Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Contents

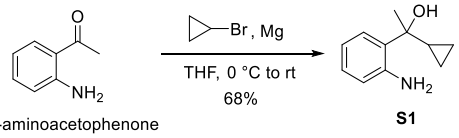
General

All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware. Analytical thin-layer chromatography was performed with Silica gel 60 (Merck). Silica gel column chromatography was performed with Kanto silica gel 60 (particle size, 63–210 μm) and Fuji silysia Chromatorex BW-300. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL JNM-ECA 500 at 500 MHz or a JEOL JNM-AL 400 at 400 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00) in $CDCl_3$ and residual $(CH_3)(CH_2D)S(O)$ (δ 2.50) in DMSO-d_6. Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL JNM-ECA 500 at 126 MHz or a JEOL JNM-AL 400 at 101 MHz. Chemical shifts are reported relative to $CDCl_3$ (δ 77.0) and DMSO-d_6 (δ 39.5). Infrared spectra were recorded on a FT/IR-4100 Fourier-transform infrared spectrometer ATR (attenuated total reflectance). Low and high resolution mass spectra (LRMS and HRMS) were recorded on JEOL JMS-HX/HX 110A mass spectrometer and JEOL JMS-700 mass spectrometer.

Material

Anhydrous CH_2Cl_2, 1,2-dichloroethane, xylene, DMF, methanol and CH_3CN were purchased from KANTO Chemical Co. Aldrich and Wako chemicals. Materials were obtained from Tokyo Chemical Industry Co., Ltd. Aldrich Inc., and other commercial suppliers and used without further purification.

Experimental Procedures

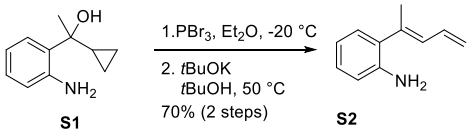


o-aminoacetophenone **S1**

Alcohol **S1**:

To a suspension of Mg (1.16 g, 46.6 mmol) in THF (40.0 mL) was added bromocyclopropane (3.60 mL, 44.4 mmol) dropwise, and the mixture was stirred at 0 °C for 1 h. *O*-aminoacetophenone (2.70 mL, 22.2 mmol) in THF (55 mL) was then added to the reaction mixture, and the mixture was stirred at room temperature for 6.5 h. The reaction mixture was then cooled to 0 °C and quenched with 2M aqueous HCl solution, followed by 10% aqueous NaOH solution to neutralize. The mixture was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The resultant residue was purified by flash column chromatography on silica gel (10-40% EtOAc/hexane) to give alcohol **S1** (2.67 g, 68%) as a light-yellow oil; ^{1}H NMR (500

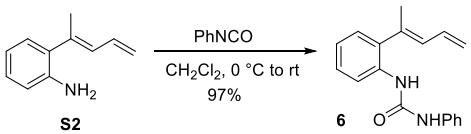
MHz, $CDCl_3$) δ 7.34 (dd, 1H, *J* = 7.7, 1.1 Hz, 1H), 7.05 (td, 1H, *J* = 7.6, 1.1 Hz), 6.69 (td, 1H, *J* = 8.2, 1.1 Hz), 6.61 (d, 1H, *J* = 7.2 Hz), 1.43 (s, 3H), 1.42 (m, 1H), 0.61 (m, 1H), 0.54-0.47 (m, 2H), 0.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 130.3, 128.0, 126.7, 117.7, 117.5, 75.5, 24.5, 21.5, 2.9, 1.1; HRMS calcd for $C_{11}H_{15}NONa$ $[M+Na]^+$ 200.1051; Found: *m/z* 200.1050.



(*E*)-Dienylaniline **S2**:

To a solution of alcohol **S1** (1.92 g, 10.83 mmol) in Et_2O (50.0 mL) was added phosphorus tribromide (1.56 mL, 21.66 mmol) in Et_2O (23.0 mL) at -20 °C to -10 °C dropwise, and the solution was stirred at -20 °C for 1.5 h. The reaction solution was then cooled to 0 °C and treated with 10% aqueous NaOH solution to pH 9. The mixture was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure to give a crude bromide.

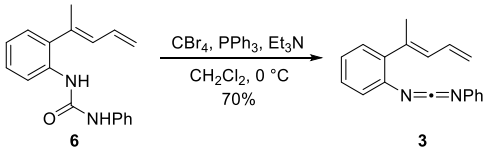
To a solution of the above crude bromide in *t*BuOH (50.0 mL) was added potassium *tert*-butoxide (2.00 g, 17.82 mmol), and the mixture was stirred at 50 °C for 2.5 h. The reaction mixture was then cooled to room temperature and diluted with Et_2O. The organic layer was washed with water and brine, and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The resultant residue was purified by flash column chromatography on silica gel (10% EtOAc/hexane) to give (*E*)-dienylaniline **S2** (1.21 g, 70% in 2 steps) as a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.07 (ddd, 1H, *J* = 7.7, 7.7, 1.6 Hz), 7.02 (dd, 1H, *J* = 7.6, 1.6 Hz), 6.78-6.70 (m, 3H), 6.16 (d, 1H, *J* = 11.7 Hz), 5.24 (d, 1H, *J* = 16.9 Hz), 5.18 (d, 1H, *J* = 10.3 Hz), 3.75 (br, 2H), 2.11 (d, 3H, *J* = 0.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 136.3, 133.0, 130.6, 130.0, 128.5, 127.9, 118.3, 117.3, 115.6, 17.8; HRMS calcd for $C_{11}H_{14}N$ $[M+H]^+$ 160.1126; Found: *m/z* 160.1133.



(*E*)-Dienylurea **6**:

To a solution of (*E*)-dienylaniline **S2** (838.1 mg, 5.26 mmol) in CH_2Cl_2 (17.0 mL) was added phenyl isocyanate (629.0 μL, 5.79 mmol) at 0 °C. The solution was stirred at room temperature for 2.5 h. The reaction solution was then concentrated under reduced pressure to give (*E*)-

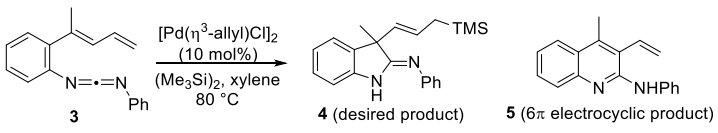
dienylurea **6** (1.42 g, 97%) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, 1H, *J* = 8.3 Hz), 7.32-7.27 (m, 5H), 7.13-7.07 (m, 3H), 6.72 (br, 1H), 6.65 (br, 1H), 6.61 (ddd, 1H, *J* = 16.9, 10.9, 10.8 Hz), 6.02 (d, 1H, *J* = 10.9 Hz, 1H), 5.21 (d, 1H, *J* = 16.9 Hz), 5.20 (d, 1H, *J* = 10.8 Hz), 2.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 137.7, 136.5, 135.5, 134.5, 132.4, 131.3, 129.4, 128.6, 128.1, 124.6, 124.1, 122.2, 121.8, 118.6, 18.2; HRMS calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$ 279.1497; Found: *m/z* 279.1493.



6 **3**

(*E*)-Dienylcarbodiimide **3**:

To a solution of (*E*)-dienylurea **6** (96.5 mg, 0.347 mmol) and PPh_3 (200.0 mg, 0.760 mmol) in CH_2Cl_2 (4.0 mL) were added Et_3N (200.0 μL, 1.43 mmol) and CBr_4 (250.0 mg, 0.754 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C. The reaction solution was stirred at 0 °C for 40 min. The resultant solution was then concentrated under reduced pressure. The obtained residue was suspended in 50% EtOAc/hexane and filtered on silica pad. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on neutral silica gel (20% EtOAc/hexane) to give (*E*)-dienylcarbodiimide **3** (62.8 mg, 70%) as a yellow oil. The product was not stable, thus it was used for the next reaction immediately; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, 2H, *J* = 7.6, 7.6 Hz), 7.24-7.19 (m, 3H), 7.16-7.12 (m, 4H), 6.65 (ddd, 1H, *J* = 16.9, 10.9, 10.6 Hz), 6.14 (d, 1H, *J* = 10.9 Hz), 5.23 (d, 1H, *J* = 16.9 Hz), 5.15 (d, 1H, *J* = 10.6 Hz), 2.16 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ140.2, 138.8, 136.5, 135.4, 132.8, 131.0, 129.4 129.3, 128.0, 125.5, 125.2, 125.1, 124.1, 117.8, 18.2. (Compound **3** was too unstable to measure HRMS.)

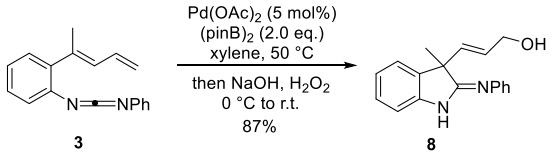


3 **4** (desired product) 55% **5** (6π electrocyclic product) 29%

2-iminoindoline **4** and quinoline **5**:

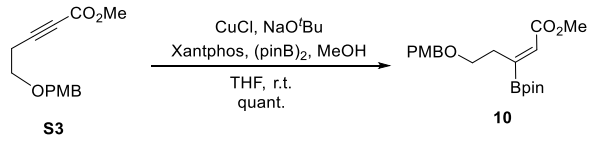
To a solution of (*E*)-dienylcarbodiimide **3** (23.2 mg, 0.0891 mmol) in anhydrous xylene (1.0 mL) was added hexamethyldisilane (40.0 μL, 0.195 mmol) and $[Pd(\eta^3\text{-allyl})Cl]_2$ (3.3 mg, 8.91×10^{-3} mmol) at room temperature. The reaction atmosphere was replaced by the Ar atmosphere. The mixture was then stirred at 80 °C for 15.5 h. The mixture was cooled to room temperature,

concentrated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel (0-50% EtOAc/hexane) to give 2-iminoindoline **4** (16.3 mg, 55%) as a white solid and quinoline **5** (6.7 mg, 29%) as a white solid; 2-iminoindoline **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, *J* = 7.8 Hz), 7.39-7.34 (m, 3H), 7.10-6.96 (m, 4H), 6.34 (br, 1H), 5.82 (dd, 1H, *J* = 15.6, 8.0, 8.0 Hz), 5.24 (d, 1H, *J* = 15.6 Hz), 1.54 (d, 2H, *J* = 8.0 Hz), 1.48 (s, 3H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 155.3, 140.5, 139.5, 129.2, 128.9, 128.0, 127.7, 123.0, 122.4, 121.6, 118.9, 117.8, 56.5, 23.0, 22.2, -1.9; HRMS calcd for $C_{21}H_{27}N_2Si$ $[M+H]^+$ 335.1944; Found: *m/z* 335.1942; quinoline **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 4H), 7.56 (ddd, 1H, *J* = 8.9, 8.9, 1.8 Hz), 7.37-7.29 (m, 3H), 7.04-7.00 (m, 2H), 6.81 (dd, 1H, *J* = 17.9, 11.6 Hz), 5.89 (dd, 1H, *J* = 11.6, 2.0 Hz), 5.61 (dd, 1H, *J* = 17.9, 2.0 Hz), 2.58 (d, 3H, *J* = 0.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 146.1, 141.2, 140.6, 132.5, 129.0, 128.8, 127.6, 124.0, 123.9, 123.7, 123.0, 122.0, 121.7, 119.2, 15.5.



Iminoindoline 8

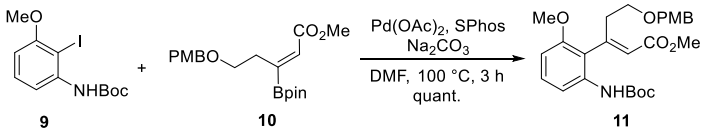
To a solution of carbodiimide **3** (30.0 mg, 0.115 mmol) in xylene (1.5 mL) were added $(pinB)_2$ (55.5 mg, 0.218 mmol) and $Pd(OAc)_2$ (1.3 mg, 0.00575 mmol) at room temperature. The resulting mixture was stirred at 50 °C overnight. After the reaction mixture was cooled to 0 °C, aqueous NaOH (10% w/v, 0.3 mL, 0.75 mmol) and aqueous H_2O_2 (30% w/v, 0.078 mL, 0.69 mmol) were added. The reaction mixture was stirred at room temperature for 2 h. After addition of saturated aqueous NH_4Cl, the reaction was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue by column chromatography on silica gel (5%-20% ethyl acetate/hexanes) gave iminoindoline **8** as a colorless oil; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.21 (s, 1H), 8.02 (d, 2H, *J* = 7.8 Hz), 7.32 (dd, 2H, *J* = 8.6, 7.4 Hz), 7.22-7.15 (m, 3H), 7.00-6.95 (m, 2H), 5.87 (d, 1H, *J* = 13.7 Hz), 5.53 (ddd, 1H, *J* = 13.7, 4.8, 4.6 Hz), 4.76 (dd, 1H, *J* = 5.4, 5.2 Hz), 3.92 (ddd, 2H, *J* = 5.2, 4.8, 1.7 Hz), 1.52 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 173.1, 155.3, 140.8, 139.7, 130.4, 129.2, 128.5, 127.7, 122.1, 121.9, 121.6, 118.9, 116.8, 60.9, 55.8, 22.0; IR (film, cm^{-1}) 3439, 2975, 2918, 2251, 2125, 1668, 1469, 1383, 1236, 1090, 1054, 1025, 1005, 891, 820**;** MS (FAB) *m/z* 279 $[M+H]^+$; HRMS calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$ 279.1497; Found: *m/z* 279.1496.



S3 10

Vinylboronate **10**:

A suspension of CuCl (12.0 mg, 0.121 mmol) and NaO^{t}Bu (23.3 mg, 0.242 mmol) and Xantphos (70.0 mg, 0.121 mmol) in anhydrous THF (1.8 mL) was stirred at room temperature for 30 min. A solution of bis(pinacolato)diboron (563.7 mg, 2.22 mmol) in anhydrous THF (1.2 mL) was added to the reaction suspension. The reaction mixture was stirred at room temperature for an additional 10 min. A solution of ester **S3** (501.7 mg, 2.02 mmol) in anhydrous THF (0.9 mL) and following anhydrous MeOH (163 μL, 4.04 mmol) were then added to the reaction mixture via cannula. After the reaction mixture was stirred at room temperature for 10.5 h, the mixture was then filtered through Celite. After concentration of the filtrate under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (10-20% EtOAc/hexane) to give vinylboronate **10** (760.0 mg, quant.) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, 2H, *J* = 8.6 Hz), 6.85 (d, 2H, *J* = 8.6 Hz), 6.47 (s, 1H), 4.44 (s, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.58 (dd, 2H, *J* = 6.9, 6.6 Hz), 3.03 (dd, 2H, *J* = 6.9, 6.1 Hz), 1.22 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 159.0, 130.8, 130.7, 129.2, 113.6, 84.1, 72.1, 69.4, 55.2, 51.1, 30.3, 24.6; IR (ATR, cm^{-1}) 2978, 1721, 1612, 1512, 1465, 1374, 1335, 1244, 1173, 1144, 1092, 1035, 894**;** MS (FAB) *m/z* 377 $[M+H]^+$; HRMS calcd for $C_{20}H_{30}BO_6$ $[M+H]^+$ 377.2135; Found: *m/z* 377.2137.

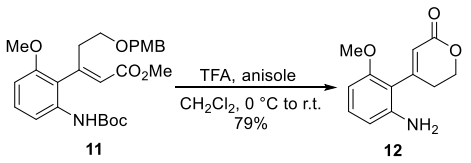


9 10 11

Coupling product **11**:

To a solution of vinylboronate **10** (771.3 mg, 2.05 mmol) and aryliodide **9** (550.6 mg, 1.58 mmol) in DMF (16.0 mL) were added 1M aqueous Na_2CO_3 (4.7 mL, 4.7 mmol), SPhos (129.7 mg, 0.316 mmol) and $Pd(OAc)_2$ (35.5 mg, 0.158 mmol) at room temperature. The reaction atmosphere was replaced with the Ar atmosphere, and the mixture was stirred at 100 °C for 3 h. After the reaction mixture was then cooled to room temperature, the mixture was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, purification by flash column chromatography on silica gel (10-20% EtOAc/hexane) gave a coupling product **11** (745.0 mg, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, 1H, *J* = 8.3 Hz), 7.30 (br, 1H), 7.24 (dd, 1H, *J* = 8.3, 8.3 Hz), 7.20-7.17 (m, 2H), 6.86-6.82 (m, 2H), 6.59 (dd, 1H, *J* = 8.3, 0.6 Hz), 5.87 (s, 1H), 4.44-4.35 (m, 2H), 4.00 (br, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.58 (m, 1H), 3.35 (br, 1H), 2.59 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (126

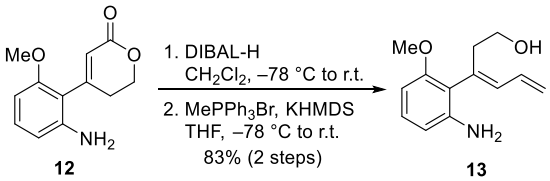
MHz, $CDCl_3$) δ 166.4, 159.1, 156.3, 154.4, 153.3, 136.7, 129.9, 129.2, 128.9, 122.8, 120.8, 113.6, 113.5, 105.2, 80.0, 72.2, 67.3, 55.6, 55.2, 51.2, 32.4, 28.3; IR (ATR, cm^{-1}) 3321, 2975, 2360, 1721, 1639, 1589, 1513, 1469, 1435, 1365, 1240, 1160, 1088, 1042, 878**;** MS (FAB) *m/z* 472 $[M+H]^+$; HRMS calcd for $C_{26}H_{34}NO_7$ $[M+H]^+$ 472.2335; Found: *m/z* 472.2338.



11 **12**

Aniline **12**:

To a solution of the coupling product **11** (998.1 mg, 2.12 mmol) in CH_2Cl_2 (15.0 mL) were added anisole (1.2 mL, 10.6 mmol) and TFA (3.0 mL) at 0 °C, and the solution was stirred at room temperature for 6.5 h. After addition of saturated aqueous $NaHCO_3$, the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, purification by flash column chromatography on silica gel (10-60% EtOAc/hexane) gave aniline **12** (366.5 mg, 79%) as a yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (dd, 1H, *J* = 8.3, 8.0 Hz), 6.38 (d, 1H, *J* = 8.0 Hz), 6.32 (d, 1H, *J* = 8.3 Hz), 6.06 (s, 1H), 4.52 (dd, 2H, *J* = 6.1, 6.1 Hz), 3.87 (br, 1H), 3.77 (s, 3H), 2.70 (dd, 2H, *J* = 6.1, 6.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 157.2, 155.7, 143.7, 130.3, 120.0, 112.3, 108.8, 100.6, 66.8, 55.5, 28.5; IR (ATR, cm^{-1}) 3464, 3367, 3239, 2942, 2838, 1710, 1621, 1579, 1466, 1438, 1399, 1302, 1254, 1222, 1132, 1081, 1045, 880; MS (FAB) *m/z* 220 $[M+H]^+$; HRMS calcd for $C_{12}H_{14}NO_3$ $[M+H]^+$ 220.0974; Found: *m/z* 220.0974; Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.58; H, 6.00; N, 6.31.



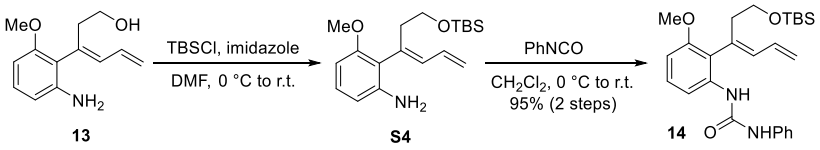
12 **13**

(*E*)-Dienylalcohol **13**:

To a solution of aniline **12** (810.0 mg, 3.69 mmol) in CH_2Cl_2 (70.0 mL) was added DIBAL-H (1M in toluene, 7.4 mL, 7.40 mmol) at –78 °C. The solution was stirred for 1 h. After addition of saturated aqueous Na/K tartrate, the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with EtOAc, washed with brine and dried over Na_2SO_4. Concentration under reduced pressure gave the crude acetal.

To a suspension of $MePPh_3Br$ (4.60 g, 12.9 mmol) in anhydrous THF (30.0 mL) was added KHMDS (0.5 M in THF, 22.2 mL, 11.1 mmol), and the suspension was stirred at 0 °C for 1 h. To

the suspension was added the above acetal in anhydrous THF (7.0 mL) via cannula. After the reaction mixture was stirred for 2 h at room temperature, it was quenched with water, extracted with EtOAc, washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, purification by flash column chromatography on silica gel (10-60% EtOAc/hexane) gave (*E*)-dienylalcohol **13** (672.4 mg, 83% in 2 steps) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, 1H, *J*= 8.3, 8.0 Hz), 6.85 (ddd, 1H, *J*= 16.6, 10.9, 10.3 Hz), 6.41-6.36 (m, 2H), 6.17 (d, 1H, *J*= 11.2 Hz), 5.25 (dd, 1H, *J*= 16.9, 1.1 Hz), 5.22 (dd, 2H, *J* = 12.9, 1.1 Hz), 3.76 (s, 3H), 3.76 (br, 1H), 3.59-3.57 (m, 2H), 2.80-2.65 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 144.4, 134.4, 133.9, 132.5, 128.4, 118.4, 117.8, 109.0, 101.3, 60.9, 55.6, 34.3; IR (ATR, cm^{-1}) 3370, 2955, 1714, 1584, 1466, 1437, 1253, 1130, 1092, 1047, 909; MS (FAB) *m/z* 220 $[M+H]^+$; HRMS calcd for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1338; Found: *m/z* 220.1340.

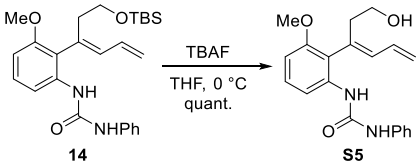


(*E*)-Dienylurea **14**:

To a solution of (*E*)-dienylalcohol **13** (649.1 mg, 2.96 mmol) in anhydrous DMF (30.0 mL) were added TBSCl (535.0 mg, 3.55 mmol) and imidazole (302.1 mg, 4.44 mmol) at 0 °C, and the solution was stirred at room temperature for 8 h. After addition of water to the reaction solution, the mixture was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, purification by flash column chromatography on silica gel (10-30% EtOAc/hexane) gave a mixture including desired (*E*)-dienylsilylether **S4**.

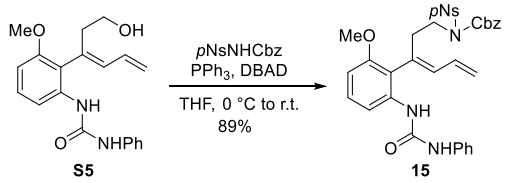
To a solution of the above (*E*)-dienylsilylether **S4** in CH_2Cl_2 (30.0 mL) was added phenyl isocyanate (406.0 μL, 3.74 mmol) at 0 °C, and the solution was stirred at room temperature for 6 h. The reaction solution was then concentrated under reduced pressure. The resultant residue was purified by flash column chromatography on silica gel (10-30% EtOAc/hexane) to give (*E*)-dienylurea **14** (1.27 g, 95% in 2 steps) as a white solid; mp. 156.5-160.3 °C (hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 1H, *J* = 8.3 Hz), 7.32-7.13 (m, 5H), 7.09-6.94 (m, 2H), 6.58 (d, 1H, *J* = 7.4 Hz), 6.44 (br, 1H), 6.21 (d, 1H, *J* = 10.9 Hz), 5.93 (ddd, 1H, J = 17.0, 10.0, 10.0 Hz), 5.13 (dd, 1H, *J* = 17.0, 1.7 Hz), 4.93 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.70 (s, 3H), 3.61 (ddd, 1H, *J* = 10.0, 6.0, 4.5 Hz), 3.45 (ddd, 1H, *J* = 12.5, 7.5, 3.1 Hz), 2.54 (ddd, 1H, *J* = 13.8, 13.8, 4.3 Hz), 2.44 (ddd, 1H, 13.8, 9.0, 6.0 Hz), 0.83 (s, 9H), 0.012 (s, 3H), 0.008 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 152.8, 138.1, 137.4, 134.1, 133.4, 132.6, 129.0, 128.8, 123.8, 121.0, 118.2, 118.0, 113.3, 105.6, 61.6, 55.7, 40.9, 26.0, 18.5, -5.0, -5.2; IR (ATR, cm^{-1}) 3331, 2954, 2856, 1657, 1598,

1551, 1466, 1436, 1315, 1294, 1246, 1088; Anal. Calcd for $C_{26}H_{36}N_2O_3Si$: C, 68.99; H, 8.02; N, 6.19. Found: C, 68.79: H, 7.99; N, 6.27.



(*E*)-Dienylalcohol **S5**:

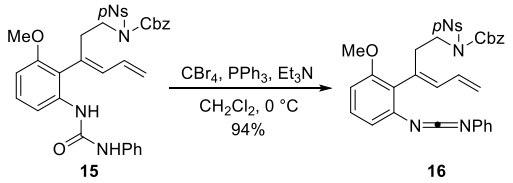
To a solution of (*E*)-dienylurea **14** (200.0 mg, 0.442 mmol) in THF (4.4 mL) was added TBAF (1M in THF, 0.5mL, 0.486 mmol) at 0 °C. The solution was stirred at 0 °C for 2 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with EtOAc, washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (10-60% EtOAc/hexane) to give (*E*)-dienylalcohol **S5** (149.0 mg, quant.) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, 1H, *J* = 8.3 Hz), 7.41 (br, 1H), 7.29-7.19 (m, 6H), 7.04 (dd, 1H, *J* = 7.2, 7.2 Hz), 6.73 (ddd, 1H, *J* = 16.6, 10.8, 10.3 Hz), 6.59 (d, 1H, *J* = 8.3 Hz), 6.10 (d, 1H, *J* = 10.8 Hz), 5.22 (d, 1H, *J* = 17.2 Hz), 5.20 (d, 1H, *J* = 10.3 Hz), 3.75 (s, 3H), 3.62 (m, 1H), 3.45 (m, 1H), 2.73 (m, 1H), 2.59-2.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 153.5, 138.1, 137.5, 135.1, 133.0, 132.2, 129.1, 128.6, 123.8, 121.6, 121.0, 119.2, 113.3, 105.4, 60.4, 55.7, 34.2; IR (ATR, cm^{-1}) 3341, 2960, 2246, 1665, 1588, 1549, 1466, 1436, 1314, 1246, 1097, 1040, 907; Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55: N, 8.28. Found: C, 70.82: H, 6.65: N, 8.21.



(*E*)-Dienylurea **15**:

To a solution of (*E*)-dienylalcohol **S5** (215.4 mg, 0.637 mmol), *p*NsNHCbz (428.5 g, 1.27 mmol) and PPh_3 (334.2 mg, 1.27 mmol) in THF (6.0 mL) was added a solution of DBAD (293.4 mg, 1.27 mmol) in THF (1.0 mL) at 0 °C. The solution was stirred at room temperature for 3 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (5-30% EtOAc/hexane) to give (*E*)-dienylurea **15** (372.4 mg, 89%) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, 2H, *J* = 8.9 Hz), 7.82 (d, 2H, *J* = 8.9 Hz), 7.76 (d, 1H, *J* = 8.3 Hz), 7.36-7.21 (m, 10H), 7.08 (d, 2H, *J* = 7.4 Hz), 7.02 (dd, 1H, *J* = 7.4, 7.2 Hz), 6.71 (ddd, 1H, *J* = 16.6, 10.6,

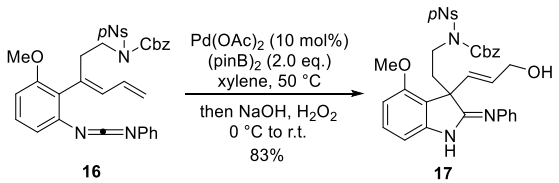
10.6 Hz), 6.62 (d, 1H, *J* = 8.3 Hz), 6.05 (d, 1H, *J* = 10.9 Hz), 5.22 (d, 1H, *J* = 16.9 Hz), 5.18 (d, 1H, *J* = 10.3 Hz), 5.01 (s, 2H), 3.88-3.85 (m, 2H), 3.74 (s, 3H), 3.00-2.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 153.2, 151.9, 150.2, 144.3, 138.1, 136.6, 134.6, 133.5, 132.0, 131.9, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 123.9, 123.8, 121.8, 120.7, 119.9, 113.6, 105.8, 69.7, 55.5, 46.5, 33.0; IR (ATR, cm^{-1}) 3369, 2977, 2917, 2252, 1733, 1665, 1588, 1533, 1468, 1437, 1350, 1236, 1171, 1089, 897; MS (FAB) *m/z* 657 $[M+H]^+$; HRMS calcd for $C_{34}H_{33}N_4O_8S$ $[M+H]^+$ 657.2019; Found: *m/z* 657.2022.



15 **16**

(*E*)-Dienylcarbodiimide **16**:

To a solution of (*E*)-dienylurea **15** (28.0 mg, 0.0426 mmol) and PPh_3 (22.4 mg, 0.0852 mmol) in CH_2Cl_2 (1.0 mL) were added Et_3N (24.0 μL, 0.170 mmol) and CBr_4 (28.3 mg, 0.0852 mmol) at 0 °C. The reaction solution was stirred at 0 °C for 2 h. The resultant solution was then concentrated under reduced pressure. The obtained residue was purified by flash column chromatography on neutral silica gel (10-30% EtOAc/hexane) to give (*E*)-dienylcarbodiimide **16** (25.7 mg, 94%) as a yellow solid. The product was not stable, thus it was used for the next reaction immediately; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 8.9 Hz), 7.92 (d, 2H, *J* = 8.9 Hz), 7.35-7.27 (m, 5H), 7.21 (dd, 1H, *J* = 8.3, 8.0 Hz), 7.17-7.09 (m, 5H), 6.86 (d, 1H, *J* = 8.0 Hz), 6.72 (d, 1H, *J* = 8.3 Hz), 6.69 (ddd, 1H, *J* = 16.6, 10.6, 10.6 Hz), 6.10 (d, 1H, *J* = 11.2 Hz), 5.21 (dd, 1H, *J* = 16.9, 1.7 Hz), 5.13 (dd, 1H, *J* = 10.0, 1.7 Hz), 5.03 (s, 2H), 3.94 (dd, 2H, *J* = 8.3, 8.3 Hz), 3.77 (s, 3H), 2.94 (dd, 2H, *J* = 8.6, 8.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 151.6, 150.2, 144.7, 138.6, 136.9, 134.4, 133.9, 133.2, 131.9, 131.2, 129.5, 129.4, 128.8, 128.6, 128.6, 128.5, 127.0, 125.2, 124.1, 123.7, 119.4, 117.4, 107.9, 69.3, 55.7, 46.3, 33.0; IR (ATR, cm^{-1}) 2919, 2138, 1733, 1578, 1532, 1467, 1352, 1264, 1234, 1171, 1088, 889; MS (FAB) *m/z* 639 $[M+H]^+$; HRMS calcd for $C_{34}H_{31}N_4O_7S$ $[M+H]^+$ 639.1913; Found: *m/z* 639.1911.

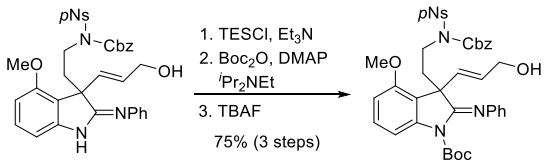


16 **17**

2-Iminoindoline **17**:

To a solution of (*E*)-dienylcarbodiimide **16** (165.0 mg, 0.258 mmol) in anhydrous xylene (4.0 mL) were added bis(pinacolato)diboron (131.0 mg, 0.518 mmol) and $Pd(OAc)_2$ (5.8 mg, 0.0258

mmol) at room temperature, and the reaction atmosphere was replaced by the Ar atmosphere. The mixture was then stirred at 50 °C for 13 h. After the mixture was cooled to 0 °C, 1M aqueous NaOH (1.6 mL, 1.55 mmol) and 30% H_2O_2 (175.0 μL, 1.55 mmol) were added to the reaction mixture. The mixture was stirred at room temperature for additional 1 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (5-60% EtOAc/hexane) to give 2-iminoindoline **17** (141.0 mg, 83%) as a yellow oil; (mixture of isomer of amidine) ^{1}H NMR (500 MHz, DMSO) δ 9.42 (s, 0.15H, minor), 9.36 (s, 1H, major), 8.27 (d, 0.30H, *J* = 8.9 Hz, minor), 8.23 (d, 2H, *J* = 8.9 Hz, major), 8.07 (d, 0.30H, *J* = 8.9 Hz, minor), 8.01 (d, 2H, *J* = 8.9 Hz, major), 8.00 (d, 2H, *J* = 7.7 Hz, major), 7.34 (dd, 2.30H, *J* = 8.0, 7.8 Hz, major + minor), 7.28-7.23 (m, 1.30H, major + minor), 7.20 (dd, 3H, *J* = 7.8, 7.7 Hz, major), 7.15 (d, 0.30H, *J* = 6.8 Hz, minor), 7.11 (dd, 0.15H, *J* = 8.3, 8.0 Hz, minor), 7.03-6.97 (m, 3.30H, major + minor), 6.90 (d, 0.30H, *J* = 7.7 Hz, minor), 6.87 (d, 1H, *J* = 7.8 Hz, major), 6.66 (d, 1H, *J* = 8.3 Hz, major), 6.56 (d, 0.15H, *J* = 8.3 Hz), 6.48 (d, 0.15H, *J* = 7.7 Hz, minor), 6.00 (d, 1H, *J* = 15.5 Hz, major), 5.89 (d, 0.15H, *J* = 15.5 Hz, minor), 5.63 (ddd, 0.15H, *J* = 15.4, 4.9, 4.8 Hz, minor), 5.43 (ddd, 1H, *J* = 15.5, 4.9, 4.6 Hz, major), 5.08-5.03 (m, 1.30H, major + minor), 4.96 (d, 1H, *J* = 12.4 Hz, major), 4.75 (dd, 1H, *J* = 5.5, 5.1 Hz, major), 4.70 (dd, 0.15H, *J* = 5.5, 5.4 Hz, minor), 3.91 (dd, 2.30H, *J* = 4.6, 3.7 Hz, major + minor), 3.81-3.73 (m, 0.15H, minor), 3.73 (s, 3.45H, major + minor), 3.59-3.54 (m, 0.15H, minor), 3.36-3.30 (m, 1H, major), 3.24-3.17 (m, 1H, major), 2.77 (ddd, 1H, *J* = 12.3, 12.3, 4.9 Hz, major), 2.59 (ddd, 1.15H, *J* = 12.1, 12.0, 4.0 Hz, major + minor), 2.40-2.35 (m, 0.15H, minor); ^{13}C NMR (126 MHz, DMSO) δ 170.9, 156.9, 155.2, 151.0, 150.1, 144.1, 140.7, 134.6, 130.3, 129.6, 129.3, 128.5, 128.3, 128.0, 126.9, 124.3, 122.1, 121.2, 119.3, 110.5, 105.8, 68.5, 60.9, 59.4, 55.4, 43.3, 32.9; IR (ATR, cm^{-1}) 2965, 2361, 1733, 1674, 1606, 1532, 1489, 1444, 1350, 1266, 1237, 1171, 1139, 1090, 1007, 970, 855; MS (FAB) *m/z* 657 $[M+H]^+$; HRMS calcd for $C_{34}H_{33}N_4O_8S$ $[M+H]^+$ 657.2019; Found: *m/z* 657.2027.



17 **18**

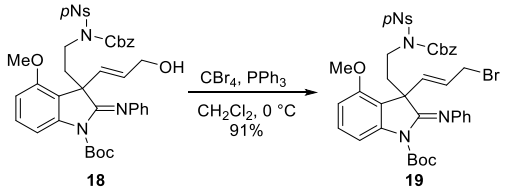
N-Boc-2-iminoindoline **18**:

To a solution of 2-iminoindoline **17** (102.2 mg, 0.156 mmol) in CH_2Cl_2 (2.0 mL) were added Et_3N (82.0 μL, 0.588 mmol) and TESCl (65.8 μL, 0.392 mmol) at 0 °C. The solution was stirred at room temperature for 4 h. After addition of water, the mixture was extracted with EtOAc. The

combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by short column chromatography on neutral silica gel (10-30% EtOAc/hexane) to give a mixture including a desired silylether.

To a solution of the above mixture in CH_2Cl_2 (2.0 mL) were added DIPEA (137.0 μL, 0.784 mmol), Boc_2O (128.3 mg, 0.588 mmol) and DMAP (23.9 mg, 0.196 mmol) at 0 °C. The solution was stirred at room temperature for 3 h. After concentration under reduced pressure, the resultant residue was purified by short column chromatography on silica gel (5-30% EtOAc/hexane) to give a mixture including the desired *N*-Boc-2-iminoindoline**.**

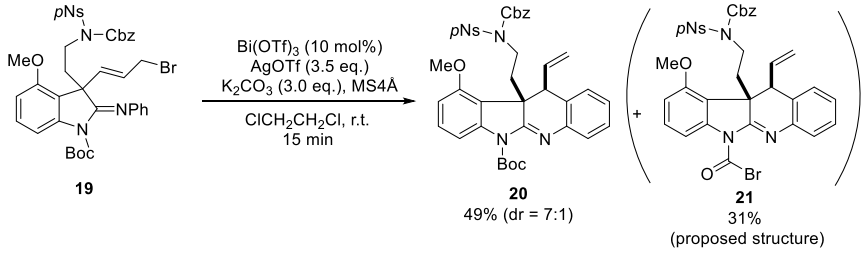
To a solution of the above *N*-Boc iminoindoline in THF (1.3 mL) was added TBAF (1M in THF, 139.0 μL, 0.139 mmol) at 0 °C. The solution was stirred at 0 °C for 15 min. After addition of saturated aqueous NH_4Cl, the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (10-40% EtOAc/hexane) to give *N*-Boc-2-iminoindoline **18** (88.8 mg, 75% in 3 steps) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, 2H, *J* = 8.9 Hz), 7.93 (d, 2H, *J* = 8.9 Hz), 7.33-7.28 (m, 5H), 7.26-7.22 (m, 3H), 7.10-7.02 (m, 5H), 6.71 (dd, lH, *J* = 3.8, 3.7 Hz), 5.98 (d, lH, *J* = 15.8 Hz), 5.76 (ddd, lH, *J* = 15.4, 5.5, 5.1 Hz), 4.95 (d, 1H, *J* = 11.7 Hz), 4.90 (d, 1H, *J* = 11.7 Hz), 4.12 (d, 2H, *J* = 5.2 Hz), 3.84 (s, 3H), 3.81-3.75 (m, 1H), 3.72-3.64 (m, 1H), 2.89 (ddd, 1H, *J* = 12.1, 11.7, 5.4 Hz), 2.55 (ddd, 1H, *J* = 12.3, 12.3, 4.3 Hz), 1.20 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 155.1, 151.6, 150.1, 149.2, 148.7, 144.9, 142.0, 134.2, 131.3, 129.8, 129.6, 129.1, 128.7, 128.7, 128.5, 123.7, 123.6, 120.3, 116.1, 107.2, 106.8, 84.0, 69.1, 63.2, 55.5, 53.9, 44.2, 34.8, 27.5; IR (ATR, cm^{-1}) 3454, 2979, 1731, 1693, 1596, 1532, 1489, 1456, 1369, 1348, 1241, 1172, 1149, 1088, 885; MS (FAB) *m/z* 757 $[M+H]^+$; HRMS calcd for $C_{39}H_{41}N_4O_{10}S$ $[M+H]^+$ 757.2543; Found: *m/z* 757.2541.



Allylbromide **19**:

To a solution of *N*-Boc-2-iminoindoline **18** (104.8 mg, 0.138 mmol) and PPh_3 (90.8 mg, 0.345 mmol) in CH_2Cl_2 (2.0 mL) was added CBr_4 (91.5 mg, 0.276 mmol) at 0 °C. The reaction solution was stirred at 0 °C for 30 min. After addition of water, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (10-30%

EtOAc/hexane) to give allylbromide **19** (102.9 mg, 91%) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, 2H, *J* = 9.2 Hz), 7.92 (d, 2H, *J* = 8.9 Hz), 7.34-7.28 (m, 5H), 7.27-7.22 (m, 2H), 7.10-7.03 (m, 5H), 6.72 (dd, 1H, *J* = 7.1, 2.0 Hz), 6.00 (d, 1H, *J* = 15.2 Hz), 5.79 (ddd, 1H, *J* = 15.2, 7.7, 7.5 Hz), 4.94 (d, 1H, *J* = 11.8 Hz), 4.90 (d, 1H, *J* = 11.8 Hz), 3.97-3.89 (m, 2H), 3.85 (s, 3H), 3.88 (m, 1H), 3.69 (m, 1H), 2.86 (ddd, 1H, *J* = 12.0, 11.8, 5.7 Hz), 2.53 (ddd, 1H, *J* = 12.3, 10.6, 4.3 Hz), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 154.5, 151.5, 150.1, 149.3, 148.5, 144.8, 142.2, 134.7, 134.2, 130.1, 129.6, 129.1, 128.8, 128.7, 128.5, 126.3, 123.8, 123.7, 120.4, 115.5, 107.3, 106.9, 84.0, 69.2, 55.5, 53.8, 44.1, 34.5, 32.4, 27.4; IR (ATR, cm^{-1}) 2975, 2936, 2255, 1730, 1691, 1596, 1532, 1489, 1455, 1347, 1253, 1147, 1087, 1013, 966, 908, 854; MS (FAB) *m/z* 819 $[M+H]^+$; HRMS calcd for $C_{39}H_{40}N_4O_9S$ $[M+H]^+$ 819.1699; Found: *m/z* 819.1704.



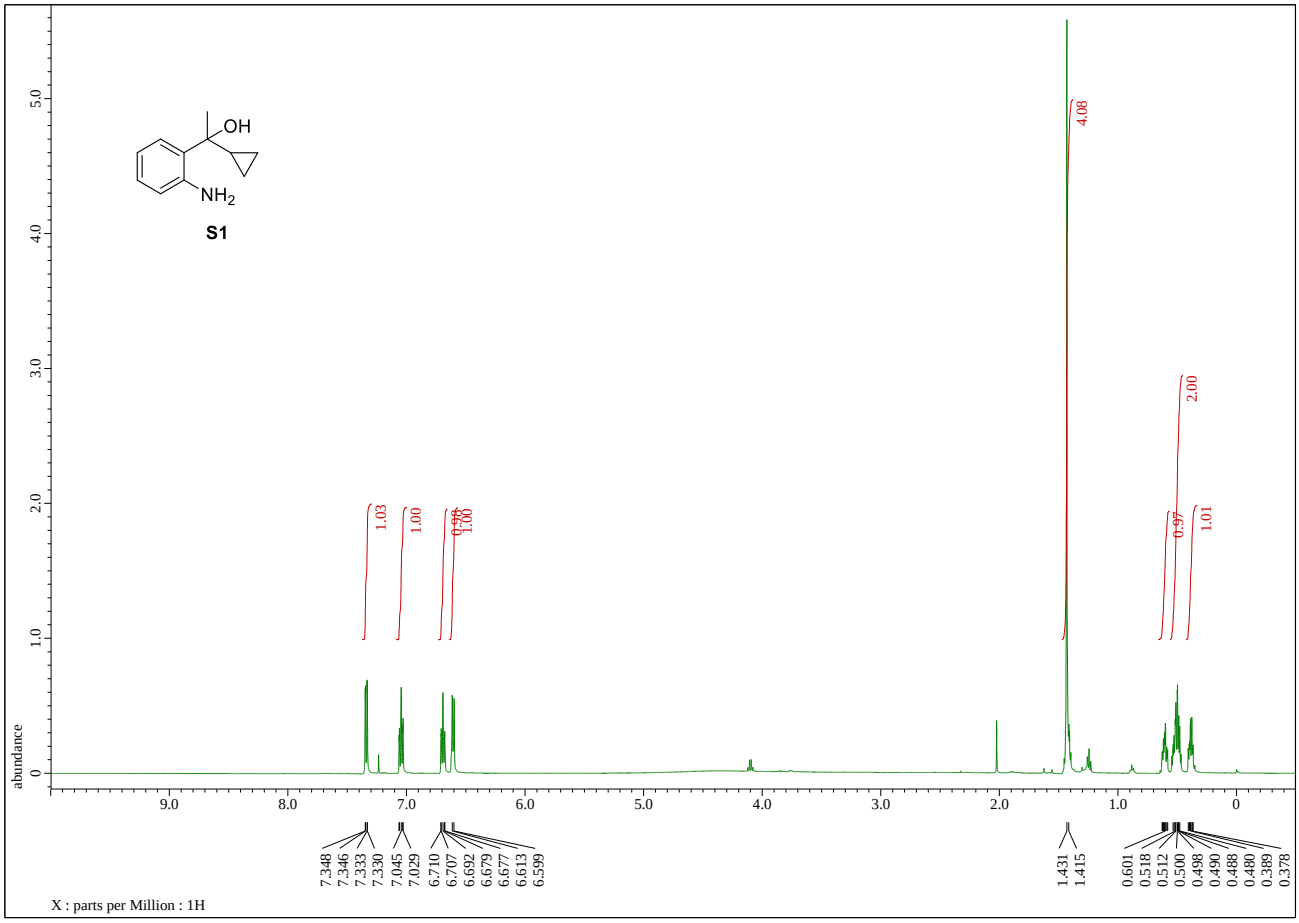
Tetracyclic compound **20** and **21**:

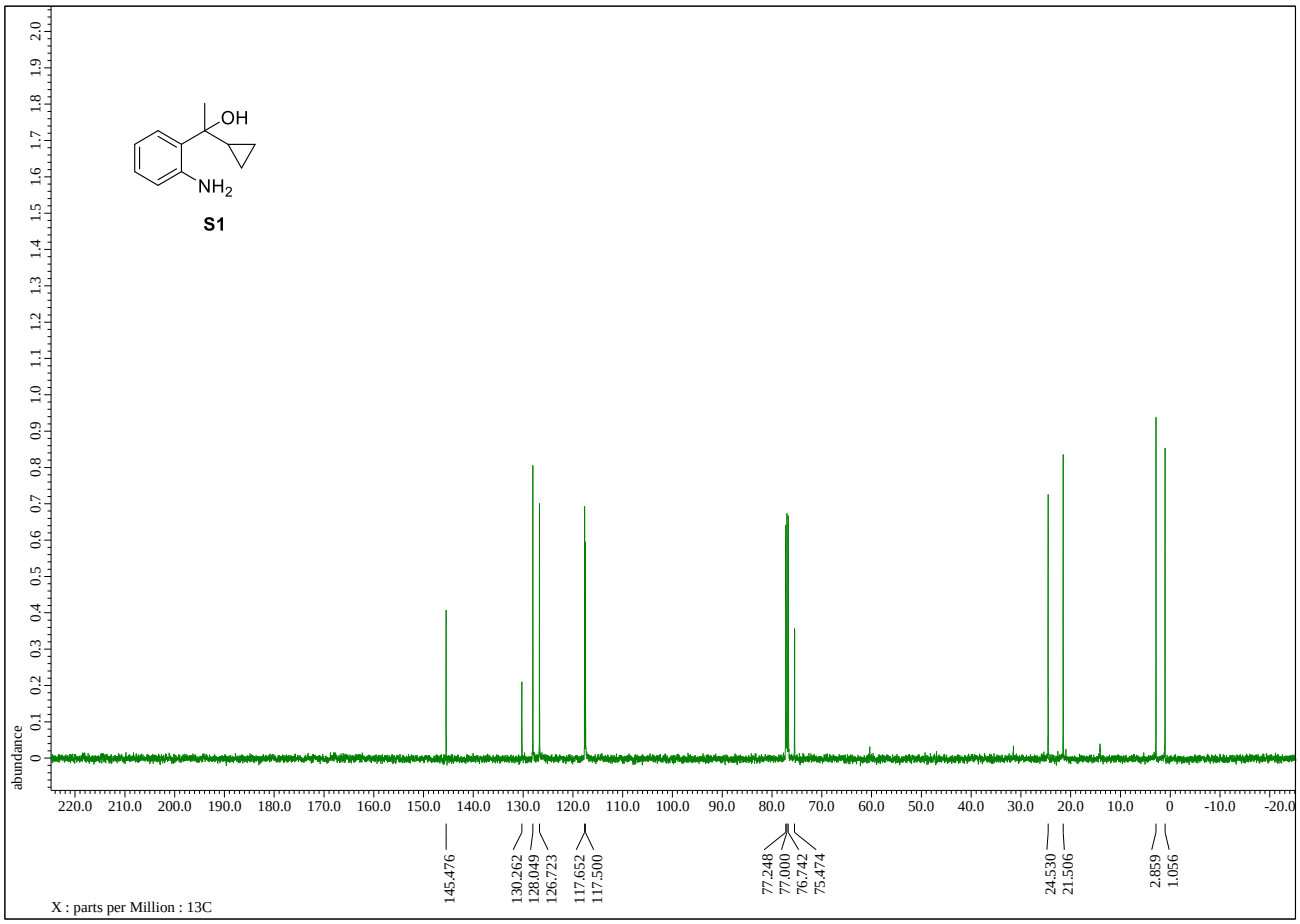
A suspension of allylbromide **19** (20.1 mg, 0.0245 mmol), $Bi(OTf)_3$ (1.6 mg, 2.45×10^{-3} mmol), AgOTf (22.0 mg, 0.0858 mmol), MS4Å (21.0 mg) and K_2CO_3 (10.2 mg, 0.0735 mmol) in CH_2Cl_2 (2.5 mL) was stirred at room temperature for 15 min. After addition of water, the mixture was filtered through Celite pad. The filtrate was extracted with EtOAc and dried over Na_2SO_4. After concentration under reduced pressure, the resultant residue was purified by flash column chromatography on silica gel (5-30% EtOAc/hexane) to give a tetracyclic compound **20** (8.9 mg, 49%, dr = 7:1) as a colorless oil and **21** (5.7 mg, 31%) as yellow oil;

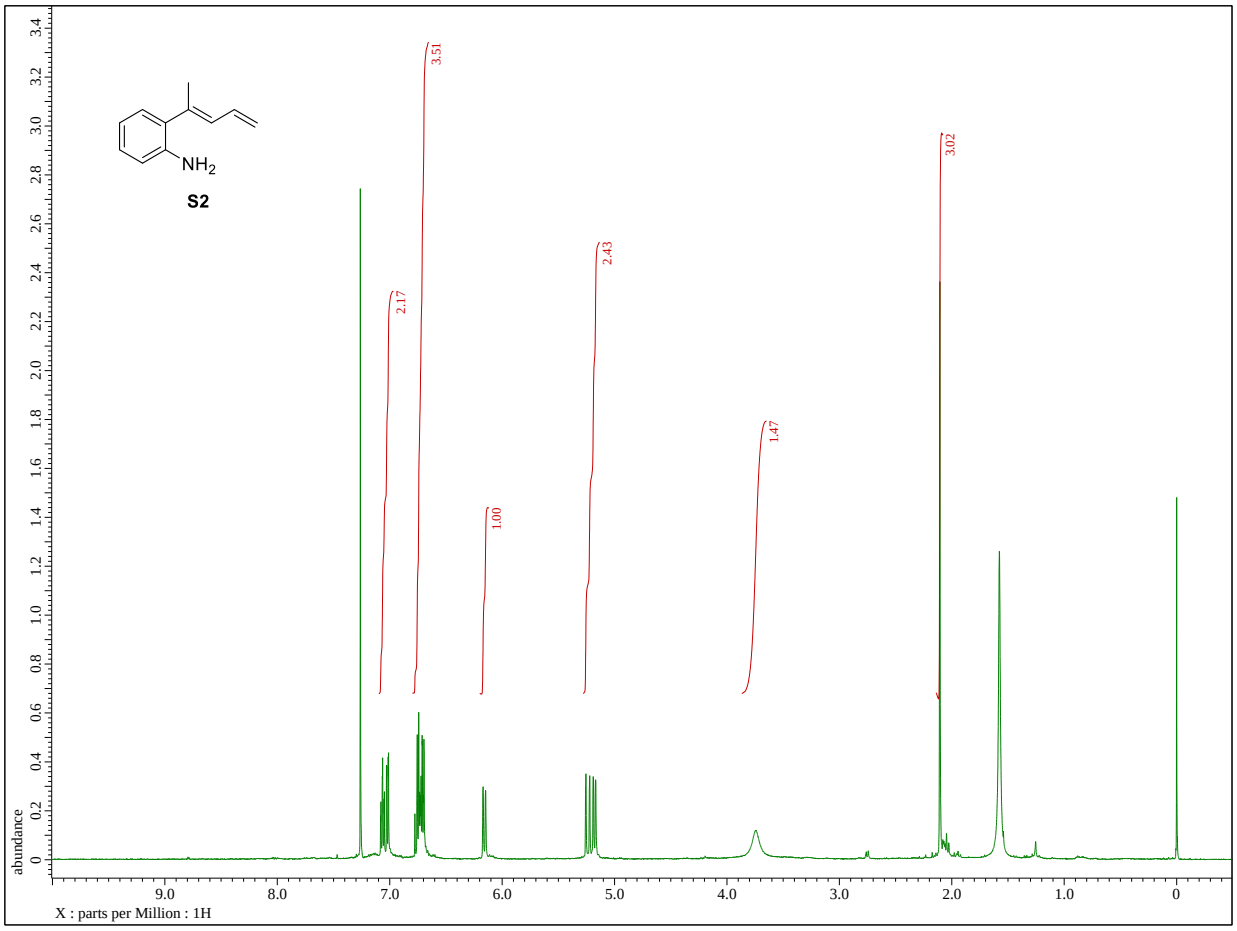
Tetracyclic compound **20** (major diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, 2H, *J* = 7.7 Hz), 7.75 (d, 2H, *J* = 7.7 Hz), 7.52 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 1H, *J* = 7.8 Hz), 7.34-7.28 (m, 5H), 7.19-7.16 (m, 2H), 7.09 (d, 2H, *J* =7.8 Hz), 6.66 (d, 1H, *J* = 8.3 Hz), 6.16 (ddd, 1H, *J* = 16.6, 10.6, 9.8 Hz), 5.35 (d, 1H, *J* = 9.8 Hz), 5.08 (d, 1H, *J* = 16.6 Hz), 4.94 (s, 2H), 3.80 (d, 1H, *J* = 10.3 Hz), 3.68 (s, 3H), 3.61-3.55 (m, 1H), 3.33-3.26 (m, 1H), 2.41-2.35 (m, 1H), 2.14-2.07 (m, 1H), 1.69 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 156.9, 151.3, 150.2, 149.3, 144.5, 144.3, 143.1, 135.1, 134.8, 134.1, 130.3, 129.7, 128.8, 128.6, 128.5, 128.1, 126.7, 125.7, 125.3, 123.7, 123.7, 117.6, 115.4, 108.0, 107.6, 84.1, 69.2, 54.6, 51.0, 47.4, 44.2, 28.3, 26.3; IR (ATR, cm^{-1}) 2979, 2915, 1733, 1650, 1580, 1533, 1465, 1350, 1282, 1248, 1145, 1070, 890, 859, 747, 627; MS (ESI) *m/z* 739 $[M+H]^+$; HRMS calcd for $C_{39}H_{39}N_4O_9S$ $[M+H]^+$ 739.2438; Found: *m/z*

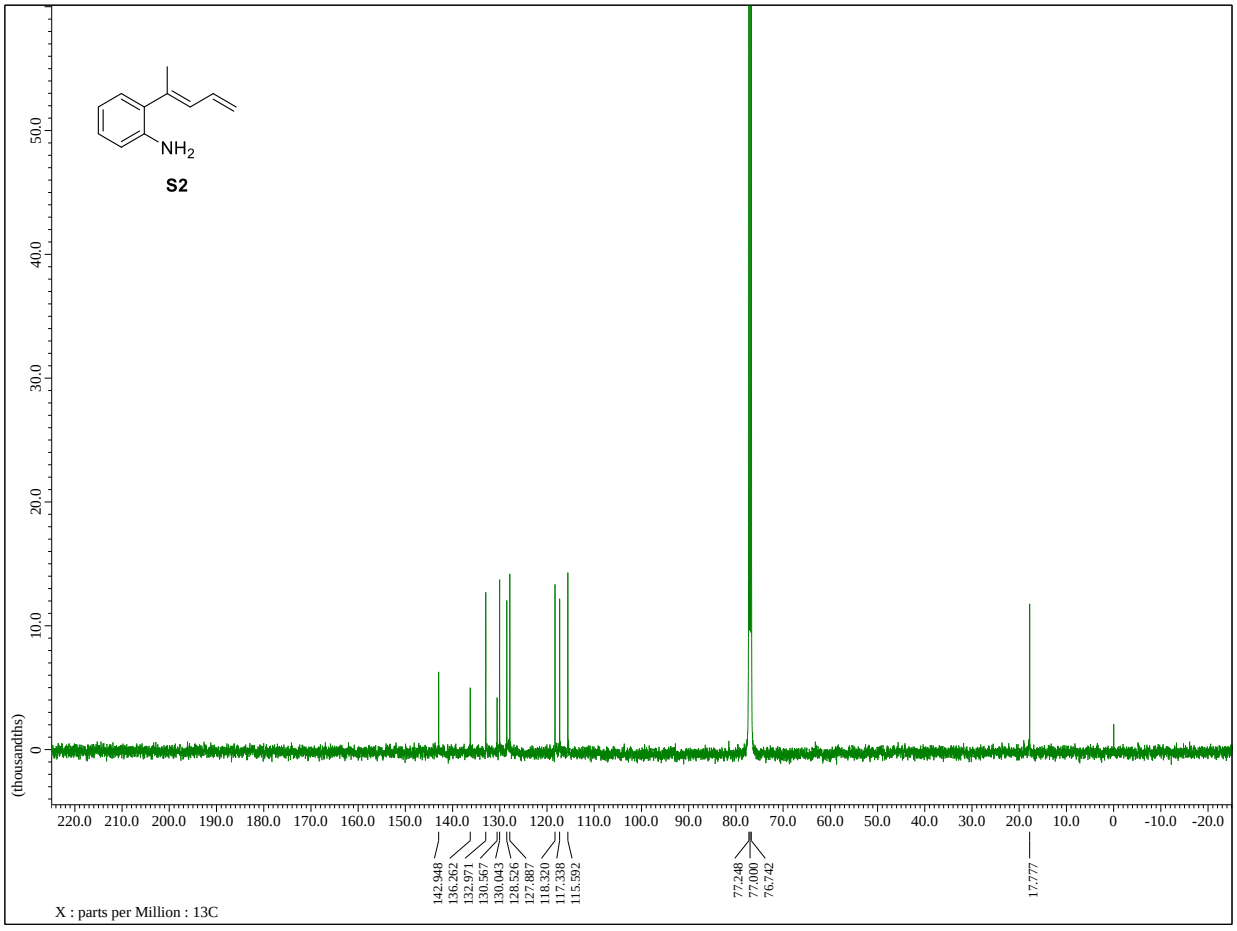
739.2427.

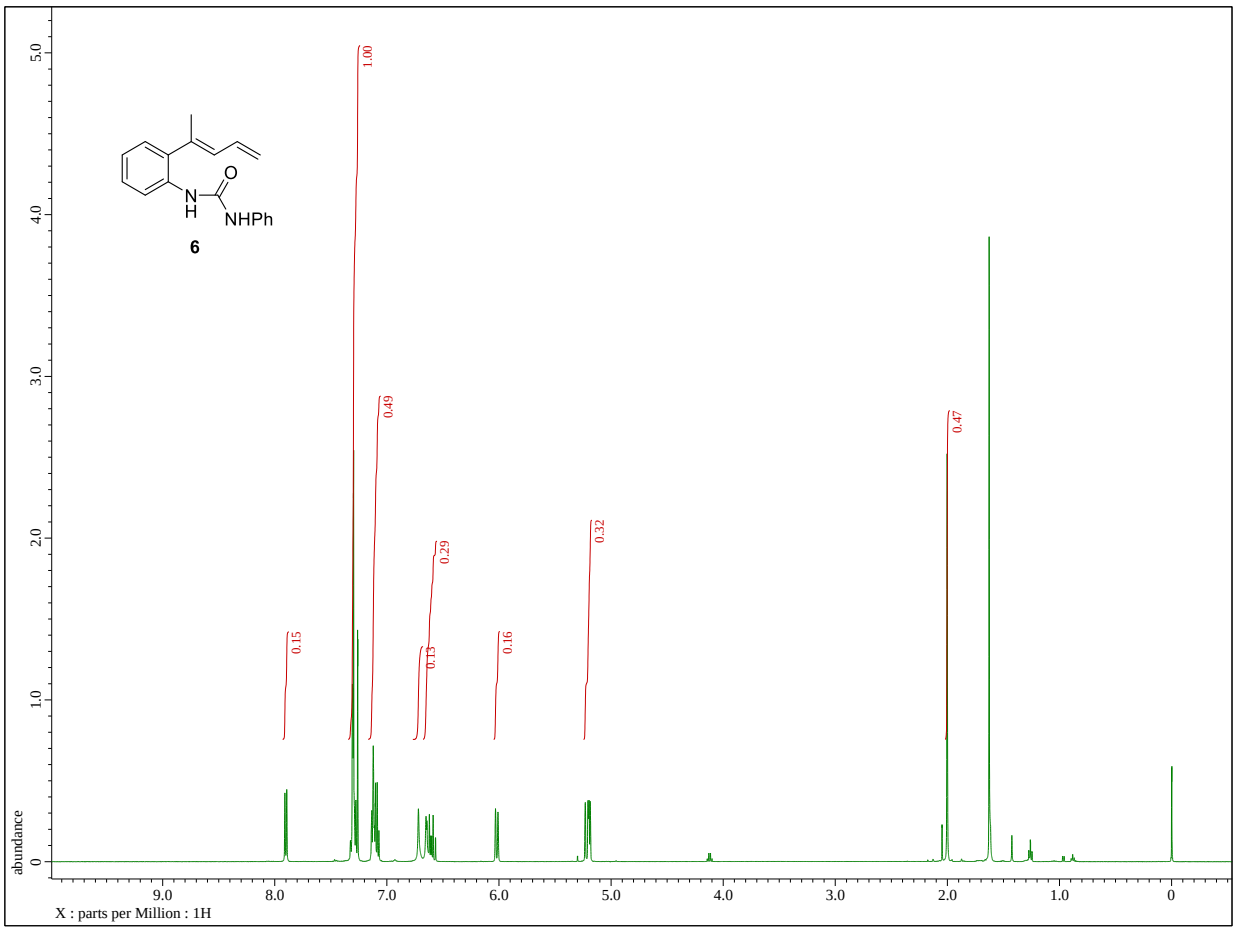
Tetracyclic compound **21:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, 2H, *J* = 8.9 Hz), 7.80 (d, 2H, *J* = 8.9 Hz), 7.31-7.23 (m, 5H), 7.20 (d, 1H, *J* = 7.8 Hz), 7.13 (d, 1H, *J* = 8.0 Hz), 7.10-7.04 (m, 3H), 6.88 (d, 1H, *J* = 8.0 Hz), 6.63 (d, 1H, *J* = 8.3 Hz), 6.22 (ddd, 1H, *J* = 16.9, 10.0, 9.8 Hz), 5.43 (d, 1H, *J* = 11.4 Hz), 5.15 (d, 1H, *J* = 16.9 Hz), 4.95 (dd, 2H, *J* = 12.1, 11.7 Hz), 3.75 (d, 1H, *J* = 9.8 Hz), 3.72 (s, 3H), 3.59-3.54 (m, 1H), 3.21 (ddd, 1H, *J* = 12.6, 12.3, 4.6 Hz), 2.63 (ddd, 1H, *J* = 12.6, 12.3, 4.5 Hz), 2.25 (ddd, 1H, *J* = 12.6, 12.3, 4.6 Hz); MS (FAB) *m/z* 745, 747 $[M+H]^+$. (Compound **21** was too unstable to measure ^{13}C NMR and IR.

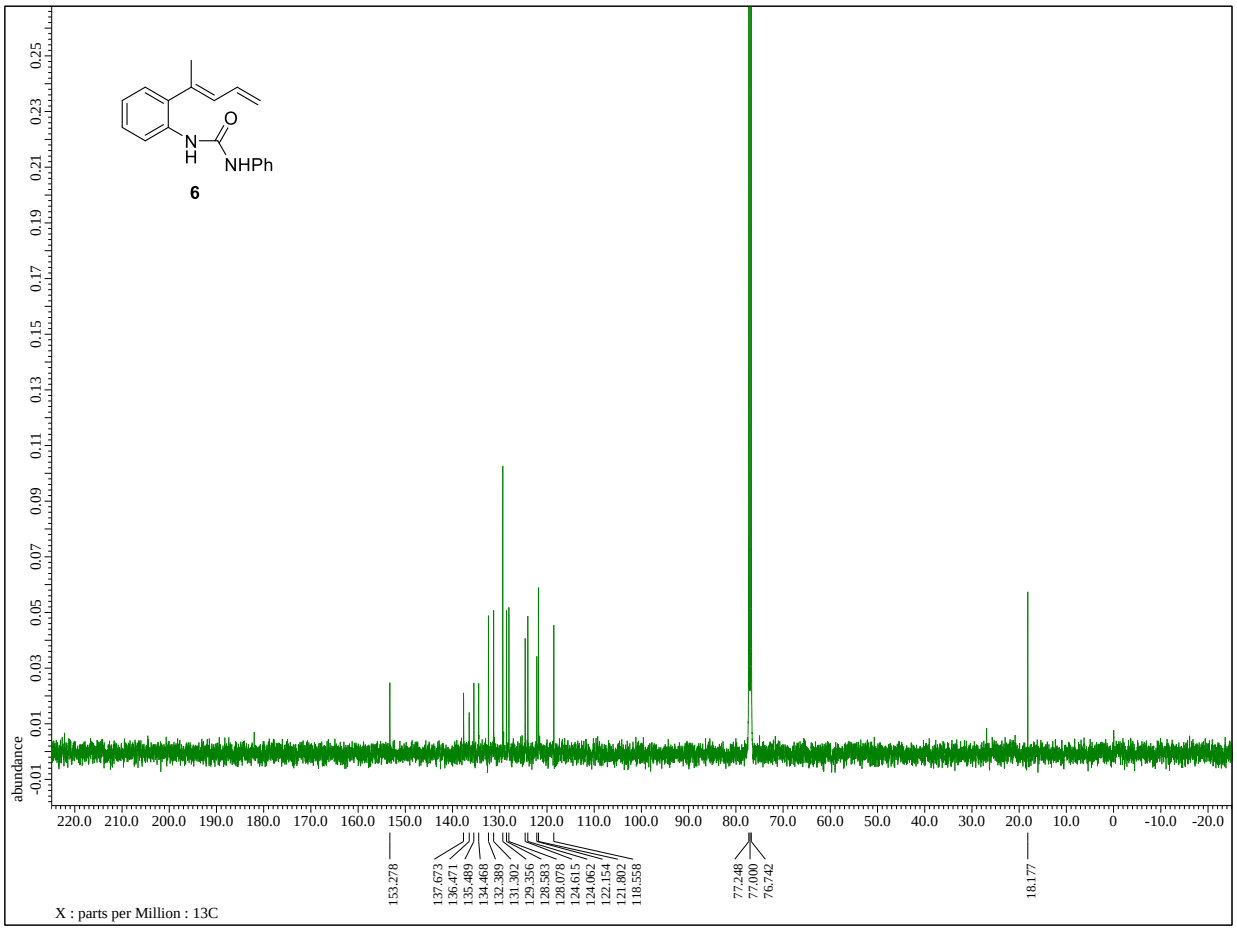

OH
NH2
S1
abundance
X : parts per Million : 1H
7.348
7.346
7.333
7.330
7.045
7.029
6.710
6.707
6.692
6.679
6.677
6.613
6.599
1.431
1.415
0.601
0.518
0.512
0.500
0.498
0.490
0.488
0.480
0.389
0.378
1.03
1.00
0.98
1.00
4.08
2.00
0.97
1.01

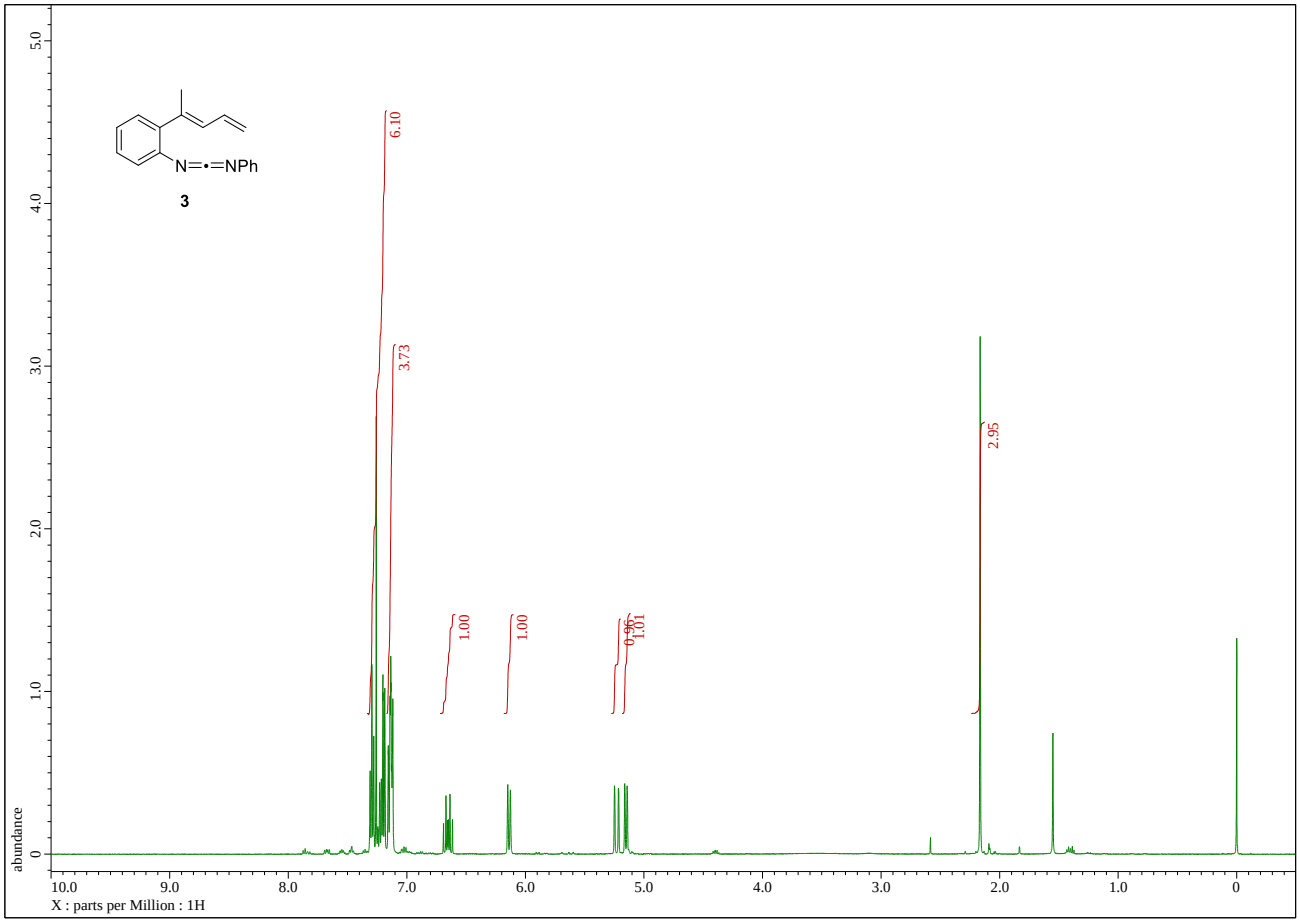

OH
NH2
S1
abundance
X : parts per Million : 13C
145.476
130.262
128.049
126.723
117.652
117.500
77.248
77.000
76.742
75.474
24.530
21.506
2.859
1.056

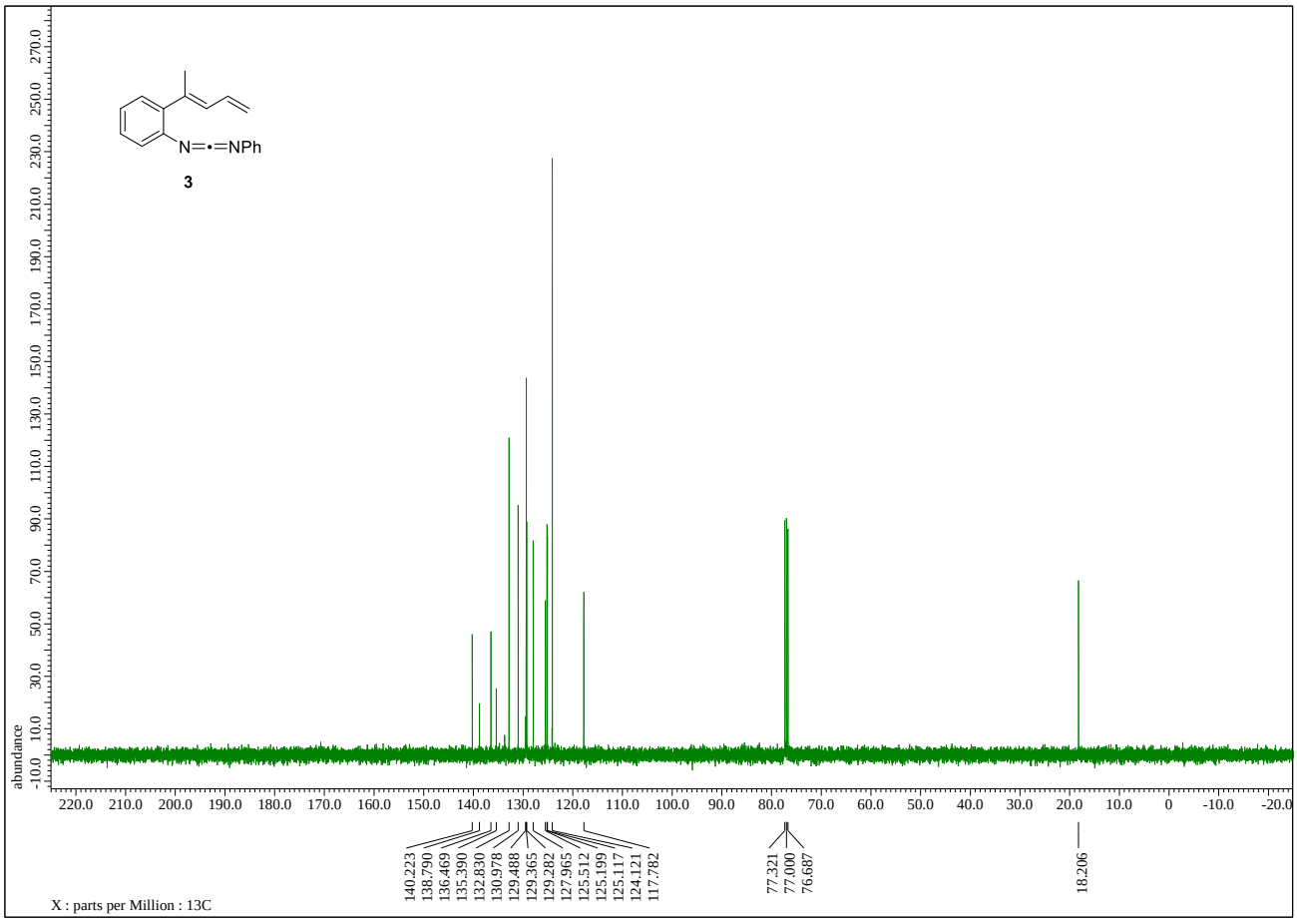

NH2
S2
3.51
2.17
1.00
2.43
1.47
3.02
abundance
X : parts per Million : 1H

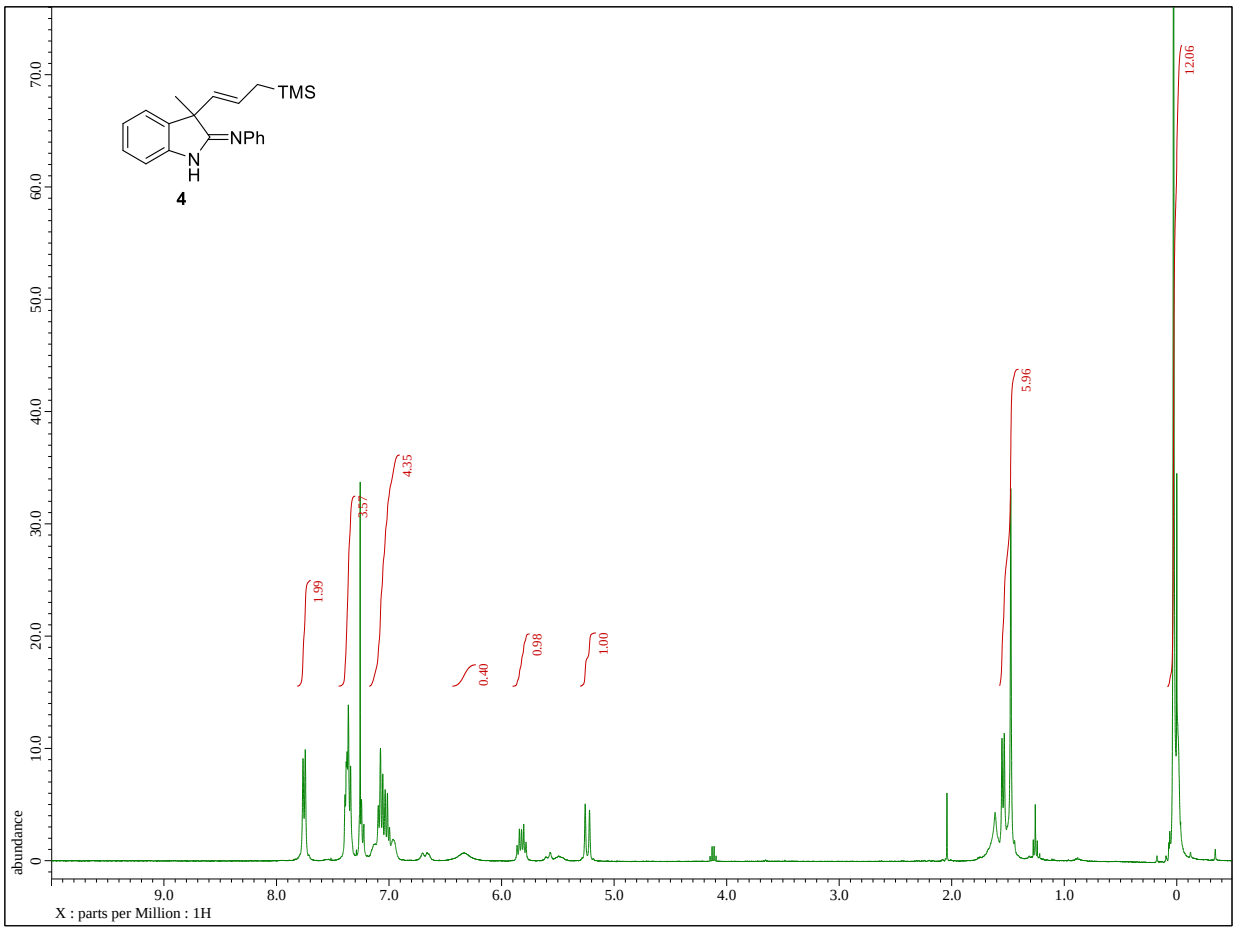

NH2
S2
(thousandths)
142.948
136.262
132.971
130.567
130.043
128.526
127.897
116.320
117.338
115.592
77.248
77.000
76.742
17.777
X : parts per Million : 13C

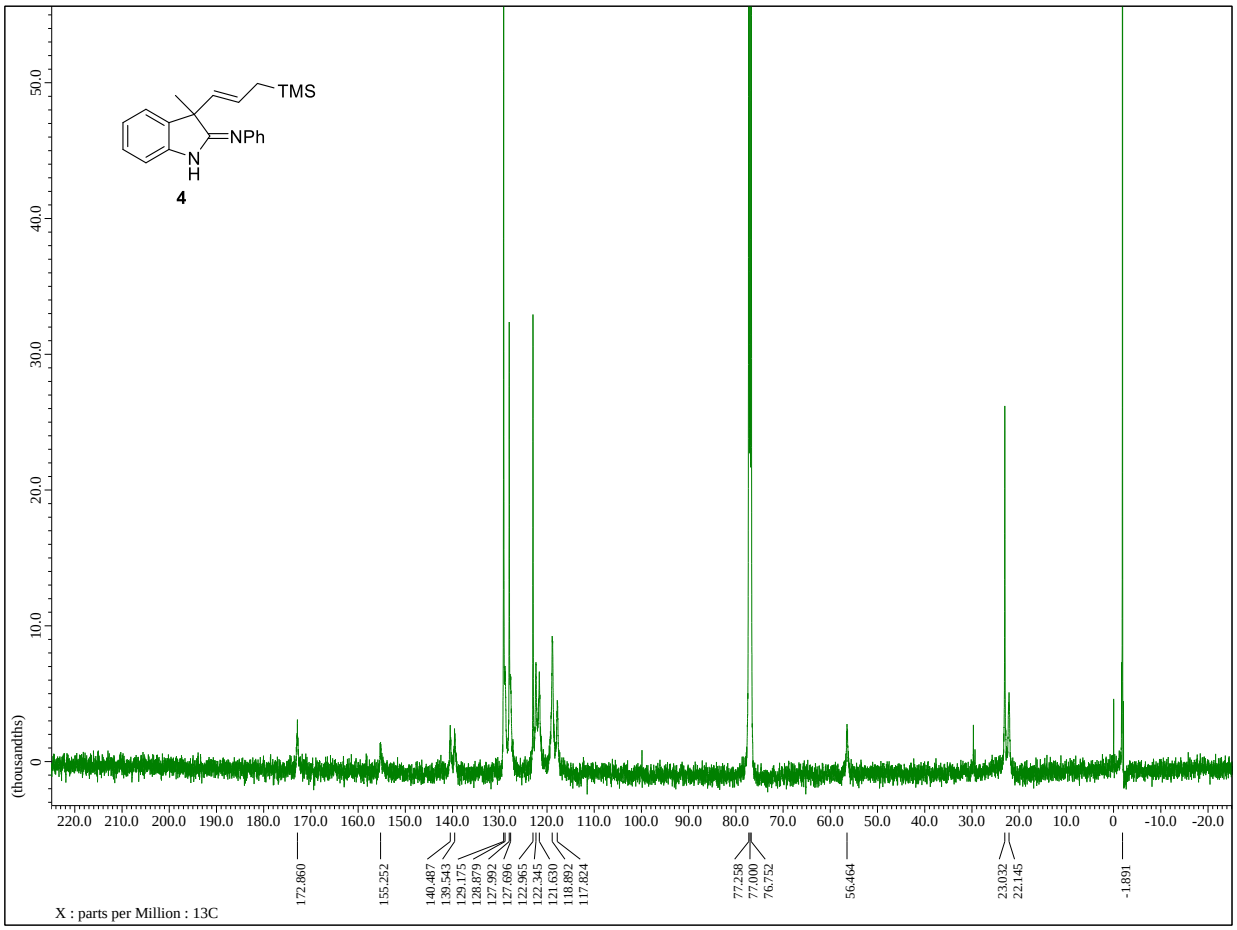

6
1.00
0.49
0.29
0.32
0.15
0.13
0.16
0.47
abundance
X : parts per Million : 1H

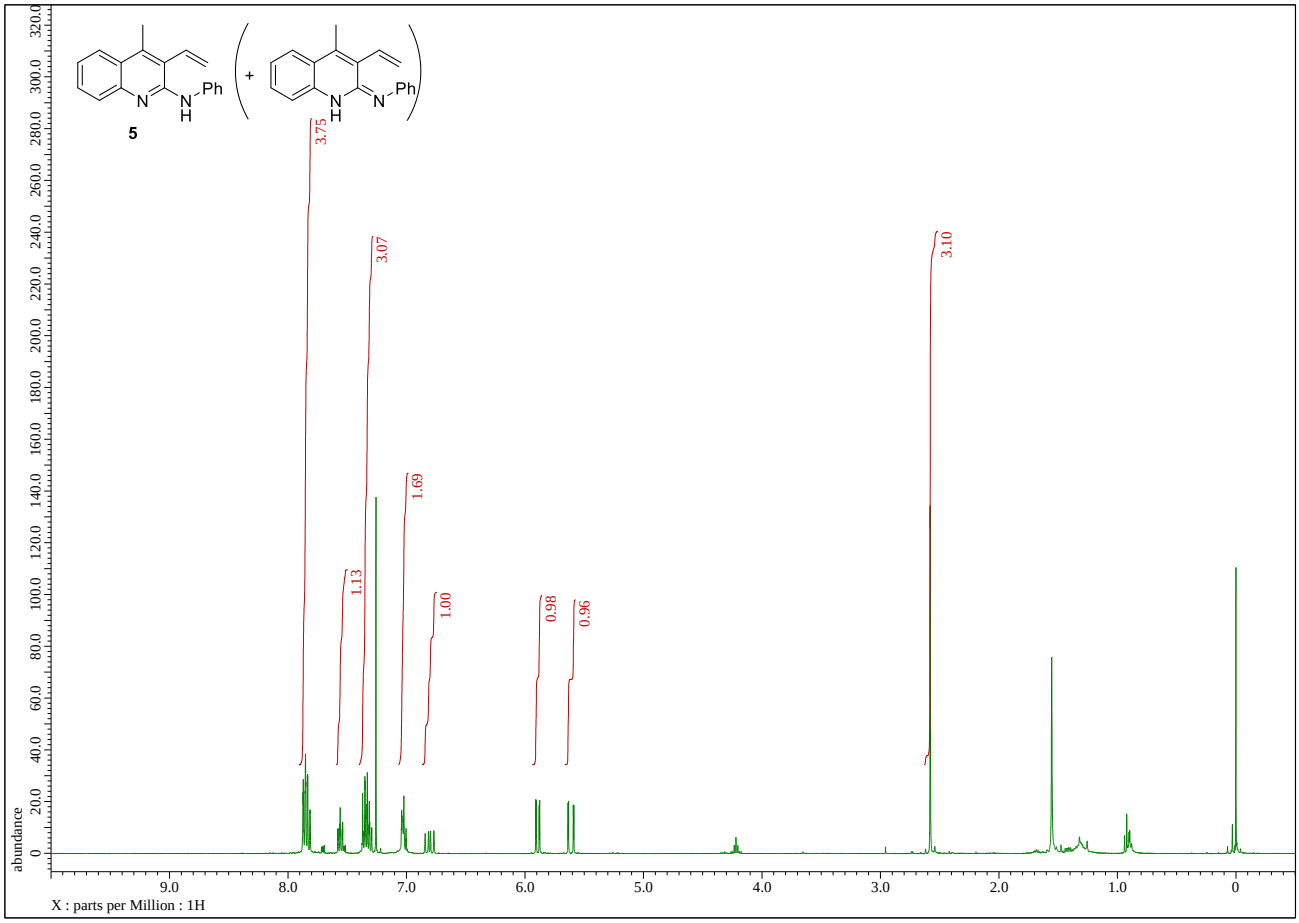

6
abundance
153.278
137.673
136.471
135.489
134.468
132.389
131.302
129.356
128.583
128.078
124.615
124.062
122.154
121.802
118.558
77.248
77.000
76.742
18.177
X : parts per Million : 13C

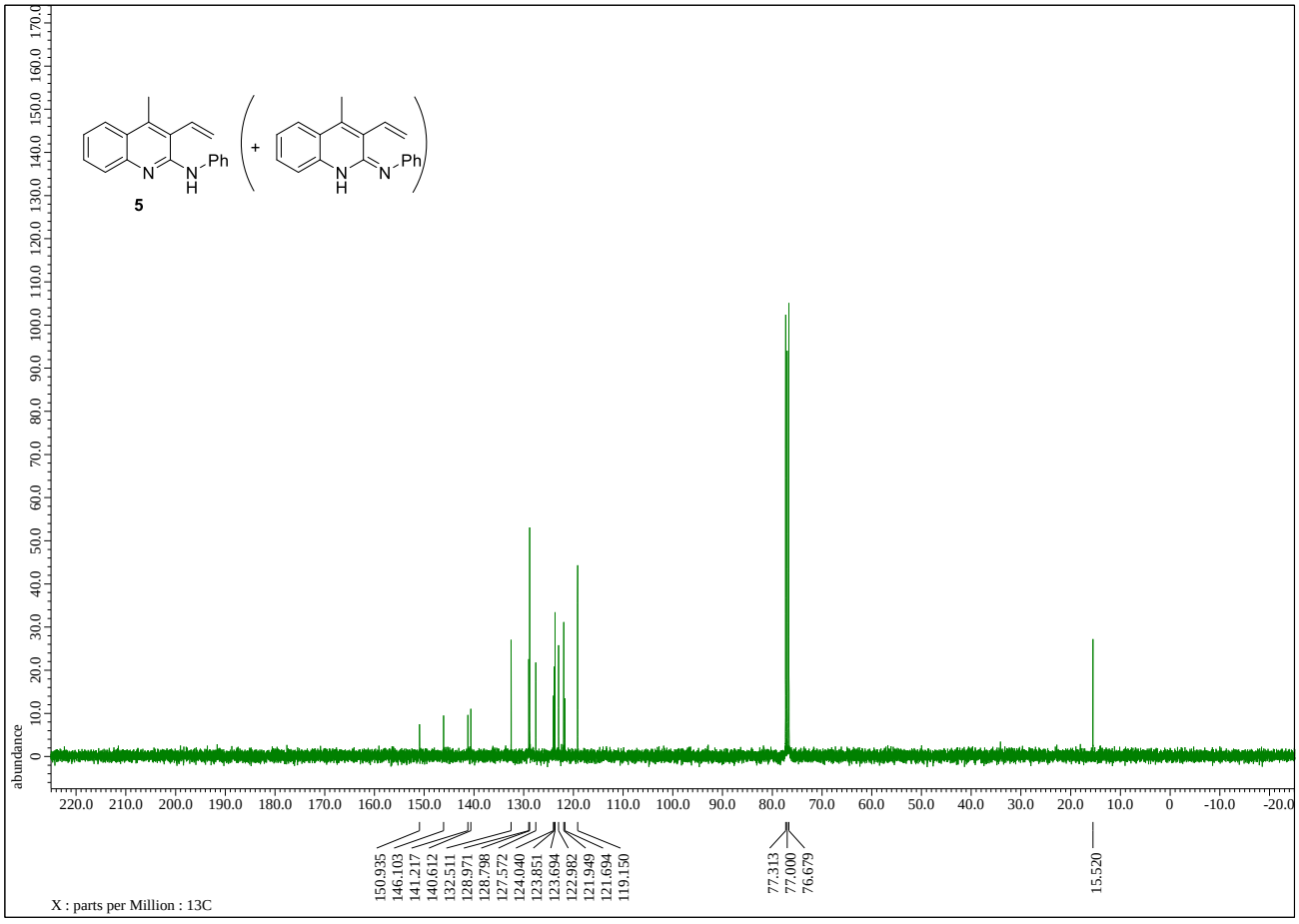

N=•=NPh
3
6.10
3.73
2.95
1.00
1.00
0.96
1.01
abundance
X : parts per Million : 1H

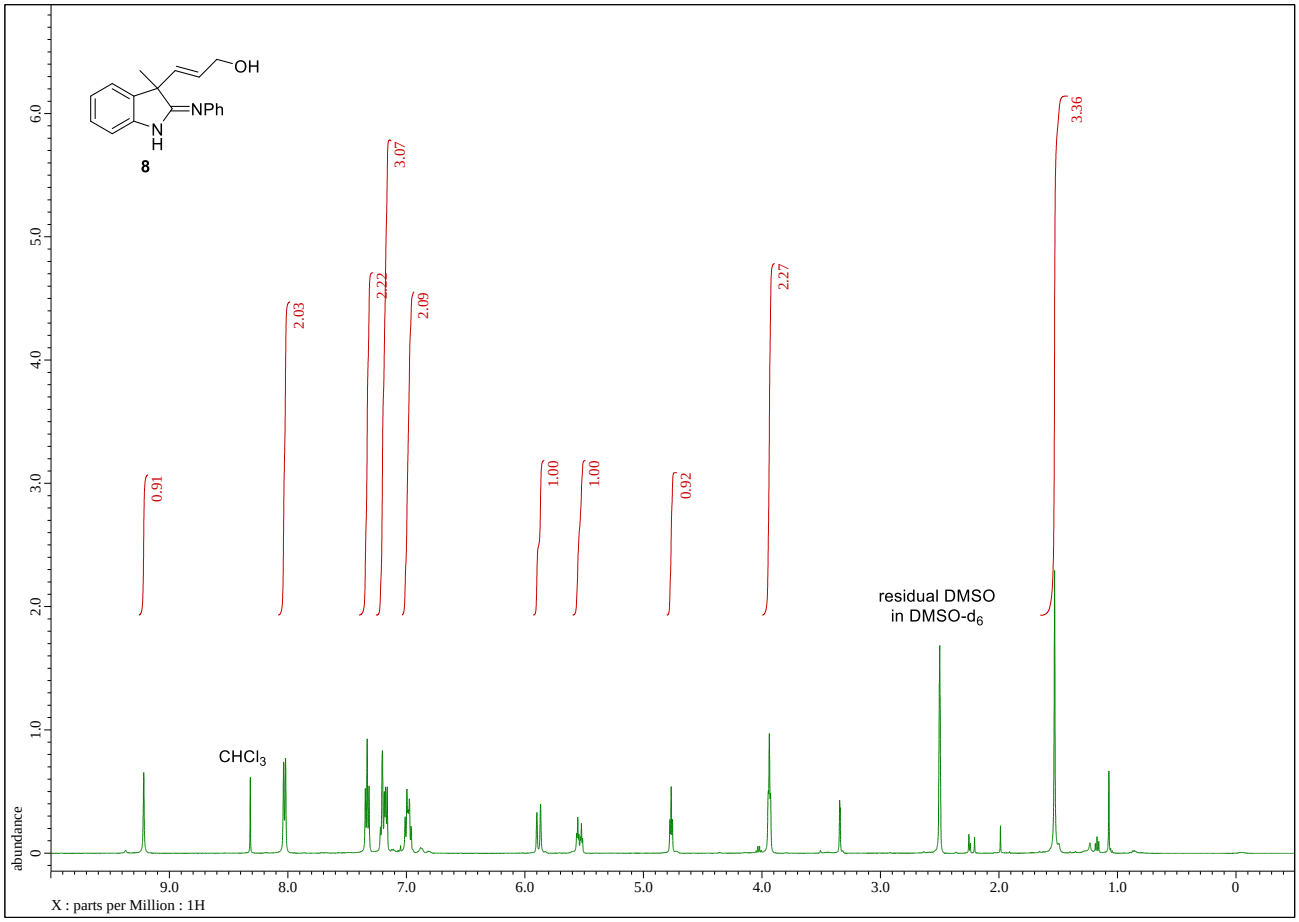

N=•=NPh
3
abundance
140.223
138.790
136.469
135.390
132.830
130.978
129.488
129.365
129.282
127.965
125.512
125.199
125.117
124.121
117.782
77.321
77.000
76.687
18.206
X : parts per Million : 13C

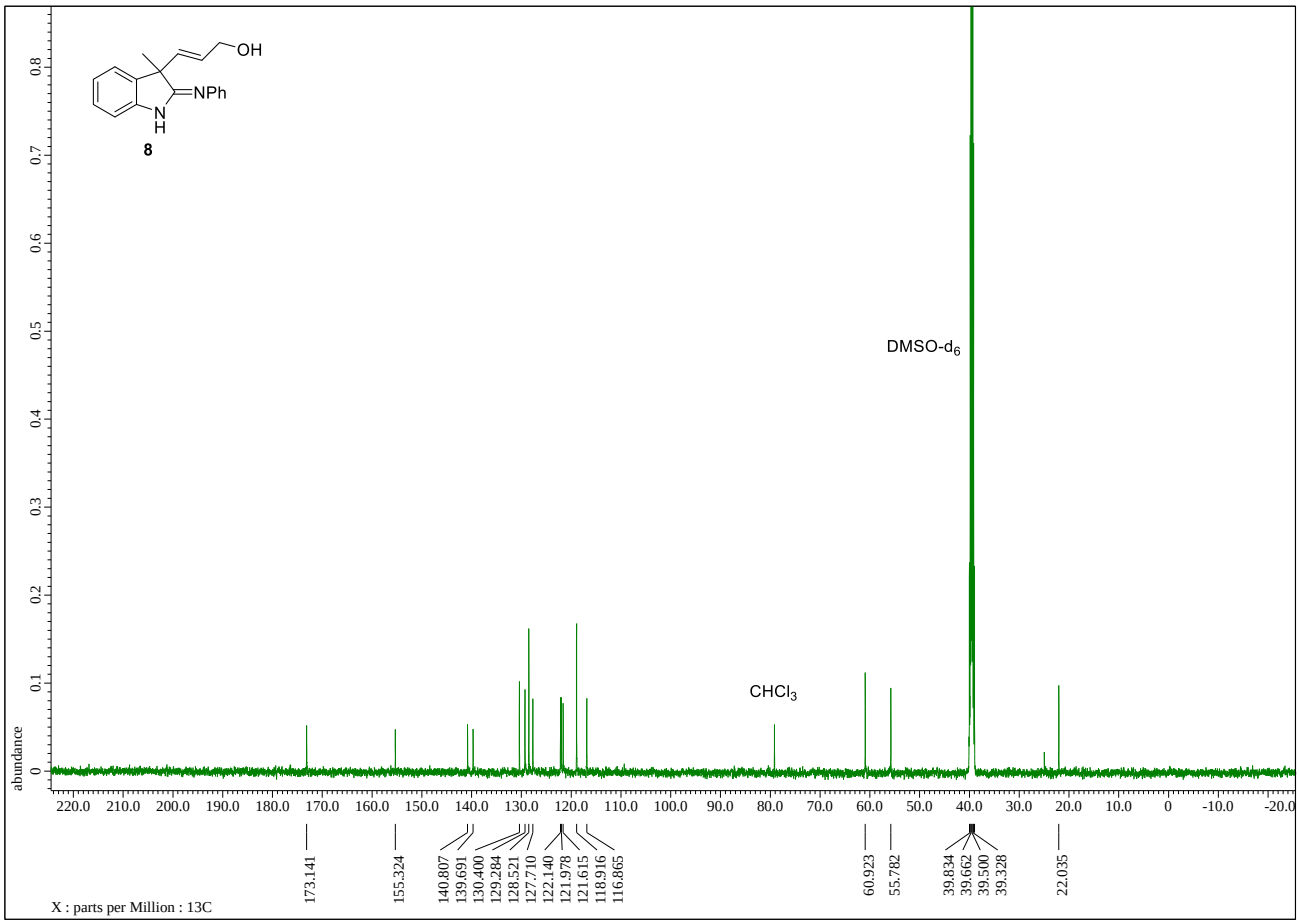

TMS
NPh
N
H
4
abundance
X : parts per Million : 1H
1.99
3.57
4.35
0.40
0.98
1.00
5.96
12.06

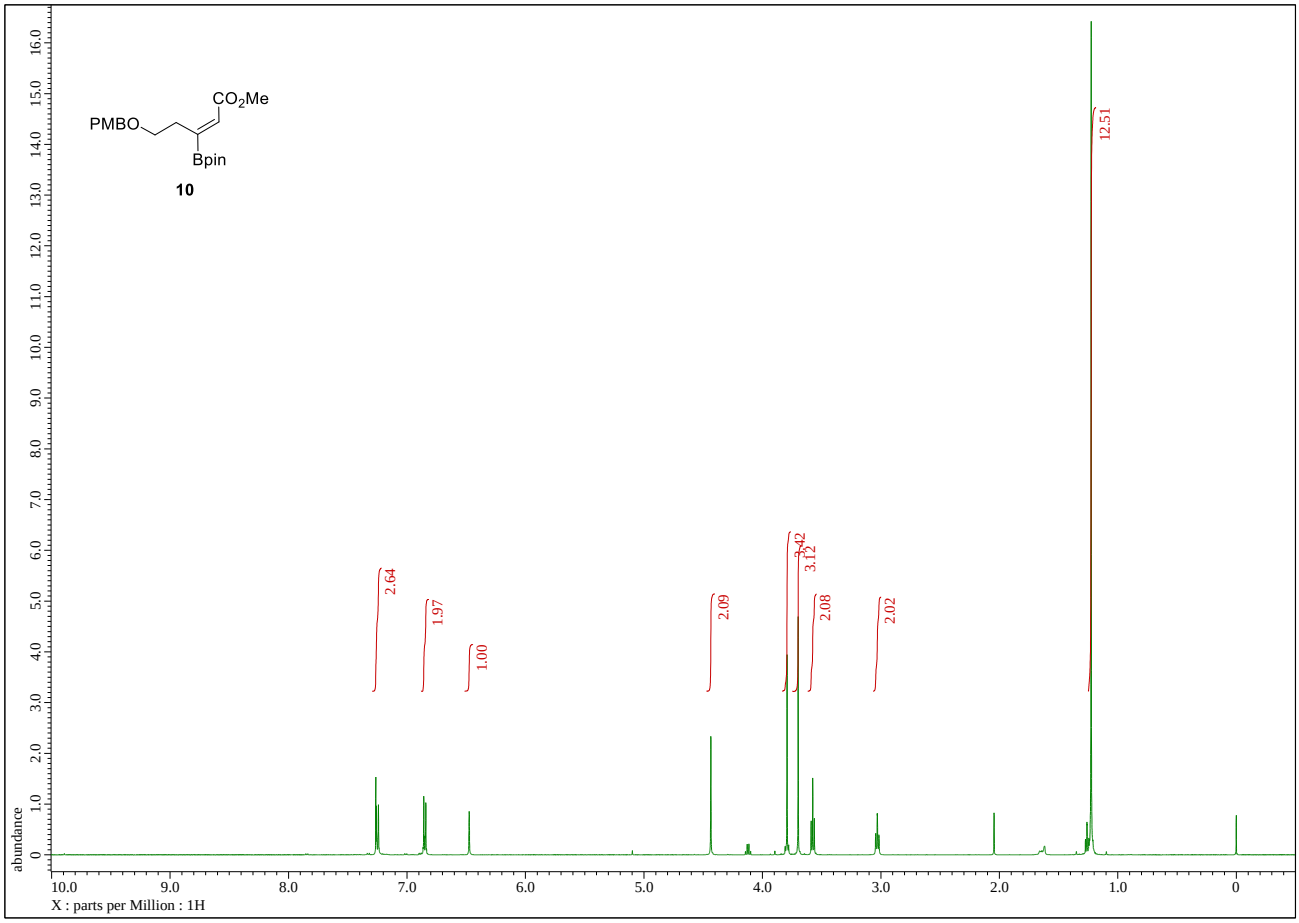

TMS
NPh
N
H
4
(thousandths)
X : parts per Million : 13C
172.860
155.252
140.487
139.543
129.175
128.879
127.992
127.696
122.965
122.345
121.630
118.892
117.824
77.258
77.000
76.752
56.464
23.032
22.145
-1.891

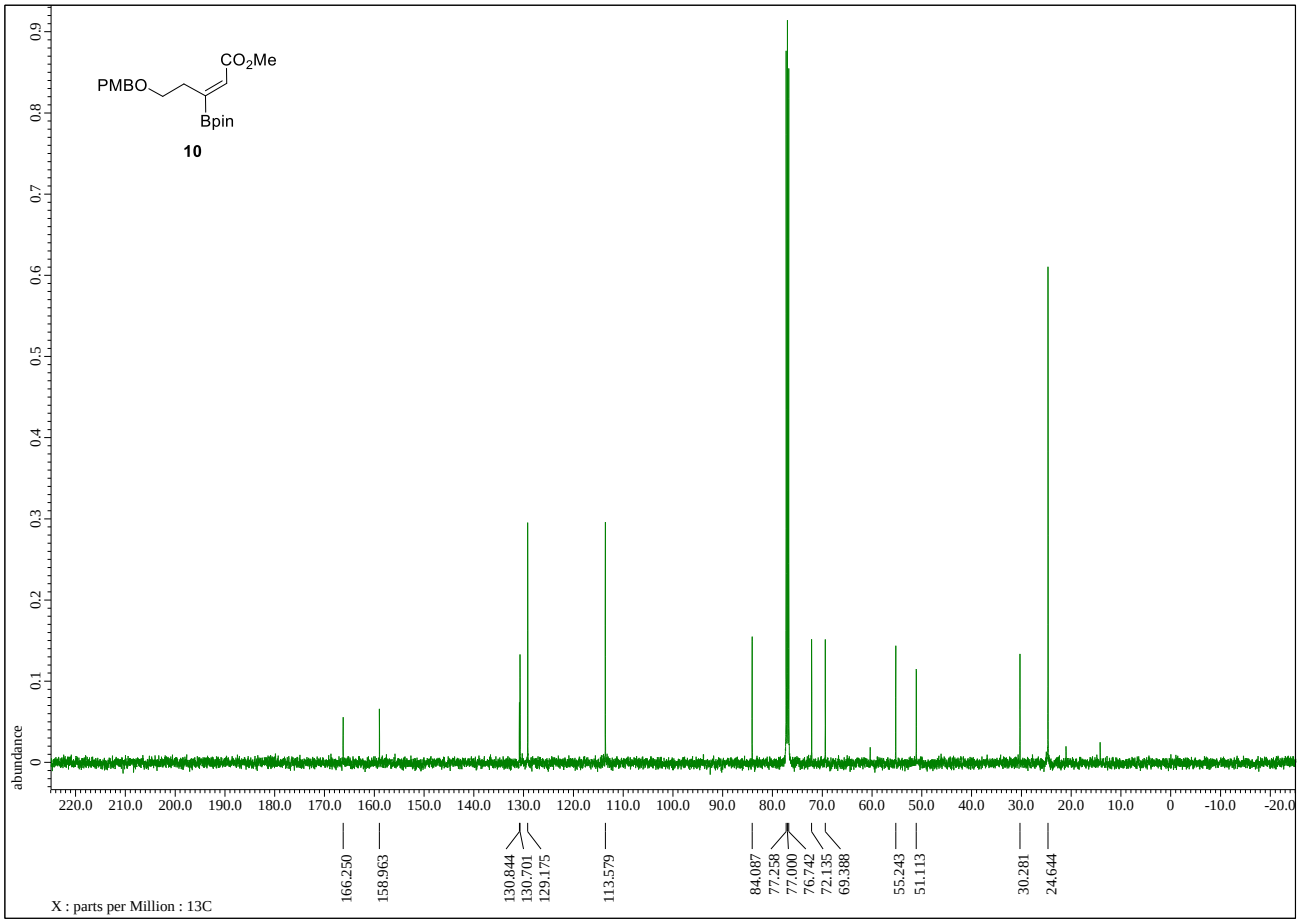

5
3.75
3.07
1.69
1.13
1.00
0.98
0.96
3.10
abundance
X : parts per Million : 1H

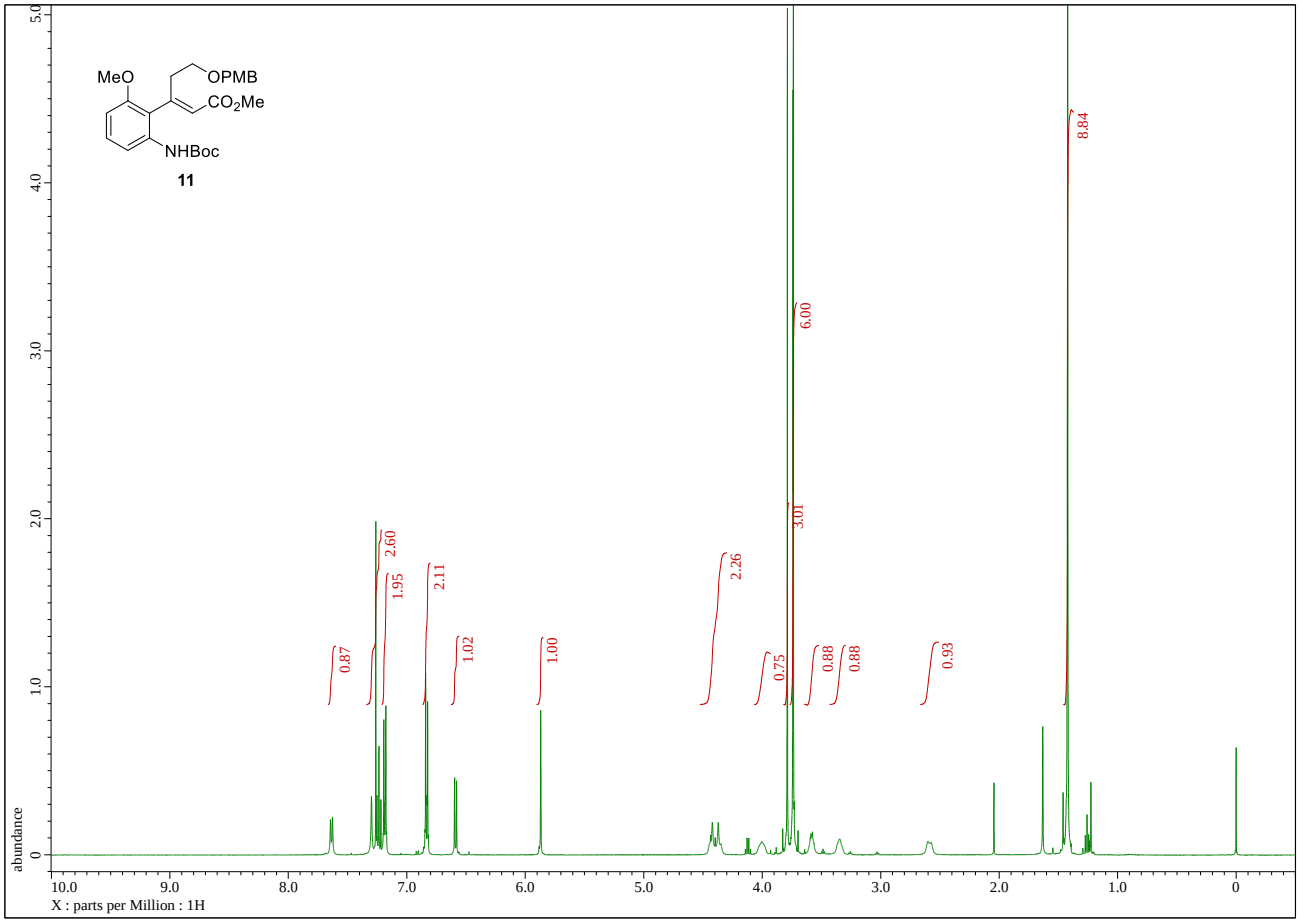

5
abundance
150.935
146.103
141.217
140.612
132.511
128.971
128.798
127.572
124.040
123.851
123.694
122.982
121.949
121.694
119.150
77.313
77.000
76.679
15.520
X : parts per Million : 13C

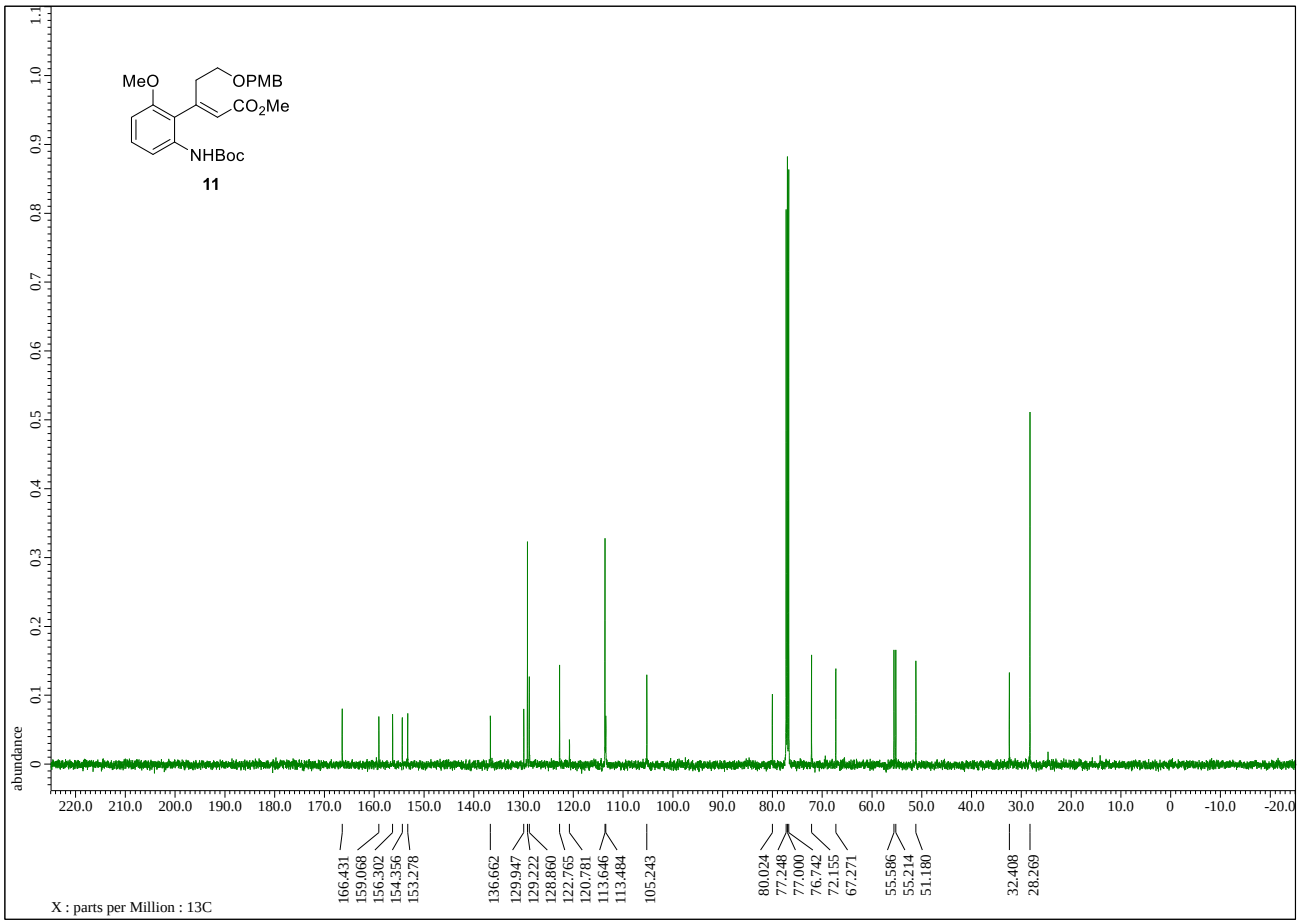

OH
NPh
N
H
8
3.07
2.22
2.09
2.03
0.91
1.00
1.00
0.92
2.27
3.36
residual DMSO
in DMSO-d6
CHCl3
abundance
X : parts per Million : 1H

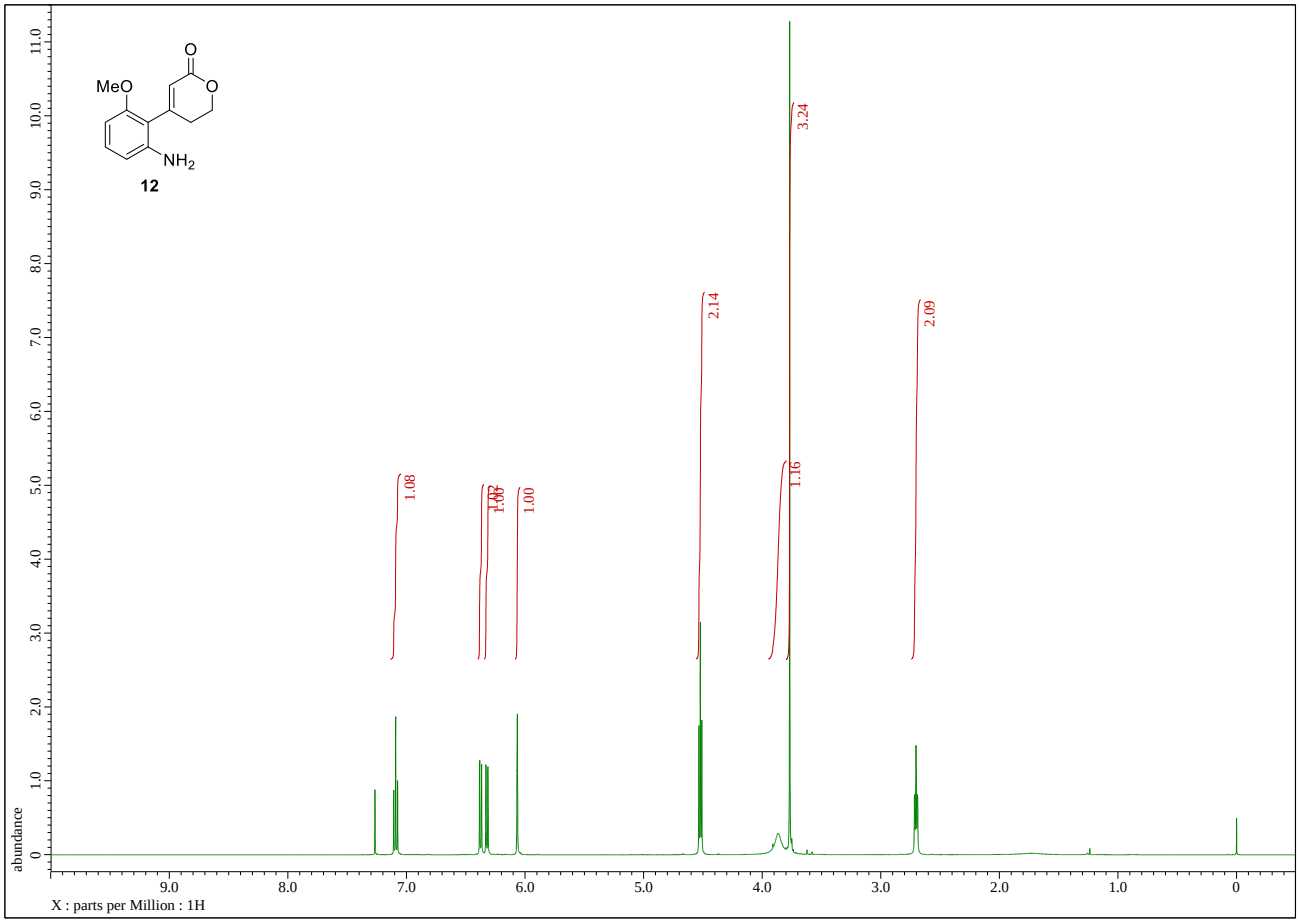

OH
NPh
N
H
8
DMSO-d6
CHCl3
abundance
173.141
155.324
140.807
139.691
130.400
129.284
128.521
127.710
122.140
121.978
121.615
118.916
116.865
60.923
55.782
39.834
39.662
39.500
39.328
22.035
X : parts per Million : 13C

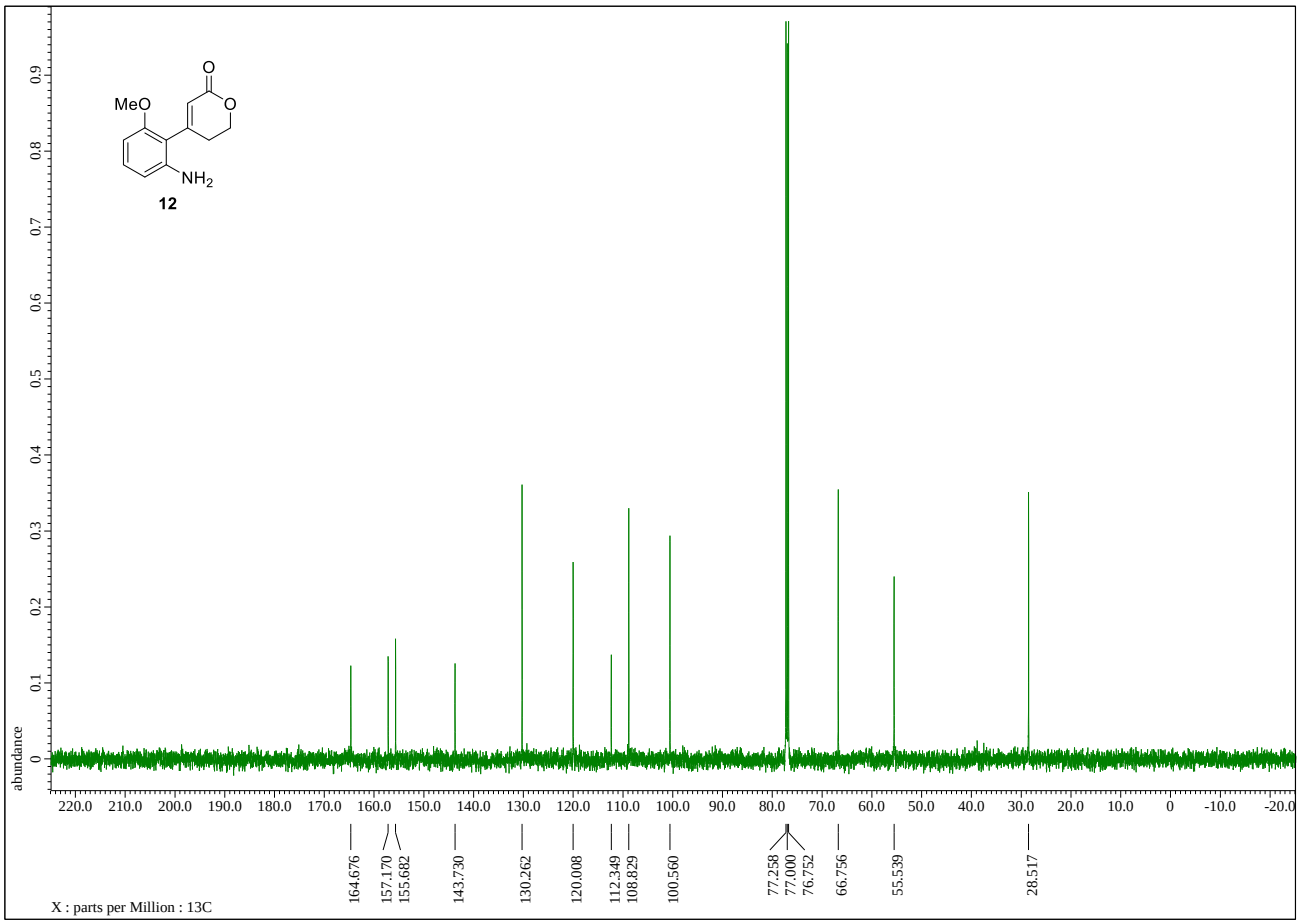

CO2Me
PMBO
Bpin
10
2.64
1.97
1.00
2.09
3.42
3.12
2.08
2.02
12.51
abundance
X : parts per Million : 1H

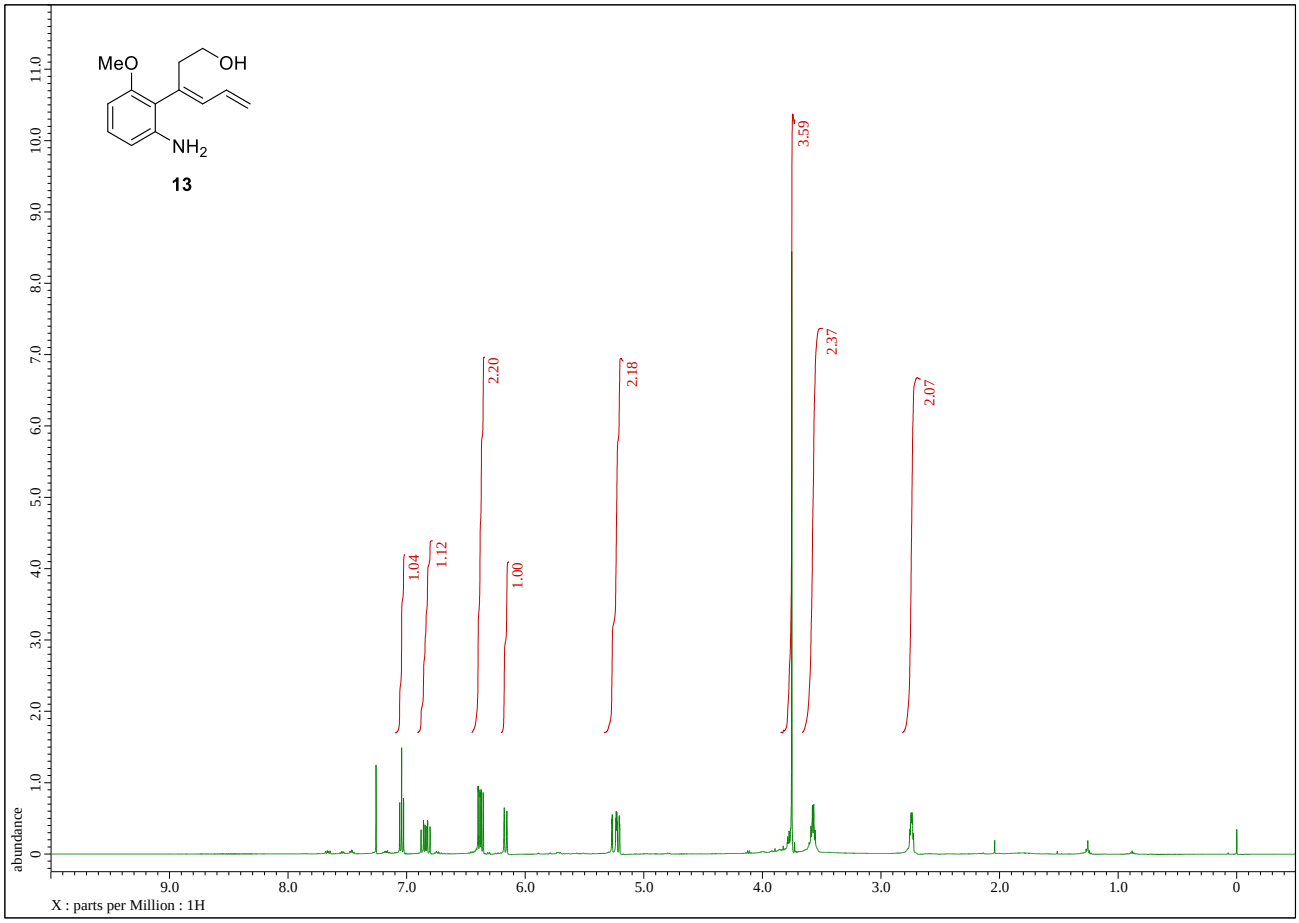

CO2Me
PMBO
Bpin
10
abundance
166.250
158.963
130.844
130.701
129.175
113.579
84.087
77.258
77.000
76.742
72.135
69.388
55.243
51.113
30.281
24.644
X : parts per Million : 13C

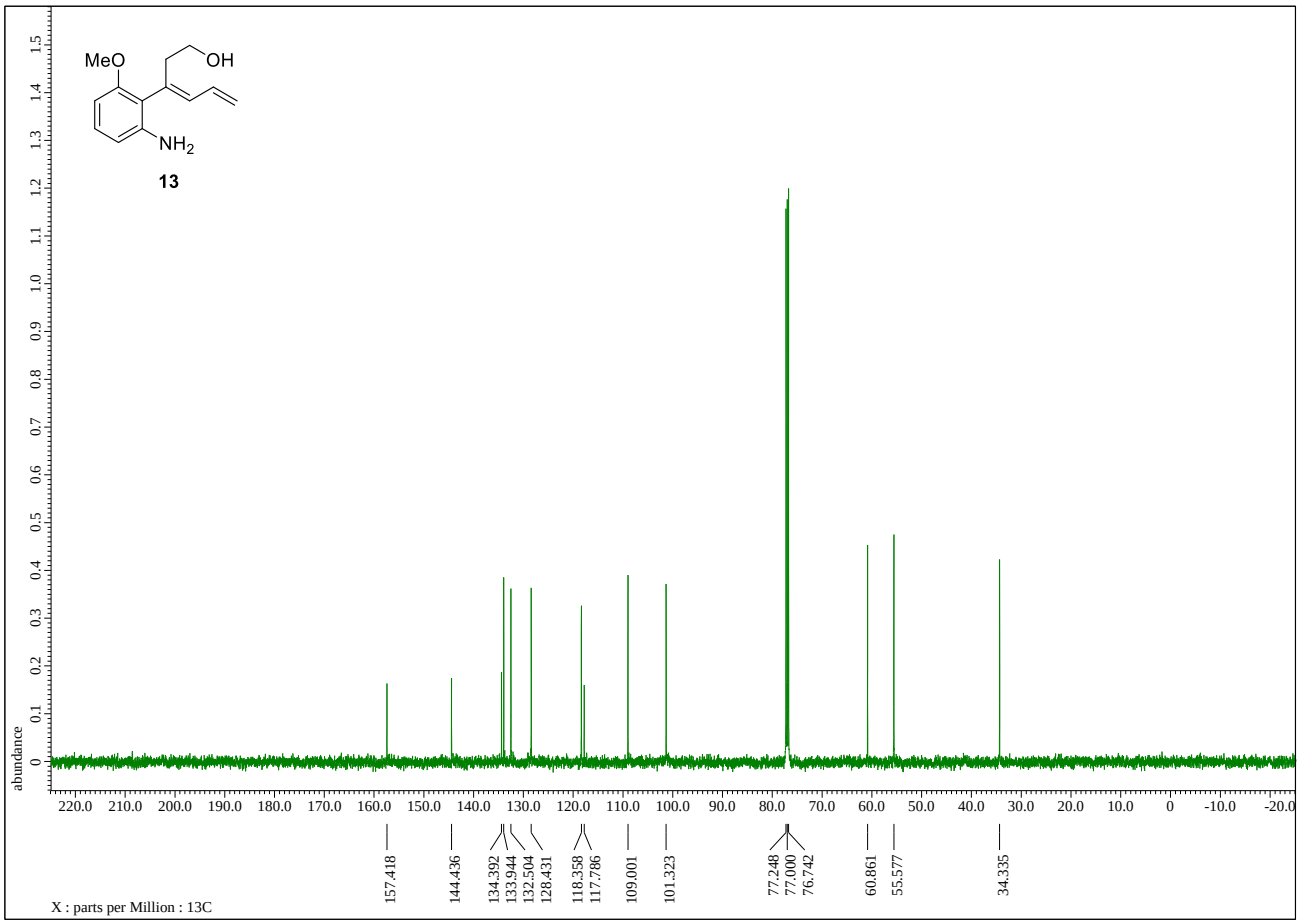

MeO
OPMB
CO2Me
NHBoc
11
abundance
X : parts per Million : 1H
0.87
2.60
1.95
2.11
1.02
1.00
2.26
3.01
6.00
0.75
0.88
0.88
0.93
8.84

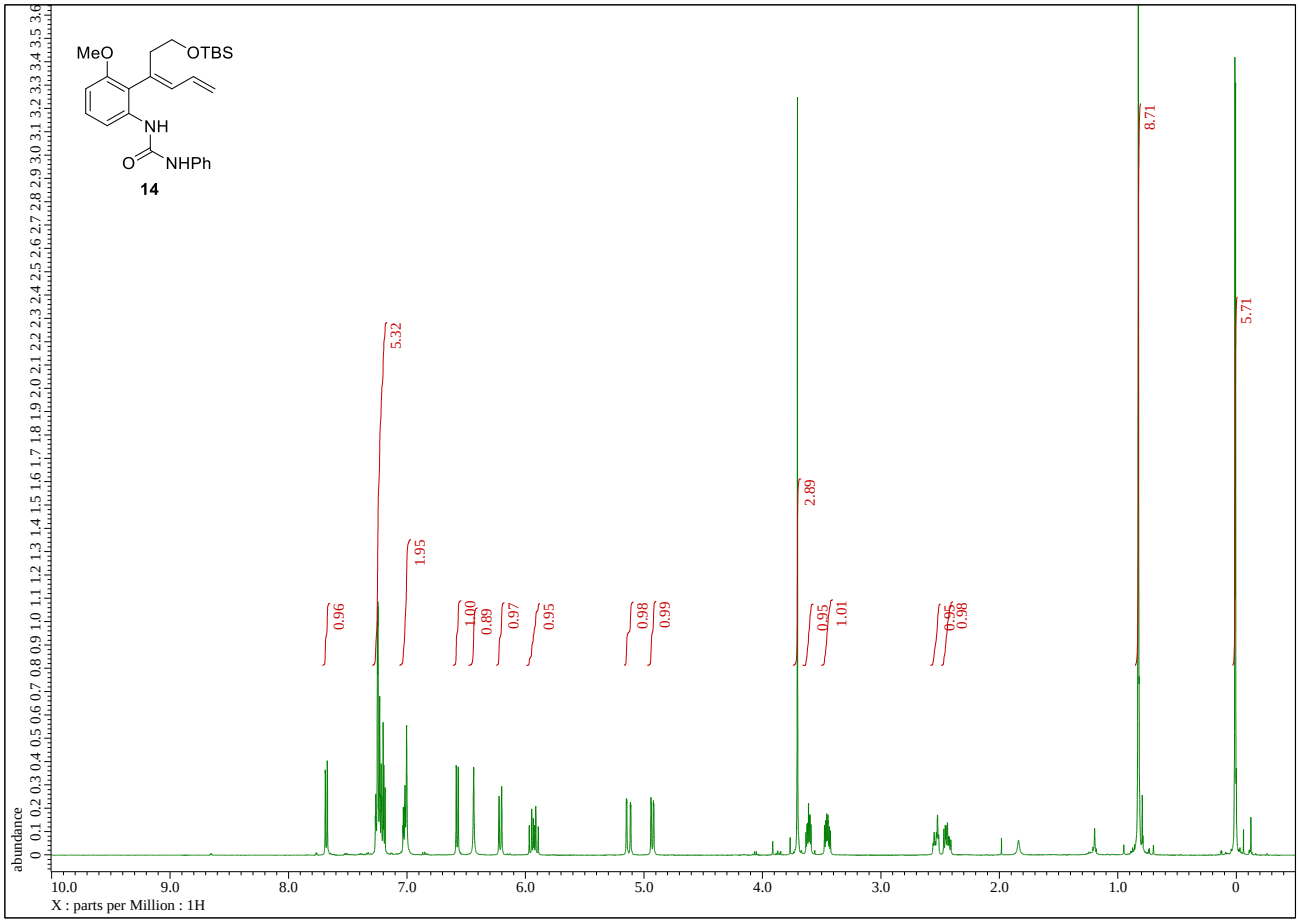

MeO
OPMB
CO2Me
NHBoc
11
abundance
X : parts per Million : 13C
166.431
159.068
156.302
154.356
153.278
136.662
129.947
129.222
128.860
122.765
120.781
113.646
113.484
105.243
80.024
77.248
77.000
76.742
72.155
67.271
55.586
55.214
51.180
32.408
28.269

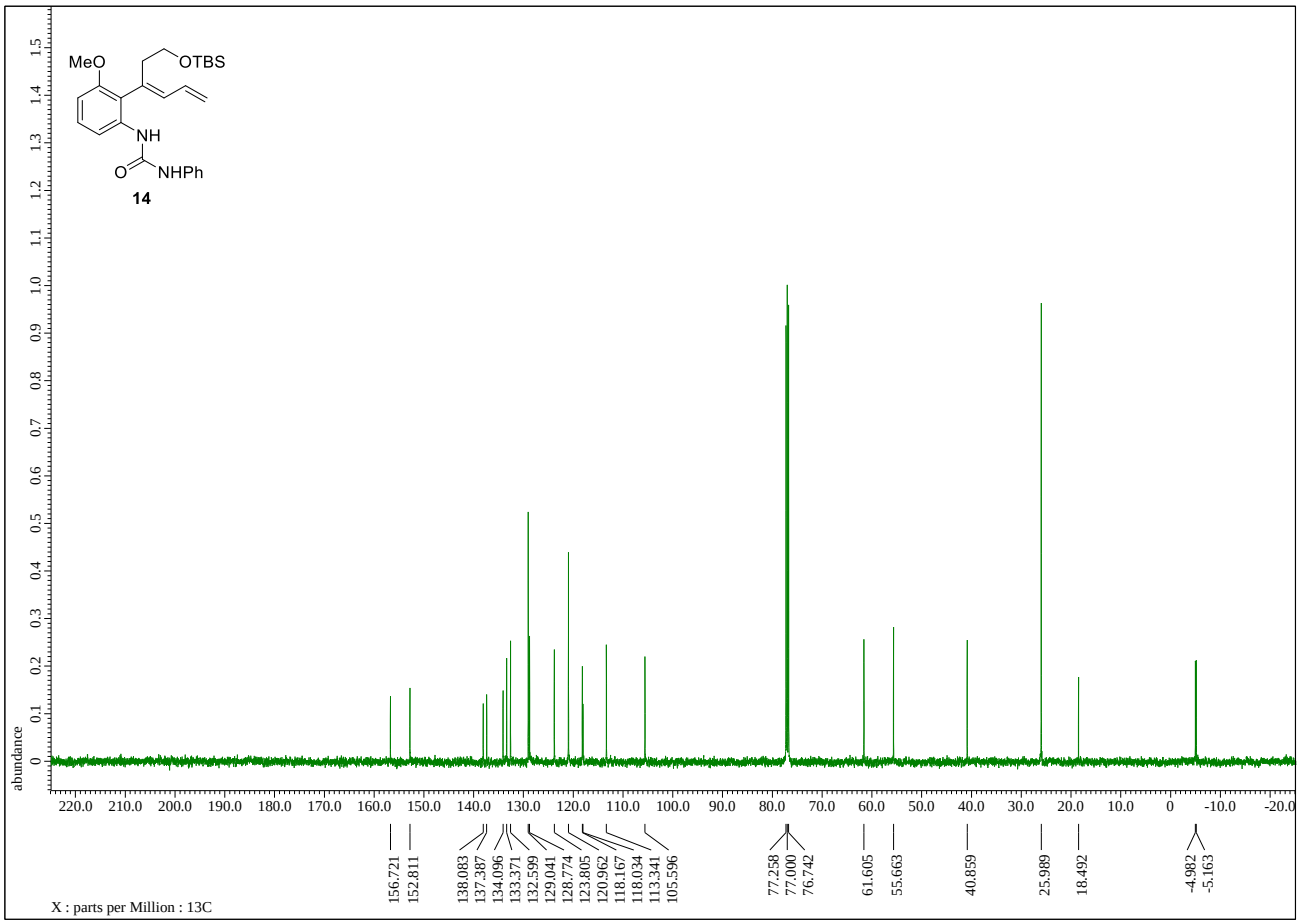

MeO
O
O
NH2
12
3.24
2.14
2.09
1.16
1.08
1.00
abundance
X : parts per Million : 1H

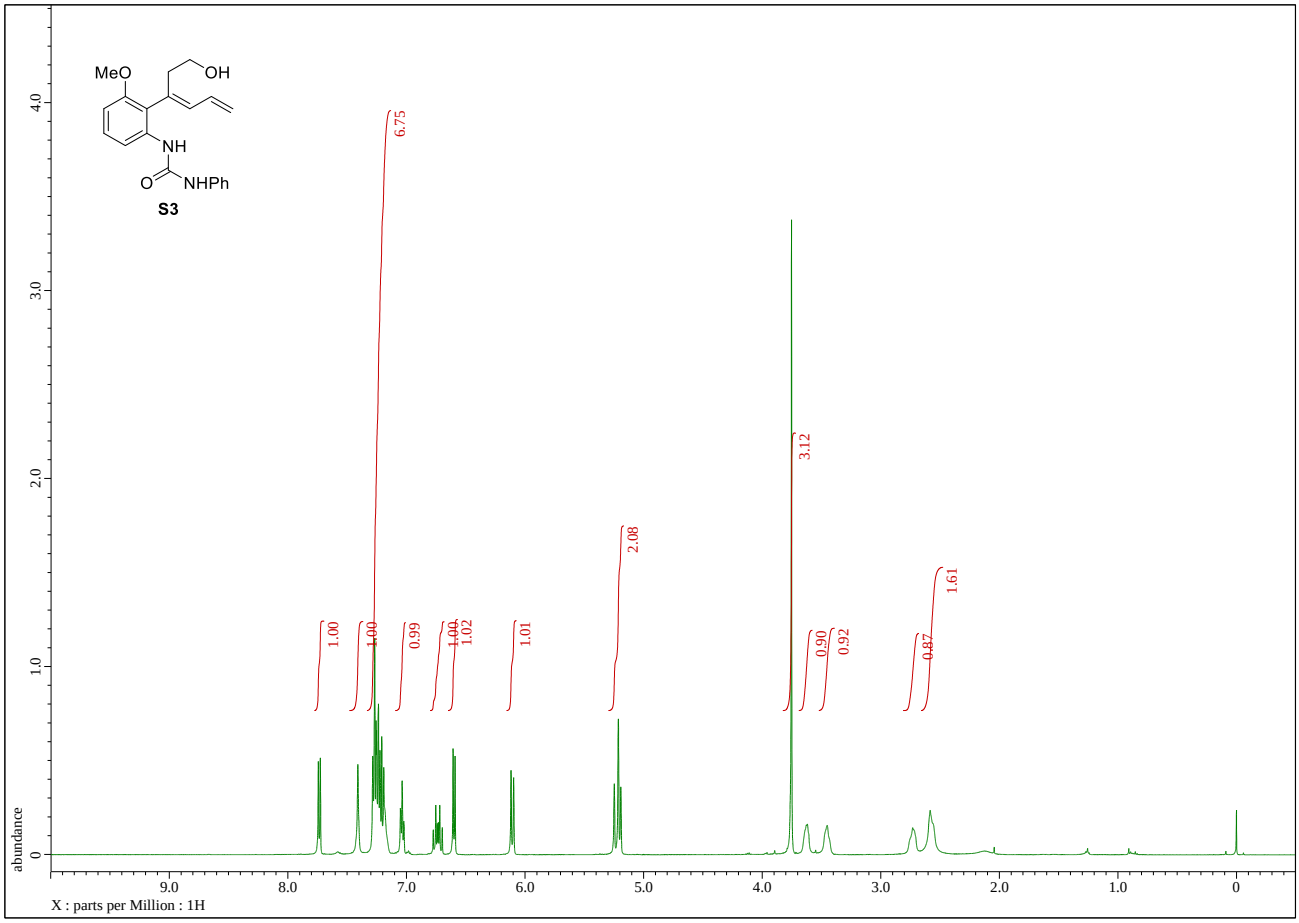

MeO
O
O
NH2
12
abundance
164.676
157.170
155.682
143.730
130.262
120.008
112.349
108.829
100.560
77.258
77.000
76.752
66.756
55.539
28.517
X : parts per Million : 13C

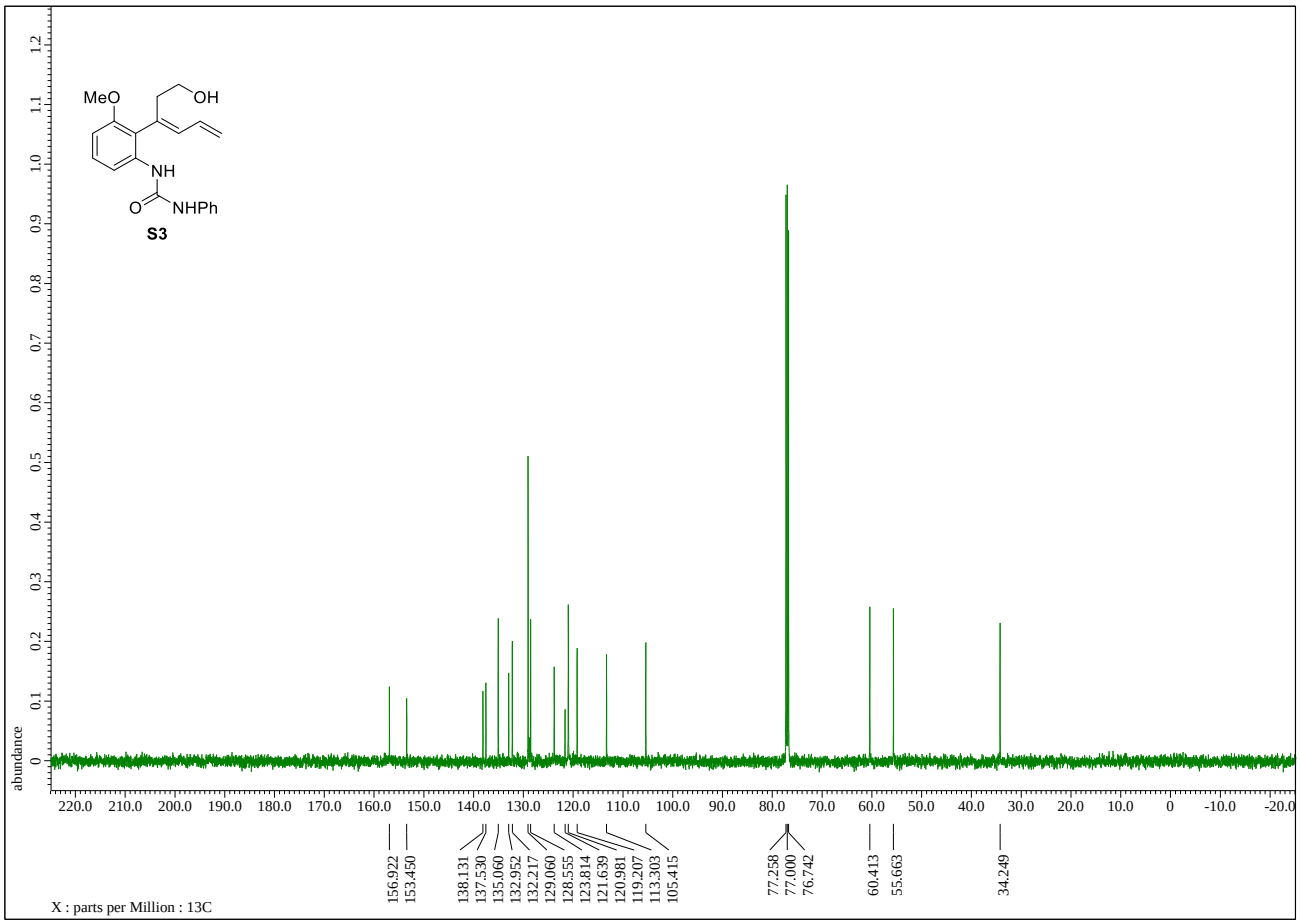

MeO
OH
NH2
13
3.59
2.37
2.20
2.18
2.07
1.04
1.12
1.00
abundance
X : parts per Million : 1H

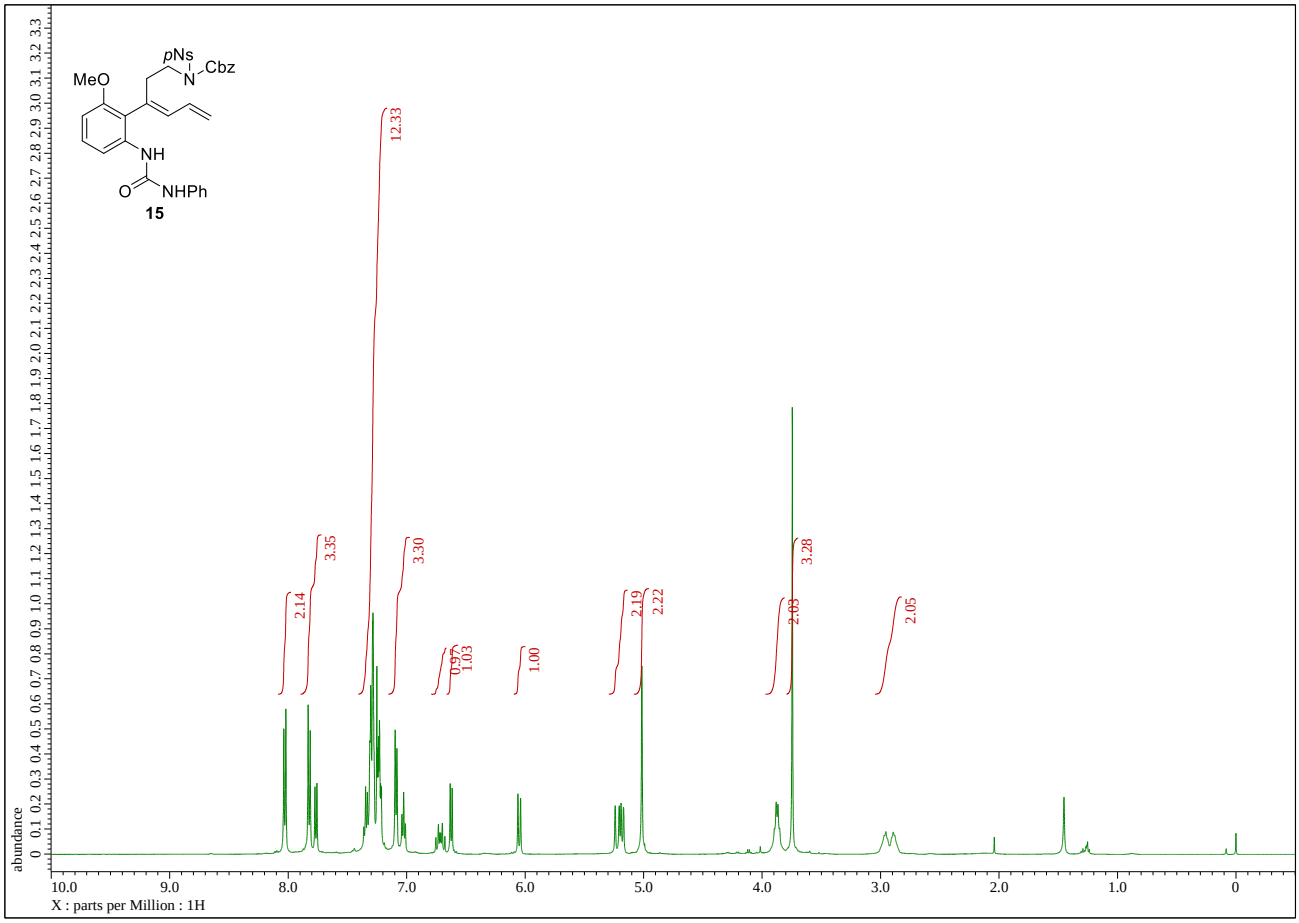

MeO
OH
NH2
13
abundance
157.418
144.436
134.392
133.944
132.504
128.431
118.358
117.786
109.001
101.323
77.248
77.000
76.742
60.861
55.577
34.335
X : parts per Million : 13C

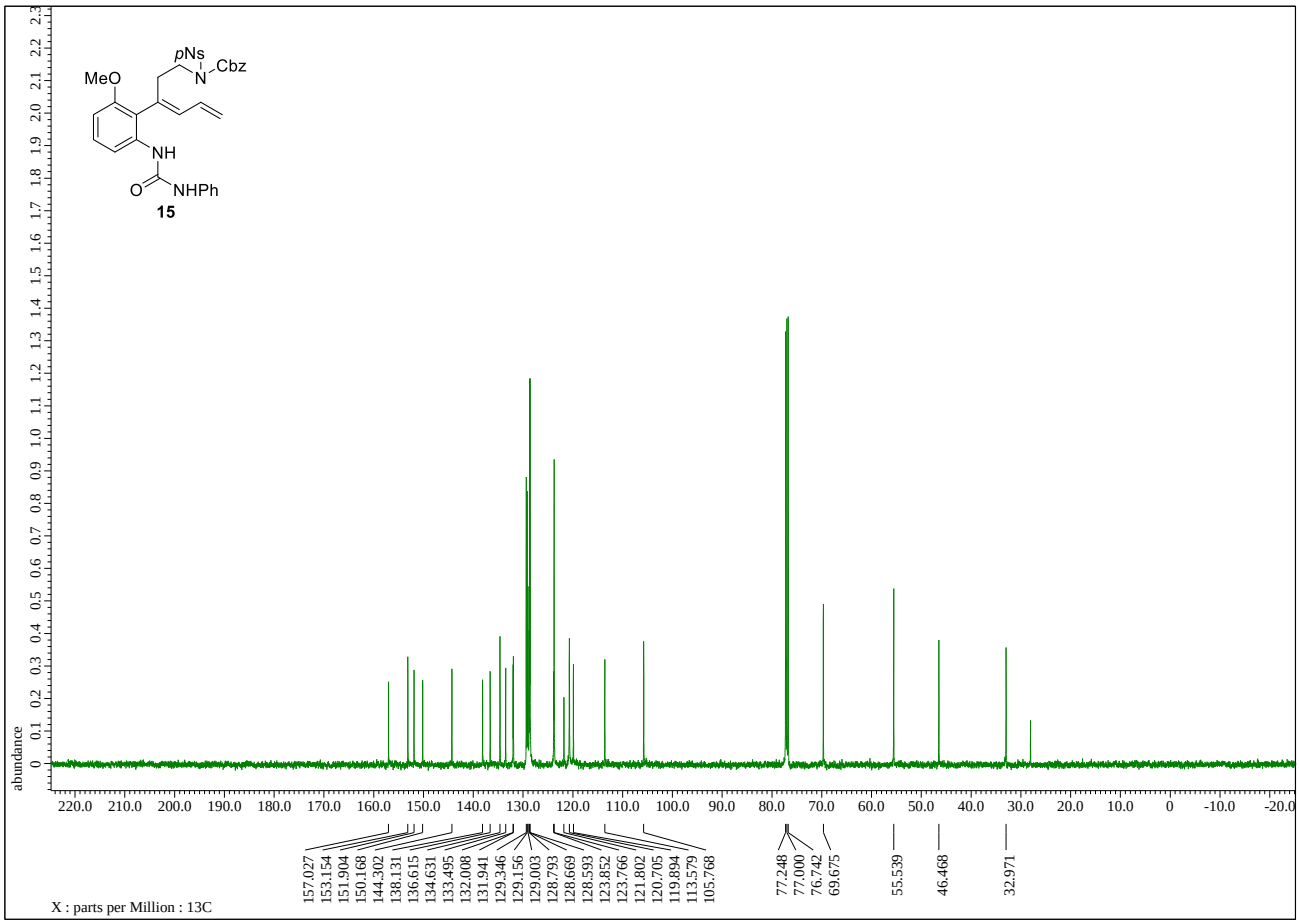

MeO
OTBS
NH
O
NHPh
14
abundance
X : parts per Million : 1H
0.96
5.32
1.95
1.00
0.89
0.97
0.95
0.98
0.99
2.89
0.95
1.01
0.95
0.98
8.71
5.71

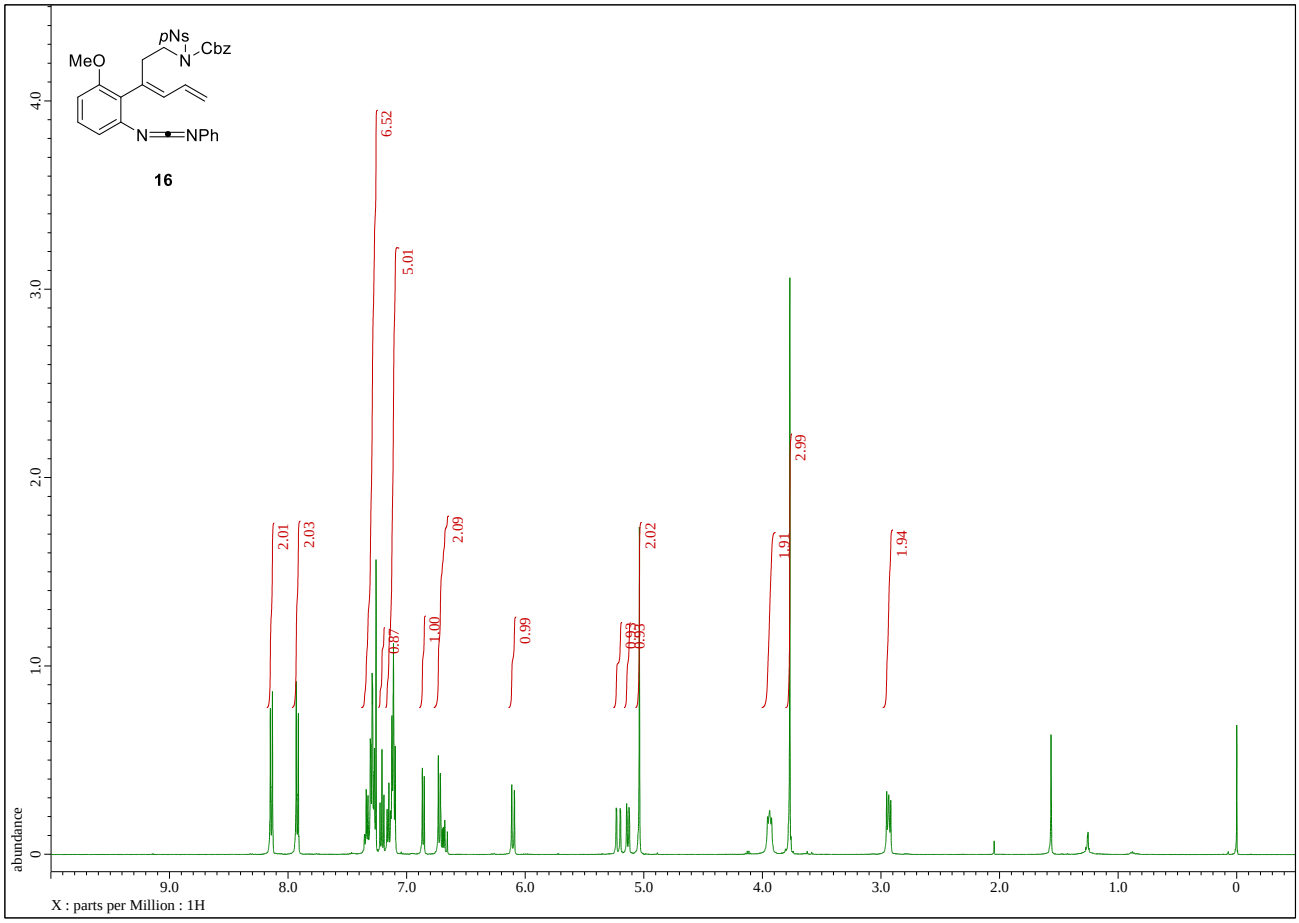

MeO
OTBS
NH
O
NHPh
14
abundance
X : parts per Million : 13C
156.721
152.811
138.083
137.387
134.096
133.371
132.599
129.041
128.774
123.805
120.962
118.167
118.034
113.341
105.596
77.258
77.000
76.742
61.605
55.663
40.859
25.989
18.492
-4.982
-5.163

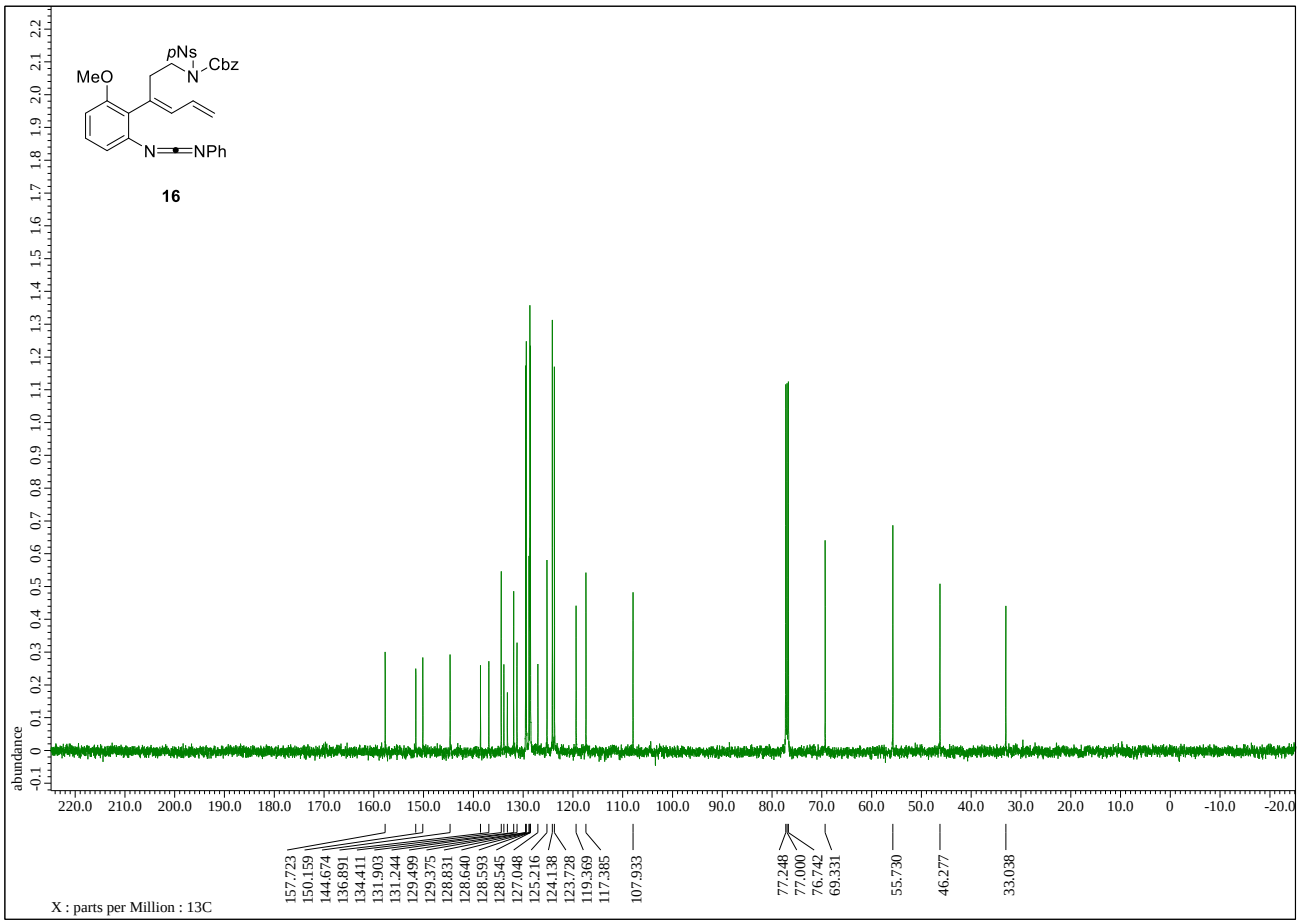

MeO
OH
NH
O
NHPh
S3
6.75
3.12
2.08
1.61
1.00
1.00
0.99
1.00
1.02
1.01
0.90
0.92
0.87
abundance
X : parts per Million : 1H

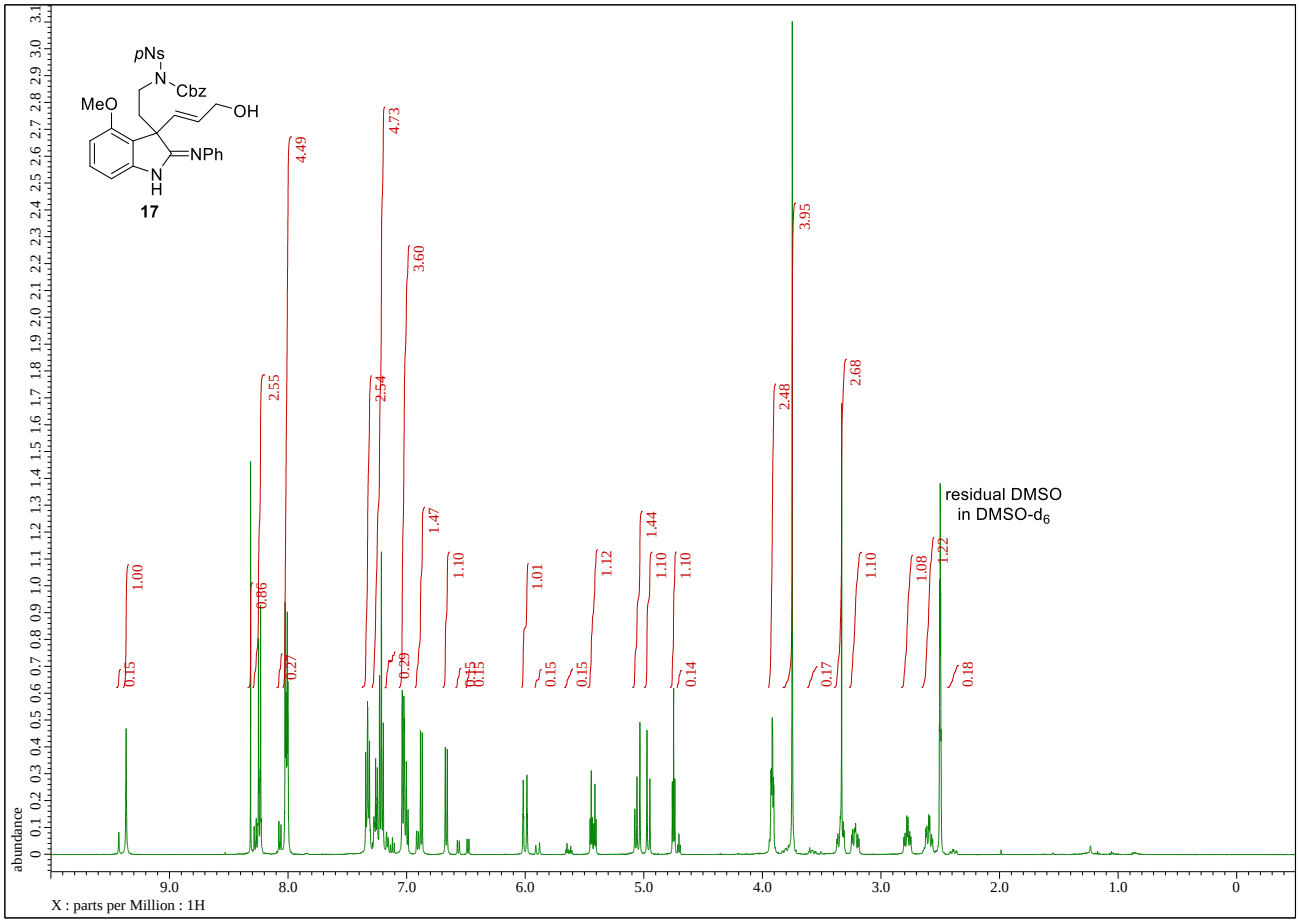

MeO
OH
NH
O
NHPh
S3
abundance
156.922
153.450
138.131
137.530
135.060
132.952
132.217
129.060
128.555
123.814
121.639
120.981
119.207
113.303
105.415
77.258
77.000
76.742
60.413
55.663
34.249
X : parts per Million : 13C

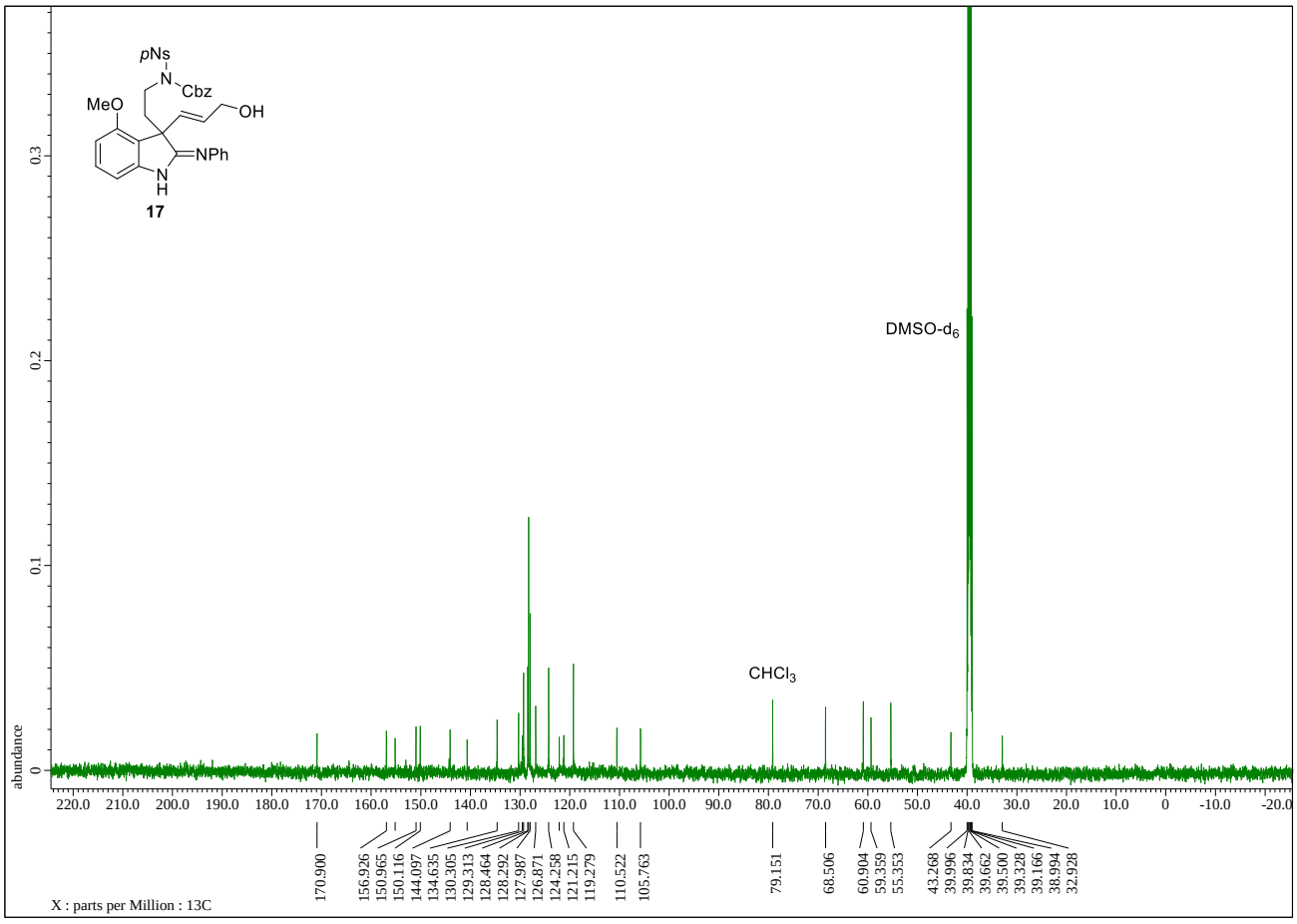

pNs
Cbz
N
MeO
NH
O
NHPh
15
12.33
3.35
3.30
3.28
2.14
2.19
2.22
2.03
2.05
0.97
1.03
1.00
abundance
X : parts per Million : 1H

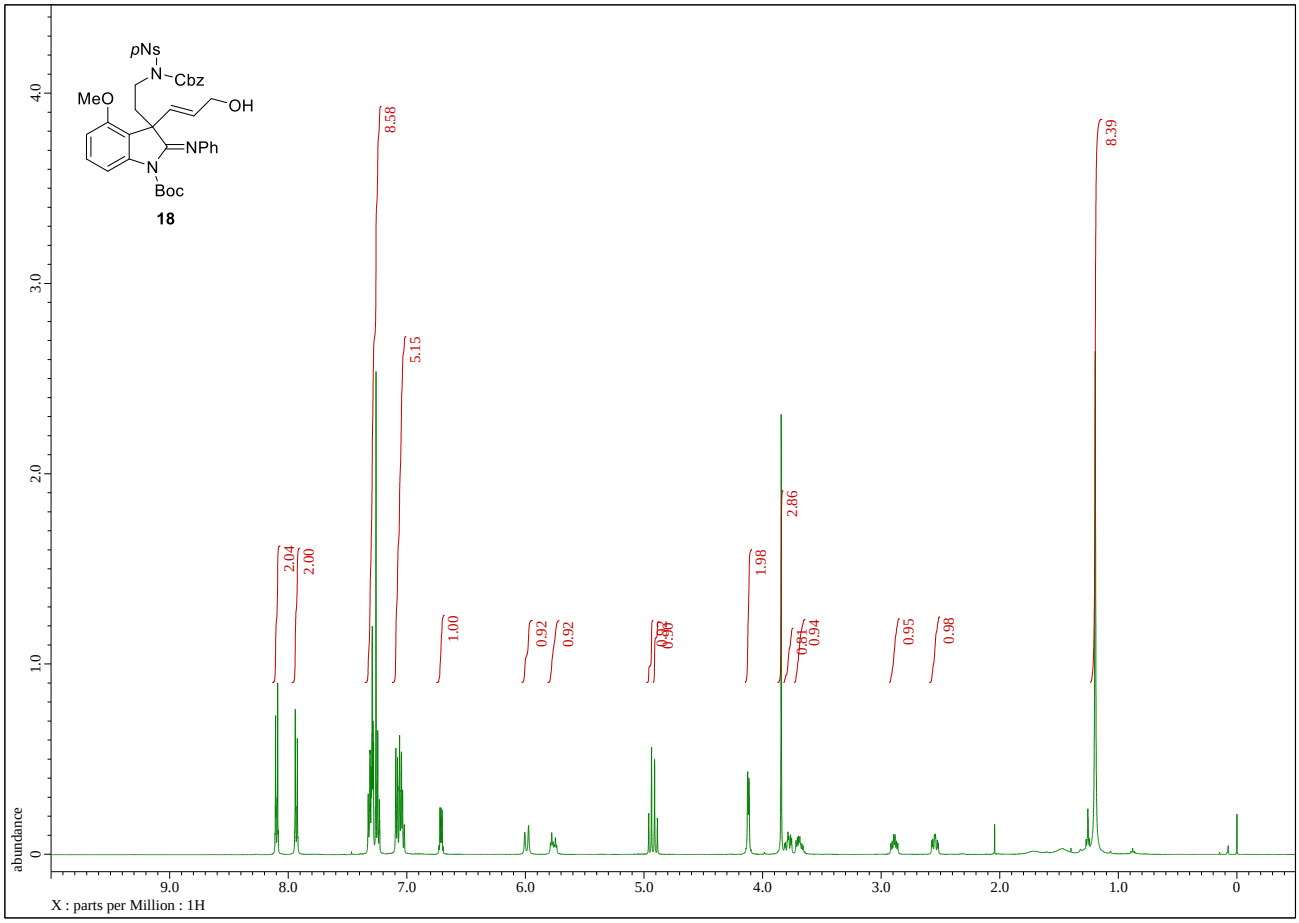

pNs
Cbz
N
MeO
NH
O
NHPh
15
abundance
157.027
153.154
151.904
150.168
144.302
138.131
136.615
134.631
133.495
132.008
131.941
129.346
129.156
129.003
128.793
128.669
128.593
123.852
123.766
121.802
120.705
119.894
113.579
105.768
77.248
77.000
76.742
69.675
55.539
46.468
32.971
X : parts per Million : 13C

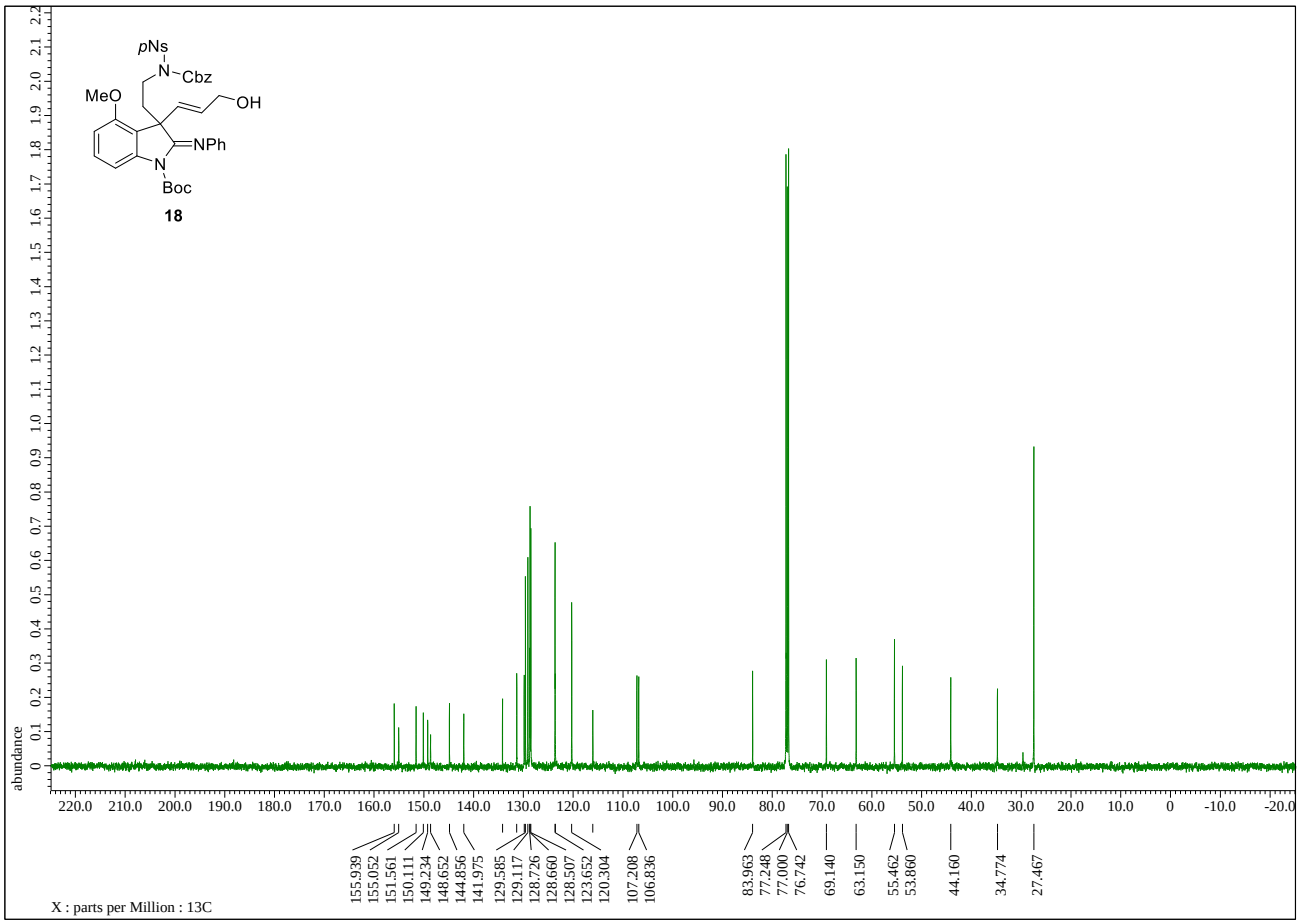

pNs
Cbz
MeO
N
N=NPh
16
6.52
5.01
2.99
2.09
2.03
2.02
2.01
1.94
1.91
1.00
0.99
0.87
abundance
X : parts per Million : 1H

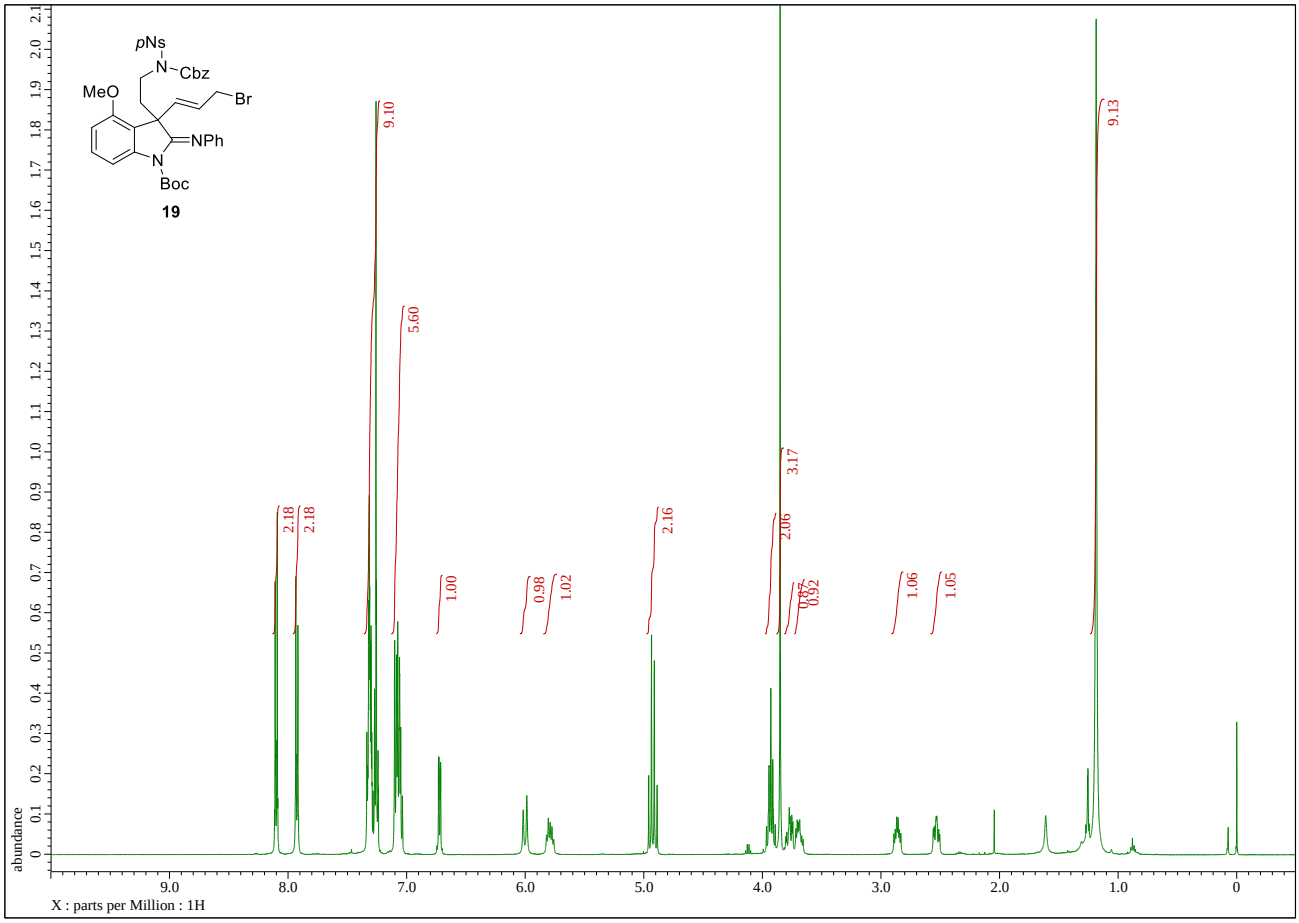

pNs
Cbz
MeO
N
N=NPh
16
abundance
157.723
150.159
144.674
136.891
134.411
131.903
131.244
129.499
129.375
128.831
128.640
128.593
128.545
127.048
125.216
124.138
123.728
119.369
117.385
107.933
77.248
77.000
76.742
69.331
55.730
46.277
33.038
X : parts per Million : 13C

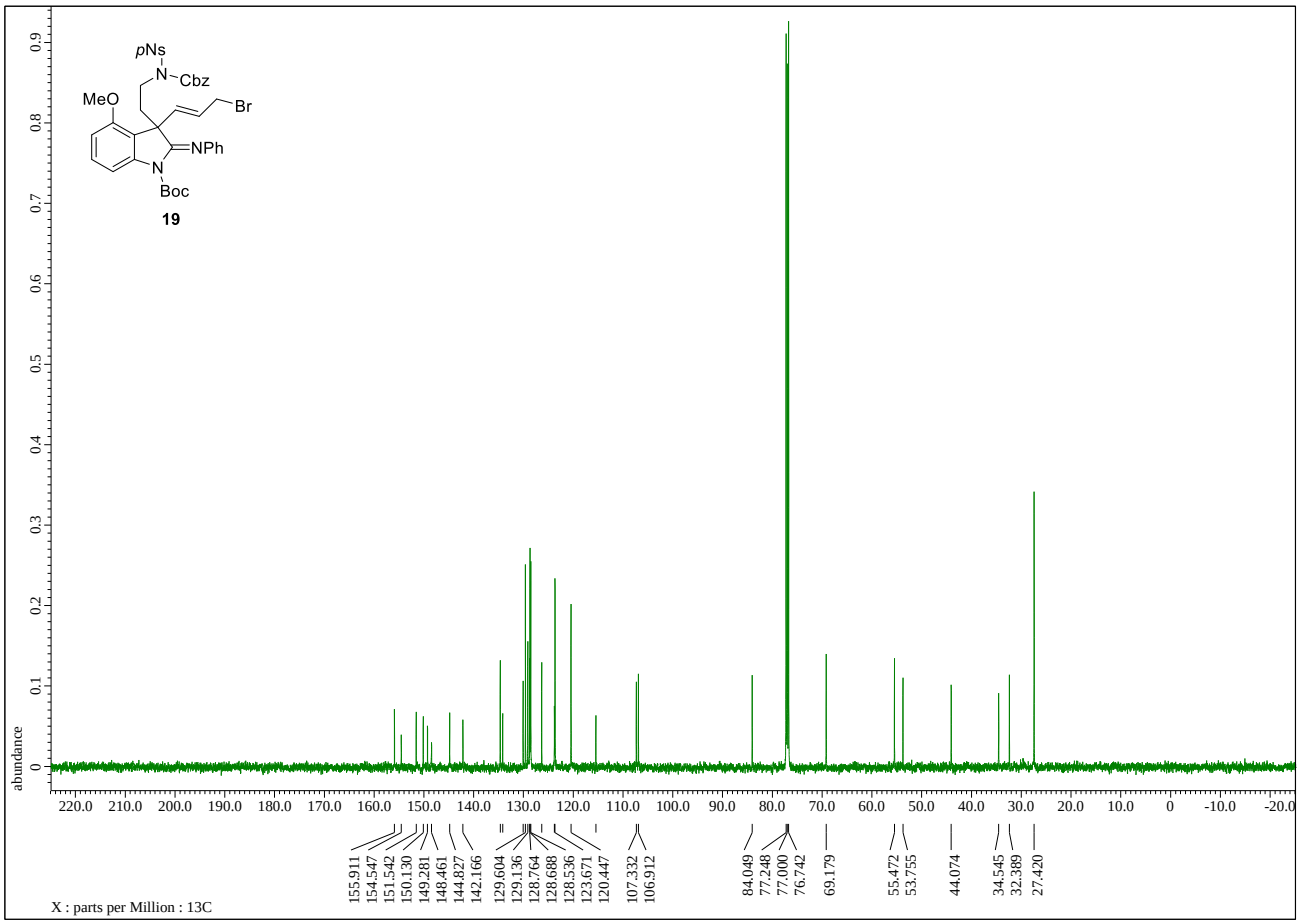

pNs
N
Cbz
MeO
OH
NPh
N
H
17
residual DMSO
in DMSO-d6
abundance
X : parts per Million : 1H

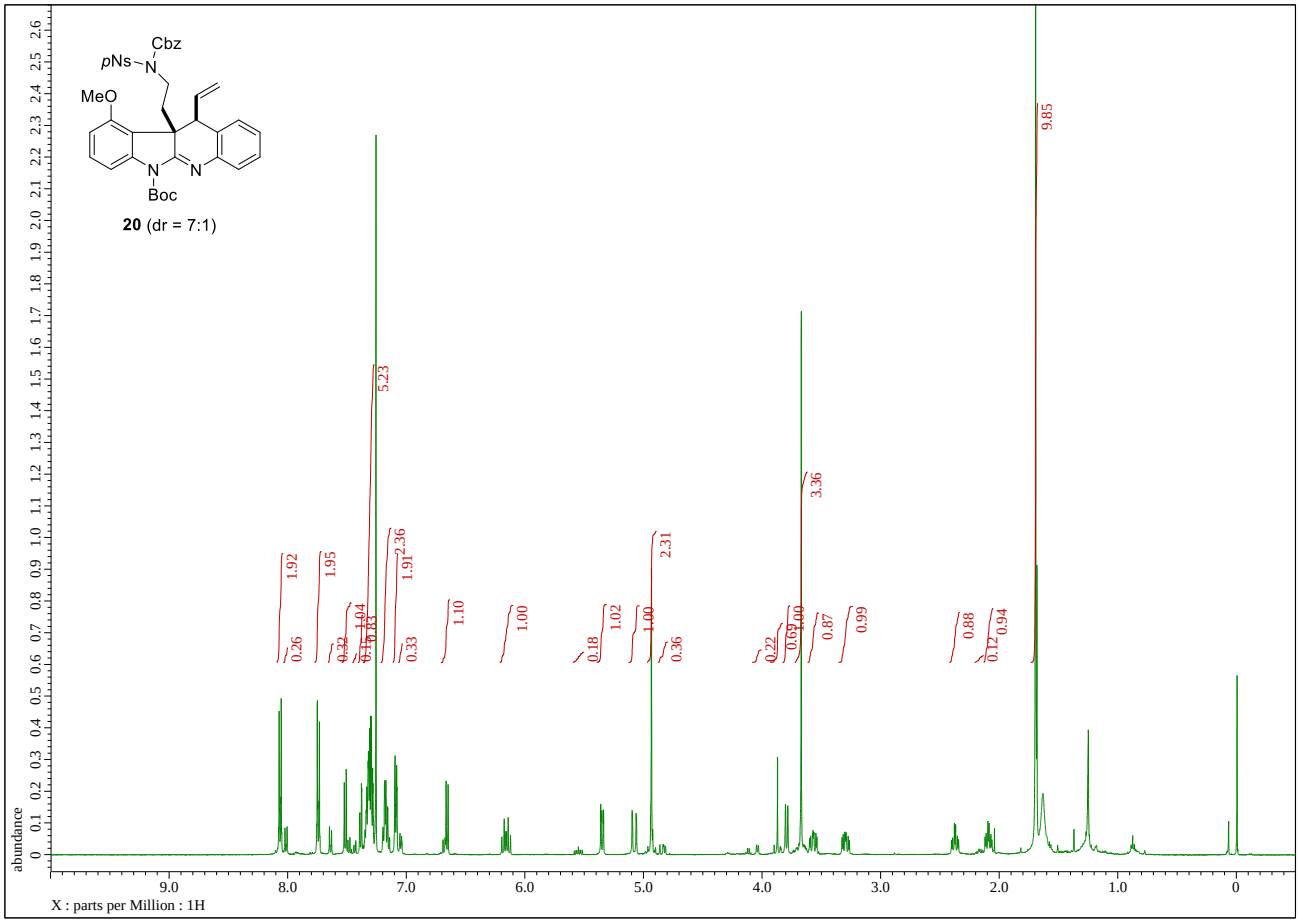

pNs
N
Cbz
MeO
OH
NPh
N
H
17
DMSO-d6
CHCl3
abundance
X : parts per Million : 13C

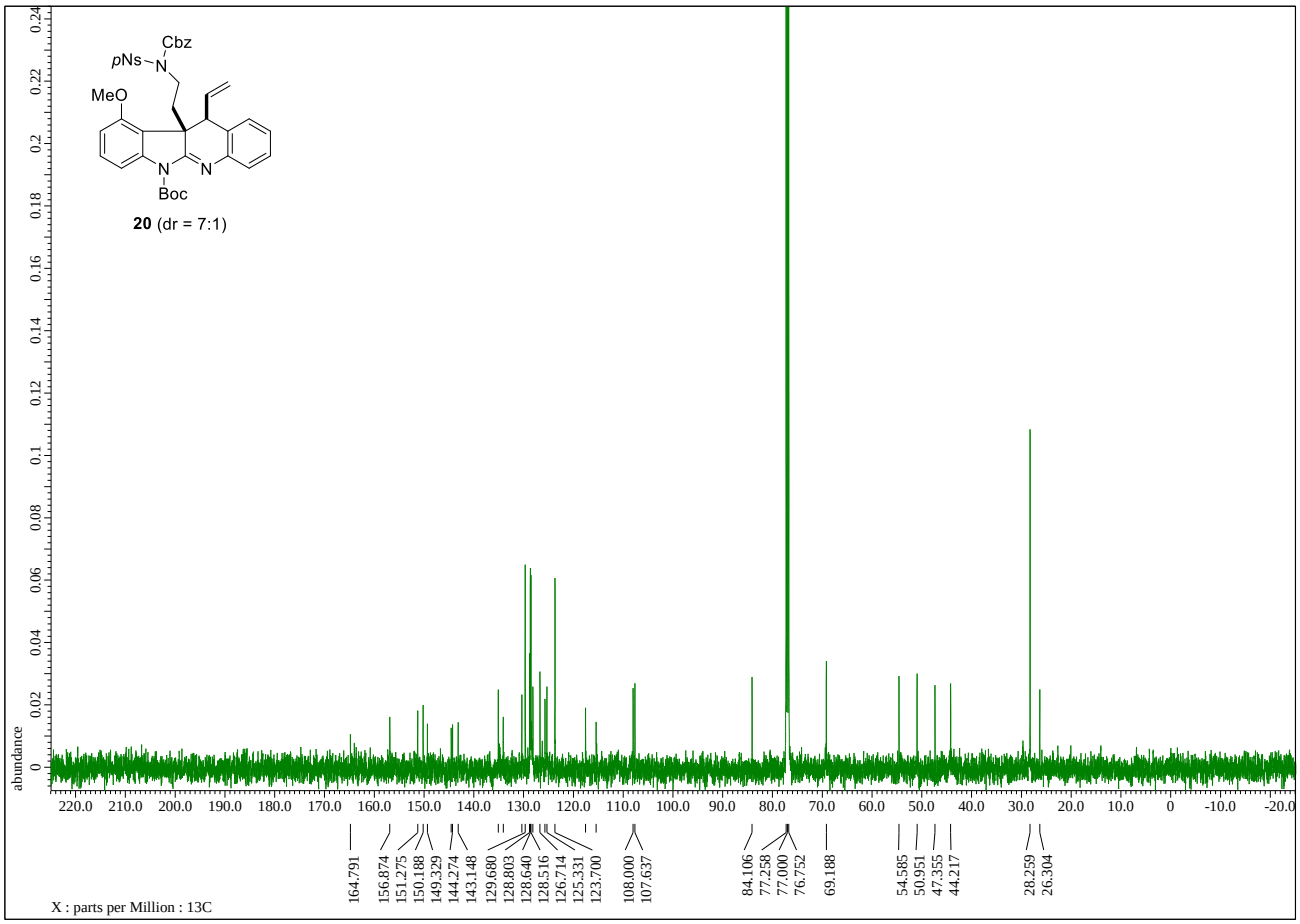

pNs
N
Cbz
MeO
OH
NPh
N
Boc
18
8.58
8.39
5.15
2.86
2.04
2.00
1.98
1.00
0.92
0.92
0.95
0.98
0.94
abundance
X : parts per Million : 1H


pNs
N
Cbz
MeO
OH
NPh
N
Boc
18
abundance
X : parts per Million : 13C


pNs
N
Cbz
MeO
Br
NPh
N
Boc
19
9.10
5.60
9.13
3.17
2.18
2.18
2.16
2.06
1.00
0.98
1.02
1.06
1.05
0.87
0.92
abundance
X : parts per Million : 1H


pNs
N
Cbz
MeO
Br
NPh
N
Boc
19
155.911
154.547
151.542
150.130
149.281
148.461
144.827
142.166
129.604
129.136
128.764
128.688
128.536
123.671
120.447
107.332
106.912
84.049
77.248
77.000
76.742
69.179
55.472
53.755
44.074
34.545
32.389
27.420
abundance
X : parts per Million : 13C


Cbz
pNs
N
MeO
N
N
Boc
20 (dr = 7:1)
abundance
X : parts per Million : 1H


Cbz
pNs
N
MeO
N
N
Boc
20 (dr = 7:1)
abundance
X : parts per Million : 13C