Direct Functionalization of Benzylic C-Hs with Vinyl Acetates via Fe-Catalysis

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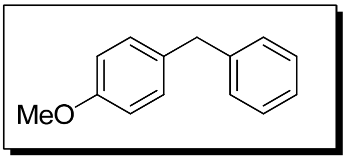
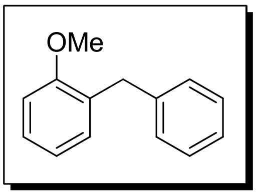
General procedure. All the reactions were carried out under nitrogen atmosphere unless otherwise noted. Most diphenylmethane derivatives were purchased as analytical pure and used without further purification. $FeCl_2$ was purchased from Strem Chemicals. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were registered on Varian 300 M spectrometers; ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) were registered on Varian 200 M spectrometers, all with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). LRMS was performed on Agilent Technologies 6890N/5973i GC-MS. HRMS were performed by the State-authorized Analytical Center in Peking University.

General procedure for 4-Benzyl anisole (1f)[1]: 4-Benzylphenol (1.5 g, 8 mmol) in THF (3 ml) was added dropwise, under an nitrogen atmosphere, to sodium hydride (70% dispersion in mineral oils) (0.31 g, 9 mmol) in THF (18 ml) at 0 °C. The mixture was refluxed for 1 h, followed by cooling to room temperature and the addition of methyl iodide (1.42 g, 10 mmol) in THF (2.5 ml). The mixture was stirred at room temperature for 15 h, quenched by saturated aq. ammonium chloride (10 ml), diluted with water (15 ml) and extracted with methylene chloride. The combined organic phases were washed with 1 M sodium hydroxide and brine, dried over $MgSO_4$. Solvent was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluting with ethyl acetate/petroleum ether = 1:9) and the fraction with an Rf = 0.8 was collected and concentrated to give the title product **1f**.



4-Benzyl anisole (1f).

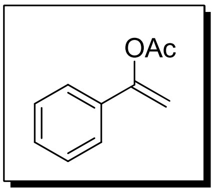
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.29-7.11 (m, 7H), 6.82 (d, 2H, *J*= 8.7), 3.91 (s, 2H), 3.76 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 157.9, 141.5, 133.2, 129.8, 128.8, 128.4, 125.9, 113.8, 55.2, 41.0 ppm.



2-Benzyl anisole (1g).

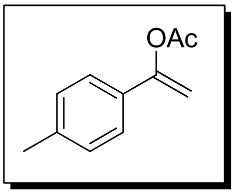
^{1}H NMR (CDCl$_3$, 200MHz) δ 7.24-7.14 (m, 6H), 7.06-7.03 (m, 1H), 6.89-6.81 (m, 2H), 3.96 (s, 2H), 3.76 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 157.3, 141.0, 130.2, 129.6, 128.9, 128.2, 127.3, 125.7, 125.7, 120.4, 110.3, 55.2, 35.8 ppm.

General procedure for 1-phenylvinyl acetate (2a) [2]**:** To a mixture of acetophenone (4.85 ml, 5 g, 42.5 mmol) and 2-propenyl acetate (23.13 ml, 0.213 mol, 5 equiv.) was added *p*-toluenesulfonic acid (0.75 g, 3.925 mmol, 0.09 equiv). The resulting mixture was refluxed for 20 h in a 100 ml flask equipped with a condenser and a drying tube. The solvent was then cooled to room temperature, and the solvent was evaporated *in vacuo*. Ether was added (100 ml), and the resulting solvent was washed with water (3 x 50 ml) and dried over MgSO$_4$. The solvent was evaporated in vacuo to give a dark orange/red oily residue. This residue was purified by column chromatography on silica gel to yield a yellow oil. Sometimes a further distillation to remove remained acetophenone is necessary.



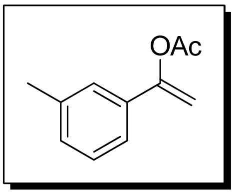
1-phenylvinyl acetate (2a)

^{1}H NMR (CDCl$_3$, 200MHz) δ 7.49-7.45 (m, 2H), 7.38-7.32 (m, 3), 5.48 (d, 1H, J = 2.0), 5.03 (d, 1H, J = 2.0), 2.27 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 50MHz) 169.2, 152.9, 134.2, 129.0, 128.5, 124.8, 102.1, 20.8 ppm.



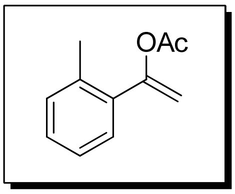
1-*p*-tolylvinyl acetate (2b)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.35 (d, 2H, *J* = 8.4), 7.14 (d, 2H, *J* = 8.1), 5.42 (d, 1H, *J* = 1.8), 4.96 (d, 1H, *J* = 1.8), 2.34 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 169.1, 153.9, 138.9, 131.4, 129.1, 124.7, 101.2, 21.2, 20.9 ppm.



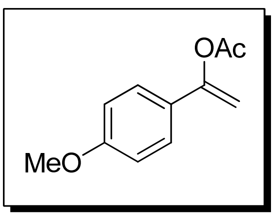
1-*m*-tolylvinyl acetate (2c)

^{1}H NMR (CDCl$_3$, 200MHz) δ 7.38-7.13 (m, 4H), 5.46 (d, 1H, *J* = 2.2), 5.00 (d, 1H, *J* = 2.0), 2.35 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 50MHz) 169.2, 153.2, 138.2, 134.2, 129.8, 128.5, 125.5, 122.0, 102.0, 21.4, 20.9 ppm.



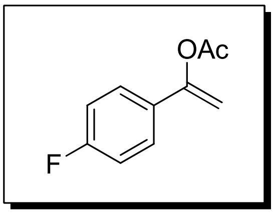
1-*o*-tolylvinyl acetate (2d)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.38-7.35 (m, 1H), 7.26-7.16 (m, 3H), 5.17 (d, 1H, *J* = 1.5), 5.01 (d, 1H, *J* = 2.0), 2.41 (s, 3H), 2.13 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 168.7, 153.8, 135.9, 135.3, 130.3, 129.0, 128.7, 125.6, 105.6, 21.0, 20.3 ppm.



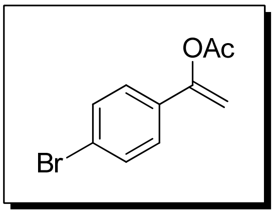
1-(4-methoxyphenyl)vinyl acetate (2e)

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.44-7.38 (m, 2H), 6.91-6.85 (m, 2H), 5.36 (d, 1H, *J* = 2.0), 4.92 (d, 1H, *J* = 2.0), 3.81 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) 169.2, 160.2, 152.8, 126.9, 126.3, 113.9, 100.2, 55.2, 20.9 ppm.



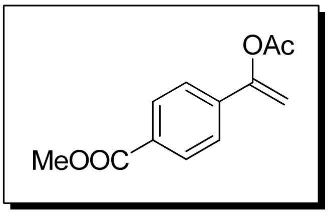
1-(4-fluorophenyl)vinyl acetate (2f)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.47-7.42 (m, 2H), 7.06-7.00 (m, 2H, *J* = 9.0), 5.40 (d, 1H, *J* = 2.1), 5.01 (d, 1H, *J* = 2.4), 2.27 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 169.0, 164.7, 152.0, 126.9, 126.7, 115.7, 115.4, 102.0, 20.9 ppm.



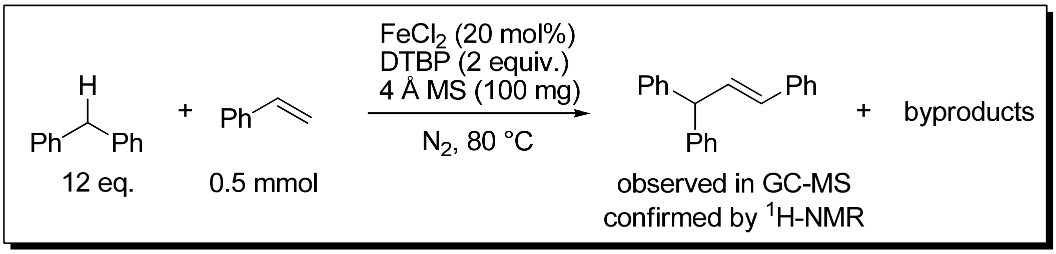
1-(4-bromophenyl)vinyl acetate (2g)

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.47 (d, 2H, *J* = 8.4), 7.32 (d, 2H, *J* = 8.1), 5.47 (d, 1H, *J* = 2.0), 5.06 (d, 1s, *J* = 2.4), 2.34 (s, 3H), 2.26 (s, 3H) ppm.



methyl 4-(1-acetoxyvinyl)benzoate (2h)

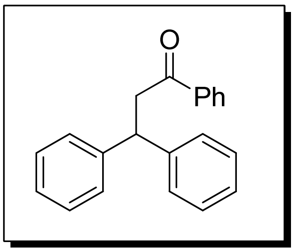
^{1}H NMR ($CDCl_3$, 300MHz) δ 8.02 (d, 2H, *J* = 8.4), 7.52 (d, 2H, *J* = 8.4), 5.59 (d, 1H, *J* = 2.1), 5.15 (d, 1H, *J* = 2.4), 3.92 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 168.9, 166.5, 152.0, 138.4, 130.3, 129.8, 124.7, 104.3, 52.1, 20.9 ppm.



Procedure for the reaction of diphenylmethane with styrene: To a mixture of $FeCl_2$ (12.6 mg, 0.1 mmol), 4Å molecular sieves (Alfa, 0.4-0.8mm beads, 100 mg) in a Schlenck tube was added diphenylmethane (1 mL, 6.0 mmol), distilled styrene (57 µl, 0.5 mmol) and di-*tert*-butyl peroxide (0.183 mL, 1.0 mmol). The septum-sealed tube was cooled dawn with aq. N_2 and then evacuated and refilled with N_2 three times. The resulting mixture was heated at 80 ^{o}C in an oil bath for 24h. After that the reaction mixture was cooled down to room temperature and then directly purified by flash column chromatography on silica gel. Use petroleum ether to remove most of the diphenylmethane and collect the rest fraction and then evacuate the eluent to get a residue. The desired product (E)-prop-2-ene-1,1,3-triyltribenzene can be confirmed from the crude ^{1}H-NMR of the residue after comparing with the data reported by DeShong, P et al.[3]. ^{1}H NMR ($CDCl_3$, 300MHz) δ 6.67 (dd, 1H, J = 15.8, 7.4), 6.35 (d, 1H, J = 16.2), 4.90 (d, 1H, J = 7.2) ppm. (Please refer to ^{1}H NMR data at page S 15).

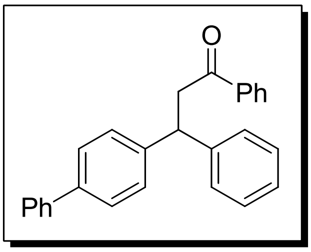
General procedure for 3: Diphenylmethane (0.67 mL, 4.0 mmol) and 1-phenylvinyl acetate (81.1 mg, 0.5 mmol) were added successively to a 25 mL Schlenk tube containing $FeCl_2$ (12.6 mg, 0.1 mmol). The septum-sealed tube was evacuated at room temperature and refilled with N_2 three times. Then di-*tert*-butyl peroxide (0.110 mL, 0.6 mmol) was added in under N_2. The resulting mixture was heated at 100 ^{o}C in an oil bath for 24 h. The reaction mixture was cooled down to room temperature and directly purified by flash column chromatography on silica gel (eluent: first petroleum ether then ethyl acetate/petroleum ether = 1/30) and the fraction with an R_f = 0.4 (ethyl acetate/petroleum ether = 1/30) was collected and concentrated to gave the titled product **3aa**.

Procedure for 3aa with the slow addition of DTBP: Diphenylmethane **1a** (0.67 mL, 4.0 mmol), 1-phenylvinyl acetate **2a** (81.1 mg, 0.5 mmol), and di-*tert*-butyl peroxide (0.010 mL, 0.05 mmol) were added successively to a 25 mL Schlenk tube containing $FeCl_2$ (6.3 mg, 0.05 mmol). The septum-sealed tube was evacuated at room temperature and refilled with N_2 three times. The mixture was heated at 100 □ in an oil bath for half an hour. Under N_2, the remaining di-*tert*-butyl peroxide (0.10 mL, 0.55 mmol) was added in 10 h (0.010 mL was added per hour). The reaction mixture was heated at 100 □ totally for 24 h and then cooled down to room temperature. The product was purified directly by flash column chromatography on silica gel (eluent: first petroleum ether then dichloromethane/petroleum ether = 1/4) to give the titled product 3**aa** 100 mg. Yield 70%.



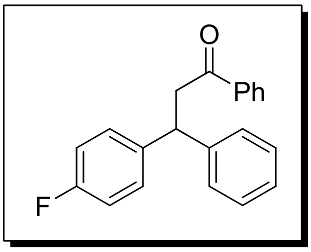
1,3,3-triphenylpropan-1-one (3aa)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.93-7.90 (m, 2H), 7.55-7.49 (m, 1H), 7.44-7.39 (m, 2H), 7.25-7.21 (m, 8H), 7.20-7.14 (m, 2H), 4.83 (t, 1H, *J* = 7.2), 3.73 (d, 2H, *J* = 7.2) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 197.9, 144.1, 137.0, 130.0, 128.5, 128.0, 127.8, 126.3, 45.8, 44.6 ppm; IR ν 2960, 2925, 2853, 1684, 1259, 1023, 865 cm^{-1}; MS (EI): (m/z) (%): 286 (29) [M$^+$], 105 (100).



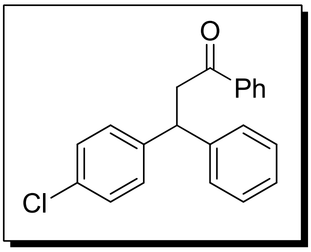
3-(biphenyl-4-yl)-1,3-diphenylpropan-1-one (3ba)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.95-7.93 (m, 2H), 7.55-7.24 (m, 16H), 7.22-7.14 (m, 1H), 4.87 (t, 1H, *J* = 7.5), 3.76 (d, 2H, *J* = 7.5) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 197.9, 144.0, 143.2, 140.8, 139.2, 137.0, 133.1, 128.6, 128.2, 128.0, 127.8, 127.2, 127.0, 126.9, 126.4, 45.6, 44.7 ppm; IR ν 2961, 2924, 1684, 1259, 1089, 1019, 800 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{27}H_{22}NaO$ 385.15629, Found: 385.15646.



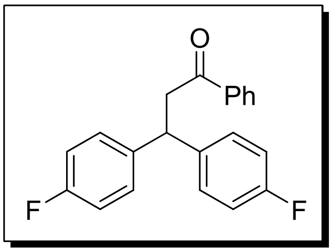
3-(4-fluorophenyl)-1,3-diphenylpropan-1-one (3ca)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.92-7.89 (m, 2H), 7.53-7.48 (m, 1H), 7.42-3.37 (m, 2H), 7.28-7.13 (m, 7H), 6.95-6.89 (m, 1H), 4.80 (t, 1H, *J* = 7.5), 3.68 (d, 2H, *J* = 7.2) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 197.7, 162.9, 159.7, 143.9, 139.8, 139.7, 136.8, 133.1, 129.2, 129.1, 128.5, 127.9, 127.6, 126.4, 115.3, 115.1, 45.1, 44.6 ppm; IR ν 2926, 2856, 1738, 1671, 1301, 1239,842 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{21}H_{17}FNaO$ 327.11556, Found: 327.11606.



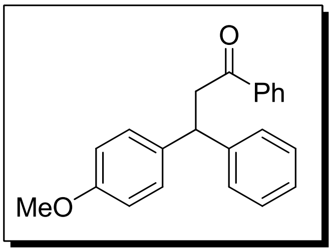
3-(4-chlorophenyl)-1,3-diphenylpropan-1-one (3da)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.90 (d, 2H, *J* = 7.8), 7.52-7.48 (m, 1H), 7.42-7.36 (m, 2H), 7.28-7.15 (m, 9H), 4.79 (t, 1H, *J* = 7.5), 3.68 (d, 2H, *J* = 7.2) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 197.5, 143.6, 142.5, 136.7, 133.1, 132.0, 139.1, 128.6, 128.5, 127.9, 127.6, 126.5, 45.1, 44.4 ppm; IR ν 2955, 2922, 2854, 1686, 1448, 1091, 985 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{21}H_{17}ClNaO$ 343.08601 Found: 343.08676.



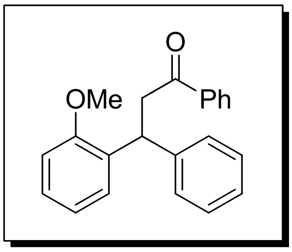
3,3-bis(4-fluorophenyl)-1-phenylpropan-1-one (3ea)

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.93-7.89 (m, 2H), 7.56-7.38 (m, 3H), 7.22-7.08 (m, 4H), 6.96-6.89 (m, 4H), 4.79 (t, 1H, *J* = 7.2), 3.66 (d, 2H, *J* = 7.2) ppm. ^{13}C NMR ($CDCl_3$, 50MHz) 197.5, 163.8, 158.9, 139.7, 139.6, 136.8, 133.2, 129.2, 129.0, 128.6, 127.9, 115.5, 115.1, 44.7, 44.3 ppm; IR ν 2955, 2923, 2853, 1684, 1507, 1458, 1377, 1225, 834 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{21}H_{16}F_2NaO$ 345.10614 Found: 345.10616.



