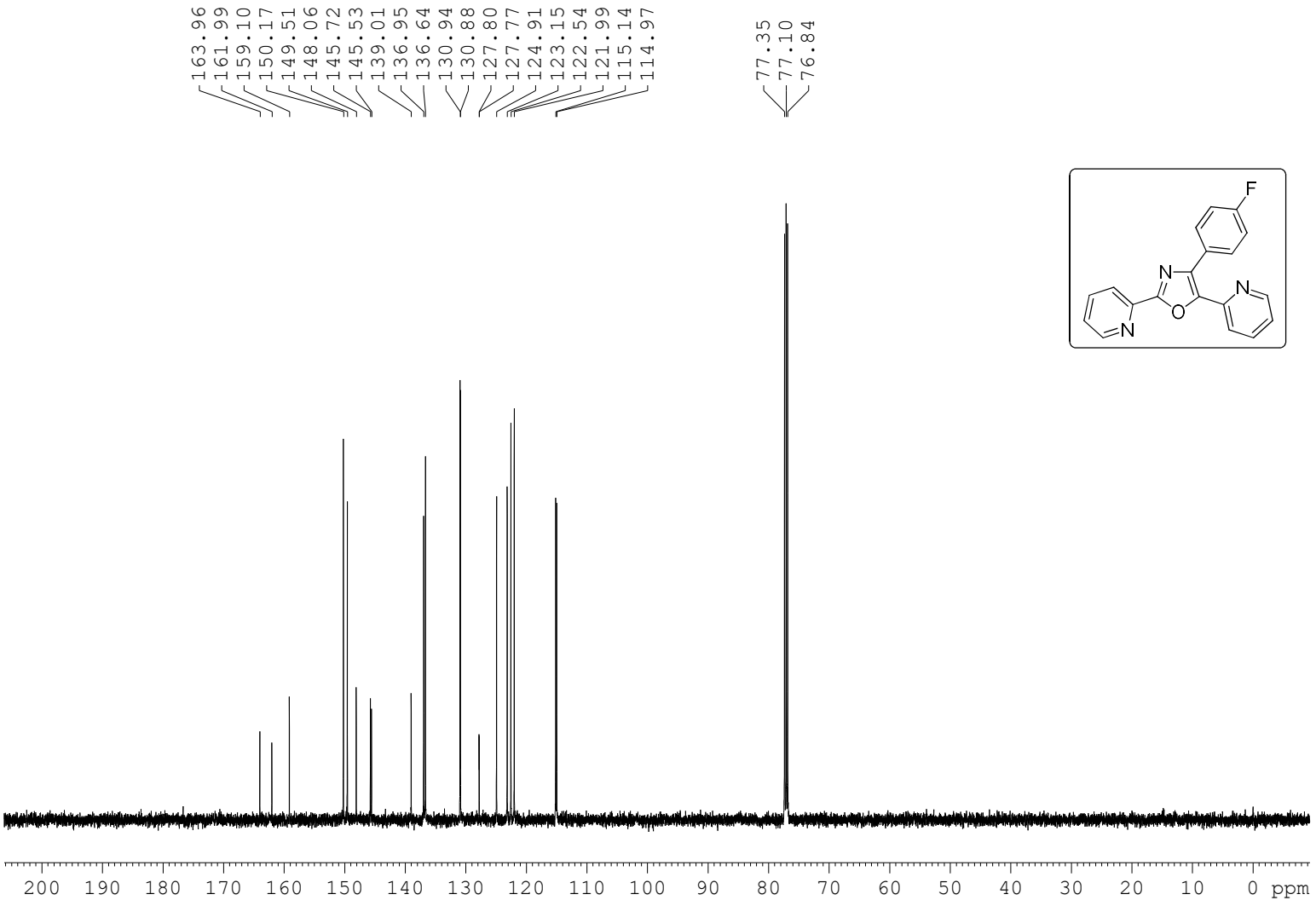
^{13}C NMR Spectrum of 3af



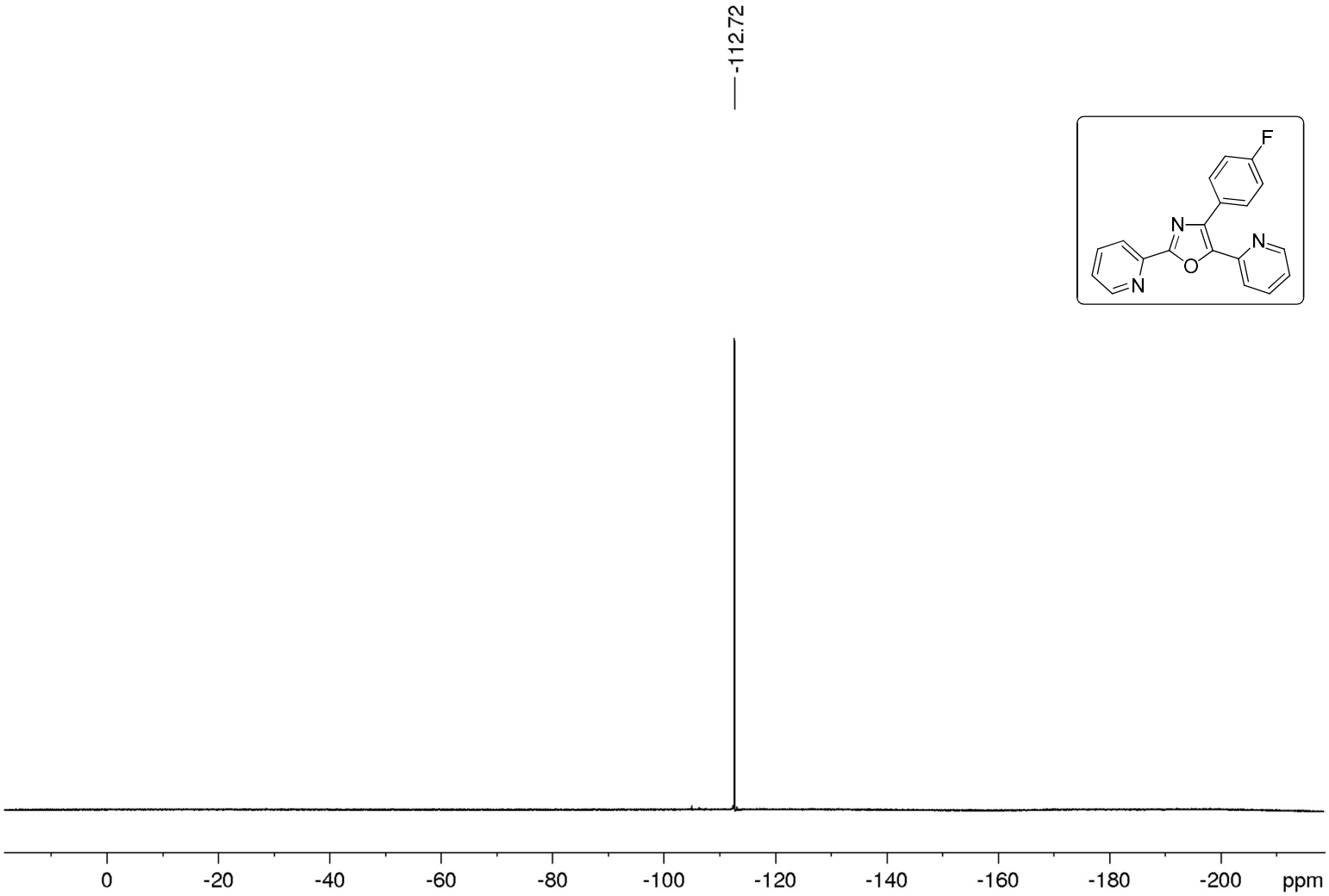
^{1}H NMR Spectrum of 3ag



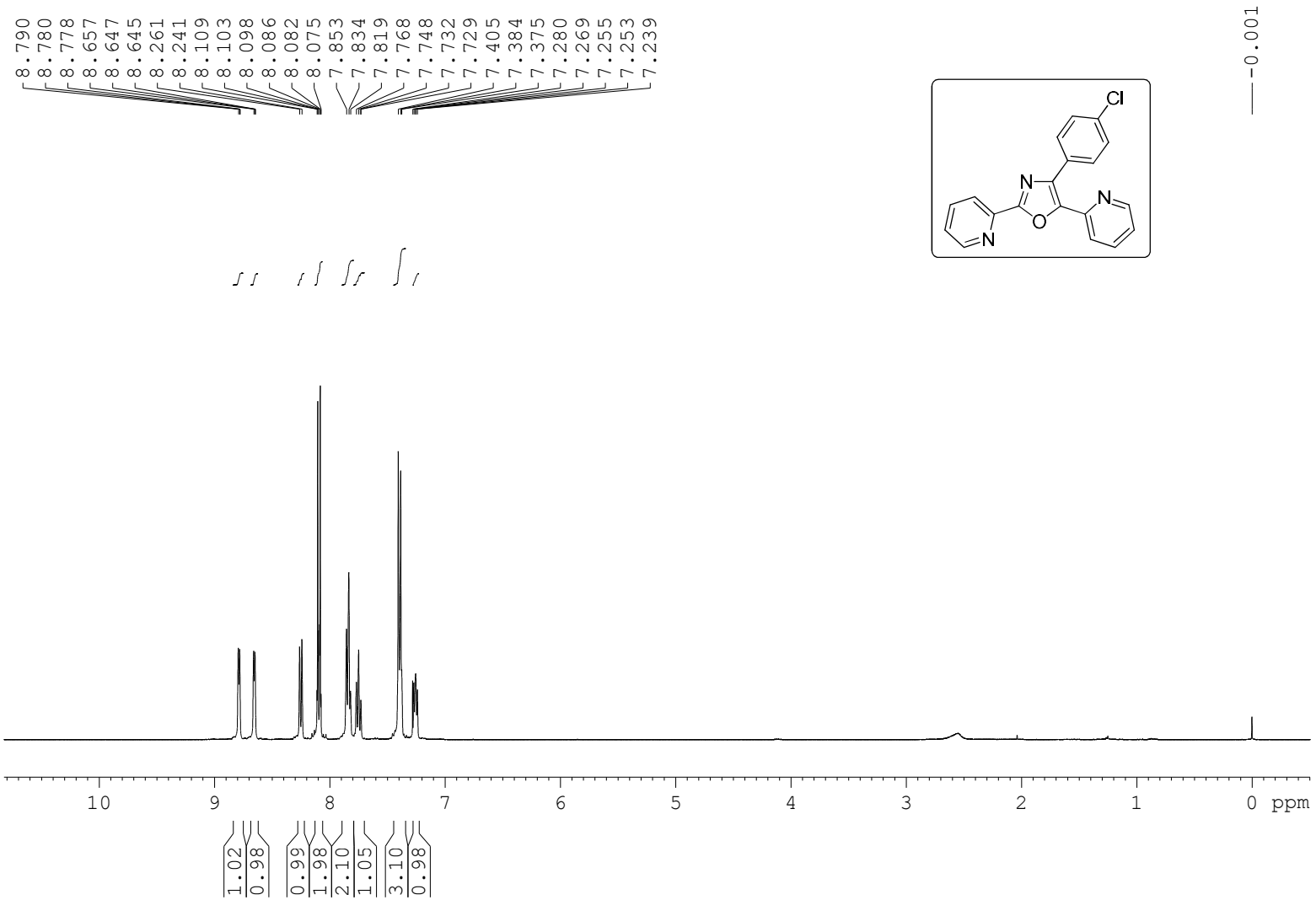
^{13}C NMR Spectrum of 3ag



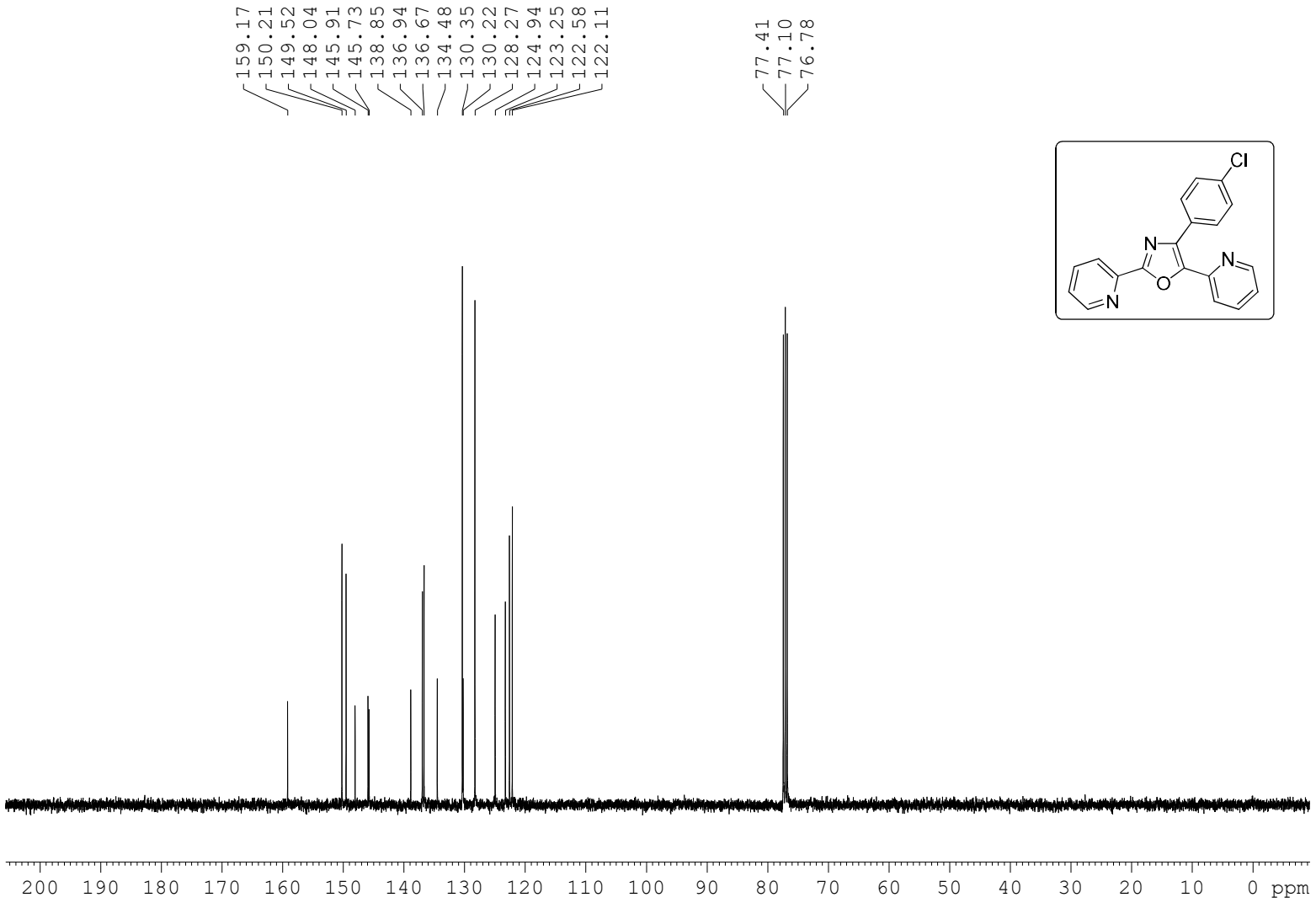
^{19}F NMR Spectrum of 3ag



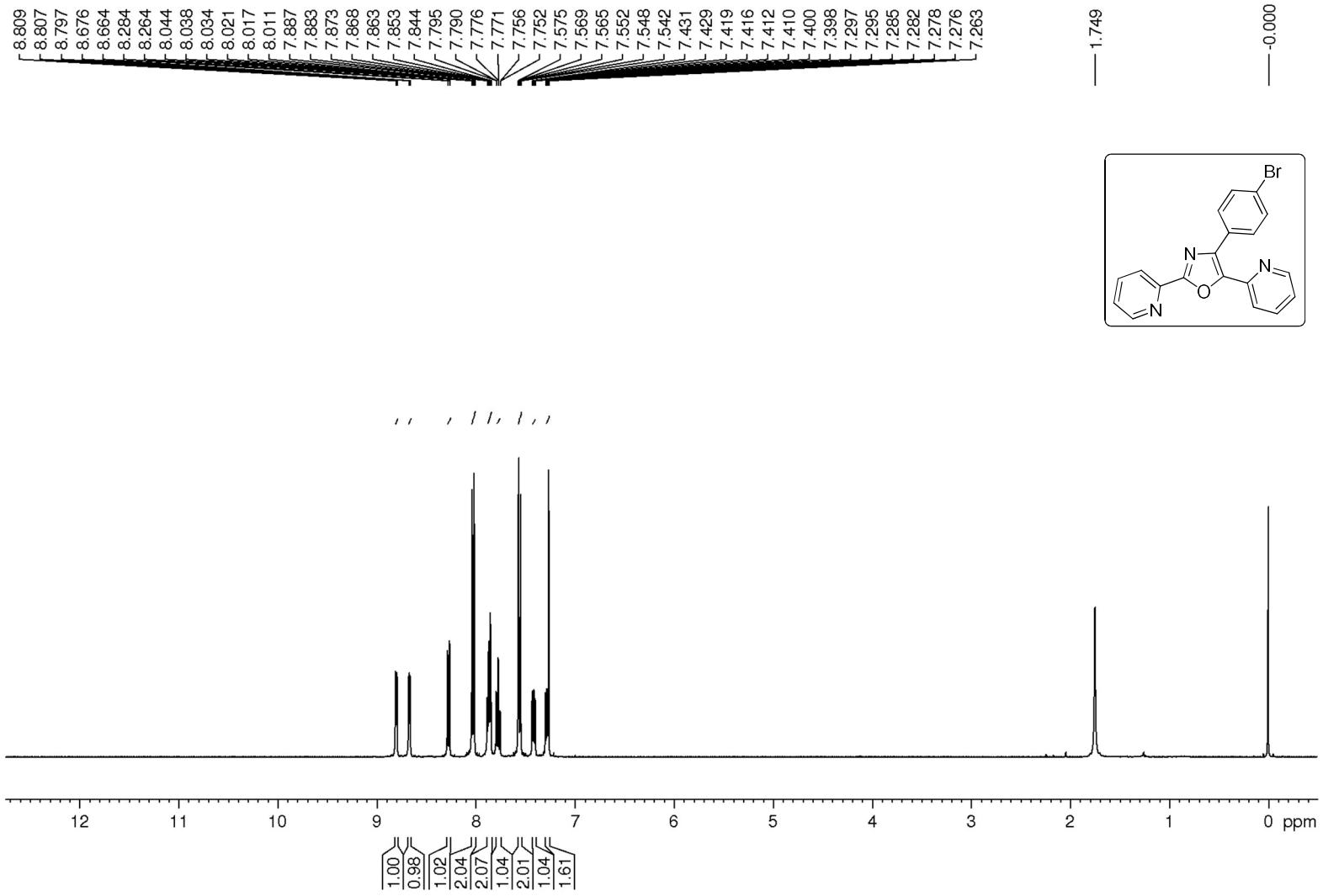
^{1}H NMR Spectrum of 3ah



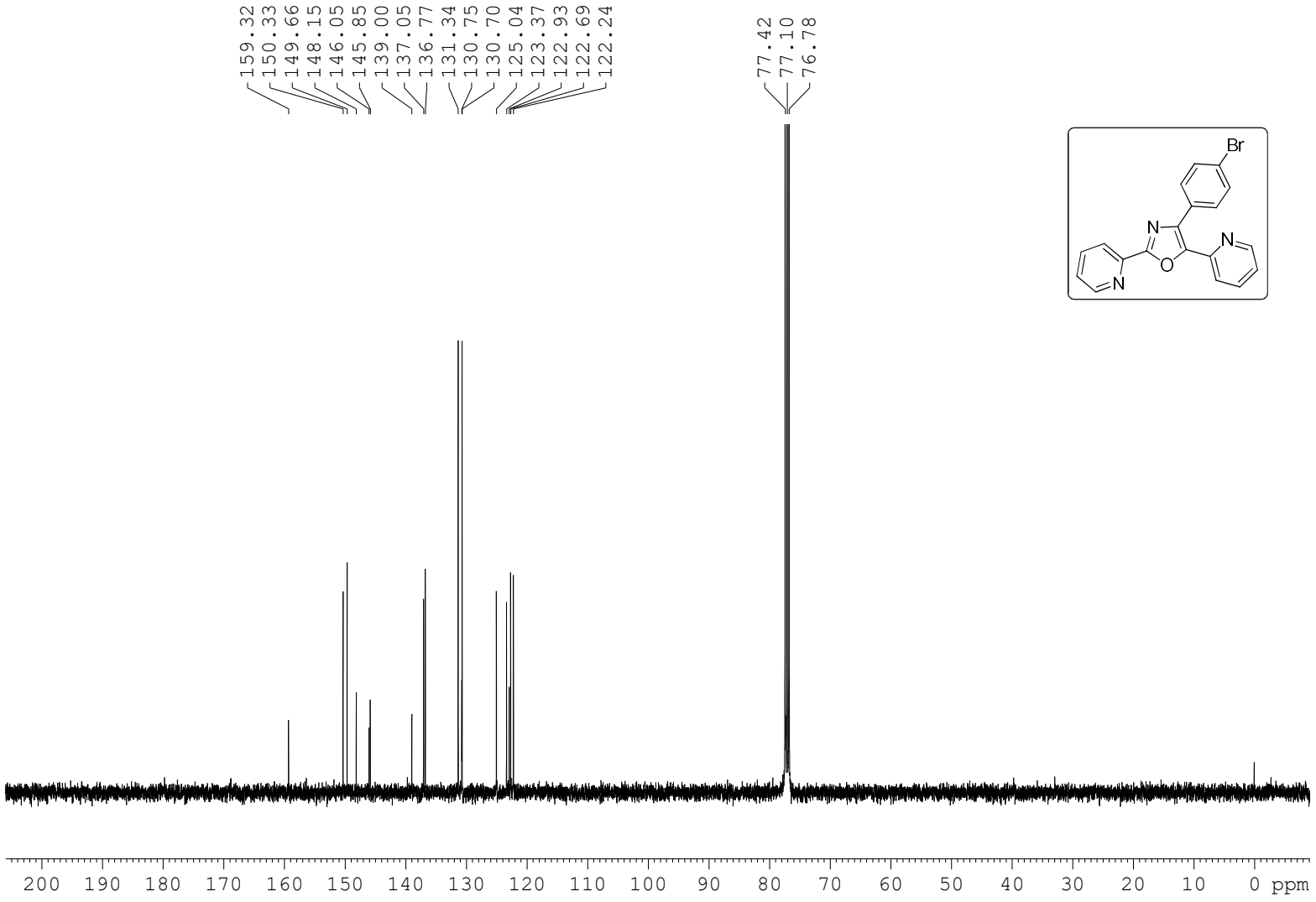
^{13}C NMR Spectrum of 3ah



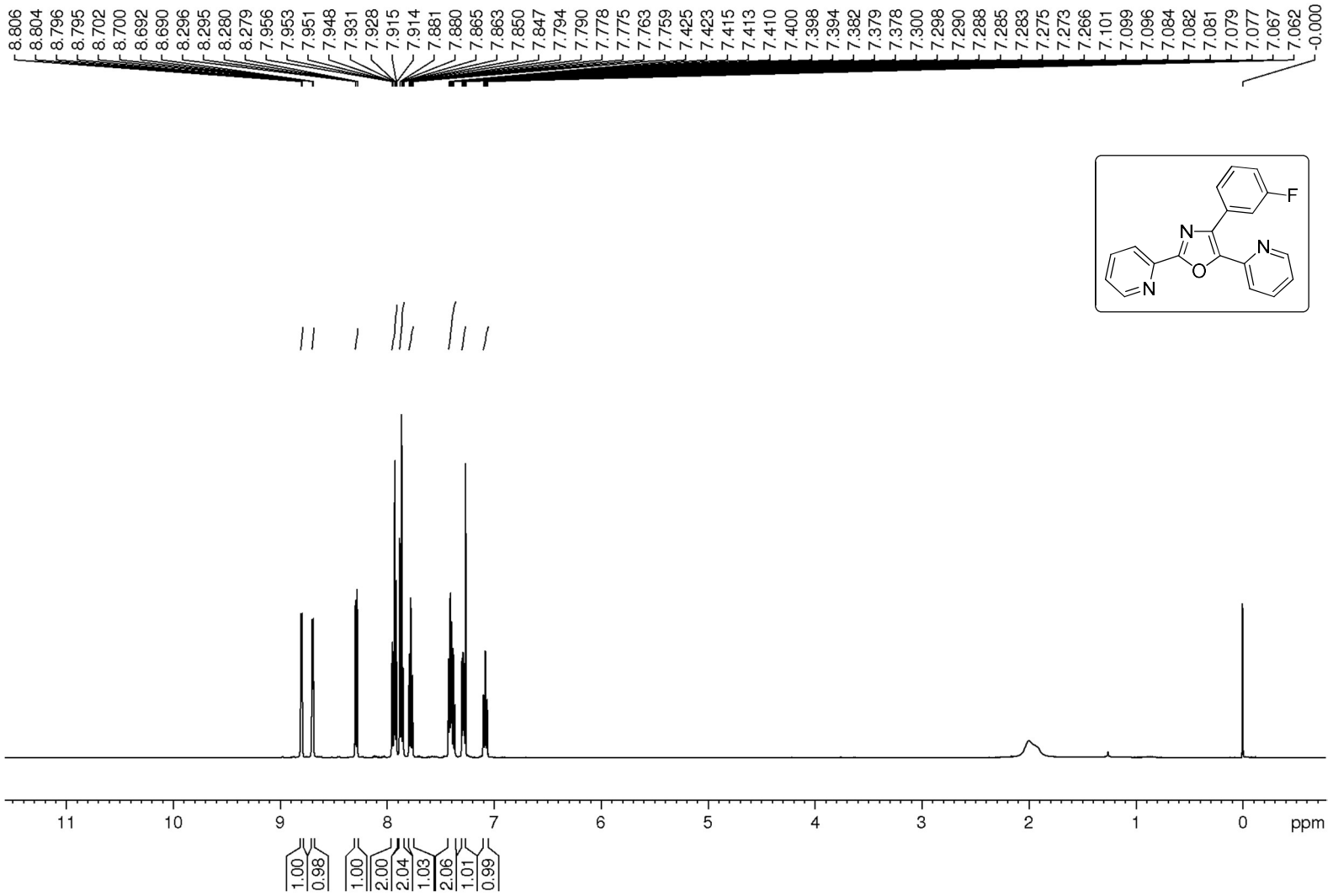
^{1}H NMR Spectrum of 3ai



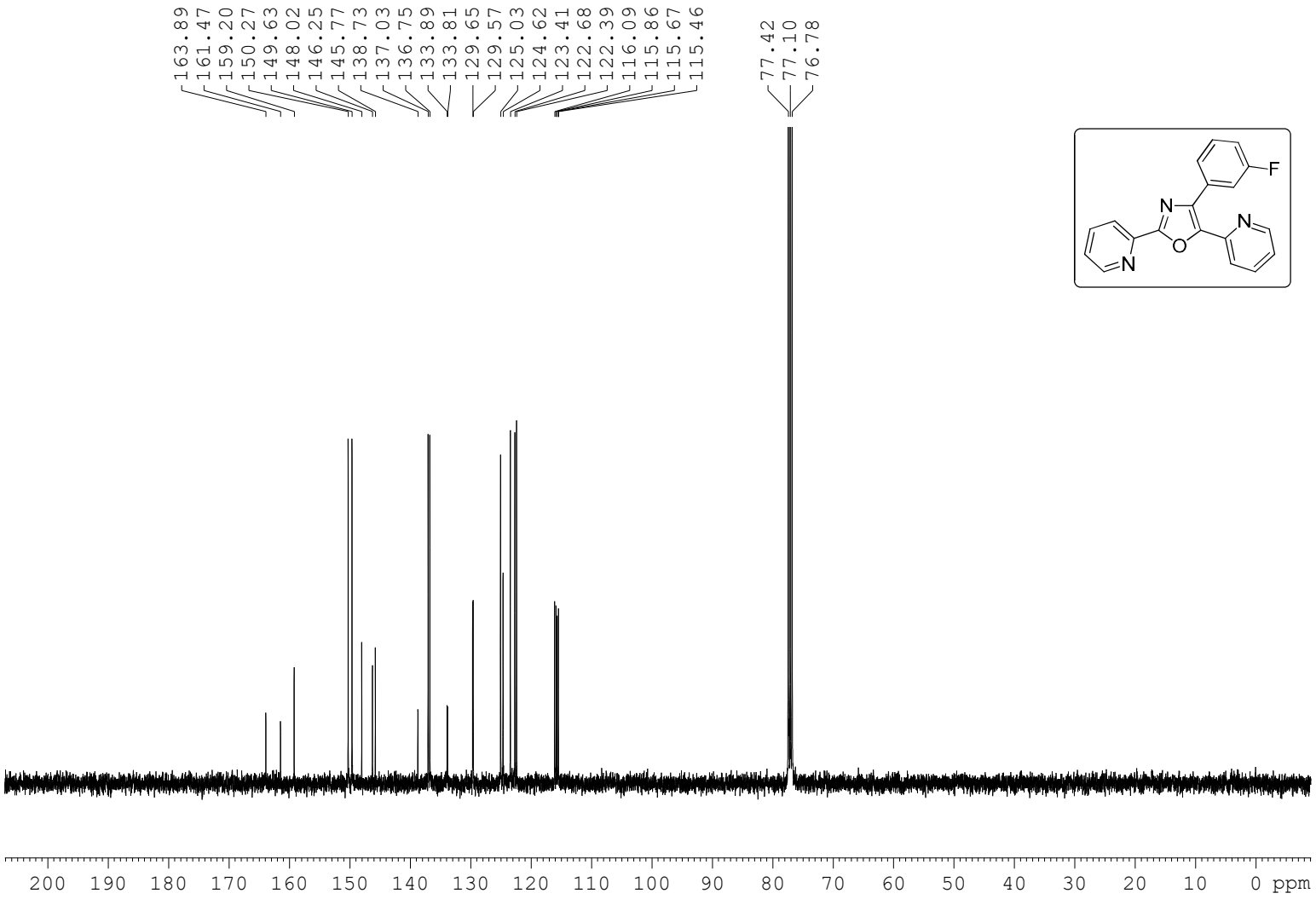
^{13}C NMR Spectrum of 3ai



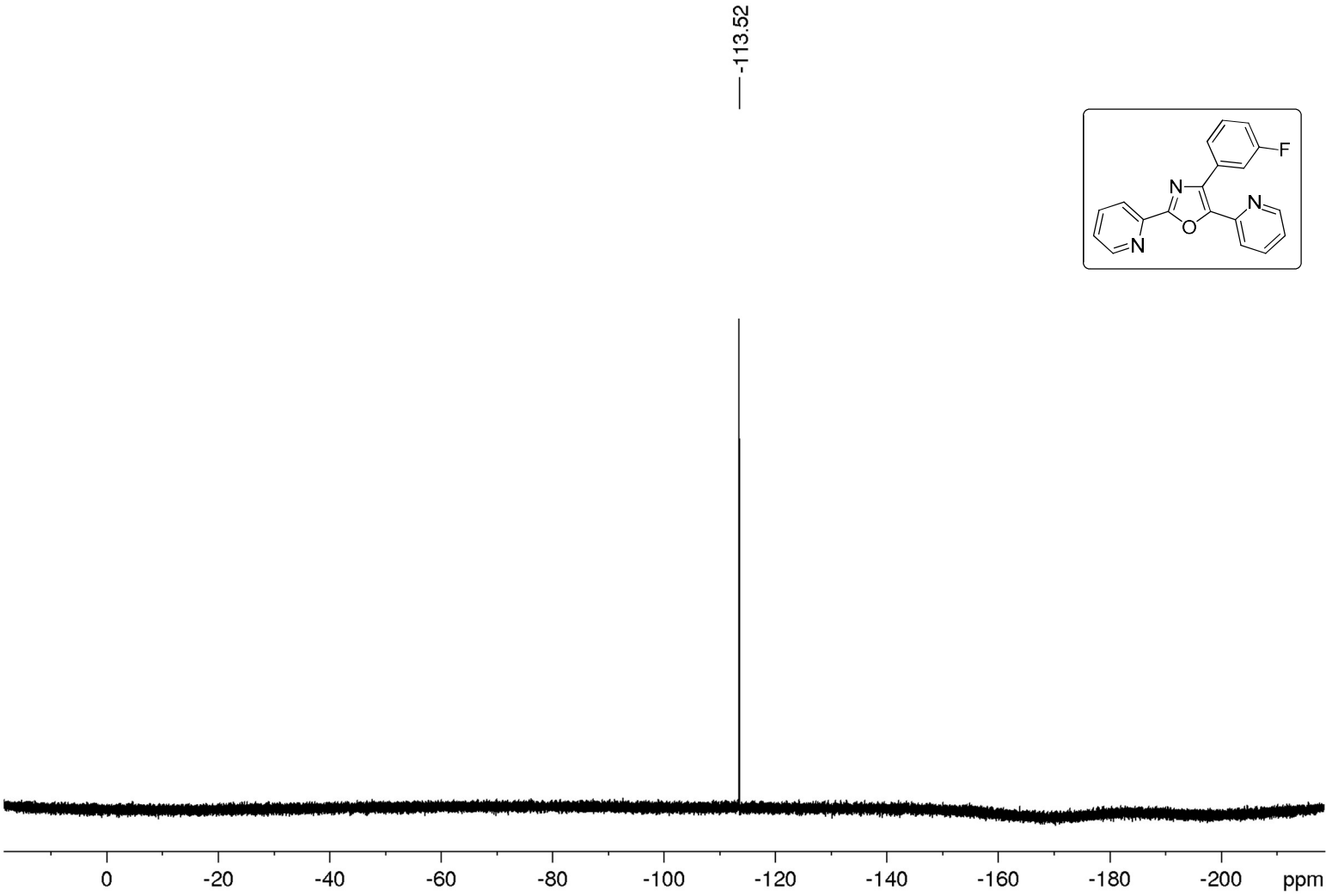
[1]H NMR Spectrum of 3aj



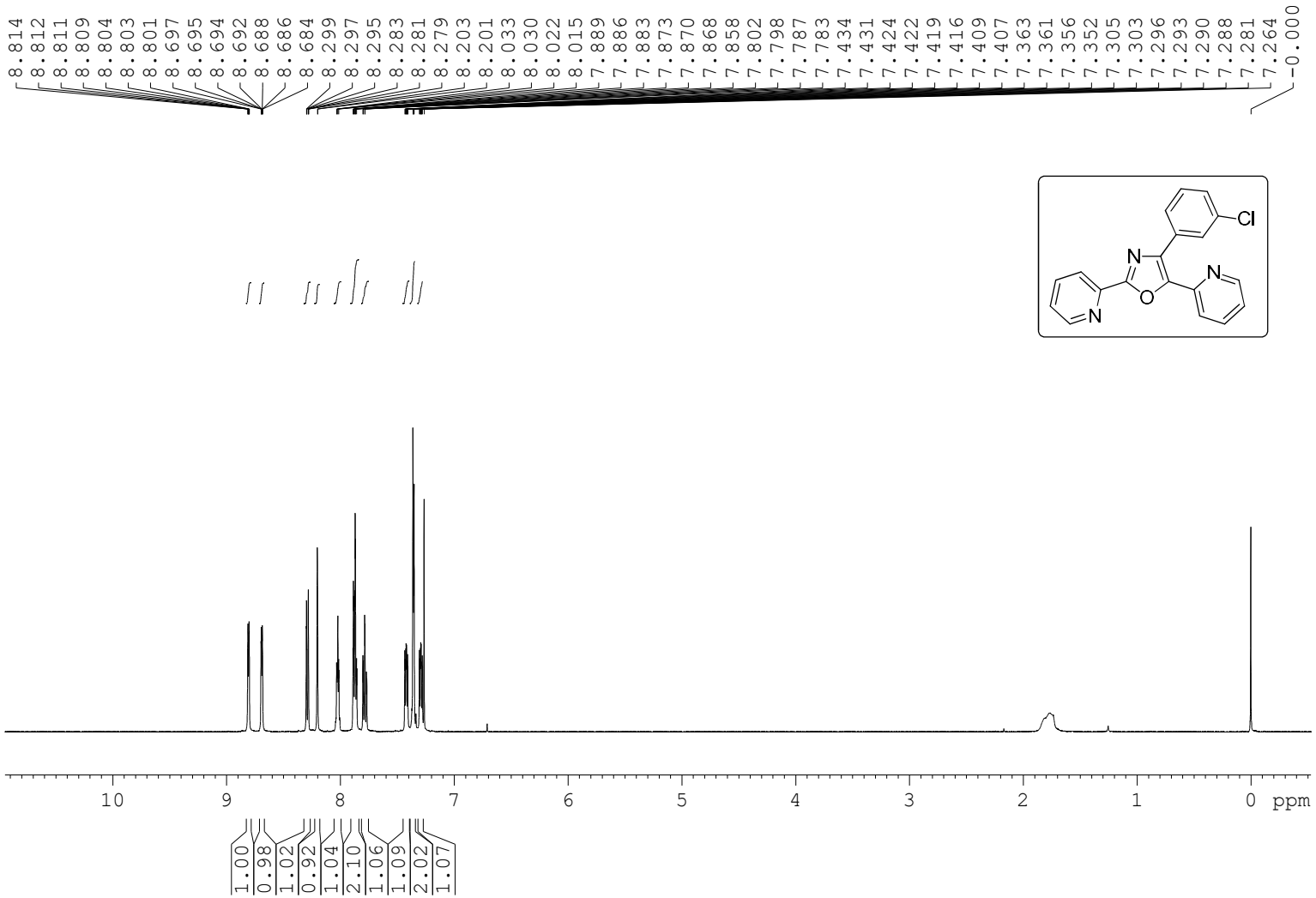
^{13}C NMR Spectrum of 3aj



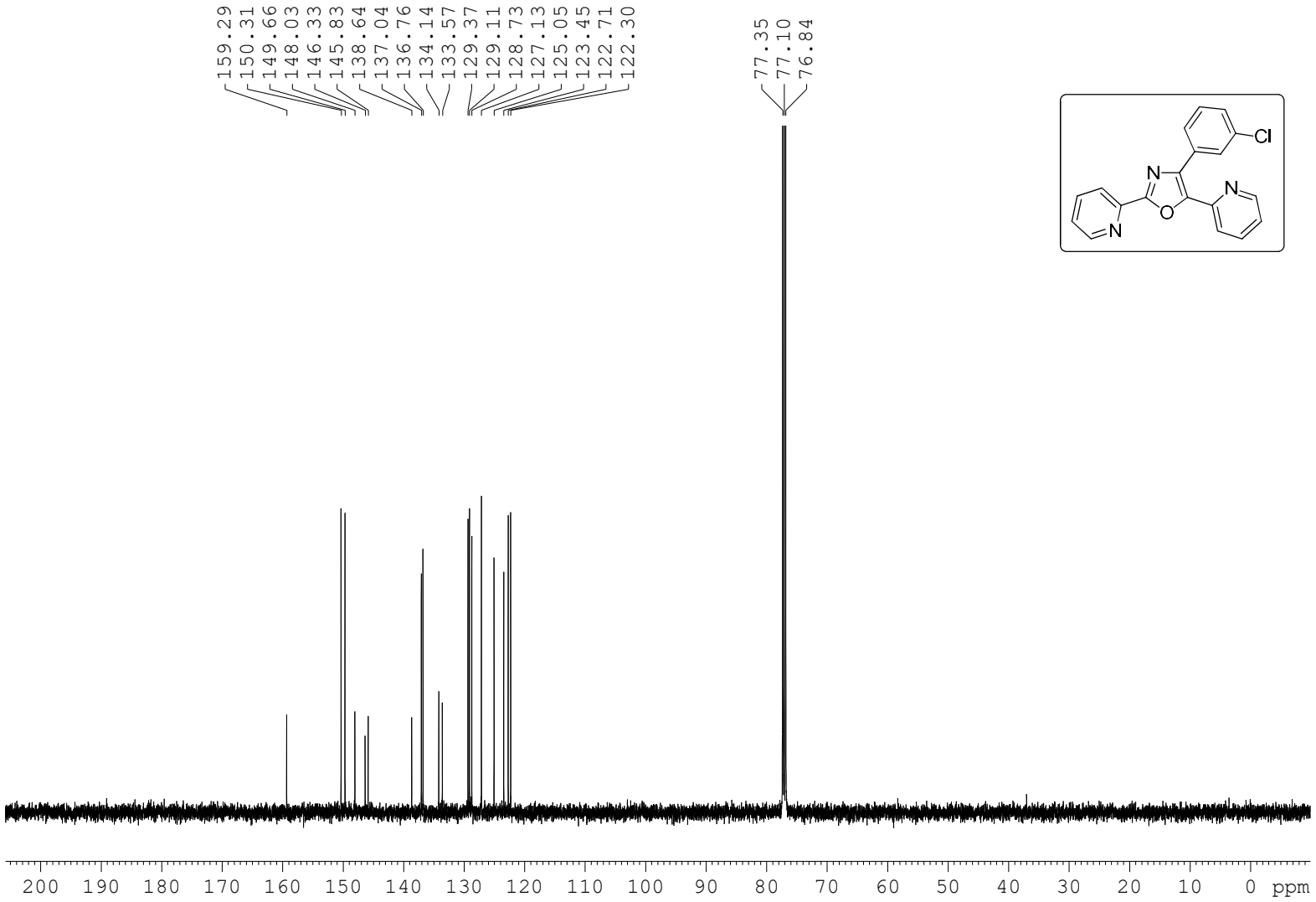
^{19}F NMR Spectrum of 3aj



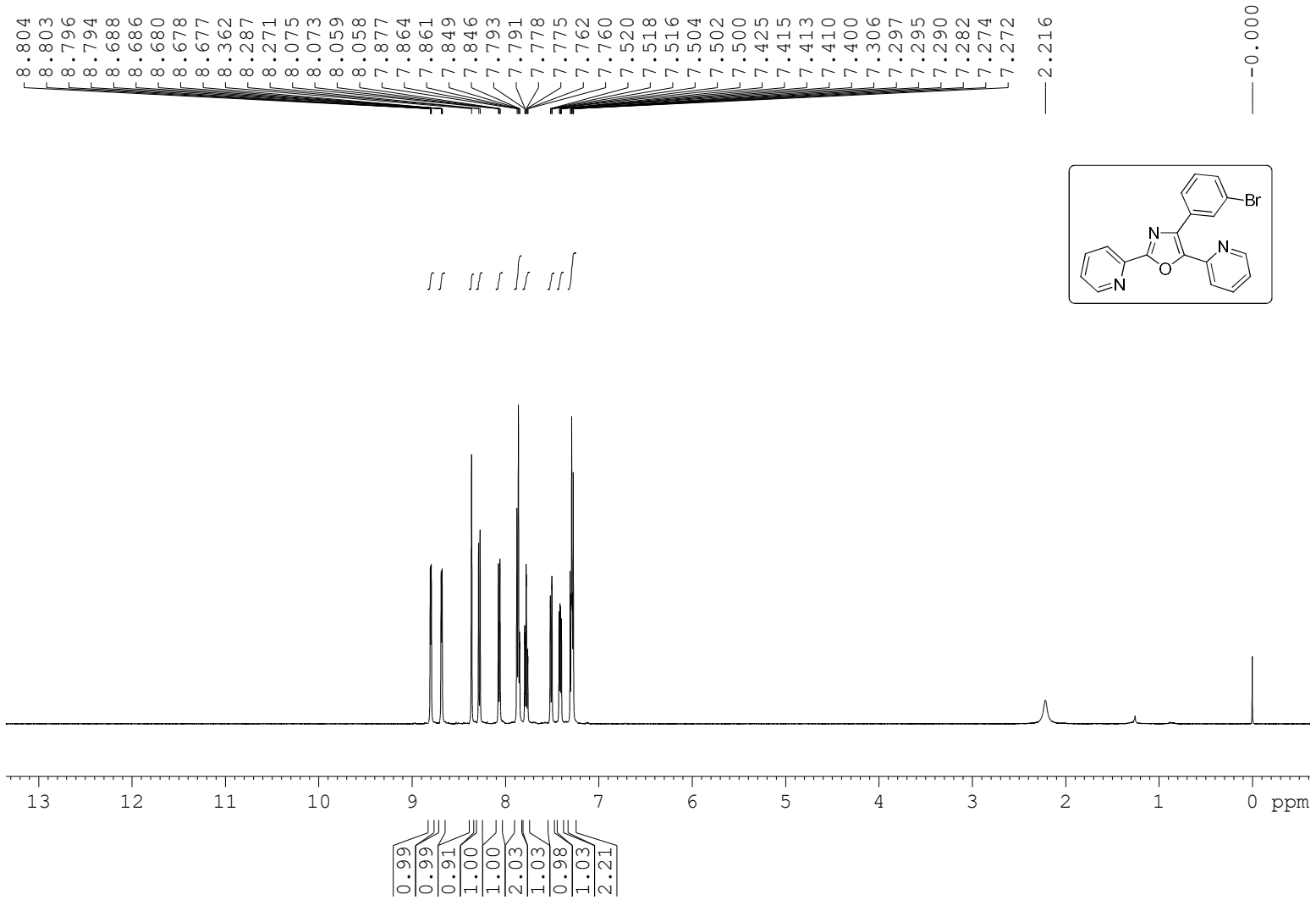
[1]H NMR Spectrum of 3ak



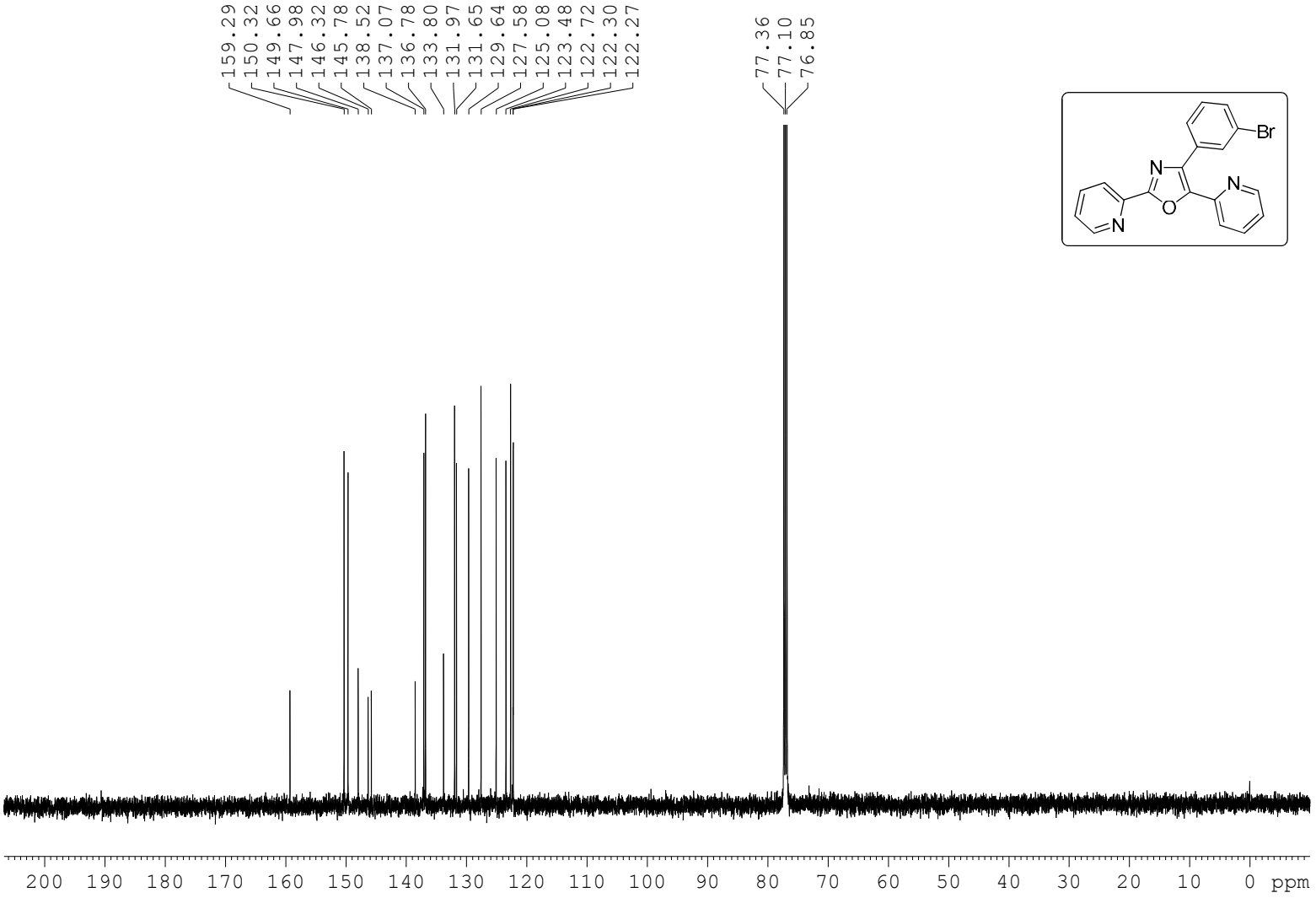
^{13}C NMR Spectrum of 3ak



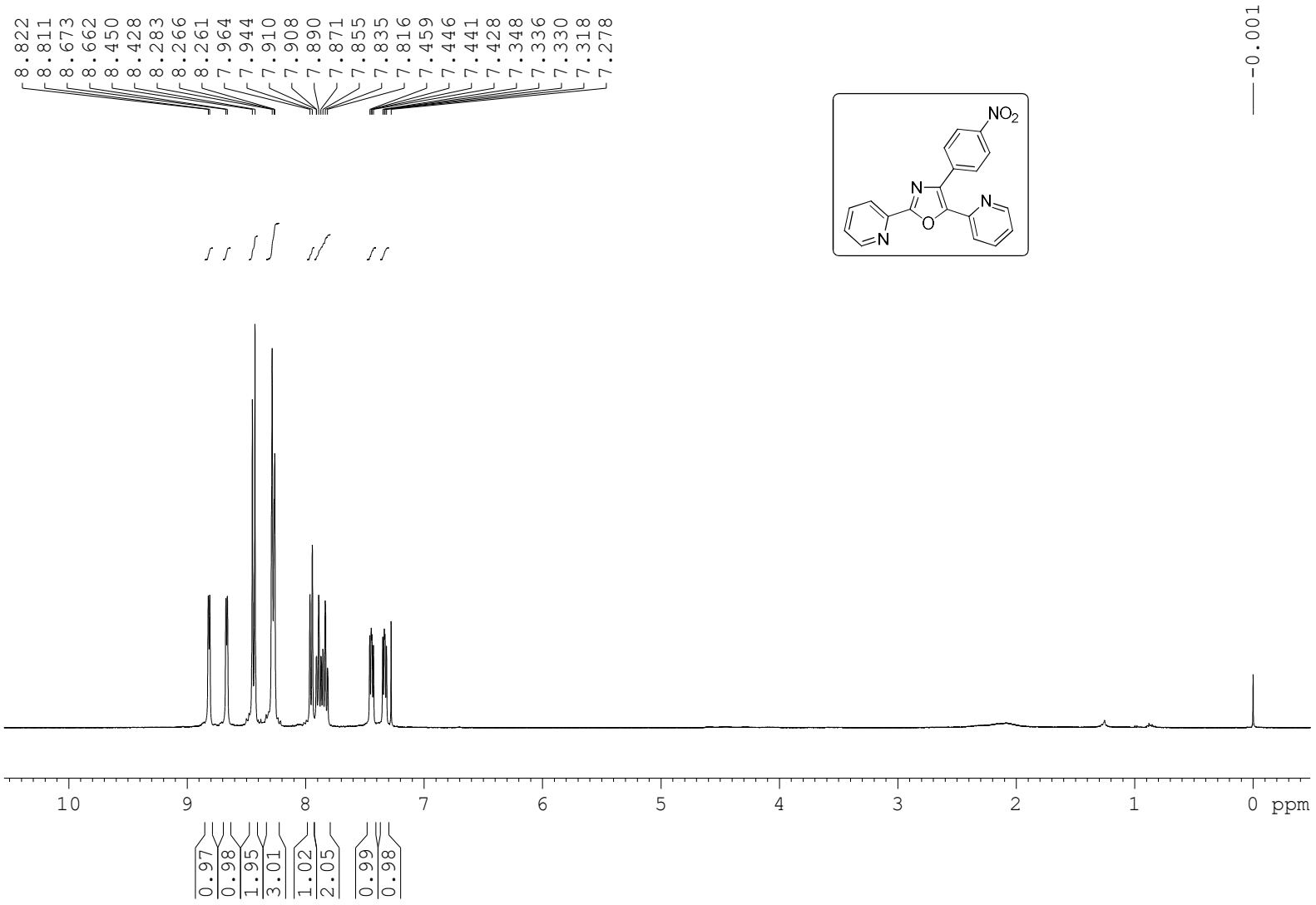
^{1}H NMR Spectrum of 3al



