Supporting Information

Aerobic oxidative iodination of ketones catalysed by sodium nitrite "on water" or in a micelle-based aqueous system

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1. General Remarks

All chemicals were purchased from commercial sources and were used without further purification. Preparative column or thin layer chromatography were carried out using silica gel 60 (0.063-0.200 mm) or PLC Silica gel 60 F_{254}, 2mm plates, respectively. NMR spectra of $CDCl_3$ solutions of samples were recorded on a Varian INOVA 300 spectrometer at 300 MHz for ^1H and 76 MHz for the ^{13}C. Chemical shifts are reported in ppm units relative to TMS as internal standard. Standard KBr pellet procedures were used to obtain IR spectra of solid products, while a film of neat material on a NaCl window was used for liquid products. Melting points of solid products were measured on a Büchi 535 apparatus. Mass spectra were obtained on an Autoscope Q instrument with EI ionization at 70eV.

2. 10 mmol Scale Synthetic Protocols and Isolation of Products without Using Organic Solvents

2.2. Aerobic Oxidative Iodination of 3,4-dihydro-2*H*-naphthalen-1-one (**3**)

3,4-Dihydro-2*H*-naphthalen-1-one (**3**) (10 mmol, 1.46 g) was placed in a two necked glass flask equipped with a magnetic stirrer bar (50 mL) and one neck was closed with a rubber septum). 8 mL of 0.1 M aqueous solution of SDS and 96% H_2SO_4 (5 mmol, 0.47 g) were added and the dispersion was stirred (500-700 rpm) for a few minutes at 60 ^oC. Afterwards finely powdered molecular iodine (1.27 g, 5 mmol) was added to the reaction mixture and the open neck then closed with a rubber balloon (3 L) filled with air. After 20 min of stirring 2 mL of aqueous solution of sodium nitrite ($NaNO_2$) catalyst (96.6 mg, 1.4 mmol dissolved in 2 mL of water) was introduced during continuing stirring through the septum into the reaction mixture in 4 portions at 1 hour intervals and the reaction system stirred (500-700 rpm) at 60 ^oC until it lost the iodine colour (overall reaction time was 5 hours). The reaction mixture was then cooled in an ice bath, discolored by adding a a few drops of 40% aqueous solution of Na_2SO_3, neutralized with few drops of saturated aqueous $NaHCO_3$ and the precipitated product filtered off under reduced pressure. The crude solid product was washed several times with water and after drying at reduced pressure 2.65 g (97%) of
2-iodo-3,4-dihydro-2*H*-naphthalen-1-one[2] (**4**) was obtained:
white crystals (from EtOH/*n*-hexane = 3 : 1); mp = 78-80 ^oC (mp[2] = 78.5-79.6 ^oC); ^1H NMR: δ = 2.15(m, 2H), 2.31(m, 1H), 2.85(dt, J = 17.0 , 3.5 Hz, 1H), 3.16(ddd, J = 17.0, 11.0, 4.1 Hz, 1H), 5.01(t, J = 3.5 Hz, 1H), 7.27-7.38(m, 3H), 8.08(dd, J = 8.0, 1.8 Hz, 1H); MS: m/z: 272(M^+, 55%), 145(100), 117(53), 90(25), 77(6).

2.1. Aerobic Oxidative Iodination of 1-(4-methoxy-phenyl)-ethanone (9a)

1-(4-methoxy-phenyl)-ethanone (**1**) (10 mmol, 1.5 g) was placed in a two necked glass flask equipped with a magnetic stirrer bar (50 mL) and one neck was closed with a rubber septum). 8 mL of 0.1 M aqueous solution of SDS and 96% H_2SO_4 (5 mmol, 0.47 g) were added and the dispersion was stirred (500-700 rpm) for a few minutes at 60 ^oC. Afterwards finely powdered molecular iodine (1.27 g, 5 mmol) was added to the reaction mixture and the open neck was then closed with a rubber balloon (3 L) filled with air. After 20 min stirring, 2 mL of aqueous solution of sodium nitrite ($NaNO_2$) catalyst (96.6 mg, 1.4 mmol dissolved in 2 mL of water) was introduced with continuous stirring the reaction mixture in 4 portions at 1 hour intervals. The reaction system was stirred (500-700 rpm) at 60 ^oC until it lost the iodine colour (overall reaction time was 5 hours). The reaction mixture was then cooled in an ice bath, discolored by adding a few drops of 40% aqueous solution of Na_2SO_3, neutralized with a few drops of saturated aqueous $NaHCO_3$ and the precipitated product filtered off under reduced pressure. The crude solid product was washed several times with water and after drying at reduced pressure 2.52 g (91%) of **2-iodo-1-(4-methoxy-phenyl)-ethanone**[1] (**10a**) was obtained:
white crystals (from EtOH/*n*-hexane = 3 : 1); mp = 58-59.5 ^oC (mp[1] = 59-61 ^oC); ^1H NMR: δ = 3.88(s, 3H), 4.31(s, 2H), 6.95(d, J = 9 Hz, 2H), 7.97(d, J = 9 Hz, 2H); MS: m/z: 276(M^+, 26%), 135(100).

3. Characterization of Known Iodinated Products Obtained

3.1. **2-Iodo-1-phenylethanone**[4] (**2**): 224 mg (91%, flash column chromatography, SiO_2, CH_2Cl_2); mp = 33.0-35.5 ^oC (mp[4] = 35-36 ^oC); ^1H NMR: δ = 4.36(s, 2H), 7.45(dd, J = 9.0, 6.2 Hz, 2H), 7.58(dd, J = 9.0, 6.2 Hz, 1H), 8.00(dd, J = 9.0, 6.2 Hz, 2H); MS: m/z: 246(M^+, 30%), 105(100), 91(22), 77(30).

3.2. **4-Iodo-nonan-5-on**[3] (**8**): 225 mg (84%, flash column chromatography, SiO_2, CH_2Cl_2); yellow liquid; ^1H NMR: δ= 0.98(t, J= 7.5 Hz, 6H), 1.33-1.64(m, 6H), 1.93(m, 2H), 2.40-2.85(m, 2H), 4.50(t, J= 6.5 Hz, 1H); MS: m/z: 268(M^+, 3%), 226(5), 211(1), 183(2), 141(17), 85(100), 57(85).

3.3. **4-*tert*-Butyl-2-iodo-cyclohexanone**[4] (**6**): 238 mg (80%); mixture of *trans* and *cis* isomers in 2 : 1 relative ratio; ^1H NMR: *trans* isomer: δ = 0.93(broad s, 9H), 1.43-1.71(m), 1.90-2.33(m), 2.71(m, 1H, $H3_e$), 3.29(dt, J = 14.9, 6.0 Hz, 1H, $H3_a$), 4.68(m, 1H, H2); *cis* isomer: δ = 0.92(broad s, 9H), 1.43-1.71(m), 1.90-2.33(m), 4.89(dd, J = 13.9, 6.0 Hz, 1H, H2); MS: m/z: 280(M^+, 1%), 153(4), 128(5), 97(18), 84(15), 57(100).

3.3. **1-(2,4-dimethoxy-phenyl)2-iodo-ethanone**[6] (**10b**): 275.4 mg (90%, flash column chromatography, SiO_2, CH_2Cl_2); mp = 55.0-57.0 ^oC (mp[6] = 56-57.4 ^oC); ^1H NMR: δ = 3.88(s, 3H), 3.95(s, 3H), 4.46(s, 2H), 6.48(d, J = 2.5 Hz, 1H), 6.60(d, J = 9.0, 2.5 Hz, 1H), 7.93(d, J = 9.0 Hz, 1H); MS: m/z: 306(M^+, 22%), 165(100), 121(14), 91(5), 77(12).

3.4. **2-Iodo-6-methoxy-3,4-dihydro-2*H*-naphthalen-1-one**[7] (**12**): 281 mg (93%, flash column chromatography, SiO_2, CH_2Cl_2); mp = 103.5-106.0 ^oC (mp[7] = 104-105 ^oC); ^1H NMR: δ = 2.11-2.16(m, 1H), 2.24-2.29(m, 1H), 2.80-2.86(m, 1H), 3.08-3.13(m, 1H), 3.87(s, 3H), 4.98(t, J = 3.5 Hz, 1H), 6.93(d, J = 2.9 Hz, 1H), 6.87(dd, J = 8.9, 2.9 Hz, 1H), 8.06(d, J = 8.9 Hz, 1H); MS: m/z: 302(M^+, 100%), 175(47), 147(58), 115(15), 91(17), 7716).

3.5. **Ethyl-2-iodo-2-oxo-3-phenylpropanoate**[5] (**20**): 258 mg (81%, column chromatography, *n*-hexane/EtOH 9.5:0.5); oily product; ^1H NMR: δ = 1.23(t, J = 7.4 Hz, 3H), 4.25(q, J = 7.4 Hz, 2H), 5.95(s, 1H), 7.46(m, 2H), 7.50(m, 1H), 7.99(m, 2H).

3.6. **1-(2,6-Dimethoxy-phenyl)-2-iodo-ethanone**[6] (**10c**): 275.4 mg (90%, column chromatography, *n*-hexane/EtOH = 9.5:0.5); mp 58.0-60.5 ^0C (mp[6] = 58.3-59.5 ^oC); ^1H NMR: δ = 3.81(s, 6H), 4.30(s, 2H), 6.57(d, J= 8.7 Hz, 2H), 7.30(m, 1H); MS: *m/z:* 306(M^+, 10%), 165(100), 150(12), 91(28), 77(15).

3.7. **1-(3-Iodo-2,6-dimethoxy-phenyl)-ethanone**[6] (**21**): 248 mg (81%, column chromatography, CH_2Cl_2 / *n*-hexane = 9.5:0.5); mp 65-68 ^0C (mp[6] = 66-69 ^oC); ^1H NMR: δ = 2.50(s, 3H), 3.80(s, 3H), 3.83(s, 3H), 6.55(d, J= 8.7 Hz, 1H), 7.70(d, J= 8.7 Hz, 1H); MS: *m/z:* 306(M^+, 30%), 291(68), 276(20), 233(11), 165(100), 150(20), 107(13), 91(3), 77(14).

4. References

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2 C. A. Horiuchi, S.-J. Ji, M. Matsushita and W. Chai, *Synthesis,* 2004, 202-204.
3 M. Jereb, M. Zupan and S. Stavber, *Chem. Commun.,* 2004, 2614-2615.
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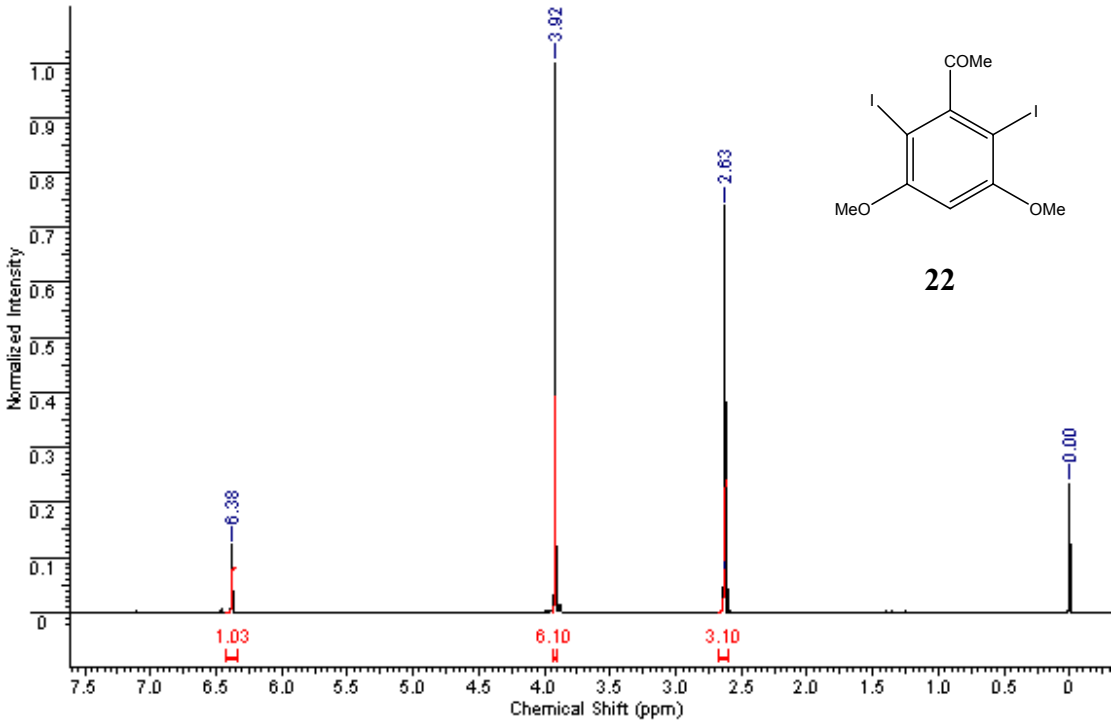
5. ^{1}H and ^{13}C NMR Spectra of New Compounds 22, 10d, 10e, 23, 14, 16, and 19



