Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information for

Palladium-catalyzed conjugate addition of arylsulfonyl hydrazides with α,β-unsaturated ketones

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General information:

All experiments were carried out under an atmosphere of oxygen. 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 structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were used as received from commercial sources without further purification. Palladium salts and (*E*)-4-phenylbut-3-en-2-one **1a** and arylsulfonyl hydrazides **2a, 2b,** and **2c** were purchased from Alfa-Aesar and were used as received without further purification.

General Procedure for the preparation of substrates (1b-1q) [1]:

Procedure for 4-(4-methylphenyl)-3-buten-2-one (**1b**): water (4 mL) and 10 % NaOH aqueous solution (1 mL) were added under stirring to the solution of 4-methylbenzaldehyde (0.24 g, 2 mmol) in acetone (2 mL). The reaction mixture was stirred for 14 h at room temperature, then the pH value was adjusted to 7.0 with 10 % hydrochloric acid, extracted with DCM (3 x 10 mL). The combined organic layer was washed with water, dried over with anhydrous sodium sulfate, filtered and concentrated to give 0.16 g of **1b** as a yellow viscous oil, yield: 51.2 %. Similarly, other *α, β*-unsaturated carbonyl compounds (**1c-1q**) were prepared from their corresponding aldehydes.

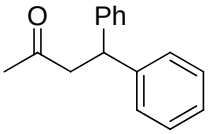
General procedure for the preparation of arylsulfonyl hydrazides (2d , 2e , 2f) :

Arylsulfonyl hydrazides **2d-f** were prepared according to the literature procedure.[2] Hydrazinemonohydrate (1.21 mL, 25 mmol) was added dropwise to a solution of arylsulfonyl chloride (10 mmol) in tetrahyrdofuran (10 mL) under nitrogen at -30 °C. During the addition the mixture became brown and a white precipitate of hydrazine hydrochloride was deposited. The mixture was stirred at -30 °C for 30 min, added ethyl acetate (20 mL), and washed with saturated brine (5 x 15 mL). The organic layer was dried over sodium sulfate, filtered, and added slowly to stirred hexane (120 mL) over 5 min. After being stirred for 10 min, the mixture was filtered, and the collected solid was dried in vacuum. The yields for the formation of arylsulfonyl hydrazides range from 65% to 89%.

General procedure for desulfitative conjugate addition reaction (3a):

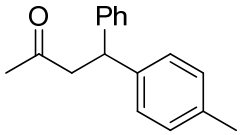
A 10 mL reaction vessel was charged with $Pd(acac)_2$ (3.0 mg, 0.01 mmol), (*E*)-4-phenylbut-3-en-2-one (**1a**, 29.2 mg, 0.2 mmol), benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) and charged with oxygen (1 atm). 1,4-Dioxane (0.6 mL) and H_2O (0.2 mL) were added to the sealed reaction vessel by syringe. The resulting solution was stirred at 80 ^oC for 24 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 = 50:1) to give 36.3 mg **3a** as pale yellow oil; yield 81%.

4,4-Diphenylbutan-2-one (3a, CAS: 5409-60-9)[3]



^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29-7.27 (m, 3H), 7.23-7.16 (m, 7H), 4.59 (t, J = 7.6 Hz, 1H), 3.18 (d, J = 7.6 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.7, 143.9, 128.6, 127.8, 126.5, 49.8, 46.2, 30.6; MS (EI) m/z (%) 224.1, 181, 167 (100), 103, 77.

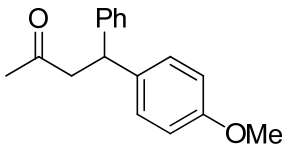
4-Phenyl-4-(p-tolyl)butan-2-one (3b, CAS: 80331-24-4)[3]



The reaction was conducted with (*E*)-4-(*p*-tolyl)but-3-en-2-one (**1b**, 32.0 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3b** as pale yellow oil; yield 82%.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28-7.26 (m, 1H), 7.24-7.07 (m, 8H), 4.54 (t, J = 7.6 Hz, 1H), 3.16 (d, J = 7.6 Hz, 2H), 2.29 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 207.0, 144.1, 140.8, 136.0, 129.3, 128.6, 127.6, 127.5, 126.4, 49.8, 45.7, 30.6, 21.0 ; MS (EI) m/z (%) 238.1, 195.1, 181.1(100), 165.1, 103.1, 77.

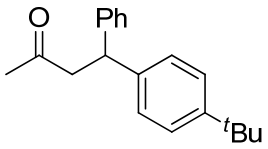
4-(4-Methoxyphenyl)-4-phenylbutan-2-one (3c, CAS: 76217-07-7)[3]



The reaction was conducted with (*E*)-4-(4-methoxyphenyl)but-3-en-2-one (**1c**, 35.2 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3c** as pale yellow oil; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29-7.12 (m, 7H), 6.81 (d, J = 8.4 Hz, 2H), 4.54 (t, J = 7. 6 Hz , 1H), 3.76 (s, 3H), 3.15 (d, J = 7.6 Hz, 2H), 2.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.9, 158.2, 144.3, 136.1, 128.6, 128.5, 127.7, 126.4, 114.1, 55.3, 50.0, 45.4, 30.6; MS (EI) m/z (%)254.1, 197.1 (100), 165.1, 103, 77.

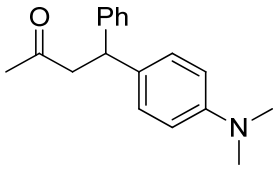
4-(4-tert-Butylphenyl)-4-phenylbutan-2-one (3d) [3]



The reaction was conducted with (*E*)-4-(4-(tert-butyl)phenyl) -but-3-en-2-one (**1d**, 40.4 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3d** as pale yellow oil; yield 76%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29-7.27 (m, 3H), 7.24-7.13 (m, 6H), 4.55 (t, J = 7.6 Hz, 1H), 3.17 (d, J = 7.6 Hz, 2H), 2.08 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.9, 149.2, 144.1, 140.8, 128.5, 127.8, 127.3, 126.4, 125.5, 49.9, 45.7, 34.4, 31.3, 30.5; MS (EI) m/z (%) 280.1, 265.1, 223.1 (100), 208.1, 165.1, 77.

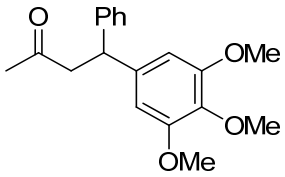
4-(4-(Dimethylamino)phenyl)-4-phenylbutan-2-one (3e)[4]



The reaction was conducted with (*E*)-4-(4-(dimethylamino)phenyl)but-3-en-2-one (**1e**, 37.8 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) using $CuSO_4$ (44.8 mg, 0.28 mmol) as co-oxidant. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **3e** as yellow solid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.27-7.13 (m, 5H), 7.08 (d, J = 8.4 Hz, 2H), 6.65(d, J = 8.8 Hz, 2H), 4.48 (t, J = 7.6 Hz, 1H), 3.13 (d, J = 7.6 Hz, 2H), 2,89 (s, 6H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 207.3, 149.3, 144.7, 131.9, 128.5, 128.3, 127.6, 126.2, 112.9, 50.1, 45.4, 40.7, 30.6; MS (EI) m/z (%) 267.1, 210.1(100), 194.1, 165.1, 103.1, 77.

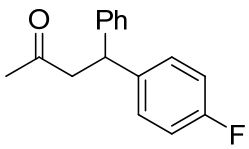
4-Phenyl-4-(3,4,5-trimethoxyphenyl)butan-2-one (3f)



The reaction was conducted with (*E*)-4-(3,4,5-trimethoxyphenyl)but-3-en-2-one (**1f**, 47.2 mg, 0.2 mmol) and **2a** (51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3f** as white solid; yield 59%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31-7.28 (m, 2H), 7.24-7.20 (m, 3H), 6.43 (s, 2H), 4.53 (t, J = 7.4 Hz, 1H), 3.81 (s, 6H), 3.80 (s, 3H), 3.15 (d, J = 7.2 Hz, 2H), 2,10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.7, 153.3, 143.7, 139.5, 136.8, 128.6, 127.6, 126.6, 105.2, 60.8, 56.2, 49.9, 46.3, 30.6; MS (EI) m/z (%) 314.1, 271.1, 257.1(100), 169, 103, 77; HRMS calcd. for: $C_{19}H_{22}NaO_4$ $[M+Na]^+$ 337.1416, found 337.1412.

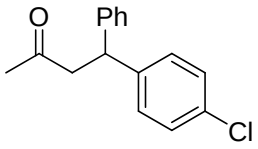
4-(4-Fluorophenyl)-4-phenylbutan-2-one (3g)[3]



The reaction was conducted with (*E*)-4-(4-fluorophenyl)but -3-en-2-one (**1g**, 32.8 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3g** as pale yellow oil; yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.28 (m, 2H), 7.20-7.16 (m, 5H), 6.98-6.94 (m, 2H), 4.58 (t, J = 7.4 Hz, 1H), 3.16 (d, J = 7.2 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.4, 161.5 (d, J = 243.5 Hz), 143.7, 139.7 (d, J = 3.3 Hz), 129.2(d, J = 7.8 Hz), 128.7, 127.6, 126.6, 115.4 (d, J = 21.1 Hz), 49.8, 45.3, 30.6; MS (EI) m/z (%) 242.1, 199.1, 185.1(100), 165.1, 103.1, 77.

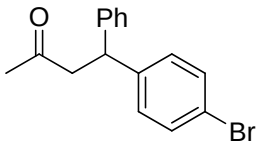
4-(4-Chlorophenyl)-4-phenylbutan-2-one (3h, CAS: 29869-86-1)[3]



The reaction was conducted with (*E*)-4-(4-chlorophenyl)but-3-en-2-one (**1h**, 36.0 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) using $CuSO_4$ (44.8 mg, 0.28 mmol) as co-oxidant. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3h** as pale yellow oil; yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.28 (m, 2H), 7.23-7.14 (m, 7H), 4.57 (t, J = 7.4 Hz, 1H), 3.16 (d, J = 7.6 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.3, 143.4, 142.5, 132.3, 129.1, 128.7, 127.6, 126.7, 49.6, 45.4, 30.6; MS (EI) m/z (%) 258.1, 223.1(100), 201., 165.1, 103, 77.

4-(4-Bromophenyl)-4-phenylbutan-2-one (3i, CAS: 1005497-31-3)[3]

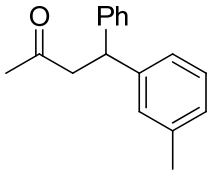


The reaction was conducted with (*E*)-4-(4-bromophenyl)but-3-en-2-one (**1i**, 44.8 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) using $CuSO_4$ (44.8 mg, 0.28 mmol) as co-oxidant. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3i** as pale yellow oil; yield 63%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7. 39 (d, J = 8.4 Hz, 2H), 7.30–7.28 (m, 2H), 7.19–7.17 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 4.55 (t, J = 7.4 Hz, 1H), 3.15 (d, J = 7.2 Hz, 2H), 2.09 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$, ppm) δ 206.4, 143.3, 143.0, 131.7, 129.5, 128.7, 127.7, 126.7, 120.3, 49.5, 45.4, 30.7; MS (EI) m/z (%) 302, 245, 178.1, 165.1 (100), 103, 77.

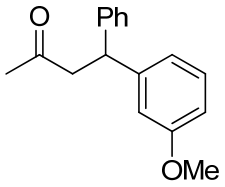
4-Phenyl-4-(m-tolyl)butan-2-one (3j)



The reaction was conducted with (*E*)-4-(m-tolyl)but-3-en-2-one (**1j**, 32.0 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3j** as pale yellow oil; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29-7.14 (m, 6H), 7.03-6.98 (m, 3H), 4.54 (t, J = 7.4 Hz, 1H), 3.17 (d, J = 7.6 Hz, 2H), 2.30 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.9, 144.0, 143.8, 138.2, 128.6, 128.5, 128.4, 127.7, 127.3, 126.4, 124.6, 49.8, 46.1, 30.6, 21.5 ; MS (EI) m/z (%) 238.1, 195.1, 181.1(100), 165.1, 103.1, 77; HRMS calcd. for: $C_{17}H_{18}NaO$ $[M+Na]^+$ 261.1256, found 261.1249.

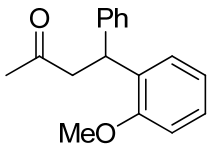
4-(3-Methoxyphenyl)-4-phenylbutan-2-one (3k)[5]



The reaction was conducted with (*E*)-4-(3-methoxyphenyl)but-3-en-2-one (**1k**, 35.2 mg, 0.2 mmol), benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3k** as white oil; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.29–7.15 (m, 6H), 6.83-6.71 (m, 3H), 4.55 (t, J = 7.4 Hz, 1H), 3.76 (s, 3H), 3.16 (d, J = 7.6 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.8, 159.8, 145.5, 143.8, 129.6, 128.6, 127.7, 126.5, 120.1, 114.0, 111.4, 55.2, 49.7, 46.1, 30.7; MS (EI) m/z (%) 254.2, 211.2, 165.1, 103.1 (100), 77.1.

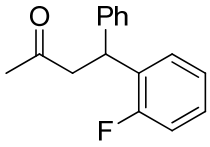
4-(2-Methoxyphenyl)-4-phenylbutan-2-one (3l)[6]



The reaction was conducted with (*E*)-4-(2-methoxyphenyl)but-3-en-2-one (**1l**, 35.2 mg, 0.2 mmol), benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3l** as white solid; yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.25–7.09 (m, 7H), 6.89-6.82 (m, 2H), 4.98 (t, J = 7.6 Hz, 1H), 3.79 (s, 3H), 3.15-3.13 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 207.3, 156.8, 143.5, 132.3, 128.4, 128.0, 127.9, 127.6, 126.2, 120.6, 110.9, 55.5, 49.0, 39.6, 30.2; MS (EI) m/z (%) 254.1, 197.1, 165.1, 91.1 (100), 77.1.

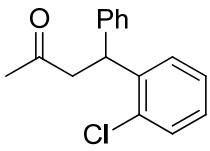
4-(2-Fluorophenyl)-4-phenylbutan-2-one (3m)



The reaction was conducted with $CuSO_4$ (44.8 mg, 0.28 mmol), (*E*)-4-(2-fluorophenyl)but-3-en-2-one (**1m**, 32.8 mg, 0.2 mmol), benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3m** as white solid; yield 53%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7. 29-7.28 (m, 2H), 7.24-7.15 (m, 5H), 7.08–6.97 (m, 2H), 4.86 (t, J = 7.6 Hz, 1H), 3.21 (d, J = 7.6 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.2, 160.6 (d, J = 244.5 Hz), 142.6, 130.8 (d, J = 14 Hz), 128.9 (d, J = 4.4 Hz), 128.6, 128.2 (d, J = 8.3 Hz),127.7 (d, J = 0.8 Hz), 126.6, 124.2 (d, J = 3.6 Hz), 115.8 (d, J = 22.4 Hz), 48.6 (d, J = 1.6 Hz), 39.8 (d, J = 2 Hz), 30.2; MS (EI) m/z (%) 242.1, 199.1, 185.1 (100), 165.1, 121.0, 77.1; HRMS calcd. for: $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.1005, found 265.1002.

