Supporting information for

Copper-Catalyzed Oxidative Cyclization of Arylamides and *β*-Diketones: New Synthesis of 2,4,5-Trisubstituted Oxazoles

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General information:

All experiments were carried out under an atmosphere of argon. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on an Agilent5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and HRMS. Unless otherwise noted, all reagents were used as received from commercial sources without further purification. Copper salts and benzamide **1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 2a, 2b** were purchased from Alfa-Aesar and were used as received without further purification, others were prepared according to the literature procedures.

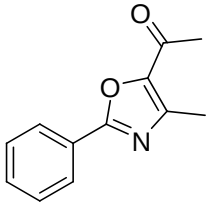
General Procedure for the preparation of *β*-diketo derivatives (2c-2j) [1]:

Procedure for 1-phenylbutane-1,3-dione (**2c**): acetophenone (1166 μL, 10 mmol) in dry ethyl acetate (10 mL) was added dropwise, at 0 ^{o}C, to a power of NaH (1.477g of a 65% power, 40 mmol) in dry ethyl acetate (10 mL) and the reaction mixture was stirred at 0 ^{o}C for 2 h and at 25 ^{o}C for further 12 h (TLC). 10% aqueous NH_4Cl was then carefully added (30 mL) and the mixture was acidified to pH 5 with HCl. The aqueous phase was separated and extracted with ethyl acetate (3 ×15 mL). The combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure; the crude product was purified by FC, with ethyl acetate/petroleum ether 9:1 as eluant, to give the diketone 1.225 g. Similarly, other diketo derivatives (**2c-2j**) were prepared from their corresponding ketone.

General procedure for oxidative cyclization reaction (3a):

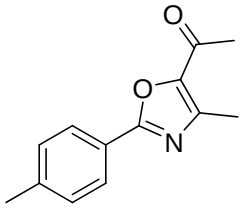
A 10 mL reaction vessel was charged with CuBr (5.7 mg, 0.04 mmol), benzamide (**1a**, 48.4 mg, 0.4 mmol), $K_2S_2O_8$ (108 mg, 2 equiv). The sealed reaction vessel was purged with argon three times. Pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol), acetic acid (23 μL, 2 equiv) and 1,1,2,2-tetrachloroethane (0.4 mL) were added to the sealed reaction vessel by syringe. The resulting solution was stirred at 140 ^{o}C for 36 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give 33.5 mg **3a** as pale yellow solid; yield 83%.

1-(4-Methyl-2-phenyloxazol-5-yl)ethanone (3a)



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (d, J = 8.0 Hz, 2H), 7.52-7.50 (m, 3H), 2.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 188.1, 162.0, 146.9, 145.8, 132.3, 129.6, 127.8, 127.1, 28.1, 14.4; MS (EI) m/z (%) 201, 186, 158, 130 (100), 77; HRMS calcd. for: $C_{12}H_{11}O_2NNa$ $[M+Na]^+$ 224.06820, found 224.06823.

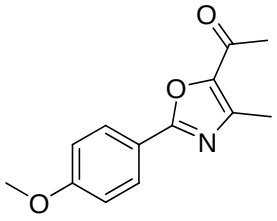
1-(4-Methyl-2-p-tolyloxazol-5-yl)ethanone (3b)



The reaction was conducted with 4-methylbenzamide (**1b**, 54.0 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give **3b** as pale yellow solid; yield 81%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.4, 161.7, 146.3, 145.0, 142.2, 129.7, 127.2, 123.8, 27.4, 21.6, 13.8; MS (EI) m/z (%) 215, 172, 144 (100), 118, 77; HRMS calcd. for: $C_{13}H_{14}O_2N$ $[M+H]^+$ 216.10191, found 216.10184.

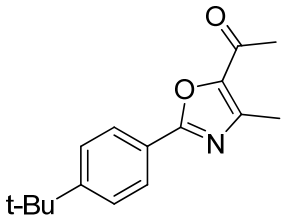
1-(2-(4-Methoxyphenyl)-4-methyloxazol-5-yl)ethanone (3c)



The reaction was conducted with 4-methoxybenzamide (**1c**, 60.4 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3c** as pale yellow solid; yield 82%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.065 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.9, 163.1, 162.3, 147.1, 145.6, 129.7, 119.8, 115.1, 56.1, 28.0, 14.5; MS (EI) m/z (%) 231, 188, 160 (100), 119, 76; HRMS calcd. for: $C_{13}H_{14}O_3N$ $[M+H]^+$ 232.09682, found 232.09673.

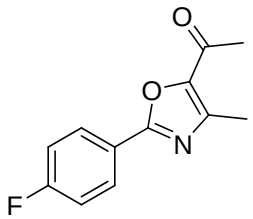
1-(2-(4-Tert-butylphenyl)-4-methyloxazol-5-yl)ethanone (3d)



The reaction was conducted with 4-(*tert*-butyl)benzamide (**1d**, 70.8 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give **3d** as pale yellow solid; yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, J = 12.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 2.57 (s, 3H), 2.56 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.4, 161.7, 155.3, 146.4, 145.0, 127.1, 125.9, 123.7, 35.1, 31.1, 27.4, 13.8; MS (EI) m/z (%) 257, 242 (100), 186, 115, 77; HRMS calcd. for: $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.14886, found 258.14874.

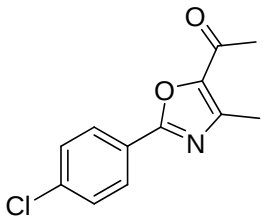
1-(2-(4-Fluorophenyl)-4-methyloxazol-5-yl)ethanone (3e)



The reaction was conducted with 4-fluorobenzamide (**1e**, 55.6 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3e** as yellow solid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13-8.10 (m, 2H), 7.21-7.17 (m, 2H), 2.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.2, 164.8 (d, J = 251.2 Hz), 160.5, 146.3, 145.2, 129.4 (d, J = 9.1 Hz), 122.8 (d, J = 3.0 Hz), 116.2 (d, J = 22.0 Hz), 27.4, 13.7; MS (EI) m/z (%) 219, 176, 148 (100), 122, 75; HRMS calcd. for: $C_{12}H_{11}O_2NF$ $[M+H]^+$ 220.07683, found 220.07677.

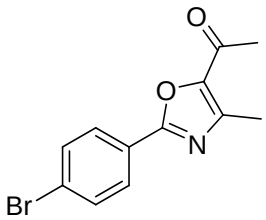
1-(2-(4-Chlorophenyl)-4-methyloxazol-5-yl)ethanone (3f)



The reaction was conducted with 4-chlorobenzamide (**1f**, 62.0 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3f** as pale yellow solid; yield 70%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 2.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.3, 160.4, 146.3, 145.3, 137.9, 129.3, 128.4, 125.0, 27.4, 13.7; MS (EI) m/z (%) 235, 192, 164 (100), 138, 75; HRMS calcd. for: $C_{12}H_{11}O_2NCl$ $[M+H]^+$ 236.04728, found 236.04720.

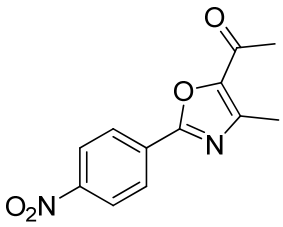
1-(2-(4-Bromophenyl)-4-methyloxazol-5-yl)ethanone (3g)



The reaction was conducted with 4-bromobenzamide (**1g**, 79.6 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3g** as pale yellow solid; yield 68%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 2.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.9, 161.2, 147.0, 146.0, 133.0, 129.2, 127.0, 126.1, 28.1, 14.4; MS (EI) m/z (%) 279, 236, 208 (100), 182, 76; HRMS calcd. for: $C_{12}H_{11}O_2NBr$ $[M+H]^+$ 279.99677, found 279.99680.

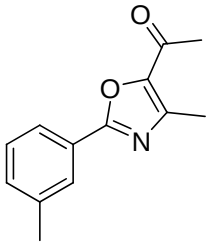
1-(4-Methyl-2-(4-nitrophenyl)oxazol-5-yl)ethanone (3h)



The reaction was conducted with 4-nitrobenzamide (**1h**, 66.4 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3h** as pale yellow solid; yield 38%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.36 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 8.0 Hz, 2H), 2.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 188.0, 159.6, 150.2, 147.2, 146.6, 132.5, 128.6, 124.9, 28.2, 14.4; MS (EI) m/z (%) 246, 203, 175 (100), 129, 76; HRMS calcd. for: $C_{12}H_{11}N_2O_4$ $[M+H]^+$ 247.07133, found 247.07163.

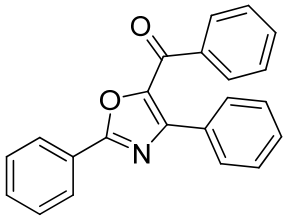
1-(4-Methyl-2-m-tolyloxazol-5-yl)ethanone (3i)



The reaction was conducted with 3-methylbenzamide (**1i**, 54.0 mg, 0.4 mmol) and pentane-2,4-dione (**2a**, 21 μL, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 95:5) to give **3i** as pale yellow solid; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (s, 1H), 7.90 (d, J = 4.0 Hz, 1H), 7.40–7.33 (m, 2H), 2.57 (s, 6H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 187.5, 161.6, 146.3, 145.0, 138.8, 132.5, 128.8, 127.7, 126.2, 124.3, 27.5, 21.3, 13.8; MS (EI) m/z (%) 215, 172, 144 (100), 118, 77; HRMS calcd. for: $C_{13}H_{14}O_2N$ $[M+H]^+$ 216.10191, found 216.10184.

(2,4-Diphenyloxazol-5-yl)(phenyl)methanone (3j)

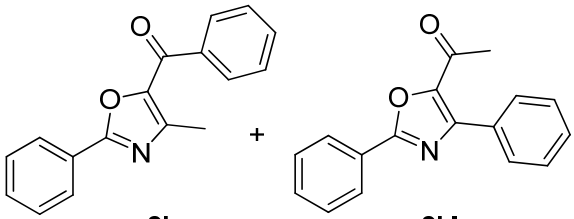


The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and 1,3-diphenylpropane-1,3-dione (**2b**, 44.8 mg, 0.2 mmol) for 48 h. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93：7) to give **3j** as pale yellow solid; yield 81%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, J = 4.0 Hz, 2H), 8.09 (d, J = 4.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.60-7.42 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 183.8, 162.6, 149.5, 144.3, 138.4, 133.5, 132.4, 131.4, 130.5, 130.3, 130.1, 129.7, 129.1, 128.9, 128.2, 127.1; MS (EI) m/z (%) 325 (100), 220, 192, 89, 77; HRMS calcd. for: $C_{22}H_{16}O_2N$ $[M+H]^+$ 326.11756, found 326.11722.

(4-Methyl-2-phenyloxazol-5-yl)(phenyl)methanone (3k) and

1-(2,4-diphenyloxazol-5-yl)ethanone (3k')



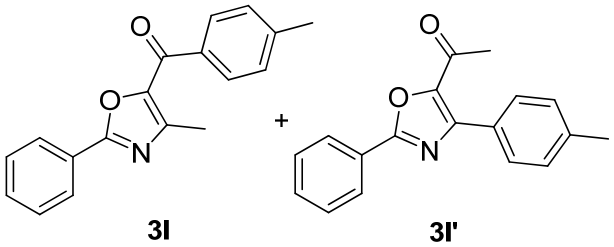
3k **3k'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol), 1-phenylbutane-1,3-dione (**2c**, 32.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give **3k** and **3k'** as pale yellow solid; yield 82%. The ratio of the regioisomers was determined by GC (3:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27–8.26 (m, 0.5H), 8.22-8.20 (m, 0.5H), 8.12-8.06 (m, 2.7H), 7.67-7.45 (m, 6.3H), 2.64-2.63 2s (2.64 s, (minor), 2.63 s, (major), 3H); MS (EI) m/z (%) 263, 246, 158, 130 (100), 77 (**3k**), 263, 248, 220, 192, 89 (100) (**3k'**); HRMS calcd. for: $C_{17}H_{14}O_2N$ $[M+H]^+$ 264.10191, found 264.10170.

(4-Methyl-2-phenyloxazol-5-yl)(p-tolyl)methanone (3l) and

1-(2-phenyl-4-p-tolyloxazol-5-yl)ethanone (3l')



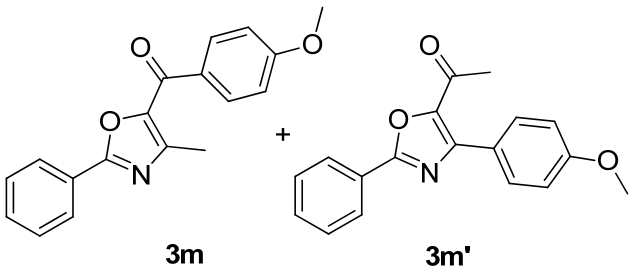
3l **3l'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol), 1-(p-tolyl)butane-1,3-dione (**2d**, 35.2 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give **3l** and **3l'** as pale yellow solid; yield 81%. The ratio of the regioisomers was determined by GC (4:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21–8.17 (m, 1.1H), 8.11 (d, J = 4.0 Hz, 1.5H), 7.99 (d, J = 8.0 Hz, 1.4H), 7.54-7.50 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.47-2.42 2s (2.47 s, (major), 2.42 s, (minor), 3H); MS (EI) m/z (%) 277, 262, 158, 130 (100), 77 (**3l**), 277 (100), 262, 234, 206, 103 (**3l'**); HRMS calcd. for: $C_{18}H_{16}O_2N$ $[M+H]^+$ 278.11756, found 278.11719.