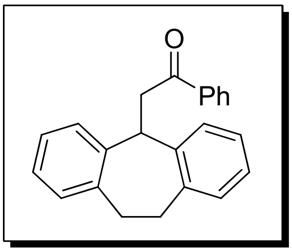
3-(4-methoxyphenyl)-1,3-diphenylpropan-1-one (3fa)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.99-7.96 (m, 2H), 7.60-7.55 (m, 1H), 7.49-7.44 (m, 2H), 7.31-7.29 (m, 4H), 7.26-7.19 (m, 3H), 6.87-6.84 (m, 2H), 4.83 (t, 1H, *J* = 7.5), 3.78 (s, 3H), 3.75 (d, 2H, *J* = 7.2) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 198.0, 157.9, 144.5, 137.0, 136.2, 133.0, 128.7, 128.5, 128.0, 127.8, 126.2, 113.8, 55.1, 45.1, 44.7 ppm; IR ν 2923, 2853, 1674, 1597, 1448, 1248, 1212, 873 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{22}H_{20}NaO_2$ 339.13555, Found: 339.13702.



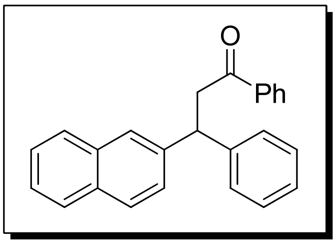
3-(2-methoxyphenyl)-1,3-diphenylpropan-1-one (3ga)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.96-7.92 (m, 2H), 7.55-6.64 (m, 12H), 5.18 (t, 1H, *J* = 7.2), 3.76-3.69 (m, 5H) ppm. IR ν 2959, 2920, 2850, 1684, 1492, 1243, 1028, 847 cm^{-1}



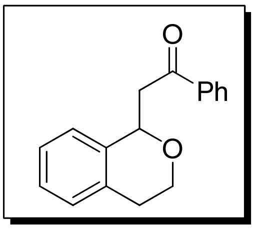
2-(10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-yl)-1-phenyl-ethane-1-one (3ha)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.87-7.84 (m, 2H), 7.49-7.42 (m, 1H), 7.40-7.33 (m, 2H), 7.09-7.04 (m, 6H), 5.02 (t, 1H, *J* = 6.6), 3.74 (d, 2H, *J* = 6.6) 3.42-3.30 (m, 2H), 3.14-3.04 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 197.8, 141.1, 139.2, 137.0, 132.9, 130.2, 129.3, 128.4, 127.9, 126.7, 126.1, 46.4, 33.2 ppm; IR ν 3059, 1736, 1685, 1596, 1492, 1447, 1245, 1202, 980, 750 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{23}H_{20}NaO$ 335.14064, Found: 335.14078.



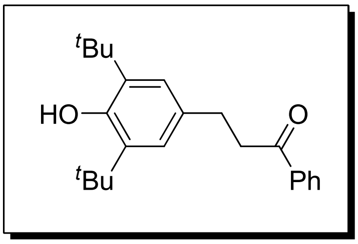
3-(naphthalen-2-yl)-1,3-diphenylpropan-1-one (3ia)

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.96-7.92 (m, 3H), 7.77-7.71 (m, 4H), 7.56-7.16 (m,13H), 4.99(t, 1H, J = 7.2), 3.83 (d, 2H, J = 6.8) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) 197.9, 143.9, 143.3, 141.5, 137.0, 133.4, 133.0, 131.9, 128.6, 128.2, 128.0, 127.9, 127.7, 127.5, 126.7, 126.4, 125.9, 125.7, 125.5, 45.9, 44.5 ppm; IR ν 2955, 2924, 1684, 1596, 1447, 1260, 1030, 800 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{25}H_{20}NaO$ 359.14064, Found: 359.14074.



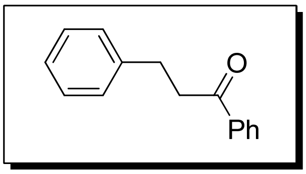
2-(isochroman-1-yl)-1-phenylethanone (3ja)

^{1}H NMR ($CDCl_3$, 200MHz) δ 7.99-7.96 (m, 2H), 7.55-7.37 (m, 4H), 7.23-7.05 (m, 5H), 5.50-5.45 (m, 1H), 4.11-4.01 (m,1H), 3.81-3.70 (m,1H), 3.69-3.51 (m,1H), 3.32-3.22 (m,1H), 3.05-2.90 (m,1H), 2.71-2.61 (m,1H) ppm; ^{13}C NMR ($CDCl_3$, 50MHz) 197.9, 137.4, 137.0, 133.8, 132.9, 128.8, 128.3, 128.1, 126.4, 126.1, 124.3, 72.5, 63.2, 45.2, 28.7 ppm; IR ν 2928, 2853, 1685, 1579, 1280, 1202, 1105, 774 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{17}H_{17}O_2$ 253.12231, Found: 253.12214.



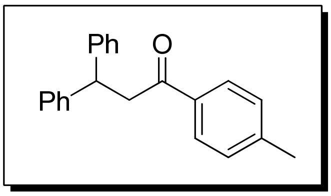
3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylpropan-1-one(3ka)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.82-7.79 (m, 2H), 7.37-7.23 (m, 3H), 6.92 (broad peak, 2H), 4.98 (broad peak, 1H), 3.14 (t, 2H, J = 7.2), 2.87 (t, 2H, J = 7.2), 1.30 (broad peak, 19H) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 199.6, 151.9, 136.9, 135.9, 132.8, 131.6, 128.4, 127.9, 124.8, 41.0, 34.2, 30.2 ppm; IR ν 2957, 1684, 1434, 1232, 1159, 977 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{23}H_{30}NaO_2$ 361.21380, Found: 361.21387.



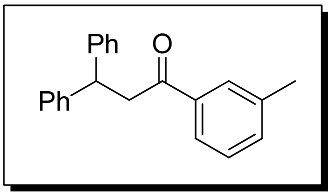
1,3-diphenylpropan-1-one(3la)

^{1}H NMR (CDCl$_3$, 200MHz) δ 7.98-7.94 (m, 2H), 7.59-7.34 (m, 3H), 7.30-7.20 (m, 5H), 3.31 (t, 2H, J = 7.2), 3.06 (t, 2H, J = 7.0), ppm; ^{13}C NMR (CDCl$_3$, 50MHz) 199.2, 141.2, 136.8, 133.0, 128.5, 128.4, 128.3, 128.0, 126.1, 40.4, 30.1 ppm; IR ν 2954, 2926, 1770, 1684, 1448, 1245, 974 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{15}H_{15}O$ 211.11174, Found: 211.11203.



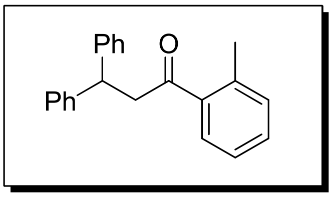
3,3-diphenyl-1-p-tolylpropan-1-one (3ab)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.80 (d, 2H, J = 8.1), 7.23-7.09 (m, 12H), 4.81 (t, 1H, J = 7.2), 3.66 (d, 2H, J = 7.5), 2.32 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$, 75MHz) 197.3, 144.1, 134.6, 134.4, 129.1, 128.4, 128.0, 127.7, 126.1, 45.8, 44.4, 21.4 ppm; IR ν 2920, 2852, 1684, 1607, 1261, 1180, 1030, 977 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{22}H_{21}O$ 301.15869, Found: 301.15919.



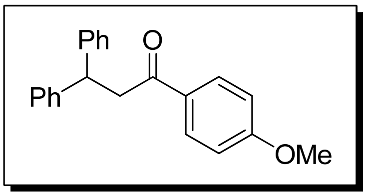
3,3-diphenyl-1-m-tolylpropan-1-one (3ac)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.71-7.69 (m, 2H), 7.31-7.10 (m, 12H), 4.82 (t, 1H, *J* = 7.5), 3.69 (d, 2H, *J* = 7.5), 2.33 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 197.7, 144.1, 138.2, 137.0, 133.7, 128.5, 128.4, 128.3, 127.7, 126.2, 125.1, 45.8, 44.6, 21.2 ppm. IR ν 3026, 2921, 1682, 1493, 1450, 1275, 1260, 1156 908 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{22}H_{21}O$ 301.15869, Found: 301.15867.



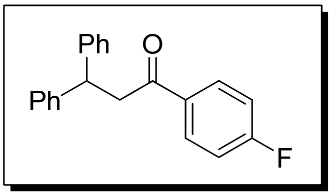
3,3-diphenyl-1-o-tolylpropan-1-one (3ad)

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.54-7.51(m, 1H), 7.35-7.15 (m, 13H), 4.74 (t, 1H, *J* = 7.8), 3.63 (d, 2H, *J* = 7.8), 2.21 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) 202.5, 143.8, 138.4, 137.9, 131.7, 131.0, 128.5, 127.8, 126.4, 125.5, 47.8, 46.5, 20.6 ppm. IR ν 2926, 1738, 1679, 1494, 1241, 1034, 940, 908 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{22}H_{21}O$ 301.15869, Found: 301.15878.



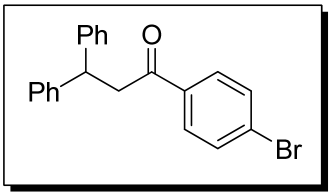
1-(4-methoxyphenyl)-3,3-diphenylpropan-1-one (3ae)

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.91 (d, 2H, *J* = 9.2), 7.26-7.14 (m, 10H), 6.89 (d, 2H, *J* = 8.8), 4.81 (t, 1H, *J* = 7.2), 3.82 (s, 3H), 3.67 (d, 2H, *J* = 7.2) ppm; ^{13}C NMR ($CDCl_3$, 100MHz) 196.5, 163.4, 144.2, 130.3, 130.1, 128.5, 127.8, 126.3, 113.7, 55.4, 46.0, 44.3 ppm. IR ν 2922, 2849, 1675, 1599, 1509, 1254, 1168, 983, 813 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{22}H_{21}O_2$ 317.15361, Found: 317.15383.



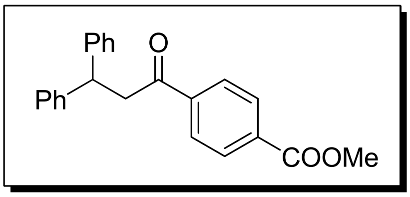
1-(4-fluorophenyl)-3,3-diphenylpropan-1-one (3af)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.95-7.90 (m, 2H), 7.28-7.23 (m, 7H), 7.23-7.14 (m, 2H), 7.09-7.04 (m, 2H), 4.80 (t, 1H, *J* = 7.2), 3.68 (d, 2H, *J* = 7.2); ^{13}C NMR (CDCl$_3$, 75MHz) 196.3, 167.3, 163.9, 143.9, 133.4, 133.5, 130.7, 130.5, 128.5, 127.7, 126.4, 115.7, 115.4, 45.9, 44.5 ppm. IR ν 2953, 2924, 2853, 1687, 1597, 1261, 1029, 985, 837 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{21}H_{18}FO$ 305.13362, Found: 305.13350.



1-(4-bromophenyl)-3,3-diphenylpropan-1-one (3ag)

^{1}H NMR (CDCl$_3$, 300MHz) δ 7.81-7.76 (m, 2H), 7.59-7.53 (m, 2H), 7.29-7.22 (m, 82H), 7.20-7.14 (m, 2H), 4.79 (t, 1H, *J* = 7.5), 3.67 (d, 2H, *J* = 7.5); ^{13}C NMR (CDCl$_3$, 75MHz) 197.0, 143.8, 135.7, 131.8, 129.5, 128.5, 128.2, 127.7, 126.4, 45.9, 44.6 ppm;. IR ν 2960, 2925, 1685, 1584, 1260, 1070, 982, 837 cm^{-1}; MS (EI) (m/z) (%): 365 (8) [M$^+$], 167 (100).



methyl 4-(3,3-diphenylpropanoyl)benzoate (3ah)

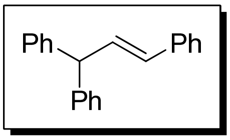
^{1}H NMR (CDCl$_3$, 200MHz) δ 7.93-7.8 (m, 2H), 7.35-7.10 (m, 9H), 6.92-6.86 (m, 9H), 4.82 (t, 1H, *J* = 7.2), 3.82 (s, 3H), 3.75 (d, 2H, *J* = 7.2) ppm. ^{13}C NMR (CDCl$_3$, 50MHz) 196.4, 163.4, 144.2, 130.2, 130.1, 128.4, 127.8, 126.2, 113.6, 55.3, 46.0, 44.2 ppm;. IR ν 2953, 2921, 2849, 1763, 1720, 1685, 1433, 1277, 1203, 1108, 1017, 859 cm^{-1}; HRMS (ESI): Anal. Calcd. for $C_{23}H_{20}NaO_3$ 367.13047, Found: 367.13064.

References:

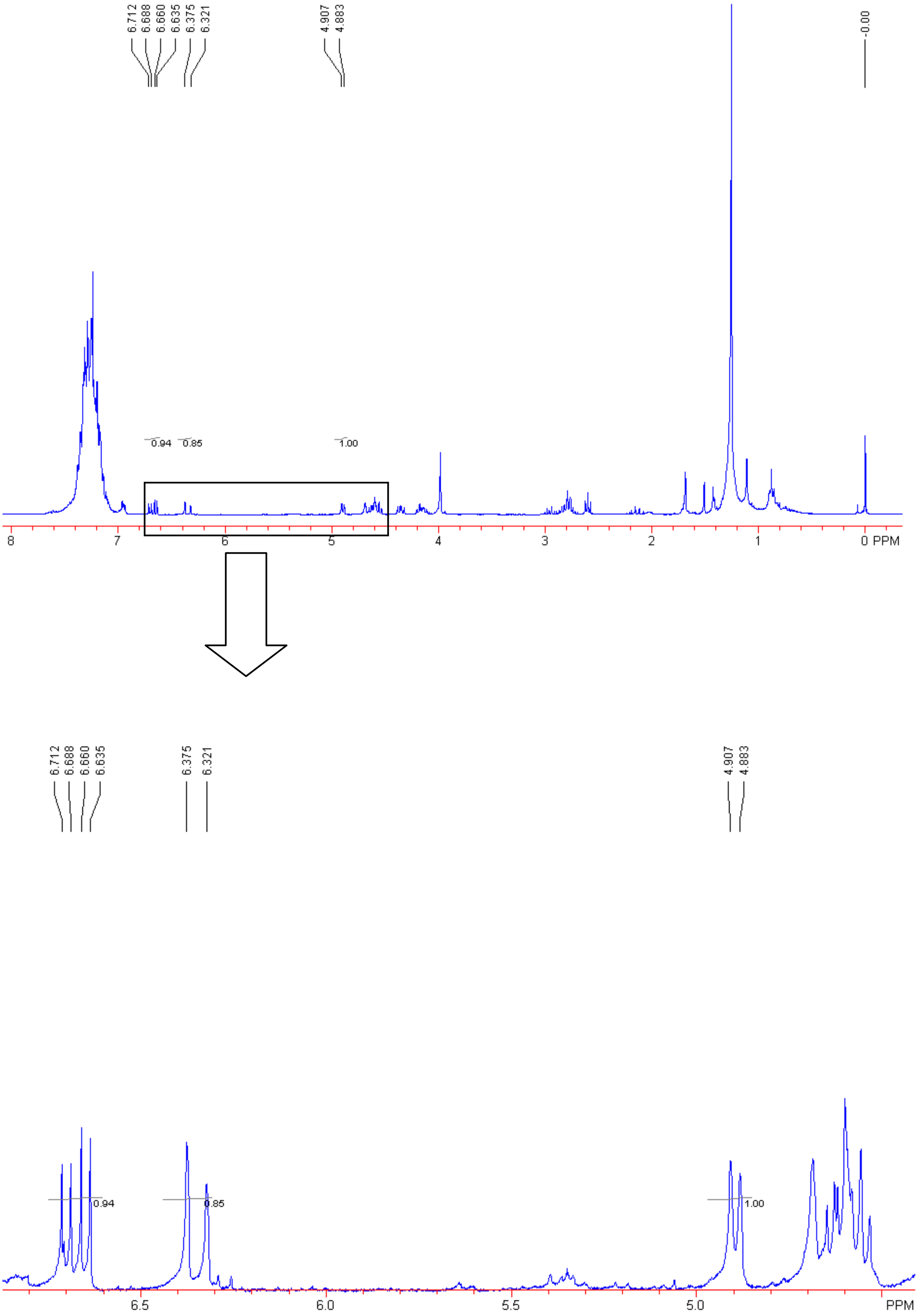
[1] J. A. Wilkinson, S. B. Rossington, S. Ducki, J. Leonard, N. Hussain, *Tetrahedron* **2006**, *62*, 1833.

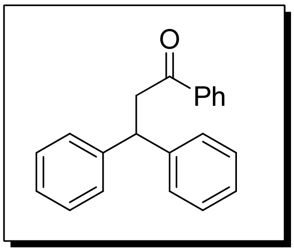
[2] A. Berkessel, M. L. Sebastian-Ibarz, T. N. Muller, *Angew. Chem. Int. Ed.* **2006**,

[3] R, Correia, P. DeShong, *J. Org. Chem.* **2001,** *66,* 7159.*45*, 6567.



