# *Supporting Information*

# *N*-Substituted Hydroxylamines as Synthetically Versatile Amino Sources in the Iridium-Catalyzed Mild C–H Amidation Reaction

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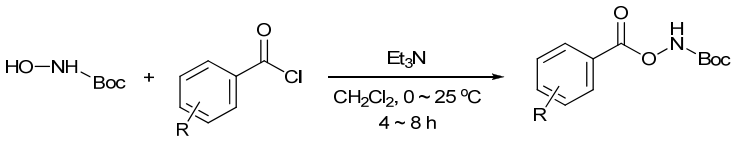
## 1. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 $F_{254}$ plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (400–630mesh) using a proper eluent system. $^1$H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). $^{13}$C NMR was recorded on FT AM 400 (100 MHz), FT AM 600 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded using diamond ATR module of ALPHA FT-IR Spectrometer from Bruker Co., Ltd. Frequencies are given in reciprocal centimeters ($cm^{-1}$) and only selected absorbance peaks are reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Dichloro($\eta^5$-pentamethylcyclopentadienyl)iridium(III) dimer (99%) was purchased from Strem Chemicals Co., Ltd and all the silver salts were purchased from Aldrich Chemicals. All the amidating reagents[1-6] and 2-phenylpyridine[7-9] substrates were prepared according to reported procedure.

## 2. General Procedure for the Preparation of Starting Materials

### 2.1. Preparation of Aminating Reagents (2)



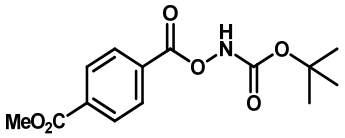

Aminating reagents were prepared according to literature procedures.[S1–S7] Spectroscopic data for all new compounds were given where as only NMR data were given for reported compounds.

**Representative procedure for the synthesis of *O*-aroyloxycarbamates:** To a solution of *N*-Boc protected hydroxyl amine (0.27 g, 2.0 mmol) in dichloromethane (5 mL) at 0 °C was added triethylamine (0.24 g, 2.3 mmol) followed by a slow addition of methyl 4-(chlorocarbonyl)benzoate (2.0 mmol) under argon in a round bottomed flask (50 mL). The reaction mixture was stirred at room temperature until completion as indicated by TLC (4 h). To the reaction mixture was quenched with wated, extracted by dichloromethane (10 mL x 3), dried over $MgSO_4$, and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica

gel with *n*-hexane/EtOAc to give methyl 4-[{(tert-butoxycarbonyl)amino}oxycarbonyl]benzoate (**2a**, 0.5 g, 83%).[S1]

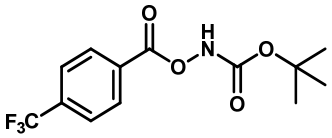
**2.2. Spectroscopic Data of Amidating Reagents.**

**Methyl 4-[{(tert-butoxycarbonyl)amino}oxycarbonyl]benzoate (2a)**



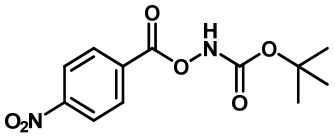
White solid; m.p. 93 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.16 – 8.06 (m, 4H), 3.95 (s, 3H), 1.51 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.3, 155.3, 134.9, 130.6, 129.8, 129.7, 52.5, 28.0; IR (diamond) 3338, 3326, 2977, 1745, 1724, 1479, 1435, 1395, 1274, 1232, 1154, 1003, 777 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{14}H_{17}NO_6$ $[M+Na]^+$: 318.0954, found: 318.0962.

***tert*-Butyl (4-trifluoromethylbenzoyl)oxycarbamate (2b)**



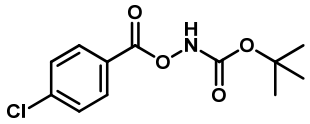
White solid; m.p. 80 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, $J$ = 8.2 Hz, 2H), 8.19 (s, 1H), 7.76 (d, $J$ = 8.1 Hz, 2H), 1.52 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 164.9, 155.3, 135.4, 130.3, 130.3, 125.7, 124.3, 122.5, 83.7, 28.0; IR (diamond) 3324, 3033, 2955, 2901, 2850, 1743, 1720, 1470, 1455, 1376, 1272, 1214, 1098, 723 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{13}H_{14}F_3NO_4$ $[M]^+$: 305.0875, found: 308.0877.

***tert*-Butyl (4-nitrobenzoyl)oxycarbamate (2c)**[7]



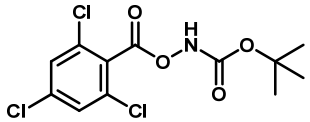
White solid; m.p. 92 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 8.7 Hz, 2H), 8.28 (d, $J$ = 8.9 Hz, 2H), 1.53 (s, 9H; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.2, 155.1, 151.1, 132.3, 131.1, 123.8, 83.9, 28.0.

***tert*-Butyl (4-chlorobenzoyl)oxycarbamate (2d)**[3]



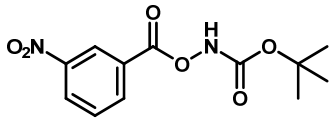
White solid; m.p. 98 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 (d, $J$ = 8.4 Hz, 2H), 7.40 (d, $J$ = 8.4 Hz, 2H), 1.45 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.3, 155.4, 140.8, 131.3, 129.1, 125.3, 83.6, 28.0.

***tert*-Butyl (2,4,6-trichlorobenzoyl)oxycarbamate (2e)**[7]



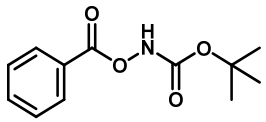
White solid; m.p. 81 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.40 (s, 2H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.2, 154.7, 137.6, 133.6, 128.8, 128.2, 83.9, 28.0.

***tert*-Butyl (3-nitrobenzoyl)oxycarbamate (2f)**



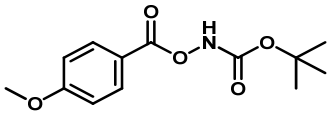
White solid; m.p. 78 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.85 (m, 1H), 8.48 – 8.44 (m, 1H), 8.39 (d, $J$ = 9.4 Hz, 1H), 8.36 (s, 1H), 7.70 (t, $J$ = 8.2 Hz, 1H), 1.49 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.2, 148.2, 135.4, 130.0, 128.7, 128.4, 124.8, 83.8, 27.9.; IR (diamond) 3278, 2981, 2937, 1743, 1732, 1458, 1368, 1271, 1252, 1151, 848 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{12}H_{14}N_2O_6$ $[M+Na]^+$: 305.0750, found: 305.0746.

***tert*-Butyl (benzoyl)oxycarbamate (2g)**[7]



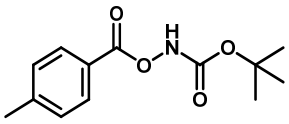
White solid; m.p. 76 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.10 (dd, $J$ = 8.2, 1.5 Hz, 2H), 7.63 (t, $J$ = 7.5 Hz, 1H), 7.48 (t, $J$ = 7.9 Hz, 2H), 1.52 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 155.5, 134.1, 129.9, 128.7, 126.9, 83.4, 28.1.

***tert*-Butyl (4-methoxybenzoyl)oxycarbamate (2h)**



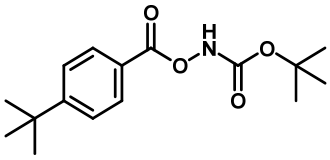
White solid; m.p. 79 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.06 (d, $J$ = 9.0 Hz, 2H), 6.95 (d, $J$ = 9.0 Hz, 2H), 3.88 (s, 3H), 1.51 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.3, 155.7, 132.1, 119.0, 113.9, 83.2, 55.5, 28.1; IR (diamond) 3279, 3032, 2980, 2934, 1783, 1730, 1455, 1368, 1272, 1227, 1156, 1098, 1009, 710 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{13}H_{17}NO_5$ $[M]^+$: 267.1107, found: 267.1110.

***tert*-Butyl (4-methylbenzoyl)oxycarbamate (2i)**



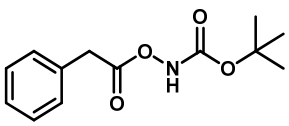
White solid; m.p. 92 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.99 (dd, $J$ = 7.9, 2.9 Hz, 2H), 7.28 (dd, $J$ = 12.8, 3.2 Hz, 2H), 2.43 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.2, 155.6, 145.1, 129.9, 129.4, 124.1, 83.3, 28.1, 21.8; IR (diamond) 3275, 2968, 1762, 1723, 1580, 1514, 1482, 1430, 1374, 1376, 1323, 1231, 1150, 1045, 1011, 835 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{13}H_{17}NO_4$ $[M]^+$: 251.1158, found: 251.1155.

***tert*-Butyl (4-*t*-butylbenzoyl)oxycarbamate (2j)**



White solid; m.p. 89 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.02 (d, $J$ = 7.8 Hz, 2H), 7.48 (d, $J$ = 7.8 Hz, 2H), 1.51 (s, 9H), 1.34 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.0, 155.6, 129.8, 125.6, 124.0, 83.2, 35.2, 31.0, 28.0; IR (diamond) 3275, 2968, 2850, 1758, 1723, 1580, 1514, 1482, 1376, 1323, 1231, 1150, 1047, 1011, 9104, 750 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{16}H_{23}NO_4$ $[M+Na]^+$: 316.1525, found: 316.1519.

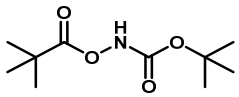
***tert*-Butyl 2-phenylacetoxycarbamate (2k)**



Sticky liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.49 – 7.09 (m, 5H), 3.74 (s, 2H), 1.44 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.7, 155.4, 132.2, 129.2, 128.6,

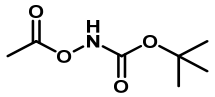
127.4, 83.1, 38.5, 27.9; IR (diamond) 3140, 3025, 2955, 2812, 1789, 1707, 1644, 1527, 1364, 1287, 1171, 1061, 847 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{13}H_{17}NO_4$ $[M]^+$: 251.1158, found: 251.1157.

***tert*-butyl pivaloyloxycarbamate (2l)**[7]



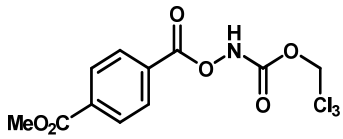
White solid; m.p. 72 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 1.49 (s, 9H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.7, 155.7, 83.0, 38.1, 28.0, 26.9.

***tert*-butyl acyloxycarbamate (2m)**[2]



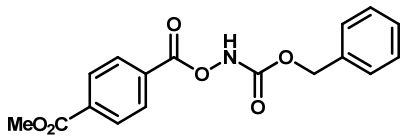
Colorless liquid; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 2.20 (s, 3H), 1.49 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 169.9, 155.4, 83.19, 27.9, 18.3.

**Methyl 4-[(2′,2′,2′-trichloroethoxycarbonyl)amino-oxycarbonyl]benzoate (2n):** Reactant for product **5** of Scheme 2.



White solid; m.p. 121 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.16 (d, $J$ = 2.4 Hz, 2H), 8.14 (d, $J$ = 2.4 Hz, 2H), 4.85 (s, 2H), 3.97 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.9, 164.7, 154.5, 135.2, 130.0, 129.9, 129.8, 94.3, 75.2, 52.6; IR (diamond) 3196, 2959, 2922, 2851, 1779, 1722, 1502, 1435, 1407, 1280, 1232, 1141, 1105, 1091, 986, 747 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{11}H_{10}Cl_3NO_6$ $[M]^+$: 356.9574, found: 356.9751.

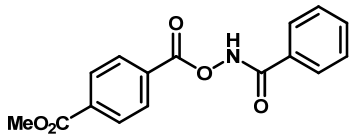
**Methyl 4-[(benzyloxycarbonyl)amino-oxycarbonyl]benzoate (2o):** Reactant for product **6** of Scheme 2.



White solid; m.p. 131 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.15 – 7.88 (m, 4H), 7.40 – 7.20 (m, 5H), 5.16 (s, 2H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ

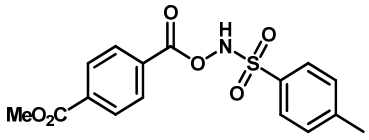
165.9, 164.9, 156.2, 135.0, 134.9, 130.3, 129.9, 129.8, 128.6, 128.6, 128.3, 68.5, 52.6; IR (diamond) 3275, 2962, 2926, 2869, 1768, 1719, 1607, 1461, 1368, 1247, 1160, 1106, 849 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{15}N_2O_6$ $[M]^+$: 329.0899, found3: 29.0895.

**Methyl 4-[(benzamidooxy)carbonyl]benzoate (2p):** Reactant for product **7** of Scheme 2.



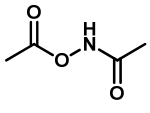
White solid; m.p. 144 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.22 – 8.15 (m, 2H), 8.14 – 8.09 (m, 2H), 7.92 – 7.80 (m, 2H), 7.56 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.45 (td, $J$ = 7.7, 0.9 Hz, 2H), 3.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.9, 164.4, 134.9 132.9, 130.5, 130.3, 129.9, 129.7, 128.8, 127.5, 52.6; IR (diamond) 3170, 3151, 2957, 1771, 1717, 1653, 1506, 1282, 1237, 1107, 1045, 993, 723 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{16}H_{13}NO_5$ $[M]^+$: 299.0794, found: 299.0796.

**Methyl 4-[(4-methylphenylsulfonamido)oxycarbonyl]benzoate (2q):** Reactant for product **8** of Scheme 2.

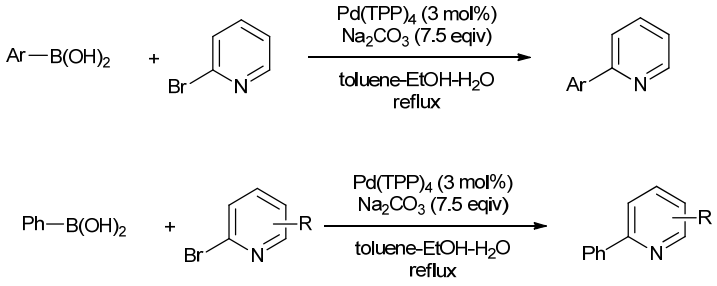


White solid; m.p. 92 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.10 (d, $J$ = 8.3 Hz, 2H), 7.97 (d, $J$ = 8.2 Hz, 2H), 7.82 (d, $J$ = 8.3 Hz, 2H), 7.29 (d, $J$ = 8.2 Hz, 2H), 3.95 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.7, 164.1, 145.8, 135.2, 132.1, 129.9, 129.8, 129.6, 129.5, 128.7, 52.6, 21.6; IR (diamond) 3352, 33259, 3136, 3043, 2959, 1720, 1595, 1438, 1387, 1279, 1175, 1059, 1007, 719 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{16}H_{15}NO_6S$ $[M]^+$: 349.0620, found: 349.0624.

***O*-Acetyl acetylhydroxamic acid (2r)[6]:** Reactant for the product **9** of Scheme 2. Acetyl hydroxamic acid (0.75 g, 10.0 mmol), $CH_2Cl_2$ (15 mL), and NaOH (2.0 M, 6 mL) were charged to a round bottomed flask. To this, $Ac_2O$ (1.1 g, 11.0 mmol) was added via syringe. After stirring at room temperature for 2 h, the $CH_2Cl_2$ layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave the product as a white solid (0.85 g, 76%). M.p. 86 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 9.15 (s, 1H), 2.22 (s, 3H), 2.06 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 168.9, 167.3, 19.7, 18.3.

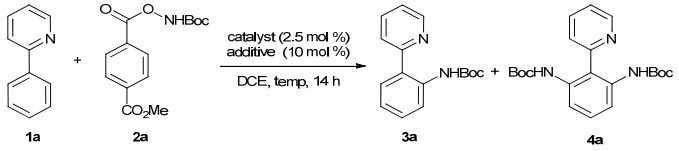


## 2.3. General Procedure for the Preparation of Arylpyridines (1)




To a solution of 2-bromopyridine (0.32 g, 2.0 mmol) in a co-solvent of toluene (7 mL), ethanol (1.5 mL) and $H_2O$ (7 mL) were added $Na_2CO_3$ (1.57 g, 14.8 mmol) followed by $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol) and the 4-methoxyphenylboronic acid (0.4 g, 2.6 mmol) under argon in a 50 mL two-necked flask. The reaction mixture was refluxed for 12 h, and cooled to room temperature. To the reaction mixture was added aqueous $NH_4Cl$ (15 mL), extracted by EtOAc for three times, dried over $MgSO_4$, and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel with *n*-hexane/EtOAc to give 2-(4-methoxyphenyl)pyridine (**1f**, 0.29 g, 78%).[S8–S9]

## 3. Experimental Procedure for Optimization Study (Table S1)




To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added 2-phenylpyridine (**1a**, 15.5 mg, 0.10 mmol), methyl 4-[(*tert*-butoxycarbonyl)-amino]oxycarbonyl-benzoate (**2a**, 32.5 mg, 0.11 mmol), catalyst, additive, and solvent (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at the indicated temperature for 14 h. The reaction mixture was cooled to room temperature in case of heating, filtered through a pad of celite and then washed with $CH_2Cl_2$ (5 mL x 3). Solvents were removed under reduced pressure and the crude yield was measured by $^1H$ NMR spectrum using an internal standard (1,1,2,2-tetrachloroethane).

| entry | catalyst (mol %) | additives (mol %) | solvent | *T* (°C) | yield % (**3a**/**4a**) |
|---|---|---|---|---|---|
| 1 | $[IrCp^*Cl_2]_2$ (3) | $AgNTf_2$ (12) | 1,2-DCE | 50 | 78:9 |
| 2 | $[IrCp^*Cl_2]_2$ (2.5) | $AgNTf_2$ (10) | 1,2-DCE | 50 | 76:9 |
| 3 | $[IrCp^*Cl_2]_2$ (2.5) | $AgNTf_2$ (10) | 1,2-DCE | 25 | 74:7 |
| 4 | $[IrCp^*Cl_2]_2$ (2.5) | – | 1,2-DCE | 25 | 11:0 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | $[IrCp^*Cl_2]_2$ (2.5) | AgOAc (10) | 1,2-DCE | 25 | 68:5 |
| 6 | $[IrCp^*Cl_2]_2$ (2.5) | $AgSbF_6$ (10) | 1,2-DCE | 25 | 72:10 |
| 7 | $[IrCp^*Cl_2]_2$ (2.5) | $AgPF_6$ (10) | 1,2-DCE | 25 | 69:8 |
| 8 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | 1,2-DCE | 25 | 81:5 |
| 9 | $[IrCp^*Cl_2]_2$ (2.5) | KOAc (100) | 1,2-DCE | 25 | 18:0 |
| 10 | $[IrCp^*Cl_2]_2$ (2.5) | AgOMs (10) | 1,2-DCE | 25 | 77:6 |
| 11 | $[IrCp^*Cl_2]_2$ (2.5) | $AgBF_4$ (10) | 1,2-DCE | 25 | 76:12 |
| 12 | $[IrCp^*Cl_2]_2$ (2.5) | $Ag_2OTf$ (10) | 1,2-DCE | 25 | 71:7 |
| 13 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | Toluene | 25 | 32:0 |
| 14 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | Acetonitrile | 25 | 18:1 |
| 15 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | Methanol | 25 | 62:28 |
| 16 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | $CH_2Cl_2$ | 25 | 72:8 |
| 17 | $[IrCp^*Cl_2]_2$ (2.5) | AgOTs (10) | 1,2-DCE | 25 | 96:0 (92)[a] |
| 18 | $IrCp^*(OAc)_2 \cdot H_2O$ (5) | – | 1,2-DCE | 25 | 81:8 |
| 19 | $IrCp^*(OAc)_2 \cdot H_2O$ (5) | – | 1,2-DCE | 25 | 91:0 |
| 20 | $[RhCp^*Cl_2]_2$ (2.5) | $AgSbF_6$ (10) | 1,2-DCE | 25 | 44:0 |
| 21 | [Ru(*p*-cymene)$Cl_2$]$_2$ (2.5) | $AgNTf_2$ (10) | 1,2-DCE | 80 | <10 |
| 22 | $Pd(OAc)_2$ (5) | $PhI(OAc)_2$ (100) | 1,2-DCE | 80 | NR |
| 23 | $Pd(OAc)_2$ (5) | $AgSbF_6$ | 1,2-DCE | 80 | NR |

[a] Substrate (**1a**) was used in 1.2 equiv relative to **2a** and reaction time 10 h. Isolated yield was mention in brackets.

## 4. Experimental Procedure of Ir-Catalyzed C–H Amidation of Arenes & Spectroscopic Data of Products.

### 4.1. Ir-Catalyzed C–N Bond Formation Using a $[IrCp^*Cl_2]_2$/AgOTs Catalyst System.

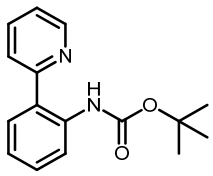

**1** **2a** **3**

To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added 2-phenylpyridine (**1a**, 37.8 mg, 0.24 mmol), methyl 4-[{(tert-butoxycarbonyl)amino}oxycarbonyl]benzoate (**2a**, 60.0 mg, 0.2 mmol), $[IrCp^*Cl_2]_2$ (4.0 mg, 2.5 mol %), AgOTs (5.6 mg, 10.0 mol %) and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 10 h, filtered through a pad of celite and then washed with $CH_2Cl_2$ (10 mL x 3). Solvents were removed under

reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product **3a** (50.5 mg, 92%).

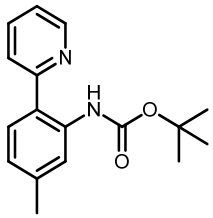
### 4.2. Spectroscopic Data of Products.

***tert*-Butyl [2-(pyridin-2-yl)phenyl]carbamate (3a)**



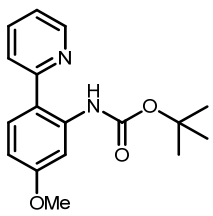
White solid; m.p. 75 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.73 – 8.59 (m, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.80 (td, *J* = 7.8, 1.9 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H), 7.25 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 7.08 (td, *J* = 7.6, 1.3 Hz, 1H), 1.51 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 158.5, 153.3, 147.7, 138.1, 137.4, 129.9, 128.9, 125.5, 122.9, 122.1, 121.6, 120.4, 79.7, 28.4; IR (diamond) 3275, 2968, 1723, 1580, 1514, 1482, 1432, 1393, 1376, 1323, 1231, 1150, 1047, 1011, 9104, 835 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{16}H_{18}N_2O_2$ $[M]^+$: 270.1368, found: 270.1366.

***tert*-Butyl [5-methyl-2-(pyridin-2-yl)phenyl]carbamate (3b)**



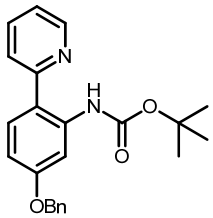
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.63 (d, J = 4.8 Hz, 1H), 8.18 (s, 1H), 7.78 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.22 (ddd, J = 7.4, 4.8, 1.2 Hz, 1H), 6.90 (d, J = 8.1, Hz, 1H), 2.39 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.4, 147.5, 140.3, 138.0, 137.4, 128.8, 123.0, 122.6, 121.3, 120.6, 79.6, 28.4, 21.6; IR (diamond) 3232, 3183, 3011, 3058, 2926, 2853, 1682, 1585, 1522, 1473, 1437, 1419, 1307, 1280, 1240, 995, 748 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1529.

***tert*-Butyl [5-methoxy-2-(pyridin-2-yl)phenyl]carbamate (3c)**



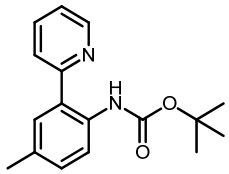
Thick colorless liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 8.61 (d, J = 4.9 Hz, 1H), 8.04 (s, 1H), 7.76 (ddd, *J* = 9.3, 7.4, 1.8 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.19 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 6.64 (dd, J = 8.6, 2.6 Hz, 1H), 3.88 (s, 3H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.9, 158.2, 153.3, 147.3, 139.9, 137.3, 129.8, 122.0, 120.8, 117.4, 109.0, 103.9, 79.7, 55.3, 28.4; IR (diamond) 3204, 2979, 2930, 2814, 2710, 1711, 1695, 1580, 1525, 1429, 1237, 1152, 1080, 927, 812, 670, 563 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_3$ $[M]^+$: 300.1474, found: 300.1474.

**_tert_-Butyl [5-(benzyloxy)-2-(pyridin-2-yl)phenyl]carbamate (3d)**



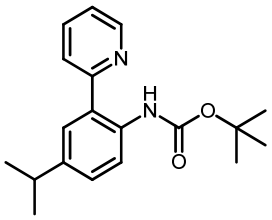

White solid; m.p. 109 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.16 (d, *J* = 2.6 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.15 (m, 1H), 6.69 (d, *J* = 11.3 Hz, 1H), 5.14 (s, 2H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.2, 158.3, 153.3, 147.4, 140.0, 137.3, 136.9, 129.9, 128.5, 127.9, 127.7, 122.0, 120.9, 117.8, 109.5, 105.2, 79.7, 69.9, 28.4; IR (diamond) 3199, 2982, 2928, 2709, 1712, 1690, 1562, 1430, 1239, 1153, 1052, 1002, 936 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{23}H_{24}N_2O_3$ $[M]^+$: 376.1787, found: 376.1785.

**_tert_-Butyl [4-methyl-2-(pyridin-2-yl)phenyl]carbamate (3e)**



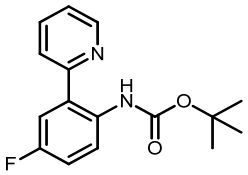

White solid; m.p. 89 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.65 (dd, J = 4.8, 1.7 Hz, 1H), 8.17 (t, *J* = 8.4 Hz, 1H), 7.80 (dt, J = 8.0, 1.9 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.37 (s, 1H), 7.24 (d, J = 7.4, 4.8, 1.1 Hz, 1H), 7.18 (dd, J = 8.8, 1.2 Hz, 1H), 2.35 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.4, 147.7, 137.4, 135.5, 131.5, 130.5, 129.5, 122.9, 125.7, 121.5, 120.5, 79.6, 28.4, 20.8; IR (diamond) 3209, 3114, 2930, 2873, 1709, 1698, 1579, 1501, 1366, 1220, 1145, 950 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1526.

***tert*-Butyl [4-isopropyl-2-(pyridin-2-yl)phenyl]carbamate (3f)**



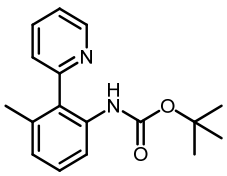
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.65 (dd, J = 4.8, 1.5 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.81 (ddd, J = 8.9, 7.6, 1.5 Hz, 1H), 7.70 (dd, J = 8.1, 0.6 Hz, 1H), 7.41 (d, J = 1.7 Hz, 2H), 7.28 – 7.22 (m, 2H), 2.91 (t, J = 6.8 Hz, 1H), 1.50 (s, 9H), 1.26 (d, J = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.4, 147.7, 142.6, 137.4, 135.6, 127.8 , 126.9, 125.8, 122.9, 121.5, 120.7, 79.6, 33.6, 28.4, 24.0; IR (diamond) 3209, 3062, 3003, 2976, 2930, 2872, 1717, 1630, 185, 1528, 1472, 1235, 1072, 877 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{19}H_{24}N_2O_2$ $[M]^+$: 312.1838, found: 312.1838.

***tert*-Butyl [4-fluoro-2-(pyridin-2-yl)phenyl]carbamate (3g)**



White solid; m.p. 85 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.68 (d, *J* = 5.5 Hz, 1H), 8.22 (s, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.28 (dd, *J* = 9.6, 3.0 Hz, 1H), 7.15 – 6.95 (m, 1H), 1.49 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 158.1 (d, *J* = 241.3 Hz), 156.9, 153.5, 147.5, 138.1, 134.1, 128.3, 123.2, 122.8, 122.3, 116.6 (CH, d, *J* = 21.6 Hz), 115.3 (CH, d, *J* = 23.9 Hz), 79.9, 28.4; IR (diamond) 3244, 3002, 2977, 2930, 1721, 1687, 1585, 1519, 1442, 1316, 1245, 1011, 955, 870, 759 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{16}H_{17}FN_2O_2$ $[M]^+$: 288.1274, found: 288.1272.

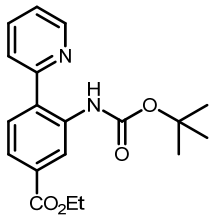
***tert*-Butyl [3-methyl-2-(pyridin-2-yl)phenyl]carbamate (3h)**



Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.5 Hz, 1H), 7.97 – 7.88 (m, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.29 – 7.23 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 2.14 (s, 3H), 1.42 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.9, 152.9, 149.7, 136.8, 136.1, 136.0, 128.7, 126.1, 125.3, 122.2, 118.5, 80.0, 28.3, 20.7; IR (diamond) 3115, 3064, 2984, 2927, 2853, 1677, 1586, 1492, 1475,

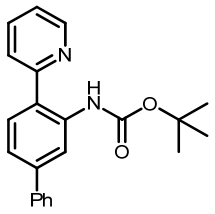
1411, 1399, 1370, 1340, 1253, 1153, 1019, 927, 812, 670, 563 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1522.

**Ethyl 3-[(*tert*-butoxycarbonyl)amino]-4-(pyridin-2-yl)benzoate (3i)**



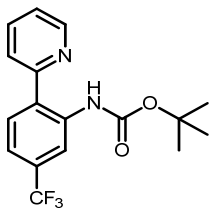

White solid; m.p. 119 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 11.08 (s, 1H), 8.93 (s, 1H), 8.74 – 8.61 (m, 1H), 7.85 (td, *J* = 7.8, 1.9 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.31 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.53 (s, 9H), 1.42 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.3, 157.5, 153.1, 147.9, 137.6, 131.7, 129.9, 128.9, 126.8, 123.4, 123.1, 122.3, 61.1, 28.4, 14.4; IR (diamond) 3115, 3064, 2984, 2927, 2853, 1677, 1586, 1492, 1475, 1411, 1399, 1370, 1340, 1253, 1153, 1019, 927, 812, 670, 563 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{19}H_{22}N_2O_4$ $[M]^+$: 342.1580, found: 342.1577.

***tert*-Butyl [4-(pyridin-2-yl)-(1,1'-biphenyl)-3-yl]carbamate (3j)**



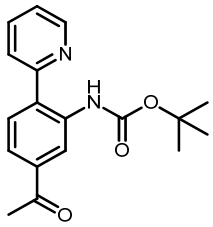

White solid; m.p. 158 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 11.34 (s, 1H), 8.72 – 8.56 (m, 2H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 18.9, 8.6 Hz, 2H), 7.27 – 7.18 (m, 1H), 1.54 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.4, 147.7, 142.7, 140.5, 138.6, 137.5, 129.3, 128.7, 127.6, 127.3, 124.0, 122.8, 121.6, 120.7, 118.8, 79.8, 28.4; IR (diamond) 3285, 3062, 3012, 2974, 2927, 1713, 1570, 1527, 1586, 1466, 1409, 1364, 1224, 1152, 755, 694 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{22}H_{22}N_2O_2$ $[M]^+$: 346.1681, found: 346.1680.

***tert*-Butyl [2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl]carbamate (3k)**



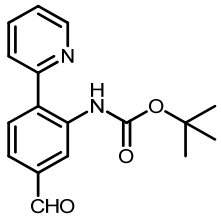
White solid; m.p. 93 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 1H), 8.70 (dd, J = 5.9, 1.7 Hz, 1H), 8.69 (s, 1H), 7.87 (dd, J = 8.0, 1.7,  Hz, 1H), 7.72 (t, J = 8.1 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.34-7.30 (m, 2H), 1.59 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.2, 153.1, 147.9, 138.7, 137.8, 129.3, 123.3, 122.5, 118.4, 117.2, 80.4, 28.3; IR (diamond) 3321, 3050, 3003, 2977, 2928, 1726, 1632, 1605, 1578, 1519, 1446, 1273, 1148, 936, 750, 651 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{17}F_3N_2O_2$ $[M]^+$: 338.1242, found: 338.1245.

**_tert_-Butyl [5-acetyl-2-(pyridin-2-yl)phenyl]carbamate (3l)**



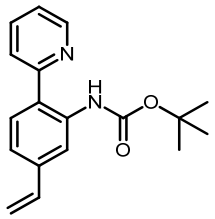
White solid; m.p. 104 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.95 (s, 1H), 8.77 – 8.64 (m, 1H), 7.86 (td, *J* = 7.8, 1.9 Hz, 1H), 7.74 (ddd, *J* = 8.2, 2.5, 1.2 Hz, 1H), 7.68 (t, *J* = 1.9 Hz, 2H), 7.34 – 7.30 (m, 1H), 2.67 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.1, 157.3, 153.2, 147.8, 138.2, 137.9, 137.7, 129.1, 128.8, 123.3, 122.4, 121.2, 120.8, 80.2, 28.47, 26.9; IR (diamond) 3207, 2994, 2974, 2922, 2852, 1753, 1700, 1632, 1609, 1319, 1230, 1118, 1008, 932 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{18}H_{20}N_2O_3$ $[M]^+$: 312.1474, found: 312.1474.

**_tert_-Butyl [5-formyl-2-(pyridin-2-yl)phenyl]carbamate (3m)**



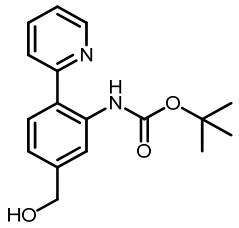
White solid; m.p. 121 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 10.06 (s, 1H), 8.89 (s, 1H), 8.71 (d, J = 4.9 Hz, 1H), 7.88 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.63 (dd, J = 8.0, 1.5 Hz, 1H), 7.35 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 1.54 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.2, 157.2, 153.2, 147.9, 139.0, 137.8, 137.1, 129.9, 129.6, 123.5, 123.4, 122.6, 121.1, 80.4, 28.3; IR (diamond) 3207, 2974, 2922, 2853, 1753, 1700, 1609, 1580, 1368, 1230, 1118, 1008, 912, 762 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{18}N_2O_3$ $[M]^+$: 298.1317, found: 298.1317.

***tert*-Butyl [2-(pyridin-2-yl)-5-vinylphenyl]carbamate (3n)**



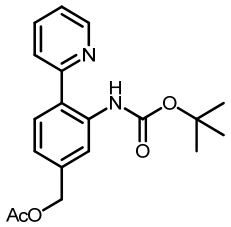
Colorless viscous liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.65 (ddd, J = 4.8, 1.9. 0.9 Hz, 1H), 8.41 (s, 1H), 7.82-7.71 (m, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.26-7.22 (m, 1H), 7.16 (dd, J = 8.1, 1.4 Hz, 1H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.7 Hz, 1H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 147.6, 139.2, 138.5, 137.4, 136.5, 129.1, 124.4, 122.7, 121.5, 119.7, 118.2, 115.0, 79.7, 28.4; IR (diamond) 3213, 3045, 2928, 2913, 2850, 1712, 1590, 1566, 1431, 1412, 1345, 1286, 1132, 1088, 945, 756 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{18}H_{20}N_2O_2$ $[M]^+$: 296.1525, found: 296.1528.

***tert*-Butyl [5-(hydroxymethyl)-2-(pyridin-2-yl)phenyl]carbamate (3o)**



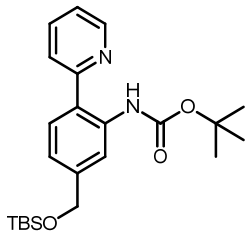
Viscous liquid; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.77 – 8.57 (m, 1H), 8.29 (s, 1H), 7.80 (td, *J* = 7.8, 1.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 9.1, 7.5 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.72 (s, 2H), 2.27 (s, 1H), 1.51 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.4, 147.6, 143.0, 138.2, 137.4, 129.2, 124.4, 122.8, 121.6, 120.6, 118.4, 79.8, 65.0, 28.3; IR (diamond) 3350, 3115, 3064, 2984, 2927, 2853, 1677, 1586, 1492, 1475, 1411, 1399, 1370, 1340, 1253, 1153, 1019, $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_3$ $[M]^+$: 300.1474, found: 300.1477.

**3-[(*tert*-Butoxycarbonyl)amino]-4-(pyridin-2-yl)benzyl acetate (3p)**



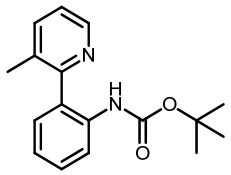
Viscous liquid; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.66 (dd, *J* = 4.5, 1.3 Hz, 1H), 8.36 (s, 1H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.13 (s, 2H), 2.13 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.9, 158.0, 153.3, 147.7, 138.4, 137.7, 137.5, 129.2, 124.9, 122.9, 121.8, 121.7, 119.8, 79.9, 66.2, 28.4, 21.0; IR (diamond) 3244, 3002, 2977, 2930, 1721, 1690, 1687, 1585, 1565, 1516, 1470, 1238, 1132, 1078, 954 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{19}H_{22}N_2O_4$ $[M]^+$: 342.1580, found: 342.1577.

***tert*-Butyl [5-(*tert*-butyldimethylsilyloxymethyl)-2-(pyridin-2-yl)phenyl]carbamate (3q)**



Viscous liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.65 (d, J = 4.4 Hz, 1H), 8.23 (s, 1H), 7.80 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.24 (ddd, J = 7.5, 4.4, 1.0 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 4.41 (s, 2H), 0.97 (s, 9H), 0.13 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.3, 147.6, 143.6, 137.9, 137.4, 129.0, 123.8, 122.7, 121.4, 119.6, 117.4, 79.7, 64.8, 28.4, 25.9, 18.4, -5.3; IR (diamond) 3211, 1931, 2976, 1720, 1616, 1585, 1509, 1449, 1418, 1236, 1163, 1013, 965, 765 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{23}H_{34}N_2O_3Si$ $[M]^+$: 414.2339, found: 414.2342.

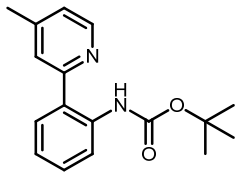
***tert*-Butyl [2-(3-methylpyridin-2-yl)phenyl]carbamate (3r)**



White solid; m.p. 89 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 2.8 Hz, 1H), 8.16 (d, J = 4.0 Hz, 1H), 7.85 (s, 1H), 7.68 – 7.66 (m, 1H), 7.39 – 7.35 (m, 1H), 7.27 – 7.21 (m, 2H), 7.11 – 7.07 (m, 1H), 2.28 (s, 3H), 1.46 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.6, 152.9, 146.7, 139.5, 136.2, 132.5, 129.9, 129.1, 128.4, 122.5, 122.2, 120.8, 80.1,

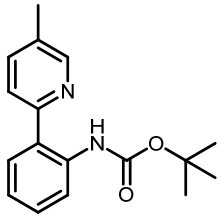
28.3, 19.8; IR (diamond) 3280, 3213, 3090, 3063, 2954, 1728, 1632, 1587, 1524, 1475, 1442, 1215, 1077, 1021, 942 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1524.

**_tert_-Butyl [2-(4-methylpyridin-2-yl)phenyl]carbamate (3s)**



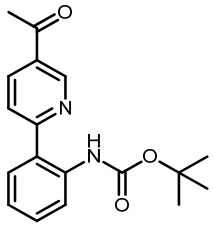
Colorless viscous liquid; $^1H$ NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 8.51 (d, J = 5.4 Hz, 1H), 8.30 (t, *J* = 8.2 Hz, 1H), 7.58 dd, J = 7.8, 1.1 Hz, 1H), 7.50 (s, 1H), 7.37 (dt, J = 7.8, 1.4 Hz, 1H), 7.09-7.06 (m 2H), 2.42 (s, 3H), 1.51 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.1, 153.3, 148.6, 147.4 , 138.0, 129.7, 128.9, 125.6, 123.8, 122.7, 122.1, 120.2, 79.7, 28.3, 21.4; IR (diamond) 3108, 3052, 2922, 2851, 1709, 1586, 1521, 1450, 1434, 1343, 1209, 1120, 735 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1528.

**_tert_-Butyl [2-(5-methylpyridin-2-yl)phenyl]carbamate (3t)**



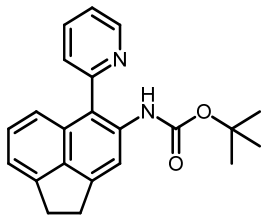
White solid; m.p. 95 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.49 (dd, *J* = 1.6, 0.7 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 17.3, 7.9 Hz, 3H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 1.51 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 155.6, 153.3, 147.9, 138.1, 137.9, 131.2, 129.5, 128.7, 125.4, 122.4, 122.1, 120.2, 79.6, 28.4, 18.1; IR (diamond) 3195, 3114, 3002, 2976, 2934, 1715, 1614, 1585, 1471, 1422, 1235, 1155, 935, 746 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M]^+$: 284.1525, found: 284.1527.

***tert*-Butyl [2-(5-acetylpyridin-2-yl)phenyl]carbamate (3u)**



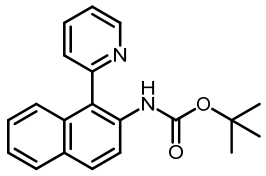
White solid; m.p. 106 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 9.20 (d, J = 2.3 Hz, 1H), 8.36 – 8.32 (m, 2H), 7.81 (d, J = 8.6 Hz, 1H), 7.65 (dd, J = 7.8, 0.9 Hz, 1H), 7.43 (dt, J = 8.5, 1.2 Hz, 1H), 7.13 – 7.09 (m, 1H), 2.69 (s, 3H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.1, 162.1, 153.2, 148.1, 138.7, 136.8, 131.0, 129.8, 129.3, 124.2, 122.6, 122.3, 120.6, 80.1, 28.3, 26.7; IR (diamond) 3245, 2976, 3019, 2926, 1728, 1729, 1583, 1565, 1516, 1470, 1238, 1078, 923, 768 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{18}H_{20}N_2O_3$ $[M]^+$: 312.1474, found: 312.1476.

***tert*-Butyl [5-(pyridin-2-yl)-1,2-dihydroacenaphthylen-4-yl]carbamate (3v)**



White solid; m.p. 142 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.81 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 8.22 (s, 1H), 7.87 – 7.83 (m, 1H), 7.64 – 7.61 (m, 1H), 7.461 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 6.8 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.19 (d, J = 6.8 Hz, 1H), 3.41 (s, 4H), 1.48 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.3, 149.4, 147.7, 146.2, 136.6, 136.4, 135.9, 129.9, 128.6, 126.9, 121.9, 119.8, 118.0, 114.2, 80.0, 30.4, 30.3, 28.3; IR (diamond) 3243, 2954, 2928, 2884, 2855, 1720, 1583, 1529, 1480, 1239,m 1155, 1097, 835 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{22}H_{22}N_2O_2$ $[M]^+$: 346.1681, found: 346.1682.

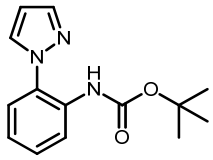
***tert*-Butyl [1-(pyridin-2-yl)naphthalen-2-yl]carbamate (3w)**



White solid; m.p. 149 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.84 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 8.34 (d, J = 8.9 Hz, 1H), 8.16 (s, 1H), 7.90 – 7.86 (m, 2H), 7.84 – 7.82 (m, 1H), 7.58 – 7.50 (m, 2H), 7.40 – 7.33 (m, 3H), 1.47 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.1, 153.0, 149.9, 136.7, 134.1 , 131.9, 130.4, 129.4, 128.1, 127.3, 126.5, 124.7, 124.3, 122.4, 120.5, 80.3, 28.3; IR (diamond) 3115, 3064, 2984, 2927, 2853, 1712, 1586, 1492,

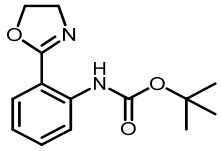
1475, 1411, 1399, 1370, 1340, 1253, 1153, 1019, 927, 812, 670, 563 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{20}H_{20}N_2O_2$ $[M]^+$: 320.1525, found: 320.1525.

**_tert_-Butyl [2-(1*H*-pyrazol-1-yl)phenyl]carbamate (10)**



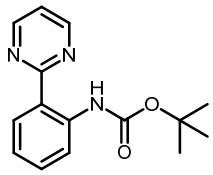
White solid; m.p. 116 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.30 (d, $J$ = 8.2 Hz, 1H), 7.81 (d, $J$ = 1.9 Hz, 1H), 7.76 (d, $J$ = 2.3 Hz, 1H), 7.33 (t, $J$ = 7.9 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.07 (t, $J$ = 8.2 Hz, 1H), 6.49 (s, 1H), 1.49 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 152.9, 141.2, 132.6, 130.2, 128.6, 128.1, 122.9, 122.6, 121.2, 106.9, 80.4, 28.3; IR (diamond) 3269, 3146, 2950, 2935, 2930, 2873, 1713, 1599, 1530, 1509, 1391, 1229, 1152, 1044, 742 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{14}H_{17}N_3O_2$ $[M]^+$: 259.1321, found: 259.1319.

**_tert_-Butyl [2-(4,5-dihydrooxazol-2-yl)phenyl]carbamate (11)**



White solid; m.p. 119 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.44 (d, $J$ = 8.5 Hz, 1H), 7.82 (dd, $J$ = 7.9, 1.6 Hz, 1H), 7.42 (t, $J$ = 1.4 Hz, 1H), 6.98 (s, 1H), 4.35 (d, $J$ = 9.4 Hz, 2H), 4.15 (t, $J$ = 9.5 Hz, 2H), 1.54 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.4, 153.2, 140.5, 132.3, 129.2, 120.8, 117.9, 112.4, 80.1, 66.0, 54.8, 28.3; IR (diamond) 3062, 2977, 2923, 2857, 1724, 1590, 1491, 1454, 1386, 1154, 1091, 754 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{14}H_{18}N_2O_2$ $[M]^+$: 262.1317, found: 262.1320.

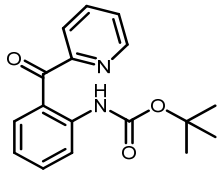
**_tert_-Butyl [2-(pyrimidin-2-yl)phenyl]carbamate (12)**



White solid; m.p. 80 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.84 (d, J = 4.8 Hz, 1H), 8.53 (dd, J = 8.0, 1.6 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.20 (t, J = 4.8 Hz, 1H), 7.13 – 7.09 (m, 1H), 1.55 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.2, 156.4, 153.3, 140.3, 131.9, 130.6, 122.2, 121.7, 119.5, 118.2, 79.9, 28.4; IR (diamond)

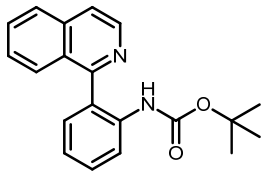
3130, 3029, 2974, 2929, 1721, 1589, 1577, 1514, 1466, 1278, 1246, 1159, 1130, 1072, 744 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{15}H_{17}N_3O_2$ $[M]^+$: 271.1321, found: 271.1324.

**_tert_-Butyl (2-picolinoylphenyl)carbamate (13)**



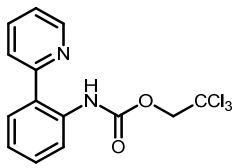
White solid; m.p. 98 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.71 (d, $J$ = 4.6 Hz, 1H), 8.46 (d, $J$ = 8.5 Hz, 1H), 7.94 – 7.81 (m, 2H), 7.73 (d, $J$ = 7.9 Hz, 1H), 7.54 (t, $J$ = 7.9 Hz, 1H), 7.47 (d, $J$ = 6.5 Hz, 1H), 7.00 (t, $J$ = 7.6 Hz, 1H), 1.53 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.8, 156.2, 152.9, 148.6, 142.4, 137.0, 134.8, 134.6, 125.8, 124.5, 121.0, 120.6, 119.5, 80.6, 28.3; IR (diamond) 3223, 3064, 2977, 2931, 2821, 1725, 1719, 1696, 1581, 1525, 1470, 1430, 1366, 1269, 1153, 1048, 785 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{17}H_{18}N_2O_3$ $[M]^+$: 298.1317, found: 298.1314.

**_tert_-Butyl [2-(isoquinolin-1-yl)phenyl]carbamate (14)**



Colorless liquid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, $J$ = 5.6 Hz, 1H), 8.31 (s, 1H), 8.27 (d, $J$ = 8.4 Hz, 1H), 8.02 (d, $J$ = 8.5 Hz, 1H), 7.88 (d, $J$ = 8.2 Hz, 1H), 7.75 – 7.63 (m, 2H), 7.53 (ddd, $J$ = 8.2, 6.6, 1.2 Hz, 1H), 7.46 (ddd, $J$ = 8.7, 7.5, 1.6 Hz, 1H), 7.38 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.15 (td, $J$ = 7.5, 1.1 Hz, 1H), 1.42 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.7, 152.9, 141.5, 137.4, 136.8, 131.5, 130.4, 129.5, 127.7, 127.5, 127.4, 127.1, 126.9, 122.0, 121.1, 120.3, 80.1, 28.2; IR (diamond) 3285, 3057, 2978, 2930, 1727, 1639, 1579, 1517, 1447, 1248, 1120, 935, 748 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{20}H_{20}N_2O_2$ $[M]^+$: 320.1525, found: 320.1523.

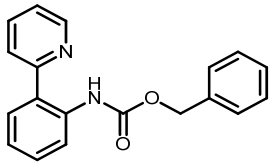
**2,2,2-Trichloroethyl [2-(pyridin-2-yl)phenyl]carbamate (5)**



White solid; m.p. 67 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.74 – 8.58 (m, 1H), 8.30 (d, $J$ = 8.4 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.76 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.69

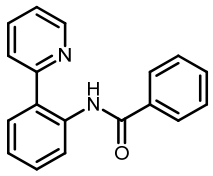
(dd, $J$ = 7.9, 1.5 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.33 – 7.24 (m, 1H), 7.22 – 7.11 (m, 1H), 4.83 (s, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 157.8, 152.1, 147.5, 137.7, 137.2, 130.1, 128.8, 125.8, 123.2, 122.7, 121.9, 120.6, 96.6, 74.3; IR (diamond) 3232, 3183, 3085, 2926, 3011, 1692, 1585, 1522, 1473, 1437, 1419, 1307, 1280, 1240, 995, 784 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{14}H_{11}Cl_3N_2O_2$ $[M+H]^+$: 344.9964, found: 344.9965.

**Benzyl [2-(pyridin-2-yl)phenyl]carbamate (6)**



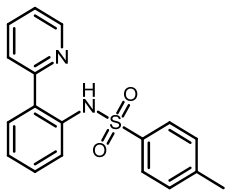
White solid; m.p. 78 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1H), 8.61(ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 8.36 (d, J = 8.1 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.61 (dd, J = 7.9, 1.3 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.23 – 7.20 (m, 1H), 7.13 – 7.09 (m, 1H), 5.20 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.8, 147.6, 137.7, 137.5, 136.6, 129.9, 128.9, 128.4, 128.1, 128.0, 122.9, 122.6, 121.7, 120.4, 66.5; IR (diamond) 3217, 3115, 2978, 1933, 1720, 1584, 1529, 1470, 1427, 1341, 1226, 1158, 759 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{19}H_{16}N_2O_2$ $[M]^+$: 304.1212, found: 304.1211.

***N*-[2-(Pyridin-2-yl)phenyl]benzamide (7)**



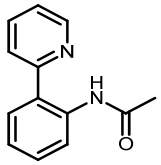
White solid; m.p. 109 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 13.30 (s, 1H), 8.80 (d, $J$ = 8.3 Hz, 1H), 8.67 (d, $J$ = 4.5 Hz, 1H), 8.11 – 7.91 (m, 2H), 7.89 – 7.81 (m, 1H), 7.79 (dd, $J$ = 7.9, 2.1 Hz, 1H), 7.72 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.57 – 7.43 (m, 4H), 7.30 – 7.26 (m, 1H), 7.23 – 7.17 (m, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.5, 158.3, 147.3, 138.1, 137.8, 135.8, 131.5, 130.2, 128.7, 128. 6, 127.3, 125.5, 123.5, 122.9, 121.9, 121.9; IR (diamond) 3321, 3050, 3012, 2974, 2918, 1726, 1632, 1605, 1519, 1446, 1273, 1244, 1148, 936, 750 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{18}H_{14}N_2O$ $[M]^+$: 274.1106, found: 274.1107.

**4-Methyl-*N*-[2-(pyridin-2-yl)phenyl]benzenesulfonamide (8)**



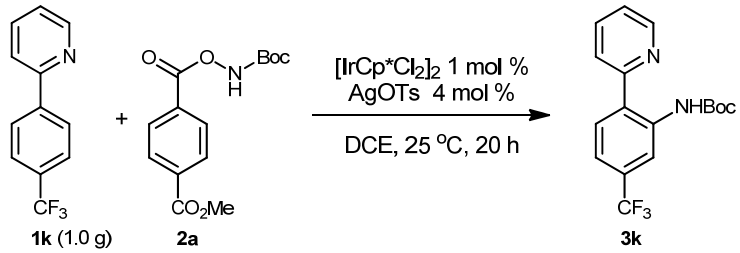
Colorless viscous liquid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.82 – 8.45 (m, 1H), 7.70 (td, *J* = 7.5, 1.9 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.24 (dd, *J* = 13.2, 5.9 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.1, 147.32, 142.9, 137.4, 136.8, 136.5, 130.1, 129.1, 128.4, 127.4, 126.7, 124.6, 123.3, 122.2, 122.0, 21.4.; IR (diamond) 3138, 3070, 3029, 2973, 2850, 1723, 1590, 1491, 1453, 1386, 1154, 1091, 754 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{18}H_{16}N_2O_2S$ $[M+Na]^+$: 347.0830, found: 347.0821.

***N*-[2-(Pyridin-2-yl)phenyl]acetamide (9)**



Colorless liquid; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.63 (dt, *J* = 4.8, 1.3 Hz, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 7.83 (td, *J* = 7.8, 1.9 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.5, 7.4, 1.6 Hz, 1H), 7.35 (d, *J* = 4.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 2.17 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 168.5, 158.3, 147.4, 137.7, 137.5, 129.9, 128.8, 128.5, 128.0, 125.5, 123.4, 123.1, 121.8, 121.8, 25.2; IR (diamond) 3163, 3106, 2976, 2034, 2881, 1722, 1710, 1634, 1587, 1569, 1447, 1372, 1239, 1153, 1044, 748 cm$^{-1}$; HRMS (EI) m/z calcd. for $C_{13}H_{12}N_2O$ $[M]^+$: 212.0950, found: 212.0950.

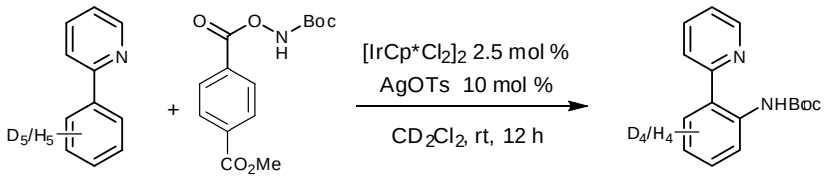
## 5. Scale-up Reaction




In a 100 mL round bottom flask with a stirbar were added 2-[4-(trifluoromethyl)phenyl]pyridine (**1k**, 1.0 g, 4.48 mmol), **2a** (1.32 g, 4.48 mmol), $[IrCp^*Cl_2]_2$ (35.7 mg, 1.0 mol %), AgOTs (50.0 mg, 4.0 mol %) and 1,2-dichloroethane (10 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 20 h, filtered through a pad of celite and then washed with $CH_2Cl_2$ (20 mL x 3). Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product **3k** (1.19 g, 78%).

## 6. Experimental Procedures of the Mechanistic Studies

### 6.1. Study of Kinetic Isotope Effects (Eq 2)




1.2 eq. each **2a**

To a J. Young valve NMR tube was added 2-phenylpyridine (**1a**, 18.6 mg, 0.12 mmol) or 2-phenylpyridine-$d_5$ (**1a**-$d_5$, 0.12 mmol), **2a** (0.1 mmol), [IrCp*$Cl_2$]$_2$ (1.6 mg, 2.0 mol %), AgOTs (3.1 mg, 8.0 mol %), 1,1,2,2-tetrachloroethane (16.8 mg, 0.1 mmol) and dichloromethane-$d_2$ (0.48 mL). The crude yield was measured at every 10 min over 45 min at room temperature. The reaction rate was obtained by plotting each point to obtain ***KIE*** value to be 1.19.

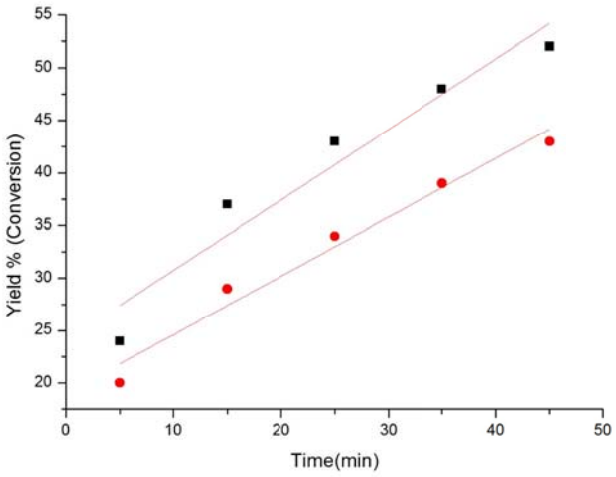
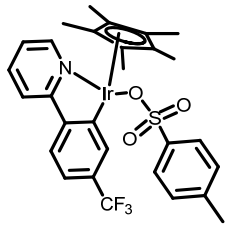



**Figure S1**. Reaction rates of 2-phenylpyridine (**1a**) and 2-phenylpyridine-$d_5$ (**1a**-$d_5$).

### 6.2. Preparation of cyclometalated complex 15 and 16 (Eq 3)

**Synthesis of complex 15**: A solution of [IrCp*$Cl_2$]$_2$ (99.5 mg, 0.125 mmol), 2-[4-(trifluoromethyl)phenyl]pyridine (55.8 mg, 0.250 mmol), silver tosylate (139.5 mg, 0.5 mmol), and lithium carbonate (9.3 mg, 0.125 mmol) in 1,2-dichloroethane (5.0 mL) was stirred for 24 h at room temperature under argon atmosphere. The reaction mixture was filtered through a cake of celite with 1,2-dichloroethane (3 mL x 3) under argon atmosphere, taken out to air, and concentrated in vacuo, to obtain the cyclometallated complex **15** (80 mg, 44 %).

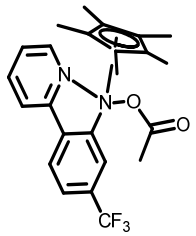
**(2-Pyridyl-5-trifluoromethylphenyl)(1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)(4-methylphenylsulphonoxy)iridium (15)**



Yellow solid; m.p. 197 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 5.6 Hz, 1H), 8.20 (s, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 16.0, 8.0 Hz, 2H), 6.79 (d, *J* = 6.9 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 2.17 (s, 3H), 1.66 (s, 15H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.5, 152.6, 148.7, 141.5, 139.1, 138.1, 132.3, 132.2, 127.8, 125.5, 123.3, 123.0, 122.9, 119.7, 119.7, 118.9, 88.1, 77.3, 77.0, 76.7, 21.1, 9.1; IR (diamond) 3057, 2994, 2923, 2898, 2845, 1630, 1602, 1592, 1487, 1378, 1230, 1120, 1106, 1071, 756 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{29}H_{29}F_3N_2O_3S$ $[M - OTs]^+$: 542.1851, found: 542.1853.

**Synthesis of complex 16**: A solution of $[IrCp^*Cl_2]_2$ (53.5 mg, 0.067 mmol), 2-[4-(trifluoromethyl)phenyl]pyridine (30.0 mg, 0.134 mmol), silver acetate (44.8 mg, 0.269 mmol), and sodium acetate (11.0 mg, 0.134 mmol) in dichloromethane (4.0 mL) was stirred for 12 h at room temperature under argon atmosphere. The reaction mixture was filtered through a cake of celite with dichloromethane (3 mL x 3) and concentrated under reduced pressure. The residue was purified by column chromatography on triethylamine-neutralized silica gel (*n*-hexane/EtOAc) to obtain cyclometallated complex **16** (58.0 mg, 72%).

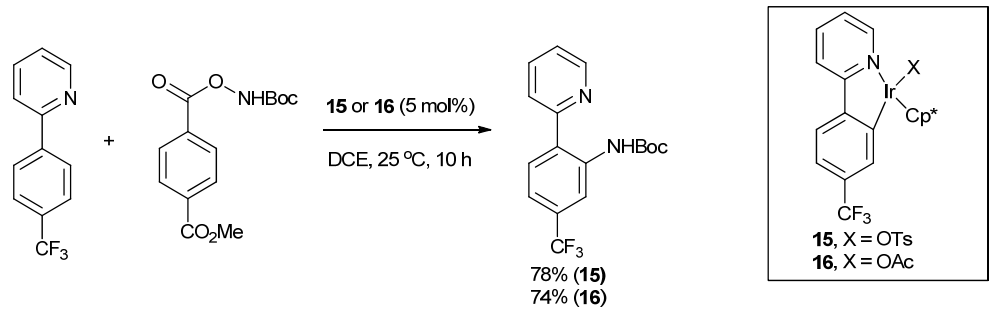
**(2-Pyridyl-5-trifluoromethylphenyl)(1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)(acetoxy)iridium (16)**



Yellow crystal; m.p. 248 °C; $^{1}$H NMR (600 MHz, $CDCl_3$) δ 9.29 – 9.14 (m, 1H), 8.37 – 8.19 (m, 1H), 7.80 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.70 (td, *J* = 7.8, 1.4 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.16 (ddd, *J* = 7.2, 5.7, 1.4 Hz, 1H), 1.71 (s, 3H), 1.65 (s, 15H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.6, 166.2, 163.7, 153.7, 148.5, 137.6, 131.8, 131.8, 131.1, 130.9, 125.5, 123.6, 123.2, 122.5, 119.3, 119.3, 118.8, 87.5, 23.3, 9.0; IR (diamond) 3065, 2954, 2917,

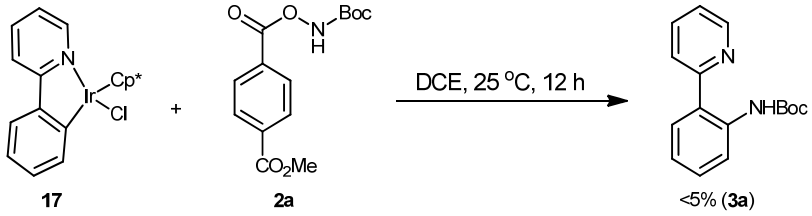
2853, 1718, 1620, 1606, 1592, 1477, 1318, 1159, 1116, 1071, 783 $cm^{-1}$; HRMS (EI) m/z calcd. for $C_{24}H_{25}F_3N_2O_2$ $[M - OAc]^+$: 542.1851, found: 542.1854.

### 6.3. Amidation Reaction Using Cyclometalated Complexes 15 or 16 (Eq 4)




To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added amidating reagent (**2a**, 29.5 mg, 0.1 mmol), 2-[4-(trifluoromethyl)phenyl]pyridine (**1k**, 26.8 mg, 0.12 mmol), complex **15** or **16** (5 mol %) and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred for 10 h at 25 °C. Upon completion, the reaction mixture was filtered through a short pad of celite, washed with EtOAc (4 mL x 3), and then solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product **3k** with the indicated yields.

### 6.4. Amidation Reaction Using Iridacycle 17 in the Absence of Silver Additives.




To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added amidating reagent **2a** (29.5 mg, 0.1 mmol), **17** (51.7 mg, 1.0 eqiv) and 1,2-dichloroethane (0.5 mL). The reaction mixture was stirred for 12 h at 25 °C. The reaction mixture was filtered through a short pad of silica, washed with $CH_2Cl_2$ (4 mL x 5), and organic solvent was removed under reduced pressure. Conversion (<5%) was determined by $^1H$ NMR using $C_2H_2Cl_4$ as an internal standard.

### 7. References

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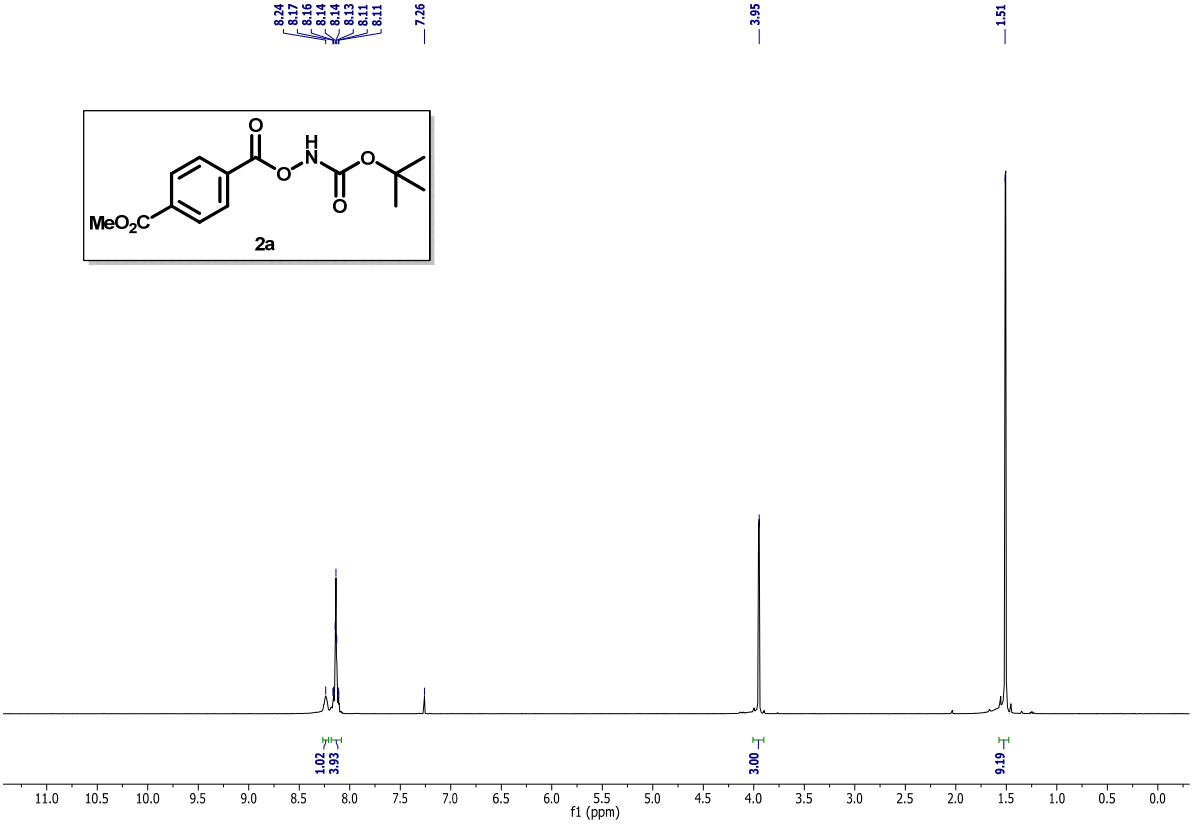
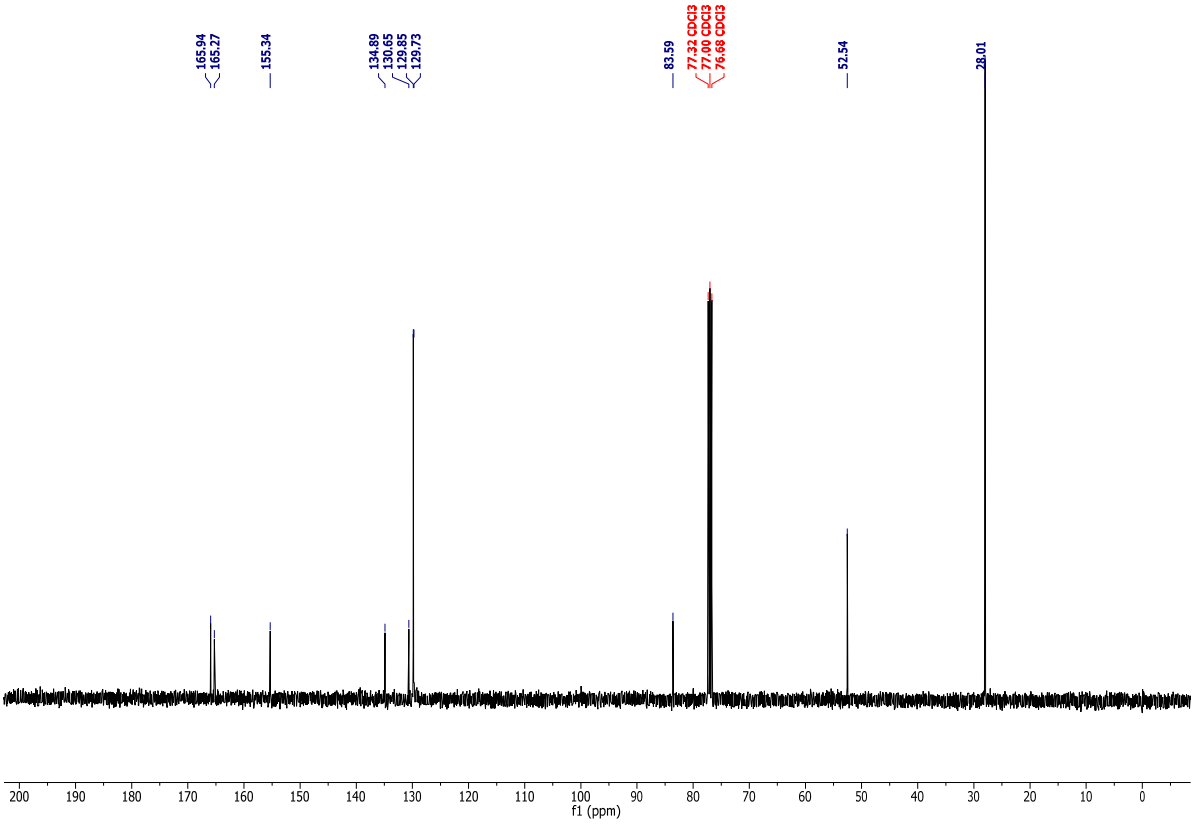
# *Appendix I*

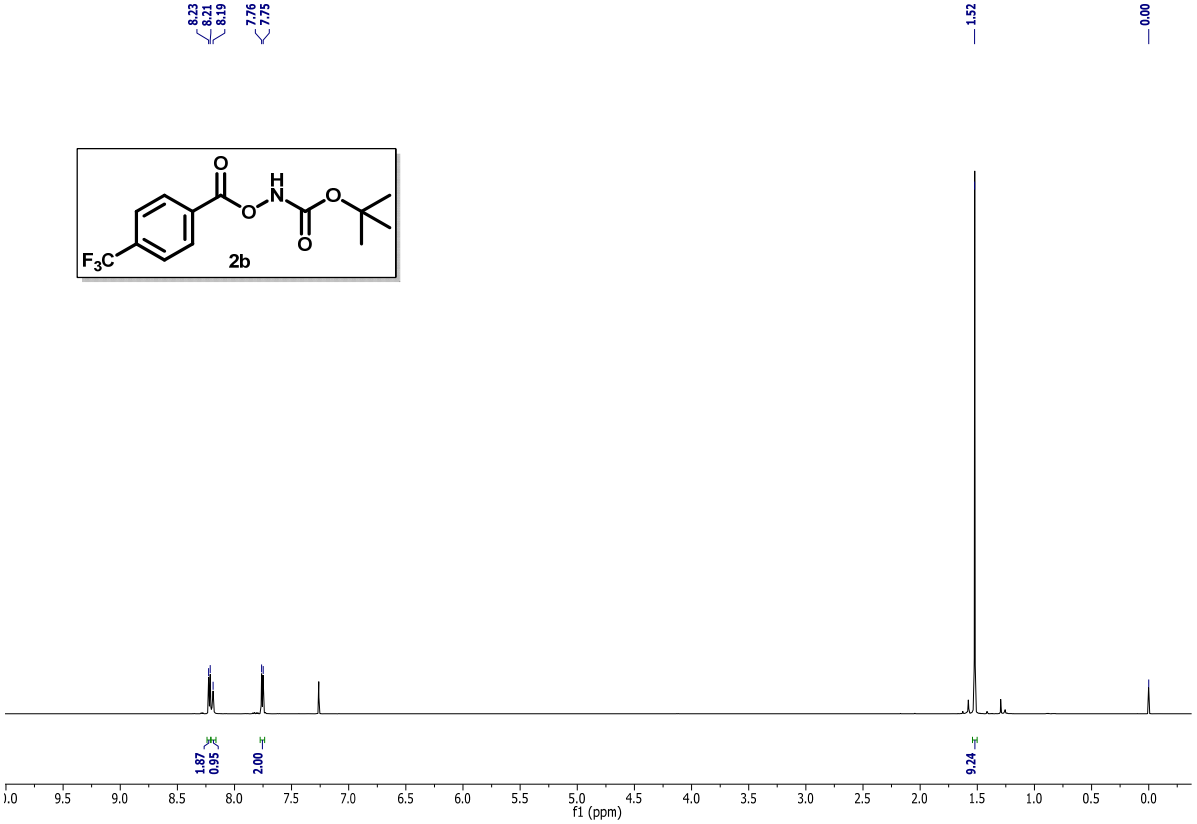
## Spectral Copies of $^{1}H$ and $^{13}C$ NMR of Compounds Obtained in this study

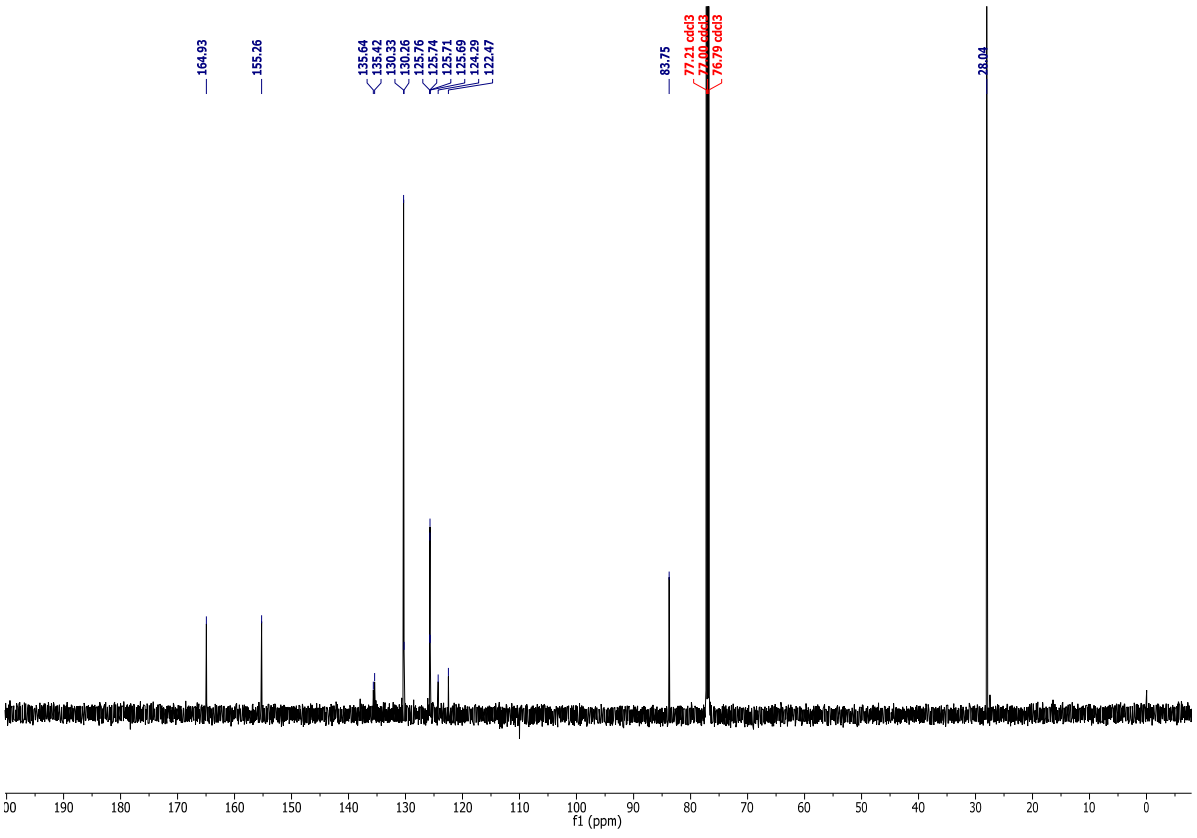
## Methyl 4-[{(tert-butoxycarbonyl)amino}oxycarbonyl]benzoate (2a)



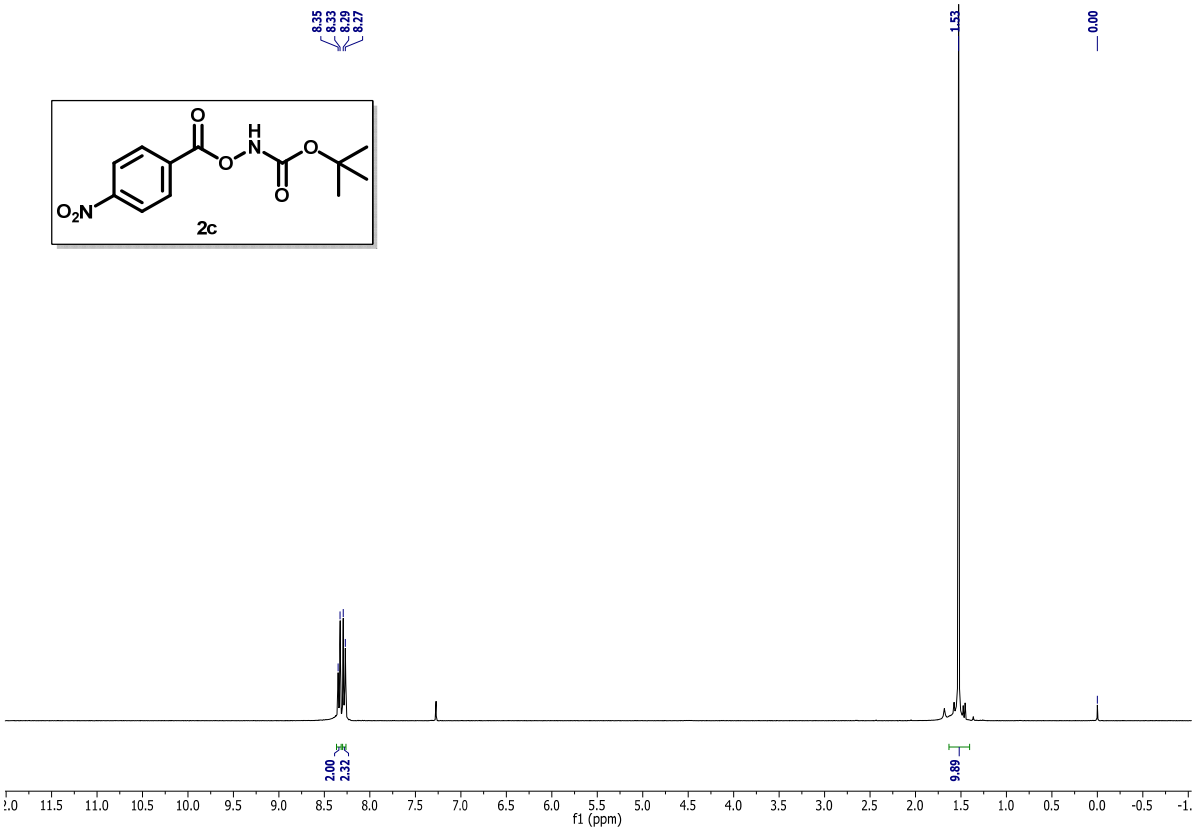



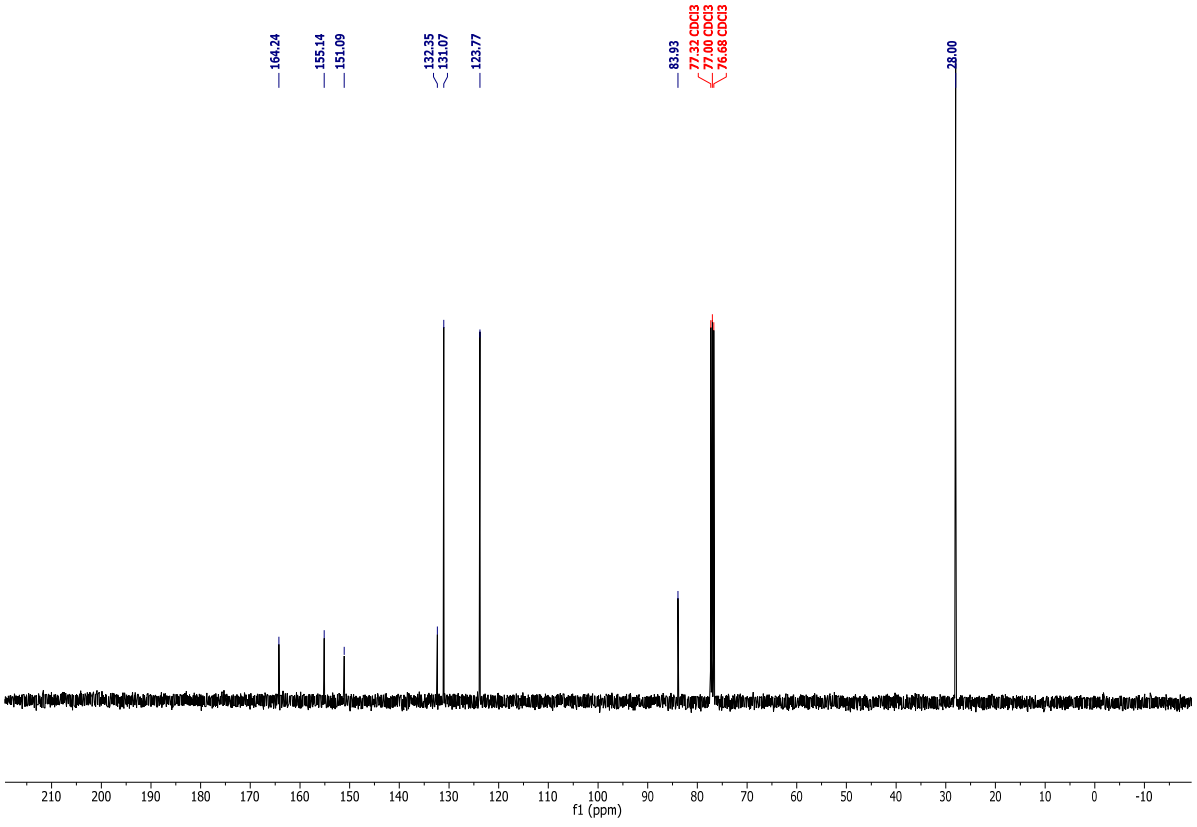
## *tert*-Butyl (4-trifluoromethylbenzoyl)oxycarbamate (2b)



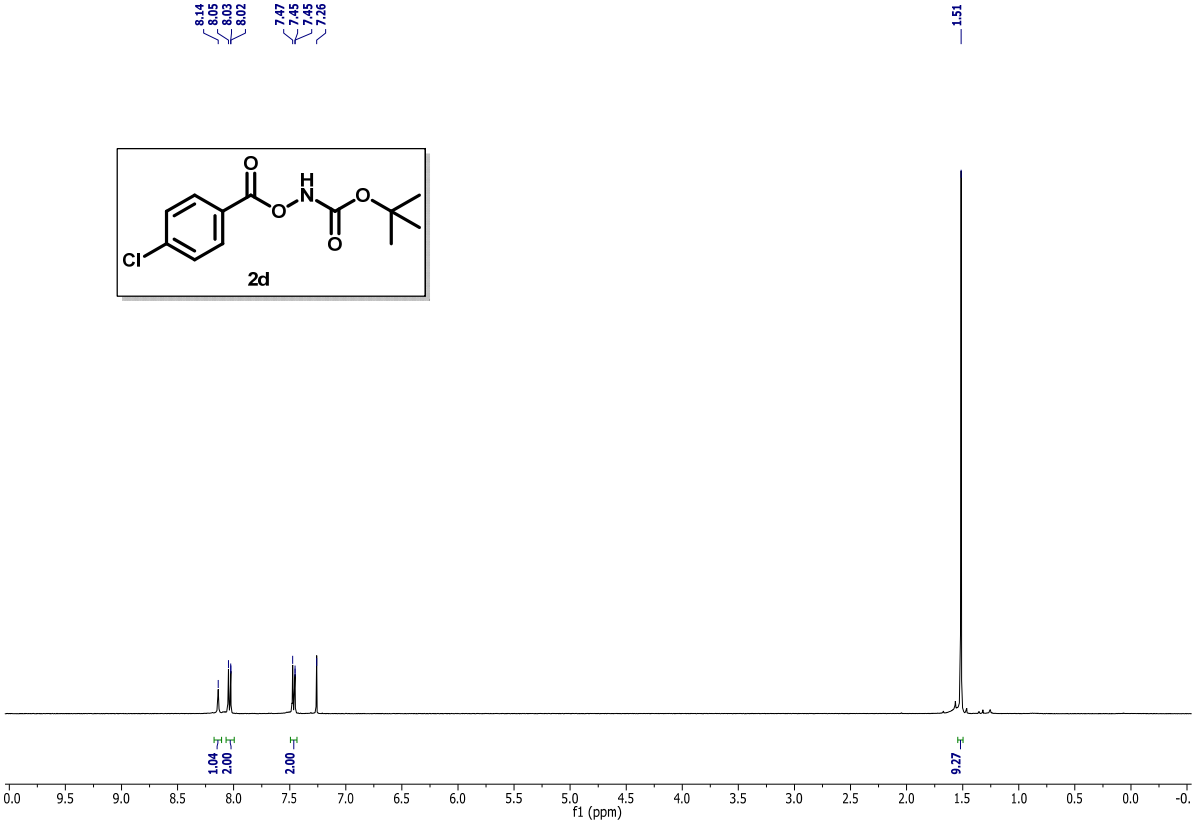



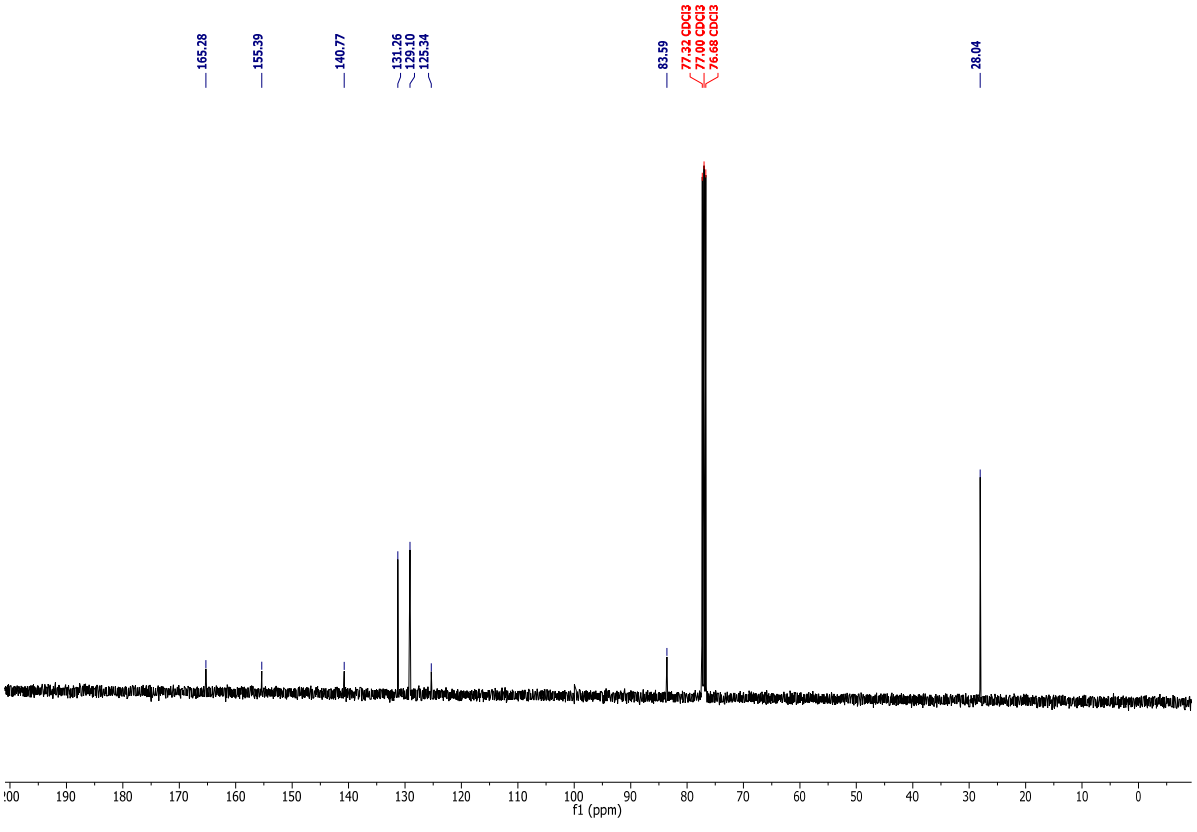
## *tert*-Butyl (4-nitrobenzoyl)oxycarbamate (2c)



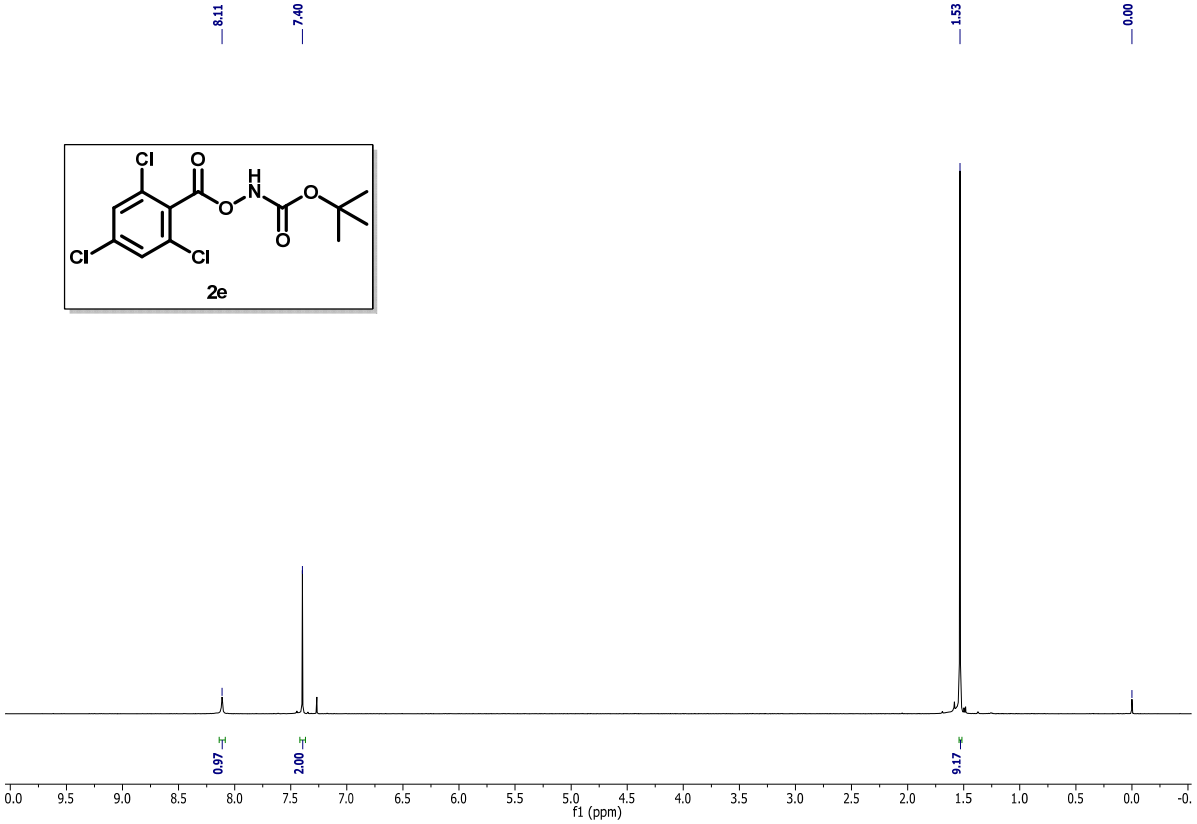



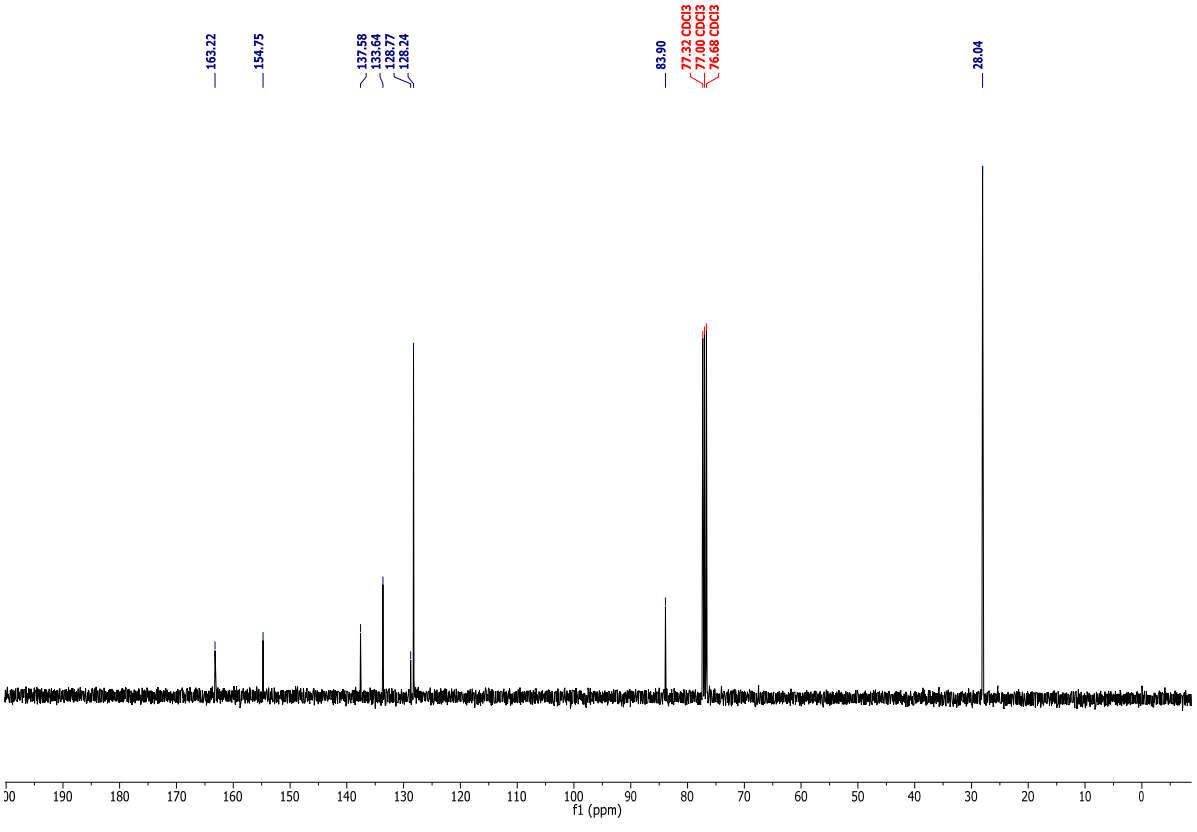
## *tert*-Butyl (4-chlorobenzoyl)oxycarbamate (2d)



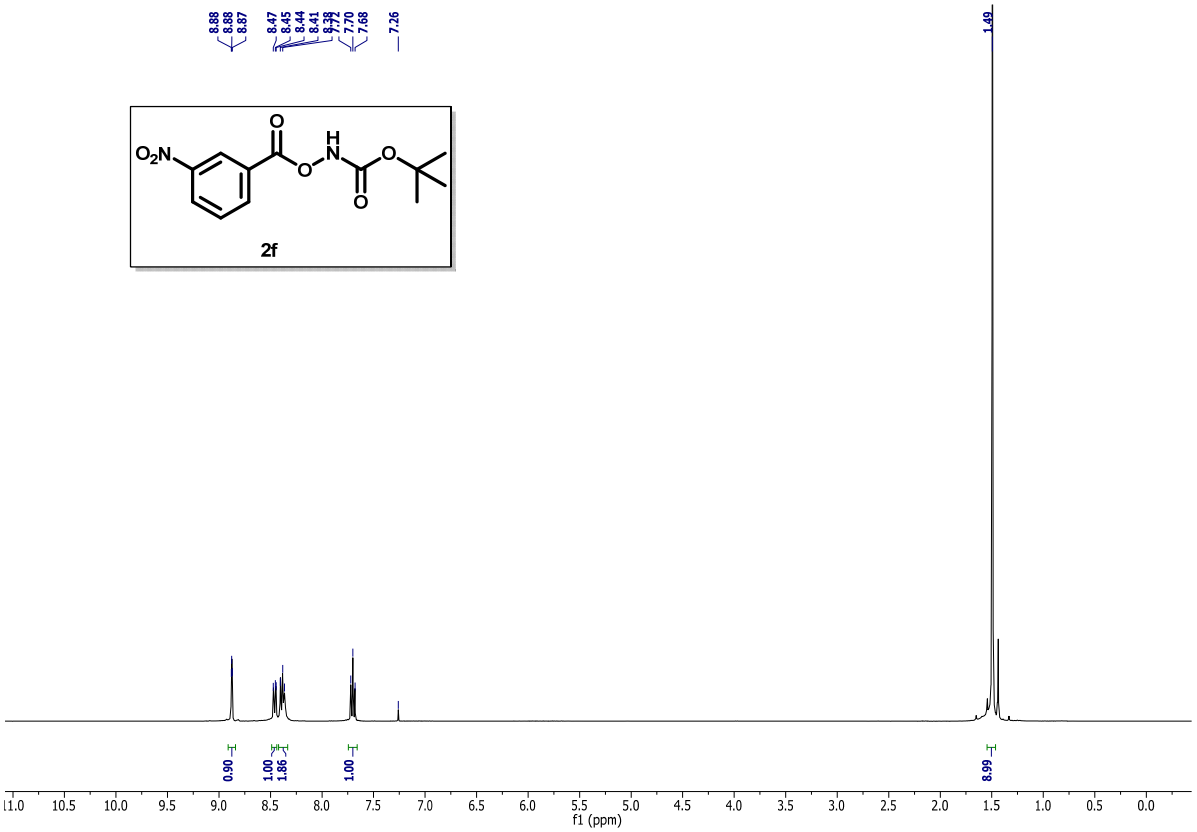



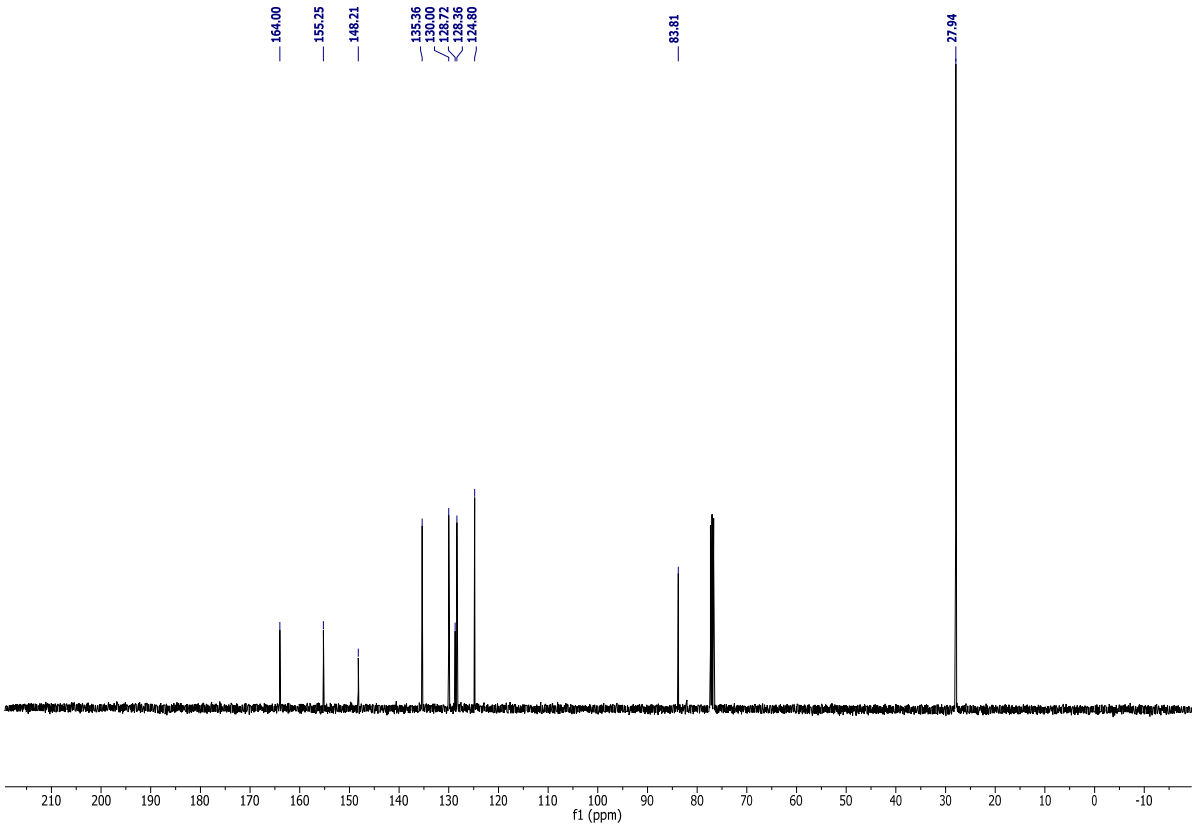
## *tert*-Butyl (2,4,6-trichlorobenzoyl)oxycarbamate (2e)



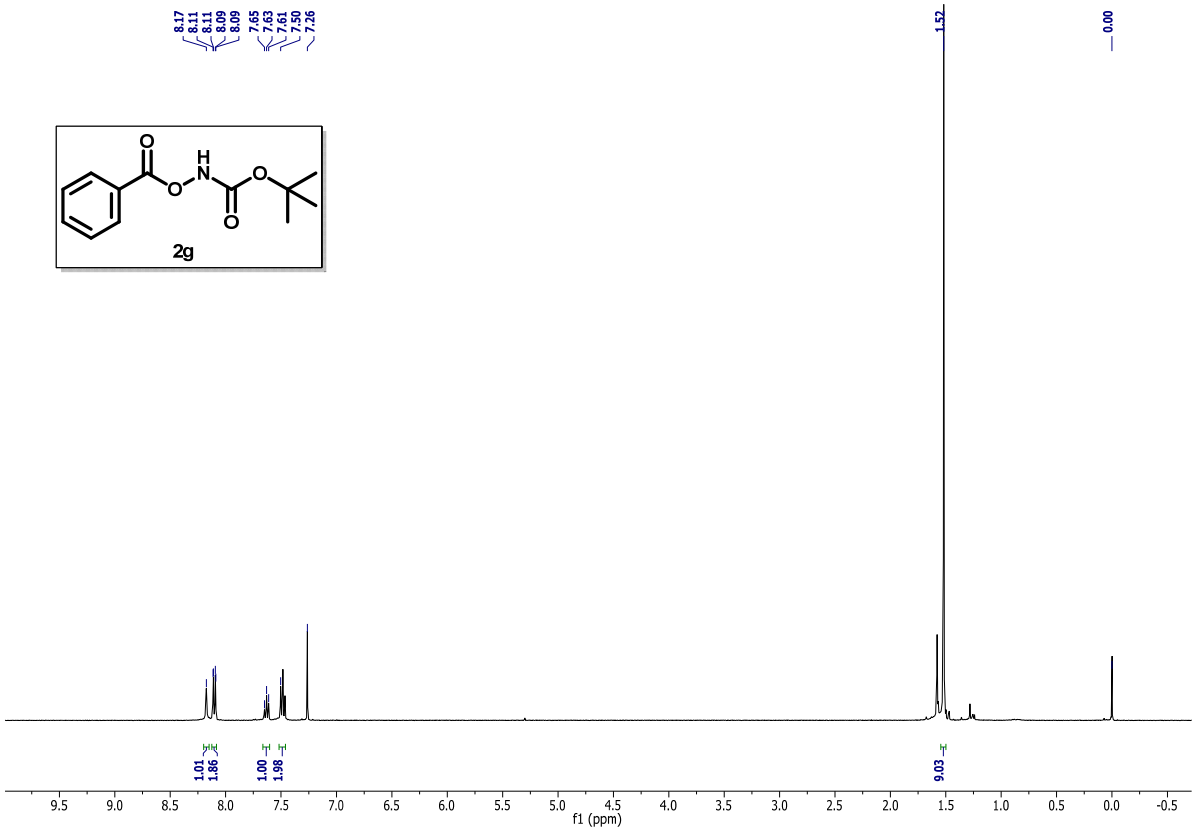



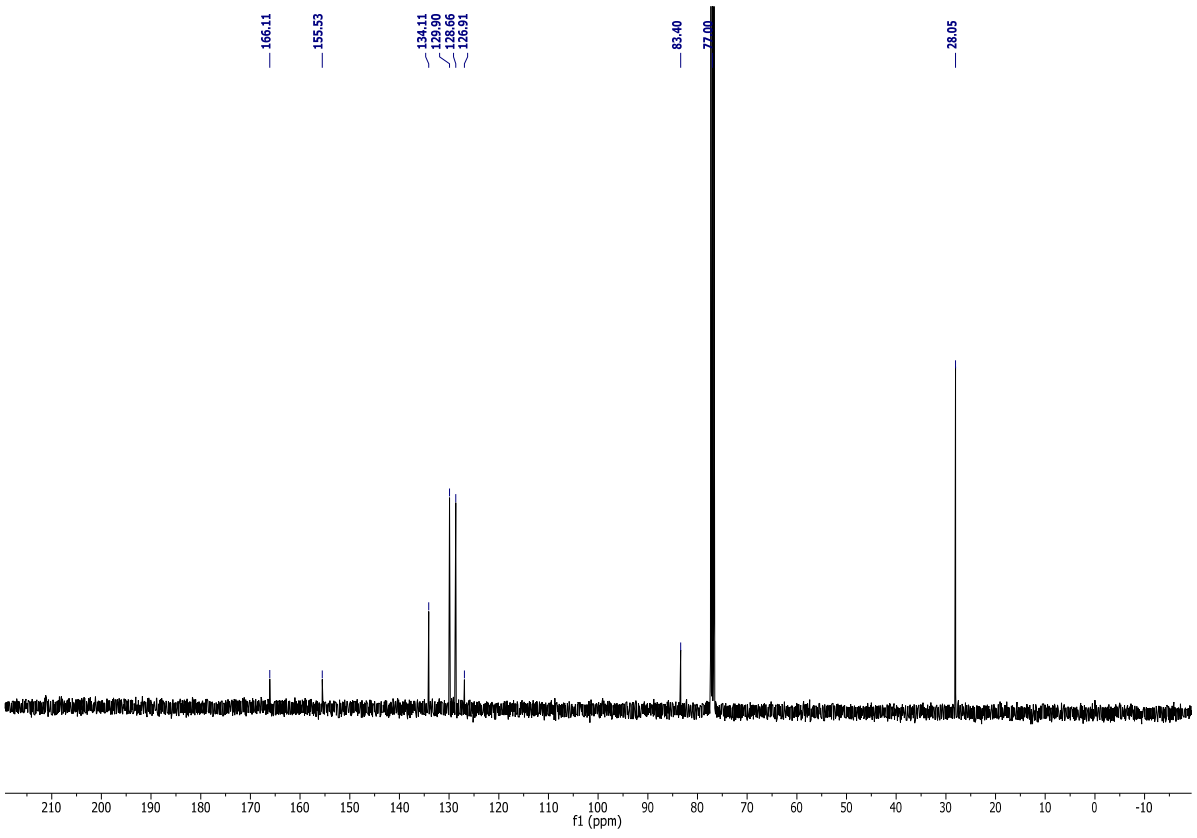
## *tert*-Butyl (3-nitrobenzoyl)oxycarbamate (2f)



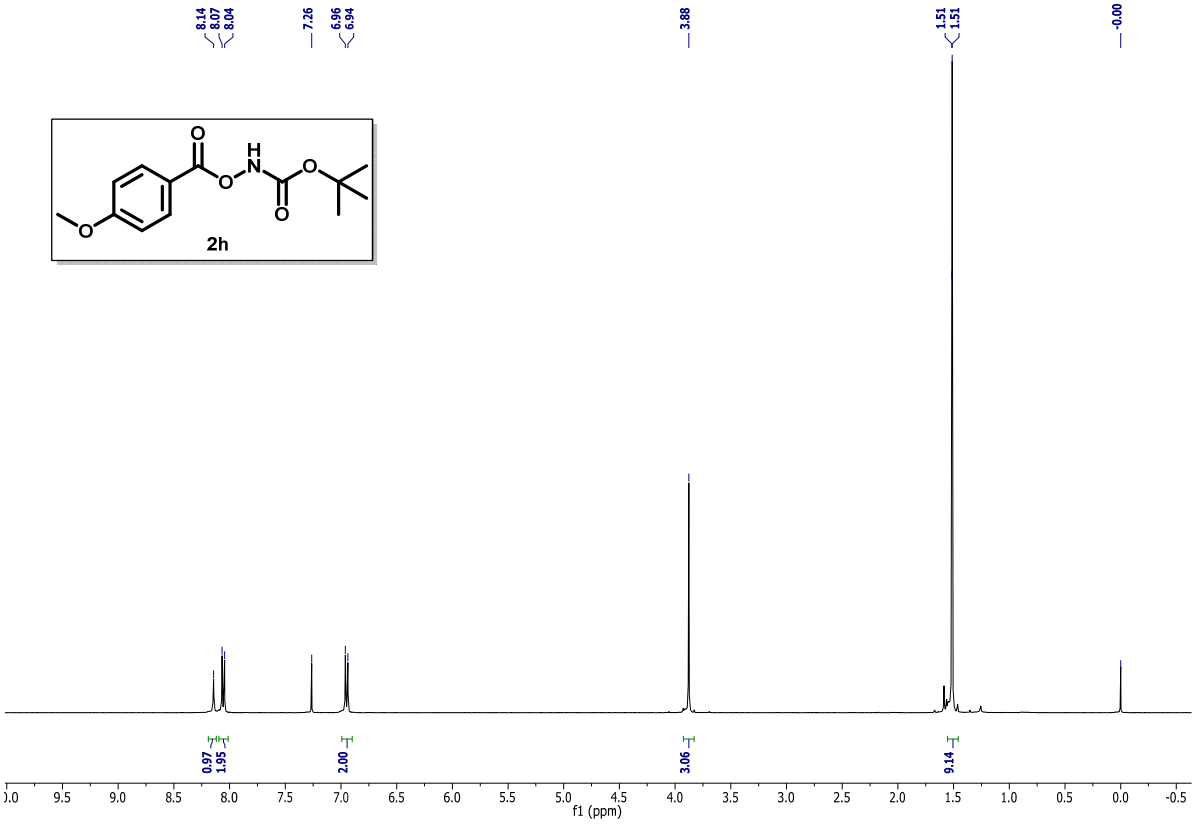



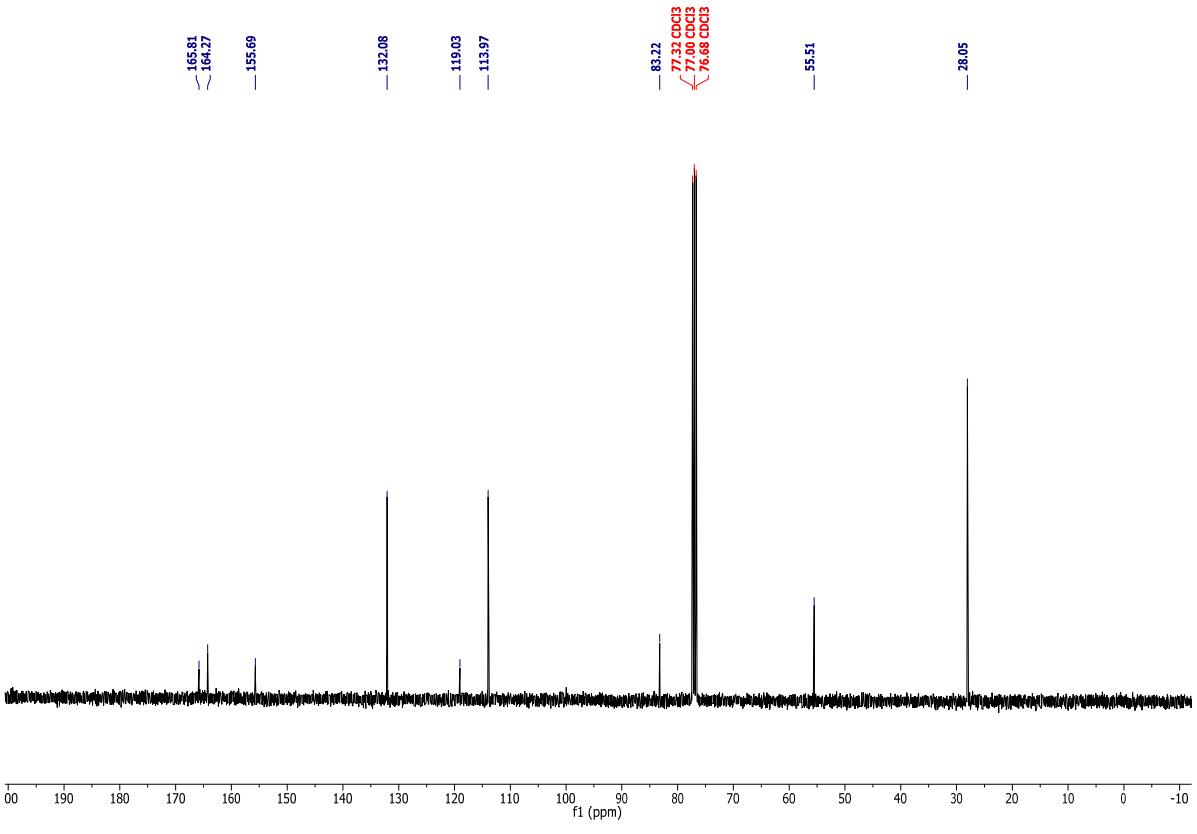
## *tert*-Butyl benzoyloxycarbamate (2g)



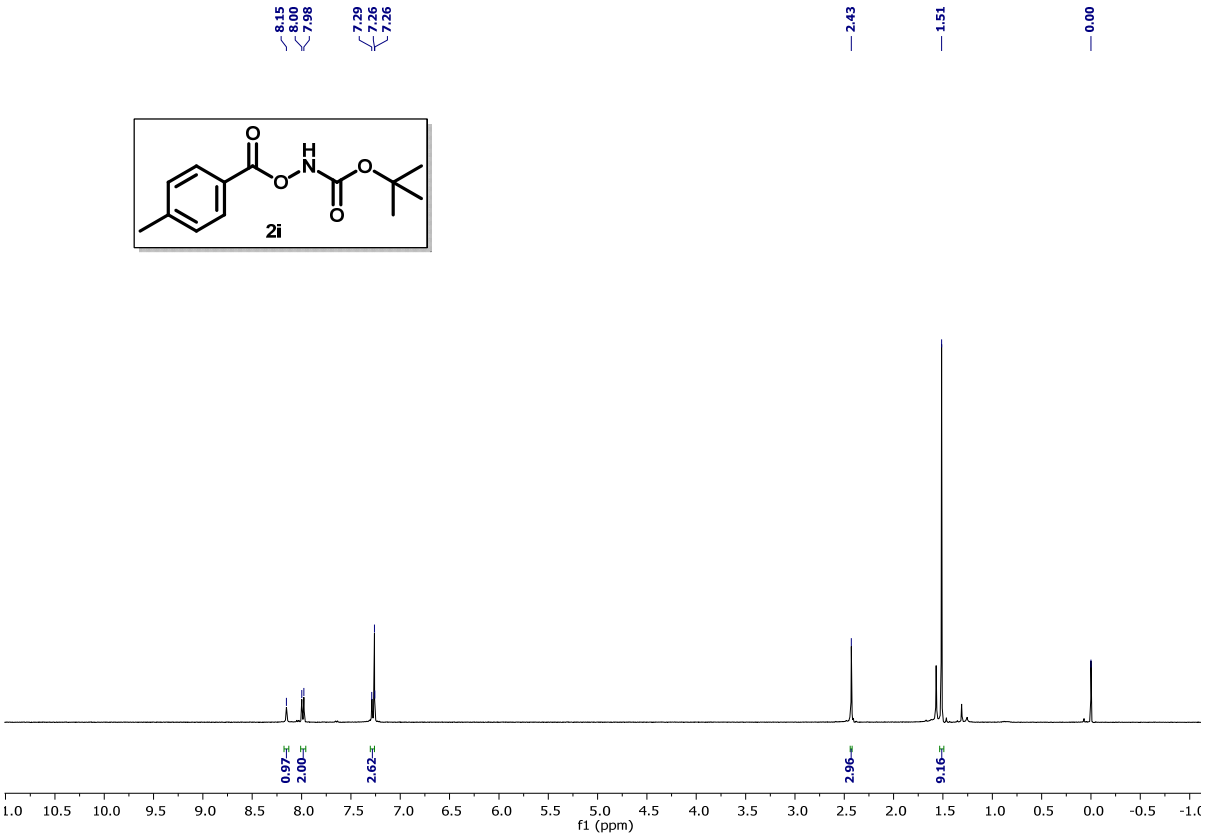



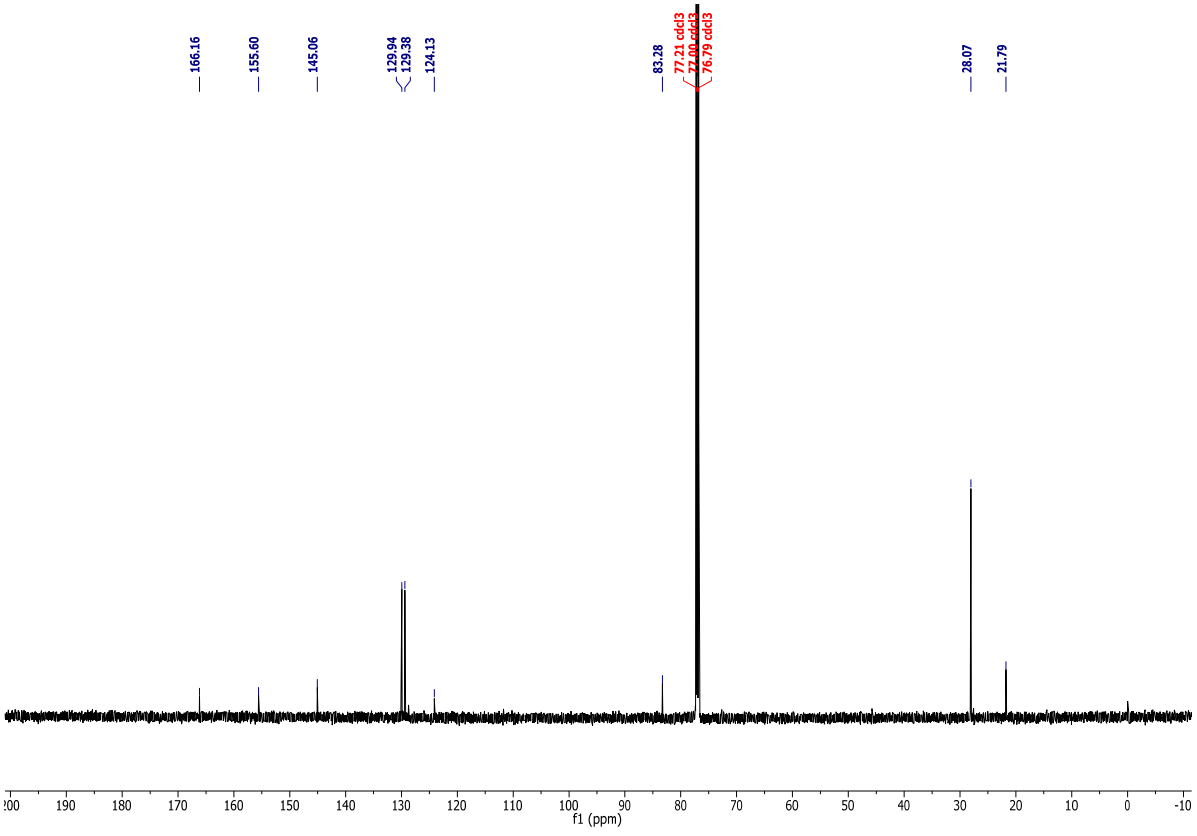
## *tert*-Butyl (4-methoxybenzoyl)oxycarbamate (2h)



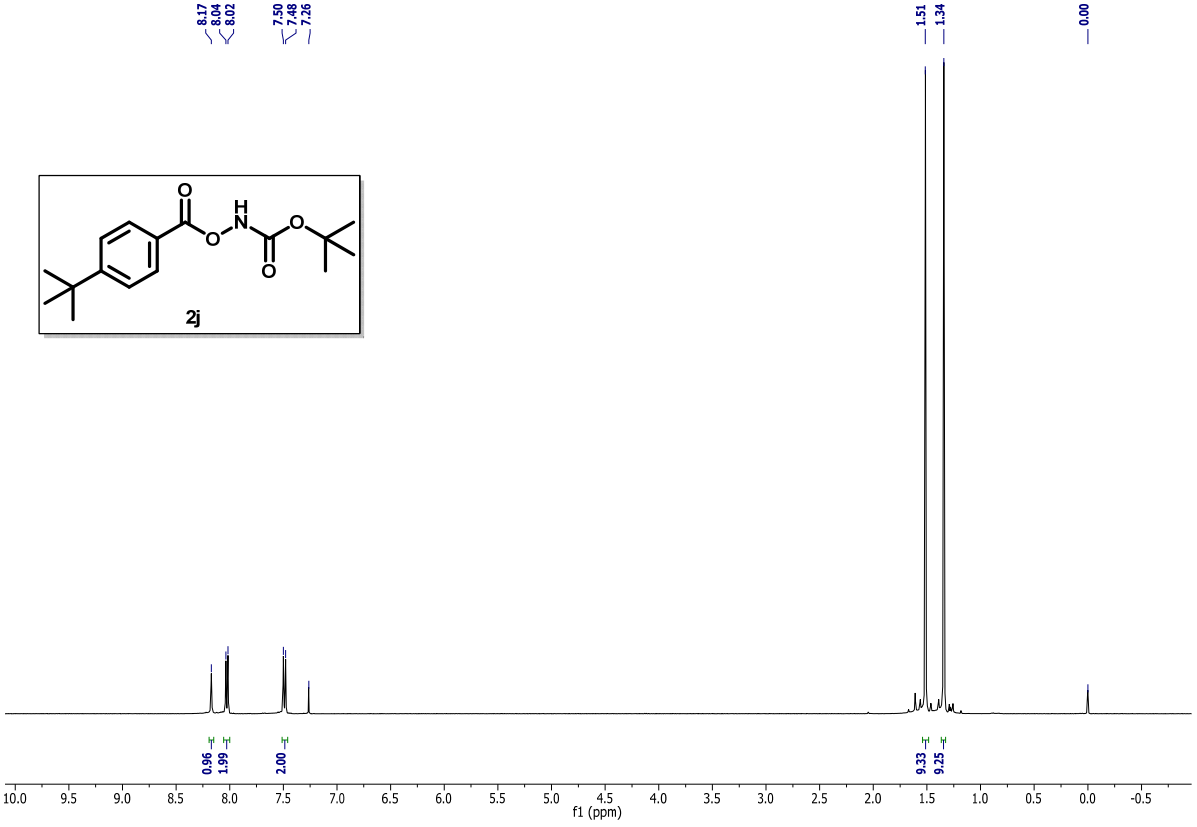



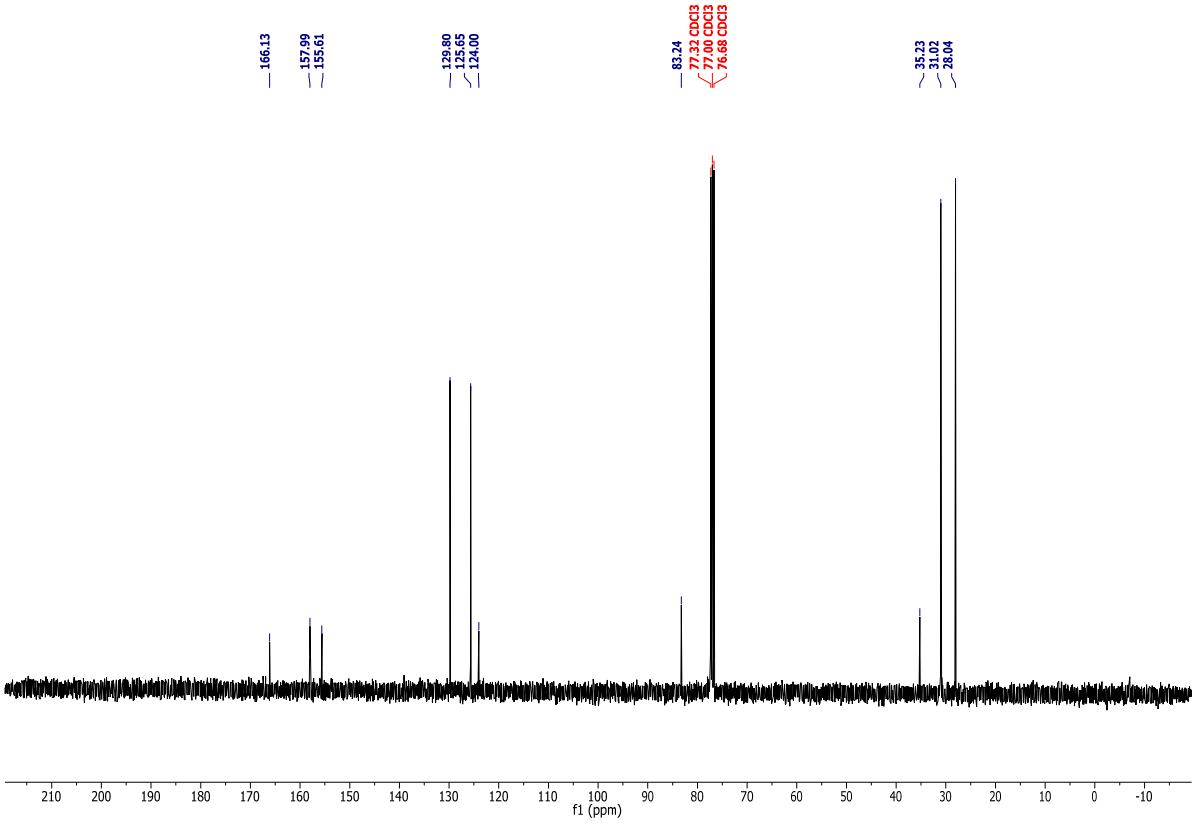
## *tert*-Butyl (4-methylbenzoyl)oxycarbamate (2i)



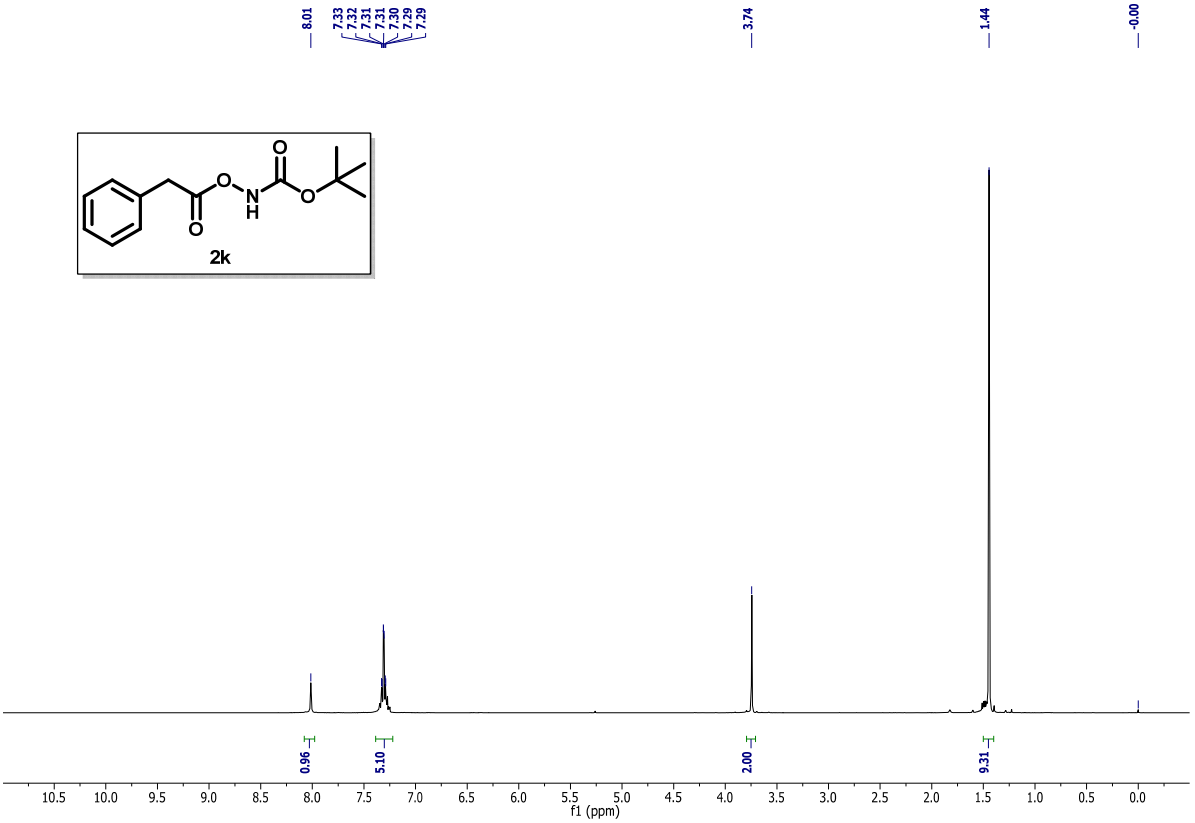



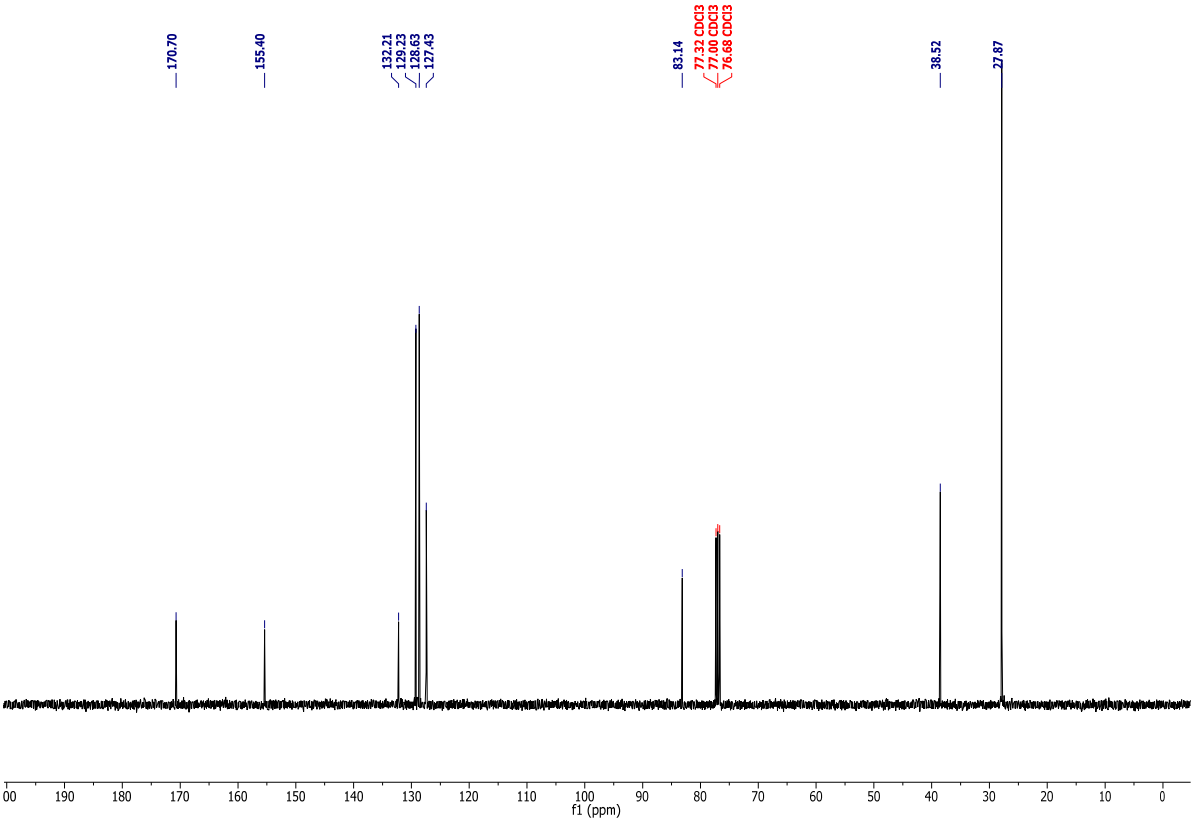
## *tert*-Butyl (4-*t*-butylbenzoyl)oxycarbamate (2j)



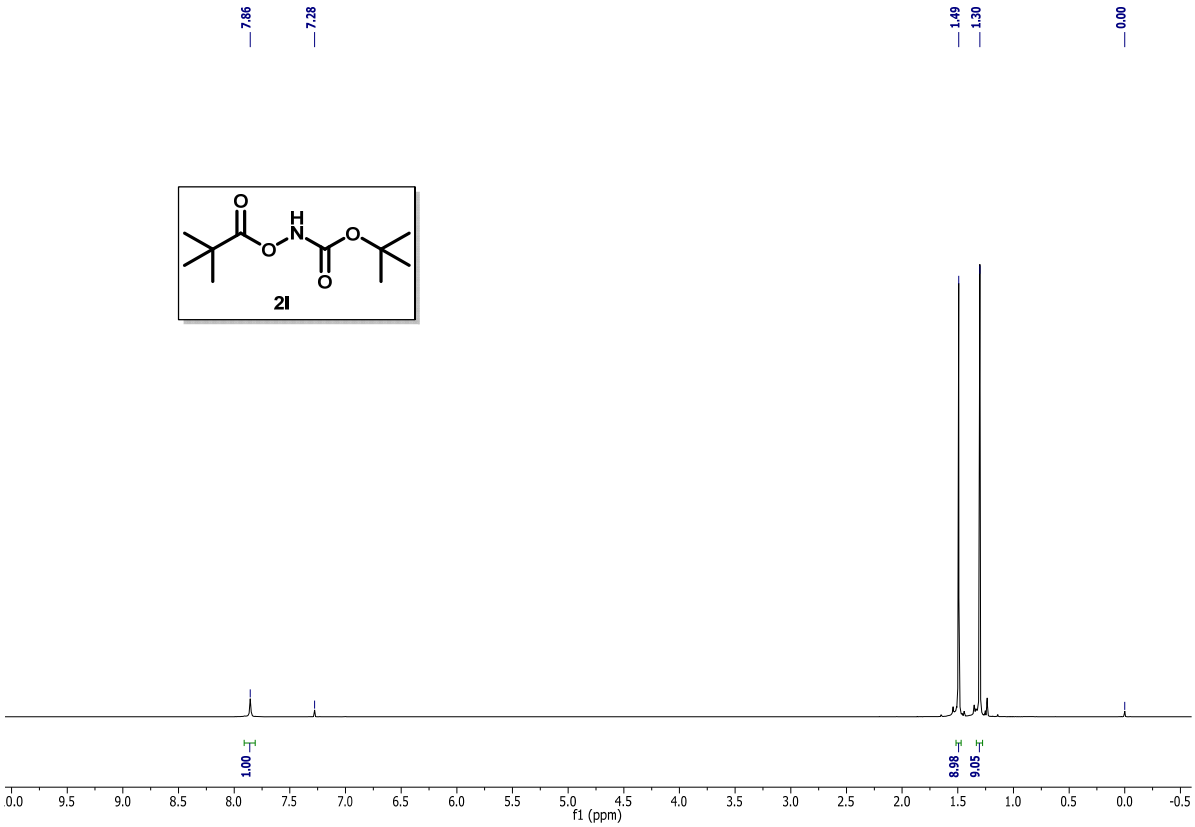



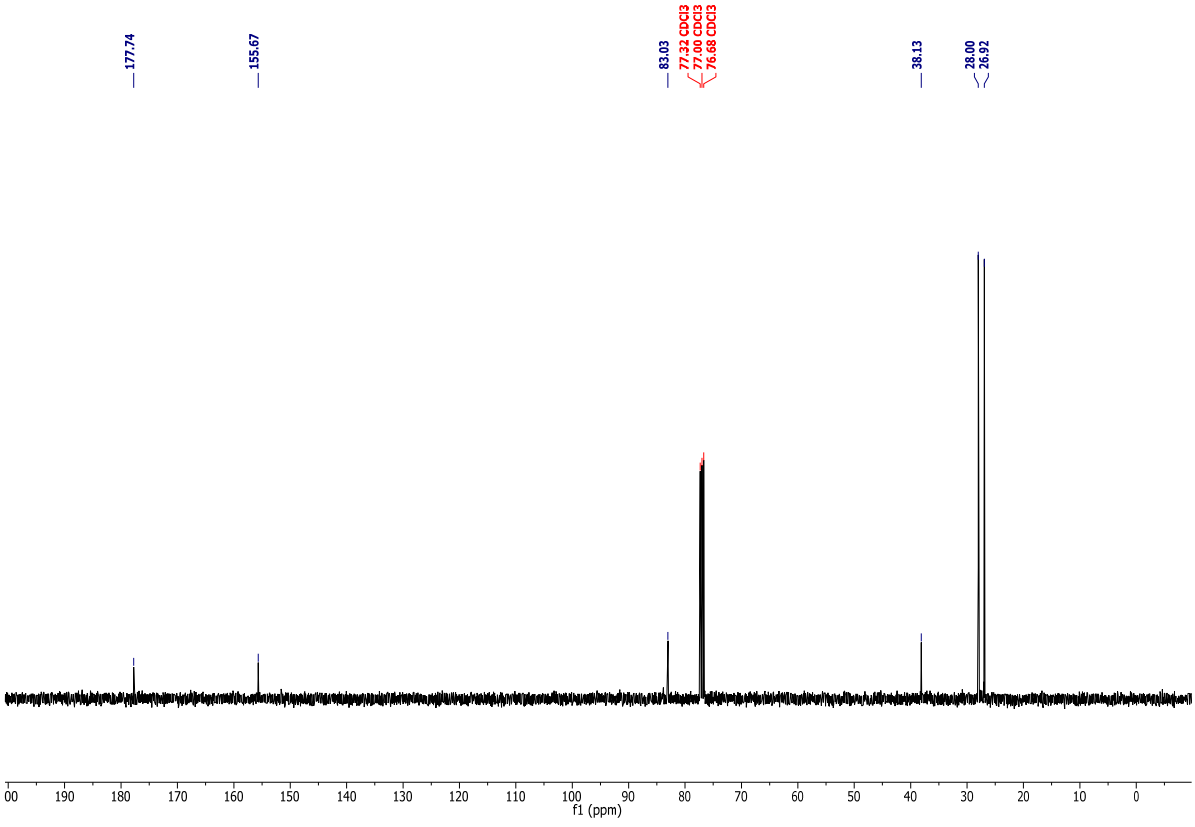
## *tert*-Butyl 2-phenylacetoxycarbamate (2k)



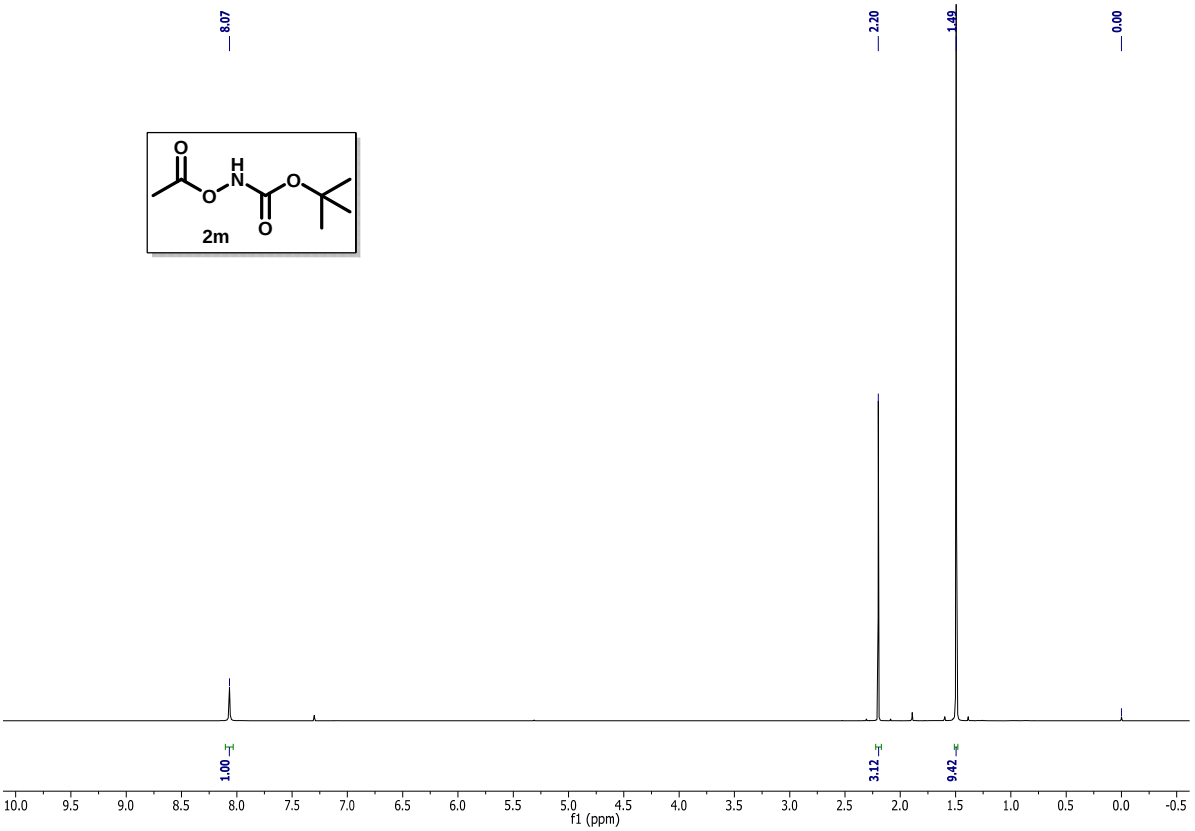



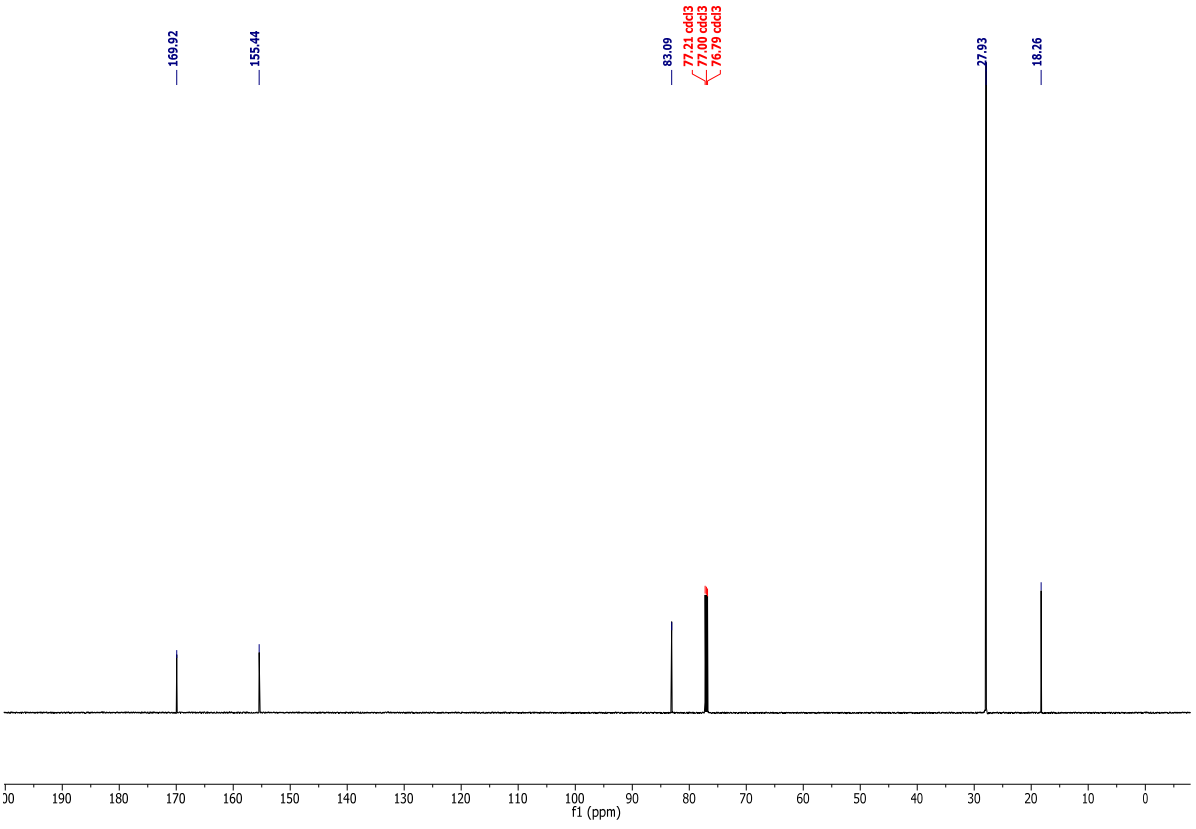
## *tert*-butyl pivaloyloxycarbamate (2l)



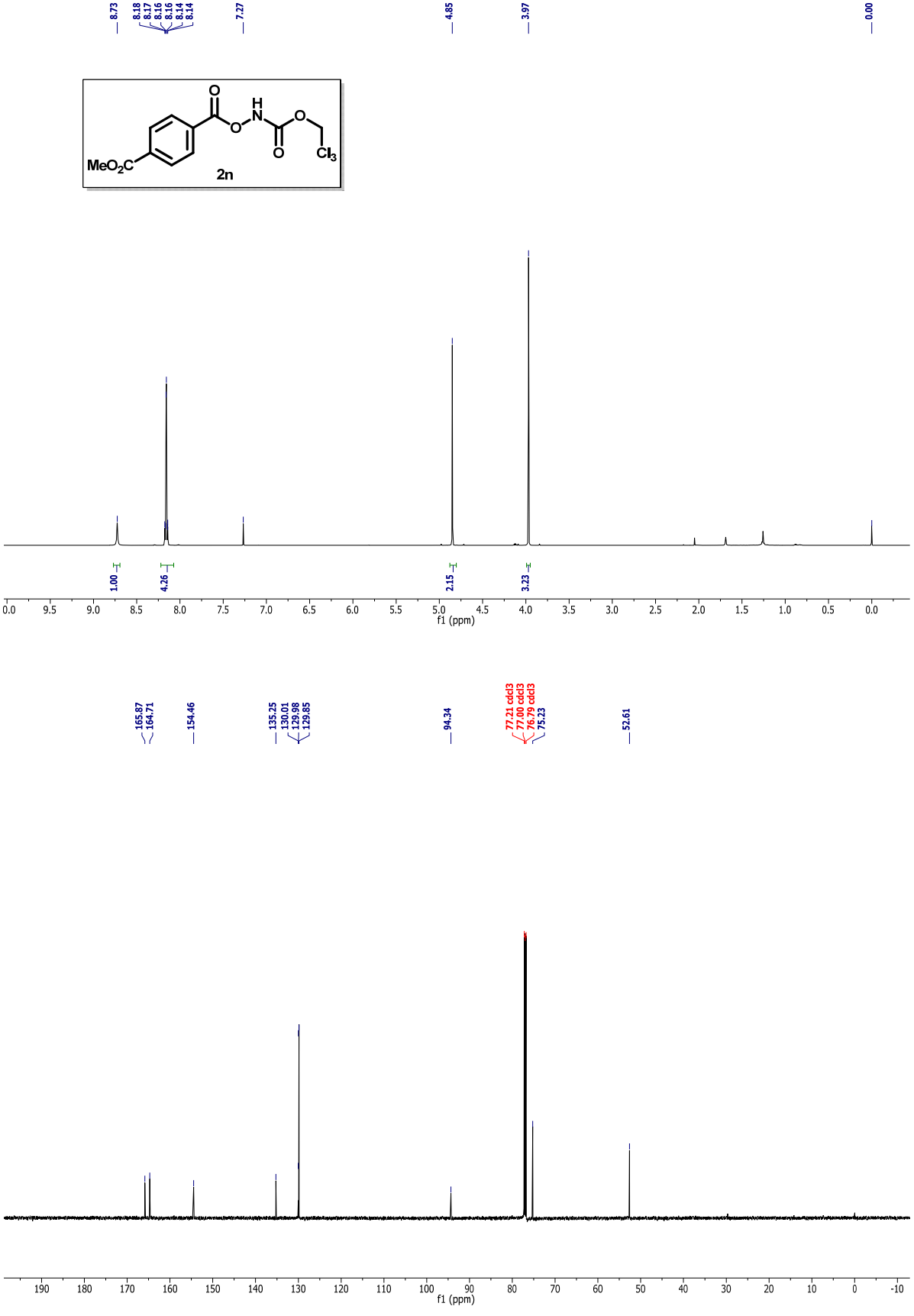



## *tert*-butyl acyloxycarbamate (2m)

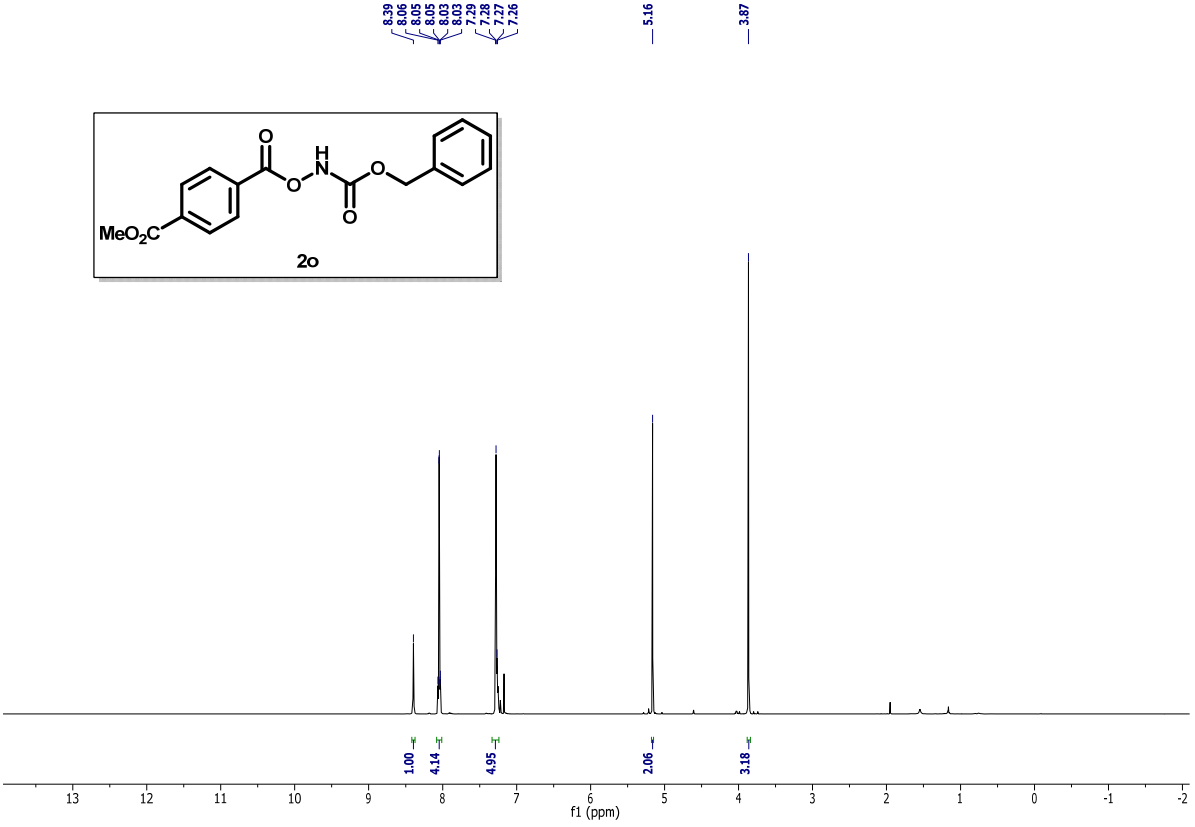


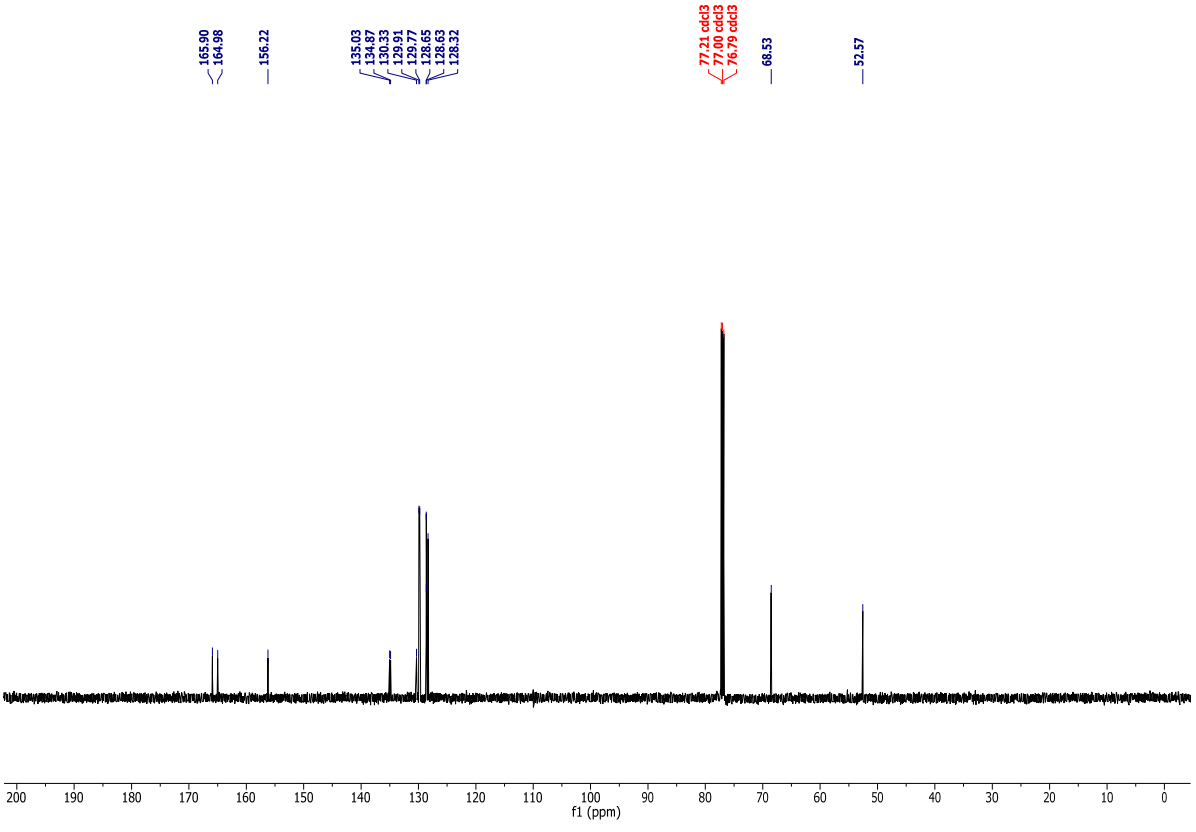



## Methyl 4-[(2′, 2′, 2′-trichloroethoxycarbonyl)amino-oxycarbonyl]benzoate (2n)

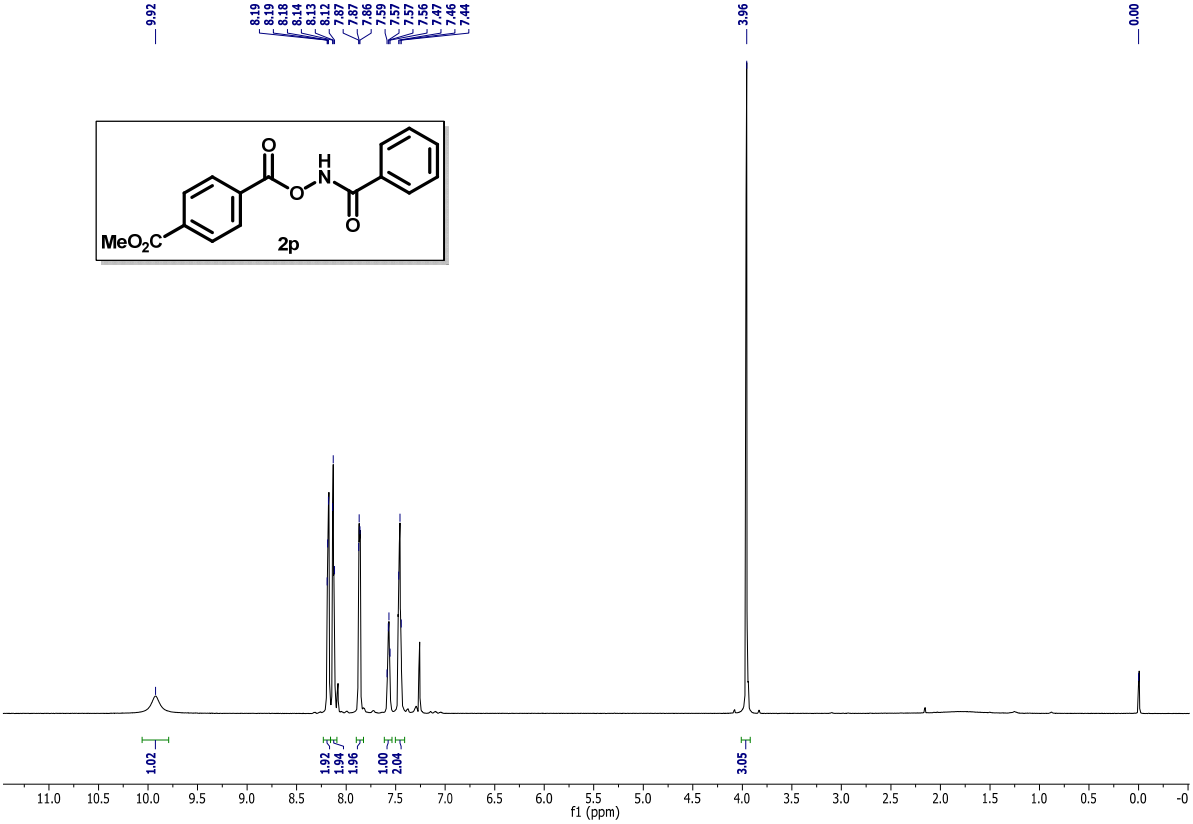


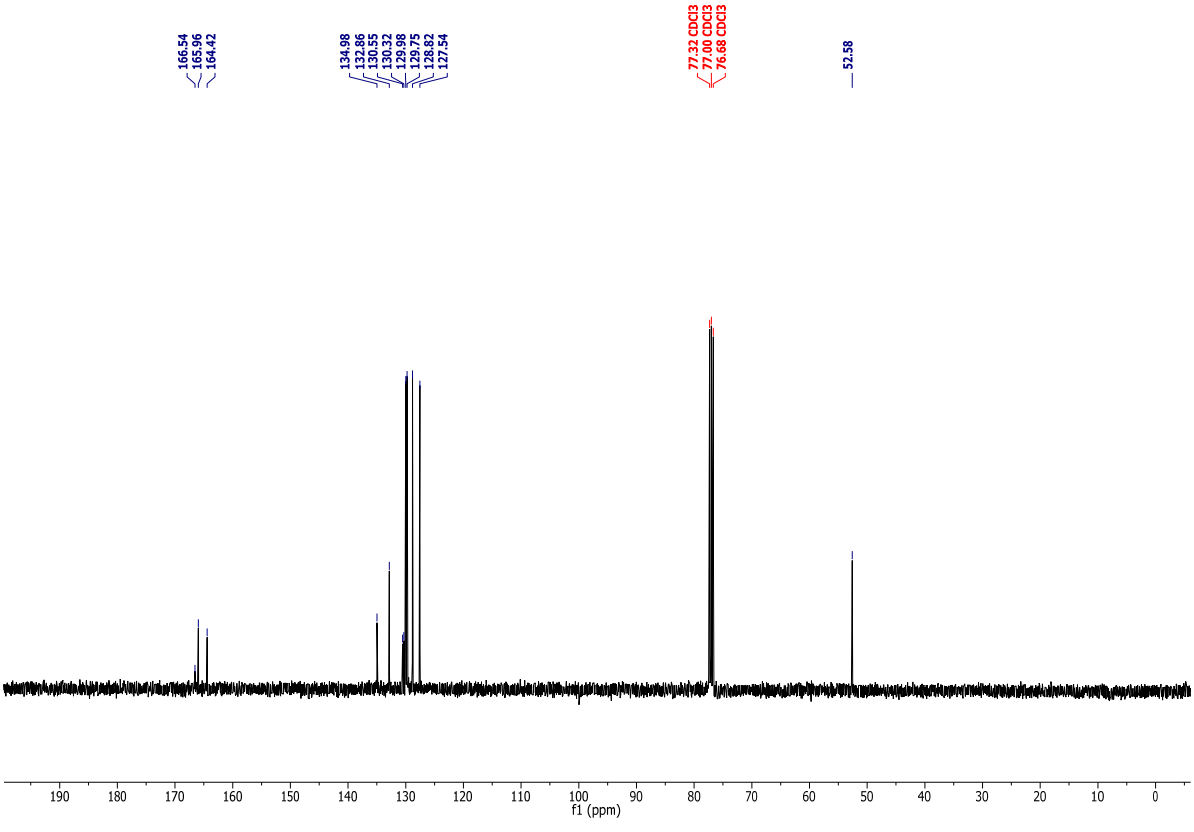
## Methyl 4-[(benzyloxycarbonyl)amino-oxycarbonyl]benzoate (2o)



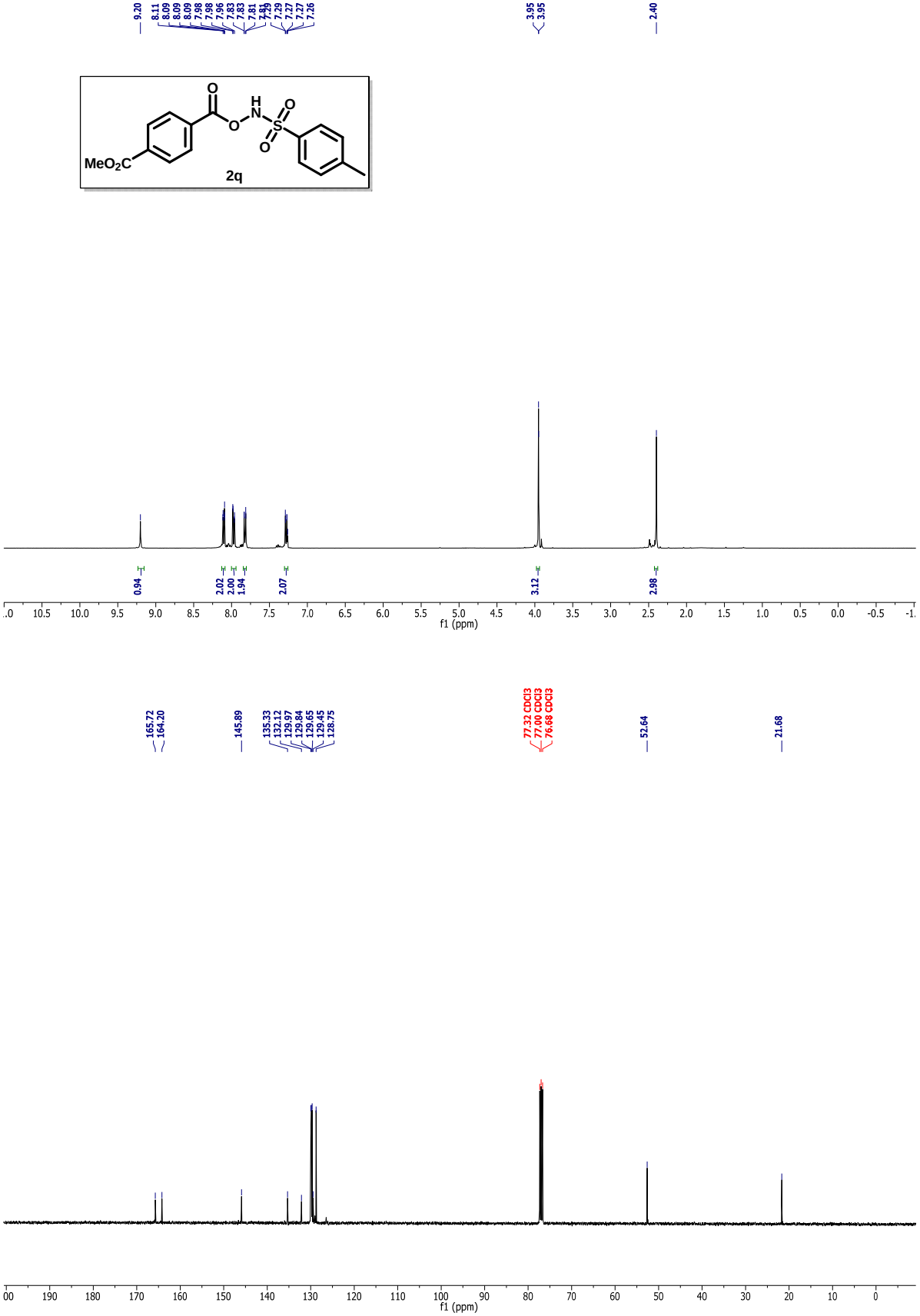



## Methyl 4-[(benzamidooxy)carbonyl]benzoate (2p)

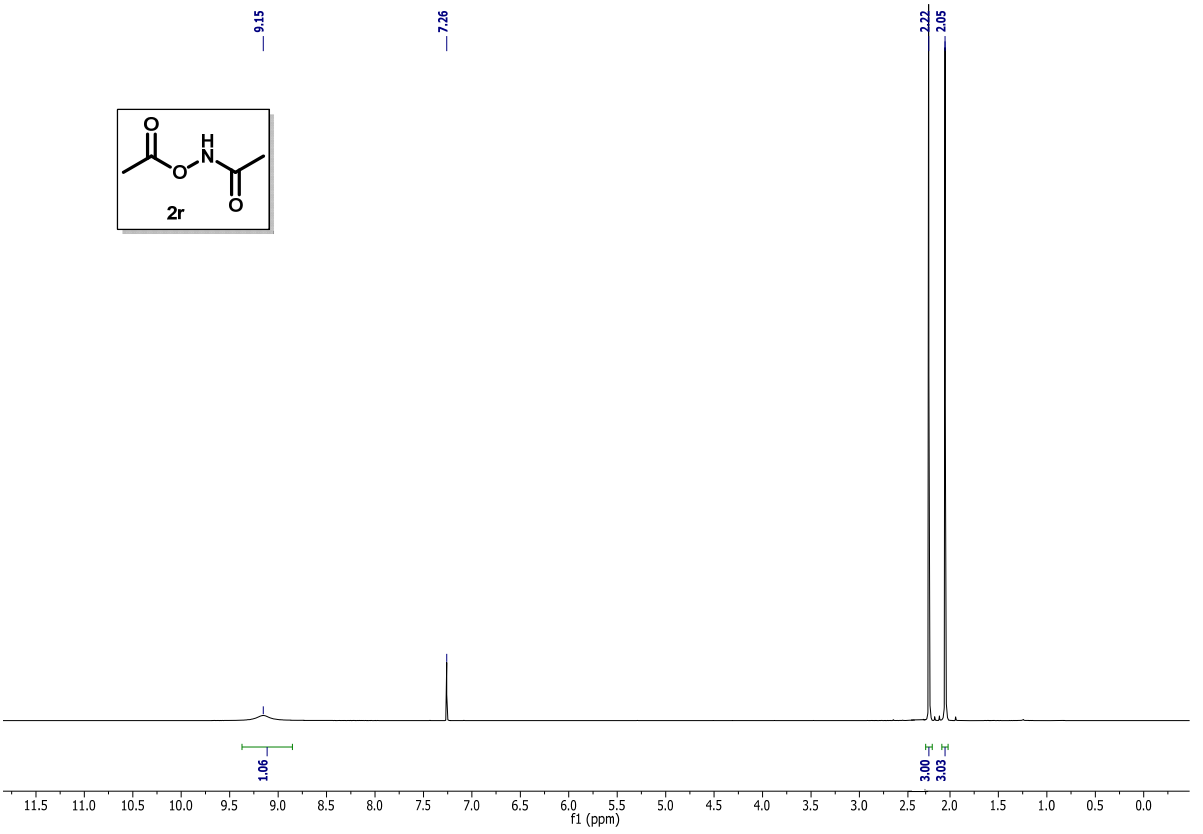


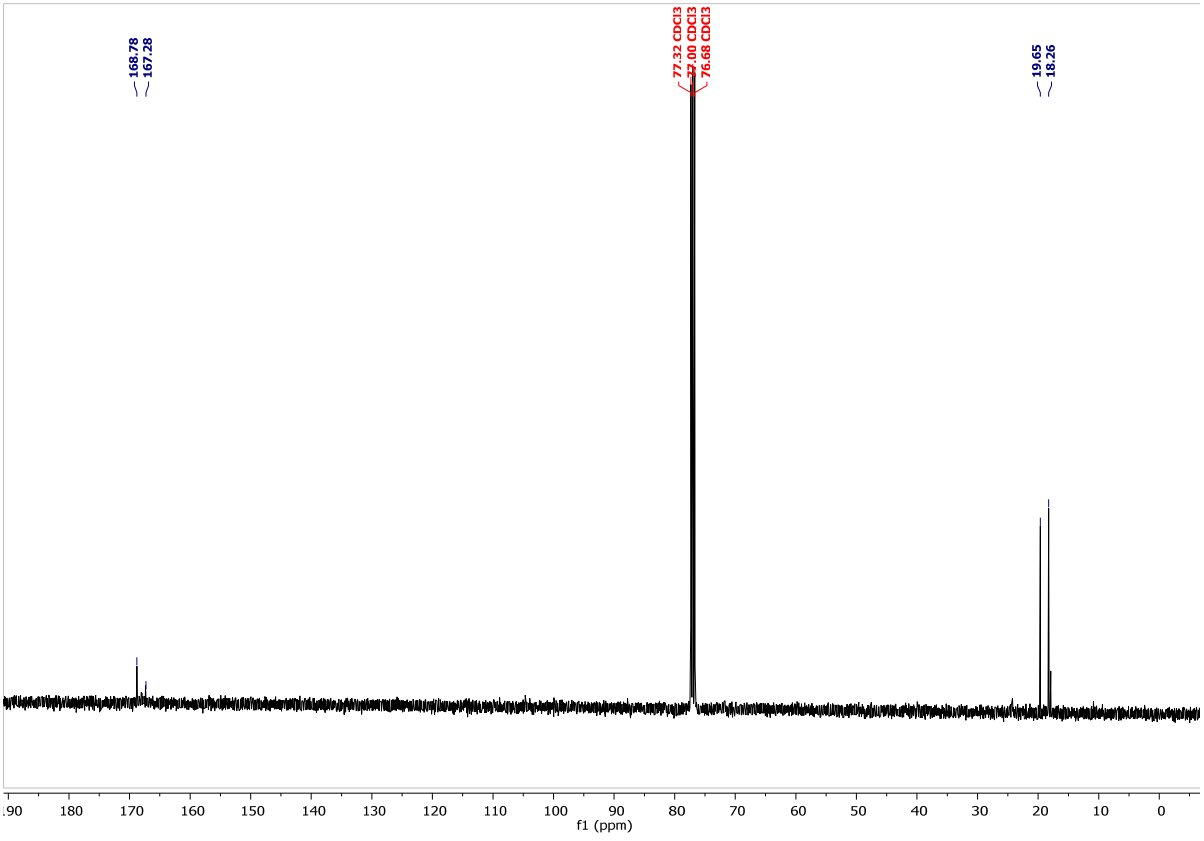



## Methyl 4-[(4-methylphenylsulfonamido)oxycarbonyl]benzoate (2q)

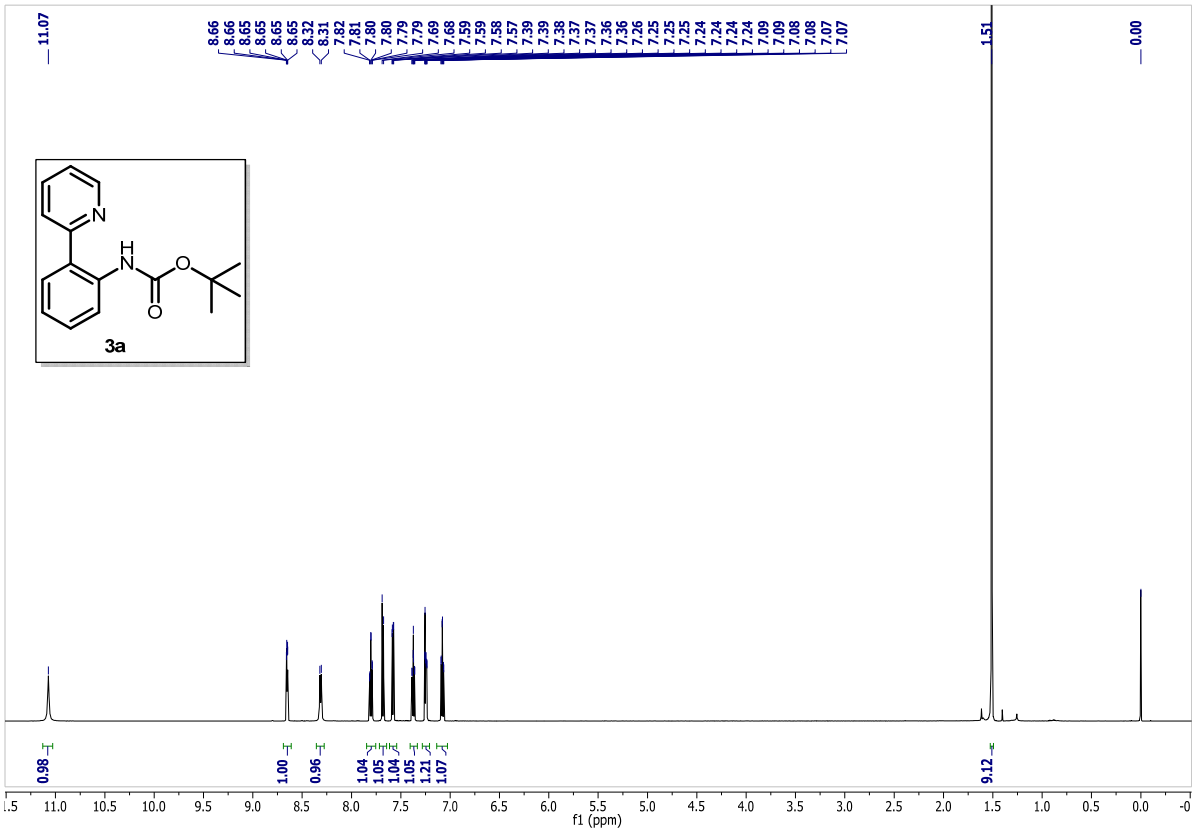


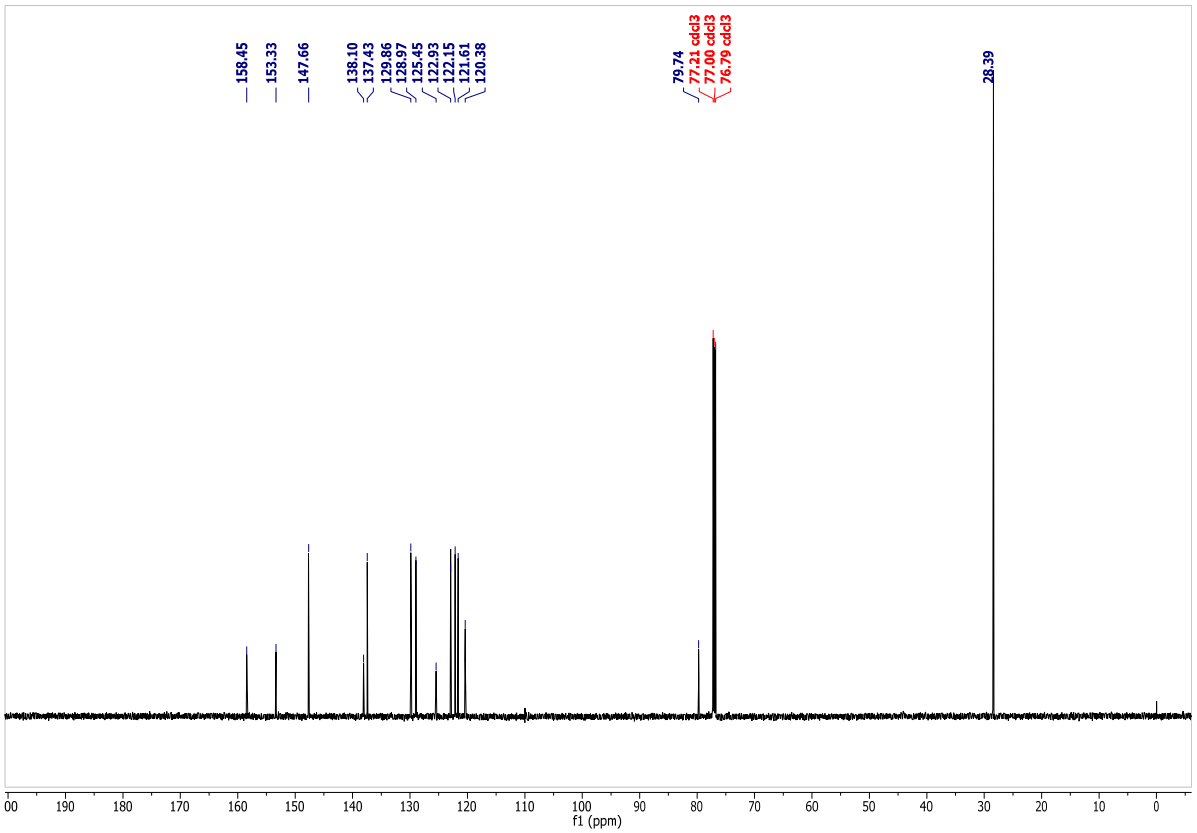
## *O*-Acetyl acetylhydroxamic acid (2r)



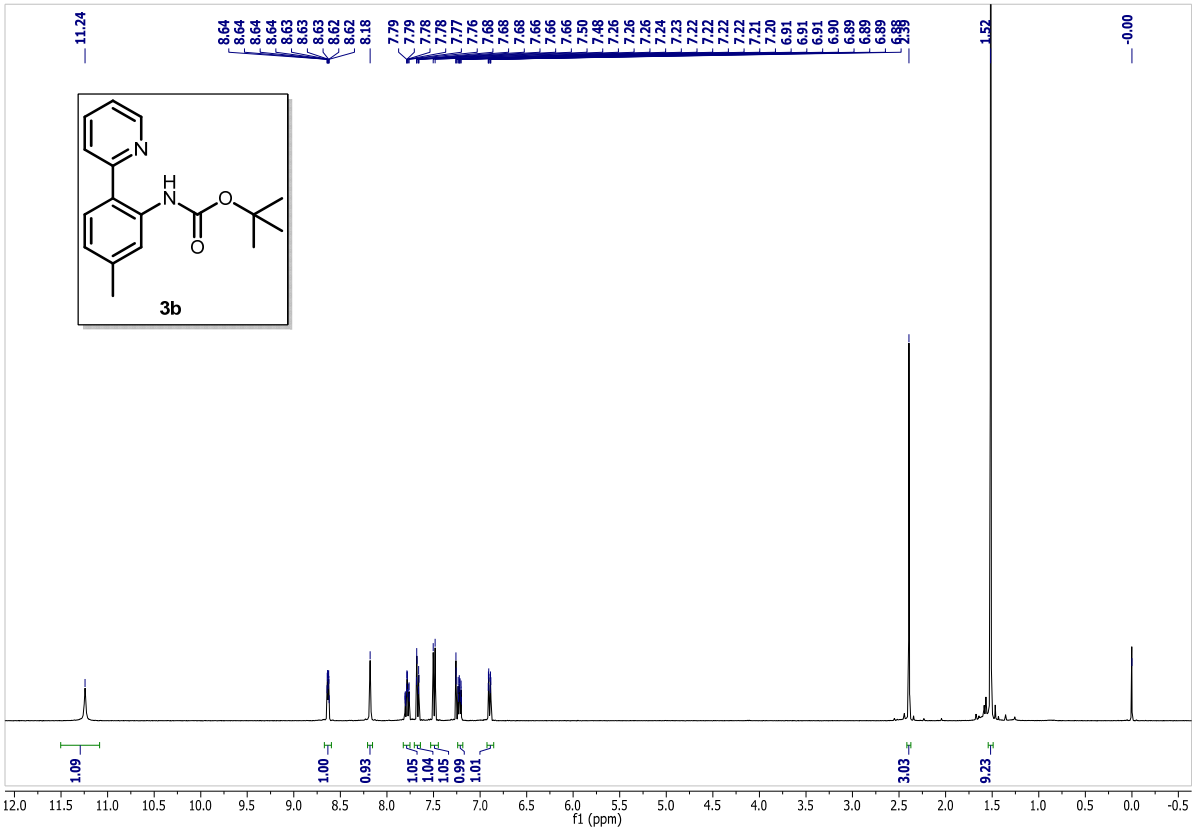



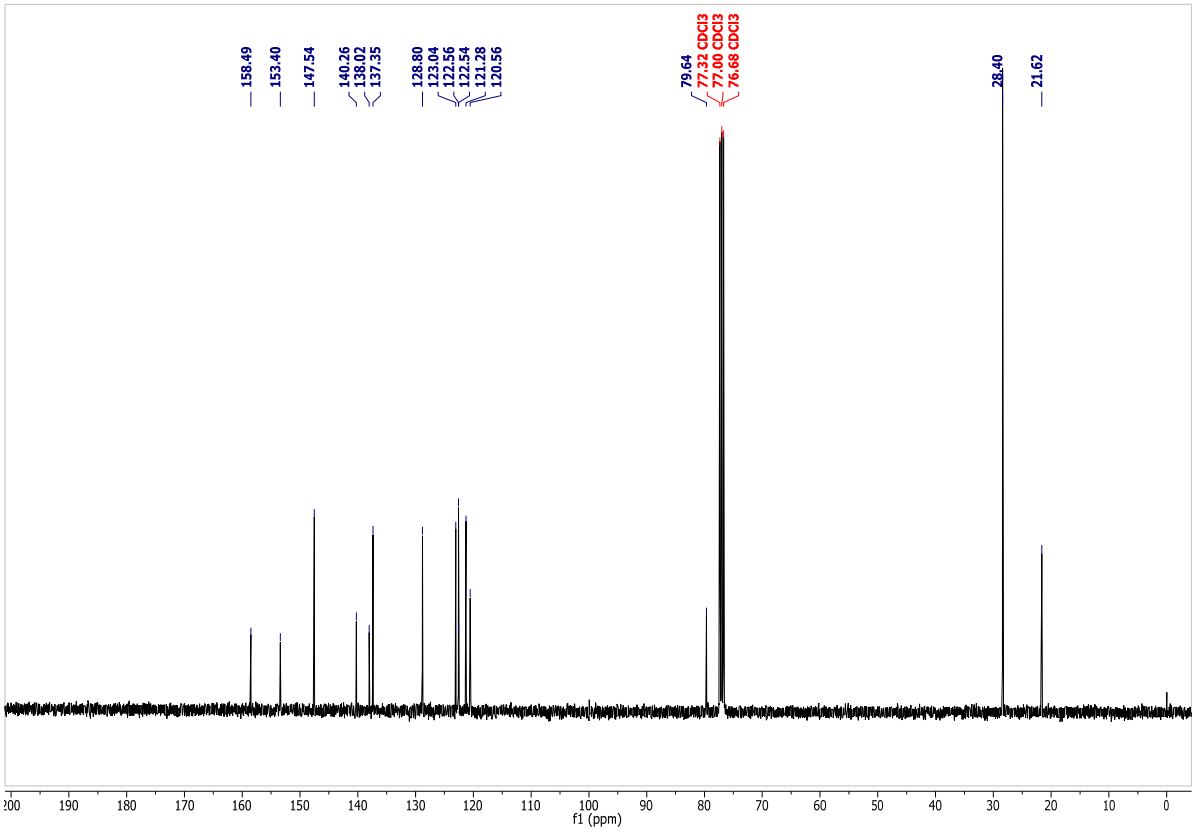
## *tert*-Butyl [2-(pyridin-2-yl)phenyl]carbamate (3a)



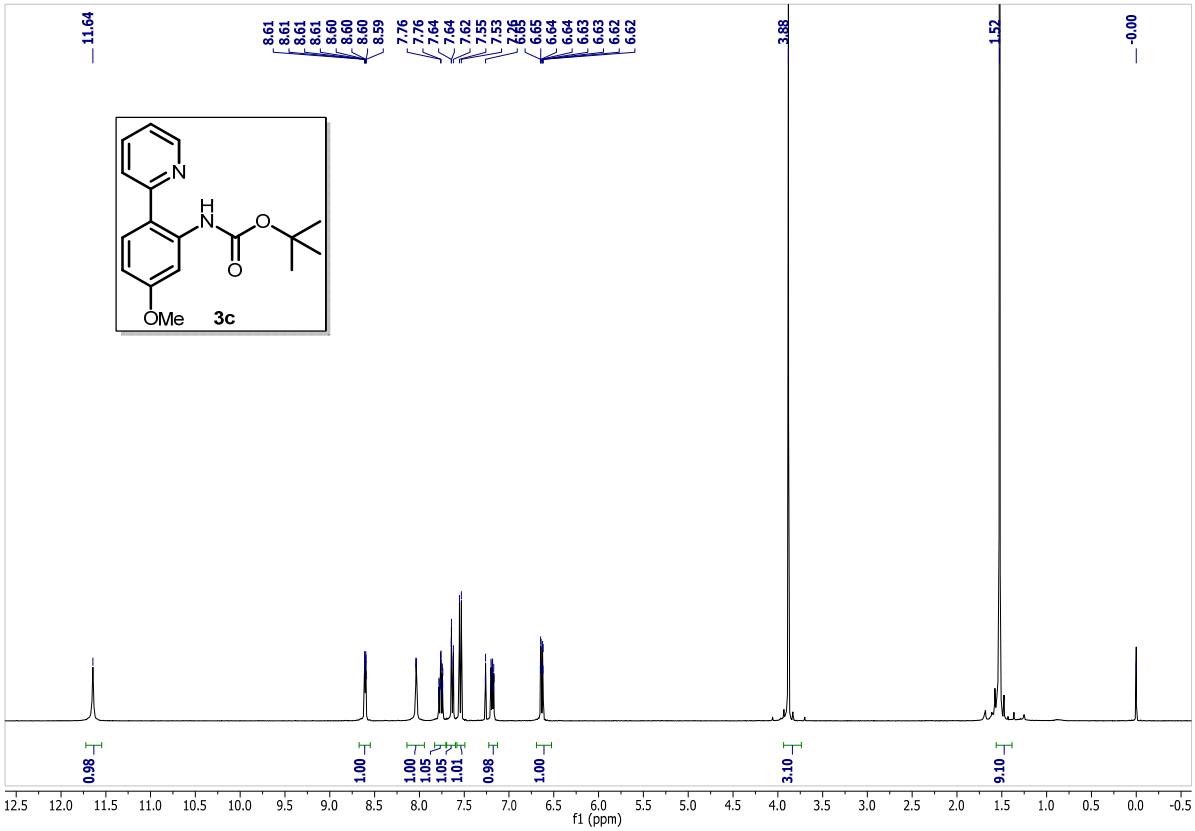



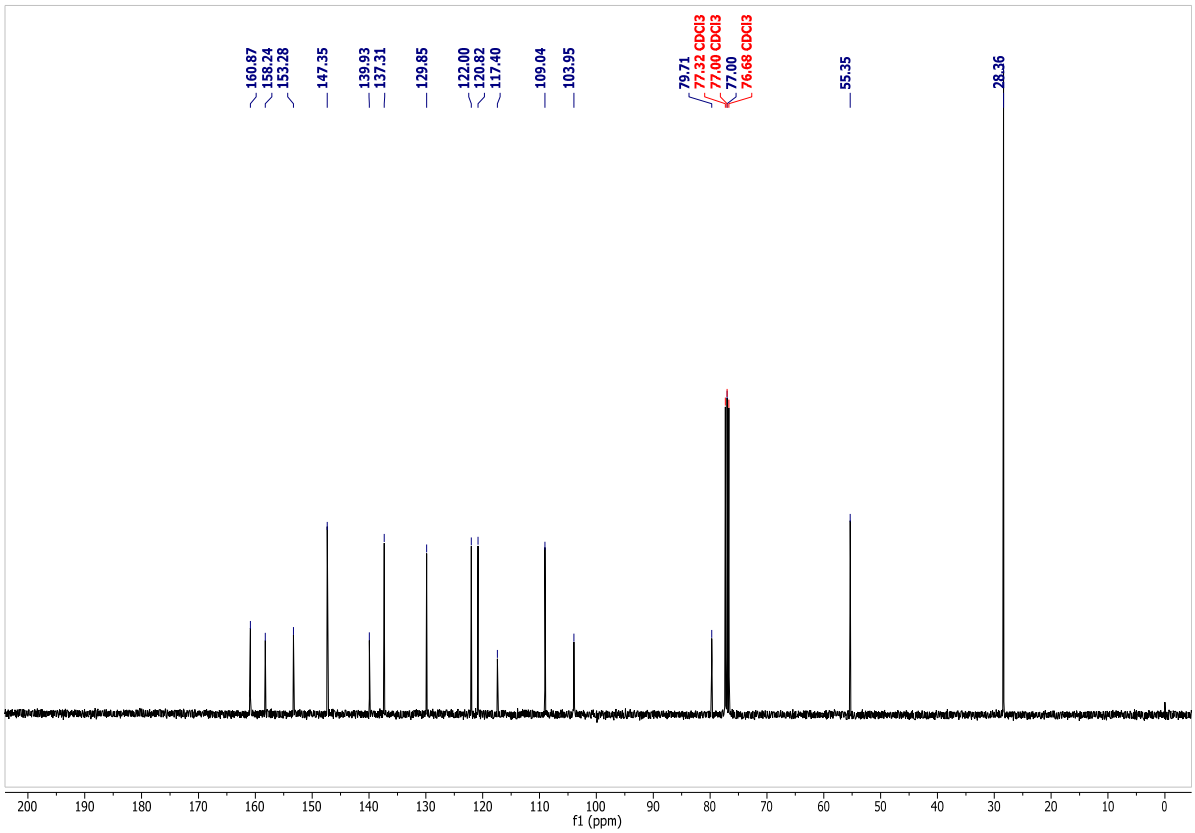
## *tert*-Butyl [5-methyl-2-(pyridin-2-yl)phenyl]carbamate (3b)



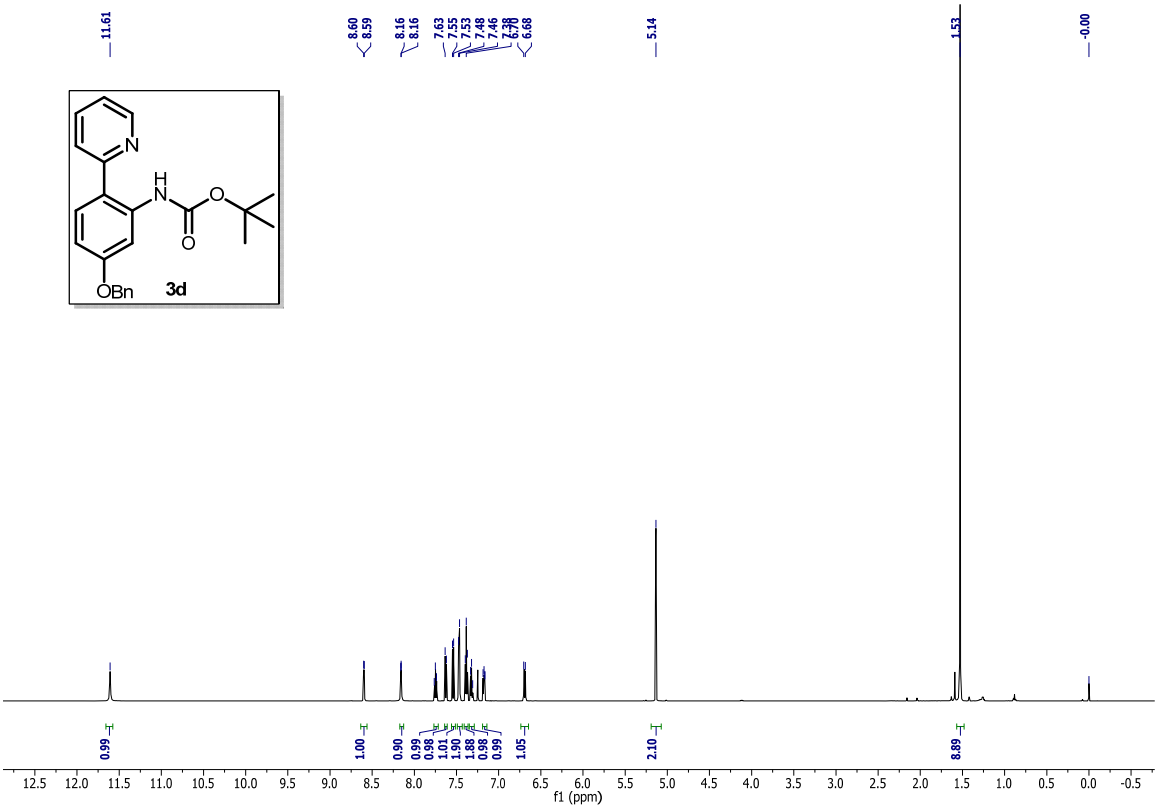



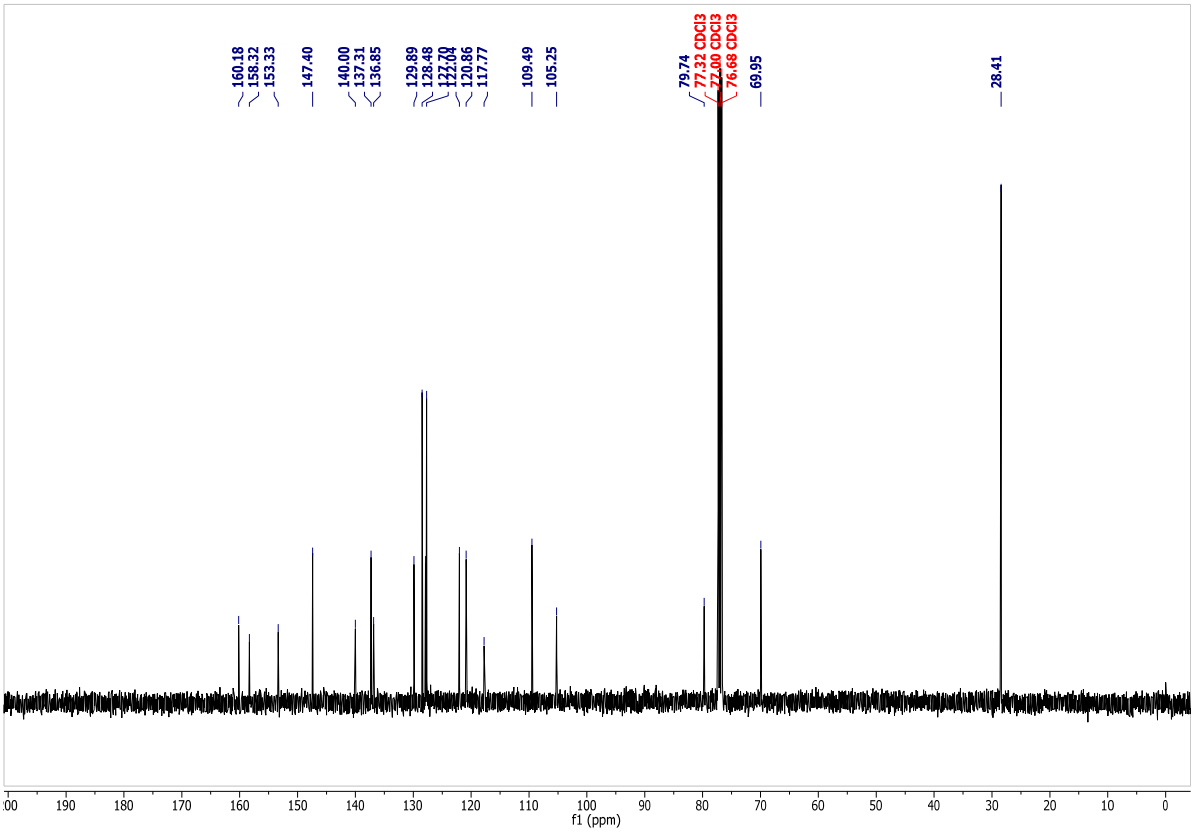
## *tert*-Butyl [5-methoxy-2-(pyridin-2-yl)phenyl]carbamate (3c)



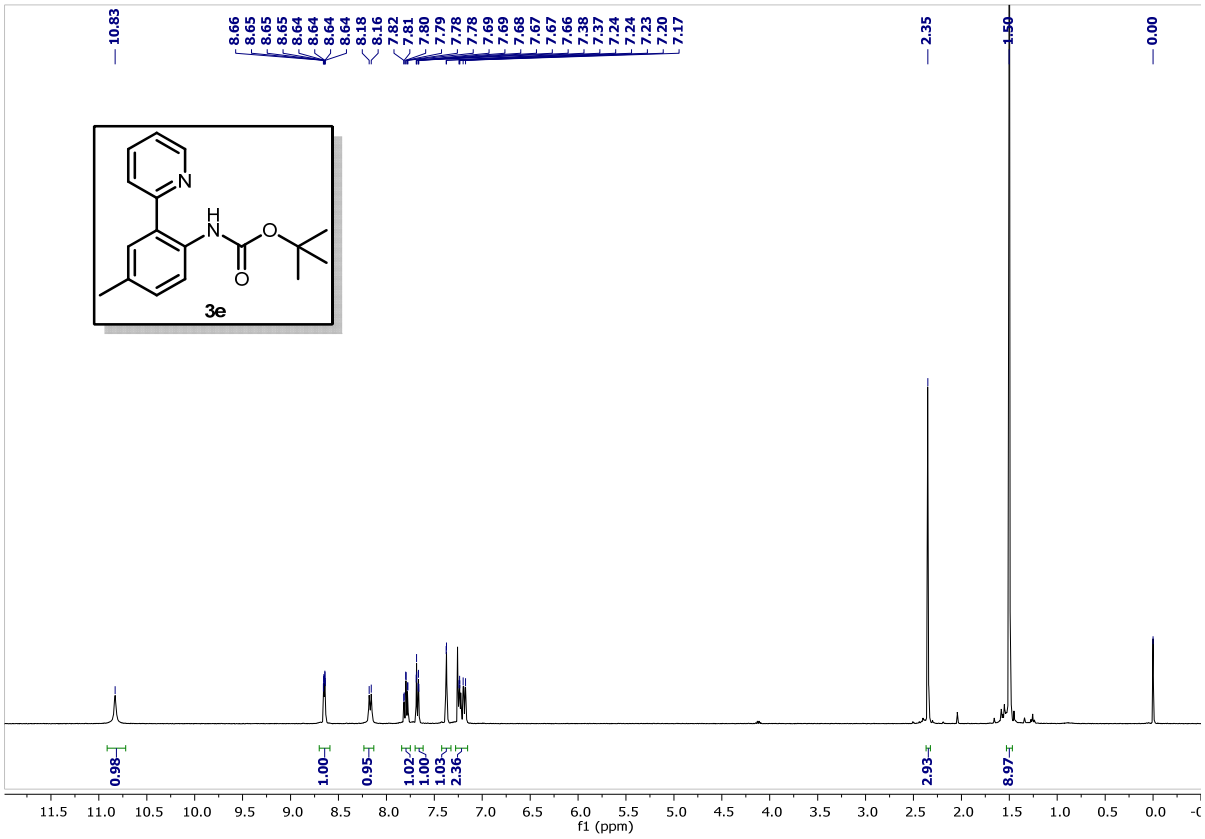



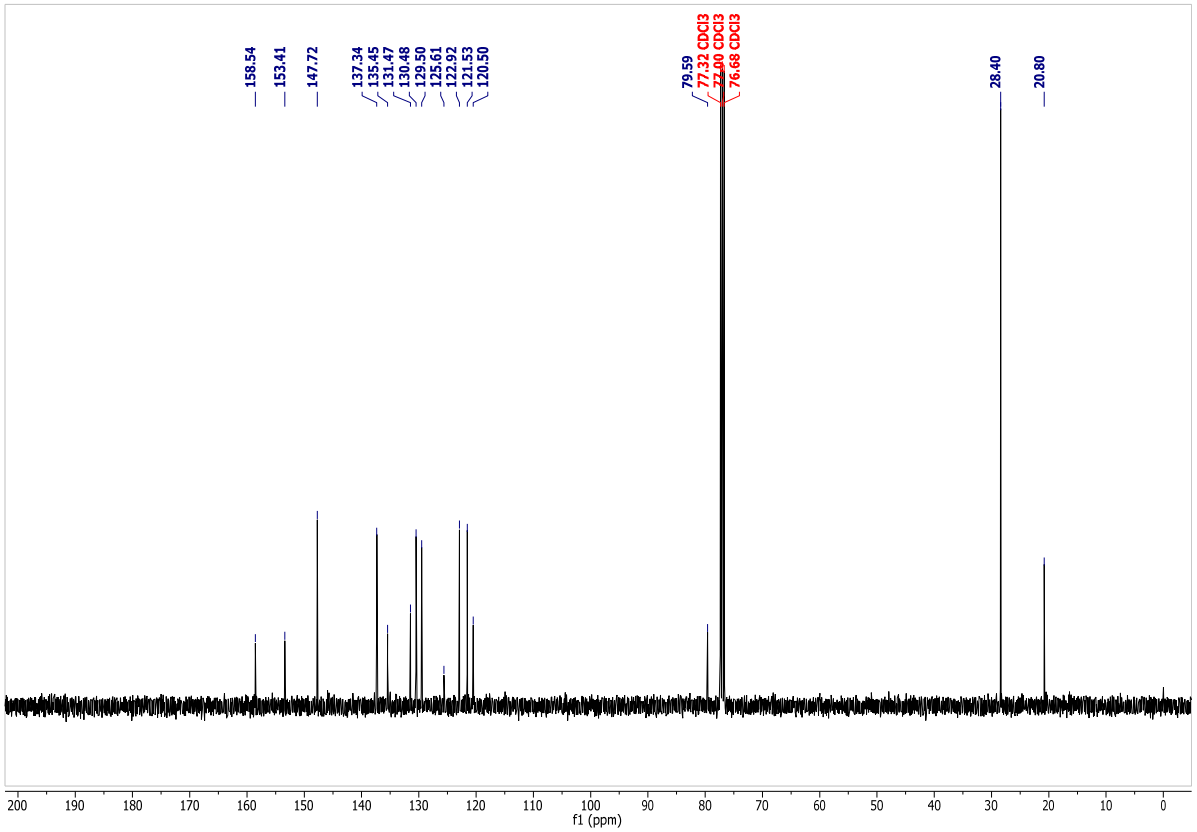
## *tert*-Butyl [5-(benzyloxy)-2-(pyridin-2-yl)phenyl]carbamate (3d)



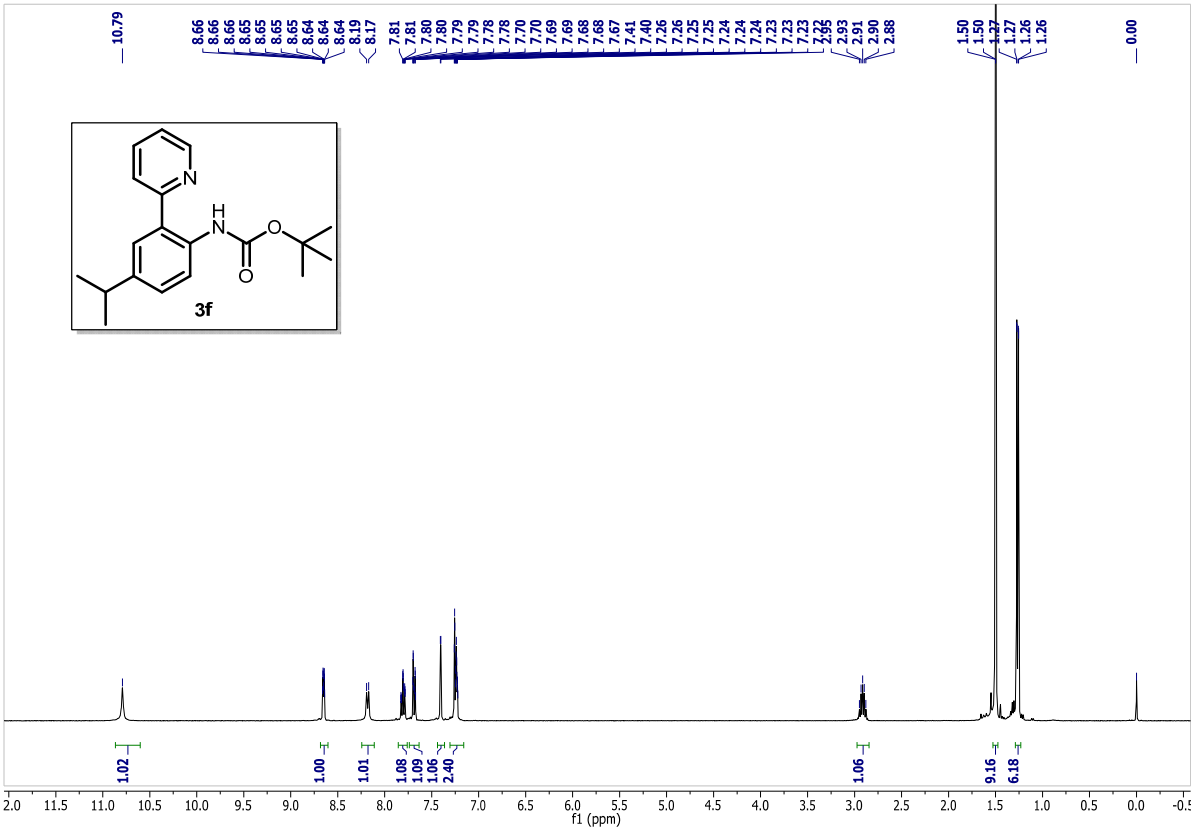



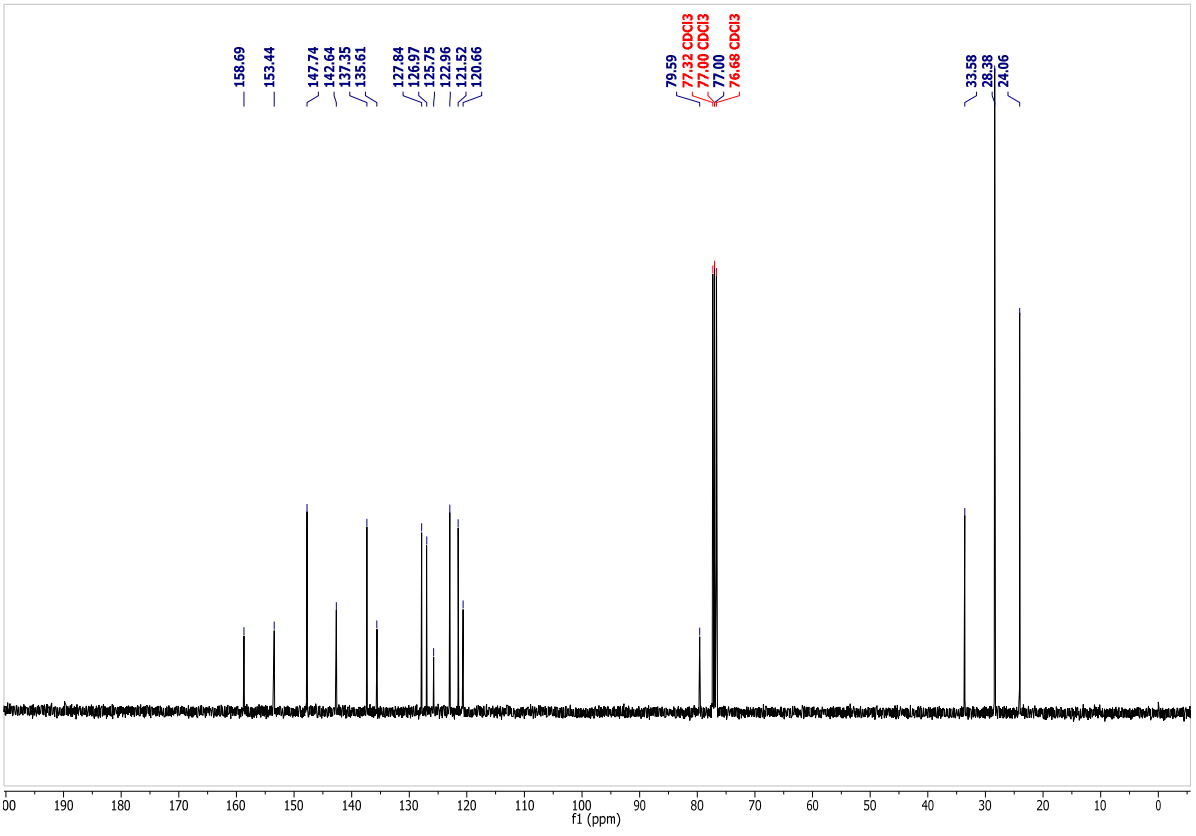
## *tert*-Butyl [4-methyl-2-(pyridin-2-yl)phenyl]carbamate (3e)



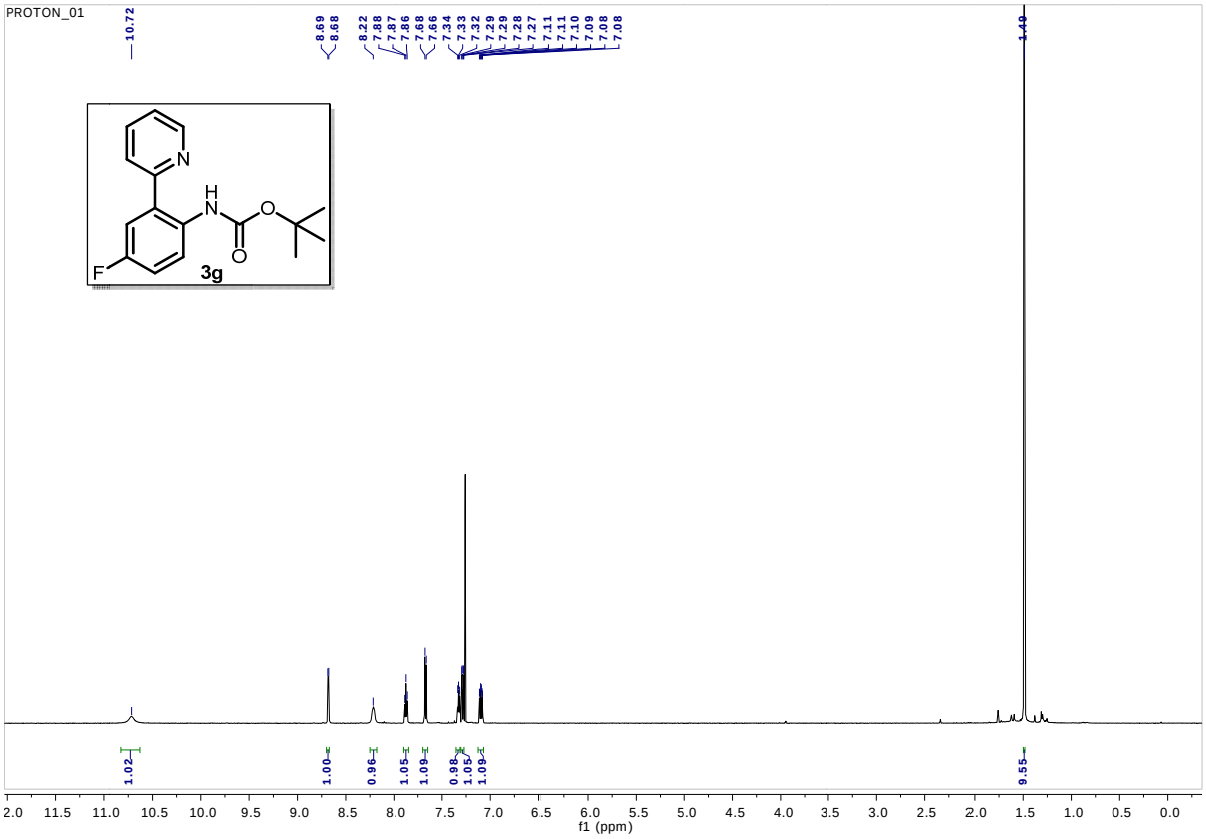



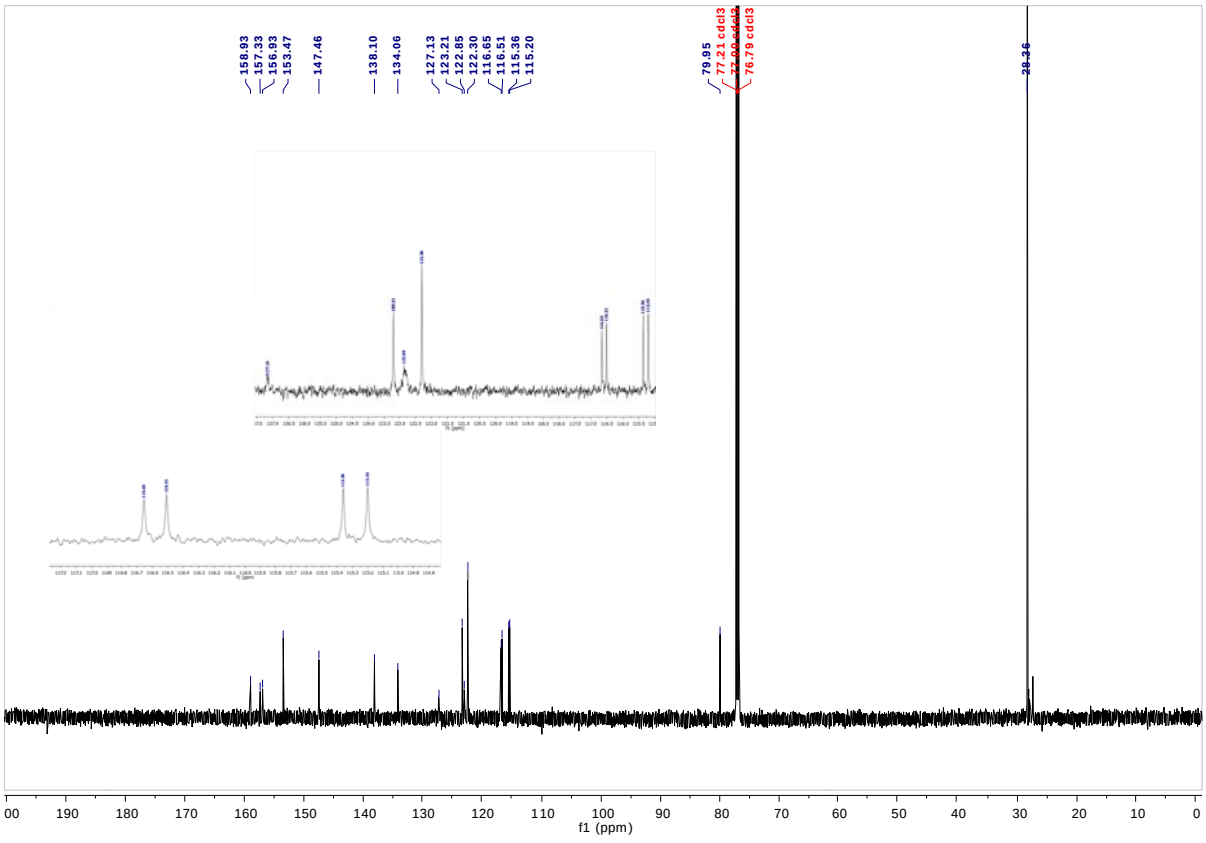
## *tert*-Butyl [4-isopropyl-2-(pyridin-2-yl)phenyl]carbamate (3f)



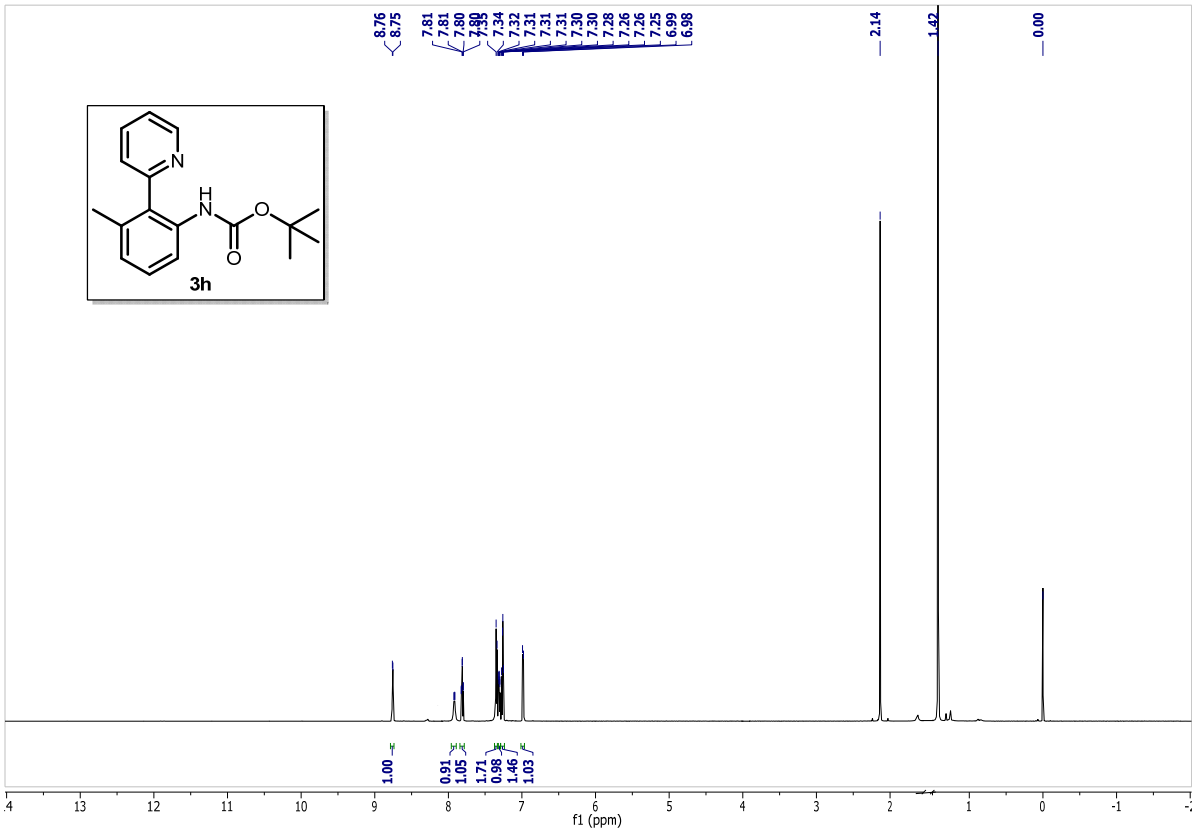



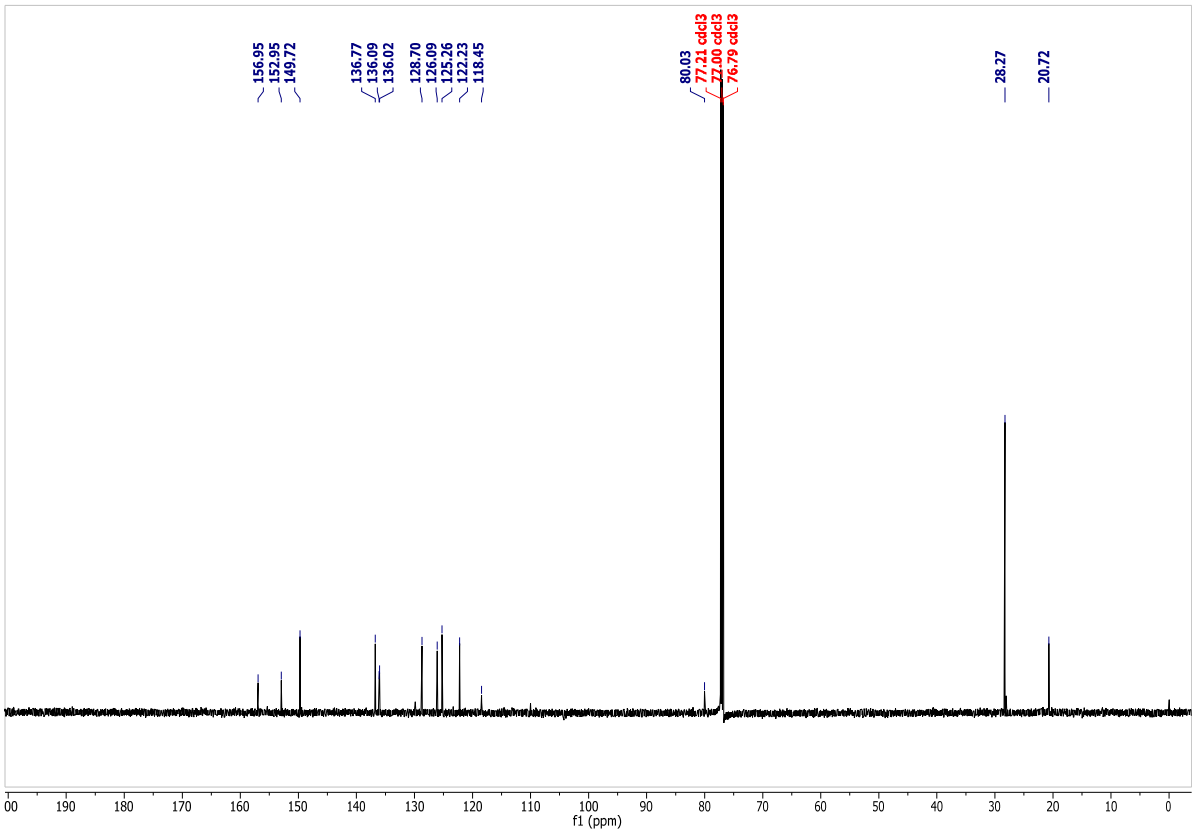
## *tert*-Butyl [4-fluoro-2-(pyridin-2-yl)phenyl]carbamate (3g)



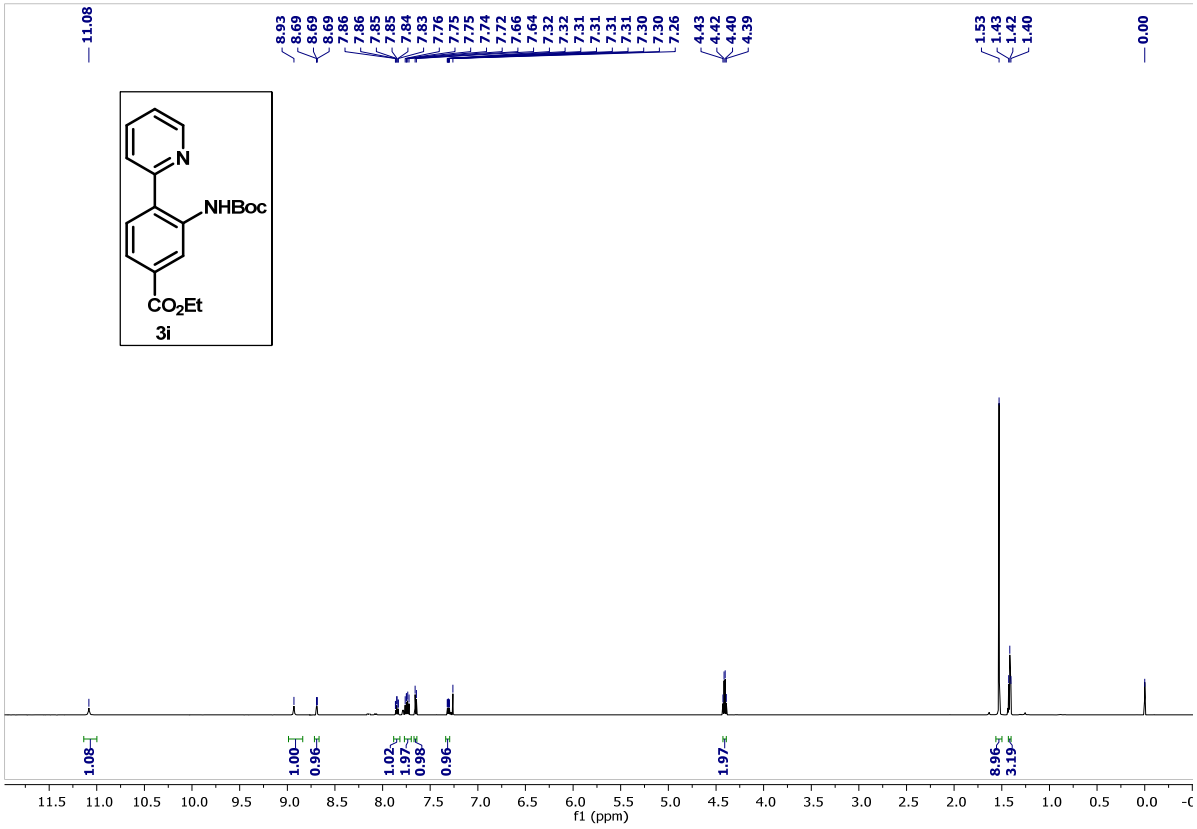



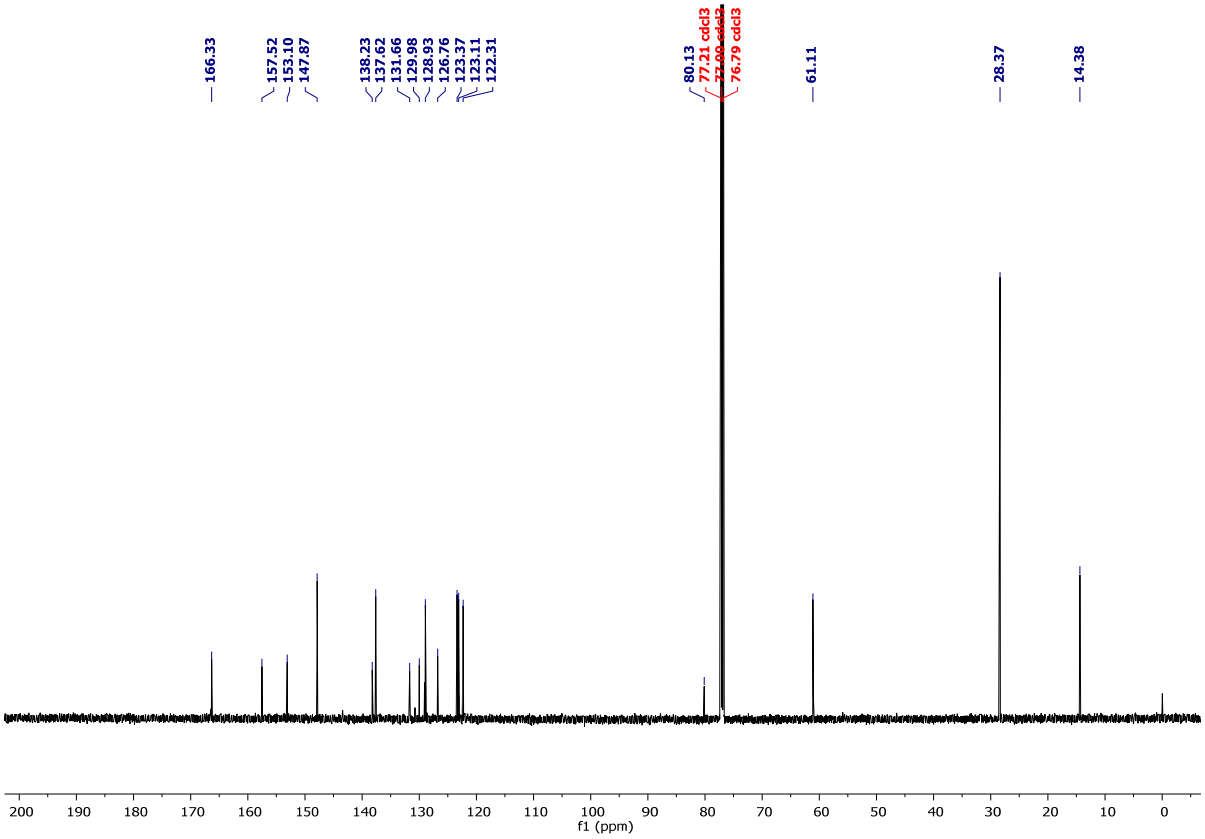
## *tert*-Butyl [3-methyl-2-(pyridin-2-yl)phenyl]carbamate (3h)



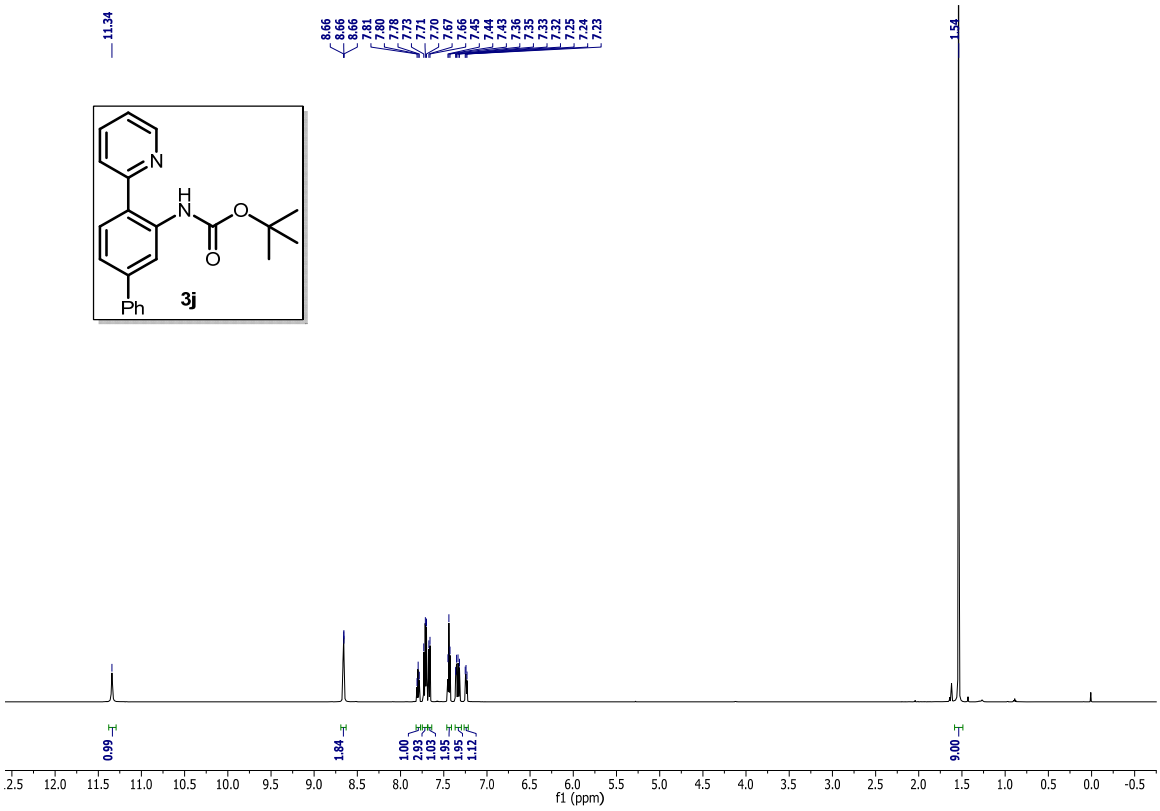



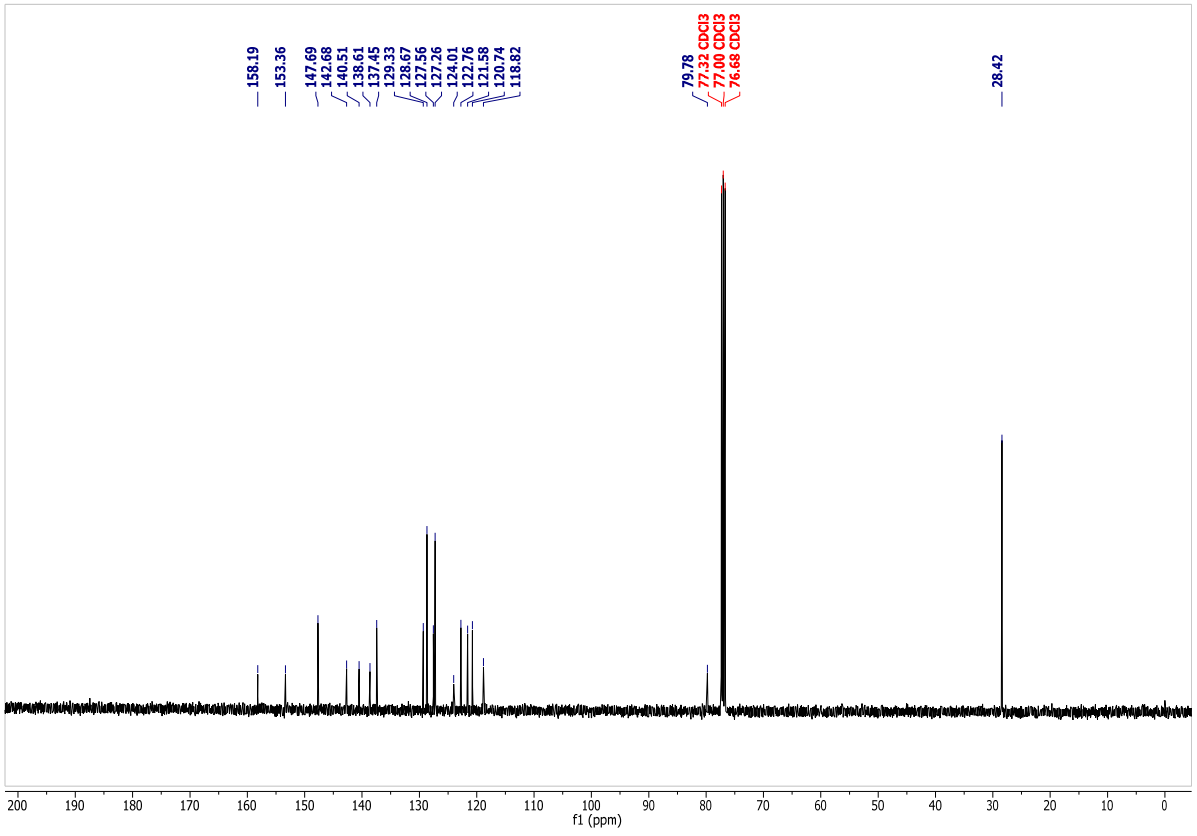
## Ethyl 3-[(*tert*-butoxycarbonyl)amino]-4-(pyridin-2-yl)benzoate (3i)



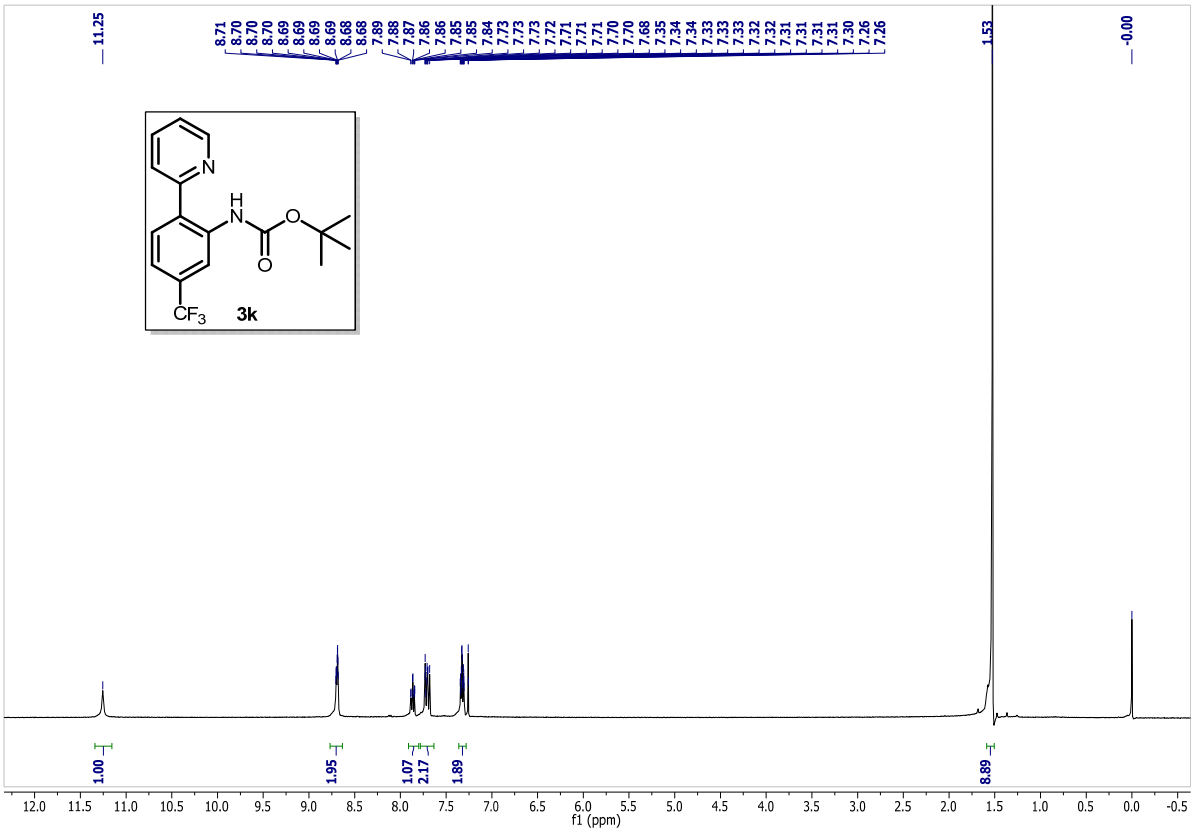



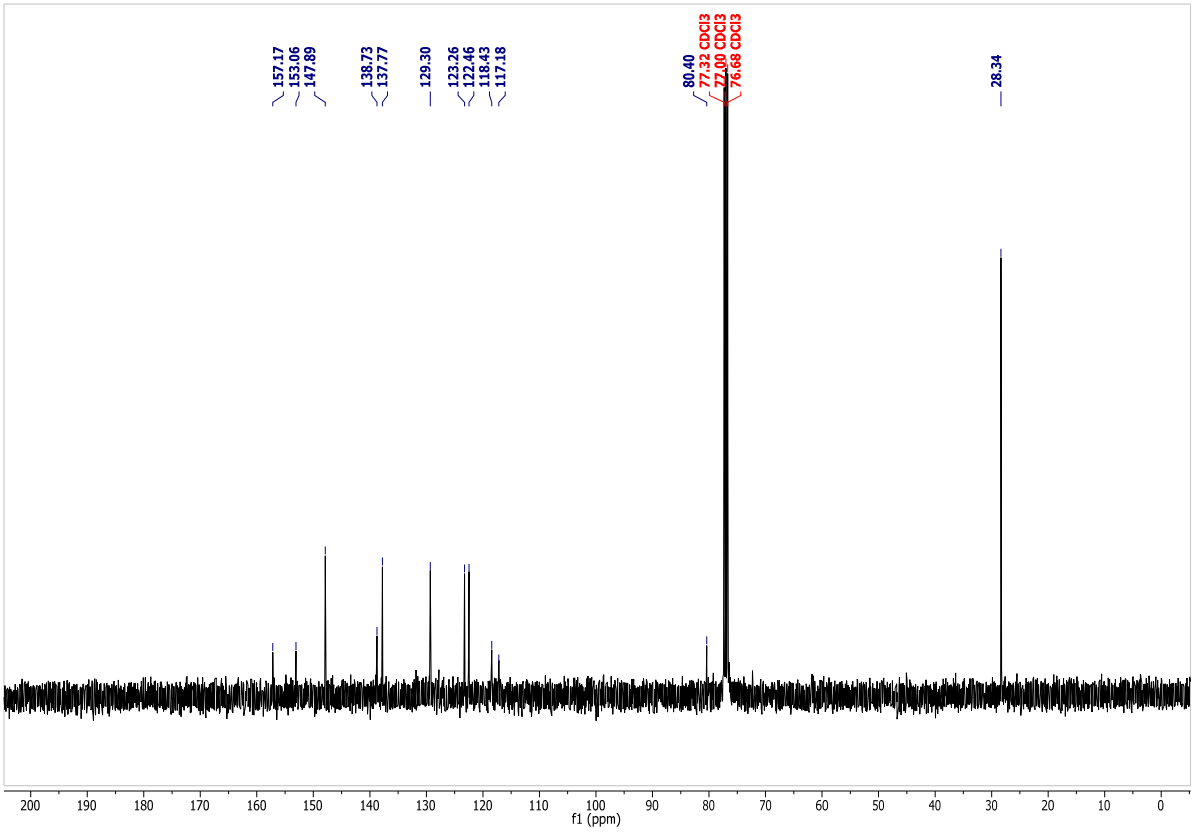
## *tert*-Butyl [4-(pyridin-2-yl)-(1,1'-biphenyl)-3-yl]carbamate (3j)



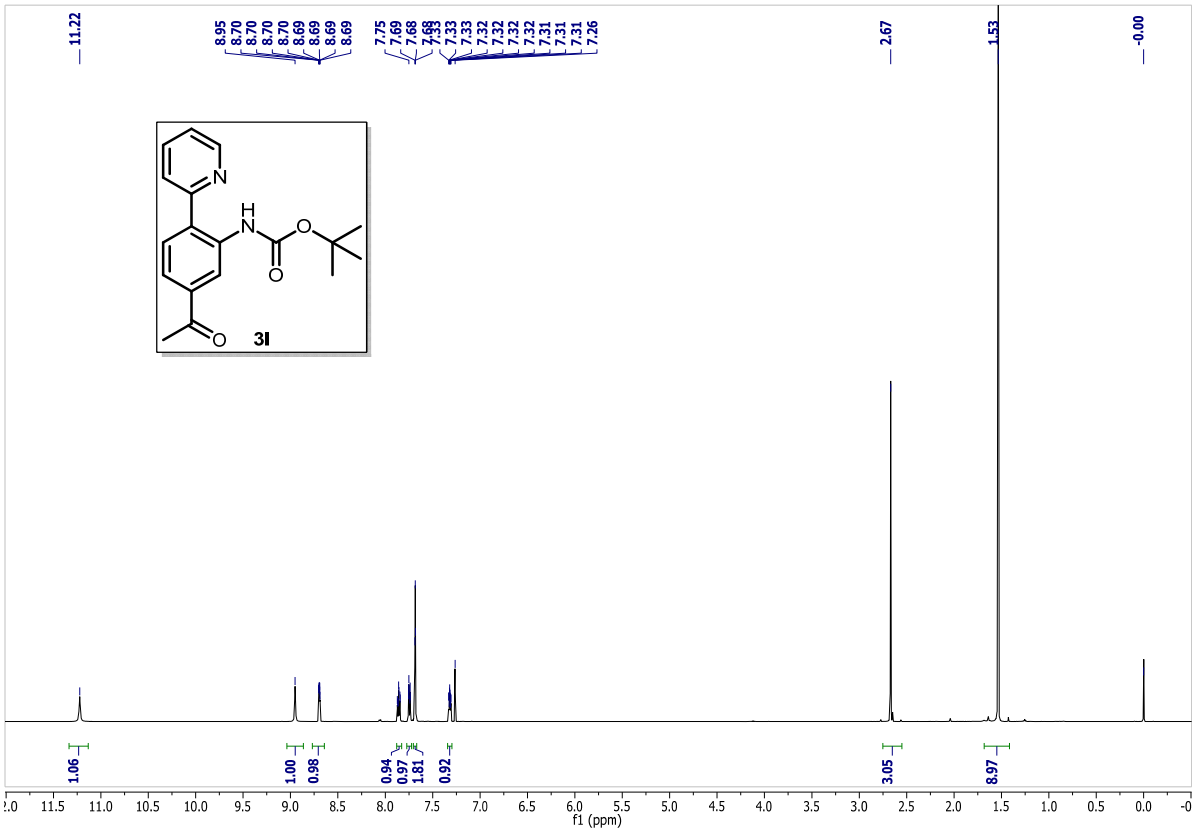



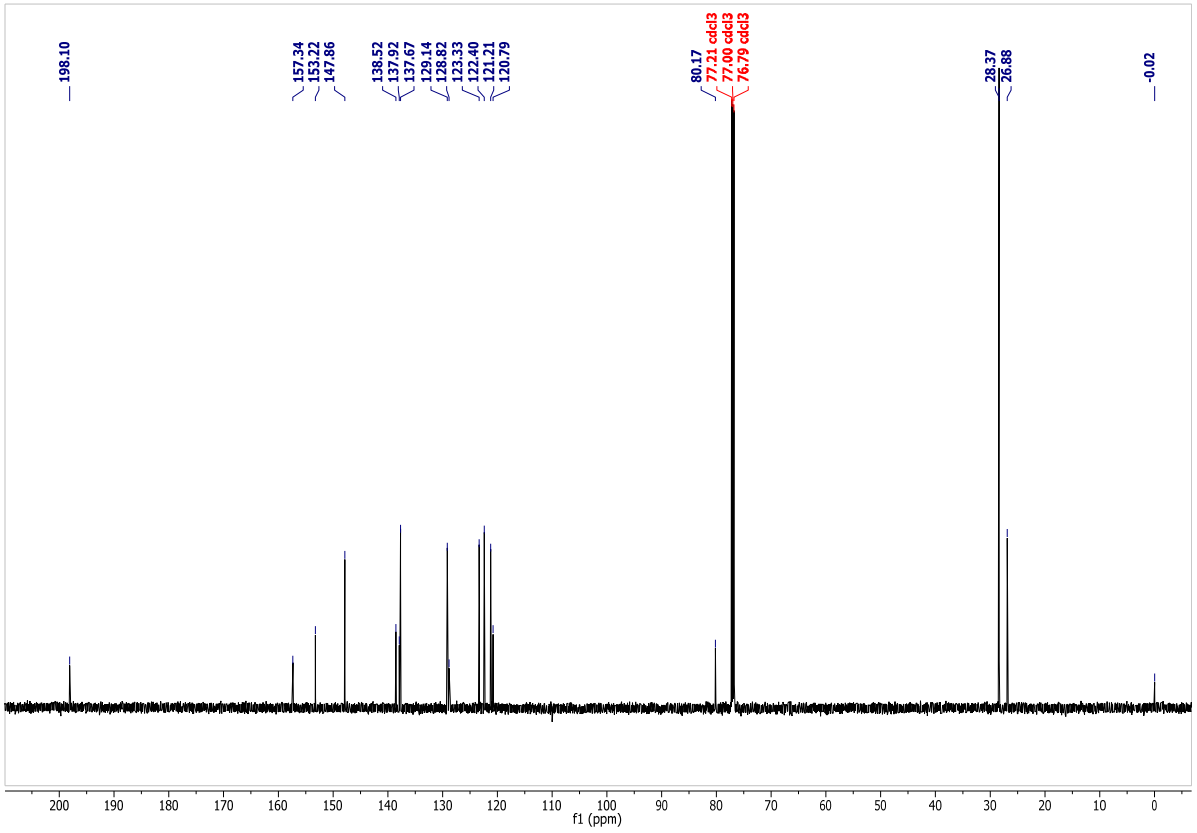
## *tert*-Butyl [2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl]carbamate (3k)



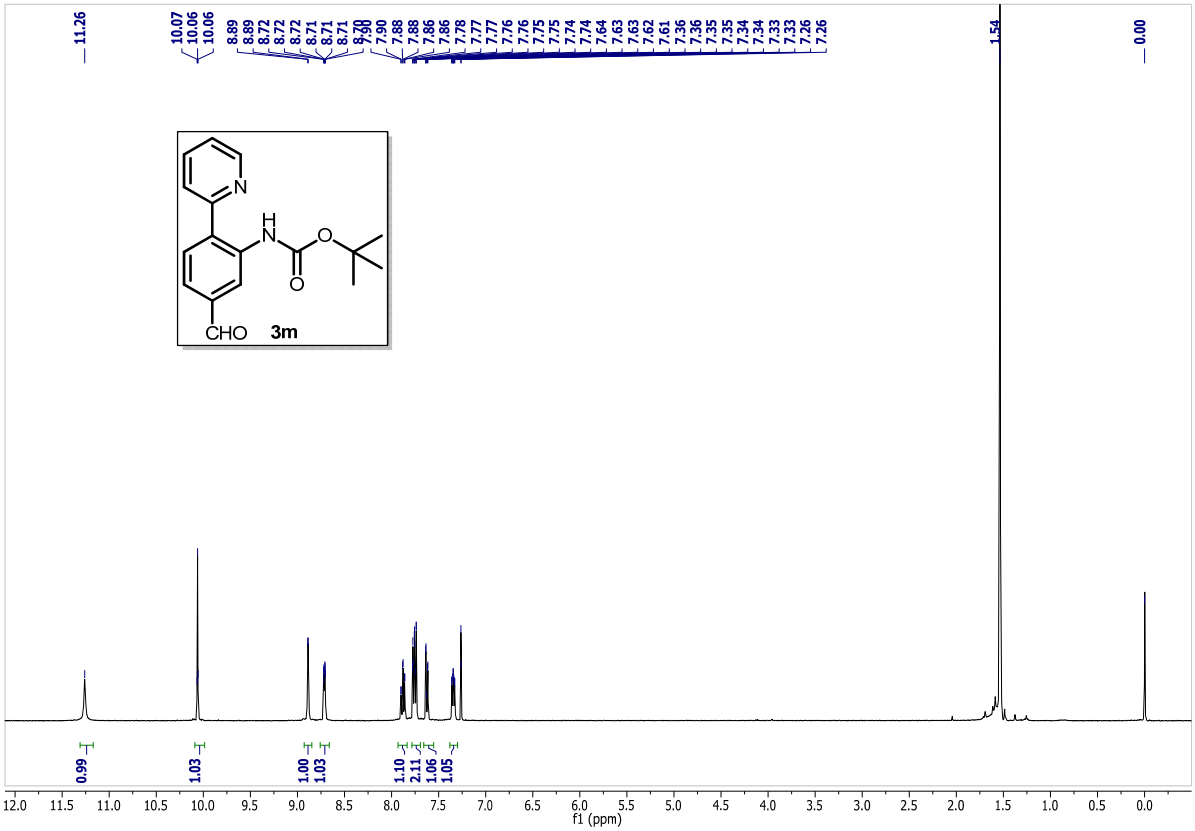



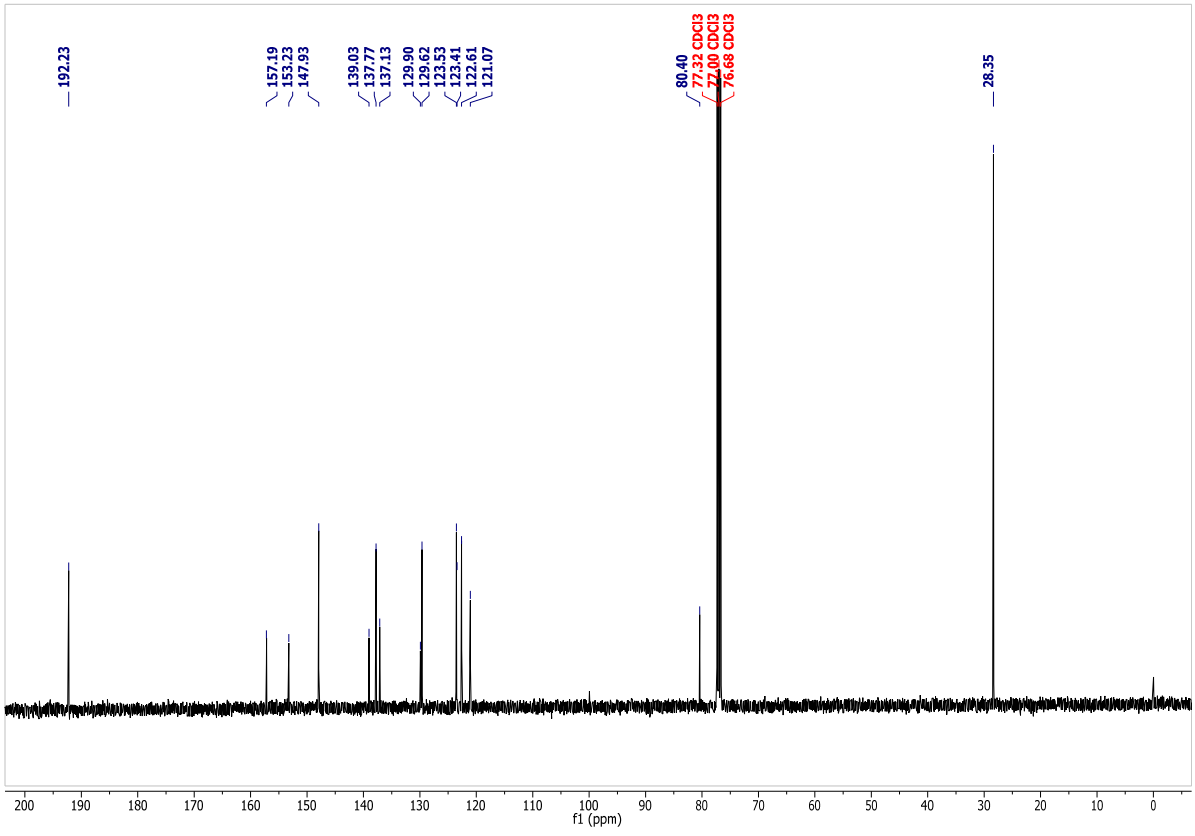
## *tert*-Butyl [5-acetyl-2-(pyridin-2-yl)phenyl]carbamate (3l)



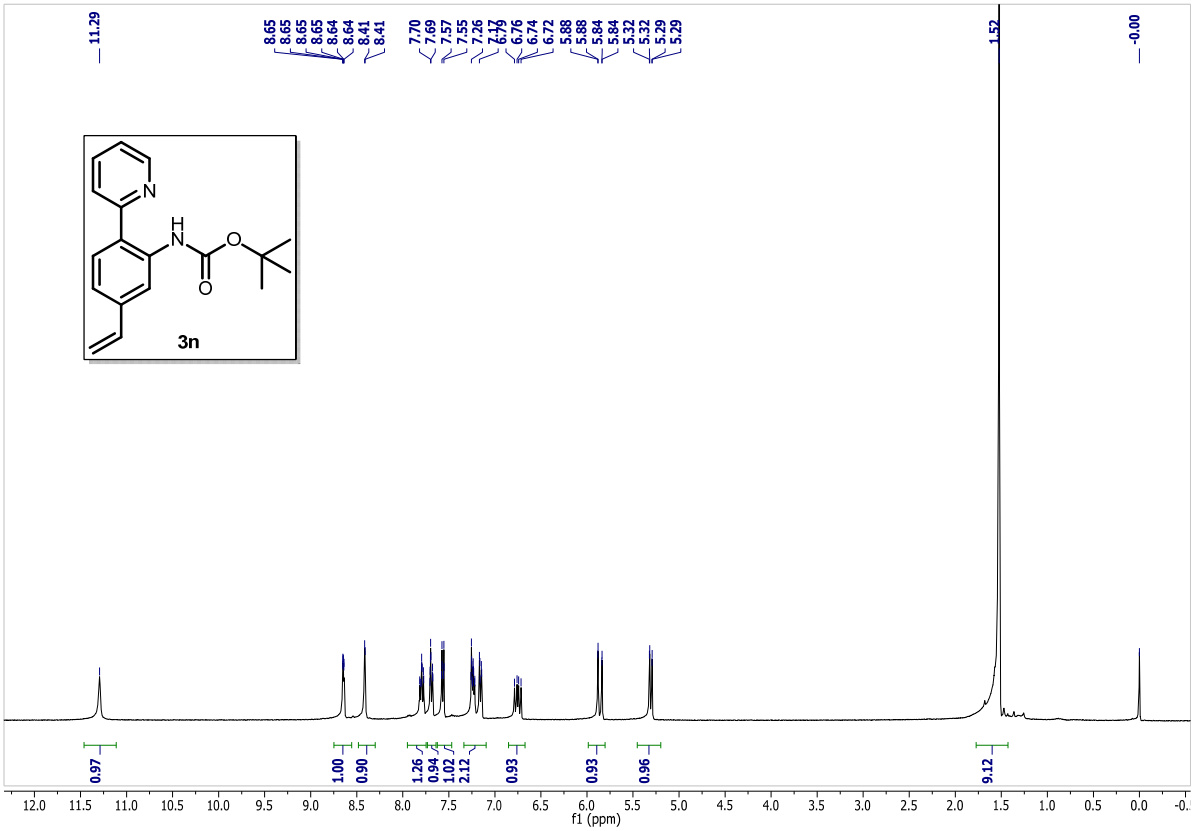



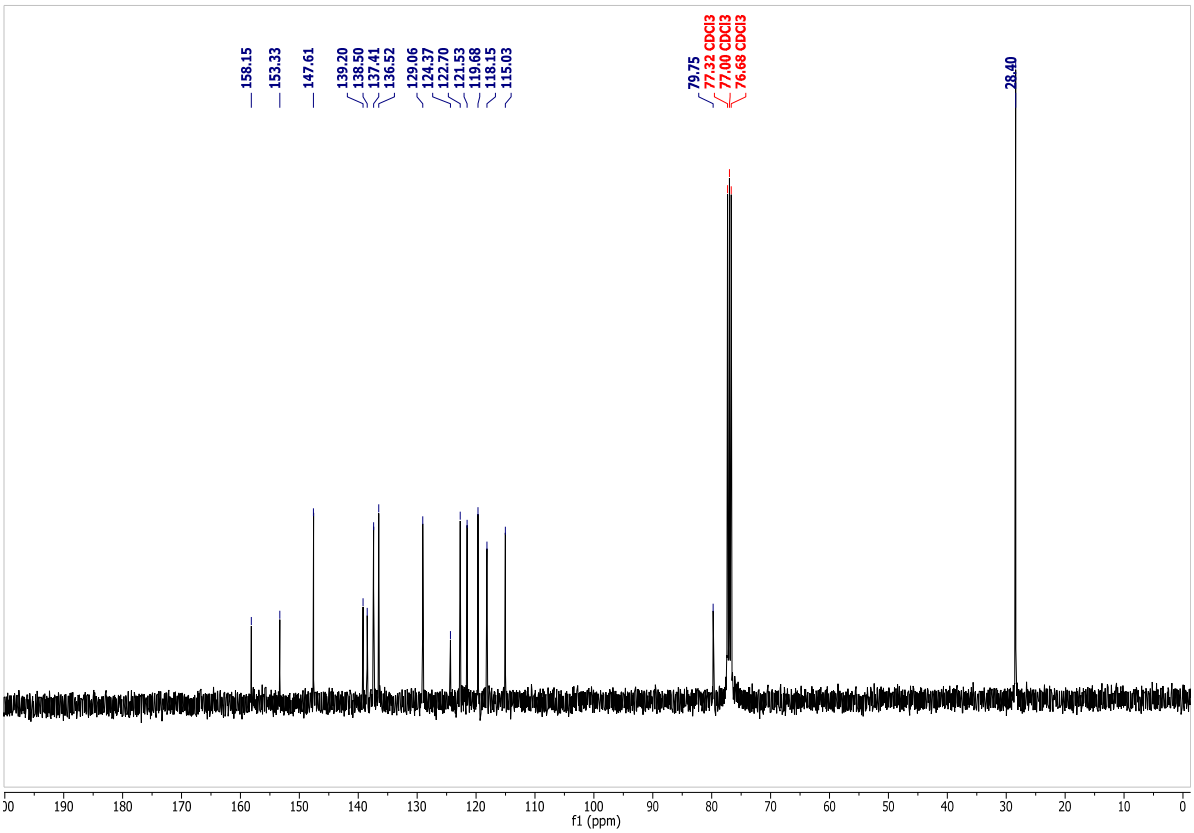
## *tert*-Butyl [5-formyl-2-(pyridin-2-yl)phenyl]carbamate (3m)



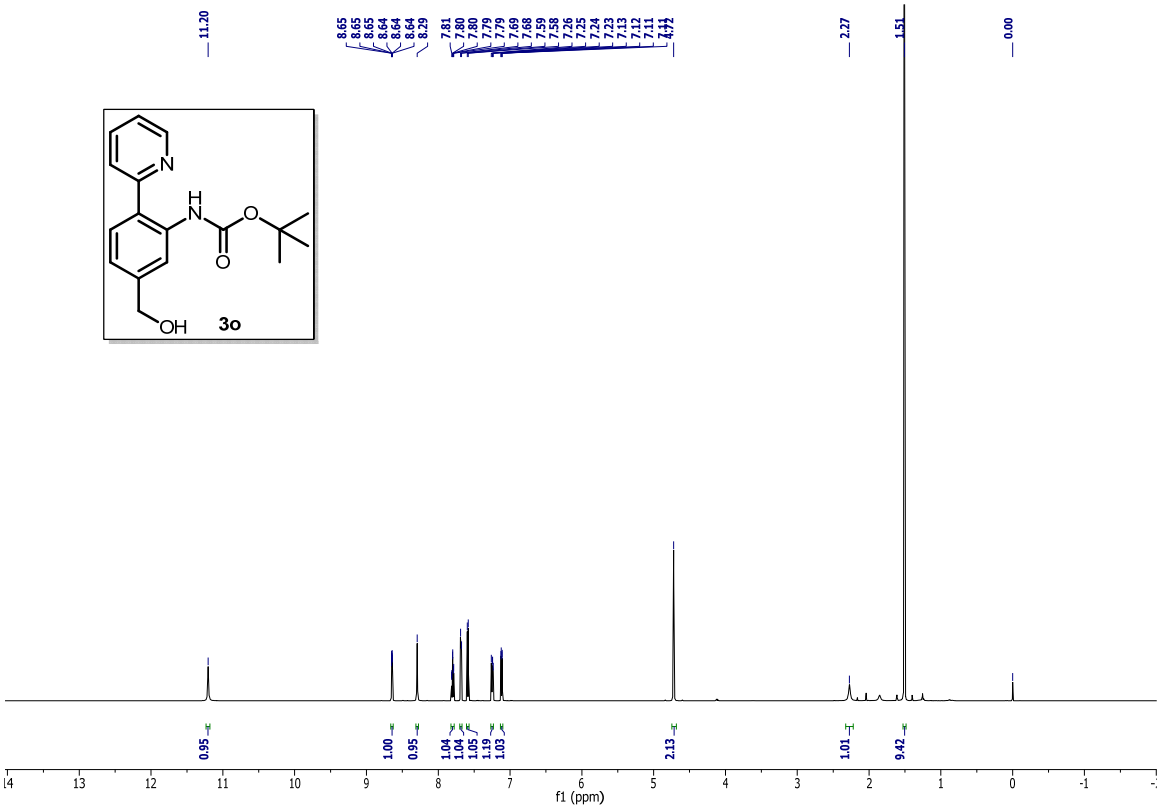



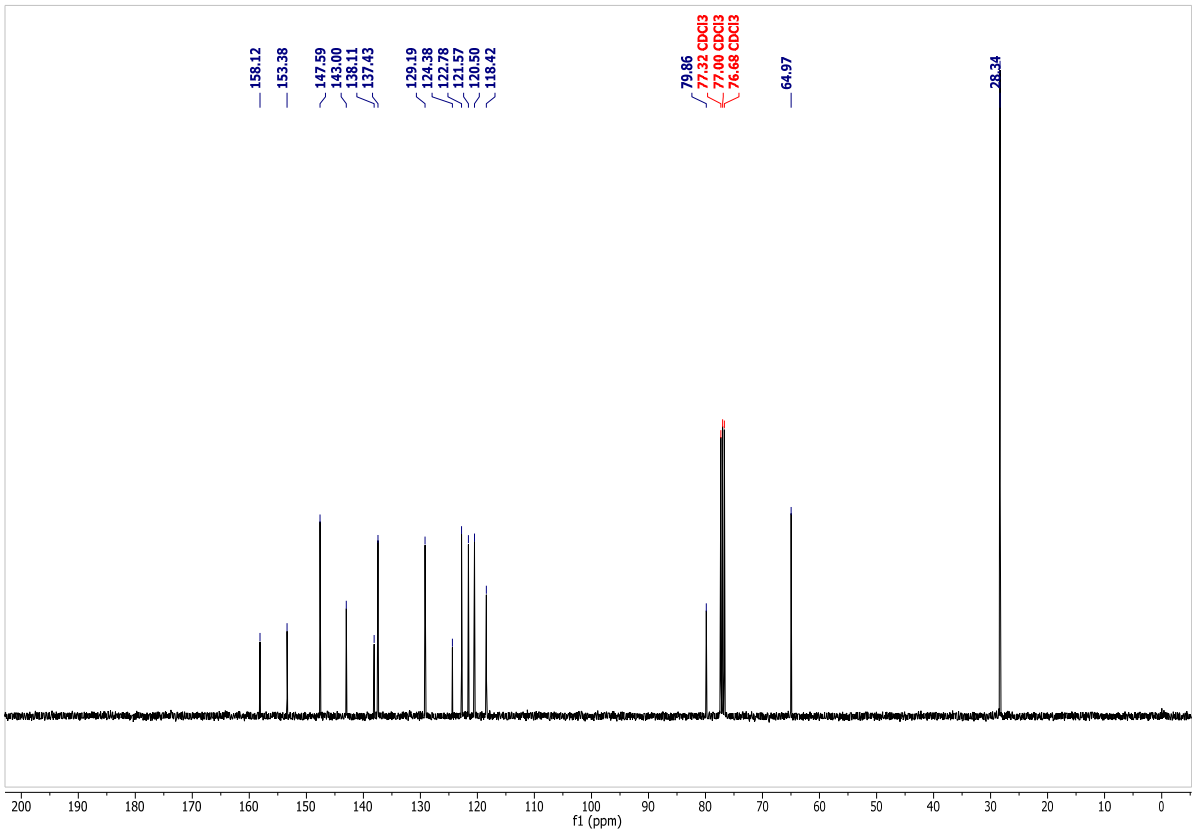
## *tert*-Butyl [2-(pyridin-2-yl)-5-vinylphenyl]carbamate (3n)



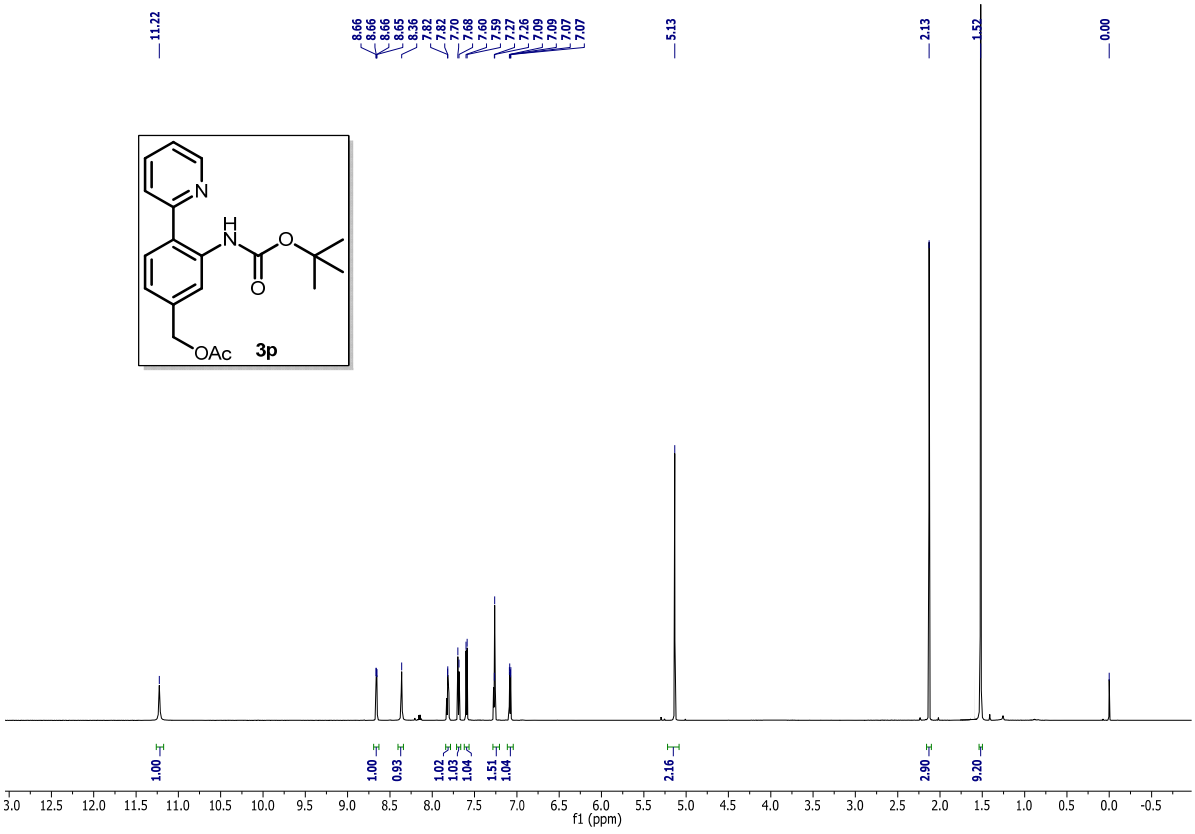



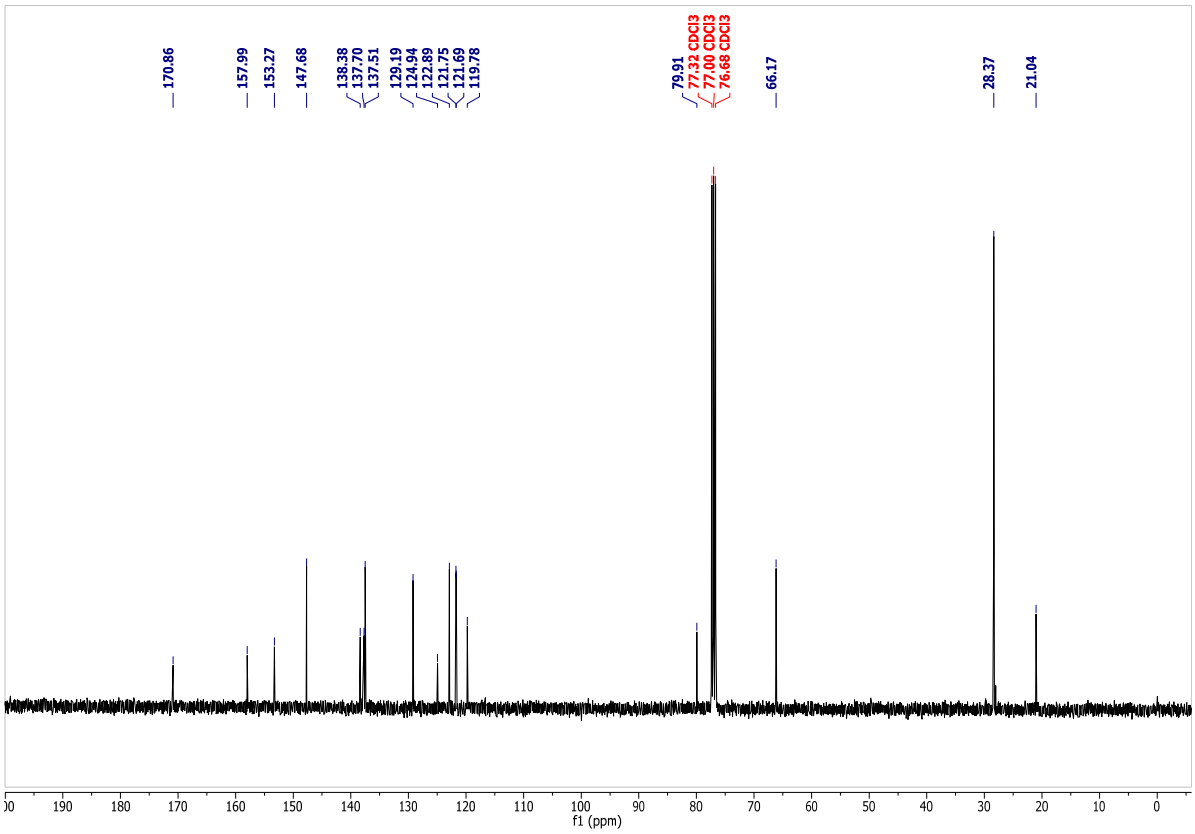
## *tert*-Butyl [5-(hydroxymethyl)-2-(pyridin-2-yl)phenyl]carbamate (3o)



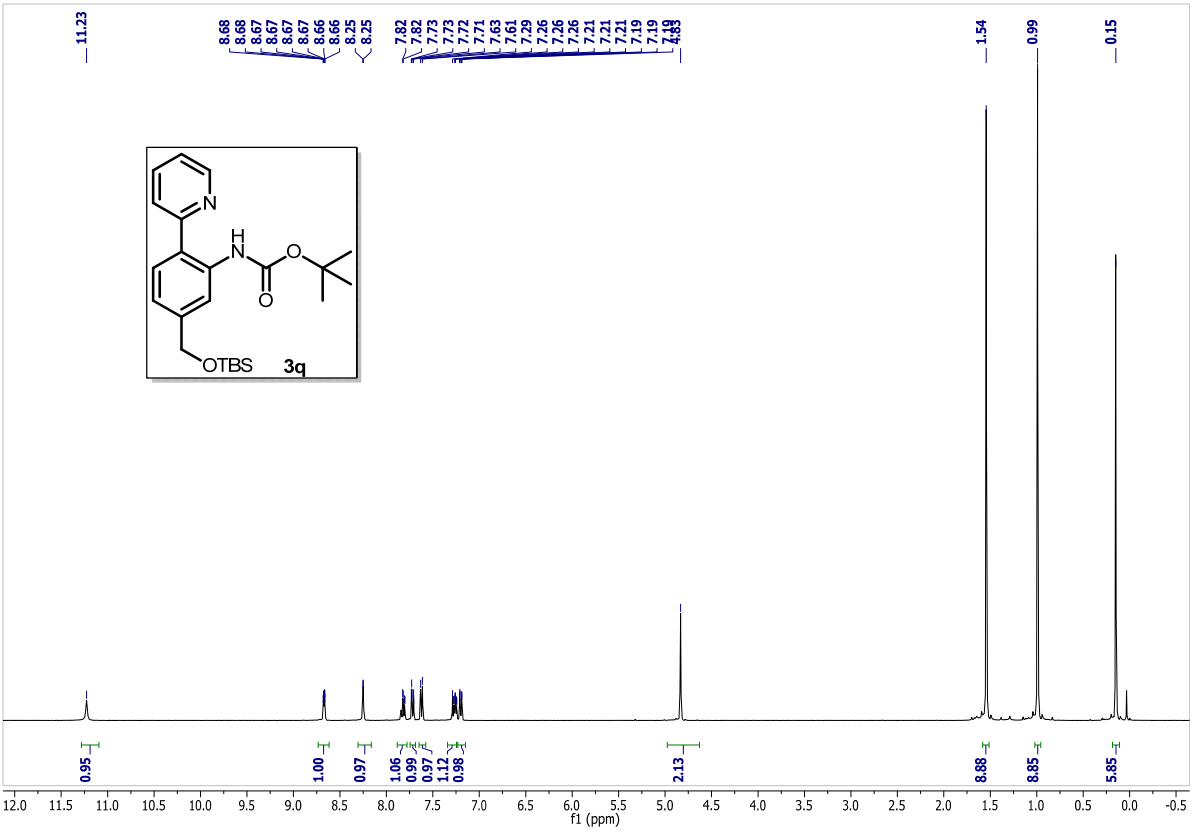



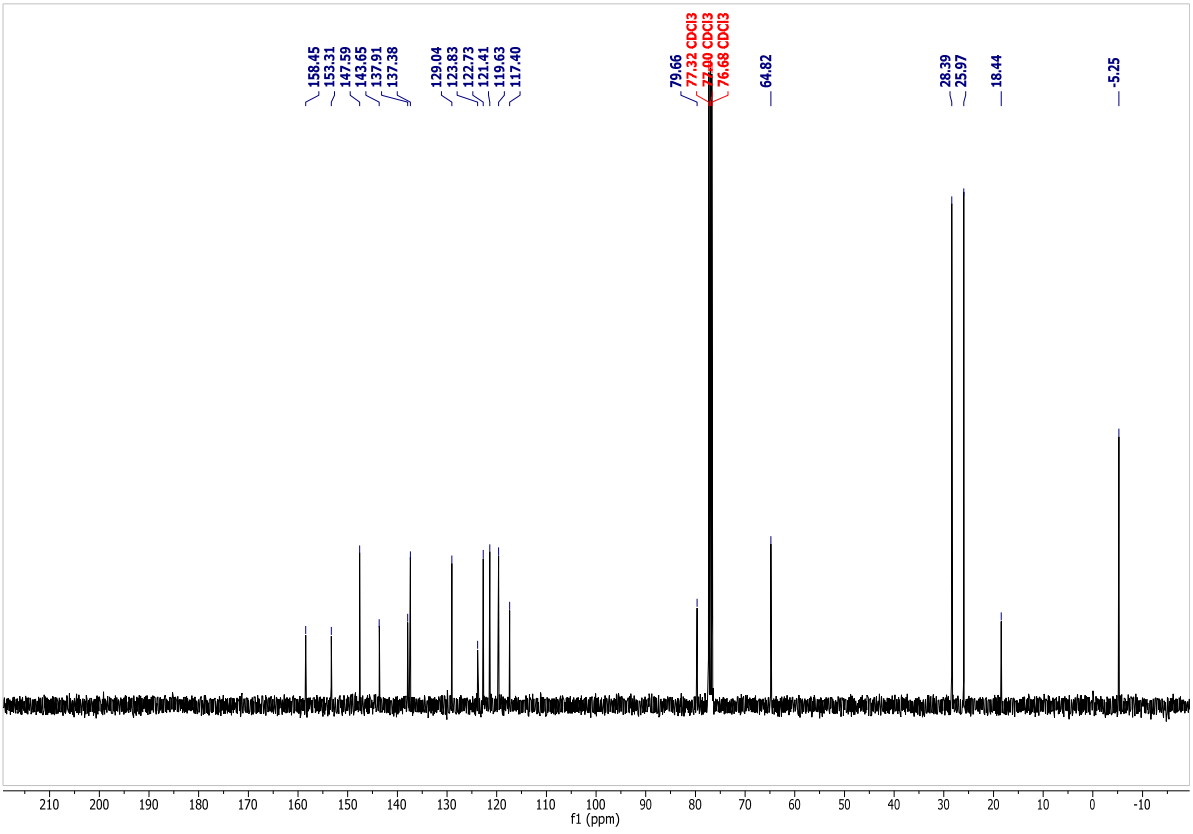
## 3-[(*tert*-Butoxycarbonyl)amino]-4-(pyridin-2-yl)benzyl acetate (3p)



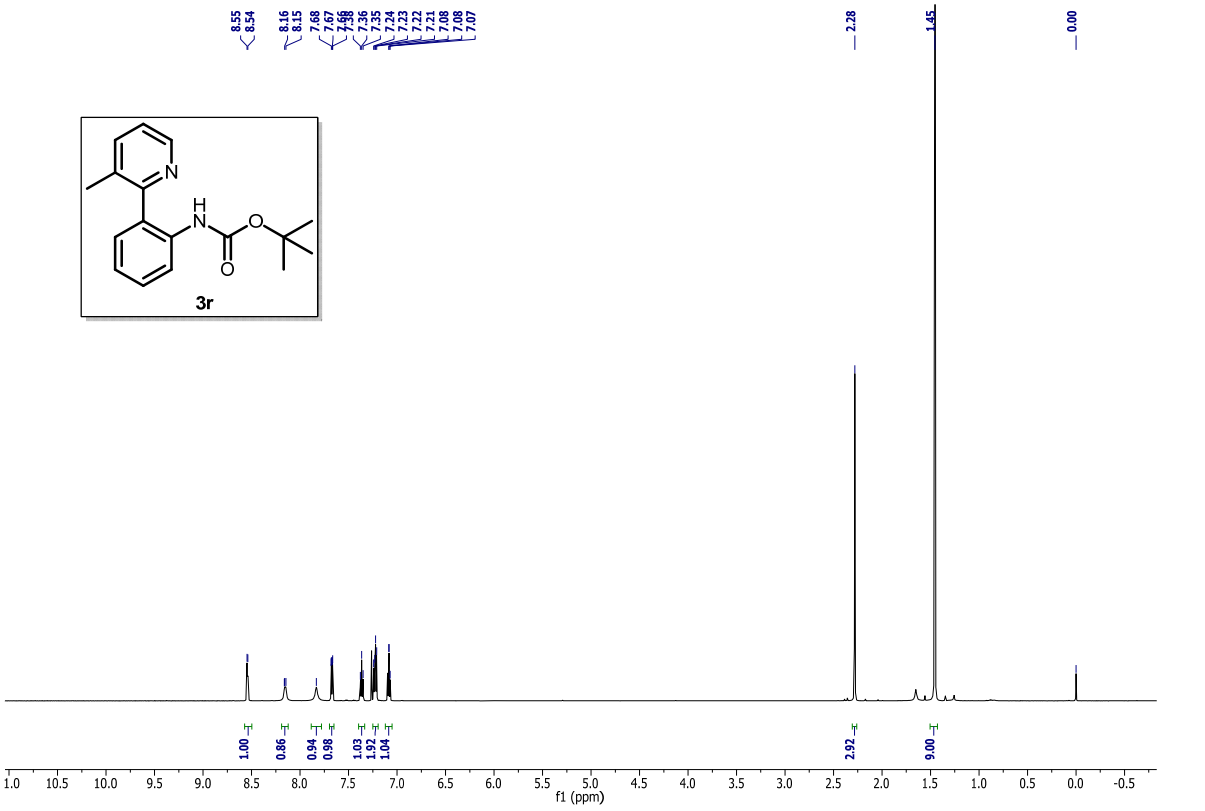



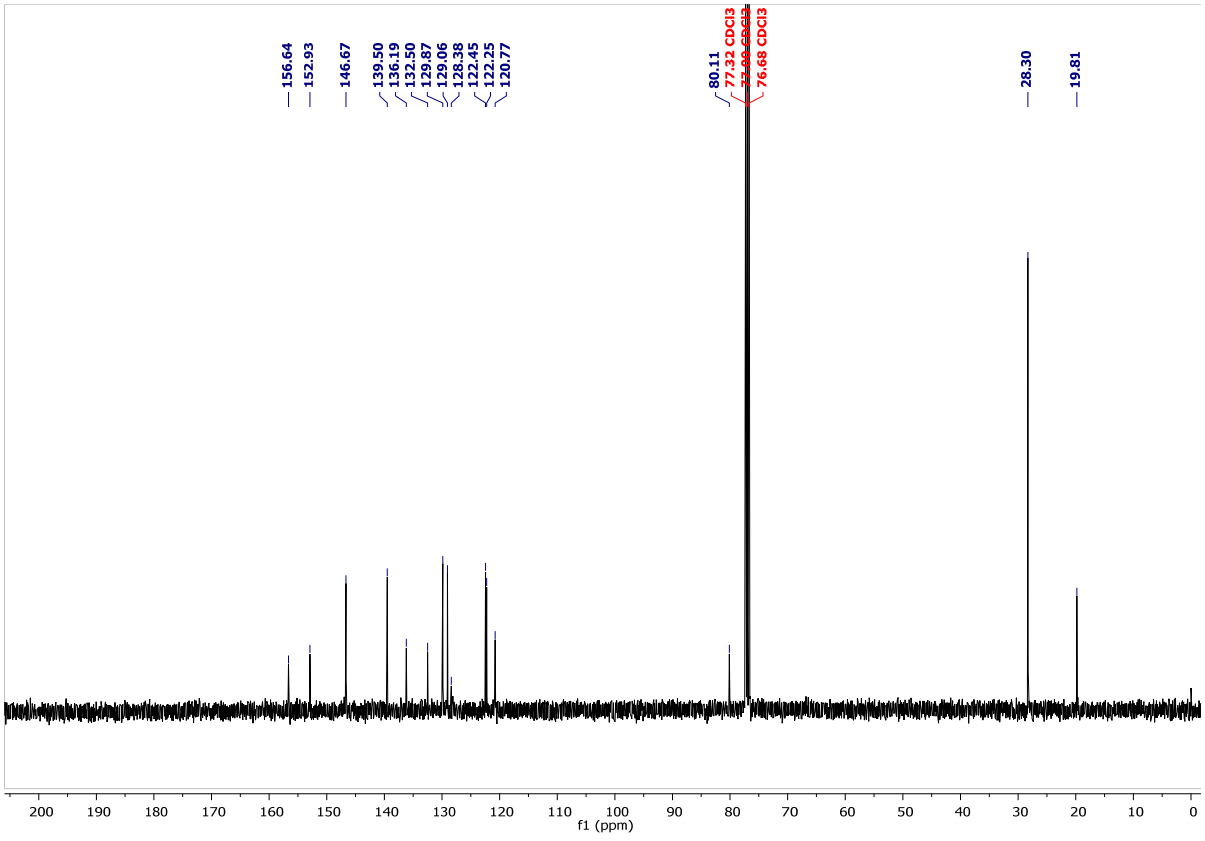
**_tert_-Butyl [5-{(_tert_-butyldimethylsilyl)oxymethyl}-2-(pyridin-2-yl)phenyl]carbamate (3q)**



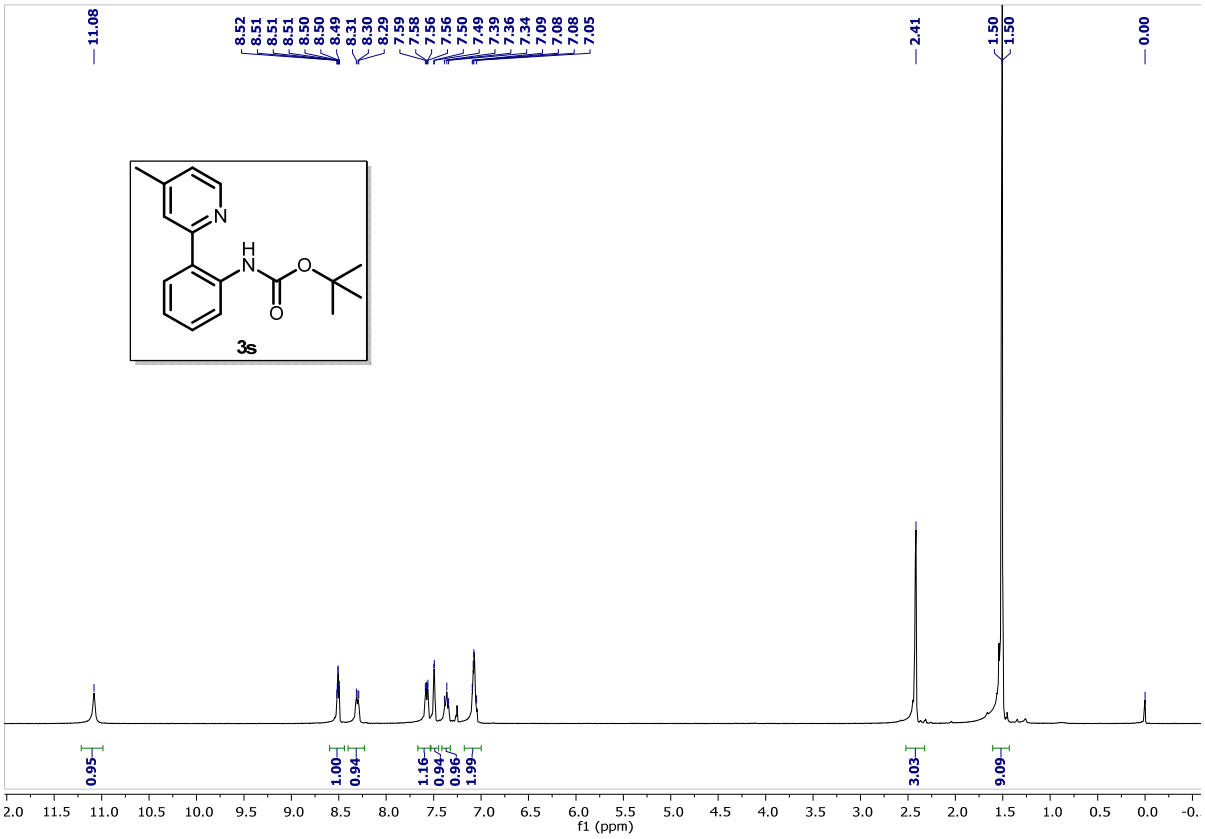



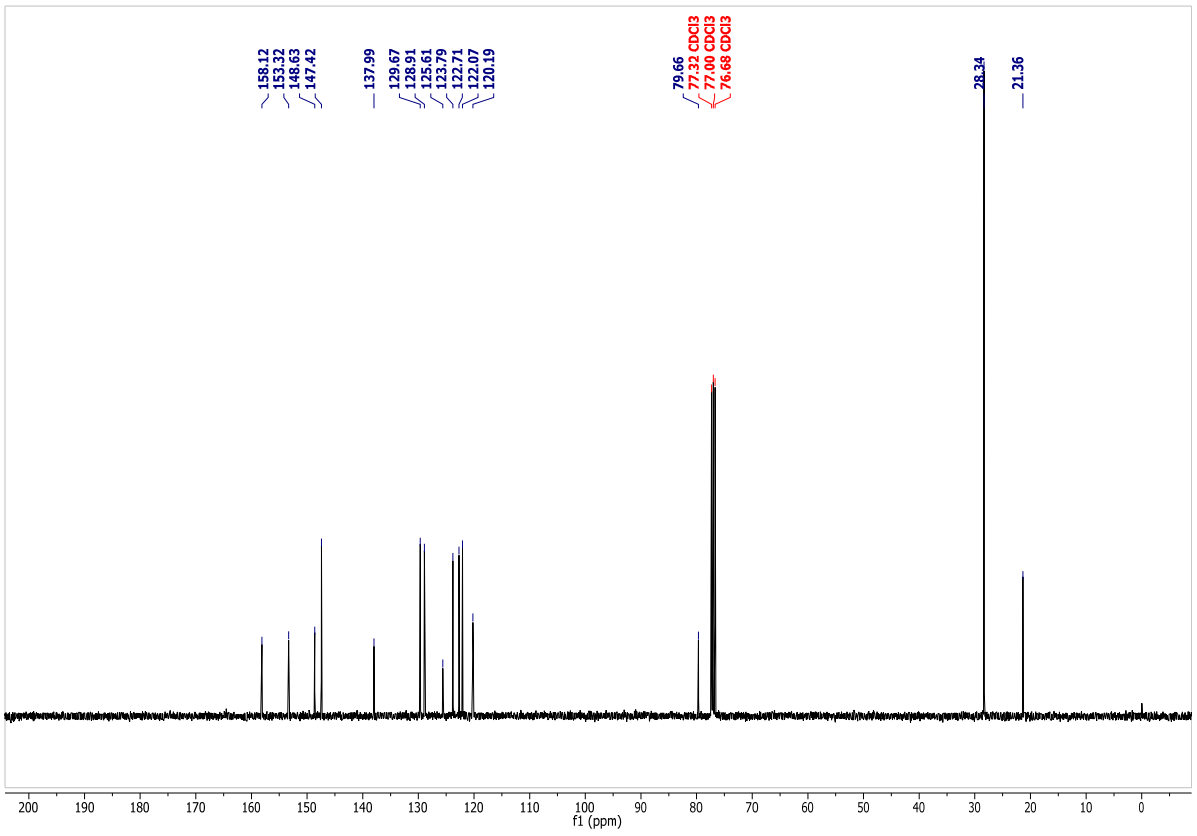
## *tert*-Butyl [2-(3-methylpyridin-2-yl)phenyl]carbamate (3r)



