Direct β-Functionalization of Cyclic Ketones with Aryl Ketones via the Merger of Photoredox and Organocatalysis

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Supporting Information

Contents:

1. General Information. Commercial reagents were purchased from Sigma Aldrich and purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an acetone-dry ice bath. Chromatographic purification of products was accomplished using forced-flow chromatography according to the method of Still[3] on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. Visualization of the developed plates was performed by fluorescence quenching, potassium permanganate, or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz), and are internally referenced to residual protio solvent signals (for $CDCl_3$, δ 7.27 and 77.0 ppm, respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of wavenumber of absorption (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility.

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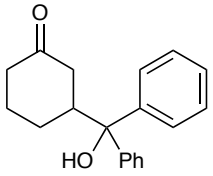
[1] Perrin, D. D.; Armarego, W. L. F. In *Purification of Laboratory Chemicals*. 3rd ed., Pergamon Press: Oxford, 1988.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *115*, 1518.
[3] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

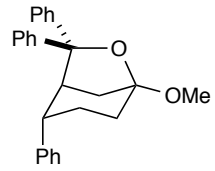
2. Experimental Procedures and Spectral Characterization of the Products

General Procedure A: A solution of tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (0.75 mmol, 1.00 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclohexanone (3.9 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in DMPU (1.5 mL) was degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature), then irradiated with a 26 W fluorescent lamp (at approximately 2 cm away from the light source). After 24 h, the reaction mixture was diluted with water, extracted with EtOAc (3 x 5 mL), combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by flash chromatography on SiO_2 (15-30% EtOAc in hexanes) provided the desired product.

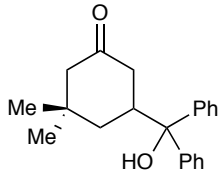
General Procedure B: A solution of Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), methyl aryl ketone (0.75 mmol, 1.00 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10.0 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) was degassed by bubbling Ar stream for 10 min, and then irradiated with two 26 W fluorescent lamps (at approximately 2 cm away from the light source; temperature at 40 °C). After 48 h, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography on SiO_2 (15-30% EtOAc in hexanes) provided the desired product.



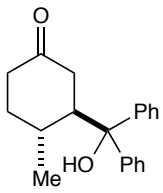
3-(Hydroxydiphenylmethyl)cyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclohexanone (0.39 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in DMPU (1.5 mL) provided the desired product (170.0 mg, 81%) as a colorless oil. The product was isolated as an inseparable mixture of the title compound and the corresponding hemiacetal in *ca.* 8:1 ratio: IR (film) 3475, 3949, 1701, 1448 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, 0.33 H, J = 8.4, 1.3 Hz), 7.50–7.46 (m, 0.34 H), 7.42–7.36 (m, 2 H), 7.36–7.31 (m, 2 H), 7.26 (dd, 2 H, J = 8.5, 7.1 Hz), 7.24–7.20 (m, 2 H), 7.17–7.09 (m, 2 H), 2.85 (ddt, 1 H, J = 11.7, 4.8, 3.2 Hz), 2.32 (ddt, 1 H, J = 14.6, 4.1, 2.3 Hz), 2.28–2.14 (m, 3 H), 2.07–1.96 (m, 1 H), 1.74 (ddt, 1 H, J = 11.9, 3.5, 1.8 Hz), 1.61 (ddq, 1 H, J = 13.3, 5.2, 3.0 Hz), 1.42 (ddt, 1 H, J = 13.0, 11.5, 3.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3, 145.6, 144.7, 128.4 (2 C), 126.9 (2 C), 125.6, 125.4, 79.7, 46.2, 42.8, 41.2, 25.8, 24.8; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}O_2Na$ [$(M+Na)^+$] 303.1361, found 303.1350.



5-Methoxy-2,7,7-triphenyl-6-oxabicyclo[3.2.1]octane: According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), 4-phenylcyclohexanone (654.0 mg, 3.750 mmol, 5.000 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in DMPU (2.0 mL) provided the crude product, which was subjected to the next step without previous purification and characterization. The crude material was dissolved in MeOH (10.0 mL), treated with *p*-TsOH•H_2O (10.0 mg, 0.0526 mmol), and stirred at room temperature for 12 h. The reaction mixture was then diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by chromatography on SiO_2 (5-10% EtOAc in hexanes) gave the desired methyl acetal (180.0 mg, 65% over two steps) as a colorless oil: IR (film) 2959, 2926, 1727, 1449 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, 2 H, J = 7.8 Hz), 7.60 (dd, 2 H, J = 8.2, 1.4 Hz), 7.38–7.30 (m, 5 H), 7.30–7.25 (m, 3 H), 7.25–7.11 (m, 3 H), 3.53–3.46 (m, 1 H), 3.24 (s, 3 H), 3.13–3.02 (m, 1 H), 2.25–2.13 (m, 1 H), 2.09–1.89 (m, 3 H), 1.84–1.75 (m, 1 H), 1.54 (d, 1 H, J = 11.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 145.6, 144.2, 128.4 (2 C), 128.1, 127.6, 126.4, 126.3, 125.9, 125.5, 125.1, 110.3, 88.6, 50.7, 50.0, 38.9, 35.3, 30.9, 22.4; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}O_2Na$ $[(M+Na)^+]$ 393.1830, found 393.1831.

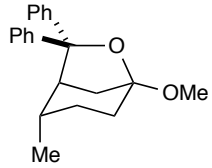


5-(Hydroxydiphenylmethyl)-3,3-dimethylcyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), 3,3-dimethylcyclohexanone (0.52 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in DMPU (1.5 mL) provided the desired product (98.7 mg, 43%) as a colorless oil: IR (film) 3480, 2955, 1701, 1448 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2 H), 7.44–7.39 (m, 2 H), 7.35 (dd, 2 H, J = 8.5, 7.1 Hz), 7.31–7.26 (m, 2 H), 7.26–7.21 (m, 1 H), 7.21–7.15 (m, 1 H), 3.10 (ddt, 1 H, J = 12.7, 11.0, 4.2 Hz), 2.33 (s, 1 H), 2.29–2.21 (m, 1 H), 2.19 (d, 1 H, J = 13.6), 2.16–2.08 (m, 2 H), 1.55–1.52 (m, 1 H), 1.03 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 145.6, 144.9, 128.5, 128.4, 126.9, 126.8, 125.5, 125.3, 79.5, 54.4, 41.8 (2 C), 38.9, 34.5, 32.1, 25.7; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}O_2Na$ [$(M+Na)^+$] 331.1674, found 331.1668.



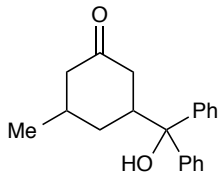
(3*R,4*R**)-3-(hydroxydiphenylmethyl)-4-methylcyclohexan-1-one:** According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol,

1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), 4-methylcyclohexanone (0.45 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (0.13 mL, 7.5 mmol, 10.0 equiv.) in DMPU (1.5 mL) provided the desired product (174.9 mg, 79%) as an inseparable mixture of the title compound and the corresponding hemiacetal in 2:1 ratio, respectively: IR (film) 3413, 2956, 1700, 1448 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2 H), 7.48 (d, 2 H, *J* = 10.0 Hz), 7.37–7.31 (m, 2 H), 7.25–7.17 (m, 6 H), 7.13–7.10 (m, 1 H), 7.08–7.04 (m, 2 H), 2.99 (dd, 1 H, *J* = 5.0 Hz), 2.89 (dt, 0.5 H, *J* = 10.0, 5.0 Hz), 2.55 (s, 1 H), 2.42 (dd, 0.5 H, *J* = 15.0, 5.0 Hz), 2.35 (dd, *J* = 0.5 H, *J* = 15.0, 5.0 Hz), 2.30–2.22 (m, 1 H), 2.16–2.08 (m, 1 H), 1.93 (dt, 1 H, *J* = 10.0, 5.0 Hz), 1.89 (d, 1 H, *J* = 10.0 Hz), 1.84–1.79 (m, 1 H), 1.78–1.70 (m, 3 H), 1.61–1.53 (m, 1 H), 1.52–1.45 (m, 1 H), 1.01–0.97 (m, 1 H), 0.95 (d, 3 H, *J* = 10.0 Hz), 0.86 (d, 1.5 H, 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.1, 148.9, 146.2, 145.8, 143.8, 128.7, 128.3, 128.2, 127.9, 127.0, 126.5, 126.3, 126.1, 125.6, 125.5, 125.4, 124.7, 106.7, 89.6, 81.9, 50.5, 48.7, 39.5, 37.0, 36.6, 34.2, 29.4, 28.0, 27.3, 25.5, 21.5, 19.4; HRMS (ESI) *m/z* calcd for $C_{20}H_{22}O_2Na$ $[(M+Na)^+]$ 317.1517, found 317.1509. The relative stereochemistry was confirmed by a single-crystal X-ray analysis (*vide infra*).



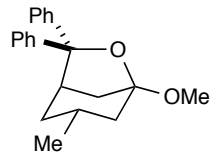
(1*S,2*S**,5*S**)-5-Methoxy-2-methyl-7,7-diphenyl-6-oxabicyclo[3.2.1]octane:** 3-(Hydroxydiphenylmethyl)-4-methylcyclohexan-1-one (22.5 mg, 0.0760 mmol) was dissolved in MeOH (0.3 mL), treated with *p*-TsOH•H_2O (1.1 mg, 5.8 μmol), and stirred

at room temperature for 12 h. The reaction mixture was then diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by chromatography on SiO_2 (5-10% EtOAc in hexanes) gave the desired methyl acetal (22.0 mg, 93%) as a colorless oil: IR (film) 2958, 1599, 1448, 1136 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2 H), 7.55–7.53 (m, 2 H), 7.29–7.24 (m, 4 H), 7.14 (tt, 2 H, *J* = 7.4, 1.2 Hz), 3.25 (s, 3 H), 3.18 (t, 1 H, *J* = 3.7 Hz), 2.10 (dt, 1 H, *J* = 11.5, 2.7 Hz), 2.13–2.06 (m, 1 H), 1.90 (ddt, 2 H, *J* = 9.3, 5.1, 1.4 Hz), 1.75–1.64 (m, 3 H), 1.03 (d, 3 H, *J* = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 144.2, 128.3, 127.8, 126.2, 125.9, 125.6, 125.0, 110.2, 89.1, 50.0, 49.0, 33.0, 30.7, 27.8, 25.3, 19.5; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}O_2Na$ [$(M+Na)^+$] 331.1674, found 331.1668.



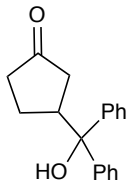
3-(Hydroxydiphenylmethyl)-5-methylcyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), 3-methylcyclohexanone (0.45 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in DMPU (1.5 mL) provided the desired product (164.8 mg, 75%) as a mixture of two diastereomers in *ca.* 1:1 ratio. **Diastereomer 1** (R_f = 0.21 (30% EtOAc in hexanes), mixture of the *trans*-diastereoisomer and the corresponding hemiacetal in 2:1 ratio,

respectively): IR (film) 2958, 1599, 1448, 1136 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63–7.58 (m, 1 H), 7.56–7.51 (m, 1 H), 7.50–7.44 (m, 2 H), 7.44–7.39 (m, 2 H), 7.33 (t, 2 H, *J* = 7.7 Hz), 7.32–7.10 (m, 7 H), 3.26 (q, 0.5 H *J* = 3.5 Hz), 3.20 (tt, 1 H, *J* = 1 H), 2.53–2.42 (m, 2 H), 2.35 (dd, 1 H, *J* = 14.2, 11.1 Hz), 2.23 (s, 1 H), 2.23–2.19 (m, 1 H), 2.17–2.09 (m, 1 H), 2.09–1.97 (m, 1 H), 1.92 (ddd, 1 H, *J* = 15.5, 5.4, 2.4 Hz), 1.78–1.63 (m, 2 H), 1.63–1.54 (m, 2 H), 1.02 (d, 3 H, *J* = 6.8 Hz), 0.75 (d, 1.5 H, *J* = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3, 148.8, 145.7, 145.1, 144.2, 128.5, 128.4, 128.2, 127.9, 126.9, 126.8, 126.2, 125.5, 125.4, 124.7, 106.5, 89.4, 80.1, 47.9, 46.1, 44.3, 42.4, 42.3, 40.8, 35.5, 32.0, 29.2, 26.1, 21.6, 19.8; HRMS (ESI) *m/z* calcd for $C_{20}H_{22}O_2Na$ $[(M+Na)^+]$ 317.1517, found 317.1512. **Diastereomer 2** (R_f = 0.1 (30% EtOAc in hexanes), *cis*-diastereoisomer): IR (film) 3493, 2957, 1704, 1492, 1448, 1267 cm^{-1}; 7.50–7.45 (m, 2 H), 7.43–7.38 (m, 2 H), 7.34 (dd, 2 H, *J* = 8.5, 7.0 Hz), 7.29 (dd, 2 H, *J* = 8.5, 7.0 Hz), 7.26–7.21 (m, 1 H), 7.21–7.16 (m, 1 H), 2.94 (tdd, 1 H, *J* = 11.9, 5.1, 2.9 Hz), 2.38 (ddt, 1 H, *J* = 13.4, 3.2, 1.7 Hz), 2.30–2.18 (m, 3 H), 2.01–1.85 (m, 2 H), 1.79 (dt, 1 H, *J* = 13.4, 2.0 Hz), 1.31–1.19 (m, 2 H), 1.00 (d, 3 H, *J* = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 145.5, 144.7, 128.4 (2 C), 126.9, 126.8, 125.6, 125.4, 79.5, 49.6, 45.1, 42.0, 34.5, 32.5, 22.5; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}O_2Na$ $[(M+Na)^+]$ 317.1517, found 317.1517. The relative stereochemistry was confirmed by a single crystal X-ray analysis (*vide infra*).



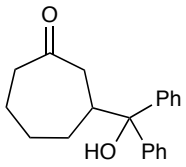
(1*R,3*R**,5*S**)-5-Methoxy-3-methyl-7,7-diphenyl-6-oxabicyclo[3.2.1]octane:** 3-(Hydroxydiphenylmethyl)-5-methylcyclohexan-1-one (18.2 mg, 0.0762 mmol) was

dissolved in MeOH (0.3 mL), treated with *p*-TsOH•H_2O (1.1 mg, 5.8 μmol), and stirred at room temperature for 12 h. The reaction mixture was then diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by chromatography on SiO_2 (5-10% EtOAc in hexanes) gave the desired methyl acetal (18.9 mg, 99%) as a white solid: IR (film) 2953, 1598, 1460, 1330 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2 H), 7.45 (d, 2 H, *J* = 7.8 Hz), 7.23–7.13 (m, 4 H), 7.04 (dt, 2 H, *J* = 7.2, 3.4 Hz), 3.30 (q, 1 H, *J* = 3.6 Hz), 3.21 (s, 3 H), 2.20 (ddt, 1 H, *J* = 10.6, 4.8, 2.4 Hz), 2.07 (ddd, 1 H, *J* = 12.9, 6.4, 2.8 Hz), 1.79–1.77 (m, 1 H), 1.67 (ddt, 1 H, *J* = 18.0, 12.2, 5.6 Hz), 1.32 (d, 1 H, *J* = 10.9 Hz), 1.20 (dd, 1 H, *J* = 13.0, 11.0 Hz), 1.07 (ddd, 1 H, *J* = 13.8, 11.5, 2.8 Hz), 0.66 (d, 3 H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 144.6, 128.2, 127.8, 126.2, 126.0, 125.4, 124.9, 109.9, 88.9, 50.1, 44.7, 42.9, 36.9, 36.1, 25.9, 21.8; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}O_2Na$ [$(M+Na)^+$] 331.1674, found 331.1671.



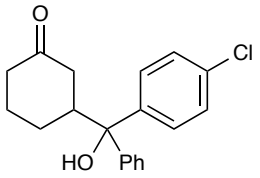
3-(Hydroxydiphenylmethyl)cyclopentan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclopentanone (0.33 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2 equiv.) in DMPU (1.5 mL) provided the desired product (129.3 mg, 65%) as a colorless oil: IR (film) 3466, 2924, 1731, 1172

cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2 H), 7.37–7.33 (m, 2 H), 7.25 (ddd, 4 H, *J* = 13.2, 8.5, 7.0 Hz), 7.19–7.12 (m, 2 H), 3.31 (tt, 1 H, *J* = 9.5, 7.6 Hz), 2.33–2.07 (m, 5 H), 1.87–1.73 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 218.9, 146.1, 145.7, 128.4, 128.3, 127.1, 127.0, 125.7, 125.6, 78.8, 45.1, 40.6, 38.5, 24.0; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}O_2Na$ [$(M+Na)^+$] 289.1204, found 289.1197.



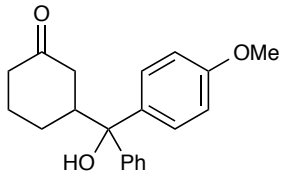
3-(Hydroxydiphenylmethyl)cycloheptan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), benzophenone (138.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cycloheptanone (0.45 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2 equiv.) in DMPU (1.5 mL) provided the desired product (24.0 mg, 11%) as a colorless oil. The product was isolated as an inseparable mixture of the title compound and the corresponding hemiacetal in *ca.* 6:1 ratio: IR (film) 3429, 2932, 1695, 1449, 1008 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66–7.58 (m, 2 H), 7.42–7.38 (m, 2 H), 7.25–7.21 (m, 2 H), 7.20–7.13 (m, 2 H), 7.10–7.03 (m, 2 H), 3.30 (dt, 1 H, *J* = 6.5, 3.6 Hz), 2.47–2.33 (m, 1 H), 2.26 (d, 1 H, *J* = 10.0 Hz), 2.07–1.96 (m, 1 H), 1.93 (ddt, 1 H, *J* = 13.6, 6.5, 1.6 Hz), 1.79 (ddd, *J* = 13.6, 5.6, 3.0 Hz), 1.72–1.60 (m, 1 H), 1.47–1.39 (m, 2 H), 1.28–1.18 (3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.6, 148.5, 143.6, 128.6, 127.9, 126.7, 125.9, 125.5, 124.9, 108.5, 89.6, 43.7, 41.8, 38.4,

30.0, 23.9, 23.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{21}ONa$ [$(M–H_2O+Na)^+$] 277.1592, found 277.1589.

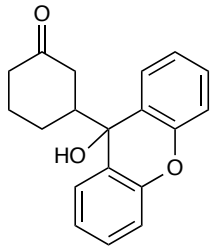


3-((4-Chlorophenyl)(hydroxy)(phenyl)methyl)cyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), 4-chlorobenzophenone (162.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclohexanone (0.39 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2 equiv.) in DMPU (1.5 mL) provided the desired product (191.0 mg, 81%) as an inseparable mixture of two diastereomeric alcohols (1:1 ratio), and the corresponding hemiacetals (20% with respect to the open form): IR (film) 3466, 2950, 1701, 1490, 1094 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59–7.57 (m, 0.4 H), 7.57–7.54 (m, 0.4 H), 7.53-7.51 (m, 0.4 H), 7.51-7.48 (m, 0.4 H), 7.45 (dd, 2 H, J = 7.6, 1.7 Hz), 7.42–7.38 (m, 3.9 H), 7.36–7.31 (m, 4.2 H), 7.31–7.14 (m, 9.8 H), 2.88 (dddd, 2 H, J = 13.3, 10.5, 5.4, 2.8 Hz), 2.40 (ddt, 2 H, J = 14.7, 5.1, 2.3), 2.35–2.14 (m, 7.8 H), 2.10 (ddt, 2 H, J = 13.2, 6.3, 3.1 Hz), 2.03–1.61 (m, 6.3 H), 1.54–1.33 (m, 3.4 H); ^{13}C NMR (125 MHz, $CDCl_3$) major peaks (mixture of diastereomeric alcohols): δ 212.0 (2 C), 145.2, 144.4, 144.2, 143.3, 128.7, 128.6, 128.5 (2 C), 127.2 (3 C), 127.0, 125.6 (2 C), 125.4 (2 C), 79.6, 79.5, 46.1 (2 C), 42.8, 42.7, 41.2 (2 C), 25.8, 25.7, 24.8 (2 C); minor peaks (mixture of hemiacetals): δ 148.2, 147.4, 143.7, 142.8, 132.7 (2 C), 128.4 (2 C), 128.1, 128.0, 126.9, 126.5, 126.4, 126.3, 125.3, 124.6,

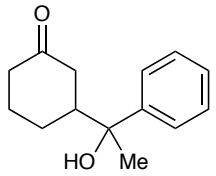
106.8 (2 C), 69.0 (2 C), 44.6, 44.5, 42.6, 42.4, 37.4, 37.2, 26.4, 26.3, 19.2 (2 C); HRMS (ESI) *m/z* calcd for $C_{19}H_{19}ClO_2Na$ [$(M+Na)^+$] 337.0971, found 337.0965.



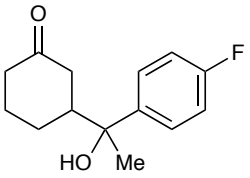
3-(Hydroxy(4-methoxyphenyl)(phenyl)methyl)cyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,N]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), 4-methoxybenzophenone (159.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclohexanone (0.39 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2 equiv.) in DMPU (1.5 mL) provided the desired product (130.5 mg, 56%) as an inseparable mixture of two diastereomeric alcohols (1:1 ratio) with *ca.* 15% of the corresponding hemiacetals: IR (film) 3481, 2949, 1702, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2.3 H), 7.42–7.36 (4.4 H), 7.36–7.26 (m, 8.5 H), 7.26–7.18 (m, 2.8 H), 6.91–6.82 (m, 4.5 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.77 (s, 0.4 H), 3.76 (s, 0.4 H), 2.90 (dt, 1 H, J = 4.8, 3.1 Hz), 2.89 (dt, 1 H, J = 4.8, 3.1 Hz), 2.42–2.38 (m, 2 H), 2.33–2.23 (7 H), 2.16–2.08 (m, 2 H), 1.91–1.76 (m, 3 H), 1.76–1.63 (m, 3 H), 1.53–1.45 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.4 (2 C), 158.3 (2 C), 145.8, 144.9, 137.7, 136.7, 128.3 (2 C), 126.9 (2 C), 126.8 (2 C), 125.6, 125.4, 113.7 (2 C), 79.5 (2 C), 55.2 (2 C), 46.3 (2 C), 42.9 (2 C), 41.2 (2 C), 25.9, 25.8, 24.9, 24.8; HRMS (ESI) *m/z* calcd for $C_{20}H_{22}O_3Na$ [$(M+Na)^+$] 333.1467, found 333.1467.



3-(9-Hydroxy-9*H*-xanthen-9-yl)cyclohexan-1-one: According to general procedure A, tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.010 equiv.), DABCO (168.0 mg, 1.500 mmol, 2.000 equiv.), $LiAsF_6$ (147.0 mg, 0.7500 mmol, 1.000 equiv.), 9-xanthene-9-one (147.3 mg, 0.7500 mmol, 1.000 equiv.), azepane (18.0 μL, 0.150 mmol, 0.200 equiv.), cyclohexanone (0.39 mL, 3.7 mmol, 5.0 equiv.), acetic acid (9.0 μL, 0.15 mmol, 0.20 equiv.) and water (27 μL, 1.5 mmol, 2 equiv.) in DMPU (2.0 mL) provided the desired product (155.1 mg, 70%) a white solid: IR (film) 3395, 2927, 1604, 1476, 1450 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, 1 H, *J* = 7.8, 1.6 Hz), 7.61 (dd, 1 H, *J* = 7.8, 1.6 Hz), 7.40–7.31 (m, 2 H), 7.20 (dq, 2 H, *J* = 7.2, 1.2 Hz), 7.15 (d, 2 H, *J* = 8.2 Hz), 2.36 (ddt, 1 H, *J* = 13.8, 3.7, 2.2 Hz), 2.23–2.19 (m, 1 H), 2.13 (tt , 1 H, *J* = 12.2, 3.2 Hz), 2.07–1.98 (m, 1 H), 1.97–1.91 (m, 1 H), 1.88 (d, 1 H, *J* = 13.7 Hz), 1.86–1.79 (m, 1 H), 1.66 (s, 1 H), 1.43 (qt, 1 H, *J* = 13.5, 3.9 Hz), 1.10 (dq, 1 H, *J* = 12.9, 3.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) 211.6, 151.0 (2 C), 129.2, 129.2, 126.7, 126.6, 126.0, 125.8, 123.4 (2 C), 116.2, 116.1, 71.0, 52.4, 42.5, 41.1, 25.2, 24.6; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_3Na$ [$(M+Na)^+$] 317.1154, found 317.1140.

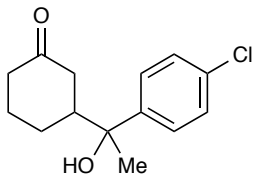


3-(1-Hydroxy-1-phenylethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), acetophenone (87 μL, 0.75 mmol, 1.0 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (126.3 mg, 77%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3456, 2946, 1702, 1447 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.33 (m, 8 H), 7.29–7.25 (m, 2 H), 2.56 (ddt, 1 H, J = 13.9, 4.2, 2.2 Hz), 2.35–2.30 (m, 2 H), 2.28–1.96 (m, 10 H), 1.65–1.27 (m, 7 H), 1.62 (s, 3 H), 1.56 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.5, 212.4, 146.7, 146.2, 128.2 (2 C), 126.9, 126.8, 125.0 (2 C), 75.9, 75.7, 49.4, 49.3, 42.9, 42.8, 41.2, 41.1, 27.8, 27.6, 25.7, 25.3, 24.9 (2 C); HRMS (ESI) *m/z* calcd for $C_{14}H_{18}O_2Na$ [(M+Na)$^+$] 241.1204, found 241.1193.



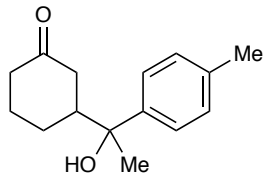
3-(1-(4-Fluorophenyl)-1-hydroxyethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 4'-fluoroacetophenone (90 μL, 0.75 mmol, 1.0 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10.0 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0

equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (114.7 mg, 65%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3447, 2942, 2868, 1704, 1508, 1224 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4 H), 7.00–6.91 (m, 4 H), 2.44 (dddd, 1 H, J = 13.9, 4.0, 2.1 Hz), 2.29–2.24 (m, 2 H), 2.21–1.89 (m, 10 H), 1.53 (s, 3 H), 1.48 (s, 3 H), 1.57–1.29 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.2 (2 C), 162.6 (d, J = 2.5 Hz), 160.7 (d, J = 2.5 Hz), 142.4 (d, J = 3.75 Hz), 142.0 (d, J = 2.5 Hz), 126.8 (d, J = 5.0 Hz), 126.7 (d, J = 5.0 Hz), 115.0 (d, J = 1.25 Hz), 114.8 (d, J = 1.25 Hz), 75.6, 75.4, 49.5 (2 C), 42.9, 42.8, 41.2, 41.1, 27.9, 27.7, 25.7, 25.3, 24.9 (2 C); HRMS (ESI) *m/z* calcd for $C_{14}H_{17}FO_2Na$ [$(M+Na)^+$] 259.1110, found 259.1109.

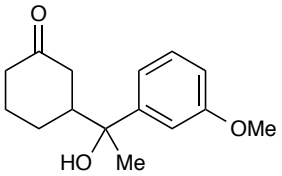


3-(1-(4-Chlorophenyl)-1-hydroxyethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 4'-chloroacetophenone (96 μL, 0.75 mmol, 1.0 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (116.1 mg, 65%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3449, 2949, 1701, 1490, 1094 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 8 H), 2.53 (ddt, 1 H, J = 14.1, 4.1, 2.1 Hz), 2.38–2.30 (m, 2 H), 2.28–2.17 (m, 4 H), 2.16–1.96 (m, 7 H), 1.62–1.30 (m, 9 H), 1.60 (s, 3 H), 1.54 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.2, 212.1, 145.2, 144.8, 132.7, 132.6, 128.3, 128.2, 126.6, 126.5, 75.6, 75.4, 49.3 (2 C), 42.8, 42.7, 41.1 (2

C), 27.8, 27.7, 25.6, 25.2, 24.8 (2 C); HRMS (ESI) *m/z* calcd for $C_{14}H_{17}ClO_2Na$ [$(M+Na)^+$] 275.0815, found 275.0813.

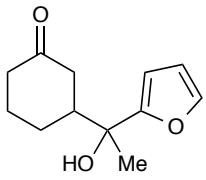


3-(1-Hydroxy-1-(*p*-tolyl)ethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 4'-methylacetophenone (100 μL, 0.750 mmol, 1.00 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (137.4 mg, 79%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3452, 2938, 2867, 1699, 1512, 818 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.25 (m, 4 H), 7.18 (t, 4 H, J = 8.5 Hz), 2.55 (ddt, 1 H, J = 14.1, 4.2, 2.1 Hz), 2.38 (s, 3 H), 2.37 (s, 3 H), 2.41–1.99 (m, 11 H), 1.79 (m, 2 H), 1.76–1.63 (m, 2 H), 1.62 (s, 3 H), 1.57 (s, 3 H), 1.63–1.26 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6 (2 C), 143.7, 143.2, 136.4 (2 C), 128.8 (2 C), 124.9 (2 C), 75.7, 75.6, 49.5, 49.4, 43.0, 42.9, 41.2, 41.1, 27.7, 27.5, 25.7, 25.4, 25.0 (2 C), 20.9 (2 C); HRMS (ESI) *m/z* calcd for $C_{15}H_{20}O_2Na$ [$(M+Na)^+$] 255.1361, found 255.1357.



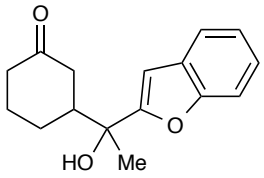
3-(1-Hydroxy-1-(3-methoxyphenyl)ethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg,

2.250 mmol, 3.000 equiv.), 3'-methoxyacetophenone (103 μL, 0.750 mmol, 1.00 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (135.2 mg, 73%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3450, 1701, 1583, 1254, 1043 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2 H), 7.00–6.95 (m, 2 H), 6.95–6.89 (m, 2 H), 6.83–6.77 (m, 2 H), 3.83 (s, 3 H), 3.82 (3 H), 2.57–2.50 (m, 1 H), 2.38–2.28 (m, 3 H), 2.28–1.97 (m, 9 H), 1.70 (d, 2 H J = 4.4 Hz), 1.67–1.61 (m, 2 H), 1.60 (s, 3 H), 1.54 (s, 3 H), 1.56–1.32 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 212.4, 159.5 (2 C), 148.6, 148.1, 129.2 (2 C), 117.4, 117.3, 111.6, 111.5, 111.4, 111.3, 75.8, 75.7, 55.2 (2 C), 49.3, 49.2, 42.9, 42.8, 41.2, 41.1, 27.8, 27.6, 25.7, 25.3, 24.9 (2 C); HRMS (ESI) *m/z* calcd for $C_{15}H_{20}O_3Na$ [$(M+Na)^+$] 271.1310, found 271.1300.

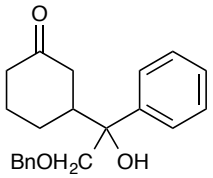


3-(1-(Furan-2-yl)-1-hydroxyethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 2-acetylfuran (82.0 mg, 0.750 mmol, 1.00 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (108.1 mg, 69%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 3441, 2939, 1706, 1450 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (dt, 2 H, J = 1.7, 0.9 Hz), 6.33 (dd, 2 H, J = 3.2, 1.8 Hz), 6.22 (ddd, 2 H, J

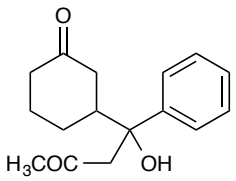
= 3.1, 2.1, 0.9 Hz), 2.44–2.32 (m, 4 H), 2.28–2.13 (m, 6 H), 2.13–2.06 (m, 3 H), 1.90–1.86 (m, 2 H), 1.64–1.55 (m, 2 H), 1.54 (s, 3 H), 1.53 (s, 3 H), 1.44–1.39 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 211.9, 158.3, 158.2, 141.7 (2 C), 110.2 (2 C), 105.6 (2 C), 73.4, 73.3, 48.1, 47.9, 42.9 (2 C), 41.3, 41.2, 23.7 (2 C), 25.0, 24.9, 24.2, 23.9; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}O_3Na$ [$(M+Na)^+$] 271.1310, found 271.1300.



3-(1-(Benzofuran-2-yl)-1-hydroxyethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 2-acetylbenzfuran (120.0 mg, 0.7500 mmol, 1.000 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (108.6 mg, 56%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 2937, 1706, 1454, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, 1 H, *J* = 1.9 Hz), 7.54 (t, 1 H, *J* = 1.9 Hz), 7.46 (dd, 1 H, *J* = 3.4, 1.1 Hz), 7.44 (dd, 1 H, *J* = 3.4, 1.1 Hz), 7.30–7.22 (m, 4 H), 6.64 (d, 1 H, *J* = 0.9 Hz), 6.63 (d, 1 H, *J* = 0.9 Hz), 2.50–2.44 (m, 1 H), 2.44–2.04 (m, 14 H), 2.01–1.95 (m, 1 H), 1.91–1.83 (m, 1 H), 1.65 (s, 3 H), 1.62 (s, 3 H), 1.56–1.46 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 211.6, 161.2, 161.0, 154.6 (2 C), 128.0 (2 C), 124.1, 124.0, 122.9 (2 C), 120.9 (2 C), 111.2 (2 C), 102.4, 102.3; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_3Na$ [$(M+Na)^+$] 281.1154, found 281.1149.



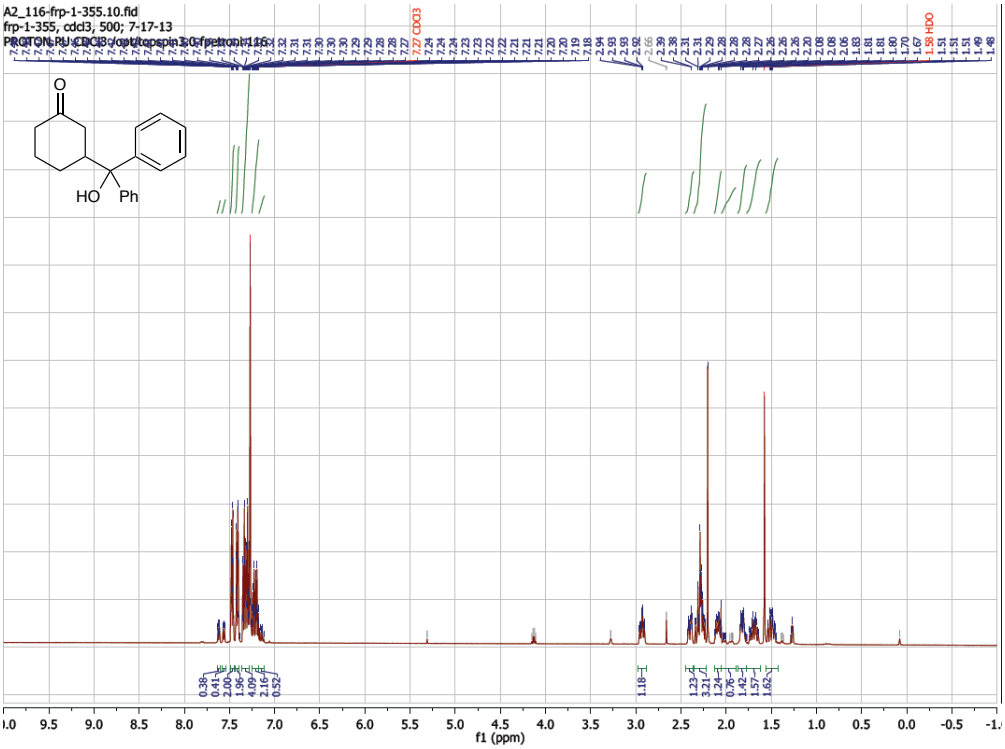
3-(2-(benzyloxy)-1-hydroxy-1-phenylethyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 2-(benzyloxy)-1-phenylethan-1-one (169.5 mg, 0.7500 mmol, 1.000 equiv.), azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (131.2 mg, 54%) as an inseparable mixture of two diastereomers (1:1 ratio): IR (film) 2933, 1706, 1450, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.26 (m, 16 H), 7.20 (dt, *J* = 8.3, 7.6, 6.1 Hz, 4 H), 4.60–4.44 (m, 4 H), 3.83–3.69 (m, 4 H), 3.02 (s, 1 H), 2.96 (s, 1 H), 2.30 (ddq, *J* =12.3, 4.1, 2.2 Hz, 2 H), 2.27–2.03 (m, 9 H), 1.97 (ddt, *J* = 12.5, 6.2, 3.1 Hz), 1.60–1.30 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 212.0, 142.8, 142.3, 128.4 (2 C), 128.1, 128.0 (2 C), 127.9, 127.7 (2 C), 127.1, 127.0, 125.5, 74.8, 74.7, 73.5 (2 C), 46.5, 46.4, 42.9, 42.8, 41.2 (2 C), 25.6, 25.3, 25.0 (2 C); HRMS (ESI) *m/z* calcd for $C_{21}H_{24}O_3Na$ [$(M+Na)^+$] 347.1623, found 347.1614.

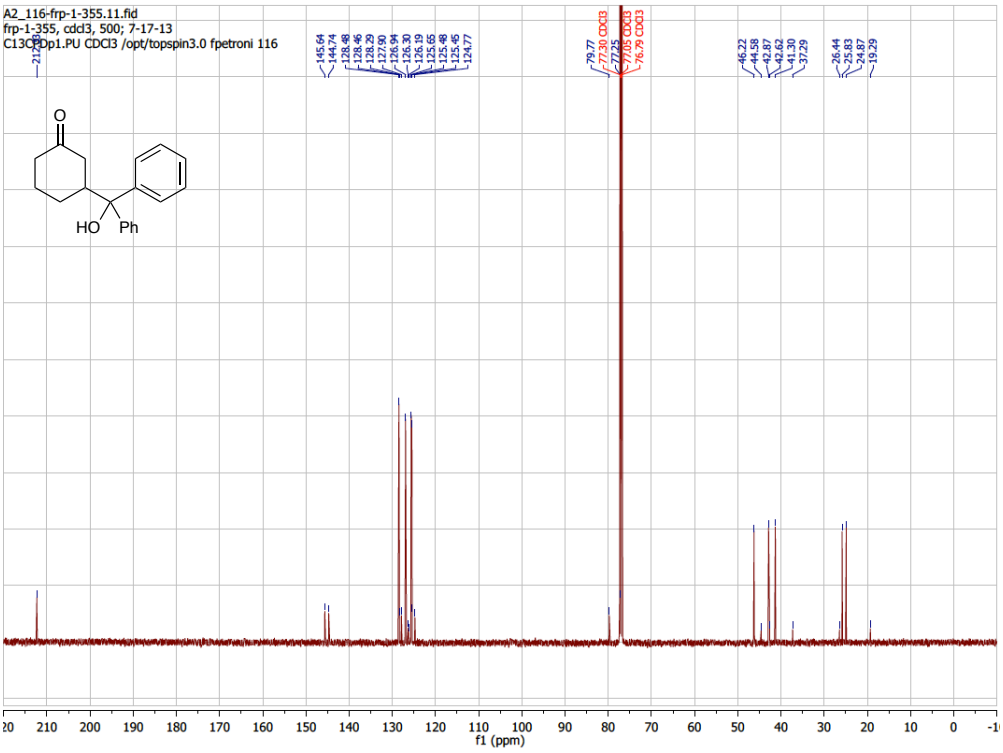


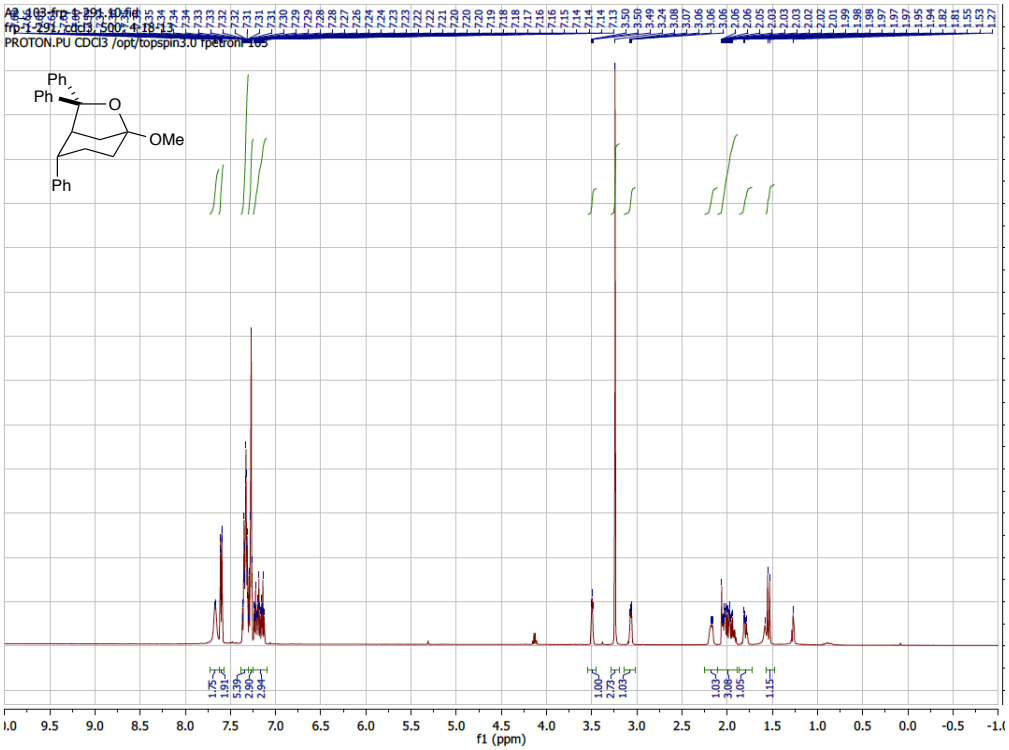
3-(1-hydroxy-3-oxo-1-phenylbutyl)cyclohexan-1-one: According to general procedure B, Ir(*p*-MeO-ppy)$_3$ (5.7 mg, 7.5 μmol, 0.010 equiv.), DABCO (252.0 mg, 2.250 mmol, 3.000 equiv.), 1,3-diphenyl-1,3-propandione (168.0 mg, 0.7500 mmol, 1.000 equiv.),

azepane (36.0 μL, 0.300 mmol, 0.400 equiv.), cyclohexanone (0.78 mL, 7.5 mmol, 10 equiv.), acetic acid (18.0 μL, 0.300 mmol, 0.400 equiv.) and water (27 μL, 1.5 mmol, 2.0 equiv.) in CH_3CN (4.5 mL) provided the desired alcohol (123.5 mg, 52%) as a mixture of two diastereomers (1.1:1 ratio). **Diastereomer 1**: IR (film) 3466, 2942, 1706, 1667, 1448, 1218 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83–7.77 (m, 2 H), 7.58–7.52 (m, 1 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.38–7.34 (m, 2 H), 7.18–7.12 (m, 1 H), 5.01 (s, 1 H), 3.95 (d, *J* = 16.9 Hz, 1 H), 3.16 (d, *J* = 16.9 Hz, 1 H), 2.66–2.57 (m, 1 H), 2.55–2.44 (m, 1 H), 2.32 (ddq, *J* = 14.4, 4.2, 1.8 Hz), 2.28–2.19 (m, 1 H), 2.15–2.05 (m, 1 H), 1.98 (ddd, *J* = 12.9, 6.1, 3.0 Hz), 1.56–1.38 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 202.0, 144.8, 136.8, 133.9, 128.7, 128.2, 128.0, 126.8, 125.3, 49.4, 44.7, 43.0, 41.3, 25.1, 25.0; HRMS (ESI) *m/z* calcd for $C_{21}H_{22}O_3Na$ $[(M+Na)^+]$ 345.1467, found 347.1458. **Diastereomer 2**: IR (film) 3463, 2943, 1704, 1666, 1448, 1219 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2 H), 7.61–7.54 (m, 1 H), 7.48–7.41 (m, 2 H), 7.35 (d, *J* = 7.3 Hz, 2 H), 7.30–7.23 (m, 3 H), 7.22–7.08 (m, 1 H), 5.08 (s, 1 H), 4.03 (d, *J* = 16.9 Hz, 1 H), 3.27 (d, *J* = 16.9 Hz, 1 H), 2.48–1.94 (m, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.2, 201.8, 144.0, 136.8, 133.8, 128.7, 128.2, 128.0, 126.9, 125.2, 49.3, 44.9, 42.3, 41.1, 25.4, 24.9; HRMS (ESI) *m/z* calcd for $C_{21}H_{22}O_3Na$ $[(M+Na)^+]$ 345.1467, found 347.1461.

3. Spectral Data



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OMe
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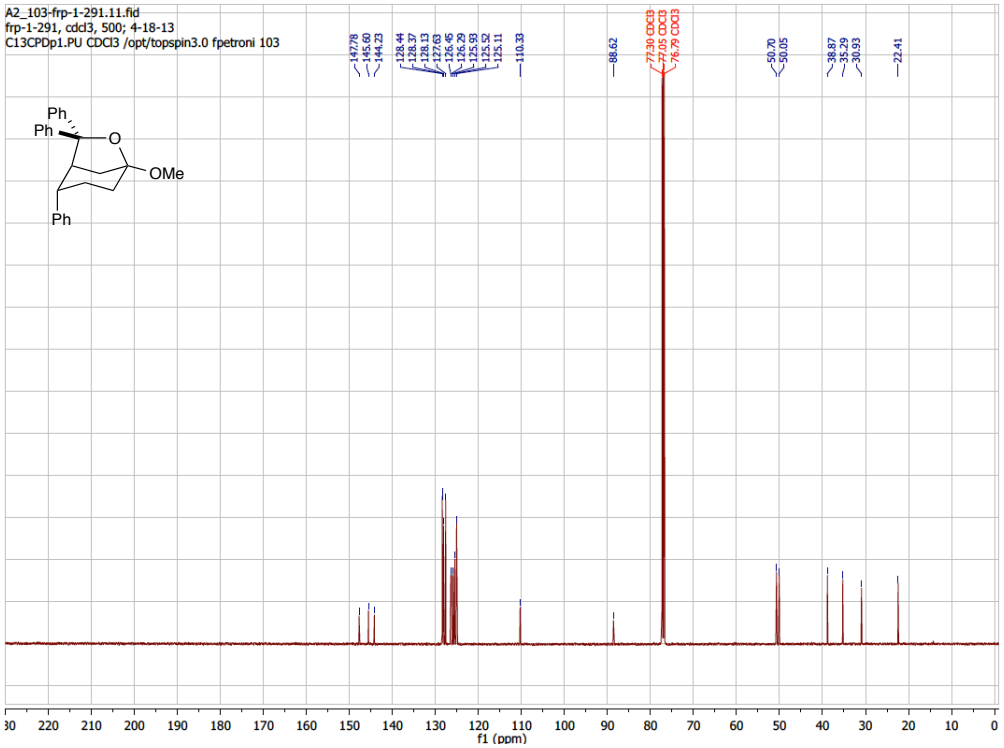
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OMe
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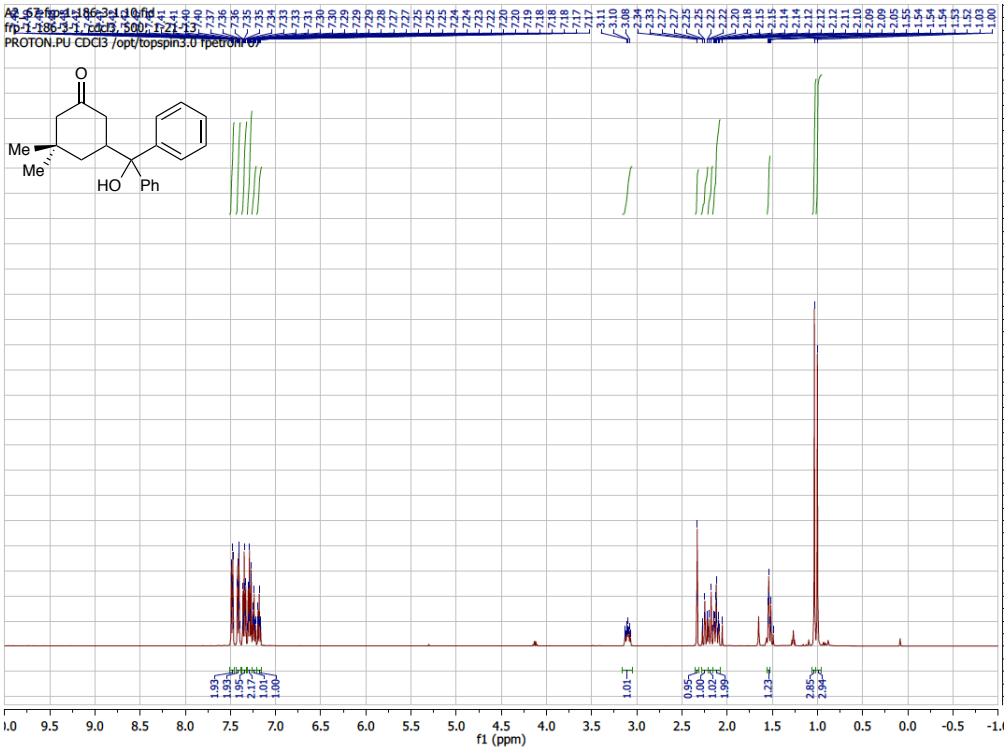
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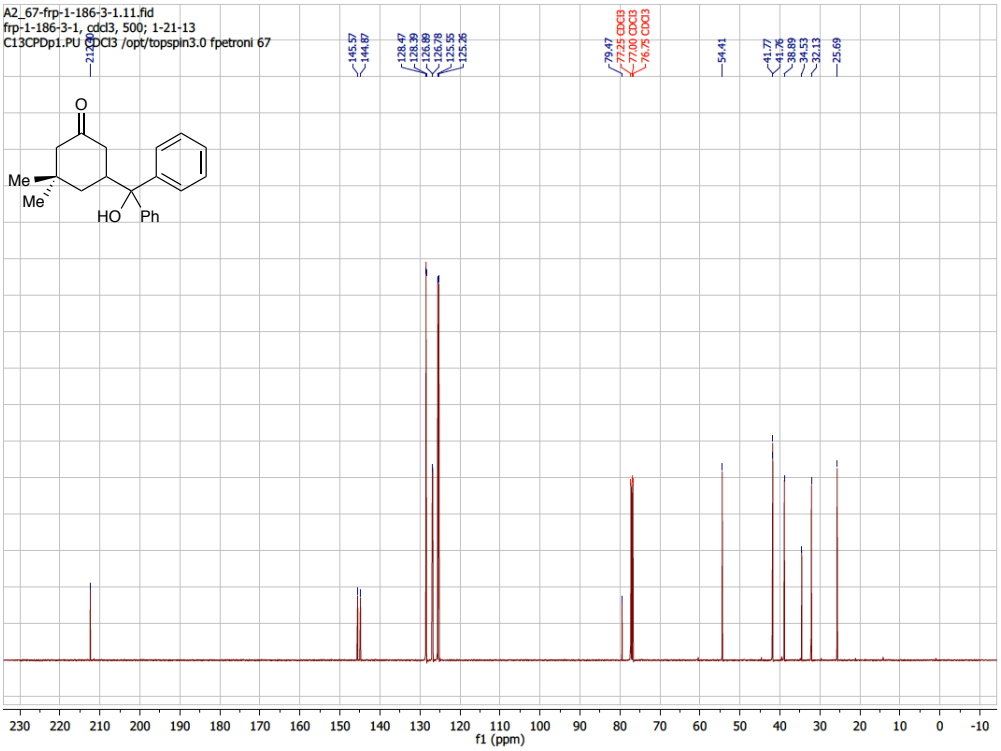
f1 (ppm)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144.87
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126.78
125.55
125.26
79.47
77.25 CDCl3
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76.75 CDCl3
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Ph
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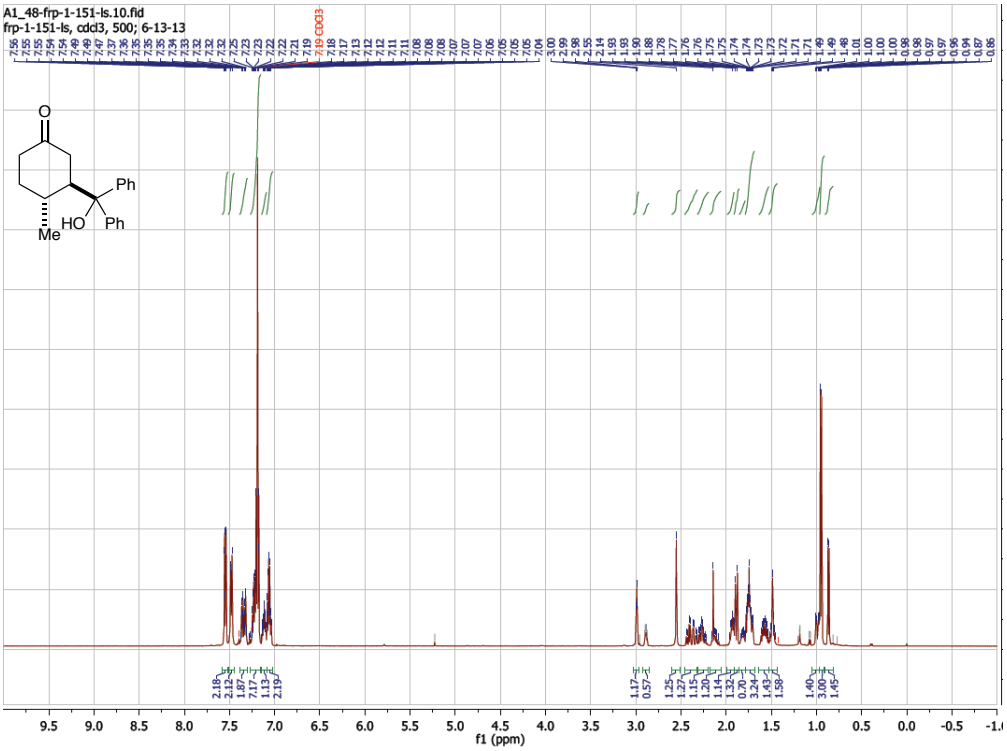
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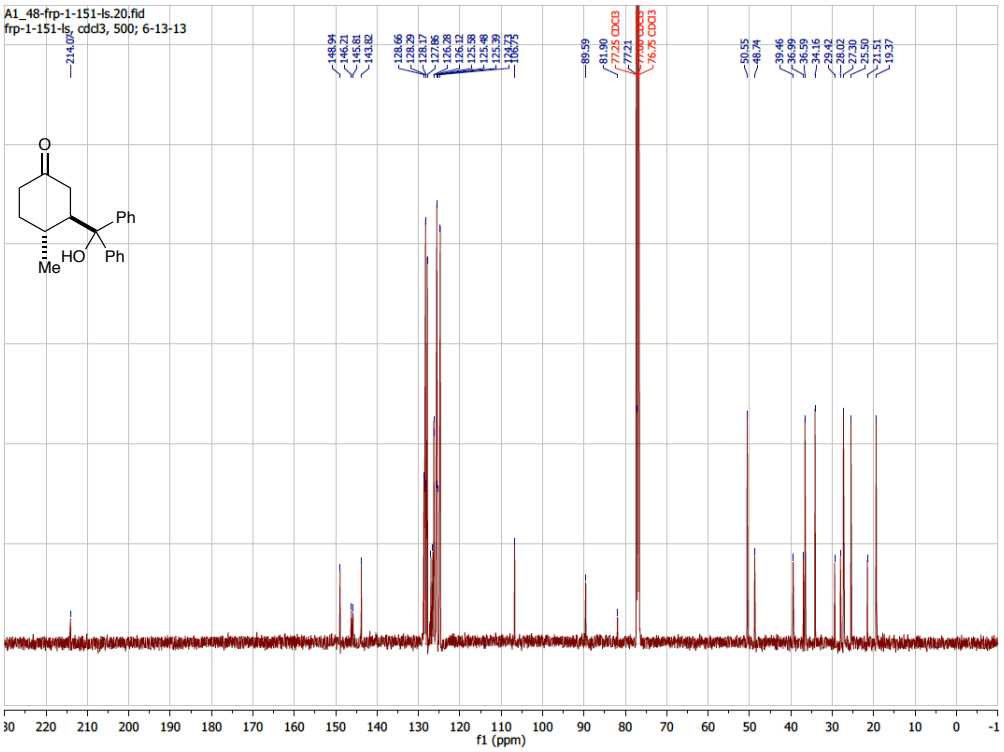
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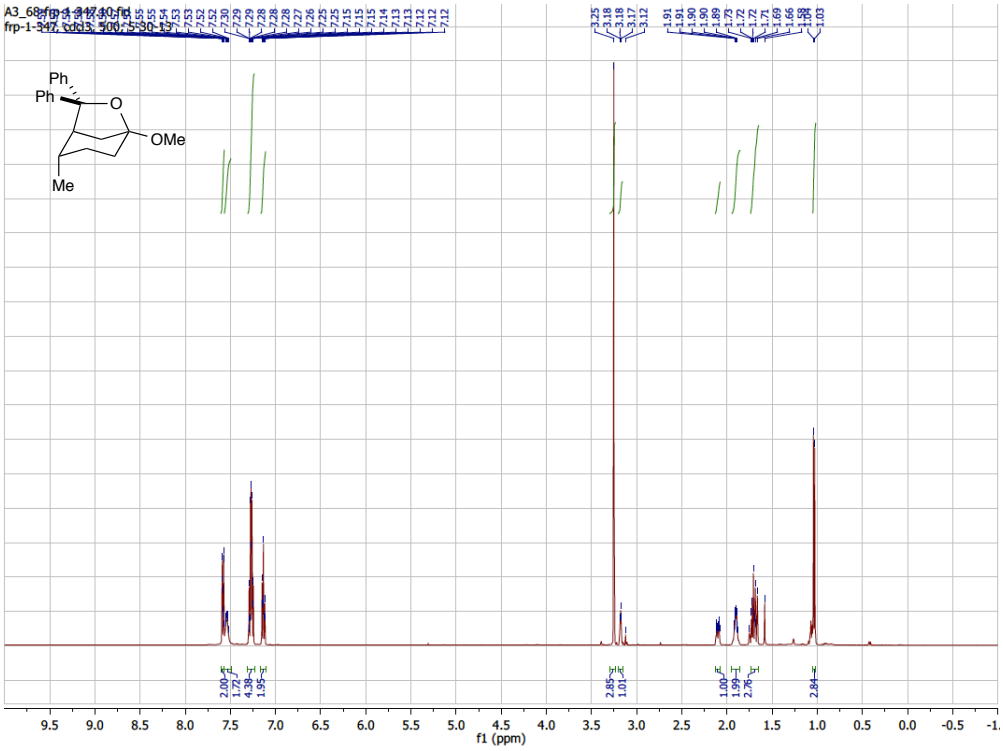
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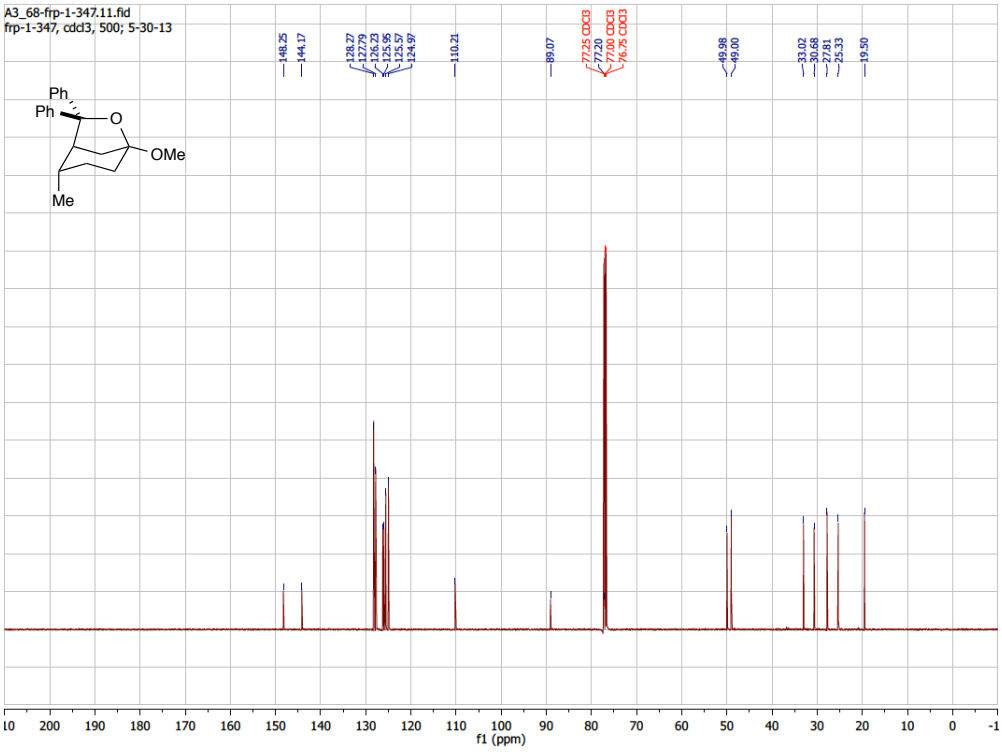
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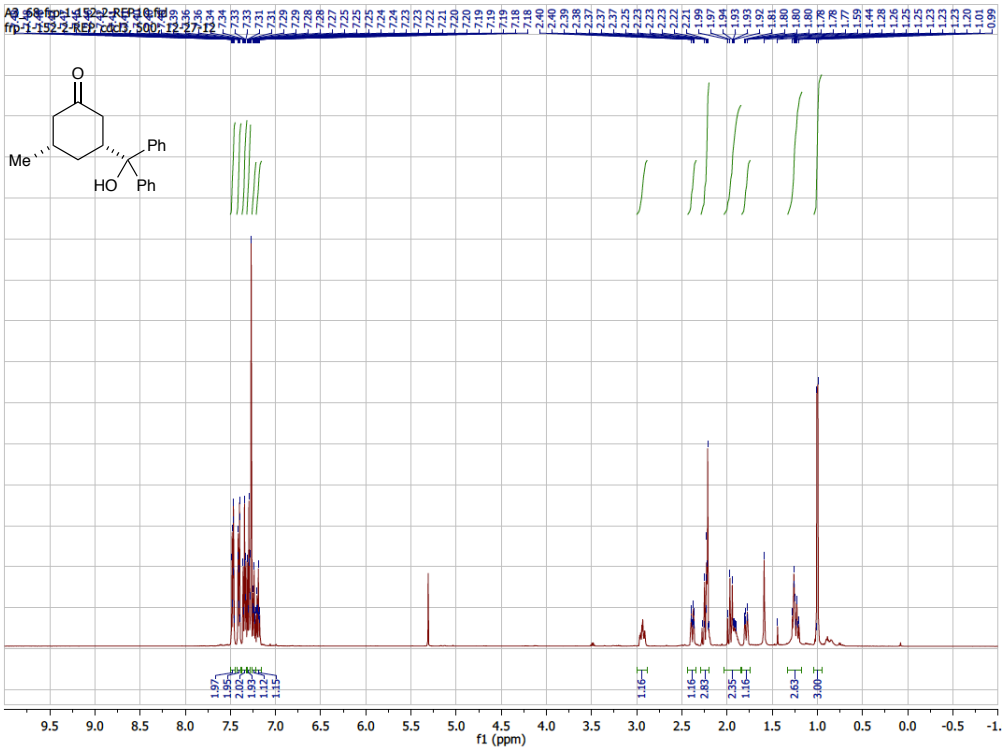
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Ph
HO
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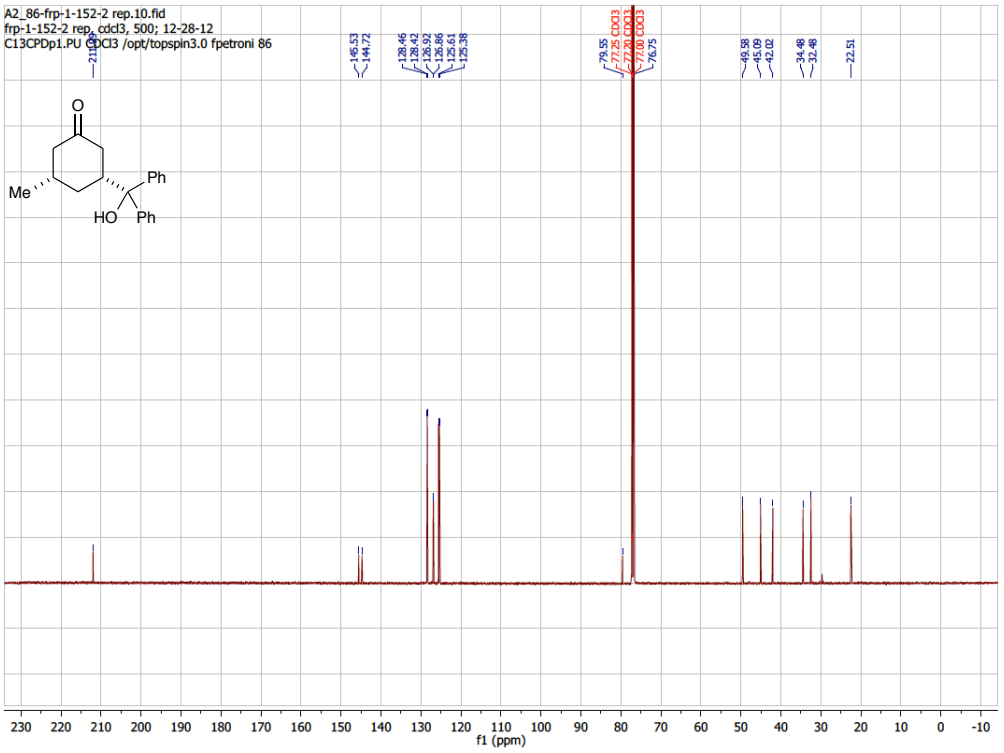
f1 (ppm)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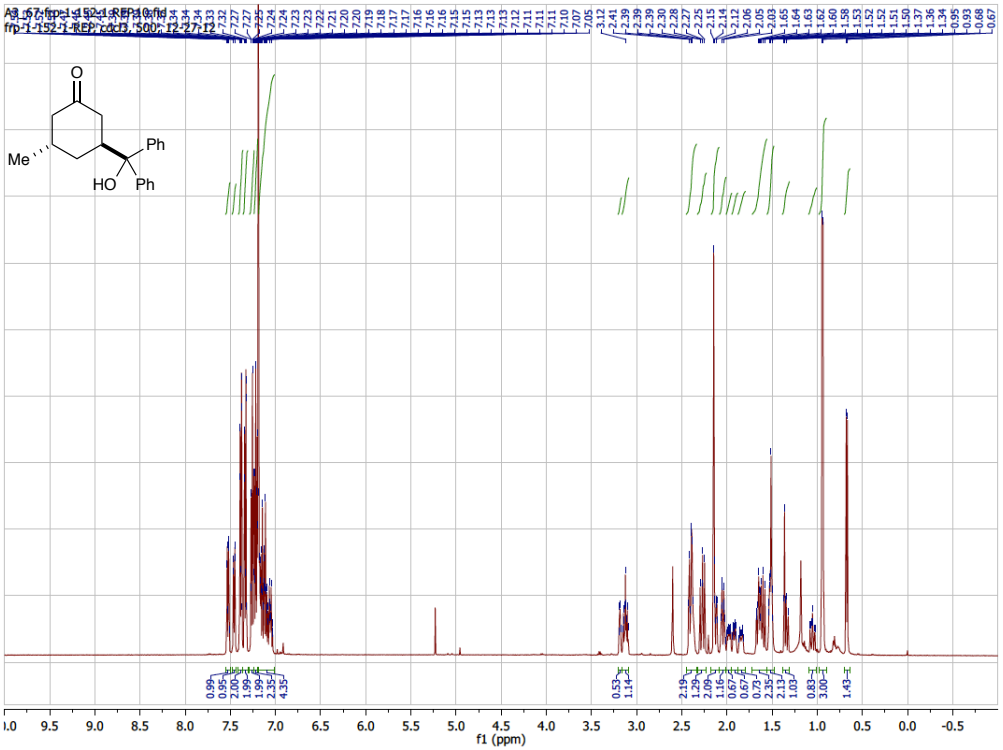
HO
Ph
f1 (ppm)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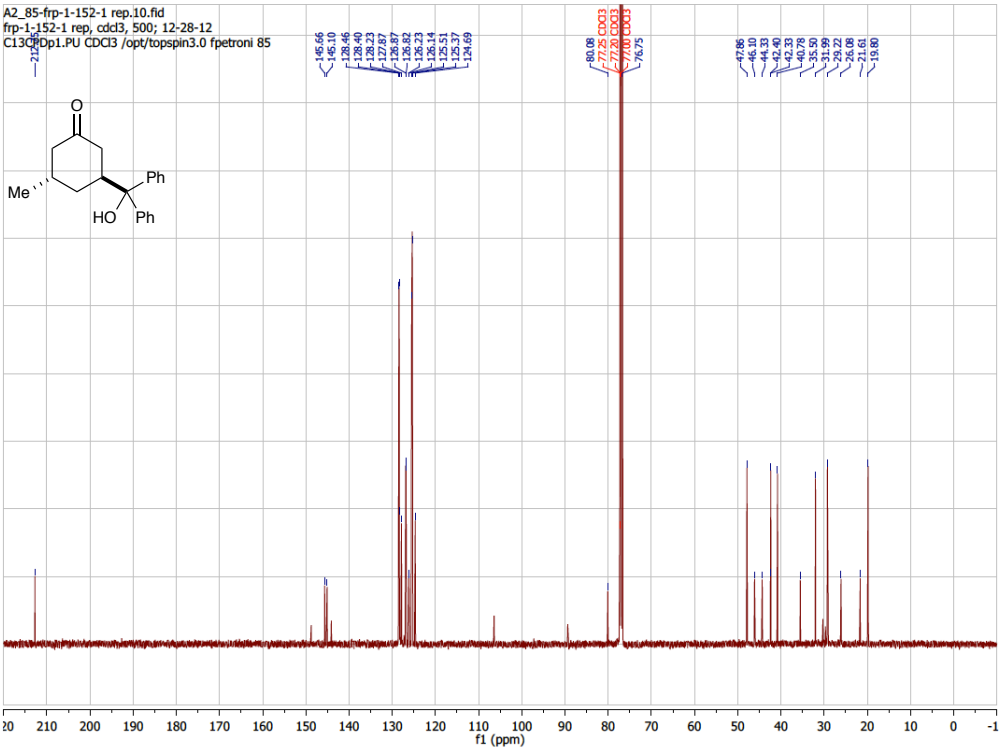
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Ph
HO
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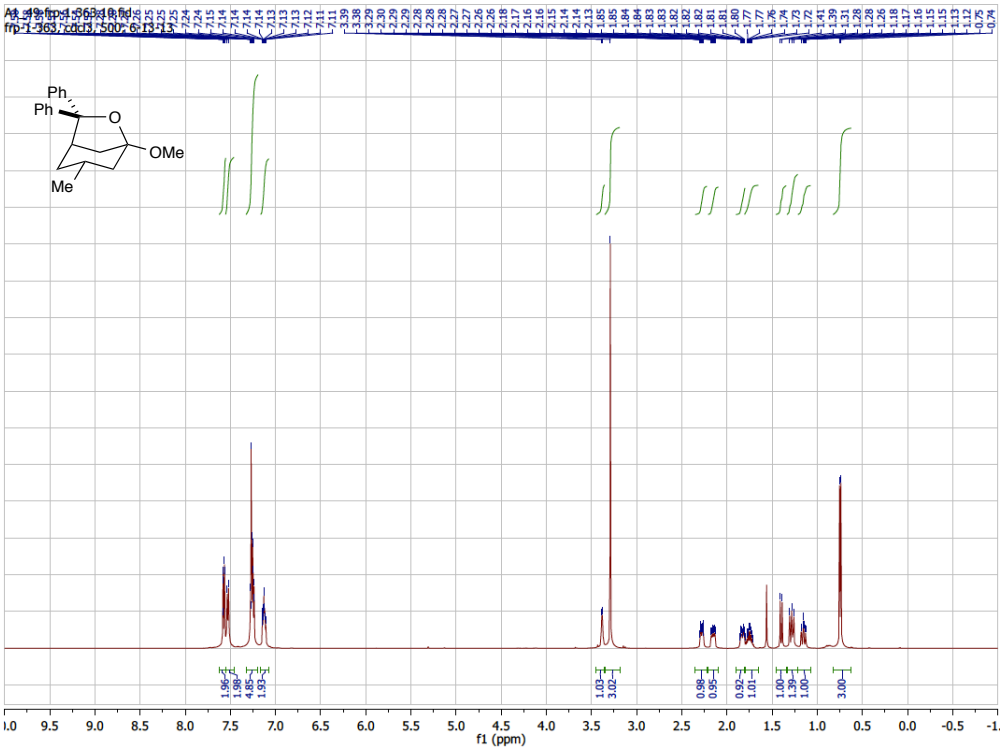
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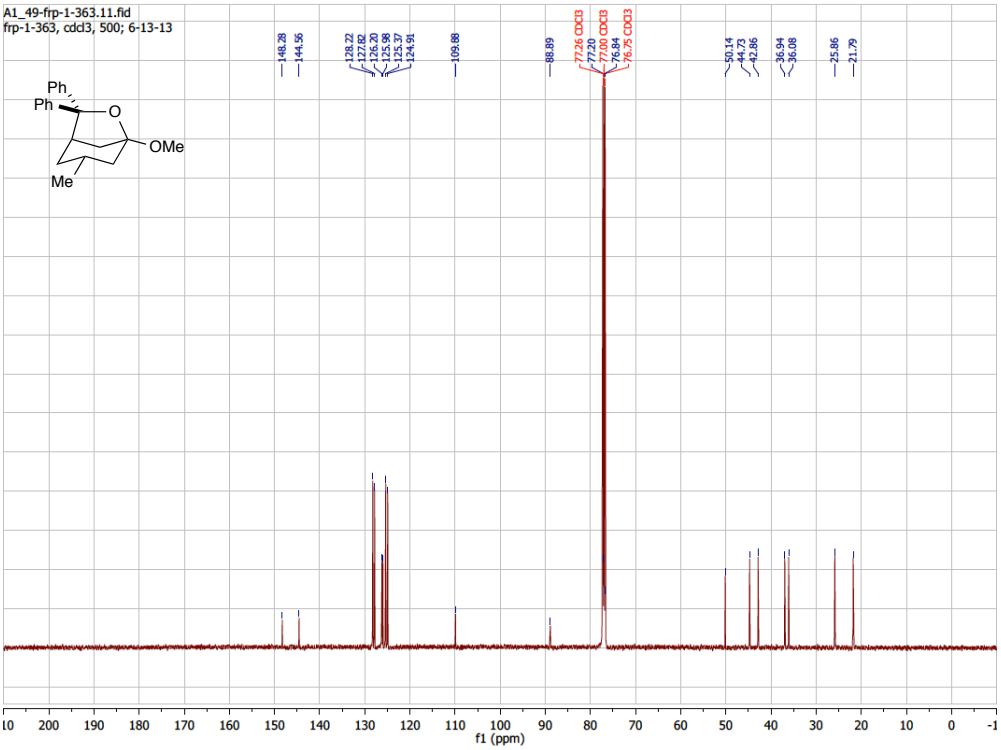
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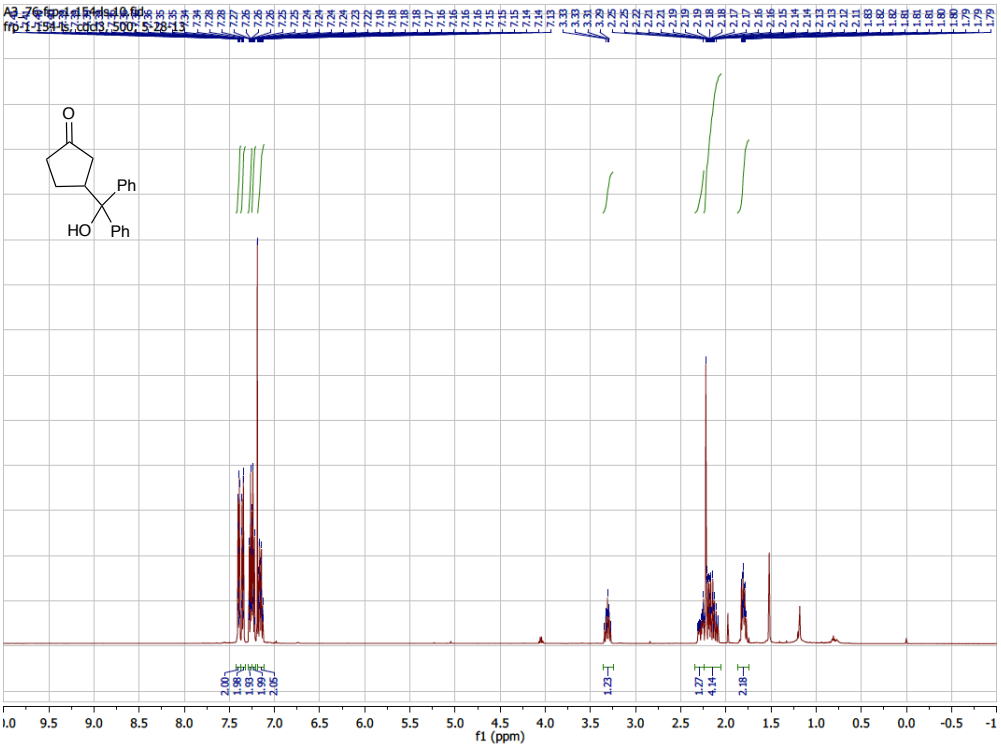
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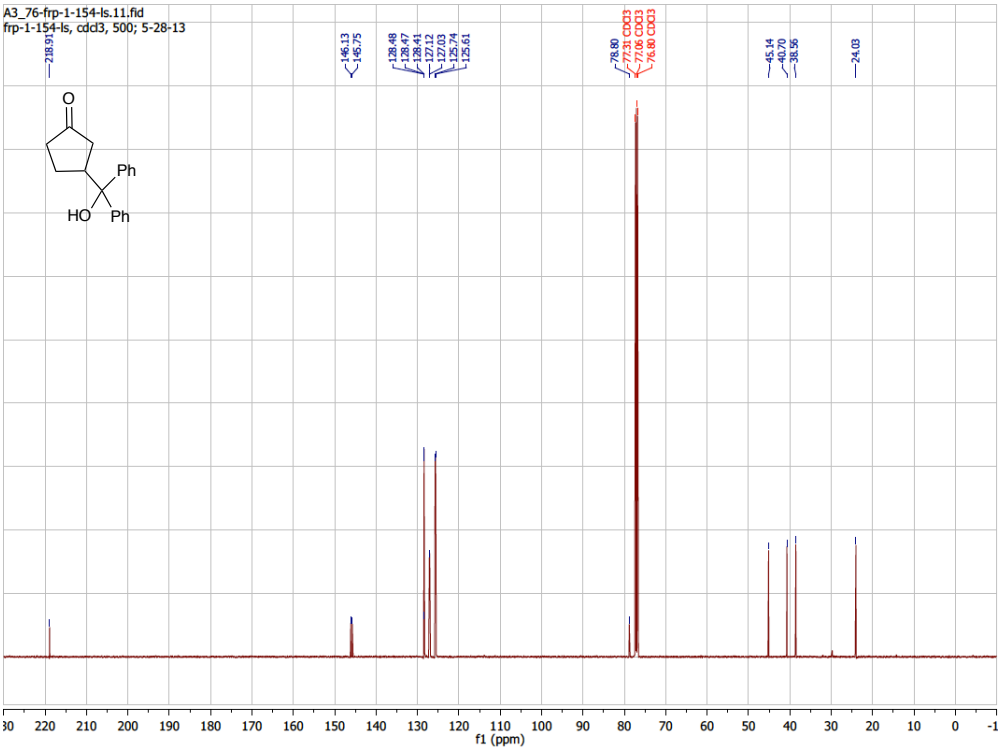
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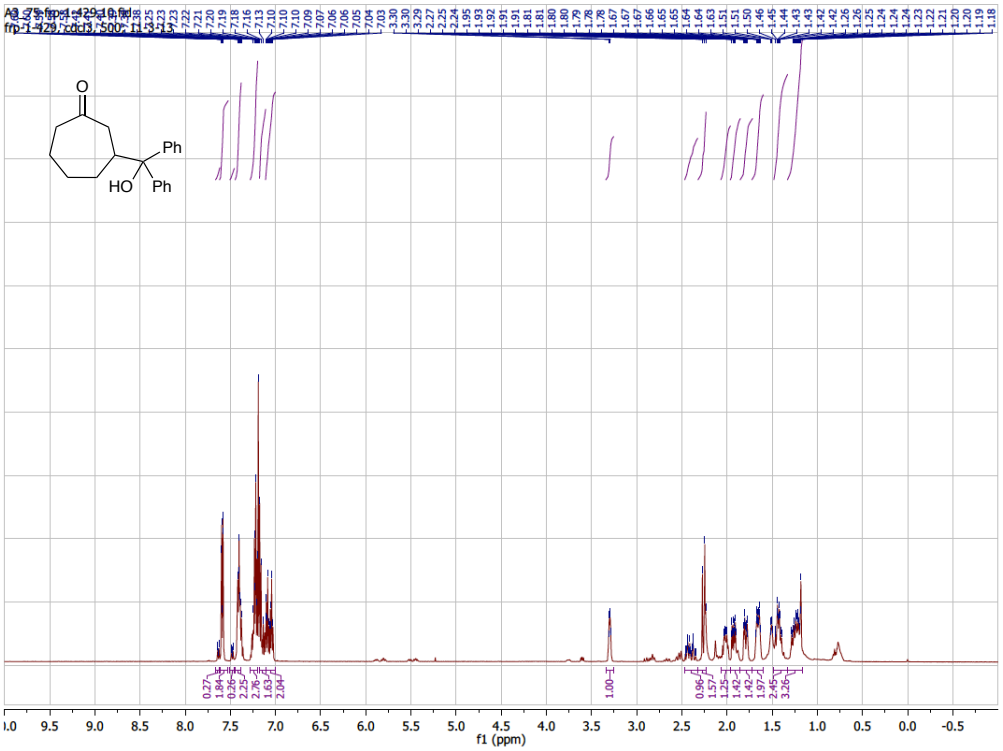
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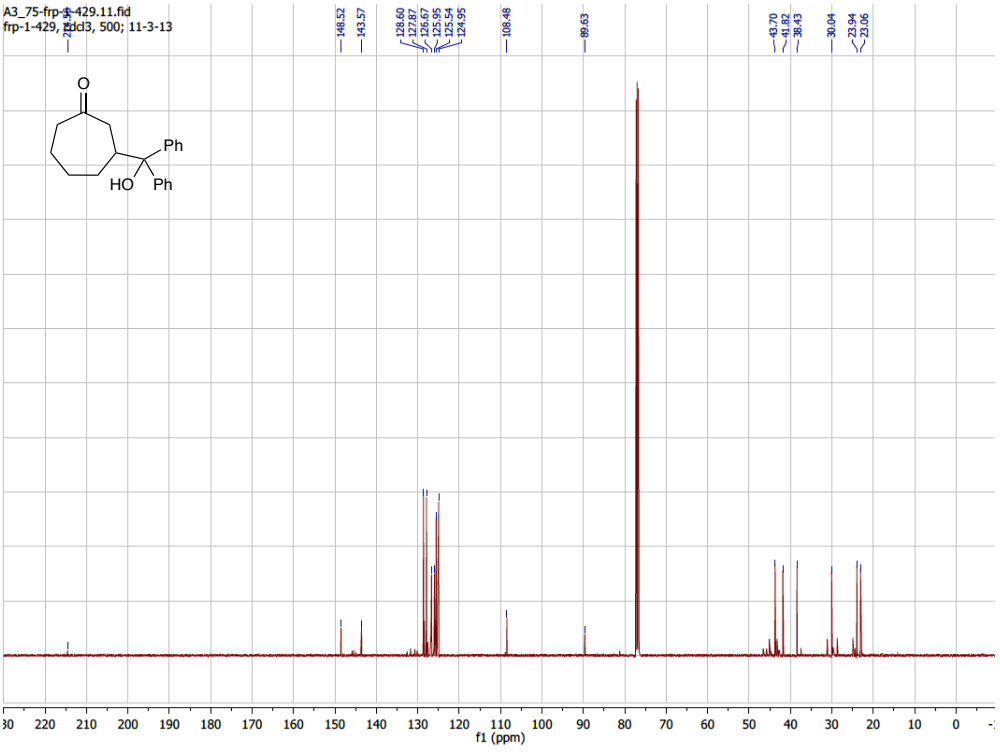
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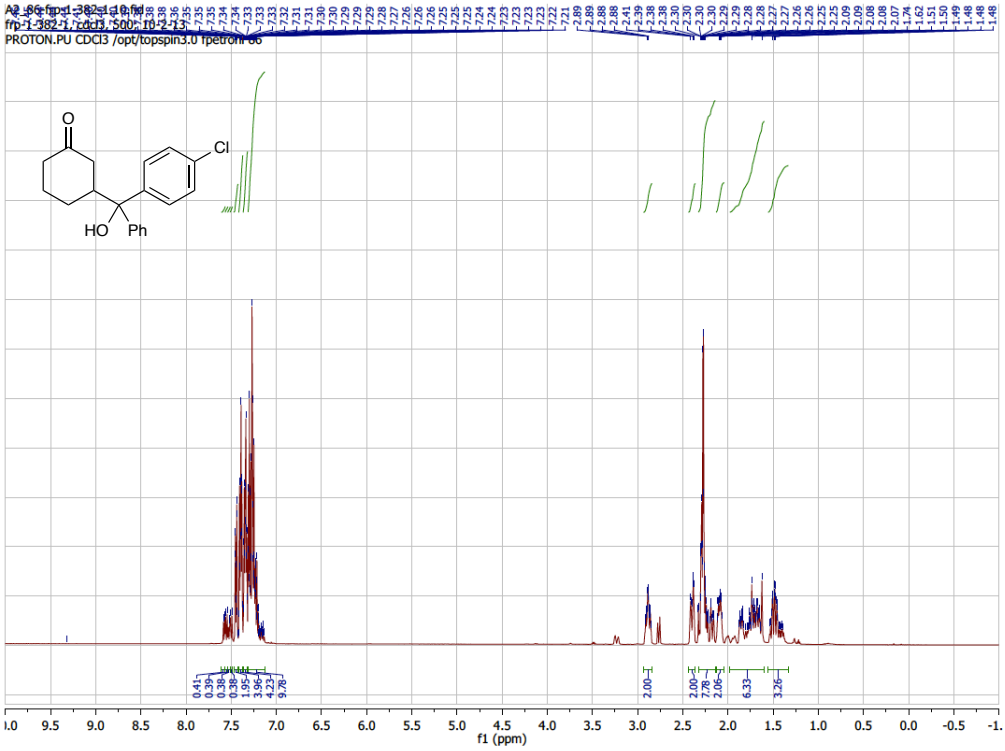
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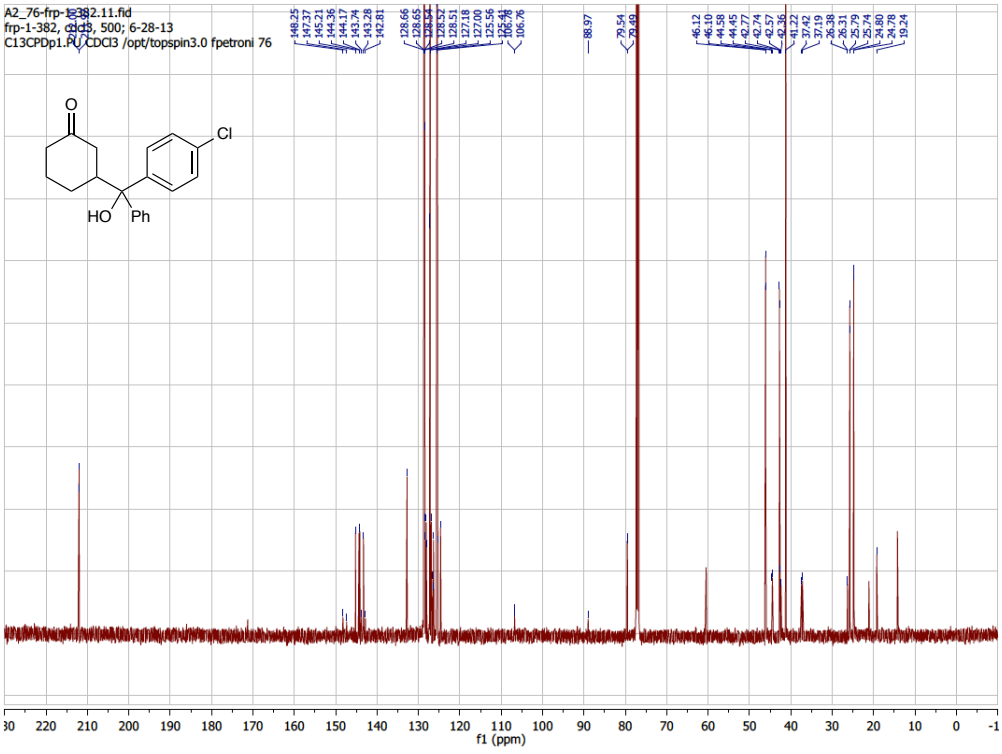
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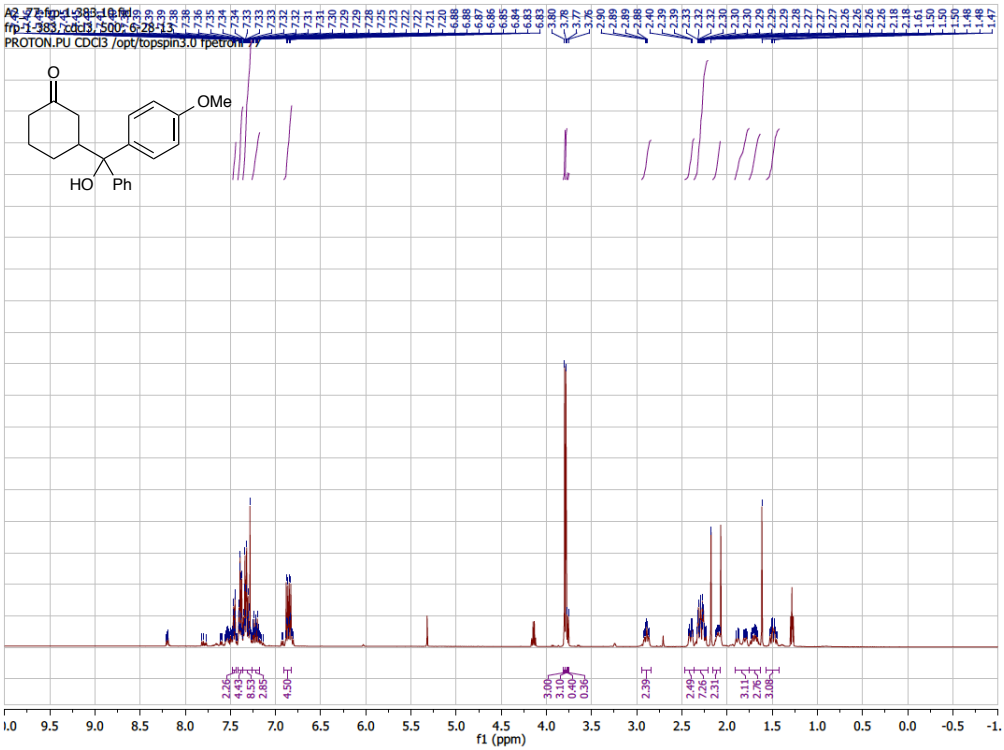
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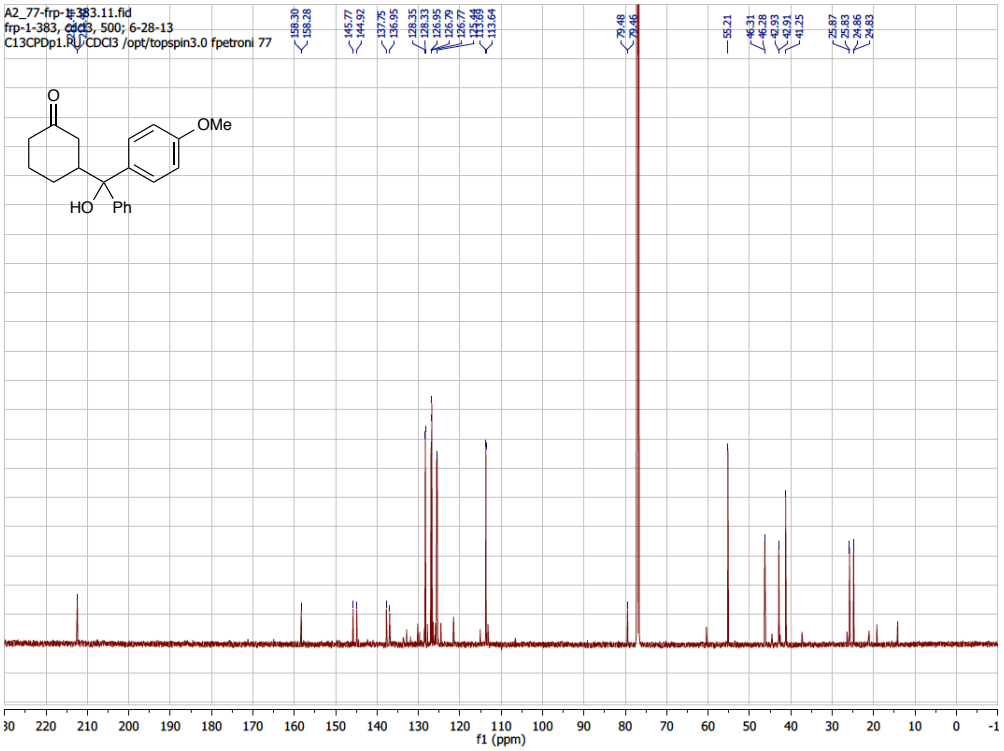
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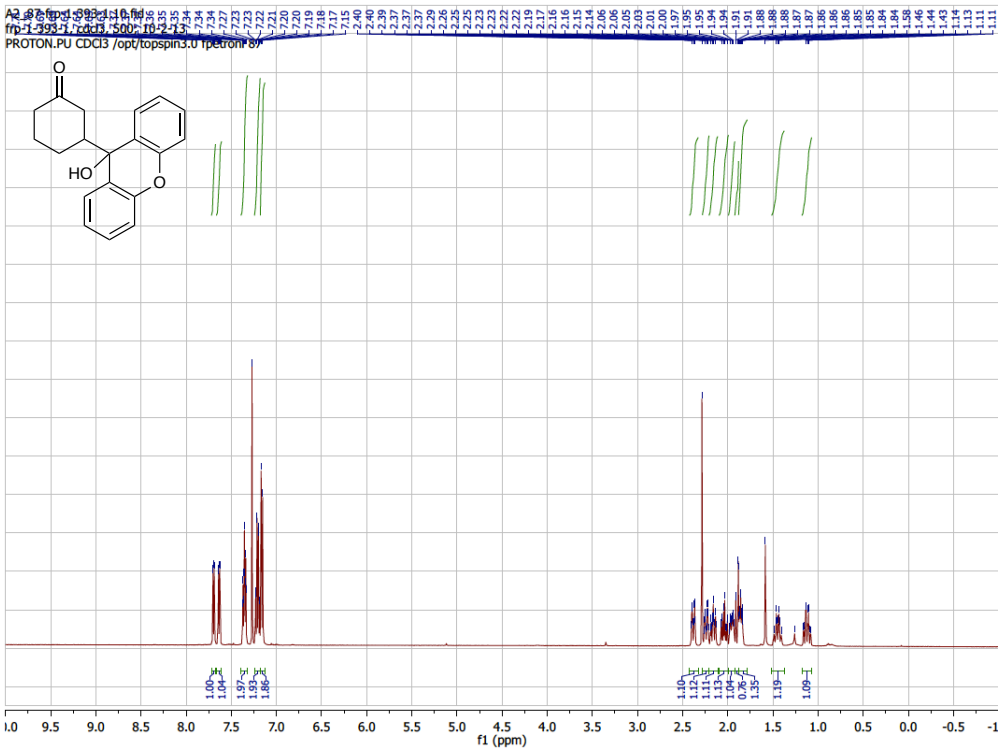
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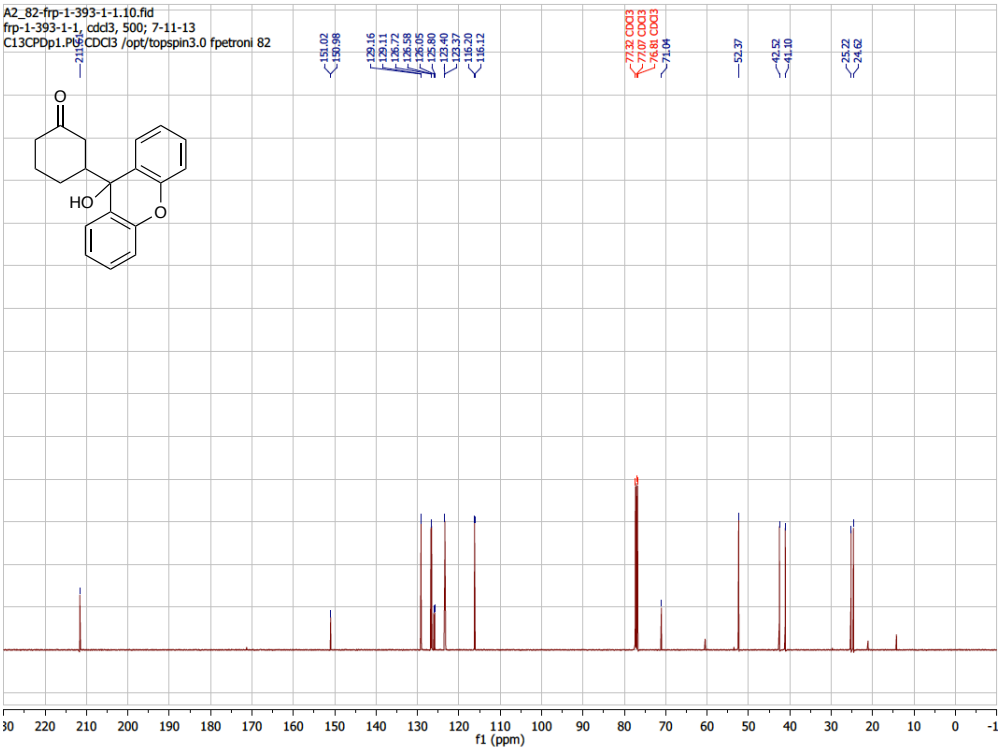
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HO
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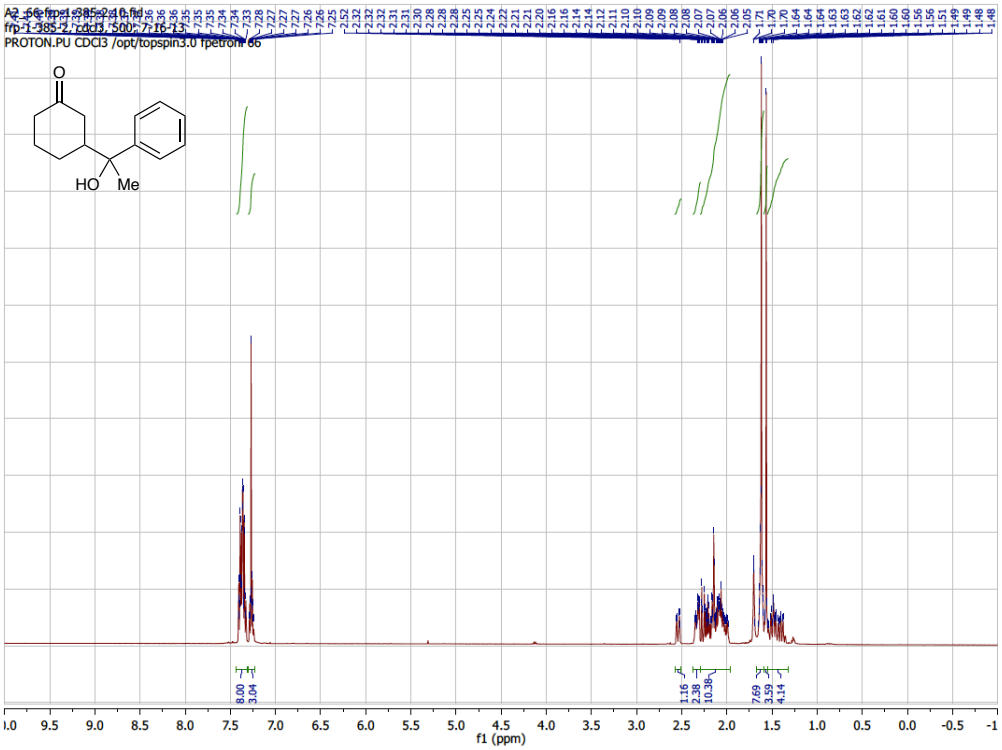
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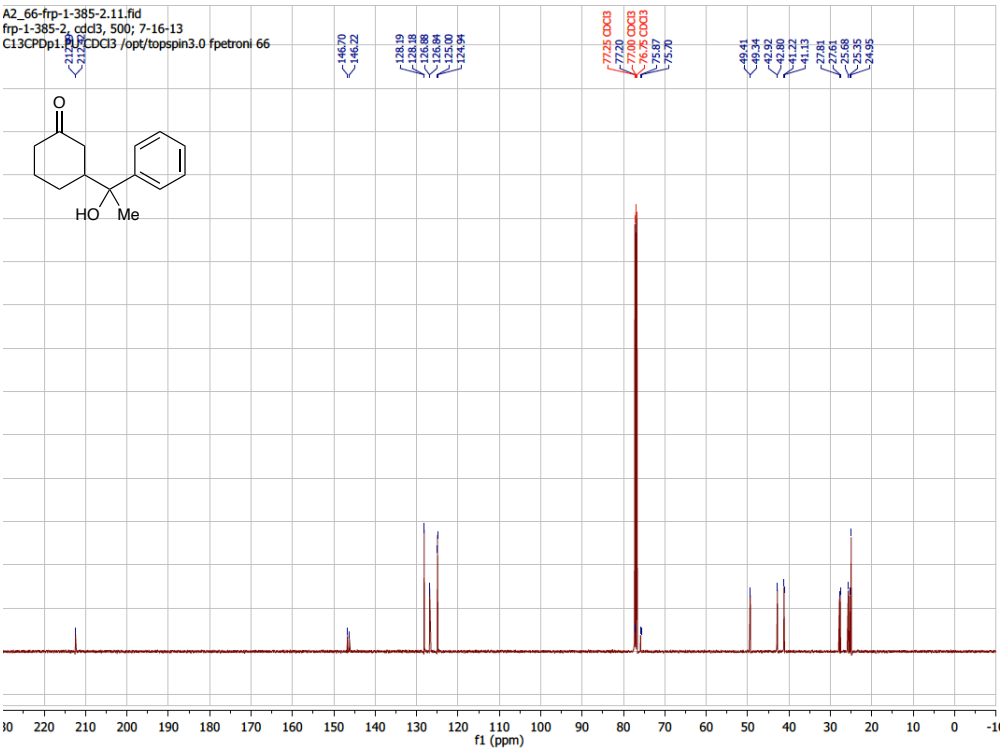
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146.22
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124.94
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77.20
77.00 CDCl3
76.75 CDCl3
75.87
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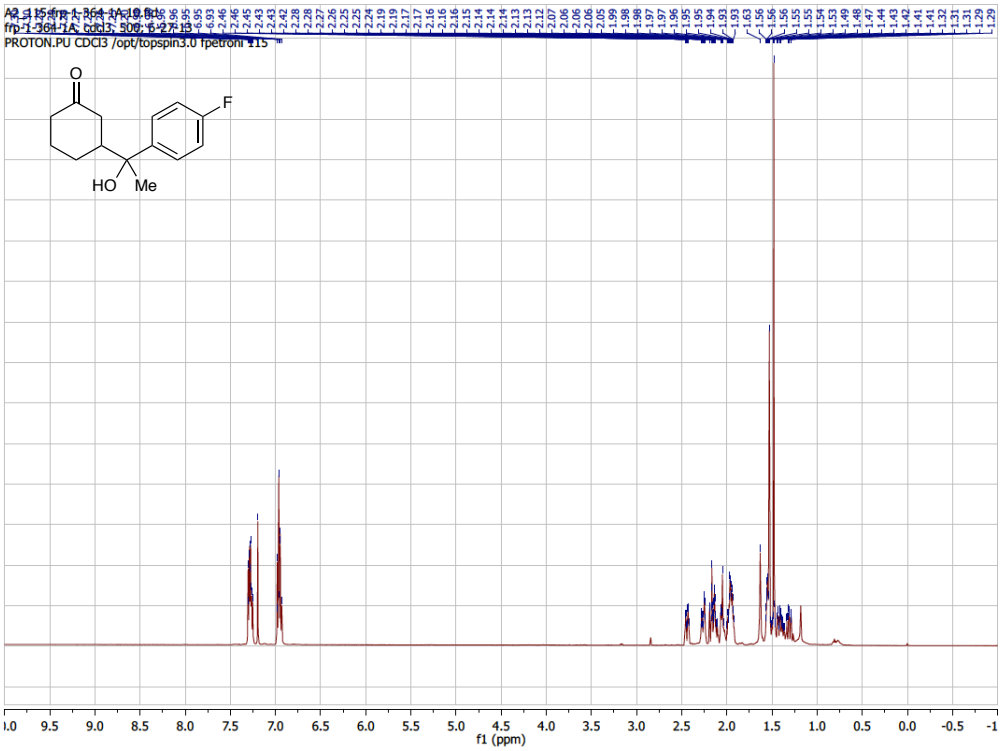
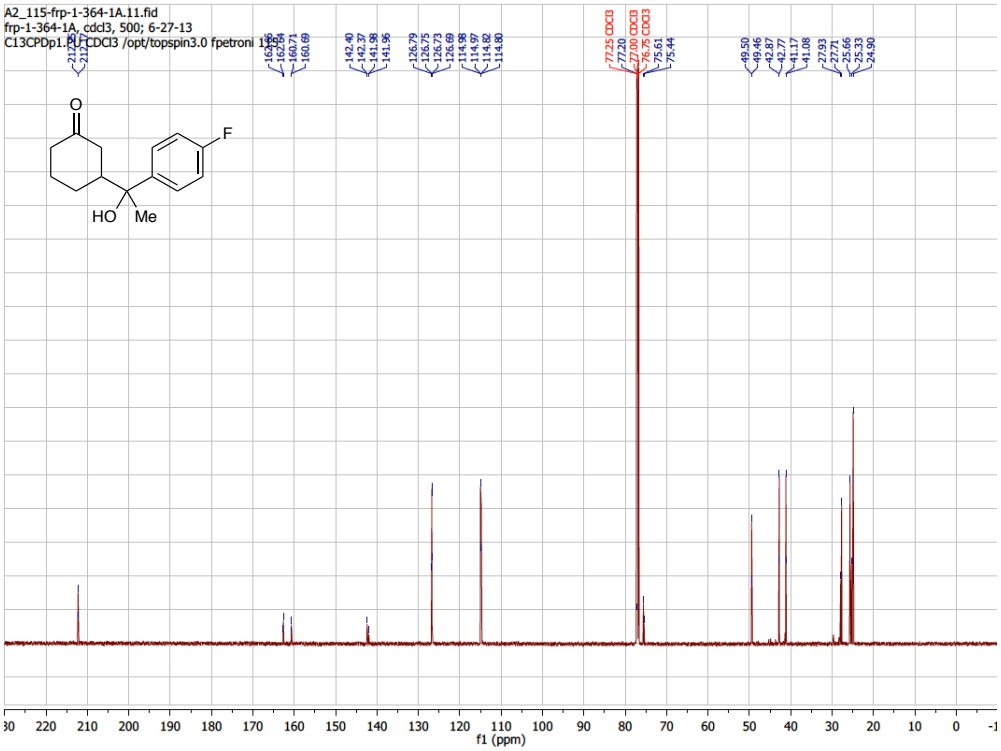
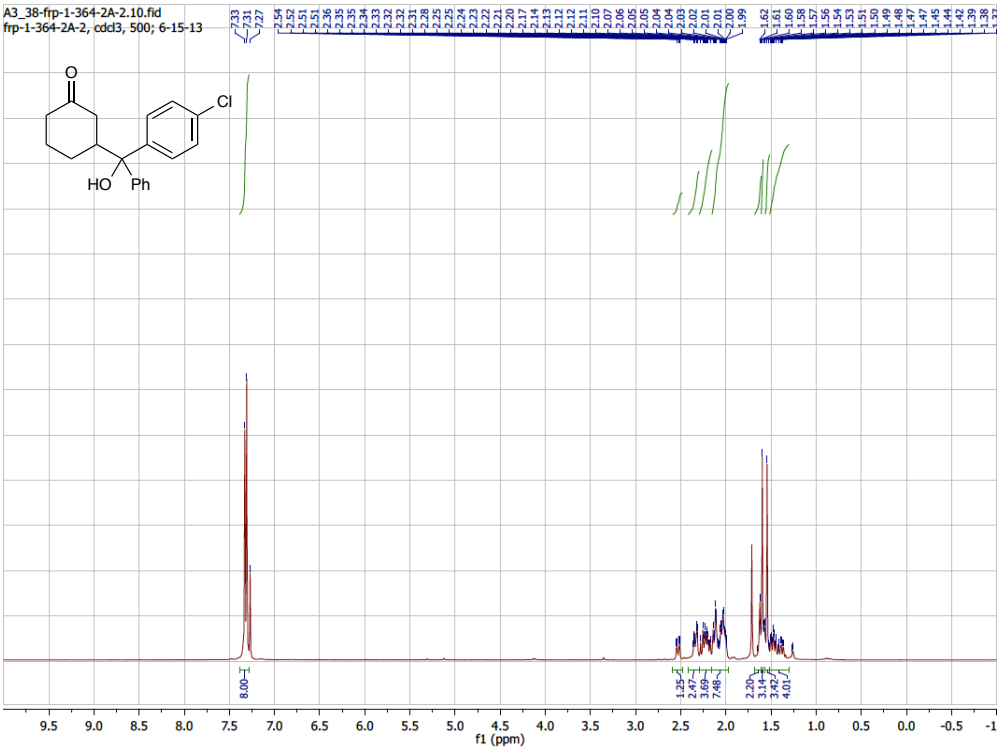
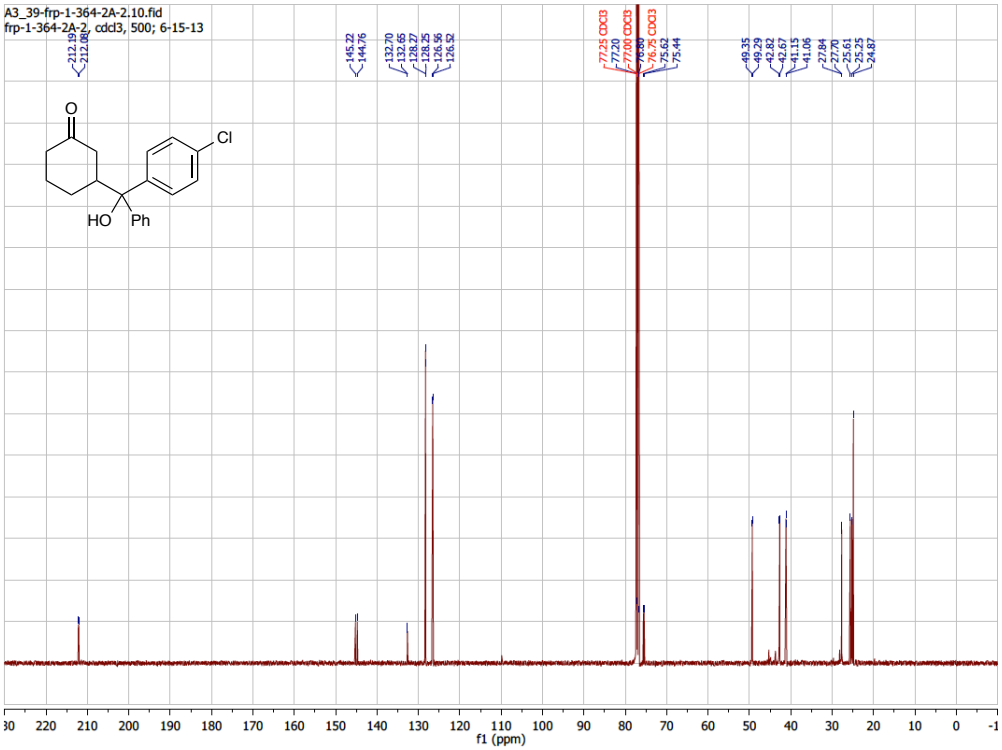
Me
f1 (ppm)


PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 115
O
F
HO
Me
f1 (ppm)


A2_115-frp-1-364-1A.11.fid
frp-1-364-1A, cdcl3, 500; 6-27-13
C13CPDp1.PU CDCl3 /opt/topspin3.0 fpetroni 115
77.25 CDCl3
77.20
77.00 CDCl3
76.75 CDCl3
O
F
HO
Me
f1 (ppm)


A3_38-frp-1-364-2A-2.10.fid
frp-1-364-2A-2, cdcl3, 500; 6-15-13
O
Cl
HO
Ph
f1 (ppm)


A3_39-frp-1-364-2A-2.10.fid
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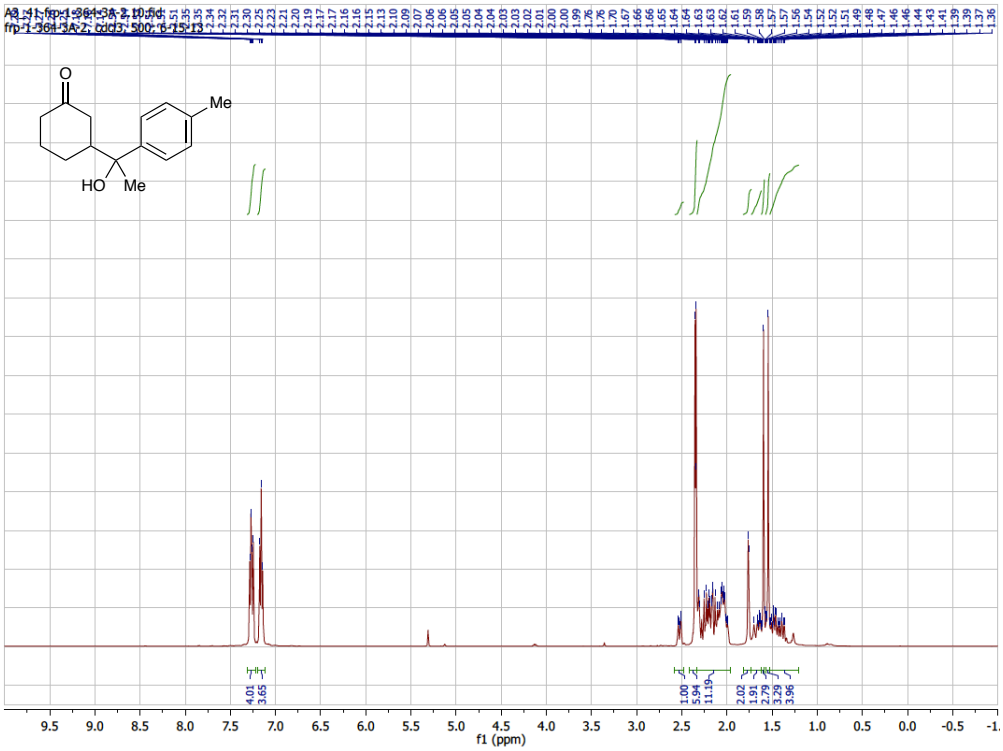
O
Cl
HO
Ph
f1 (ppm)


A3_41-frp-1-364-3A-2.10.fid
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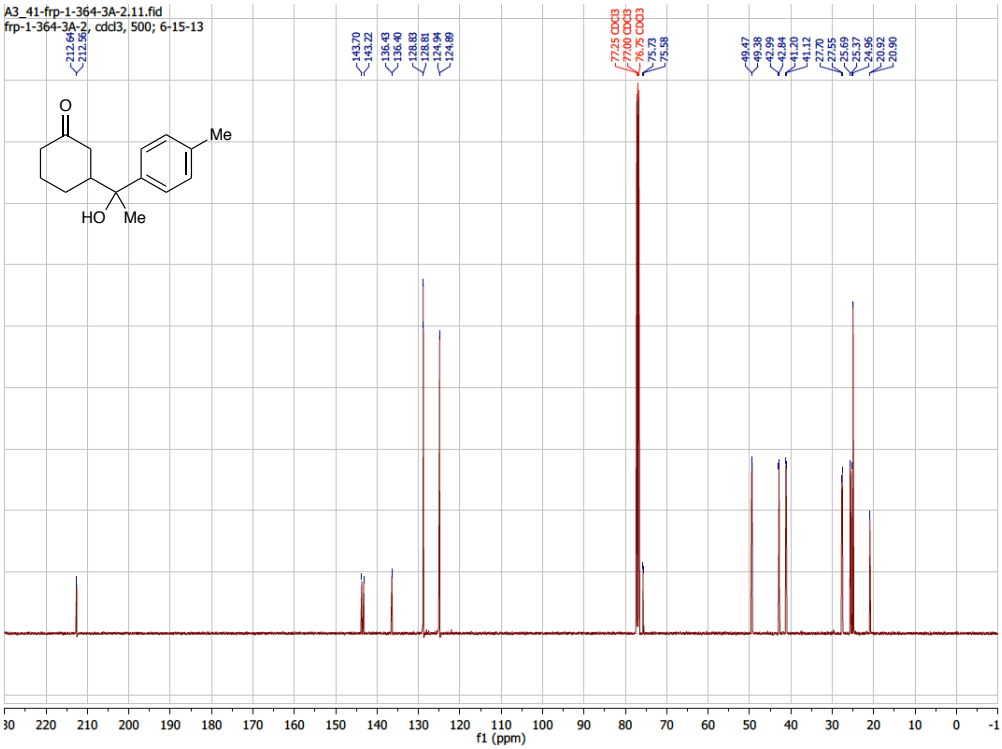
O
Me
HO
Me
4.01
3.65
1.00
5.94
11.19
2.02
1.91
2.79
3.28
3.96
f1 (ppm)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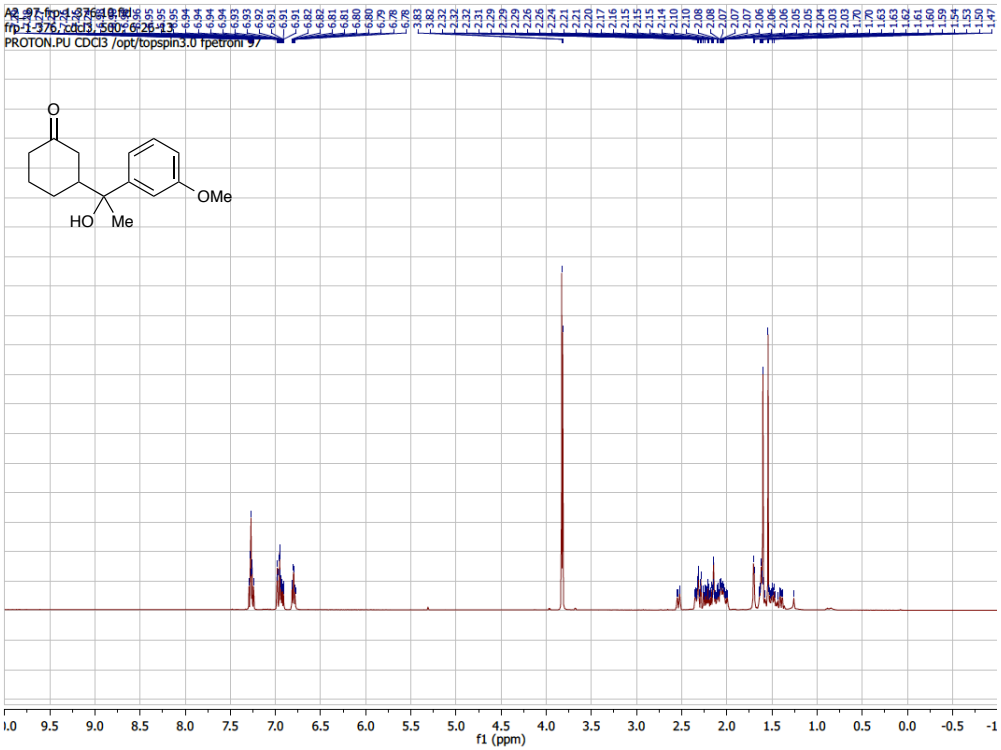
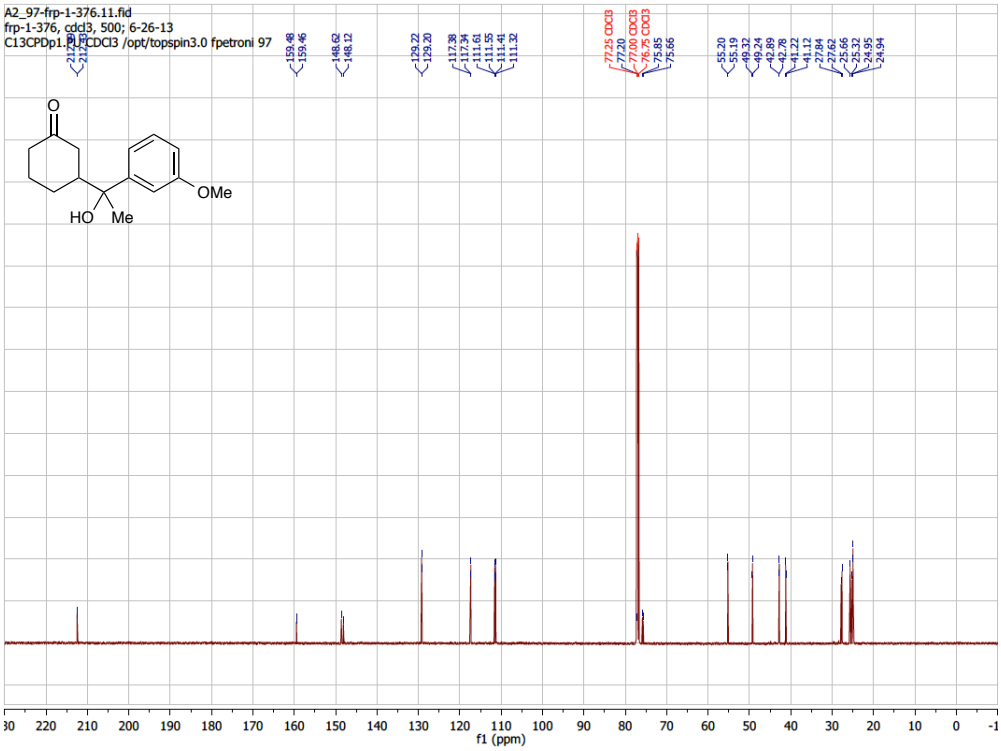
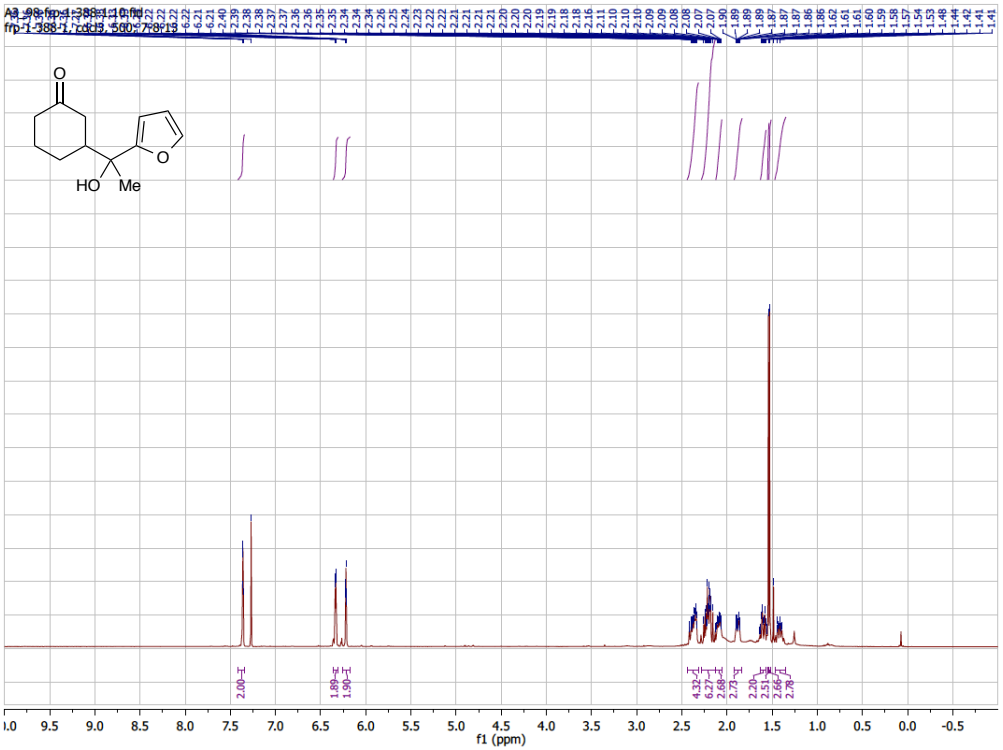
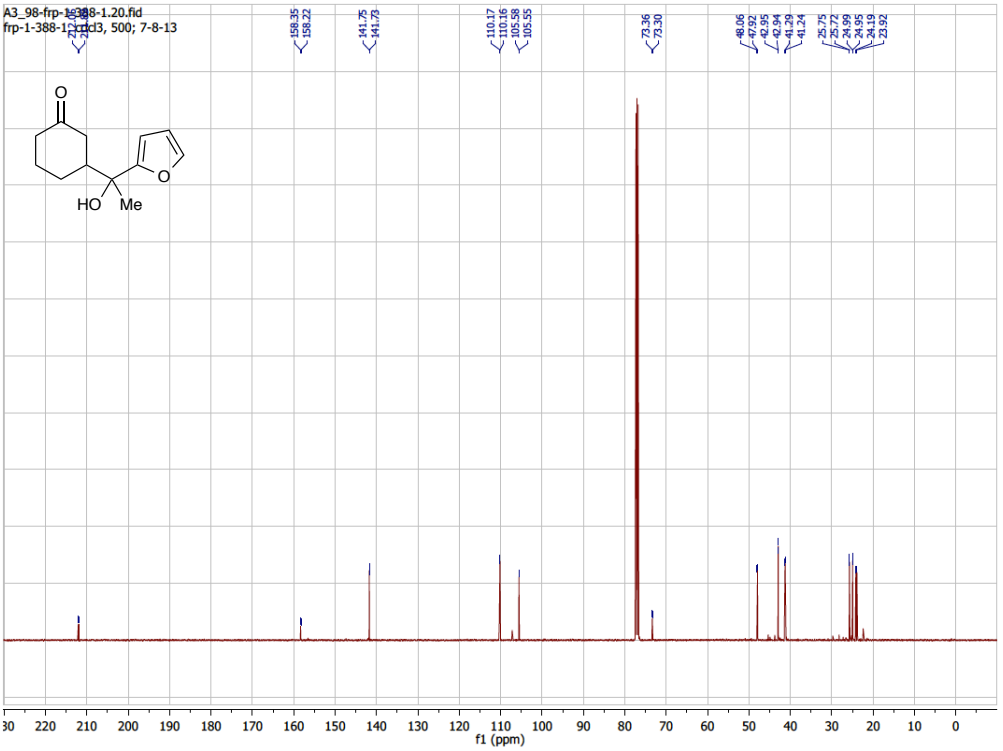
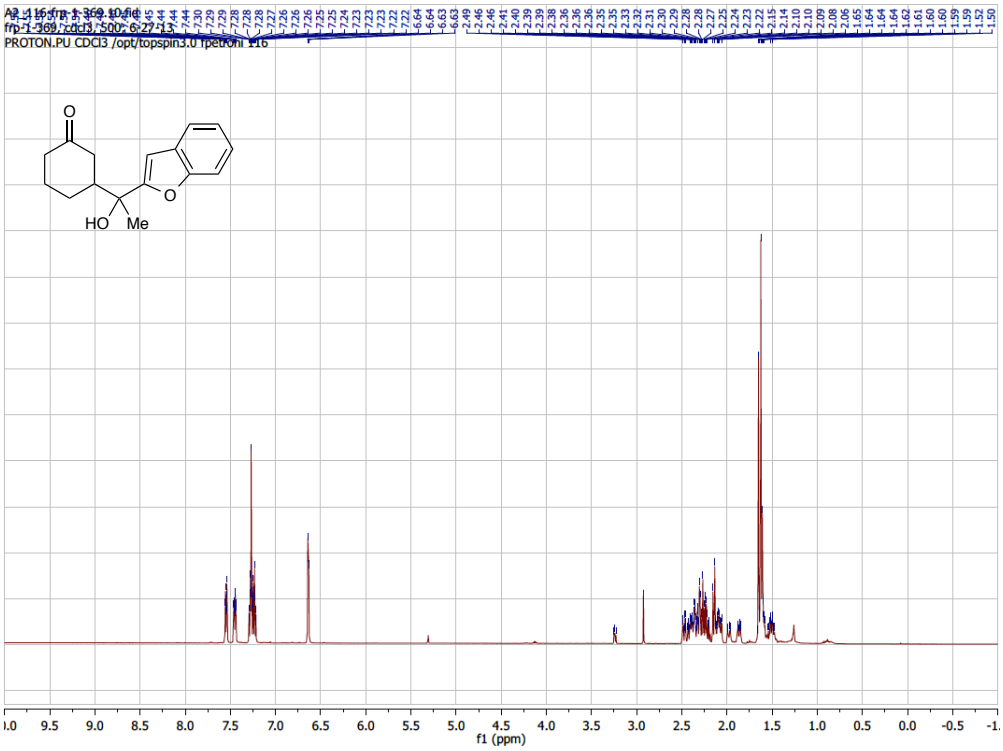
212.64
212.56
143.70
143.22
136.43
136.40
128.83
128.81
124.94
124.89
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
75.73
75.58
49.47
49.38
42.99
42.84
41.20
41.12
27.70
27.55
25.69
25.37
24.96
20.92
20.90
O
Me
HO
Me
f1 (ppm)

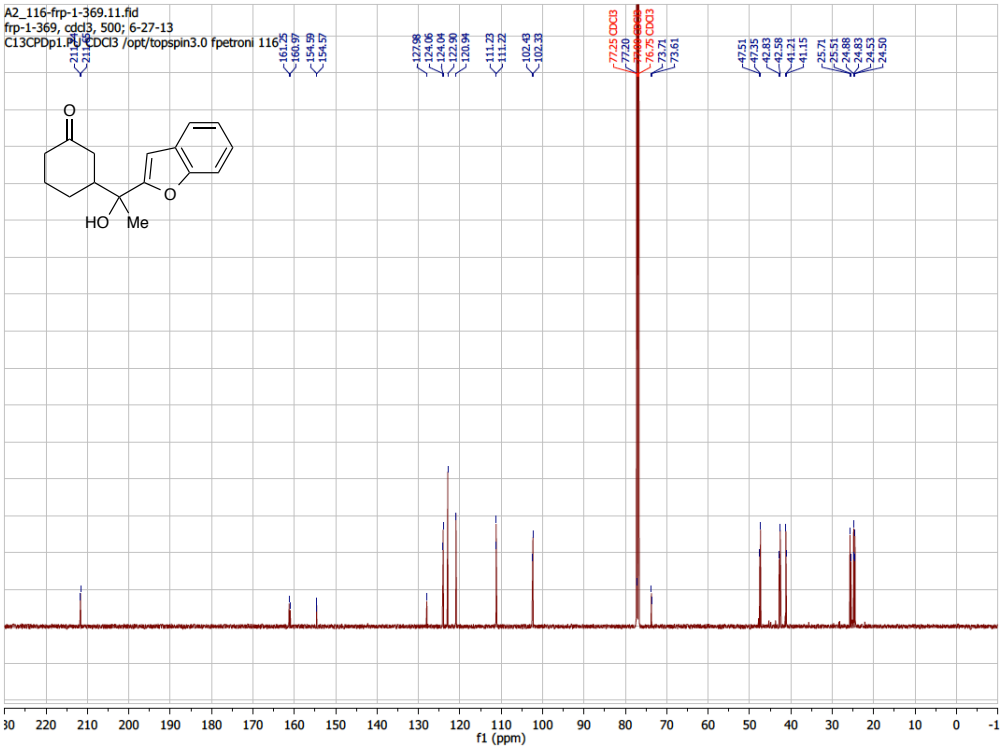

PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 97
O
OMe
HO
Me
f1 (ppm)

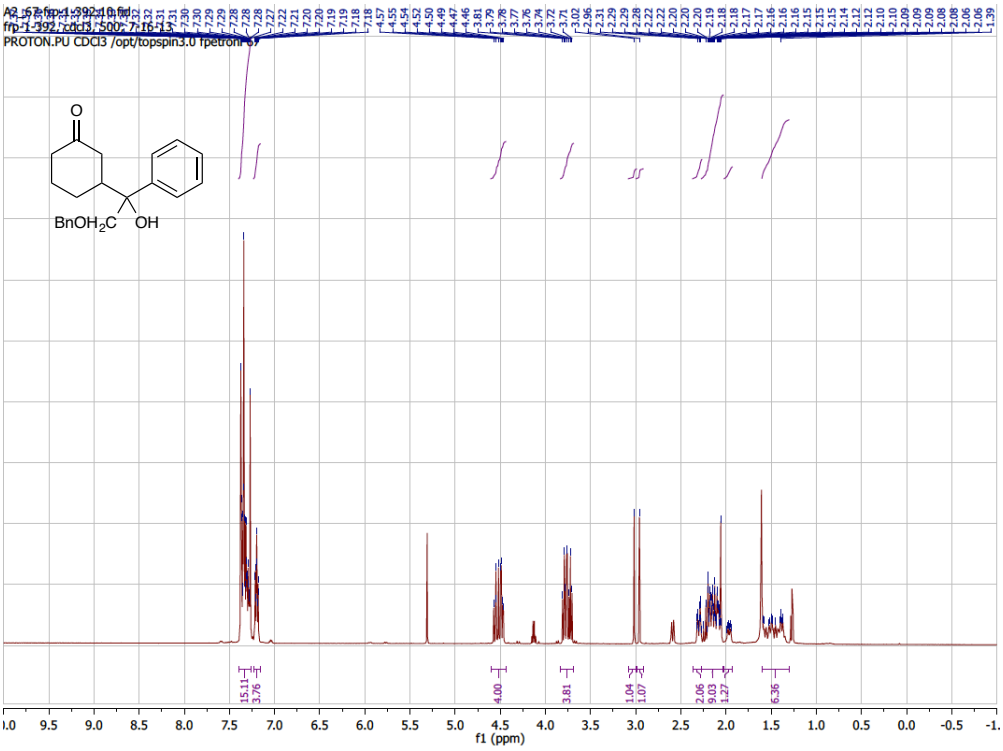

A2_97-frp-1-376.11.fid
frp-1-376, cdcl3, 500; 6-26-13
C13CPDp1.2 CDCl3 /opt/topspin3.0 fpetroni 97
O
OMe
HO
Me
f1 (ppm)

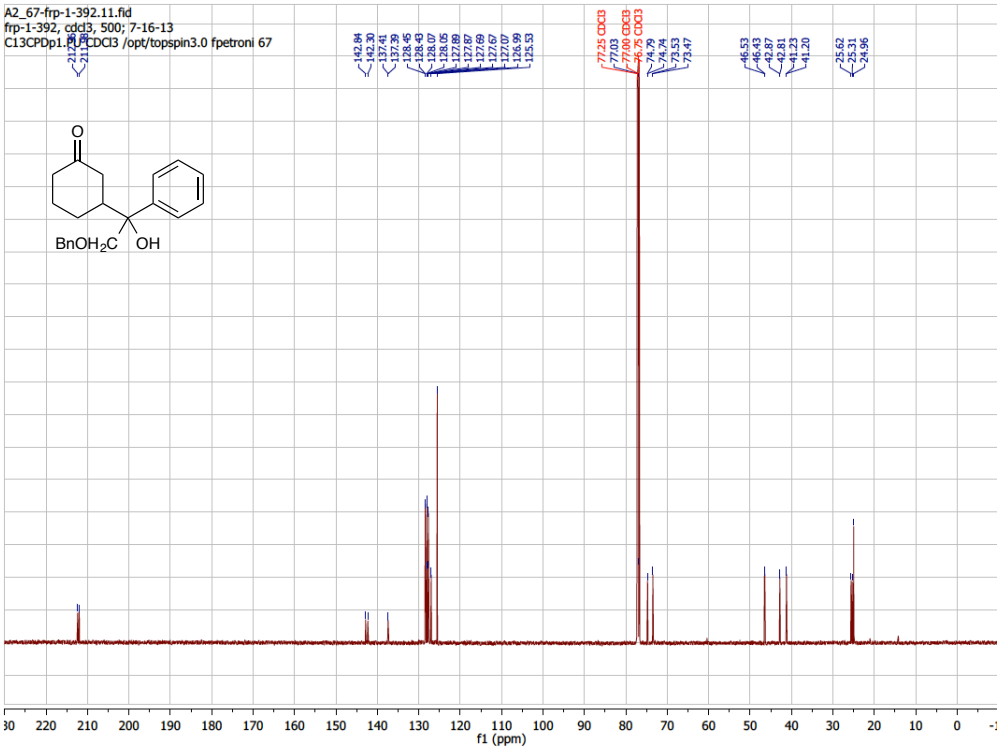

O
O
HO
Me
2.00
1.89
1.90
4.32
6.27
2.68
2.73
2.20
2.51
2.46
2.28
f1 (ppm)

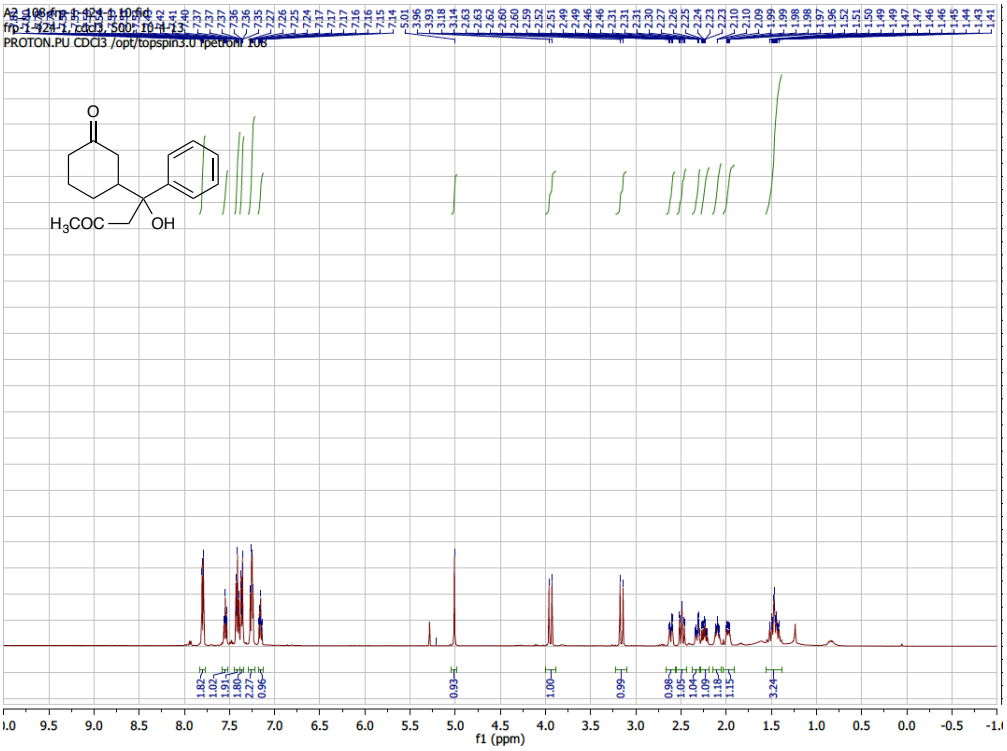

158.35
158.22
141.75
141.73
110.17
110.16
105.58
105.55
73.36
73.30
48.06
47.92
42.95
42.64
41.29
41.24
25.75
25.72
24.98
24.95
24.19
23.92
O
O
HO
Me
f1 (ppm)

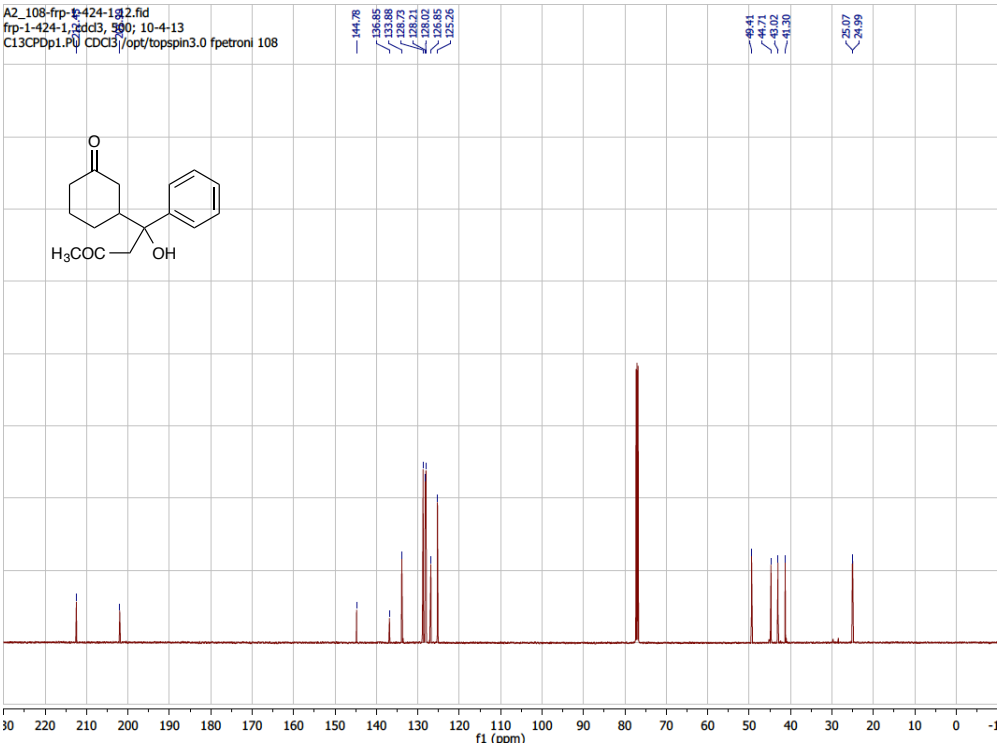

A2_116-frp-1-369.10.fid
frp-1-369, cdcl3, 500; 6-27-13
PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 116
O
O
HO
Me
f1 (ppm)

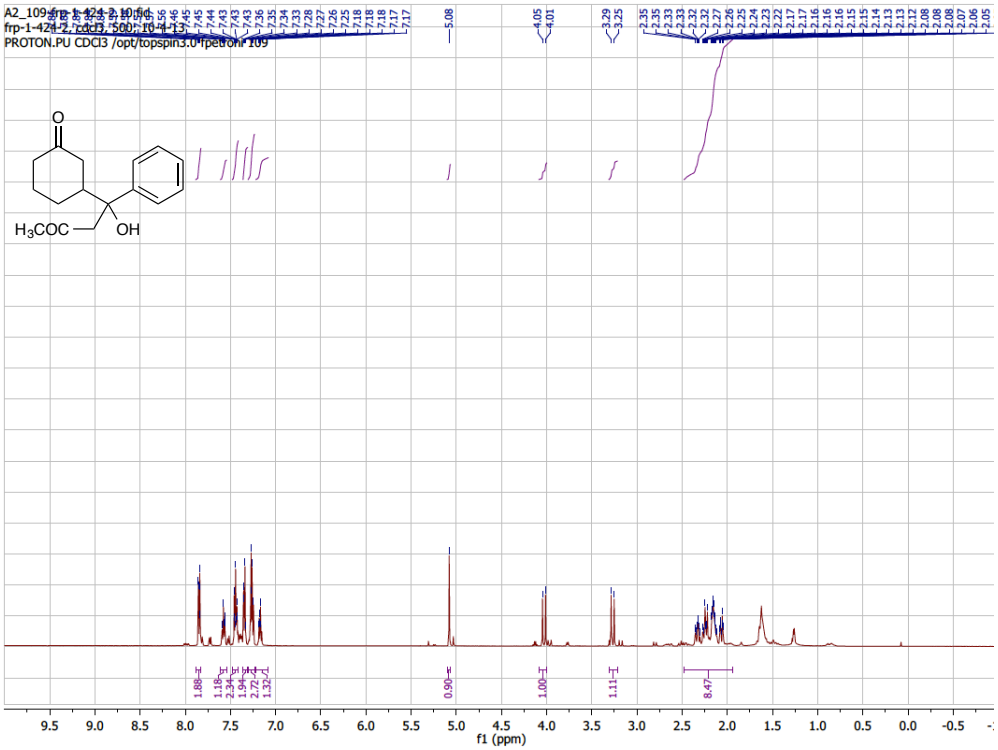

A2_116-frp-1-369.11.fid
frp-1-369, cdcl3, 500; 6-27-13
C13CPDp1.PU CDCl3 /opt/topspin3.0 fpetroni 116
O
O
HO
Me
f1 (ppm)

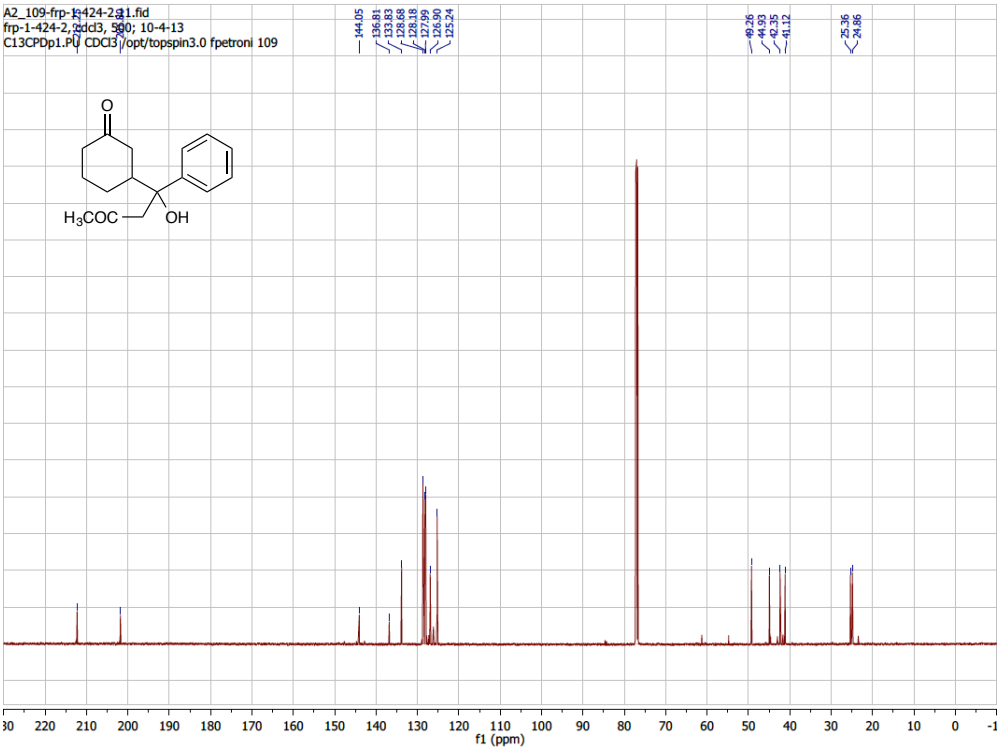

A2_67-frp-1-392.10.fid
frp-1-392, cdcl3, 500; 7-16-13
PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 67
O
BnOH2C
OH
15.11
3.76
4.00
3.81
1.04
1.07
2.06
9.03
1.27
6.36
f1 (ppm)


A2_67-frp-1-392.11.fid
frp-1-392, cdcl3, 500; 7-16-13
C13CPDp1.PU CDCl3 /opt/topspin3.0 fpetroni 67
O
BnOH2C
OH
77.25 CDCl3
77.03
76.80 CDCl3
76.75 CDCl3
f1 (ppm)


PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 108
O
H3COC
OH
1.82
1.02
1.91
1.80
2.27
0.96
0.93
1.00
0.99
0.98
1.05
1.04
1.09
1.18
1.15
3.24
f1 (ppm)

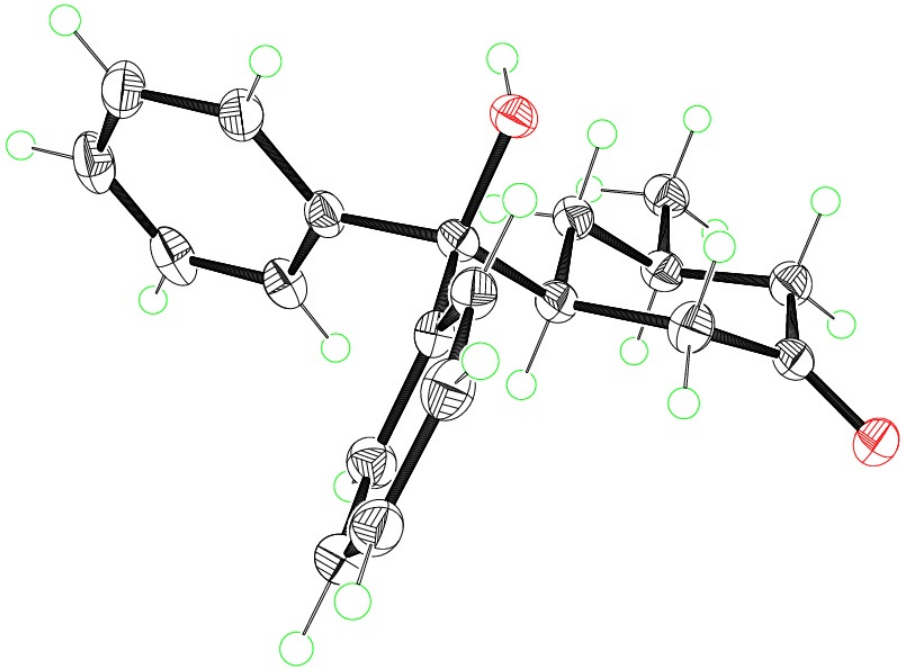

C13CPDp1.PU CDCl3 /opt/topspin3.0 fpetroni 108
144.78
136.85
133.88
128.73
128.21
128.02
126.85
125.26
49.41
44.71
43.02
41.30
25.07
24.99
O
H3COC
OH
f1 (ppm)


PROTON.PU CDCl3 /opt/topspin3.0 fpetroni 109
O
H3COC
OH
f1 (ppm)


C13CPDp1.PU CDCl3 /opt/topspin3.0 fpetroni 109
O
H3COC
OH
f1 (ppm)

4. X-Ray Crystal Structures

a) *Trans*-3-(hydroxydiphenylmethyl)-5-methylcyclohexan-1-one



• Sample and crystal data:

Chemical formula	$C_{20}H_{22}O_2$	
Formula weight	294.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.270 x 0.380 x 0.440 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.318(3) Å	α = 90°
	b = 16.115(6) Å	β = 99.129(5)°
	c = 10.684(4) Å	γ = 90°
Volume	1584.0(9) $Å^3$	
Z	4	
Density (calculated)	1.234 Mg/cm^3	
Absorption coefficient	0.611 mm^{-1}	
F(000)	632	

• Data collection and structure refinement:

Theta range for data collection	5.01 to 64.72°	
Index ranges	-10<=h<=10, -18<=k<=16, -12<=l<=11	
Reflections collected	8974	
Independent reflections	2517 [R(int) = 0.0287]	
Coverage of independent reflections	94.1%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8514 and 0.7726	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2517 / 0 / 202	
Goodness-of-fit on F^2	1.052	
Δ/σ_{max}	0.002	
Final R indices	2480 data; I>2σ(I)	R1 = 0.0362, wR2 = 0.0865
	all data	R1 = 0.0367, wR2 = 0.0868
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0295P)^2+0.7329P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0047(6)	
Largest diff. peak and hole	0.208 and -0.184 eÅ^{-3}	
R.M.S. deviation from mean	0.035 eÅ^{-3}	

• Atomic coordinates and equivalent isotropic atomic displacement (Å^2):

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.89870(10)	0.82607(6)	0.85598(8)	0.0277(3)

	x/a	y/b	z/c	U(eq)
O2	0.13040(9)	0.62901(6)	0.21700(8)	0.0224(2)
C1	0.18733(15)	0.95655(9)	0.21780(13)	0.0277(3)
C2	0.07240(14)	0.89448(8)	0.15938(12)	0.0239(3)
C3	0.09189(14)	0.81136(8)	0.22816(12)	0.0227(3)
C4	0.97316(14)	0.74865(8)	0.17707(12)	0.0217(3)
C5	0.99785(13)	0.66334(8)	0.24513(12)	0.0207(3)
C6	0.87732(14)	0.60158(8)	0.19375(11)	0.0207(3)
C7	0.90767(14)	0.53065(8)	0.12918(12)	0.0234(3)
C8	0.79769(15)	0.47440(9)	0.08502(12)	0.0260(3)
C9	0.65715(15)	0.48774(9)	0.10720(12)	0.0263(3)
C10	0.97290(14)	0.81645(8)	0.96004(12)	0.0227(3)
C11	0.07826(15)	0.88172(9)	0.01810(12)	0.0253(3)
C12	0.96722(15)	0.73709(8)	0.03312(12)	0.0256(3)
C13	0.00420(14)	0.66987(8)	0.38979(12)	0.0220(3)
C14	0.93516(15)	0.73269(9)	0.44785(13)	0.0261(3)
C15	0.94497(16)	0.73537(9)	0.57910(14)	0.0317(3)
C16	0.02135(16)	0.67518(10)	0.65406(13)	0.0340(4)
C17	0.08794(16)	0.61113(10)	0.59775(13)	0.0331(4)
C18	0.07888(15)	0.60879(9)	0.46645(13)	0.0269(3)
C19	0.73462(15)	0.61534(9)	0.21329(12)	0.0251(3)
C20	0.62574(15)	0.55883(9)	0.17086(13)	0.0272(3)

• Bond lengths (Å):

O1-C10	1.2224(17)	O2-C5	1.4282(15)
O2-H2	0.84	C1-C2	1.5248(19)
C1-H1A	0.98	C1-H1B	0.98
C1-H1C	0.98	C2-C3	1.5247(19)
C2-C11	1.5330(19)	C2-H2A	1.0
C3-C4	1.5335(18)	C3-H3A	0.99
C3-H3B	0.99	C4-C12	1.5415(19)
C4-C5	1.5551(18)	C4-H4	1.0
C5-C6	1.5356(18)	C5-C13	1.5410(18)
C6-C7	1.3872(19)	C6-C19	1.3960(19)
C7-C8	1.393(2)	C7-H7	0.95
C8-C9	1.384(2)	C8-H8	0.95
C9-C20	1.387(2)	C9-H9	0.95

C10-C11	1.5038(19)	C10-C12	1.5038(19)
C11-H11A	0.99	C11-H11B	0.99
C12-H12A	0.99	C12-H12B	0.99
C13-C18	1.394(2)	C13-C14	1.3966(19)
C14-C15	1.391(2)	C14-H14	0.95
C15-C16	1.381(2)	C15-H15	0.95
C16-C17	1.390(2)	C16-H16	0.95
C17-C18	1.392(2)	C17-H17	0.95
C18-H18	0.95	C19-C20	1.385(2)
C19-H19	0.95	C20-H20	0.95

• Bond angles (˚):

C5-O2-H2	109.5	C2-C1-H1A	109.5
C2-C1-H1B	109.5	H1A-C1-H1B	109.5
C2-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	C3-C2-C1	110.90(11)
C3-C2-C11	109.68(11)	C1-C2-C11	111.02(11)
C3-C2-H2A	108.4	C1-C2-H2A	108.4
C11-C2-H2A	108.4	C2-C3-C4	112.54(11)
C2-C3-H3A	109.1	C4-C3-H3A	109.1
C2-C3-H3B	109.1	C4-C3-H3B	109.1
H3A-C3-H3B	107.8	C3-C4-C12	110.15(10)
C3-C4-C5	111.80(10)	C12-C4-C5	109.81(10)
C3-C4-H4	108.3	C12-C4-H4	108.3
C5-C4-H4	108.3	O2-C5-C6	106.35(10)
O2-C5-C13	109.92(10)	C6-C5-C13	108.20(10)
O2-C5-C4	108.23(10)	C6-C5-C4	111.12(10)
C13-C5-C4	112.83(10)	C7-C6-C19	118.65(12)
C7-C6-C5	121.11(11)	C19-C6-C5	120.23(11)
C6-C7-C8	120.50(12)	C6-C7-H7	119.8
C8-C7-H7	119.8	C9-C8-C7	120.40(13)
C9-C8-H8	119.8	C7-C8-H8	119.8
C8-C9-C20	119.42(12)	C8-C9-H9	120.3
C20-C9-H9	120.3	O1-C10-C11	121.64(12)
O1-C10-C12	121.24(12)	C11-C10-C12	117.07(11)
C10-C11-C2	112.15(11)	C10-C11-H11A	109.2

C2-C11-H11A	109.2	C10-C11-H11B	109.2
C2-C11-H11B	109.2	H11A-C11-H11B	107.9
C10-C12-C4	114.62(11)	C10-C12-H12A	108.6
C4-C12-H12A	108.6	C10-C12-H12B	108.6
C4-C12-H12B	108.6	H12A-C12-H12B	107.6
C18-C13-C14	118.23(12)	C18-C13-C5	118.51(12)
C14-C13-C5	123.23(12)	C15-C14-C13	120.60(13)
C15-C14-H14	119.7	C13-C14-H14	119.7
C16-C15-C14	120.53(14)	C16-C15-H15	119.7
C14-C15-H15	119.7	C15-C16-C17	119.66(13)
C15-C16-H16	120.2	C17-C16-H16	120.2
C16-C17-C18	119.77(14)	C16-C17-H17	120.1
C18-C17-H17	120.1	C17-C18-C13	121.18(13)
C17-C18-H18	119.4	C13-C18-H18	119.4
C20-C19-C6	120.81(13)	C20-C19-H19	119.6
C6-C19-H19	119.6	C19-C20-C9	120.20(13)
C19-C20-H20	119.9	C9-C20-H20	119.9

• Anisotropic atomic displacement parameters ($Å^2$):

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

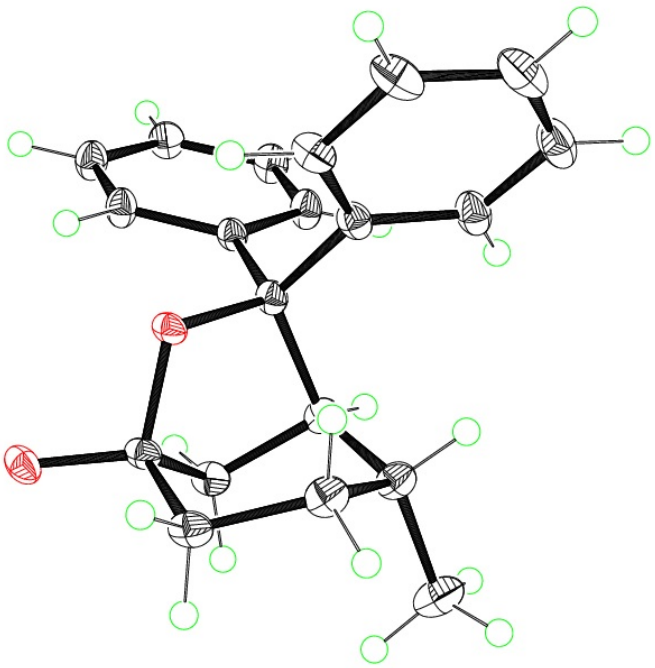
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0279(5)	0.0324(6)	0.0223(5)	0.0030(4)	0.0027(4)	0.0036(4)
O2	0.0185(5)	0.0259(5)	0.0232(5)	-0.0012(4)	0.0048(3)	0.0017(4)
C1	0.0265(7)	0.0256(7)	0.0318(7)	0.0006(6)	0.0065(6)	-0.0010(5)
C2	0.0226(7)	0.0236(7)	0.0260(7)	-0.0005(5)	0.0054(5)	0.0010(5)
C3	0.0228(7)	0.0244(7)	0.0215(6)	-0.0002(5)	0.0055(5)	0.0000(5)
C4	0.0207(7)	0.0228(7)	0.0220(7)	0.0009(5)	0.0048(5)	0.0015(5)
C5	0.0188(6)	0.0232(7)	0.0210(6)	0.0002(5)	0.0061(5)	0.0022(5)
C6	0.0219(7)	0.0232(7)	0.0173(6)	0.0039(5)	0.0038(5)	0.0003(5)
C7	0.0246(7)	0.0262(7)	0.0199(6)	0.0026(5)	0.0053(5)	0.0023(5)
C8	0.0322(7)	0.0239(7)	0.0218(6)	-0.0008(5)	0.0038(5)	0.0007(5)
C9	0.0267(7)	0.0273(7)	0.0236(7)	0.0033(6)	0.0001(5)	-0.0056(5)
C10	0.0212(7)	0.0269(7)	0.0211(7)	0.0000(5)	0.0070(5)	0.0055(5)
C11	0.0264(7)	0.0238(7)	0.0264(7)	0.0046(5)	0.0064(5)	0.0025(5)
C12	0.0299(7)	0.0239(7)	0.0226(7)	-0.0001(5)	0.0030(5)	-0.0012(5)
C13	0.0210(7)	0.0248(7)	0.0210(7)	0.0001(5)	0.0057(5)	-0.0058(5)
C14	0.0265(7)	0.0263(7)	0.0273(7)	-0.0020(6)	0.0097(5)	-0.0048(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	0.0346(8)	0.0339(8)	0.0301(7)	-0.0090(6)	0.0162(6)	-0.0119(6)
C16	0.0372(8)	0.0460(9)	0.0200(7)	-0.0032(6)	0.0086(6)	-0.0167(7)
C17	0.0336(8)	0.0412(9)	0.0241(7)	0.0075(6)	0.0036(6)	-0.0072(6)
C18	0.0277(7)	0.0299(8)	0.0236(7)	0.0022(6)	0.0061(5)	-0.0025(6)
C19	0.0256(7)	0.0254(7)	0.0253(7)	-0.0005(6)	0.0067(5)	0.0018(5)
C20	0.0222(7)	0.0315(8)	0.0281(7)	0.0028(6)	0.0048(5)	-0.0004(

• Hydrogen atomic coordinates and istropic atomic displacement ($Å^2$):

	x/a	y/b	z/c	U(eq)
H2	1.2011	0.6511	0.2637	0.034
H1A	1.1831	0.9625	0.3084	0.042
H1B	1.1689	1.0104	0.1758	0.042
H1C	1.2839	0.9366	0.2067	0.042
H2A	0.9745	0.9170	0.1680	0.029
H3A	1.0905	0.8204	0.3196	0.027
H3B	1.1880	0.7880	0.2191	0.027
H4	0.8774	0.7712	0.1923	0.026
H7	1.0042	0.5204	0.1150	0.028
H8	0.8193	0.4266	0.0394	0.031
H9	0.5828	0.4485	0.0791	0.032
H11A	1.0557	0.9348	-0.0273	0.03
H11B	1.1780	0.8652	0.0076	0.03
H12A	1.0497	0.7016	0.0187	0.031
H12B	0.8764	0.7073	-0.0010	0.031
H14	0.8810	0.7740	0.3973	0.031
H15	0.8988	0.7789	0.6175	0.038
H16	1.0283	0.6776	0.7437	0.041
H17	1.1395	0.5691	0.6486	0.04
H18	1.1244	0.5648	0.4284	0.032
H19	0.7119	0.6641	0.2562	0.03
H20	0.5293	0.5688	0.1854	0.033

b) *Trans*-3-(hydroxydiphenylmethyl)-4-methylcyclohexan-1-one



• Sample and crystal data:

Chemical formula	$C_{20}H_{21}O_2$	
Formula weight	293.37	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal size	0.280 x 0.370 x 0.450 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.45(2) Å	α = 90°
	b = 9.900(17) Å	β = 114.30(3)°
	c = 12.67(2) Å	γ = 90°
Volume	1538.(5) $Å^3$	
Z	4	
Density (calculated)	1.267 Mg/cm^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	628	

• Data collection and structure refinement:

Theta range for data collection	2.64 to 35.85°
Index ranges	-21<=h<=22, -16<=k<=16, -20<=l<=20

Reflections collected	38210	
Independent reflections	7098 [R(int) = 0.0204]	
Coverage of independent reflections	98.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9778 and 0.9647	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7098 / 0 / 201	
Goodness-of-fit on F^2	1.037	
Δ/σ_{max}	4.683	
Final R indices	6270 data; I>2σ(I)	R1 = 0.0530, wR2 = 0.1564
	all data	R1 = 0.0589, wR2 = 0.1633
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0982P)^2+0.5255P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.012 and -0.281 eÅ^{-3}	
R.M.S. deviation from mean	0.077 eÅ^{-3}	

• Atomic coordinates and equivalent isotropic atomic displacement (Å^2):

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1	0.86260(4)	0.57788(6)	0.87921(5)	0.01503(11)
O2	0.04451(5)	0.56782(7)	0.90910(5)	0.01945(13)
C1	0.50276(8)	0.66798(13)	0.89122(10)	0.0304(2)
C2	0.58938(8)	0.58170(12)	0.95059(10)	0.0285(2)
C3	0.67391(7)	0.56613(10)	0.91456(8)	0.02199(16)
C4	0.67303(6)	0.63687(9)	0.81840(7)	0.01747(14)

	x/a	y/b	z/c	U(eq)
C5	0.76696(6)	0.62390(8)	0.78121(6)	0.01486(13)
C6	0.73936(6)	0.52111(8)	0.68192(6)	0.01504(13)
C7	0.79843(7)	0.40163(9)	0.69702(7)	0.01913(14)
C8	0.77668(7)	0.31167(9)	0.60491(8)	0.02134(16)
C9	0.69554(7)	0.34036(9)	0.49649(8)	0.02130(16)
C10	0.80479(7)	0.75978(8)	0.74759(6)	0.01682(14)
C11	0.92096(7)	0.71958(9)	0.76720(7)	0.01784(14)
C12	0.95741(6)	0.65628(8)	0.88664(6)	0.01591(13)
C13	0.97842(7)	0.76497(9)	0.97912(7)	0.01956(15)
C14	0.87312(7)	0.84446(9)	0.95651(7)	0.02049(15)
C15	0.80683(7)	0.87946(9)	0.82772(7)	0.01953(15)
C16	0.84739(10)	0.00775(10)	0.79075(9)	0.0278(2)
C17	0.63536(7)	0.45890(10)	0.48074(7)	0.02205(16)
C18	0.65687(7)	0.54807(9)	0.57276(7)	0.02008(15)
C19	0.58425(7)	0.72150(10)	0.75797(8)	0.02200(16)
C20	0.50049(7)	0.73762(11)	0.79487(9)	0.0271(2)

• Bond lengths (Å):

O1-C5	1.445(2)	O1-C12	1.462(2)
O2-C12	1.395(2)	C1-C2	1.390(2)
C1-C20	1.391(3)	C1-H1	0.93
C2-C3	1.397(2)	C2-H2	0.93
C3-C4	1.401(2)	C3-H3	0.93
C4-C19	1.401(2)	C4-C5	1.525(3)
C5-C6	1.540(2)	C5-C10	1.558(2)
C6-C7	1.394(2)	C6-C18	1.397(2)
C7-C8	1.400(2)	C7-H7	0.93
C8-C9	1.387(2)	C8-H8	0.93
C9-C17	1.393(2)	C9-H9	0.93
C10-C11	1.530(3)	C10-C15	1.553(2)
C10-H10	0.98	C11-C12	1.521(3)
C11-H11A	0.97	C11-H11B	0.97
C12-C13	1.529(2)	C13-C14	1.541(3)
C13-H13A	0.97	C13-H13B	0.97
C14-C15	1.543(3)	C14-H14A	0.97
C14-H14B	0.97	C15-C16	1.530(2)

C15-H15	0.98	C16-H16A	0.96
C16-H16B	0.96	C16-H16C	0.96
C17-C18	1.395(2)	C17-H17	0.93
C18-H18	0.93	C19-C20	1.395(2)
C19-H19	0.93	C20-H20	0.93

• Bond angles (˚):

C5-O1-C12	109.40(12)	C2-C1-C20	119.35(12)
C2-C1-H1	120.3	C20-C1-H1	120.3
C1-C2-C3	120.31(15)	C1-C2-H2	119.8
C3-C2-H2	119.8	C2-C3-C4	120.81(11)
C2-C3-H3	119.6	C4-C3-H3	119.6
C19-C4-C3	118.33(11)	C19-C4-C5	120.66(13)
C3-C4-C5	121.00(9)	O1-C5-C4	108.59(15)
O1-C5-C6	108.88(12)	C4-C5-C6	110.87(9)
O1-C5-C10	103.40(11)	C4-C5-C10	114.65(9)
C6-C5-C10	110.07(13)	C7-C6-C18	118.27(9)
C7-C6-C5	121.10(10)	C18-C6-C5	120.58(12)
C6-C7-C8	120.92(11)	C6-C7-H7	119.5
C8-C7-H7	119.5	C9-C8-C7	120.30(13)
C9-C8-H8	119.9	C7-C8-H8	119.9
C8-C9-C17	119.24(9)	C8-C9-H9	120.4
C17-C9-H9	120.4	C11-C10-C15	110.49(7)
C11-C10-C5	99.06(10)	C15-C10-C5	113.56(13)
C11-C10-H10	111.1	C15-C10-H10	111.1
C5-C10-H10	111.1	C12-C11-C10	99.11(8)
C12-C11-H11A	111.9	C10-C11-H11A	111.9
C12-C11-H11B	111.9	C10-C11-H11B	111.9
H11A-C11-H11B	109.6	O2-C12-O1	108.47(15)
O2-C12-C11	111.19(8)	O1-C12-C11	103.84(8)
O2-C12-C13	114.24(10)	O1-C12-C13	107.70(9)
C11-C12-C13	110.78(15)	C12-C13-C14	110.56(9)
C12-C13-H13A	109.5	C14-C13-H13A	109.5
C12-C13-H13B	109.5	C14-C13-H13B	109.5
H13A-C13-H13B	108.1	C13-C14-C15	113.47(9)
C13-C14-H14A	108.9	C15-C14-H14A	108.9
C13-C14-H14B	108.9	C15-C14-H14B	108.9
H14A-C14-H14B	107.7	C16-C15-C14	112.74(10)

C16-C15-C10	110.23(14)	C14-C15-C10	111.54(13)
C16-C15-H15	107.3	C14-C15-H15	107.3
C10-C15-H15	107.3	C15-C16-H16A	109.5
C15-C16-H16B	109.5	H16A-C16-H16B	109.5
C15-C16-H16C	109.5	H16A-C16-H16C	109.5
H16B-C16-H16C	109.5	C9-C17-C18	120.35(11)
C9-C17-H17	119.8	C18-C17-H17	119.8
C17-C18-C6	120.91(12)	C17-C18-H18	119.5
C6-C18-H18	119.5	C20-C19-C4	120.63(14)
C20-C19-H19	119.7	C4-C19-H19	119.7
C1-C20-C19	120.54(11)	C1-C20-H20	119.7
C19-C20-H20	119.7		

• Anisotropic atomic displacement parameters ($Å^2$):

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0118(2)	0.0186(2)	0.0112(2)	0.00248(17)	0.00127(17)	-0.00177(17)
O2	0.0136(2)	0.0264(3)	0.0163(2)	0.0051(2)	0.00409(19)	0.0008(2)
C1	0.0178(3)	0.0412(5)	0.0331(5)	-0.0126(4)	0.0115(3)	-0.0035(3)
C2	0.0207(4)	0.0401(5)	0.0280(4)	-0.0036(4)	0.0133(3)	-0.0046(3)
C3	0.0173(3)	0.0282(4)	0.0208(3)	0.0000(3)	0.0082(3)	-0.0019(3)
C4	0.0141(3)	0.0204(3)	0.0154(3)	-0.0034(2)	0.0035(2)	-0.0001(2)
C5	0.0135(3)	0.0169(3)	0.0109(3)	-0.0001(2)	0.0017(2)	0.0008(2)
C6	0.0131(3)	0.0166(3)	0.0127(3)	-0.0010(2)	0.0027(2)	0.0006(2)
C7	0.0184(3)	0.0193(3)	0.0159(3)	-0.0009(2)	0.0031(2)	0.0040(3)
C8	0.0216(3)	0.0193(3)	0.0203(3)	-0.0026(3)	0.0058(3)	0.0034(3)
C9	0.0214(3)	0.0212(3)	0.0182(3)	-0.0055(3)	0.0050(3)	-0.0004(3)
C10	0.0193(3)	0.0165(3)	0.0112(3)	0.0007(2)	0.0027(2)	-0.0002(2)
C11	0.0186(3)	0.0208(3)	0.0123(3)	0.0023(2)	0.0046(2)	-0.0028(2)
C12	0.0138(3)	0.0194(3)	0.0120(3)	0.0021(2)	0.0027(2)	-0.0030(2)
C13	0.0198(3)	0.0221(3)	0.0121(3)	-0.0005(2)	0.0019(2)	-0.0049(3)
C14	0.0243(4)	0.0205(3)	0.0136(3)	-0.0016(2)	0.0047(3)	-0.0021(3)
C15	0.0223(3)	0.0178(3)	0.0154(3)	-0.0010(2)	0.0047(3)	-0.0016(3)
C16	0.0375(5)	0.0198(4)	0.0223(4)	0.0003(3)	0.0086(4)	-0.0058(3)
C17	0.0209(3)	0.0230(4)	0.0151(3)	-0.0039(3)	0.0003(3)	0.0013(3)
C18	0.0180(3)	0.0205(3)	0.0144(3)	-0.0027(2)	-0.0007(2)	0.0035(3)
C19	0.0161(3)	0.0255(4)	0.0194(3)	-0.0047(3)	0.0022(3)	0.0028(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	0.0154(3)	0.0331(5)	0.0275(4)	-0.0114(4)	0.0035(3)	0.0023(3)

• Hydrogen atomic coordinates and istropic atomic displacement ($Å^2$):

	x/a	y/b	z/c	U(eq)
H1	0.4469	0.6791	0.9157	0.036
H2	0.5911	0.5341	1.0146	0.034
H3	0.7315	0.5081	0.9549	0.026
H7	0.8531	0.3814	0.7693	0.023
H8	0.8168	0.2323	0.6165	0.026
H9	0.6815	0.2811	0.4350	0.026
H10	0.7610	0.7819	0.6661	0.02
H11A	0.9217	0.6550	0.7100	0.021
H11B	0.9650	0.7974	0.7678	0.021
H13A	1.0343	0.8264	0.9785	0.023
H13B	1.0046	0.7230	1.0549	0.023
H14A	0.8921	0.9275	1.0010	0.025
H14B	0.8277	0.7915	0.9838	0.025
H15	0.7314	0.8960	0.8170	0.023
H16A	0.8351	1.0841	0.8306	0.042
H16B	0.8085	1.0201	0.7087	0.042
H16C	0.9240	0.9995	0.8098	0.042
H17	0.5805	0.4787	0.4085	0.026
H18	0.6157	0.6266	0.5613	0.024
H19	0.5811	0.7674	0.6926	0.026
H20	0.4427	0.7954	0.7547	0.033

5. Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a Perkin Elmer LS50 luminescence spectrophotometer. All $Ir(ppy)_3$ solutions were excited at 320 nm and the emission intensity was collected at 518 nm. In a typical experiment, to a $1.2•10^{-5}$ M solution of $Ir(ppy)_3$ in DMPU was added the appropriate amount of quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission

of the sample was collected. All Ir(*p*-MeO-ppy)$_3$ solutions were excited at 350 nm and the emission intensity was collected at 500 nm. In a typical experiment, to a $2.0 \bullet 10^{-6}$ M solution of Ir(*p*-MeO-ppy)$_3$ in acetonitrile was added the appropriate amount of quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

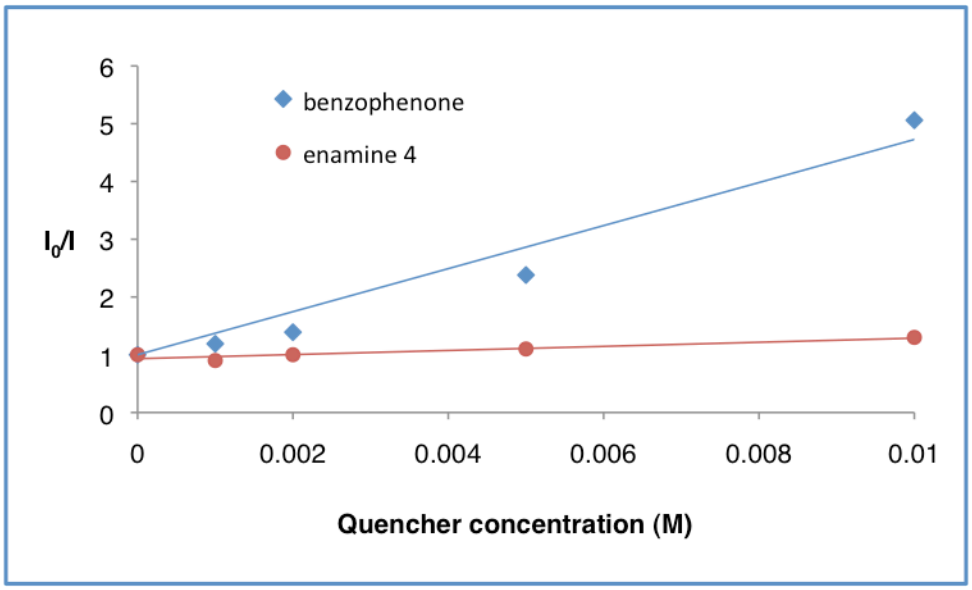


Figure 1. Ir(ppy)$_3$ emission quenching with benzophenone or enamine **4**.

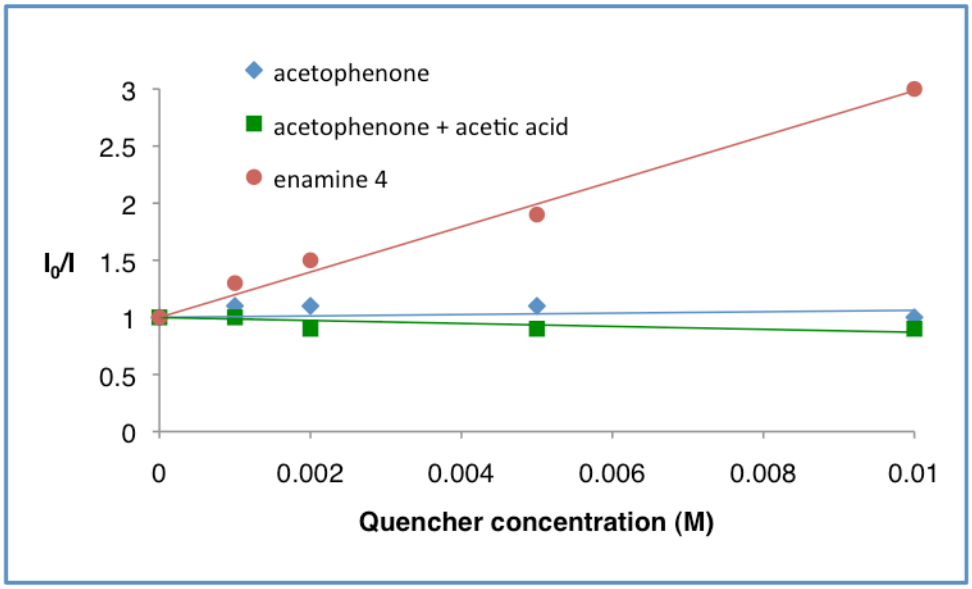


Figure 2. Ir(*p*-MeO-ppy)$_3$ emission quenching with acetophenone, acetophenone in the presence of acetic acid (20 mol%) or and enamine **4**.