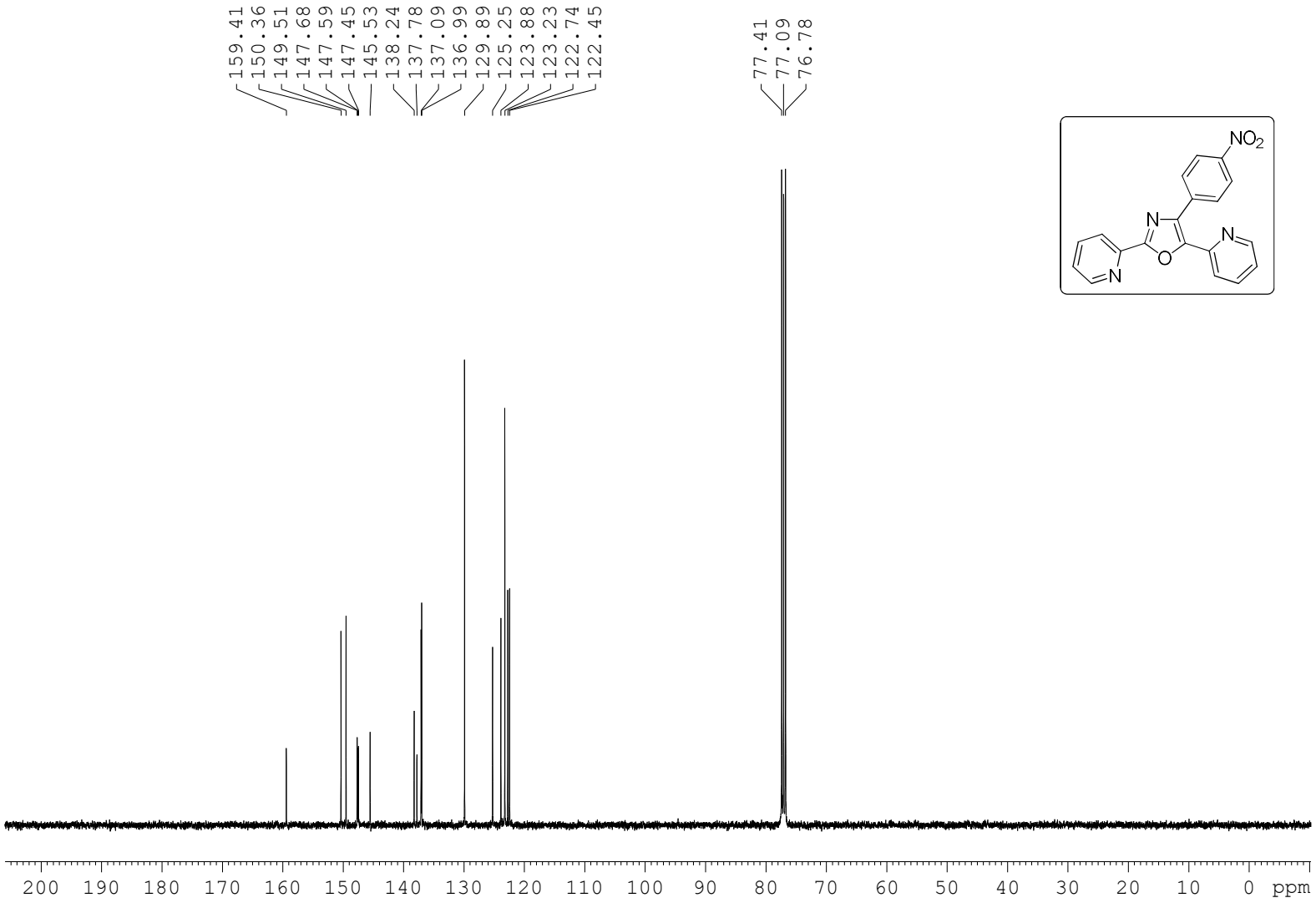
^{13}C NMR Spectrum of 3al



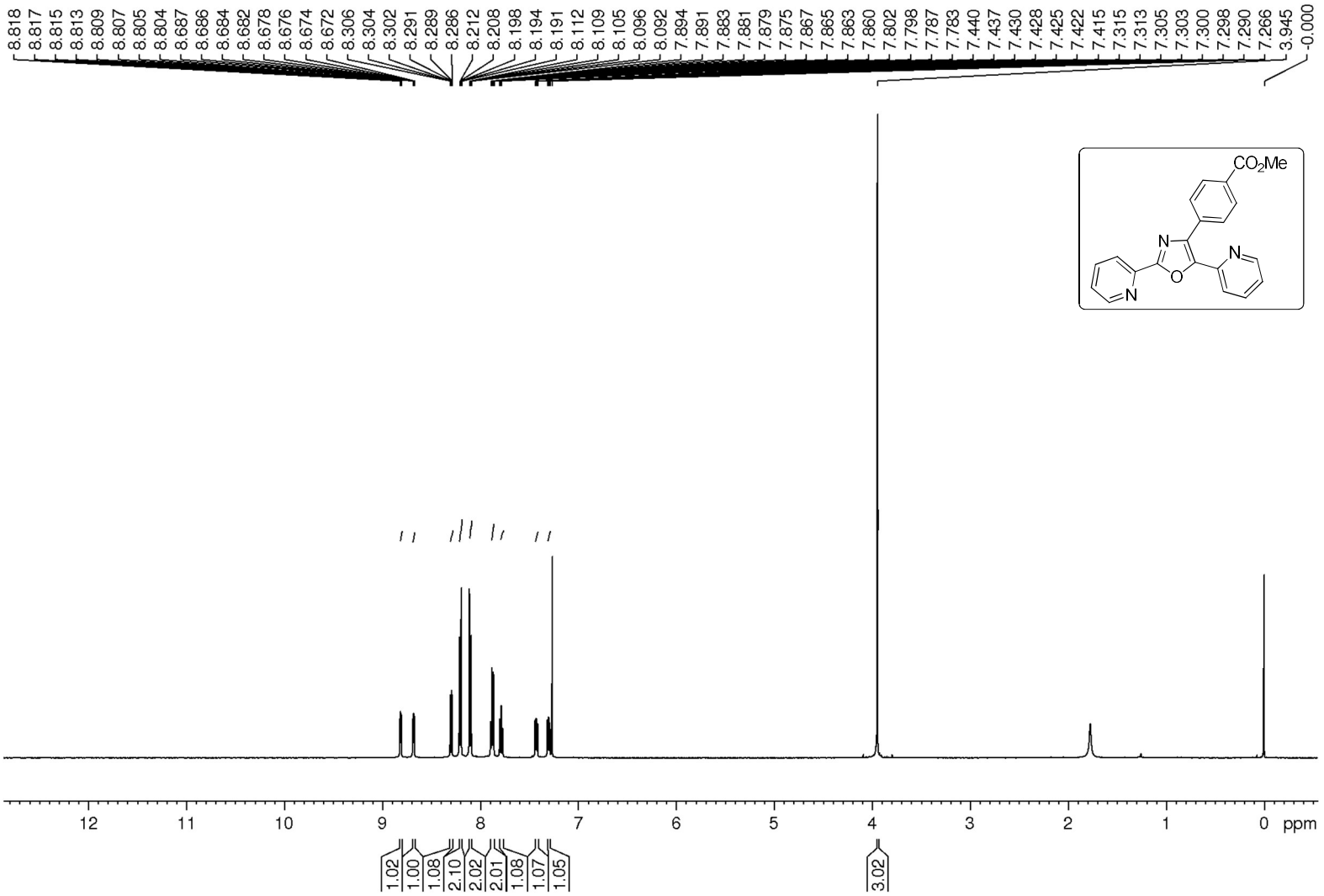
^{1}H NMR Spectrum of 3am



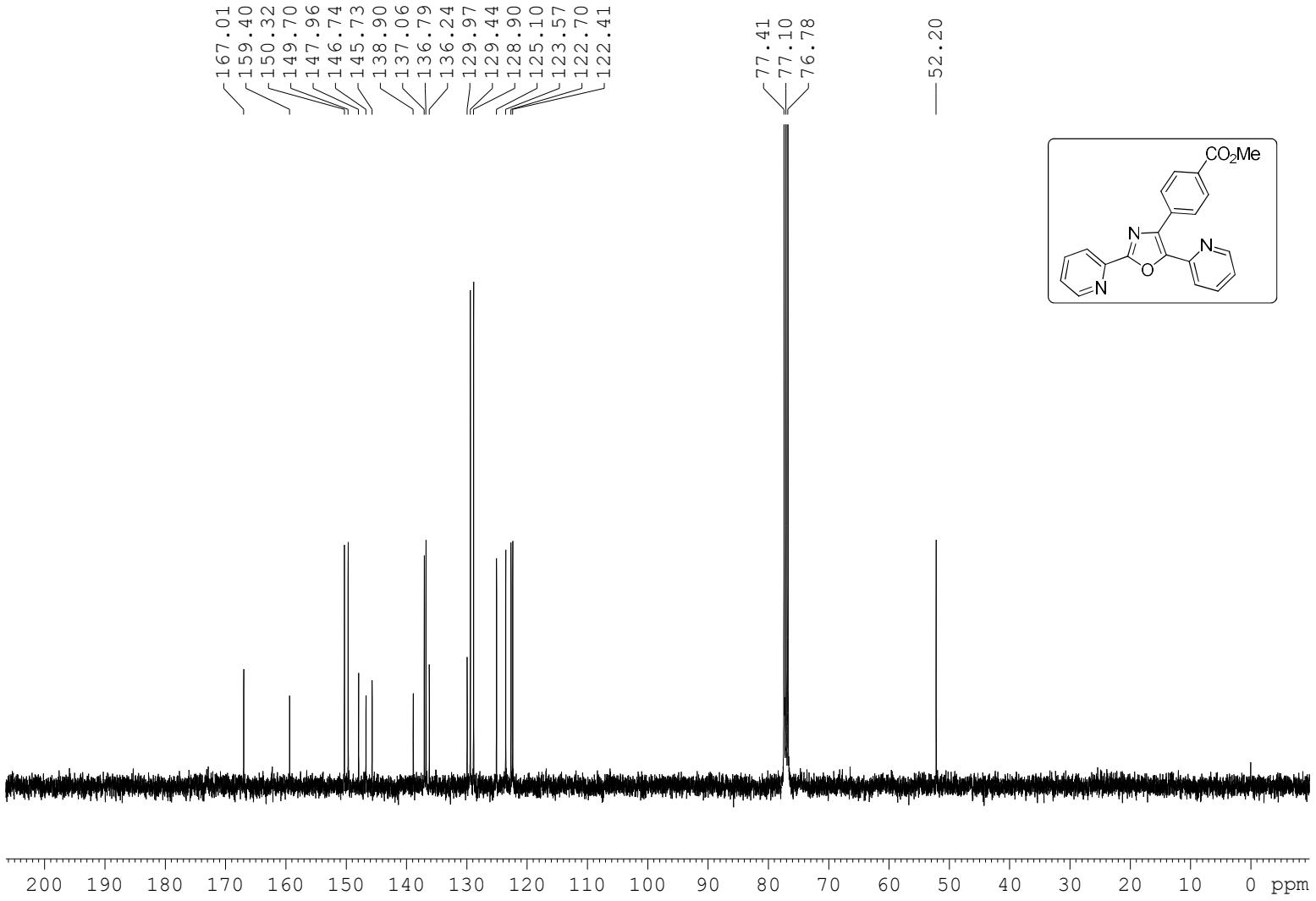
^{13}C NMR Spectrum of 3am



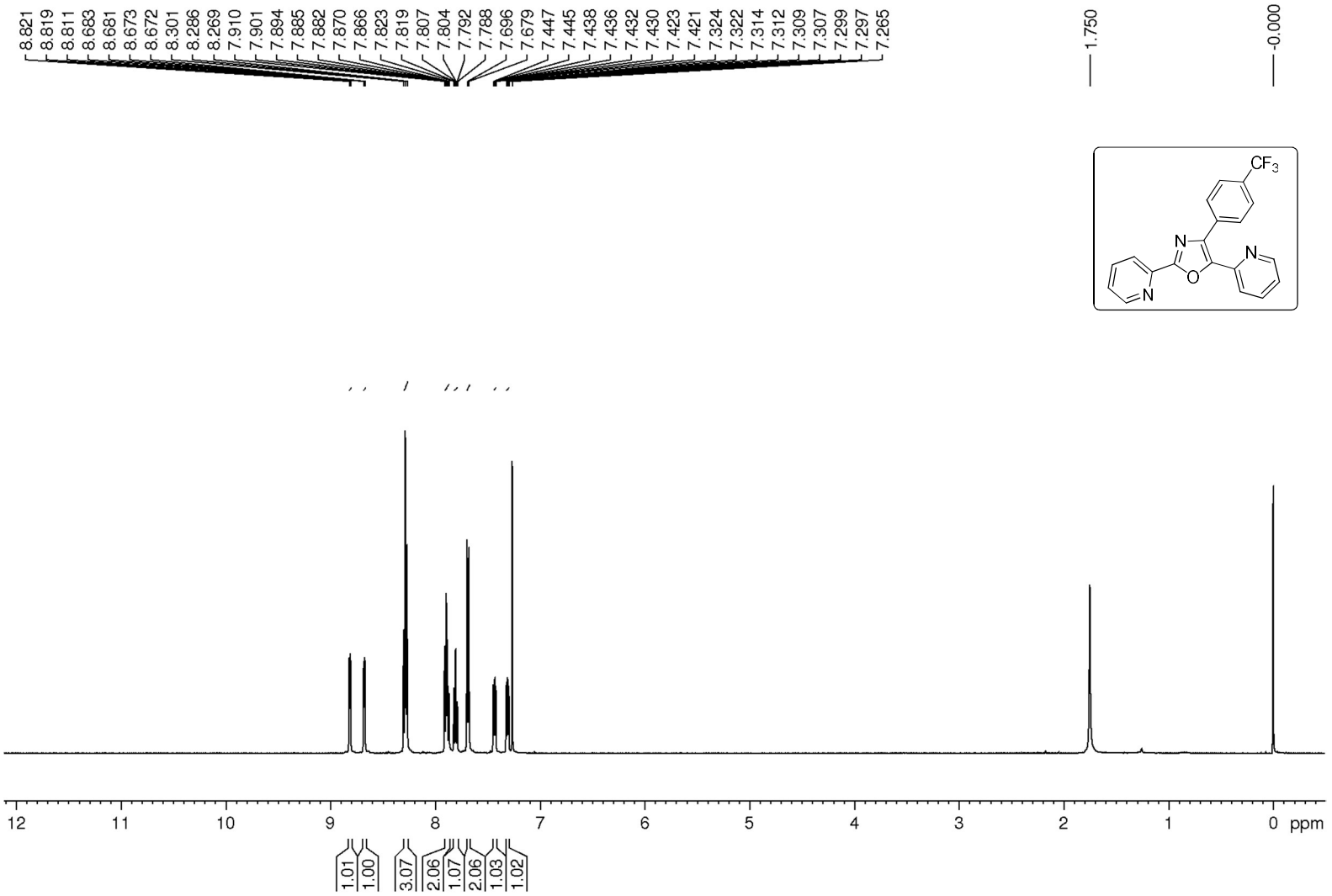
[1]H NMR Spectrum of 3an



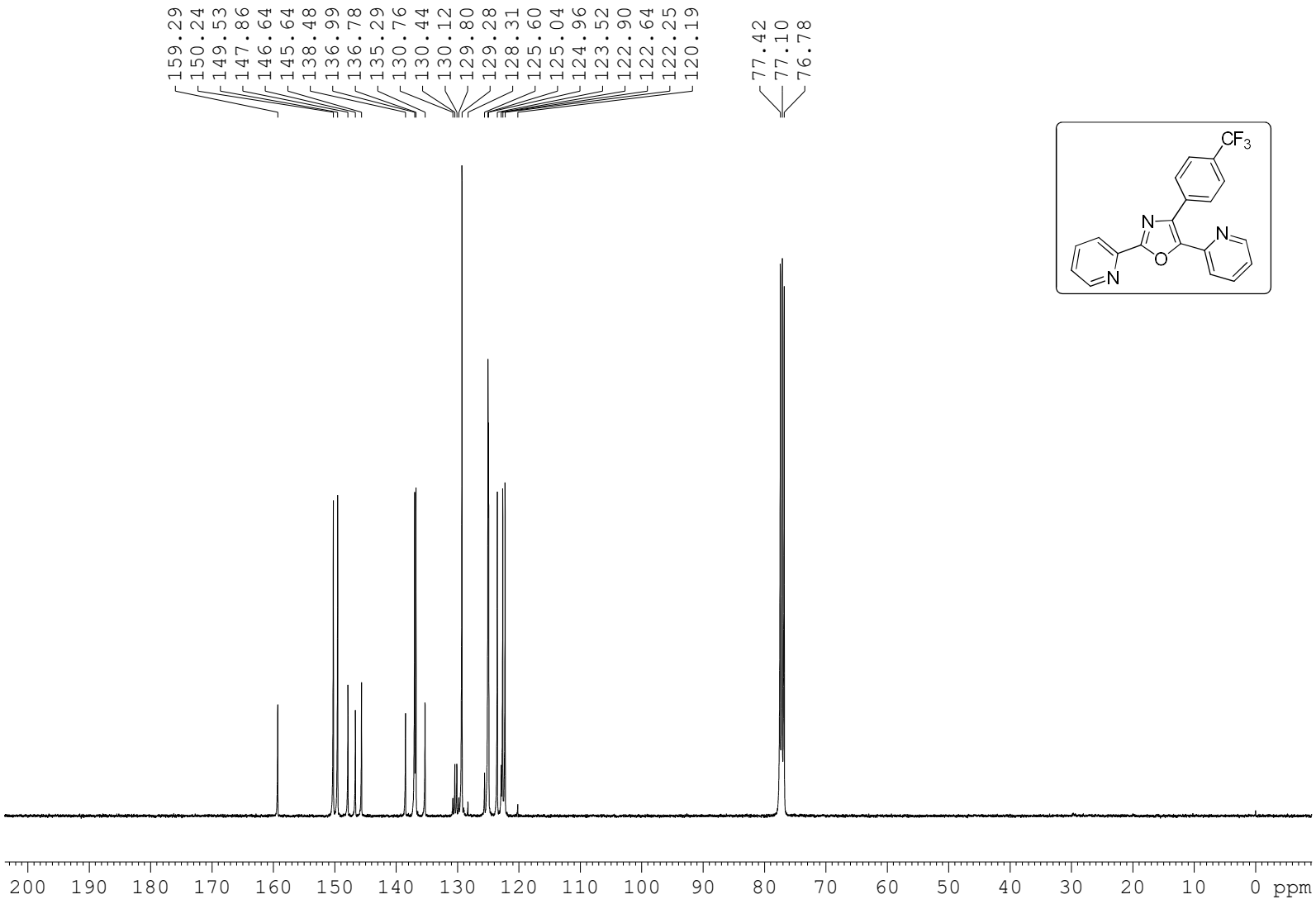
^{13}C NMR Spectrum of 3an



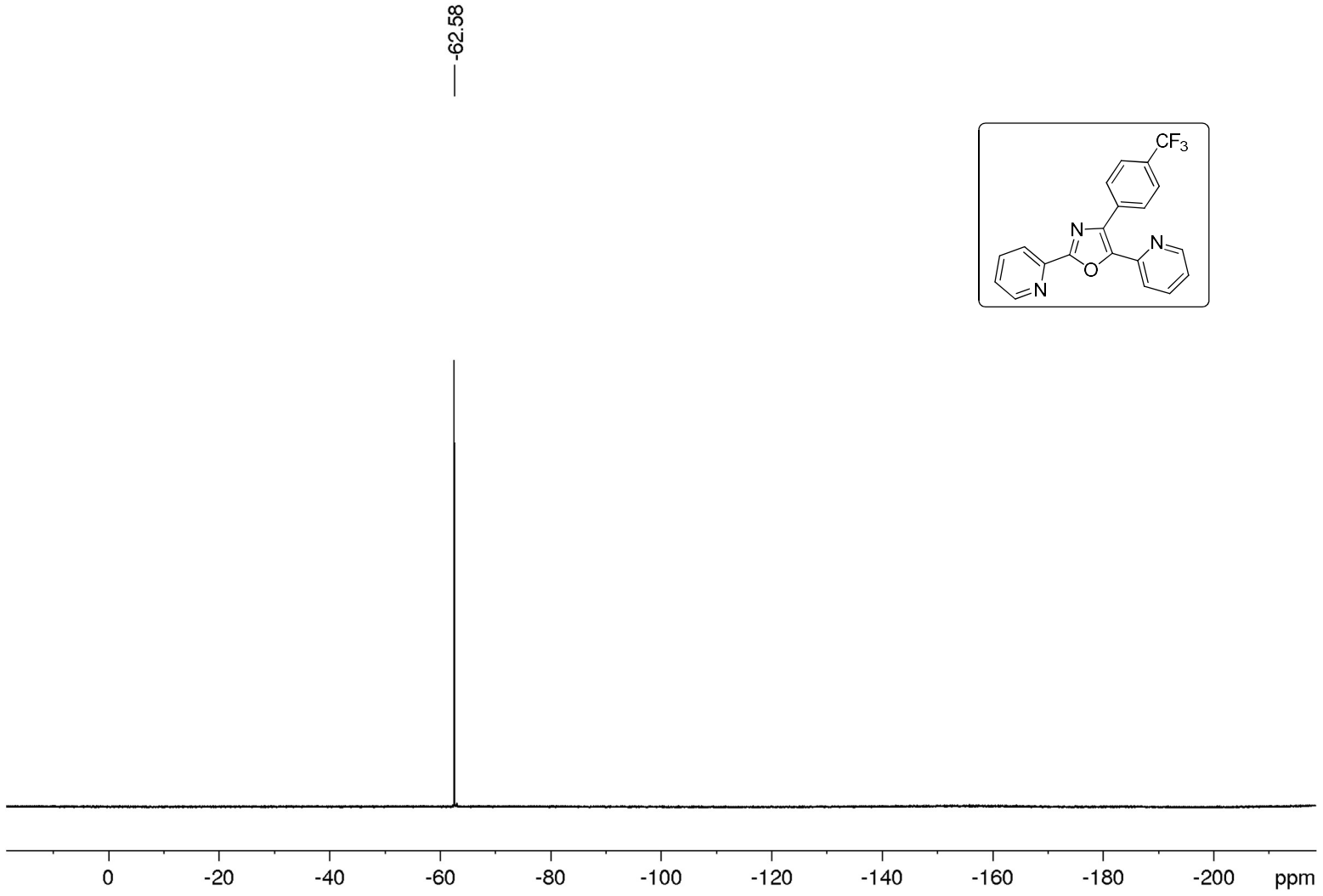
[1]H NMR Spectrum of 3ao



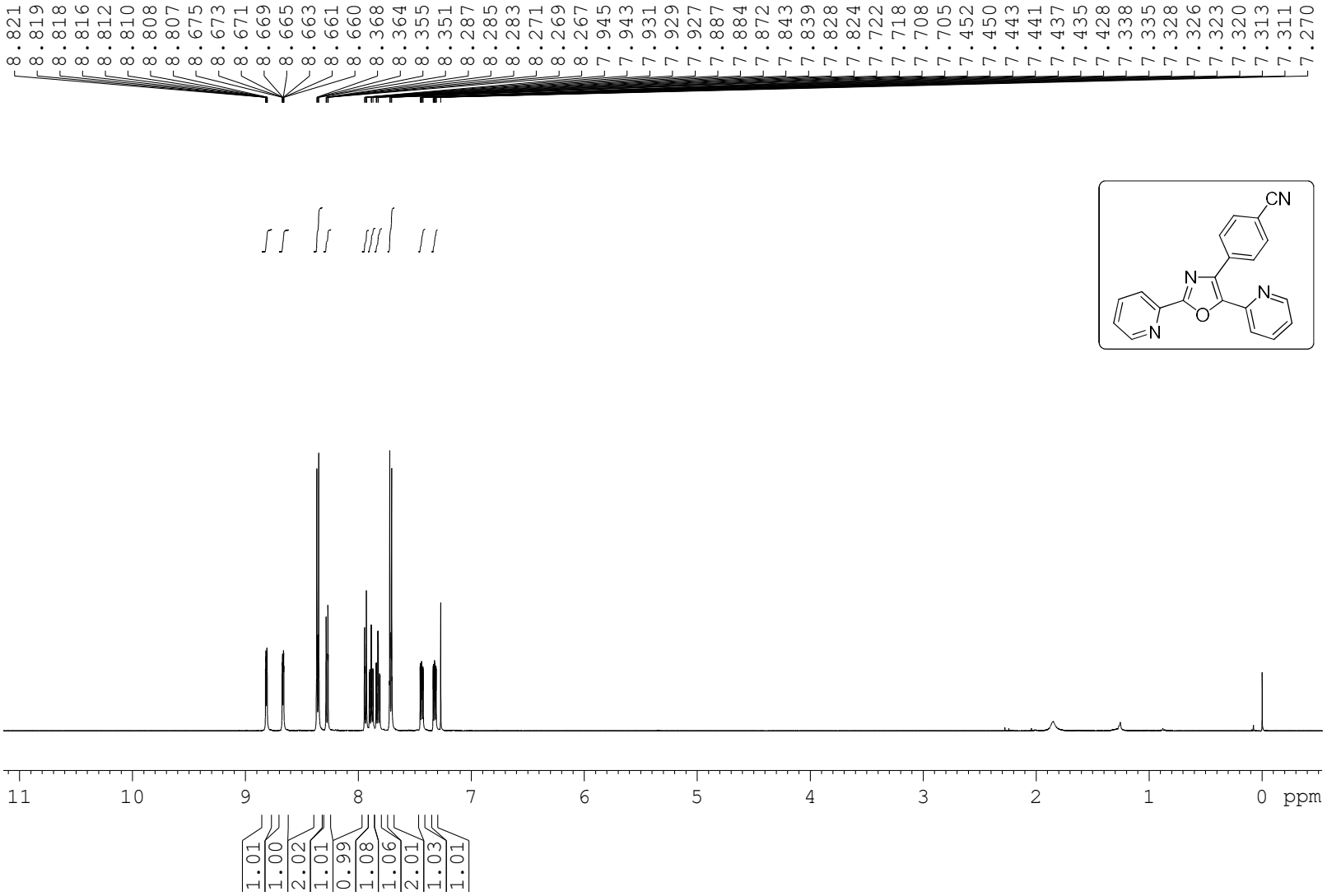
^{13}C NMR Spectrum of 3ao



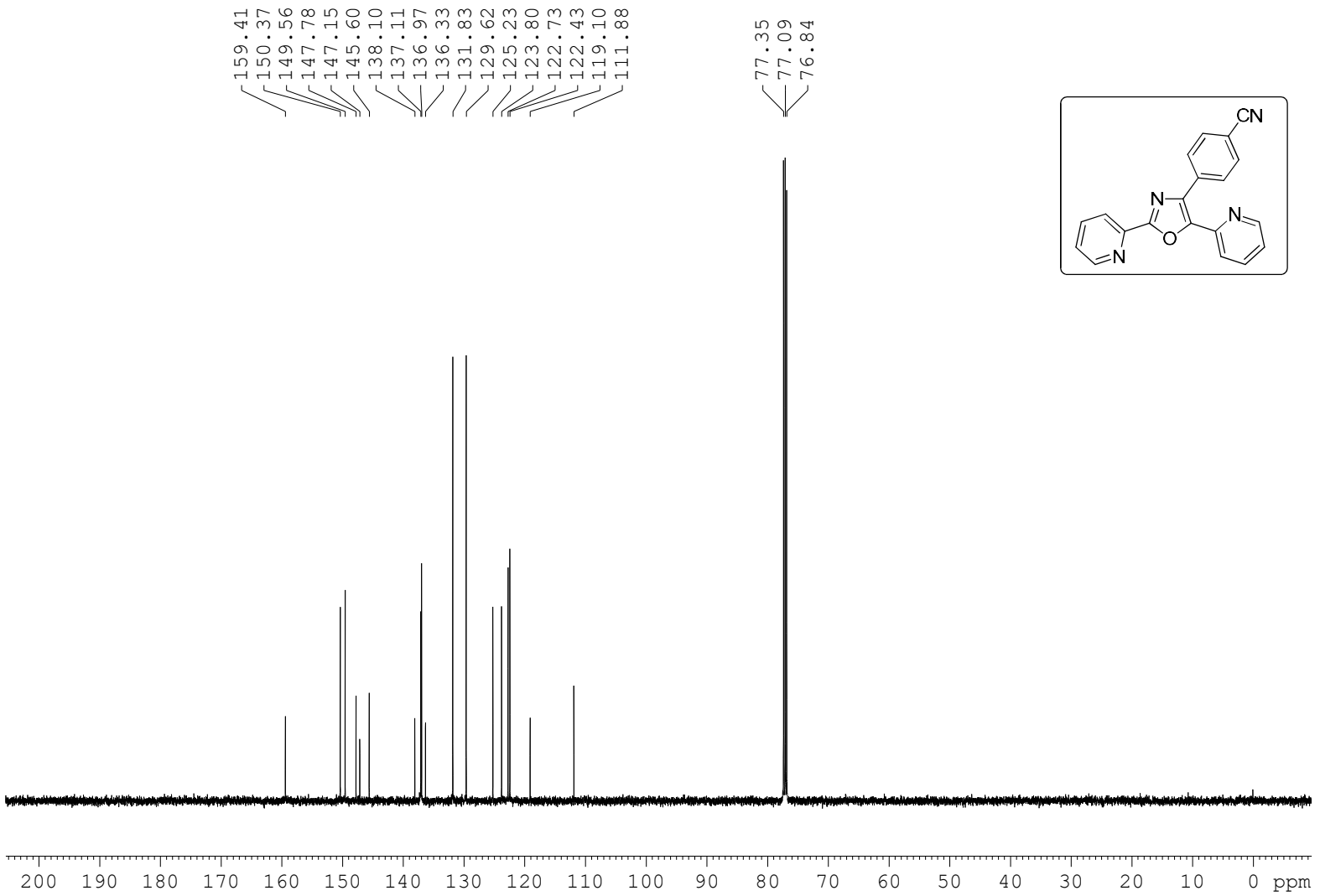
^{19}F NMR Spectrum of 3ao



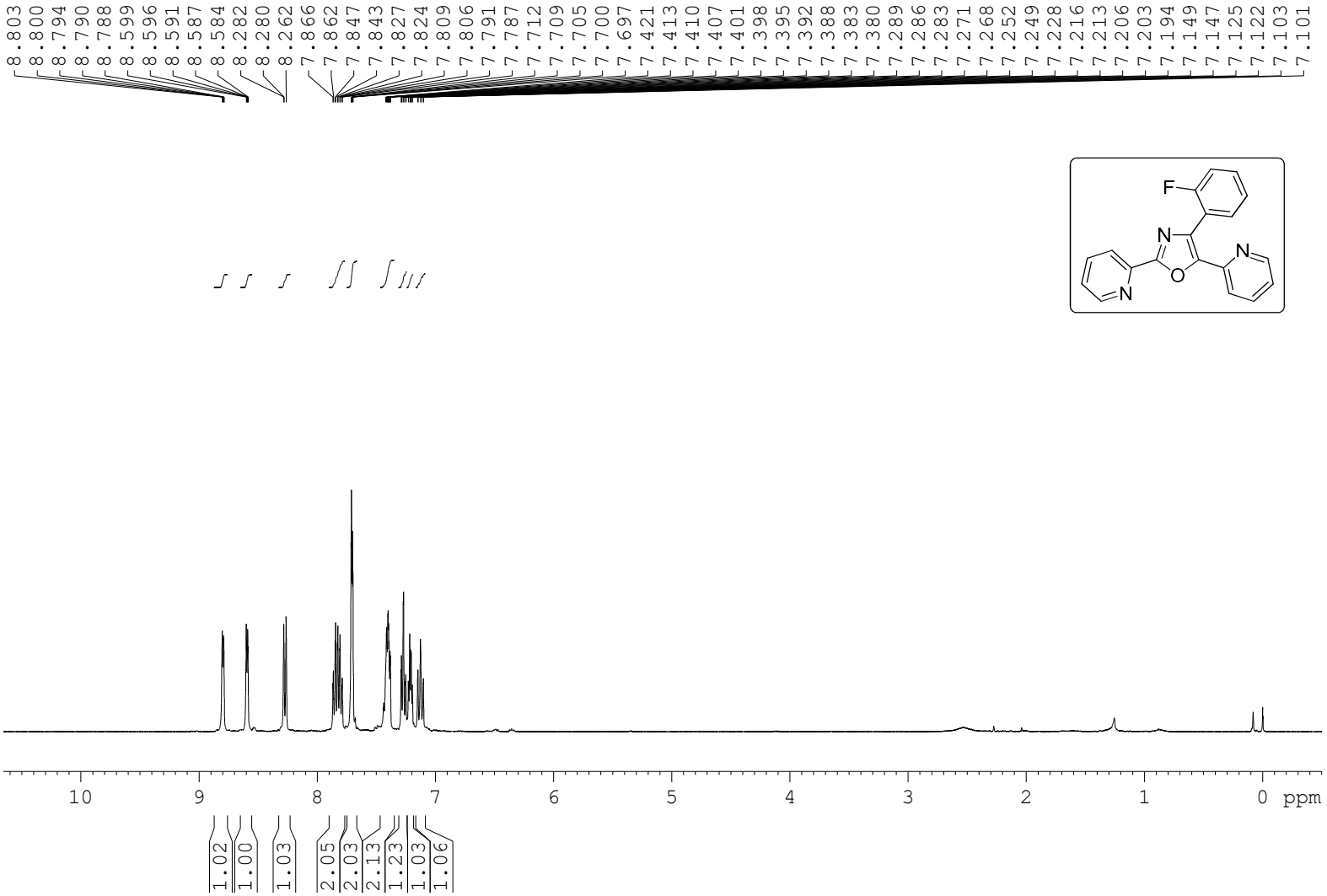
^{1}H NMR Spectrum of 3ap



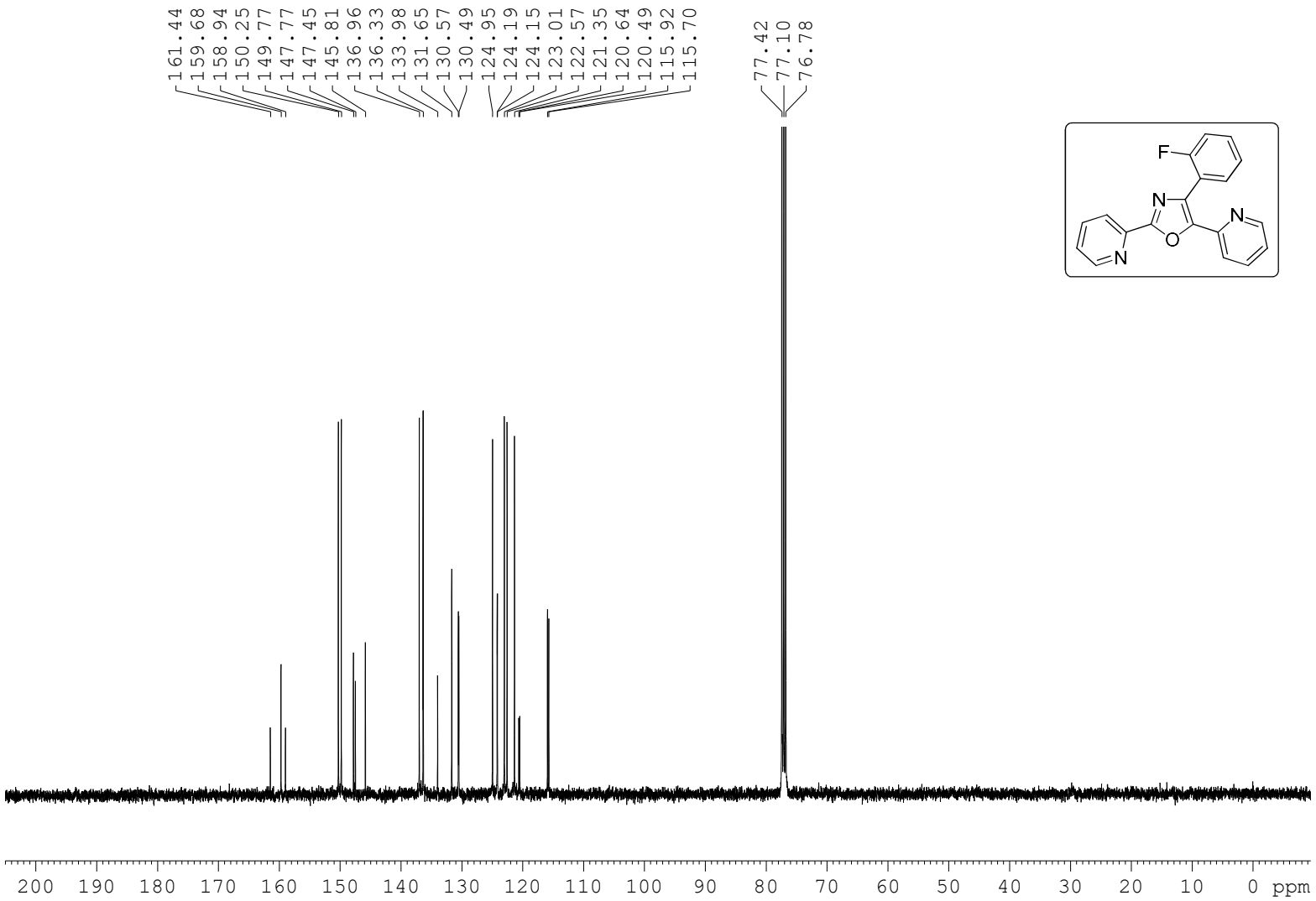
^{13}C NMR Spectrum of 3ap



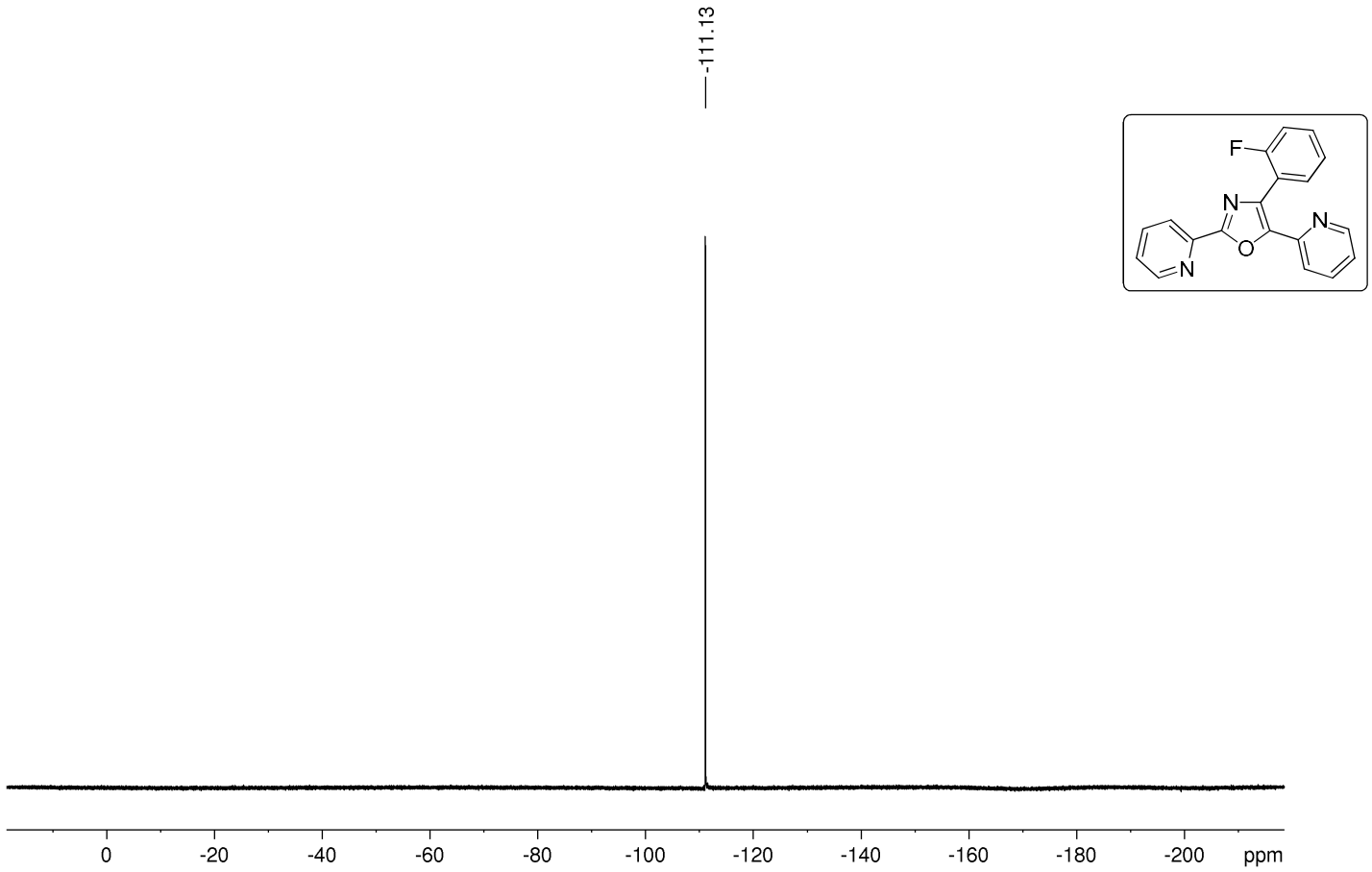
[1]H NMR Spectrum of 3aq



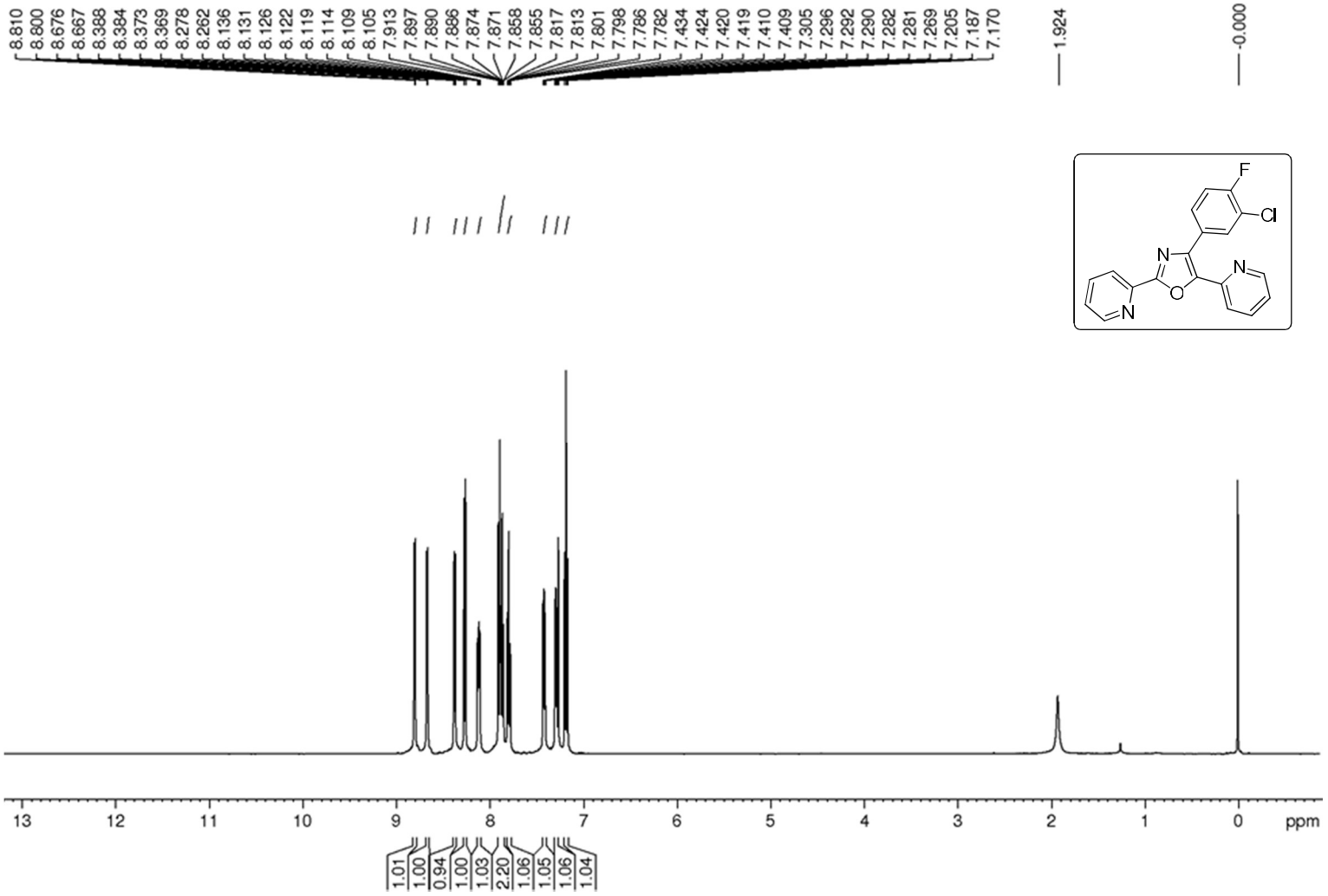
^{13}C NMR Spectrum of 3aq



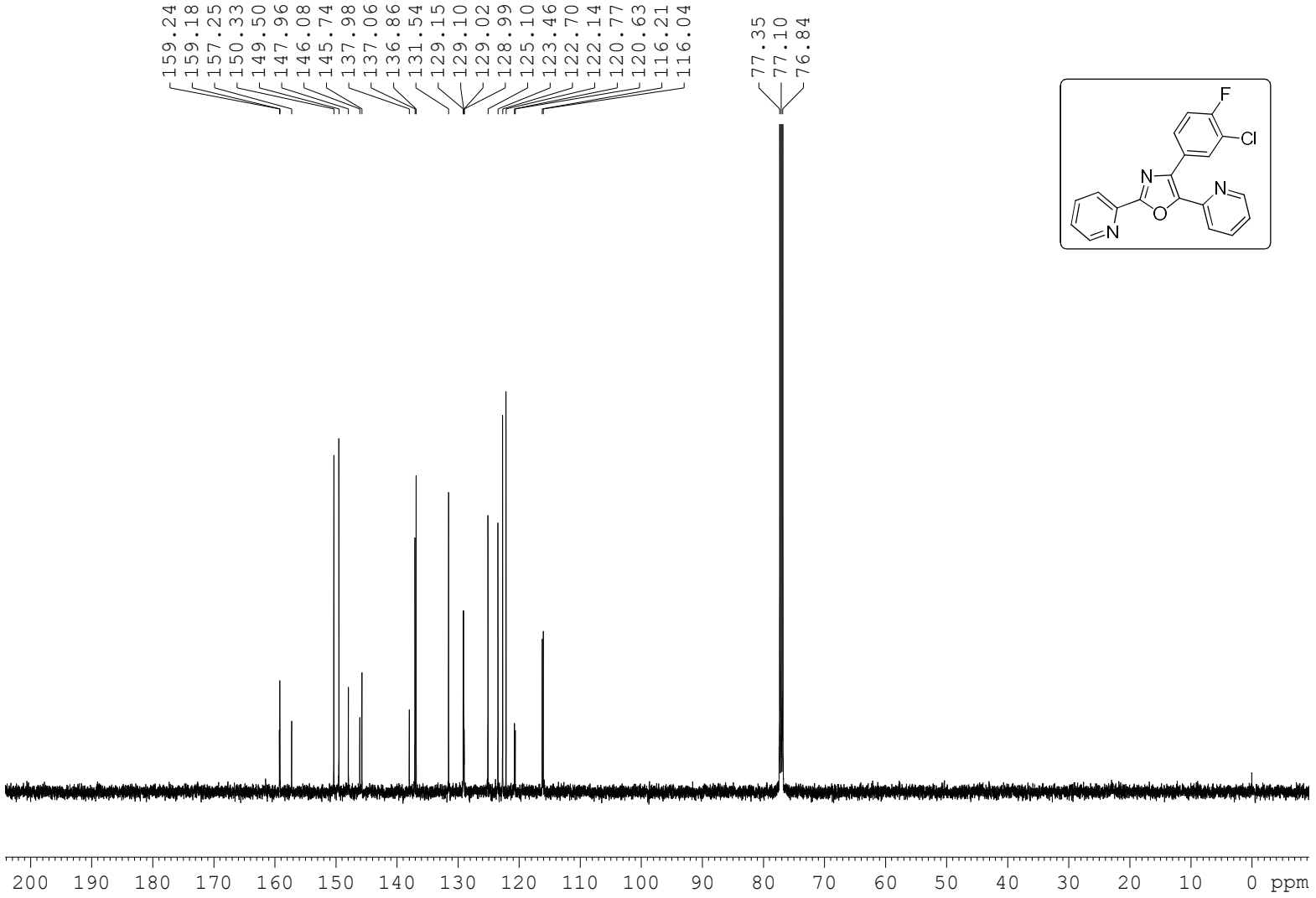
^{19}F NMR Spectrum of 3aq



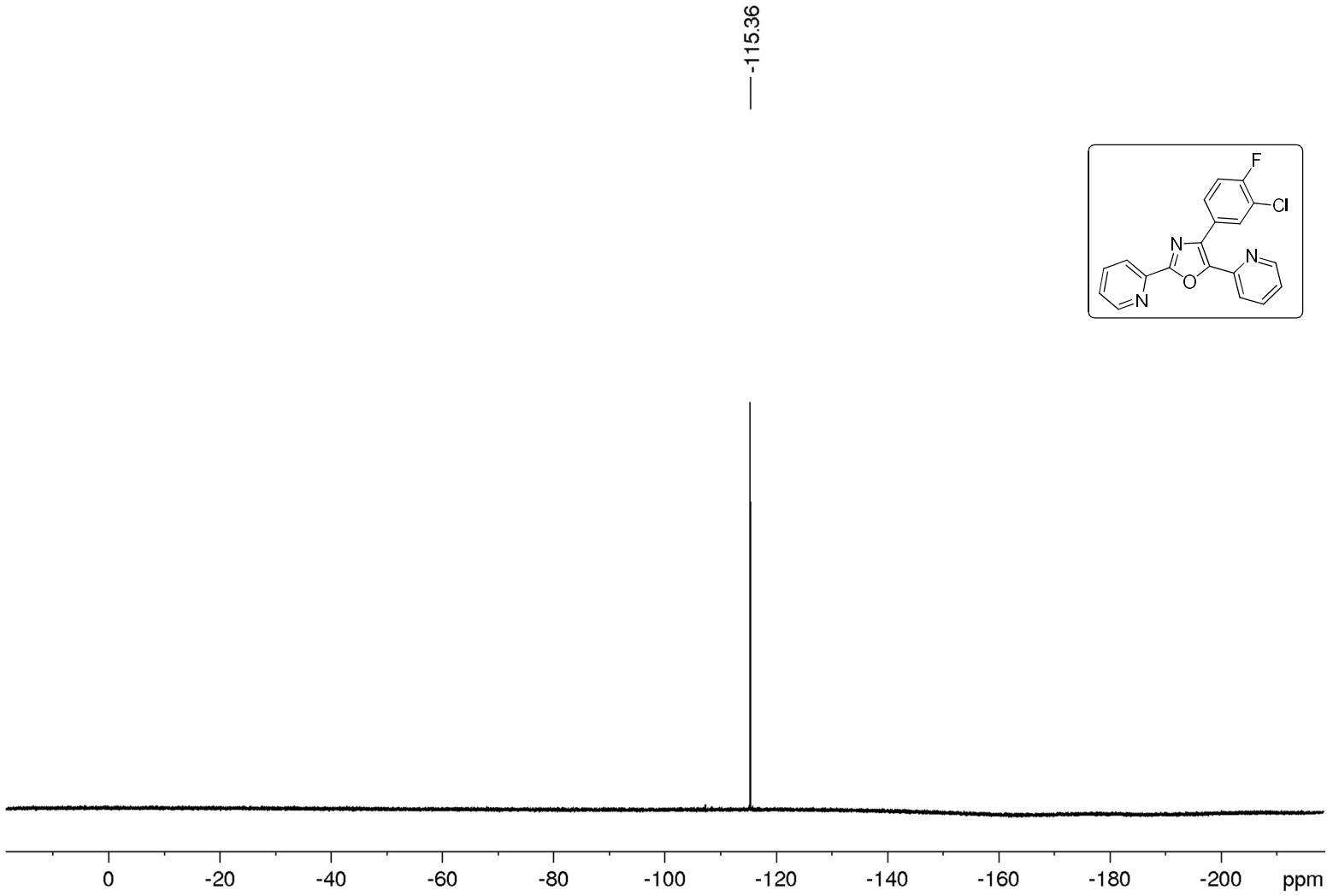
^{1}H NMR Spectrum of 3ar



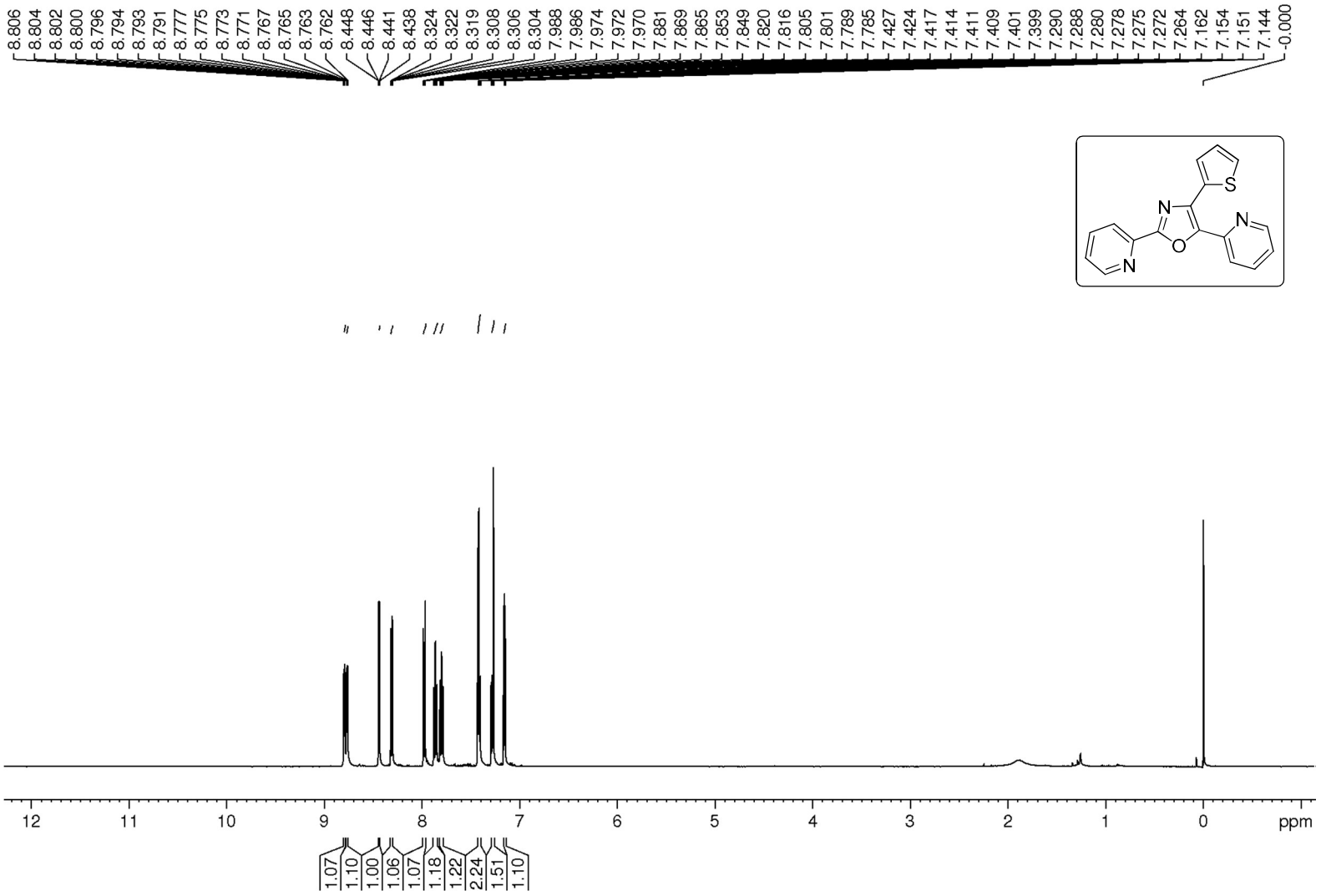
