Supplementary Information

Copper(II)-catalyzed highly diastereoselective three-component reaction of aryldiazoacetates with alcohols and chalcones: an easy access to furan derivatives

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General Considerations:

Dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($ClCH_2CH_2Cl$) and chloroform ($CHCl_3$) were freshly distilled over calcium hydride prior to use. All commercially available reagents were directly used as received from vendors, unless otherwise stated. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR spectra were recorded on a Brucker-500 MHz spectrometer, and ^{13}C NMR spectra were recorded on a JNM-EX400 MHz spectrometer. Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^{1}H NMR and deuteriochloroform (δ = 77.00 ppm) for ^{13}C NMR spectroscopy. HRMS spectra were recorded on a Bruker micrOTOF II instrument.

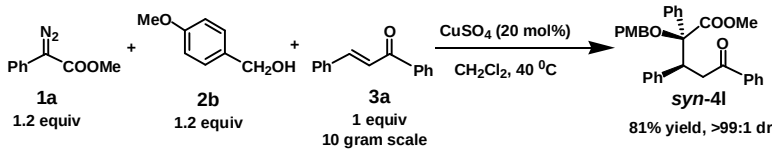
Synthesis of Substrates:

Chalcones **3a**-**3j** were prepared according to the literature procedure.[1] **3k** was synthesized following another literature procedure.[2] Aryl diazoacetates **1a**-**1c** were prepared by the treatment of corresponding arylacetate with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in the presence of DBU following the general procedure.[3]

General Procedure for Copper(II)-Catalyzed Highly Diastereoselective Three-Component Reaction of Aryldiazoacetates with Alcohols and Chalcones:

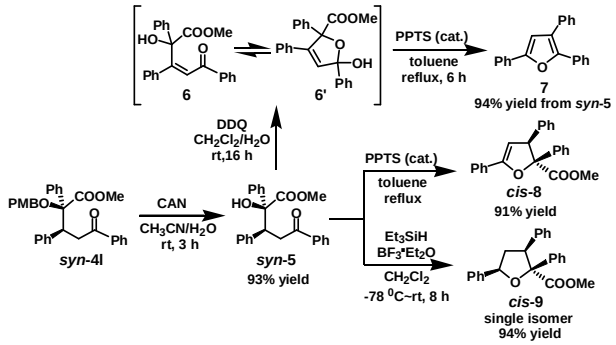
A mixture of $Cu(OTf)_2$ (10.8 mg, 0.03 mmol), alcohols **2** (0.36 mmol), chalcones **3** (0.3 mmol) and CH_2Cl_2 (3 mL) was stirred for 20 min at room temperature, then to the mixture was added diazo compounds **1** (0.36 mmol) in 1.5 mL of CH_2Cl_2 over 3 h via a syringe pump at 40 ^{o}C. After completion of the addition, the reaction mixture was cooled to room temperature. Solvent was removed, and a portion of crude product was subjected to ^{1}H NMR analysis for determination of the product ratio. The crude product was purified by flash chromatography on silica gel (ethyl acetate / petroleum ether = 1:30 ~ 1:20) to give the corresponding pure products **4**.

Scale-up of the Michael-type Theree-Component Reaction:

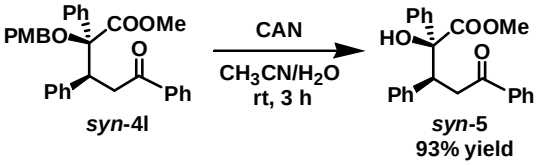


A mixture of $CuSO_4$ (1.53 g, 9.61 mmol), *p*-methoxy benzylalcohol **2b** (7.97 g, 57.64 mmol), chalcone **3a** (10.0 g, 48.03 mmol) and CH_2Cl_2 (200 mL) was vigorously stirred for 20 min at room temperature, then to the mixture was added methyl phenyldiazoacetate **1a** (10.16 g, 57.64 mmol) in 50 mL of CH_2Cl_2 over 4 h via a syringe pump at 40 ^oC. After completion of the addition, the reaction mixture was stirred for another 2 h at the same temperature. The reaction mixture was cooled to room temperature. CH_2Cl_2 was removed, and a portion of crude product was subjected to ^1H NMR analysis for determination of the product ratio (*syn* : *anti* >99 : 1). The crude product was purified by flash chromatography on silica gel (ethyl acetate / petroleum ether = 1:20 ~ 1:10) to give product *syn*-**4l** (19.24 g, 81% yield) as a white solid.

Syntheses of *syn*-5, Polysubstituted Furan 7, 2,3-Dihydrofuran *cis*-8 and Tetrahydrofuran *cis*-9:



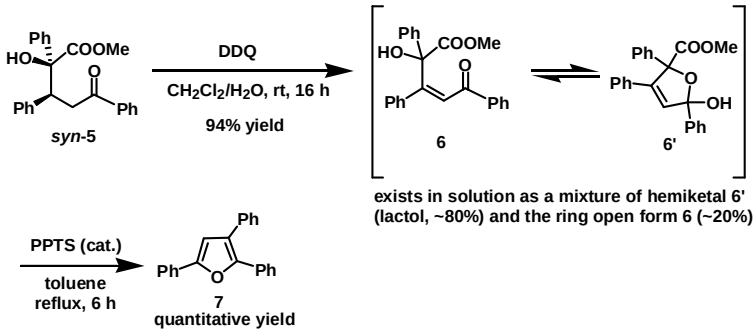
The procedure for preparation of *syn*-5 from three-component product *syn*-4l:



To a stirred solution of compound *syn*-**4l** (1.70 g, 3.44 mmol) in the mixed solvents of CH_3CN and water (v/v = 3:1, 48 mL) was added dropwise the solution of ammonium cerium (IV) nitrate (CAN) (5.10 g, 9.28 mmol) in wet CH_3CN (8 mL) at 0 ^0C. After

addition, the reaction mixture was warmed to room temperature and stirred for 3 h. TLC indicated that the starting material was consumed completely. Then, saturated aq. $NaHCO_3$ solution (20 mL) was added. The precipitated solid was removed by filtration. The filtrate was extracted with EtOAc (3×30 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo* to give the crude product. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:10) to afford the corresponding product *syn*-**5** (1.20 g, 93% yield) as a white solid.

The procedure for preparation of polysubstituted furan 7 from *syn*-5:

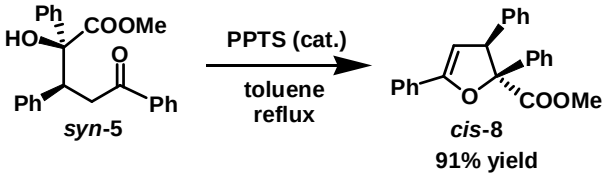


To a mixture of compound *syn*-**5** (0.60 g, 1.60 mmol) in the mixed solvents of CH_2Cl_2 and water (v/v = 9:1, 30 mL) was added 2, 3-dichloro-5, 6-dicyanobenzoquinone (DDQ, 0.44 g, 1.92 mmol) at room temperature. The resulting reaction mixture was stirred at room temperature for 16 h. TLC showed the starting material was completely consumed. The aqueous solution of Na_2CO_3 was added to adjust PH = 10. The organic lay was separated and aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo* to give the crude product. The crude product was purified by column chromatography on silica gel (eluent: EtOAc / petroleum ether = 1:20 ~ 1:10) to afford the dehydrogenated product **6** (560 mg, 94% yield) as a white solid. ^1H NMR analysis showed that this product exists in solution as a mixture of hemiketal **6'** (lactol, ~80%) and the ring open form **6** (~20%).

A mixture of the obtained dehydrogenated product **6** (450 mg, 1.21 mmol), pyridinium *p*-toluenesulfonate (PPTS) (60.3 mg, 0.24 mmol) and toluene (18 mL) was

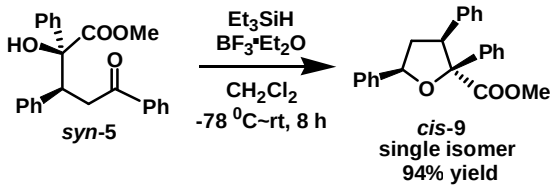
refluxed for 6 h under azeotropic distillation conditions. TLC indicated the reaction was complete. The reaction mixture was cooled to room temperature. The solvent was removed under vacuum to give the crude product. The resulted crude product was purified by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:50) to give the product **7** (340.3 mg, almost quantitative yield) as a colorless crystalline solid.

The procedure for preparation of 2,3-dihydrofuran *cis*-8 from *syn*-5:[4]



A mixture of compound ***syn*-5** (270 mg, 0.72 mmol), pyridinium *p*-toluenesulfonate (PPTS) (36 mg, 0.144 mmol) and toluene (12 mL) was refluxed for 8 h under azeotropic distillation conditions. TLC indicated the reaction was complete. The reaction mixture was cooled to room temperature. The solvent was removed under vacuum to give the crude product. The resulted crude product was purified by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:40) to give the product *cis*-**8** (234 mg, 91% yield) as a white solid.

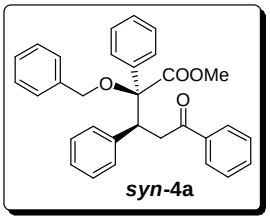
The procedure for preparation of tetrahydrofuran *cis*-9 from *syn*-5:[5]



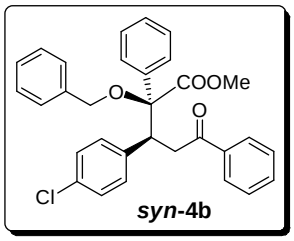
To a stirred solution of compound *syn*-**5** (300 mg, 0.80 mmol) and triethylsilane (186 mg, 1.60 mmol) in dry CH_2Cl_2 (8 mL) was added dropwise a solution of $BF_3 \cdot Et_2O$ (227 mg, 1.60 mmol) in dry CH_2Cl_2 (2 mL) at -78 ^{0}C for 10 min. After addition, the reaction mixture was stirred for 30 min at -78 ^{0}C and for 8 h at room temperature. TLC showed the starting material was completely consumed. Then, saturated aq. $NaHCO_3$ solution (10 mL) was added. The organic lay was separated and aqueous

phase was extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo* to give the crude product. The crude product was purified by column chromatography on silica gel (eluent: EtOAc / petroleum ether = 1:25) to afford the corresponding product *cis*-**9** (269 mg, 94% yield) as a white solid.

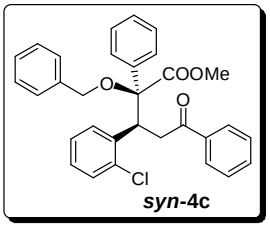
Characterization Data of Products:



(2S*,3S*)-2-benzyloxy-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4a): White solid, mp 156-157 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.39-7.25 (m, 12H), 7.16-7.13 (m, 5H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.42 (dd, *J* = 10.3, 3.2 Hz, 1H), 4.30 (d, *J* = 11.9 Hz, 1H), 3.76 (dd, *J* = 17.5, 10.3 Hz, 1H), 3.77 (s, 3H), 3.35 (dd, *J* = 17.5, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.96, 172.00, 138.88, 138.65, 137.06, 136.37, 132.77, 130.02, 128.36, 128.13, 128.08, 127.98, 127.84, 127.47, 127.07, 126.95, 126.87, 88.72, 68.03, 51.87, 50.72, 39.71; HRMS (ESI) *m/z* calcd for $C_{31}H_{28}NaO_4$ $(M + Na)^+$ 487.1880, found 487.1879.

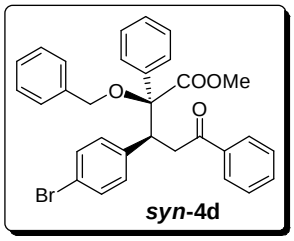


(2S*,3S*)-2-benzyloxy-3-(4-chloro-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4b): White solid, mp 135-137 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.41-7.30 (m, 12H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.39 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.31 (d, *J* = 11.8 Hz, 1H), 3.79 (s, 3H), 3.77 (dd, *J* = 17.8, 10.6 Hz, 1H), 3.34 (dd, *J* = 17.8, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.67, 171.84, 138.69, 137.31, 136.84, 136.23, 132.91, 132.71, 131.30, 128.40, 128.27, 128.17, 127.99, 127.91, 127.85, 127.61, 127.19, 126.91, 88.53, 68.14, 51.94, 50.21, 39.67; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}ClNaO_4$ $(M + Na)^+$ 521.1490, found 521.1490.

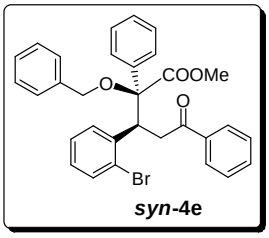


(2S*,3S*)-2-benzyloxy-3-(2-chloro-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4c): White solid, mp 98-100 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40-7.36 (m, 6H), 7.31-7.20 (m, 6H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14-7.11 (m, 1H), 7.09-7.05 (m, 1H), 5.06 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz,

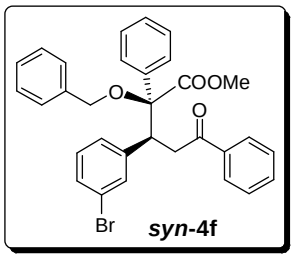
1H), 3.92 (dd, *J* = 17.4, 10.6 Hz, 1H), 3.88 (s, 3H), 3.44 (dd, *J* = 17.4, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.56, 172.40, 139.02, 137.04, 136.82, 136.71, 135.95, 132.79, 129.59, 129.00, 128.35, 128.16, 128.06, 127.97, 127.85, 127.71, 126.98, 126.86, 125.81, 88.56, 68.12, 52.01, 45.89, 41.03; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}ClNaO_4$ $(M + Na)^+$ 521.1490, found 521.1495.



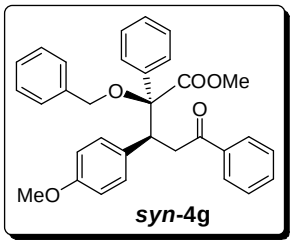
(2S*,3S*)-2-benzyloxy-3-(4-bromo-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4d): White solid, mp 141-142 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.36-7.28 (m, 12H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.38 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.31 (d, *J* = 11.8 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, *J* = 17.7, 10.6 Hz, 1H), 3.34 (dd, *J* = 17.7, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.63, 171.82, 138.67, 137.86, 136.83, 136.21, 132.92, 131.69, 130.55, 128.41, 128.29, 128.17, 128.01, 127.91, 127.85, 127.19, 126.91, 120.97, 88.46, 68.14, 51.95, 50.27, 39.63; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}BrNaO_4$ $(M + Na)^+$ 565.0985, found 565.0981.



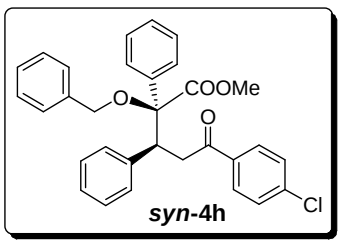
(2S*,3S*)-2-benzyloxy-3-(2-bromo-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4e): White solid, mp 82-84 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.52-7.46 (m, 2H), 7.41-7.35 (m, 7H), 7.32-7.28 (m, 2H), 7.27-7.20 (m, 4H), 7.19-7.16 (m, 1H), 7.01-6.98 (m, 1H), 5.01 (dd, *J* = 10.7, 3.1 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 3.93 (dd, *J* = 17.3, 10.7 Hz, 1H), 3.89 (s, 3H), 3.43 (dd, *J* = 17.3, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.65, 172.47, 139.05, 138.44, 136.74, 135.86, 132.83, 132.45, 129.82, 128.69, 128.38, 128.22, 128.17, 128.07, 127.89, 127.76, 127.02, 126.98, 126.49, 88.65, 68.17, 52.06, 48.65, 41.31; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}BrNaO_4$ $(M + Na)^+$ 565.0985, found 565.0988.



(2S*,3S*)-2-benzyloxy-3-(3-bromo-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4f): White solid, mp 95-97 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40-7.27 (m, 14H), 7.24-6.98 (m, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.33 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.76 (s, 3H), 3.73 (dd, *J* = 18.0, 10.0 Hz, 1H), 3.30 (dd, *J* = 18.0, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.52, 171.81, 141.28, 138.72, 136.83, 136.20, 132.99, 132.96, 130.02, 128.92, 128.75, 128.44, 128.35, 128.24, 128.06, 127.97, 127.82, 127.14, 126.82, 121.62, 88.54, 68.12, 51.96, 50.55, 39.56; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}BrNaO_4$ $(M + Na)^+$ 565.0985, found 565.0991.

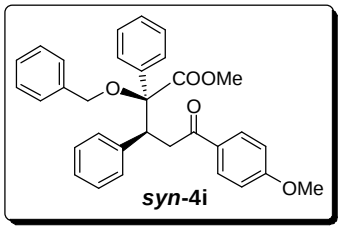


(2S*,3S*)-2-benzyloxy-3-(4-methoxy-phenyl)-5-oxo-2,5-diphenyl-pentanoic acid methyl ester (4g): White solid, mp 96-97 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.50-7.47 (m, 1H), 7.39-7.27 (m, 12H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.36 (dd, *J* = 10.8, 3.0 Hz, 1H), 4.29 (d, *J* = 11.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.68 (dd, *J* = 17.3, 10.8 Hz, 1H), 3.31 (dd, *J* = 17.3, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.06, 171.99, 158.44, 138.83, 137.03, 136.32, 132.70, 130.91, 130.49, 128.31, 128.09, 128.05, 127.93, 127.76, 127.05, 126.86, 112.87, 88.75, 67.96, 54.98, 51.82, 49.89, 39.74; HRMS (ESI) *m/z* calcd for $C_{32}H_{30}NaO_5$ $(M + Na)^+$ 517.1985, found 517.1992.

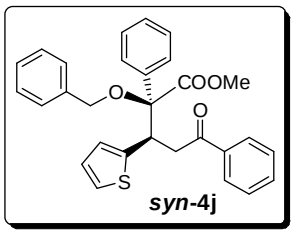


(2S*,3S*)-2-benzyloxy-5-(4-chloro-phenyl)-5-oxo-2,3-diphenyl-pentanoic acid methyl ester (4h): White solid, mp 141-143 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.32-7.21 (m, 12H), 7.14-7.09 (m, 5H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.37 (dd, *J* = 10.1, 3.3 Hz, 1H), 4.28 (d, *J* = 11.9 Hz, 1H), 3.74 (s, 3H), 3.66 (dd, *J* = 17.4, 10.1 Hz, 1H), 3.32 (dd, *J* = 17.4, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.82, 171.89, 139.11, 138.74, 138.44, 136.19, 135.31, 129.94, 129.38, 128.62, 128.14, 128.10, 128.03, 127.82, 127.48, 127.09, 127.01,

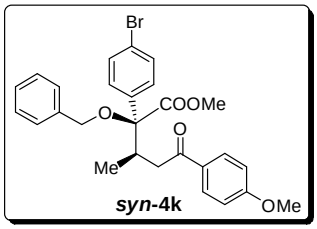
126.87, 88.64, 68.06, 51.86, 50.82, 39.65; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}ClNaO_4$ $(M + Na)^+$ 521.1490, found 521.1497.



(2S*,3S*)-2-benzyloxy-5-(4-methoxy-phenyl)-5-oxo-2,3-diphenyl-pentanoic acid methyl ester (4i): White solid, mp 155-156 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.33-7.21 (m, 10H), 7.14-7.11 (m, 5H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.40 (dd, *J* = 10.3, 3.0 Hz, 1H), 4.28 (d, *J* = 11.9 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.71 (dd, *J* = 17.3, 10.3 Hz, 1H), 3.27 (dd, *J* = 17.3, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.41, 171.98, 163.18, 138.88, 138.70, 136.40, 130.19, 130.12, 129.99, 128.07, 128.03, 127.77, 127.38, 127.01, 126.85, 126.82, 113.44, 88.72, 67.96, 55.29, 51.78, 50.83, 39.21; HRMS (ESI) *m/z* calcd for $C_{32}H_{30}NaO_5$ $(M + Na)^+$ 517.1985, found 517.1983.

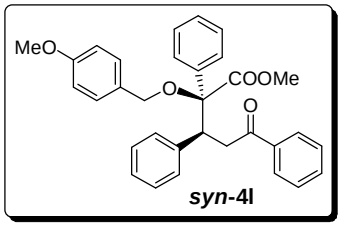


(2S*,3S*)-2-benzyloxy-5-oxo-2,5-diphenyl-3-thiophen-2-yl-pentanoic acid methyl ester (4j): White solid, mp 123-125 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38-7.26 (m, 12H), 7.08 (d, *J* = 5.0 Hz, 1H), 6.79 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 4.76 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.32 (d, *J* = 11.8 Hz, 1H), 3.79 (s, 3H), 3.70 (dd, *J* = 17.5, 10.5 Hz, 1H), 3.27 (dd, *J* = 17.5, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.39, 171.67, 141.64, 138.59, 136.87, 136.10, 132.86, 128.38, 128.29, 128.12, 127.97, 127.94, 127.86, 127.14, 127.01, 126.77, 125,96, 124.38, 88.56, 68.26, 51.98, 46.01, 41.12; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}NaO_4S$ $(M + Na)^+$ 493.1444, found 493.1441.

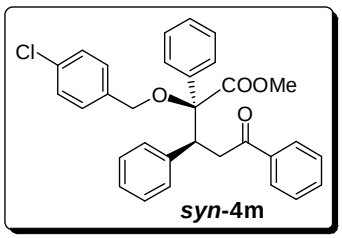


(2S*,3S*)-2-benzyloxy-2-(4-bromo-phenyl)-5-(4-methoxy-phenyl)-3-methyl-5-oxo-pentanoic acid methyl ester (4k): colorless viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.37-7.33 (m, *J* = 8.8 Hz, 4H), 7.31-7.27 (m, 1H), 6.89 (d, *J* = 8.8 Hz,

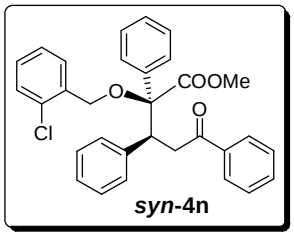
2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 3.85 (s, 6H, overlap), 3.26-3.22 (m, 1H), 3.05 (dd, *J* = 16.4, 2.2 Hz, 1H), 2.59 (dd, *J* = 16.4, 10.4 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.25, 171.50, 163.19, 138.17, 135.73, 131.05, 130.17, 129.96, 129.62, 128.11, 127.24, 126.93, 122.15, 113.44, 87.91, 67.74, 55.20, 51.90, 40.37, 38.67, 15.60; HRMS (ESI) *m/z* calcd for $C_{27}H_{27}BrNaO_5$ $(M + Na)^+$ 533.0934, found 533.0941.



(2S*,3S*)-2-(4-methoxy-benzyloxy)-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4l): White solid, mp 118-119 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40-7.30 (m, 7H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.18-7.13 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.57 (d, *J* = 11.3 Hz, 1H), 4.45 (dd, *J* = 10.2, 3.0 Hz, 1H), 4.26 (d, *J* = 11.3 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.75 (dd, *J* = 17.5, 10.2 Hz, 1H), 3.39 (dd, *J* = 17.5, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.95, 171.99, 158.78, 138.64, 137.04, 136.38, 132.70, 130.91, 130.00, 128.43, 128.31, 128.12, 128.03, 127.92, 127.73, 127.41, 126.89, 113.53, 88.59, 67.70, 55.18, 51.81, 50.57, 39.64; HRMS (ESI) *m/z* calcd for $C_{32}H_{30}NaO_5$ $(M + Na)^+$ 517.1985, found 517.1985.

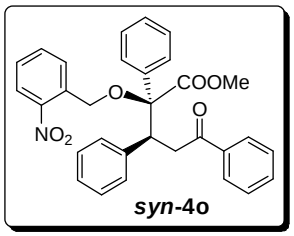


(2S*,3S*)-2-(4-chloro-benzyloxy)-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4m): White solid, mp 168-169 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.40-7.35 (m, 4H), 7.32-7.29 (m, 5H), 7.22-7.18 (m, 7H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.44 (dd, *J* = 10.2, 3.1 Hz, 1H), 4.24 (d, *J* = 12.1 Hz, 1H), 3.82 (dd, *J* = 17.6, 10.2 Hz, 1H), 3.78 (s, 3H), 3.31 (dd, *J* = 17.6, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.76, 171.82, 138.61, 137.38, 136.96, 136.31, 132.77, 132.68, 129.90, 128.34, 128.24, 128.19, 127.96, 127.92, 127.90, 127.49, 126.99, 88.84, 67.37, 51.85, 50.76, 39.68; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}ClNaO_4$ $(M + Na)^+$ 521.1490, found 521.1497.



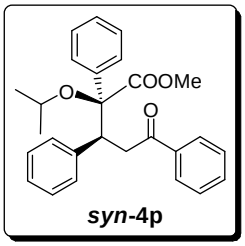
***syn*-4n**

(2S*,3S*)-2-(2-chloro-benzyloxy)-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4n): White solid, mp 83-85 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41-7.38 (m, 4H), 7.31-7.27 (m, 5H), 7.22-7.19 (m, 6H), 4.67 (d, *J* = 13.4 Hz, 1H), 4.45 (dd, *J* = 10.4, 3.0 Hz, 1H), 4.42 (d, *J* = 13.4 Hz, 1H), 3.83 (dd, *J* = 17.6, 10.4 Hz, 1H), 3.77 (s, 3H), 3.34 (dd, *J* = 17.6, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.82, 171.82, 138.69, 138.67, 136.97, 136.66, 136.27, 132.79, 131.76, 129.92, 128.79, 128.39, 128.35, 128.25, 128.01, 127.93, 127.80, 127.52, 126.99, 126.58, 88.92, 65.37, 51.91, 51.04, 39.79; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}ClNaO_4$ $(M + Na)^+$ 521.1490, found 521.1484.



***syn*-4o**

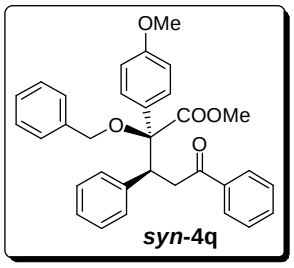
(2S*,3S*)-2-(2-nitro-benzyloxy)-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4o): light yellow solid, mp 118-119 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42-7.37 (m, 5H), 7.33-7.30 (m, 3H), 7.25-7.19 (m, 5H), 4.91 (d, *J* = 15.3 Hz, 1H), 4.62 (d, *J* = 15.3 Hz, 1H), 4.45 (dd, *J* = 10.5, 2.7 Hz, 1H), 3.92 (dd, *J* = 17.8, 10.5 Hz, 1H), 3.74 (s, 3H), 3.23 (dd, *J* = 17.8, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.64, 171.60, 146.87, 138.81, 136.87, 136.31, 135.54, 133.34, 132.82, 129.76, 128.88, 128.51, 128.35, 128.30, 127.91, 127.64, 127.55, 127.41, 127.07, 124.21, 89.27, 65.27, 51.90, 51.23, 39.86; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}NNaO_6$ $(M + Na)^+$ 532.1730, found 532.1734.



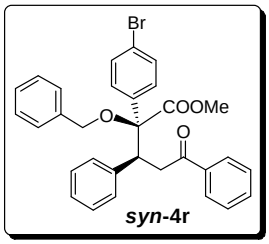
***syn*-4p**

(2S*,3S*)-2-isopropoxy-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (4p): White solid, mp 110-112 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30-7.24 (m, 5H), 7.14-7.12 (m, 3H), 7.08-7.06 (m, 2H), 4.51 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.83 (septet, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 3.60 (dd, *J* = 18.0, 10.0 Hz, 1H), 3.45 (dd, *J* = 18.0, 2.5 Hz, 1H), 1.11 (d, *J* =

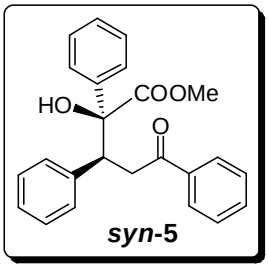
6.0 Hz, 3H), 0.93 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.32, 172.51, 139.02, 137.79, 137.27, 132.68, 130.12, 128.60, 128.34, 127.93, 127.89, 127.34, 127.24, 126.69, 88.01, 68.95, 51.56, 49.02, 39.69, 23.92, 23.44; HRMS (ESI) *m/z* calcd for $C_{27}H_{28}NaO_4$ $(M + Na)^+$ 439.1880, found 439.1886.



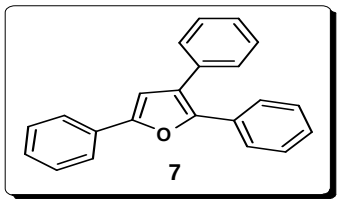
(2S*,3S*)-2-benzyloxy-2-(4-methoxy-phenyl)-5-oxo-3,5-diphenyl-pentanoic acid methyl ester (4q): White solid, mp 135-137 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41-7.37 (m, 2H), 7.31-7.20 (m, 7H), 7.20-7.17 (m, 5H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.44 (dd, *J* = 10.3, 3.2 Hz, 1H), 4.29 (d, *J* = 11.9 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.78 (dd, *J* = 17.5, 10.3 Hz, 1H, overlap), 3.38 (dd, *J* = 17.5, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.98, 172.13, 159.23, 138.93, 138.75, 137.04, 132.70, 129.98, 129.41, 128.30, 128.23, 128.06, 127.93, 127.45, 126.99, 126.89, 126.83, 113.11, 88.41, 67.79, 55.11, 51.75, 50.82, 39.69; HRMS (ESI) *m/z* calcd for $C_{32}H_{30}NaO_5$ $(M + Na)^+$ 517.1985, found 517.1983.



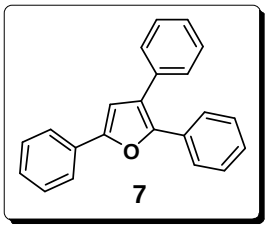
(2S*,3S*)-2-benzyloxy-2-(4-bromo-phenyl)-5-oxo-3,5-diphenyl-pentanoic acid methyl ester (4r): White solid, mp 134-135 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.44-7.31 (m, 9H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.21-7.19 (m, 3H), 7.15-7.13 (m, 2H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.46 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.33 (d, *J* = 11.8 Hz, 1H), 3.79 (s, 3H), 3.73 (dd, *J* = 17.5, 9.9 Hz, 1H), 3.46 (dd, *J* = 17.5, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.58, 171.46, 138.34, 138.19, 136.88, 135.27, 132.77, 130.75, 129.94, 129.91, 128.32, 128.15, 127.87, 127.53, 127.21, 127.06, 126.82, 122.29, 88.22, 68.09, 51.96, 50.50, 39.36; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}BrNaO_4$ $(M + Na)^+$ 565.0985, found 565.0989.



(2S*,3S*)-2-hydroxy-5-oxo-2,3,5-triphenyl-pentanoic acid methyl ester (*syn*-5): White solid, mp 140-141 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.51-7.49 (m, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.18-7.11 (m, 5H), 7.01-6.97 (m, 3H), 4.41 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.94 (s, 1H), 3.89 (dd, *J* = 17.0, 9.5 Hz, 1H), 3.84 (s, 3H), 3.13 (dd, *J* = 17.0, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.96, 175.40, 140.16, 138.89, 136.97, 132.97, 129.75, 128.47, 128.06, 127.78, 127.47, 127.45, 126.45, 125.76, 81.49, 53.58, 48.51, 40.91; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NaO_4$ $(M + Na)^+$ 397.1410, found 397.1418

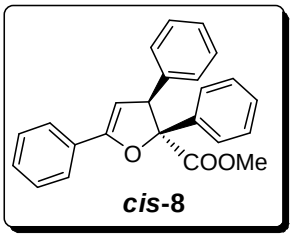


Dehydrogenated product exists in solution as a mixture of hemiketal 6' (lactol, ~80%) and the ring open form 6 (~20%): White solid, mp 94-95 ^{0}C; hemiketal **6'** (lactol, ~80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.42-7.32 (m, 7H), 7.30-7.23 (m, 6H), 6.61 (s, 1H), 4.49 (s, 1H, exchanged by D_2O addition, O<u>H</u>), 3.84 (s, 3H); the ring open form **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.54-7.52 (m, 2H), 7.43-7.32 (m, 5H), 7.31-7.23 (m, 6H), 646 (s, 1H), 3.74 (s, 3H), 3.09 (s, 1H, exchanged by D_2O addition, O<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.17 (170.76), (143.52) 141.55, 140.71 (139.35), 137.39, 131.81, 130.80 (130.19), 128.61, 128.45, 128.30, 128.17, 128.11, 128.03, 127.96, 127.86, 127.74, 127.33, 125.88, (109.83) 109.67, (94.51) 94.23, 53.24 (52.31); HRMS (ESI) *m/z* calcd for $C_{24}H_{20}NaO_4$ $(M + Na)^+$ 395.1254, found 395.1266.



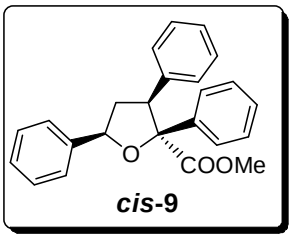
2,3,5-triphenyl-furan (7): colorless crystalline solid, mp 90-91 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.42-7.36 (m, 4H), 7.33-7.27 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.53, 147.87, 134.30, 131.09, 130.51, 128.69,

128.67, 128.63, 128.36, 127.48, 127.45, 127.26, 126.10, 124.51, 123.79, 109.43; HRMS (ESI) *m/z* calcd for $C_{22}H_{17}O\,(M + H)^+$ 297.1274, found 297.1264.



***cis*-8**

(2S*,3S*)-2,3,5-triphenyl-2,3-dihydro-furan-2-carboxylic acid methyl ester (*cis*-8): White solid, mp 104-105 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.47-7.39 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.11-7.00 (m, 8H), 5.64 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.24, 155.32, 138.77, 135.83, 130.21, 129.24, 128.99, 128.44, 127.72, 127.52, 127.33, 126.77, 126.04, 125.65, 101.20, 93.55, 56.80, 53.15; HRMS (ESI) *m/z* calcd for $C_{24}H_{20}NaO_3\,(M + Na)^+$ 379.1304, found 379.1311

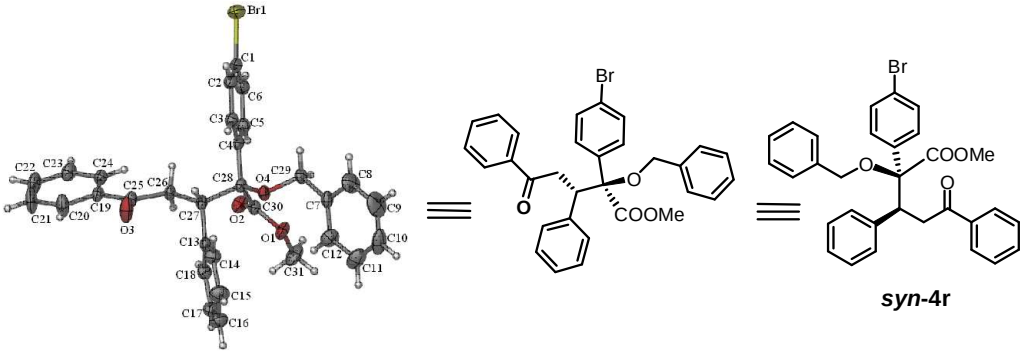


***cis*-9**

(2S*,3S*,5R*)-2,3,5-triphenyl-tetrahydro-furan-2-carboxylic acid methyl ester (*cis*-9): White solid, mp 96-97 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21-7.19 (m, 2H), 7.07-7.05 (m, 3H), 7.01-6.99 (m, 3H), 6.94-6.91 (m, 2H), 5.21 (dd, *J* = 10.1, 5.9 Hz, 1H), 4.57 (dd, *J* = 8.9, 7.6 Hz, 1H), 3.77 (s, 3H), 2.81 (ddd, *J* = 12.4, 10.1, 8.9 Hz, 1H), 2.26 (ddd, *J* = 12.4, 7.6, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.27, 140.47, 139.74, 137.81, 129.21, 128.43, 127.66, 127.56, 127.29, 127.10, 126.32, 126.09, 126.04, 90.68, 79.95, 52.84, 52.82, 41.92; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NaO_3\,(M + Na)^+$ 381.1461, found 381.1474.

Single-crystal X-ray structure determinations were performed on a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software. Scaling and absorption corrections were applied using SADABS multi-scan technique supplied by George Sheldrick.[6] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97.[7]

Crystal data of the three-component product *syn*-4r

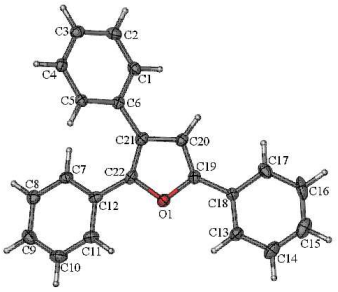


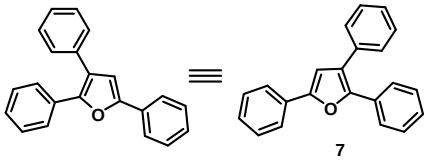
***syn*-4r**

Identification code	z
Empirical formula	$C_{31}H_{27}BrO_4$
Formula weight	543.44
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 11.0837(4) Å alpha = 90 deg.
	b = 12.5162(4) Å beta = 105.7030(10) deg.
	c = 19.9846(7) Å gamma = 90 deg.
Volume	2668.91(16) $Å^3$
Z, Calculated density	4, 1.352 Mg/m^3
Absorption coefficient	1.574 mm^{-1}
F(000)	1120

Crystal size	0.48 x 0.26 x 0.22 mm
Theta range for data collection	1.91 to 25.01 deg.
Limiting indices	-13<=h<=13, -14<=k<=14, -23<=l<=23
Reflections collected / unique	30268 / 4691 [R(int) = 0.0283]
Completeness to theta = 25.01	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.606688
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4691 / 0 / 325
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1131
R indices (all data)	R1 = 0.0630, wR2 = 0.1251
Largest diff. peak and hole	0.646 and -0.768 e. $Å^{-3}$

Crystal data of polysubstituted furan 7



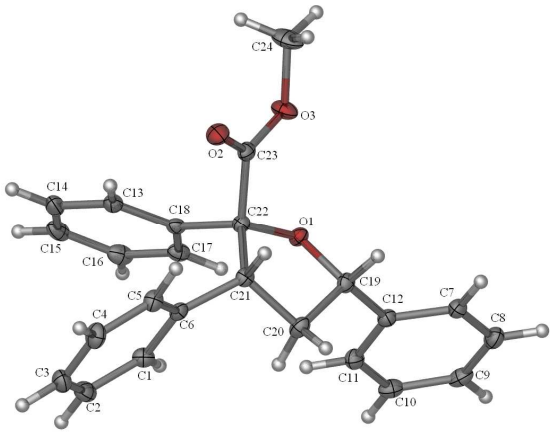


7

Identification code	z
Empirical formula	$C_{22}H_{16}O$
Formula weight	296.35
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 7.7124(4) Å alpha = 90 deg.
	b = 19.8082(9) Å beta = 90 deg.

	c = 20.3303(10) Å gamma = 90 deg.
Volume	3105.8(3) Å^3
Z, Calculated density	8, 1.268 Mg/m^3
Absorption coefficient	0.076 mm^{-1}
F(000)	1248
Crystal size	0.52 x 0.48 x 0.36 mm
Theta range for data collection	2.06 to 25.01 deg.
Limiting indices	-9<=h<=9, -23<=k<=23, -24<=l<=24
Reflections collected / unique	32737 / 2731 [R(int) = 0.0247]
Completeness to theta = 25.01	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9731 and 0.9615
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2731 / 0 / 208
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1258
R indices (all data)	R1 = 0.0559, wR2 = 0.1334
Largest diff. peak and hole	0.308 and -0.391 e.A^{-3}

Crystal data of polysubstituted tetrahydrofuran *cis*-9



Identification code	z

Empirical formula	$C_{24}H_{22}O_3$
Formula weight	358.42
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 8.6978(3) Å alpha = 90 deg.
	b = 9.0256(3) Å beta = 90 deg.
	c = 23.8222(9) Å gamma = 90 deg.
Volume	1870.11(11) $Å^3$
Z, Calculated density	4, 1.273 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	760
Crystal size	0.52 x 0.44 x 0.32 mm
Theta range for data collection	2.41 to 25.01 deg.
Limiting indices	-10<=h<=10, -10<=k<=10, -28<=l<=28
Reflections collected / unique	21736 / 1903 [R(int) = 0.0862]
Completeness to theta = 25.01	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9740 and 0.9582
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1903 / 0 / 244
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0293, wR2 = 0.0734
R indices (all data)	R1 = 0.0302, wR2 = 0.0742
Largest diff. peak and hole	0.135 and -0.180 $e.A^{-3}$

Notes and references

1 X.-C. Luo, H. Zhang, H. Duan, Q. Liu, L.-Z. Zhu, T. Zhang and A.-W. Lei, *Org. Lett.*, 2007, **9**, 4571.

2 R. P. Mariella and R. R. Raube, *J. Am. Chem. Soc.*, 1952, **74**, 521.

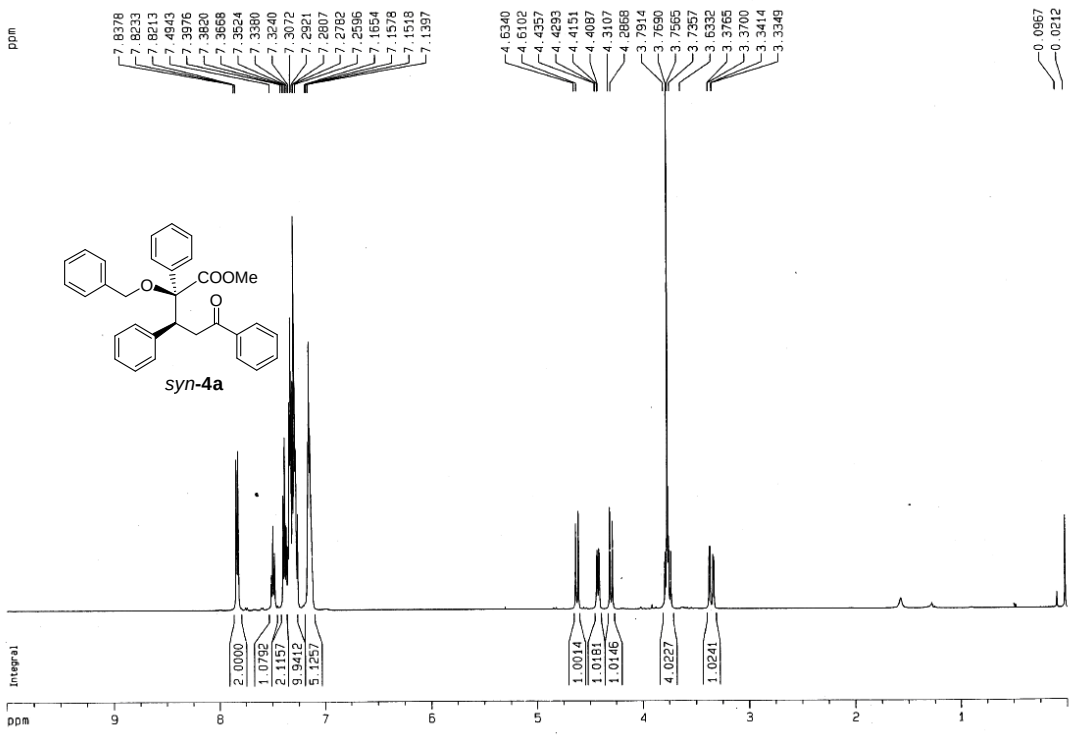
3 M. P. Doyle, M. A. McKervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, 1998.

4 T. Mukaiyama, M. Hayashi and J. Ichikawa, *Chem. Lett.*, 1986, 1157.

5 H.-U. Reissig, H. Holzinger and G. Glomsda, *Tetrahedron*, 1989, **45**, 3139.

6 SAINT V 7.34 Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Madison, WI, 2001.

7 Sheldrick, G. M. *SHELX-97*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.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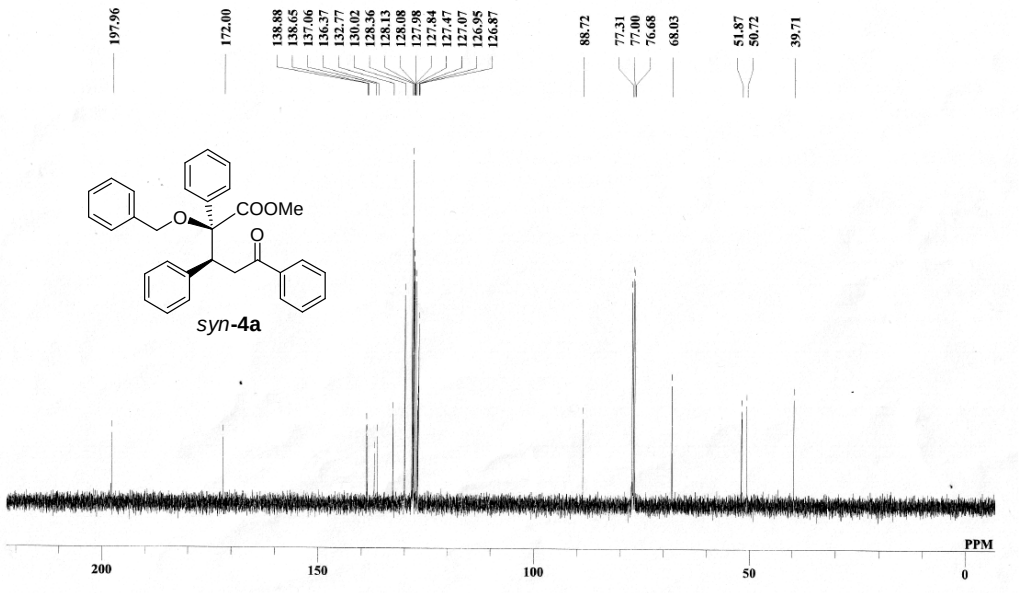
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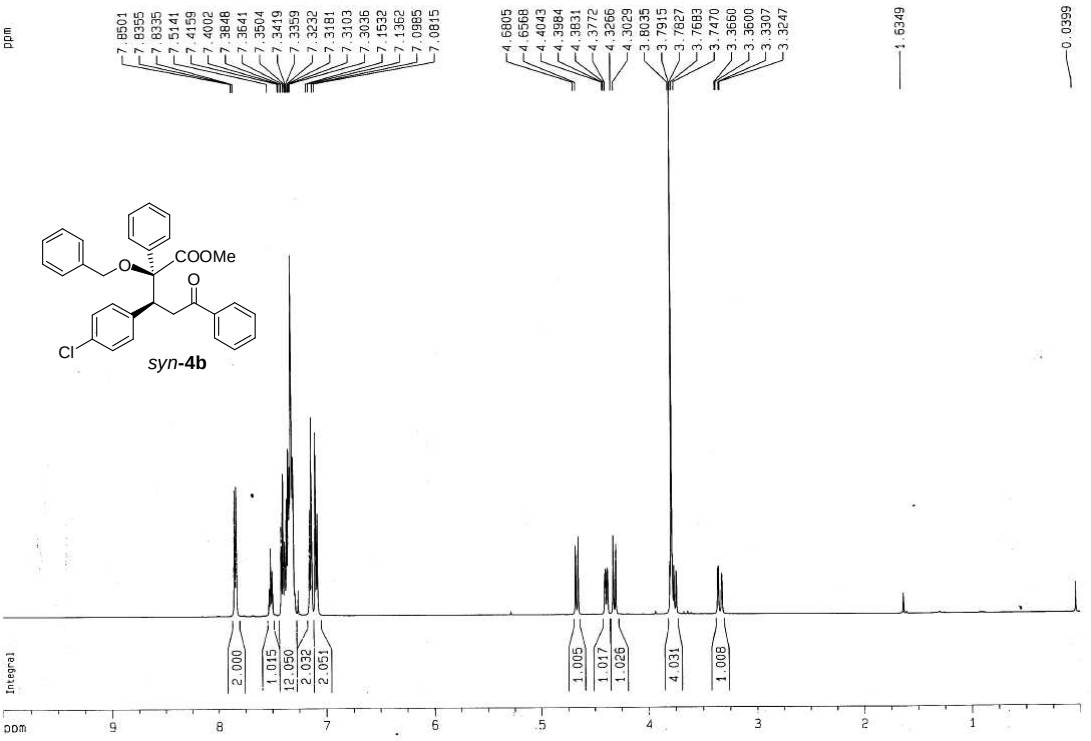
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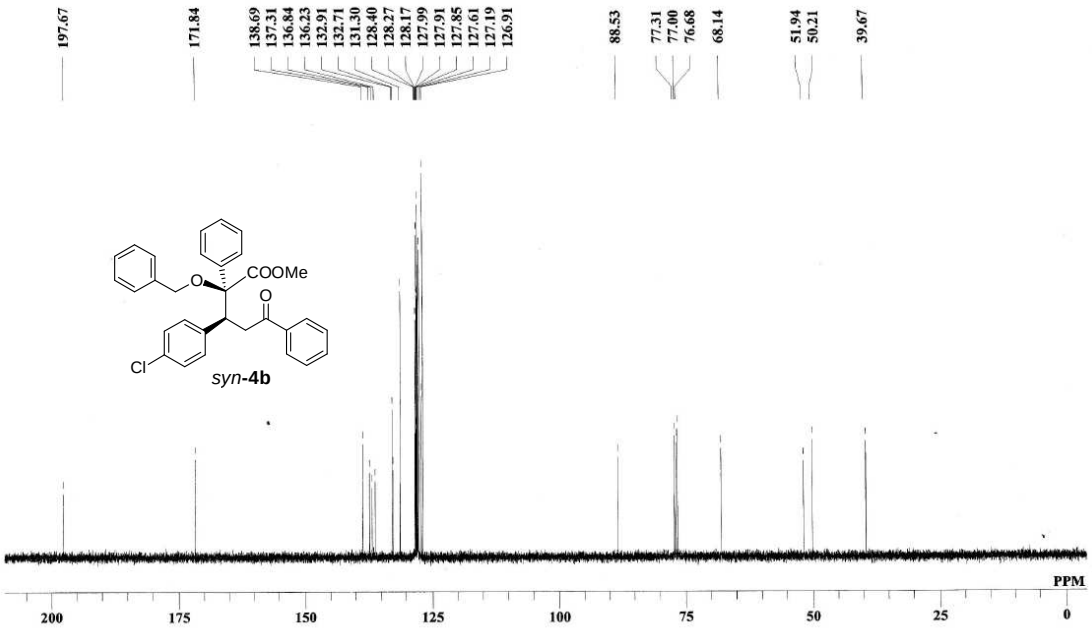
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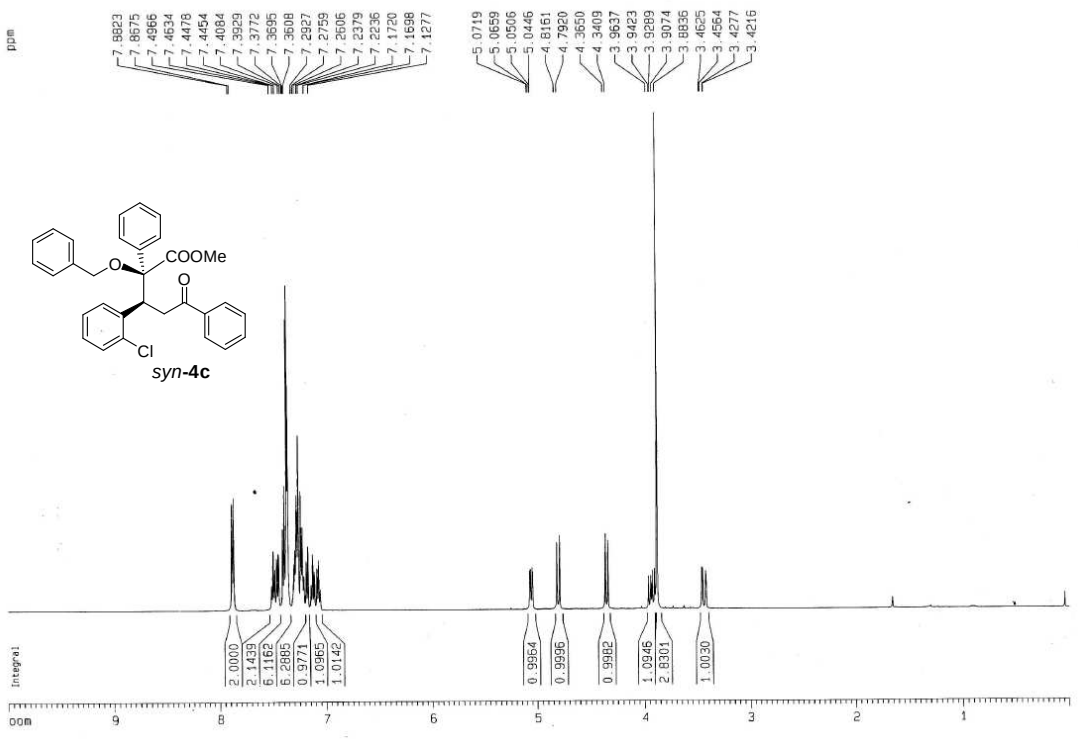
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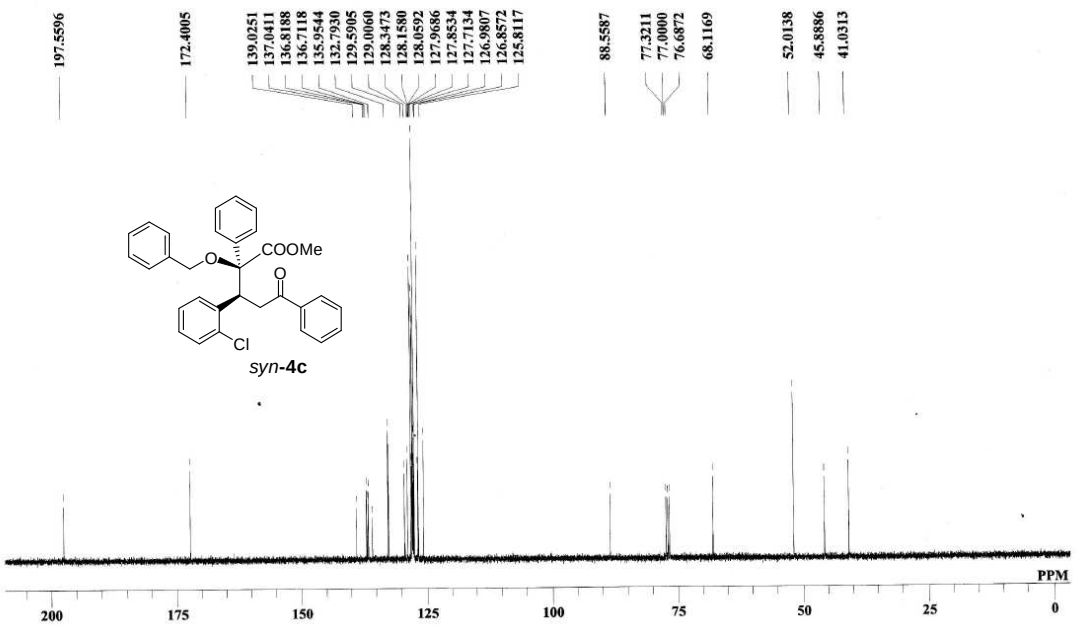
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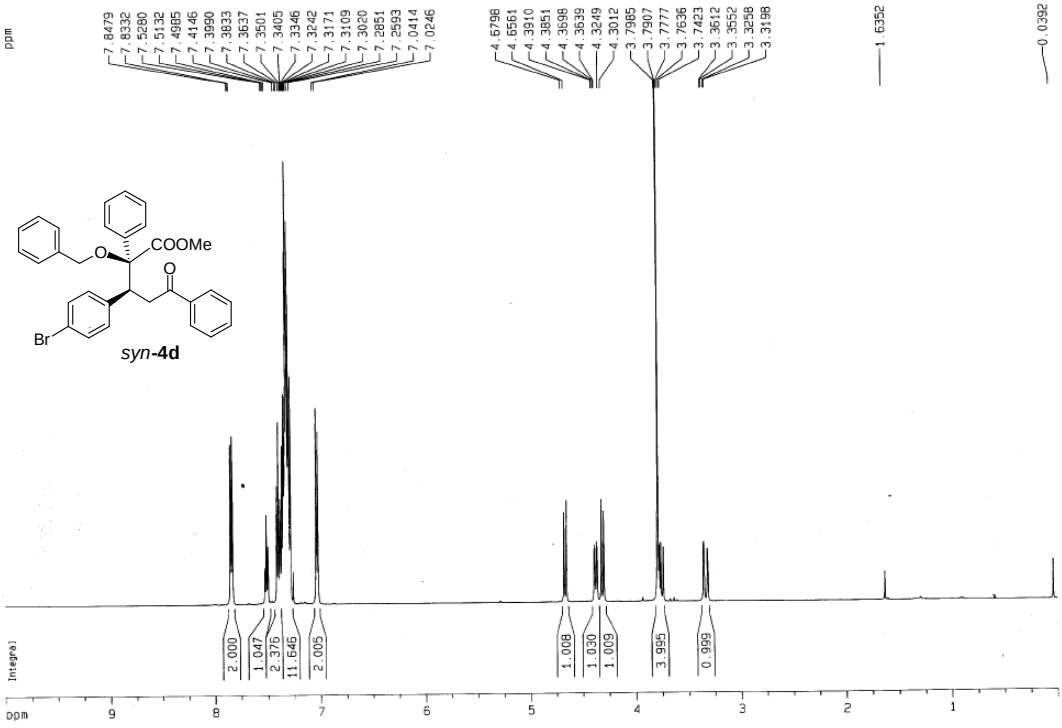
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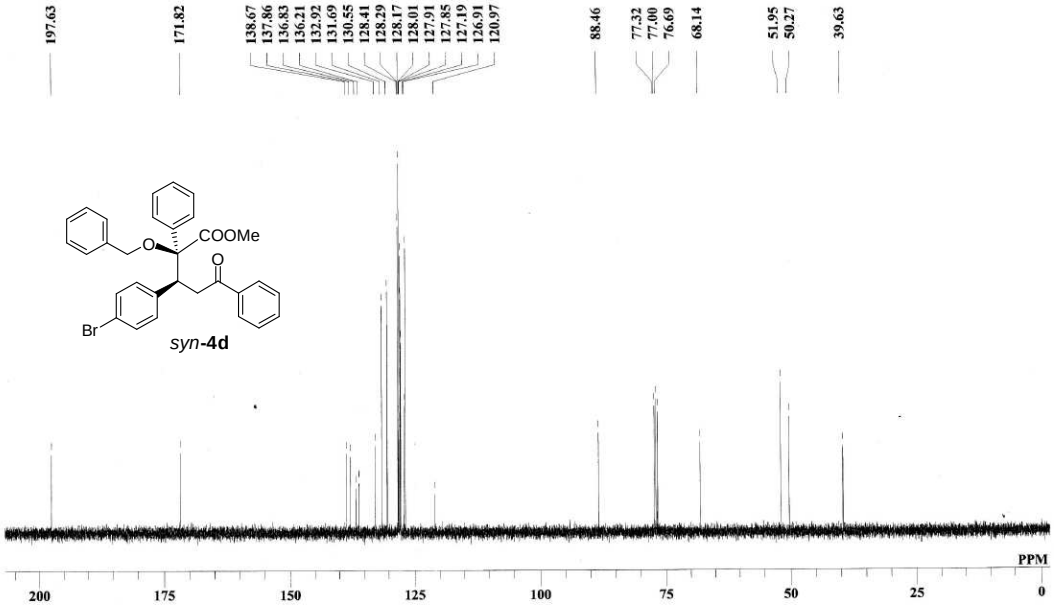
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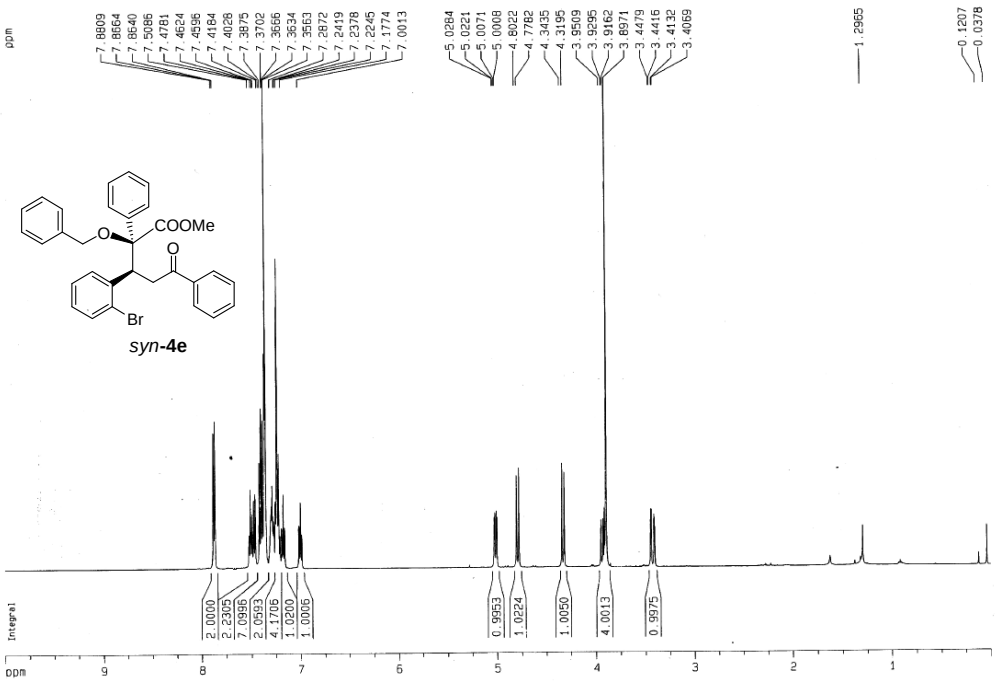
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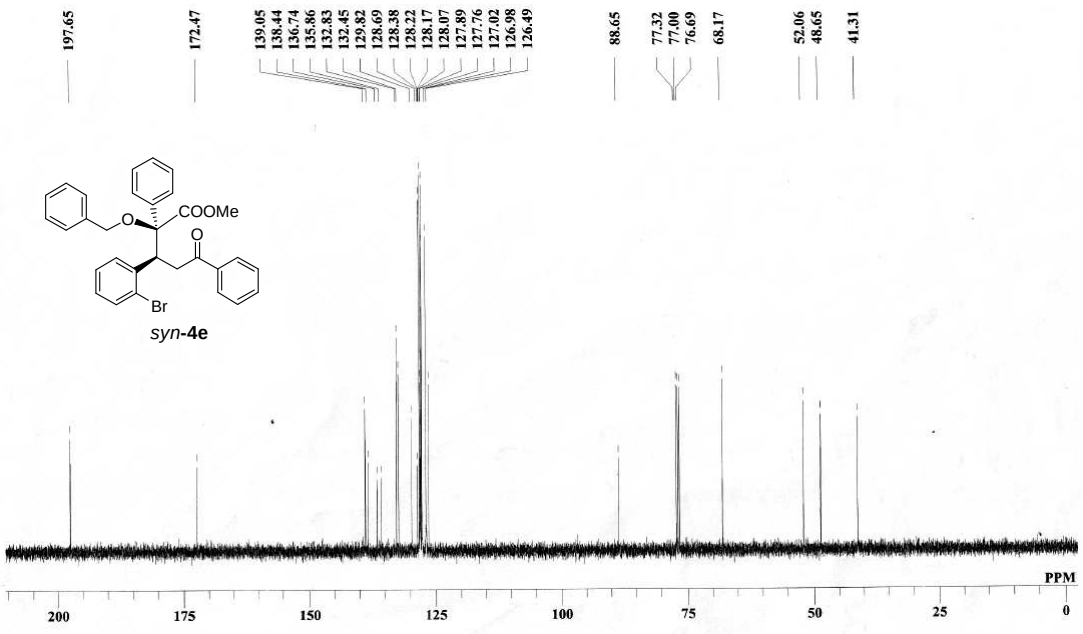
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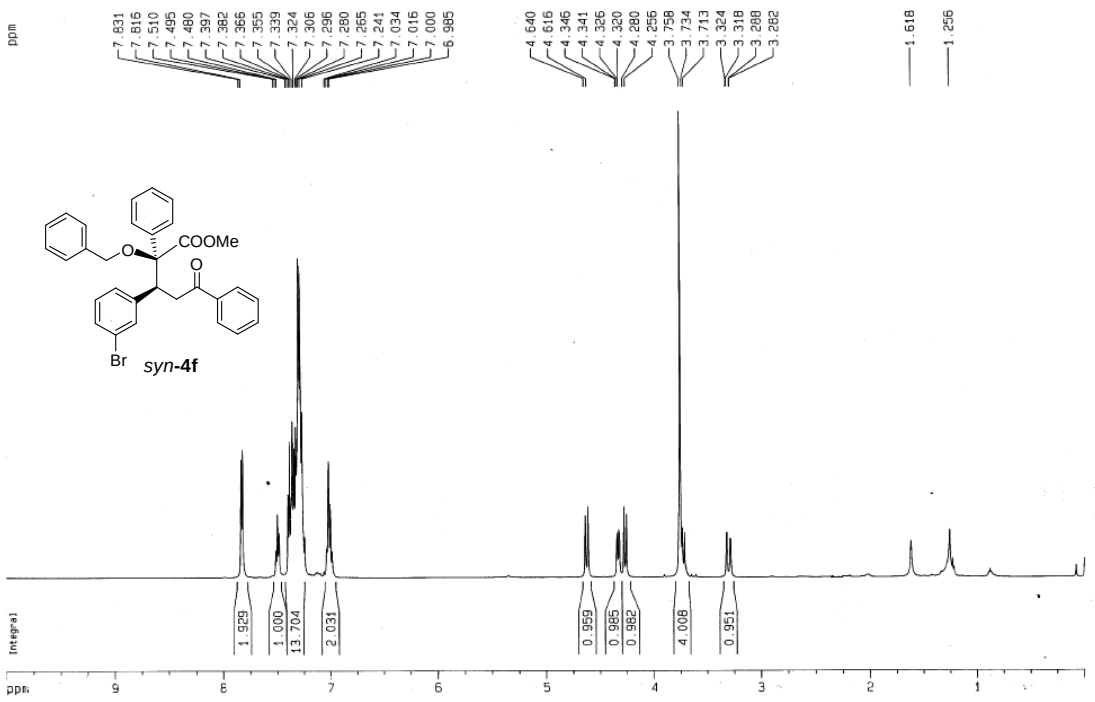
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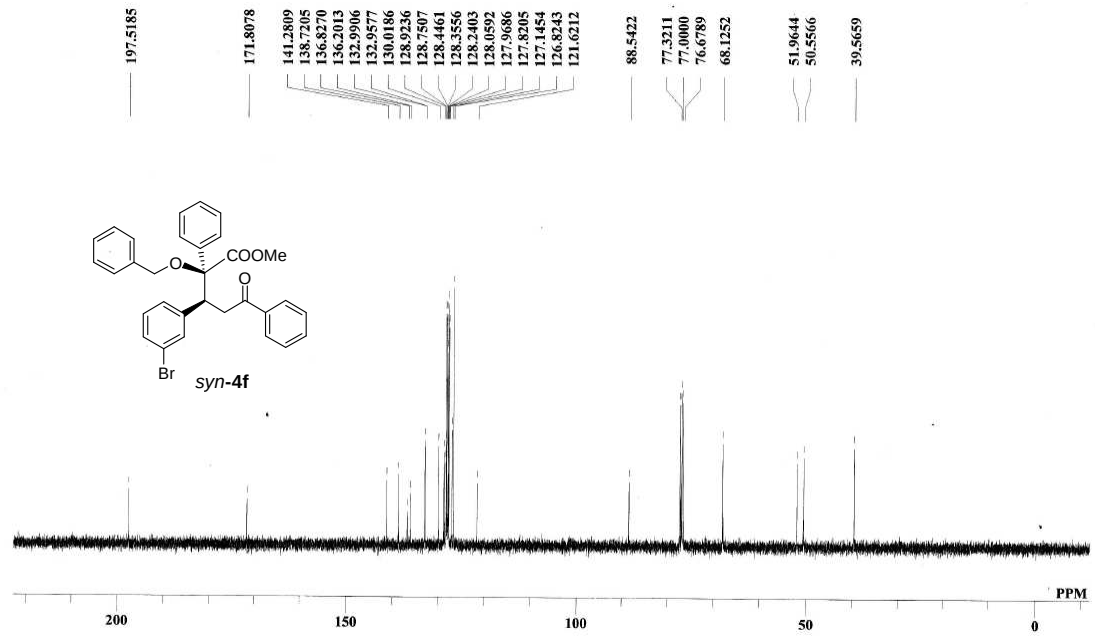
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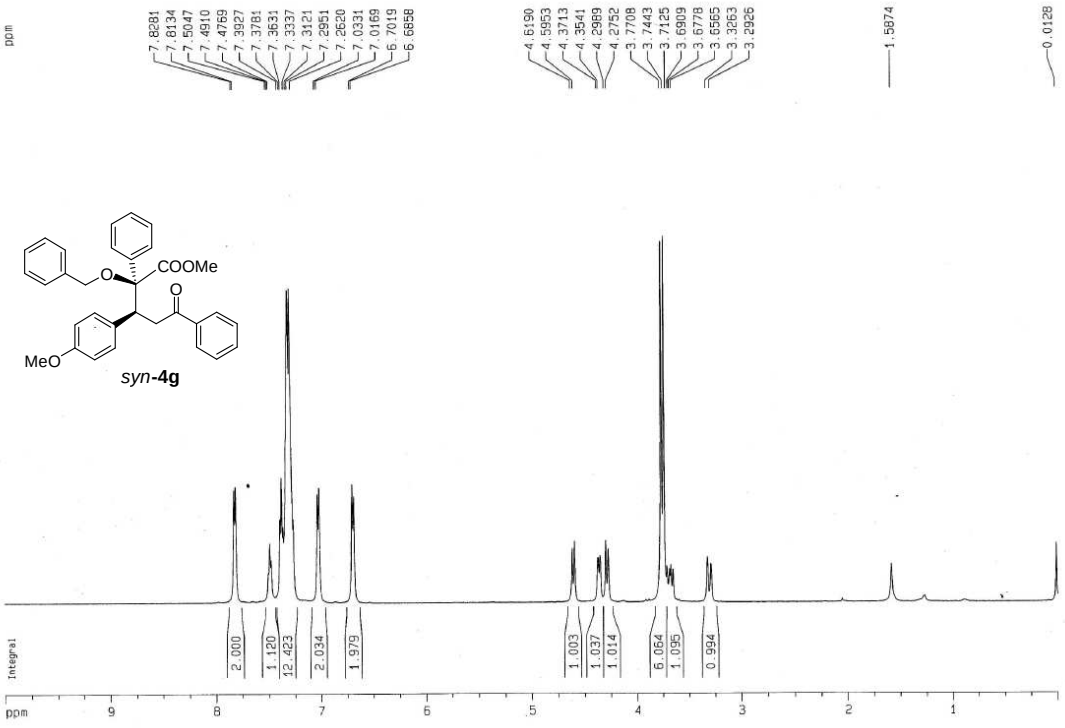
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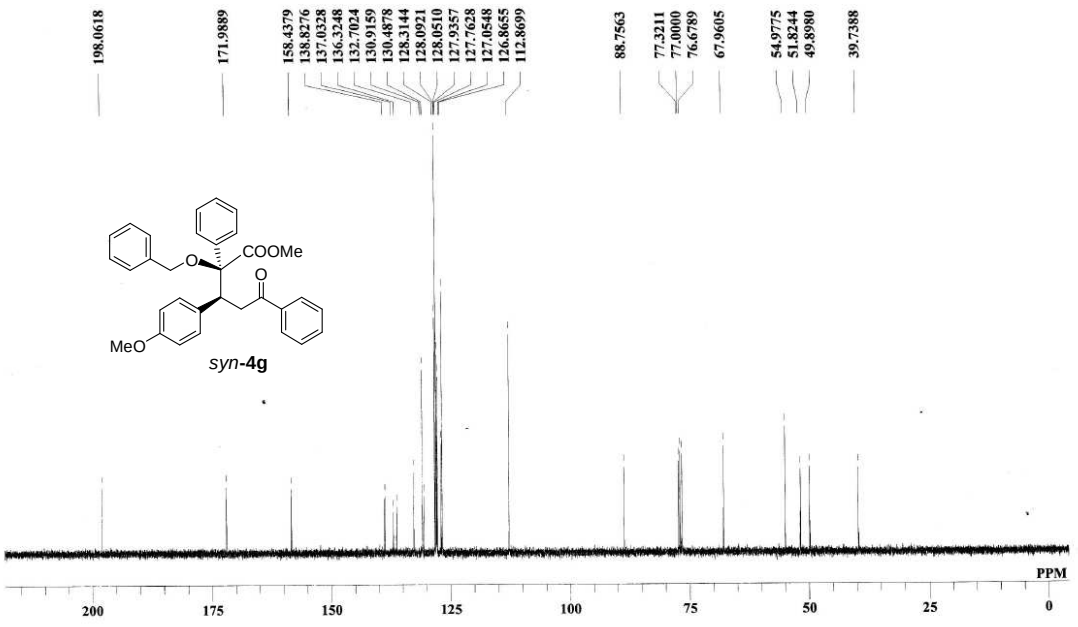
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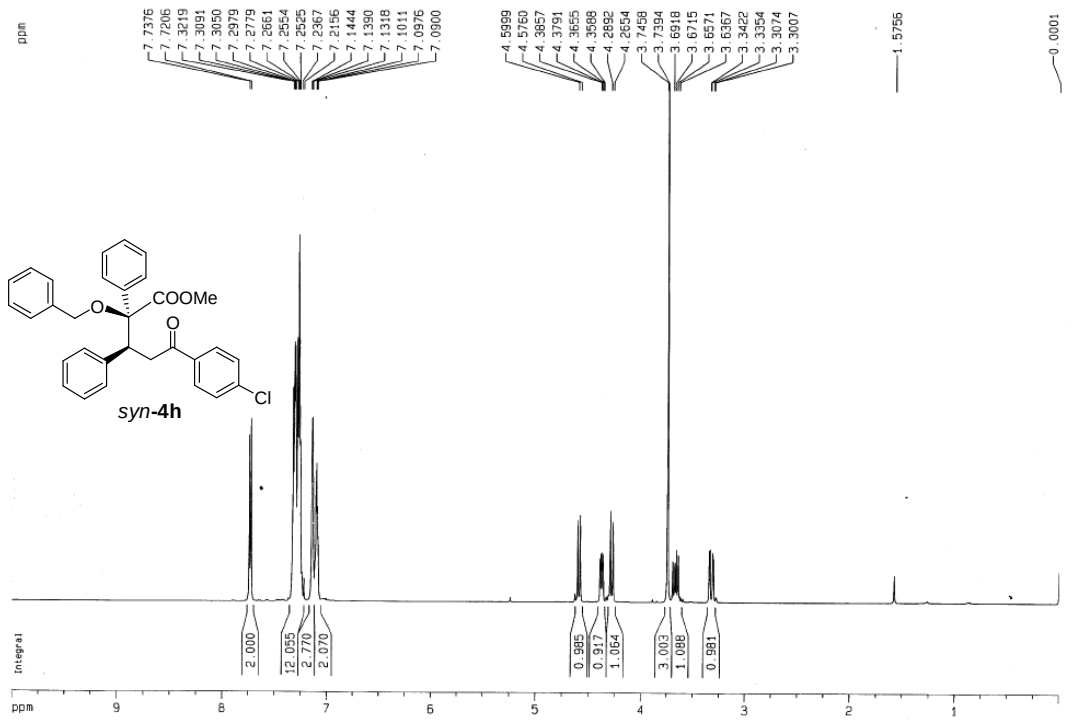
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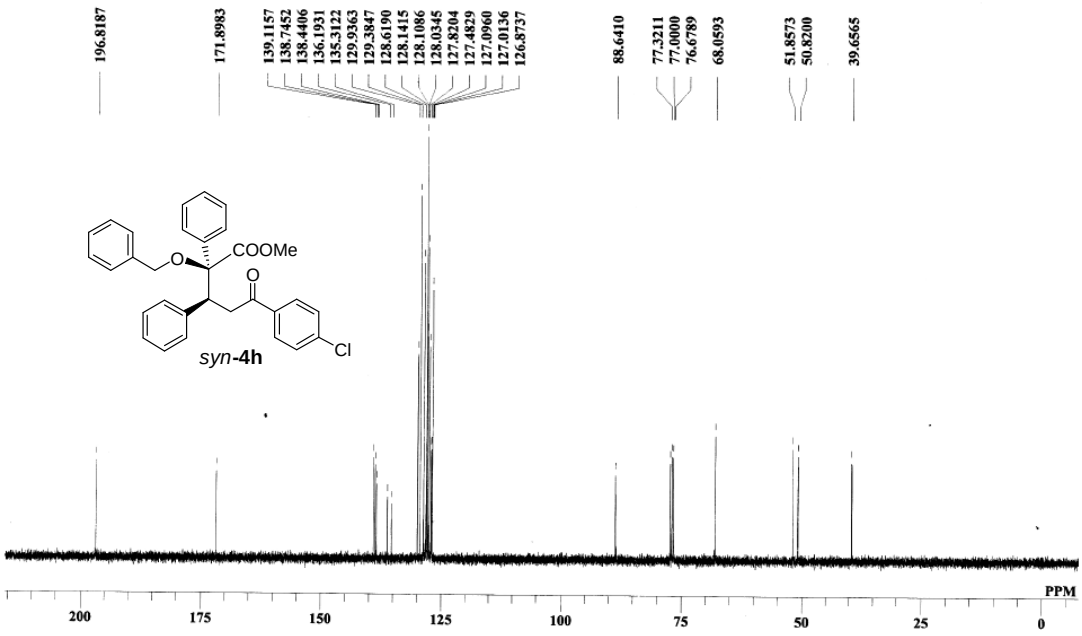
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76.6789
68.0593
51.8573
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O
Cl
syn-4h
PPM
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75
50
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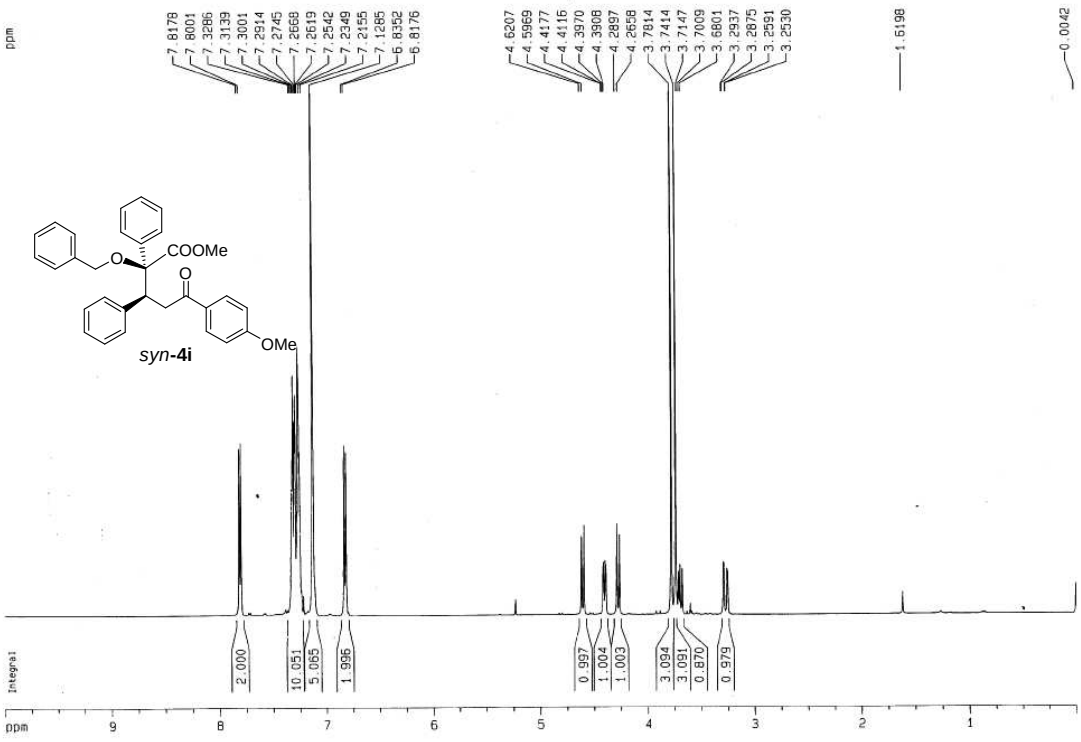
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7.3001
7.2914
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7.2668
7.2619
7.2542
7.2349
7.2155
7.1285
6.8352
6.8176
4.6207
4.5969
4.4177
4.4116
4.3970
4.3908
4.2897
4.2658
3.7814
3.7414
3.7147
3.7009
3.6801
3.2937
3.2875
3.2591
3.2530
1.6198
0.0042
COOMe
O
OMe
syn-4i
Integral
2.000
10.051
5.065
1.996
0.997
1.004
1.003
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3.091
0.870
0.979
ppm
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8
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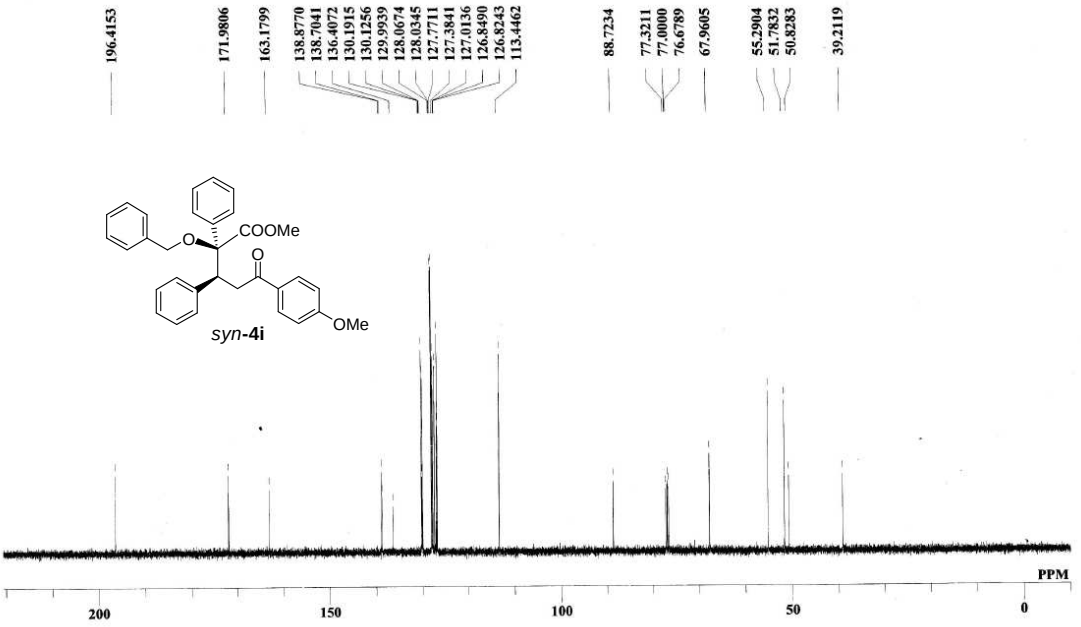
1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127.7711
127.3841
127.0136
126.8490
126.8243
113.4462
88.7234
77.3211
77.0000
76.6789
67.9605
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O
OMe
syn-4i
PPM
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150
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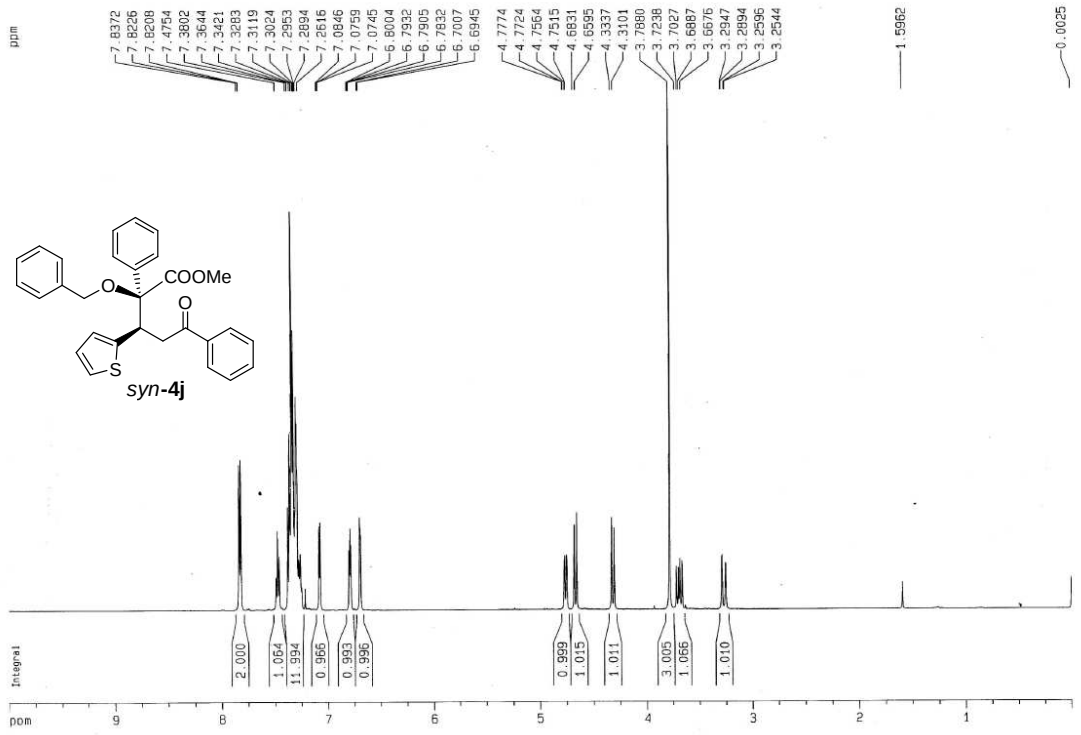
50
0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7.3119
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7.2953
7.2894
7.2616
7.0846
7.0759
7.0745
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6.7932
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6.7832
6.7007
6.6945
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4.7724
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4.7515
4.6831
4.6595
4.3337
4.3101
3.7880
3.7238
3.7027
3.6887
3.6676
3.2947
3.2894
3.2596
3.2544
1.5962
0.0025
COOMe
O
O
S
syn-4j
Integral
2.000
1.064
11.994
0.966
0.993
0.996
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1.011
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1.010
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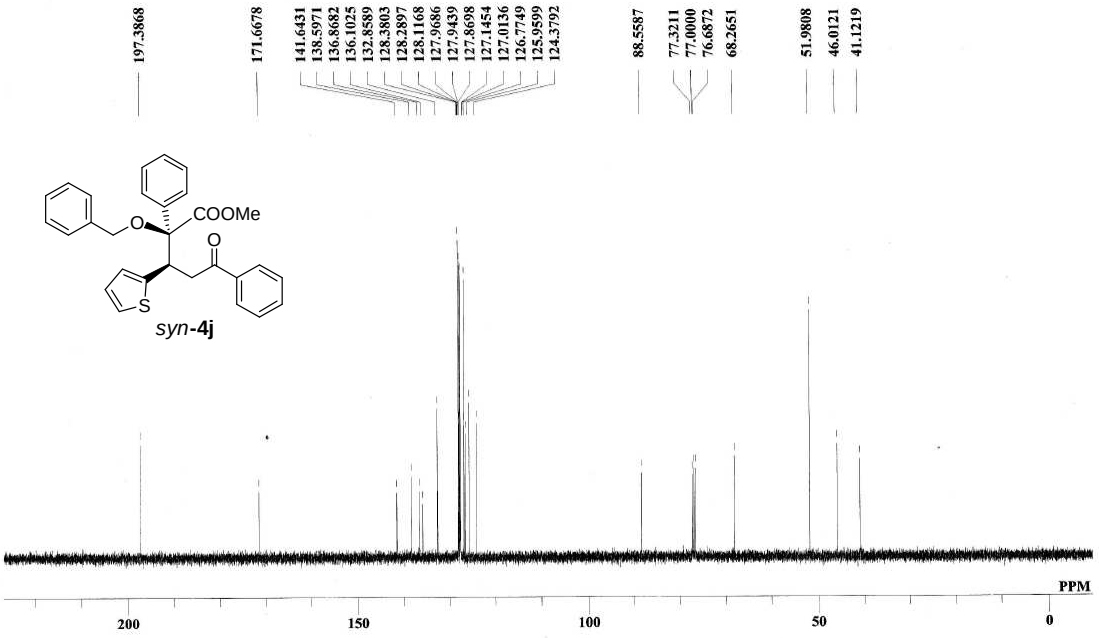
1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127.1454
127.0136
126.7749
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124.3792
88.5587
77.3211
77.0000
76.6872
68.2651
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41.1219
COOMe
O
O
S
syn-4j
PPM
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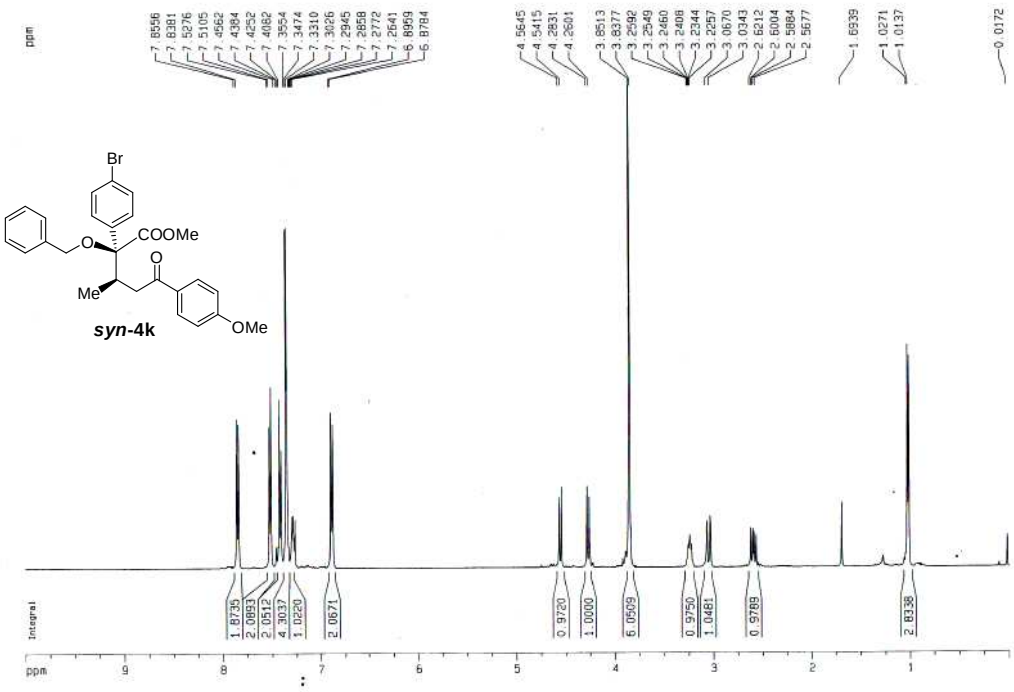
150
100
50
0


Br
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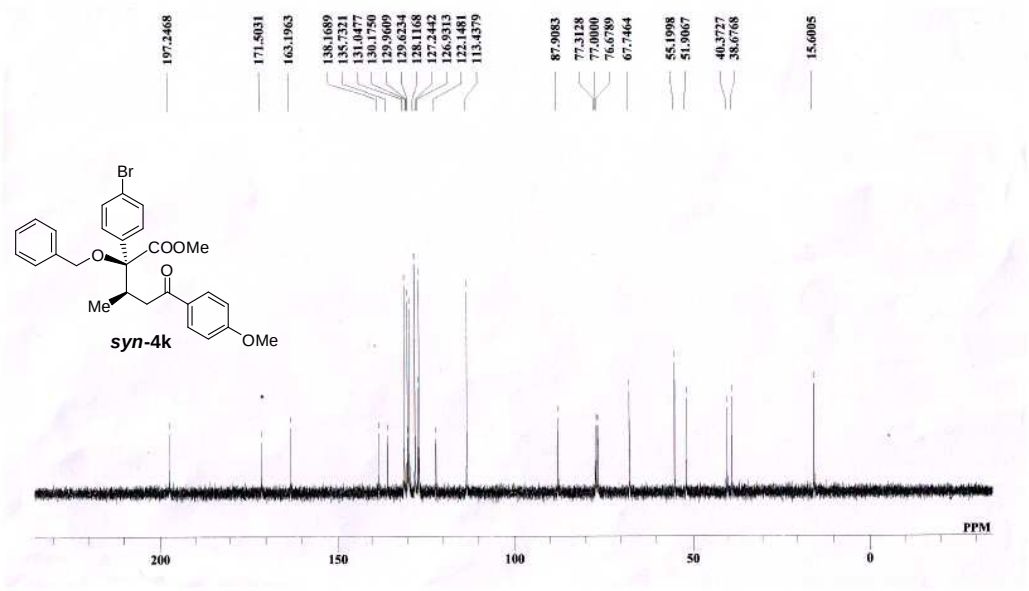
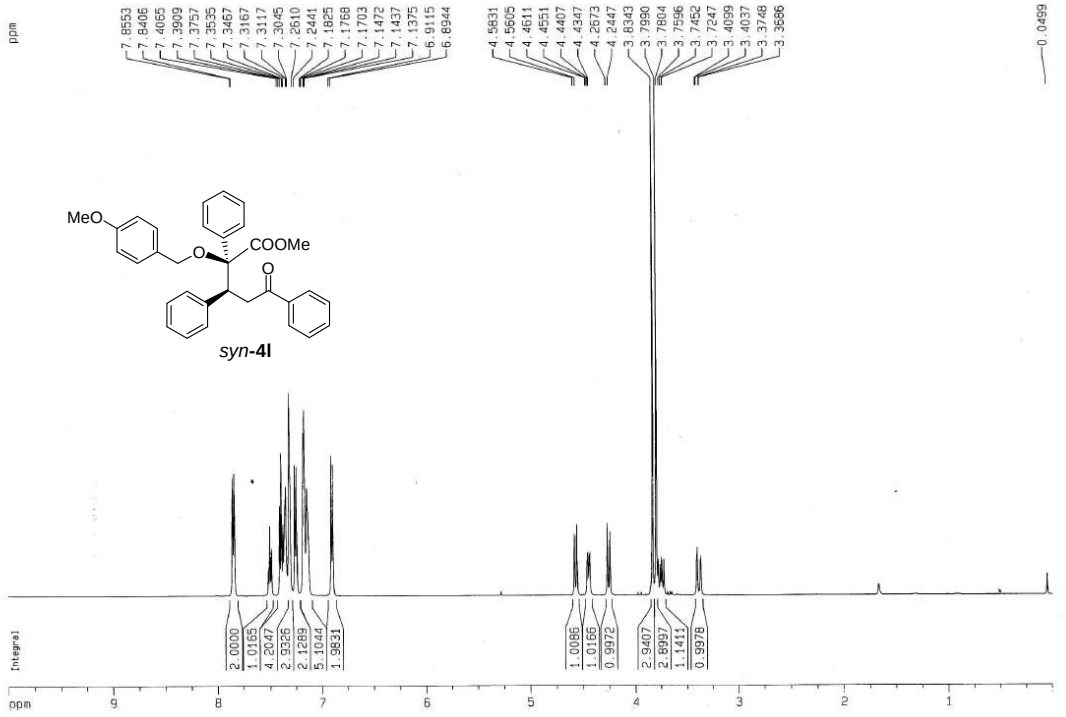
O
Me
O
OMe
syn-4k
ppm
Integral


Br
COOMe
O
Me
O
OMe
syn-4k
PPM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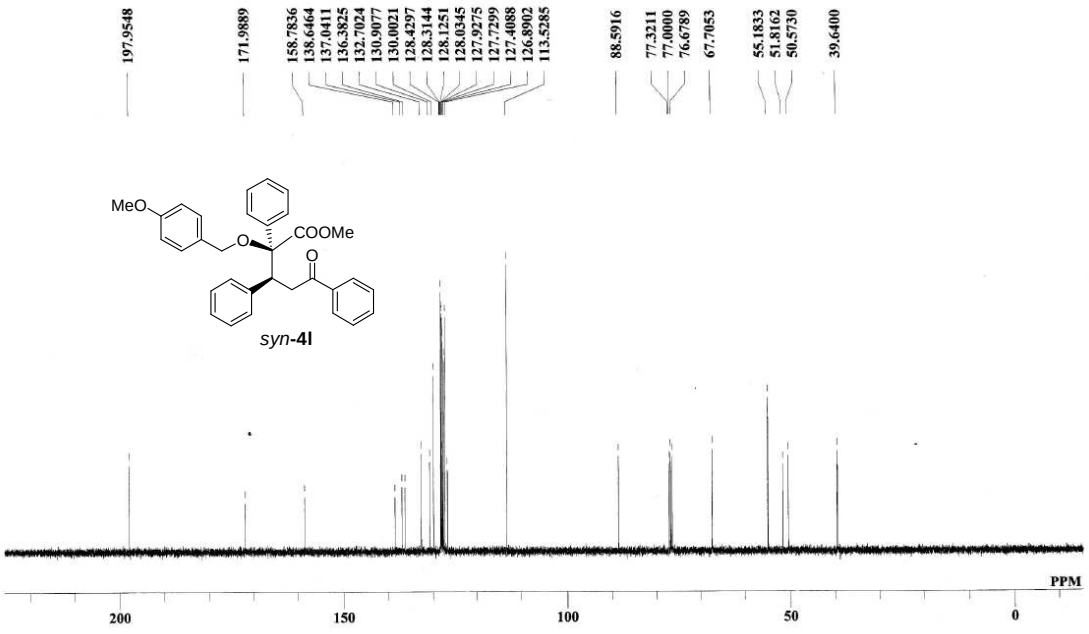
O
O
syn-4l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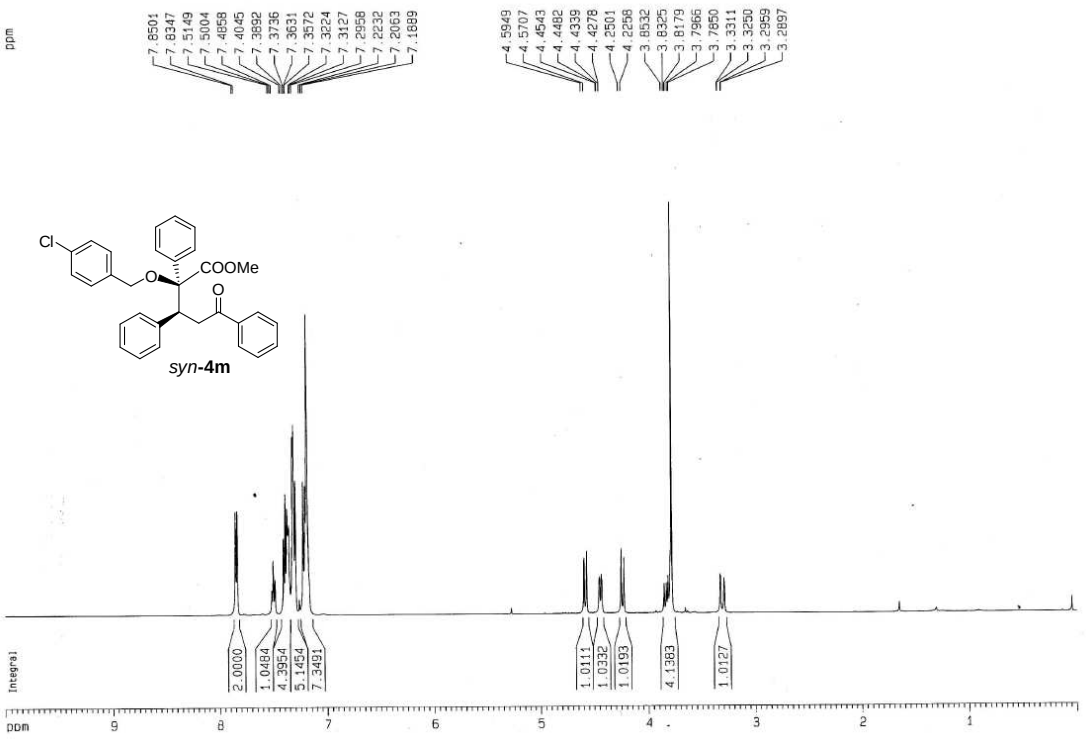
COOMe
O
O
syn-4l
PPM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7.3631
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7.3224
7.3127
7.2958
7.2232
7.2063
7.1889
4.5949
4.5707
4.4543
4.4482
4.4339
4.4278
4.2501
4.2256
3.8532
3.8325
3.8179
3.7966
3.7850
3.3311
3.3250
3.2959
3.2897
Cl
O
COOMe
O
syn-4m
Integral
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1.0484
4.3954
5.1454
7.3491
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1.0332
1.0193
4.1383
1.0127
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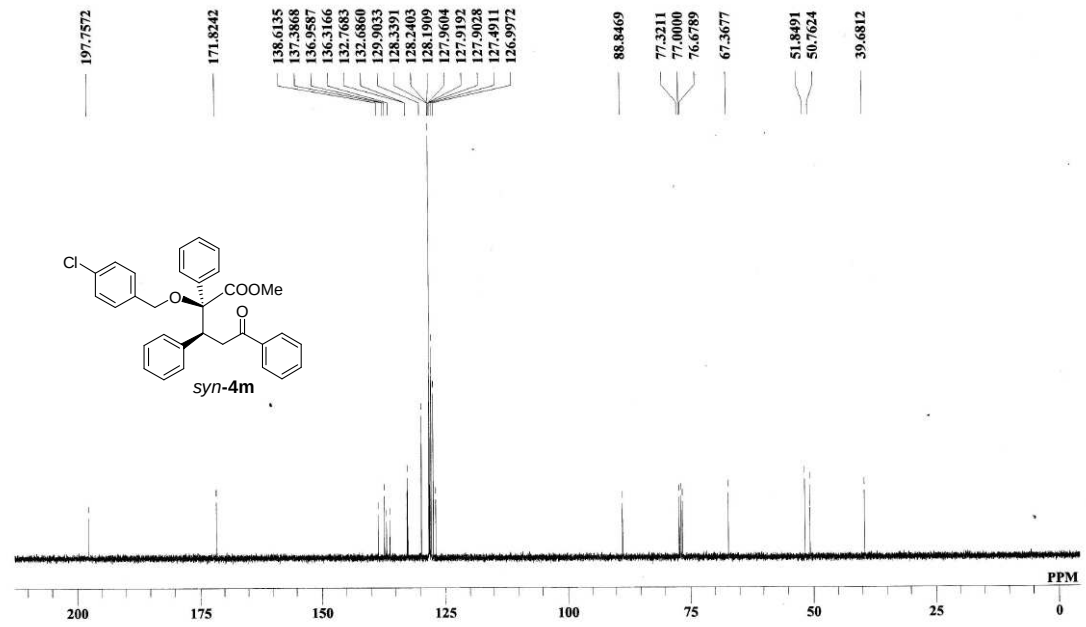
5
4
3
2
1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136.3166
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132.6860
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128.2403
128.1909
127.9604
127.9192
127.9028
127.4911
126.9972
88.8469
77.3211
77.0000
76.6789
67.3677
51.8491
50.7624
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Cl
O
COOMe
O
syn-4m
PPM
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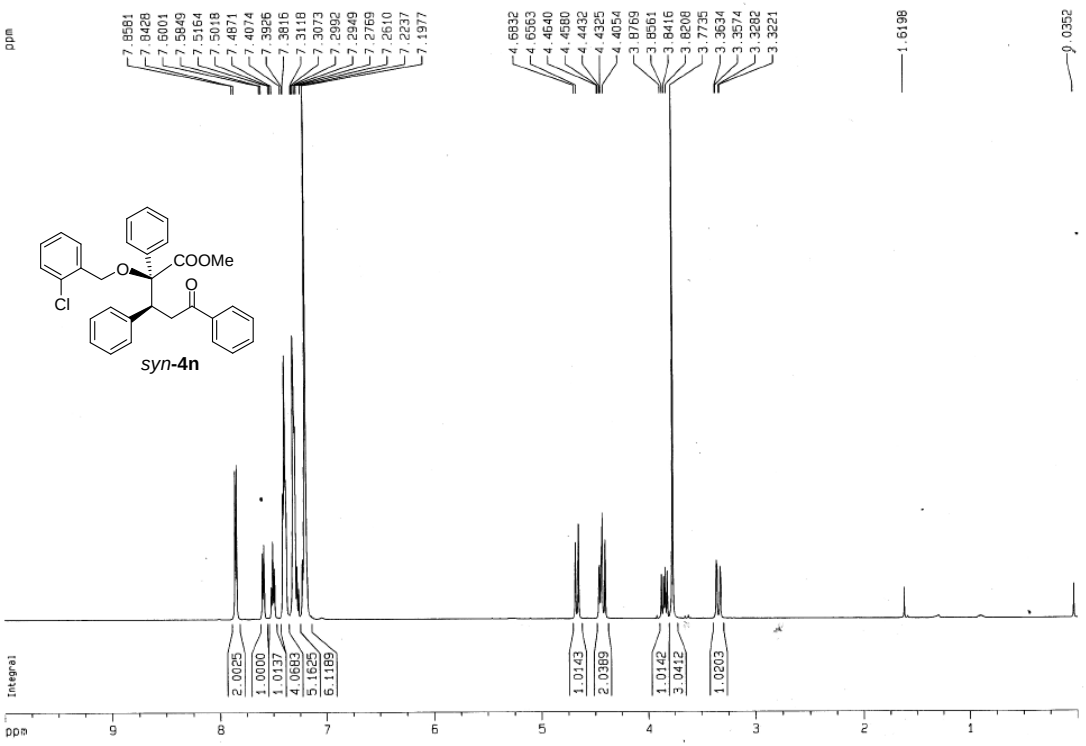
150
125
100
75
50
25
0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7.3118
7.3073
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7.2949
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7.2237
7.1977
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4.6563
4.4640
4.4580
4.4432
4.4325
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3.8208
3.7735
3.3634
3.3574
3.3282
3.3221
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0.0352
COOMe
O
O
Cl
syn-4n
Integral
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6.1189
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1.0203
ppm
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2
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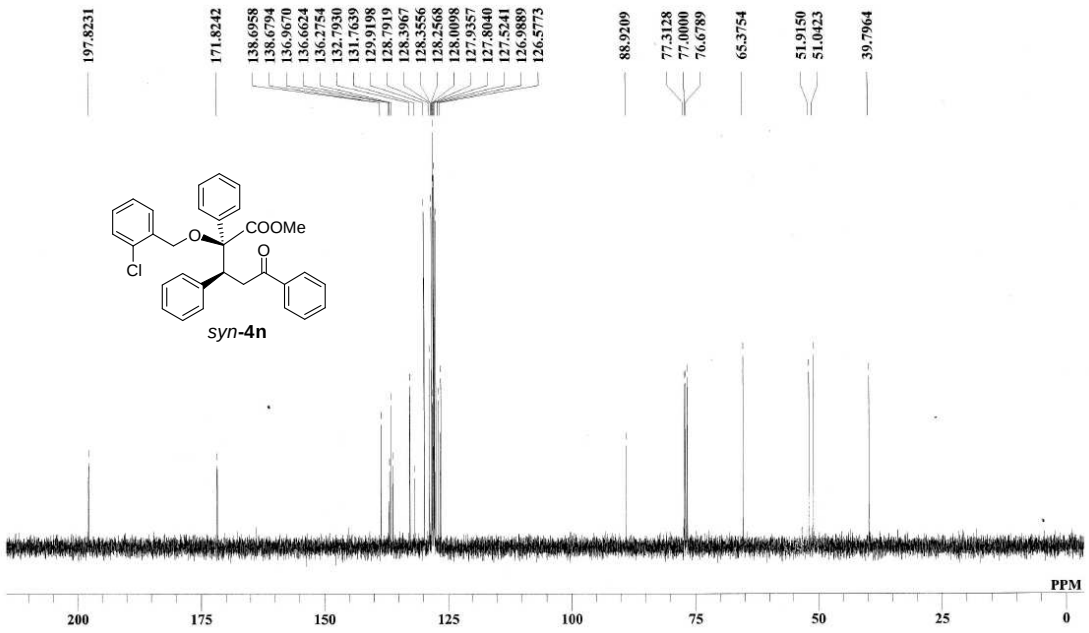
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127.5241
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77.0000
76.6789
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51.9150
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O
O
Cl
syn-4n
PPM
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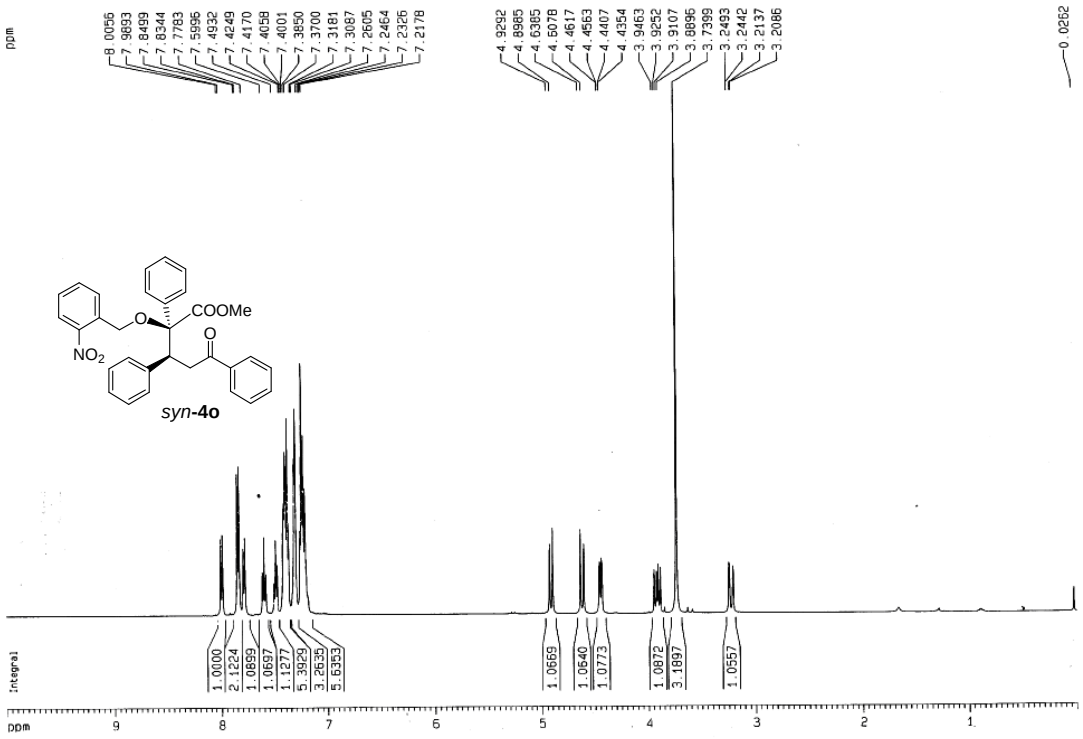
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7.3850
7.3700
7.3181
7.3087
7.2605
7.2464
7.2326
7.2178
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4.4563
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4.4354
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3.9252
3.9107
3.8896
3.7399
3.2493
3.2442
3.2137
3.2086
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COOMe
O
NO2
syn-4o
Integral
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1.0697
1.1277
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3.2635
5.6353
1.0669
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1.0872
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1.0557
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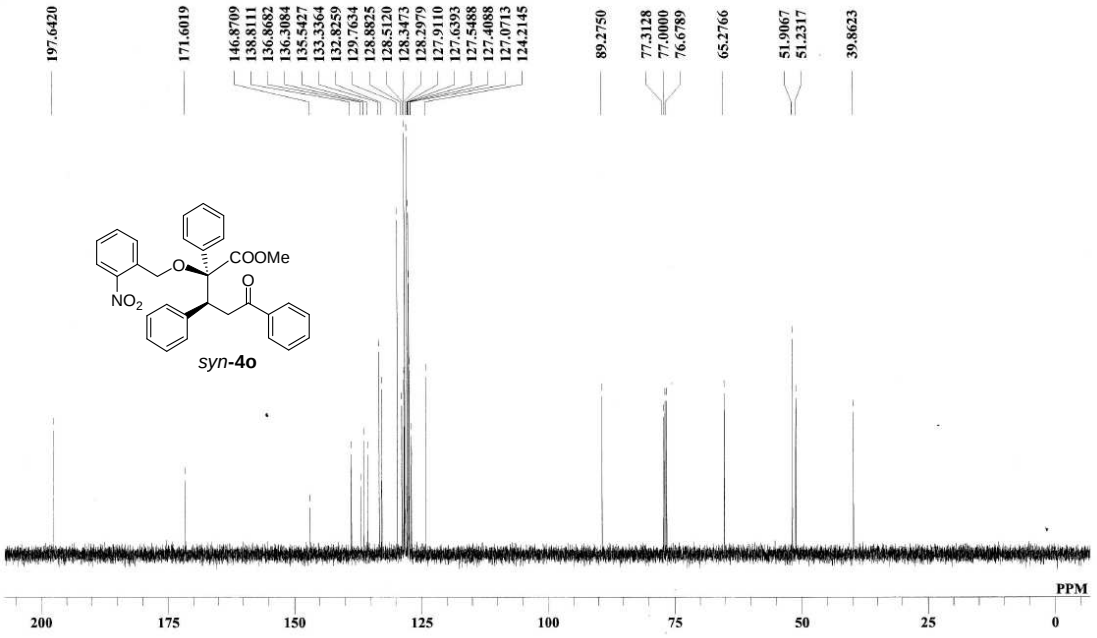
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127.5488
127.4088
127.0713
124.2145
89.2750
77.3128
77.0000
76.6789
65.2766
51.9067
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COOMe
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NO2
syn-4o
PPM
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75
50
25
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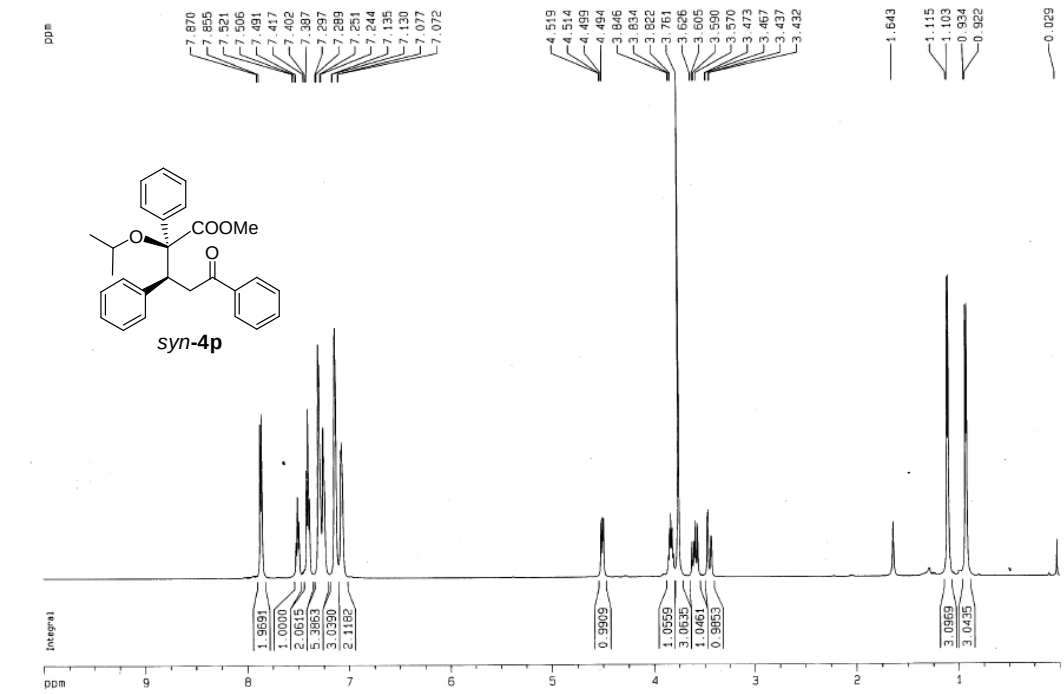
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7.289
7.251
7.244
7.135
7.130
7.077
7.072
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4.499
4.494
3.846
3.834
3.822
3.761
3.626
3.605
3.590
3.570
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3.467
3.437
3.432
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1.115
1.103
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0.922
0.029
COOMe
O
O
syn-4p
Integral
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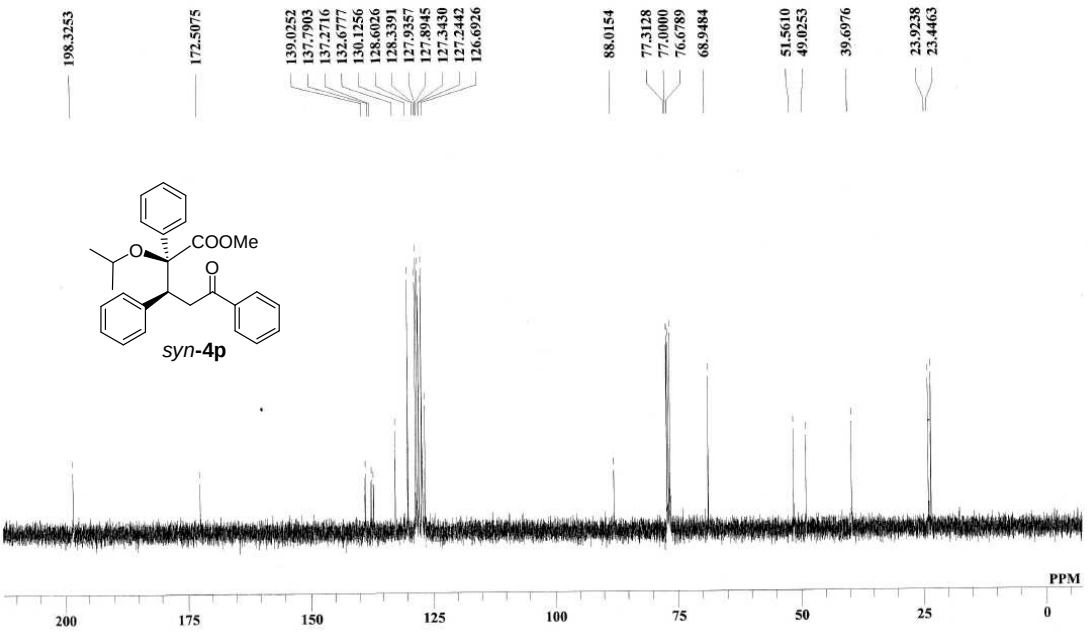
ppm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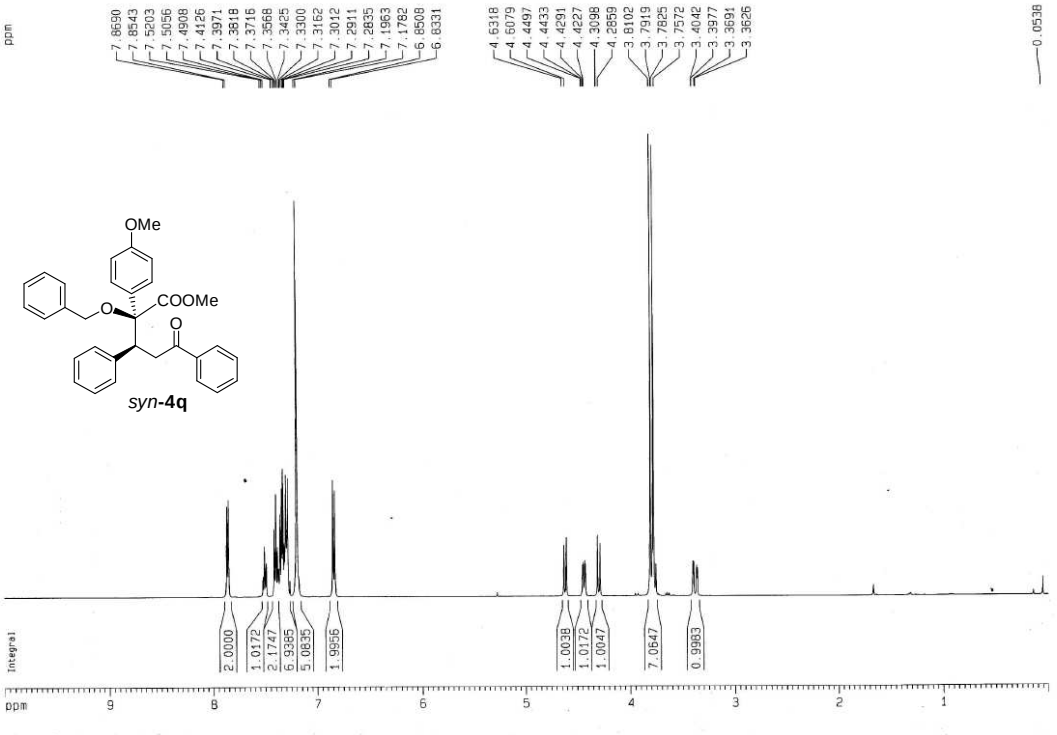
syn-4p
PPM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7.2911
7.2835
7.1963
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3.8102
3.7919
3.7825
3.7572
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3.3691
3.3626
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COOMe
O
O
syn-4q
Integral
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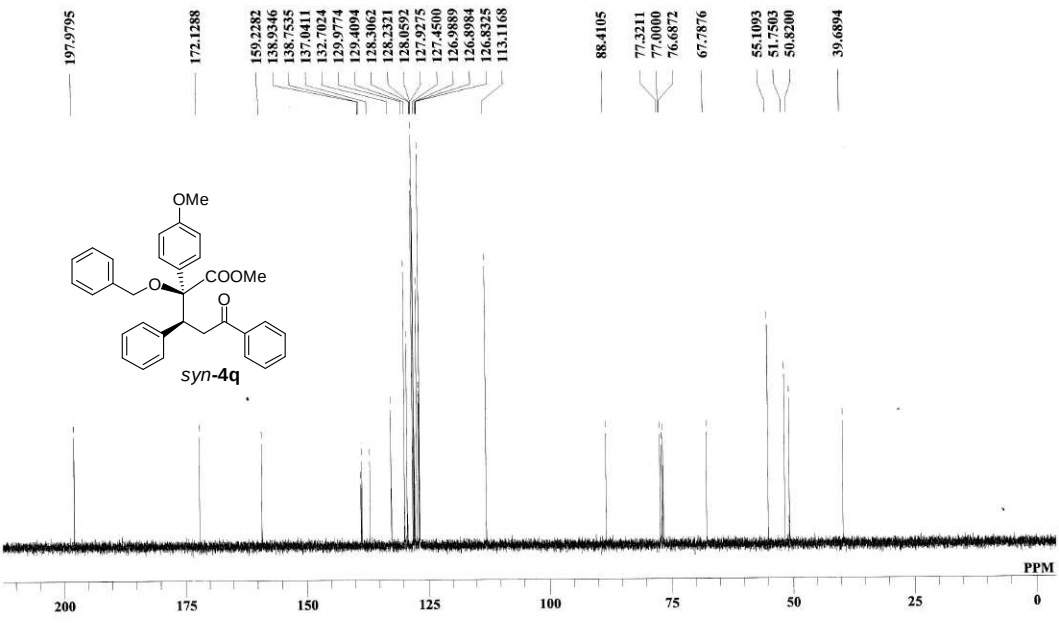
1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76.6872
67.7876
55.1093
51.7503
50.8200
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OMe
COOMe
O
O
syn-4q
PPM
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75
50
25
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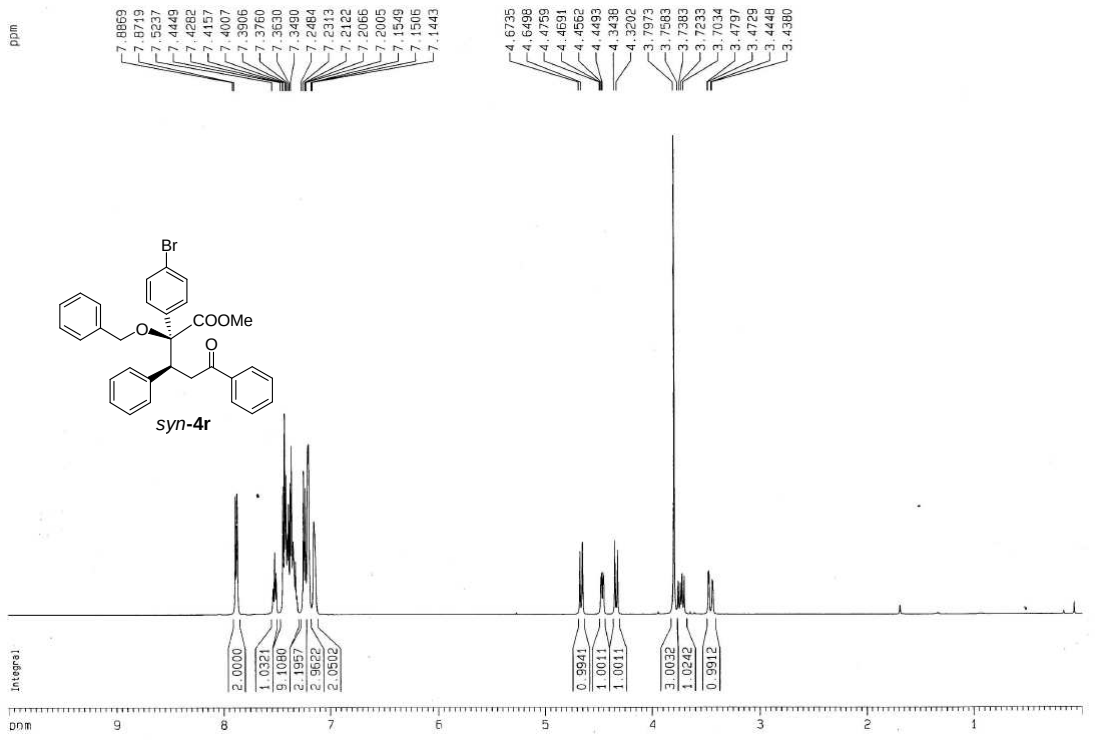
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7.1443
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4.4562
4.4493
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3.4797
3.4729
3.4448
3.4380
Br
COOMe
O
O
syn-4r
Integral
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2.9622
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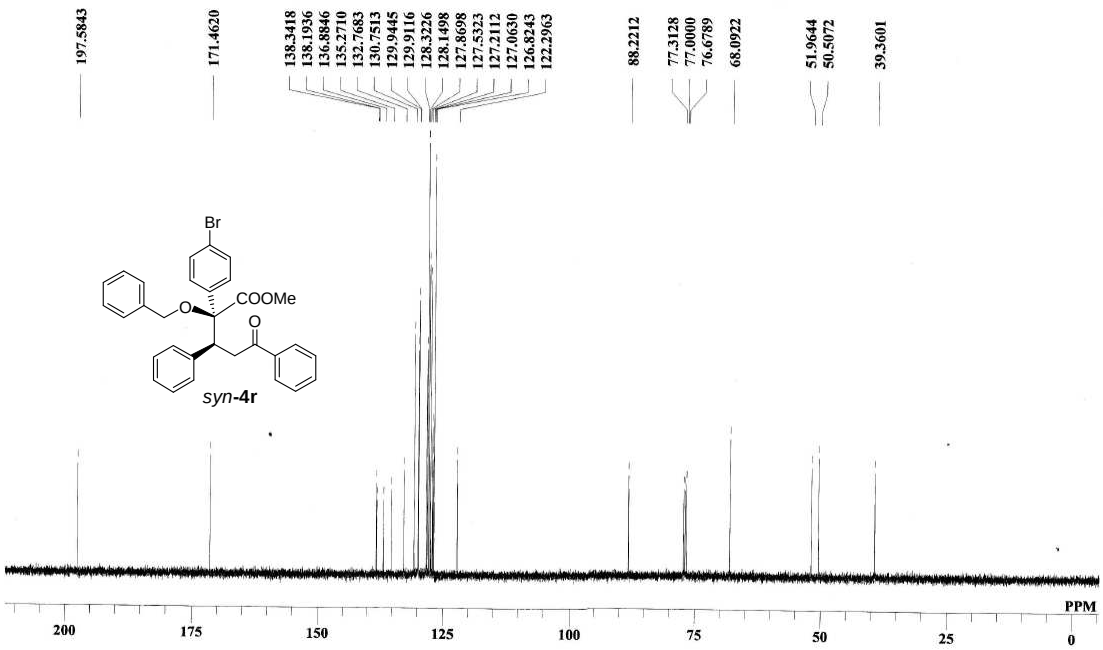
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128.1498
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127.2112
127.0630
126.8243
122.2963
88.2212
77.3128
77.0000
76.6789
68.0922
51.9644
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COOMe
O
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syn-4r
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150
125
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75
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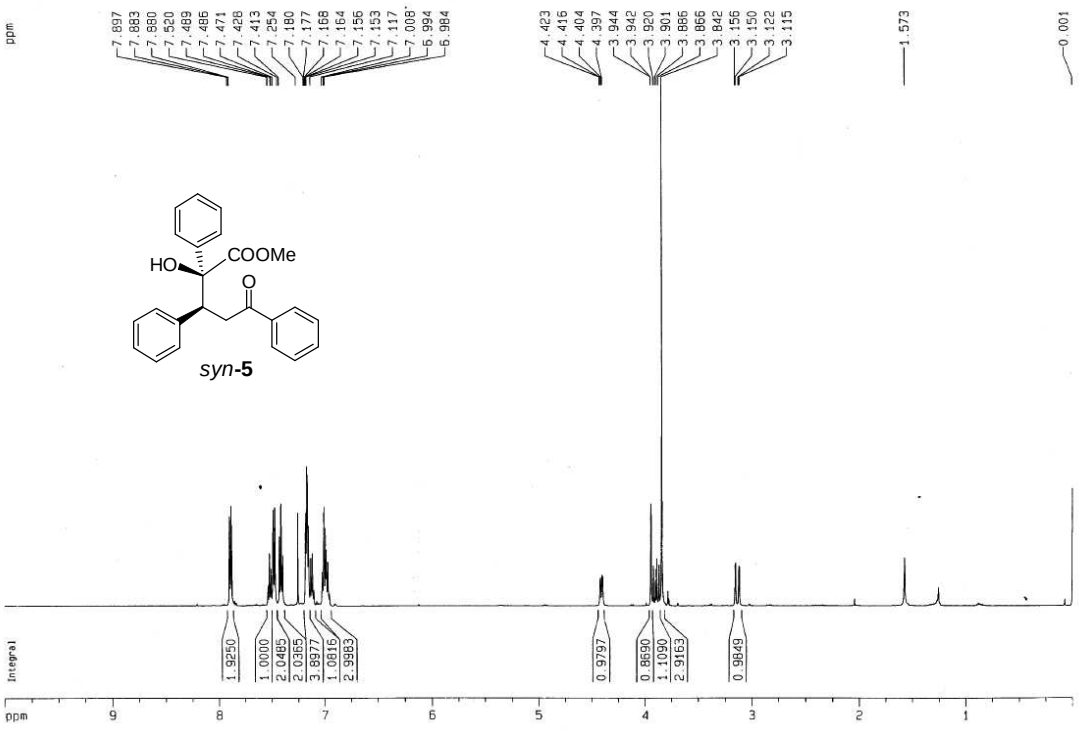
PPM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7.156
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7.117
7.008
6.994
6.984
4.423
4.416
4.404
4.397
3.944
3.942
3.920
3.901
3.886
3.866
3.842
3.156
3.150
3.122
3.115
1.573
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COOMe
O
syn-5
Integral
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2.0365
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1.0816
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1.1090
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ppm
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2
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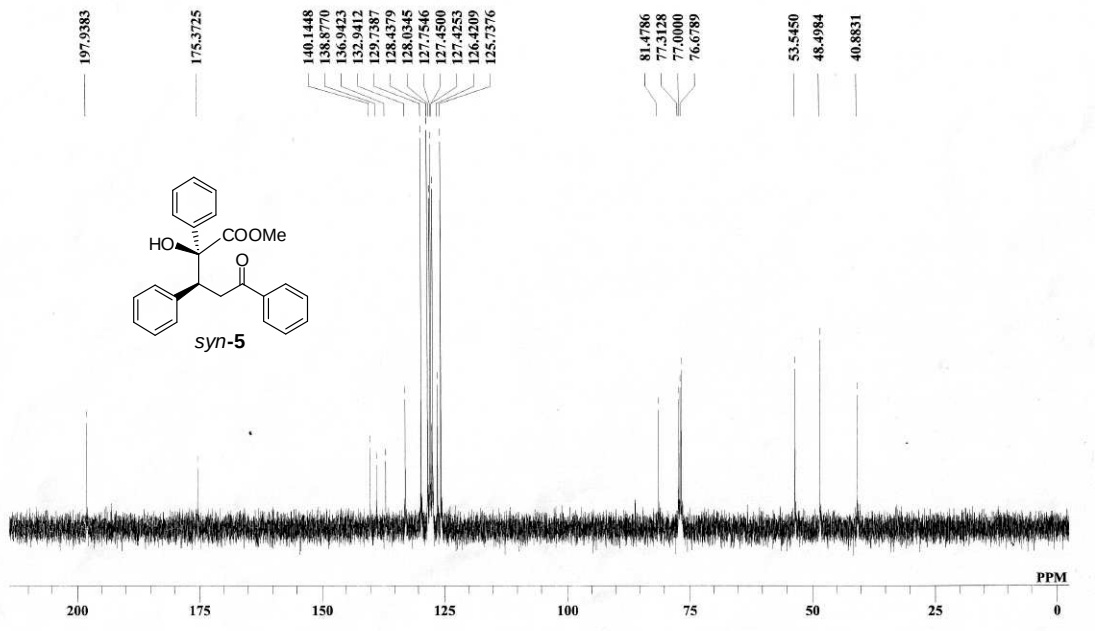
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128.0345
127.7546
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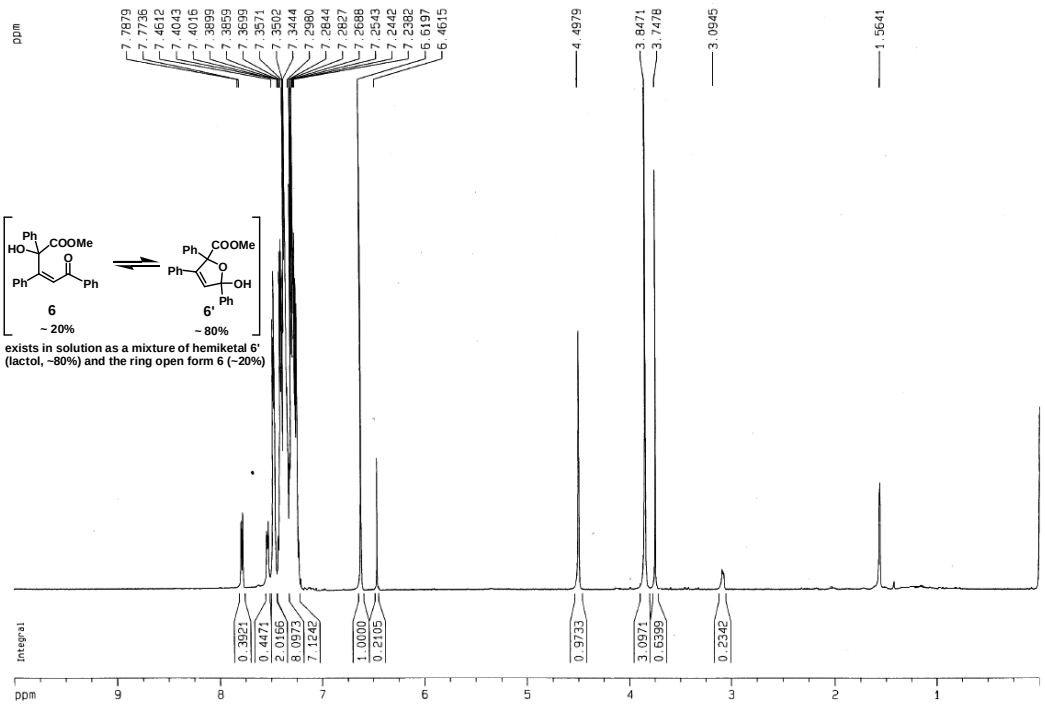
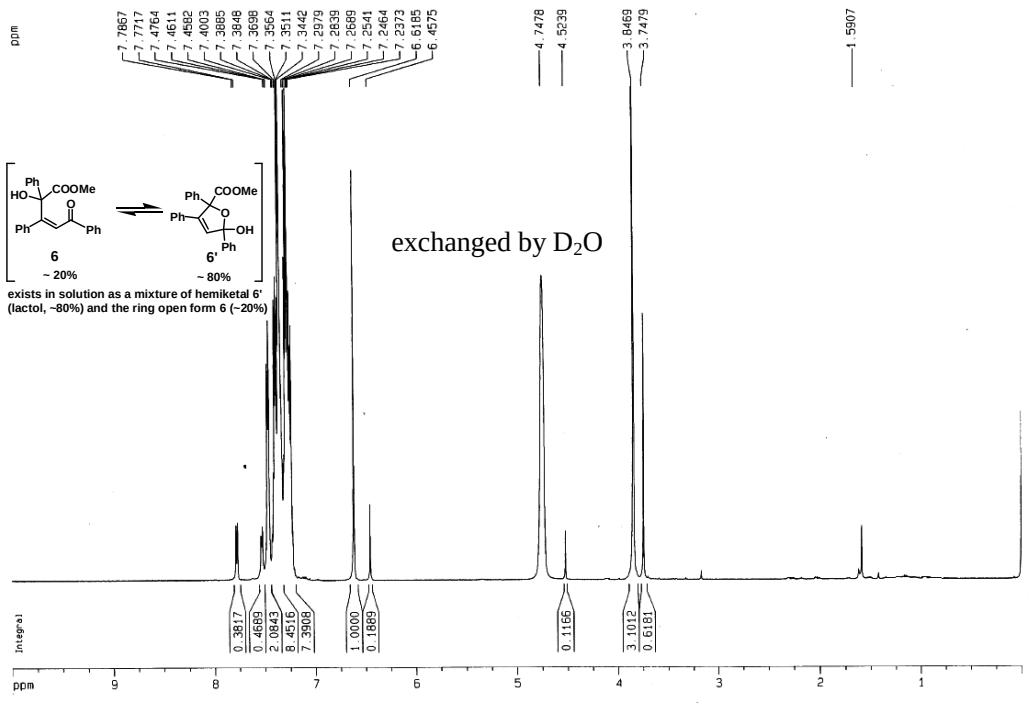
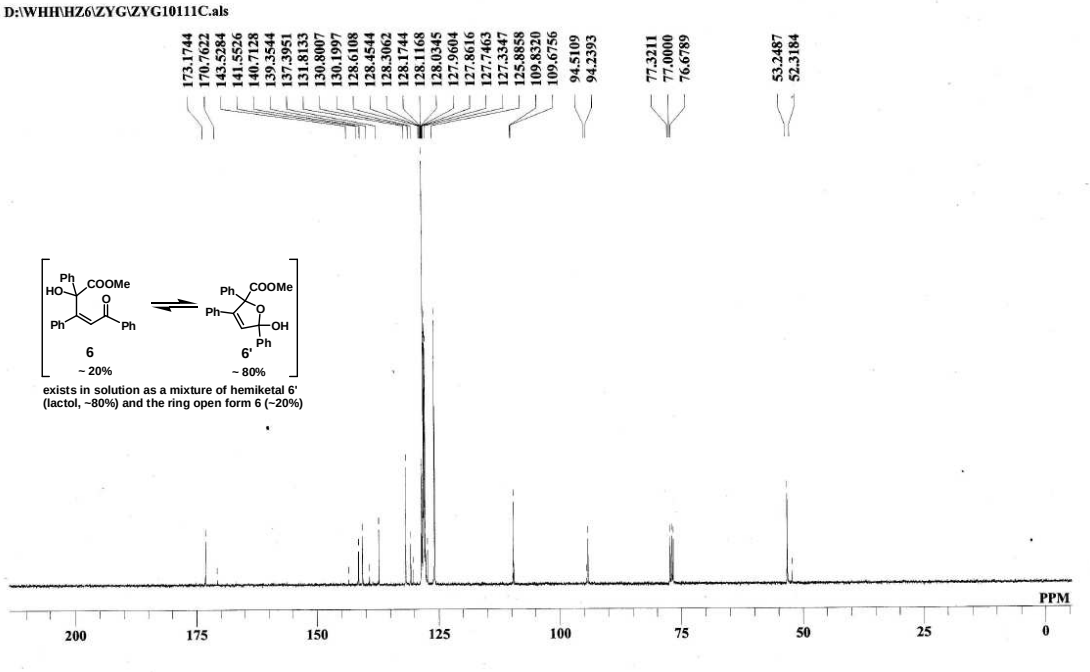
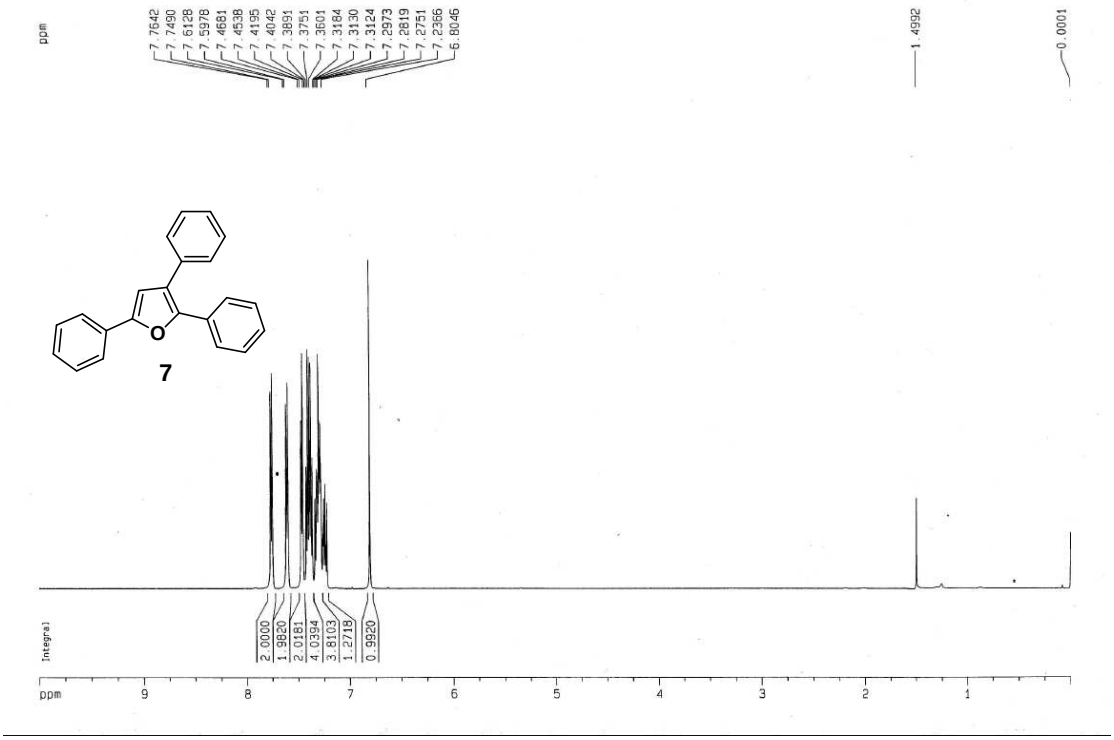
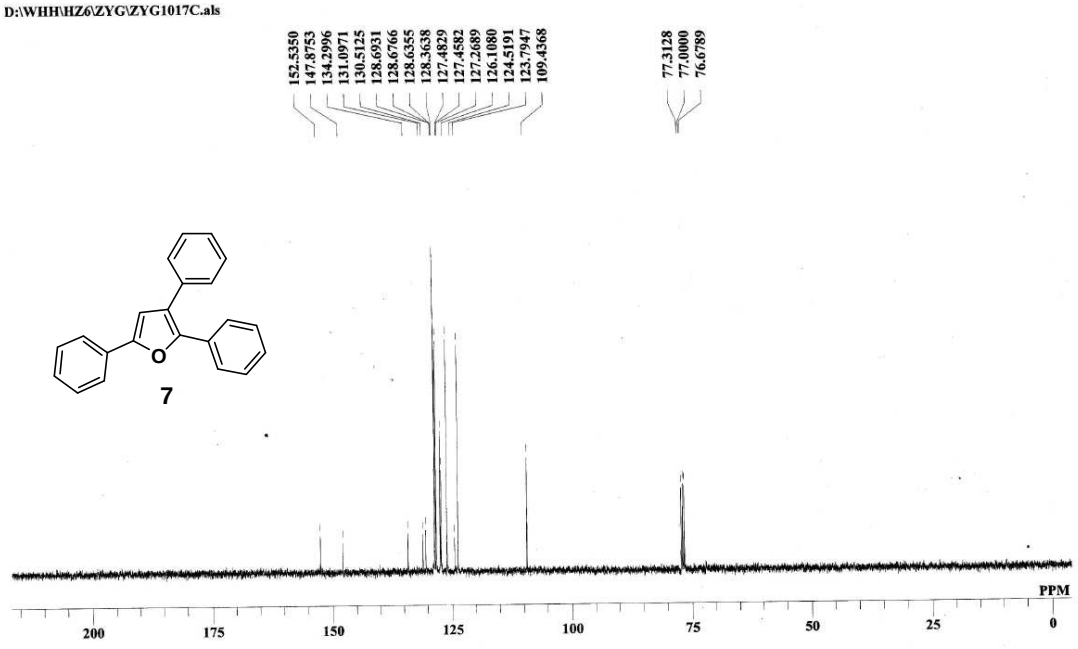
126.4209
125.7376
81.4786
77.3128
77.0000
76.6789
53.5450
48.4984
40.8831
HO
COOMe
O
syn-5
PPM
200
175
150
125
100
75
50
25
0

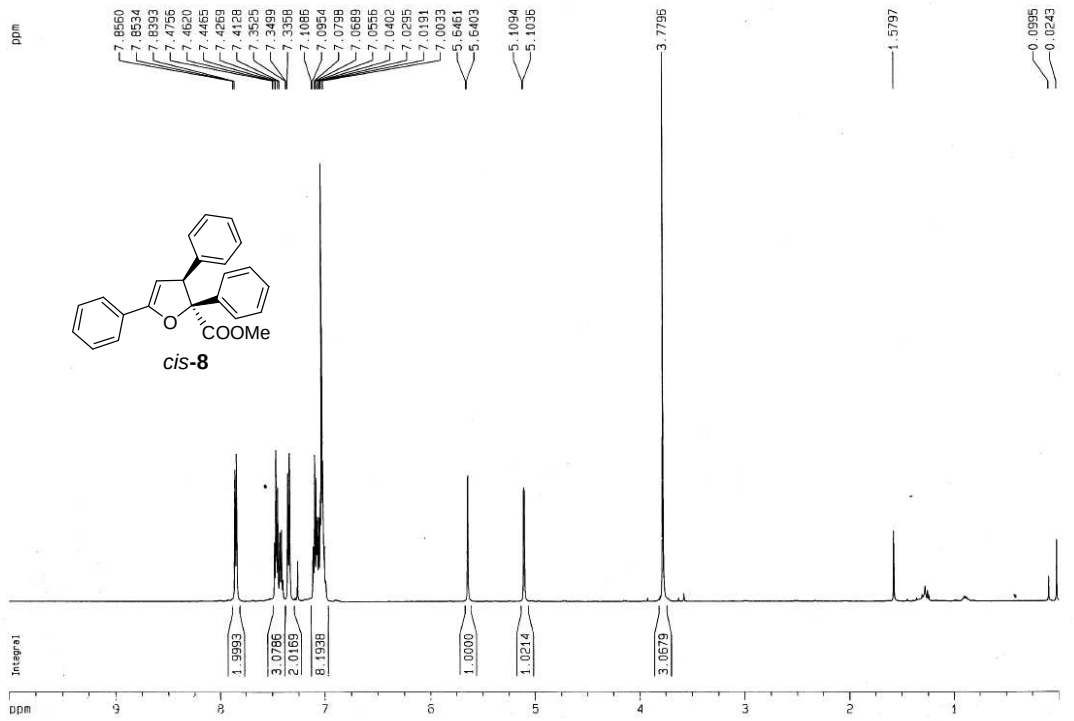

ppm
7.7879
7.7736
7.4612
7.4043
7.4016
7.3899
7.3859
7.3699
7.3571
7.3502
7.3444
7.2980
7.2844
7.2827
7.2688
7.2543
7.2442
7.2382
6.6197
6.4615
4.4979
3.8471
3.7478
3.0945
1.5641
Ph
HO
COOMe
O
Ph
Ph
6
~ 20%
Ph
COOMe
Ph
O
OH
Ph
6'
~ 80%
exists in solution as a mixture of hemiketal 6' (lactol, ~80%) and the ring open form 6 (~20%)
Integral
0.3921
0.4471
2.0166
8.0973
7.1242
1.0000
0.2105
0.9733
3.0971
0.6399
0.2342
ppm
9
8
7
6
5
4
3
2
1

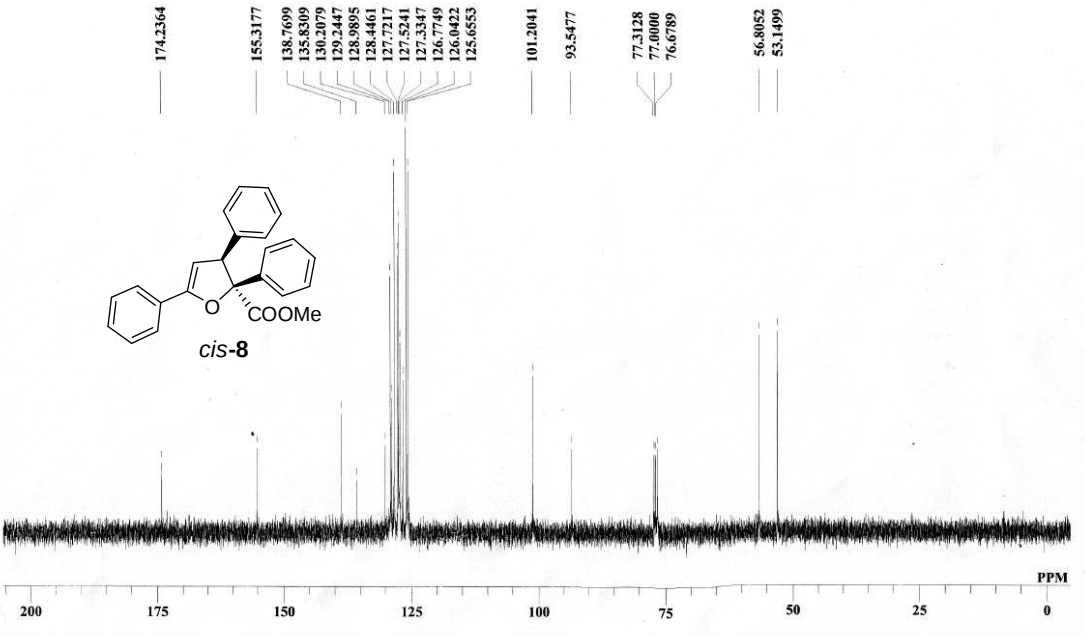

ppm
7.7867
7.7717
7.4764
7.4611
7.4582
7.4003
7.3885
7.3848
7.3698
7.3564
7.3511
7.3442
7.2979
7.2839
7.2689
7.2541
7.2464
7.2373
6.6185
6.4575
4.7478
4.5239
3.8469
3.7479
1.5907
Ph
HO
COOMe
O
Ph
Ph
6
~ 20%
Ph
COOMe
Ph
O
OH
Ph
6'
~ 80%
exists in solution as a mixture of hemiketal 6' (lactol, ~80%) and the ring open form 6 (~20%)
exchanged by D2O
Integral
0.3817
0.4689
2.0843
8.4516
7.3908
1.0000
0.1889
0.1166
3.1012
0.6181
ppm
9
8
7
6
5
4
3
2
1

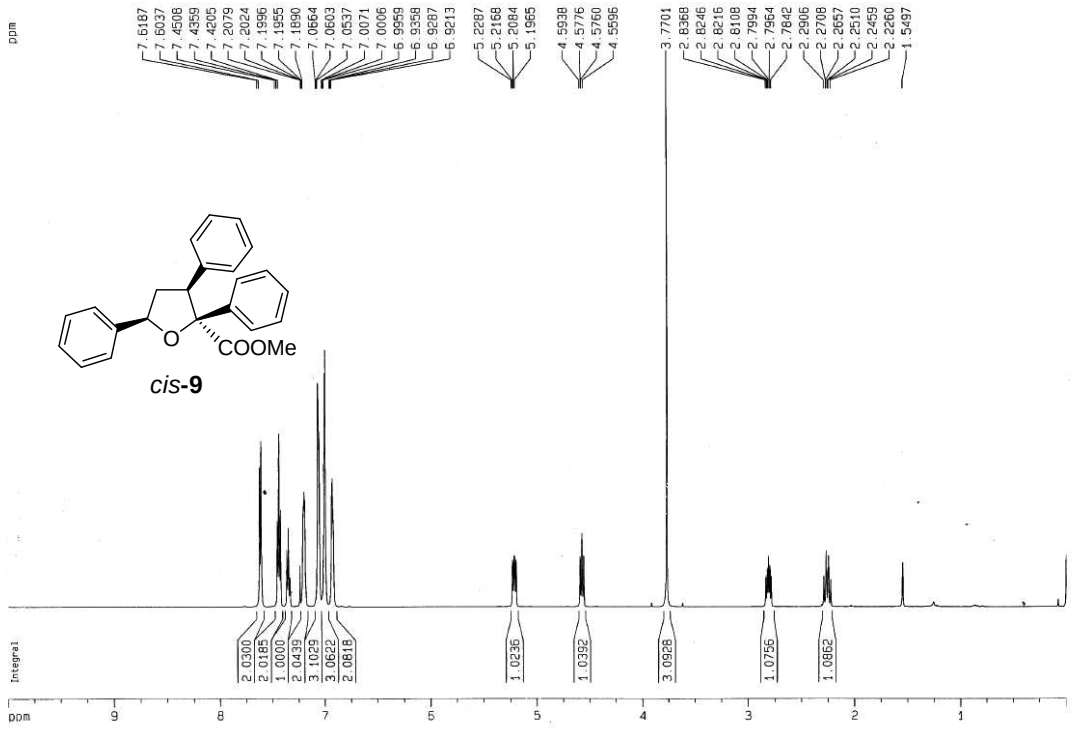

D:\WHH\HZ6\ZYG\ZYG10111C.als
173.1744
170.7622
143.5284
141.5526
140.7128
139.3544
137.3951
131.8133
130.8007
130.1997
128.6108
128.4544
128.3062
128.1744
128.1168
128.0345
127.9604
127.8616
127.7463
127.3347
125.8858
109.8320
109.6756
94.5109
94.2393
77.3211
77.0000
76.6789
53.2487
52.3184
Ph
HO
COOMe
O
Ph
Ph
6
~ 20%
Ph
COOMe
Ph
O
OH
Ph
6'
~ 80%
exists in solution as a mixture of hemiketal 6' (lactol, ~80%) and the ring open form 6 (~20%)
PPM
200
175
150
125
100
75
50
25
0

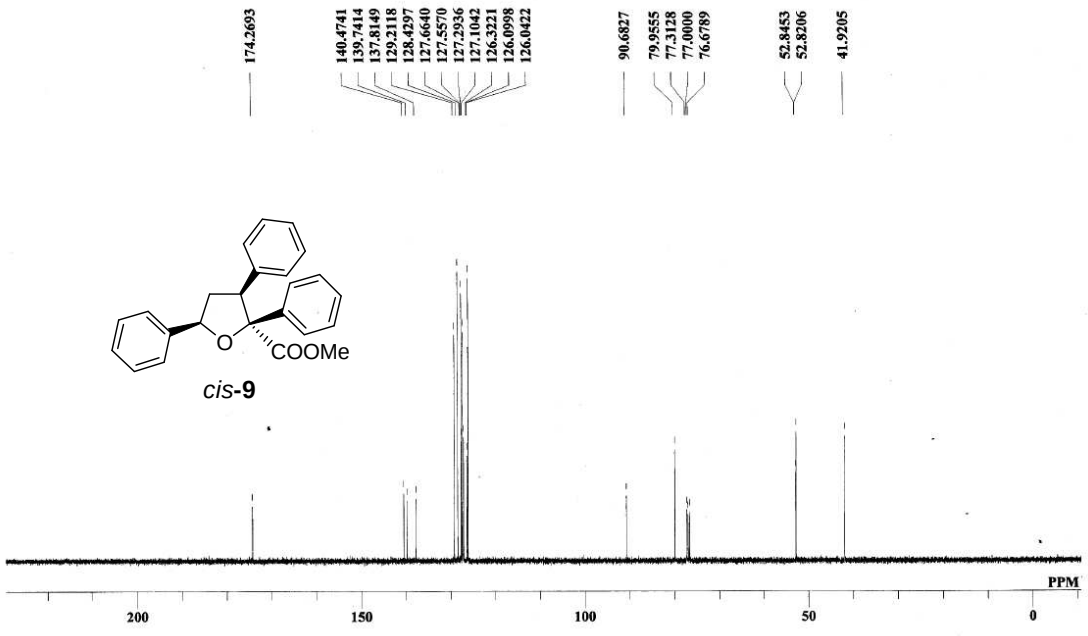

ppm
7.7642
7.7490
7.6128
7.5978
7.4681
7.4538
7.4195
7.4042
7.3891
7.3751
7.3601
7.3184
7.3130
7.3124
7.2973
7.2819
7.2751
7.2366
6.8046
1.4992
0.0001
7
Integral
2.0000
1.9880
2.0181
4.0394
3.8103
1.2718
0.9920
ppm
9
8
7
6
5
4
3
2
1


D:\WHH\HZ6\ZYG\ZYG1017C.als
152.5350
147.8753
134.2996
131.0971
130.5125
128.6931
128.6766
128.6355
128.3638
127.4829
127.4582
127.2689
126.1080
124.5191
123.7947
109.4368
77.3128
77.0000
76.6789
7
PPM
200
175
150
125
100
75
50
25
0


ppm
7.8560
7.8534
7.8393
7.4756
7.4620
7.4465
7.4269
7.4128
7.3525
7.3499
7.3358
7.1086
7.0954
7.0798
7.0689
7.0556
7.0402
7.0295
7.0191
7.0033
5.6461
5.6403
5.1094
5.1036
3.7796
1.5797
0.0995
0.0243
COOMe
cis-8
Integral
1.9993
3.0786
2.0169
8.1938
1.0000
1.0214
3.0679
ppm


174.2364
155.3177
138.7699
135.8309
130.2079
129.2447
128.9895
128.4461
127.7217
127.5241
127.3347
126.7749
126.0422
125.6553
101.2041
93.5477
77.3128
77.0000
76.6789
56.8052
53.1499
COOMe
cis-8
PPM


ppm
7.6187
7.6037
7.4506
7.4359
7.4205
7.2079
7.2024
7.1996
7.1955
7.1890
7.0664
7.0603
7.0537
7.0071
7.0006
6.9959
6.9358
6.9287
6.9213
5.2287
5.2168
5.2084
5.1965
4.5938
4.5776
4.5760
4.5596
3.7701
2.8368
2.8246
2.8216
2.8108
2.7994
2.7964
2.7842
2.2906
2.2708
2.2657
2.2510
2.2459
2.2260
1.5497
O
COOMe
cis-9
Integral
2.0300
2.0185
1.0000
2.0439
3.1029
3.0622
2.0818
1.0236
1.0392
3.0928
1.0756
1.0862
ppm
9
8
7
6
5
4
3
2
1


174.2693
140.4741
139.7414
137.8149
129.2118
128.4297
127.6640
127.5570
127.2936
127.1042
126.3221
126.0998
126.0422
90.6827
79.9555
77.3128
77.0000
76.6789
52.8453
52.8206
41.9205
O
COOMe
cis-9
PPM
200
150
100
50
0