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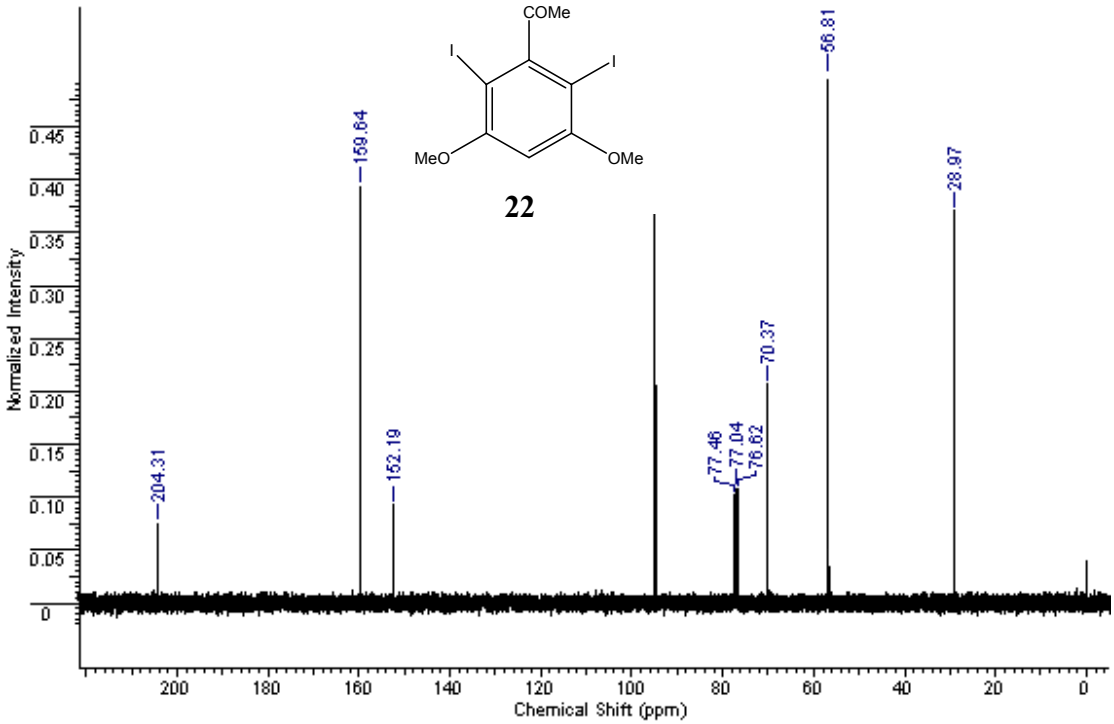