3 crude ^{1}H NMR

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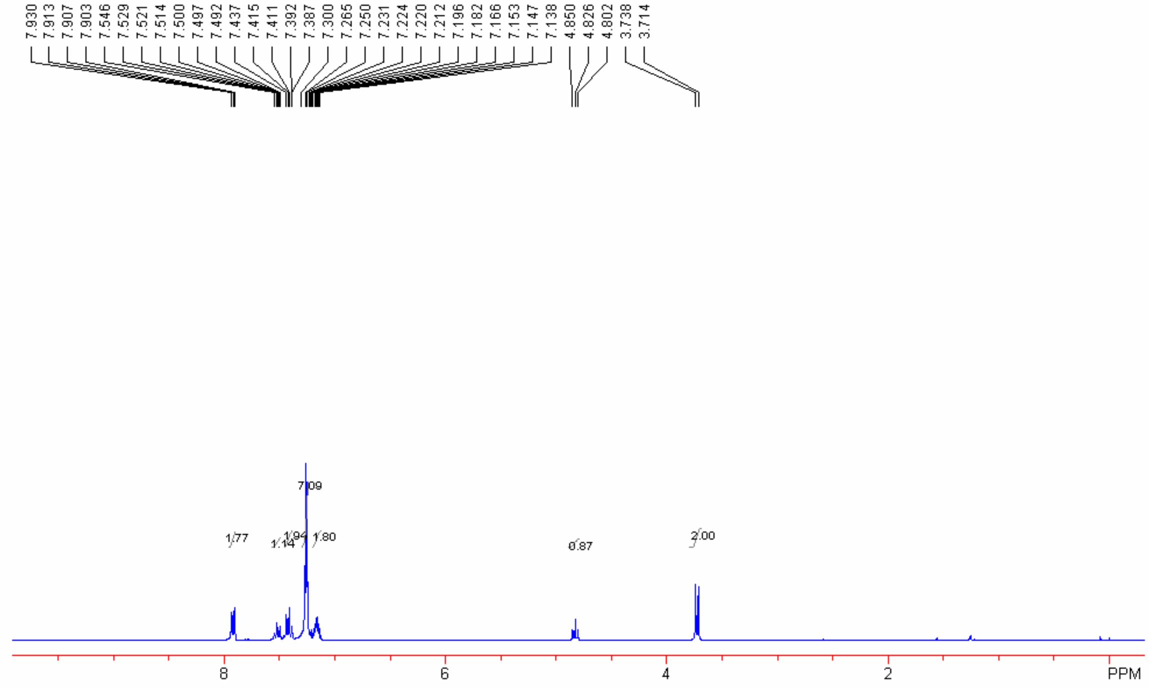
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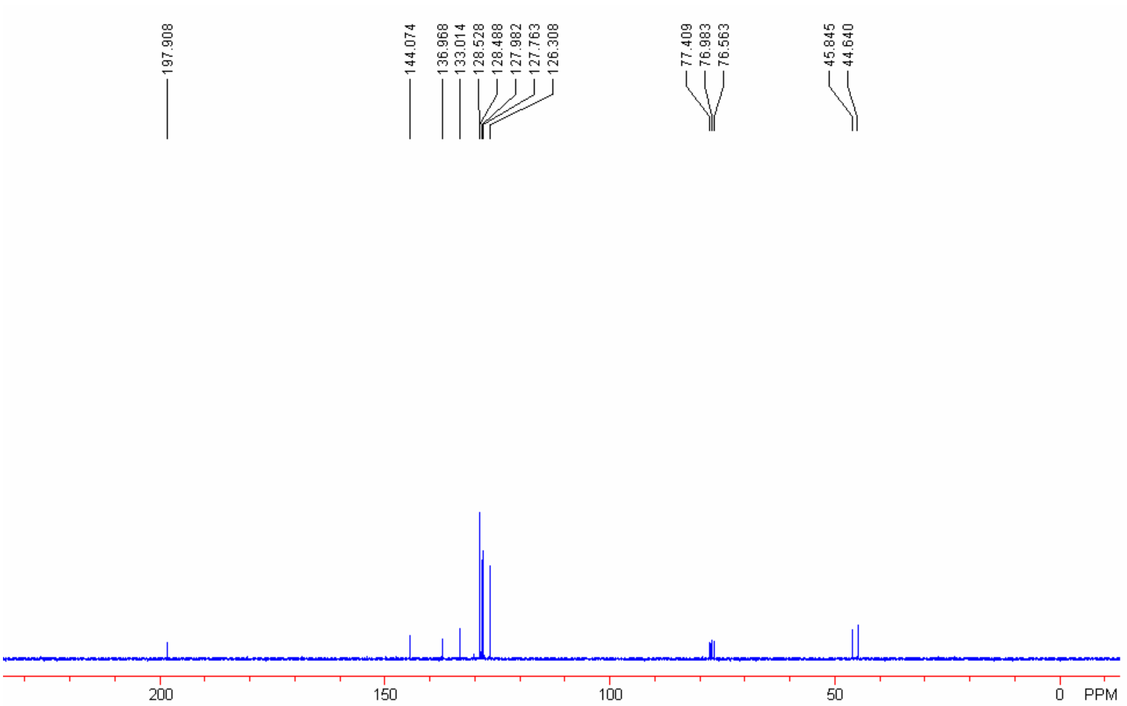
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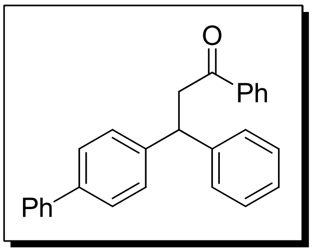
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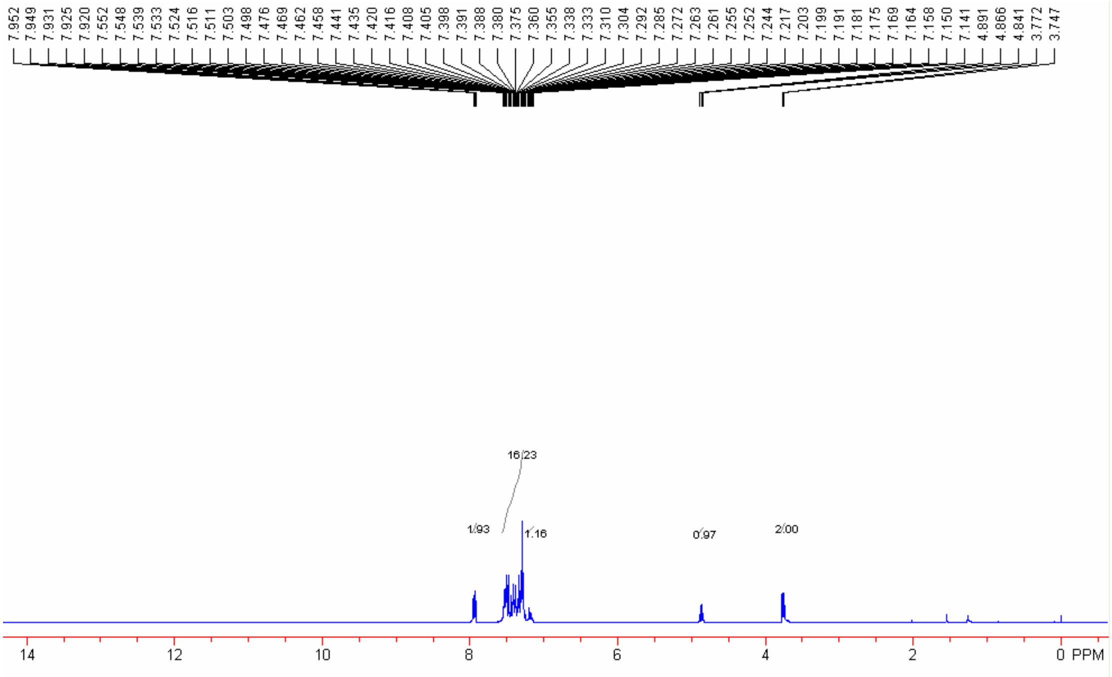
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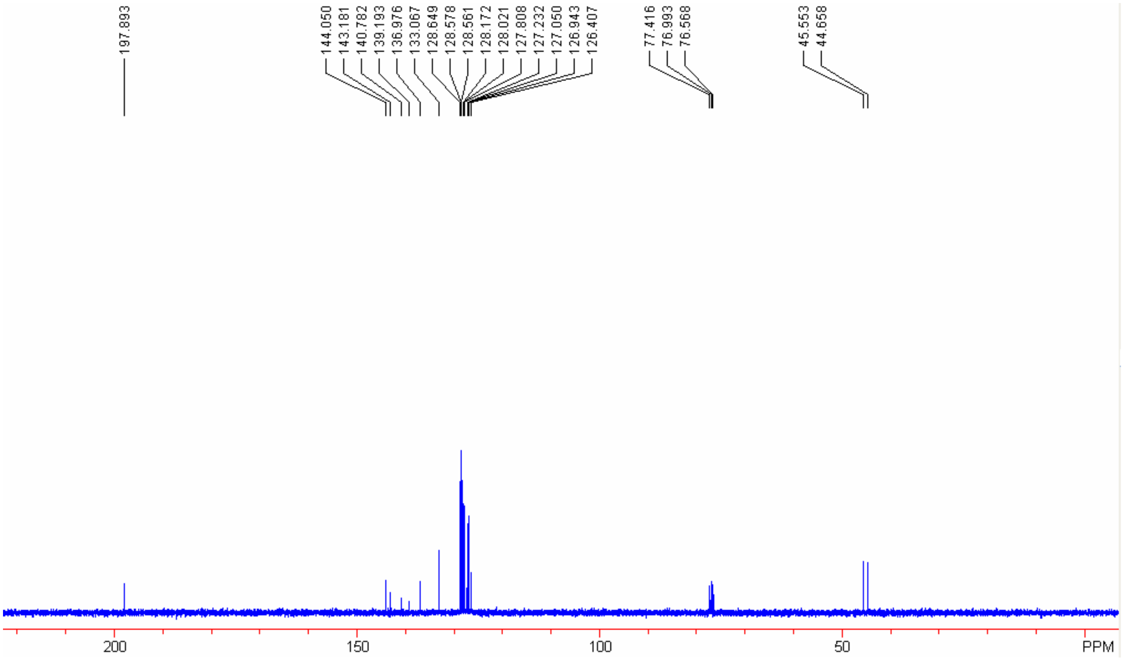
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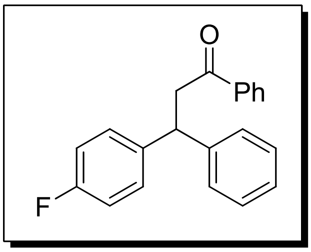
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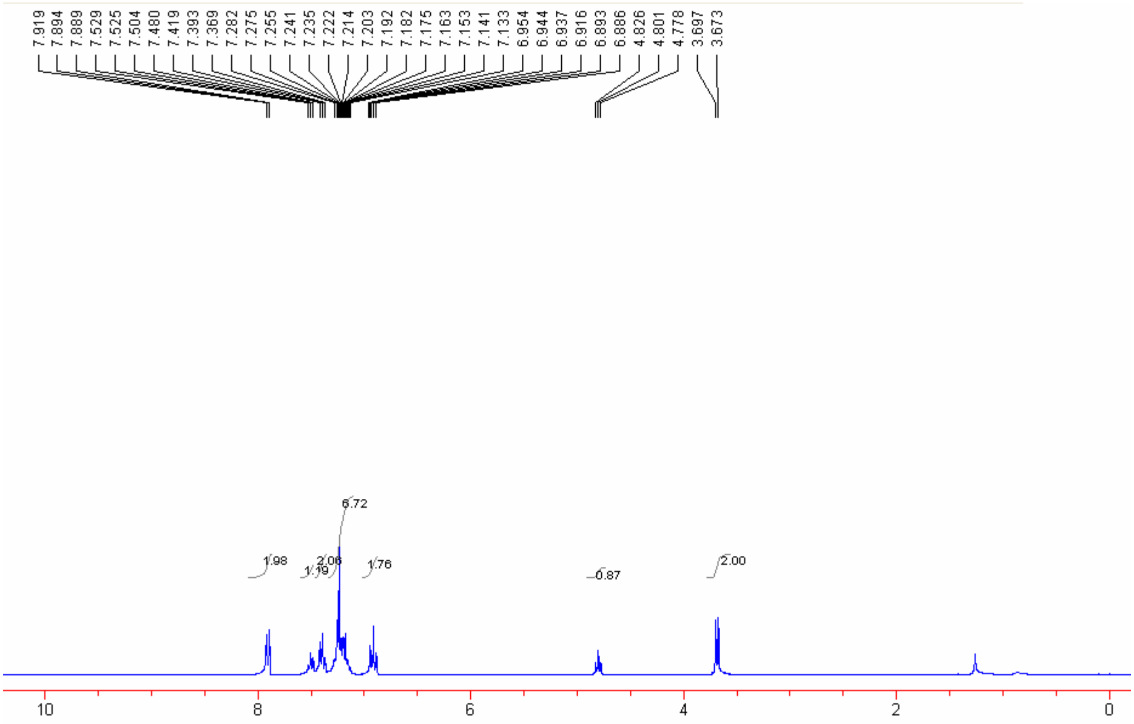
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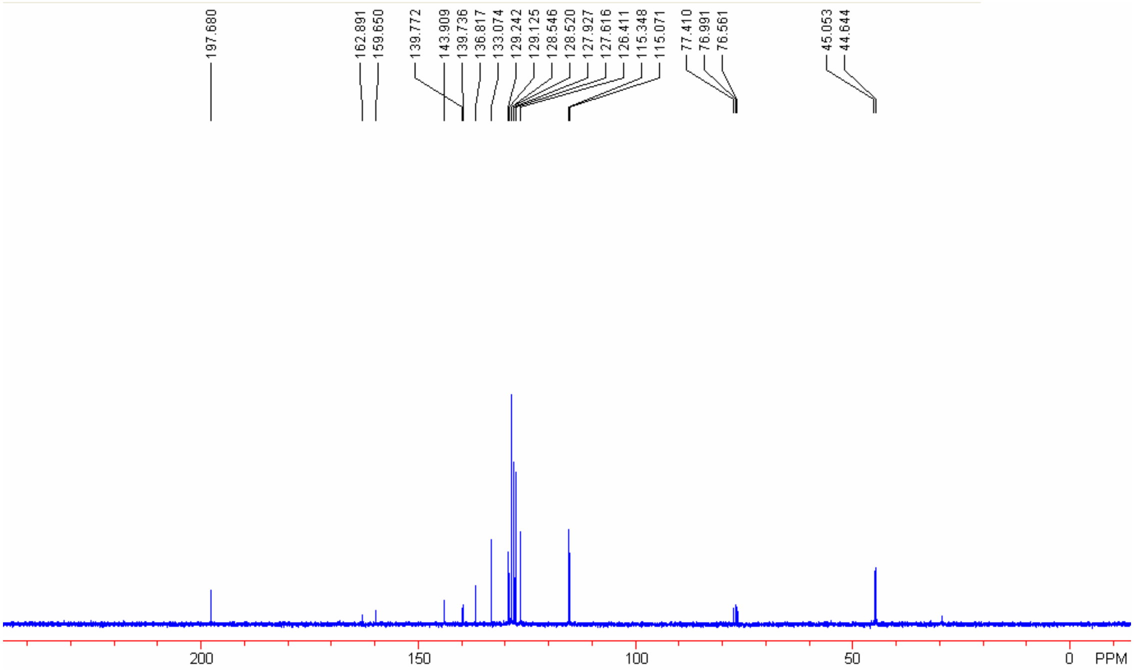
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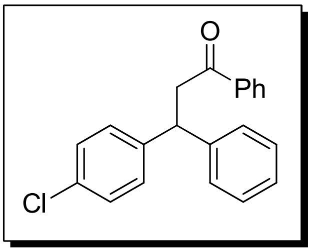
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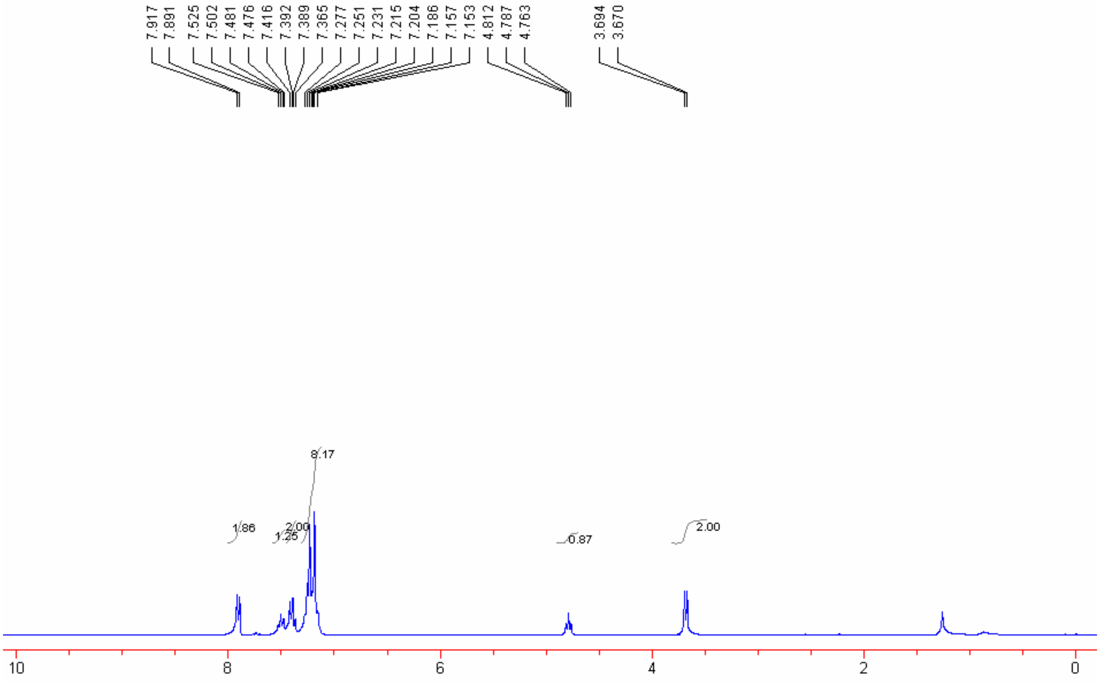
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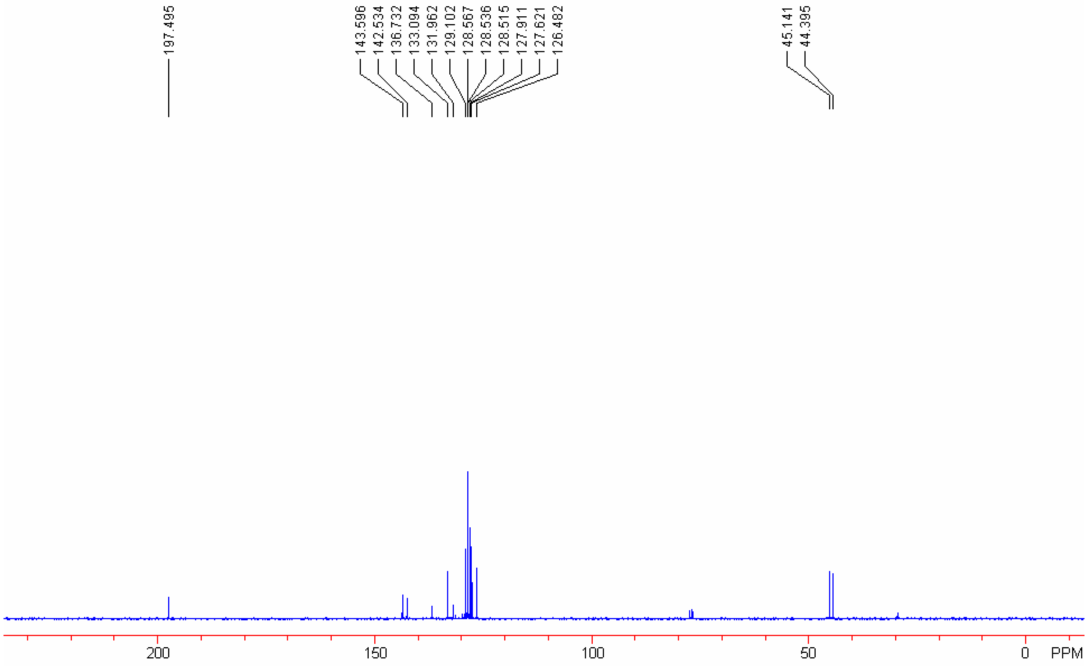
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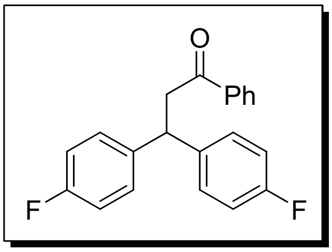
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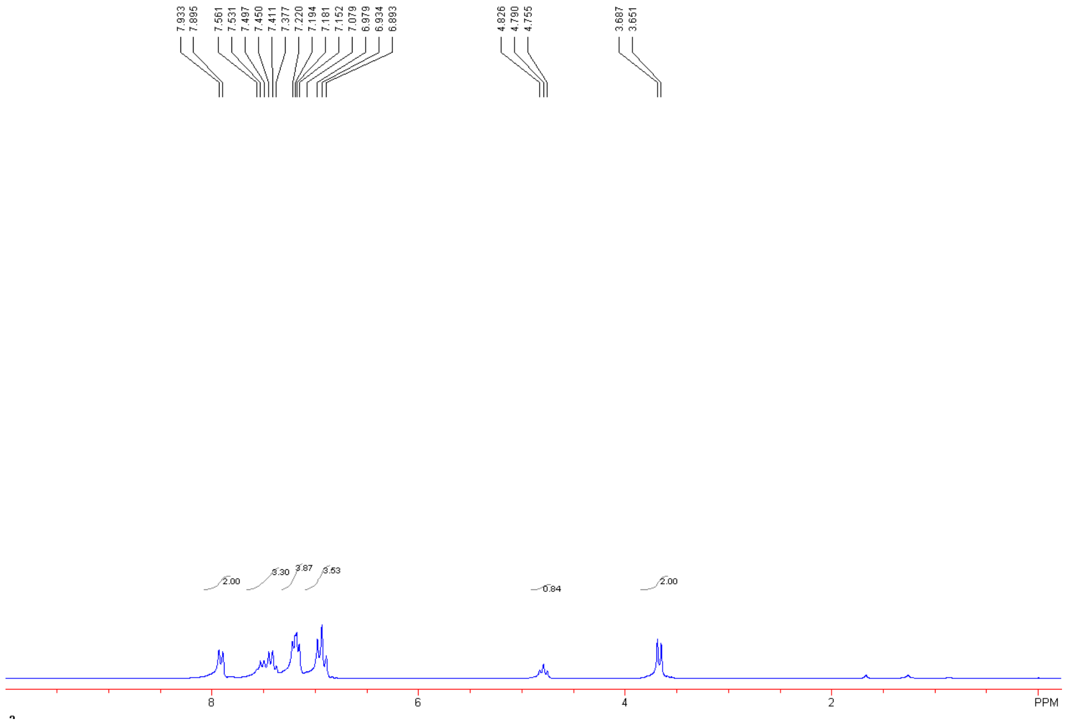
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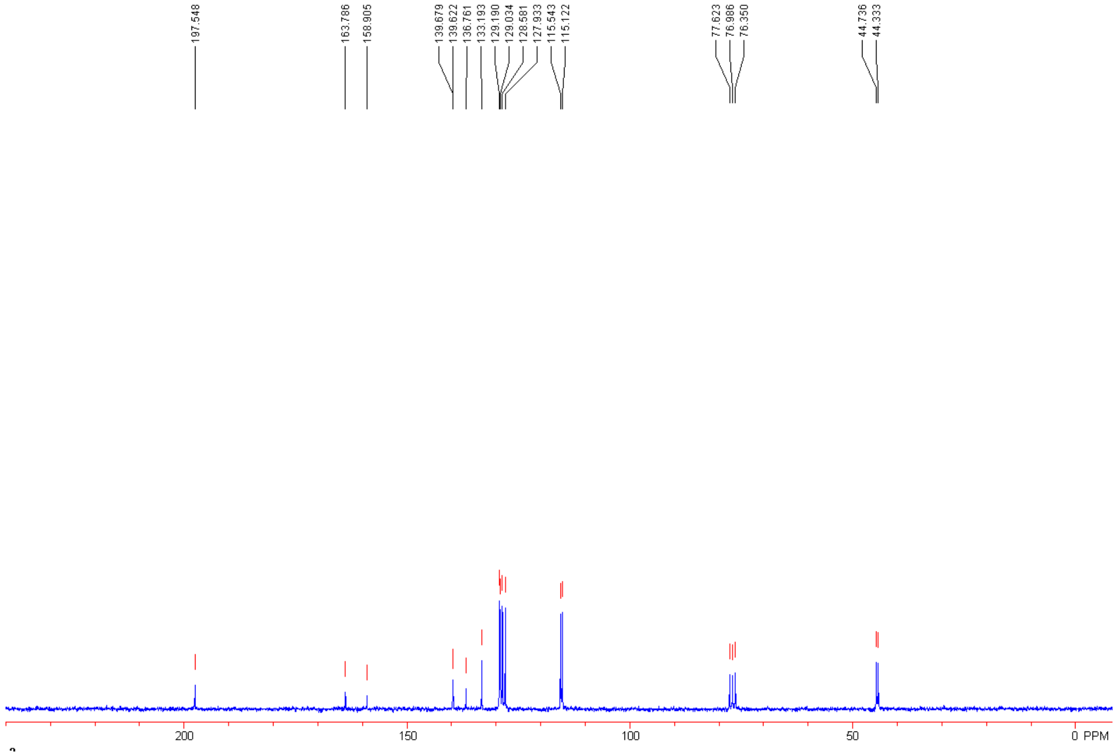
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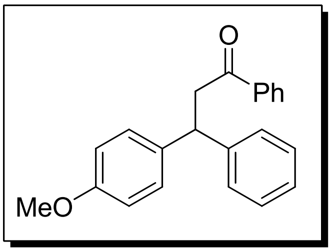
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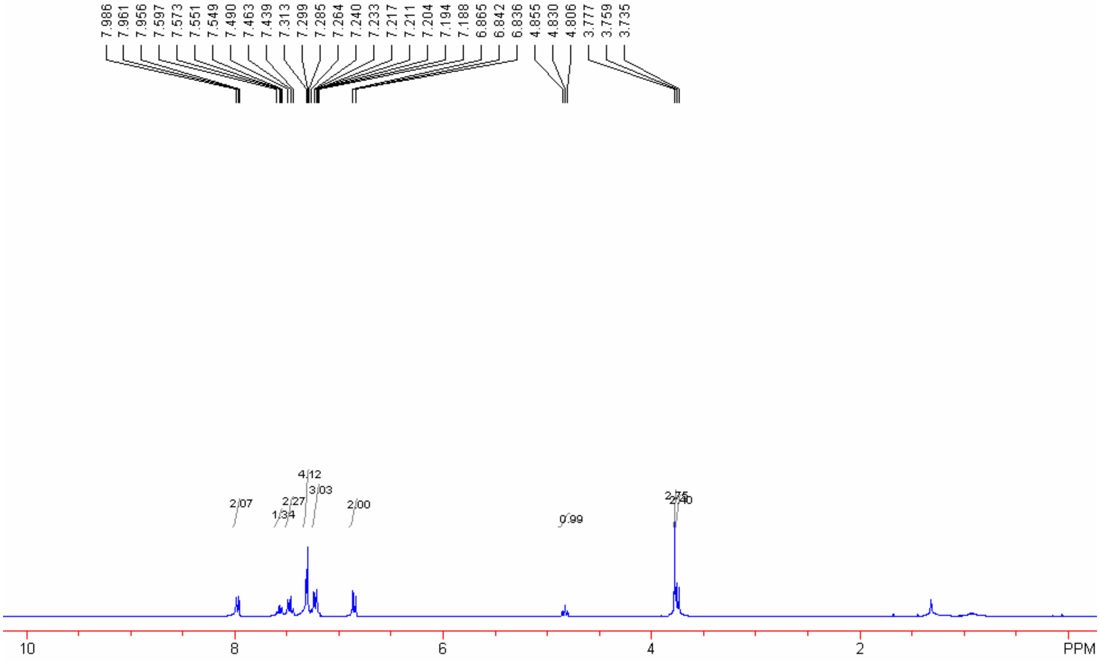
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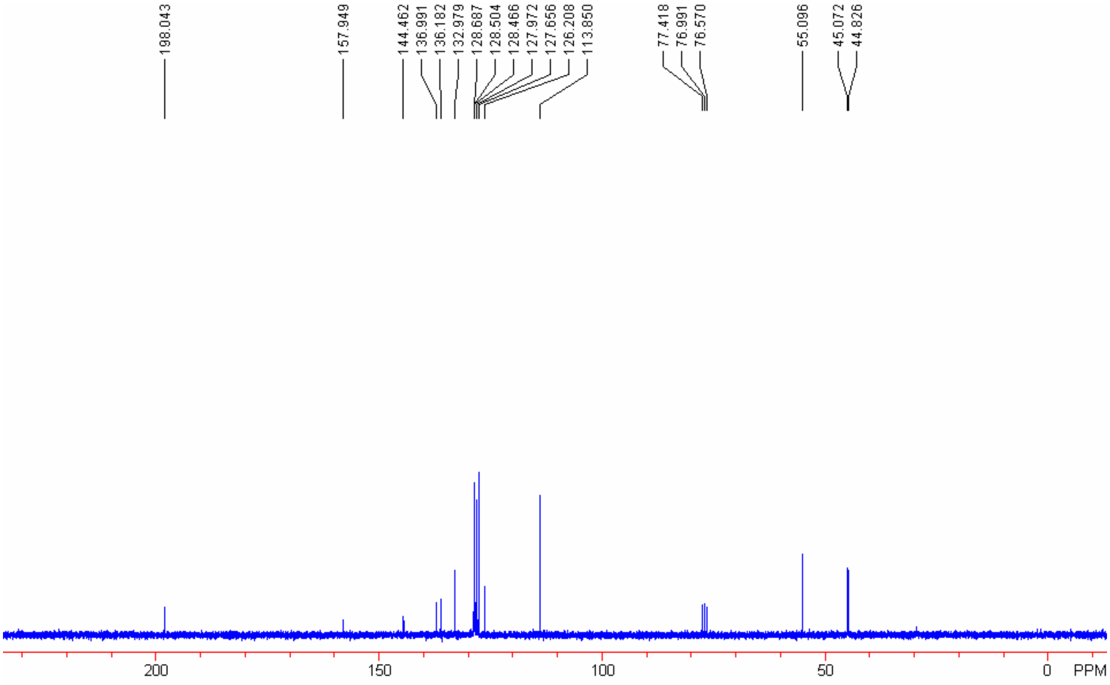
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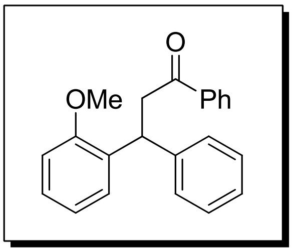
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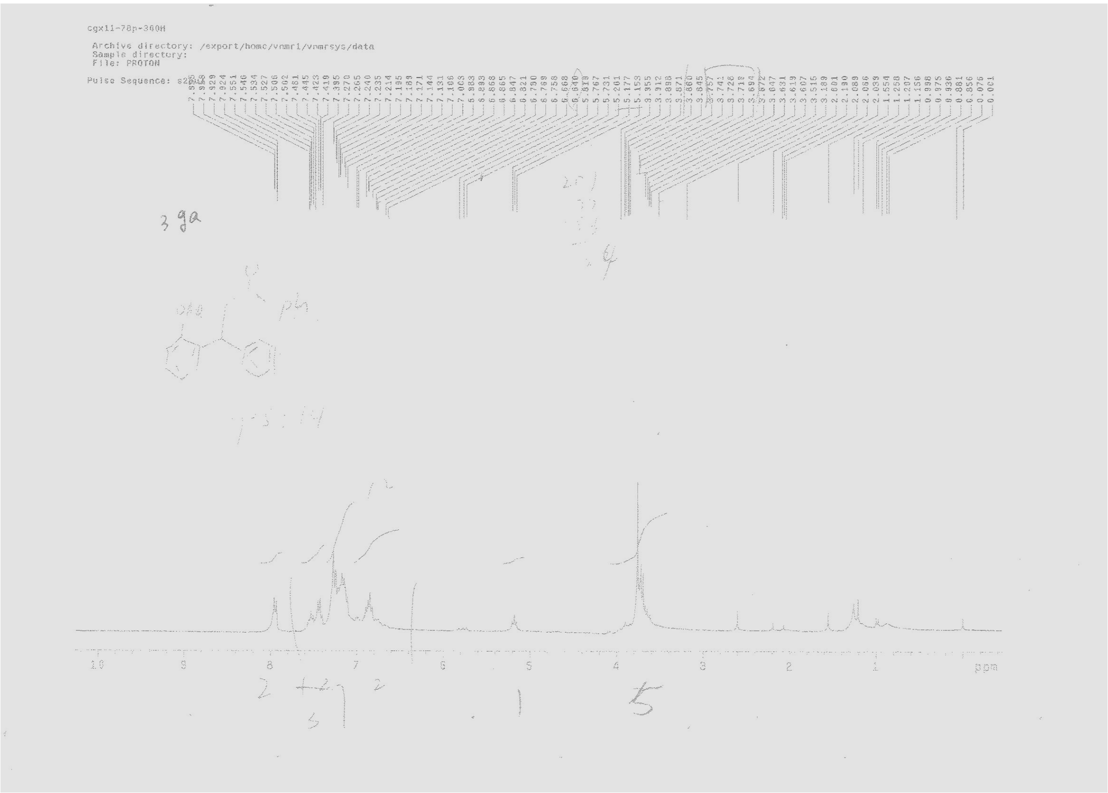