(4-Methoxyphenyl)(4-methyl-2-phenyloxazol-5-yl)methanone (3m)

and 1-(4-(4-methoxyphenyl)-2-phenyloxazol-5-yl)ethanone (3m')



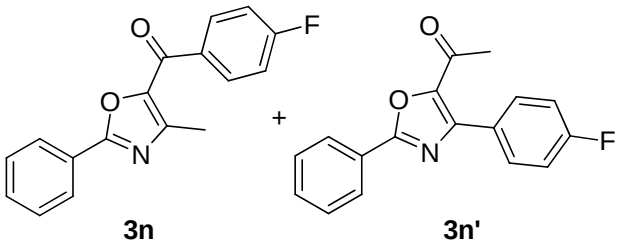
3m **3m'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol), 1-(4-methoxyphenyl)butane-1,3-dione (**2e**, 38.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 85:15) to give **3m** and **3m'** as pale yellow solid; yield 76%. The ratio of the regioisomers was determined by GC (4:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.34-8.32 (m, 0.4H), 8.19-8.11 (m, 3.8H), 7.61-7.45 (m, 3.1H), 7.04-7.02 (m, 1.7H), 3.92-3.87 2s (3.92 s, (major), 3.87 s, (minor), 3H), 2.63 (s, 3H); MS (EI) m/z (%) 293, 262, 158, 130 (100), 77 (**3m**), 293, 278, 250, 147 (100), 76 (**3m'**); HRMS calcd. for: $C_{18}H_{16}O_3N$ $[M+H]^+$ 294.11247, found 294.11215.

(4-Fluorophenyl)(4-methyl-2-phenyloxazol-5-yl)methanone (3n)

and 1-(4-(4-fluorophenyl)-2-phenyloxazol-5-yl)ethanone (3n')



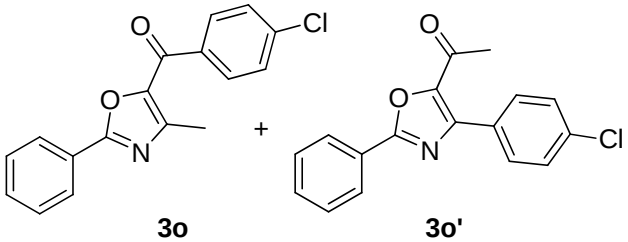
3n **3n'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and 1-(4-fluorophenyl)butane-1,3-dione (**2f**, 36.0 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 93:7) to give **3n** and **3n'** as pale yellow solid; yield 66%. The ratio of the regioisomers was determined by GC (3:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.38-8.36 (m, 0.3H), 8.34-8.09 (m, 3.7H), 7.54-7.49(m, 3H), 7.24-7.13 (m, 2H), 2.65-2.64 2s (2.65 s, (minor), 2.64 s, (major), 3H); MS (EI) m/z (%) 281, 264, 158, 130 (100), 77 (**3n**), 281, 266, 238, 210, 107 (100) (**3n**'); HRMS calcd. for: $C_{17}H_{13}O_2NF$ $[M+H]^+$ 282.09248, found 282.09216.

(4-Chlorophenyl)(4-methyl-2-phenyloxazol-5-yl)methanone (3o)

and 1-(4-(4-chlorophenyl)-2-phenyloxazol-5-yl)ethanone (3o')



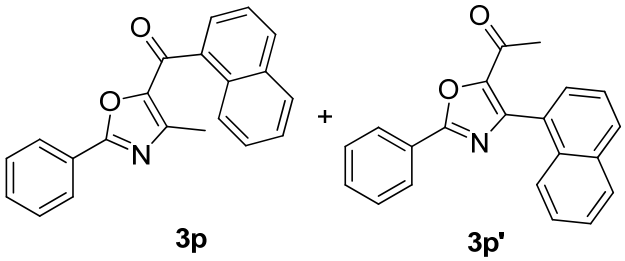
3o **3o'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and 1-(4-chlorophenyl)butane-1,3-dione (**2g**, 39.2 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =93:7) to give **3o** and **3o'** as pale yellow solid; yield 73%. The ratio of the regioisomers was determined by GC (4:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.31 (d, J = 8.0 Hz, 0.3H), 8.20-8.19 (m, 0.3H), 8.10 (d, J = 8.0 Hz, 1.5H), 8.03 (d, J = 12.0 Hz, 1.5H), 7.54-7.44 (m, 5.4H), 2.66-2.64 2s (2.66 s, (minor), 2.64 s, (major), 3H); MS (EI) m/z (%) 297, 262, 158, 130 (100), 77 (**3o**), 297, 262 (100), 226, 123, 77 (**3o'**); HRMS calcd. for: $C_{17}H_{13}O_2NCl$ $[M+H]^+$ 298.06293, found 298.06257.

(4-Methyl-2-phenyloxazol-5-yl)(naphthalen-1-yl)methanone (3p)

and 1-(4-(naphthalen-1-yl)-2-phenyloxazol-5-yl)ethanone (3p')



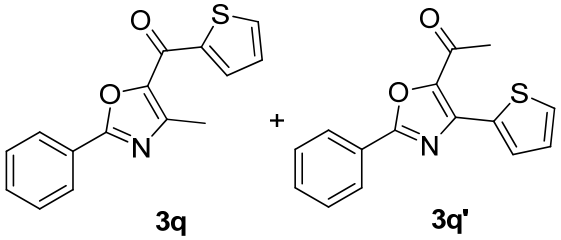
3p **3p'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and 1-(naphthalen-1-yl)butane-1,3-dione (**2h**, 42.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =93:7) to give **3p** and **3p'** as pale yellow solid; yield 75%. The ratio of the regioisomers was determined by GC (80:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21-8.19 (m, 1H), 8.06-8.03 (m, 2H), 7.96-7.93 (m, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.60-7.44 (m, 7H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 184.7, 162.6, 149.1, 145.6, 135.7, 133.8, 131.8, 131.7, 130.5, 128.9, 128.5, 127.5, 127.4, 127.3, 126.6, 126.3, 125.2, 124.5, 14.3; MS (EI) m/z (%) 313, 285, 158, 130 (100), 77 (**3p**), 313, 298, 242, 139 (100), 77 (**3p'**); HRMS calcd. for: $C_{21}H_{16}O_2N$ $[M+H]^+$ 314.11756, found 314.11706.

(4-Methyl-2-phenyloxazol-5-yl)(thiophen-2-yl)methanone (3q)

and 1-(2-phenyl-4-(thiophen-2-yl)oxazol-5-yl)ethanone (3q')



3q **3q'**

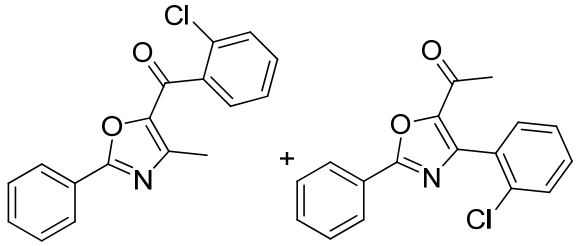
The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and 1-(thiophen-2-yl)butane-1,3-dione (**2i**, 33.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =20:1) to give **3q** and **3q'** as pale yellow solid; yield 77%. The ratio of the regioisomers was determined by GC (8:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50-8.49 (m, 0.1H), 8.25-8.24 (m, 0.9H), 8.17-8.15 (m, 2H), 7.765 (d, J = 8.0 Hz, 1H), 7.54-7.53 (m, 3.3H), 7.26-7.25 (m, 0.6H), 7.18-7.16 (m, 0.1H), 2.67-2.66 2s (2.67 s, (minor), 2.66 s, (major), 3H); MS (EI) m/z (%) 269, 252, 158, 130 (100), 77

(**3q**), 269, 222, 207, 123 (100), 77 (**3q'**); HRMS calcd. for: $C_{15}H_{12}O_2NS$ $[M+H]^+$ 270.05833, found 270.05795.

(2-Chlorophenyl)(4-methyl-2-phenyloxazol-5-yl)methanone (3r)

and 1-(4-(2-chlorophenyl)-2-phenyloxazol-5-yl)ethanone (3r')

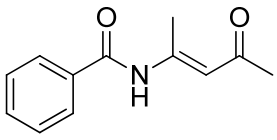


3r **3r'**

The reaction was conducted with benzamide (**1a**, 48.4 mg, 0.4 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =50:1) to give **3r** and **3r'** as pale yellow solid; yield 50%. The ratio of the regioisomers was determined by GC (4:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, J = 8.0 Hz, 0.3H), 8.06 (d, J = 8.0 Hz, 1.3H), 7.56-7.39 (m, 7.4H), 2.42-2.39 2s, (2.42 s, (major), 2.39 s, (minor), 3H); MS (EI) m/z (%) 297, 262, 158, 130 (100), 77 (**3r**), 297, 262 (100), 226, 123, 77 (**3r'**); HRMS calcd. for: $C_{17}H_{13}O_2NCl$ $[M+H]^+$ 298.06293, found 298.06286.

(*E*)-*N*-(4-Oxopent-2-en-2-yl)benzamide (4a)

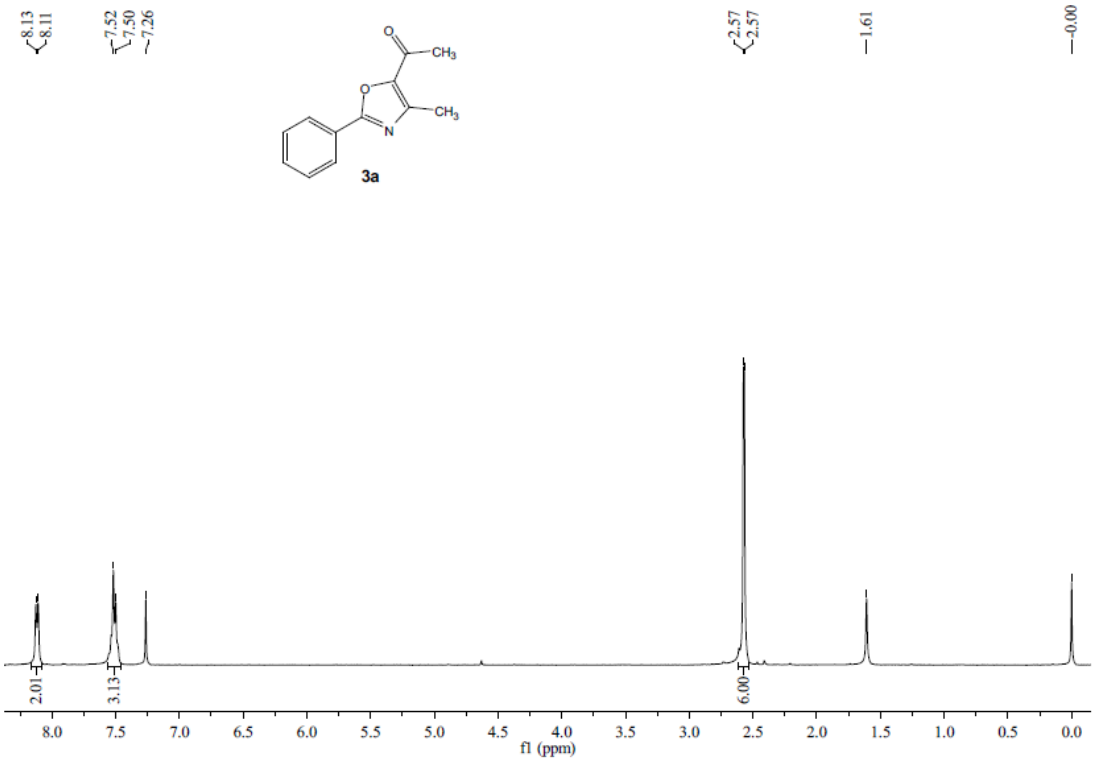


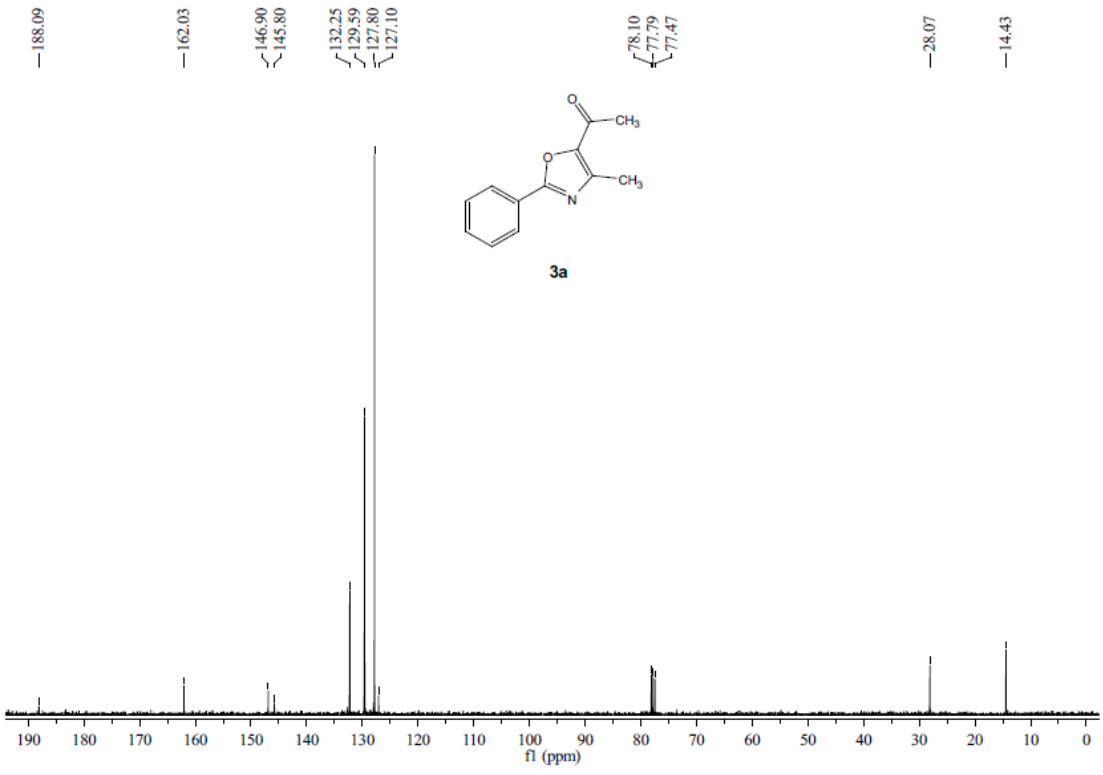
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 13.39 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.59-7.48 (m, 3H), 5.48 (s, 1H), 2.54 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 200.06, 166.01, 156.08, 133.65, 132.62, 128.88, 127.95, 106.16, 30.44, 22.00; MS (EI) m/z (%) 203, 185, 160, 105 (100), 77.