^{13}C NMR Spectrum of 3ar



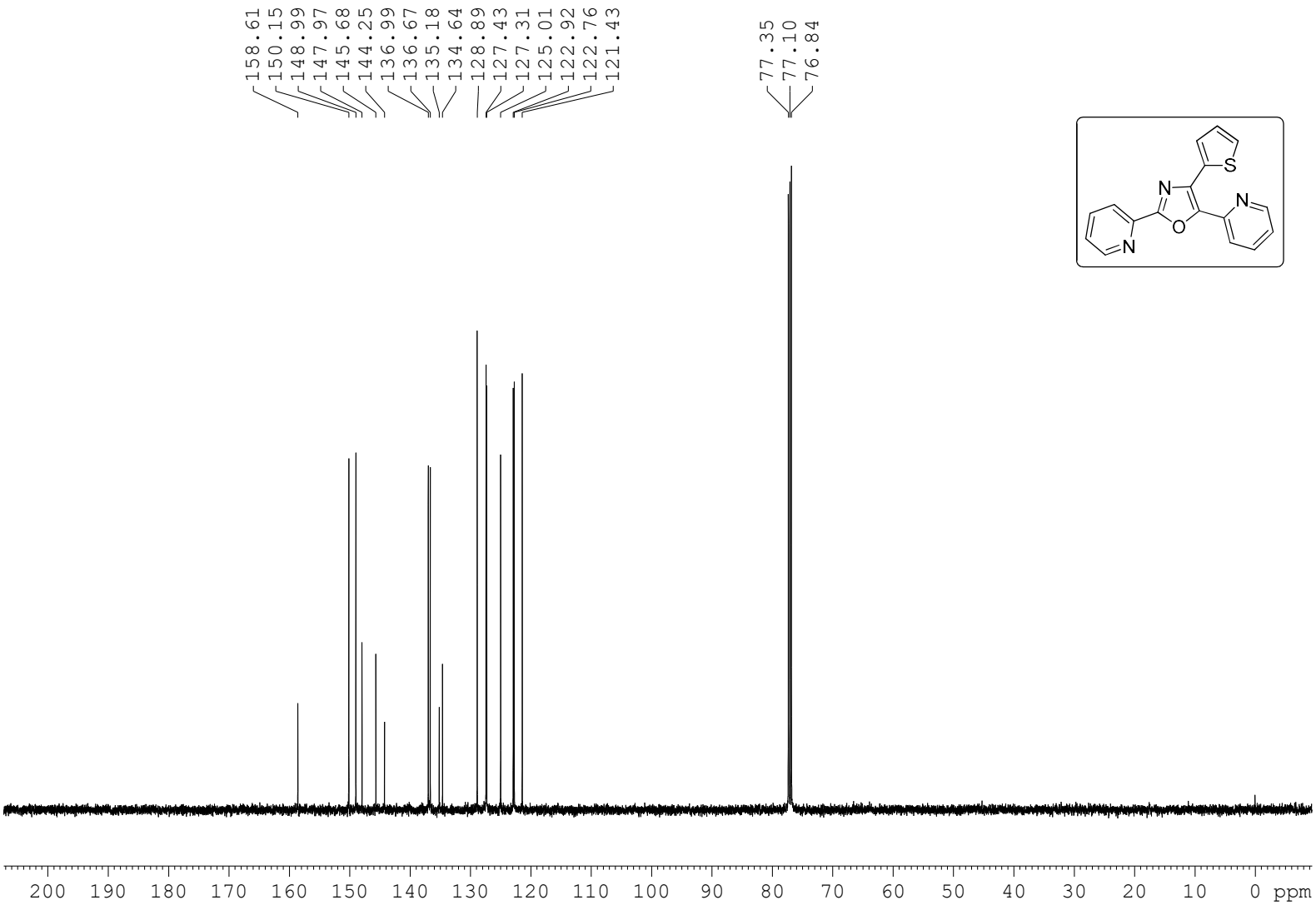
^{19}F NMR Spectrum of 3ar



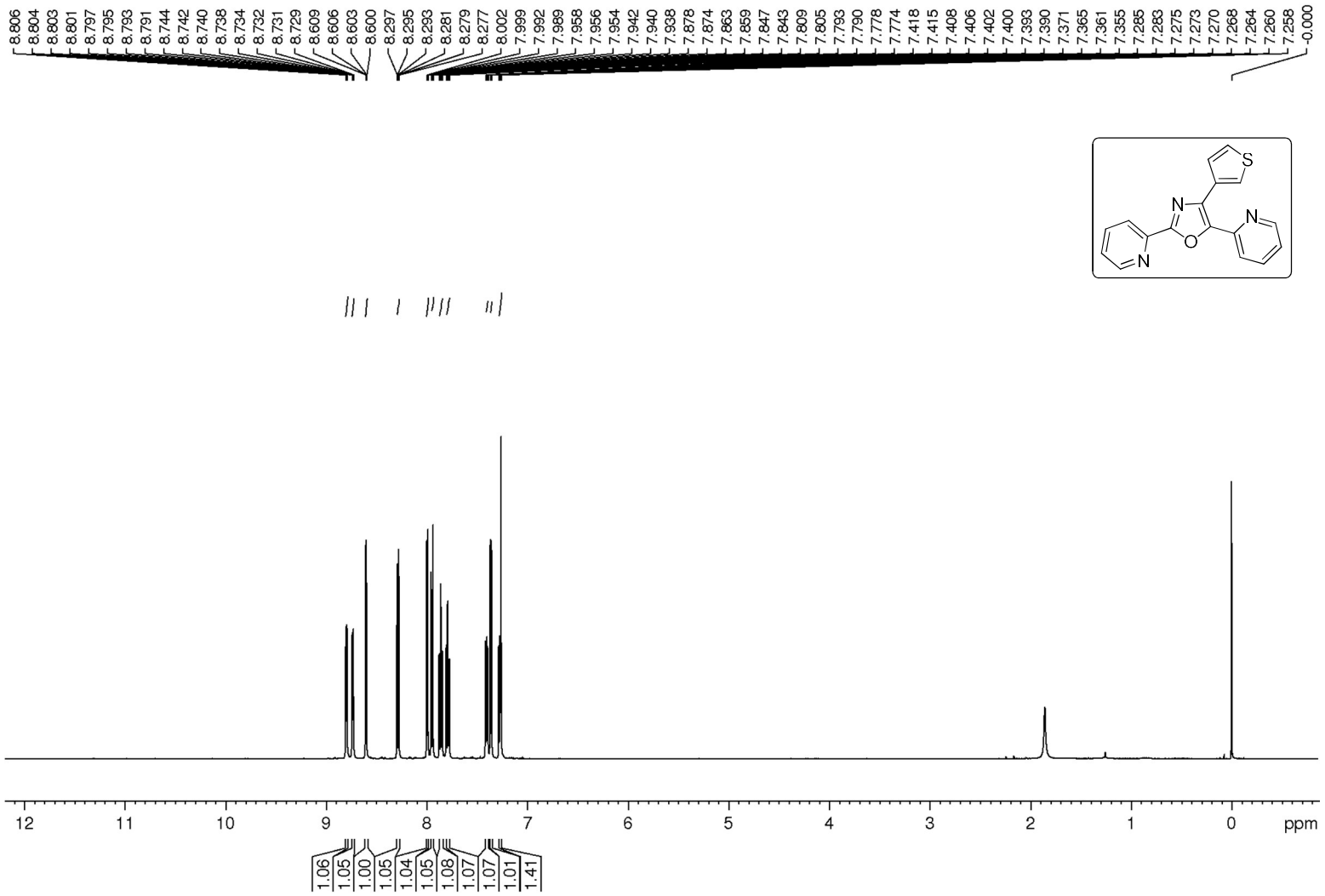
^{1}H NMR Spectrum of 3as



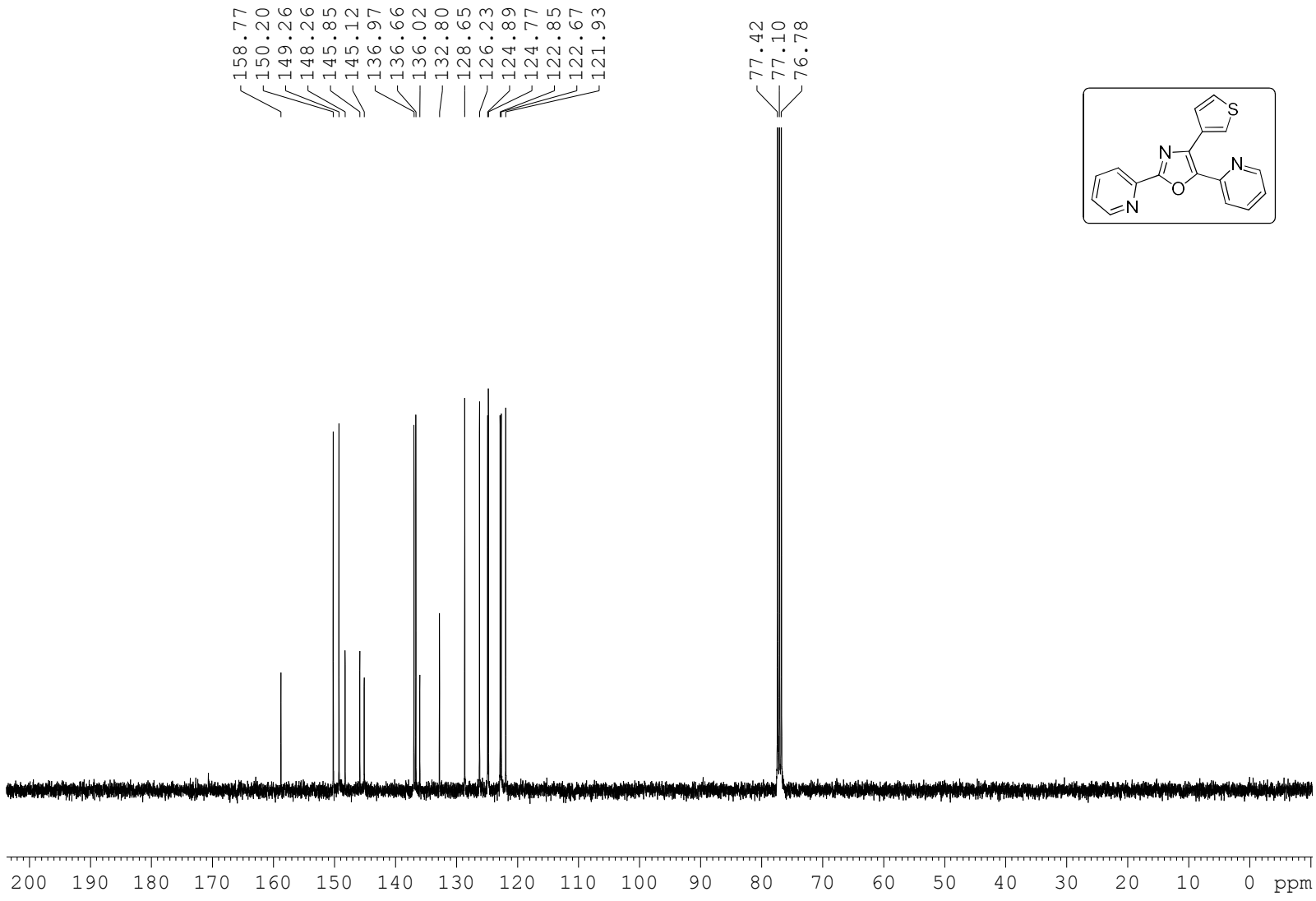
^{13}C NMR Spectrum of 3as



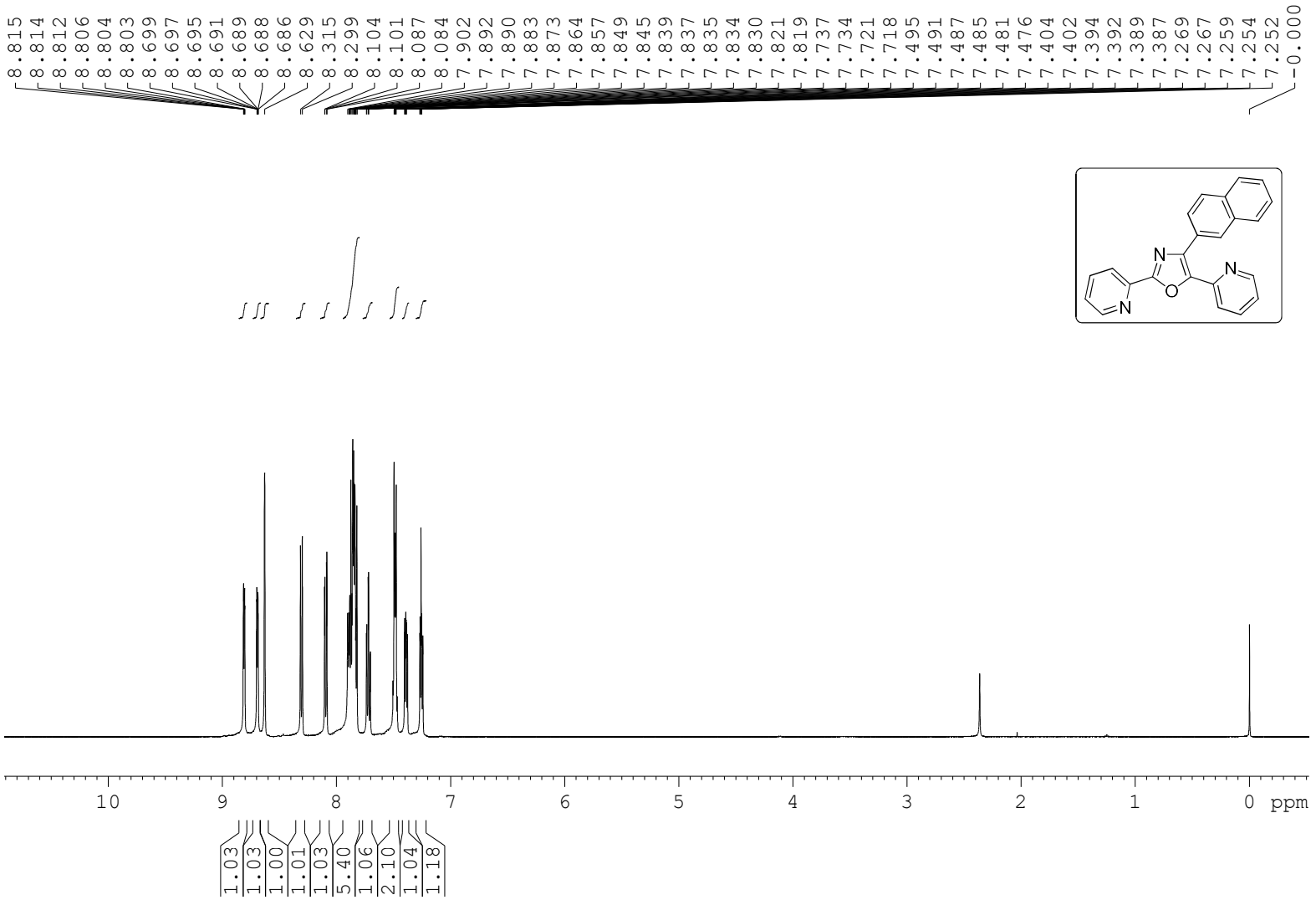
^{1}H NMR Spectrum of 3at



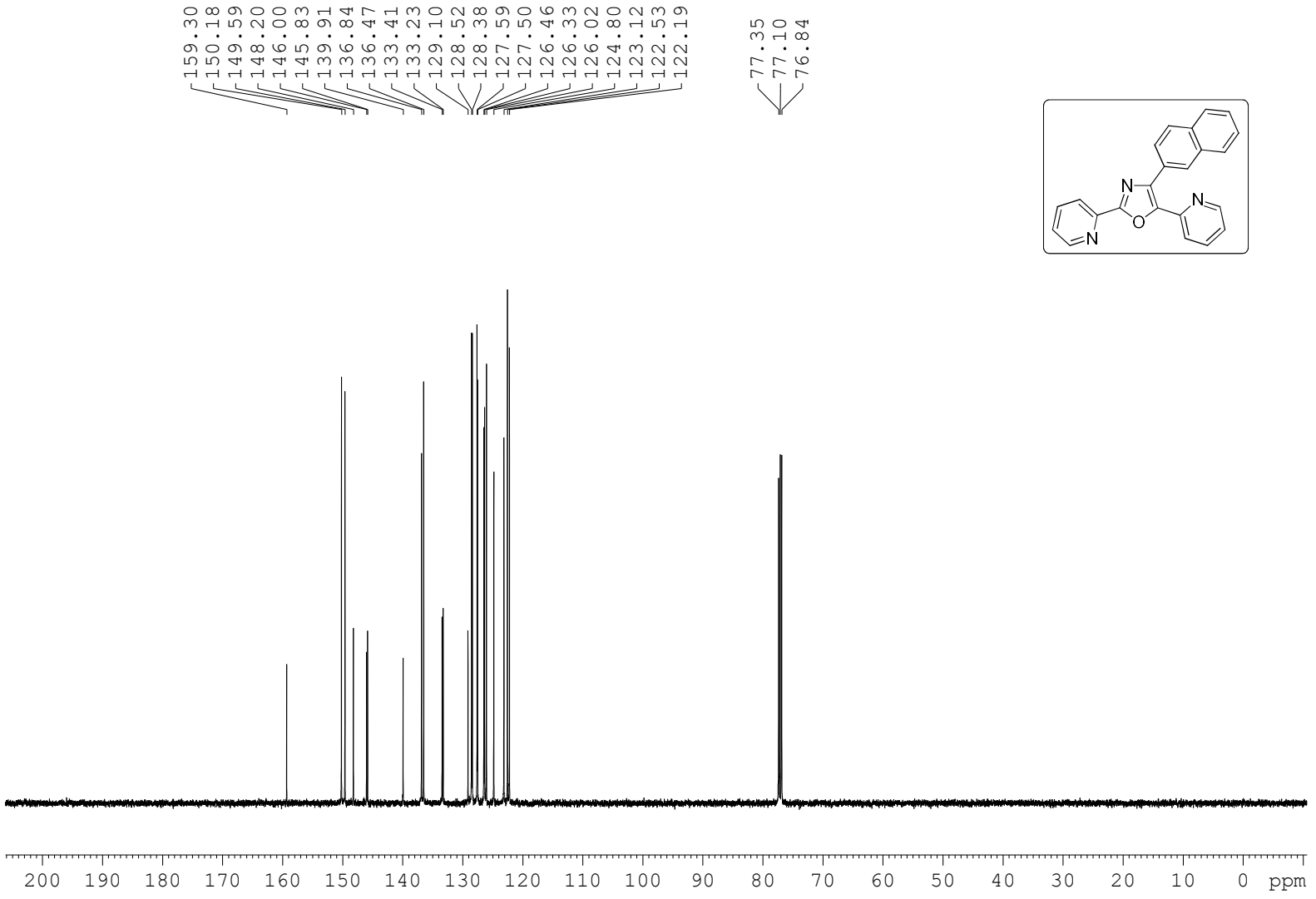
^{13}C NMR Spectrum of 3at



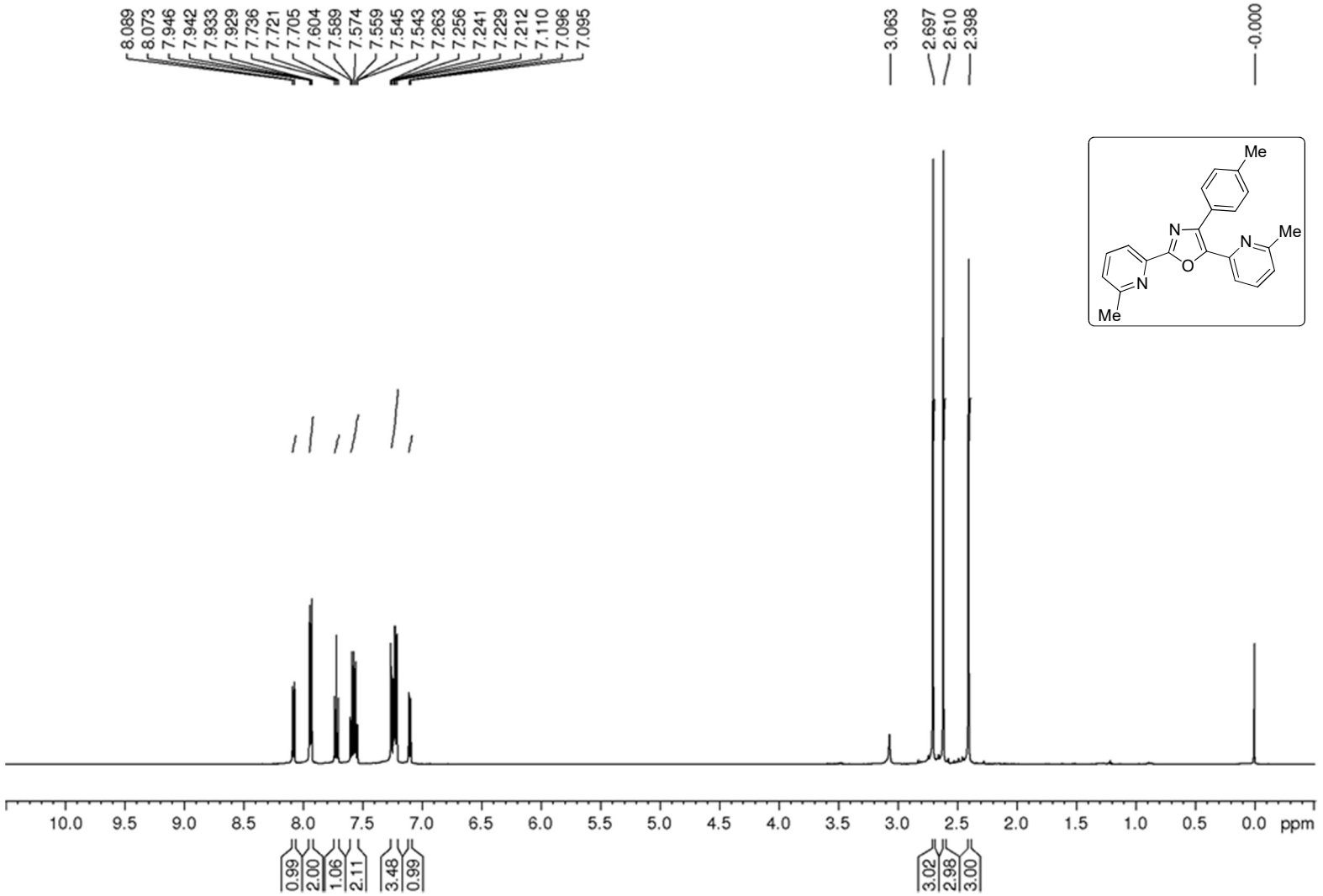
^{1}H NMR Spectrum of 3au



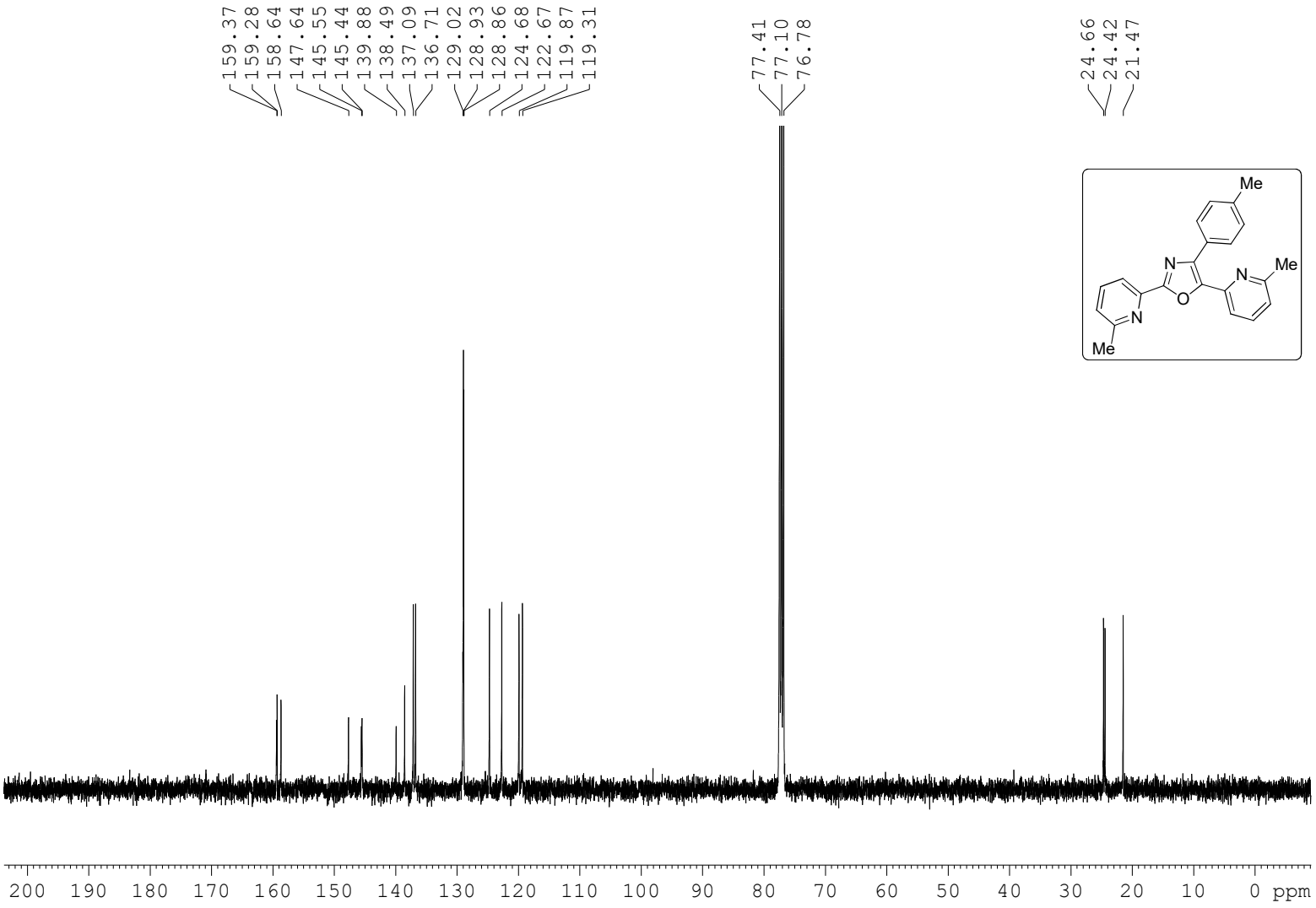
^{13}C NMR Spectrum of 3au



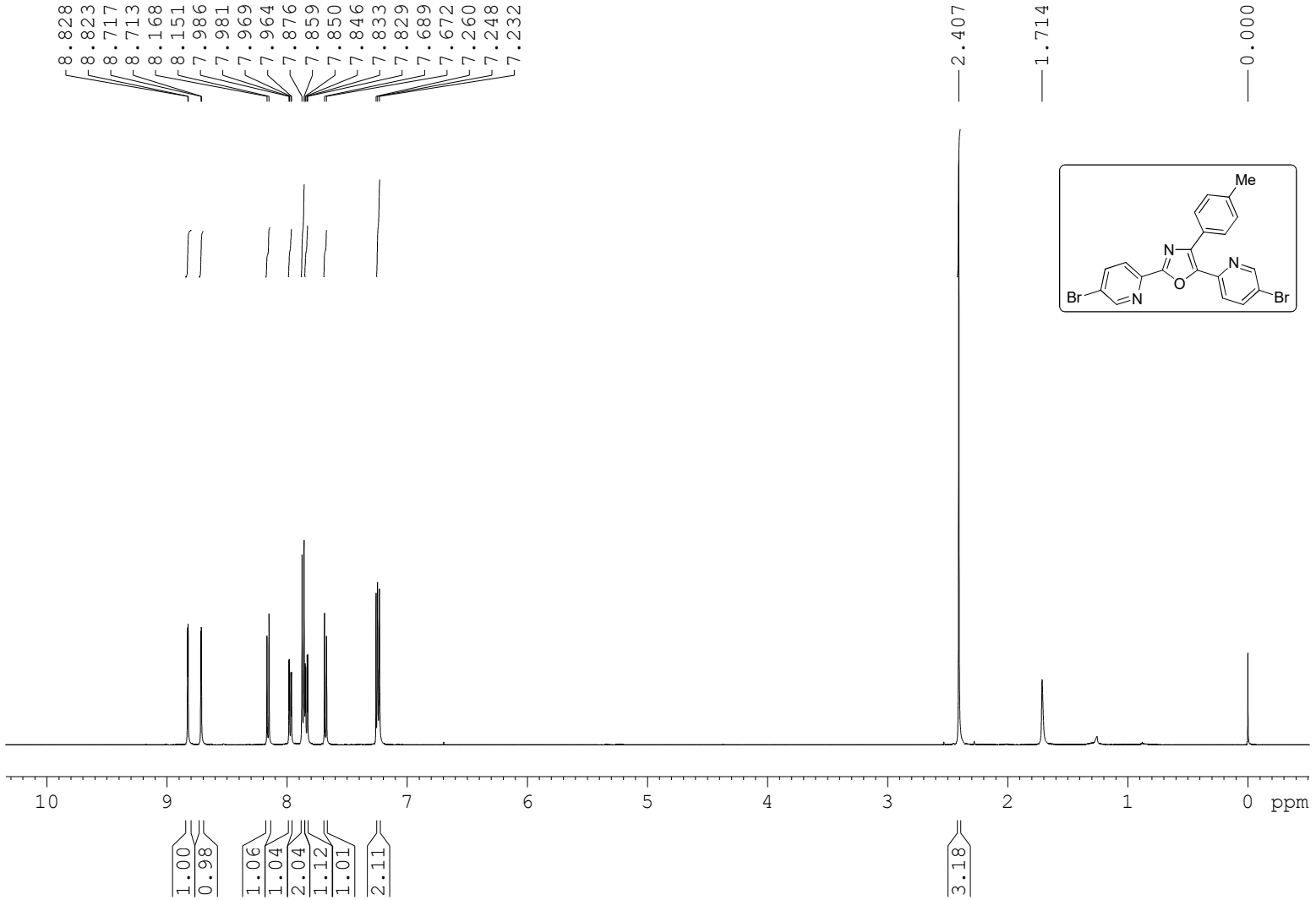
^{1}H NMR Spectrum of 3bb



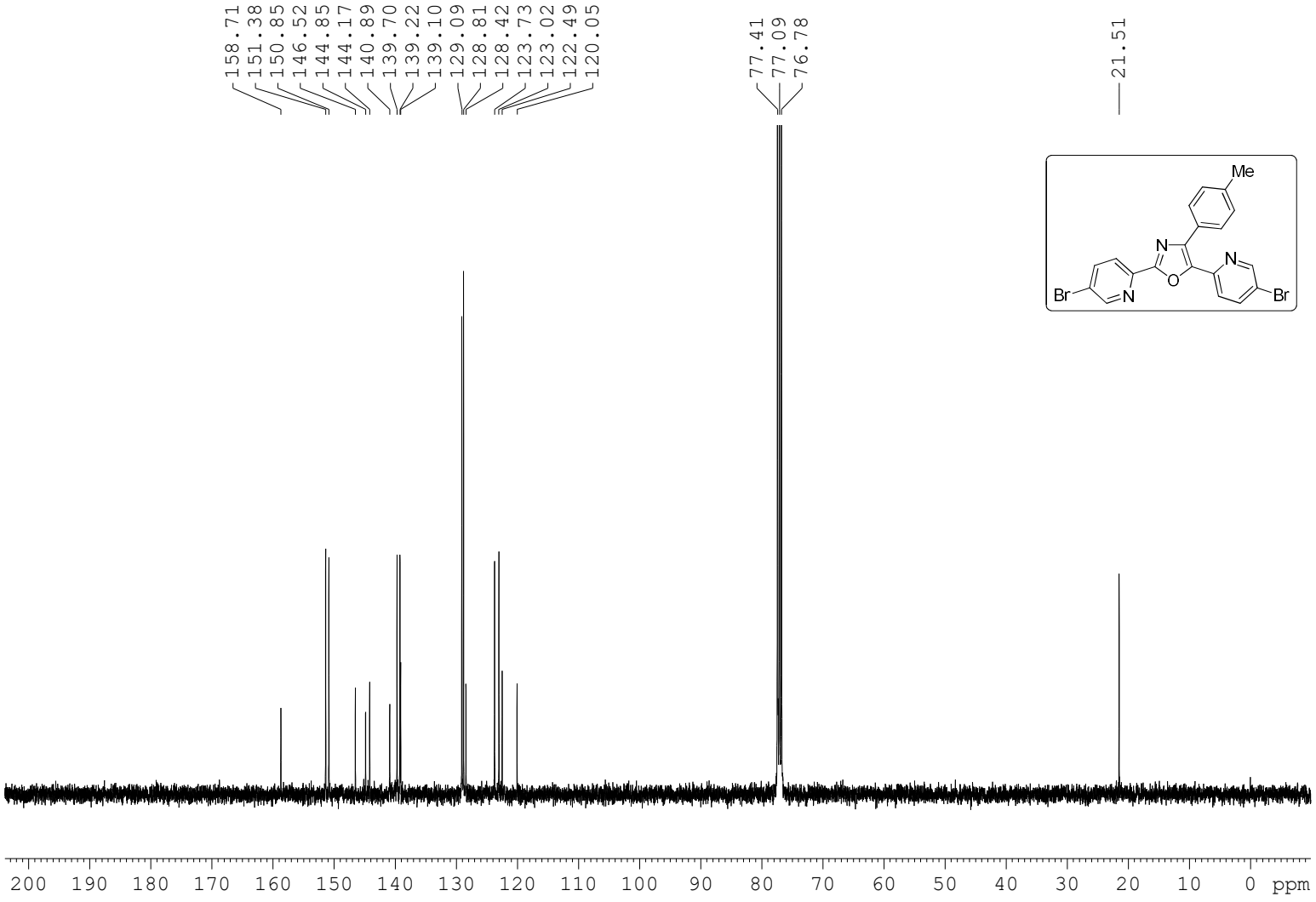
^{13}C NMR Spectrum of 3bb



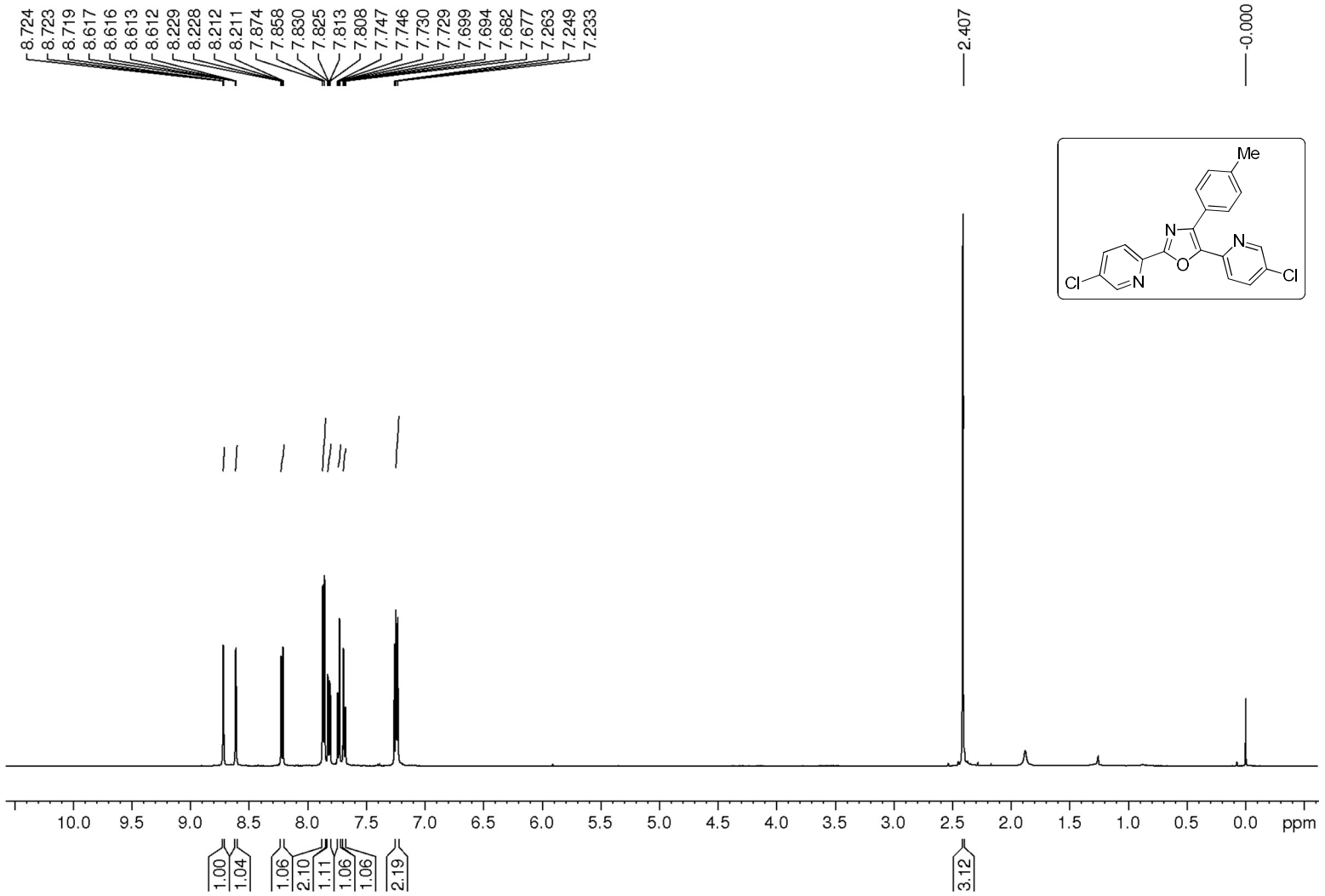
^{1}H NMR Spectrum of 3cb



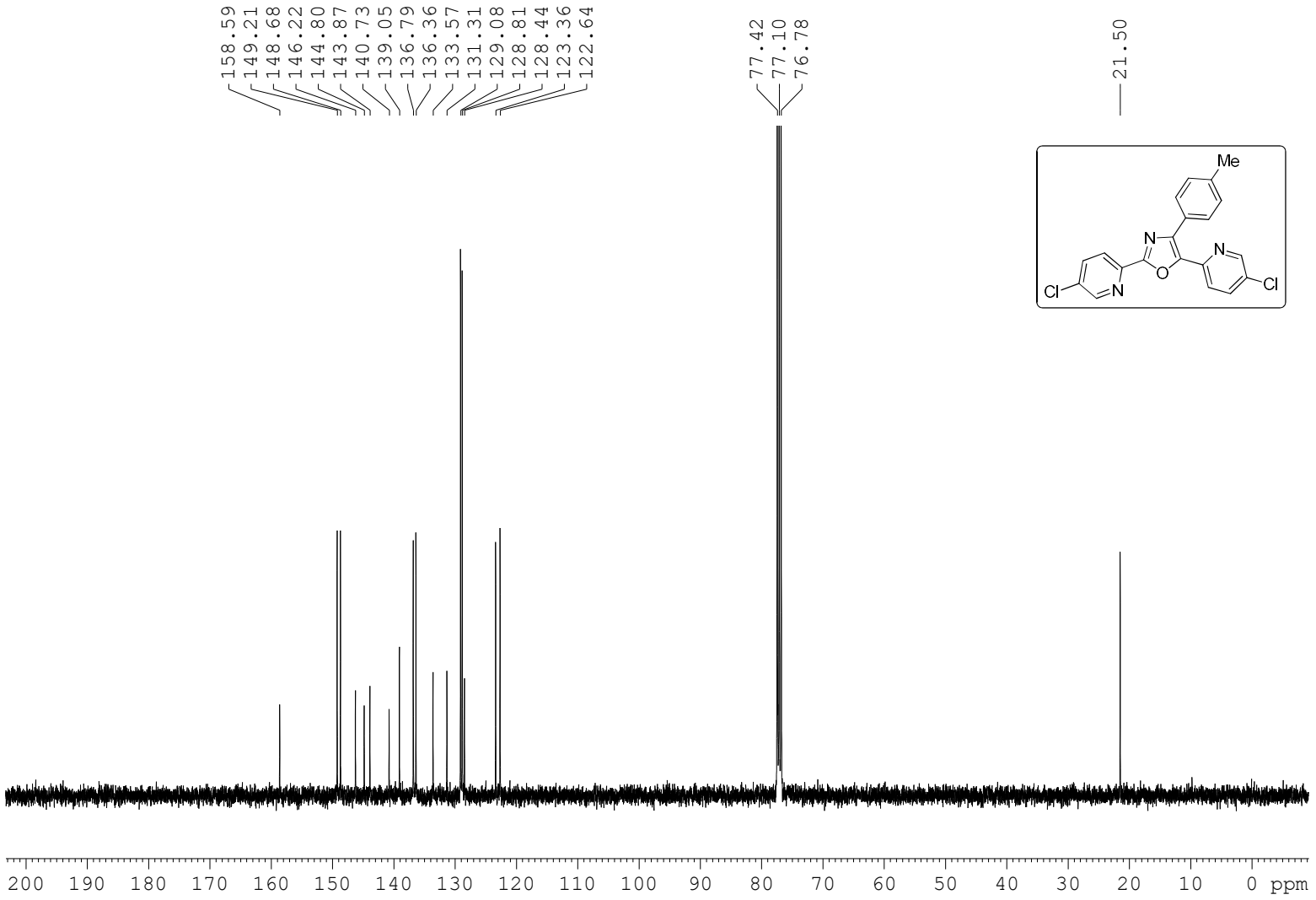
^{13}C NMR Spectrum of 3cb



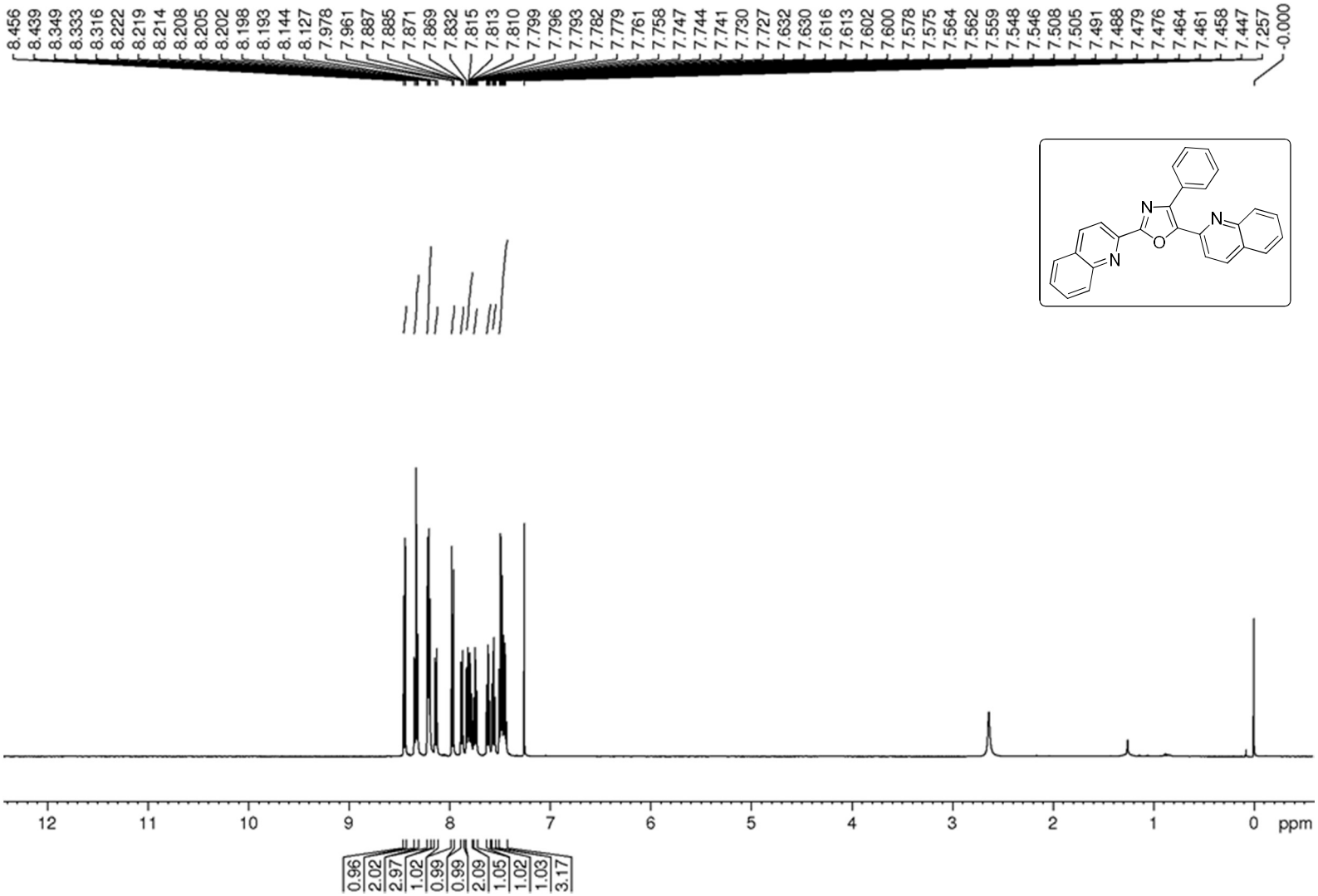
[1]H NMR Spectrum of 3db



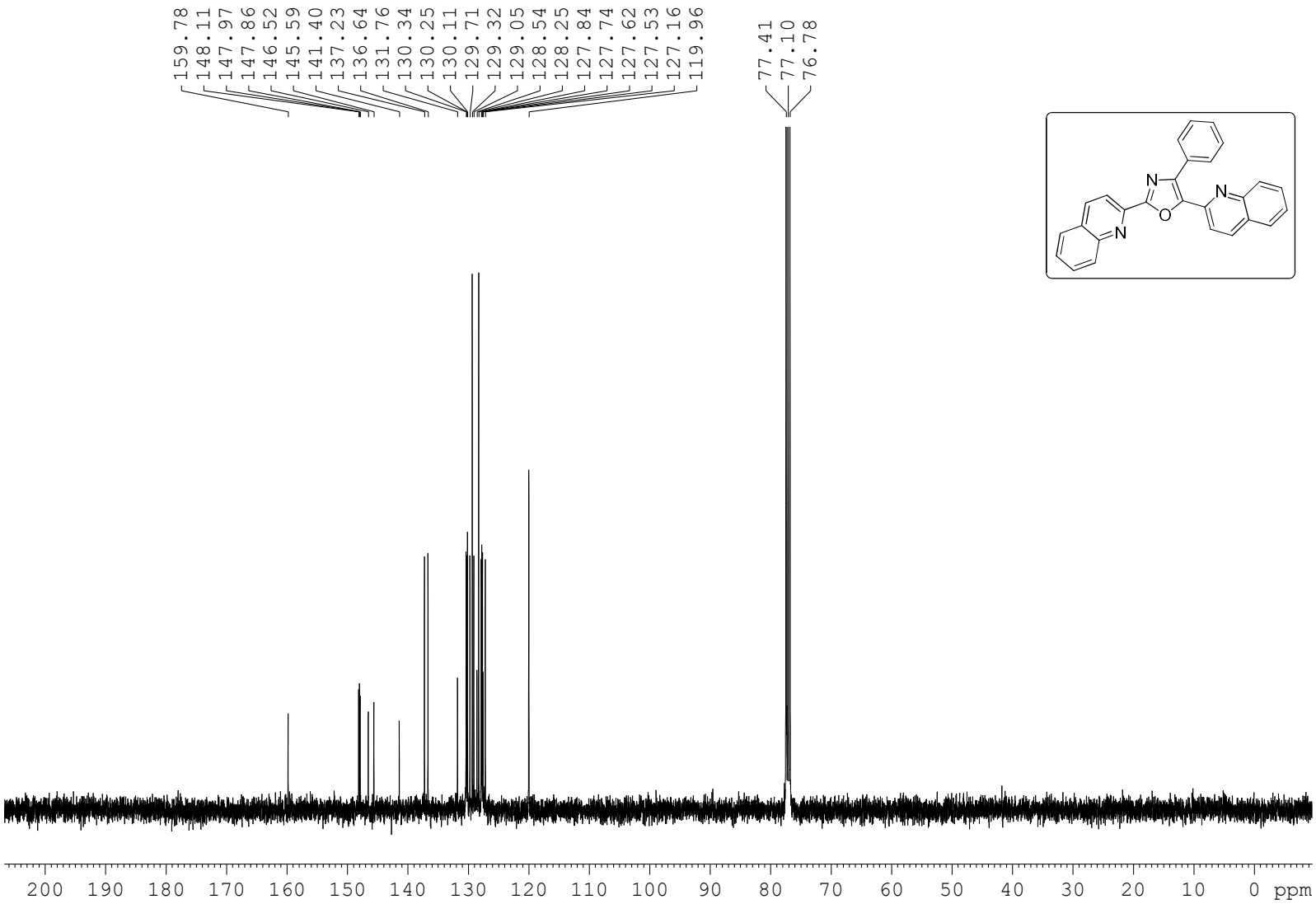
^{13}C NMR Spectrum of 3db



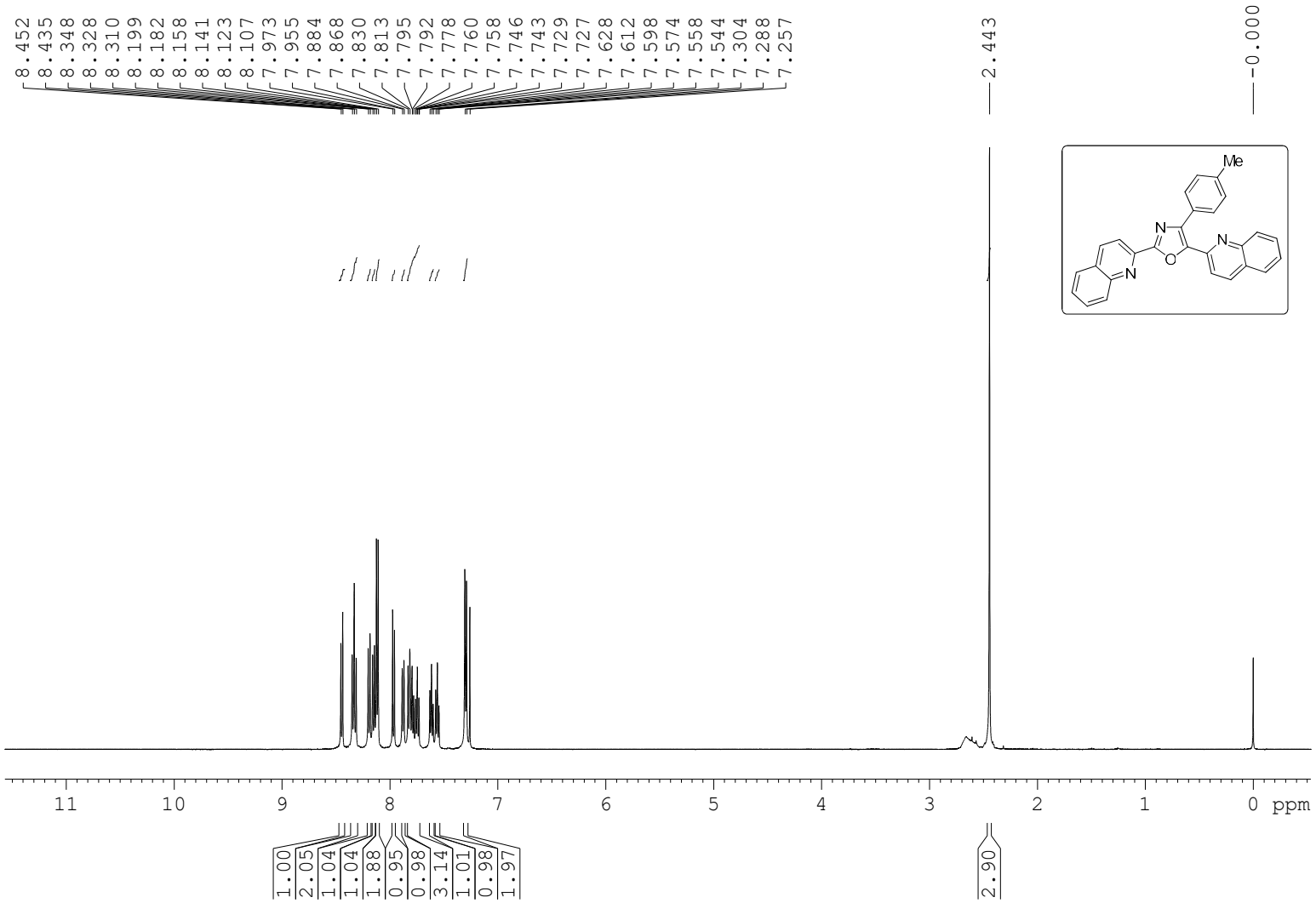