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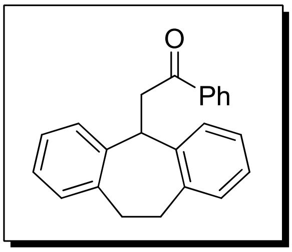
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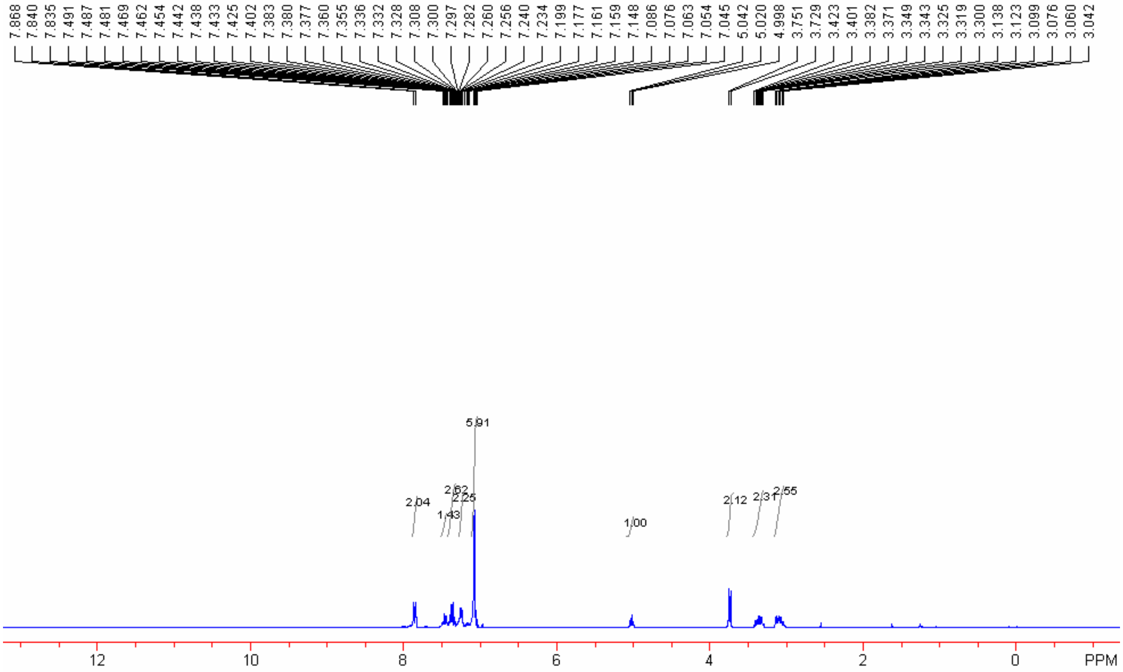
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7.045
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3.325
3.319
3.300
3.138
3.123
3.099
3.076
3.060
3.042
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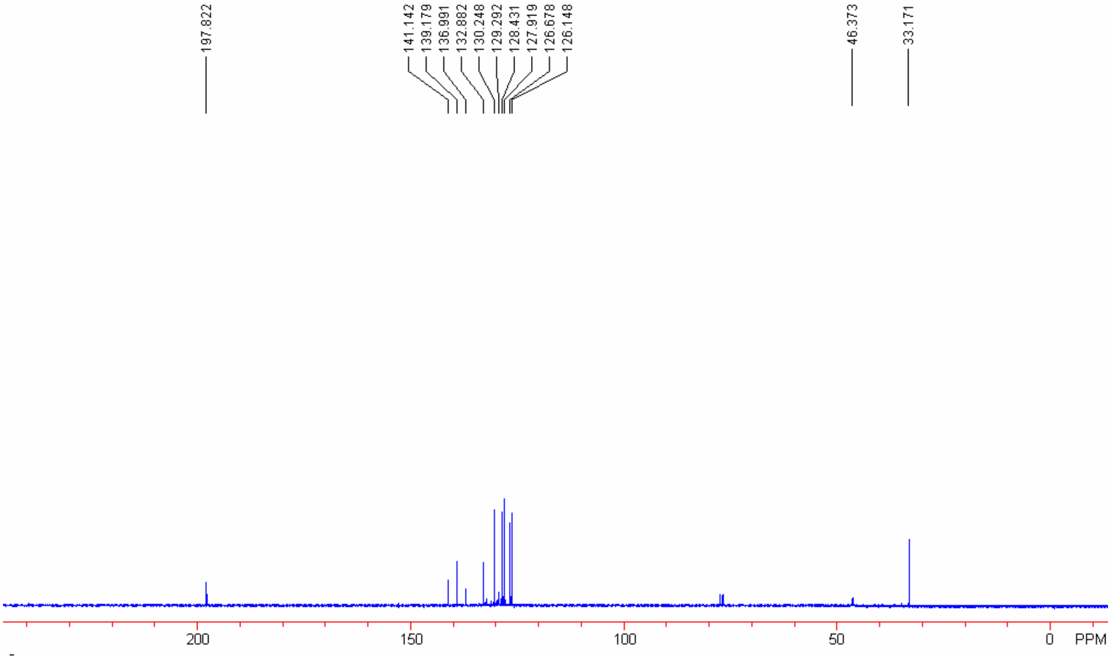
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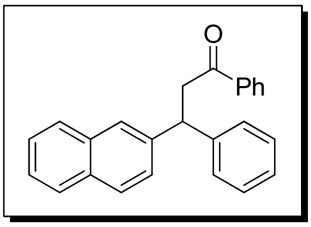
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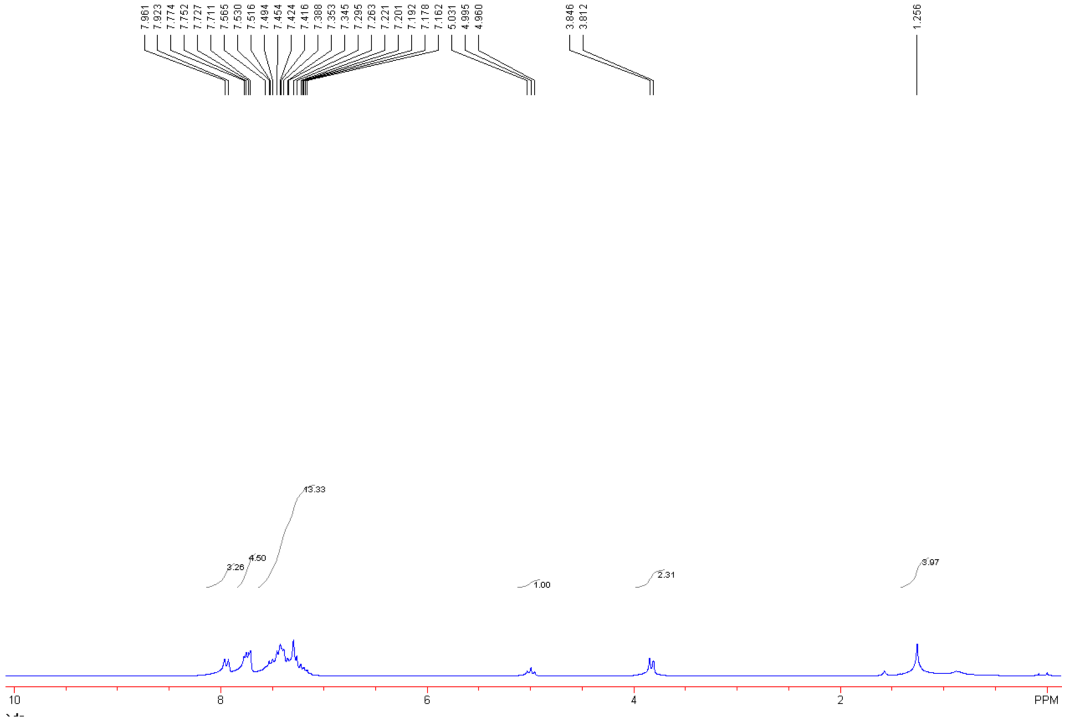
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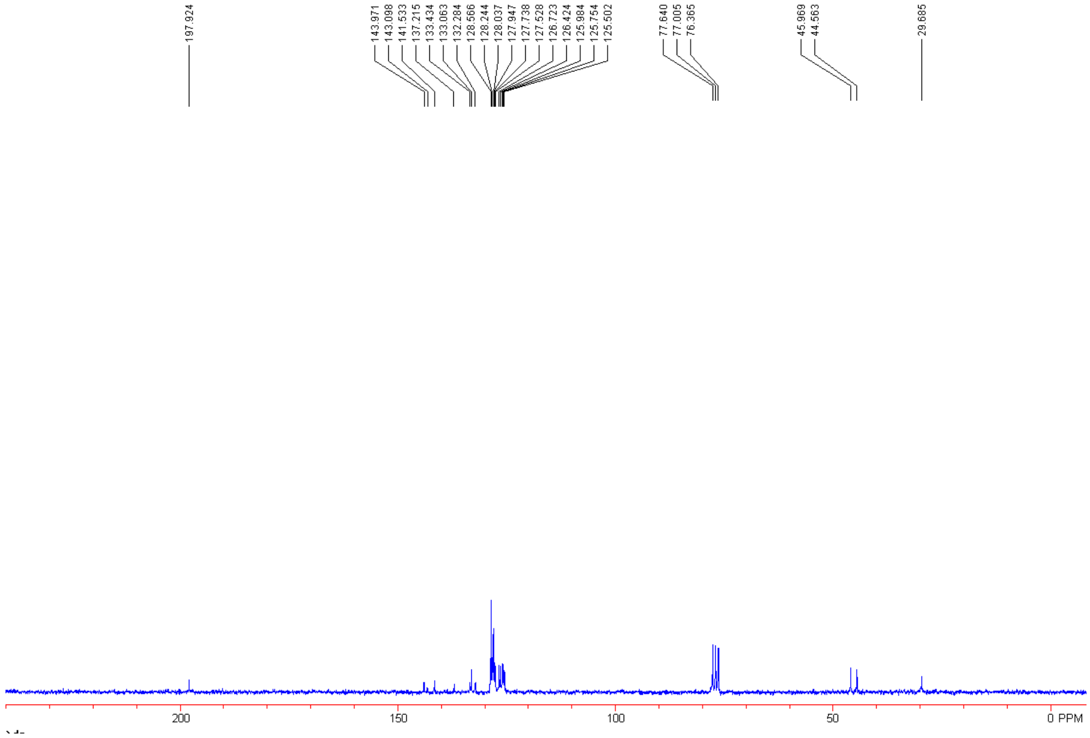
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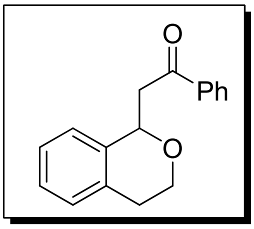
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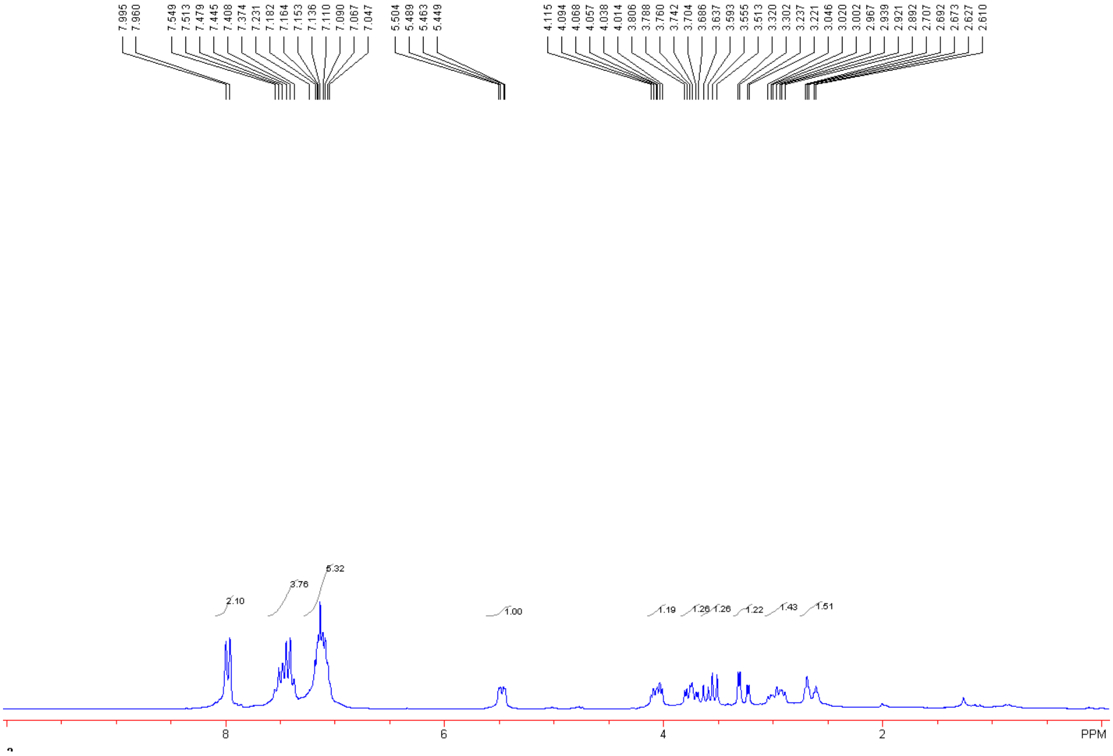
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7.067
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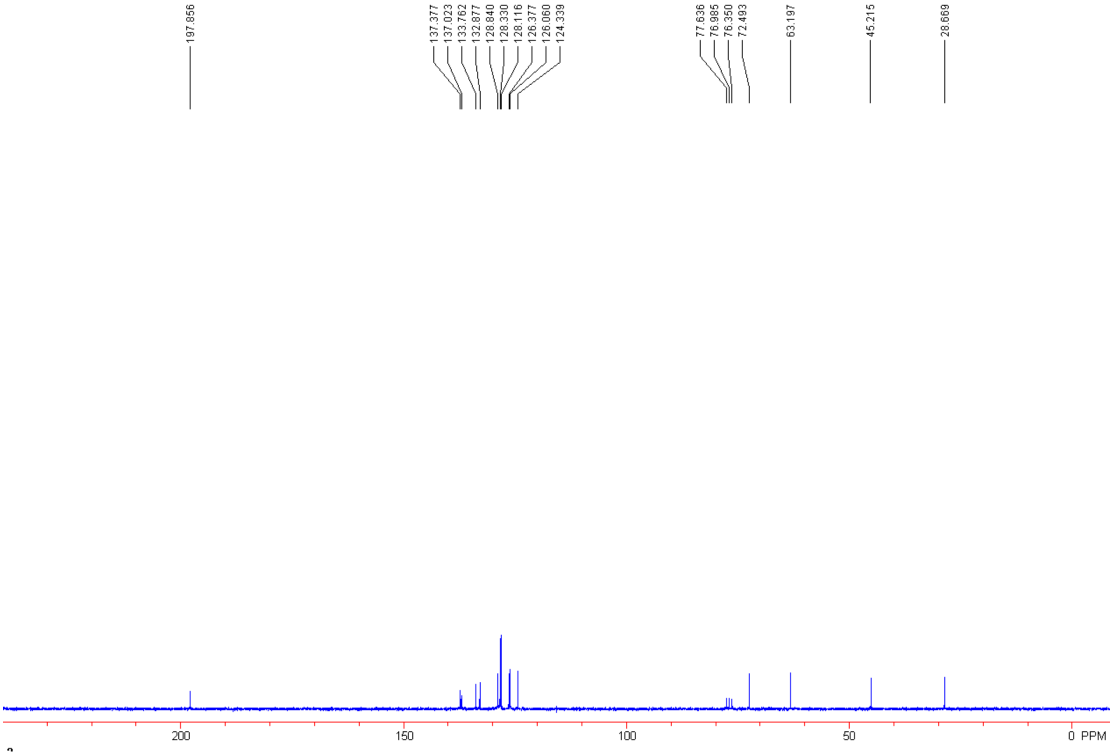
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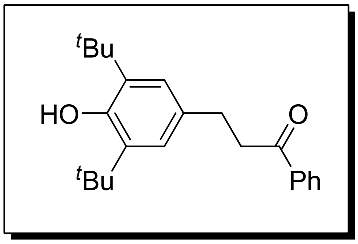
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HO
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tBu
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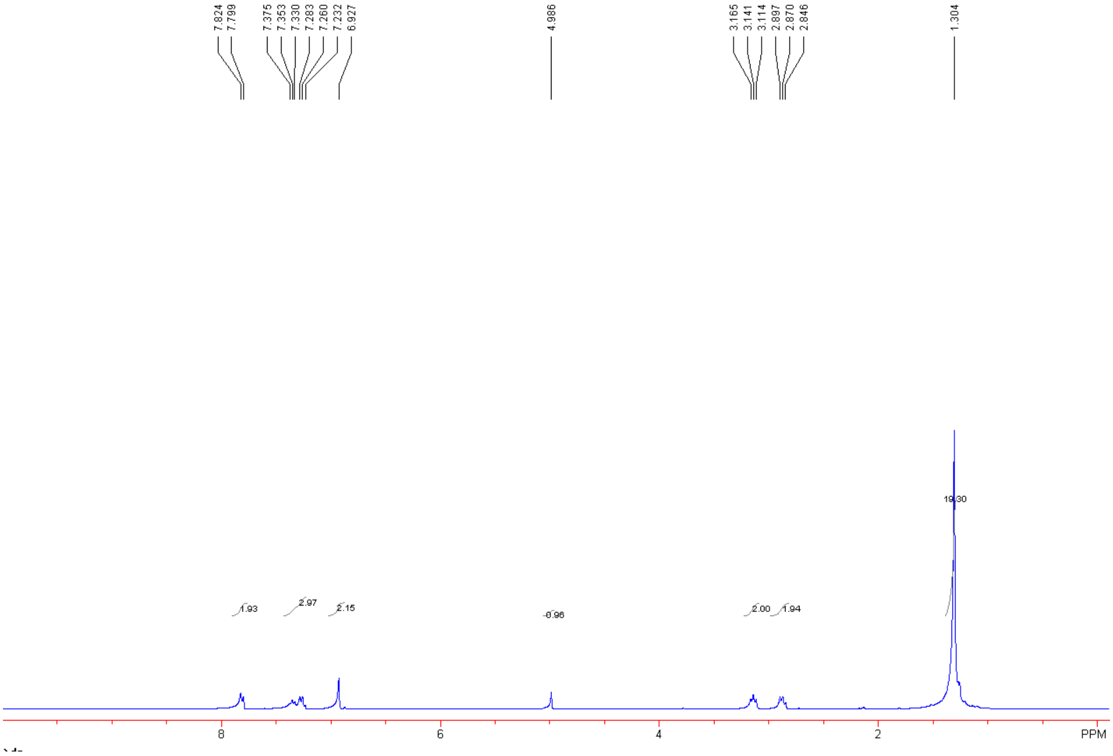
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7.232
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3.141
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2.870
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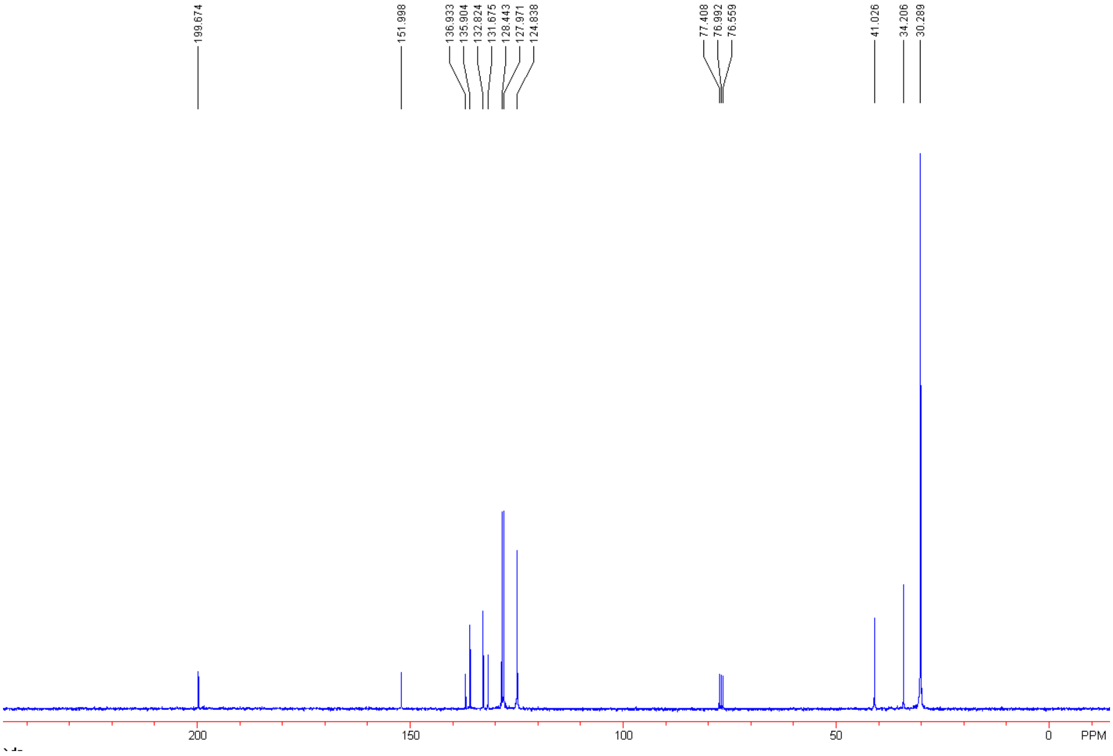
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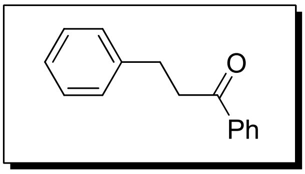
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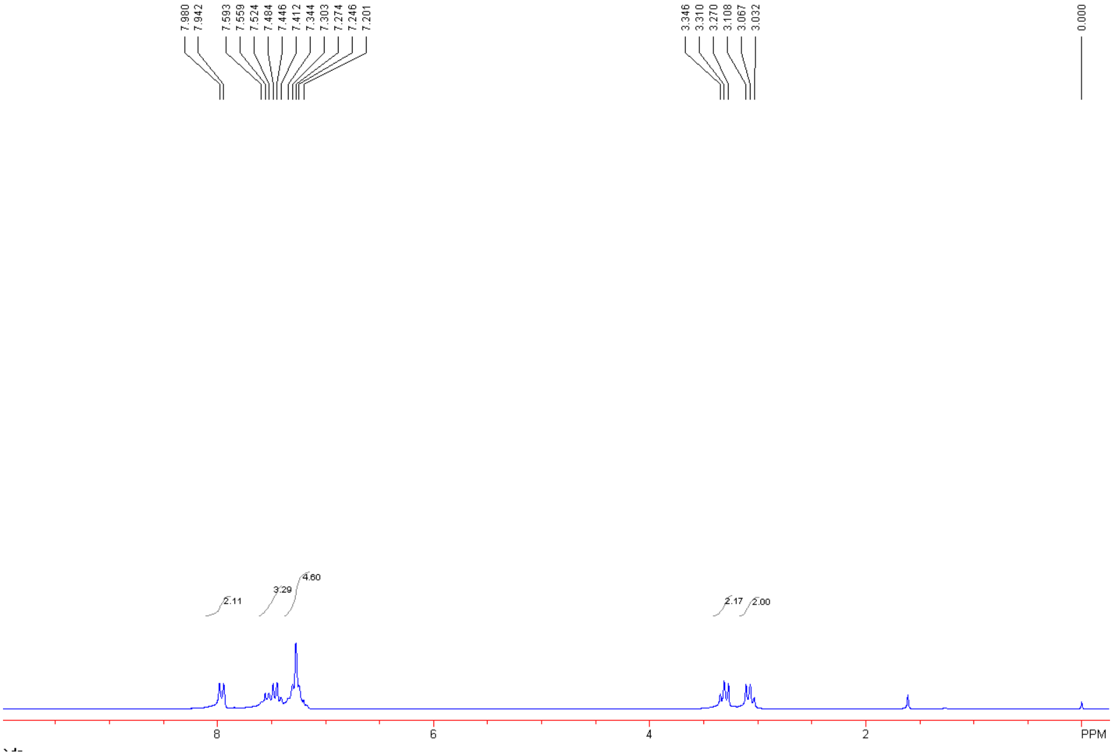
Ph