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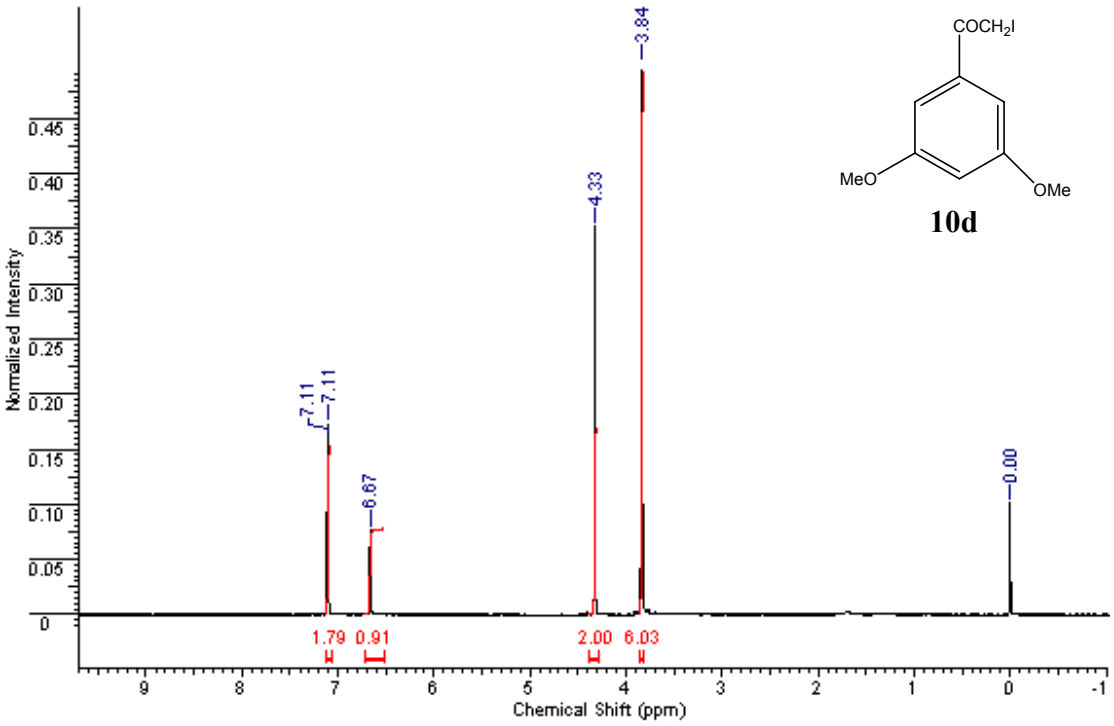
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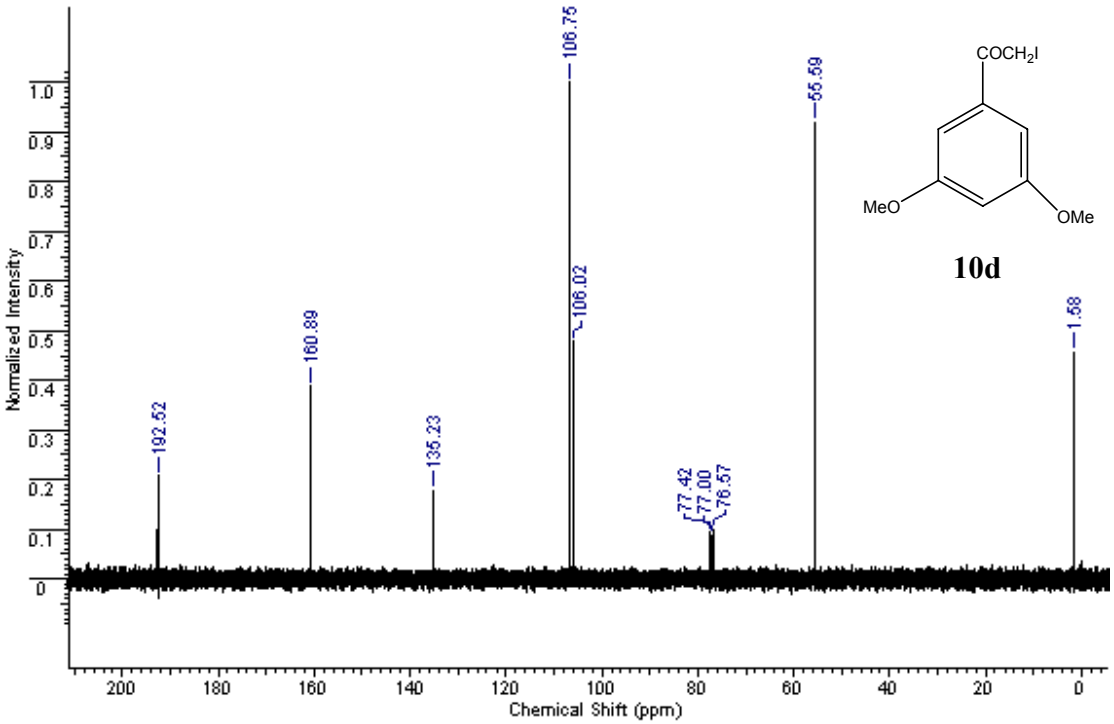
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