SUPPORTING INFORMATION

Palladium-Catalyzed Three-Component Transformation of Homoallenols: A Regio- and Stereoselective Route to 1,5-Amino Alcohols

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1. General

^{1}H NMR (400 and 500 MHz) and ^{13}C (100 and 125 MHz) spectra were recorded with 400 or 500 MHz spectrometers using tetramethylsilane as an internal standard. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. High-resolution mass spectra (HRMS) were reported as m/z. Infrared spectra were recorded on Fourier transform instrument. Optical rotation values were measured at room temperature with a polarimeter. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60 F_{254} or on plastic sheets precoated with aluminium oxide 60 F_{254}, neutral. Column chromatography separations were performed using silica gel (0.040-0.060 mm). The enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) with chiral column. HPLC grade heptane and ethanol were used as the eluting solvents. All reactions were carried out under a nitrogen atmosphere in flame-dried Schlenk tubes. Solvents were dried immediately before use by distillation from standard drying agents. Et_3N was distilled over powder KOH and stored under nitrogen. All amines were distilled over powder KOH prior to use. Chiral β-allenols were prepared according to the procedure described in literature.[1] Racemic β-allenols were also prepared according to known literature procedures.[2,3]

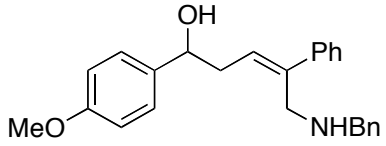
2. Experimental section for the palladium-catalyzed three-component reaction

2.1 General procedure

A flame-dried Schlenk tube flushed with nitrogen was charged with homoallenol **1** (0.52 mmol), the corresponding electrophile (0.65 mmol) and amine (0.78 mmol). To this mixture was added Et_3N (1.04 mmol), anhydrous CH_2Cl_2 (2.5 mL) and $Pd(PPh_3)_4$ (13 μmol). The tube was allowed to reflux under nitrogen for the appropriate length of time. The solvent was removed *in vacuo*. The conversion and regioselectivity of the reaction was determined at this stage from the ^1H NMR spectrum of the crude product. The crude mixture was then purified by flash column chromatography on silica gel using pentane:EtOAc as the eluent to give the corresponding 1,5-amino alcohol **2**.

2.2 Characterization data of Amino Alcohols 2a-l and 3a

(*Z*)-5-(Benzylamino)-1-(4-methoxyphenyl)-4-phenylpent-3-en-1-ol (2a)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane:EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.58 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = +34.0 (c =0.2 in $CHCl_3$) for 96% *ee* (*R*).

^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.35-7.27 (m, 12H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.93 (t, *J* = 8.5 Hz, 1H), 4.80 (app. dd, *J* = 7.5, 3.8 Hz, 1H), 3.81 (s, 2H), 3.79 (s, 3H), 3.64 (d, *J* = 12.0 Hz, 1H), 3.56 (d, *J* = 12.0 Hz, 1H), 2.70 - 2.56 (m, 2H).

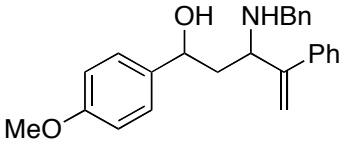
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.6, 141.8, 140.0, 138.9, 137.5, 129.0, 128.5, 128.4 (2C), 127.2, 127.1, 126.7 (2C), 126.0 (2C), 113.6 (2C), 71.9, 55.2, 53.8, 47.1, 39.6.

IR (neat): ν = 3414, 2092, 1644, 1512, 1443 cm^{-1}.

HRMS (ESI) Calcd. for $C_{25}H_{28}NO_2$ [M+H]: 374.2120, found: 374.2120.

Enantiomeric excess has been determined by HPLC analysis using an IA column (heptane/ethanol, 90/10, 1.0 mL/min), t_r = 23.7 min for (*S*) and t_r = 25.4 min for (*R*).

3-(Benzylamino)-1-(4-methoxyphenyl)-4-phenylpent-4-en-1-ol (3a)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.15 (EtOAc: pentane / 3:2).

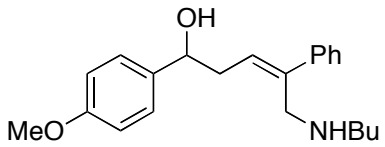
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.38 – 7.21 (m, 12H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.35 (s, 1H), 5.18 (s, 1H), 4.87 (dd, *J* = 10.4, 2.2 Hz, 1H), 3.94 (m, 2H), 3.77 (s, 3H), 3.76 (app d, *J* = 12.4 Hz, 1H), 3.48 (q, *J* = 7.0 Hz, 1H), 2.04 (s, 1H), 1.86 (dt, *J* = 14.5, 2.2 Hz, 1H), 1.68 (app dt, *J* = 14.5, 10.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.0, 150.4, 140.8, 139.3, 137.5, 128.9 (2C), 128.8 (2C), 128.8 (2C), 128.1, 127.7, 127.3 (2C), 127.1 (2C), 113.9 (2C) , 113.6, 75.4, 63.2, 55.6, 51.1, 44.8.

IR (neat): ν = 3485, 3393, 1644, 1513, 1377 cm^{-1}.

HRMS (ESI) Calcd. for $C_{25}H_{28}NO_2$ [M+H]: 374.2120, found: 374.2118.

(*Z*)-5-(Butylamino)-1-(4-methoxyphenyl)-4-phenylpent-3-en-1-ol (2b)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.30 (EtOAc: pentane / 3:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.33-7.29 (m, 7H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.96 (q, *J* = 8.0 Hz, 1H), 4.85 – 4.77 (m, 1H), 3.81 (s, 3H), 3.68 (d, *J* = 12.0 Hz, 1H),

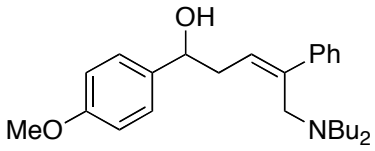
3.62 (d, *J* = 12.0 Hz, 1H), 2.68 (m, 4H), 1.54 (quintet, *J* = 7.0 Hz, 2H), 1.34 (sextet, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 157.9, 141.4 (2C), 137.0, 131.5, 131.4, 131.3, 127.8, 127.7, 126.5, 126.1 (2C), 125.4, 112.9, 70.9, 54.6, 52.7, 39.1, 30.9, 28.9, 19.7, 13.2.

IR (neat): ν = 3392, 2957, 2928, 2856, 1650, 1611, 1512, 1463, 1175 cm^{-1}.

HRMS (ESI) Calcd. for $C_{22}H_{30}NO_2$ [M+H]: 340.2277, found: 340.2291.

(*Z*)-5-(Dibutylamino)-1-(4-methoxyphenyl)-4-phenylpent-3-en-1-ol (2c)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 4:1).

TLC: R_f = 0.20 (EtOAc: pentane / 3:2).

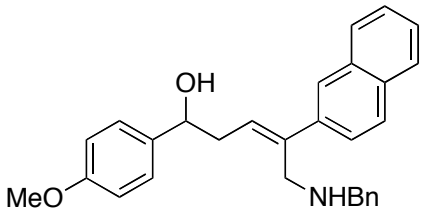
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.18 (m, 7H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.95 (t, *J* = 8.5 Hz, 1H), 4.82 (dd, *J* = 7.5, 3.5 Hz, 1H), 3.82 (s, 3H), 3.51 (d, *J* = 12.0 Hz, 1H), 3.37 (d, *J* = 12.0 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.48 (m, 4H), 1.45 (quint, *J* = 7.0 Hz, 4H), 1.17 (sext, *J* = 7.0 Hz, 4H), 0.83 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 158.9, 144.3, 139.25, 138.7, 128.6 (2C), 127.1, 127.0 (2C), 126.5 (2C), 113.9 (2C), 112.3, 71.7, 55.6, 53.3, 52.5, 40.3, 27.5, 21.1, 14.3.

IR (neat): *v* = 3394, 2936, 2930 2861, 1511, 1246, 1036 cm^{-1}.

HRMS (ESI) Calcd. for $C_{26}H_{39}NO_2$. [M+H]: 396.2903, found: 396.2919.

(*Z*)-5-(Benzylamino)-1-(4-methoxyphenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (2d)



The product was obtained as an orange oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.13 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = +137.0 (c =0.2 in $CHCl_3$) for 96% *ee* (*R*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.81 – 7.76 (m, 3H), 7.69 (m, 1H), 7.55 – 7.44 (m, 3H), 7.35 – 7.21 (m, 7H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.10 (t, *J* = 8.5 Hz, 1H), 4.85 (dd, *J* = 7.0, 4.5 Hz, 1H), 3.86 (s, 2H), 3.82 (s, 3H), 3.78 (d, *J* = 7.5 Hz, 1), 3.71 (d, *J* = 7.5 Hz, 1H), 2.75 – 2.62 (m, 2H).

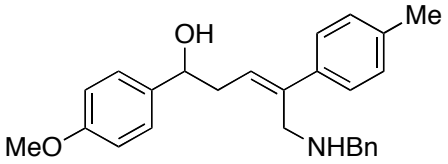
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.0, 140.6, 139.4, 137.9, 133.7, 132.9, 132.5, 132.4, 132.3, 129.9, 128.9 (3C), 128.8, 128.4, 128.3, 127.8, 127.7, 127.2, 126.6, 126.2, 124.8, 124.8, 113.9, 72.3, 55.6, 54.2, 47.3, 40.1.

IR (neat): ν = 3844, 2954, 1889, 1510, 1215, 1033 cm^{-1}.

HRMS (ESI) Calcd. for $C_{29}H_{30}NO_2$ [M+H]: 424.2277, found: 424.2260.

Enantiomeric excess has been determined by HPLC analysis using an IA column (heptane/ethanol, 90/10, 1.0mL/min), t_r = 39.6 min for (*S*) and t_r = 43.8 min for (*R*).

(*Z*)-5-(Benzylamino)-1-(4-methoxyphenyl)-4-p-tolylpent-3-en-1-ol (2e)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.23 (EtOAc: pentane / 3:2).

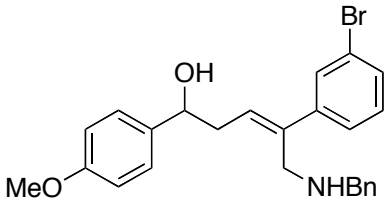
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.39 – 7.28 (m, 6H), 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.91 (t, *J* = 8.5 Hz, 1H), 4.86 – 4.71 (m, 1H, C*H*OH), 3.82 (s, 2H), 3.80 (s, 3H), 3.62 (d, *J* = 12.0 Hz, 1H), 3.56 (d, *J* = 12.0 Hz, 1H), 2.61 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.6, 140.1, 138.9, 138.8, 137.5, 136.9, 129.2 (2C), 128.5 (2C), 128.5 (2C), 128.3, 127.3, 127.0, 126.8 (2C), 125.9 (2C), 113.6, 71.9, 55.3, 53.8, 47.0, 39.5, 21.0.

IR (neat): ν = 3304, 2952, 2922, 2854, 1732, 1611, 1511, 1246, 1112 cm^{-1}.

HRMS (ESI) Calcd. for $C_{26}H_{30}NO_2$ [M+H]: 388.2273, found: 388.2277.

((*Z*)-5-(Benzylamino)-4-(3-bromophenyl)-1-(4-methoxyphenyl)pent-3-en-1-ol (2f)



The product was obtained as a white solid after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.33 (EtOAc: pentane / 3:2).

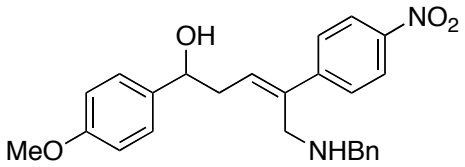
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.45 (m, 1H), 7.41 – 7.12 (m, 10H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.93 (t, *J* = 8.5 Hz, 1H), 4.80 (dd, *J* = 6.5, 5.0 Hz, 1H), 3.81 (app s, 5H), 3.58 (d, *J* = 12.0 Hz, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 2.68 – 2.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 159.1, 144.5, 139.6, 139.2, 137.6, 130.6, 130.4, 130.3, 129.6, 128.9 (2C), 128.8 (2C), 127.7, 127.1 (2C), 125.0, 114.1 (2C), 110.4, 72.3, 55.6, 54.1, 47.3, 39.8.

IR (neat): ν = 3436, 2966, 1683, 1558, 1511, 1454, 1363, 1035 cm^{-1}.

HRMS (ESI) Calcd. for $C_{25}H_{27}BrNO_2$ [M+H]: 452.1225, found: 452.1220.

(*Z*)-5-(Benzylamino)-1-(4-methoxyphenyl)-4-(4-nitrophenyl)pent-3-en-1-ol (2g)



The product was obtained as a yellow oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.23 (EtOAc: pentane / 3:2).

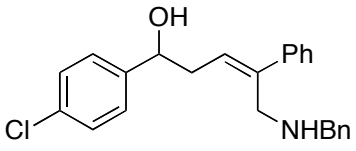
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.14 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.30 (m, 7H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.09 (t, *J* = 9.0 Hz, 1H), 4.83 (t, *J* = 5.0 Hz, 1H), 3.82 (s, 2H) 3.81 (s, 3H), 3.62 (d, *J* = 12.5 Hz, 1H), 3.56 (d, *J* = 12.5 Hz, 1H), 2.67 (dd, *J* = 10.5, 5.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 159.3, 148.9, 147.1, 139.3, 139.3, 137.2, 132.9, 129.0, 128.9 (2C), 128.7 (2C), 127.8, 127.1 (2C), 127.0 (2C), 124.1 (2C), 114.1, 72.4, 55.6, 54.2, 47.2, 39.8.

IR (neat): ν = 3436, 1638, 1512, 1243, 1246, 1032 cm^{-1}.

HRMS (ESI) Calcd. for $C_{25}H_{27}N_2O_4$. [M+H]: 419.1971, found: 419.1985.

(*Z*)-5-(Benzylamino)-1-(4-chlorophenyl)-4-phenylpent-3-en-1-ol (2h)



The product was obtained as a pale yellow solid after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.15 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = +10.8 (*c*=1.0 in $CHCl_3$) for 97% *ee* (*R*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.49-7.43 (m, 1H), 7.36 – 7.19 (m, 13H), 5.91 (t, *J* = 8.5 Hz, 1H), 4.81 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.91 – 3.76 (m, 2H), 3.61 (d, *J* = 12.0 Hz, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 2.64 (ddd, *J* = 14.0, 8.0, 3.0 Hz, 1H), 2.56 (ddd, *J* = 14.0, 8.0, 3.0 Hz, 1H).

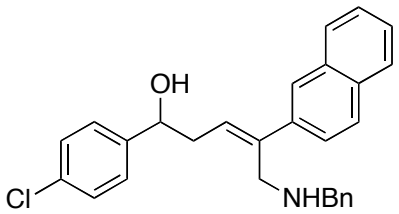
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 159.1, 144.5, 139.6, 139.2, 137.6, 130.6, 130.4, 130.3, 129.6, 128.9 (2C), 128.8 (2C), 127.7, 127.1 (2C), 125.0, 123.0, 114.0, 110.4, 72.3, 55.6, 54.1, 39.8.

IR (neat): ν = 3583, 3368, 3299, 3060, 1947, 1640, 1494, 1066 cm^{-1}.

HRMS (ESI) Calcd. for $C_{24}H_{25}NOCl$ [M+H]: 378.1643, found: 378.1625.

Enantiomeric excess has been determined by HPLC analysis using an IA column (heptane/ethanol, 90/10, 1.0 mL/min), t_r = 16.9 min for (*S*) and t_r = 19.6 min for (*R*).