3la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7.201
3.346
3.310
3.270
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2.00
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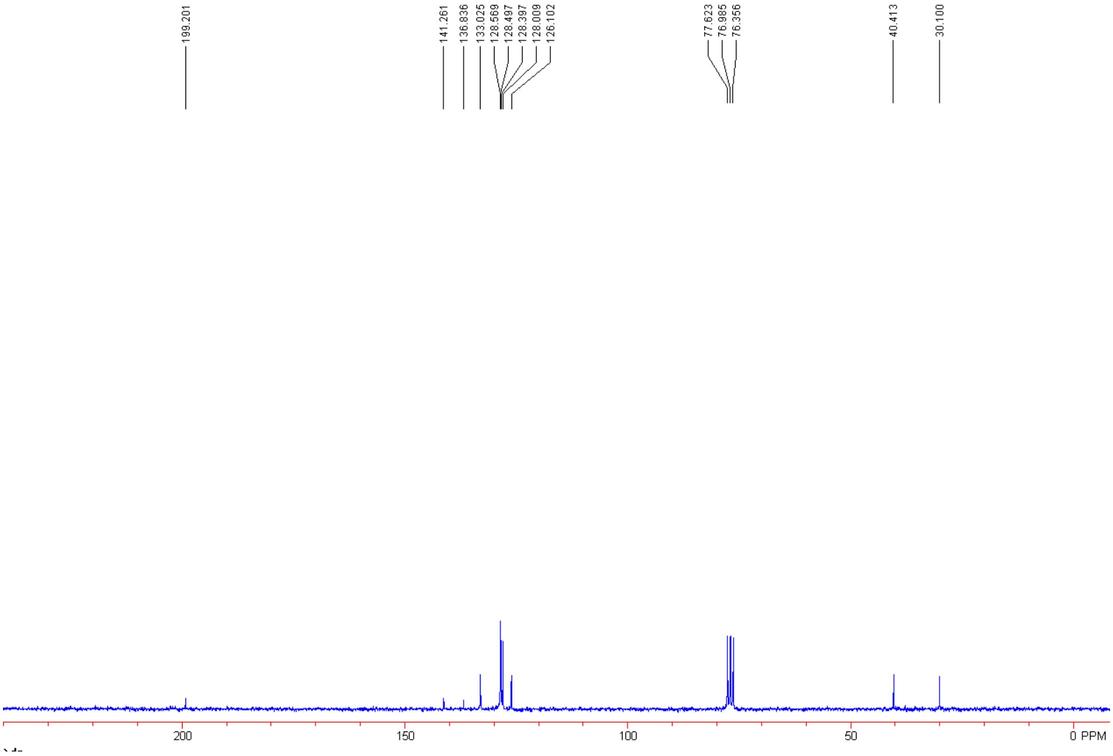
PPM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100
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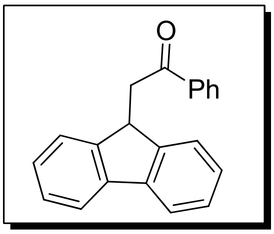
0 PPM



