Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Highly Efficient and Stereocontrolled Oxidative Coupling of Tetrahydropyrroloindoles: Synthesis of Chimonanthines, (+)-WIN 64821 and (+)-WIN 64745

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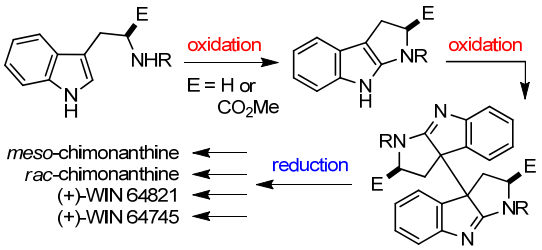

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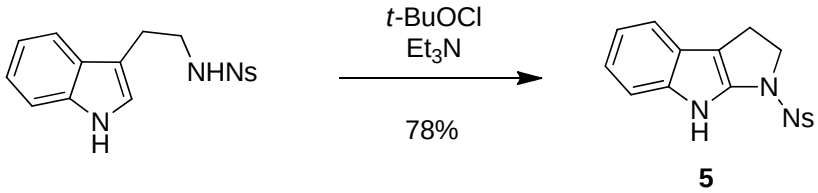
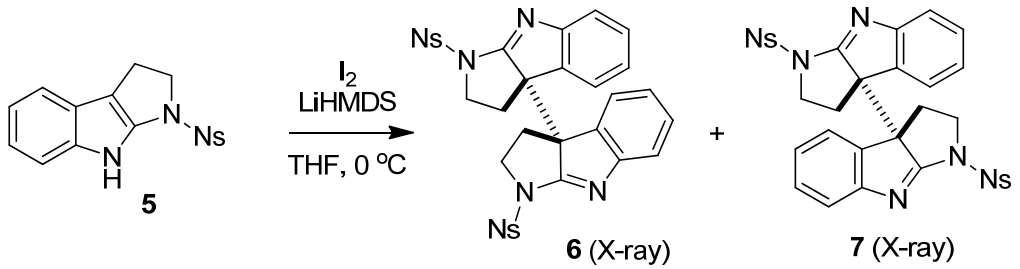
1. Synthesis of Compounds 5–7.



1-((2-Nitrophenyl)sulfonyl)-1,2,3,8-tetrahydropyrrolo[2,3-*b*]indole (5). To a solution of *N*-nosyl tryptamine (2.875 g, 8.3 mmol) and Et_3N (5 mL, 35.9 mmol) in CH_2Cl_2 (83 mL) at 0 ^oC under nitrogen was slowly added *t*-BuOCl (1.0 mL, 9.1 mmol). The reaction mixture was stirred at 0 ^oC for 3 h, and warmed to room temperature for 18 h. Et_2O (200 mL) and H_2O (200 mL) were added into the mixture. The two layers were separated, and the organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel with CH_2Cl_2-hexane (4:5, v:v) as the eluent to give the product **5** (2.230 g, 78% yield) as a red solid. Mp 127-128 ^oC. IR (KBr): υ (cm^{-1}) 3420, 1557, 1480, 1505, 1450, 1374, 1358, 1167, 1007, 771, 743, 660, 609. ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.62-7.54 (m, 2H), 7.36-7.31 (m, 2H), 7.16-7.11 (m, 2H), 4.38 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 140.5, 138.1, 134.5, 131.9, 130.0, 129.2, 124.3, 124.0, 121.0, 120.9, 117.9, 112.2, 103.8, 56.0, 23.3. ESI-MS (*m/z*): $(M+H)^+$ 344. Anal. calcd for $C_{16}H_{13}N_3O_4S$: C, 55.97; H, 3.82; N, 12.24. Found: C, 55.89; H, 3.98; N, 12.03.



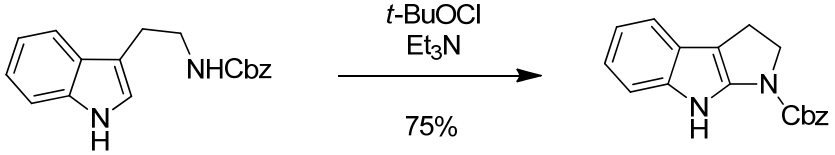
Lithium bis(trimethylsilyl)amide (1.0 M solution in THF, 0.55 mL, 0.55 mmol) was added into the solution of compound **5** (172 mg, 0.5 mmol) in dry THF (5 mL) at 0 ^oC under nitrogen atmosphere. After 30 min, I_2 (95 mg, 0.375 mmol) was added and the mixture was stirred for 10 min. The resulting mixture was quenched with saturated aqueous $Na_2S_2O_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and dried

over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude products were purified by column chromatography on silica gel with hexane-ethyl acetate (4:3, v:v) as the eluent to give the mixture of **6** and **7**. Further separation by HPLC produced **6** (68 mg, 40%) and **7** (23 mg, 13%).

Compound 6. White solid. Mp 152-154 ^{o}C (dec.). IR (KBr): υ (cm^{-1}) 1623, 1586, 1545, 1447, 1368, 1251, 1172, 1082, 990, 765, 741, 656, 604, 579. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.94 (t, *J* = 7.6 Hz, 2H), 7.87 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 7.2 Hz, 2H), 4.39-4.34 (m, 4H), 3.02 (dd, *J* = 14.0, 3.6 Hz, 2H), 2.17-2.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.2, 158.5, 148.2, 137.5, 136.4, 133.1, 131.9, 130.1, 129.6, 124.9, 123.8, 123.6, 119.8, 64.9, 57.1, 26.5. ESI-MS (*m/z*): (M^{+}+Na) 707; HRMS calcd for $C_{32}H_{25}N_6O_8S_2$ (M+H) 685.1170, found: 685.1166. The structure was further confirmed by its X-ray diffractional experiments.

Compound 7. Yellow solid. Mp 146-148 ^{o}C (dec.). IR (KBr): υ (cm^{-1}) 2924, 1626, 1592, 1541, 1447, 1377, 1250, 1180, 1061, 768, 741, 654, 584. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.80-7.72 (m, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.31-7.23 (m, 4H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 2H), 4.78-4.71 (m, 2H), 4.64-4.59 (m, 2H), 2.02 (dd, *J* = 13.6, 6.0 Hz, 2H), 1.91-1.82 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 179.2, 159.9, 148.6, 137.1, 135.6, 133.7, 131.8, 130.6, 129.8, 124.6, 124.0, 122.8, 118.9, 64.4, 57.6, 26.8. ESI-MS (*m/z*): (M^{+}+Na) 707. HRMS calcd for $C_{32}H_{25}N_6O_8S_2$ (M+H) 685.1170, found: 685.1186. The structure was further confirmed by its X-ray diffractional experiments.

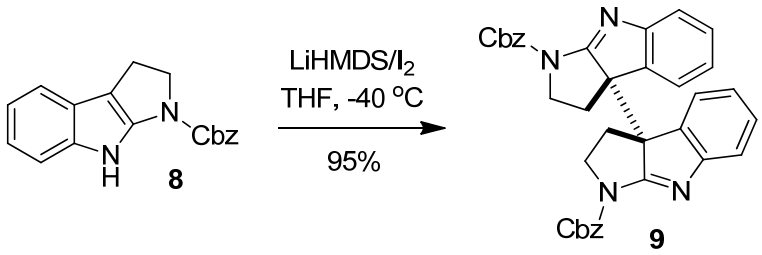
2. Synthesis of *meso*-Chimonanthine 1.



8

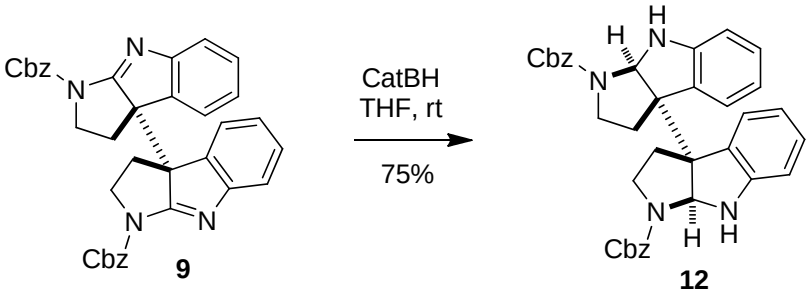
Benzyl 2,3-dihydropyrrolo[2,3-*b*]indole-1(8*H*)-carboxylate (8). To a solution of

N-(benzoxycarbonyl)tryptamine (0.294 g, 1.0 mmol) and Et_3N (1.4 mL, 10 mmol) in CH_2Cl_2 (10 mL) at 0 °C under nitrogen was slowly added *t*-BuOCl (0.122 mL, 1.1 mmol). The reaction mixture was stirred at 0 °C for 3 h, and warmed to room temperature for 18 h. The solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2-hexane-Et_3N (40:50:1, v:v:v) as the eluent to give the product **8** (0.219 g, 75% yield) as a white solid. Mp 152-154 °C. IR (KBr): ν (cm^{-1}) 3368, 1697, 1585, 1537, 1421, 1350, 1304, 1208, 1164, 734, 689. ^1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 8.76/8.13 (2br, 1H), 7.46-7.19 (m, 7H), 7.10-7.02 (m, 2H), 5.33/5.26 (2s, 2H), 4.46-4.37 (m, 2H), 3.15-3.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (mixture of rotamers) δ 152.5/151.2, 142.5/140.9, 137.2/136.0, 128.9, 128.6, 128.4, 128.2/128.0, 124.6/124.4, 120.6/120.4, 119.7/119.4, 117.2/117.0, 111.7/111.5, 101.2/100.1, 67.9/67.4, 53.4/53.1, 23.2/22.5. ESI-MS (*m/z*): $(M+H)^+$ 293; HRMS calcd for $C_{18}H_{17}N_2O_2$ (M+H) 293.1285, found 293.1292.

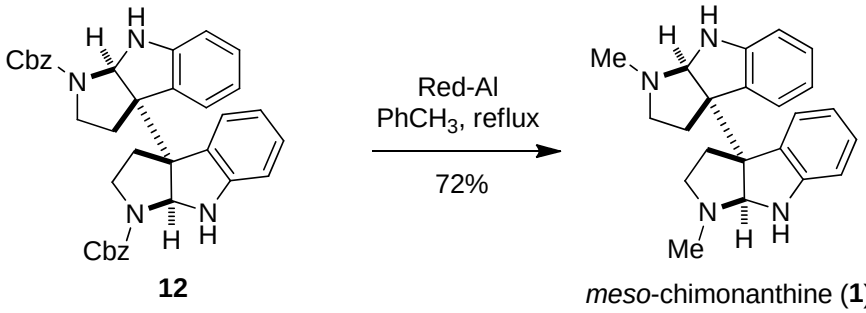


Compound 9. The solution of **8** (58 mg, 0.2 mmol) in dry THF (2 mL) was cooled to -40 °C under nitrogen atmosphere, A LiHMDS solution (1.0 M solution in THF, 0.22 mL, 0.22 mmol) was added slowly. After 30 min, I_2 (38 mg, 0.15 mmol) was added and the mixture was stirred for 10 min. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with CH_2Cl_2-ethyl acetate (5:1, v:v) as the eluent to give the product (55 mg, 95% yield) as a white solid. Mp 218-220 °C (decomposed). IR (KBr): ν (cm^{-1}) 3054, 2964, 1735, 1574, 1449, 1406, 1309, 1211, 1137, 1033, 919, 747, 702. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.29 (m, 14H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 2H), 5.34 (s, 4H), 3.73 (t, *J* = 10.4 Hz, 2H), 2.66 (dd, *J* = 17.2, 10.0 Hz, 2H), 2.12 (dd, *J* = 14.0, 6.8 Hz, 2H), 1.78-1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

179.9, 160.0, 150.6, 136.6, 135.6, 130.0, 128.6, 128.5, 123.5, 123.2, 120.0, 68.4, 65.4, 54.1, 23.4. MALDI-MS (*m/z*): (M^+) 582; HRMS calcd for $C_{36}H_{31}N_4O_4$ (M+H) 583.2340, found 583.2334.

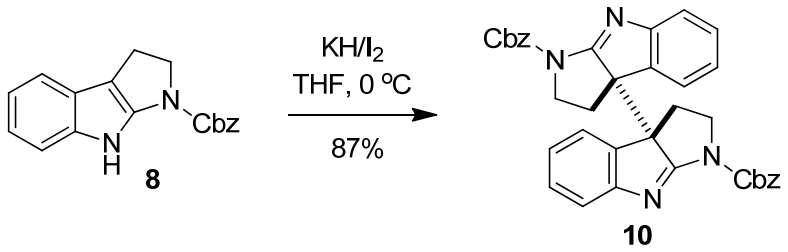


Compound 12. To a solution of compound **9** (29 mg, 0.05 mmol) in dry THF (0.5 mL) was added catecholborane (1.0 M solution in THF, 0.2 mL, 0.2 mmol) at 0 ^oC under nitrogen atmosphere. After 2 hours, the reaction mixture was warmed to room temperature and stirred for another 12 h. Water (1 mL) was added to the reaction mixture. The resulting mixture was then extracted with CH_2Cl_2 (4 × 3 ml). The organic phases were combined and then washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel with CH_2Cl_2-ethyl acetate (2:1, v:v) as the eluent to give the product **12** (22 mg, 75% yield) as a white solid. Mp 208-210 ^oC. IR (KBr): ν (cm^{-1}) 3332, 1692, 1606, 1468, 1420, 1199, 892, 746, 696. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 10H), 7.10-7.04 (m, 2H), 6.75-6.61 (m, 4H), 6.55-6.43 (m, 2H), 5.50-5.03 (m, 6H), 4.59 (br, 2H), 3.80-3.63 (m, 2H), 3.04-2.97 (m, 2H), 2.31-2.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7/153.8, 150.4/150.3/150.0, 136.7/136.5, 129.1, 128.8/128.7, 128.5, 128.3/128.1, 127.9, 124.1, 118.9/118.7, 109.4/109.2, 77.9, 67.1/66.9, 62.5/62.4/61.3/61.2, 45.6/45.3, 33.2/33.1/33.0. ESI-MS (*m/z*): (M^++Na) 609; HRMS calcd for $C_{36}H_{34}N_4O_4Na$ (M+Na) 609.2472, found 609.2489.



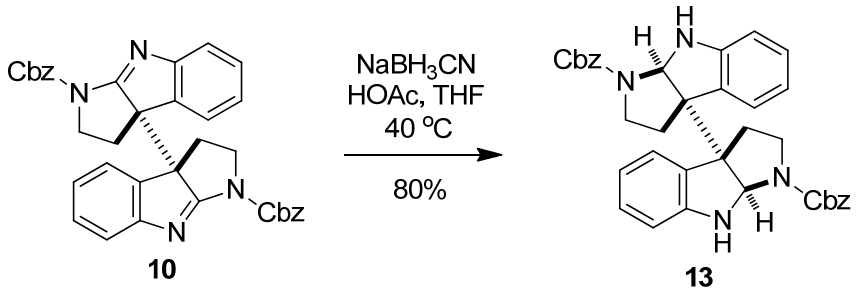
***meso*-Chimonanthine (1)**. To a solution of compound **12** (59 mg, 0.1 mmol) in toluene (1 mL) was added Red-Al (65% in toluene, 0.28 mL, 1 mmol) dropwise. The reaction mixture was heated to reflux. After 3 h, the mixture was cooled down to room temperature, diluted with CH_2Cl_2, and quenched with saturated aqueous Na-K tartrate (5 mL). The resulting mixture was vigorously stirred for 1 h at room temperature. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and then washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (10% methanol in dichloromethane saturated with ammonia) to afford *meso*-chimonanthine (**1**) (25 mg, 72%) as a white solid. Mp 190-192 ^oC (lit.[4a] mp 199-201 ^oC). IR (KBr): ν (cm^{-1}) 3374, 2965, 2926, 2854, 2809, 1604, 1485, 1247, 1158, 1024, 745. ^1H NMR (400 MHz, CD_3OD) δ 6.84 (br s, 2H), 6.41 (br, 2H), 6.34 (d, *J* = 8.0 Hz, 4H), 4.47 (br, 2H), 2.63 (br s, 2H), 2.40 (br s, 2H), 2.24 (br, 8H), 1.95 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 153.6, 133.9, 129.1, 125.4, 118.6, 109.5, 84.3, 64.9, 53.5, 37.3, 36.3. ESI-MS (*m/z*): (M^++H) 347; HRMS calcd for $C_{22}H_{27}N_4$ (M+H) 347.2230, found 347.2233.