(*Z*)-5-(Benzylamino)-1-(4-chlorophenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (2i)



The product was obtained as a after yellow oil purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.31 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = +120.5 (c=1.0 in $CHCl_3$) for 97% *ee* (*R*).

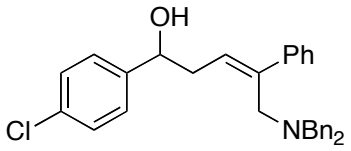
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.80- 7.75 (m, 3H), 7.70- 7.75 (m, 1H), 7.54 – 7.40 (m, 4H), 7.33 (t, *J* = 6.5 Hz, 4H), 7.31 – 7.18 (m, 3H), 6.05 (t, *J* = 8.0, 1H), 4.86 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.98 – 3.78 (m, 2H), 3.71 (d, *J* = 12.0 Hz, 1H), 3.66 (d, *J* = 12.0 Hz, 1H), 2.71 (ddd, *J* = 13.5, 8.0, 3.0 Hz, 1H), 2.67 – 2.58 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 148.0, 141.0, 139.2, 138.9, 134.5, 133.6, 132.9, 129.5, 128.8 (2C), 128.8 (2C), 128.4, 128.3, 127.8, 127.7, 127.3, 126.5, 126.2, 126.2 , 124.8, 124.6, 124.1, 110.2, 71.8, 54.2, 47.1, 39.8.

IR (neat): ν = 3409, 3392, 3058, 3029, 1638, 1628, 1454, 1432, 1264, 1197 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}NOCl$ [M+H]: 428.1781, found: 428.1778.

Enantiomeric excess has been determined by HPLC analysis using an AS-H column (heptane/ethanol, 95/05, 1.0 mL/min), t_r = 7.7 min for (*S*) and t_r = 8.6 min for (*R*).

(*Z*)-1-(4-Chlorophenyl)-5-(dibenzylamino)-4-phenylpent-3-en-1-ol (2j)



The product was obtained as a after yellow oil purification by flash chromatography on silica gel (pentane: EtOAc/ 4:1).

TLC: R_f = 0.23 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = +38.7 (c=1.0 in $CHCl_3$) for 97% *ee* (*R*).

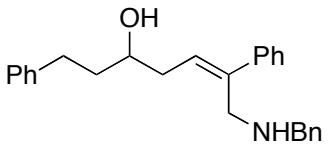
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.45 - 7.40 (m, 1H), 7.39 – 7.01 (m, 18H), 5.81 (t, *J* = 8.1 Hz, 1H), 4.85 – 4.72 (m, 1H), 3.47 – 3.40 (m, 4H), 3.37 (d, *J* = 12.5 Hz, 1H), 3.32 (d, *J* = 12.5 Hz, 1H), 2.59 – 2.36 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 147.1, 143.6, 141.5, 138.6, 134.6, 130.0 (2C), 129.9, 129.1, 128.9, 128.9, 128.5, 128.5 (3C), 128.4, 128.2 (2C), 127.7, 127.5 (2C), 127.3, 127.0 (2C), 126.4, 124.4 , 72.7, 59.2, 52.7, 38.8.

IR (neat): ν = 3565, 3388, 3060, 3028, 1641, 1597, 1493, 1453, 1054, 1028, 901 cm^{-1}. HRMS (ESI) Calcd. for $C_{31}H_{31}NOCl$ [M+H]: 468.2094, found: 468.2116.

Enantiomeric excess has been determined by HPLC analysis using an AD column (hexane/2-propanol, 90/10, 0.1% DEA, 1.0 mL/min), t_r = 62.0 min for (*S*) and t_r = 81.1 min for (*R*).

(*Z*)-7-(Benzylamino)-1,6-diphenylhept-5-en-3-ol (2k)



The product was obtained as an orange oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.24 (EtOAc: pentane / 3:2).

$[\alpha]_D^{20}$ = 15.2 (c=1.0 in $CHCl_3$) for 95% *ee* (*S*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.44 – 7.09 (m, 15H), 6.0 (t, *J* = 8.0 Hz, 1H), 3.82 (d, *J* = 13.0 Hz, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 3.17 (br s, 1H), 2.94 – 2.80 (m, 1H), 2.73 (m 1H), 2.50 – 2.30 (m, 2H), 1.96 – 1.72 (m, 2H).

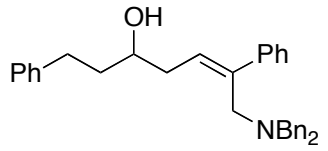
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.43, 141.85, 140.07, 138.79, 129.35, 128.53 (2C), 128.48 (2C), 128.46 (2C), 128.32 (2C), 127.30, 127.15, 125.98 (2C), 125.67 (2C), 115.83, 69.40, 53.60, 46.83, 39.70, 36.93, 32.31.

IR (neat): ν = 3407, 3020, 2925, 2833, 1494, 1453, 1121, 1028, 909 cm^{-1}.

HRMS (ESI) Calcd. for $C_{21}H_{27}NO$ [M+H]: 372.2327, found: 372.2337.

Enantiomeric excess has been determined by HPLC analysis using an IB column (heptane/ethanol, 75/25, 1.0 mL/min), t_r = 7.2 min for (*S*) and t_r = 10.4 min for (*R*).

(*Z*)-7-(Dibenzylamino)-1,6-diphenylhept-5-en-3-ol (2l)



The product was obtained as an orange oil after purification by flash chromatography on silica gel (pentane: EtOAc/ 2:1 to 1:1).

TLC: R_f = 0.70 (EtOAc: pentane / 3:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 16H), 7.07 (d, *J* = 7.0 Hz, 4H), 5.81 (t, *J* = 8.0 Hz, 1H), 3.63 (s, 1H), 3.43 (d, *J* = 12.5 Hz, 1H), 3.38 (d, *J* = 12.5 Hz, 1H),

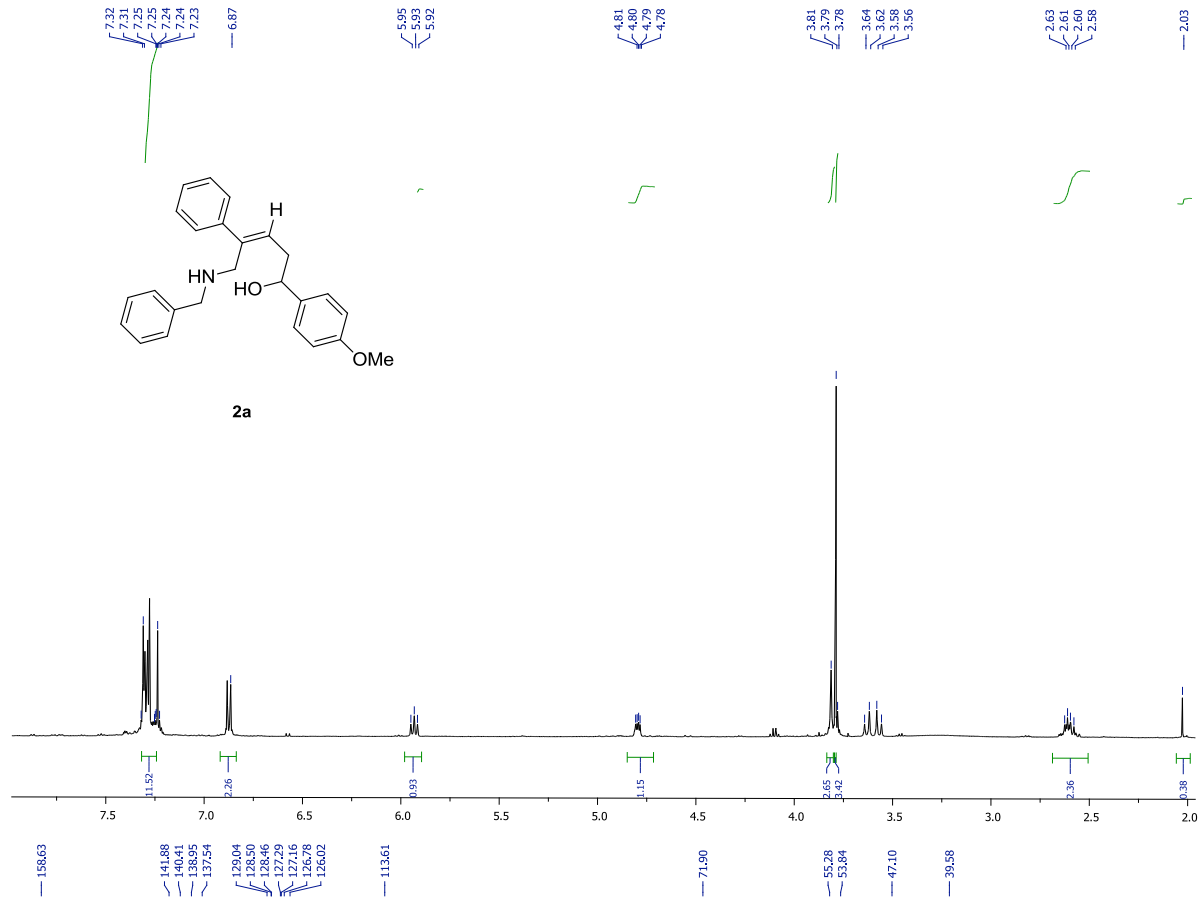
3.29 (d, J = 12.5 Hz, 2H), 2.87 – 2.70 (m, 2H), 2.62 (dd, J = 14.5, 9.0 Hz, 2H), 2.37 – 2.11 (m, 2H), 1.82 – 1.64 (m, 2H).

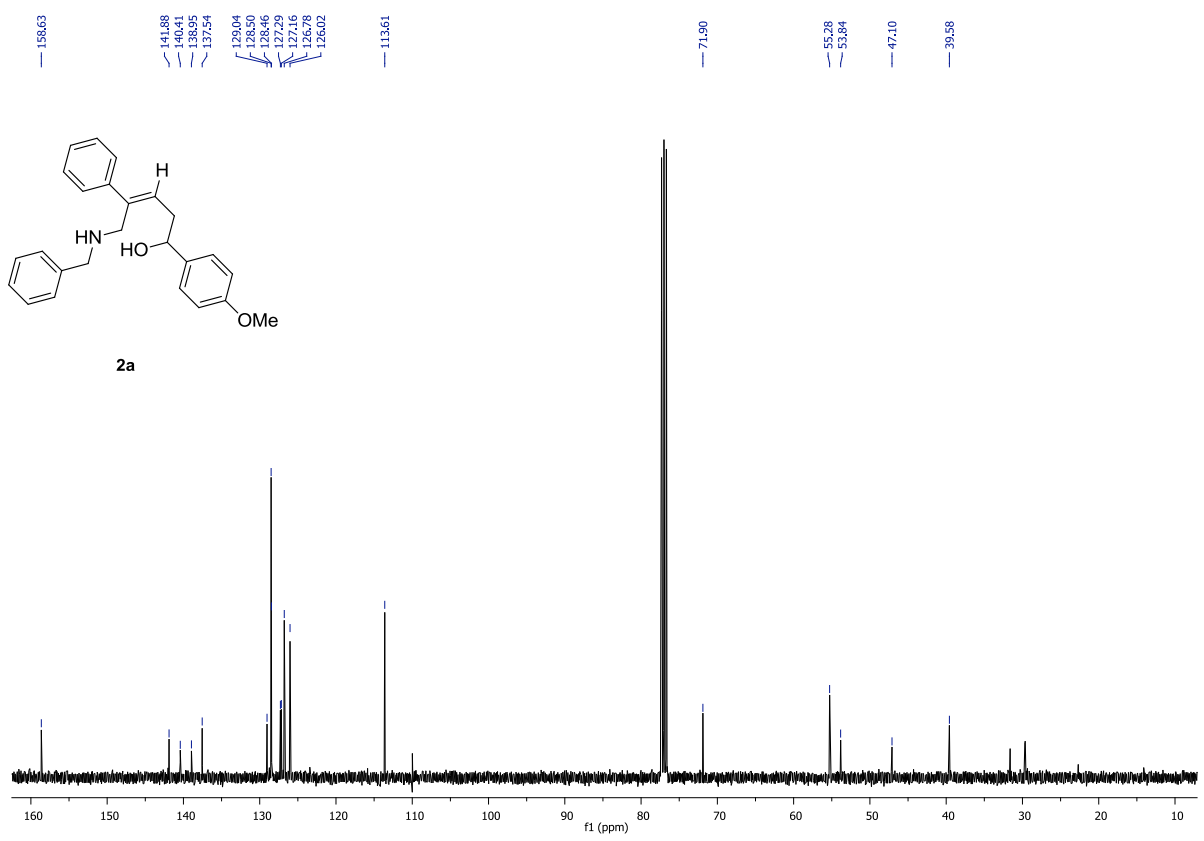
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 141.9, 141.1, 139.7, 138.6, 137.8, 128.4 (4C), 128.1, 127.4 (2C), 127.4 (2C) 127.3 (2C), 127.0 (4C), 126.9 (2C), 125.8 (2C), 125.8, 124.8, 69.5, 57.5, 51.2, 37.9, 35.6, 31.2.

IR (neat): v = 3407, 3020, 2925, 2833, 1494, 1453, 1121, 1028, 909 cm^{-1}.

HRMS (ESI) Calcd. for $C_{33}H_{36}NO$ [M+H]: 462.2797, found: 462.2809.

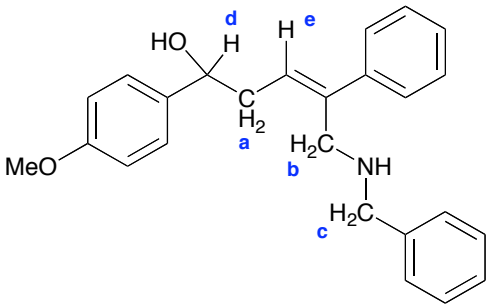
3. ^{1}H and ^{13}C NMR spectra of 2a-l, 3a and nOe spectrum of (*Z*)-2a

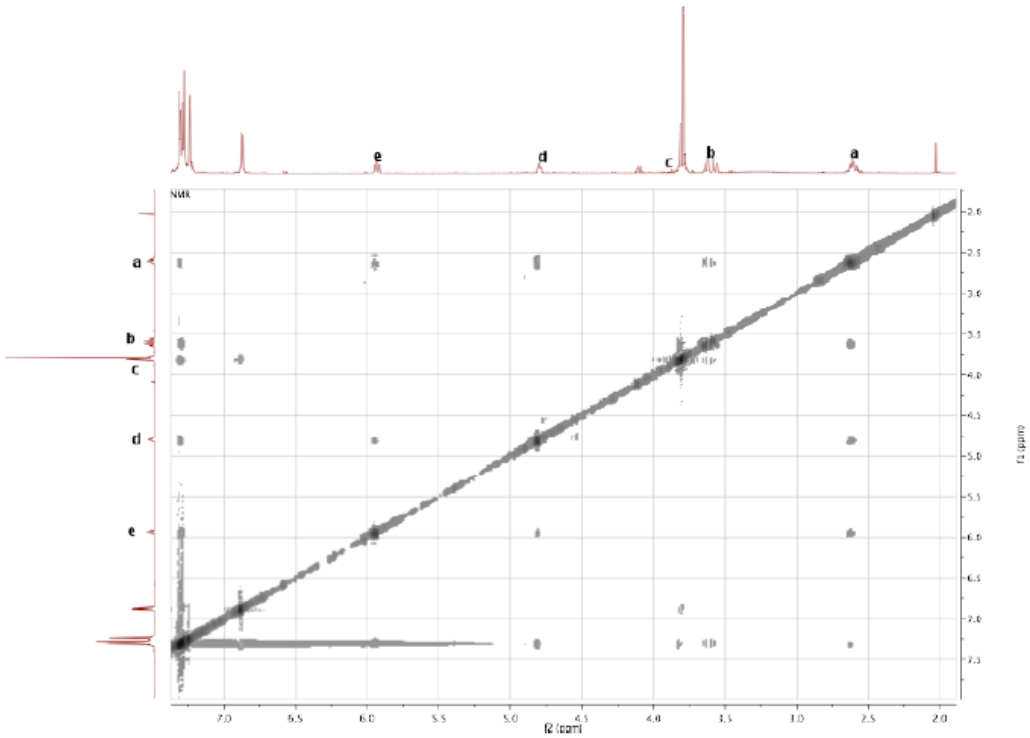


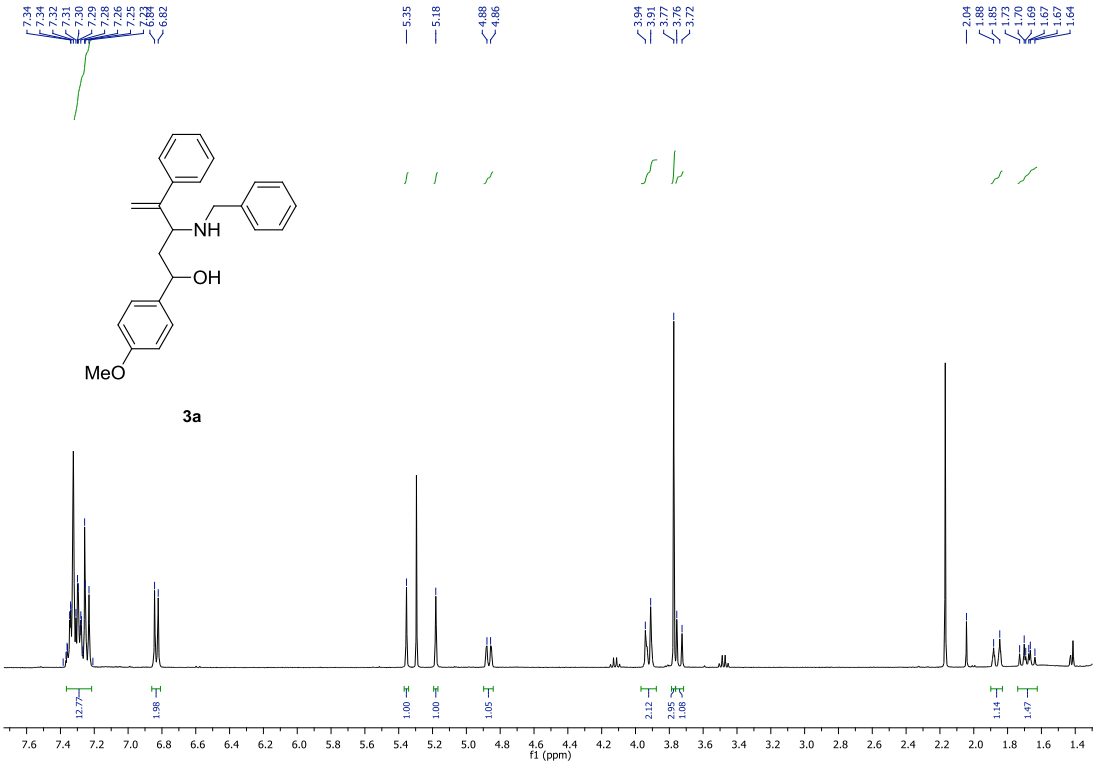


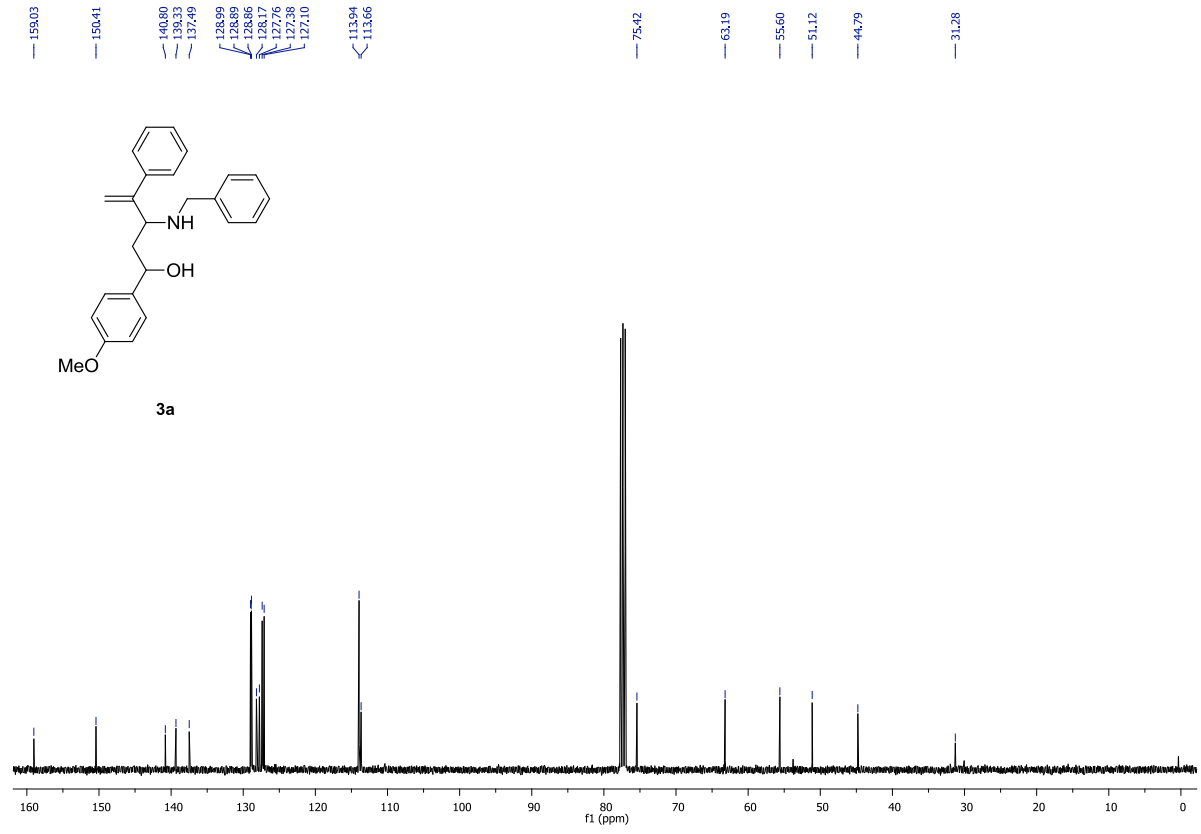
^{1}H-^{1}H nOe spectrum of (*Z*)-2a

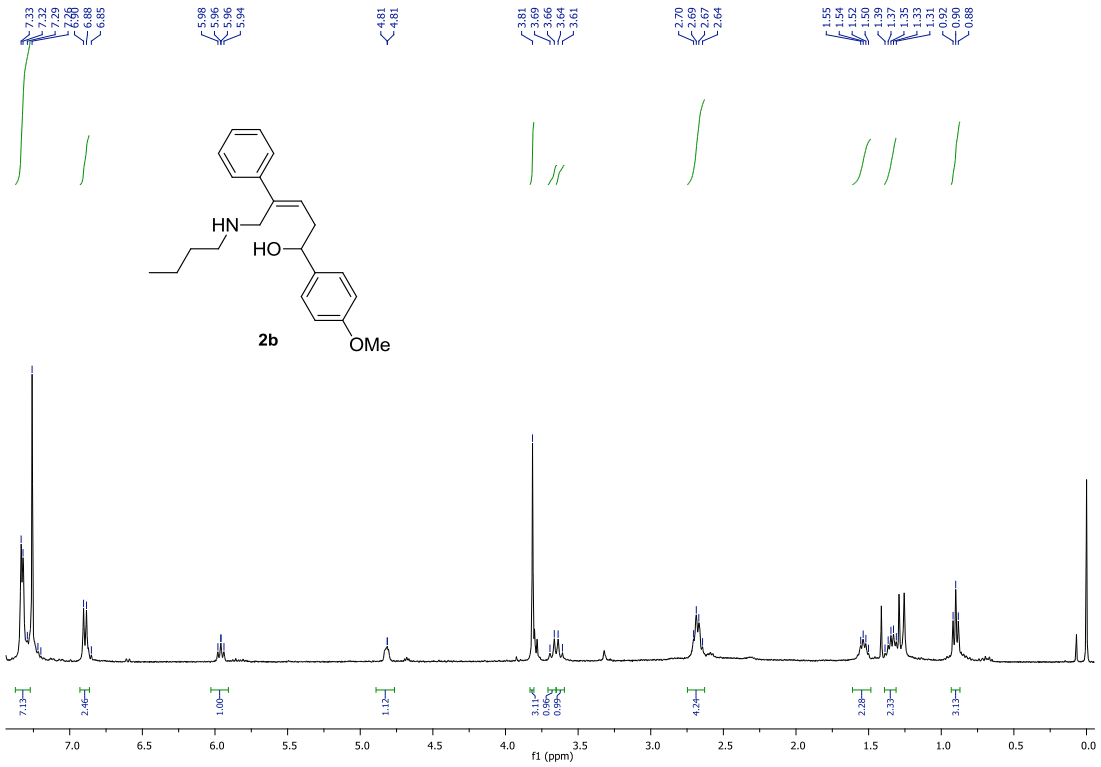
This figure shows the contour plot of the ^{1}H-^{1}H Noesy 2D spectrum of the compound (*Z*)-2a registered on a 500 MHz spectrometer. Spectral acquisition parameters were 90º-pulse (9.4 µs), sweep width (4248 Hz), mixing time (0.5 s), 128 increments, acquisition time (0.15 s) and a relaxation time of 2s.






NH
OH
MeO
3a
f1 (ppm)


NH
OH
MeO
3a
f1 (ppm)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5.98
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5.96
5.94
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4.81
3.81
3.69
3.66
3.64
3.61
2.70
2.69
2.67
2.64
1.55
1.54
1.52
1.50
1.39
1.37
1.35
1.33
1.31
0.92
0.90
0.88
HN
HO
OMe
2b
7.19
2.46
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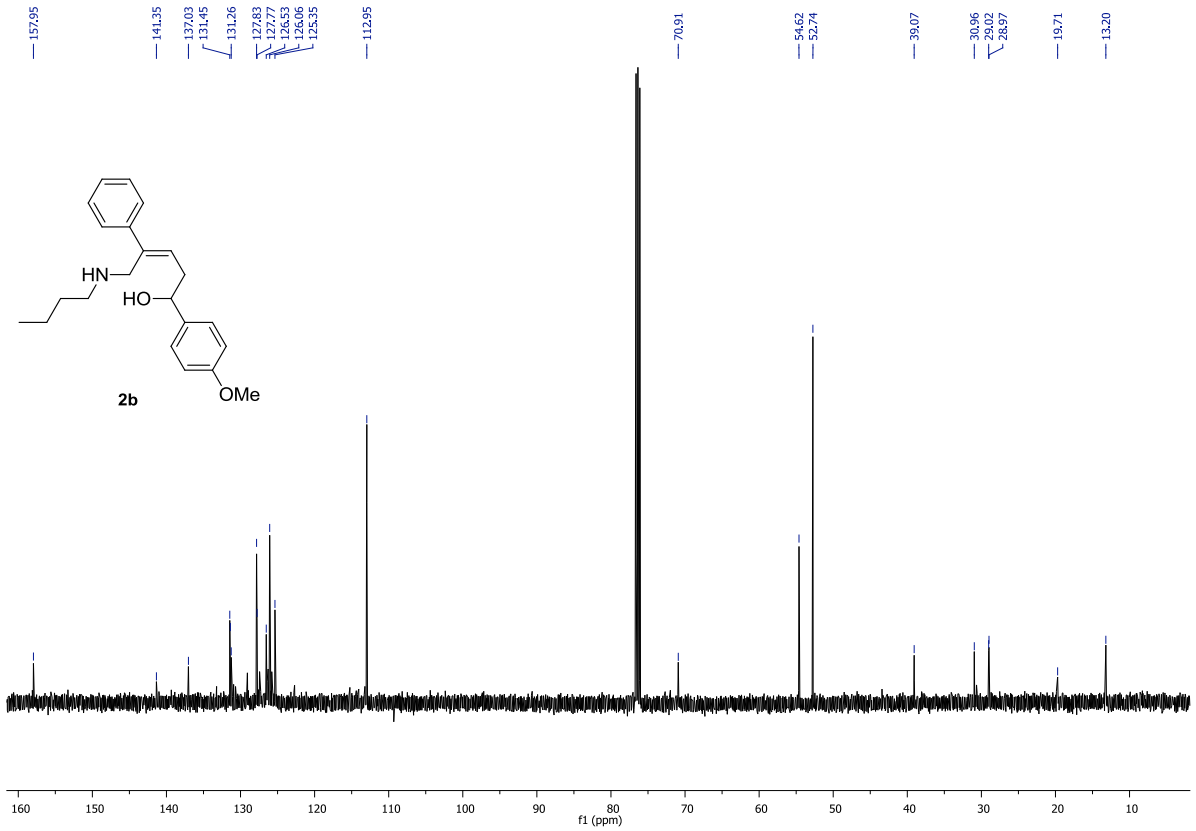
1.12
3.11
0.96
0.99
4.24
2.28
2.33
3.13
f1 (ppm)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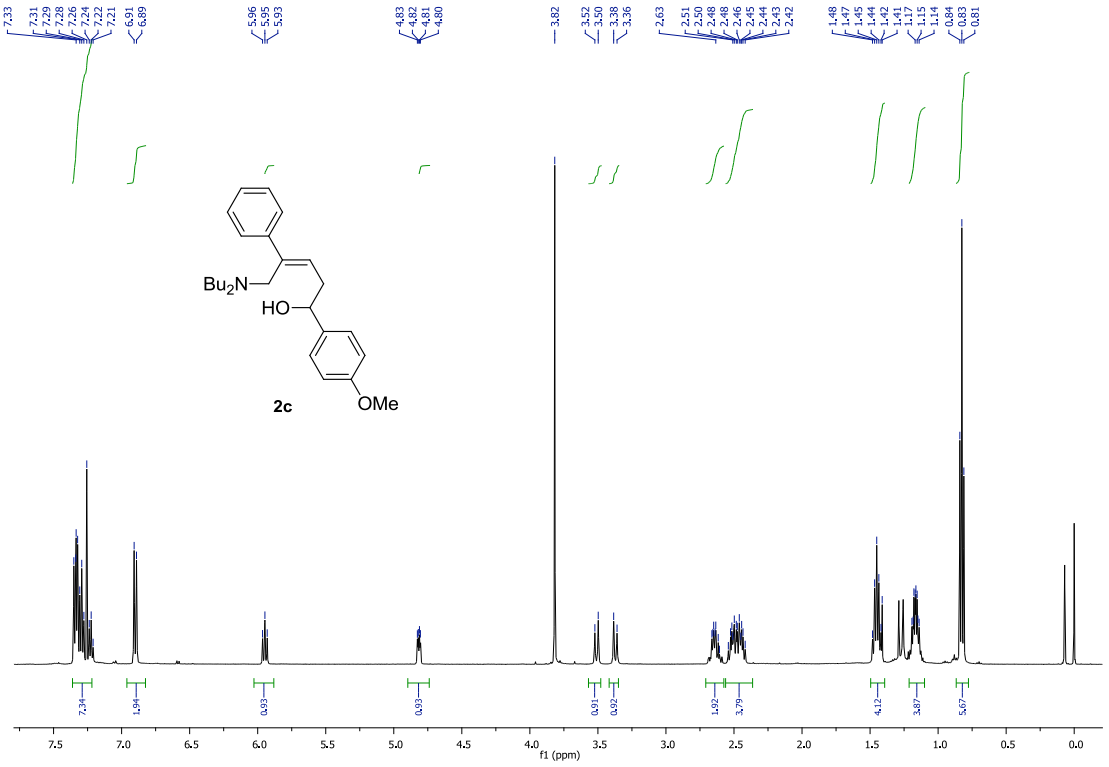
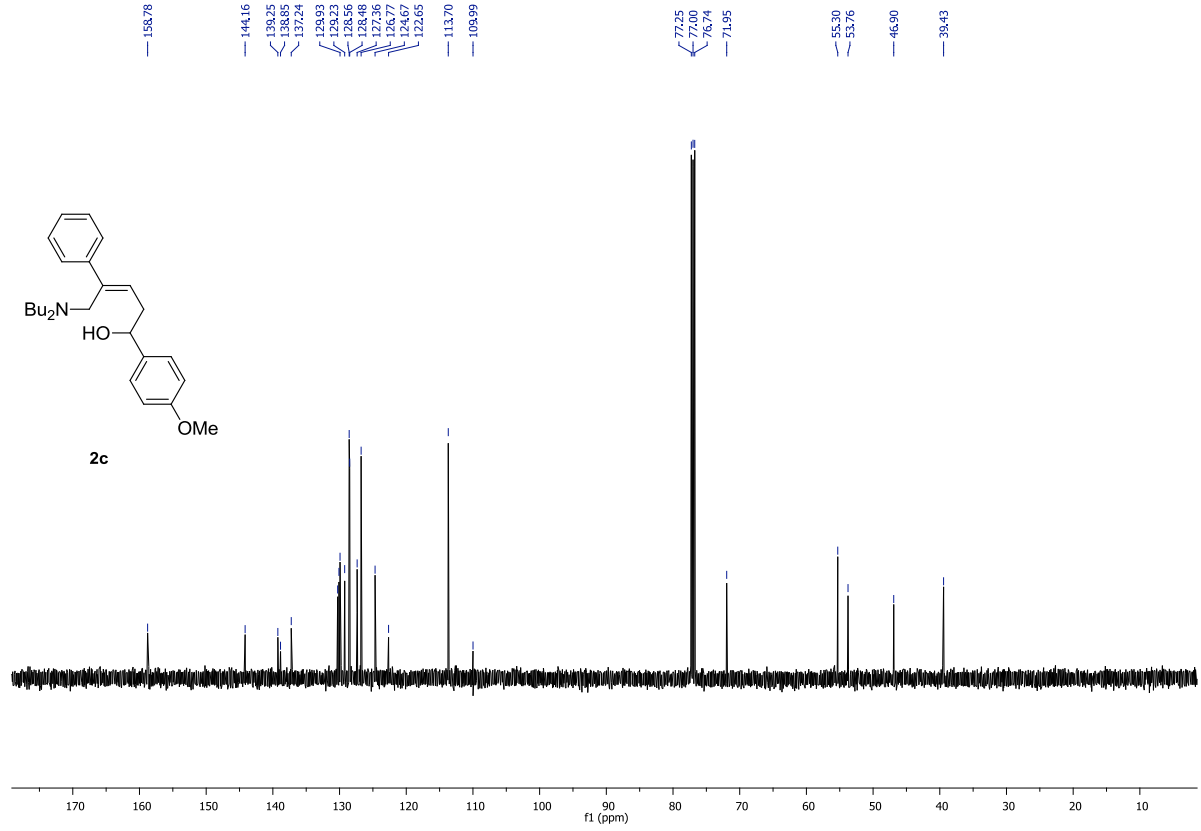
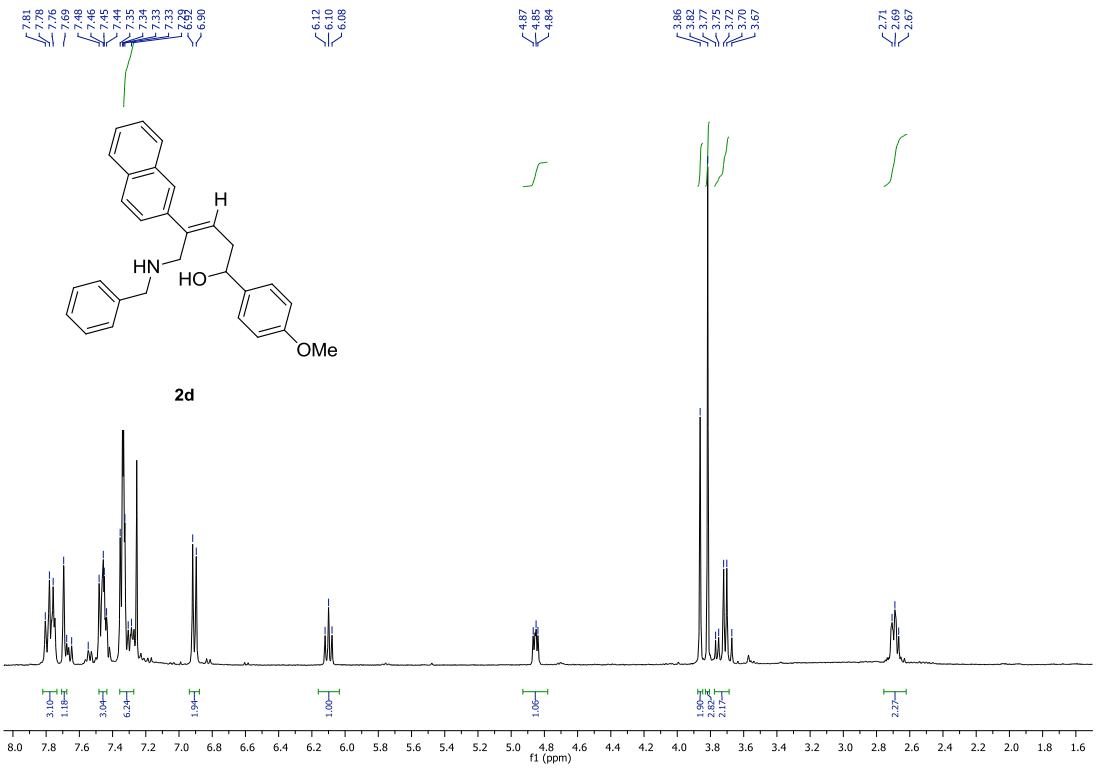
125.35
112.95
70.91
54.62
52.74
39.07
30.96
29.02
28.97
19.71
13.20
HN
HO
OMe
2b
f1 (ppm)


Bu2N
HO
OMe
2c
f1 (ppm)


Bu2N
HO
OMe
2c
f1 (ppm)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6.08
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4.84
3.86
3.82
3.77
3.75
3.72
3.70
3.67
2.71
2.69
2.67
H
HN
HO
OMe
2d
3.10
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1.06
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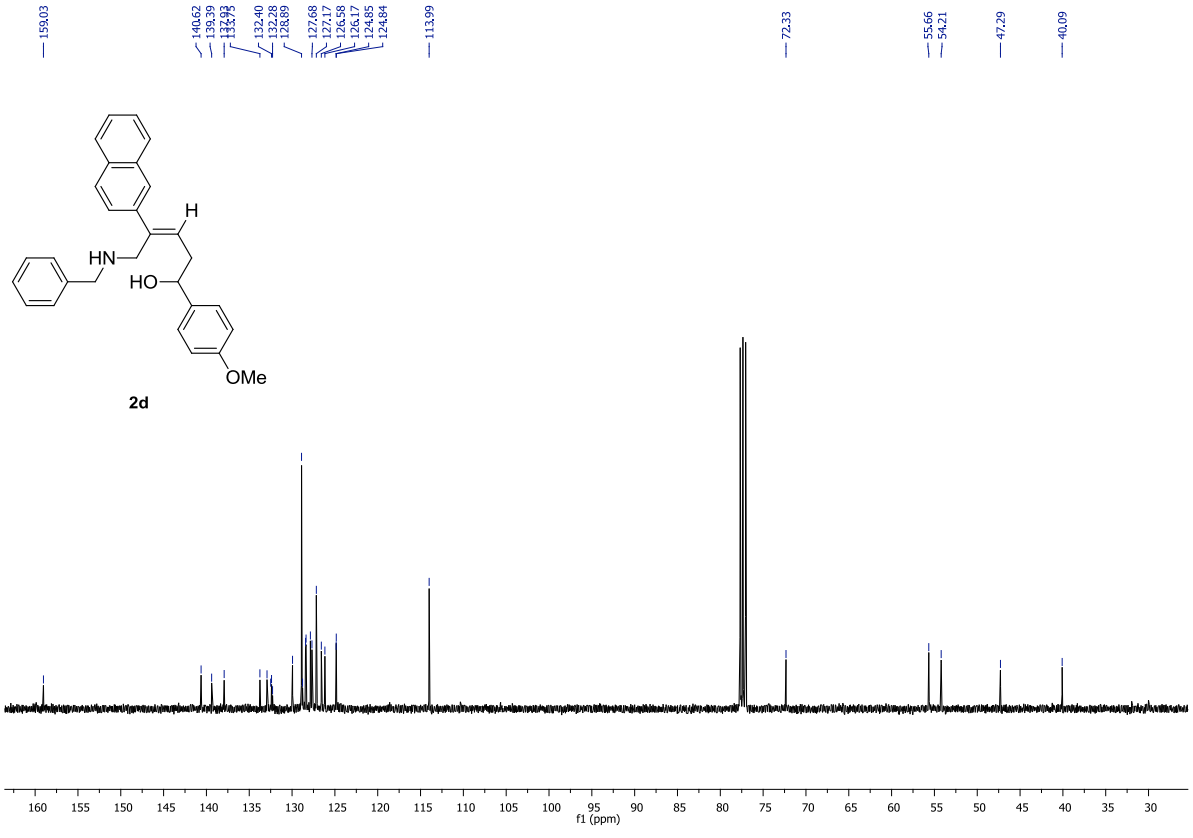
2.17
2.27
f1 (ppm)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127.68
127.17
126.58
126.17
124.85
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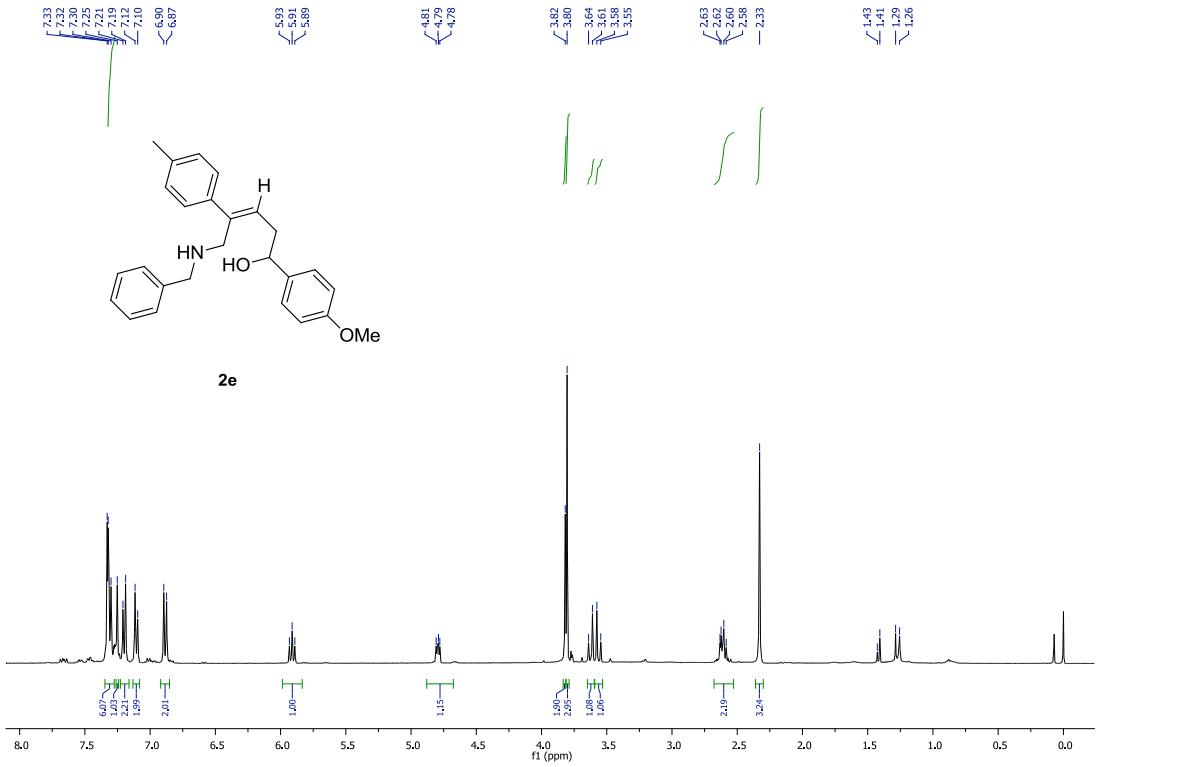
113.99
72.33
55.66
54.21
47.29
40.09
H
HN
HO
OMe
2d
f1 (ppm)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7.32
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7.19
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7.10
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6.87
5.93
5.91
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4.81
4.79
4.78
3.82
3.80
3.64
3.61
3.58
3.55
2.63
2.62
2.60
2.58
2.33
1.43
1.41
1.29
1.26
H
HN
HO
OMe
2e
6.07
1.03
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1.90
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1.08
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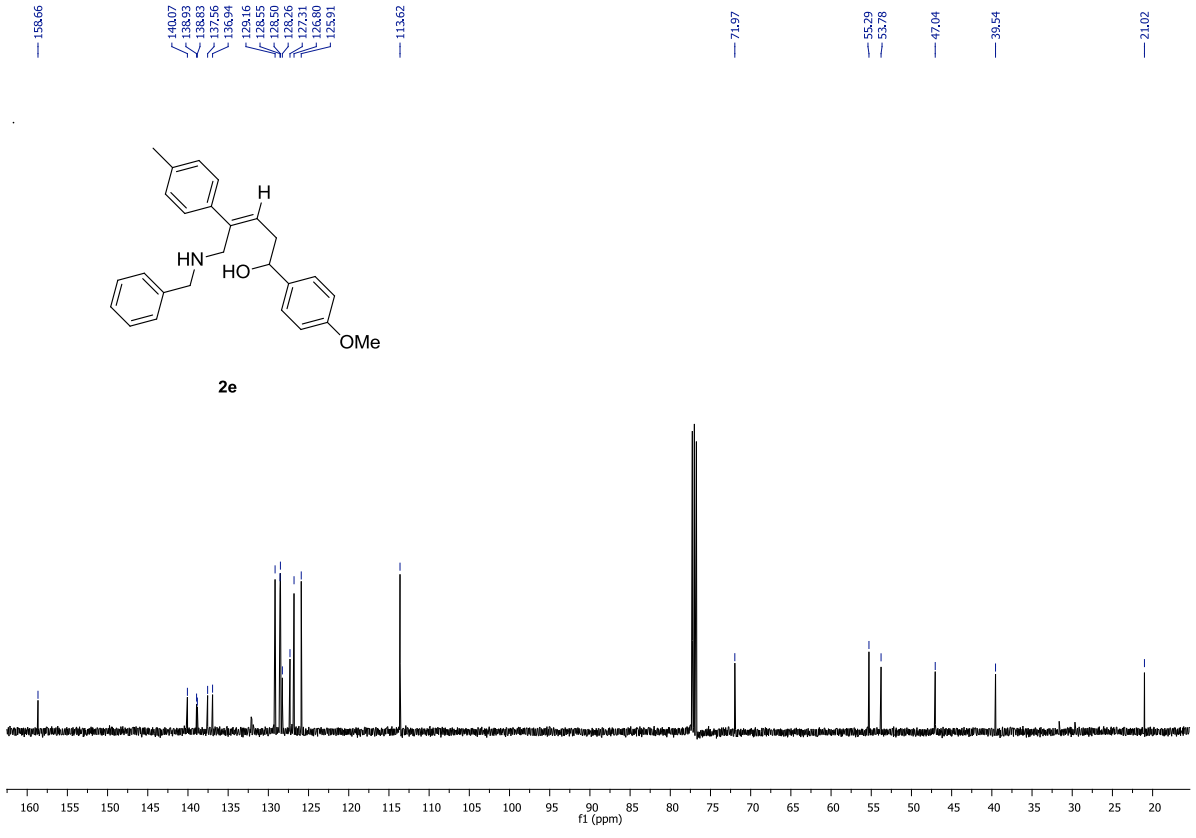
3.24
f1 (ppm)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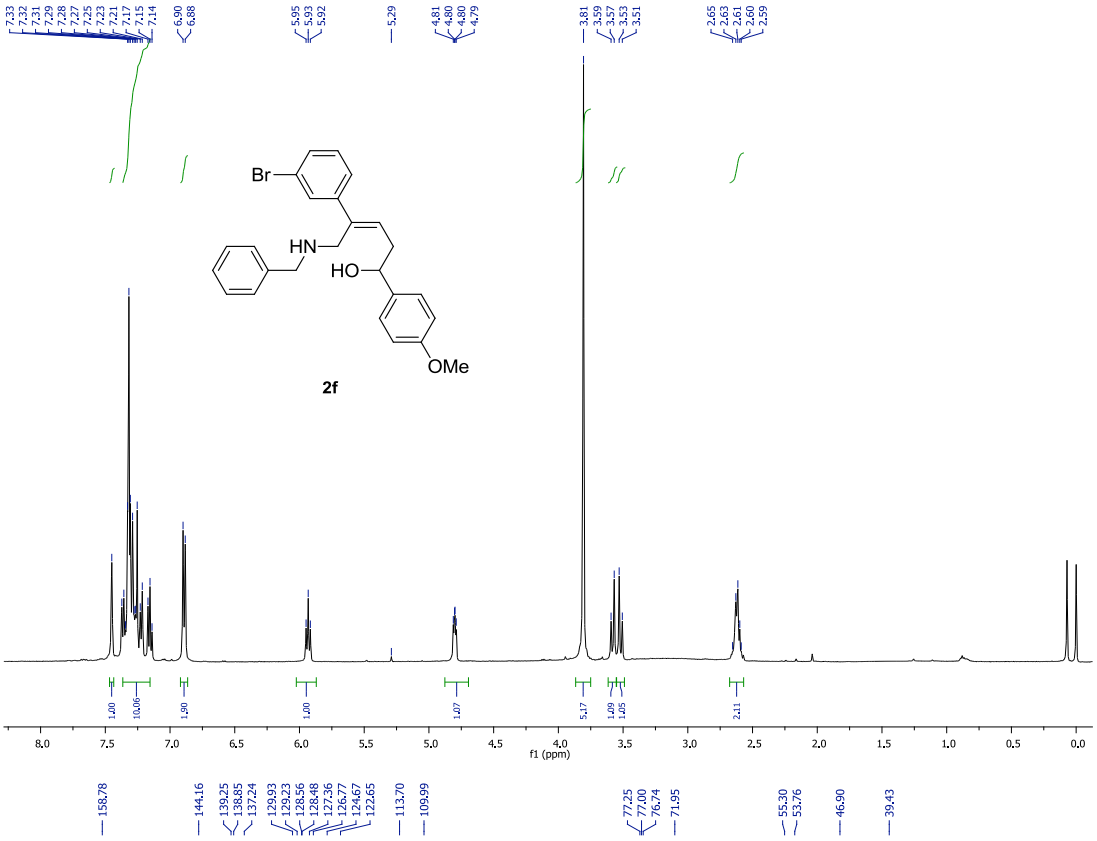
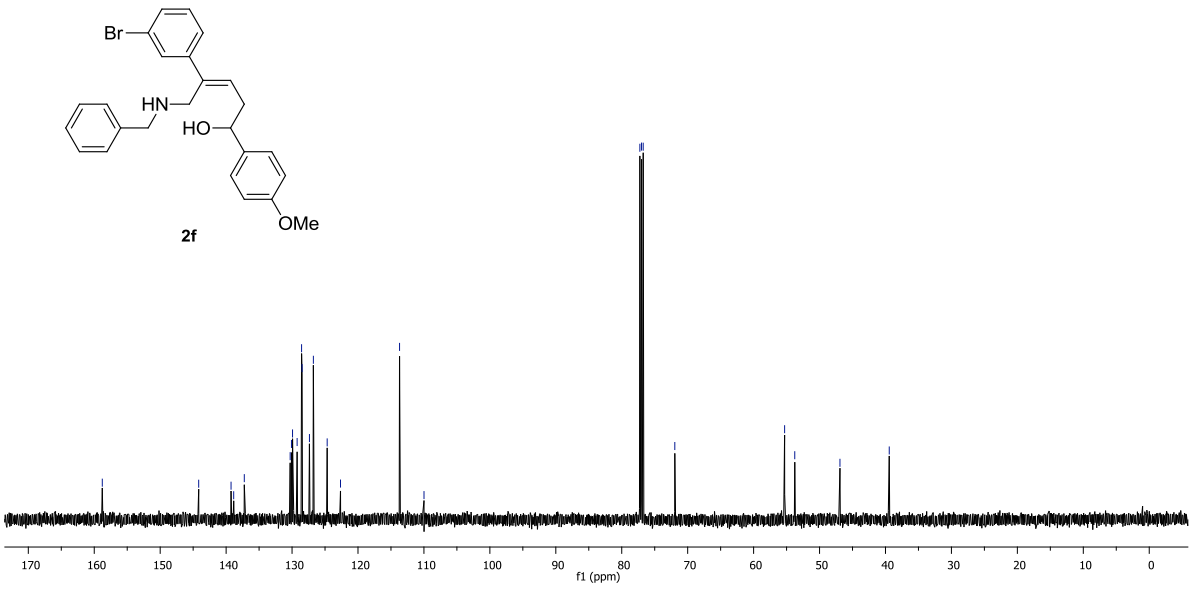
136.94
129.16
128.55
128.50
128.26
127.31
126.80
125.91
113.62
71.97
55.29
53.78
47.04
39.54
21.02
H
HN
HO
OMe
2e
f1 (ppm)


Br
HN
HO
OMe
2f
f1 (ppm)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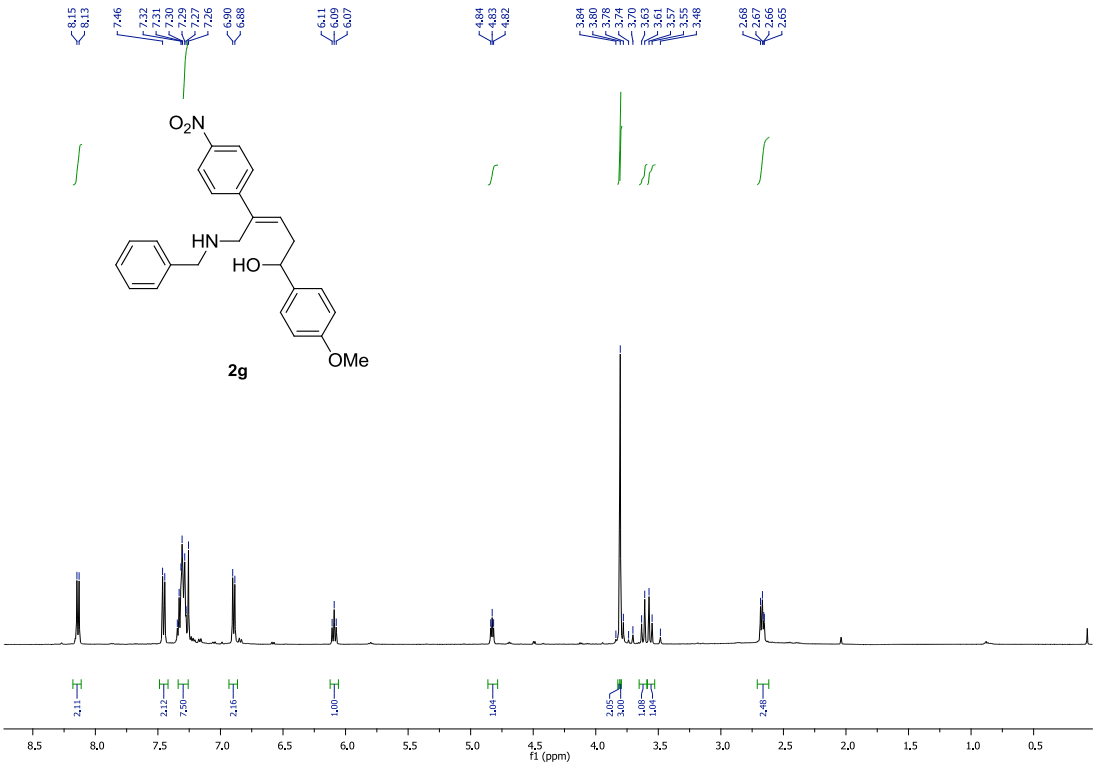
HO
OMe
2f
f1 (ppm)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7.27
7.26
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6.88
6.11
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6.07
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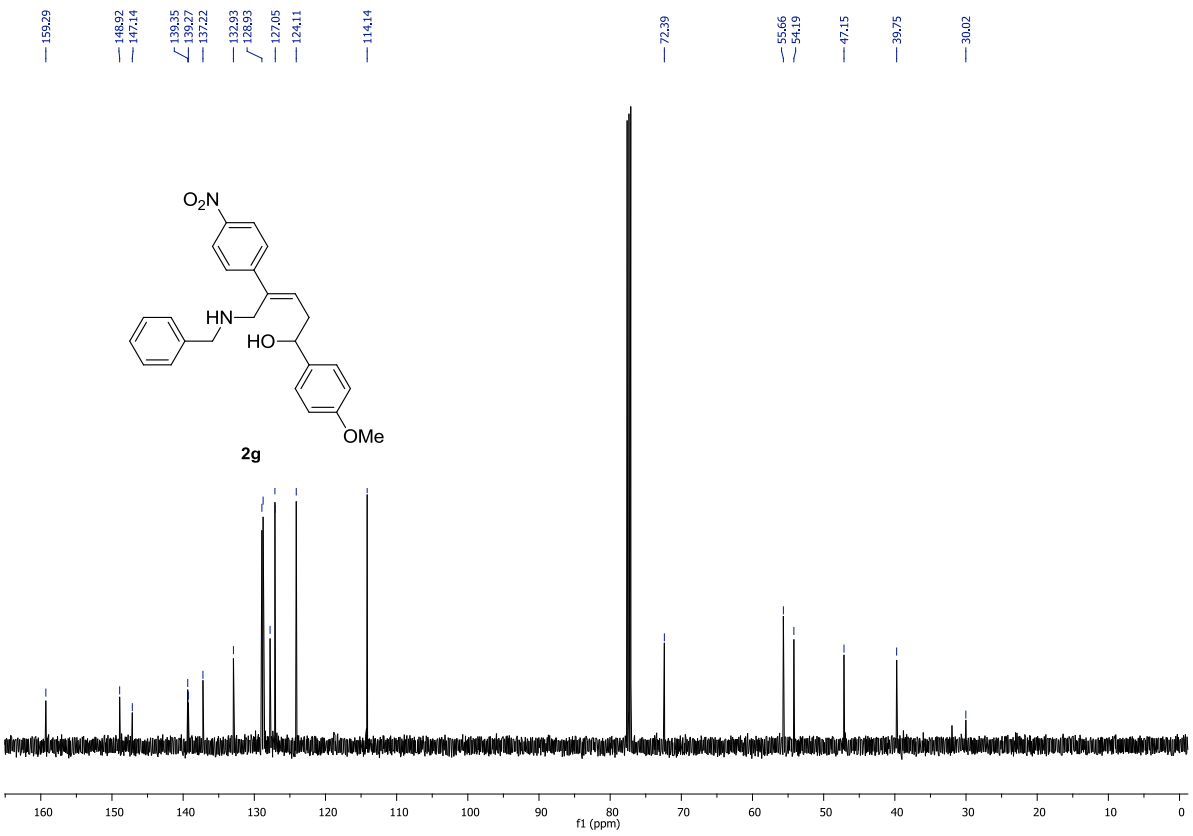
4.83
4.82
3.84
3.80
3.78
3.74
3.70
3.63
3.61
3.57
3.55
3.48
2.68
2.67
2.66
2.65
O2N
HN
HO
OMe
2g
2.11
2.12
7.50
2.16
1.00
1.04
2.05
3.00
1.08
1.04
2.48
f1 (ppm)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39.75
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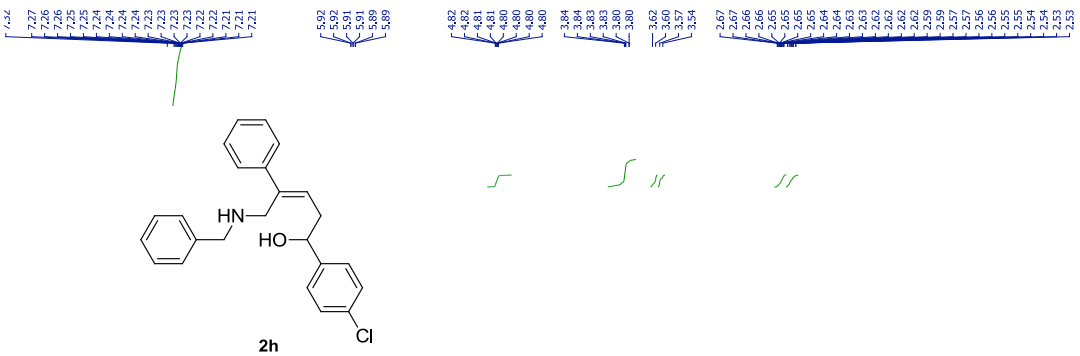
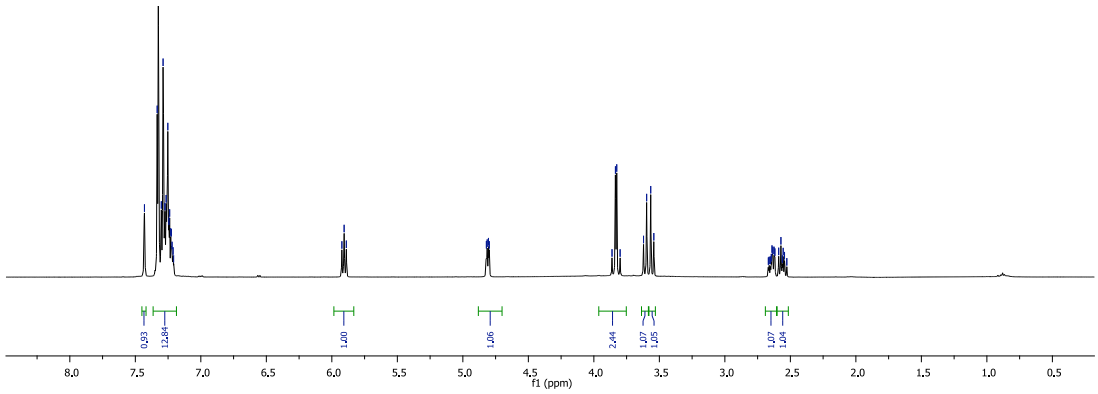
O2N
HN
HO
OMe
2g
f1 (ppm)



HN
HO
Cl

2h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1.07
1.04
f1 (ppm)


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139.21
137.60
130.45
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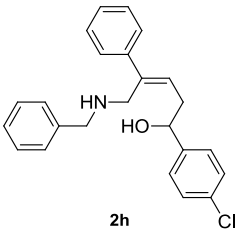
39.79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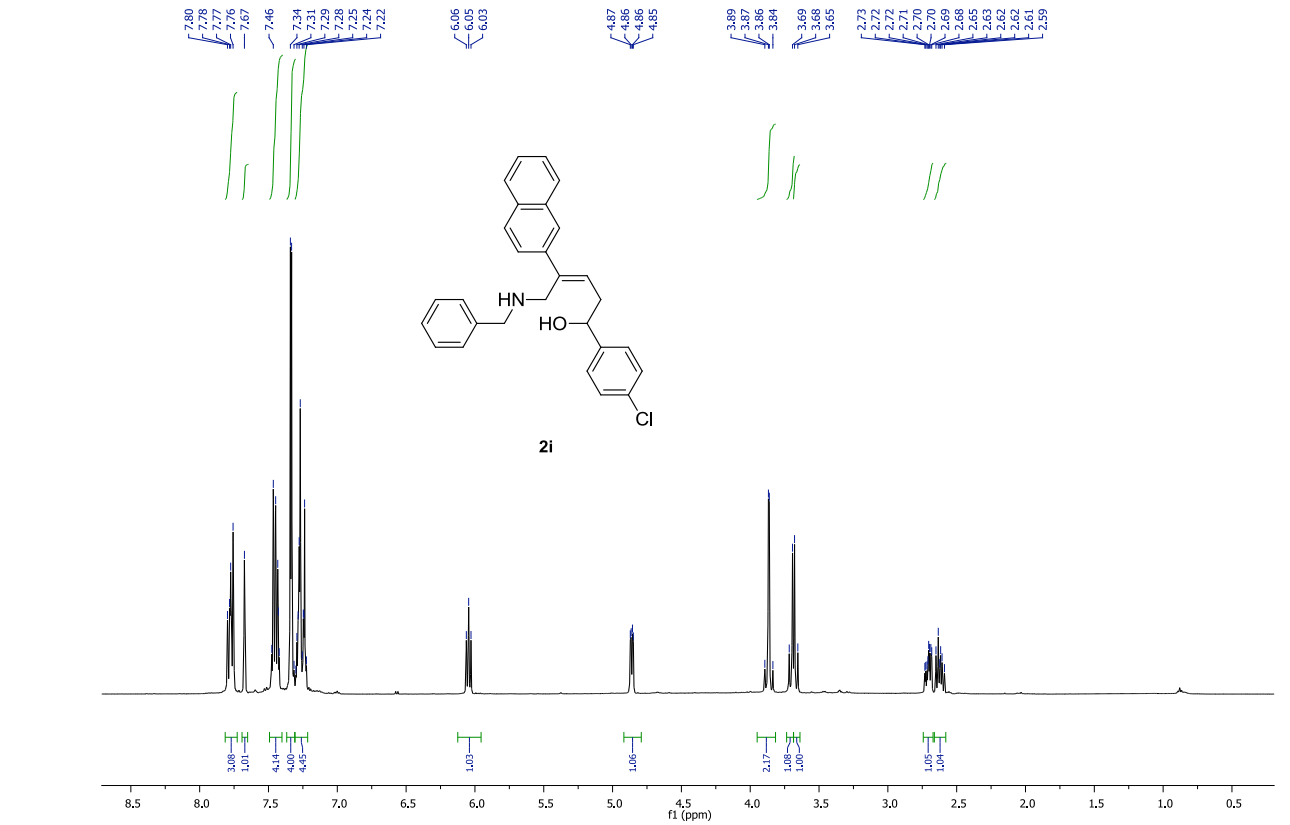
HO
Cl

2h

f1 (ppm)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2.72
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2.71
2.70
2.70
2.69
2.68
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2.63
2.62
2.62
2.61
2.59
HN
HO
Cl
2i
3.08
1.01
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4.45
1.03
1.06
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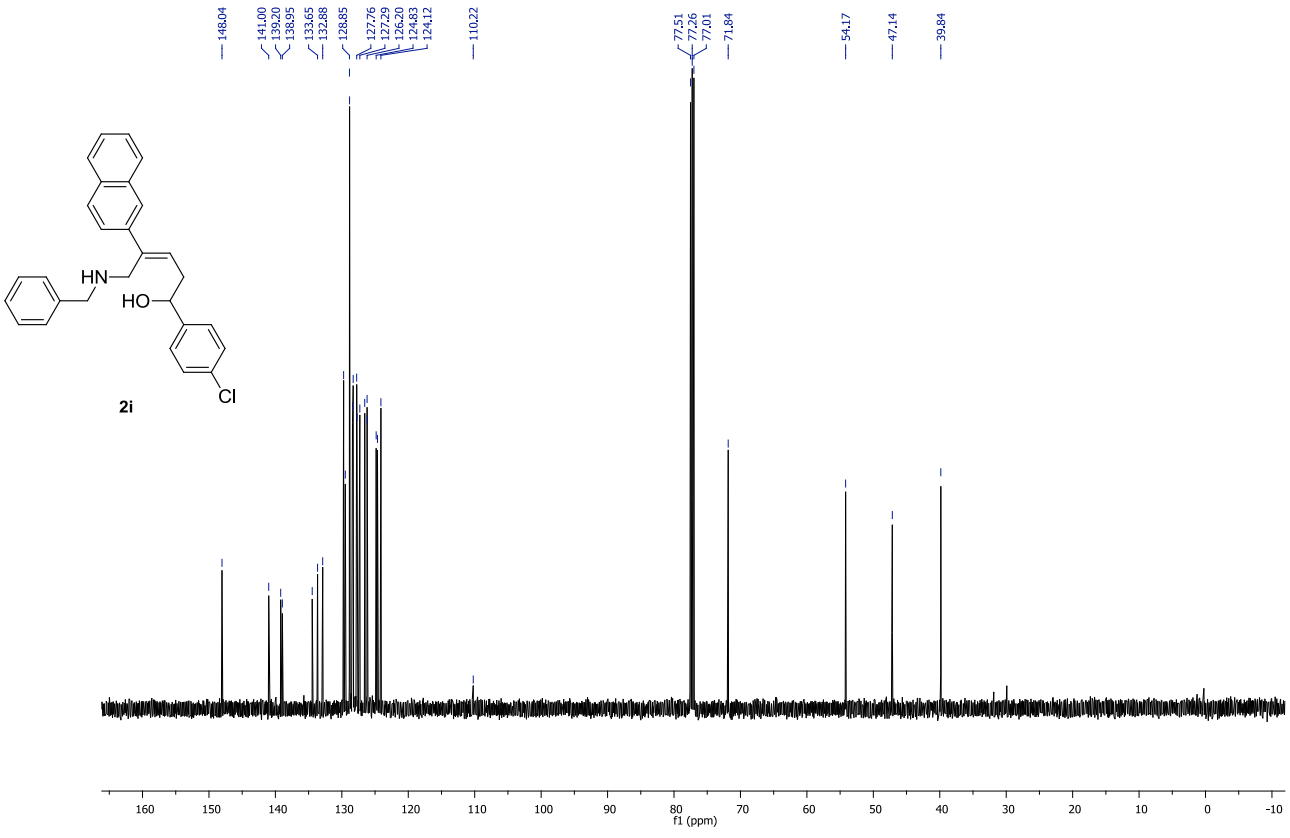
1.00
1.05
1.04
f1 (ppm)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39.84
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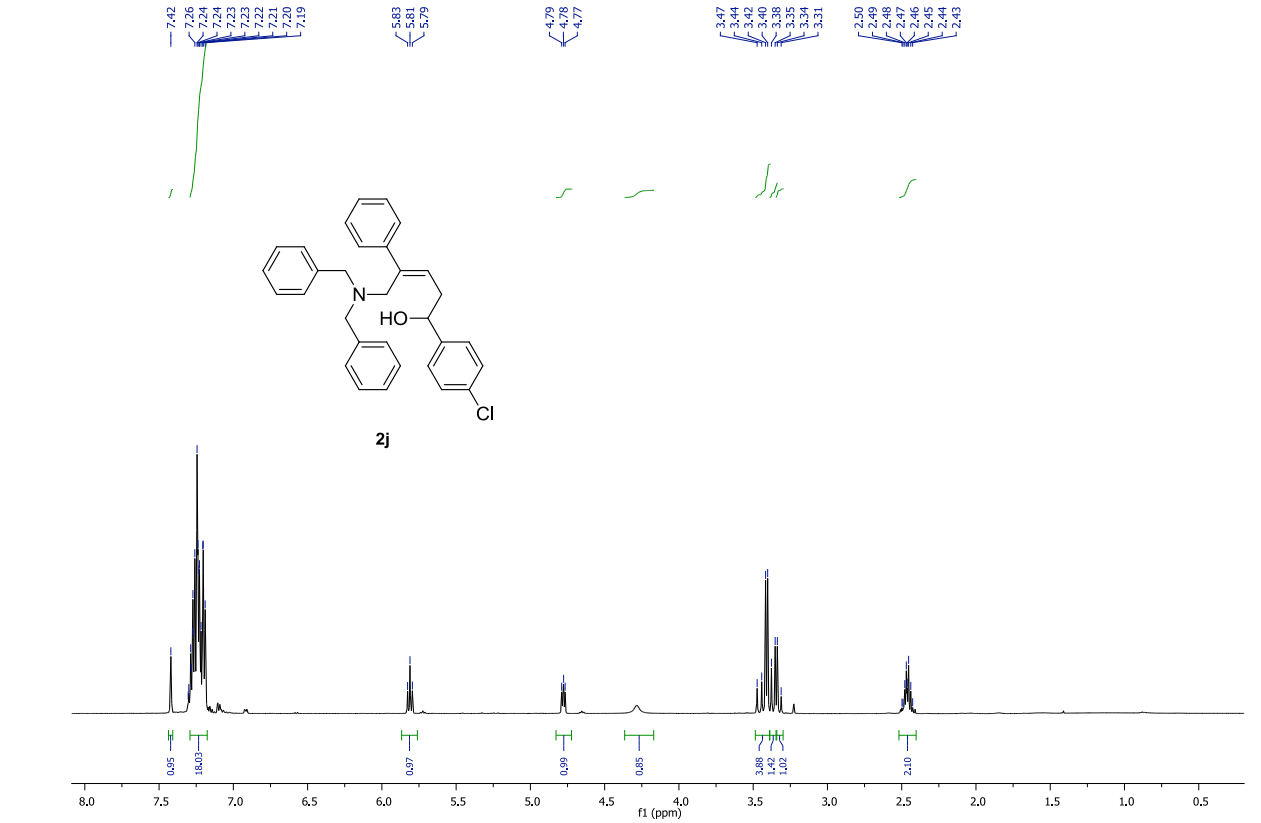
HO
Cl
2i
f1 (ppm)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4.78
4.77
3.47
3.44
3.42
3.42
3.40
3.38
3.35
3.34
3.31
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.43
N
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Cl
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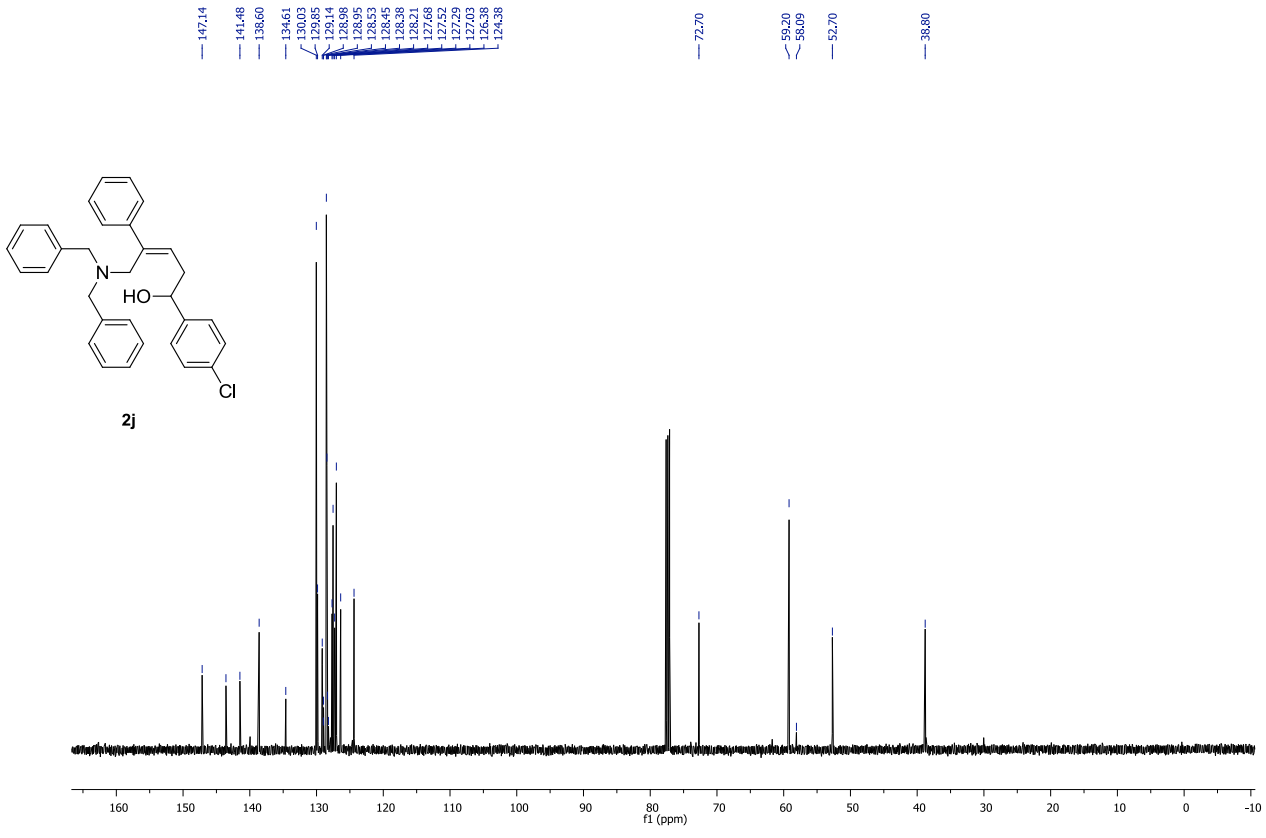
2.10
f1 (ppm)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127.52
127.29
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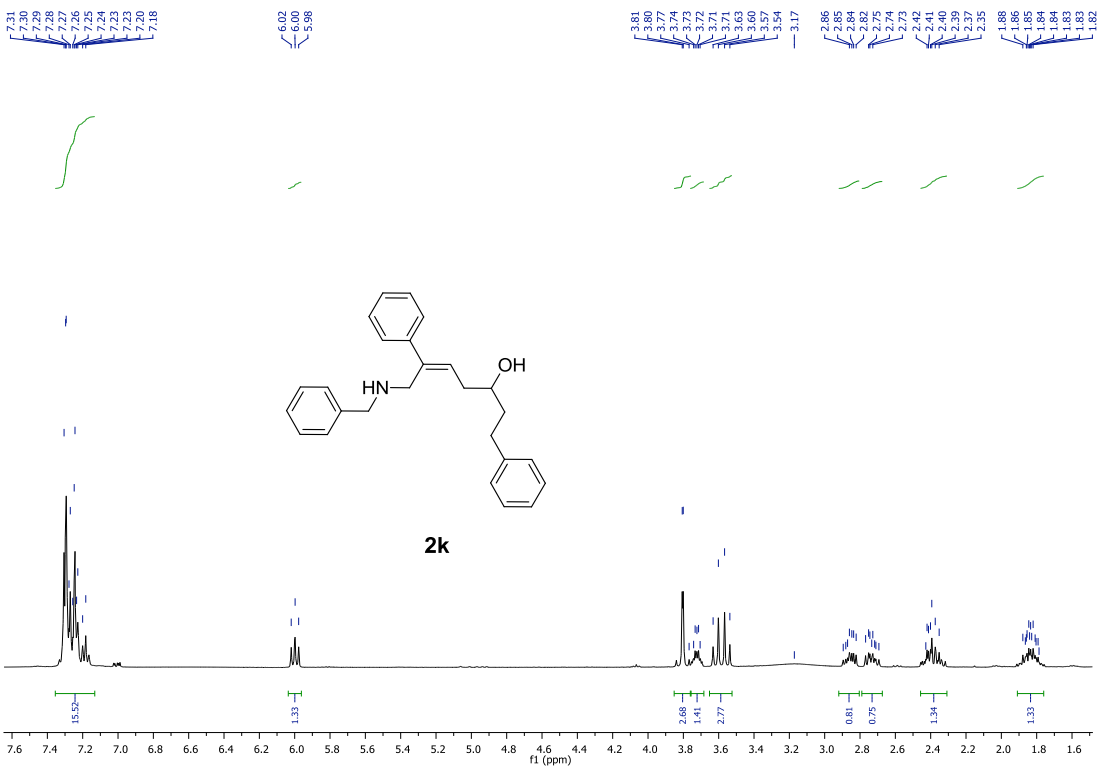
Cl
2j
f1 (ppm)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7.23
7.20
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6.00
5.98
3.81
3.80
3.77
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3.73
3.72
3.71
3.71
3.63
3.60
3.57
3.54
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2.86
2.85
2.84
2.82
2.75
2.74
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1.84
1.83
1.83
1.82
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OH
2k
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0.75
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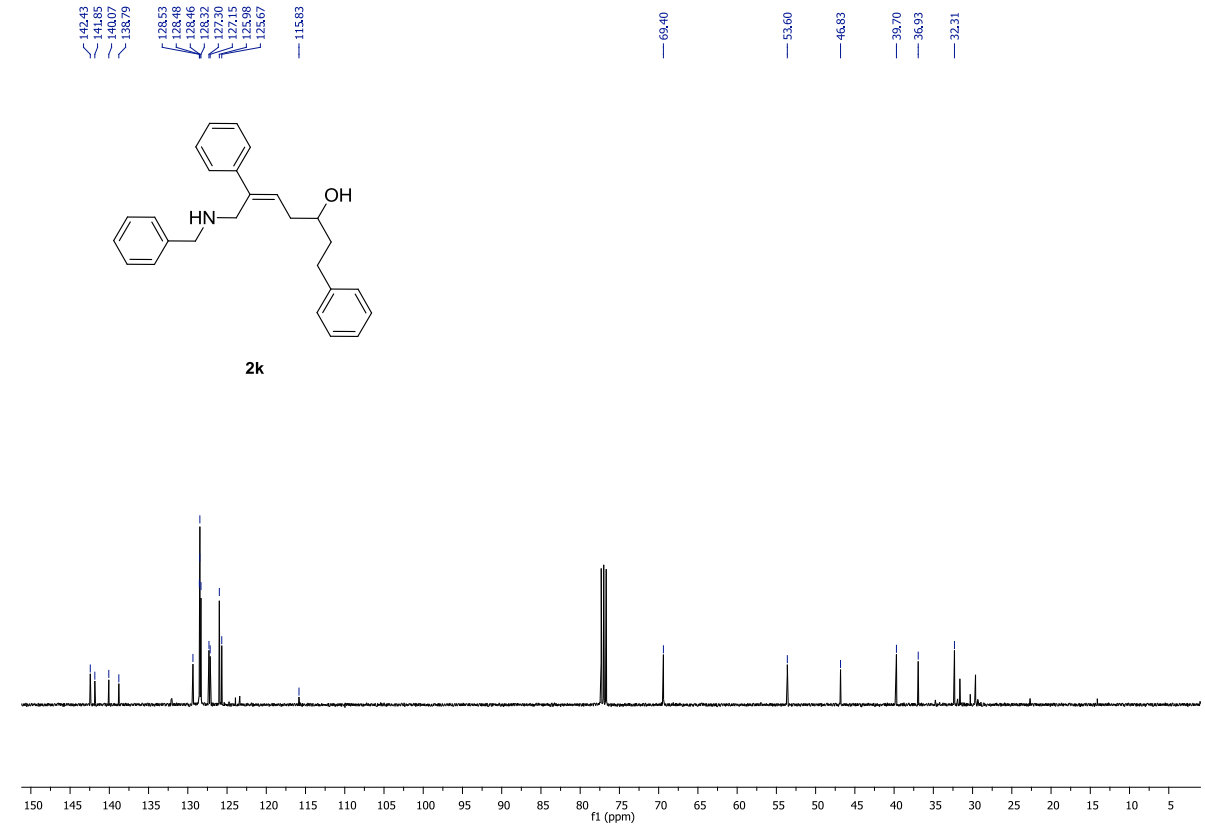
f1 (ppm)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69.40
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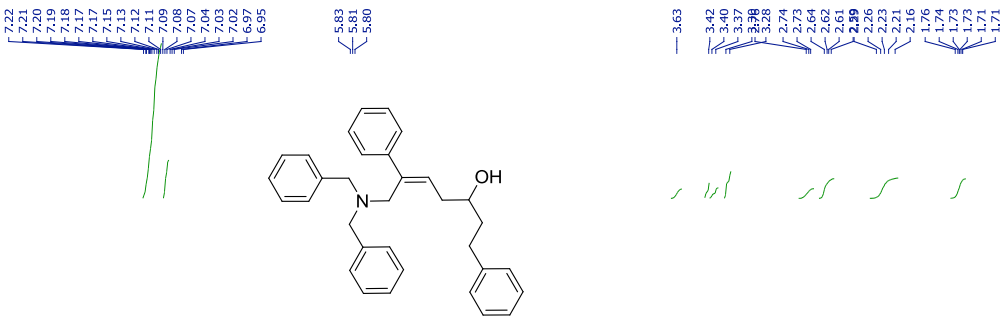
46.83
39.70
36.93
32.31
HN
OH
2k
f1 (ppm)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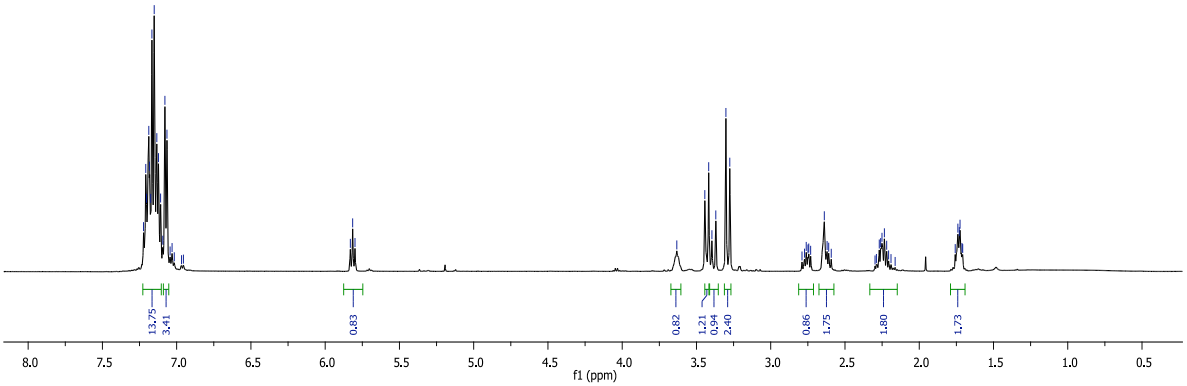
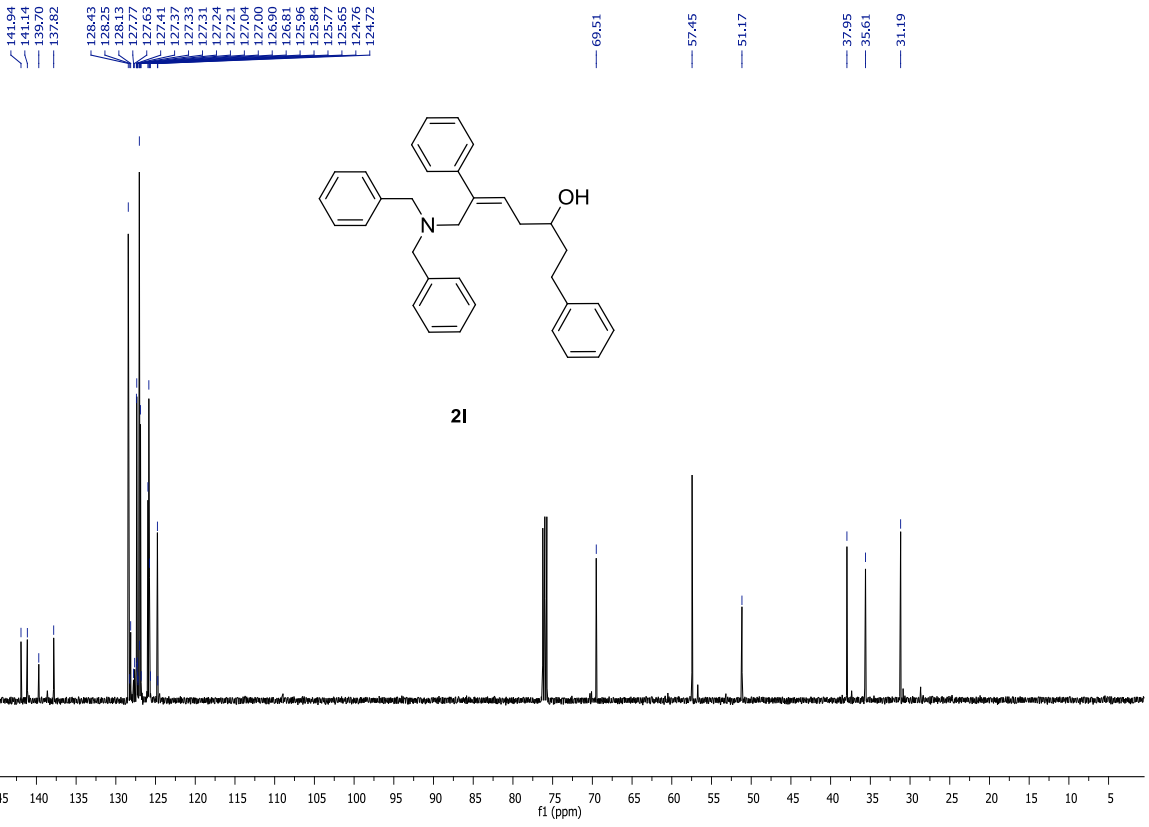
2.23
2.21
2.16
1.76
1.74
1.73
1.73
1.71
1.71
OH
N

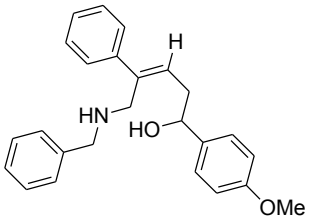
2l


13.75
3.41
0.83
0.82
1.21
0.94
2.40
0.86
1.75
1.80
1.73
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

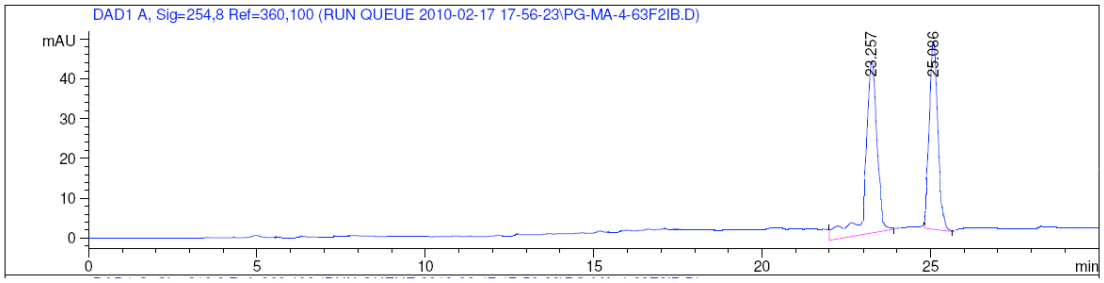

141.94
141.14
139.70
137.82
128.43
128.25
128.13
127.77
127.63
127.41
127.37
127.33
127.31
127.24
127.21
127.04
127.00
126.90
126.81
125.96
125.84
125.77
125.65
124.76
124.72
69.51
57.45
51.17
37.95
35.61
31.19
OH
N
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

2l

4. HPLC data



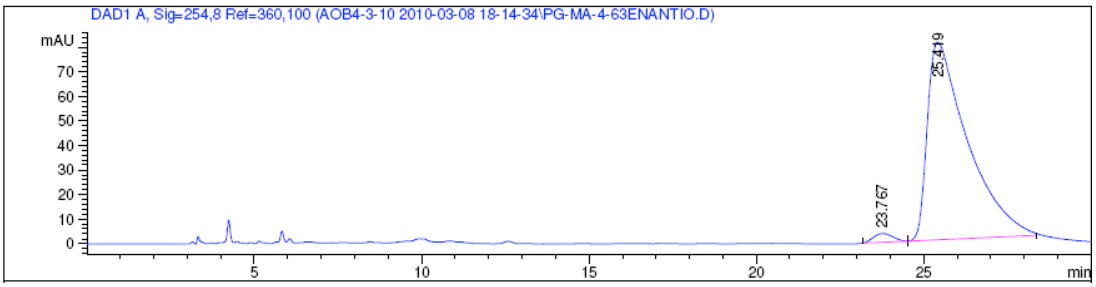
(Z)-5-(benzylamino)-1-(4-methoxyphenyl)-4-phenylpent-3-en-1-ol (racemic) 2a



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

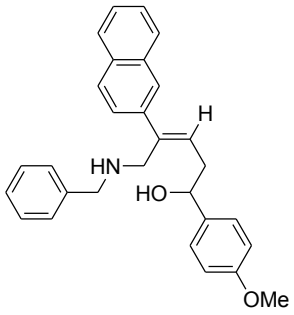
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.255	VB	0.3208	756.34857	34.90895	51.0834
2	25.086	VB	0.2878	724.26575	37.09712	48.9166
Totals :				1480.61432	72.00607	

(Z)-5-(benzylamino)-1-(4-methoxyphenyl)-4-phenylpent-3-en-1-ol (enantioenriched) 2a

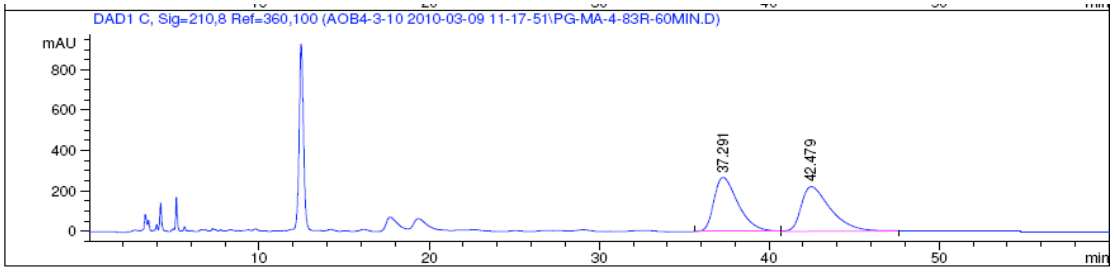


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.767	BV	0.5866	143.75719	3.56427	2.0953
2	25.419	VB	1.1670	6717.12891	80.53705	97.9047
Totals :				6860.88609	84.10132	



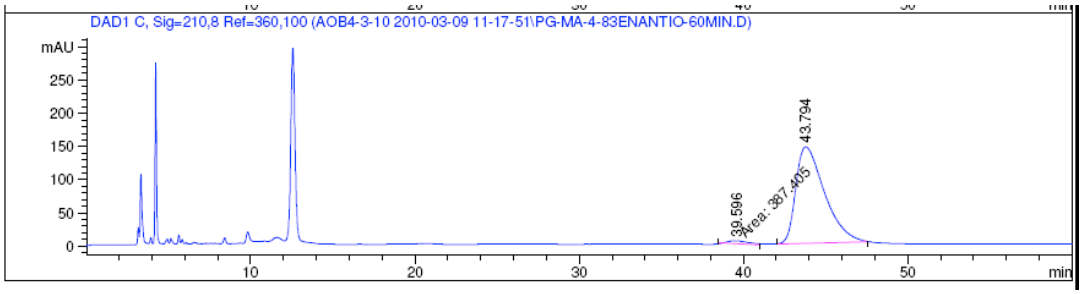
(Z)-5-(benzylamino)-1-(4-methoxyphenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (racemic) 2d



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

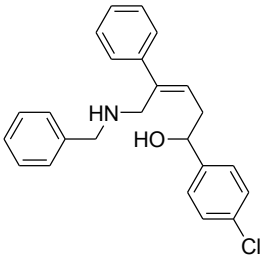
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.291	BV	1.5102	2.64849e4	268.17197	50.1907
2	42.479	VB	1.7941	2.62836e4	220.58551	49.8093
Totals :				5.27685e4	488.75748	

(Z)-5-(benzylamino)-1-(4-methoxyphenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (enantioenriched) 2d

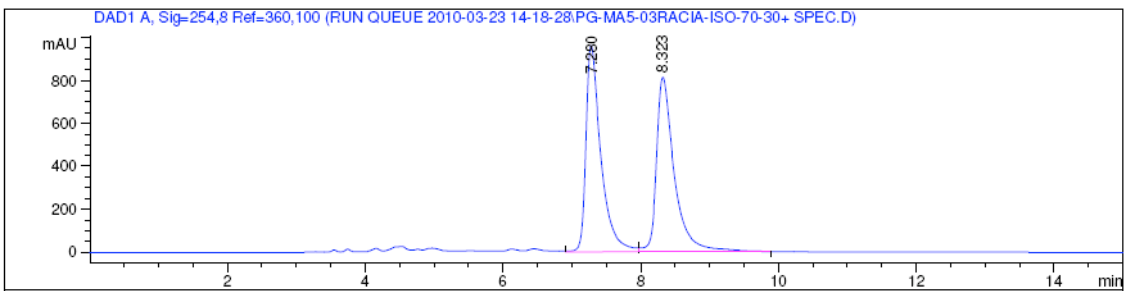


Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.596	MM	1.4811	387.40546	4.35930	2.1394
2	43.794	BB	1.8439	1.77211e4	145.19997	97.8606
Totals :				1.81085e4	149.55927	



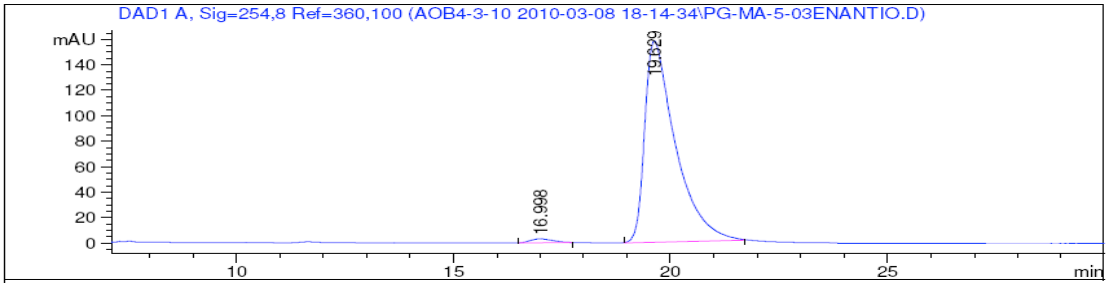
(Z)-5-(benzylamino)-1-(4-chlorophenyl)-4-phenylpent-3-en-1-ol (racemic) 2h



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

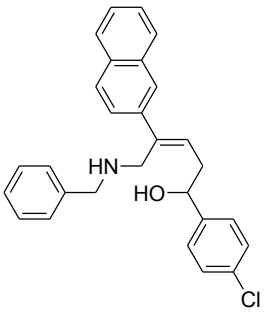
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.280	BV	0.2173	1.44246e4	960.11169	49.7564
2	8.323	VB	0.2611	1.45658e4	812.71686	50.2436
Totals :				2.89904e4	1772.82855	

(Z)-5-(benzylamino)-1-(4-chlorophenyl)-4-phenylpent-3-en-1-ol (enantioenriched) 2h

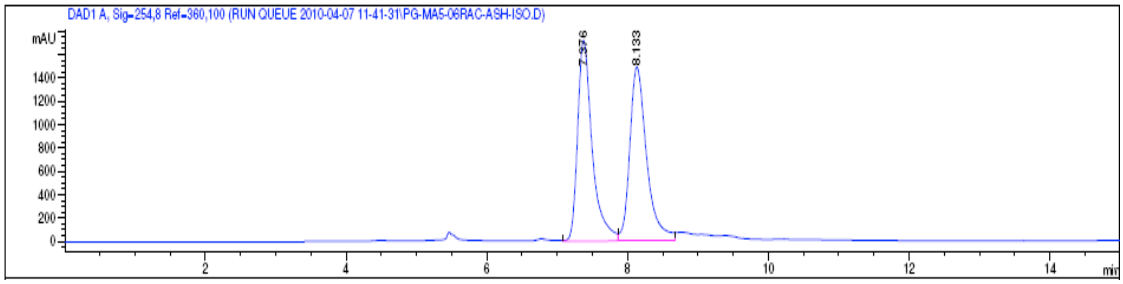


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.998	BB	0.5351	111.11090	3.06416	1.4042
2	19.629	BB	0.7171	7801.78857	158.26292	98.5958
Totals :				7912.89948	161.32708	



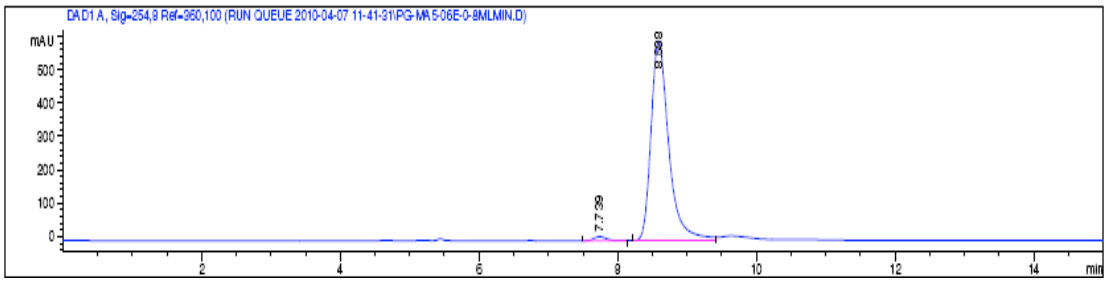
(Z)-5-(benzylamino)-1-(4-chlorophenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (racemic) 2i



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

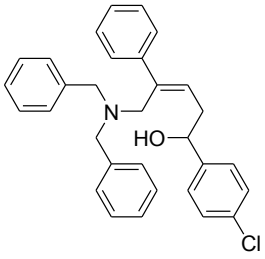
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.376	VV	0.2163	2.47538e4	1716.28833	49.7743
2	8.133	VV	0.2519	2.49783e4	1487.28857	50.2257
Totals :				4.97320e4	3203.57690	

(Z)-5-(benzylamino)-1-(4-chlorophenyl)-4-(naphthalen-2-yl)pent-3-en-1-ol (enantioenriched) 2i

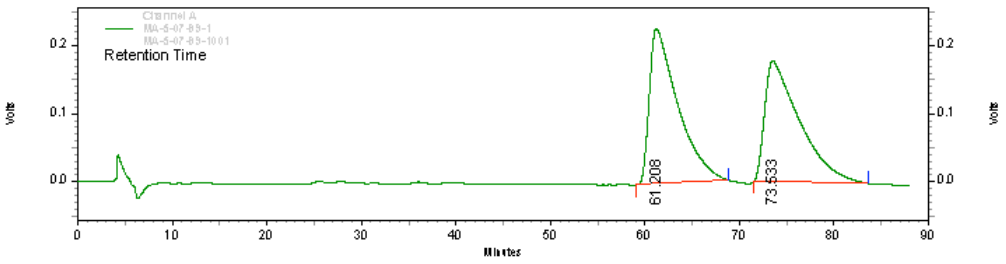


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.739	BB	0.2083	176.96802	13.04377	1.6368
2	8.588	BV	0.2696	1.06349e4	597.57434	98.3632
Totals :				1.08118e4	610.61811	



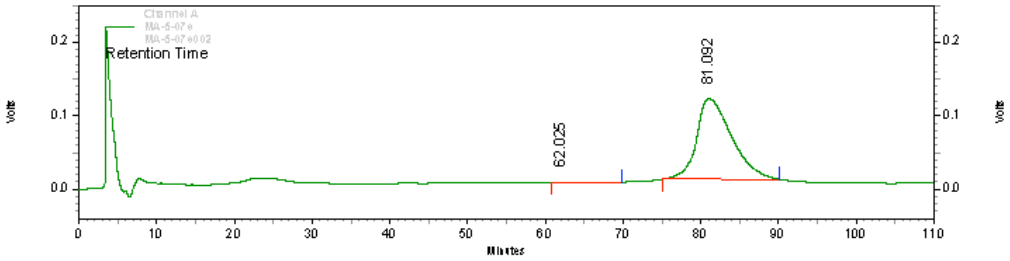
(Z)-1-(4-chlorophenyl)-5-(dibenzylamino)-4-phenylpent-3-en-1-ol (racemic) 2j



Detector A (254nm)

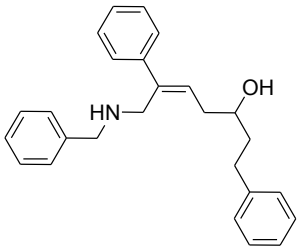
Pk#	Retention Time	Area	Area %	Height	Height %
1	61.208	47869140	51.178	228352	56.265
2	73.533	45665623	48.822	177496	43.735
Totals		93534763	100.000	405848	100.000

(Z)-1-(4-chlorophenyl)-5-(dibenzylamino)-4-phenylpent-3-en-1-ol (enantioenriched) 2j

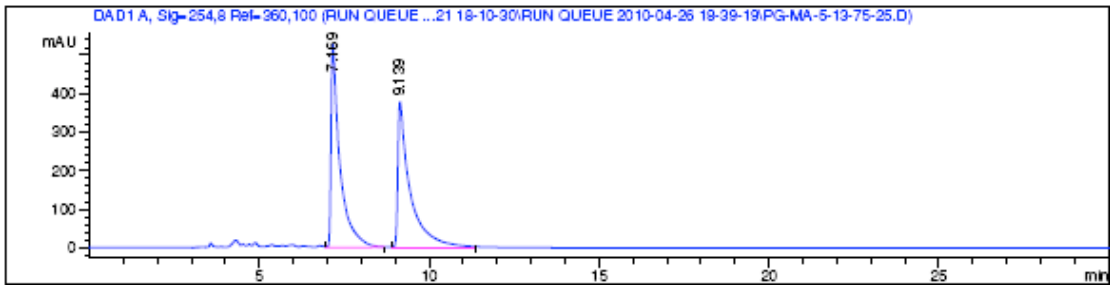


Detector A (254nm)

Pk#	Retention Time	Area	Area %	Height	Height %
1	62.025	66806	1.194	203	1.185
2	81.092	34449053	98.806	109345	98.815
Totals		34515859	100.000	109548	100.000



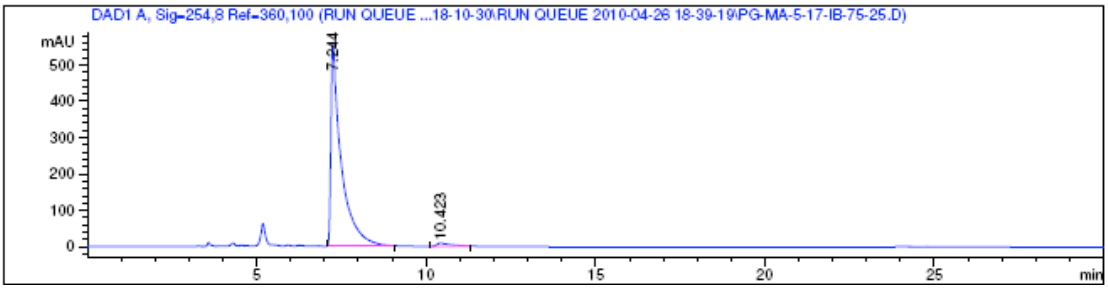
(Z)-7-(benzylamino)-1,6-diphenylhept-5-en-3-ol (racemic) 2k



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.169	VB	0.2388	9463.00098	528.78851	50.2987
2	9.139	BB	0.3247	9350.61035	377.85101	49.7013
Totals :				1.88136e4	906.63953	

(Z)-7-(benzylamino)-1,6-diphenylhept-5-en-3-ol (enantioenriched) 2k



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.244	BB	0.2756	1.17993e4	560.53143	97.7692
2	10.423	BB	0.4291	269.22833	8.60382	2.2308
Totals :				1.20686e4	569.13525	

5. References for Supporting Information

[1] Coeffard, V.; Aylward, M.; Guiry, P. J. *Angew. Chem. Int. Ed.* 2009, *48*, 9152-9155.

[2] Lee, A. S.-Y.; Chu, S.-F.; Chang, Y.-T.; Wang, S.-H. *Tetrahedron. Lett.* 2004, *45*, 1551-1553.

[3] Kuang, J.; Ma, S. *J. Org. Chem.* 2009, *74*, 1763-1765.