[1]H NMR Spectrum of 3ea



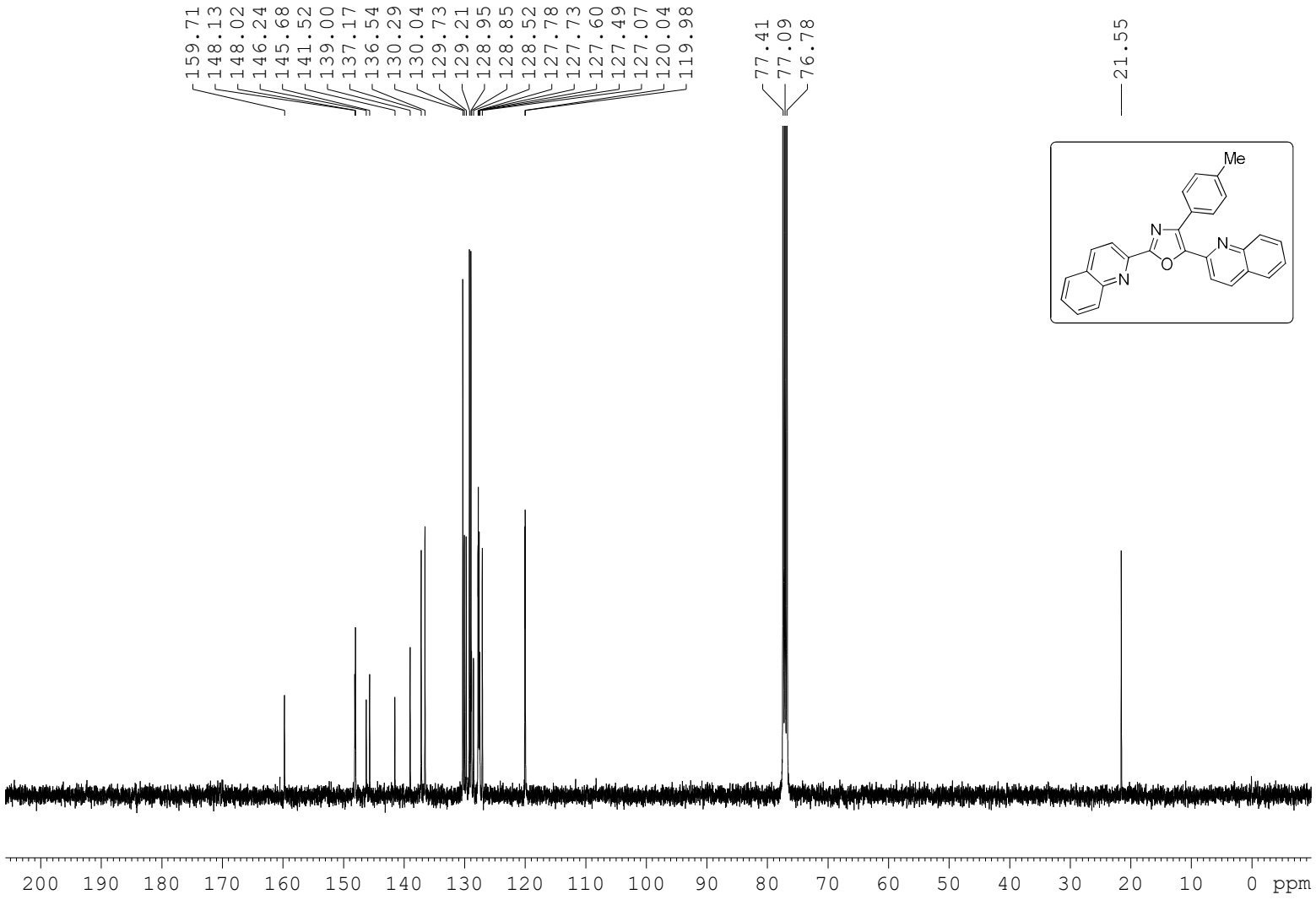
^{13}C NMR Spectrum of 3ea



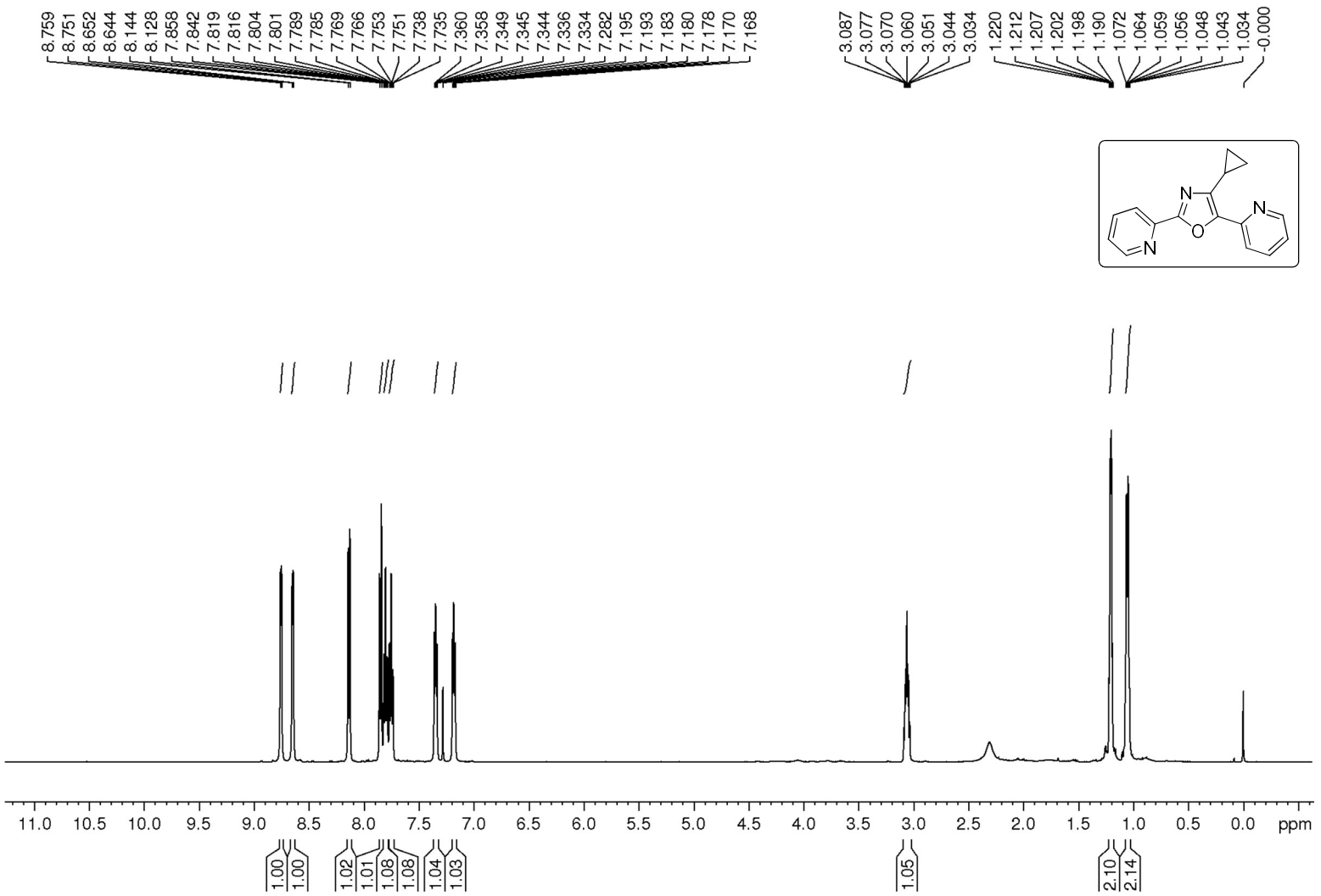
^{1}H NMR Spectrum of 3eb



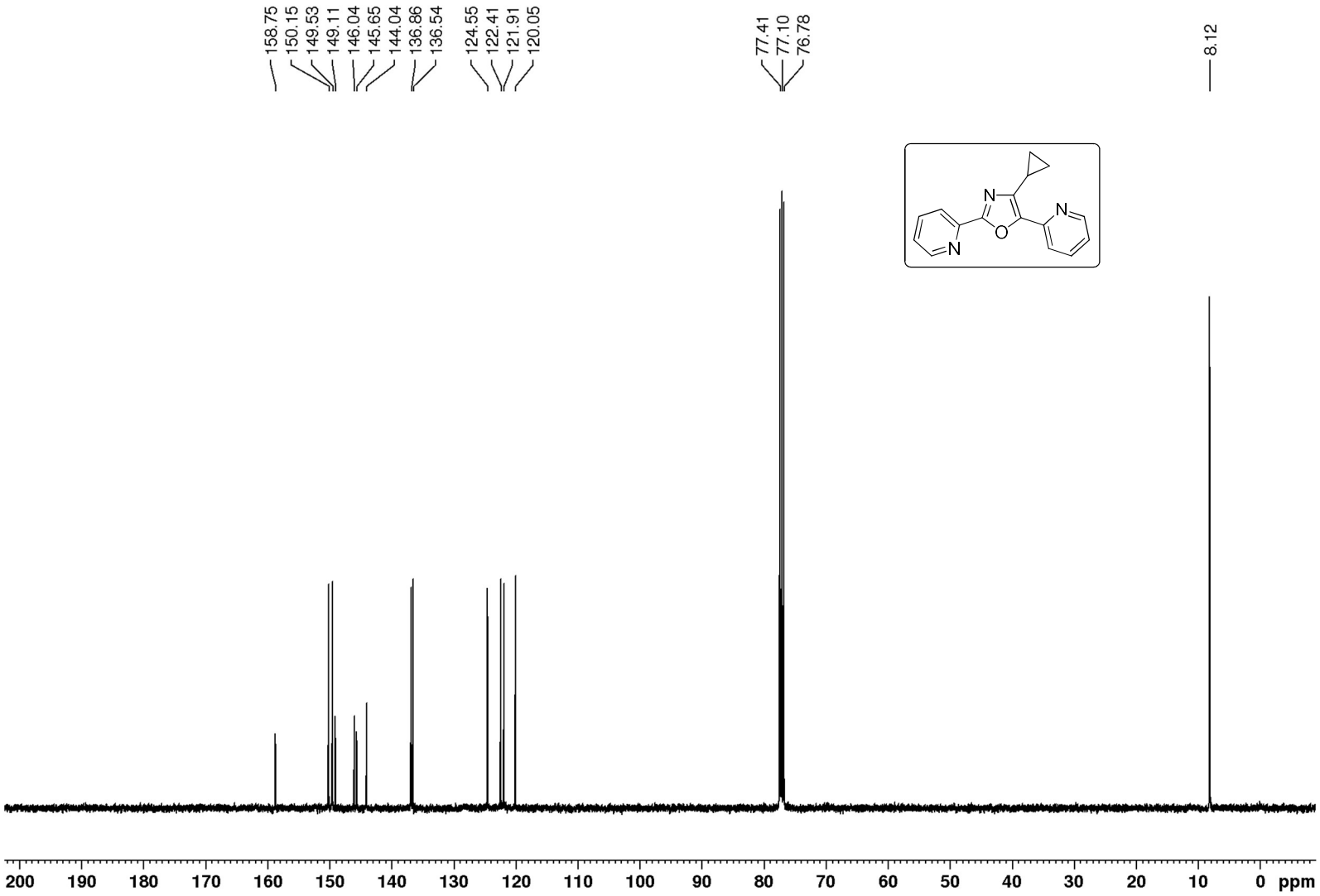
^{13}C NMR Spectrum of 3eb



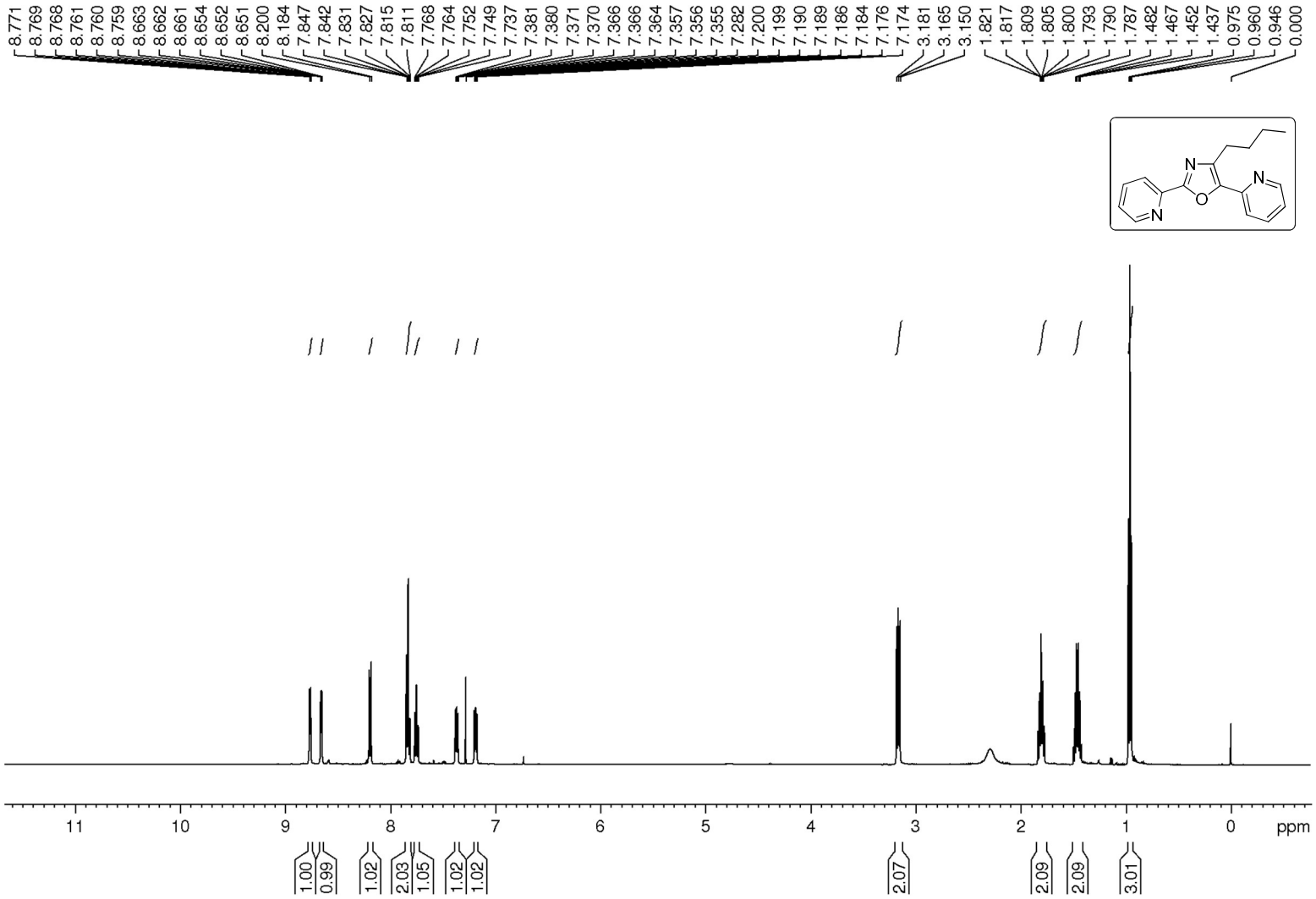
[1]H NMR Spectrum of 3av



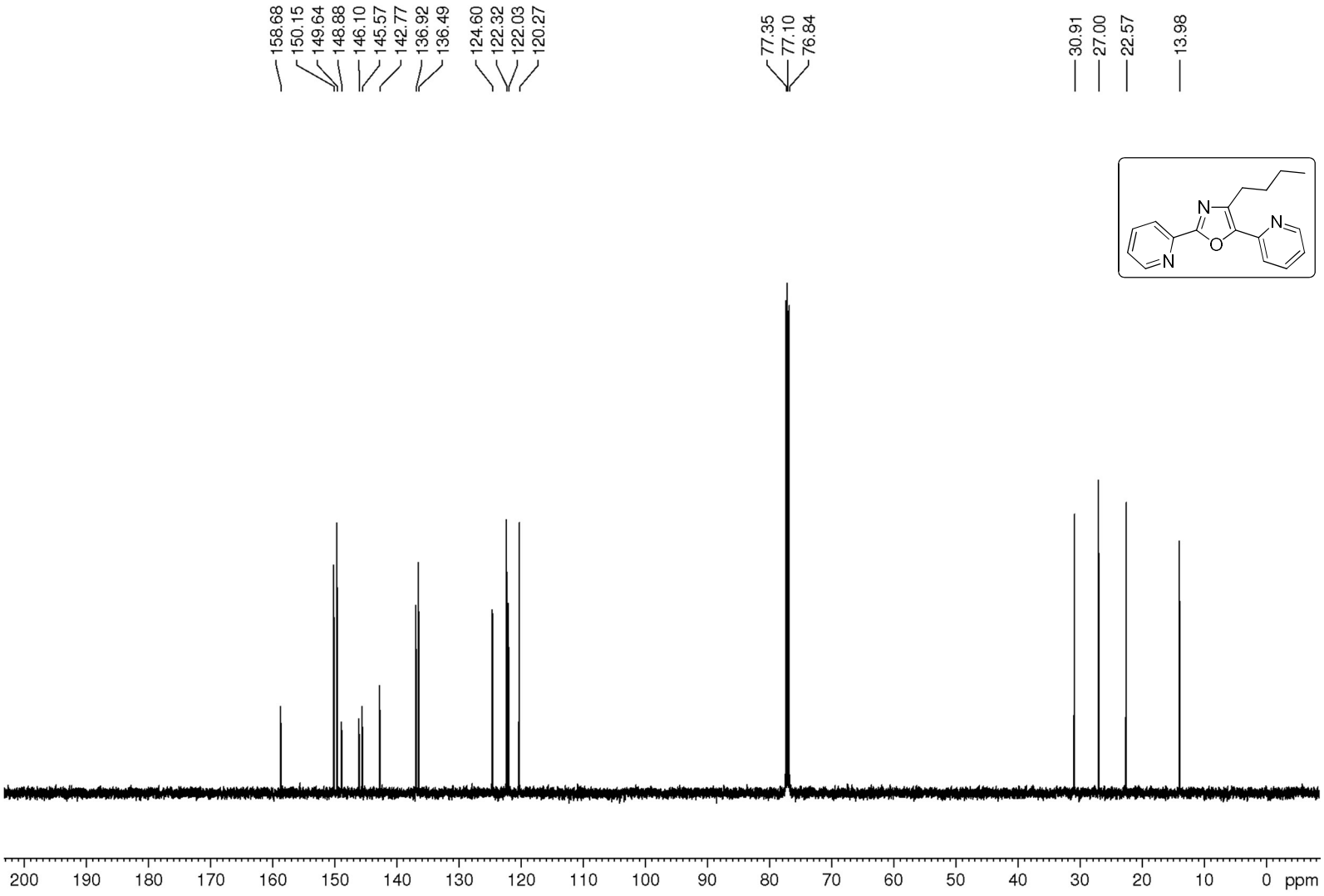
^{13}C NMR Spectrum of 3av



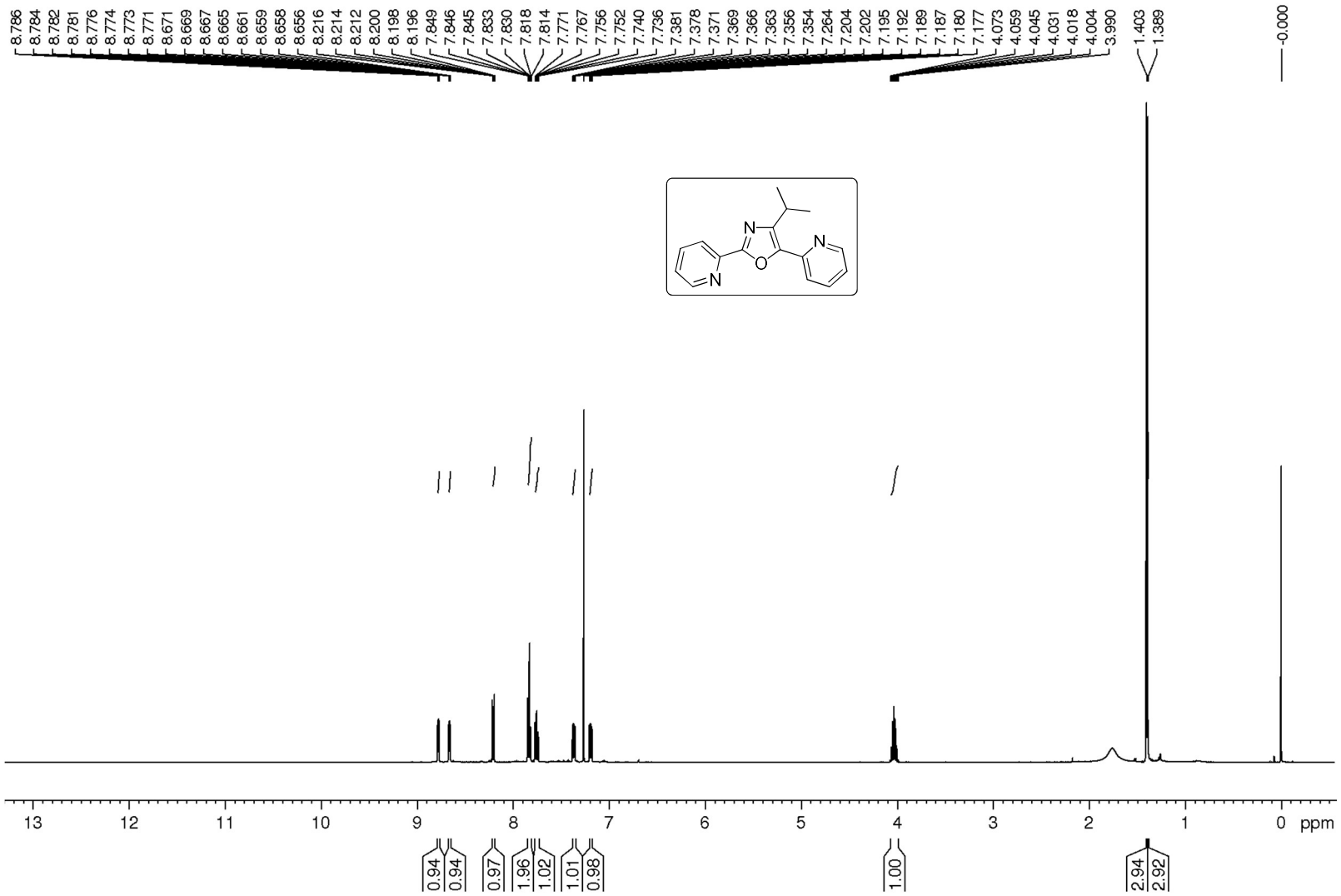
[1]H NMR Spectrum of 3aw



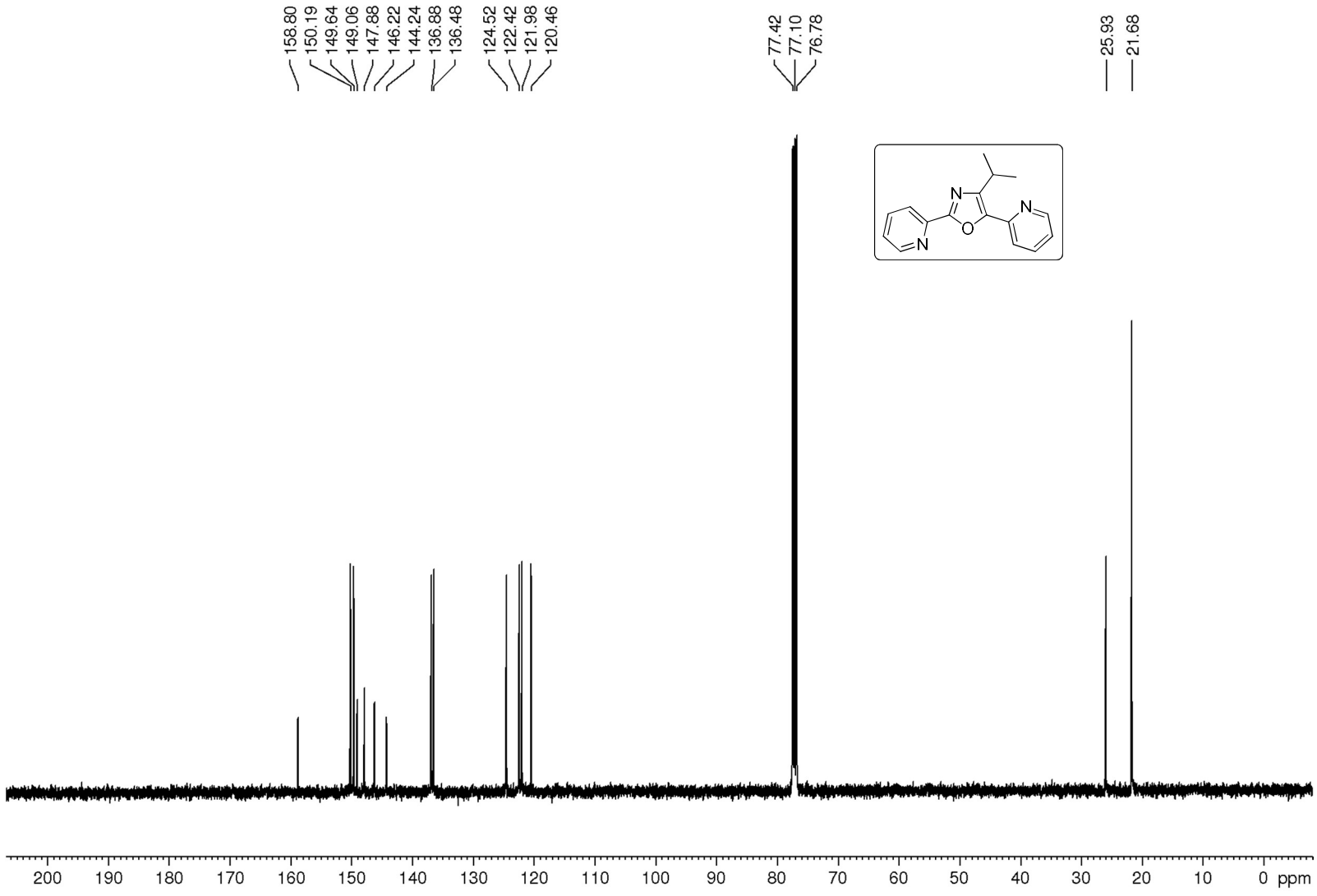
^{13}C NMR Spectrum of 3aw



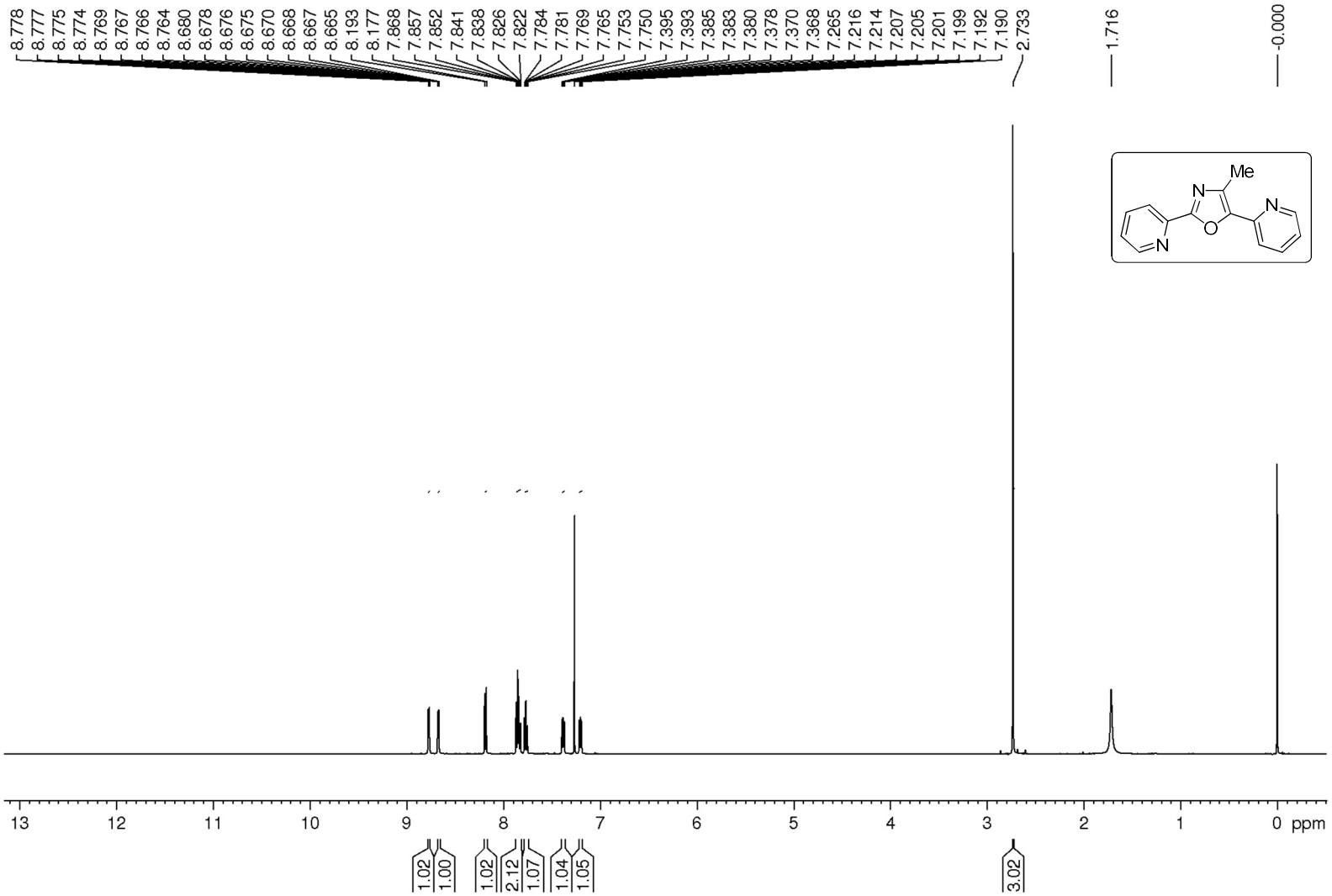
[1]H NMR Spectrum of 3ax



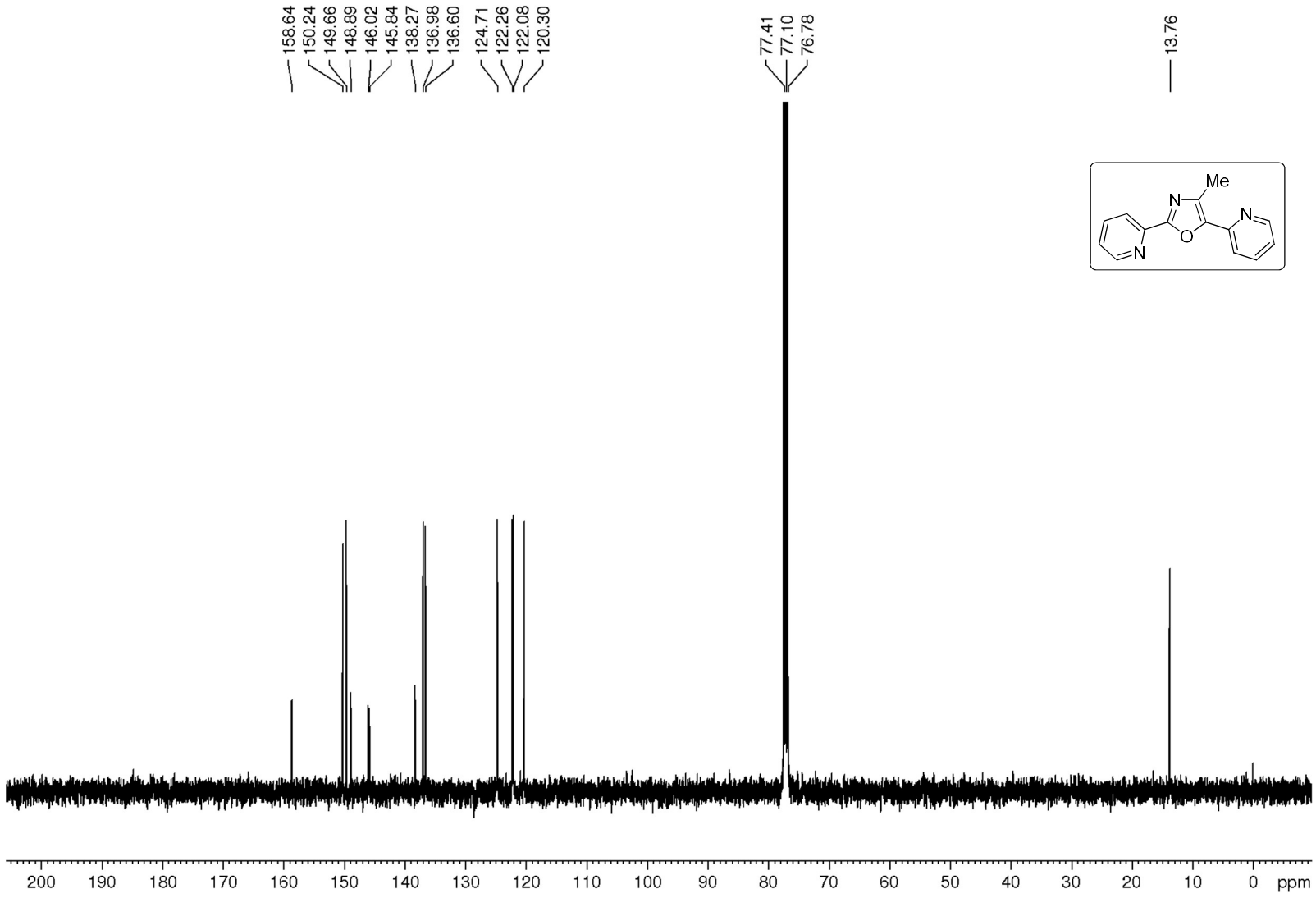
^{13}C NMR Spectrum of 3ax



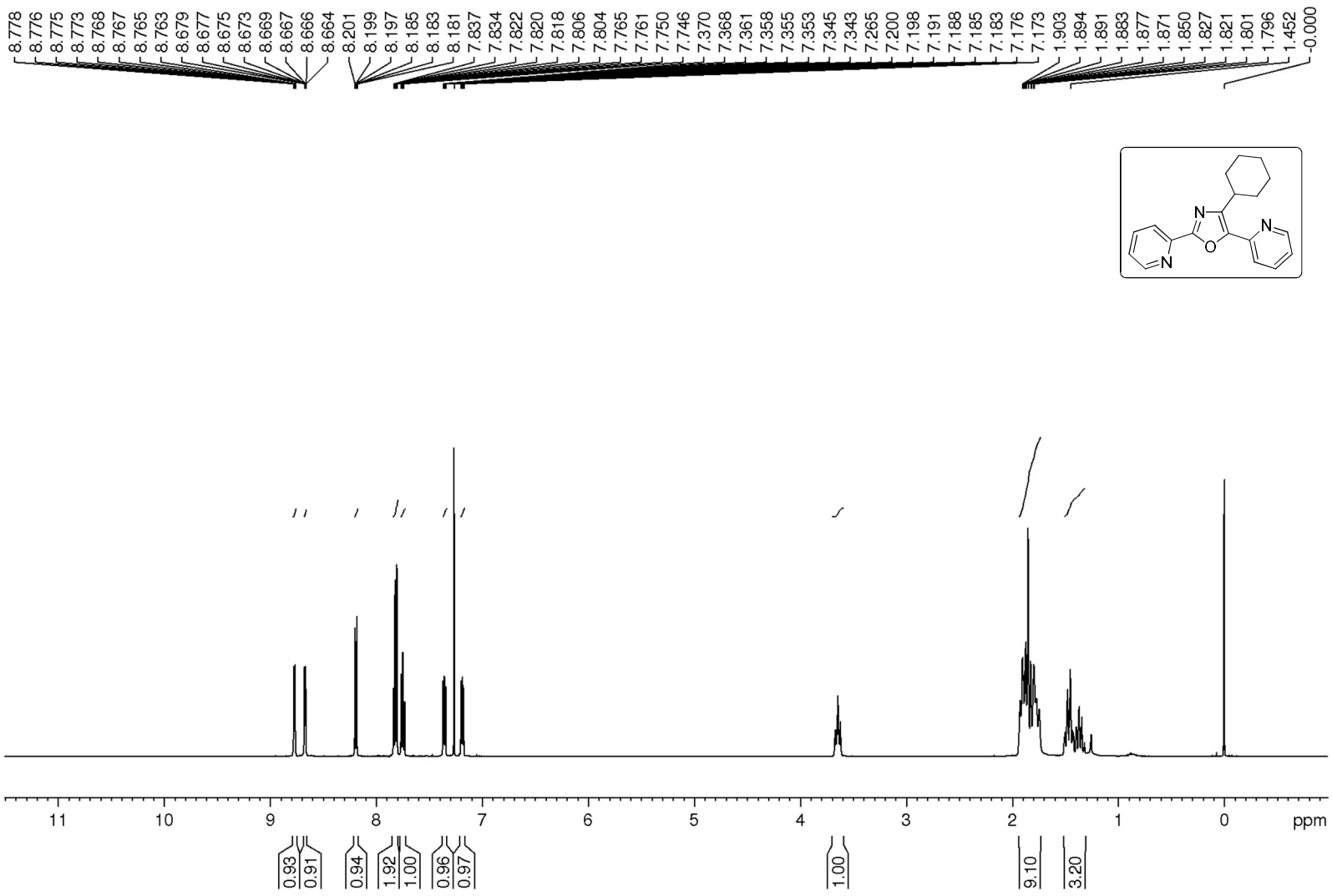
[1]H NMR Spectrum of 3ay



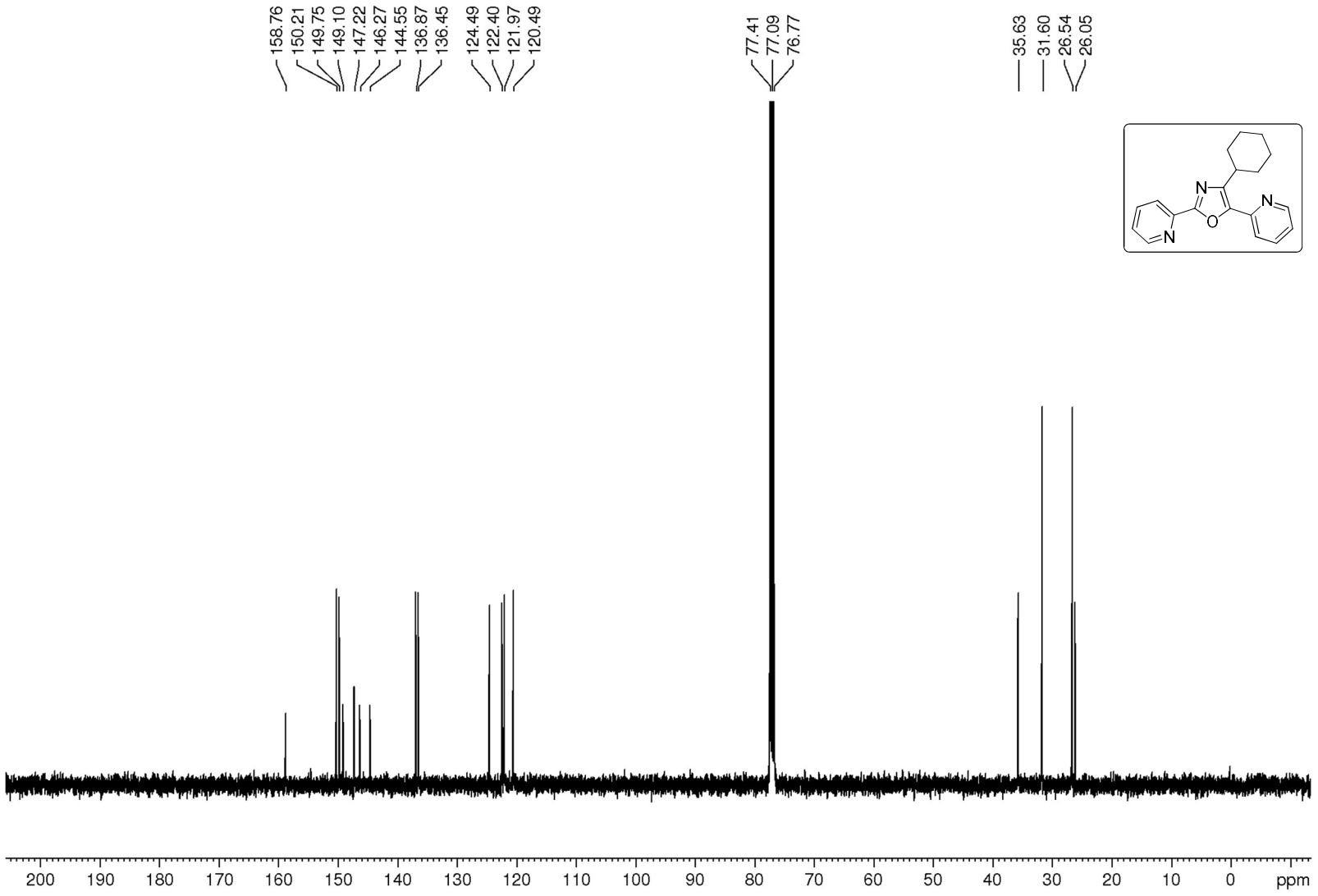
^{13}C NMR Spectrum of 3ay



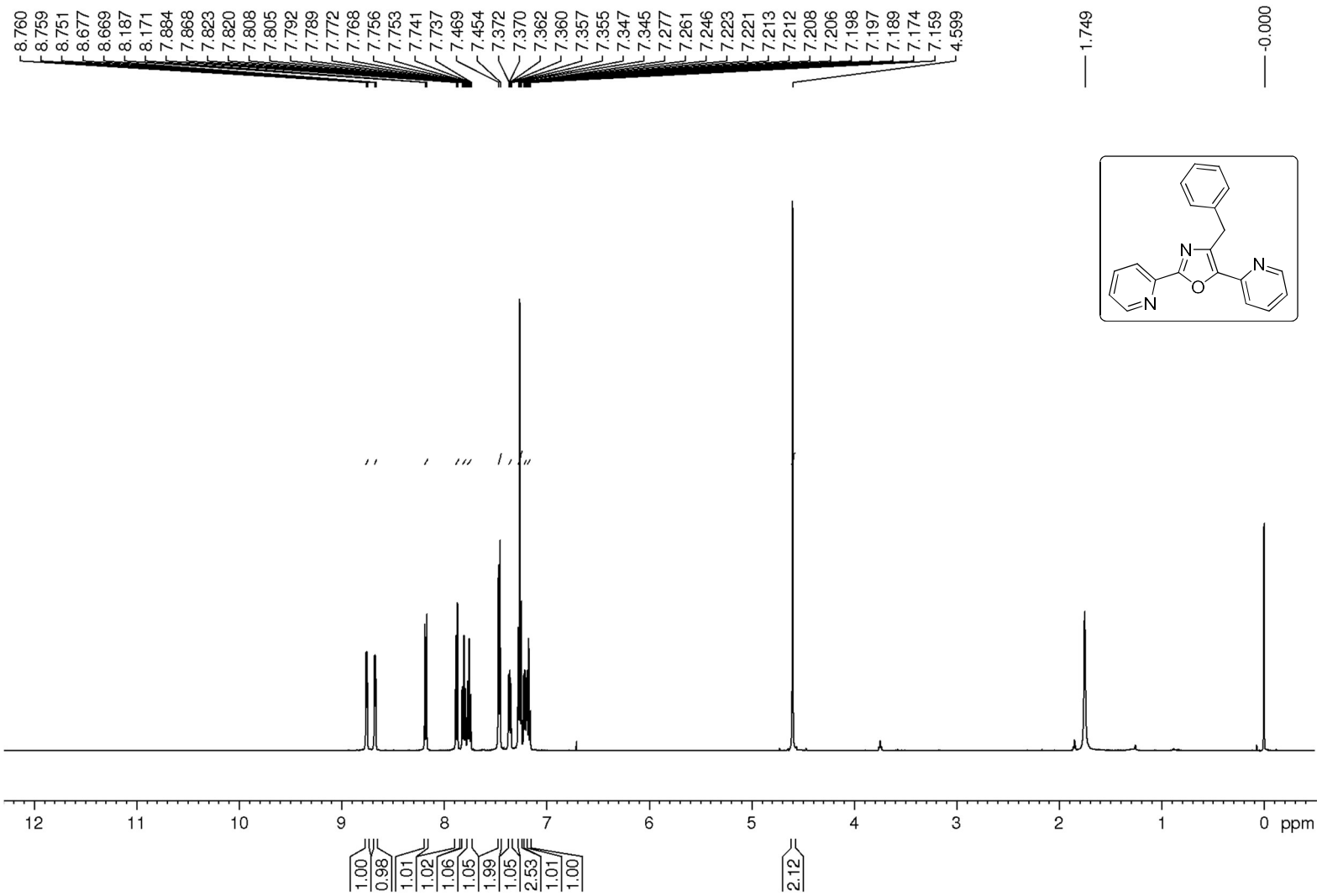
^{1}H NMR Spectrum of 3az



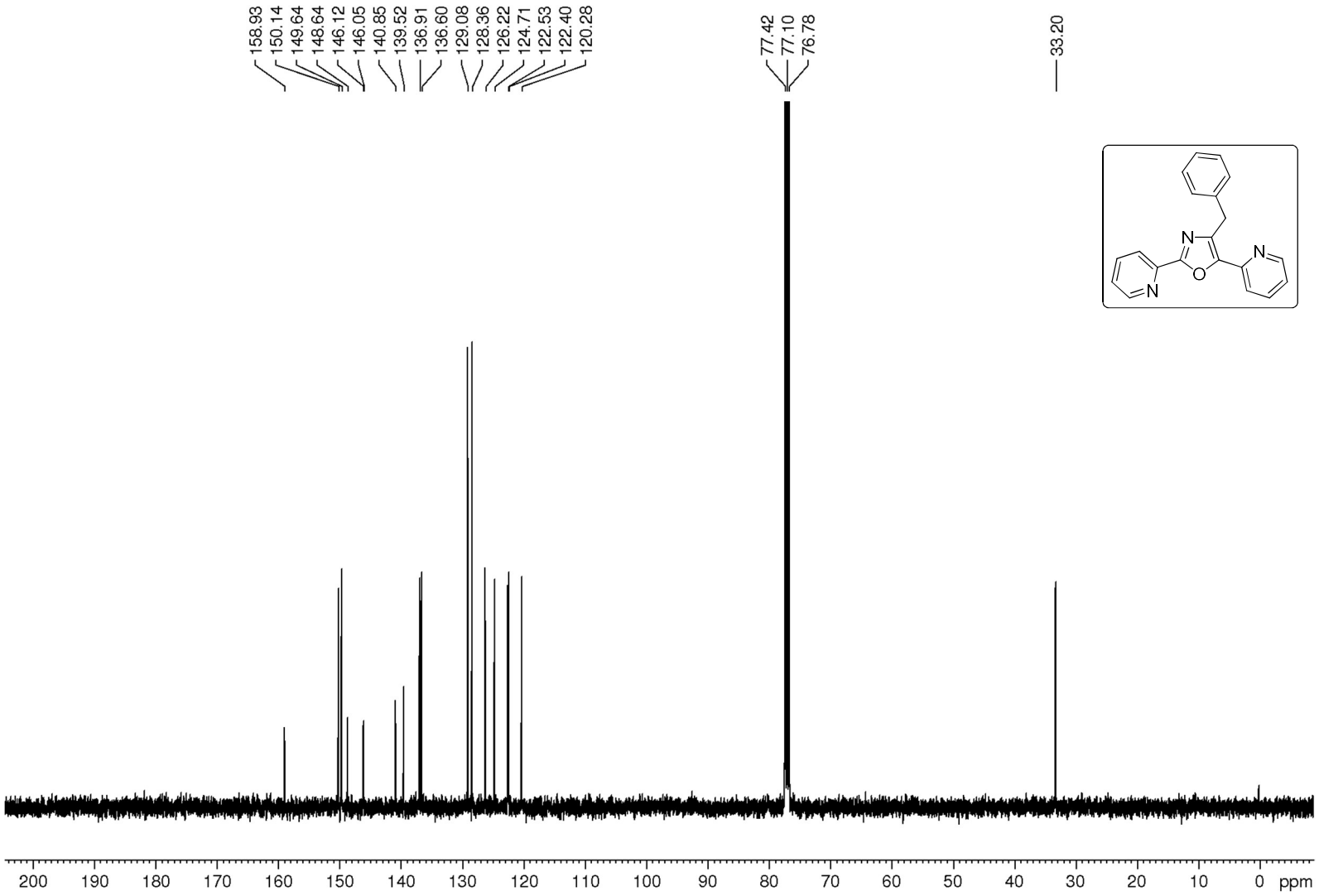
^{13}C NMR Spectrum of 3az



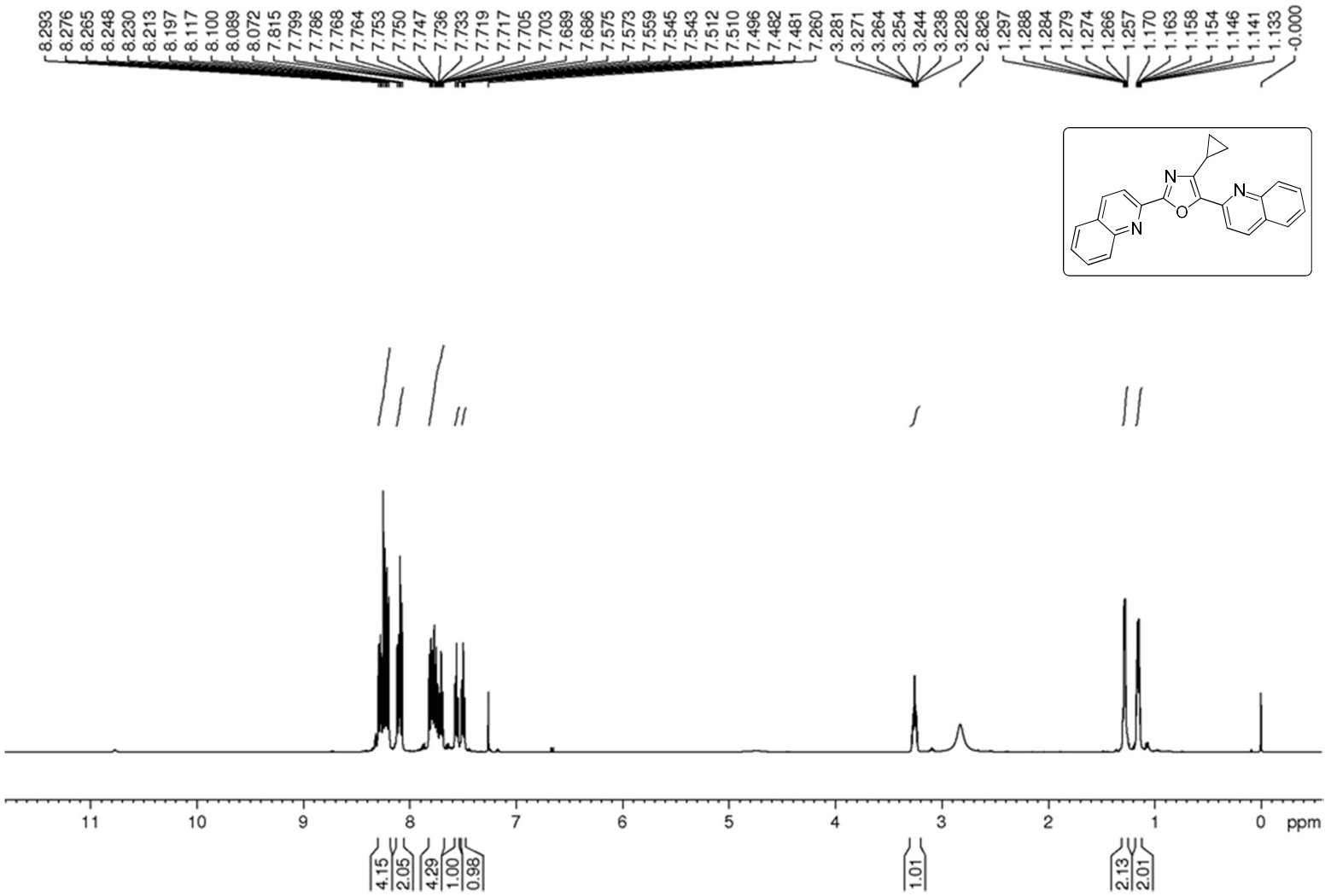
[1]H NMR Spectrum of 3az'