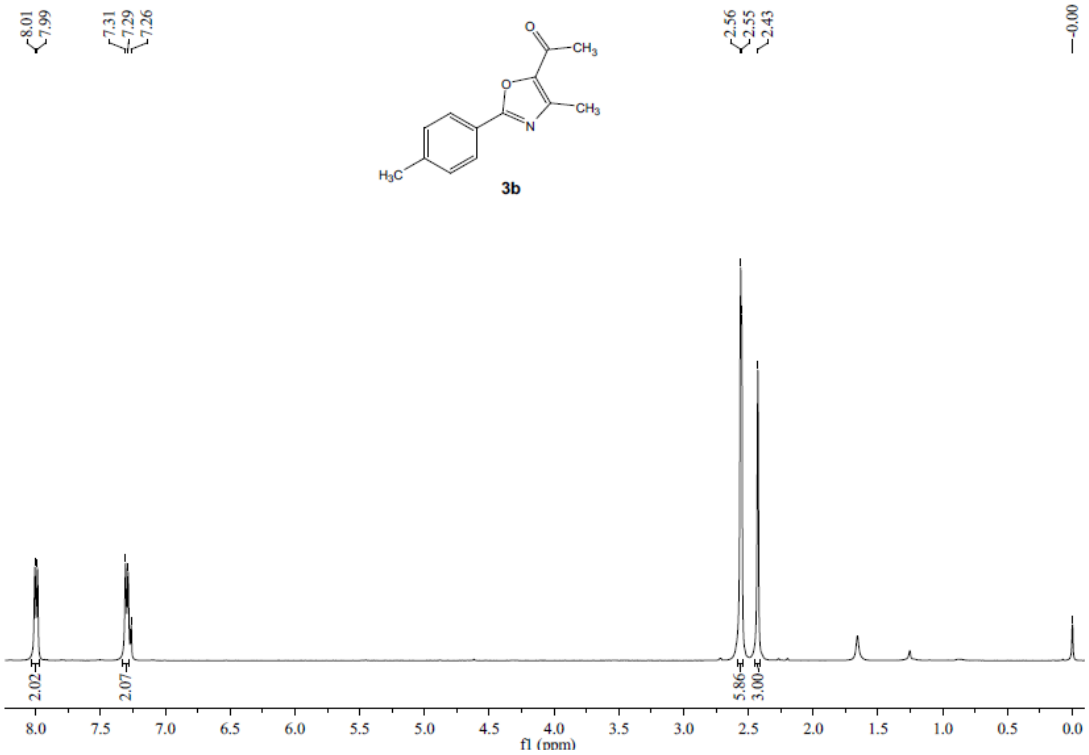
Reference

1. F. Berti, S. Bincoletto, I. Donati, G. Fontanive, M. Fregonese, F. Benedetti, *Org. Biomol. Chem.* **2011**, *9*, 1987.