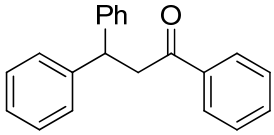
4-(2-Chlorophenyl)-4-phenylbutan-2-one (3n)



The reaction was conducted with (*E*)-4-(2-chlorophenyl)but-3-en-2-one (**1n**, 36.0 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3n** as pale yellow oil; yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36–7.28 (m, 2H), 7.24-7.13 (m, 7H), 5.09 (t, J = 7.6 Hz, 1H), 3.18-3.14 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.2, 142.2, 141.1, 134.0, 130.0, 128.6, 128.5, 128.0, 127.8, 127.0, 126.6, 49.1, 42.4, 30.1; MS (EI) m/z (%) 258.1, 223.1(100), 201., 165.1, 103, 77; HRMS calcd. for: $C_{16}H_{15}ClNaO$ $[M+Na]^+$ 281.0708, found 281.0712.

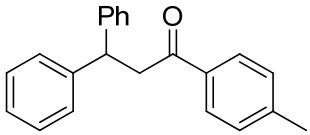
1,3,3-Triphenylpropan-1-one (3o, CAS: 606-86-0)[7]



The reaction was conducted with (*E*)-chalcone (**1o**, 41.6 mg, 0.2 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 **3o** as white solid; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (d, J = 7.6 Hz, 2H), 7.55-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.27-7.26 (m, 8H), 7.19-7.16 (m, 2H), 4.83 (t, J = 7.2 Hz , 1H), 3.74 (d, J = 7.2 Hz , 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 198.0, 144.2, 137.2, 133.0, 128.6, 128.5, 128.1, 127.9, 126.4, 46.1, 44.8; MS (EI) m/z (%) 286.1, 167.1, 152.1, 105.0 (100), 77.

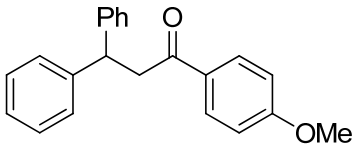
3,3-Diphenyl-1-(p-tolyl)propan-1-one (3p, CAS: 37620-42-1)[7]



The reaction was conducted with (*E*)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (**1p**, 44.4 mg, 0.2 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 **3p** as white solid; yield 81%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, J = 8.0 Hz, 2H), 7.27-7.15 (m, 12H), 4.82 (t, J = 7.2 Hz, 1H), 3.71 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 197.6, 144.3, 143.8, 134.8, 129.3, 128.5, 128.2, 127.9, 126.3, 46.1, 44.7, 21.6; MS (EI) m/z (%) 300.1, 167.1, 152.0, 119.1(100), 91.1.

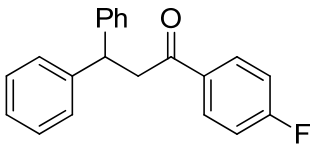
1-(4-Methoxyphenyl)-3,3-diphenylpropan-1-one (3q, CAS: 2657-24-1)[7]



The reaction was conducted with (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**1q**, 47.6 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) under oxygen (1 atm) for 32 h. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =20:1) to give **3q** as white solid; yield 81%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (d, J = 8.0 Hz, 2H), 7.27-7.17 (m, 10H), 6.91 (d, J = 8.4 Hz, 2H), 4.82 (t, J = 7.0 Hz, 1H), 3.86 (s, 3H), 3.69 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.5, 163.5, 144.4, 130.4, 130.2, 128.5, 127.9, 126.3, 113.8, 55.5, 46.2, 44.4; MS (EI) m/z (%) 316.2, 239.2, 167.1, 135.1(100), 77.1.

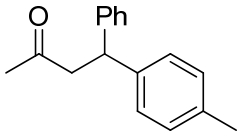
1-(4-Fluorophenyl)-3,3-diphenylpropan-1-one (3r, CAS: 67800-16-2)[7]



The reaction was conducted with (*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (**1r**, 45.2 mg, 0.2 mmol) and benzenesulfonylhydrazine (**2a**, 51.6 mg, 0.3 mmol) under oxygen (1 atm) for 32 h. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =50:1) to give **3r** as white solid; yield 82%.

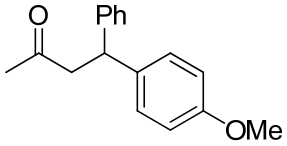
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.97-7.94 (m, 2H), 7.26-7.18(m, 10H), 7.13-7.08 (m, 2H), 4.81 (t, J = 7.2 Hz, 1H), 3.71 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.5, 165.8 (d, J = 253.3 Hz), 144.1, 133.6 (d, J = 2.7 Hz), 130.7 (d, J = 9.3 Hz), 128.6, 127.9, 126.5, 115.7 (d, J = 21.8 Hz), 46.1, 44.7; MS (EI) m/z (%) 304.1, 286.1, 167.1, 123(100), 95.

4-Phenyl-4-(p-tolyl)butan-2-one (3s, CAS: 80331-24-4)[3]



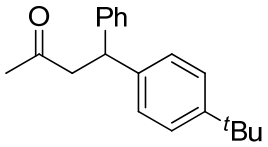
The reaction was conducted with **1a** (29.2 mg, 0.2 mmol) and 4-methylbenzenesulfonohydrazide (**2b**, 55.8 mg, 0.3 mmol) under oxygen (1 atm) for 24 h. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3s** as pale yellow oil; yield 87%. This product is same as **3b**.

4-(4-Methoxyphenyl)-4-phenylbutan-2-one (3t, CAS: 76217-07-7)[3]



The reaction was conducted with **1a** (29.2 mg, 0.2 mmol) and 4-methoxybenzenesulfonohydrazide (**2c**, 60.6 mg, 0.3 mmol) under oxygen (1 atm) for 24 h. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3t** as pale yellow oil; yield 85%. This product is same as **3c**.

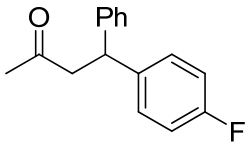
4-(4-tert-Butylphenyl)-4-phenylbutan-2-one (3u)[3]



The reaction was conducted with **1a** (29.2 mg, 0.2 mmol) and 4-(tert-butyl)benzenesulfonohydrazide (**2d**, 68.4 mg, 0.3 mmol) using $CuSO_4$ (44.8 mg, 0.28

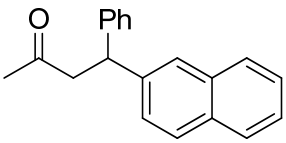
mmol) as co-oxidant. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 40:1) to give **3u** as pale yellow oil; yield 80%. This product is same as **3d**.

4-(4-Fluorophenyl)-4-phenylbutan-2-one (3v)[3]



The reaction was conducted with **1a** (29.2 mg, 0.2 mmol) and 4-fluorobenzenesulfonohydrazide (**2e**, 57.0 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **3v** as pale yellow oil; yield 88%. This product is same as **3g**.

4-(Naphthalen-2-yl)-4-phenylbutan-2-one (3w)[3]



The reaction was conducted with **1a** (29.2 mg, 0.2 mmol) and naphthalene-2-sulfonohydrazide (**2f**, 66.6 mg, 0.3mmol) using $CuSO_4$ (44.8 mg, 0.28 mmol) as co-oxidant. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate =50:1) to give **3w** as white solid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78-7.68 (m, 4H), 7.46-7.42 (m, 2H), 7.33-7.19 (m, 6H), 4.76 (t, J = 7.2 Hz, 1H), 3.34-3.23 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 206.7, 143.7, 141.3, 133.5, 132.3, 128.9, 128.6, 128.3, 127.9, 127.8, 127.6, 126.6, 126.1, 125.8, 125.6, 49.6, 46.2, 30.7; MS (EI) m/z (%) 274.1, 217.1 (100), 202.1, 153.1, 103.1.

Reference

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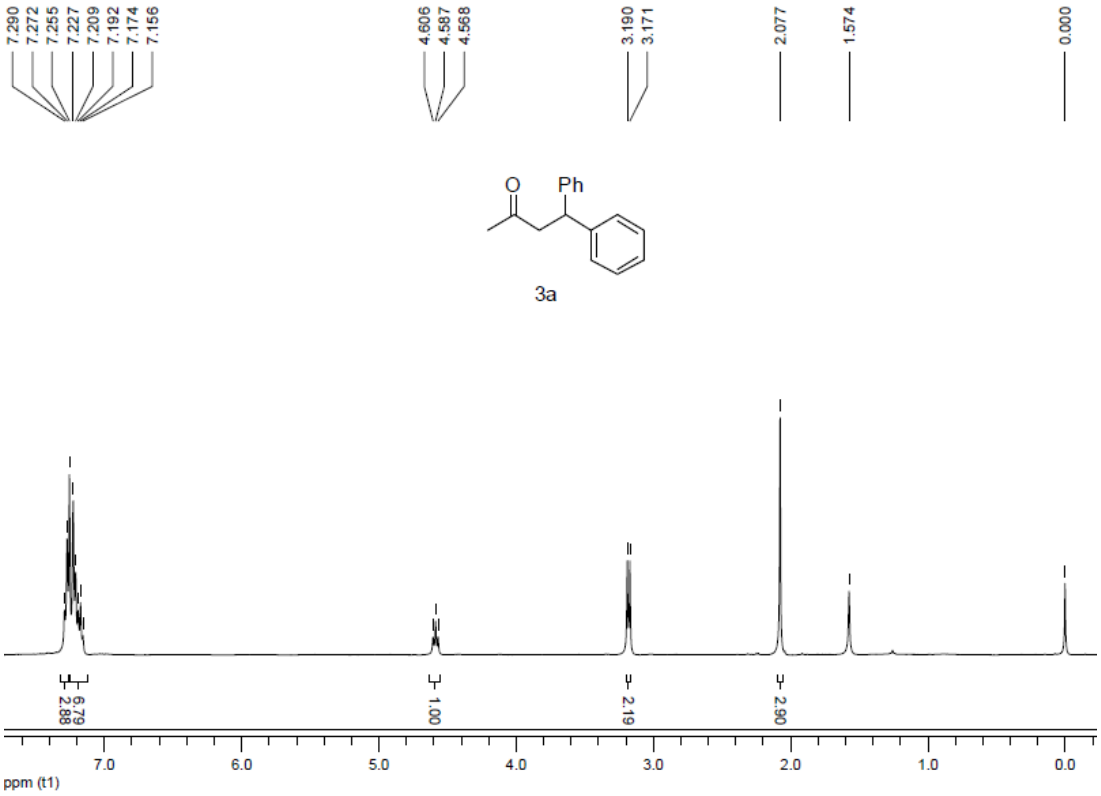
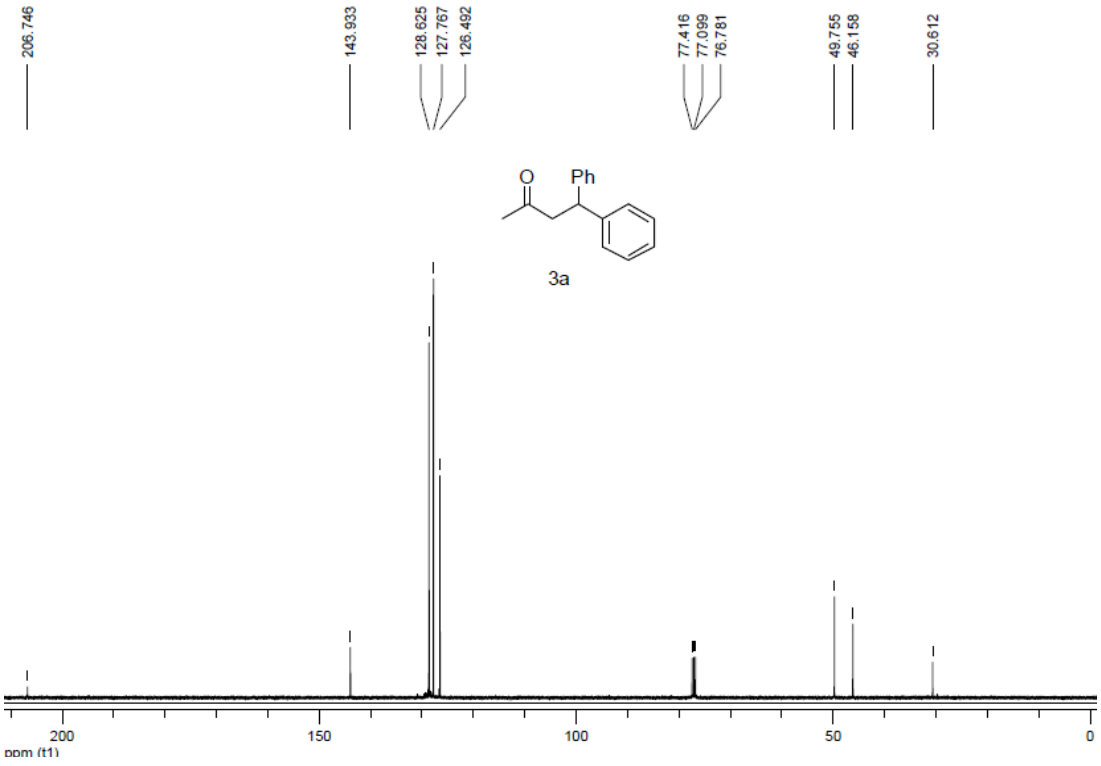
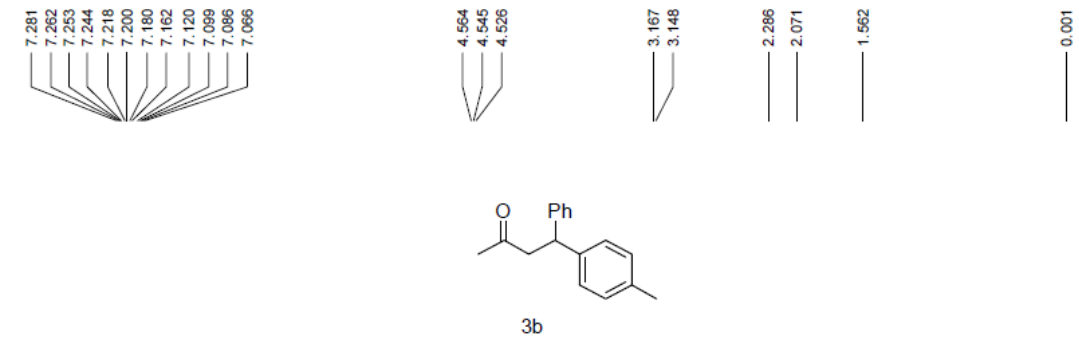
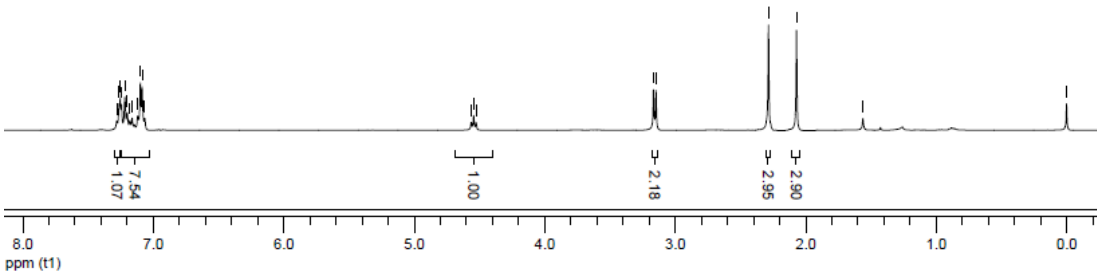
^{1}H NMR and ^{13}C NMR spectra

