Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis, characterisation, and reactivity of novel pseudocyclic hypervalent iodine reagents with heteroaryl carbonyl substituents

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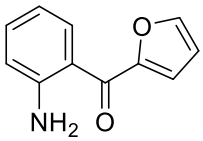
General information

All solvents and reagents were used as received without purification or drying. Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualized by UV radiation (254 nm). Automated column chromatography was performed on a Biotage® Isolera Four using Biotage® cartridges SNAP Ultra. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on Bruker DPX 300, 400 or 500 apparatus and were referenced to the residual proton solvent peak (^{1}H: $CDCl_3$, δ 7.26 ppm; DMSO-d_6, δ 2.50 ppm; MeOH-d_4, δ 3.31 ppm) and solvent ^{13}C signal ($CDCl_3$, δ 77.2 ppm, DMSO-d_6, δ 39.5, MeOH-d_4, δ 49.0). Chemical shifts δ were reported in ppm, multiplicity of the signals was declared as followed: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, hep = septet, dd = doublet of doublets, m = multiplet, b = broad; and coupling constants (*J*) in Hertz. IR spectra were recorded on a Shimadzu FTIR Affinity-1S apparatus. Wavenumbers are quoted in cm^{-1}. All compounds were measured neat directly on the crystal of the IR machine.

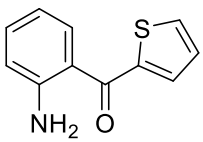
X-Ray crystallographic studies were carried out at the X-Ray Crystallography Service at Cardiff University. The data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator, equipped with an Oxford cryosystems cooling apparatus. Crystal structures were solved and refined using SHELX. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealised positions. The structure was solved by a direct method and refined by a full matrix least-squares procedure on F2 for all reflections (SHELXL-97).

(2-Aminophenyl)(furan-2-yl)methanone (**8**):[1]



To a stirred solution of furan (9.0 mL, 114 mmol, 4.5 equiv) in dry THF (100 mL) at –78 °C *n*-BuLi (2.5 M in hexane, 45 mL, 114 mmol, 4.5 equiv) was added. The solution left to warm to room temperature overnight, diluted with dry THF. The solution was then added slowly to a cooled (–78°C) stirred solution of 2-cyanoaniline (3.0 g, 25 mmol, 1 equiv) in dry THF (100 mL). Stirring was continued at room temperature for 12 h. The reaction mixture was then poured into ice and acidified with HCl (4 N) and stirred for 30 min. Solid Na_2CO_3 was then added portionwise with stirring until pH > 10, then extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2/pentane, 8:2) to afford pure **8** as brown oil (3.0 g, 16 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.66 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.29 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.12 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.76 – 6.65 (m, 2H), 6.55 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.88 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.9, 152.7, 150.5, 146.4, 134.1, 132.3, 119.6, 118.3, 117.1, 116.1, 112.0 ppm. Spectral data agree with literature.[1]

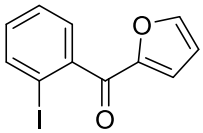
(2-Aminophenyl)(thiophen-2-yl)methanone (**9**):[1]



To a stirred solution of thiophene (6.0 mL, 76.5 mmol,4.5 equiv) in dry THF (50 mL) at –78 °C *n*-BuLi (2.5 M in hexane, 30.6 mL, 76.5 mmol, 4.5 equiv) was added. The solution left to warm to room temperature overnight, diluted with dry THF. The solution was then added slowly to a cooled (–78°C) stirred solution of 2-cyanoaniline (2.0 g, 17 mmol, 1 equiv) in dry THF (50 mL). Stirring was continued at room temperature for 12 hours. The reaction mixture was then poured into ice and acidified with HCl (4 N) and stirred for 30 min. Solid Na_2CO_3 was then added portionwise with stirring until pH > 10, then extracted with diethyl ether (3 x 80 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, the

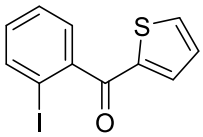
residue was purified by column chromatography (CH_2Cl_2) to afford pure **9** as brown oil (2.75 g, 13.5 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (dd, *J* = 8.0, 1.6, 1H), 7.65 (dd, *J* = 5.0, 1.1, 1H), 7.57 (dd, *J* = 3.8, 1.1, 1H), 7.29 (ddd, *J* = 14.4, 8.0, 4.4, 1H), 7.13 (dd, *J* = 5.0, 3.8, 1H), 6.77 – 6.65 (m, 2H), 5.55 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 189.6, 150.0, 144.9, 134.0, 133.9, 132.9, 132.9, 127.7, 119.2, 117.1, 116.1 ppm. Spectral data agree with literature.[1]

Furan-2-yl(2-iodophenyl)methanone (**10**):



To a cold stirred solution of (2-aminophenyl)(furan-2-yl)methanone(**8**) (3.0 g, 16.0 mmol, 1 equiv) in water (40 mL) and concentrated HCl (2 mL) was added slowly a solution of sodium nitrite (1.13 g, 16.3 mmol, 1 equiv) in water (2.5 mL). After stirring for additional 5 min, a solution of potassium iodide (2.71 g, 16.3 mmol, 1 equiv) in water (5 mL) was added. After removing the cooling bath and stirring at room temperature for 5 min, the reaction mixture was heated to 90 °C with stirring for 10 min. After cooling to room temperature, the precipitated solid was filtered off and washed with water. The crude product was purified by column chromatography (hexane/ethyl acetate 9:1) to give pure **10** as a pale yellow solid (3.15 g, 10.6 mmol, 66%). m.p. 75 – 77 °C; IR (solid) u/cm^{-1}: 3068,1639, 1577; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.91 (m, 1H), 7.71 (dd, *J* = 1.7, 0.8, 1H), 7.47 – 7.38 (m, 2H), 7.19 (ddd, *J* = 8.0, 7.1, 2.1, 1H), 7.03 (dd, *J* = 3.6, 0.7, 1H), 6.58 (dd, *J* = 3.6, 1.7, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 184.1, 151.1, 148.2, 142.9, 139.9, 131.7, 128.6, 127.8, 122.2, 112.8, 92.5 ppm. HRMS: m/z calcd for $C_{11}H_8IO_2$ $[M+H]^+$ = 298.9563; found: 298.9561.

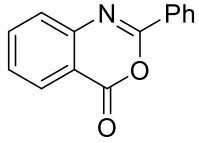
(2-Iodophenyl)(thiophen-2-yl)methanone (**11**):



(2-Aminophenyl)(thiophen-2-yl)methanone (**9**) (2.0 g, 9.84 mmol, 1 equiv) was added to a solution of *p*-TsOH·H_2O (5.6 g, 29.5 mmol, 3 equiv) in MeCN (7 mL). The reaction mixture was cooled to 10–15 °C, then a solution of $NaNO_2$ (1.357 g, 19.68 mmol, 2 equiv) and KI (4.0 g, 24.6 mmol, 2.5 equiv) in H_2O (3 mL) was added slowly. The

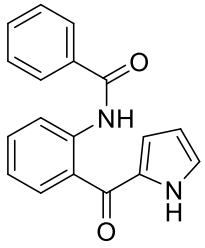
cooling bath was removed, and the reaction mixture was stirred at room temperature for 4 h. Water (30 mL) was then added followed by $NaHCO_3$ solution (1 M) until pH 9–10 then $Na_2S_2O_3$ solution (2 M, 4 mL). The mixture was extracted with CH_2Cl_2 and purified by flash chromatography (Hexane/Et_2O 9:1) to give pure **11** as a brown oil (2.856 g, 9 mmol, 95%). IR (neat) υ/cm^{-1}: 3089,1633, 1514; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.78 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.44 (td, *J* = 7.4, 1.0 Hz, 1H), 7.39 (dt, *J* = 3.3, 2.1 Hz, 2H), 7.18 (ddd, *J* = 7.9, 7.3, 1.9 Hz, 1H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 189.5, 144.3, 143.1, 140.0, 136.3, 135.9, 131.4, 128.5, 128.3, 127.8, 92.3 ppm. HRMS: m/z calcd for $C_{11}H_8IOS$ $[M+H]^+$ = 314.9335; found: 314.9333.

2-Phenyl-4*H*-benzoxazin-4-one (**13**):[2]



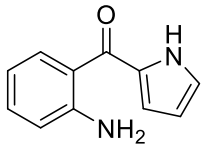
Powdered Na_2CO_3 (13.73 g, 129.6 mmol, 2 equiv) was added to a cooled (ice bath) stirred mixture of anthranilic acid (8.88 g, 64.8 mmol, 1 equiv) in THF (130 ml), followed by the addition of benzoyl chloride (18.8 ml, 162 mmol, 2.5 equiv). The cooling bath was removed after 10 min stirring was continued at room temperature overnight. Water (130 ml), was then added, stirring was continued for additional 10. The formed yellow solid was filtered off, washed with water and 50% aqueous methanol. A second crop was obtained from the filtrate upon standing. The combined crops were dried at 50 °C under high vacuum to give **13** (13.9 g, 62.3 mmol, 96%) as a pale yellow solid, m.p. 122 – 125 °C, (lit:[17] 119 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.36 – 8.29 (m, 2H), 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.71 (dd, *J* = 8.1, 0.6, 1H), 7.60 – 7.49 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.8, 157.3, 147.1, 136.7, 132.8, 130.3, 128.9, 128.8, 128.5, 128.4, 127.4, 117.2 ppm. Spectral data agree with literature.[2]

N-[2-(1*H*-Pyrrol-2-carbonyl)phenyl]benzamide (**14**):



A solution of EtMgCl (2.8 M in THF, 9.75 mL, 27.3 mmol, 2.1 equiv) in dry THF (5 mL) was cooled to 0 °C, then a solution of pyrrole (2.1 mL, 30.3 mmol, 2.3 equiv) in dry toluene (2 mL) was added dropwise over 20 min. The mixture was then stirred at room temperature for 20 min, then a suspension of **13** (2.9 g, 13.0 mmol, 1 equiv) in THF (3 mL) was added. After stirring for additional 45 min, the reaction mixture was heated under reflux for 3 h. Sat. aq. NH_4Cl solution (3 mL) was then added to the hot mixture over 5 min, stirring was continued for 20 min, then Na_2SO_4 (3 g) was added. The mixture was stirred for additional 20 min then filtered off. The collected solid was washed with THF, and the combined organic filtrate and washes were evaporated under reduced pressure. The residue was suspended in toluene (15 mL), and cooled in an ice bath, the formed solid was collected by filtration and washed with hexane, dried at room temperature overnight under high vacuum to give **14** as light green crystals (3.66 g, 12.6 mmol, 97%). ^{1}H NMR (400 MHz, DMSO) δ = 12.17 (s, 1H), 11.12 (s, 1H), 8.27 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.84 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 – 7.50 (m, 4H), 7.30 (td, *J* = 7.6, 1.1 Hz, 1H), 7.23 (dd, *J* = 2.3, 1.4 Hz, 1H), 6.76 (dd, *J* = 3.8, 1.3 Hz, 1H), 6.27 (dd, *J* = 3.8, 2.4 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 184.6, 164.7, 137.8, 134.4, 132.2, 132.0, 131.0, 130.9, 128.8, 127.2, 127.1, 123.7, 122.5, 120.3, 110.7 ppm. Spectral data agree with literature.[2]

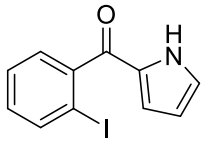
(2-Aminophenyl)(1*H*-pyrrol-2-yl)methanone (**15**):[2]



A mixture of *N*-[2-(1*H*-pyrrol-2-carbonyl)phenyl]benzamide (**14**) (3.5 g, 12 mmol), methanol (24 mL) and aqueous NaOH (10 M, 6 mL) was refluxed for 24 h. Water (17 mL) was added to the solution while hot and stirred for 3 h at room temperature. The formed precipitate was filtered and washed with cold water then dried under vacuum and crystallised from toluene to give **15** as off-white solid (1.97 g, 10.6 mmol, 99%). m.p. 125 – 127 °C (lit:[2] 125 – 126 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 7.86 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.09 (td, J = 2.7, 1.3 Hz, 1H), 6.85 (ddd, *J* = 3.8, 2.4, 1.3 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.33 (dt, *J* = 3.8, 2.6 Hz, 1H), 5.54 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 186.0, 149.4, 133.3, 132.2,

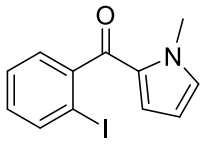
131.9, 124.4, 119.9, 118.7, 117.0, 116.3, 111.0 ppm. Spectral data agree with literature.[2]

(2-Iodophenyl)(1*H*-pyrrol-2-yl)methanone (**16**):



(2-Aminophenyl)(1*H*-pyrrol-2-yl)methanone (**15**) (1.22 g, 6.5 mmol, 1 equiv) was added to a solution of *p*-TsOH·H_2O (3.7 g, 19.6 mmol, 3 equiv) in MeCN (5 mL). The reaction mixture was cooled to 10–15 °C, then a solution of $NaNO_2$ (0.9 g, 13.7 mmol, 2 equiv) and KI (2.5 g, 16.3 mmol, 2.5 equiv) in H_2O (4 mL) was added slowly. The cooling bath was removed, and the reaction mixture was stirred at room temperature overnight. Water (20 mL) was then added followed by $NaHCO_3$ solution (1 M) until pH 9–10 then $Na_2S_2O_3$ solution (2 M, 4 mL). The mixture was extracted with CH_2Cl_2 and purified by flash chromatography (hexane/ethyl acetate 3:2) to give pure **16** as a red solid (1.74 g, 5.8 mmol, 92%); m.p. 105 – 107 °C. IR (solid) u/cm^{-1}: 3221, 3122, 1602, 1577. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.75 (s, 1H), 7.94 (d, *J* = 7.89 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.22 – 7.13 (m, 2H), 6.57 (ddd, *J* = 3.8, 2.4, 1.4 Hz, 1H), 6.31 (dt, *J* = 3.8, 2.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 186.0, 143.7, 140.1, 131.3, 131.0, 128.9, 127.7, 126.8, 121.2, 111.5, 93.0 ppm. HRMS: m/z calcd for $C_{11}H_9INO$ $[M+H]^+$ = 297.9723; found: 297.9727.

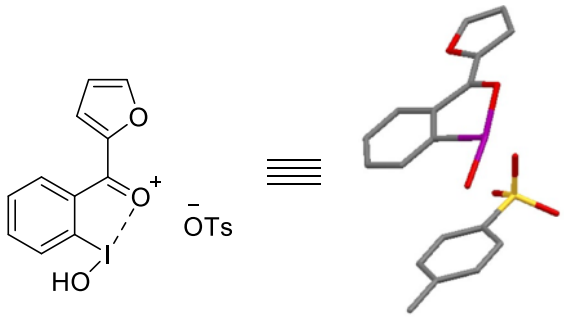
(2-Iodophenyl)(1-methyl-1*H*-pyrrol-2-yl)methanone (**17**):



To a solution of the **16** (50 mg, 0.168 mmol, 1equiv) in dry THF (1 mL), NaH (13.5 mg, 0.337 mmol, 2 equiv) and methyl iodide (59 µL, 0.95 mmol, 5.6 equiv) were added. The reaction mixture was stirred at room temperature under N_2 atmosphere for 24 h and the solvent removed under reduced pressure. The residue was dissolved in ether (2 mL) and washed with water (2 mL). The aqueous phase was extracted with ether (3 x 2 mL). The combined ether extracts were washed with 10% $Na_2S_2O_3$ solution (2 mL) and water (2 mL), dried over $MgSO_4$, filtered and the filtrate was evaporated under

vacuum to give **17** as a red solid (44 mg, 0.14 mmol, 88%); m.p. 112 – 114 °C. IR (solid) u/cm^{-1}: 3124, 1624, 1521. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 4.4, 4.0 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.12 (ddd, *J* = 8.0, 6.9, 2.3 Hz, 1H), 6.95 (t, *J* = 2.0 Hz, 1H), 6.42 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.11 (dd, *J* = 4.1, 2.4 Hz, 1H), 4.09 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 186.9, 145.4, 139.6, 132.7, 130.7, 129.9, 128.4, 127.6, 124.3, 108.8, 93.1, 37.7 ppm. HRMS: m/z calcd for $C_{12}H_{11}INO$ $[M+H]^+$ = 311.9880; found: 311.9879.

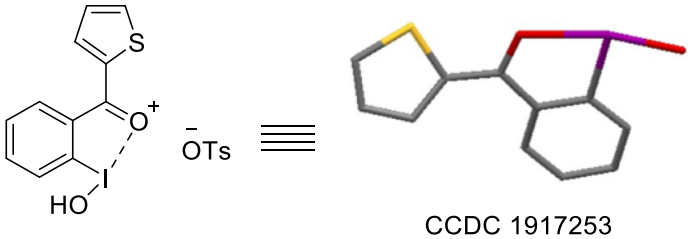
3-(Furan-2-yl)-1-hydroxy-1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**18**):



CCDC 1917254

m-Chloroperbenzoic acid (135 mg, 0.6 mmol, 1.2 equiv) was added to a stirred solution of **10** (150 mg, 0.5 mmol, 1 equiv) in dichloromethane/TFE (1:1 v/v, 5 mL), followed by TsOH•H_2O (96 mg, 0.50 mmol, 1 equiv). Stirring was continued at room temperature for 30 min. The reaction mixture was then concentrated under a stream of air, diethyl ether (10 mL) was then added to the residue. The resulting precipitate was filtered off and dried to give **18** as a yellow solid (211 mg, 0.43 mmol, 86%); m.p. 130 – 133 °C. IR (solid) u/cm^{-1}: 3406, 3128, 1716, 1585. ^{1}H NMR (400 MHz, CD_3OD) δ = 9.34 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.37 (dd, *J* = 1.6, 0.7 Hz, 1H), 8.26 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 8.22 – 8.16 (m, 2H), 8.03 (ddd, *J* = 8.2, 5.6, 1.2 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.03 (dd, *J* = 3.9, 1.6 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, CD_3OD) δ = 182.8, 155.2, 152.1, 143.5, 141.7, 139.6, 137.8, 133.0, 132.2, 130.6, 129.8, 128.6, 127.0, 124.5, 116.4, 21.3 ppm.

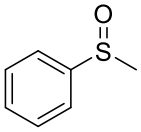
1-Hydroxy-3-(thiophen-2-yl)- 1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**19**):



CCDC 1917253

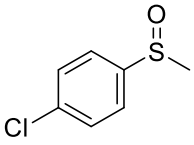
m-Chloroperbenzoic acid (128 mg, 0.57 mmol, 1.2 equiv) was added to a stirred solution of **11** (150 mg, 0.48 mmol, 1 equiv) in CH_2Cl_2/TFE (1:1 v/v, 5 mL), followed by TsOH•H_2O (91 mg, 0.48 mmol, 1 equiv). Stirring was continued at room temperature for 30 min. The reaction mixture was then concentrated under a stream of air, diethyl ether (10 mL) was then added to the residue. The resulting precipitate was filtered off and dried to give **19** as a red gummy material (204 mg, 0.41 mmol, 85%). IR (neat) υ/cm^{-1}: 3421, 3088, 2922, 1583. ^{1}H NMR (400 MHz, CD_3OD) δ= 9.02 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.60 (dd, *J* = 4.1, 1.0 Hz, 1H), 8.45 (dd, *J* = 4.9, 1.0 Hz, 1H), 8.29 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.07 – 8.02 (m, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 4.9, 4.1 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C NMR (126 MHz, CD_3OD) δ = 190.3, 143.4, 143.2, 141.9, 141.7, 139.6, 138.3, 137.4, 133.0, 132.6, 131.5, 129.9, 128.9, 126.9, 124.5, 21.3 ppm.