^{1}H NMR and ^{13}C NMR spectra



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7.99
7.31
7.29
7.26
2.56
2.55
2.43
0.00
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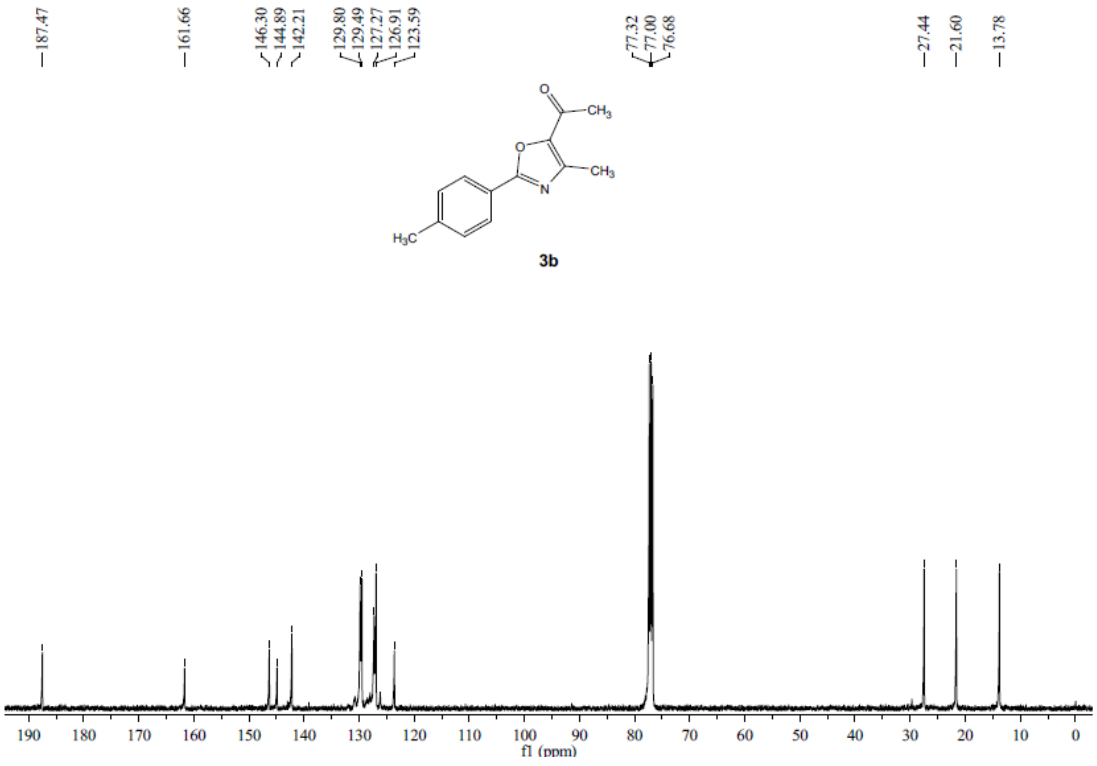
CH3
O
CH3
N
H3C
3b
2.02
2.07
5.86
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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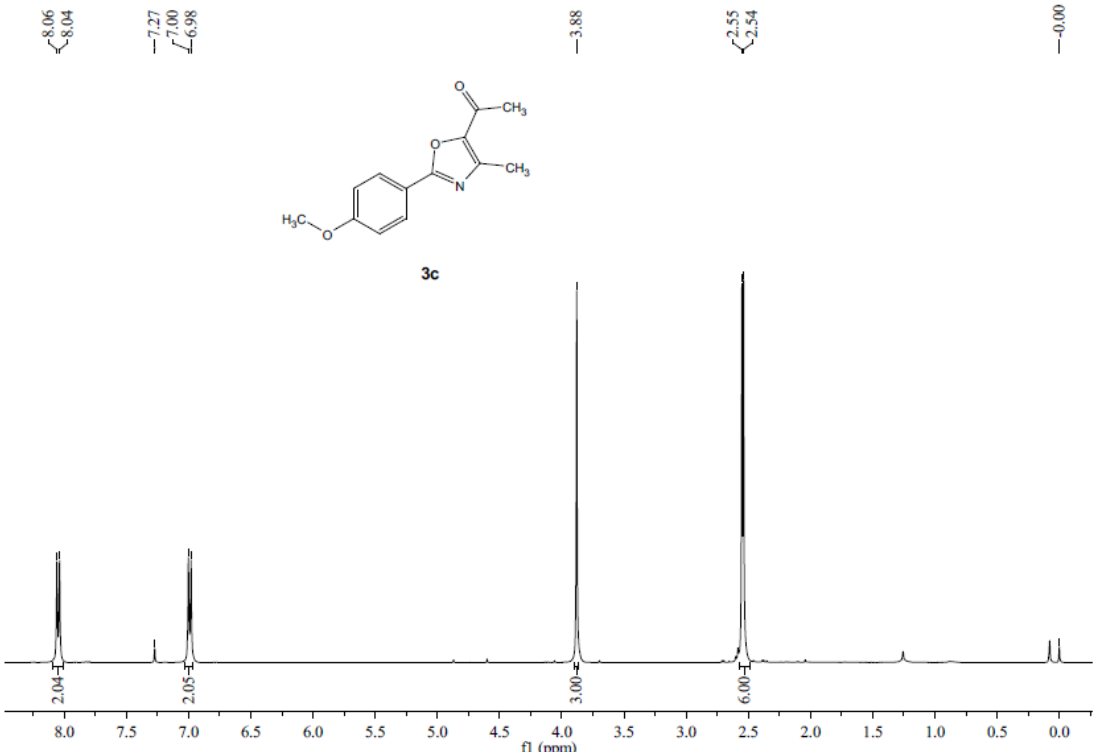
161.66
146.30
144.89
142.21
129.80
129.49
127.27
126.91
123.59
77.32
77.00
76.68
27.44
21.60
13.78
O
CH3
O
CH3
N
H3C
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.04
7.27
7.00
6.98
3.88
2.55
2.54
0.00
3c
2.04
2.05
3.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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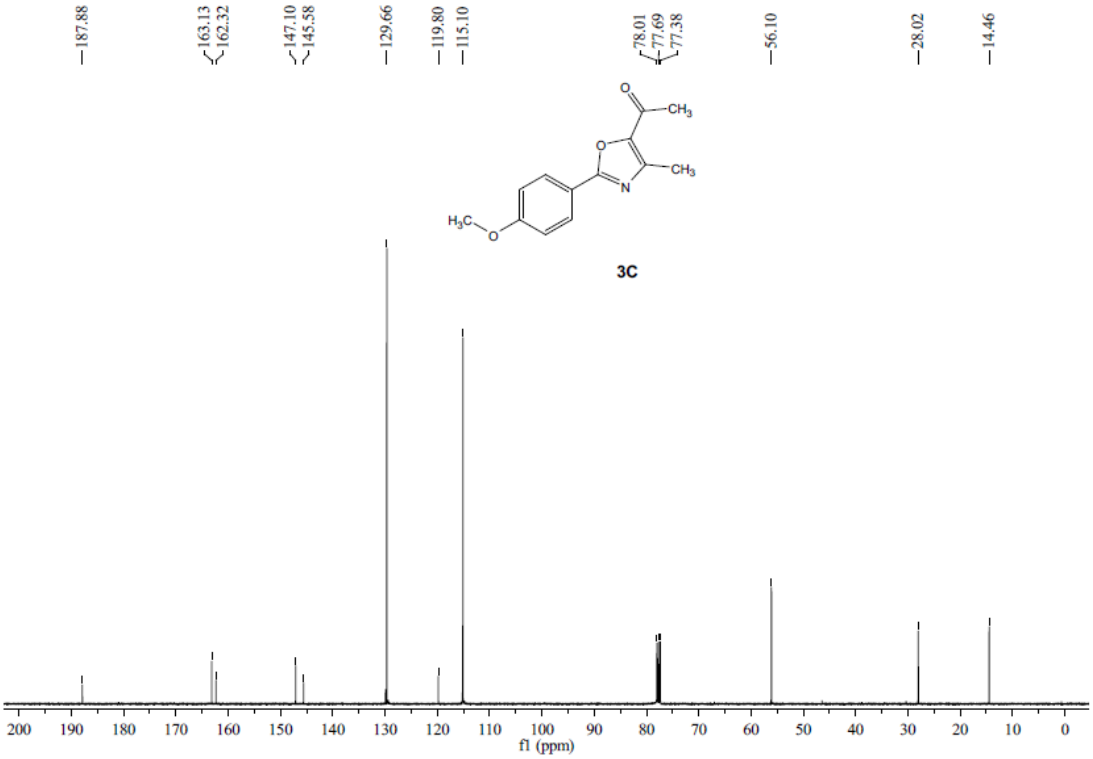
0.0
f1 (ppm)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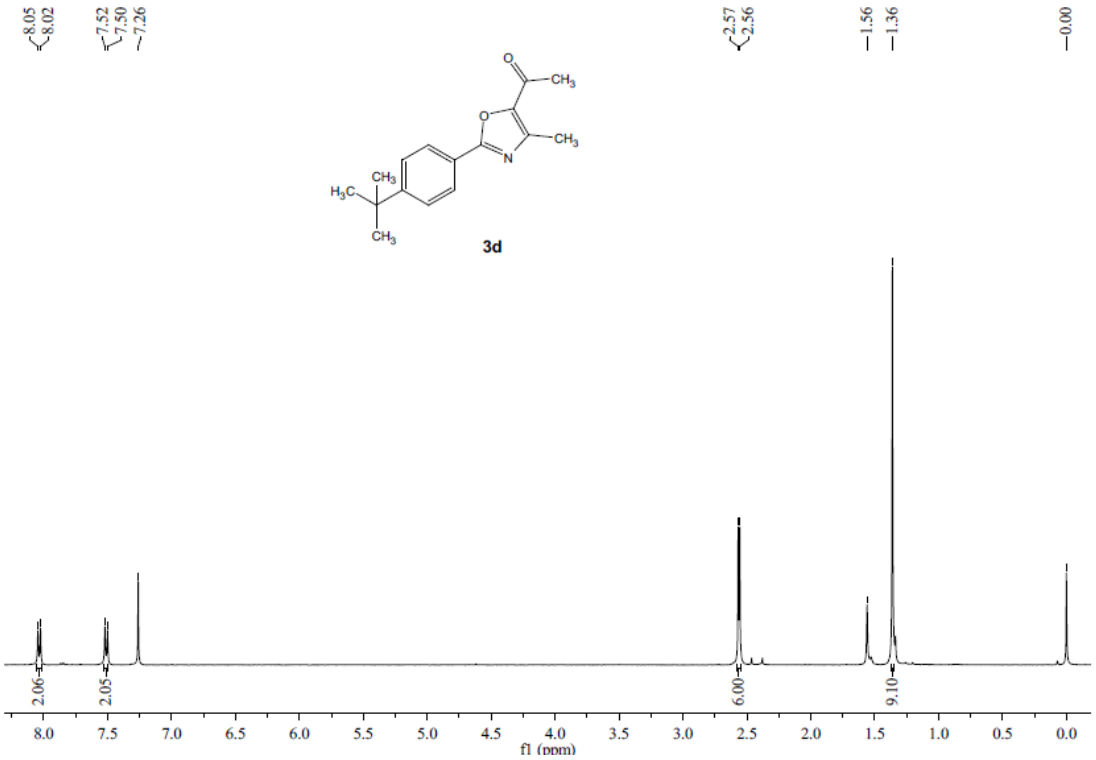
163.13
162.32
147.10
145.58
129.66
119.80
115.10
78.01
77.69
77.38
56.10
28.02
14.46
3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.02
7.52
7.50
7.26
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1.56
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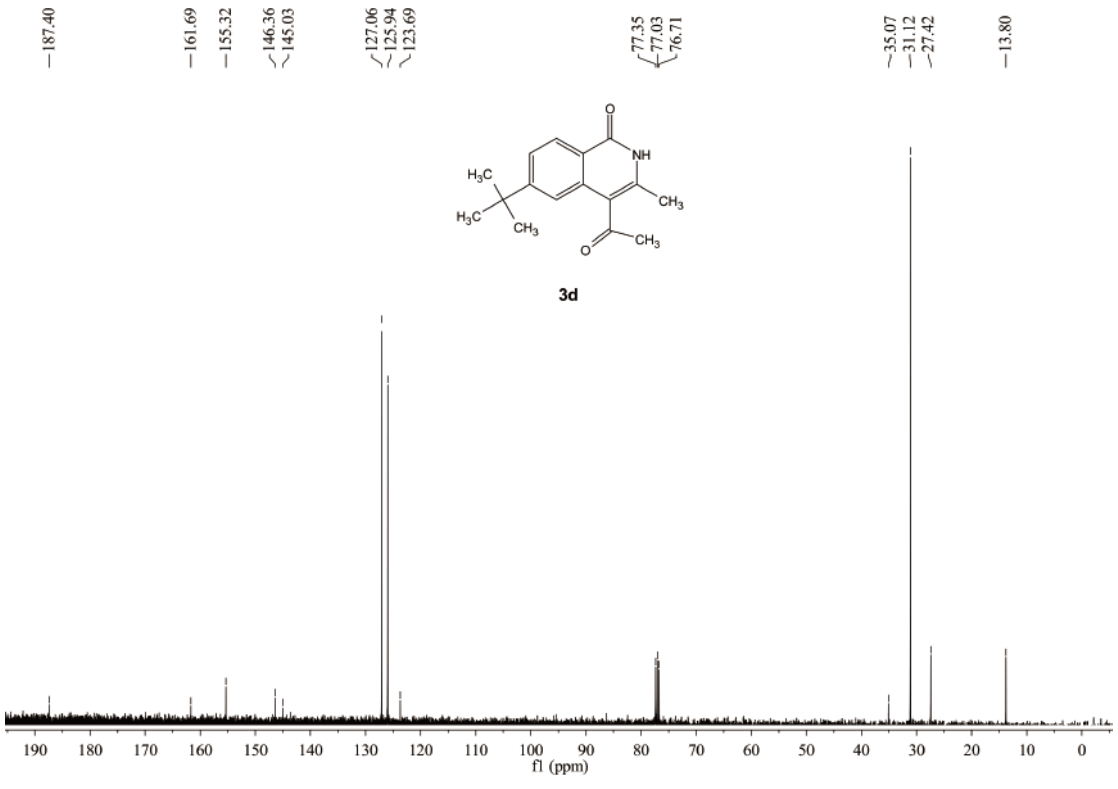
3d
2.06
2.05
6.00
9.10
f1 (ppm)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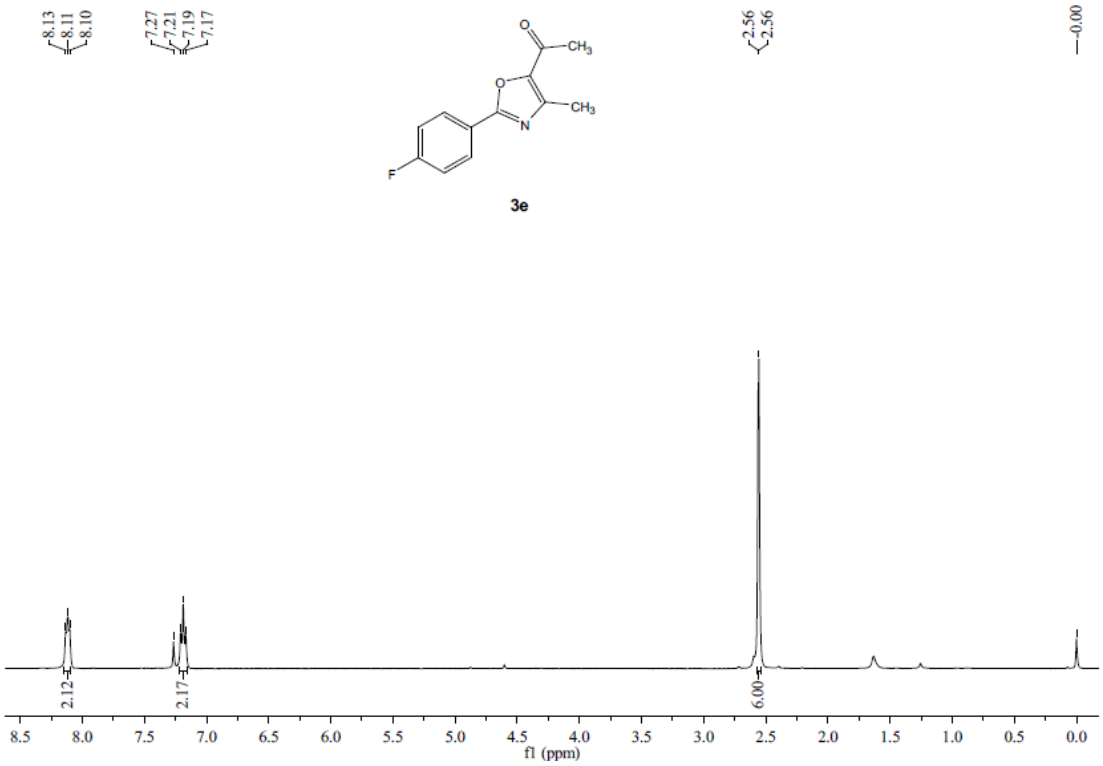
155.32
146.36
145.03
127.06
125.94
123.69
77.35
77.03
76.71
35.07
31.12
27.42
13.80
3d