3. Synthesis of *rac*-Chimonanthine 2.

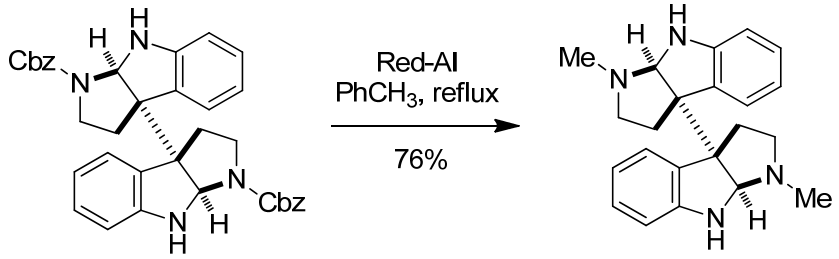


Compound 10. To the solution of **8** (58 mg, 0.2 mmol) in dry THF (10 mL) at 0 ^oC under nitrogen atmosphere was added KH (9 mg, 0.23 mmol). After 30 min, I_2 (38 mg, 0.15 mmol) was added and the mixture was stirred for 10 min. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (4:3, v:v) as the eluent to give the product **10** (51 mg, 87% yield) as a

white solid. Mp 194-196 ^{o}C (dec.). IR (KBr): ν (cm^{-1}) 1717, 1627, 1589, 1411, 1321, 1246, 1133, 772, 754. ^{1}H NMR (400 MHz, CD_3Cl) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.42-7.29 (m, 14H), 7.12 (t, *J* = 7.6 Hz, 2H), 5.20 (d, *J* = 12.0 Hz, 2H), 5.12 (d, *J* = 12.4 Hz, 2H), 4.40-4.33 (m, 2H), 4.08 (t, *J* = 10.0 Hz, 2H), 1.82 (dd, *J* = 13.6, 6.0 Hz, 2H), 1.71-1.62 (m, 2H); ^{13}C NMR (100 MHz, CD_3Cl) δ 180.7, 161.0, 150.5, 136.8, 135.2, 129.9, 128.6, 128.3, 128.2, 124.5, 123.0, 119.9, 68.3, 64.4, 54.8, 25.3. MALDI-MS (*m/z*): (M^{+}+K) 621; HRMS calcd for $C_{36}H_{31}N_4O_4$ (M+H) 583.2340, found 583.2351.



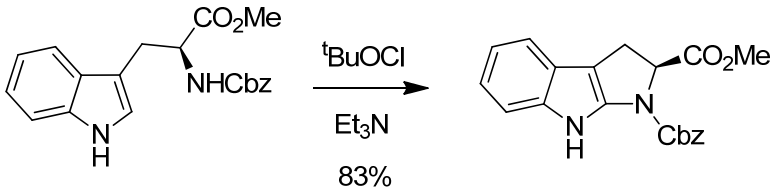
Compound 13. To the solution of compound **10** (15 mg, 0.025 mmol) in dry THF (0.6 mL) at room temperature under nitrogen atmosphere was added HOAc (3 μL, 0.05 mmol). After 1 h, $NaBH_3CN$ (9 mg, 0.15 mmol) was added and then the mixture was stirred at 40 ^{o}C for 18 hours, the reaction was quenched with saturated aqueous NH_4Cl (1 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The organic phases were combined and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (2:1, v:v) as the eluent to give the product **13** (12 mg, 80% yield) as a white solid. Mp 114-116 ^{o}C. IR (KBr): ν (cm^{-1}) 3337, 3034, 2956, 1686, 1425, 1356, 1202, 889, 731, 699. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.38-7.24 (m, 10H), 7.20-7.09 (m, 4H), 6.80-6.54 (m, 4H), 5.22-4.87 (m, 6H), 4.50 (br s, 2H), 3.70-3.56 (m, 2H), 2.92-2.86 (m, 2H), 2.65-2.55 (m, 2H), 2.16-2.00 (m, 2H); ^{13}C NMR (100 MHz, CD_3Cl) (mixture of rotamers) δ 154.6/153.7, 150.5/150.2/150.1, 136.6/136.4, 129.3/129.2, 128.7, 128.5/128.4, 128.2/128.1, 127.9, 125.4/125.2/125.1, 119.2/118.9/118.8/118.6, 110.0/109.8, 79.3/79.1/78.4, 67.0/66.9, 61.9/60.9, 45.6/45.4, 31.6/31.5/31.4. ESI-MS (*m/z*): (M^{+}+Na) 609; HRMS calcd for $C_{36}H_{34}N_4O_4Na$ (M+Na) 609.2472, found 609.2491.



13 *rac*-chimonanthine (**2**)

***rac*-Chimonanthine (2)**. *rac*-Chimonanthine **2** was synthesized from **13** according to the procedure outlined for *meso*-chimonanthine **1**. Compound **2** was obtained in 76% yield as a white solid. Mp 150-152 ^{o}C (lit.[12a] mp 168-172 ^{o}C). IR (KBr): ν (cm^{-1}) 3408, 2932, 2790, 1605, 1486, 1466, 1353, 1247, 1154, 1024, 736. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 6.8 Hz, 2H), 6.98 (t, *J* = 6.8 Hz, 2H), 6.67 (d, *J* = 6.4 Hz, 2H), 6.54 (d, *J* = 7.2 Hz, 2H), 4.32 (br s, 4H), 2.56-2.51 (m, 6H), 2.31 (s, 6H), 2.09-2.07 (m, 2H); ^{13}C NMR (100 MHz, CD_3Cl) δ 150.7, 133.3, 128.1, 124.5, 118.7, 109.3, 85.3, 63.4, 52.7, 37.3, 35.7. ESI-MS (*m/z*): (M^{+}+H) 347; HRMS calcd for $C_{22}H_{27}N_4$ (M+H)347.2230, found 347.2229.

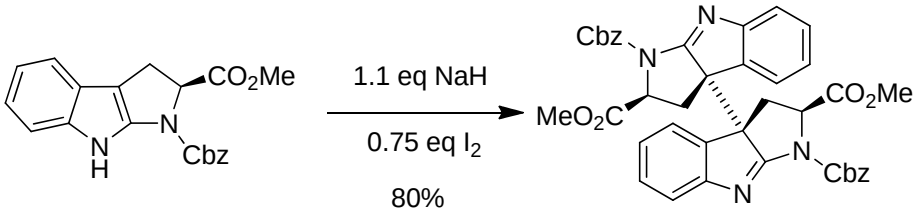
4. Synthesis of (+)-WIN 64821 (3) and (+)-WIN 64745 (4).



14 **15**

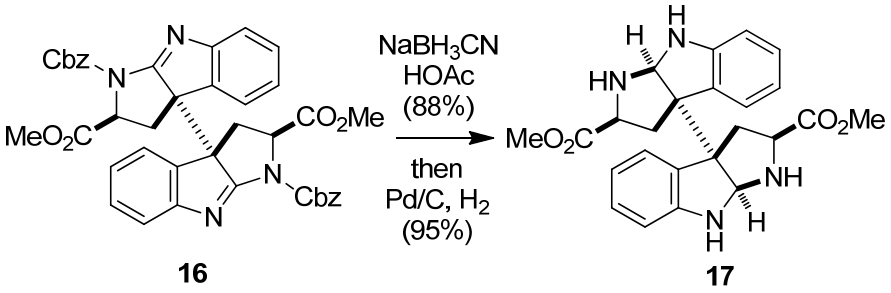
(*S*)-1-Benzyl 2-methyl 2,3-dihydropyrrolo[2,3-*b*]indole-1,2(8*H*)-dicarboxylate (15). To a solution of *N*-(benzoxycarbonyl)tryptophan methyl ester (3.987 g, 0.011 mol) and Et_3N (15.3 mL, 0.11 mol) in CH_2Cl_2 (110 mL) at 0 ^{o}C under nitrogen was slowly added *t*-BuOCl (1.4 mL, 0.012 mol). The reaction mixture was stirred at 0 ^{o}C for 3 h, and then warmed up to room temperature for 18 h. Et_2O and H_2O were added to the mixture. The two layers were separated, and the organic layer was washed with saturated aqueous Na_2CO_3 for three times, dried over Na_2SO_4, and evaporated. The residue was recrystallized from CH_2Cl_2/Et_2O to give the tricyclic compound as white powder (2.293 g). The mother liquor was concentrated and purified by column chromatography on silica gel with hexane-ethyl acetate-Et_3N (40:10:0.5,

v:v:v) as the eluent to afford the second crop of product **15** (0.895 g, 3.188 g total, 83 % yield). Mp 154-156 ^{o}C. $[\alpha]^{26}_{D}$ = -38.2 (c 1.00, $CHCl_3$). IR (KBr): ν (cm^{-1}) 3320, 2955, 1756, 1687, 1589, 1536, 1452, 1425, 1347, 1164, 737, 696. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 8.88/8.22 (2 br s, 1H), 7.44-7.18 (m, 7H), 7.09-7.01 (m, 2H), 5.38-5.15 (m, 3H), 3.78/3.62 (2s, 3H), 3.57-3.50 (m, 1H), 3.17-3.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (mixture of rotamers) δ 171.4/171.2, 152.0/151.2, 142.1/140.5, 137.4/137.3/135.7, 128.9/128.7, 128.6/128.5, 128.2/128.1, 127.8, 124.2/124.0, 120.8/120.6, 120.0/119.8, 117.2/117.0, 111.9/111.7, 98.6/97.5, 68.3/67.9, 65.6/65.5, 52.7/52.5, 29.5/28.5. ESI-MS (*m/z*): (M^{+}+Na) 373; HRMS calcd for $C_{20}H_{18}N_2O_4Na$ (M+Na) 373.1159, found 373.1144.



15 **16**

Compound 16. To the solution of compound **15** (70 mg, 0.2 mmol) in dry THF (10 mL) at -40 ^{o}C under nitrogen atmosphere was added sodium hydride (60%, 9 mg, 0.22 mmol). After 30 min, the reaction mixture was warmed to 0 ^{o}C, then I_2 (38 mg, 0.15 mmol) was added and the mixture was stirred for 15 min. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (4:3, v:v) as the eluent to give the product **16** (56 mg, 80% yield) as a white solid. Mp 182-184 ^{o}C. $[\alpha]^{24}_{D}$ = 113.6 (c 0.20, $CHCl_3$); IR (KBr): ν (cm^{-1}) 1752, 1717, 1627, 1591, 1407, 1298, 1218, 768, 689; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.45-7.31 (m, 14H), 7.15 (t, *J* = 7.6 Hz, 2H), 5.33 (d, *J* = 12.0 Hz, 2H), 5.13-5.09 (m, 4H), 3.38 (br s, 6H), 2.11 (dd, *J* = 13.2, 6.4 Hz, 2H), 1.59 (dd, *J* = 13.6, 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 170.3, 160.7, 149.9, 136.3, 134.7, 130.3, 128.5, 128.4, 124.2, 123.8, 120.7, 68.8, 66.5, 64.0, 52.3, 29.1; ESI-MS (*m/z*): (M^{+}+H) 699; HRMS calcd for $C_{40}H_{35}N_4O_8$ (M+H) 699.2449, found 699.2471. The structure was further confirmed by its X-ray diffractional experiments.

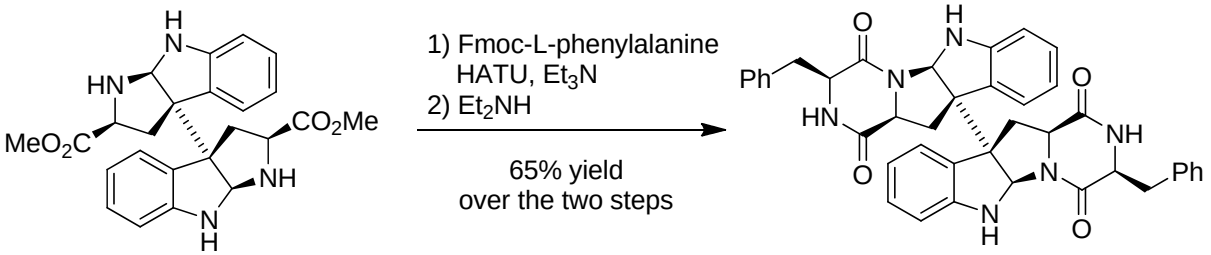


16 **17**

Compound 17. To the solution of compound **16** (35 mg, 0.05 mmol) in dry THF (1 mL) at room temperature under nitrogen atmosphere was added HOAc (6 μL, 0.1 mmol). After 1 h, $NaBH_3CN$ (18 mg, 0.3 mmol) was added and the mixture was stirred at reflux for 20 hours. The reaction was quenched with saturated aqueous NH_4Cl (1 mL) and extracted with Et_2O (3 × 2 mL). The organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (2:1, v:v) as the eluent to give the reductive product (31 mg, 88% yield) as a white solid. Mp 206-208 ^oC; $[\alpha]^{26}_D = 245.5$ (c 0.20, $CHCl_3$); IR (KBr): ν (cm^{-1}) 3324, 1726, 1695, 1604, 1455, 1412, 1356, 1279, 1223, 1106, 750, 693; ^1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.29-7.12 (m, 10H), 7.05-6.94 (m, 4H), 6.68-6.51 (m, 4H), 5.28-4.76 (m, 8H), 4.47-4.33 (m, 2H), 3.04-2.95 (m, 6H), 2.86-2.76 (m, 2H), 2.52-2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (mixture of rotamers) δ 171.3/171.0, 154.4/153.7, 151.4/151.3/150.9/150.8, 136.3/136.2/136.1, 129.9/129.8, 128.7/128.6/128.4, 128.2/128.1, 127.8/127.7, 126.9/126.8/126.7, 126.2/126.1/126.0/125.9, 118.9/118.7/118.5/118.3, 110.0, 80.2/80.0/79.4/79.2, 67.4/67.2, 60.9/59.8/59.7, 59.3/59.1/59.0, 52.1/52.0, 35.8/35.6/35.2; ESI-MS (*m/z*): (M^++H) 703; HRMS calcd for $C_{40}H_{38}N_4O_8Na$ (M+Na) 725.2582, found 725.2563.

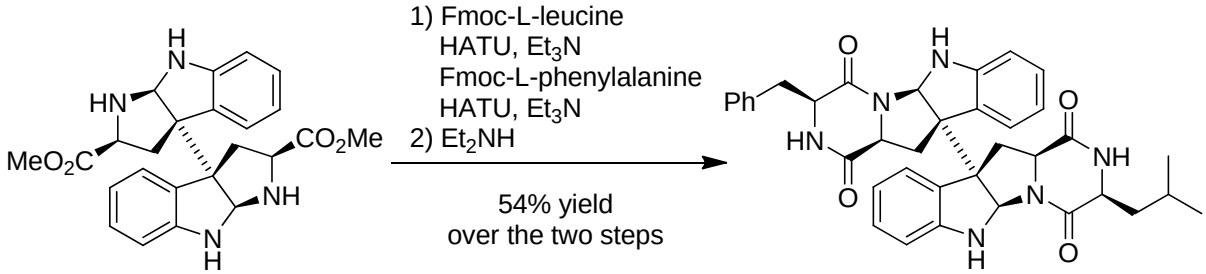
The above reduction product was dissolved in a 5:1 mixture of MeOH/THF (6 mL), 10% Pd/C (50 mg) was added and the vessel purged three times with H_2. The mixture was stirred under 1 atm of H_2 overnight and then filtered over a pad of Celite. The precipitate was washed with MeOH and the combined filtrates concentrated in vacuo. The residue was purified by flash chromatography on silica gel with CH_2Cl_2/MeOH (10:1, v:v) as the eluent to give the product **17** (103 mg, 95% yield) as a white solid. Mp 164-166 ^oC. $[\alpha]^{24}_D = 192.6$ (c 0.16, MeOH). IR (KBr): ν (cm^{-1}) 3377, 2946, 1731, 1604, 1487, 1473, 1321, 1236, 1103, 1013, 763, 743, 550. ^1H NMR (400 MHz, CD_3OD) δ 7.08 (d, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H),

6.56 (t, *J* = 7.2 Hz, 2H), 6.44 (d, *J* = 7.6 Hz, 2H), 4.54 (s, 2H), 3.61 (dd, *J* = 8.0, 2.8 Hz, 2H), 3.15 (s, 6H), 2.72 (dd, *J* = 12.8, 8.4 Hz, 2H), 2.40 (dd, *J* = 12.8, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 174.0, 151.5, 129.6, 128.7, 125.8, 117.7, 109.4, 80.5, 61.8, 59.5, 51.0, 38.0.



17 **(+)-WIN 64821**

(+)-WIN 64821 (3). HATU (84 mg, 0.22 mmol) and Et_3N (40 μL, 0.26 mmol) were added to the solution of the *N*-Fmoc-L-phenylalanine (85 mg, 0.22 mmol) in DMF (1 mL). The mixture was cooled to -10 ^{o}C. After 15 min, compound **17** (43 mg, 0.1 mmol) was added. The mixture was stirred at -10 ^{o}C for 2 h, then warmed up to room temperature and stirred overnight. The reaction was quenched by the addition of H_2O (5 mL) and extracted with CH_2Cl_2 by three times. The combined organic phases were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The residue was then directly used in the next step without further purification. Diethylamine (0.2 mL) was added to the solution of the crude condensation product in MeOH (3 mL) and the mixture was stirred for 10 h at room temperature. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel with CH_2Cl_2-acetone-hexane (6:1:0.5, v:v:v) as the eluent to afford product **3** (43 mg, 65% combined yield over the two steps) as a white solid. Mp 180-182 ^{o}C (lit.[7a] mp 193-196 ^{o}C). $[\alpha]^{26}_{D}$ = 253.8 (c 0.15, MeOH) (lit.[7a] $[\alpha]^{20}_{D}$ = 227 (c 0.15, MeOH)). IR (KBr): ν (cm^{-1}) 3376, 1670, 1406, 1314, 1182, 1095, 749, 701. ^{1}H NMR (400 MHz, CD_3CN) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.21-7.13 (m, 12H), 6.77 (t, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 5.99 (s, 2H), 5.91 (s, 2H), 4.92 (s, 2H), 4.19 (t, *J* = 5.6 Hz, 2H), 4.10 (t, *J* = 8.8 Hz, 2H), 3.14 (dd, *J* = 14.8, 4.8 Hz, 2H), 3.06-2.99 (m, 4H), 2.55 (dd, *J* = 14.0, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 168.8, 168.0, 149.1, 136.5, 130.5, 129.4, 129.2, 128.4, 126.7, 125.1, 119.3, 117.3, 109.5, 79.7, 60.1, 56.9, 56.0, 35.8, 35.2. ESI-MS (*m/z*): (M^{+}+H) 665; HRMS calcd for $C_{40}H_{36}N_6O_4Na$ (M+Na) 687.2690, found 687.2682.