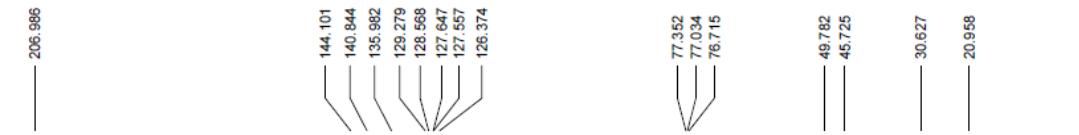


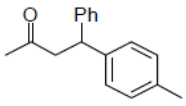




3b







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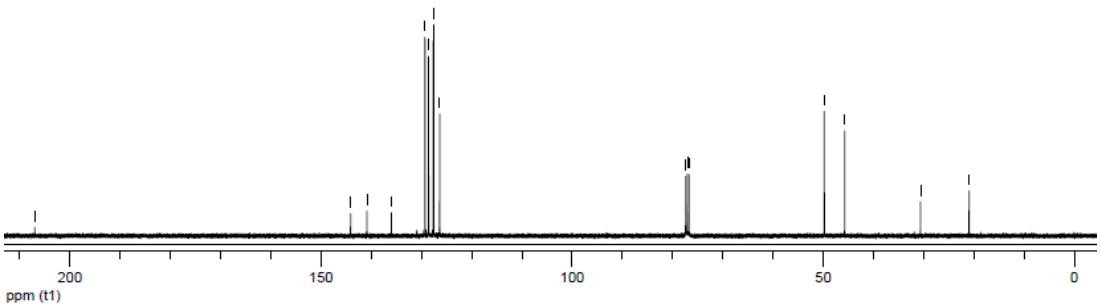

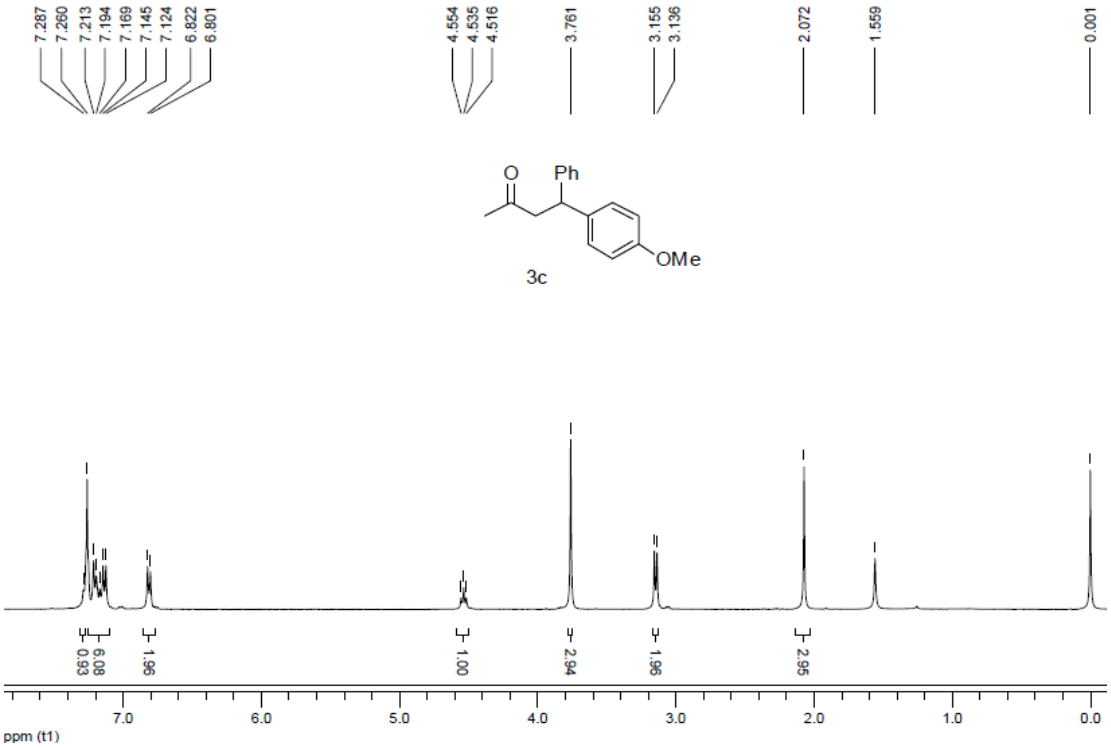
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3.155
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Ph
OMe
3c
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6.08
1.96
1.00
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7.0
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2.0
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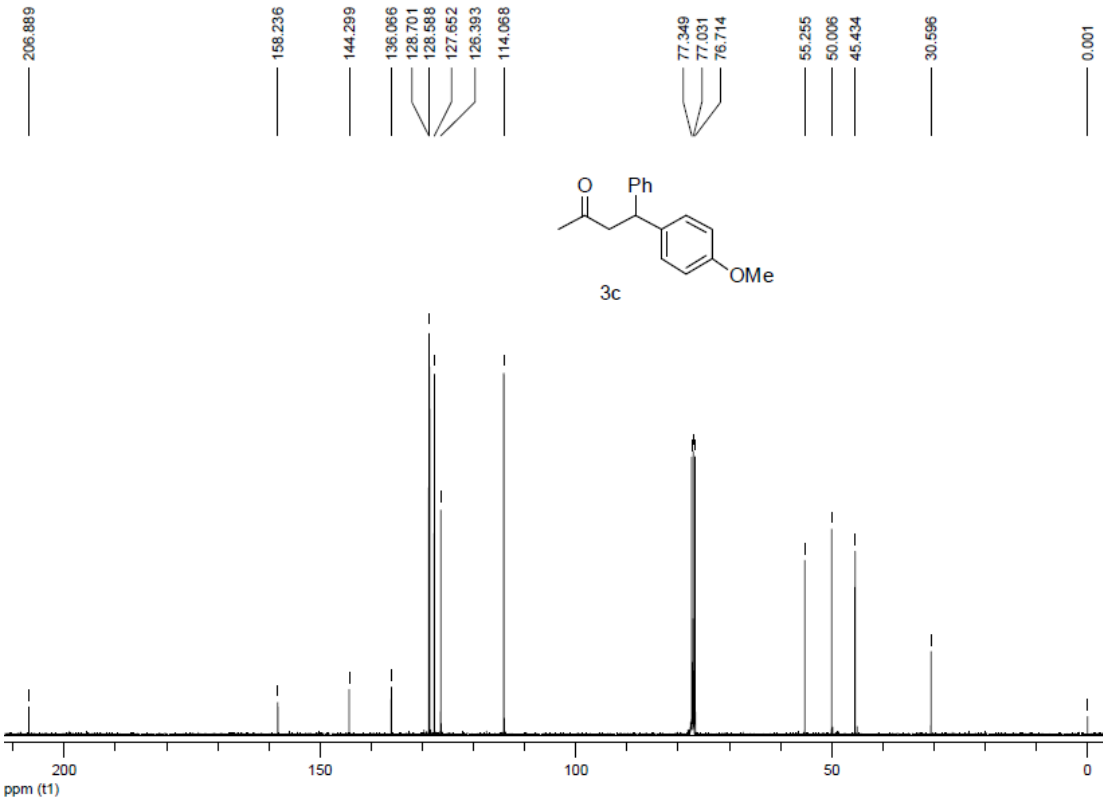
ppm (t1)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O
Ph
OMe
3c
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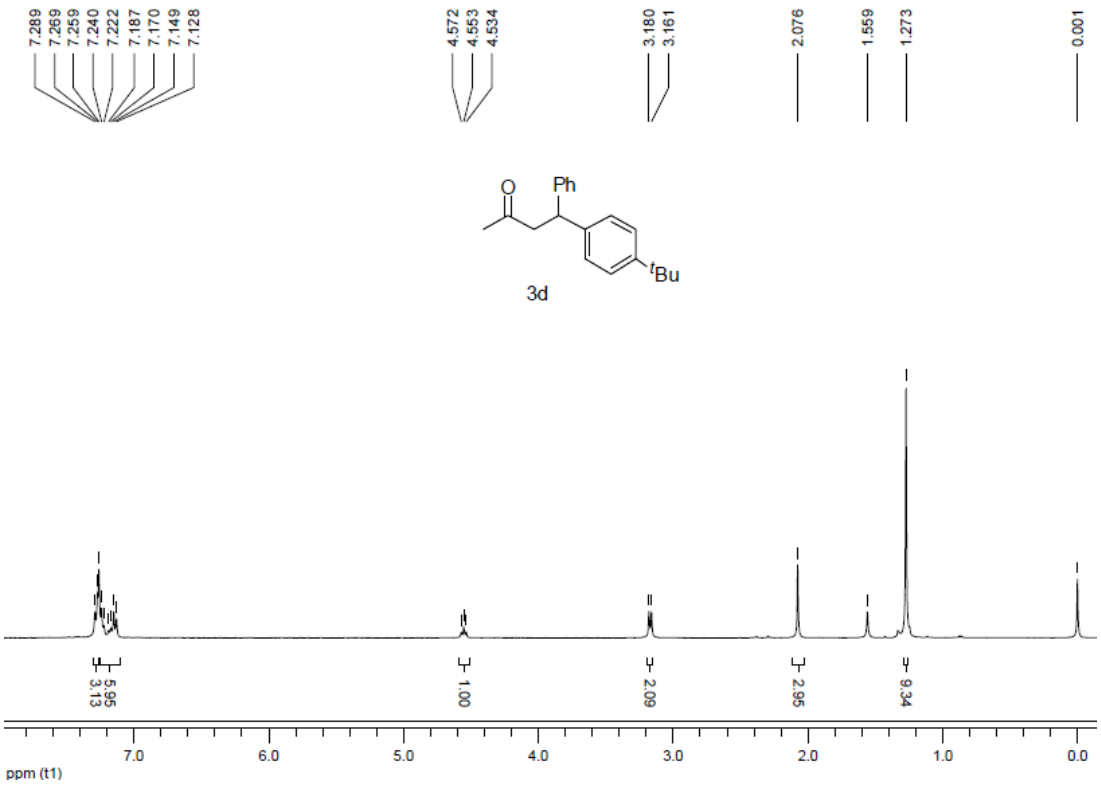
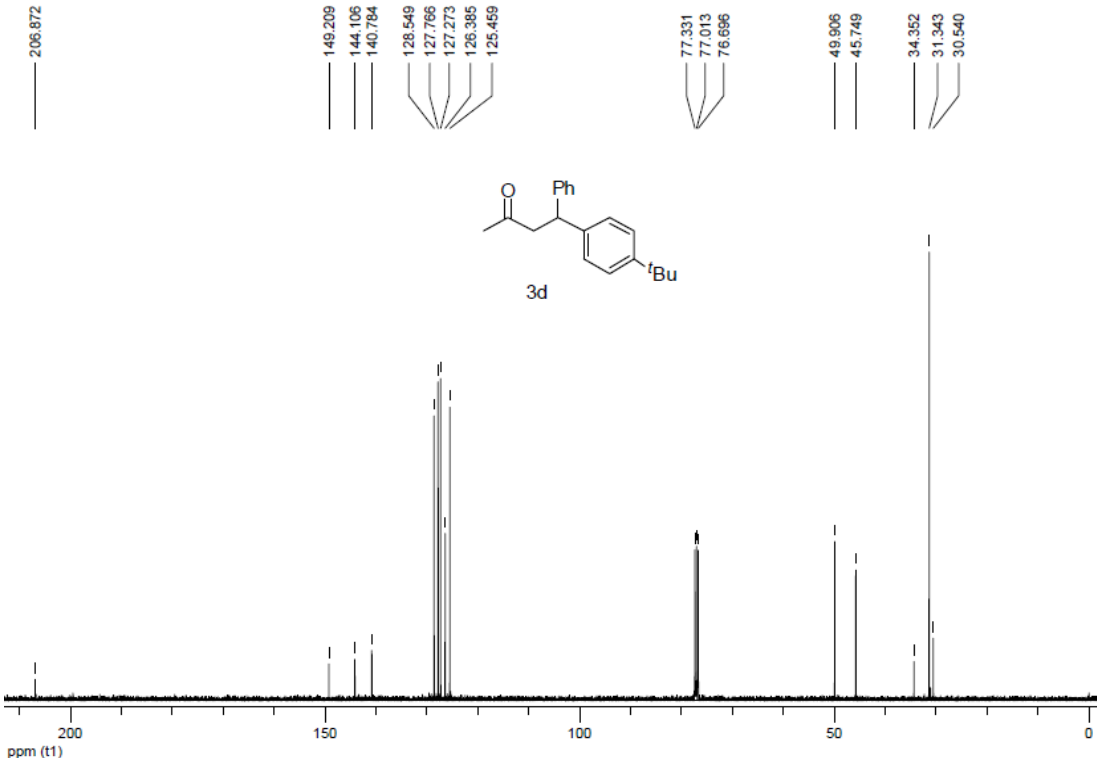
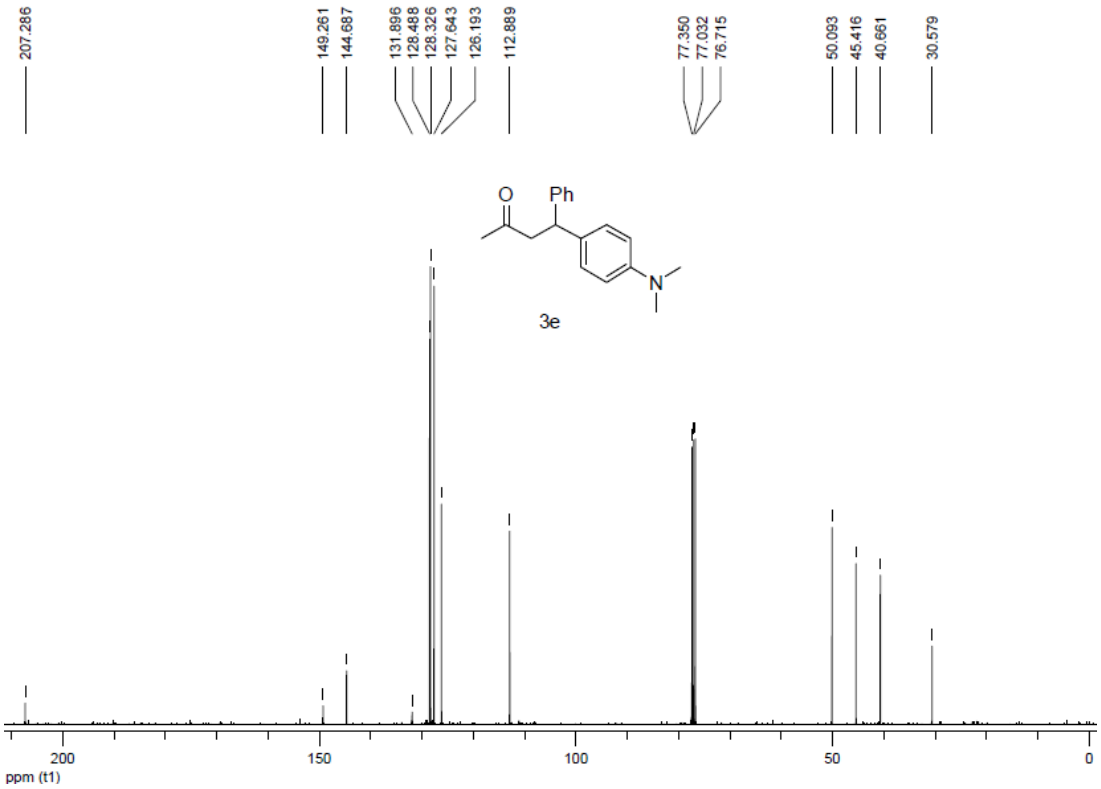
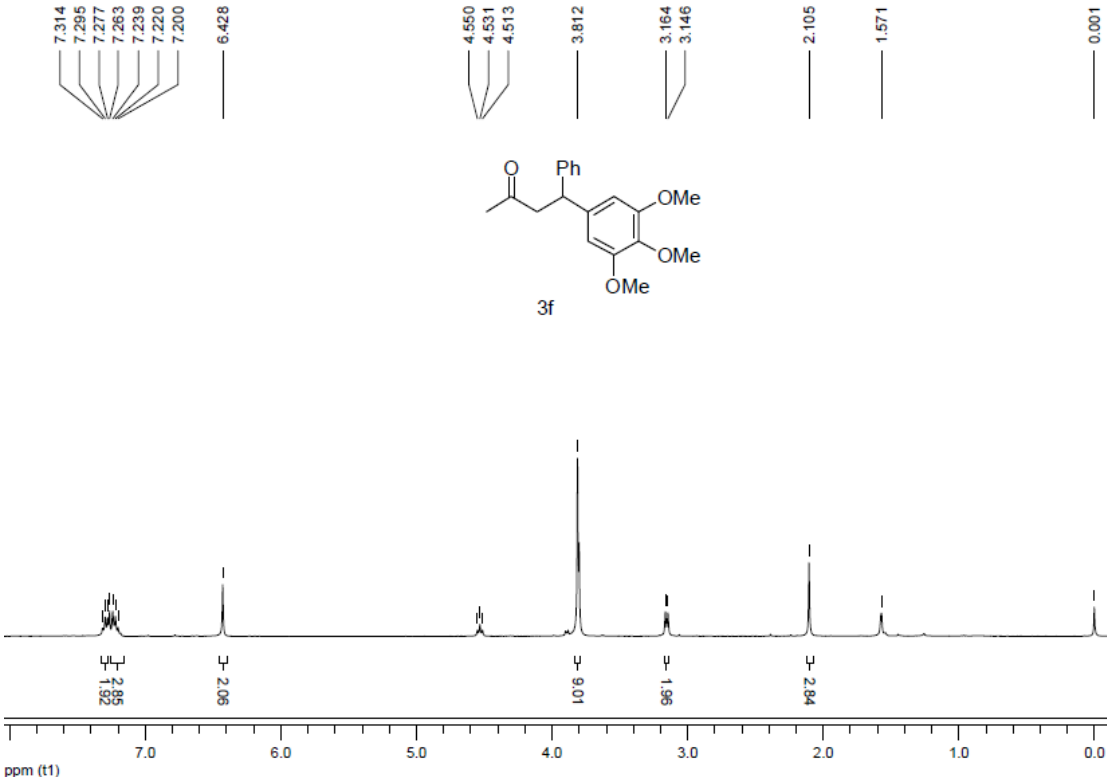
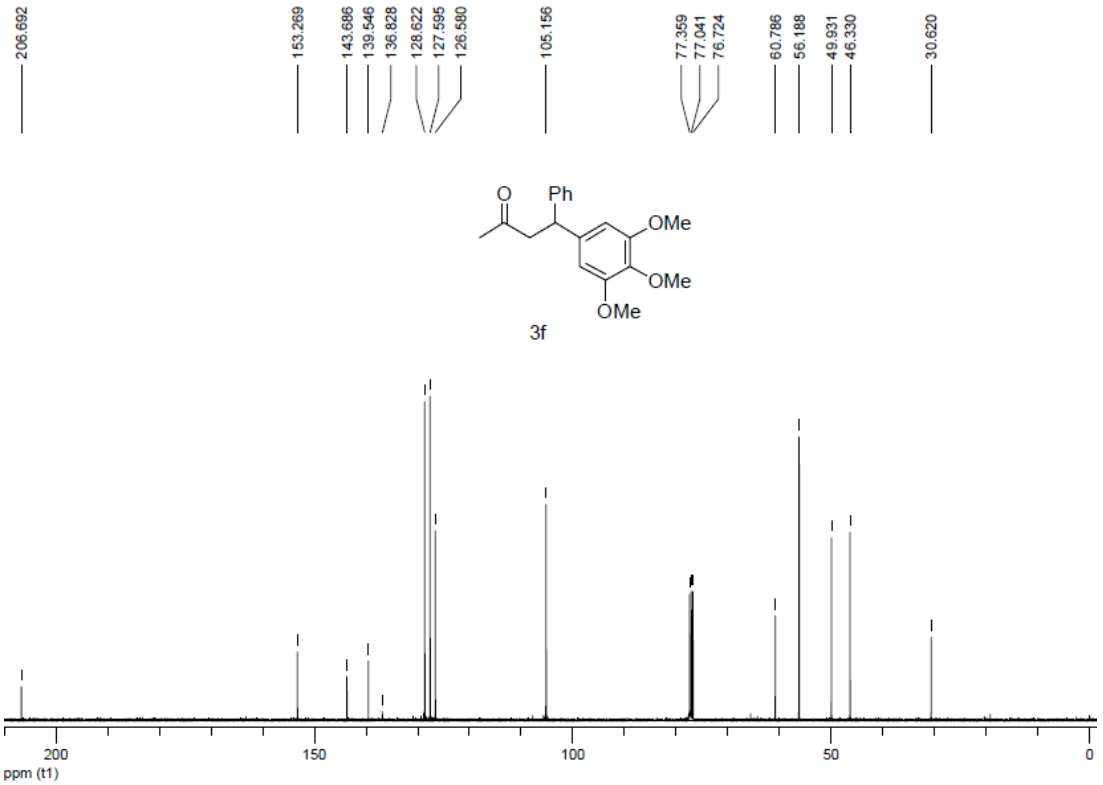
50
0
ppm (t1)

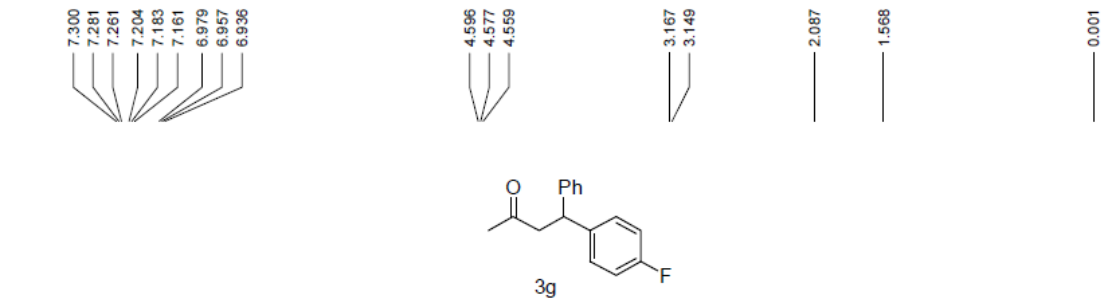




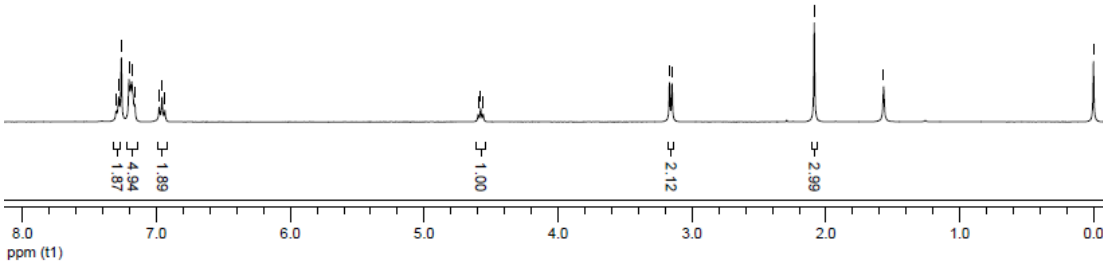


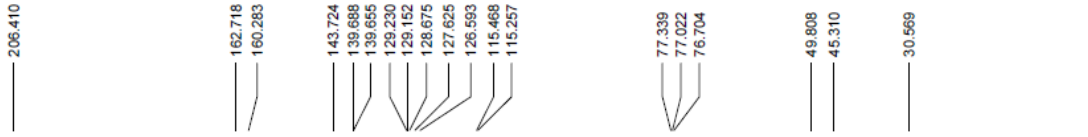


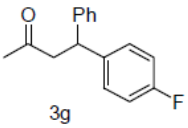




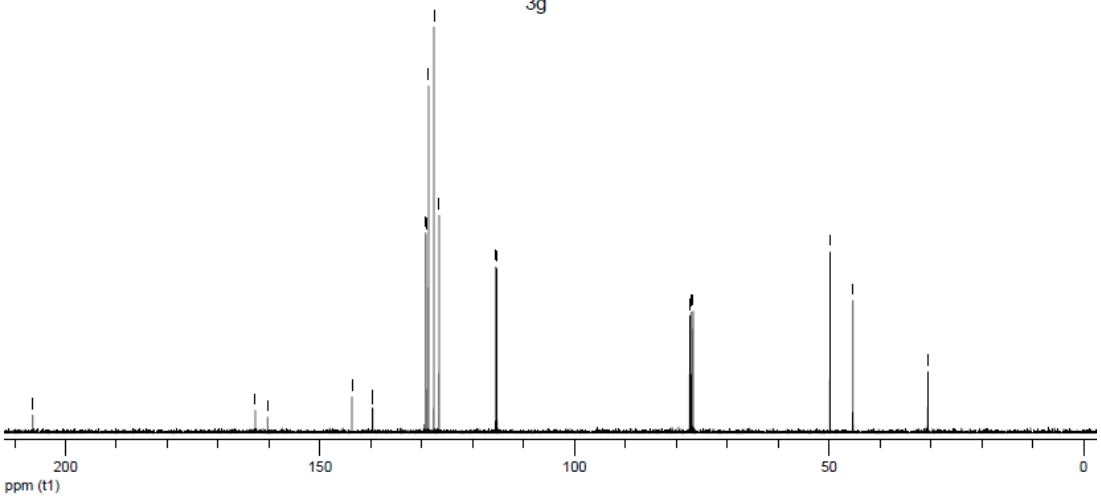
3g

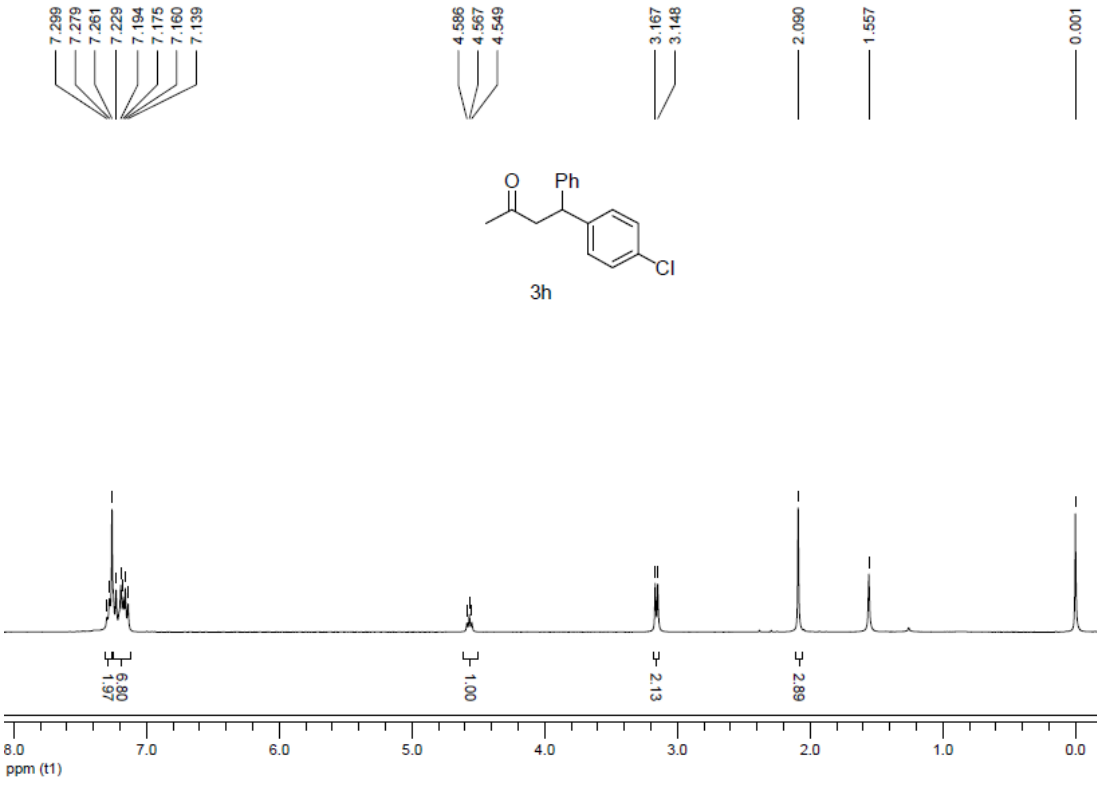


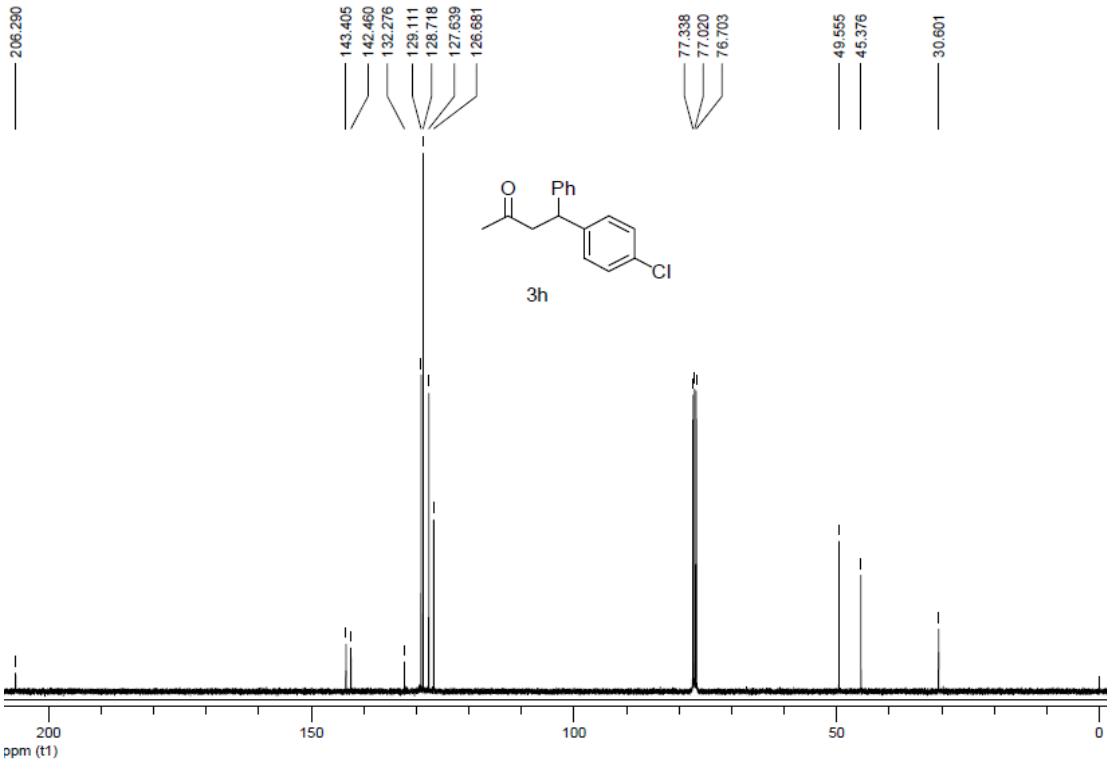


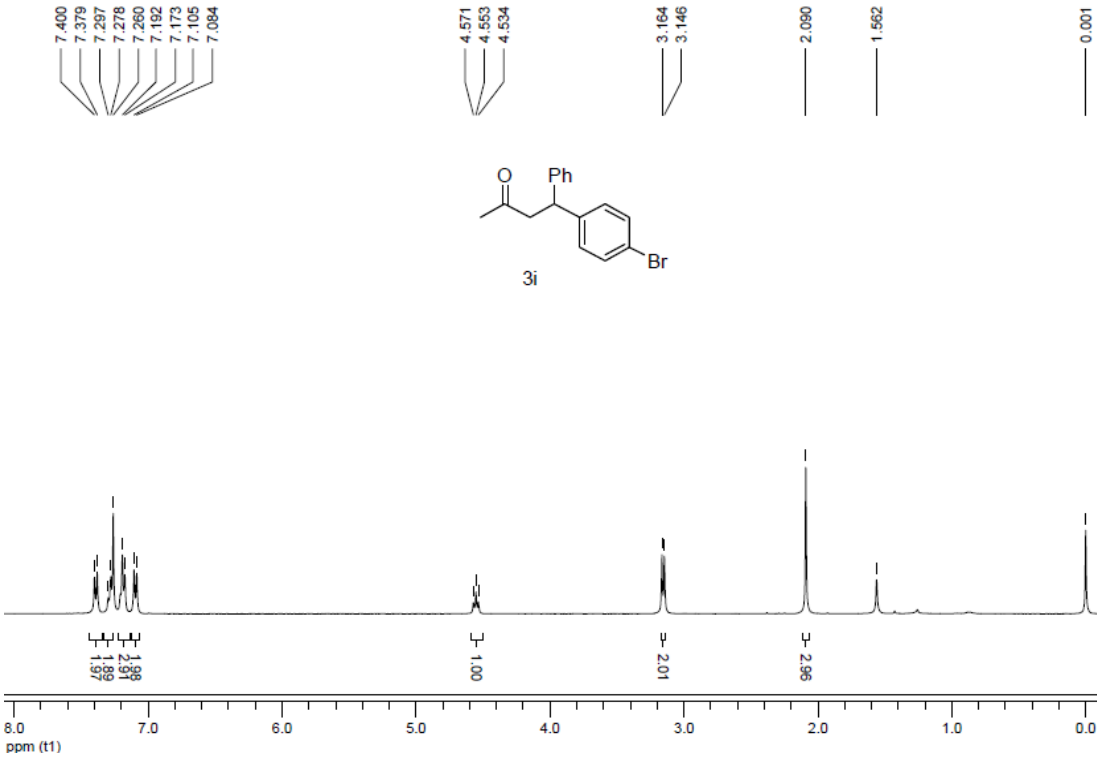


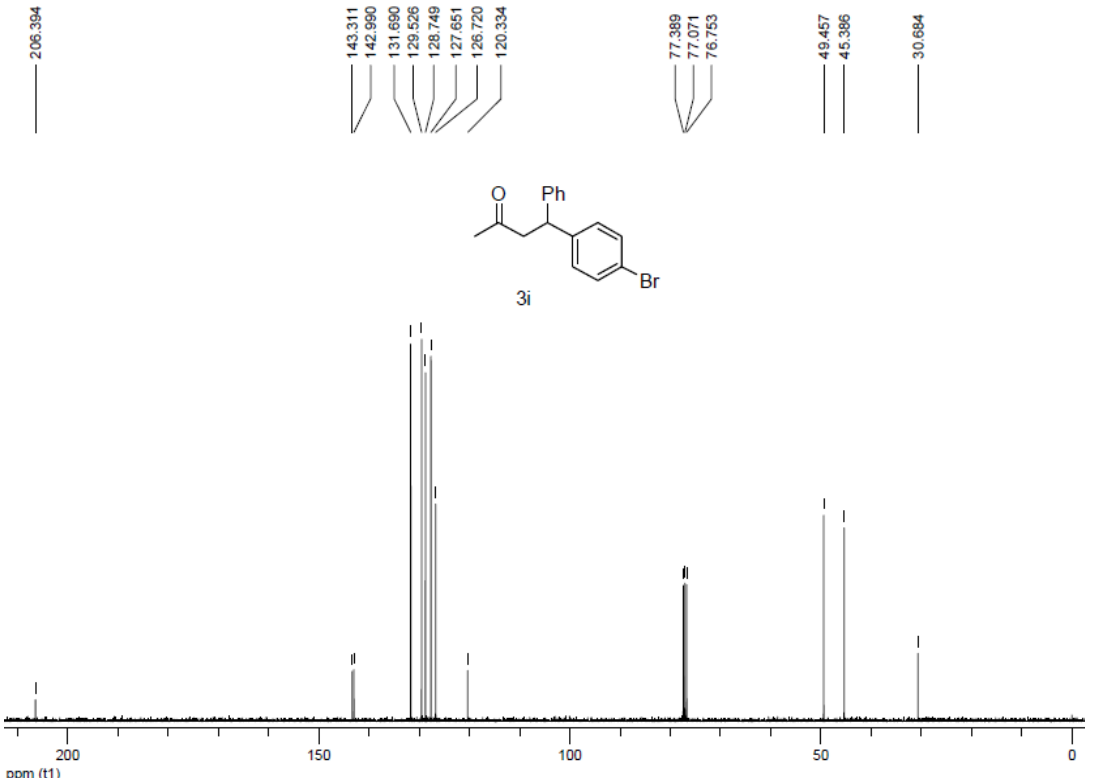
3g

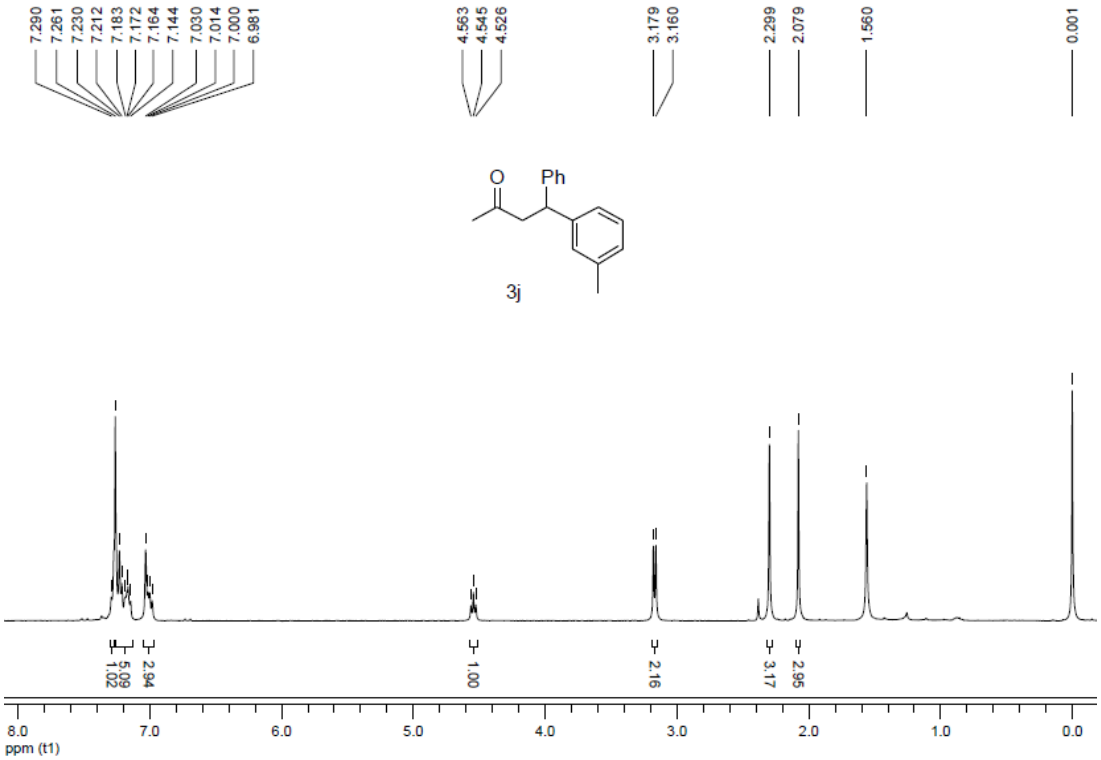








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4.526
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Ph
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1.00
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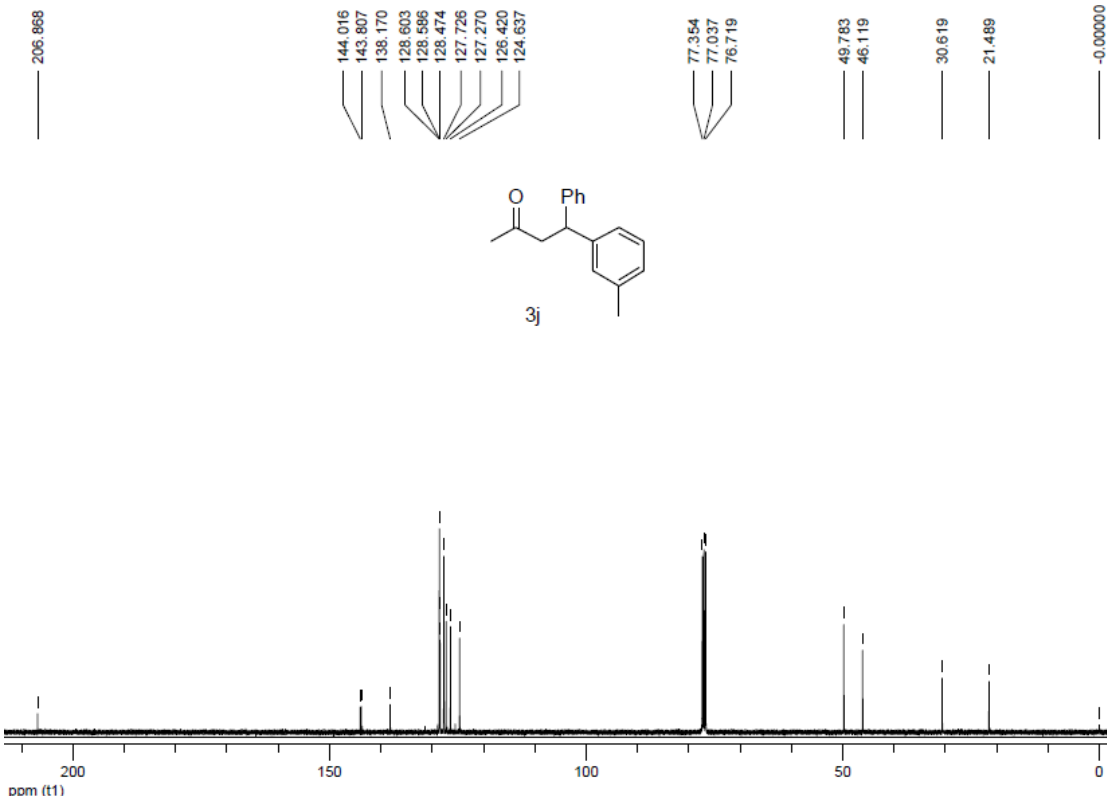
ppm (t1)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O
Ph
3j
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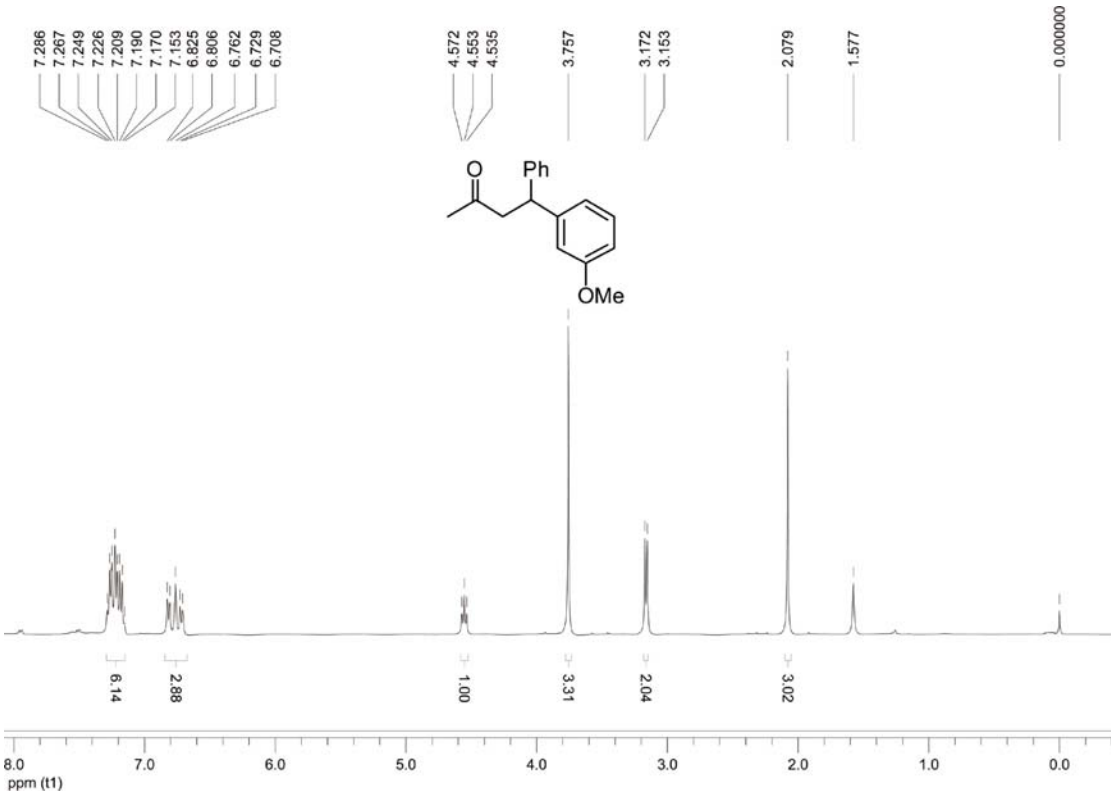
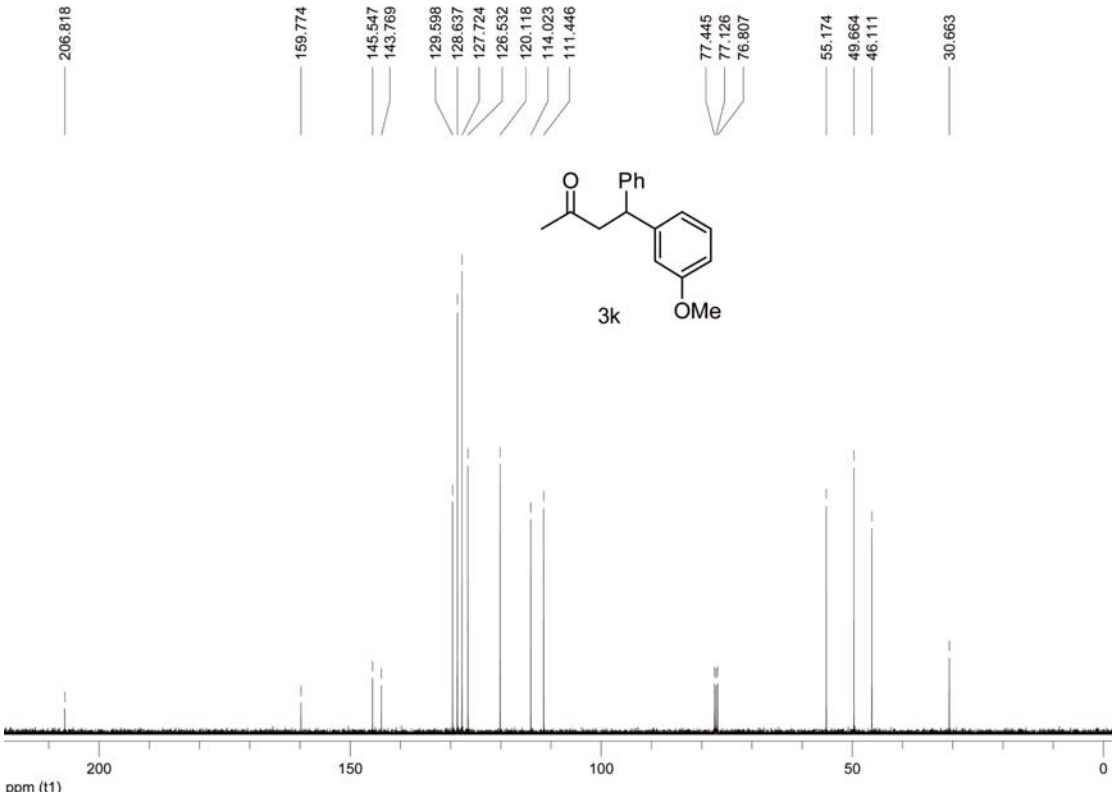
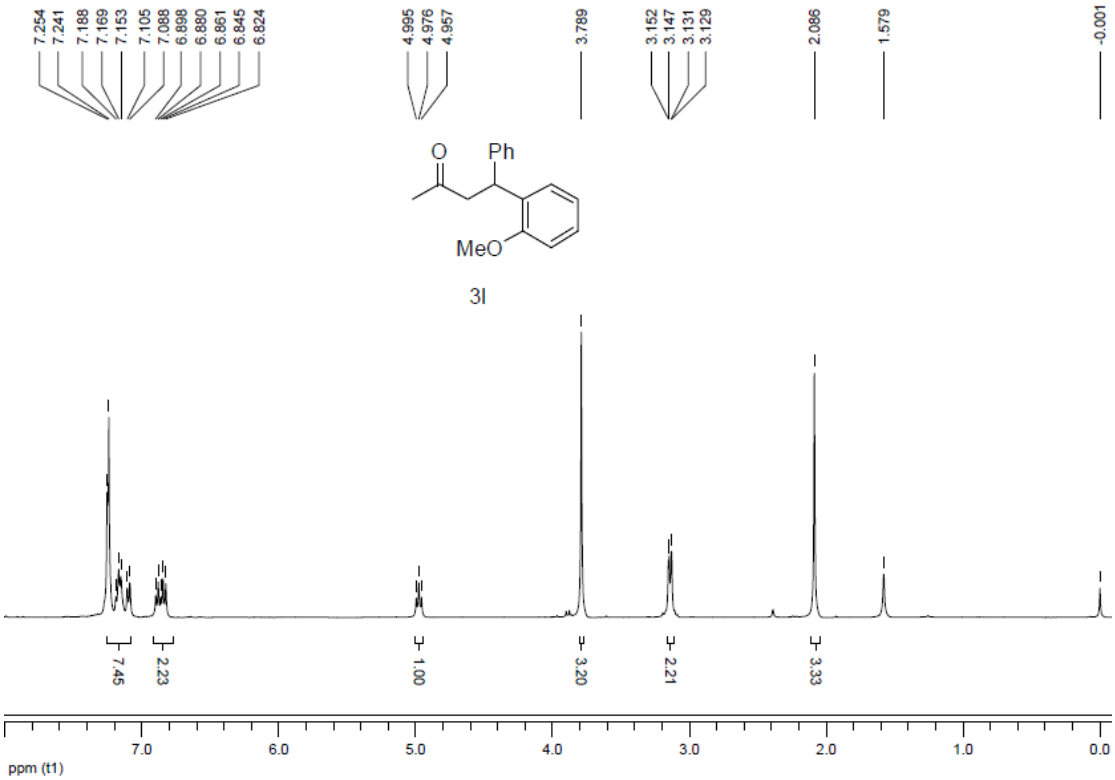
ppm (t1)



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3.131
3.129
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O
Ph
MeO
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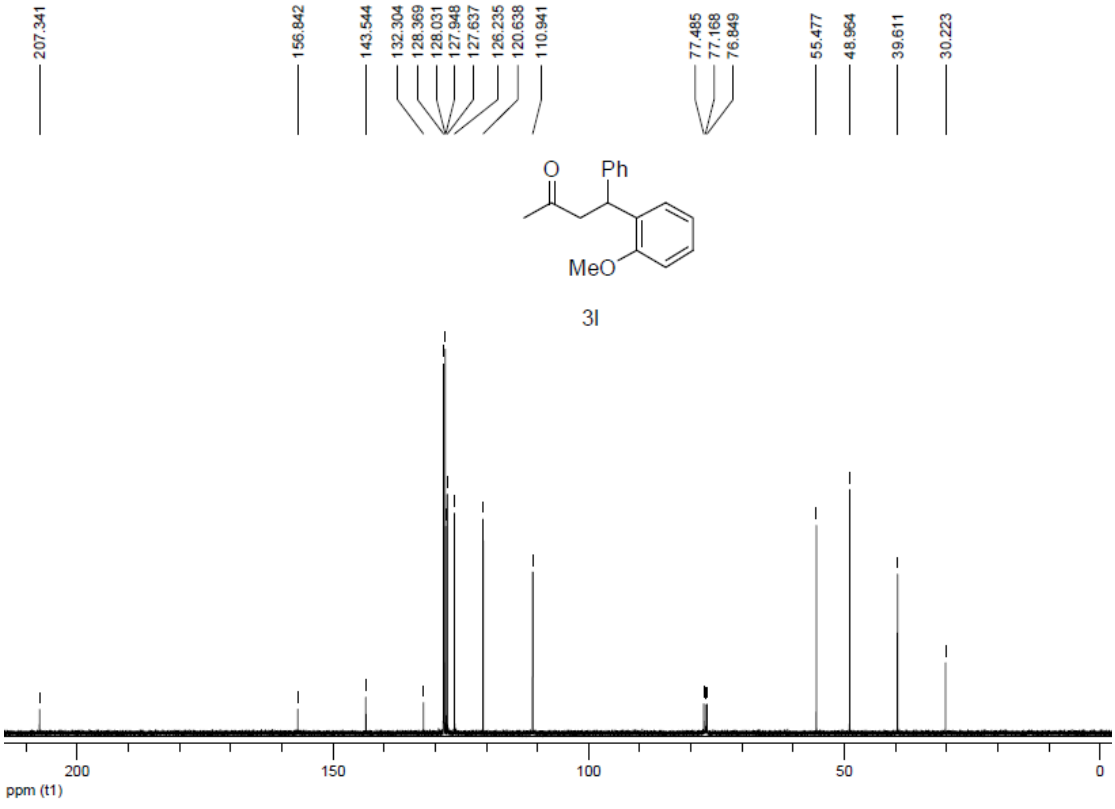
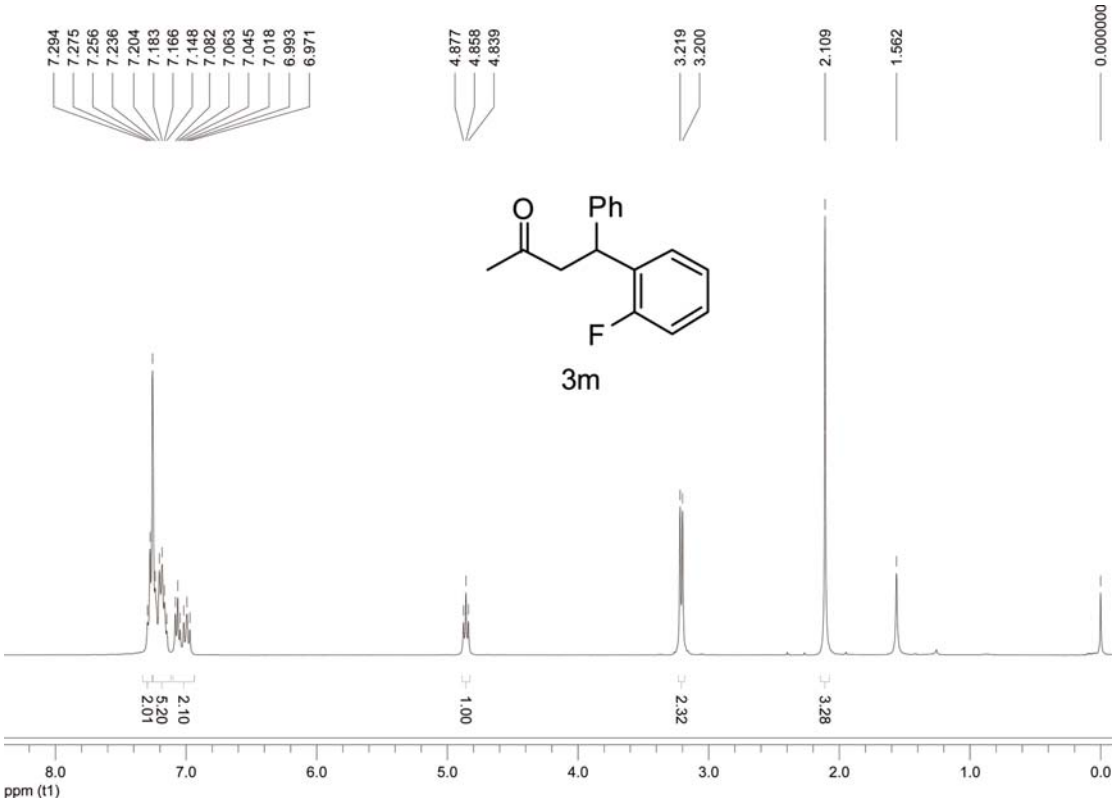
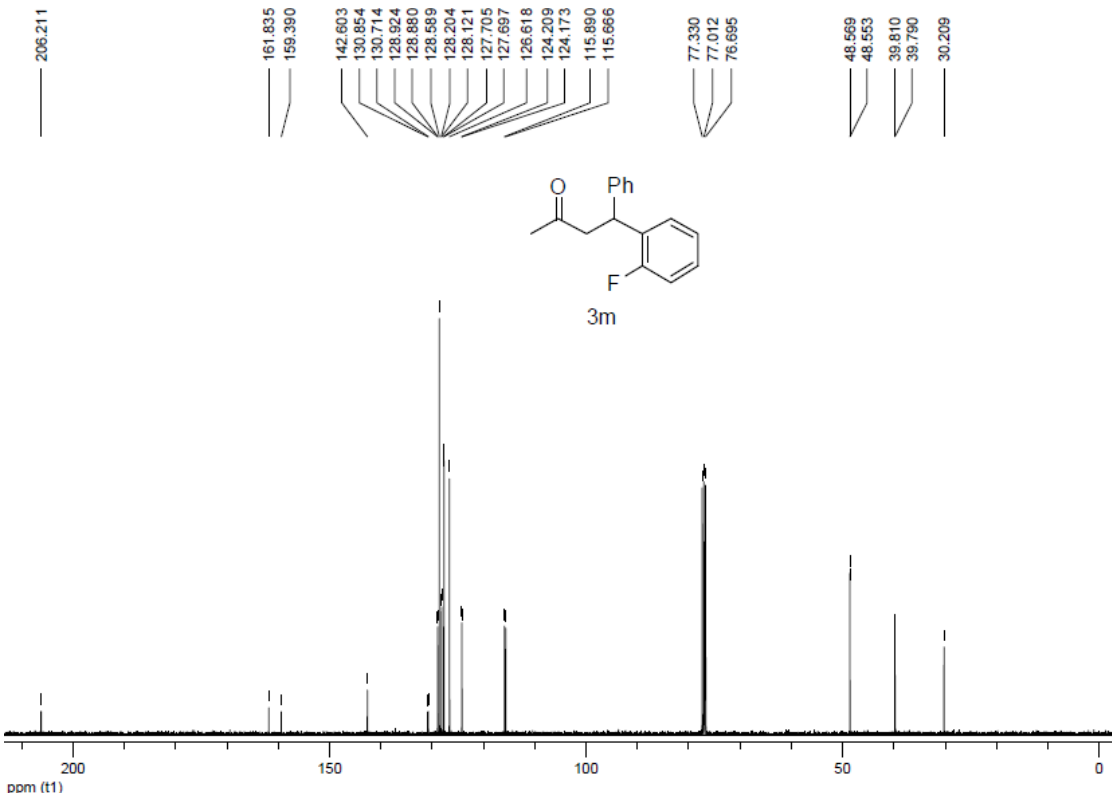
2.23
1.00
3.20
2.21
3.33
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

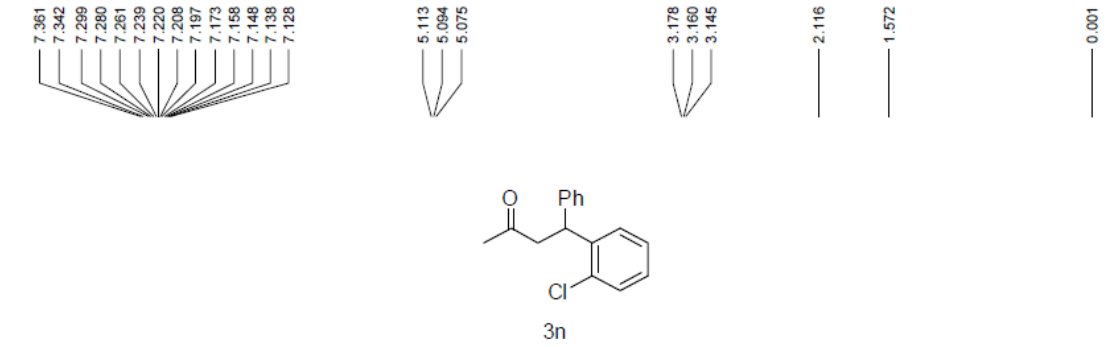
3l


207.341
156.842
143.544
132.304
128.369
128.031
127.948
127.637
126.235
120.638
110.941
77.485
77.168
76.849
55.477
48.964
39.611
30.223
O
Ph
MeO
200
150
100
50
0
ppm (t1)

3l

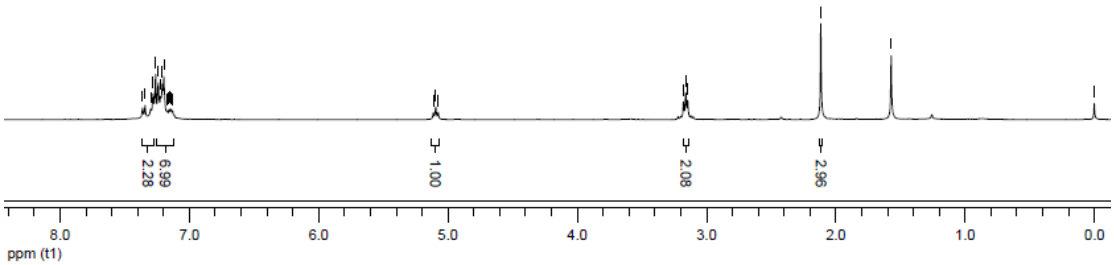


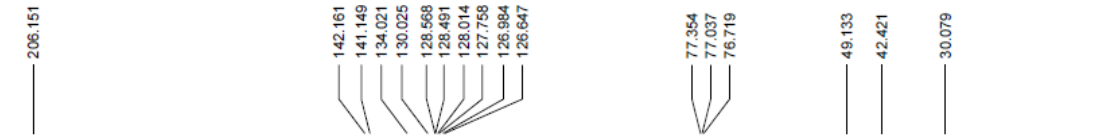


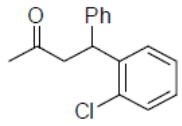

7.361
7.342
7.299
7.280
7.261
7.239
7.220
7.208
7.197
7.173
7.158
7.148
7.138
7.128
5.113
5.094
5.075
3.178
3.160
3.145
2.116
1.572
0.001

O
Ph
Cl

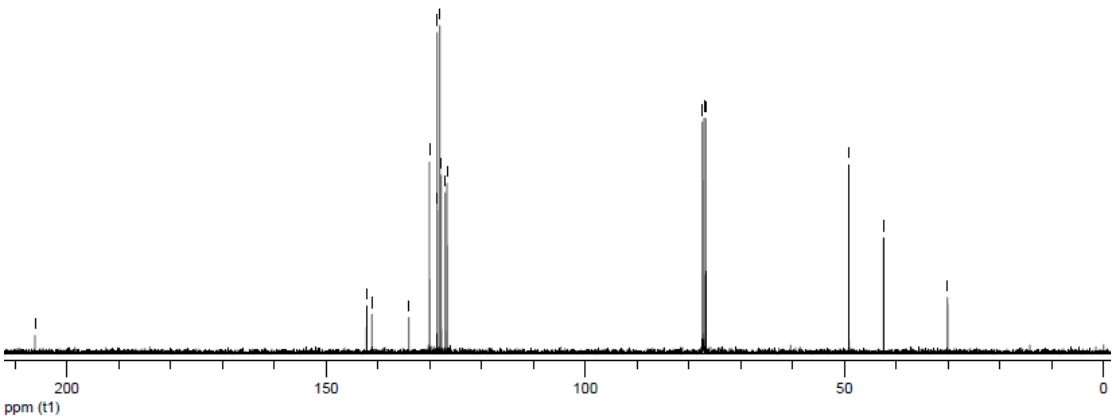
3n

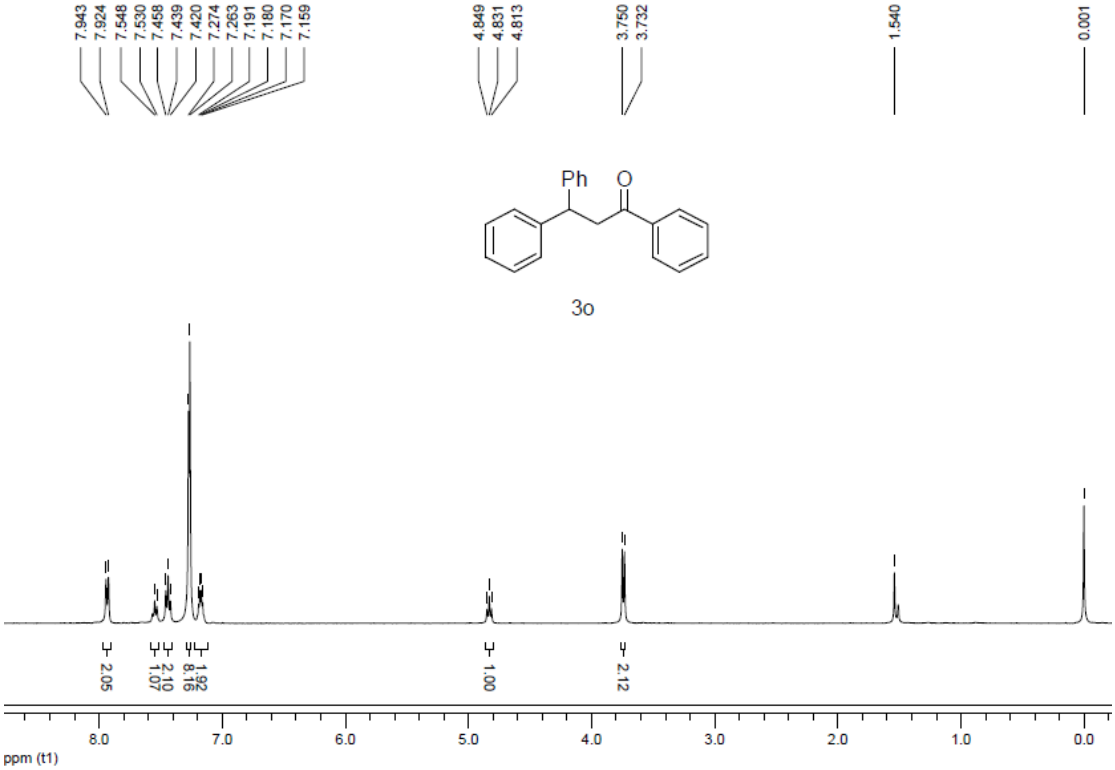

6.99
2.28
1.00
2.08
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

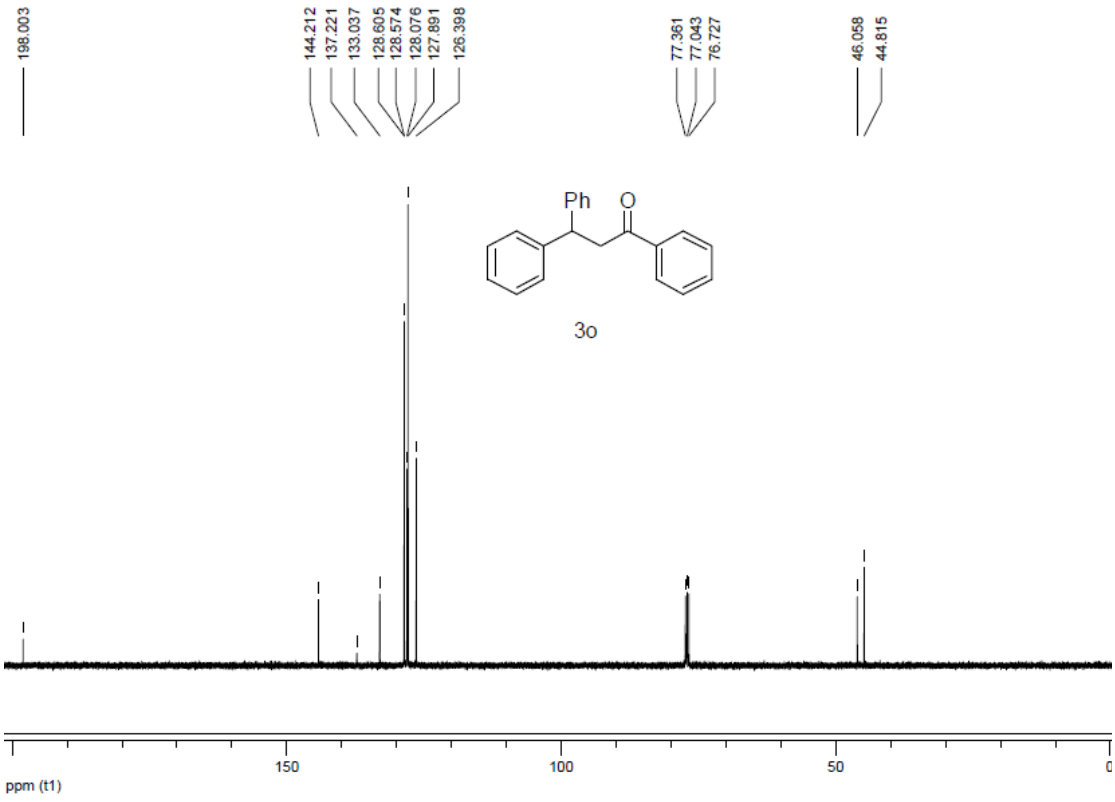

206.151
142.161
141.149
134.021
130.025
128.568
128.491
128.014
127.758
126.984
126.647
77.354
77.037
76.719
49.133
42.421
30.079

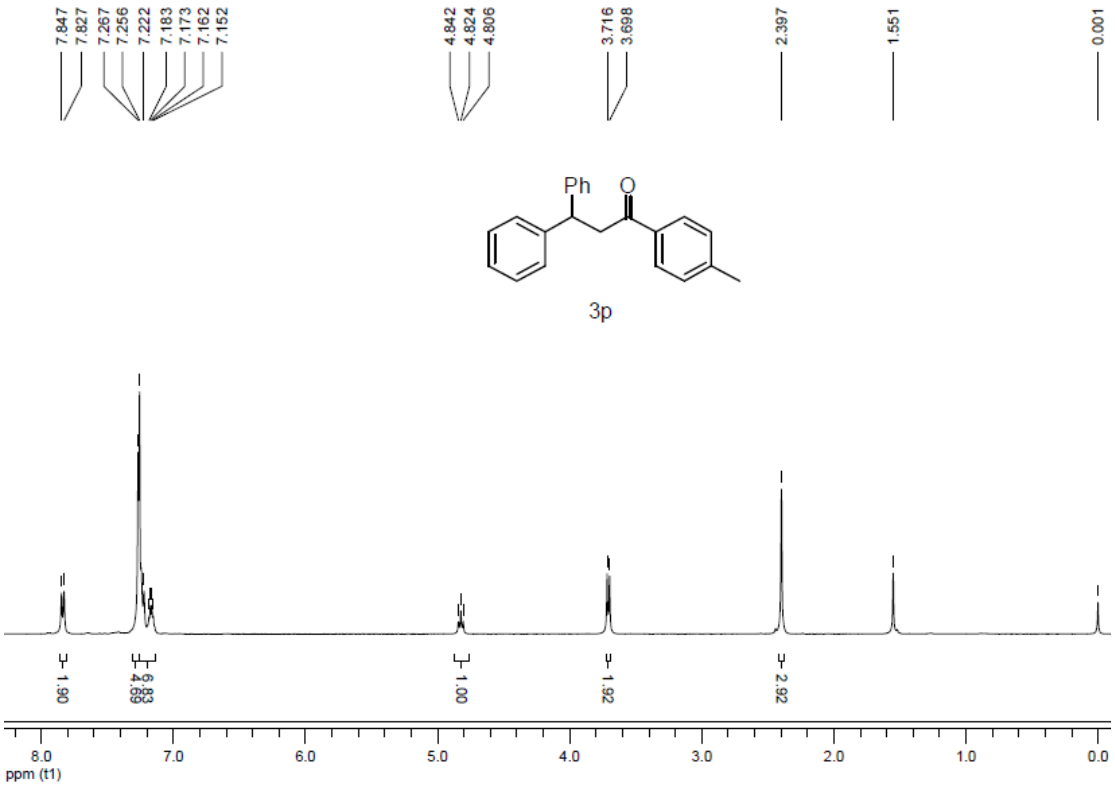

O
Ph
Cl

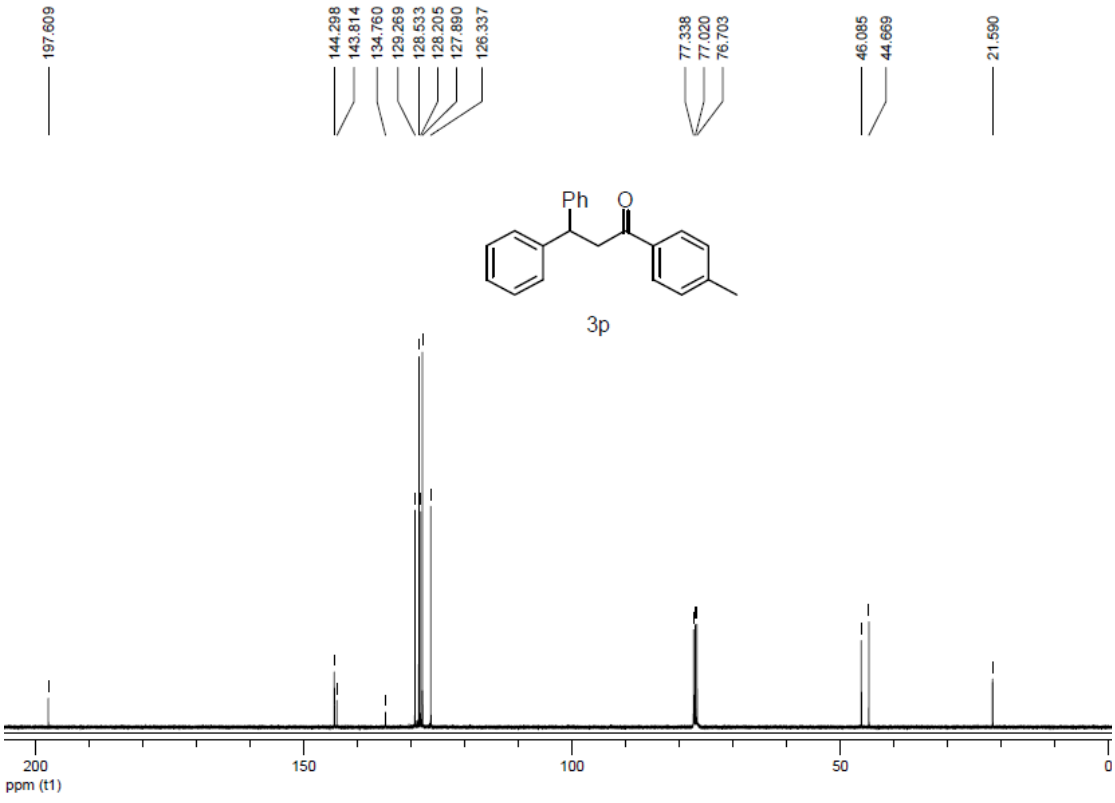
3n

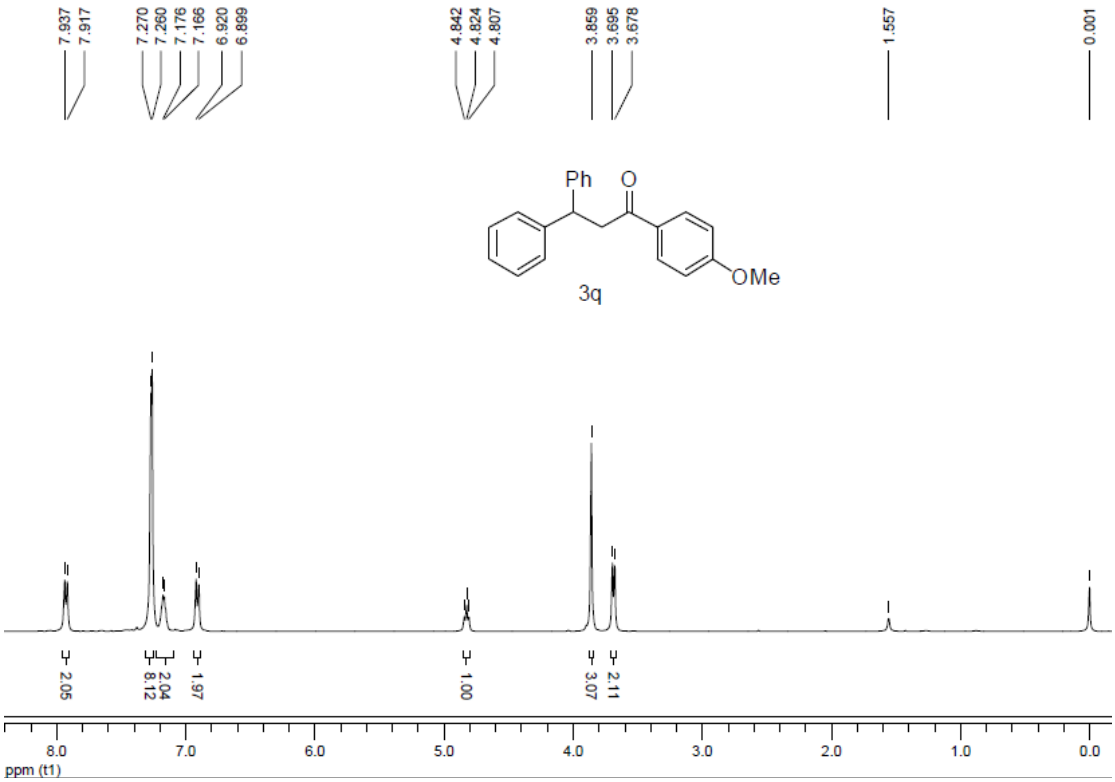

200
150
100
50
0
ppm (t1)

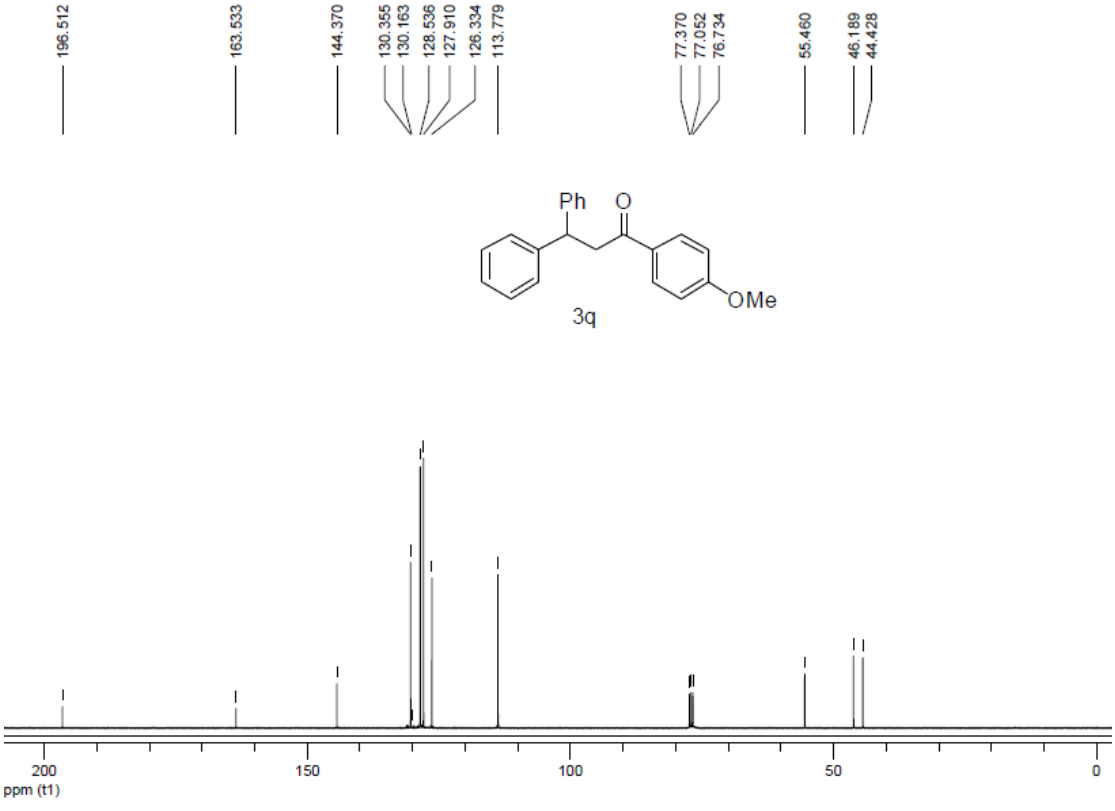

7.943
7.924
7.548
7.530
7.458
7.439
7.420
7.274
7.263
7.191
7.180
7.170
7.159
4.849
4.831
4.813
3.750
3.732
1.540
0.001
Ph
O
3o
2.05
1.07
2.10
8.16
1.00
2.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


198.003
144.212
137.221
133.037
128.605
128.574
128.076
127.891
126.398
77.361
77.043
76.727
46.058
44.815
Ph
O
3o
150
100
50
ppm (t1)

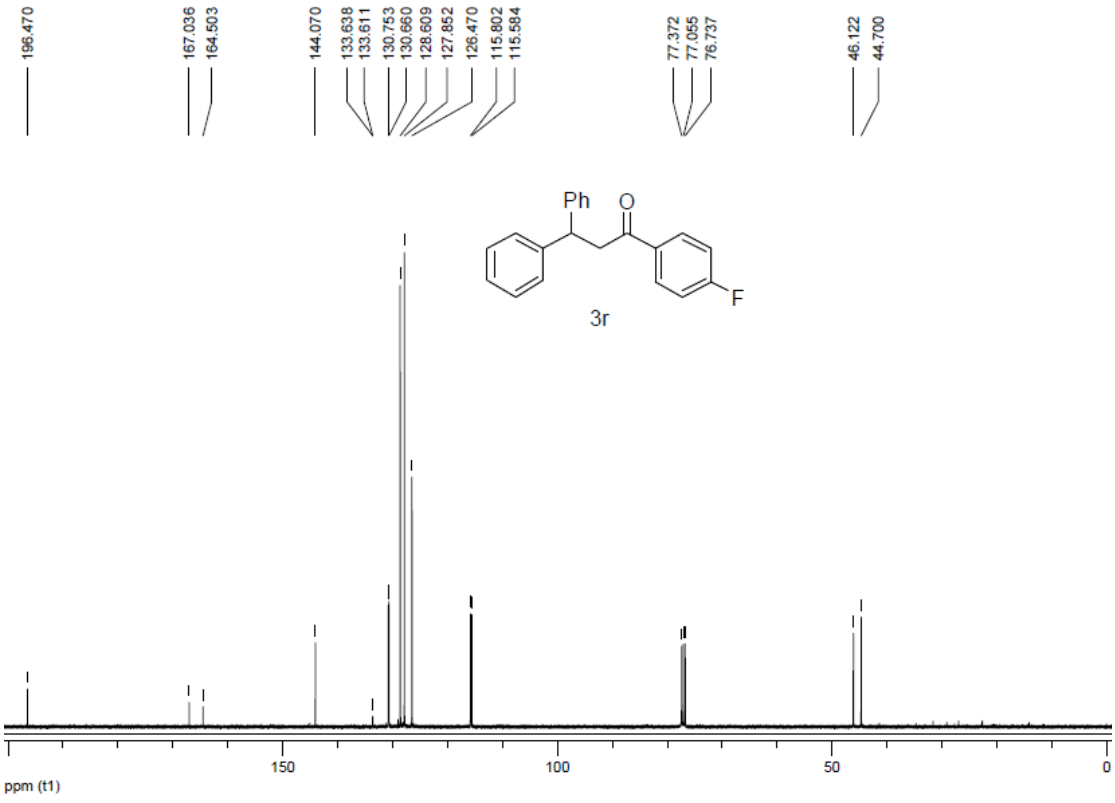

7.847
7.827
7.267
7.256
7.222
7.183
7.173
7.162
7.152
4.842
4.824
4.806
3.716
3.698
2.397
1.551
0.001
Ph
O
3p
1.90
6.89
4.69
1.00
1.92
2.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


197.609
144.298
143.814
134.760
129.269
128.533
128.205
127.890
126.337
77.338
77.020
76.703
46.085
44.669
21.590
Ph
O
3p
200
150
100
50
0
ppm (t1)


7.937
7.917
7.270
7.260
7.176
7.166
6.920
6.899
4.842
4.824
4.807
3.859
3.695
3.678
1.557
0.001
Ph
O
OMe
3q
2.05
8.12
2.04
1.97
1.00
3.07
2.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


196.512
163.533
144.370
130.355
130.163
128.536
127.910
126.334
113.779
77.370
77.052
76.734
55.460
46.189
44.428
Ph
O
OMe
3q
200
150
100
50
0
ppm (t1)


7.974
7.960
7.953
7.939
7.261
7.190
7.181
7.126
7.104
7.083
4.827
4.809
4.791
3.717
3.699
1.528
0.001
Ph
O
F
3r
1.96
10.14
1.91
1.00
2.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


196.470
167.036
164.503
144.070
133.638
133.611
130.753
130.660
128.609
127.852
126.470
115.802
115.584
77.372
77.055
76.737
46.122
44.700
Ph
O
F
3r
150
100
50
0
ppm (t1)