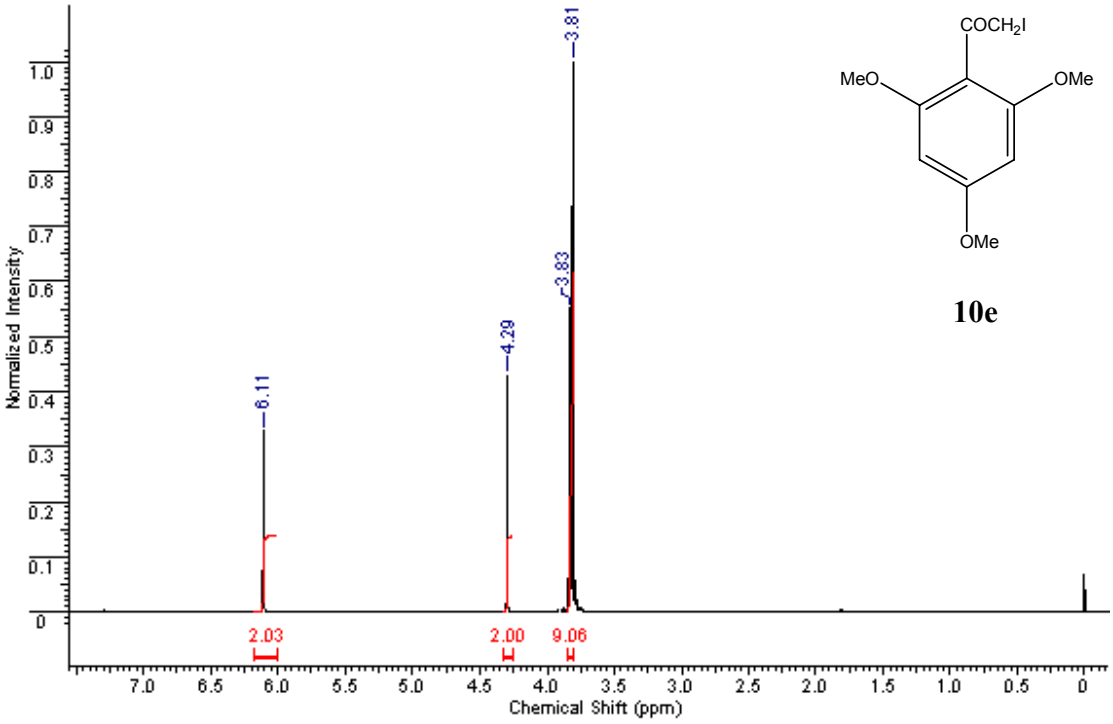
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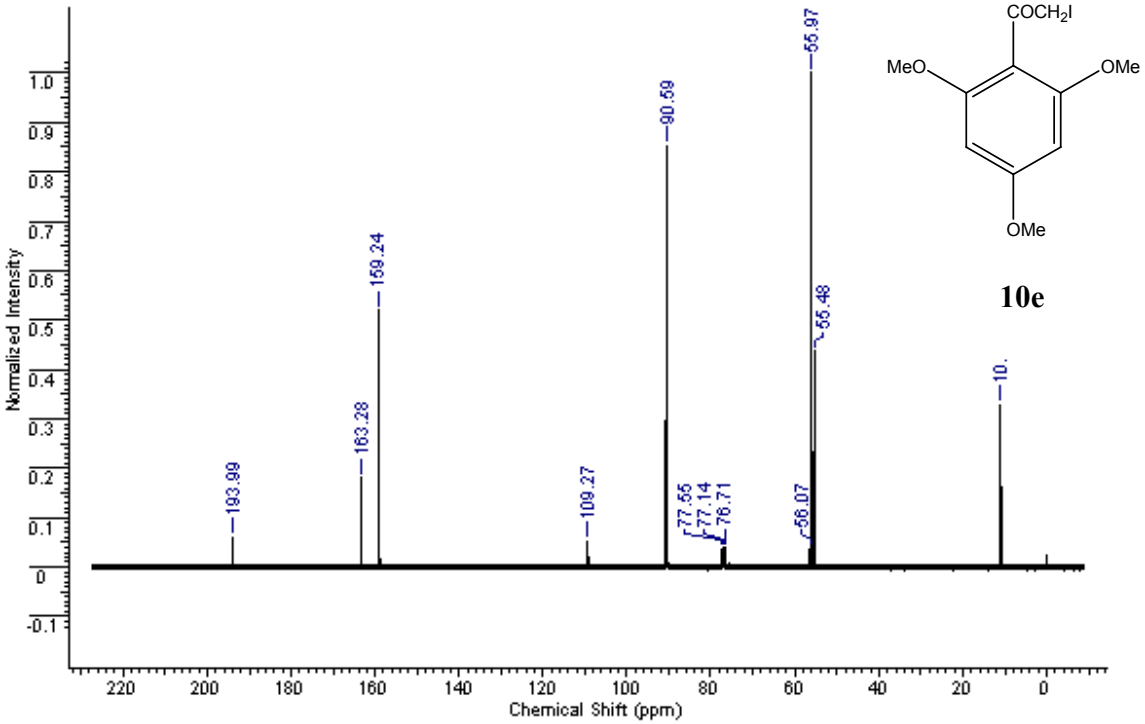
10e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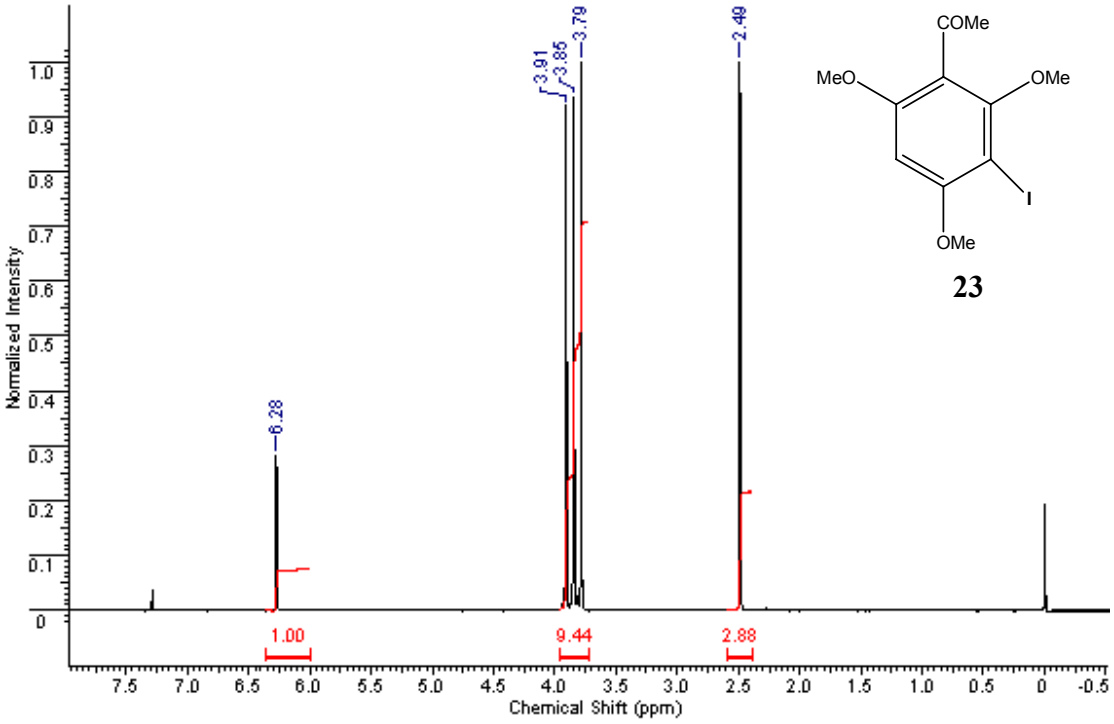
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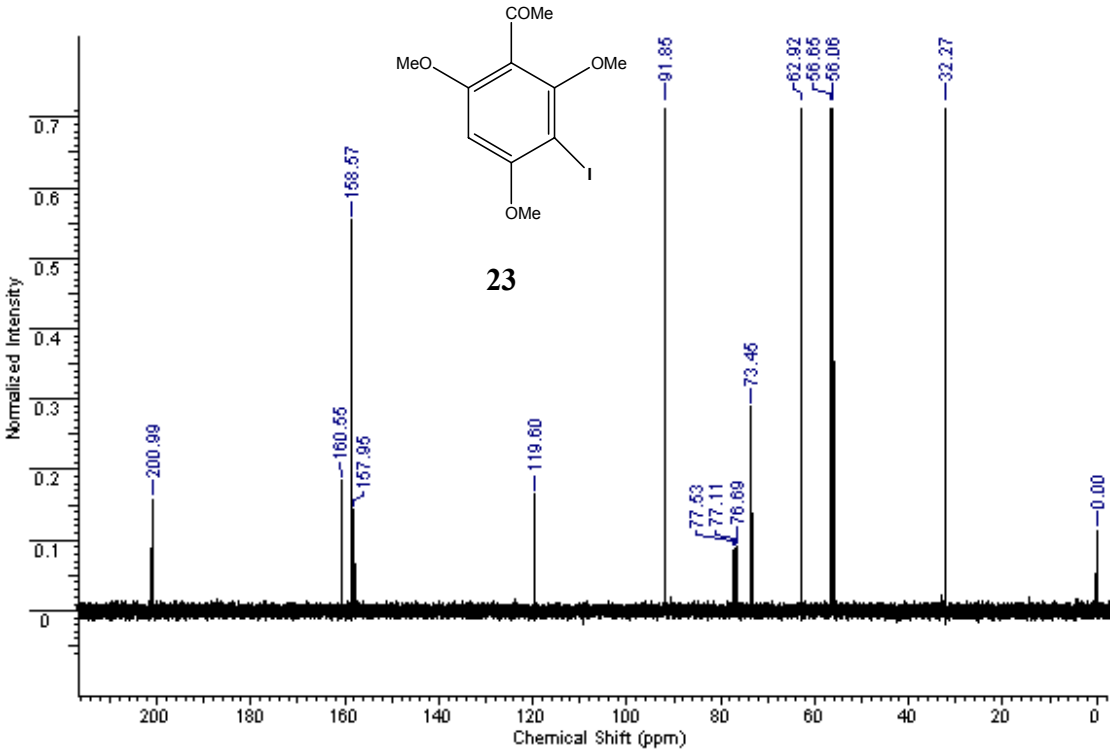
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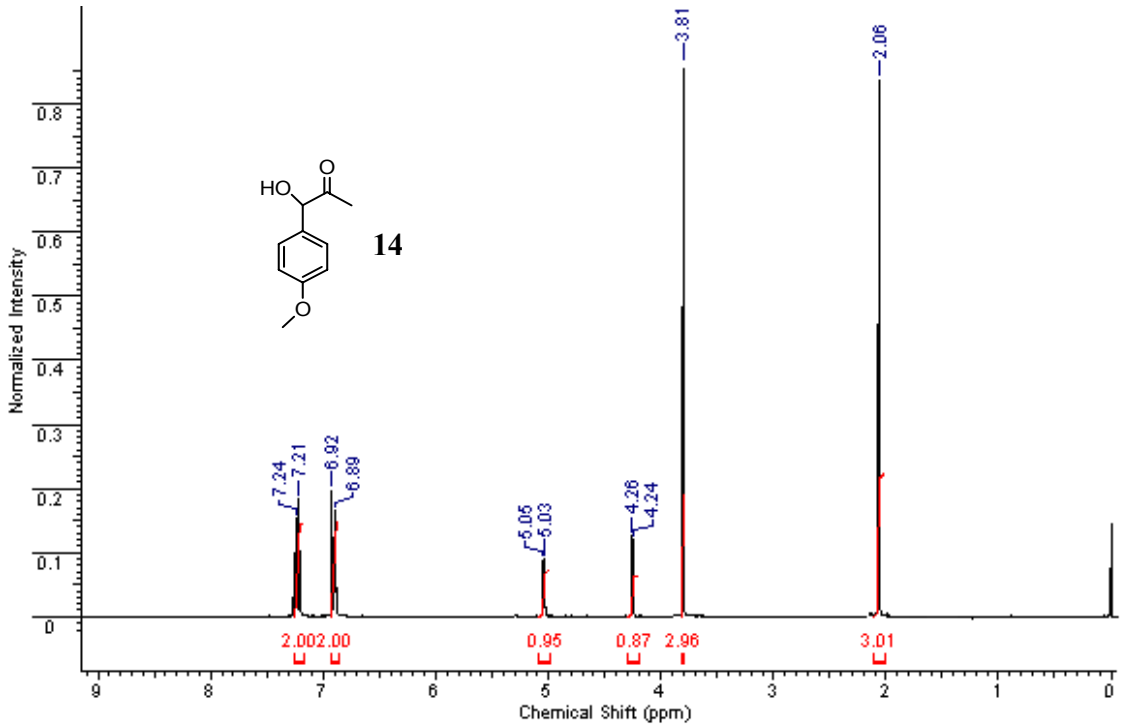
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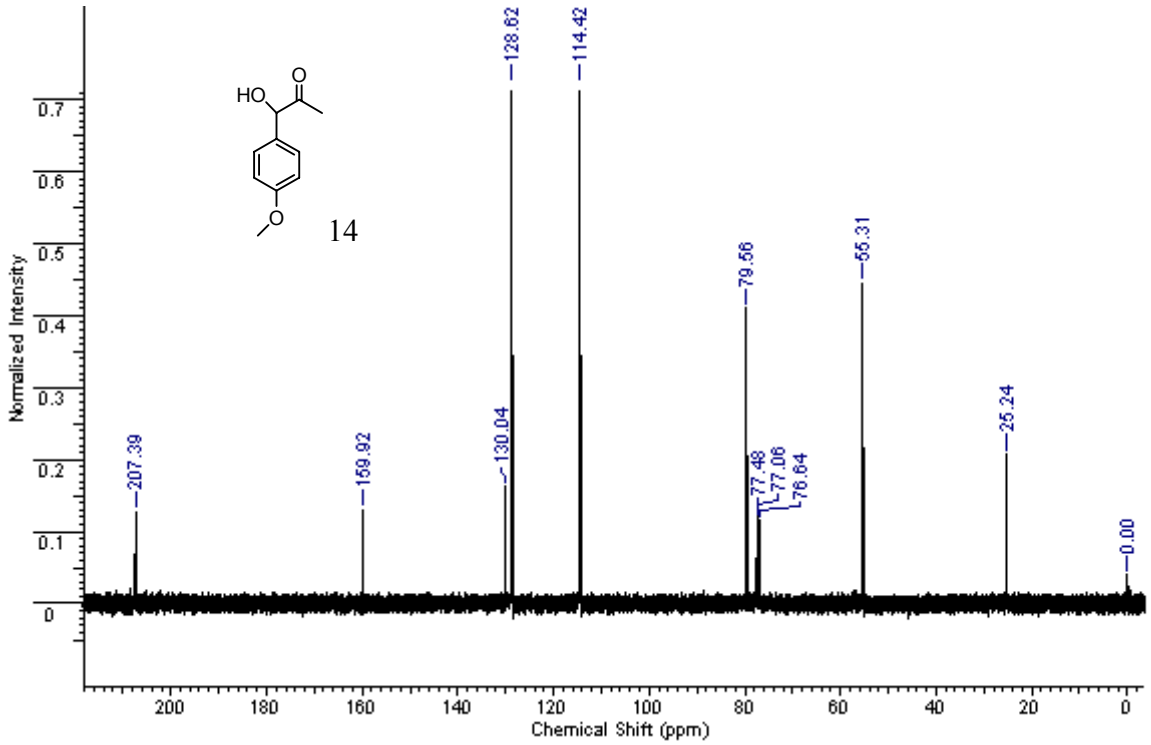
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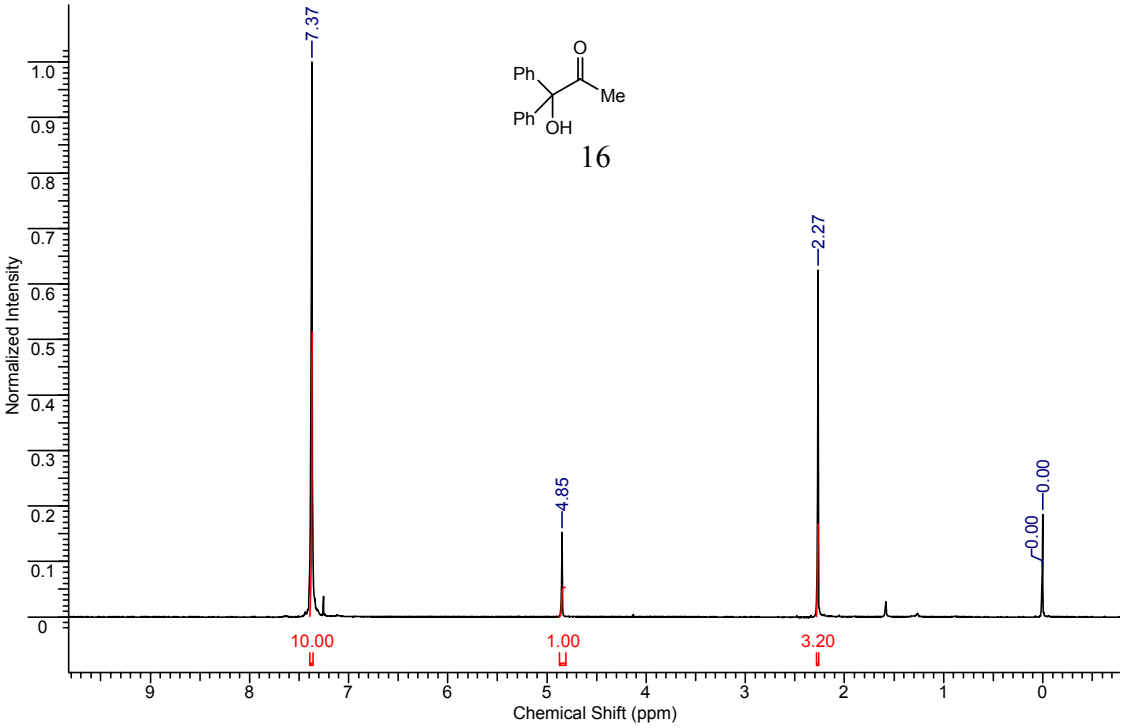
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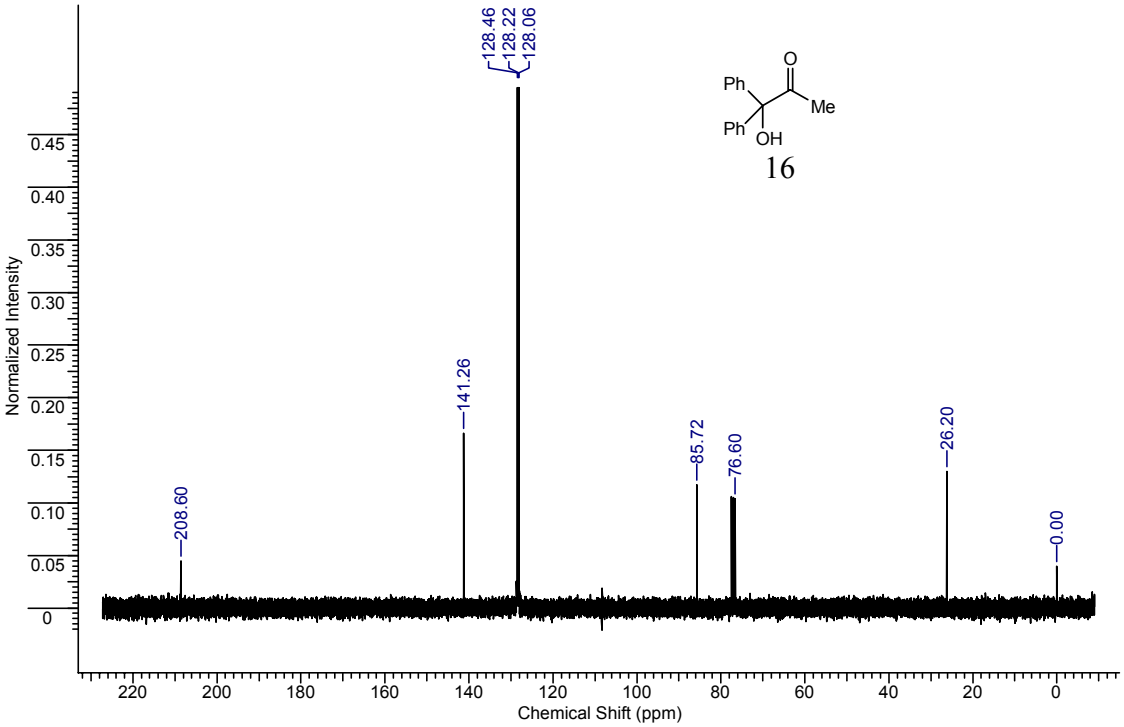
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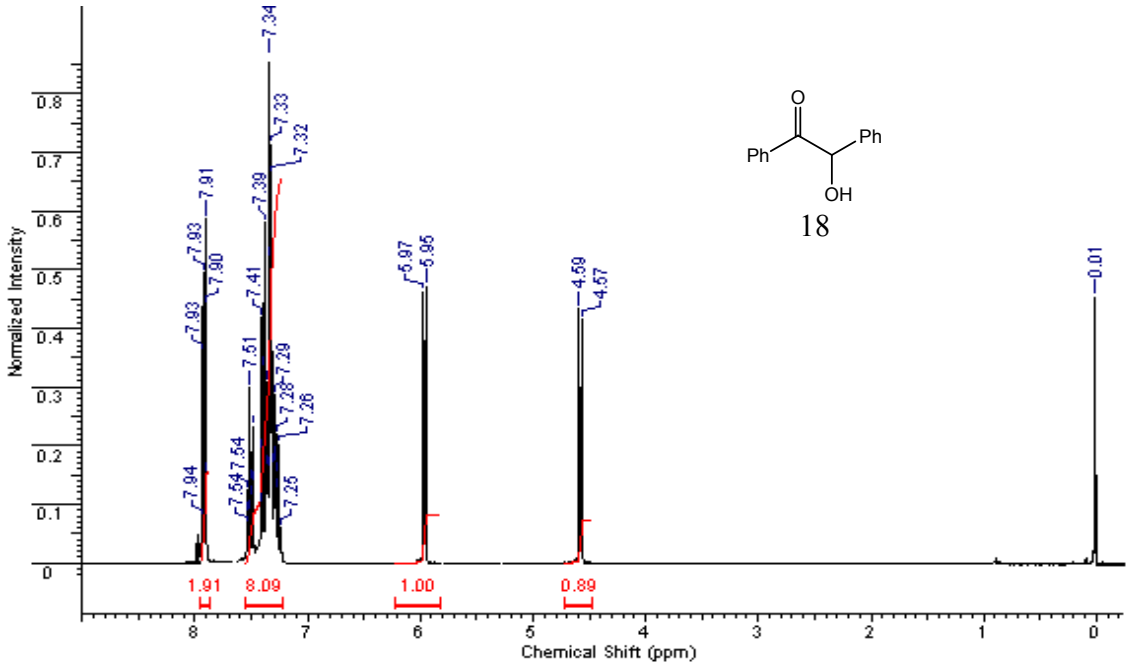
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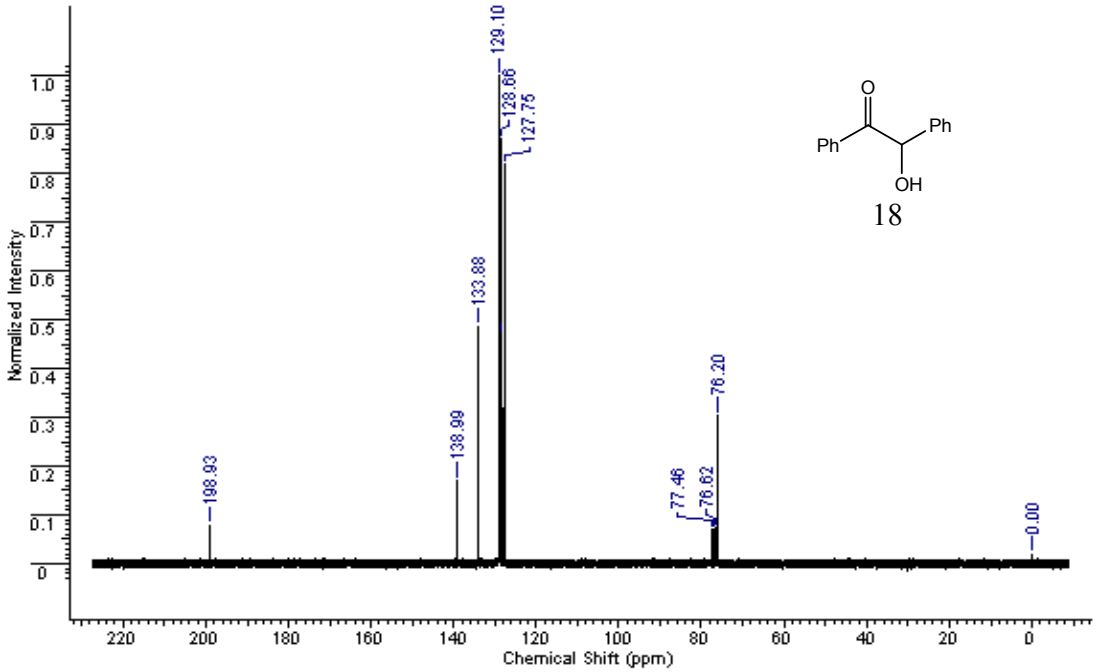
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