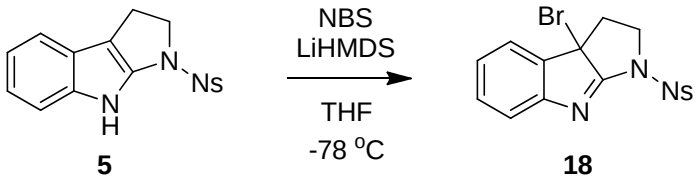


17 **(+)-WIN 64745**

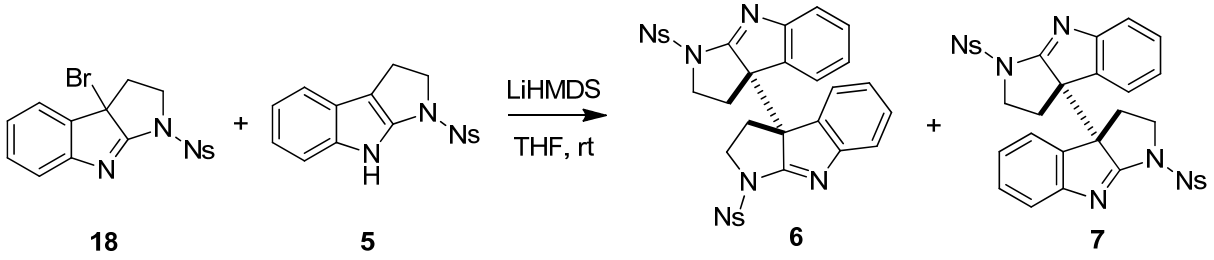
(+)-WIN 64745. HATU (42 mg, 0.11 mmol) and Et_3N (30 μL, 0.2 mmol) were added to the solution of *N*-Fmoc-L-leucine (42 mg, 0.11 mmol) in DMF (0.5 mL) and the mixture was cooled down to -10 ^oC. After 15 min, a solution of compound **17** (43 mg, 0.1 mmol) in DMF (0.5 mL) was added. The reaction mixture was stirred at -10 ^oC for 5 h and then warmed up to 0 ^oC, *N*-Fmoc-L-phenylalanine (46 mg, 0.12 mmol), Et_3N (30 μL, 0.2 mmol) and HATU (46 mg, 0.12 mmol) were added. After 2 hours, the resulting mixture was warmed up to room temperature and stirred overnight. The reaction mixture was quenched by H_2O (5 mL) and extracted with CH_2Cl_2 for three times. The combined organic phases were dried over anhydrous Na_2SO_4. After the removal of solvents under reduced pressure, the residue was then directly used in the next step without further purification. Diethylamine (0.2 mL) was added into the solution of the crude product in MeOH (3 mL) and the mixture was stirred for 10 h at room temperature. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel with hexane-ethyl acetate (1:4, v:v) as the eluent to give (+)-WIN 64745 (34 mg, 54% combined yield over the two steps) as a white solid. Mp 186-188 ^oC (lit.[7a] mp 190-192 ^oC). $[\alpha]^{26}_D$ = 265.3 (c 0.012, MeOH) (lit.[7a] $[\alpha]^{27}_D$ = 301 (c 0.012, MeOH). IR (neat): ν (cm^{-1}) 3383, 2956, 1671, 1606, 1408, 1339, 1314, 1188, 1096, 747, 701. ^1H NMR (400 MHz, CD_3CN) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.19-7.10 (m, 7H), 6.80-6.75 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 6.08 (s, 1H), 5.92 (br s, 1H), 5.84 (br s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 4.22-4.11 (m, 3H), 3.88 (q, *J* = 4.4 Hz, 1H), 3.14 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.09-2.99 (m, 3H), 2.80 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.57 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.82-1.69 (m, 2H), 1.42-1.35 (m, 1H), 0.86 (dd, *J* = 6.4, 2.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ 169.8, 169.3, 169.0, 168.0, 149.1, 149.1, 136.4, 130.5, 130.4, 129.4, 129.2, 128.4, 126.7, 125.2, 125.2, 119.2, 119.2, 117.3, 109.5, 79.7, 79.6, 60.4, 60.1, 57.1, 56.9, 56.1, 53.6, 37.7, 35.8, 35.2, 35.1, 24.2, 22.1, 20.9. ESI-MS (*m/z*): (M^++H) 631; HRMS calcd for $C_{37}H_{39}N_6O_4$ (M+H) 631.3027, found

631.3022.

5. Synthesis and Reaction of Compound 18.



3a-Bromo-1-((2-nitrophenyl)sulfonyl)-1,2,3,3a-tetrahydropyrrolo[2,3-*b*]indole (18). The solution of **5** (2.506 g, 7.3 mmol) in dry THF (73 mL) was cooled to -78 °C under nitrogen atmosphere. A LiHMDS solution (1.0 M solution in THF, 8.0 mL, 8.0 mmol) was added slowly. After 30 min, NBS (1.424 g, 8 mmol) was added and the mixture was stirred for 3 h at -78 °C. The reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 × 100 ml). The combined organic phases were dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (2:1, v:v) as the eluent to give the product (2.557 g, 83% yield) as a yellow solid. Mp 94-96 °C (dec.). IR (KBr): υ (cm^{-1}) 1630, 1590, 1552, 1447, 1383, 1259, 1179, 1067, 998, 787, 764, 744, 607. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62-8.59 (m, 1H), 7.82-7.77 (m, 2H), 7.72-7.70 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 4.0 Hz, 2H), 7.12-7.08 (m, 1H), 4.76 (td, *J* = 10.4, 4.4 Hz, 1H), 4.60 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.72 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.28 (ddd, *J* = 13.6, 10.0, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.0, 156.4, 147.4, 136.4, 136.3, 133.0, 131.4, 130.9, 129.2, 125.0, 124.9, 124.2, 120.0, 64.4, 56.9, 33.9. ESI-MS (*m/z*): (M^++H) 422. HRMS calcd for $C_{16}H_{13}O_4N_3BrS$ (M+H) 421.9805, found: 421.9800.



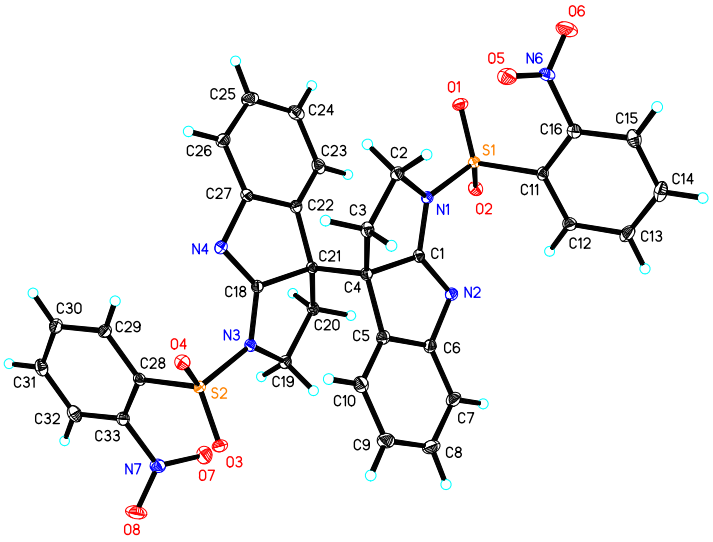
Compound **5** (34 mg, 0.1 mmol) and anhydrous LiI (26 mg, 0.2 mmol) were dissolved in dry

THF (1 mL), and the mixture was cooled to -40 ^{o}C under nitrogen atmosphere. A LiHMDS solution (1.0 M solution in THF, 0.12 mL, 0.12 mmol) was added slowly. After 30 min, the reaction mixture was warmed up to room temperature, and compound **18** was added. After stirring overnight, the reaction was quenched with water (2 mL) and extracted with CH_2Cl_2 (4 × 5 ml). The combined organic phases were dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (4:3, v:v) as the eluent to give the mixture of **6** and **7** (32 mg, 47% yield, **6**:**7** = 3:2).

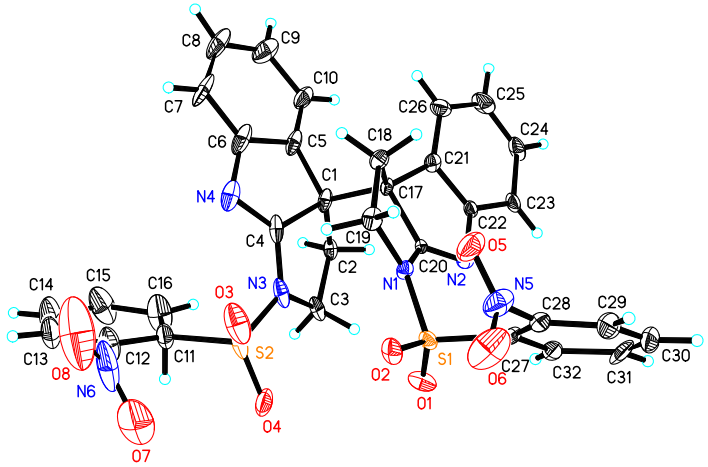
6. References for Known Compounds.

No.	reference	compound
1	Link, J. T.; Overman, L. E. *J. Am. Chem. Soc.* **1996**, *118*, 8166.	**1**
2	Araki, T.; Manabe, Y.; Fujioka, K.; Yokoe, H.; Kanematsu, M.; Yoshida, M.; Shishido, K. *Tetrahedron Lett.* **2013**, *54*, 1012.	**2**
3	Barrow, C. J.; Cai, P.; Snyder, J. K.; Sedlock, D. M.; Sun, H. H.; Cooper, R. *J. Org. Chem.* **1993**, *58*, 6016.	**3, 4**
4	Kawano, M.; Kiuchi, T.; Negishi, S.; Tanaka, H.; Hoshikawa, T.; Matsuo, J.-i.; Ishibashi, H. *Angew. Chem. Int. Ed.* **2013**, *52*, 906.	**8**
5	Okada, M.; Sato, I.; Cho, S. J.; Dubnau, D.; Sakagami, Y. *Tetrahedron* **2006**, *62*, 8907.	**15**
6	Pérez-Balado, C.; de Lera, Á. R. *Org. Lett.* **2008**, *10*, 3701.	**17**
7	Gore, S.; Baskaran, S.; König, B. *Org. Lett.* **2012**, *14*, 4568.	**19**

7. X-Ray Crystal Structure of 6, 7 and 16.



Compound 6



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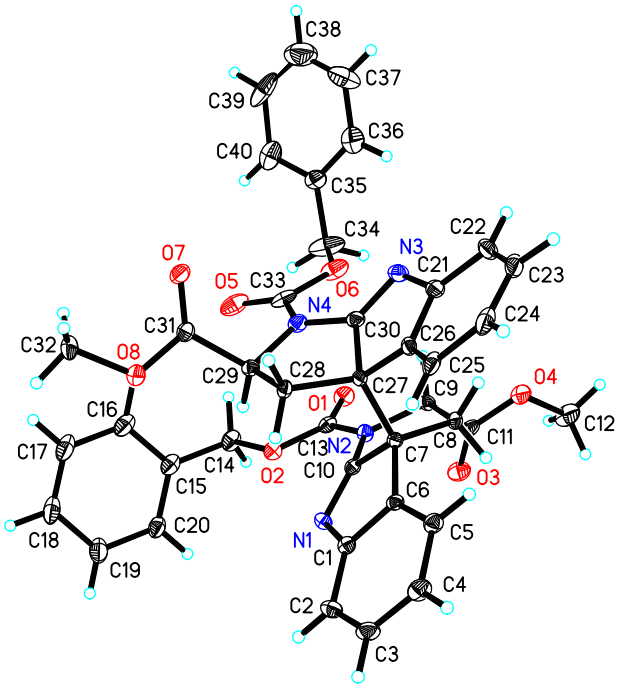
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C7
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O3
C15
C6
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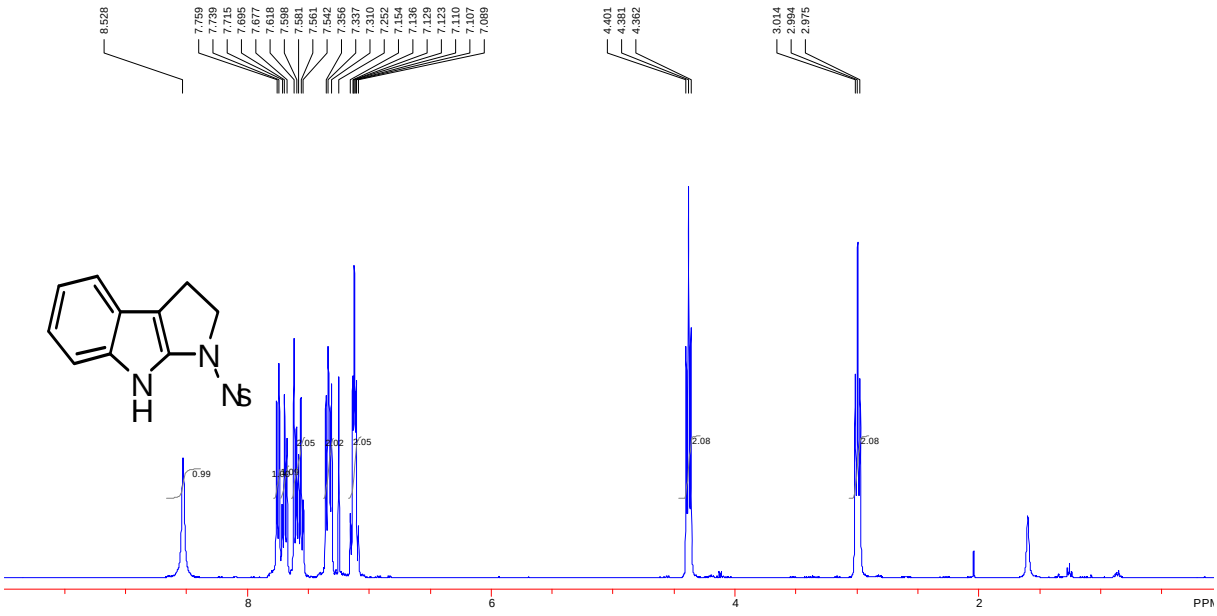
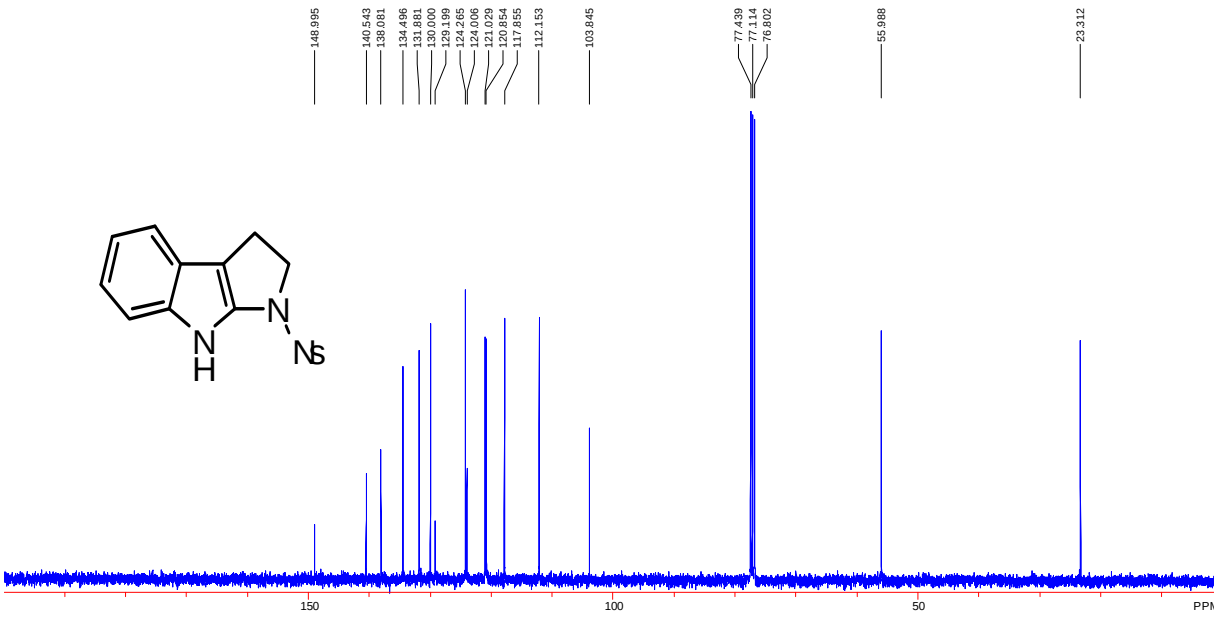
Compound 16

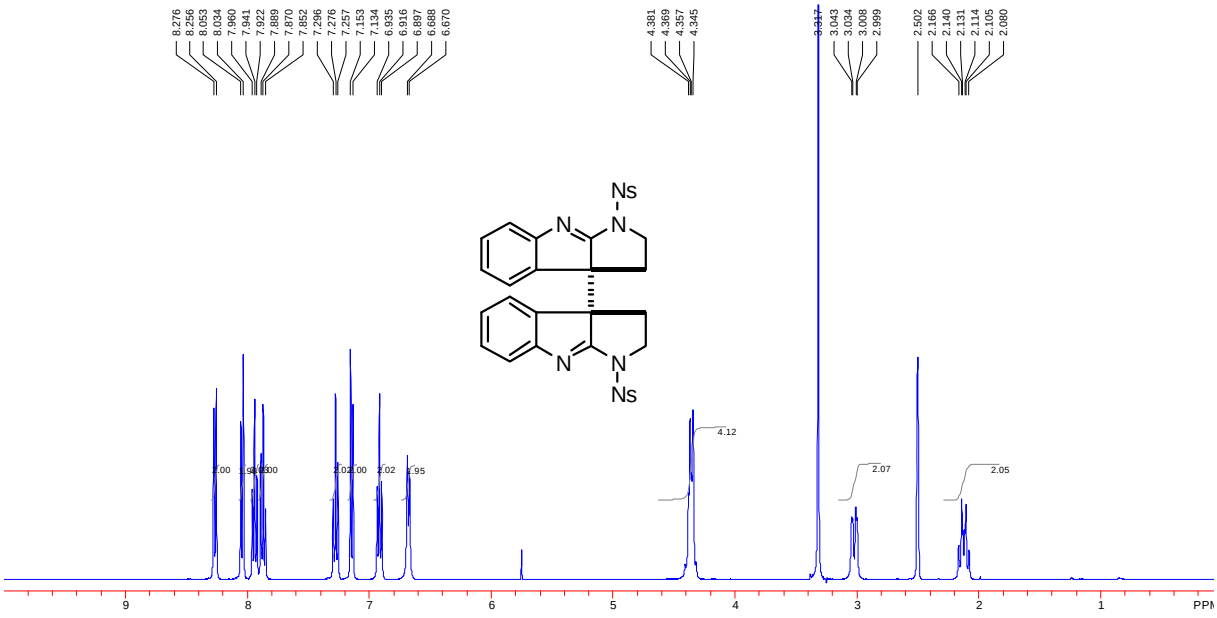
8. ^{1}H and ^{13}C NMR Spectra.

Compound 5





Compound 6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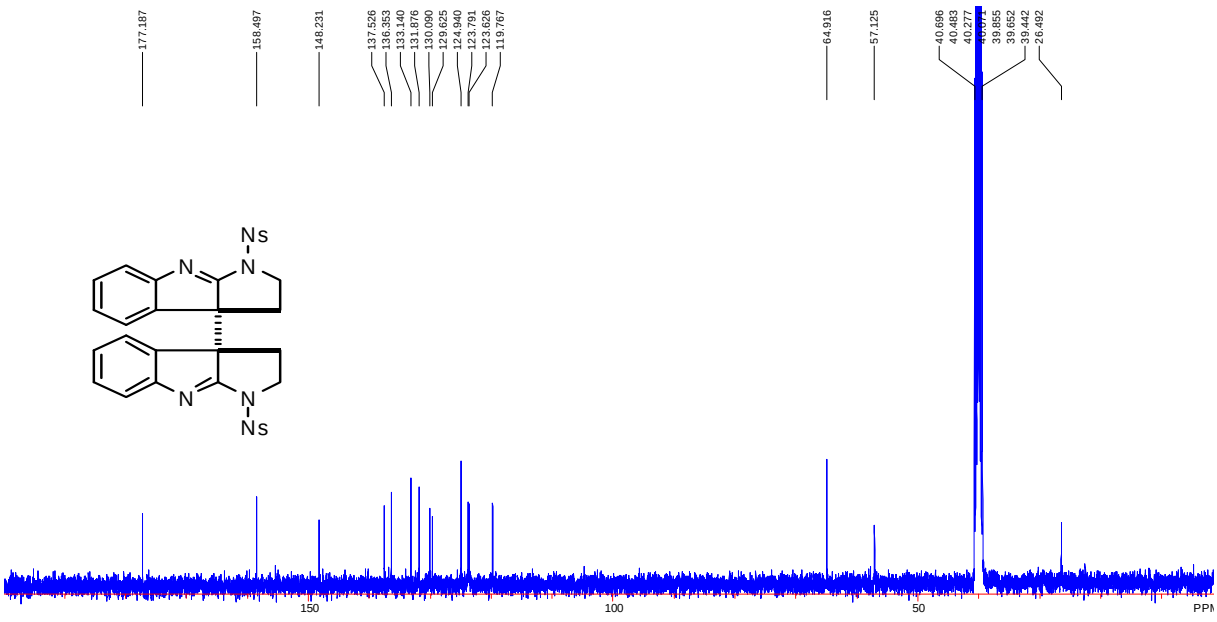
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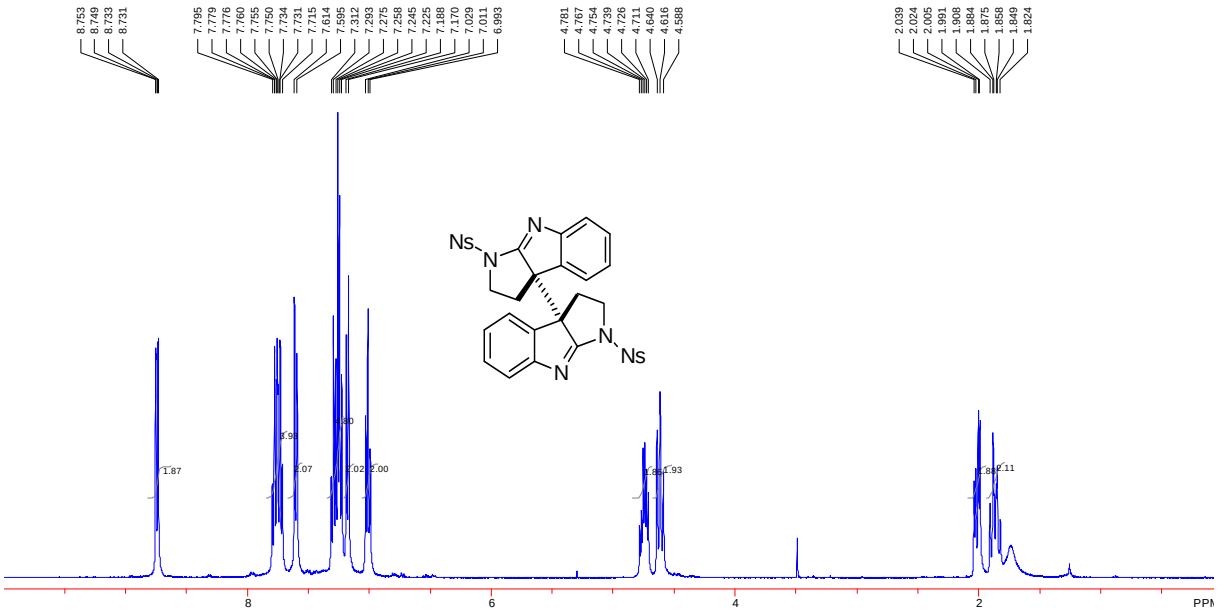
Compound 7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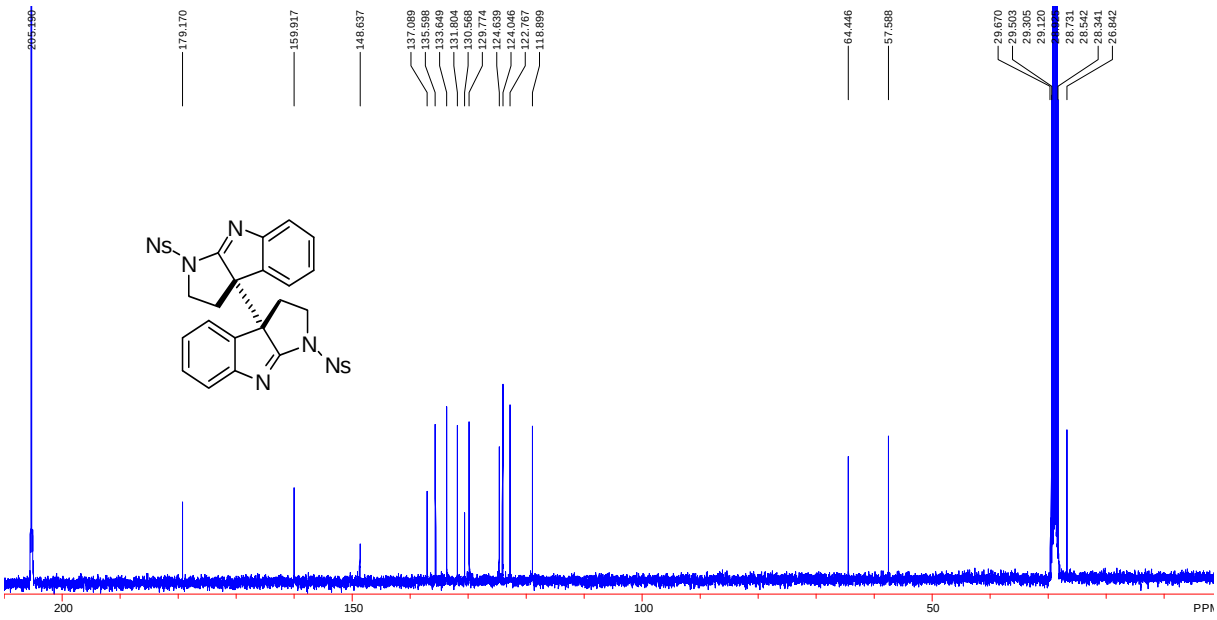
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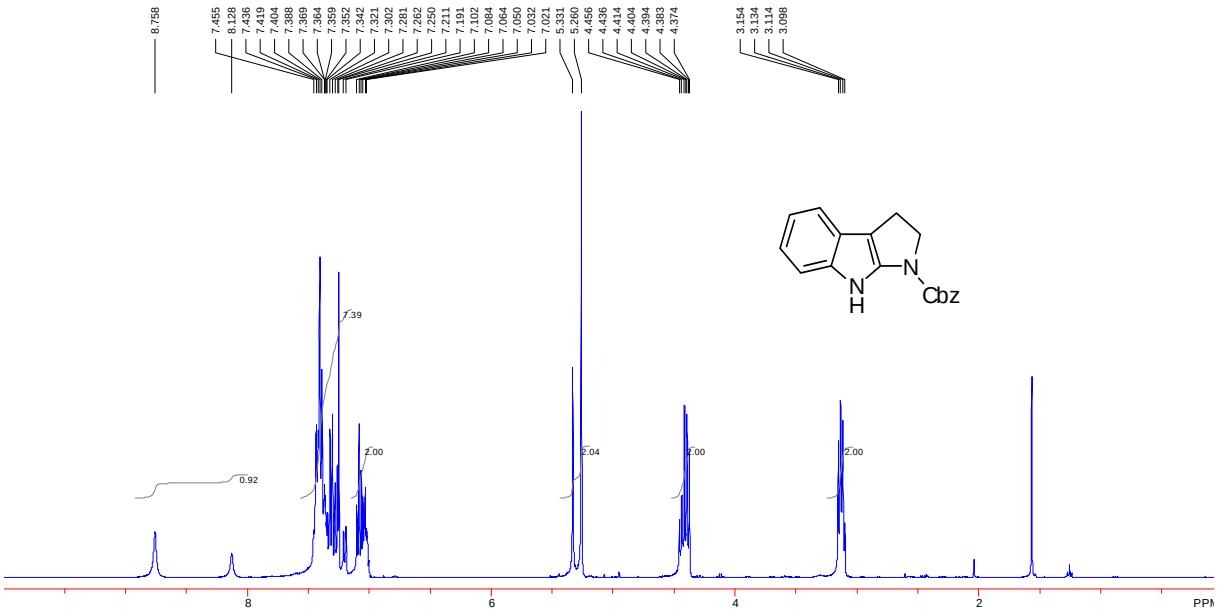
Compound 8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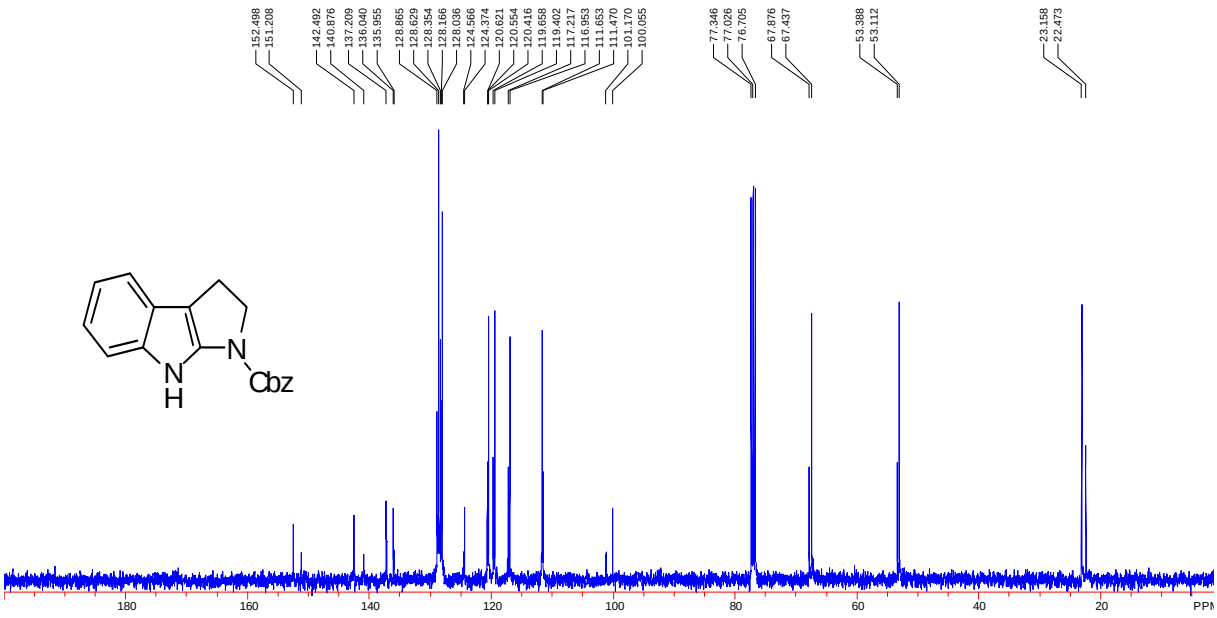
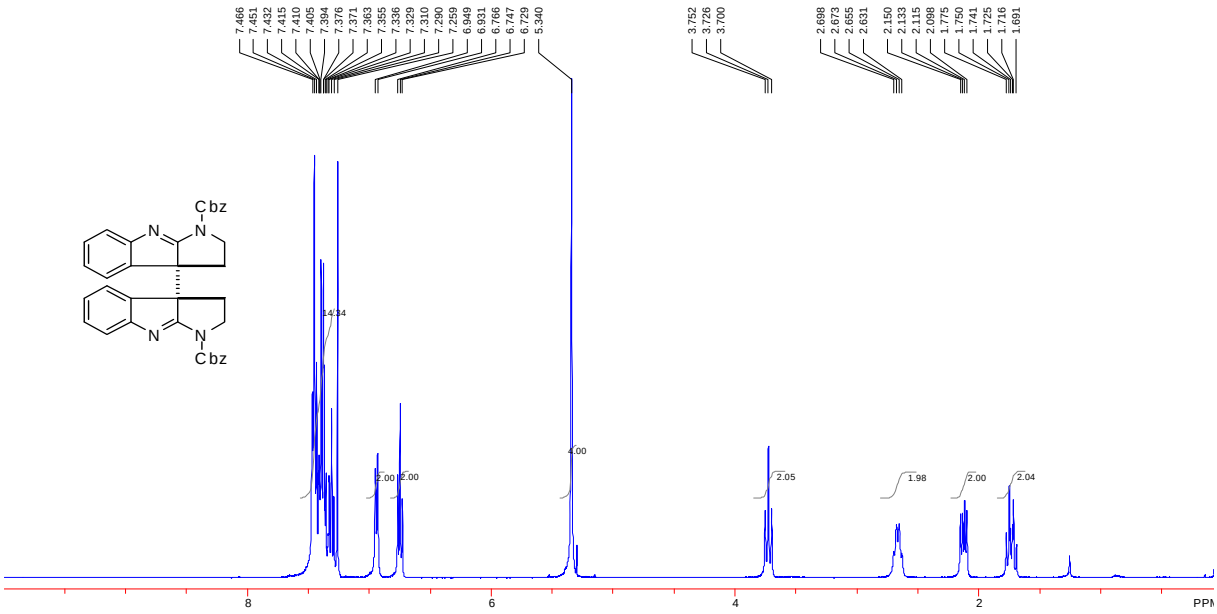
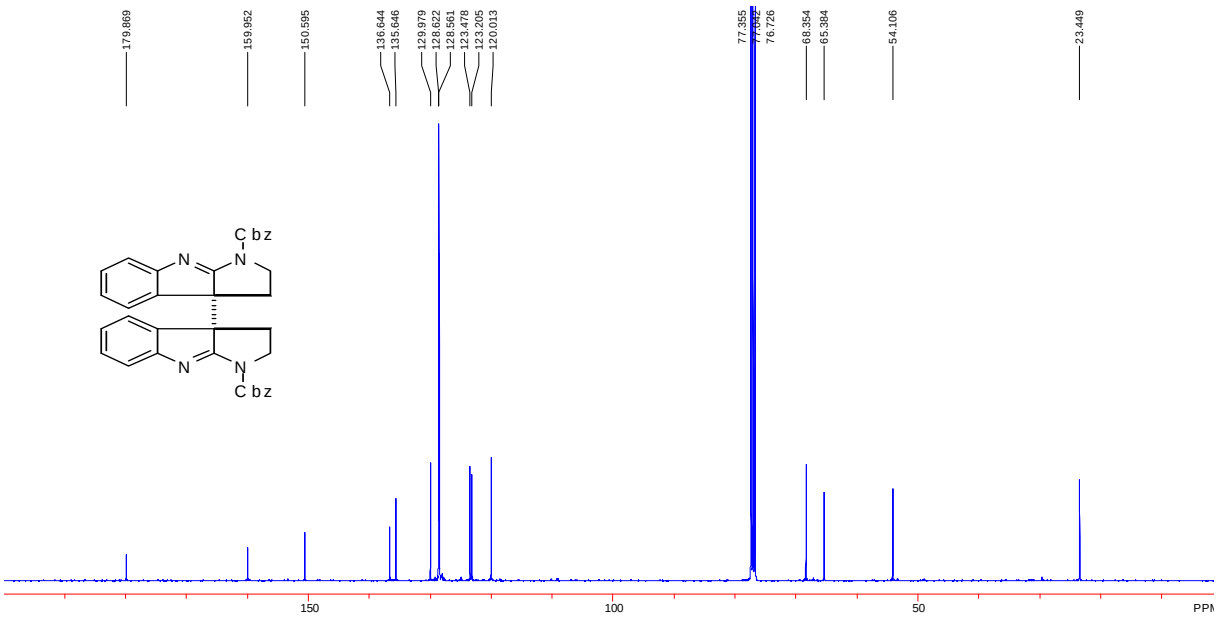
1.39
2.00
0.92
2.04
2.00
2.00
N
H
N
Cbz
8
6
4
2
PPM

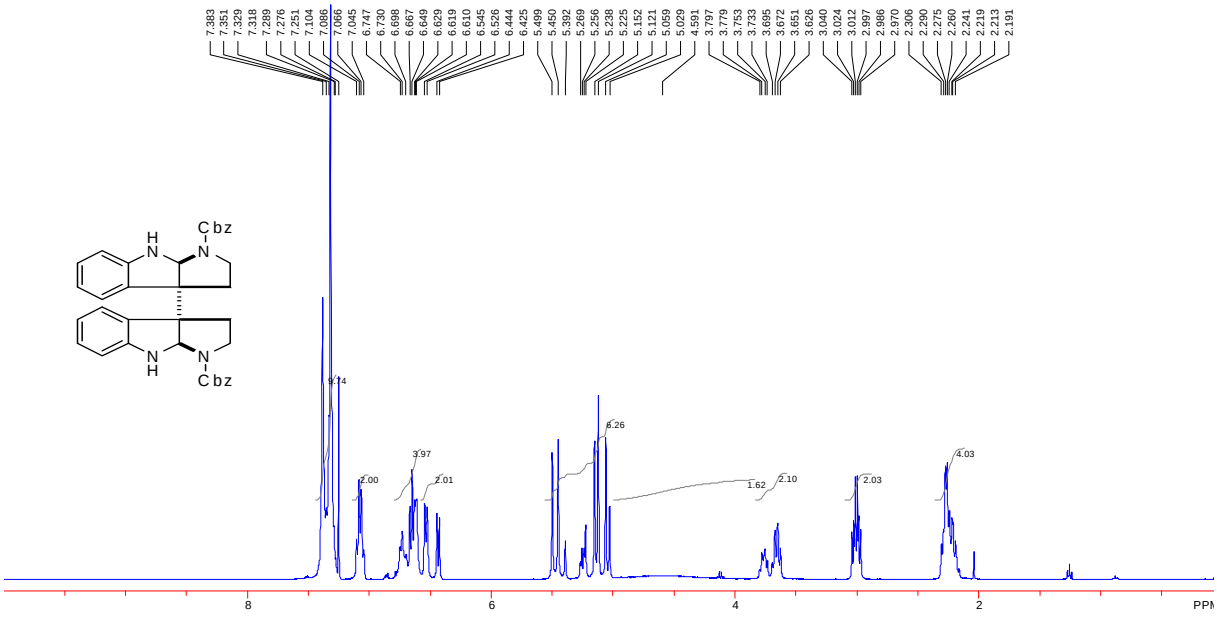

152.498
151.208
142.492
140.876
137.209
136.040
135.955
128.865
128.629
128.354
128.166
128.036
124.566
124.374
120.621
120.554
120.416
119.658
119.402
117.217
116.953
111.653
111.470
101.170
100.055
77.346
77.026
76.705
67.876
67.437
53.388
53.112
23.158
22.473
N
H
N
Cbz
180
160
140
120
100
80
60
40
20
PPM

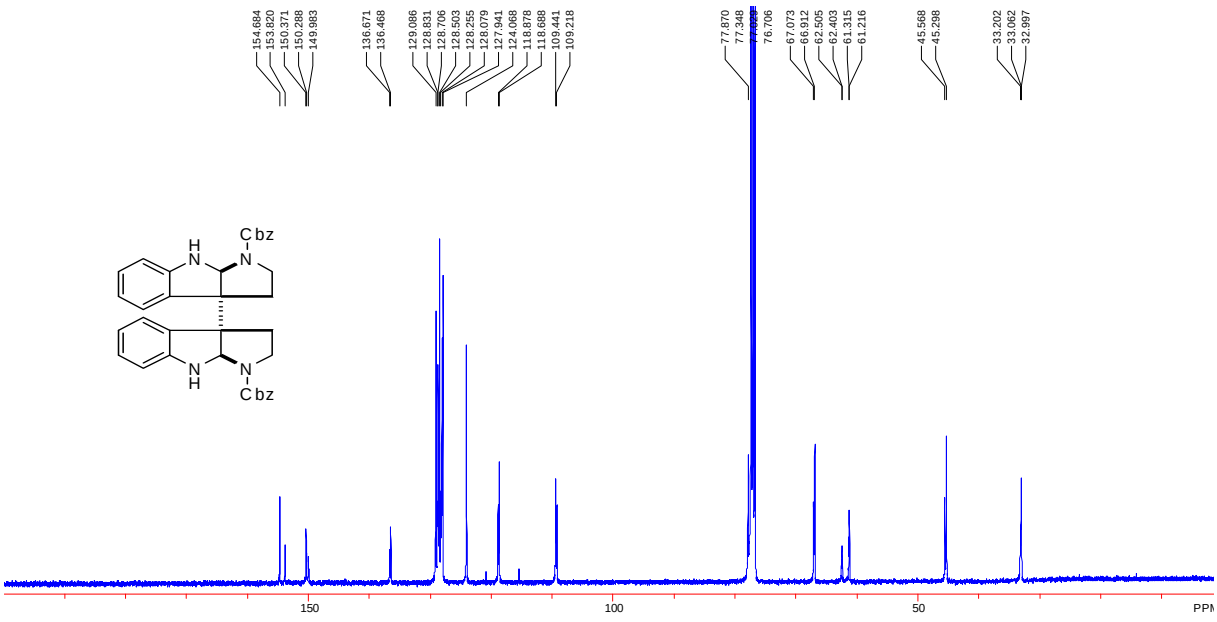
Compound 9


7.466
7.451
7.432
7.415
7.410
7.405
7.394
7.376
7.371
7.363
7.355
7.336
7.329
7.310
7.290
7.259
6.949
6.931
6.766
6.747
6.729
5.340
3.752
3.726
3.700
2.698
2.673
2.655
2.631
2.150
2.133
2.115
2.098
1.775
1.750
1.741
1.725
1.716
1.691
Cbz
N
N
N
N
Cbz
14.34
2.00
2.00
4.00
2.05
1.98
2.00
2.04
8
6
4
2
PPM


179.869
159.952
150.595
136.644
135.646
129.979
128.622
128.561
123.478
123.205
120.013
77.355
77.042
76.726
68.354
65.384
54.106
23.449
Cbz
N
N
N
N
Cbz
150
100
50
PPM

Compound 12


7.383
7.351
7.329
7.318
7.289
7.276
7.251
7.104
7.086
7.066
7.045
6.747
6.730
6.698
6.667
6.649
6.629
6.619
6.610
6.545
6.526
6.444
6.425
5.499
5.450
5.392
5.269
5.256
5.238
5.225
5.152
5.121
5.059
5.029
4.591
3.797
3.779
3.753
3.733
3.695
3.672
3.651
3.626
3.040
3.024
3.012
2.997
2.986
2.970
2.306
2.290
2.275
2.260
2.241
2.219
2.213
2.191
Cbz
H
N
N
N
H
N
Cbz
8.14
2.00
3.97
2.01
6.26
1.62
2.10
2.03
4.03
8
6
4
2
PPM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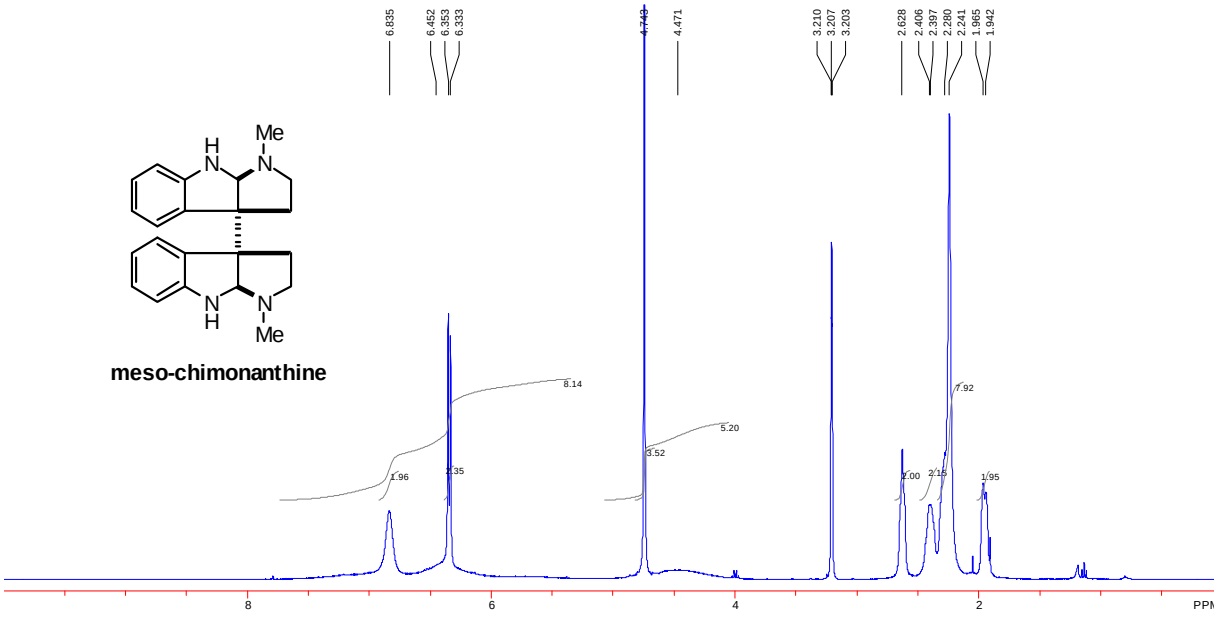
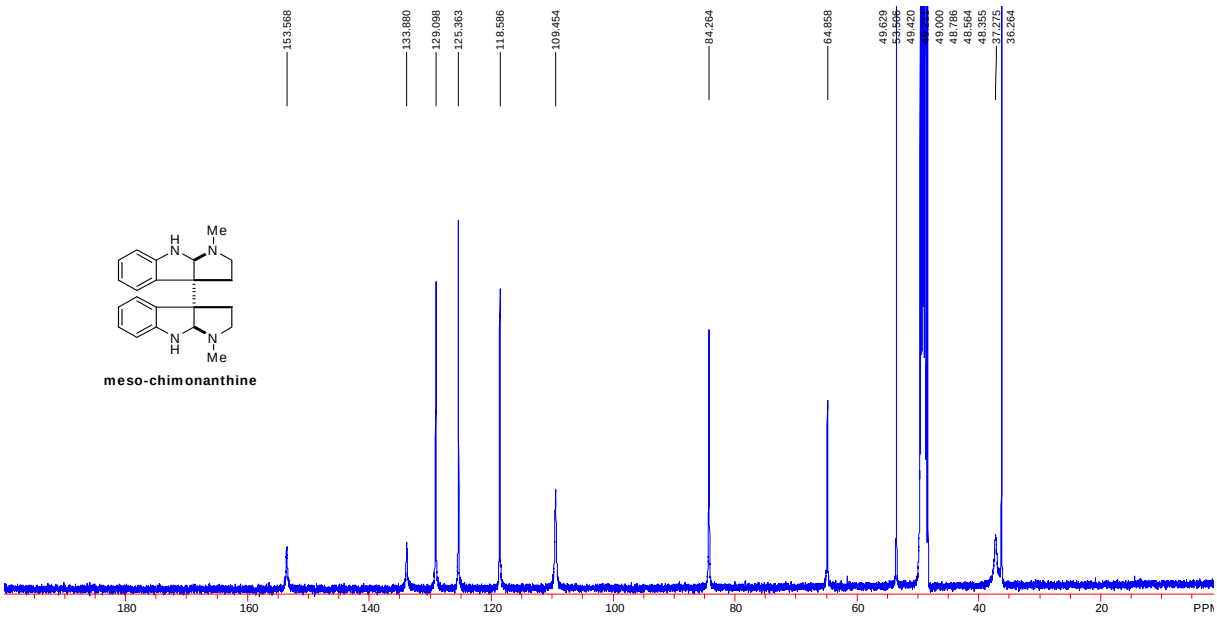
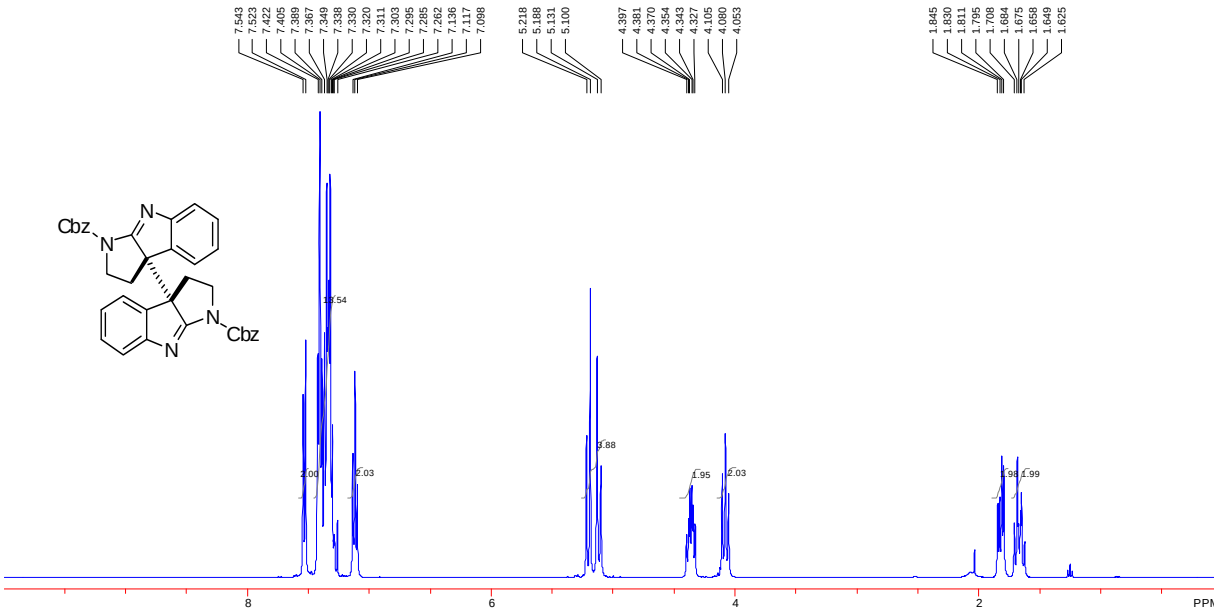
153.820
150.371
150.288
149.983
136.671
136.468
129.086
128.831
128.706
128.503
128.255
128.079
127.941
124.068
118.878
118.688
109.441
109.218
77.870
77.348
76.706
67.073
66.912
62.505
62.403
61.315
61.216
45.568
45.298
33.202
33.062
32.997
Cbz
H
N
N
N
H
N
Cbz
150
100
50
PPM

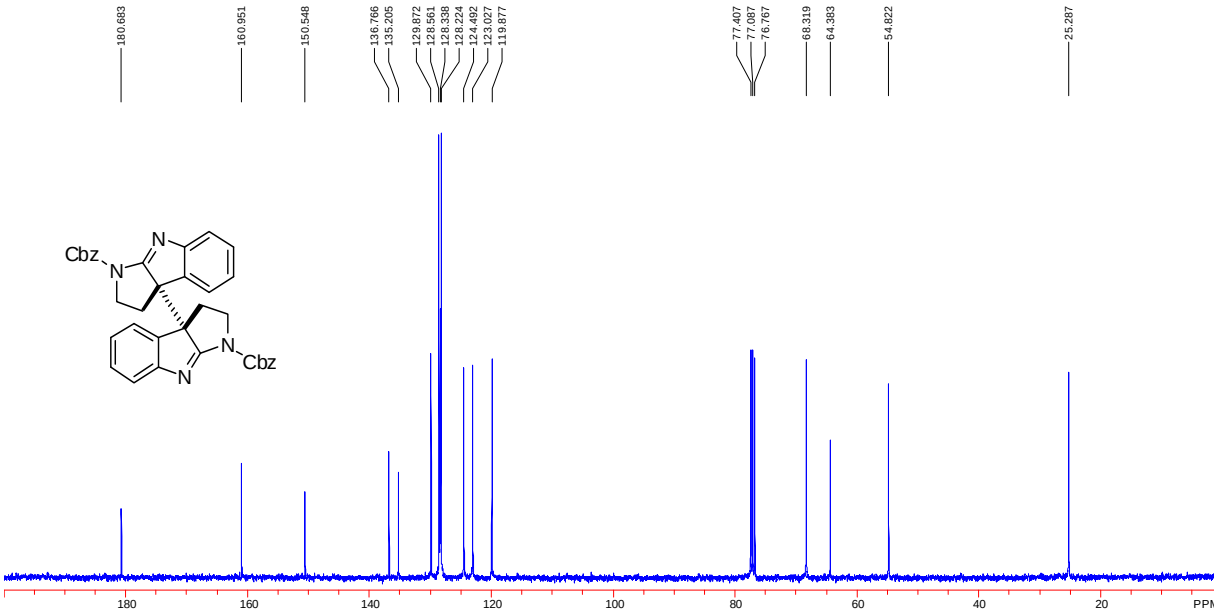
Compound 1


6.835
6.452
6.353
6.333
4.748
4.471
3.210
3.207
3.203
2.628
2.406
2.397
2.280
2.241
1.965
1.942
meso-chimonanthine
8.14
5.20
3.52
1.96
2.35
1.00
2.15
7.92
1.95
8
6
4
2
PPM

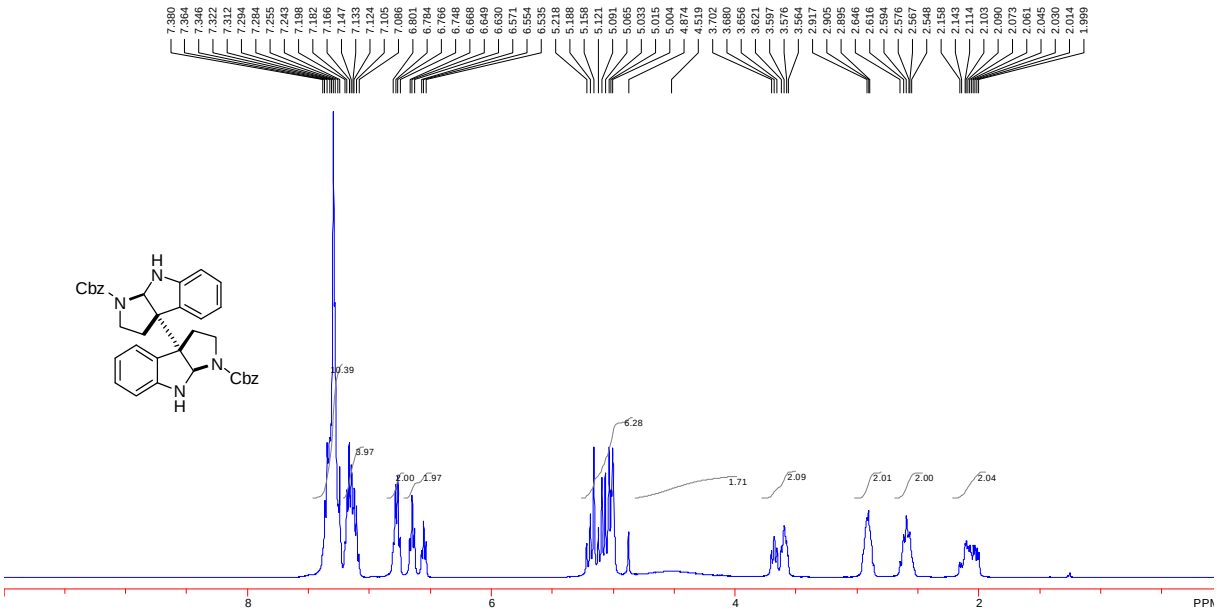

153.568
133.880
129.098
125.363
118.586
109.454
84.264
64.858
49.629
49.420
49.000
48.786
48.564
48.355
37.275
36.264
meso-chimonanthine
180
160
140
120
100
80
60
40
20
PPM

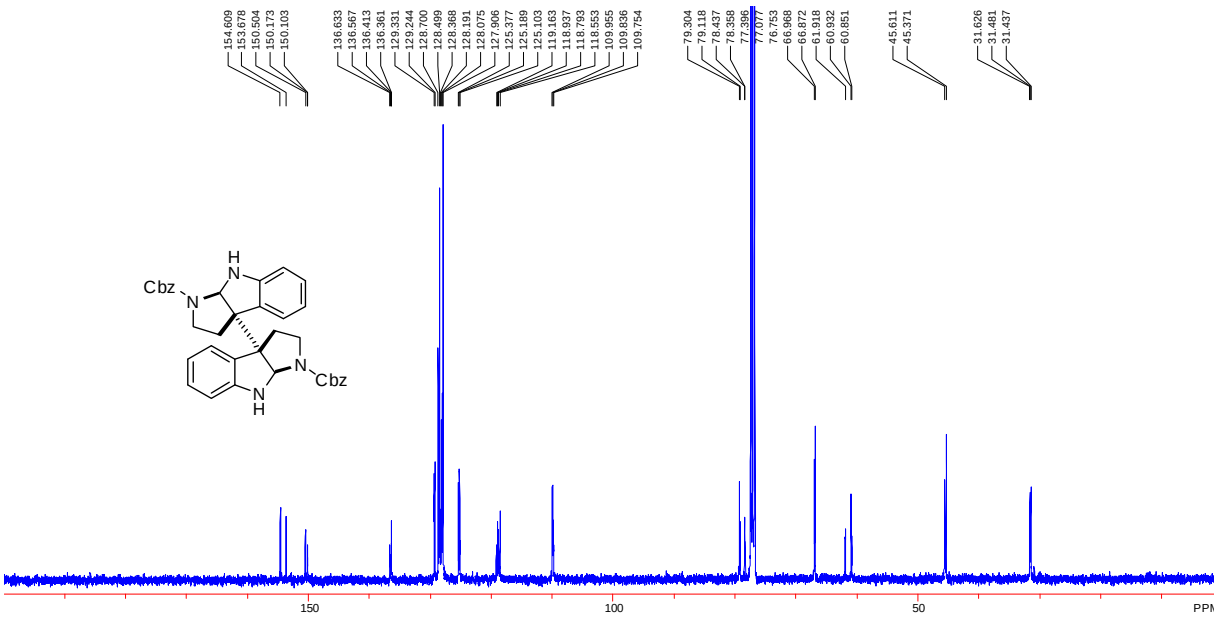
Compound 10


7.543
7.523
7.422
7.405
7.389
7.367
7.349
7.338
7.330
7.320
7.311
7.303
7.295
7.285
7.262
7.136
7.117
7.098
5.218
5.188
5.131
5.100
4.397
4.381
4.370
4.354
4.343
4.327
4.105
4.080
4.053
1.845
1.830
1.811
1.795
1.708
1.694
1.675
1.658
1.649
1.625
Cbz
N
Cbz
N
N
14.54
2.00
2.03
3.88
1.95
2.03
1.98
1.99
8
6
4
2
PPM

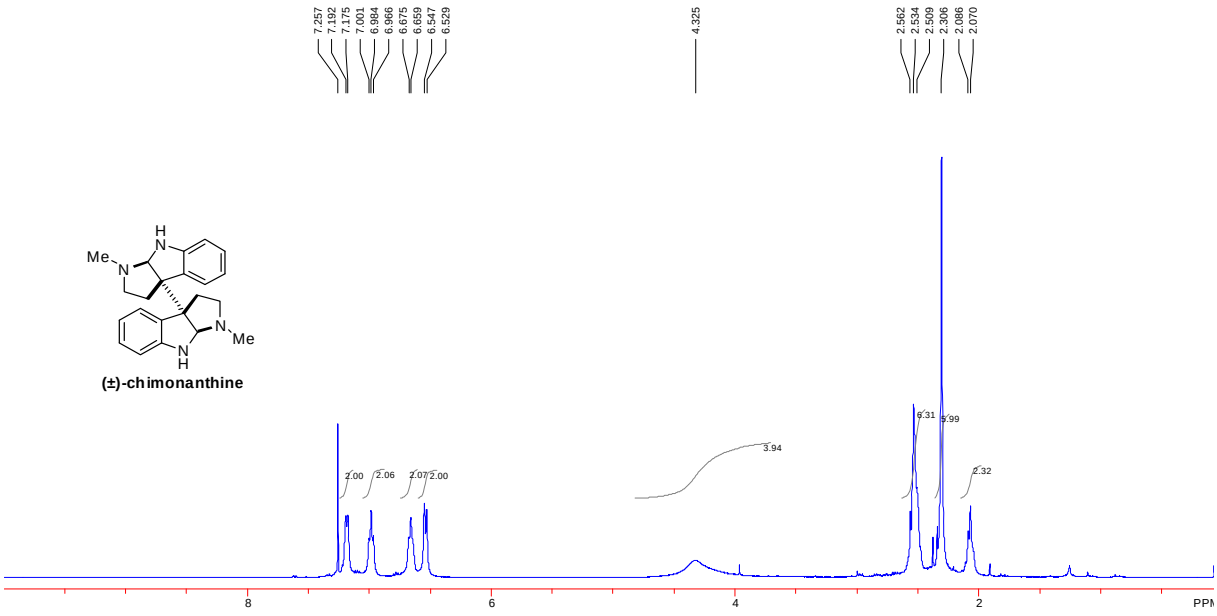

180.683
160.951
150.548
136.766
135.205
129.872
128.561
128.338
128.224
124.492
123.027
119.877
77.407
77.087
76.767
68.319
64.383
54.822
25.287
Cbz
N
N
Cbz
N
180
160
140
120
100
80
60
40
20
PPM

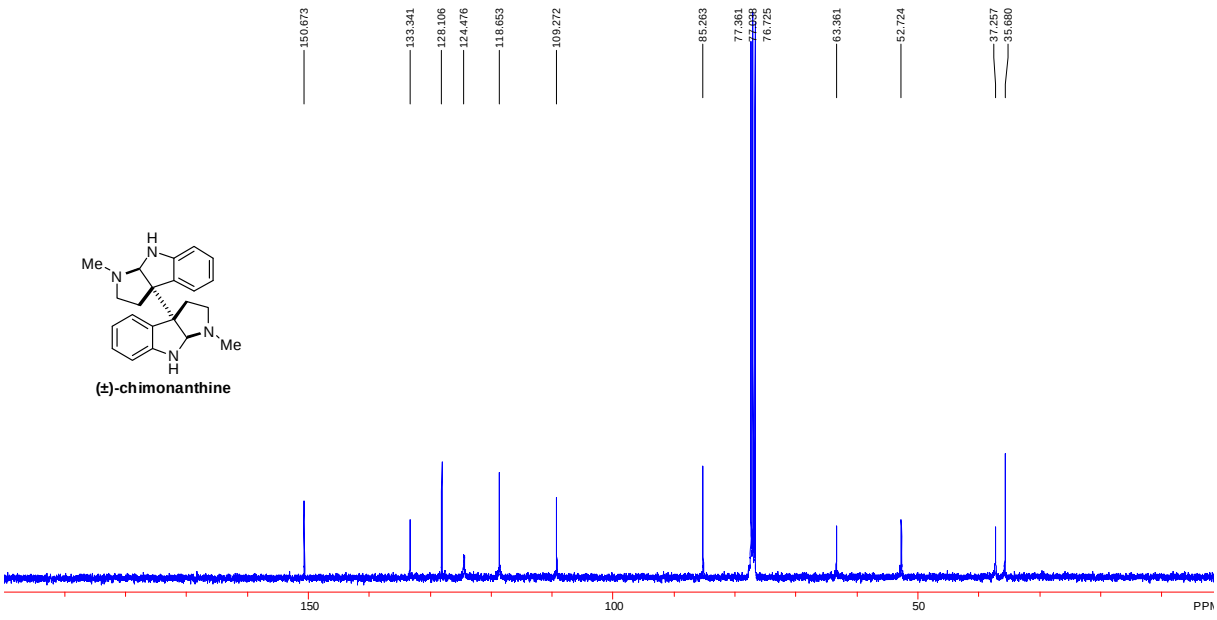
Compound 13


7.380
7.364
7.346
7.322
7.312
7.294
7.284
7.255
7.243
7.198
7.182
7.166
7.147
7.133
7.124
7.105
7.086
6.801
6.784
6.766
6.748
6.668
6.649
6.630
6.571
6.554
6.535
5.218
5.188
5.158
5.121
5.091
5.065
5.033
5.015
5.004
4.874
4.519
3.702
3.680
3.656
3.621
3.597
3.576
3.564
2.917
2.905
2.895
2.646
2.616
2.594
2.576
2.567
2.548
2.158
2.143
2.114
2.103
2.090
2.073
2.061
2.045
2.030
2.014
1.999
Cbz
N
H
N
Cbz
N
H
10.39
5.97
2.00
1.97
6.28
1.71
2.09
2.01
2.00
2.04
8
6
4
2
PPM

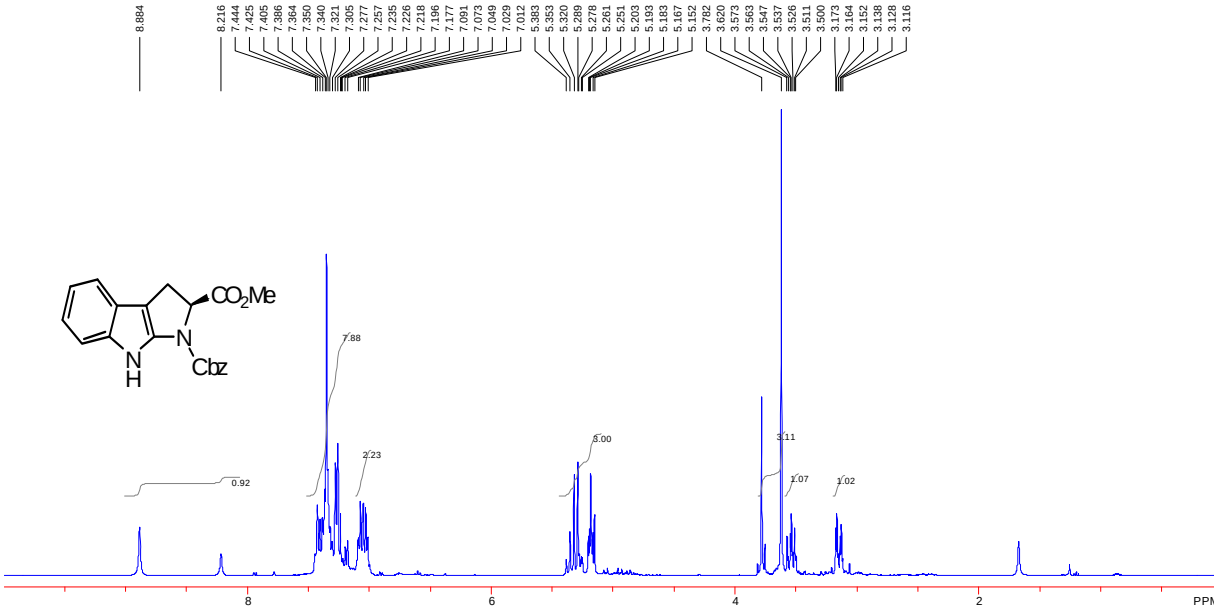

154.609
153.678
150.504
150.173
150.103
136.633
136.567
136.413
136.361
129.331
129.244
128.700
128.499
128.368
128.191
128.075
127.906
125.377
125.189
125.103
119.163
118.937
118.793
118.553
109.955
109.836
109.754
79.304
79.118
78.437
78.358
77.396
77.077
76.753
66.968
66.872
61.918
60.932
60.851
45.611
45.371
31.626
31.461
31.437
Cbz
N
H
N
Cbz
N
H
150
100
50
PPM

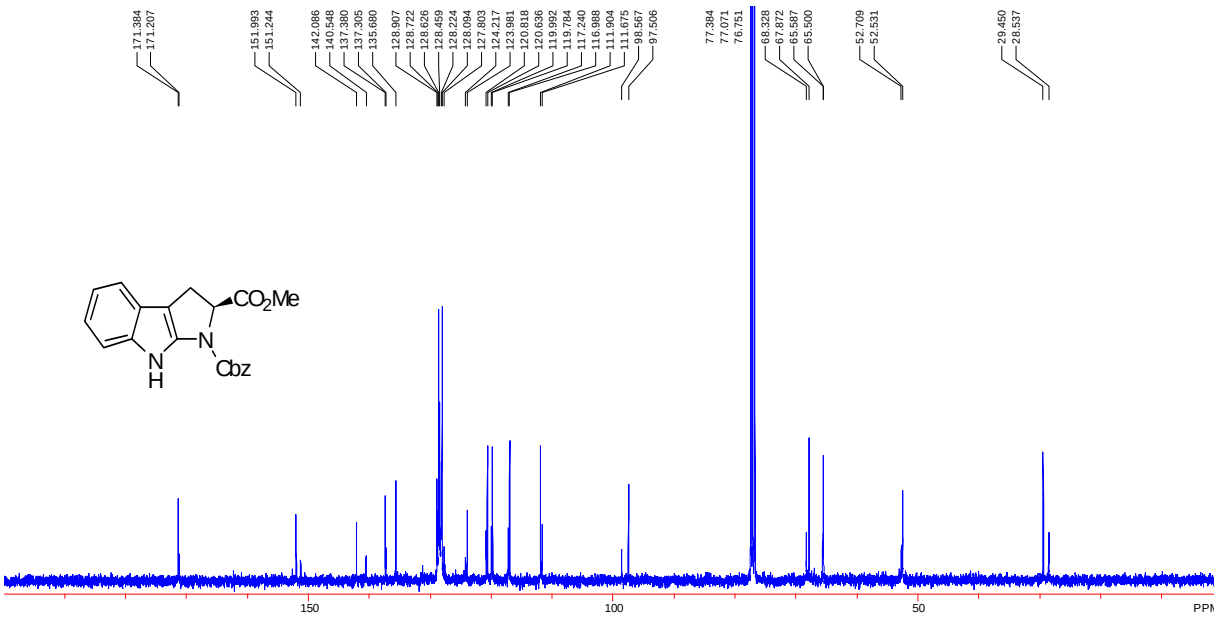
Compound 2


7.257
7.192
7.175
7.001
6.984
6.966
6.675
6.659
6.547
6.529
4.325
2.562
2.534
2.509
2.306
2.086
2.070
Me
N
H
N
Me
N
H
(±)-chimonanthine
2.00
2.06
2.07
2.00
3.94
9.31
5.99
2.32
8
6
4
2
PPM

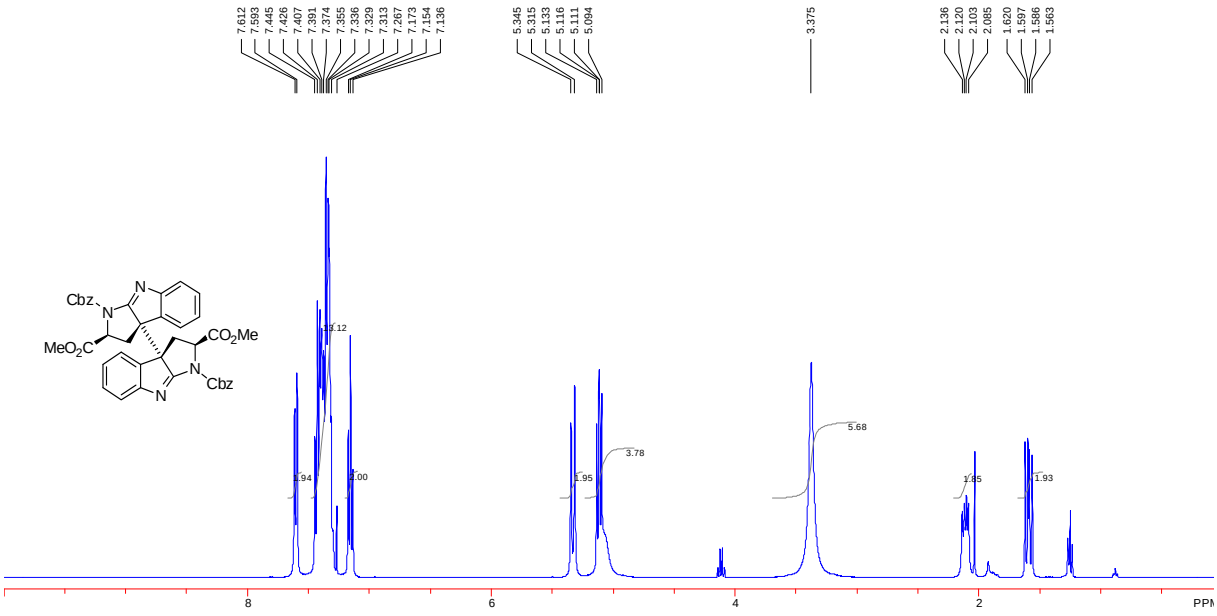

150.673
133.341
128.106
124.476
118.653
109.272
85.263
77.361
77.098
76.725
63.361
52.724
37.257
35.680
Me
N
H
N
Me
N
H
(±)-chimonanthine
150
100
50
PPM

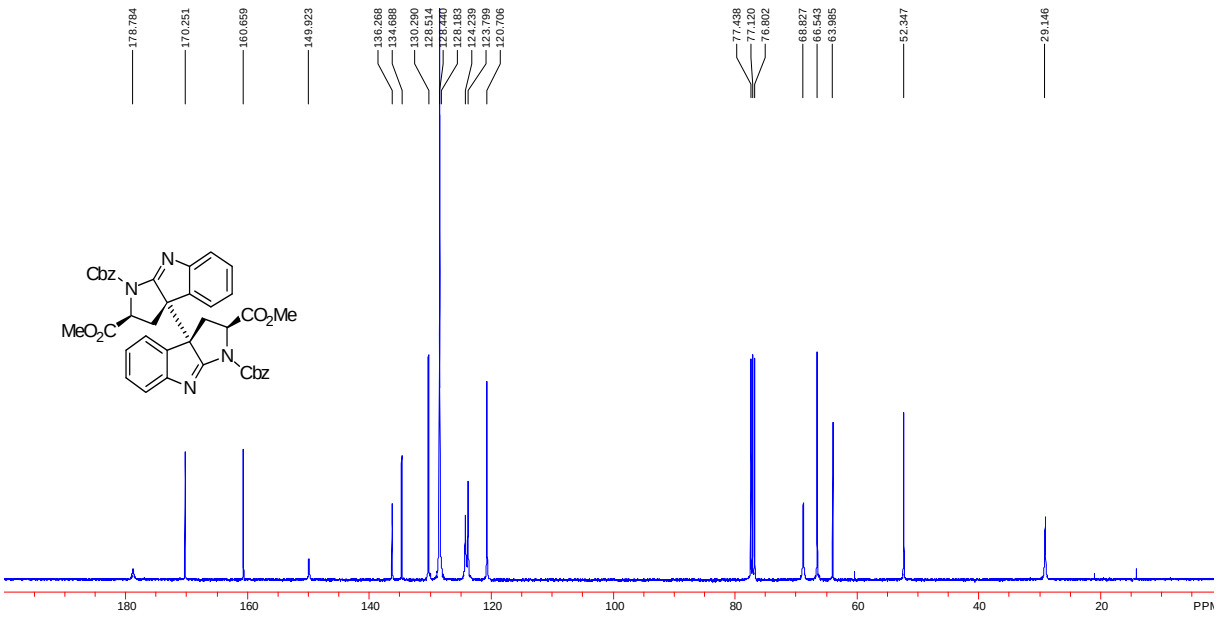
Compound 15


8.884
8.216
7.444
7.425
7.405
7.386
7.364
7.350
7.340
7.321
7.305
7.277
7.257
7.235
7.226
7.218
7.196
7.177
7.091
7.073
7.049
7.029
7.012
5.383
5.353
5.320
5.289
5.278
5.261
5.251
5.203
5.193
5.183
5.167
5.152
3.782
3.620
3.573
3.563
3.547
3.537
3.526
3.511
3.500
3.173
3.164
3.152
3.138
3.128
3.116
CO2Me
N
H
Cbz
7.88
2.23
0.92
3.00
3.11
1.07
1.02
8
6
4
2
PPM

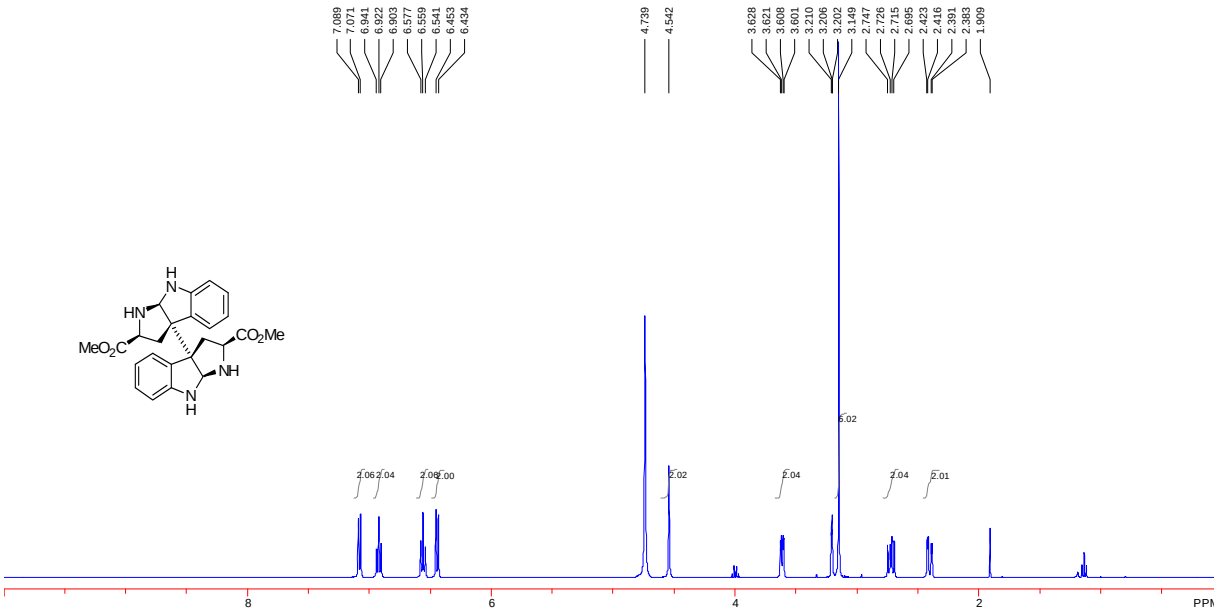

171.384
171.207
151.993
151.244
142.086
140.548
137.380
137.305
135.680
128.907
128.722
128.626
128.459
128.224
128.094
127.803
124.217
123.981
120.818
120.636
119.992
119.784
117.240
116.988
111.904
111.675
98.567
97.506
77.384
77.071
76.751
68.328
67.872
65.587
65.500
52.709
52.531
29.450
28.537
CO2Me
N
H
Cbz
150
100
50
PPM

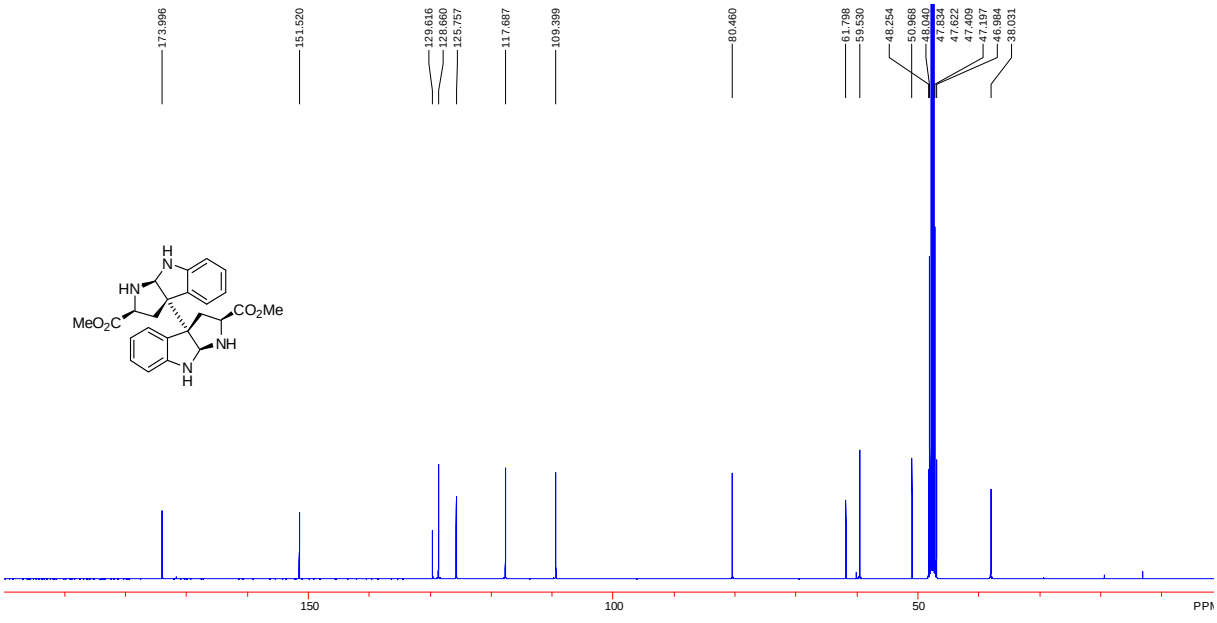
Compound 16


7.612
7.593
7.445
7.426
7.407
7.391
7.374
7.355
7.336
7.329
7.313
7.267
7.173
7.154
7.136
5.345
5.315
5.133
5.116
5.111
5.094
3.375
2.136
2.120
2.103
2.085
1.620
1.597
1.586
1.563
Cbz
N
MeO2C
CO2Me
Cbz
4.12
1.94
2.00
1.95
3.78
5.68
1.85
1.93
8
6
4
2
PPM

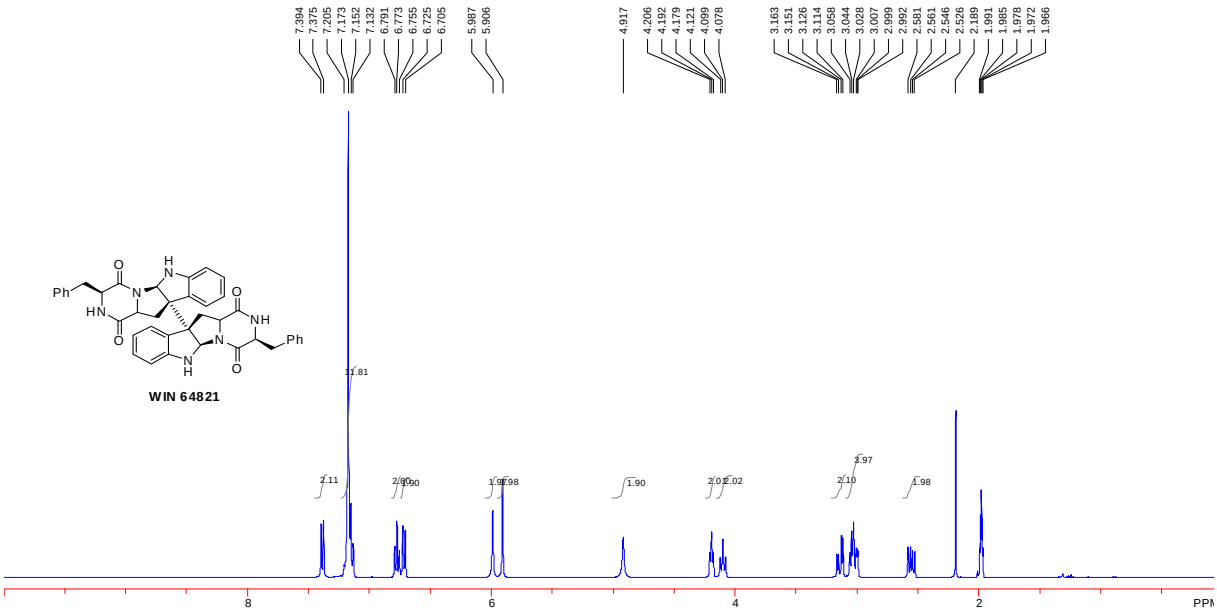

178.784
170.251
160.659
149.923
136.268
134.688
130.290
128.514
128.440
126.183
124.239
123.799
120.706
77.438
77.120
76.802
68.827
66.543
63.985
52.347
29.146
Cbz
N
MeO2C
CO2Me
Cbz
180
160
140
120
100
80
60
40
20
PPM

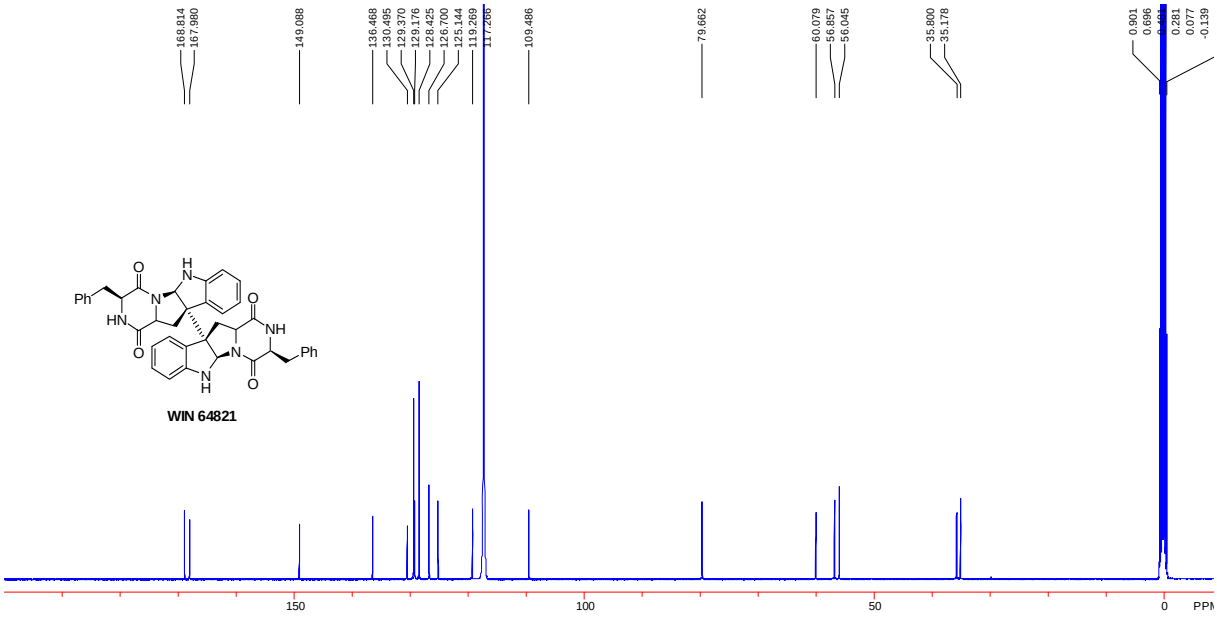
Compound 17


7.089
7.071
6.941
6.922
6.903
6.577
6.559
6.541
6.453
6.434
4.739
4.542
3.628
3.621
3.608
3.601
3.210
3.206
3.202
3.149
2.747
2.726
2.715
2.695
2.423
2.416
2.391
2.383
1.909
2.06
2.04
2.08
2.00
2.02
2.04
5.02
2.04
2.01
8
6
4
2
PPM

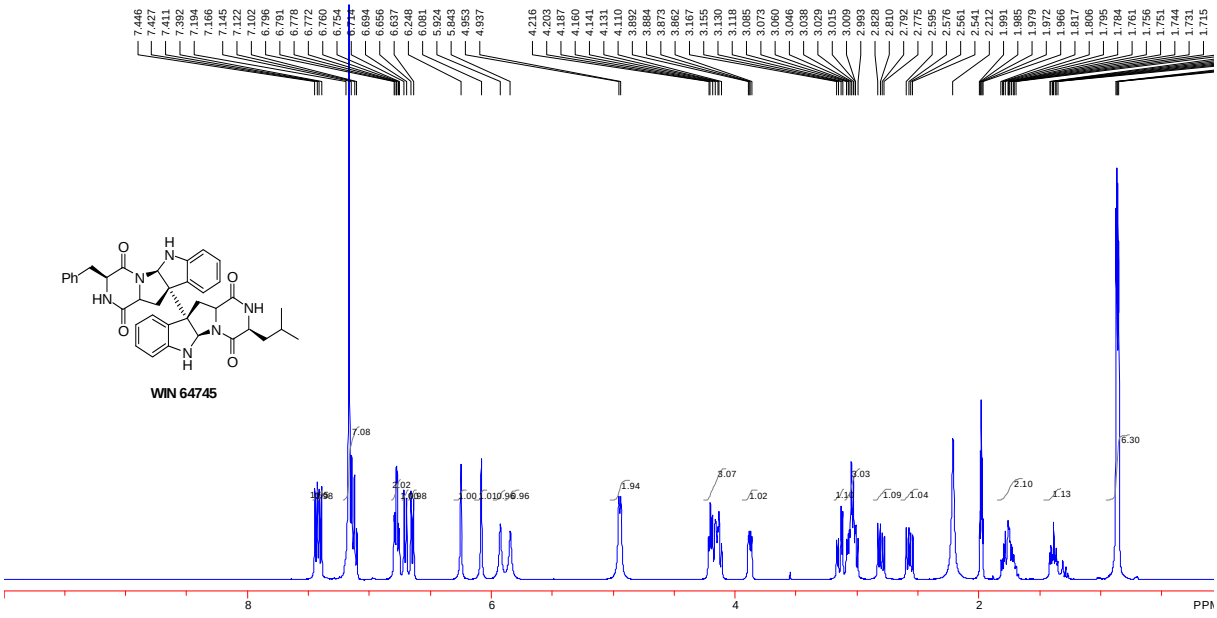

173.996
151.520
129.616
128.660
125.757
117.687
109.399
80.460
61.798
59.530
48.254
50.968
48.040
47.834
47.622
47.409
47.197
46.984
38.031
150
100
50
PPM

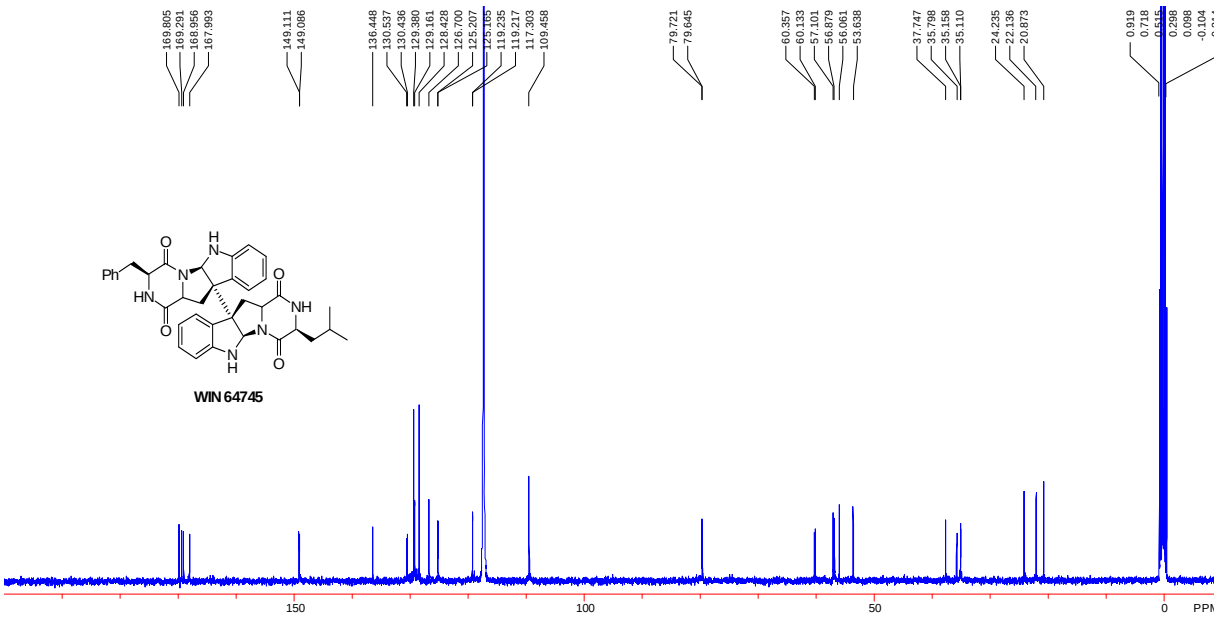
Compound 3


7.394
7.375
7.205
7.173
7.152
7.132
6.791
6.773
6.755
6.725
6.705
5.987
5.906
4.917
4.206
4.192
4.179
4.121
4.099
4.078
3.163
3.151
3.126
3.114
3.058
3.044
3.028
3.007
2.999
2.992
2.581
2.561
2.546
2.526
2.189
1.991
1.985
1.978
1.972
1.966
11.81
2.11
2.00
2.00
1.97
1.98
1.90
2.01
2.02
3.97
2.10
1.98
WIN 64821
8
6
4
2
PPM

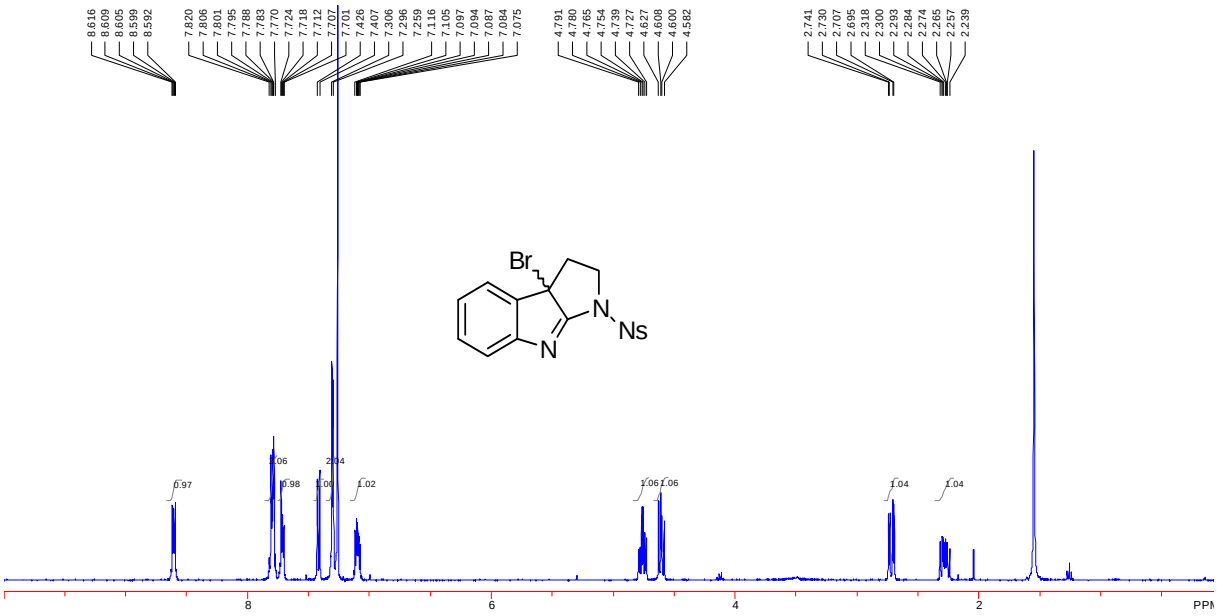

168.814
167.980
149.088
136.468
130.495
129.370
129.176
128.425
126.700
125.144
119.269
117.266
109.486
79.662
60.079
56.857
56.045
35.800
35.178
0.901
0.696
0.281
0.077
-0.139
WIN 64821
150
100
50
0
PPM

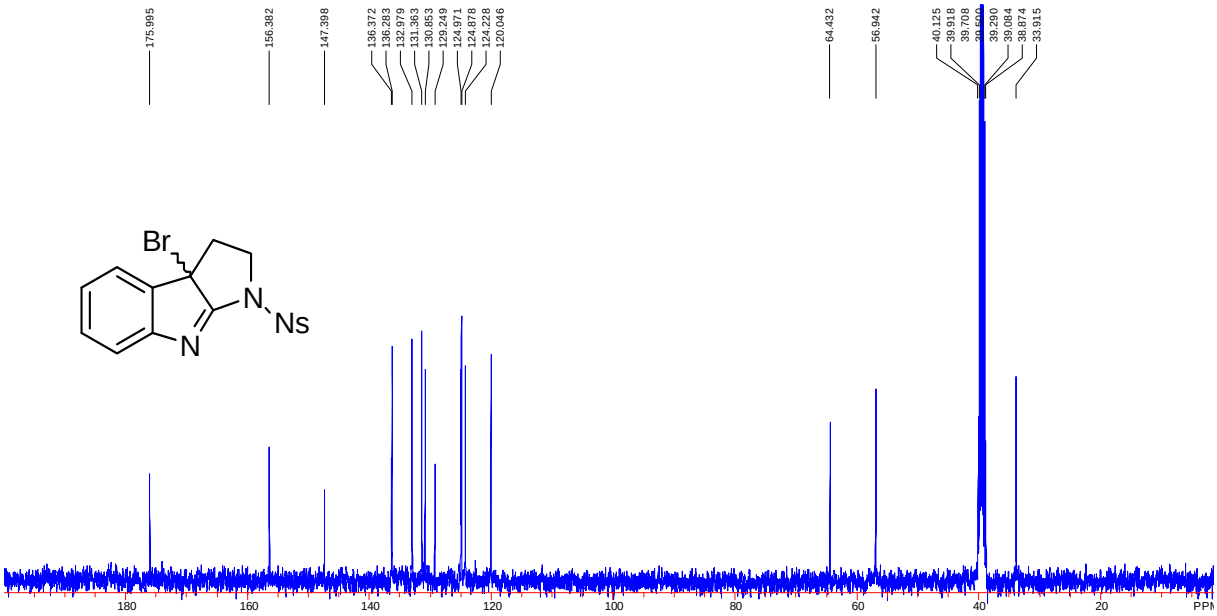
Compound 4



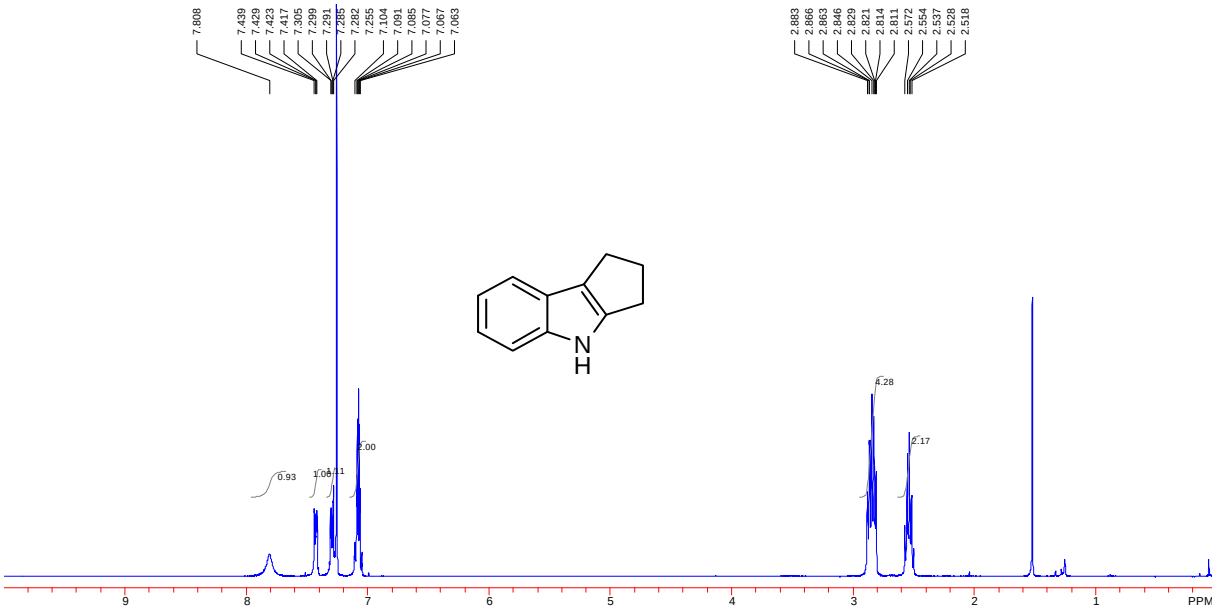


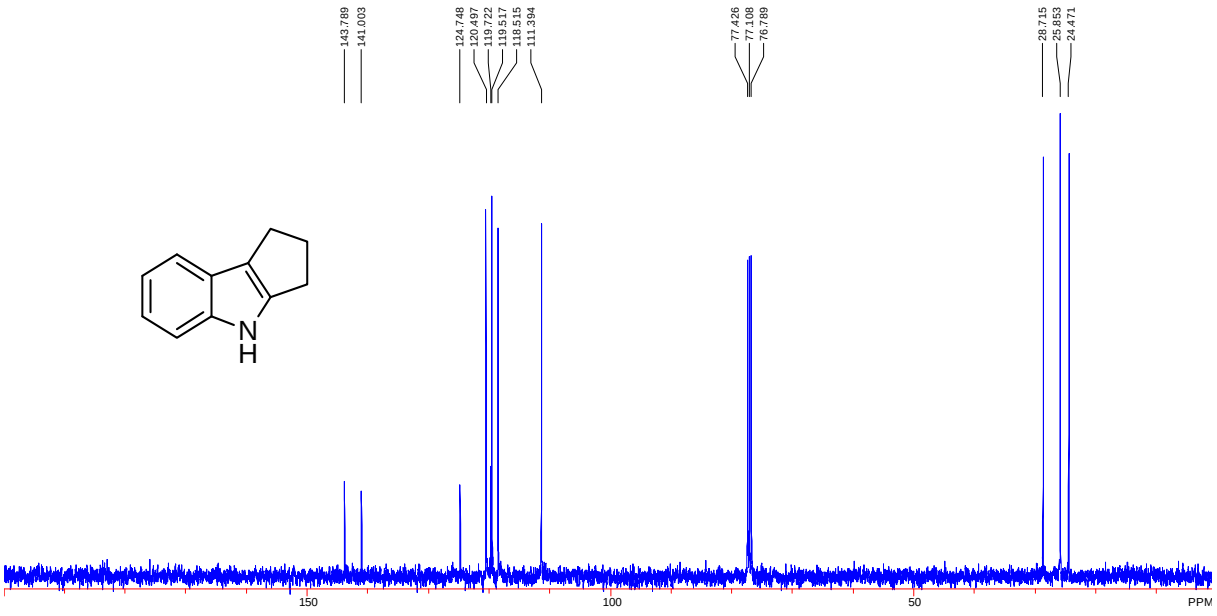
Compound 18


8.616
8.609
8.605
8.599
8.592
7.820
7.806
7.801
7.795
7.788
7.783
7.770
7.724
7.718
7.712
7.707
7.701
7.426
7.407
7.306
7.296
7.259
7.116
7.105
7.097
7.094
7.087
7.084
7.075
4.791
4.780
4.765
4.754
4.739
4.727
4.627
4.608
4.600
4.582
2.741
2.730
2.707
2.695
2.318
2.300
2.293
2.284
2.274
2.265
2.257
2.239
Br
N
Ns
N
0.97
2.06
0.98
1.00
2.04
1.02
1.06
1.06
1.04
1.04
8
6
4
2
PPM


175.995
156.382
147.398
136.372
136.283
132.979
131.363
130.853
129.249
124.971
124.878
124.228
120.046
64.432
56.942
40.125
39.918
39.708
39.290
39.084
38.874
33.915
Br
N
Ns
N
180
160
140
120
100
80
60
40
20
PPM

Compound 19


7.808
7.439
7.429
7.423
7.417
7.305
7.299
7.291
7.285
7.282
7.255
7.104
7.091
7.085
7.077
7.067
7.063
2.883
2.866
2.863
2.846
2.829
2.821
2.814
2.811
2.572
2.554
2.537
2.528
2.518
0.93
1.04
1.11
1.00
4.28
2.17
N
H
9
8
7
6
5
4
3
2
1
PPM


143.789
141.003
124.748
120.497
119.722
119.517
118.515
111.394
77.426
77.108
76.789
28.715
25.853
24.471
N
H
150
100
50
PPM