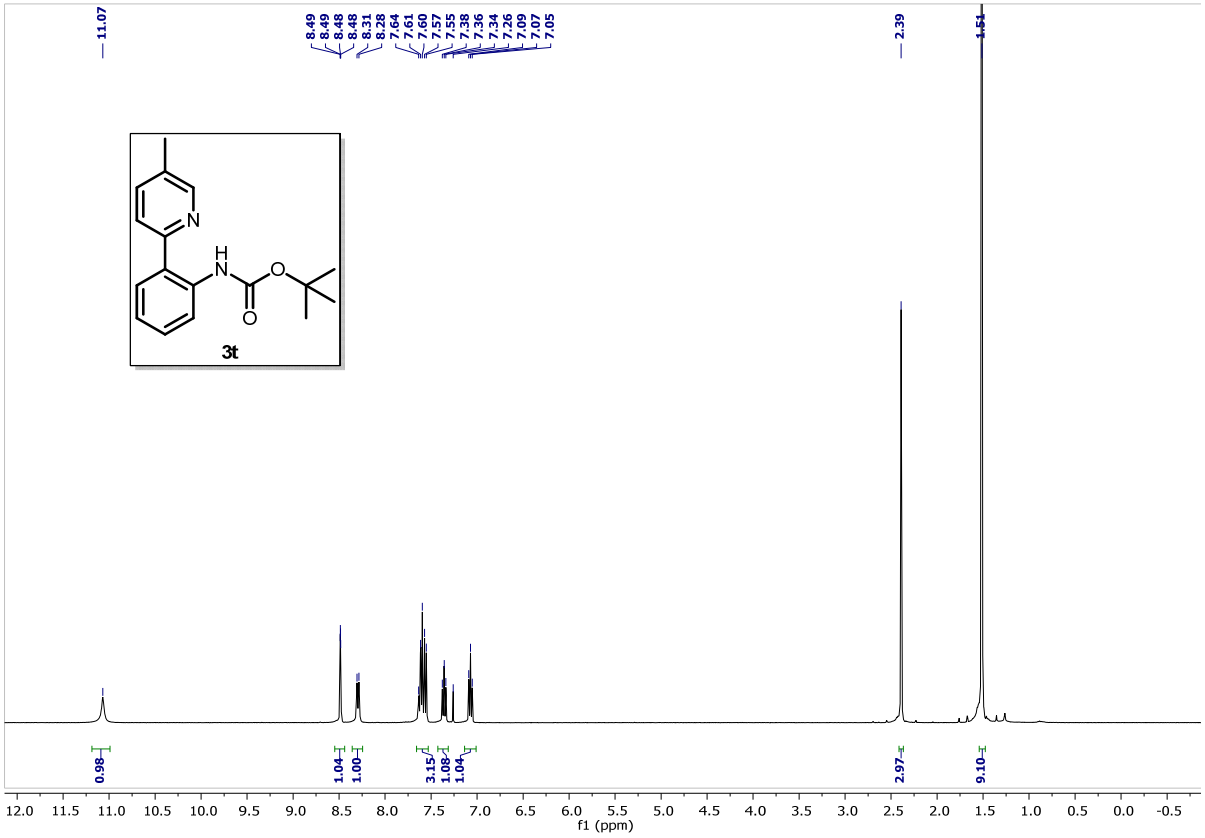



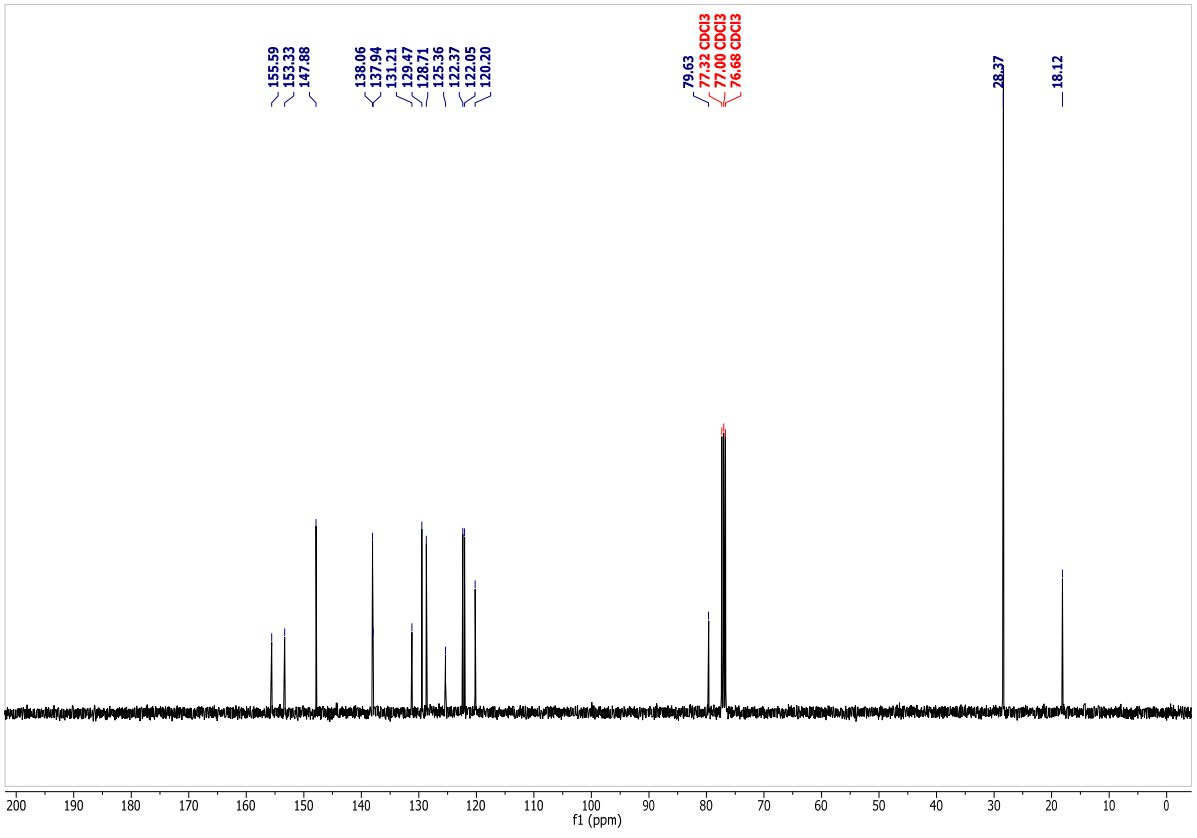
## *tert*-Butyl [2-(4-methylpyridin-2-yl)phenyl]carbamate (3s)



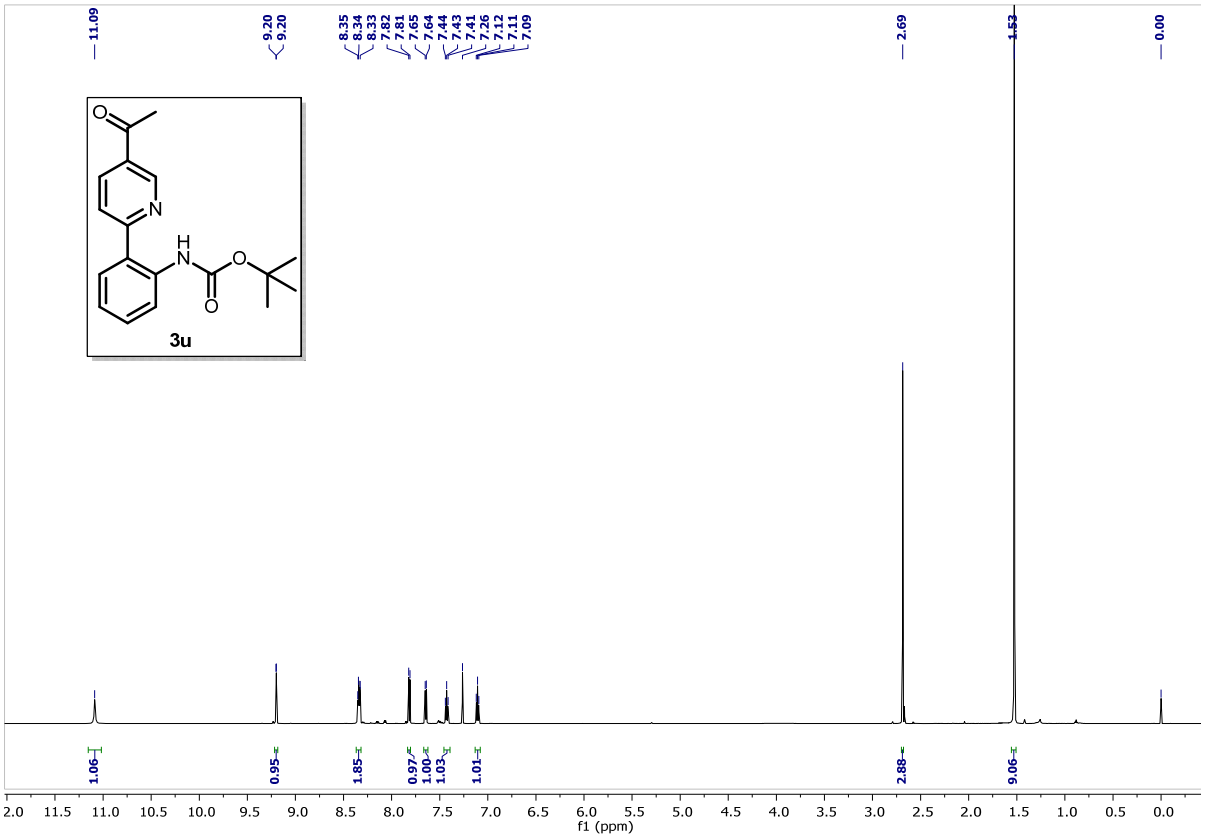



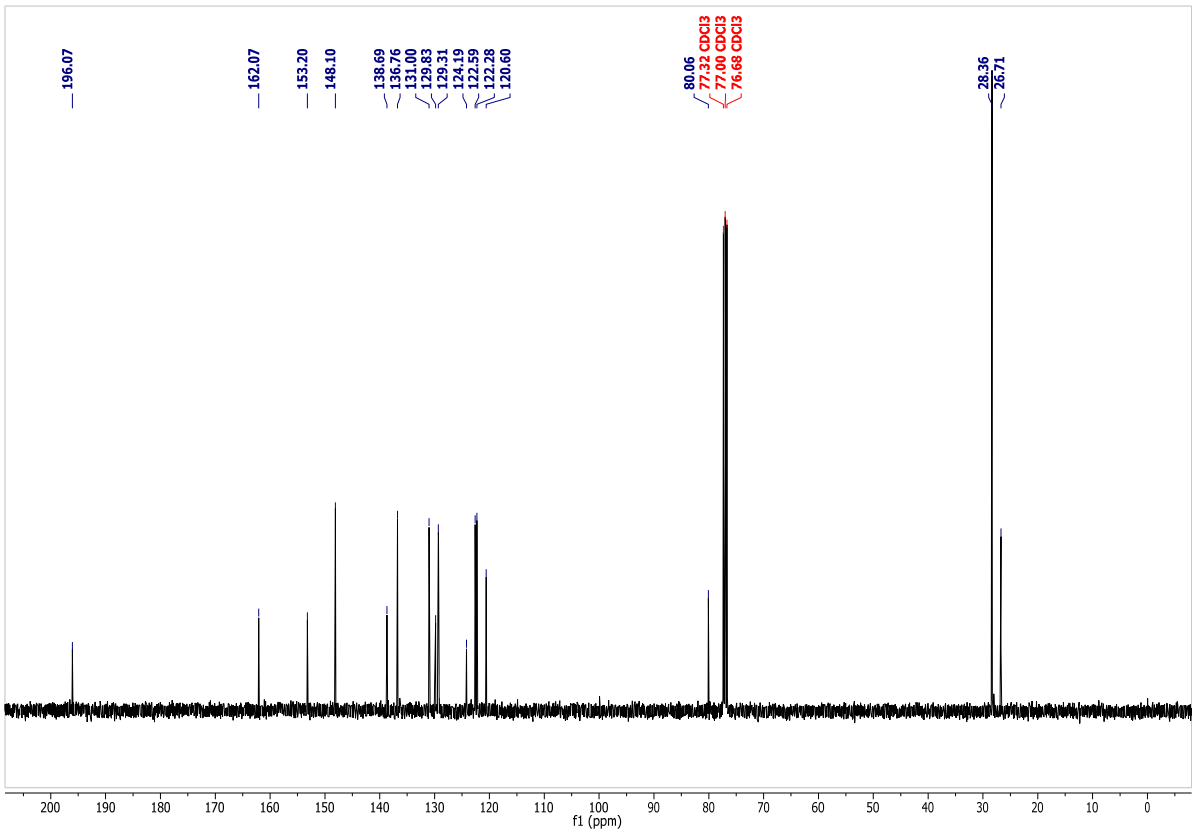
## *tert*-Butyl [2-(5-methylpyridin-2-yl)phenyl]carbamate (3t)



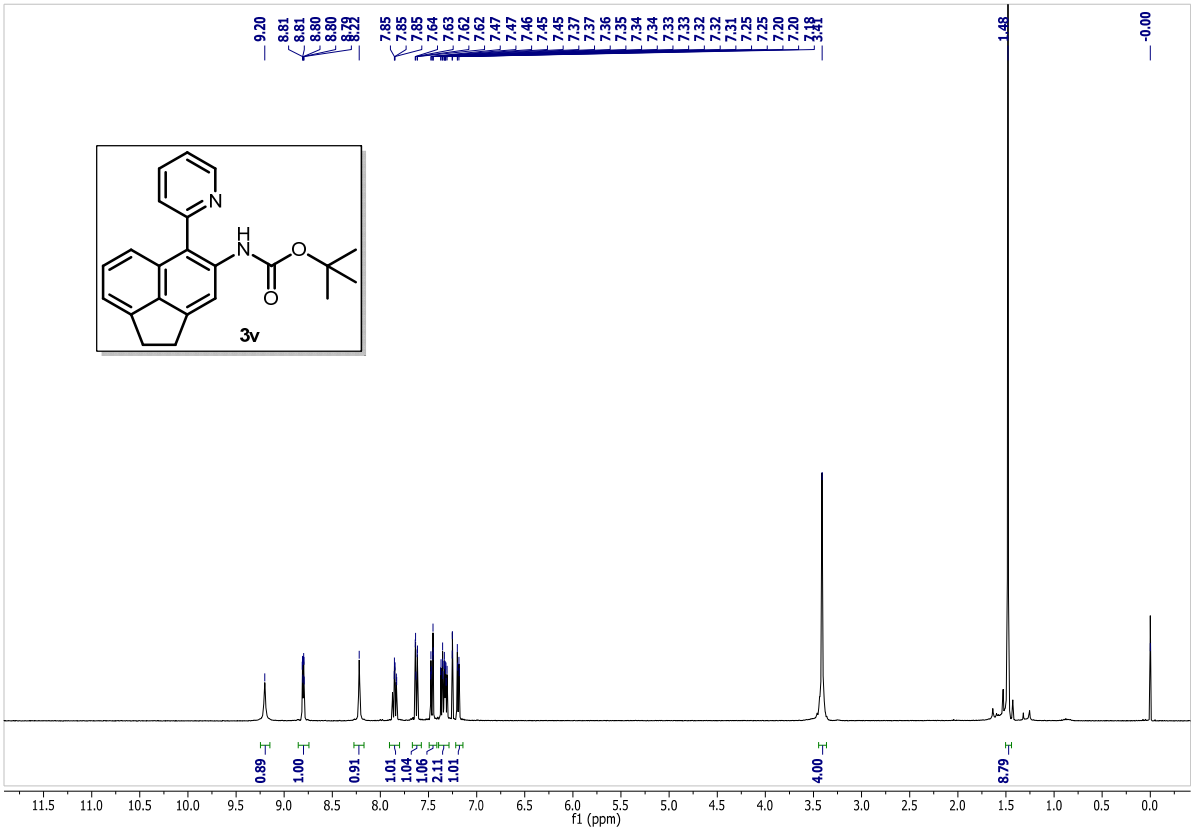



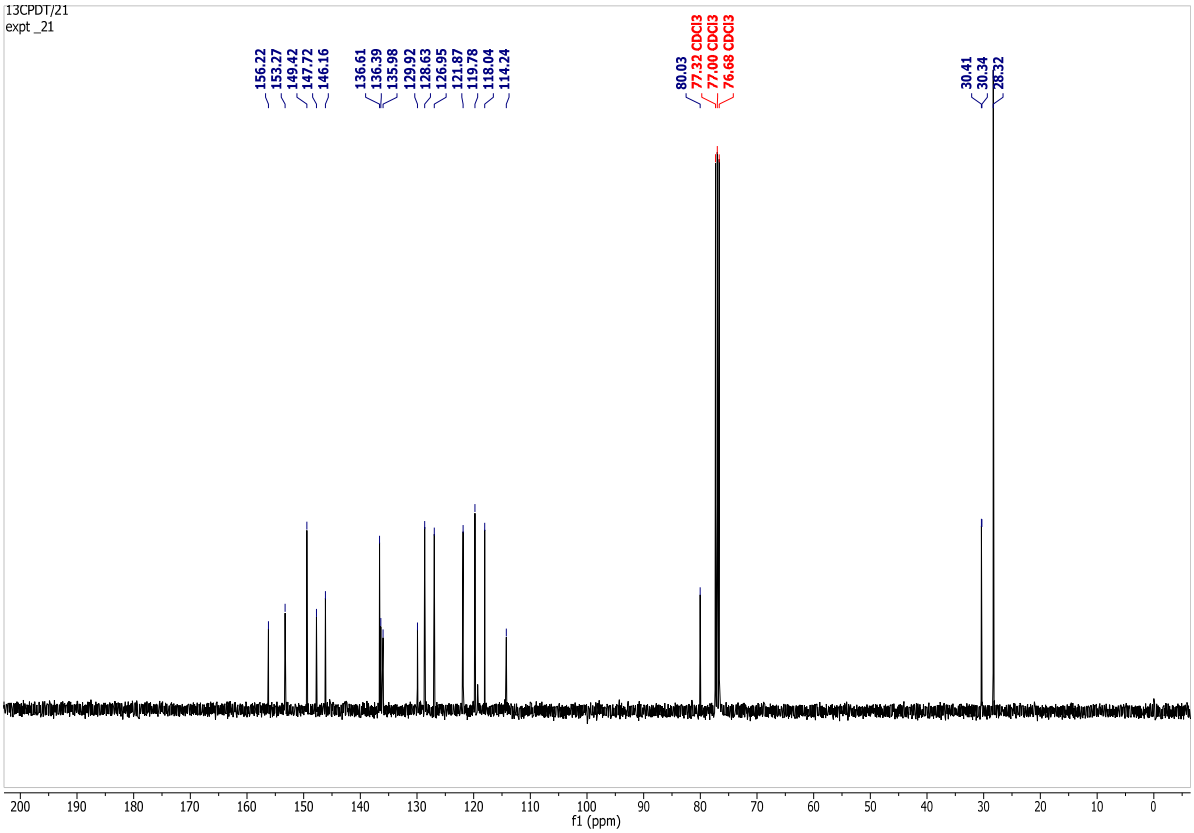
## *tert*-Butyl [2-(5-acetylpyridin-2-yl)phenyl]carbamate (3u)



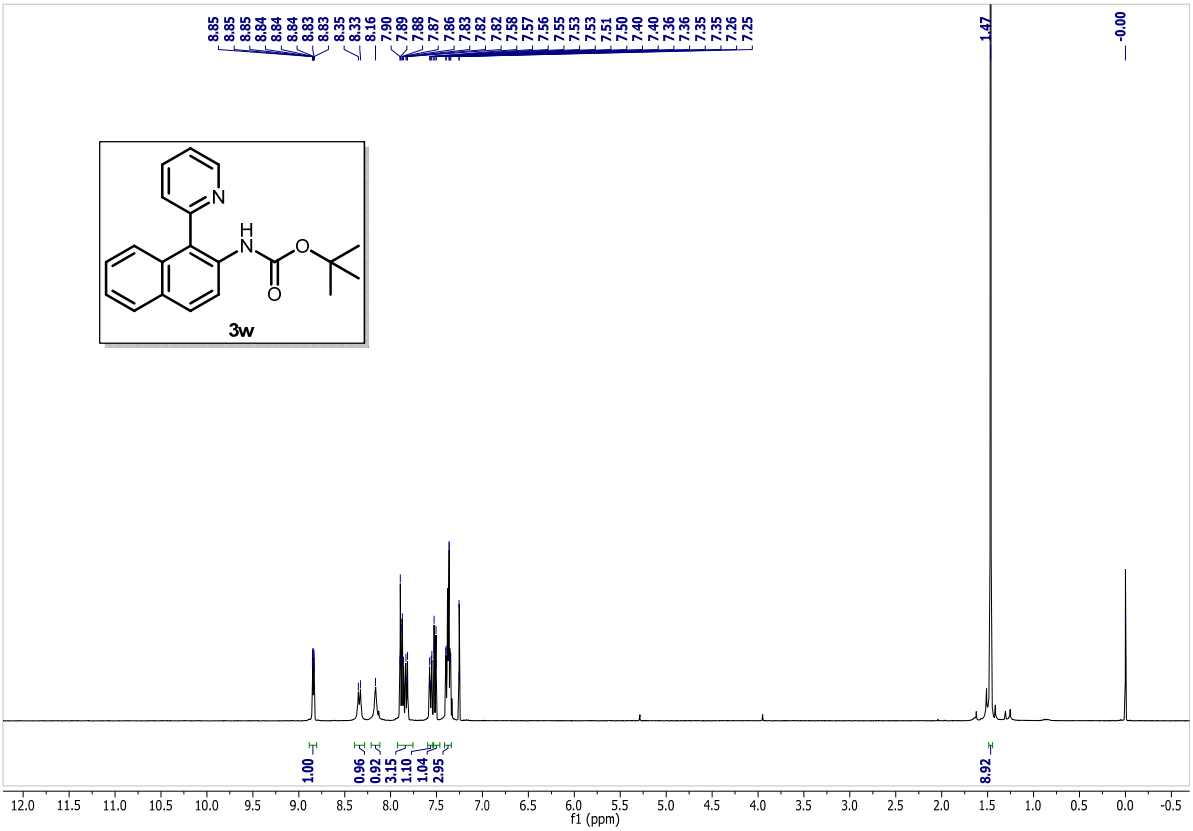



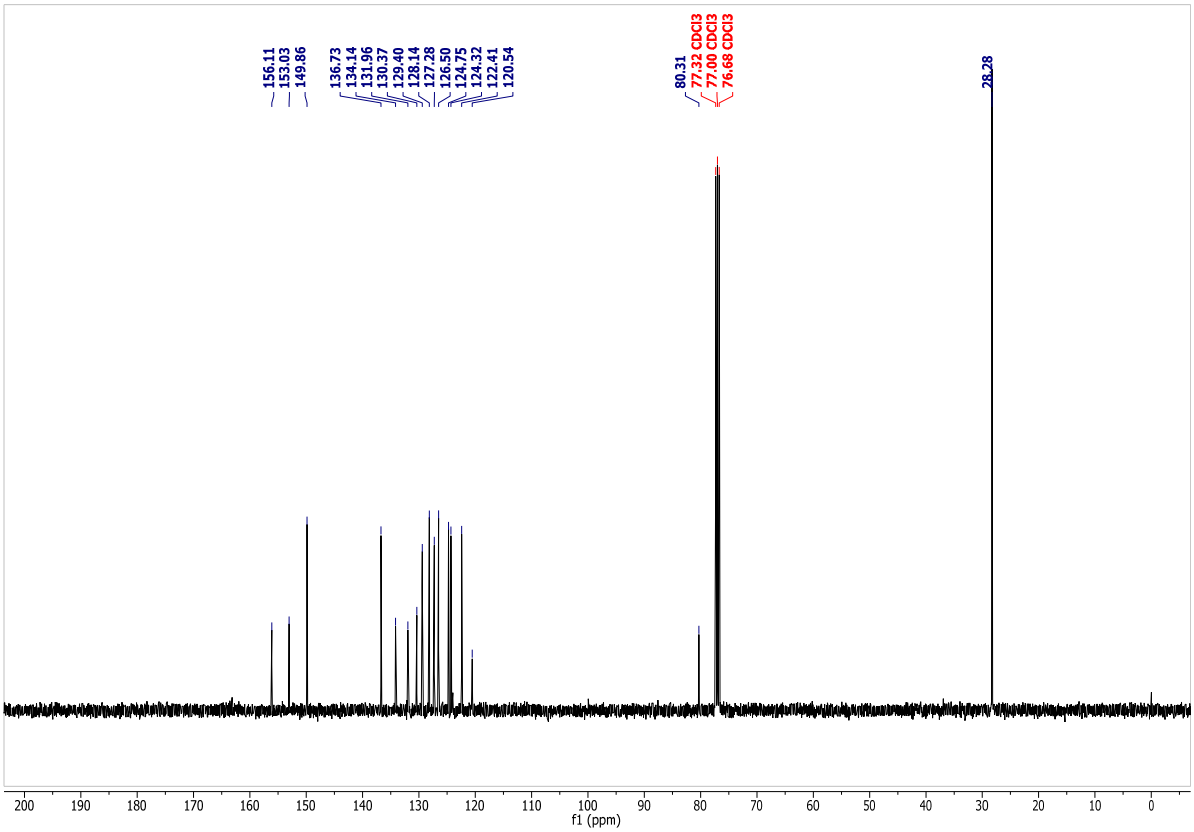
## *tert*-Butyl [5-(pyridin-2-yl)-1,2-dihydroacenaphthylen-4-yl]carbamate (3v)



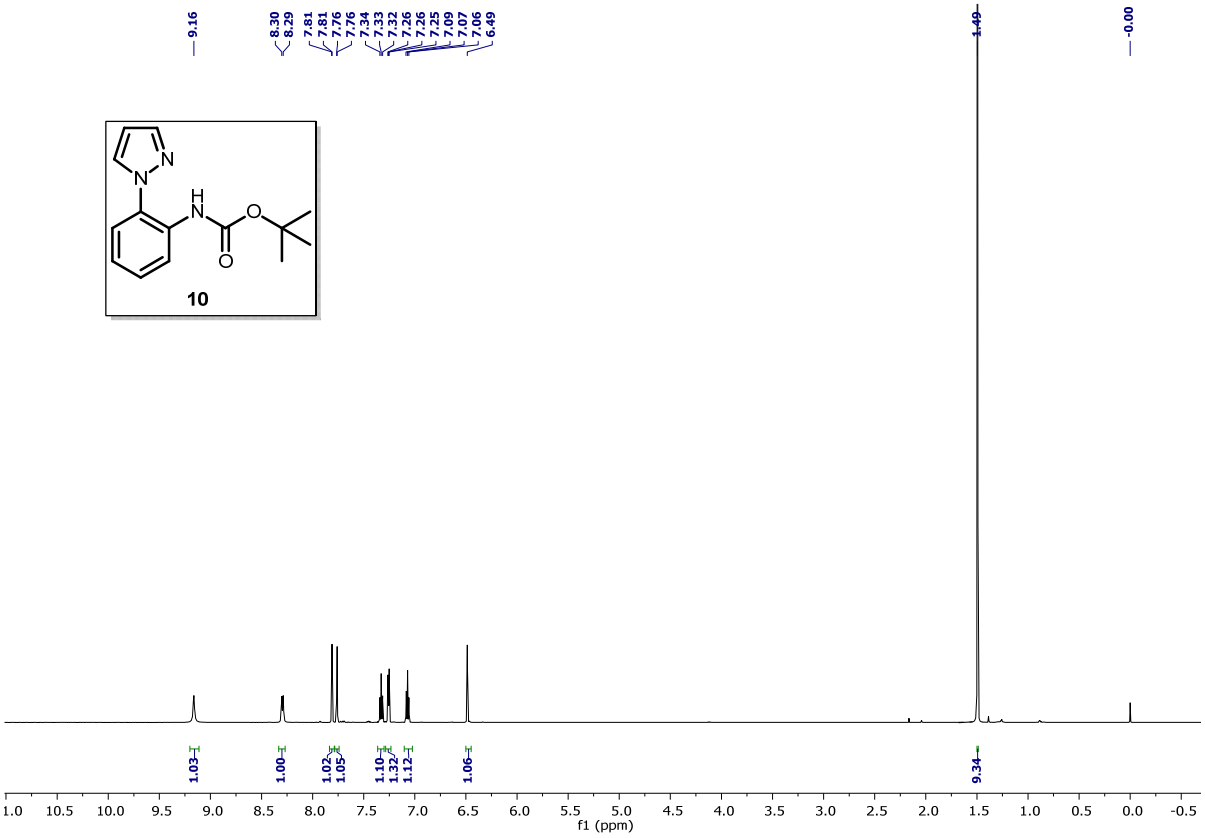



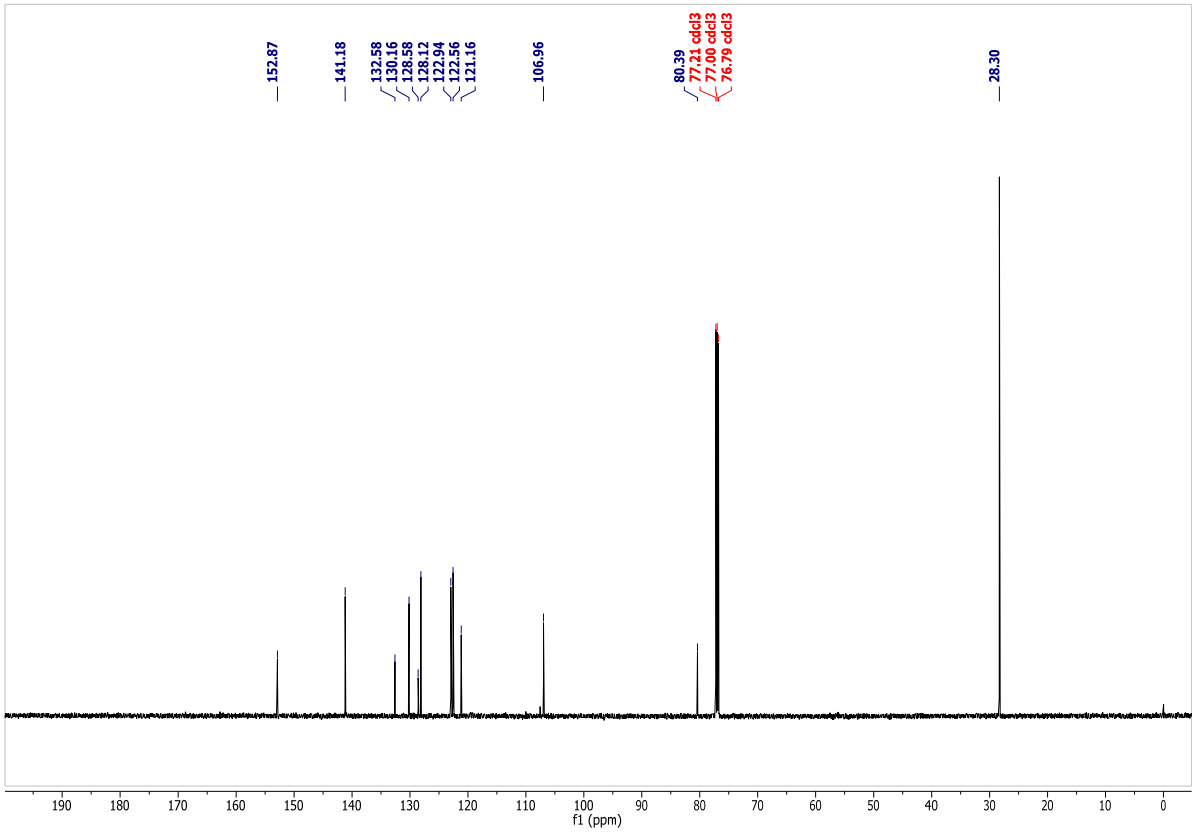
## *tert*-Butyl [1-(pyridin-2-yl)naphthalen-2-yl]carbamate (3w)



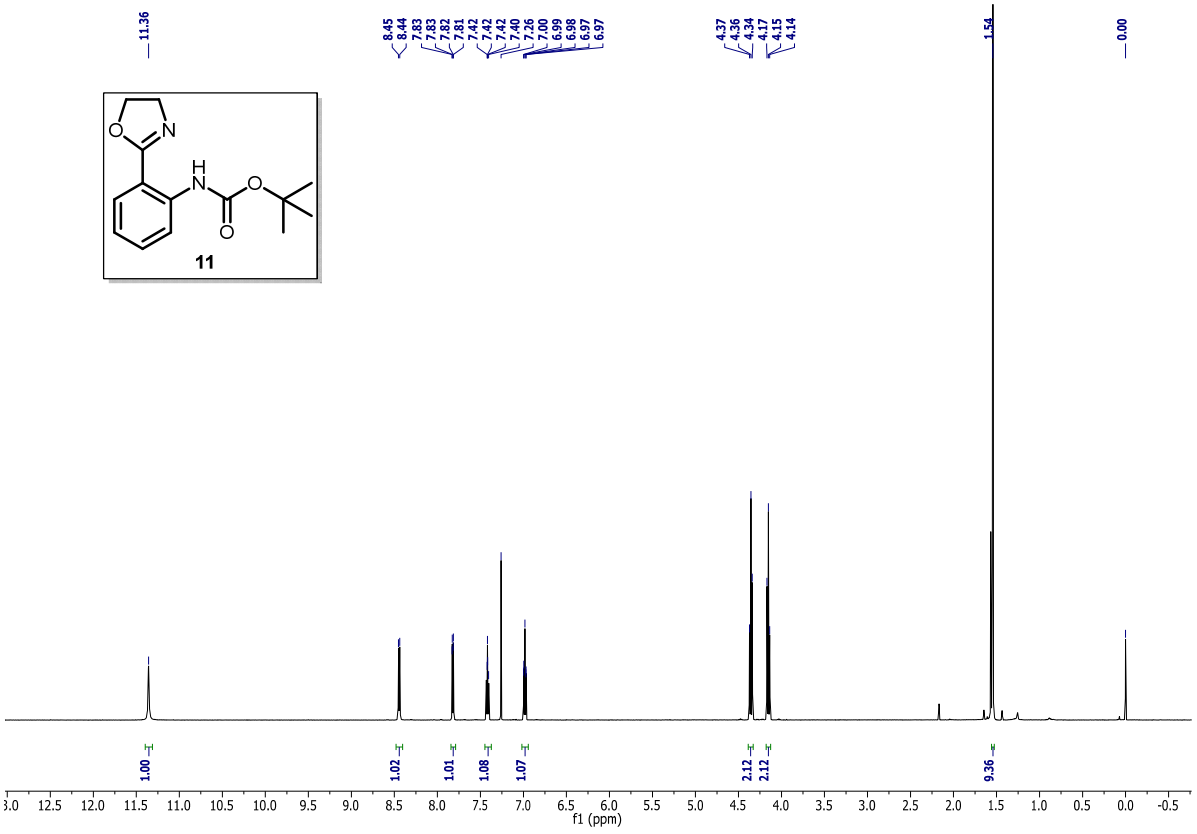



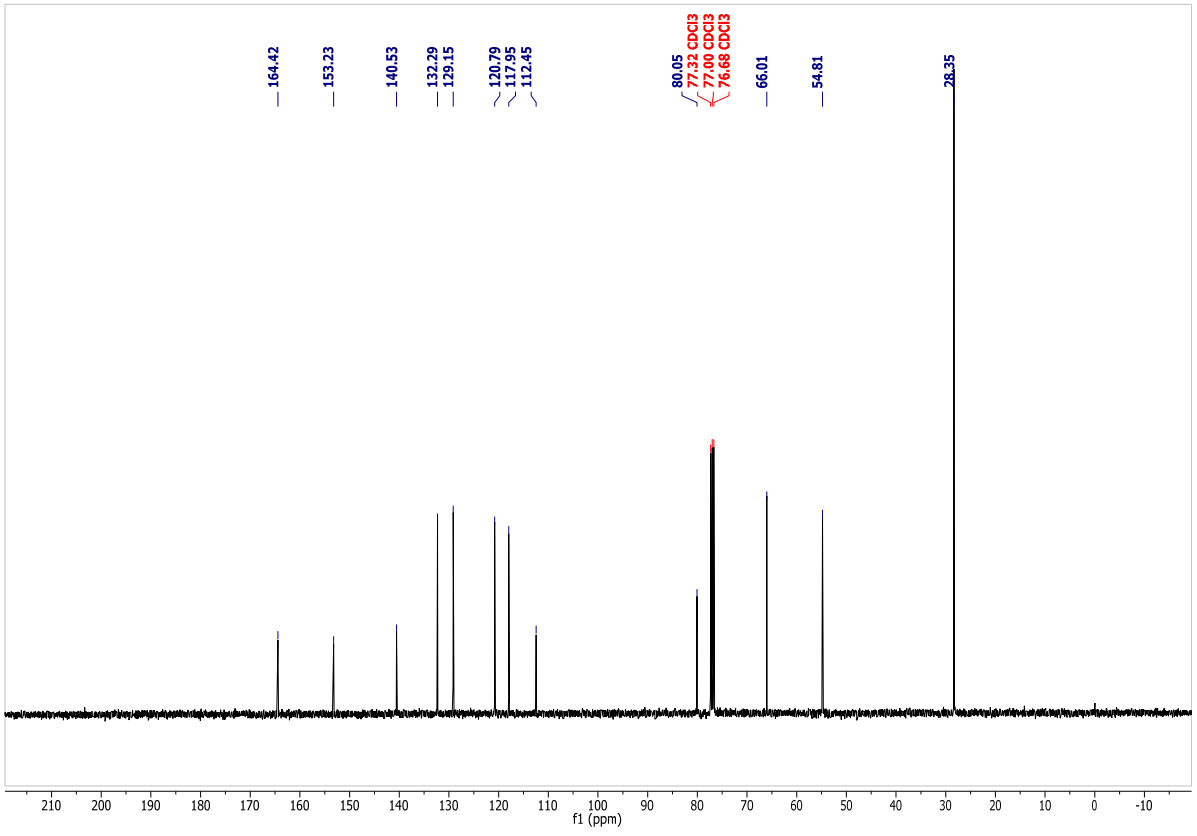
## *tert*-Butyl [2-(1*H*-pyrazol-1-yl)phenyl]carbamate (10)



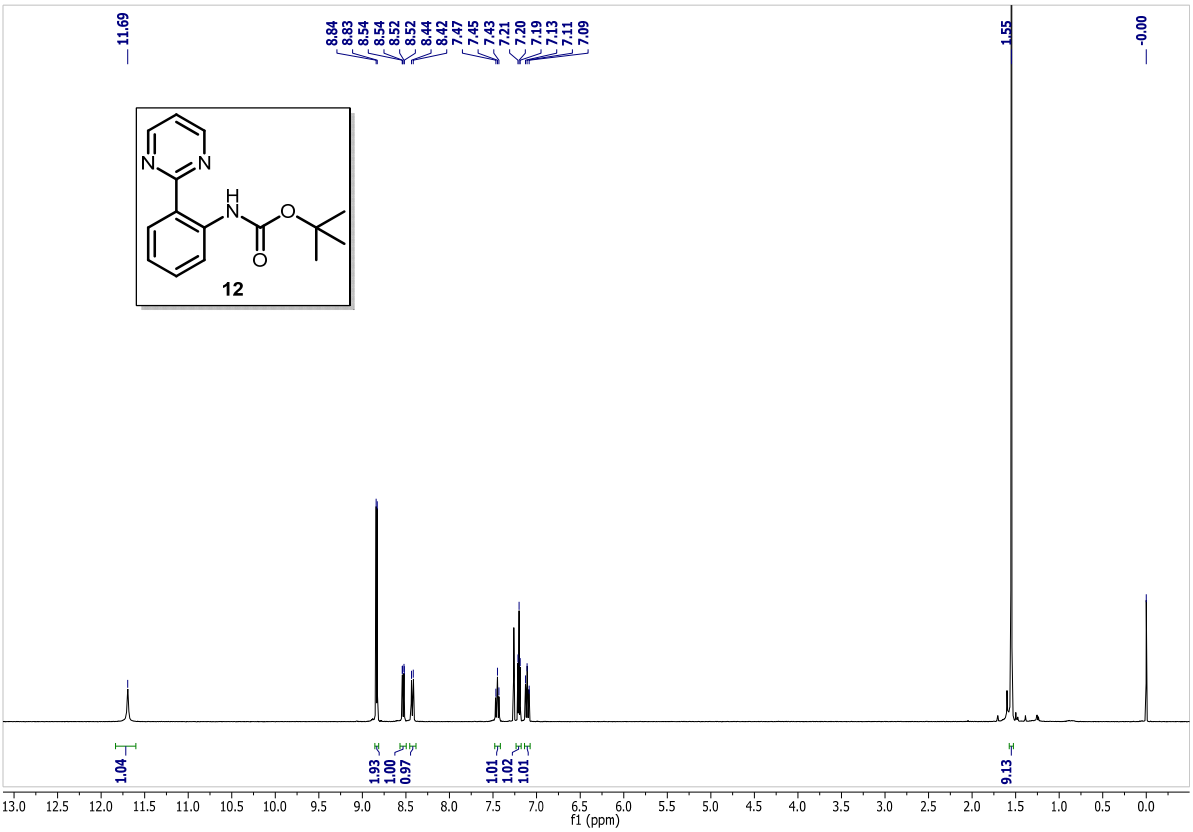



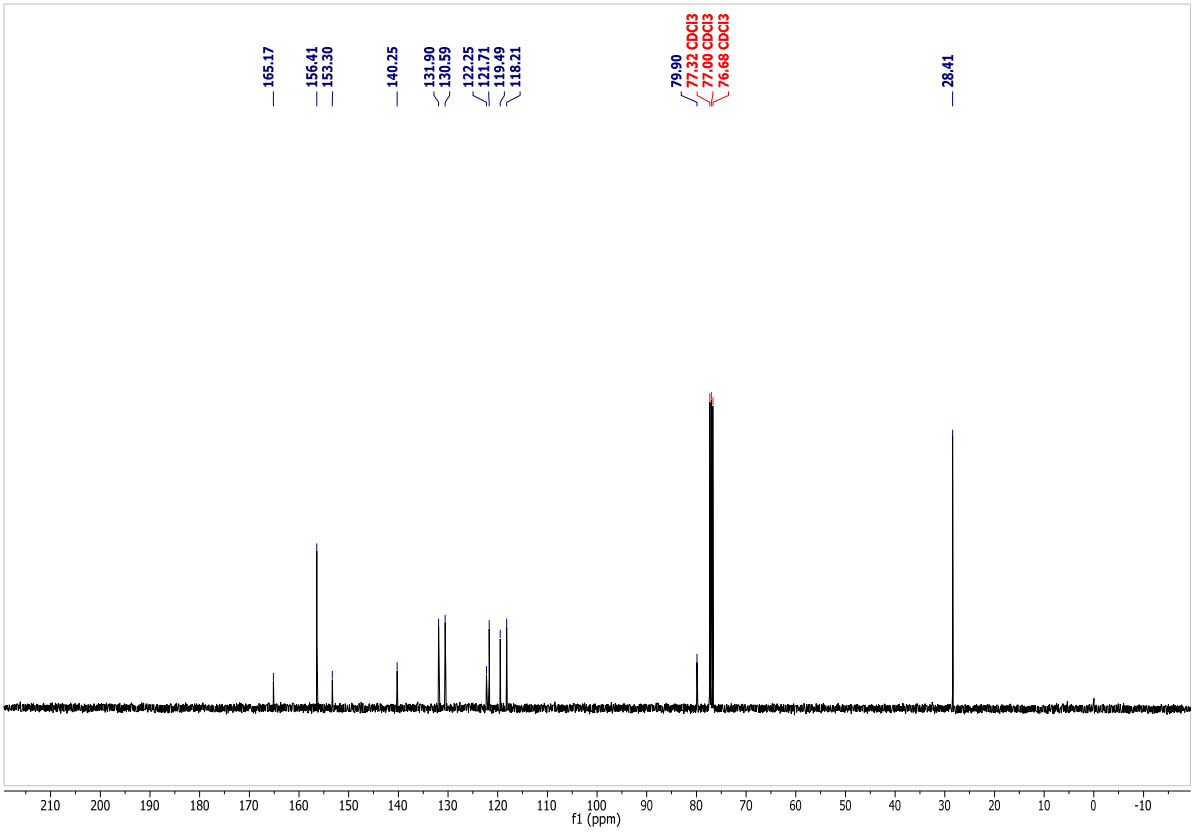
## *tert*-Butyl [2-(4,5-dihydrooxazol-2-yl)phenyl]carbamate (11)



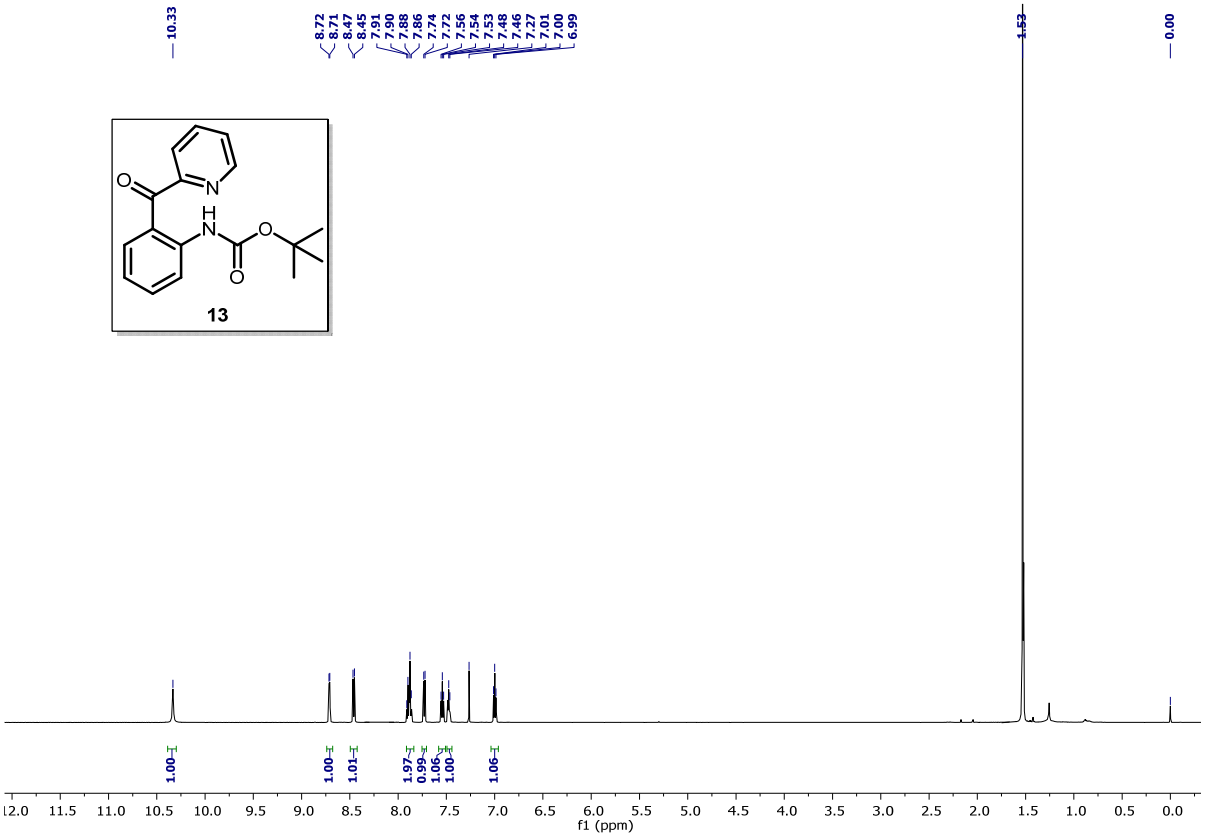



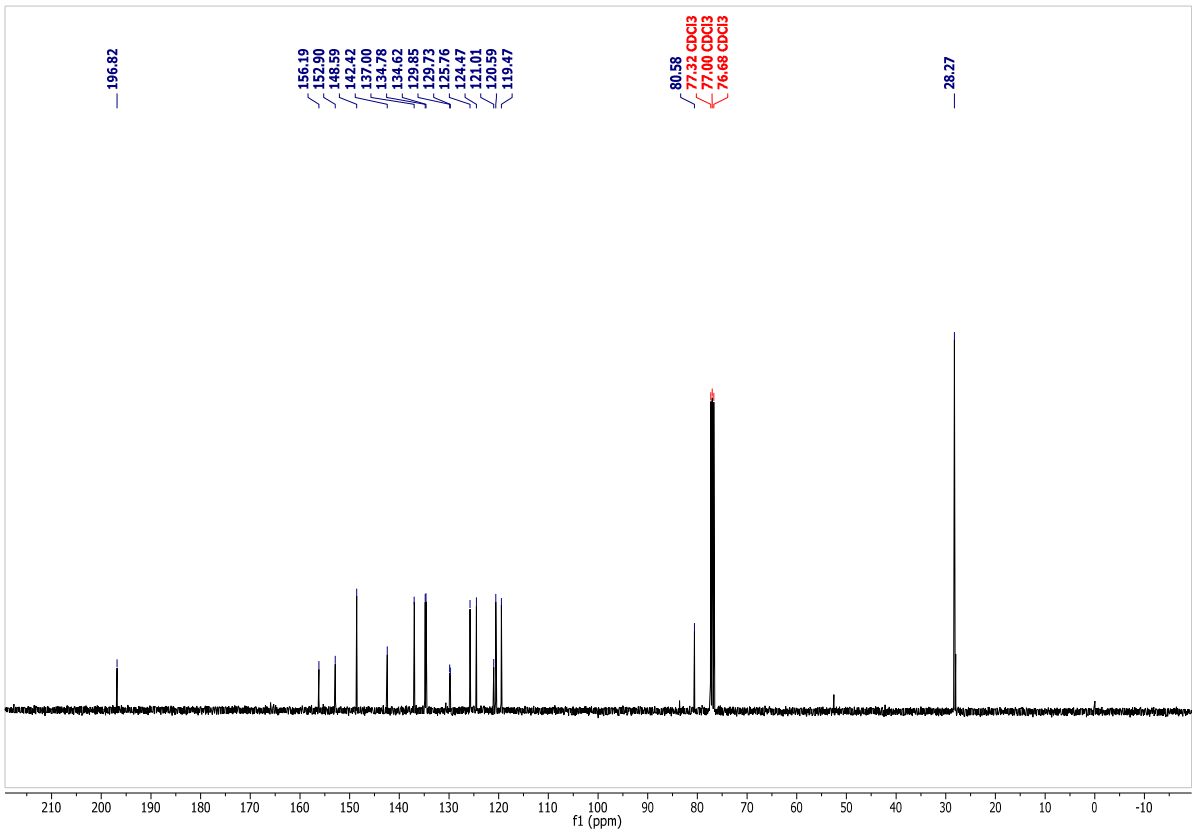
## *tert*-Butyl [2-(pyrimidin-2-yl)phenyl]carbamate (12)



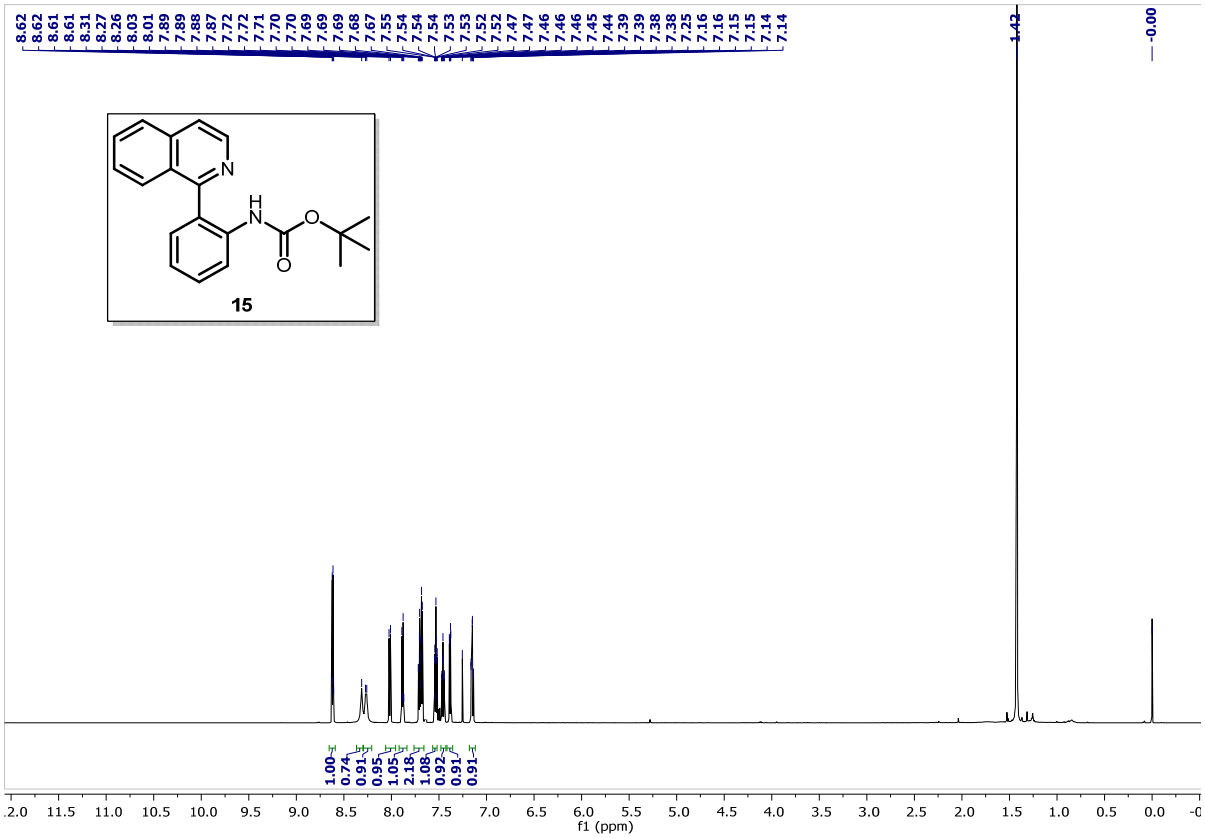



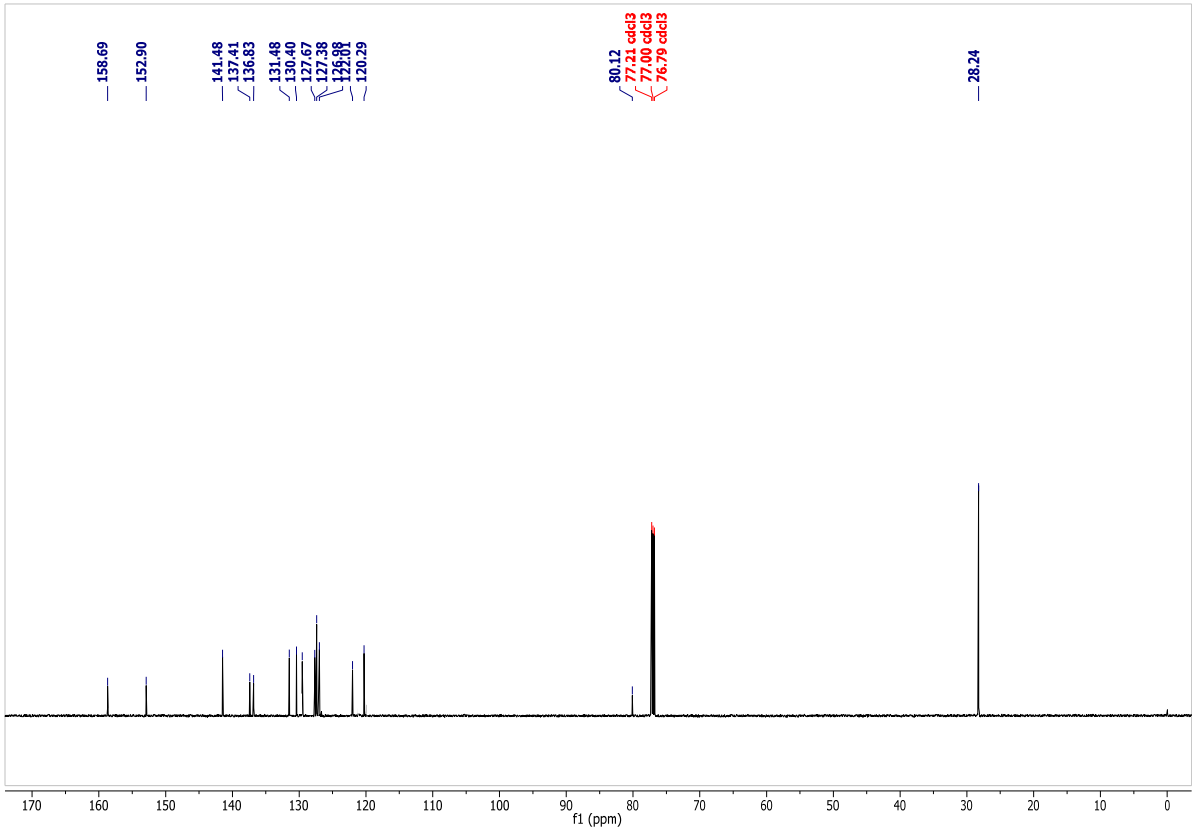
## *tert*-Butyl (2-picolinoylphenyl)carbamate (13)



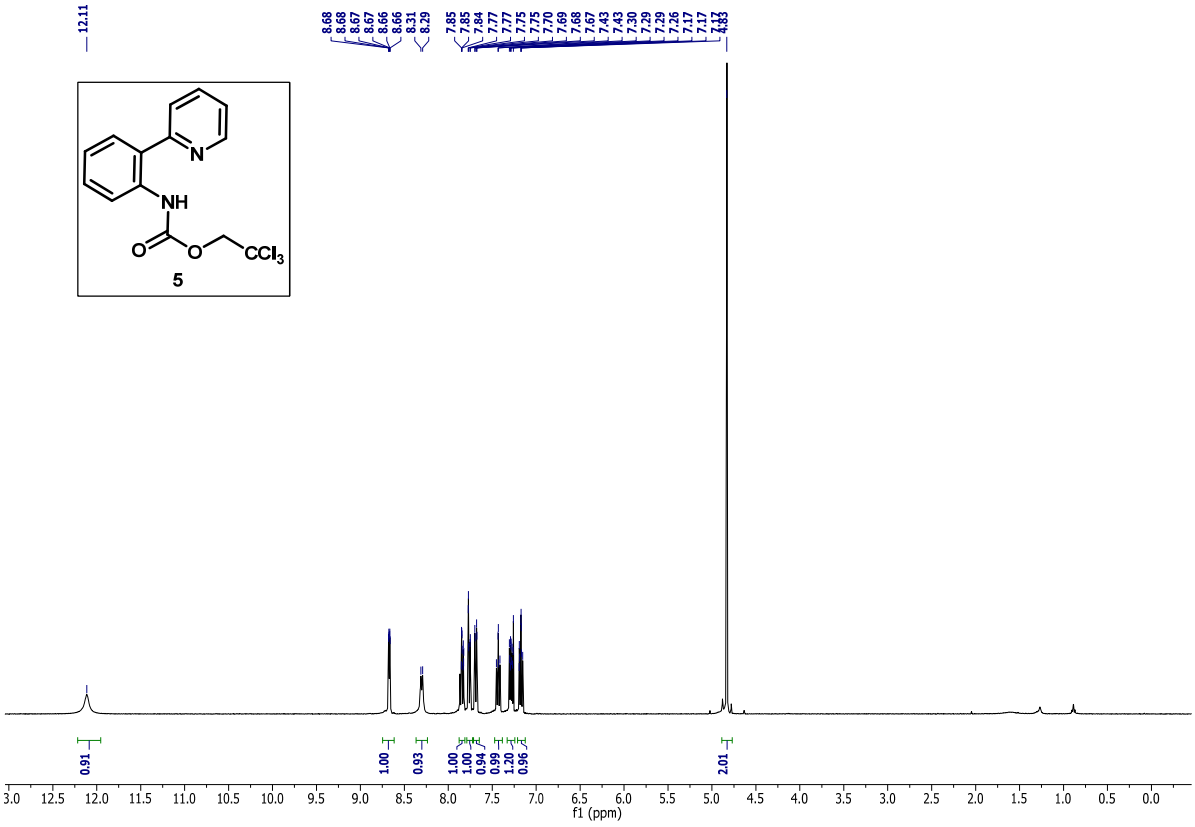



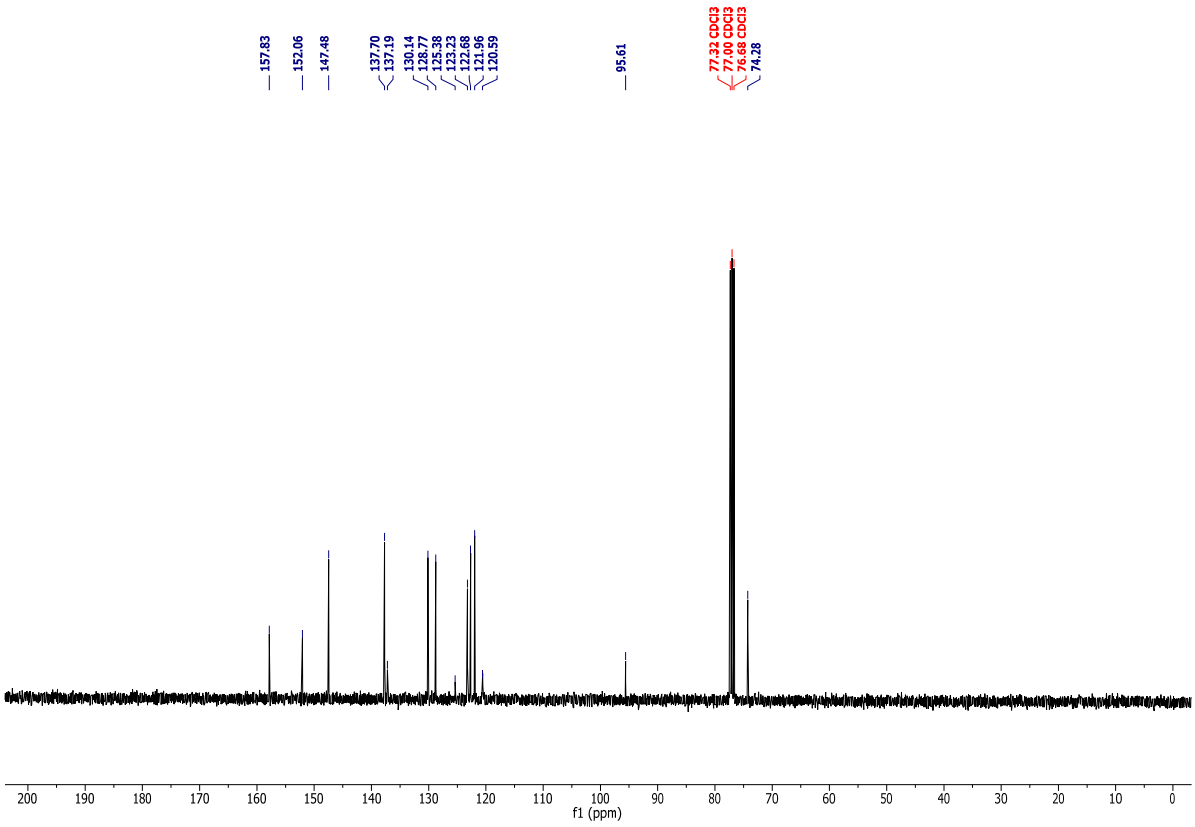
## *tert*-Butyl [2-(isoquinolin-1-yl)phenyl]carbamate (14)



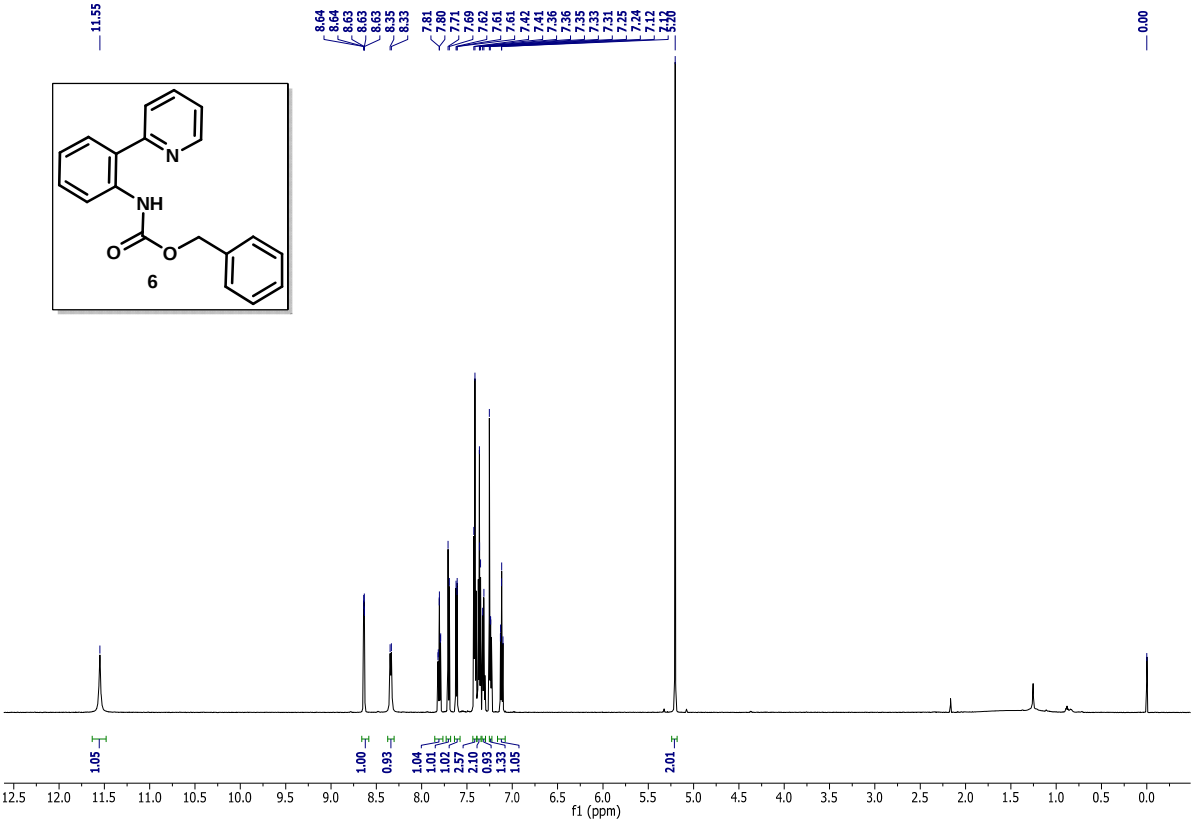



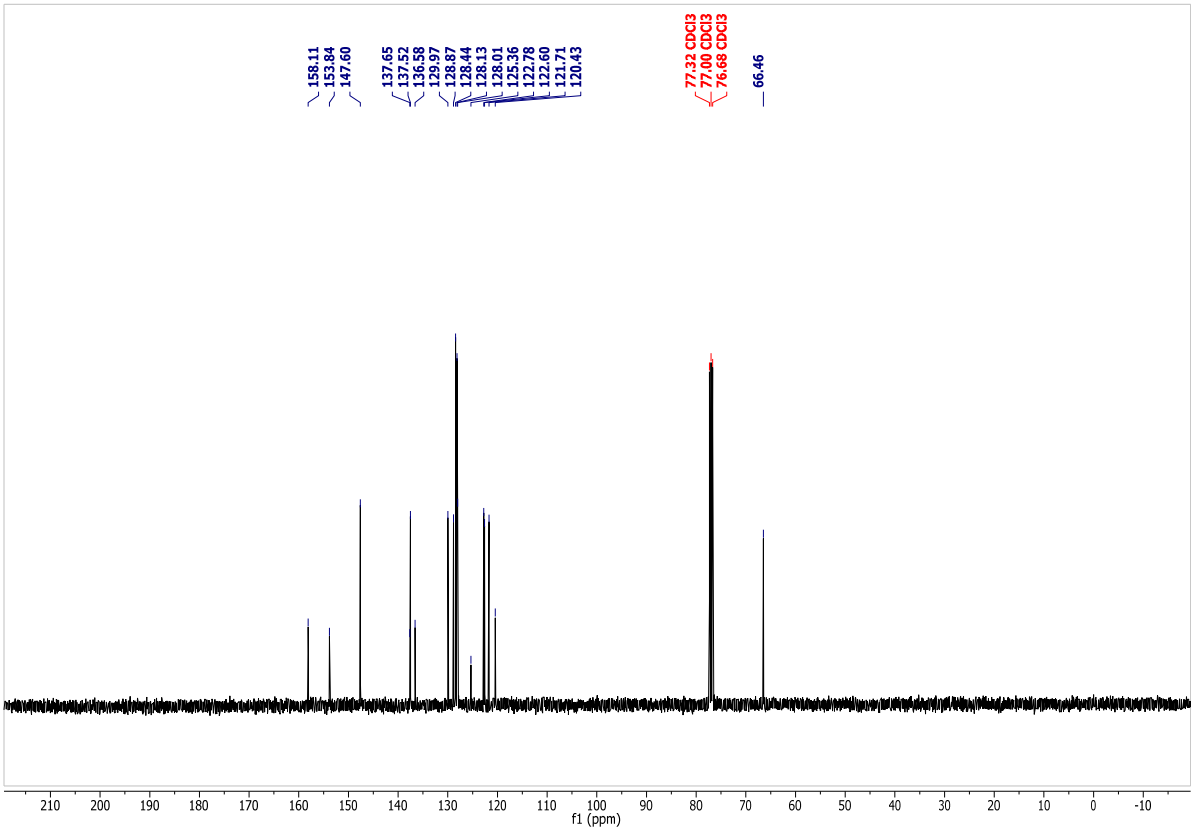
**2,2,2-Trichloroethyl [2-(pyridin-2-yl)phenyl]carbamate (5)**



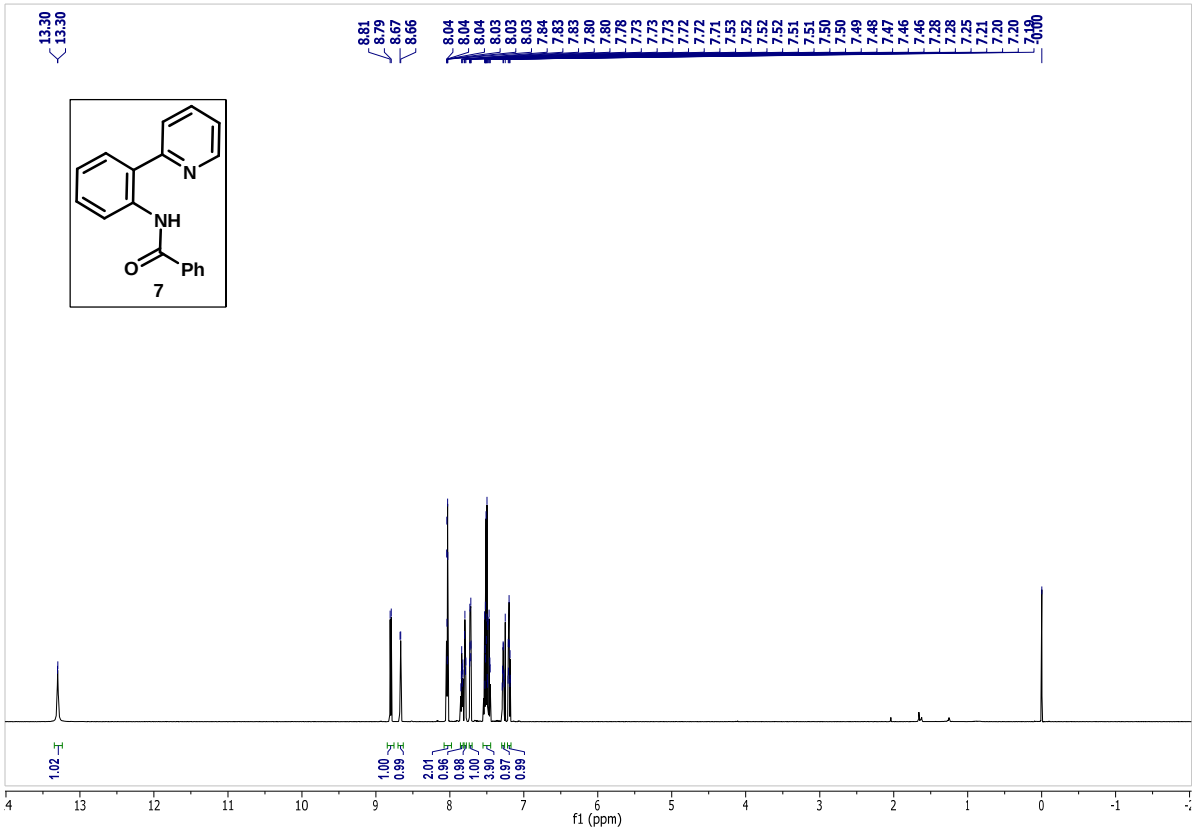



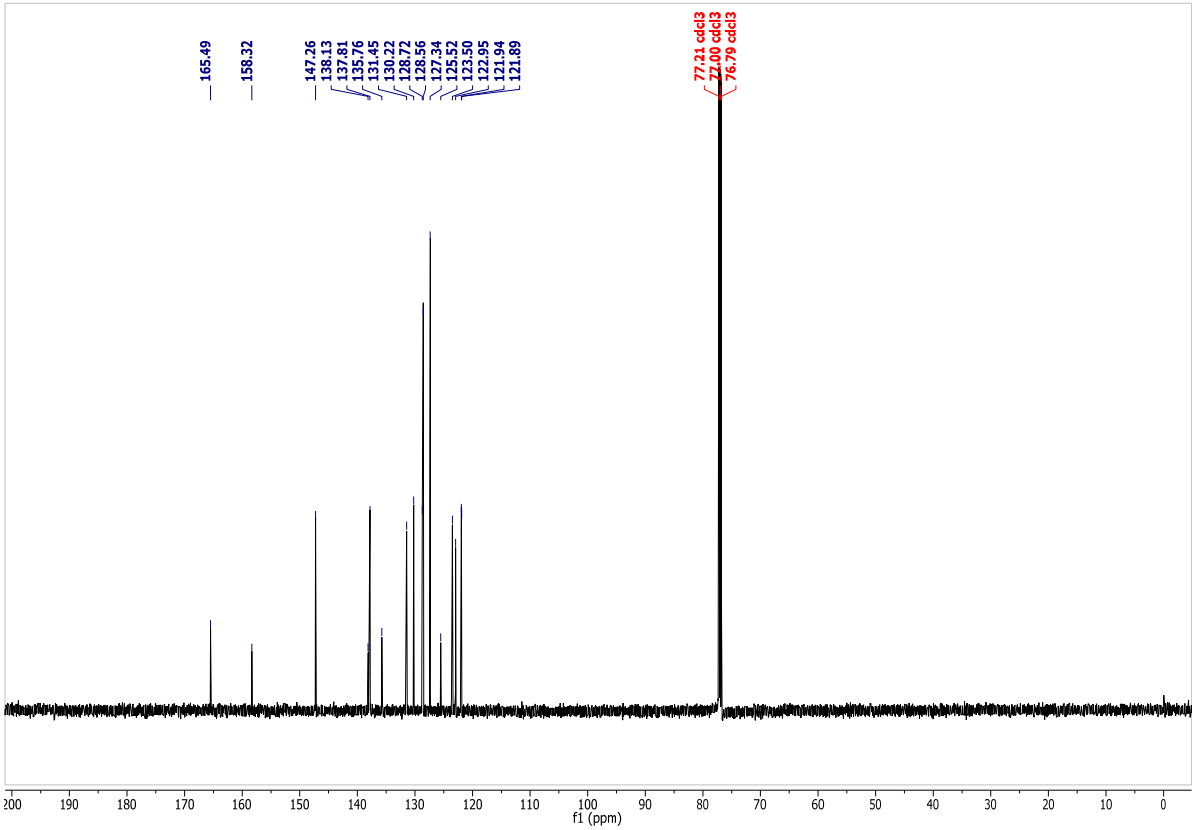
## Benzyl [2-(pyridin-2-yl)phenyl]carbamate (6)



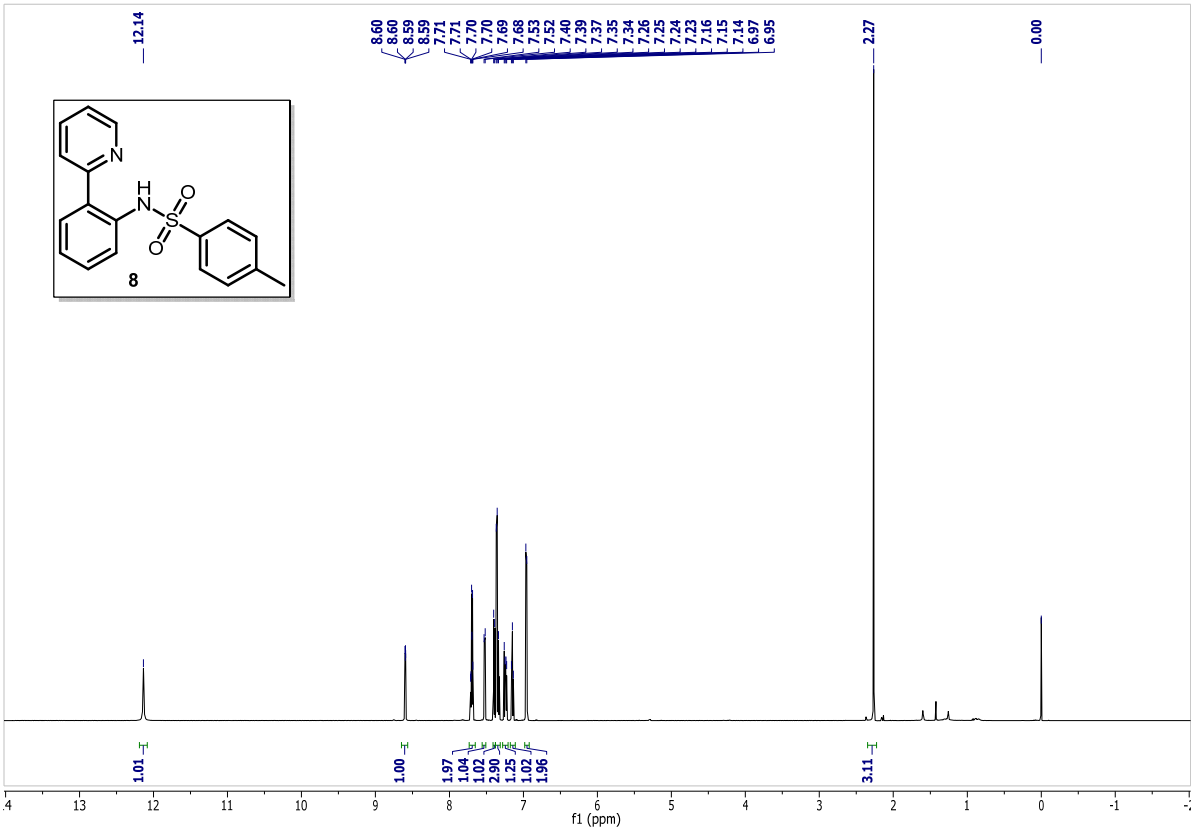



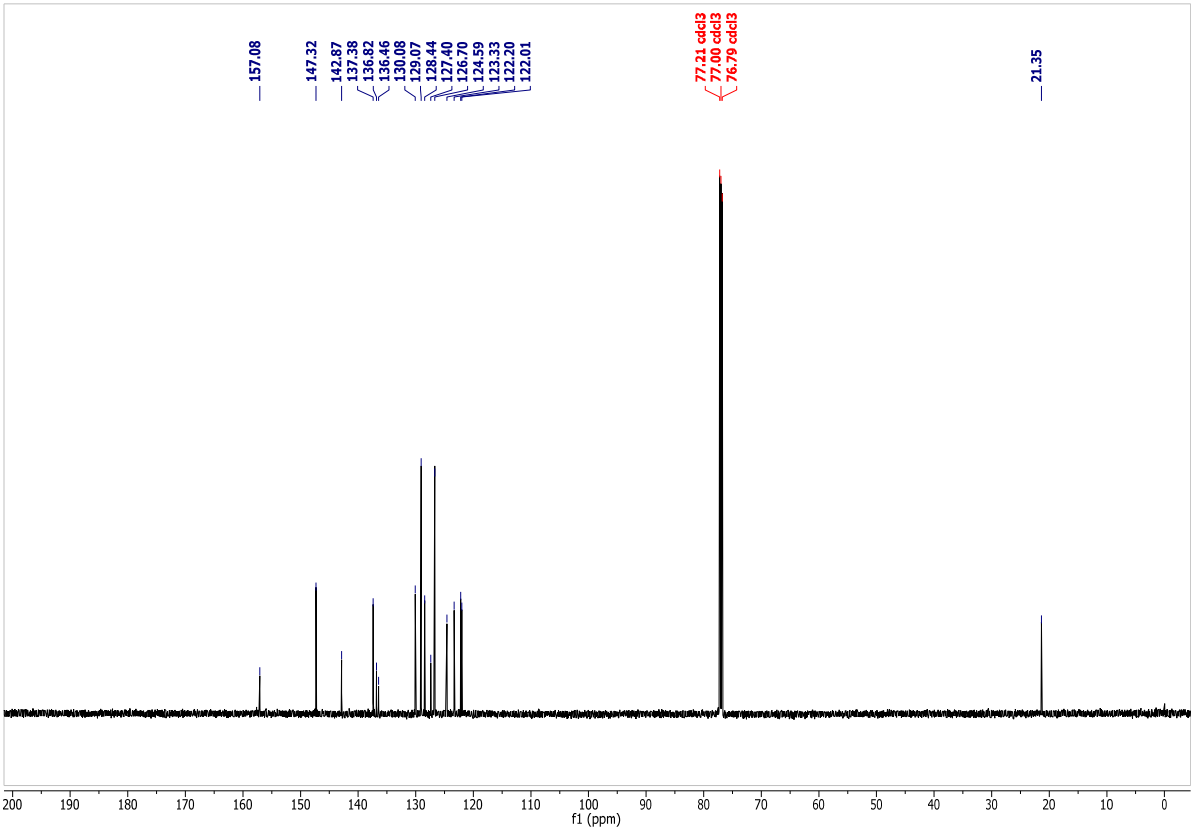
***N*-[2-(Pyridin-2-yl)phenyl]benzamide (7)**



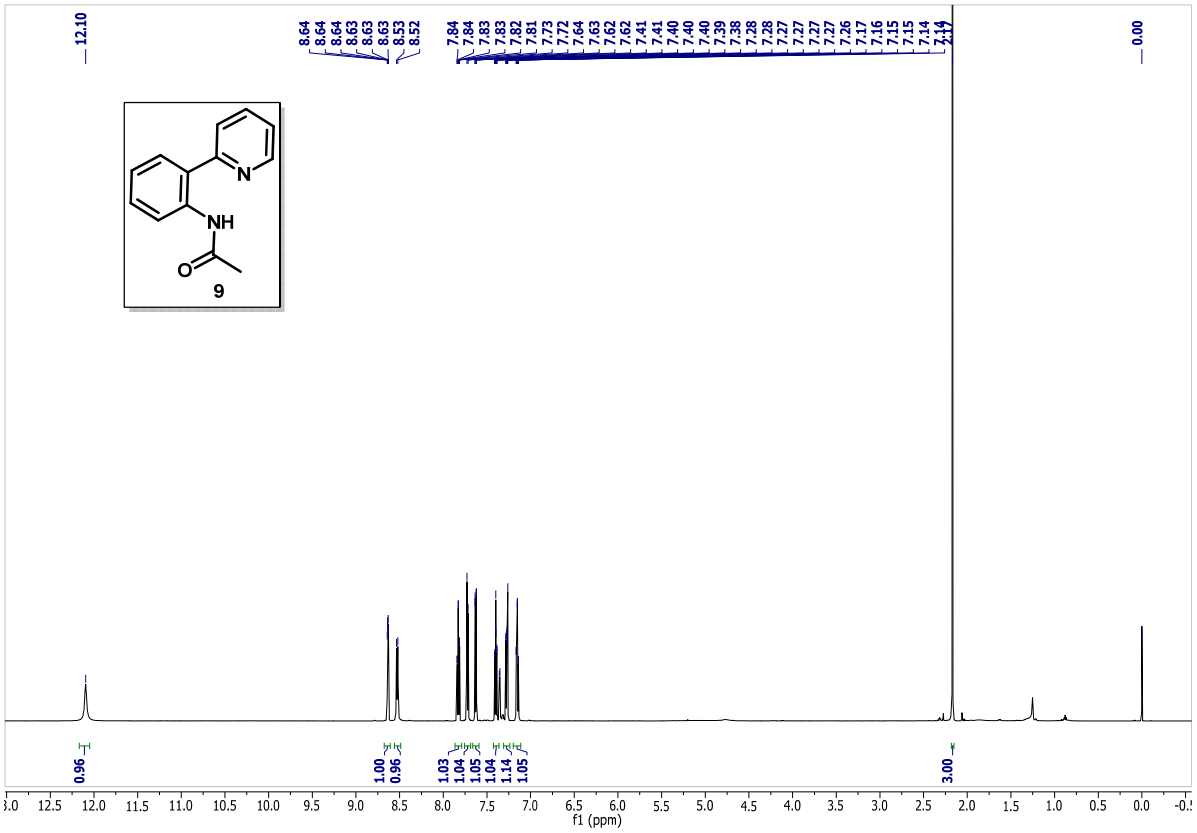



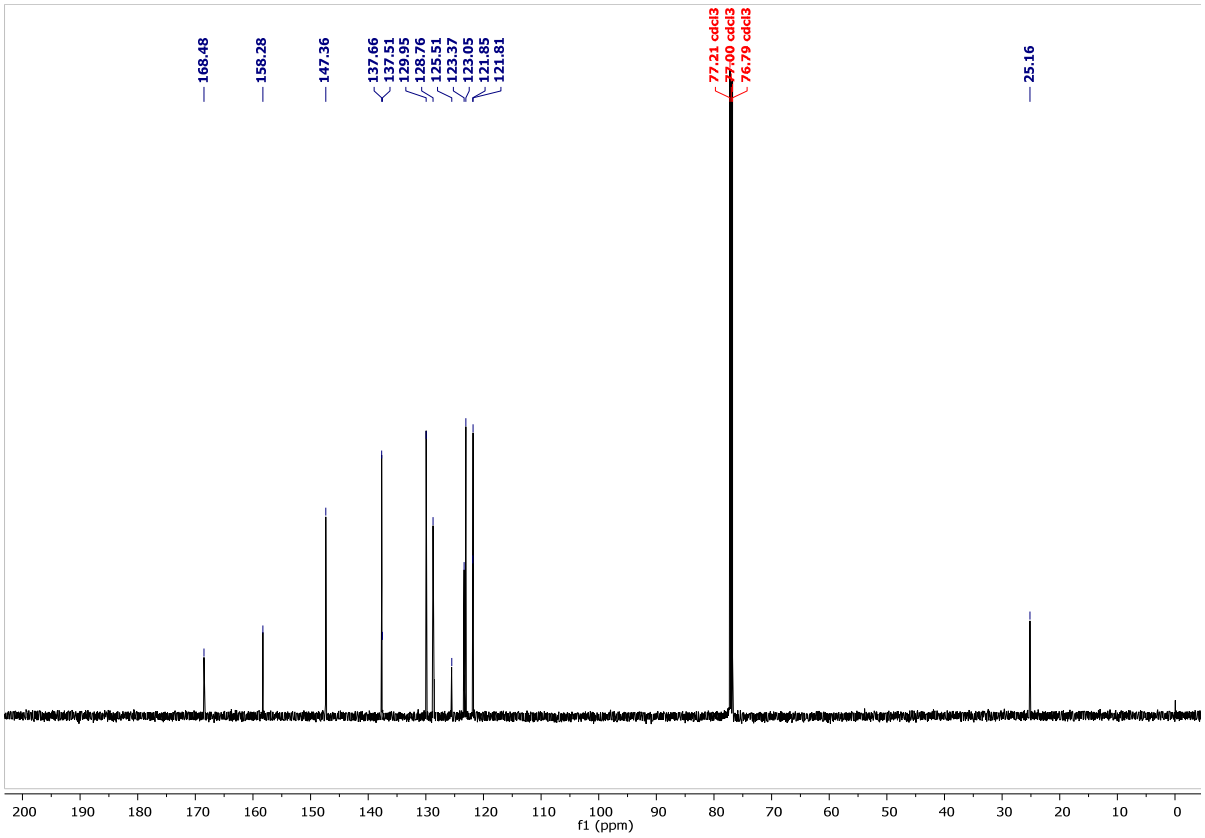
## 4-Methyl-*N*-[2-(pyridin-2-yl)phenyl]benzenesulfonamide (8)



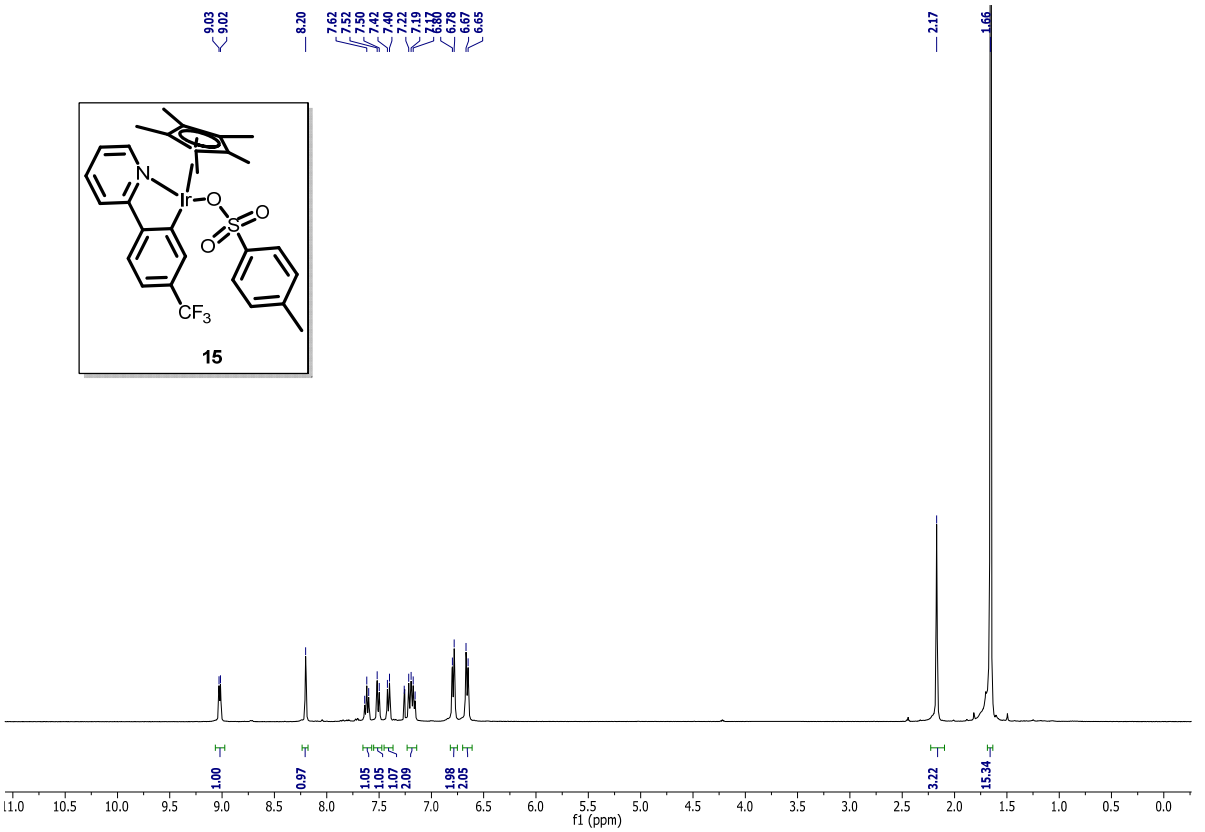



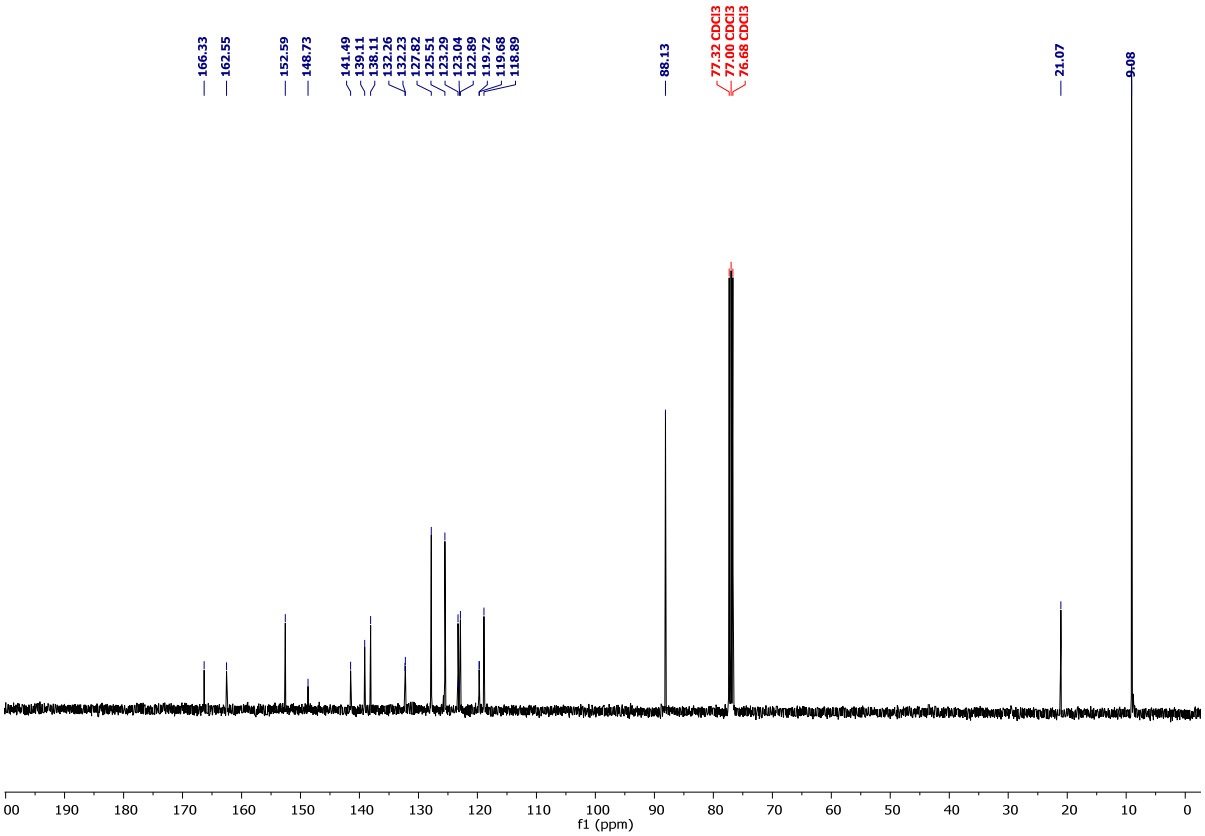
***N*-[2-(Pyridin-2-yl)phenyl]acetamide (9)**



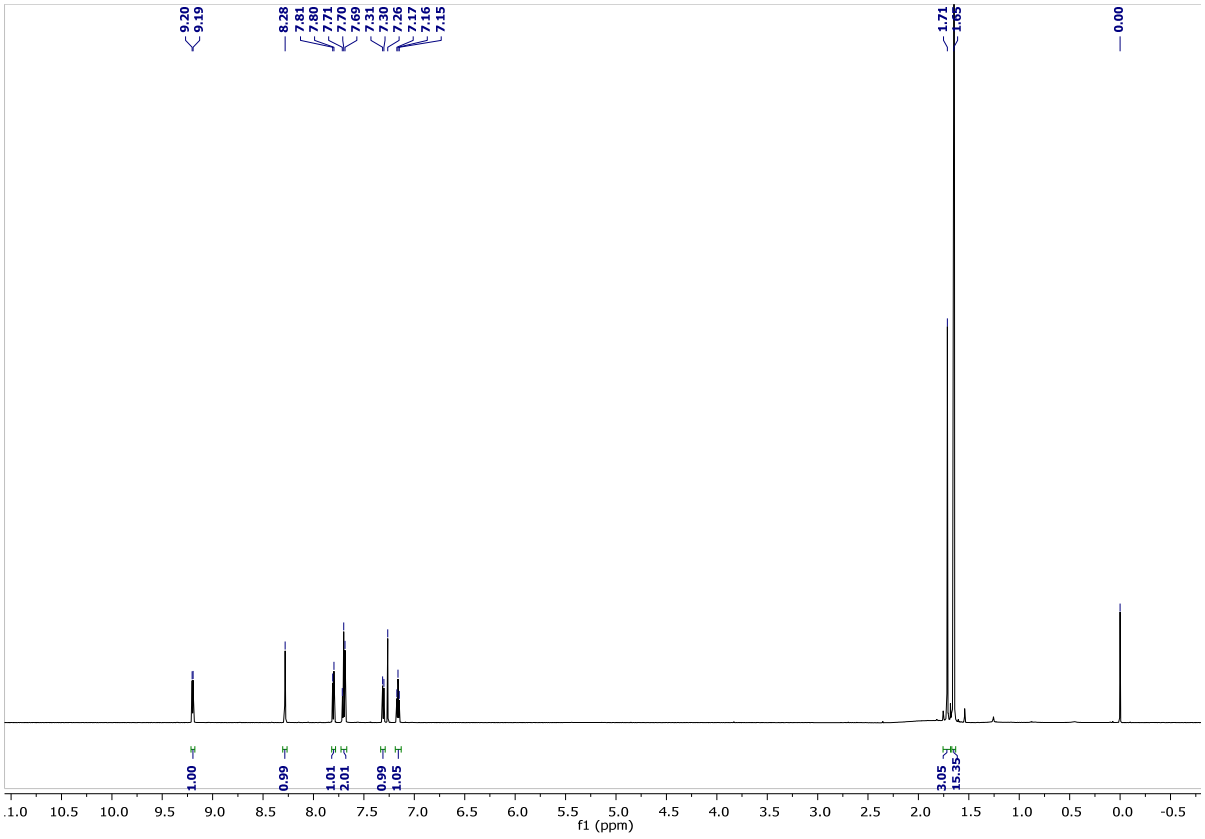



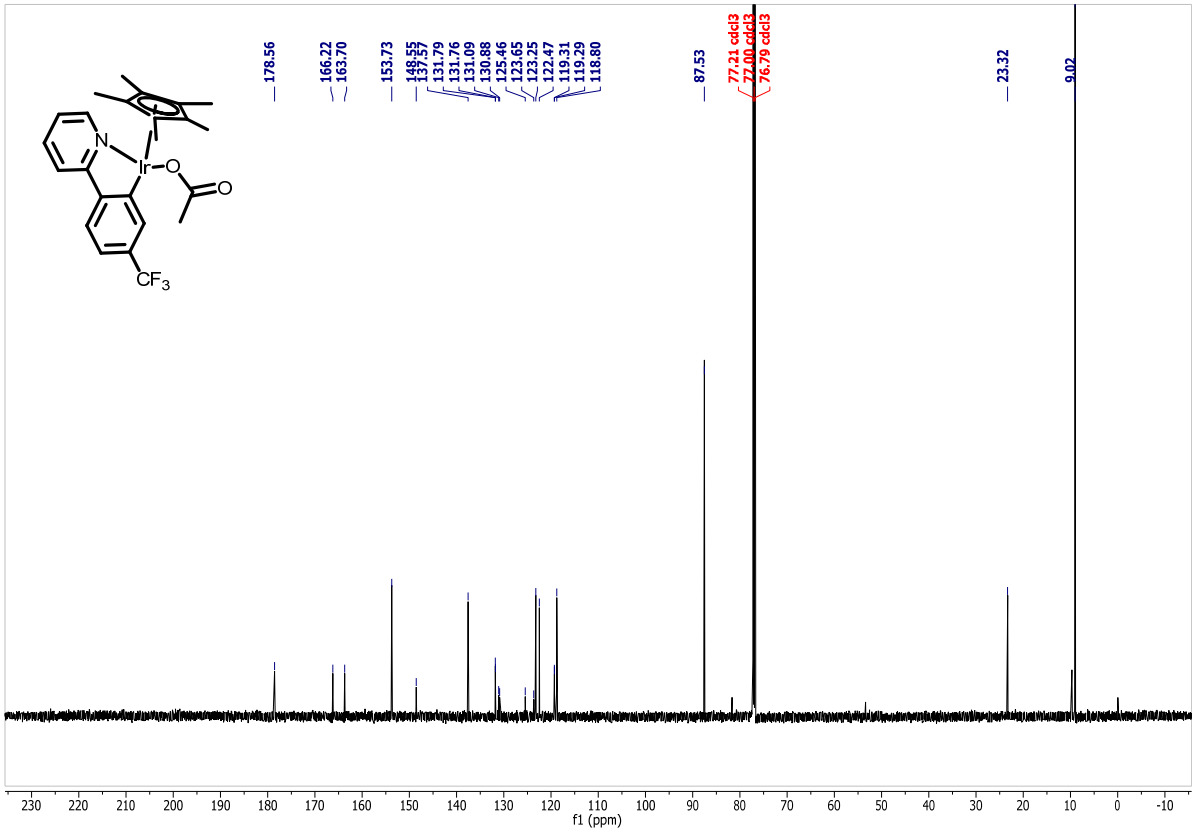
**(2-Pyridyl-5-trifluoromethylphenyl)(1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)(4-methylphenylsulphonoxy)iridium (15)**



**(2-Pyridyl-5-trifluoromethylphenyl)(1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)(acetoxy)iridium (16)**



# *Appendix II*

## Crystallographic Data

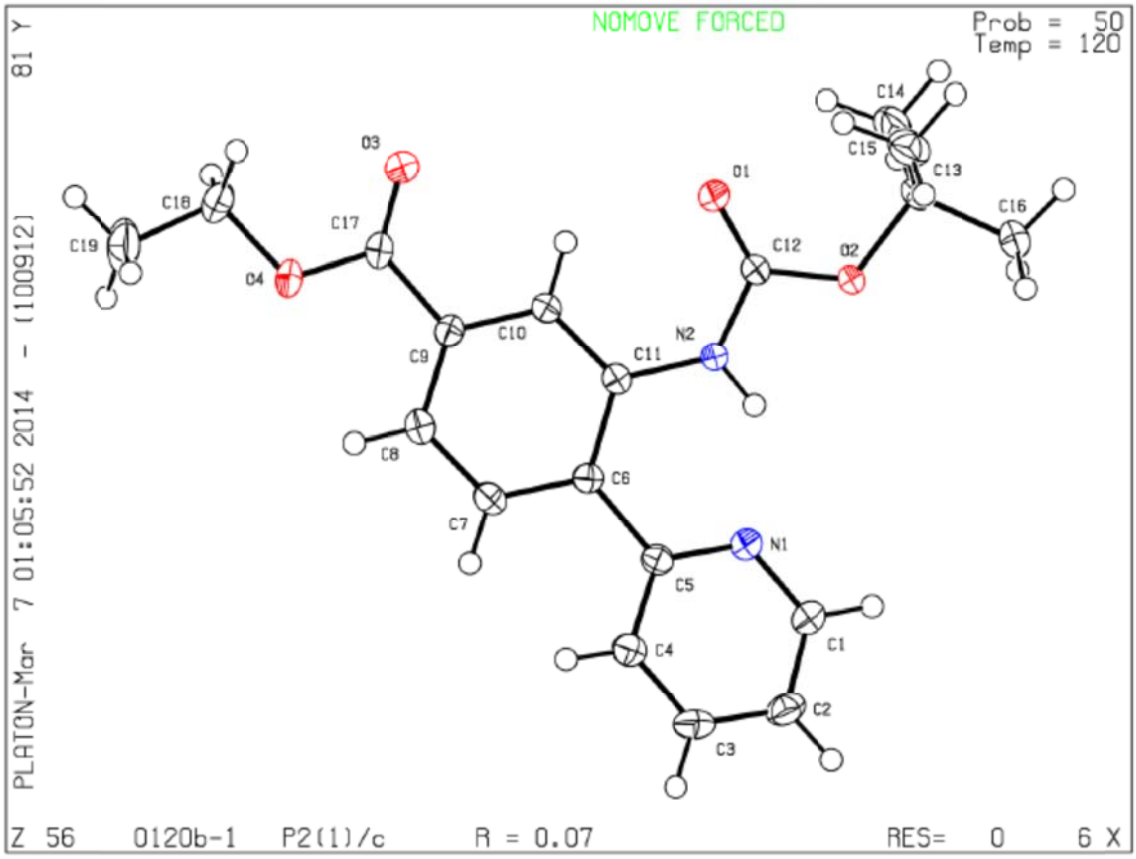



**Figure S2:** Crystal XRD image of **3i**

**Table S2**. Crystal data and structure refinement for **3i**.

| | | |
|---|---|---|
| Identification code | **3i** | |
| Empirical formula | C19 H22 N2 O4 | |
| Formula weight | 342.39 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | ? | |
| Space group | ? | |
| Unit cell dimensions | a = 7.297(2) Å | α= 90°. |
| | b = 12.192(4) Å | β= 94.898(4)°. |
| | c = 19.971(6) Å | γ = 90°. |
| Volume | 1770.2(9) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.285 $Mg/m^3$ | |
| Absorption coefficient | 0.091 $mm^{-1}$ | |
| F(000) | 728 | |
| Crystal size | 0.19 x 0.08 x 0.07 $mm^3$ | |
| Theta range for data collection | 1.96 to 29.24°. | |
| Index ranges | -9<=h<=9, -16<=k<=16, -27<=l<=27 | |
| Reflections collected | 23250 | |
| Independent reflections | 4428 [R(int) = 0.0452] | |
| Completeness to theta = 25.00° | 99.9 % | |
| Max. and min. transmission | 0.9937 and 0.9830 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4428 / 0 / 226 | |
| Goodness-of-fit on $F^2$ | 1.174 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0708, wR2 = 0.2266 | |
| R indices (all data) | R1 = 0.0943, wR2 = 0.2461 | |
| Largest diff. peak and hole | 0.467 and -0.381 $e.Å^{-3}$ | |

**Table S3**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3i**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(2) | 2611(3) | 9481(2) | 354(1) | 22(1) |
| O(1) | 2937(4) | 8558(2) | 1345(1) | 35(1) |
| O(4) | 1975(3) | 3851(2) | 2215(1) | 28(1) |
| O(3) | 1482(5) | 5600(2) | 2489(1) | 44(1) |
| N(1) | 2081(4) | 6982(2) | -942(1) | 23(1) |
| C(11) | 2325(4) | 6579(2) | 517(1) | 20(1) |
| N(2) | 2421(4) | 7684(2) | 328(1) | 22(1) |
| C(8) | 2054(4) | 4356(3) | 871(2) | 24(1) |
| C(6) | 2417(4) | 5754(2) | 18(1) | 20(1) |
| C(12) | 2680(4) | 8573(2) | 740(1) | 21(1) |
| C(5) | 2637(4) | 5995(2) | -707(1) | 20(1) |
| C(1) | 2210(5) | 7205(3) | -1594(2) | 26(1) |
| C(10) | 2099(4) | 6269(2) | 1177(1) | 22(1) |
| C(7) | 2261(4) | 4659(3) | 214(2) | 24(1) |
| C(9) | 1975(4) | 5174(2) | 1355(1) | 21(1) |
| C(4) | 3374(4) | 5215(3) | -1120(2) | 25(1) |
| C(17) | 1785(5) | 4915(3) | 2074(2) | 25(1) |
| C(2) | 2888(5) | 6465(3) | -2041(2) | 28(1) |
| C(3) | 3466(5) | 5458(3) | -1795(2) | 29(1) |
| C(13) | 2703(4) | 10583(2) | 662(2) | 22(1) |
| C(18) | 1836(6) | 3550(3) | 2914(2) | 35(1) |
| C(14) | 1067(5) | 10749(3) | 1078(2) | 32(1) |
| C(15) | 4524(5) | 10760(3) | 1076(2) | 33(1) |
| C(16) | 2560(5) | 11329(3) | 48(2) | 32(1) |
| C(19) | 2387(7) | 2372(3) | 2990(2) | 48(1) |

**Table S4**. Bond lengths [Å] and angles [°] for **3i**.

| | |
|---|---|
| O(2)-C(12) | 1.348(3) |
| O(2)-C(13) | 1.476(3) |
| O(1)-C(12) | 1.207(4) |
| O(4)-C(17) | 1.332(4) |
| O(4)-C(18) | 1.455(4) |
| O(3)-C(17) | 1.210(4) |
| N(1)-C(1) | 1.341(4) |
| N(1)-C(5) | 1.343(4) |
| C(11)-C(10) | 1.394(4) |
| C(11)-N(2) | 1.403(4) |
| C(11)-C(6) | 1.422(4) |
| N(2)-C(12) | 1.364(4) |
| C(8)-C(7) | 1.385(4) |
| C(8)-C(9) | 1.394(4) |
| C(6)-C(7) | 1.400(4) |
| C(6)-C(5) | 1.497(4) |
| C(5)-C(4) | 1.397(4) |
| C(1)-C(2) | 1.389(5) |
| C(10)-C(9) | 1.387(4) |
| C(9)-C(17) | 1.487(4) |
| C(4)-C(3) | 1.386(4) |
| C(2)-C(3) | 1.376(5) |
| C(13)-C(15) | 1.518(5) |
| C(13)-C(16) | 1.524(4) |
| C(13)-C(14) | 1.524(4) |
| C(18)-C(19) | 1.496(5) |

| | |
|---|---|
| C(12)-O(2)-C(13) | 120.7(2) |
| C(17)-O(4)-C(18) | 115.7(3) |
| C(1)-N(1)-C(5) | 118.6(3) |
| C(10)-C(11)-N(2) | 121.8(3) |
| C(10)-C(11)-C(6) | 119.2(3) |
| N(2)-C(11)-C(6) | 118.9(3) |
| C(12)-N(2)-C(11) | 127.4(2) |
| C(7)-C(8)-C(9) | 118.8(3) |
| C(7)-C(6)-C(11) | 117.9(3) |
| C(7)-C(6)-C(5) | 118.4(3) |

| | |
|---|---|
| C(11)-C(6)-C(5) | 123.7(3) |
| O(1)-C(12)-O(2) | 125.4(3) |
| O(1)-C(12)-N(2) | 126.5(3) |
| O(2)-C(12)-N(2) | 108.1(2) |
| N(1)-C(5)-C(4) | 121.5(3) |
| N(1)-C(5)-C(6) | 117.4(3) |
| C(4)-C(5)-C(6) | 121.1(3) |
| N(1)-C(1)-C(2) | 123.4(3) |
| C(9)-C(10)-C(11) | 121.2(3) |
| C(8)-C(7)-C(6) | 122.6(3) |
| C(10)-C(9)-C(8) | 120.2(3) |
| C(10)-C(9)-C(17) | 117.7(3) |
| C(8)-C(9)-C(17) | 122.0(3) |
| C(3)-C(4)-C(5) | 118.8(3) |
| O(3)-C(17)-O(4) | 123.2(3) |
| O(3)-C(17)-C(9) | 123.6(3) |
| O(4)-C(17)-C(9) | 113.2(3) |
| C(3)-C(2)-C(1) | 117.7(3) |
| C(2)-C(3)-C(4) | 120.0(3) |
| O(2)-C(13)-C(15) | 111.3(3) |
| O(2)-C(13)-C(16) | 102.1(2) |
| C(15)-C(13)-C(16) | 110.5(3) |
| O(2)-C(13)-C(14) | 109.7(2) |
| C(15)-C(13)-C(14) | 112.0(3) |
| C(16)-C(13)-C(14) | 110.8(3) |
| O(4)-C(18)-C(19) | 107.4(3) |

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Symmetry transformations used to generate equivalent atoms:

**Table S5**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(2) | 34(1) | 13(1) | 18(1) | 0(1) | 4(1) | -1(1) |
| O(1) | 66(2) | 21(1) | 17(1) | 0(1) | 2(1) | -5(1) |
| O(4) | 40(1) | 19(1) | 25(1) | 7(1) | 6(1) | 1(1) |
| O(3) | 88(2) | 24(1) | 22(1) | 0(1) | 14(1) | 1(1) |
| N(1) | 31(1) | 21(1) | 19(1) | 0(1) | 2(1) | -2(1) |
| C(11) | 24(1) | 16(1) | 19(1) | 0(1) | 2(1) | 0(1) |
| N(2) | 38(2) | 14(1) | 15(1) | 0(1) | 4(1) | -1(1) |
| C(8) | 28(2) | 18(1) | 25(1) | 1(1) | 3(1) | -2(1) |
| C(6) | 22(1) | 19(1) | 18(1) | -1(1) | 1(1) | 1(1) |
| C(12) | 29(2) | 16(1) | 19(1) | 0(1) | 4(1) | 1(1) |
| C(5) | 21(1) | 19(1) | 19(1) | -2(1) | -1(1) | -3(1) |
| C(1) | 34(2) | 26(2) | 19(1) | 1(1) | 2(1) | 0(1) |
| C(10) | 30(2) | 17(1) | 19(1) | -1(1) | 5(1) | 3(1) |
| C(7) | 29(2) | 18(2) | 24(1) | -2(1) | 1(1) | 0(1) |
| C(9) | 25(2) | 20(2) | 19(1) | 3(1) | 4(1) | 0(1) |
| C(4) | 28(2) | 23(2) | 23(1) | -2(1) | 2(1) | 1(1) |
| C(17) | 32(2) | 20(2) | 23(1) | 5(1) | 3(1) | -1(1) |
| C(2) | 33(2) | 34(2) | 17(1) | -1(1) | 1(1) | -5(1) |
| C(3) | 31(2) | 33(2) | 22(1) | -8(1) | 6(1) | 1(1) |
| C(13) | 31(2) | 12(1) | 25(1) | -3(1) | 6(1) | 0(1) |
| C(18) | 53(2) | 29(2) | 24(2) | 8(1) | 3(2) | -7(2) |
| C(14) | 37(2) | 22(2) | 37(2) | -3(1) | 15(1) | 1(1) |
| C(15) | 36(2) | 28(2) | 34(2) | -8(1) | 1(1) | -6(1) |
| C(16) | 46(2) | 18(2) | 31(2) | 2(1) | 9(2) | 1(1) |
| C(19) | 62(3) | 32(2) | 49(2) | 18(2) | 2(2) | 3(2) |