Methyl phenyl sulfoxide (**20**):[3]



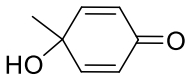
To a solution **18**, **19**, or Koser's reagent (0.24 mmol, 1.2 equiv) in acetonitrile (1 mL) was added thioanisole (25.0 mg, 23.5 µl, 0.2 mmol, 1 equiv). The mixture was stirred at room temperature for overnight, then 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification by preparative TLC (hexane/ethyl acetate 3:1) afforded 26 mg (92%) of pure **20** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2H), 7.57-7.48 (m, 3H), 2.73 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.9, 131.2, 129.5, 123.7, 44.2 ppm. Spectral data agree with literature.[3]

p-Chlorophenyl methyl sulfoxide (**21**):[3]



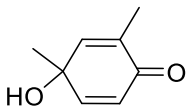
To a solution **18** or **19** (0.15 mmol, 1.2 equiv) in acetonitrile (1 mL) was added *p*-Chlorophenyl methyl sufide (20 mg, 0.125 mmol, 1 equiv.). The mixture was stirred at room temperature for overnight, then 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification by preparative TLC (hexane/ethyl acetate 3:1) afforded 20 mg (90%) of pure **21** as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 2.72 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.4, 137.4, 129.8, 125.1, 44.2 ppm. Spectral data agree with literature.[3,4]

4-Hydroxy-4-methylcyclohexa-2,5-dienone (**22**):[3]



To a solution **18** or **19** or Koser's reagent (0.15 mmol, 1.2 equiv) in CH_2Cl_2 (1.5 mL) and water (75 µL) *p*-cresol (14 mg, 0.125 mmol, 1 equiv) was added. The mixture was stirred at 0 °C to room temperature for 24 h, then 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification by preparative TLC (hexane/ethyl acetate 3:1) afforded 13 mg (81%) of pure **22** as a colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ =.6.88 (d, *J* = 10 Hz, 2H), 6.15 (d, *J* = 10 Hz, 2H), 1.49 (s, 3H) ppm. Spectral data agree with literature.[3]

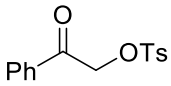
4-Hydroxy-2,4-dimethylcyclohexa-2,5-dien-1-one (**23**)[5]:



To a solution **18** or **19** (0.15 mmol, 1.2 equiv) in methylene chloride (1.5 mL) and water (75 µL) 2,4-dimethylphenol (15 mg, 0.125 mmol, 1 equiv) was added. The mixture was stirred at 0 °C to room temperature for 24 h, then 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under

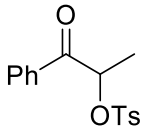
vacuum. Purification by preparative TLC (hexane/ethyl acetate 3:1) afforded 15 mg (83%) of pure **23** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) 6.84 (dd, *J* = 9.9, 3.1 Hz, 1H), 6.64 (dq, *J* = 3.0, 1.5 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 1.87 (d, *J* = 1.5 Hz, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 186.1, 151.8, 147.4, 134.0, 127.2, 67.7, 27.0, 15.7. Spectral data agree with literature.[5]

2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**24**):[6]



To a solution **18** or **19** (0.165 mmol, 1.5 equiv) in acetonitrile (1.5 mL) was added acetophenone (13.2 mg, 0.11 mmol, 1 equiv.). The mixture was heated under reflux for 2 h. After cooling down to room temperature then sat. aq. $NaHCO_3$ solution (5 mL) was added, then extracted with CH_2Cl_2 (3 X 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **24** as a colourless oil (22.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87– 7.81 (m, 4H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.34 (d, *J* = 7.95 Hz, 2H), 5.27 (s, 2H), 2.44 (s, 3H). ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.5, 145.4, 134.3, 133.9, 132.7, 130.0, 129.0, 128.3, 128.1, 70.1, 21.8 ppm. Spectral data agree with literature.[6]

1-Oxo-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**25**):[7]



Method A:

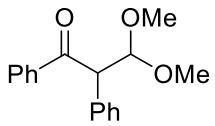
To a solution **18** or **19** (0.165 mmol, 1.5 equiv) in acetonitrile (1.5 mL) propiophenone (15 mg, 15 µL, 0.11 mmol, 1 equiv.) was added. The mixture was heated under reflux for 2 h. After cooling down to room temperature then sat. aq. $NaHCO_3$ solution (5 mL) was added, then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **25** as a colourless oil (24 mg, 72%).

Method B:

To a solution of propiophenone (40 mg, 0.3 mmol, 1 equiv.) in MeCN (2 mL) was added the iodoarene catalyst, **10**, **11**, or **17** (10 mmol %) followed by *p*-TsOH•H_2O (0.9 mmol, 3 equiv.) and *m*-chloroperbenzoic acid (0.9 mmol, 3 equiv.). The reaction mixture was stirred at room temperature for 48 h, then quenched with sat. aq. $Na_2S_2O_3$ solution and neutralized with sat. aq. $NaHCO_3$ solution. The aqueous layer was extracted with AcOEt (3× 10 mL). The combined organic layers were washed brine and dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude mixture was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **25** as a colourless oil.

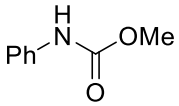
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.85 (m, 2H), 7.77 – 7.73 (m, 2H), 7.62 – 7.56 (m, 1H), 7.48 – 7.43 (m, 2H), 7.29 – 7.24 (m, 3H), 5.78 (q, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 1.60 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.0, 145.2, 134.0, 133.8, 133.6, 129.9, 128.9, 128.9, 128.8, 128.1, 77.5, 21.8, 18.9 ppm. Spectral data agree with literature.[7]

3,3-Dimethoxy-1,2-diphenylpropan-1-one (**26**):[3]



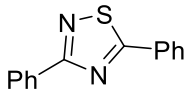
To a stirred solution **18** or **19** (0.15 mmol, 1.2 equiv) in methanol (1.5 mL) chalcone (26 mg, 0.125 mmol, 1 equiv.) was added. Stirring was continued for 24 h at room temperature. The reaction was quenched with 5% $Na_2S_2O_3$ solution (5 mL) and sat. $NaHCO_3$ solution (5 mL) then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 5:1) to give pure **26** as a white solid (19 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.46-7.38 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25-7.22 (m, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 3.44 (s, 3H), 3.21 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.9, 137.0, 134.9, 133.3, 129.2, 128.9, 128.8, 128.7, 127.7, 107.0, 57.1, 56.3, 54.6 ppm. Spectral data agree with literature.[3]

Methyl phenylcarbamate (**27**):[8]



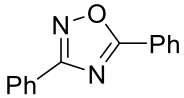
To a stirred solution **18** or **19** (0.15 mmol, 1.2 equiv) in methanol (2 mL) benzamide (15 mg, 0.125 mmol, 1 equiv.) was added. The reaction mixture was heated under reflux for 8 h. After cooling down to room temperature then sat. aq. $NaHCO_3$ solution (5 mL) was added, then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **27** as a light yellow oil (15 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.64 (s, 1H), 3.78 (s, 3H) ppm.^{13}C NMR (126 MHz, $CDCl_3$) δ = 154.1, 138.0, 129.2, 123.6, 118.8, 52.5. ppm. Spectral data agree with literature.[8]

3,5-Diphenyl-1,2,4-thiadiazole (**28**):[3]



To a stirred solution **18** or **19** (0.24 mmol, 1.6 equiv) in acetonitrile (1 mL) thiobenzamide (21 mg, 0.15 mmol, 1 equiv.) was added. Stirring was continued at r.t. for 1 h. The reaction was quenched with 5% $Na_2S_2O_3$ solution (5 mL) and sat. $NaHCO_3$ solution (5 mL) then extracted with CH_2Cl_2 (3 X 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **28** as a white solid (15 mg, 86%). M.p. 89 – 90 °C (lit.[3], m.p. 87.3 – 88.0 °C). ^{1}H NMR (400 MHz, d^6-acetone) δ 8.44 – 8.37 (m, 2H), 8.20 – 8.13 (m, 2H), 7.66 – 7.53 (m, 6H) ppm. ^{13}C NMR (101 MHz, d^6-acetone) δ = 189.3, 174.4, 133.8, 133.2, 131.4, 130.4, 129.7, 129.0, 128.3. ppm. Spectral data agree with literature.[3]

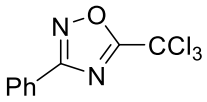
3,5-Diphenyl-1,2,4-oxadiazole (**29**):[3]



To a stirred solution **18** or **19** (0.15 mmol, 1.2 equiv) in benzonitrile (1 mL) benzaldoxime (15 mg, 0.125 mmol, 1 equiv.) was added. Stirring was continued at room temperature for 1 h. The reaction was quenched with 5% $Na_2S_2O_3$ solution (5

mL) and sat. $NaHCO_3$ solution (5 mL) then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 3:1) to give pure **29** as a white solid (26 mg, 93%). M.p. 106 – 107 °C (lit.[3], m.p. 107.3 – 107.6 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (ddd, *J* = 6.8, 1.4, 0.7 Hz, 2H), 8.19 (ddt, *J* = 3.1, 2.2, 1.7 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.59 – 7.46 (m, 5H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.9, 169.1, 132.9, 131.3, 129.2, 129.0, 128.3, 127.7, 127.1, 124.5 ppm. Spectral data agree with literature.[3]

3-Phenyl-5-(trichloromethyl)-1,2,4-oxadiazole (**30**):[3]



To a stirred solution **18** or **19** (0.15 mmol, 1.2 equiv) in trichloroacetonitrile (1 mL) benzaldoxime (15 mg, 0.125 mmol, 1 equiv.) was added. Stirring was continued at room temperature for 1 h. The reaction was quenched with 5% $Na_2S_2O_3$ solution (5 mL) and sat. aq. $NaHCO_3$ solution (5 mL) then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and removed under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc 5:1) to give pure **30** as a colourless oil (27 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 – 8.09 (m, 2H), 7.60 – 7.49 (m, 3H) ppm. Spectral data agree with literature.[3]

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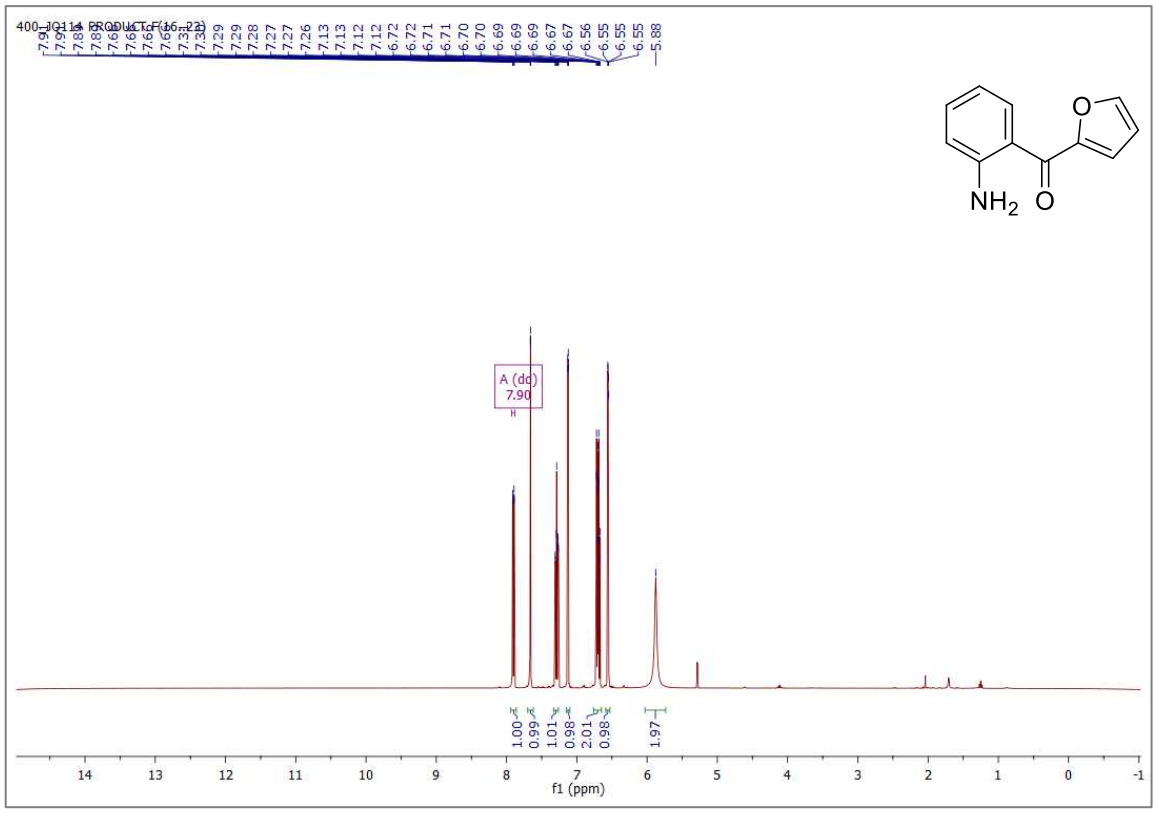
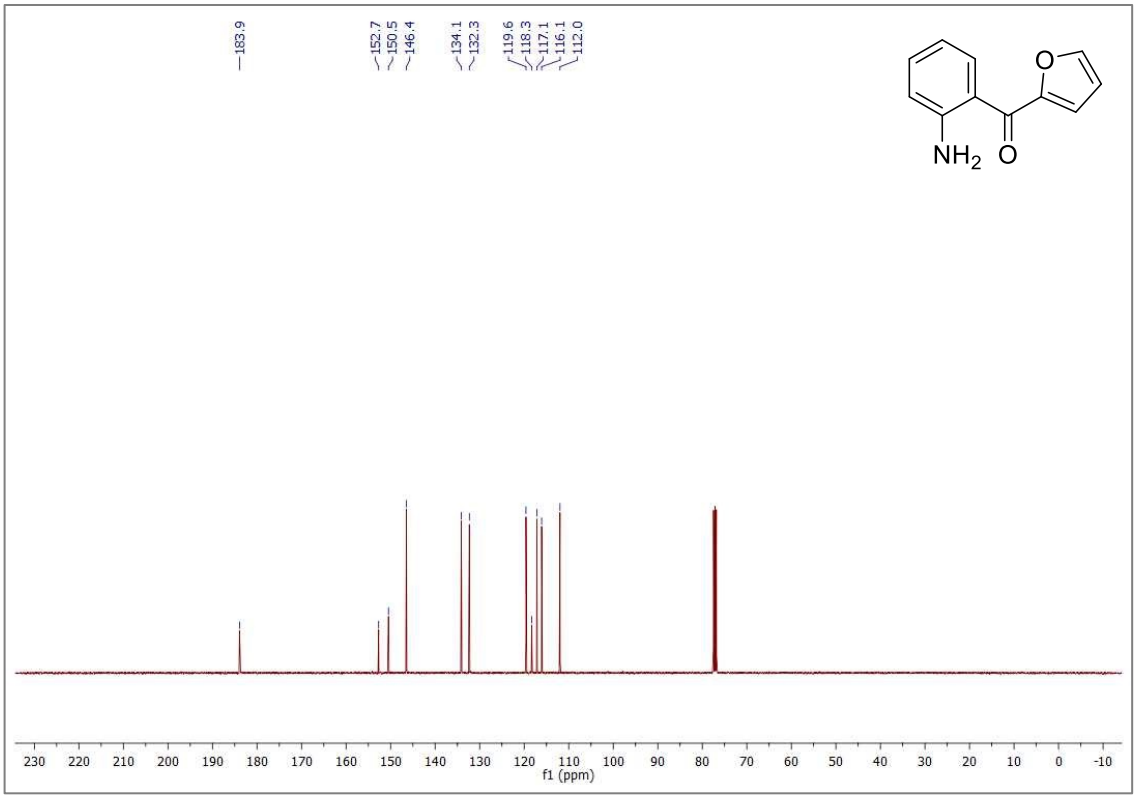
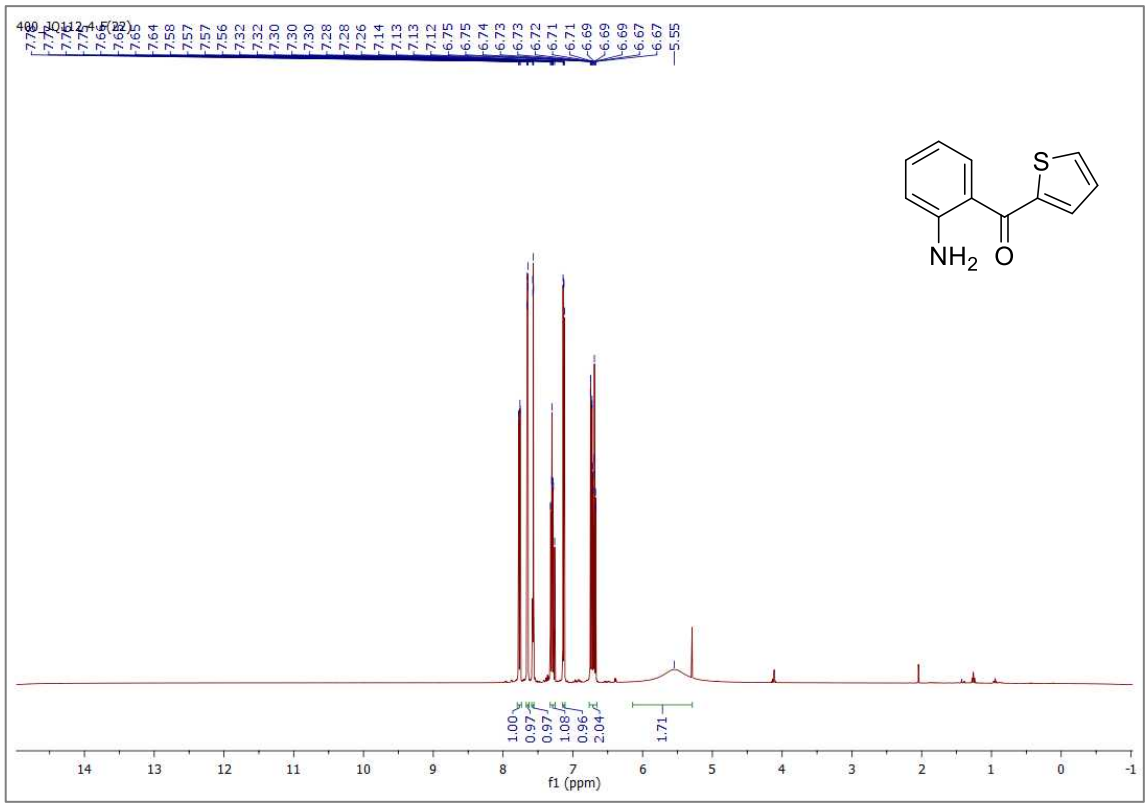
(2-Aminophenyl)(furan-2-yl)methanone (**8**), ^{1}H NMR:



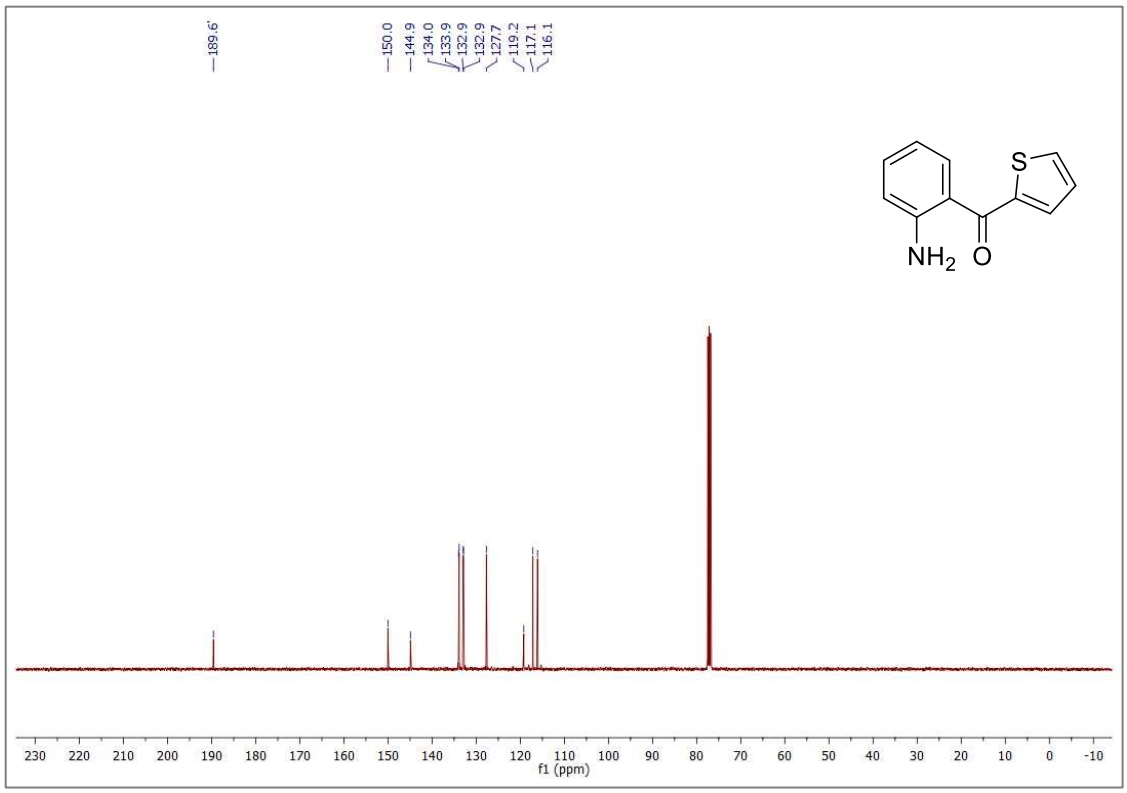
(2-Aminophenyl)(furan-2-yl)methanone (**8**), ^{13}C NMR:



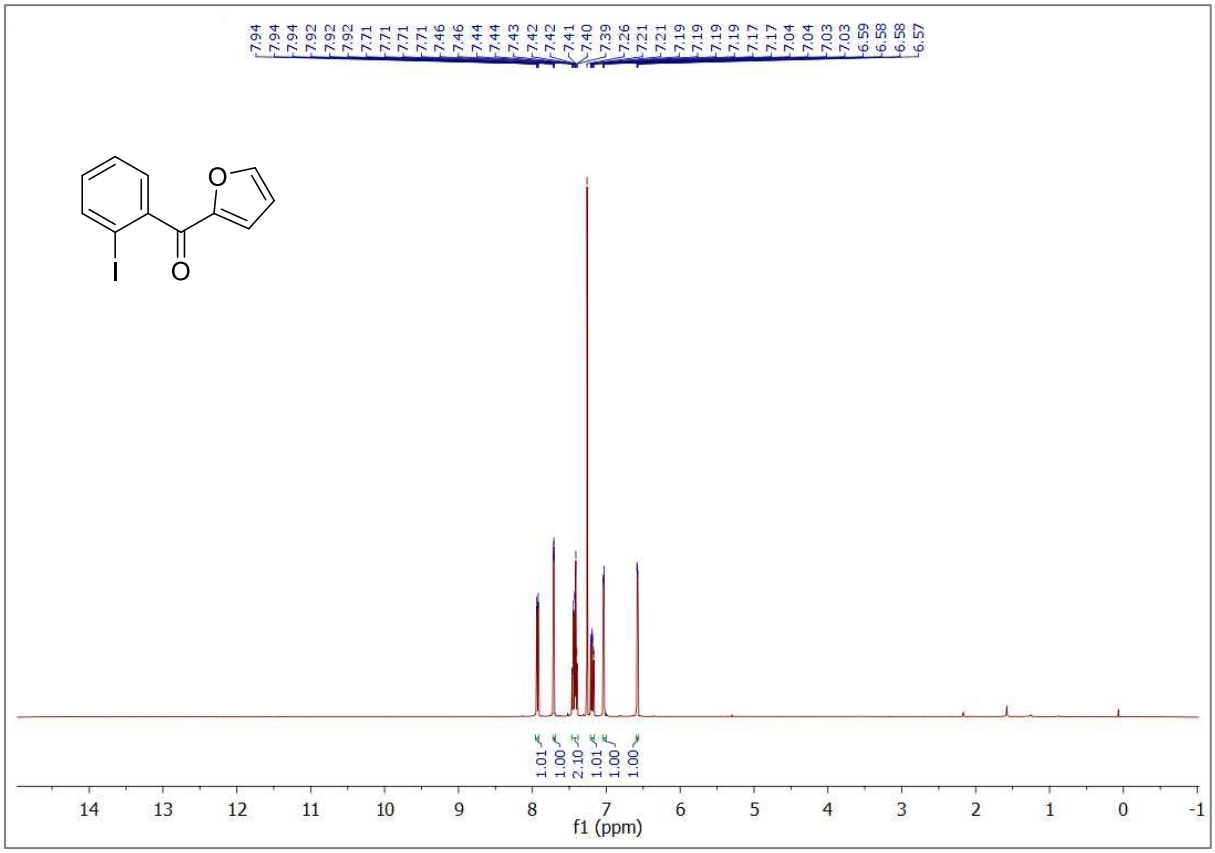
2-Aminophenyl)(thiophen-2-yl)methanone (**9**), ^{1}H NMR:



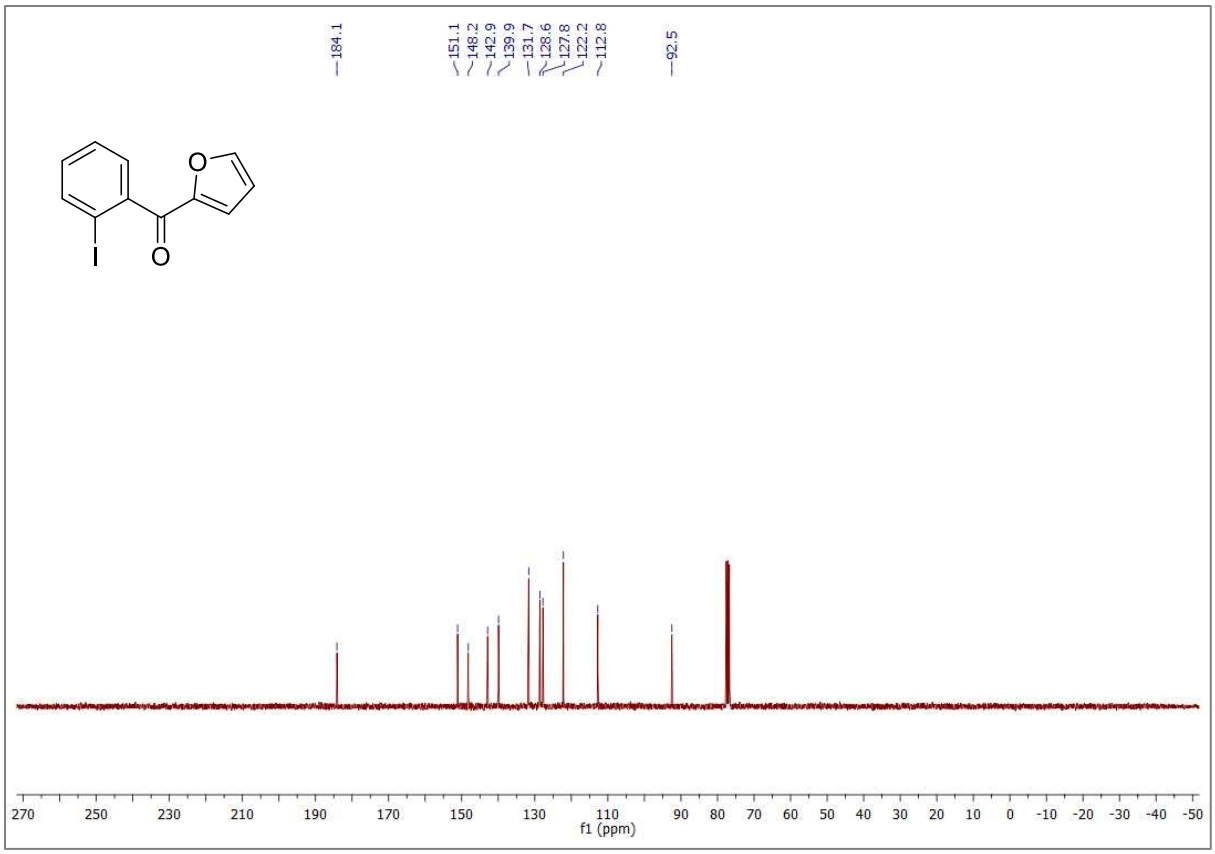
2-Aminophenyl)(thiophen-2-yl)methanone (**9**), ^{13}C NMR:



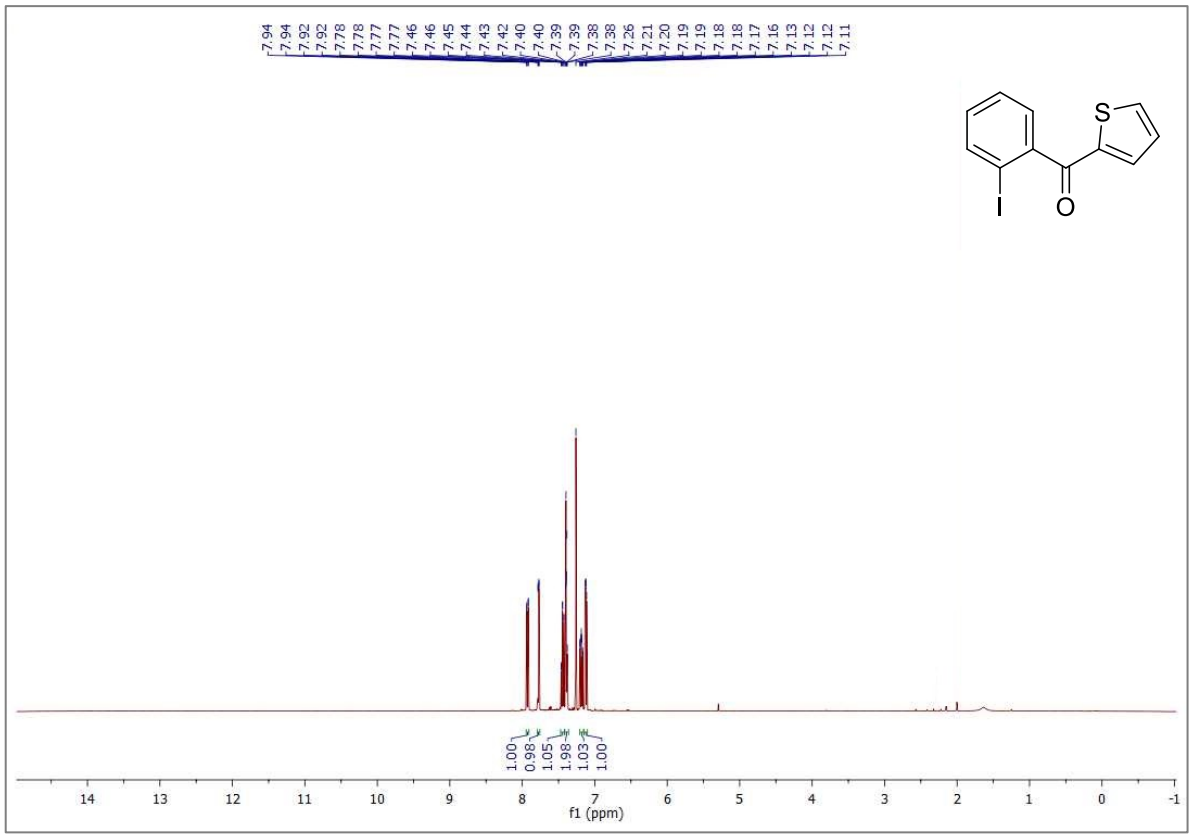
Furan-2-yl(2-iodophenyl)methanone (**10**), ^{1}H NMR:



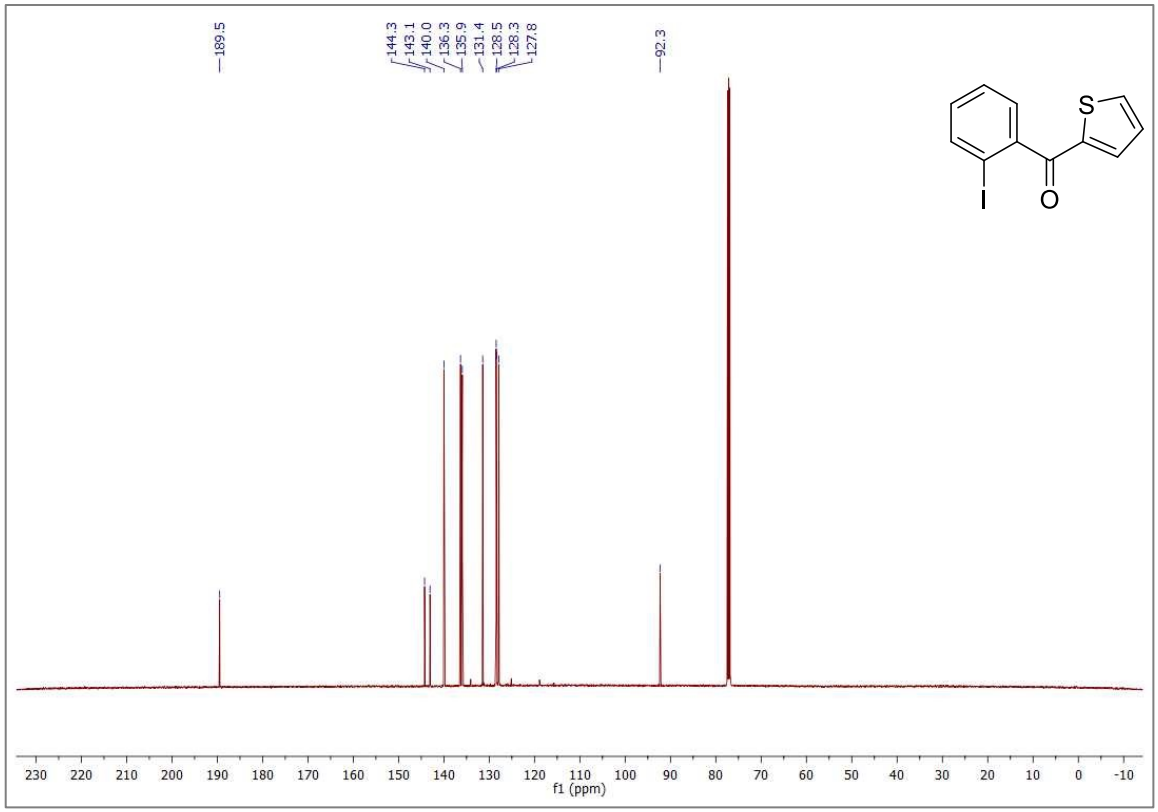
Furan-2-yl(2-iodophenyl)methanone (**10**), ^{13}C NMR:



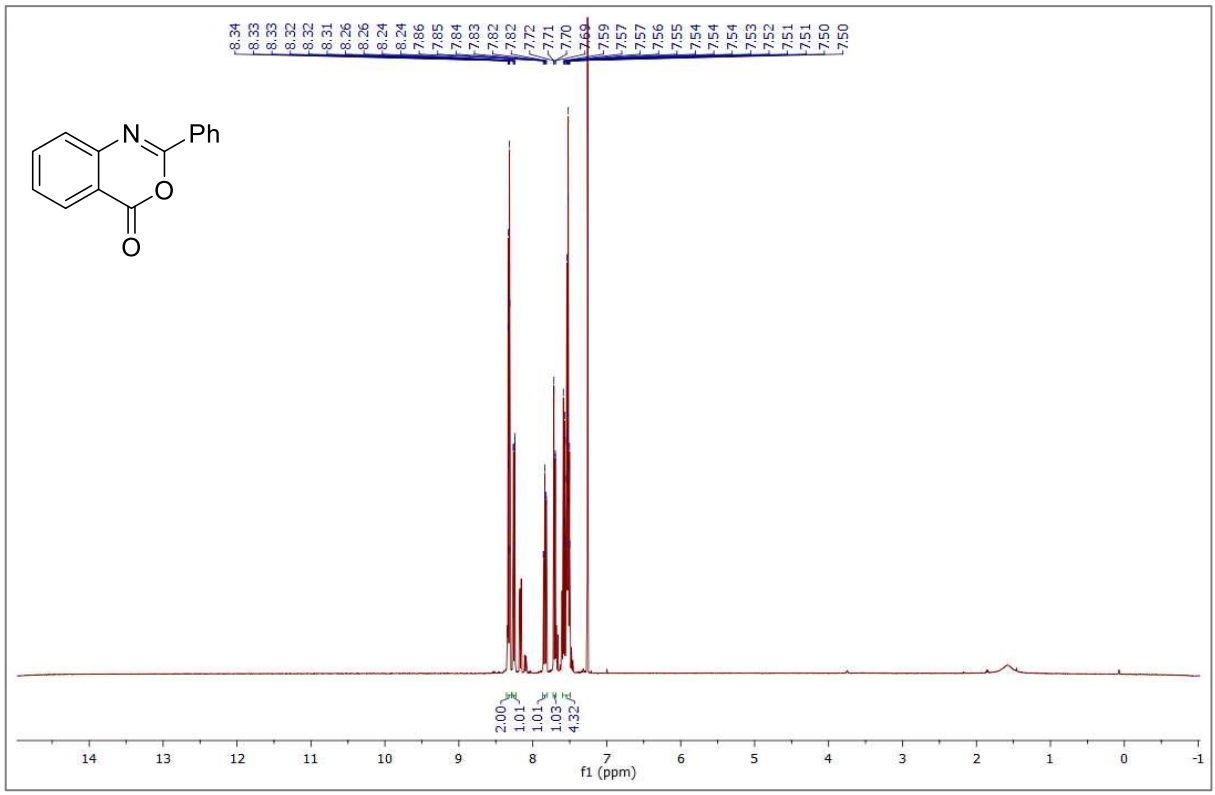
(2-Iodophenyl)(thiophen-2-yl)methanone (**11**), ^{1}H NMR:



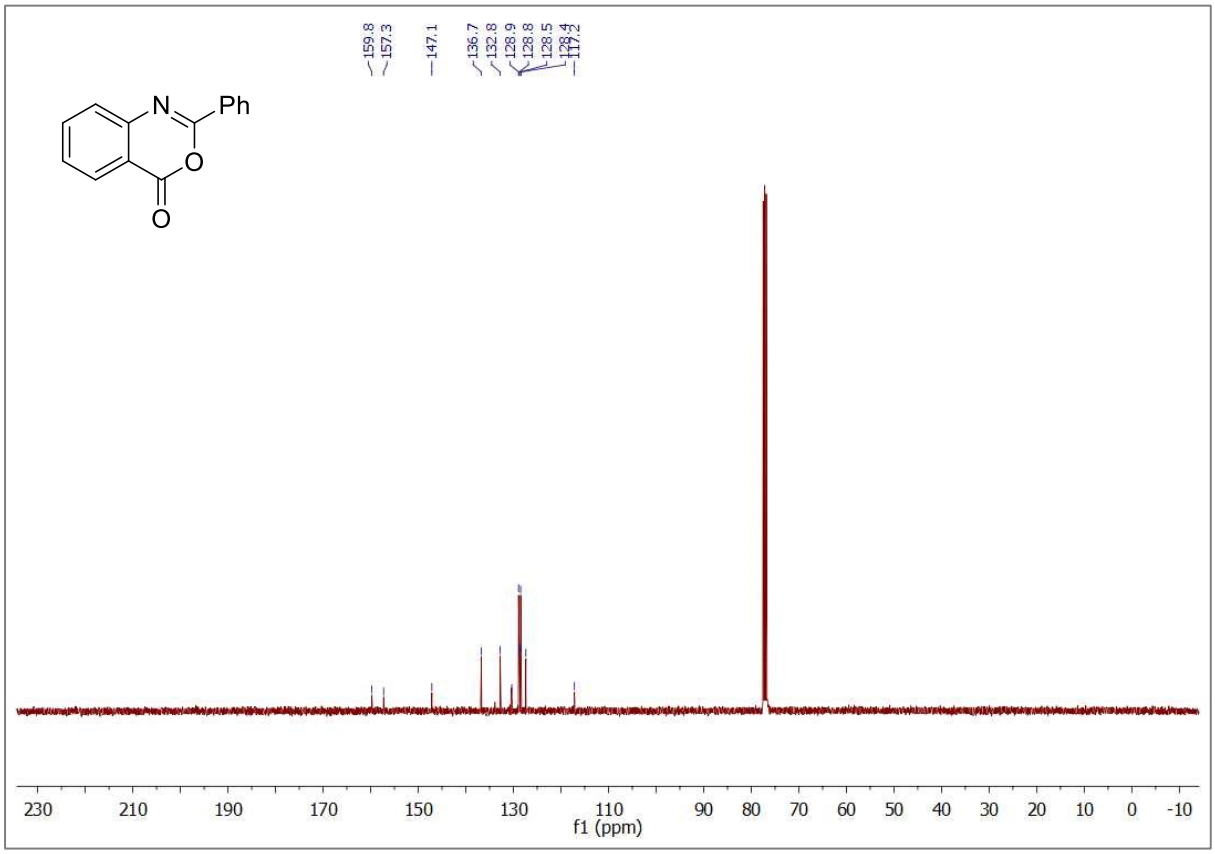
(2-iodophenyl)(thiophen-2-yl)methanone (**11**), ^{13}C NMR:



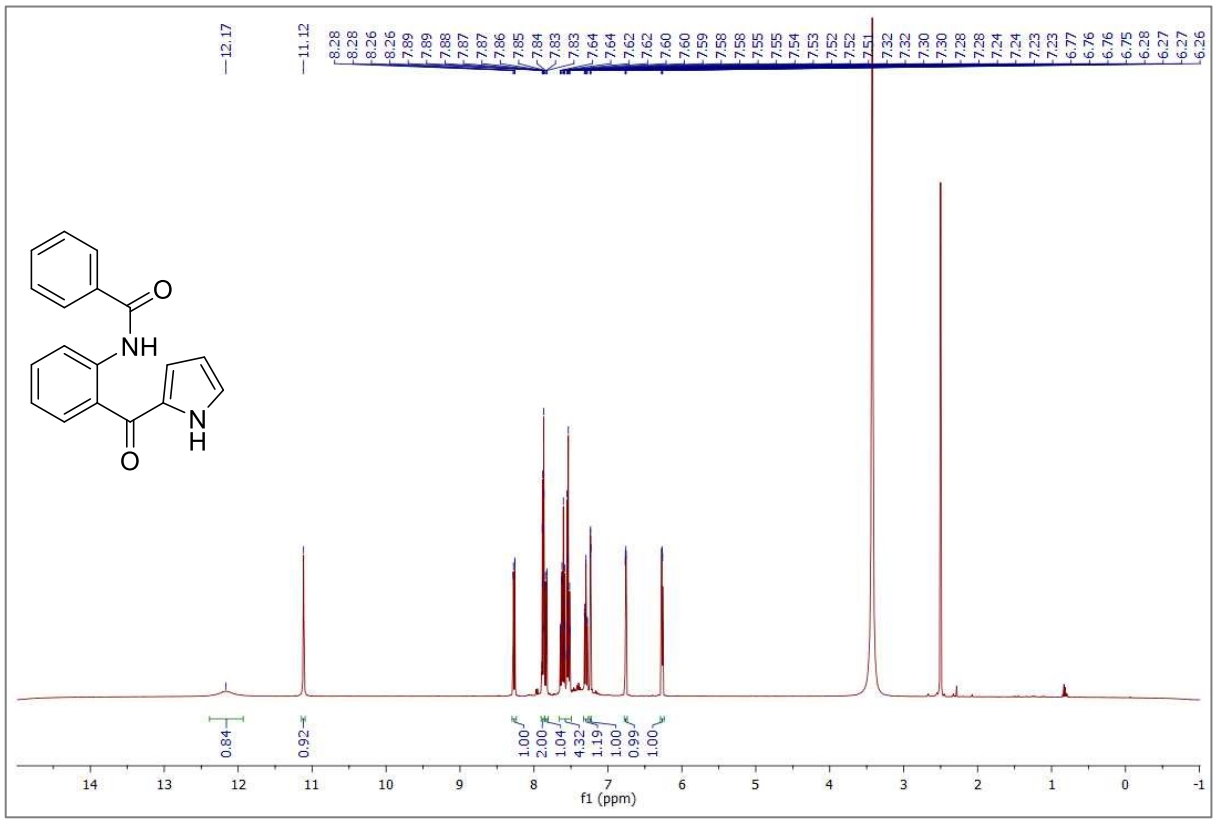
2-Phenyl-4*H*-benzoxazin-4-one (**13**), ^{1}H NMR:



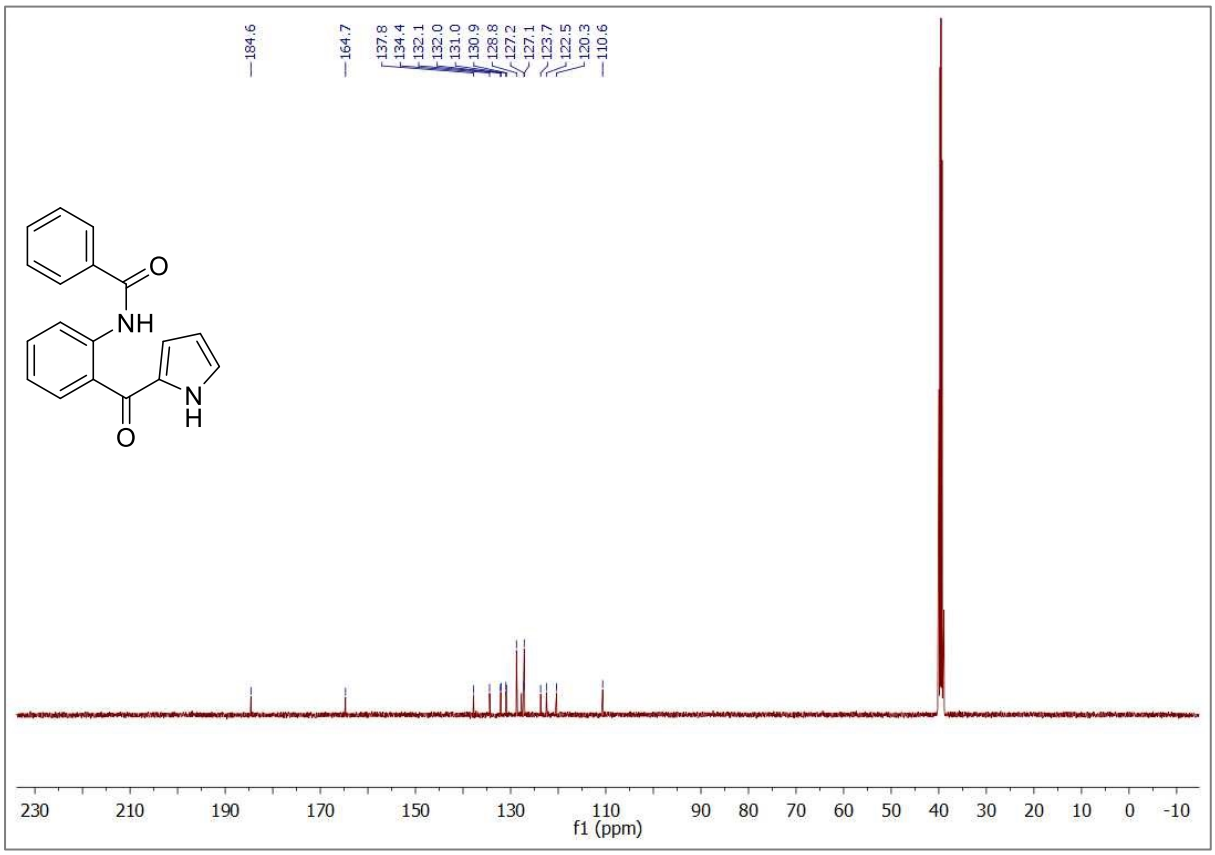
2-Phenyl-4*H*-benzoxazin-4-one (**13**), ^{13}C NMR:



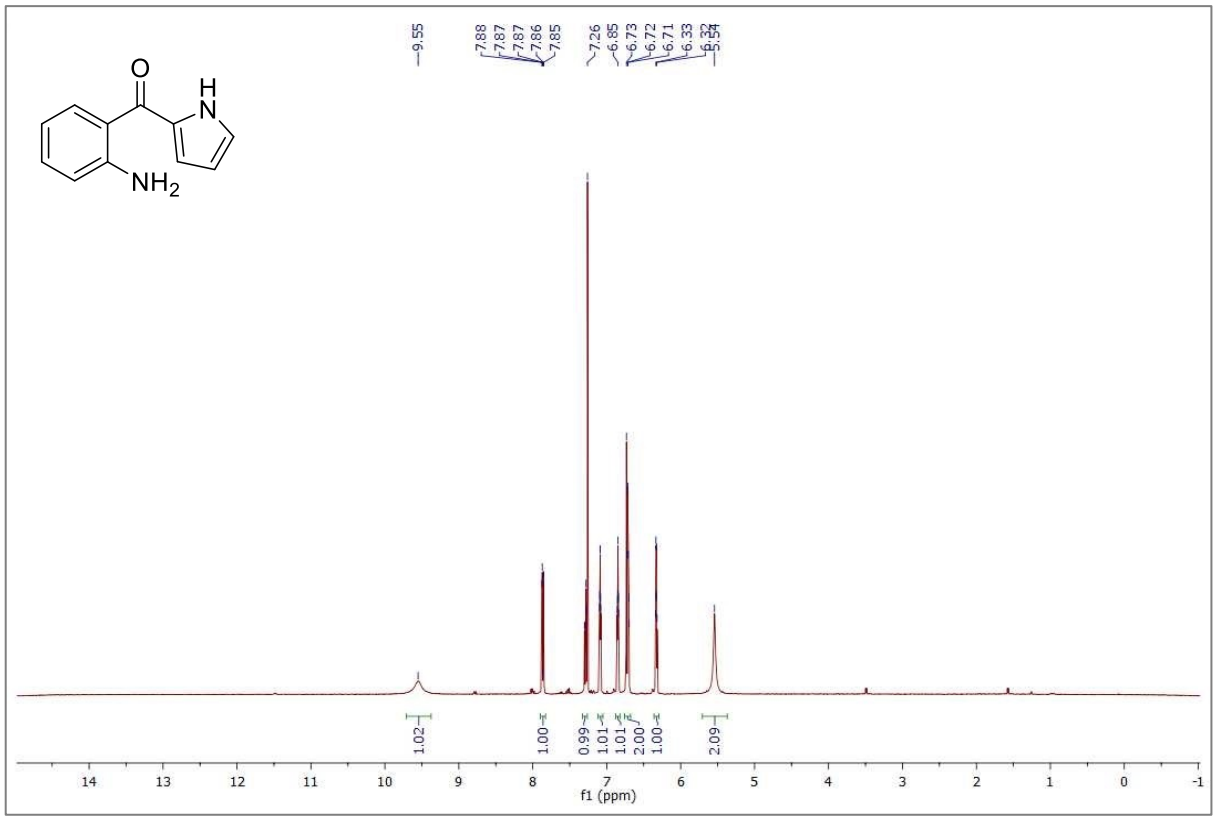
N-[2-(1*H*-Pyrrol-2-carbonyl)phenyl]benzamide (**14**), ^{1}C NMR:



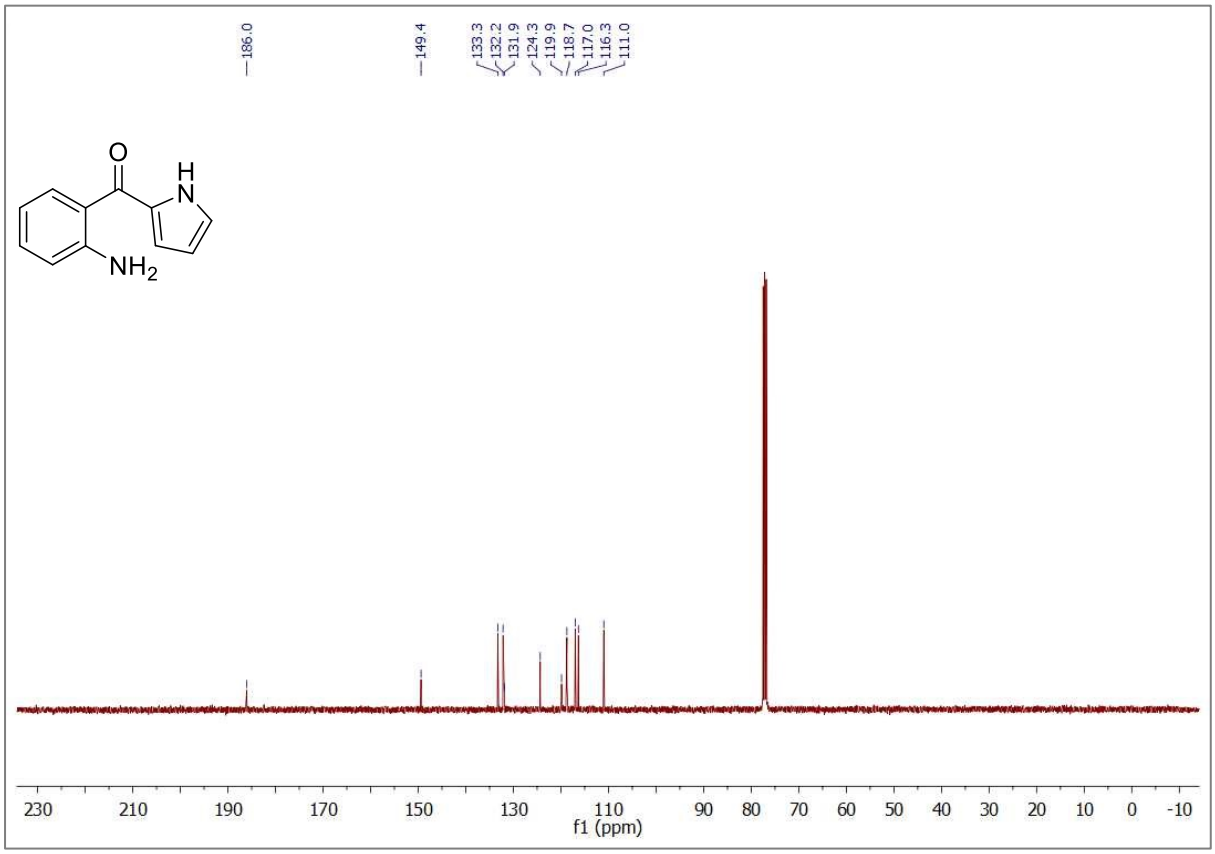
N-[2-(1*H*-Pyrrol-2-carbonyl)phenyl]benzamide (**14**), ^{13}C NMR:



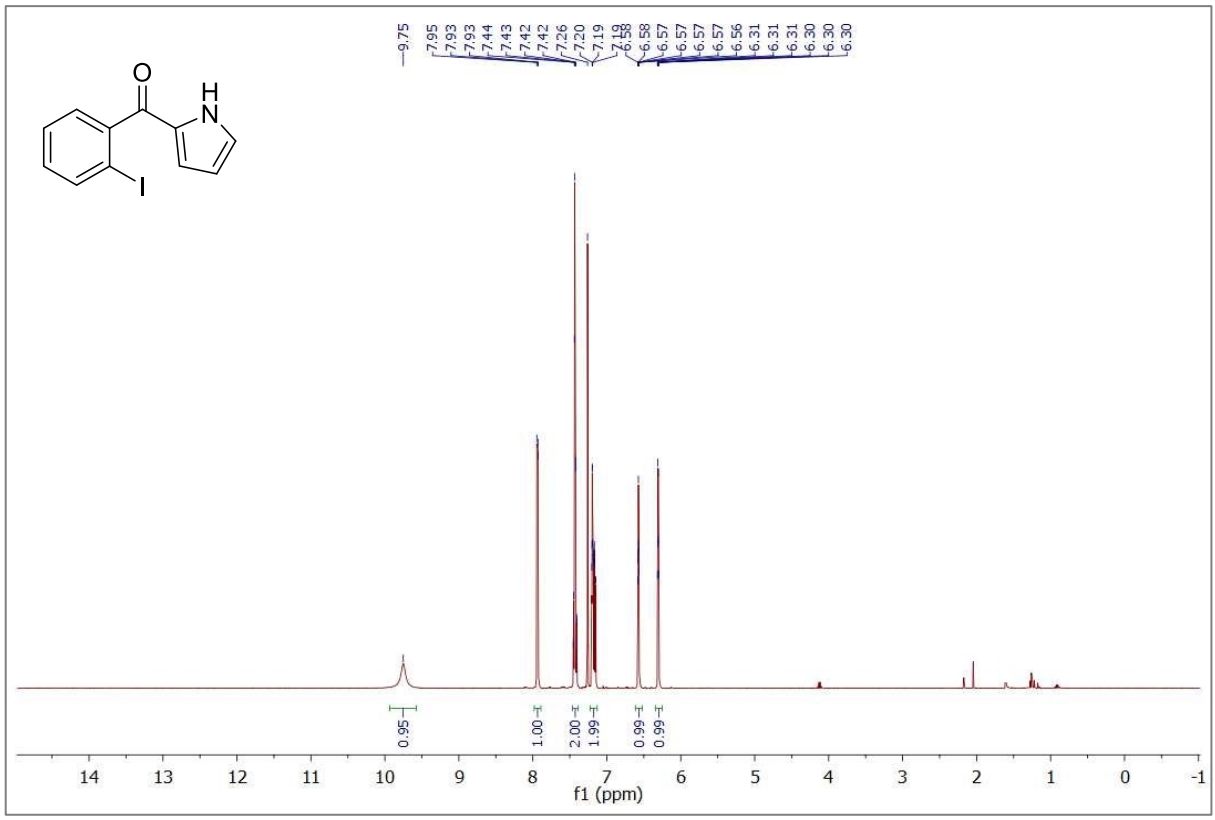
(2-Aminophenyl)(1*H*-pyrrol-2-yl)methanone (**15**), ^{1}H NMR:



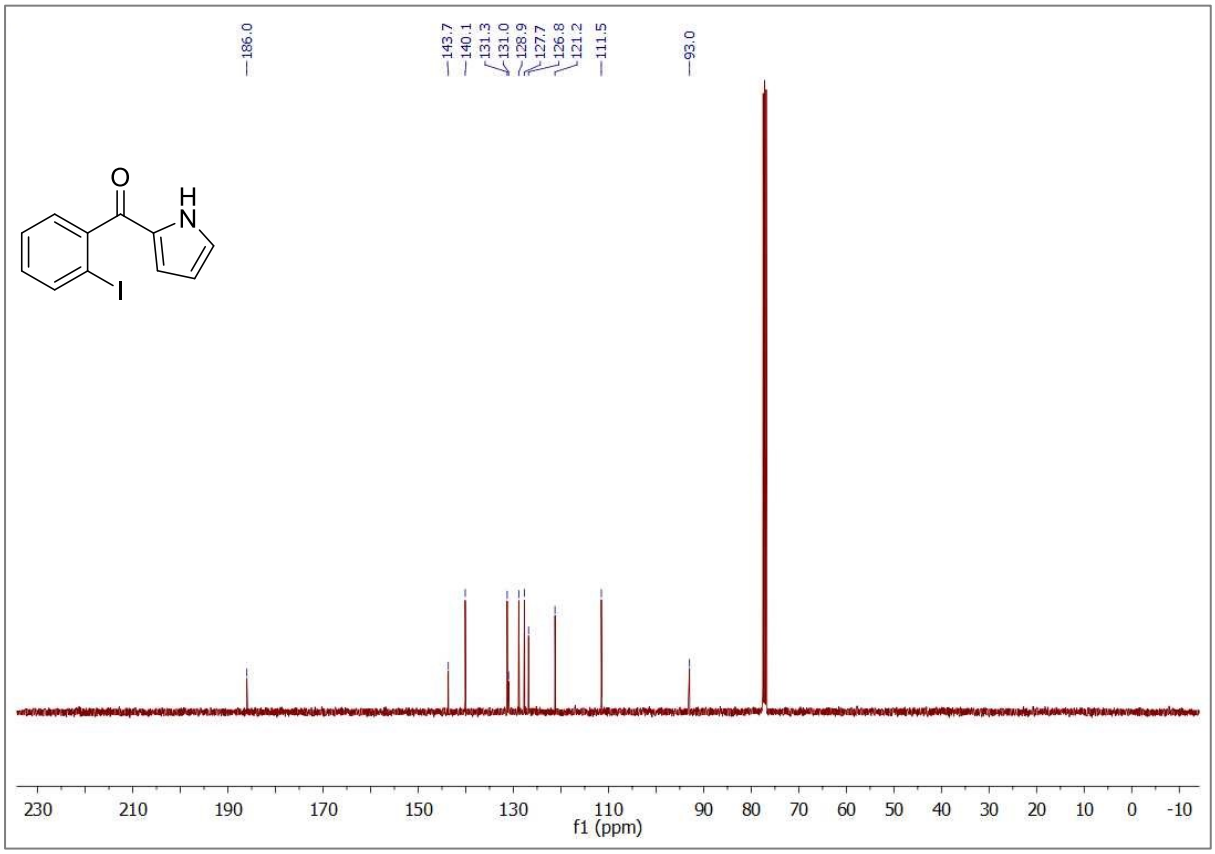
(2-Aminophenyl)(1*H*-pyrrol-2-yl)methanone (**15**), ^{13}C NMR:



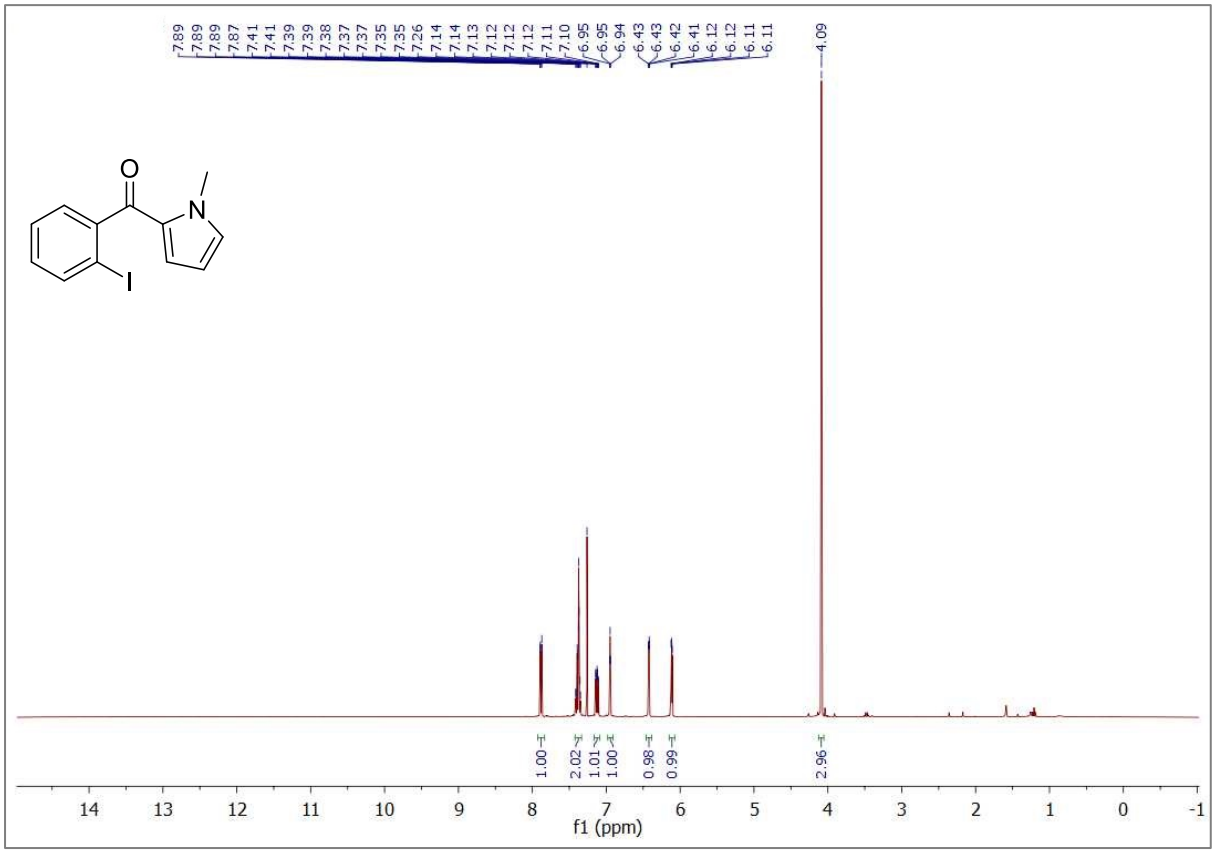
(2-Iodophenyl)(1*H*-pyrrol-2-yl)methanone (**16**), ^{1}H NMR:



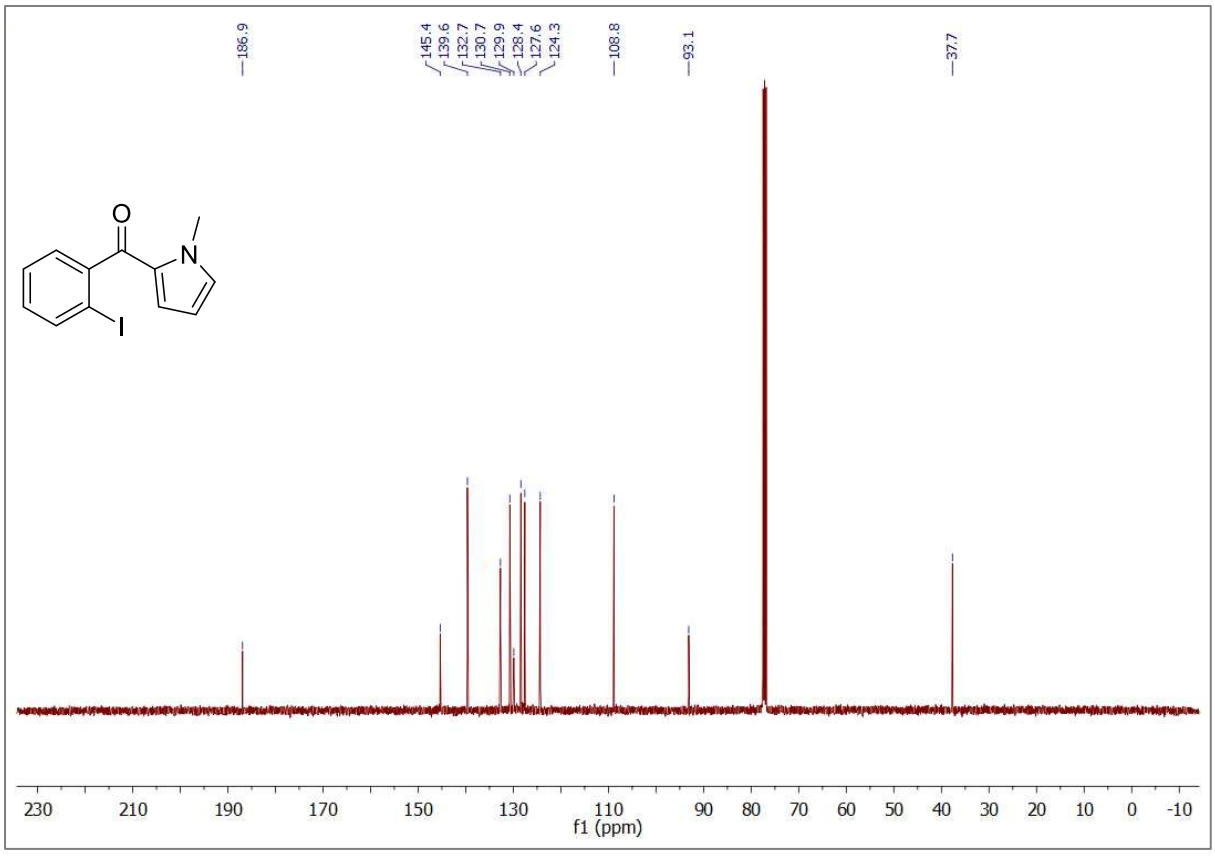
(2-Iodophenyl)(1*H*-pyrrol-2-yl)methanone (**16**), ^{13}C NMR:



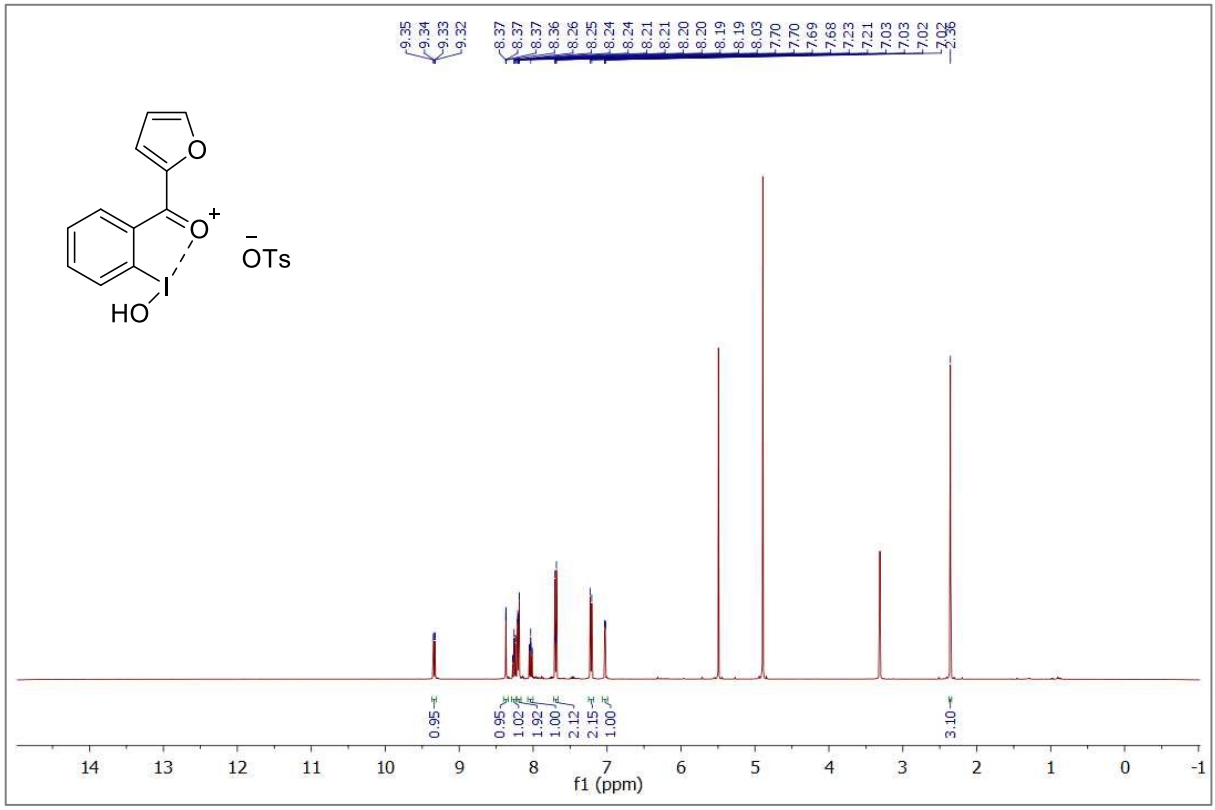
(2-Iodophenyl)(1-methyl-1*H*-pyrrol-2-yl)methanone (**17**), ^{1}H NMR:



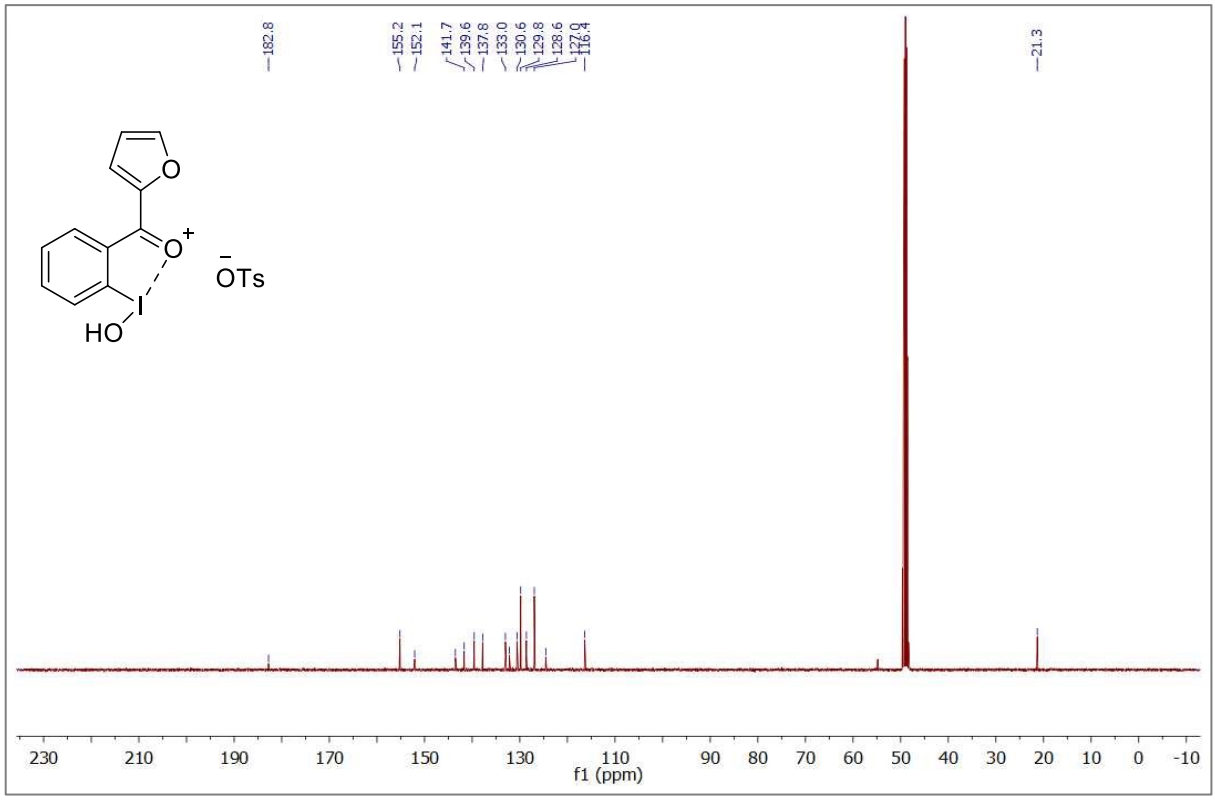
(2-Iodophenyl)(1-methyl-1*H*-pyrrol-2-yl)methanone (**17**), ^{13}C NMR:



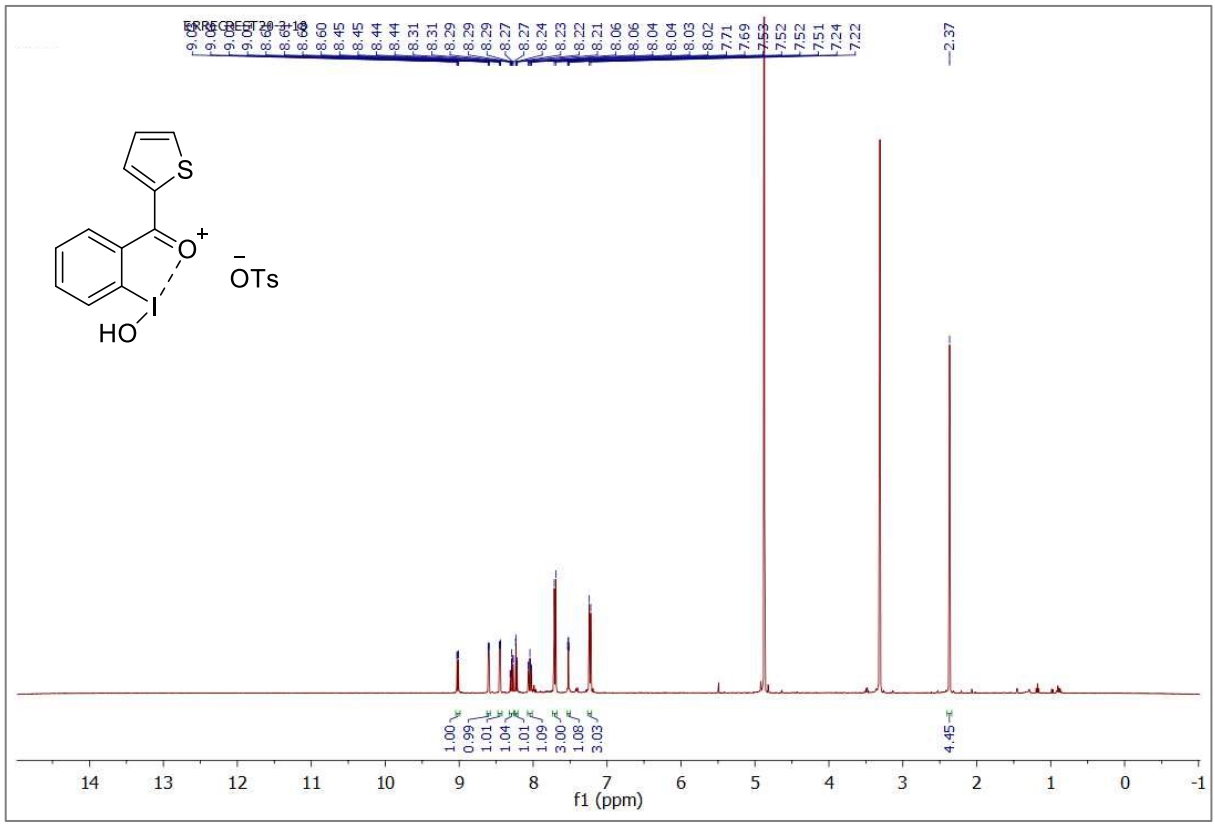
3-(Furan-2-yl)-1-hydroxy-1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**18**), ^{1}H NMR:



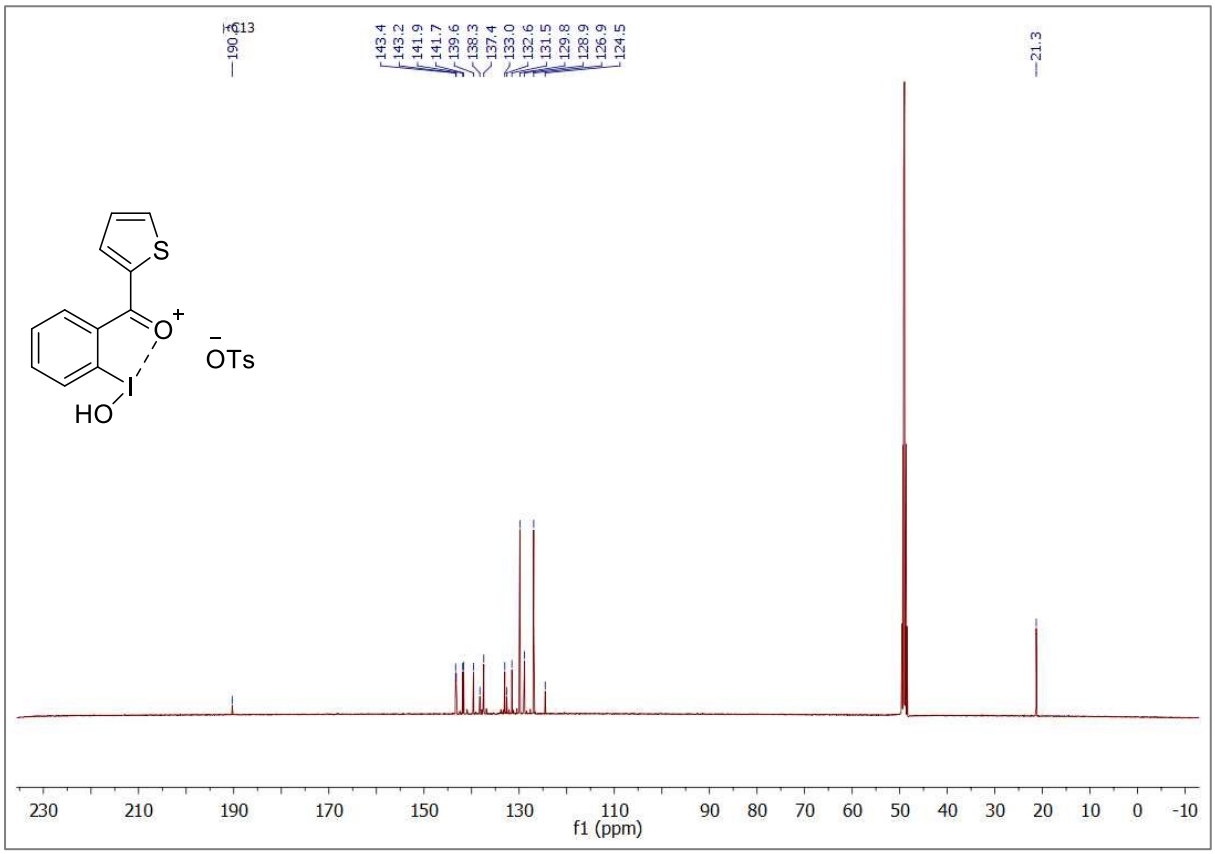
3-(Furan-2-yl)-1-hydroxy-1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**18**), ^{13}C NMR:



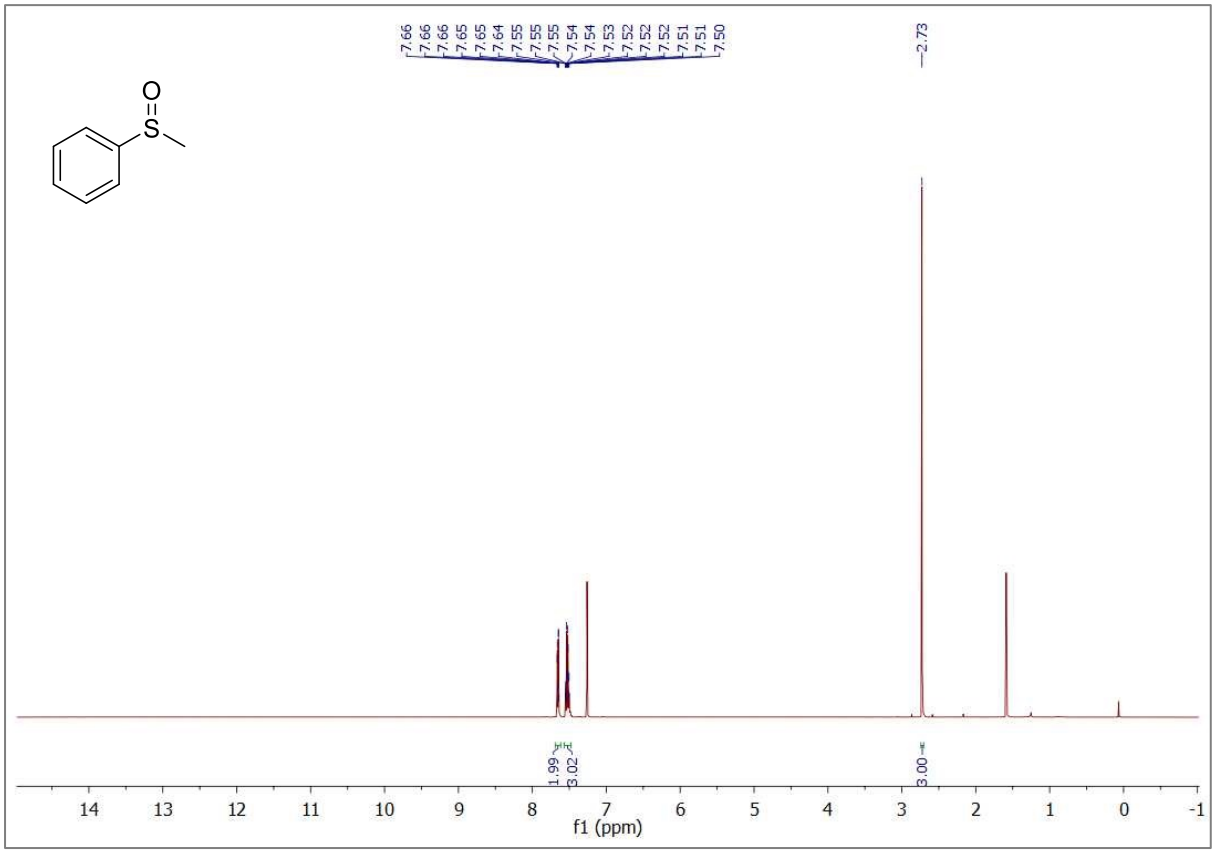
1-Hydroxy-3-(thiophen-2-yl)- 1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**19**), ^{1}H NMR:



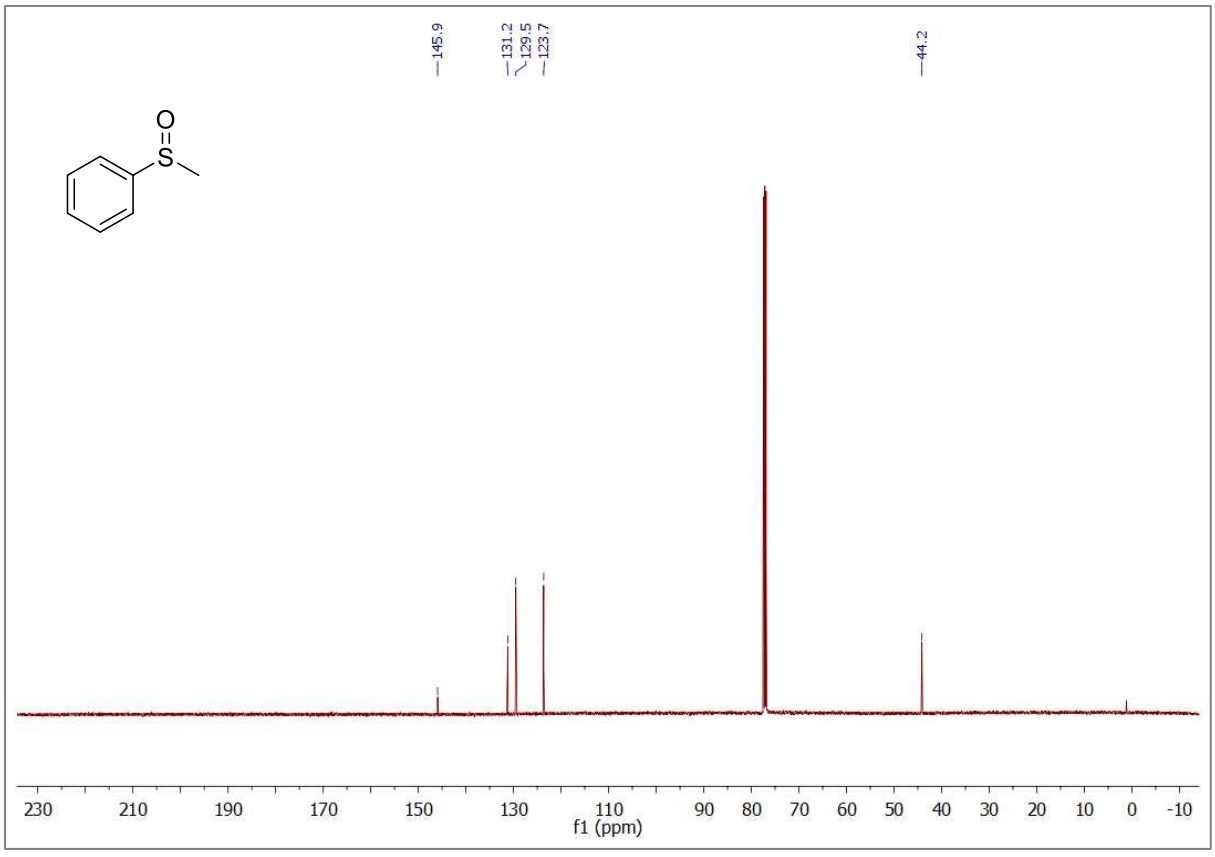
1-Hydroxy-3-(thiophen-2-yl)- 1*H*-λ^3-benzo[d][1,2]iodaoxol-2-ium 4-methylbenzenesulfonate (**19**), ^{13}C NMR:



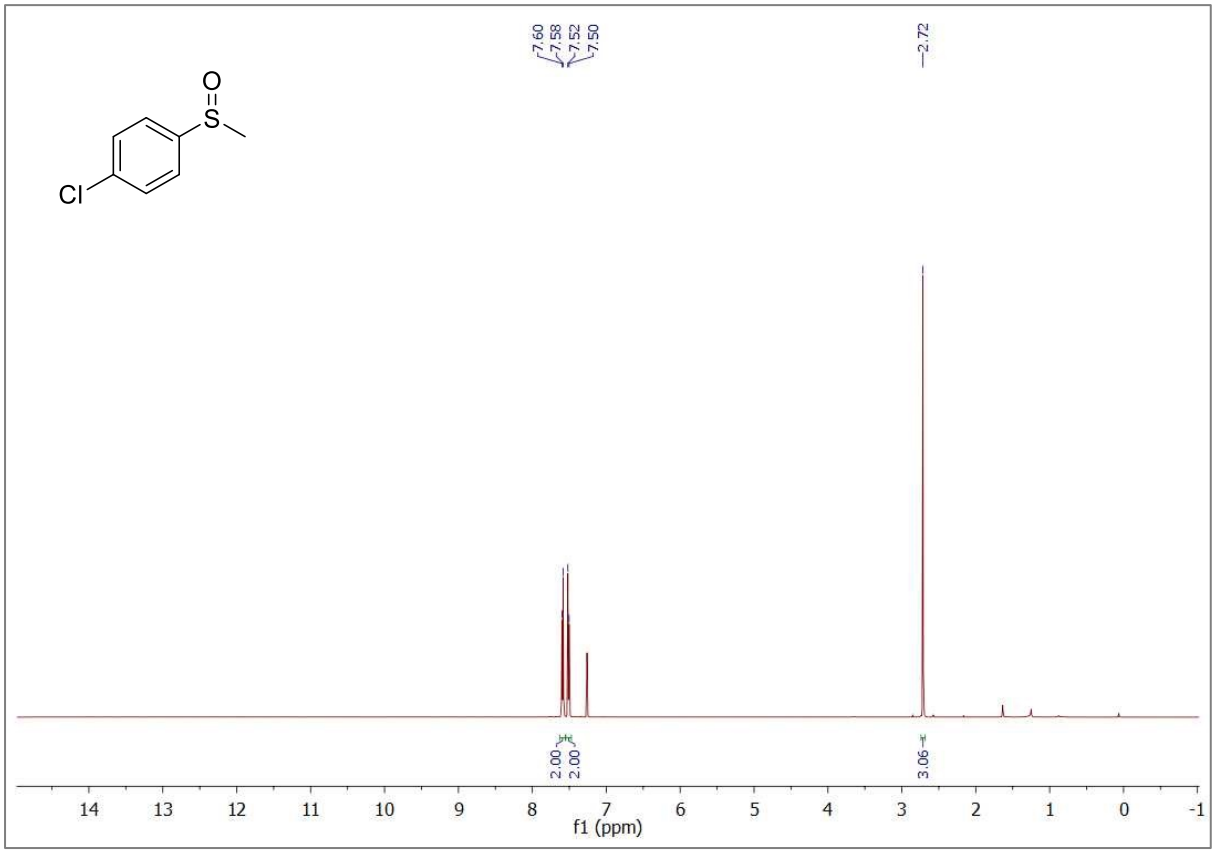
Methyl phenyl sulfoxide (**20**), ^{1}H NMR:



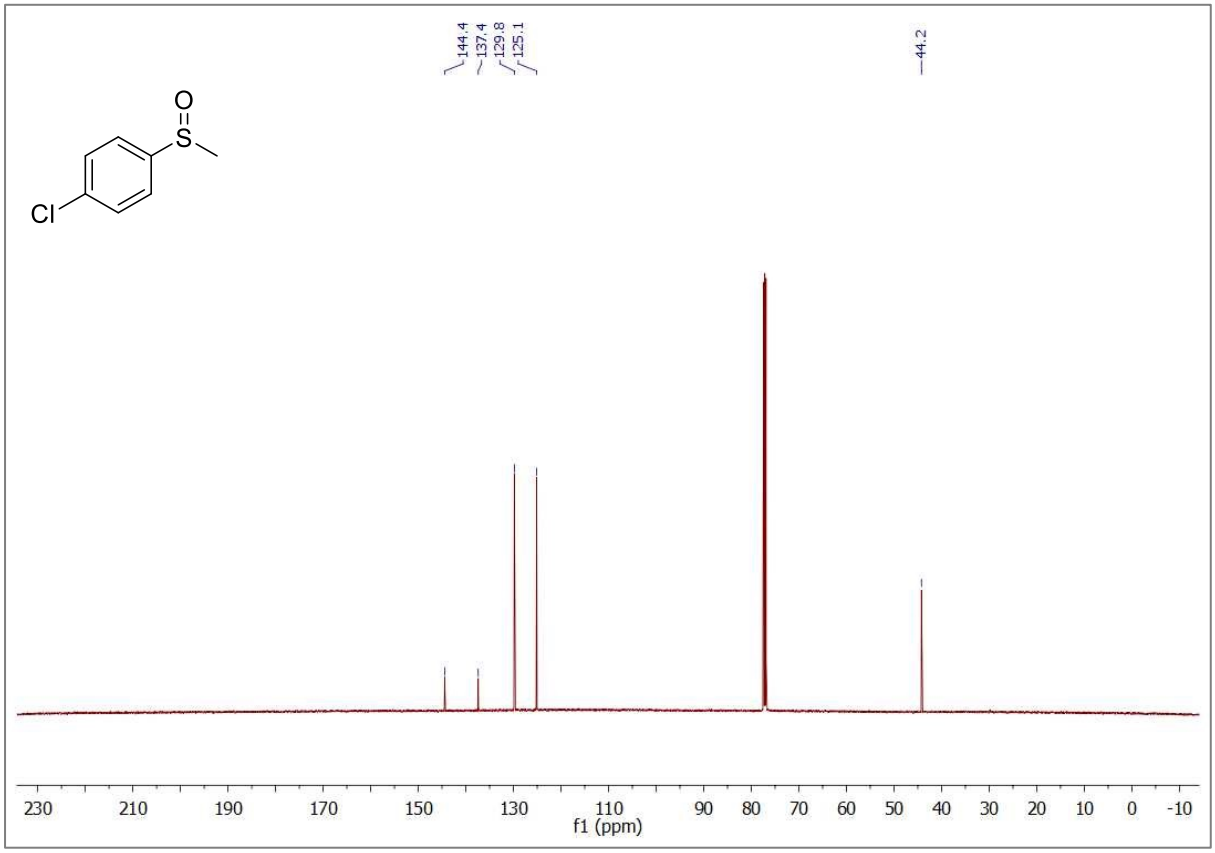
Methyl phenyl sulfoxide (**20**), ^{13}C NMR:



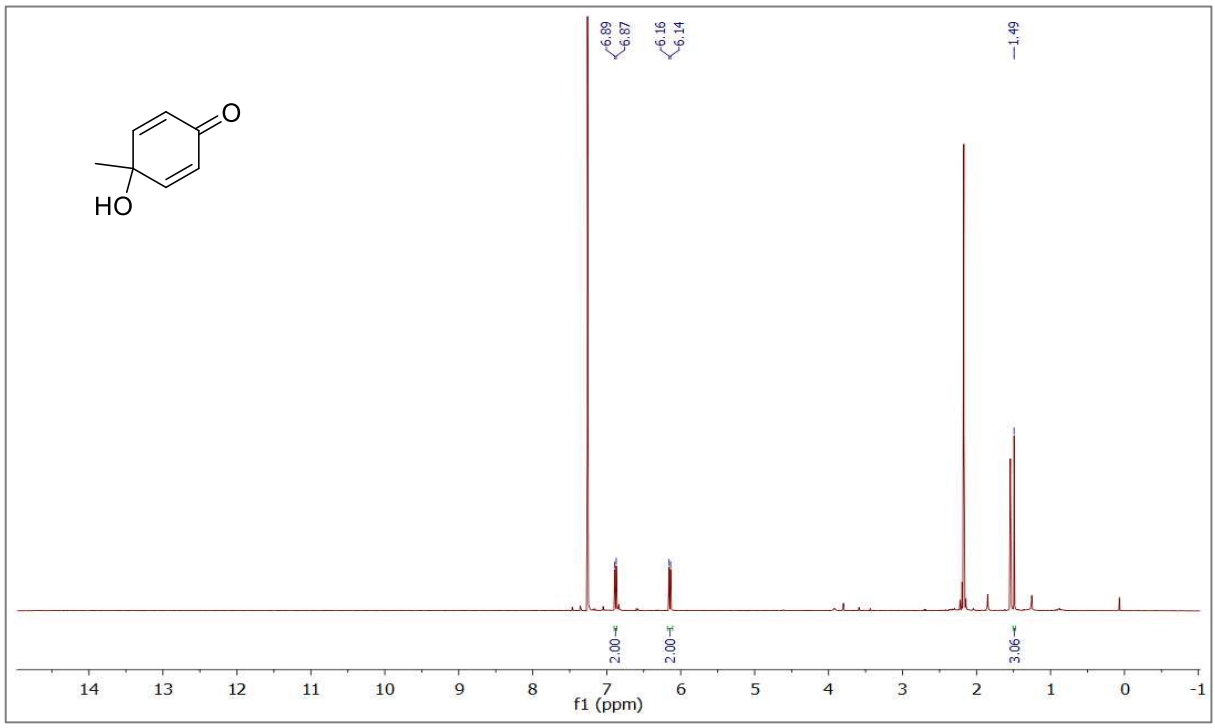
p-Chlorophenyl methyl sulfoxide (**21**), ^{1}H NMR:



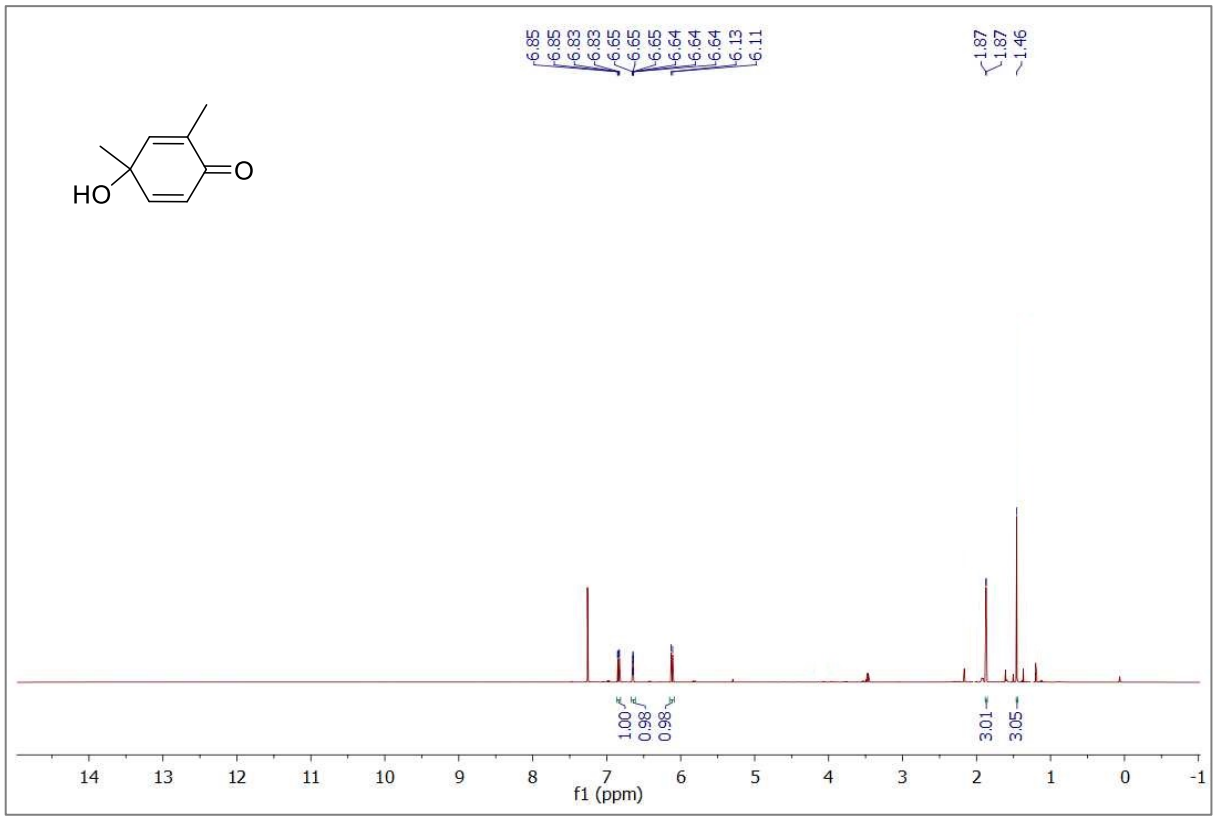
p-Chlorophenyl methyl sulfoxide (**21**), ^{13}C NMR:



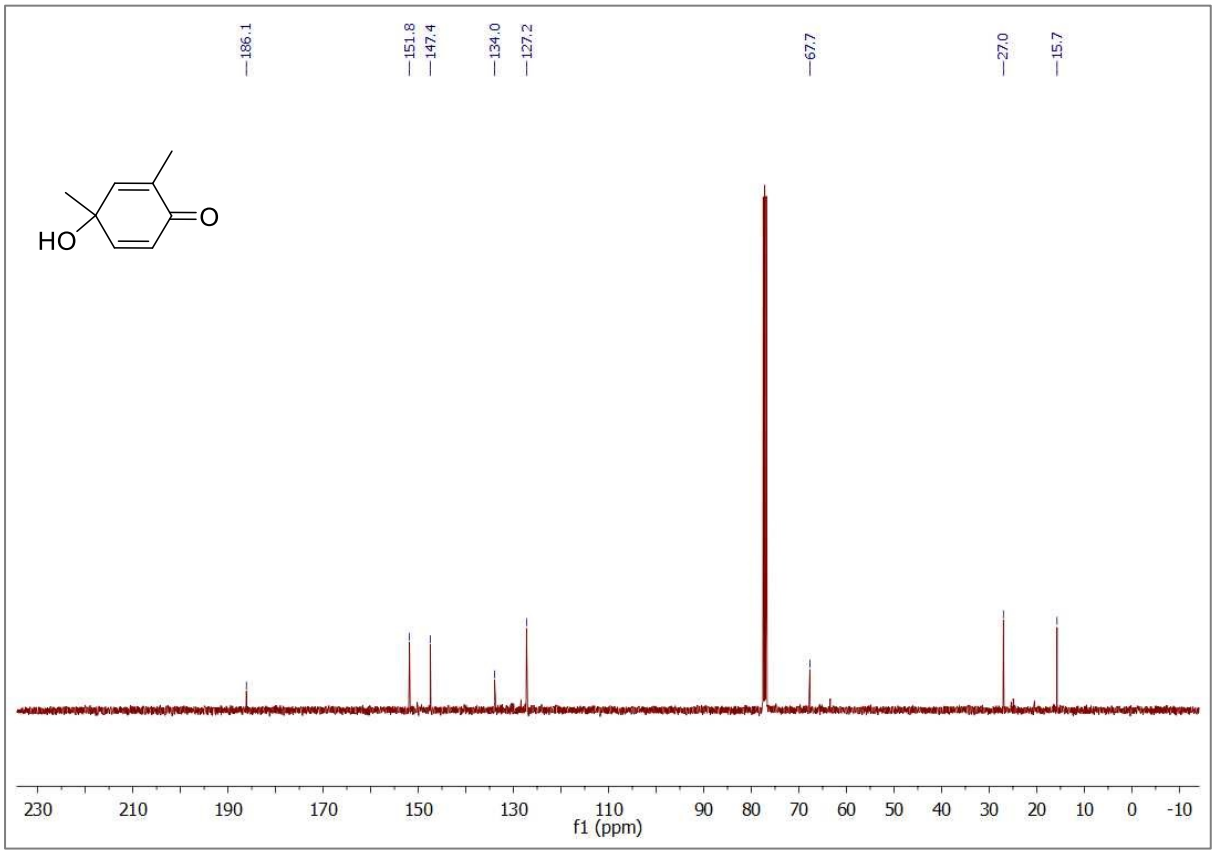
4-Hydroxy-4-methylcyclohexa-2,5-dienone (**22**), ^{1}H NMR:



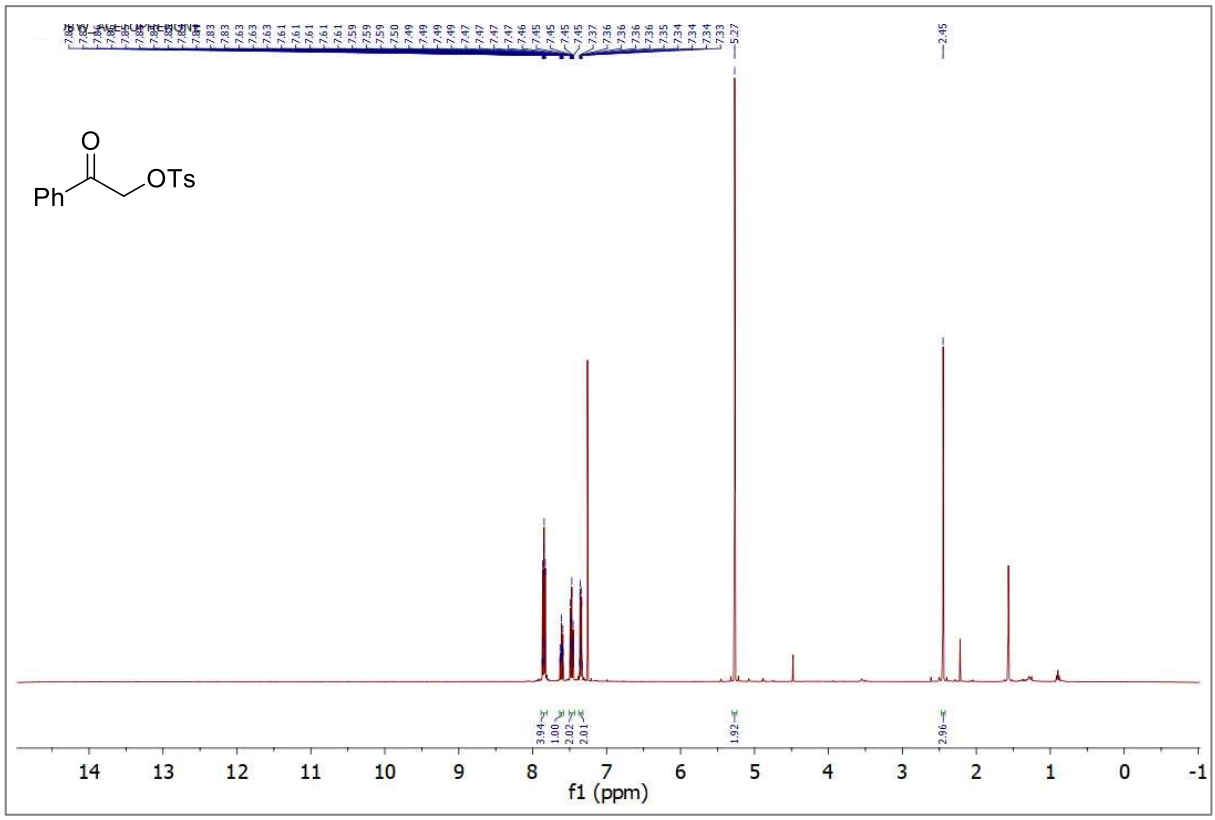
4-Hydroxy-2,4-dimethylcyclohexa-2,5-dien-1-one (**23**), ^{1}H NMR:



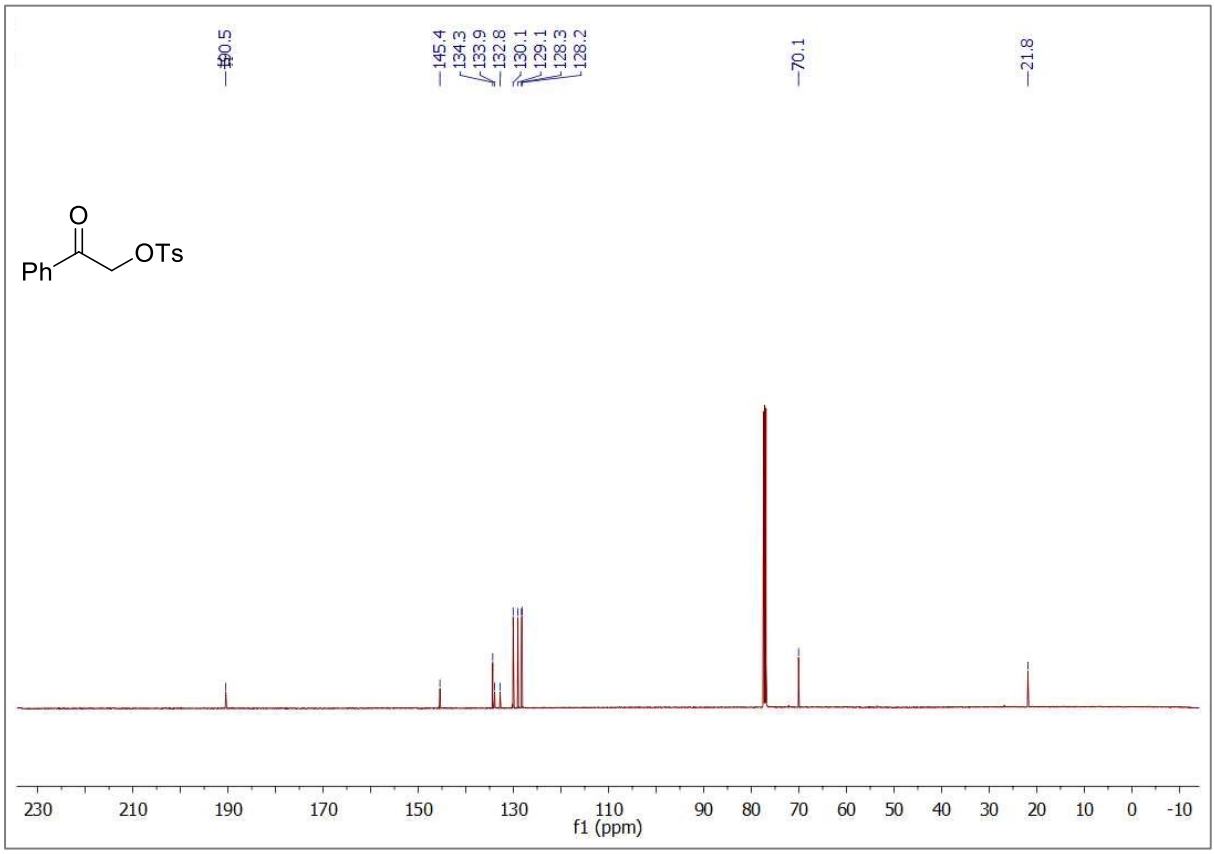
4-Hydroxy-2,4-dimethylcyclohexa-2,5-dien-1-one (**23**), ^{13}C NMR:



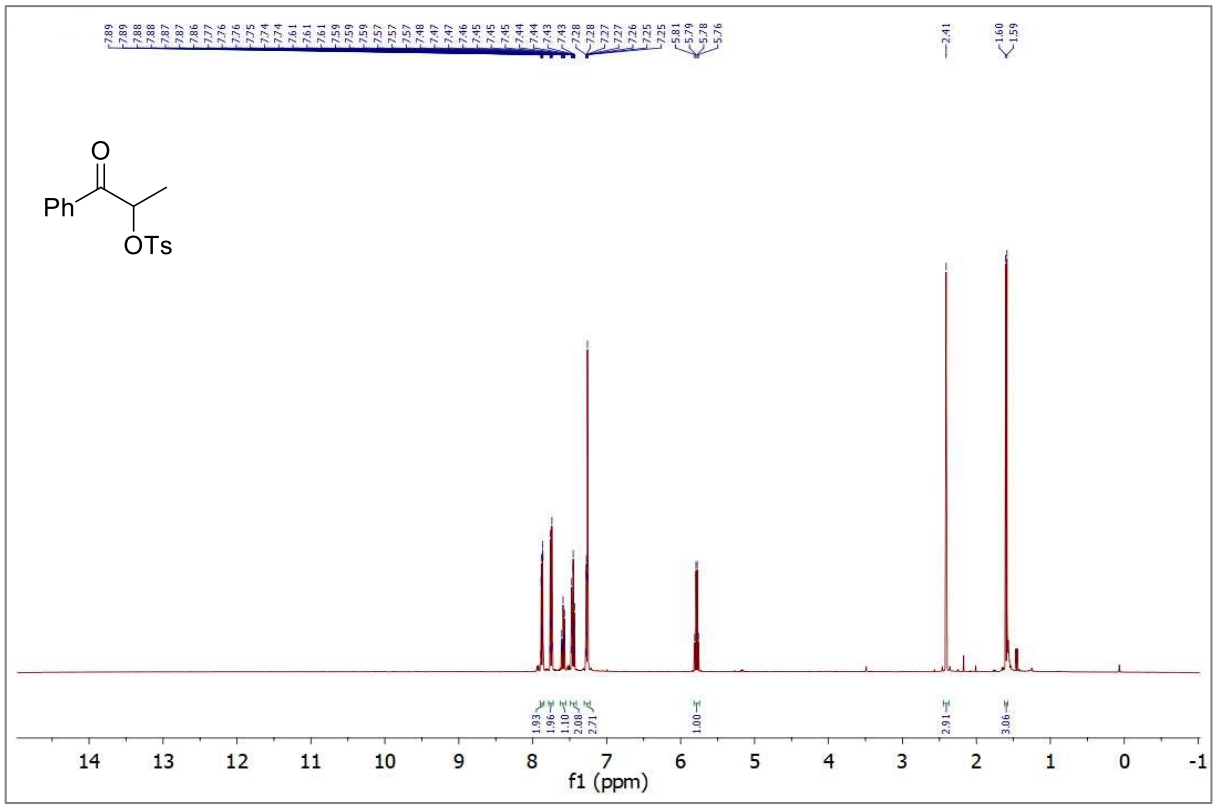
2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**24**), ^{1}H NMR:



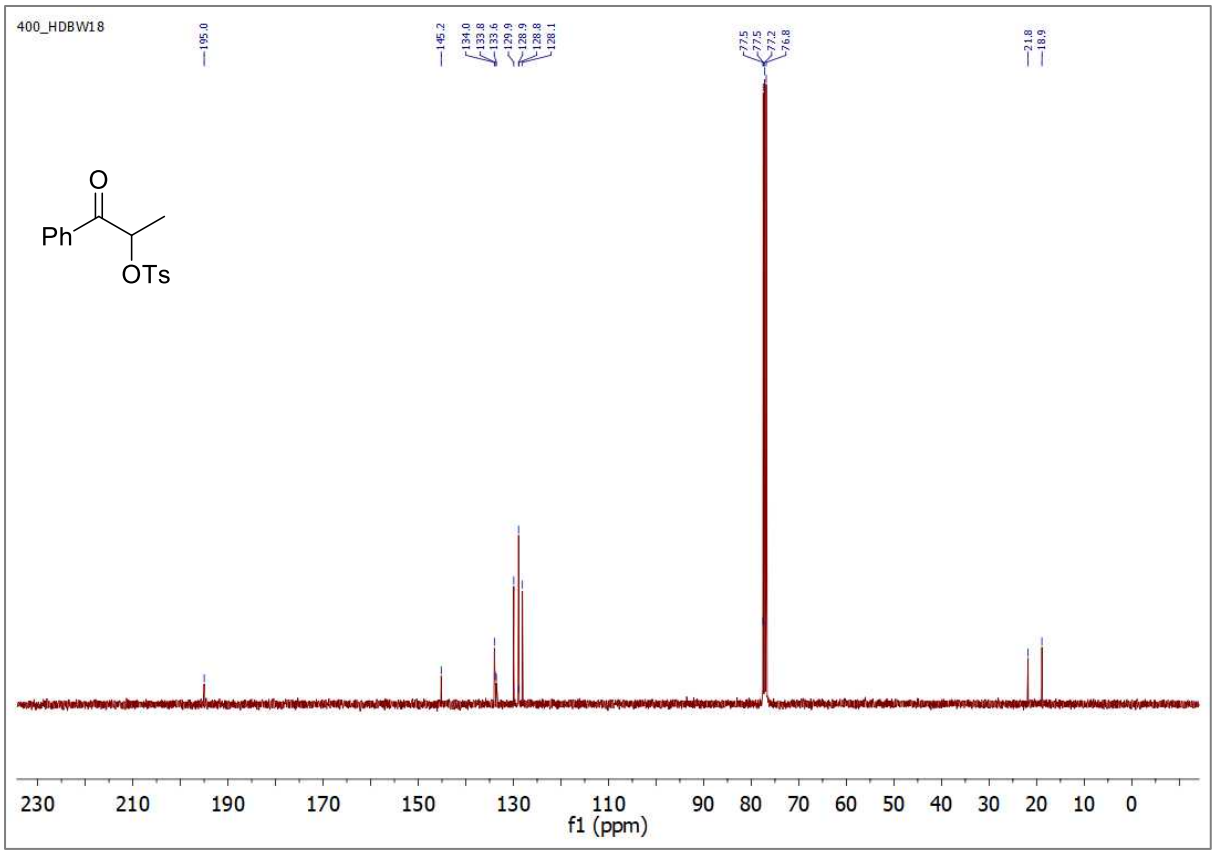
2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**24**), ^{13}C NMR:



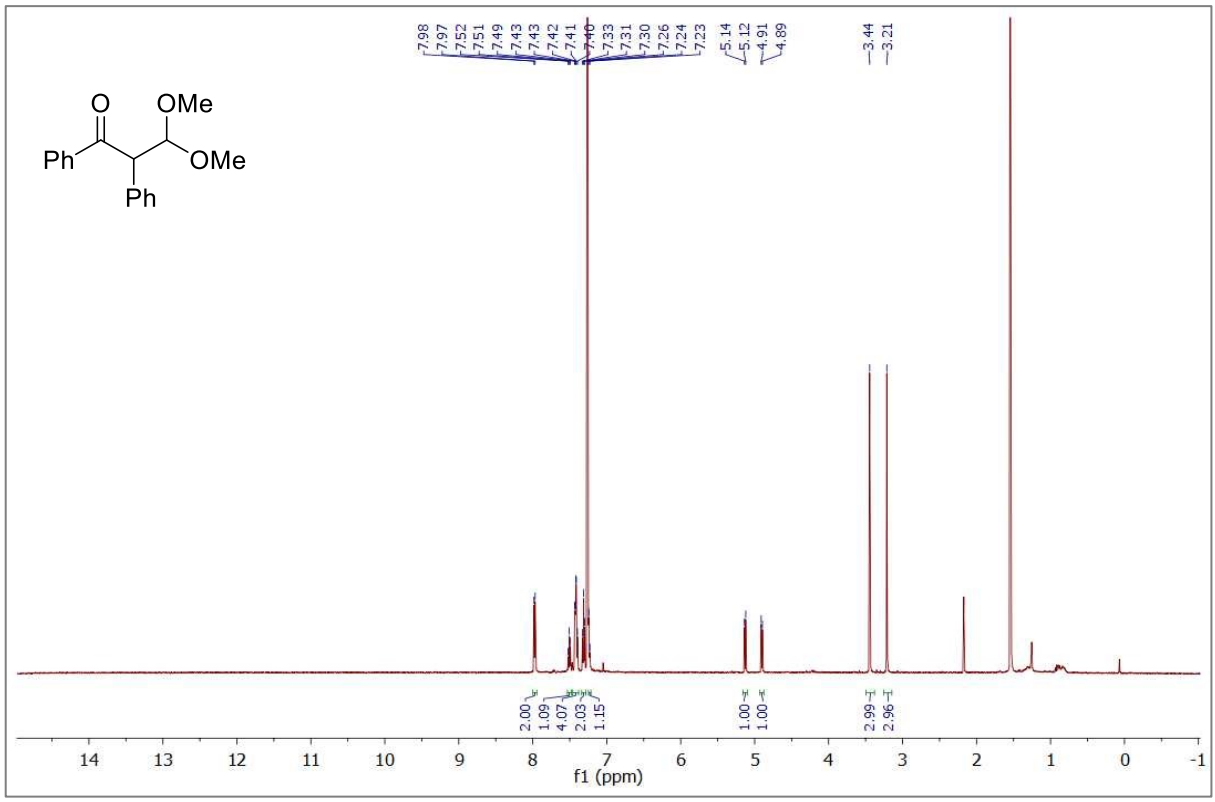
4-Phenyl-1-tosyl-but-3-en-2-one (**25**), ^{1}H NMR:



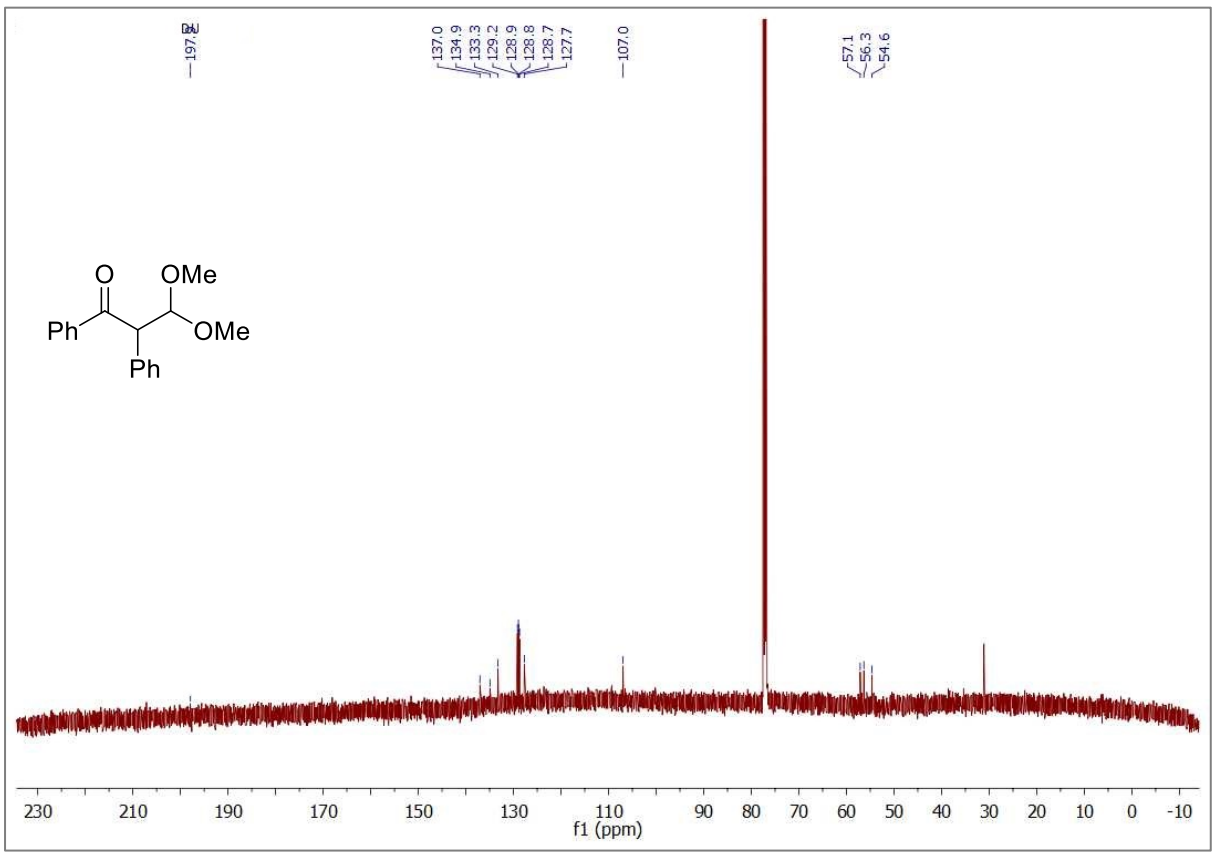
4-Phenyl-1-tosyl-but-3-en-2-one (**25**), ^{13}C NMR:



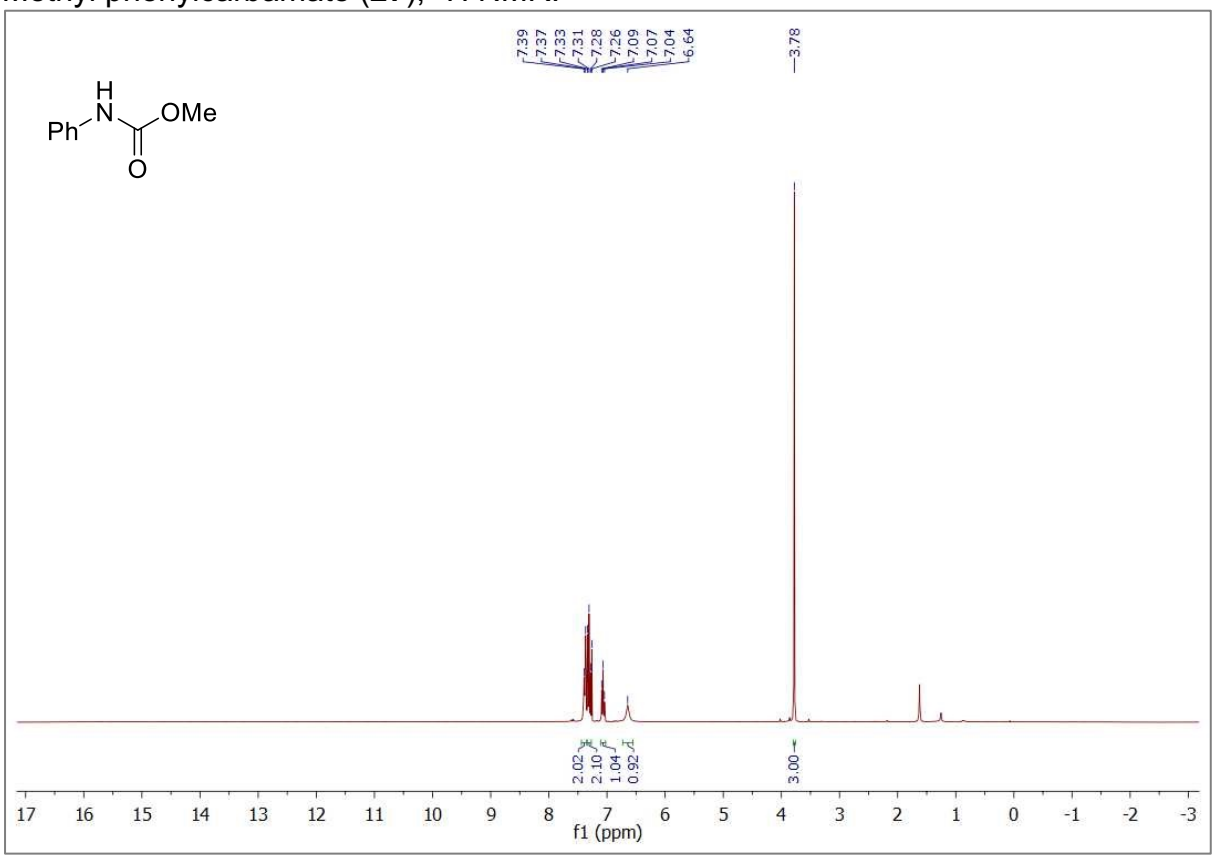
3,3-Dimethoxy-1,2-diphenylpropan-1-one (**26**), ^{1}H NMR:



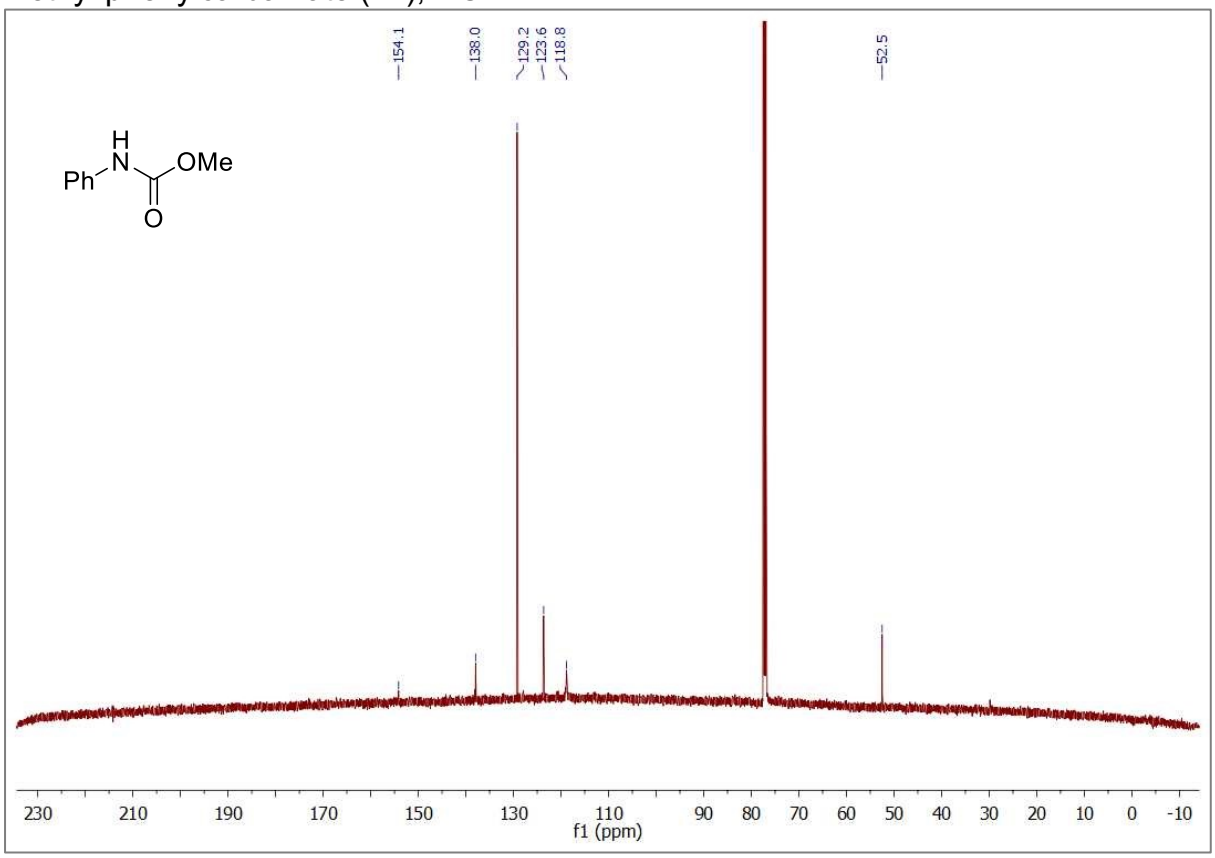
3,3-Dimethoxy-1,2-diphenylpropan-1-one (**26**), ^{13}C NMR:



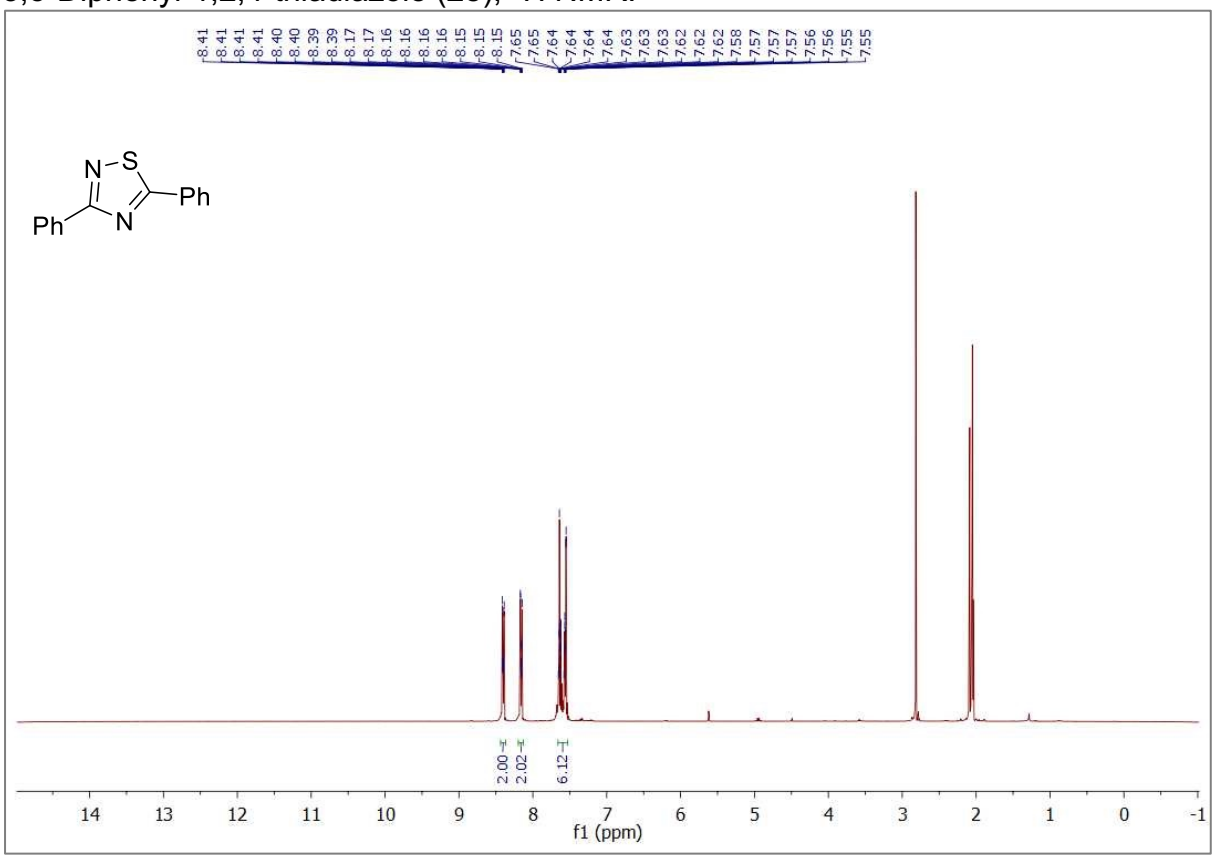
Methyl phenylcarbamate (**27**), ^{1}H NMR:



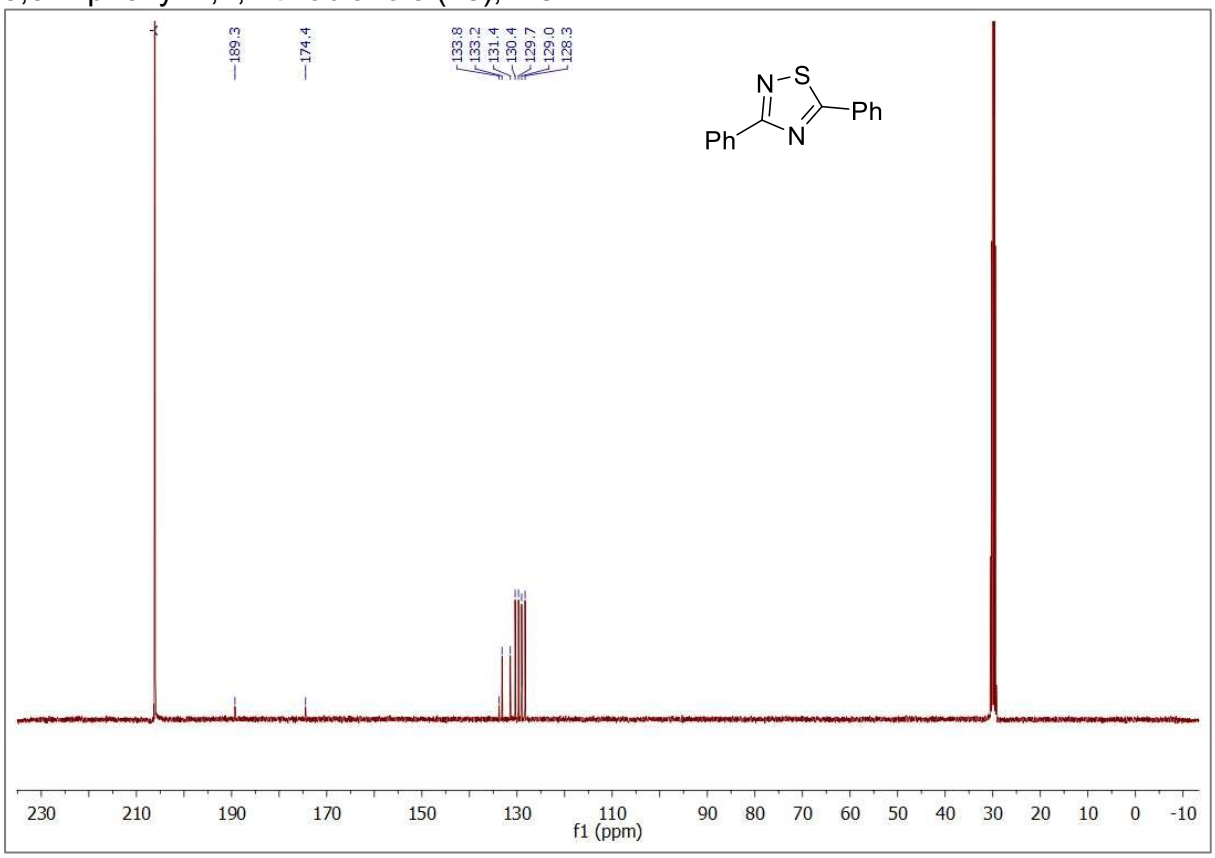
Methyl phenylcarbamate (**27**), ^{13}C NMR:



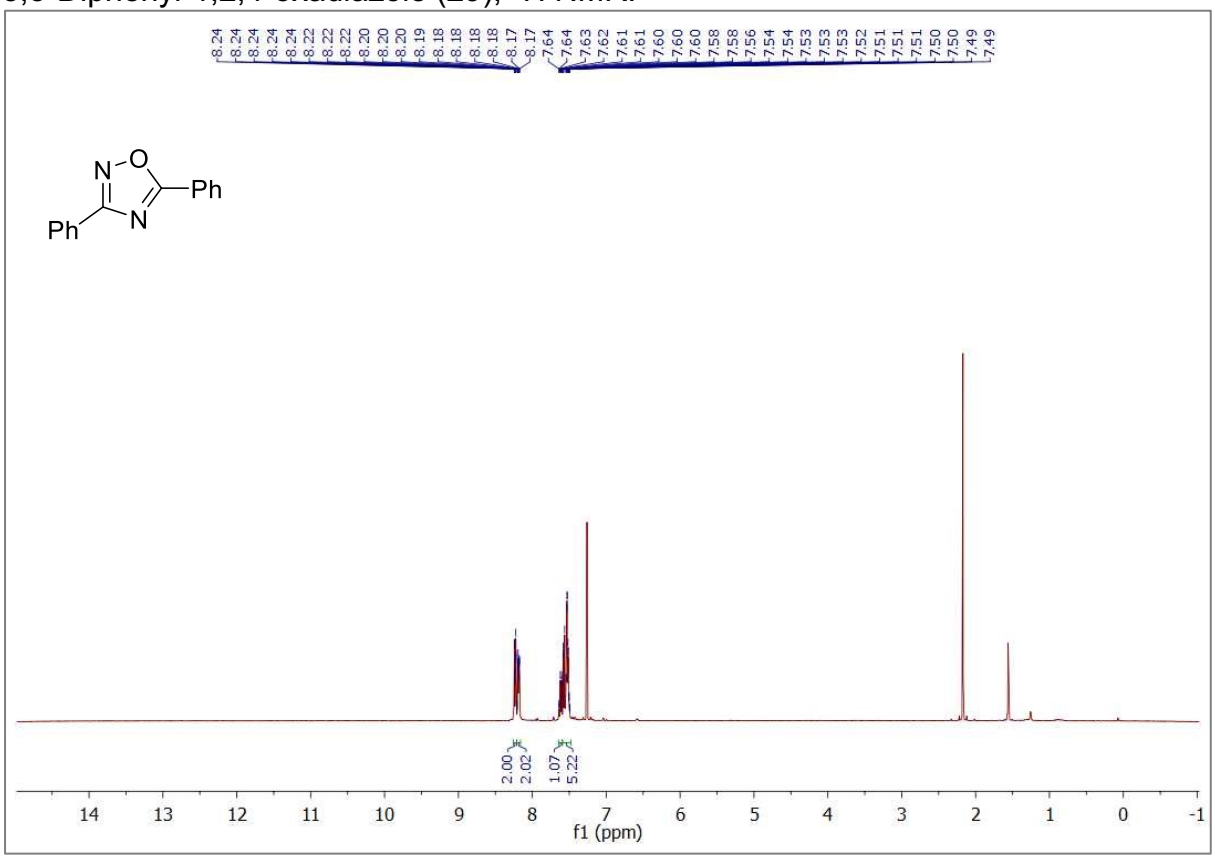
3,5-Diphenyl-1,2,4-thiadiazole (**28**), ^{1}H NMR:



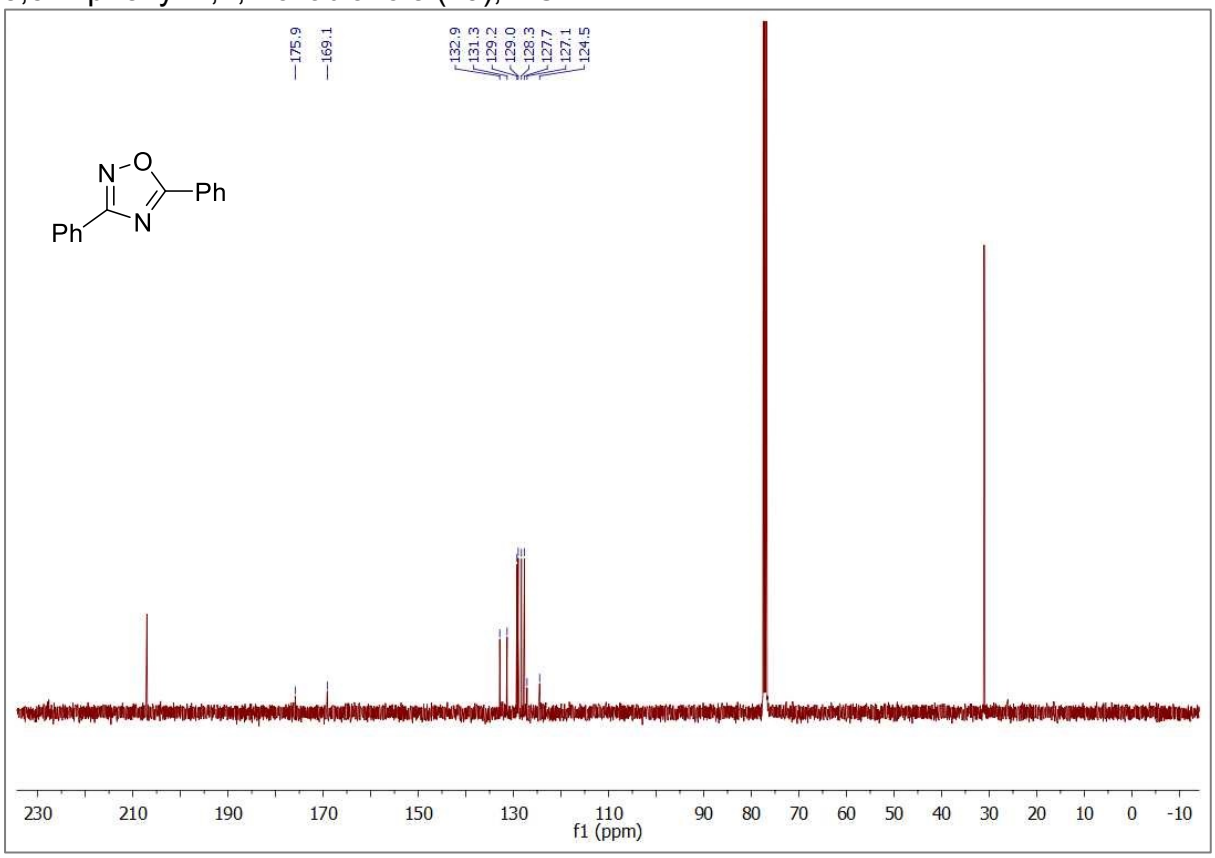
3,5-Diphenyl-1,2,4-thiadiazole (**28**), ^{13}C NMR:



3,5-Diphenyl-1,2,4-oxadiazole (**29**), ^{1}H NMR:



3,5-Diphenyl-1,2,4-oxadiazole (**29**), ^{13}C NMR:



3-Phenyl-5-(trichloromethyl)-1,2,4-oxadiazole (**30**), ^{1}H NMR: