Supporting Information available

Sustainable Byproduct Catalyzed Domino Strategy: Facile Synthesis of α- formyloxy and Acetoxy Ketones via Iodination/Nucleophilic Substitution/Hydrolyzation/Oxidation Sequences

Yan-Ping Zhu, Qing-He Gao, Mi Lian, Jing-Jing Yuan, Mei-Cai Liu, Qin Zhao, Yan Yang, An-Xin Wu*

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, Central China Normal University, Wuhan 430079, P. R. China

E-mail: chwuax@mail.ccnu.edu.cn

Table of Contents **Pages**

1. General……S2
2. Synthesis of **3a-3m, 5a-5f**……S2
3. Evidence in support of the hypothetic mechanism……S2-S5
4. Crystallographic data and molecular structure……S5-S6
5. Spectral data of compound **3a-3m**, **5a-5f**…… S6-S12
6. Appendix: spectral copies of ^{1}H NMR, and ^{13}C NMR ……S12-S48

1. General

All aryl methyl ketones (**1a-1n**), and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer Chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of **2e** and **3d** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. Synthesis of 2a-2x, 3a-3m

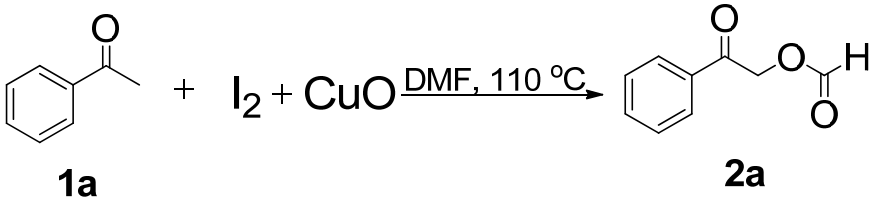
2.1. General procedure for preparation of 2 and 3 (2b as an example)

A mixture of benzalacetone **1b** (120 mg, 1 mmol), iodine (254 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in common DMF (3.0 mL) was heated at 110 ℃ for 1 h, after disappearance of the reactant (monitored by TLC), and added 50mL water to the residue, then extracted with EtOAc 3 times (3 × 50mL). The extract was washed with 10% $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as the eluent to give the expected products **2b** in 96% yield.

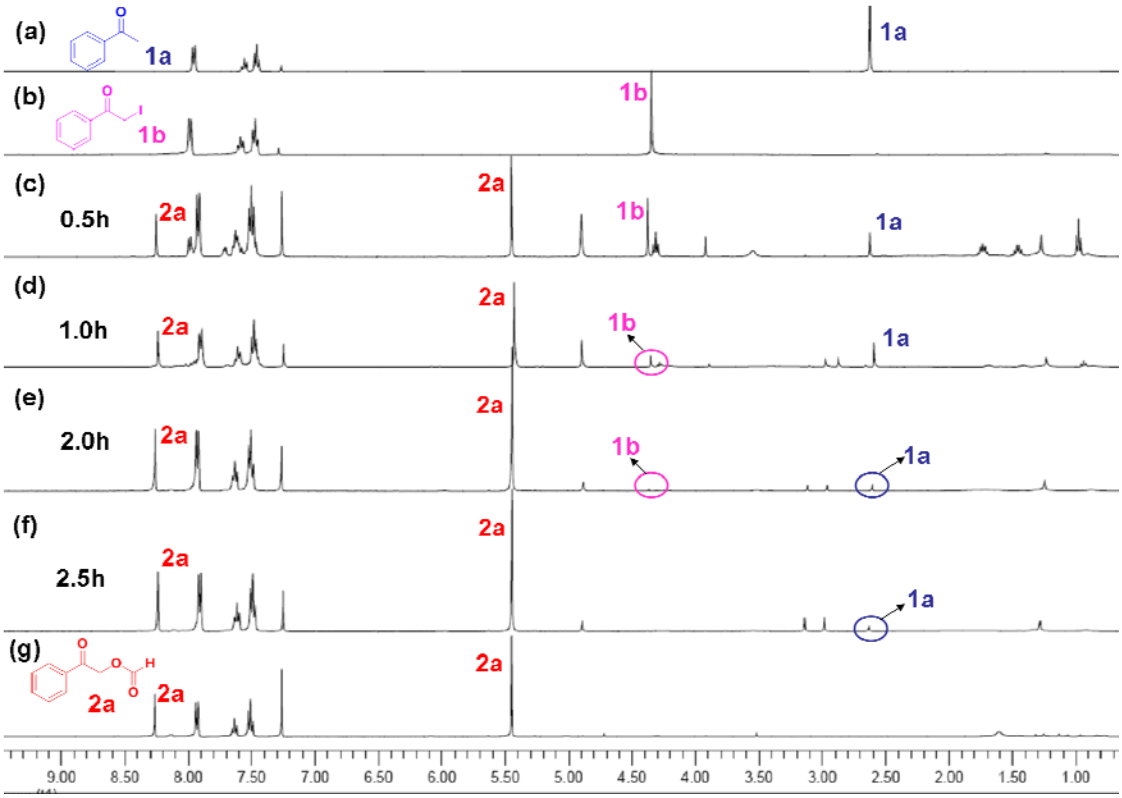
3. In order to support the hypothetic mechanism following experiments were carried out.

(a) The reaction process of Acetophenone **1a,** iodine and CuO in DMF at 110 °C**:**

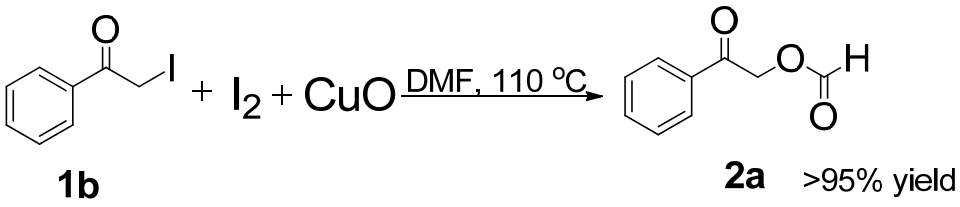
The reaction process of acetophenone **1a** (120 mg, 1.0 mmol), iodine (254 mg, 1.0 mmol) and CuO (80 mg, 1.0 mmol) in DMF (6mL) at 110°C was monitored by ^1H NMR (400 MHz, $CDCl_3$, 298 K) over time.



1a **2a**



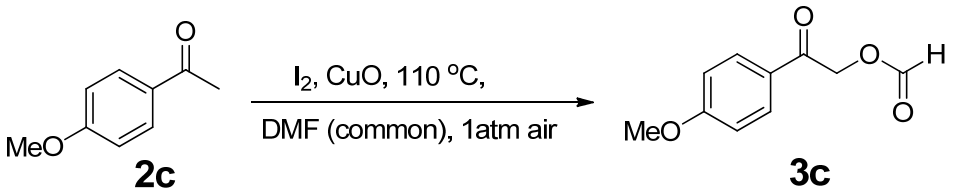
(b) A mixture of phenacyl iodine (246 mg, 1.0 mmol), I_2 (253.81 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in DMF (3-4 mL) was stirred at 110°C for 2 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with $Na_2S_2O_3$ (5% w/w, aq.), and brine successively. After drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 2a (>95% yield) as a yellow oil.

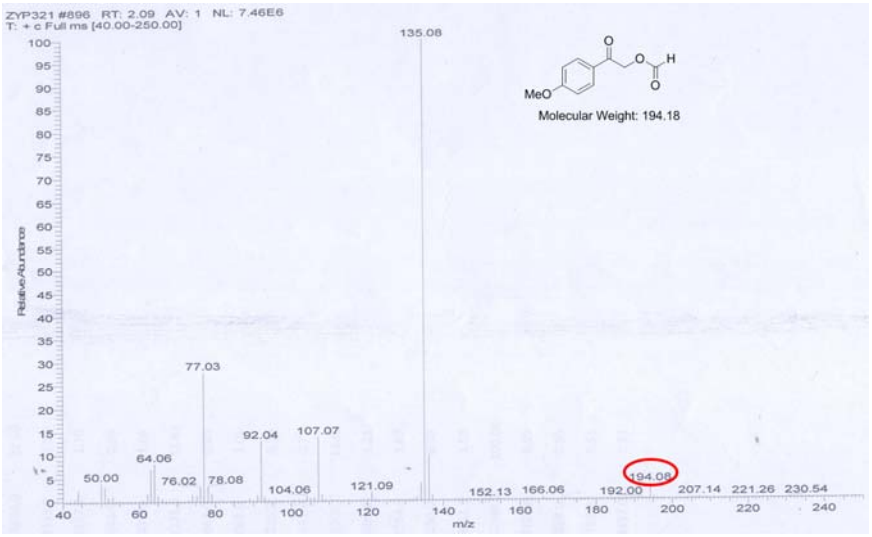


1b **2a** >95% yield

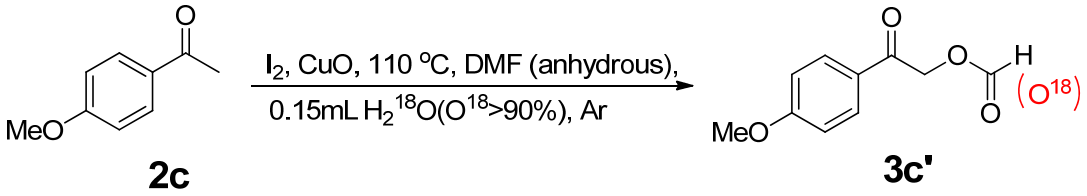
(c) The isotope labeling experiment

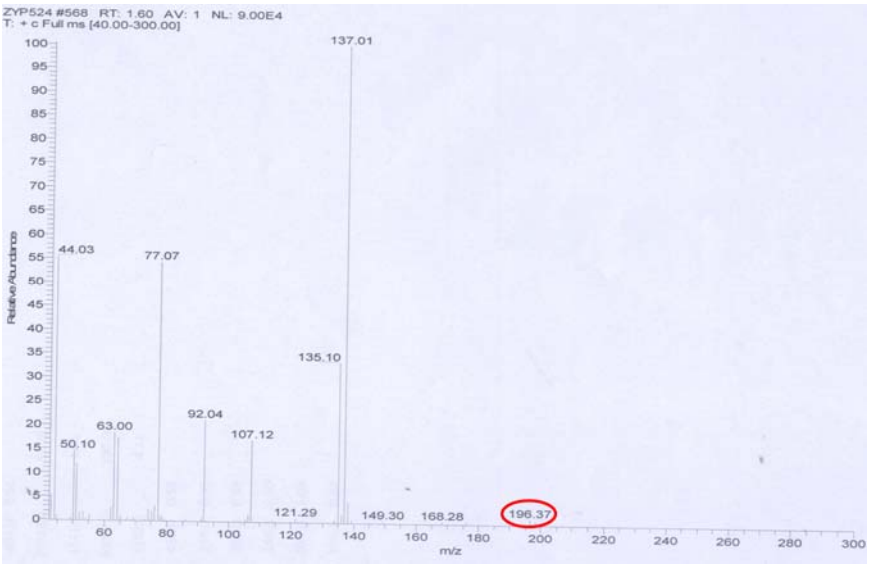
1. A mixture of 1-(4-methoxyphenyl)ethanone (150.17 mg, 1.0 mmol), I_2 (253.81 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in DMF (3-4 mL) was stirred at 110°C for 2 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with $Na_2S_2O_3$ (5% w/w, aq.), and brine successively. After drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 2a (>95% yield).



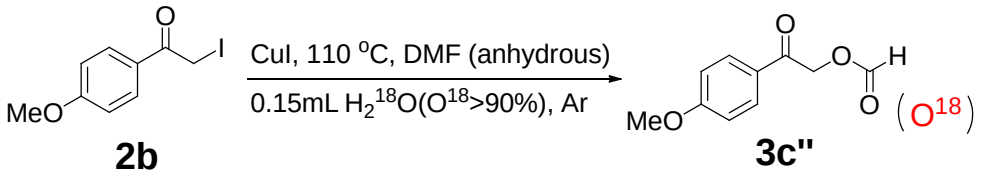


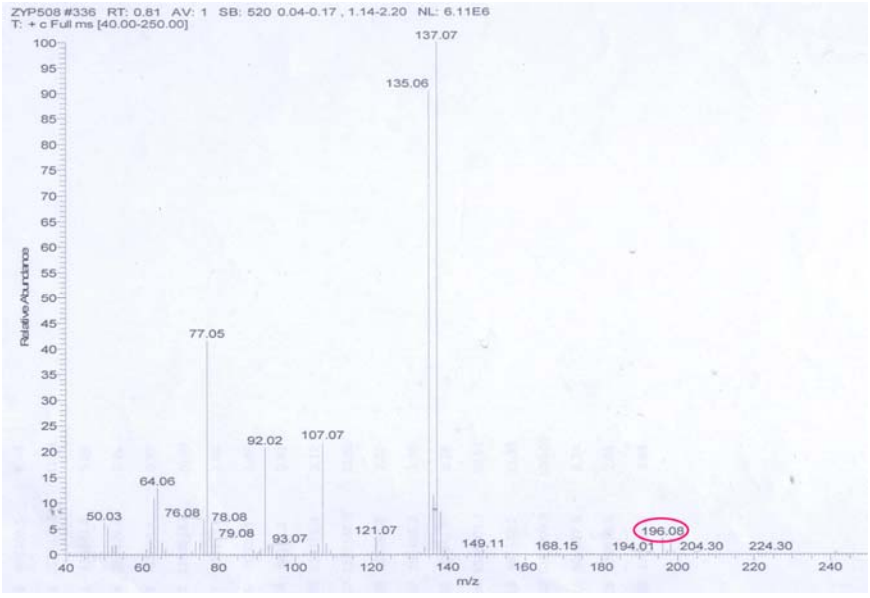
2. A mixture of 1-(4-methoxyphenyl)ethanone (150.17 mg, 1.0 mmol), I_2 (253.81 mg, 1.0 mmol), CuO (80 mg, 1.0 mmol) and 0.15mL H_2O (O^{18}>90%) in anhydrous DMF (3-4 mL) under the Ar atmosphere was stirred at 110°C for 4 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with $Na_2S_2O_3$ (5% w/w, aq.), and brine successively. After drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product **3c'** (92% yield)





3. A mixture of 4-methoxyphenacyl iodine (246 mg, 1.0 mmol), CuI (190 mg, 1.0 mmol) and 0.15mL H_2O (O^{18}>90%) in anhydrous DMF (3-4 mL) under the Ar atmosphere was stirred at 110°C for 4 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with $Na_2S_2O_3$ (5% w/w, aq.), and brine successively. After drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product **3c"** (>95% yield).





4. Crystallographic data and molecular structure

Crystal structure data for macrocycle **2e**: CCDC 844753.

$C_9H_7NO_5$, chemical formula weight: 209.16, Orthorhombic space group P2(1)/c, *a* = 9.6790(1), *b* = 15.1737(15), *c* = 6.3703(6) Å; α = 90.00°, β = 92.00°, γ = 90.00°, U = 927.02(16) Å3, T = 298(2) K, Z = 4, DC = 1.499 Mg/M^3, μ = 0.125 mm^{-1}, λ = 0.71073 Å, F(000) 432, crystal size 0.20 × □0.10× □0.10 mm^3, 2289 independent reflections[R(int) = 0.1244], reflections collected 11219, refinementmethod: full-matrix least-squares on F^2: goodness-of-fit on F^2 1.049, final R indices [I > 2σ(I)], R1 = 0.1007, wR2 = 0.2348, largest diff. peak and hole 0.688Å^{-3} and –0.438e·Å^{-3}.

Crystal Structure of **2e**

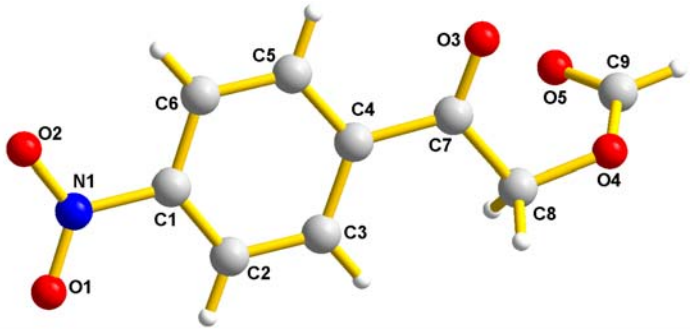


Figure 1 The X-Ray crystal structure of compound **2e**

Crystal structure data for macrocycle **3d**: CCDC 844754.

$C_{10}H_9NO_5$, chemical formula weight: 227.69, Orthorhombic space group P2(1)/c, *a* = 9.077(5), *b* = 12.606(7), *c* = 9.405(5) Å; α = 90.00°, β = 102.097()9°, γ = 90.00°, U = 1052.3(10) Å3, T = 298(2) K, Z = 4, DC = 1.437 Mg/M^3, μ = 0.118 mm^{-1}, λ = 0.71073 Å, F(000) 474, crystal size 0.20 × □0.20 × □0.20 mm^3, 1954 independent reflections[R(int) = 0.0300], reflections collected 10229, refinementmethod: full-matrix least-squares on F^2: goodness-of-fit on F^2 1.074, final R indices [I > 2σ(I)], R1 = 0.0561, wR2 = 0.1588, largest diff. peak and hole 0.318Å^{-3} and –0.133e·Å^{-3}.

Crystal Structure of **3d**

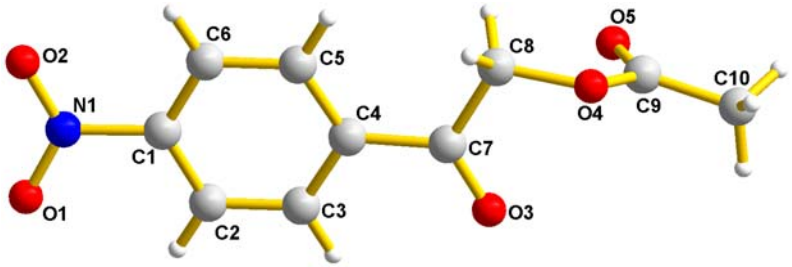
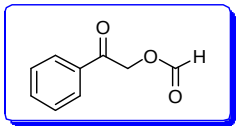


Figure 1 The X-Ray crystal structure of compound **3d**

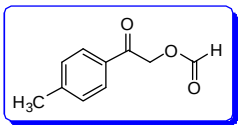
5. Spectral data of compound 3a-3m, 5a-5f

2-oxo-2-phenylethyl formate (**2a**)



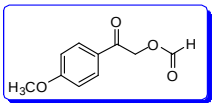
IR (KBr): 3425, 3064, 2933, 1731, 1693, 1598, 1450, 1288, 1234, 1171, 1103 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.93 (d, J = 7.8 Hz, 2H), 7.61-7.64 (t, J = 7.2 Hz, 1H), 7.49-7.52 (t, J = 7.8 Hz, 2H), 5.44 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.1, 160.0, 134.1, 133.9, 128.9, 127.8, 65.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_9O_3$: 165.05369; found: 165.05462.

2-oxo-2-(p-tolyl)ethyl formate (**2b**)



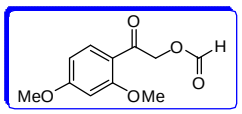
IR (KBr): 3437, 3046, 2951, 1726, 1692, 1606, 1420, 1371, 1281, 1239, 1170, 1012 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.25 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 5.41 (s, 2H), 2.42 （s, 3H）; ^{13}C NMR (150 MHz, $CDCl_3$): δ =190.6, 160.0, 145.0, 131.1, 129.5, 127.8, 65.2, 21.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_{10}O_3$: 179.0703; found: 179.0711.

2-(4-methoxyphenyl)-2-oxoethyl formate (**2c**)



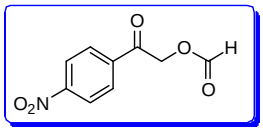
IR (KBr): 3413, 2944, 2847, 1731, 1682, 1601, 1572, 1512, 1464, 1424, 1372, 1316, 1267, 1111, 1014 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.25 (s, 1H), 7.89 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 2H), 5.40 (s, 2H), 3.87 （s, 3H）; ^{13}C NMR (150 MHz, $CDCl_3$): δ =189.5, 164.0, 160.1, 130.0, 129.9, 114.0, 65.0, 55.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_{10}O_4$: 195.0652; found: 195.0143.

2-(2,4-dimethoxyphenyl)-2-oxoethyl formate (**2d**)



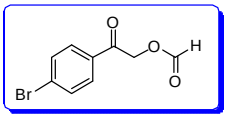
IR (KBr): 3411, 3314, 3097, 2953, 2844, 1729, 1665, 1605, 1478, 1421, 1370, 1336, 1289, 1258, 1219, 1111, 1017 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.25 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 6.46 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =190.0, 165.6, 161.4, 160.4, 133.2, 117.3, 105.9, 97.9, 69.2, 55.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{12}O_5$: 225.0757; found: 225.0753.

2-(4-nitrophenyl)-2-oxoethyl formate (**2e**)



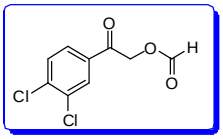
IR (KBr): 3444, 3109, 2949, 1727, 1702, 1605, 1529, 1372, 1348, 1321, 1284, 1226, 1156, 1006 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.36 (d, J = 8.4 Hz, 2H), 8.26 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 5.47 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =190.0, 159.8, 150.7, 138.2, 128.9, 124.1, 65.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_7NO_5$: 210.0216; found: 210.0404.

2-(4-bromophenyl)-2-oxoethyl formate (**2f**)



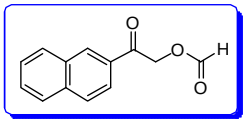
IR (KBr): 3427, 3094, 2945, 1719, 1690, 1585, 1427, 1399, 1283, 1240, 1180, 1070, 1003 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.25 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 5.40 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =190.2, 159.9, 132.5, 132.3, 129.3, 129.2, 65.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_7BrO_3$: 290.9627; found: 290.9872.

2-(3,4-dichlorophenyl)-2-oxoethyl formate (**2g**)



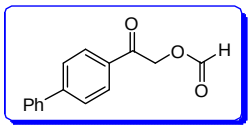
IR (KBr): 3449, 3090, 3011, 2942, 1731, 1696, 1582, 1429, 1398, 1287, 1264, 1223, 1172, 1042 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.24 (s, 1H), 8.00 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1 H), 5.38 (s, 2H); ^{13}C NMR (150 MHz, d6-DMSO): δ =189.2, 159.8, 138.8, 133.7, 133.3, 131.1, 129.8, 126.7, 65.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_6Cl_2O_3$: 234.9767; found: 234.9773.

2-(naphthalen-2-yl)-2-oxoethyl formate (**2h**)



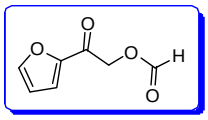
IR (KBr): 3444, 3109, 2949, 1727, 1702, 1605, 1529, 1372, 1348, 1321, 1284, 1226, 1156, 1006 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.44 (s, 1H), 8.30 (s, 1H), 7.89-7.99 (m, 4H), 7.63-7.66 (t, J = 7.8 Hz, 1H), 7.58-7.60 (t, J = 7.8 Hz, 1H), 5.59 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.0, 160.1, 135.9, 132.3, 131.2, 129.6, 129.0, 128.9, 127.9, 127.1, 123.2, 65.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{10}O_3$: 237.0522; found: 237.0520.

2-([1,1'-biphenyl]-4-yl)-2-oxoethyl formate (**2i**)



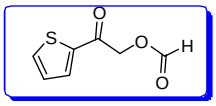
IR (KBr): 3419, 3036, 2943, 1728, 1697, 1604, 1447, 1422, 1402, 1373, 1286, 1237, 1167, 1005 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.27 (s, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.46-7.49 (t, J = 7.8 Hz, 2H), 7.40-7.43 (t, J = 7.8 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.6, 160.0, 146.7, 139.4, 132.5, 129.0, 128.4, 127.5, 127.2, 65.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{12}O_3$: 263.0679; found: 263.0677.

2-(furan-2-yl)-2-oxoethyl acetate (**2j**)



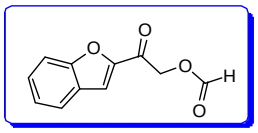
IR (KBr): 3422, 3131, 2929, 2856, 1730, 1688, 1570, 1468, 1399, 1276, 1161, 1021 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.23 (s, 1H), 7.65 (d, J = 1.2 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 6.60-6.61 (q, J = 1.8 Hz, 1H), 5.29 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =180.5, 159.9, 150.1, 146.9, 117.9, 112.5, 64.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_7H_6O_4$: 192.9930; found: 192.9979.

2-oxo-2-(thiophen-2-yl)ethyl acetate (**2k**)



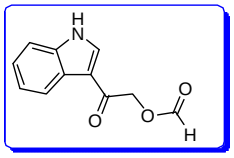
IR (KBr): 3429, 3096, 3001, 2942, 1724, 1671, 1520, 1413, 1387, 1274, 1252, 1194, 1059 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.24 (s, 1H), 7.77 (d, J = 4.2 Hz, 1H), 7.74 (d, J = 4.2 Hz, 1H), 7.18-7.19 (q, J = 4.2 Hz, 1H), 5.34 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =180.5, 159.9, 150.1, 146.9, 117.9, 112.5, 64.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_7H_7SO_3$: 171.00996; found: 171.01104.

2-(benzofuran-2-yl)-2-oxoethyl formate (**2l**)



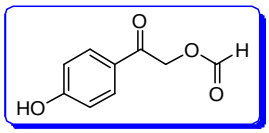
IR (KBr): 3414, 2926, 1723, 1695, 1609, 1562, 1189, 1157, 1138 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.26 (s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50-7.52 （t, J = 7.2 Hz, 1H）, 7.32-7.36 (q, J = 7.2 Hz, 1H), 5.43 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =182.6, 159.9, 155.5, 150.0, 128.8, 126.5, 124.2, 123.5, 113.6, 112.4, 65.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_9O_4$: 205.04858; found: 205.04954.

2-(1H-indol-3-yl)-2-oxoethyl formate (**2m**)



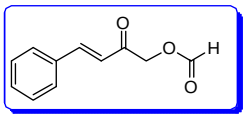
IR (KBr): 3237, 2931, 1729, 1649, 1579, 1520, 1425, 1313, 1238, 1195, 1156 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.76 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 7.94 (s, 1H), 7.45 (s, 1H), 7.33 (s, 1H), 5.31 (s, 2H) ; ^{13}C NMR (150 MHz, d6-DMSO): δ =187.1, 161.9, 136.3, 133.8, 125.3, 123.3, 122.2, 121.2, 112.8, 112.4, 65.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_9NO_3$: 204.0655; found: 204.0653.

2-(4-hydroxyphenyl)-2-oxoethyl formate (**2n**)



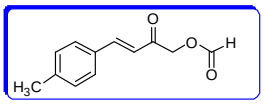
IR (KBr): 3349, 2923, 1727, 1677, 1604, 1577, 1515, 1432, 1370, 1352, 1289, 1250, 1217, 1192, 1168, 1034, 951, 847 cm^{-1}; ^1H NMR (600 MHz, DMSO): δ =10.58 (s, 1H), 8.40 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.49 (s, 2H); ^{13}C NMR (150 MHz, d6-DMSO): δ =190.3, 162.6, 161.7, 130.5, 125.4, 115.6, 115.5, 65.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_9H_8O_4$: 181.0495; found: 181.0501.

(E)-2-oxo-4-phenylbut-3-en-1-yl formate (**2o**)



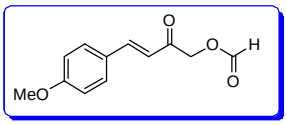
IR (KBr): 3435, 3060, 3029, 2934, 1730, 1685, 1613, 1576, 1495, 1450, 1376, 1332, 1268, 1170, 1091, 1053 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.21 (s, 1H), 7.67 (d, J = 16.2 Hz, 1H), 7.55 (d, J =9.0 Hz, 2H), 7.38-7.41 (m, 3H), 6.79 (d, J = 16.2 Hz, 1H), 5.03 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.3, 160.0, 144.5, 133.8, 131.1, 129.0, 128.5, 121.1, 66.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}O_3$: 191.0703; found: 191.0865.

(E)-2-oxo-4-(p-tolyl)but-3-en-1-yl formate (**2p**)



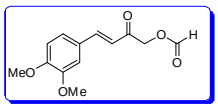
IR (KBr): 3440, 2942, 1728, 1690, 1599, 1511, 1415, 1372, 1270, 1167, 1087, 1037 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.23 (s, 1H), 7.65-7.68 (q, J = 16.2 Hz, 1H), 7.46 (d, J =7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.75-6.78 (q, J = 16.2 Hz, 1H), 5.03 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.3, 160.0, 144.6, 141.8, 131.1, 129.8, 128.5, 120.1, 66.5, 21.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{12}H_{12}O_3$: 227.0679; found: 227.5765.

(E)-4-(4-methoxyphenyl)-2-oxobut-3-en-1-yl formate (**2q**)



IR (KBr): 3445, 2934, 2837, 1671, 1594, 1511, 1421, 1209, 1254, 1172, 1095, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ =8.15 (s, 1H), 7.58 (d, J = 15.6 Hz, 1H), 7.45 (d, J =8.8 Hz, 2H), 7.85 (d, J =8.4 Hz, 2H), 6.61 (d, J = 16.4 Hz, 1H), 4.96 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =191.2, 162.1, 160.0, 144.3, 130.4, 126.5, 118.8, 114.5, 66.6, 55.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}O_4$: 2243.0628; found: 243.0651.

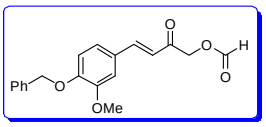
(E)-4-(3,4-dimethoxyphenyl)-2-oxobut-3-en-1-yl formate (**2r**)



IR (KBr): 3417, 2937, 2841, 1716, 1680, 1620, 1594, 1515, 1423, 1268, 1234, 1166, 1139, 1084, 1022 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.24 (s, 1H), 7.65 (d, J = 16.2 Hz, 1H), 7.17 (d, J =7.8 Hz, 1H), 7.08 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 16.2 Hz, 1H), 5.05 (s, 2H), 3.94 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.2, 160.0, 151.8, 149.2, 144.6, 126.7, 123.7, 118.9, 111.0, 110.0, 66.5, 55.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{15}O_5$: 251.09061; found: 251.09140.

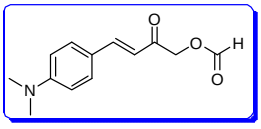
(E)-4-(4-(benzyloxy)-3-methoxyphenyl)-2-oxobut-3-en-1-yl formate (**2s**)

IR (KBr): 3442, 2943, 1724, 1676, 1619, 1593, 1515, 1469, 1425, 1384, 1271, 1235, 1141, 1087, 1034 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.21 (s, 1H), 7.61 (d, J = 16.2 Hz, 1H), 7.38-7.36 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.08 (s, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 16.2 Hz, 1H), 5.19 (s, 2H), 5.01 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.1, 159.9, 151.0, 149.7, 144.5, 136.3, 128.6, 128.0, 127.1, 123.3, 119.1, 113.3, 110.4, 70.7, 66.5, 56.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{18}O_5$: 349.1046; found: 349.1040.

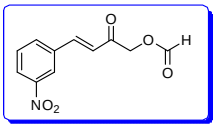


(E)-4-(4-(dimethylamino)phenyl)-2-oxobut-3-en-1-yl formate (**2t**)

IR (KBr): 3437, 2925, 1725, 1688, 1666, 1580, 1528, 1436, 1370, 1268, 1227, 1173, 1144, 1083 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ =8.23 (s, 1H), 7.64 (d, J = 16.2 Hz, 1H), 7.46 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 16.2 Hz, 1H), 5.01 (s, 2H), 3.05 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.1, 160.1, 152.3, 145.4, 130.6, 121.5, 115.8, 111.8, 66.5, 40.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{13}NO_3$: 256.0944; found: 256.0940.

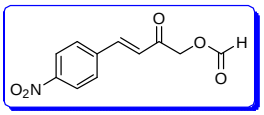


(E)-4-(3-nitrophenyl)-2-oxobut-3-en-1-yl formate (**2u**)



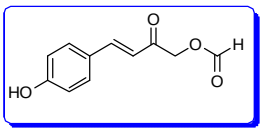
IR (KBr): 3436, 3071, 2929, 1727, 0718, 1680, 1629, 1526, 1430, 1354, 1206, 1171, 1099 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.21 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 16.2 Hz, 1H), 7.60-7.69 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 16.8 Hz, 1H), 5.04 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.0, 159.9, 159.8, 148.6, 141.4, 135.6, 134.2, 130.1, 125.1, 123.4, 122.6, 122.5, 66.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{10}NO_5$: 236.05444; found: 236.05535.

(E)-4-(4-nitrophenyl)-2-oxobut-3-en-1-yl formate (**2v**)



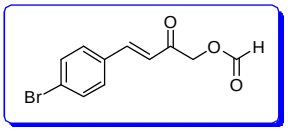
IR (KBr): 3421, 3112, 3065, 2931, 1718, 1681, 1593, 1513, 1343, 1178, 1106 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.4 Hz, 2H), 8.24 (s, 1H), 7.74 (d, J = 8.4 Hz, 3H), 6.94 (d, J = 15.6 Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.0, 159.8, 148.8, 141.4, 140.0, 129.1, 124.4, 124.3, 66.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_9NO_5$: 236.0553; found: 236.0558.

(E)-4-(4-hydroxyphenyl)-2-oxobut-3-en-1-yl formate (**2w**)



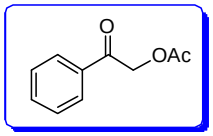
IR (KBr): 3380, 2925, 2855, 1729, 1682, 1584, 1515, 1453, 1379, 1286, 1171, 1024 cm^{-1}; ^1H NMR (600 MHz, DMSO): δ = 10.21 (s, 1H), 8.39 (s, 1H), 7.65 (d, J = 16.8 Hz, 1H), 7.61 (d, J =8.4 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 16.8 Hz, 1H), 5.15 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =192.0, 160.3, 143.9, 130.9, 125.2, 119.0, 116.0, 66.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{10}O_4$: 229.0471; found: 229.0782.

(E)-4-(4-bromophenyl)-2-oxobut-3-en-1-yl formate (**2x**)



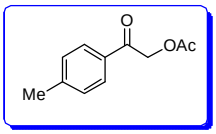
IR (KBr): 3433, 2998, 2934, 1725, 1666, 1620, 1584, 1486, 1428, 1391, 1285, 1261, 1190, 1164, 1072, 1008 cm^{-1}; ^1H NMR (600 MHz, DMSO): δ = 8.22 (s, 1H), 7.62 (d, J = 16.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.43 (d, J =8.4 Hz, 2H), 6.80 (d, J = 16.2 Hz, 1H), 5.02 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =191.2, 159.9, 143.1, 132.7, 132.3, 129.8, 125.5, 121.5, 66.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_9BrO_3$: 29.09627; found: 290.9631.

2-oxo-2-phenylethyl acetate (**3a**)



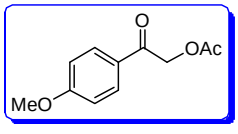
IR (KBr): 3472, 3064, 2937, 1750, 1703, 1597, 1448, 1422, 1375, 1221, 1085, 998 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.59-7.63 (t, J = 7.2 Hz, 1H), 7.47-4.51 (t, J = 7.2 Hz), 5.35 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =192.1, 170.4, 134.0, 133.8, 128.8, 127.7, 66.0, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_{11}O_3$: 179.07027; found: 179.06977.

2-oxo-2-(p-tolyl)ethyl acetate (**3b**)



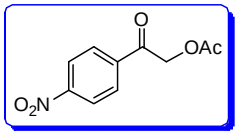
IR (KBr): 3465, 2954, 1749, 1699, 1605, 1420, 1372, 1289, 1226, 1180, 1085, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.25 (s, 2H), 5.35 (s, 3H), 2.16 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ =191.7, 144.8, 131.6, 129.5, 129.4, 128.7, 127.8, 65.9, 21.7, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{12}O_3$: 215.0679; found: 215.0680.

2-(4-methoxyphenyl)-2-oxoethyl acetate (**3c**)



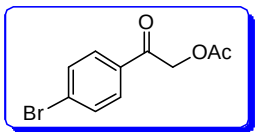
IR (KBr): 3465, 3040, 2954, 1926, 1749, 1696, 1605, 1571, 1420, 1372, 1289, 1226, 1180, 1085, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.92 (m, 2H), 7.95-7.98 (m, 2H), 5.31 (s, 2H), 3.89 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.6, 170.5, 164.0, 130.0, 127.1, 65.7, 55.5, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{13}O_4$: 209.07980; found: 209.08084.

2-(4-nitrophenyl)-2-oxoethyl acetate (**3d**)



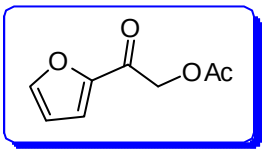
IR (KBr): 3478, 3119, 2926, 2855, 1748, 1703, 1603, 1524, 1416, 1373, 1348, 1319, 1284, 1248, 1218, 1107, 1081 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 5.34 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 170.3, 150.7, 138.6, 128.9, 124.1, 66.0, 29.7, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_{10}NO_5$: 224.05463; found: 224.05535.

2-(4-bromophenyl)-2-oxoethyl acetate (**3e**)



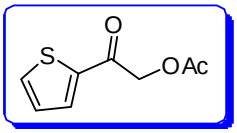
IR (KBr): 3487, 3376, 2990, 2950, 1746, 1694, 1585, 1430, 1398, 1378, 1292, 1225, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77-7.80 (m, 2H), 7.63-7.65 (m, 2H), 5.30 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 170.3, 132.8, 132.2, 129.2, 129.1, 65.8, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_9BrO_3$: 278.9627; found: 278.9631.

2-(furan-2-yl)-2-oxoethyl acetate (**3f**)



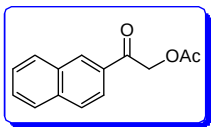
IR (KBr): 3484, 3135, 2942, 1751, 1693, 1572, 1469, 1421, 1400, 1374, 1229, 1162, 1080, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 4.0 Hz, 1H), 6.58-6.59 (q, J = 2 Hz, 1H), 5.19 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.7, 170.3, 150.5, 146.7, 117.7, 112.5, 65.3, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_8H_8O_4$: 191.0315; found: 191.0312.

2-oxo-2-(thiophen-2-yl)ethyl acetate (**3g**)



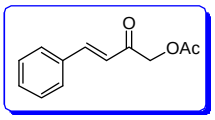
IR (KBr): 3484, 3135, 2942, 1751, 1693, 1572, 1469, 1421, 1400, 1374, 1229, 1162, 1080, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 4.8 Hz, 1H), 7.16-7.18 (t, J = 4.4 Hz, 1H), 5.23 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.4, 170.3, 134.3, 131.9, 128.2, 65.7, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_8H_8O_3S$: 207.0086; found: 207.0082.

2-(naphthalen-2-yl)-2-oxoethyl acetate (**3h**)



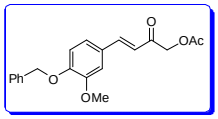
IR (KBr): 3466, 3062, 2943, 1750, 1696, 1624, 1592, 1467, 1417, 1375, 1235, 1176, 1081, 1026, 1008 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 7.951-7.976 (q, J = 8.4 Hz, 2H), 7.891-7.938 (t, J = 8.4 Hz, 1H), 7.56-7.62 (m, 2H), 5.47 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 170.5, 135.9, 132.3, 131.5, 129.5, 128.8, 127.8, 127.0, 123.2, 66.1, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{12}O_3$: 251.0679; found: 251.0885.

(E)-2-oxo-4-phenylbut-3-en-1-yl acetate (**3o**)



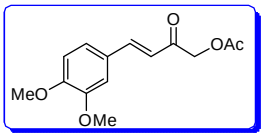
IR (KBr): 3457, 2932, 1751, 1705, 1688, 1615, 1450, 1419, 1377, 1232, 1195, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 16.4 Hz, 1H), 7.55-7.58 (q, J = 6.8 Hz, 2H), 6.79 (s, J = 16.0 Hz, 1H), 4.95 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.41, 170.3, 144.2, 134.0, 131.0, 129.0, 128.5, 121.5, 67.4, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}O_3$: 227.0679; found: 227.5765.

(E)-4-(4-(benzyloxy)-3-methoxyphenyl)-2-oxobut-3-en-1-yl acetate (**3r**)



IR (KBr): 3452, 3016, 2923, 1724, 1680, 1620, 1513, 1454, 1424, 1384, 1367, 1326, 1271, 1226, 1200, 1168, 1137, 1066, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.36-7.40 (m, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.071-7.091 (q, J = 6.0 Hz, 1H), 6.89 (d, J = 9.2 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 5.21 (s, 2H), 4.94 (s, 2H), 3.93 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 170.4, 150.9, 149.7, 144.1, 136.3, 128.7, 128.1, 127.2, 123.2, 119.5, 113.3, 110.3, 70.8, 67.2, 56.0, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{20}O_5$: 341.1384; found: 341.1387.

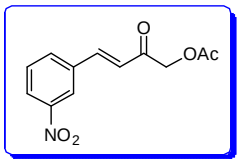
(E)-4-(3,4-dimethoxyphenyl)-2-oxobut-3-en-1-yl acetate (**3s**)



IR (KBr): 3444, 2998, 2916, 1837, 1736, 1696, 1593, 1512, 1466, 1424, 1378, 1263, 1162, 1143, 1112, 1052, 1021 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 16.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 15.6 Hz, 1H), 4.96 (s, 2H), 3.93 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 170.4, 150.9, 149.7, 144.1, 136.3, 128.7, 128.1, 127.2, 123.2, 119.5,

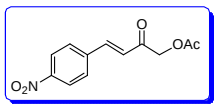
113.3, 110.3, 70.8, 67.2, 56.0, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}O_5$: 287.0890; found: 287.0888.

(E)-4-(3-nitrophenyl)-2-oxobut-3-en-1-yl acetate (**3v**)



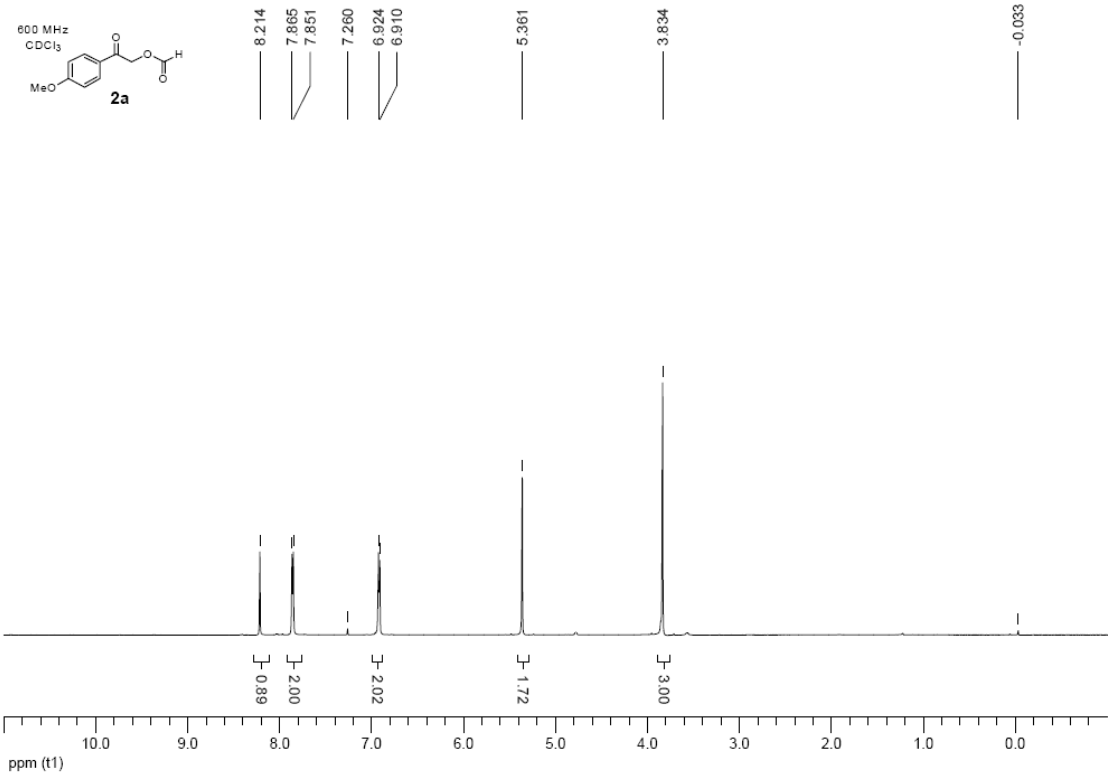
IR (KBr): 3460, 3067, 2927, 2855, 1740, 1667, 1630, 1528, 1439, 1384, 1351, 1250, 1199, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 8.26 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 16.04 Hz, 1H), 7.612-7.685 (t, J = 8.4 Hz, 1H), 6.91 (d, J = 16.4 Hz, 2H), 4.95 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 141.1, 134.2, 130.1, 125.1, 123.7, 122.6, 67.6, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}NO_5$: 250.07035; found: 250.07100.

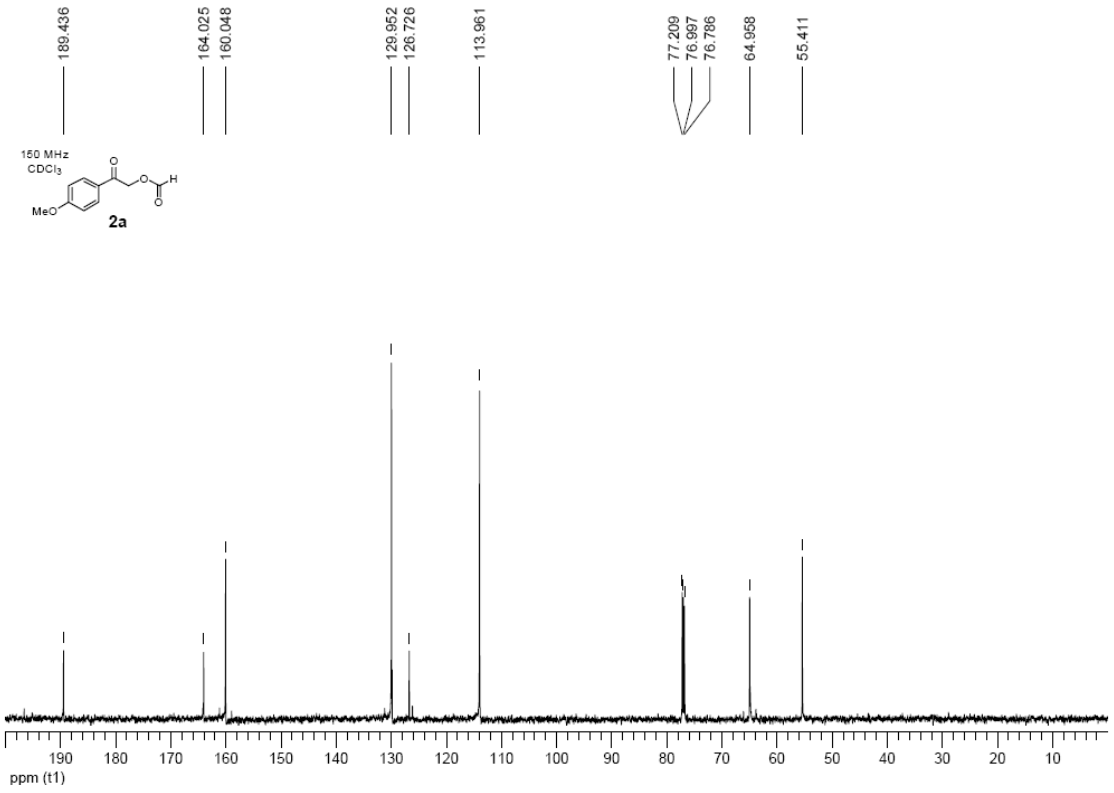
(E)-4-(4-nitrophenyl)-2-oxobut-3-en-1-yl acetate (**3w**)

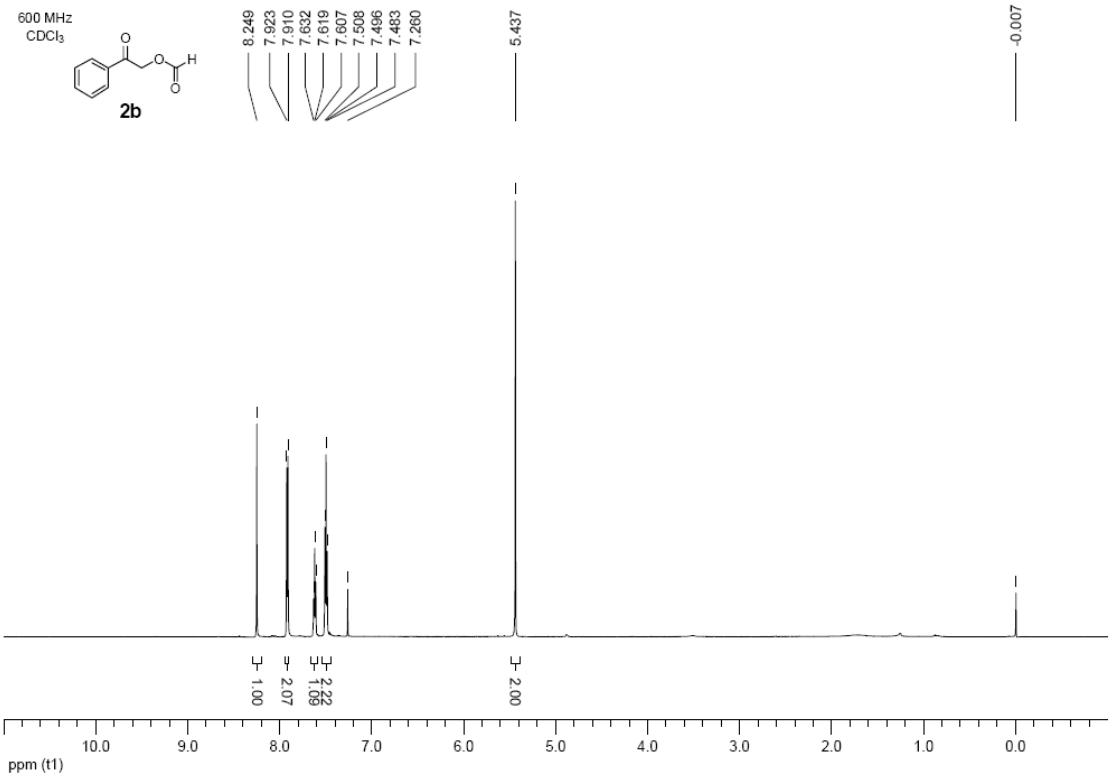


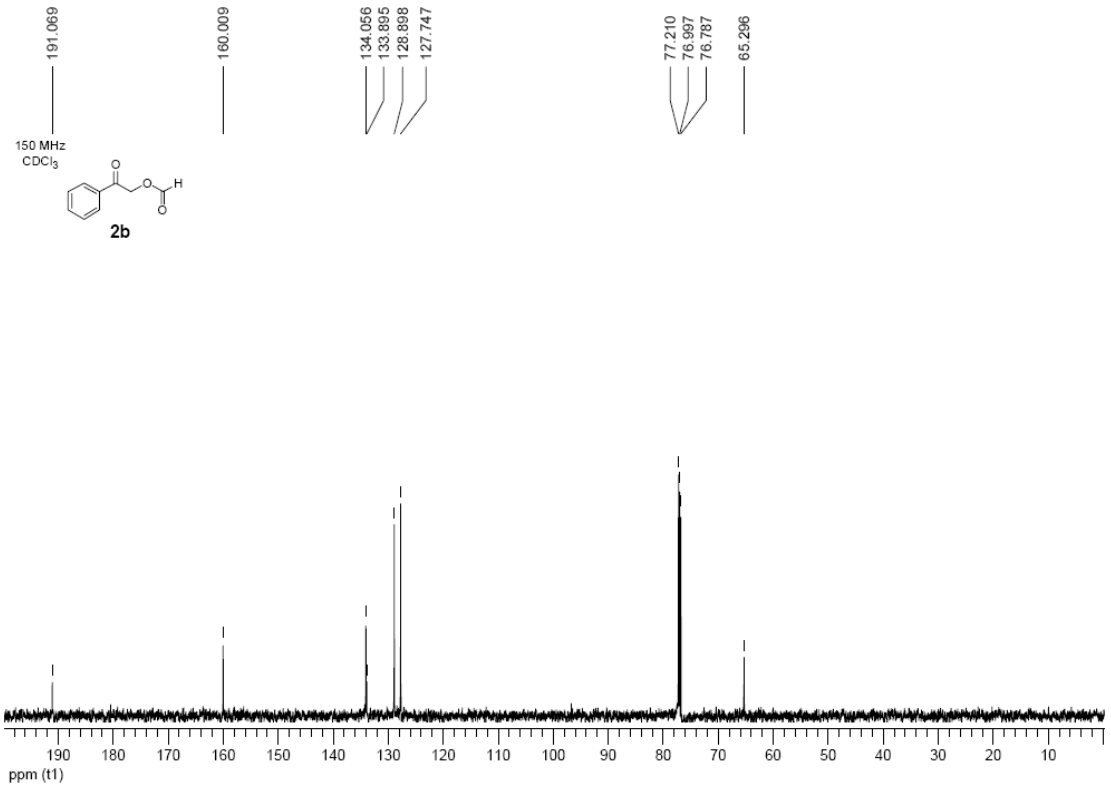
IR (KBr): 3443, 2927, 1740, 1702, 1621, 1594, 1513, 1415, 1349, 1265, 1235, 1115, 1058, 1002cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.68 (s, 1H), 6.90 (d, J = 16.4 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 170.2, 148.8, 141.0, 140.1, 129.0, 124.8, 124.2, 67.6, 20.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}NO_5$: 250.07035; found: 250.07100.

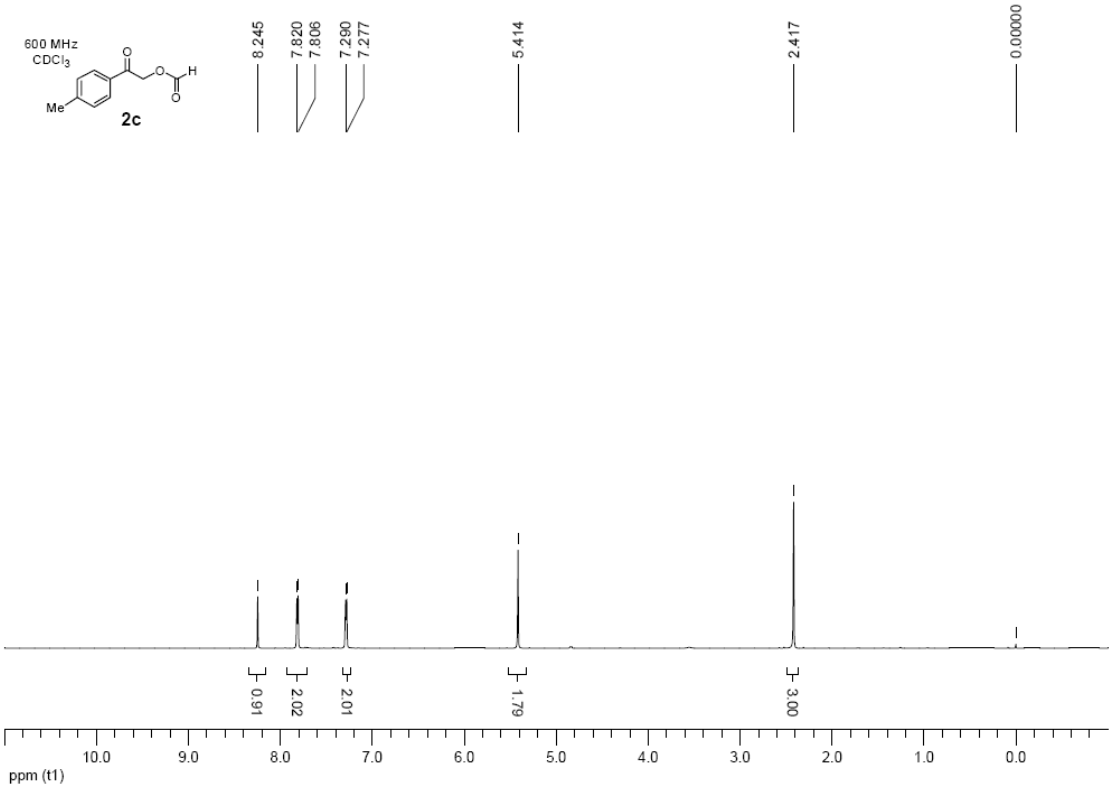
7. **Appendix:** spectral Copies of ^1H NMR and ^{13}C NMR of compounds obtained in this Study

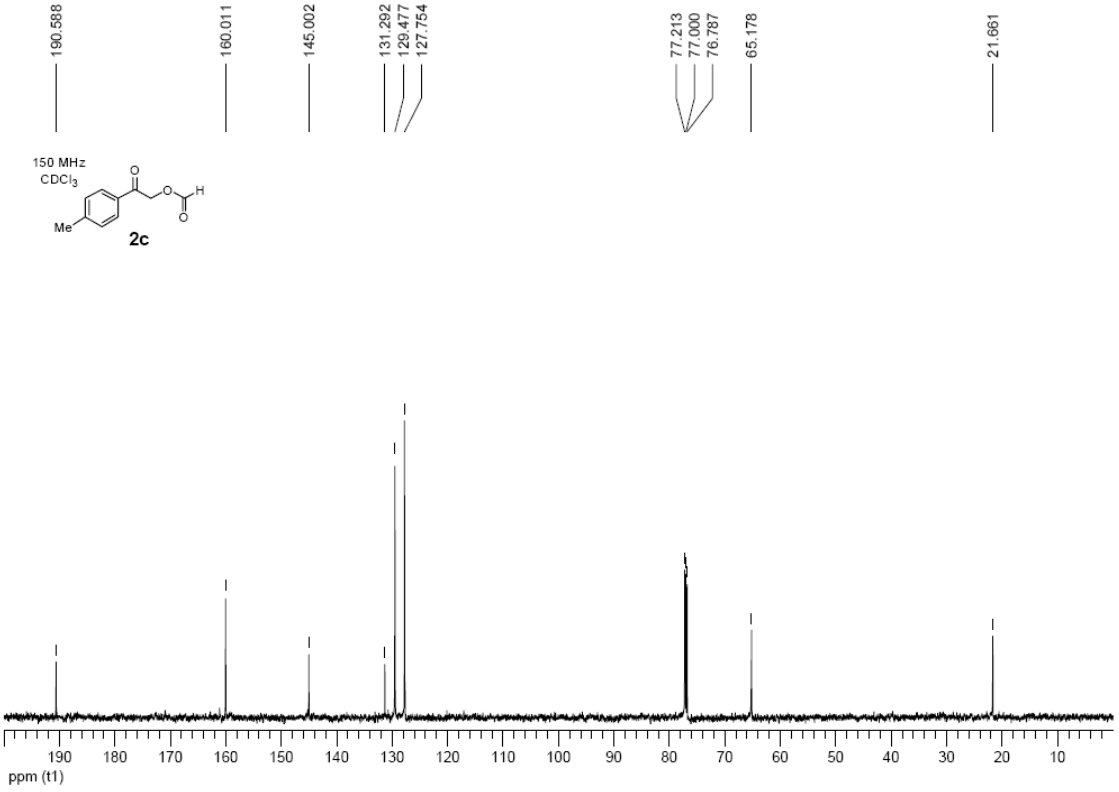


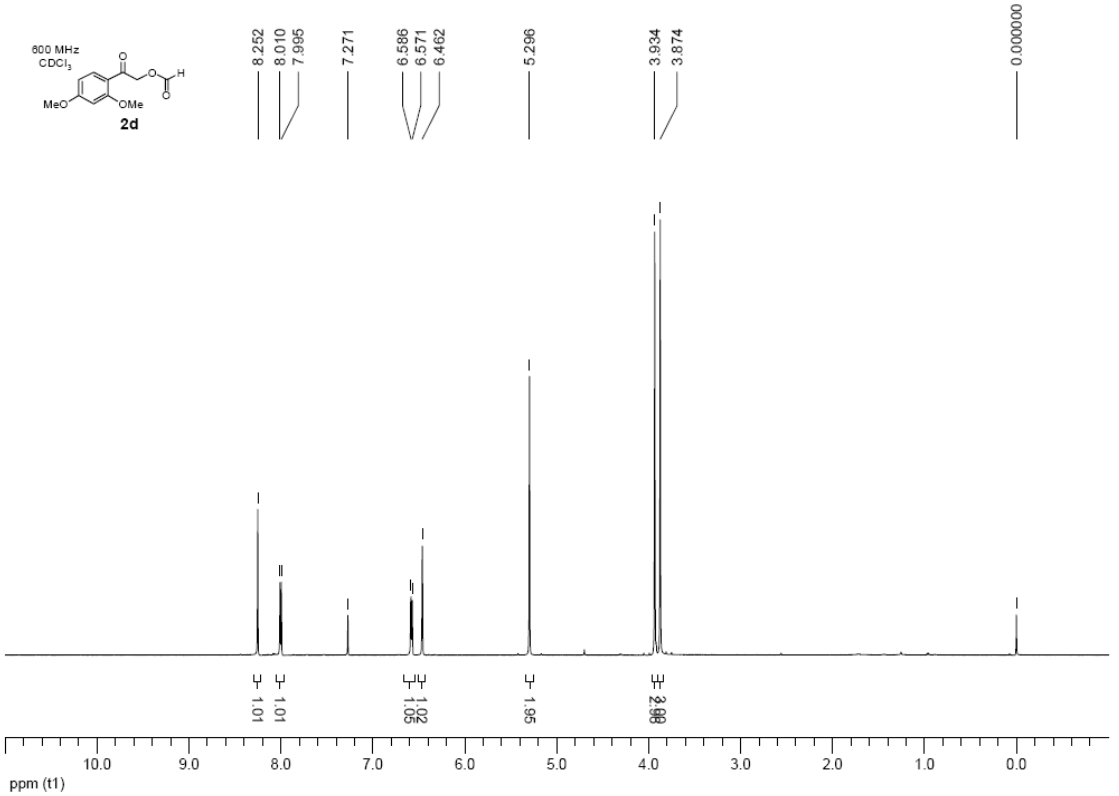

189.436
164.025
160.048
129.952
126.726
113.961
77.209
76.997
76.786
64.958
55.411
150 MHz
CDCl3
MeO
2a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

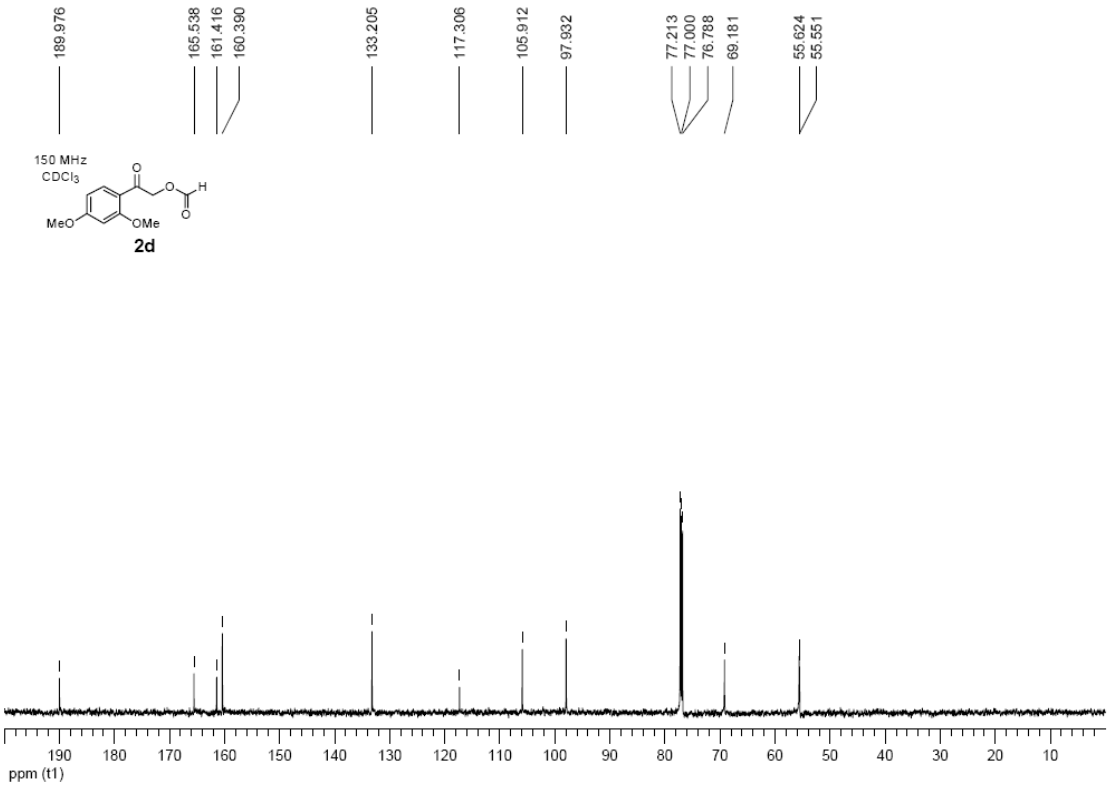

600 MHz
CDCl3
2b
8.249
7.923
7.910
7.632
7.619
7.607
7.508
7.496
7.483
7.260
5.437
-0.007
1.00
2.07
1.09
2.22
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

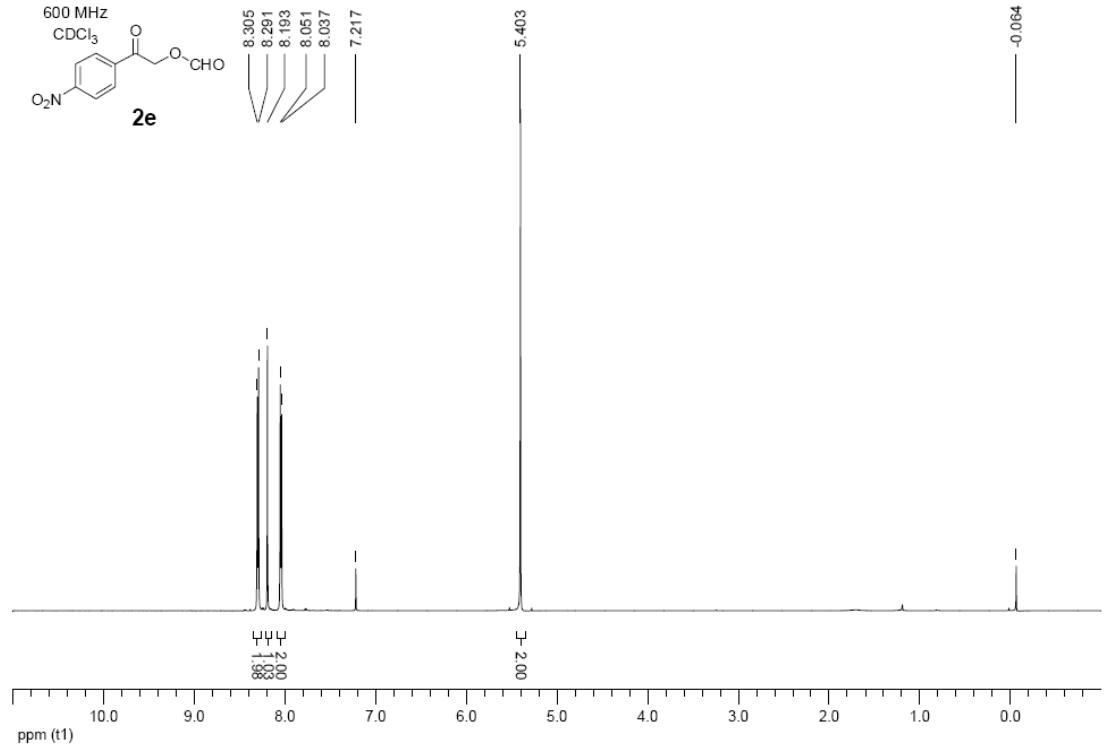

191.069
160.009
134.056
133.895
128.898
127.747
77.210
76.997
76.787
65.296
150 MHz
CDCl3
2b
ppm (t1)

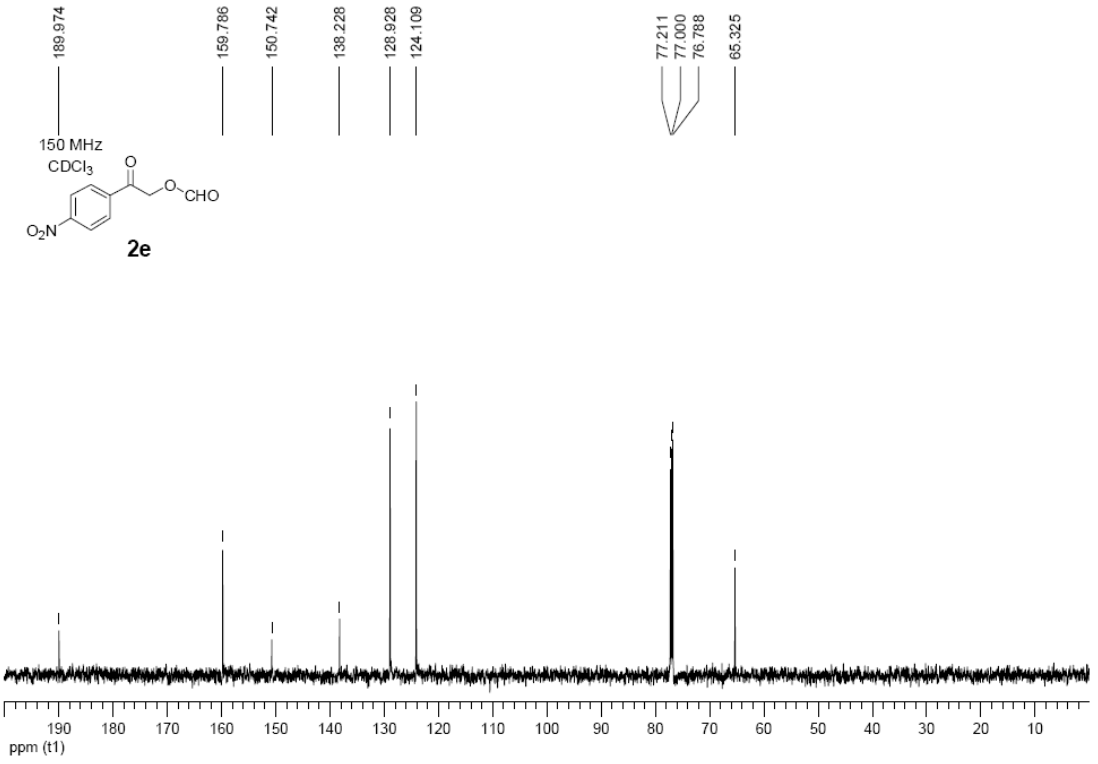

600 MHz
CDCl3
Me
2c
8.245
7.820
7.806
7.290
7.277
5.414
2.417
0.00000
0.91
2.02
2.01
1.79
3.00
ppm (t1)

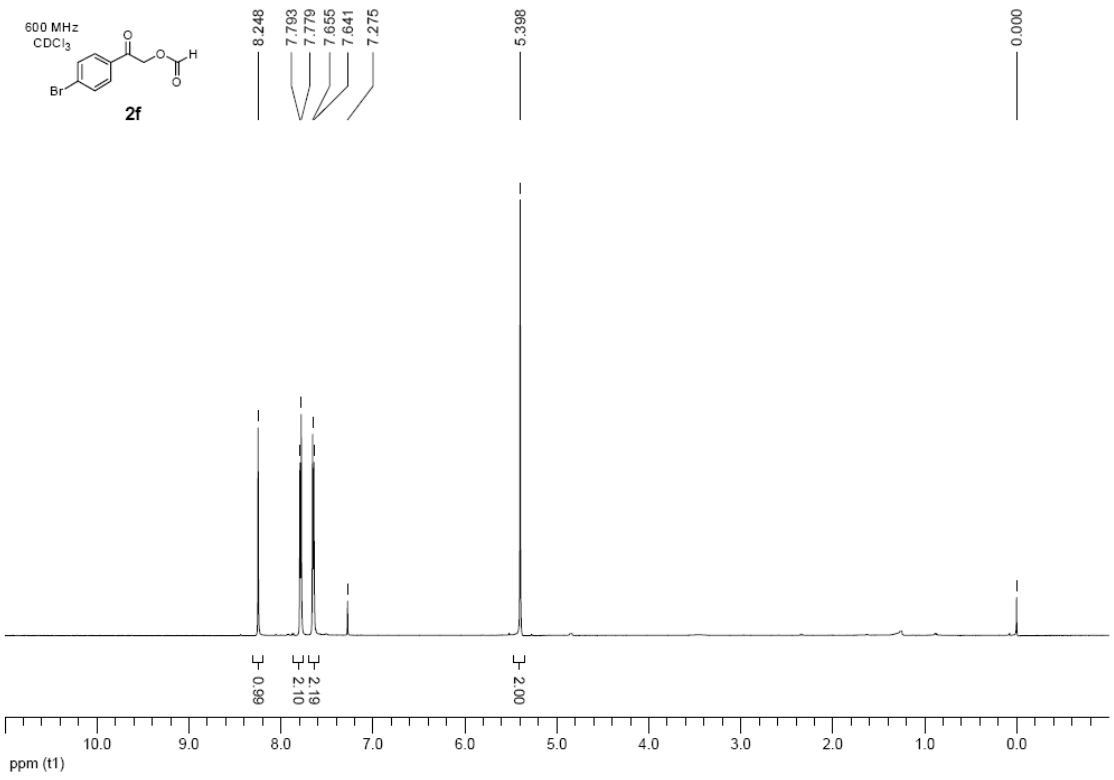

190.588
160.011
145.002
131.292
129.477
127.754
77.213
77.000
76.787
65.178
21.661
150 MHz
CDCl3
Me
2c
ppm (t1)

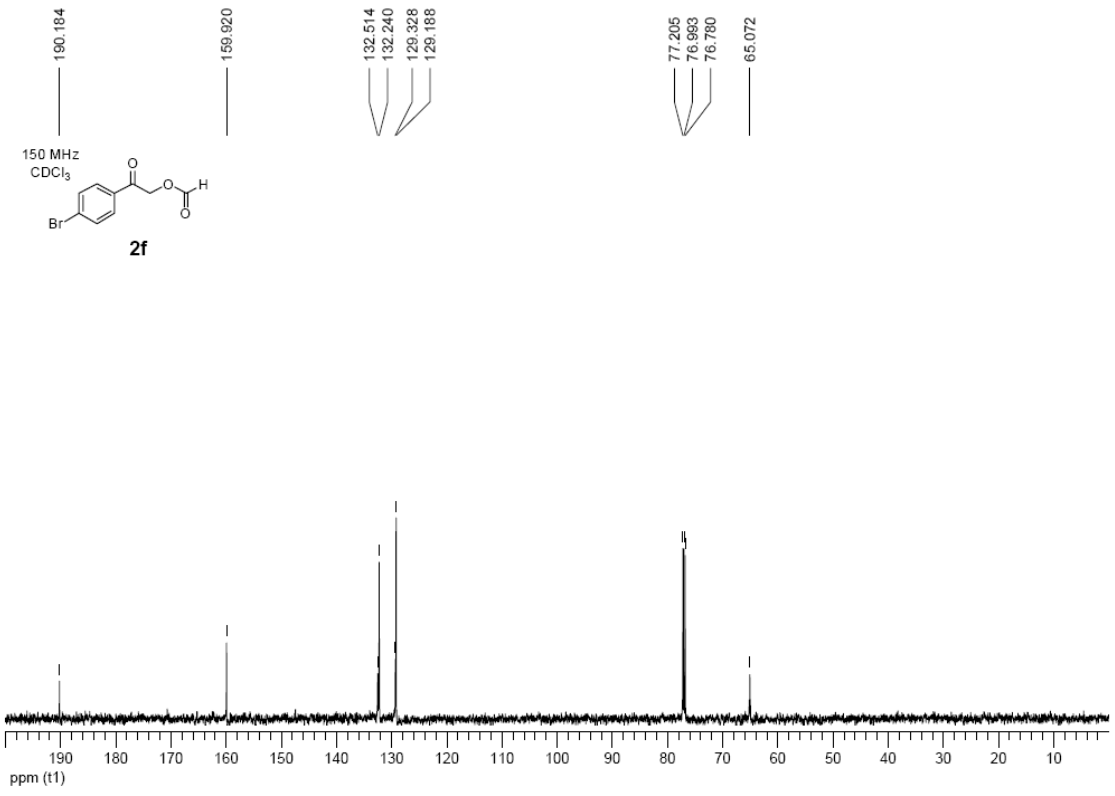

600 MHz
CDCl3
MeO
OMe
2d
8.252
8.010
7.995
7.271
6.586
6.571
6.462
5.296
3.934
3.874
0.000000
1.01
1.01
1.02
2.00
1.96
3.00
ppm (t1)

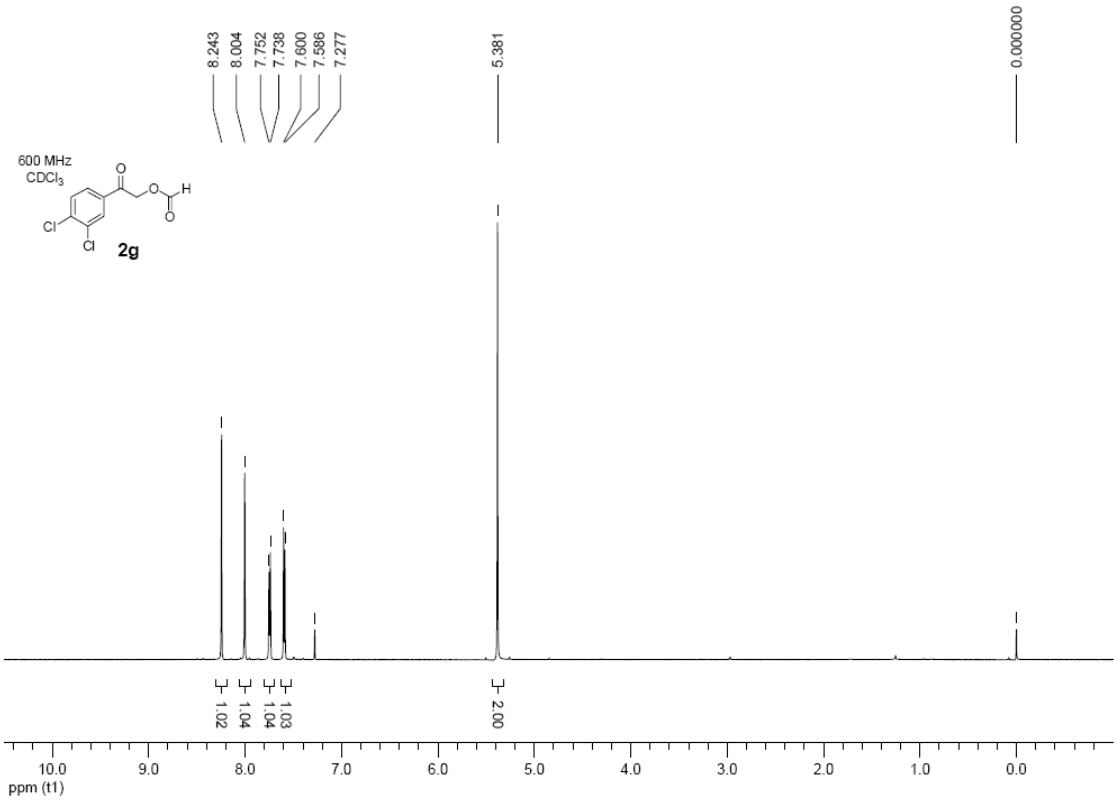

189.976
165.538
161.416
160.390
133.205
117.306
105.912
97.932
77.213
77.000
76.788
69.181
55.624
55.551
150 MHz
CDCl3
MeO
OMe
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

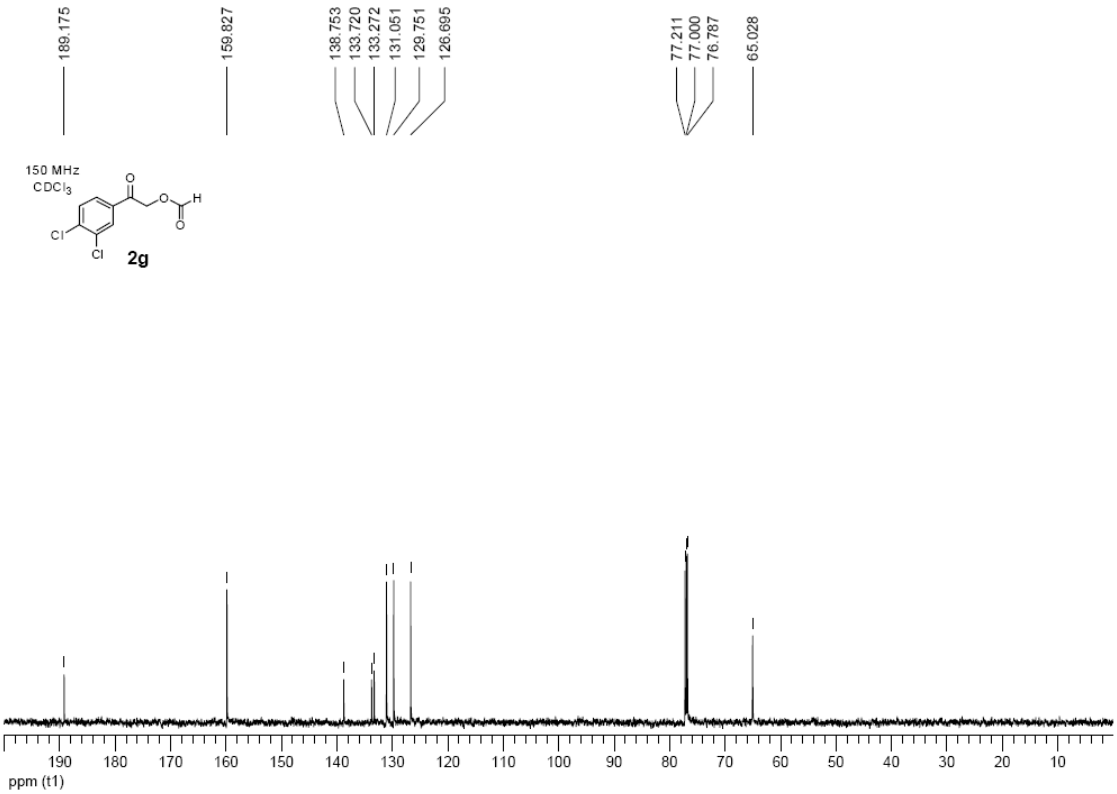

600 MHz
CDCl3
O2N
CHO
2e
8.305
8.291
8.193
8.051
8.037
7.217
5.403
-0.064
1.98
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

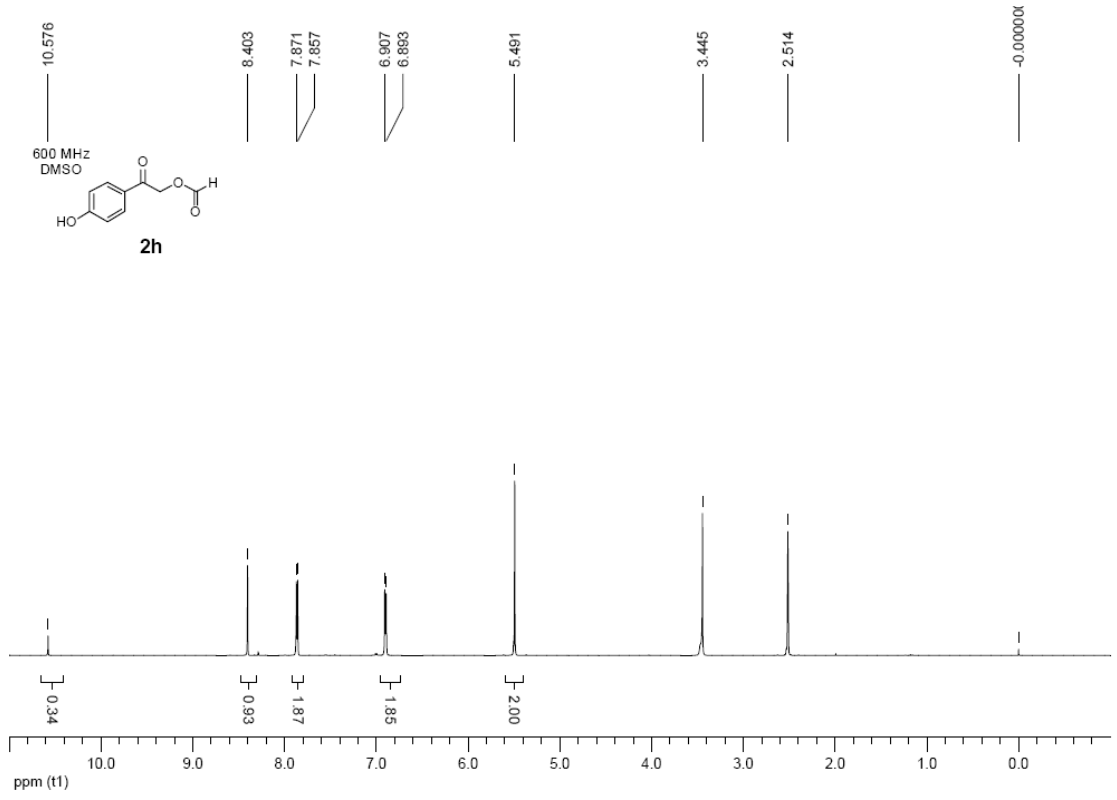

189.974
159.786
150.742
138.228
128.928
124.109
77.211
77.000
76.788
65.325
150 MHz
CDCl3
O
O
CHO
O2N
2e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

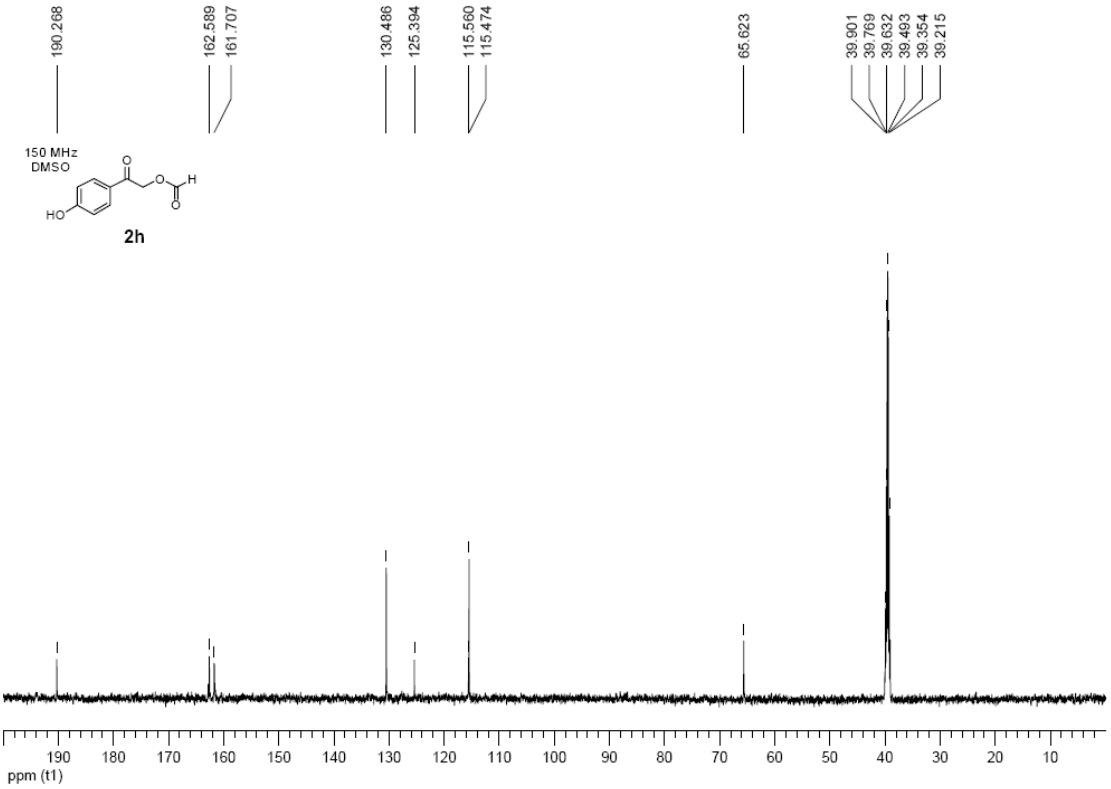

600 MHz
CDCl3
O
O
H
O
Br
2f
8.248
7.793
7.779
7.655
7.641
7.275
5.398
0.000
0.99
2.10
2.19
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

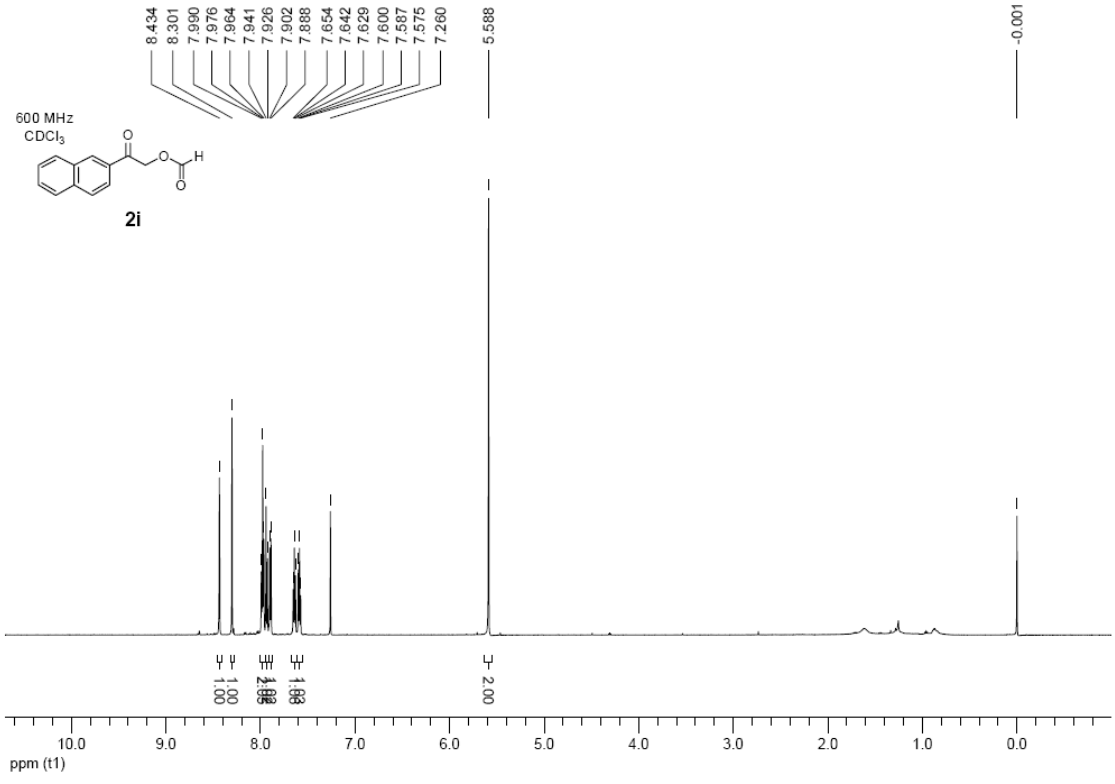

190.184
159.920
132.514
132.240
129.328
129.188
77.205
76.983
76.780
65.072
150 MHz
CDCl3
Br
2f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

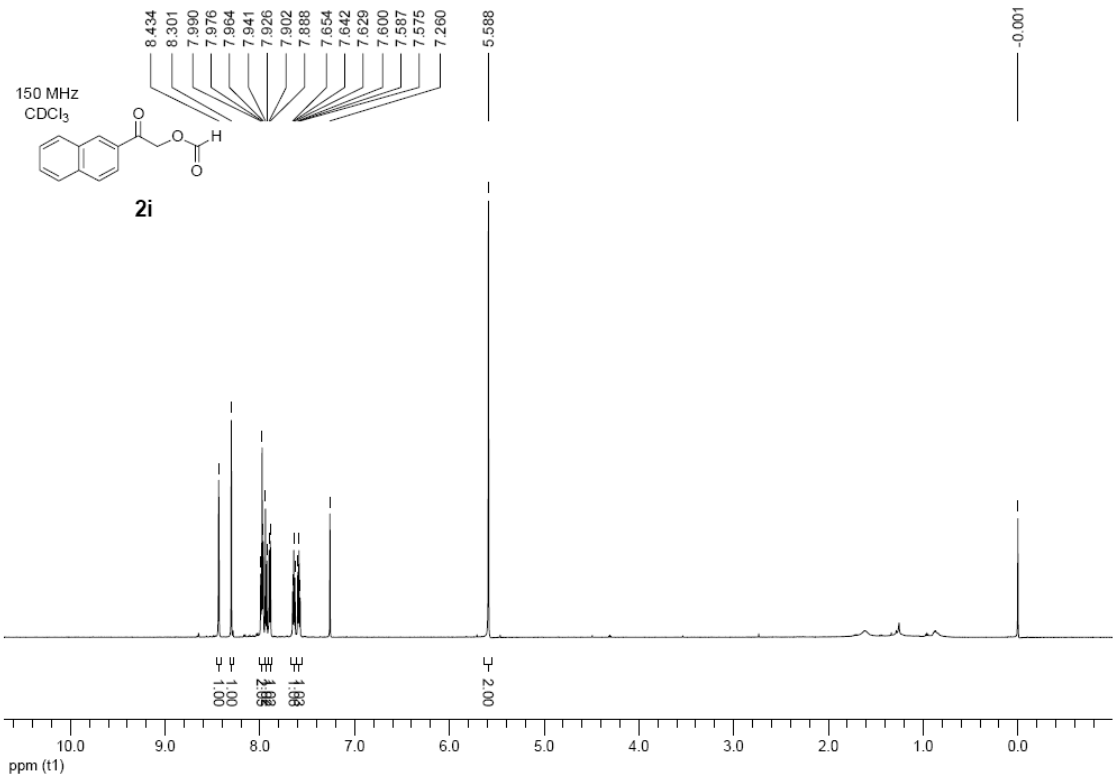

8.243
8.004
7.752
7.738
7.600
7.586
7.277
5.381
0.000000
600 MHz
CDCl3
Cl
Cl
2g
1.02
1.04
1.04
1.03
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

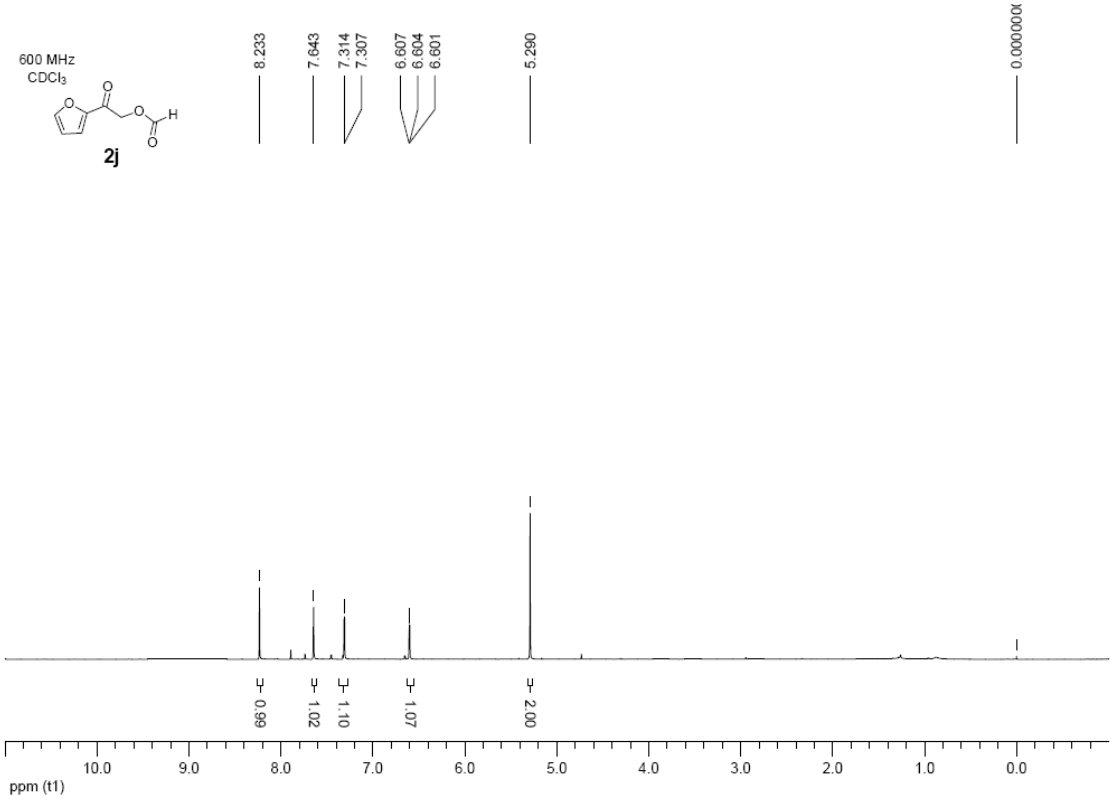

189.175
159.827
138.753
133.720
133.272
131.051
129.751
126.695
77.211
77.000
76.787
65.028
150 MHz
CDCl3
Cl
Cl
2g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

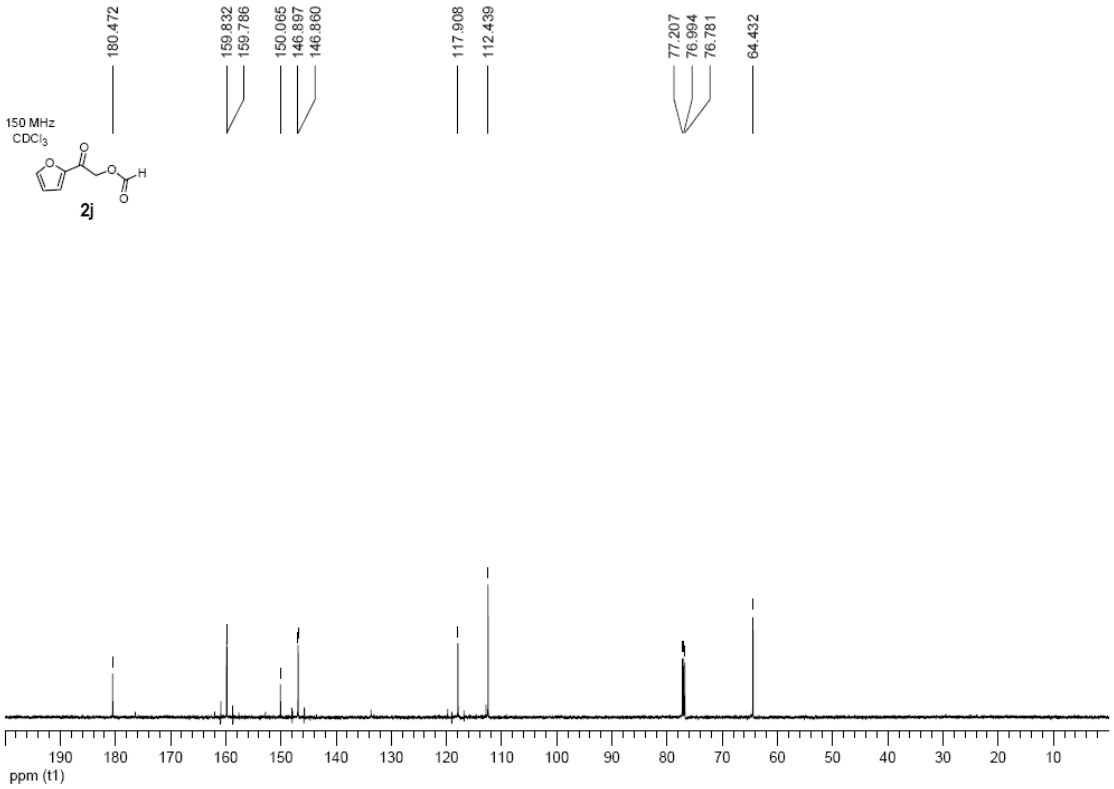

10.576
8.403
7.871
7.857
6.907
6.893
5.491
3.445
2.514
-0.000000
600 MHz
DMSO
HO
2h
0.34
0.93
1.87
1.85
2.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

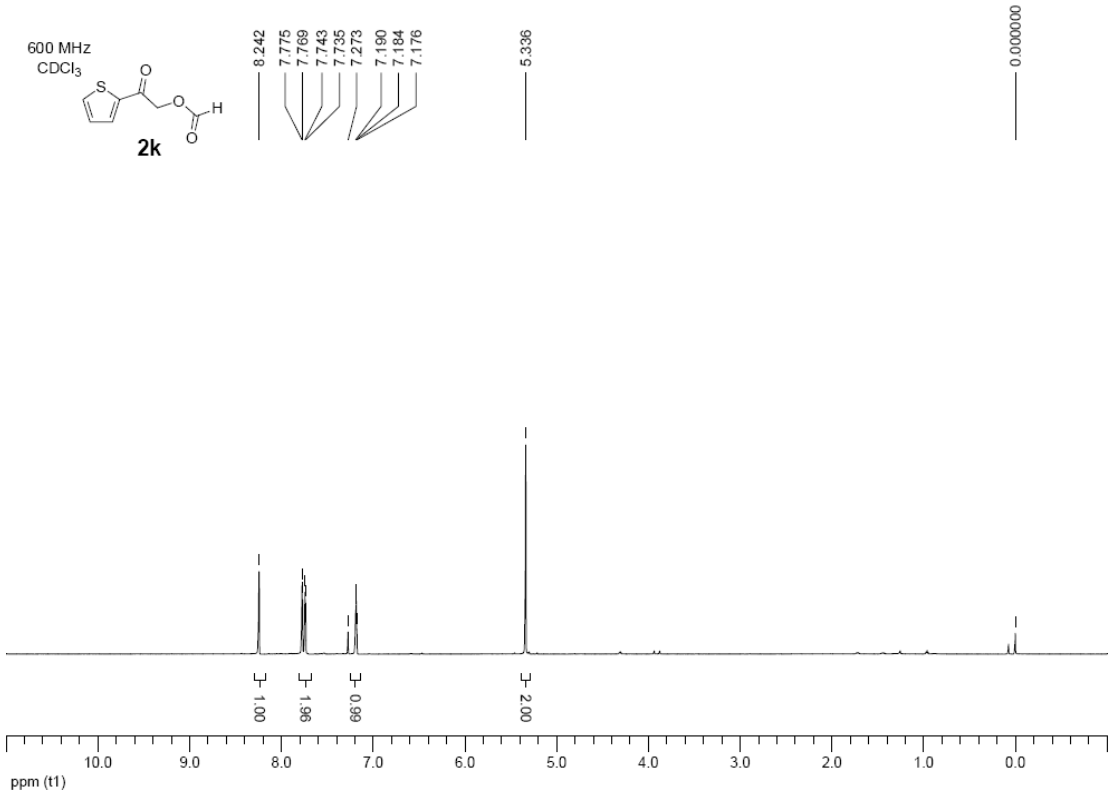

190.268
162.589
161.707
130.486
125.394
115.560
115.474
65.623
39.901
39.769
39.632
39.493
39.354
39.215
150 MHz
DMSO
HO
O
O
O
H
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

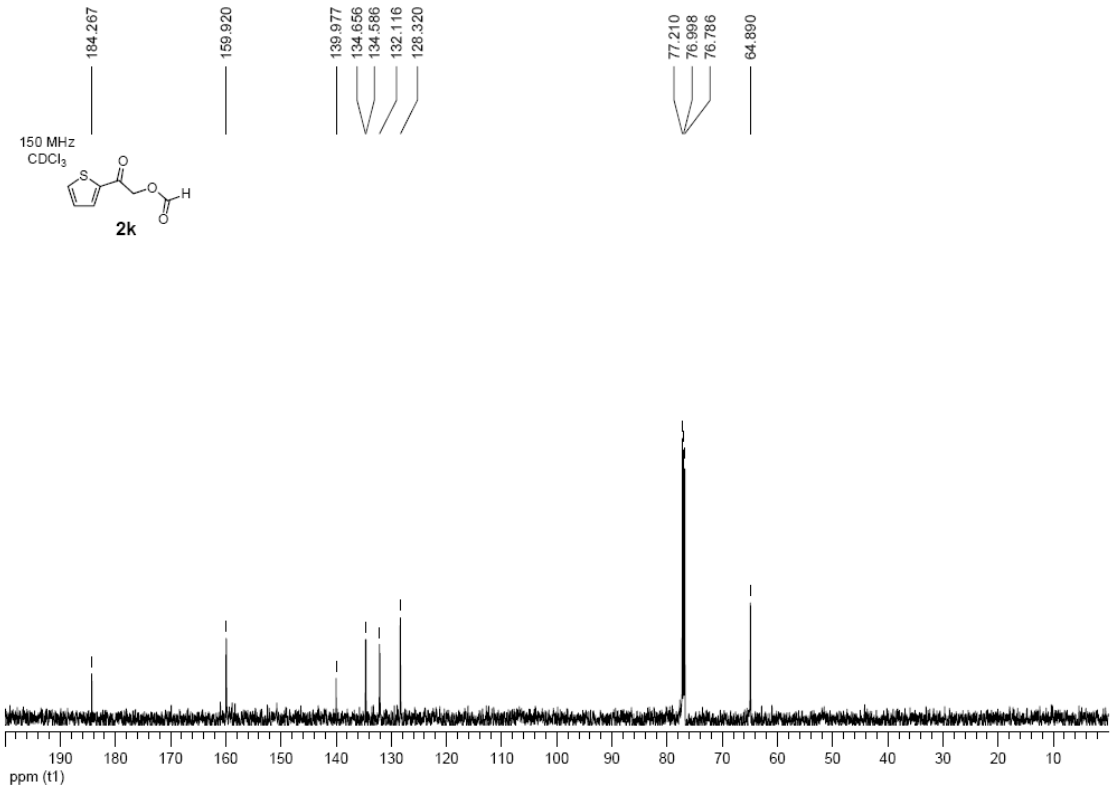

8.434
8.301
7.990
7.976
7.964
7.941
7.926
7.902
7.888
7.654
7.642
7.629
7.600
7.587
7.575
7.260
5.588
-0.001
600 MHz
CDCl3
O
O
O
H
2i
1.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

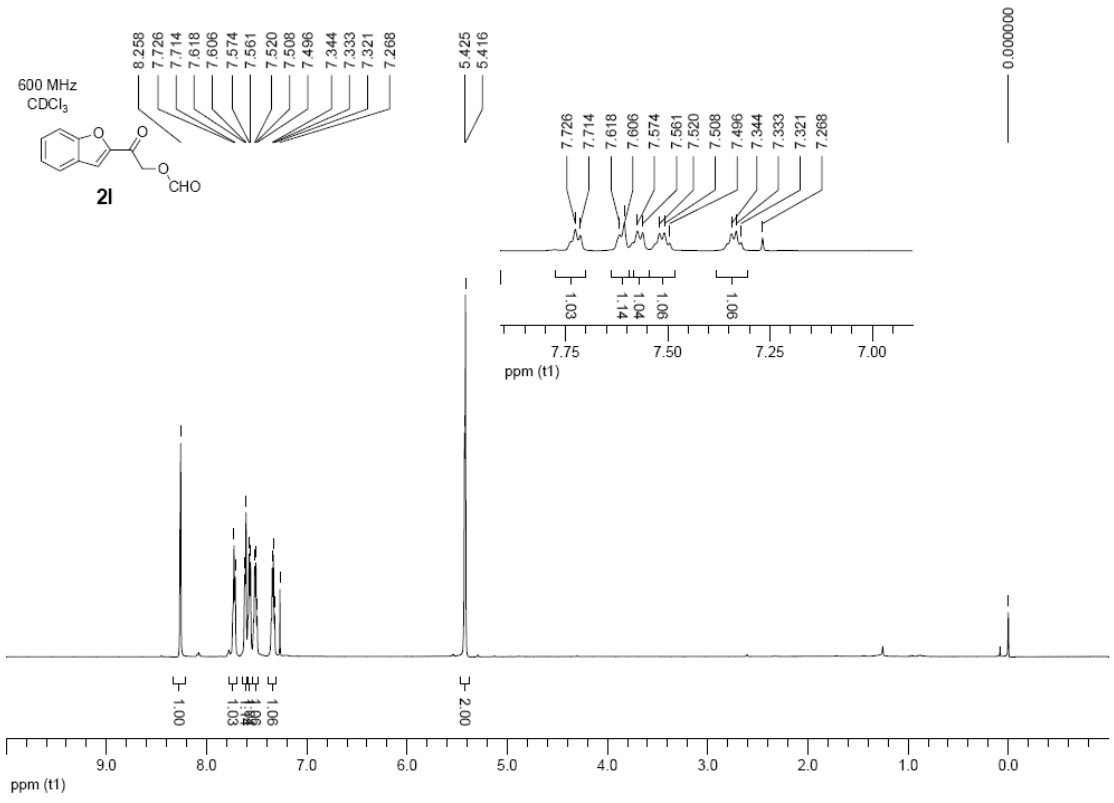

8.434
8.301
7.990
7.976
7.964
7.941
7.926
7.902
7.888
7.654
7.642
7.629
7.600
7.587
7.575
7.260
5.588
-0.001
150 MHz
CDCl3
2i
1.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

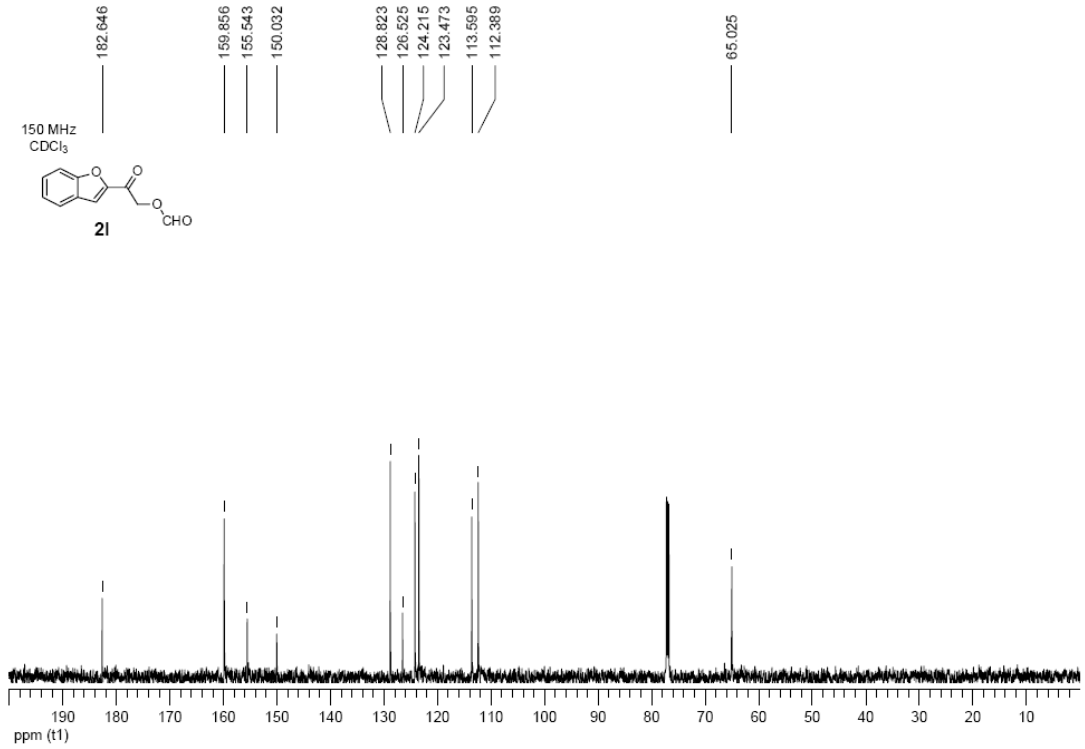

8.233
7.643
7.314
7.307
6.607
6.604
6.601
5.260
0.000000
600 MHz
CDCl3
2j
0.99
1.02
1.10
1.07
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

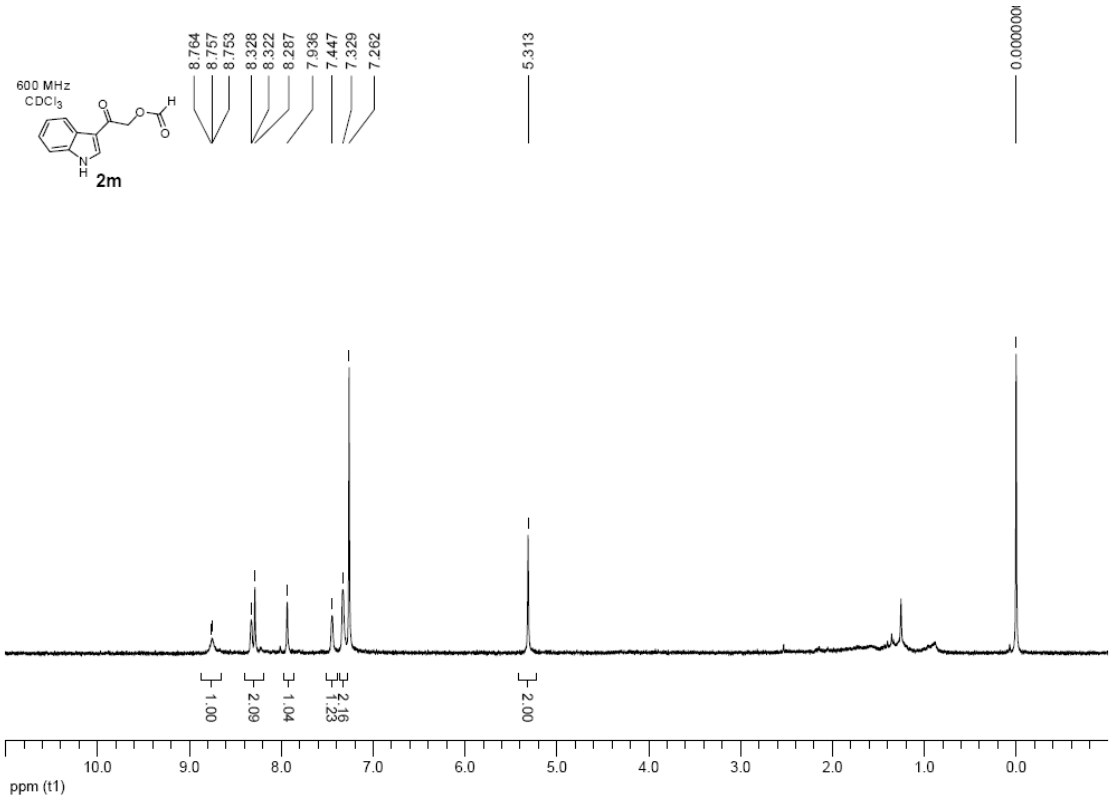

180.472
159.832
159.786
150.065
146.897
146.860
117.908
112.439
77.207
76.994
76.781
64.432
150 MHz
CDCl3
2j
ppm (t1)

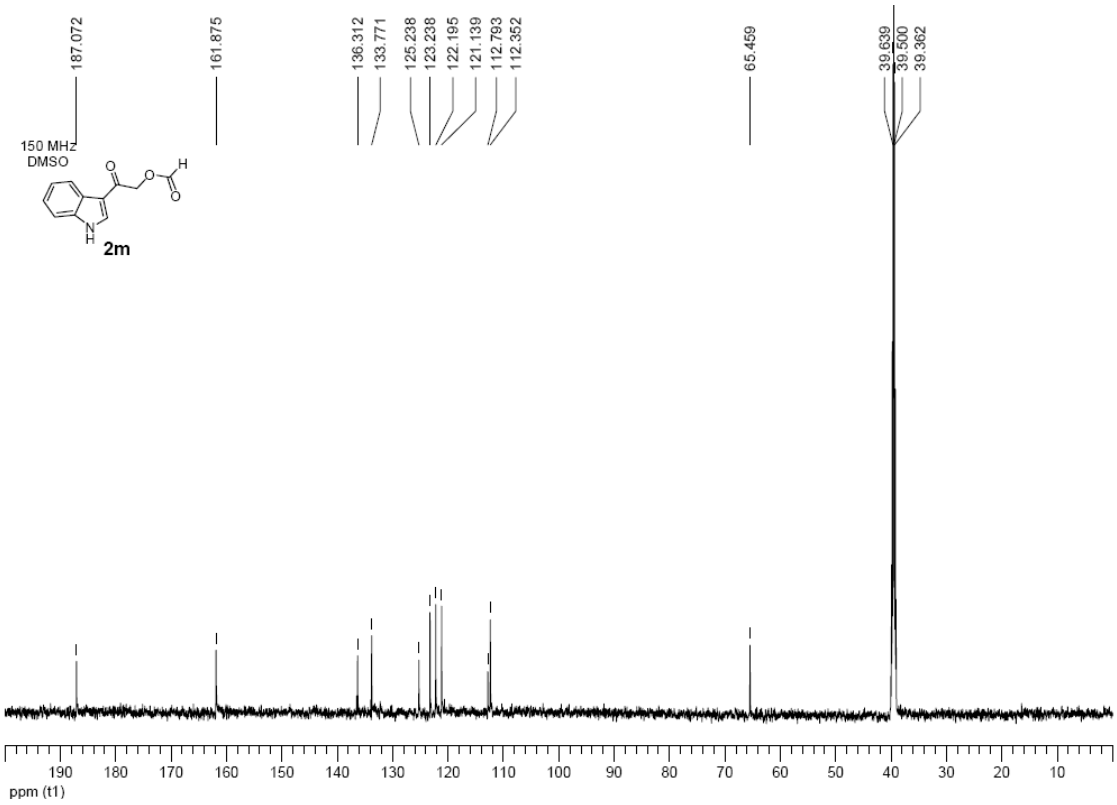

600 MHz
CDCl3
8.242
7.775
7.769
7.743
7.735
7.273
7.190
7.184
7.176
5.336
0.000000
2k
1.00
1.96
0.99
2.00
ppm (t1)

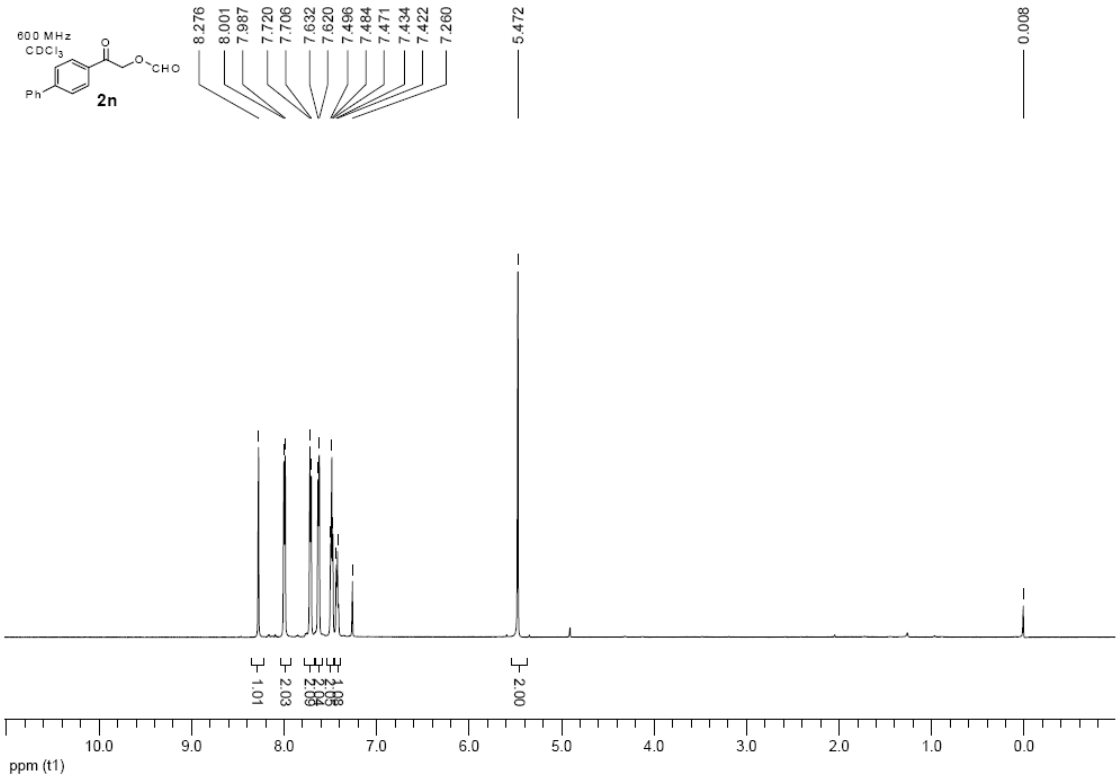

184.267
159.920
139.977
134.656
134.586
132.116
128.320
77.210
76.998
76.786
64.890
150 MHz
CDCl3
2k
ppm (t1)

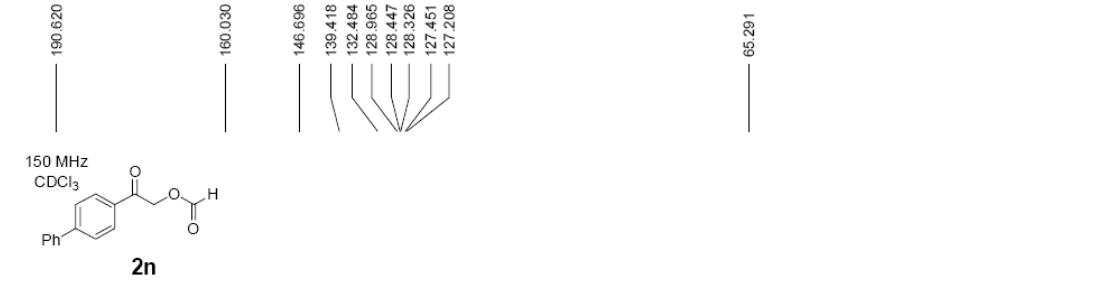

8.258
7.726
7.714
7.618
7.606
7.574
7.561
7.520
7.508
7.496
7.344
7.333
7.321
7.268
5.425
5.416
0.000000
600 MHz
CDCl3
2l
CHO
1.00
1.03
1.06
2.00
ppm (t1)


182.646
159.856
155.543
150.032
128.823
126.525
124.215
123.473
113.595
112.389
65.025
150 MHz
CDCl3
O
O
O
CHO
2l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

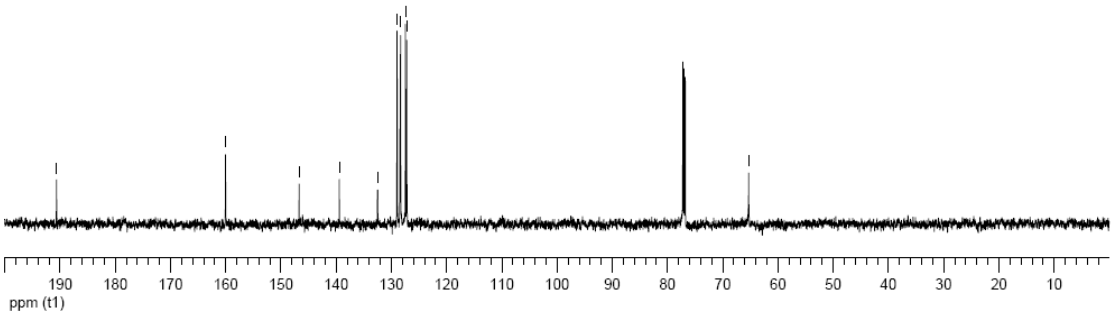

8.764
8.757
8.753
8.328
8.322
8.287
7.936
7.447
7.329
7.262
5.313
0.000000
600 MHz
CDCl3
O
O
H
O
N
H
2m
1.00
2.09
1.04
2.16
1.23
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

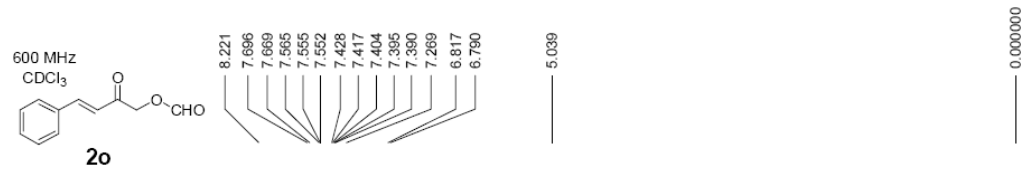

187.072
161.875
136.312
133.771
125.238
123.238
122.195
121.139
112.793
112.352
65.459
39.639
39.500
39.362
150 MHz
DMSO
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


8.276
8.001
7.987
7.720
7.706
7.632
7.620
7.496
7.484
7.471
7.434
7.422
7.260
5.472
0.008
600 MHz
CDCl3
2n
1.01
2.03
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

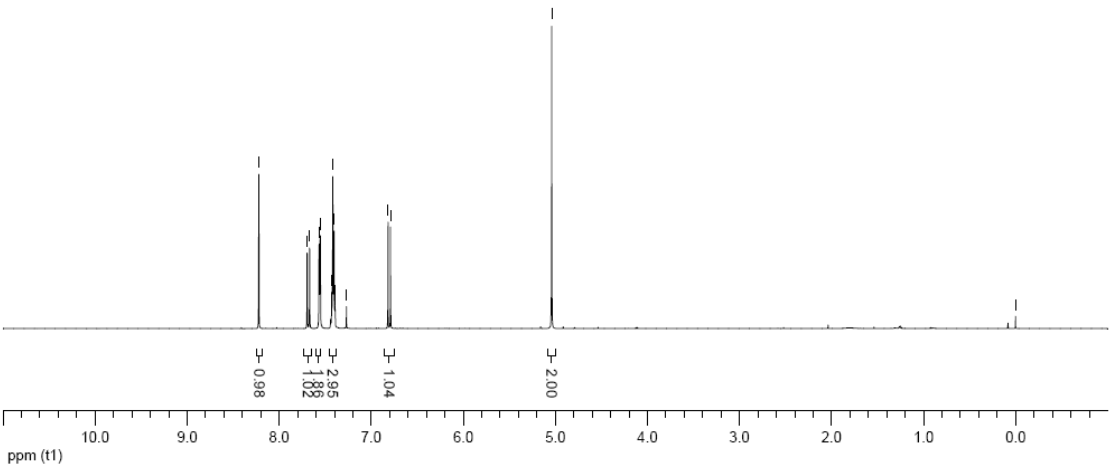

190.620
160.030
146.696
139.418
132.484
128.965
128.447
128.326
127.451
127.208
65.291
150 MHz
CDCl3
Ph
O
O
H
O

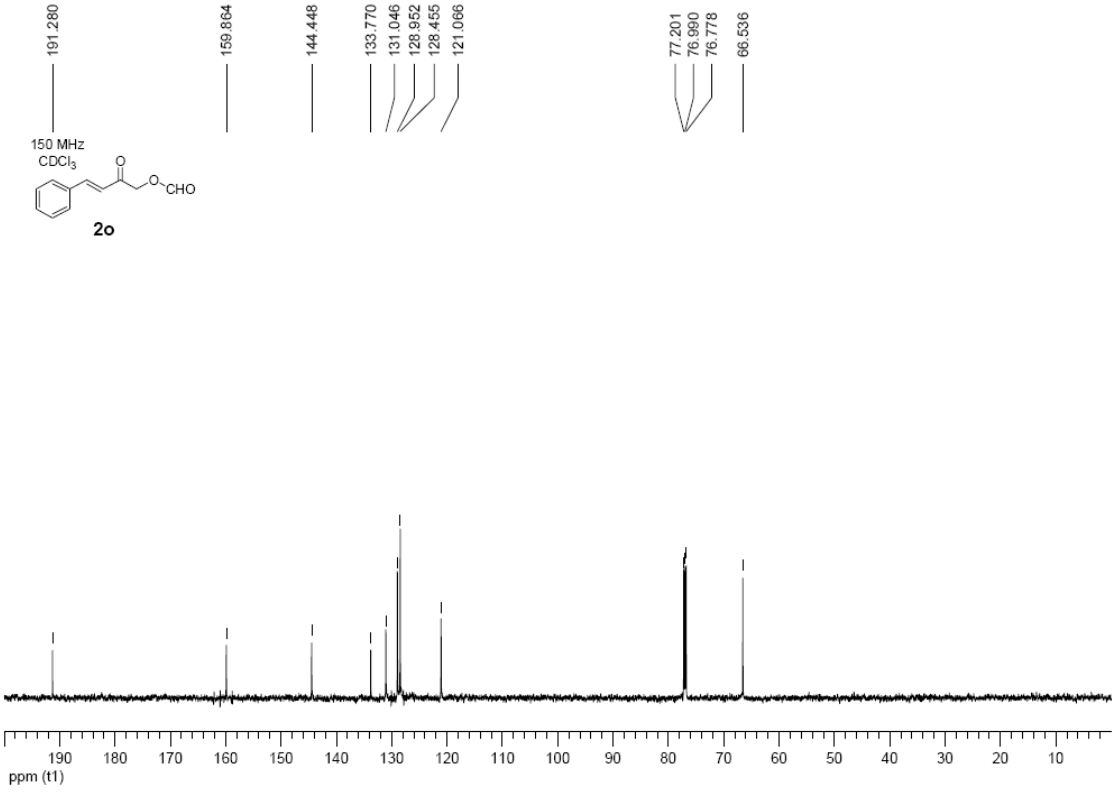
2n

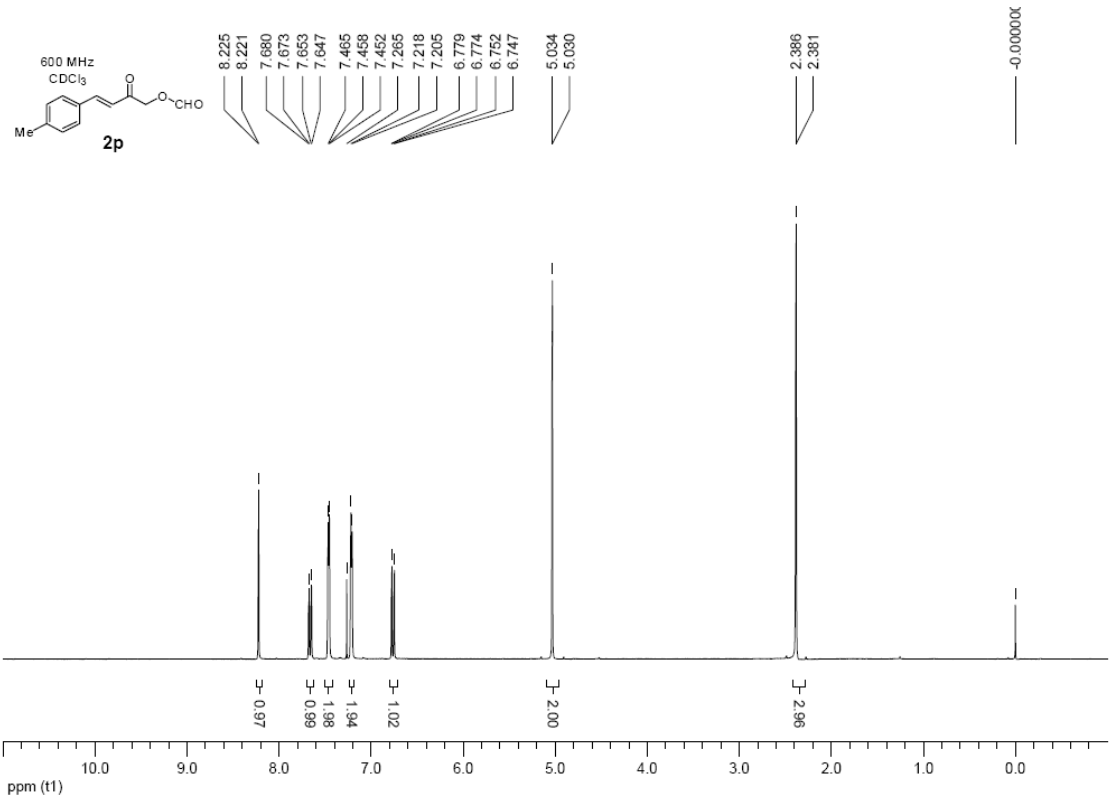

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

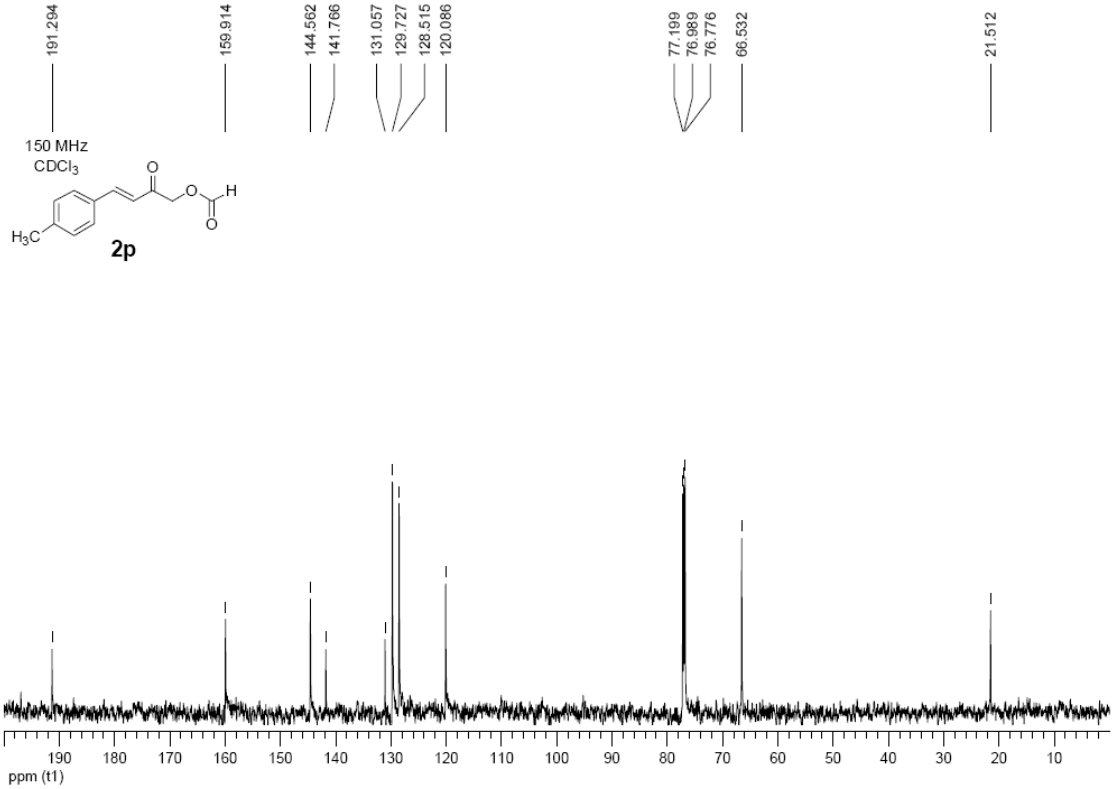

600 MHz
CDCl3
O
O
CHO
8.221
7.696
7.669
7.565
7.555
7.552
7.428
7.417
7.404
7.395
7.390
7.269
6.817
6.790
5.039
0.000000

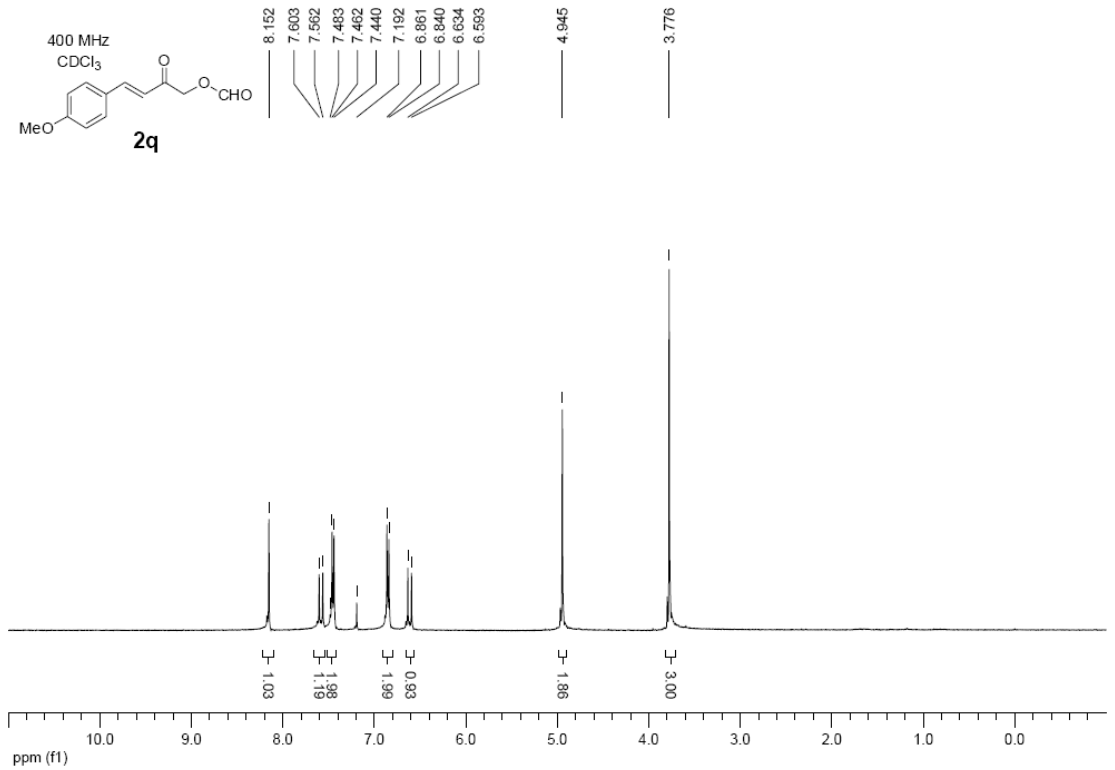
2o

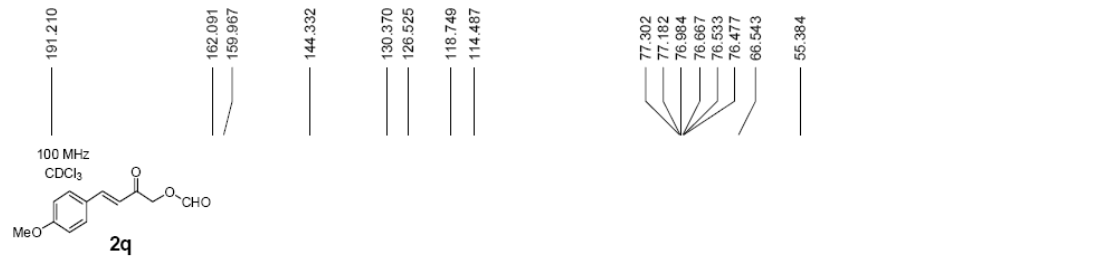

0.98
1.02
1.06
2.95
1.04
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

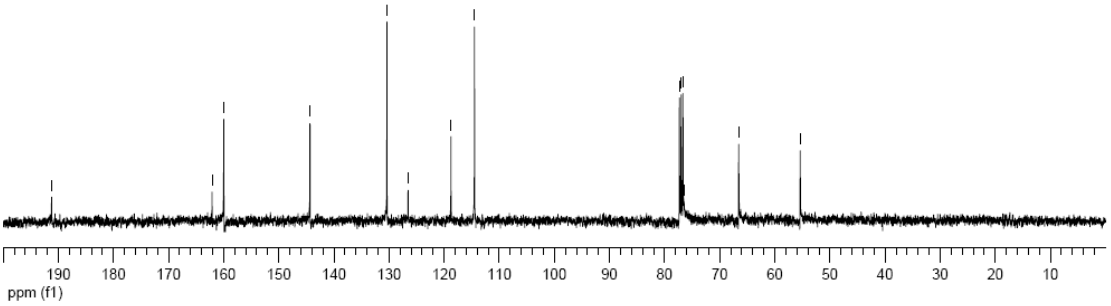

191.280
159.864
144.448
133.770
131.046
128.952
128.455
121.066
77.201
76.990
76.778
66.536
150 MHz
CDCl3
O
O
CHO
2o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

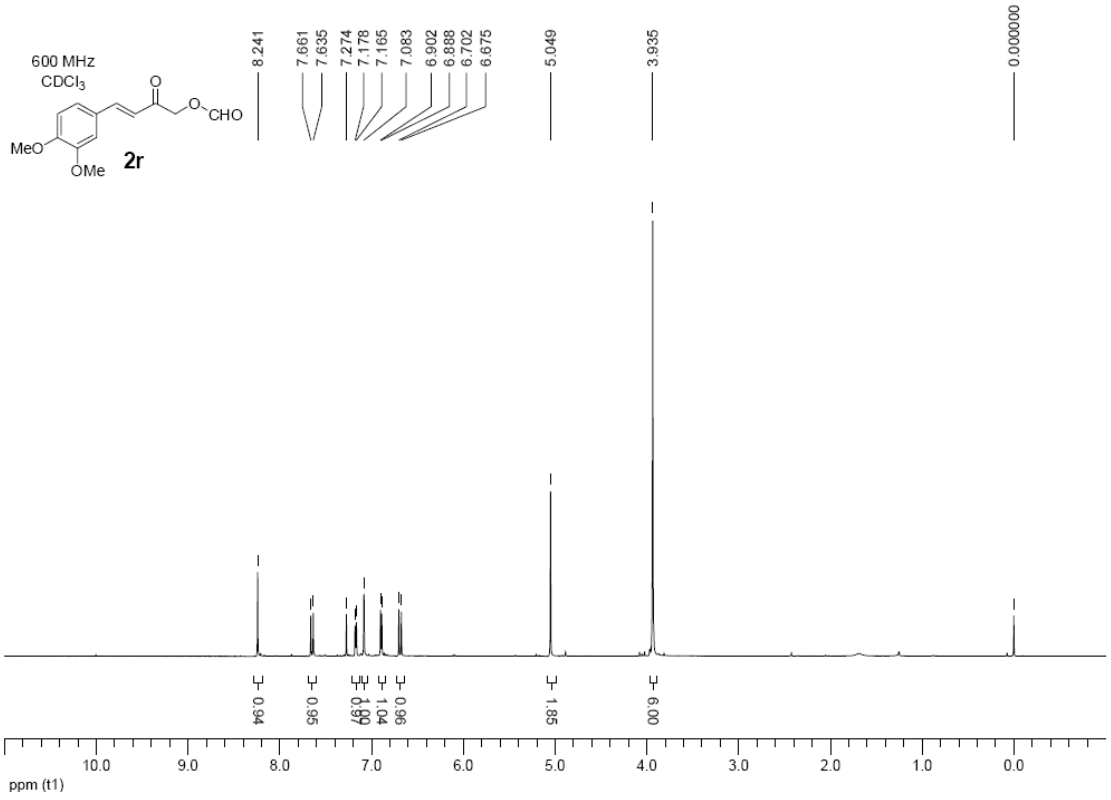

8.225
8.221
7.680
7.673
7.653
7.647
7.465
7.458
7.452
7.265
7.218
7.205
6.779
6.774
6.752
6.747
5.034
5.030
2.386
2.381
-0.000001
600 MHz
CDCl3
O
O
CHO
Me
2p
0.97
0.99
1.98
1.94
1.02
2.00
2.96
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

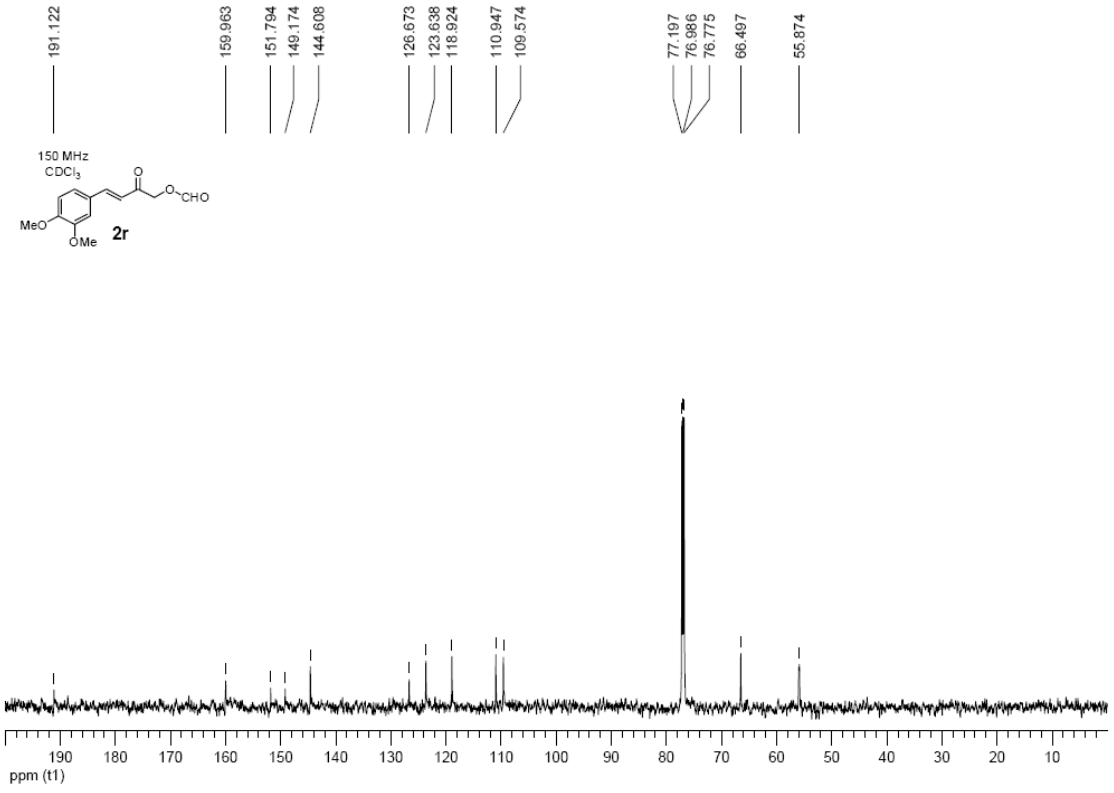

191.294
159.914
144.562
141.766
131.057
129.727
128.515
120.086
77.199
76.989
76.776
66.532
21.512
150 MHz
CDCl3
2p
ppm (t1)

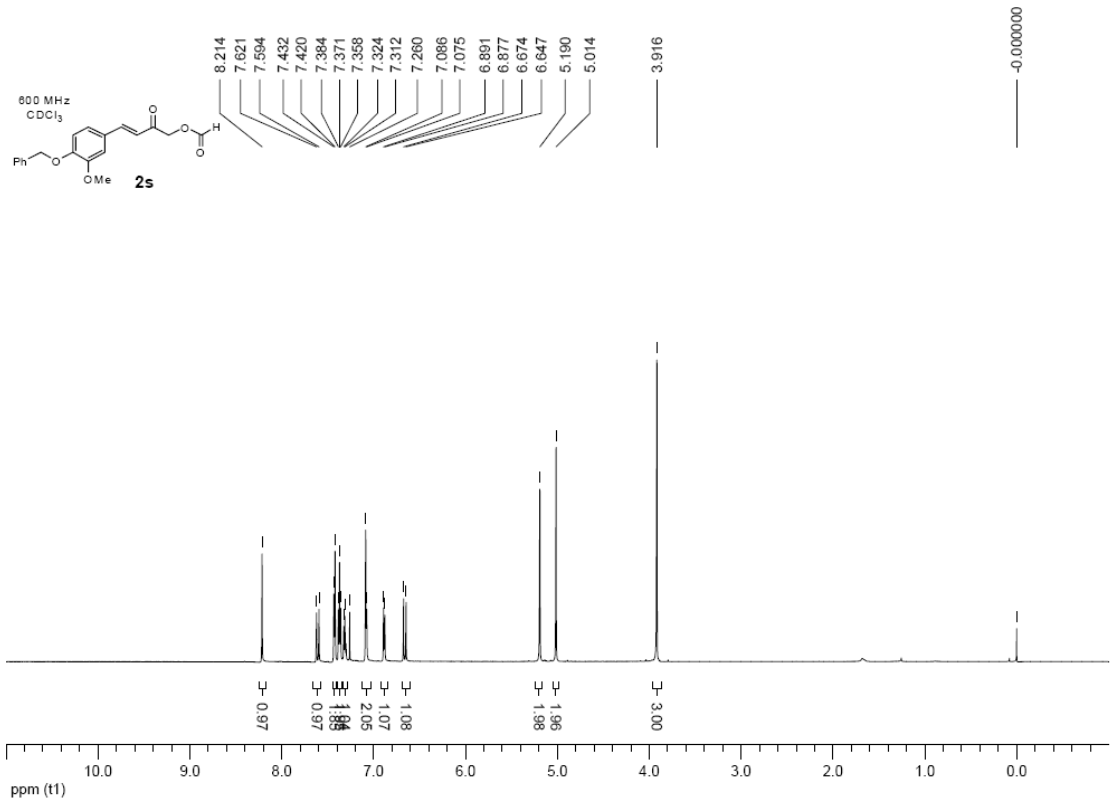

8.152
7.603
7.562
7.483
7.462
7.440
7.192
6.861
6.840
6.634
6.593
4.945
3.776
400 MHz
CDCl3
2q
1.03
1.19
1.98
1.99
0.93
1.86
3.00
ppm (f1)

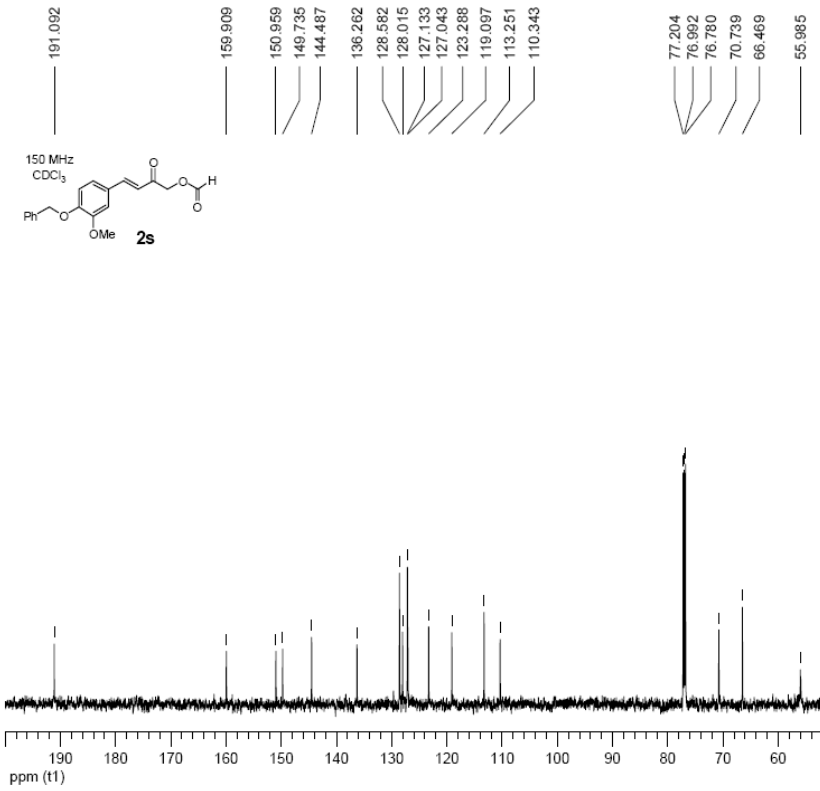

191.210
162.091
159.967
144.332
130.370
126.525
118.749
114.487
77.302
77.182
76.984
76.667
76.533
76.477
66.543
55.384
100 MHz
CDCl3
MeO
CHO
2q

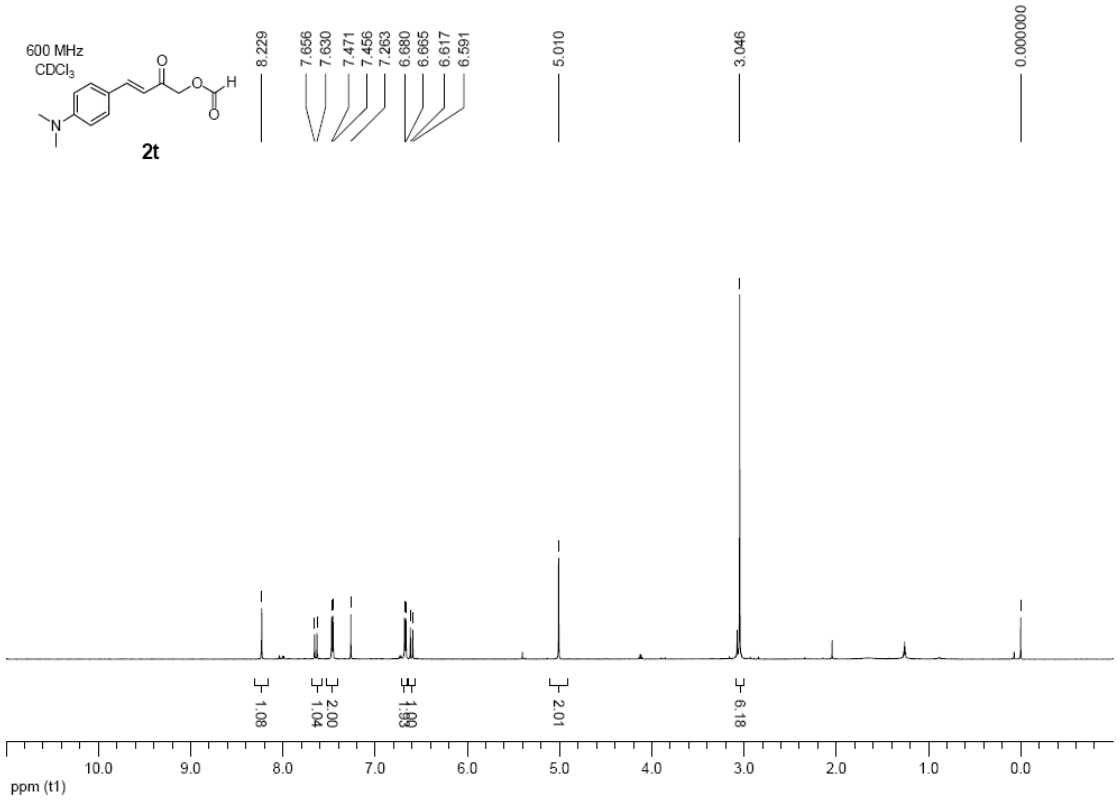

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

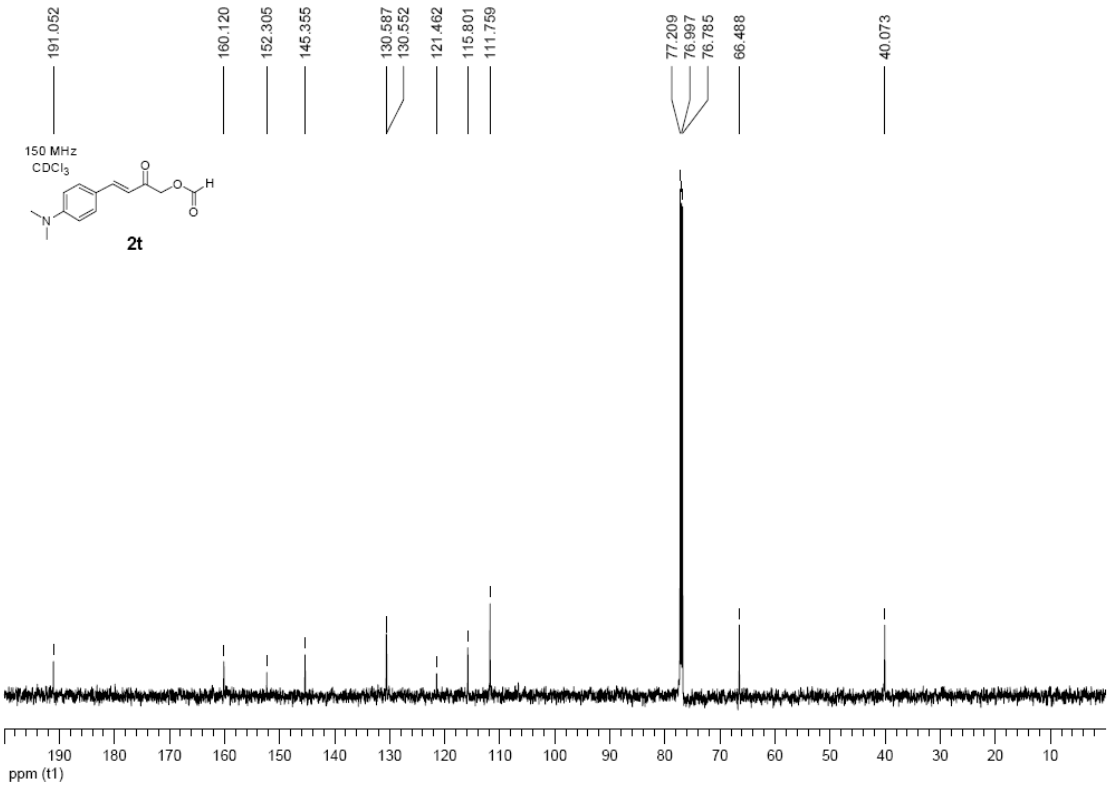

600 MHz
CDCl3
MeO
OMe
CHO
2r
8.241
7.661
7.635
7.274
7.178
7.165
7.083
6.902
6.888
6.702
6.675
5.049
3.935
0.000000
0.94
0.96
0.89
1.04
0.96
1.85
6.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

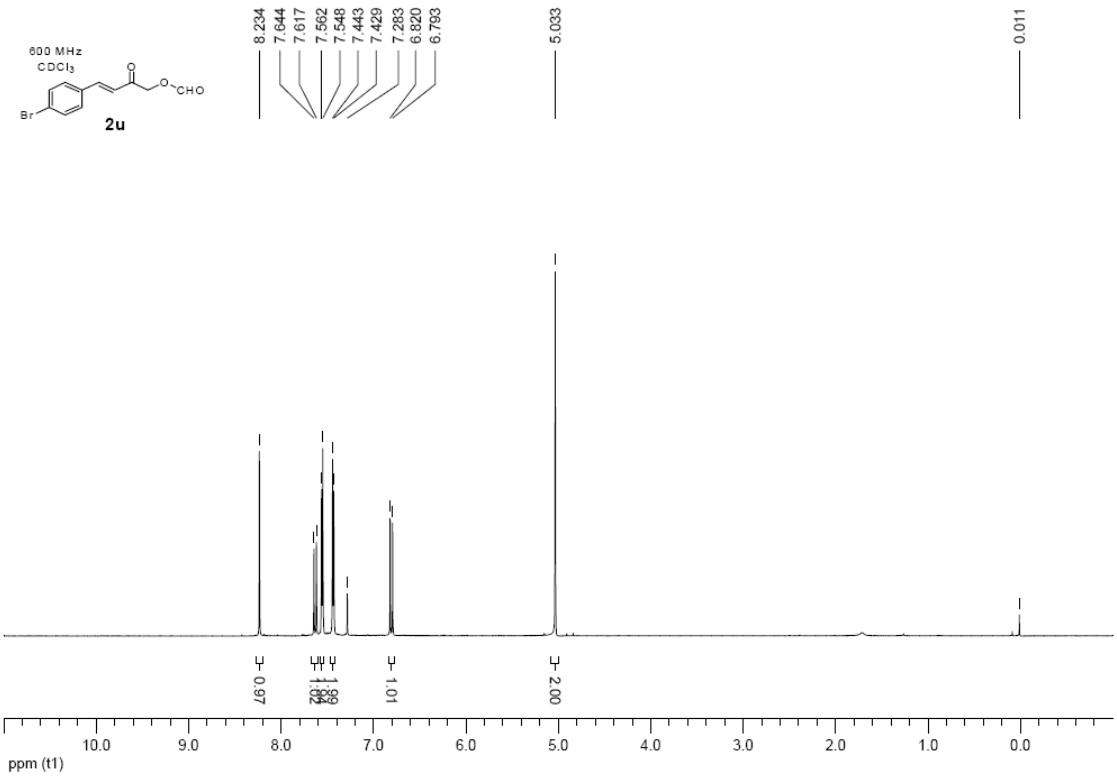

191.122
159.963
151.794
149.174
144.608
126.673
123.638
118.924
110.947
109.574
77.197
76.986
76.775
66.497
55.874
150 MHz
CDCl3
MeO
OMe
CHO
2r
ppm (t1)

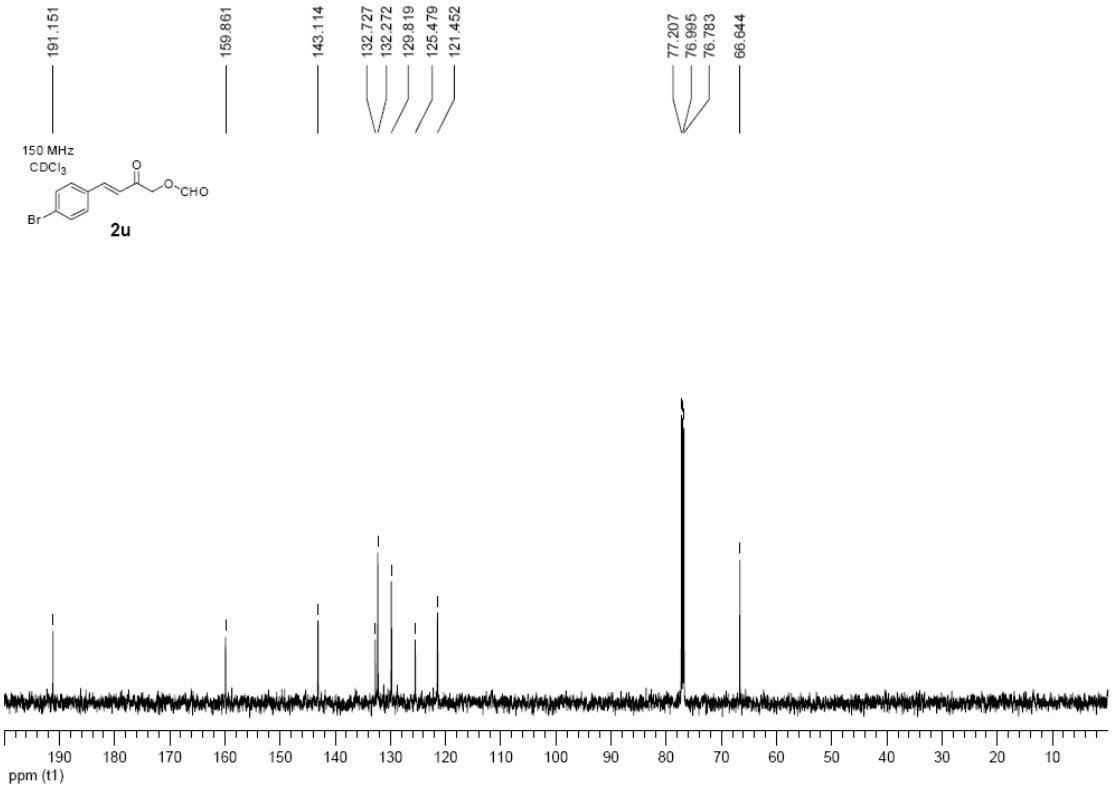

8.214
7.621
7.594
7.432
7.420
7.384
7.371
7.358
7.324
7.312
7.260
7.086
7.075
6.891
6.877
6.674
6.647
5.190
5.014
3.916
-0.000000
600 MHz
CDCl3
Ph
OMe
2s
0.97
0.97
2.05
1.07
1.08
1.98
1.96
3.00
ppm (t1)

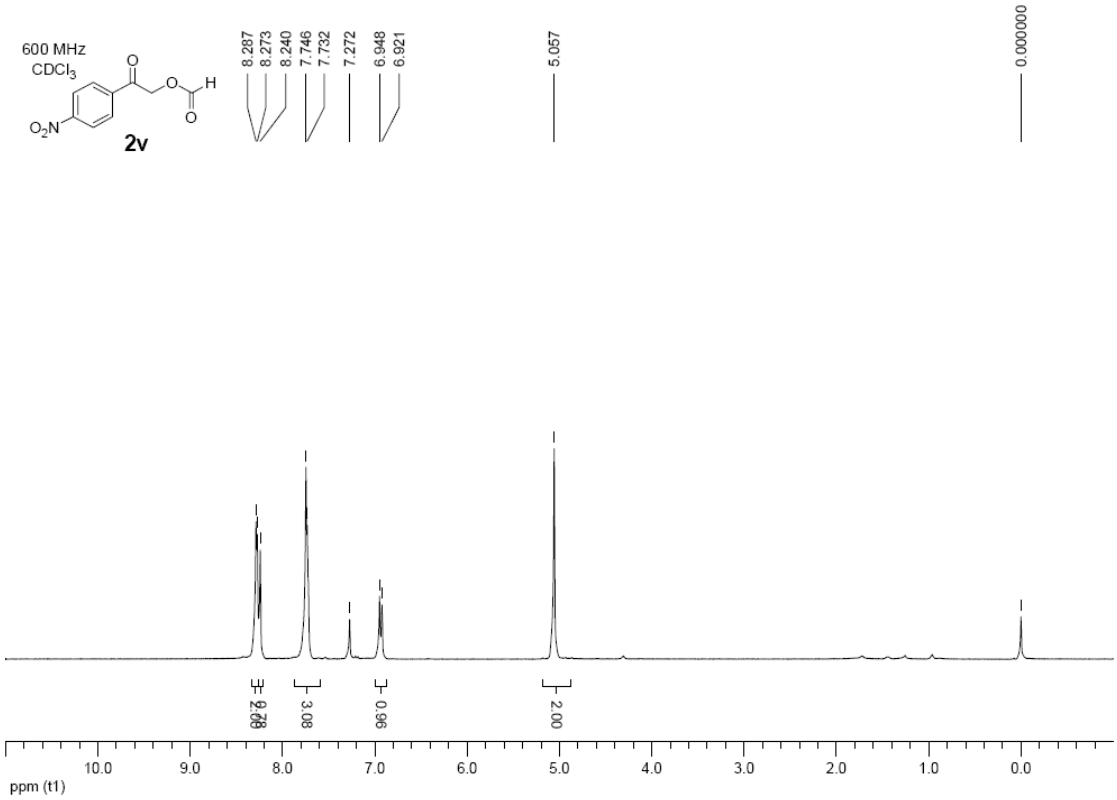

191.092
159.909
150.959
149.735
144.487
136.262
128.582
128.015
127.133
127.043
123.288
119.097
113.251
110.343
77.204
76.992
76.780
70.739
66.469
55.985
150 MHz
CDCl3
Ph
OMe
2s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

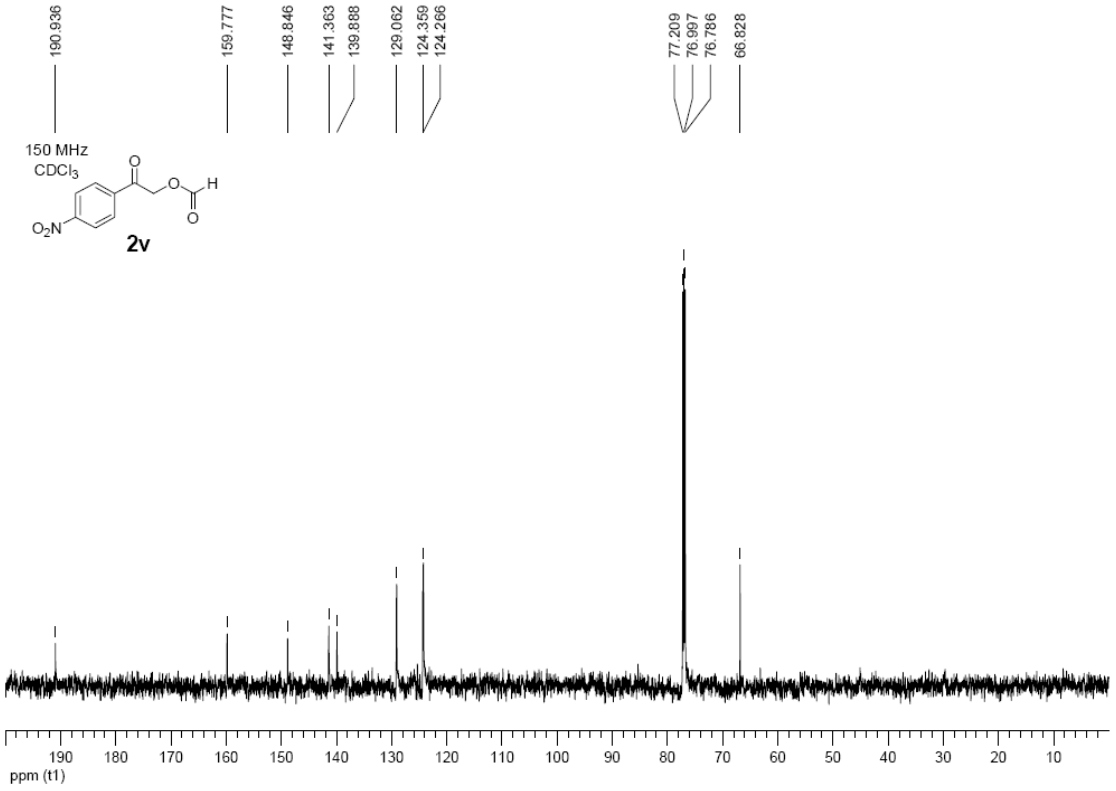

600 MHz
CDCl3
2t
8.229
7.656
7.630
7.471
7.456
7.263
6.680
6.665
6.617
6.591
5.010
3.046
0.000000
1.08
1.04
2.00
1.09
2.01
6.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

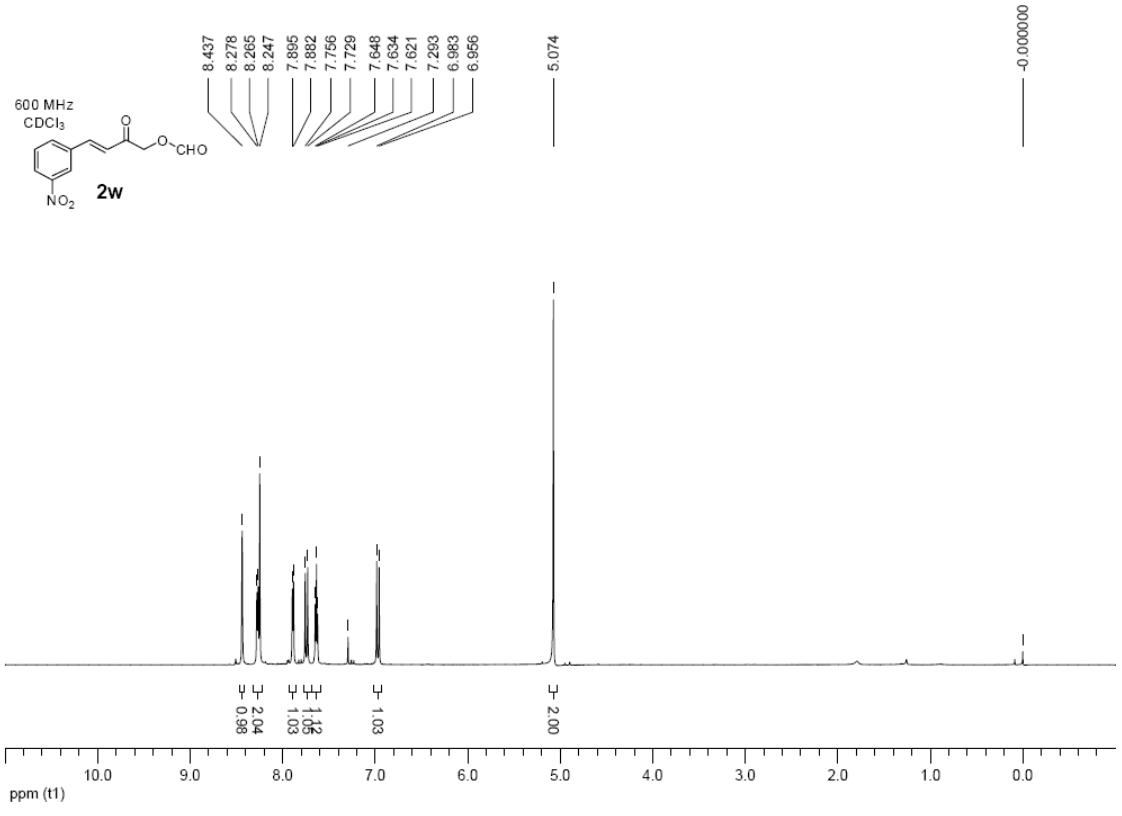

191.052
160.120
152.305
145.355
130.587
130.552
121.462
115.801
111.759
77.209
76.997
76.785
66.488
40.073
150 MHz
CDCl3
2t
ppm (t1)

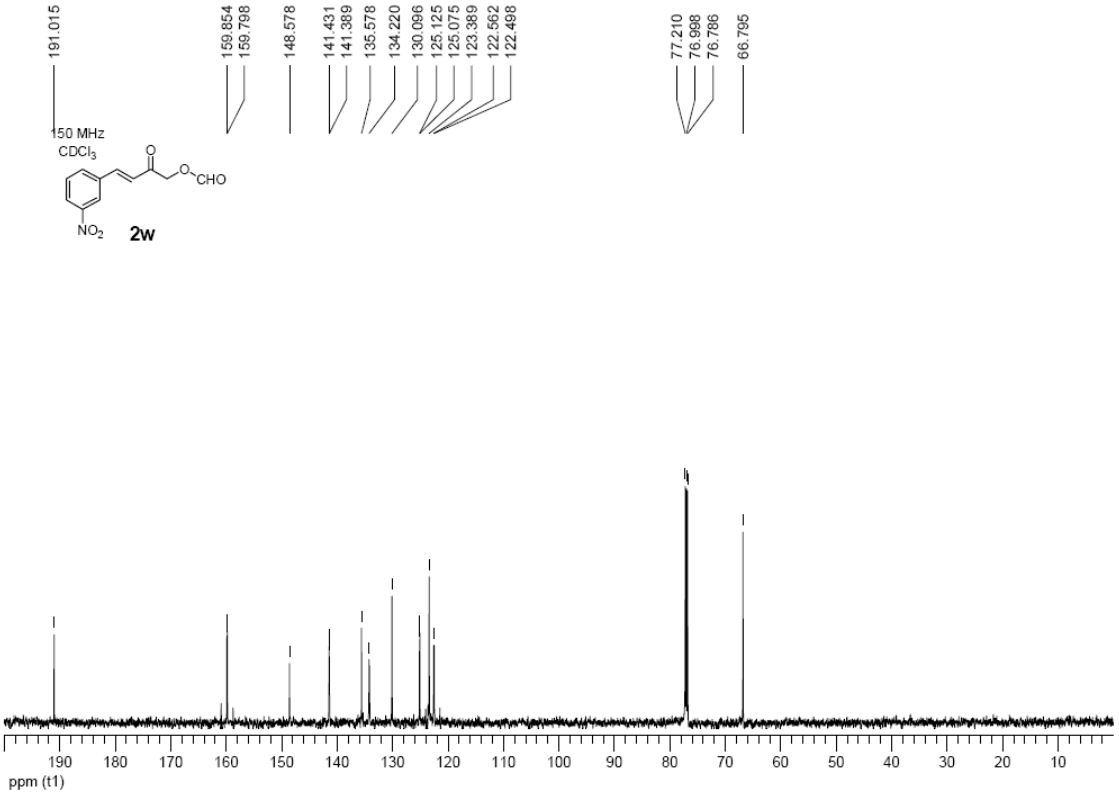

8.234
7.644
7.617
7.562
7.548
7.443
7.429
7.283
6.820
6.793
5.033
0.011
600 MHz
CDCl3
2u
0.97
1.89
1.01
2.00
ppm (t1)

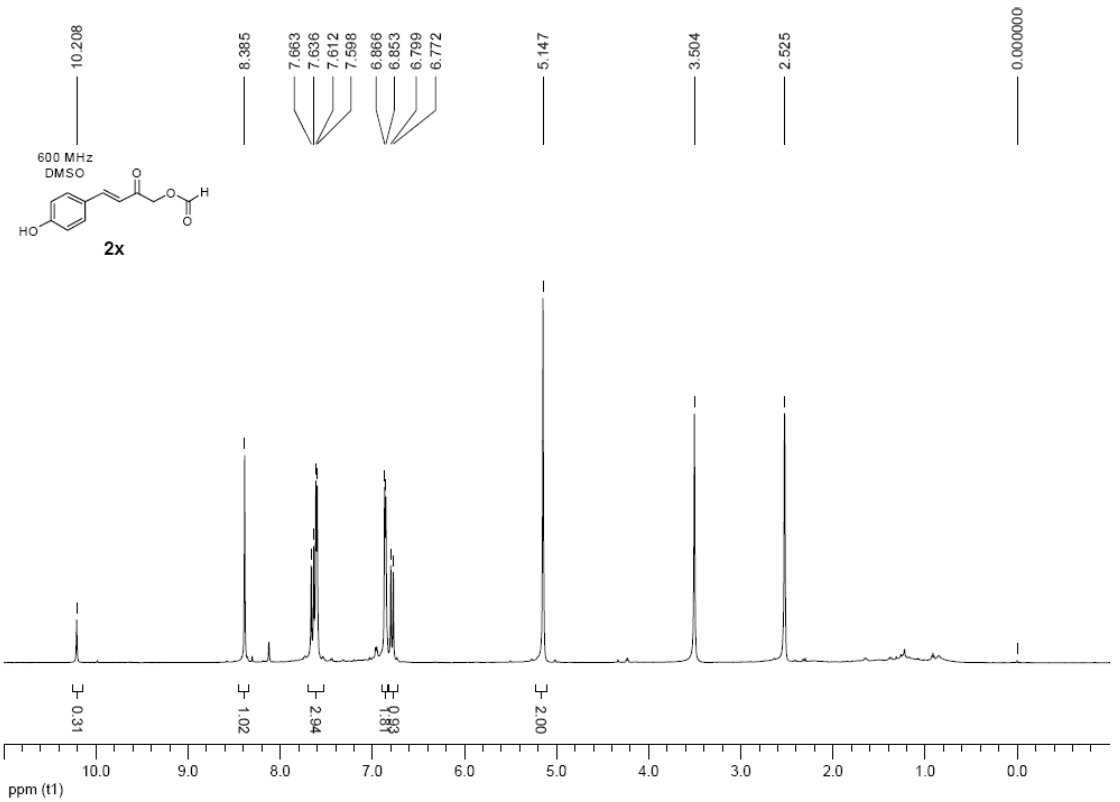

191.151
159.861
143.114
132.727
132.272
129.819
125.479
121.452
77.207
76.995
76.783
66.644
150 MHz
CDCl3
Br
O
CHO
2u
ppm (t1)

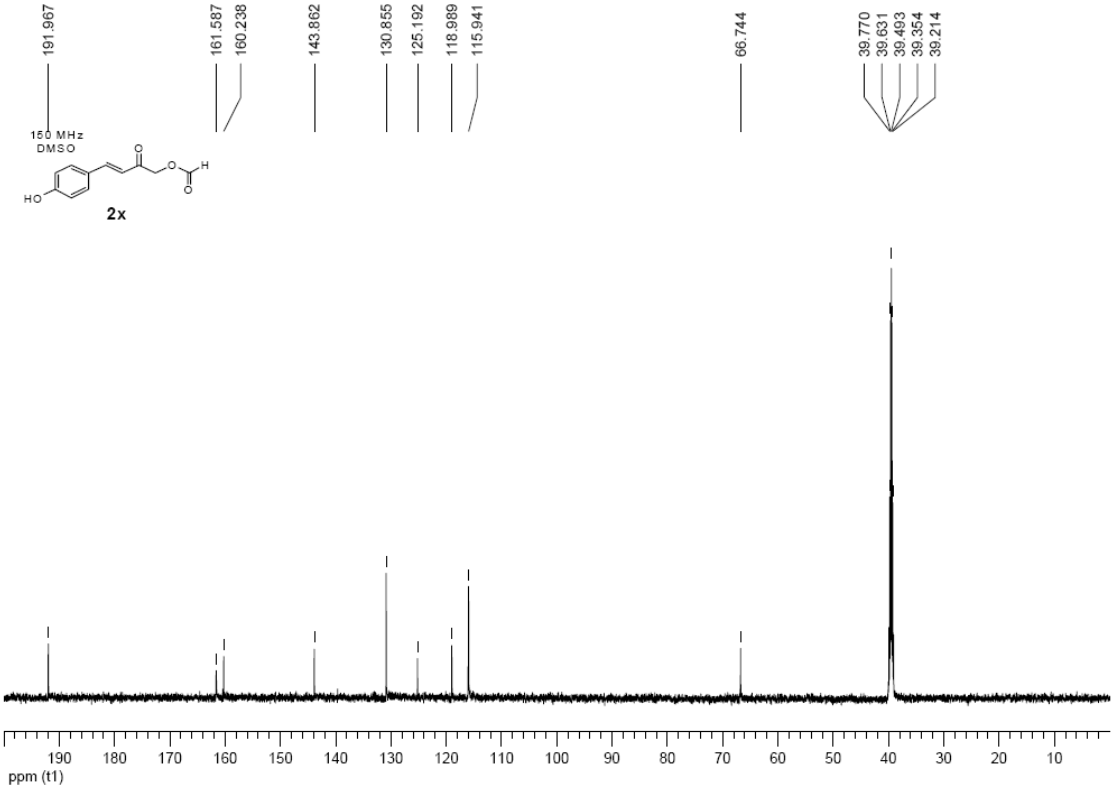

600 MHz
CDCl3
O2N
O
H
2v
8.287
8.273
8.240
7.746
7.732
7.272
6.948
6.921
5.057
0.000000
2.08
3.08
0.96
2.00
ppm (t1)

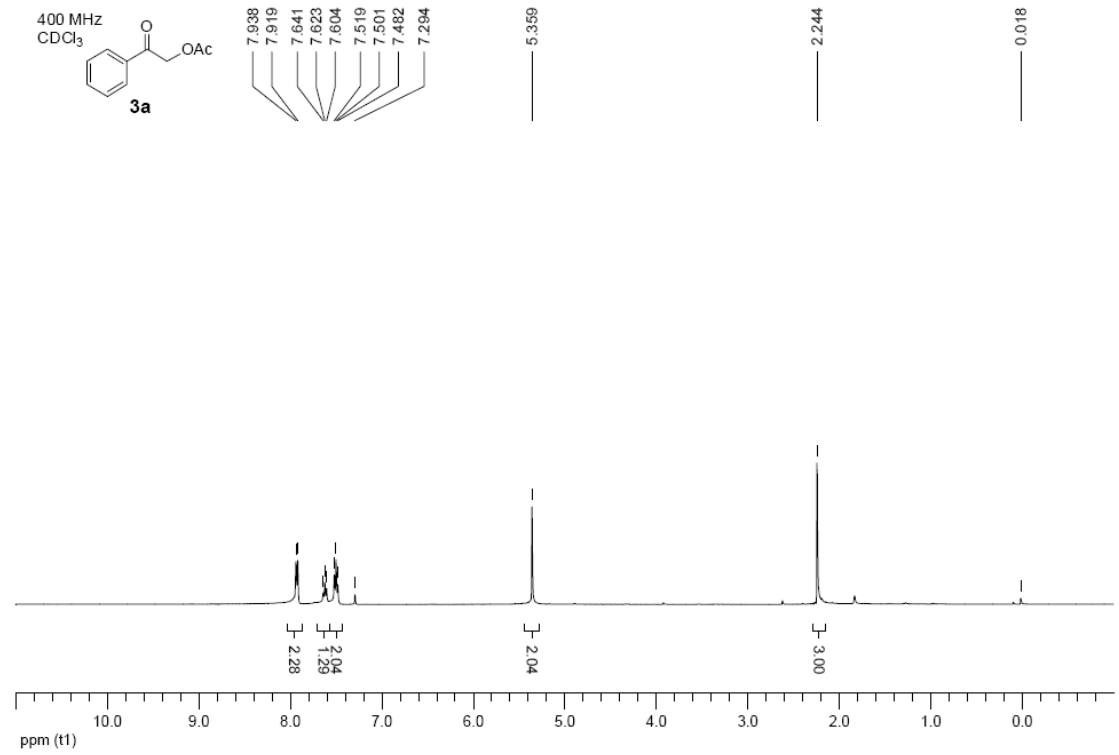

190.936
159.777
148.846
141.363
139.888
129.062
124.359
124.266
77.209
76.997
76.786
66.828
150 MHz
CDCl3
2v
ppm (t1)

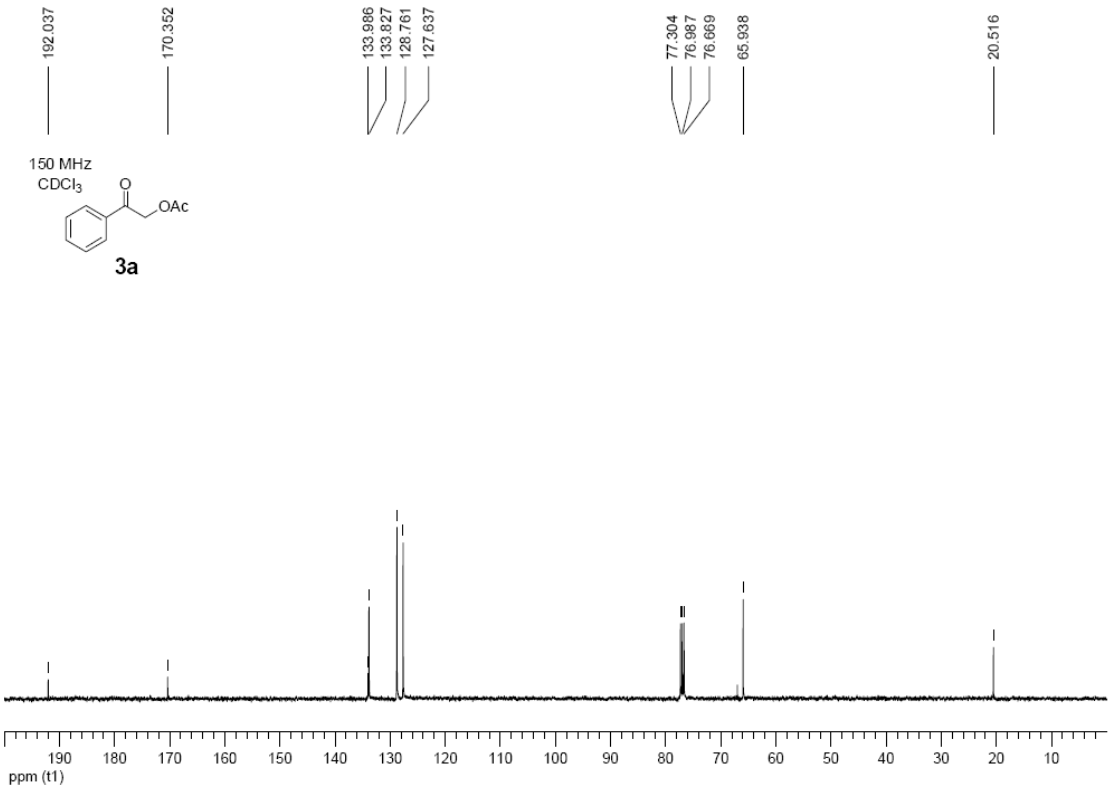

8.437
8.278
8.265
8.247
7.895
7.882
7.756
7.729
7.648
7.634
7.621
7.293
6.983
6.956
5.074
-0.000000
600 MHz
CDCl3
2w
0.98
2.04
1.03
1.12
1.05
1.03
2.00
ppm (t1)

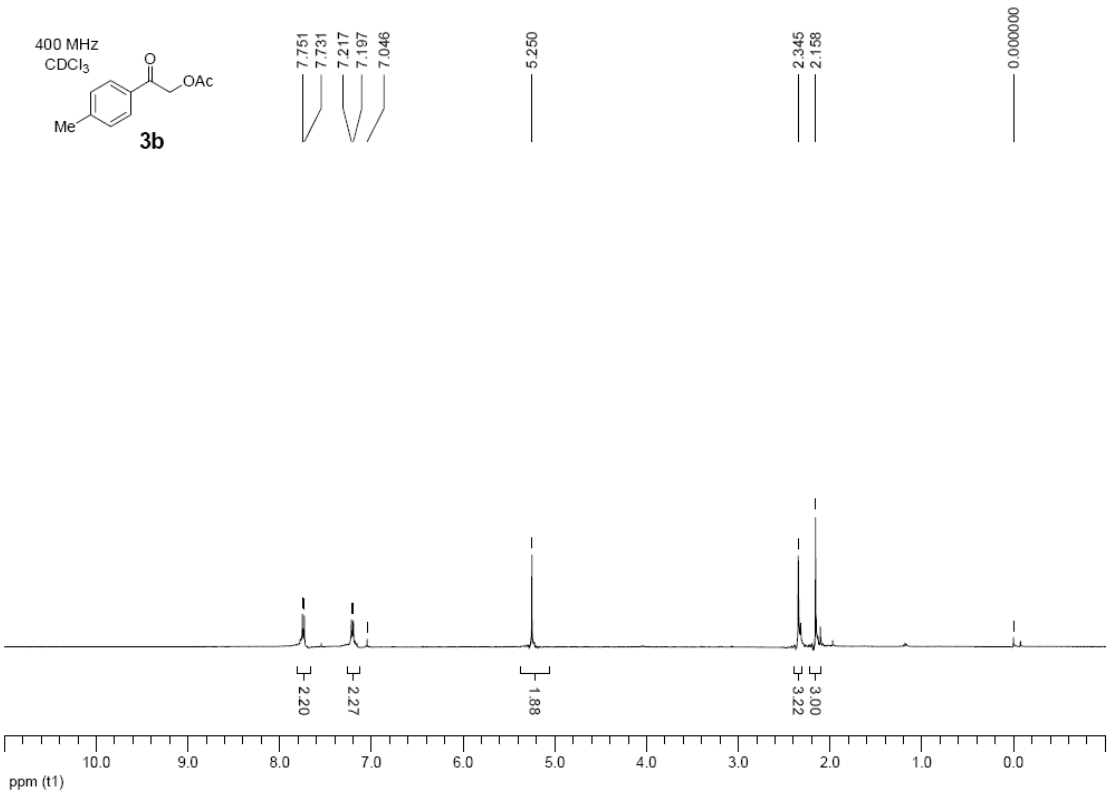

191.015
159.854
159.798
148.578
141.431
141.389
135.578
134.220
130.096
125.125
125.075
123.389
122.562
122.498
77.210
76.998
76.786
66.795
150 MHz
CDCl3
O
O
CHO
NO2
2w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

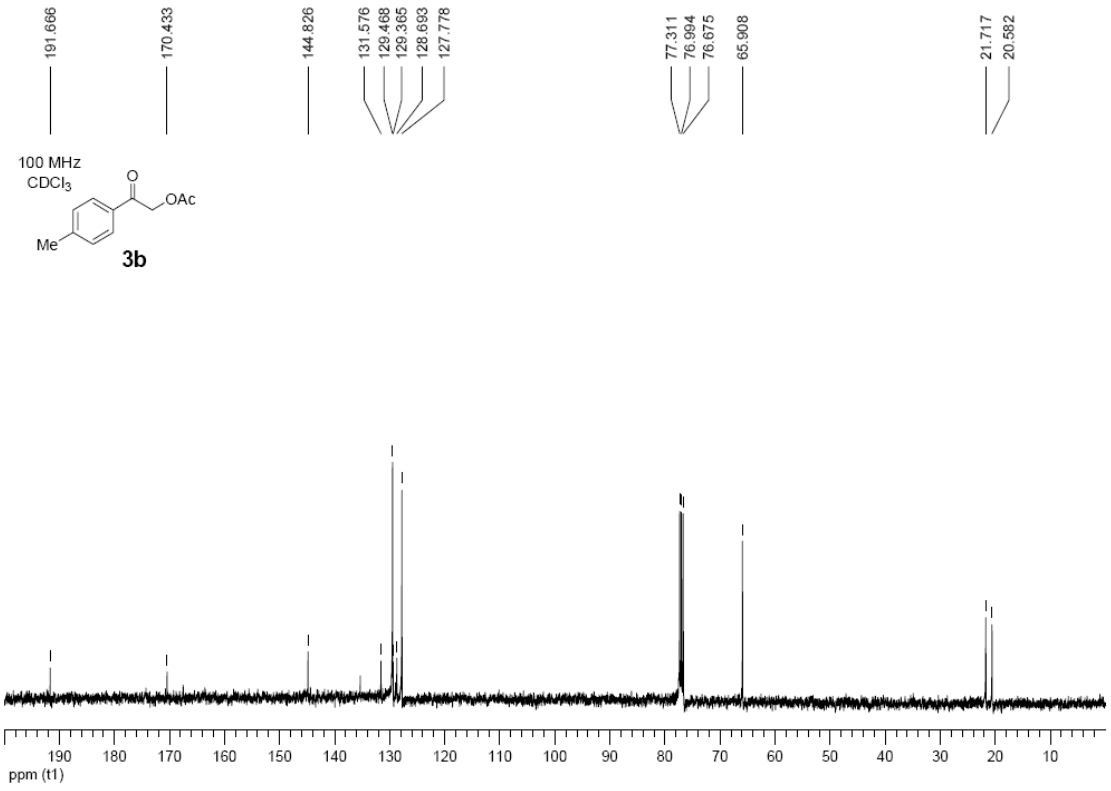

10.208
8.385
7.663
7.636
7.612
7.598
6.866
6.853
6.799
6.772
5.147
3.504
2.525
0.000000
600 MHz
DMSO
O
O
H
O
HO
2x
0.31
1.02
2.94
3.83
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

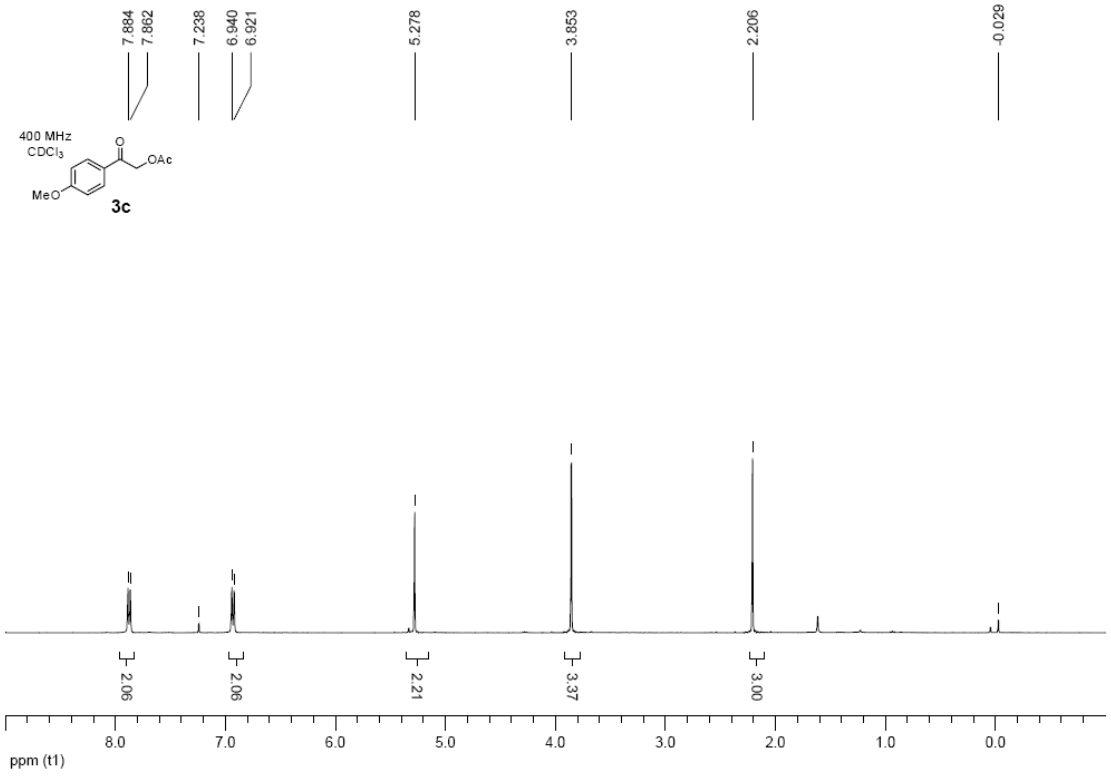

191.967
161.587
160.238
143.862
130.855
125.192
118.989
115.941
66.744
39.770
39.631
39.493
39.354
39.214
150 MHz
DMSO
2x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

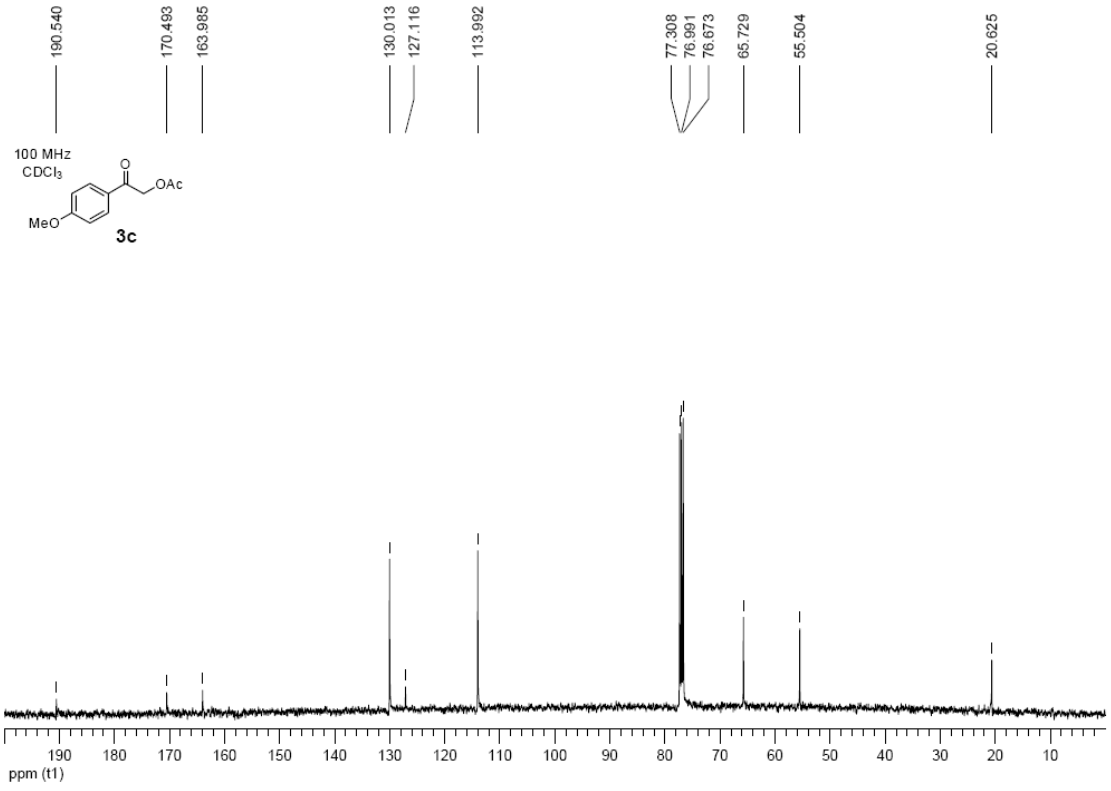

400 MHz
CDCl3
OAc
3a
7.938
7.919
7.641
7.623
7.604
7.519
7.501
7.482
7.294
5.359
2.244
0.018
2.28
2.04
1.29
2.04
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

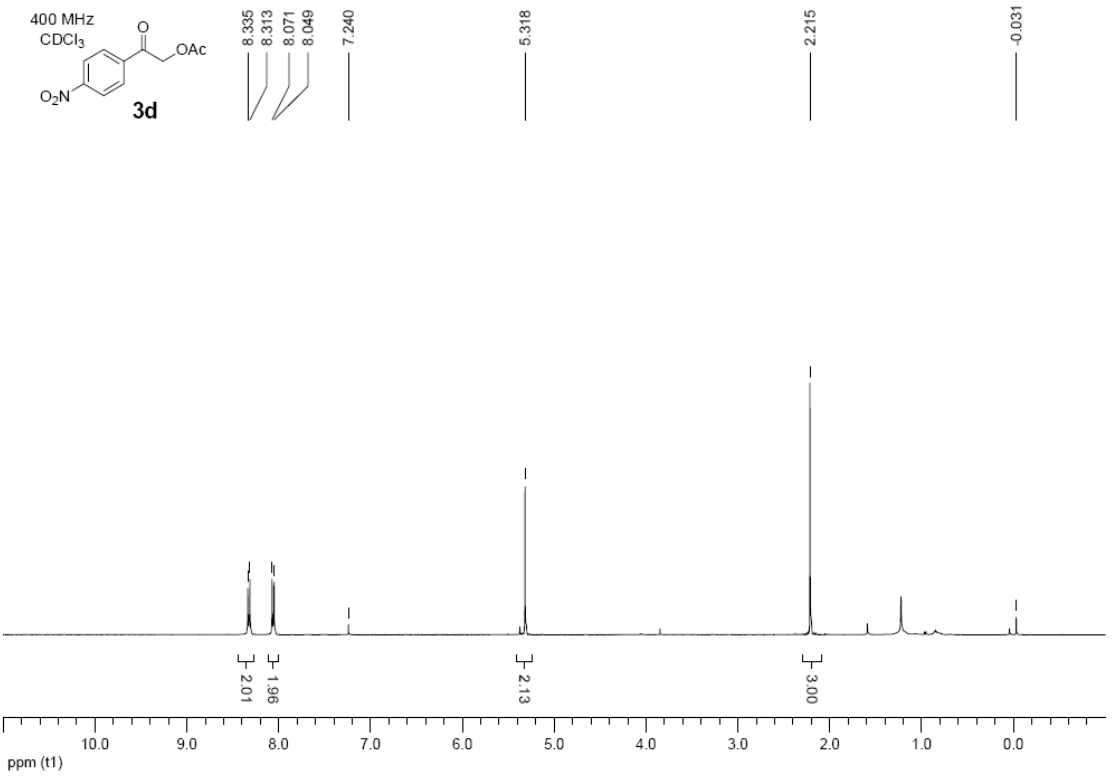

192.037
170.352
133.986
133.827
128.761
127.637
77.304
76.987
76.669
65.938
20.516
150 MHz
CDCl3
O
OAc
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

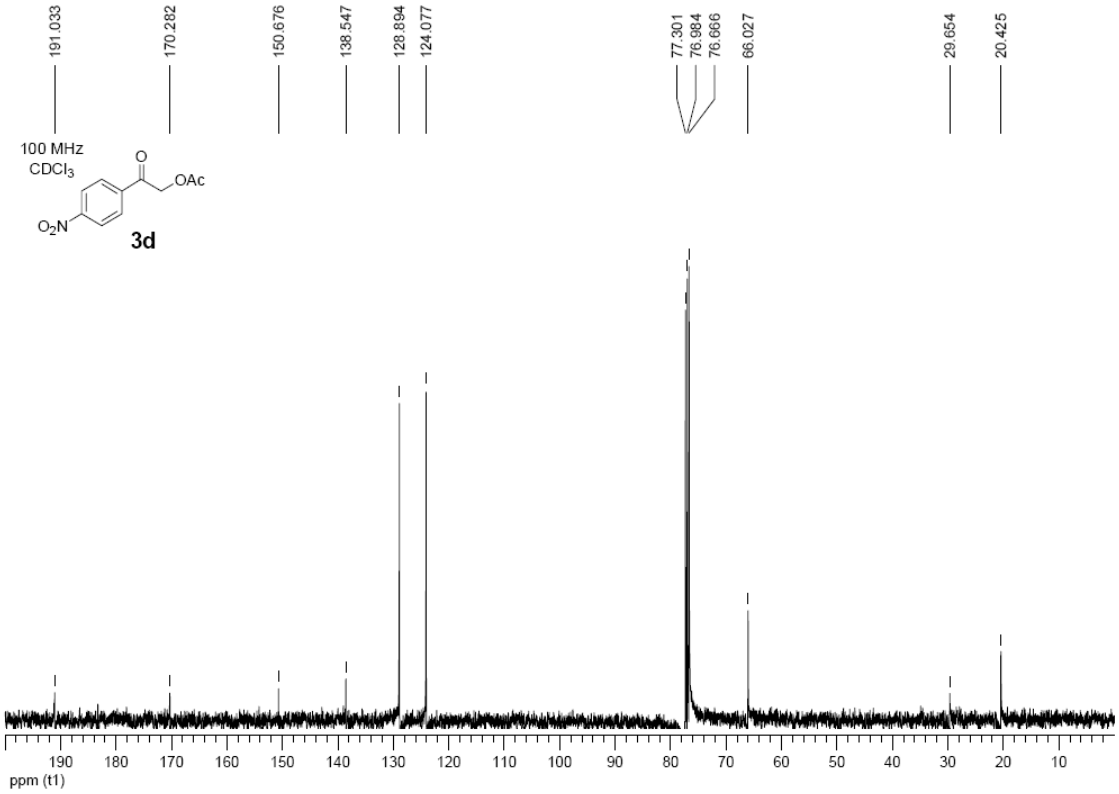

400 MHz
CDCl3
O
OAc
Me
3b
7.751
7.731
7.217
7.197
7.046
5.250
2.345
2.158
0.000000
2.20
2.27
1.88
3.22
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

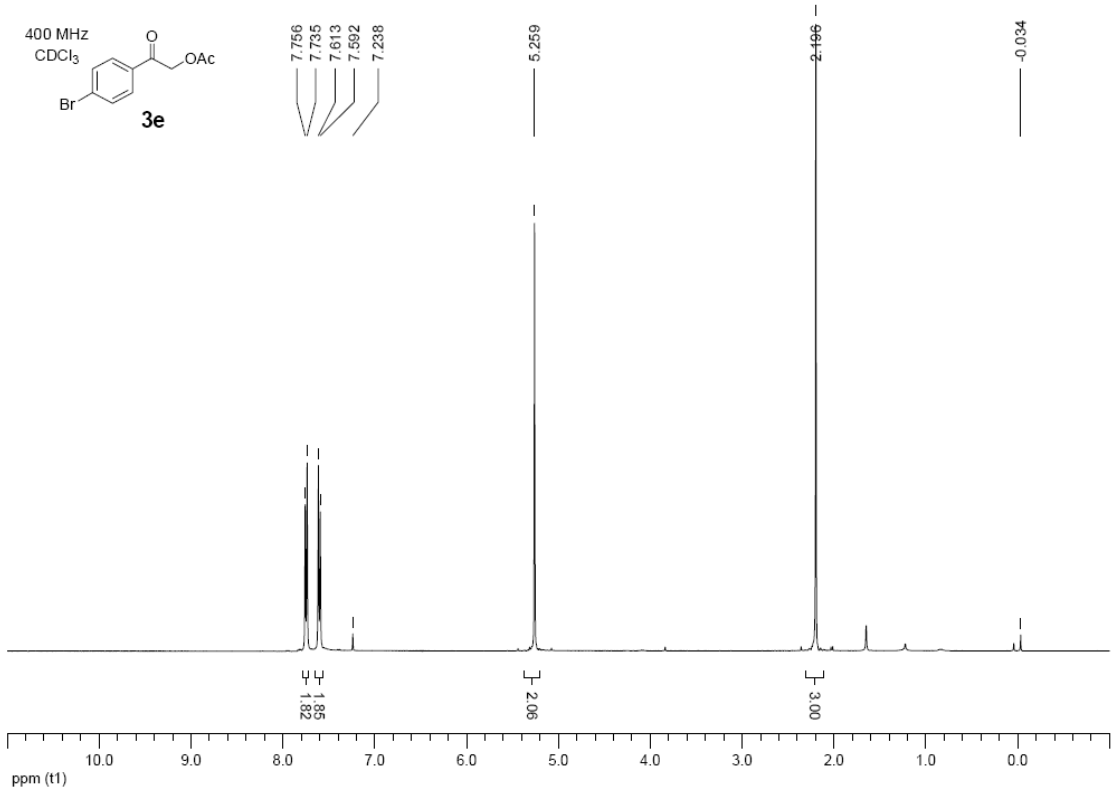

191.666
170.433
144.826
131.576
129.468
129.365
128.693
127.778
77.311
76.994
76.675
65.908
21.717
20.582
100 MHz
CDCl3
O
OAc
Me
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

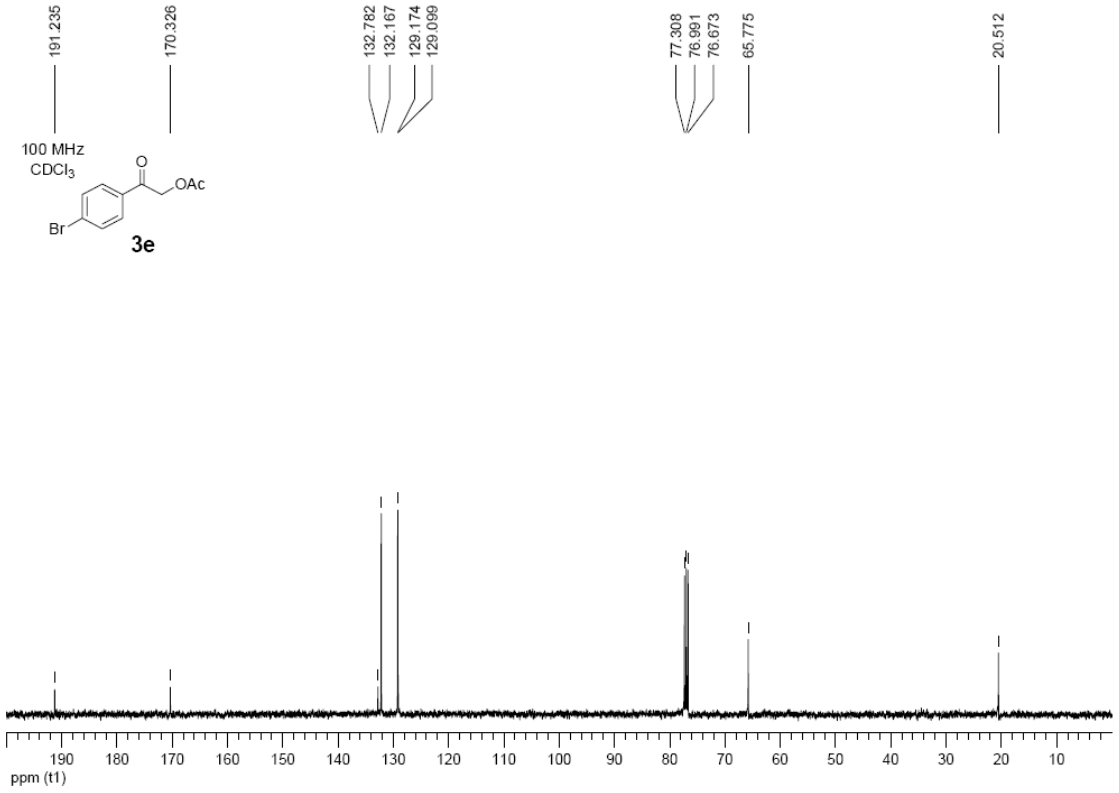

7.884
7.862
7.238
6.940
6.921
5.278
3.853
2.206
-0.029
400 MHz
CDCl3
O
OAc
MeO
3c
2.06
2.00
2.21
3.37
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

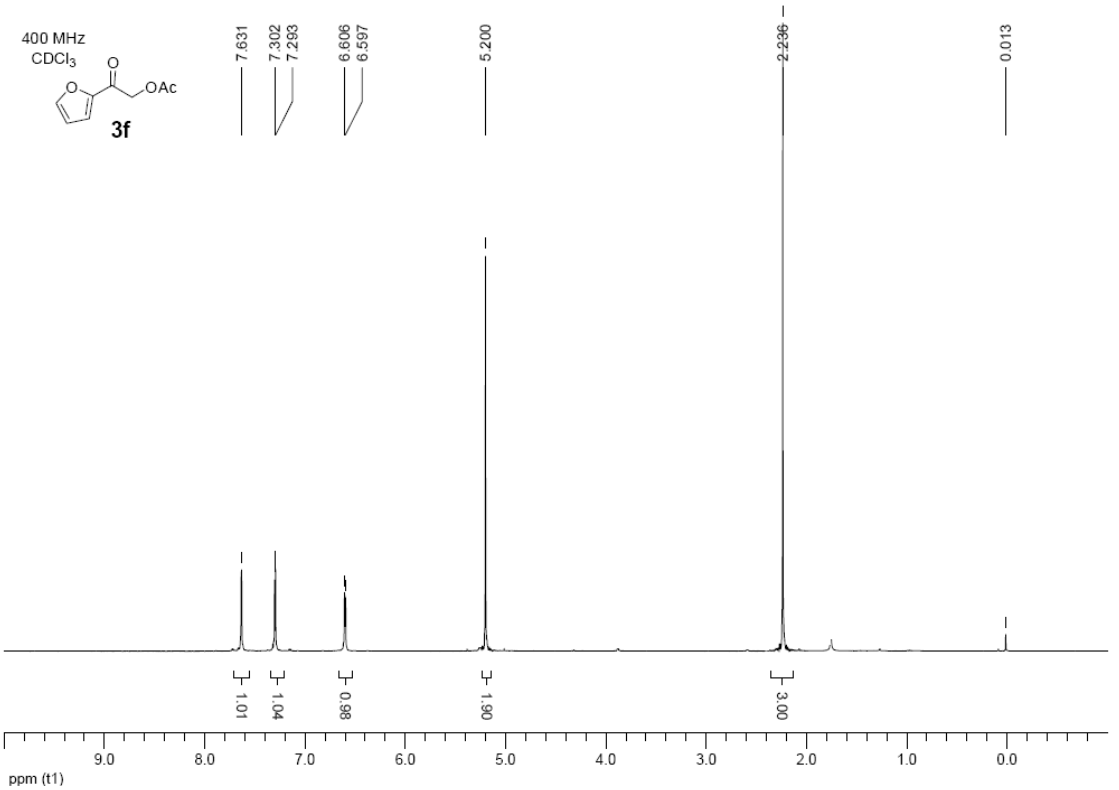

190.540
170.493
163.985
130.013
127.116
113.992
77.308
76.991
76.673
65.729
55.504
20.625
100 MHz
CDCl3
O
OAc
MeO
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

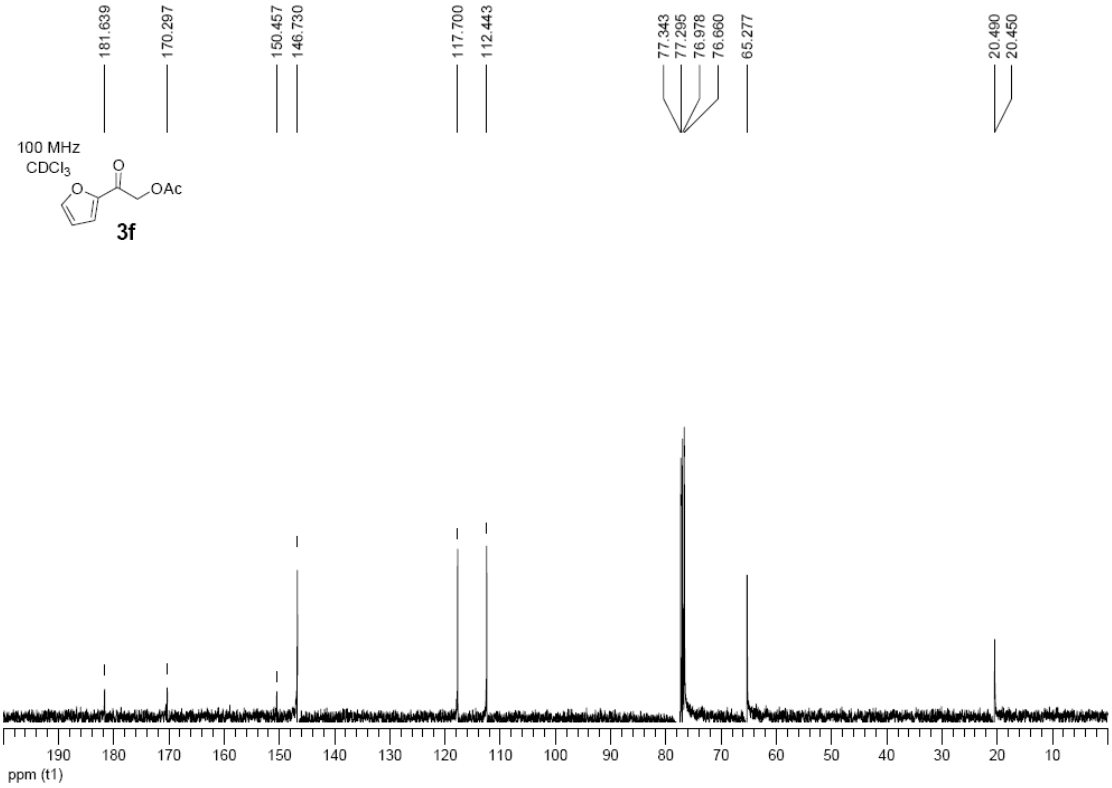

400 MHz
CDCl3
O
OAc
O2N
3d
8.335
8.313
8.071
8.049
7.240
5.318
2.215
-0.031
2.01
1.96
2.13
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

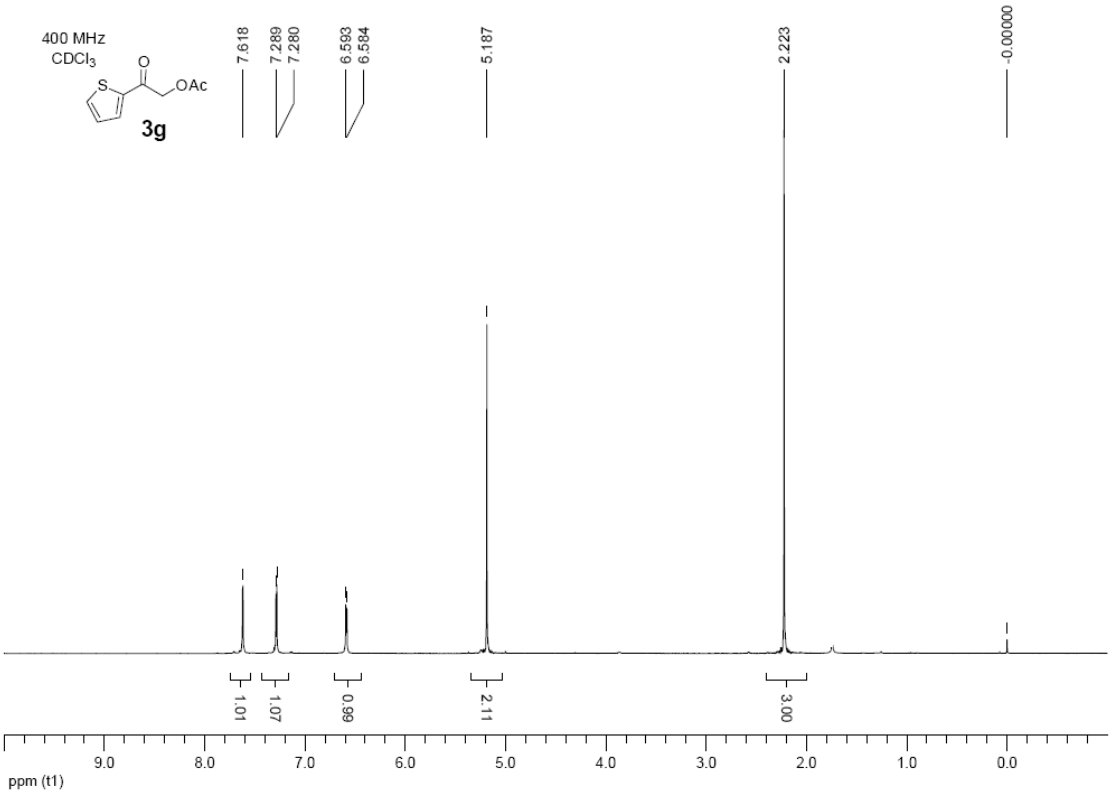

191.033
170.282
150.676
138.547
128.894
124.077
77.301
76.984
76.666
66.027
29.654
20.425
100 MHz
CDCl3
O
OAc
O2N
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

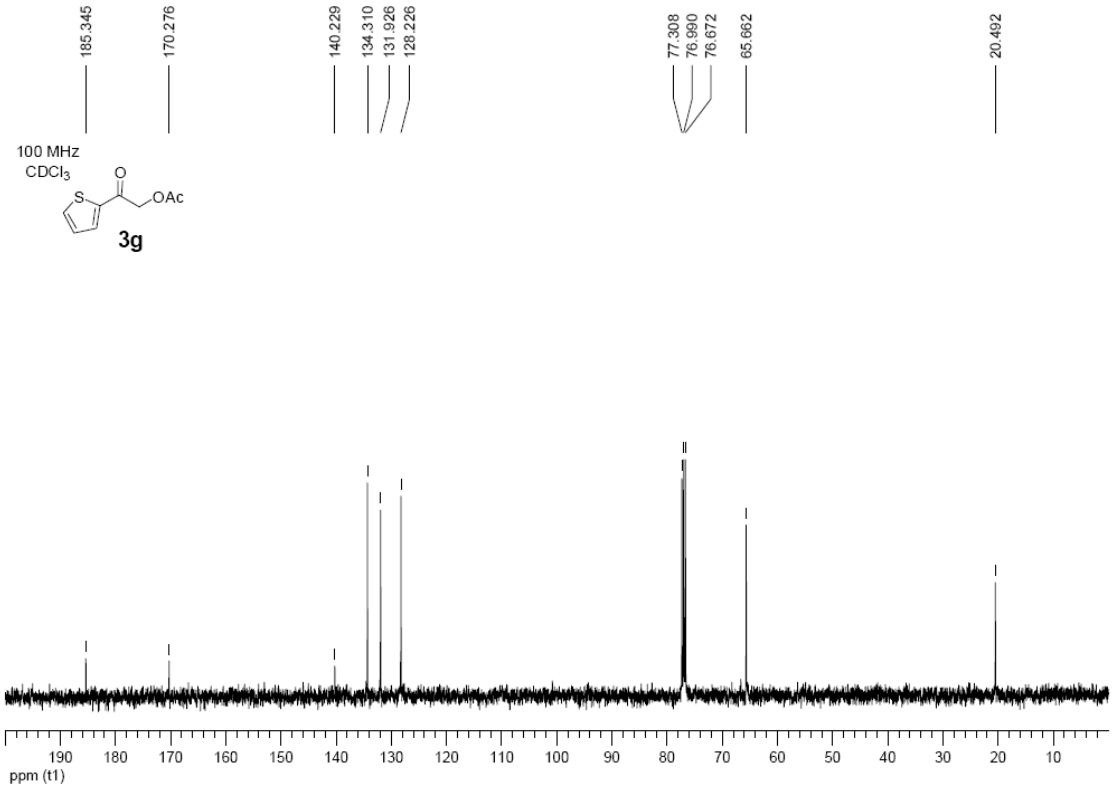

400 MHz
CDCl3
O
OAc
Br
3e
7.756
7.735
7.613
7.592
7.238
5.259
2.196
-0.034
1.82
1.85
2.06
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

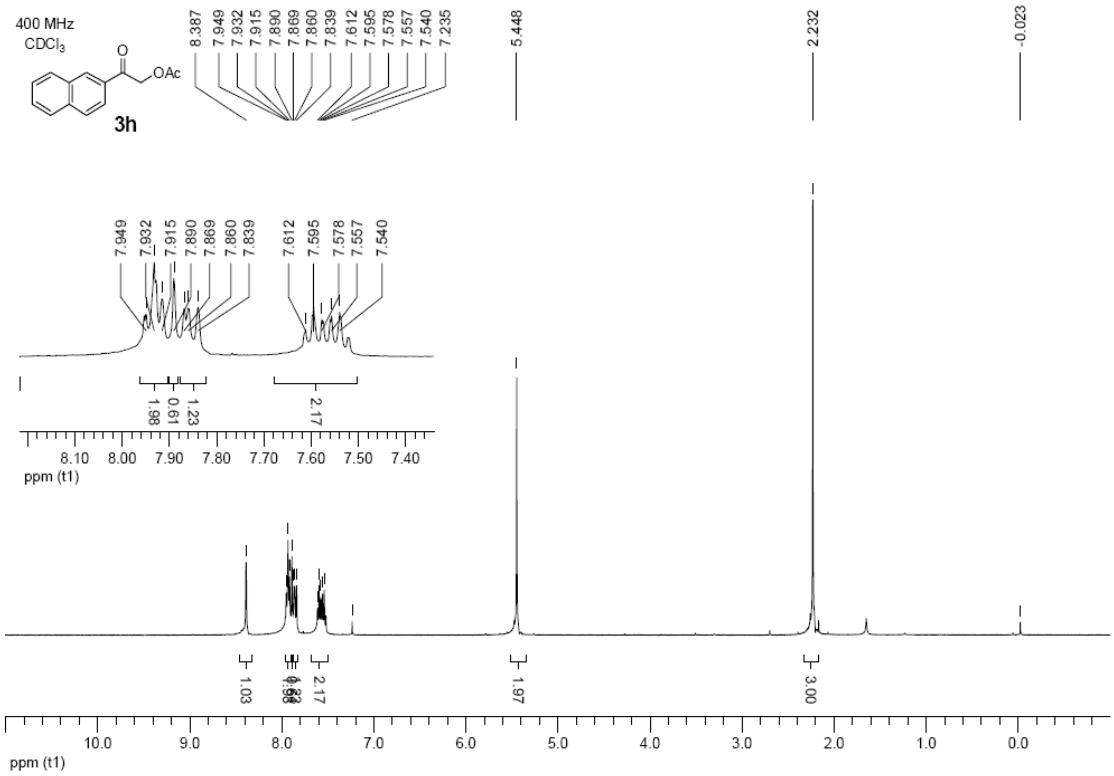

191.235
170.326
132.782
132.167
129.174
129.099
77.308
76.991
76.673
65.775
20.512
100 MHz
CDCl3
O
OAc
Br
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

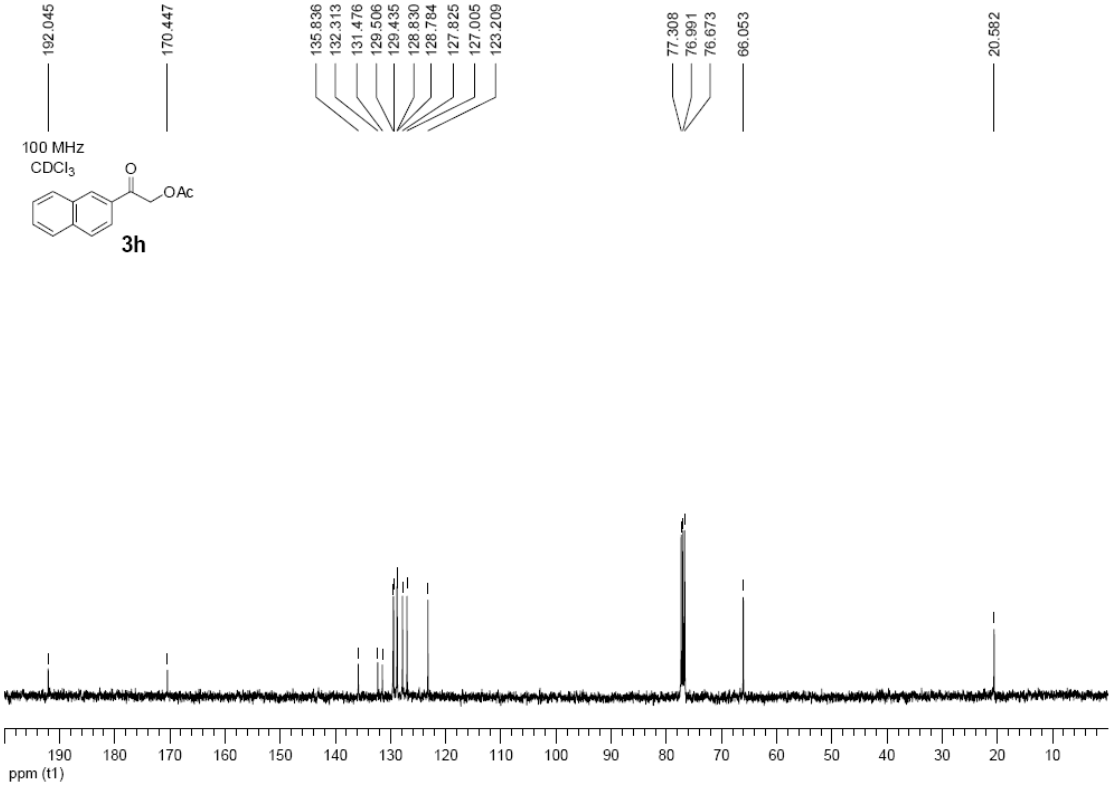

400 MHz
CDCl3
O
O
OAc
3f
7.631
7.302
7.293
6.606
6.597
5.200
2.296
0.013
1.01
1.04
0.98
1.98
3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

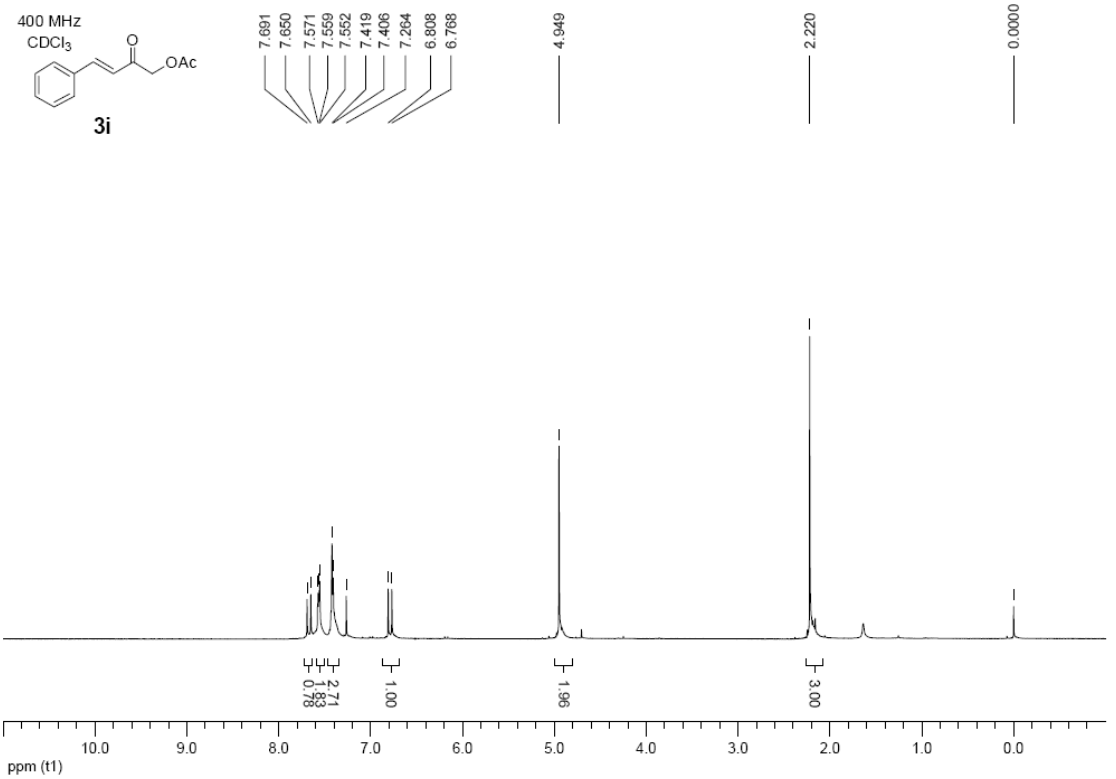

181.639
170.297
150.457
146.730
117.700
112.443
77.343
77.295
76.978
76.660
65.277
20.490
20.450
100 MHz
CDCl3
O
O
OAc
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

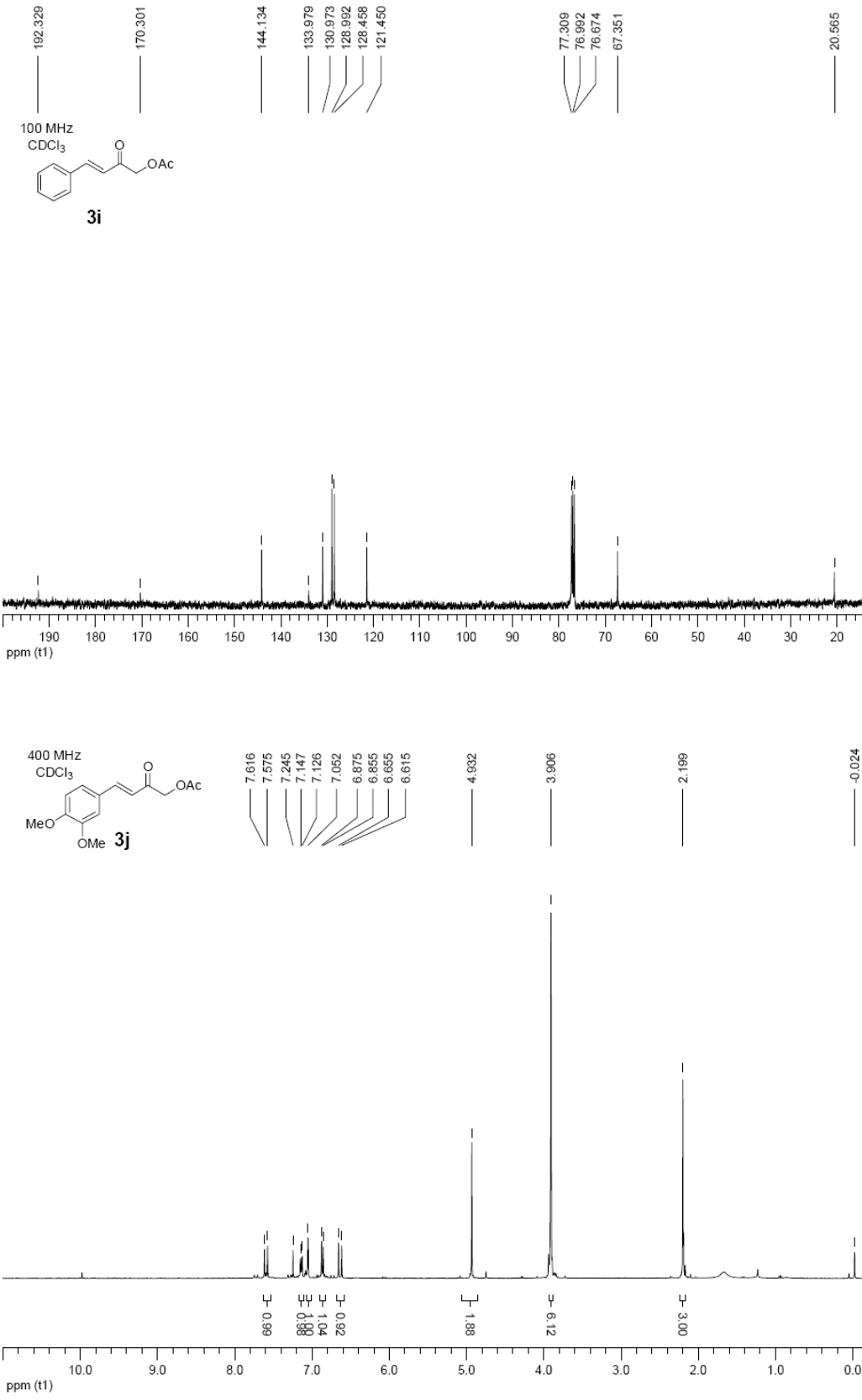

400 MHz
CDCl3
S
O
OAc
3g
7.618
7.289
7.280
6.593
6.584
5.187
2.223
-0.00000
1.01
1.07
0.99
2.11
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

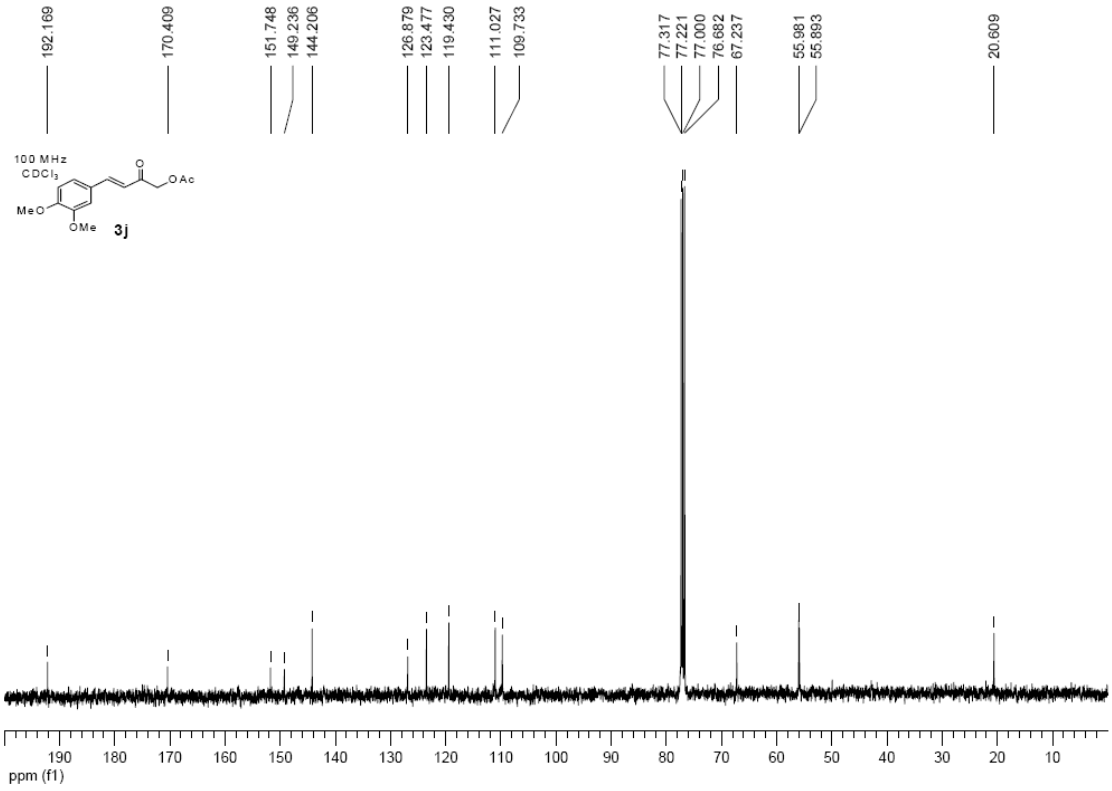

185.345
170.276
140.229
134.310
131.926
128.226
77.308
76.990
76.672
65.662
20.492
100 MHz
CDCl3
O
S
OAc
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

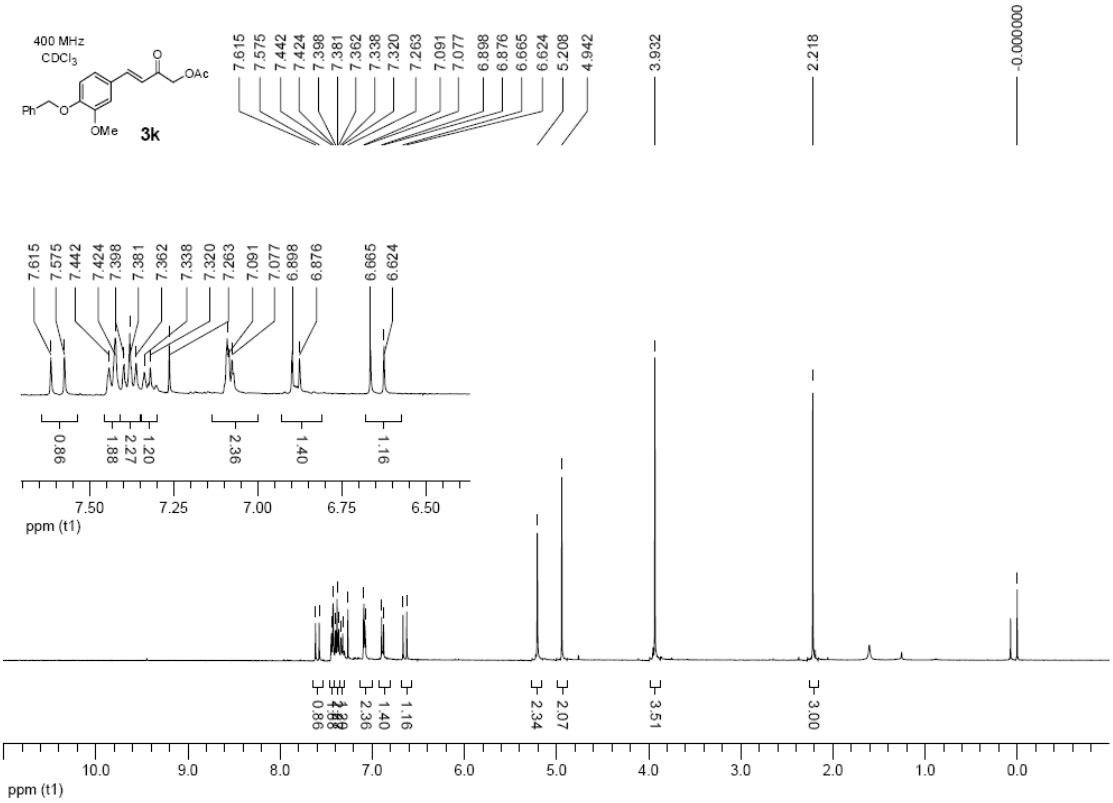

400 MHz
CDCl3
O
OAc
3h
8.387
7.949
7.932
7.915
7.890
7.869
7.860
7.839
7.612
7.595
7.578
7.557
7.540
7.235
5.448
2.232
-0.023
1.88
0.61
1.23
2.17
8.10 8.00 7.90 7.80 7.70 7.60 7.50 7.40
ppm (t1)
1.03
2.17
1.97
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

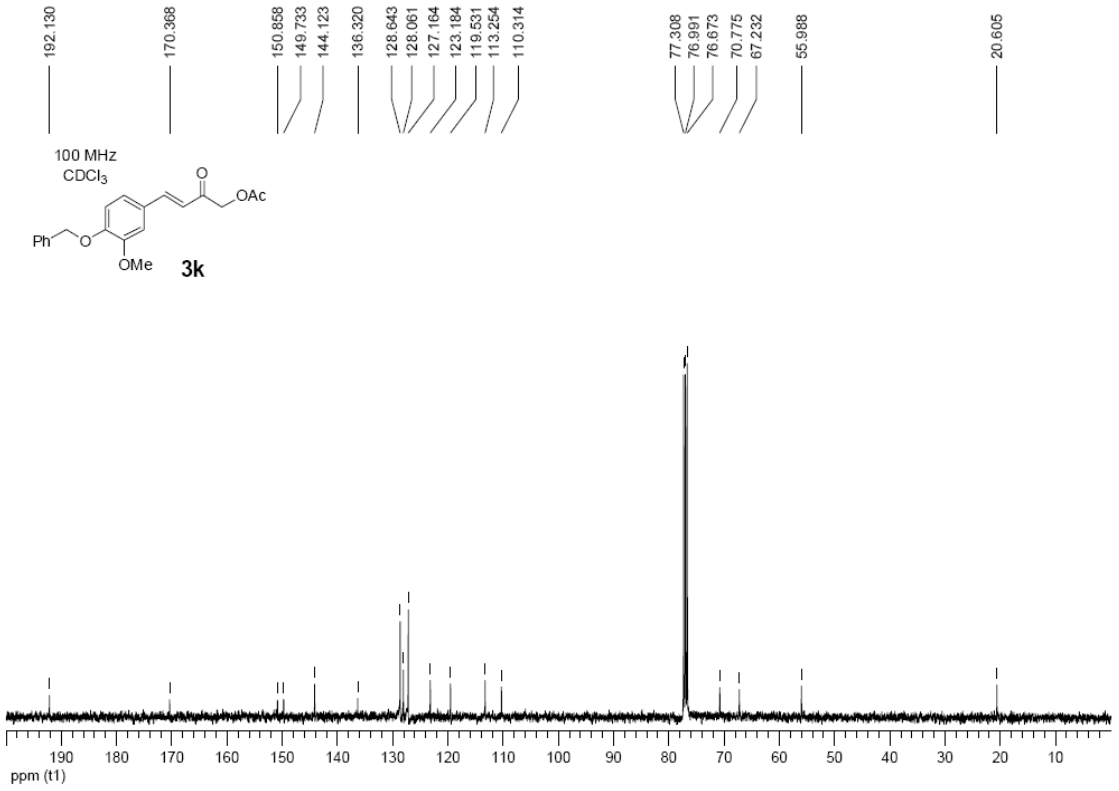

192.045
170.447
135.836
132.313
131.476
129.506
129.435
128.830
128.784
127.825
127.005
123.209
77.308
76.991
76.673
66.053
20.582
100 MHz
CDCl3
O
OAc
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

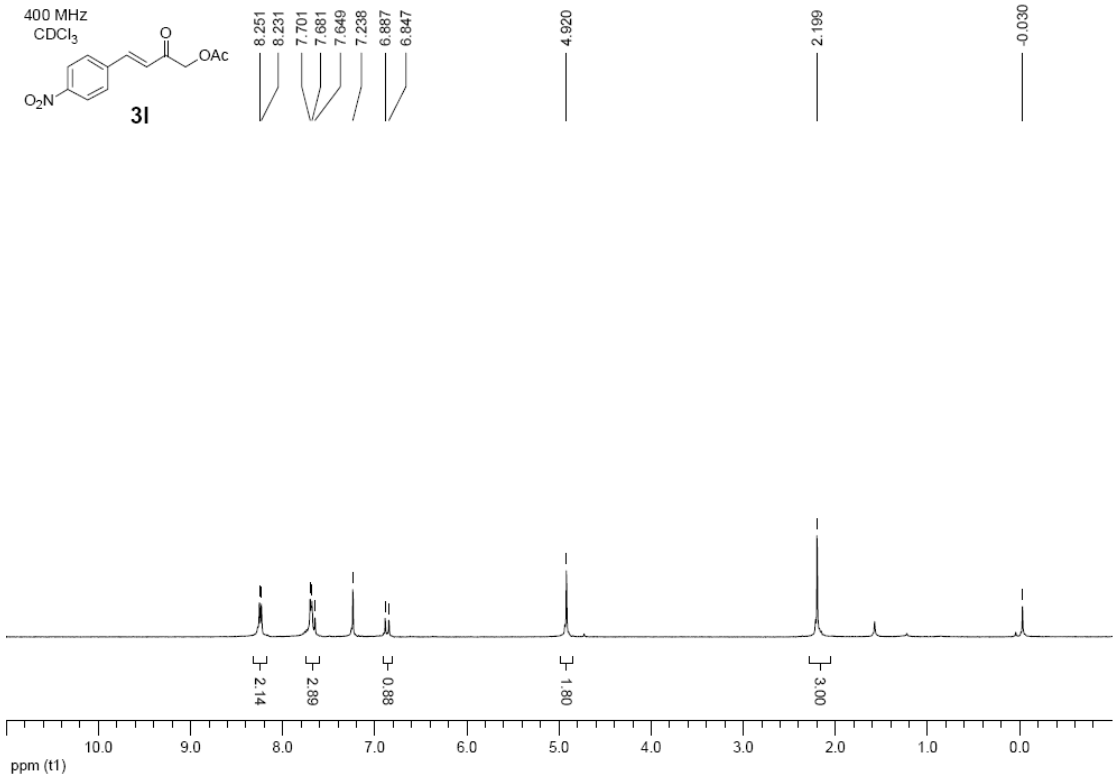

400 MHz
CDCl3
O
OAc
3i
7.691
7.650
7.571
7.559
7.552
7.419
7.406
7.264
6.808
6.768
4.949
2.220
0.0000
0.78
1.83
2.71
1.00
1.96
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

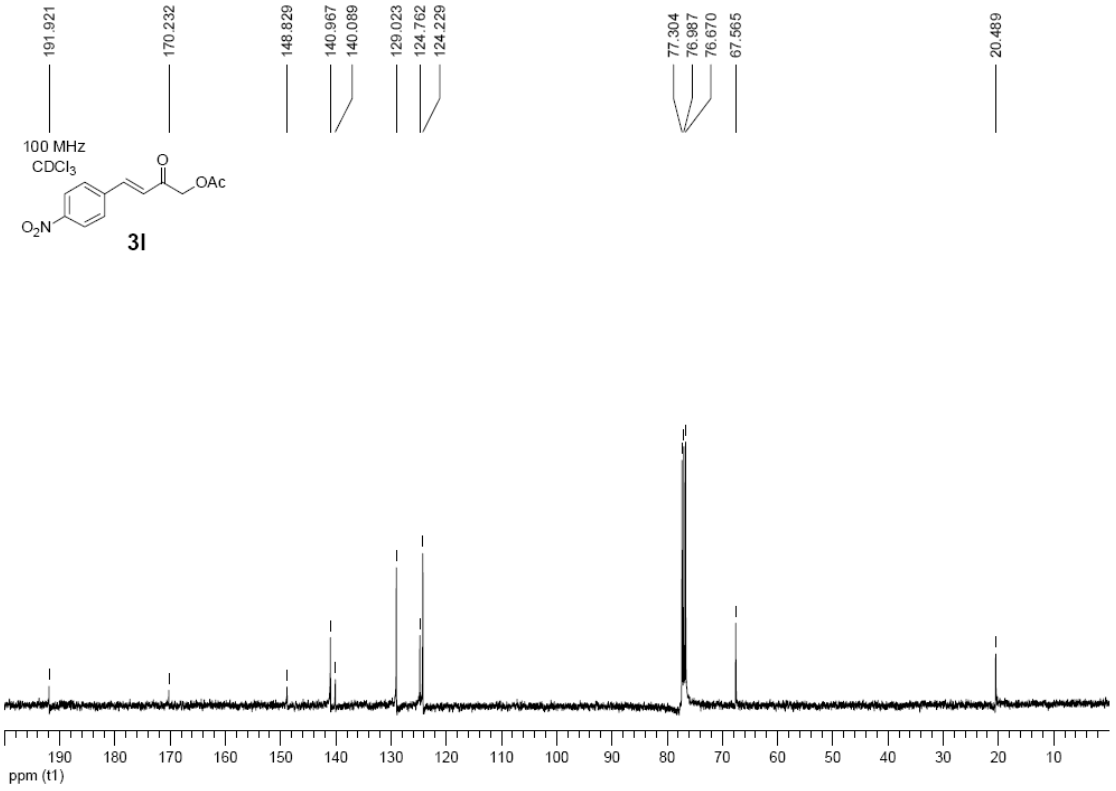

192.329
170.301
144.134
133.979
130.973
128.992
128.458
121.450
77.309
76.992
76.674
67.351
20.565
100 MHz
CDCl3
O
OAc
3i
ppm (t1)
400 MHz
CDCl3
O
OAc
MeO
OMe
3j
7.616
7.575
7.245
7.147
7.126
7.052
6.875
6.855
6.655
6.615
4.932
3.906
2.199
-0.024
0.99
1.04
0.92
1.88
6.12
3.00
ppm (t1)

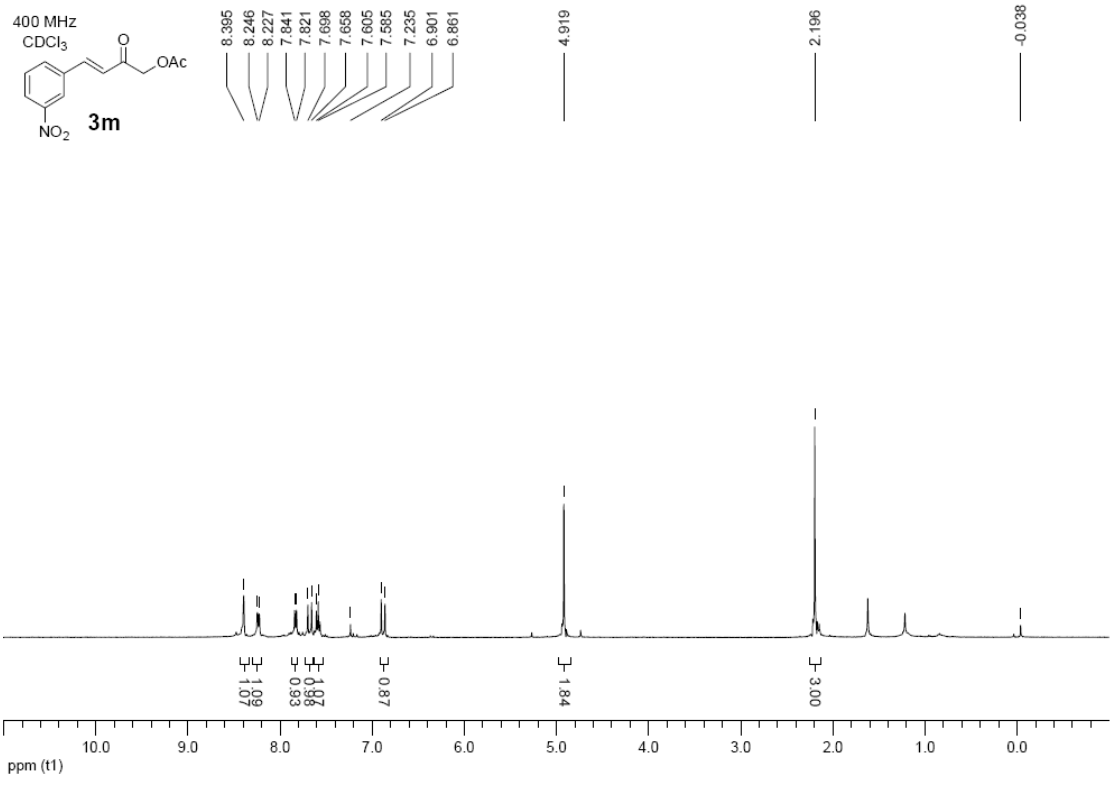

192.169
170.409
151.748
149.236
144.206
126.879
123.477
119.430
111.027
109.733
77.317
77.221
77.000
76.682
67.237
55.981
55.893
20.609
100 MHz
CDCl3
MeO
OMe
OAc
3j
ppm (f1)

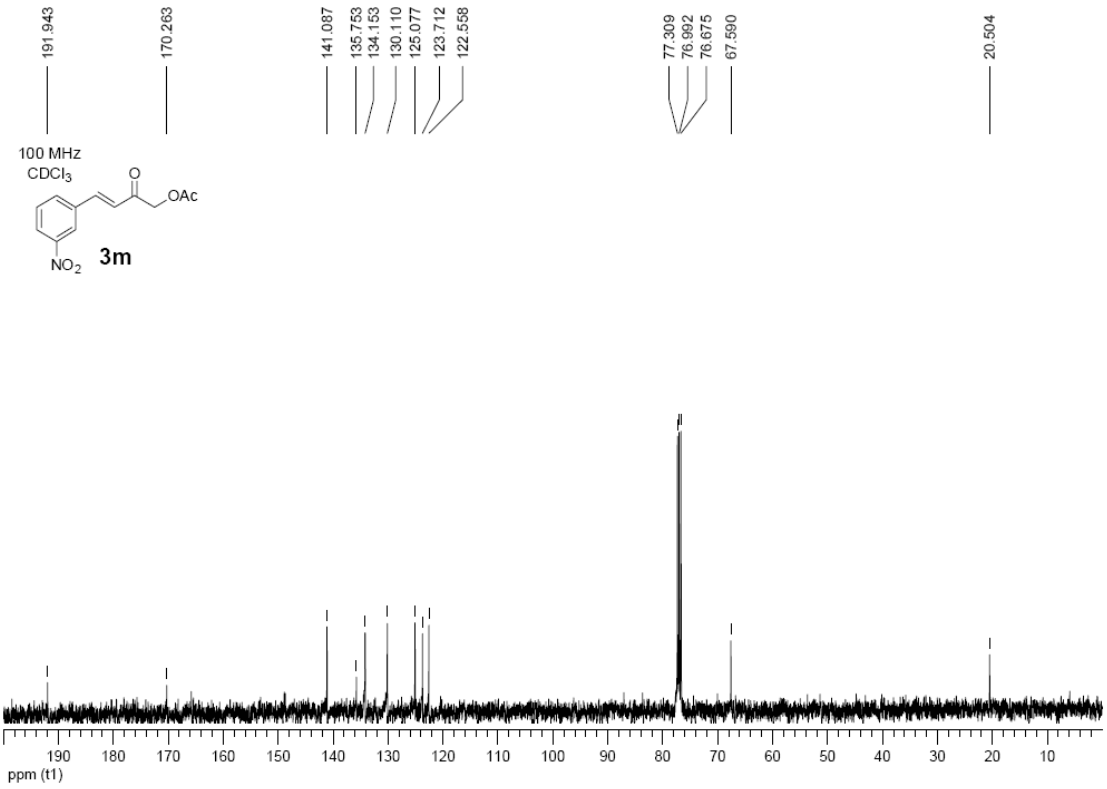

400 MHz
CDCl3
Ph
OMe
OAc
3k
7.615
7.575
7.442
7.424
7.398
7.381
7.362
7.338
7.320
7.263
7.091
7.077
6.898
6.876
6.665
6.624
5.208
4.942
3.932
2.218
-0.000000
0.86
1.88
2.27
1.20
2.39
1.40
1.16
ppm (t1)
0.89
2.36
1.40
1.16
2.34
2.07
3.51
3.00
ppm (t1)


192.130
170.368
150.858
149.733
144.123
136.320
128.643
128.061
127.164
123.184
119.531
113.254
110.314
77.308
76.991
76.673
70.775
67.232
55.988
20.605
100 MHz
CDCl3
O
OAc
Ph
O
OMe
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


400 MHz
CDCl3
O
OAc
O2N
3l
8.251
8.231
7.701
7.681
7.649
7.238
6.887
6.847
4.920
2.199
-0.030
2.14
2.89
0.88
1.80
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


191.921
170.232
148.829
140.967
140.089
129.023
124.762
124.229
77.304
76.987
76.670
67.565
20.489
100 MHz
CDCl3
O
OAc
O2N
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)


400 MHz
CDCl3
O
OAc
NO2
3m
8.395
8.246
8.227
7.841
7.821
7.698
7.658
7.605
7.585
7.235
6.901
6.861
4.919
2.196
-0.038
1.09
1.07
0.93
0.98
1.02
1.20
0.87
1.84
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)


191.943
170.263
141.087
135.753
134.153
130.110
125.077
123.712
122.558
77.309
76.992
76.675
67.590
20.504
100 MHz
CDCl3
O
OAc
NO2
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)