**Table S6**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **3i**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2B) | 2299 | 7820 | -107 | 27 |
| H(8A) | 1967 | 3604 | 990 | 28 |
| H(1A) | 1818 | 7905 | -1759 | 32 |
| H(10A) | 2029 | 6819 | 1511 | 26 |
| H(7A) | 2299 | 4101 | -117 | 28 |
| H(4A) | 3805 | 4530 | -943 | 30 |
| H(2A) | 2951 | 6649 | -2501 | 34 |
| H(3A) | 3927 | 4929 | -2086 | 34 |
| H(18A) | 558 | 3651 | 3034 | 42 |
| H(18B) | 2659 | 4016 | 3213 | 42 |
| H(14A) | -77 | 10624 | 794 | 47 |
| H(14B) | 1081 | 11500 | 1252 | 47 |
| H(14C) | 1146 | 10229 | 1453 | 47 |
| H(15A) | 5538 | 10640 | 792 | 49 |
| H(15B) | 4629 | 10242 | 1452 | 49 |
| H(15C) | 4579 | 11512 | 1250 | 49 |
| H(16A) | 1381 | 11202 | -214 | 47 |
| H(16B) | 3569 | 11167 | -231 | 47 |
| H(16C) | 2637 | 12096 | 193 | 47 |
| H(19A) | 2299 | 2141 | 3456 | 72 |
| H(19B) | 3657 | 2283 | 2874 | 72 |
| H(19C) | 1567 | 1919 | 2690 | 72 |

**Table S7**. Torsion angles [°] for **3i**.

| | |
|---|---|
| C(10)-C(11)-N(2)-C(12) | 14.1(5) |
| C(6)-C(11)-N(2)-C(12) | -167.5(3) |
| C(10)-C(11)-C(6)-C(7) | 0.5(4) |
| N(2)-C(11)-C(6)-C(7) | -178.0(3) |
| C(10)-C(11)-C(6)-C(5) | 179.3(3) |
| N(2)-C(11)-C(6)-C(5) | 0.8(4) |
| C(13)-O(2)-C(12)-O(1) | -5.1(5) |
| C(13)-O(2)-C(12)-N(2) | 175.2(3) |
| C(11)-N(2)-C(12)-O(1) | 2.7(5) |
| C(11)-N(2)-C(12)-O(2) | -177.6(3) |
| C(1)-N(1)-C(5)-C(4) | 1.4(4) |
| C(1)-N(1)-C(5)-C(6) | -177.9(3) |
| C(7)-C(6)-C(5)-N(1) | 154.7(3) |
| C(11)-C(6)-C(5)-N(1) | -24.2(4) |
| C(7)-C(6)-C(5)-C(4) | -24.6(4) |
| C(11)-C(6)-C(5)-C(4) | 156.5(3) |
| C(5)-N(1)-C(1)-C(2) | 0.1(5) |
| N(2)-C(11)-C(10)-C(9) | 178.9(3) |
| C(6)-C(11)-C(10)-C(9) | 0.4(5) |
| C(9)-C(8)-C(7)-C(6) | 0.8(5) |
| C(11)-C(6)-C(7)-C(8) | -1.1(5) |
| C(5)-C(6)-C(7)-C(8) | 180.0(3) |
| C(11)-C(10)-C(9)-C(8) | -0.7(5) |
| C(11)-C(10)-C(9)-C(17) | 178.4(3) |
| C(7)-C(8)-C(9)-C(10) | 0.1(5) |
| C(7)-C(8)-C(9)-C(17) | -179.0(3) |
| N(1)-C(5)-C(4)-C(3) | -2.4(5) |
| C(6)-C(5)-C(4)-C(3) | 176.9(3) |
| C(18)-O(4)-C(17)-O(3) | -1.3(5) |
| C(18)-O(4)-C(17)-C(9) | 179.0(3) |
| C(10)-C(9)-C(17)-O(3) | 10.5(5) |
| C(8)-C(9)-C(17)-O(3) | -170.4(3) |
| C(10)-C(9)-C(17)-O(4) | -169.8(3) |
| C(8)-C(9)-C(17)-O(4) | 9.3(4) |
| N(1)-C(1)-C(2)-C(3) | -0.5(5) |
| C(1)-C(2)-C(3)-C(4) | -0.5(5) |
| C(5)-C(4)-C(3)-C(2) | 1.9(5) |

| | |
|---|---|
| C(12)-O(2)-C(13)-C(15) | 62.6(3) |
| C(12)-O(2)-C(13)-C(16) | -179.5(3) |
| C(12)-O(2)-C(13)-C(14) | -61.9(4) |
| C(17)-O(4)-C(18)-C(19) | -170.9(3) |

Symmetry transformations used to generate equivalent atoms:

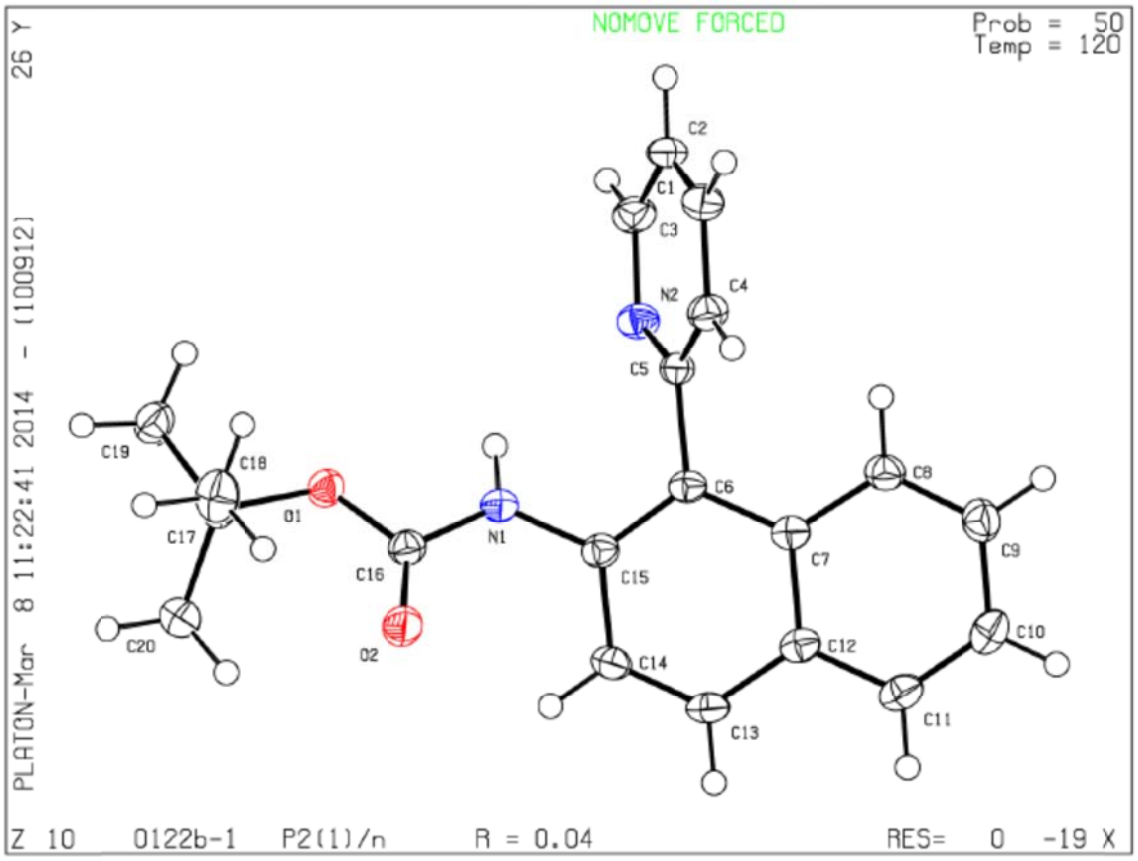


**Figure S3**: Crystal XRD image of **3w.**

**Table S8**. Crystal data and structure refinement for **3w**.

| | | |
|---|---|---|
| Identification code | **3w** | |
| Empirical formula | C20 H20 N2 O2 | |
| Formula weight | 320.38 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 9.5080(4) Å | α= 90°. |
| | b = 10.4245(4) Å | β= 98.3970(17)°. |
| | c = 17.1939(7) Å | γ = 90°. |
| Volume | 1685.92(12) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.262 $Mg/m^3$ | |
| Absorption coefficient | 0.082 $mm^{-1}$ | |
| F(000) | 680 | |
| Crystal size | 0.43 x 0.39 x 0.37 $mm^3$ | |
| Theta range for data collection | 2.29 to 26.37°. | |
| Index ranges | -11<=h<=11, -13<=k<=13, -21<=l<=21 | |
| Reflections collected | 21326 | |
| Independent reflections | 3436 [R(int) = 0.0296] | |
| Completeness to theta = 26.37° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9702 and 0.9655 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3436 / 63 / 218 | |
| Goodness-of-fit on $F^2$ | 1.093 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0382, wR2 = 0.0995 | |
| R indices (all data) | R1 = 0.0411, wR2 = 0.1023 | |
| Extinction coefficient | 0.0270(19) | |
| Largest diff. peak and hole | 0.316 and -0.254 $e.Å^{-3}$ | |

**Table S9**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3w**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 5538(1) | 3030(1) | 4812(1) | 24(1) |
| O(2) | 7379(1) | 1767(1) | 5353(1) | 30(1) |
| N(2) | 8009(1) | 4805(1) | 3000(1) | 24(1) |
| N(1) | 7406(1) | 2844(1) | 4195(1) | 24(1) |
| C(15) | 8721(1) | 2393(1) | 4012(1) | 21(1) |
| C(16) | 6816(1) | 2475(1) | 4840(1) | 22(1) |
| C(7) | 10892(1) | 2720(1) | 3439(1) | 20(1) |
| C(5) | 9205(1) | 4578(1) | 3502(1) | 20(1) |
| C(12) | 11285(1) | 1422(1) | 3616(1) | 22(1) |
| C(6) | 9595(1) | 3205(1) | 3660(1) | 20(1) |
| C(13) | 10364(1) | 636(1) | 3984(1) | 24(1) |
| C(14) | 9113(1) | 1096(1) | 4171(1) | 24(1) |
| C(11) | 12592(1) | 947(1) | 3429(1) | 27(1) |
| C(1) | 7694(1) | 6034(1) | 2815(1) | 28(1) |
| C(4) | 10066(1) | 5563(1) | 3851(1) | 26(1) |
| C(8) | 11829(1) | 3480(1) | 3055(1) | 25(1) |
| C(17) | 4725(1) | 2905(1) | 5482(1) | 24(1) |
| C(10) | 13485(1) | 1718(1) | 3085(1) | 30(1) |
| C(9) | 13088(1) | 2992(1) | 2890(1) | 29(1) |
| C(3) | 9715(1) | 6823(1) | 3649(1) | 30(1) |
| C(2) | 8518(1) | 7066(1) | 3111(1) | 30(1) |
| C(19) | 3406(1) | 3694(1) | 5200(1) | 28(1) |
| C(18) | 5573(1) | 3491(2) | 6215(1) | 34(1) |
| C(20) | 4327(1) | 1510(1) | 5592(1) | 34(1) |

**Table S10**. Bond lengths [Å] and angles [°] for **3w**.

| | |
|---|---|
| O(1)-C(16) | 1.3403(13) |
| O(1)-C(17) | 1.4848(13) |
| O(2)-C(16) | 1.2127(14) |
| N(2)-C(1) | 1.3436(15) |
| N(2)-C(5) | 1.3445(15) |
| N(1)-C(16) | 1.3695(14) |
| N(1)-C(15) | 1.4136(14) |
| C(15)-C(6) | 1.3855(16) |
| C(15)-C(14) | 1.4189(16) |
| C(7)-C(8) | 1.4243(16) |
| C(7)-C(12) | 1.4249(15) |
| C(7)-C(6) | 1.4340(15) |
| C(5)-C(4) | 1.3930(16) |
| C(5)-C(6) | 1.4937(15) |
| C(12)-C(13) | 1.4154(16) |
| C(12)-C(11) | 1.4175(16) |
| C(13)-C(14) | 1.3630(16) |
| C(11)-C(10) | 1.3650(18) |
| C(1)-C(2) | 1.3832(19) |
| C(4)-C(3) | 1.3868(17) |
| C(8)-C(9) | 1.3675(17) |
| C(17)-C(19) | 1.5193(16) |
| C(17)-C(18) | 1.5202(17) |
| C(17)-C(20) | 1.5208(17) |
| C(10)-C(9) | 1.4085(18) |
| C(3)-C(2) | 1.3820(19) |

| | |
|---|---|
| C(16)-O(1)-C(17) | 120.39(8) |
| C(1)-N(2)-C(5) | 117.28(10) |
| C(16)-N(1)-C(15) | 124.53(9) |
| C(6)-C(15)-N(1) | 120.00(10) |
| C(6)-C(15)-C(14) | 120.60(10) |
| N(1)-C(15)-C(14) | 119.38(10) |
| O(2)-C(16)-O(1) | 126.18(10) |
| O(2)-C(16)-N(1) | 124.81(10) |
| O(1)-C(16)-N(1) | 109.01(9) |
| C(8)-C(7)-C(12) | 117.68(10) |

| | |
|---|---|
| C(8)-C(7)-C(6) | 123.19(10) |
| C(12)-C(7)-C(6) | 119.13(10) |
| N(2)-C(5)-C(4) | 122.38(10) |
| N(2)-C(5)-C(6) | 116.70(10) |
| C(4)-C(5)-C(6) | 120.92(10) |
| C(13)-C(12)-C(11) | 121.27(10) |
| C(13)-C(12)-C(7) | 119.06(10) |
| C(11)-C(12)-C(7) | 119.67(10) |
| C(15)-C(6)-C(7) | 119.63(10) |
| C(15)-C(6)-C(5) | 121.08(10) |
| C(7)-C(6)-C(5) | 119.30(10) |
| C(14)-C(13)-C(12) | 121.31(10) |
| C(13)-C(14)-C(15) | 120.24(10) |
| C(10)-C(11)-C(12) | 120.91(11) |
| N(2)-C(1)-C(2) | 124.03(11) |
| C(3)-C(4)-C(5) | 119.08(11) |
| C(9)-C(8)-C(7) | 121.00(11) |
| O(1)-C(17)-C(19) | 101.72(9) |
| O(1)-C(17)-C(18) | 109.57(9) |
| C(19)-C(17)-C(18) | 111.10(10) |
| O(1)-C(17)-C(20) | 110.38(9) |
| C(19)-C(17)-C(20) | 110.38(10) |
| C(18)-C(17)-C(20) | 113.10(11) |
| C(11)-C(10)-C(9) | 119.75(11) |
| C(8)-C(9)-C(10) | 120.92(11) |
| C(2)-C(3)-C(4) | 119.02(11) |
| C(3)-C(2)-C(1) | 118.12(11) |

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Symmetry transformations used to generate equivalent atoms:

**Table S11**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3w**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 23(1) | 27(1) | 22(1) | 3(1) | 5(1) | 4(1) |
| O(2) | 29(1) | 34(1) | 28(1) | 10(1) | 6(1) | 9(1) |
| N(2) | 29(1) | 23(1) | 21(1) | 2(1) | 1(1) | 3(1) |
| N(1) | 25(1) | 21(1) | 26(1) | 6(1) | 6(1) | 5(1) |
| C(15) | 24(1) | 19(1) | 19(1) | -1(1) | 2(1) | 1(1) |
| C(16) | 22(1) | 20(1) | 24(1) | 0(1) | 3(1) | 0(1) |
| C(7) | 25(1) | 19(1) | 17(1) | -1(1) | 0(1) | 1(1) |
| C(5) | 24(1) | 18(1) | 19(1) | 1(1) | 6(1) | 2(1) |
| C(12) | 27(1) | 20(1) | 18(1) | -2(1) | 1(1) | 3(1) |
| C(6) | 24(1) | 17(1) | 17(1) | -1(1) | 1(1) | 1(1) |
| C(13) | 34(1) | 15(1) | 23(1) | 1(1) | 2(1) | 4(1) |
| C(14) | 30(1) | 18(1) | 23(1) | 2(1) | 5(1) | -1(1) |
| C(11) | 31(1) | 23(1) | 25(1) | -2(1) | 3(1) | 7(1) |
| C(1) | 34(1) | 28(1) | 22(1) | 6(1) | 4(1) | 9(1) |
| C(4) | 25(1) | 21(1) | 31(1) | -1(1) | 3(1) | 1(1) |
| C(8) | 31(1) | 21(1) | 23(1) | 0(1) | 6(1) | 1(1) |
| C(17) | 23(1) | 27(1) | 22(1) | 2(1) | 6(1) | 3(1) |
| C(10) | 28(1) | 34(1) | 29(1) | -4(1) | 7(1) | 6(1) |
| C(9) | 31(1) | 31(1) | 27(1) | -1(1) | 10(1) | -2(1) |
| C(3) | 33(1) | 18(1) | 42(1) | -2(1) | 11(1) | -2(1) |
| C(2) | 40(1) | 18(1) | 35(1) | 8(1) | 16(1) | 8(1) |
| C(19) | 27(1) | 32(1) | 27(1) | 3(1) | 5(1) | 7(1) |
| C(18) | 31(1) | 48(1) | 24(1) | -2(1) | 3(1) | 2(1) |
| C(20) | 31(1) | 29(1) | 43(1) | 8(1) | 11(1) | 2(1) |

**Table S12**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x 10 $^3$) for **3w**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1B) | 6934 | 3401 | 3871 | 29 |
| H(13A) | 10622 | -230 | 4104 | 29 |
| H(14A) | 8503 | 546 | 4409 | 28 |
| H(11A) | 12850 | 80 | 3545 | 32 |
| H(1A) | 6853 | 6205 | 2459 | 34 |
| H(4A) | 10881 | 5374 | 4222 | 31 |
| H(8A) | 11576 | 4339 | 2912 | 30 |
| H(10A) | 14371 | 1395 | 2977 | 36 |
| H(9A) | 13703 | 3521 | 2641 | 35 |
| H(3A) | 10290 | 7510 | 3878 | 37 |
| H(2A) | 8268 | 7917 | 2948 | 36 |
| H(19A) | 2878 | 3295 | 4730 | 43 |
| H(19B) | 3687 | 4565 | 5073 | 43 |
| H(19C) | 2802 | 3731 | 5615 | 43 |
| H(18A) | 5801 | 4385 | 6109 | 52 |
| H(18B) | 6455 | 3005 | 6359 | 52 |
| H(18C) | 5008 | 3460 | 6648 | 52 |
| H(20A) | 3789 | 1184 | 5103 | 50 |
| H(20B) | 3741 | 1449 | 6015 | 50 |
| H(20C) | 5193 | 1000 | 5730 | 50 |

**Table S13**. Torsion angles [°] for **3w**.

| | |
|---|---|
| C(16)-N(1)-C(15)-C(6) | -145.06(11) |
| C(16)-N(1)-C(15)-C(14) | 36.75(16) |
| C(17)-O(1)-C(16)-O(2) | 5.89(17) |
| C(17)-O(1)-C(16)-N(1) | -173.54(9) |
| C(15)-N(1)-C(16)-O(2) | 3.87(19) |
| C(15)-N(1)-C(16)-O(1) | -176.69(10) |
| C(1)-N(2)-C(5)-C(4) | 2.90(16) |
| C(1)-N(2)-C(5)-C(6) | -175.92(10) |
| C(8)-C(7)-C(12)-C(13) | -178.90(10) |
| C(6)-C(7)-C(12)-C(13) | 1.81(15) |
| C(8)-C(7)-C(12)-C(11) | 1.82(15) |
| C(6)-C(7)-C(12)-C(11) | -177.47(10) |
| N(1)-C(15)-C(6)-C(7) | -176.77(9) |
| C(14)-C(15)-C(6)-C(7) | 1.39(16) |
| N(1)-C(15)-C(6)-C(5) | 2.94(16) |
| C(14)-C(15)-C(6)-C(5) | -178.90(10) |
| C(8)-C(7)-C(6)-C(15) | 178.23(10) |
| C(12)-C(7)-C(6)-C(15) | -2.52(15) |
| C(8)-C(7)-C(6)-C(5) | -1.49(16) |
| C(12)-C(7)-C(6)-C(5) | 177.77(9) |
| N(2)-C(5)-C(6)-C(15) | -62.84(14) |
| C(4)-C(5)-C(6)-C(15) | 118.32(12) |
| N(2)-C(5)-C(6)-C(7) | 116.87(11) |
| C(4)-C(5)-C(6)-C(7) | -61.97(14) |
| C(11)-C(12)-C(13)-C(14) | 179.32(10) |
| C(7)-C(12)-C(13)-C(14) | 0.05(16) |
| C(12)-C(13)-C(14)-C(15) | -1.22(17) |
| C(6)-C(15)-C(14)-C(13) | 0.49(17) |
| N(1)-C(15)-C(14)-C(13) | 178.66(10) |
| C(13)-C(12)-C(11)-C(10) | -178.95(11) |
| C(7)-C(12)-C(11)-C(10) | 0.31(17) |
| C(5)-N(2)-C(1)-C(2) | -0.30(17) |
| N(2)-C(5)-C(4)-C(3) | -2.95(17) |
| C(6)-C(5)-C(4)-C(3) | 175.82(10) |
| C(12)-C(7)-C(8)-C(9) | -2.42(16) |
| C(6)-C(7)-C(8)-C(9) | 176.84(10) |
| C(16)-O(1)-C(17)-C(19) | 178.64(10) |

| | |
|---|---|
| C(16)-O(1)-C(17)-C(18) | 60.99(13) |
| C(16)-O(1)-C(17)-C(20) | -64.20(13) |
| C(12)-C(11)-C(10)-C(9) | -1.91(18) |
| C(7)-C(8)-C(9)-C(10) | 0.89(18) |
| C(11)-C(10)-C(9)-C(8) | 1.33(19) |
| C(5)-C(4)-C(3)-C(2) | 0.34(18) |
| C(4)-C(3)-C(2)-C(1) | 2.06(18) |
| N(2)-C(1)-C(2)-C(3) | -2.18(18) |

Symmetry transformations used to generate equivalent atoms:

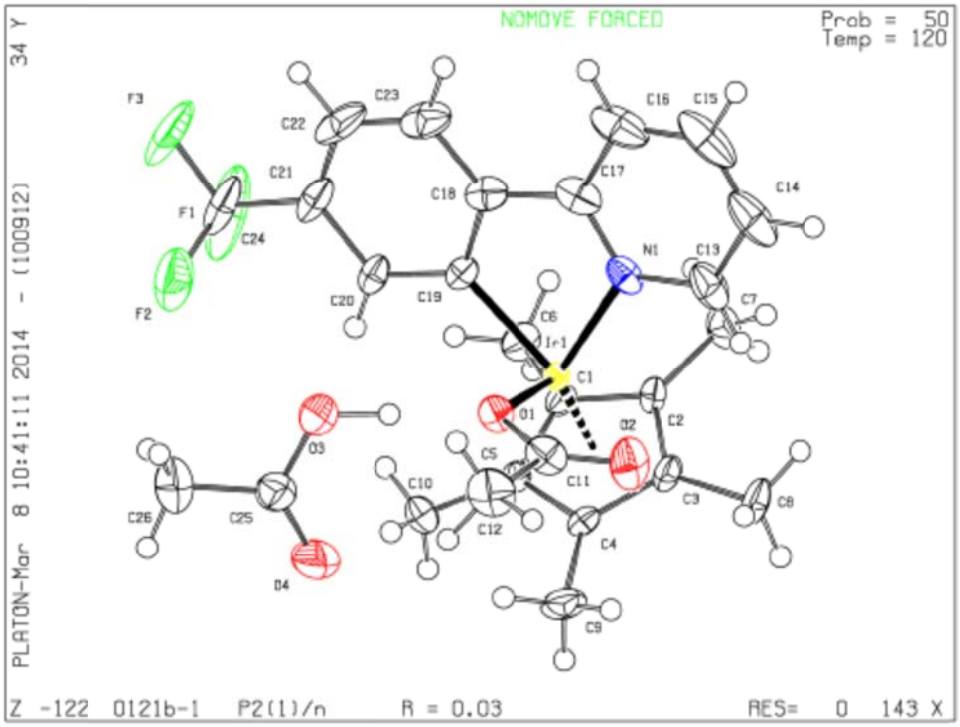


**Figure S4**: Crystal XRD image of complex **16**.

**Table S14**. Crystal data and structure refinement for **16**.

| | | |
|---|---|---|
| Identification code | **16** | |
| Empirical formula | C26 H29 F3 Ir N O4 | |
| Formula weight | 668.70 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | ? | |
| Space group | ? | |
| Unit cell dimensions | a = 16.4790(8) Å | α= 90°. |
| | b = 8.8550(4) Å | β= 103.143(2)°. |
| | c = 17.7803(9) Å | γ = 90°. |
| Volume | 2526.6(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.758 $Mg/m^3$ | |
| Absorption coefficient | 5.339 $mm^{-1}$ | |
| F(000) | 1312 | |
| Crystal size | 0.56 x 0.24 x 0.22 $mm^3$ | |
| Theta range for data collection | 1.52 to 30.47°. | |
| Index ranges | -23<=h<=23, -12<=k<=12, -18<=l<=25 | |
| Reflections collected | 37402 | |
| Independent reflections | 7176 [R(int) = 0.0348] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Max. and min. transmission | 0.3863 and 0.1540 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7176 / 0 / 323 | |
| Goodness-of-fit on $F^2$ | 1.048 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0253, wR2 = 0.0585 | |
| R indices (all data) | R1 = 0.0334, wR2 = 0.0628 | |
| Largest diff. peak and hole | 1.235 and -1.376 $e.Å^{-3}$ | |

**Table S15**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **16**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 7423(1) | 5066(1) | 164(1) | 17(1) |
| N(1) | 7972(2) | 6184(3) | -629(1) | 26(1) |
| O(1) | 7976(1) | 3091(2) | -182(1) | 26(1) |
| O(2) | 7149(2) | 3144(3) | -1371(1) | 42(1) |
| O(3) | 8959(2) | 1549(3) | 884(2) | 47(1) |
| O(4) | 7892(2) | 240(3) | 1088(3) | 70(1) |
| F(1) | 9657(2) | 5569(4) | 3227(2) | 93(1) |
| F(2) | 9955(2) | 3387(3) | 2857(1) | 64(1) |
| F(3) | 10860(2) | 5140(3) | 3029(2) | 81(1) |
| C(1) | 6730(2) | 5991(3) | 938(2) | 22(1) |
| C(2) | 6388(2) | 6529(3) | 172(2) | 23(1) |
| C(3) | 6036(2) | 5248(3) | -303(2) | 26(1) |
| C(4) | 6216(2) | 3945(3) | 157(2) | 24(1) |
| C(5) | 6653(2) | 4374(3) | 927(2) | 22(1) |
| C(6) | 7050(2) | 6947(4) | 1635(2) | 30(1) |
| C(7) | 6333(2) | 8155(4) | -72(2) | 35(1) |
| C(8) | 5543(2) | 5281(4) | -1126(2) | 38(1) |
| C(9) | 6006(2) | 2347(4) | -87(2) | 37(1) |
| C(10) | 6847(2) | 3330(4) | 1610(2) | 33(1) |
| C(11) | 7668(2) | 2522(3) | -872(2) | 31(1) |
| C(12) | 8020(3) | 986(4) | -991(2) | 45(1) |
| C(13) | 7565(3) | 6476(4) | -1360(2) | 39(1) |
| C(14) | 7936(3) | 7218(4) | -1868(2) | 51(1) |
| C(15) | 8744(3) | 7625(4) | -1637(3) | 56(1) |
| C(16) | 9178(3) | 7327(4) | -893(3) | 49(1) |
| C(17) | 8775(2) | 6597(3) | -386(2) | 32(1) |
| C(18) | 9145(2) | 6190(3) | 421(2) | 29(1) |
| C(19) | 8597(2) | 5471(3) | 809(2) | 22(1) |
| C(20) | 8918(2) | 5052(3) | 1576(2) | 26(1) |
| C(21) | 9748(2) | 5356(4) | 1932(2) | 35(1) |
| C(22) | 10273(2) | 6047(4) | 1535(3) | 48(1) |
| C(23) | 9975(2) | 6464(4) | 777(2) | 42(1) |
| C(24) | 10054(2) | 4874(5) | 2756(2) | 49(1) |

| | | | | |
|---|---|---|---|---|
| C(25) | 8626(2) | 490(4) | 1228(2) | 36(1) |
| C(26) | 9255(3) | -361(5) | 1811(3) | 52(1) |

**Table S16**. Bond lengths [Å] and angles [°] for **16**.

| | |
|---|---|
| Ir(1)-C(19) | 2.044(3) |
| Ir(1)-N(1) | 2.090(2) |
| Ir(1)-O(1) | 2.127(2) |
| Ir(1)-C(1) | 2.140(3) |
| Ir(1)-C(2) | 2.145(3) |
| Ir(1)-C(5) | 2.145(3) |
| Ir(1)-C(4) | 2.220(3) |
| Ir(1)-C(3) | 2.253(3) |
| N(1)-C(13) | 1.345(4) |
| N(1)-C(17) | 1.346(4) |
| O(1)-C(11) | 1.318(4) |
| O(2)-C(11) | 1.215(4) |
| O(3)-C(25) | 1.307(4) |
| O(4)-C(25) | 1.199(5) |
| F(1)-C(24) | 1.326(5) |
| F(2)-C(24) | 1.344(5) |
| F(3)-C(24) | 1.327(5) |
| C(1)-C(2) | 1.432(4) |
| C(1)-C(5) | 1.437(4) |
| C(1)-C(6) | 1.495(4) |
| C(2)-C(3) | 1.454(4) |
| C(2)-C(7) | 1.500(4) |
| C(3)-C(4) | 1.407(4) |
| C(3)-C(8) | 1.503(4) |
| C(4)-C(5) | 1.444(4) |
| C(4)-C(9) | 1.498(4) |
| C(5)-C(10) | 1.502(4) |
| C(11)-C(12) | 1.512(4) |
| C(13)-C(14) | 1.369(5) |
| C(14)-C(15) | 1.350(6) |
| C(15)-C(16) | 1.379(6) |
| C(16)-C(17) | 1.394(5) |
| C(17)-C(18) | 1.470(5) |
| C(18)-C(23) | 1.392(4) |

| | |
|---|---|
| C(18)-C(19) | 1.408(4) |
| C(19)-C(20) | 1.396(4) |
| C(20)-C(21) | 1.397(4) |
| C(21)-C(22) | 1.377(6) |
| C(21)-C(24) | 1.497(6) |
| C(22)-C(23) | 1.377(6) |
| C(25)-C(26) | 1.492(5) |

| | |
|---|---|
| C(19)-Ir(1)-N(1) | 78.20(11) |
| C(19)-Ir(1)-O(1) | 83.85(10) |
| N(1)-Ir(1)-O(1) | 85.10(9) |
| C(19)-Ir(1)-C(1) | 98.47(11) |
| N(1)-Ir(1)-C(1) | 128.92(11) |
| O(1)-Ir(1)-C(1) | 145.80(10) |
| C(19)-Ir(1)-C(2) | 122.90(11) |
| N(1)-Ir(1)-C(2) | 100.66(11) |
| O(1)-Ir(1)-C(2) | 153.22(10) |
| C(1)-Ir(1)-C(2) | 39.06(10) |
| C(19)-Ir(1)-C(5) | 108.38(11) |
| N(1)-Ir(1)-C(5) | 166.02(11) |
| O(1)-Ir(1)-C(5) | 107.58(10) |
| C(1)-Ir(1)-C(5) | 39.18(11) |
| C(2)-Ir(1)-C(5) | 65.38(11) |
| C(19)-Ir(1)-C(4) | 144.47(12) |
| N(1)-Ir(1)-C(4) | 137.14(11) |
| O(1)-Ir(1)-C(4) | 94.22(10) |
| C(1)-Ir(1)-C(4) | 64.31(11) |
| C(2)-Ir(1)-C(4) | 63.74(11) |
| C(5)-Ir(1)-C(4) | 38.60(10) |
| C(19)-Ir(1)-C(3) | 161.03(11) |
| N(1)-Ir(1)-C(3) | 106.02(11) |
| O(1)-Ir(1)-C(3) | 114.72(10) |
| C(1)-Ir(1)-C(3) | 64.21(11) |
| C(2)-Ir(1)-C(3) | 38.51(11) |
| C(5)-Ir(1)-C(3) | 63.75(11) |
| C(4)-Ir(1)-C(3) | 36.66(11) |
| C(13)-N(1)-C(17) | 119.7(3) |
| C(13)-N(1)-Ir(1) | 123.1(2) |
| C(17)-N(1)-Ir(1) | 117.2(2) |

| | |
|---|---|
| C(11)-O(1)-Ir(1) | 118.95(19) |
| C(2)-C(1)-C(5) | 107.7(2) |
| C(2)-C(1)-C(6) | 126.0(3) |
| C(5)-C(1)-C(6) | 126.1(3) |
| C(2)-C(1)-Ir(1) | 70.66(16) |
| C(5)-C(1)-Ir(1) | 70.62(16) |
| C(6)-C(1)-Ir(1) | 127.7(2) |
| C(1)-C(2)-C(3) | 108.1(2) |
| C(1)-C(2)-C(7) | 125.4(3) |
| C(3)-C(2)-C(7) | 126.3(3) |
| C(1)-C(2)-Ir(1) | 70.29(16) |
| C(3)-C(2)-Ir(1) | 74.77(17) |
| C(7)-C(2)-Ir(1) | 125.0(2) |
| C(4)-C(3)-C(2) | 107.4(3) |
| C(4)-C(3)-C(8) | 125.3(3) |
| C(2)-C(3)-C(8) | 127.3(3) |
| C(4)-C(3)-Ir(1) | 70.41(16) |
| C(2)-C(3)-Ir(1) | 66.72(16) |
| C(8)-C(3)-Ir(1) | 129.7(2) |
| C(3)-C(4)-C(5) | 109.2(2) |
| C(3)-C(4)-C(9) | 127.0(3) |
| C(5)-C(4)-C(9) | 123.7(3) |
| C(3)-C(4)-Ir(1) | 72.94(17) |
| C(5)-C(4)-Ir(1) | 67.90(15) |
| C(9)-C(4)-Ir(1) | 124.9(2) |
| C(1)-C(5)-C(4) | 107.4(2) |
| C(1)-C(5)-C(10) | 126.9(3) |
| C(4)-C(5)-C(10) | 124.9(3) |
| C(1)-C(5)-Ir(1) | 70.21(16) |
| C(4)-C(5)-Ir(1) | 73.50(17) |
| C(10)-C(5)-Ir(1) | 129.7(2) |
| O(2)-C(11)-O(1) | 124.4(3) |
| O(2)-C(11)-C(12) | 122.3(3) |
| O(1)-C(11)-C(12) | 113.3(3) |
| N(1)-C(13)-C(14) | 122.1(4) |
| C(15)-C(14)-C(13) | 119.0(4) |
| C(14)-C(15)-C(16) | 120.1(4) |
| C(15)-C(16)-C(17) | 119.4(4) |
| N(1)-C(17)-C(16) | 119.8(4) |

| | |
|---|---|
| N(1)-C(17)-C(18) | 113.9(3) |
| C(16)-C(17)-C(18) | 126.3(4) |
| C(23)-C(18)-C(19) | 122.0(3) |
| C(23)-C(18)-C(17) | 123.2(3) |
| C(19)-C(18)-C(17) | 114.8(3) |
| C(20)-C(19)-C(18) | 117.1(3) |
| C(20)-C(19)-Ir(1) | 127.0(2) |
| C(18)-C(19)-Ir(1) | 115.8(2) |
| C(19)-C(20)-C(21) | 120.4(3) |
| C(22)-C(21)-C(20) | 121.2(3) |
| C(22)-C(21)-C(24) | 121.1(3) |
| C(20)-C(21)-C(24) | 117.7(4) |
| C(23)-C(22)-C(21) | 119.7(3) |
| C(22)-C(23)-C(18) | 119.6(4) |
| F(1)-C(24)-F(3) | 106.5(3) |
| F(1)-C(24)-F(2) | 106.1(4) |
| F(3)-C(24)-F(2) | 105.4(3) |
| F(1)-C(24)-C(21) | 112.4(3) |
| F(3)-C(24)-C(21) | 113.2(4) |
| F(2)-C(24)-C(21) | 112.7(3) |
| O(4)-C(25)-O(3) | 123.1(4) |
| O(4)-C(25)-C(26) | 124.0(4) |
| O(3)-C(25)-C(26) | 112.9(3) |

---

Symmetry transformations used to generate equivalent atoms:

**Table S17**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 21(1) | 17(1) | 10(1) | 0(1) | 0(1) | -1(1) |
| N(1) | 41(2) | 22(1) | 19(1) | 0(1) | 13(1) | 1(1) |
| O(1) | 33(1) | 22(1) | 22(1) | -3(1) | 6(1) | 1(1) |
| O(2) | 62(2) | 38(1) | 20(1) | -9(1) | 0(1) | 7(1) |
| O(3) | 26(1) | 47(2) | 64(2) | 17(1) | 0(1) | 1(1) |
| O(4) | 37(2) | 57(2) | 110(3) | 36(2) | 4(2) | -9(1) |
| F(1) | 89(2) | 140(3) | 37(1) | -29(2) | -15(1) | 75(2) |
| F(2) | 71(2) | 68(2) | 38(1) | 1(1) | -16(1) | 13(1) |
| F(3) | 42(2) | 103(3) | 74(2) | -17(2) | -38(2) | 8(1) |
| C(1) | 20(1) | 26(1) | 17(1) | -2(1) | 1(1) | -2(1) |
| C(2) | 22(1) | 25(1) | 21(1) | 2(1) | 0(1) | 5(1) |
| C(3) | 22(1) | 31(2) | 20(1) | -1(1) | -4(1) | 1(1) |
| C(4) | 20(1) | 26(1) | 22(1) | -2(1) | -2(1) | -5(1) |
| C(5) | 21(1) | 25(1) | 18(1) | 2(1) | 3(1) | -2(1) |
| C(6) | 33(2) | 35(2) | 21(2) | -9(1) | 7(1) | -3(1) |
| C(7) | 39(2) | 27(2) | 36(2) | 6(1) | 4(2) | 9(1) |
| C(8) | 32(2) | 49(2) | 25(2) | -1(2) | -12(1) | 6(2) |
| C(9) | 33(2) | 30(2) | 46(2) | -10(2) | 2(2) | -12(1) |
| C(10) | 36(2) | 35(2) | 26(2) | 12(1) | 6(1) | -4(1) |
| C(11) | 44(2) | 24(2) | 28(2) | -7(1) | 12(1) | -1(1) |
| C(12) | 61(3) | 28(2) | 44(2) | -14(2) | 11(2) | 4(2) |
| C(13) | 66(3) | 31(2) | 21(2) | 5(1) | 12(2) | 2(2) |
| C(14) | 99(4) | 34(2) | 30(2) | 7(2) | 34(2) | 5(2) |
| C(15) | 101(4) | 30(2) | 57(3) | 12(2) | 61(3) | 14(2) |
| C(16) | 56(2) | 34(2) | 74(3) | 5(2) | 49(2) | 2(2) |
| C(17) | 39(2) | 22(2) | 42(2) | -3(1) | 26(2) | 3(1) |
| C(18) | 23(2) | 27(2) | 40(2) | -8(1) | 14(1) | 1(1) |
| C(19) | 19(1) | 22(1) | 24(1) | -6(1) | 2(1) | 2(1) |
| C(20) | 23(1) | 29(2) | 24(2) | -7(1) | -1(1) | 5(1) |
| C(21) | 24(2) | 34(2) | 40(2) | -16(2) | -10(1) | 10(1) |
| C(22) | 17(2) | 45(2) | 75(3) | -23(2) | -3(2) | 3(1) |
| C(23) | 21(2) | 38(2) | 71(3) | -9(2) | 15(2) | 0(1) |
| C(24) | 35(2) | 62(3) | 38(2) | -22(2) | -18(2) | 22(2) |
| C(25) | 34(2) | 31(2) | 43(2) | 0(2) | 6(2) | -1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 55(3) | 50(2) | 47(2) | 11(2) | 3(2) | 15(2) |

**Table S18**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **16**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | 8585 | 1975 | 551 | 71 |
| H(6A) | 6590 | 7201 | 1878 | 44 |
| H(6B) | 7291 | 7878 | 1481 | 44 |
| H(6C) | 7479 | 6390 | 2003 | 44 |
| H(7A) | 5805 | 8582 | -8 | 53 |
| H(7B) | 6362 | 8226 | -615 | 53 |
| H(7C) | 6798 | 8718 | 248 | 53 |
| H(8A) | 5749 | 4496 | -1423 | 58 |
| H(8B) | 5604 | 6272 | -1352 | 58 |
| H(8C) | 4953 | 5097 | -1138 | 58 |
| H(9A) | 5515 | 2024 | 97 | 56 |
| H(9B) | 6479 | 1691 | 136 | 56 |
| H(9C) | 5886 | 2280 | -651 | 56 |
| H(10A) | 7225 | 3836 | 2042 | 49 |
| H(10B) | 7114 | 2413 | 1472 | 49 |
| H(10C) | 6330 | 3061 | 1761 | 49 |
| H(12A) | 7784 | 641 | -1519 | 67 |
| H(12B) | 7876 | 267 | -623 | 67 |
| H(12C) | 8627 | 1056 | -907 | 67 |
| H(13A) | 7003 | 6156 | -1529 | 47 |
| H(14A) | 7629 | 7444 | -2376 | 62 |
| H(15A) | 9014 | 8117 | -1988 | 67 |
| H(16A) | 9745 | 7617 | -727 | 59 |
| H(20A) | 8570 | 4558 | 1858 | 31 |
| H(22A) | 10838 | 6234 | 1784 | 57 |
| H(23A) | 10334 | 6935 | 498 | 51 |
| H(26A) | 9432 | 254 | 2278 | 78 |
| H(26B) | 9738 | -593 | 1597 | 78 |

| | | | | |
|---|---|---|---|---|
| H(26C) | 9007 | -1304 | 1941 | 78 |

**Table S19**. Torsion angles [°] for **16**.

| | |
|---|---|
| C(19)-Ir(1)-N(1)-C(13) | -180.0(3) |
| O(1)-Ir(1)-N(1)-C(13) | 95.3(3) |
| C(1)-Ir(1)-N(1)-C(13) | -88.5(3) |
| C(2)-Ir(1)-N(1)-C(13) | -58.3(3) |
| C(5)-Ir(1)-N(1)-C(13) | -60.3(5) |
| C(4)-Ir(1)-N(1)-C(13) | 4.4(3) |
| C(3)-Ir(1)-N(1)-C(13) | -19.0(3) |
| C(19)-Ir(1)-N(1)-C(17) | 1.2(2) |
| O(1)-Ir(1)-N(1)-C(17) | -83.5(2) |
| C(1)-Ir(1)-N(1)-C(17) | 92.6(2) |
| C(2)-Ir(1)-N(1)-C(17) | 122.9(2) |
| C(5)-Ir(1)-N(1)-C(17) | 120.8(4) |
| C(4)-Ir(1)-N(1)-C(17) | -174.4(2) |
| C(3)-Ir(1)-N(1)-C(17) | 162.1(2) |
| C(19)-Ir(1)-O(1)-C(11) | -150.5(2) |
| N(1)-Ir(1)-O(1)-C(11) | -71.9(2) |
| C(1)-Ir(1)-O(1)-C(11) | 113.5(2) |
| C(2)-Ir(1)-O(1)-C(11) | 32.1(3) |
| C(5)-Ir(1)-O(1)-C(11) | 102.1(2) |
| C(4)-Ir(1)-O(1)-C(11) | 65.1(2) |
| C(3)-Ir(1)-O(1)-C(11) | 33.5(2) |
| C(19)-Ir(1)-C(1)-C(2) | 133.47(17) |
| N(1)-Ir(1)-C(1)-C(2) | 51.8(2) |
| O(1)-Ir(1)-C(1)-C(2) | -135.01(18) |
| C(5)-Ir(1)-C(1)-C(2) | -117.7(2) |
| C(4)-Ir(1)-C(1)-C(2) | -79.25(18) |
| C(3)-Ir(1)-C(1)-C(2) | -38.39(17) |
| C(19)-Ir(1)-C(1)-C(5) | -108.78(17) |
| N(1)-Ir(1)-C(1)-C(5) | 169.58(15) |
| O(1)-Ir(1)-C(1)-C(5) | -17.3(2) |
| C(2)-Ir(1)-C(1)-C(5) | 117.7(2) |
| C(4)-Ir(1)-C(1)-C(5) | 38.50(15) |
| C(3)-Ir(1)-C(1)-C(5) | 79.36(17) |

| | |
|---|---|
| C(19)-Ir(1)-C(1)-C(6) | 12.4(3) |
| N(1)-Ir(1)-C(1)-C(6) | -69.3(3) |
| O(1)-Ir(1)-C(1)-C(6) | 103.9(3) |
| C(2)-Ir(1)-C(1)-C(6) | -121.1(3) |
| C(5)-Ir(1)-C(1)-C(6) | 121.1(3) |
| C(4)-Ir(1)-C(1)-C(6) | 159.6(3) |
| C(3)-Ir(1)-C(1)-C(6) | -159.5(3) |
| C(5)-C(1)-C(2)-C(3) | 4.5(3) |
| C(6)-C(1)-C(2)-C(3) | -171.2(3) |
| Ir(1)-C(1)-C(2)-C(3) | 65.7(2) |
| C(5)-C(1)-C(2)-C(7) | 179.2(3) |
| C(6)-C(1)-C(2)-C(7) | 3.5(5) |
| Ir(1)-C(1)-C(2)-C(7) | -119.5(3) |
| C(5)-C(1)-C(2)-Ir(1) | -61.2(2) |
| C(6)-C(1)-C(2)-Ir(1) | 123.0(3) |
| C(19)-Ir(1)-C(2)-C(1) | -58.7(2) |
| N(1)-Ir(1)-C(2)-C(1) | -141.51(16) |
| O(1)-Ir(1)-C(2)-C(1) | 118.1(2) |
| C(5)-Ir(1)-C(2)-C(1) | 37.95(16) |
| C(4)-Ir(1)-C(2)-C(1) | 80.85(18) |
| C(3)-Ir(1)-C(2)-C(1) | 116.1(2) |
| C(19)-Ir(1)-C(2)-C(3) | -174.85(17) |
| N(1)-Ir(1)-C(2)-C(3) | 102.39(18) |
| O(1)-Ir(1)-C(2)-C(3) | 2.0(3) |
| C(1)-Ir(1)-C(2)-C(3) | -116.1(2) |
| C(5)-Ir(1)-C(2)-C(3) | -78.15(19) |
| C(4)-Ir(1)-C(2)-C(3) | -35.25(17) |
| C(19)-Ir(1)-C(2)-C(7) | 61.2(3) |
| N(1)-Ir(1)-C(2)-C(7) | -21.5(3) |
| O(1)-Ir(1)-C(2)-C(7) | -121.9(3) |
| C(1)-Ir(1)-C(2)-C(7) | 120.0(3) |
| C(5)-Ir(1)-C(2)-C(7) | 157.9(3) |
| C(4)-Ir(1)-C(2)-C(7) | -159.2(3) |
| C(3)-Ir(1)-C(2)-C(7) | -123.9(3) |
| C(1)-C(2)-C(3)-C(4) | -4.0(4) |
| C(7)-C(2)-C(3)-C(4) | -178.6(3) |
| Ir(1)-C(2)-C(3)-C(4) | 58.9(2) |
| C(1)-C(2)-C(3)-C(8) | 174.1(3) |
| C(7)-C(2)-C(3)-C(8) | -0.6(5) |

| | |
|---|---|
| Ir(1)-C(2)-C(3)-C(8) | -123.1(3) |
| C(1)-C(2)-C(3)-Ir(1) | -62.8(2) |
| C(7)-C(2)-C(3)-Ir(1) | 122.5(3) |
| C(19)-Ir(1)-C(3)-C(4) | -106.5(4) |
| N(1)-Ir(1)-C(3)-C(4) | 153.08(17) |
| O(1)-Ir(1)-C(3)-C(4) | 61.1(2) |
| C(1)-Ir(1)-C(3)-C(4) | -80.96(19) |
| C(2)-Ir(1)-C(3)-C(4) | -119.9(3) |
| C(5)-Ir(1)-C(3)-C(4) | -37.16(17) |
| C(19)-Ir(1)-C(3)-C(2) | 13.4(4) |
| N(1)-Ir(1)-C(3)-C(2) | -87.03(18) |
| O(1)-Ir(1)-C(3)-C(2) | -178.99(16) |
| C(1)-Ir(1)-C(3)-C(2) | 38.93(17) |
| C(5)-Ir(1)-C(3)-C(2) | 82.74(19) |
| C(4)-Ir(1)-C(3)-C(2) | 119.9(3) |
| C(19)-Ir(1)-C(3)-C(8) | 133.4(4) |
| N(1)-Ir(1)-C(3)-C(8) | 33.0(3) |
| O(1)-Ir(1)-C(3)-C(8) | -59.0(3) |
| C(1)-Ir(1)-C(3)-C(8) | 158.9(3) |
| C(2)-Ir(1)-C(3)-C(8) | 120.0(4) |
| C(5)-Ir(1)-C(3)-C(8) | -157.3(3) |
| C(4)-Ir(1)-C(3)-C(8) | -120.1(4) |
| C(2)-C(3)-C(4)-C(5) | 1.9(4) |
| C(8)-C(3)-C(4)-C(5) | -176.2(3) |
| Ir(1)-C(3)-C(4)-C(5) | 58.4(2) |
| C(2)-C(3)-C(4)-C(9) | -177.8(3) |
| C(8)-C(3)-C(4)-C(9) | 4.2(5) |
| Ir(1)-C(3)-C(4)-C(9) | -121.2(3) |
| C(2)-C(3)-C(4)-Ir(1) | -56.6(2) |
| C(8)-C(3)-C(4)-Ir(1) | 125.4(3) |
| C(19)-Ir(1)-C(4)-C(3) | 147.6(2) |
| N(1)-Ir(1)-C(4)-C(3) | -39.8(2) |
| O(1)-Ir(1)-C(4)-C(3) | -127.11(18) |
| C(1)-Ir(1)-C(4)-C(3) | 80.66(19) |
| C(2)-Ir(1)-C(4)-C(3) | 37.01(18) |
| C(5)-Ir(1)-C(4)-C(3) | 119.7(3) |
| C(19)-Ir(1)-C(4)-C(5) | 27.8(3) |
| N(1)-Ir(1)-C(4)-C(5) | -159.51(17) |
| O(1)-Ir(1)-C(4)-C(5) | 113.16(17) |

| | |
|---|---|
| C(1)-Ir(1)-C(4)-C(5) | -39.07(17) |
| C(2)-Ir(1)-C(4)-C(5) | -82.73(18) |
| C(3)-Ir(1)-C(4)-C(5) | -119.7(3) |
| C(19)-Ir(1)-C(4)-C(9) | -88.8(3) |
| N(1)-Ir(1)-C(4)-C(9) | 83.9(3) |
| O(1)-Ir(1)-C(4)-C(9) | -3.5(3) |
| C(1)-Ir(1)-C(4)-C(9) | -155.7(3) |
| C(2)-Ir(1)-C(4)-C(9) | 160.7(3) |
| C(5)-Ir(1)-C(4)-C(9) | -116.6(3) |
| C(3)-Ir(1)-C(4)-C(9) | 123.7(3) |
| C(2)-C(1)-C(5)-C(4) | -3.4(3) |
| C(6)-C(1)-C(5)-C(4) | 172.4(3) |
| Ir(1)-C(1)-C(5)-C(4) | -64.6(2) |
| C(2)-C(1)-C(5)-C(10) | -173.4(3) |
| C(6)-C(1)-C(5)-C(10) | 2.3(5) |
| Ir(1)-C(1)-C(5)-C(10) | 125.4(3) |
| C(2)-C(1)-C(5)-Ir(1) | 61.2(2) |
| C(6)-C(1)-C(5)-Ir(1) | -123.0(3) |
| C(3)-C(4)-C(5)-C(1) | 0.9(3) |
| C(9)-C(4)-C(5)-C(1) | -179.5(3) |
| Ir(1)-C(4)-C(5)-C(1) | 62.44(19) |
| C(3)-C(4)-C(5)-C(10) | 171.2(3) |
| C(9)-C(4)-C(5)-C(10) | -9.2(5) |
| Ir(1)-C(4)-C(5)-C(10) | -127.3(3) |
| C(3)-C(4)-C(5)-Ir(1) | -61.5(2) |
| C(9)-C(4)-C(5)-Ir(1) | 118.1(3) |
| C(19)-Ir(1)-C(5)-C(1) | 80.67(17) |
| N(1)-Ir(1)-C(5)-C(1) | -35.6(5) |
| O(1)-Ir(1)-C(5)-C(1) | 169.92(15) |
| C(2)-Ir(1)-C(5)-C(1) | -37.84(15) |
| C(4)-Ir(1)-C(5)-C(1) | -115.9(2) |
| C(3)-Ir(1)-C(5)-C(1) | -80.64(17) |
| C(19)-Ir(1)-C(5)-C(4) | -163.38(17) |
| N(1)-Ir(1)-C(5)-C(4) | 80.3(5) |
| O(1)-Ir(1)-C(5)-C(4) | -74.13(17) |
| C(1)-Ir(1)-C(5)-C(4) | 115.9(2) |
| C(2)-Ir(1)-C(5)-C(4) | 78.11(18) |
| C(3)-Ir(1)-C(5)-C(4) | 35.31(16) |
| C(19)-Ir(1)-C(5)-C(10) | -41.4(3) |

| | |
|---|---|
| N(1)-Ir(1)-C(5)-C(10) | -157.7(4) |
| O(1)-Ir(1)-C(5)-C(10) | 47.9(3) |
| C(1)-Ir(1)-C(5)-C(10) | -122.0(3) |
| C(2)-Ir(1)-C(5)-C(10) | -159.9(3) |
| C(4)-Ir(1)-C(5)-C(10) | 122.0(4) |
| C(3)-Ir(1)-C(5)-C(10) | 157.3(3) |
| Ir(1)-O(1)-C(11)-O(2) | 9.5(5) |
| Ir(1)-O(1)-C(11)-C(12) | -170.1(2) |
| C(17)-N(1)-C(13)-C(14) | -1.6(5) |
| Ir(1)-N(1)-C(13)-C(14) | 179.6(3) |
| N(1)-C(13)-C(14)-C(15) | 2.4(6) |
| C(13)-C(14)-C(15)-C(16) | -1.7(6) |
| C(14)-C(15)-C(16)-C(17) | 0.4(6) |
| C(13)-N(1)-C(17)-C(16) | 0.2(5) |
| Ir(1)-N(1)-C(17)-C(16) | 179.1(2) |
| C(13)-N(1)-C(17)-C(18) | -179.1(3) |
| Ir(1)-N(1)-C(17)-C(18) | -0.3(3) |
| C(15)-C(16)-C(17)-N(1) | 0.4(5) |
| C(15)-C(16)-C(17)-C(18) | 179.7(3) |
| N(1)-C(17)-C(18)-C(23) | 177.6(3) |
| C(16)-C(17)-C(18)-C(23) | -1.7(5) |
| N(1)-C(17)-C(18)-C(19) | -1.4(4) |
| C(16)-C(17)-C(18)-C(19) | 179.3(3) |
| C(23)-C(18)-C(19)-C(20) | 0.7(4) |
| C(17)-C(18)-C(19)-C(20) | 179.7(2) |
| C(23)-C(18)-C(19)-Ir(1) | -176.6(2) |
| C(17)-C(18)-C(19)-Ir(1) | 2.4(3) |
| N(1)-Ir(1)-C(19)-C(20) | -178.9(3) |
| O(1)-Ir(1)-C(19)-C(20) | -92.6(3) |
| C(1)-Ir(1)-C(19)-C(20) | 52.9(3) |
| C(2)-Ir(1)-C(19)-C(20) | 85.9(3) |
| C(5)-Ir(1)-C(19)-C(20) | 13.9(3) |
| C(4)-Ir(1)-C(19)-C(20) | -4.0(4) |
| C(3)-Ir(1)-C(19)-C(20) | 76.0(5) |
| N(1)-Ir(1)-C(19)-C(18) | -1.9(2) |
| O(1)-Ir(1)-C(19)-C(18) | 84.3(2) |
| C(1)-Ir(1)-C(19)-C(18) | -130.1(2) |
| C(2)-Ir(1)-C(19)-C(18) | -97.1(2) |
| C(5)-Ir(1)-C(19)-C(18) | -169.2(2) |

| | |
|---|---|
| C(4)-Ir(1)-C(19)-C(18) | 173.0(2) |
| C(3)-Ir(1)-C(19)-C(18) | -107.0(4) |
| C(18)-C(19)-C(20)-C(21) | 0.4(4) |
| Ir(1)-C(19)-C(20)-C(21) | 177.4(2) |
| C(19)-C(20)-C(21)-C(22) | -1.2(5) |
| C(19)-C(20)-C(21)-C(24) | -179.8(3) |
| C(20)-C(21)-C(22)-C(23) | 0.8(5) |
| C(24)-C(21)-C(22)-C(23) | 179.4(3) |
| C(21)-C(22)-C(23)-C(18) | 0.4(5) |
| C(19)-C(18)-C(23)-C(22) | -1.1(5) |
| C(17)-C(18)-C(23)-C(22) | 180.0(3) |
| C(22)-C(21)-C(24)-F(1) | 118.6(4) |
| C(20)-C(21)-C(24)-F(1) | -62.8(5) |
| C(22)-C(21)-C(24)-F(3) | -2.0(5) |
| C(20)-C(21)-C(24)-F(3) | 176.6(3) |
| C(22)-C(21)-C(24)-F(2) | -121.6(4) |
| C(20)-C(21)-C(24)-F(2) | 57.1(4) |

Symmetry transformations used to generate equivalent atoms:

**Table S20**. Hydrogen bonds for **16** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3A)...O(1) | 0.84 | 1.76 | 2.585(3) | 168.0 |

Symmetry transformations used to generate equivalent atoms: