Enantioselective Rhodium-Catalyzed [4+2] Cycloaddition of Alpha, Beta-Unsaturated Imines and Isocyanates

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Supporting Information

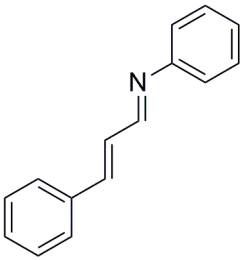
General Methods:

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Column chromatography was performed on Silicycle Inc. silica gel 60 (230-400 mesh). Thin layer chromatography was performed on Silicycle Inc. 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light (254 nm), anisaldehyde, and $KMnO_4$.

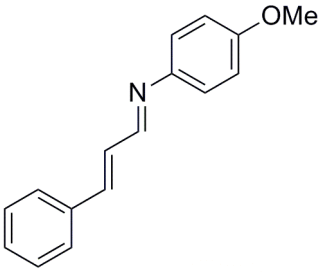
^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ or D_3COD at ambient temperature and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm ($CHCl_3$) and carbon chemical shifts are referenced to 77.0 ppm ($CDCl_3$). Data reporting uses the following abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet; and *J*, coupling constant in Hz.

Unless otherwise indicated, commercially available starting material were purchased from Aldrich Chemicals. $[Rh(C_2H_4)_2Cl]_2$ was purchased from Strem Chemicals. Amines were distilled over KOH under reduced pressure before use. Ligands **L1 - L3** were synthesized as previously reported.[1]

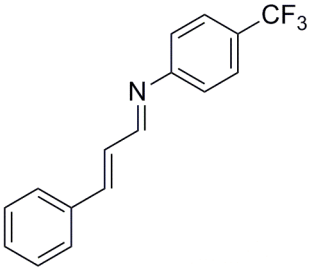
Synthesis of Starting Materials:



1,4-diphenyl-1-azabuta-1,3-diene (1a). Trans-cinnamaldehyde (6.3 ml, 50 mmol) and aniline (4.6 ml, 50 mmol) were dissolved in toluene and $MgSO_4$ was added. The reaction was stirred at 23 °C for 6 h, filtered, and concentrated *in vacuo*. Recrystallization from Et_2O resulted in yellow-orange needles (6.5 g, 62%, mp: 107 - 109 °C). Spectral data matches literature values.[2] ^1H NMR (300 MHz, $CDCl_3$) δ 8.29 (m, 1H), 7.55 (m, 2H), 7.44 - 7.37 (m, 5H), 7.24 - 7.16 (m, 5H).

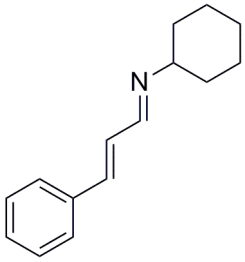


1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (1b). Trans-cinnamaldehyde (2.1 ml, 16.5 mmol) and *p*-anisidine (2.02 g, 16.5 mmol) were dissolved in toluene and $MgSO_4$ was added. The reaction mixture was stirred at 23 °C for 12 h, filtered, and concentrated *in vacuo*. Recrystallization from Et_2O resulted in yellow flakes (2.53 g, 65%, mp: 119 - 121 °C). Spectral data matches literature values.[2] ^1H NMR (300 MHz, $CDCl_3$) δ 8.29 (m, 1H), 7.53 (m, 2H), 7.42 - 7.34 (m, 3H), 7.22 (m, 2H), 7.12 (m, 2H), 6.92 (m, 2H), 3.82 (s, 3H).

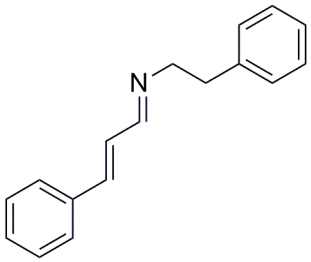


1-(4-trifluoromethylphenyl)-4-phenyl-1-azabuta-1,3-diene (1c). Trans-cinnamaldehyde (1.3 ml, 10 mmol) and 4-(trifluoromethyl)aniline (1.2 ml, 10 mmol) were dissolved in toluene and Na_2SO_4 was added. The reaction mixture was stirred at 23 °C for 2 h, filtered, and concentrated *in vacuo*. Recrystallization from Et_2O resulted in a yellow powder (0.77 g, 28%, mp:

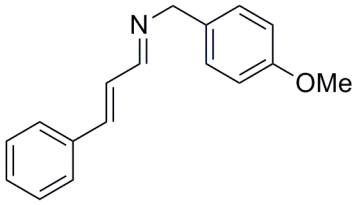
106 - 108 °C). Spectral data matches literature values.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (m, 1H), 7.64 (m, 2H), 7.56 (m, 2H), 7.46 - 7.38 (m, 3H), 7.23 (m, 3H), 7.15 (m, 1H).



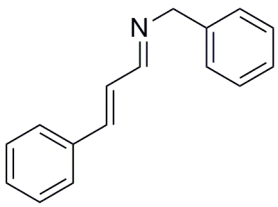
1-cyclohexyl-4-phenyl-1-azabuta-1,3-diene (1d). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. Trans-cinnamaldehyde (2.5 ml, 20 mmol) and cyclohexyl amine (2.3 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (2.99 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.44 (m, 2H), 7.31 (m, 3H), 6.89 (m, 2H), 3.04 (m, 1H), 1.82 - 1.15 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 140.9, 135.7, 128.8, 128.6, 128.4, 127.0, 69.5, 34.3, 25.4, 24.6. IR (NaCl, Thin Film) 3027, 2928, 2852, 1636, 1449, 1166, 981, 749 cm^{-1}. HRMS (ESI) *m/z* $[C_{15}H_{20}N]^+$ calcd 214.1590, found 214.1594.



1-phenethyl-4-phenyl-1-azabuta-1,3-diene (1e). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. Trans-cinnamaldehyde (1.9 ml, 15 mmol) and phenethylamine (1.9 ml, 15 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo*. Recrystallization from Et_2O resulted in clear cubic crystals with a slight yellow hue (1.00 g, 28%, mp: 52 -53 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.51 - 7.22 (m, 10H), 6.92 (m, 2H), 3.81 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 141.4, 139.7, 135.6, 128.9, 128.8, 128.6, 128.2, 127.9, 127.0, 126.0, 62.9, 37.3. IR (NaCl, Thin Film) 3028, 2943, 2826, 1634, 1453, 978, 743 cm^{-1}. HRMS (ESI) *m/z* $[C_{17}H_{18}N]^+$ calcd 236.1434, found 236.1436.

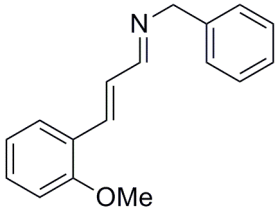


1-(4-methoxybenzyl)-4-phenyl-1-azabuta-1,3-diene (1f). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. Trans-cinnamaldehyde (2.5 ml, 20 mmol) and 4-methoxybenzyl amine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 36 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulted in an amorphous pale brown powder (0.98 g, 26%). Spectral data matches literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (m, 1H), 7.48 (m, 2H), 7.36 (m, 3H), 7.25 (m, 2H), 6.98 (m, 2H), 6.89 (m, 2H), 4.66 (s, 2H), 3.80 (s, 3H).

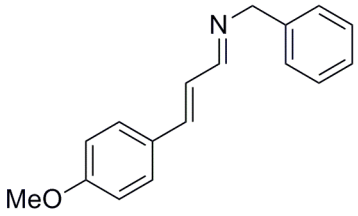


1-benzyl-4-phenyl-1-azabuta-1,3-diene (1g). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was

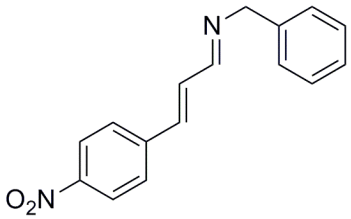
added under Ar. Trans-cinnamaldehyde (2.5 ml, 20 mmol) and benzylamine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 36 h. The resulting mixture was filtered through Celite and concentrated *in vacuo* resulting in a brown oil (3.77 g, 85%). Spectral data matches literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.49 (m, 2H), 7.40 - 7.25 (m, 8H), 7.00 (m, 2H), 4.73 (s, 2H).



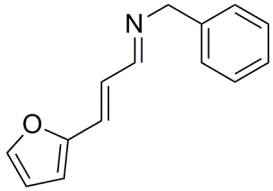
1-benzyl-4-(2-methoxyphenyl)-1-azabuta-1,3-diene (1h). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. *O*-methoxy-trans-cinnamaldehyde (3.2 g, 20 mmol) and benzylamine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (3.78 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.55 (m, 1H), 7.42 - 7.26 (m, 7H), 7.12 - 6.90 (m, 3H), 4.74 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 157.2, 139.2, 137.0, 130.2, 128.5, 128.4, 127.9, 127.4, 126.8, 124.4, 120.6, 110.8, 65.1, 55.2. IR (NaCl, Thin Film) 3028, 2837, 1633, 1488, 1246, 1027, 751 cm^{-1}. HRMS (ESI) *m/z* $[C_{17}H_{18}NO]^+$ calcd 252.1383, found 252.1387.



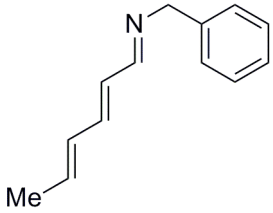
1-benzyl-4-(4-methoxyphenyl)-1-azabuta-1,3-diene (1i). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. *P*-methoxy-trans-cinnamaldehyde (3.2 g, 20 mmol) and benzylamine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo*. Recrystallization from Et_2O resulted in off-white prisms (3.78 g, 75%, mp: 73 - 75 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (m, 1H), 7.44 (m, 2H), 7.40 - 7.26 (m, 5H), 6.91 (m, 4H), 4.72 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 160.3, 141.6, 139.2, 128.6, 128.4, 128.3, 127.9, 126.8, 125.9, 114.1, 65.0, 55.1. IR (NaCl, Thin Film) 3018, 2929, 2837, 1573, 1425, 1207, 1033, 738 cm^{-1}. HRMS (ESI) *m/z* $[C_{17}H_{18}NO]^+$ calcd 252.1383, found 252.1385.



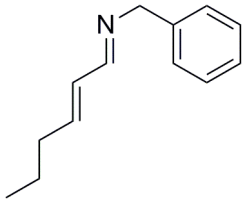
1-benzyl-4-(4-nitrophenyl)-1-azabuta-1,3-diene (1j). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. 4-nitrocinnamaldehyde (1.8 g, 10 mmol) and benzyl amine (1.1 ml, 10 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo*. Recrystallization from Et_2O resulted in pale yellow flakes (1.74 g, 65%, 104 - 105 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 3H), 7.58 (m, 2H), 7.38-7.27 (m, 5H), 7.04 (m, 2H), 4.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 147.5, 141.8, 138.6, 132.1, 128.5, 127.9, 127.6, 127.0, 124.0, 65.2. IR (NaCl, Thin Film) 3058, 3027, 2922, 2814, 1617, 1513, 1345, 741 cm^{-1}. HRMS (ESI) *m/z* $[C_{16}H_{15}N_2O_2]^+$ calcd 267.1128, found 267.1132.



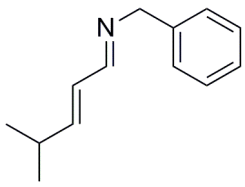
1-benzyl-4-(2-furyl)-1-azabuta-1,3-diene (1k). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. Trans-3-(2furyl)-acrolein (1.8 g, 15 mmol) and benzyl amine (1.6 ml, 15 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (2.76 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (m, 1H), 7.44 - 7.32 (m, 6H), 6.94 - 6.74 (m, 2H), 6.46 (m, 2H), 4.72 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 151.7, 143.6, 139.1, 128.5, 128.4, 127.9, 126.8, 126.1, 111.8, 111.6, 65.1. IR (NaCl, Thin Film) 3062, 3028, 2842, 1633, 1453, 1155, 963, 698 cm^{-1}. HRMS (ESI) *m/z* $[C_{14}H_{14}NO]^+$ calcd 212.1070, found 212.1072.



1-benzyl-6-methyl-1-azabuta-1,3,5-triene (1l). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. 2,4-hexadienal (2.2 ml, 20 mmol) and benzyl amine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (3.22 g, 87%) as a 1:10 mixture of isomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 1H), 7.28 (m, 5H), 6.60 (m, 1H), 6.27 (m, 2H), 5.98 (m, 1H), 4.65 (s, 2H), 1.83 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 142.2, 139.2, 136.6, 135.0, 130.7, 129.1, 128.3, 127.8, 126.8, 65.0, 18.4. IR (NaCl, Thin Film) 3386, 3028, 2925, 1631, 1452, 1171, 1001, 698, 665 cm^{-1}. HRMS (ESI) *m/z* $[C_{14}H_{16}N]^+$ calcd 186.1277, found 186.1278.



1-benzyl-4-(n-propyl)-1-azabuta-1,3-diene (1m). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. trans-2-hexenal (2.3 ml, 20 mmol) and benzyl amine (2.2 ml, 20 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (3.07 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (m, 1H), 7.35 - 7.22 (m, 6H), 6.31 (m, 1H), 4.66 (s, 2H), 2.23 (dd, *J* = 13.2, 7.2 Hz, 2H), 1.53 (dt, *J* = 7.5, 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 145.8, 139.3, 130.6, 128.4, 128.2, 128.1, 127.9, 126.8, 64.9, 34.6, 21.6, 13.6. IR (NaCl, Thin Film) 3028, 2958, 2930, 2871, 1655, 1454, 969, 698 cm^{-1}. HRMS (ESI) *m/z* $[C_{13}H_{18}N]^+$ calcd 188.1434, found 188.1431.



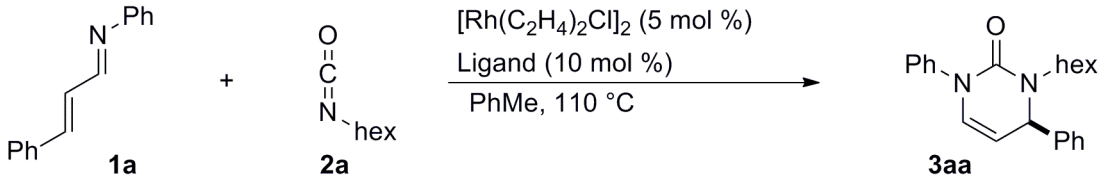
1-benzyl-4-(i-propyl)-1-azabuta-1,3-diene (1n). In a round bottom flask, 3 Å molecular sieves were activated by flame drying under vacuum and toluene was added under Ar. 4-methyl-2-pentenal (1.7 ml, 15 mmol) and benzyl amine (1.6 ml, 15 mmol) were added and the reaction mixture was stirred at 23 °C for 24 h. The

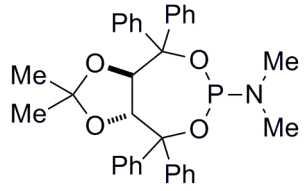
resulting mixture was filtered through $MgSO_4$ and Celite and concentrated *in vacuo* resulting in a brown oil (2.49 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 1H), 7.35 - 7.25 (m, 6H), 6.26 (m, 1H), 4.65 (s, 2H), 2.50 (m, 1H), 1.09 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 152.5, 139.2, 128.4, 127.9, 127.7, 126.8, 64.9, 31.0, 21.5. IR (NaCl, Thin Film) 3029, 2961, 2869, 1652, 1454, 973, 698cm^{-1}. HRMS (ESI) *m/z* $[C_{13}H_{18}N]^+$ calcd 188.1434, found 188.1439.

General Procedure for Rhodium-Catalyzed [4+2] Cycloaddition:

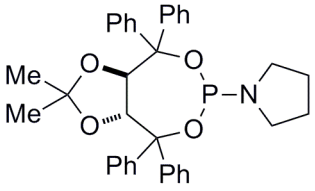
$[Rh(C_2H_4)_2Cl]_2$ (5.8 mg, 0.015 mmol) and ligand (0.03 mmol) were added to an oven-dried 10 ml round bottom flask and the flask was fitted with an oven-dried reflux condenser in an inert atmosphere (Ar) glove box. Upon removal from the glove box, the reaction vessel was put under Ar and 4 ml of toluene was added via syringe and the resulting gold solution was stirred at 23 °C for 15 min. To this solution, imine (0.3 mmol) and isocyanate (0.375 mmol) in 2 ml of toluene was added via syringe. The reaction mixture was heated to 110 °C in an oil bath and kept at reflux for 12 h. The reaction mixture was cooled to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (typically 2:1 Hex:CH_2Cl_2, followed by CH_2Cl_2). Evaporation of solvent afforded the analytically pure products.

Ligand screen.

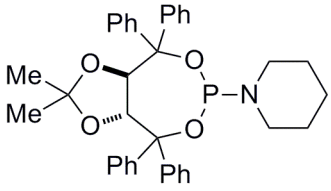




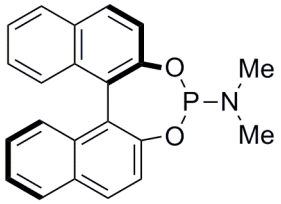
29%, 81% ee



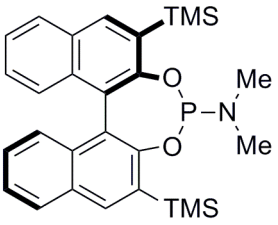
54%, 90% ee



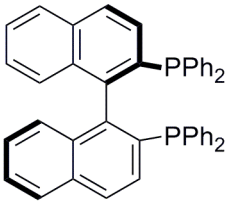
22%, 79% ee



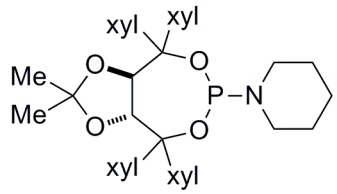
<5%, ee nd



92%, 33% ee

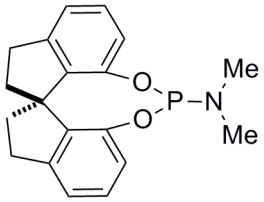


NR, ee nd

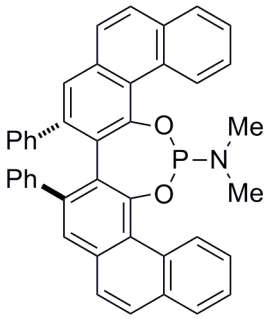


xyl = 3,5-Me-C_6H_3

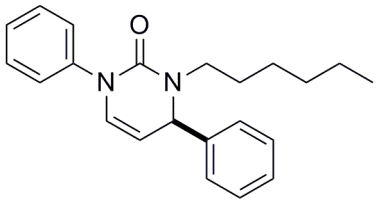
29%, 84% ee



21%, -52% ee

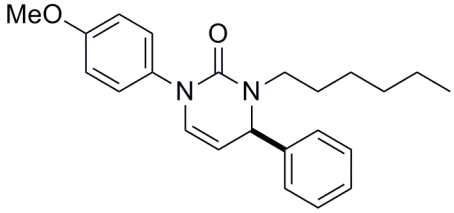


79%, 74% ee

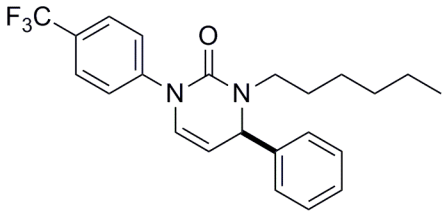


(*R*)-3-hexyl-1,4-diphenyl-3,4-dihydropyrimidine-2-one (3aa). General procedure yielded brown oil (56%). 90% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 7.68 min, RT_{minor} = 11.08 min, 210 nm. $[\alpha]^{20}_{D}$ = +110.0, c = 0.0118 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.23 (m, 10H), 6.30 (d, *J* = 7.8 Hz, 1H), 5.10 (d, *J* = 4.5 Hz, 1H), 4.97 (dd, *J* = 7.8, 4.5 Hz, 1H), 3.74 (ddd, *J* = 15.6, 9.6, 6.0 Hz, 1H), 2.76 (ddd, *J* = 14.4, 9.3, 5.4 Hz, 1H), 1.61 (m, 1H), 1.50 (m, 1H), 1.26 (m, 6H), 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 142.6, 141.3, 128.9, 128.7, 128.0, 127.9, 126.5, 126.2,

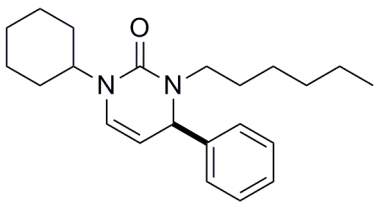
103.0, 61.6, 46.2, 31.4, 26.8, 26.5, 22.5, 14.0. R_f = 0.42 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2957, 2928, 2857, 1665, 1450, 1289, 697 cm^{-1}. HRMS (ESI) *m/z* $[C_{22}H_{27}N_2O]^+$ calcd 335.2118, found 335.2127.



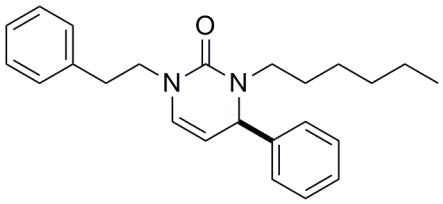
(*R*)-3-hexyl-1-(4-methoxyphenyl)-4-phenyl-3,4-dihydropyrimidin-2-one (3ba). General procedure yielded a brown syrup (49%). 89% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 8.76 min, RT_{minor} = 20.42 min, 230 nm. $[\alpha]^{20}_D$ = +151.3, c = 0.0099 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 - 7.32 (m, 5H), 7.26 (m, 2H), 6.91 (m, 2H), 6.22 (d, *J* = 7.8 Hz, 1H), 5.08 (d, *J* = 4.5 Hz, 1H), 4.92 (dd, *J* = 7.8, 4.5 Hz, 1H), 3.80 (s, 3H), 3.72 (ddd, *J* = 15.6, 9.6, 6.0 Hz, 1H), 2.73 (ddd, *J* = 14.4, 9.3, 5.4 Hz, 1H), 1.59 (m, 1H), 1.48 (m, 1H), 1.24 (m, 6H), 0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 152.6, 142.7, 134.3, 128.8, 128.3, 127.9, 127.6, 126.5, 114.0, 102.5, 61.6, 55.4, 46.2, 31.4, 26.8, 26.5, 22.5, 14.0. R_f = 0.16 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3029, 2930, 2857, 1655, 1512, 1246, 1031, 829, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{29}N_2O_2]^+$ calcd 365.2224, found 365.2229.



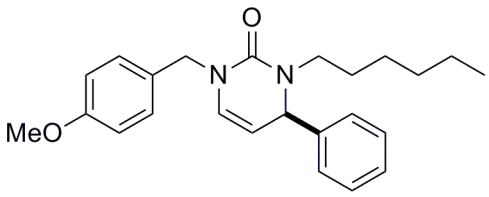
(*R*)-3-hexyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2-one (3ca). General procedure yielded a brown syrup (65%). 91% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 6.40 min, RT_{minor} = 7.11 min, 254 nm. $[\alpha]^{20}_D$ = +159.3°, c = 0.0145 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.50 (m, 2H), 7.39 - 7.33 (m, 5H), 6.32 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 4.5 Hz, 1H), 5.04 (dd, *J* = 7.8, 4.5 Hz, 1H), 3.71 (ddd, *J* = 15.6, 9.6, 6.0 Hz, 1H), 2.76 (ddd, *J* = 14.4, 9.3, 5.1 Hz, 1H), 1.60 (m, 1H), 1.49 (m, 1H), 1.24 (m, 6H), 0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 144.2, 142.1, 129.0, 128.2, 127.0, 126.5, 126.0, 125.9, 125.8, 104.4, 61.6, 46.4, 31.4, 26.8, 26.5, 22.5, 14.0. R_f = 0.32 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2958, 2931, 2859, 1667, 1326, 1124, 699 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{26}F_3N_2O]^+$ calcd 403.1992, found 403.1991.



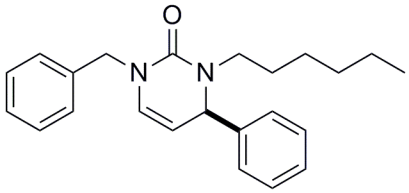
(*R*)-1-cyclohexyl-3-hexyl-4-phenyl-3,4-dihydropyrimidin-2-one (3da). General procedure yielded a brown syrup (80%). 80% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 4.24 min, RT_{minor} = 4.64 min, 210 nm. $[\alpha]^{20}_D$ = +221.0°, c = 0.0090 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.22 (m, 5H), 6.09 (d, *J* = 8.1 Hz, 1H), 4.92 (d, *J* = 4.8 Hz, 1H), 4.83 (dd, *J* = 8.1, 4.8 Hz, 1H), 4.33 (m, 1H), 3.67 (ddd, *J* = 15.3, 9.6, 6.0 Hz, 1H), 2.68 (ddd, *J* = 14.4, 9.3, 5.1 Hz, 1H), 1.82 - 1.64 (m, 5H), 1.39 - 1.08 (m, 16H), 0.84 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 143.2, 128.7, 127.7, 126.4, 123.1, 101.9, 60.8, 52.6, 46.2, 32.0, 31.5, 31.3, 27.0, 26.5, 25.9, 25.7, 25.5, 22.5, 14.0. R_f = 0.44 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2929, 2856, 1649, 1460, 1226, 699 cm^{-1}. HRMS (ESI) *m/z* $[C_{22}H_{33}N_2O]^+$ calcd 341.2587, found 341.2582.



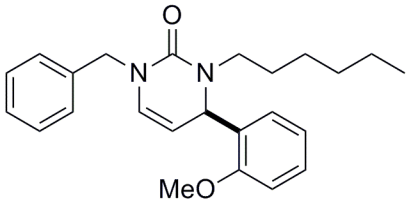
(*R*)-3-hexyl-1-phenethyl-4-phenyl-3,4-dihydropyrimidin-2-one(3ea). General procedure yielded a brown syrup (69%). 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 7.31 min, RT_{minor} = 8.52 min, 254 nm. $[\alpha]^{20}_D$ = +149.6°, c = 0.0147 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 - 7.19 (m, 10H), 5.82 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 4.5 Hz, 1H), 4.70 (dd, *J* = 7.8, 4.5 Hz, 1H), 3.86 (dt, *J* = 13.8, 7.5 Hz, 1H), 3.72 (ddd, *J* = 15.3, 9.3, 6.3 Hz, 1H), 3.58 (dt, *J* = 13.8, 7.5 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.66 (ddd, *J* = 14.4, 9.0, 5.4 Hz, 1H), 1.54 (m, 1H), 1.45 (m, 1H), 1.26 (m, 6H), 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 142.9, 138.8, 129.0, 128.7, 128.4, 127.7, 127.6, 126.4, 126.2, 101.6, 61.3, 49.3, 45.7, 35.5, 31.5, 26.9, 26.5, 22.5, 14.0. R_f = 0.50 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3028, 2929, 2858, 1653, 1455, 1255, 699 cm^{-1}. HRMS (ESI) *m/z* $[C_{24}H_{31}N_2O]^+$ calcd 363.2431, found 363.2431.



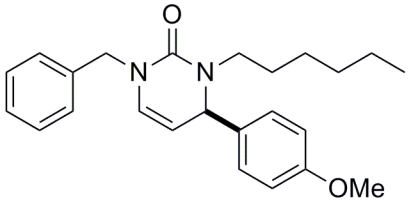
(*R*)-3-hexyl-1-(4-methoxybenzyl)-4-phenyl-3,4-dihydropyrimidin-2-one (3fa). General procedure yielded a brown oil (75%). 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 10.37 min, RT_{minor} = 9.20 min, 230 nm. $[\alpha]^{20}_D$ = +171.3, c = 0.0150 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.21 (m, 7H), 6.74 (m, 2H), 5.98 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 4.5 Hz, 1H), 4.80 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.69 (d, *J* = 15.0 Hz, 1H), 4.59 (d, *J* = 15.0 Hz, 1H), 3.80 (s, 3H), 3.74 (ddd, *J* = 15.3, 9.3, 6.3 Hz, 1H), 2.68 (ddd, *J* = 14.3, 9.0, 5.3 Hz, 1H), 1.55 (m, 1H), 1.47 (m, 1H), 1.24 (m, 6H), 0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 153.4, 142.8, 130.3, 128.9, 128.7, 127.8, 126.9, 126.4, 113.9, 102.4, 61.3, 55.2, 49.8, 45.9, 31.5, 26.9, 26.5, 22.5, 14.0. R_f = 0.48 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2955, 2929, 2858, 1652, 1248, 1035, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{24}H_{31}N_2O_2]^+$ calcd 379.2380, found 379.2360.



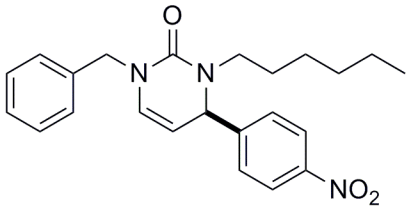
(*R*)-1-benzyl-3-hexyl-4-phenyl-3,4-dihydropyrimidin-2-one (3ga). General procedure yielded a brown oil (67%). 93% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 8.12 min, RT_{minor} = 7.56 min, 210 nm. $[\alpha]^{20}_D$ = +38.4, c = 0.0076 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 - 7.24 (m, 10H), 5.99 (d, J = 7.8 Hz, 1H), 5.02 (d, J = 4.5 Hz, 1H), 4.82 (dd, J = 7.8, 4.5 Hz, 1H), 4.82 (d, J = 15.3 Hz, 1H), 4.66 (d, J = 15.3 Hz, 1H), 3.77 (ddd, J = 15.6, 9.3, 6.3 Hz, 1H), 2.69 (ddd, J = 14.1, 9.0, 5.1 Hz, 1H), 1.56 (m, 1H), 1.48 (m, 1H), 1.26 (m, 6 H), 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.7, 138.2, 128.7, 128.5, 127.8, 127.5, 127.2, 127.0, 126.4, 102.4, 61.3, 50.3, 45.9, 31.5, 26.9, 26.5, 22.5, 14.0. R_f = 0.33 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3030, 2929, 2858, 1655, 1453, 1253, 701 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{29}N_2O]^+$ calcd 349.2274, found 349.2277.



(*R*)-1-benzyl-3-hexyl-4-(2-methoxyphenyl)-3,4-dihydropyrimidin-2-one (3ha). General procedure yielded a brown oil (67%). 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 9.75 min, RT_{minor} = 7.15 min, 230 nm. $[\alpha]^{20}_D$ = +219.7, c = 0.0081 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.20 (m, 7H), 6.97 - 6.86 (m, 2 H), 5.95 (d, *J* = 7.8 Hz, 1H), 5.46 (d, *J* = 4.8 Hz, 1H), 4.96 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.78 (d, *J* = 15.3 Hz, 1H), 4.63 (d, *J* = 15.3 Hz, 1H), 3.89 (ddd, *J* = 15.3, 8.7, 6.9 Hz, 1H), 3.82 (s, 3H), 2.62 (ddd, *J* = 14.1, 8.4, 5.7 Hz, 1H), 1.66 - 1.49 (m, 2H), 1.28 (m, 6H), 0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 154.2, 138.4, 130.3, 128.5, 128.4, 127.4, 127.3, 127.1, 126.8, 120.9, 110.3, 101.8, 55.2, 54.7, 50.2, 46.0, 31.5, 27.3, 26.4, 22.5, 14.0. R_f = 0.32 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2954, 2929, 2857, 1654, 1464, 1239, 1029, 704 cm^{-1}. HRMS (ESI) *m/z* $[C_{24}H_{31}N_2O_2]^+$ calcd 379.2380, found 379.2386.

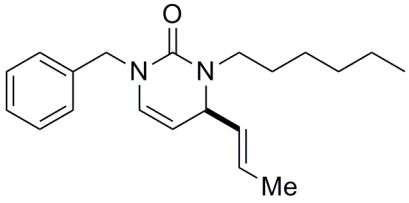


(*R*)-1-benzyl-3-hexyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2-one (3ia). General procedure yielded a gold oil (69%). 92% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 10.55 min, RT_{minor} = 9.7 min, 210 nm. $[\alpha]^{20}_D$ = +177.8, c = 0.0086 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.20 (m, 5H), 7.16 (m, 2H), 6.85 (m, 2H), 5.98 (d, *J* = 7.8 Hz, 1H), 4.95 (d, *J* = 4.5 Hz, 1H), 4.78 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.75 (d, *J* = 15.3 Hz, 1H), 4.65 (d, *J* = 15.3 Hz, 1H), 3.80 (s, 3H), 3.71 (ddd, *J* = 15.3, 9.3, 6.3 Hz, 1H), 2.69 (ddd, *J* = 14.1, 9.0, 5.1 Hz, 1H), 1.55 (m, 1H), 1.46 (m, 1H), 1.24 (m, 6H), 0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 153.3, 138.3, 134.9, 128.6, 127.7, 127.5, 127.3, 126.8, 114.0, 102.7, 60.7, 55.2, 50.3, 45.7, 31.5, 26.9, 26.5, 22.6, 14.0. R_f = 0.35 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2929, 2857, 1653, 1510, 1249, 1034, 832, 703 cm^{-1}. HRMS (ESI) *m/z* $[C_{24}H_{31}N_2O_2]^+$ calcd 379.2380, found 379.2376.

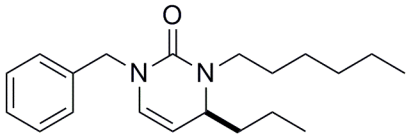


(*R*)-1-benzyl-3-hexyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2-one (3ja). General procedure yielded a brown syrup (36%). 95% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 16.76 min, RT_{minor} = 19.91 min, 210 nm. $[\alpha]^{20}_D$ = +227.3, c = 0.0077 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) 8.18 (m, 2H), 7.39 - 7.28 (m, 7H), 6.04 (d, *J* = 7.8 Hz, 1H), 5.12 (d, *J* = 4.8 Hz, 1H), 4.80 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.78 (d, *J* = 15.0 Hz, 1H), 4.63 (d, *J* = 15.0 Hz, 1H), 3.80 (ddd, *J* = 15.3, 9.3, 6.3 Hz, 1H), 2.62 (ddd, *J* = 14.4, 9.0, 5.4 Hz, 1H), 1.52 (m, 2H), 1.25 (m, 6H), 0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 149.9, 147.5, 137.9, 128.7, 128.3, 127.6, 127.1, 124.2, 101.0, 60.8, 50.5, 46.4, 31.5, 27.0, 26.4, 22.5, 14.0. R_f = 0.44 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2930, 2858, 1654, 1522, 1348, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{28}N_3O_3]^+$ calcd 394.2125, found 394.2130.

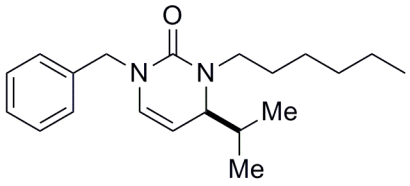
(*R*)-1-benzyl-4-(furan-2-yl)-3-hexyl-3,4-dihydropyrimidin-2-one (3ka). General procedure yielded a brown syrup (82%). 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 8.86 min, RT_{minor} = 8.00 min, 210 nm. $[\alpha]^{20}_{D}$ = +138.7, c = 0.0140 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) 7.36 - 7.22 (m, 6H), 6.32 (dd, J = 3.0, 1.8 Hz, 1H), 6.18 (d, 3.0 Hz, 1H), 6.08 (d, 7.8 Hz, 1H), 5.05 (d, J = 4.8 Hz, 1H), 4.83 (dd, J = 7.8, 4.8 Hz, 1H), 4.79 (d, J = 15.3 Hz, 1H), 4.63 (d, J = 15.3 Hz, 1H), 3.72 (ddd, J = 15.0, 9.3, 6.0 Hz, 1H), 2.98 (ddd, J = 14.1, 9.0, 5.1 Hz, 1H), 1.59 (m, 1H), 1.40 (m, 1H), 1.28 (m, 6H), 0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 153.2, 142.2, 138.1, 129.1, 128.4, 127.3, 127.1, 110.2, 106.8, 98.9, 54.1, 50.1, 46.1, 31.5, 27.1, 26.4, 22.5, 14.0. R_f = 0.46 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2957, 2929, 2858, 1654, 1497, 1254, 737 cm^{-1}. HRMS (ESI) *m/z* $[C_{21}H_{27}N_2O_2]^+$ calcd 339.2067, found 339.2075.



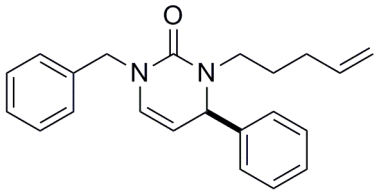
(*S,E*)-1-benzyl-3-hexyl-4-(prop-1-en-1-yl)-3,4-dihydropyrimidin-2-one (3la). General procedure yielded yellow oil (60%) as a 1:10 mixture of cis:trans isomers. 89% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 6.79 min, RT_{minor} = 6.53 min, 230 nm. $[\alpha]^{20}_{D}$ = +121.6, c = 0.0124 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 - 7.23 (m, 5H), 5.92 (d, *J* = 7.8 Hz, 1H), 5.59 - 5.33 (m, 2H), 4.70 (d, *J* = 15.3 Hz, 1H), 4.65 (m, 1H), 4.57 (d, *J* = 15.3 Hz, 1H), 4.30 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.72 (ddd, *J* = 15.0, 7.8, 7.2 Hz, 1H), 2.90 (ddd, *J* = 14.1, 8.1, 6.0 Hz, 1H), 1.69 (d, *J* = 6.0 Hz, 3H), 1.56 (m, 2H), 1.29 (m, 6H), 0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 138.4, 130.8, 128.4, 127.8, 127.3, 127.1, 126.4, 101.2, 59.1, 50.0, 45.3, 31.5, 27.3, 26.5, 22.6, 17.4, 14.0. R_f = 0.31 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3029, 2929, 2857, 1653, 1456, 1253, 964, 703 cm^{-1}. HRMS (ESI) *m/z* $[C_{20}H_{29}N_2O]^+$ calcd 313.2274, found 313.2277.



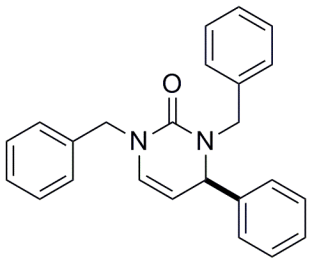
(*S*)-1-benzyl-3-hexyl-4-propyl-3,4-dihydropyrimidin-2-one (3ma). General procedure yielded gold syrup (38%). 77% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 5.75 min, RT_{minor} = 5.16 min, 230 nm. $[\alpha]^{20}_{D}$ = +27.0, c = 0.0117 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 - 7.23 (m, 5H), 5.95 (d, *J* = 7.8 Hz, 1H), 4.74 (m, 1H), 4.71 (d, *J* = 15.3 Hz, 1H), 4.53 (d, *J* = 15.3 Hz, 1H), 3.93 (m, 1H), 3.78 (ddd, *J* = 14.4, 8.7, 6.6 Hz, 1H), 2.88 (ddd, *J* = 14.4, 8.7, 5.7 Hz, 1H), 1.58 (m, 2H), 1.30 (m, 10H), 0.89 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 138.4, 128.4, 127.4, 127.1, 101.7, 56.2, 50.0, 45.8, 37.1, 31.6, 27.8, 26.5, 22.6, 17.0, 14.0. R_f = 0.42 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3065, 3032, 2930, 2859, 1653, 1454, 1372, 1259, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{20}H_{31}N_2O]^+$ calcd 315.2431, found 315.2431.



(*S*)-1-benzyl-3-hexyl-4-isopropyl-3,4-dihydropyrimidin-2-one (3na). General procedure yielded gold syrup (53%). 83% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 6.19 min, RT_{minor} = 5.43 min, 210 nm. $[\alpha]^{20}_{D}$ = +59.0, c = 0.0116 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 - 7.23 (m, 5H), 6.02 (d, J = 8.1 Hz, 1H), 4.74 (d, J = 15.3 Hz, 1H), 4.64 (dd, J = 8.1, 4.5 Hz, 1H), 4.48 (d, J = 15.3 Hz, 1H), 3.85 (dd, J = 4.5, 4.2 Hz, 1H), 3.77 (ddd, J = 15.3, 9.3, 6.3 Hz, 1H), 2.91 (ddd, J = 14.4, 9.0, 5.4 Hz, 1H), 1.97 (dd, J = 6.6, 4.2 Hz, 1H), 1.59 (m, 2H), 1.30 (m, 6H), 0.89 (m, 3H), 0.83 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 138.2, 129.5, 128.4, 127.6, 127.1, 97.5, 62.0, 50.0, 46.3, 31.6, 31.4, 27.7, 26.6, 22.6, 17.8, 15.2, 14.0. R_f = 0.43 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 2959, 2929, 2871, 1652, 1455, 1257, 702 cm^{-1}. HRMS (ESI) *m/z* $[C_{20}H_{31}N_2O]^+$ calcd 315.2431, found 315.2421.

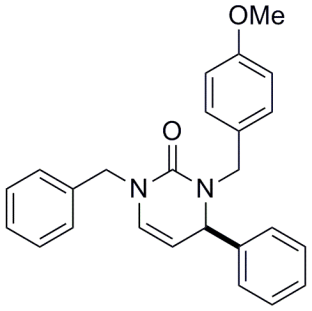


(*R*)-1-benzyl-3-(pent-4-en-1-yl)-4-phenyl-3,4-dihydropyrimidin-2-one (3gb). General procedure yielded gold syrup (53%). 91% ee by HPLC: Chiralcel IC column, 95:5 Hex:iPrOH, 1ml/min, RT_{major} = 20.89 min, RT_{minor} = 18.37 min, 210 nm. $[\alpha]^{20}_{D}$ = +120.4, c = 0.0098 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 - 7.23 (m, 10H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.78 (ddt, *J* = 16.8, 10.2, 6.6, 1H), 5.02 - 4.92 (m, 3H), 4.82 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.78 (d, *J* = 15.3 Hz, 1H), 4.65 (d, *J* = 15.3 Hz, 1H), 3.74 (ddd, *J* = 15.3, 9.3, 6.3 Hz, 1H), 2.74 (ddd, *J* = 14.4, 9.0, 5.4 Hz, 1H), 2.03 (dt, *J* = 7.2, 6.6 Hz, 2H), 1.72 - 1.56 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.7, 138.2, 138.0, 128.8, 128.6, 127.9, 127.5, 127.3, 127.1, 126.4, 114.8, 102.5, 61.6, 50.3, 45.6, 31.0, 26.2. R_f = 0.24 (4:1 Hex:EtOAc). IR (NaCl, Thin Film) 3064, 3030, 2930, 1653, 1452, 1246, 913, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{22}H_{25}N_2O]^+$ calcd 333.1961, found 333.1965.

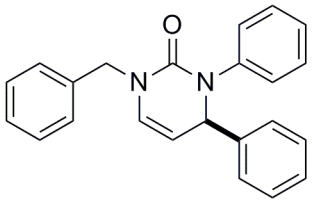


(*R*)-1,3-dibenzyl-4-phenyl-3,4-dihydropyrimidin-2-one (3gc). General procedure yielded gold syrup (65%). 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 10.53 min, RT_{minor} = 7.97 min, 230 nm. $[\alpha]^{20}_{D}$ = +202.5, c = 0.0100 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 - 7.23 (m, 15H), 6.03 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 15.3 Hz, 1H), 4.89 (d, *J* = 15.3 Hz, 1H), 4.88 (d, *J* = 4.5 Hz, 1H), 4.79 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.71 (d, *J* = 15.3 Hz, 1H), 3.56 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 141.8, 138.1, 137.1, 128.8, 128.6, 128.5, 128.0, 127.5, 127.4, 127.3, 126.9, 126.7, 60.0, 50.6, 47.8. R_f = 0.42 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3063, 3029, 2926, 1652, 1449, 1246, 698 cm^{-1}. HRMS (ESI) *m/z* $[C_{24}H_{23}N_2O]^+$ calcd 355.1805, found 355.1808. $[Rh(C_2H_4)_2Cl]_2$ (17.5 mg, 0.045 mmol) and **L2** (50.9 mg, 0.09 mmol) were added to an oven-dried 50 ml round bottom flask and the flask was fitted with an oven-dried reflux condenser in an inert atmosphere (Ar) glove box. Upon removal from the glove box, the reaction vessel was put under Ar and 20 ml of toluene was added via syringe and the resulting gold solution was stirred at 23 °C for 15 min. To this solution, imine **1d** (1.0 g, 4.5 mmol) and isocyanate **2c** (0.75 g, 5.6 mmol) in 15 ml of toluene was added via syringe. The reaction mixture was heated to 110 °C in an oil bath and kept at reflux for 12 h. The reaction mixture was cooled

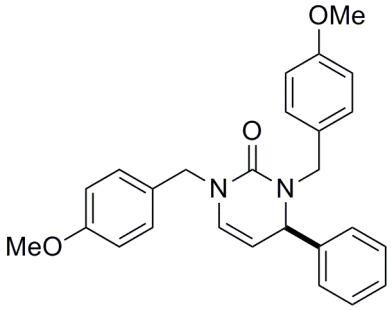
to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (2:1 Hex:CH_2Cl_2, followed by CH_2Cl_2). Evaporation of solvent afforded 1.13g (71%, 94% ee) of **3gc**.



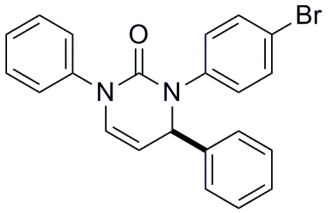
(*R*)-1-benzyl-3-(4-methoxybenzyl)-4-phenyl-3,4-dihydropyrimidin-2-one (3gd). General procedure yielded gold syrup (75%). 93% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1 ml/min, RT_{major} = 14.91 min, RT_{minor} = 11.61 min, 210 nm. $[\alpha]^{20}_D$ = +182.6, c = 0.0113 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 - 6.88 (m, 12H), 6.89 (m, 2H), 6.00 (d, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 15.0 Hz, 1H), 4.88 (d, *J* = 15.3 Hz, 1H), 4.88 (d, *J* = 4.5 Hz, 1H), 4.77 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.70 (d, *J* = 15.3 Hz, 1H), 3.82 (s, 3H), 3.49 (d, *J* = 15.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 153.6, 141.9, 138.1, 129.4, 129.0, 128.8, 128.6, 127.9, 127.5, 127.3, 126.8, 126.6, 113.8, 102.7, 59.7, 55.2, 50.6, 47.1. R_f = 0.42 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3028, 2933, 1650, 1511, 1370, 1246, 700 cm^{-1}. HRMS (ESI) *m/z* $[C_{25}H_{25}N_2O_2]^+$ calcd 385.1911, found 385.1892.



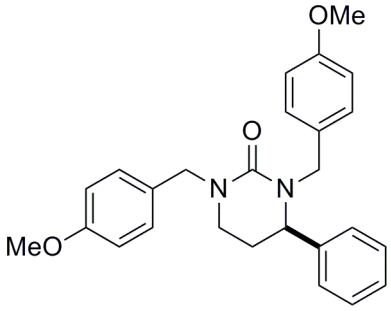
(*R*)-1-benzyl-3,4-diphenyl-3,4-dihydropyrimidin-2-one (3ge). General procedure yielded brown syrup (42%). 84% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1 ml/min, RT_{major} = 13.74 min, RT_{minor} = 15.11 min, 230 nm. $[\alpha]^{20}_D$ = +246.5, c = 0.0123 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 - 7.07 (m, 15H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.29 (d, *J* = 4.8 Hz, 1H), 5.06 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.84 (d, *J* = 15.0 Hz, 1H), 4.74 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 142.1, 142.0, 137.8, 128.8, 128.6, 127.9, 127.8, 127.6, 127.5, 127.3, 126.7, 126.5, 64.8, 50.4. R_f = 0.50 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3062, 3030, 1656, 1416, 1248, 697 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{21}N_2O]^+$ calcd 341.1648, found 341.1656.



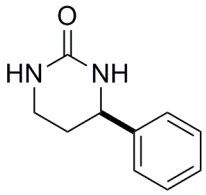
(*R*)-1,3-bis(4-methoxybenzyl)-4-phenyl-3,4-dihydropyrimidin-2-one (3fd). General procedure yielded gold syrup (78%). 92% ee by HPLC: Chiralcel IC column, 80:20 Hex:iPrOH, 1 ml/min, RT_{major} = 32.25 min, RT_{minor} = 22.60 min, 230 nm. $[\alpha]^{20}_D$ = +139.5, c = 0.0124 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.17 (m, 9H), 6.92 - 6.86 (m, 4H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.38 (d, *J* = 15.0 Hz, 1H), 4.83 (d, J = 4.5 Hz, 1H), 4.79 (d, *J* = 14.7 Hz, 1H), 4.74 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.62 (d, *J* = 15.0 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.46 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 158.8, 153.7, 142.0, 130.2, 129.4, 129.1, 129.0, 128.8, 127.9, 126.8, 126.7, 114.0, 113.8, 102.7, 59.7, 55.2, 50.1, 47.1. R_f = 0.27 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3029, 3002, 2933, 2836, 1651, 1512, 1247, 1034, 828, 665 cm^{-1}. HRMS (ESI) *m/z* $[C_{26}H_{27}N_2O_3]^+$ calcd 415.2016, found 415.2018.



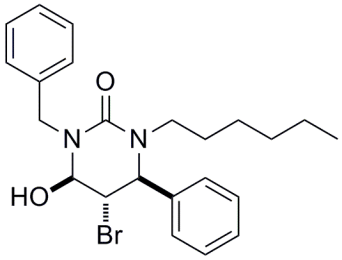
(*R*)-3-(4-bromophenyl)-1,4-diphenyl-3,4-dihydropyrimidin-2-one (3af). General procedure yielded brown solid (37%). 81% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 11.44 min, RT_{minor} = 20.74 min, 210 nm. $[\alpha]^{20}_D$ = +161.8, c = 0.0126 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 - 6.97 (m, 12H), 6.98 (m, 2H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.8 Hz, 1H), 5.20 (dd, *J* = 7.8, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 141.4, 140.8, 140.6, 131.9, 129.5, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 126.8, 126.7, 126.2, 120.3, 104.1, 65.0. R_f = 0.40 (98:2 CH_2Cl_2:EtOAc). IR (NaCl, Thin Film) 3061, 3029, 2924, 1672, 1489, 1264, 697 cm^{-1}. HRMS (ESI) *m/z* $[C_{22}H_{18}BrN_2O]^+$ calcd 405.0597, found 405.0594. Slow crystallization from CH_2Cl_2 layered with heptanes yielded clear X-ray quality crystals (<99% ee by HPLC: Chiralcel IA column, 90:10 Hex:iPrOH, 1ml/min, RT_{major} = 11.70 min).



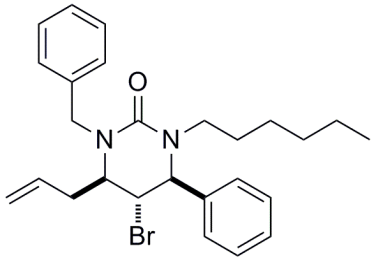
(*R*)-1,3-bis(4-methoxybenzyl)-4-phenyltetrahydropyrimidin-2-one (4). In a 10 ml round bottom, **3fd** (127 mg, 0.31 mmol) was dissolved in MeOH and 10% Pd/C (4 mg) was added. The reaction flask was evacuated and refilled with H_2. After stirring at 23 °C for 12 h, the reaction was filtered through Celite, concentrated *in vacuo*, and purified by flash column chromatography to yield 104.5 mg of **4** (82%) as a clear amorphous solid. 92% ee by HPLC: Chiralcel IA column, 85:15 Hex:iPrOH, 1 ml/min, RT_{major} = 18.96 min, RT_{minor} = 16.46 min, 254 nm. $[\alpha]^{20}_D$ = +11.5, c = 0.0132 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.24 (m, 5H), 7.18 - 7.11 (m, 4H), 6.88 - 6.83 (m, 4H), 5.50 (d, *J* = 15.0 Hz, 1H), 4.63 (d, *J* = 14.8 Hz, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 4.43 (dd, *J* = 4.8, 3.3 Hz, 1H), 3.80 (s, 6H), 3.51 (d, *J* = 15.0 Hz, 1H), 3.02 - 2.97 (m, 2H), 2.14 (dddd, *J* = 16.8, 12.9, 5.4, 5.4 Hz, 1H), 1.80 (dddd, *J* = 13.2, 3.3, 3.3, 3.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 156.3, 141.0, 130.5, 130.3, 129.1, 129.0, 128.5, 127.3, 126.2, 113.6, 56.9, 55.0, 50.9, 48.4, 40.7, 29.5. R_f = 0.19 (2:1 Hex:EtOAc). IR (NaCl, Thin Film) 2931, 2835, 1630, 1510, 1245, 1034 cm^{-1}. HRMS (ESI) *m/z* $[C_{26}H_{29}N_2O_3]^+$ calcd 417.2173, found 417.2162.



(*R*)-4-phenyltetrahydropyrimidin-2-one (5).[5] In a 10 ml round bottom, **4** (91.4 mg, 0.22 mmol) was dissolved in 6 ml TFA and heated to 80 °C for 3 h. The reaction was cooled to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (elute 10:1 EtOAc:MeOH). The resulting white powder was tritrated with EtOAc to yield 25.4 mg of **5** (66%) as a white powder. 94% ee by HPLC: Chiralcel IA column, 70:30 Hex:iPrOH, 1 ml/min, RT_{major} = 6.80 min, RT_{minor} = 6.33 min, 254 nm. $[\alpha]^{20}_D$ = +41.7, c = 0.0081 g/ml MeOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.24 (m, 5H), 4.57 (dd, *J* = 6.0, 5.2 Hz, 1H), 3.27 (s, 1H), 3.26 (s, 1H), 3.23 (ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 3.10 (ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 2.09 (m, 1H), 1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 129.7, 128.6, 127.2, 55.5, 38.4, 30.9. R_f = 0.18 (10:1 EtOAc:MeOH). IR (NaCl, Thin Film) 3222, 3074, 2968, 2917, 1684, 1515, 13362, 757 cm^{-1}. HRMS (ESI) *m/z* $[C_{10}H_{13}N_2O]^+$ calcd 177.1022, found 177.1021.

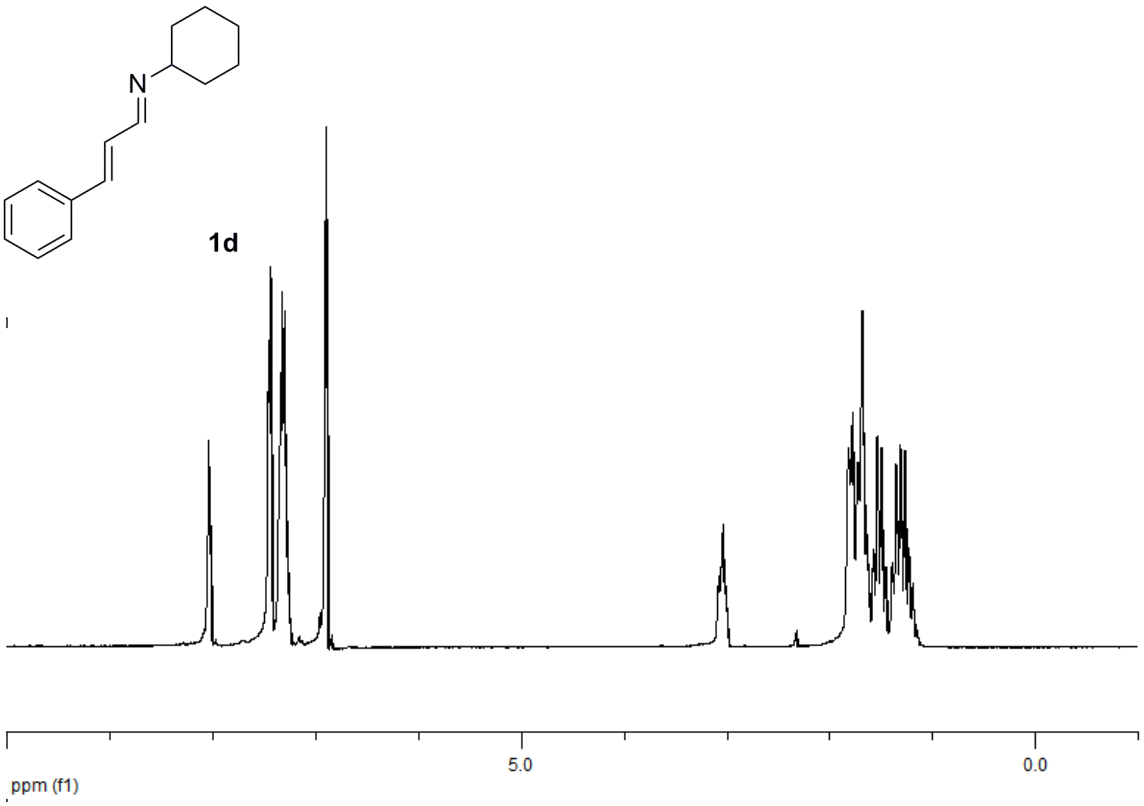


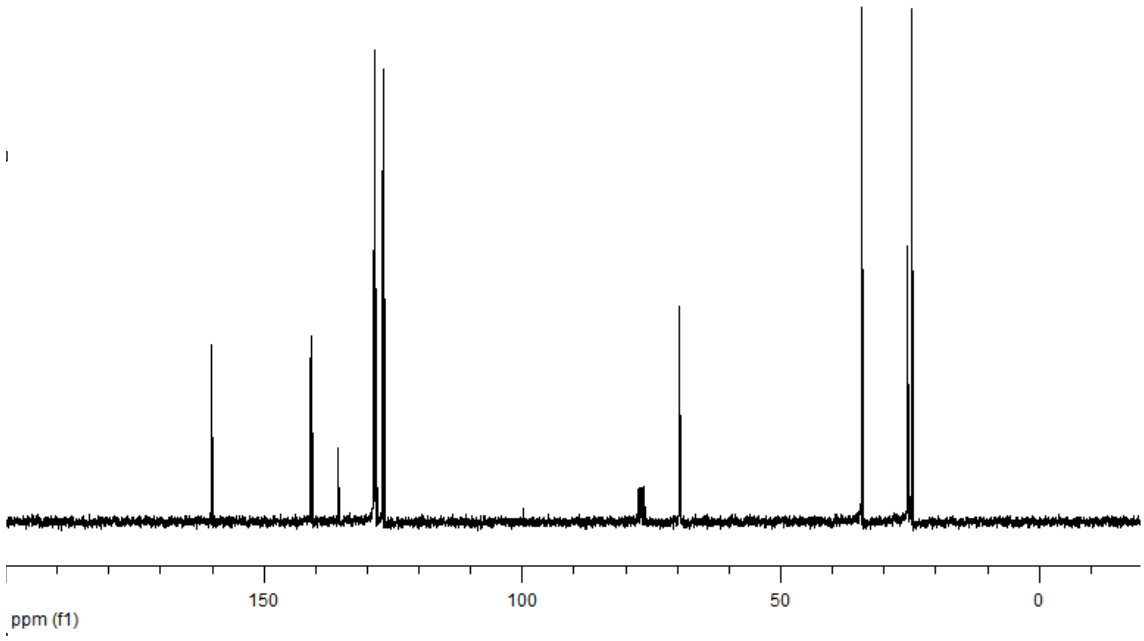
(*4S,5S,6R*)-1-benzyl-5-bromo-3-hexyl-6-hydroxy-4-phenyltetrahydropyrimidin-2-one (6). In a 10 ml round bottom, **3ga** (101.2 mg, 0.29 mmol) was dissolved in 6 ml of wet DMF, NBS (52.7 mg, 0.29 mmol) was added, and the reaction was stirred for 3 h at 23 °C. The reaction was diluted with 50 ml Et_2O and the organic layer was washed with H_2O (3 X 50 ml), concentrated *in vacuo*, dried with $MgSO_4$, and purified by flash column chromatography (elute 4:1 Hex:EtOAc) to yield 96.7 mg of **6** (75%) as a clear amorphous solid. 94% ee by HPLC: Chiralcel IC column, 80:20 Hex:iPrOH, 1 ml/min, RT_{major} = 7.14 min, RT_{minor} = 5.23 min, 230 nm. $[\alpha]^{20}_D$ = -20.6, c = 0.0060 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.24 (m, 10H), 5.13 (d, *J* = 15.3 Hz, 1H), 4.83 (bs, 1H), 4.77 (bd, *J* = 10.2 Hz, 1H), 4.59 (dd, *J* = 2.1, 2.1 Hz, 1H), 4.27 (d, *J* = 15.3 Hz, 1H), 4.08 (ddd, *J* = 15.6, 9.3, 6.6 Hz, 1H), 2.70 (ddd, *J* = 14.4, 9.3, 5.1 Hz, 1H), 1.62 (m, 3H), 1.28 (m, 6H), 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 137.9, 137.5, 129.7, 128.7, 128.3, 128.2, 127.2, 126.0, 83.1, 63.4, 48.4, 48.3, 47.7, 31.6, 27.8, 26.6, 22.6, 14.0. R_f = 0.26 (2:1 Hex:EtOAc). IR (NaCl, Thin Film) 3330, 2955, 2928, 2857, 1616, 1502, 1227, 1045, 696 cm^{-1}. HRMS (ESI) *m/z* $[C_{23}H_{30}BrN_2O_2]^+$ calcd 445.1485, found 445.1494.

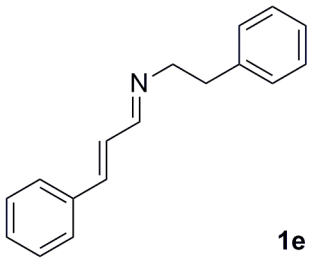


(*4S,5S,6R*)-6-allyl-1-benzyl-5-bromo-3-hexyl-4-phenyltetrahydropyrimidin-2-one (7). In a 10 ml round bottom, **6** (54.1 mg, 0.12 mmol) and allyltrimethylsilane (41.4 mg, 0.36 mmol) was dissolved in DCM and cooled to -78 °C. After cooling, 50 µl of boron trifluoride diethyl etherate was added and the reaction vessel was removed from the cooling bath and allowed to warm to 23 °C. The reaction was concentrated *in vacuo*, and purified by flash column chromatography (elute 10:1 Hex:EtOAc) to yield 43.1 mg of **7** (72%) as a clear syrup. 94% ee by HPLC: Chiralcel ODH column, 90:10 Hex:iPrOH, 1 ml/min, RT_{major} = 5.40 min, RT_{minor} = 4.62 min, 254 nm. $[\alpha]^{20}_D$ = +15.4, c = 0.0105 g/ml $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 - 7.22 (m, 10H), 5.29 (d, *J* = 15.3 Hz, 1H), 5.25 (m, 1H), 4.86 (bs, 1H), 4.84 (bd, *J* = 10.8 Hz, 1H), 4.72 (bs, 1H), 4.21 (bd, *J* = 16.5 Hz, 1H), 4.16 (m, 1H), 4.13 (d, *J* = 15.3 Hz, 1H), 3.49 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.62 (ddd, *J* 14.3, 9.9, 4.5 Hz, 1H), 2.14 (dt, *J* = 13.8, 5.1 Hz, 1H), 1.72 (m, 1H), 1.57 (m, 1H), 1.41 (m, 2H), 1.29 (m, 5H), 0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 138.8, 137.7, 132.6, 129.0, 128.3, 128.2, 128.1, 127.2, 126.7, 119.2, 65.3, 62.3, 49.1, 47.5, 47.2, 37.3, 31.7, 27.7, 26.6, 22.6, 14.0. R_f = 0.38 (4:1 Hex:EtOAc). IR (NaCl, Thin Film) 3063, 3028, 2955, 2928, 2857, 1636, 1482, 1230, 923, 818, 702 cm^{-1}. HRMS (ESI) *m/z* $[C_{26}H_{34}BrN_2O]^+$ calcd 469.1849, found 469.1841.

^{1}H NMR and ^{13}C NMR Spectra of New Compounds







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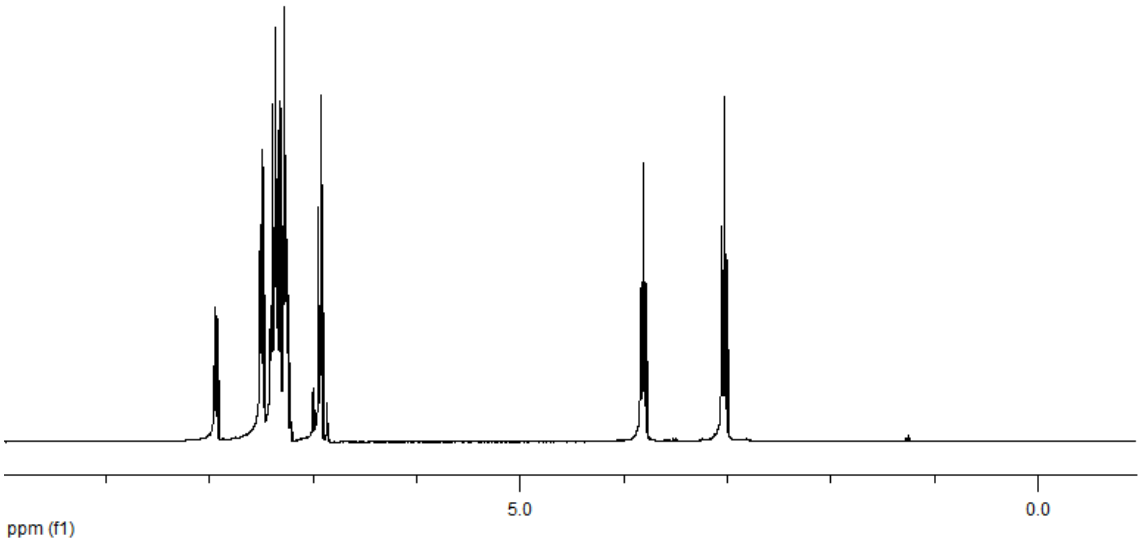

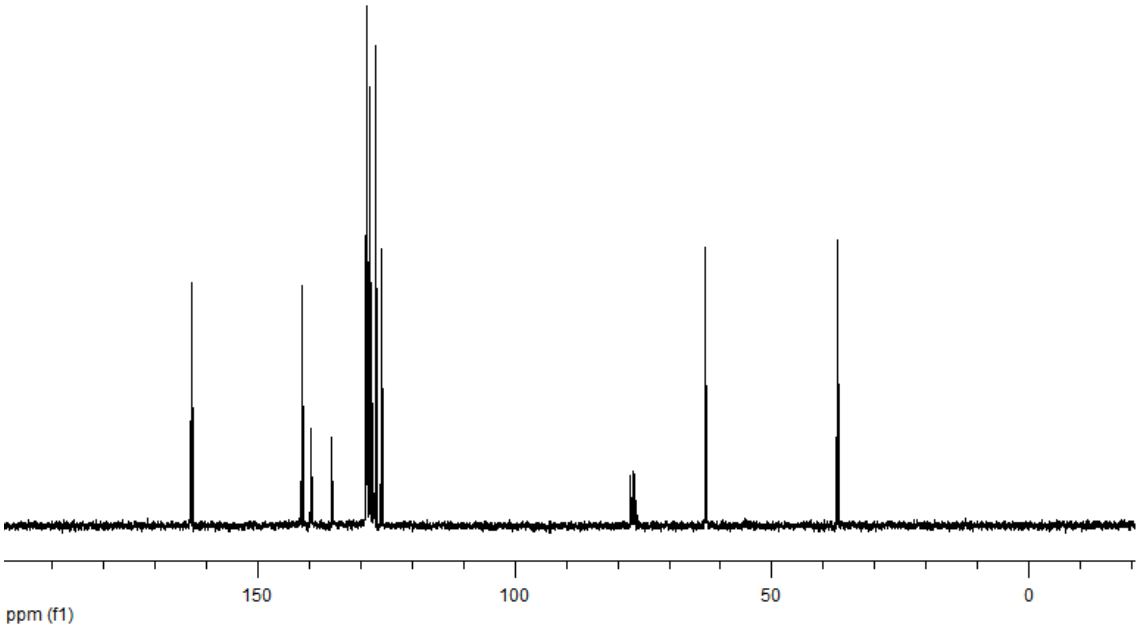

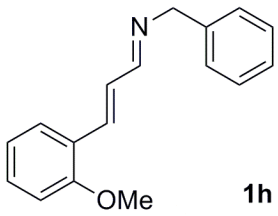

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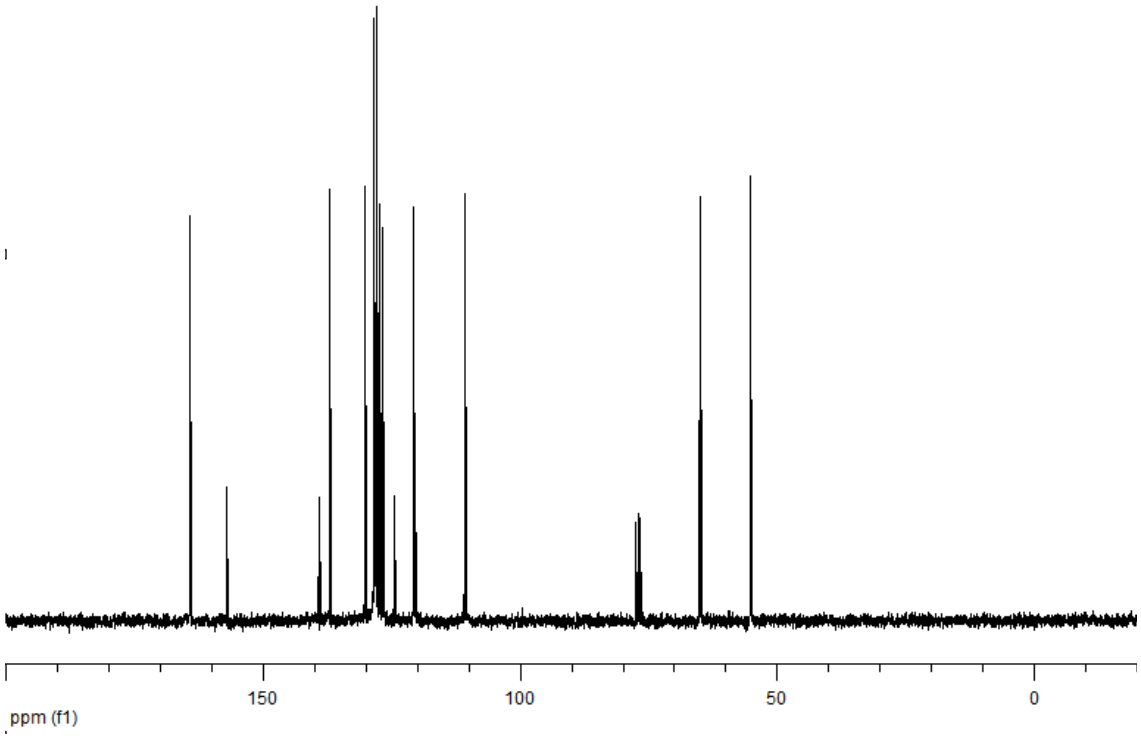

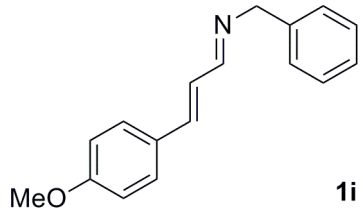

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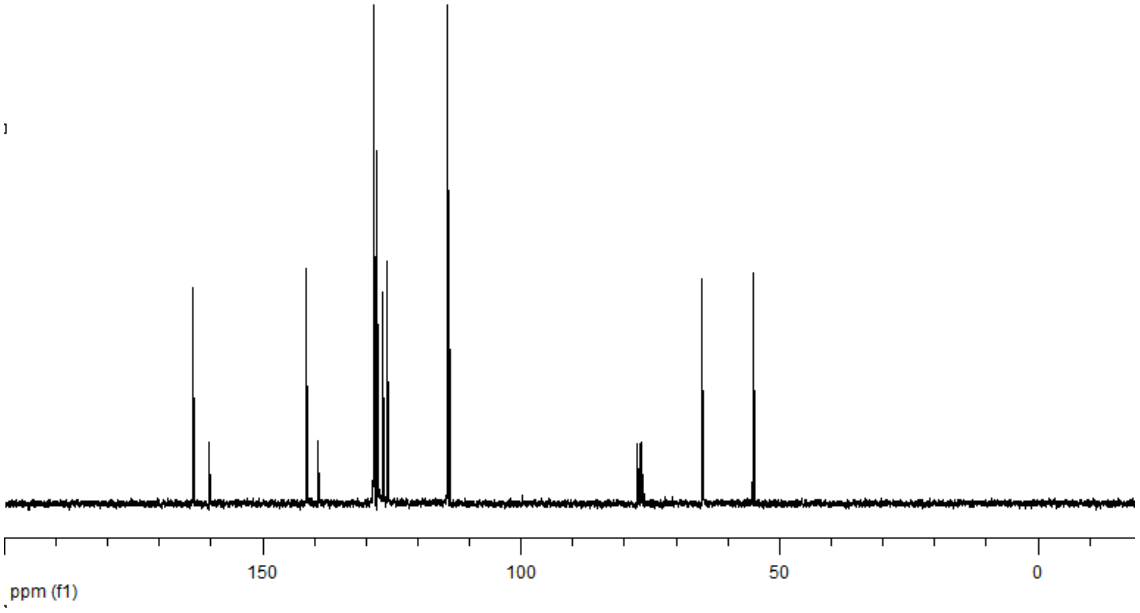

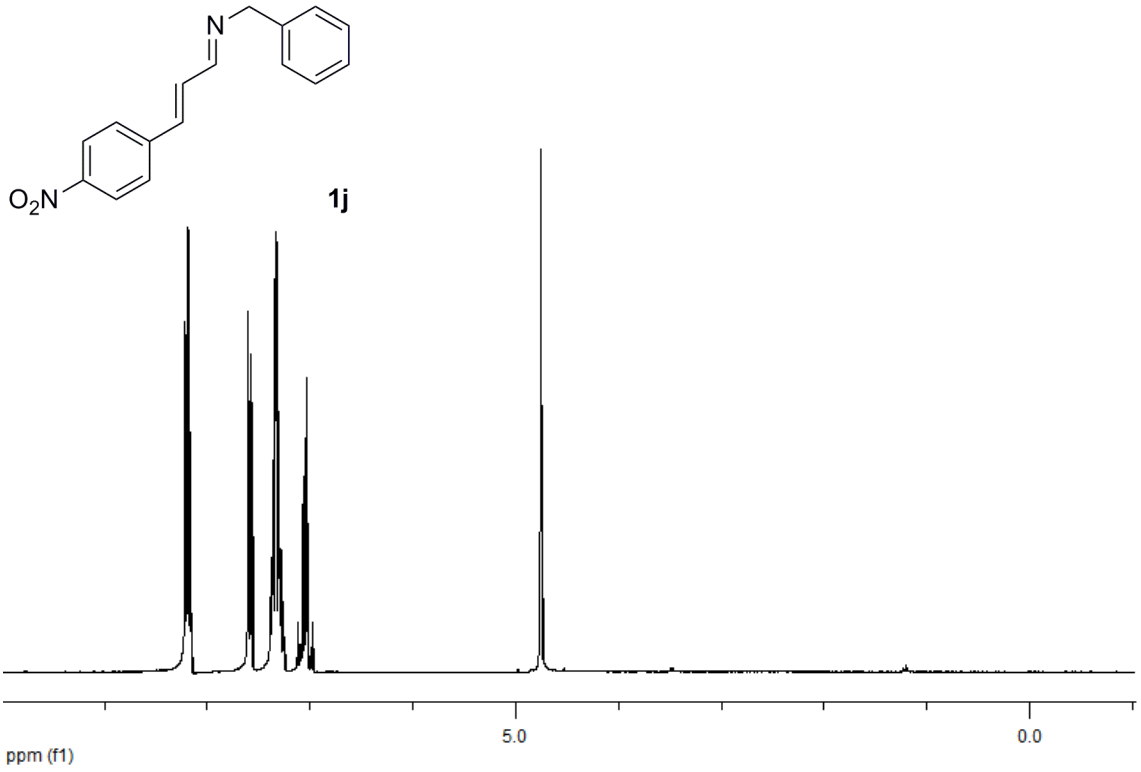
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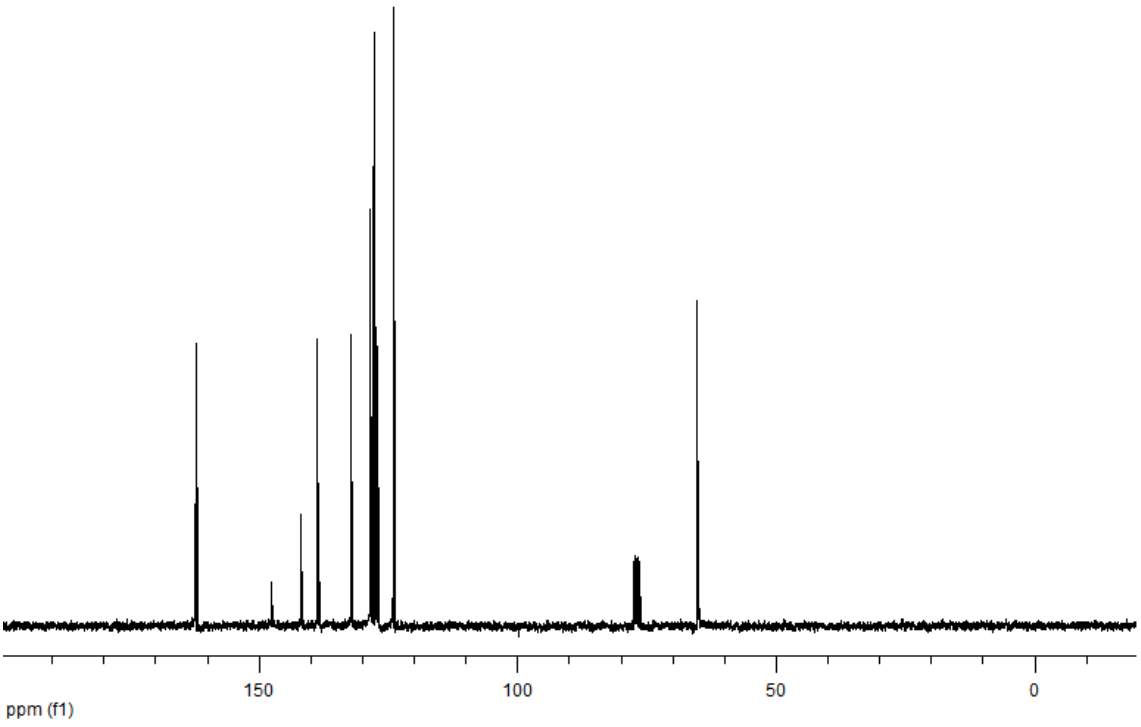
0.0
ppm (f1)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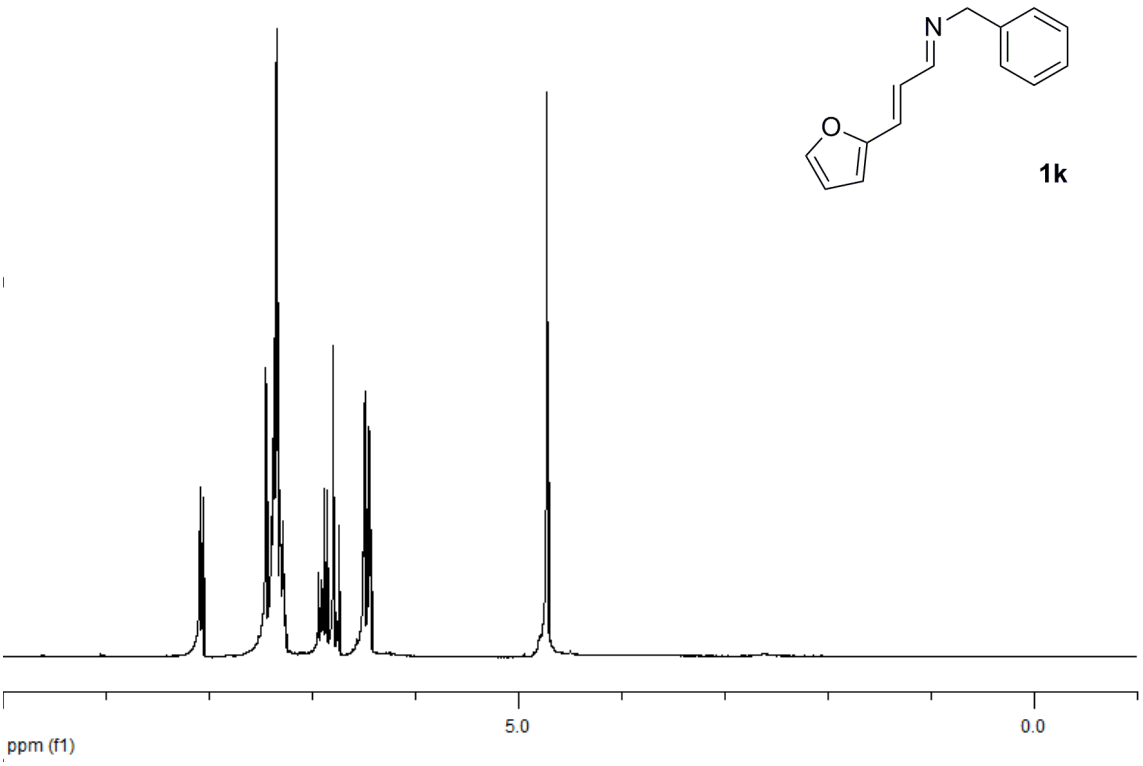
100
50
0
ppm (f1)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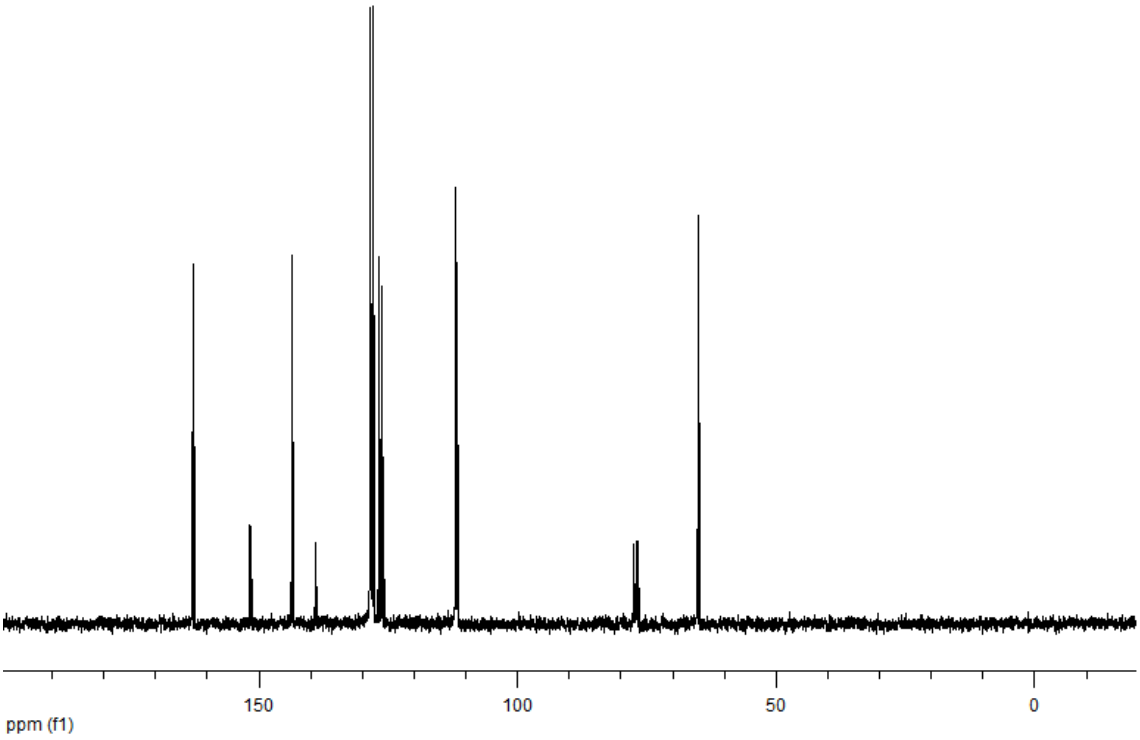
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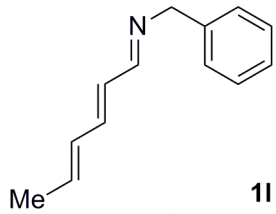

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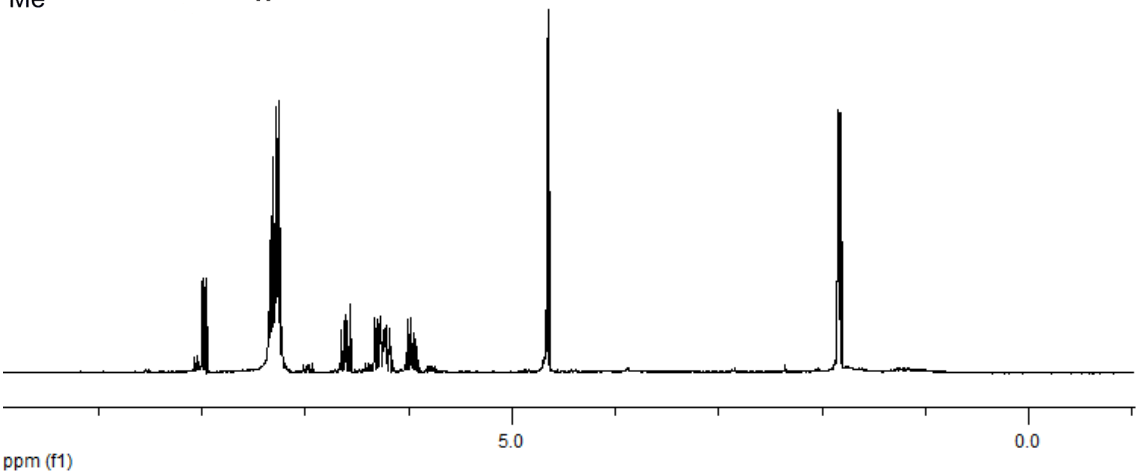

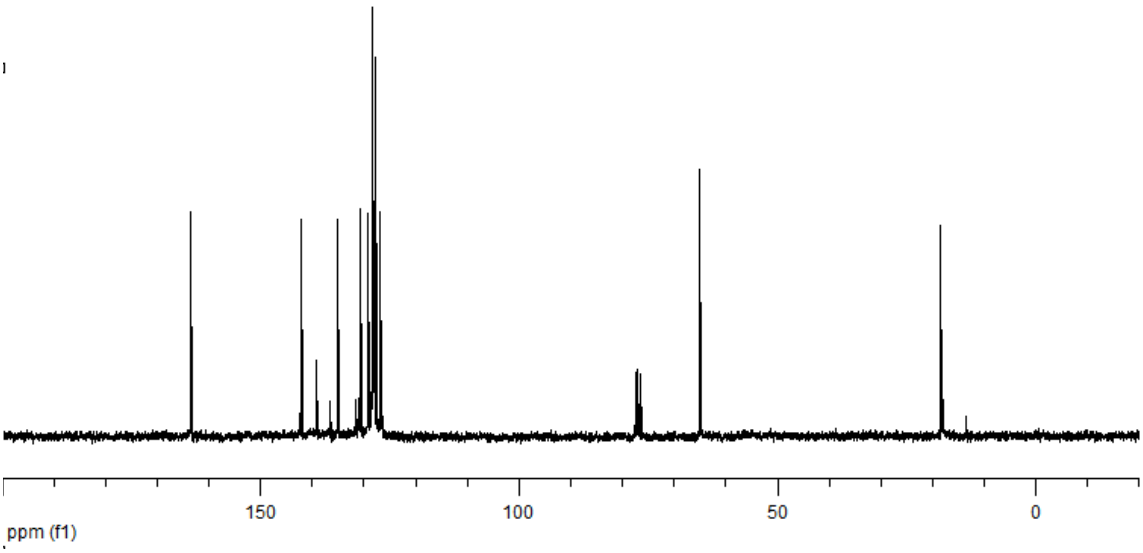

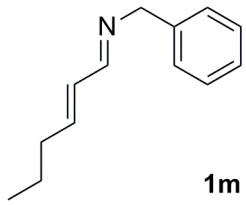

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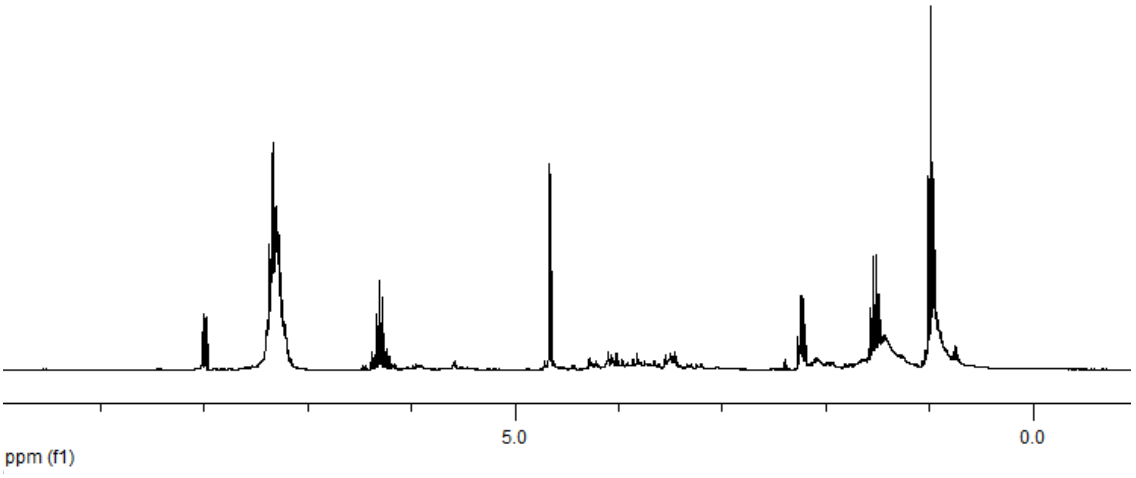

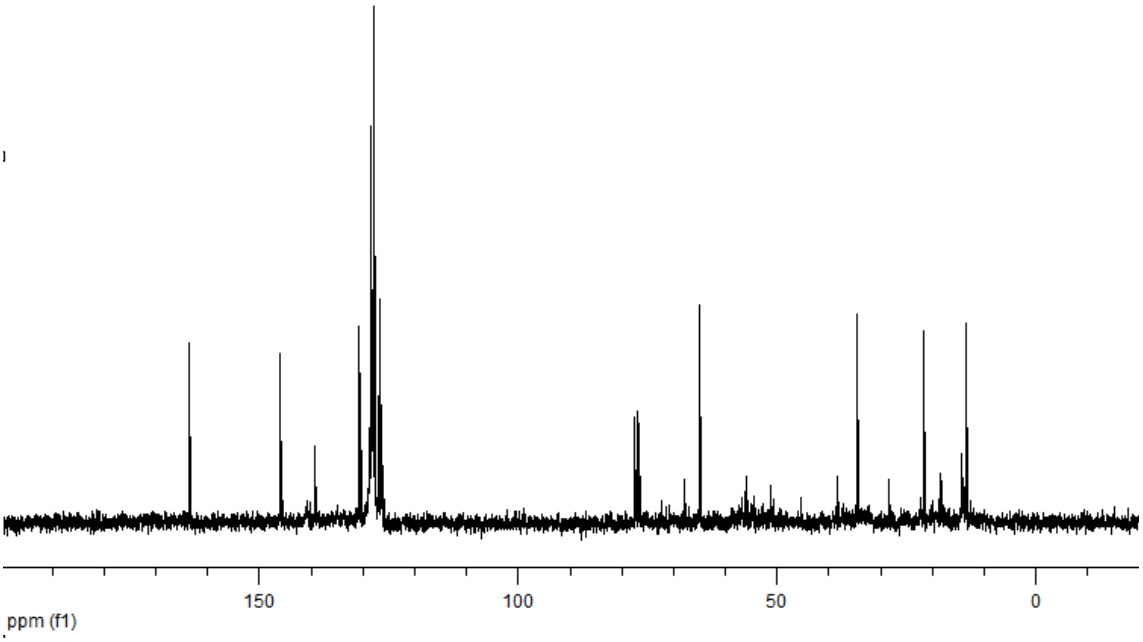

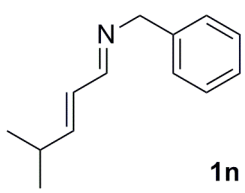

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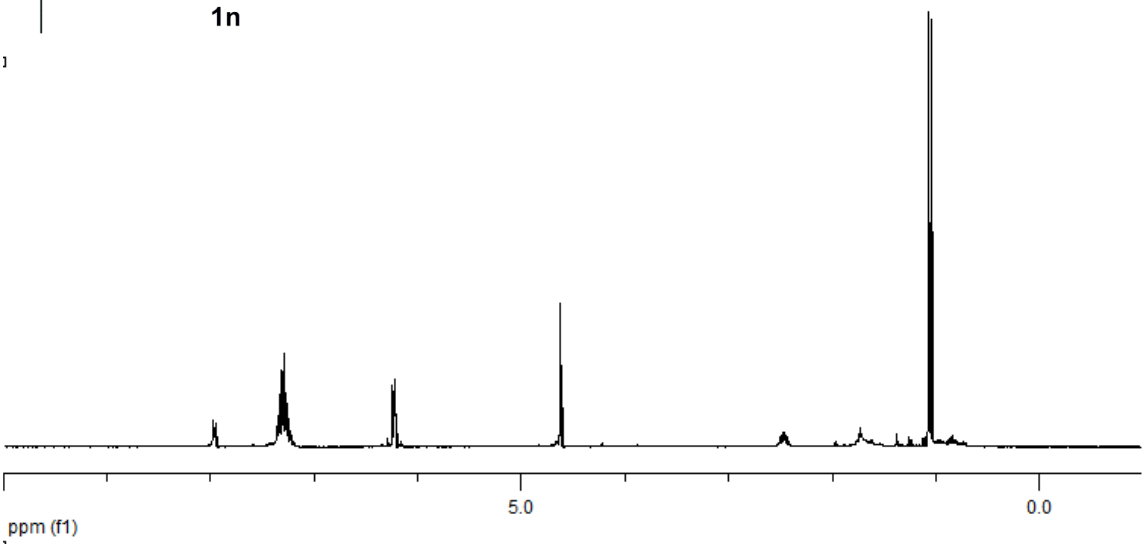

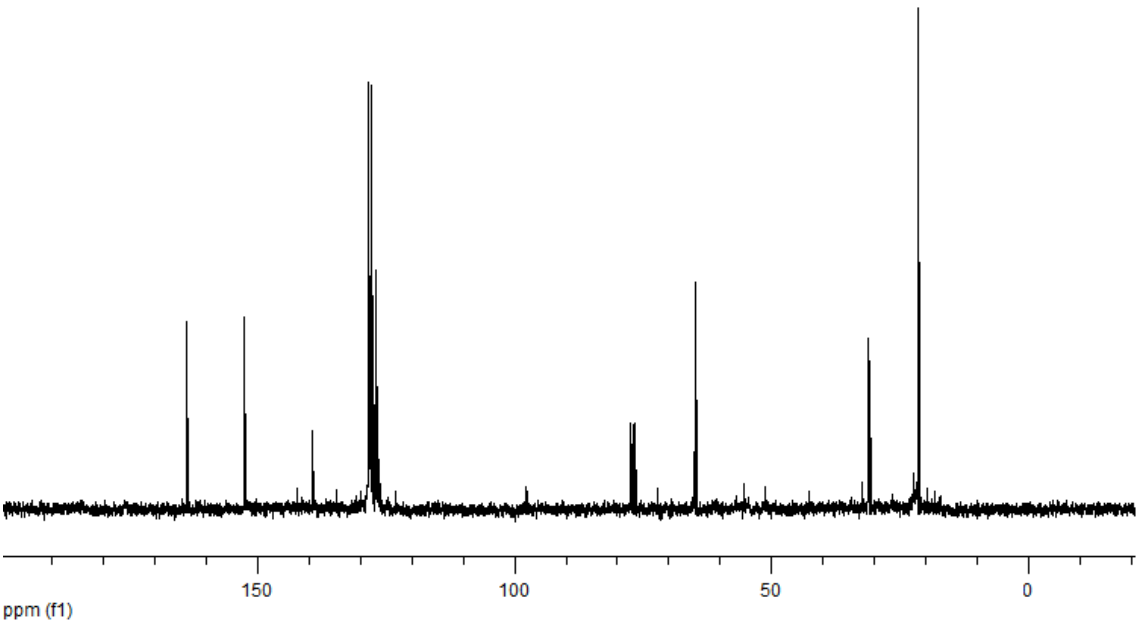

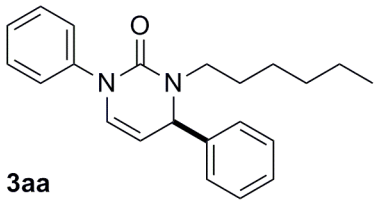

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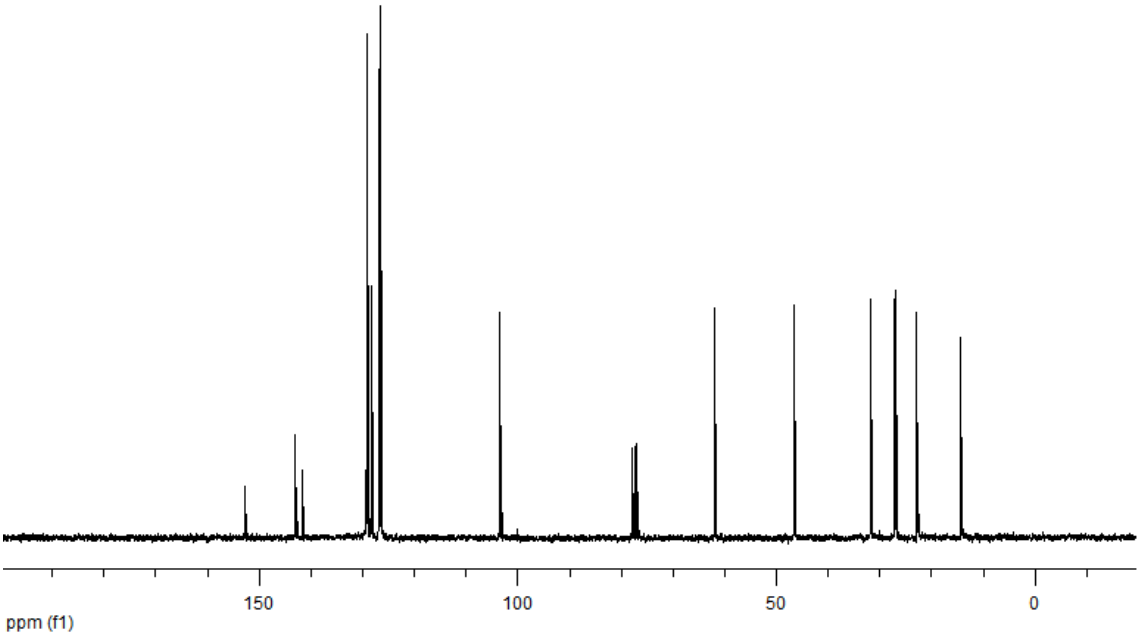

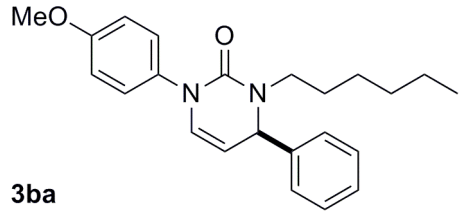

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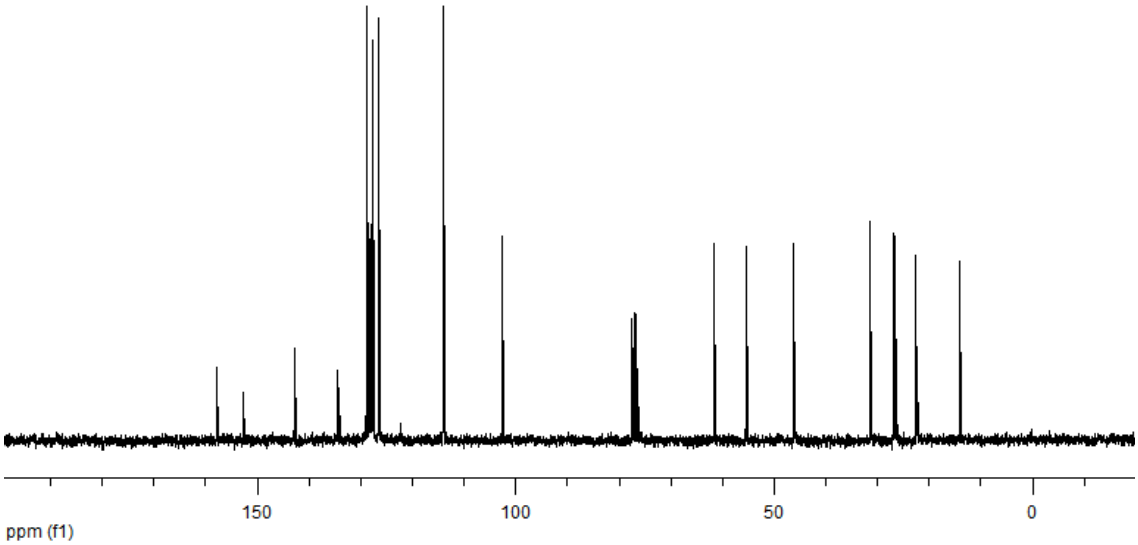

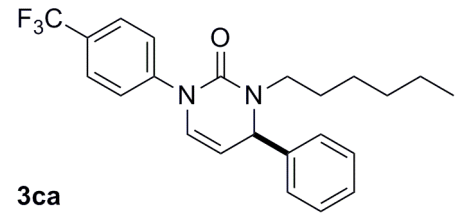

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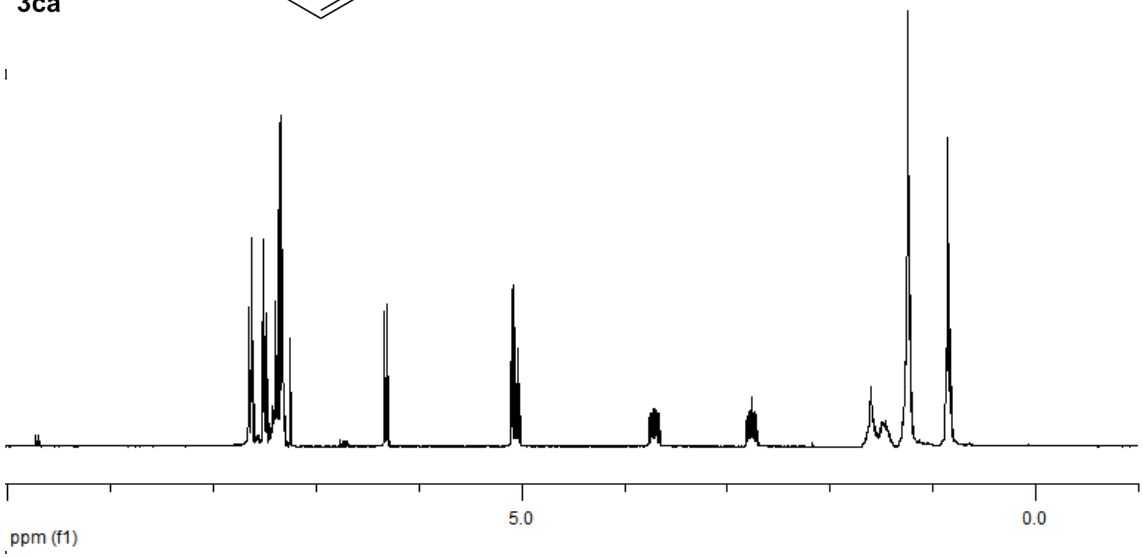

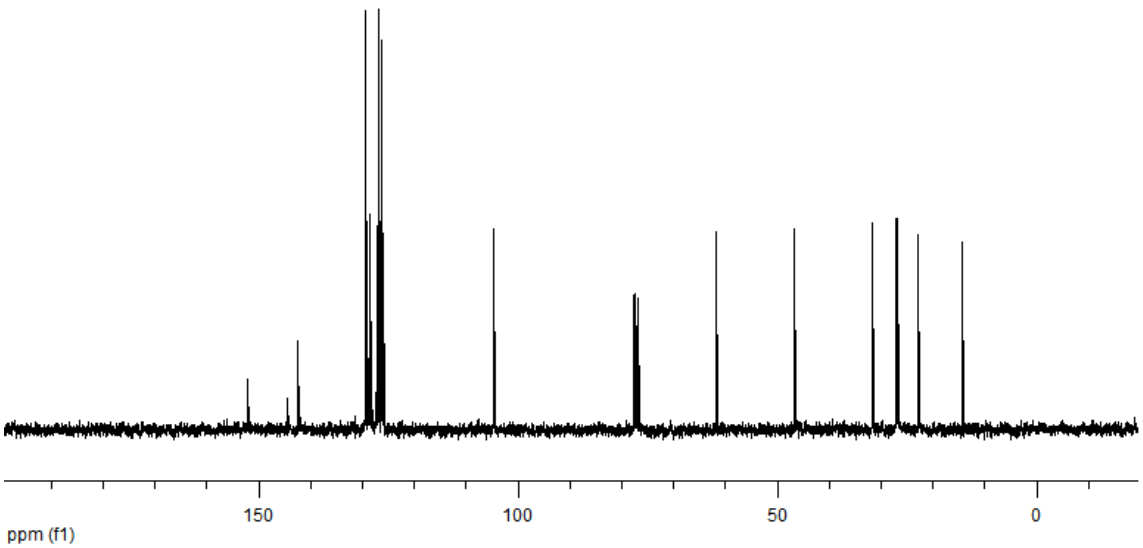

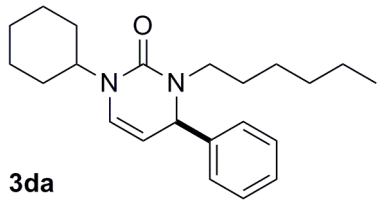

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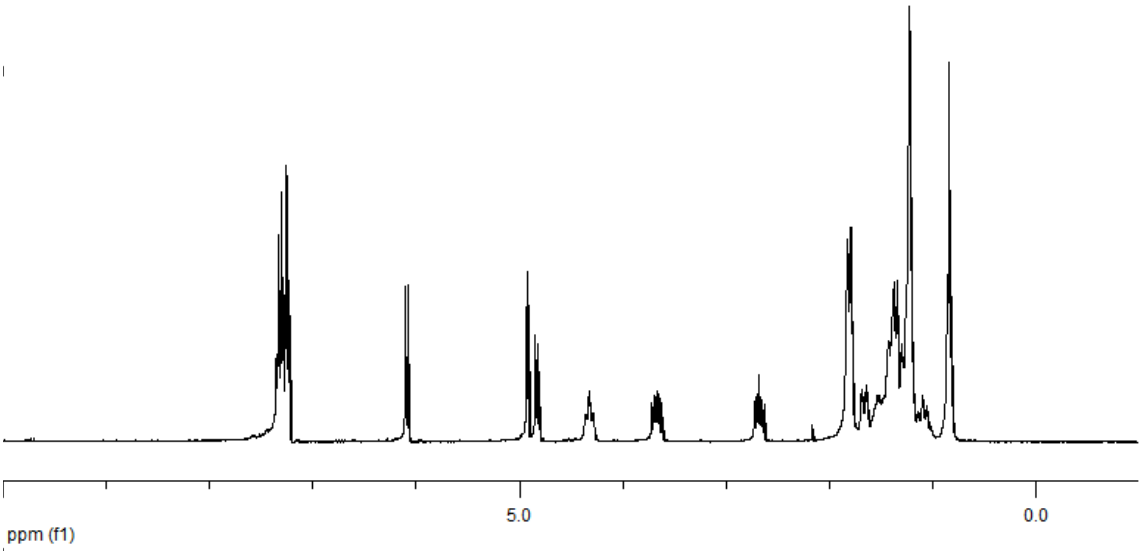

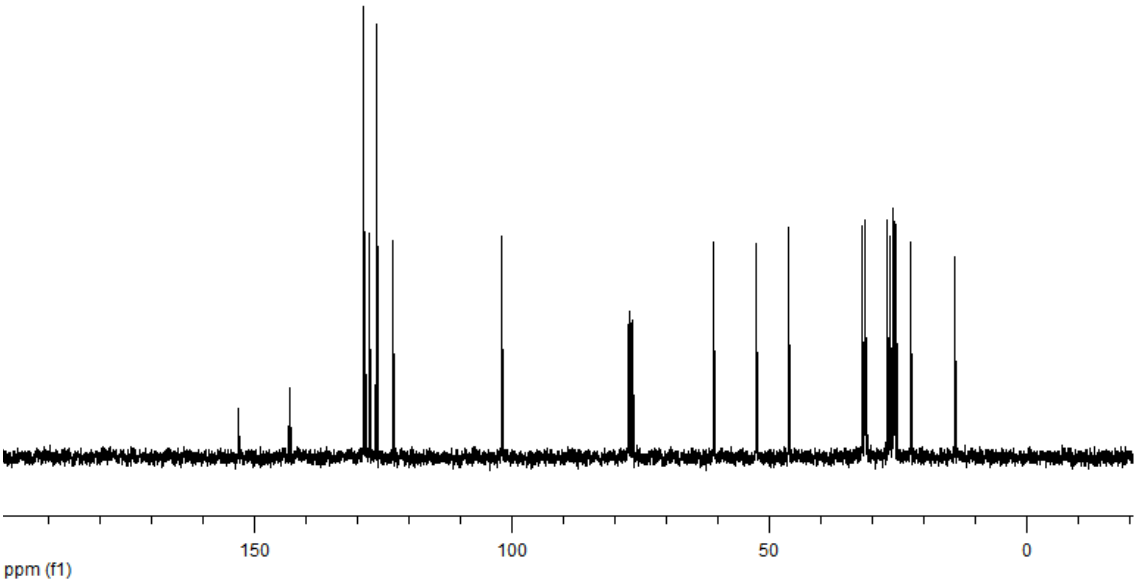

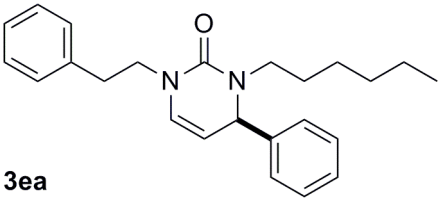

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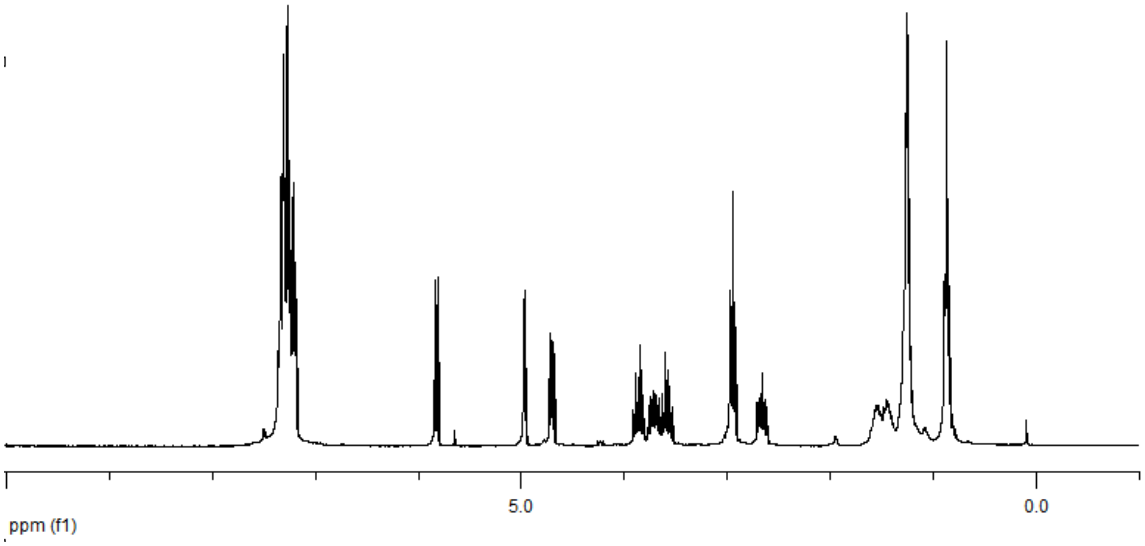

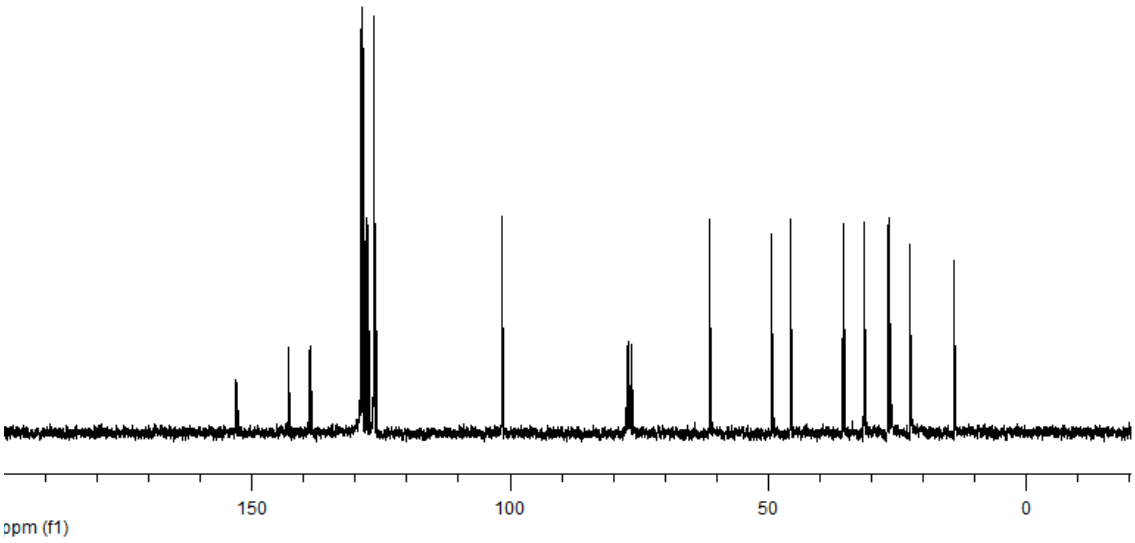

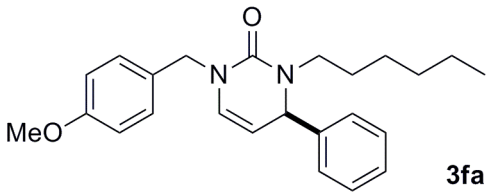

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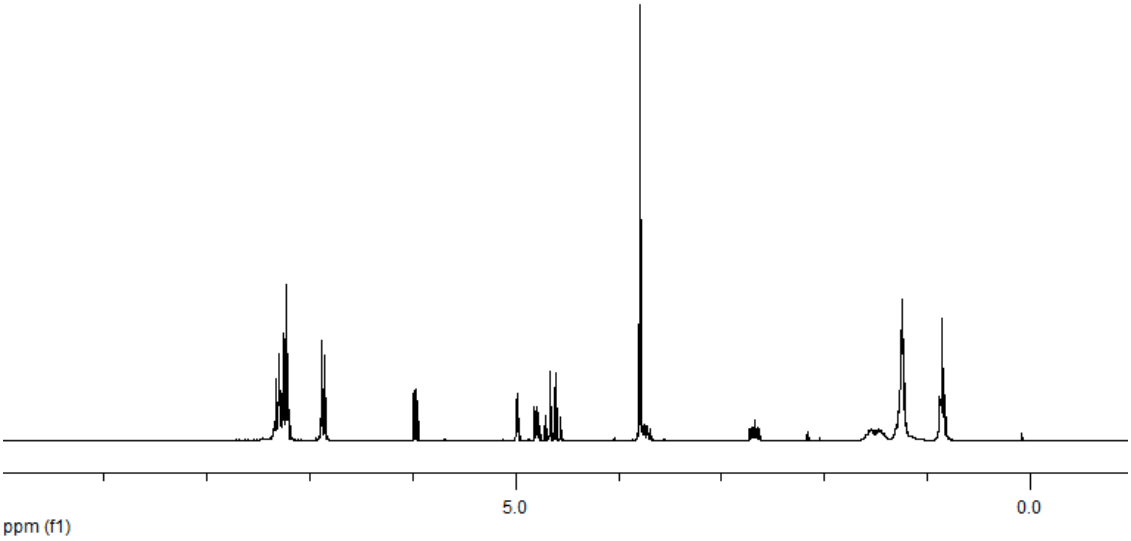

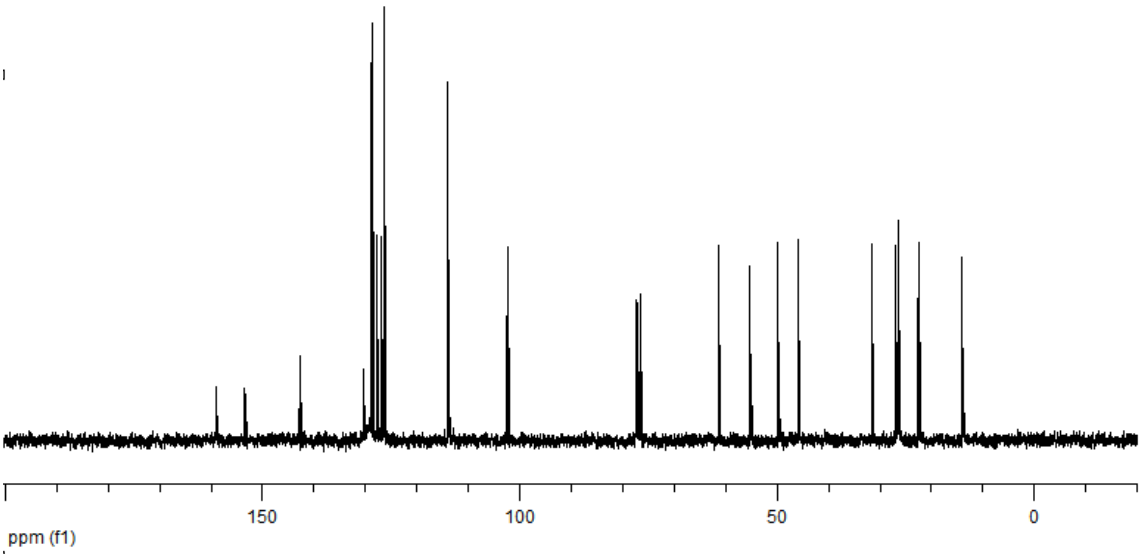

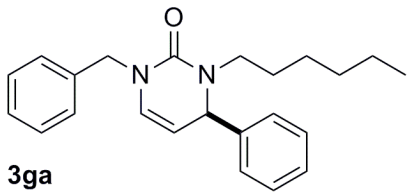

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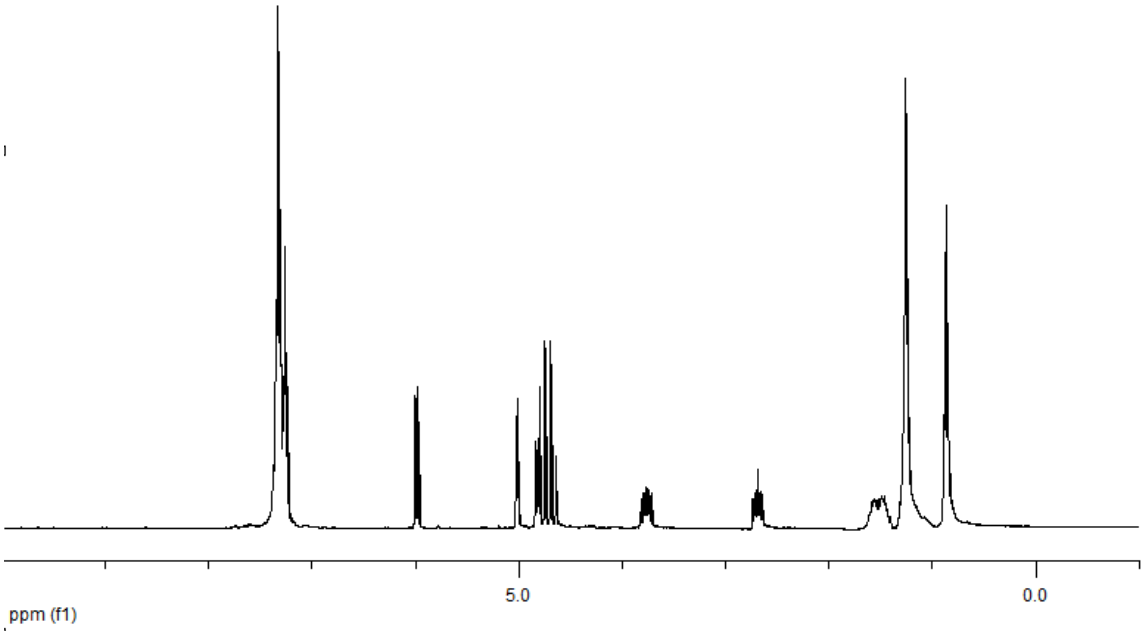

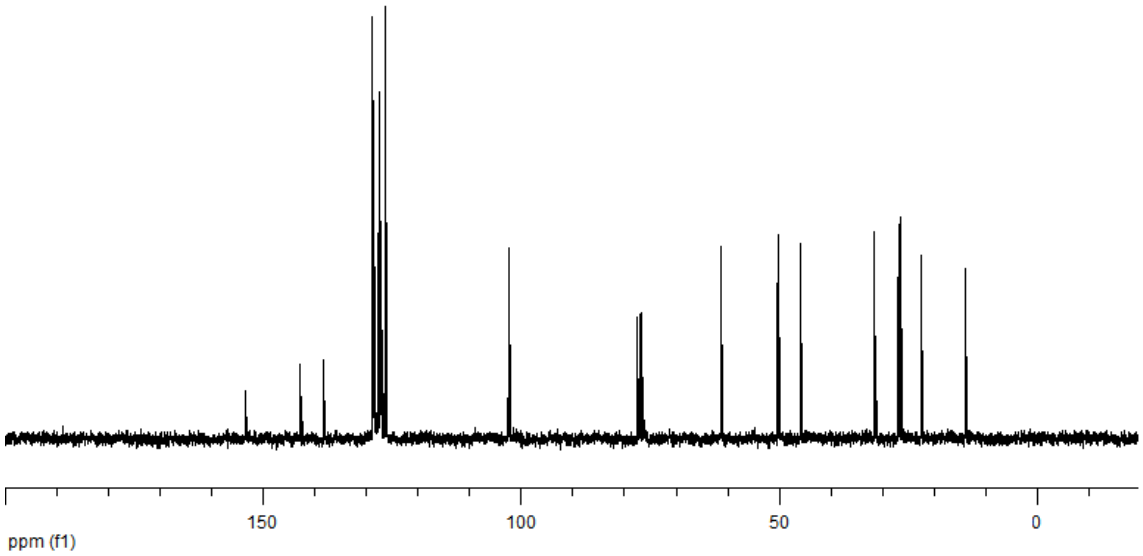

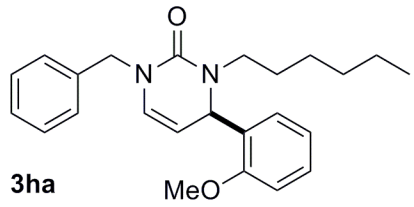

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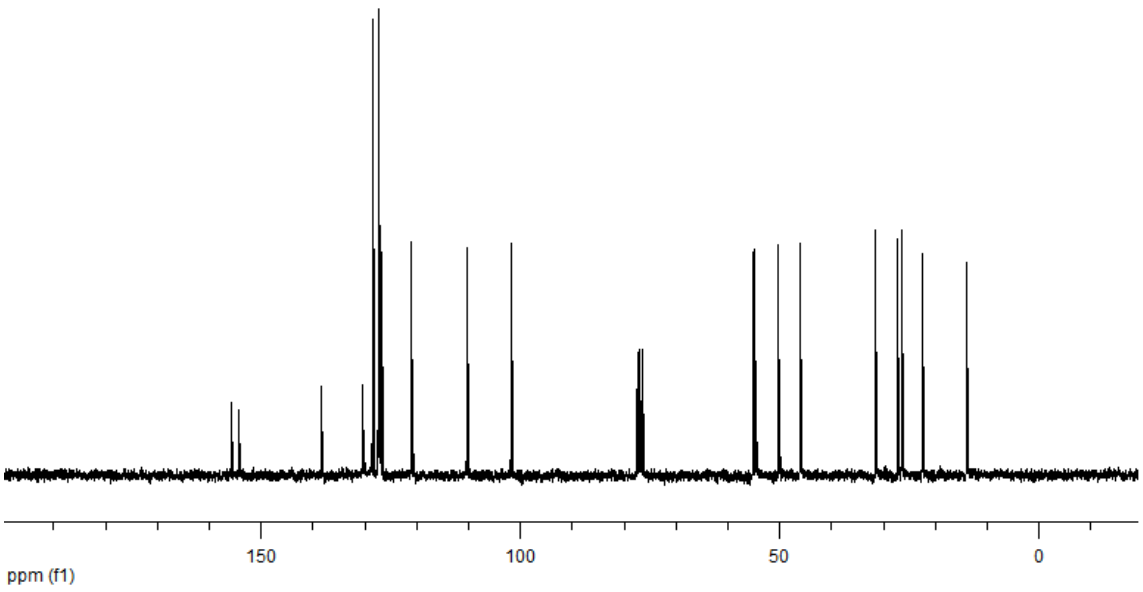

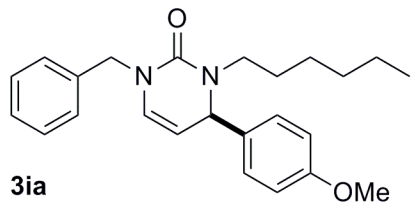

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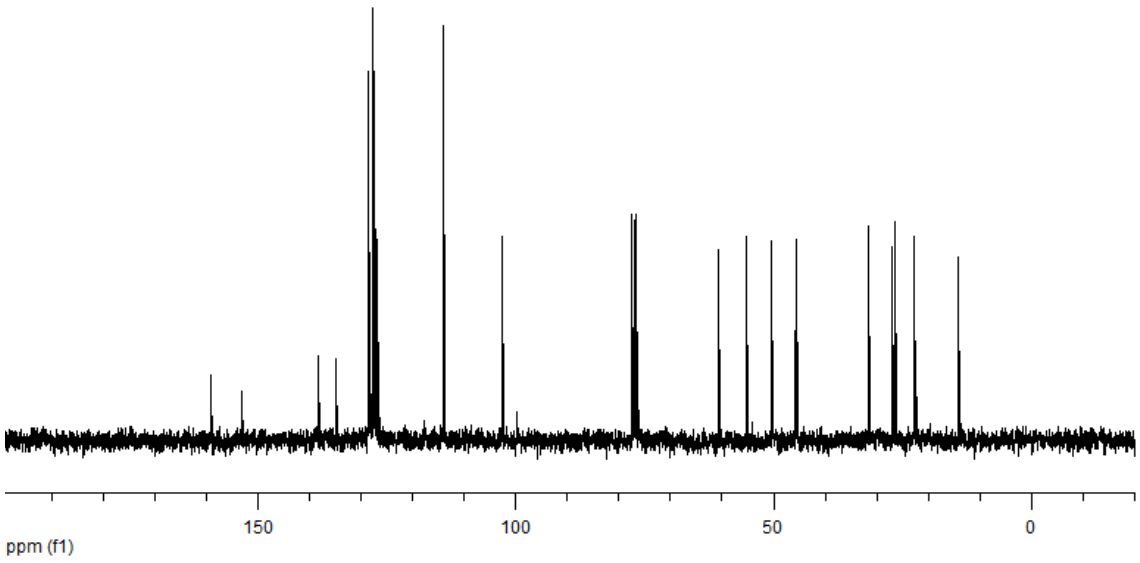

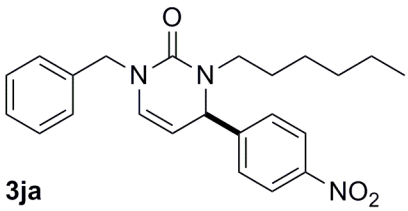

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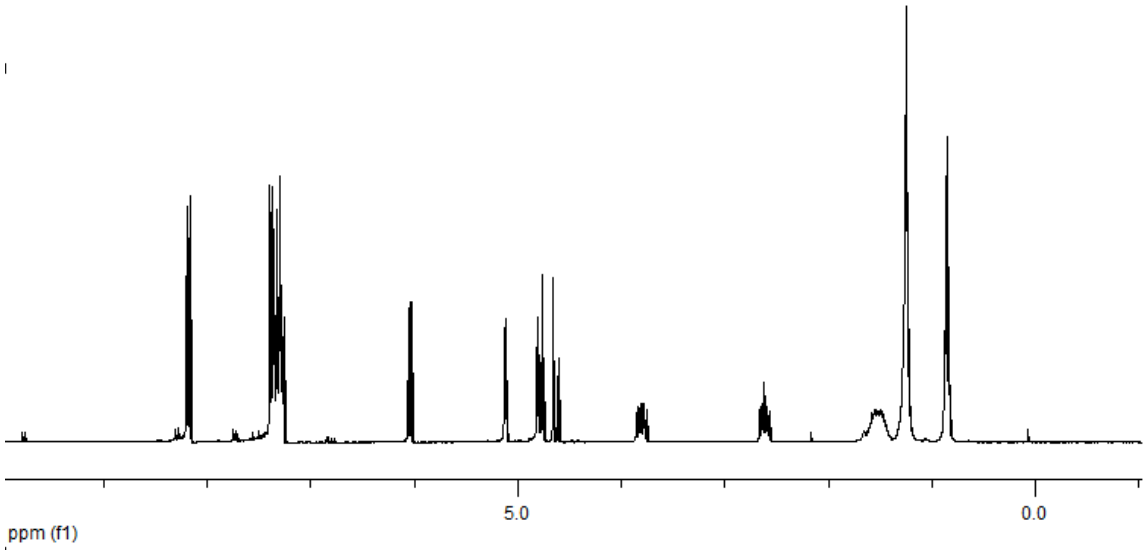

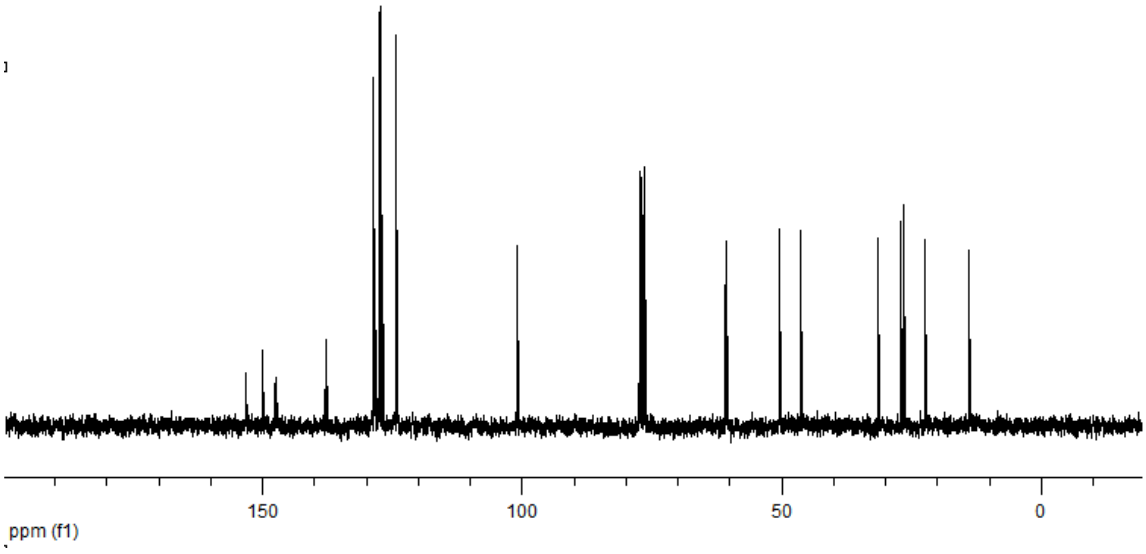

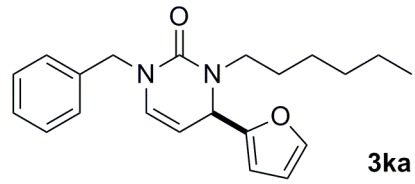

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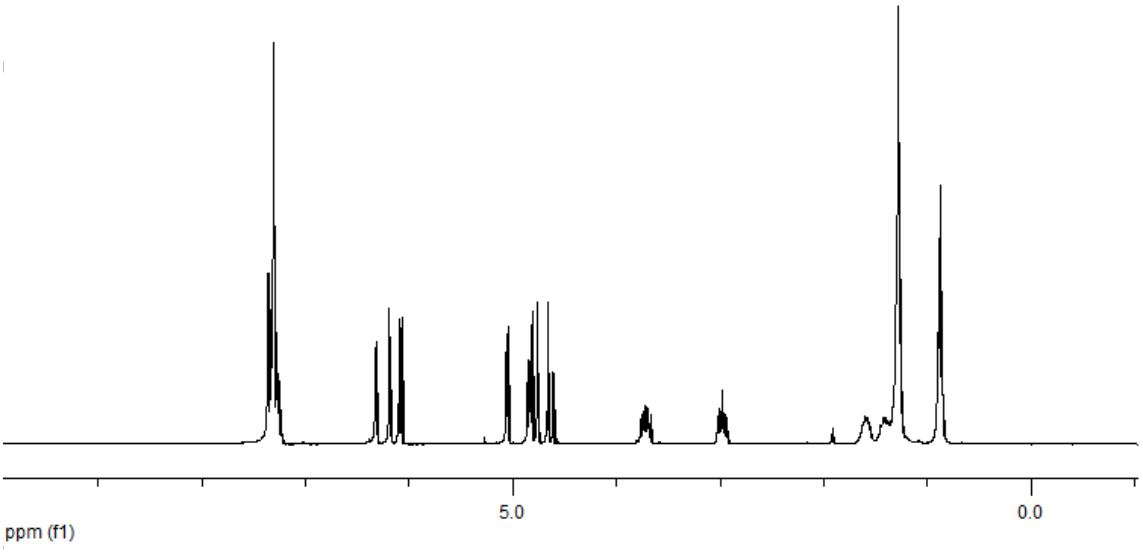

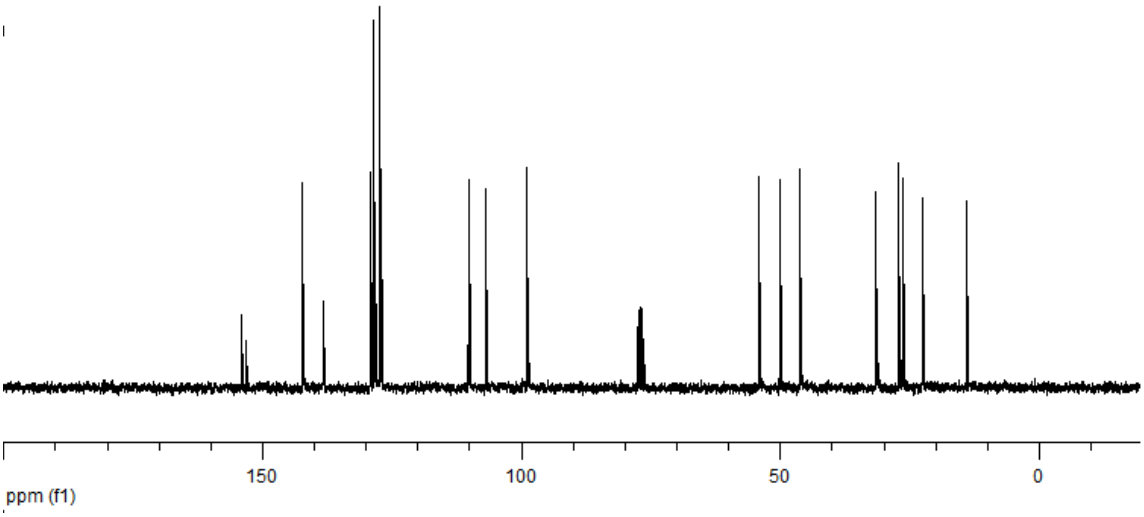

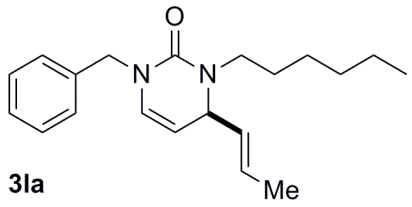

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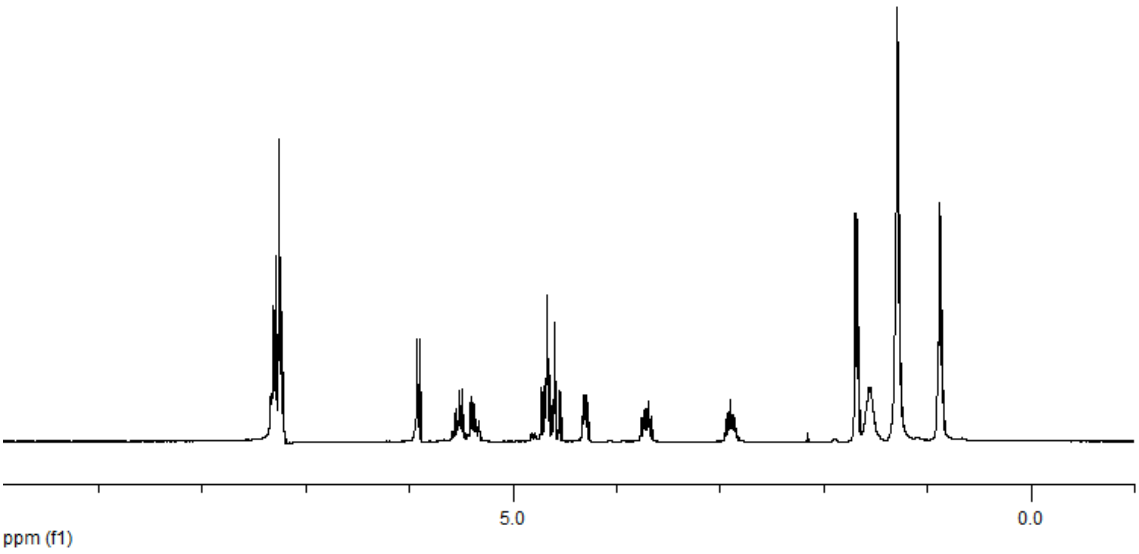

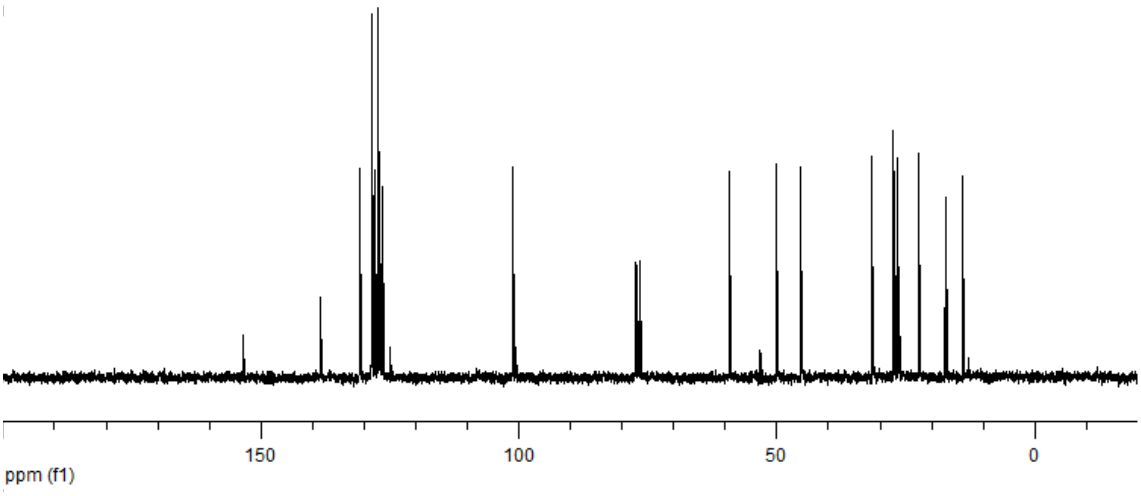

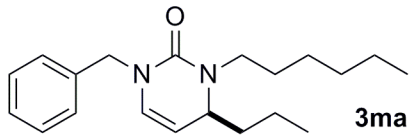

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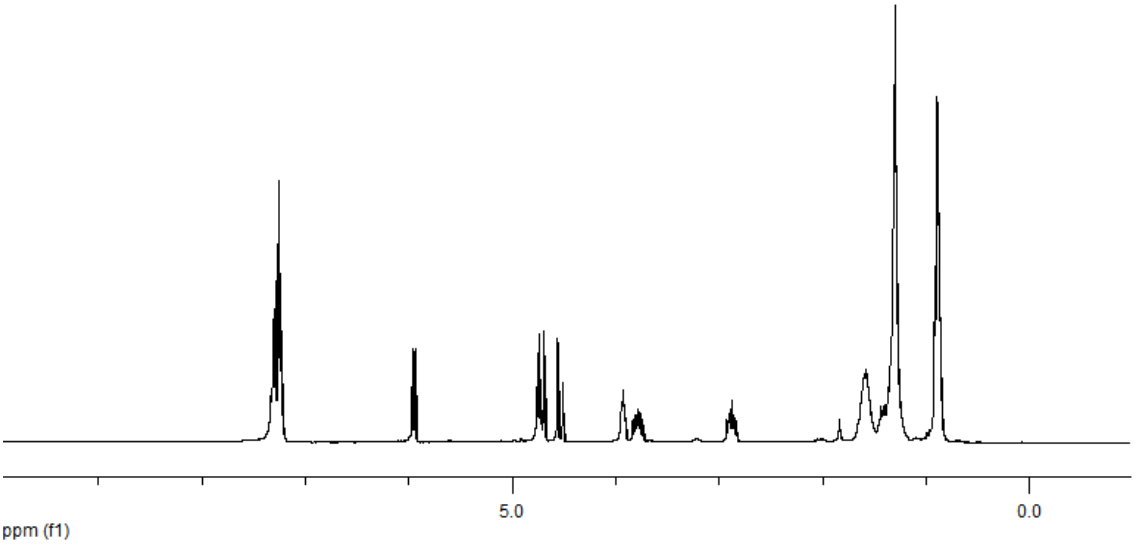

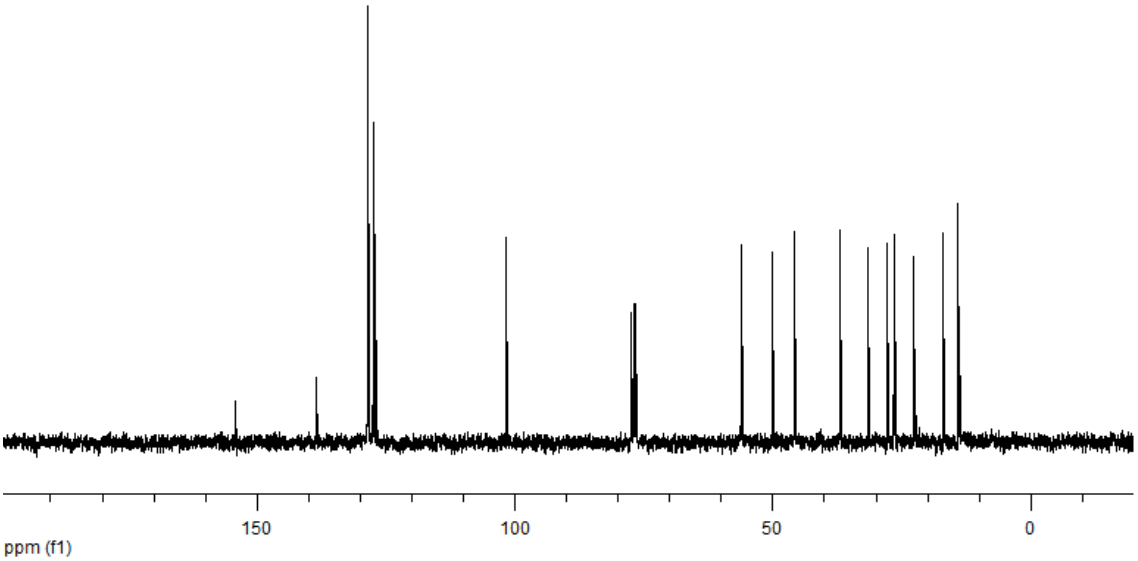

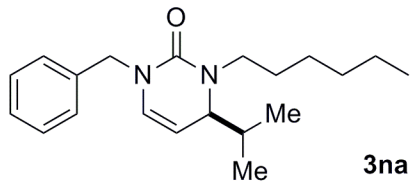

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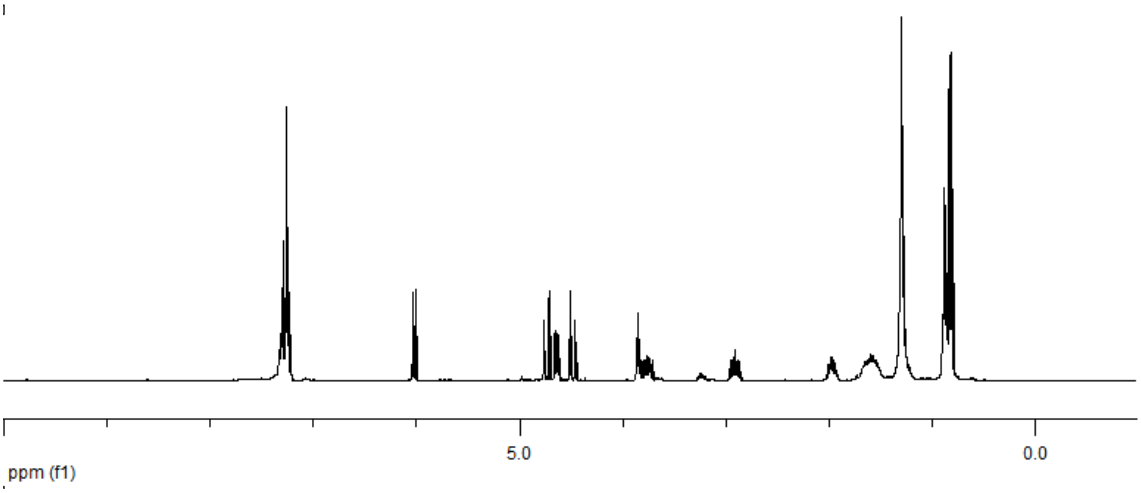

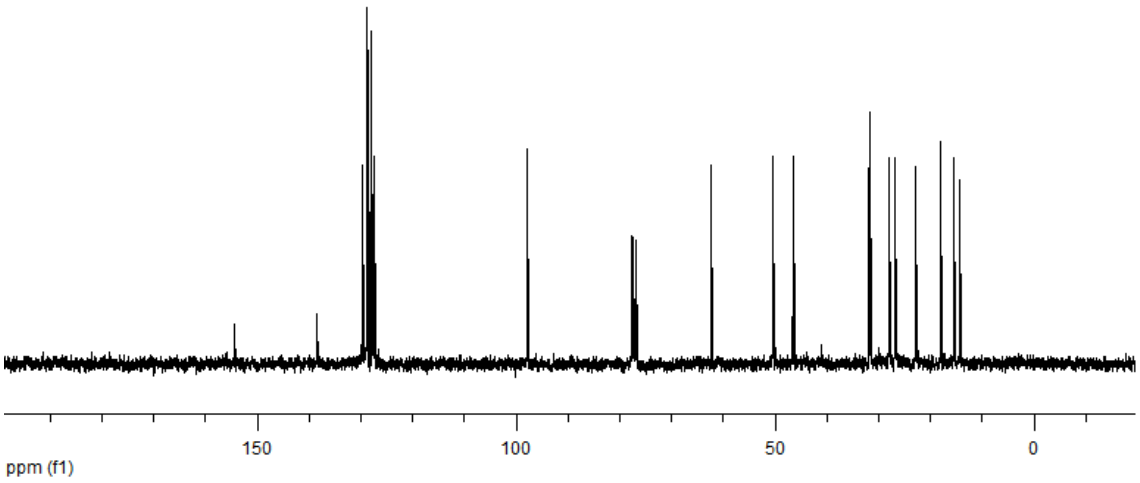

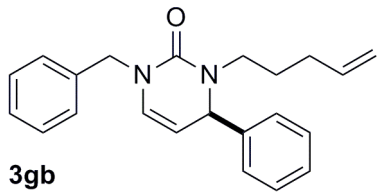

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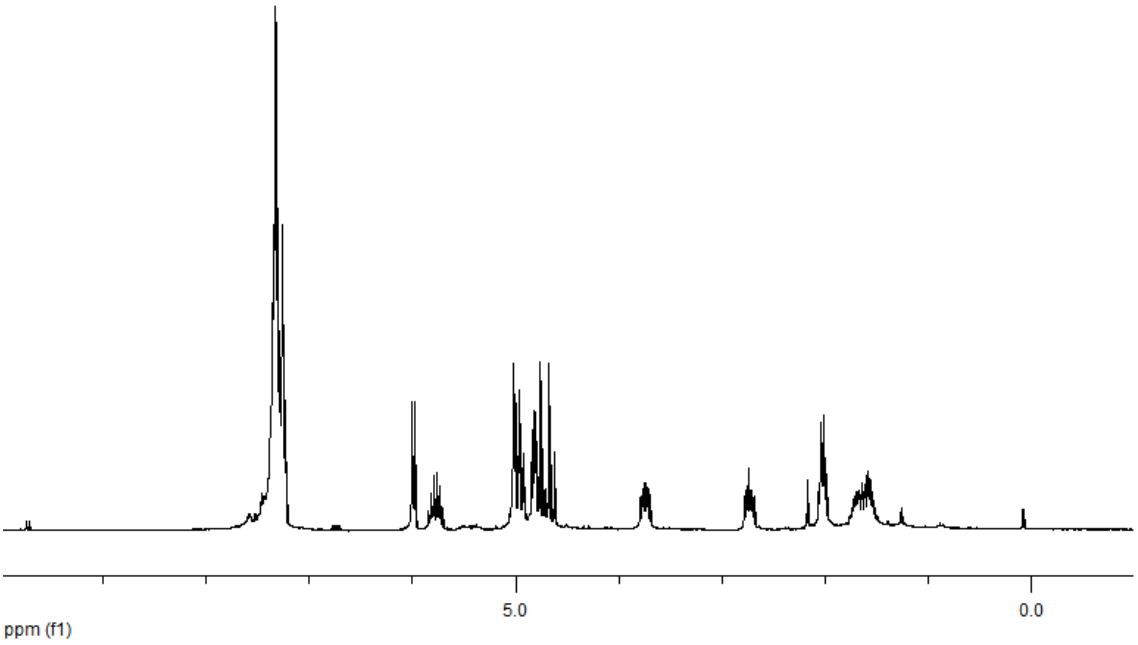

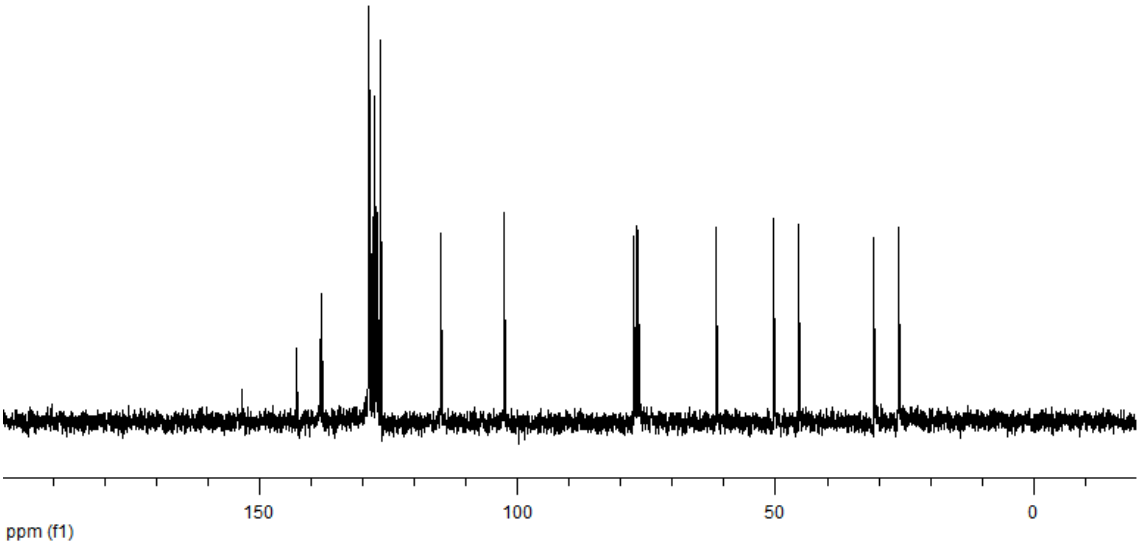

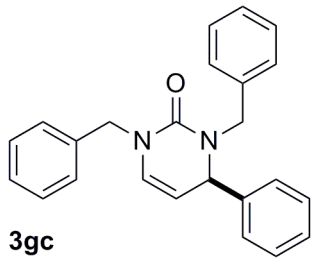

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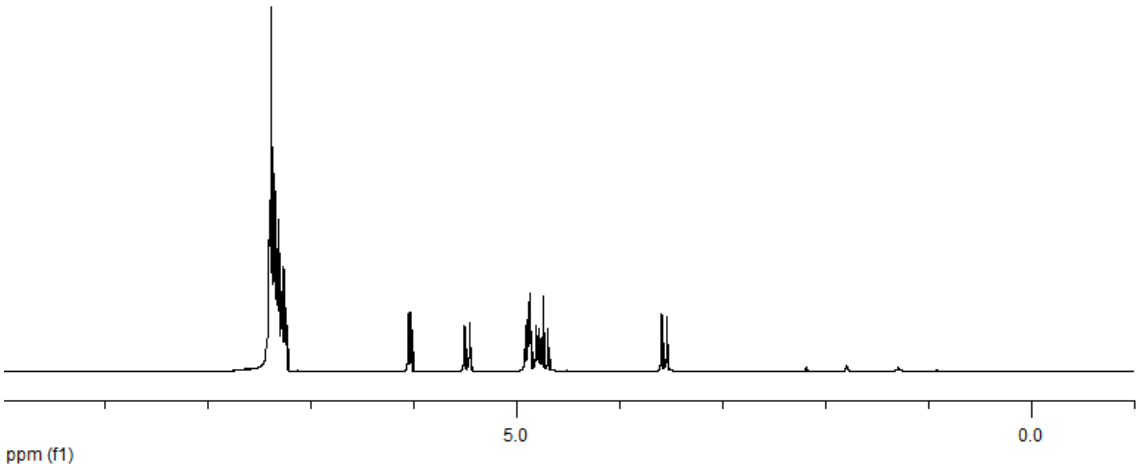

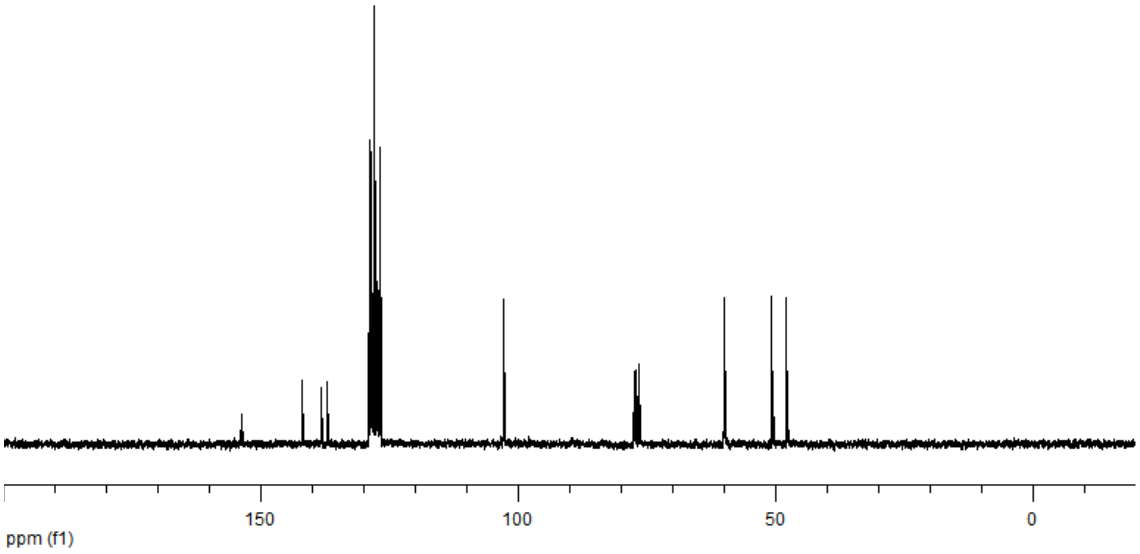

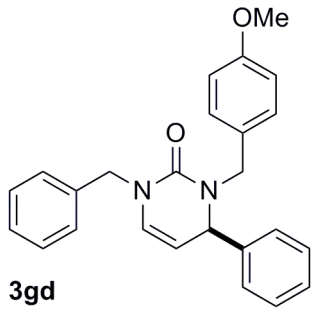

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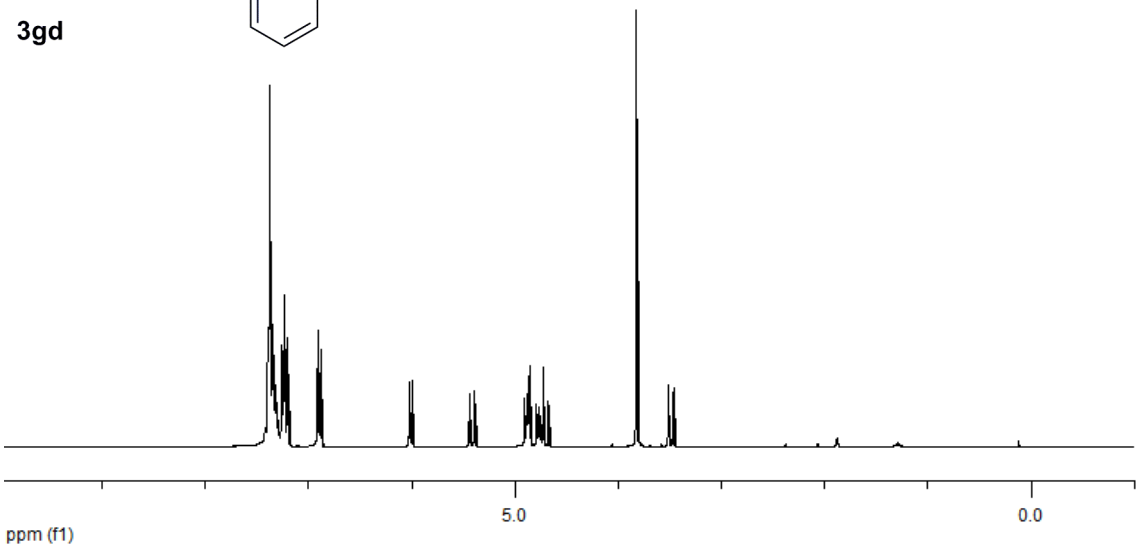

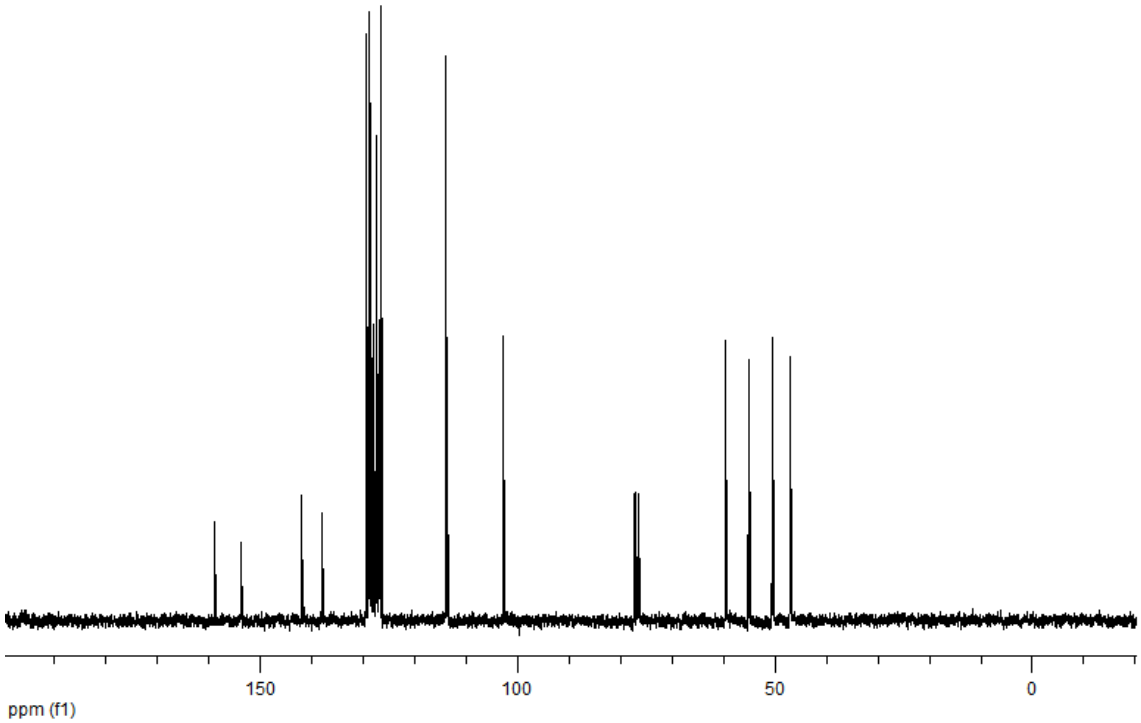

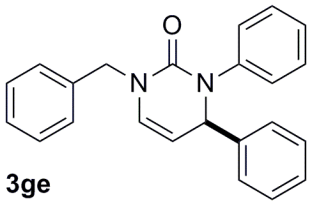

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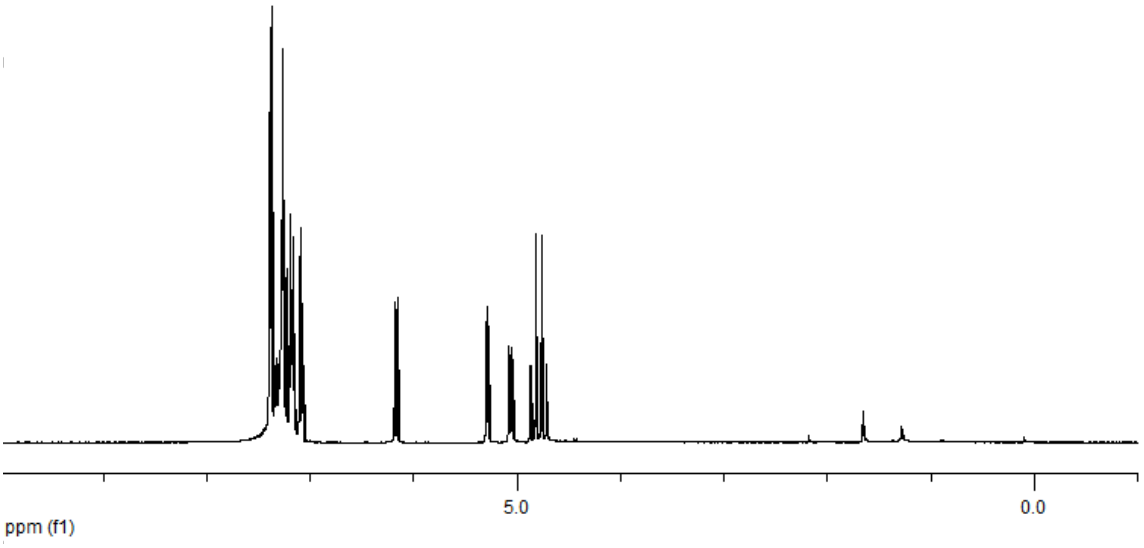

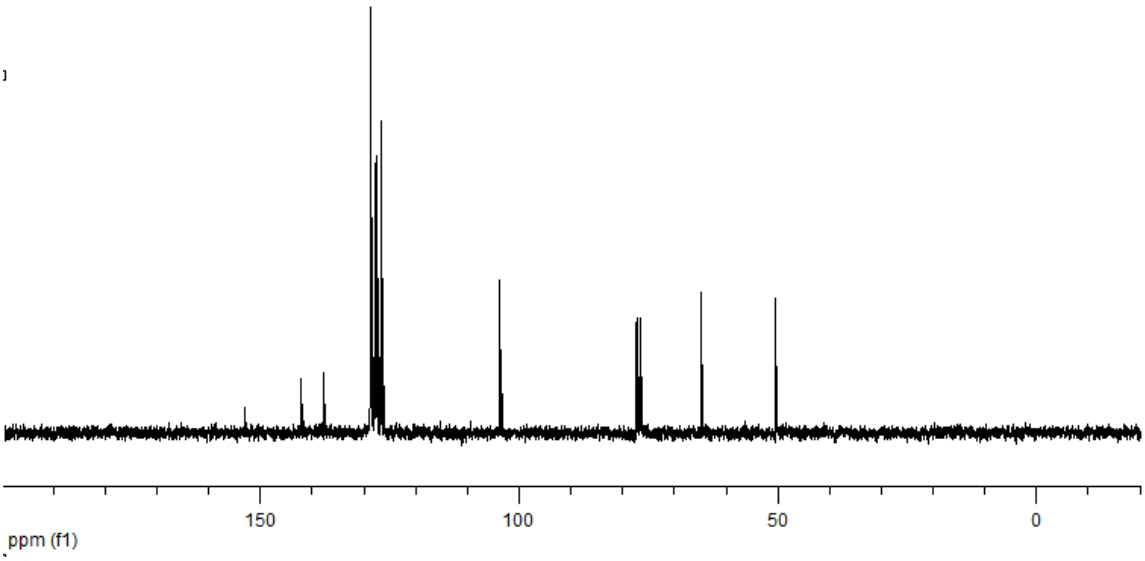

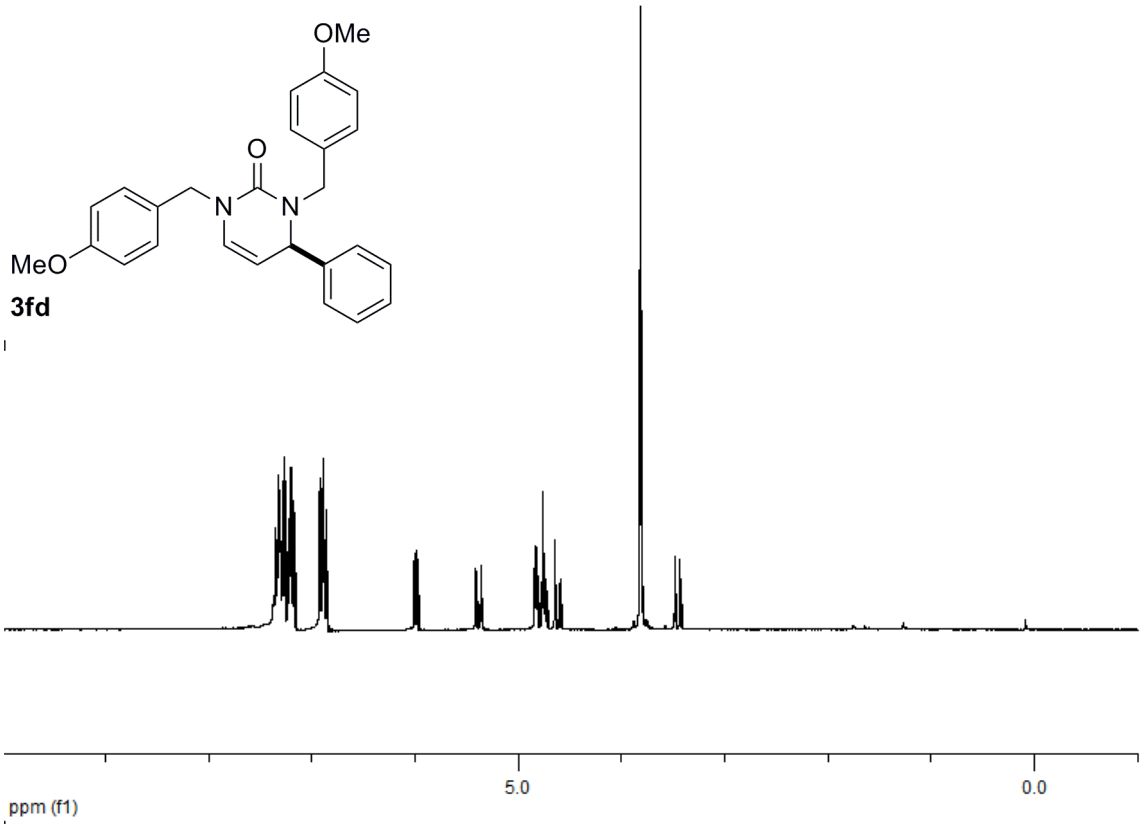
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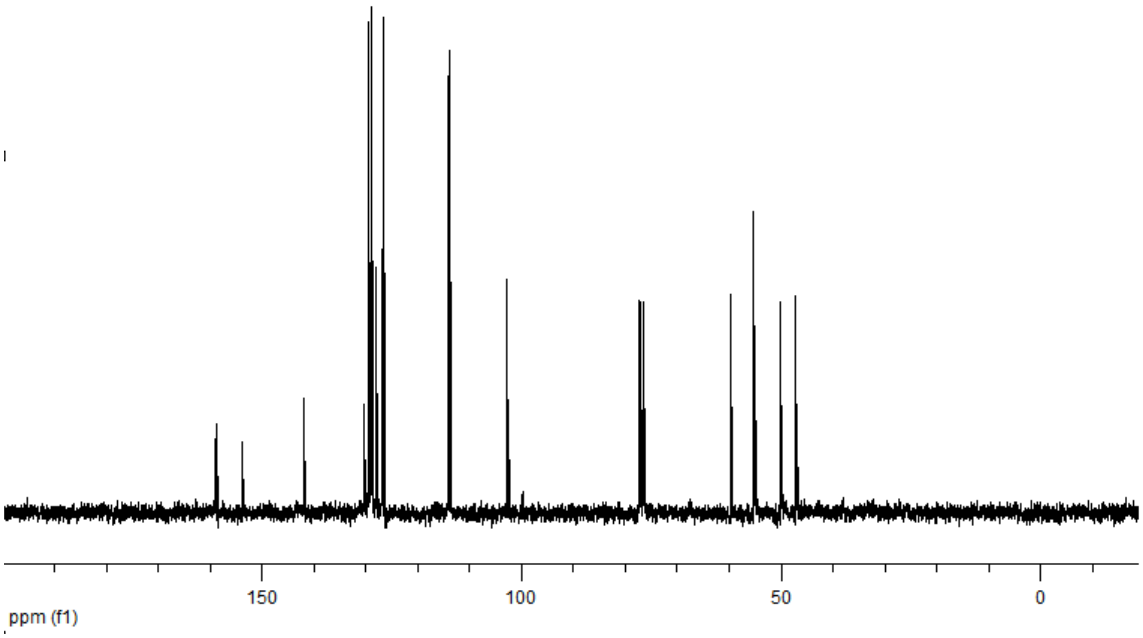
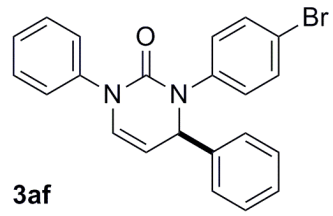
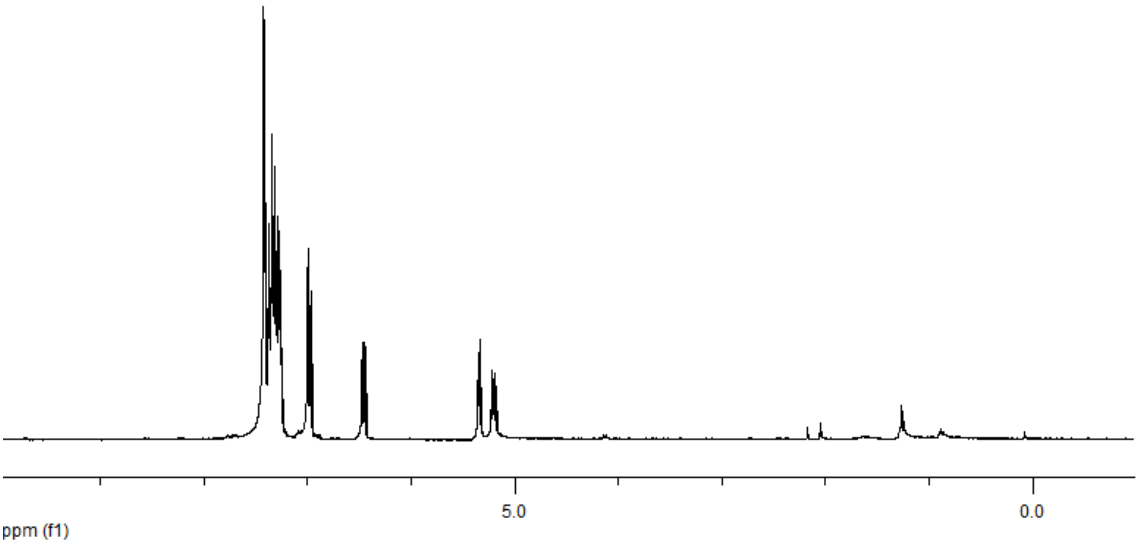
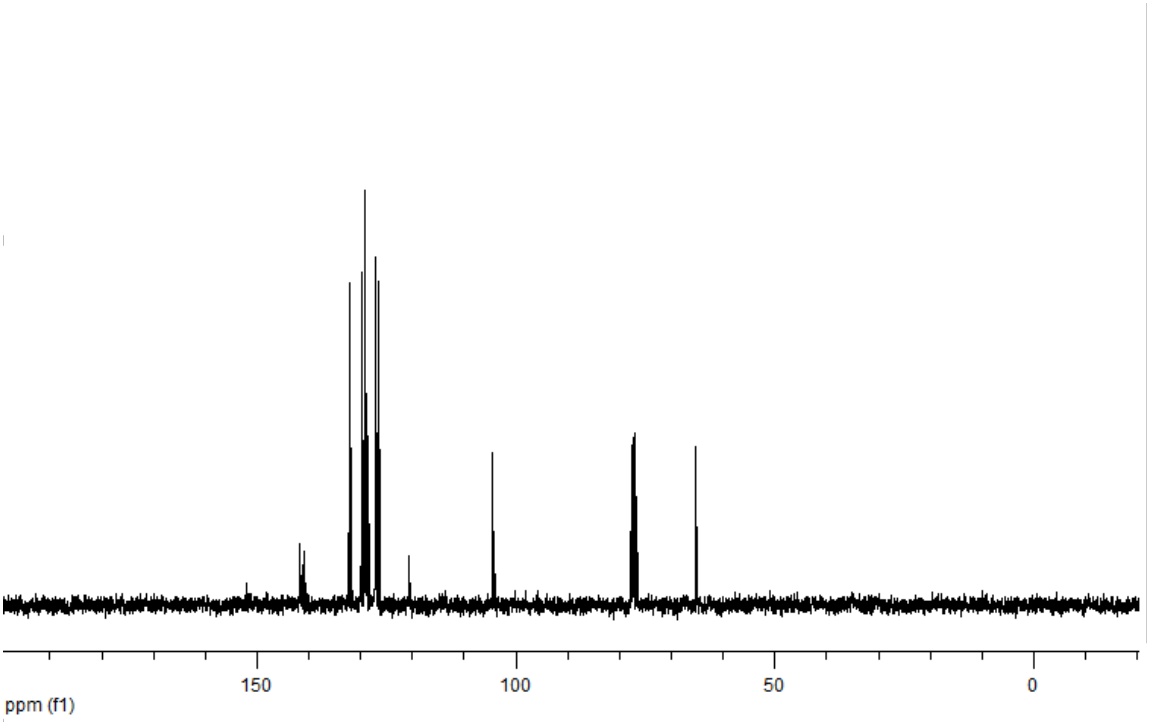
O
N
N
MeO
3fd
5.0
0.0
ppm (f1)

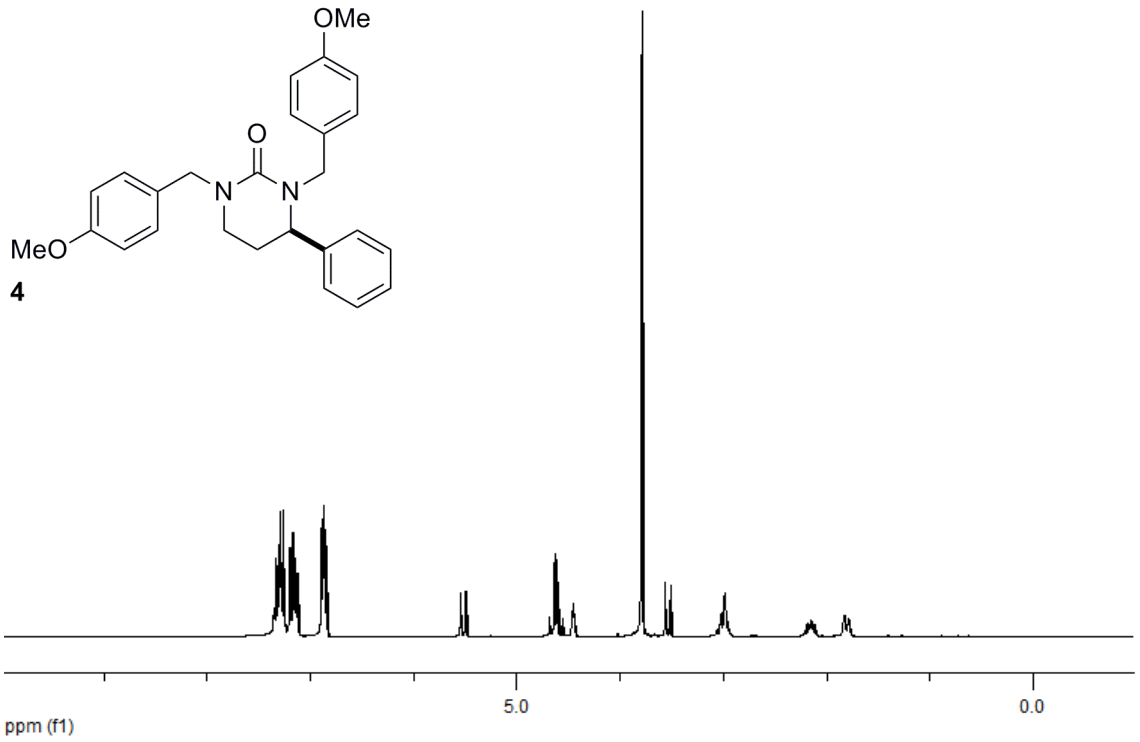

150
100
50
0
ppm (f1)



3af







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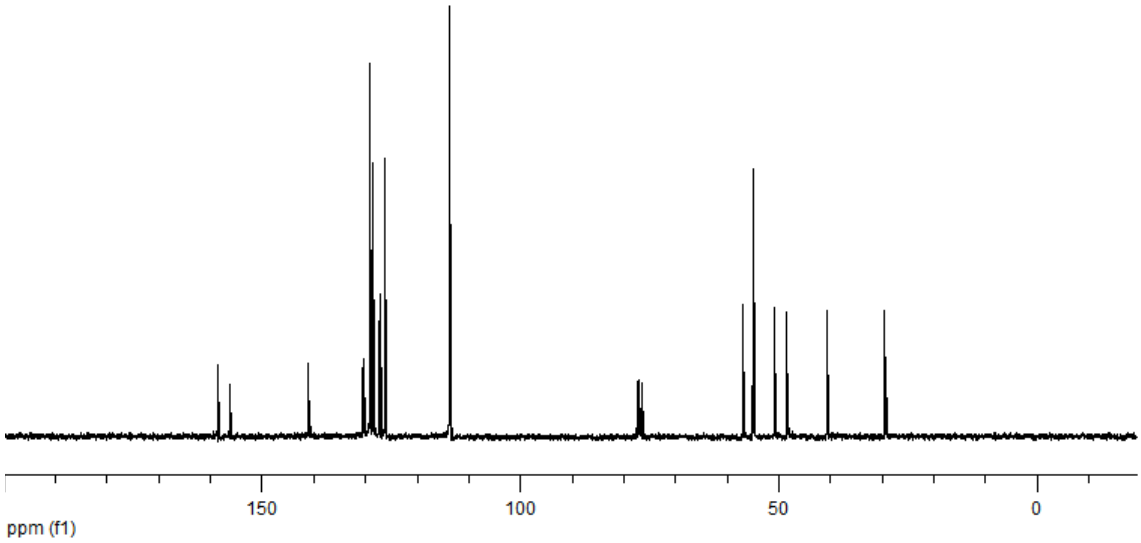

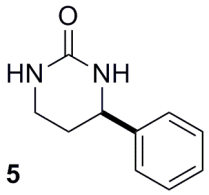

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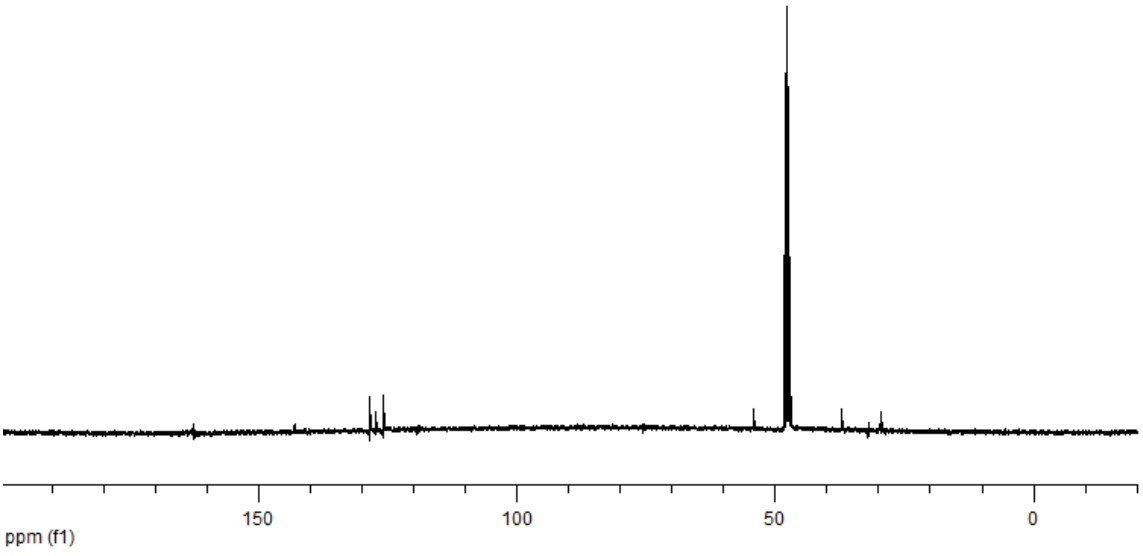

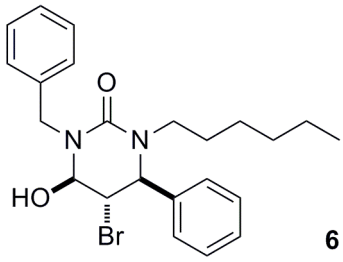

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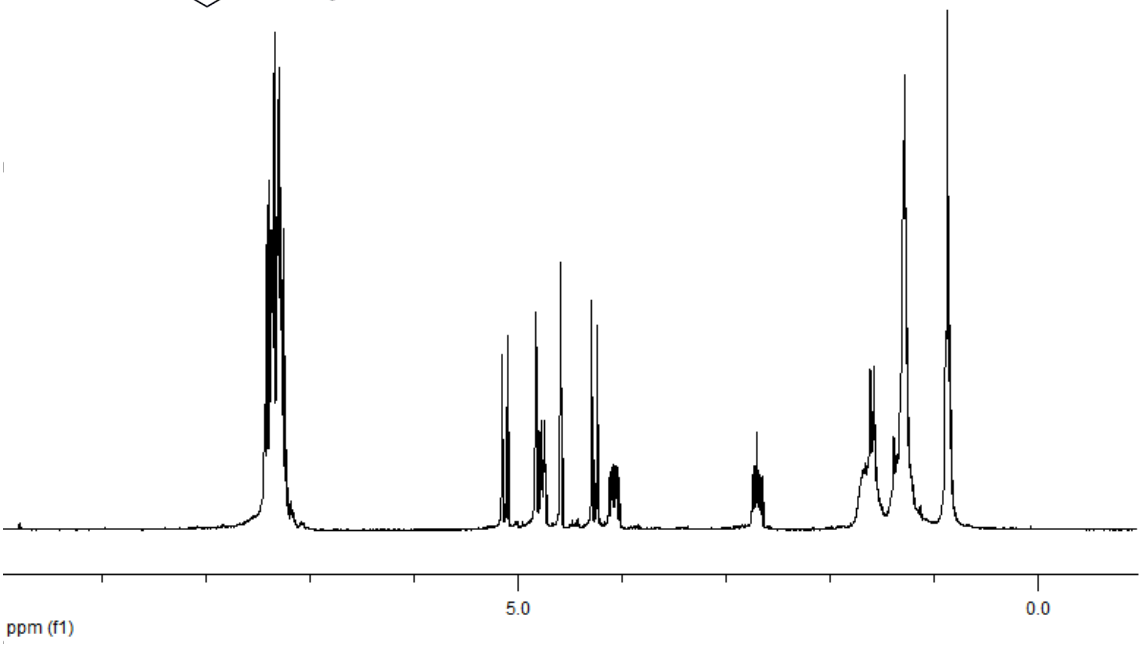

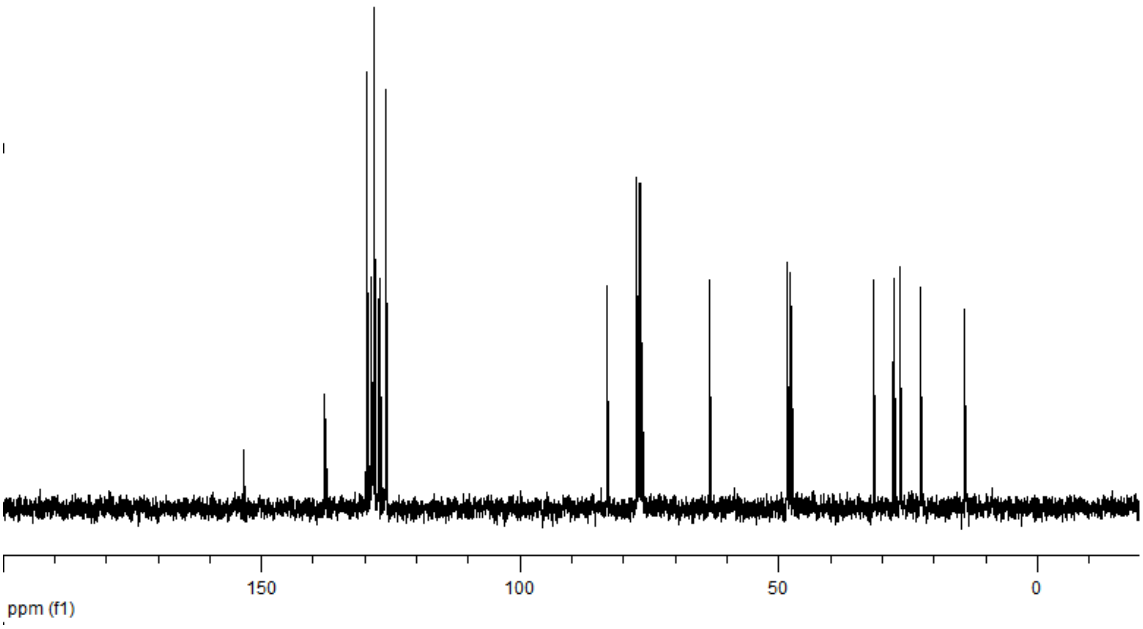

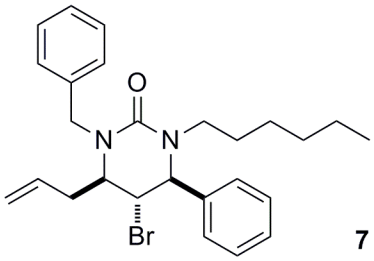

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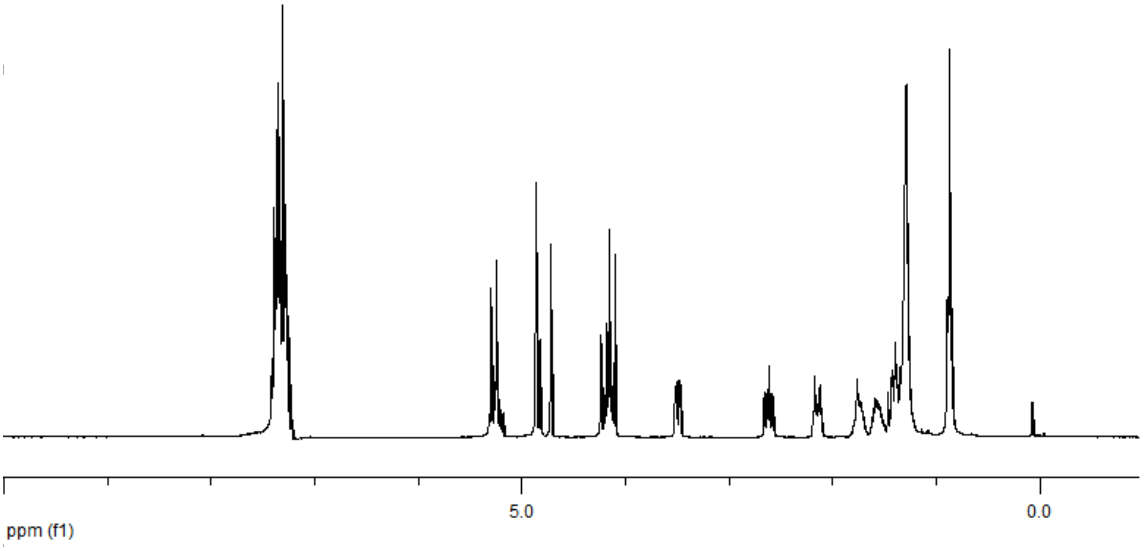
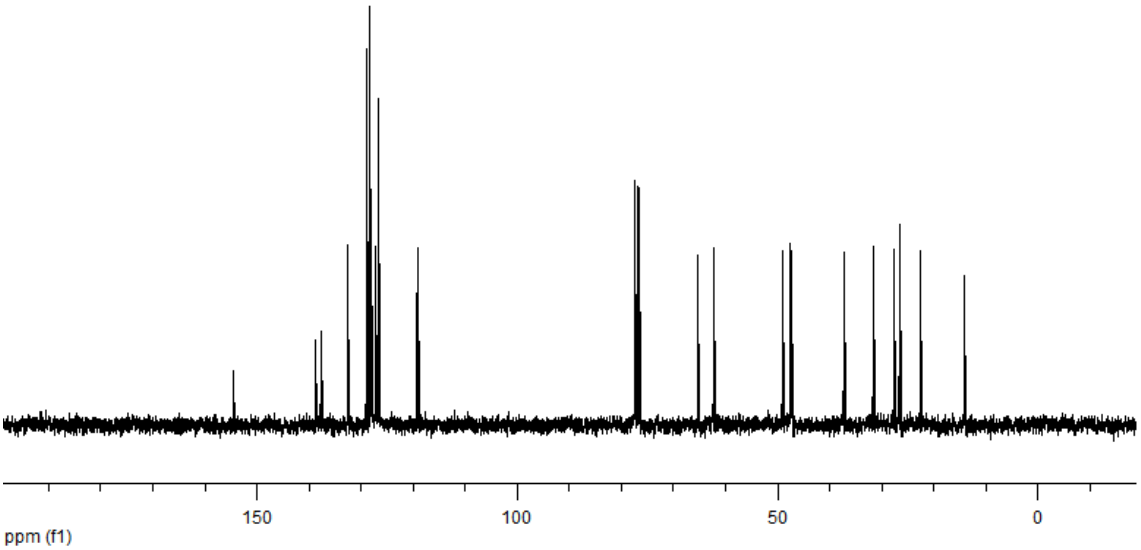




NOE of 7 in C_6D_6

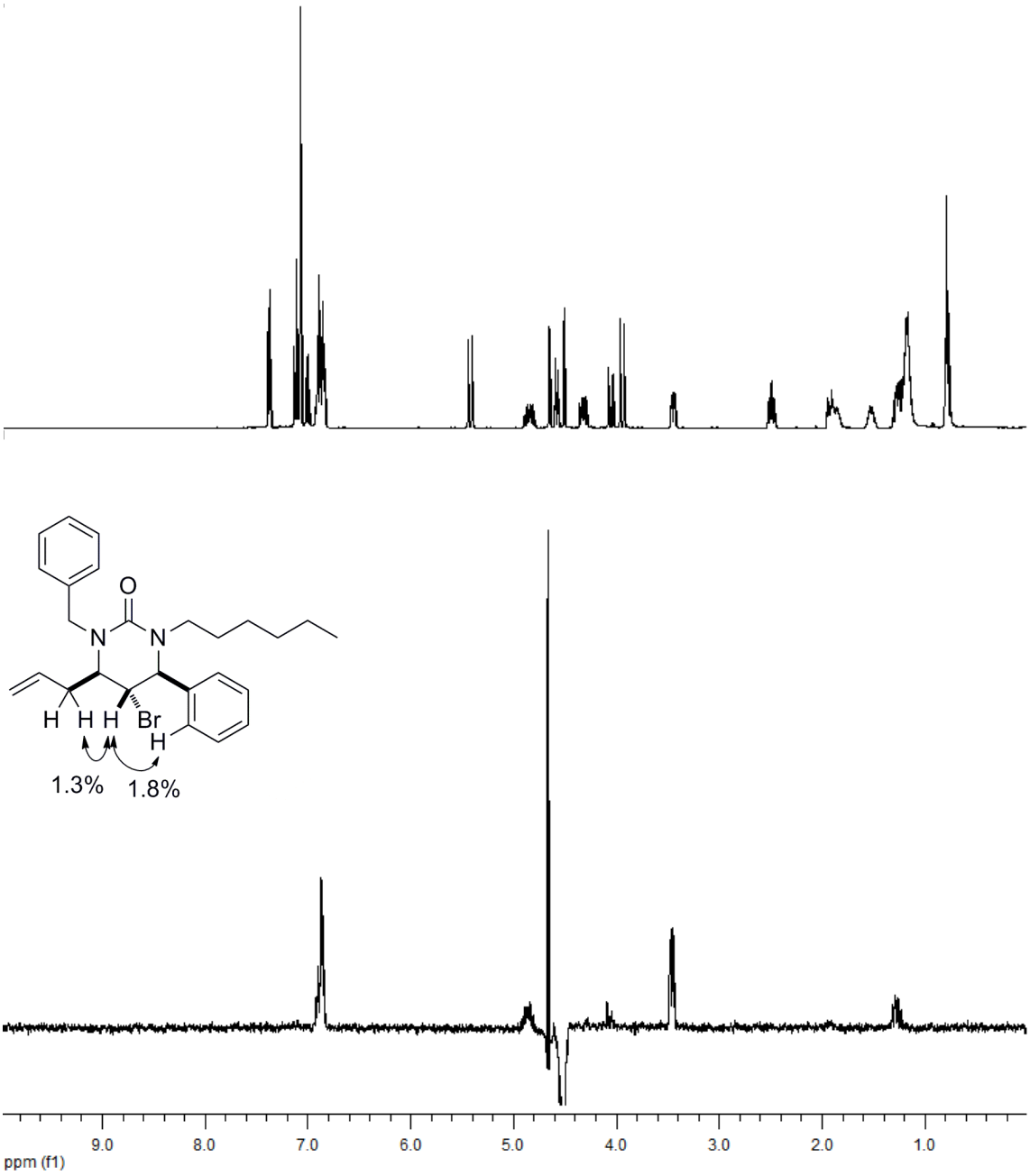


Table 1. Crystal data and structure refinement for **3af**.

Identification code	rovis102	
Empirical formula	$C_{22}H_{17}BrN_2O$	
Formula weight	405.29	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\,2_12_12_1$	
Unit cell dimensions	a = 5.8881(2) Å	α = 90°
	b = 12.0278(3) Å	β = 90°
	c = 24.8051(7) Å	γ = 90°
Volume	1756.72(9) Å^3	
Z	4	
Density (calculated)	1.532 Mg/m^3	
Absorption coefficient	2.353 mm^{-1}	
F(000)	824	
Crystal size	0.24 x 0.18 x 0.14 mm^3	
Theta range for data collection	1.64 to 30.52°.	
Index ranges	-8<=h<=8, -17<=k<=17, -35<=l<=35	
Reflections collected	42873	
Independent reflections	5374 [R(int) = 0.0753]	
Completeness to theta = 30.52°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7387 and 0.5997	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5374 / 0 / 236	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1249	
R indices (all data)	R1 = 0.0869, wR2 = 0.1933	
Absolute structure parameter	-0.013(15)	
Largest diff. peak and hole	0.932 and -1.240 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3af**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	13764(1)	-2018(1)	447(1)	29(1)
C(1)	7278(8)	1149(4)	2161(2)	17(1)
C(2)	6856(9)	3101(4)	2386(2)	23(1)
C(3)	8429(10)	3419(4)	2029(2)	27(1)
C(4)	9688(9)	2609(4)	1677(2)	20(1)
C(5)	4767(9)	1725(4)	2903(2)	19(1)
C(6)	2777(10)	2333(5)	2945(2)	27(1)
C(7)	1268(10)	2130(5)	3355(2)	32(1)
C(8)	1788(11)	1320(5)	3740(2)	36(2)
C(9)	3831(12)	722(4)	3715(2)	32(1)
C(10)	5316(10)	929(4)	3296(2)	24(1)
C(11)	9860(8)	616(4)	1460(2)	17(1)
C(12)	8836(10)	167(4)	1004(2)	20(1)
C(13)	9999(9)	-645(4)	708(2)	21(1)
C(14)	12136(9)	-972(4)	877(2)	20(1)
C(15)	13142(8)	-538(4)	1332(2)	20(1)
C(16)	12003(8)	258(4)	1619(2)	20(1)
C(17)	9548(8)	3018(4)	1101(2)	19(1)
C(18)	7535(9)	2892(4)	801(2)	23(1)
C(19)	7386(10)	3370(4)	293(2)	26(1)
C(20)	9191(10)	3991(4)	92(2)	30(1)
C(21)	11140(11)	4138(4)	392(2)	29(1)
C(22)	11365(10)	3638(4)	897(2)	23(1)
N(1)	6325(7)	1983(3)	2475(1)	19(1)
N(2)	8716(8)	1489(3)	1749(1)	19(1)
O(1)	6856(6)	158(3)	2231(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for **3af**.

Br(1)-C(14)	1.908(5)	C(3)-C(2)-N(1)	122.3(4)
C(1)-O(1)	1.231(6)	C(2)-C(3)-C(4)	122.7(4)
C(1)-N(2)	1.388(6)	N(2)-C(4)-C(3)	109.3(4)
C(1)-N(1)	1.388(6)	N(2)-C(4)-C(17)	112.9(4)
C(2)-C(3)	1.336(7)	C(3)-C(4)-C(17)	108.1(4)
C(2)-N(1)	1.398(6)	C(6)-C(5)-C(10)	120.2(5)
C(3)-C(4)	1.504(7)	C(6)-C(5)-N(1)	118.8(4)
C(4)-N(2)	1.475(6)	C(10)-C(5)-N(1)	120.8(4)
C(4)-C(17)	1.514(6)	C(7)-C(6)-C(5)	120.7(5)
C(5)-C(6)	1.385(8)	C(6)-C(7)-C(8)	119.2(5)
C(5)-C(10)	1.402(7)	C(7)-C(8)-C(9)	121.0(5)
C(5)-N(1)	1.438(6)	C(10)-C(9)-C(8)	118.9(5)
C(6)-C(7)	1.371(8)	C(9)-C(10)-C(5)	120.0(5)
C(7)-C(8)	1.399(9)	C(12)-C(11)-C(16)	120.3(4)
C(8)-C(9)	1.403(9)	C(12)-C(11)-N(2)	119.1(4)
C(9)-C(10)	1.381(7)	C(16)-C(11)-N(2)	120.6(4)
C(11)-C(12)	1.390(6)	C(11)-C(12)-C(13)	119.0(5)
C(11)-C(16)	1.390(7)	C(14)-C(13)-C(12)	119.0(4)
C(11)-N(2)	1.439(6)	C(15)-C(14)-C(13)	122.1(4)
C(12)-C(13)	1.400(7)	C(15)-C(14)-Br(1)	119.5(4)
C(13)-C(14)	1.383(7)	C(13)-C(14)-Br(1)	118.4(4)
C(14)-C(15)	1.378(7)	C(16)-C(15)-C(14)	118.7(5)
C(15)-C(16)	1.369(7)	C(15)-C(16)-C(11)	121.0(4)
C(17)-C(22)	1.398(7)	C(22)-C(17)-C(18)	120.7(4)
C(17)-C(18)	1.408(7)	C(22)-C(17)-C(4)	118.2(4)
C(18)-C(19)	1.386(7)	C(18)-C(17)-C(4)	120.7(4)
C(19)-C(20)	1.392(8)	C(19)-C(18)-C(17)	119.3(5)
C(20)-C(21)	1.379(9)	C(18)-C(19)-C(20)	120.0(5)
C(21)-C(22)	1.396(6)	C(21)-C(20)-C(19)	120.6(5)
		C(20)-C(21)-C(22)	120.6(5)
O(1)-C(1)-N(2)	120.8(4)	C(21)-C(22)-C(17)	118.8(5)
O(1)-C(1)-N(1)	122.6(4)	C(1)-N(1)-C(2)	121.0(4)
N(2)-C(1)-N(1)	116.6(4)	C(1)-N(1)-C(5)	121.1(4)

C(2)-N(1)-C(5)	117.8(4)
C(1)-N(2)-C(11)	116.0(4)
C(1)-N(2)-C(4)	126.4(3)
C(11)-N(2)-C(4)	115.1(4)

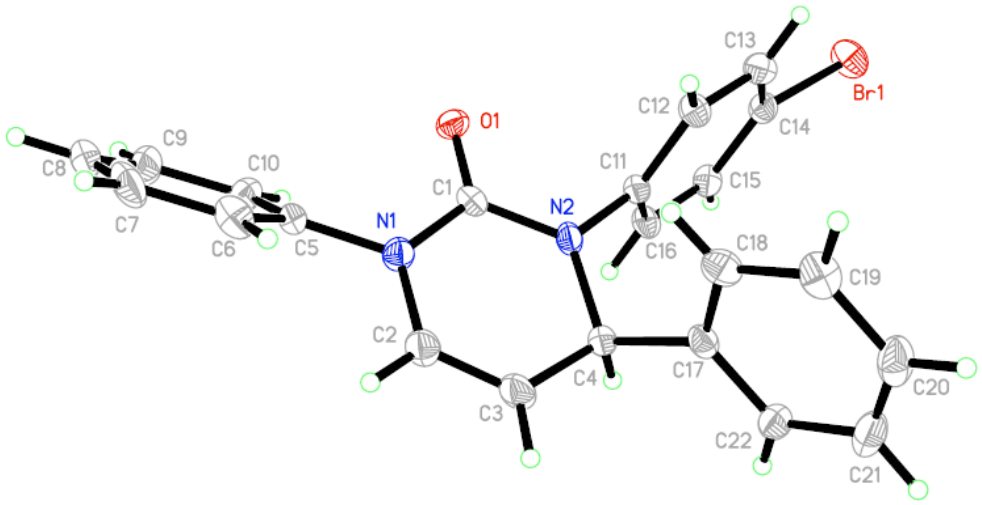
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **3af**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	30(1)	26(1)	30(1)	-7(1)	2(1)	9(1)
C(1)	18(2)	17(2)	15(2)	-3(2)	-2(2)	2(2)
C(2)	31(3)	16(2)	22(2)	1(2)	3(2)	3(2)
C(3)	44(3)	14(2)	23(2)	-3(2)	5(2)	0(2)
C(4)	27(2)	18(2)	15(2)	-1(2)	3(2)	-4(2)
C(5)	21(2)	21(2)	15(2)	-4(2)	3(2)	-4(2)
C(6)	28(3)	29(3)	23(2)	-5(2)	-3(2)	6(2)
C(7)	24(2)	42(3)	28(2)	-18(2)	2(2)	6(3)
C(8)	48(4)	34(3)	27(3)	-13(2)	17(3)	-15(3)
C(9)	43(3)	25(2)	27(2)	0(2)	14(3)	-6(3)
C(10)	27(3)	20(2)	26(2)	1(2)	7(2)	-3(2)
C(11)	22(2)	17(2)	13(2)	0(2)	1(2)	-2(2)
C(12)	21(2)	21(2)	18(2)	-1(2)	-1(2)	2(2)
C(13)	22(3)	20(2)	21(2)	-1(2)	-1(2)	0(2)
C(14)	22(2)	17(2)	22(2)	-2(2)	6(2)	1(2)
C(15)	17(2)	25(2)	18(2)	2(2)	0(2)	1(2)
C(16)	22(2)	24(2)	13(2)	1(2)	-3(2)	1(2)
C(17)	26(2)	15(2)	15(2)	-2(2)	1(2)	3(2)
C(18)	25(3)	20(2)	25(2)	-3(2)	-2(2)	3(2)
C(19)	28(3)	26(2)	24(2)	2(2)	-3(2)	9(2)
C(20)	45(4)	23(2)	23(2)	7(2)	7(2)	8(2)
C(21)	34(3)	29(2)	26(2)	7(2)	9(3)	0(2)
C(22)	28(3)	20(2)	22(2)	1(2)	4(2)	-2(2)
N(1)	22(2)	17(2)	19(2)	1(1)	3(2)	1(2)
N(2)	26(2)	16(2)	14(2)	-1(1)	5(2)	1(2)
O(1)	20(2)	16(1)	24(2)	-1(1)	3(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3af**.

	x	y	z	U(eq)
H(2)	6087	3643	2582	28
H(3)	8758	4173	1998	32
H(4)	11286	2595	1788	24
H(6)	2463	2885	2694	32
H(7)	-85	2527	3376	38
H(8)	765	1175	4017	44
H(9)	4179	194	3976	38
H(10)	6680	542	3273	29
H(12)	7400	402	898	24
H(13)	9345	-959	403	25
H(15)	14567	-782	1443	24
H(16)	12672	565	1924	24
H(18)	6320	2492	941	28
H(19)	6080	3276	88	31
H(20)	9082	4310	-249	36
H(21)	12314	4574	257	35
H(22)	12699	3715	1094	28



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