Supporting Information for

Diastereoselective One-Pot Synthesis of 7- and 8-Substituted 5-Phenylmorphans[∞]

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[∞]Probes for Narcotic Receptor Mediated Phenomena. 45

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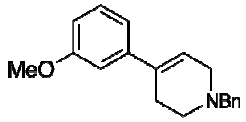
Contents:

General methods

General methods: All chemicals and solvents were used directly without further purification. *n*-BuLi was titrated and THF was dried over molecular sieves before use. Chemicals were purchased from Sigma-Aldrich or Alfa Aesar. NMR experiments were performed using $CDCl_3$ with $CHCl_3$ (δ 7.24) as an internal standard. 3-Bromo and 4-chlorophenyl allyl bromides[1] **5c-d**, 1-(bromomethyl)cyclohex-1-ene[2] **5g,** and (2-(bromomethyl)allyloxy)(*tert*-butyl)diphenyl-silane[3] **5m**, and 1-benzyl-4-(2,5-dimethoxyphenyl)-1,2,3,6-tetrahydropyridine[4] **3iii** were prepared by reported procedures. Proton and carbon nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard on a Varian Gemini-300 spectrometer and a Bruker DMX500 wide-bore spectrometer ((proton frequency 500.13 MHz) running XWINNMR v3.1, carbon 125.757) in $CDCl_3$ (unless otherwise noted) with the values given in ppm (TMS as internal standard) and *J* (Hz) assignments of ^{1}H resonance coupling. Mass spectra (HRMS) were recorded on a VG 7070E spectrometer or a JEOL SX102a mass spectrometer. Thin layer chromatography (TLC) analyses were carried out on Analtech silica gel GHLF 0.25 mm plates using various gradients of $CHCl_2$/MeOH containing 1% NH_4OH or gradients of EtOAc:*n*-hexane. Visualization was accomplished under UV light or by staining in an iodine chamber. Flash column chromatography was performed with Fluka silica gel 60 (mesh 220-400). Atlantic Microlabs, Inc., Norcross, GA or Micro-Analysis, Inc, Wilmington, DE, performed elemental analyses, and the results were within ±0.4% of the theoretical values.

1-Benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine (3ii)

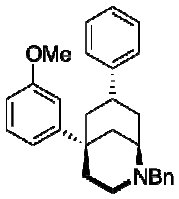


1-Benzyl-4-piperidone (50 g, 0.264 mol) was added dropwise to a stirred solution of 3-methoxyphenyl magnesium bromide (1 M in THF, 528 mL, 0.528 mol) in THF (500 mL) at 0 °C. The resulting mixture was stirred for 1.5 h under Ar atmosphere. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with Et_2O (500 mL×2). The combined organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography to yield the colorless oil **3ii** (79 g, >99%). ^{1}H NMR δ ($CDCl_3$): 7.37-7.26 (m, 6H), 7.10-7.07 (m, 2H), 6.80-6.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.79 (s, 3H), 3.58 (s, 2H), 2.78-2.76 (d, *J* = 9.0 Hz, 2H), 2.50-2.45 (tt, *J* = 0.5, 12.0 Hz, 2H), 2.18-2.12 (dt, *J* = 4.0, 13.0 Hz, 2H), 1.73-1.70 (d, *J* = 12.0 Hz, 2H); ^{13}C NMR δ ($CDCl_3$): 159.7, 150.6, 138.5, 129.4, 128.3, 127.1, 117.1, 112.2, 110.8, 71.4, 63.4, 55.3, 49.5, 38.6. The crude

alcohol (79 g, 0.26 mol) was dissolved in toluene (500 mL) and the solution was treated with *p*-TsOH•H_2O (74.1 g, 0.39 mol). The resulting mixture was refluxed for 8 h using a Dean-Stark apparatus to remove H_2O. After the reaction was cooled to r.t., the mixture was basified with 3 N NaOH and the product was extracted with Et_2O (500 mL×2). The combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography to yield **3ii** as a colorless oil (62 g, 85%). ^{1}H NMR δ ($CDCl_3$): 7.39-7.30 (m, 6H), 6.99-6.93 (m, 2H), 6.79-6.78 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.07 (br s, 1H), 3.79 (s, 3H), 3.63 (s, 2H), 2.71-2.69 (m, 2H), 2.54 (br s, 2H); ^{13}C NMR δ ($CDCl_3$): 159.7, 142.6, 138.4, 135.0, 129.3, 128.4, 127.2, 122.4, 117.6, 112.3, 111.0, 62.9, 55.3, 53.5, 50.1, 28.3.

1) Entry 1, Table 1, general procedure under Evans et al.,[5] conditions using HCO_2H/H_3PO_4)

2-Benzyl-5-(3-methoxyphenyl)-7-phenyl-2-azabicyclo[3.3.1]nonane (8b)



To a stirred solution of 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (3.3 g, 12.1 mmol) in THF (50 mL) at -78 °C was added pre-titrated 1.89 M *n*-BuLi in *n*-hexane (7.0 mL, 13.3 mmol) dropwise. The internal temperature was maintained at less than -70 °C during addition. The mixture was stirred for 15 min and warmed to -15 °C. After 15 min stirring at -15 °C, (3-bromoprop-1-en-2-yl)benzene, **5b** (3.1 g, 15.7 mmol) in THF (10 mL) was added slowly, maintaining the internal temperature at less than -10 °C. Then the mixture was slowly warmed to r.t. and stirred overnight. The reaction was quenched with 50 mL of brine and the organic layer was separated. The product was extracted with EtOAc (50 mL ×2). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated. The crude product was dissolved in HCO_2H/H_3PO_4 (1:1, 20 mL). The resulting solution was stirred at r.t. for 7 d. The mixture was poured into ice-water (20 mL), and basified with 40% NaOH to pH 8. The product was extracted with EtOAc (10 mL×3). The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The resulting cyclized imine was dissolved in $MeOH/CH_2Cl_2$ (1:1, 20 mL). The solution was treated with $NaBH_4$ (2.7 g, 60.5 mmol), and the mixture was stirred at r.t. for 8 h. The reaction was quenched with H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (200 mL×2). The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The crude

product **8b** was purified by column chromatography (2.3 g, 48%, pale yellow oil). All spectral data was identical to the sample obtained by *p*-TsOH cyclization (entry 2, Table 1).

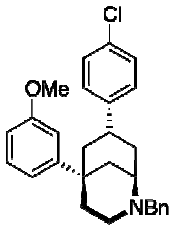
2) Entry 2, Table 1 & entry 1, Table 2, general procedure with optimized cyclization conditions using *p*-TsOH)

To a stirred solution of 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (1.0 g, 3.58 mmol) in THF (10 mL) at -78 ^{o}C was added pre-titrated 1.89 M *n*-BuLi in *n*-hexane (2.2 ml, 3.94 mmol) dropwise. The internal temperature was maintained at less than -70 ^{o}C during the addition. The mixture was stirred for 15 min then warmed to -15 ^{o}C. After 15 min stirring at -15 ^{o}C, (3-bromoprop-1-en-2-yl)benzene, **5b** (0.92 g, 4.66 mmol) in THF (5 mL) was added slowly to keep the internal temperature below -10 ^{o}C. Then the mixture was slowly warmed to r.t. and stirred overnight. The reaction was quenched with 10 mL of brine and the organic layer was separated. The product was extracted with EtOAc (10 mL×2). The combined organic solution was washed with brine, dried over K_2CO_3, filtered, and evaporated. The crude product was dissolved in toluene (10 mL) and treated with *p*-TsOH·H_2O (1.36 g, 7.16 mmol). The resulting solution was refluxed for 2 d. The reaction was cooled to r.t., and then diluted with MeOH/CH_2Cl_2 (1:1, 20 mL). The resulting solution with the cyclized imine was directly reduced by adding $NaBH_4$ (0.68 g, 17.9 mmol), and the mixture was stirred at r.t. for 3 h. The reaction was quenched with H_2O (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (20 mL×2). The combined organics were washed with brine, dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by column chromatography (0.56 g, 56%, pale yellow oil). ^{1}H NMR δ ($CDCl_3$): 7.39-7.14 (m, 11H), 6.95-6.92 (m, 2H), 6.71-6.69 (dd, *J* = 1.5, 4.5 Hz, 1H), 3.81-3.74 (m, 5H), 3.72-3.56 (m, 1H), 3.23 (br s, 1H), 3.16-3.10 (dt, *J* = 5.0, 11.0 Hz, 1H), 2.92-2.87 (m, 1H), 2.38-2.14 (m, 4H), 2.01-1.91 (m, 2H), 1.70-1.65 (t, *J* = 12.5 Hz, 1H), 1.50-1.44 (dt, *J* = 3.5, 12.5 Hz, 1H); ^{13}C NMR δ ($CDCl_3$): 159.6, 153.6, 147.5, 139.7, 129.3, 128.9, 128.5, 128.3, 127.1, 127.0, 126.3, 117.4, 111.5, 110.5, 60.4, 55.2, 52.8, 52.7, 49.4, 47.4, 40.2, 38.4, 37.4, 36.4, 33.9; IR cm^{-1} (neat): 3083.2, 3026.7, 2921.0, 2833.0, 1600.3, 1581.6, 1492.9, 1452.9, 1289.3, 1264.8, 1167.3, 1051.2, 1026.5; HRMS calcd for $C_{28}H_{32}NO$ ($M+H^+$), 398.2482; found, 398.2484.

3) Entry 3-5, Table 1

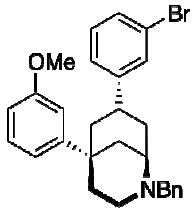
Other than the cyclization conditions, the reaction conditions were the same as the general conditions used in entry 2, Table 1.

2-Benzyl-7-(4-chlorophenyl)-5-(3-methoxyphenyl)-2-azabicyclo[3.3.1]nonane (8c, Entry 2, Table 2)



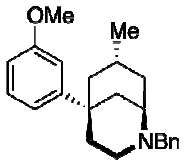
Using 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (0.5 g, 1.79 mmol) and 1-(3-bromoprop-1-en-2-yl)-4-chlorobenzene, **5c** (0.54 g, 2.34 mmol), **8c** was obtained as a pale yellow oil (0.38 g, 49%). ^{1}H NMR δ ($CDCl_3$): 7.39-7.15 (m, 10H), 6.95-6.90 (m, 2H), 6.74-6.71 (d, *J* = 10.5 Hz, 1H), 3.83-3.76 (m, 5H), 3.60-3.55 (m, 1H), 3.24 (br s, 1H), 3.13-3.08 (dt, *J* = 5.0, 6.0 Hz, 1H), 2.92-2.88 (m, 1H), 2.34-2.15 (m, 4H), 2.02-1.90 (m, 2H), 1.64-1.59 (t, *J* = 13.0 Hz, 1H), 1.45-1.39 (dt, *J* = 7.5, 12.5 Hz, 1H); ^{13}C NMR δ ($CDCl_3$): 159.8, 153.5, 146.0, 139.7, 131.8, 129.4, 128.9, 128.7, 128.5, 128.4, 127.1, 117.4, 111.6, 110.6, 60.5, 55.4, 52.8, 49.3, 47.3, 39.6, 38.3, 37.4, 36.4, 34.1; IR cm^{-1} (neat): 3060.9, 3027.2, 2925.4, 1601.0, 1581.7, 1491.4, 1288.3, 1264.2, 1167.3, 1092.5, 1051.7, 1027.3, 1012.8; HRMS calcd for $C_{28}H_{31}NOCl$ ($M+H^+$), 432.2081; found, 432.2094.

2-Benzyl-7-(3-bromophenyl)-5-(3-methoxyphenyl)-2-azabicyclo[3.3.1]-nonane (8d - entry 3, Table 2)



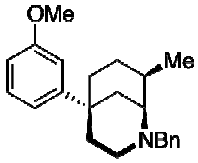
Using 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (0.5 g, 1.79 mmol) and 1-bromo-3-(3-bromoprop-1-en-2-yl)benzene, **5d** (0.64 g, 2.33 mmol), **8d** was obtained as a pale yellow oil (0.35 g, 41%). ^{1}H NMR δ ($CDCl_3$): 7.39-7.10 (m, 16H), 6.74-6.67 (m, 2H), 3.84-3.78 (m, 5H), 3.44-3.41 (d, *J* = 13.0 Hz, 1H), 3.29-3.26 (d, *J* = 13.0 Hz, 1H), 2.57-2.54 (m, 1H), 2.03-1.66 (m, 5H), 1.36-1.25 (m, 4H); ^{13}C NMR δ ($CDCl_3$): 159.9, 151.0, 139.1, 131.8, 129.5, 129.4, 128.9, 128.5, 128.4, 127.1, 124.8, 113.1, 110.2, 108.1, 61.6, 60.2, 55.6, 48.1, 47.4, 36.2, 36.0, 35.8, 26.5, 23.8; IR cm^{-1} (neat): 3061.2, 3026.6, 2953.4, 2928.1, 1063.5, 1585.5, 1476.5, 1344.5, 1282.4, 1256.0, 1071.6, 1029.4; HRMS calcd for $C_{28}H_{31}NOBr$ ($M+H^+$), 476.1573; found, 476.1589.

2-Benzyl-5-(3-methoxyphenyl)-7-methyl-2-azabicyclo[3.3.1]nonane (8e - entry 4, Table 2)



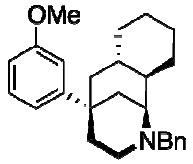
Using 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (4 g, 14.3 mmol) and 3-bromo-2-methylprop-1-ene, **5e** (2.53 g, 18.7 mmol), **8e** was obtained as a pale yellow oil (3.15 g, 64%). ^{1}H NMR δ ($CDCl_3$): 7.44-7.27 (m, 6H), 7.11-6.99 (dd, *J* = 3.0, 0.5 Hz, 1H), 6.96 (s, 1H), 6.79-6.77 (d, *J* = 8.0 Hz, 1H), 3.84-3.72 (m, 5H), 3.17 (br s, 1H), 3.08-3.02 (dt, *J* = 12.0, 5.0 Hz, 1H), 2.89-2.85 (m, 1H), 2.40-2.28 (m, 2H), 2.18-2.07 (m, 3H), 1.99-1.92 (m, 1H), 1.85-1.82 (d, *J* = 11.5 Hz, 1H), 1.24-1.19 (t, *J* = 12.5 Hz, 1H), 1.10-0.92 (m, 4H); ^{13}C NMR δ ($CDCl_3$): 159.7, 154.0, 139.9, 129.2, 128.9, 128.3, 126.9, 117.4, 111.6, 110.4, 60.2, 55.3, 52.9, 49.5, 48.3, 39.2, 37.3, 36.4, 34.5, 29.0, 24.8; IR cm^{-1} (neat): 3061, 3026, 2948, 2919, 2835, 1607, 1601, 1493, 1485, 1432, 1366, 1292, 1258, 1171, 1052, 1027; HRMS calcd for $C_{23}H_{30}NO$ ($M+H^+$), 336.2326; found, 336.2327.

2-Benzyl-5-(3-methoxyphenyl)-8-methyl-2-azabicyclo[3.3.1]nonane (8f, entry 5, Table 2)



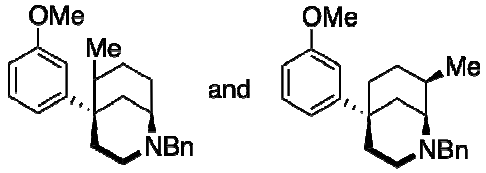
Using 1-benzyl-4-(3-methoxyphenyl)-1,2,3,6-tetrahydropyridine, **3ii** (4 g, 14.3 mmol) and (*E*)-1-bromobut-2-ene, **5f** (2.53 g, 18.7 mmol), **8f** was obtained as a pale yellow oil (3.1 g, 64%). ^{1}H NMR δ ($CDCl_3$): 7.43-7.23 (m, 6H), 6.94-6.90 (m, 2H), 6.73-6.71 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.91-3.73 (m, 5H), 2.92-2.86 (m, 2H), 2.54-2.50 (m, 1H), 2.42-2.38 (d, *J* = 15.5 Hz, 1H), 2.00-1.89 (m, 4H), 1.57-1.55 (m, 4H), 1.10-1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR δ ($CDCl_3$): 159.6, 155.3, 141.0, 129.2, 128.4, 128.3, 126.8, 117.7, 111.8, 110.1, 63.1, 59.2, 55.3, 46.1, 40.6, 37.7, 36.4, 35.1, 34.9, 28.7, 19.5; IR cm^{-1} (neat): 3061.0, 3026.5, 2928.4, 2866.9, 1607.2, 1582.4, 1493.5, 1452.9, 1291.7, 1264.3, 1166.7, 1051.0; HRMS calcd for $C_{23}H_{30}NO$ ($M+H^+$), 336.2315; found, 336.2327.

2-Benzyl-5-(3-methoxyphenyl)-7,8-cyclohexyl-2-azabicyclo[3.3.1]nonane (8g, entry 6, Table 2)



Using **3ii** (2.0 g, 7.1 mmol) and 1-(bromomethyl)cyclohex-1-ene **5g** (1.6 g, 9.1 mmol), **8g** was obtained as a pale yellow oil (1.4 g, 52%). ^{1}H NMR δ ($CDCl_3$): 7.46-7.25 (m, 6H), 6.97-6.93 (m, 2H), 6.76-6.74 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.93-3.73 (m, 5H), 2.93 (br s, 1H), 2.87-2.82 (m, 1H), 2.59-2.54 (m, 1H), 2.44-2.41 (d, *J* = 12.5 Hz, 1H), 2.13-2.04 (m, 2H), 1.99-1.60 (m, 8H), 1.43-1.19 (m, 3H), 1.06-0.92 (m, 2H); ^{13}C NMR δ ($CDCl_3$): 159.6, 155.4, 140.9, 129.2, 128.4, 128.3, 126.8, 117.6, 111.8, 110.0, 63.4, 59.5, 55.3, 50.2, 46.1, 37.3, 36.1, 36.0, 35.9, 35.6, 31.8, 30.6, 26.9, 22.9. IR cm^{-1} (neat): 3.60.7, 3026.6, 2920.3, 2849.0, 1606.3, 1581.9, 1485.5, 1450.2, 1291.0, 1256.8, 1164.5, 1050.9; HRMS calcd for $C_{26}H_{34}NO$ (M+H$^+$), 376.2628; found, 376.2640).

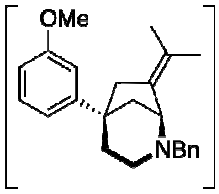
Synthesis of 2-benzyl-5-(3-methoxyphenyl)-6-methyl-2-azabicyclo[3.3.1]nonane 8h (entry 7, Table 2)



8h **8f**

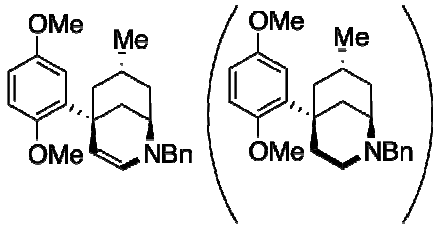
Using **3ii** (4.0 g, 14.3 mmol) and 3-chlorobut-1-ene **5h** (1.68 g, 18.7 mmol), an inseparable diastereomeric mixture **of 8h** (0.15 g, 60%) and **8f** (0.72 g, 20%) was obtained as pale yellow oil. All spectral data of the minor product was matched with **8f** (entry 5, Table 2). **8h** (inseparable diastereomeric mixture), ^{1}H NMR δ ($CDCl_3$): 7.36-7.15 (m, 6H), 7.02-6.69 (m, 3H), 3.78-3.68 (m, 5H), 3.02-2.77 (m, 3H), 2.31-1.46 (m, 9H), 0.66-0.58 (d, *J* = 7.0 Hz, 3H, diastereomeric ratio: 1:1.5); ^{13}C NMR δ ($CDCl_3$): 159.7, 159.4, 153.4, 152.2, 140.0, 139.9, 129.1, 128.9, 128.7, 126.9, 118.6, 117.8, 112.9, 111.8, 110.0, 60.3, 59.9, 55.3, 55.2, 52.5, 52.3, 49.8, 49.3, 41.3, 41.2, 39.6, 39.5, 38.5, 38.4, 32.5, 32.2, 29.7, 17.8, 17.7, 17.2, 17.1; IR cm^{-1} (neat): 3061.4, 2932.2, 2832.2, 1600.6, 1581.6, 1493.1, 1453.5, 1291.4, 1257.9, 1166.0, 1045.9; HRMS calcd for $C_{23}H_{30}NO$ (M+H$^+$), 336.2314; found, 336.2327.

2-Benzyl-5-(3-methoxyphenyl)-7-(propan-2-ylidene)-2-azabicyclo[3.2.1]octane (8i, entry 8, Table 2)



Using **3ii** (0.20 g, 0.72 mmol) and 1-bromo-3-methylbut-2-ene **5i** (0.14 g, 0.94 mmol), **8i** (0.15 g, 60%) was obtained as pale yellow oil. ^{1}H NMR δ ($CDCl_3$): 7.39-7.21 (m, 6H), 6.89-6.84 (m, 2H), 6.74-6.72 (dd, *J* = 2.0, 9.0 Hz, 1H), 3.74-3.70 (m, 5H), 3.39-3.36 (d, *J* = 13.5 Hz, 1H), 2.67-2.64 (m, 1H), 2.48-2.27 (m, 3H), 2.14-2.12 (d, *J* = 9.5 Hz, 1H), 1.87-1.82 (m, 2H), 1.71 (s, 6H), 1.60-1.57 (d, *J* = 12.5Hz, 1H); ^{13}C NMR δ ($CDCl_3$): 159.7, 151.5, 139.8, 133.9, 129.3, 128.8, 128.3, 126.8, 126.2, 118.5, 112.4, 110.7, 61.5, 60.5, 55.3, 47.4, 45.9, 43.8, 41.6, 40.2, 22.4, 21.0; IR cm^{-1} (neat): 3061.0, 3027.2, 2912.8, 2851.9, 2832.6, 2801.2, 1602.0, 1581.9, 1493.5, 1430.7, 1290.6, 1243.7, 1170.2, 1051.2, 1023.9; HRMS calcd for $C_{24}H_{30}NO$ ($M+H^+$), 348.2322; found, 348.2327.

2-Benzyl-5-(2,5-dimethoxyphenyl)-7-methyl-2-azabicyclo[3.3.1]non-3-ene 7j and 2-benzyl-5-(3-methoxyphenyl)-6-methyl-2-azabicyclo[3.3.1]nonane (8j, entry 9, Table 2)

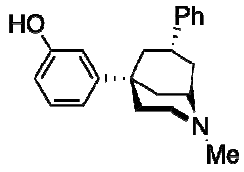


7j **8j**

Using **3iii**[4] (1.6 g, 5.0 mmol) and 3-bromo-2-methylprop-1-ene, **5e** (0.65 ml, 0.65 mmol), the enamine **7j** (0.68 g, 36%) was obtained as pale yellow oil. ^{1}H NMR δ ($CDCl_3$): 7.34-7.30 (m, 5H), 6.94-6.93 (d, *J* = 3.0 Hz, 1H), 6.85-6.83 (d, *J* = 9.0 Hz, 1H), 6.73-6.70 (dd, *J* = 2.5, 9.0 Hz, 1H), 6.22-6.20 (d, *J* = 8.0 Hz, 1H), 4.76-4.74 (dd, *J* = 1.5, 8.0 Hz, 1H), 4.17 (s, 3H), 3.82 (s, 3H), 3.77 (s, 1H), 3.36 (br s, 1H), 2.41-2.38 (m, 1H), 2.10-2.03 (m, 2H), 1.95-1.86 (m, 2H), 1.18-1.13 (t, *J* = 12.0 Hz, 1H), 1.05-1.00 (t, *J* = 10.5 Hz, 1H), 0.92-0.91 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR δ ($CDCl_3$): 153.6, 152.9, 139.9, 138.5, 135.7, 129.4, 128.5, 128.4, 127.7, 127.2, 127.1, 113.8, 112.5, 110.1, 100.0, 56.9, 55.8, 55.7, 51.5, 46.9, 41.4, 38.1, 35.3, 26.1, 22.2; IR cm^{-1} (neat): 3060.5, 2993.7, 2925.8, 2832.3, 1666.6, 1635.1, 1492.9, 1222.1, 1048.1.; HRMS calcd for $C_{24}H_{30}NO_2$ ($M+H^+$), 364.2267; found, 364.2277). The enamine **7j** was further reduced to get the desired amine **8j**. ^{1}H NMR δ ($CDCl_3$): 7.39-7.23 (m, 5H), 6.81-6.79 (m, 2H), 6.69-6.67 (m, 1H), 3.78-3.68 (m, 8H), 3.13 (br s, 1H), 2.94-2.88 (dt, *J* = 5.0, 5.5 Hz, 1H), 2.76-2.73 (m, 1H), 2.63-2.59 (m, 1H), 2.35-2.29 (m, 1H), 2.20-2.11 (m, 2H), 1.77-1.71 (m, 2H), 1.30-1.25 (m, 1H), 0.98-

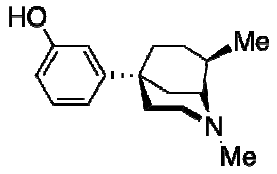
0.86 (m, 4H); ^{13}C NMR δ ($CDCl_3$): 153.6, 152.8, 141.1, 140.2, 129.0, 128.3, 126.8, 113.2, 112.6, 110.0, 60.6, 55.8, 55.7, 53.4, 48.9, 44.5, 38.6, 36.7, 35.8, 34.3, 28.0, 24.4; IR cm^{-1} (neat): 2947.7, 2832.6, 1585.5, 1494.6, 1463.3, 1280.0, 1223.7, 1052.5, 1028.4; HRMS calcd for $C_{24}H_{32}NO_2$ (M+H), 366.2423; found, 366.2433.

3-(2-Methyl-7-phenyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol (9b)



Using the reported 3-step procedure,[6] *N*-Bn compound **8b** (0.25 g, 0.63 mmol) was converted into the phenolic *N*-Me compound **9b** (0.19 g, 96%). ^{1}H NMR δ ($CDCl_3$): 9.50 (br s, 1H), 7.26-7.06 (m, 6H), 6.77-6.74 (m, 2H), 6.59-6.57 (d, *J* = 9.5 Hz, 1H), 3.43-3.37 (m, 1H), 3.23 (br s, 1H), 3.15-3.09 (dt, *J* = 5.0, 12.0 Hz, 1H), 2.97-2.93 (m, 1H), 2.46 (s, 3H), 2.40-2.37 (d, *J* = 12.0 Hz, 1H), 2.25-2.20 (t, *J* = 7.5 Hz, 2H), 2.07-1.91 (m, 3H), 1.67-1.61 (t, *J* = 13.0 Hz, 1H), 1.54-1.48 (dt, *J* = 3.0, 13.0 Hz, 1H); ^{13}C NMR δ ($CDCl_3$): 157.3, 152.5, 146.9, 129.5, 128.6, 126.9, 126.4, 116.1, 113.6, 112.7, 54.7, 51.3, 46.8, 42.8, 40.2, 38.1, 36.5, 35.5, 32.1; IR cm^{-1} (neat): 3060.4, 3027.3, 2934.6, 1598.0, 1582.1, 1492.4, 1451.8, 1376.6, 1279.4, 1245.5.; HRMS calcd for $C_{21}H_{26}NO$ ($M+H^+$), 308.2011; found, 308.2014. The title compound **9b** was converted into its HBr salt and the salt crystallized in MeOH/EtOAc (0.14 g); mp 268.8-270.1 ^{o}C; Anal. calcd for $C_{21}H_{26}BrNO$ + 0.3 M H_2O: C, 64.06; H, 6.81; N, 3.56. Found: C, 63.84; H, 6.73; N, 3.54.

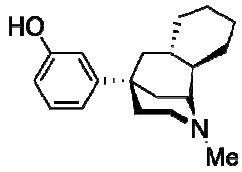
3-(2-Methyl-8-methyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol (9f)



Using the reported 3-step procedure,[6] **8f** (0.25 g, 0.75 mmol) was converted into the phenolic *N*-Me **9f** (0.17 g, 92%). ^{1}H NMR δ ($CDCl_3$): 7.16-7.13 (t, *J* = 8.0 Hz, 1H), 6.85-6.83 (d, *J* = 8.0 Hz, 1H), 6.76-6.75 (d, *J* = 4.0 Hz, 1H), 6.63-6.61 (d, *J* = 8.0 Hz, 1H), 3.02-2.97 (m, 1H), 2.77 (br s, 1H), 2.68-2.63 (m, 1H), 2.51 (m, 3H), 2.33-2.29 (m, 1H), 1.99-1.81 (m, 4H), 1.58-1.50 (m, 4H), 1.07-1.06 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR δ ($CDCl_3$): 156.3, 155.0, 129.4, 117.0, 113.0, 112.8, 60.6, 49.7, 46.6, 40.2, 37.6, 36.1, 35.3, 34.4, 29.1, 19.8.; IR cm^{-1} (neat): 3049.9, 2929.4, 2868.7, 1598.6, 1583.2, 1450.4, 1273.4, 1166.3; HRMS calcd for $C_{16}H_{24}NO$ ($M+H^+$), 246.1855; found, 246.1858. The base **9f** was converted into its HBr salt and the salt crystallized in EtOH/EtOAc

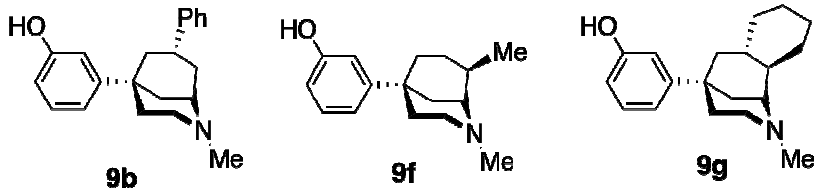
(0.13 g); mp 200.4-201.8 °C; Anal. calcd for $C_{16}H_{24}BrNO$: C, 58.90; H, 7.41; N, 4.29. Found: C, 58.62; H, 7.20; N, 4.21.

3-(2-Methyl-7,8-cyclohexyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol (9g)



Using the reported 3-step procedure,[6] *N*-Bn compound **8g** (0.25 g, 0.67 mmol) was converted into the phenolic *N*-Me compound **9g** (0.18 g, 98%). ^{1}H NMR δ ($CDCl_3$): 8.00 (br s, 1H), 7.10-7.06 (t, *J* = 8.5 Hz, 1H), 6.75 (s, 2H), 6.63-6.61 (d, *J* = 7.5 Hz, 1H), 3.02-2.97 (m, 1H), 2.76 (br s, 1H), 2.67-2.62 (m, 1H), 2.48 (m, 3H), 2.26-2.23 (d, *J* = 14.5 Hz, 1H), 1.99-1.81 (m, 3H), 1.78-1.73 (m, 2H), 1.64-1.50 (m, 5H), 1.28-1.02 (m, 4H), 0.82-0.75 (m, 1H); ^{13}C NMR δ ($CDCl_3$): 156.9, 154.2, 129.3, 116.3, 113.3, 112.9, 60.8, 49.5, 48.1, 46.3, 45.8, 36.9, 36.3, 35.8, 35.3, 35.1, 31.1, 27.6, 26.6; IR cm^{-1} (neat): 3044.3, 2920.2, 2849.1, 1597.4, 1583.2, 1446.1, 1273.1, 1246.2; HRMS calcd for $C_{19}H_{28}NO$ ($M+H^+$), 286.2171; found, 286.2171. The base **9g** was converted into its HBr salt and then crystallized in EtOH (0.14 g); mp 223.8-225.3 °C; Anal. calcd for $C_{19}H_{28}BrNO$ + 0.5 M H_2O: C, 60.80; H, 7.79; N, 3.73. Found: C, 60.85; H, 8.02; N, 3.48.

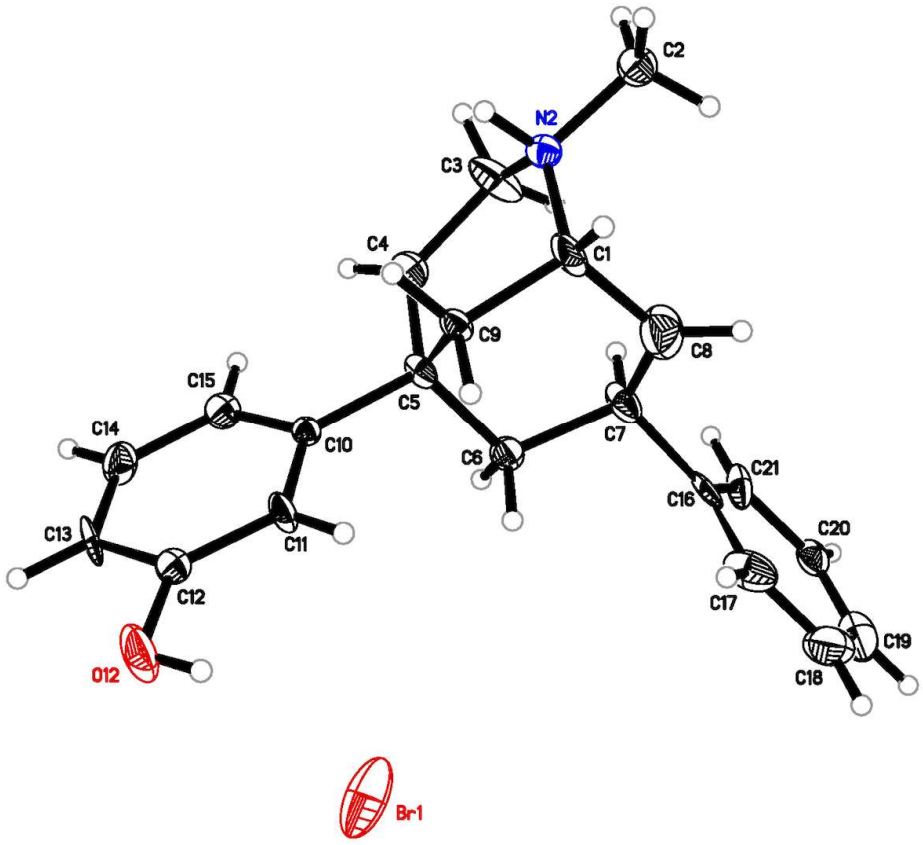
X-ray Crystallographic Structures and Data for 9b, 9f, and 9g.



Single-crystal X-ray diffraction data on compounds **9b**, **9f**, and **9g** were collected at 100 °K using MoKα radiation (λ = 0.71073 Å) and a Bruker APEX 2 CCD area detector. The structures were solved by direct methods and refined by full-matrix least squares on F^2 values using the programs found in the SHELXTL suite (Bruker, SHELXTL v6.10, 2000, Bruker AXS Inc., Madison, WI). Parameters refined included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on carbons were included using a riding model [coordinate shifts of C applied to H atoms] with C-H distance set at 0.96 Å. Atomic coordinates for these compounds have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 837805 (**9b**), CCDC 837804 (**9f**), and CCDC 837806 (**9g**)). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

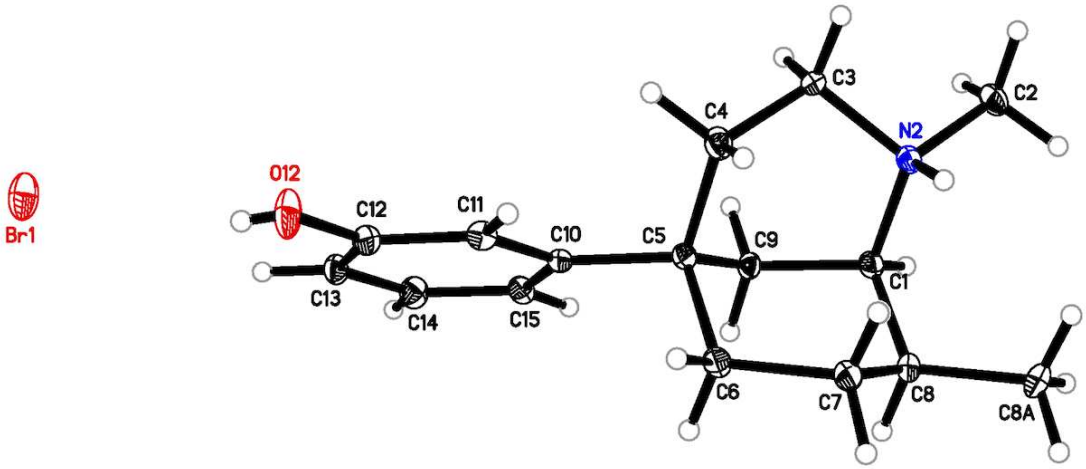
3-(2-Methyl-7-phenyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol ($C_{21}H_{26}BrNO$; **9b)**

A 0.594 x 0.332 x 0.281 mm^3 crystal of **9b** was prepared for data collection coating with high viscosity microscope oil (Paratone-N, Hampton Research). The oil-coated crystal was placed on a MicroMesh mount (MiTeGen, Ithaca, NY) and transferred immediately to the cold stream on the diffractometer. The crystal was monoclininc in space group *C* c with unit cell dimensions *a* = 10.8145(7) Å, *b* = 15.7537(8) Å, *c* = 11.0523(6) Å, and β= 104.512(3)°. Corrections were applied for Lorentz, polarization, and absorption effects. Data were 96.6% complete to 29.17° θ (approximately 0.73 Å) with an average redundancy of 3.88.



3-(2-Methyl-8-methyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol ($C_{16}H_{24}BrNO$; **9f)**

A 0.476 x 0.367 x 0.233 mm^3 crystal of **9f** was prepared for data collection coating with high viscosity microscope oil (Paratone-N, Hampton Research). The oil-coated crystal was placed on a MicroMesh mount (MiTeGen, Ithaca, NY) and transferred immediately to the cold stream on the diffractometer. The crystal was monoclininc in space group $P\ 2_1$ with unit cell dimensions a = 7.5772(8) Å, b = 11.7826(13) Å, c = 8.5116(9) Å, and β= 95.802(1)°. Corrections were applied for Lorentz, polarization, and absorption effects. Data were 96.5% complete to 29.44° θ (approximately 0.72 Å) with an average redundancy of 3.58.



3-(2-Methyl-7,8-cyclohexyl-2-azabicyclo[3.3.1]nonan-5-yl)phenol ($C_{19}H_{28}BrNO$; **9g)**

A 0.588 x 0.213 x 0.084 mm^3 crystal of **9g** was prepared for data collection coating with high viscosity microscope oil (Paratone-N, Hampton Research). The oil-coated crystal was placed on a MicroMesh mount (MiTeGen, Ithaca, NY) and transferred immediately to the cold stream on the diffractometer. The crystal was monoclininc in space group $P\ 2_1/n$ with unit cell dimensions a = 6.2638(3) Å, b = 23.3149(12) Å, c = 11.9322(6) Å, and β= 98.450(2)°. Corrections were applied for Lorentz, polarization, and absorption effects. Data were 99.2% complete to 29.17° θ (approximately 0.73 Å) with an average redundancy of 4.18.

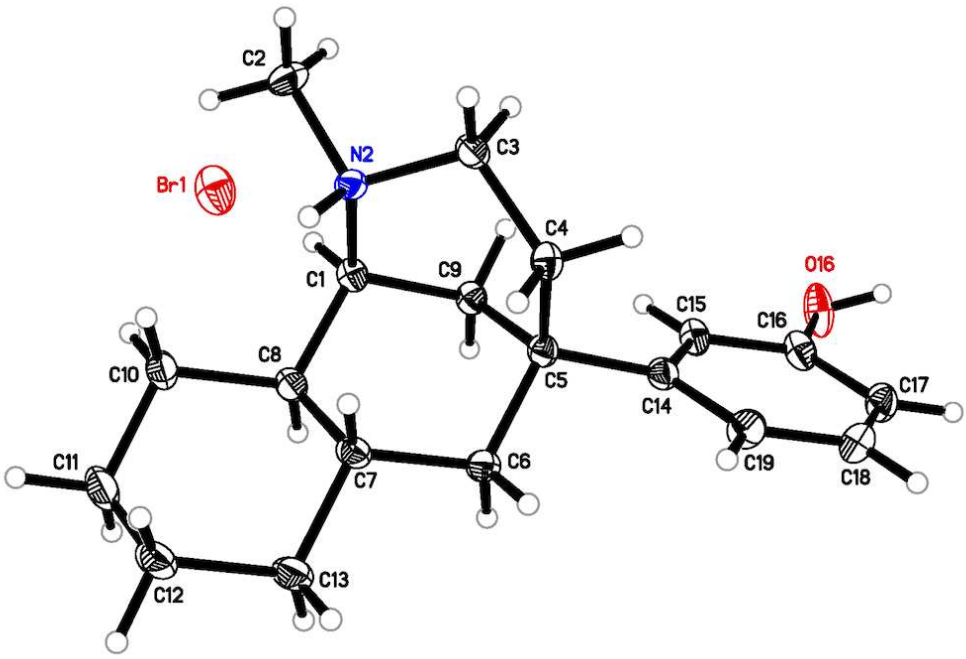


Table 1. Crystal data and structure refinement for **9b**.

Empirical formula	$C_{21}H_{24}BrNO$	
Formula weight	386.32	
Temperature	100(2) °K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 10.8145(7) Å	α= 90°
	b = 15.7537(8) Å	β= 104.512(3)°
	c = 11.0523(6) Å	γ = 90°
Volume	1822.89(18) $Å^3$	
Z	4	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	2.262 mm^{-1}	
F(000)	800	
Crystal size	0.594 x 0.332 x 0.281 mm^3	
θ range for data collection	2.34 to 29.17°	
Index ranges	-14<=h<=14, -21<=k<=21, -11<=l<=14	
Reflections collected	9721	
Independent reflections	4077 [R(int) = 0.0206]	
Completeness to θ = 25.00°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5690 and 0.3468	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4077 / 26 / 204	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2σ(I)]	R1 = 0.0934, wR2 = 0.2493	
R indices (all data)	R1 = 0.0975, wR2 = 0.2536	
Absolute structure parameter	0.05(3)	
Largest diff. peak and hole	4.130 and -2.284 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-2489(1)	1847(1)	2535(1)	42(1)
C(1)	3075(8)	2887(7)	1265(10)	33(2)
N(2)	3962(6)	2821(4)	418(6)	17(1)
C(2)	5074(8)	3393(5)	750(9)	22(2)
C(3)	4308(9)	1937(6)	127(13)	36(2)
C(4)	3127(8)	1351(5)	-117(9)	24(2)
C(5)	2117(6)	1468(4)	636(7)	16(1)
C(6)	2563(7)	1107(5)	1959(7)	18(1)
C(7)	3802(8)	1536(5)	2733(9)	28(2)
C(8)	3749(10)	2482(6)	2582(11)	37(2)
C(9)	1825(6)	2428(4)	688(7)	14(1)
C(10)	886(6)	1015(4)	-39(7)	12(1)
C(11)	-269(6)	1209(5)	268(8)	19(1)
O(12)	-2569(6)	1026(5)	-130(7)	37(2)
C(12)	-1391(7)	830(5)	-377(7)	17(1)
C(13)	-1420(6)	244(5)	-1302(8)	21(2)
C(14)	-285(8)	33(5)	-1590(8)	24(2)
C(15)	862(7)	408(5)	-977(8)	20(1)
C(16)	4113(6)	1239(5)	4101(8)	20(2)
C(17)	3433(8)	1490(6)	4920(11)	31(2)
C(18)	3775(9)	1237(7)	6166(11)	35(2)
C(19)	4814(10)	717(6)	6594(10)	35(2)
C(20)	5510(8)	451(5)	5774(8)	23(2)
C(21)	5159(7)	709(5)	4531(8)	22(2)

Table 3. Bond lengths [Å] and angles [°] for **9b**.

C(1)-N(2)	1.503(10)	C(1)-C(9)	1.525(10)
C(1)-C(8)	1.589(16)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.473(10)	N(2)-C(3)	1.498(11)
N(2)-H(2D)	0.9300	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(4)	1.543(11)	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(5)	1.541(12)
C(4)-H(4A)	0.9500	C(5)-C(10)	1.530(9)
C(5)-C(6)	1.530(10)	C(5)-C(9)	1.549(10)
C(6)-C(7)	1.553(10)	C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900	C(7)-C(8)	1.499(12)
C(7)-C(16)	1.537(12)	C(7)-H(7A)	1.0000
C(8)-H(8A)	0.9500	C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900	C(10)-C(11)	1.408(9)
C(10)-C(15)	1.405(10)	C(11)-C(12)	1.380(9)
C(11)-H(11A)	0.9500	O(12)-C(12)	1.402(9)
O(12)-H(12A)	0.8400	C(12)-C(13)	1.372(11)
C(13)-C(14)	1.384(12)	C(13)-H(13A)	0.9500
C(14)-C(15)	1.387(11)	C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500	C(16)-C(17)	1.360(14)
C(16)-C(21)	1.390(10)	C(17)-C(18)	1.392(15)
C(17)-H(17A)	0.9500	C(18)-C(19)	1.374(14)
C(18)-H(18A)	0.9500	C(19)-C(20)	1.381(15)
C(19)-H(19A)	0.9500	C(20)-C(21)	1.391(12)
C(20)-H(20A)	0.9500	C(21)-H(21A)	0.9500
N(2)-C(1)-C(9)	110.1(7)	N(2)-C(1)-C(8)	109.0(8)
C(9)-C(1)-C(8)	110.4(8)	N(2)-C(1)-H(1A)	109.1
C(9)-C(1)-H(1A)	109.1	C(8)-C(1)-H(1A)	109.1
C(2)-N(2)-C(3)	113.0(6)	C(2)-N(2)-C(1)	114.3(6)
C(3)-N(2)-C(1)	115.5(7)	C(2)-N(2)-H(2D)	104.1
C(3)-N(2)-H(2D)	104.1	C(1)-N(2)-H(2D)	104.1
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	110.7(7)	N(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3A)	109.5	N(2)-C(3)-H(3B)	109.5
C(4)-C(3)-H(3B)	109.5	H(3A)-C(3)-H(3B)	108.1
C(3)-C(4)-C(5)	120.1(7)	C(3)-C(4)-H(4A)	120.0
C(5)-C(4)-H(4A)	120.0	C(10)-C(5)-C(6)	108.6(6)
C(10)-C(5)-C(4)	109.2(6)	C(6)-C(5)-C(4)	112.1(6)
C(10)-C(5)-C(9)	108.3(5)	C(6)-C(5)-C(9)	110.2(6)
C(4)-C(5)-C(9)	108.4(6)	C(5)-C(6)-C(7)	112.7(6)
C(5)-C(6)-H(6A)	109.0	C(7)-C(6)-H(6A)	109.0
C(5)-C(6)-H(6B)	109.0	C(7)-C(6)-H(6B)	109.0
H(6A)-C(6)-H(6B)	107.8	C(8)-C(7)-C(16)	113.9(8)
C(8)-C(7)-C(6)	111.6(7)	C(16)-C(7)-C(6)	110.8(6)
C(8)-C(7)-H(7A)	106.7	C(16)-C(7)-H(7A)	106.7
C(6)-C(7)-H(7A)	106.7	C(7)-C(8)-C(1)	119.8(8)
C(7)-C(8)-H(8A)	120.1	C(1)-C(8)-H(8A)	120.1
C(1)-C(9)-C(5)	108.1(6)	C(1)-C(9)-H(9A)	110.1
C(5)-C(9)-H(9A)	110.1	C(1)-C(9)-H(9B)	110.1
C(5)-C(9)-H(9B)	110.1	H(9A)-C(9)-H(9B)	108.4

Table 3. (continued)

C(11)-C(10)-C(15)	118.2(6)	C(11)-C(10)-C(5)	119.8(6)
C(15)-C(10)-C(5)	122.0(6)	C(12)-C(11)-C(10)	120.0(7)
C(12)-C(11)-H(11A)	120.0	C(10)-C(11)-H(11A)	120.0
C(12)-O(12)-H(12A)	109.5	C(13)-C(12)-O(12)	116.1(6)
C(13)-C(12)-C(11)	121.9(7)	O(12)-C(12)-C(11)	121.9(7)
C(14)-C(13)-C(12)	118.5(6)	C(14)-C(13)-H(13A)	120.8
C(12)-C(13)-H(13A)	120.8	C(13)-C(14)-C(15)	121.4(7)
C(13)-C(14)-H(14A)	119.3	C(15)-C(14)-H(14A)	119.3
C(14)-C(15)-C(10)	120.0(7)	C(14)-C(15)-H(15A)	120.0
C(10)-C(15)-H(15A)	120.0	C(17)-C(16)-C(21)	118.5(8)
C(17)-C(16)-C(7)	123.0(8)	C(21)-C(16)-C(7)	118.5(8)
C(16)-C(17)-C(18)	121.4(8)	C(16)-C(17)-H(17A)	119.3
C(18)-C(17)-H(17A)	119.3	C(17)-C(18)-C(19)	120.2(10)
C(17)-C(18)-H(18A)	119.9	C(19)-C(18)-H(18A)	119.9
C(20)-C(19)-C(18)	119.2(9)	C(20)-C(19)-H(19A)	120.4
C(18)-C(19)-H(19A)	120.4	C(19)-C(20)-C(21)	120.0(8)
C(19)-C(20)-H(20A)	120.0	C(21)-C(20)-H(20A)	120.0
C(20)-C(21)-C(16)	120.7(8)	C(20)-C(21)-H(21A)	119.6
C(16)-C(21)-H(21A)	119.6		

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **9b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	64(1)	32(1)	21(1)	3(1)	-8(1)	22(1)
C(1)	22(4)	53(6)	31(5)	-23(4)	17(3)	-24(4)
N(2)	16(1)	17(1)	18(1)	1(1)	5(1)	0(1)
C(3)	22(4)	30(4)	61(8)	-7(4)	18(4)	-10(3)
C(4)	22(2)	23(2)	25(2)	0(1)	6(1)	0(1)
C(5)	7(3)	15(3)	21(4)	7(3)	-4(2)	1(2)
C(6)	17(2)	18(2)	18(2)	1(1)	3(1)	-1(1)
C(7)	21(3)	26(4)	28(5)	14(3)	-12(3)	-11(3)
C(8)	46(5)	28(4)	33(6)	-3(4)	1(4)	-7(4)
C(9)	11(3)	15(3)	18(4)	-4(2)	6(2)	-2(2)
C(10)	11(1)	12(1)	13(2)	0(1)	3(1)	0(1)
C(11)	9(3)	24(3)	21(4)	-5(3)	0(3)	-4(2)
O(12)	13(3)	58(5)	36(4)	-16(3)	1(2)	-7(3)
C(13)	8(3)	21(3)	26(4)	-4(3)	-10(3)	-2(2)
C(14)	29(4)	24(4)	18(4)	-6(3)	4(3)	-3(3)
C(16)	8(3)	18(3)	29(4)	4(3)	-5(3)	-8(2)
C(17)	16(3)	32(4)	44(6)	11(4)	7(4)	2(3)
C(18)	30(4)	40(5)	38(6)	4(4)	14(4)	-6(4)
C(19)	41(5)	24(4)	29(5)	10(3)	-9(4)	-9(3)
C(20)	26(4)	17(3)	21(4)	4(3)	-1(3)	-7(3)
C(21)	23(4)	17(3)	19(4)	-1(3)	-9(3)	-2(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **9b**.

	x	y	z	U(eq)
H(1A)	2891	3499	1384	40
H(2D)	3485	3028	-344	20
H(2A)	5703	3222	294	34
H(2B)	5460	3359	1651	34
H(2C)	4798	3977	525	34
H(3A)	4977	1712	837	44
H(3B)	4656	1945	-620	44
H(4A)	3022	918	-733	28
H(6A)	2715	490	1907	21
H(6B)	1877	1185	2397	21
H(7A)	4514	1332	2379	34
H(8A)	4116	2838	3272	45
H(9A)	1448	2647	-165	17
H(9B)	1207	2524	1200	17
H(11A)	-275	1601	920	22
H(12A)	-2450	1346	496	55
H(13A)	-2202	-12	-1734	25
H(14A)	-291	-377	-2222	29
H(15A)	1630	255	-1191	24
H(17A)	2709	1846	4635	37
H(18A)	3290	1423	6722	42
H(19A)	5049	543	7444	42
H(20A)	6229	92	6059	27
H(21A)	5639	522	3970	27

Table 6. Torsion angles [°] for **9b**.

C(9)-C(1)-N(2)-C(2)	167.4(7)
C(8)-C(1)-N(2)-C(2)	-71.4(9)
C(9)-C(1)-N(2)-C(3)	-59.0(11)
C(8)-C(1)-N(2)-C(3)	62.2(9)
C(2)-N(2)-C(3)-C(4)	175.8(8)
C(1)-N(2)-C(3)-C(4)	41.6(12)
N(2)-C(3)-C(4)-C(5)	-36.2(12)
C(3)-C(4)-C(5)-C(10)	162.7(8)
C(3)-C(4)-C(5)-C(6)	-76.9(9)
C(3)-C(4)-C(5)-C(9)	45.0(10)
C(10)-C(5)-C(6)-C(7)	-179.2(7)
C(4)-C(5)-C(6)-C(7)	60.1(8)
C(9)-C(5)-C(6)-C(7)	-60.7(8)
C(5)-C(6)-C(7)-C(8)	44.5(11)
C(5)-C(6)-C(7)-C(16)	172.5(7)
C(16)-C(7)-C(8)-C(1)	-163.0(8)
C(6)-C(7)-C(8)-C(1)	-36.7(13)
N(2)-C(1)-C(8)-C(7)	-77.8(11)
C(9)-C(1)-C(8)-C(7)	43.3(12)
N(2)-C(1)-C(9)-C(5)	65.8(9)
C(8)-C(1)-C(9)-C(5)	-54.6(9)
C(10)-C(5)-C(9)-C(1)	-175.5(7)
C(6)-C(5)-C(9)-C(1)	65.9(8)
C(4)-C(5)-C(9)-C(1)	-57.2(8)
C(6)-C(5)-C(10)-C(11)	74.3(8)
C(4)-C(5)-C(10)-C(11)	-163.2(7)
C(9)-C(5)-C(10)-C(11)	-45.4(9)
C(6)-C(5)-C(10)-C(15)	-106.4(8)
C(4)-C(5)-C(10)-C(15)	16.1(9)
C(9)-C(5)-C(10)-C(15)	133.9(7)
C(15)-C(10)-C(11)-C(12)	-2.3(11)
C(5)-C(10)-C(11)-C(12)	177.0(7)
C(10)-C(11)-C(12)-C(13)	1.8(12)
C(10)-C(11)-C(12)-O(12)	-177.9(7)
O(12)-C(12)-C(13)-C(14)	179.5(8)
C(11)-C(12)-C(13)-C(14)	-0.2(12)
C(12)-C(13)-C(14)-C(15)	-0.7(13)
C(13)-C(14)-C(15)-C(10)	0.1(12)
C(11)-C(10)-C(15)-C(14)	1.4(11)
C(5)-C(10)-C(15)-C(14)	-177.9(7)
C(8)-C(7)-C(16)-C(17)	54.3(11)
C(6)-C(7)-C(16)-C(17)	-72.5(10)
C(8)-C(7)-C(16)-C(21)	-123.8(9)
C(6)-C(7)-C(16)-C(21)	109.5(8)
C(21)-C(16)-C(17)-C(18)	0.8(13)
C(7)-C(16)-C(17)-C(18)	-177.2(8)
C(16)-C(17)-C(18)-C(19)	-0.5(14)
C(17)-C(18)-C(19)-C(20)	0.0(14)
C(18)-C(19)-C(20)-C(21)	0.0(12)
C(19)-C(20)-C(21)-C(16)	0.3(11)
C(17)-C(16)-C(21)-C(20)	-0.8(11)
C(7)-C(16)-C(21)-C(20)	177.4(7)

Table 7. Crystal data and structure refinement for **9f**.

Empirical formula	$C_{16}H_{24}BrNO$	
Formula weight	326.27	
Temperature	100(2) °K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 7.5772(8) Å	α= 90°
	b = 11.7826(13) Å	β= 95.802(1)°
	c = 8.5116(9) Å	γ = 90°
Volume	756.02(14) $Å^3$	
Z	2	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	2.712 mm^{-1}	
F(000)	340	
Crystal size	0.476 x 0.367 x 0.233 mm^3	
θ range for data collection	2.41 to 29.44°	
Index ranges	-10<=h<=10, -16<=k<=16, -11<=l<=11	
Reflections collected	7851	
Independent reflections	3835 [R(int) = 0.0166]	
Completeness to θ = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5707 and 0.3584	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3835 / 1 / 176	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2σ(I)]	R1 = 0.0285, wR2 = 0.0760	
R indices (all data)	R1 = 0.0297, wR2 = 0.0765	
Absolute structure parameter	0.035(8)	
Largest diff. peak and hole	1.903 and -0.260 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	546(1)	2506(1)	11617(1)	20(1)
C(1)	8514(3)	-634(2)	3507(3)	12(1)
N(2)	8119(3)	349(2)	2332(2)	11(1)
C(2)	8021(3)	-35(2)	649(3)	16(1)
C(3)	6477(3)	996(2)	2614(3)	13(1)
C(4)	6532(3)	1390(2)	4322(3)	14(1)
C(5)	6998(3)	430(2)	5559(2)	10(1)
C(6)	8868(3)	646(2)	6461(3)	14(1)
C(7)	10378(4)	619(2)	5404(3)	16(1)
C(8)	10361(3)	-459(2)	4399(3)	16(1)
C(8A)	11868(4)	-487(3)	3342(3)	22(1)
C(9)	7111(3)	-700(2)	4678(3)	10(1)
C(10)	5650(3)	398(2)	6784(2)	11(1)
C(11)	5212(3)	1412(2)	7503(3)	12(1)
O(12)	3674(2)	2446(3)	9286(2)	21(1)
C(12)	4011(3)	1427(2)	8644(3)	14(1)
C(13)	3227(3)	417(2)	9081(3)	13(1)
C(14)	3665(3)	-588(2)	8380(3)	15(1)
C(15)	4883(3)	-610(2)	7250(3)	12(1)

Table 9. Bond lengths [Å] and angles [°] for **9f**.

C(1)-C(9)	1.531(3)	C(1)-C(8)	1.538(3)
C(1)-N(2)	1.540(3)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.497(3)	N(2)-C(3)	1.499(3)
N(2)-H(2D)	0.9300	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(4)	1.523(3)	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(5)	1.562(3)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(5)-C(10)	1.532(3)	C(5)-C(9)	1.535(3)
C(5)-C(6)	1.563(3)	C(6)-C(7)	1.526(3)
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-C(8)	1.531(3)	C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900	C(8)-C(8A)	1.524(3)
C(8)-H(8A)	1.0000	C(8A)-H(8AA)	0.9800
C(8A)-H(8AB)	0.9800	C(8A)-H(8AC)	0.9800
C(9)-H(9A)	0.9900	C(9)-H(9B)	0.9900
C(10)-C(15)	1.397(3)	C(10)-C(11)	1.397(3)
C(11)-C(12)	1.396(3)	C(11)-H(11A)	0.9500
O(12)-C(12)	1.354(4)	O(12)-H(12)	0.57(3)
C(12)-C(13)	1.397(4)	C(13)-C(14)	1.382(4)
C(13)-H(13A)	0.9500	C(14)-C(15)	1.399(3)
C(14)-H(14A)	0.9500	C(15)-H(15A)	0.9500
C(9)-C(1)-C(8)	110.01(18)	C(9)-C(1)-N(2)	111.07(18)
C(8)-C(1)-N(2)	109.11(19)	C(9)-C(1)-H(1A)	108.9
C(8)-C(1)-H(1A)	108.9	N(2)-C(1)-H(1A)	108.9
C(2)-N(2)-C(3)	110.16(17)	C(2)-N(2)-C(1)	112.42(18)
C(3)-N(2)-C(1)	112.84(17)	C(2)-N(2)-H(2D)	107.0
C(3)-N(2)-H(2D)	107.0	C(1)-N(2)-H(2D)	107.0
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	111.38(18)	N(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3A)	109.4	N(2)-C(3)-H(3B)	109.4
C(4)-C(3)-H(3B)	109.4	H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(5)	113.90(19)	C(3)-C(4)-H(4A)	108.8
C(5)-C(4)-H(4A)	108.8	C(3)-C(4)-H(4B)	108.8
C(5)-C(4)-H(4B)	108.8	H(4A)-C(4)-H(4B)	107.7
C(10)-C(5)-C(9)	112.67(19)	C(10)-C(5)-C(4)	110.86(19)
C(9)-C(5)-C(4)	108.61(18)	C(10)-C(5)-C(6)	107.64(17)
C(9)-C(5)-C(6)	106.79(19)	C(4)-C(5)-C(6)	110.17(19)
C(7)-C(6)-C(5)	113.80(19)	C(7)-C(6)-H(6A)	108.8
C(5)-C(6)-H(6A)	108.8	C(7)-C(6)-H(6B)	108.8
C(5)-C(6)-H(6B)	108.8	H(6A)-C(6)-H(6B)	107.7
C(6)-C(7)-C(8)	112.5(2)	C(6)-C(7)-H(7A)	109.1
C(8)-C(7)-H(7A)	109.1	C(6)-C(7)-H(7B)	109.1
C(8)-C(7)-H(7B)	109.1	H(7A)-C(7)-H(7B)	107.8
C(8A)-C(8)-C(7)	112.6(3)	C(8A)-C(8)-C(1)	113.8(2)
C(7)-C(8)-C(1)	110.0(2)	C(8A)-C(8)-H(8A)	106.6
C(7)-C(8)-H(8A)	106.6	C(1)-C(8)-H(8A)	106.6
C(8)-C(8A)-H(8AA)	109.5	C(8)-C(8A)-H(8AB)	109.5
H(8AA)-C(8A)-H(8AB)	109.5	C(8)-C(8A)-H(8AC)	109.5
H(8AA)-C(8A)-H(8AC)	109.5	H(8AB)-C(8A)-H(8AC)	109.5

Table 9. (continued)

C(1)-C(9)-C(5)	110.53(19)	C(1)-C(9)-H(9A)	109.5
C(5)-C(9)-H(9A)	109.5	C(1)-C(9)-H(9B)	109.5
C(5)-C(9)-H(9B)	109.5	H(9A)-C(9)-H(9B)	108.1
C(15)-C(10)-C(11)	118.6(2)	C(15)-C(10)-C(5)	122.6(2)
C(11)-C(10)-C(5)	118.8(2)	C(12)-C(11)-C(10)	121.1(2)
C(12)-C(11)-H(11A)	119.5	C(10)-C(11)-H(11A)	119.5
C(12)-O(12)-H(12)	111(5)	O(12)-C(12)-C(11)	117.1(2)
O(12)-C(12)-C(13)	123.0(2)	C(11)-C(12)-C(13)	119.9(2)
C(14)-C(13)-C(12)	119.2(2)	C(14)-C(13)-H(13A)	120.4
C(12)-C(13)-H(13A)	120.4	C(13)-C(14)-C(15)	121.1(2)
C(13)-C(14)-H(14A)	119.4	C(15)-C(14)-H(14A)	119.4
C(10)-C(15)-C(14)	120.1(2)	C(10)-C(15)-H(15A)	119.9
C(14)-C(15)-H(15A)	119.9		

Table 10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **9f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	22(1)	15(1)	24(1)	-2(1)	13(1)	-3(1)
C(1)	14(1)	13(1)	10(1)	1(1)	3(1)	3(1)
N(2)	11(1)	13(1)	9(1)	0(1)	2(1)	0(1)
C(2)	18(1)	21(1)	8(1)	-2(1)	2(1)	0(1)
C(3)	10(1)	18(1)	10(1)	2(1)	1(1)	5(1)
C(4)	18(1)	12(1)	14(1)	2(1)	6(1)	3(1)
C(5)	10(1)	11(1)	9(1)	1(1)	2(1)	0(1)
C(6)	9(1)	21(1)	10(1)	-1(1)	0(1)	-4(1)
C(7)	12(1)	27(1)	11(1)	1(1)	1(1)	1(1)
C(8)	11(1)	25(1)	11(1)	2(1)	4(1)	3(1)
C(8A)	12(1)	35(2)	19(1)	2(1)	6(1)	7(1)
C(9)	11(1)	10(1)	11(1)	-1(1)	3(1)	2(1)
C(10)	9(1)	15(1)	8(1)	1(1)	0(1)	1(1)
C(11)	13(1)	11(1)	13(1)	0(1)	1(1)	-1(1)
O(12)	27(1)	14(1)	24(1)	1(1)	17(1)	0(1)
C(12)	14(1)	16(1)	12(1)	-2(1)	1(1)	3(1)
C(13)	10(1)	19(1)	12(1)	-1(1)	3(1)	-1(1)
C(14)	13(1)	17(1)	16(1)	1(1)	4(1)	-3(1)
C(15)	13(1)	14(1)	10(1)	0(1)	1(1)	-2(1)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **9f**.

	x	y	z	U(eq)
H(1A)	8510	-1363	2905	15
H(2D)	9065	854	2488	13
H(2A)	7770	618	-52	23
H(2B)	7072	-598	452	23
H(2C)	9155	-376	446	23
H(3A)	5425	506	2359	15
H(3B)	6359	1663	1905	15
H(4A)	5362	1713	4496	17
H(4B)	7422	2004	4500	17
H(6A)	8862	1396	6986	16
H(6B)	9094	63	7295	16
H(7A)	11524	670	6071	20
H(7B)	10282	1290	4699	20
H(8A)	10563	-1109	5151	19
H(8AA)	13001	-369	3984	33
H(8AB)	11691	114	2547	33
H(8AC)	11881	-1226	2814	33
H(9A)	7421	-1317	5447	13
H(9B)	5943	-879	4104	13
H(11A)	5739	2102	7211	14
H(13A)	2402	422	9851	16
H(14A)	3130	-1276	8670	18
H(15A)	5189	-1311	6798	15
H(12)	3220(40)	2400(40)	9780(40)	16(9)

Table 12. Torsion angles [°] for **9f**.

C(9)-C(1)-N(2)-C(2)	-125.4(2)
C(8)-C(1)-N(2)-C(2)	113.1(2)
C(9)-C(1)-N(2)-C(3)	-0.1(3)
C(8)-C(1)-N(2)-C(3)	-121.5(2)
C(2)-N(2)-C(3)-C(4)	179.56(19)
C(1)-N(2)-C(3)-C(4)	53.0(3)
N(2)-C(3)-C(4)-C(5)	-50.4(3)
C(3)-C(4)-C(5)-C(10)	-129.4(2)
C(3)-C(4)-C(5)-C(9)	-5.1(3)
C(3)-C(4)-C(5)-C(6)	111.6(2)
C(10)-C(5)-C(6)-C(7)	176.0(2)
C(9)-C(5)-C(6)-C(7)	54.8(3)
C(4)-C(5)-C(6)-C(7)	-63.0(3)
C(5)-C(6)-C(7)-C(8)	-52.0(3)
C(6)-C(7)-C(8)-C(8A)	180.0(2)
C(6)-C(7)-C(8)-C(1)	51.8(3)
C(9)-C(1)-C(8)-C(8A)	174.9(2)
N(2)-C(1)-C(8)-C(8A)	-63.1(3)
C(9)-C(1)-C(8)-C(7)	-57.7(3)
N(2)-C(1)-C(8)-C(7)	64.4(2)
C(8)-C(1)-C(9)-C(5)	64.1(2)
N(2)-C(1)-C(9)-C(5)	-56.8(2)
C(10)-C(5)-C(9)-C(1)	-178.29(18)
C(4)-C(5)-C(9)-C(1)	58.5(2)
C(6)-C(5)-C(9)-C(1)	-60.3(2)
C(9)-C(5)-C(10)-C(15)	11.7(3)
C(4)-C(5)-C(10)-C(15)	133.6(2)
C(6)-C(5)-C(10)-C(15)	-105.8(2)
C(9)-C(5)-C(10)-C(11)	-170.4(2)
C(4)-C(5)-C(10)-C(11)	-48.5(3)
C(6)-C(5)-C(10)-C(11)	72.1(2)
C(15)-C(10)-C(11)-C(12)	-1.1(3)
C(5)-C(10)-C(11)-C(12)	-179.0(2)
C(10)-C(11)-C(12)-O(12)	179.6(2)
C(10)-C(11)-C(12)-C(13)	-0.1(3)
O(12)-C(12)-C(13)-C(14)	-179.1(2)
C(11)-C(12)-C(13)-C(14)	0.5(3)
C(12)-C(13)-C(14)-C(15)	0.3(4)
C(11)-C(10)-C(15)-C(14)	1.8(3)
C(5)-C(10)-C(15)-C(14)	179.7(2)
C(13)-C(14)-C(15)-C(10)	-1.5(3)

Table 13. Crystal data and structure refinement for **9g**.

Empirical formula	$C_{19}H_{28}BrNO$	
Formula weight	366.33	
Temperature	100(2) °K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.2638(3) Å	α= 90°
	b = 23.3149(12) Å	β= 98.450(2)°
	c = 11.9322(6) Å	γ = 90°
Volume	1723.66(15) $Å^3$	
Z	4	
Density (calculated)	1.412 Mg/m^3	
Absorption coefficient	2.387 mm^{-1}	
F(000)	768	
Crystal size	0.588 x 0.213 x 0.084 mm^3	
θ range for data collection	1.75 to 29.17°	
Index ranges	-8<=h<=8, -31<=k<=31, -16<=l<=16	
Reflections collected	19683	
Independent reflections	4626 [R(int) = 0.0288]	
Completeness to θ = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8246 and 0.3342	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4626 / 0 / 201	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2σ(I)]	R1 = 0.0270, wR2 = 0.0640	
R indices (all data)	R1 = 0.0355, wR2 = 0.0670	
Largest diff. peak and hole	0.658 and -0.261 e.$Å^{-3}$	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7525(1)	2895(1)	6542(1)	20(1)
C(1)	3396(2)	3527(1)	8931(1)	15(1)
N(2)	4572(2)	3003(1)	8534(1)	14(1)
C(2)	3011(3)	2555(1)	8045(1)	22(1)
C(3)	6201(2)	2742(1)	9446(1)	17(1)
C(4)	7710(2)	3194(1)	10036(1)	16(1)
C(5)	6494(2)	3722(1)	10468(1)	14(1)
C(6)	7001(3)	4267(1)	9809(1)	17(1)
C(7)	6238(3)	4235(1)	8528(1)	17(1)
C(8)	3845(2)	4068(1)	8281(1)	16(1)
C(9)	4055(2)	3608(1)	10199(1)	15(1)
C(10)	3004(3)	4038(1)	7013(1)	20(1)
C(11)	3407(3)	4606(1)	6437(1)	27(1)
C(12)	5792(3)	4766(1)	6656(1)	27(1)
C(13)	6636(3)	4798(1)	7926(1)	25(1)
C(14)	7210(2)	3802(1)	11741(1)	15(1)
C(15)	5810(2)	3709(1)	12533(1)	18(1)
O(16)	5101(2)	3614(1)	14407(1)	28(1)
C(16)	6566(3)	3739(1)	13696(1)	19(1)
C(17)	8700(3)	3872(1)	14084(1)	21(1)
C(18)	10091(3)	3968(1)	13299(1)	23(1)
C(19)	9365(3)	3934(1)	12146(1)	21(1)

Table 15. Bond lengths [Å] and angles [°] for **9g**.

C(1)-C(9)	1.5207(19)	C(1)-C(8)	1.528(2)
C(1)-N(2)	1.5357(18)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.4902(19)	N(2)-C(3)	1.5067(19)
N(2)-H(2D)	0.9300	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(4)	1.518(2)	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(5)	1.573(2)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(5)-C(14)	1.5309(19)	C(5)-C(9)	1.537(2)
C(5)-C(6)	1.553(2)	C(6)-C(7)	1.535(2)
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-C(13)	1.535(2)	C(7)-C(8)	1.535(2)
C(7)-H(7A)	1.0000	C(8)-C(10)	1.529(2)
C(8)-H(8A)	1.0000	C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900	C(10)-C(11)	1.529(2)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.525(3)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-C(13)	1.531(2)
C(12)-H(12A)	0.9900	C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900	C(13)-H(13B)	0.9900
C(14)-C(15)	1.397(2)	C(14)-C(19)	1.400(2)
C(15)-C(16)	1.401(2)	C(15)-H(15A)	0.9500
O(16)-C(16)	1.3698(19)	O(16)-H(16A)	0.8400
C(16)-C(17)	1.384(2)	C(17)-C(18)	1.389(2)
C(17)-H(17A)	0.9500	C(18)-C(19)	1.386(2)
C(18)-H(18A)	0.9500	C(19)-H(19B)	0.9500
C(9)-C(1)-C(8)	111.01(12)	C(9)-C(1)-N(2)	109.47(11)
C(8)-C(1)-N(2)	111.57(11)	C(9)-C(1)-H(1A)	108.2
C(8)-C(1)-H(1A)	108.2	N(2)-C(1)-H(1A)	108.2
C(2)-N(2)-C(3)	109.55(12)	C(2)-N(2)-C(1)	111.16(12)
C(3)-N(2)-C(1)	113.84(11)	C(2)-N(2)-H(2D)	107.3
C(3)-N(2)-H(2D)	107.3	C(1)-N(2)-H(2D)	107.3
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	111.25(12)	N(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3A)	109.4	N(2)-C(3)-H(3B)	109.4
C(4)-C(3)-H(3B)	109.4	H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(5)	113.39(12)	C(3)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4A)	108.9	C(3)-C(4)-H(4B)	108.9
C(5)-C(4)-H(4B)	108.9	H(4A)-C(4)-H(4B)	107.7
C(14)-C(5)-C(9)	111.45(12)	C(14)-C(5)-C(6)	110.50(12)
C(9)-C(5)-C(6)	107.83(12)	C(14)-C(5)-C(4)	109.62(11)
C(9)-C(5)-C(4)	108.13(11)	C(6)-C(5)-C(4)	109.24(12)
C(7)-C(6)-C(5)	114.02(12)	C(7)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6A)	108.7	C(7)-C(6)-H(6B)	108.7
C(5)-C(6)-H(6B)	108.7	H(6A)-C(6)-H(6B)	107.6
C(13)-C(7)-C(8)	110.41(13)	C(13)-C(7)-C(6)	112.06(12)
C(8)-C(7)-C(6)	110.81(12)	C(13)-C(7)-H(7A)	107.8
C(8)-C(7)-H(7A)	107.8	C(6)-C(7)-H(7A)	107.8
C(1)-C(8)-C(10)	113.69(13)	C(1)-C(8)-C(7)	111.10(12)
C(10)-C(8)-C(7)	112.69(12)	C(1)-C(8)-H(8A)	106.2

Table 15. (continued)

C(10)-C(8)-H(8A)	106.2	C(7)-C(8)-H(8A)	106.2
C(1)-C(9)-C(5)	110.19(11)	C(1)-C(9)-H(9A)	109.6
C(5)-C(9)-H(9A)	109.6	C(1)-C(9)-H(9B)	109.6
C(5)-C(9)-H(9B)	109.6	H(9A)-C(9)-H(9B)	108.1
C(11)-C(10)-C(8)	110.48(13)	C(11)-C(10)-H(10A)	109.6
C(8)-C(10)-H(10A)	109.6	C(11)-C(10)-H(10B)	109.6
C(8)-C(10)-H(10B)	109.6	H(10A)-C(10)-H(10B)	108.1
C(12)-C(11)-C(10)	110.93(14)	C(12)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11A)	109.5	C(12)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	108.0
C(11)-C(12)-C(13)	111.64(14)	C(11)-C(12)-H(12A)	109.3
C(13)-C(12)-H(12A)	109.3	C(11)-C(12)-H(12B)	109.3
C(13)-C(12)-H(12B)	109.3	H(12A)-C(12)-H(12B)	108.0
C(12)-C(13)-C(7)	111.37(13)	C(12)-C(13)-H(13A)	109.4
C(7)-C(13)-H(13A)	109.4	C(12)-C(13)-H(13B)	109.4
C(7)-C(13)-H(13B)	109.4	H(13A)-C(13)-H(13B)	108.0
C(15)-C(14)-C(19)	118.05(14)	C(15)-C(14)-C(5)	122.03(13)
C(19)-C(14)-C(5)	119.77(13)	C(14)-C(15)-C(16)	120.53(14)
C(14)-C(15)-H(15A)	119.7	C(16)-C(15)-H(15A)	119.7
C(16)-O(16)-H(16A)	109.5	O(16)-C(16)-C(17)	122.84(14)
O(16)-C(16)-C(15)	116.34(14)	C(17)-C(16)-C(15)	120.79(14)
C(16)-C(17)-C(18)	118.78(14)	C(16)-C(17)-H(17A)	120.6
C(18)-C(17)-H(17A)	120.6	C(19)-C(18)-C(17)	120.89(15)
C(19)-C(18)-H(18A)	119.6	C(17)-C(18)-H(18A)	119.6
C(18)-C(19)-C(14)	120.95(15)	C(18)-C(19)-H(19B)	119.5
C(14)-C(19)-H(19B)	119.5		

Table 16. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **9g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	22(1)	24(1)	16(1)	1(1)	6(1)	6(1)
C(1)	15(1)	16(1)	13(1)	1(1)	4(1)	2(1)
N(2)	17(1)	13(1)	13(1)	0(1)	3(1)	-2(1)
C(2)	25(1)	17(1)	23(1)	-4(1)	1(1)	-7(1)
C(3)	21(1)	14(1)	15(1)	2(1)	2(1)	2(1)
C(4)	15(1)	19(1)	13(1)	0(1)	2(1)	2(1)
C(5)	17(1)	15(1)	12(1)	0(1)	3(1)	0(1)
C(6)	22(1)	15(1)	14(1)	0(1)	3(1)	-3(1)
C(7)	23(1)	14(1)	14(1)	1(1)	5(1)	-1(1)
C(8)	22(1)	14(1)	13(1)	0(1)	4(1)	4(1)
C(9)	16(1)	16(1)	12(1)	0(1)	4(1)	1(1)
C(10)	26(1)	20(1)	14(1)	2(1)	1(1)	2(1)
C(11)	42(1)	22(1)	15(1)	5(1)	2(1)	5(1)
C(12)	47(1)	19(1)	17(1)	4(1)	9(1)	-6(1)
C(13)	42(1)	16(1)	17(1)	2(1)	8(1)	-6(1)
C(14)	18(1)	14(1)	14(1)	0(1)	2(1)	2(1)
C(15)	19(1)	19(1)	14(1)	1(1)	1(1)	4(1)
O(16)	23(1)	48(1)	13(1)	6(1)	4(1)	8(1)
C(16)	23(1)	22(1)	14(1)	1(1)	4(1)	7(1)
C(17)	27(1)	21(1)	14(1)	-2(1)	-1(1)	2(1)
C(18)	22(1)	24(1)	21(1)	-3(1)	-2(1)	-3(1)
C(19)	21(1)	23(1)	19(1)	-1(1)	4(1)	-3(1)

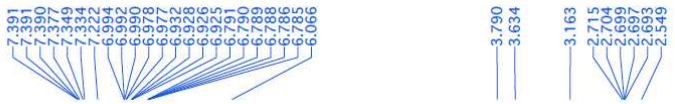
Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **9g**.

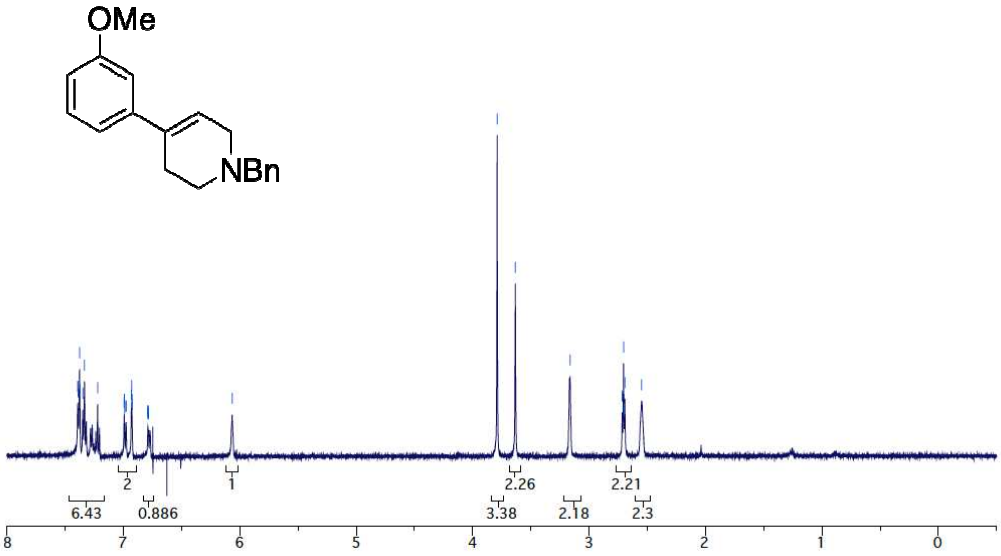
	x	y	z	U(eq)
H(1A)	1809	3450	8785	18
H(2D)	5317	3126	7959	17
H(2A)	3800	2232	7780	33
H(2B)	2033	2717	7407	33
H(2C)	2173	2422	8626	33
H(3A)	7055	2449	9105	20
H(3B)	5437	2548	10010	20
H(4A)	8668	3333	9503	19
H(4B)	8629	3016	10689	19
H(6A)	6306	4601	10119	20
H(6B)	8580	4333	9939	20
H(7A)	7089	3927	8212	20
H(8A)	3029	4385	8592	20
H(9A)	3685	3260	10605	18
H(9B)	3253	3936	10462	18
H(10A)	3741	3724	6665	24
H(10B)	1438	3955	6900	24
H(11A)	2933	4572	5611	32
H(11B)	2546	4913	6730	32
H(12A)	5999	5142	6302	33
H(12B)	6634	4477	6299	33
H(13A)	5906	5116	8268	30
H(13B)	8203	4881	8035	30
H(15A)	4334	3625	12280	21
H(16A)	5749	3478	15015	42
H(17A)	9203	3897	14873	25
H(18A)	11561	4059	13555	27
H(19B)	10345	4001	11623	25

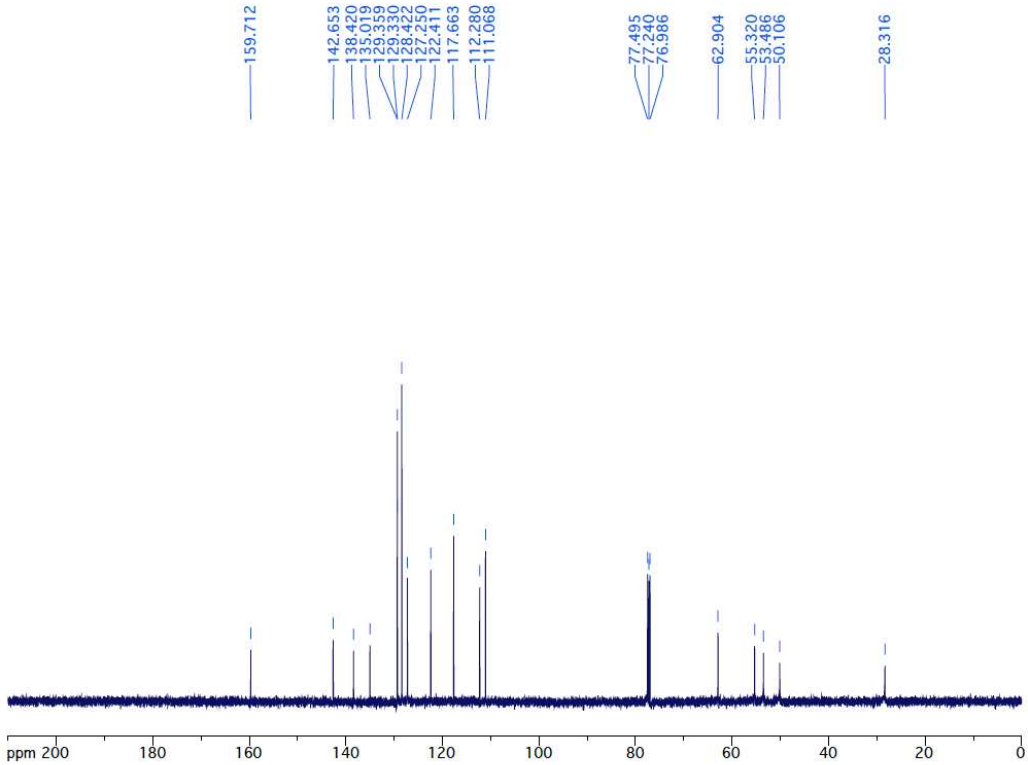
Table 18. Torsion angles [°] for **9g**.

C(9)-C(1)-N(2)-C(2)	118.78(13)
C(8)-C(1)-N(2)-C(2)	-117.95(13)
C(9)-C(1)-N(2)-C(3)	-5.51(16)
C(8)-C(1)-N(2)-C(3)	117.76(13)
C(2)-N(2)-C(3)-C(4)	-175.20(12)
C(1)-N(2)-C(3)-C(4)	-50.05(16)
N(2)-C(3)-C(4)-C(5)	51.47(16)
C(3)-C(4)-C(5)-C(14)	123.99(13)
C(3)-C(4)-C(5)-C(9)	2.30(16)
C(3)-C(4)-C(5)-C(6)	-114.80(13)
C(14)-C(5)-C(6)-C(7)	-177.30(12)
C(9)-C(5)-C(6)-C(7)	-55.27(16)
C(4)-C(5)-C(6)-C(7)	62.02(16)
C(5)-C(6)-C(7)-C(13)	176.11(13)
C(5)-C(6)-C(7)-C(8)	52.28(17)
C(9)-C(1)-C(8)-C(10)	-173.92(12)
N(2)-C(1)-C(8)-C(10)	63.69(16)
C(9)-C(1)-C(8)-C(7)	57.70(15)
N(2)-C(1)-C(8)-C(7)	-64.69(15)
C(13)-C(7)-C(8)-C(1)	-176.63(12)
C(6)-C(7)-C(8)-C(1)	-51.86(16)
C(13)-C(7)-C(8)-C(10)	54.45(16)
C(6)-C(7)-C(8)-C(10)	179.22(12)
C(8)-C(1)-C(9)-C(5)	-62.01(15)
N(2)-C(1)-C(9)-C(5)	61.60(15)
C(14)-C(5)-C(9)-C(1)	-179.68(12)
C(6)-C(5)-C(9)-C(1)	58.88(15)
C(4)-C(5)-C(9)-C(1)	-59.13(15)
C(1)-C(8)-C(10)-C(11)	176.94(13)
C(7)-C(8)-C(10)-C(11)	-55.50(17)
C(8)-C(10)-C(11)-C(12)	55.78(18)
C(10)-C(11)-C(12)-C(13)	-56.60(19)
C(11)-C(12)-C(13)-C(7)	55.81(19)
C(8)-C(7)-C(13)-C(12)	-53.87(18)
C(6)-C(7)-C(13)-C(12)	-177.92(14)
C(9)-C(5)-C(14)-C(15)	7.22(19)
C(6)-C(5)-C(14)-C(15)	127.10(15)
C(4)-C(5)-C(14)-C(15)	-112.45(15)
C(9)-C(5)-C(14)-C(19)	-177.27(13)
C(6)-C(5)-C(14)-C(19)	-57.39(18)
C(4)-C(5)-C(14)-C(19)	63.06(17)
C(19)-C(14)-C(15)-C(16)	-1.1(2)
C(5)-C(14)-C(15)-C(16)	174.52(14)
C(14)-C(15)-C(16)-O(16)	-176.85(14)
C(14)-C(15)-C(16)-C(17)	1.3(2)
O(16)-C(16)-C(17)-C(18)	177.19(15)
C(15)-C(16)-C(17)-C(18)	-0.9(2)
C(16)-C(17)-C(18)-C(19)	0.2(2)
C(17)-C(18)-C(19)-C(14)	0.0(3)
C(15)-C(14)-C(19)-C(18)	0.4(2)
C(5)-C(14)-C(19)-C(18)	-175.30(14)

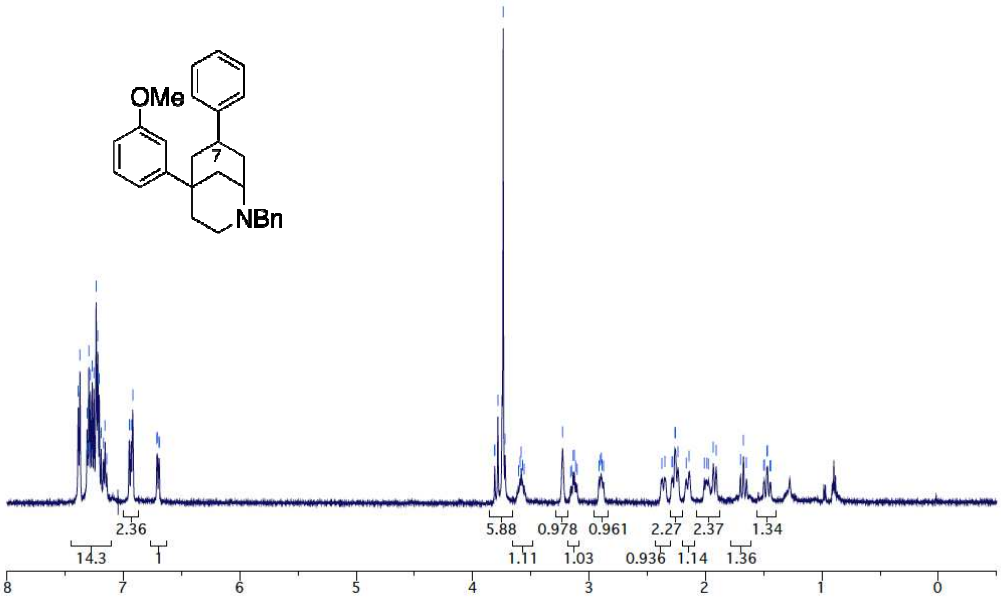
^{1}H and ^{13}C NMR Spectra of **3ii**

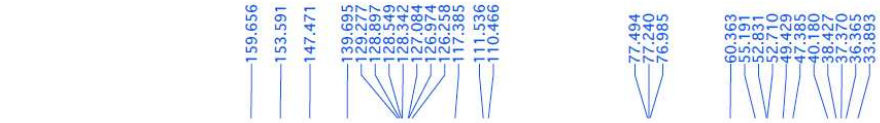


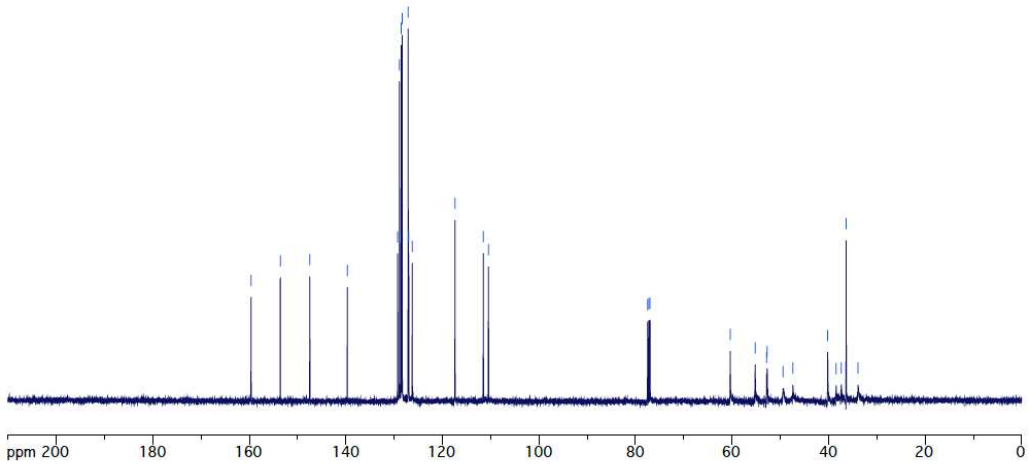




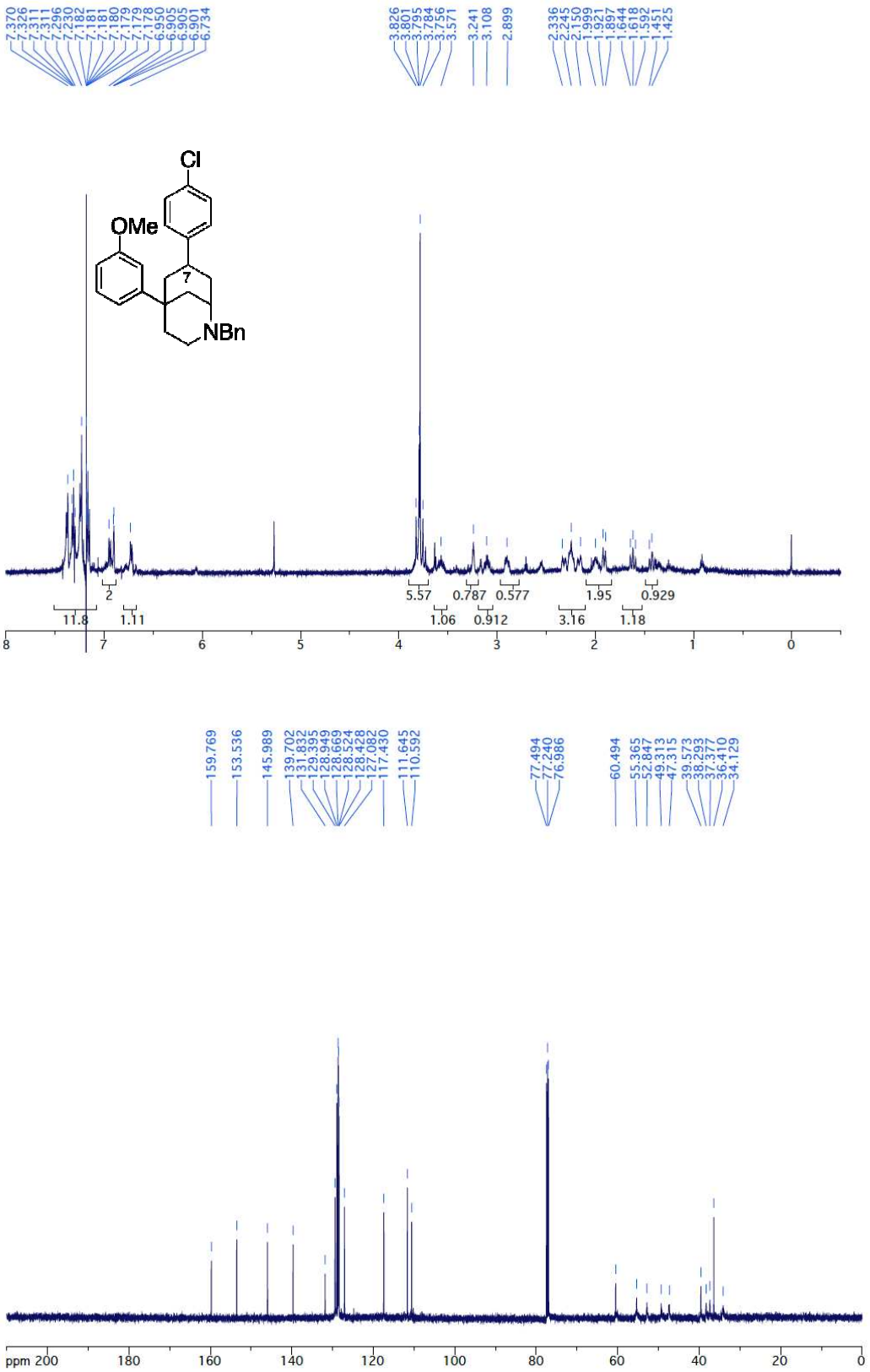
^{1}H and ^{13}C NMR Spectra of **8b**



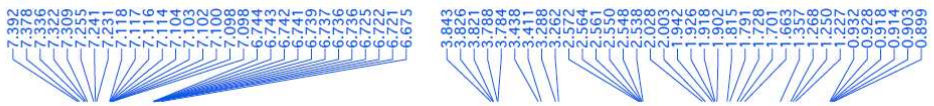


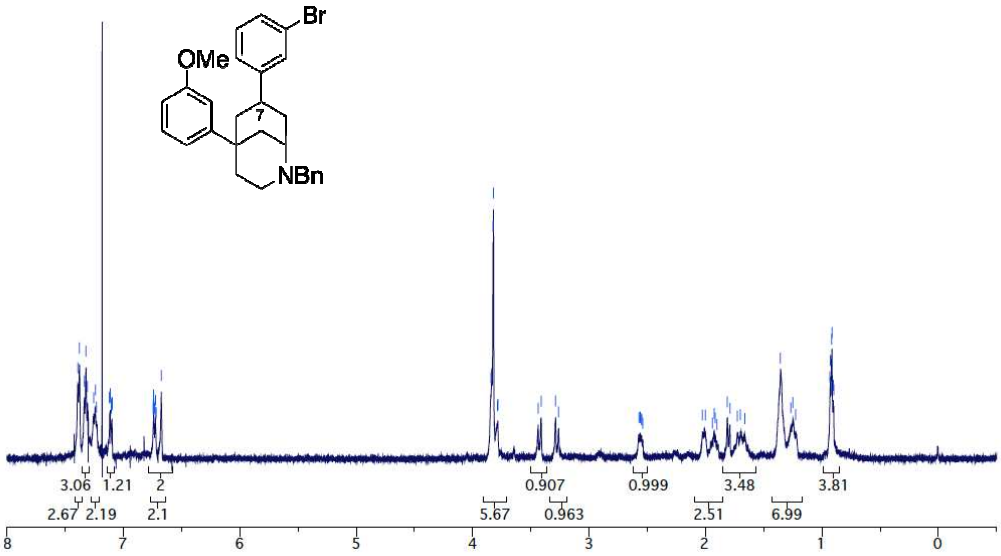


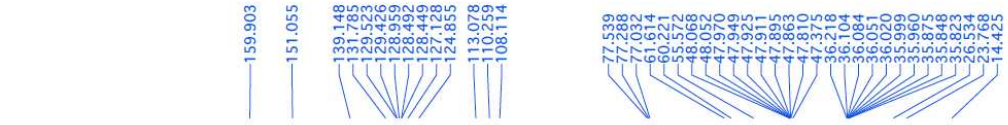
^{1}H and ^{13}C NMR Spectra of **8c**

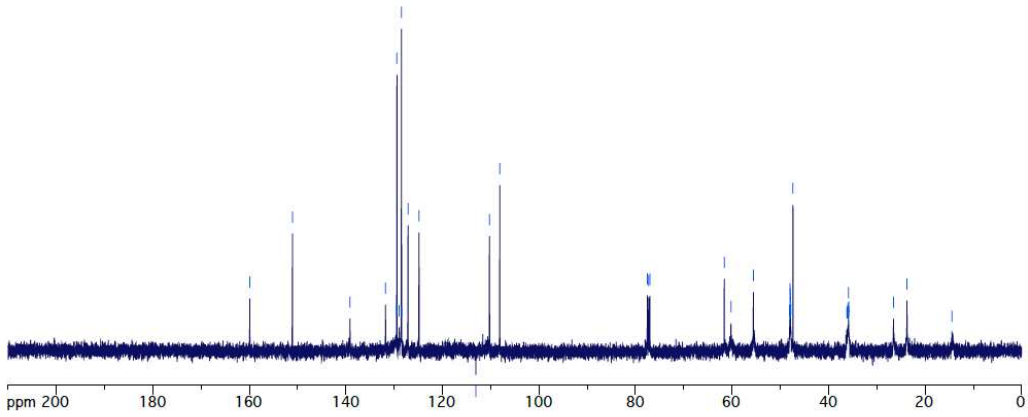


^{1}H and ^{13}C NMR Spectra of **8d**

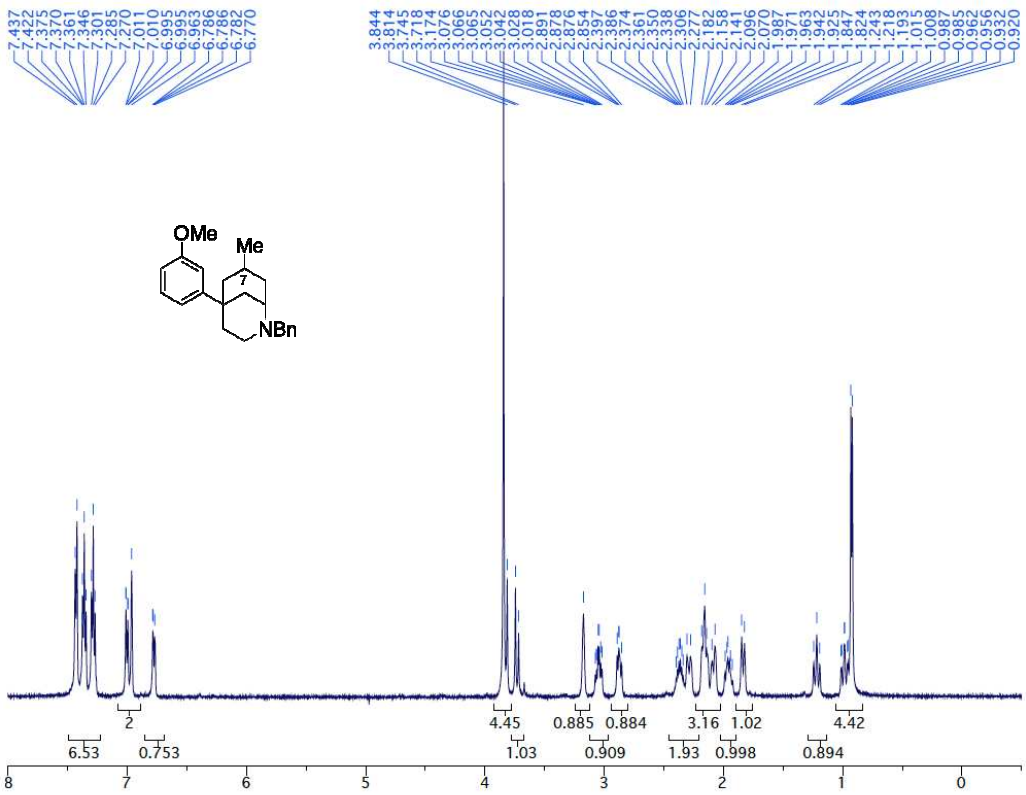


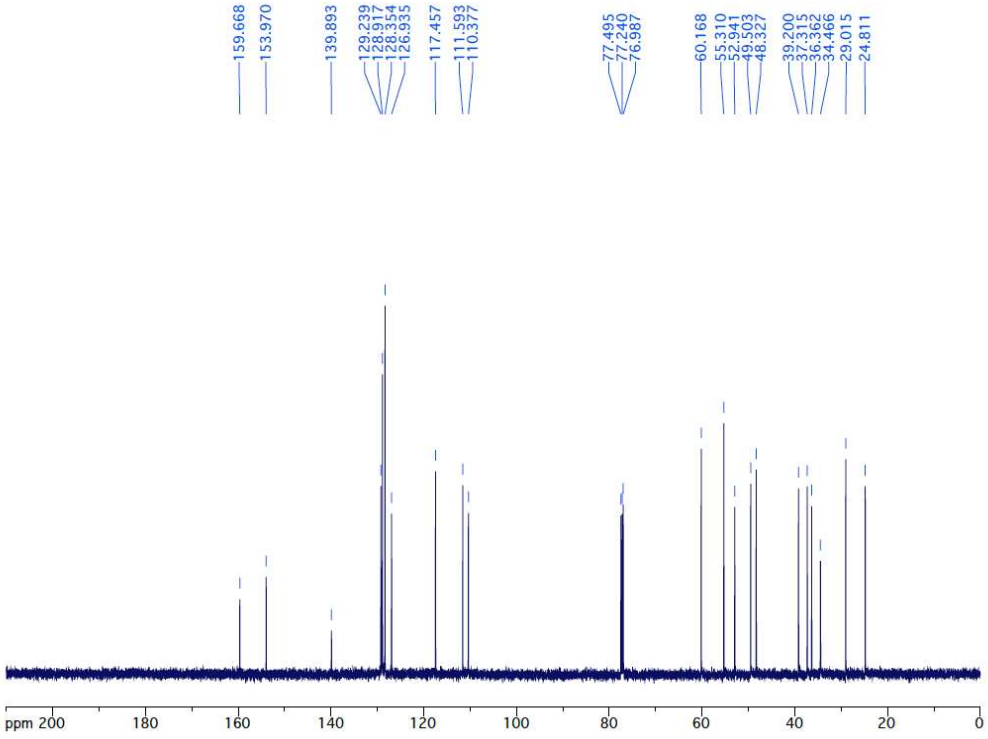




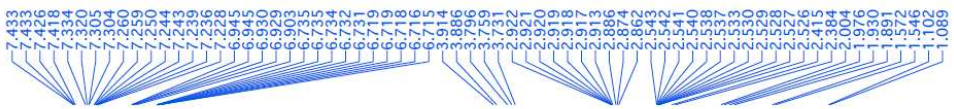


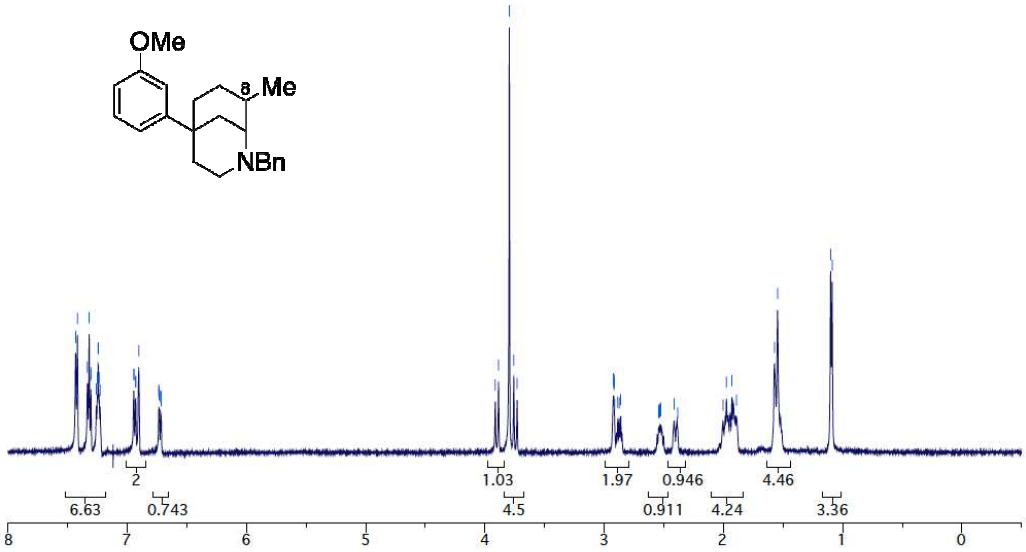
^{1}H and ^{13}C NMR Spectra of **8e**

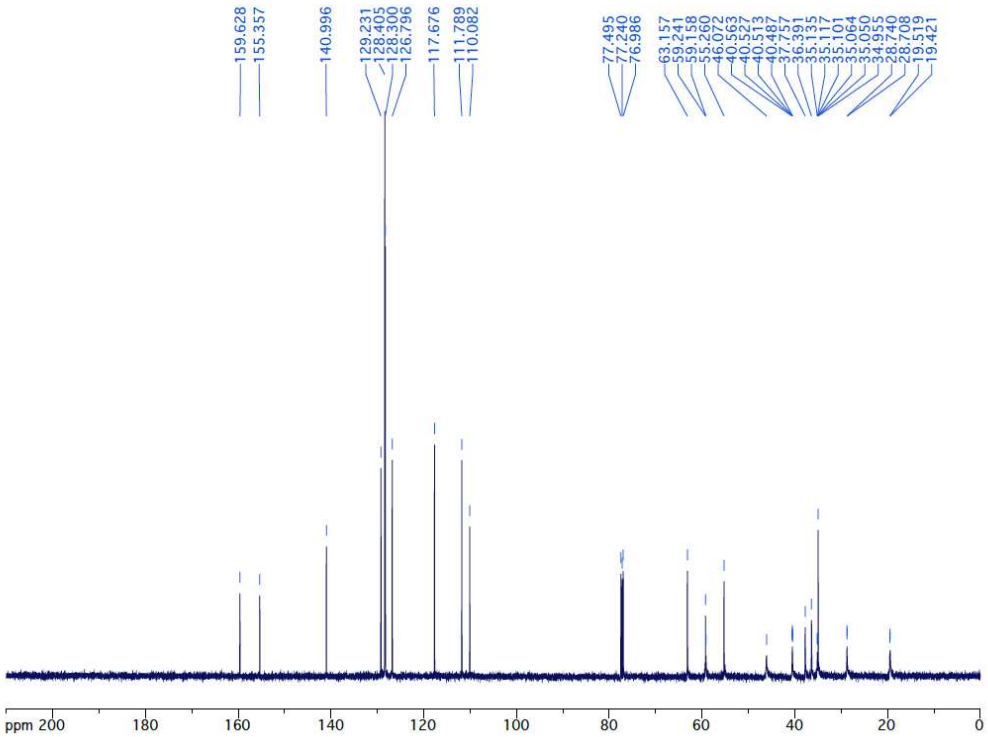




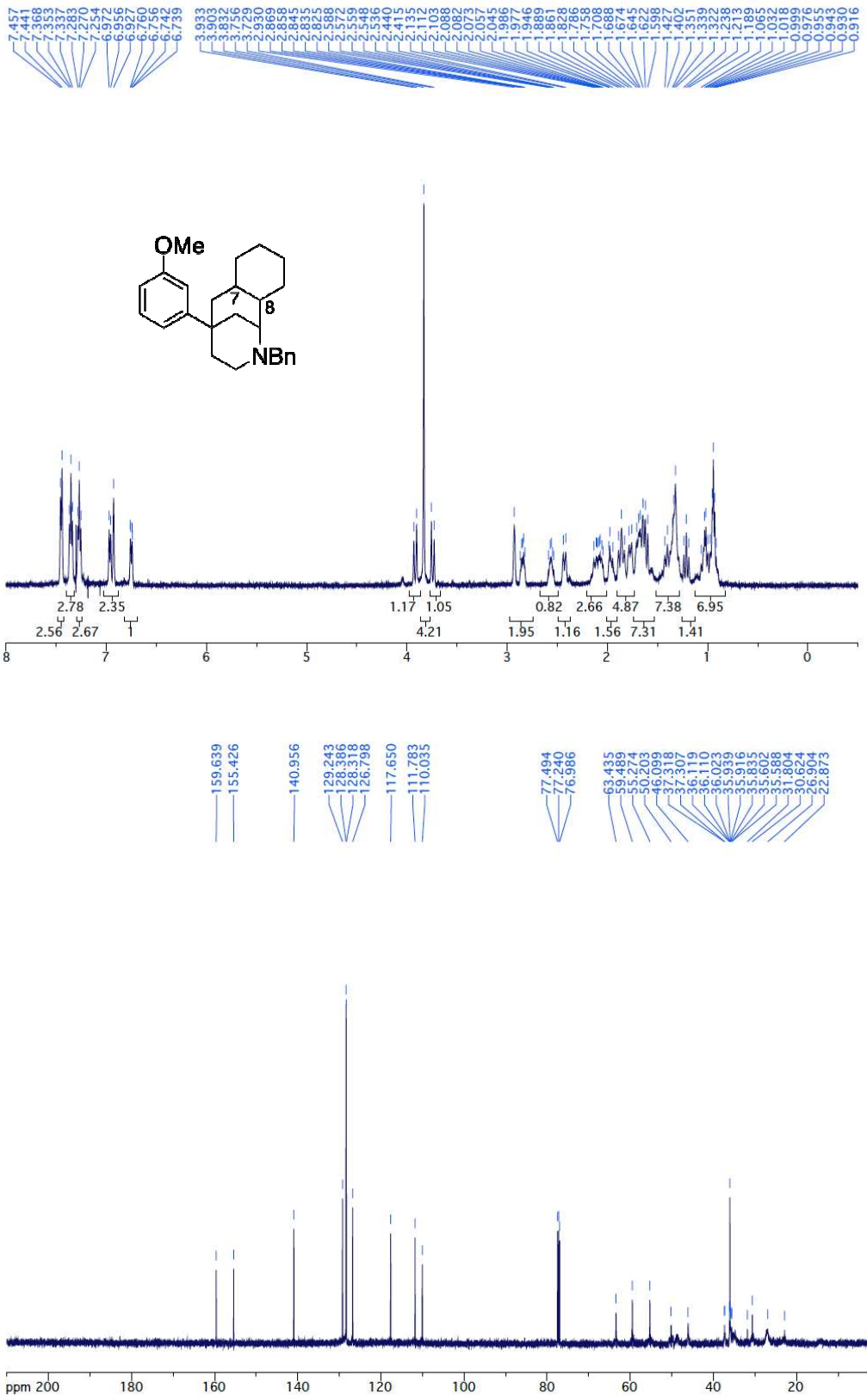
^{1}H and ^{13}C NMR Spectra of **8f**



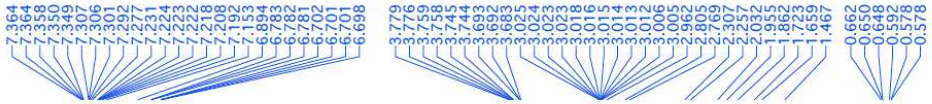


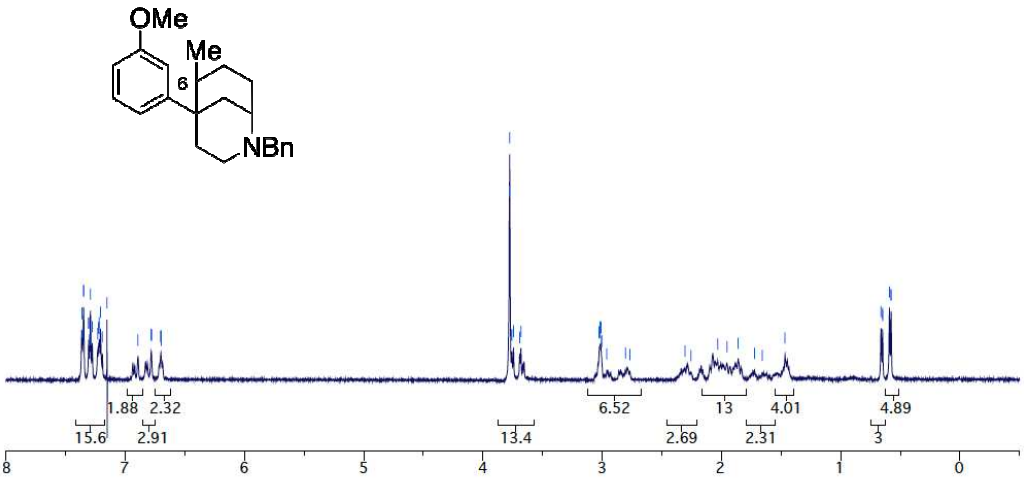


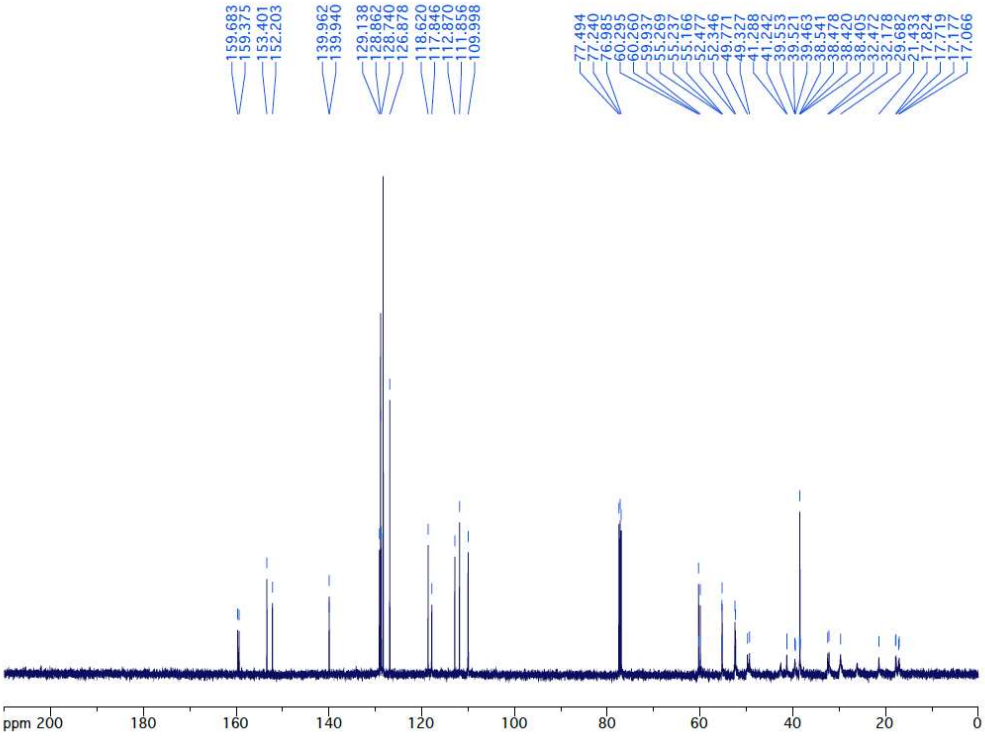
^{1}H and ^{13}C NMR Spectra of **8g**



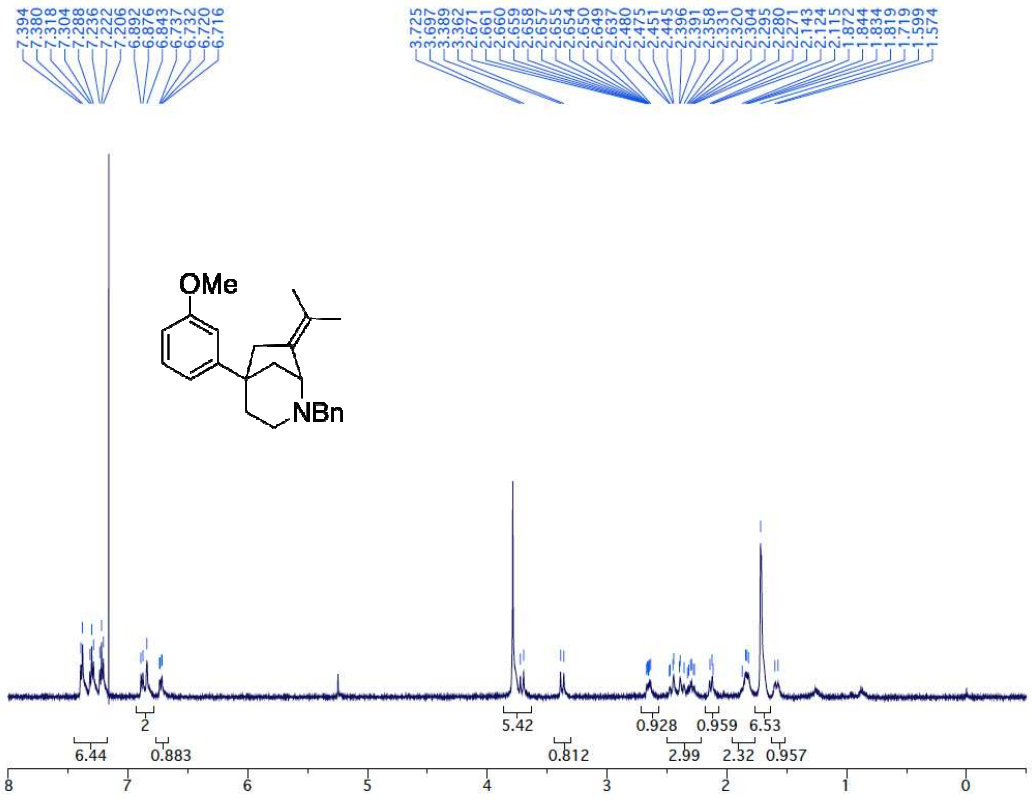
^{1}H and ^{13}C NMR Spectra of **8h**

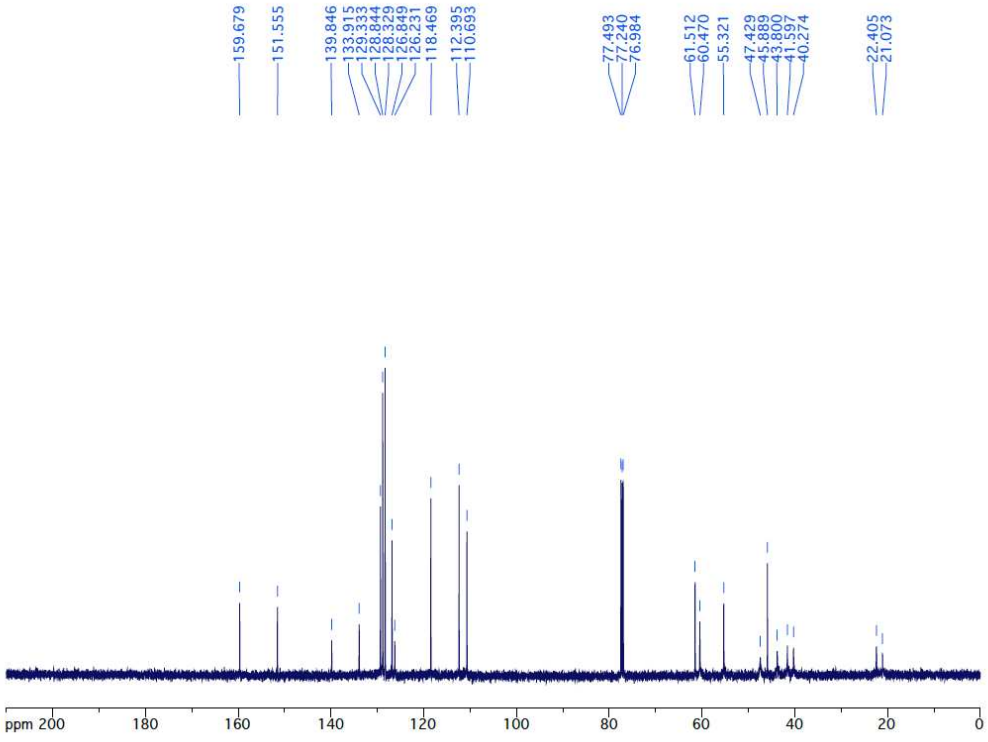




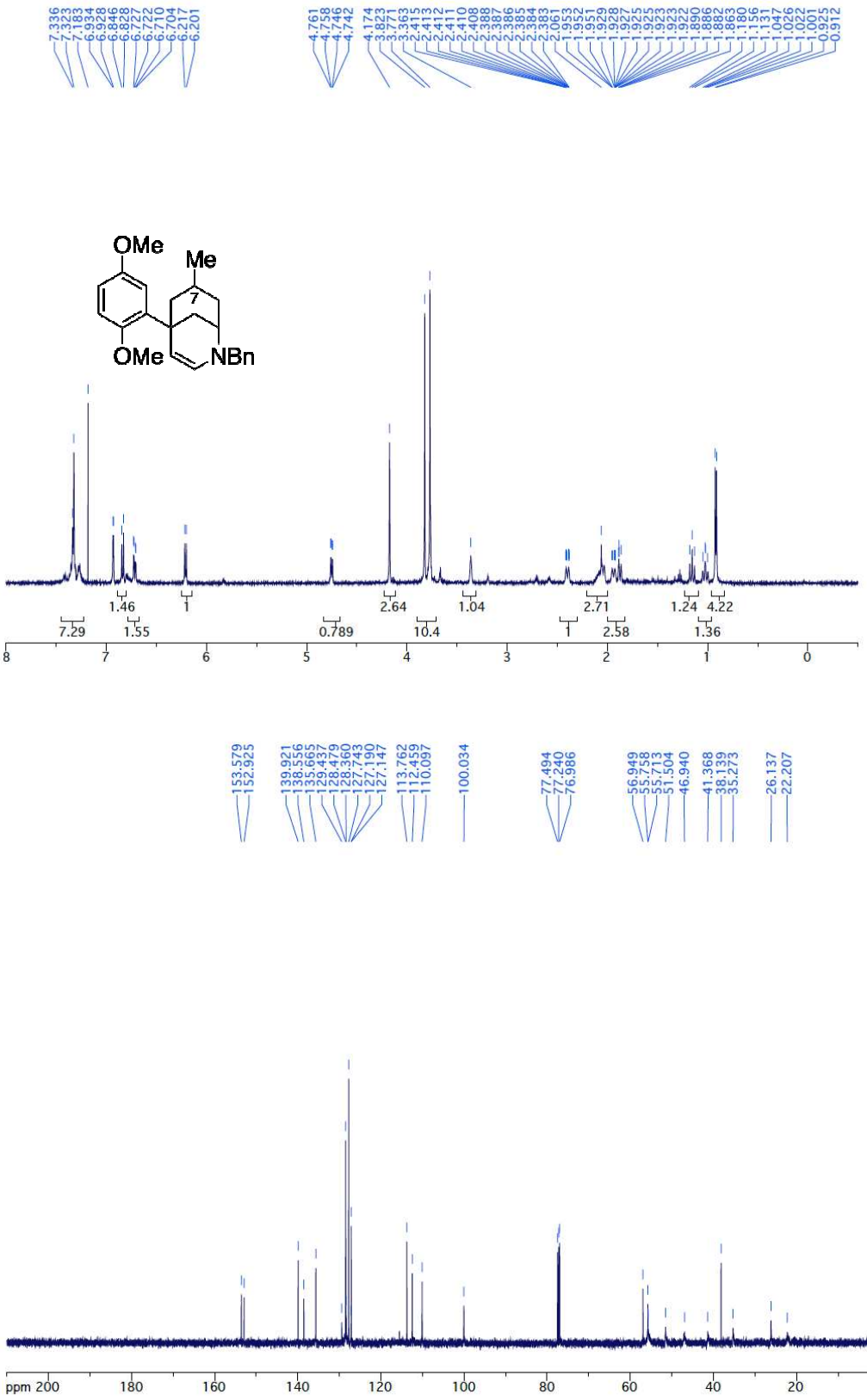


^{1}H and ^{13}C NMR Spectra of **8i**

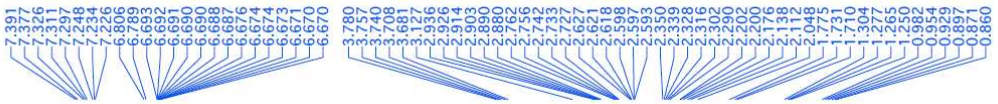


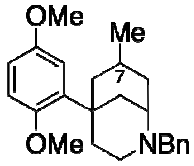


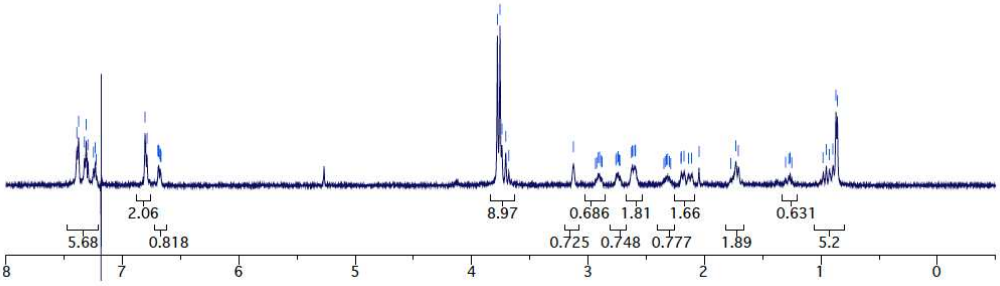
^{1}H and ^{13}C NMR Spectra of **7j**

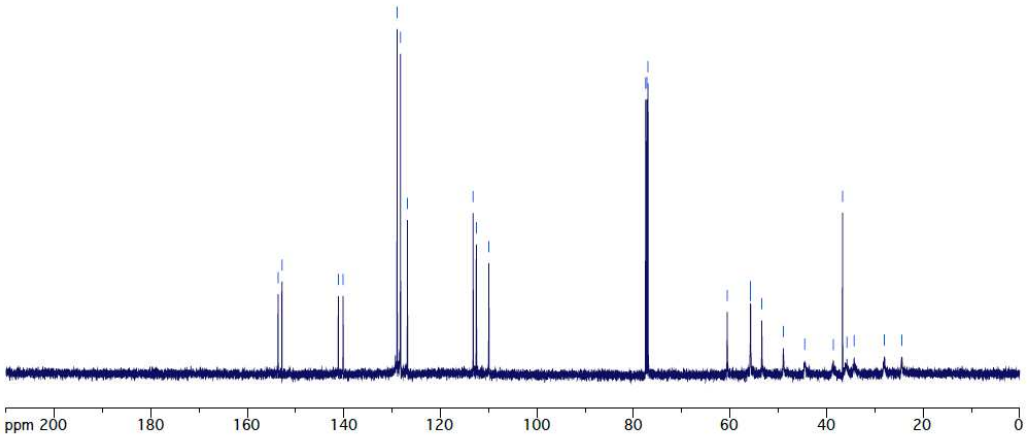


^{1}H and ^{13}C NMR Spectra of **8j**

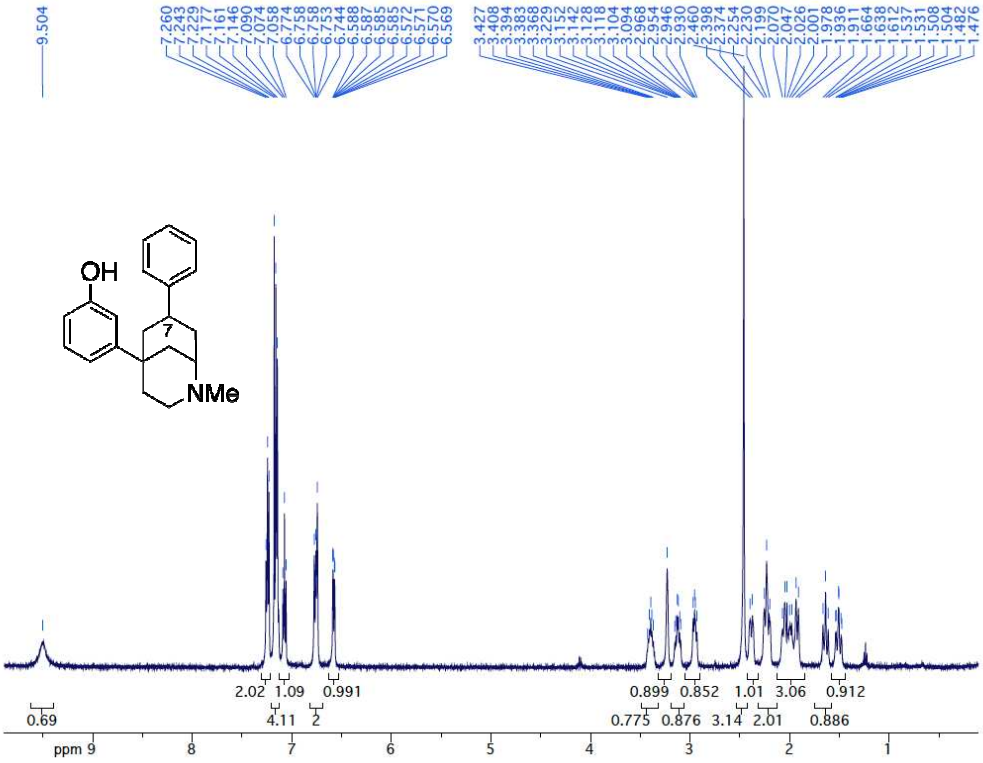


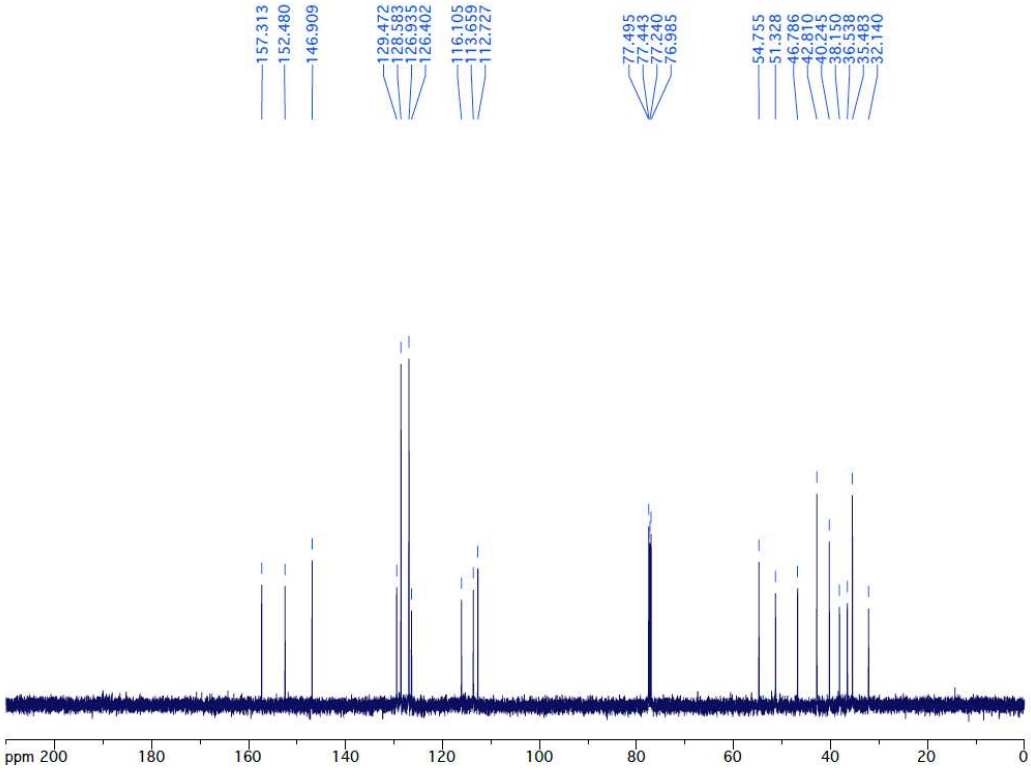




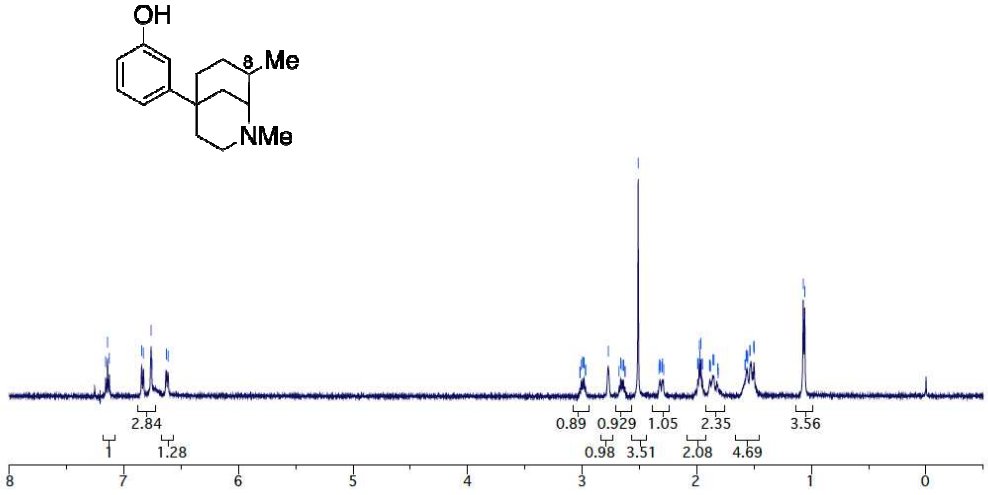


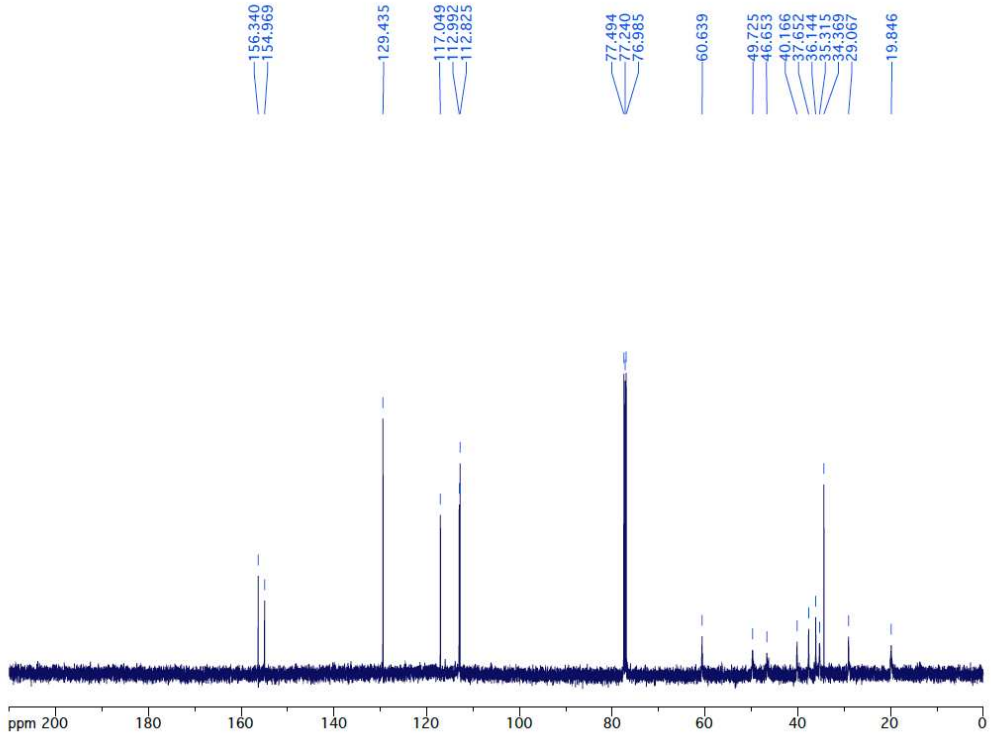
^{1}H and ^{13}C NMR Spectra of **9b**



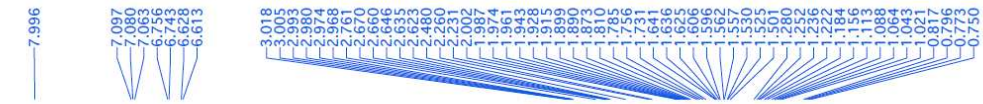


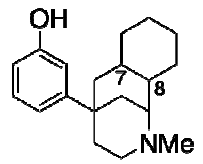
^{1}H and ^{13}C NMR Spectra of **9f**

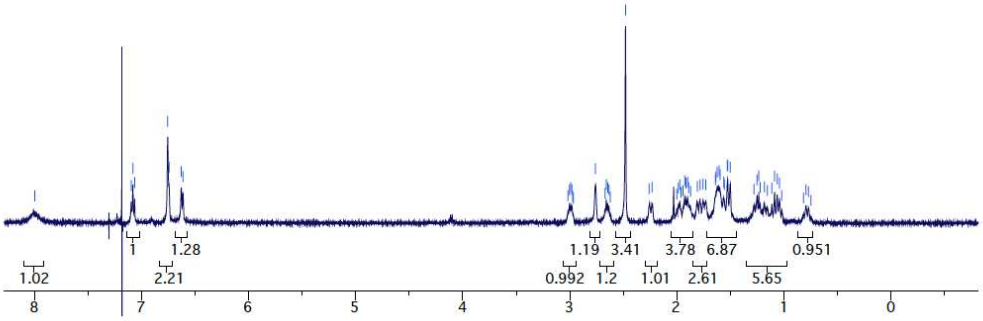


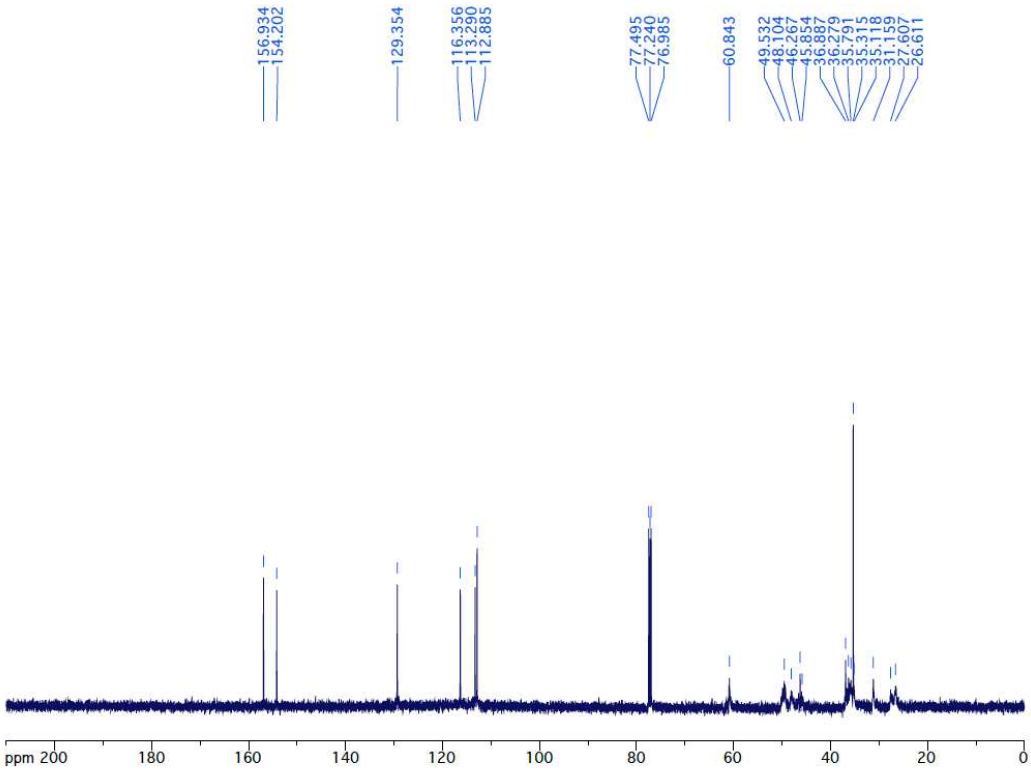


^{1}H and ^{13}C NMR Spectra of **9g**









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