$Fe(OTf)_3$-Catalyzed Annulation of *α,β*-Unsaturated Ketoxime Acetates with Enaminones for the Synthesis of Functionalized 2,4-Diarylpyridines

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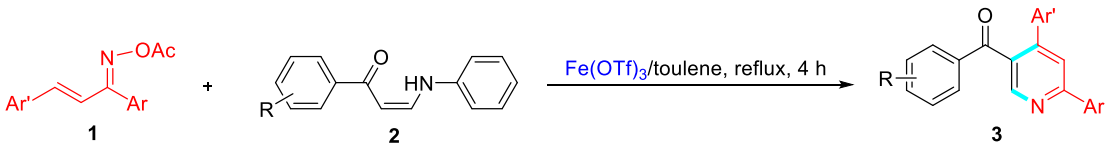
General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX600 or DRX500 or DRX400. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated DMSO-d_6 was used as solvent, the solvent residue in DMSO-d_6 (^{13}CNMR: 40.16 ppm, ^{1}H NMR, 2.50 ppm) and in $CDCl_3$ (^{13}CNMR: 77.16 ppm, ^{1}H NMR, 7.26 ppm). IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument.

The α,β-unsaturated ketoximes **1** were synthesized by known literature procedures.[1] The enaminones **2** were synthesized by known literature procedures.[2] All the other chemicals and solvents were used as received without further purification unless otherwise stated. Two kinds of reagents which were used in the experiment were commercially available reagents.

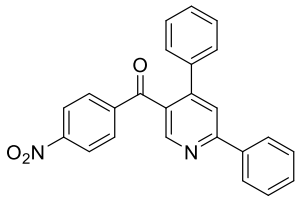
General Procedure for the Preparation of 3



A round-bottomed flask was charged with α,β-unsaturated ketoximes **1** (1.0 mmol, 1.0 equiv), enaminones **2** (1.1 mmol, 1.1 equiv), and $Fe(OTf)_3$ (0.05 mmol, 0.05 equiv). The flask was supplemented with toluene (3 mL), and the mixture was stirred under reflux (in an oil bath) for 4 h. At this stage, the substrates were completely consumed in the reaction system. After cooling the reaction mixture to room temperature, it was extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with water and brine. Then, the combined organic phases were dried over $MgSO_4$. Finally, the organic phases were filtered and concentrated under reduced pressure to obtain the crude product. Finally, the product **3** was isolated from the crude mixture by flash column chromatography over silica gel using a mixture of petroleum ether/ethyl acetate (8:1–6:1, v/v) as the eluent.

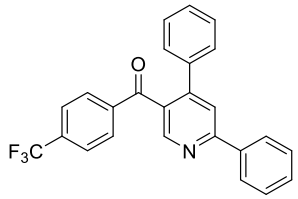
Spectroscopic Data of 3a-3p'

(4,6-Diphenylpyridin-3-yl)(4-nitrophenyl)methanone (3a)



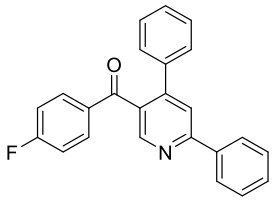
White solid (86%, 328 mg); Mp: 163.4–163.9 °C; IR (KBr): 3788, 3574, 2784, 1767, 1666, 1529, 1493, 1244, 577 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.90 (s, 1H, ArH), 8.14–8.12 (m, 2H, ArH), 8.08–8.06 (m, 2H, ArH), 7.88 (s, 1H, ArH), 7.76–7.74 (m, 2H, ArH), 7.56–7.49 (m, 3H, ArH) , 7.30–7.23 (m,5H, ArH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.2, 160.0， 150.1, 149.9, 149.8, 141.8, 138.1, 137.6, 131.5, 130.4, 130.1, 129.2, 129.0, 128.9, 128.7, 127.4, 123.4, 120.8. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}N_2O_3$ 381.1234; found, 381.1342.

(4,6-Diphenylpyridin-3-yl)(4-(trifluoromethyl)phenyl)methanone (3b)



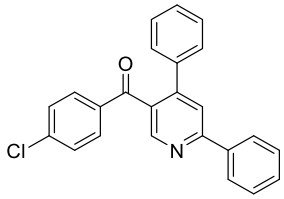
White solid (81%, 327 mg); Mp: 160.8–161.3°C; IR (KBr): 3865, 2930, 1667, 1584, 1411, 1323, 1134, 775, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.05–8.03 (m, 2H, ArH), 7.79 (s, 1H, ArH), 7.68–7.67 (m, 2H, ArH), 7.47–7.40 (m, 4H, ArH) , 7.23–7.17 (m,6H, ArH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.6, 159.6， 149.9，149.9， 140.0, 138.3, 137.7, 134.4, 134.2, 131.9, 129.9, 128.9 (d, J = 7.5 Hz), 128.6, 127.3, 125.3, 125.3, 122.5, 120.9. ^{19}F NMR (560 MHz, $CDCl_3$): δ = –63.2 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{16}F_3NO$ 404.1257; found, 404.1262.

(4,6-Diphenylpyridin-3-yl)(4-fluorophenyl)methanone (3c)



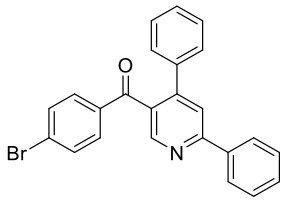
White solid (88%, 312 mg); Mp: 142.0–142.5°C; IR (KBr): 3854, 1799, 1662, 1595, 1407, 706, 547 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.79 (s, 1H, ArH), 8.29–8.28 (m, 2H, ArH), 8.13 (s, 1H, ArH), 7.74–7.72 (m, 2H, ArH), 7.57–7.52 (m, 3H, ArH), 7.41–7.40 (m, 2H, ArH), 7.35–7.31 (m, 3H, ArH), 7.22–7.19 (m, 2H, ArH). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.1, 165.5 (d, J = 252.0 Hz), 158.4, 149.5, 149.4 (d, J = 10.5 Hz), 138.3, 137.9, 133.9, 133.0 (d, J = 9.0 Hz), 132.7, 130.3, 129.3, 129.2, 129.1, 129.1, 127.6, 121.1, 116.2 (d, J = 22.5 Hz).^{19}F NMR (560 MHz, DMSO-d_6): δ = –104.9 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}FNO$ 354.1289; found, 354.1302.

(4-Chlorophenyl)(4,6-diphenylpyridin-3-yl)methanone (3d)



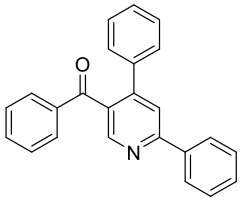
White solid (89%, 330 mg); Mp: 194.4–194.9 °C; IR (KBr): 3877, 1721, 1659, 1586, 1488, 757, 586 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.81 (s, 1H, ArH), 8.12–8.10 (m, 2H, ArH), 7.85 (s, 1H, ArH), 7.85–7.61 (m, 2H, ArH), 7.54–7.47 (m, 3H, ArH) , 7.33–7.25 (m, 7H, ArH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.4, 159.3, 149.6, 149.6, 139.8, 138.4, 137.8, 135.5, 132.2, 131.1, 129.8, 129.0, 129.0, 128.8, 128.7, 128.6, 127.3, 120.9. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}ClNO$ 370.0993; found, 370.1003.

(4-Bromophenyl)(4,6-diphenylpyridin-3-yl)methanone (3e)



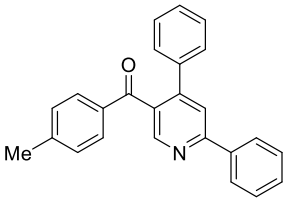
White solid (79%, 327 mg); Mp: 191.9–192.4 °C; IR (KBr): 3862, 3603, 3534, 1705, 1663, 1577, 1450, 679, 584 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.80 (s, 1H, ArH), 8.12–8.11 (m, 2H, ArH), 8.11 (s, 1H, ArH), 7.85–7.43 (m, 7H, ArH), 7.33–7.26 (m, 5H, ArH). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.6, 159.3, 149.7, 149.6, 138.4, 137.8, 135.9, 132.2, 131.7, 131.2, 129.8, 129.8, 129.0, 128.8, 128.8, 128.6, 127.3, 120.9. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}BrNO$ 414.0488; found, 414.0498.

(4,6-Diphenylpyridin-3-yl)(phenyl)methanone (3f)



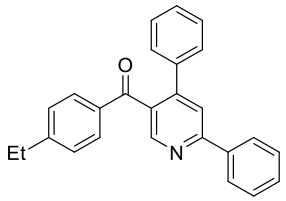
White solid (88%, 295 mg); Mp: 129.0–129.5 °C; IR (KBr): 3842, 1722, 1650, 1598, 1453, 841, 756, 565 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.80 (s, 1H, ArH), 8.29–8.27 (m, 2H, ArH), 8.13 (s, 1H, ArH), 7.61–7.52 (m, 8H, ArH), 7.41–7.33 (m, 5H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 195.6, 158.5, 149.6, 149.5, 138.2, 137.8, 136.1, 132.5, 132.2, 131.8, 130.4, 129.4, 129.3, 129.2, 129.1, 128.2, 127.7, 121.1; HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}NO$ 336.1383; found, 336.1386.

(4,6-Diphenylpyridin-3-yl)(p-tolyl)methanone (3g)



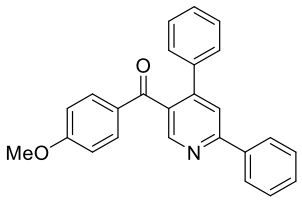
White solid (86%, 301 mg); Mp: 142.2–142.7 °C; IR (KBr): 3820, 1712, 1655, 1598, 1450, 852, 755, 562 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 8.78 (s, 1H, ArH), 8.12–8.10 (m, 2H, ArH), 7.84 (s, 1H, ArH), 7.64–7.62 (m, 2H, ArH), 7.53–7.47 (m, 3H, ArH) , 7.37–7.25 (m, 5H, ArH) , 7.13–7.11 (m, 2H, ArH) , 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.1, 158.8, 149.7, 149.5, 144.4, 138.7, 138.0, 134.6, 132.9, 130.1, 129.7, 129.1, 128.9, 128.7, 128.6, 127.2, 121.1, 21.7; HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}NO$ 350.1539; found, 350.1536.

(4,6-Diphenylpyridin-3-yl)(4-ethylphenyl)methanone (3h)



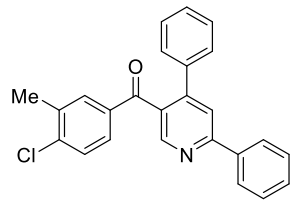
White solid (84%, 306 mg); Mp: 141.5–142.0 °C; IR (KBr): 3884, 1730, 1657, 1598, 1508, 1469, 1293, 697, 554 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.11–8.09 (m, 2H, ArH), 7.84 (s, 1H, ArH), 7.84–7.69 (m, 2H, ArH), 7.54–7.46 (m, 3H, ArH), 7.38–7.31 (m, 2H, ArH), 7.30–7.27 (m, 3H, ArH) , 6.80–6.78 (m, 2H, ArH), 4.06–4.02 (m, 2H, CH_2), 1.42–1.39 (m, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 196.1, 158.8, 150.5, 149.7, 149.5, 138.6, 138.0, 134.9, 132.9, 130.2, 129.7, 128.9, 128.7, 128.6, 128.6, 127.9, 127.2, 121.1, 29.0, 15.0. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NO$ 364.1696; found, 364.1699.

(4,6-diphenylpyridin-3-yl)(4-methoxyphenyl)methanone (3i)



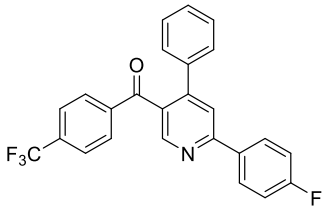
White solid (85%, 311 mg); Mp: 148.5–149.0 °C; IR (KBr): 3811, 2917, 1721, 1657, 1597, 1449, 1149, 788, 549 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.80 (s, 1H, ArH), 8.14–8.12 (m, 2H, ArH), 7.87 (s, 1H, ArH), 7.87–7.73(m, 2H, ArH), 7.73–7.48 (m, 3H, ArH), 7.41–7.38 (m, 2H, ArH), 7.33–7.28 (m, 3H, ArH) , 6.84–6.81 (m, 2H, ArH), 3.83 (s, 3H, OCH_3) . ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.0, 163.8, 158.7, 149.4, 149.4, 138.6, 138.1, 133.0, 132.3, 130.2, 129.6, 128.9, 128.7, 128.7, 128.6, 127.2, 121.0, 113.7, 55.5. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}NO_2$ 366.1489; found, 366.1491.

(4-Chloro-3-methylphenyl)(4,6-diphenylpyridin-3-yl)methanone (3j)



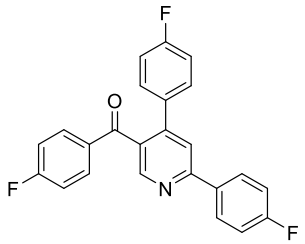
White solid (85%, 326 mg); Mp: 166.1–166.6 °C; IR (KBr): 3866, 1712, 1653, 1589, 1452, 760, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1H, ArH), 8.12–8.10 (m, 2H, ArH), 8.10 (s, 1H, ArH), 7.85–7.43 (m, 5H, ArH), 7.35–7.25 (m, 6H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 159.2, 149.8, 149.6, 140.0, 138.4, 137.9, 136.4, 135.4, 132.3, 132.2, 129.8, 129.2, 129.0, 128.9, 128.8, 128.6, 128.6, 127.3, 121.0, 19.9; HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}ClNO$ 384.1150; found, 384.1154.

(6-(4-Fluorophenyl)-4-phenylpyridin-3-yl)(4-(trifluoromethyl)phenyl)methanone (3k)



White solid (80%, 338 mg); Mp: 140.5–150.0 °C; IR (KBr): 3864, 3609, 2924, 1762, 1668, 1583, 1412, 1322, 1139, 845, 629 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.83 (s, 1H, ArH), 8.83–8.11 (m, 2H, ArH), 7.82 (s, 1H, ArH), 7.75–7.74 (m, 2H, ArH), 7.54–7.53 (m, 2H, ArH), 7.30–7.25 (m, 5H, ArH), 7.23–7.19 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.5, 164.1 (d, J = 207.5 Hz), 158.5, 149.9 (d, J = 17.5 Hz), 139.9, 137.6, 134.0, 131.8, 129.9, 129.2 (d, J = 7.5 Hz), 129.1, 128.8, 128.6, 125.3, 125.3, 123.4 (d, J = 226.3 Hz), 120.5, 116.0 (d, J = 18.8 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.2, –111.2 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{15}F_4NO$ 422.0918; found, 422.0919.

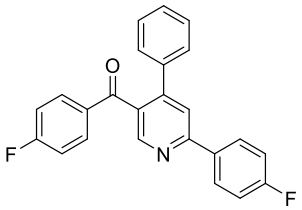
(4,6-Bis(4-fluorophenyl)pyridin-3-yl)(4-fluorophenyl)methanone (3l)



White solid (77%, 300 mg); Mp: 151.5–152.0 °C; IR (KBr): 3898, 3351, 2916, 1708, 1667, 1599, 1509, 1412, 1228, 1154, 843 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.12–8.09 (m, 2H, ArH), 7.76 (s, 1H, ArH), 7.72–7.69 (m, 2H, ArH), 7.32–7.29 (m, 2H, ArH), 7.21–7.17 (m, 2H, ArH), 7.01–6.97 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.7, 165.9 (d, J = 255.0 Hz), 164.0 (d, J = 248.8 Hz), 163.1 (d, J = 248.8 Hz), 158.1, 149.6, 148.6, 134.4, 133.8, 133.4, 132.4 (d, J = 10.0 Hz), 132.3 (d, J = 20.0 Hz), 130.4 (d, J = 7.5 Hz), 129.2 (d, J = 8.8 Hz), 120.5, 115.9 (d, J = 21.3

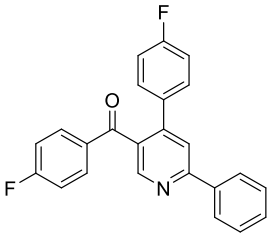
Hz), 115.9 (d, J = 22.5 Hz), 115.7 (d, J = 22.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ = –103.7, –111.3, –112.0 ppm. HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{24}H_{14}F_3NO$ 390.1100; found, 390.1099.

(4-Fluorophenyl)(6-(4-fluorophenyl)-4-phenylpyridin-3-yl)methanone (3m)



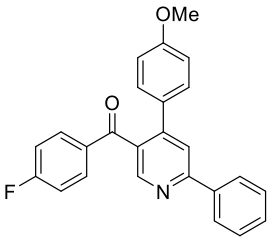
White solid (85%, 317 mg); Mp: 145.0–145.5 °C; IR (KBr): 3690, 2360, 1721, 1662, 1598, 1408, 570 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.77–8.75 (m, 1H, ArH), 8.36–8.33 (m, 2H, ArH), 8.13 (s, 1H, ArH), 7.74–7.71 (m, 2H, ArH), 7.41–7.29 (m, 8H, ArH), 7.22–7.18 (m, 2H, ArH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 195.0, 165.7 (d, J = 212.5 Hz), 164.5, 162.8, 157.4, 149.5, 149.5, 137.8, 134.8, 132.9 (d, J = 10.0 Hz), 132.6, 129.9 (d, J = 8.8 Hz), 129.2 (d, J = 12.5 Hz), 129.1 (d, J = 8.8 Hz), 120.9, 116.3, 116.2 (d, J = 16.3 Hz), 116.1. HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}F_2NO_3$ 372.1194; found, 372.1202.

(4-Fluorophenyl)(4-(4-fluorophenyl)-6-phenylpyridin-3-yl)methanone (3n)



White solid (86%, 320 mg); Mp: 154.3–154.8 °C; IR (KBr): 3948, 1723, 1658, 1596, 1410, 1282, 1106, 547 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.80 (s, 1H, ArH), 8.11–8.10 (m, 2H, ArH), 7.81 (s, 1H, ArH), 7.74–7.70 (m, 2H, ArH), 7.55–7.47 (m, 3H, ArH), 7.33–7.26 (m, 2H, ArH), 7.02–6.97 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.9, 165.9 (d, J = 255 Hz), 163.0 (d, J = 248.8 Hz), 159.3, 149.6, 148.5, 138.3, 133.9, 133.5, 132.4 (d, J = 8.8 Hz), 132.3, 130.4 (d, J = 7.5 Hz), 129.9, 129.0, 127.3, 120.8, 115.9 (d, J = 22.5 Hz), 115.6. ^{19}F NMR (470 MHz, CDCl3): δ = –103.7, –112.1 ppm. HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}F_2NO$ 372.1194; found, 372.1200.

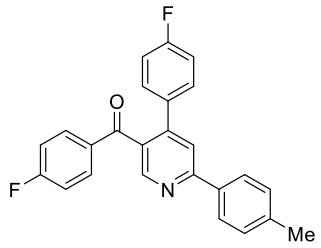
(4-Fluorophenyl)(4-(4-methoxyphenyl)-6-phenylpyridin-3-yl)methanone (3o)



White solid (77%, 296 mg); Mp: 141.0–141.5°C; IR (KBr): 3863, 1708, 1662, 1534, 1405, 1145, 710, 669, 576 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 1H, ArH),

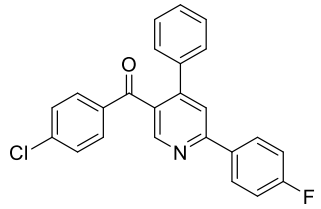
8.79–8.12 (m, 2H, ArH), 7.84 (s, 1H, ArH), 7.75–7.72(m, 2H, ArH), 7.55–7.49 (m, 3H, ArH), 7.31–7.28 (m, 2H, ArH), 7.01–6.97 (m, 2H, ArH) , 6.84–6.82 (m, 2H, ArH), 3.76 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.3, 165.7 (d, J = 253.8 Hz), 160.2, 159.1, 149.6, 149.1, 138.5, 133.5, 132.4 (d, J = 10.0 Hz), 132.2, 130.1, 130.0, 129.7, 128.1 (d, J = 208.8 Hz), 120.7, 115.6 (d, J = 21.3 Hz), 114.3, 55.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –104.2 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}FNO_2$ 384.1394; found, 384.1402.

(4-Fluorophenyl)(4-(4-fluorophenyl)-6-(p-tolyl)pyridin-3-yl)methanone (3p)



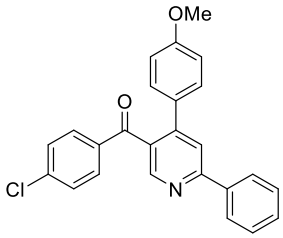
White solid (86%, 332 mg); Mp: 110.4–110.9 °C; IR (KBr): 3898, 1723, 1667, 1538, 1410, 635, 573 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.02–8.00 (m, 2H, ArH), 7.78 (s, 1H, ArH), 7.73–7.70 (m, 2H, ArH), 7.33–7.29 (m, 4H, ArH), 7.00–6.96 (m, 4H, ArH), 2.43 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.9, 165.8 (d, J = 255.0 Hz), 163.0 (d, J = 247.5 Hz), 159.3, 149.6, 148.5, 140.1, 135.5, 134.1, 134.0, 133.6, 132.5 (d, J = 8.8 Hz), 132.0, 130.4 (d, J = 8.8 Hz), 129.7, 127.1, 120.5, 115.9 (d, J = 21.3 Hz), 115.7 (d, J = 22.5 Hz), 21.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –103.9, –112.2 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{17}F_2NO$ 386.1351; found, 386.1357.

(4-Chlorophenyl)(6-(4-fluorophenyl)-4-phenylpyridin-3-yl)methanone (3q)



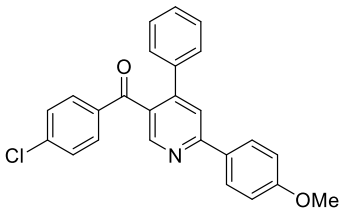
White solid (86%, 334 mg); Mp: 189.3–189.8 °C; IR (KBr): 3874, 1728, 1664, 1577, 1455, 762, 593 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.78 (s, 1H, ArH), 8.78–8.09 (m, 2H, ArH), 7.80 (s, 1H, ArH), 7.62–7.60 (m, 2H, ArH), 7.33–7.21 (m, 7H, ArH), 7.20–7.18 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.3, 164.0 (d, J = 248.8 Hz), 158.2, 149.8, 149.6, 139.8, 137.7, 135.4, 134.5, 134.5, 132.1, 131.1, 129.2 (d, J = 8.8 Hz), 129.0, 128.8, 128.6 (d, J = 17.5 Hz), 120.6, 115.9 (d, J = 21.3 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ = –111.4 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}F_2NO_3$ 372.1194; found, 372.1202. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}ClFNO$ 388.0899; found, 388.0902.

(4-Chlorophenyl)(4-(4-methoxyphenyl)-6-phenylpyridin-3-yl)methanone (3r)



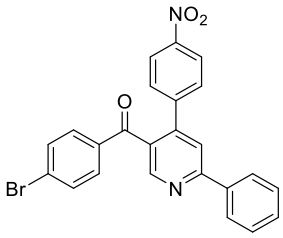
White solid (77%, 308 mg); Mp: 163.8–164.3 °C; IR (KBr): 3839, 2930, 2375, 1729, 1656, 1593, 1468, 1298, 825, 690, 559 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.76 (s, 1H, ArH), 8.11–8.09 (m, 2H, ArH), 7.82 (s, 1H, ArH), 7.64–7.62 (m, 2H, ArH), 7.54–7.48 (m, 3H, ArH), 7.29–7.26 (m, 4H, ArH), 6.82–6.80 (m, 2H, ArH) , 3.77 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.7, 160.3, 159.2, 149.6, 149.2, 139.8, 138.5, 135.5, 132.1, 131.1, 130.1, 129.9, 129.7, 128.9, 128.7, 127.2, 120.7, 114.3, 55.3. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}ClNO_2$ 400.1099; found, 400.1104.

(4-Chlorophenyl)(6-(4-methoxyphenyl)-4-phenylpyridin-3-yl)methanone (3s)



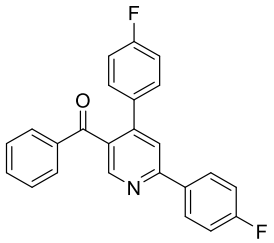
White solid (84%, 336 mg); Mp: 155.0–150.5 °C; IR (KBr): 3813, 1723, 1656, 1585, 1495, 841, 709, 566 cm^{-1}; ^1H NMR (500 MHz, CDCl3): δ = 8.76 (s, 1H, ArH), 8.09–8.07 (m, 2H, ArH), 7.78 (s, 1H, ArH), 7.62–7.60 (m, 2H, ArH), 7.32–7.25 (m, 7H, ArH), 7.05–7.03 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.4, 161.2, 158.9, 149.6, 139.6, 138.0, 135.6, 131.5, 131.1, 130.9, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 120.0, 114.4, 55.4. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}ClNO_2$ 400.1099; found, 400.1101.

(4-Bromophenyl)(4-(4-nitrophenyl)-6-phenylpyridin-3-yl)methanone (3t)



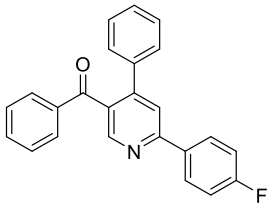
White solid (82%, 376 mg); Mp: 186.5–187.0 °C; IR (KBr): 3824, 3383, 3164, 1736, 1662, 1585, 1450, 1280, 823, 679, 556 cm^{-1}; ^1H NMR (500 MHz, CDCl3): δ = 8.84 (s, 1H, ArH), 8.20–8.18 (m, 2H, ArH), 8.12–8.11 (m, 2H, ArH), 7.83 (s, 1H, ArH), 7.63–7.61 (m, 2H, ArH), 7.55–7.49 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.4, 159.7, 149.9, 147.9, 147.8, 144.4, 137.8, 135.6, 132.1, 131.6, 131.3, 130.3, 129.5, 129.3, 129.1, 127.3, 124.0, 120.9. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}BrN_2O_3$ 459.0339; found, 459.0343.

(4,6-Bis(4-fluorophenyl)pyridin-3-yl)(phenyl)methanone (3u)



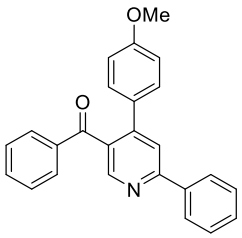
White solid (86%, 320 mg); Mp: 161.0–161.5 °C; IR (KBr): 3836, 1707, 1661, 1533, 1410, 763, 685, 548 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.78 (s, 1H, ArH), 8.12–8.09 (m, 2H, ArH), 7.76 (s, 1H, ArH), 7.70–7.69 (m, 2H, ArH), 7.50–7.47 (m, 1H, ArH), 7.35–7.30 (m, 4H, ArH), 7.22–7.19 (m, 2H, ArH), 6.99–6.95 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.3, 163.0 (d, J = 248.8 Hz), 162.0 (d, J = 248.8 Hz), 157.0, 148.7, 147.8, 136.0, 133.5, 133.0, 132.9, 131.5, 129.4 (d, J = 7.5 Hz), 128.8, 128.1 (d, J = 7.5 Hz), 127.5, 119.5, 114.9 (d, J = 21.3 Hz), 114.8 (d, J = 21.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ = –111.5, –112.3 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{15}F_2NO$ 372.1194; found, 372.1201.

(6-(4-Fluorophenyl)-4-phenylpyridin-3-yl)(phenyl)methanone (3v)



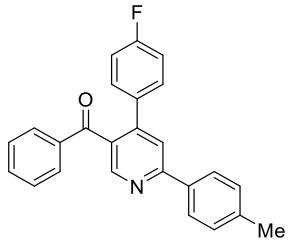
White solid (89%, 316 mg); Mp: 139.9–140.4 °C; IR (KBr): 3870, 2931, 1729, 1641, 1595, 1469, 779, 696, 541 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.75 (s, 1H, ArH), 8.36–8.33 (m, 2H, ArH), 8.12 (s, 1H, ArH), 7.66–7.65 (m, 2H, ArH), 7.56–7.53 (m, 1H, ArH), 7.42–7.28 (m, 9H, ArH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 196.4, 163.8 (d, J = 246.7 Hz), 157.3, 149.4 (d, J = 11.3 Hz), 137.9, 137.1, 134.8, 134.8, 134.0, 132.9, 130.0, 129.9, 129.9, 129.2 (d, J = 10.0 Hz), 129.1, 129.0, 121.0, 116.2 (d, J = 22.5 Hz). HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}FNO$ 354.1289; found, 372.1202.

(4-(4-Methoxyphenyl)-6-phenylpyridin-3-yl)(phenyl)methanone (3w)



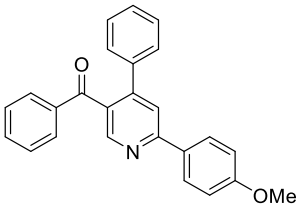
White solid (77%, 282 mg); Mp: 135.3–135.8 °C; IR (KBr): 3812, 3598, 1727, 1663, 1588, 1454, 1178, 612, 575 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.11–8.10 (m, 2H, ArH), 7.82 (s, 1H, ArH), 7.72–7.70 (m, 2H, ArH), 7.53–7.44 (m, 4H, ArH), 7.33–7.25 (m, 4H, ArH), 6.81–6.78 (m, 2H, ArH) , 3.74 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.8, 160.1, 158.9, 149.6, 149.3, 138.6, 137.1, 133.3, 132.5, 130.3, 130.0, 129.9, 129.6, 128.9, 128.4, 127.2, 120.8, 114.2, 55.3. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}NO_2$ 366.1489; found, 366.1496.

(4-(4-Fluorophenyl)-6-(p-tolyl)pyridin-3-yl)(phenyl)methanone (3x)



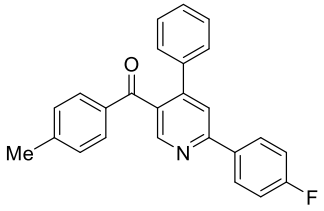
White solid (82%, 302 mg); Mp: 127.2–127.7 °C; IR (KBr): 3877, 1722, 1640, 1588, 1440, 688, 578 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 1H, ArH), 8.02–8.00 (m, 2H, ArH), 7.78 (s, 1H, ArH), 7.71–7.69 (m, 2H, ArH), 7.69–7.46 (m, 1H, ArH), 7.35–7.25 (m, 6H, ArH), 6.99–6.94 (m, 2H, ArH), 2.44 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.4, 163.0 (d, J = 247.5 Hz), 159.1, 149.7, 148.7, 140.1, 137.1, 135.6, 134.2, 133.4, 132.2, 130.4 (d, J = 8.8 Hz), 129.8, 129.7, 128.4, 127.1, 120.5, 115.7 (d, J = 21.3 Hz), 21.4. ^{19}F NMR (470 MHz, CDCl3): δ = –112.6 ppm. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}FNO$ 368.1445; found, 368.1451.

(6-(4-Methoxyphenyl)-4-phenylpyridin-3-yl)(phenyl)methanone (3y)



White solid (88%, 323 mg); Mp: 118.0–118.5 °C; IR (KBr): 3899, 1729, 1662, 1583, 1450, 1281, 672, 542 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.09–8.07 (m, 2H, ArH), 7.78 (s, 1H, ArH), 7.71–7.69 (m, 2H, ArH), 7.45–7.42 (m, 1H, ArH), 7.34–7.24 (m, 7H, ArH), 7.02–7.01 (m, 2H, ArH), 3.87 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.6, 161.2, 158.7, 149.8, 149.7, 138.2, 137.3, 133.2, 131.9, 131.0, 129.8, 129.8, 128.6, 128.6, 128.3, 128.3, 120.1, 114.3, 55.4. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}NO_2$ 366.1489; found, 366.1498.

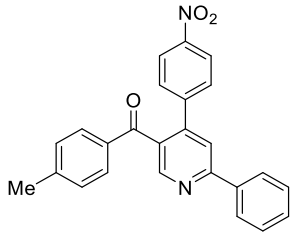
(6-(4-Fluorophenyl)-4-phenylpyridin-3-yl)(p-tolyl)methanone (3z)



White solid (85%, 312 mg); Mp: 128.3–128.8 °C; IR (KBr): 3750, 1729, 1645, 1598, 1473, 1296, 839, 697, 568 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.68 (s, 1H, ArH), 8.04–8.01 (m, 2H, ArH), 7.72 (s, 1H, ArH), 7.56–7.54 (m, 2H, ArH), 7.28–7.26 (m, 2H, ArH), 7.22–7.18 (m, 3H, ArH), 7.14–7.10 (m, 2H, ArH), 7.06–7.04 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.9, 162.9 (d, J = 248.8 Hz), 156.7, 148.7, 148.5, 143.4, 136.9, 133.7, 133.7, 133.6, 131.8, 129.0, 128.1, 128.1, 127.7, 127.5, 119.7, 114.9 (d, J = 21.3 Hz), 20.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –111.8 ppm. HRMS

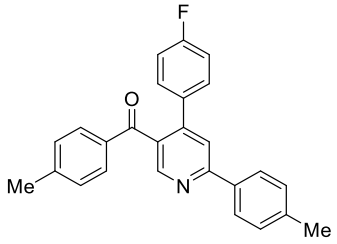
(TOF ES$^+$) m/z: [M+H]$^+$ calcd for $C_{25}H_{18}FNO$ 368.1445; found, 368.1448.

(4-(4-Nitrophenyl)-6-phenylpyridin-3-yl)(p-tolyl)methanone (3a')



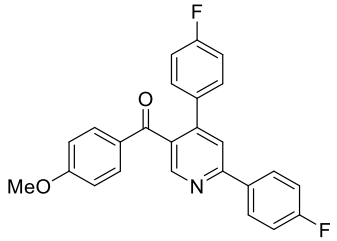
White solid (83%, 328 mg); Mp: 145.9–146.4 °C; IR (KBr): 3872, 1730, 1658, 1599, 1519, 1468, 1348, 1292, 695, 565 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.84 (s, 1H, ArH), 8.18–8.16 (m, 2H, ArH), 8.12–8.10 (m, 2H, ArH), 7.83 (s, 1H, ArH), 7.67–7.66 (m, 2H, ArH), 7.55–7.47 (m, 5H, ArH) , 7.26–7.19 (m, 2H, ArH), 2.39 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.1, 159.3, 149.9, 147.8, 147.7, 145.1, 144.7, 138.0, 134.4, 132.4, 130.2, 130.1, 129.5, 129.5, 129.0, 127.3, 123.9, 120.8, 21.8. HRMS (TOF ES$^+$) m/z: [M+H]$^+$ calcd for $C_{25}H_{18}N_2O_3$ 395.1390; found, 395.1399.

(4-(4-Fluorophenyl)-6-(p-tolyl)pyridin-3-yl)(p-tolyl)methanone (3b')



White solid (89%, 340 mg); Mp: 150.4–150.9 °C; IR (KBr): 3809, 1755, 1614, 1581, 1447, 1241, 631, 568 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.75 (s, 1H, ArH), 8.01–8.00 (m, 2H, ArH), 7.77 (s, 1H, ArH), 7.63–7.62 (m, 2H, ArH), 7.34–7.31 (m, 4H, ArH), 7.15–7.14 (m, 2H, ArH), 7.00–6.96 (m, 2H, ArH), 2.44 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.0, 163.0 (d, J = 247.5 Hz), 158.8, 149.5, 148.5, 144.5, 140.0, 135.6, 134.6, 134.2, 132.5, 130.4 (d, J = 8.8 Hz), 130.1, 129.7, 129.2, 127.1, 120.6, 115.7 (d, J = 22.5 Hz), 21.7, 21.3. ^{19}F NMR (470 MHz, CDCl3): δ = –112.7 ppm. HRMS (TOF ES$^+$) m/z: [M+H]$^+$ calcd for $C_{26}H_{20}FNO$ 382.1602; found, 382.1608.

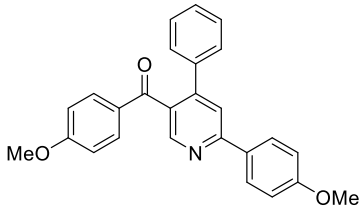
(4,6-Bis(4-fluorophenyl)pyridin-3-yl)(4-methoxyphenyl)methanone (3c')



White solid (87%, 350 mg); Mp: 131.9–132.4 °C; IR (KBr): 3877, 1728, 1614, 1597, 1510, 1426, 1164, 691, 566 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.74 (s, 1H, ArH), 8.11–8.08 (m, 2H, ArH), 7.75 (s, 1H, ArH), 7.70–7.69 (m, 2H, ArH), 7.35–7.32 (m, 2H,

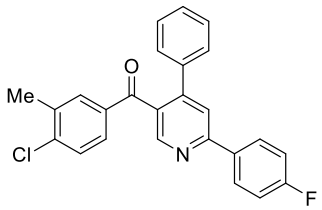
ArH), 7.20–7.17 (m, 2H, ArH), 7.00–6.97 (m, 2H, ArH), 6.83–6.81 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.7, 165.0, 164.0, 163.0 (d, J = 245.0 Hz), 157.7, 149.4, 148.4, 134.6, 134.0, 132.9, 132.3, 130.3 (d, J = 8.8 Hz), 130.0, 129.1 (d, J = 8.8 Hz), 120.5, 115.9 (d, J = 10.0 Hz), 115.8 (d, J = 10.0 Hz), 113.8, 55.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –111.6, –112.4 ppm. HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{25}H_{17}F_2NO_2$ 402.1300; found, 402.1306.

(4-Methoxyphenyl)(6-(4-methoxyphenyl)-4-phenylpyridin-3-yl)methanone (3d')



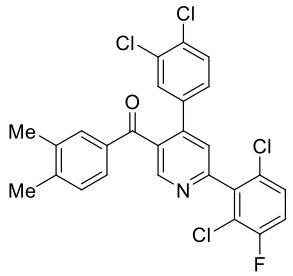
White solid (88%, 349 mg); Mp: 152.0–152.5 °C; IR (KBr): 3820, 1719, 1661, 1591, 1450, 848, 760, 516 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.73 (s, 1H, ArH), 8.08–8.06 (m, 2H, ArH), 7.77 (s, 1H, ArH), 7.72–7.70 (m, 2H, ArH), 7.37–7.35 (m, 2H, ArH), 7.29–7.26 (m, 3H, ArH), 7.04–7.02 (m, 2H, ArH), 6.81–6.79 (m, 2H, ArH), 3.88 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.0, 163.7, 161.1, 158.4, 149.5, 149.4, 138.2, 132.3, 131.1, 130.3, 128.6, 128.6, 128.6, 128.5, 120.2, 114.3, 114.3, 113.6, 55.5, 55.4; HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NO_3$ 396.1594; found, 396.1601.

(4-Chloro-3-methylphenyl)(6-(4-fluorophenyl)-4-phenylpyridin-3-yl)methanone (3e')



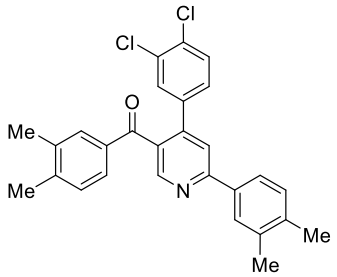
White solid (86%, 346 mg); Mp: 160.3–160.8°C; IR (KBr): 3859, 1717, 1650, 1592, 1450, 772, 585 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 8.13–8.08 (m, 2H, ArH), 7.79 (s, 1H, ArH), 7.58–7.43 (m, 1H, ArH), 7.38–7.36 (m, 1H, ArH), 7.33–7.20 (m, 6H, ArH), 7.19–7.11 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 165.3, 162.8, 158.0, 149.7 (d, J = 22.0 Hz), 140.0, 138.9 (d, J = 220.0 Hz), 136.4, 135.4, 134.6, 134.3, 132.1, 129.2, 1290 (d, J = 19.0 Hz), 128.8, 128.7 (d, J = 18.0 Hz), 128.5, 120.6, 115.9 (d, J = 22.0 Hz), 19.9; HRMS (TOF ES$^+$) m/z: $[M+H]^+$ calcd for $C_{25}H_{17}ClFNO$ 402.1055; found, 402.1058.

(6-(2,6-dichloro-3-fluorophenyl)-4-(3,4-dichlorophenyl)pyridin-3-yl)(3,4-dimethylphenyl)methanone (3f')



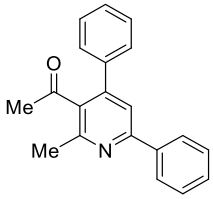
Yellow solid (84%, 434 mg); Mp: 149.4–149.9°C; IR (KBr): 3636, 3459, 1739, 1673, 1596, 1531, 1444, 1328, 1247, 1127, 991, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H, ArH), 7.68 (s, 1H, ArH), 7.62 (s, 2H, ArH), 7.35–7.34 (d, 1H, ArH), 7.29–7. 27 (d, 1H, ArH), 7.12–7.09 (m, 2H, ArH), 7.03–7.01 (m, 1H, ArH), 6.86–6.85 (m, 1H, ArH), 2.33 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 164.1 (d, J = 11.0 Hz), 161.6 (d, J = 12.0 Hz), 160.4, 149.9, 147.5, 140.0, 139.8, 138.7, 137.7, 133.5, 133.2, 132.0, 130.8, 130.7, 130.3, 127.8, 125.2, 120.9, 112.6 (d, J = 18.0 Hz), 112.6(d, J = 19.0 Hz), 109.2, 108.9, 108.7, 21.4, 21.4. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{26}H_{16}Cl_4FNO$ 518.0043; found, 518.0045.

(4-(3,4-dichlorophenyl)-6-(3,4-dimethylphenyl)pyridin-3-yl)(3,4-dimethylphenyl)methanone (3g')



Yellow liquid (80%, 367 mg); IR (KBr): 3807, 3527, 3346, 3277, 3155, 2982, 1919, 1758, 1659, 1583, 1539, 1245, 907, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H, ArH), 7.76 (s, 1H, ArH), 7.71 (s, 2H, ArH), 7.54 (s, 1H, ArH), 7.48–7. 45 (m, 2H, ArH), 7.34–7.32 (d, 1H, ArH), 7.15–7.12 (m, 3H, ArH), 2.42 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 159.4, 149.7, 147.3, 143.7, 138.6, 138.2, 138.2, 138.1, 137.2, 134.8, 133.0, 132.9, 132.9, 132.4, 131.7, 131.0, 130.5, 130.3, 129.9, 128.0, 127.9, 125.1, 120.9, 21.4, 21.4, 20.1, 19.7. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{28}H_{23}Cl_2NO$ 460.1229; found, 460.1232.

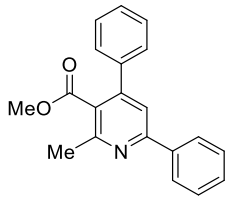
1-(2-methyl-4,6-diphenylpyridin-3-yl)ethan-1-one (3h')



White solid (84%, 241 mg); Mp: 112.5–113.0 °C; IR (KBr): 3748, 3550, 1698, 1582, 1545, 1498, 1244, 762 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 2H, ArH), 7.49 (s, 1H, ArH), 7.41–7.37 (m, 5H, ArH), 7.36–7.33 (m, 3H, ArH), 2.55 (, 3H, CH_3),

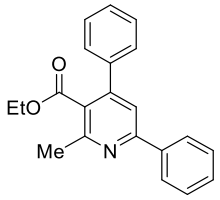
1.93 (s, 3H, CH_3CO). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 206.3, 157.0, 154.1, 147.3, 138.8, 138.4, 134.5, 129.3, 129.0, 128.8, 128.6, 128.5, 127.2, 118.6, 32.1, 23.1. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}NO$ 288.1383; found, 288.1383.

methyl 2-methyl-4,6-diphenylnicotinate (3i')



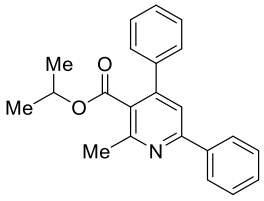
Yellow solid (82%, 249 mg); Mp: 97.3–97.8 °C; IR (KBr): 3762, 1738, 1584, 1546, 1441, 1273, 1079, 701, 670 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.94–7.93 (m, 2H, ArH), 7.47 (s, 1H, ArH), 7.37–7.30 (m, 8H, ArH), 3.53 (s, 3H, CH_3O), 2.61 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.6, 157.5, 155.8, 149.0, 138.9, 138.8, 129.4, 128.8, 128.7, 128.6, 127.8, 127.3, 126.6, 118.5, 52.2, 23.2. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}NO_2$ 304.1332; found, 304.1327.

ethyl 2-methyl-4,6-diphenylnicotinate (3j')



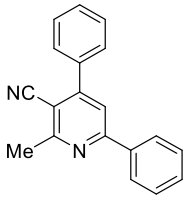
Yellow solid (79%, 251 mg); Mp: 110.1–110.6 °C; IR (KBr): 3915, 3492, 3277, 1766, 1638, 1529, 1464, 1245, 842, 716 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.95–7.93 (m, 2H, ArH), 7.48 (s, 1H, ArH), 7.39–7.36 (m, 2H, ArH) , 7.35–7.31 (m, 6H, ArH), 4.05–4.01 (m, 2H, CH_2), 2.64 (s, 3H, CH_3Ar), 0.92–0.90 (m, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 157.4, 155.8, 149.0, 139.0, 138.8, 129.4, 128.8, 128.6, 128.5, 128.0, 127.2, 126.8, 118.6, 61.4, 23.2, 13.7. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}NO_2$ 318.1489; found, 318.1493.

isopropyl 2-methyl-4,6-diphenylnicotinate (3k')



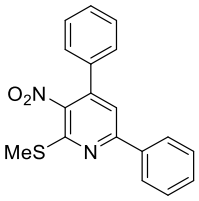
Yellow liquid (77%, 255 mg); IR (KBr): 3896, 3686, 3562, 3227, 1722, 1584, 1547, 1458, 1381, 1244, 1098, 832, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.92–7.91 (m, 2H, ArH), 7.44 (s, 1H, ArH), 7.36–7.29 (m, 8H, ArH), 4.94–4.92 (m, 1H, CH), 2.62 (s, 3H, CH_3Ar), 0.94 (s, 3H, CH_3), 0.92 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.4, 157.3, 155.5, 148.9, 138.9, 138.9, 129.3, 128.8, 128.6, 128.5 , 128.5, 128.1, 127.3, 118.6, 69.1, 23.1, 21.4, 21.4. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}NO_2$ 332.1645; found, 332.1642.

2-methyl-4,6-diphenylnicotinonitrile (3l')



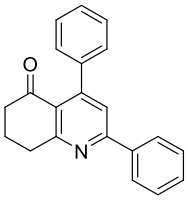
White solid (89%, 240 mg); Mp: 126.0–126.5 °C; IR (KBr): 3935, 3808, 3620, 3040, 2224, 1764, 1592, 1546, 1504, 1382, 1246, 1164, 1000, 878, 792, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.01–7.99 (m, 2H, ArH), 7.60 (s, 1H, ArH), 7.57–7.55 (m, 2H, ArH), 7.47–7.40 (m, 6H, ArH), 2.84 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.8, 159.2, 153.9, 137.8, 136.6, 130.4, 129.9, 129.0, 129.0, 128.5, 127.5, 118.0, 117.3, 105.9, 24.4. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{19}H_{14}N_2$ 271.1230; found, 271.1229.

2-(methylthio)-3-nitro-4,6-diphenylpyridine (3m')



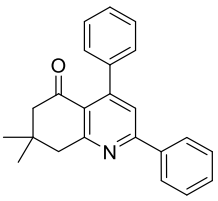
Yellow solid (77%, 248 mg); Mp: 137.4–137.9 °C; IR (KBr): 3825, 3745, 3333, 3069, 1771, 1580, 1435, 1243, 880, 697, 589 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.03–8.01 (m, 2H, ArH), 7.41–7.27 (m, 6H, ArH), 7.26–7.25 (m, 2H, ArH), 6.94 (s, 1H, ArH), 3.17 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.0, 152.5, 149.1, 138.3, 137.7, 130.5, 128.8, 128.7, 128.5, 127.9, 127.6, 127.0, 111.8, 28.6. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}N_2O_2S$ 323.0849; found, 323.0850.

2,4-diphenyl-7,8-dihydroquinolin-5(6*H*)-one (3n')



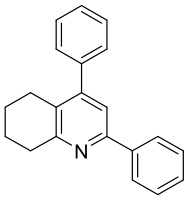
Yellow solid (87%, 260 mg); Mp: 120.0–120.5 °C; IR (KBr): 3878, 3565, 3066, 2952, 1739, 1696, 1580, 1532, 1498, 1441, 1368, 1241, 764, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.99–7.98 (m, 2H, ArH), 7.44 (s, 1H, ArH), 7.41–7.37 (m, 3H, ArH), 7.36–7.32 (m, 3H, ArH), 7.21–7.19 (m, 2H, ArH), 3.22–3.20 (m, 2H, CH_2Ar), 2.61–2.59 (m, 2H, CH_2CO), 2.16–2.12 (m, 2H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.7, 164.9, 159.0, 152.7, 140.6, 138.1, 130.1, 128.9, 128.1, 127.8, 127.8, 127.5, 124.9, 122.0, 40.1, 34.0, 21.7. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}NO$ 300.1383; found, 300.1386.

7,7-dimethyl-2,4-diphenyl-7,8-dihydroquinolin-5(6*H*)-one (3o')



White solid (83%, 271 mg); Mp: 135.1–135.6 °C; IR (KBr): 3854, 3464, 2960, 1692, 1581, 1542, 1451, 1372, 1280, 1239, 888, cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.00–7.99 (m, 2H, ArH), 7.44 (s, 1H, ArH), 7.40–7.38 (m, 3H, ArH), 7.35–7.33 (m, 3H, ArH), 7.21–7.20 (m, 2H, ArH), 3.13 (s, 2H, CH_2Ar), 2.47 (s, 2H, CH_2CO), 1.08 (s, 6H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.8, 163.5, 159.4, 152.3, 140.5, 138.2, 130.0, 128.9, 128.0, 127.8, 127.8, 127.5, 123.9, 121.8, 53.8, 47.8, 32.7, 28.3, 28.3. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}NO$ 328.1696; found, 328.1698.

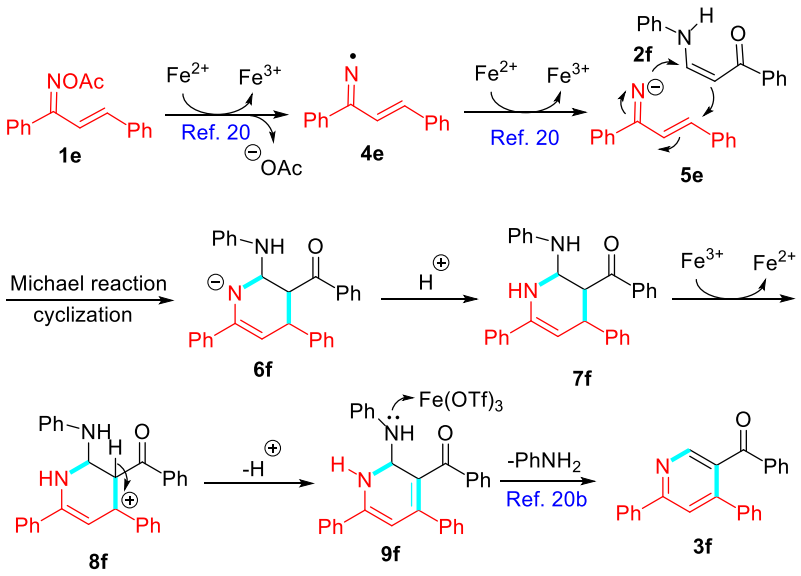
2,4-diphenyl-5,6,7,8-tetrahydroquinoline (3p')



White solid (83%, 237 mg); Mp: 117.3–117.8 °C; IR (KBr): 3805, 3631, 2937, 2863, 1587, 1546, 1442, 1381, 1244, 768, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.89–7.88 (m, 2H, ArH), 7.36–7.23 (m, 9H, ArH), 3.02–3.00 (m, 2H, CH_2), 2.57–2.55 (m, 2H, CH_2), 1.86–1.82 (m, 2H, CH_2), 1.68–1.64 (m, 2H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.6, 154.3, 150.4, 139.7, 139.7, 128.7, 128.6, 128.6, 128.5, 128.4, 127.8, 127.0, 119.2, 33.3, 27.3, 23.1, 23.1. HRMS (TOF ES^+) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N$ 286.1590; found, 286.1588.

The proposed mechanism of the cascade reaction

The proposed mechanism is shown in Scheme 2. Initially, *α,β*-unsaturated ketoxime acetate **1e** was formed **4e** via SET mechanism. Subsequently, the radical intermediate **4e** acquired one electron from the Fe^{2+} to form the intermediate **5e**. Then, the intermediate **5e** undergoes a bis-Michael reaction with the substrate **2f**, yielding the key intermediate **6f**. The intermediate was further oxidized by Fe^{3+} and formed the intermediate **7f** after losing two electrons. The intermediate **7f** produced the intermediate **8f** after losing one proton. Finally, the intermediate **8f** lost one molecule of $PhNH_2$ to yield the final product **3f**.



Scheme S1. The mechanism were tested by HPLC-HRMS

Furthermore, we tried to make the mixture of **1e** (0.1 mmol), **2f** (0.11 mmol) and $Fe(OTf)_3$ (0.05 equiv.) in toluene and carried out refluxing for 0.5 h. Following this, we immediately injected the reaction mixture into the high-pressure liquid chromatography-high-resolution mass spectrometry (HPLC-HRMS) system. Some intermediate molecular ion peaks appeared (ESI, Figures S101–S108). The molecular ion peaks that appeared in the high-resolution mass spectrum were: HRMS (TOF ES^+): *m/z* calcd. for $C_{17}H_{15}NNaO_2$ $[M+Na]^+$, 288.0995; found, 288.0996, which is the HRMS spectrum of **1e** (SI, Figure S102); HRMS (TOF ES^+): *m/z* calcd. for $C_2H_5O_2$ $[M+H]^+$, 61.0284; found, 61.0281 , which is the HRMS spectrum of HOAc (SI, Figure S103). HRMS (TOF ES^+): *m/z* calcd. for $C_{15}H_{14}NO$ $[M+H]^+$, 224.1070; found, 224.1070 , which is the HRMS spectrum of **2f** (SI, Figure S104); HRMS (TOF ES^+): *m/z* calcd. for $C_{15}H_{12}N^{\cdot+}$ $[M]^+$, 206.0964; found, 206.0965, which is the HRMS spectrum of **4e** (SI, Figure S105); HRMS (TOF ES^+): *m/z* calcd. for $C_{15}H_{14}N^{\cdot}$ $[M+H]^+$, 208.1121; found, 208.1117, which is the HRMS spectrum of **5e** (SI, Figure S106); HRMS (TOF ES^+): *m/z* calcd. for $C_{30}H_{27}N_2O$ $[M+H]^+$, 431.2118; found, 431.2115, which is the HRMS spectrum of **7f** (SI, Figure S107); HRMS (TOF ES^+): *m/z* calcd. for $C_{30}H_{25}N_2O$ $[M+H]^+$, 429.1961; found, 429.1957, which is the HRMS spectra of intermediates 8f or **9f** (SI, Figures S108); HRMS (TOF ES^+): *m/z* calcd. for $C_{24}H_{18}NO$ $[M+H]^+$, 336.1383; found, 336.1380, which is the HRMS spectrum of target compound **3f** (SI, Figure S109). Based on the molecular ion peaks of intermediates **4e**−**5e** and **7f**−**9f** (ESI, Figures

S105–S108). We believe there exist ample evidence in support of the proposed mechanism.