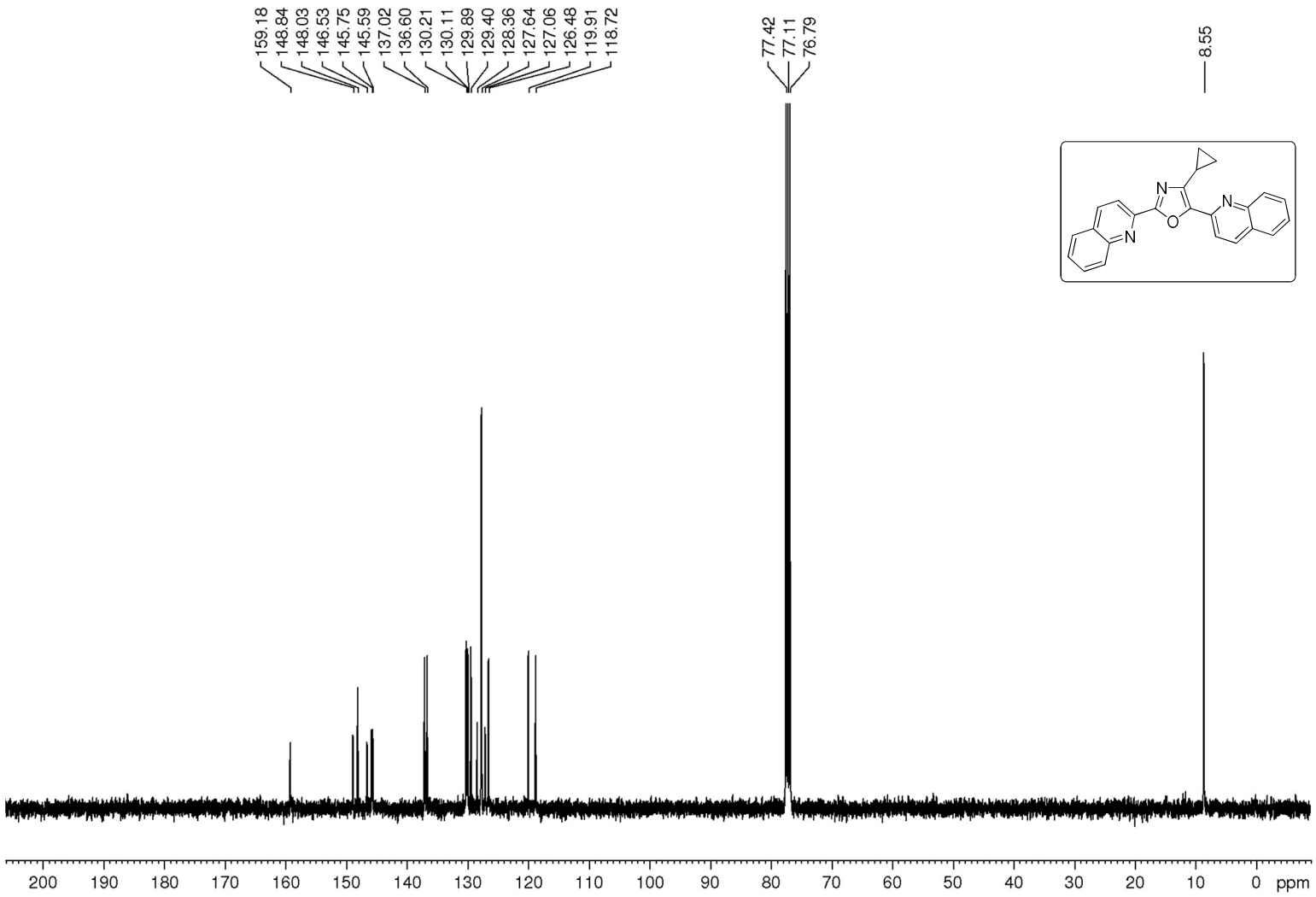
^{13}C NMR Spectrum of 3az'



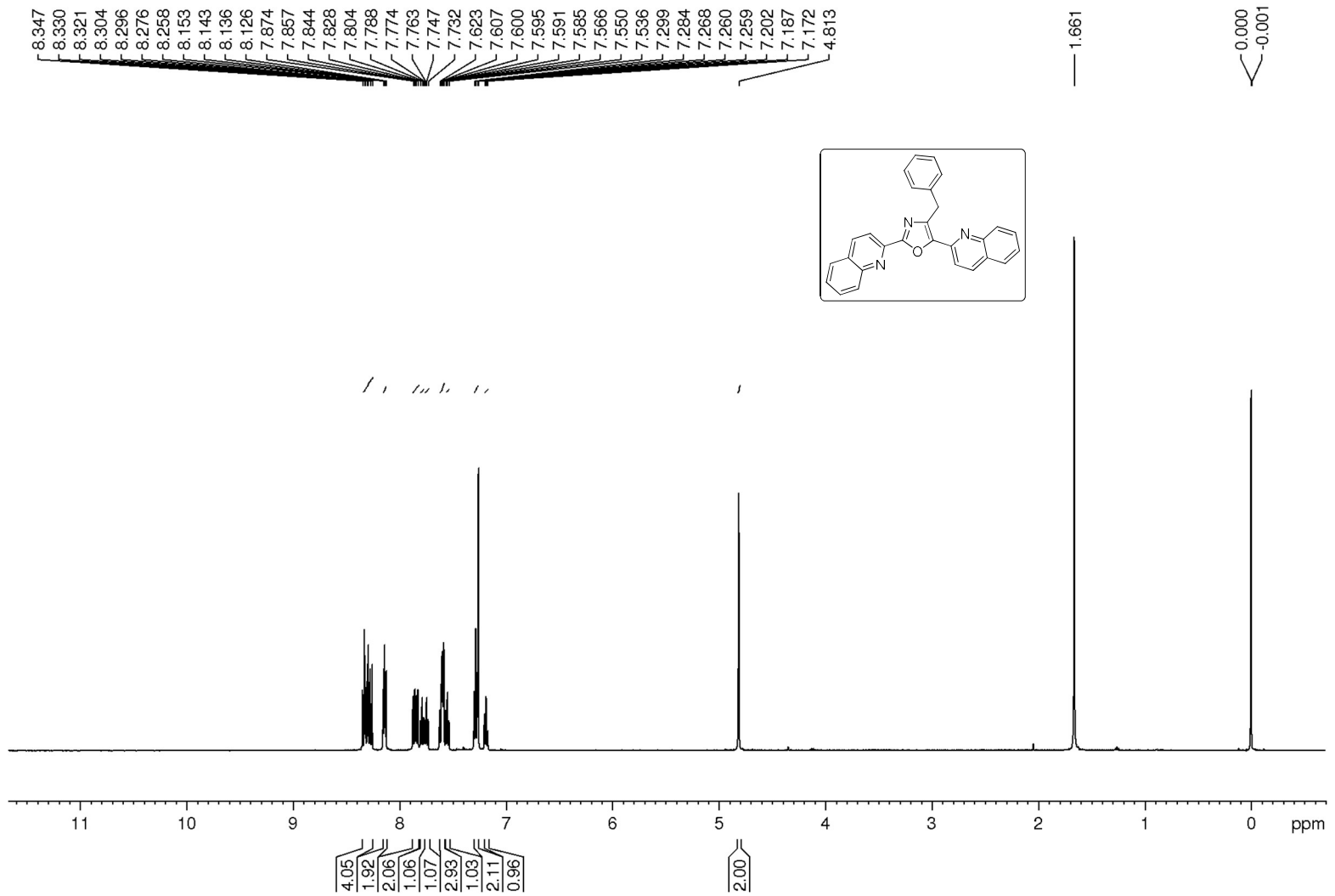
^{1}H NMR Spectrum of 3ev



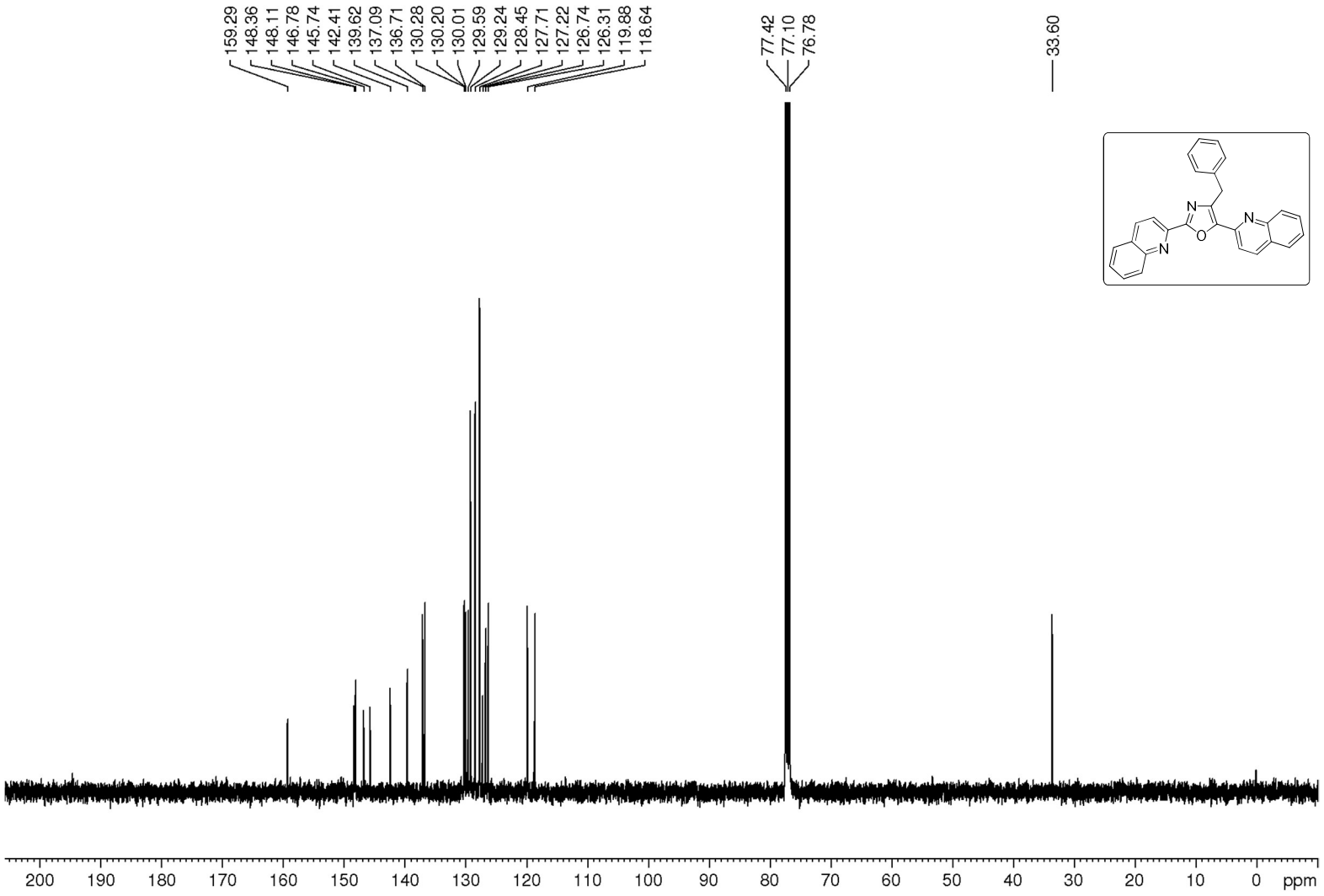
^{13}C NMR Spectrum of 3ev



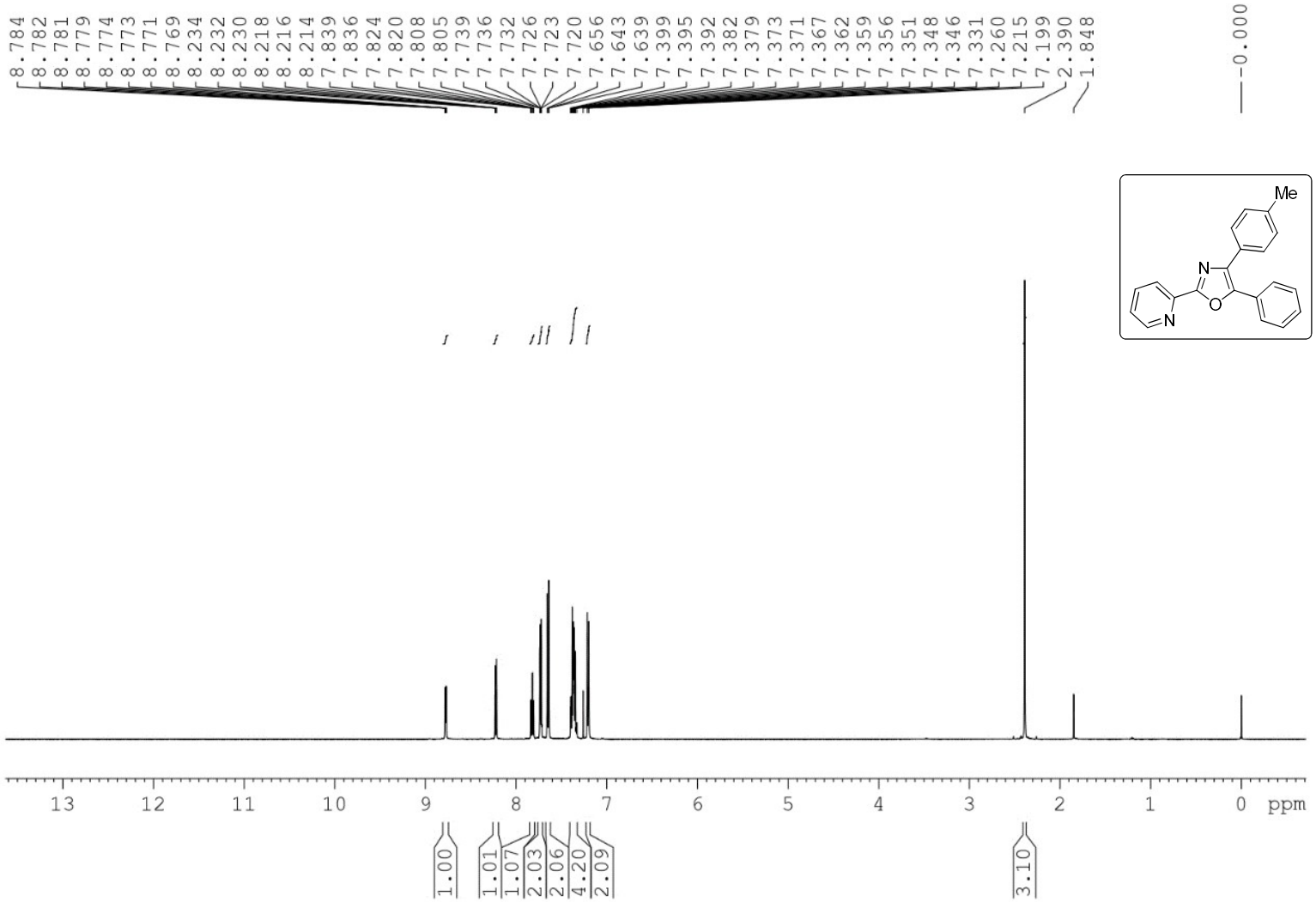
^{1}H NMR Spectrum of 3ez'



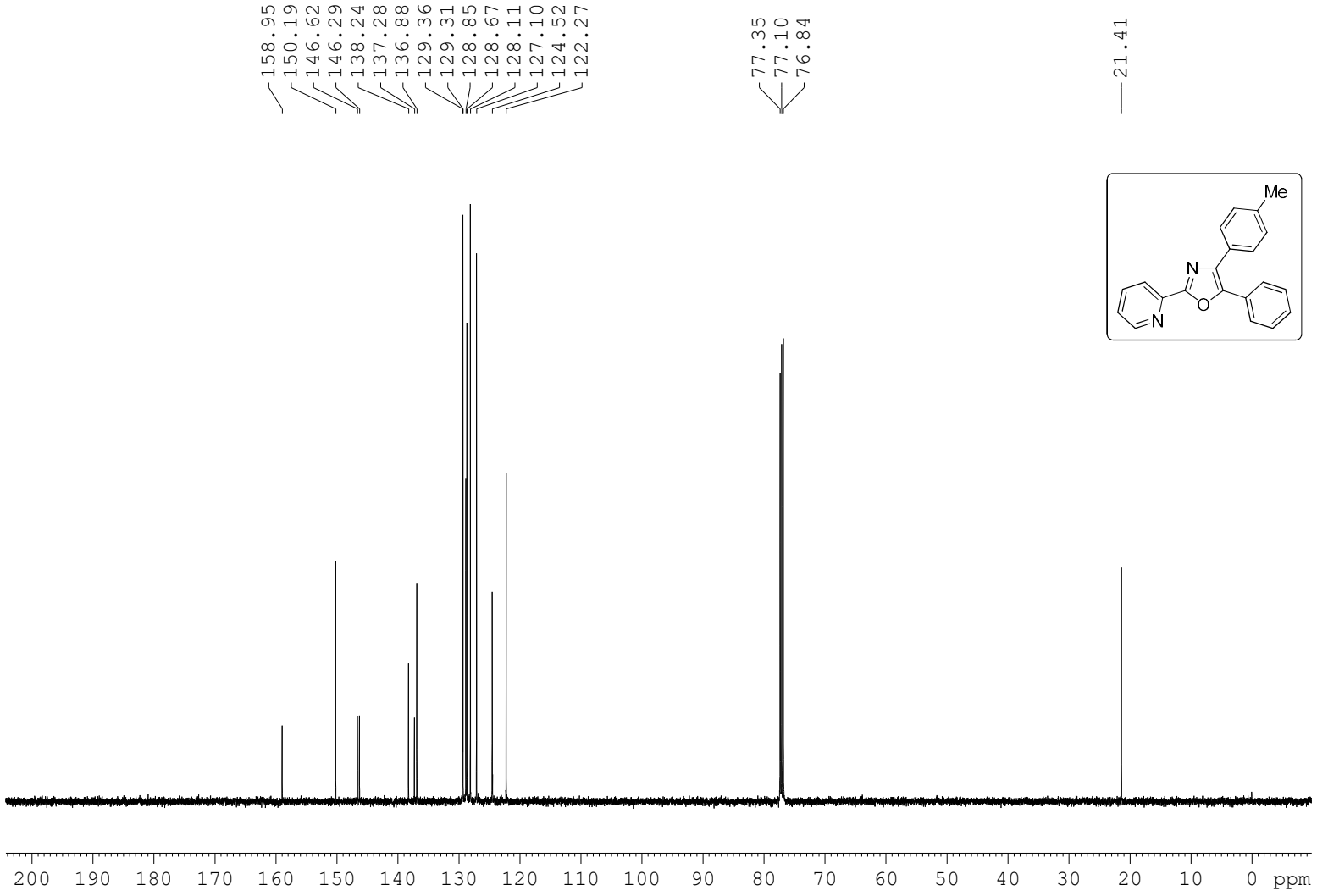
^{13}C NMR Spectrum of 3ez'



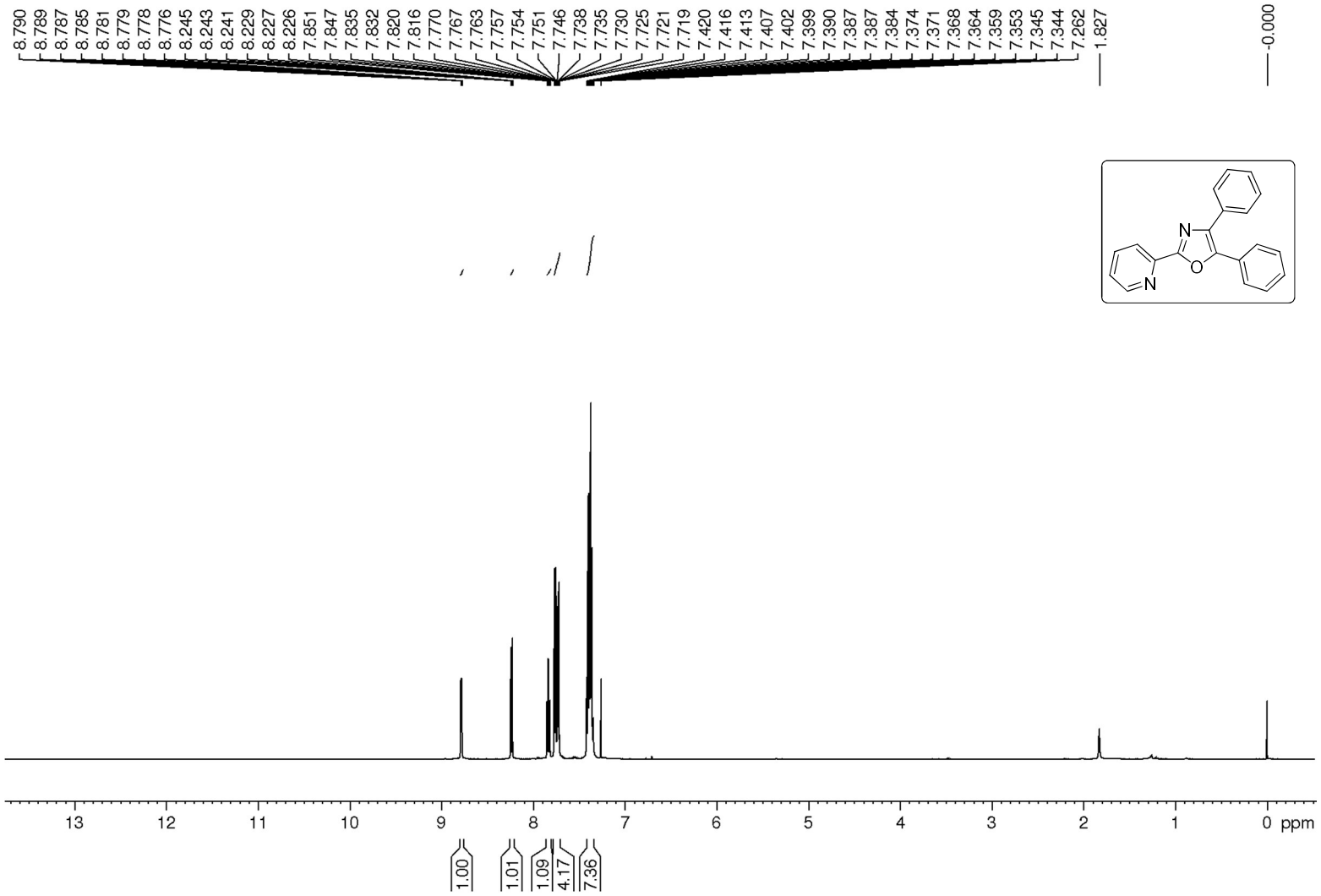
[1]H NMR Spectrum of 5aab



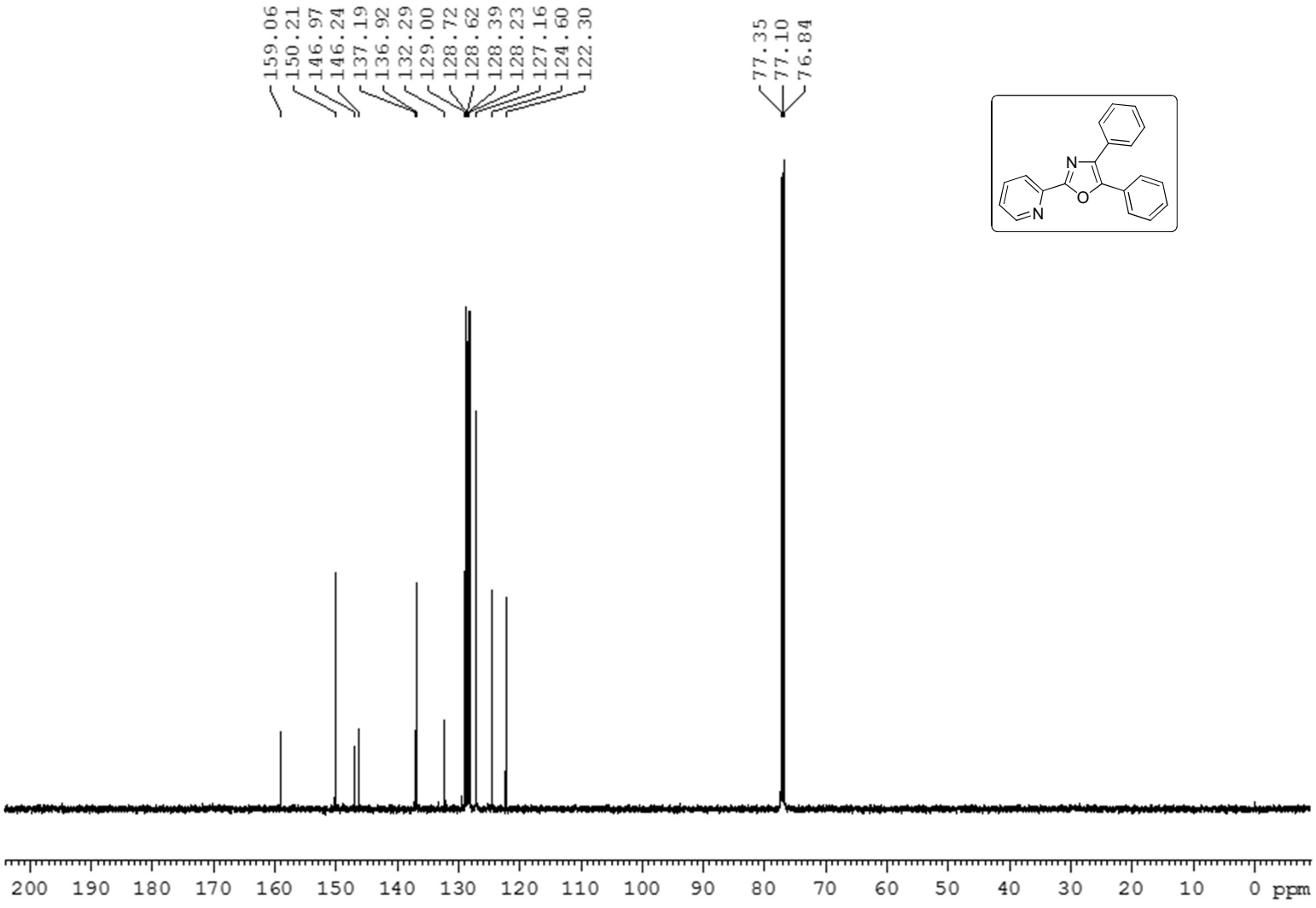
^{13}C NMR Spectrum of 5aab



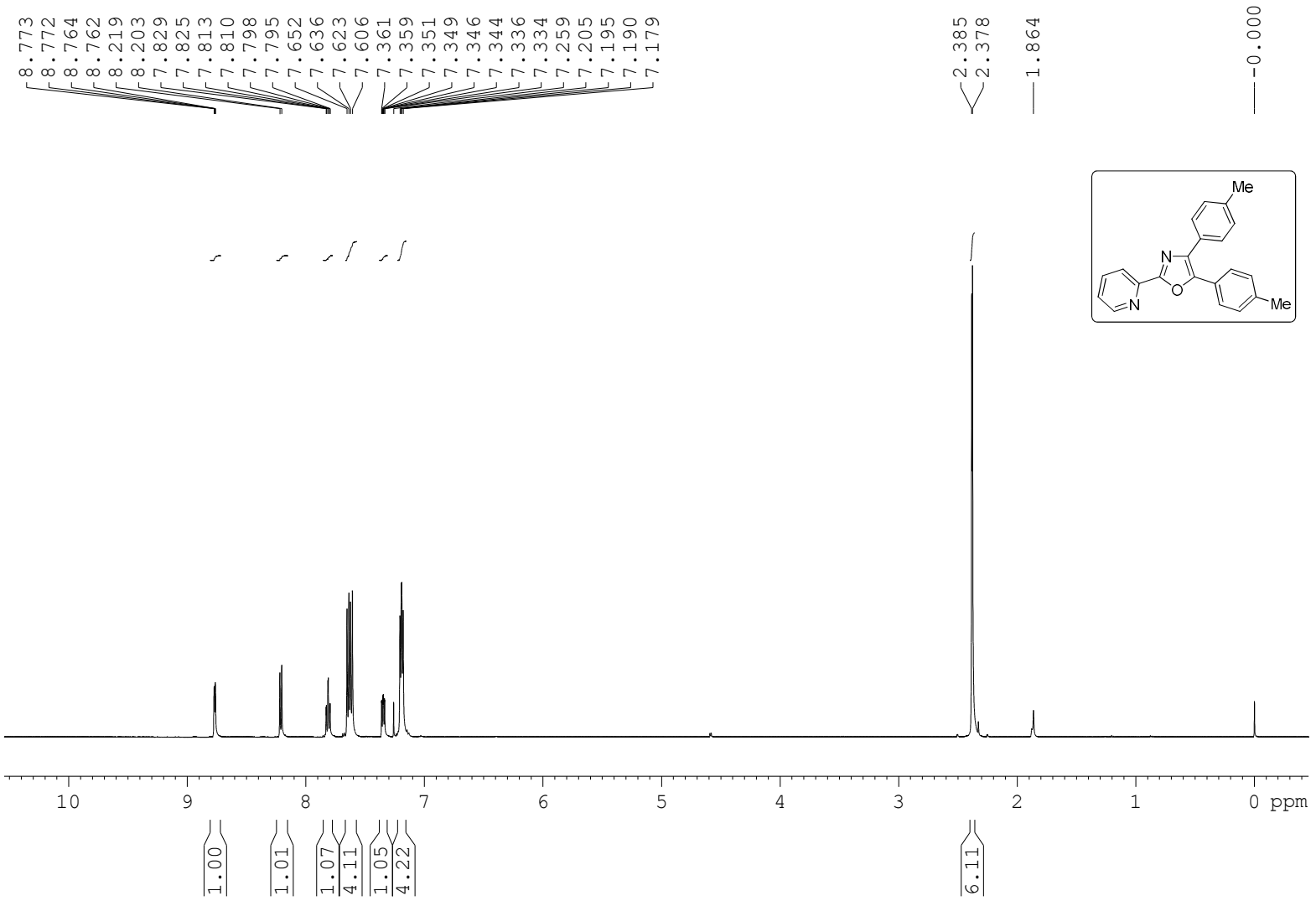
^{1}H NMR Spectrum of 5aaa



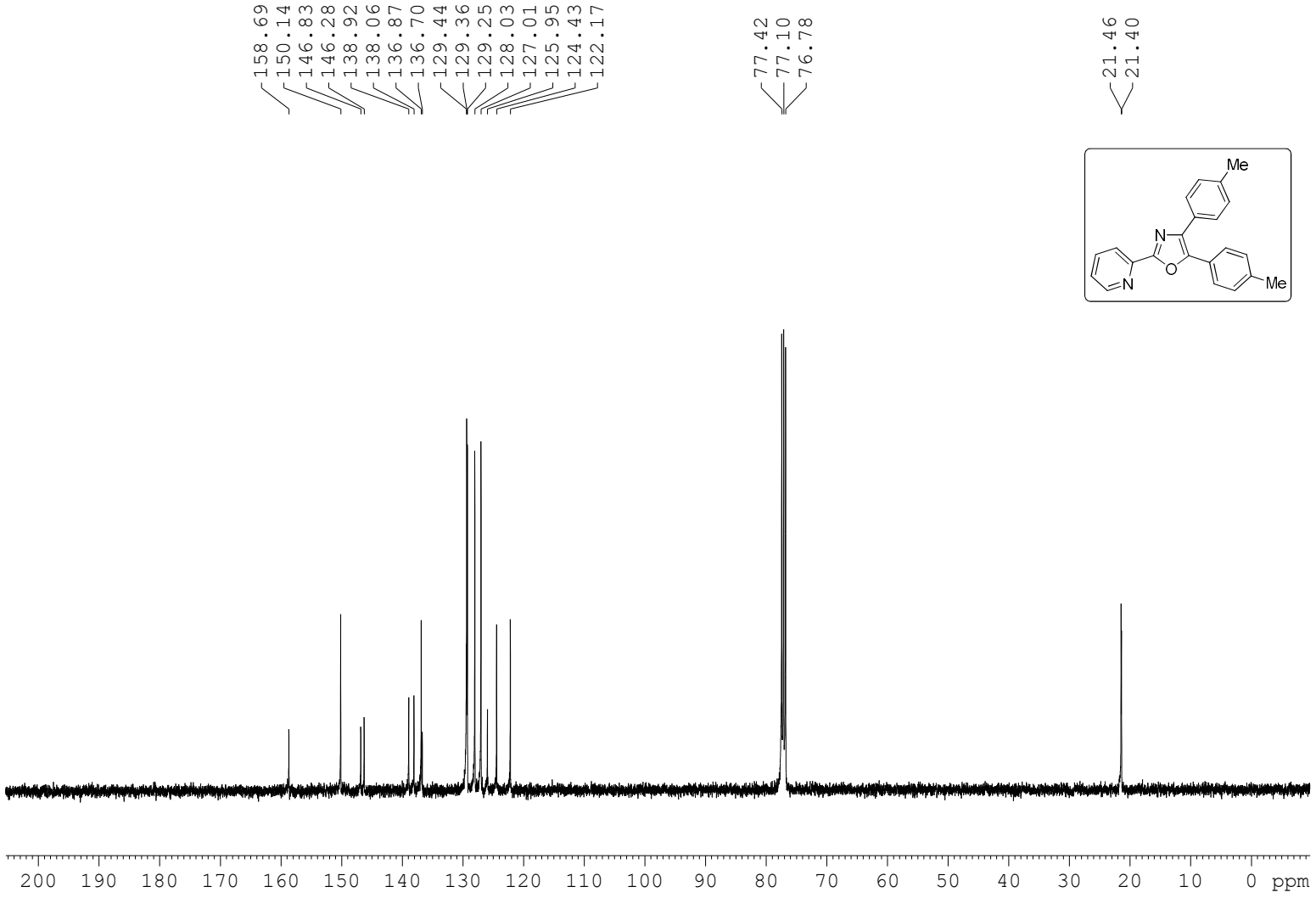
^{13}C NMR Spectrum of 5aaa



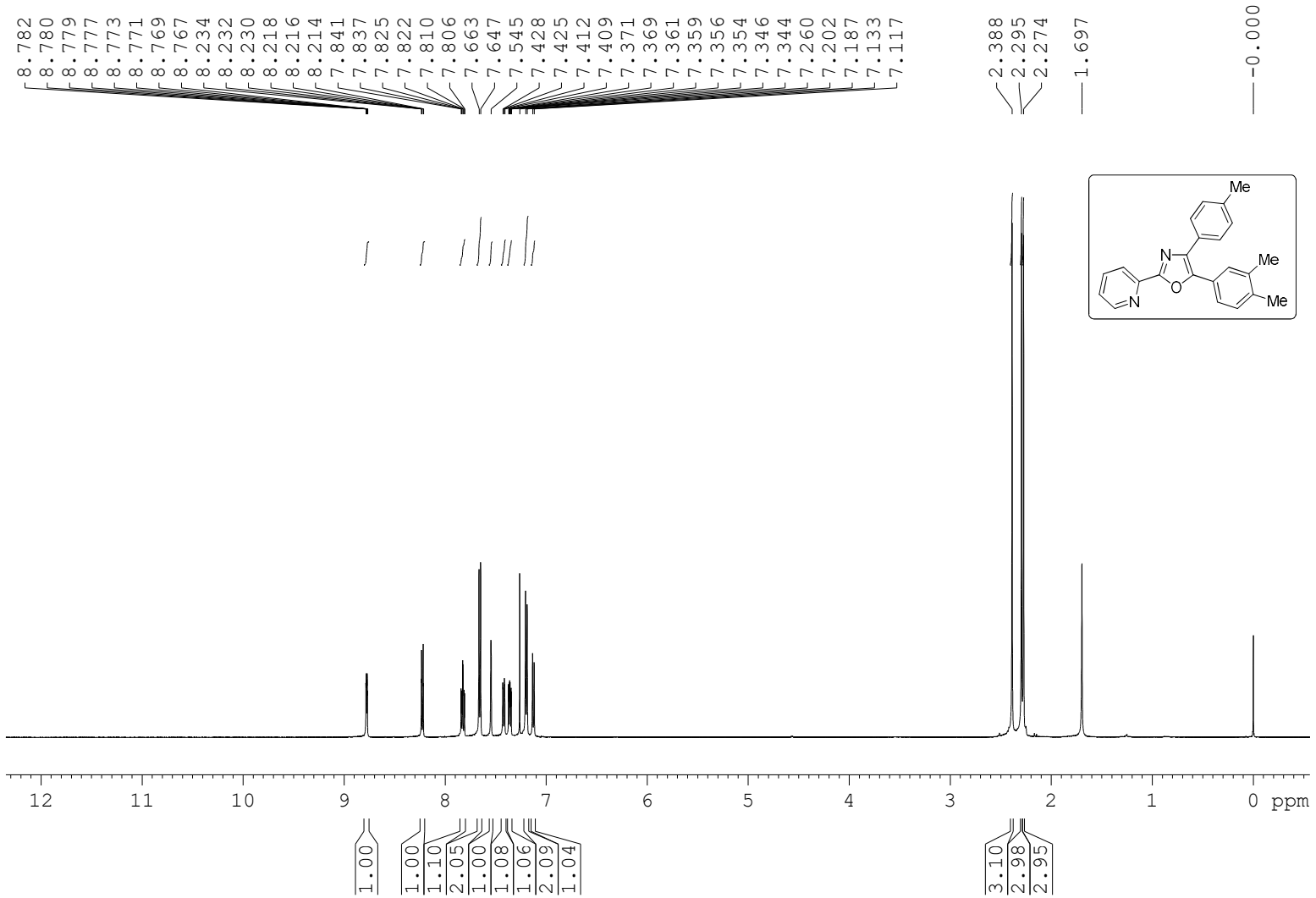
^{1}H NMR Spectrum of 5abb



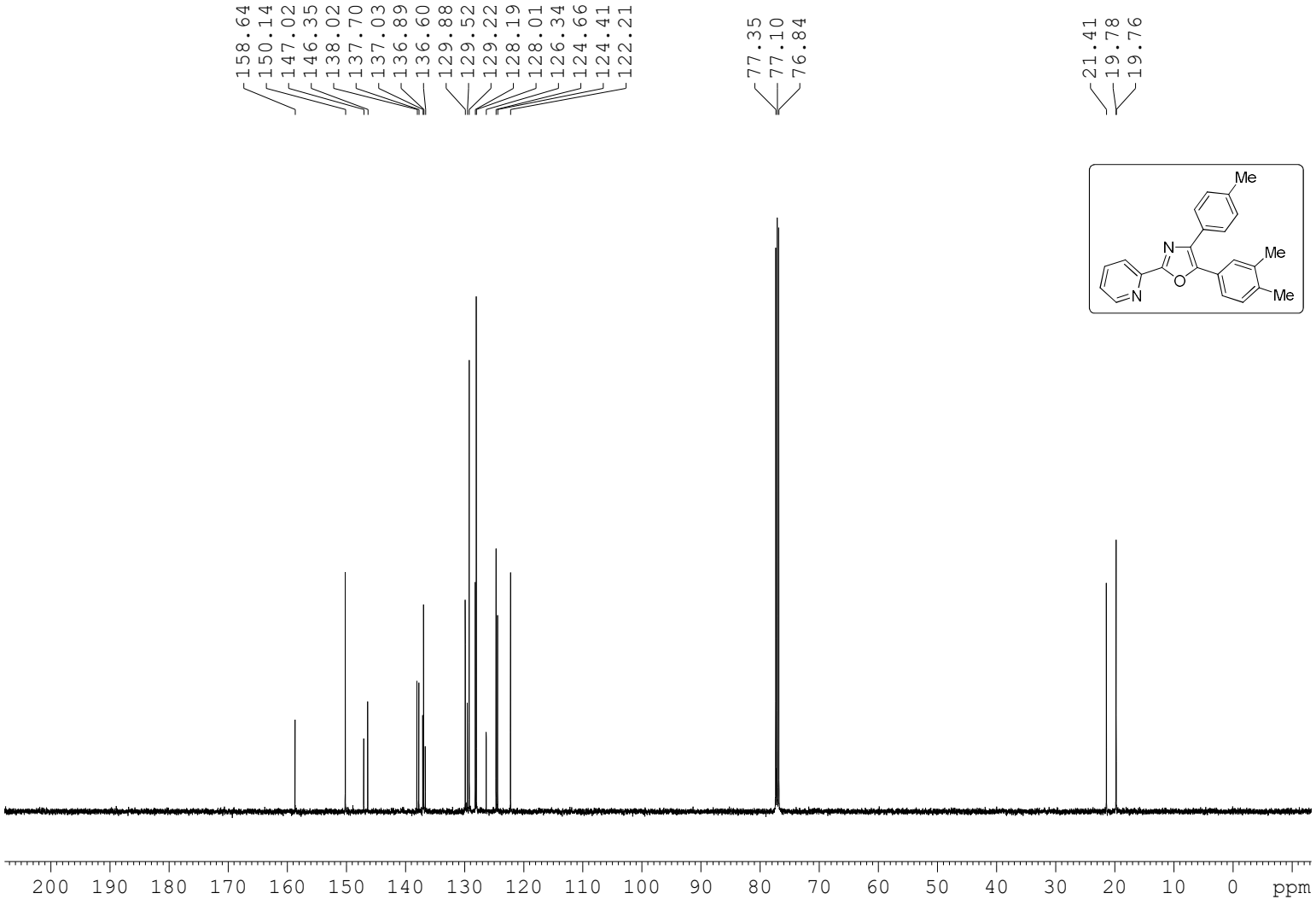
^{13}C NMR Spectrum of 5abb



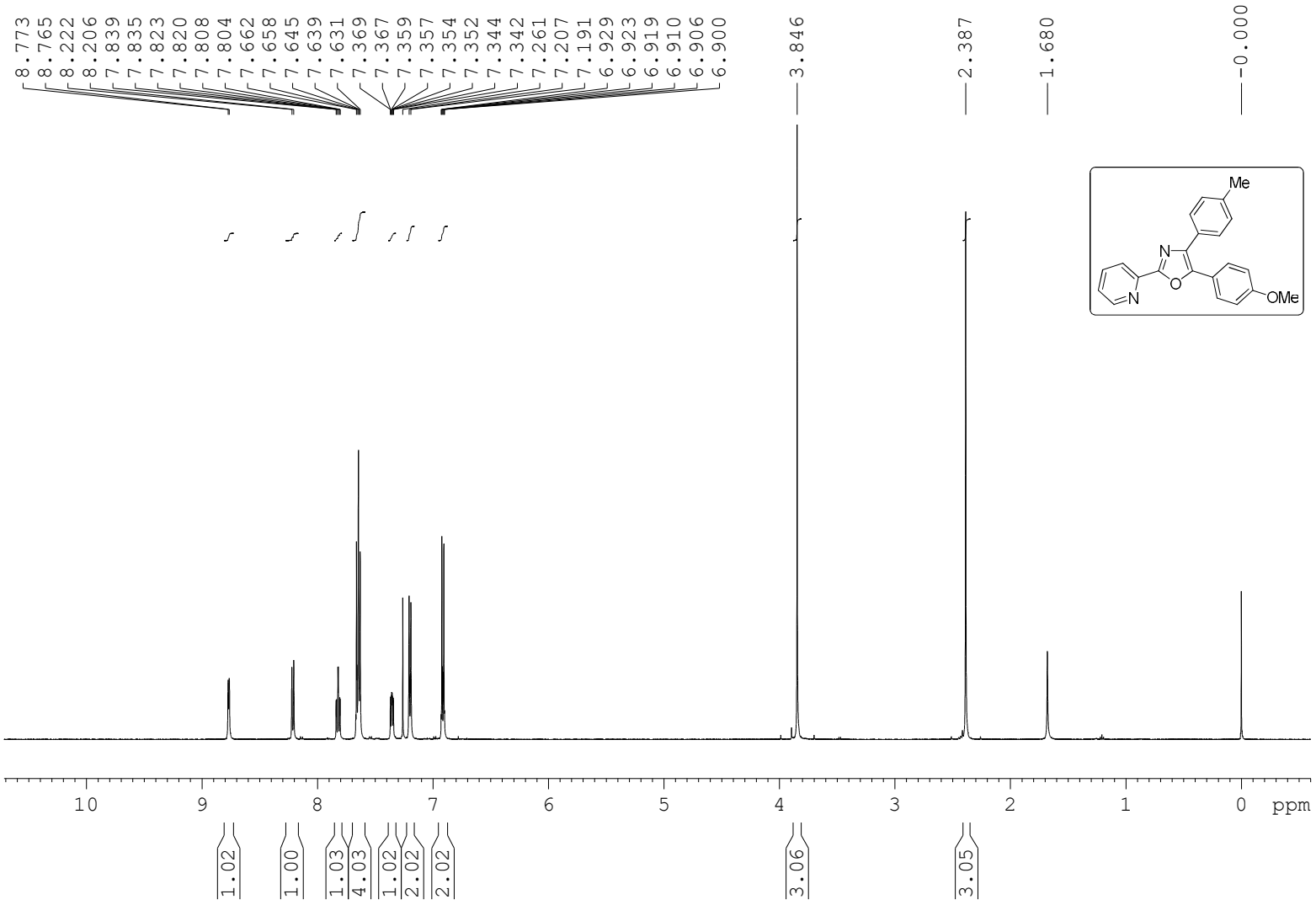
^{1}H NMR Spectrum of 5acb



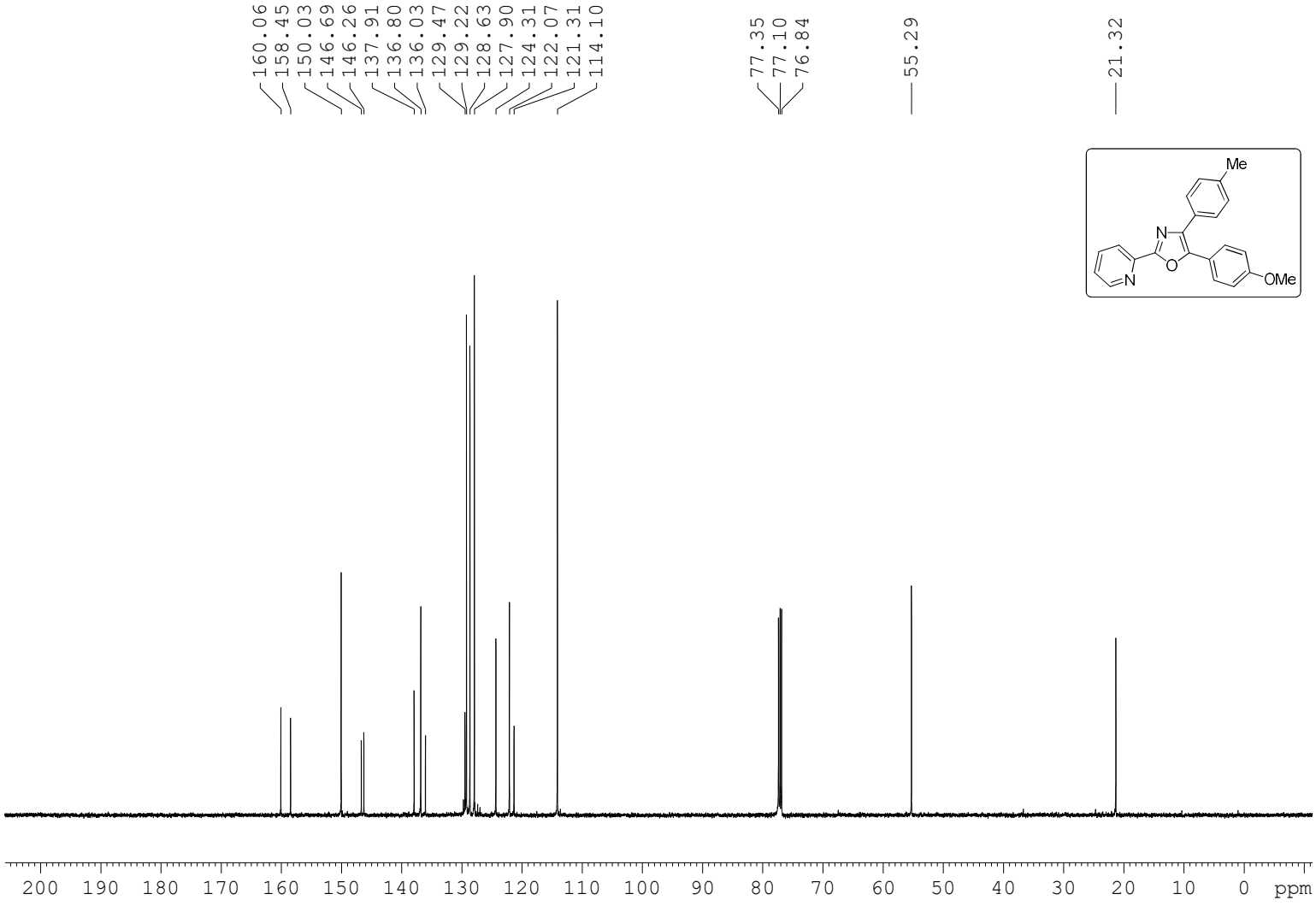
^{13}C NMR Spectrum of 5acb



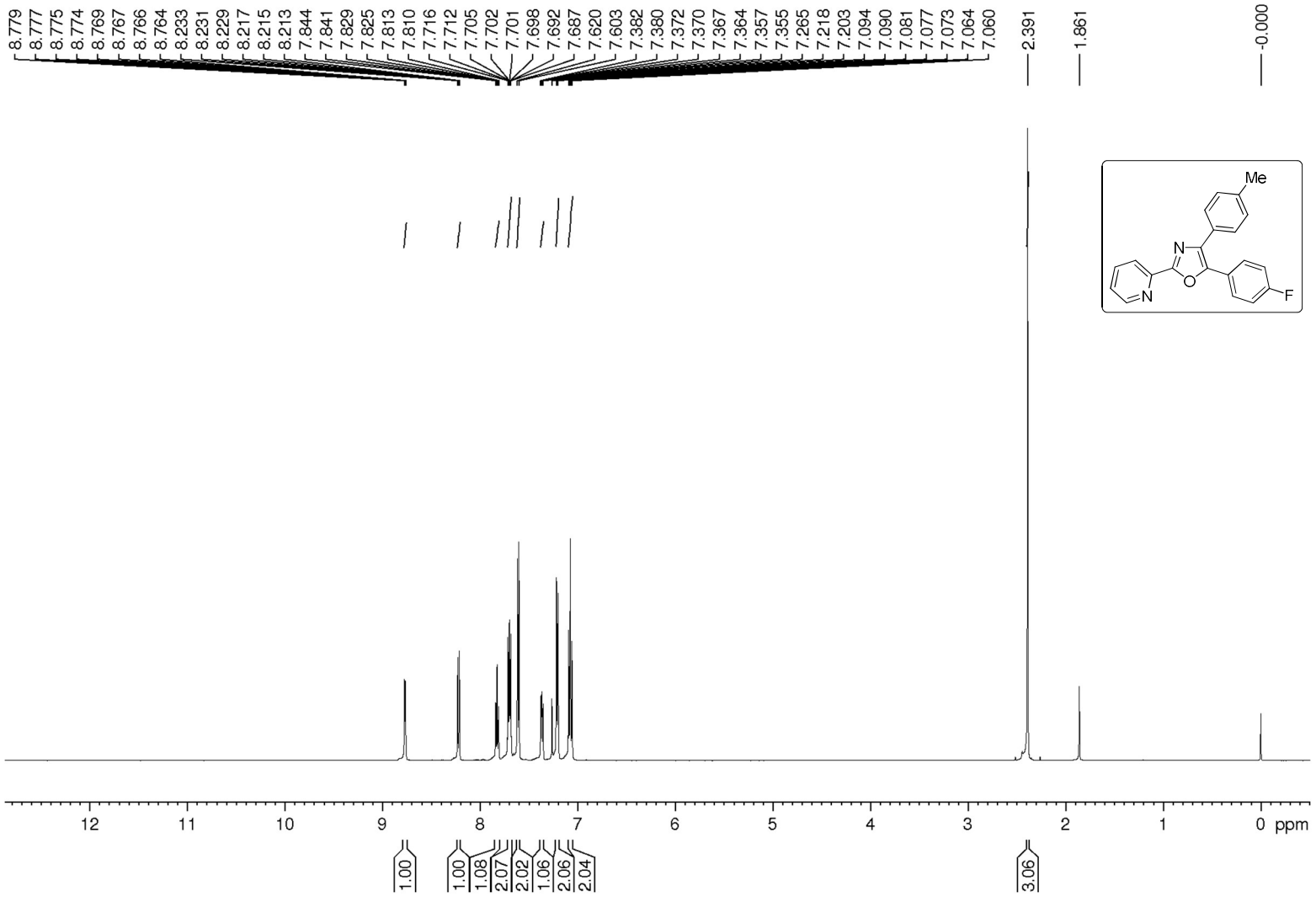
^{1}H NMR Spectrum of 5adb



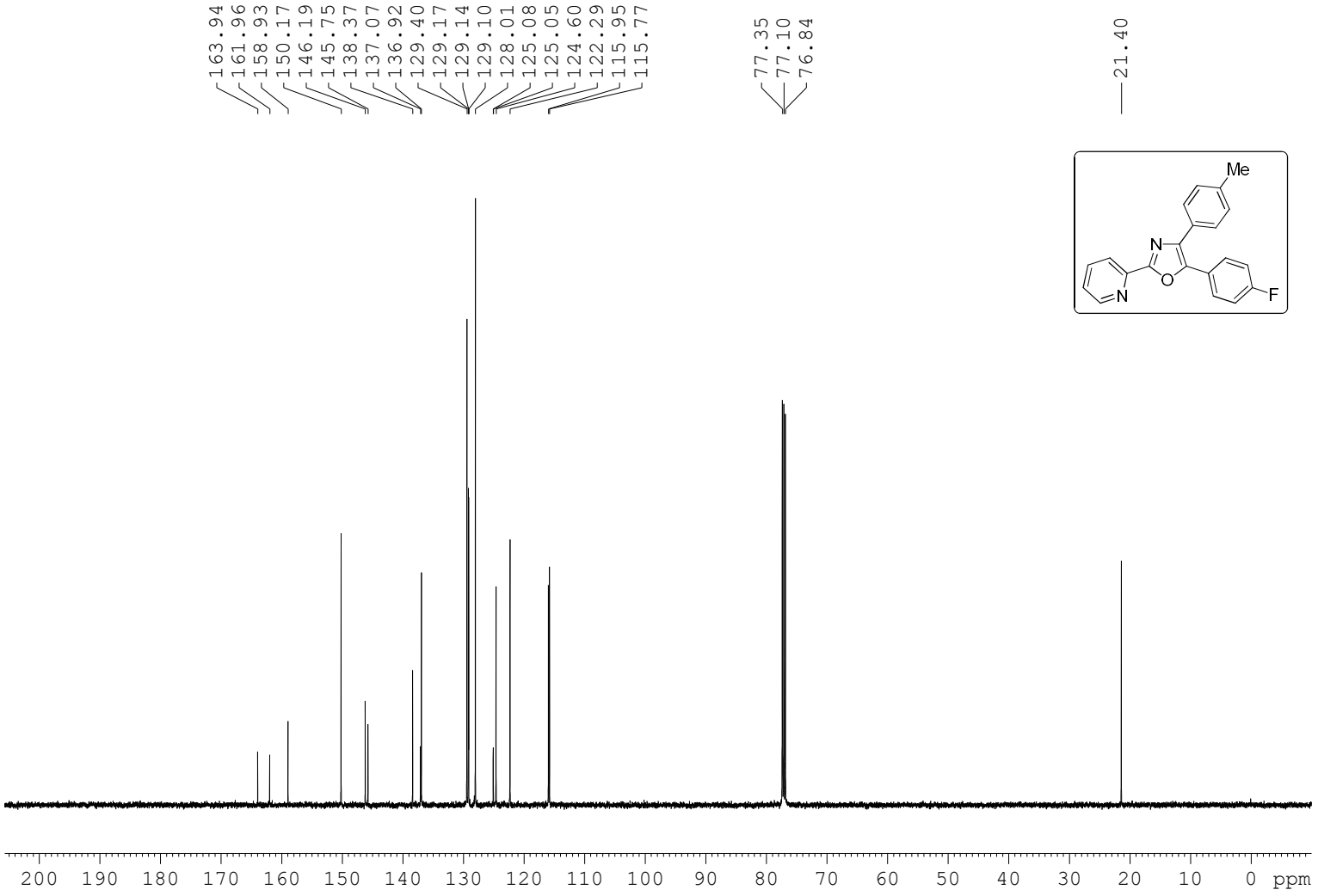
^{13}C NMR Spectrum of 5adb



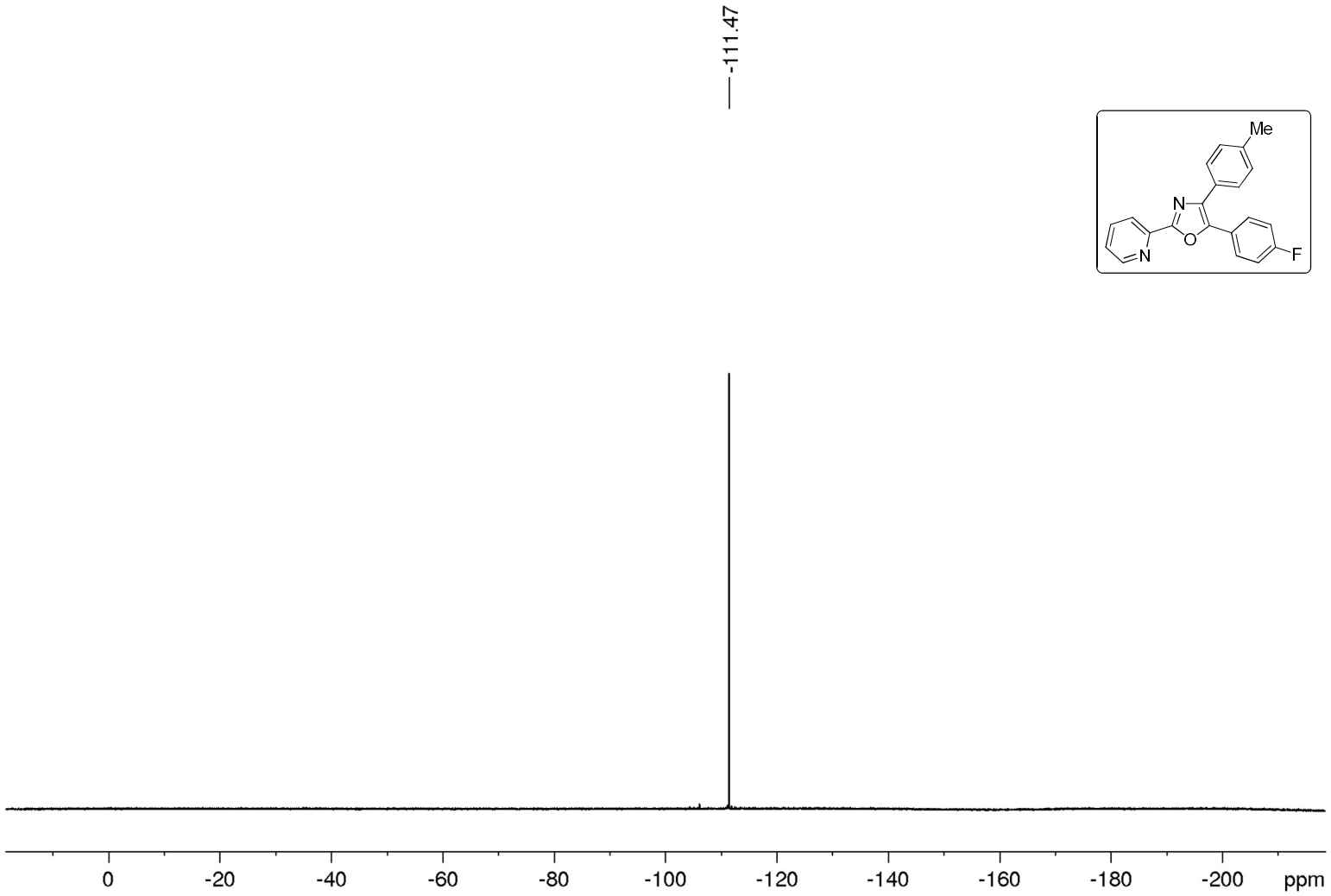
[1]H NMR Spectrum of 5aeb



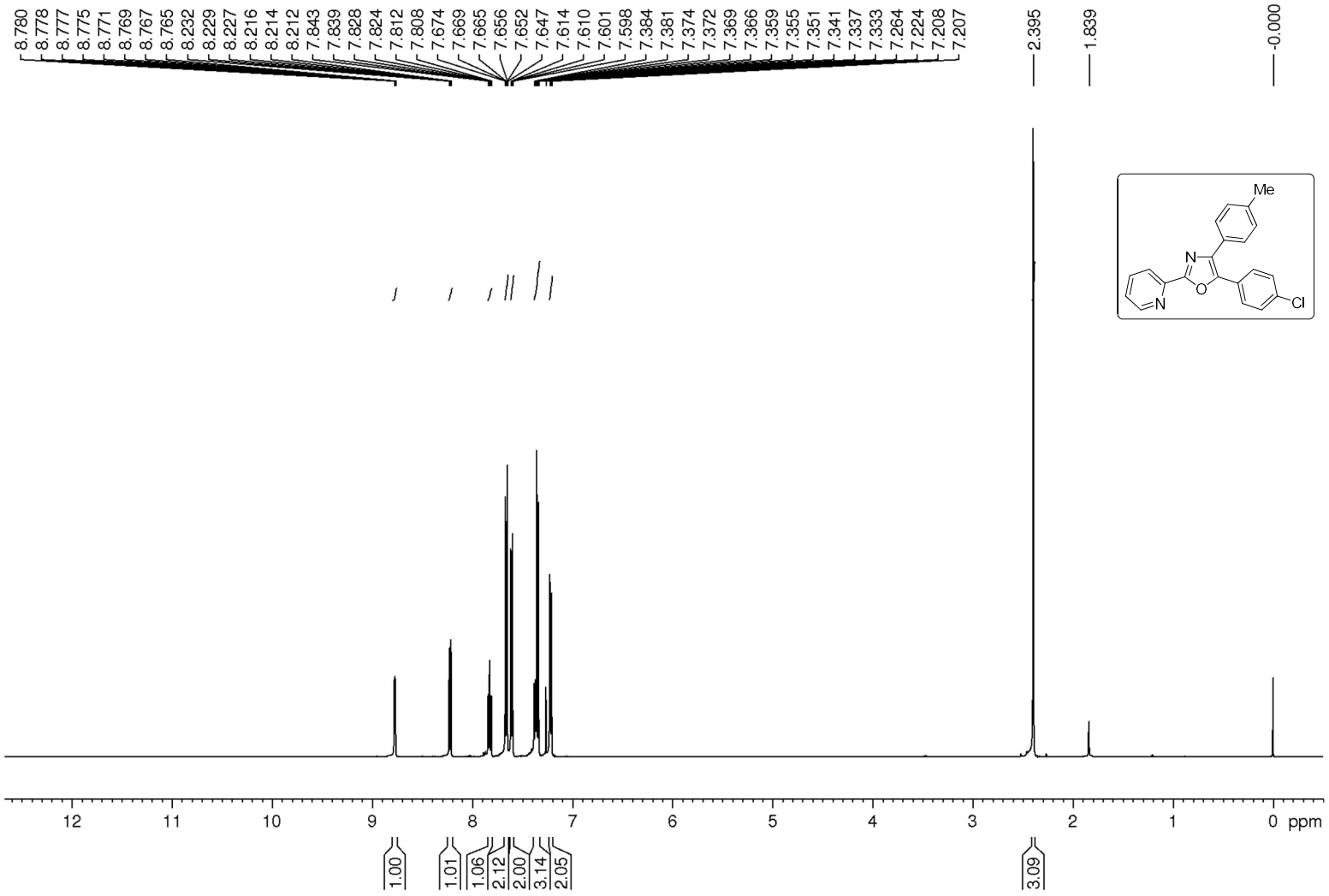
^{13}C NMR Spectrum of 5aeb



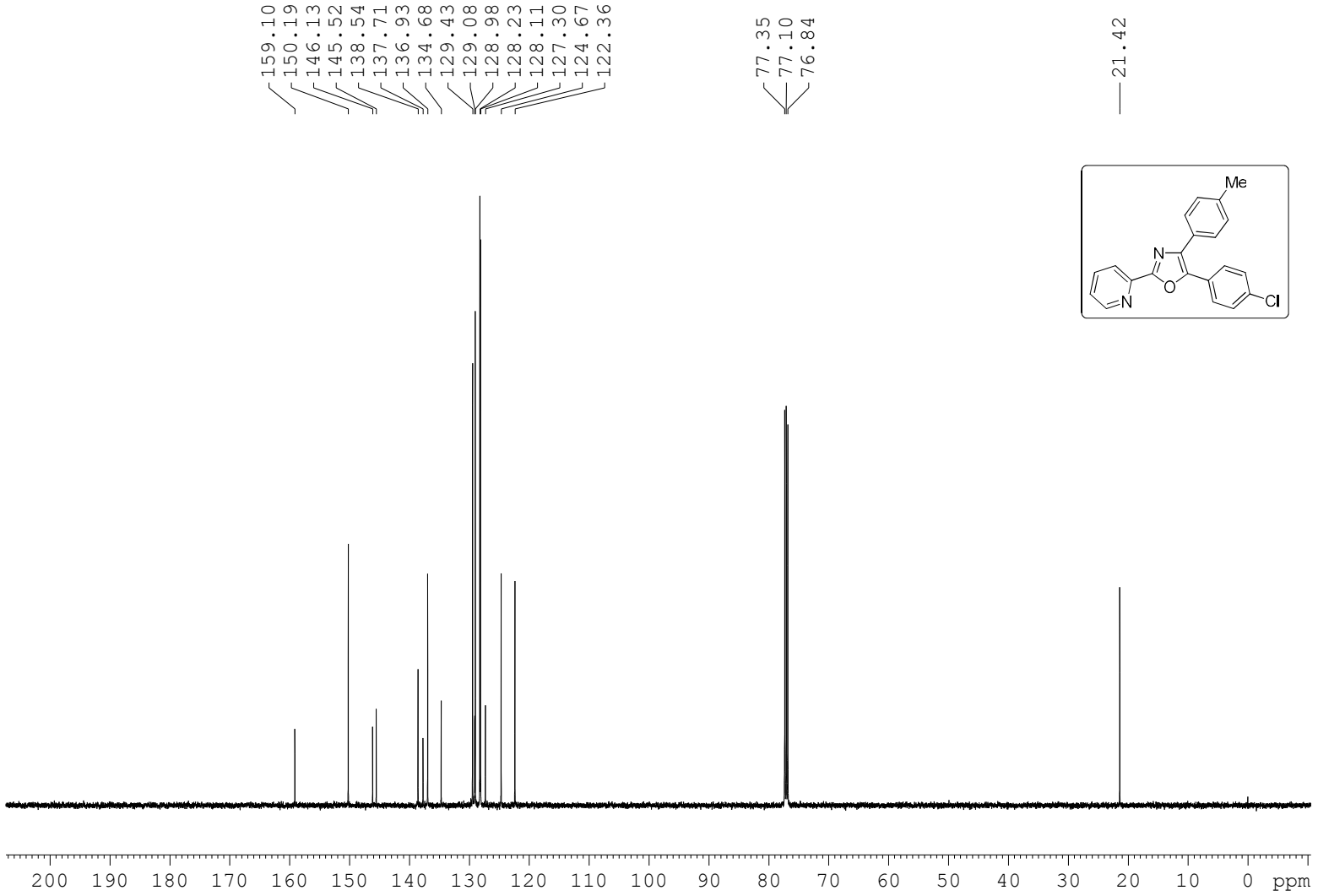
^{19}F NMR Spectrum of 5aeb



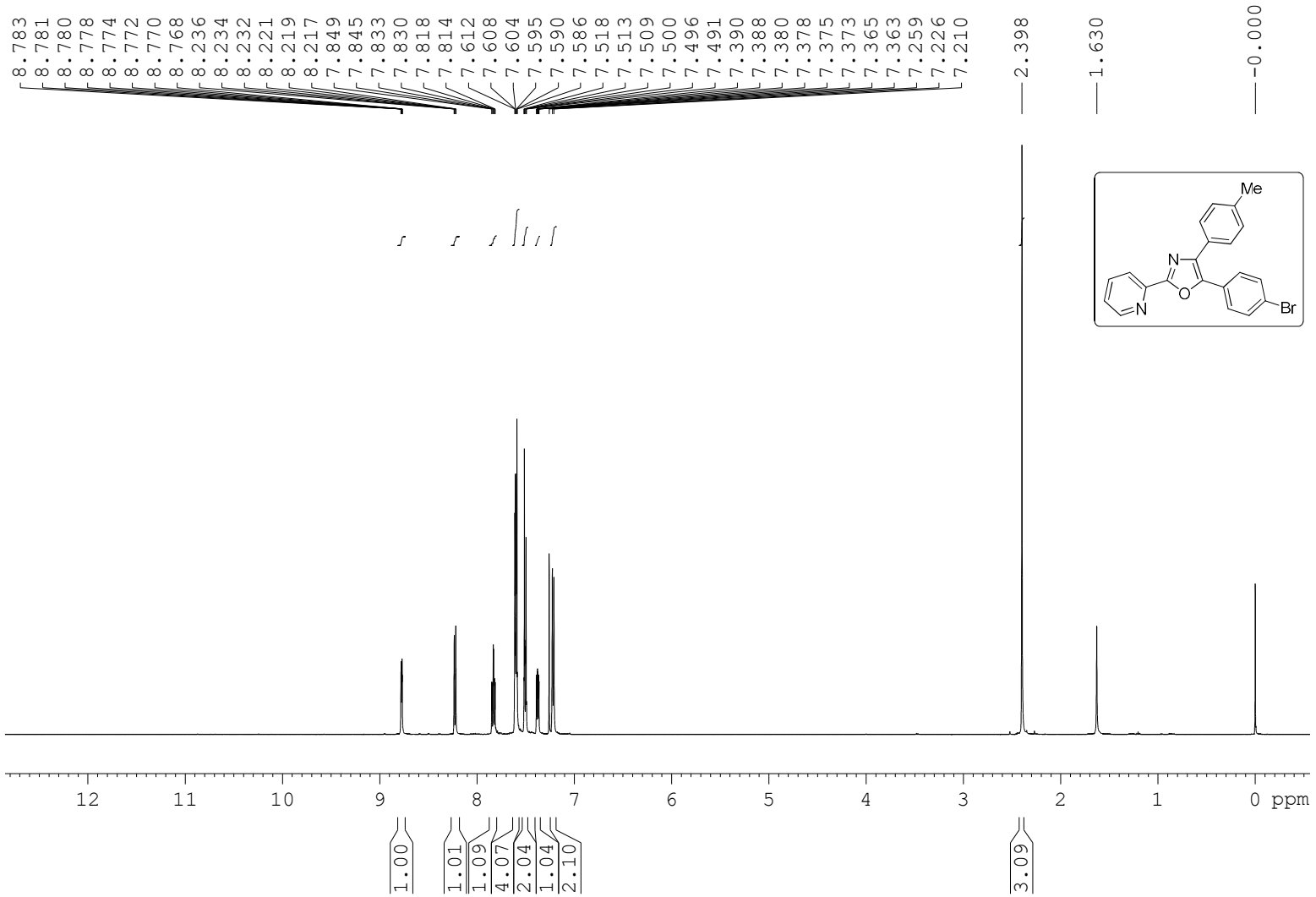
^{1}H NMR Spectrum of 5afb



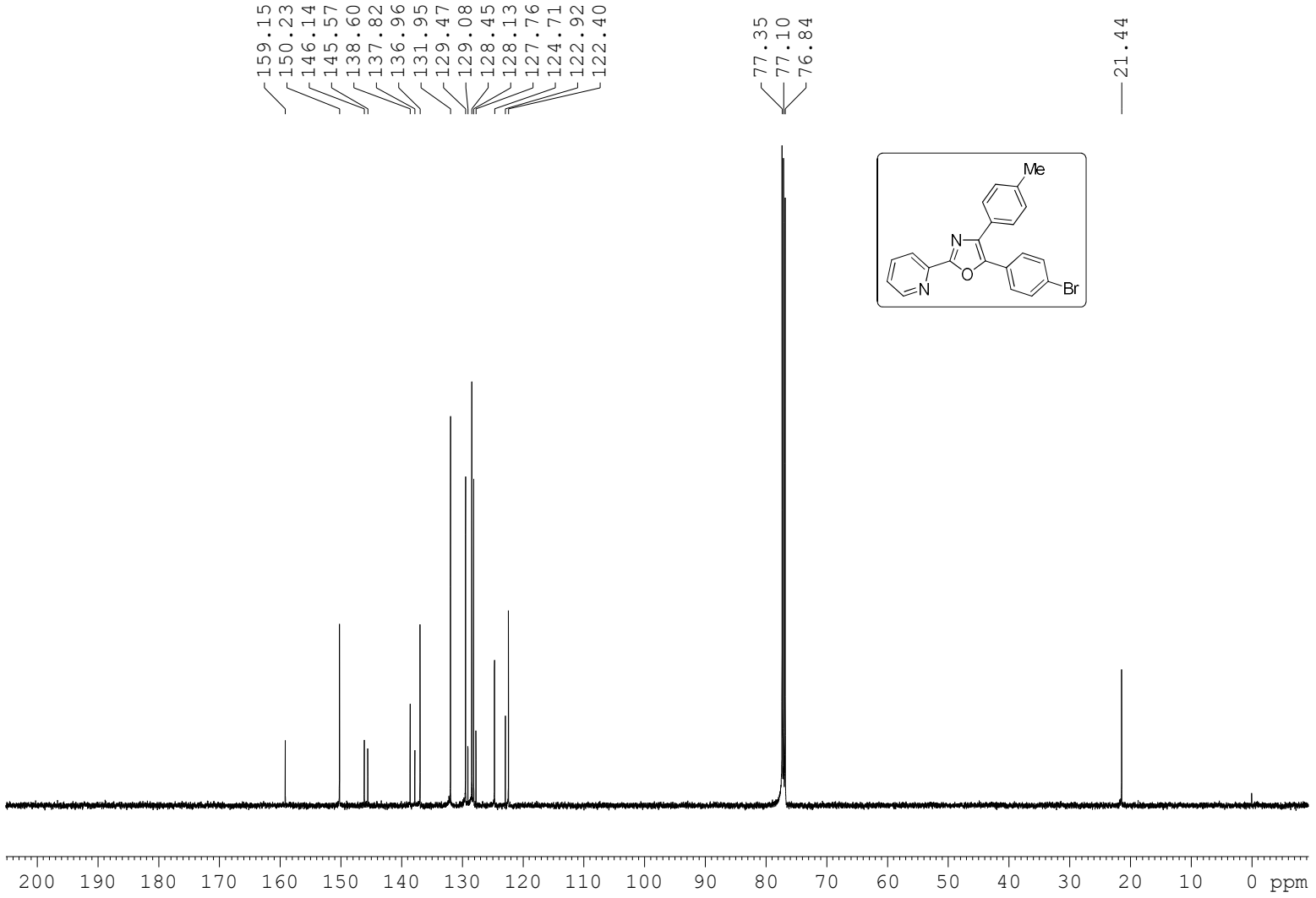
^{13}C NMR Spectrum of 5afb



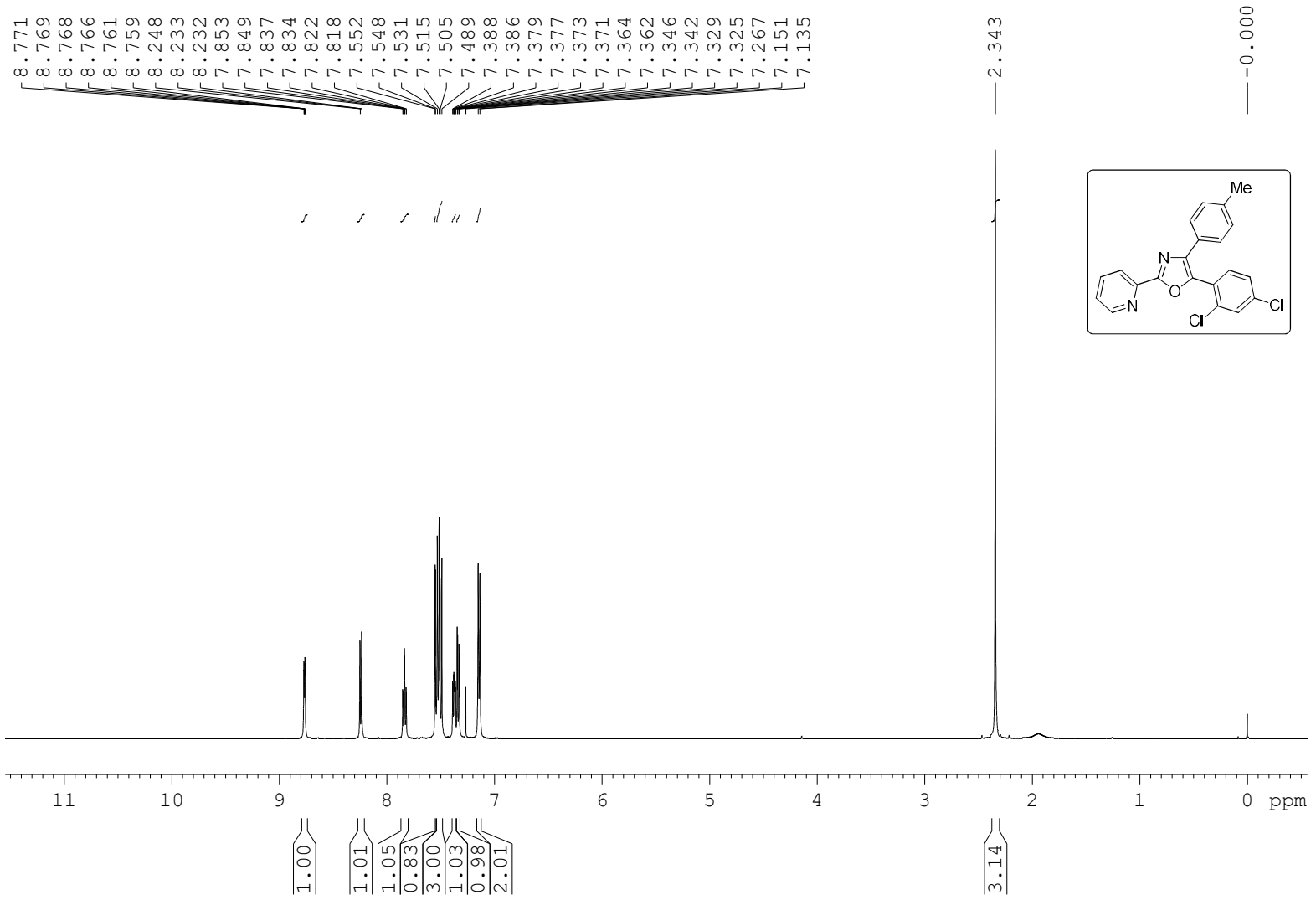
^{1}H NMR Spectrum of 5agb



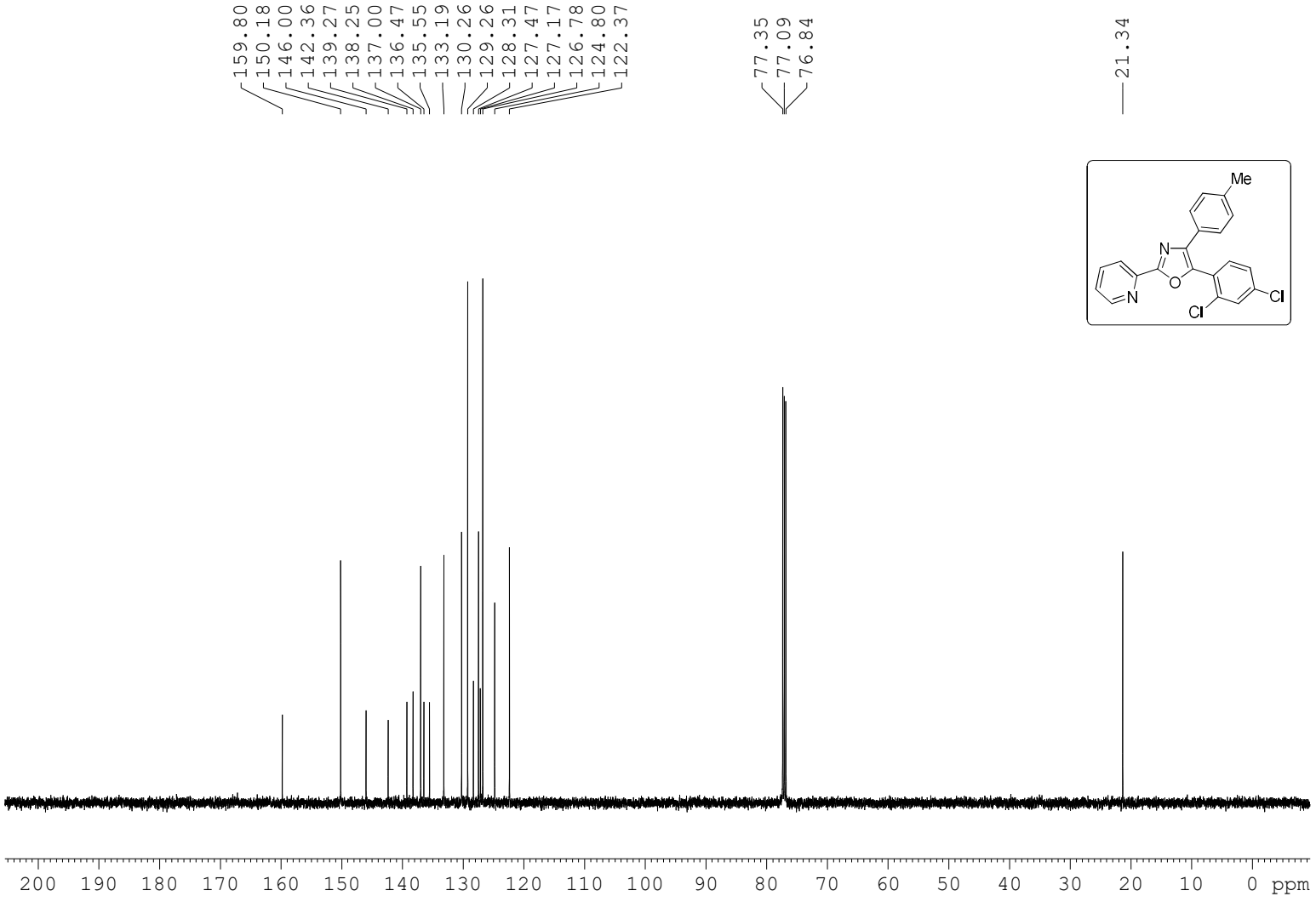
^{13}C NMR Spectrum of 5agb



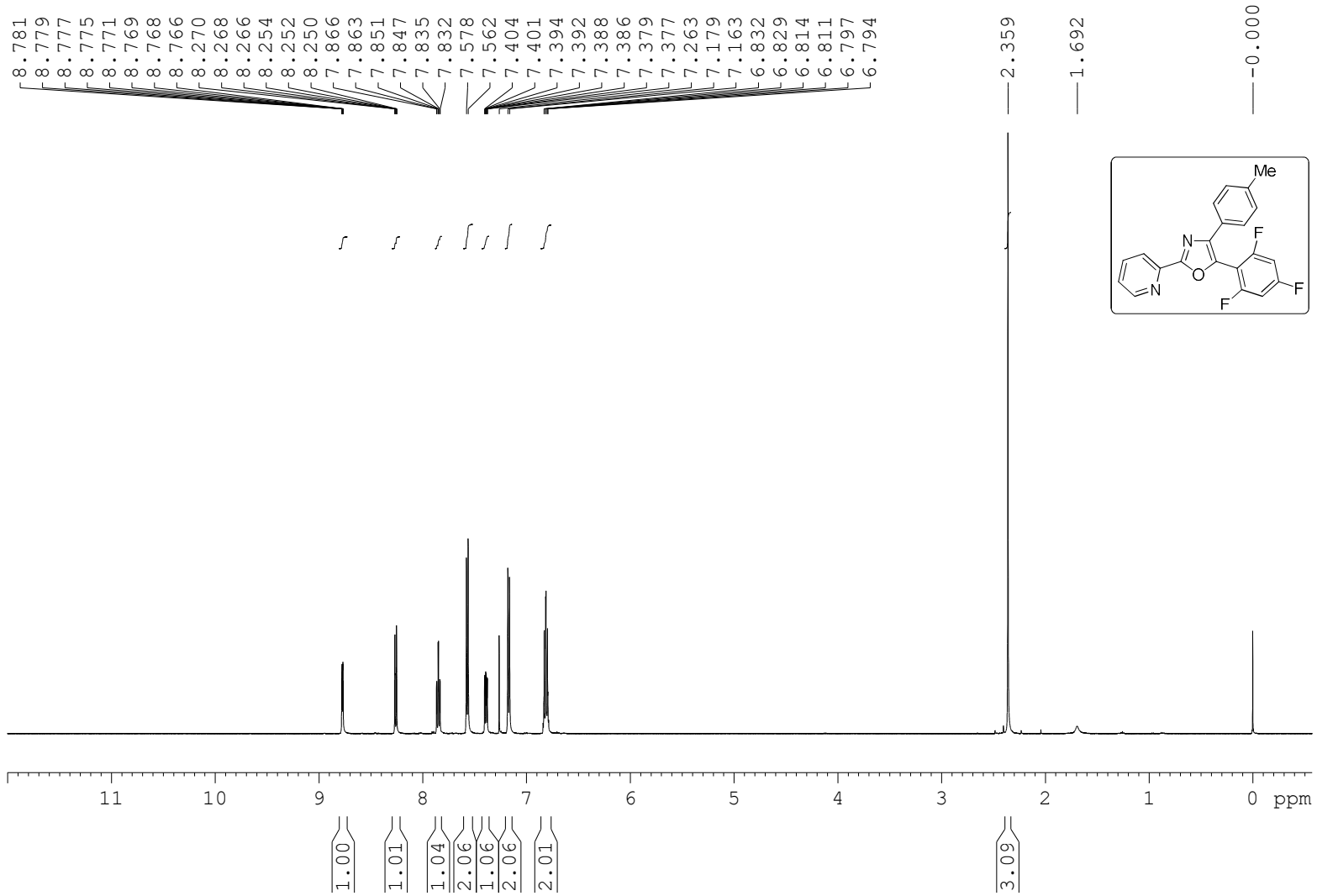
[1]H NMR Spectrum of 5ahb



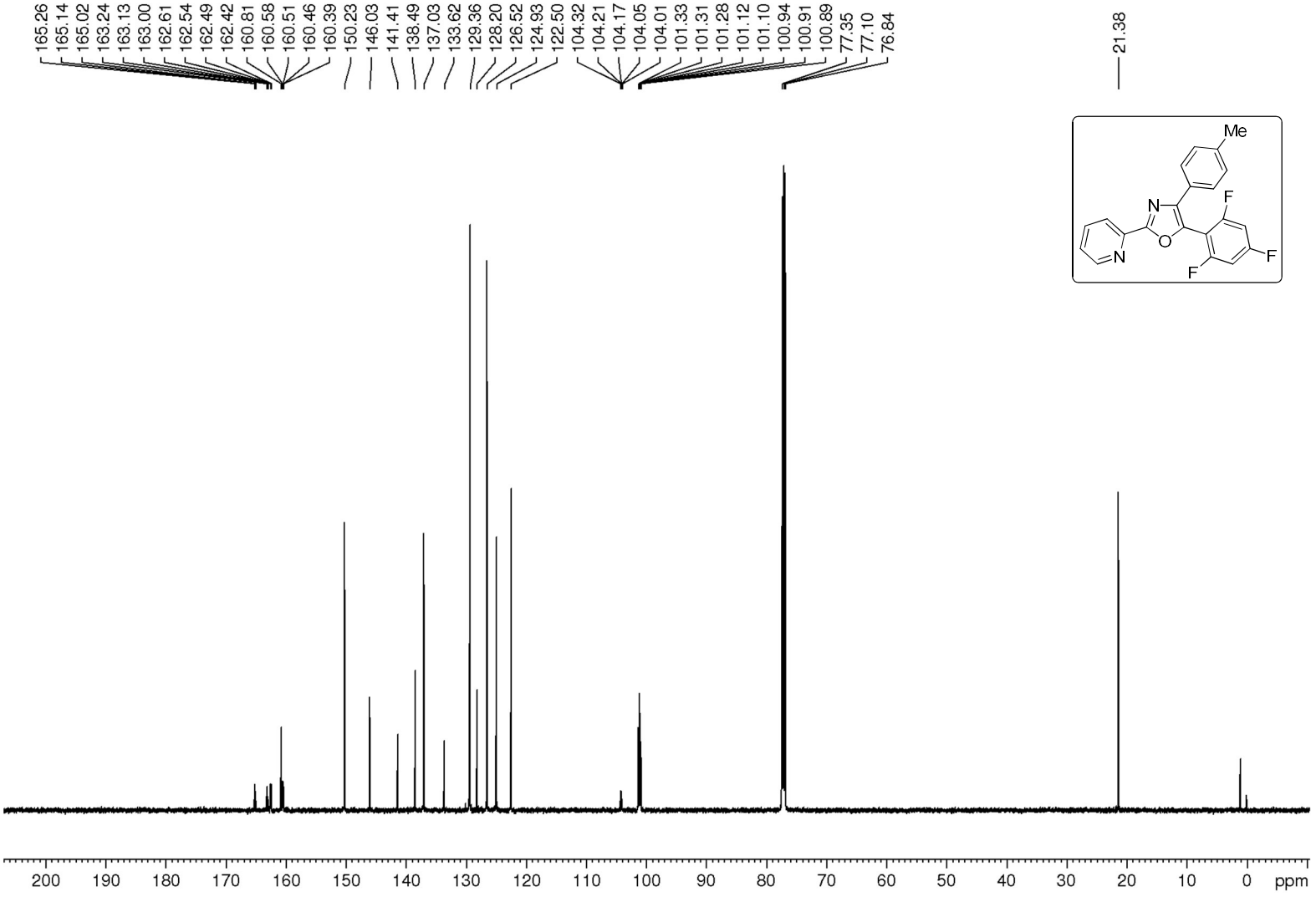
^{13}C NMR Spectrum of 5ahb



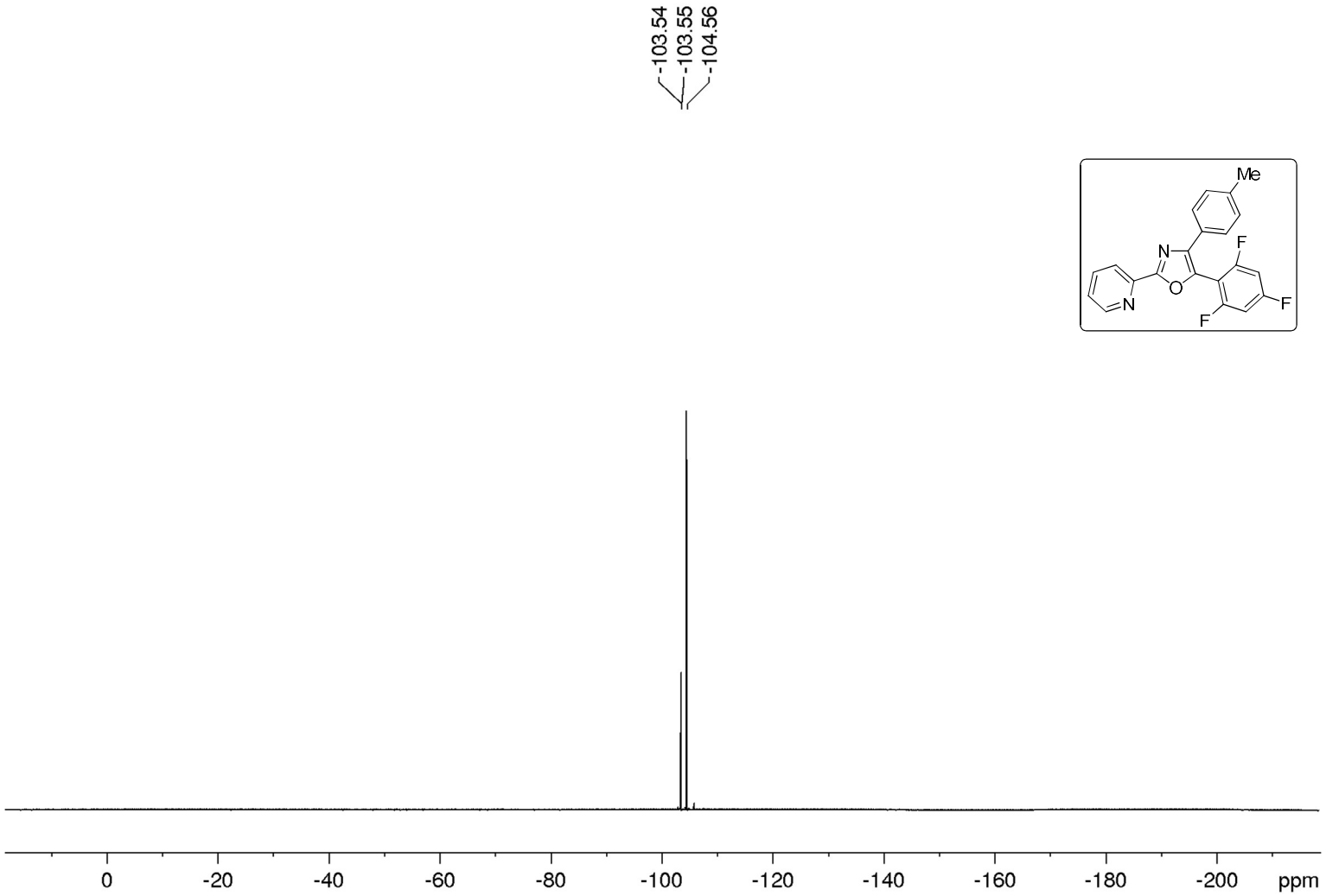
[1]H NMR Spectrum of 5aib



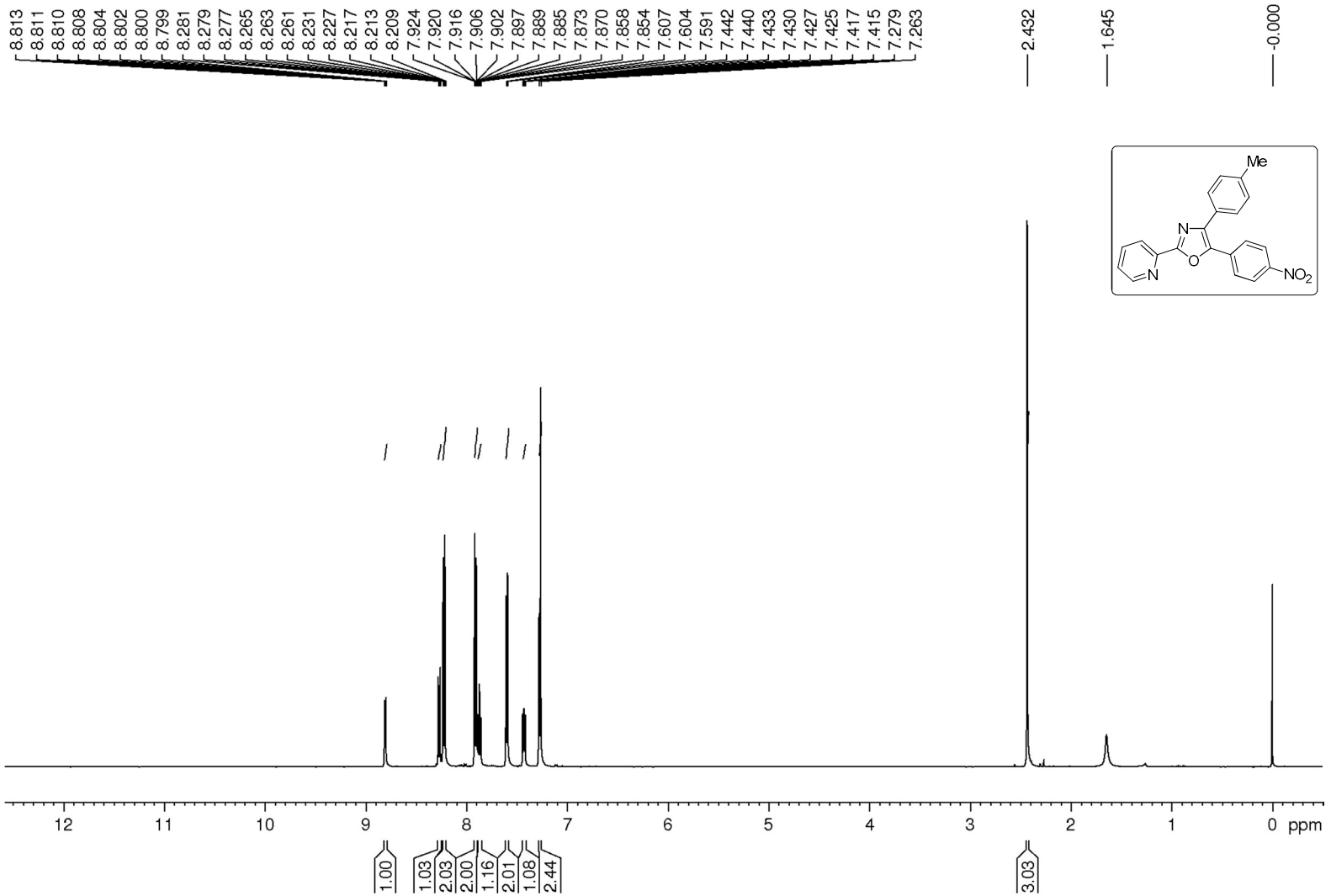
^{13}C NMR Spectrum of 5aib



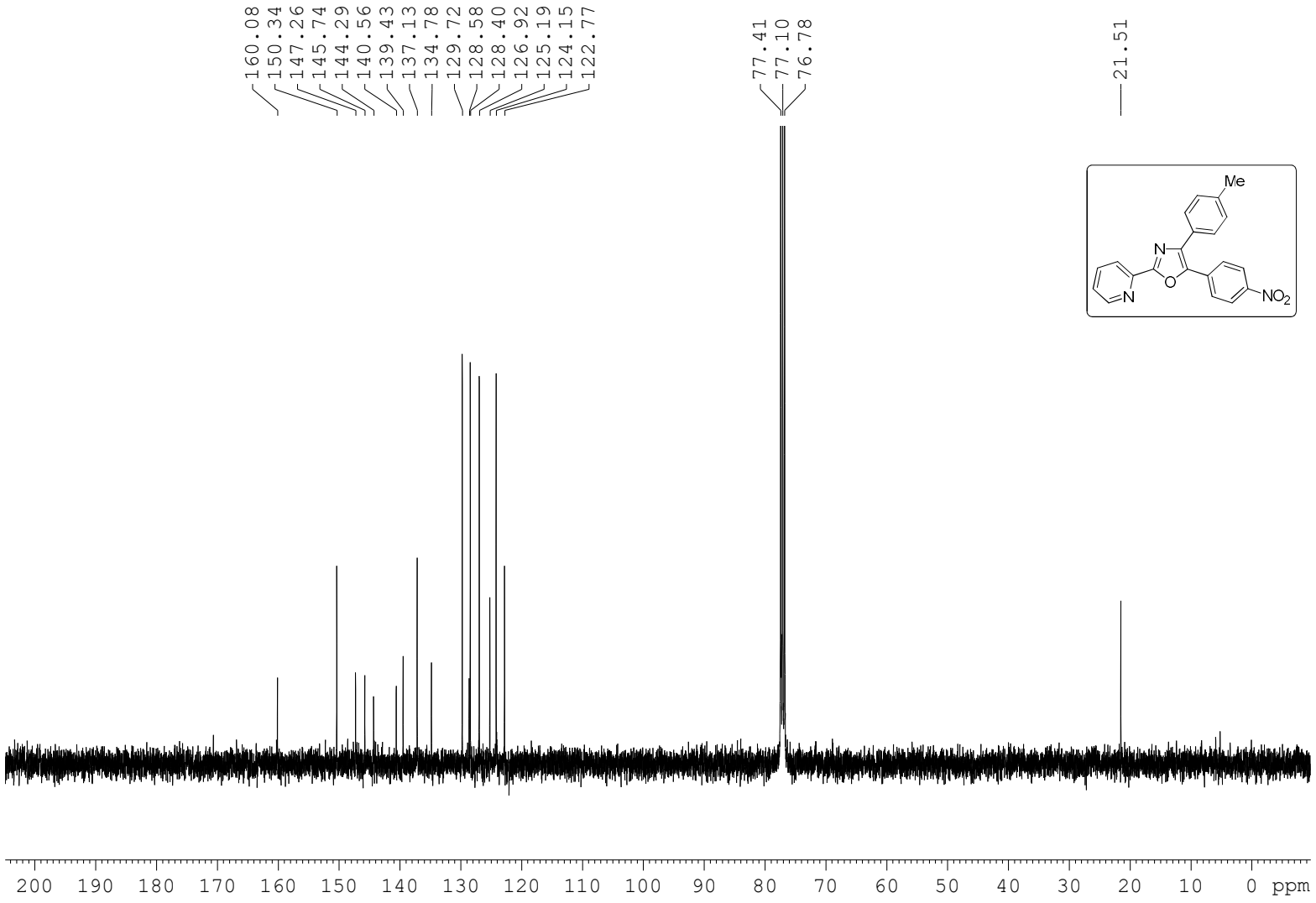
^{19}F NMR Spectrum of 5aib



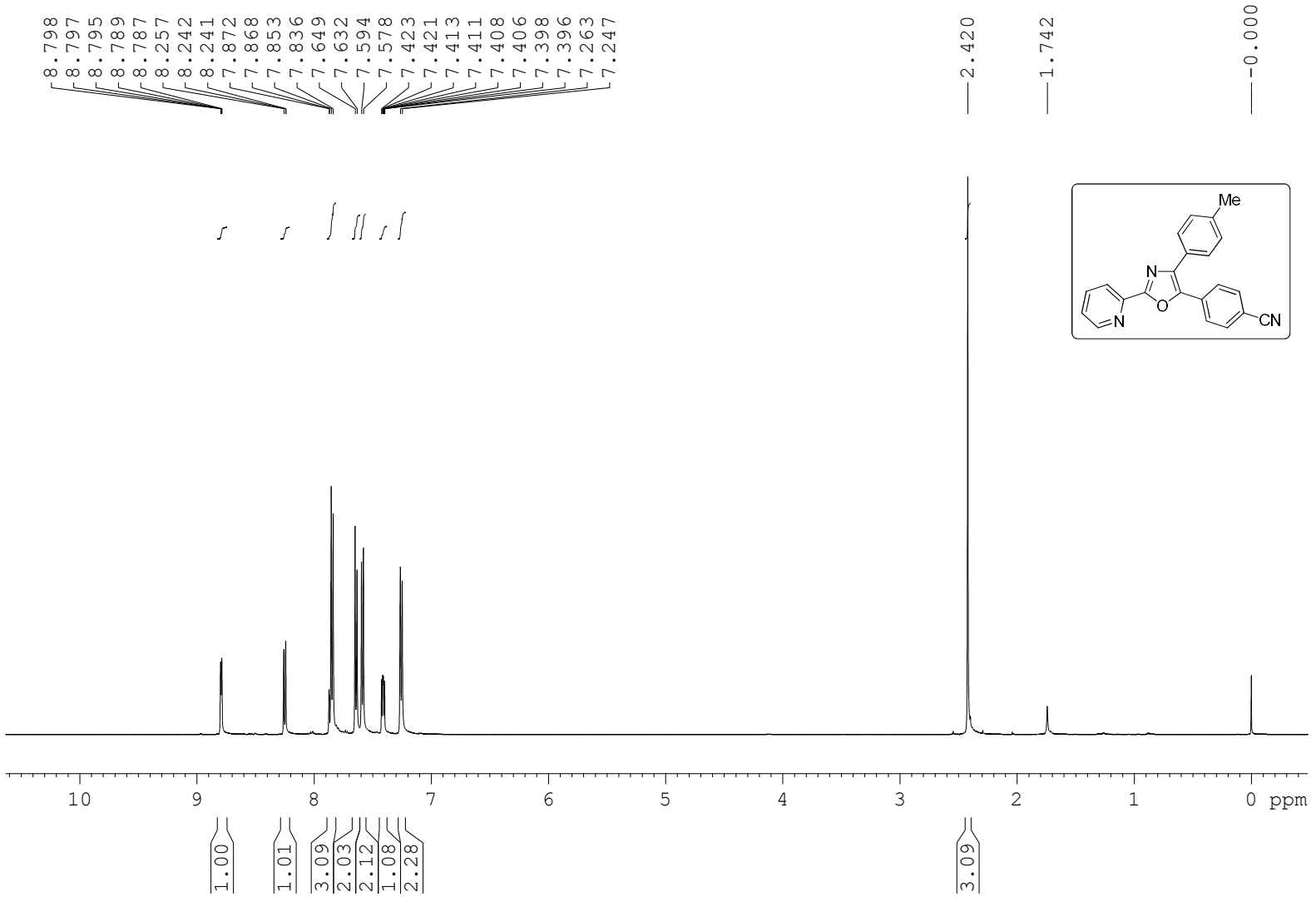
^{1}H NMR Spectrum of 5ajb



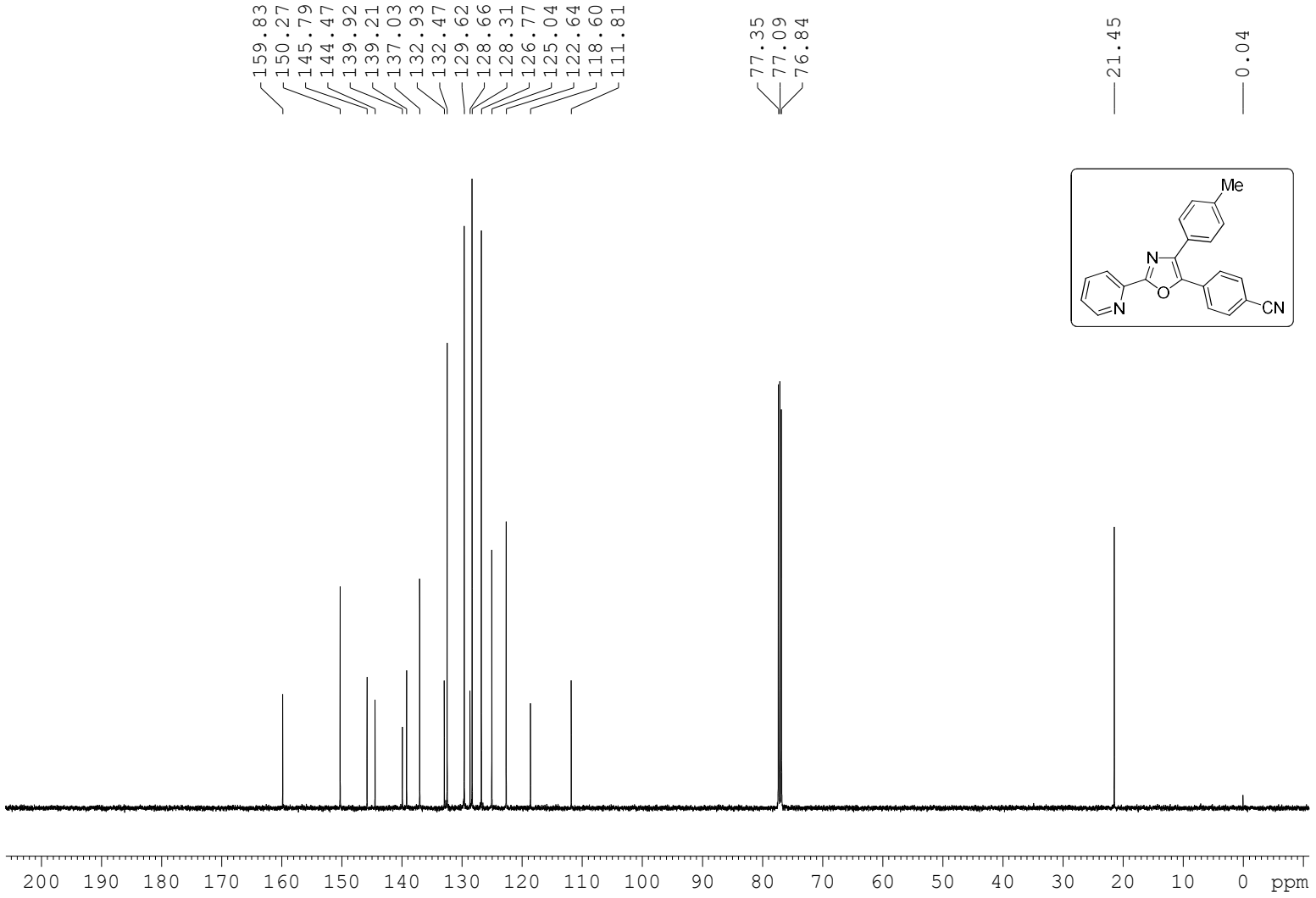
^{13}C NMR Spectrum of 5ajb



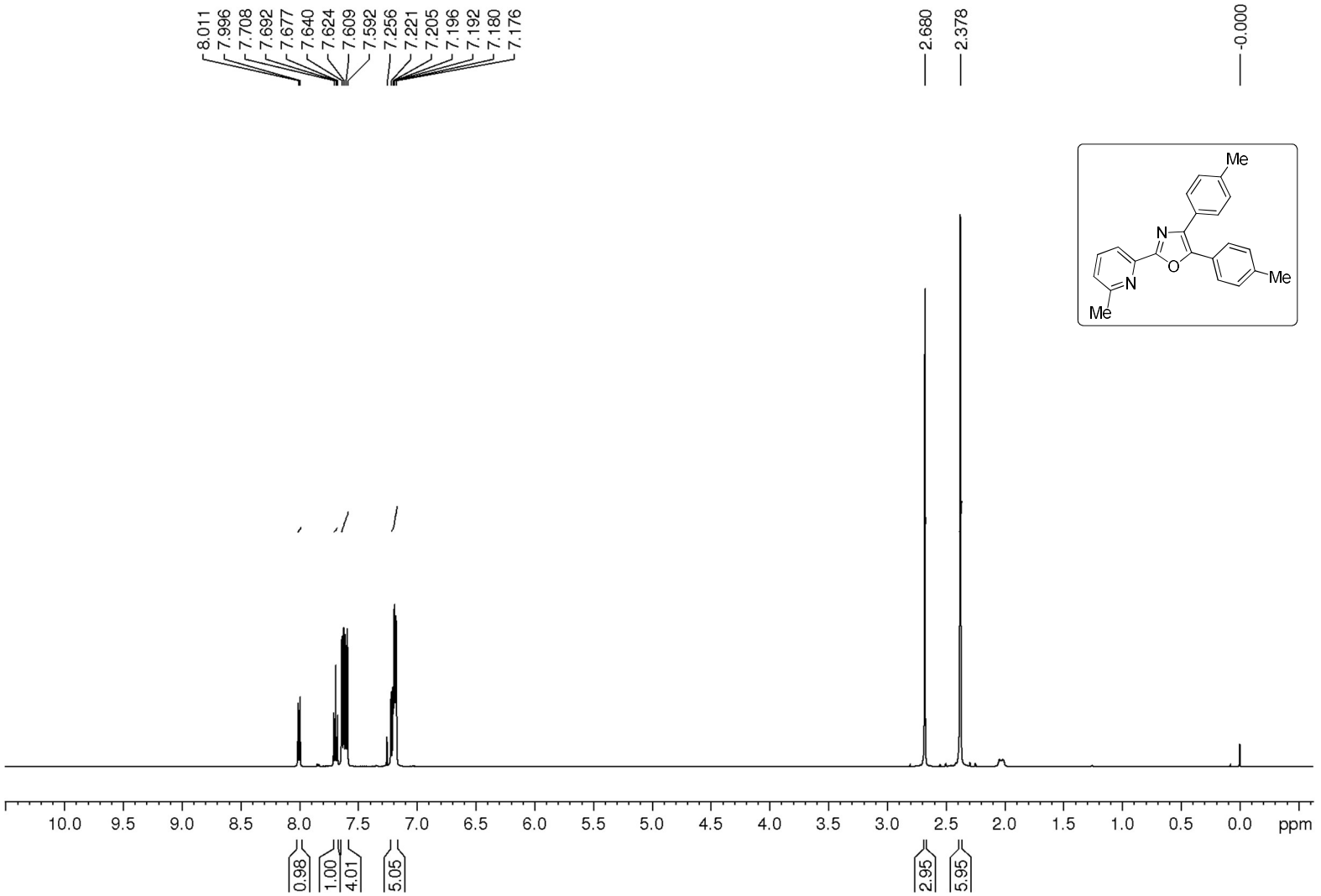
^{1}H NMR Spectrum of 5akb



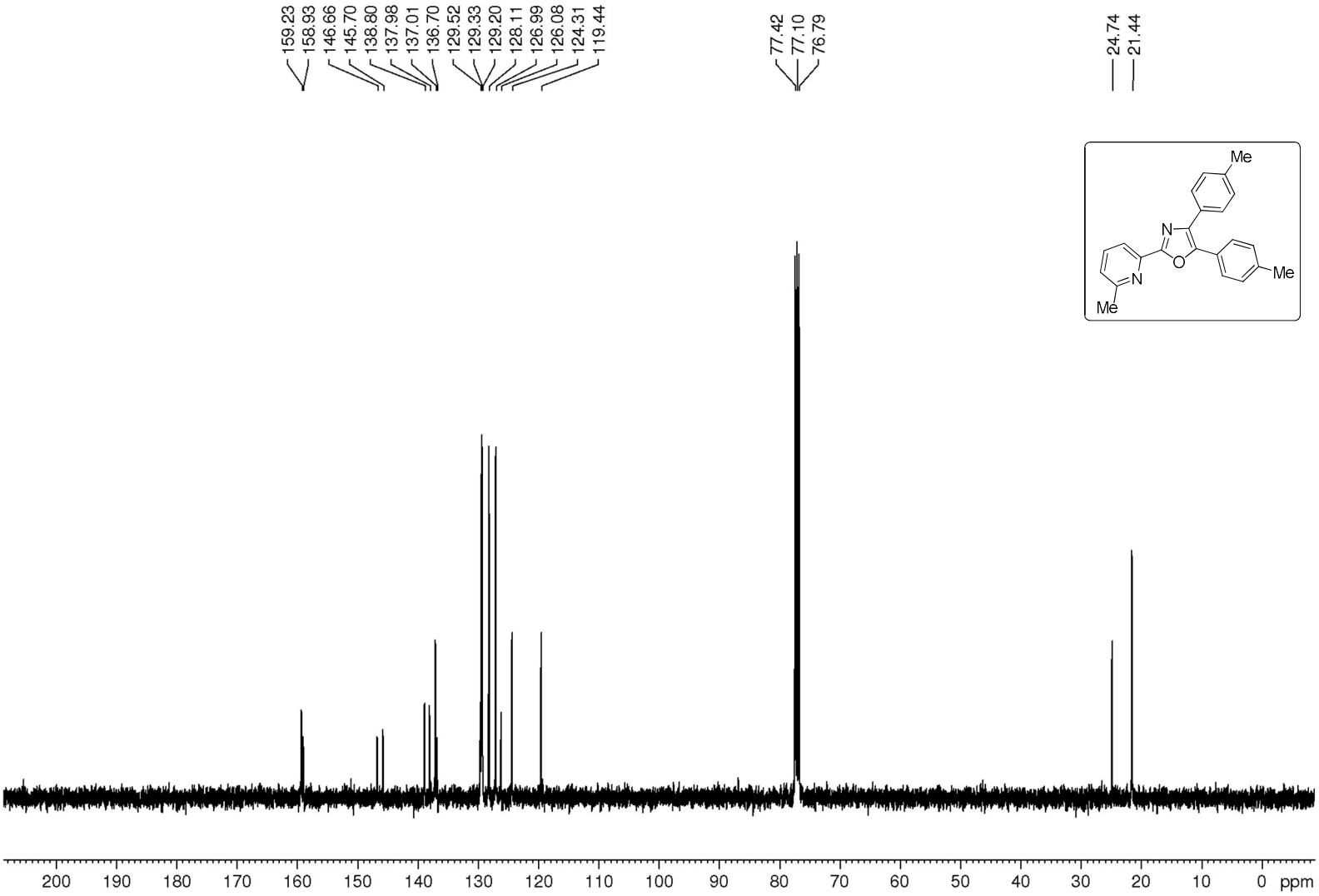
^{13}C NMR Spectrum of 5akb



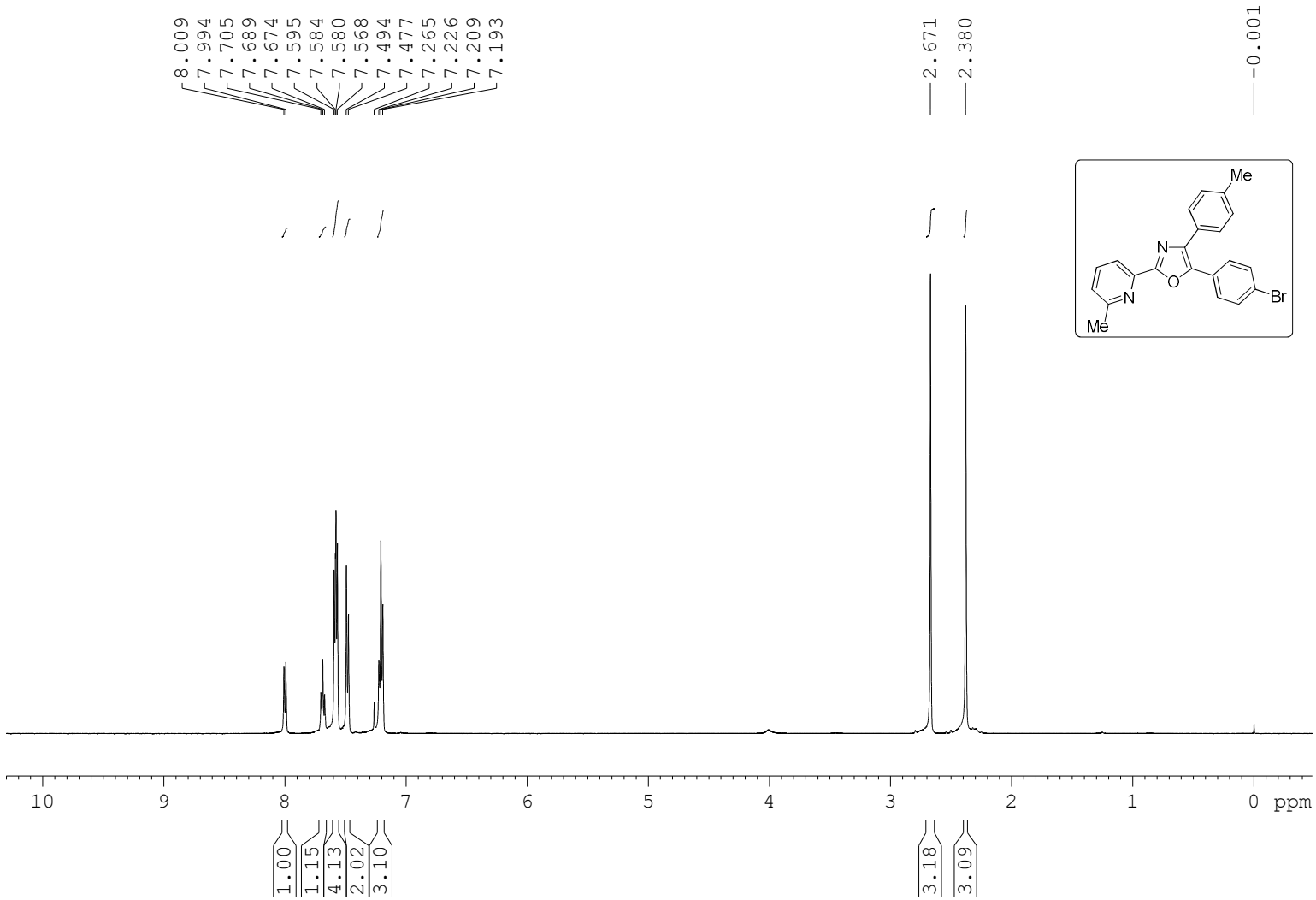
[1]H NMR Spectrum of 5bbb



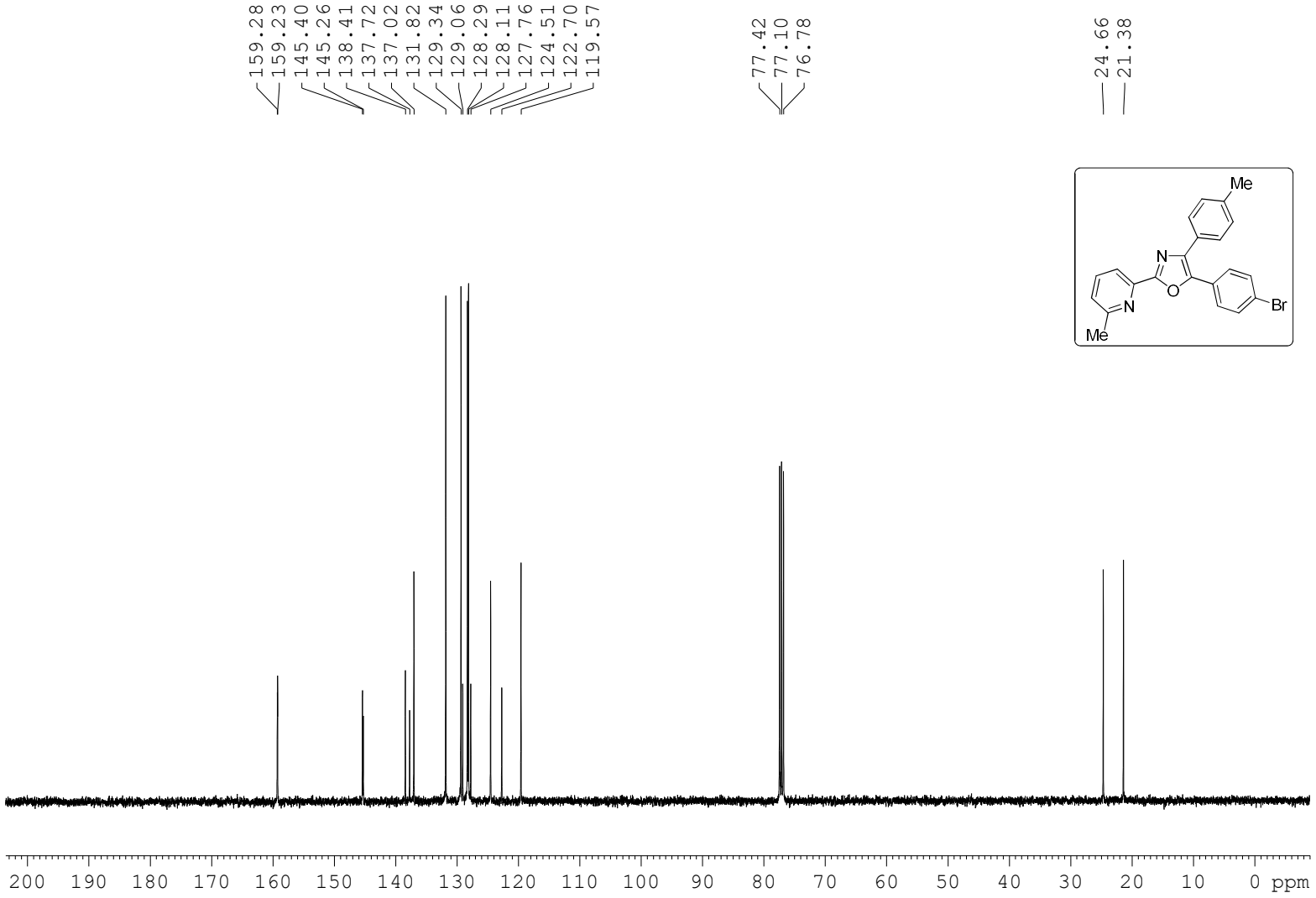
^{13}C NMR Spectrum of 5bbb



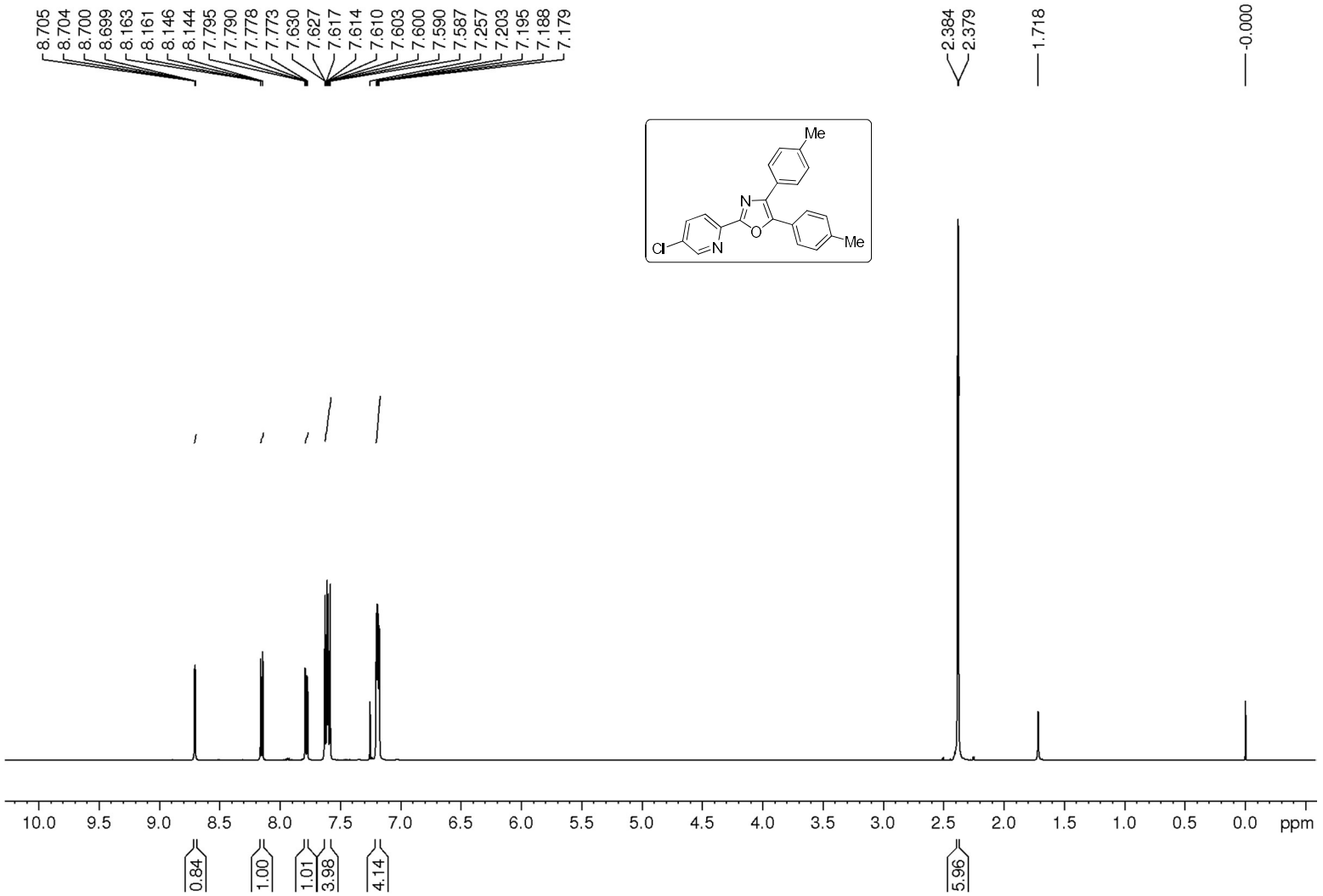
^{1}H NMR Spectrum of 5bgb



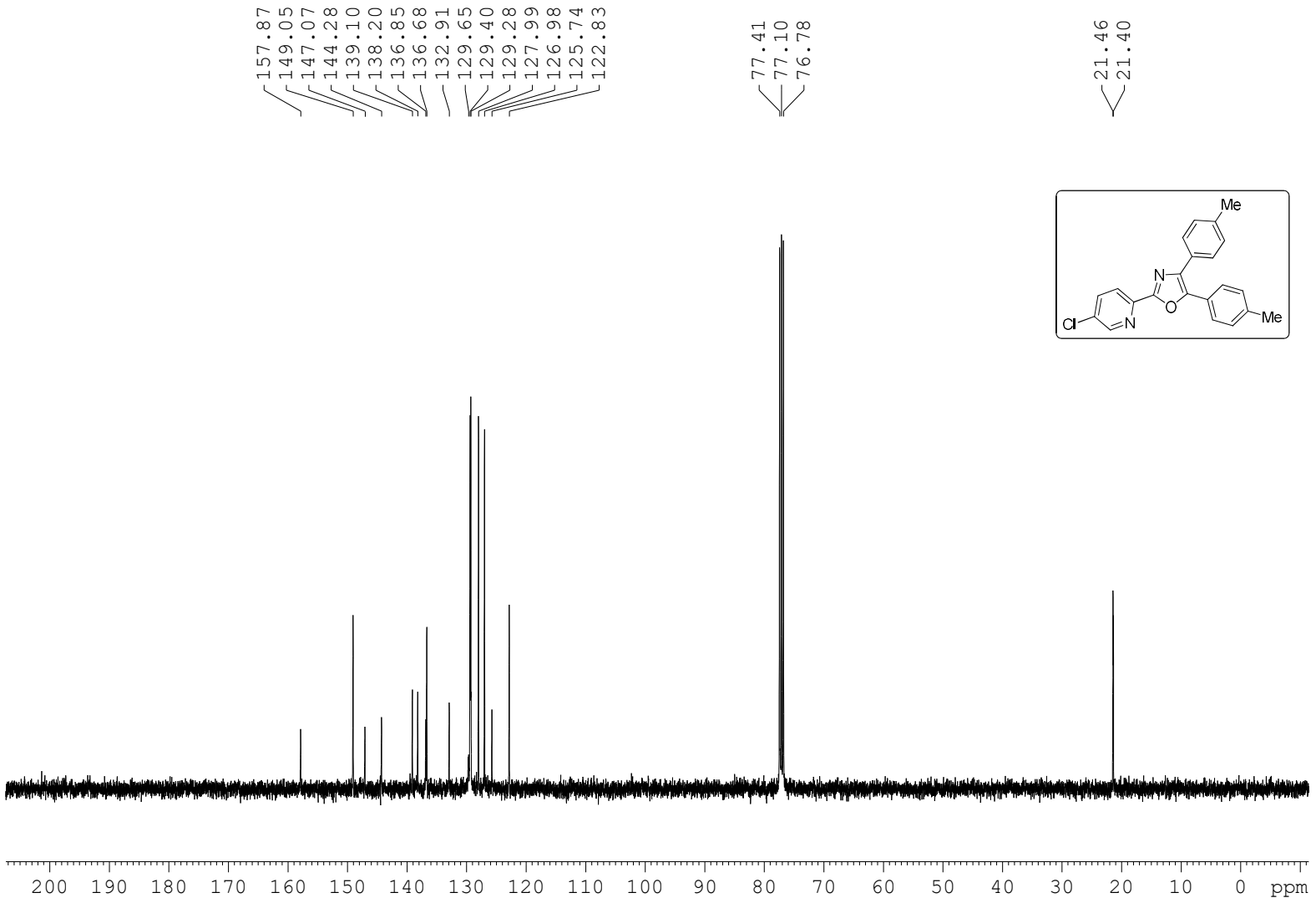
^{13}C NMR Spectrum of 5bgb



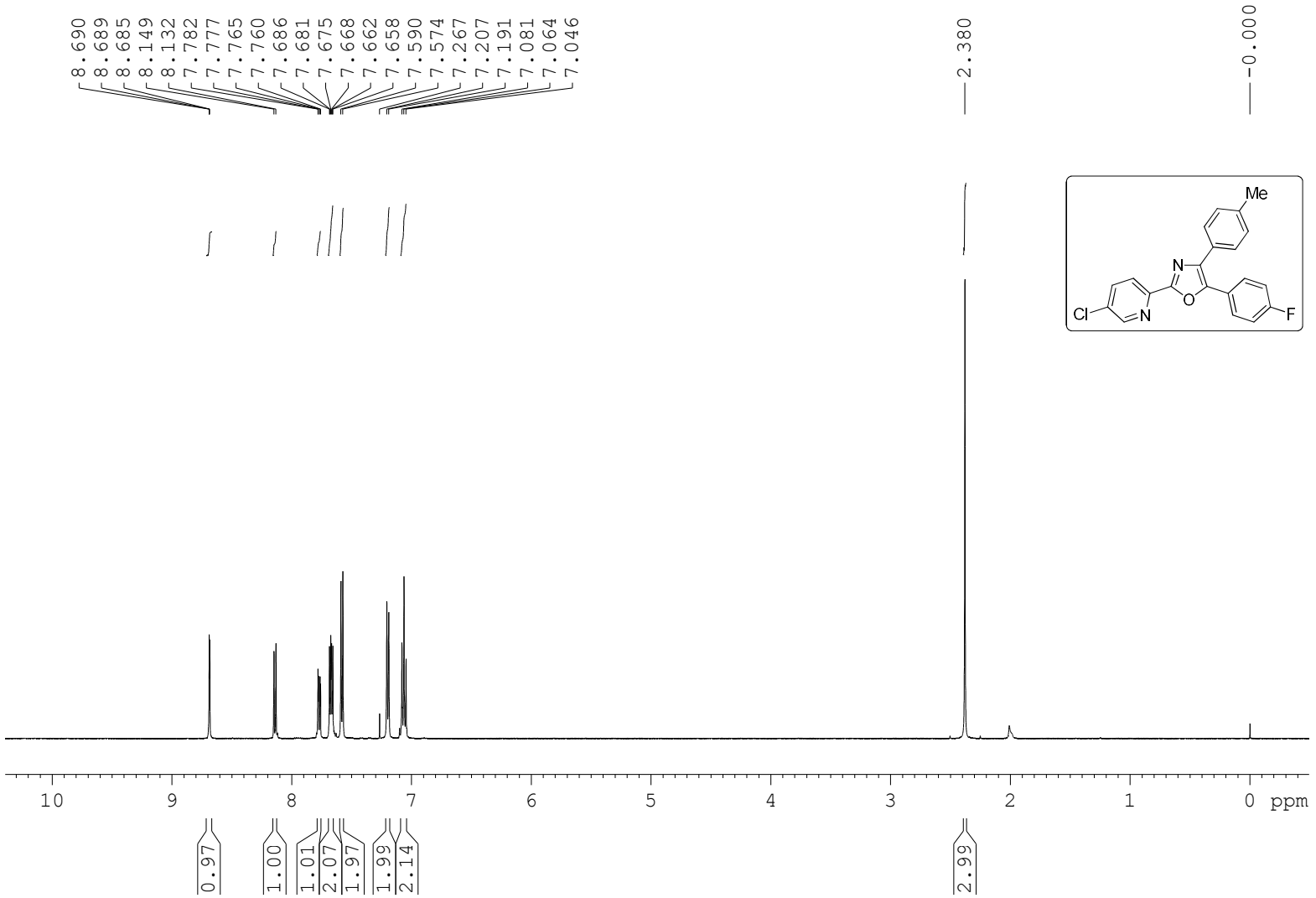
^{1}H NMR Spectrum of 5dbb



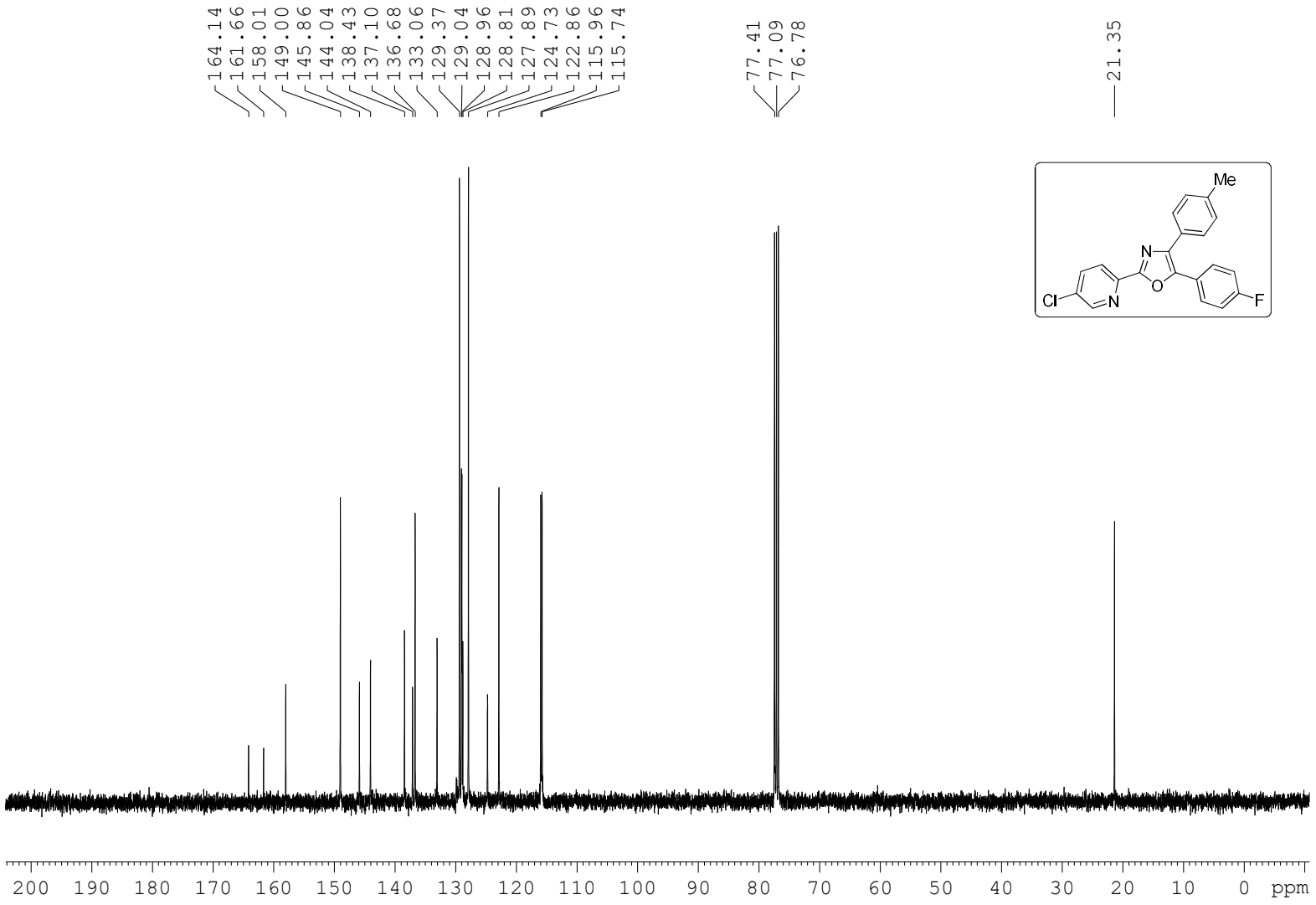
^{13}C NMR Spectrum of 5dbb



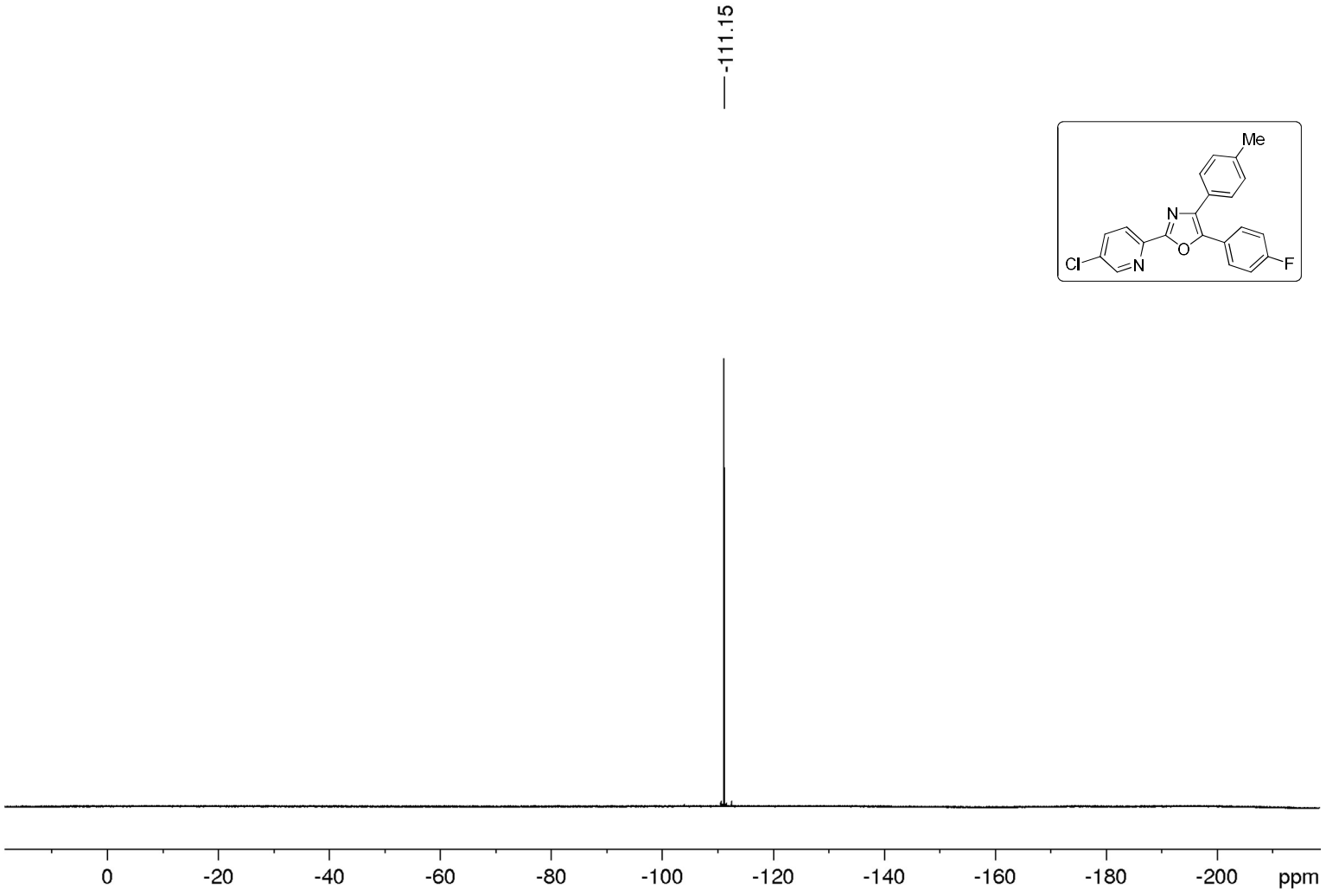
^{1}H NMR Spectrum of 5deb



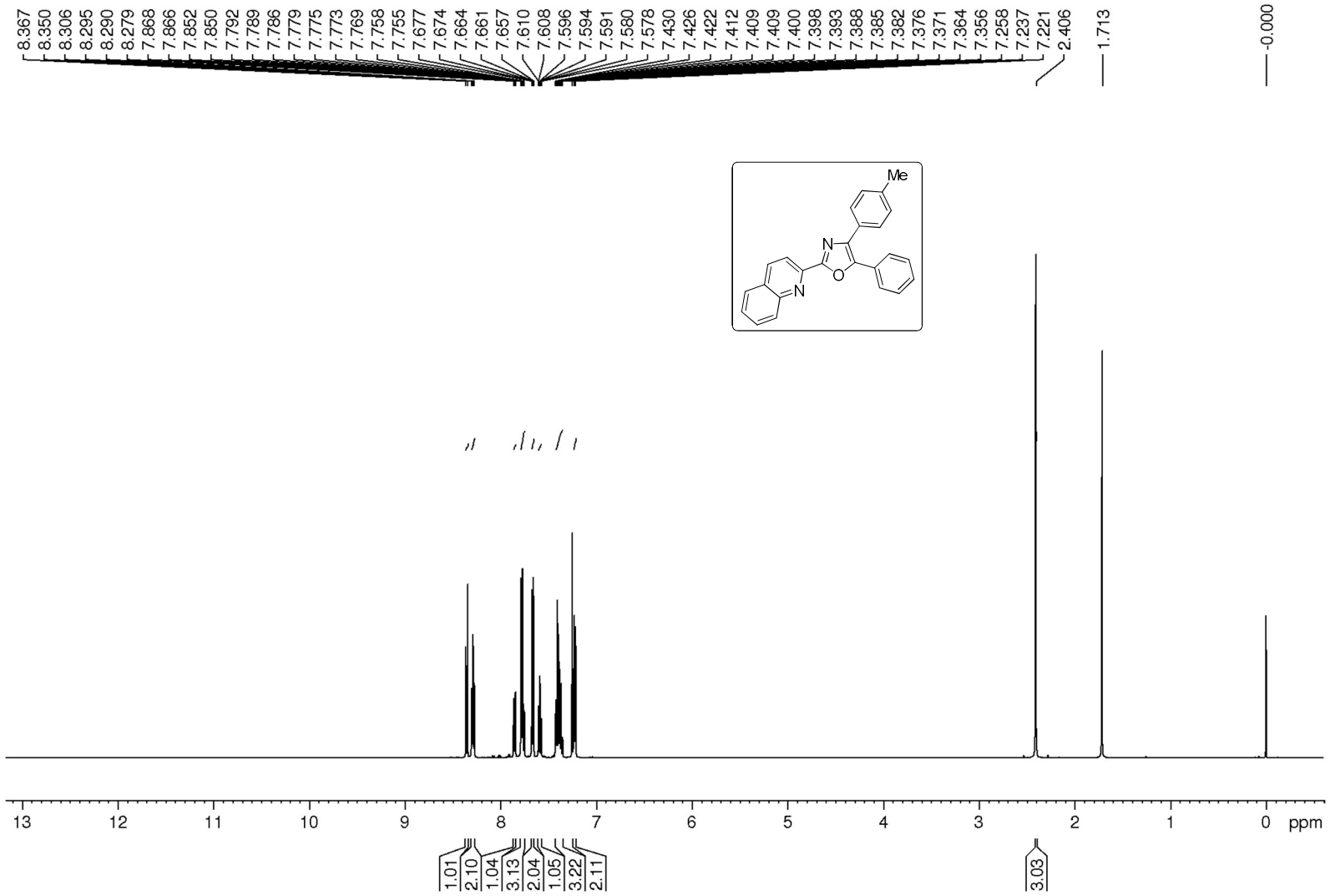
^{13}C NMR Spectrum of 5deb



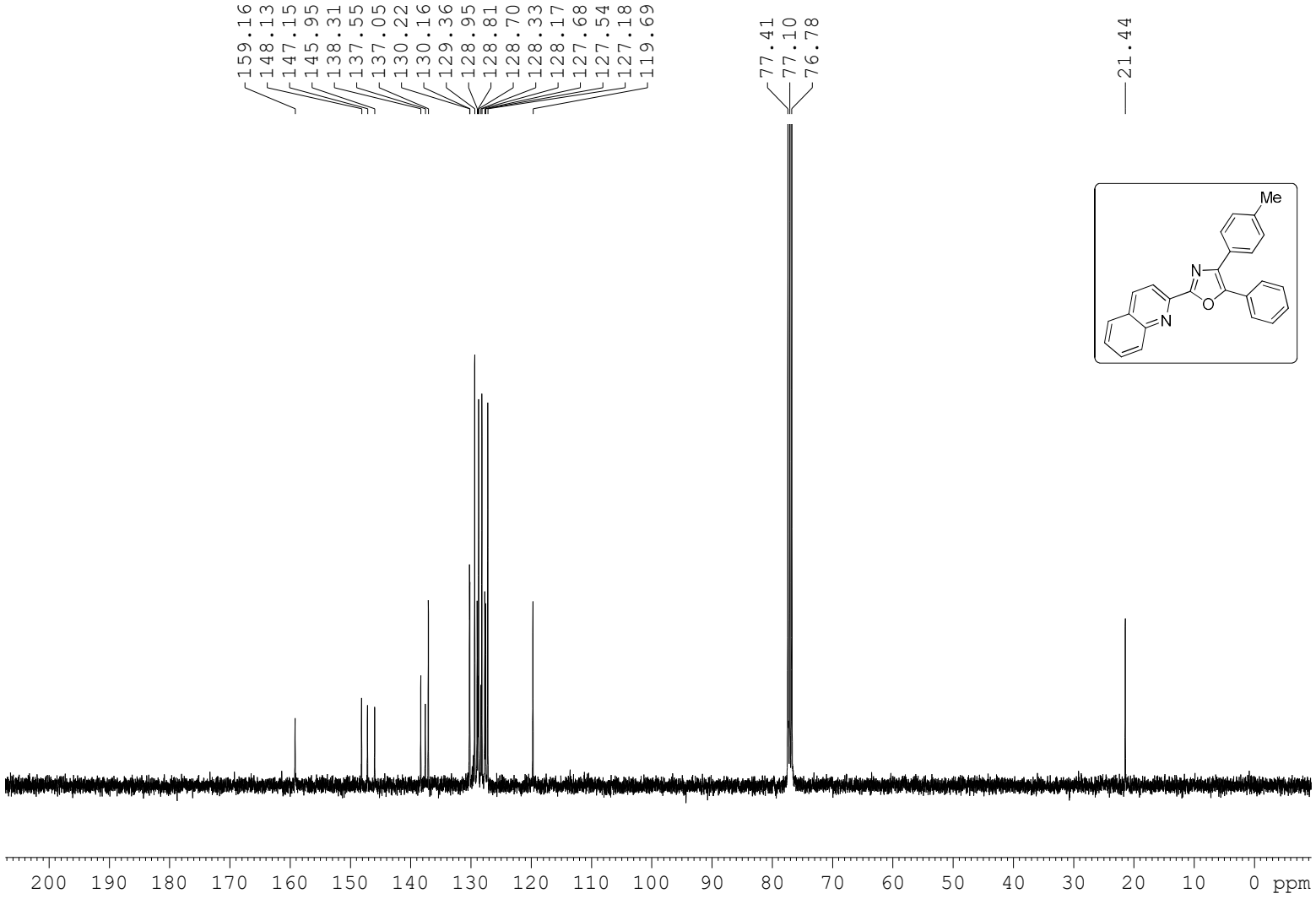
^{19}F NMR Spectrum of 5deb



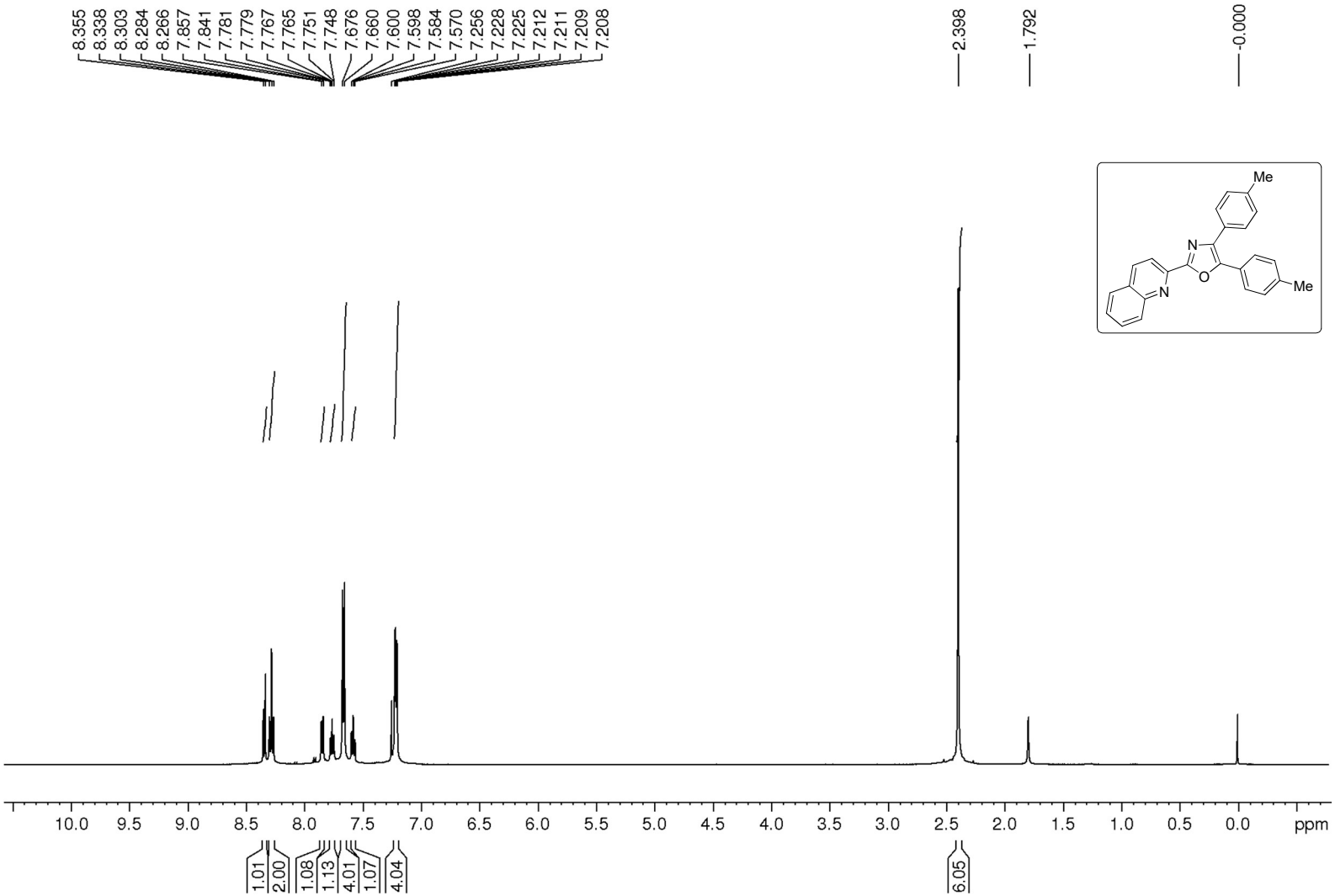
[1]H NMR Spectrum of 5eab



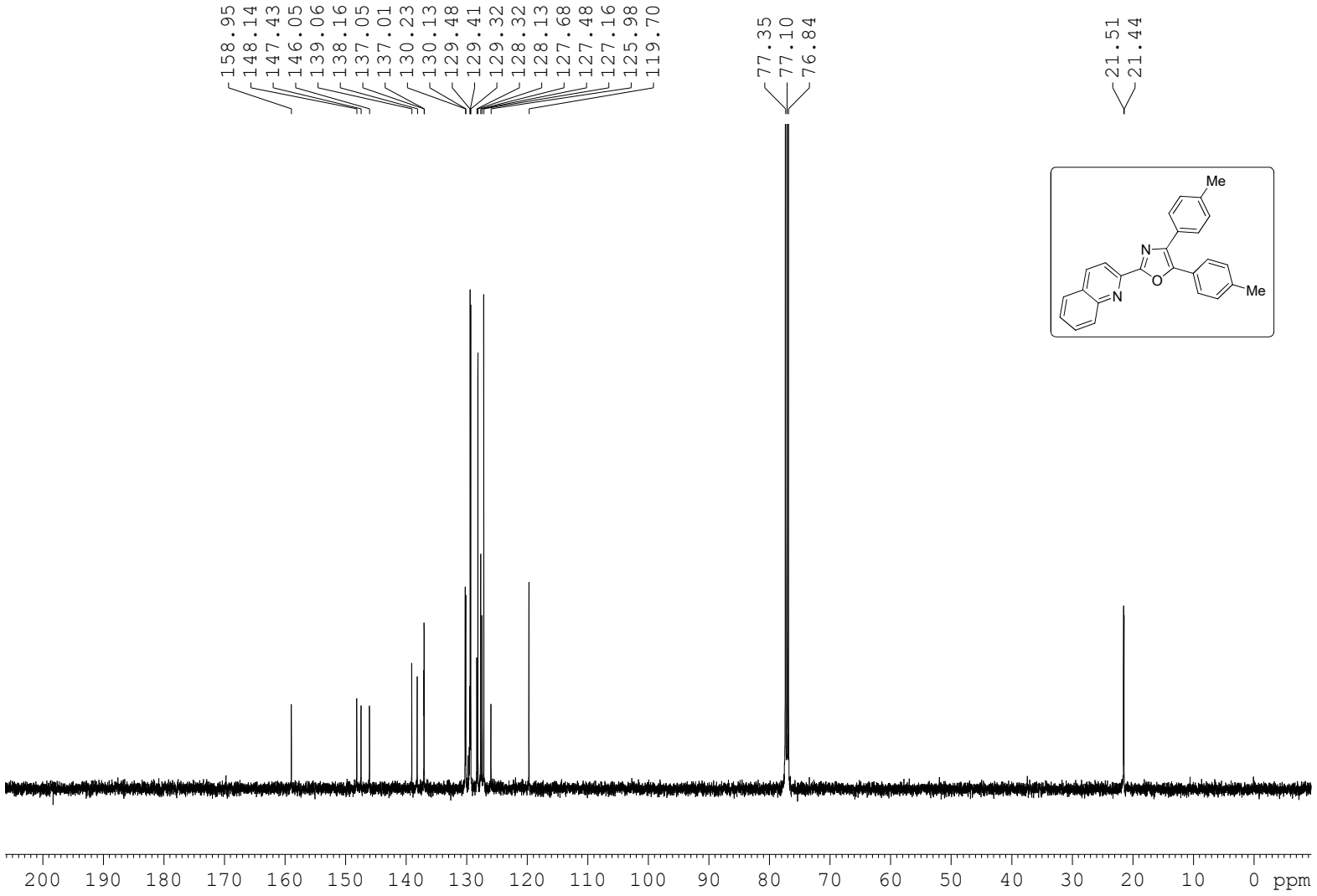
^{13}C NMR Spectrum of 5eab



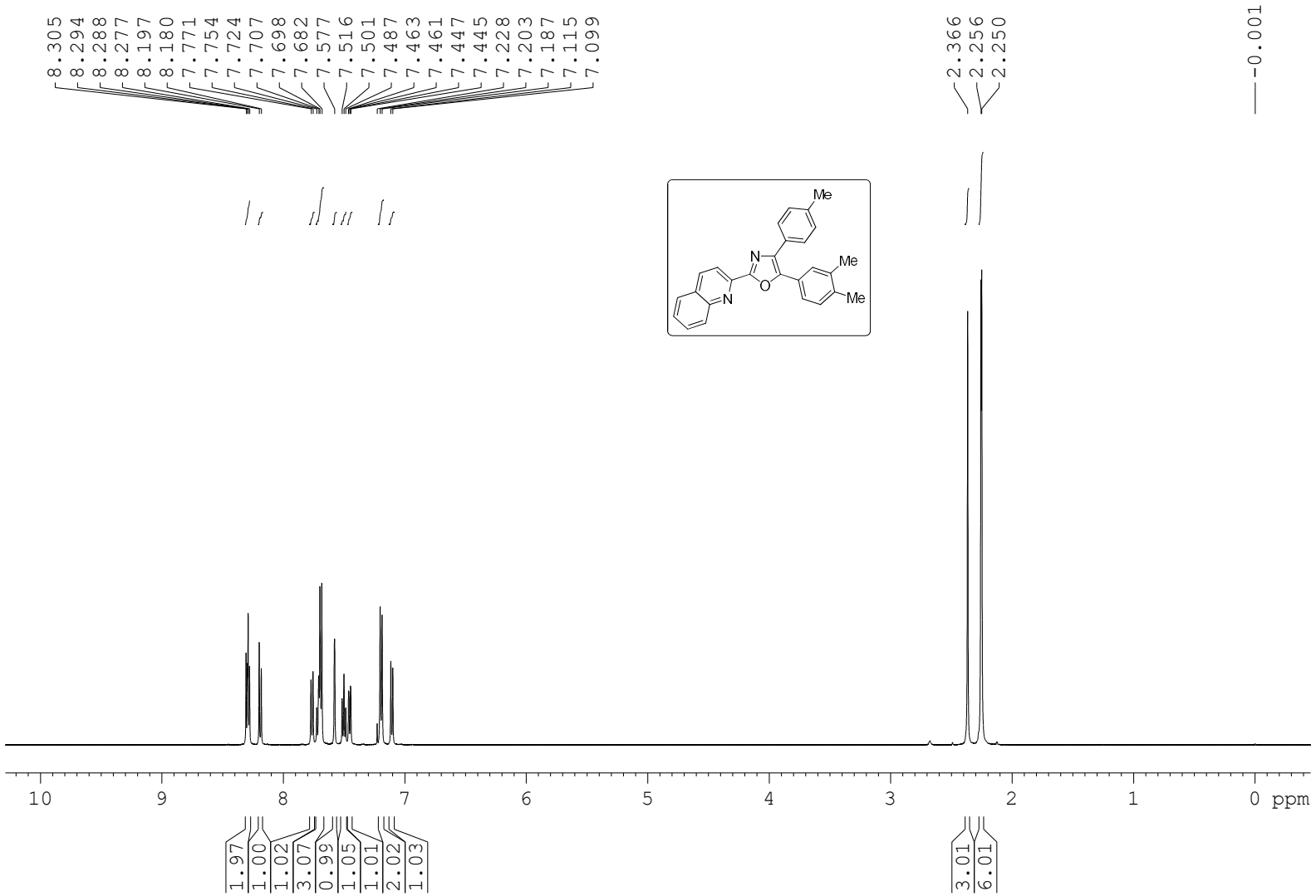
^{1}H NMR Spectrum of 5ebb



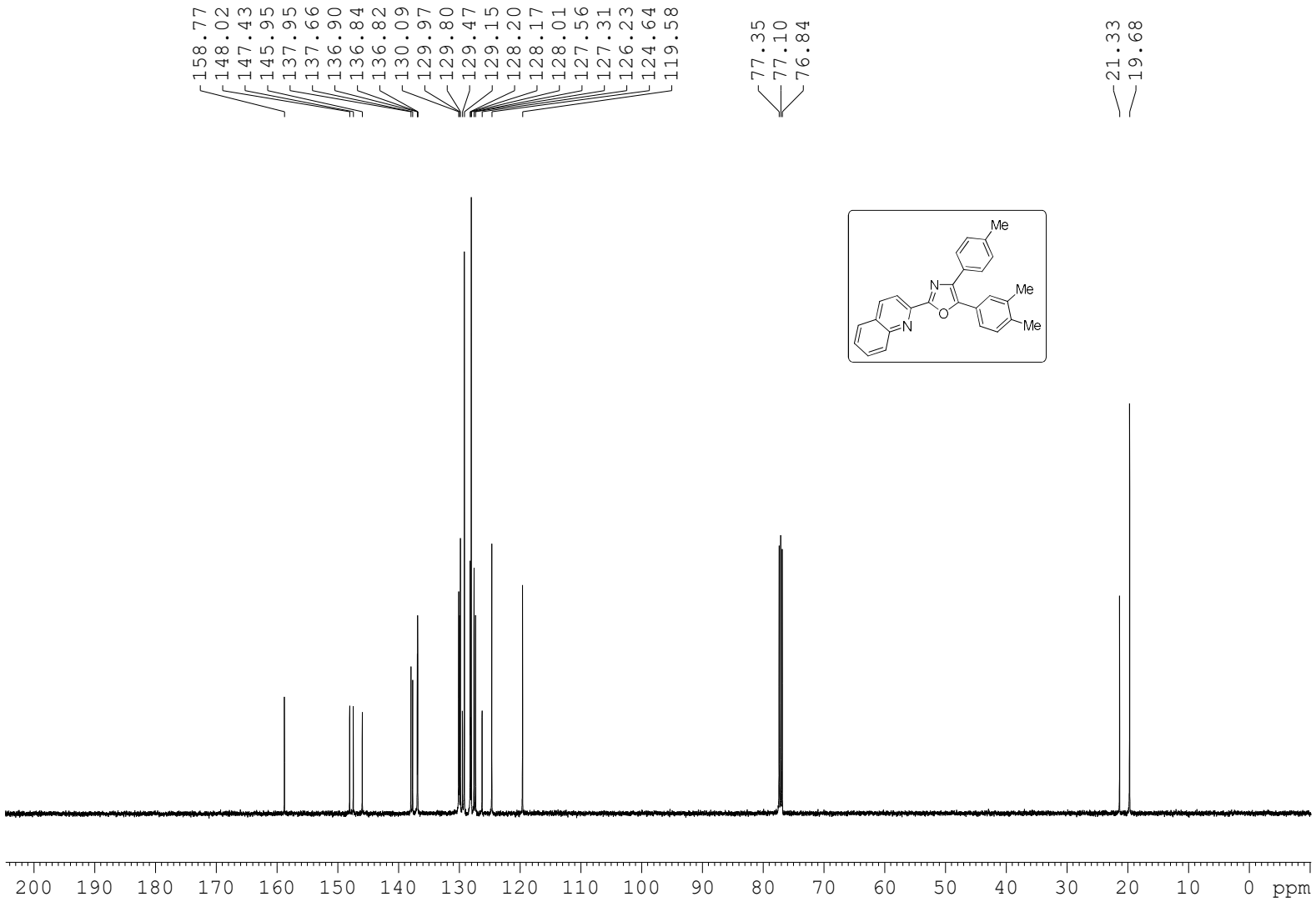
^{13}C NMR Spectrum of 5ebb



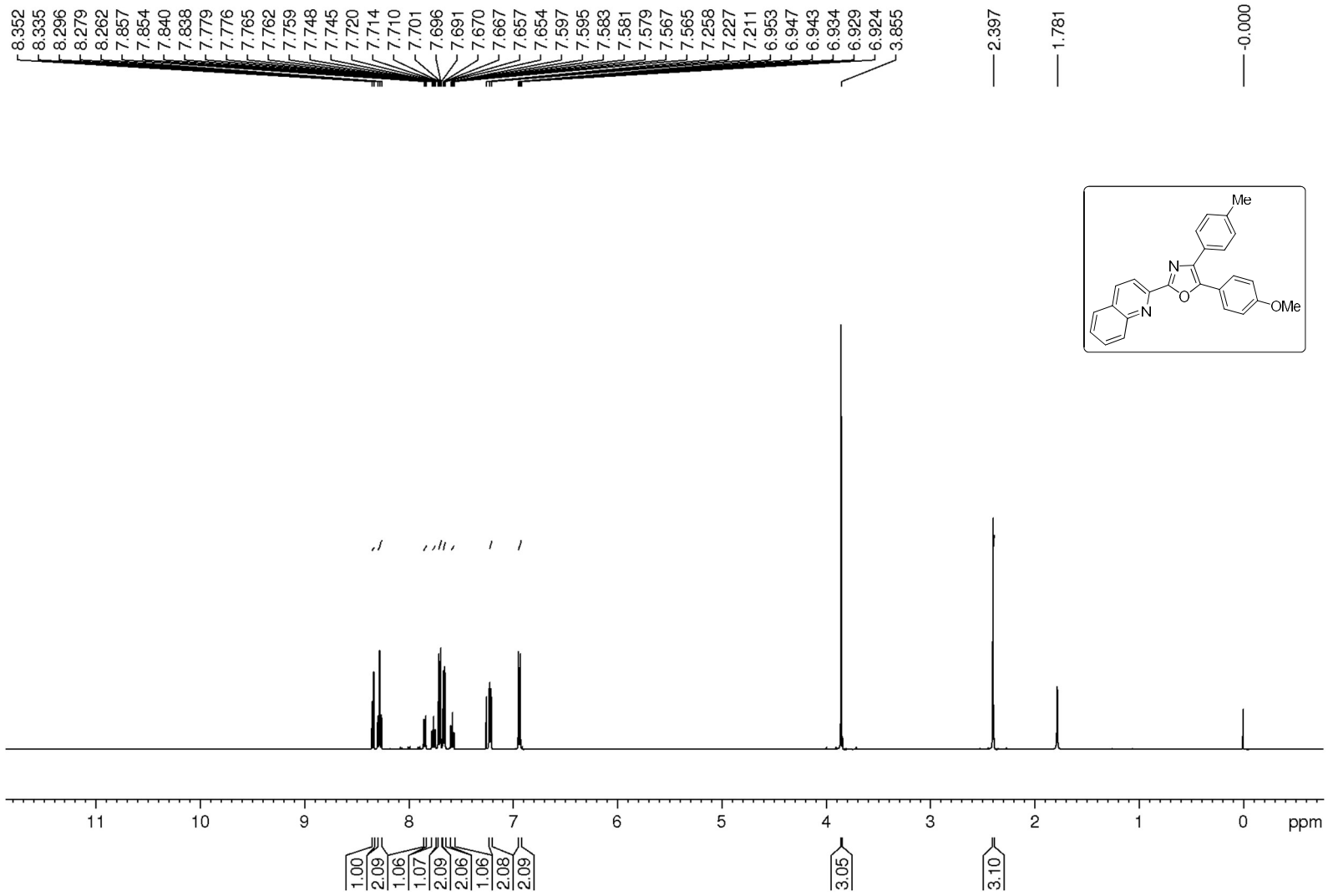
^{1}H NMR Spectrum of 5ecb



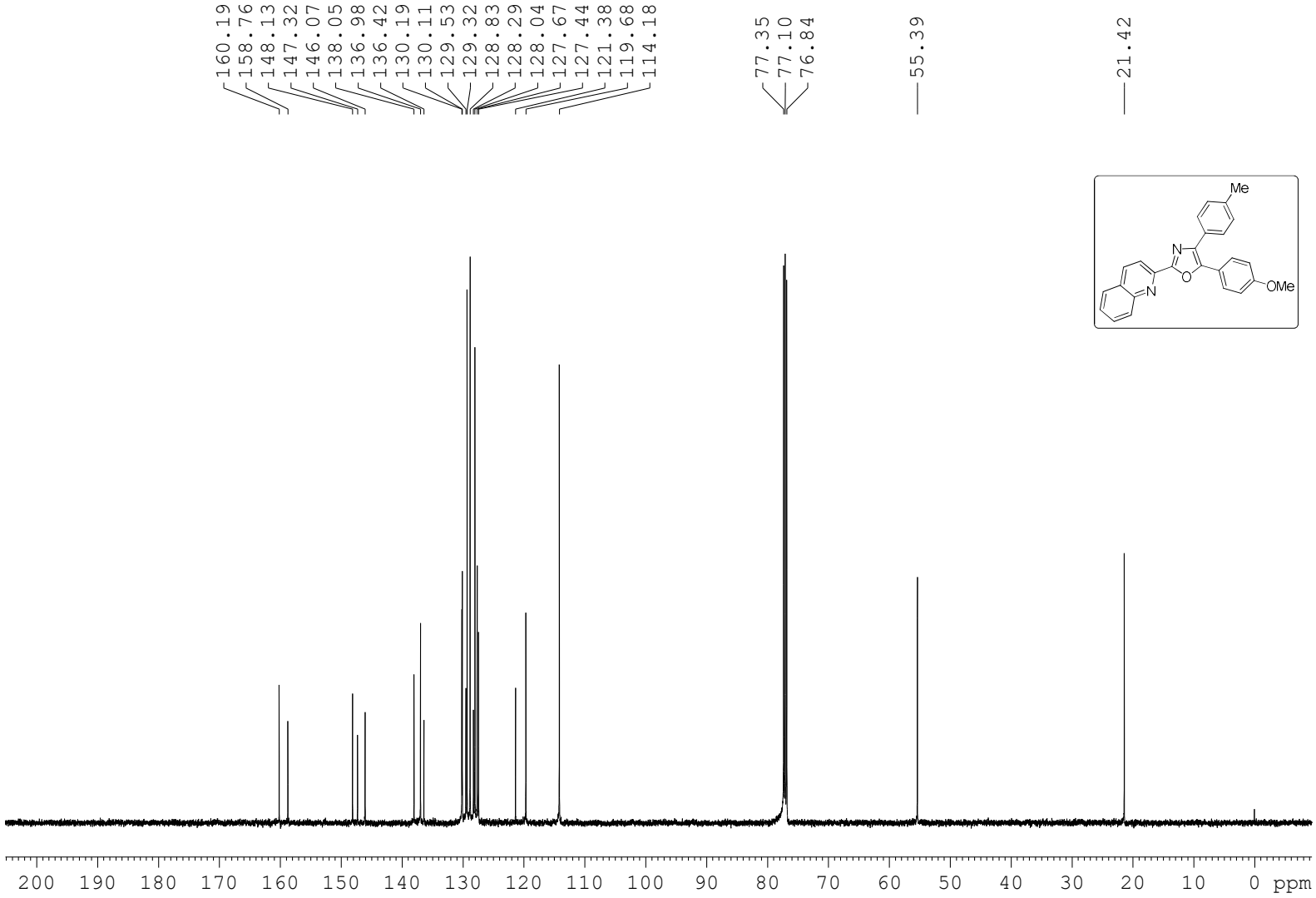
^{13}C NMR Spectrum of 5ecb



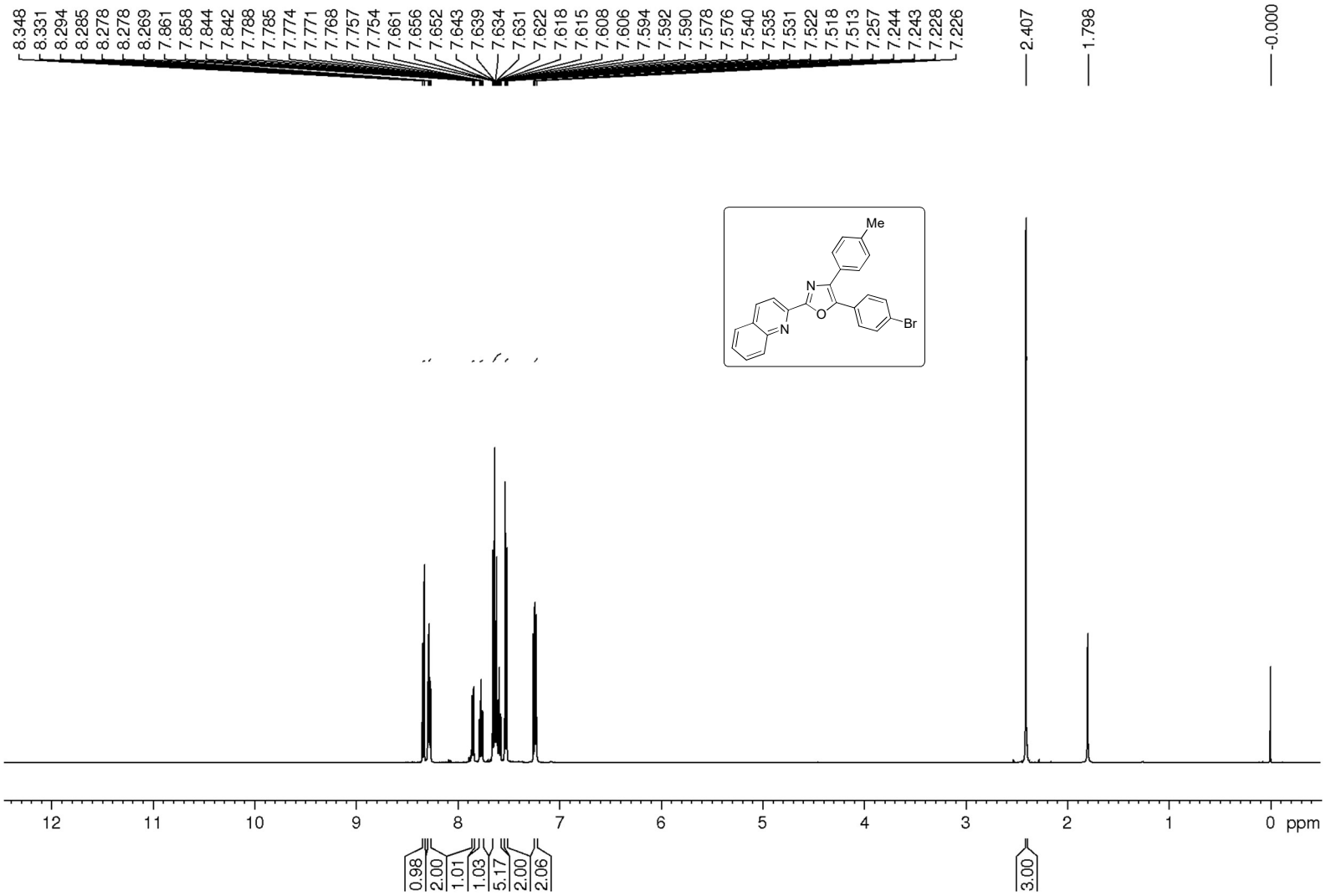
^{1}H NMR Spectrum of 5edb



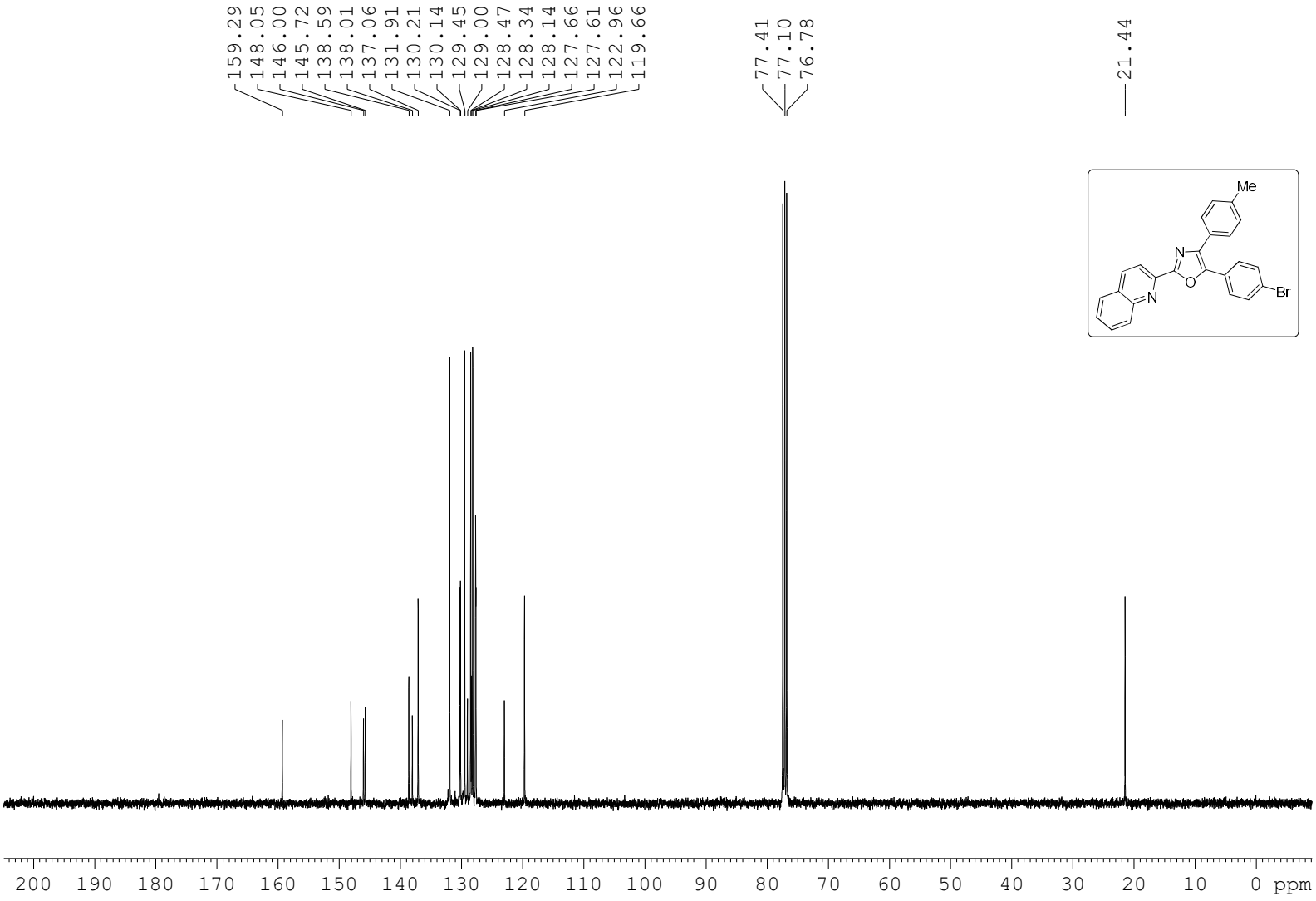
^{13}C NMR Spectrum of 5edb



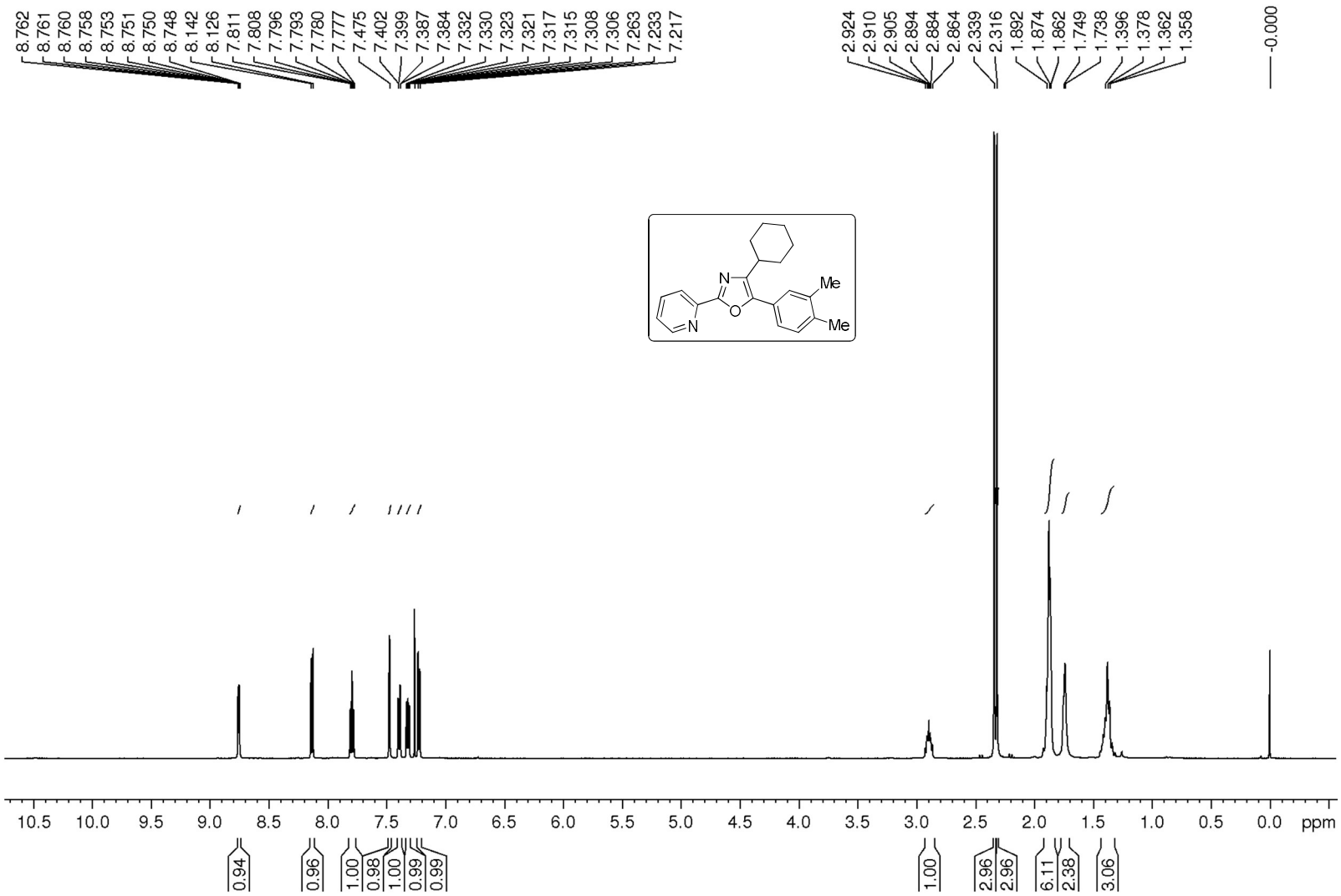
^{1}H NMR Spectrum of 5egb



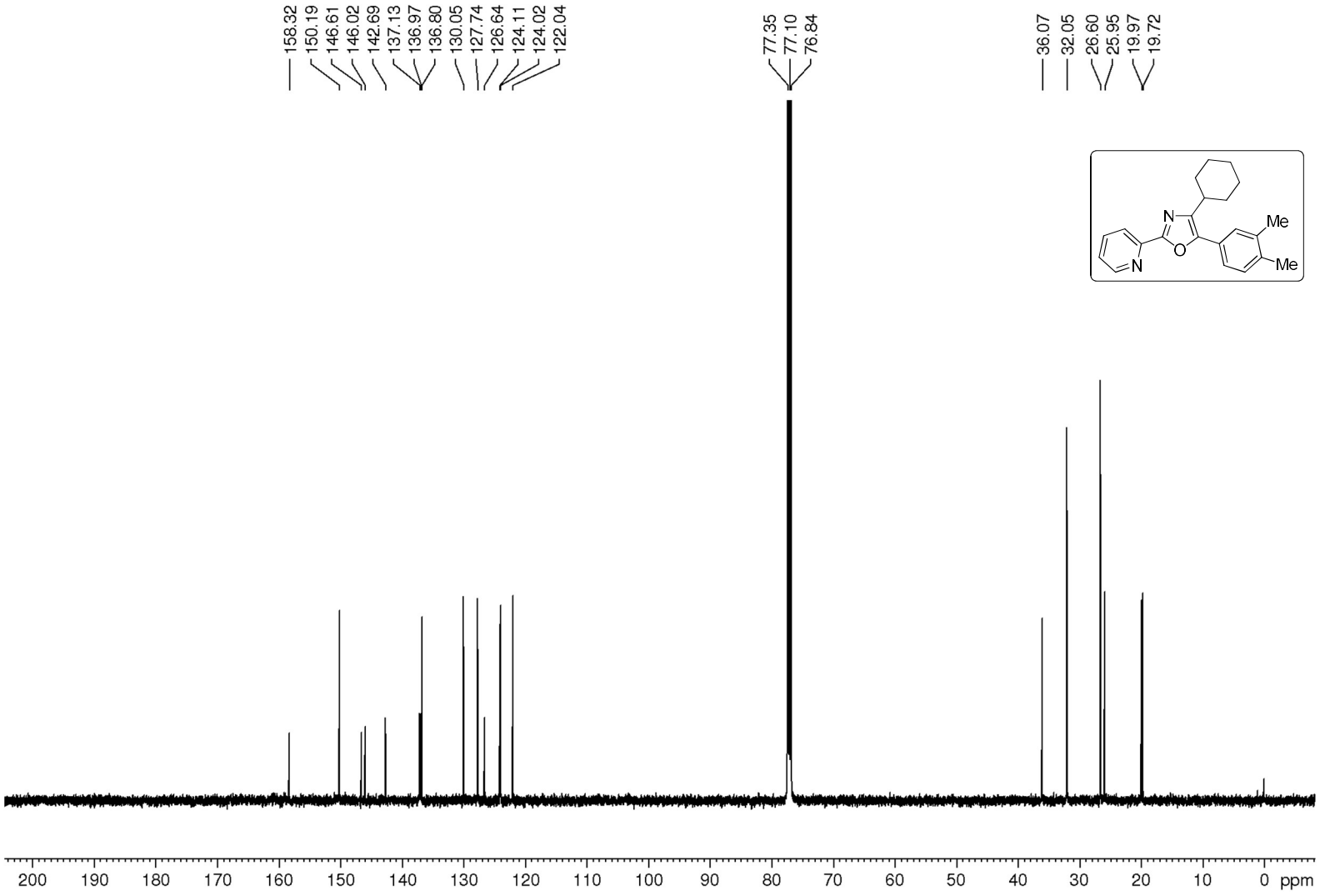
^{13}C NMR Spectrum of 5egb



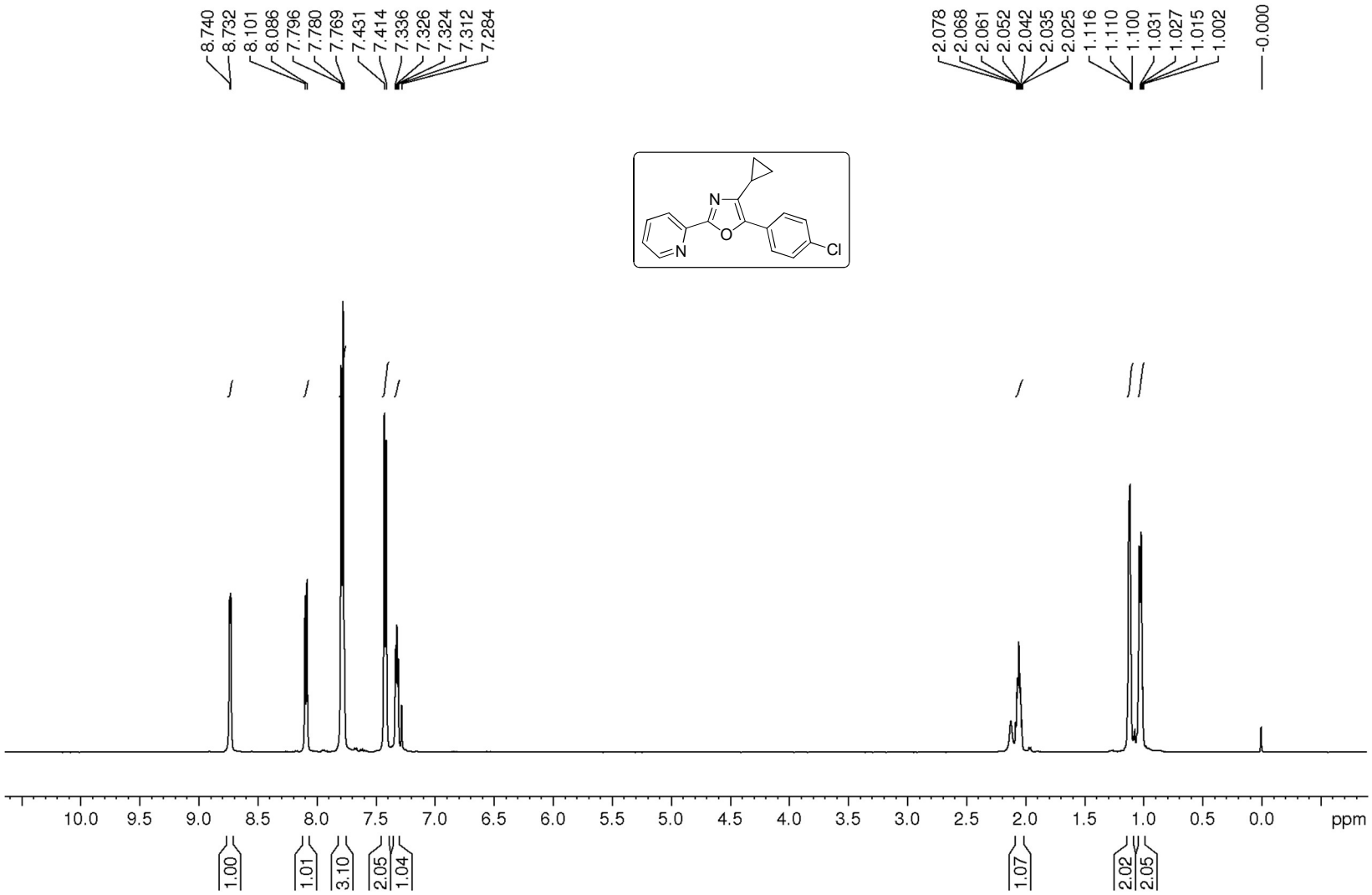
^{1}H NMR Spectrum of 5acz



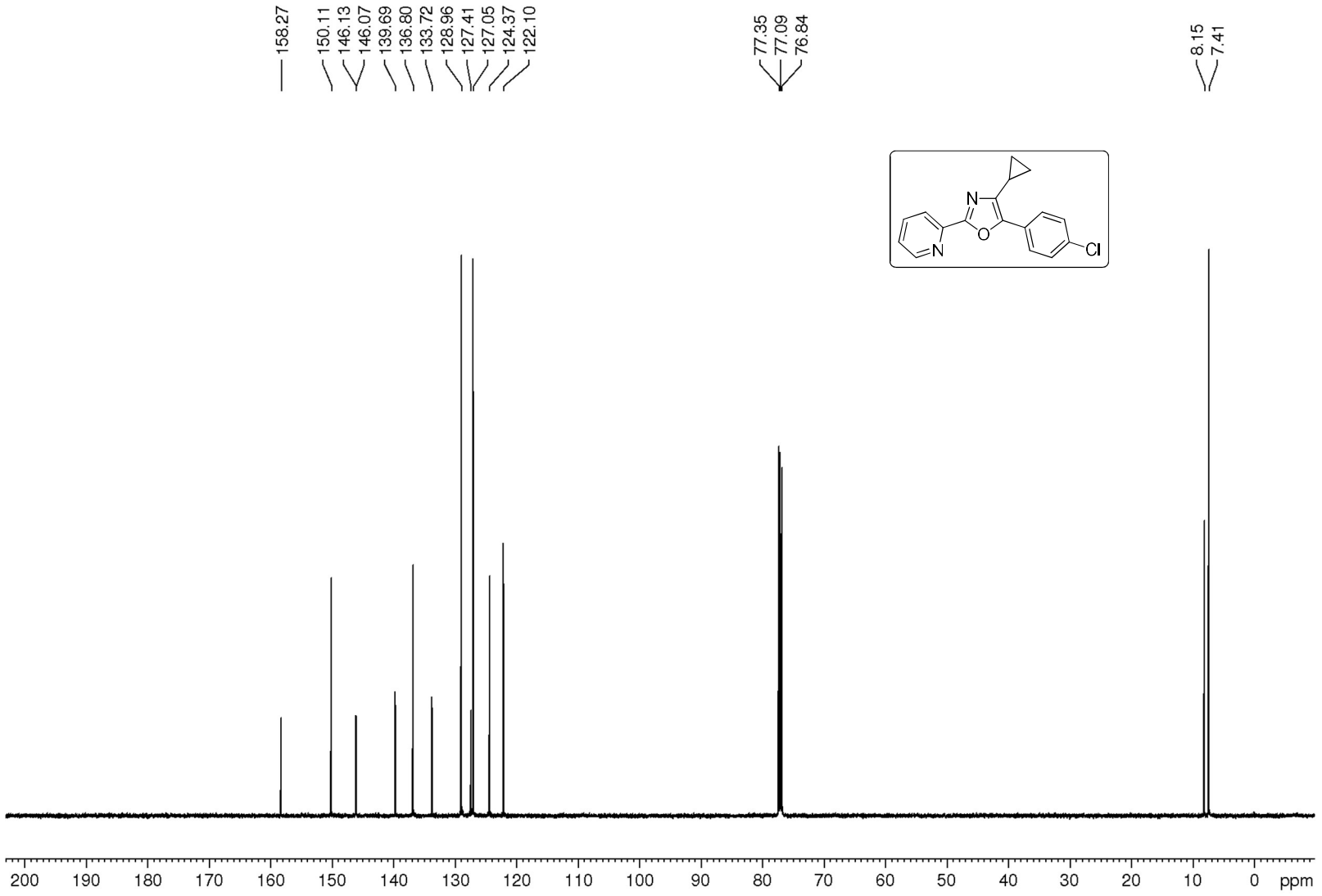
^{13}C NMR Spectrum of 5acz



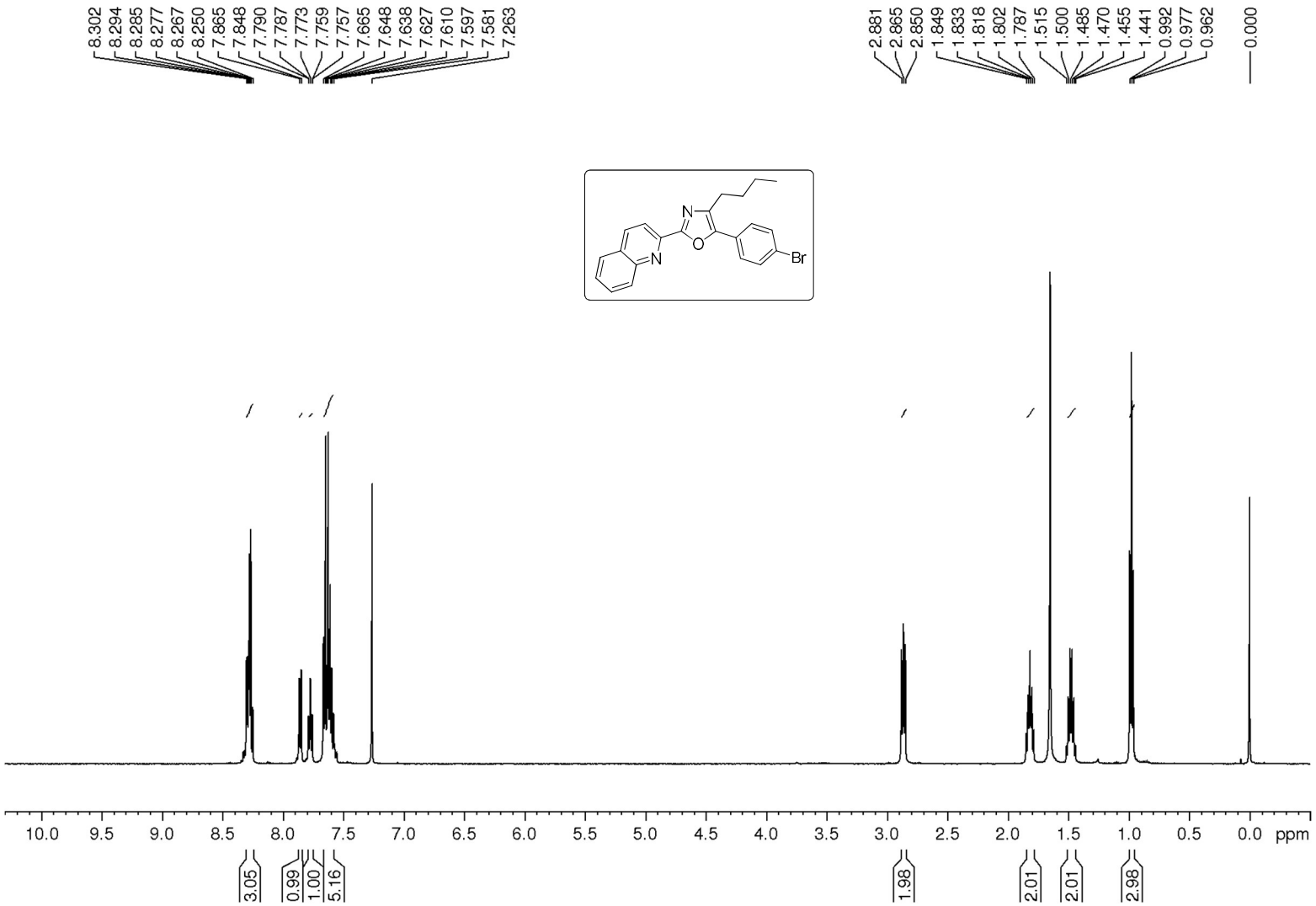
[1]H NMR Spectrum of 5afv



^{13}C NMR Spectrum of 5afv



[1]H NMR Spectrum of 5egw



^{13}C NMR Spectrum of 5egw