f1 (ppm)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8.11
8.10
7.27
7.21
7.19
7.17
2.56
2.56
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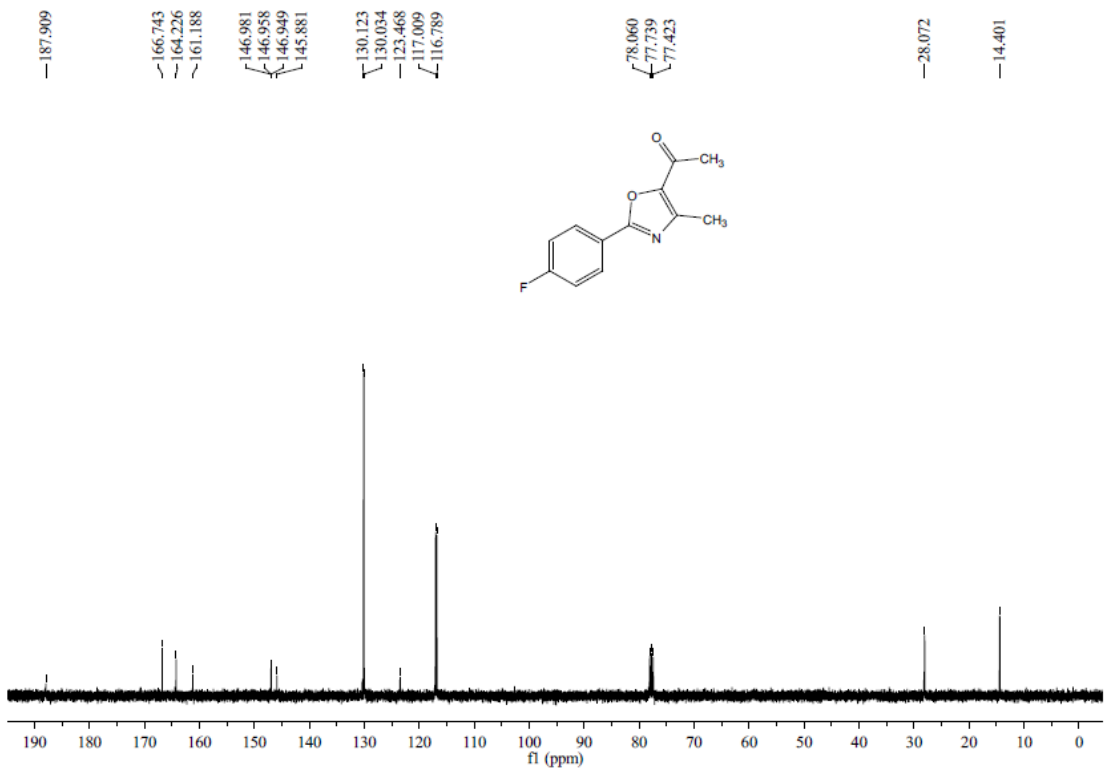
CH3
O
CH3
N
F
2.12
2.17
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3e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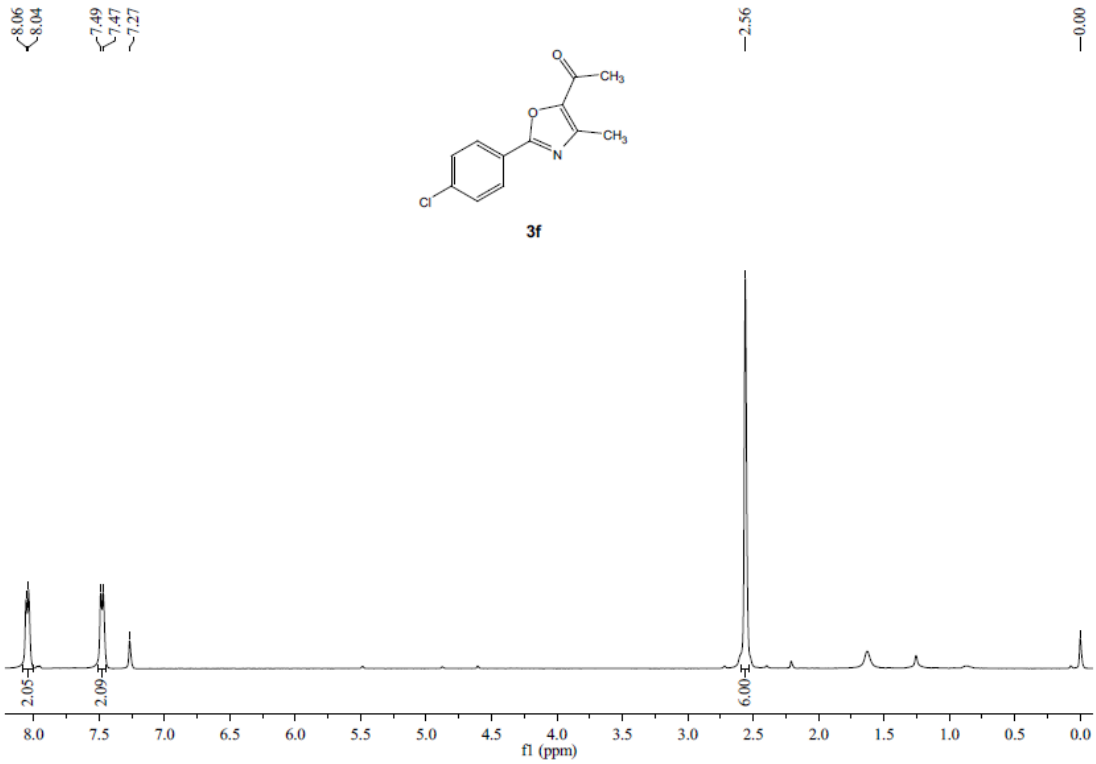
164.226
161.188
146.981
146.958
146.949
145.881
130.123
130.034
123.468
117.009
116.789
78.060
77.739
77.423
28.072
14.401
O
CH3
O
CH3
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.06
8.04
7.49
7.47
7.27
2.56
0.00
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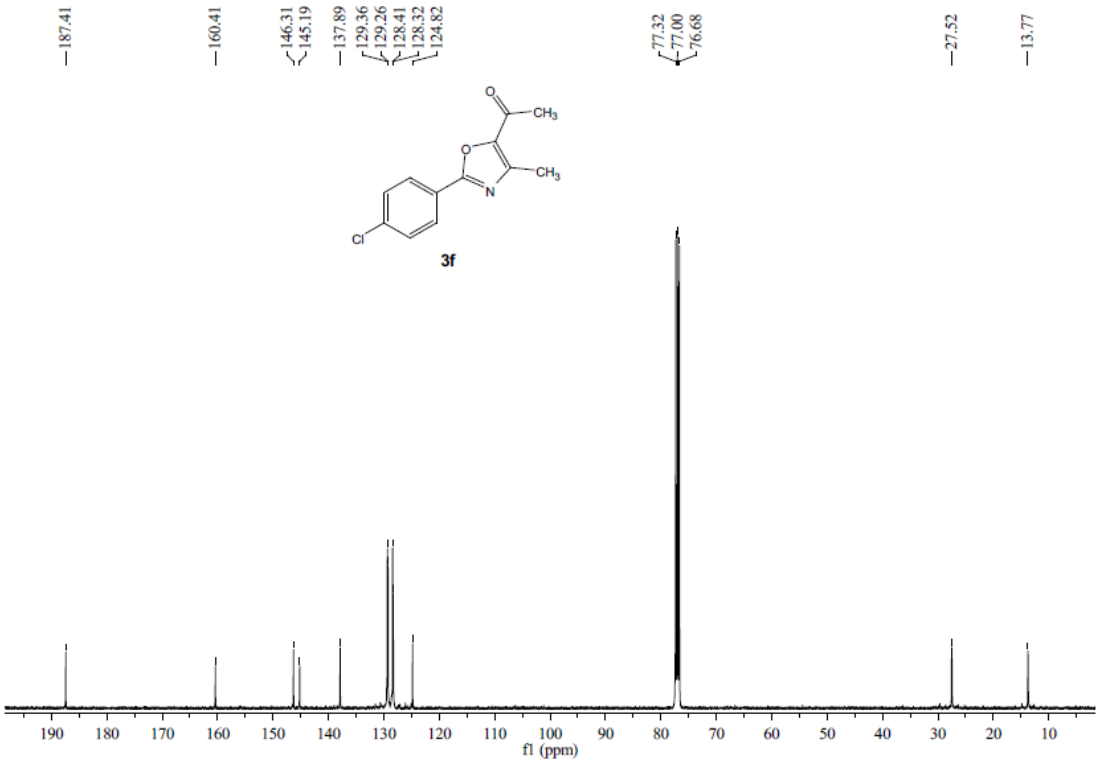
CH3
O
CH3
N
Cl
3f
2.05
2.09
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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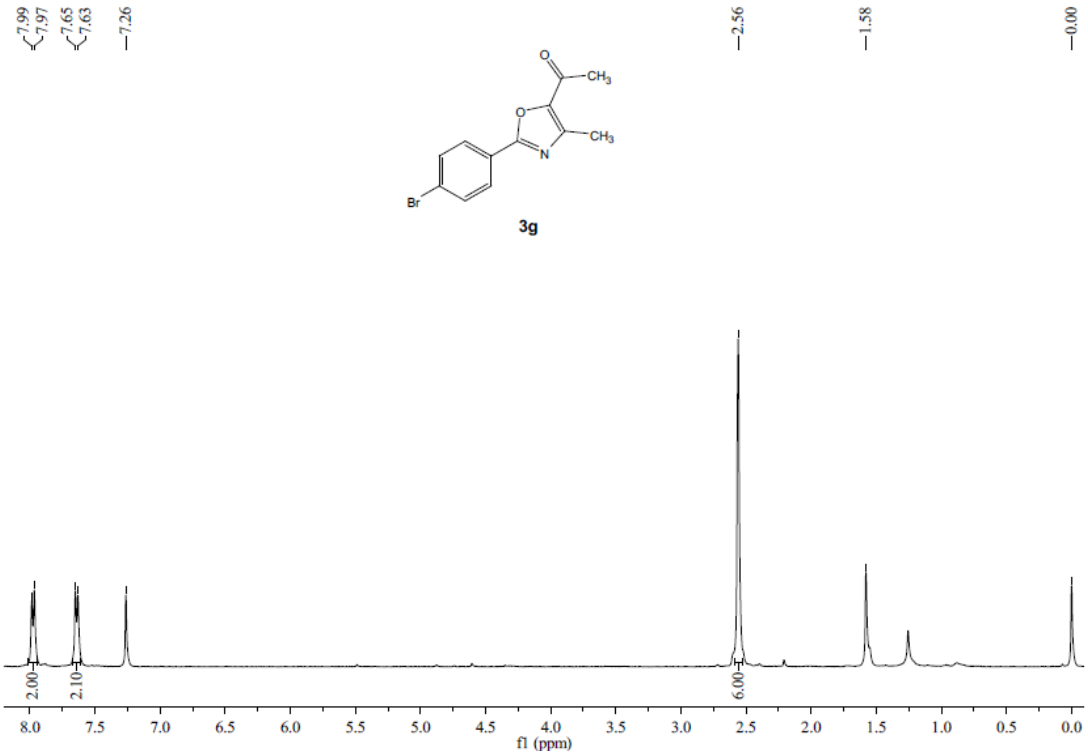
145.19
137.89
129.36
129.26
128.41
128.32
124.82
77.32
77.00
76.68
27.52
13.77
O
CH3
O
CH3
N
Cl
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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1.58
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O
CH3
N
Br
3g
2.00
2.10
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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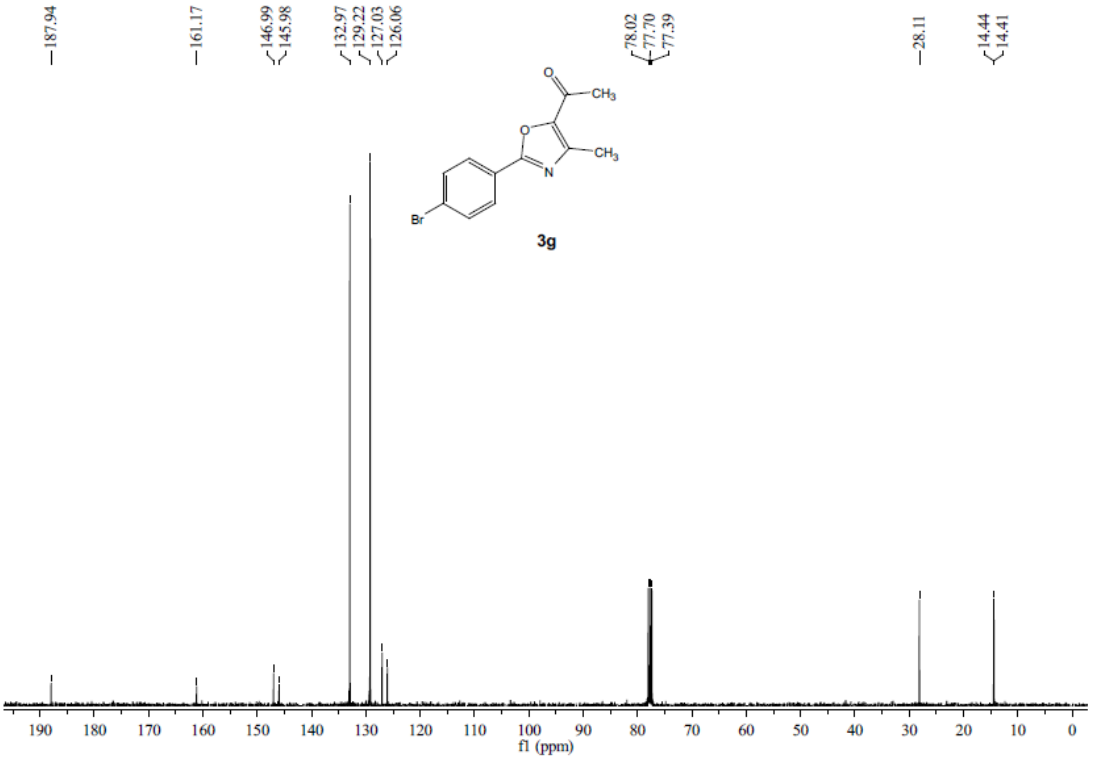
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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14.44
14.41
O
CH3
O
CH3
N
Br
3g
190
180
170
160
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140
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110
100
90
80
70
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50
40
30
20
10
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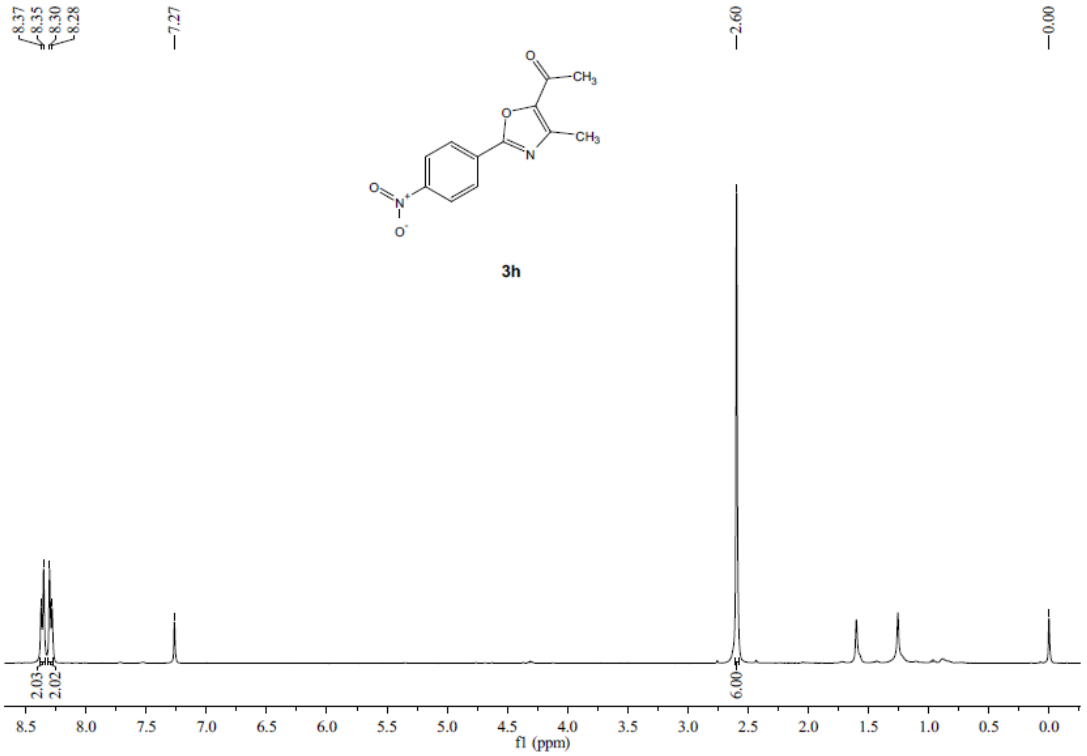
f1 (ppm)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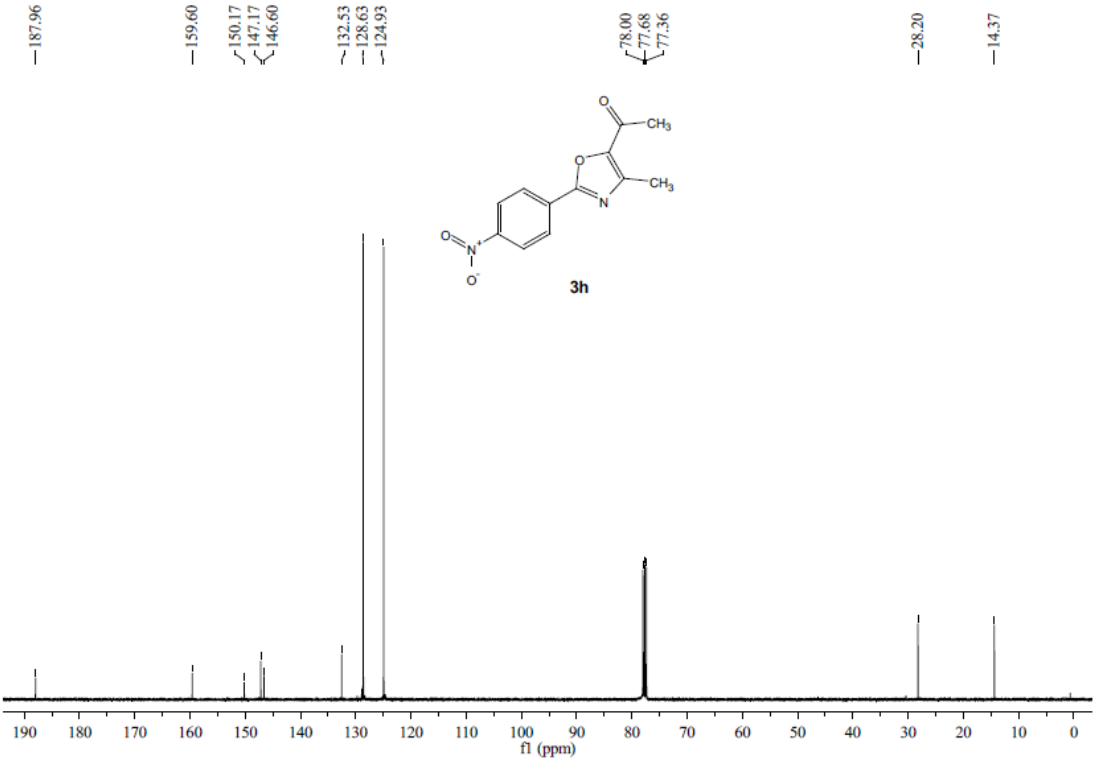
2.60
0.00
3h
2.03
2.02
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.36
28.20
14.37
3h
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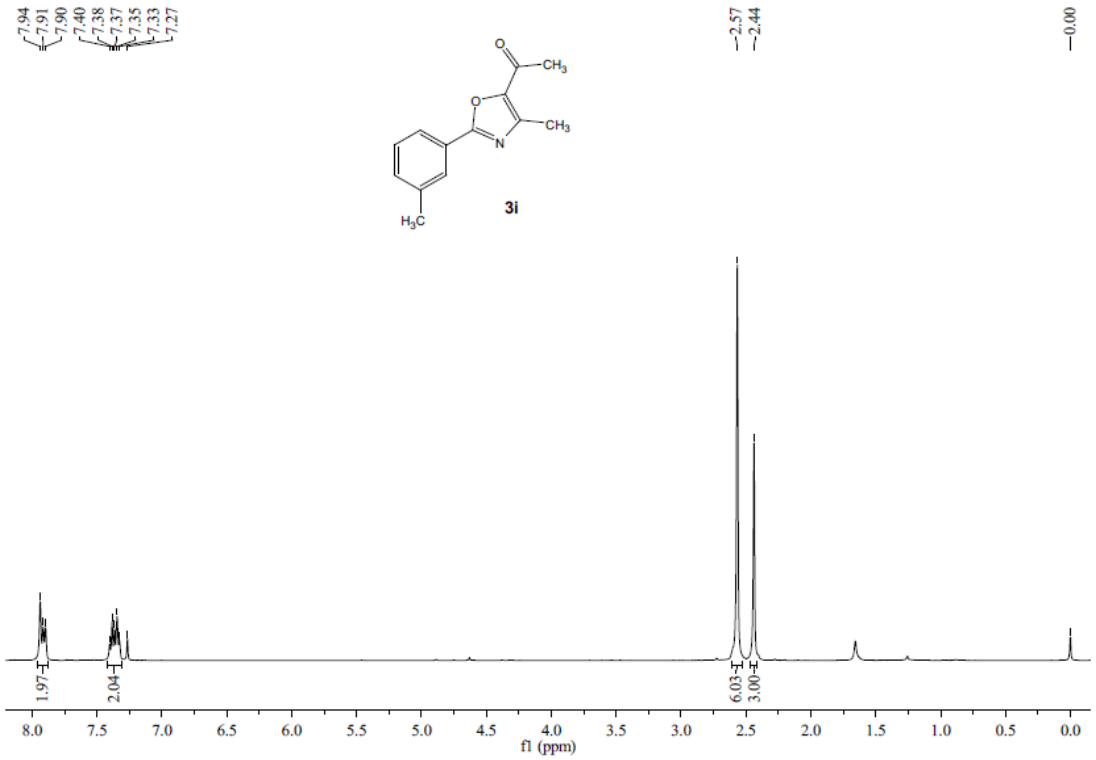
f1 (ppm)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7.35
7.33
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2.44
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O
CH3
O
CH3
N
H3C
3i
1.97
2.04
6.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
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1.0
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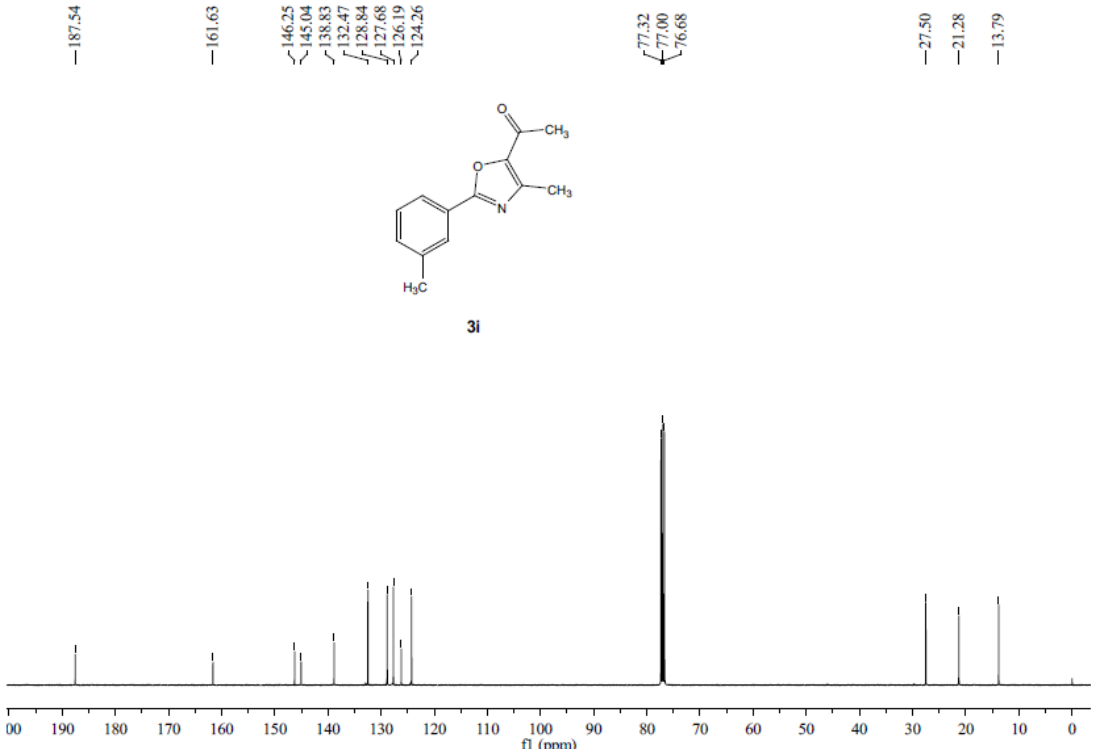
f1 (ppm)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76.68
27.50
21.28
13.79
O
CH3
O
CH3
N
H3C
3i
190
180
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160
150
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130
120
110
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90
80
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50
40
30
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10
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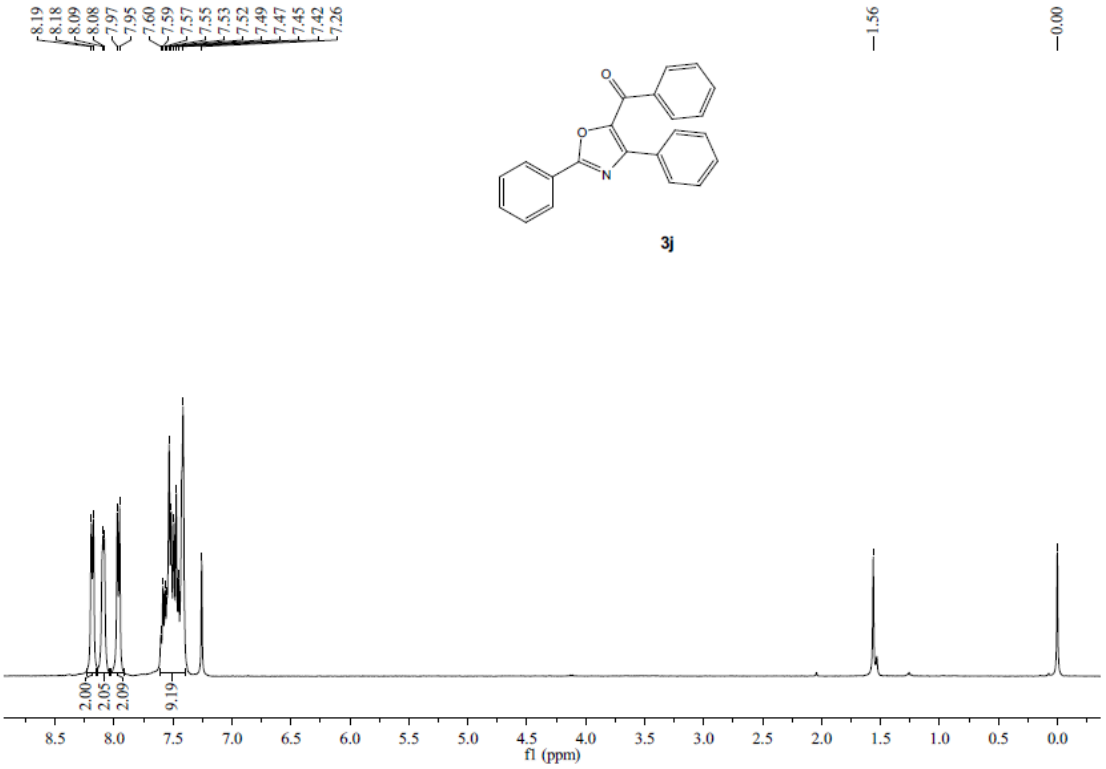
f1 (ppm)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7.52
7.49
7.47
7.45
7.42
7.26
1.56
0.00
O
O
N
3j
2.00
2.05
2.09
9.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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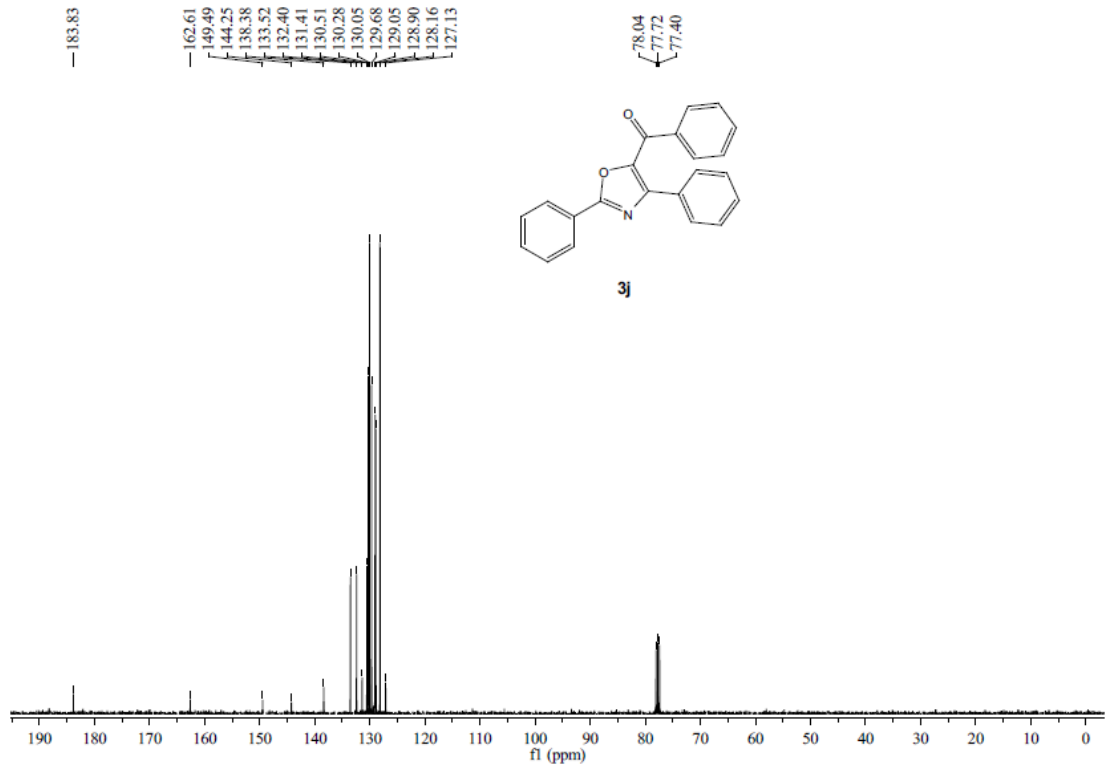
f1 (ppm)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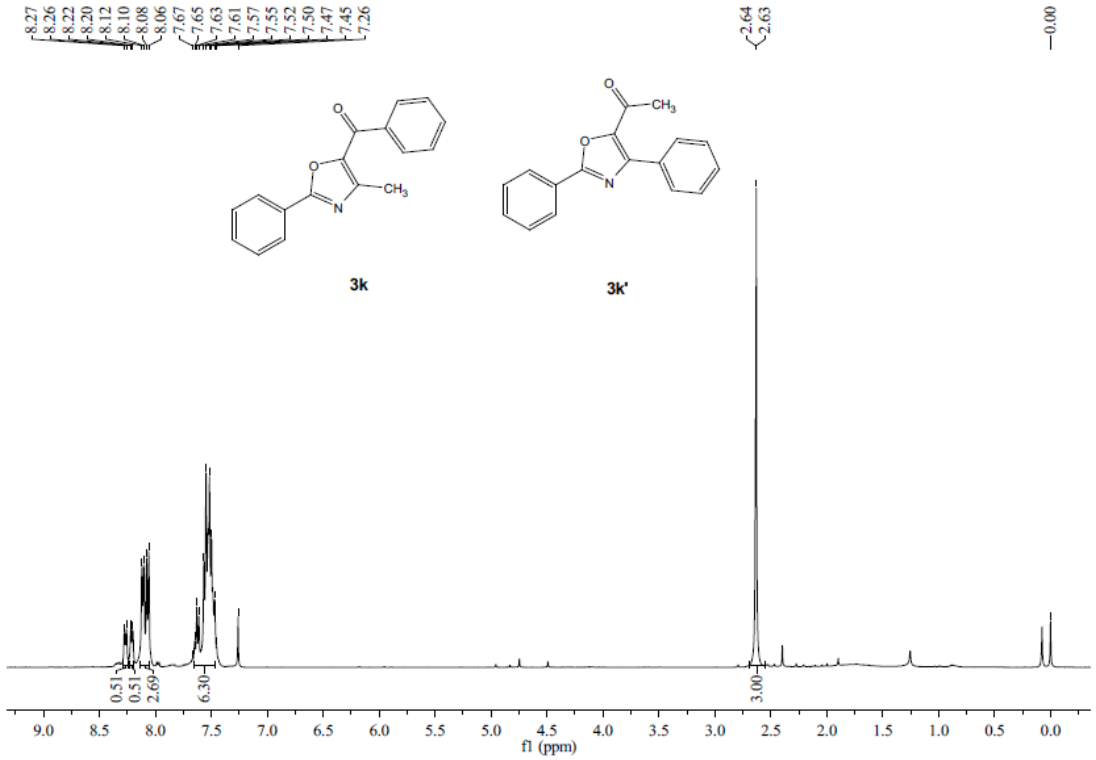
129.05
128.90
128.16
127.13
78.04
77.72
77.40
O
O
N
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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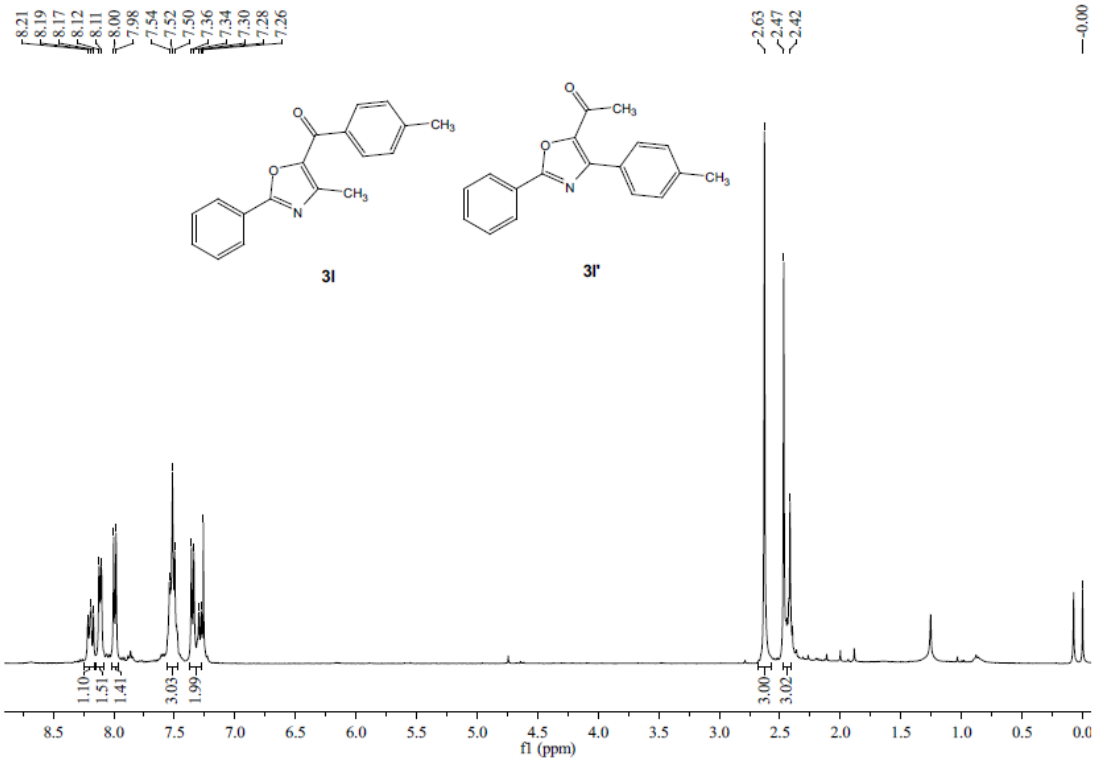
8.10
8.08
8.06
7.67
7.65
7.63
7.61
7.57
7.55
7.52
7.50
7.47
7.45
7.26
2.64
2.63
0.00
3k
3k'
0.51
0.51
2.69
6.30
3.00
fl (ppm)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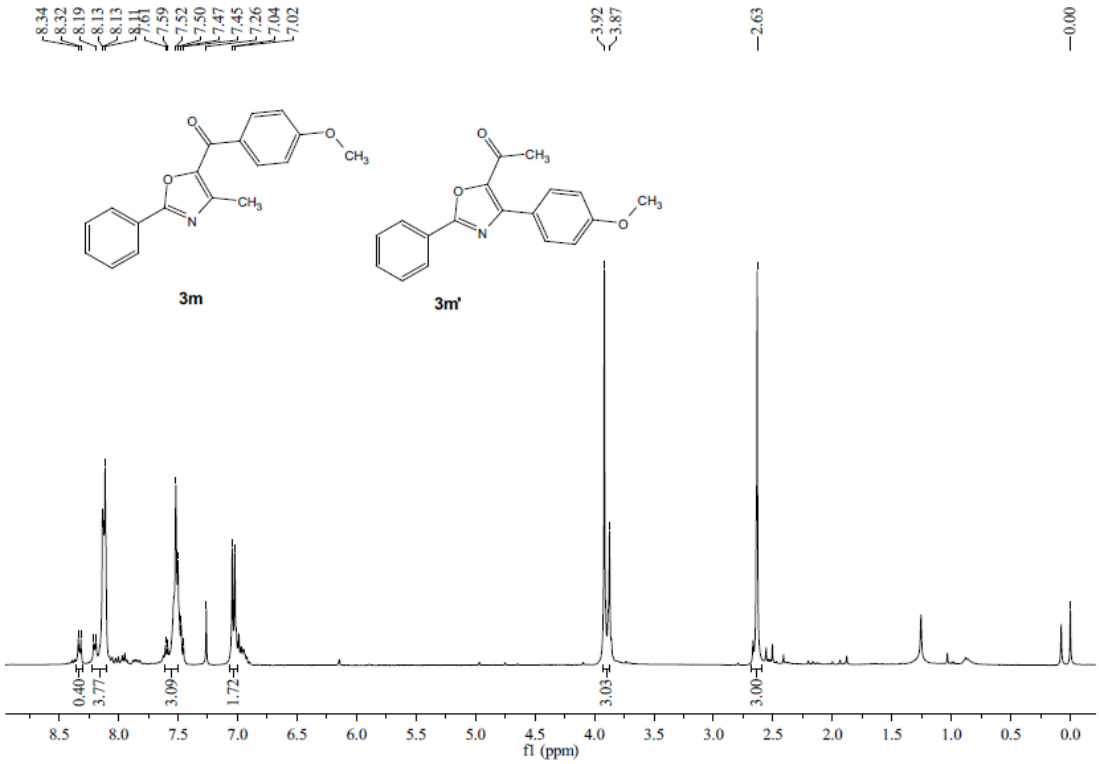
7.54
7.52
7.50
7.36
7.34
7.30
7.28
7.26
2.63
2.47
2.42
-0.00
3l
3l'
1.10
1.51
1.41
3.03
1.99
3.00
3.02
fl (ppm)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8.13
8.11
8.01
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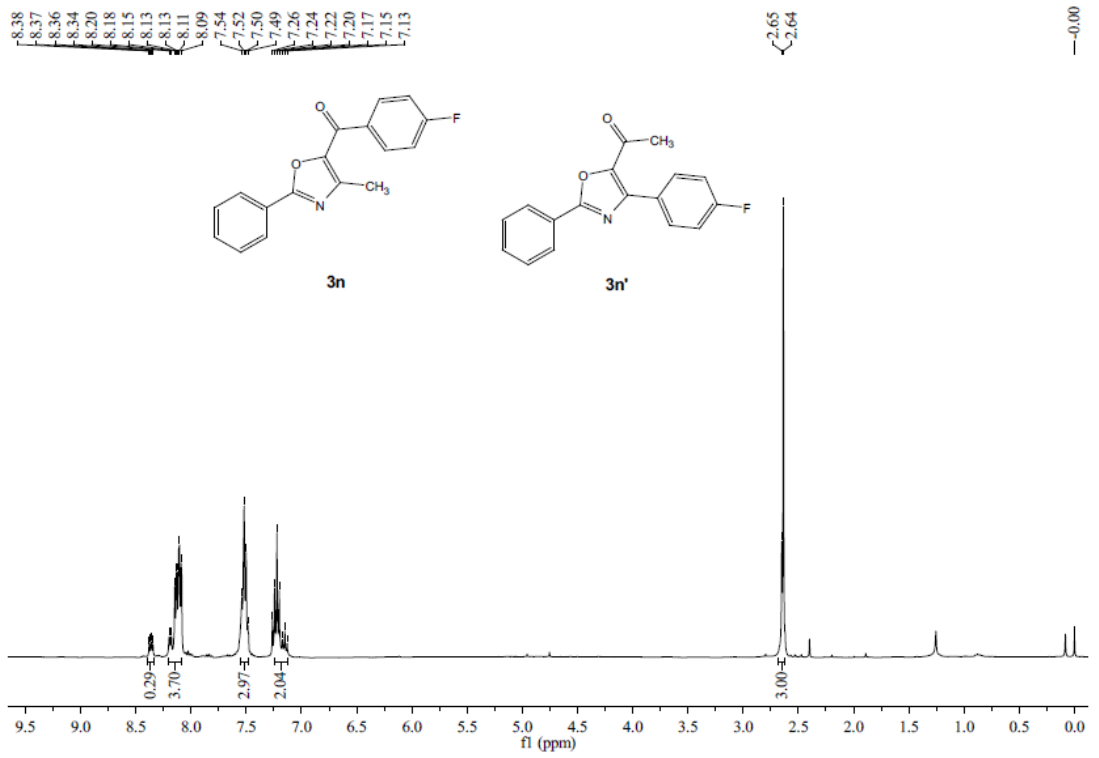
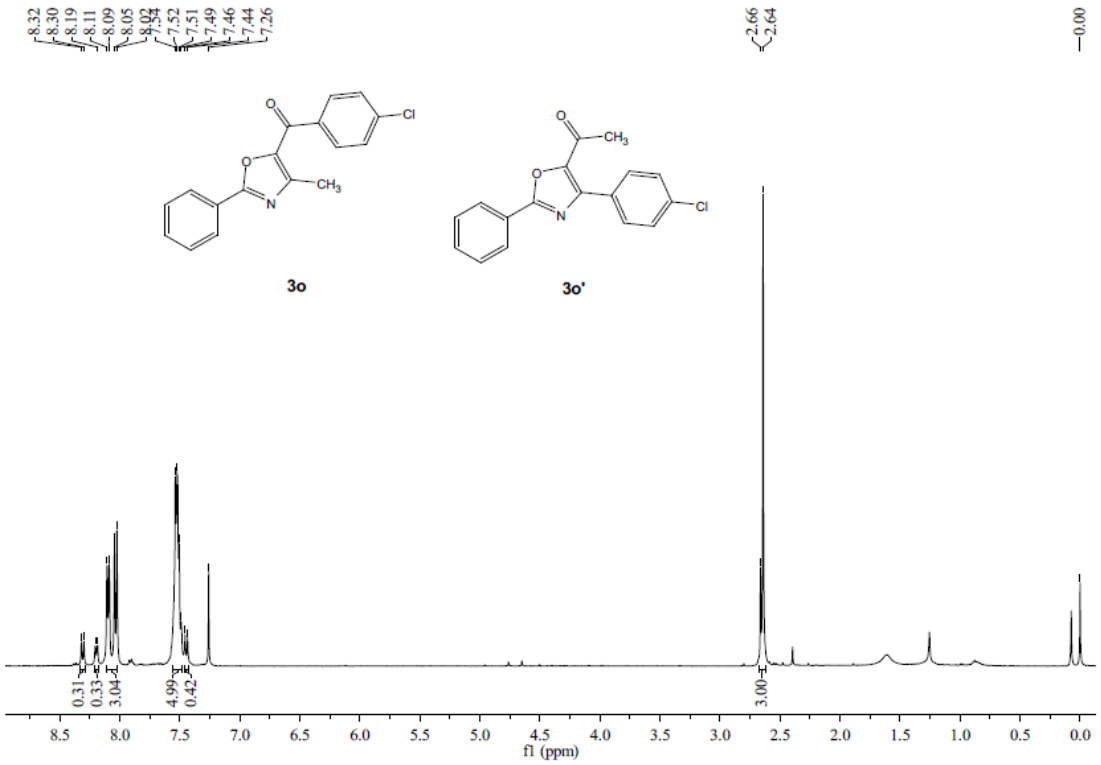
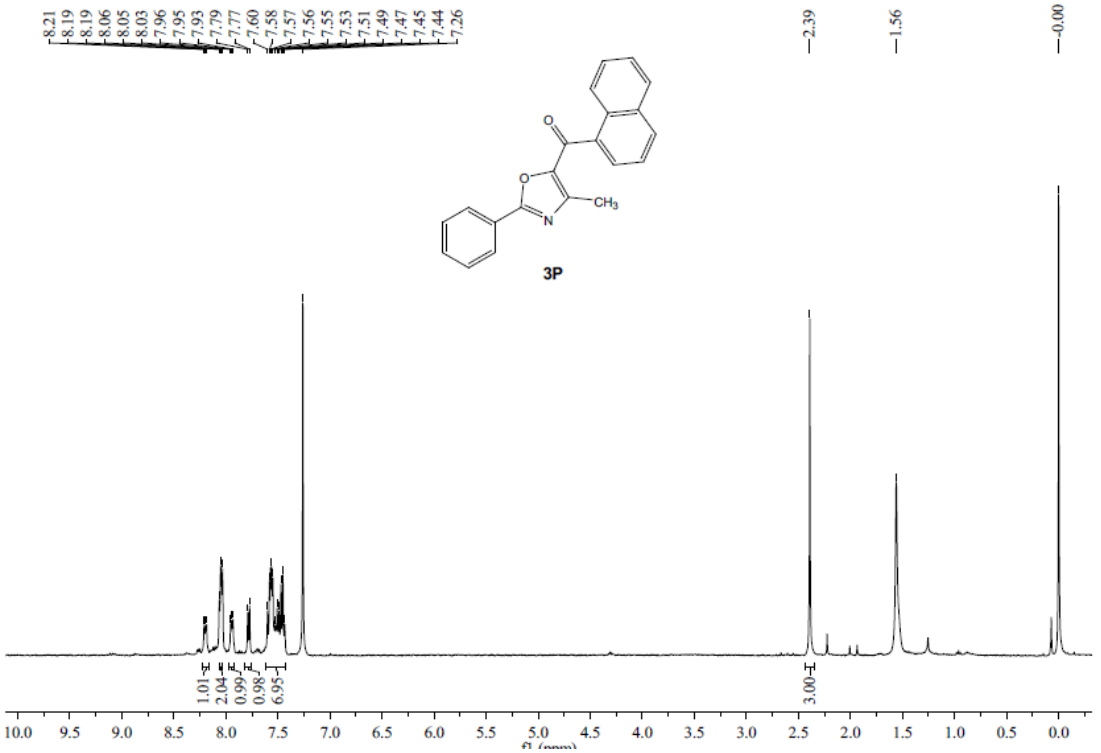
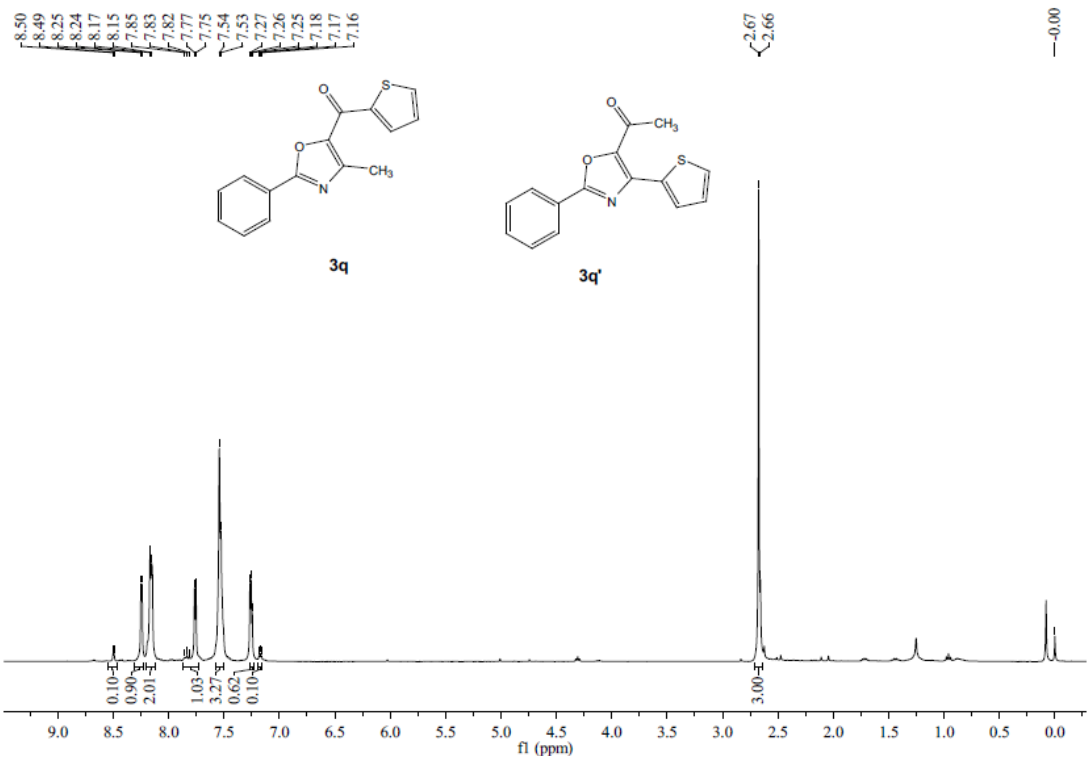
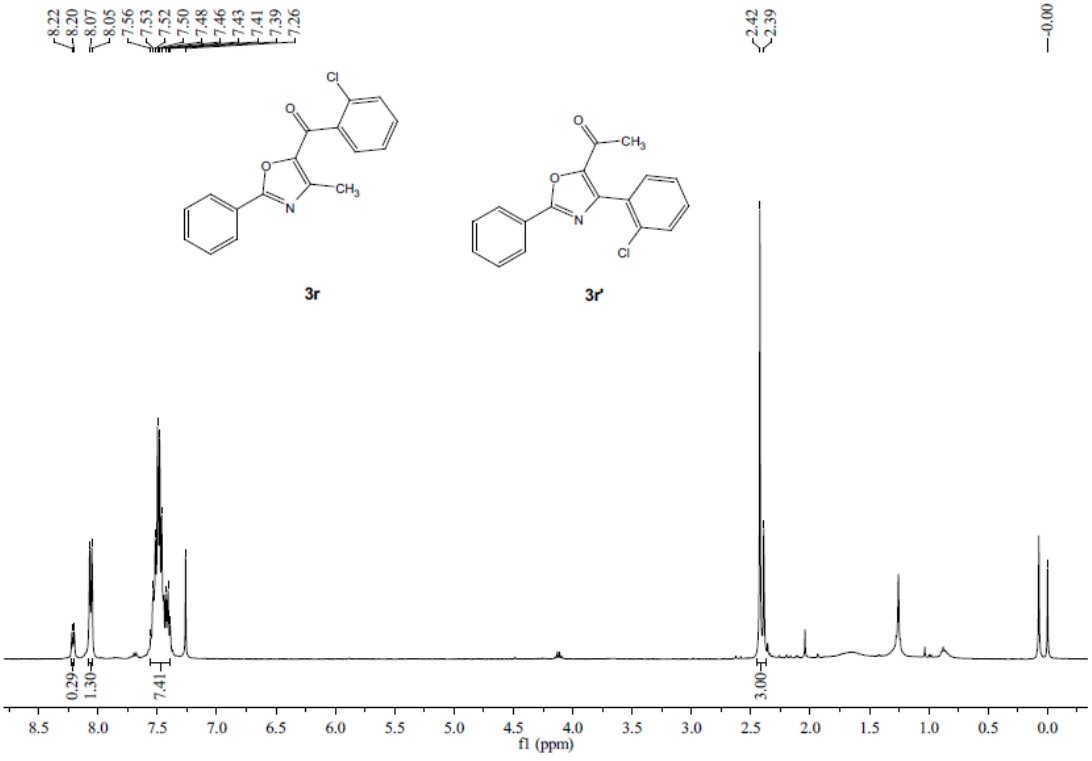
7.52
7.50
7.47
7.45
7.26
7.04
7.02
3.92
3.87
2.63
0.00
3m
3m'
0.40
3.77
3.09
1.72
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

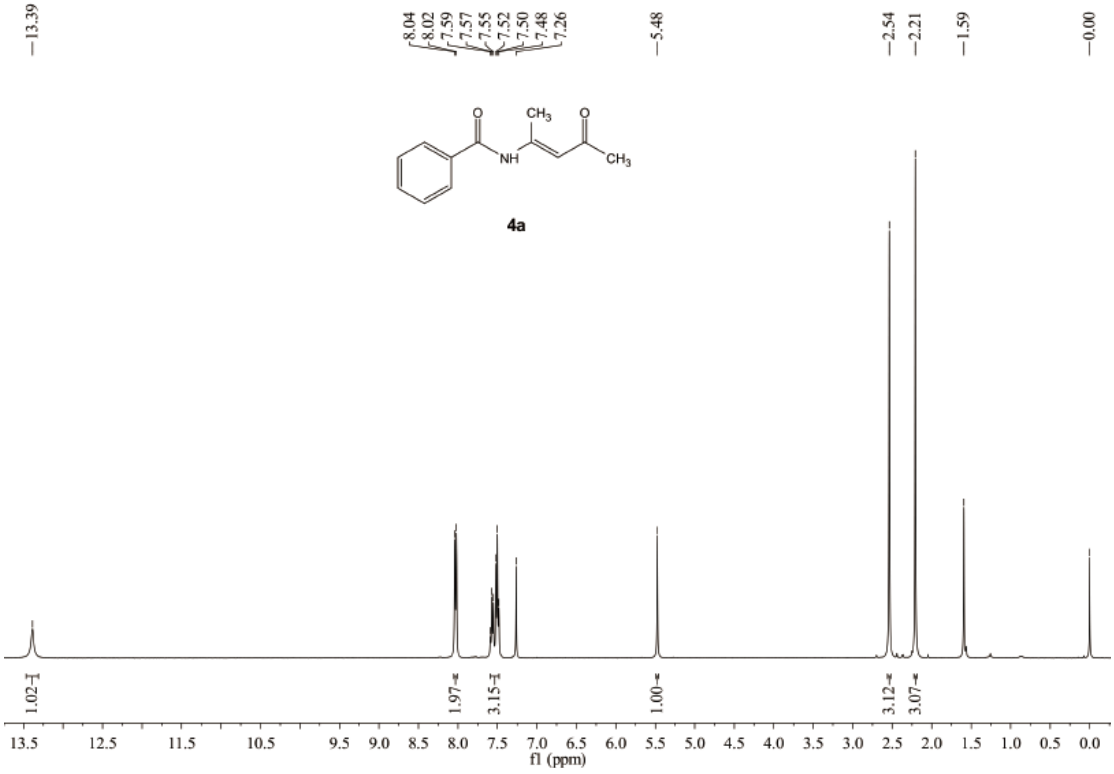

8.38
8.37
8.36
8.34
8.20
8.18
8.15
8.13
8.13
8.11
8.09
7.54
7.52
7.50
7.49
7.26
7.24
7.22
7.20
7.17
7.15
7.13
2.65
2.64
0.00
3n
3n'
0.29
3.70
2.97
2.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

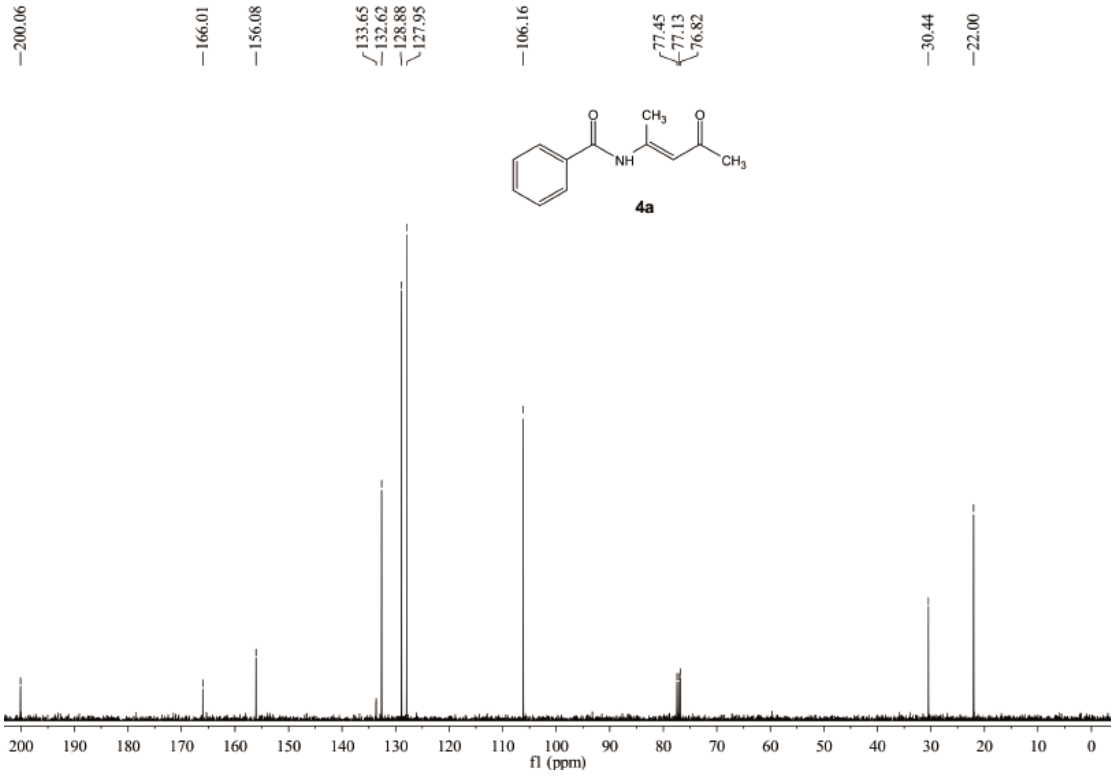

8.32
8.30
8.19
8.11
8.09
8.05
8.02
7.54
7.52
7.51
7.49
7.46
7.44
7.26
2.66
2.64
0.00
O
Cl
O
CH3
N
3o
O
CH3
O
N
Cl
3o'
0.31
0.33
3.04
4.99
0.42
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8.21
8.19
8.19
8.06
8.05
8.03
7.96
7.95
7.93
7.79
7.77
7.60
7.58
7.57
7.56
7.55
7.53
7.51
7.49
7.47
7.45
7.44
7.26
2.39
1.56
0.00
O
O
CH3
N
3P
1.01
2.04
0.99
0.98
6.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


8.50
8.49
8.25
8.24
8.17
8.15
7.85
7.83
7.82
7.77
7.75
7.54
7.53
7.27
7.26
7.25
7.18
7.17
7.16
2.67
2.66
0.00
3q
3q'
0.10
0.90
2.01
1.03
3.27
0.62
0.10
3.00
fl (ppm)


8.22
8.20
8.07
8.05
7.56
7.53
7.52
7.50
7.48
7.46
7.43
7.41
7.39
7.26
2.42
2.39
0.00
3r
3r'
0.29
1.30
7.41
3.00
fl (ppm)


13.39
8.04
8.02
7.59
7.57
7.55
7.52
7.50
7.48
7.26
5.48
2.54
2.21
1.59
0.00
4a
1.02
1.97
3.15
1.00
3.12
3.07
f1 (ppm)


200.06
166.01
156.08
133.65
132.62
128.88
127.95
106.16
77.45
77.13
76.82
30.44
22.00
4a
f1 (ppm)