X-ray Structure and Data of 3u[3]

Single crystal culture and confirmation: First, compound **3u** (20 mg) was added to a bottle and dissolved by the addition of ethyl acetate (0.5 mL). Then, the bottle was placed in a dry, ventilated place at room temperature for 10 days. Some crystals appeared, and for single crystal parsing, crystals were selected with sizes of 0.34 mm x 0.24 mm x 0.18 mm. The Bruker D8 VENTURE was used to obtain single crystal diffraction at 100.0 K with the use of three-circle diffractometer MoK (lambda = 0.71073 A) for diffraction intensity data collection, using Φ and omega scanning. The crystal structure was solved by the atomic method using the SHELXL 2018/3 (Sheldrick, 2015) program (Supporting Information, Figure S1, CCDC 2260760).[3]

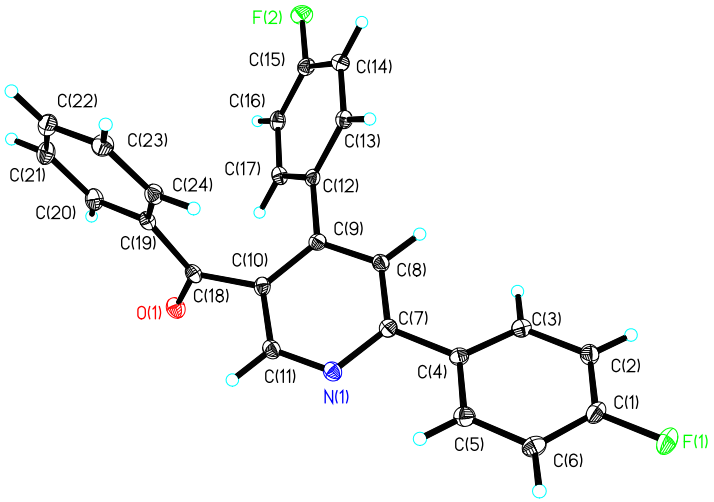


Figure S1. X-Ray crystal structure of **3u**, ellipsoid is drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **3u**

Identification code	1
Empirical formula	$C_{24}H_{15}F_2NO$
Formula weight	371.37
Temperature	100.00 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.7520(7) A alpha = 88.991(3) deg.
	b = 9.0608(6) A beta = 76.810(3) deg.
	c = 11.3766(9) A gamma = 82.972(3) deg.
Volume	871.72(11) A^3
Z, Calculated density	2, 1.415 Mg/m^3
Absorption coefficient	0.101 mm^-1
F(000)	384
Crystal size	0.34 x 0.24 x 0.18 mm
Theta range for data collection	2.265 to 28.446 deg.
Limiting indices	-11<=h<=11, -12<=k<=11, -15<=l<=15
Reflections collected / unique	19045 / 4364 [R(int) = 0.0457]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7046
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4364 / 0 / 253
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0956
Rindices (all data)	R1 = 0.0671, wR2 = 0.1068
Extinction coefficient	n/a
Largest diff. peak and hole	0.269 and -0.213 e.A^-3

Table S2. Bond Lengths for **3u**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(1)	C(1)	1.3622(16)	C(11)	H(11)	0.9500
F(2)	C(15)	1.3576(16)	C(12)	C(13)	1.398(2)
O(1)	C(18)	1.2209(17)	C(12)	C(17)	1.396(2)
N(1)	C(7)	1.3456(18)	C(13)	H(13)	0.9500
N(1)	C(11)	1.3318(19)	C(13)	C(14)	1.387(2)
C(1)	C(2)	1.376(2)	C(14)	H(14)	0.9500
C(1)	C(6)	1.374(2)	C(14)	C(15)	1.377(2)
C(2)	H(2)	0.9500	C(15)	C(16)	1.374(2)
C(2)	C(3)	1.389(2)	C(16)	H(16)	0.9500
C(3)	H(3)	0.9500	C(16)	C(17)	1.386(2)
C(3)	C(4)	1.395(2)	C(17)	H(17)	0.9500
C(4)	C(5)	1.397(2)	C(18)	C(19)	1.491(2)
C(4)	C(7)	1.4863(19)	C(19)	C(20)	1.398(2)
C(5)	H(5)	0.9500	C(19)	C(24)	1.394(2)
C(5)	C(6)	1.383(2)	C(20)	H(20)	0.9500
C(6)	H(6)	0.9500	C(20)	C(21)	1.384(2)
C(7)	C(8)	1.3958(19)	C(21)	H(21)	0.9500
C(8)	H(8)	0.9500	C(21)	C(22)	1.390(2)
C(8)	C(9)	1.3916(19)	C(22)	H(22)	0.9500
C(9)	C(10)	1.4008(19)	C(22)	C(23)	1.387(2)
C(9)	C(12)	1.4861(19)	C(23)	H(23)	0.9500
C(10)	C(11)	1.393(2)	C(23)	C(24)	1.388(2)
C(10)	C(18)	1.503(2)	C(24)	H(24)	0.9500

Table S3. Bond Angles for **3u**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(11)	N(1)	C(7)	117.44(12)	C(14)	C(13)	C(12)	121.03(13)
F(1)	C(1)	C(2)	118.52(14)	C(14)	C(13)	H(13)	119.5
F(1)	C(1)	C(6)	118.43(13)	C(13)	C(14)	H(14)	120.9
C(6)	C(1)	C(2)	123.04(14)	C(15)	C(14)	C(13)	118.24(14)
C(1)	C(2)	H(2)	120.9	C(15)	C(14)	H(14)	120.9
C(1)	C(2)	C(3)	118.17(14)	F(2)	C(15)	C(14)	118.73(13)
C(3)	C(2)	H(2)	120.9	F(2)	C(15)	C(16)	118.43(13)
C(2)	C(3)	H(3)	119.6	C(16)	C(15)	C(14)	122.83(13)
C(2)	C(3)	C(4)	120.82(13)	C(15)	C(16)	H(16)	120.9
C(4)	C(3)	H(3)	119.6	C(15)	C(16)	C(17)	118.30(13)
C(3)	C(4)	C(5)	118.63(13)	C(17)	C(16)	H(16)	120.9
C(3)	C(4)	C(7)	121.63(12)	C(12)	C(17)	H(17)	119.4
C(5)	C(4)	C(7)	119.74(13)	C(16)	C(17)	C(12)	121.12(14)
C(4)	C(5)	H(5)	119.4	C(16)	C(17)	H(17)	119.4
C(6)	C(5)	C(4)	121.17(14)	O(1)	C(18)	C(10)	119.46(13)
C(6)	C(5)	H(5)	119.4	O(1)	C(18)	C(19)	120.89(13)
C(1)	C(6)	C(5)	118.12(13)	C(19)	C(18)	C(10)	119.50(12)
C(1)	C(6)	H(6)	120.9	C(20)	C(19)	C(18)	118.65(13)
C(5)	C(6)	H(6)	120.9	C(24)	C(19)-	C(18)	121.42(13)
N(1)	C(7)	C(4)	115.80(12)	C(24)	C(19)	C(20)	119.78(13)
N(1)	C(7)	C(8)	121.76(13)	C(19)	C(20)	H(20)	120.0
C(8)	C(7)	C(4)	122.44(13)	C(21)	C(20)	C(19)	119.95(14)
C(7)	C(8)	H(8)	119.7	C(21)	C(20)	H(20)	120.0
C(9)	C(8)	C(7)	120.65(13)	C(20)	C(21)	H(21)	120.0
C(9)	C(8)	H(8)	119.7	C(20)	C(21)	C(22)	120.08(14)
C(8)	C(9)	C(10)	117.28(13)	C(22)	C(21)	H(21)	120.0
C(8)	C(9)	C(12)	120.07(12)	C(21)	C(22)	H(22)	119.9
C(10)	C(9)	C(12)	122.61(13)	C(23)	C(22)	C(21)	120.18(14)
C(9)	C(10)	C(18)	125.17(13)	C(23)	C(22)	H(22)	119.9
C(11)	C(10)	C(9)	118.09(13)	C(22)	C(23)	H(23)	120.0
C(11)	C(10)	C(18)	116.75(12)	C(22)	C(23)	C(24)	120.06(14)
N(1)	C(11)	C(10)	124.69(13)	C(24)	C(23)	H(23)	120.0
N(1)	C(11)	H(11)	117.7	C(19)	C(24)	H(24)	120.0
C(10)	C(11)	H(11)	117.7	C(23)	C(24)	C(19)	119.93(14)
C(13)	C(12)	C(9)	120.57(13)	C(23)	C(24)	H(24)	120.0
C(17)	C(12)	C(9)	120.95(13)	C(14)	C(13)	C(12)	121.03(13)
C(17)	C(12)	C(13)	118.45(13)	C(14)	C(13)	H(13)	119.5
C(12)	C(13)	H(13)	119.5				

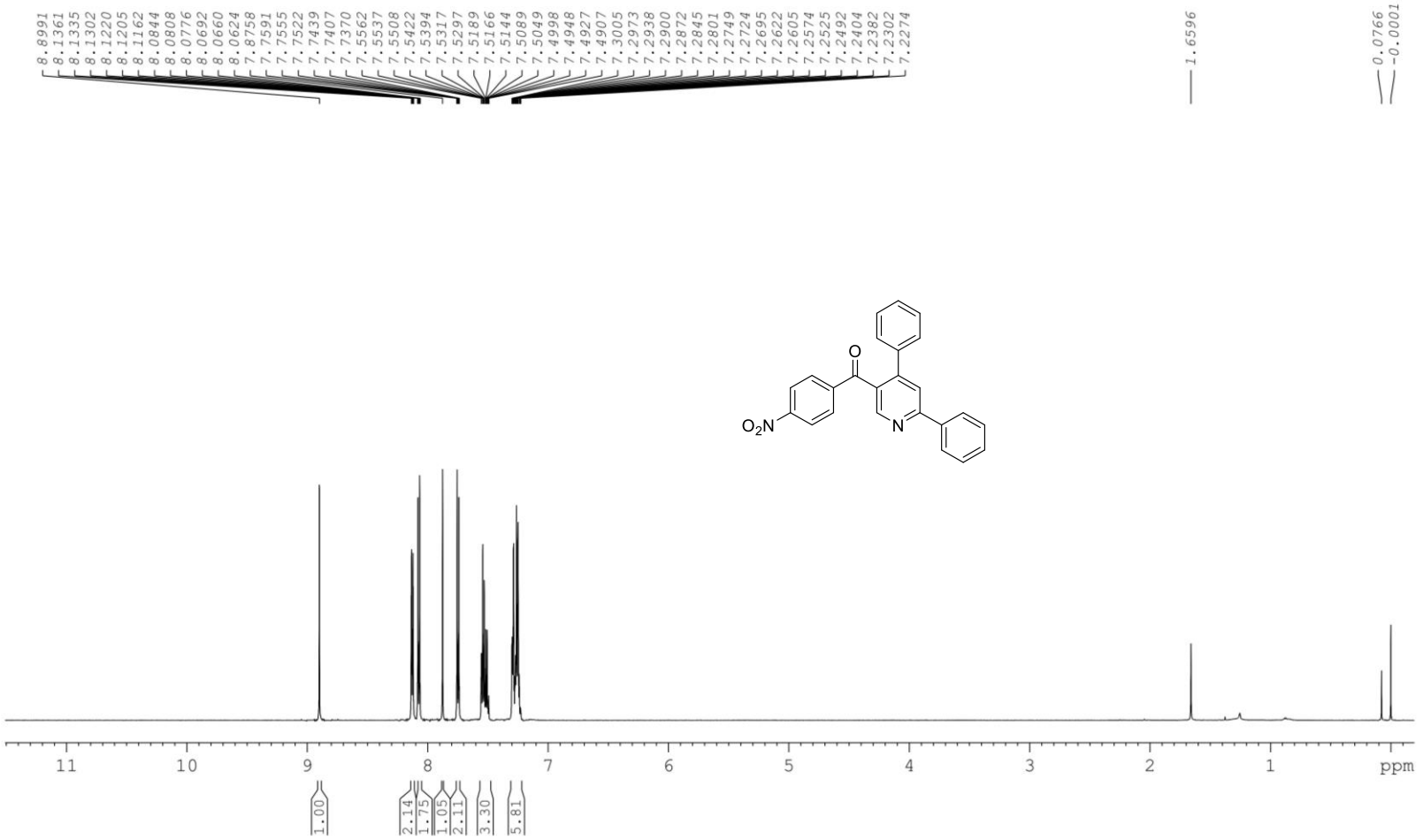


Figure S2. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3a**

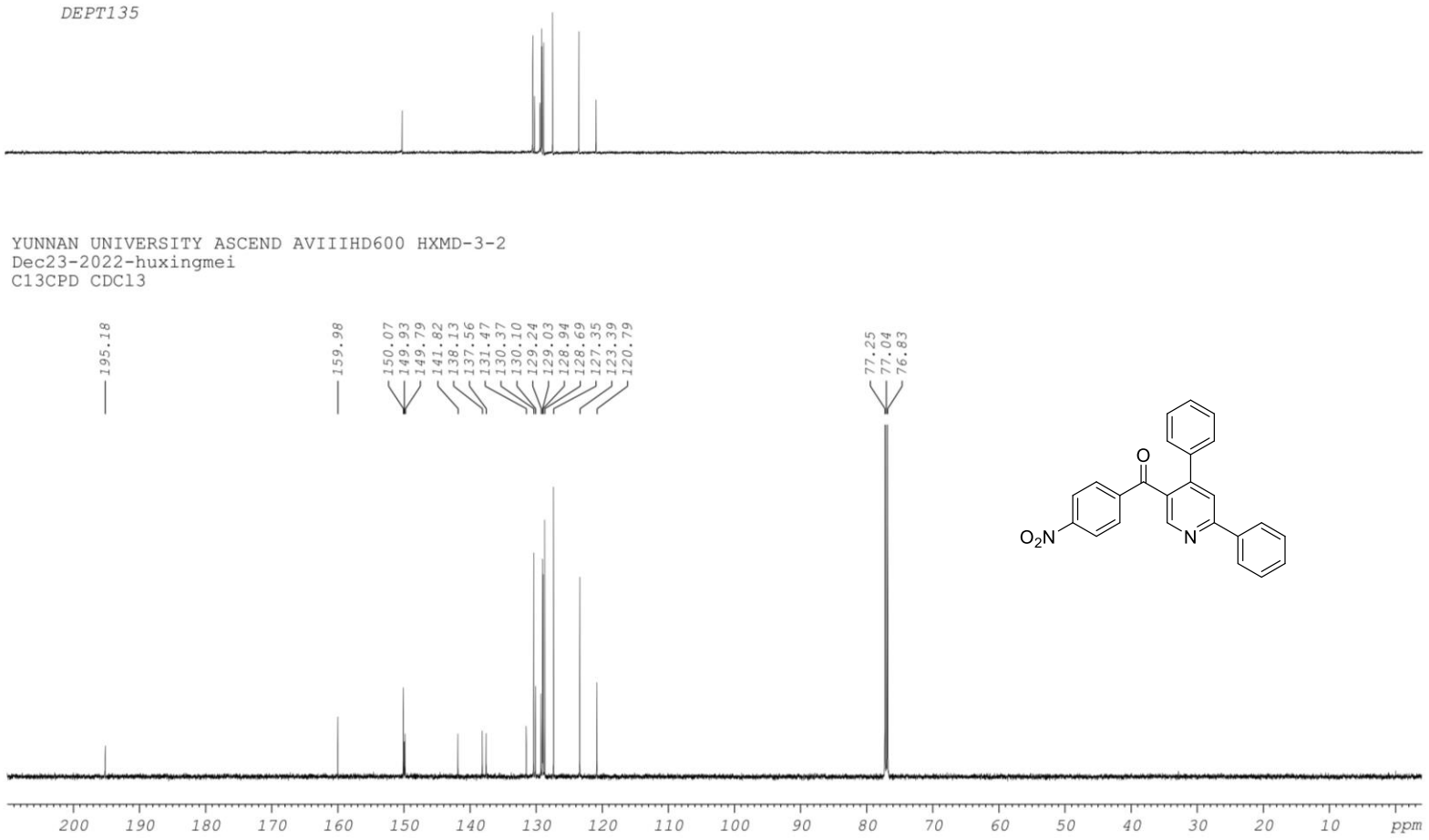


Figure S3. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3a**

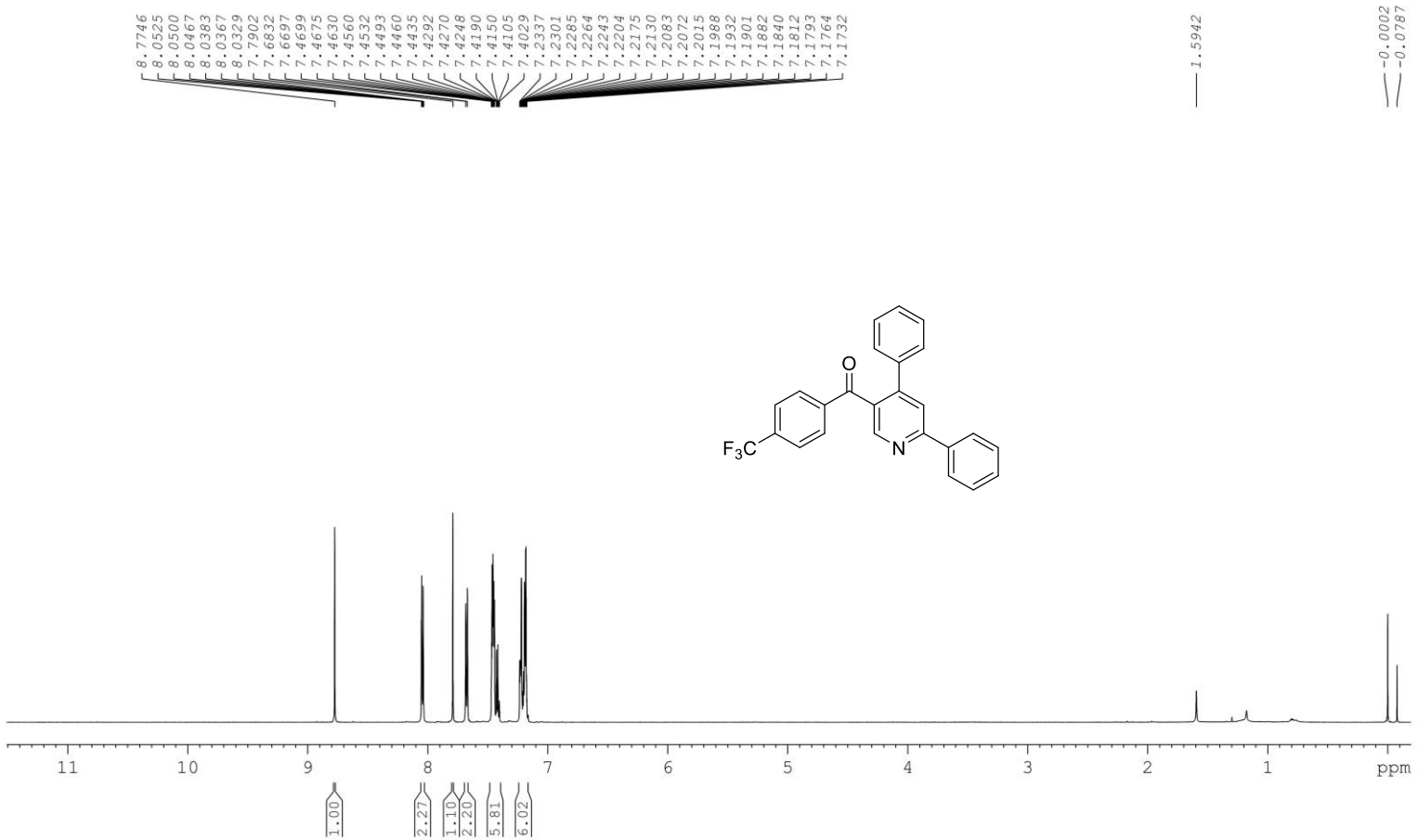


Figure S4. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3b**

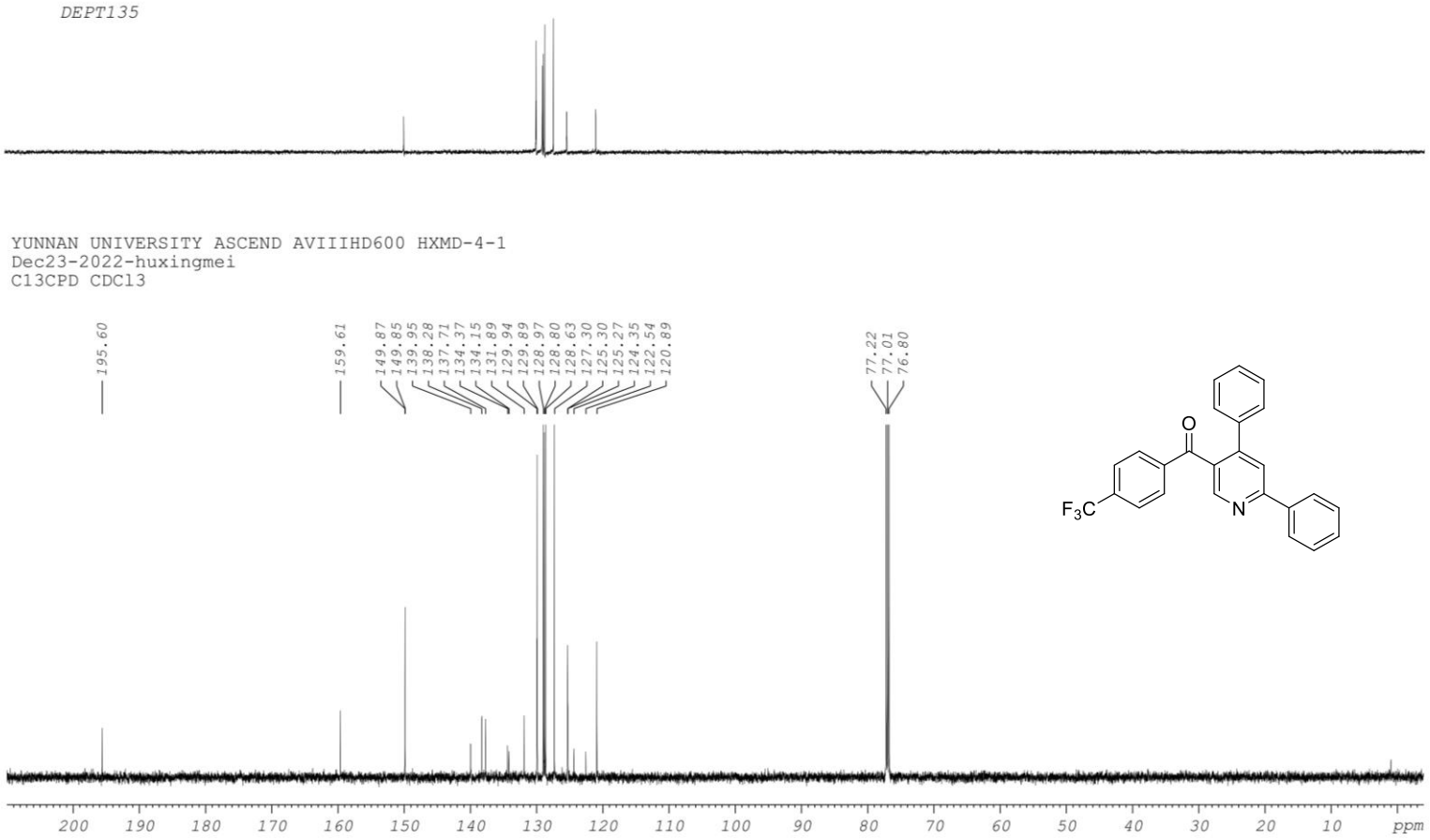


Figure S5. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3b**

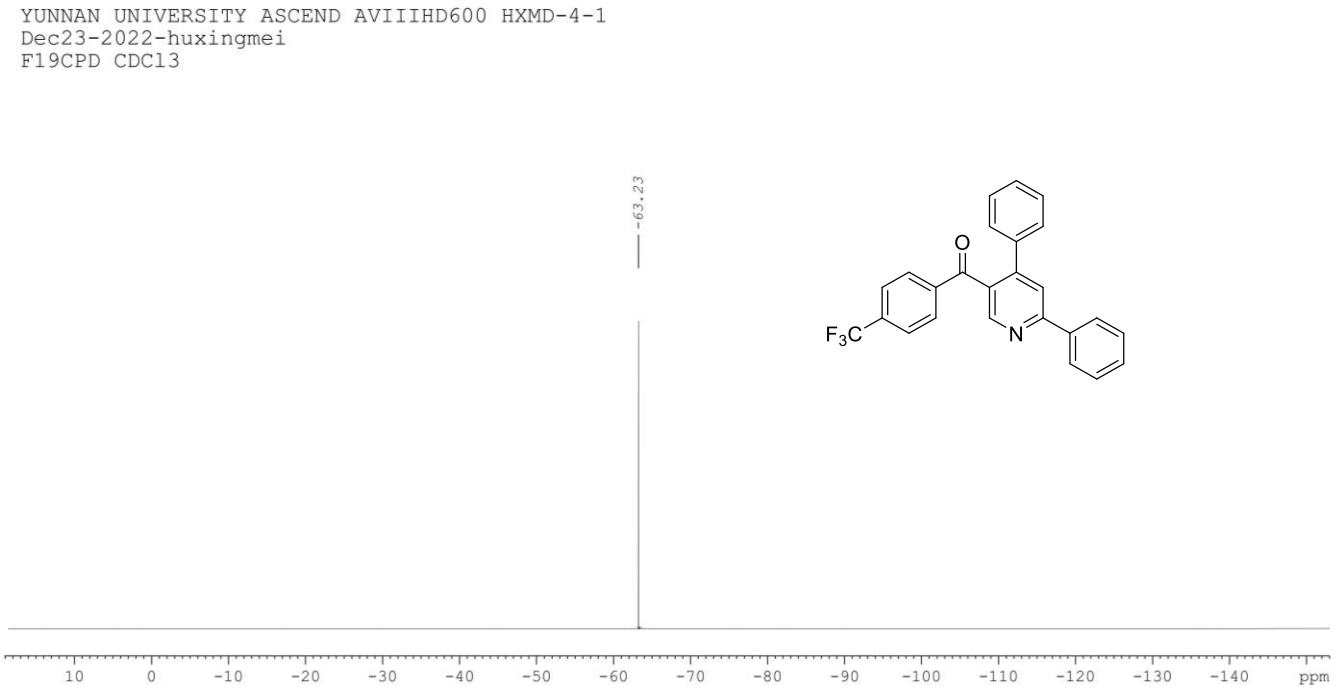


Figure S6. ^{19}F NMR (564 MHz, $CDCl_3$) spectra of compound **3b**

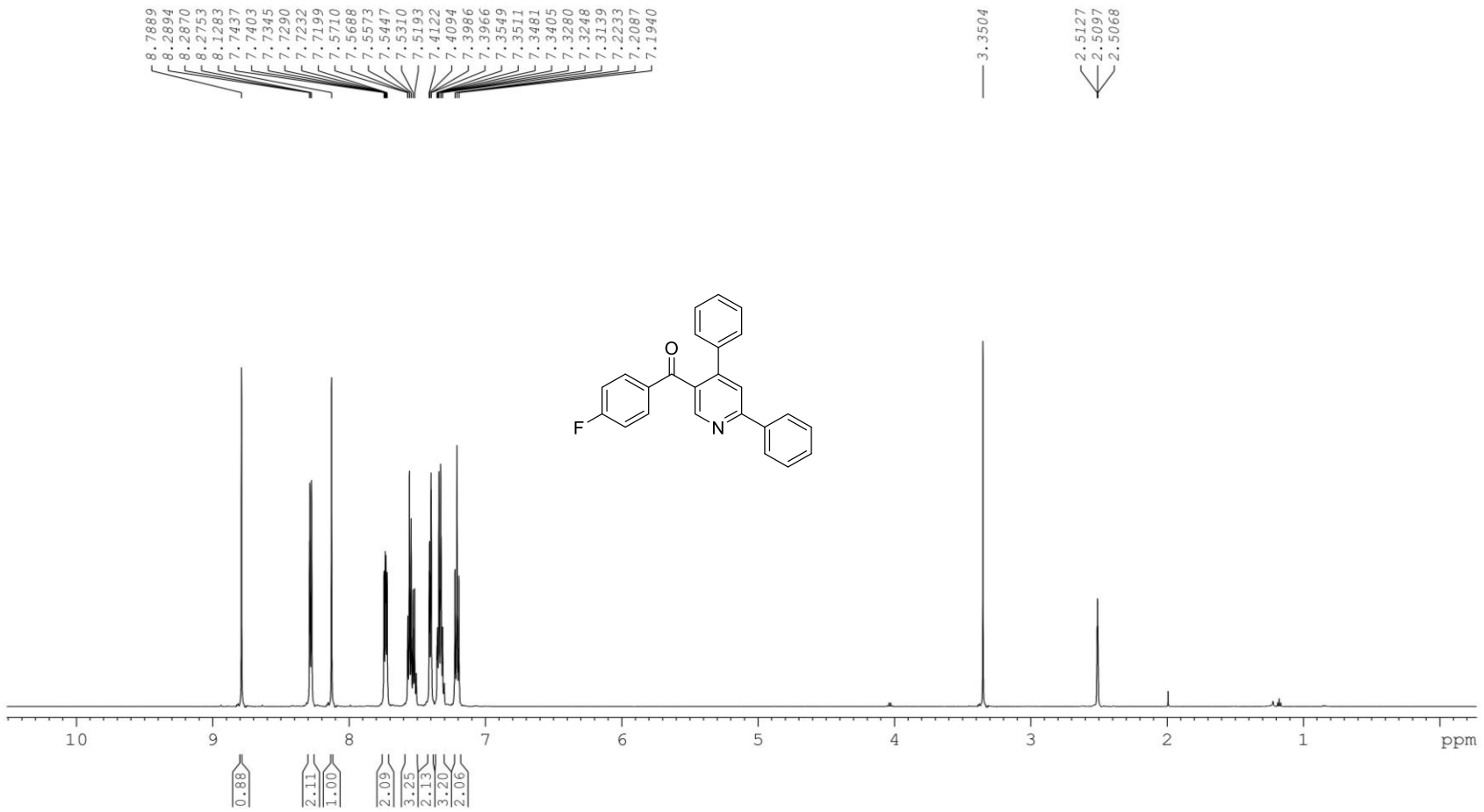


Figure S7. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3c**

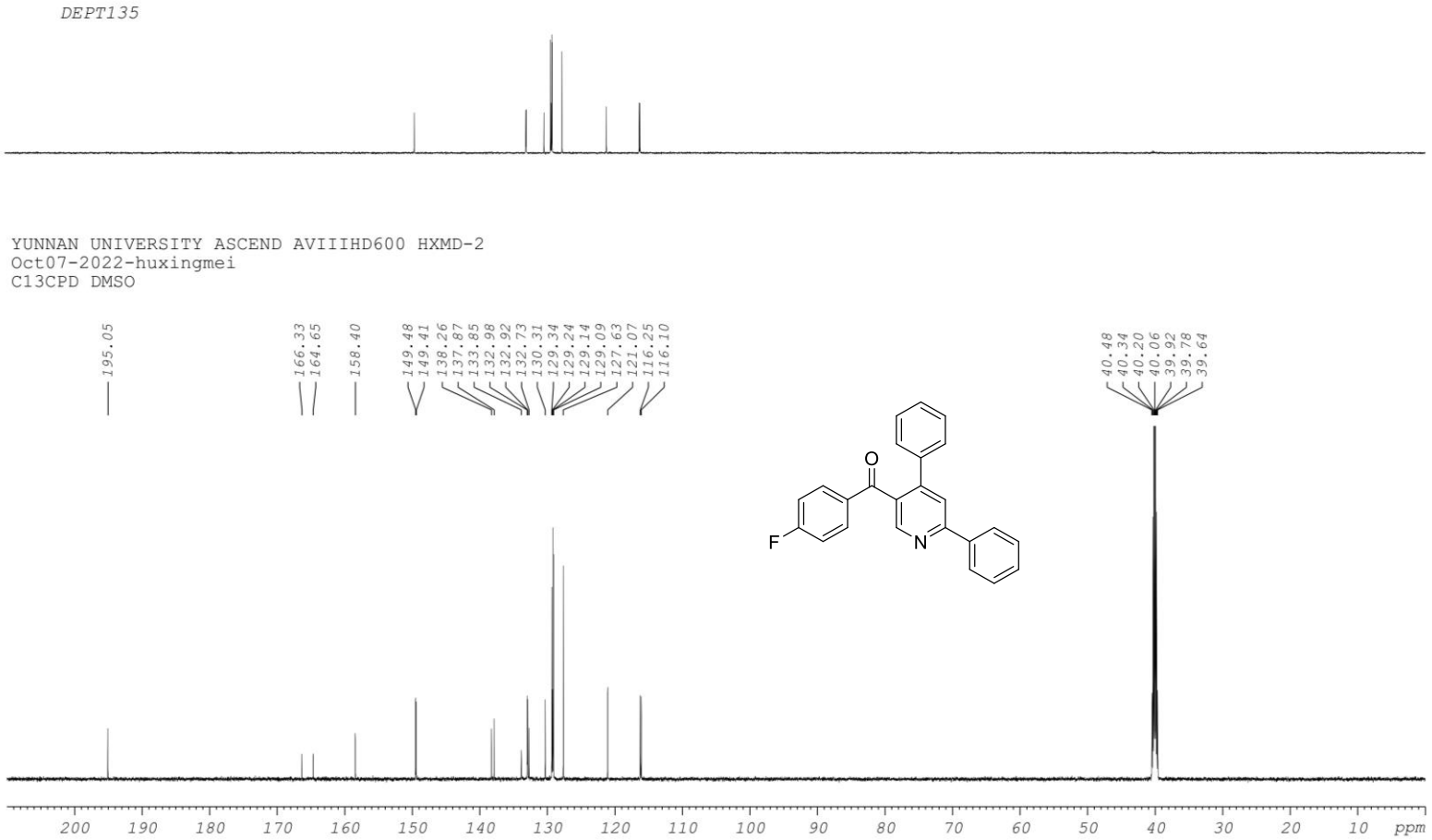


Figure S8. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3c**

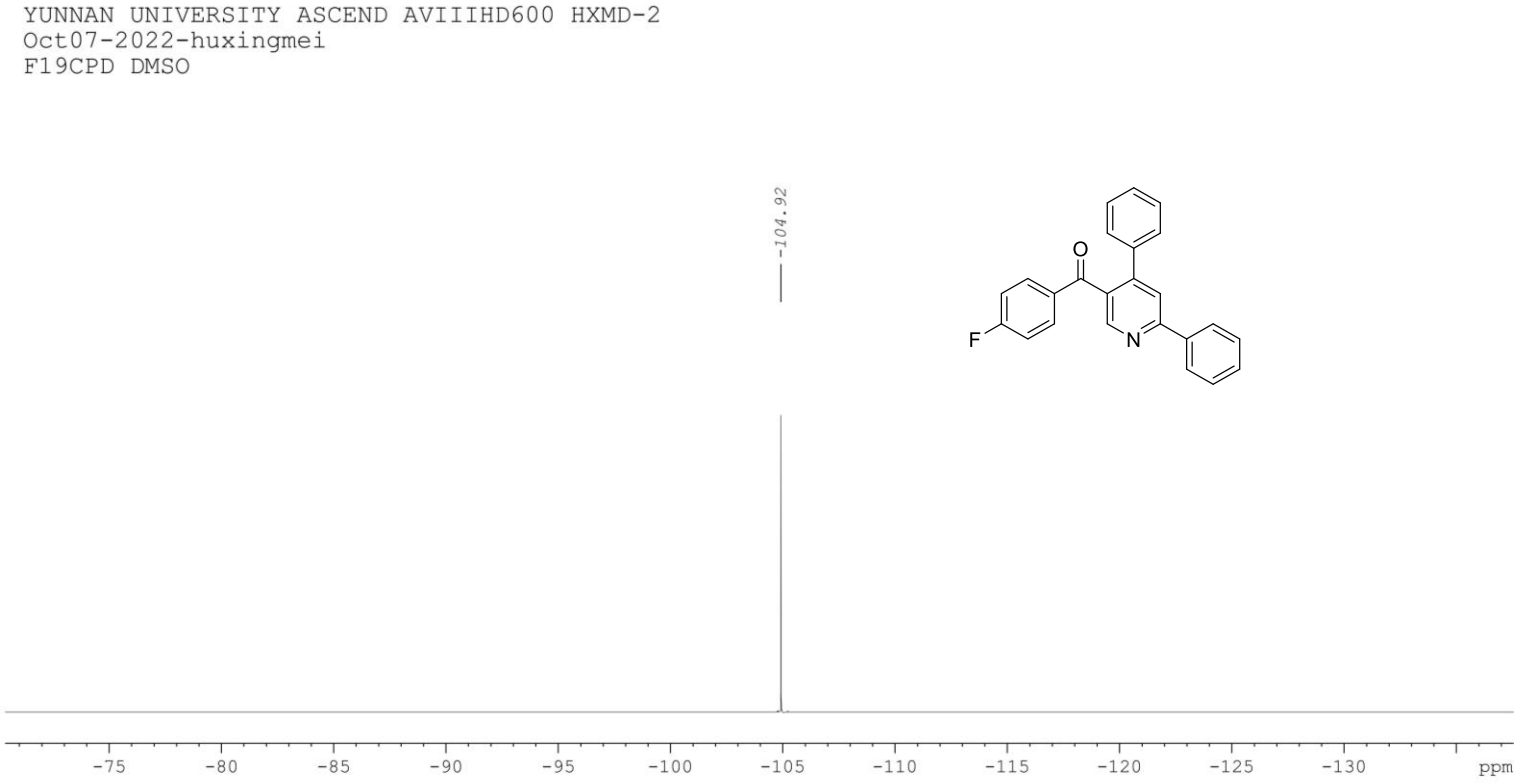


Figure S9. ^{19}F NMR (564 MHz, DMSO-d_{63}) spectra of compound **3c**

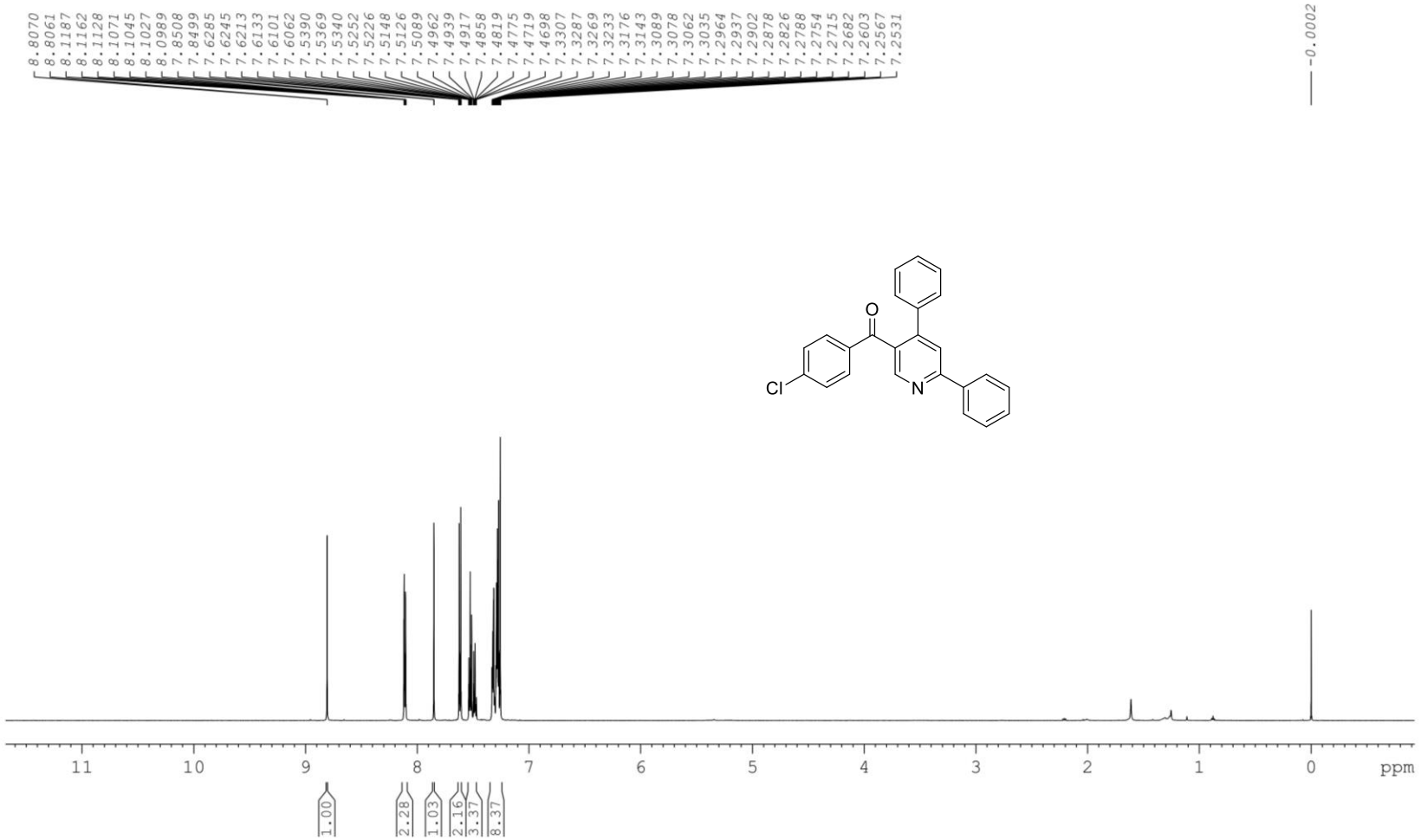


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3d**

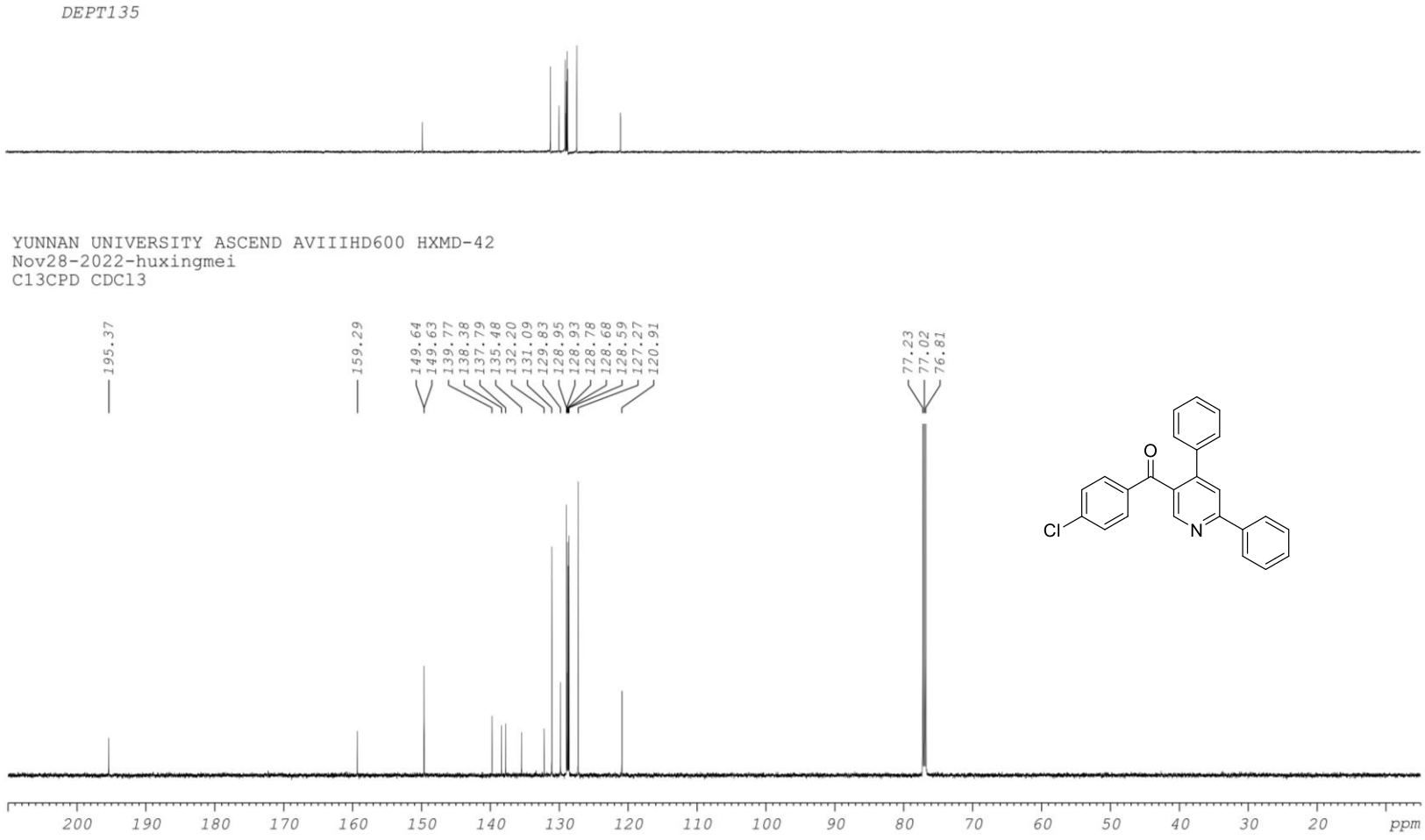


Figure S11. ^{12}C NMR (150 MHz, $CDCl_3$) spectra of compound **3d**

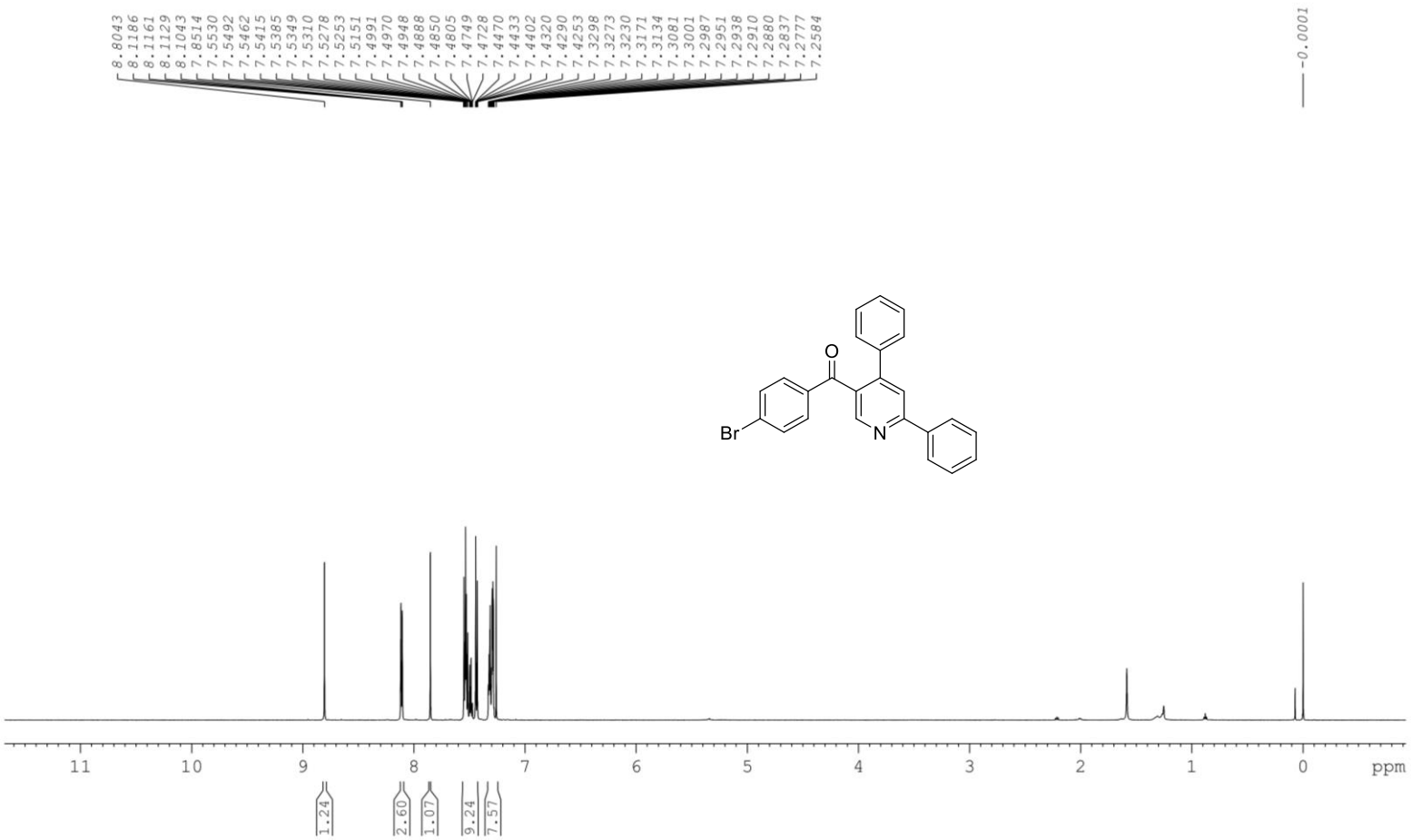


Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3e**

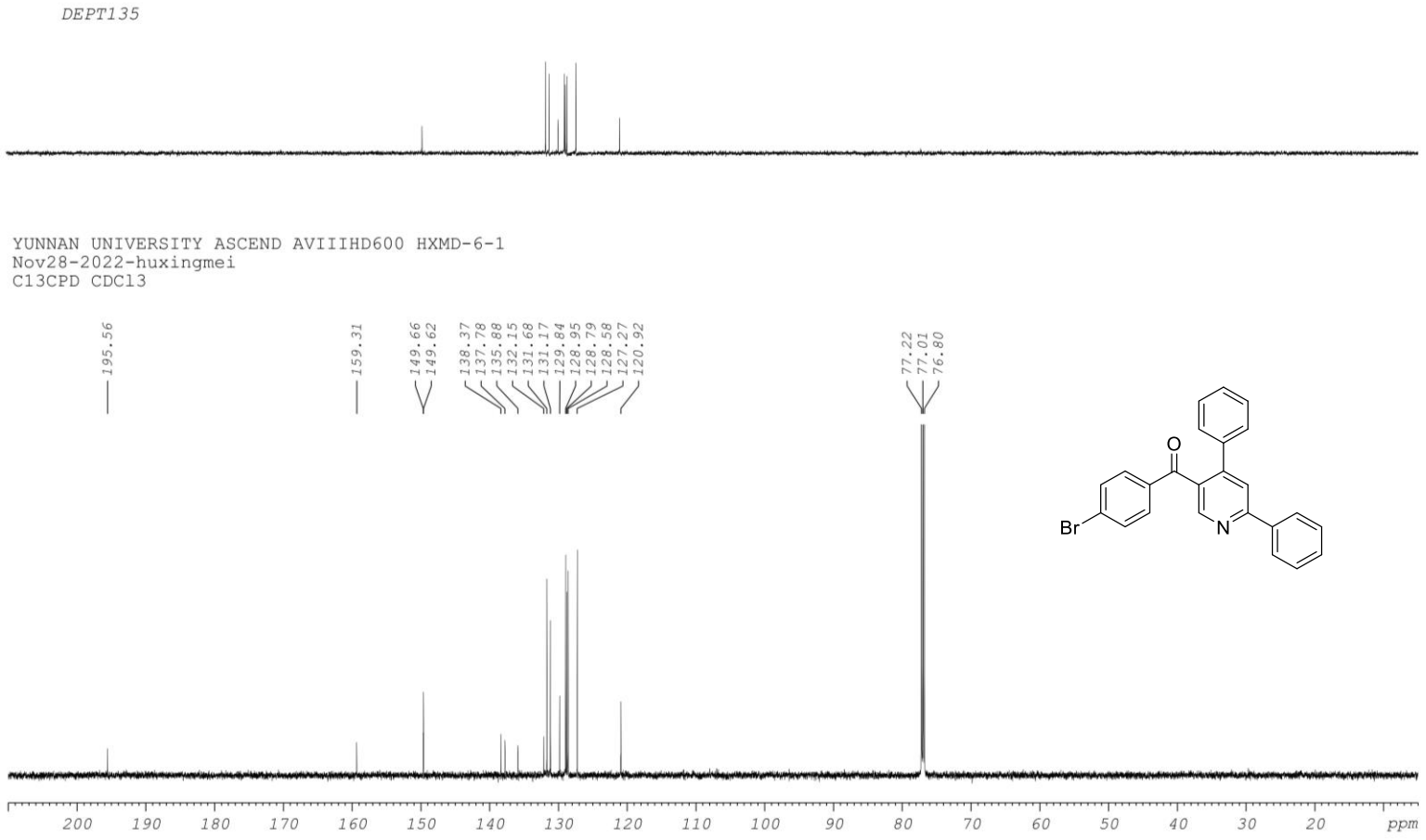


Figure S13. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3e**

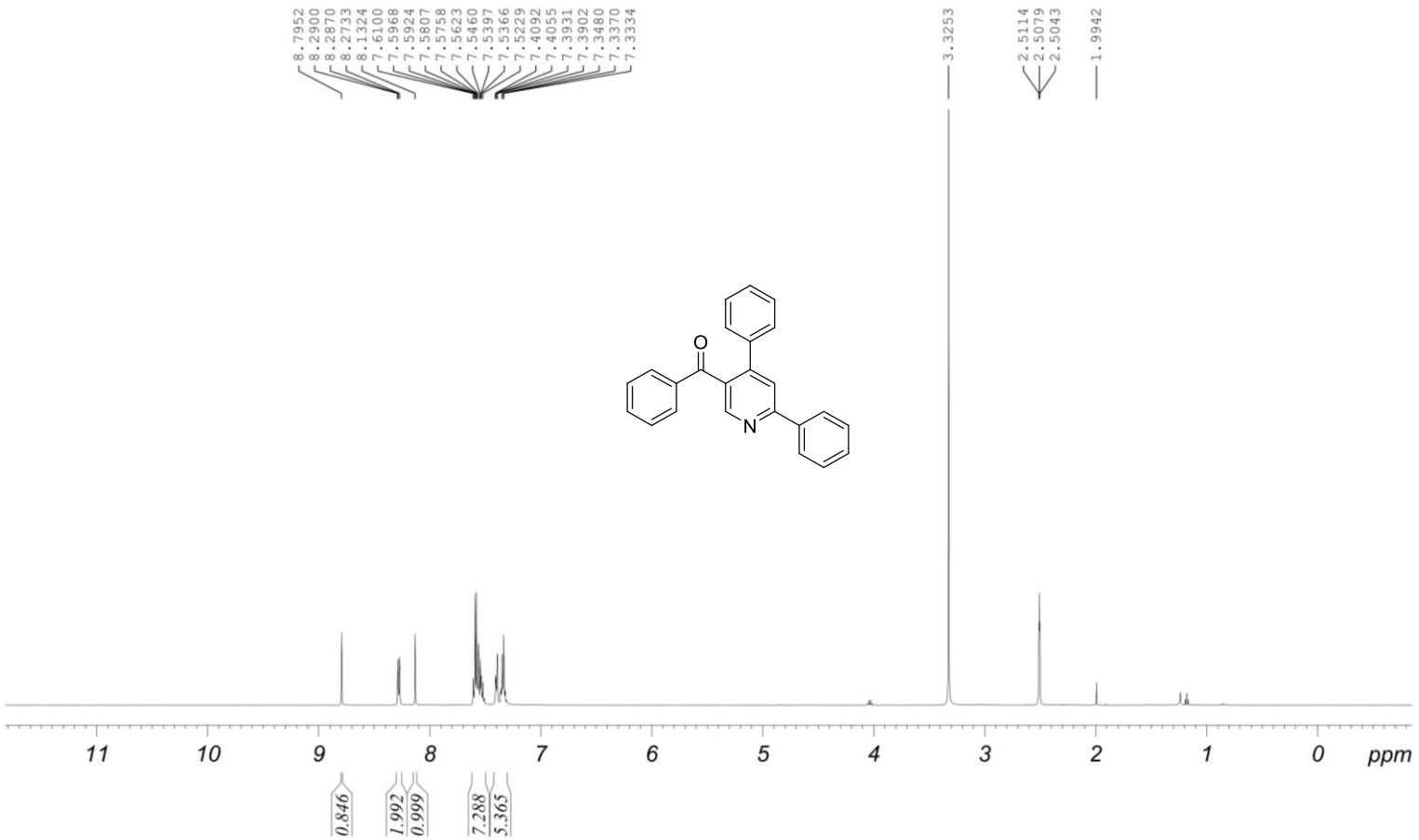


Figure S14. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **3f**

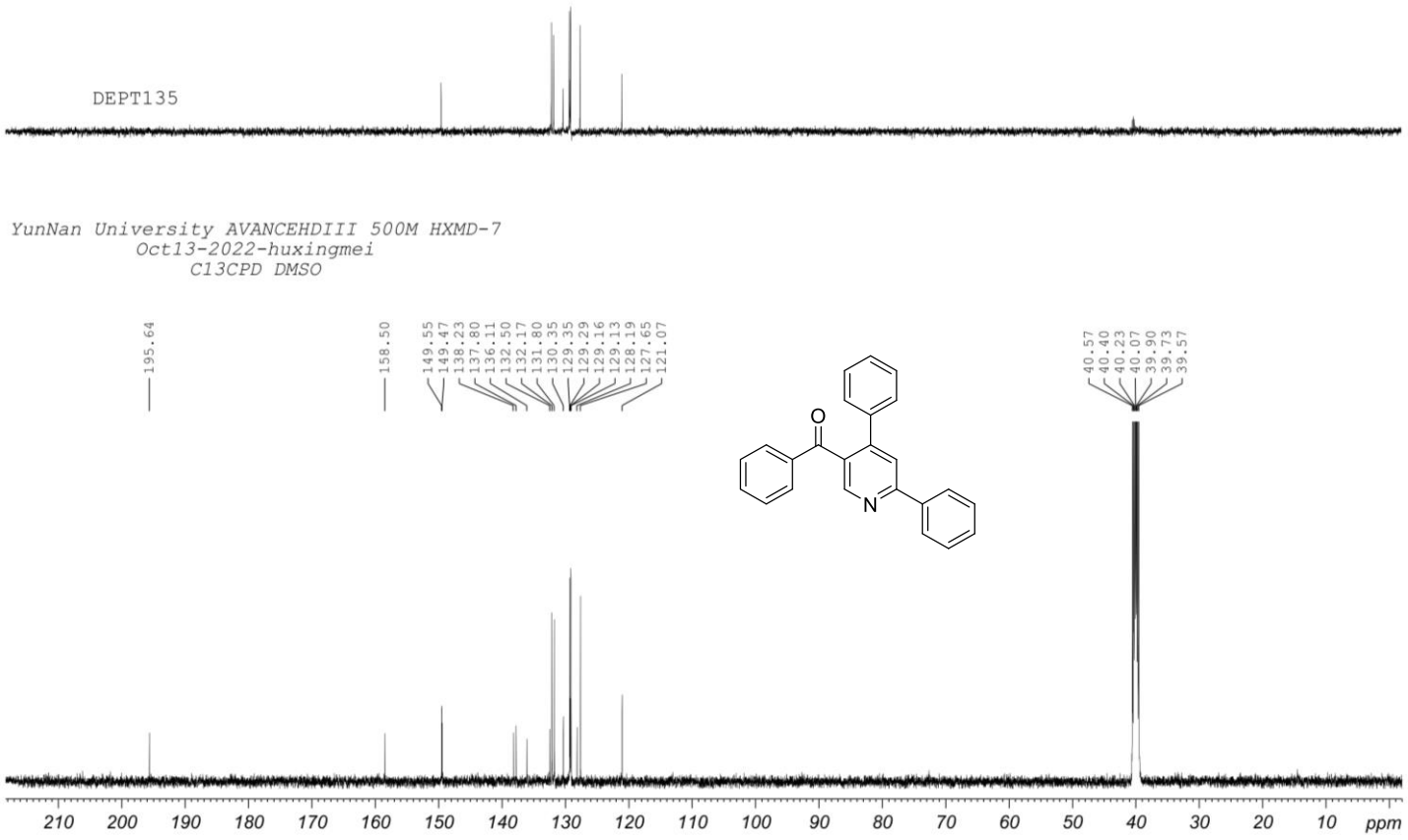


Figure S15. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **3f**

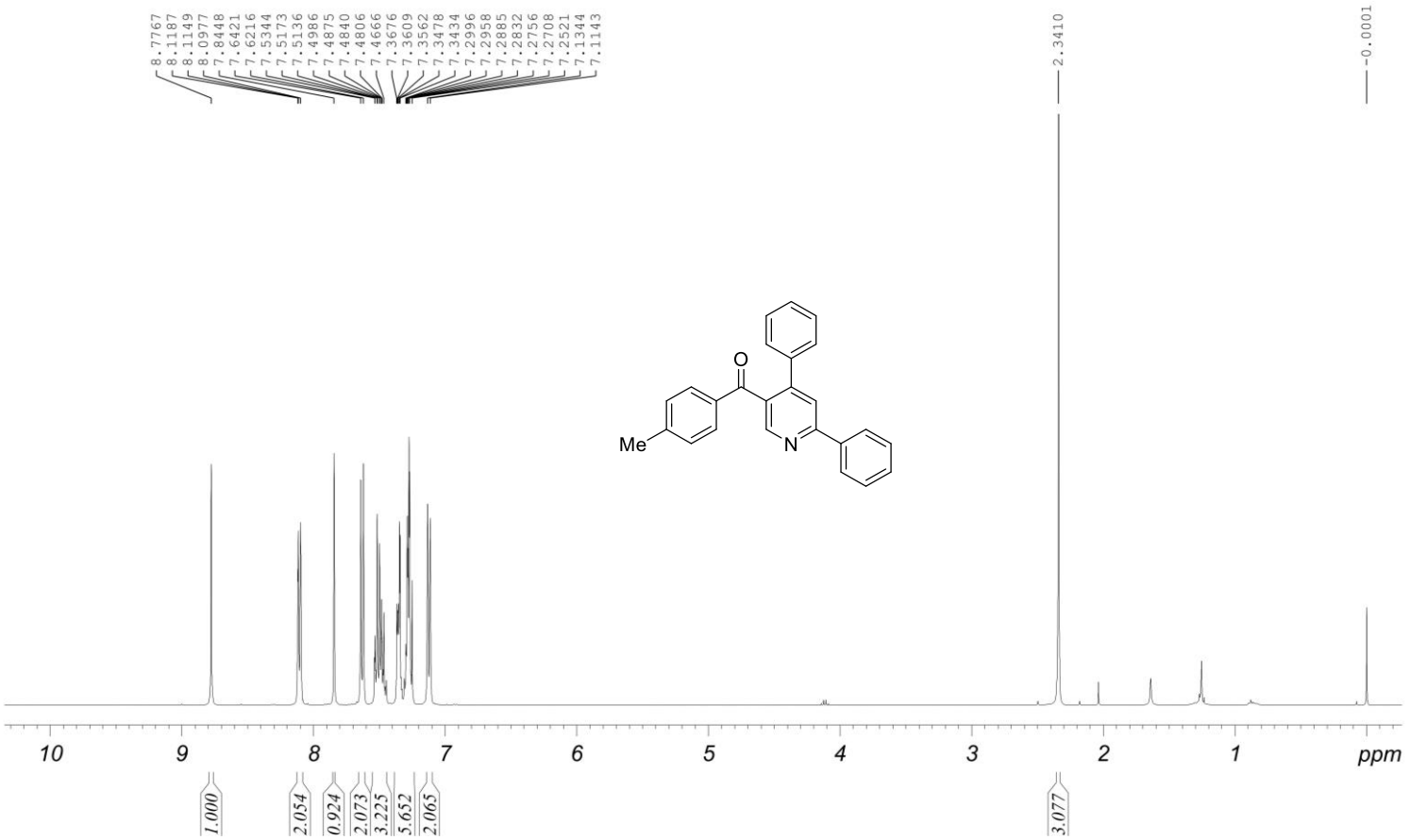


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g**

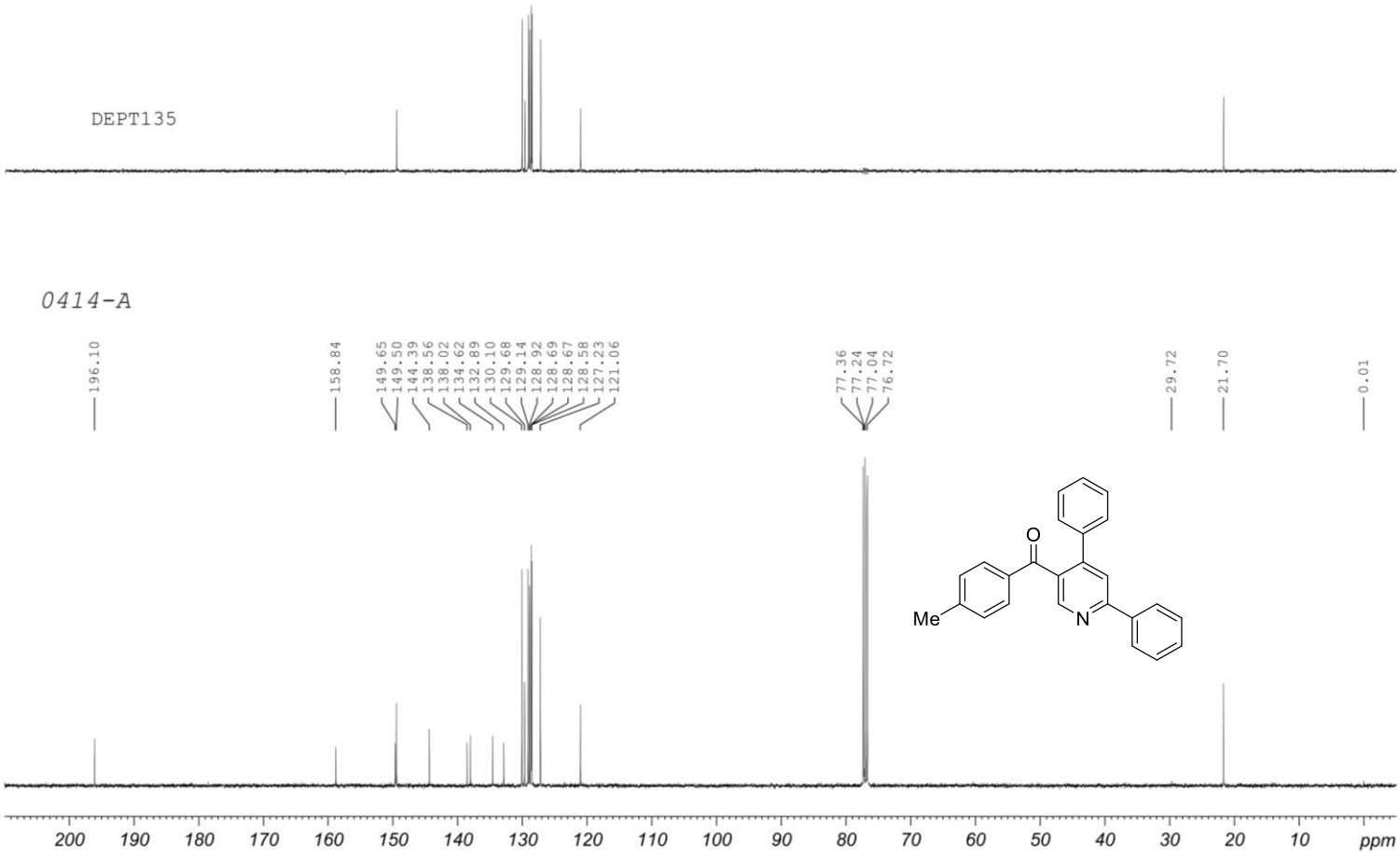


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3g**

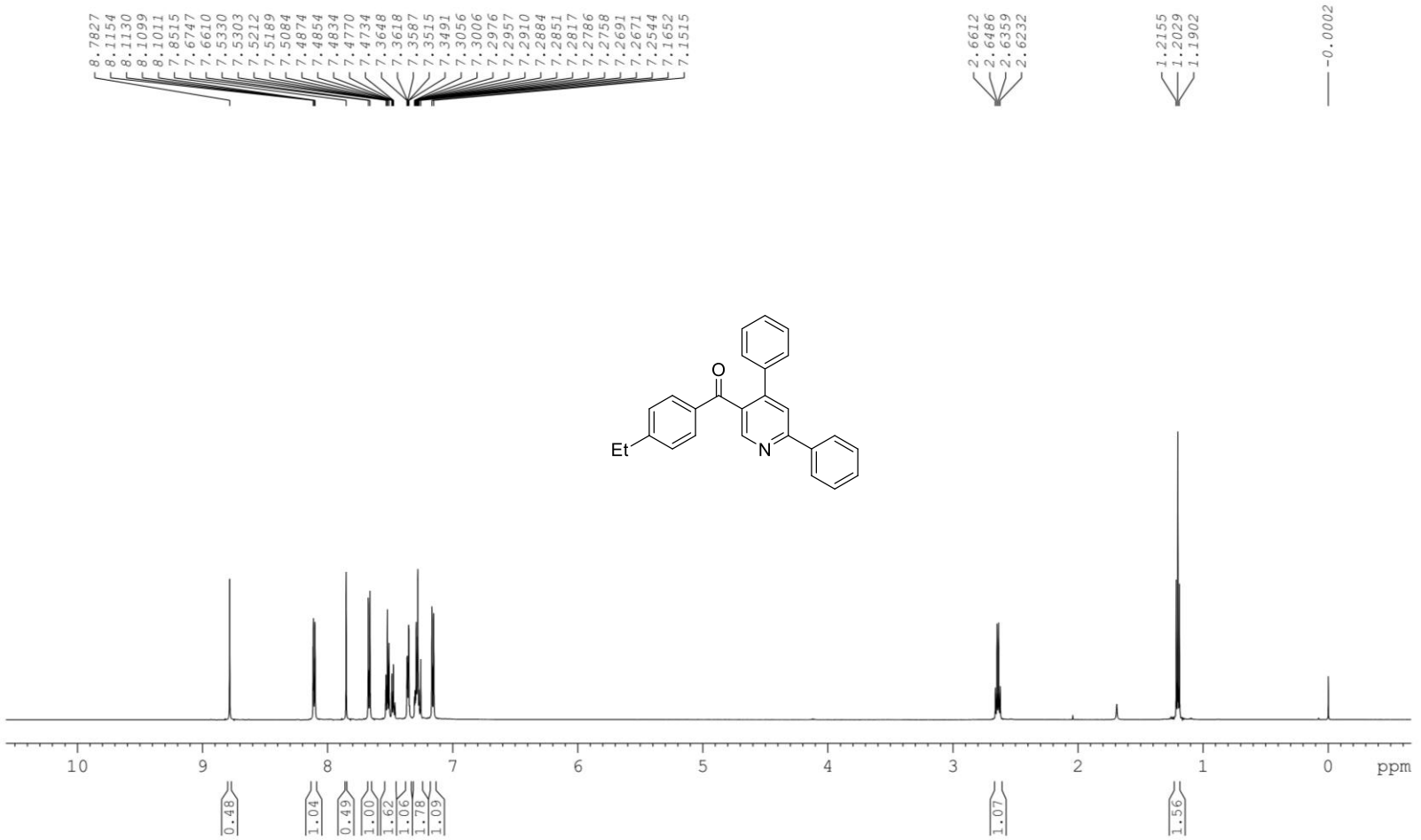


Figure S18. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3h**

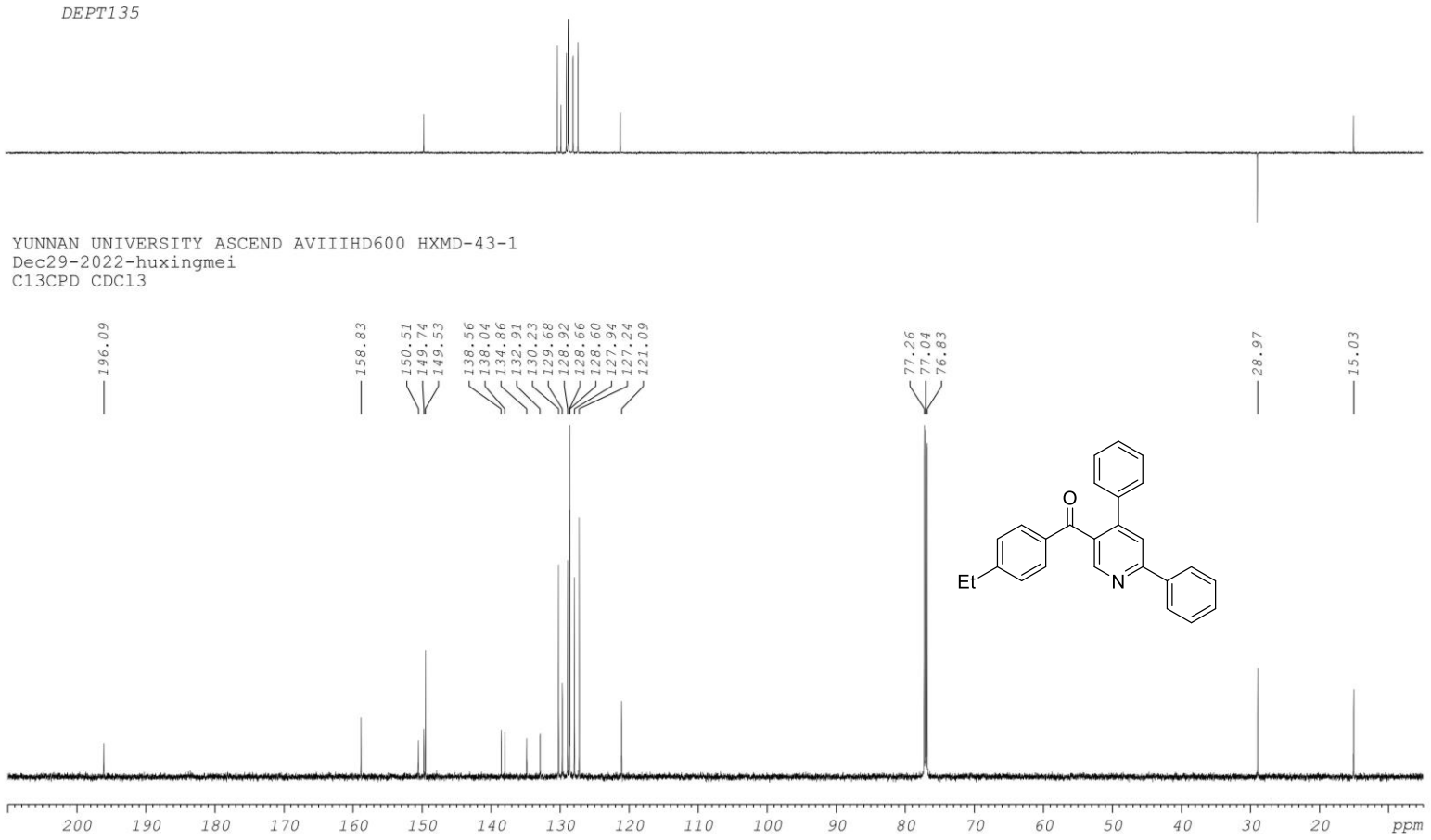


Figure S19. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3h**

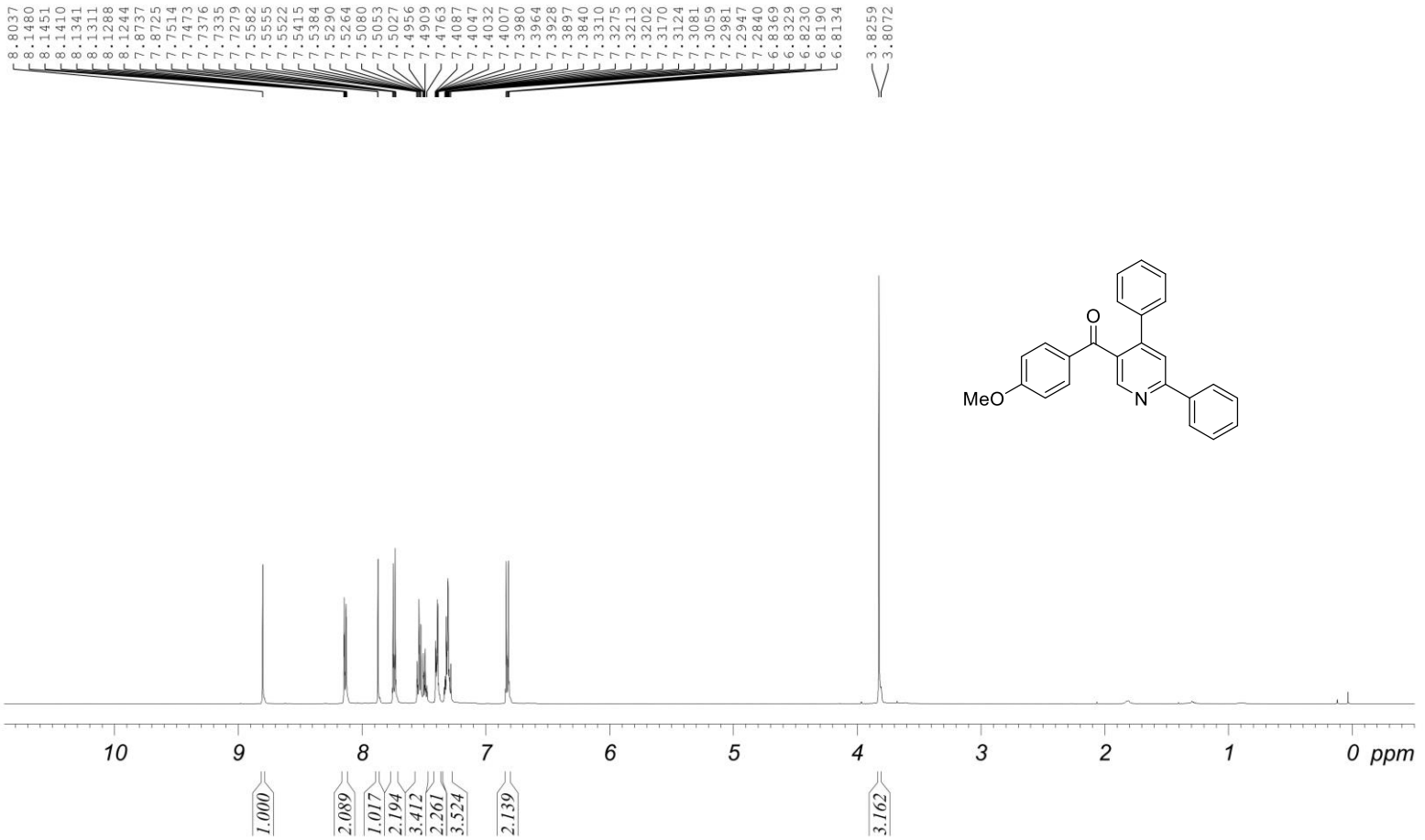


Figure S20. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3i**

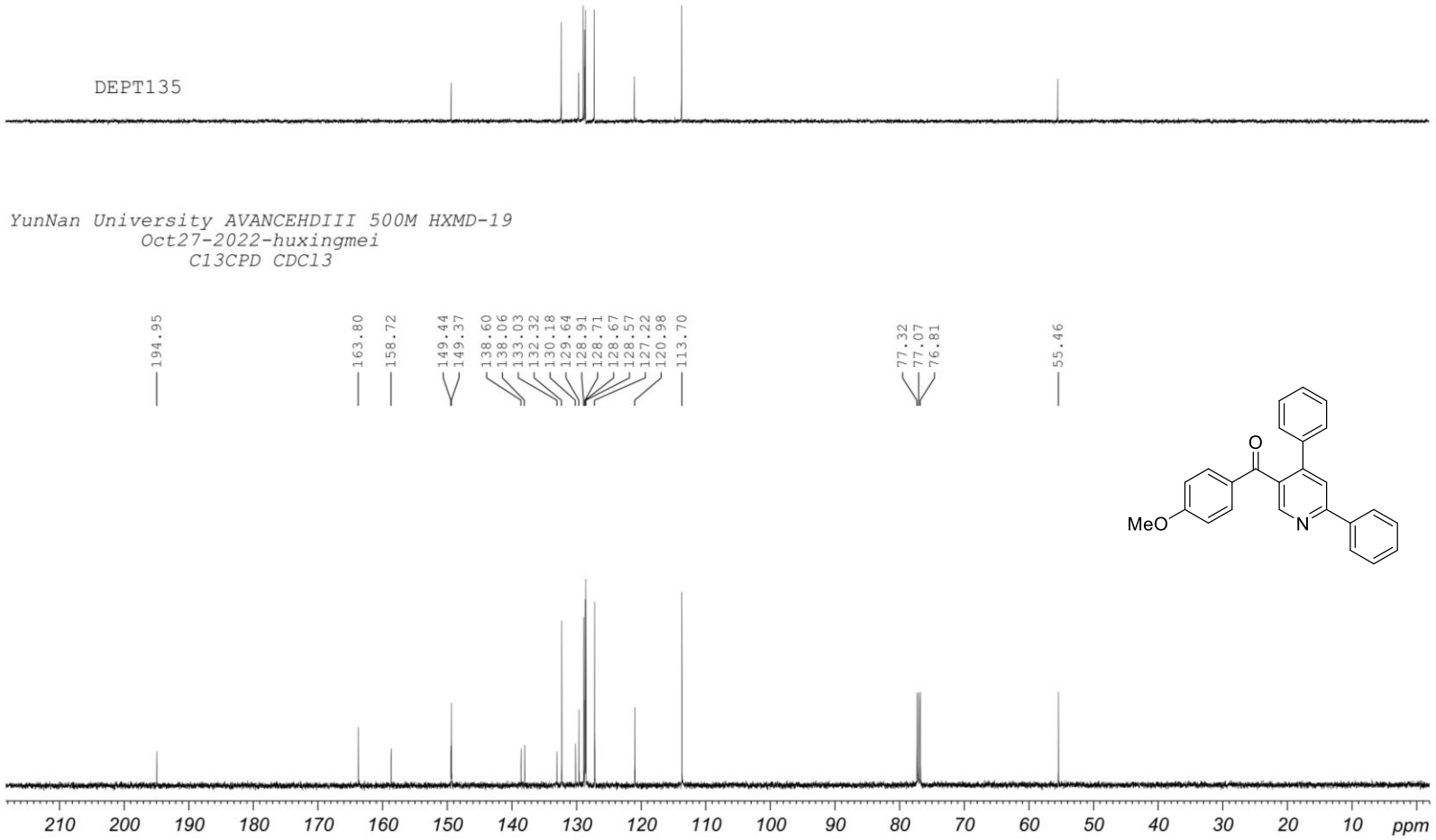


Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3i**

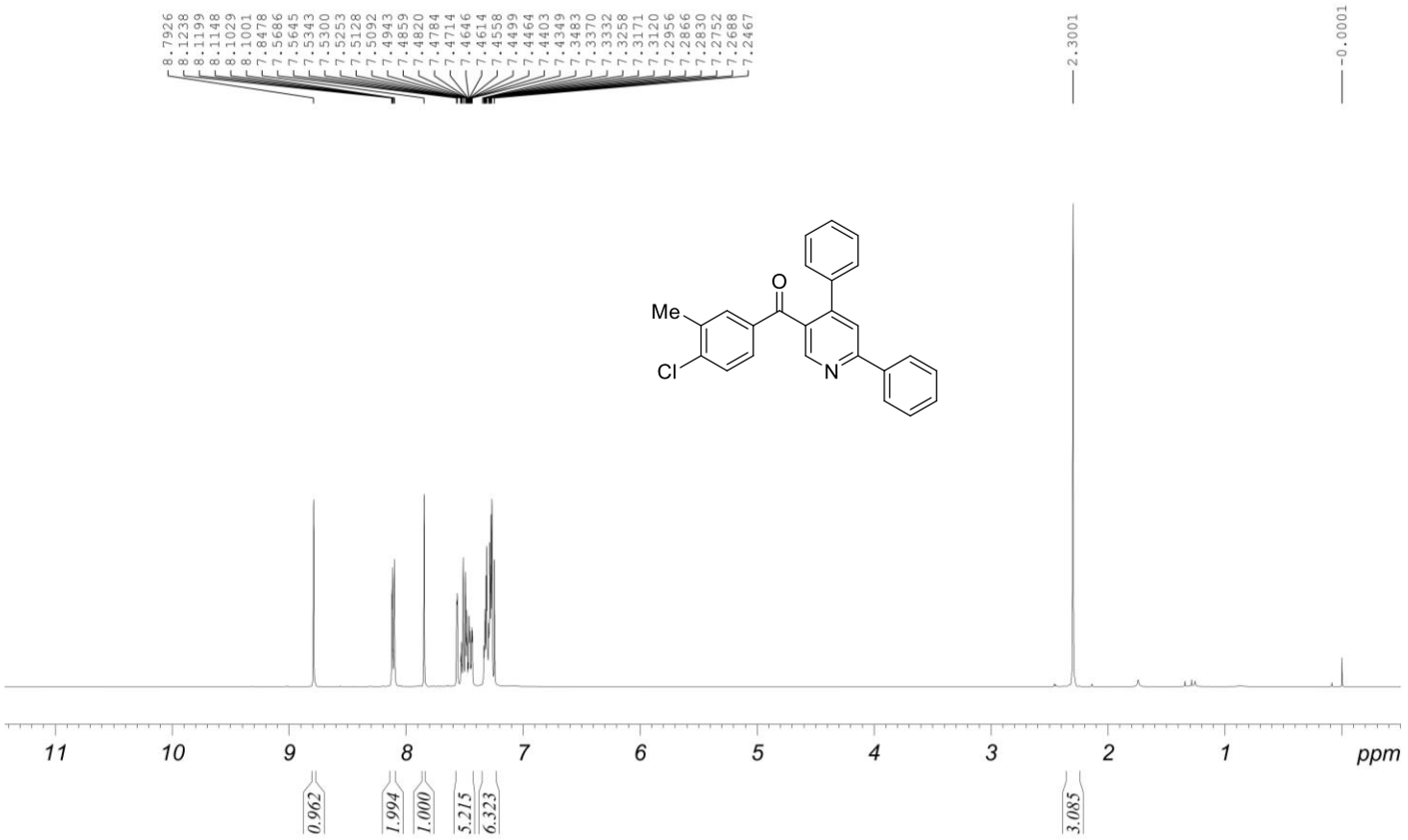


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3j**

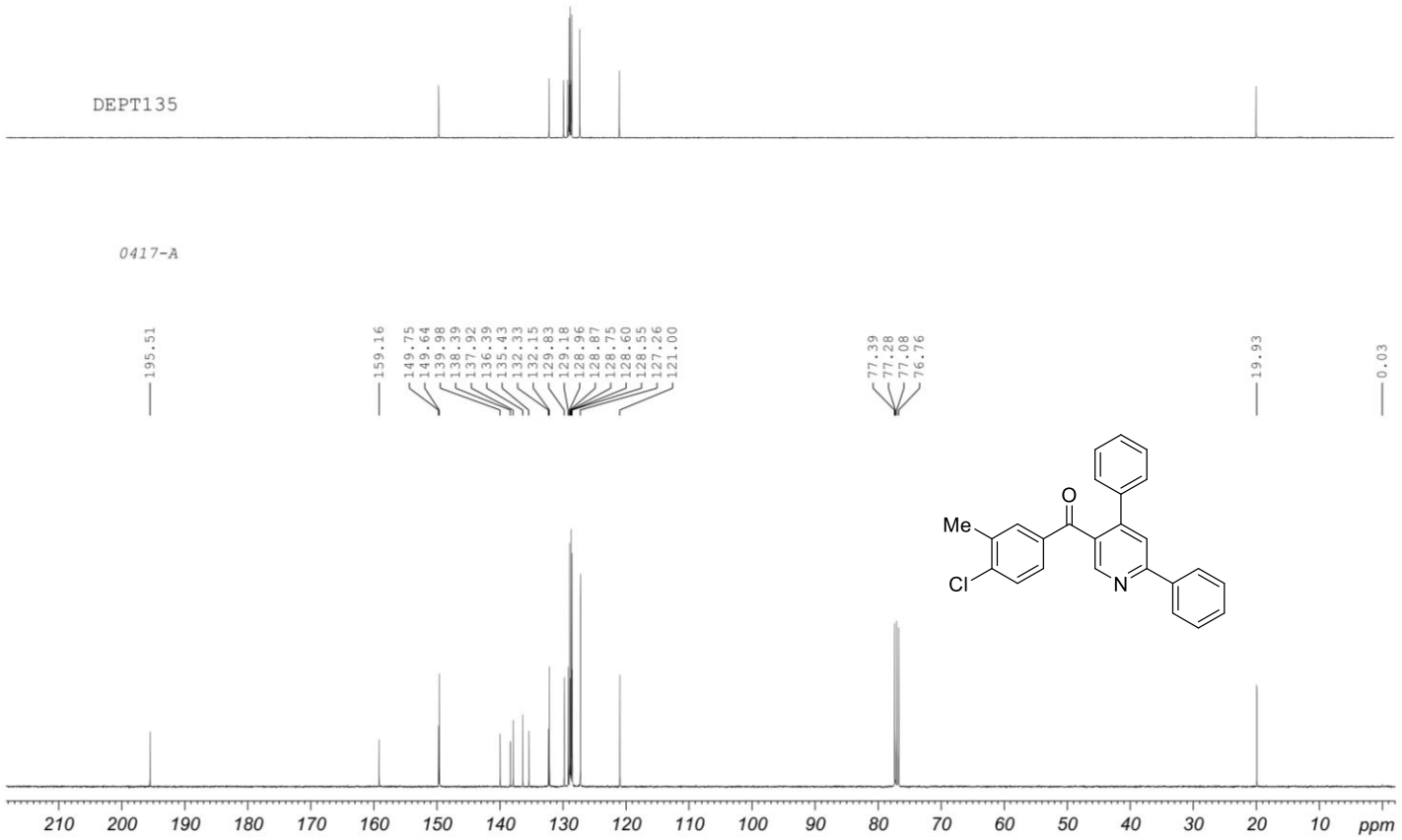


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3j**

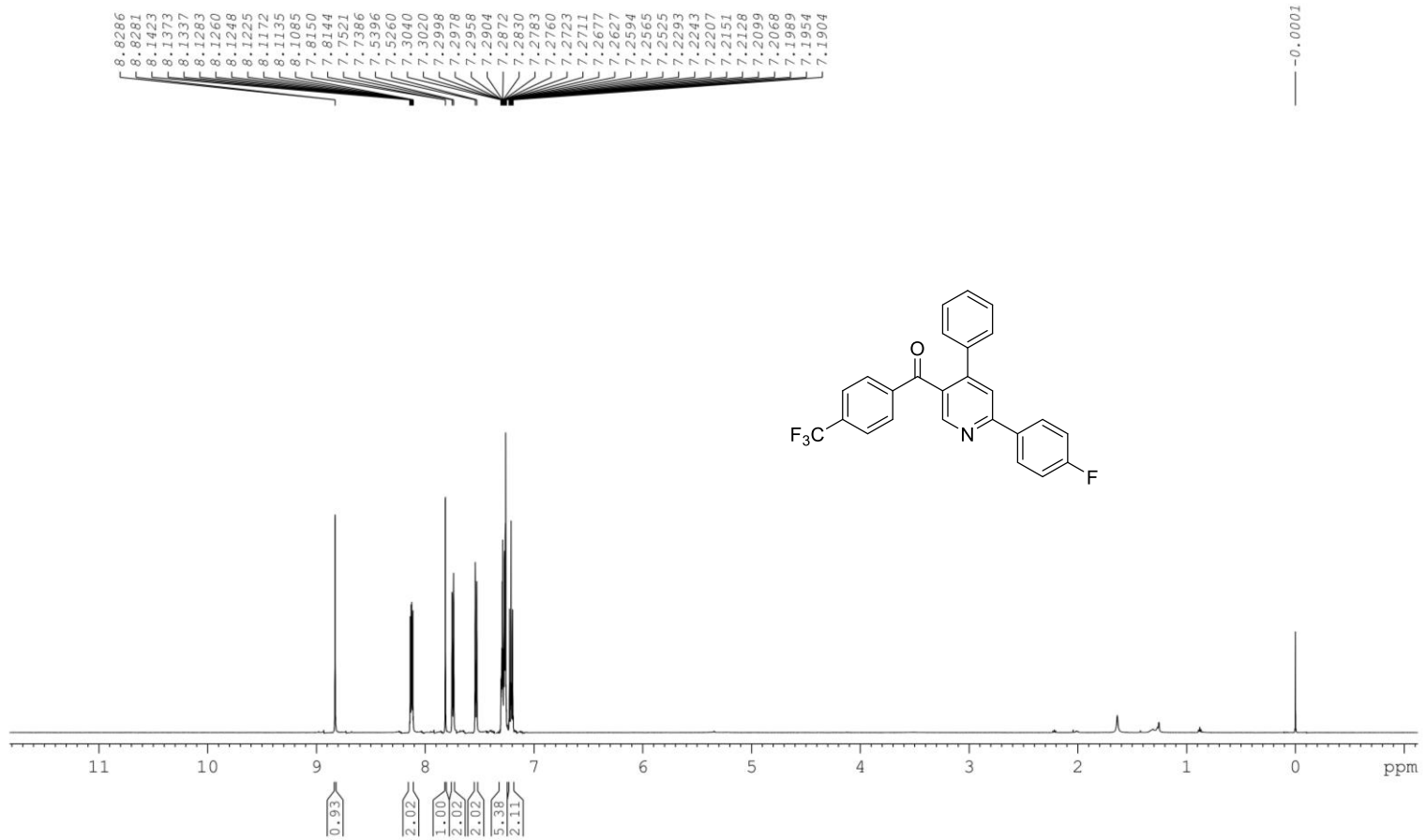


Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3k**

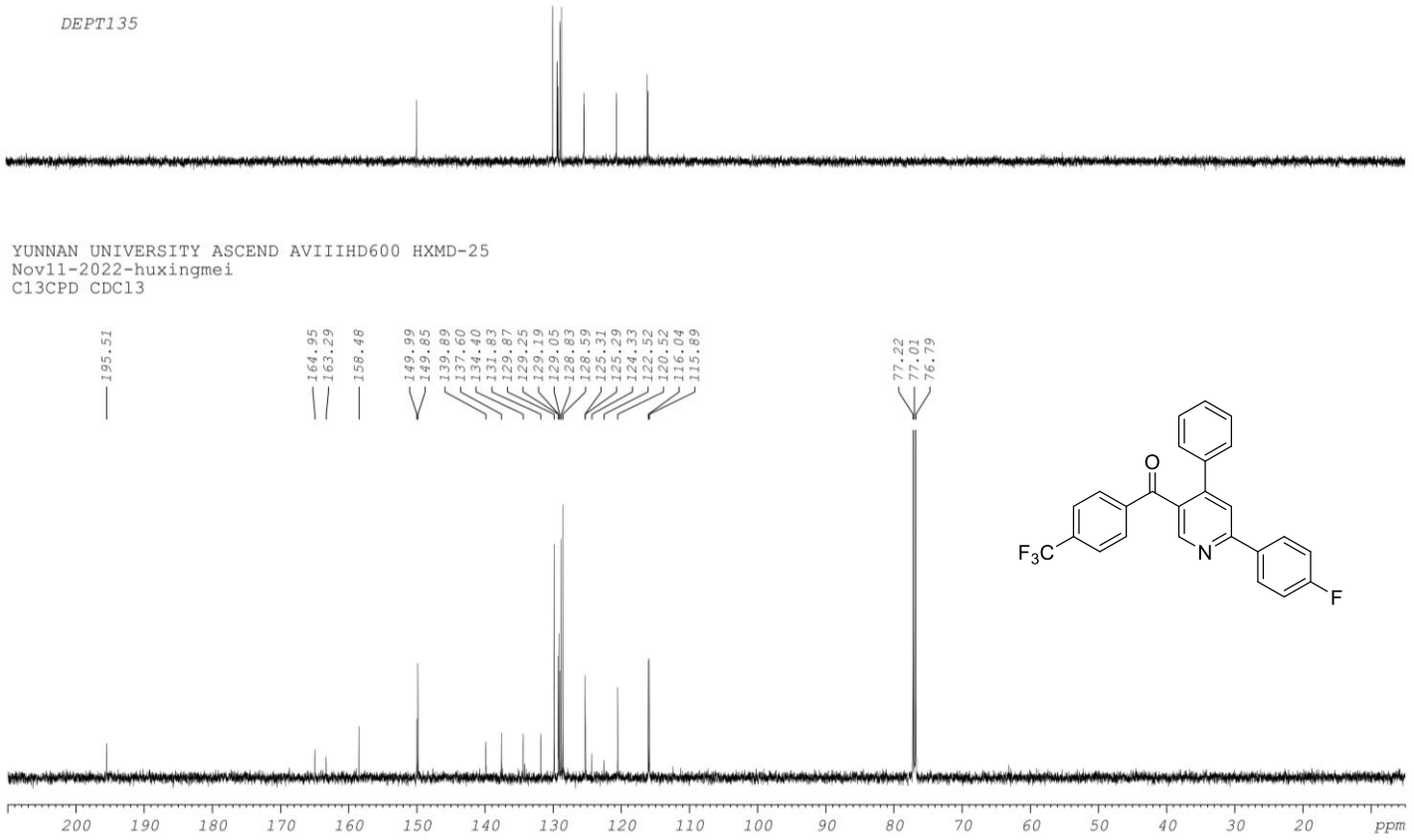


Figure S25. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3k**

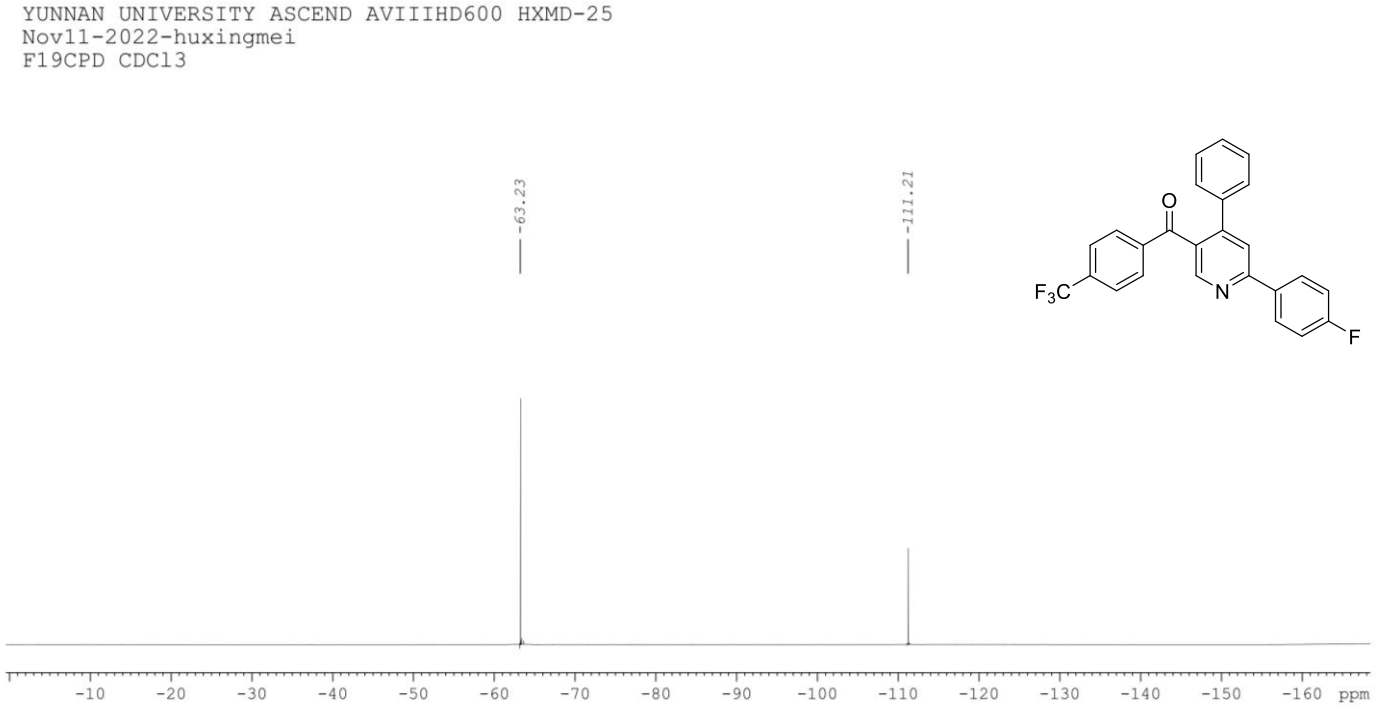


Figure S26. ^{19}F NMR (564 MHz, $CDCl_3$) spectra of compound **3k**

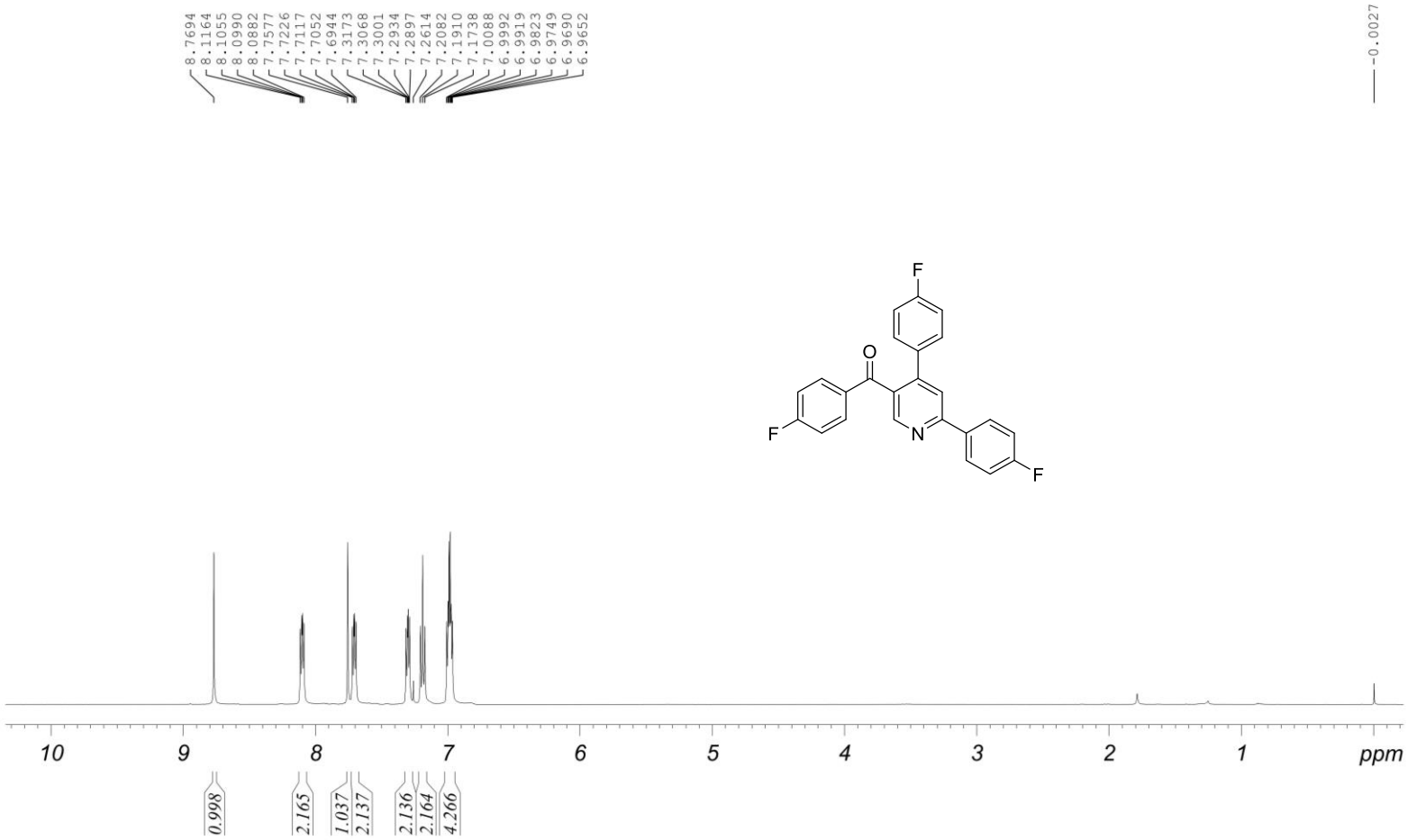


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3l**

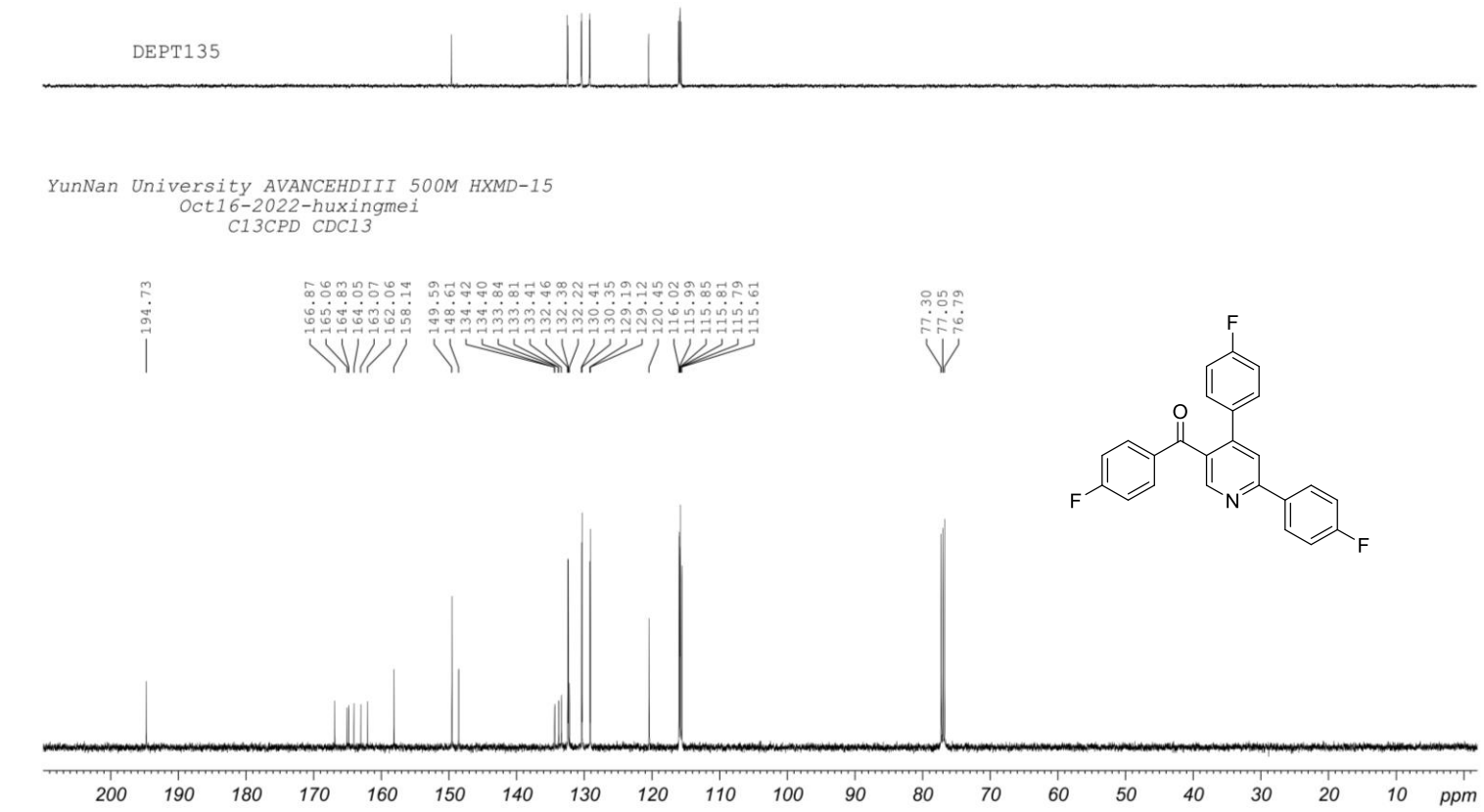


Figure S28. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3l**

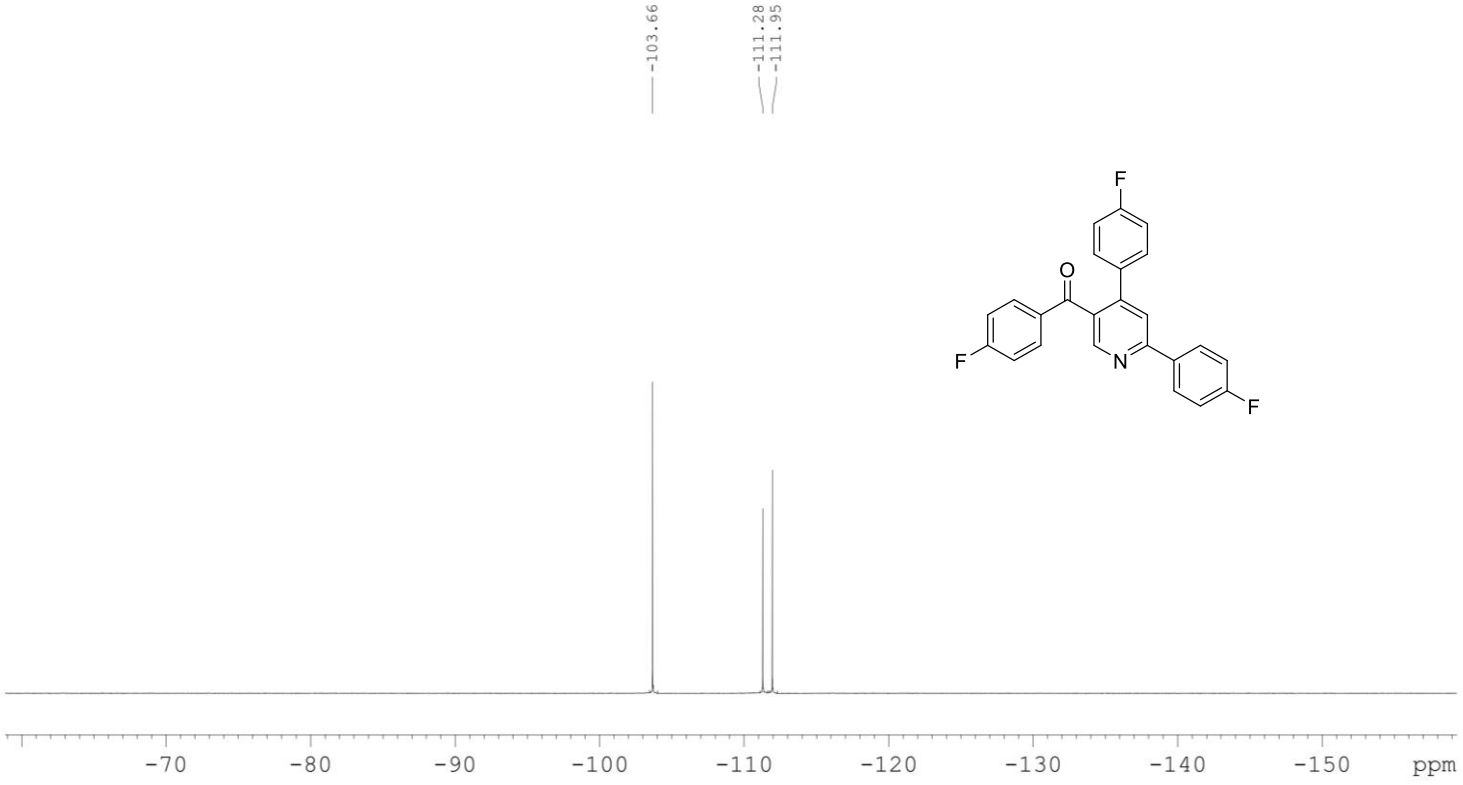


Figure S29. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3l**

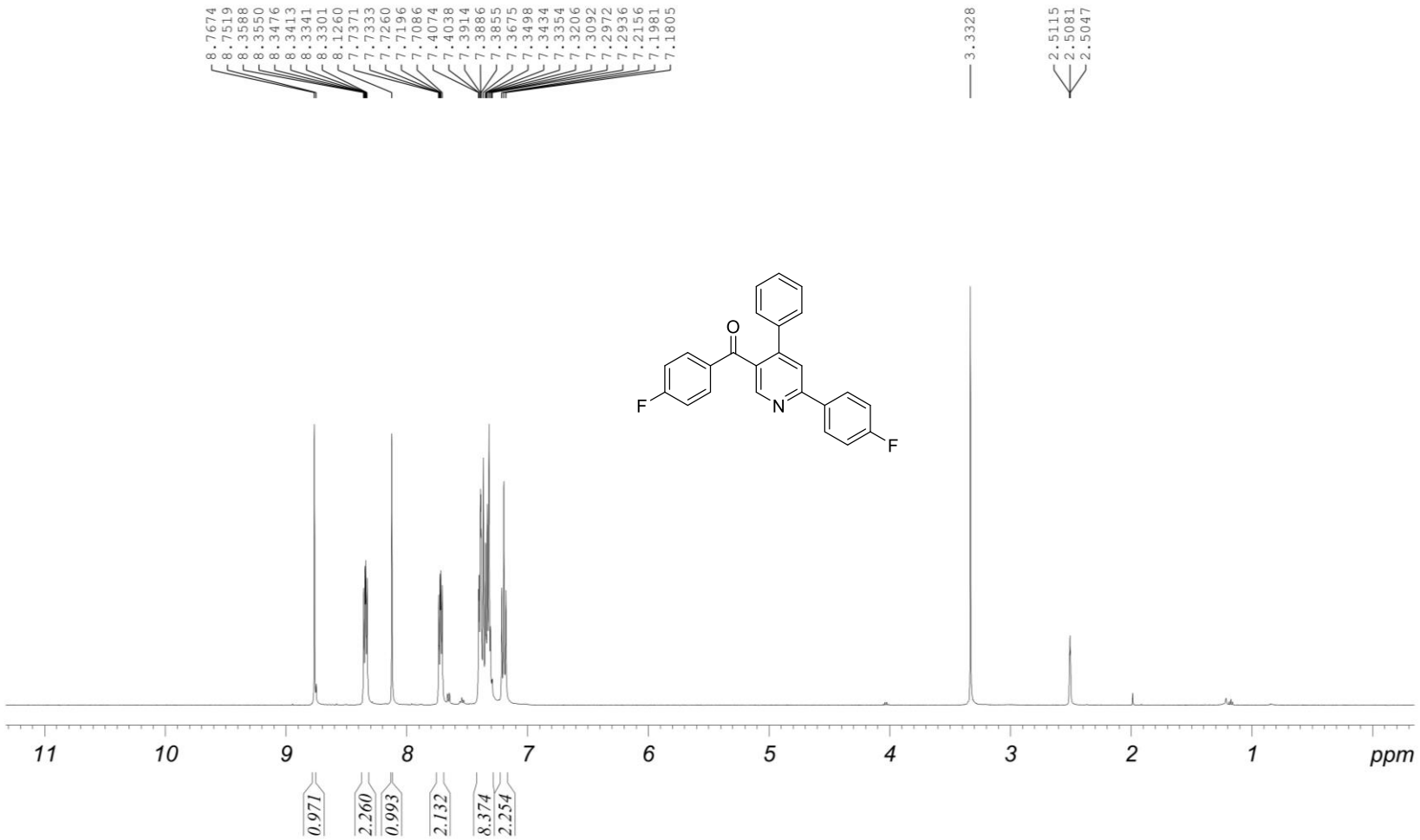


Figure S30. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **3m**

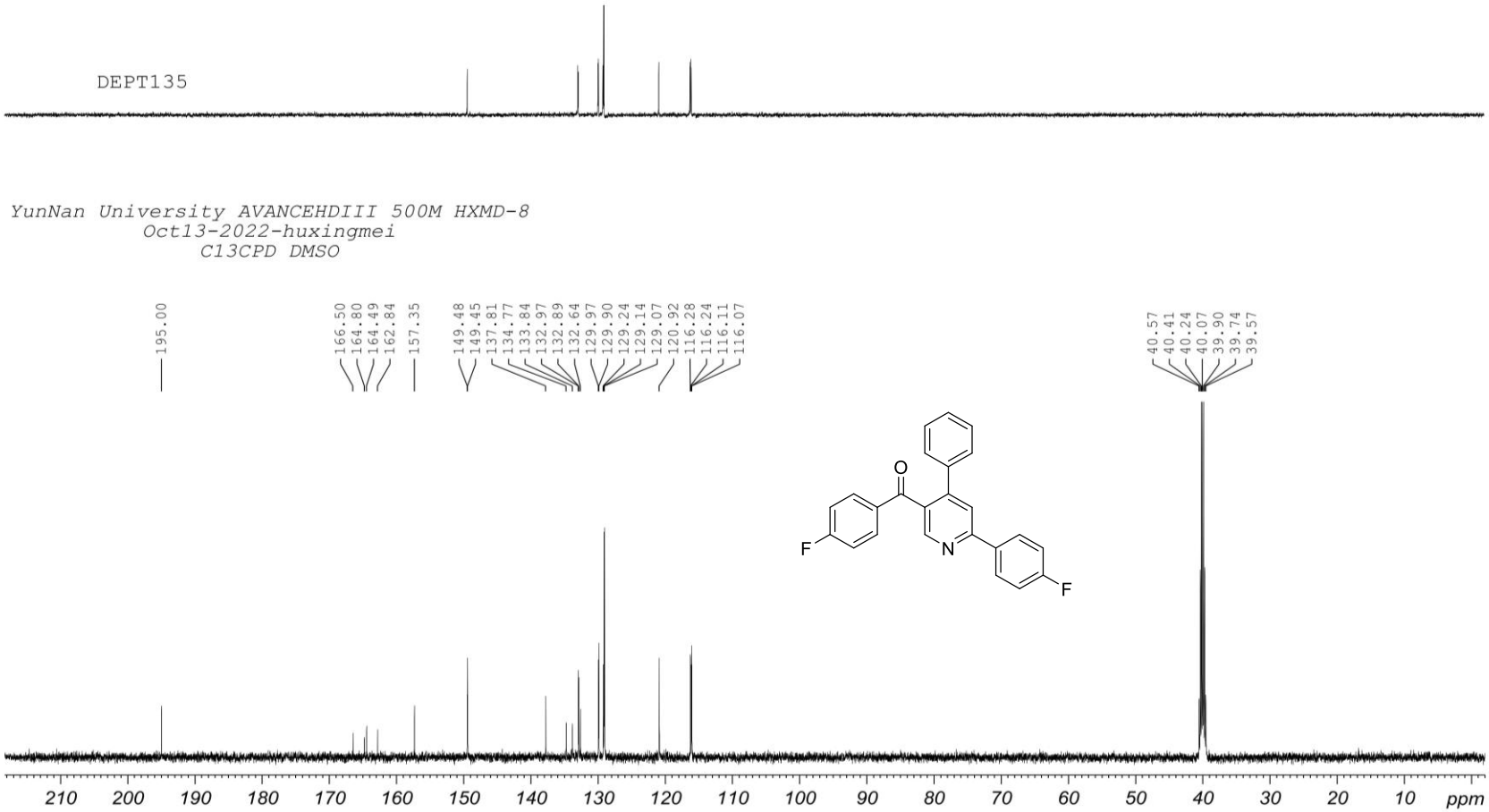


Figure S31. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **3m**

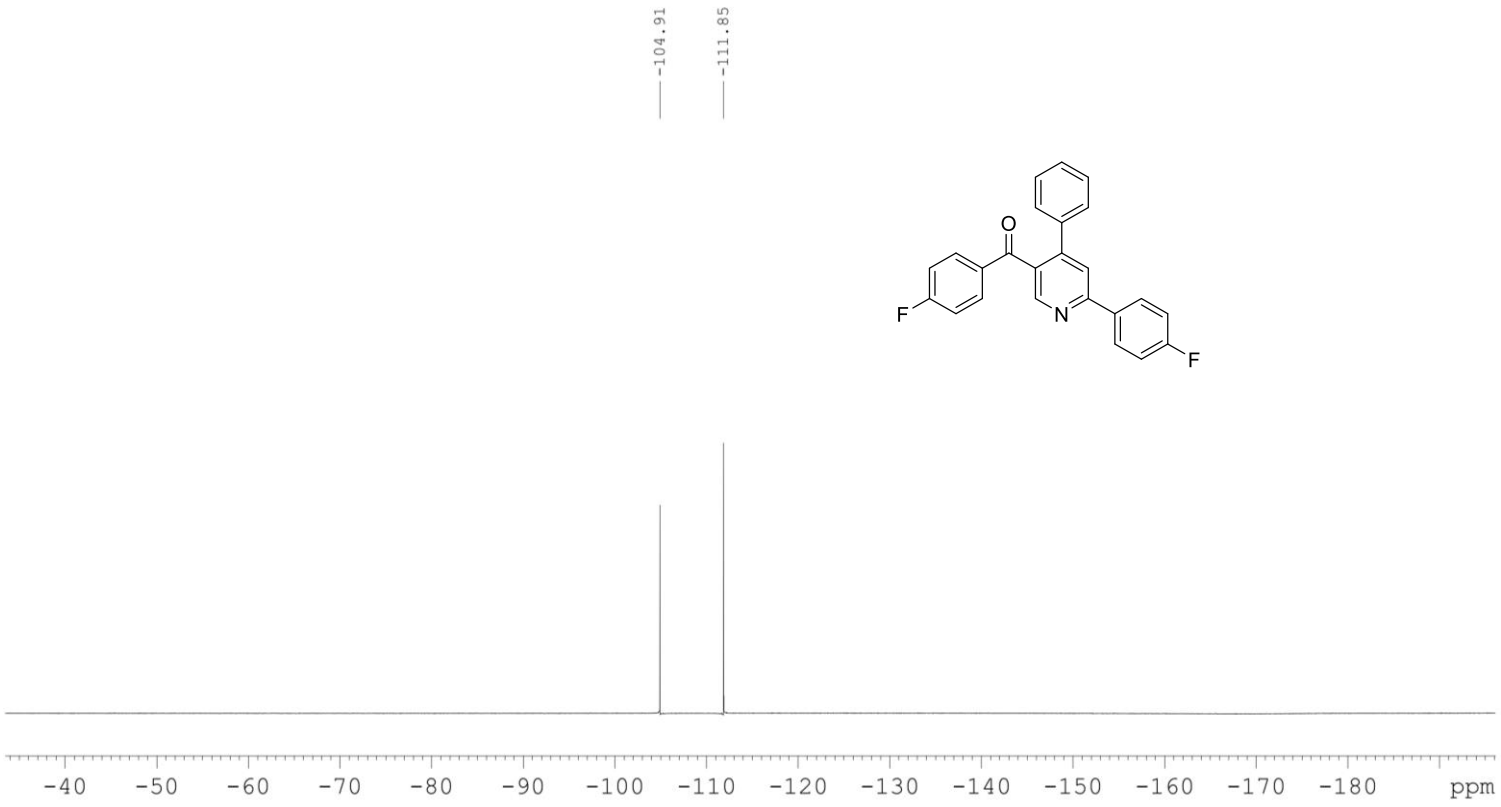


Figure S32. ^{19}F NMR (470 MHz, DMSO-d_6) spectra of compound **3m**

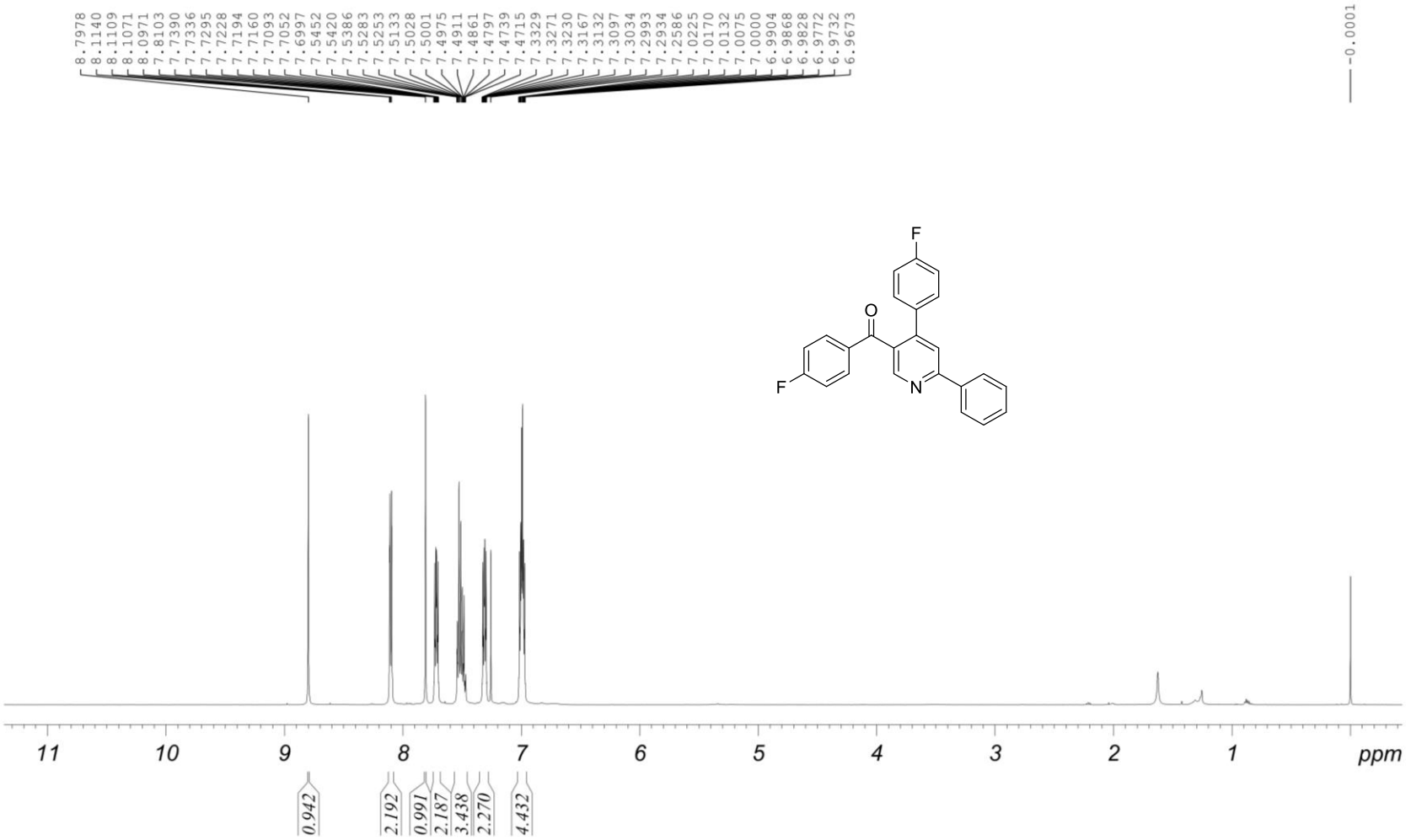


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3n**

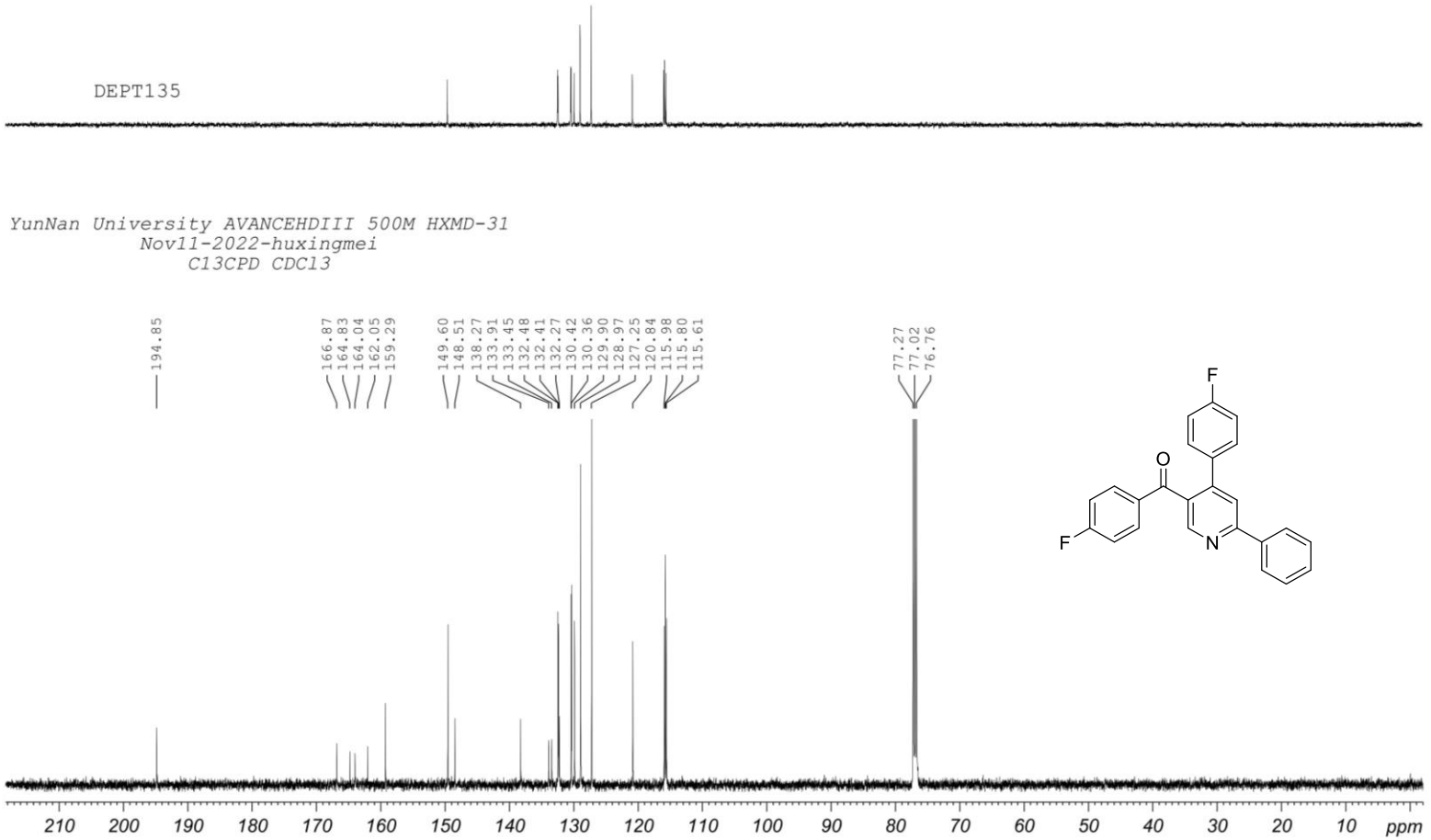


Figure S34. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3n**

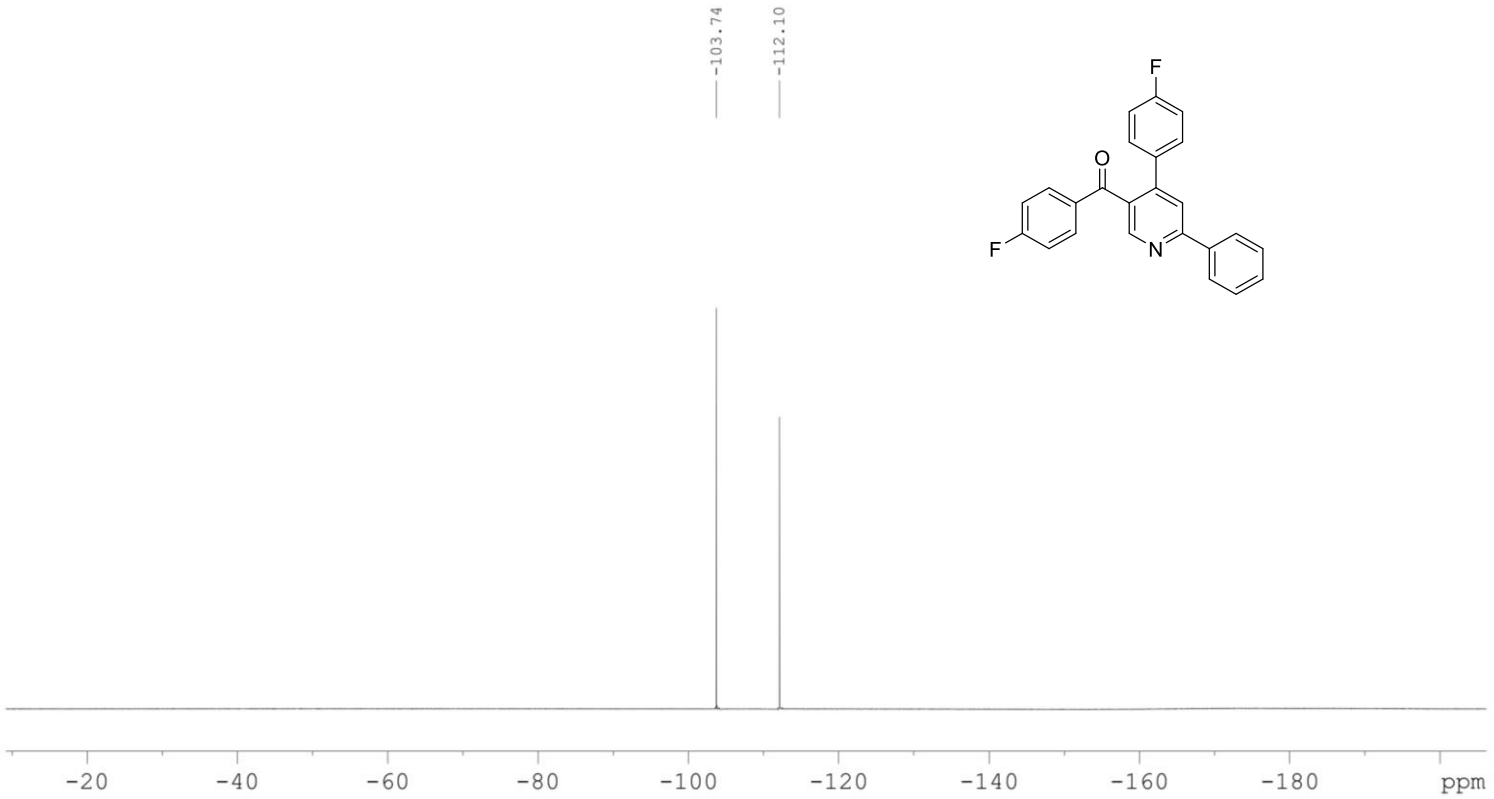


Figure S35. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3n**

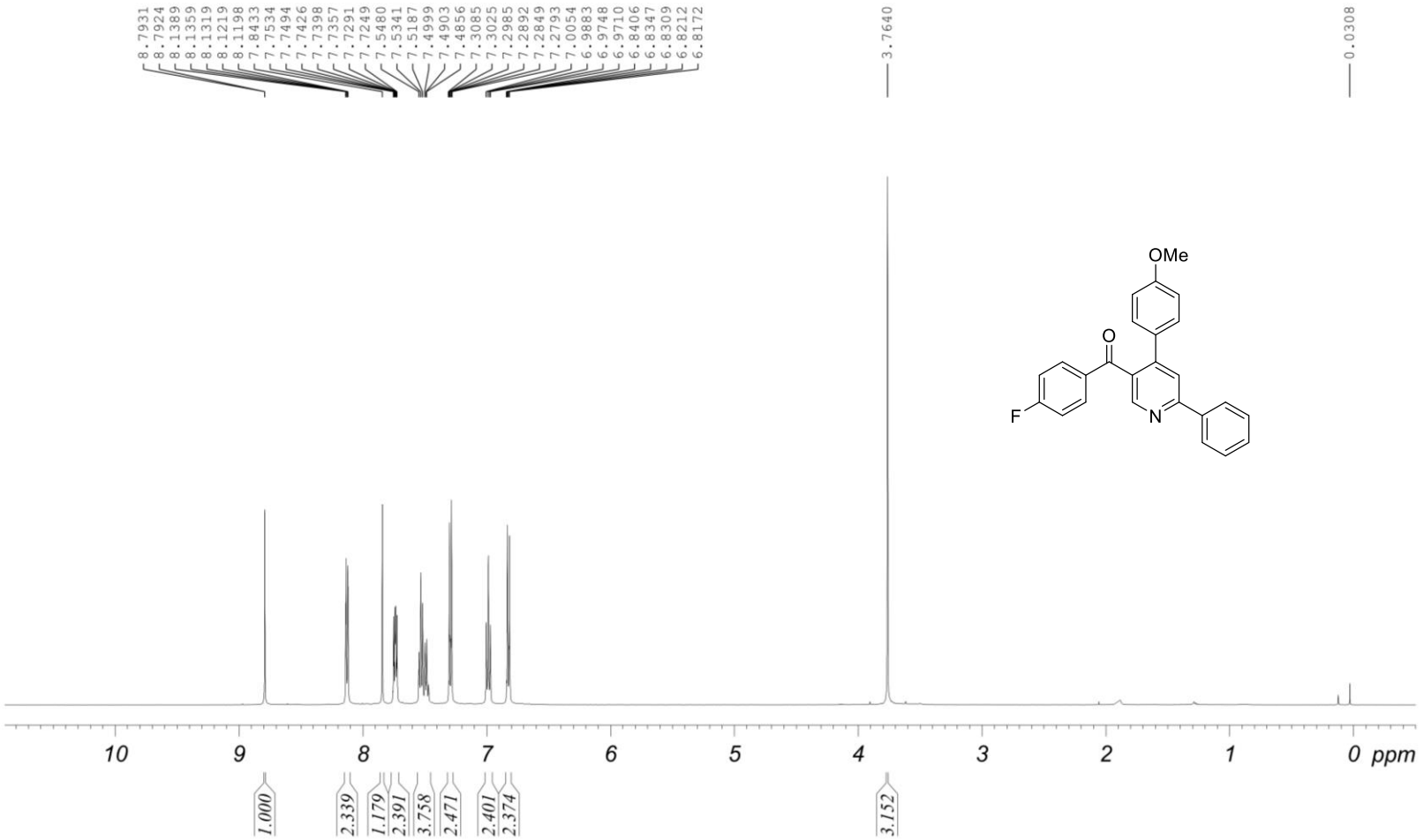


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3o**

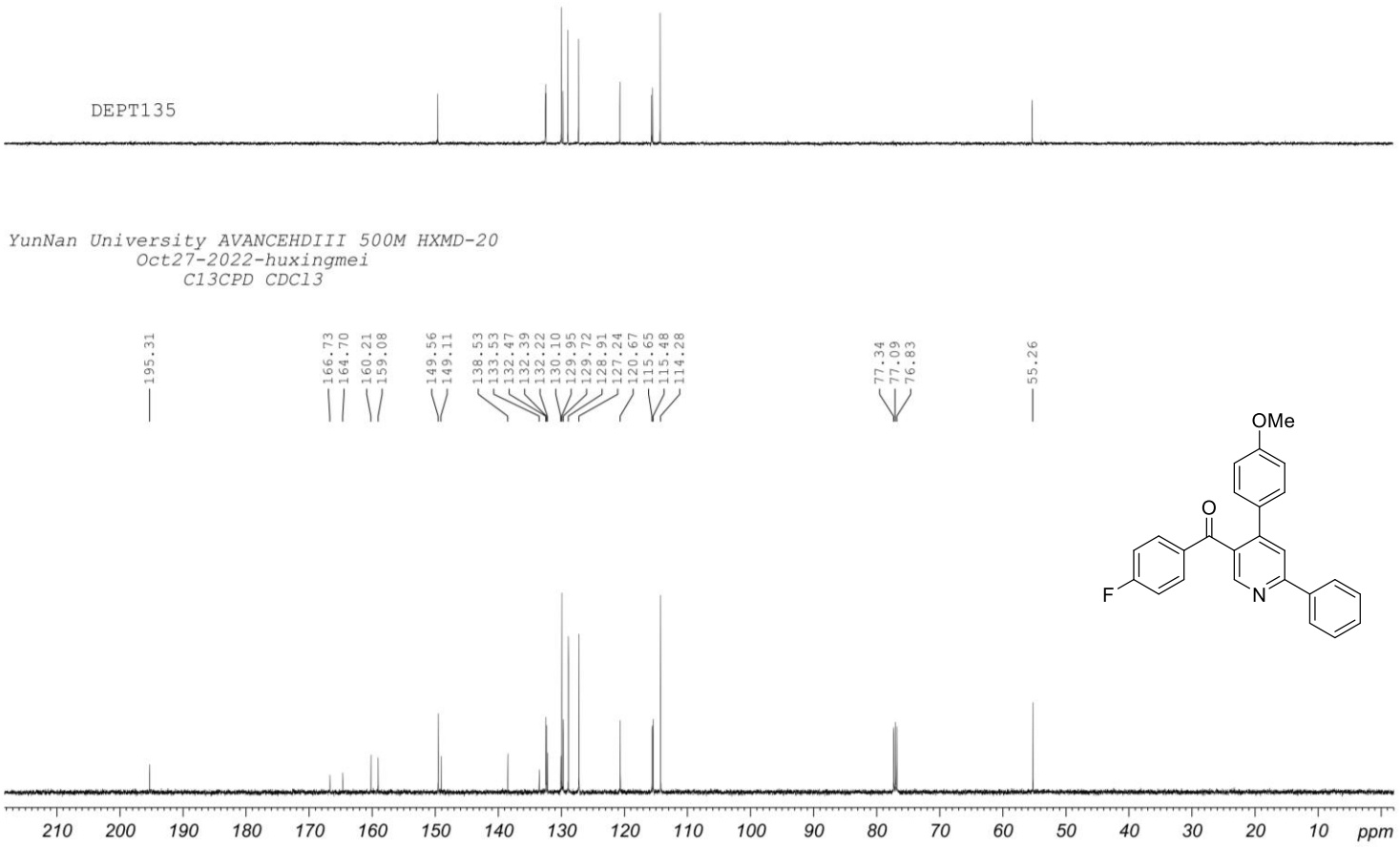


Figure S37. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3o**

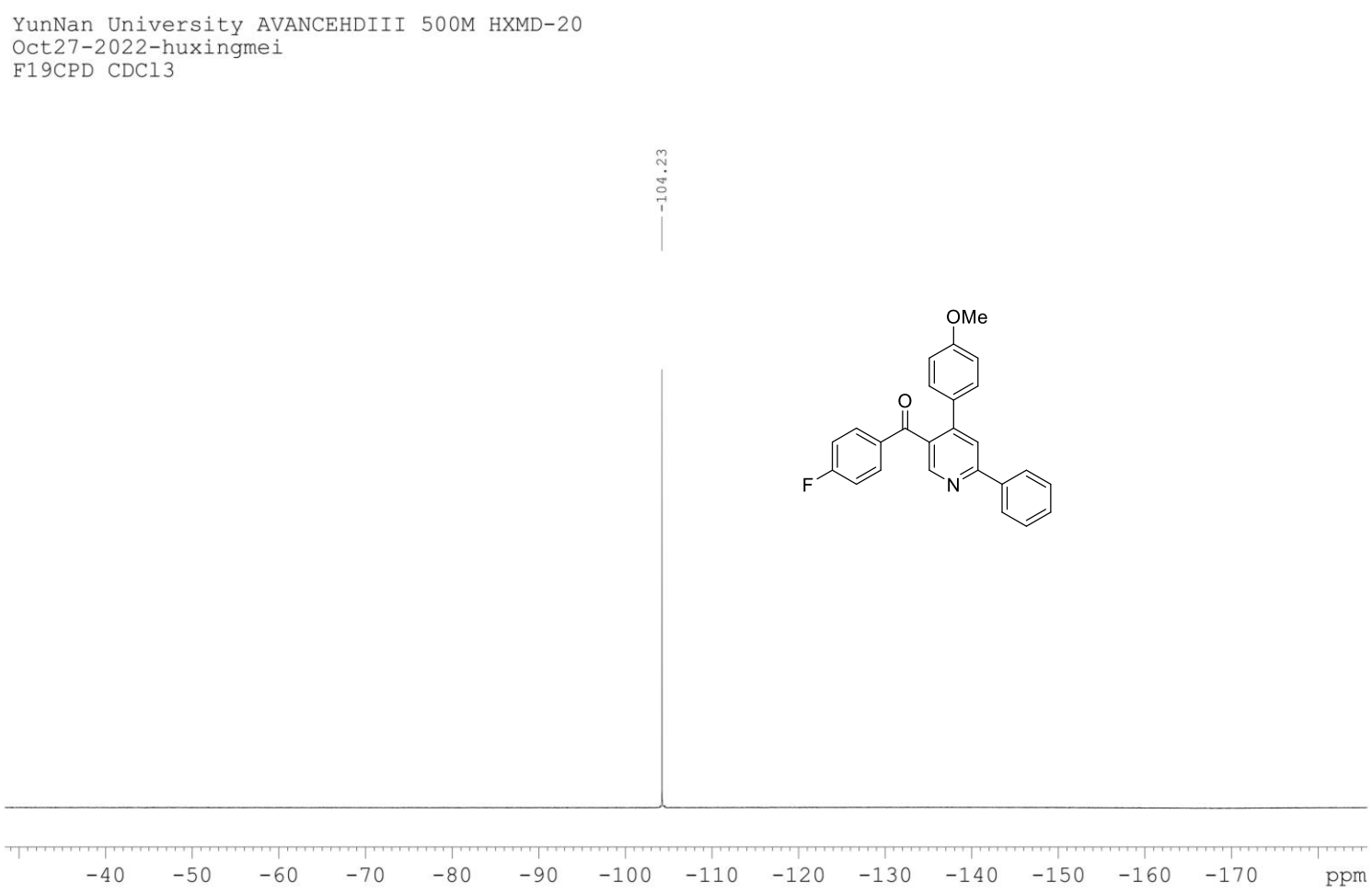


Figure S38. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3o**

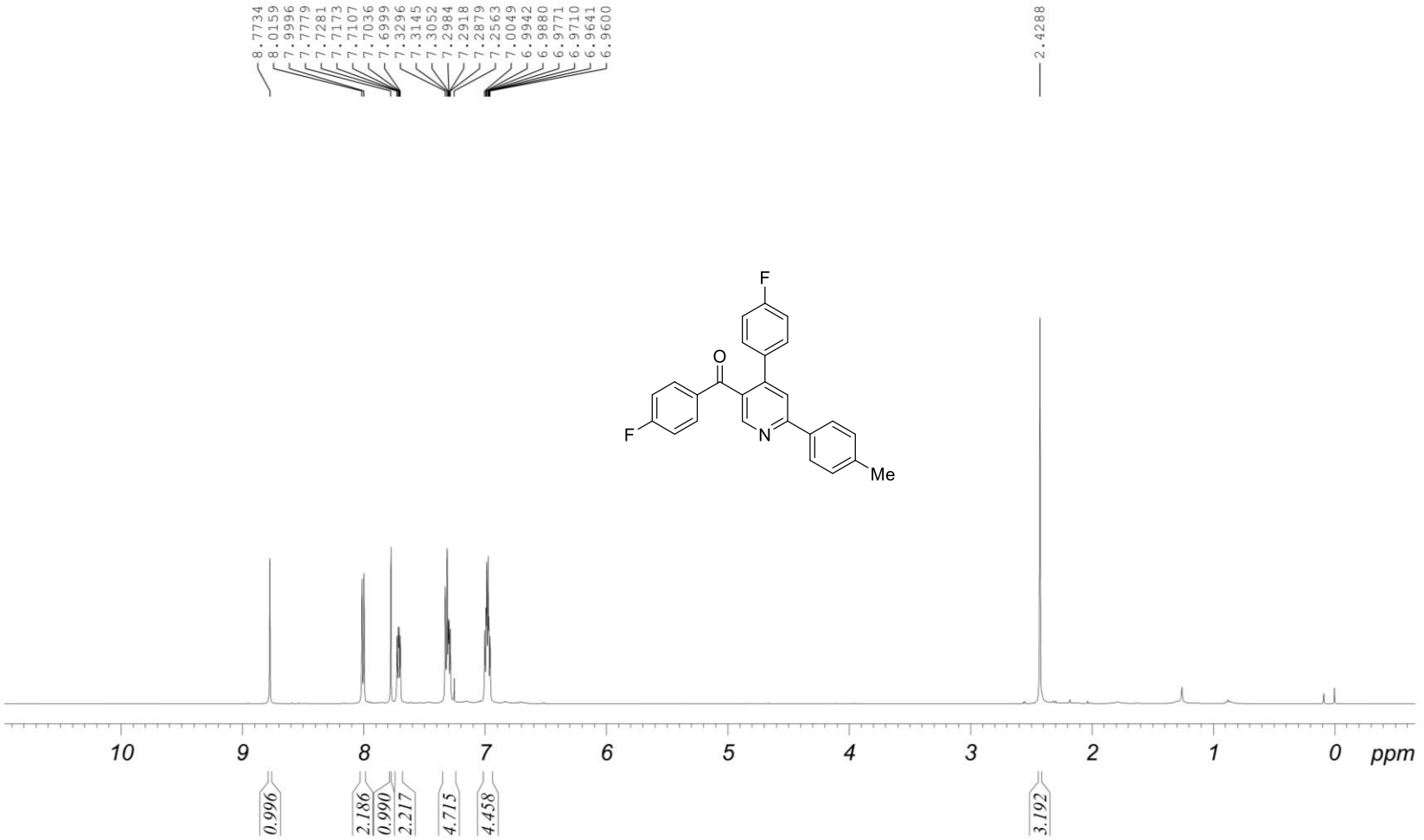


Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3p**

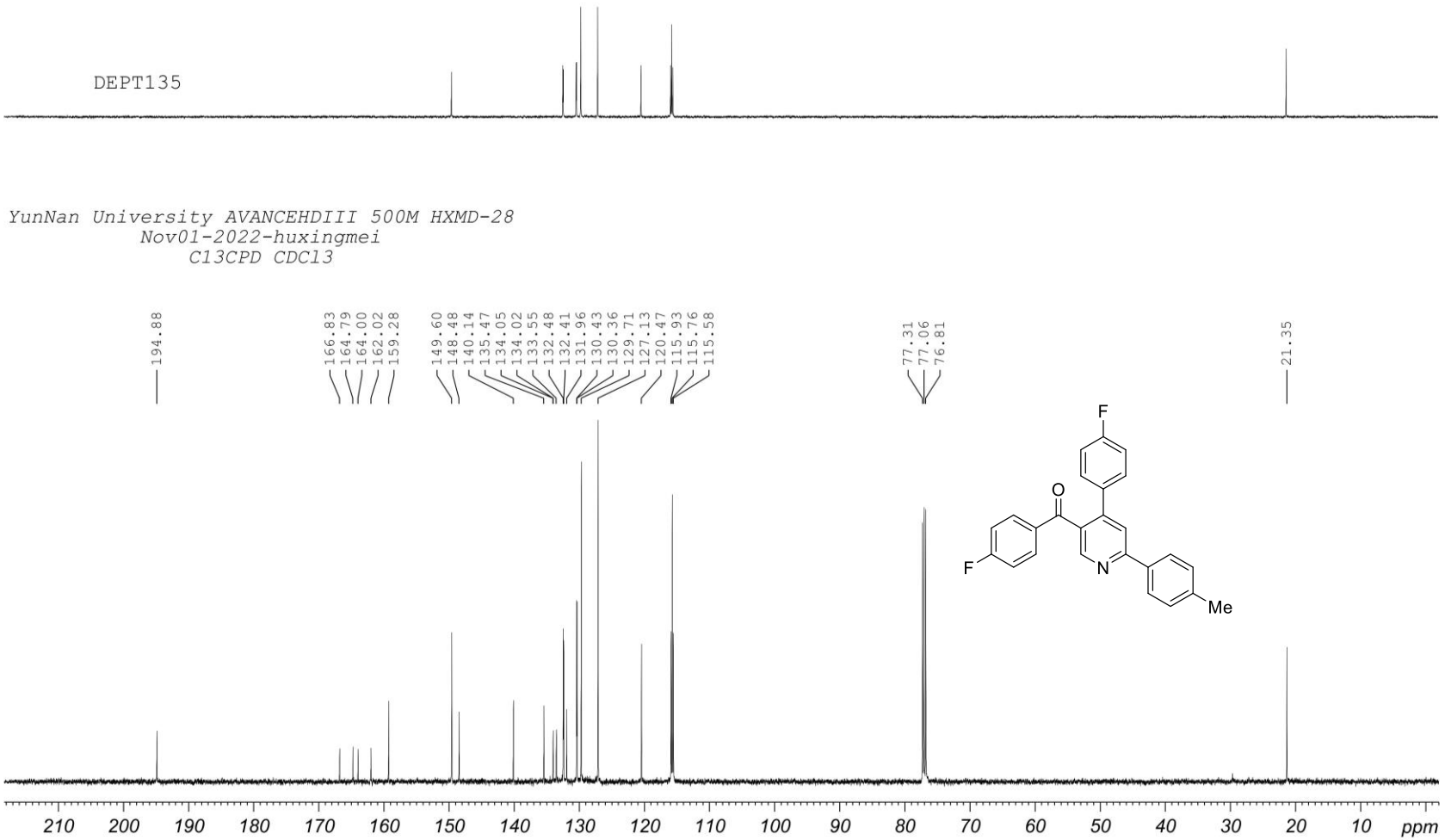


Figure S40. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3p**

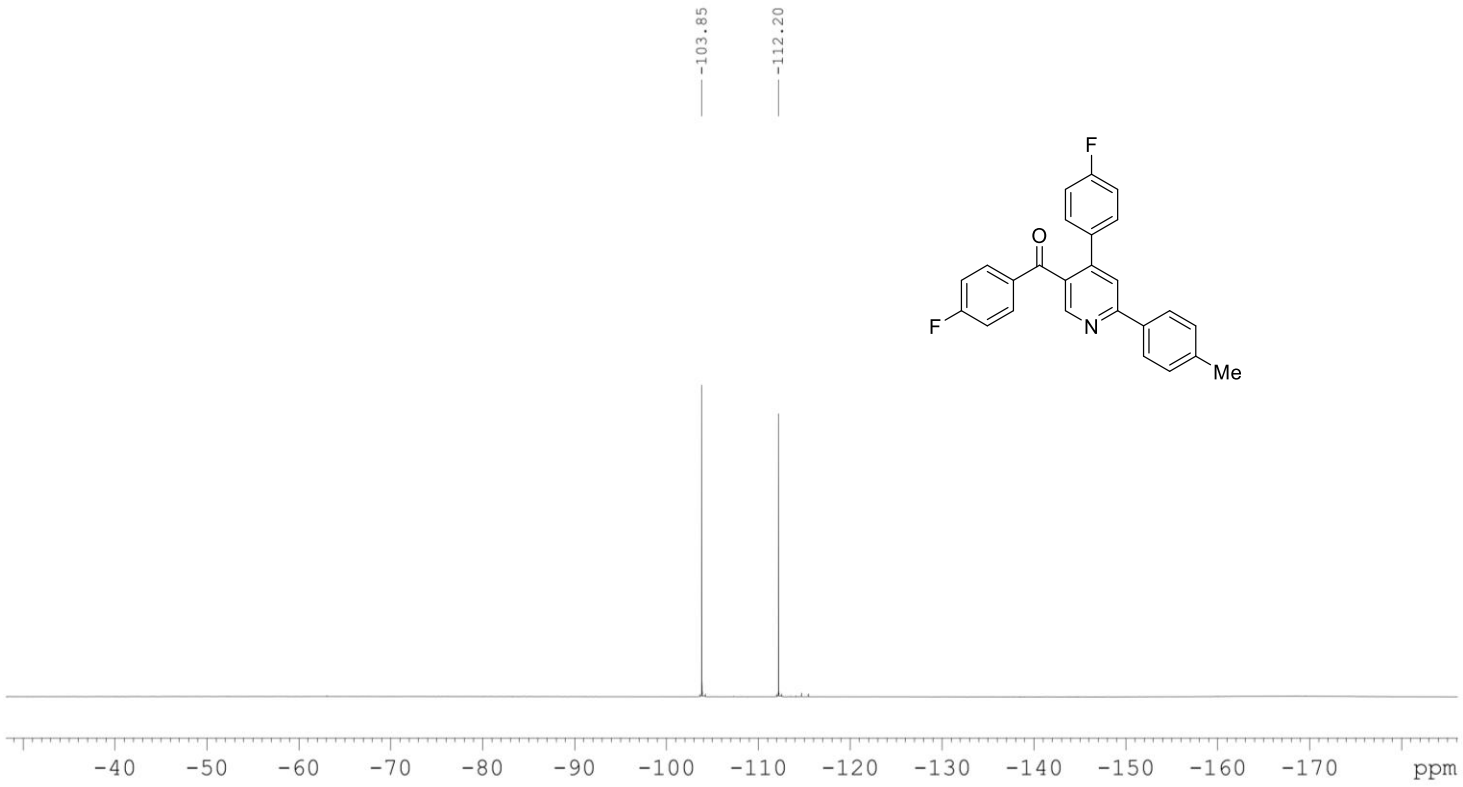


Figure S41. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3p**

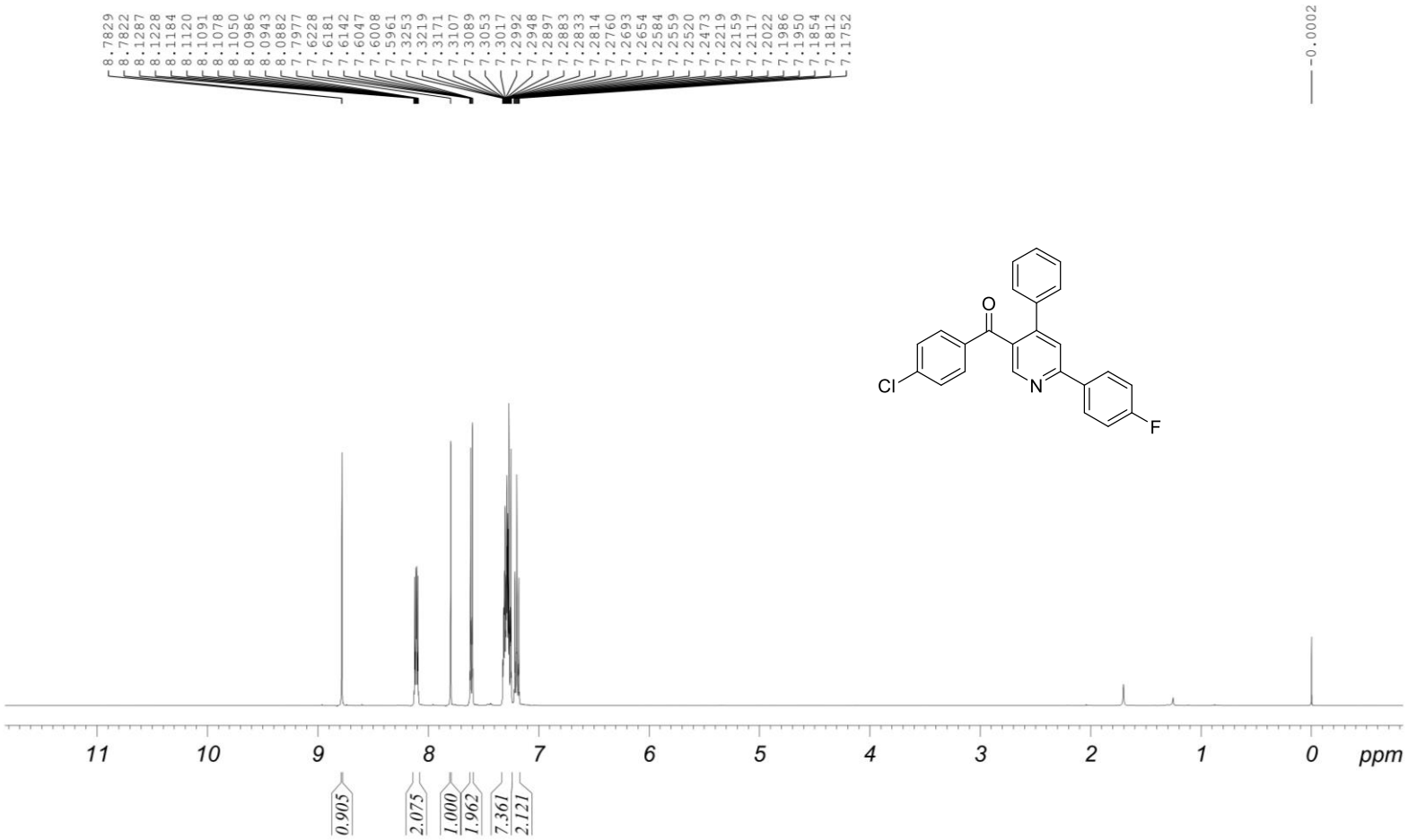


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3q**

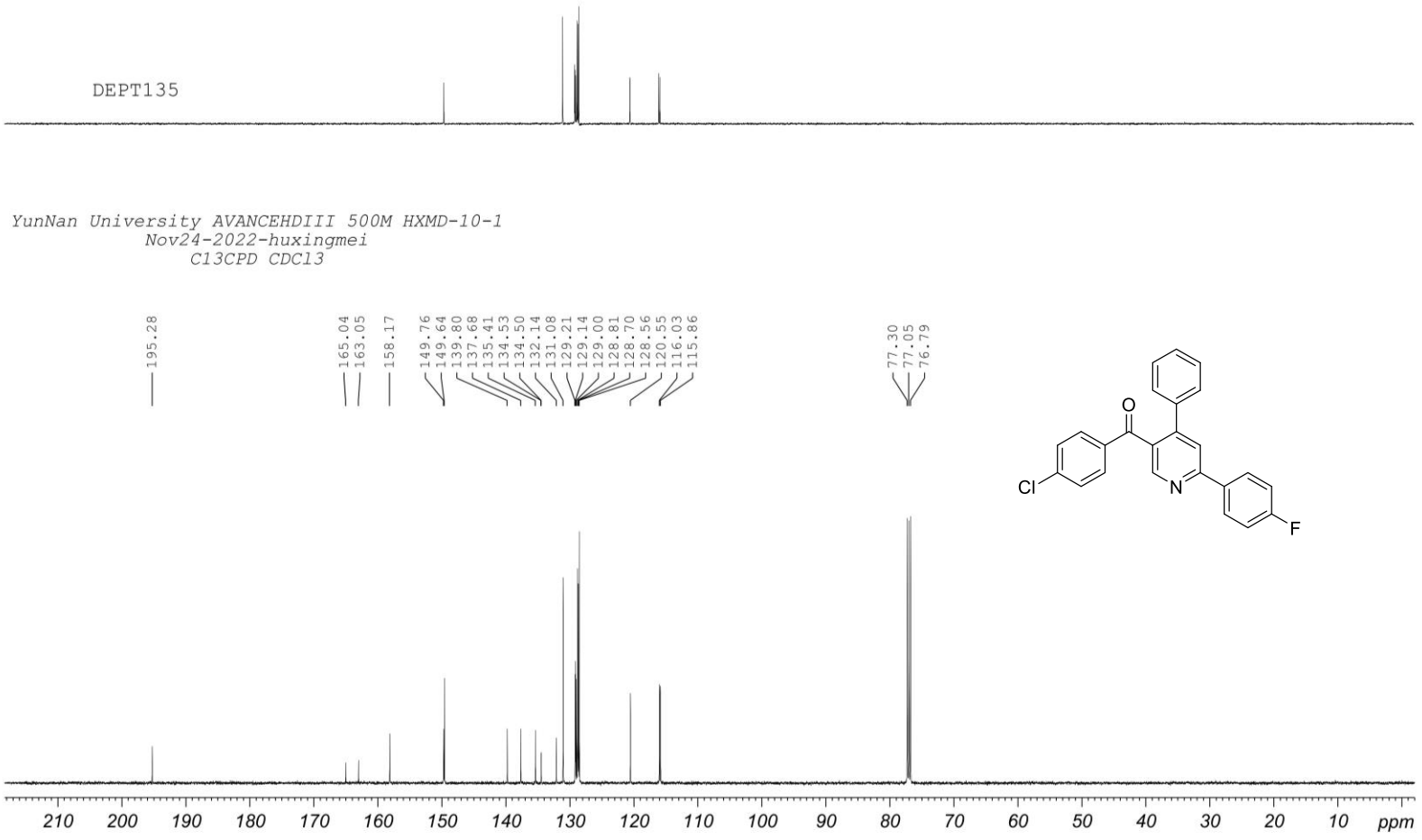


Figure S43. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3q**

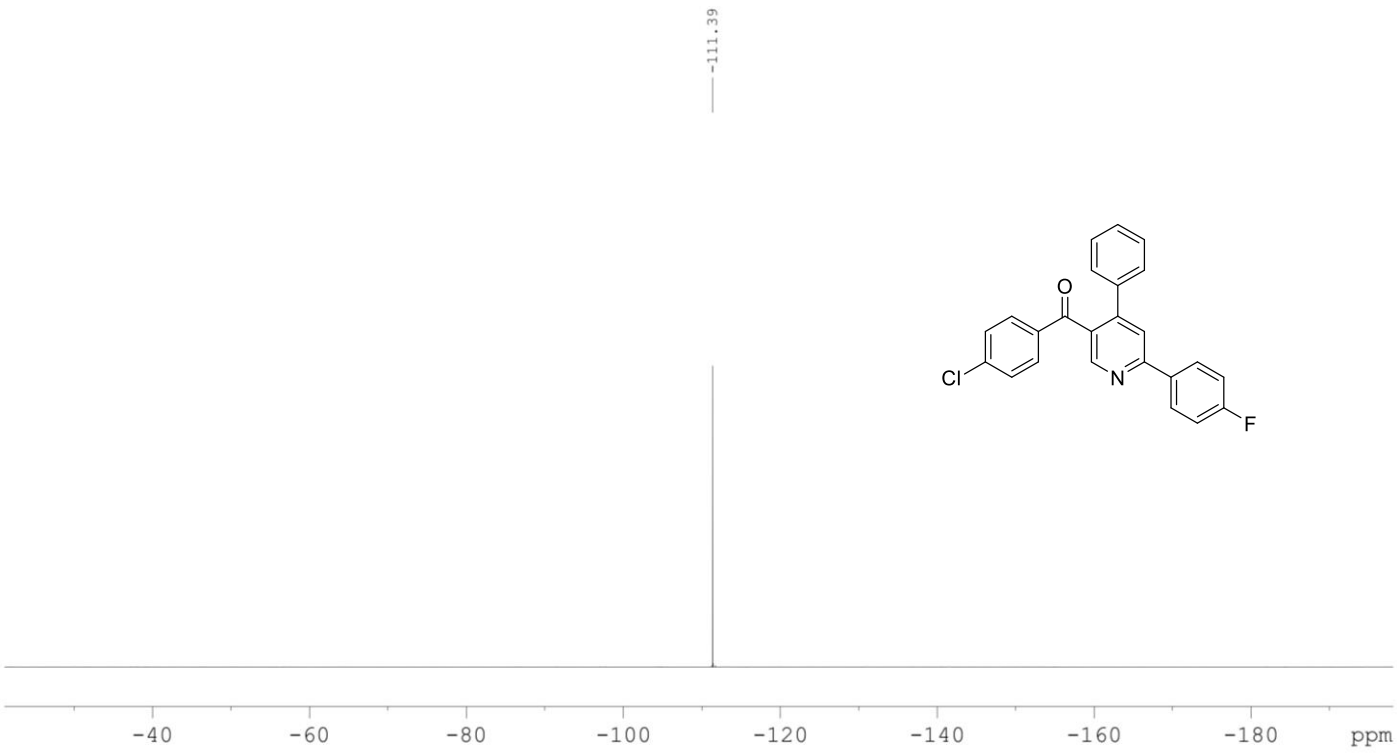


Figure S44. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3q**

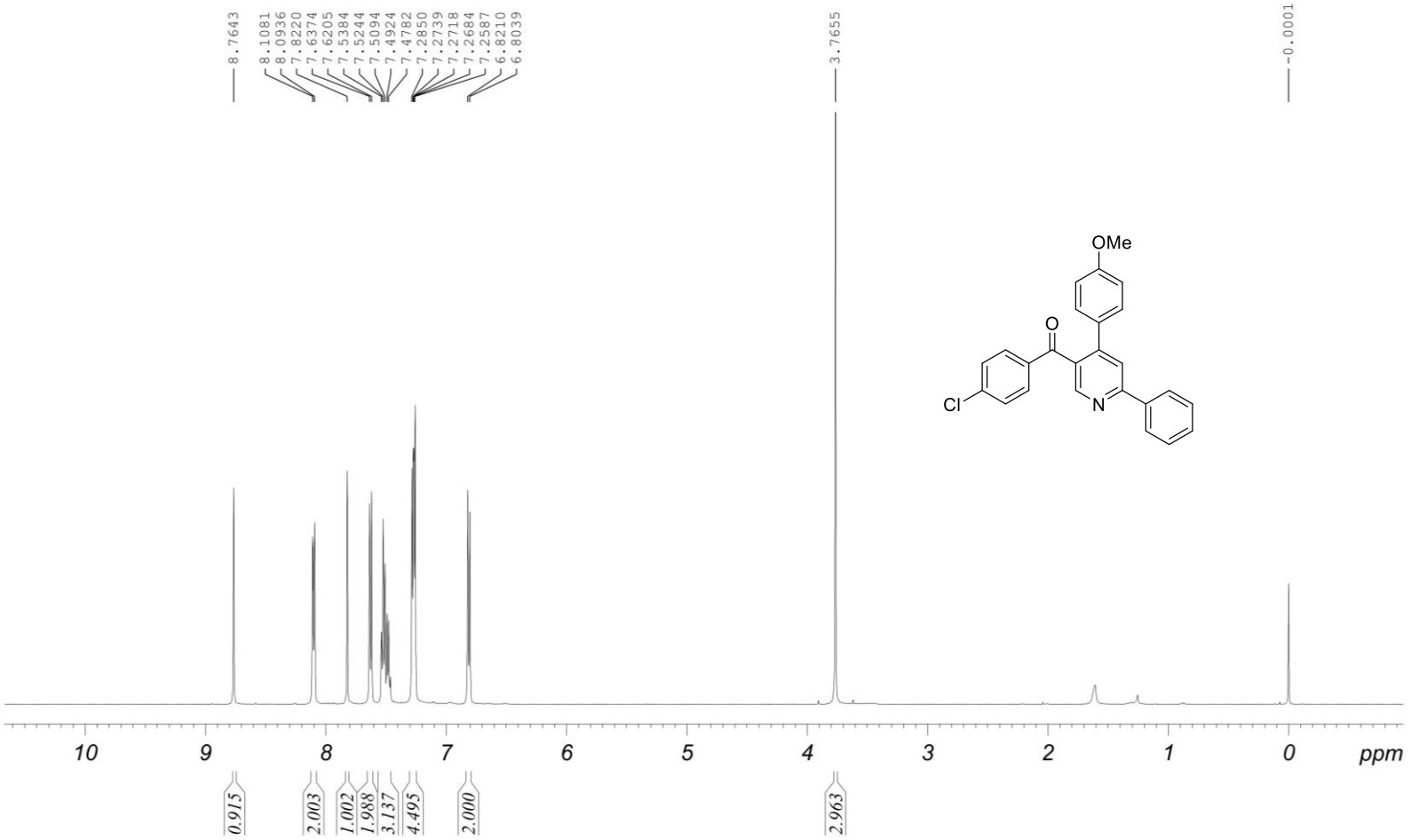


Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3r**

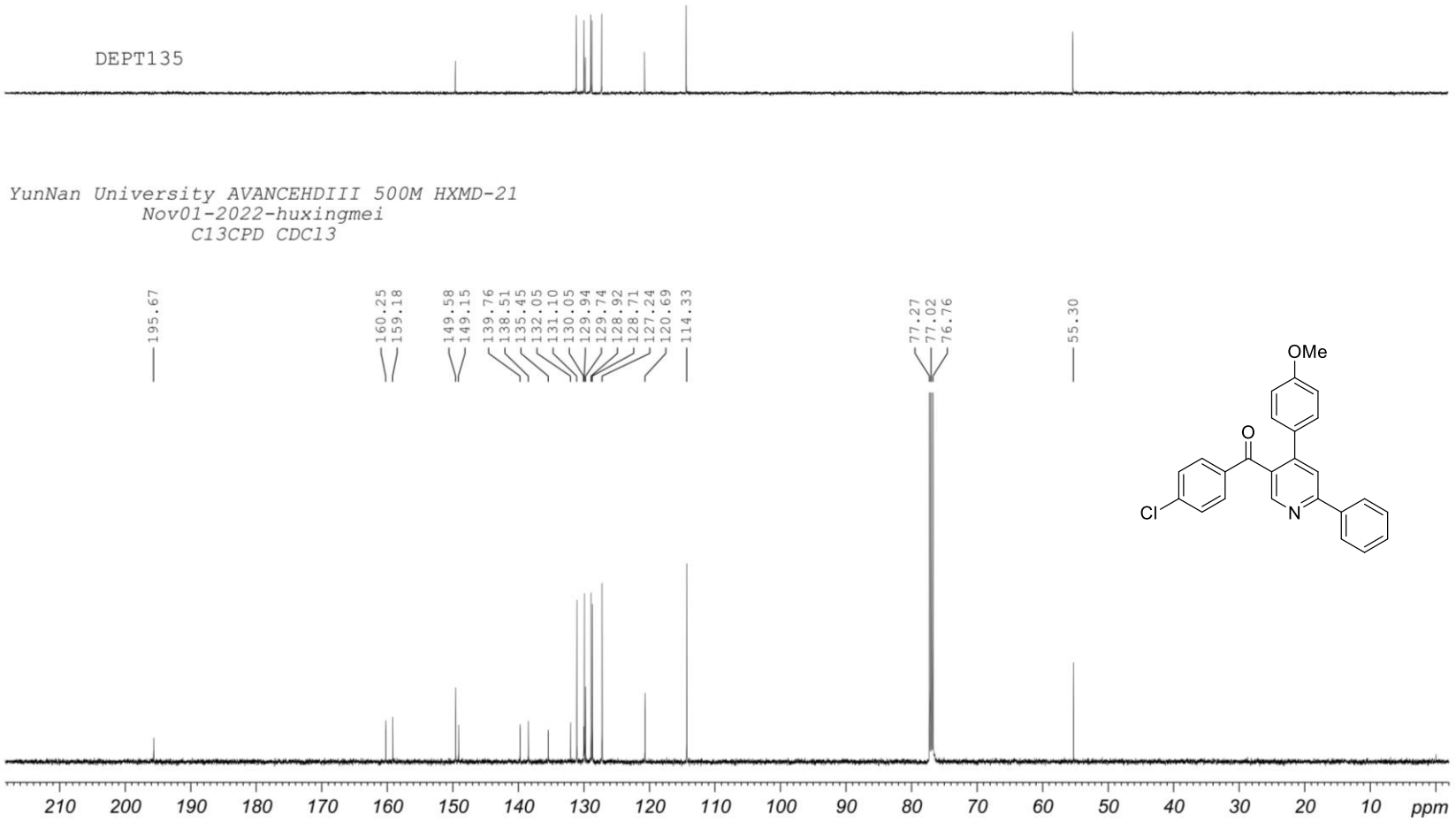


Figure S46. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3r**

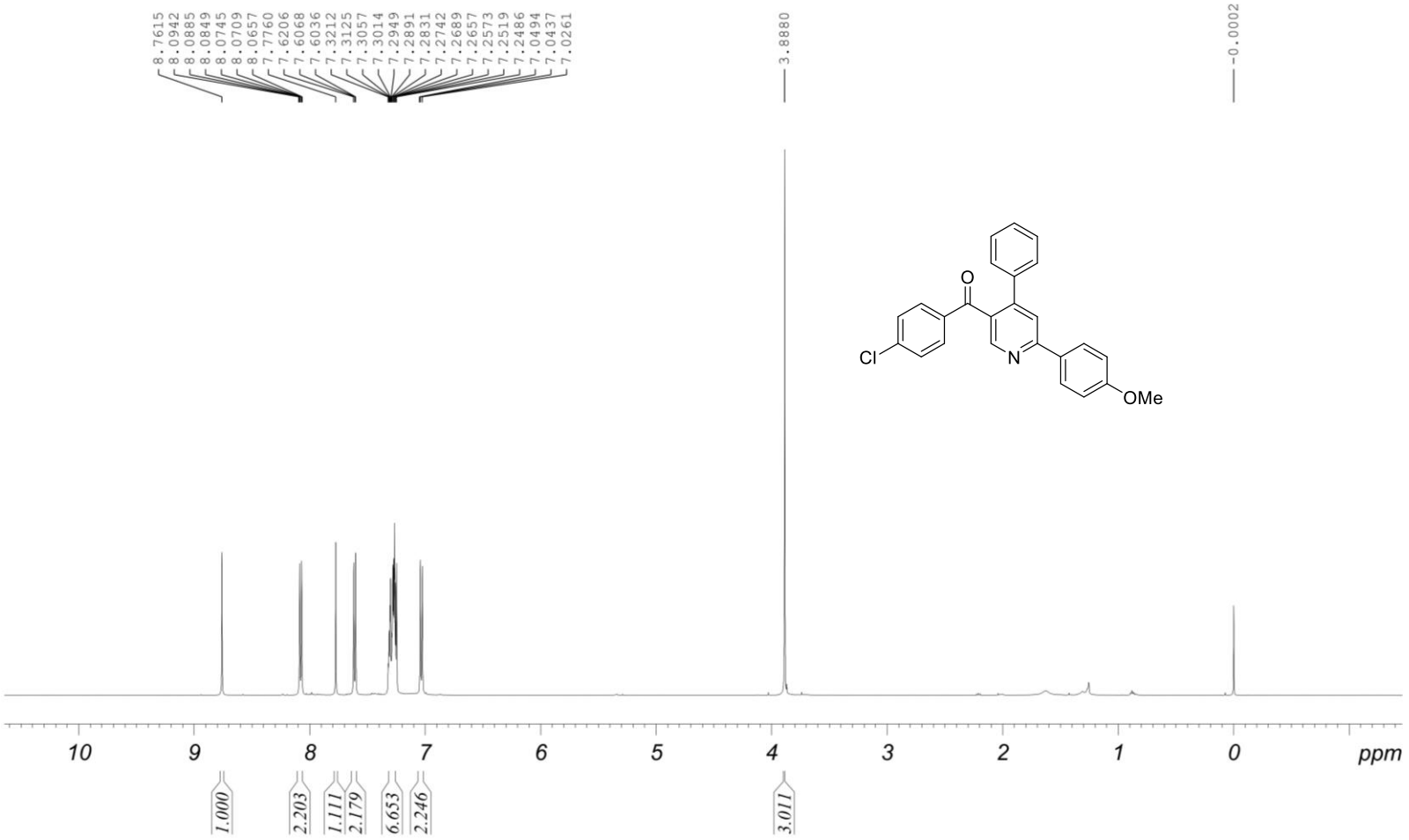


Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3s**

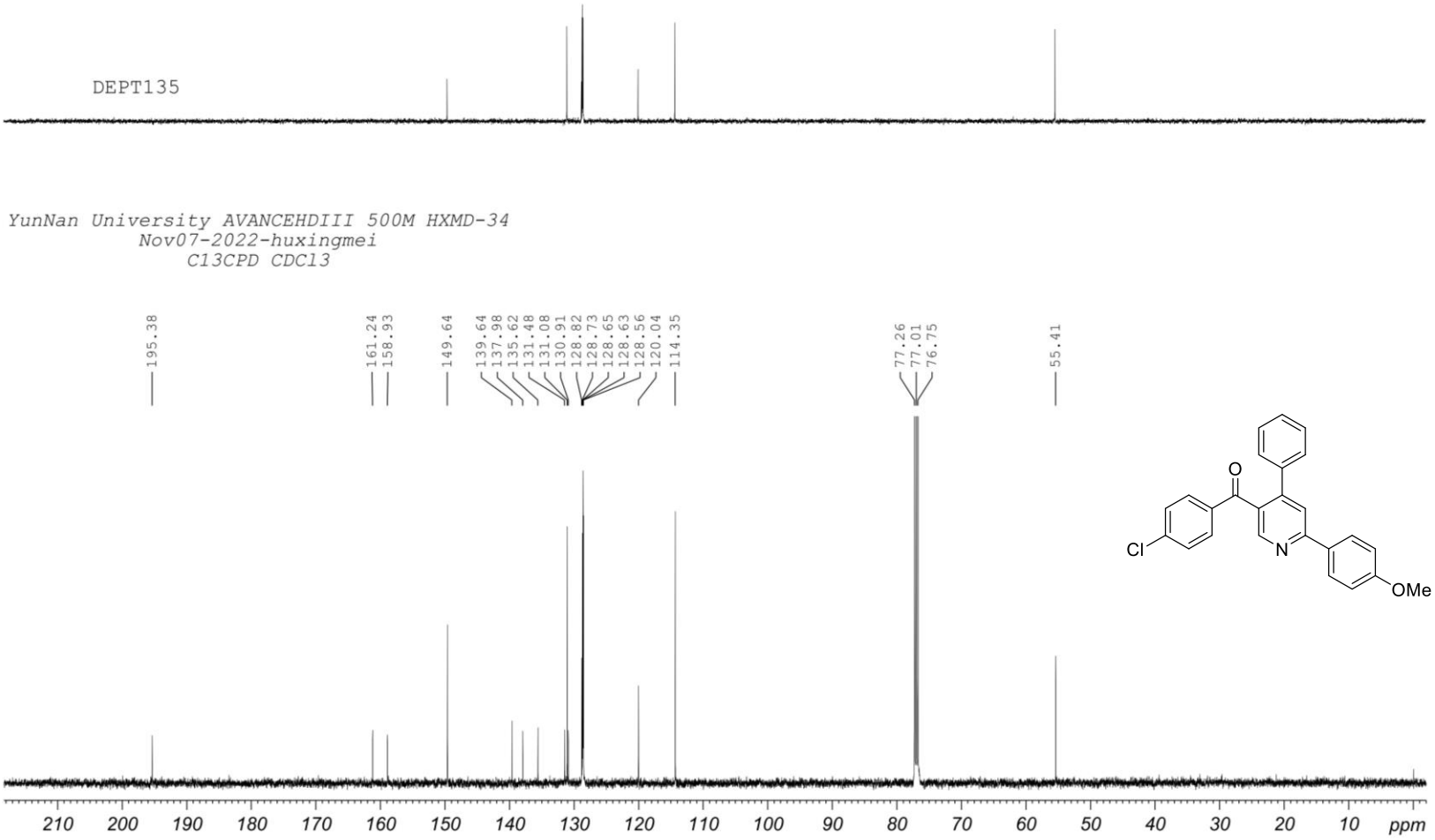


Figure S48. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3s**

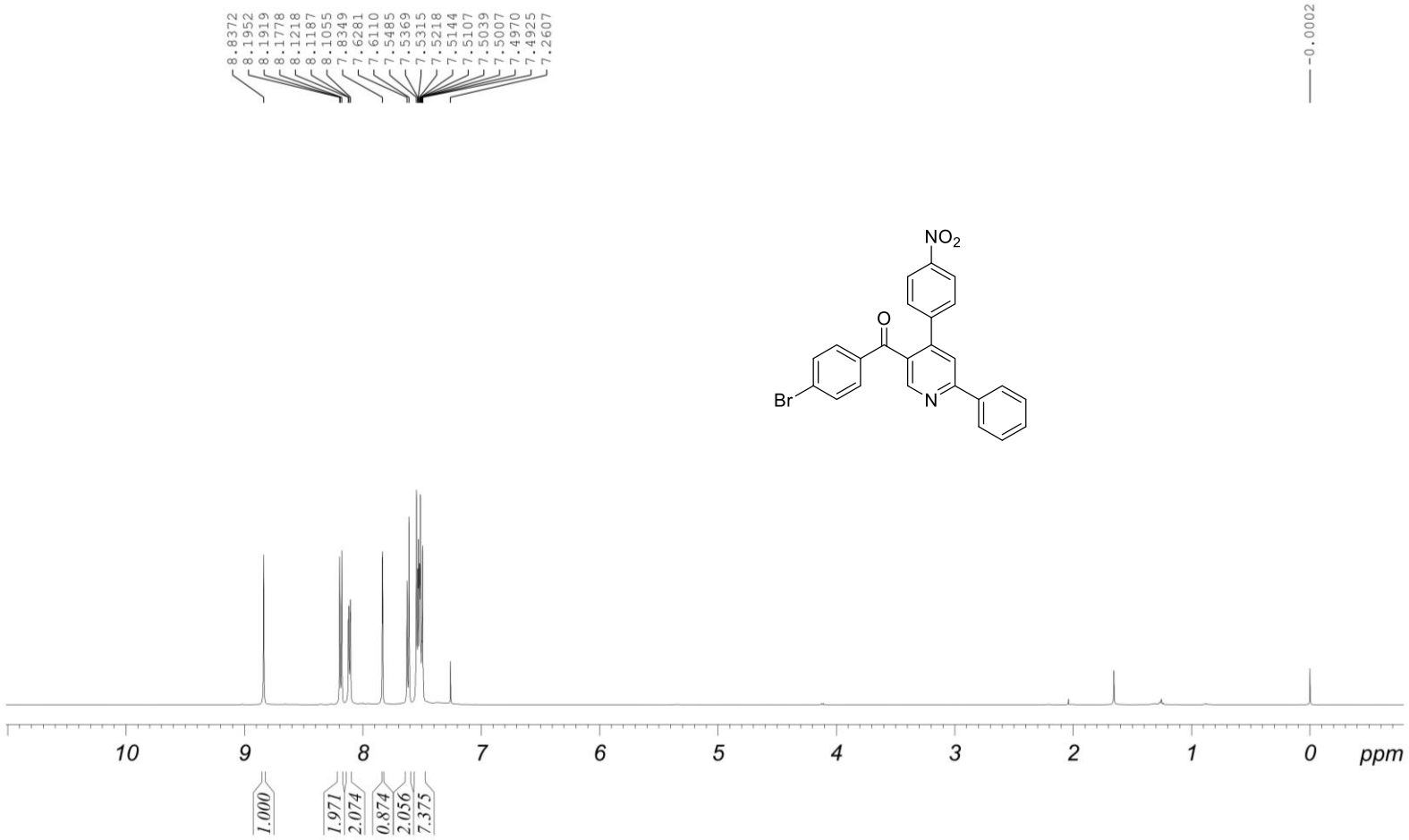


Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3t**

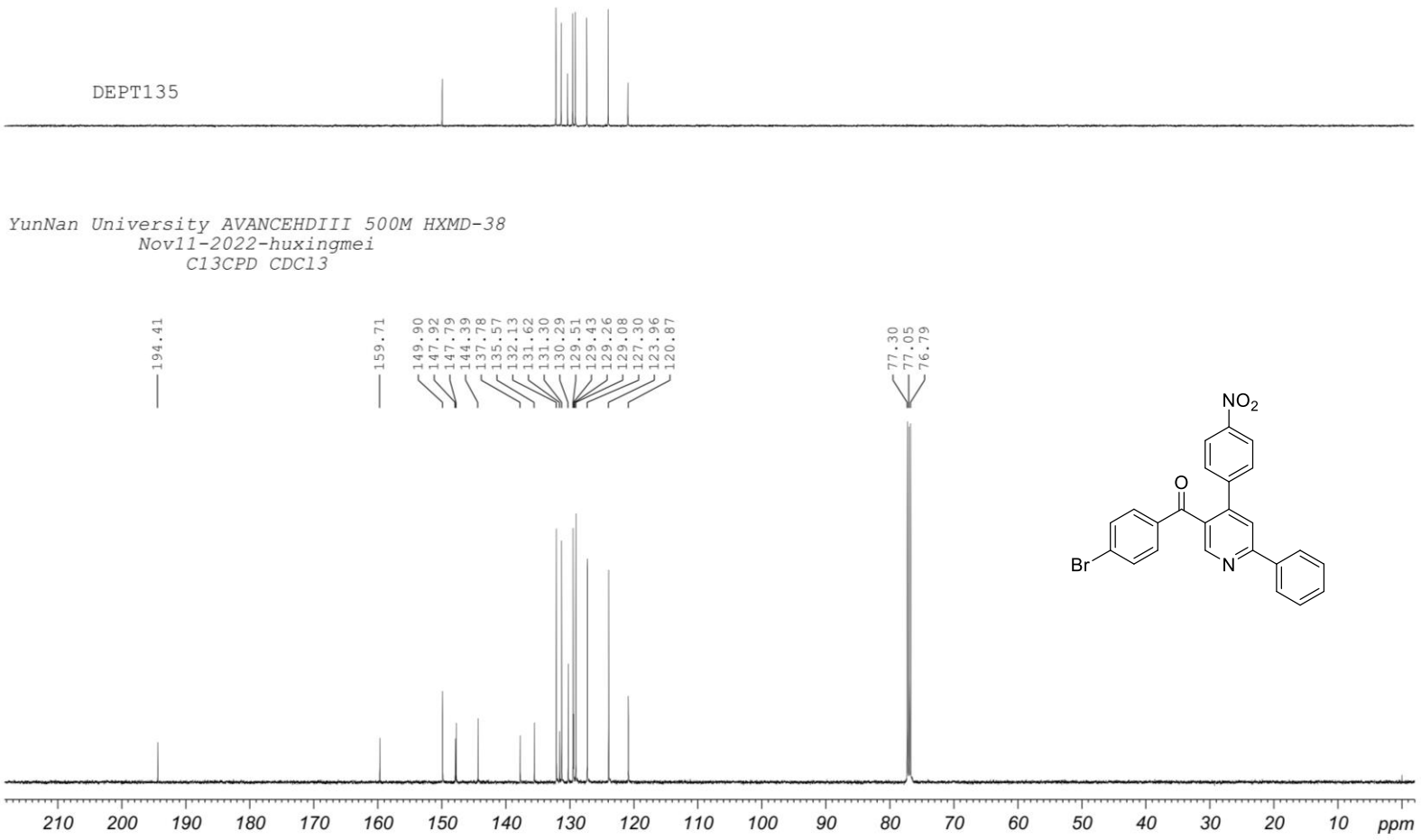


Figure S50. ^{12}C NMR (125 MHz, $CDCl_3$) spectra of compound **3t**

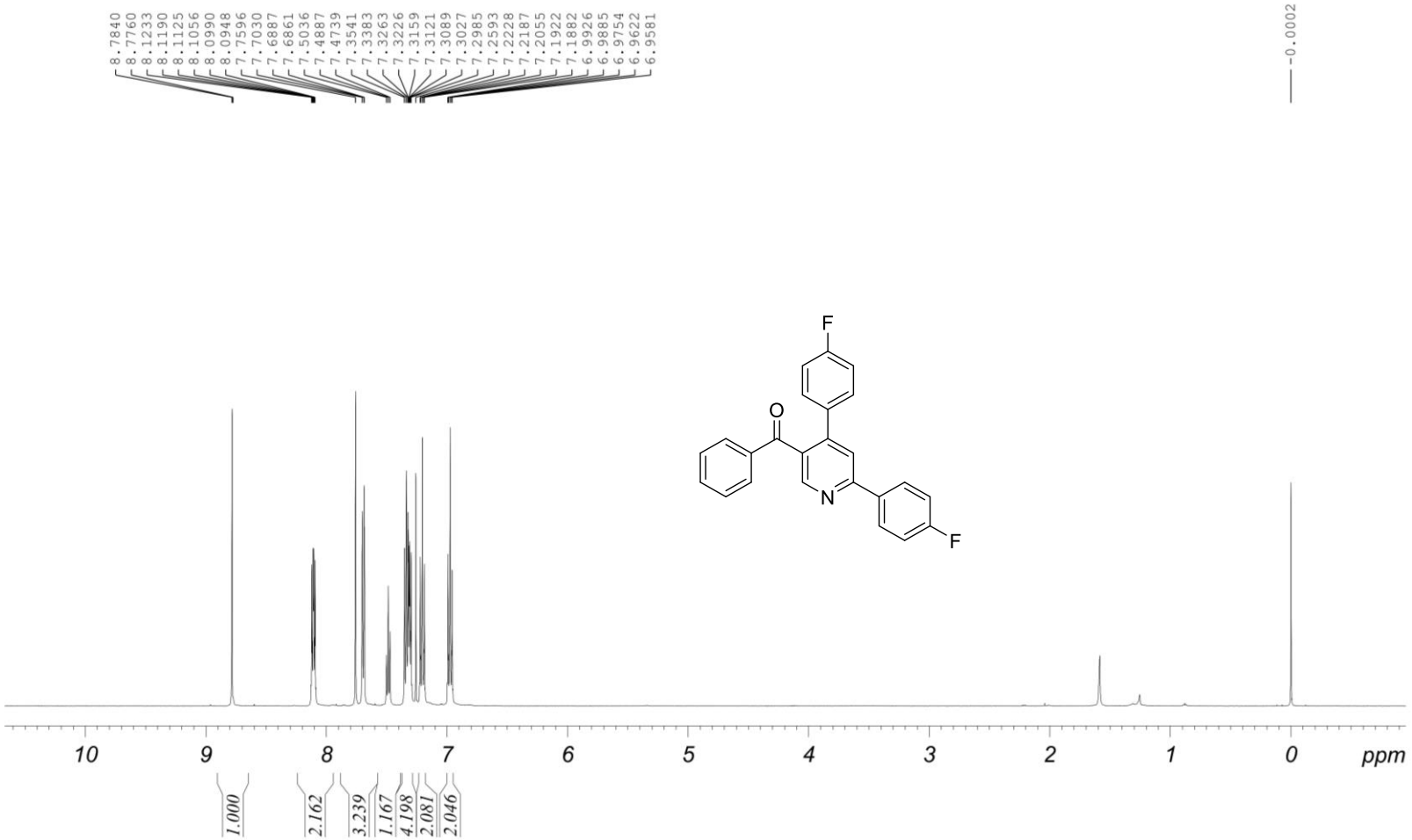


Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3u**

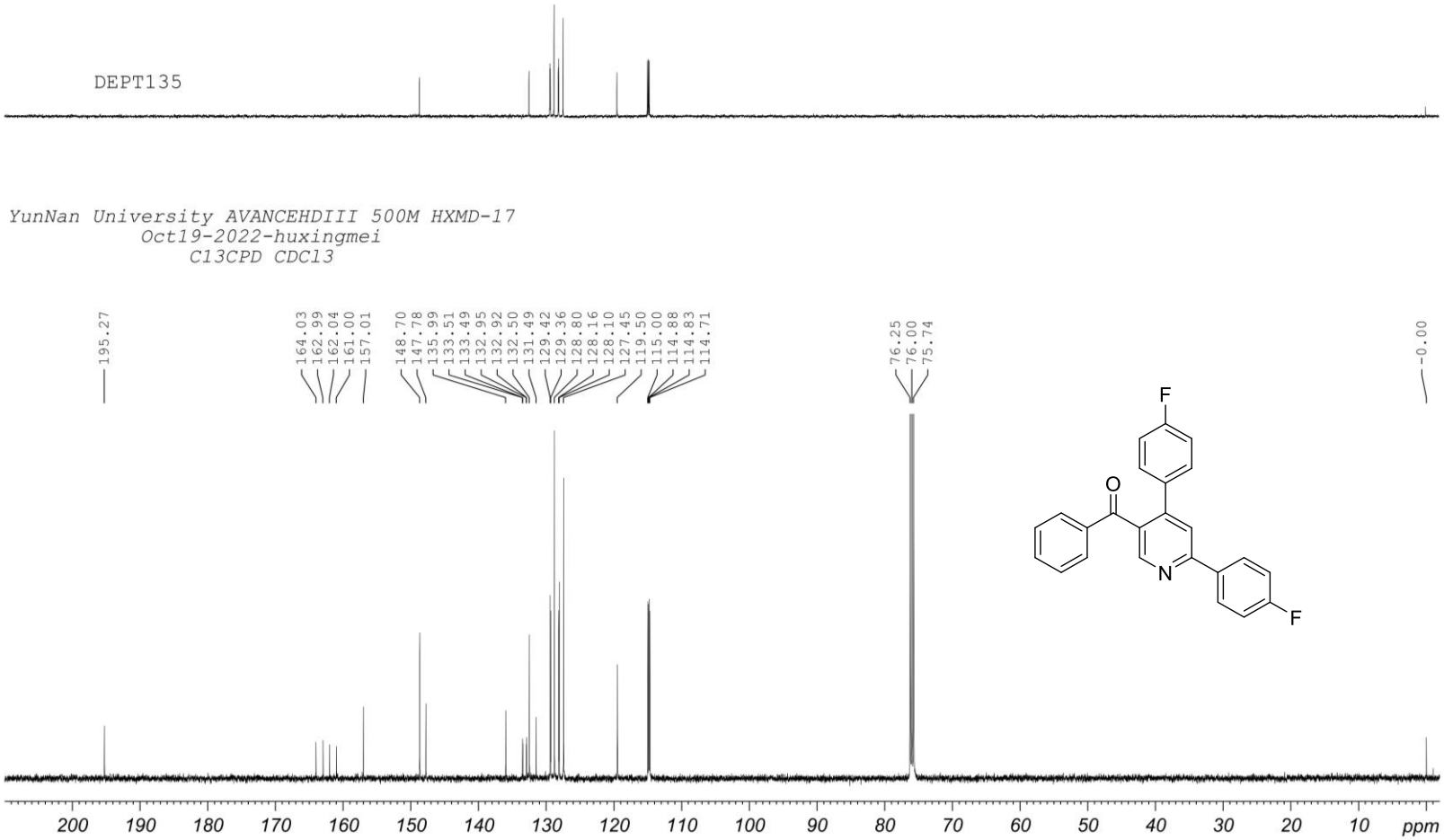


Figure S52. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3u**

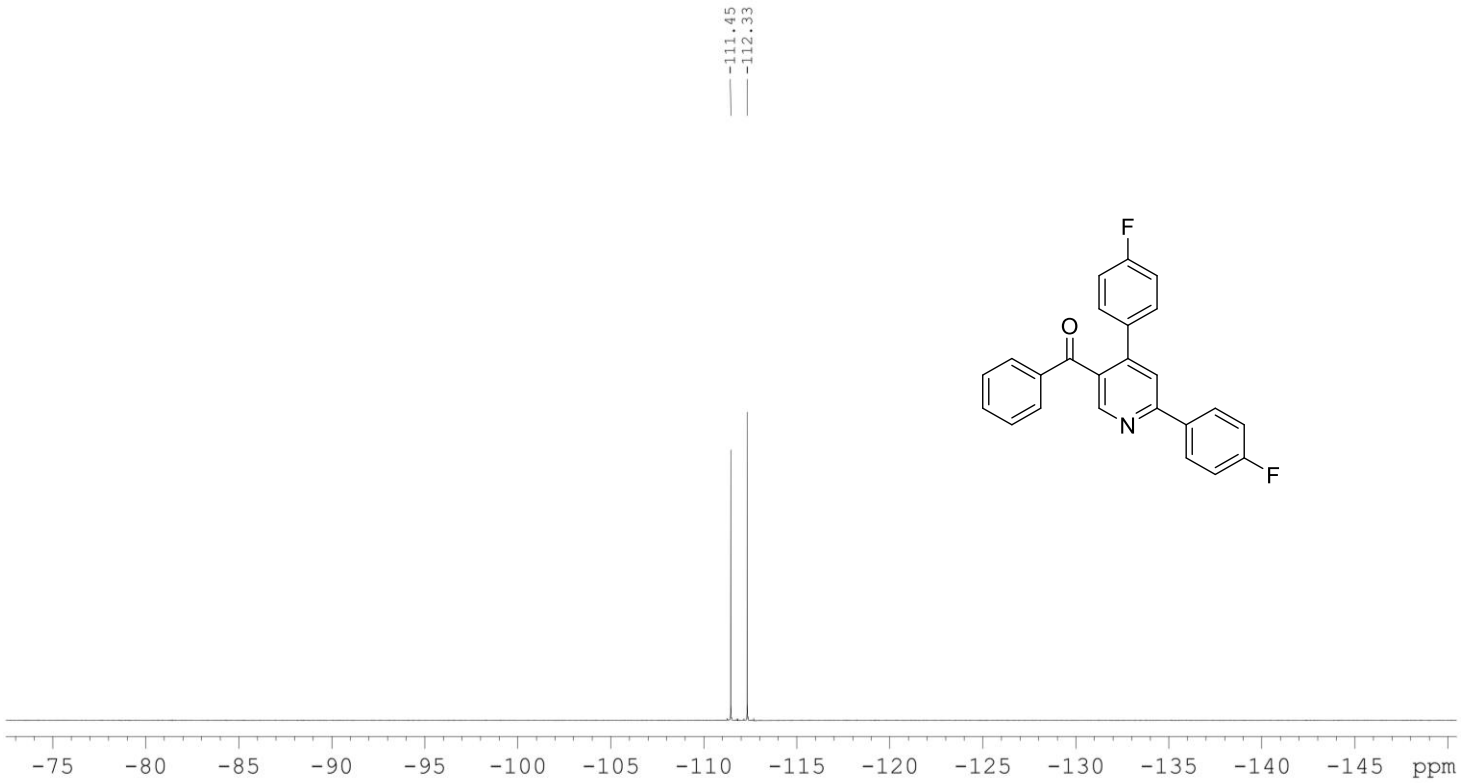


Figure S53. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3u**

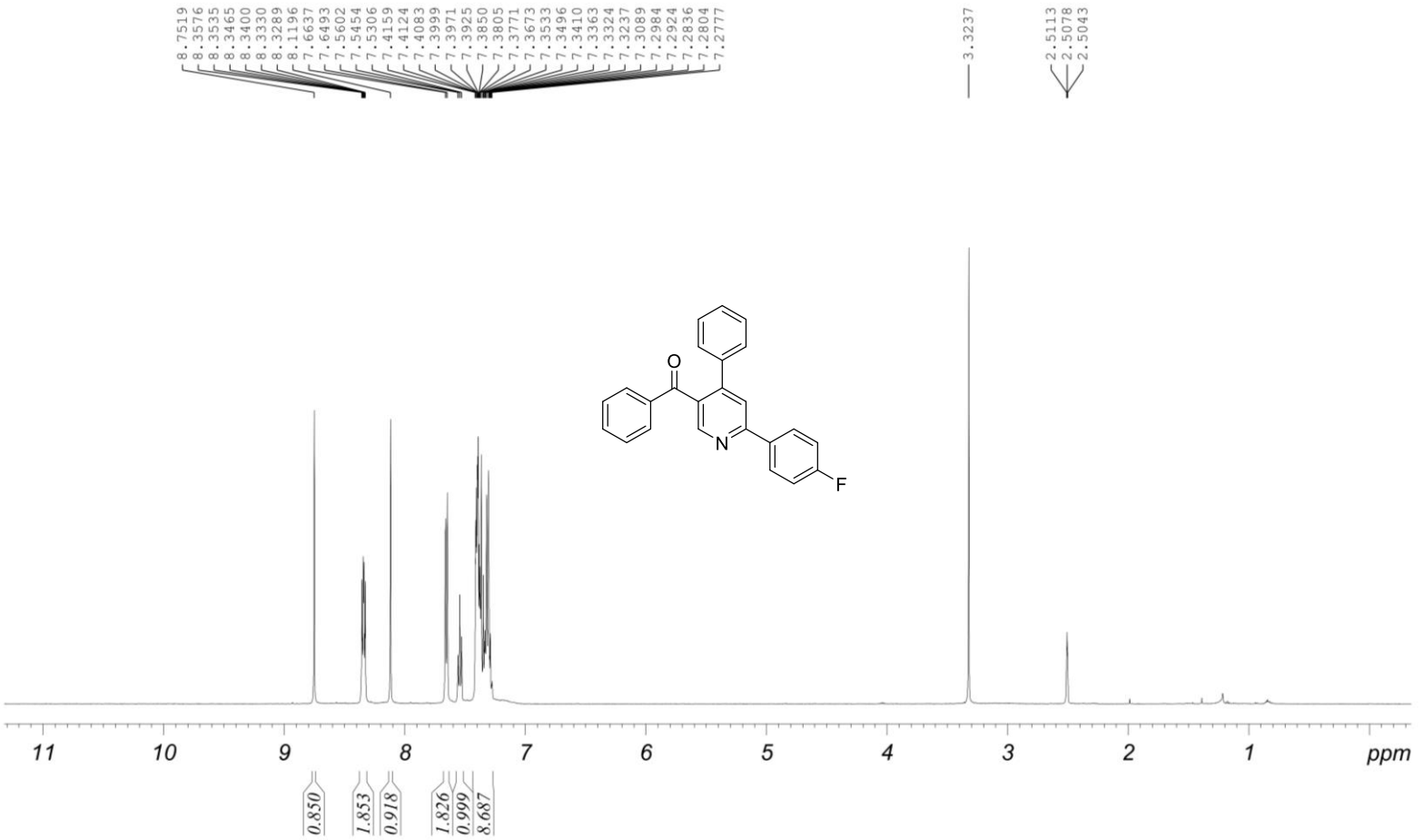


Figure S54. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **3v**

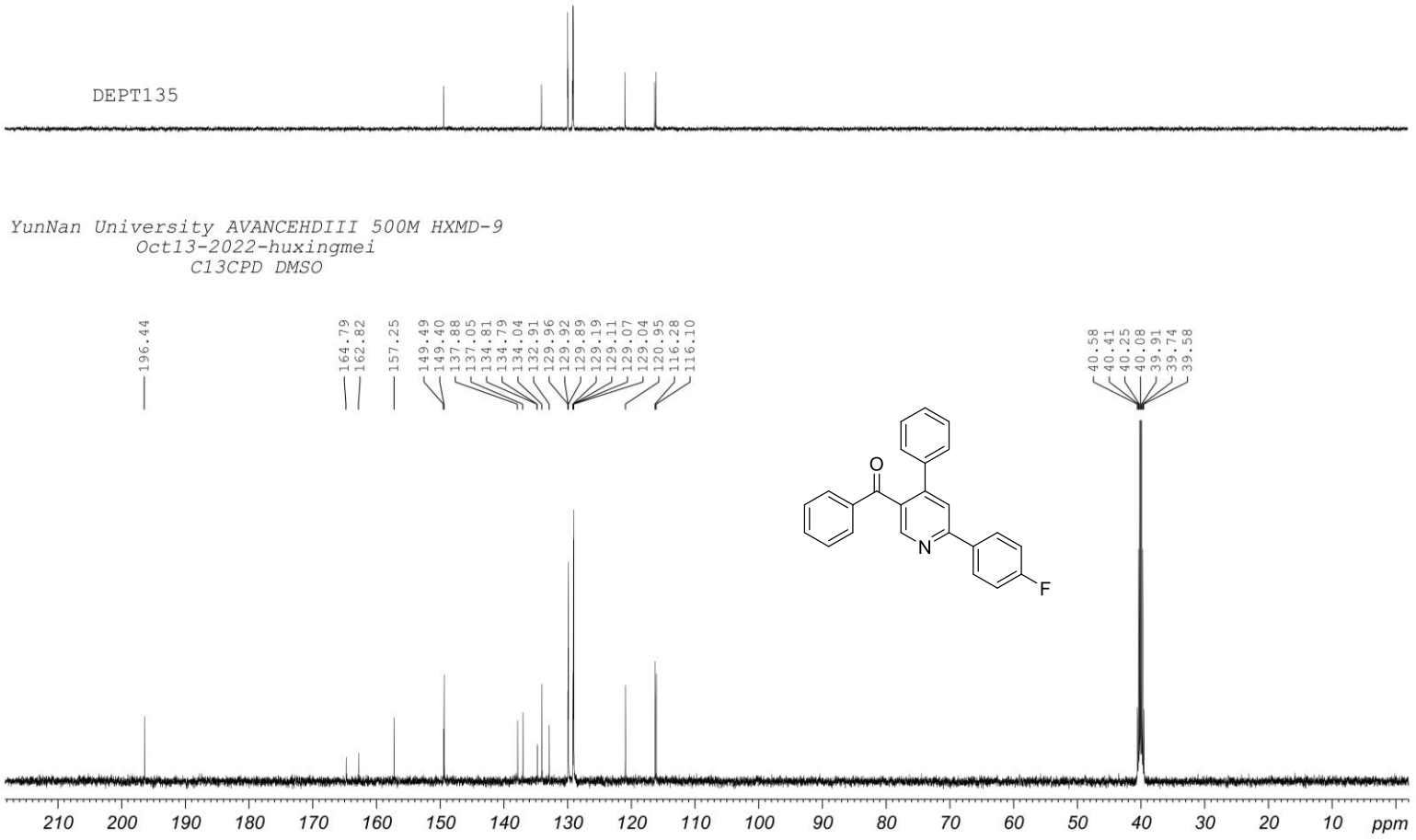


Figure S55. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **3v**

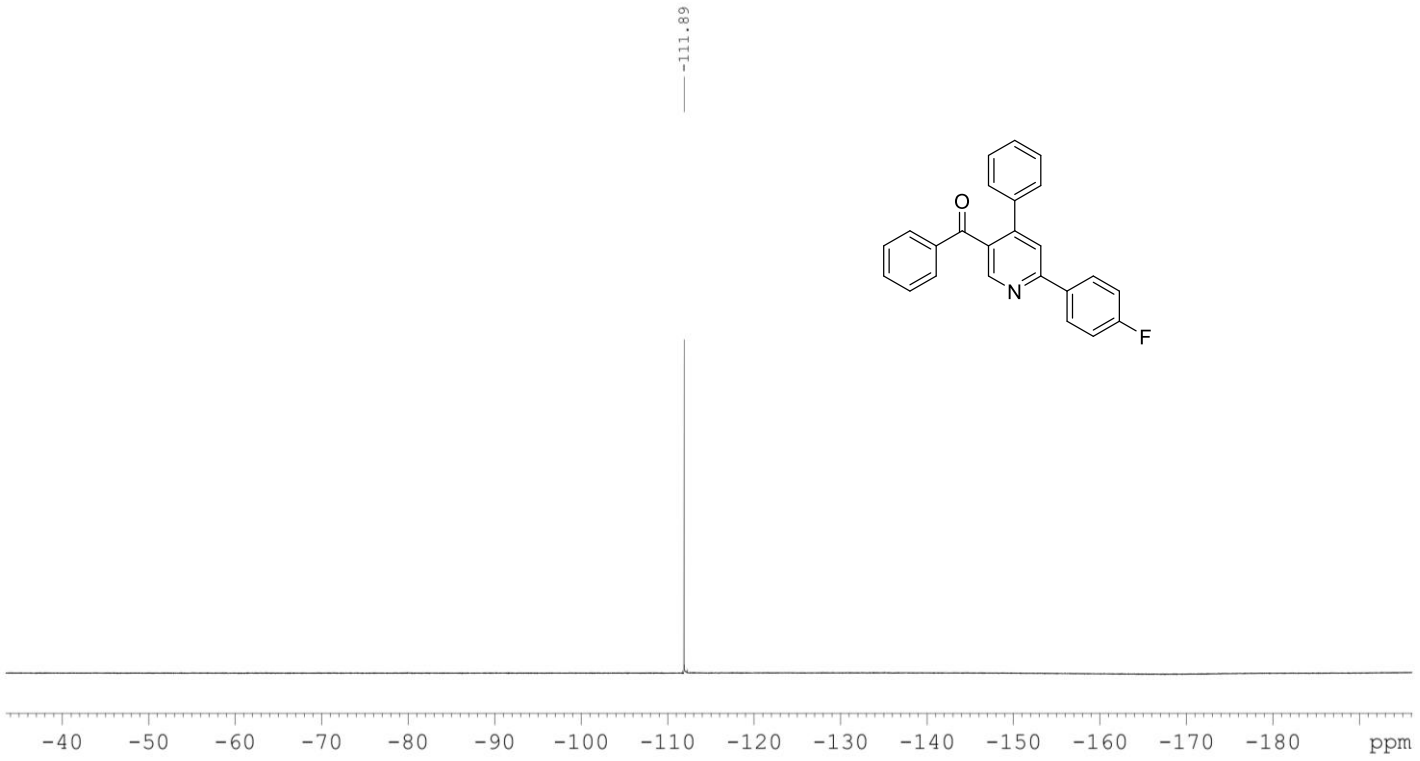


Figure S56. ^{19}F NMR (470 MHz, DMSO-d_6) spectra of compound **3v**

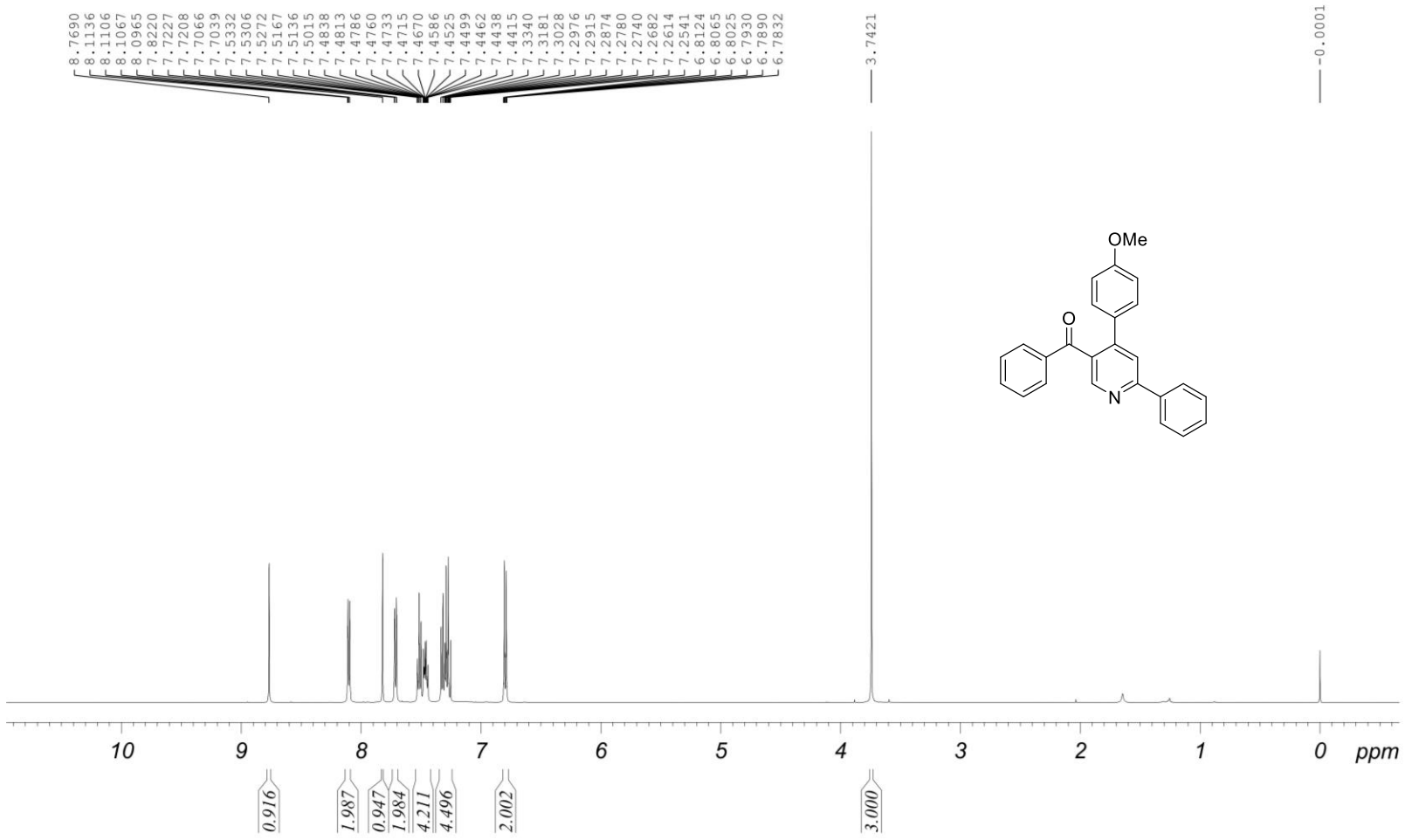


Figure S57. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3w**

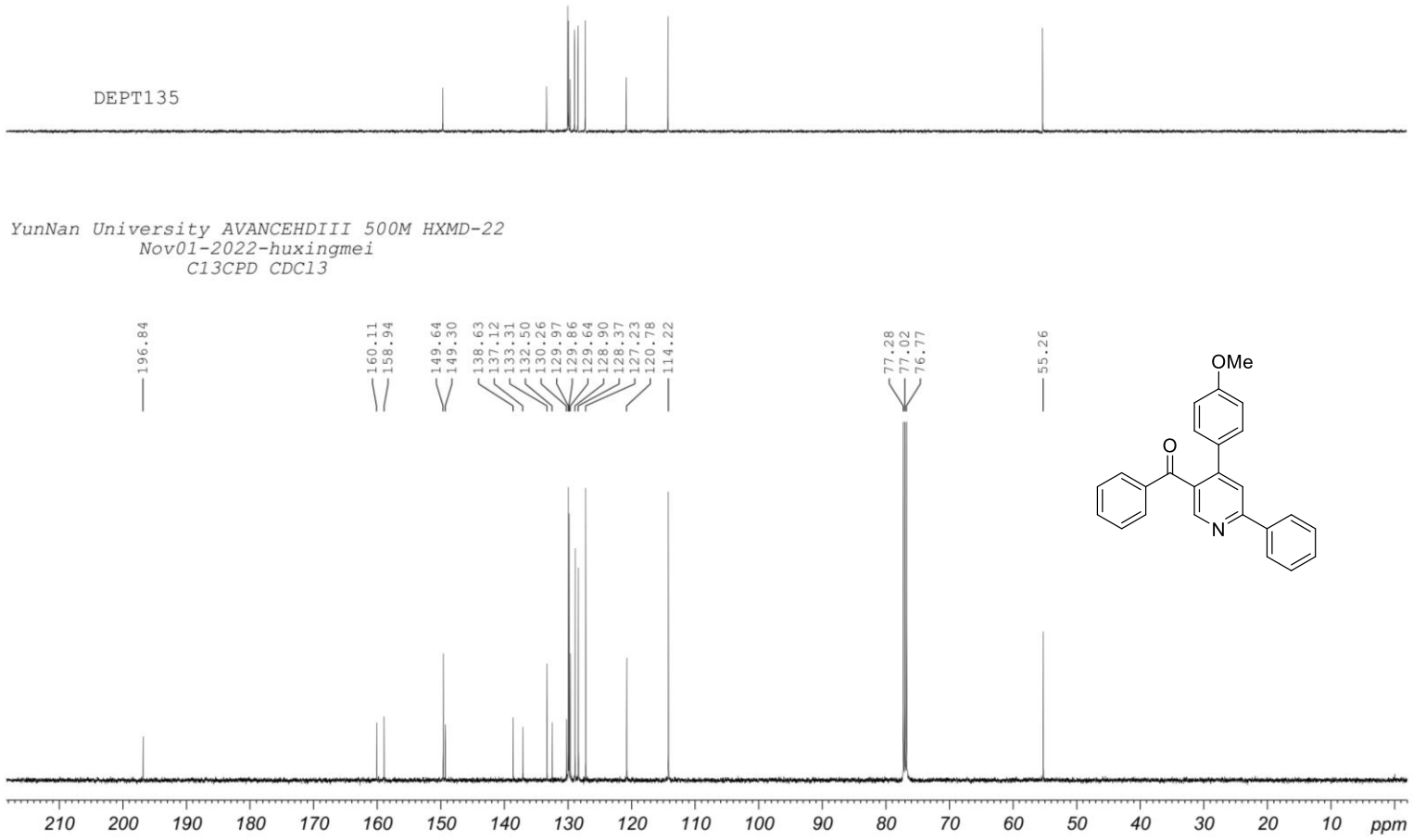


Figure S58. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3w**

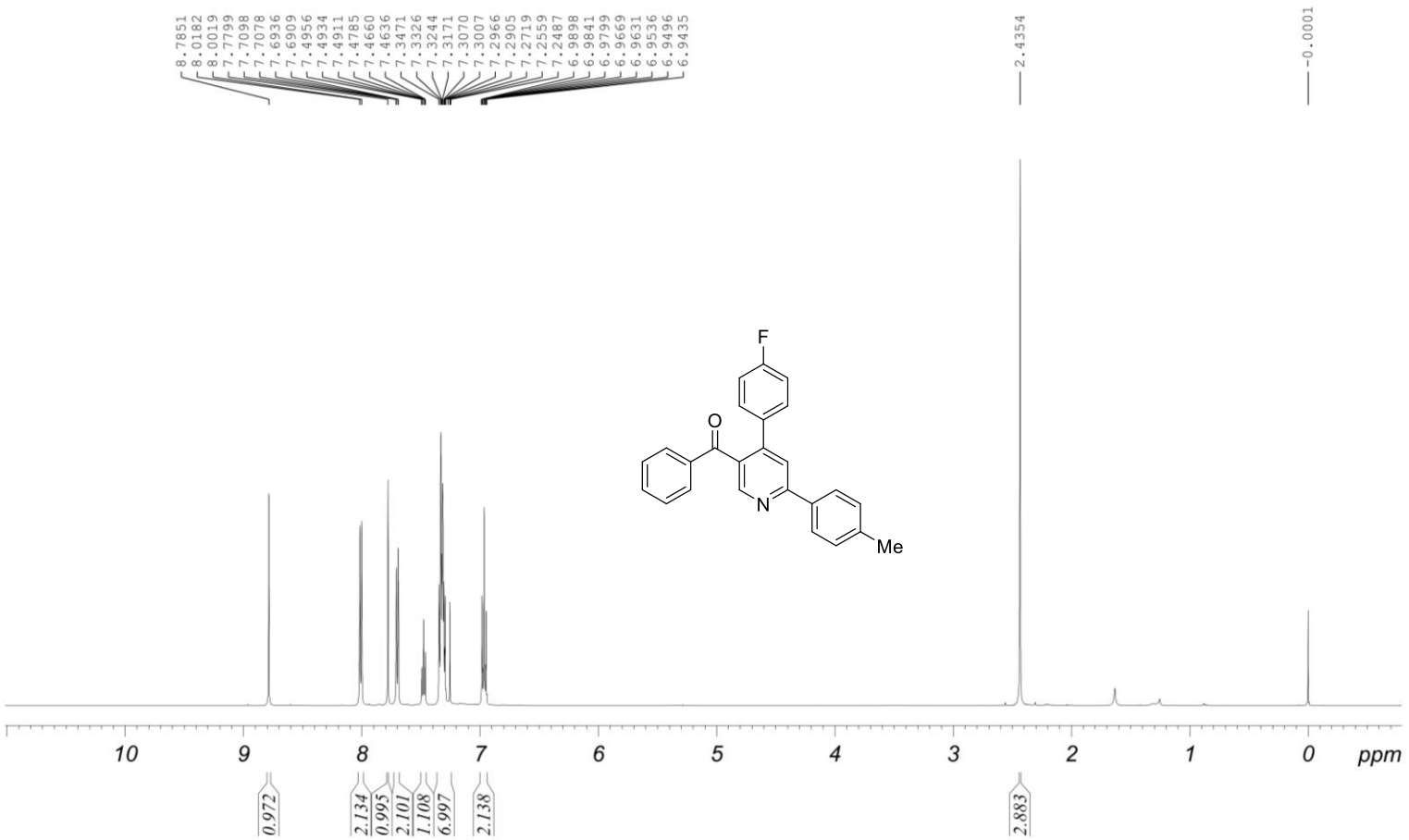


Figure S59. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3x**

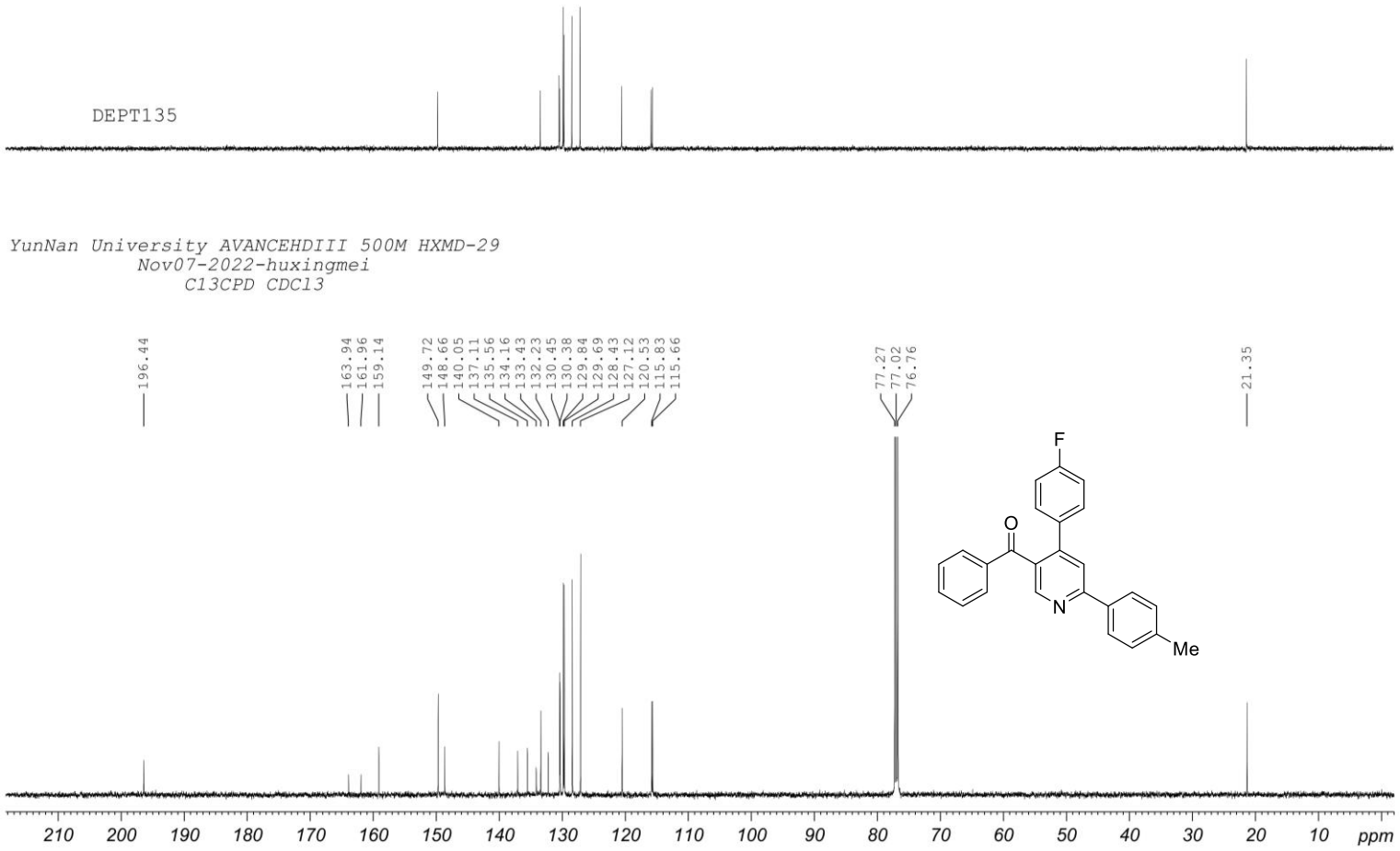


Figure S60. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3x**

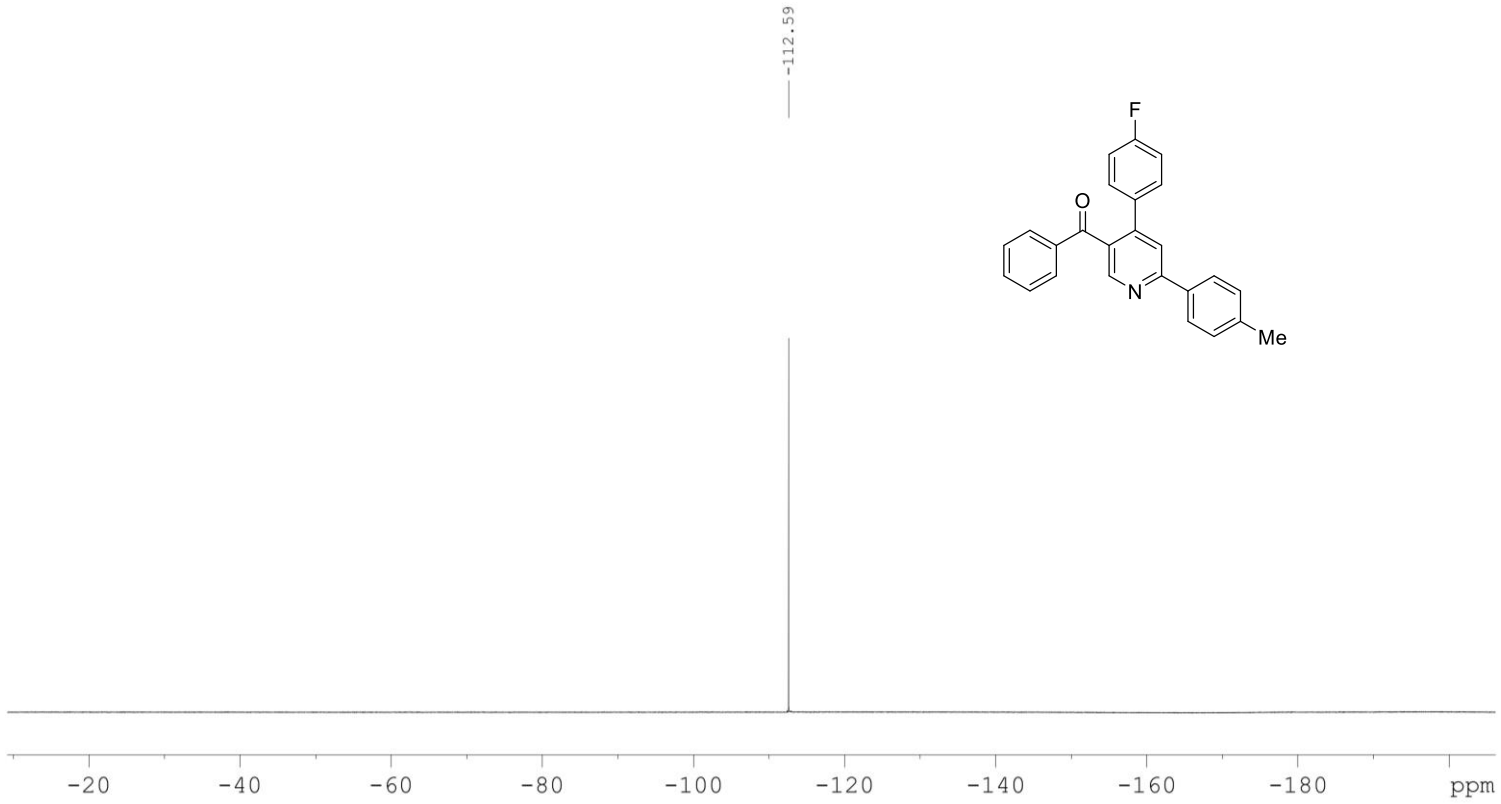


Figure S61. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3x**

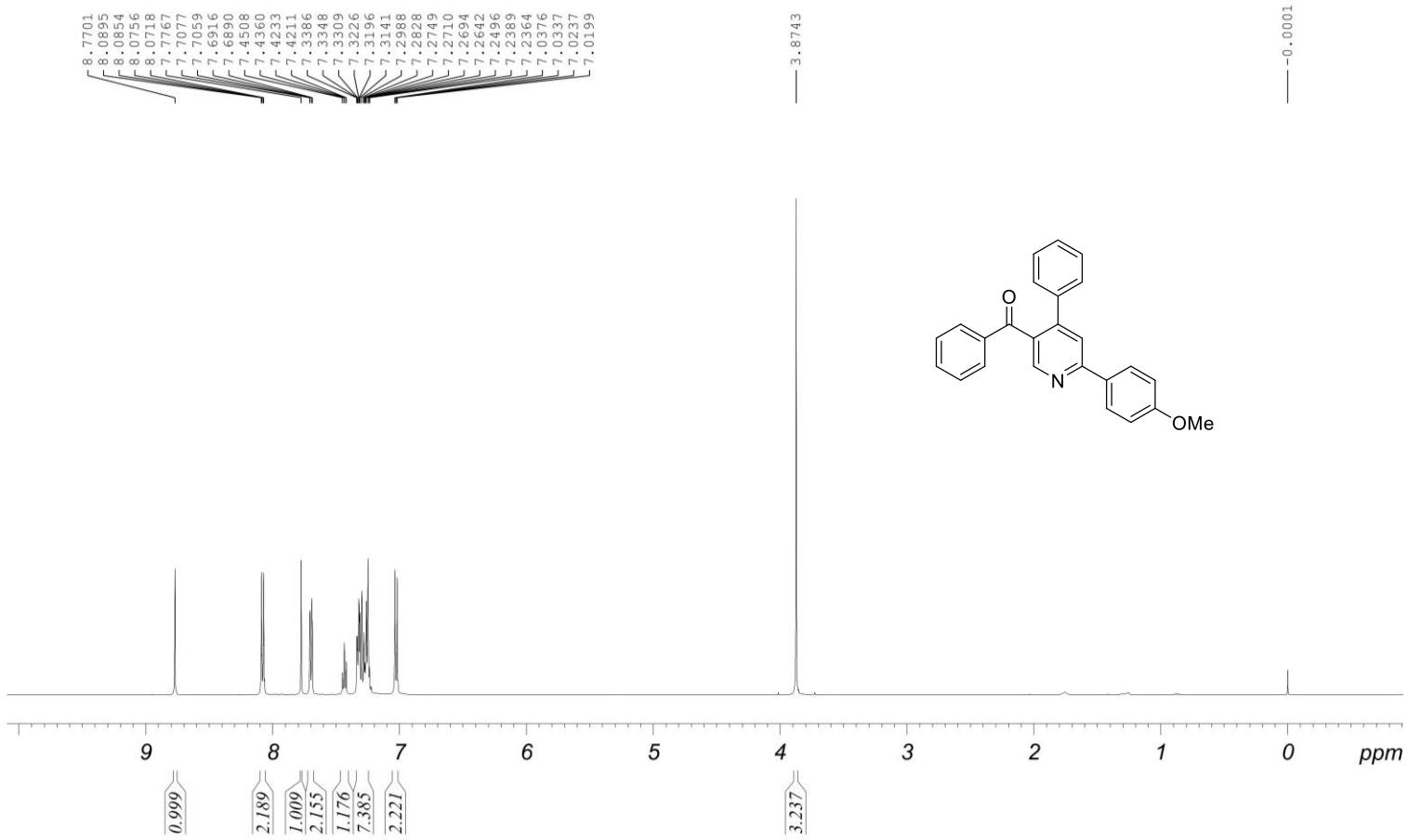


Figure S62. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3y**

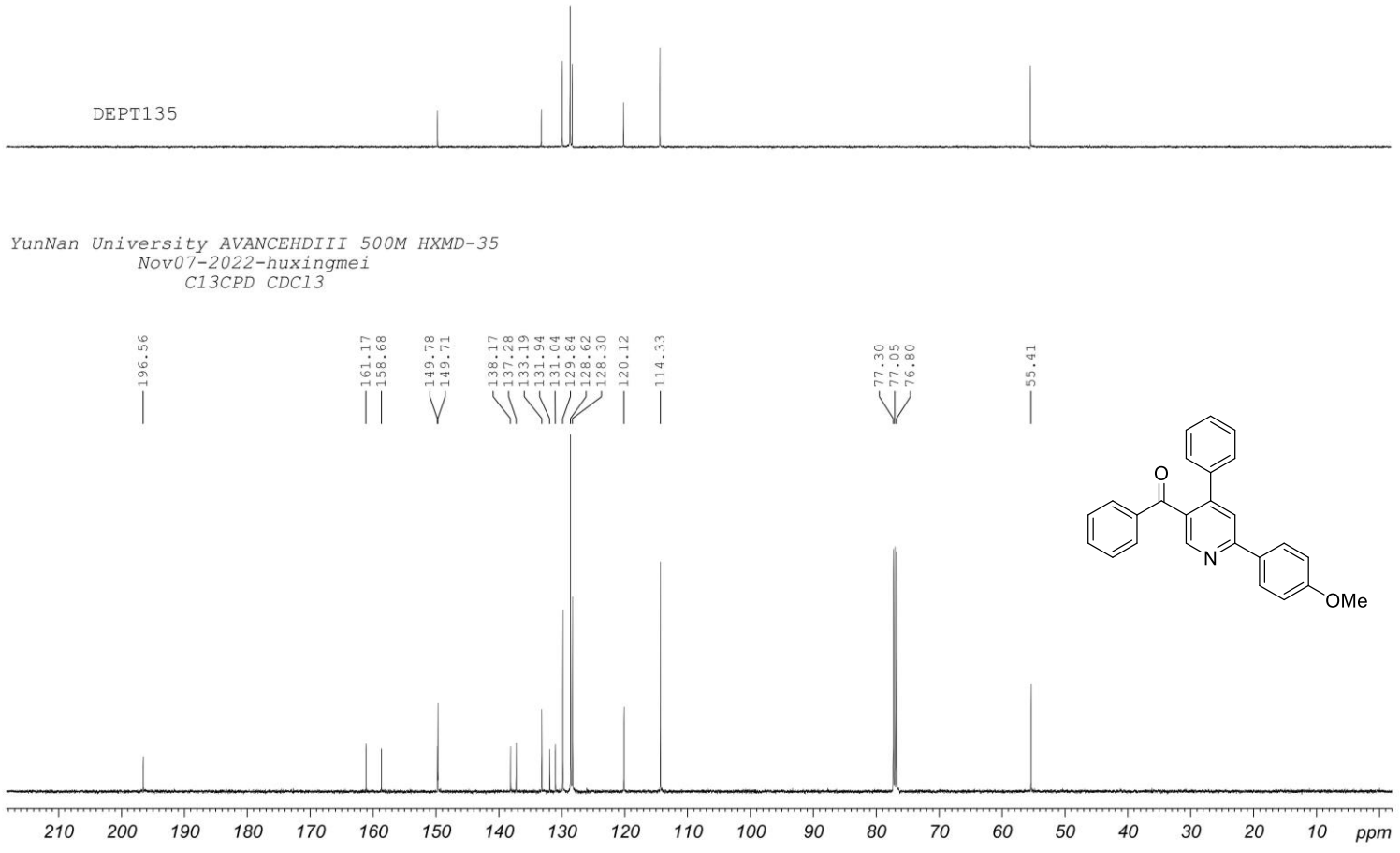


Figure S63. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3y**

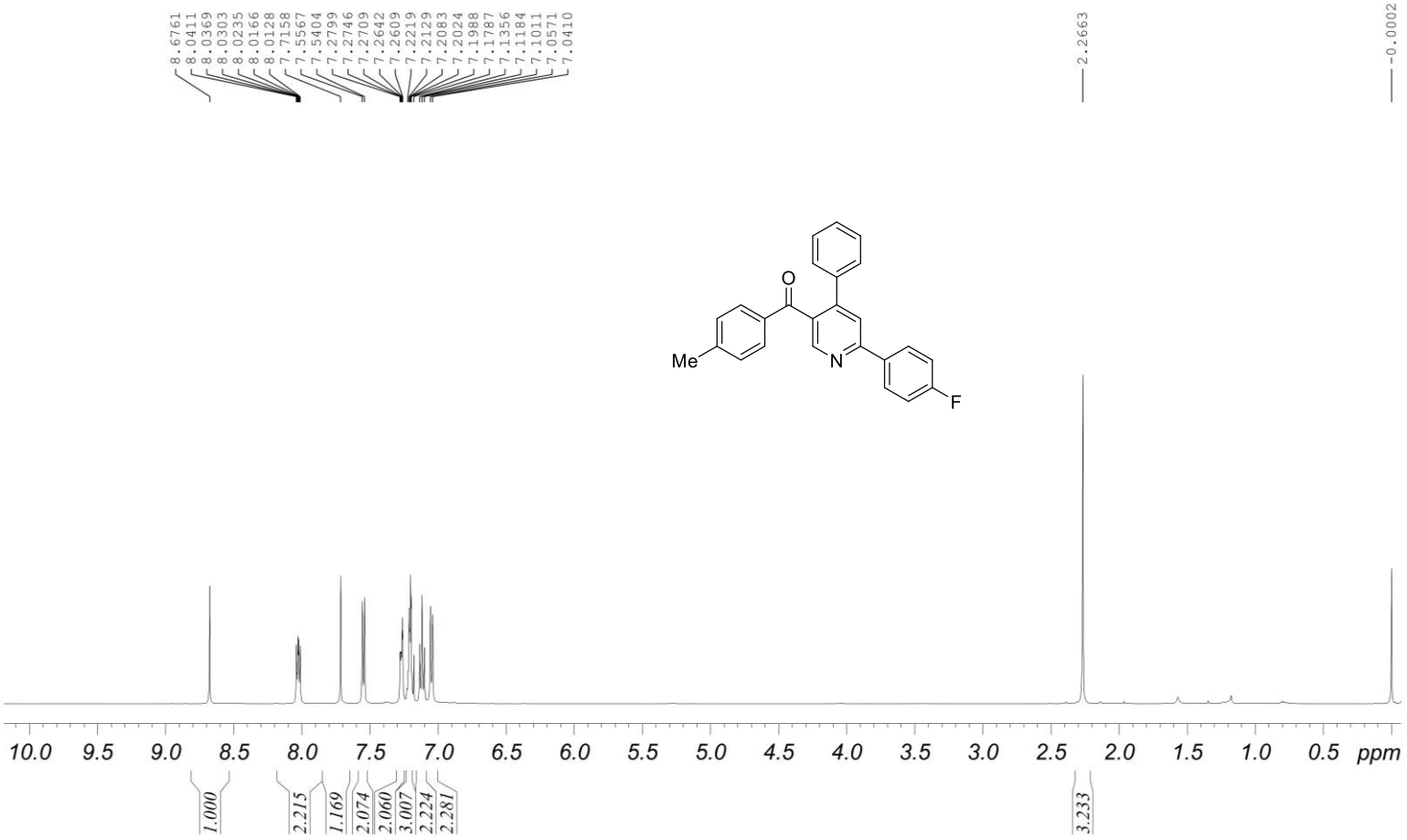


Figure S64. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3z**

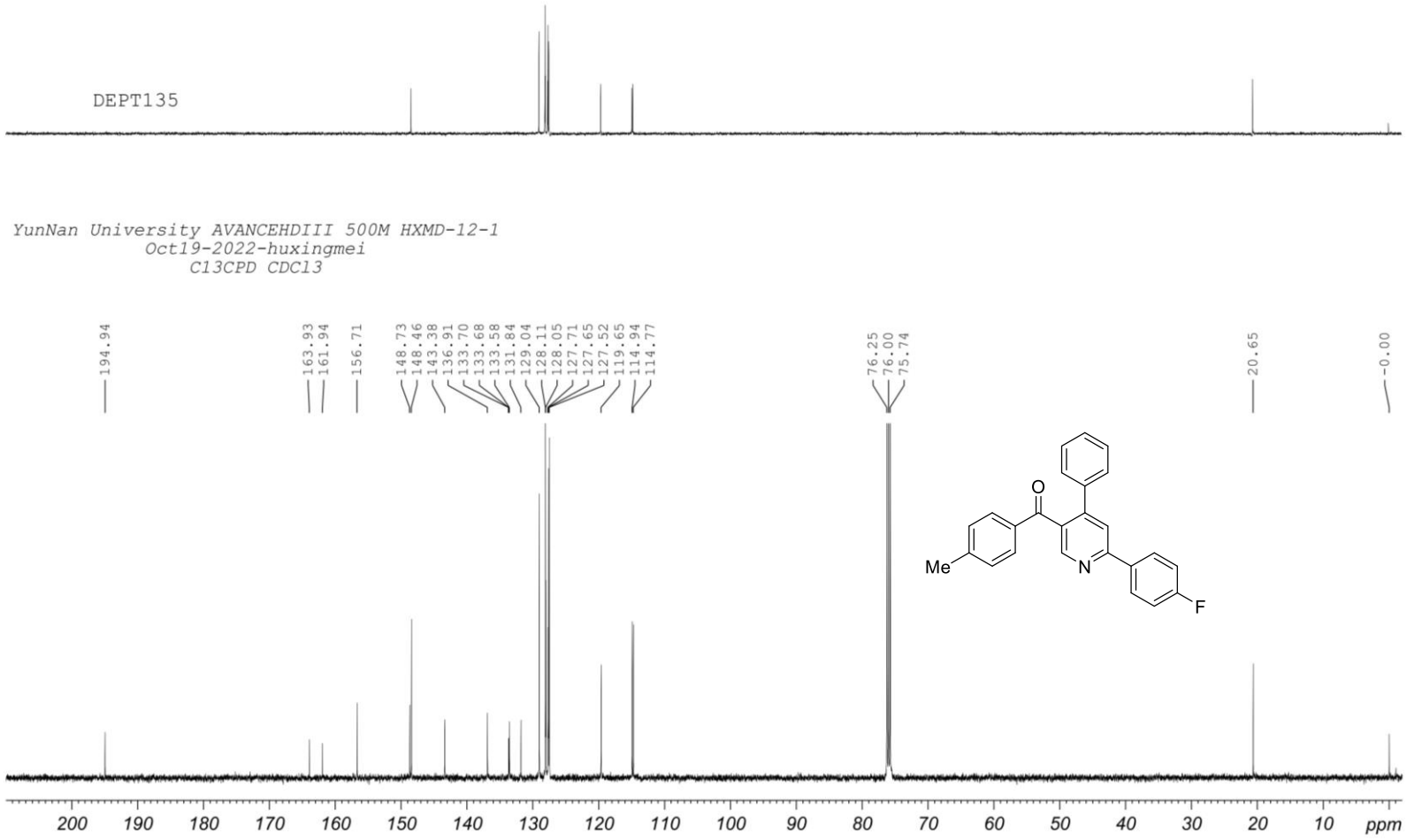


Figure S65. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3z**

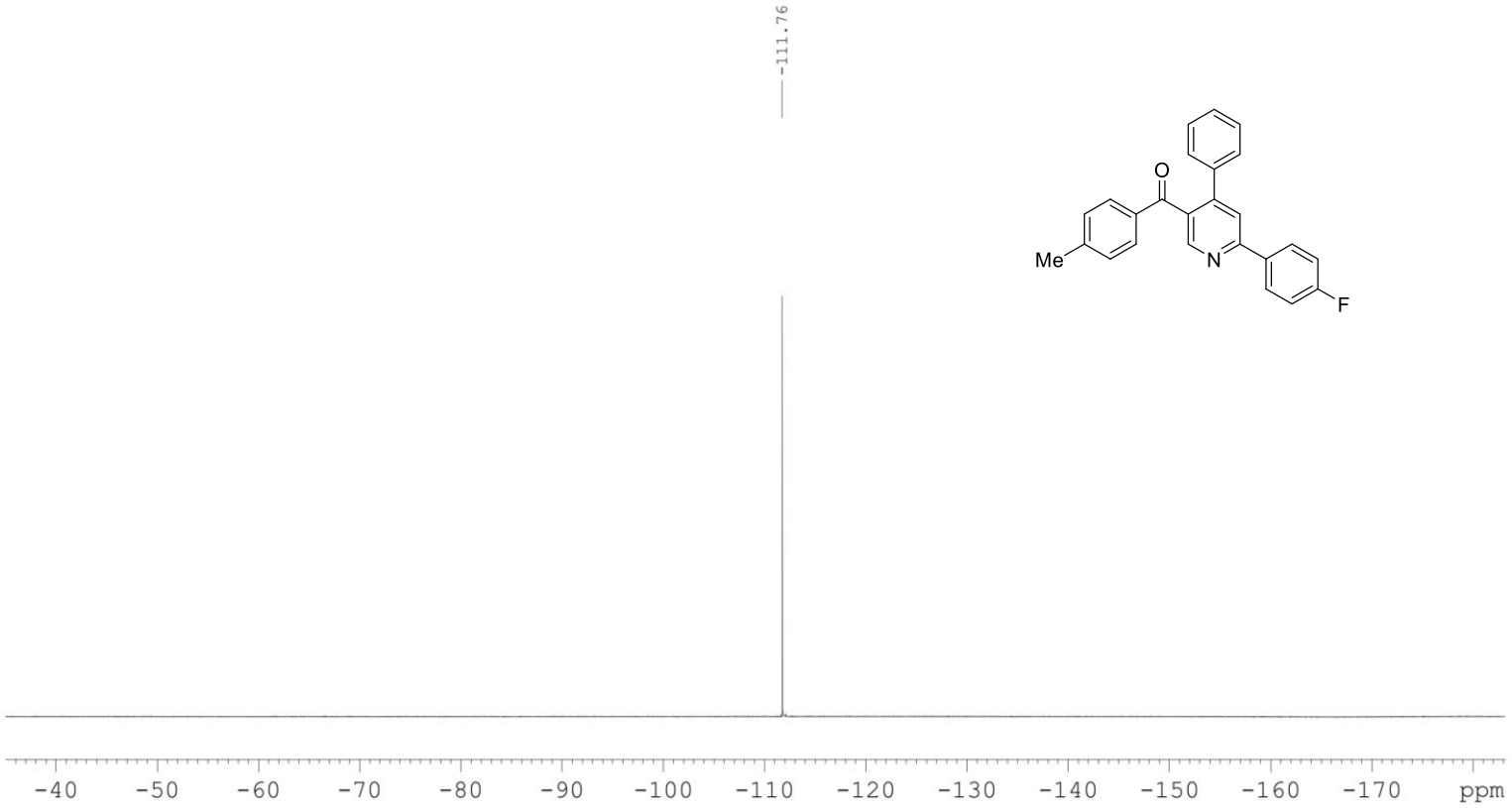


Figure S66. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3z**

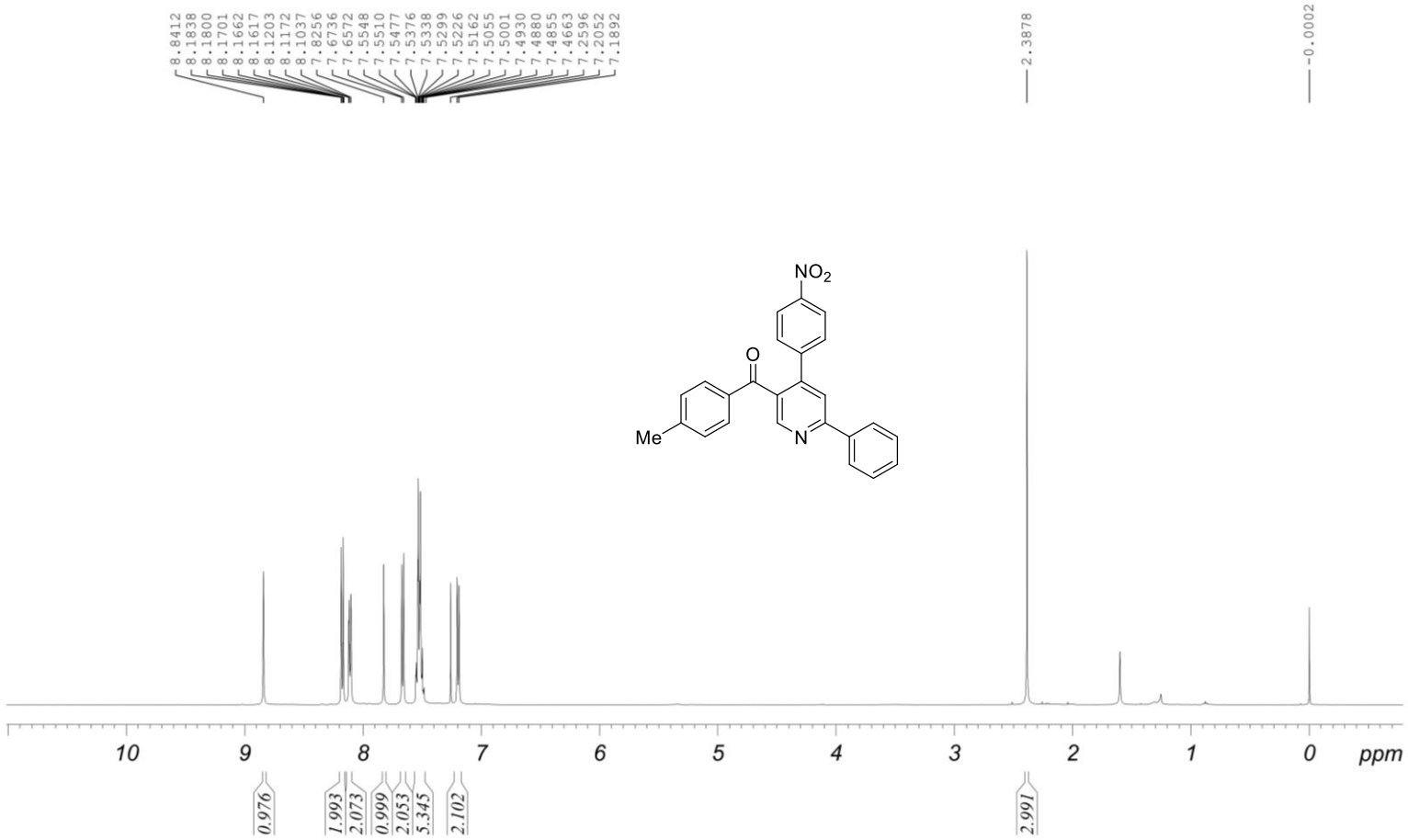


Figure S67. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3a'**

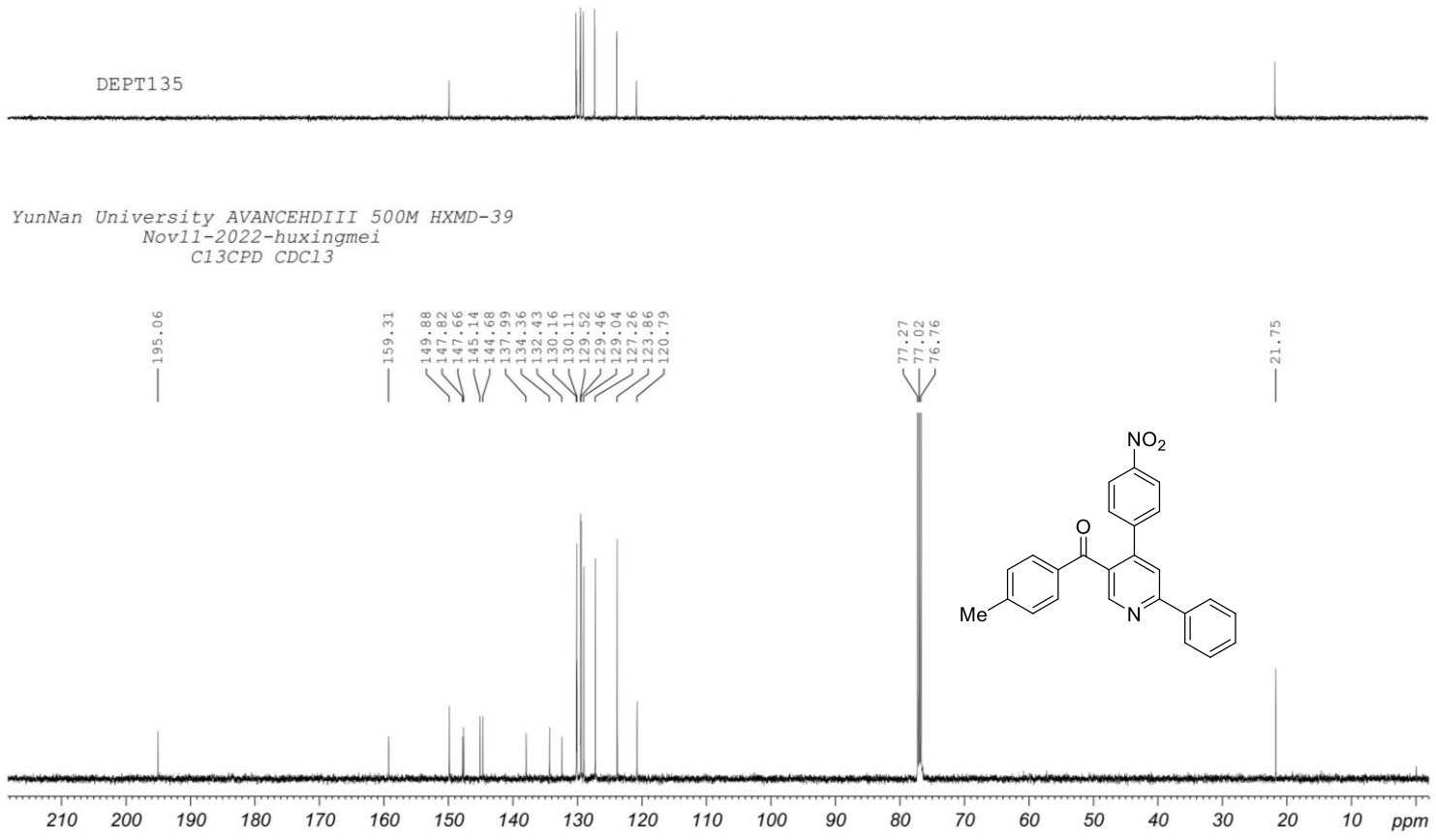


Figure S68. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3a'**

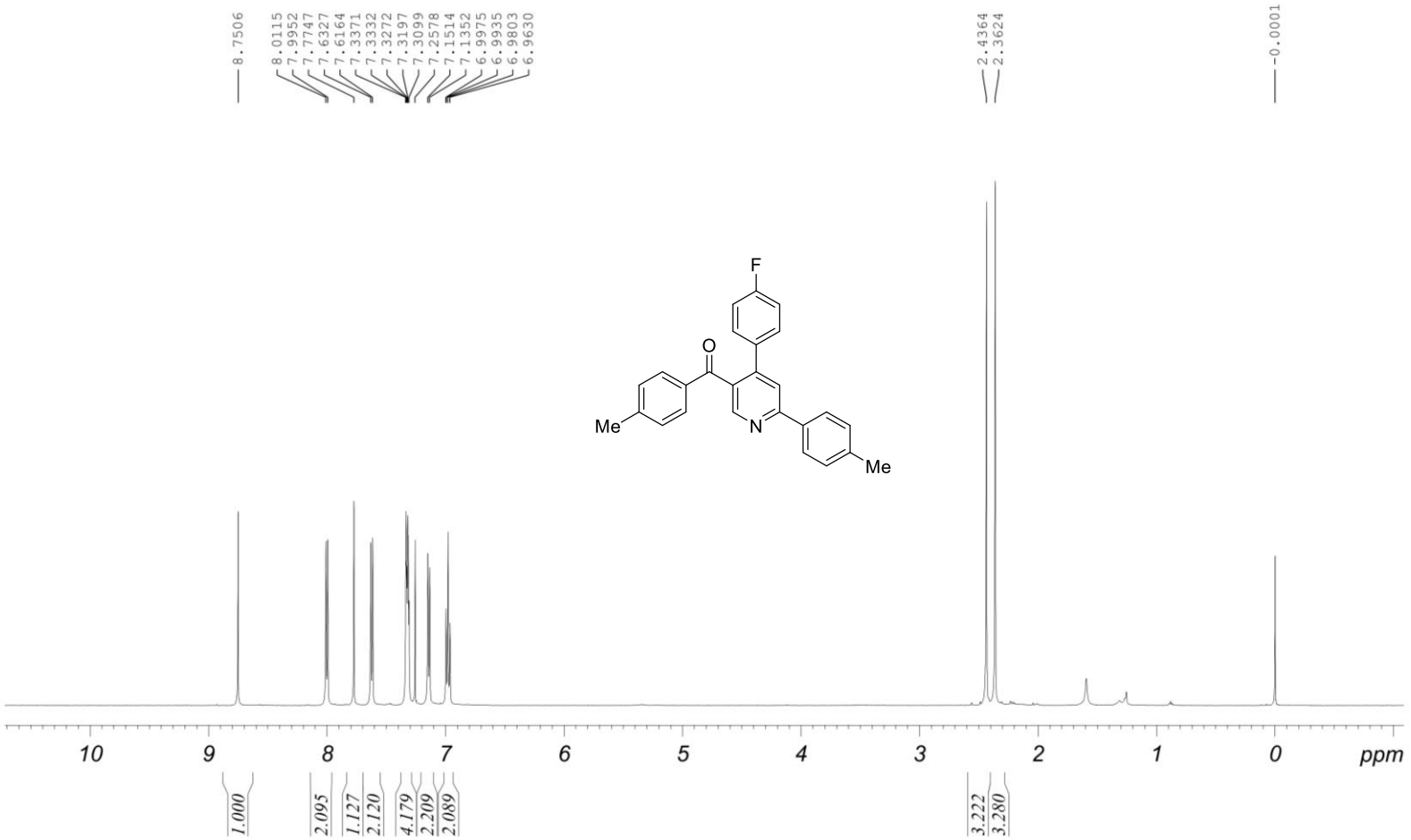


Figure S69. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3b'**

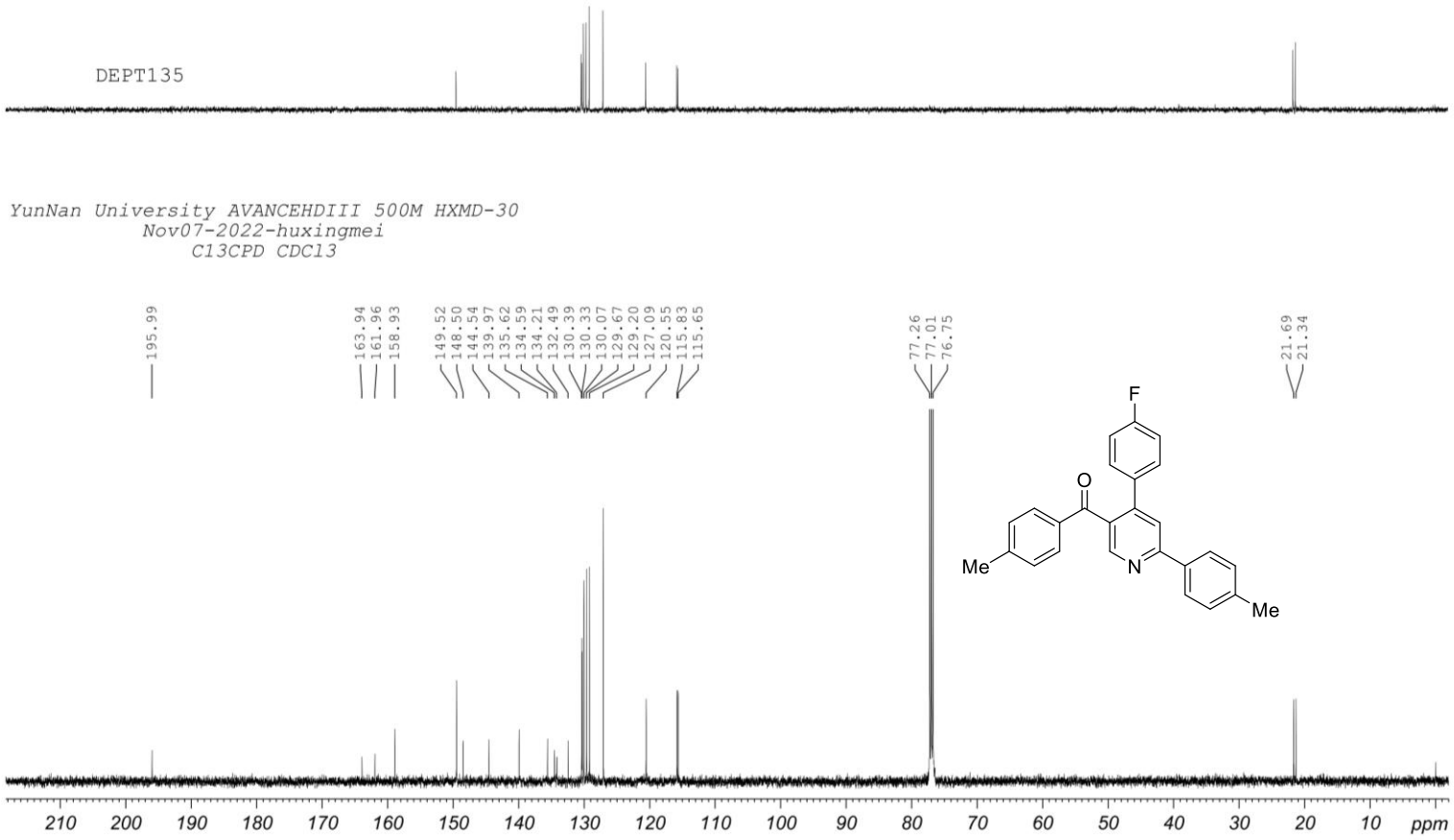


Figure S70. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3b'**

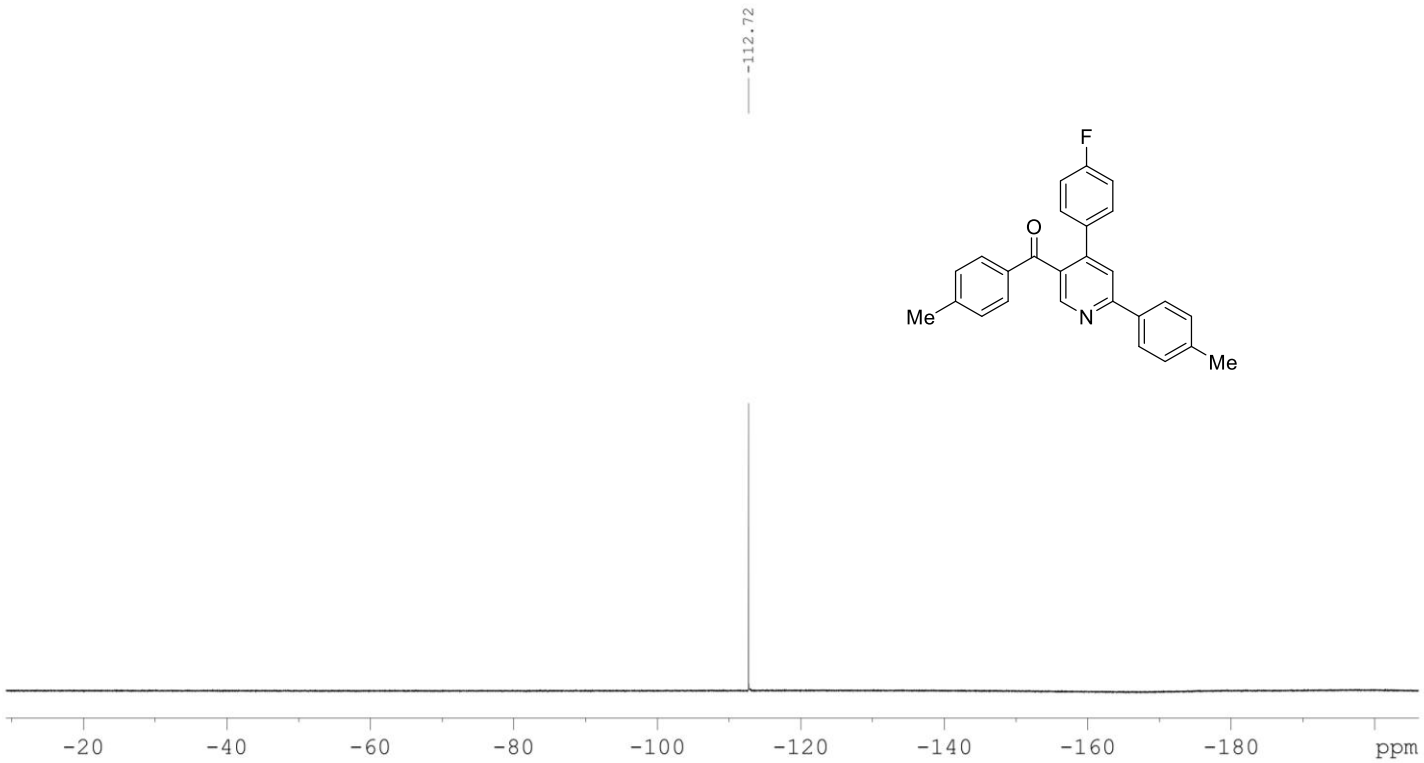


Figure S71. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3b'**

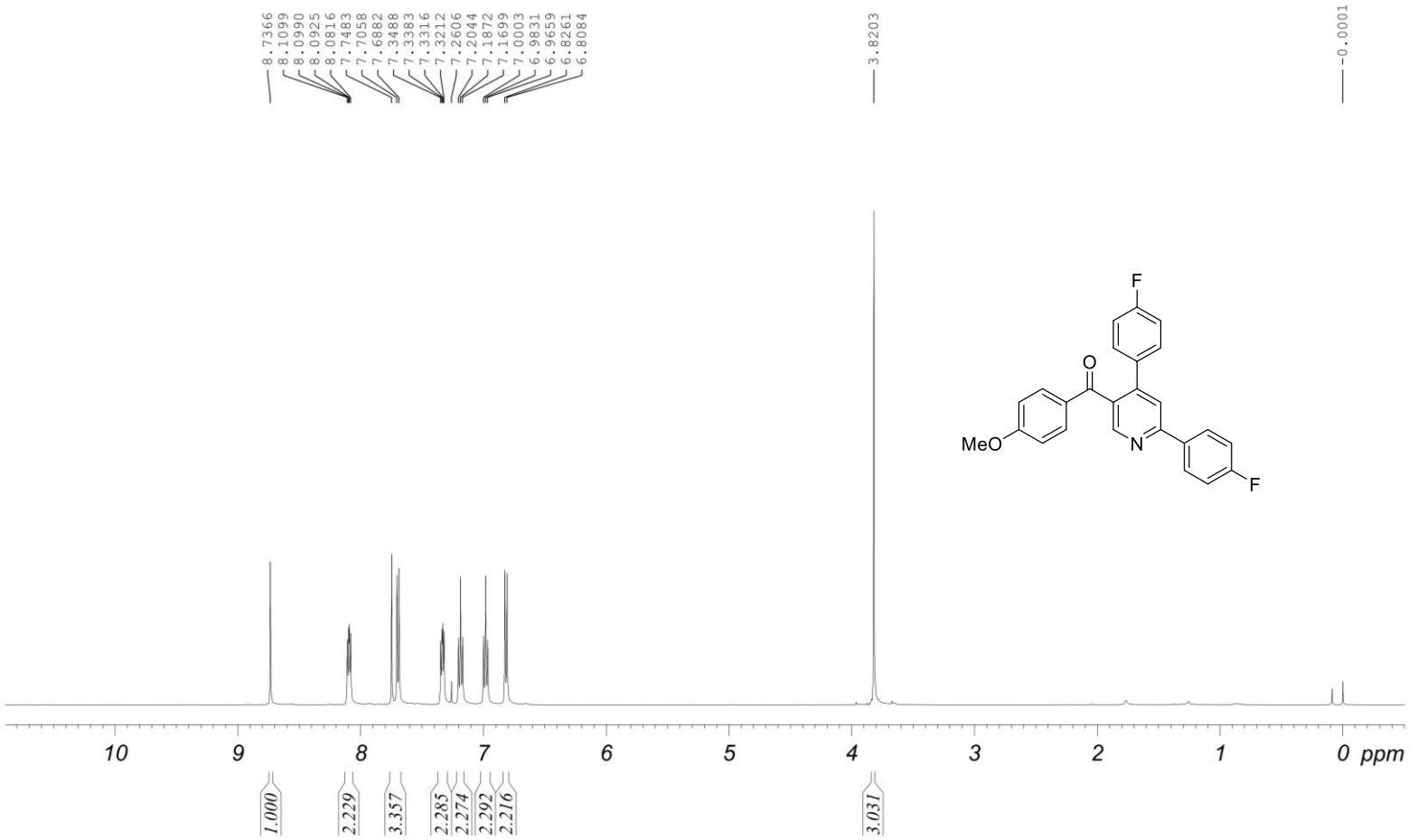


Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3c'**

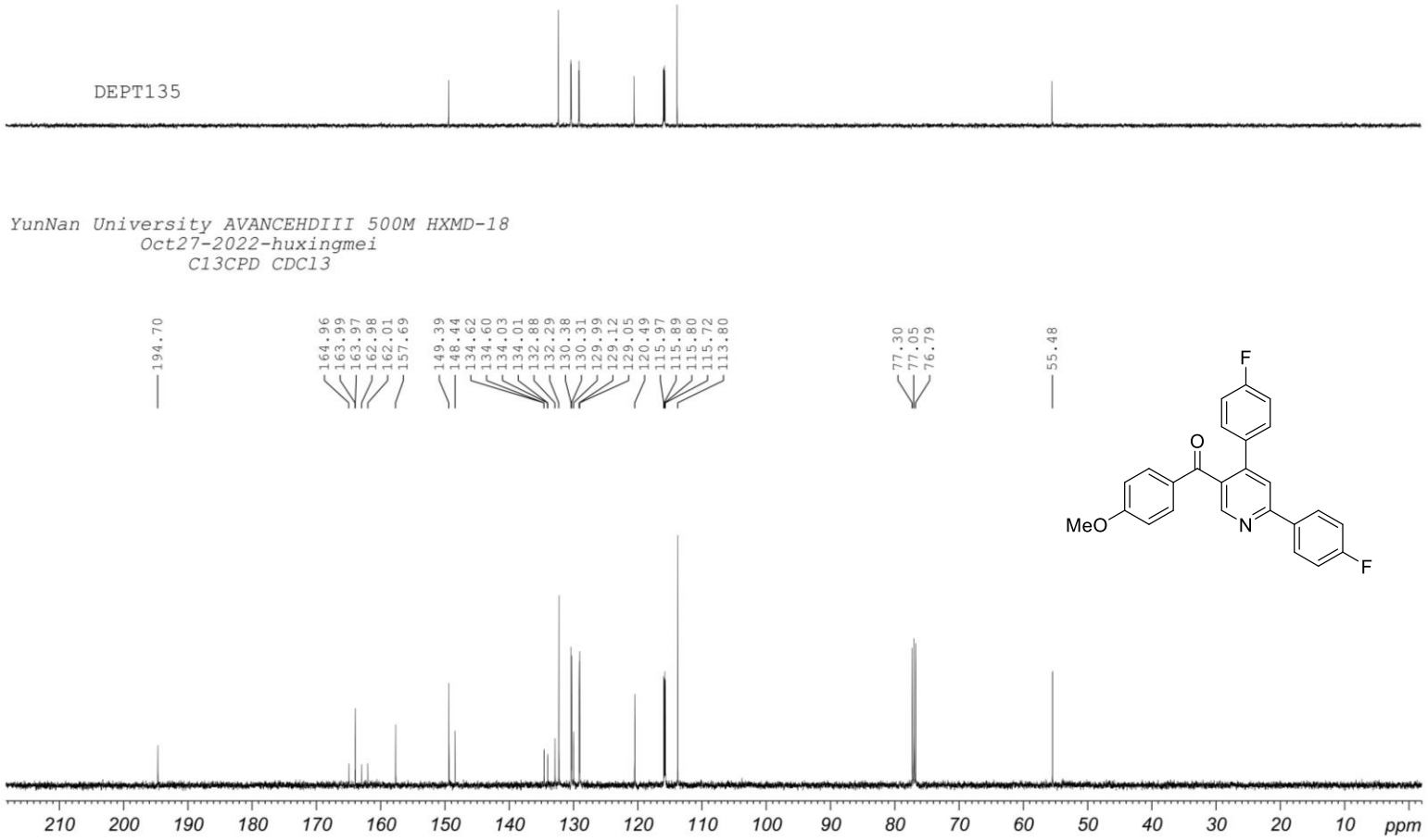


Figure S73. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3c'**

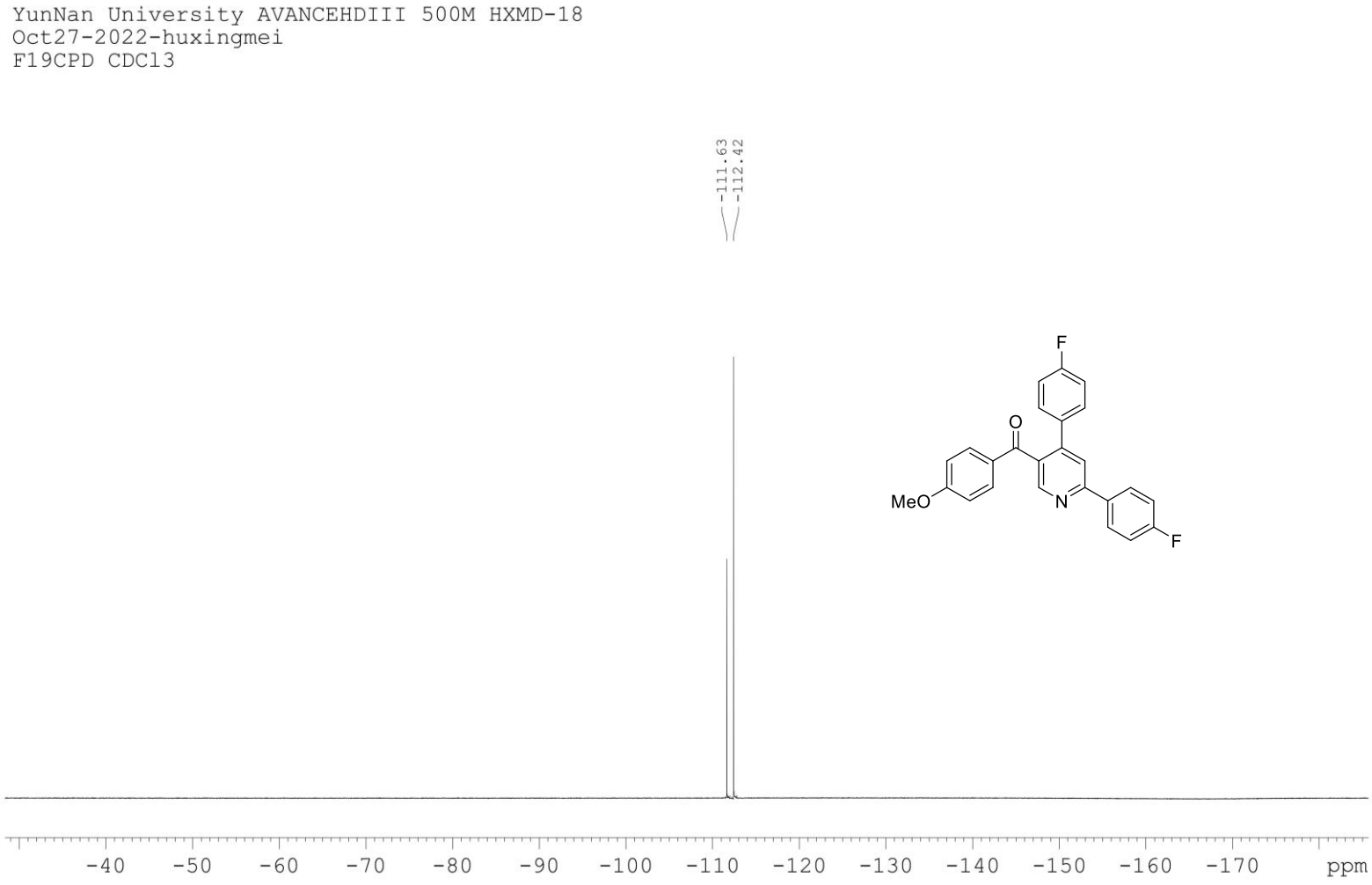


Figure S74. ^{19}F NMR (470 MHz, $CDCl_3$) spectra of compound **3c'**

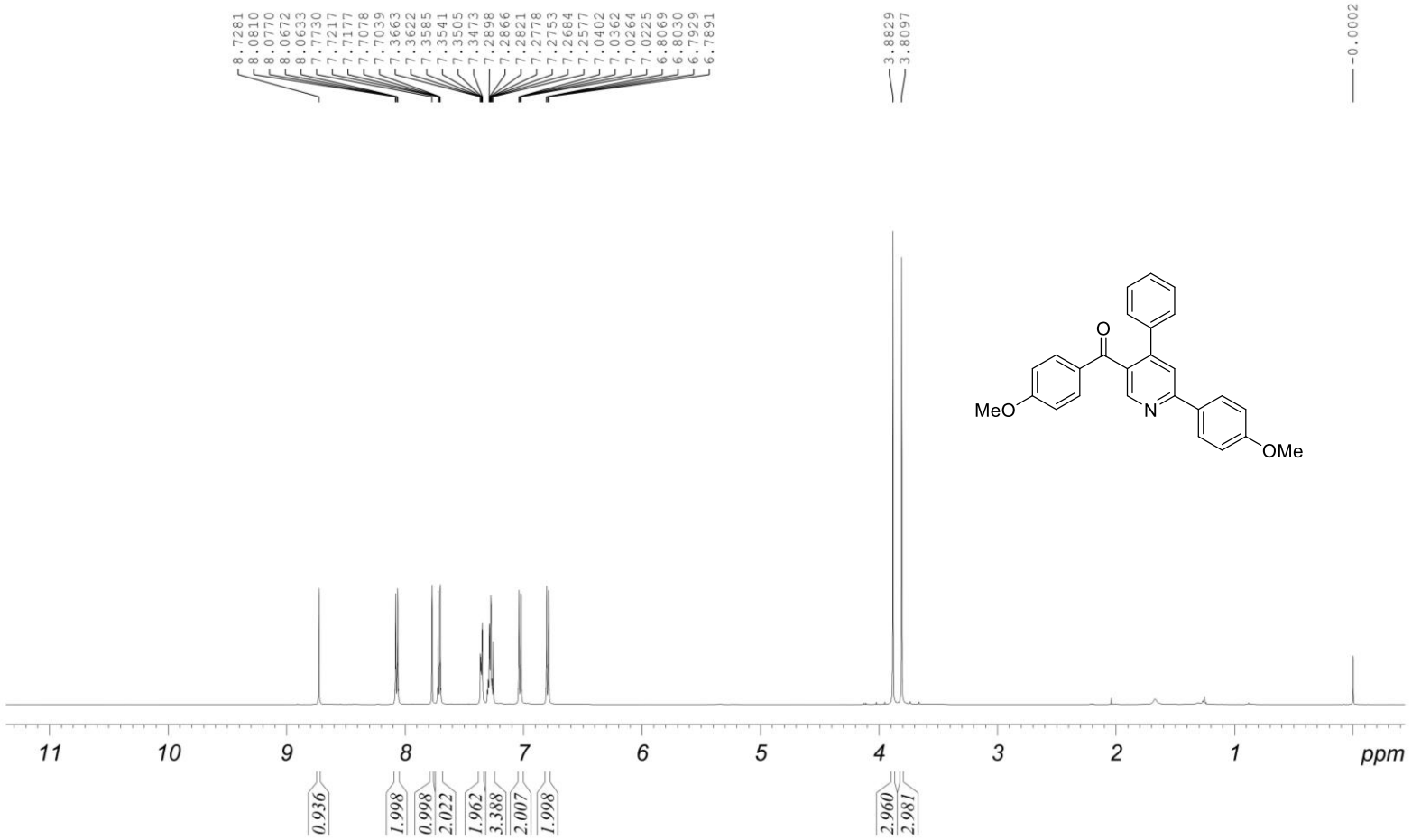


Figure S75. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3d'**

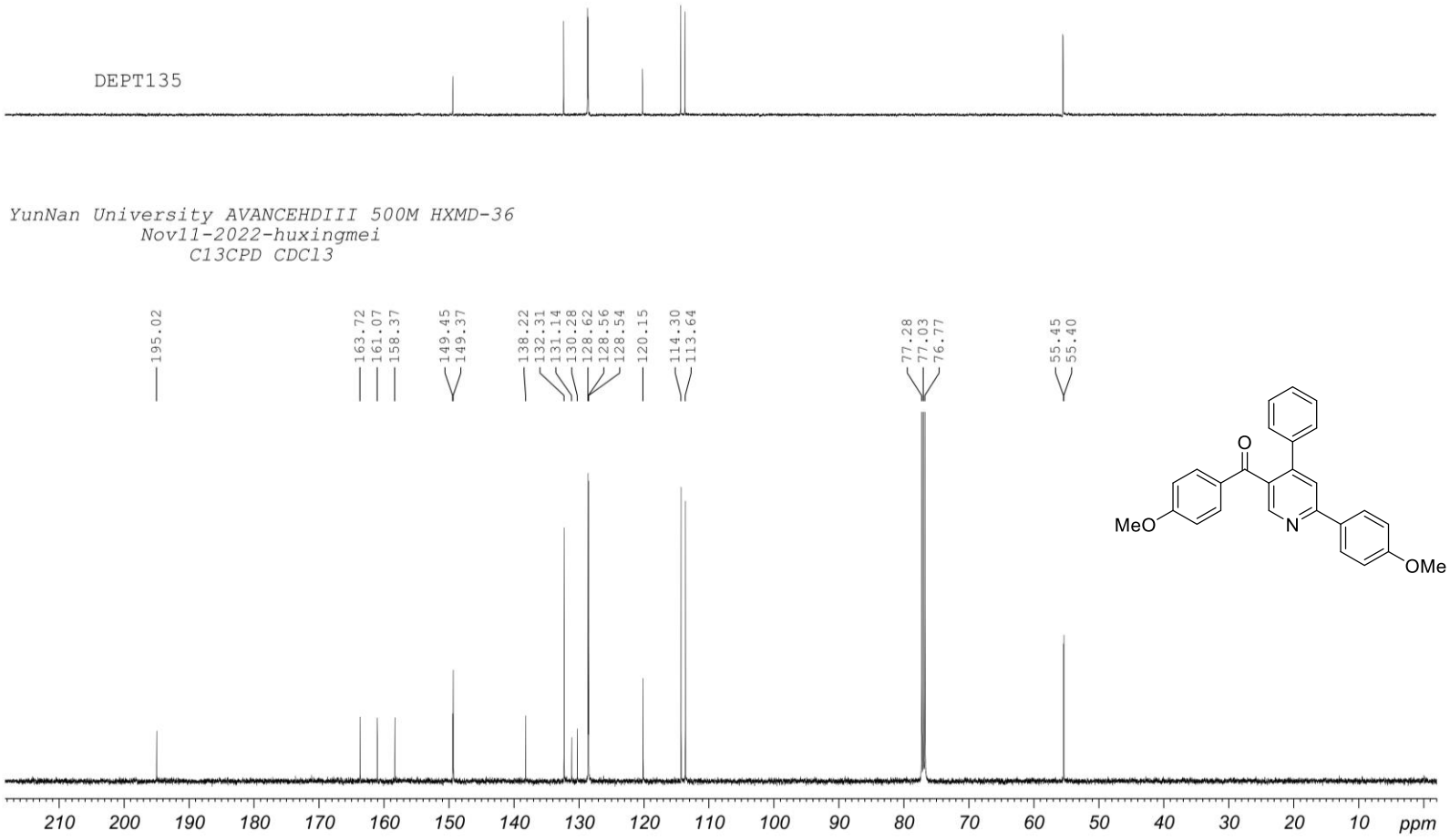


Figure S76. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3d'**

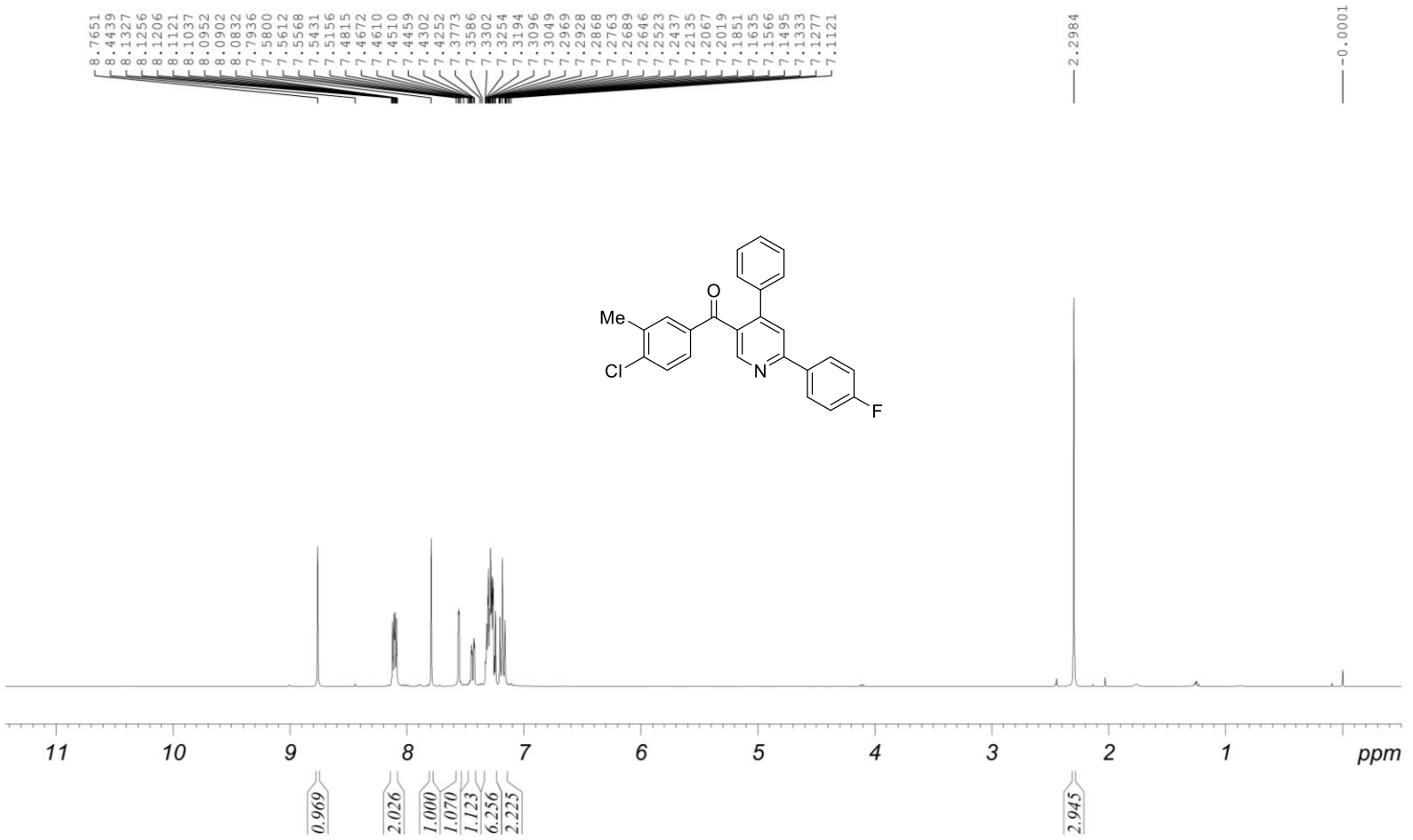


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3e'**

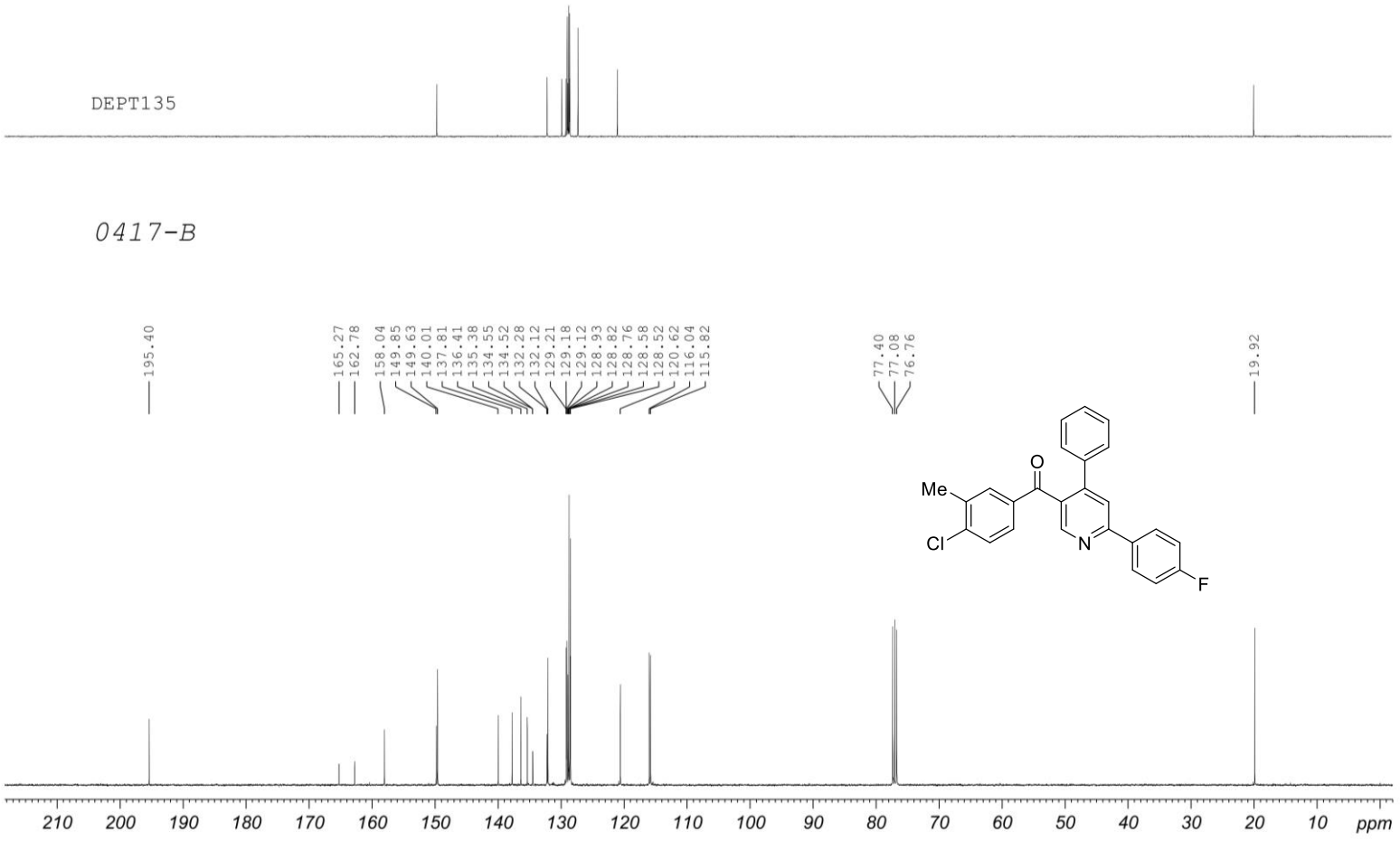


Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3e'**

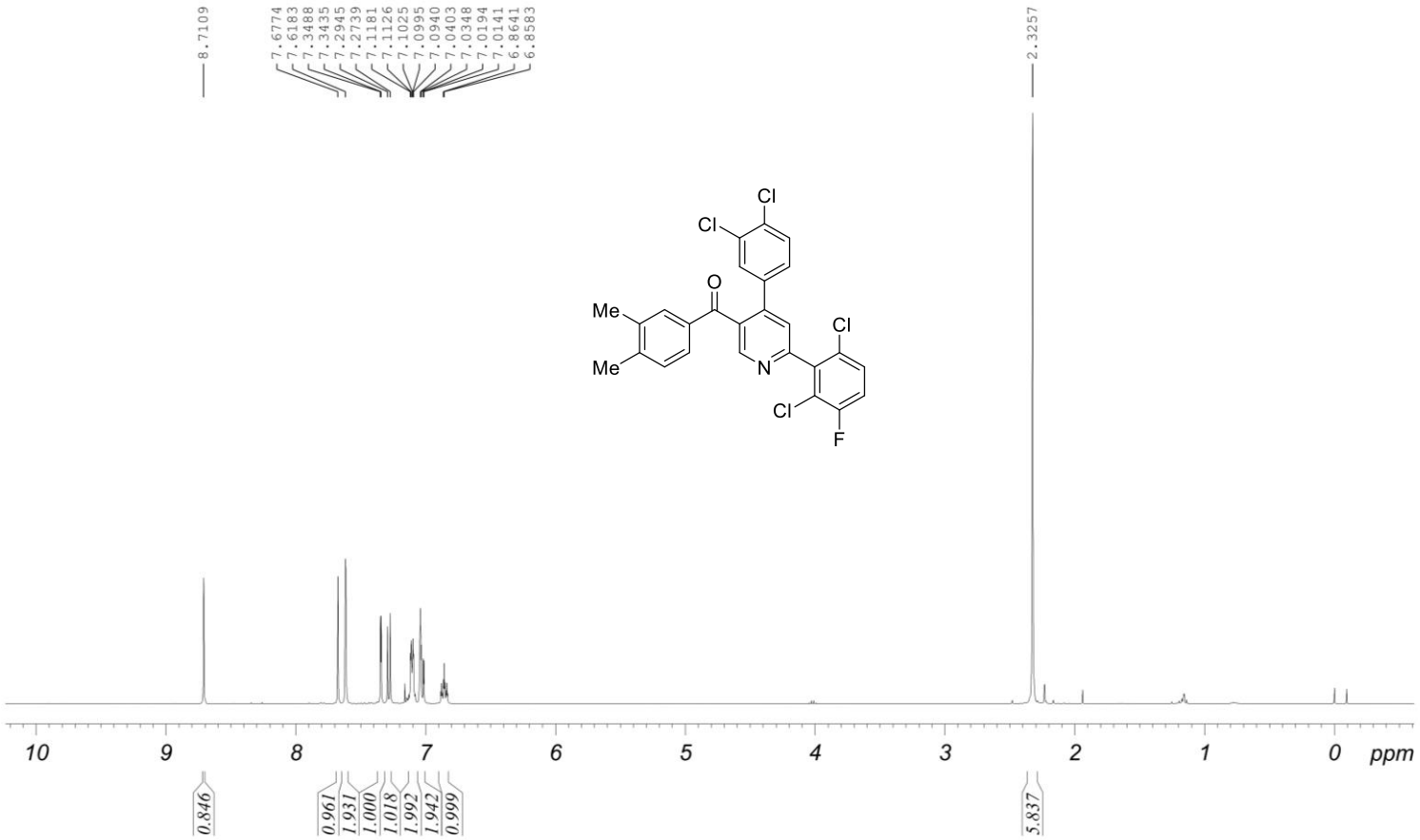


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3f'**

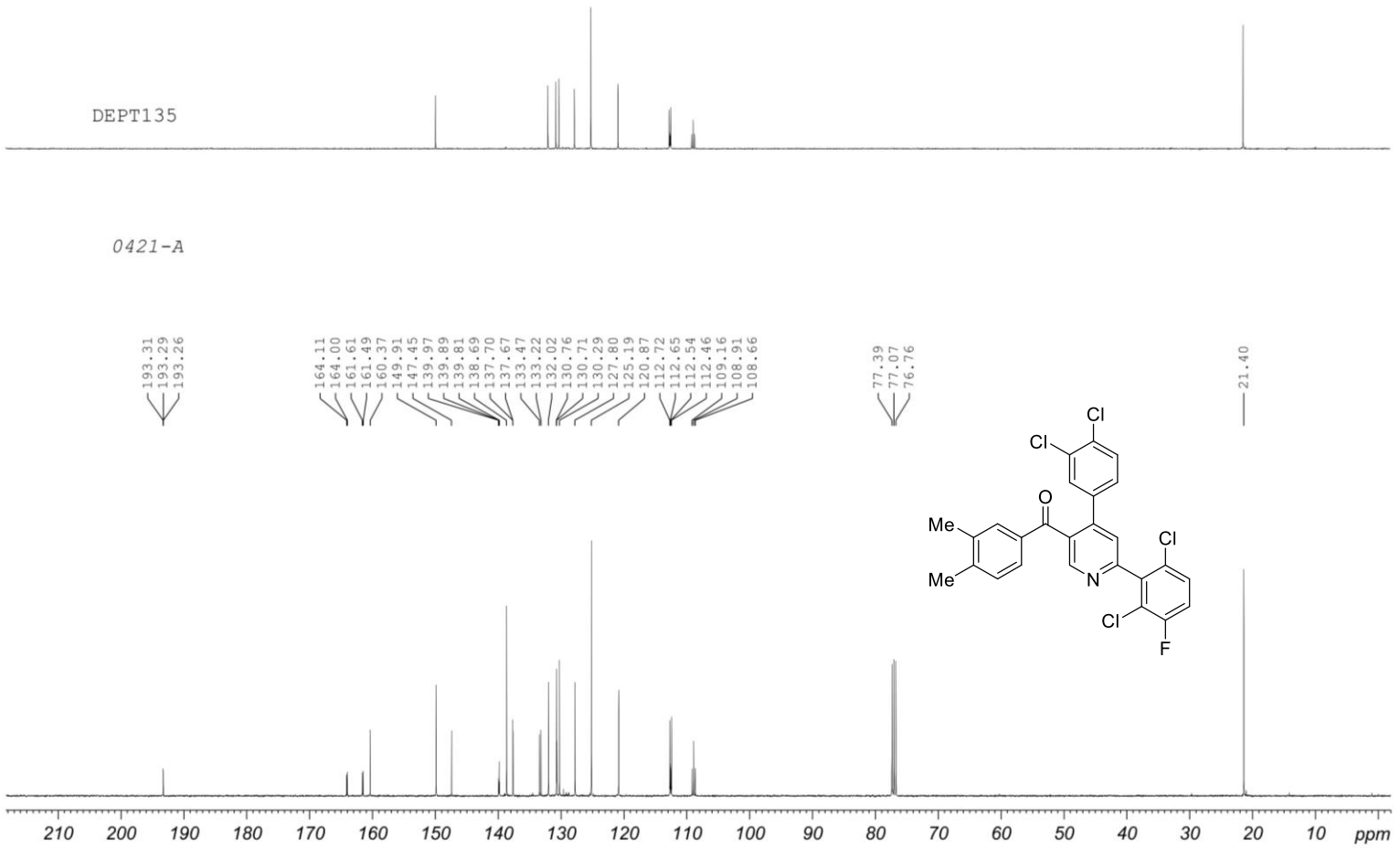


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3f'**

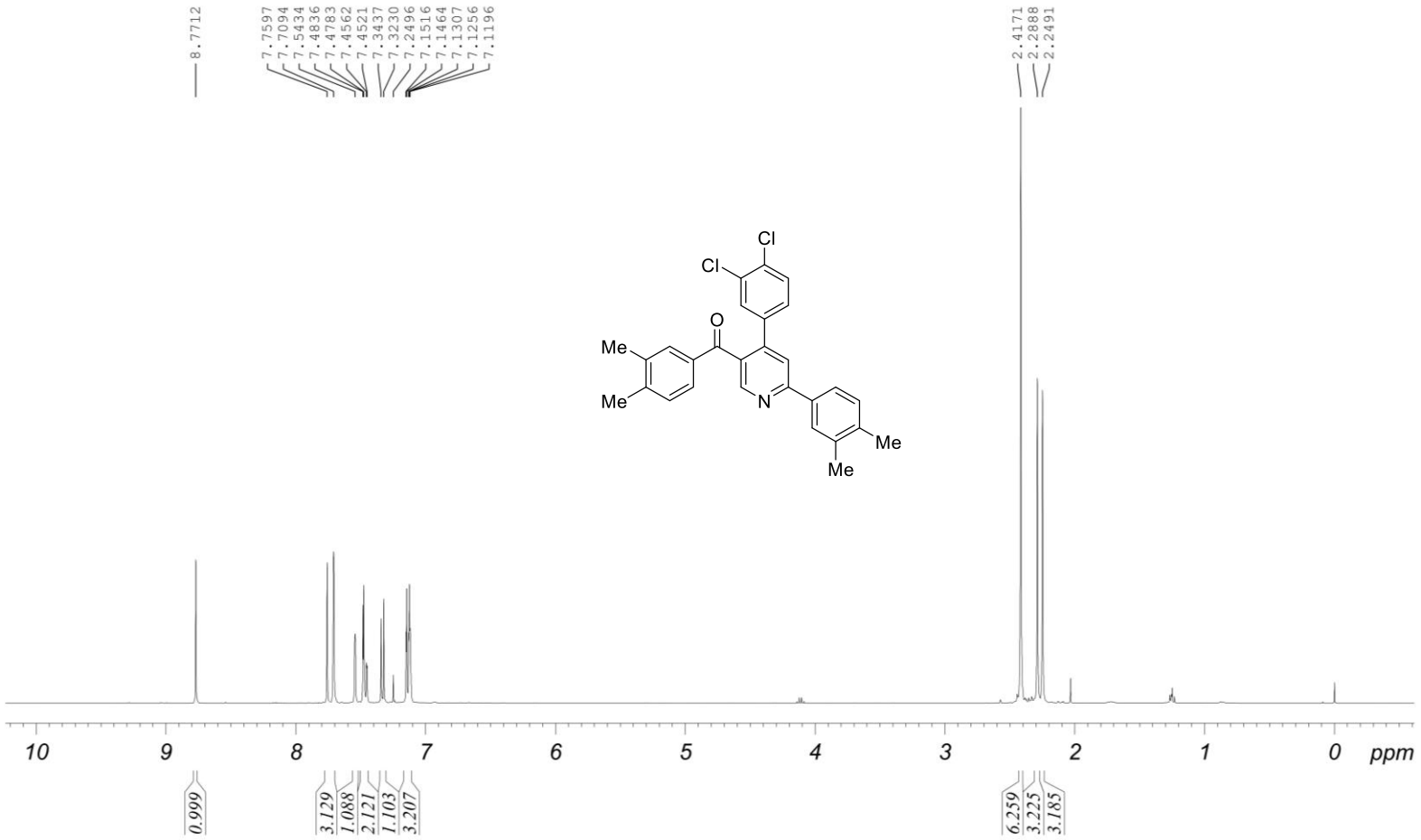


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g'**

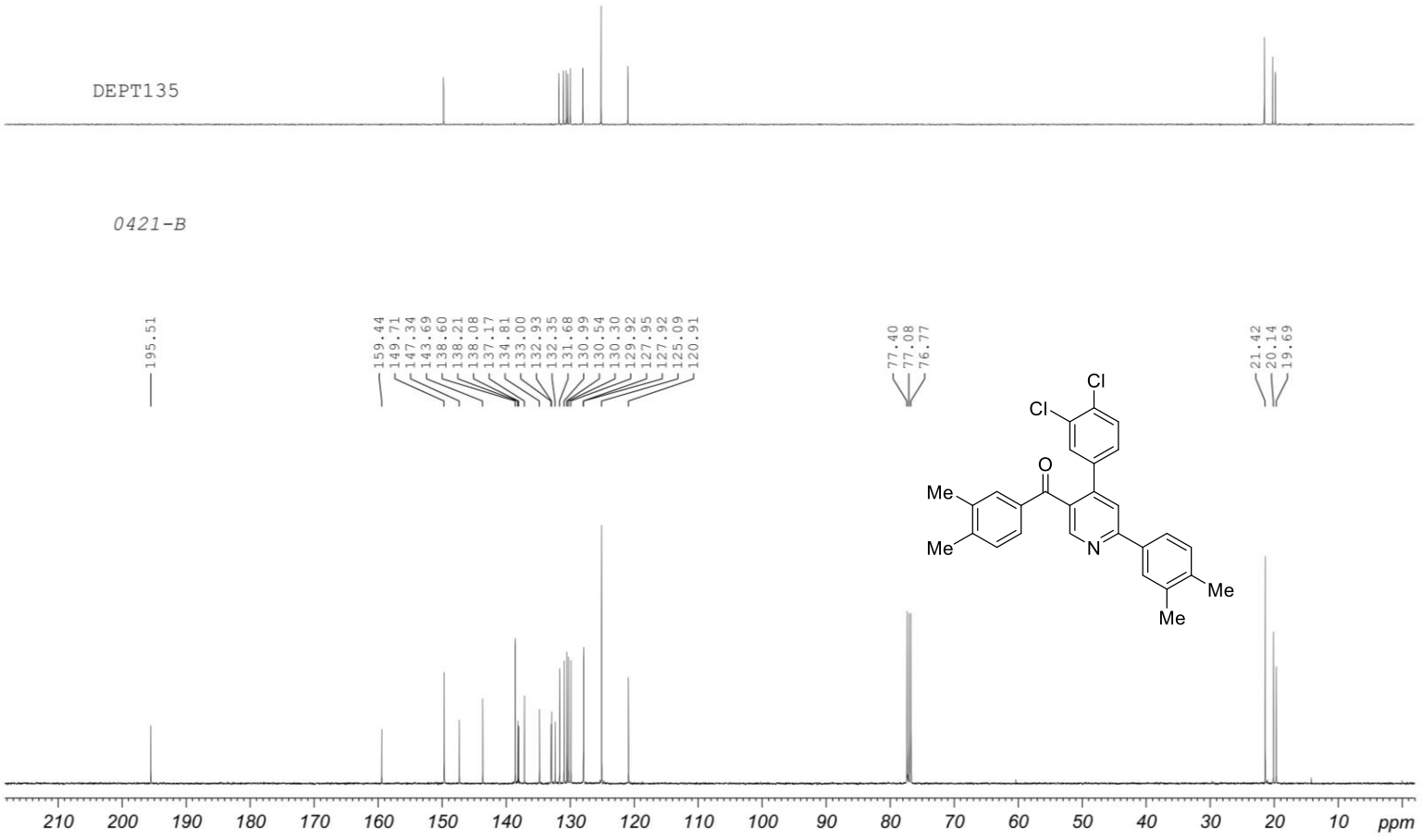


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3g'**

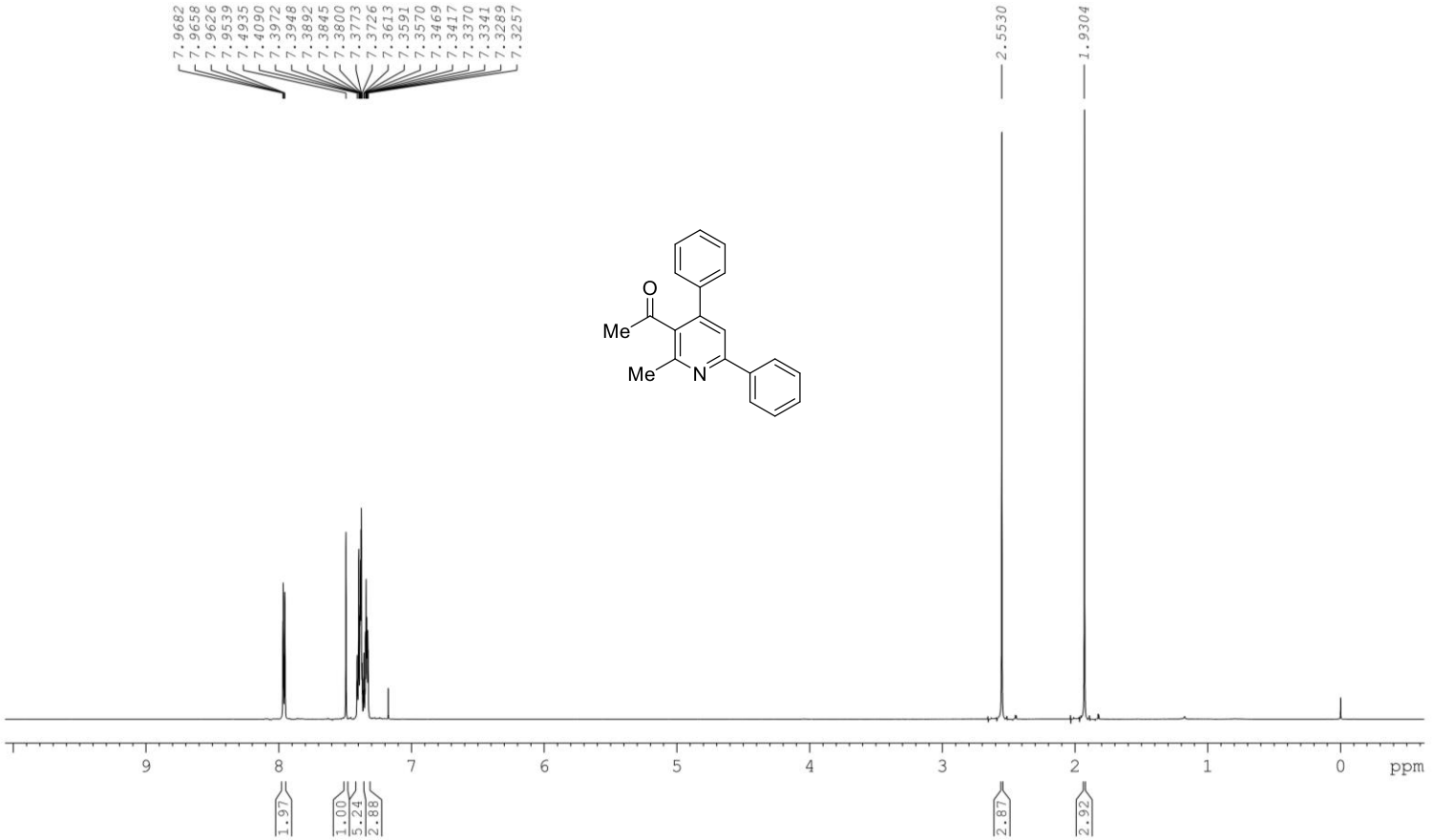


Figure S83. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3h'**

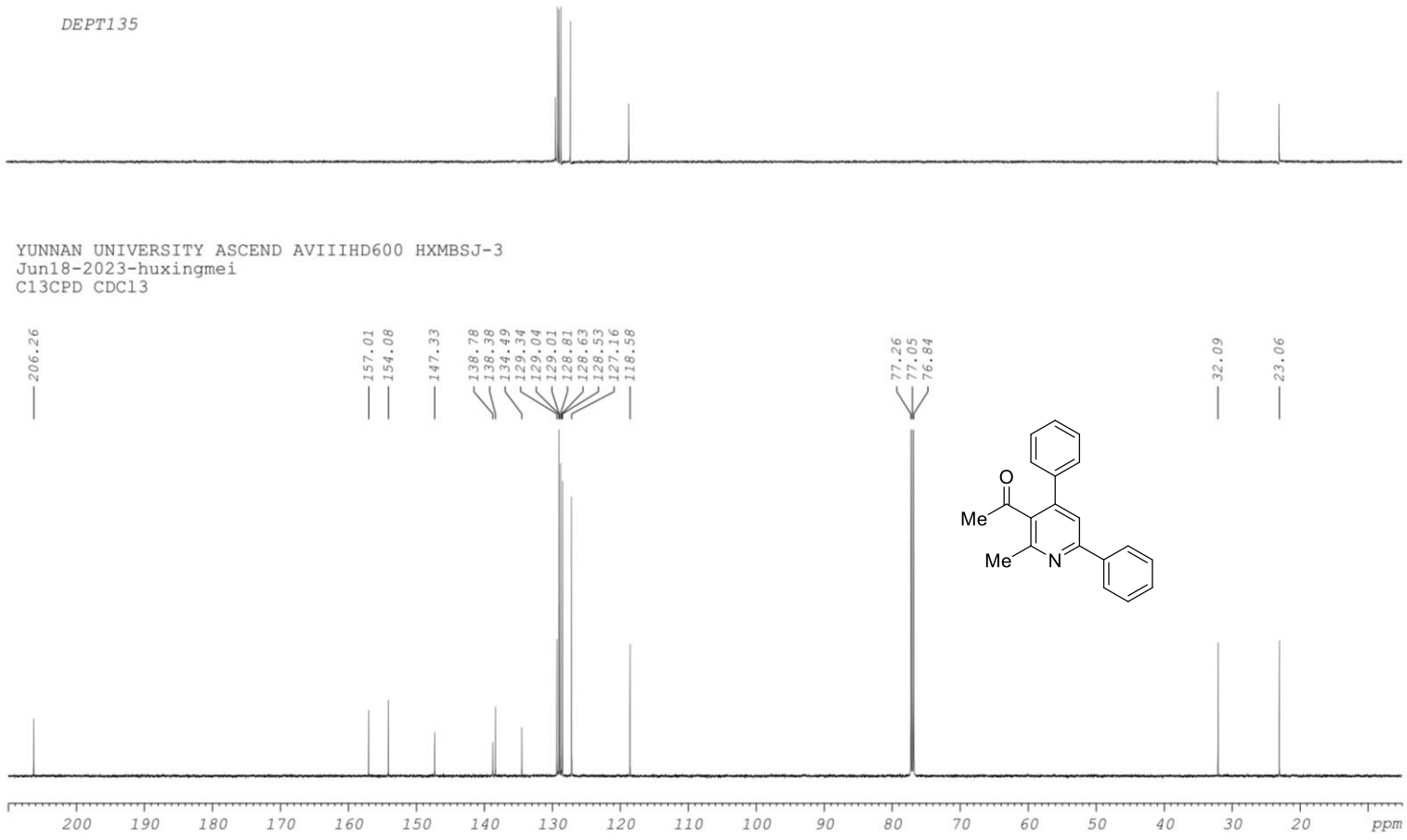


Figure S84. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3h'**

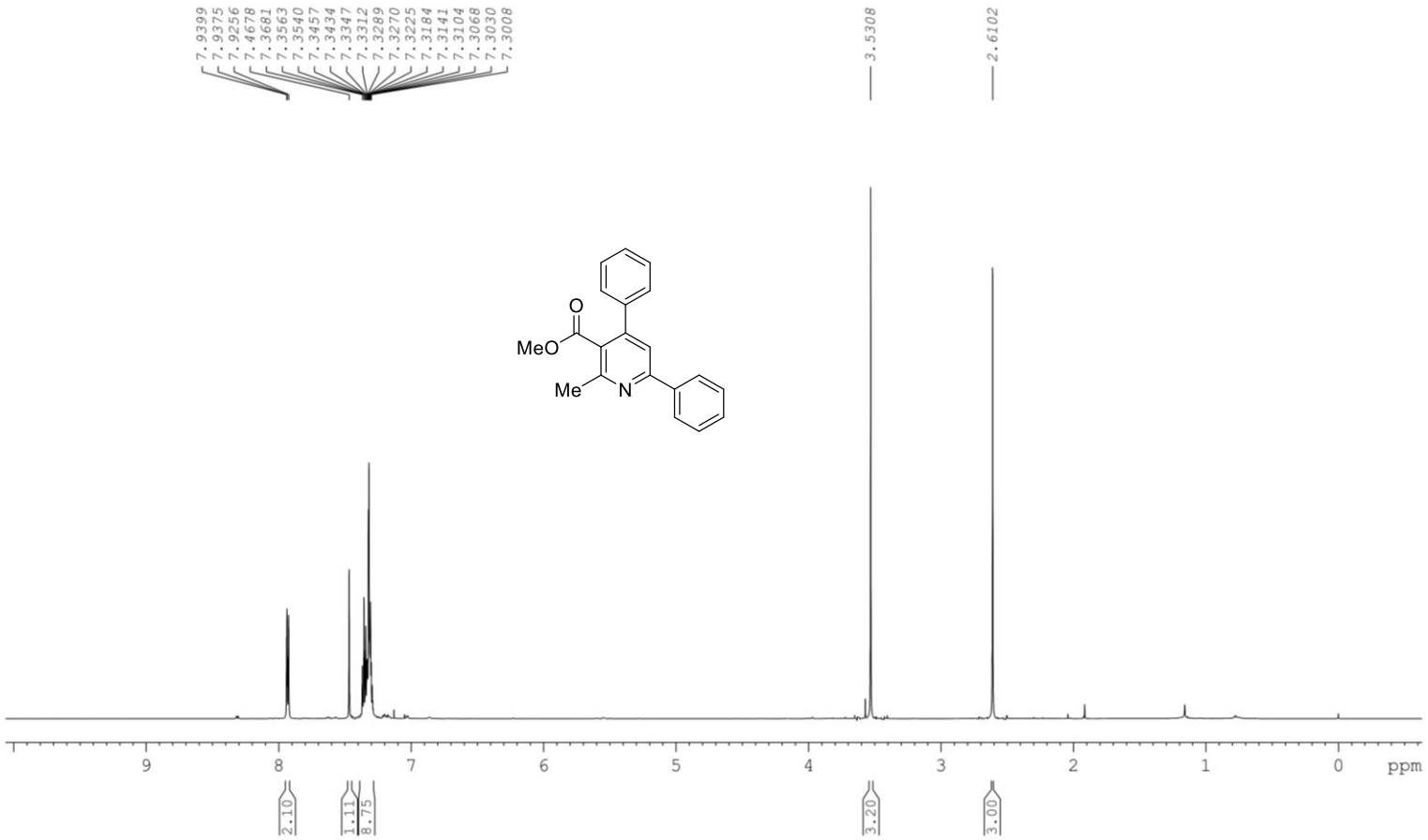


Figure S85. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3i'**

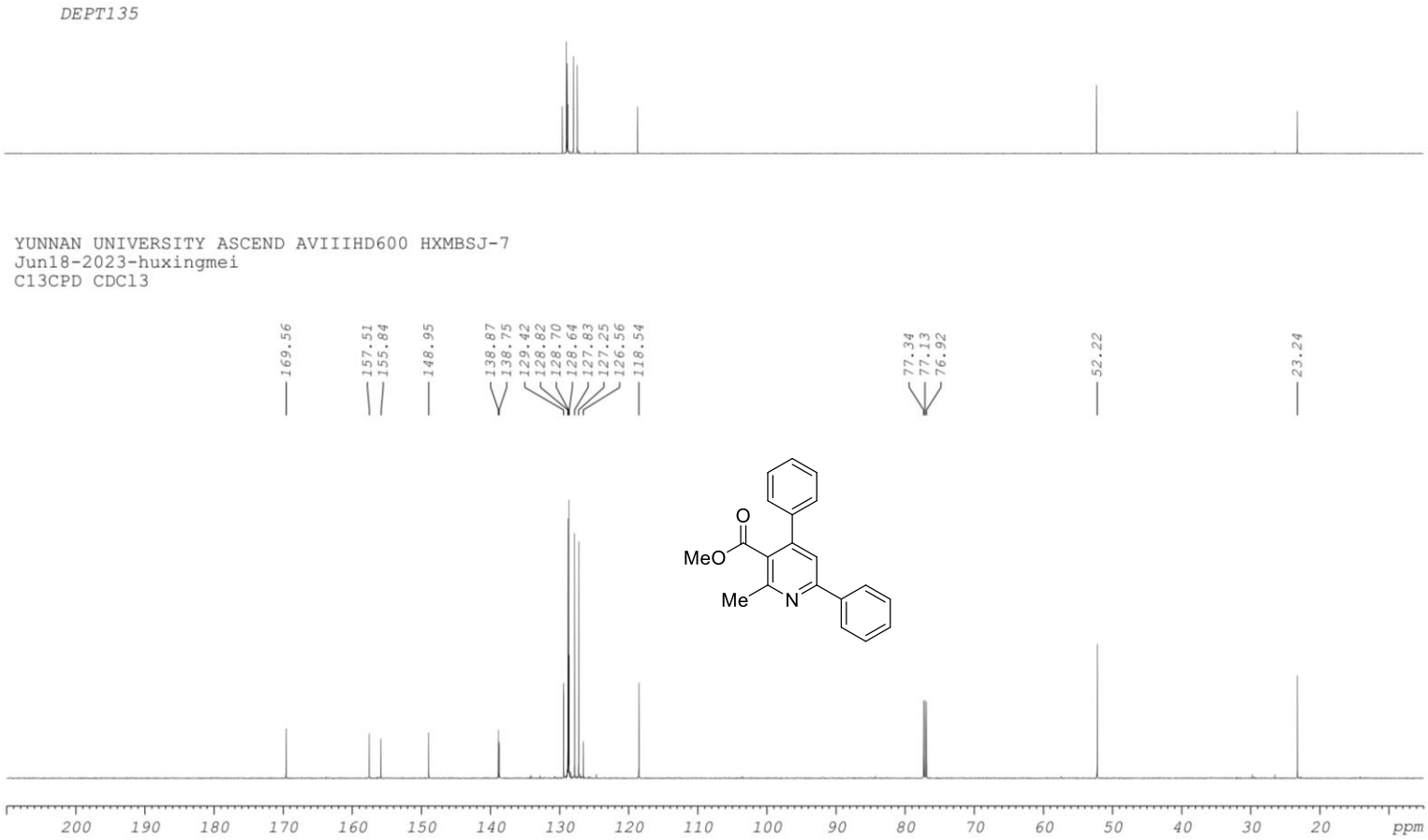


Figure S86. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3i'**

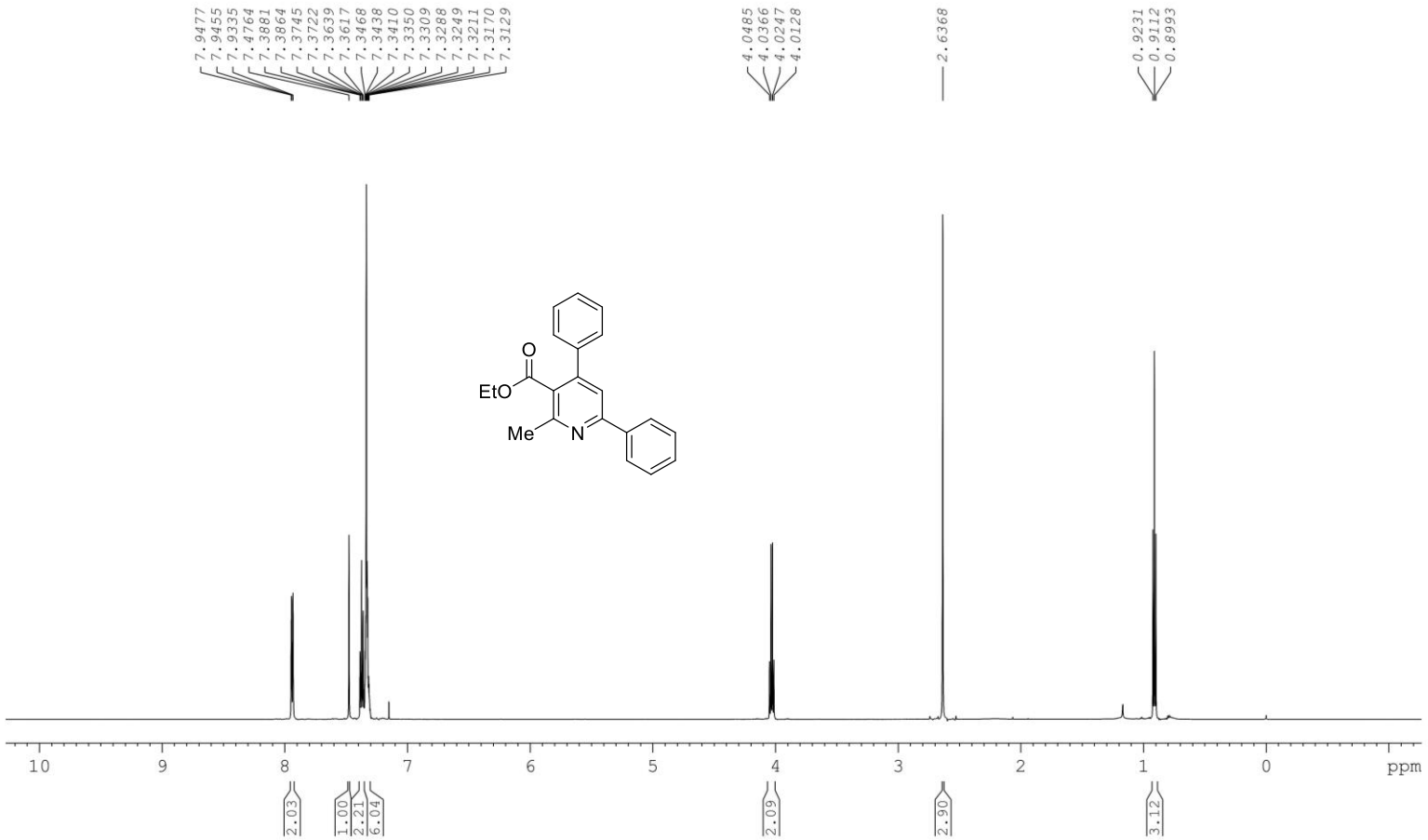


Figure S87. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3j'**

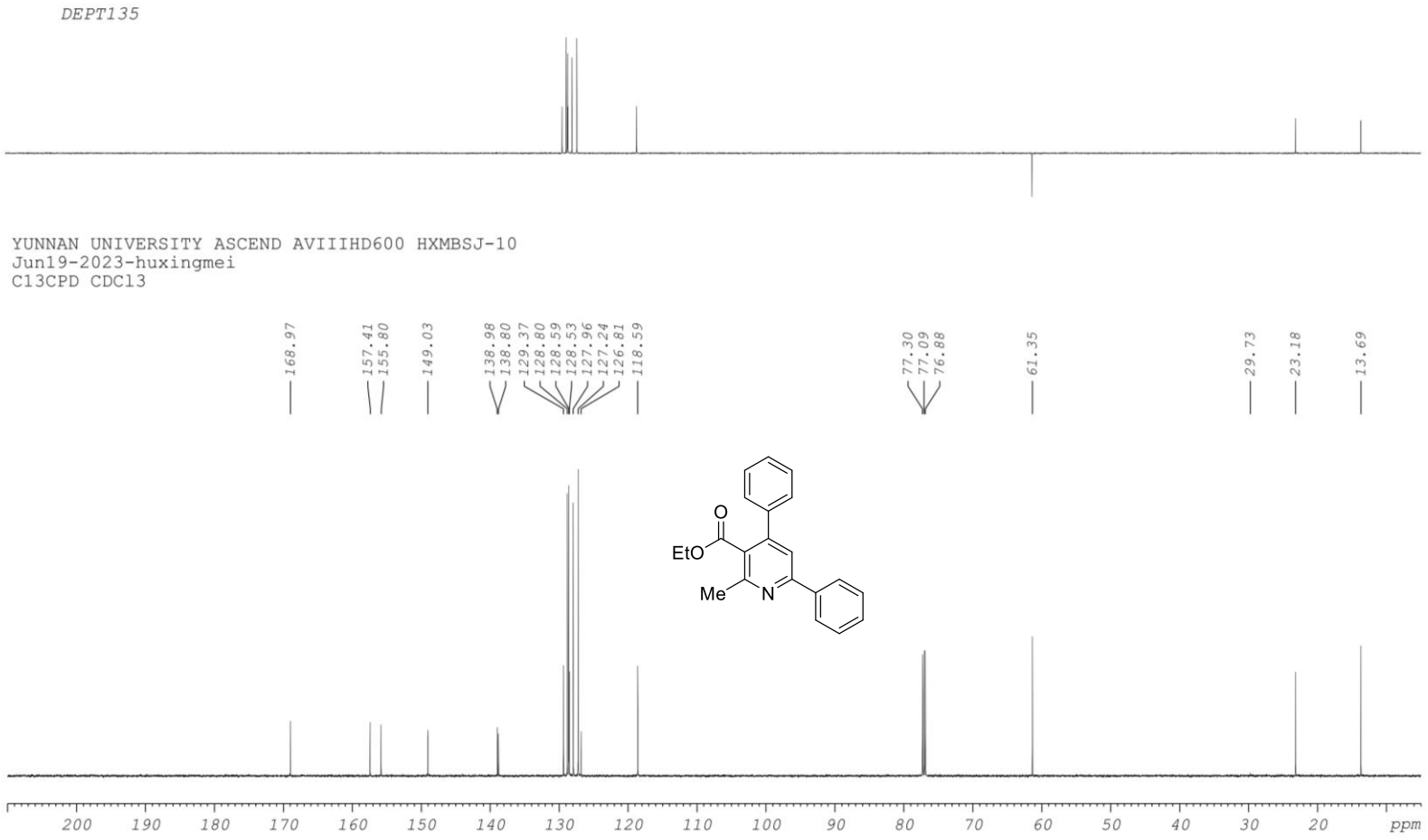


Figure S88. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3j'**

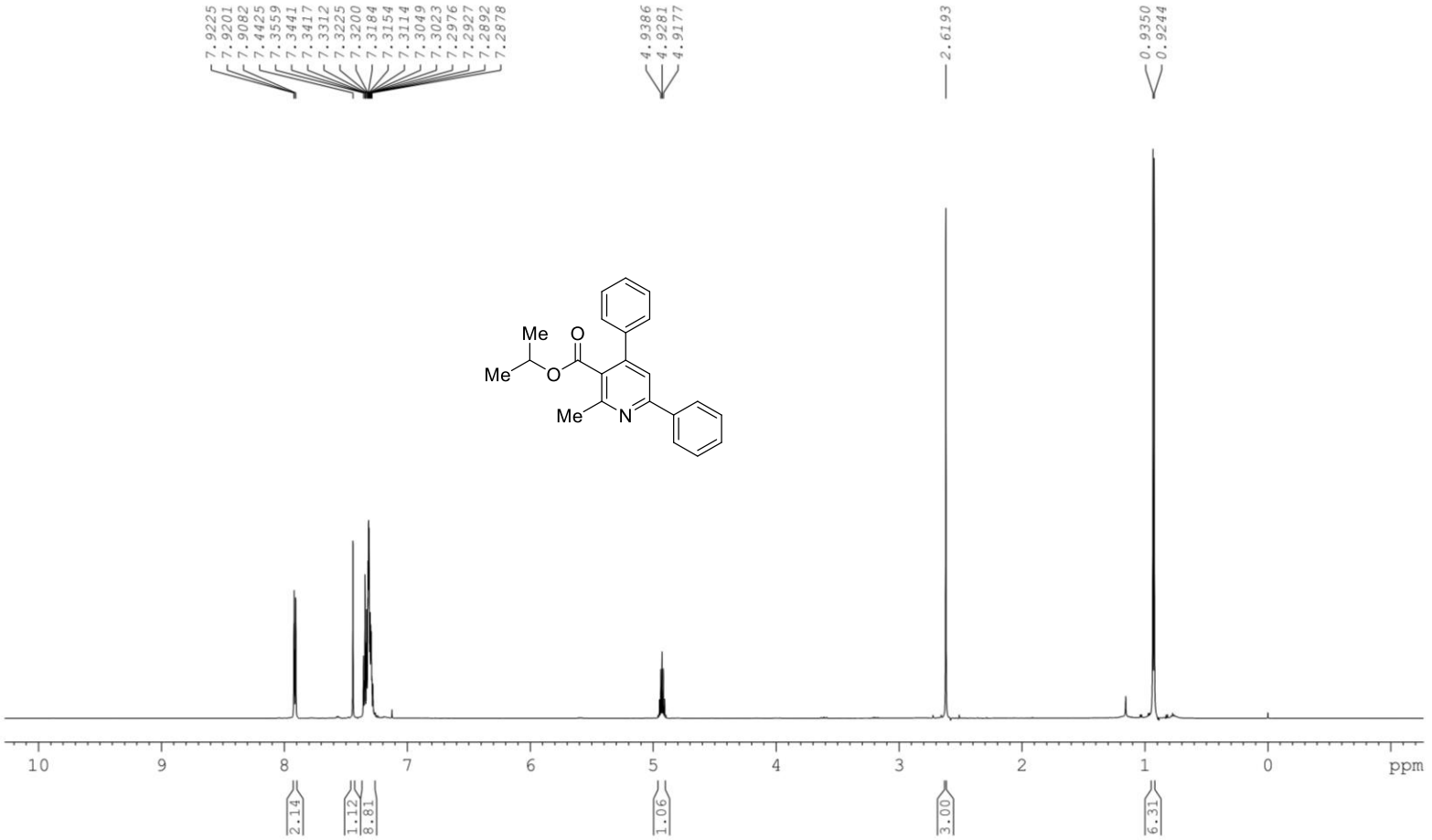


Figure S89. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3k'**

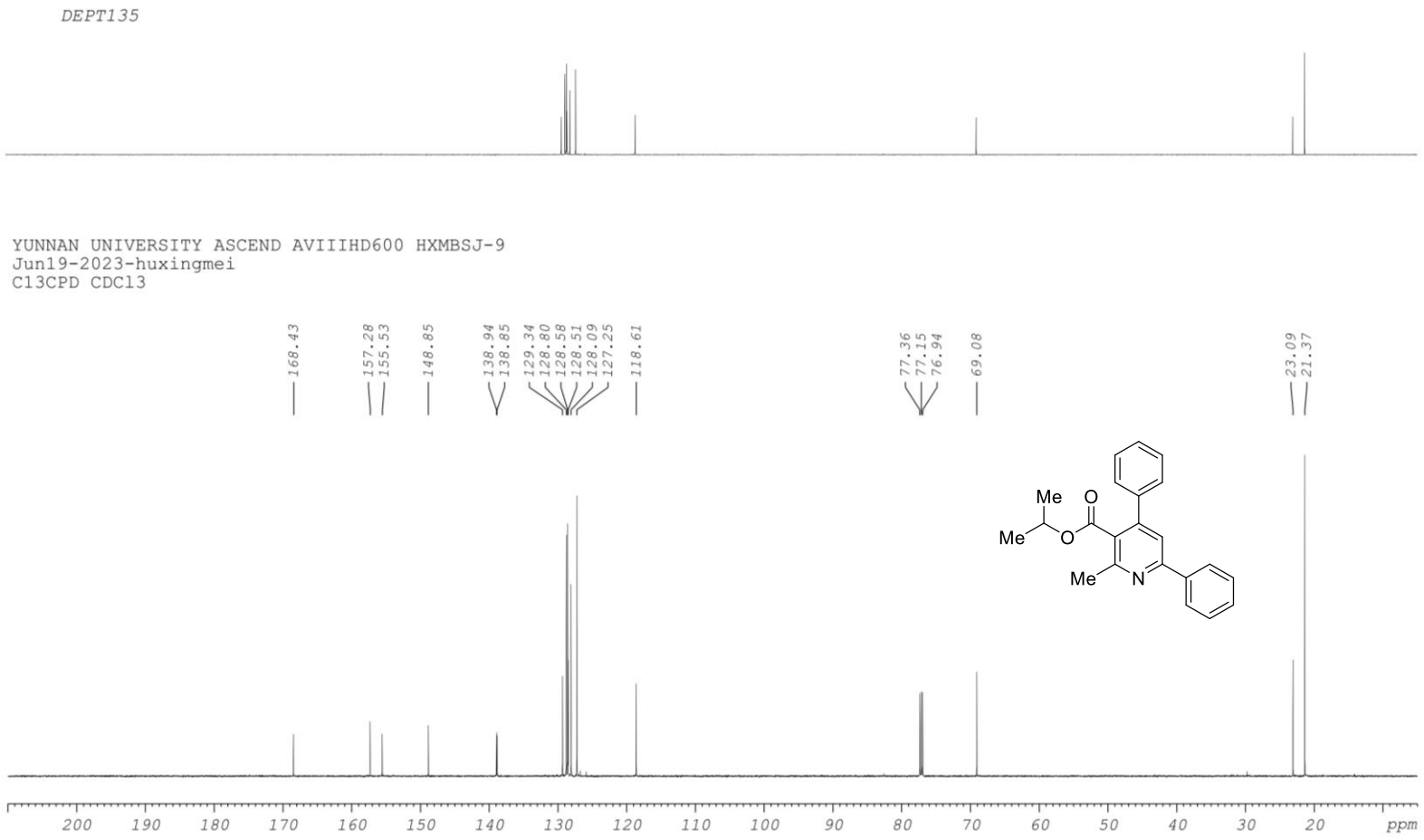


Figure S90. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3k'**

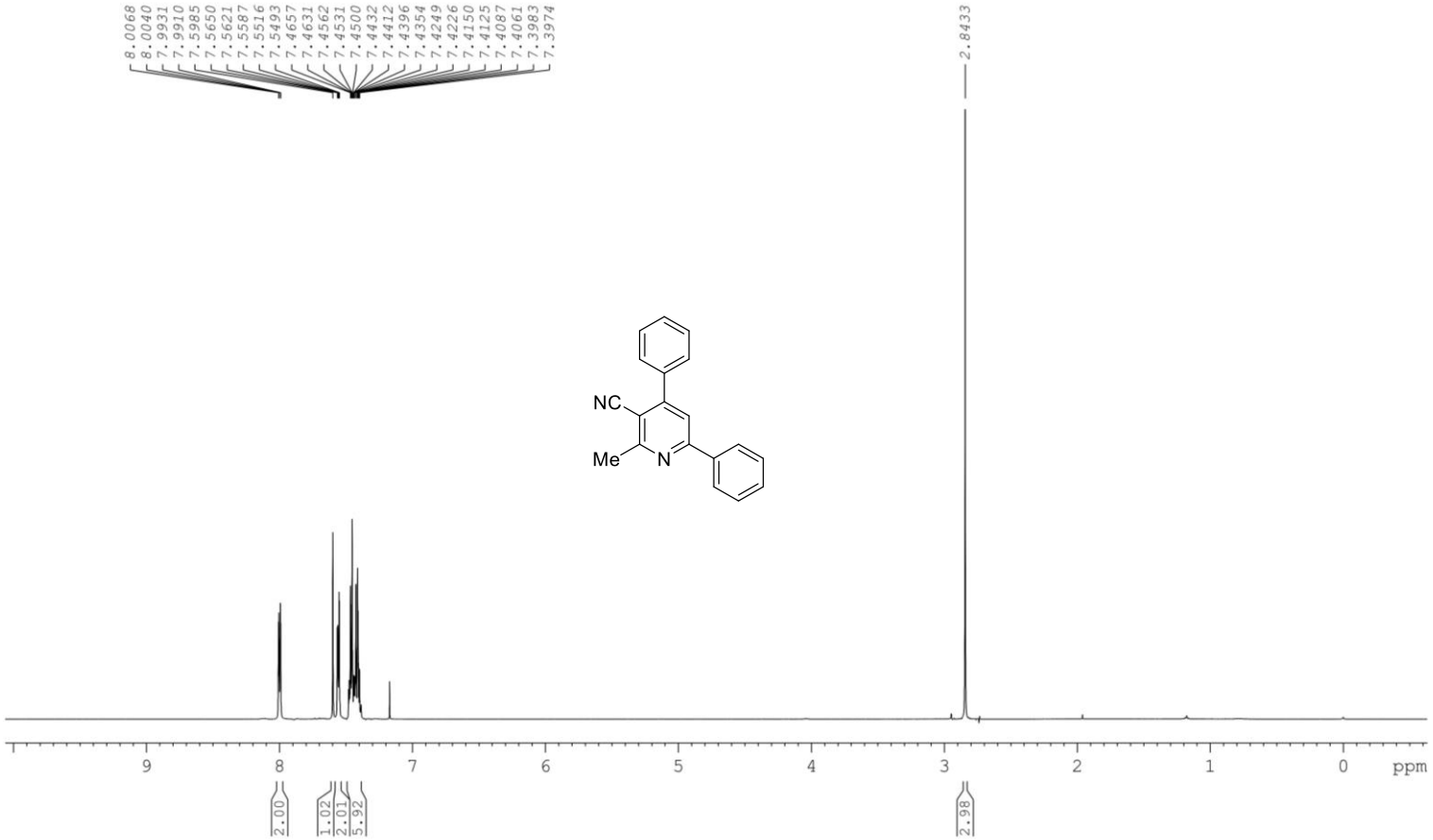


Figure S91. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3l'**

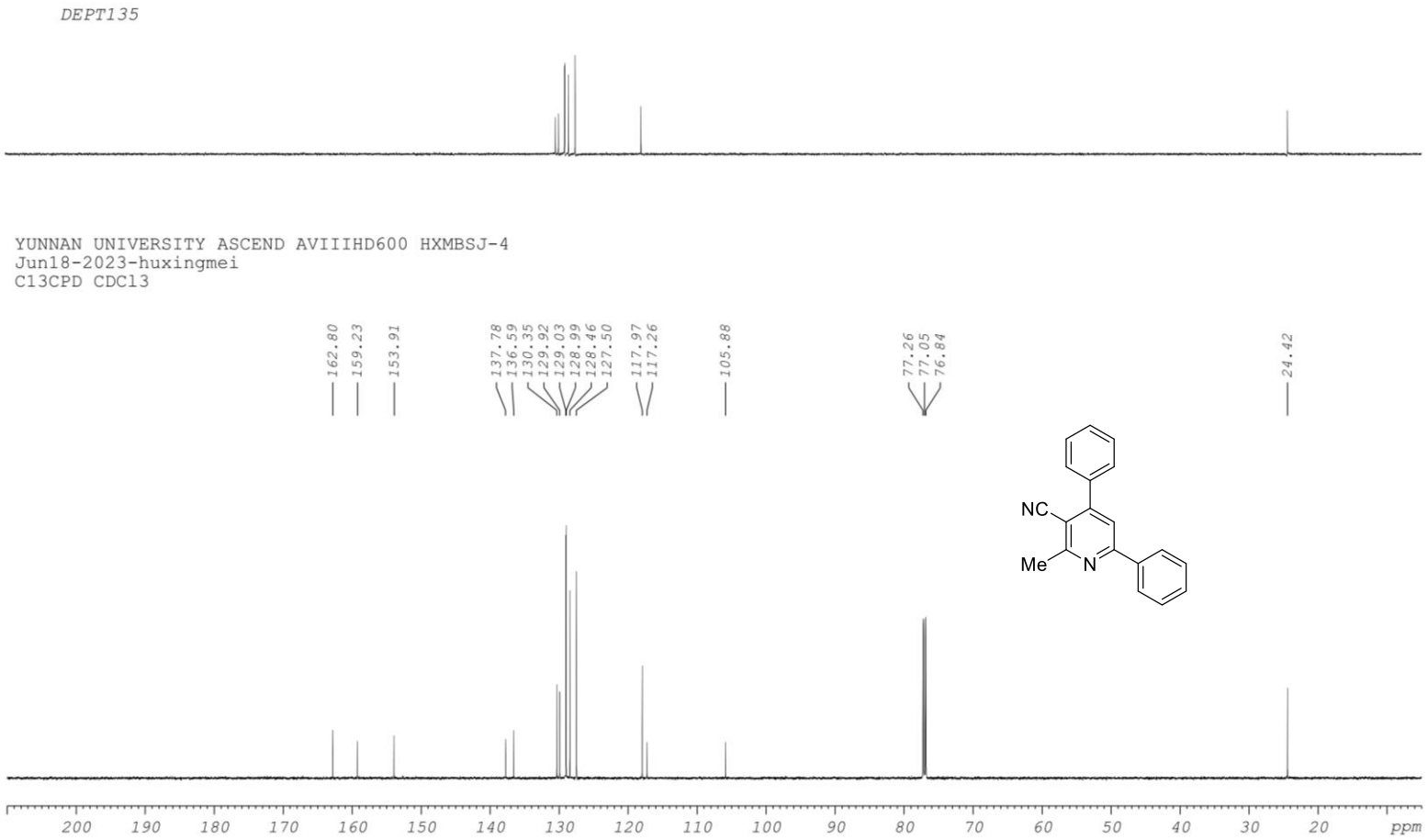


Figure S92. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3l'**

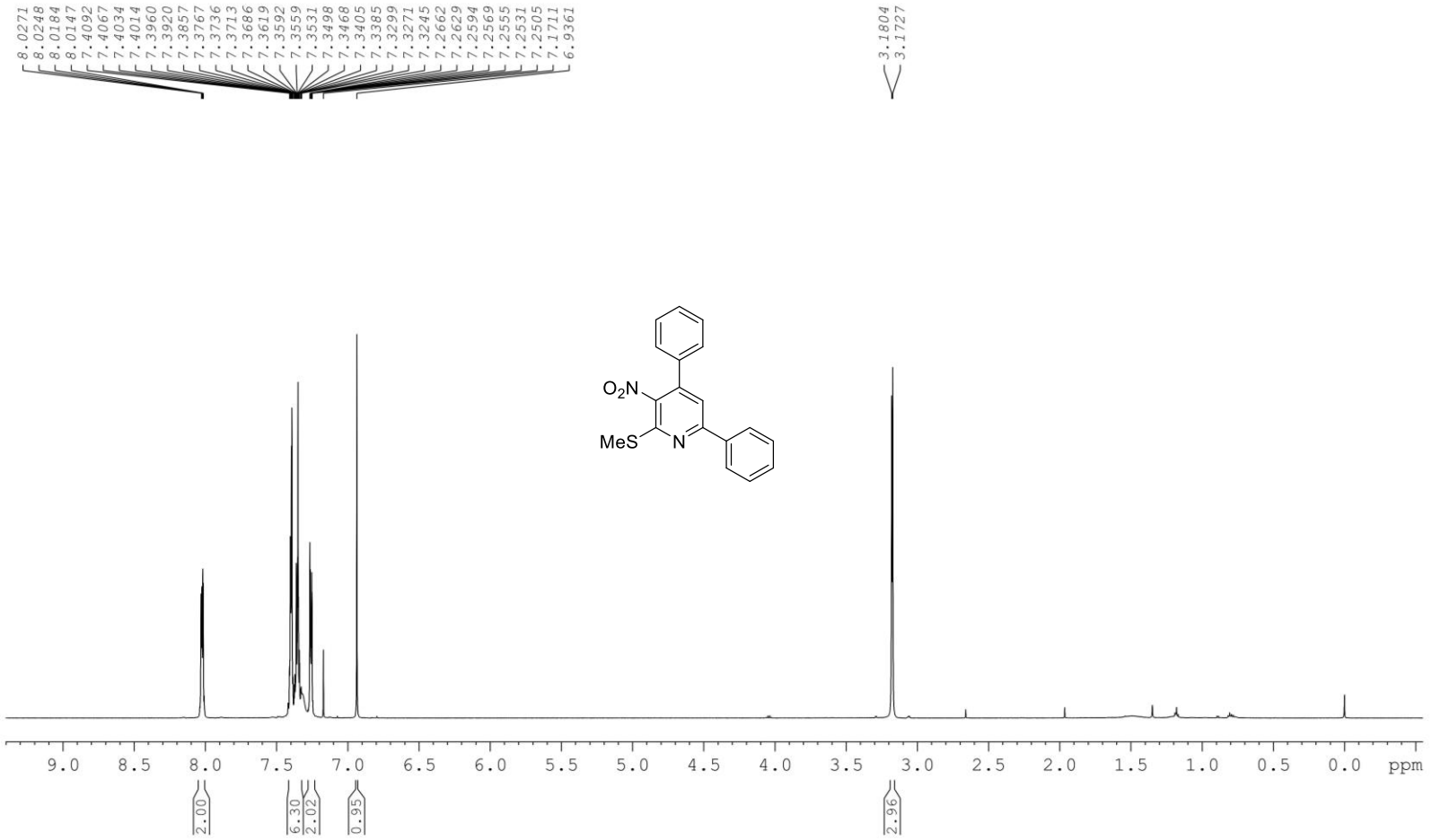


Figure S93. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3m'**

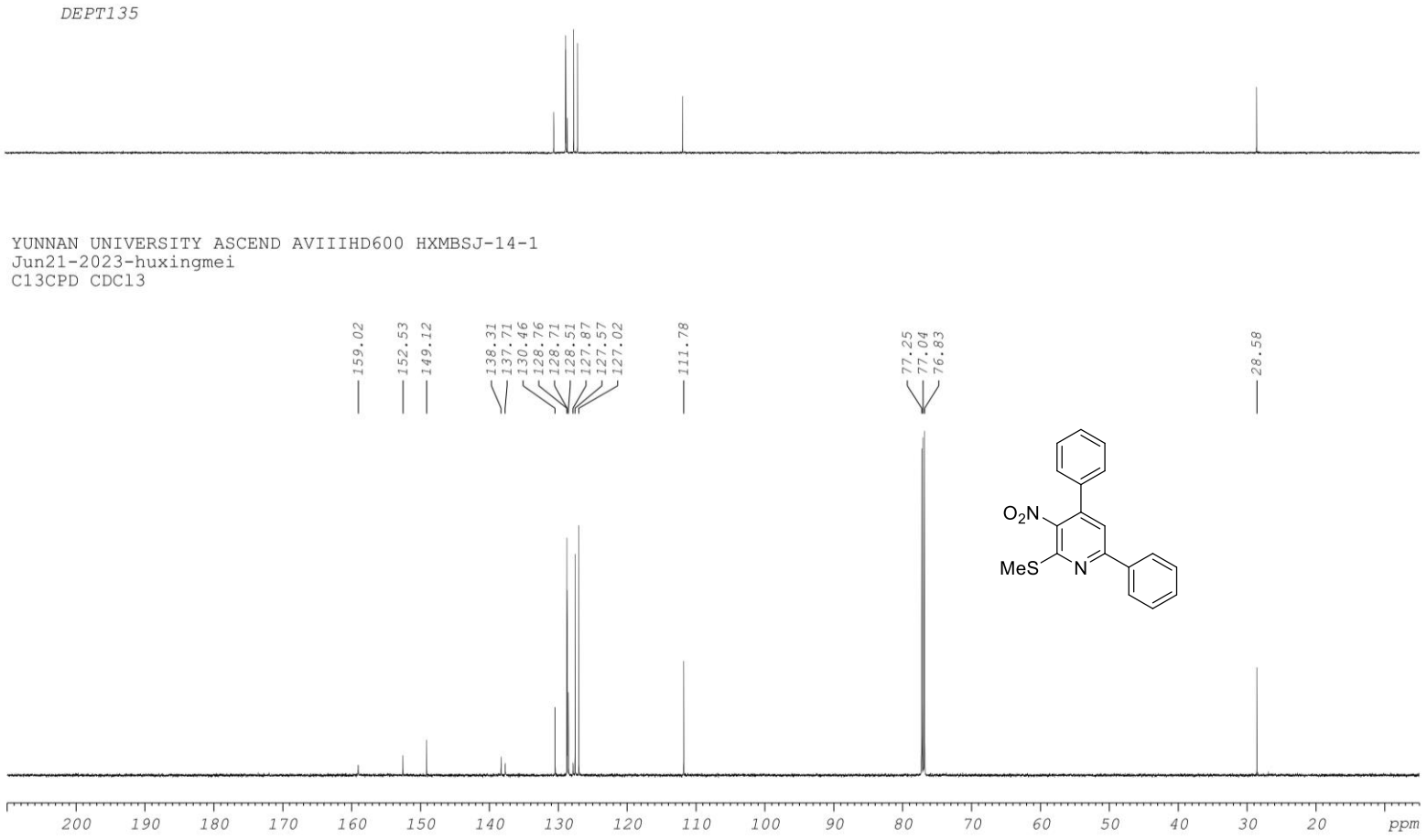


Figure S94. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3m'**

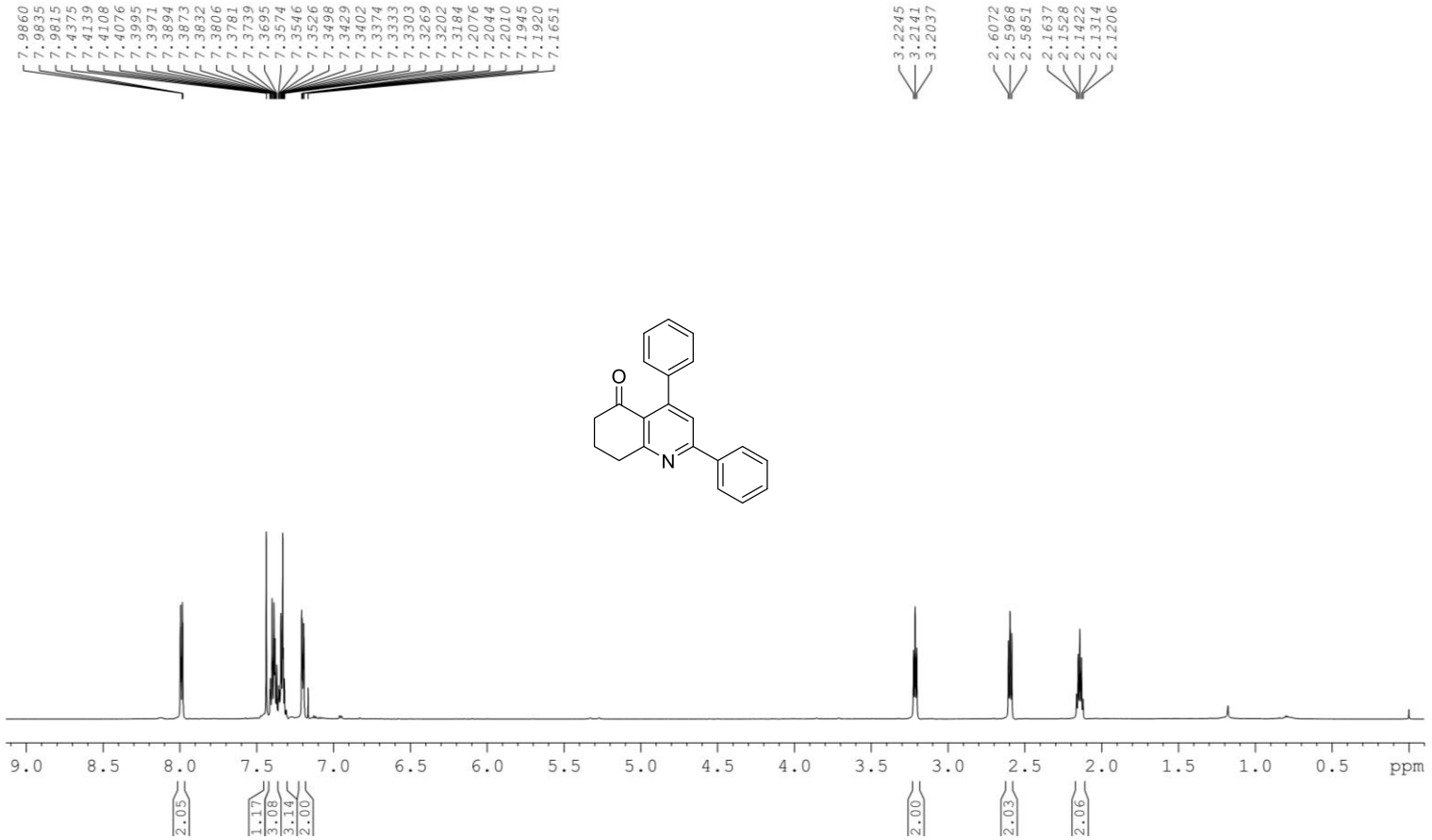