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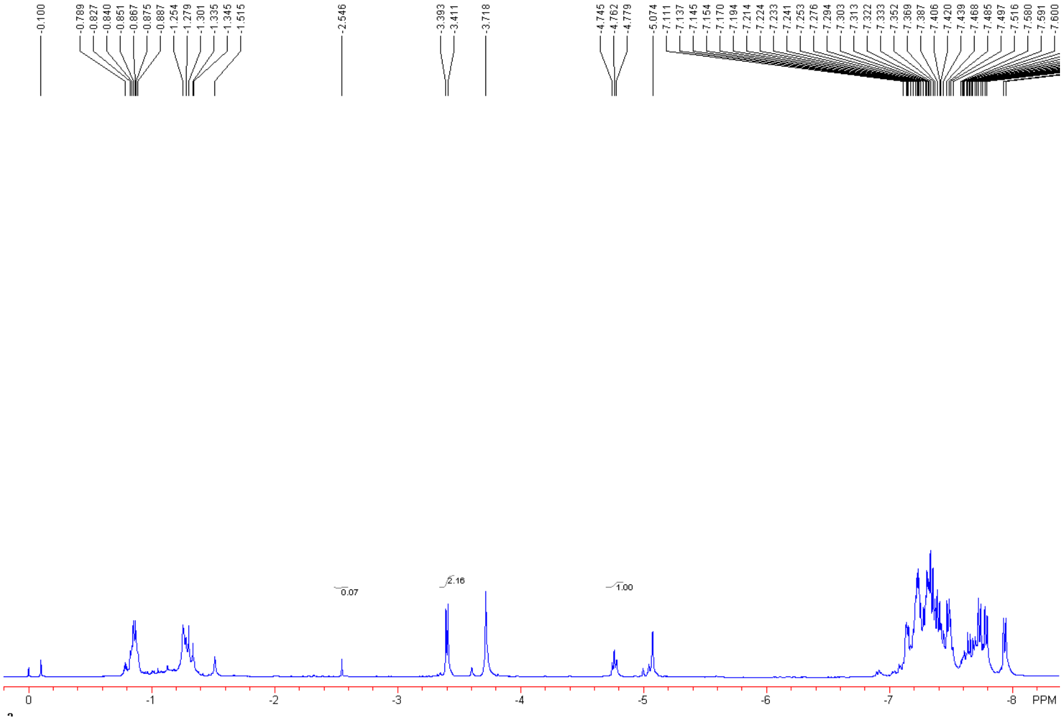

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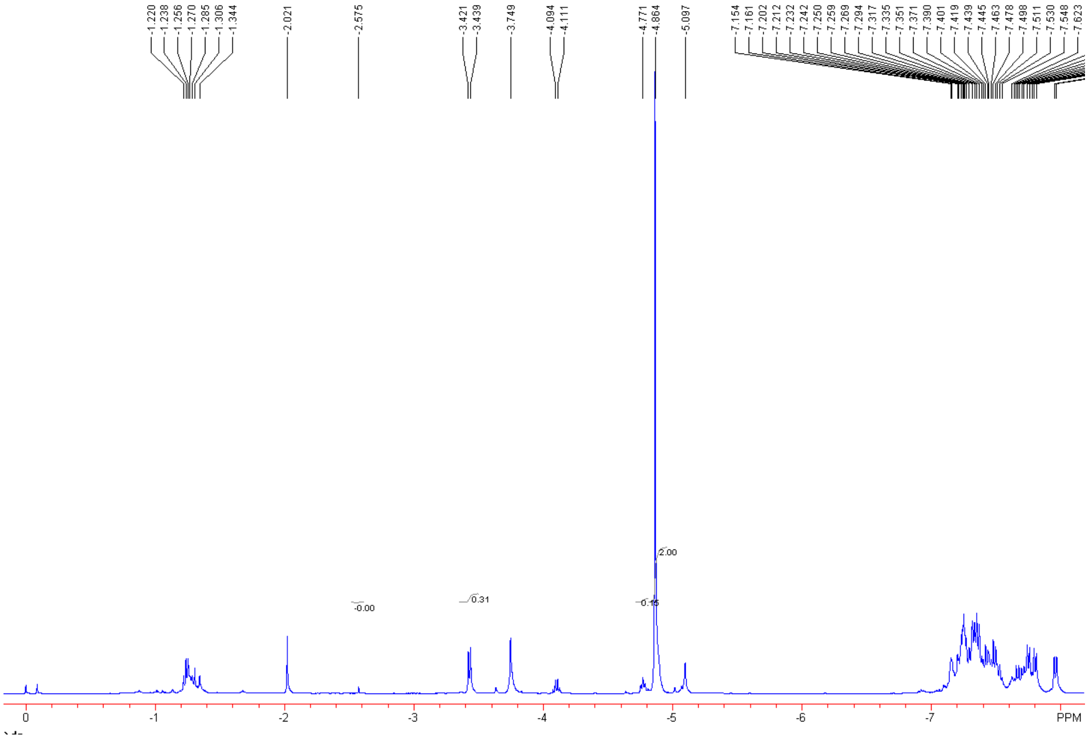

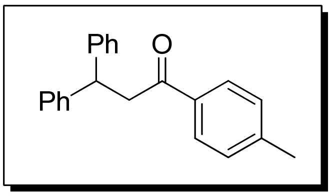
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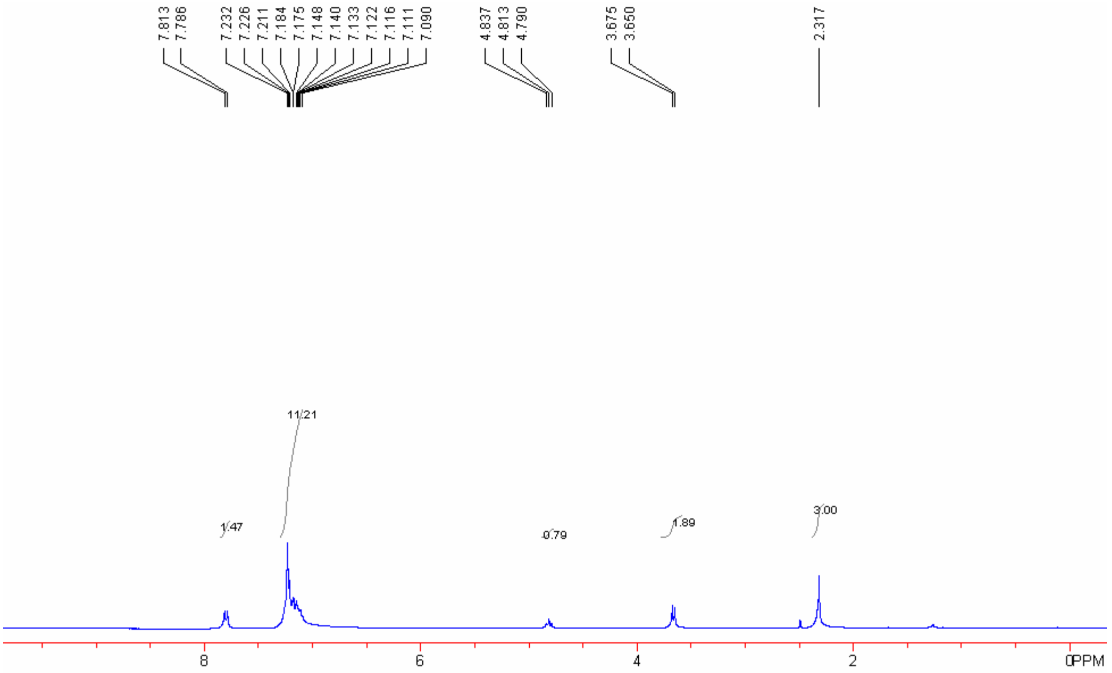
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7.133
7.122
7.116
7.111
7.090
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4.813
4.790
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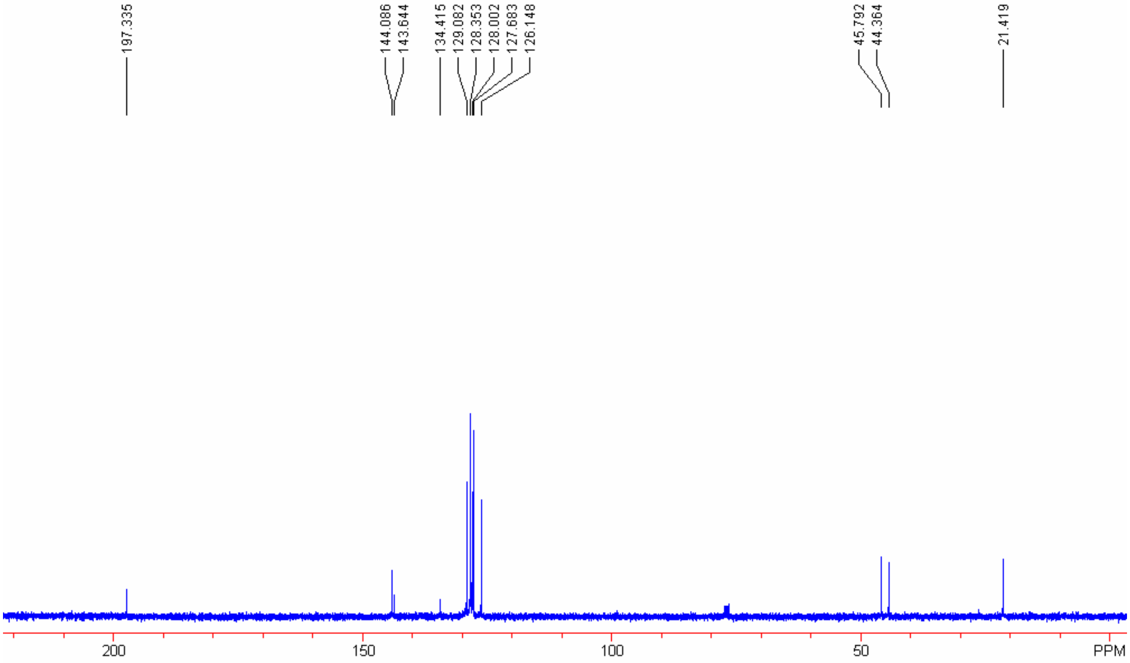
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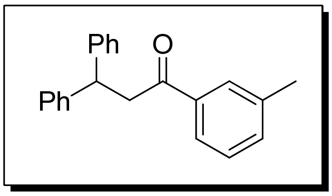
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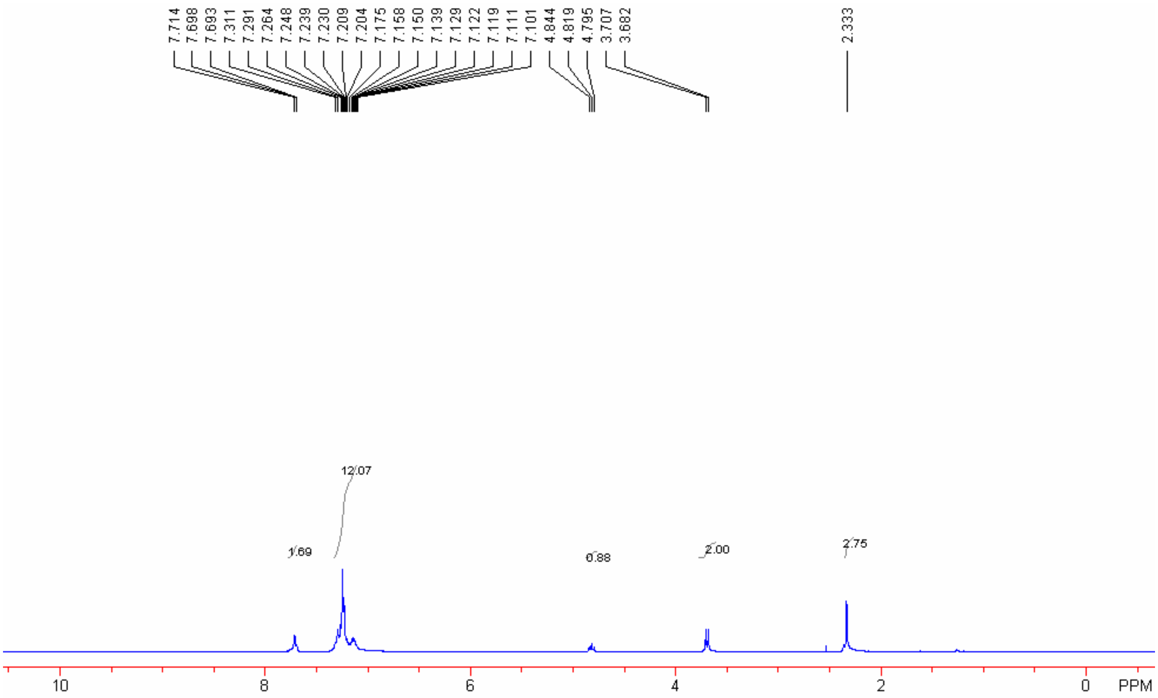
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7.158
7.150
7.139
7.129
7.122
7.119
7.111
7.101
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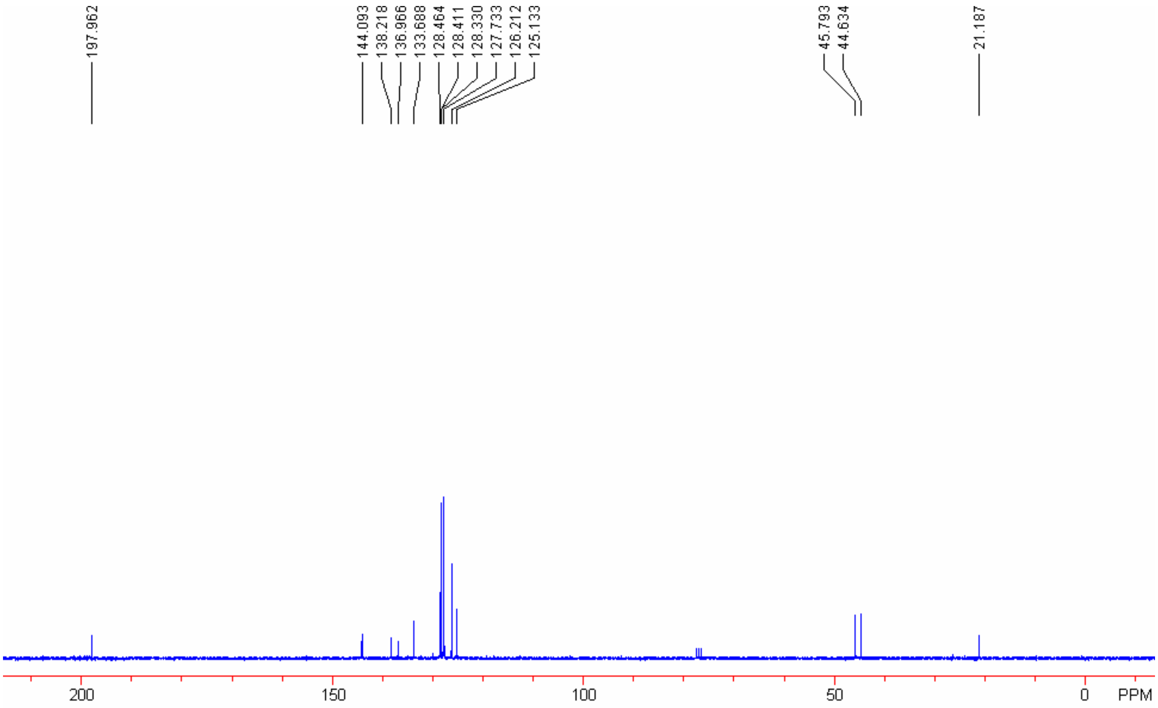
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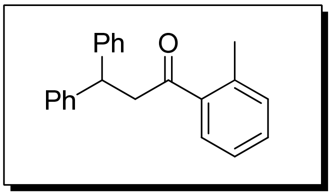
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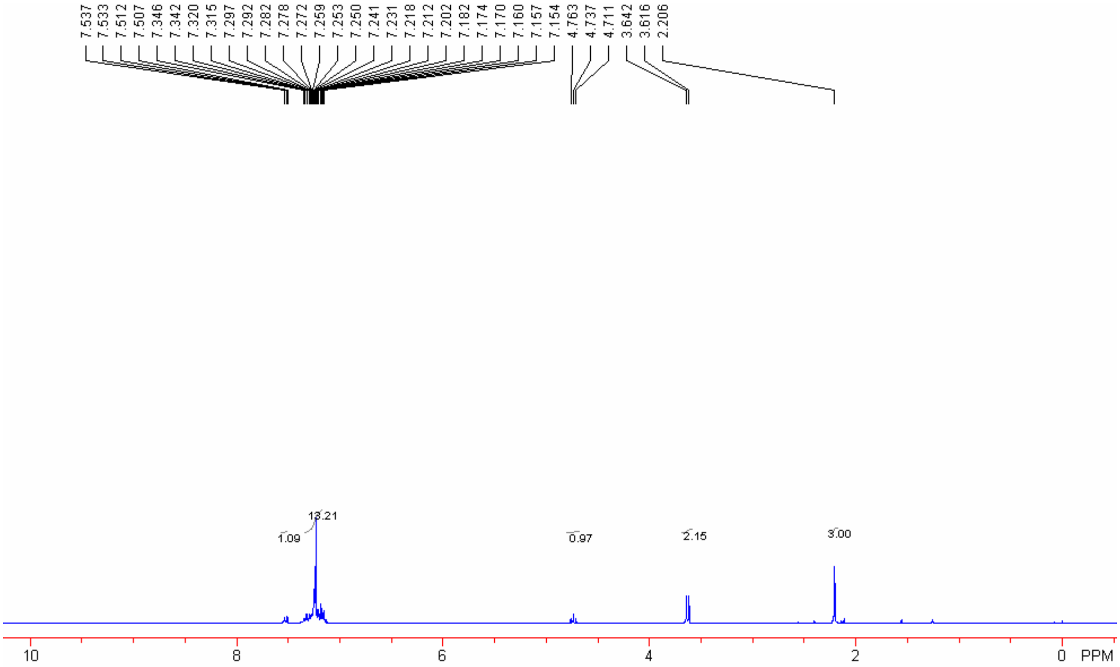
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7.272
7.259
7.253
7.250
7.241
7.231
7.218
7.212
7.202
7.182
7.174
7.170
7.160
7.157
7.154
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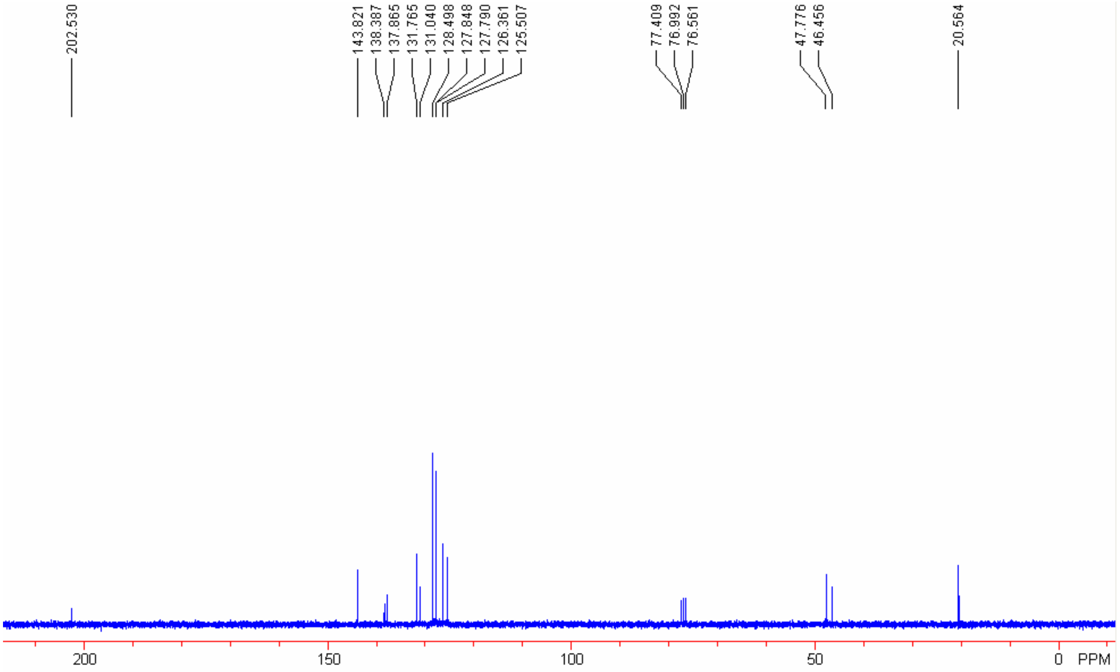
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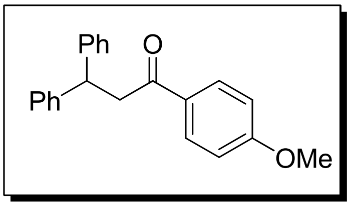
PPM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Ph
OMe

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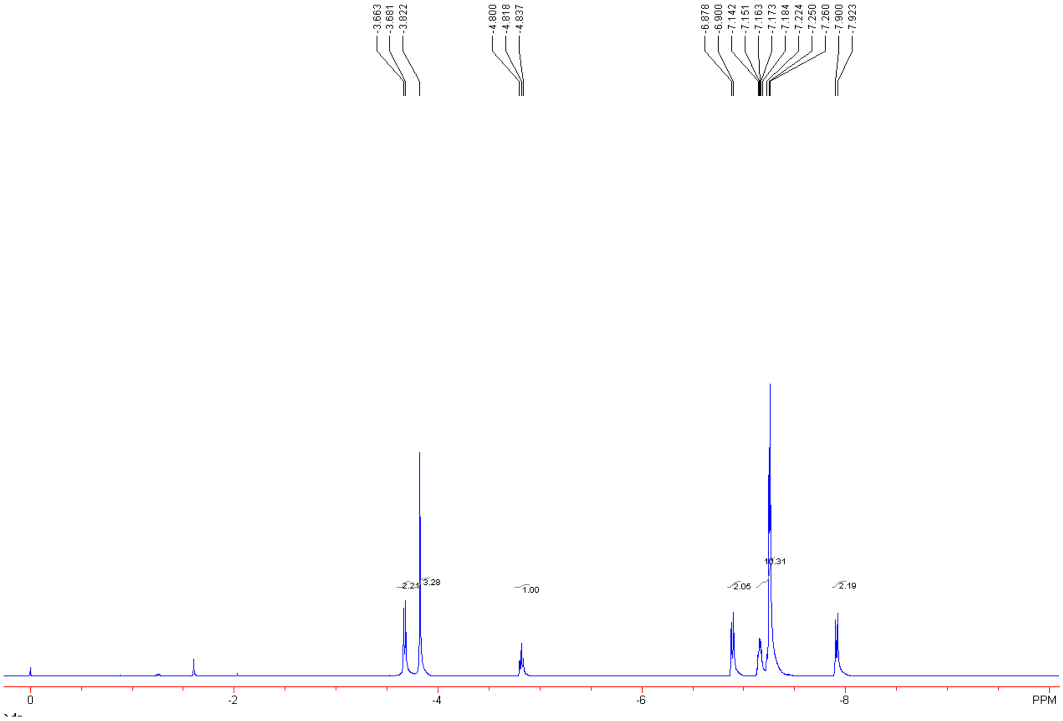
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7.184
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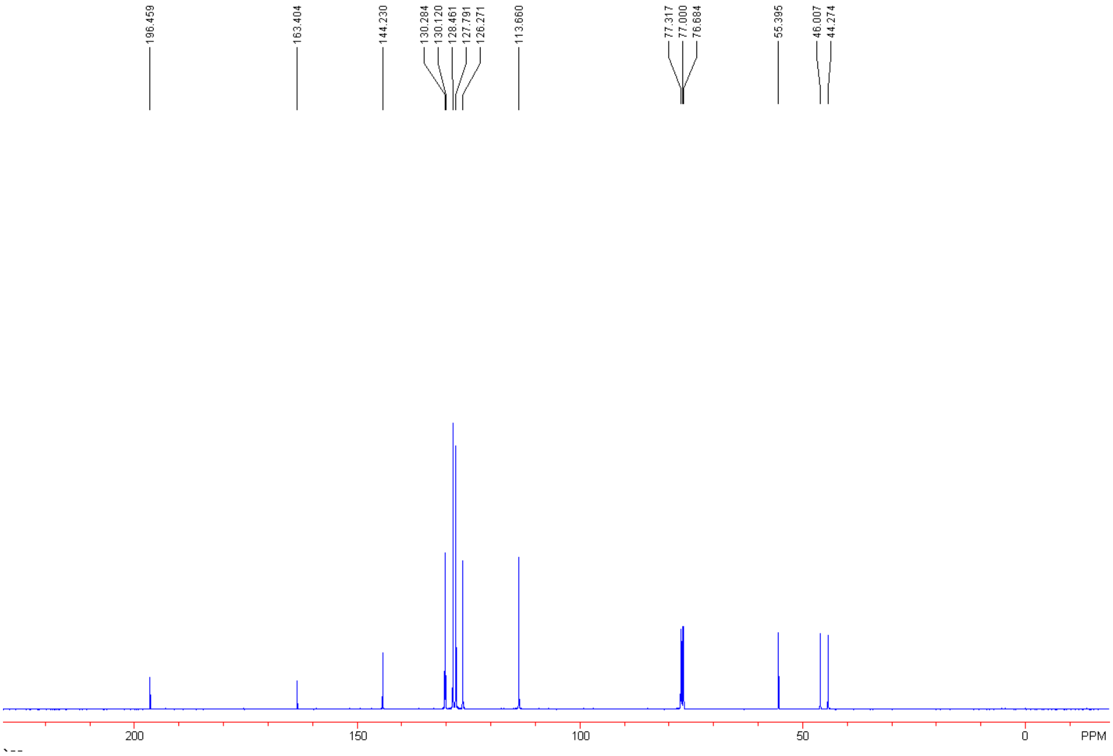
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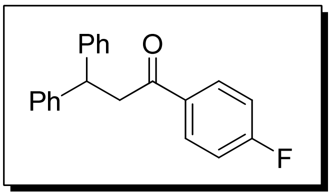
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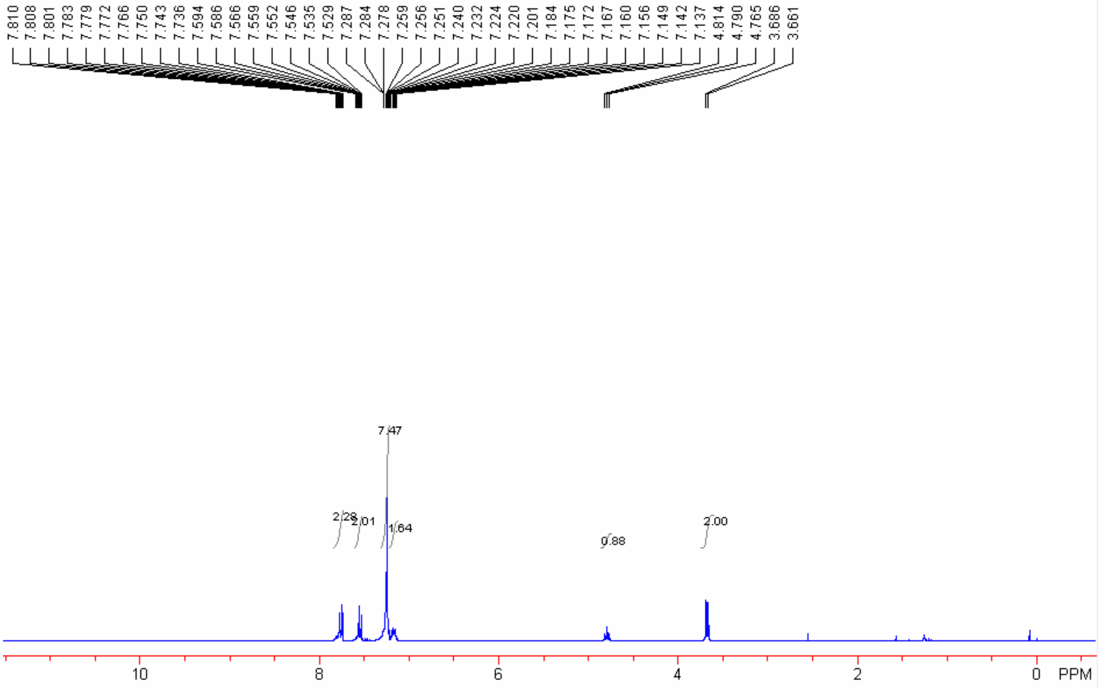
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7.750
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7.736
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7.586
7.566
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7.552
7.546
7.535
7.529
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7.284
7.278
7.259
7.256
7.251
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7.220
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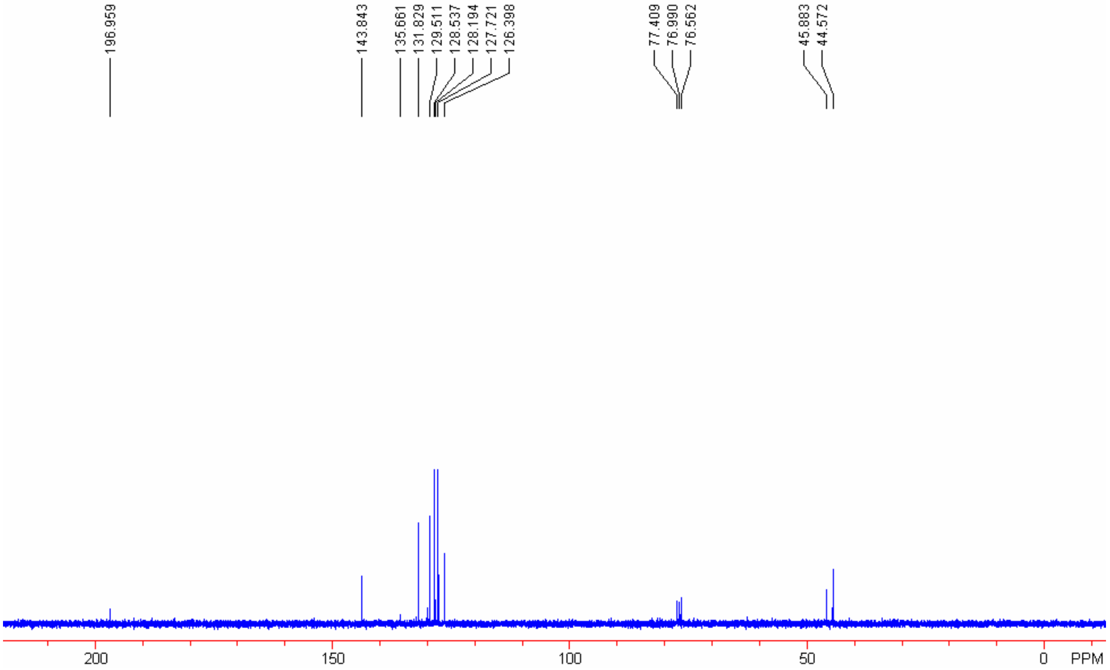
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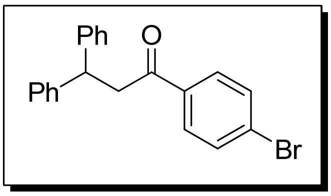
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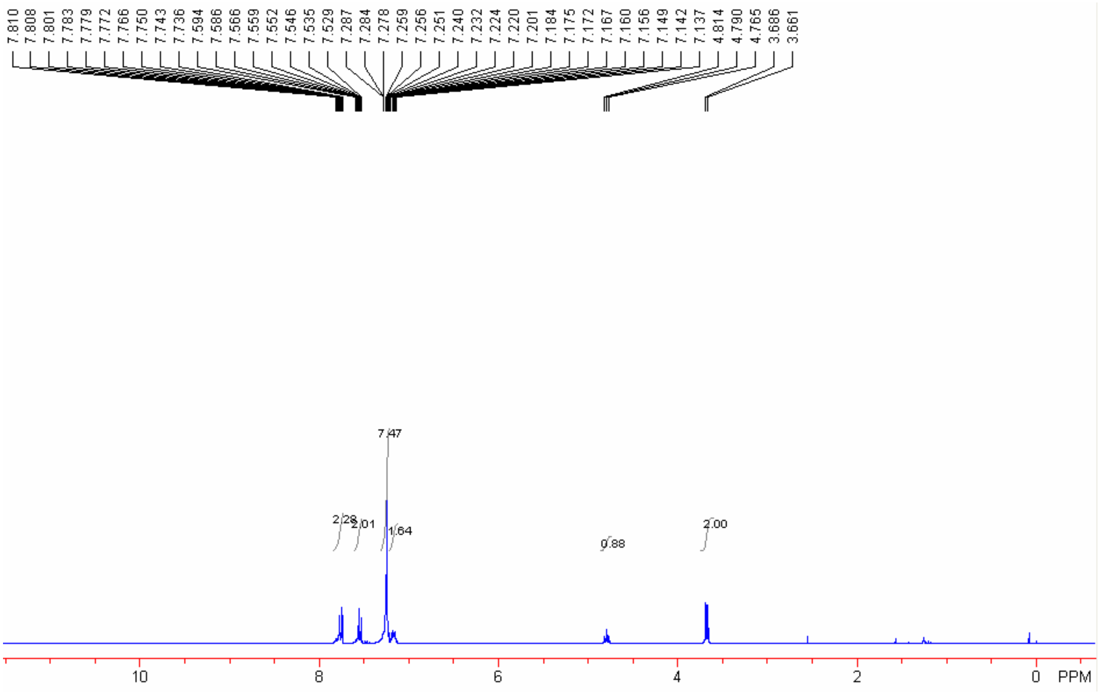
Ph
Br

3ag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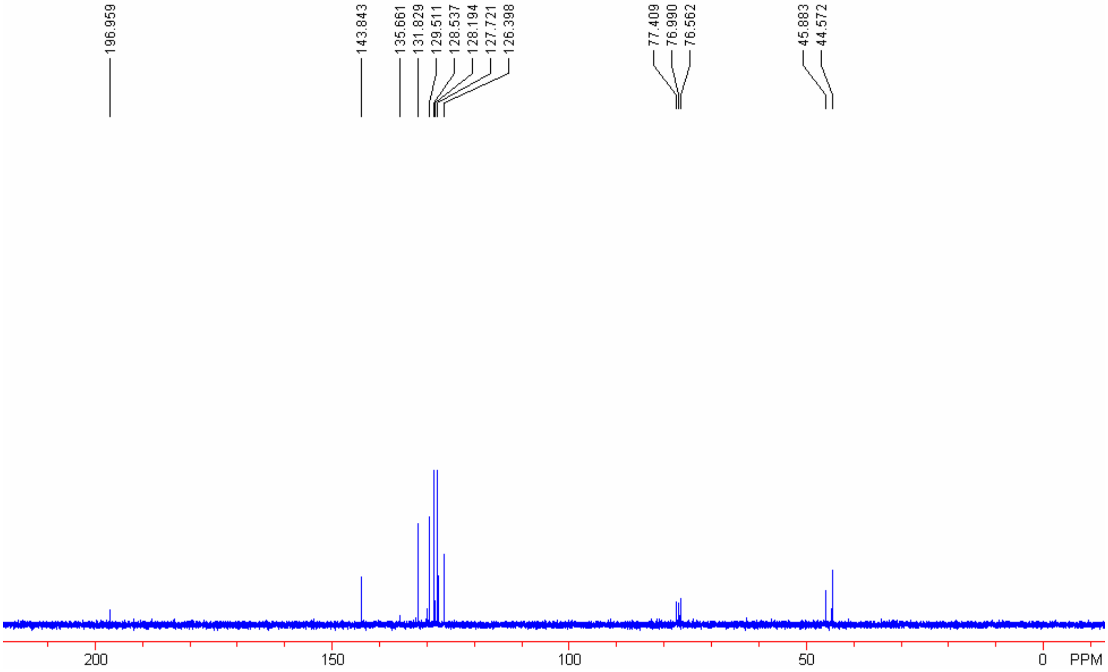
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45.883
44.572
200
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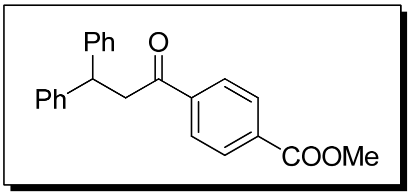
PPM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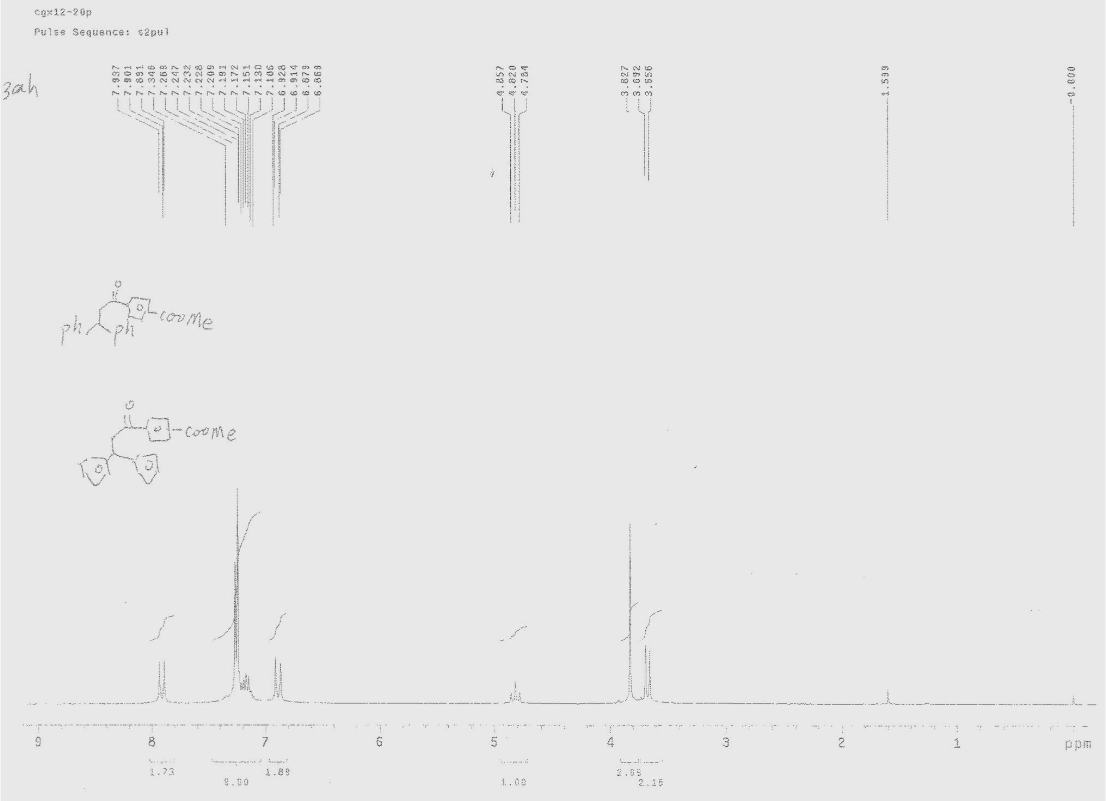
O
Ph
COOMe

3ah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7.209
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7.151
7.130
7.106
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6.914
6.879
6.869
4.857
4.820
4.784
3.827
3.692
3.656
1.599
-0.000
ph
ph
COOMe
COOMe
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5
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1
ppm
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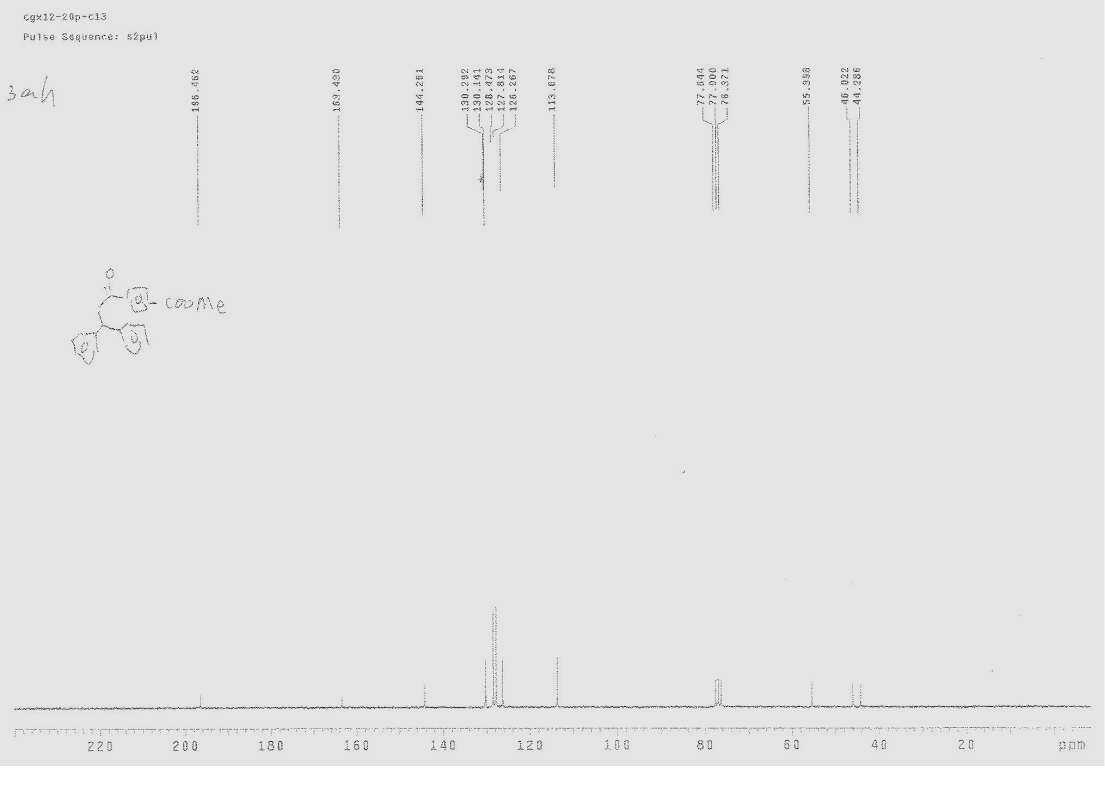
2.16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163.430
144.281
130.292
130.141
128.473
127.814
126.267
113.678
77.644
77.000
76.371
55.398
46.022
44.286
COOMe
220
200
180
160
140
120
100
80
60
40
20
ppm