Figure S95. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3n'**

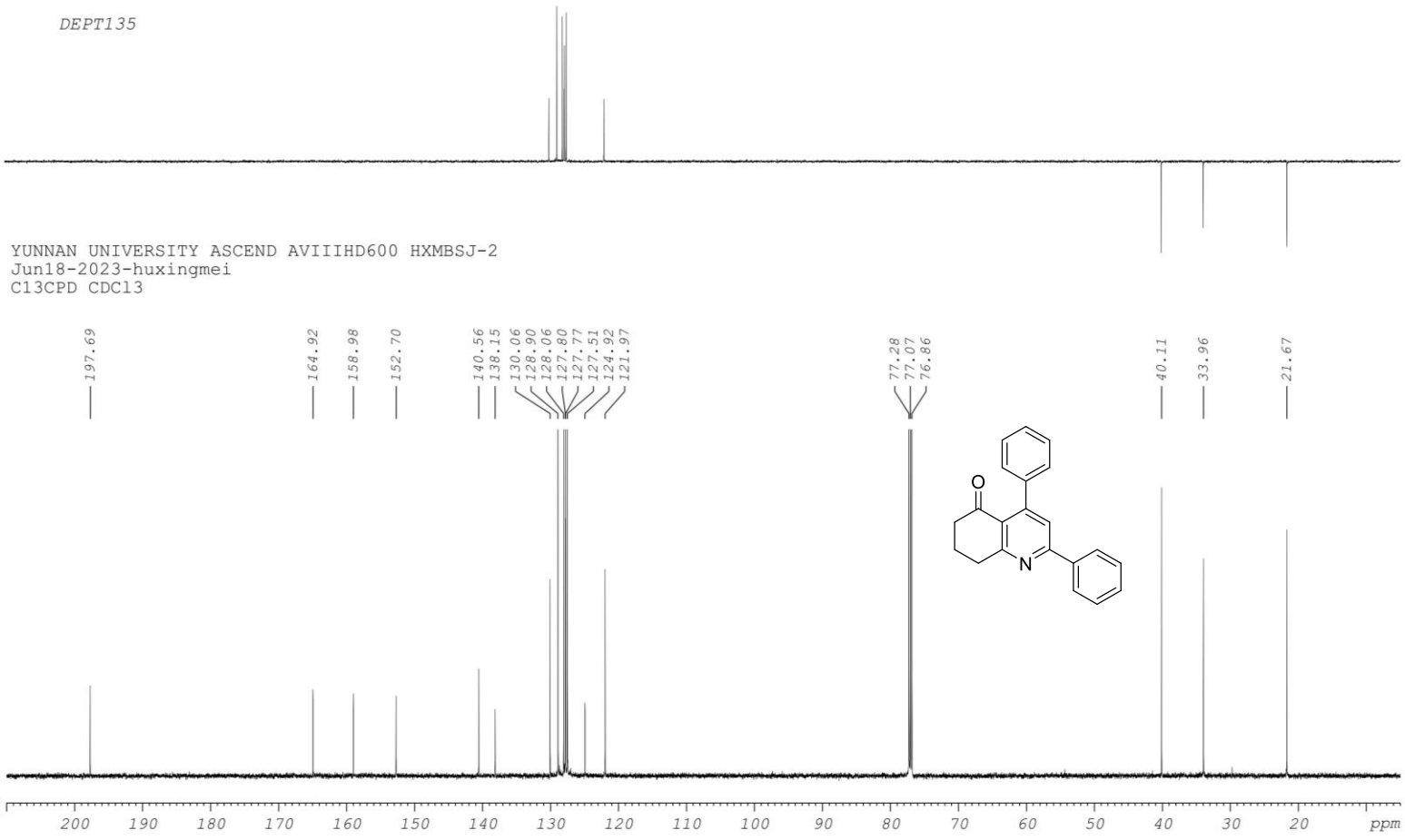


Figure S96. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3n'**

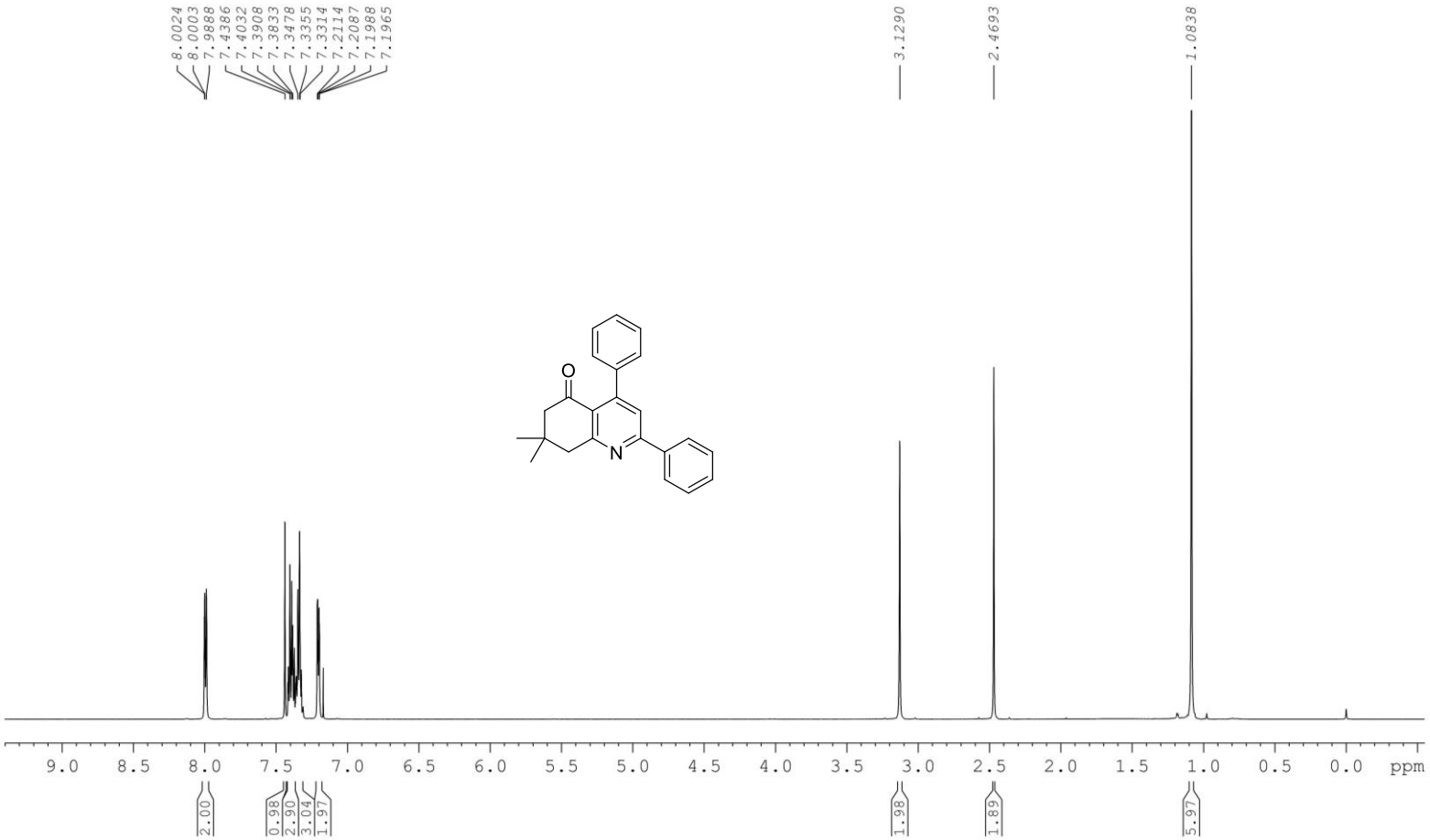


Figure S97. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3o'**

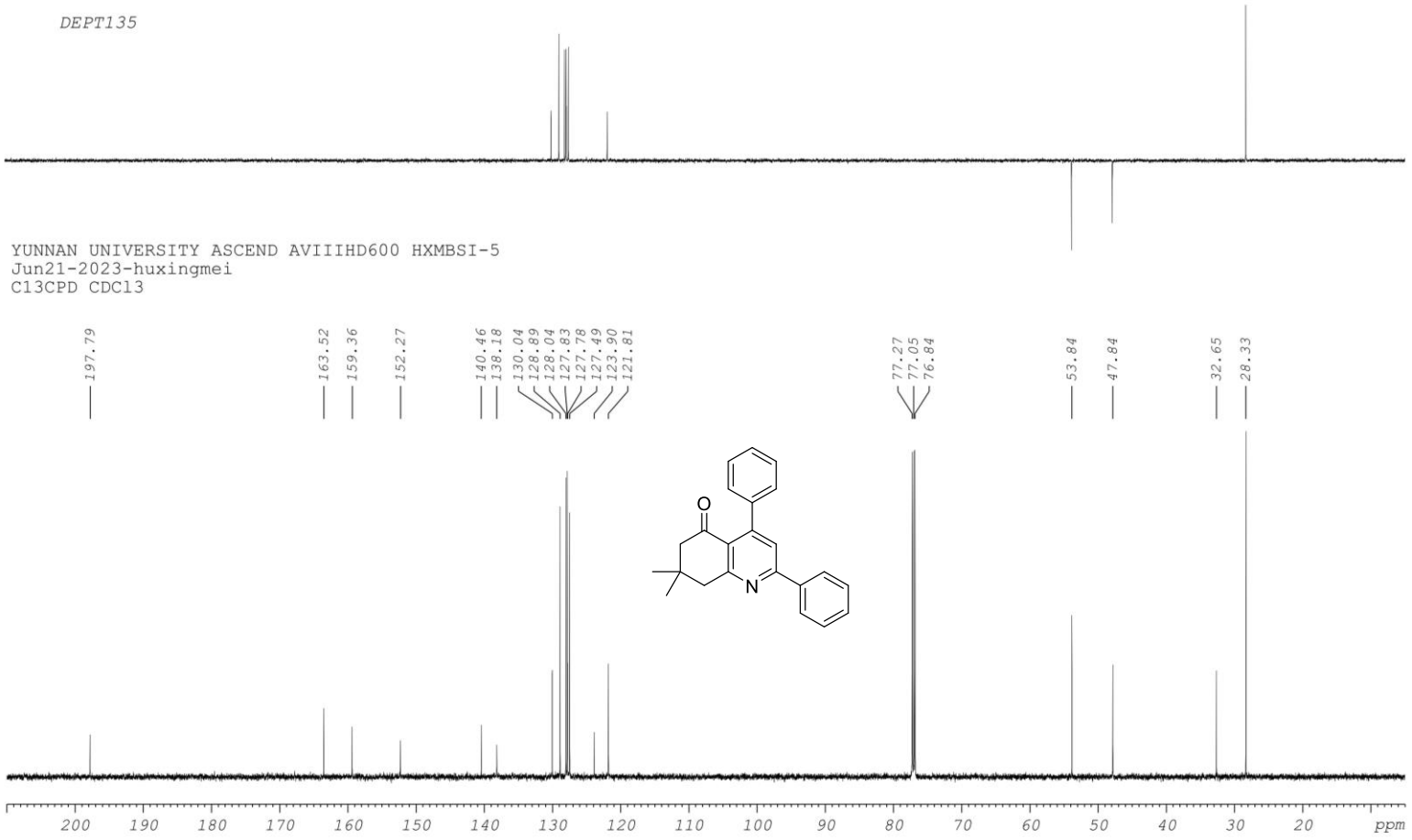


Figure S98. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3o'**

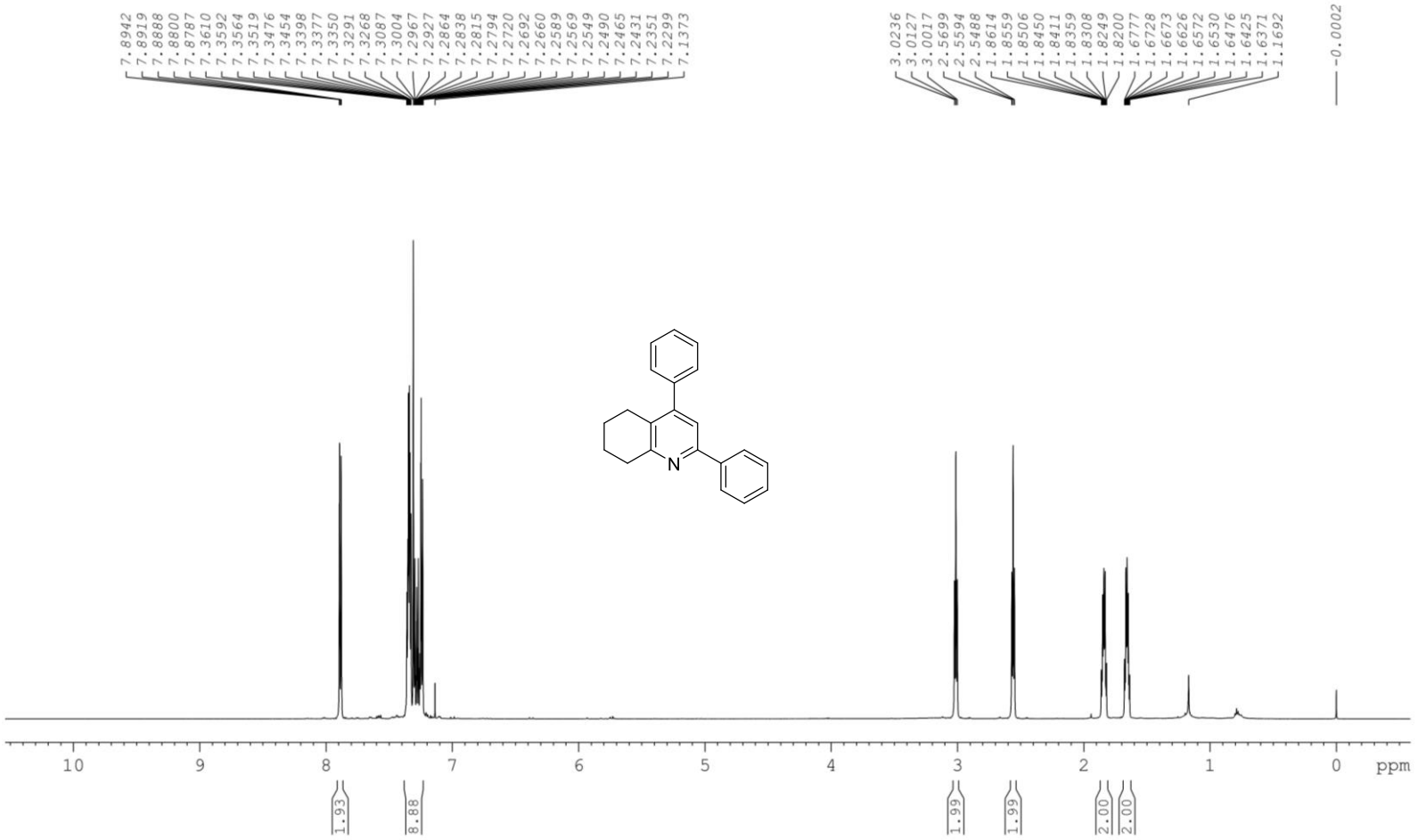


Figure S99. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3p'**

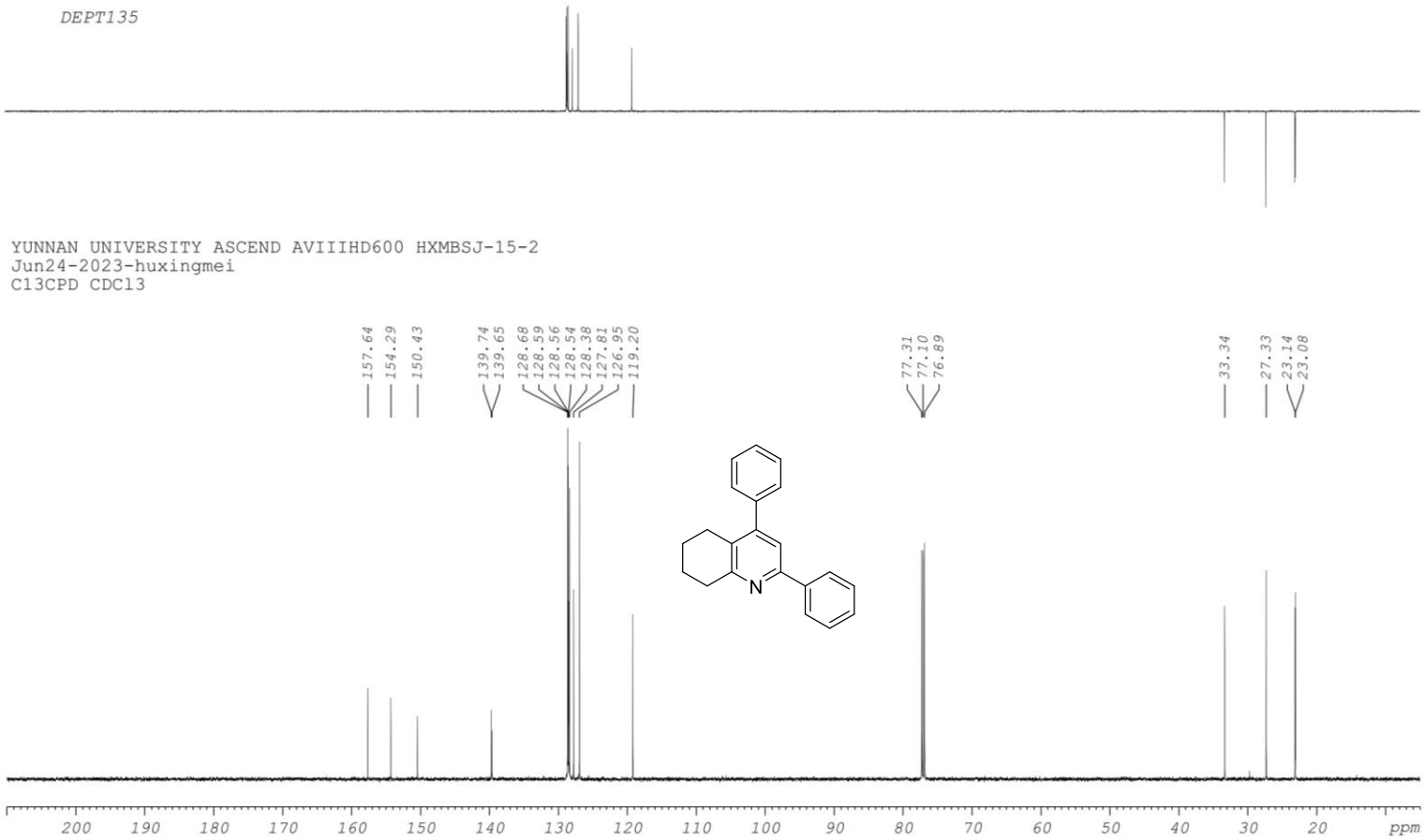


Figure S100. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3p'**

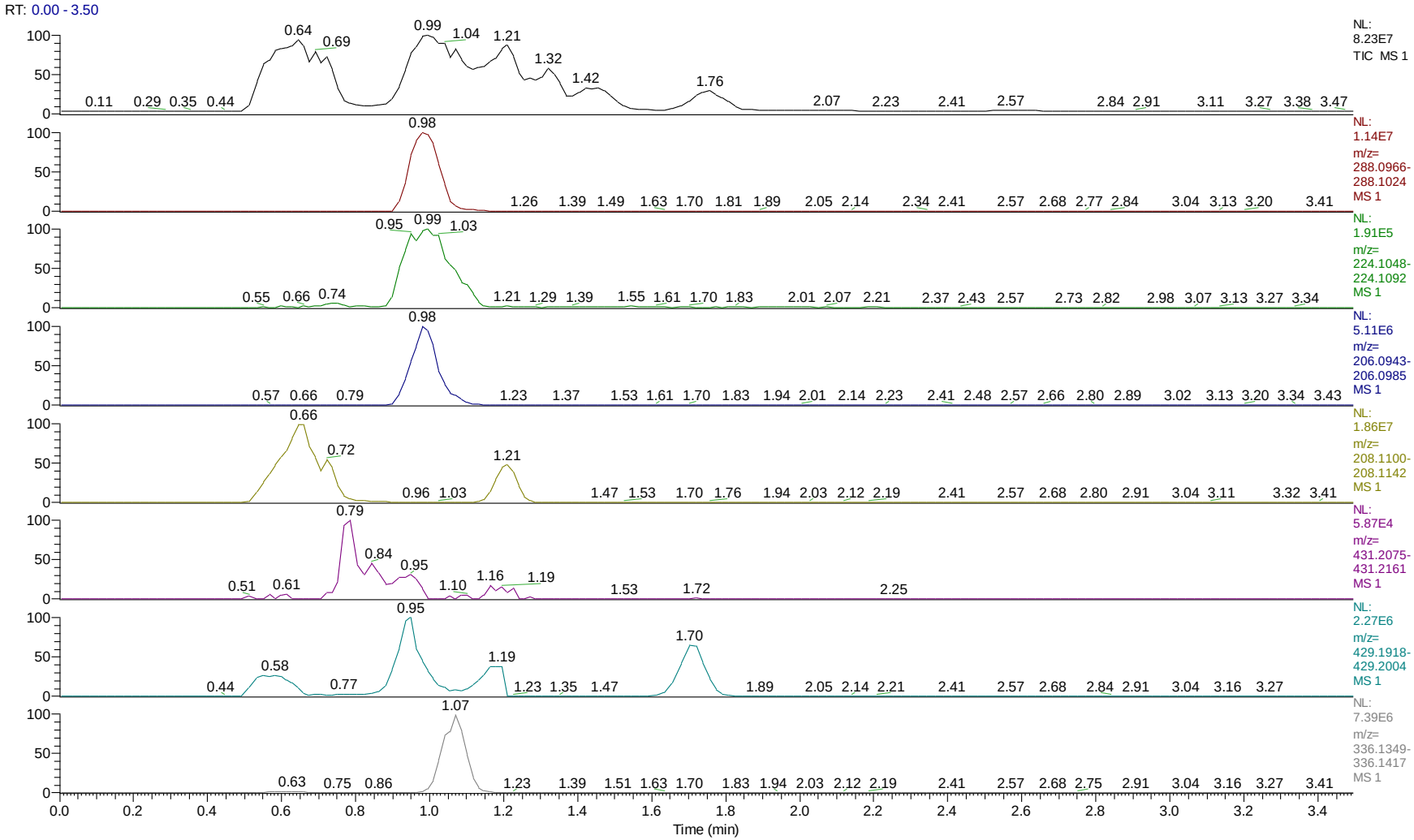


Figure S101. HPLC extracted ion flow diagrams of the reaction mixture

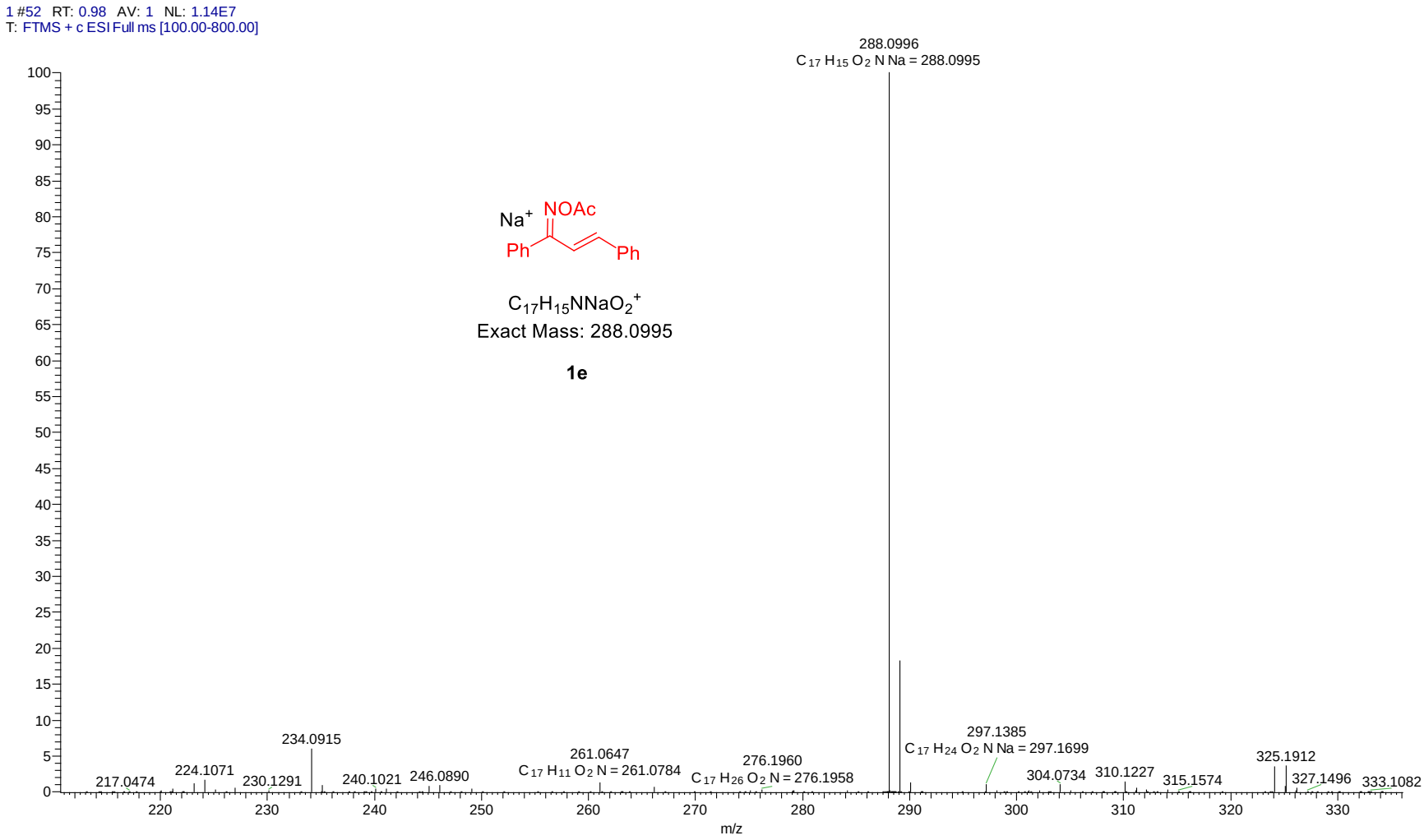


Figure S102. HRMS of substrate **1e**

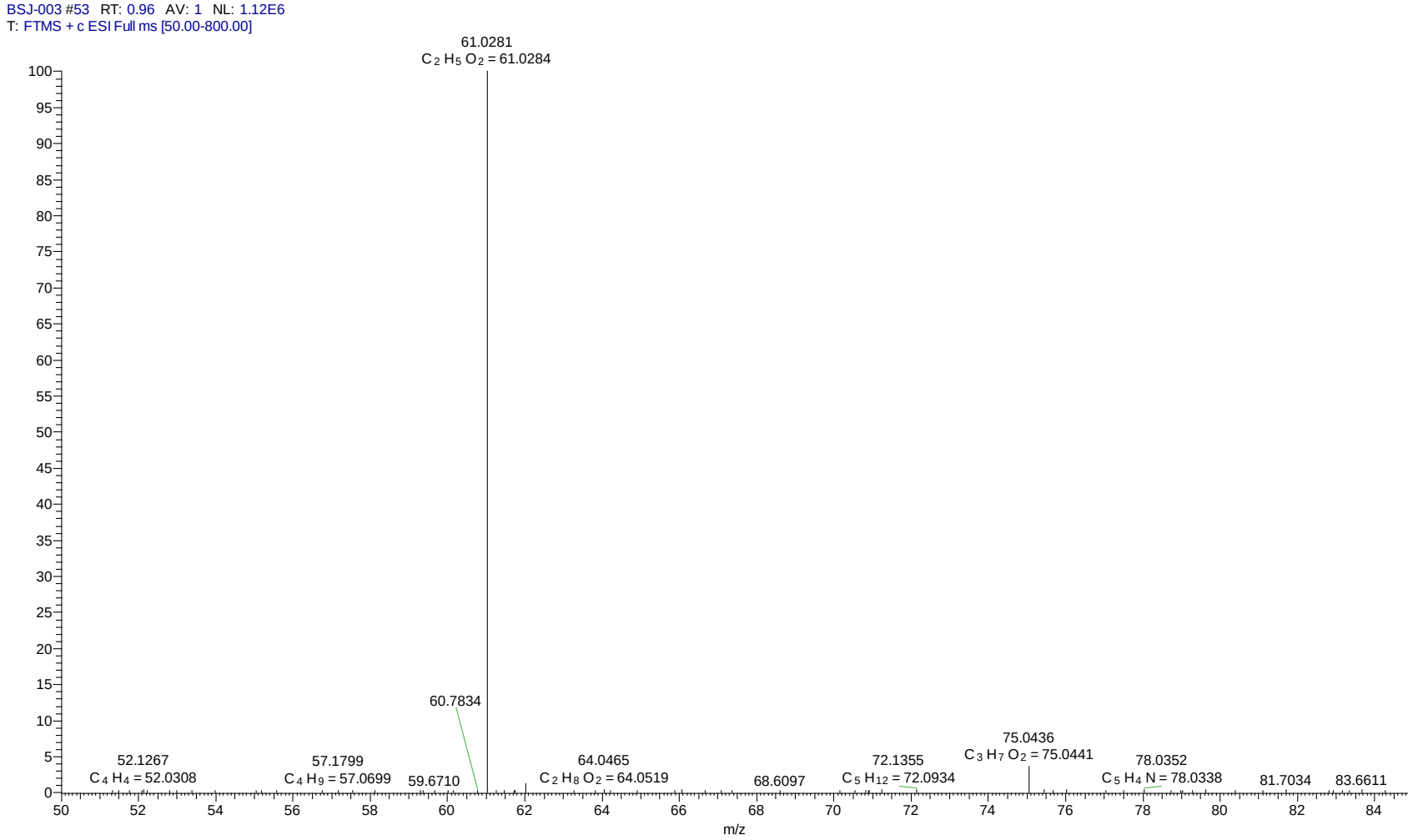


Figure S103. HRMS of HOAc

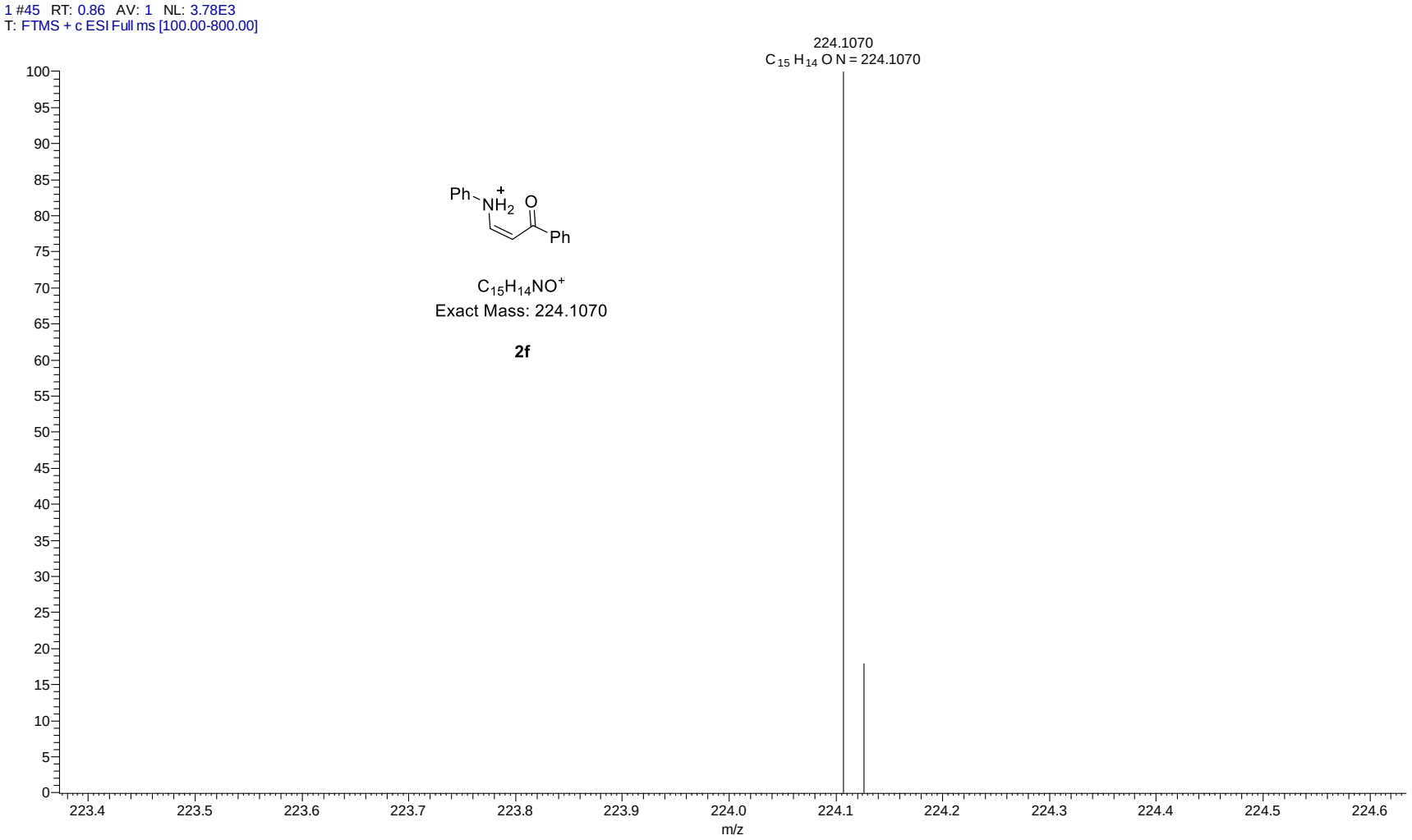


Figure S104. HRMS of substrate **2f**

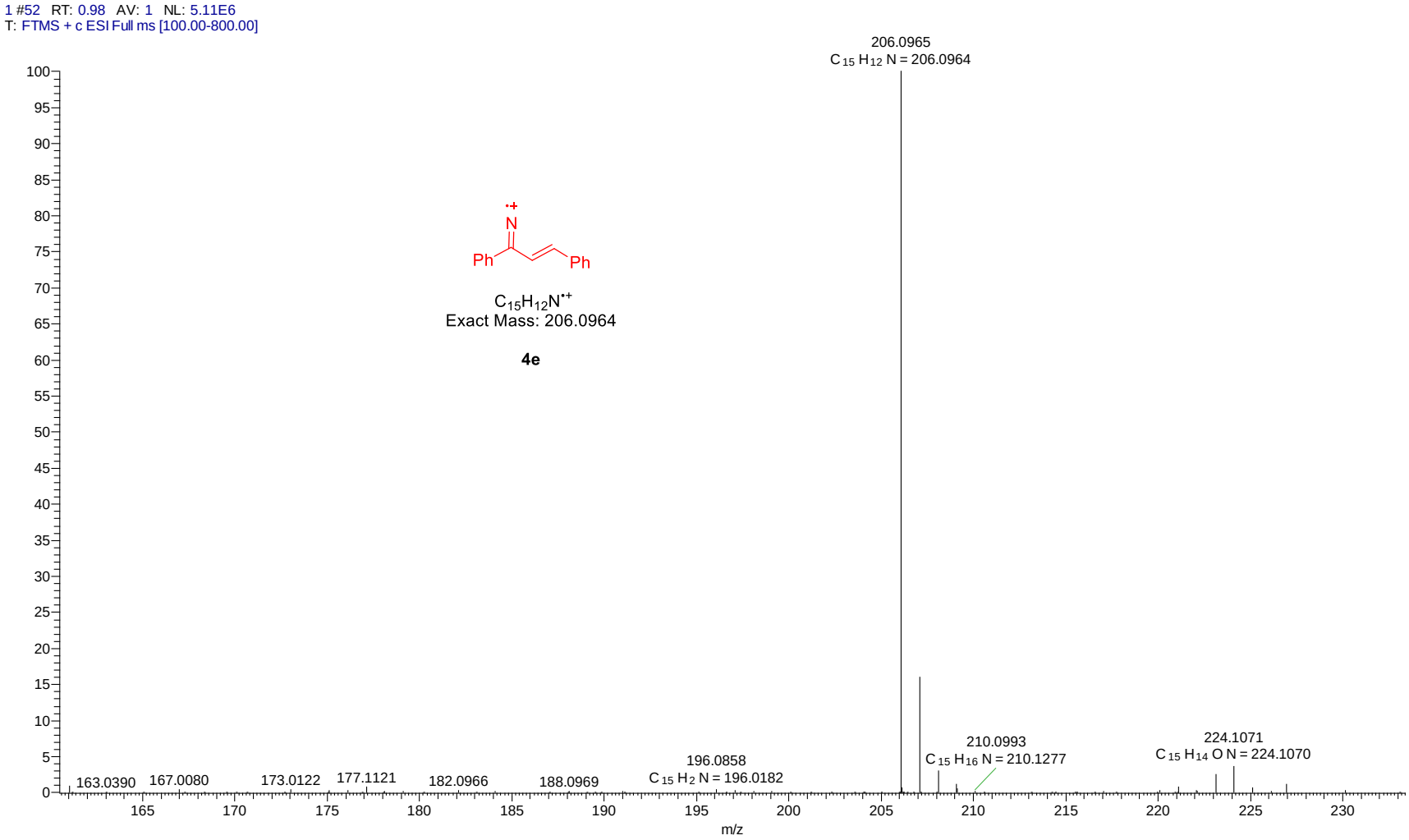


Figure S105. HRMS of intermediate **4e**

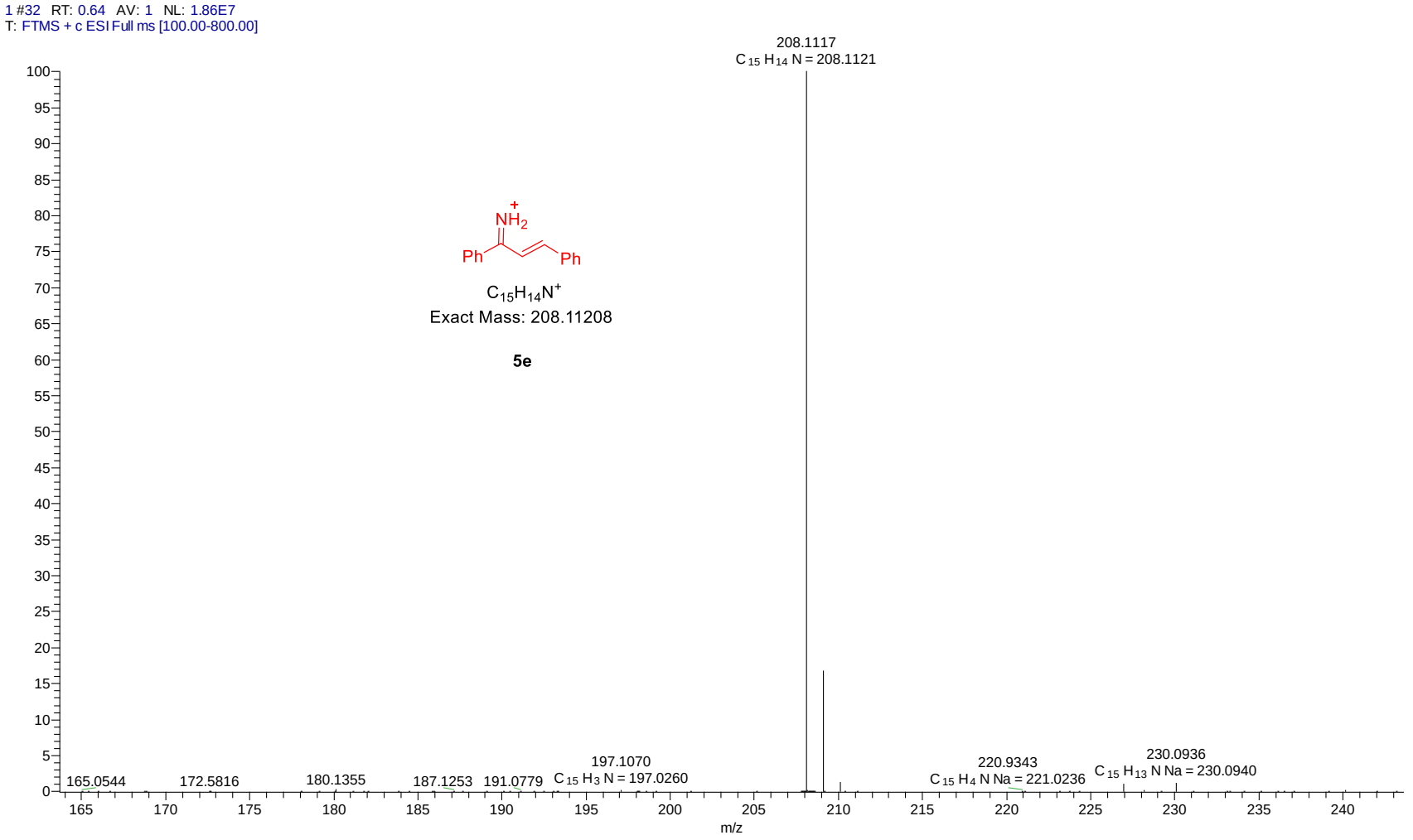


Figure S106. HRMS of intermediate **5e**

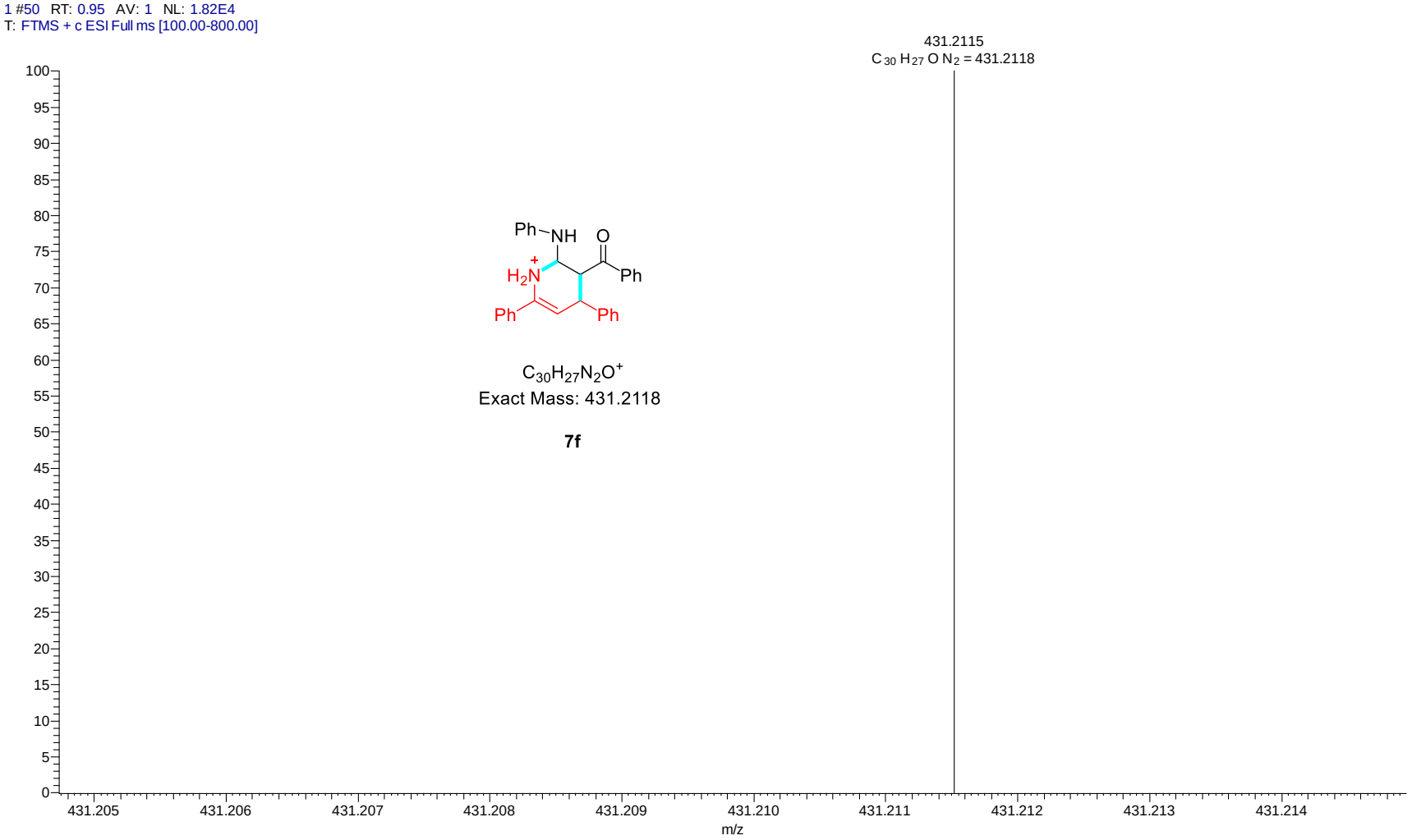


Figure S107. HRMS of intermediate **7f**

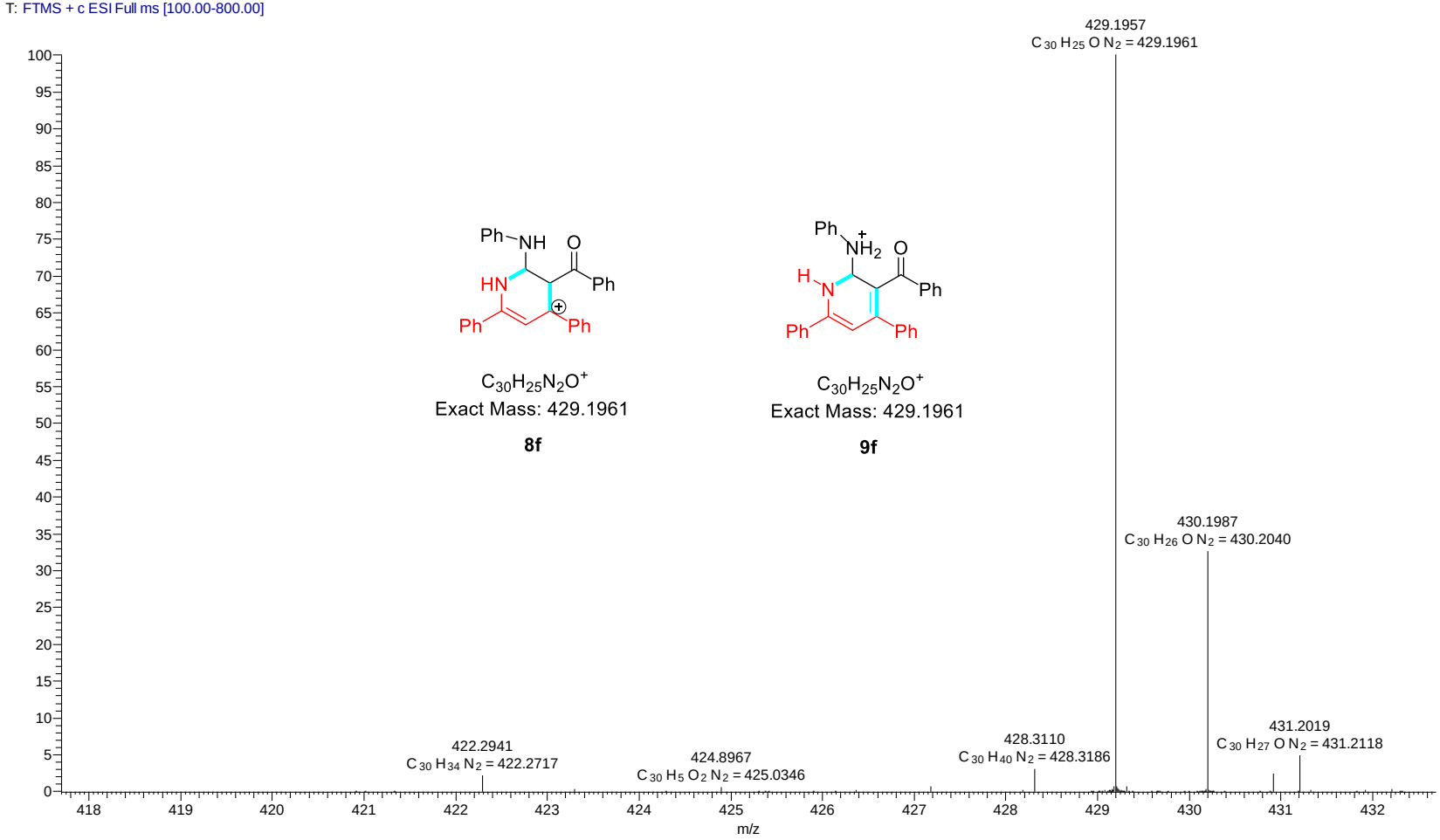


Figure S108. HRMS of intermediate **8f** or **9f**

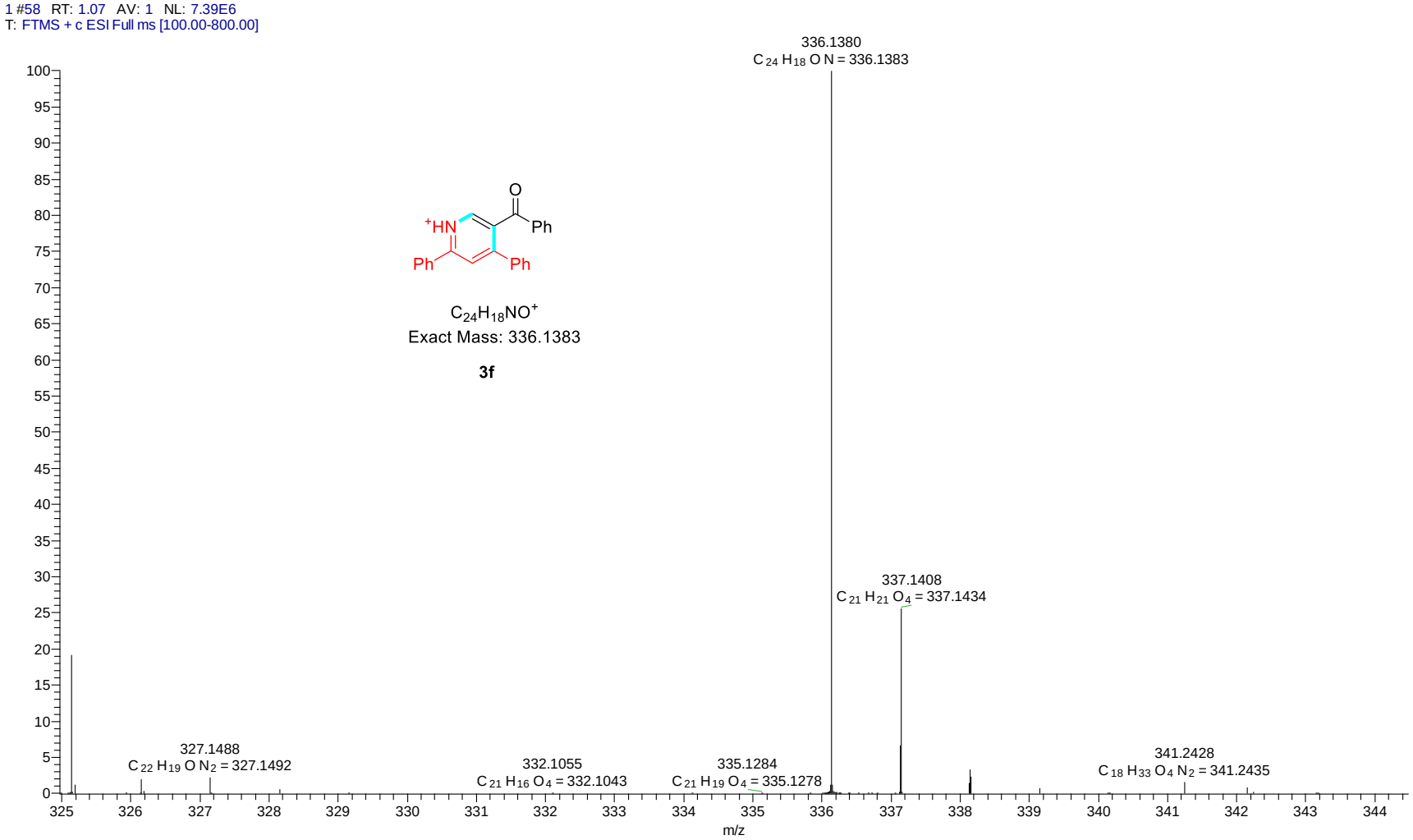


Figure S109. HRMS of the target compound **3f**

References and Notes

1. I. Erray, F. Rezgui, J. Oble, G. Poli, Microwave-Assisted Palladium-Catalyzed Allylation of β-Enaminones, *Synlett*, 2014, **25**, 2196–2200.

2. Miao, C.-B.; Qiang, X.-Q.; Xu, X.; Song, X.-Q.; Zhou, S.-Q.; Lu, X.; Yang, H.-T. Synthesis of Stable N–H Imines with a Benzo[7,8]indolizine Core and Benzo[7,8]indolizino[1,2-c]quinolines via Copper-Catalyzed Annulation of *α,β*-Unsaturated O-Acyl Ketoximes with Isoquinolinium N-Ylides. *Org. Lett.*, 2022**, 24**, 3828–3833.

3. CCDC 2260760 contains the supplementary crystallographic data for compounds **3u**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif