Supporting Information

Imidoyl dichlorides as new reagents for the rapid formation of 2-aminobenzimidazoles and related azoles

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General Information:
All reagents were used as purchased. THF, CH_2Cl_2 used in reactions were dried using a solvent delivery system (neutral alumina column). All ^1H and ^{13}C NMR spectra were recorded on 400 MHz or 500 MHz Varian Mercury spectrometers as noted. ^1H spectra were referenced to $CHCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm, or CD_3OD at 3.31 ppm. ^{13}C spectra were referenced to $CDCl_3$ at 77.0 ppm, DMSO-d_6 at 39.5 ppm, or CD_3OD at 49.0 ppm. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F254 glass backed plates and visualized using 254 nm UV light. Flash chromatographic purifications were performed using silica gel (40-60 μm) or using an MPLC system equipped with silica gel columns.

Dimethyl carbonimidodithioate, 4. Following literature procedures,[1] ammonia gas was bubbled into carbon disulfide **1** (16.7g, 0.22 mol) in THF (100 ml) keeping the temperature below 45 °C. After 1 hr, the reaction was stopped by allowing the temperature to decrease to rt. The excess ammonia gas was removed by streaming N_2 for 30 min or by rotary evaporation under vacuum. The precipitate was collected by filtration to afford white solid ammonium dithiocarbamate **2** (23.1 g, 96%). Methyl iodide (17.8 g, 0.125 mol) was added to a solution of **2** (5.5 g, 0.05 mol) in acetone (100 ml) at rt and the mixture was stirred for 24 hr. The solid was collected by filtration, washed with chilled acetone (20 ml) and dried under vacuum to provide white solid S,S'-dimethyliminodithiocarbonate hydroiodide ammonium iodide **3** (18.9 g, 96%). **3** (7.9 g, 0.02 mol) was treated with sat. aq. $NaHCO_3$ solution (100 ml x 2) and the organic products extracted with dichloromethane (50 ml). The organic layer was dried over Na_2SO_4 and concentrated in vacuo to a clear, colorless liquid **4** (2.3 g, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 172.10, 14.50. HRMS (ESI^+) *m/z* calcd for $C_3H_8N^+$ 122.0098, found 122.0096.

Benzyl (bis(methylthio)methylene)carbamate, 5: To a solution of **4** (1.2 g, 0.01 mol) and *N*-methylmorpholine (1.1 g, 0.011 mol) in THF (10 ml) was added dropwise chloro benzylcarbonate (2.05 g, 0.012 mol) at -20 °C. The reaction mixture was stirred for 1 hr allowing the temperature to rise to rt. The reaction was monitored with silica TLC (25% EtOAc in hexanes, rf 0.6). Once starting material disappeared on TLC, the reaction mixture was washed with water to remove ammonium salt and extracted with ethyl acetate (30 ml x 3). The product was purified by followed by column chromatography (20 % EtOAc in hexanes) to provide an off-white solid **5** (2.3 g, 90%). ^1H NMR (499 MHz, $CDCl_3$) δ 7.53 – 7.23 (m, 5H), 5.24 (s, 2H), 2.53 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1, 159.8, 136.0, 128.8, 128.8, 128.6, 68.6, 16.1. HRMS (ESI^+) *m/z* calcd for $C_{11}H_{14}NO_2S_2^+$ 256.0466, found 256.0470.

Benzyl (bis(chloro)methylene)carbamate, carboxybenzyl imidoyl dichloride, 6: To a solution of Benzyloxycarbonylimino-S, S'-dimethylthiocarbonate (1.0 g, 0.004 mol) in DCM (3 ml) was added 10% Chlorine in CCl4 (5.0 g, 0.07 mol) at -78 °C and stirred for 30 min at the same temperature. The excess chlorine and solvent were removed using a stream of N_2 gas at

rt. The residual liquid was pure enough to use a next reaction without further purification. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.41 (m, 5H), 5.30 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 135.5, 134.4, 129.2, 129.0, 128.9, 70.0. Elemental analysis: Found C, 43.68; H, 3.06; N, 5.32. $C_9H_7Cl_2NO_2$ 0.12Cl_2 requires C, 43.73; H, 2.82; N, 5.59%.

Representative example for the synthesis of 8a-8i. benzyl 1H-benzo[d]imidazol-2-ylcarbamate, 8a: *o*-Phenylenediamine (103 mg, 1 mmol) and K_2CO_3 (180 mg, 2.5 mmol, 2.5 equiv.) were suspended in 10 mL THF. **6** (241 mg, 1.2 mmol, 1.2 equiv.) was dissolved in 10 mL of THF and added at once via a pipet to the stirring solution. The reaction was stirred for 1 hour to ensure complete consumption of starting material. The reaction mixture was poured on 100 mL ice cold water. The product was isolated by vacuum filtration, rinsed with cold water, and dried in a vacuum desiccator to generate 264.9 mg (97% yield) of pure **8a**. ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.50 – 7.31 (m, 7H), 7.06 (dd, J = 5.9, 3.2 Hz, 2H), 5.24 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.3, 137.0, 129.2, 129.0, 128.8, 128.7, 121.9, 114.0, 67.3. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{14}N_3O_2^+$ 286.1086, found 286.1082.

Benzyl (5-bromo-1H-benzo[d]imidazol-2-yl)carbamate, 8b: As for the synthesis of **8a:** 4-bromo-1,2-diaminobenzene (22 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (35 mg, 0.25 mmol), **6** (38 mg, 0.12 mmol), producing 30.7 mg (76% yield) of **8b.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.57 (d, J = 2.0 Hz, 1H), 7.50 – 7.32 (m, 5H), 7.23 (dd, J = 8.5, 2.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.43, 148.13, 136.62, 129.20, 129.00, 128.96, 128.87, 128.38, 124.75, 117.04, 115.94, 114.00, 67.63.HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_3O_2Br^+$ 346.0191, found 346.0191.

Benzyl (5-fluoro-1H-benzo[d]imidazol-2-yl)carbamate, 8c: As for the synthesis of **8a:** 4-fluoro-1,2-diaminobenzene (13 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (36 mg, 0.25 mmol), **6** (41 mg, 0.12 mmol), producing 21.0 mg (71% yield) of **8c.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.49 – 7.33 (m, 6H), 7.26 (dd, J = 9.2, 2.6 Hz, 1H), 7.03 (ddd, J = 9.9, 8.7, 2.6 Hz, 1H), 5.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.12, 158.25, 153.91, 147.34, 136.37, 129.21, 129.17, 129.05, 129.00, 128.96, 128.37, 114.79, 110.74, 110.55, 101.23, 101.02, 67.99.^{19}F NMR (470 MHz, DMSO-d6) δ -76.60. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_3O_2F^+$ 286.0992, found 286.0993.

Benzyl (5-chloro-1H-benzo[d]imidazol-2-yl)carbamate, 8d: As for the synthesis of **8a:** 4-chloro-*o*-phenylenediamine (14 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (34 mg, 0.25 mmol), **6** (45 mg, 0.12 mmol), producing 23.8 mg (78% yield) of **8d.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.49 – 7.31 (m, 7H), 7.13 (dd, J = 8.5, 2.1 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.35, 148.15, 136.58, 129.20, 129.00, 128.97, 128.89, 128.37, 126.40, 122.24, 115.41, 114.17, 67.69.HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_3O_2Cl^+$ 302.0696, found 302.0695.

Benzyl (5,6-dichloro-1H-benzo[d]imidazol-2-yl)carbamate, 8e: As for the synthesis of **8a:** 4,5-dichloro-*o*-phenylenediamine (19 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (35 mg, 0.25 mmol), **6** (38 mg, 0.12 mmol), producing 34.4 mg (97% yield) of **8e.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.63 (s, 2H), 7.50 – 7.30 (m, 5H), 5.28 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.95, 148.65, 136.39, 135.44, 129.21, 129.04, 129.00, 128.94, 128.37, 124.61, 115.65, 67.94.HRMS (ESI^+) *m/z* calcd for $C_{15}H_{12}N_3O_2Cl_2^+$ 336.0307, found 336.0300.

Benzyl (5-cyano-1H-benzo[d]imidazol-2-yl)carbamate, 8f: As for the synthesis of **8a:** 3,4-diaminobenzonitrile (13 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (37 mg, 0.25 mmol), **6** (35 mg, 0.12 mmol), producing 20.2 mg (70% yield) of **8f.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.58 – 7.31 (m, 7H), 5.28 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.24, 149.80, 136.50, 129.21,

129.00, 128.92, 128.37, 125.88, 120.80, 118.75, 115.51, 103.60, 67.77.HRMS (ESI^+) *m/z* calcd for $C_{16}H_{13}N_4O_2^+$ 293.1039, found 293.1041.

Benzyl (5-methoxy-1H-benzo[d]imidazol-2-yl)carbamate, 8g: As for the synthesis of **8a:** 4-methoxy-*o*-phenylenediamine hydrochloride (21 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (72 mg, 0.5 mmol), **6** (41 mg, 0.12 mmol), producing 20.7 mg (70% yield) of **8g.** ^1H NMR (499 MHz, DMSO-d_6) δ 7.54 – 7.25 (m, 6H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.25 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.62, 157.27, 152.79, 144.02, 138.04, 135.84, 130.61, 129.25, 129.21, 129.15, 129.00, 128.38, 128.36, 123.70, 114.69, 113.54, 97.74, 68.73, 56.38. HRMS (ESI^+) *m/z* calcd for $C_{16}H_{16}N_3O_3^+$ 298.1192, found 298.1190.

Benzyl (5-nitro-1H-benzo[d]imidazol-2-yl)carbamate, 8h: As for the synthesis of **8a:** 4-nitro-*o*-phenylenediamine (17 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (38 mg, 0.25 mmol), **6** (45 mg, 0.12 mmol), producing 28.8 mg (81% yield) of **8h.** ^1H NMR (499 MHz, DMSO-d_6) δ 8.29 (d, *J* = 2.3 Hz, 1H), 8.03 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.31 (m, 5H), 5.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.3, 151.2, 142.5, 136.5, 129.2, 129.0, 128.9, 118.1, 110.3, 67.8. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_4O_4^+$ 313.0937, found 313.0933.

2-(((Benzyloxy)carbonyl)amino)-1H-benzo[d]imidazole-5-carboxylic acid, 8i: As for the synthesis of **8a:** 3,4-diaminobenzoic acid (15 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (41 mg, 0.25 mmol), **6** (46 mg, 0.12 mmol), producing 22.1 mg (70% yield) of **8f.** ^1H NMR (499 MHz, DMSO-d_6) δ 8.12 (d, *J* = 1.5 Hz, 1H), 7.89 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.52 –7.31 (m, 5H), 5.33 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.7, 157.3, 153.4, 138.1, 136.1, 129.2, 129.2, 129.1, 129.0, 128.4, 125.7, 115.4, 113.4, 68.5. HRMS (ESI^+) *m/z* calcd for $C_{16}H_{14}N_3O_4^+$ 312.0984, found 312.0990.

Representative example for the synthesis of 11a-f, 12-14. benzyl (1-ethyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11a: 10a (28 mg, 0.2 mmol) and K_2CO_3 (78 mg, 0.5 mmol, 2.5 equiv.) were suspended in 2 mL THF. **6** (87 mg, 0.24 mmol, 1.2 equiv.) was dissolved in 2 mL of THF and added at once via a pipet to the stirring solution. The reaction was stirred for 1 hour to ensure complete consumption of starting material. The reaction mixture was poured on 20 mL ice cold water. The product was isolated by extraction with EtOAc (2 x 10 mL), washing with saturated NaCl, drying over $MgSO_4$, and concentrating to generate 54.0 mg (89% yield) of pure **11a**.^1H NMR (499 MHz, $CDCl_3$) δ 11.21 (bs, 1H), 7.35 – 7.32 (m, 2H), 7.25 – 7.20 (m, 3H), 7.19 – 7.13 (m, 1H), 7.11 – 7.03 (m, 3H), 5.10 (s, 2H), 4.03 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 154.3, 137.5, 136.4, 129.7, 128.6, 128.5, 128.2, 127.9, 122.8, 110.9, 109.0, 67.3, 36.9, 13.7.HRMS (ESI^+) *m/z* calcd for $C_{17}H_{18}N_3O_2^+$ 296.1399, found 296.1399.

Benzyl (1-propyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11b: As for the synthesis of **11a: 10b** (18 mg, 0.1 mmol), 4 mL THF, K_2CO_3 (37 mg, 0.25 mmol), **6** (31 mg, 0.12 mmol), producing 34.8 mg (93% yield) of **11a.** ^1H NMR (499 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H), 7.39 – 7.25 (m, 3H), 7.24 – 7.15 (m, 4H), 5.24 (s, 2H), 4.10 – 4.02 (m, 2H), 1.90 – 1.78 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 154.7, 137.6, 130.2, 128.5, 128.4, 128.3, 127.9, 122.9, 122.8, 110.8, 109.4, 67.3, 43.6, 21.7, 11.4. HRMS (ESI^+) *m/z* calcd for $C_{18}H_{20}N_3O_2^+$ 310.1556, found 310.1546.

Benzyl (1-butyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11c: As for the synthesis of **11a: 10c** (34 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (78 mg, 0.5 mmol), **6** (76 mg, 0.24 mmol), producing 48.6 mg (73% yield) of **11c.**^1H NMR (499 MHz, $CDCl_3$) δ 7.55 – 7.11 (m, 9H), 5.24 (s, 2H), 4.20 – 4.08 (m, 2H), 1.83 – 1.73 (m, 2H), 1.45 – 1.35 (m, 2H), 1.01 – 0.91 (m, 3H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 163.7, 154.1, 137.4, 130.1, 129.1, 128.9, 128.8, 128.5, 128.4, 128.2, 127.9, 123.0, 122.9, 110.9, 109.4, 67.4, 42.1, 30.5, 20.2, 13.9. HRMS (ESI^+) *m/z* calcd for $C_{19}H_{22}N_3O_2^+$ 324.1712, found 324.1717.

Benzyl (1-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11d: As for the synthesis of **11a: 10d** (35 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (74 mg, 0.5 mmol), **6** (83 mg, 0.24 mmol), producing 48.2 mg (70% yield) of **11d.** ^1H NMR (499 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 1H), 7.52 – 7.45 (m, 2H), 7.46 – 7.33 (m, 3H), 7.34 – 7.25 (m, 1H), 7.24 – 7.07 (m, 2H), 5.30 (s, 1H), 5.27 (s, 2H), 1.93 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 155.4, 137.9, 130.34, 129.1, 128.9, 128.5, 127.8, 122.3, 113.8, 110.8, 69.9, 67.5, 61.3, 30.4. HRMS (ESI^+) *m/z* calcd for $C_{19}H_{22}N_3O_2^+$ 324.1712, found 324.1714.

Benzyl (1-benzyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11e: As for the synthesis of **11a: 10e** (40 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (79 mg, 0.5 mmol), **6** (75 mg, 0.24 mmol), producing 75.2 mg (97% yield) of **11e.** ^1H NMR (499 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.48 (dd, J = 7.9, 1.3 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.22 (m, 7H), 7.15 (dtd, J = 25.0, 7.5, 1.2 Hz, 2H), 7.06 – 7.02 (m, 1H), 5.34 (s, 2H), 5.26 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 135.3, 129.7, 128.7, 128.4, 128.3, 128.1, 127.8, 127.8, 127.4, 122.9, 110.6, 109.8, 67.3, 45.5. HRMS (ESI^+) *m/z* calcd for $C_{22}H_{20}N_3O_2^+$ 385.1556 found 385.1554.

Benzyl (1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 11f: As for the synthesis of **11a: 10f** (35 mg, 0.1 mmol), 4 mL THF, K_2CO_3 (75 mg, 0.5 mmol), **6** (84 mg, 0.24 mmol), producing 65.2 mg (70% yield) of **11f.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.05 (m, 14H), 5.18 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 134.0, 129.9, 128.9, 128.5, 128.4, 127.9, 127.4, 123.6, 123.2, 111.0, 110.2, 110.0, 67.5. HRMS (ESI^+) *m/z* calcd for $C_{21}H_{18}N_3O_2^+$ 344.1399, found 344.1398.

Benzyl (1H-perimidin-2-yl)carbamate, 12: As for the synthesis of **11a:** 1,8-aminonaphthalene (17 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (35 mg, 0.25 mmol), **6** (34 mg, 0.12 mmol), producing 20.5 mg (78% yield) of **12.** ^1H NMR (499 MHz, DMSO-d_6) δ 10.98 (s, 2H), 7.41 – 7.35 (m, 4H), 7.35 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 7.17 (dd, J = 8.4, 1.0 Hz, 2H), 6.71 (dd, J = 7.3, 1.0 Hz, 2H), 5.12 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.8, 137.8, 136.4, 134.9, 129.1, 128.9, 128.4, 128.2, 119.7, 117.3, 106.9, 66.6. HRMS (ESI^+) *m/z* calcd for $C_{19}H_{16}N_3O_2^+$ 318.1243, found 318.1249.

Benzyl benzo[*d*]oxazol-2-ylcarbamate, 13: As for the synthesis of **11a:** 2-aminophenol (19 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (74 mg, 0.5 mmol), **6** (78 mg, 0.24 mmol), producing 40.0 mg (85% yield) of **13.** ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.3, 1.2 Hz, 1H), 7.42 – 7.28 (m, 6H), 7.26 – 7.15 (m, 2H), 5.24 (s, 2H), 4.36 (bs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.6, 128.3, 128.2, 128.1, 128.0, 124.5, 123.4, 117.1, 109.6, 69.6, 67.6. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_2O_3^+$ 269.0926, found 269.0919.

Benzyl benzo[d]thiazol-2-ylcarbamate, 14: As for the synthesis of **11a:** 2-aminothiophenol (12 mg, 0.1 mmol), 2 mL THF, K_2CO_3 (36 mg, 0.25 mmol), **6** (38 mg, 0.12 mmol), producing 17.2 mg (65% yield) of **14.** ^1H NMR (499 MHz, DMSO-d_6) δ 12.15 (bs, 1H), 7.95 (dd, J = 8.2, 1.1 Hz, 1H), 7.74 – 7.60 (m, 1H), 7.48 – 7.32 (m, 6H), 7.31 – 7.20 (m, 1H), 5.27 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 136.4, 132.2, 129.2, 129.0, 128.9, 126.7, 124.0, 122.24, 120.9, 67.9. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{13}N_2O_2S^+$ 285.0698, found 285.0696.

***N*-methyl-3-nitropyridin-2-amine, 15:** To a solution of 3-nitro-2-chloropyridine (4.0 g, 25.2 mmol) in 15 mL 2-methoxyethanol was added methylamine (2.0 M in THF, 32 mL). The reaction

was stirred for 8 hr at 80 °C in a sealed tube. After cooling to rt, the reaction mixture was evaporated to afford **15** quantitatively (3.6 g, 23.2 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.37 (m, 2H), 8.20 (s, 1H), 6.64 (dd, J = 8.3, 4.4 Hz, 1H), 3.17 (d, J = 4.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 153.5, 135.4, 111.7, 28.4. HRMS (ESI^+) *m/z* calcd for $C_6H_8N_3O_2^+$ 154.0617, found 154.0610.

5-bromo-*N*-methyl-3-nitropyridin-2-amine, 16: 15 (2.0 g, 13.1 mmol) was dissolved into glacial acetic acid (20 mL) and pyridinium tribromide (4.2 g, 13.1 mmol) was added. After stirring for 6 hrs at rt, DI water (100 mL) was added producing a yellow solid that was collected by filtration. Recrystallization in ethanol afforded **16** (2.8 g, 93%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.54 (d, J = 2.3 Hz, 1H), 8.47 (d, J = 2.3 Hz, 1H), 8.18 (bs, 1H), 3.17 (d, J = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 156.7, 152.0, 136.9, 104.5, 28.6. HRMS (ESI^+) *m/z* calcd for $C_6H_7N_3O_2Br^+$ 231.9722, found 231.9722.

***N*-methyl-3-nitro-5-phenylpyridin-2-amine, 17:** A mixture of **16** (2.8 g, 12.1 mmol), sodium carbonate (12 mL aqueous 2M solution), benzene (35 mL), phenylboronic acid (1.2 g, 9.9 mmol), and tetrakis(triphenylphosphine)palladium(0) (300 mg) was heated 80 °C monitoring by TLC. After complete consumption of **16**, EtOAc was added; the crude material was concentrated under vacuum, loaded directly onto a silica gel column, and eluted with 10% EtOAc in hexane to provide the orange **17** (2.1 g, 78%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.71 (d, J = 2.4 Hz, 1H), 8.62 (d, J = 2.4 Hz, 1H), 8.23 (s, 1H), 7.60 – 7.29 (m, 5H), 3.21 (d, J = 4.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.46, 152.52, 136.23, 133.01, 129.42, 127.98, 126.46, 125.58, 28.57. HRMS (ESI^+) *m/z* calcd for $C_{12}H_{12}N_3O_2^+$ 230.0930, found 230.0921.

***N*^{2}-methyl-5-phenylpyridine-2,3-diamine, 18: 17** (450 mg, 1.97 mmol) was dissolved methanol (10 mL) in a pressure bottle and PtO_2 (20 mg) was added. Hydrogen (30 psi) was applied using a Parr shaker. After shaking 30 min at 30 psi H_2, the solution had changed from orange to clear. The crude mixture was passed through celite and evaporation afforded **18** (389 mg, 99.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 2.1 Hz, 1H), 7.48 (dd, J = 8.3, 1.3 Hz, 2H), 7.38 (dd, J = 8.4, 6.9 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.06 (d, J = 2.1 Hz, 1H), 3.04 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 139.0, 137.5, 129.0, 128.7, 127.0, 126.8, 126.5, 120.8, 29.1. HRMS (ESI^+) *m/z* calcd for $C_{12}H_{14}N_3^+$ 200.1188, found 200.1181.

benzyl (3-methyl-6-phenyl-3H-imidazo[4,5-b]pyridin-2-yl)carbamate, 19: To a solution of **18** (433 mg, 2.2 mmol) in dichloromethane (10 mL) was added **6** (700 mg, 6.16 mmol) and subsequently dropwise trimethylamine (913 uL, 3.0 mmol) at rt. After complete consumption of **18** as monitored by TLC, the solvent was evaporated. The residue was dissolved into methylene chloride and a white solid precipitated after addition of methanol. Filtration provided pure **19** (780 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.41 (d, J = 1.9 Hz, 1H), 7.72 – 7.08 (m, 10H), 5.22 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.9, 138.1, 137.1, 132.8, 129.4, 128.6, 128.4, 128.2, 128.1, 127.5, 115.9, 67.7, 27.4. HRMS (ESI^+) *m/z* calcd for $C_{21}H_{19}N_4O_2^+$ 359.1508, found 359.1497.

3-methyl-6-phenyl-3H-imidazo[4,5-b]pyridin-2-amine, 20: Hydrogenation (30 psi) of **19** (400 mg, 1.1 mmol) over 10% Pd/C in a MeOH for 1 hr afforded **20** (265 mg, >99%). ^{1}H NMR (400 MHz, CD_3OD) δ 8.47 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 1.8 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.52 –

7.32 (m, 3H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 152.0, 143.4, 141.8, 137.5, 133.9, 129.1, 128.0, 127.1, 123.2, 117.4, 26.8. HRMS (ESI^+) *m/z* calcd for $C_{13}H_{13}N_4^+$ 225.1140, found 225.1133.

***tert*-Butyl (bis(methylthio)methylene)carbamate, 21:** To a solution of **4** (590 mg, 4.88 mmol) and pyridine (385 mg, 4.88 mmol) in toluene (10 ml) was added dropwise phosgene solution (20% in toluene, 2.45 g, 4.95 mmol) at -78 °C. After stirring for 4 hr at the same temperature, t-butanol (900 mg, 9.60 mmol) was added and successively pyridine (385 mg, 4.88 mmol) was added into the reaction mixture at rt. The reaction mixture was washed with water and dried over $MgSO_4$. The solution was concentrated under vacuum to load SiO_2 column. Elution with the mixture of EA/n-Hex (10:90, v/v) afforded colorless liquid (900 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 6H), 1.53 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 159.2, 82.1, 28.2, 15.8.HRMS (ESI^+) *m/z* calcd for $C_8H_{16}NO_2S_2^+$ 222.0622, found 222.0627.

***tert*-butyl (bis(chloro)methylene)carbamate, t-butylcarboxy imidoyl dichloride, 22:** To the solution of t-butyloxycarbonylimino-S, S'-dimethylthiocarbonate (400 mg, 1.80 mmol) in CH_2Cl_2 (3 ml) was added 10% chlorine in carbon tetrachloride (3.0 g, 4.22 mmol) at -78 °C and stirred for 2 hr at same temperature. The excess chlorine and solvent was removed under a stream of N_2 gas at rt. The residual liquid was pure enough to use a next reaction without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 133.8, 85.4, 28.0. Elemental analysis: Found C, 28.83; H, 2.94; N, 4.97. $C_6H_9Cl_2NO_2$ requires C, 28.51; H, 3.32; N, 5.12%.

Representative example for the synthesis of 23a-e. *tert*-butyl (1*H*-benzo[*d*]imidazol-2-yl)carbamate, 23a: *o*-Phenylenediamine (28 mg, 0.2 mmol) and K_2CO_3 (74 mg, 0.5 mmol, 2.5 equiv.) were suspended in 2 mL THF. **22** (54 mg, 0.24 mmol, 1.2 equiv.) was dissolved in 2 mL of THF and added at once via a pipet to the stirring solution. The reaction was stirred for 1 hour to ensure complete consumption of starting material. The reaction mixture was poured on 20 mL ice cold water. The product was isolated by extraction into Et_2O (3x 10 mL), washed with brine, dried over $MgSO_4$, and concentrated to give 49.4 mg (81% yield) of a yellow solid. ***tert*-butyl (1*H*-benzo[*d*]imidazol-2-yl)carbamate, 23a:** ^{1}H NMR (499 MHz, CD_3OD) δ 7.41 (dd, J = 5.9, 3.2 Hz, 2H), 7.13 (dd, J = 6.0, 3.2 Hz, 2H), 4.91 (s, 2H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 154.7, 148.7, 136.7, 126.1, 123.0, 114.5, 83.0, 30.9, 28.5. HRMS (ESI^+) *m/z* calcd for $C_{12}H_{16}N_3O_2^+$ 234.1243, found 234.1239.

(*tert*-butyl (5-methoxy-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 23b: As for the synthesis of **23a:** 4-methoxy-*o*-phenylenediamine hydrochloride (60 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (150 mg, 1 mmol), **22** (57 mg, 0.24 mmol), producing 52.6 mg (70% yield) of **23b.** ^{1}H NMR (499 MHz, CD_3OD) δ 7.28 (d, J = 8.7 Hz, 1H), 6.98 (d, J = 2.5 Hz, 1H), 6.76 (dd, J = 8.7, 2.4 Hz, 1H), 3.80 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 27.30, 55.06, 81.56, 97.49, 110.12, 113.76, 130.34, 136.60, 147.48, 153.58, 156.18.HRMS (ESI^+) *m/z* calcd for $C_{13}H_{18}N_3O_3^+$ 264.1348, found 264.1343.

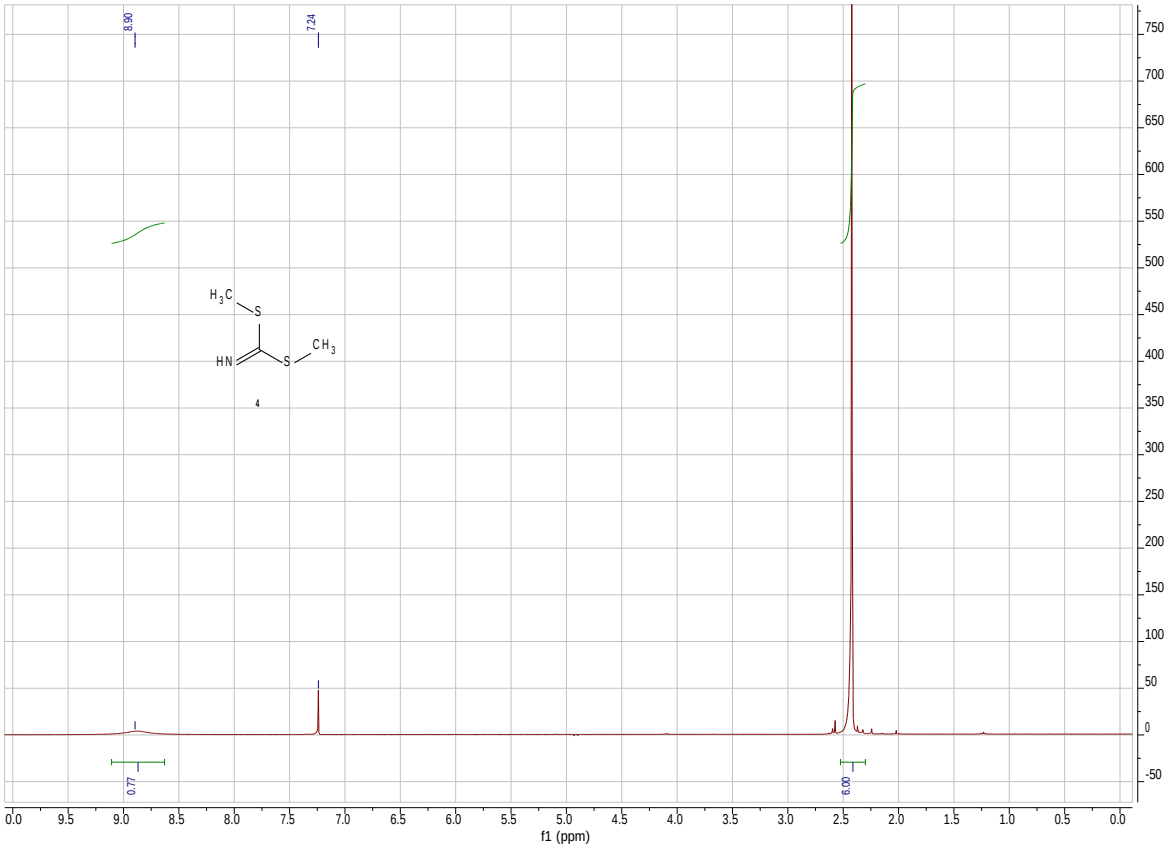
***tert*-butyl (5-nitro-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 23c:** As for the synthesis of **23a:** 4-nitro-*o*-phenylenediamine (34 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (75 mg, 0.5 mmol), **22** (61 mg, 0.24 mmol), producing 56.8 mg (93% yield) of **23c.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 8.29 (d, J = 2.4 Hz, 1H), 8.06 (dd, J = 8.8, 2.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 1.54 (s, 8H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.4, 150.2, 142.0, 117.7, 114.0, 109.4, 82.0, 30.4, 27.8. HRMS (ESI^+) *m/z* calcd for $C_{12}H_{15}N_4O_4^+$ 279.1093, found 279.1086.

***tert*-butyl (1-propyl-1*H*-benzo[*d*]imidazol-2-yl)carbamate, 23d:** As for the synthesis of **23a:** **10b** (21 mg, 0.2 mmol), 4 mL THF, K_2CO_3 (73 mg, 0.5 mmol), **22** (58 mg, 0.24 mmol), producing 34.6 mg (88% yield) of **23d.** ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.27 – 7.16 (m, 3H), 4.19 (m, 1H), 1.94 – 1.72 (m, 2H), 1.57 (s, 9H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.2, 128.5, 123.1, 111.0, 109.6, 44.1, 30.5, 28.6, 21.8, 11.3. HRMS (ESI^+) *m/z* calcd for $C_{15}H_{22}N_3O_2^+$ 276.1712, found 276.1710.

***tert*-butyl benzo[*d*]oxazol-2-ylcarbamate, 23e:** As for the synthesis of **23a:** 2-aminophenol (41 mg, 0.4 mmol), 8 mL THF, K_2CO_3 (142 mg, 1 mmol), **22** (121 mg, 0.24 mmol), producing 50.5 mg (57% yield) of **23e.** ^{1}H NMR (499 MHz, DMSO-d_6) δ 7.50 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.19 (dd, J = 7.6, 1.2 Hz, 1H), 7.17 – 7.13 (m, 1H), 1.49 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.3, 151.1, 147.9, 140.9, 124.8, 123.5, 118.2, 110.1, 81.9, 30.9, 28.5. HRMS (ESI^+) *m/z* calcd for $C_{12}H_{15}N_2O_3^+$ 235.1083, found 235.1082.

References:

1. Brandsma, L.; OE Jong, R.L.P.; Verkruijsse, H. D. *Synthesis*, **1985**, 948.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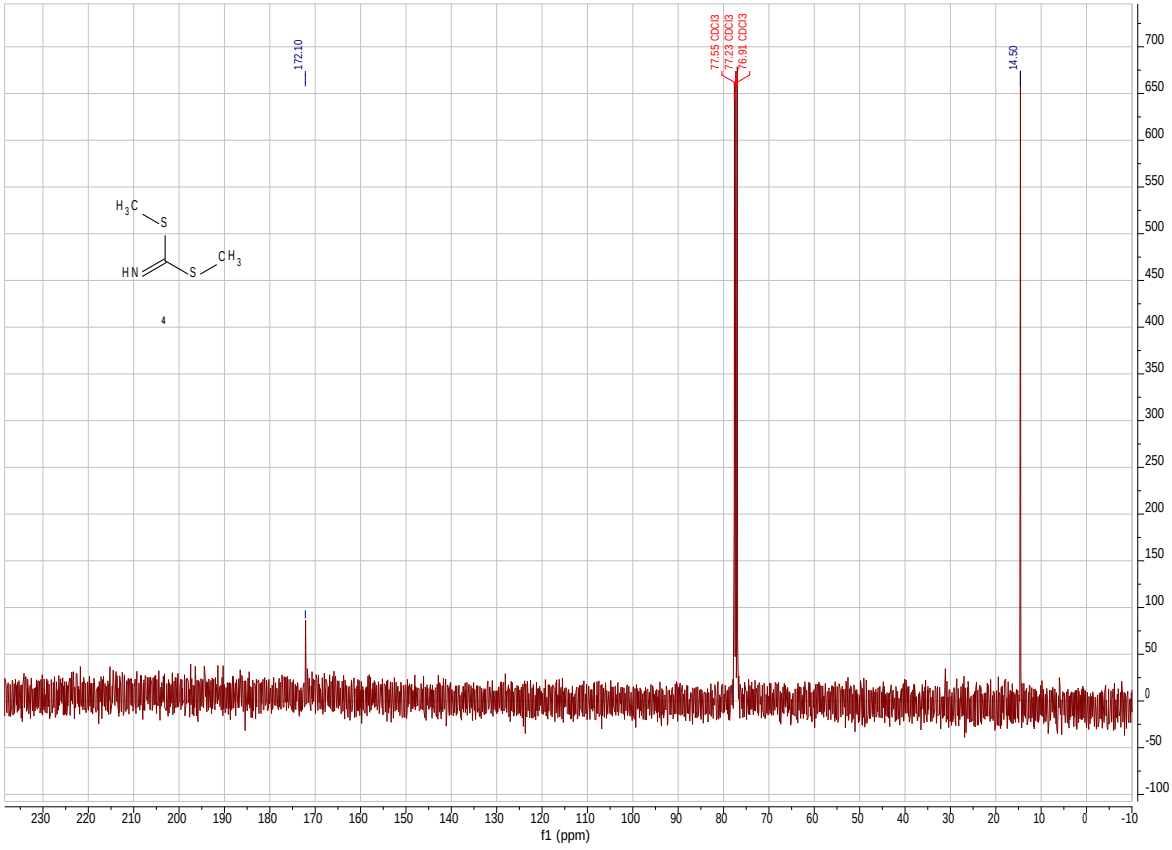
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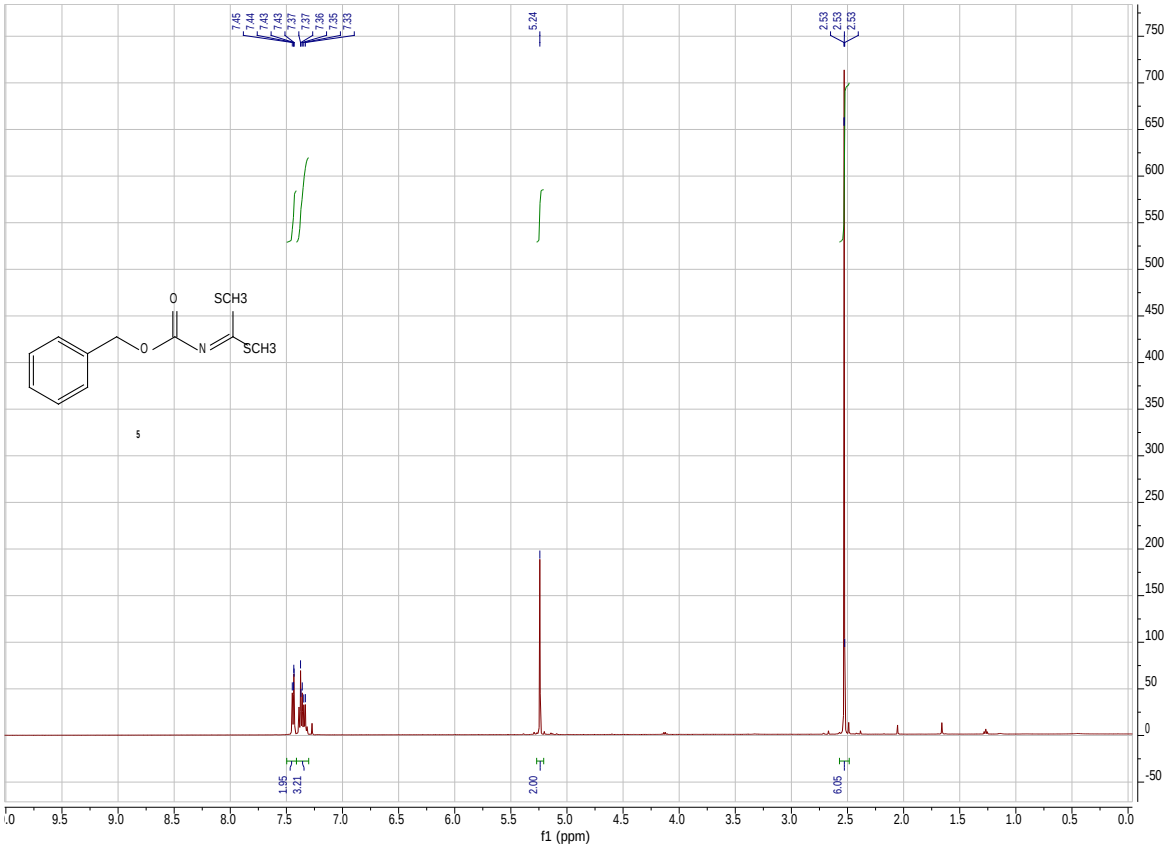
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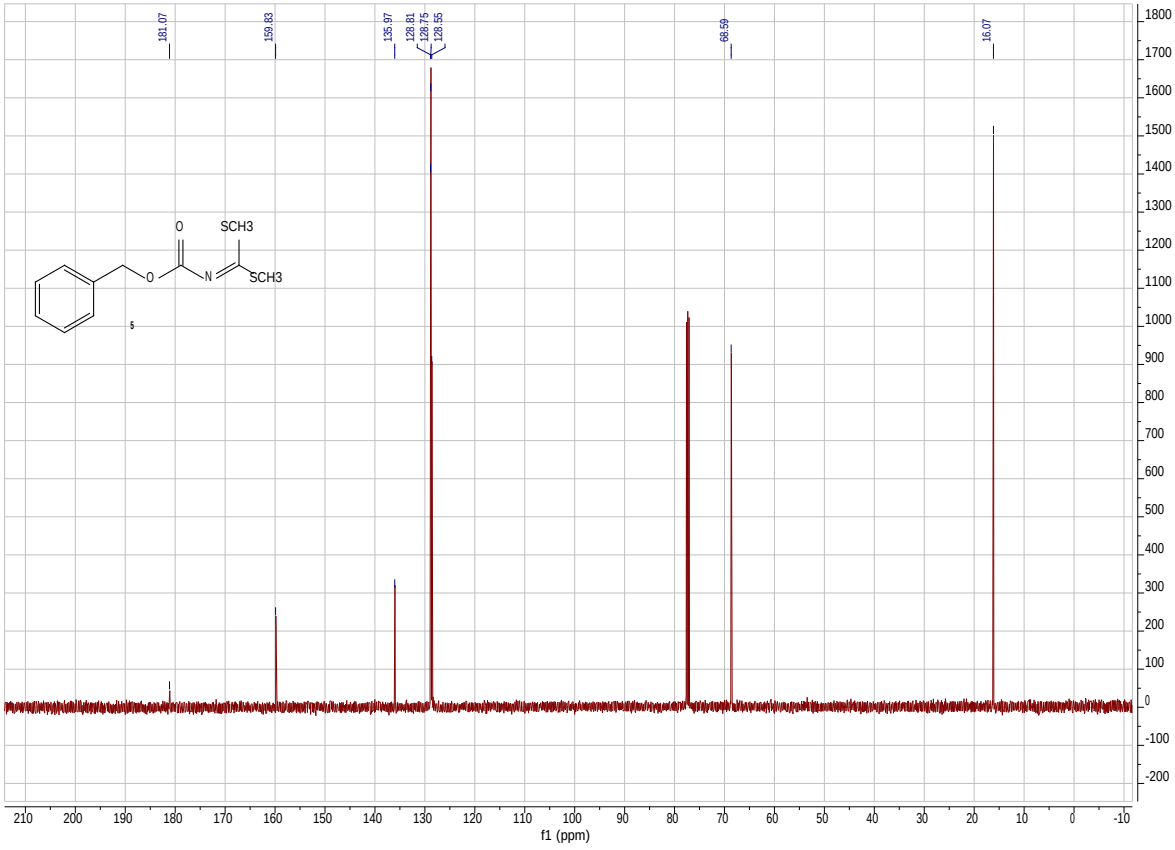
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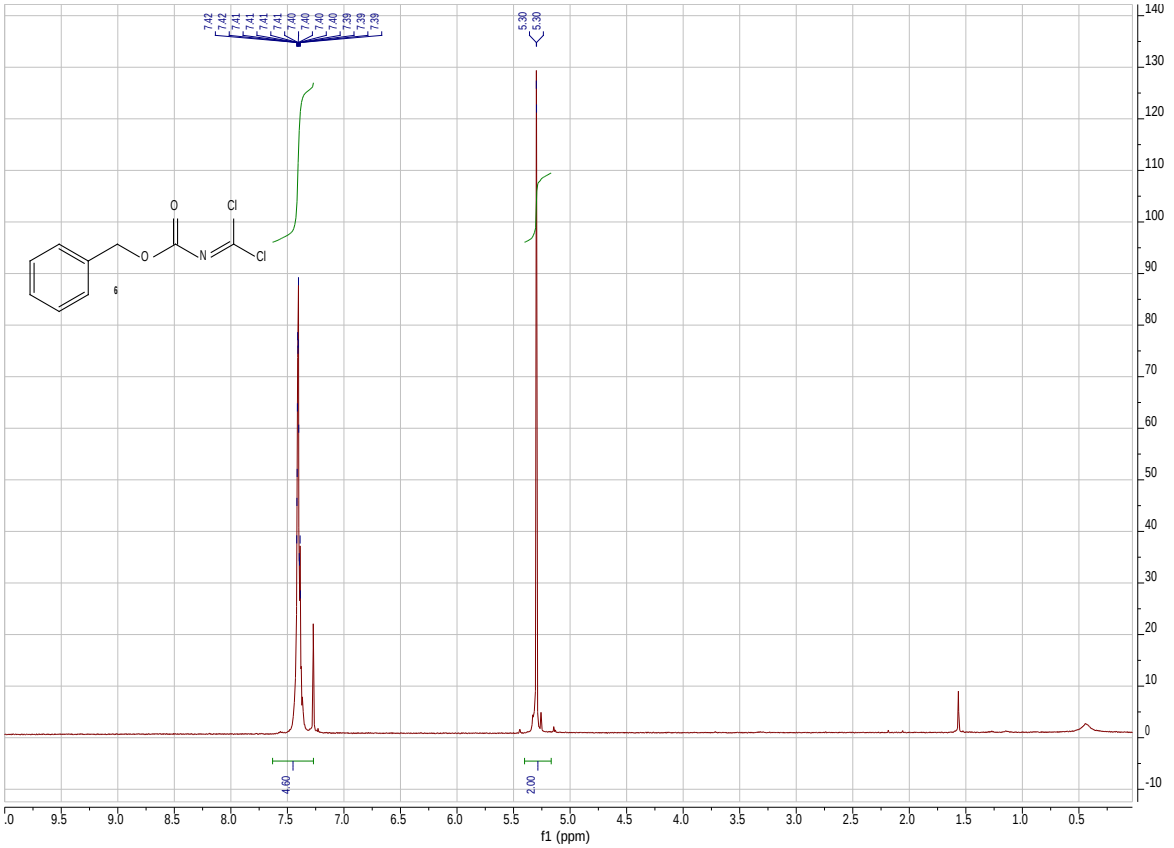
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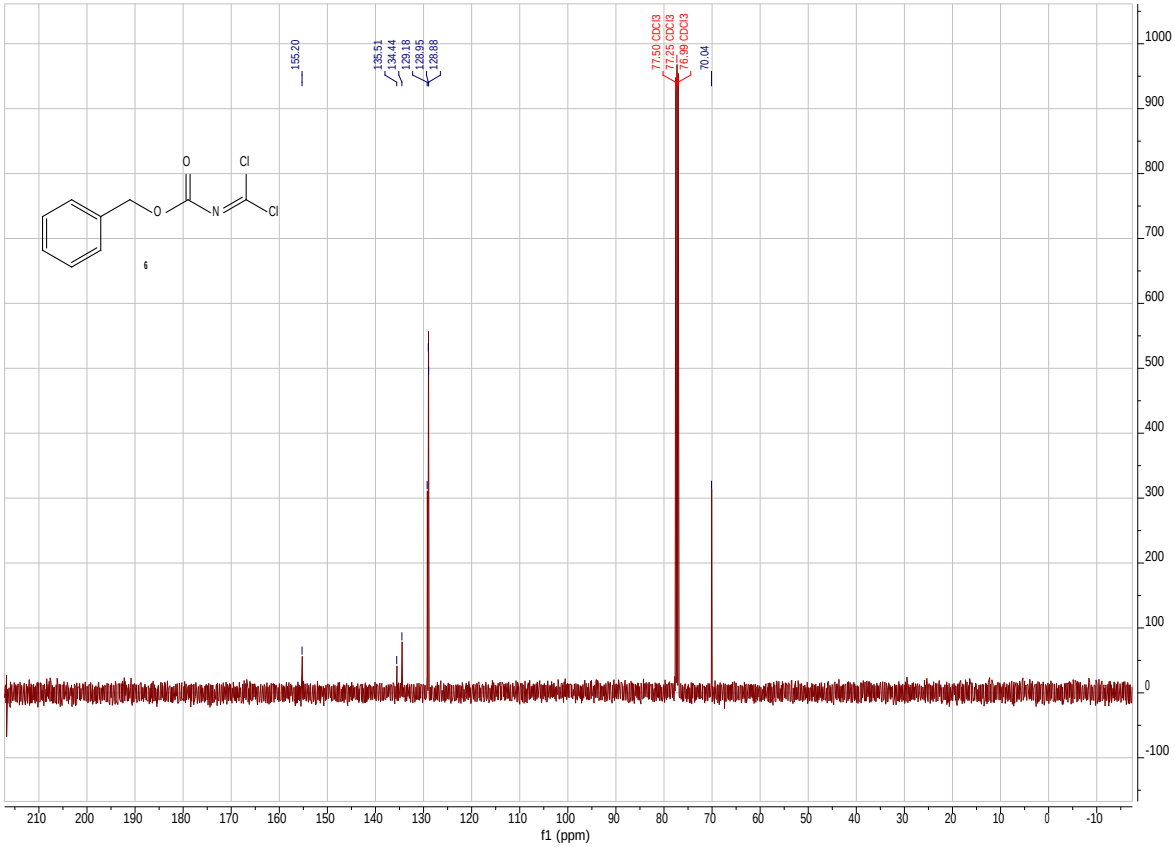
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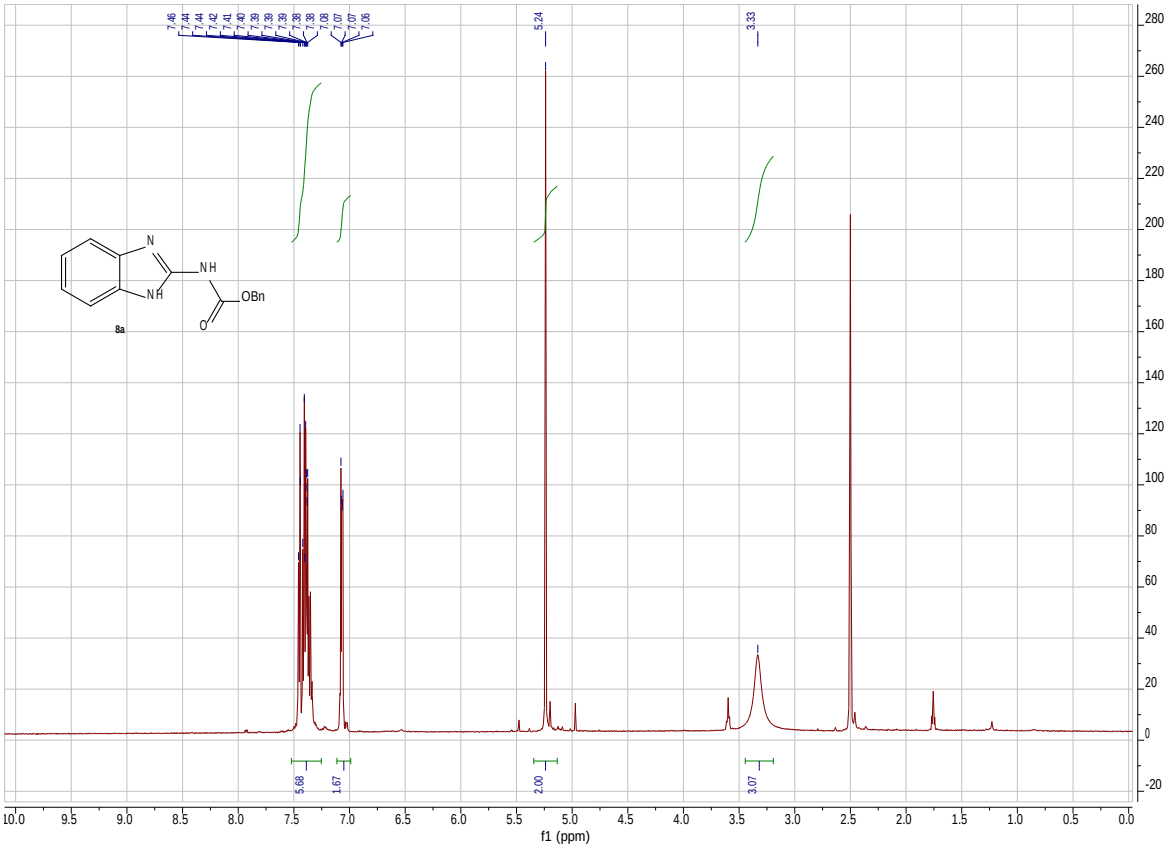
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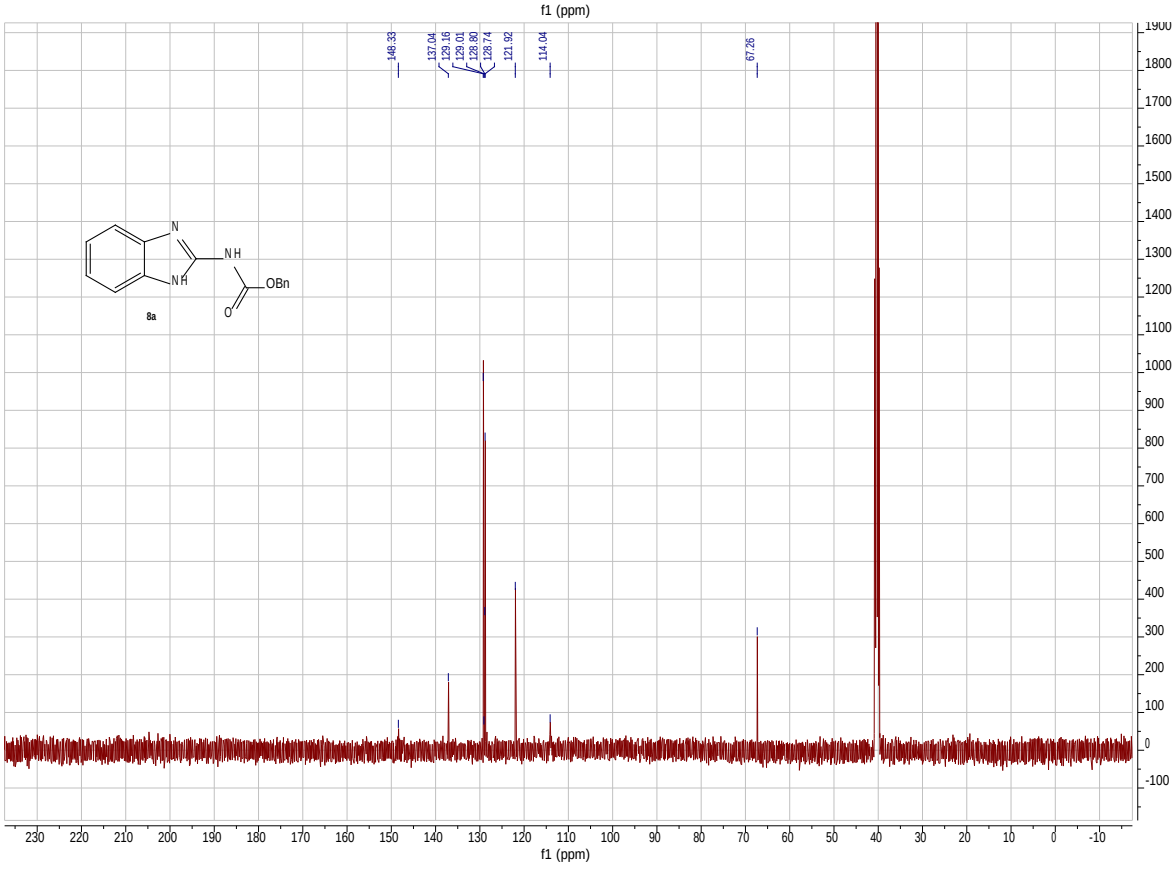
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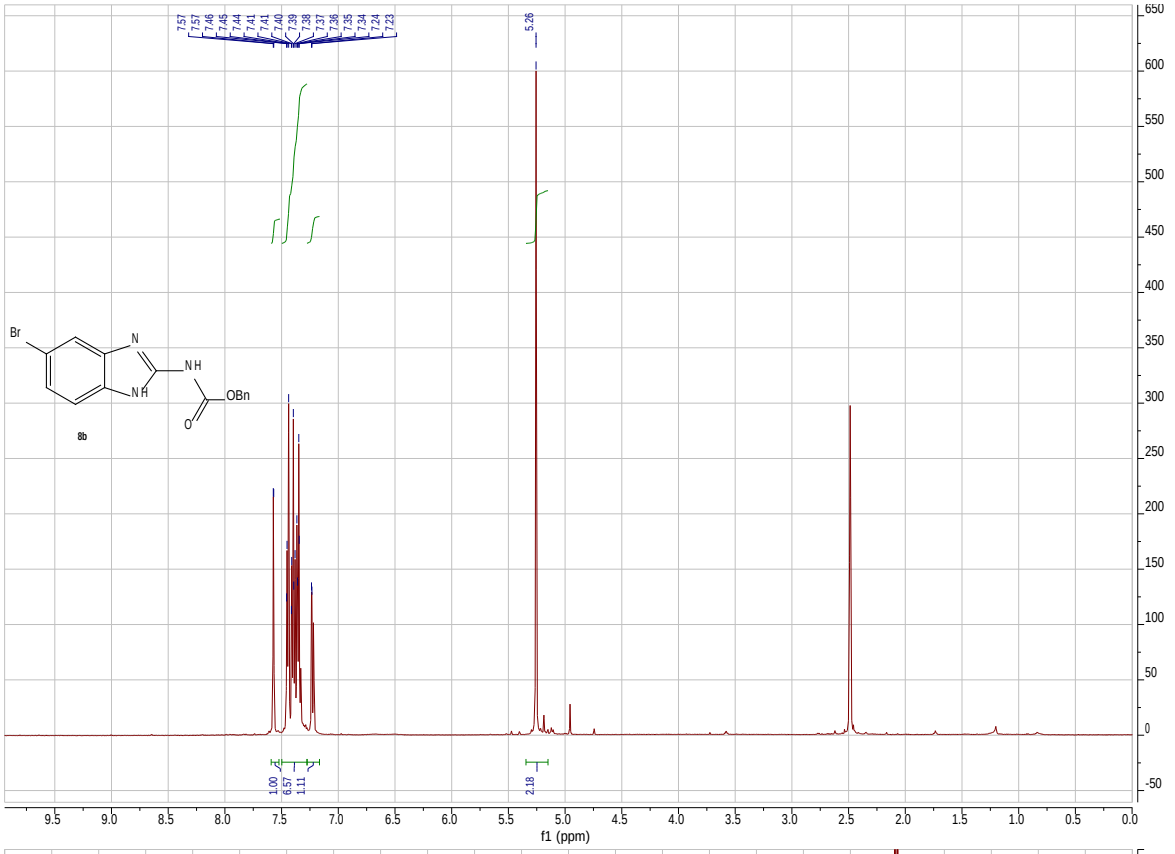
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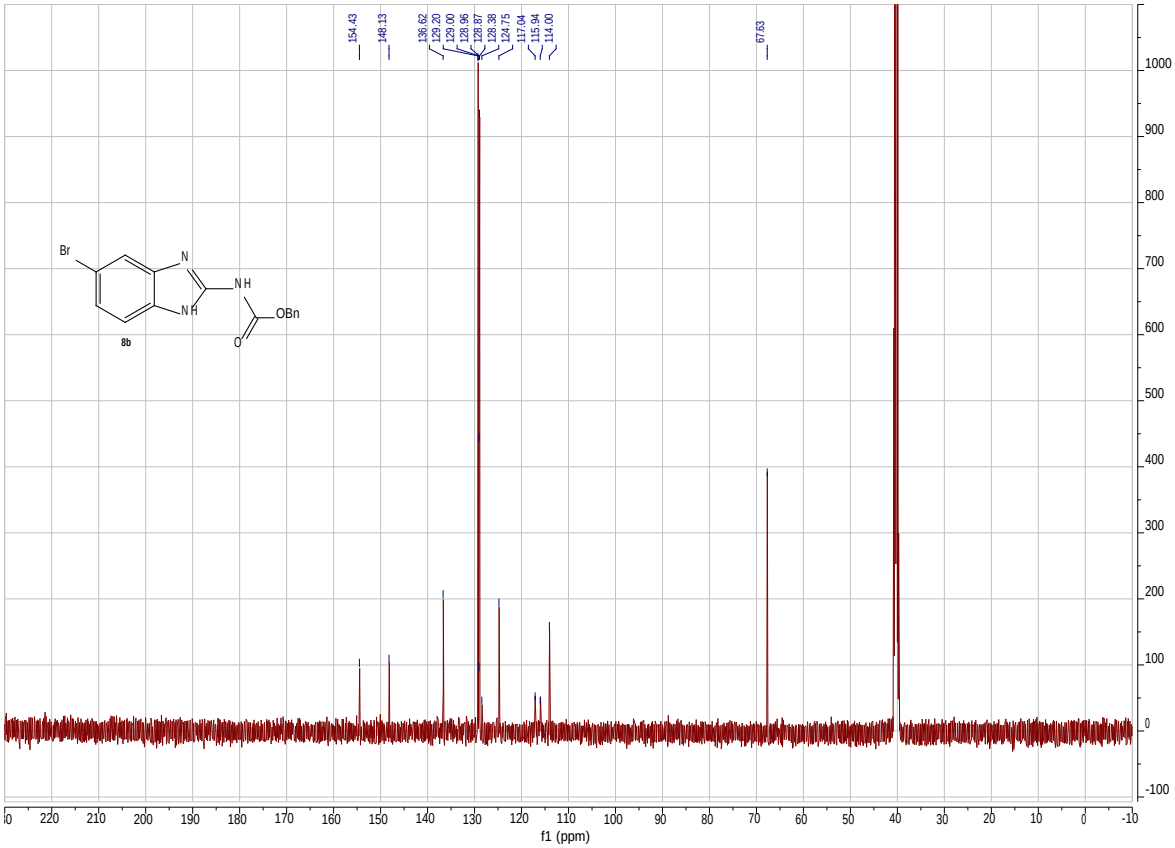
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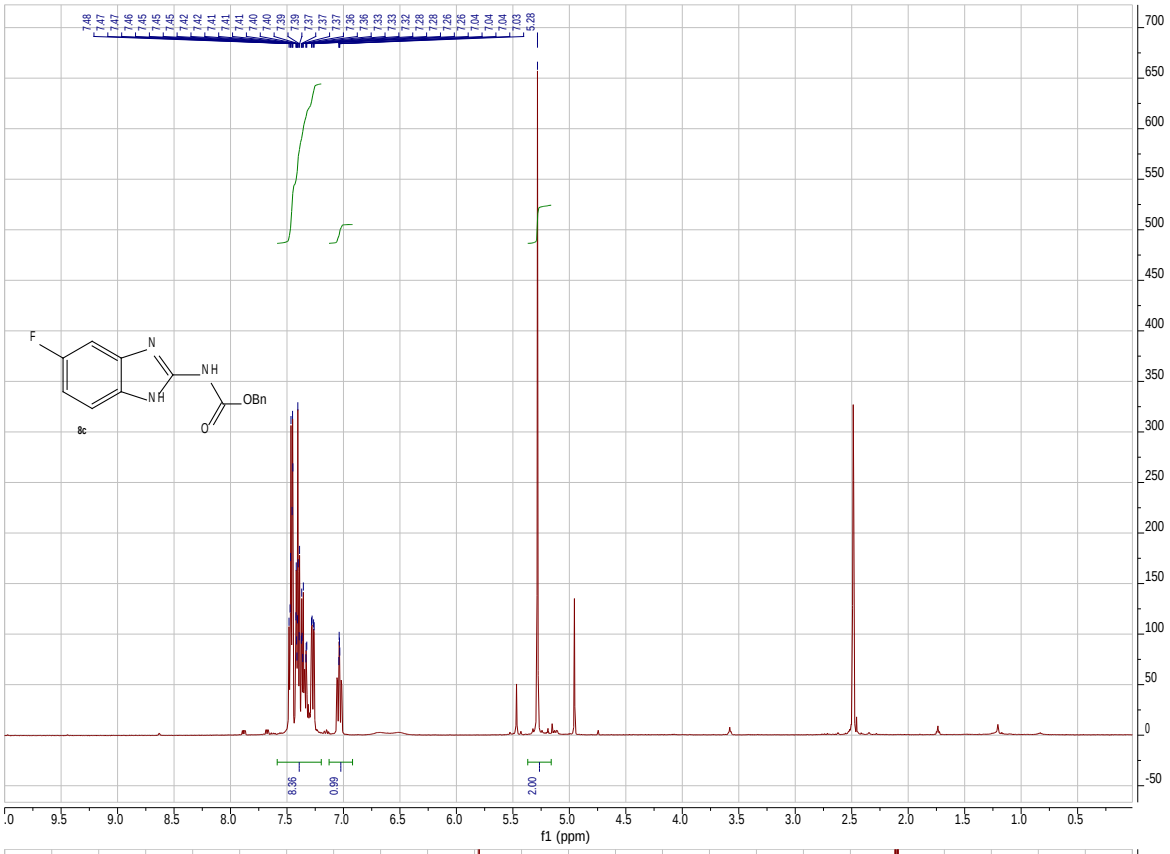
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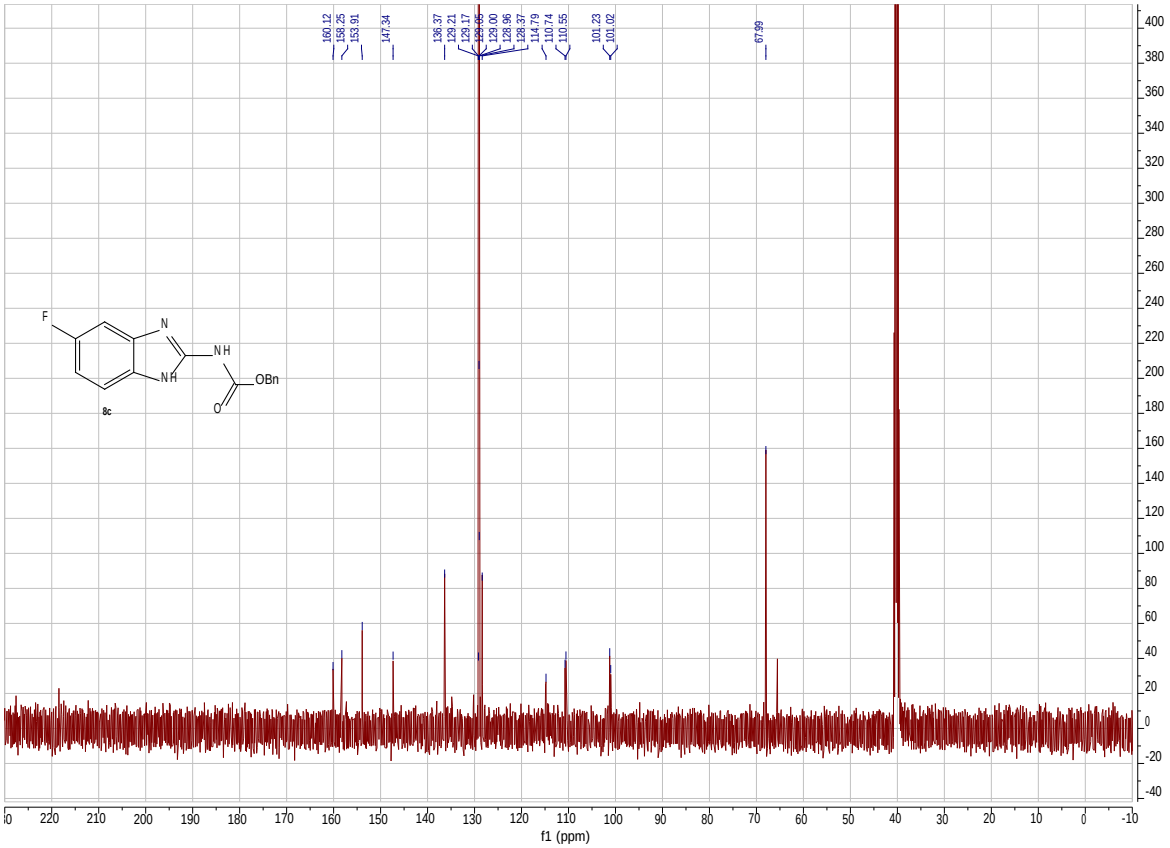
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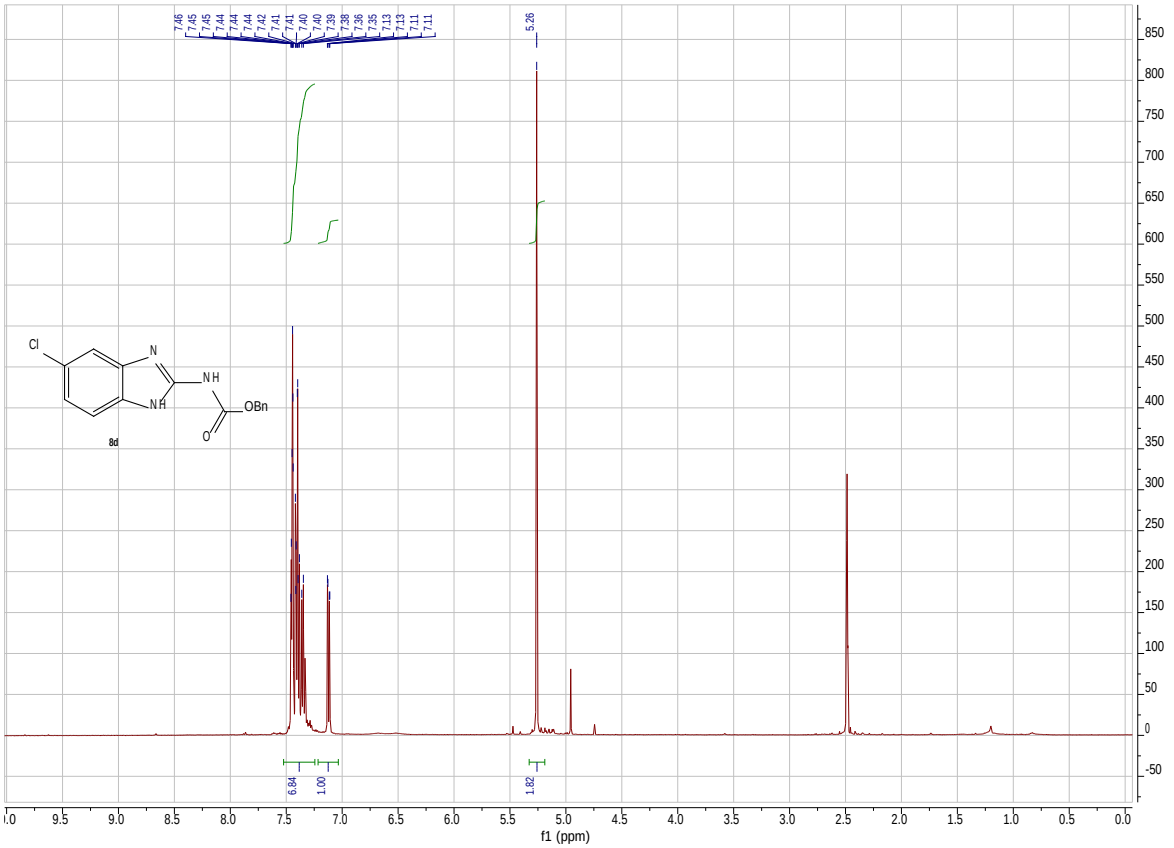
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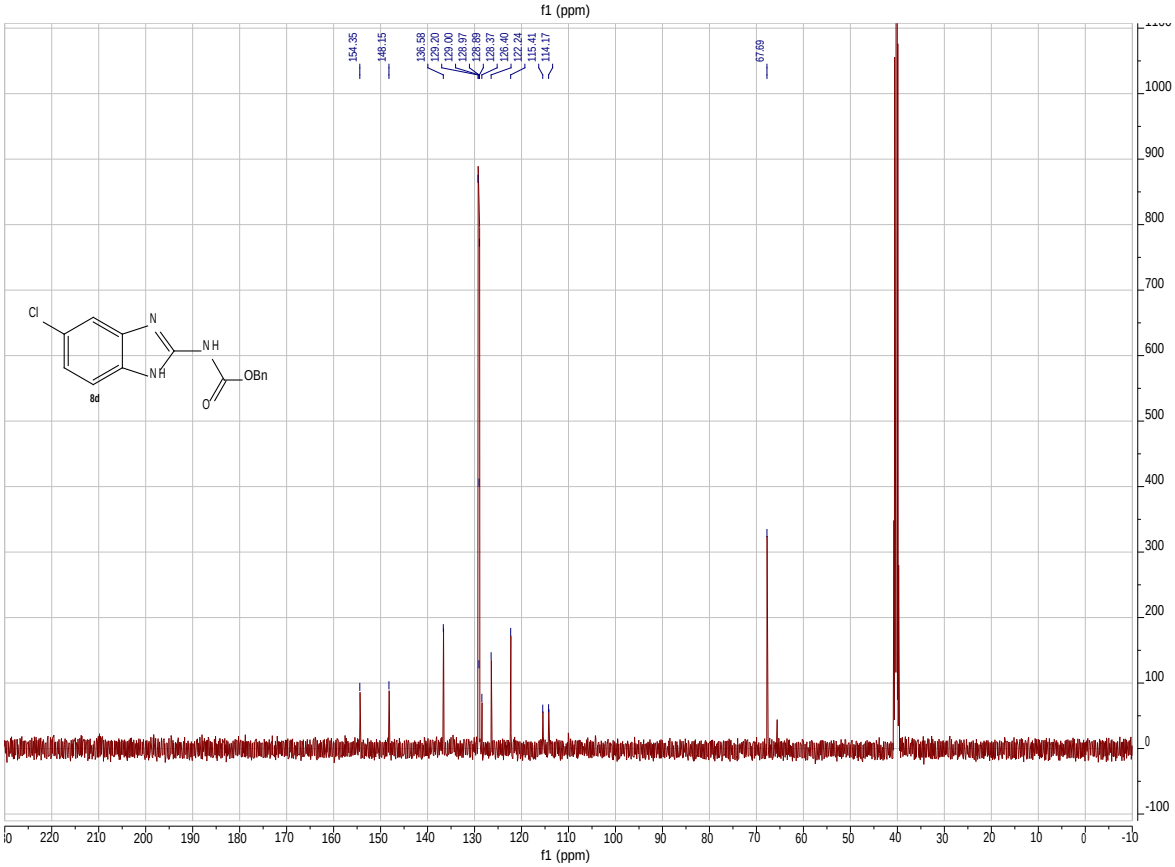
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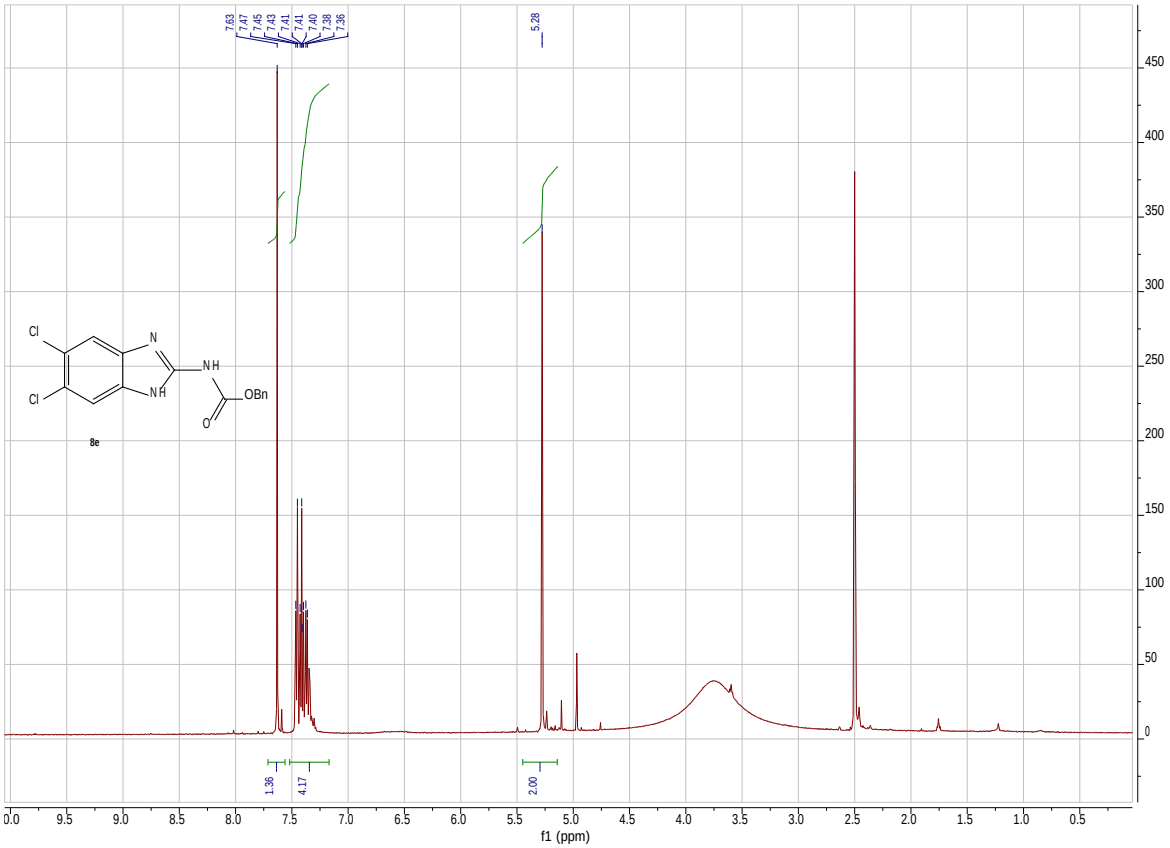
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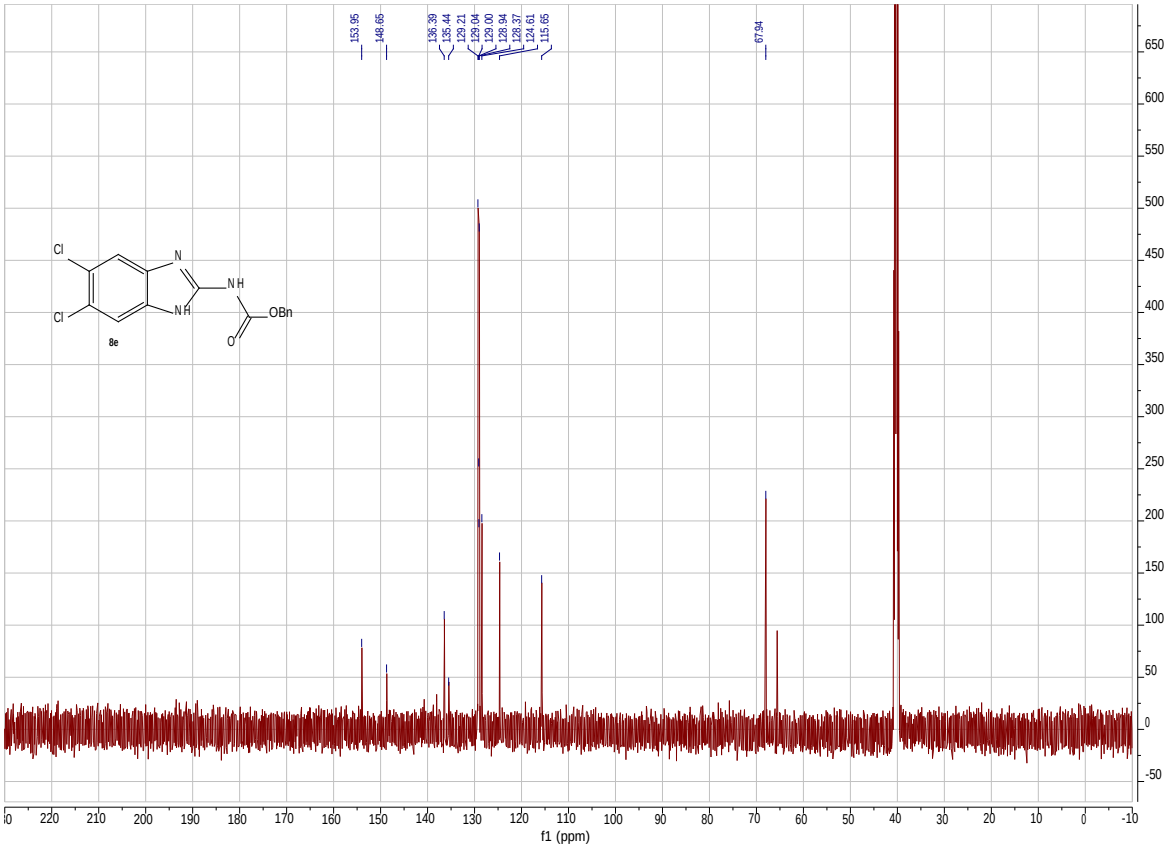
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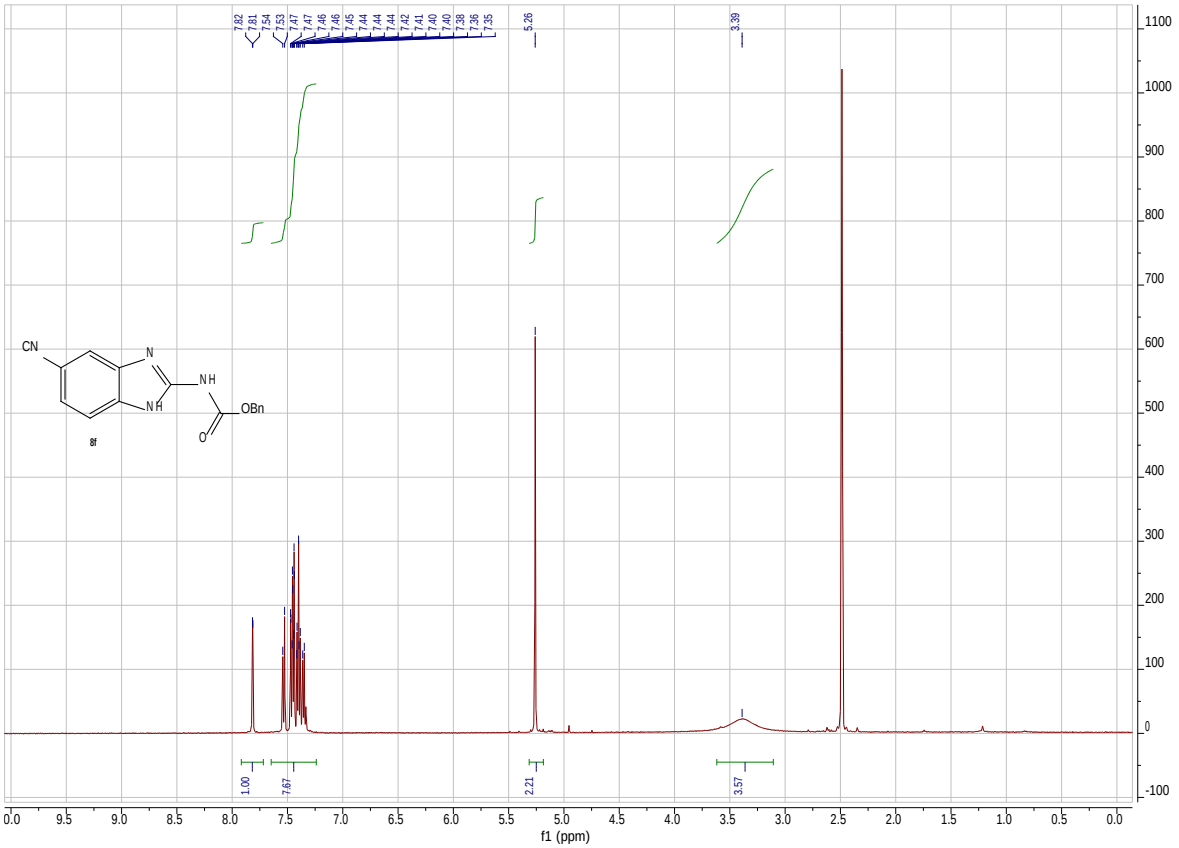
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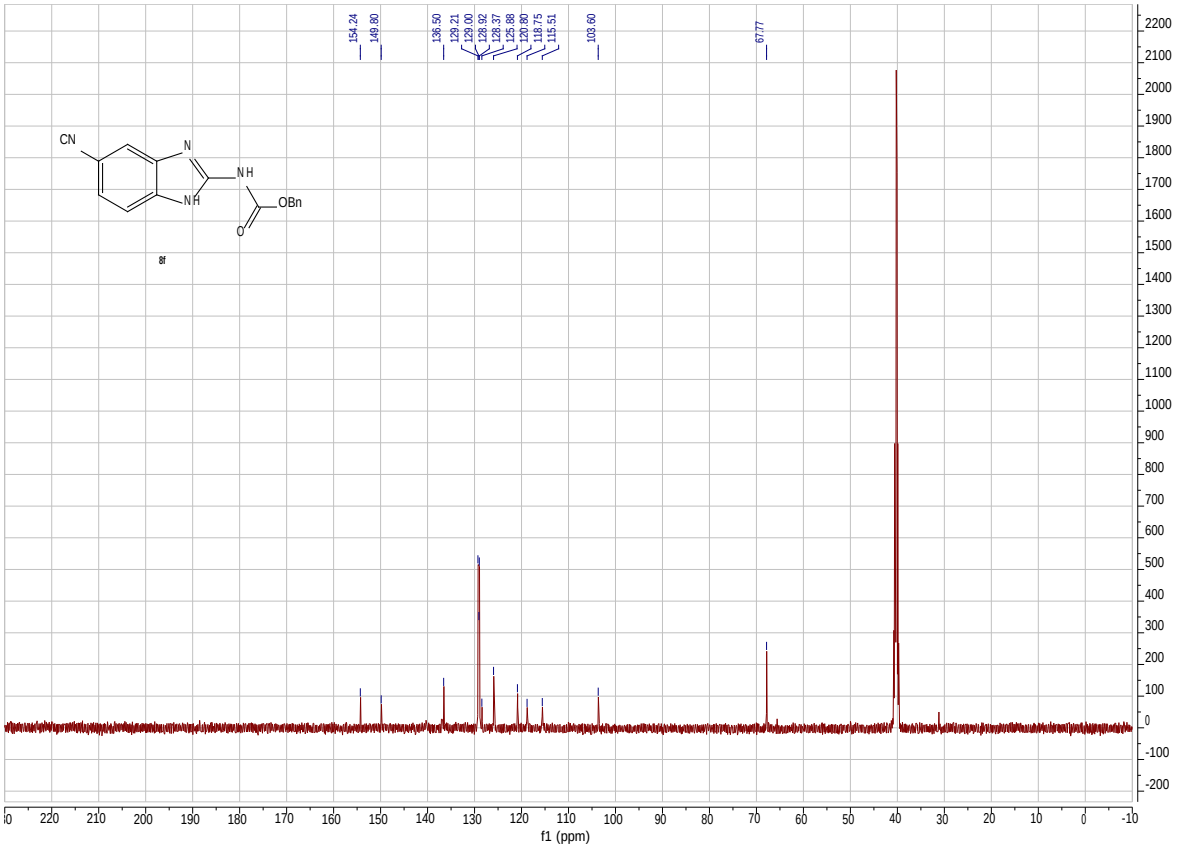
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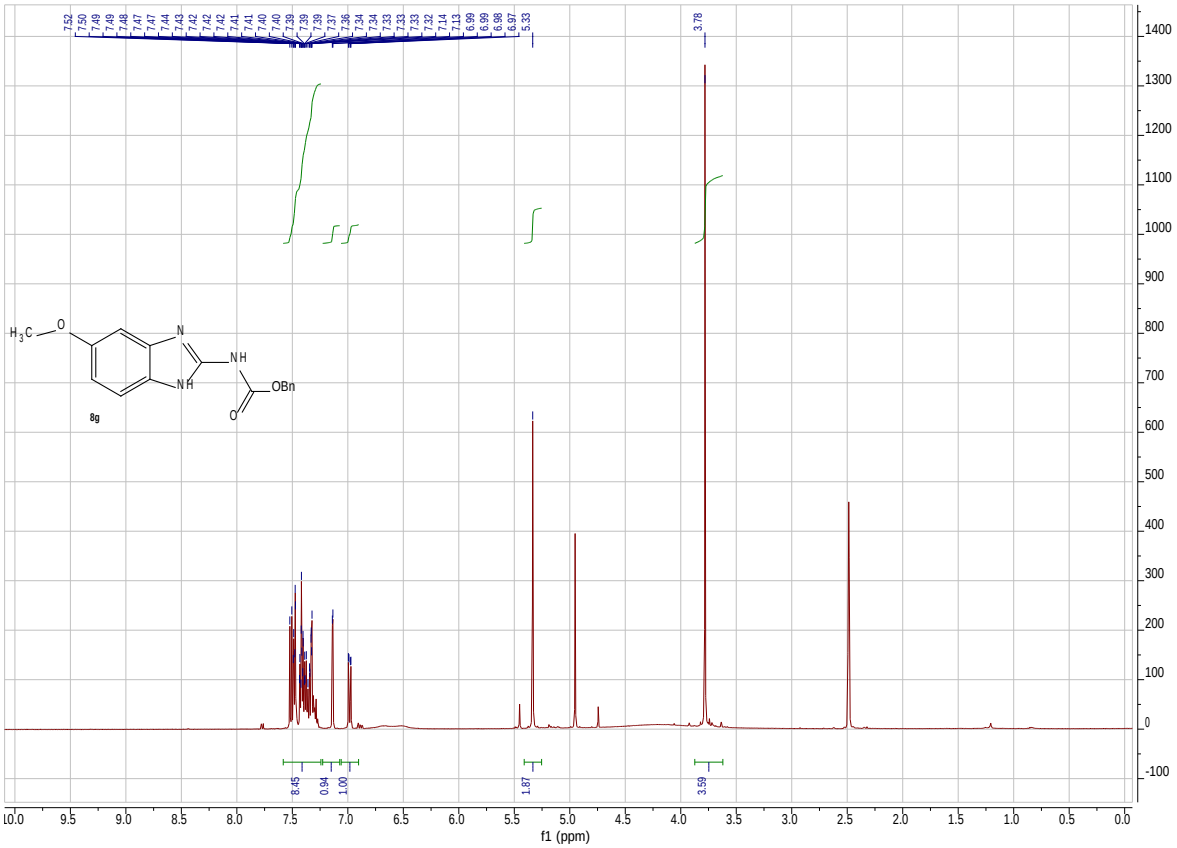
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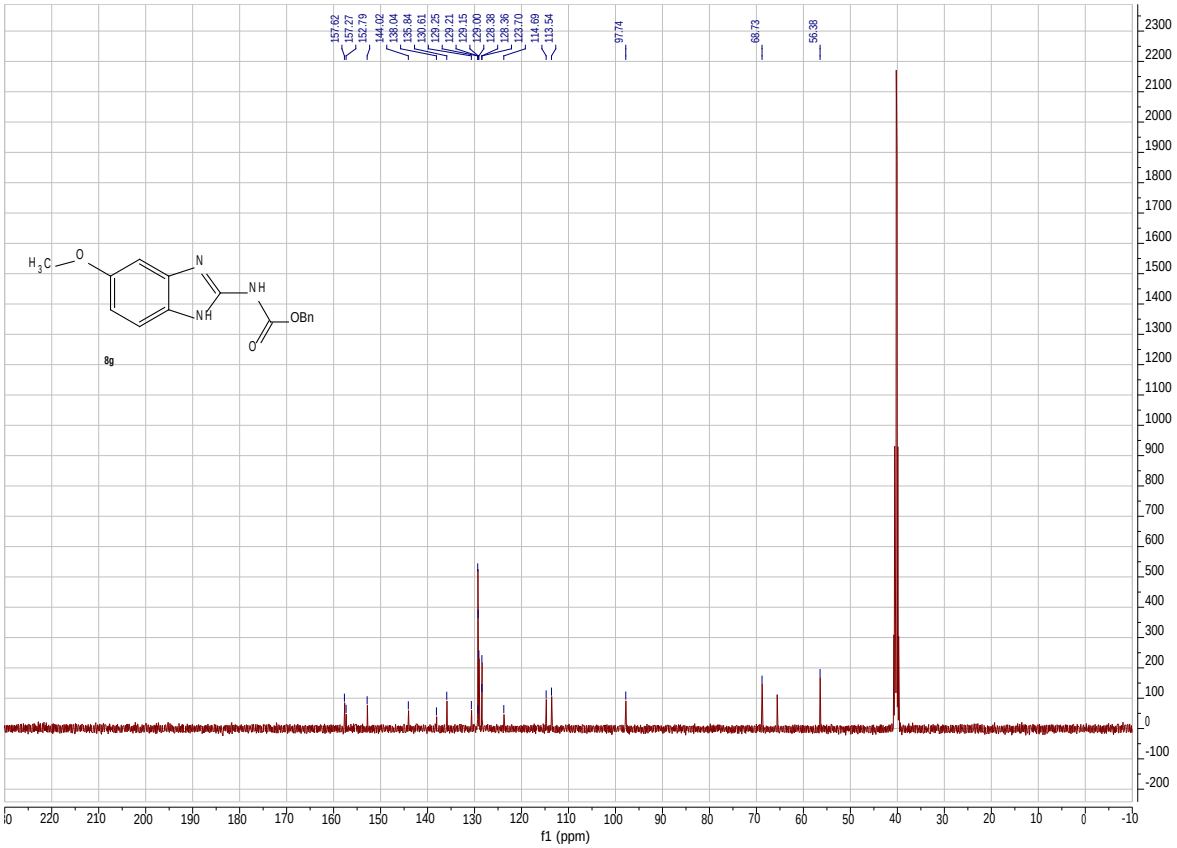
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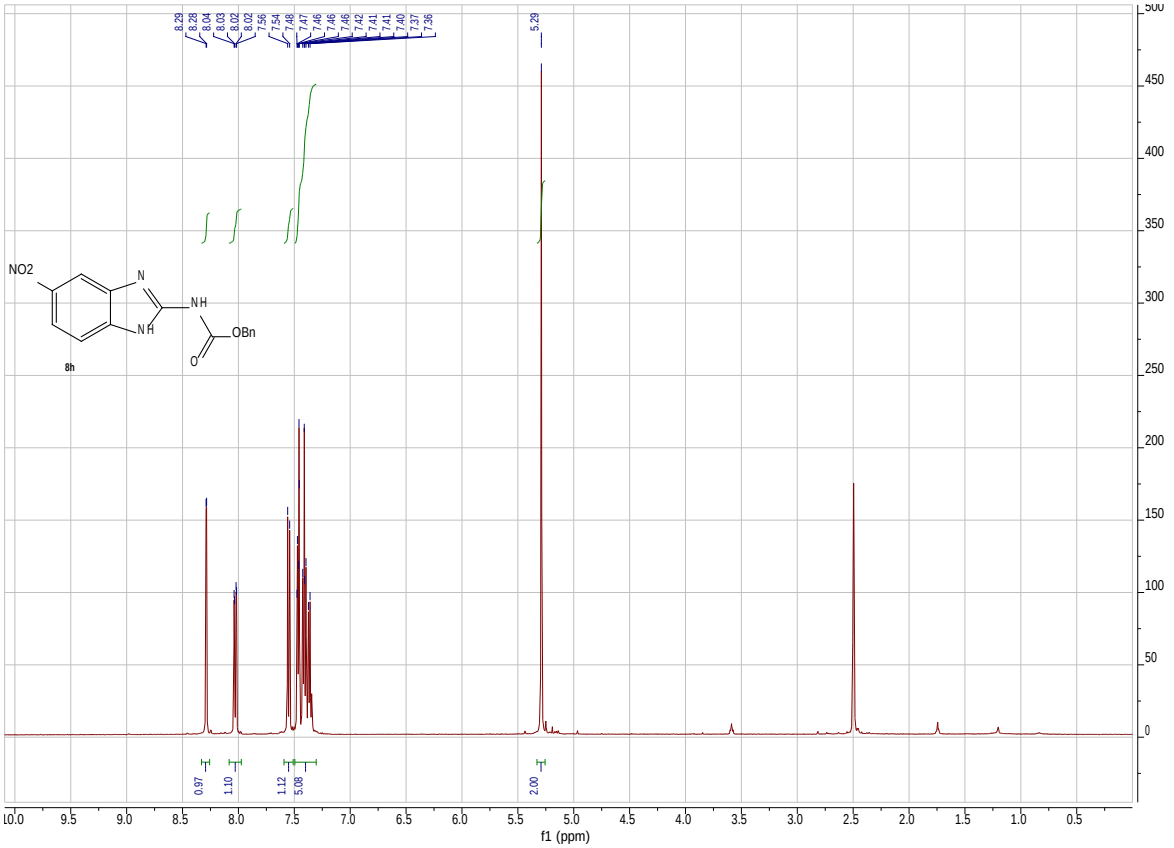
138.04
135.84
130.61
129.25
129.21
129.15
129.00
128.38
128.36
123.70
114.69
113.54
97.74
68.73
56.38
H3C
O
N
NH
NH
OBn
O
8g
f1 (ppm)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8.28
8.04
8.03
8.02
8.02
7.56
7.54
7.48
7.47
7.46
7.46
7.46
7.42
7.41
7.41
7.40
7.37
7.36
5.29
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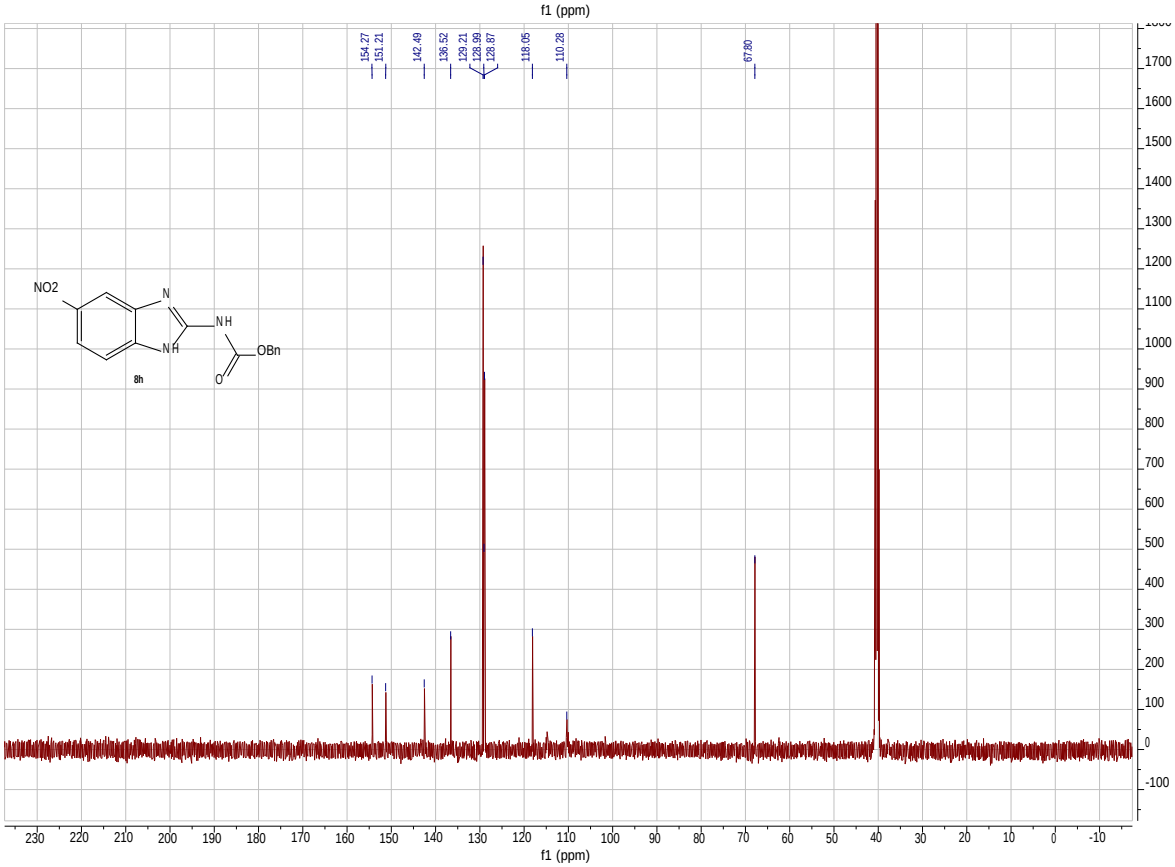
NH
NH
OBn
O
8h
0.97
1.10
1.12
5.08
2.00
f1 (ppm)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151.21
142.49
136.52
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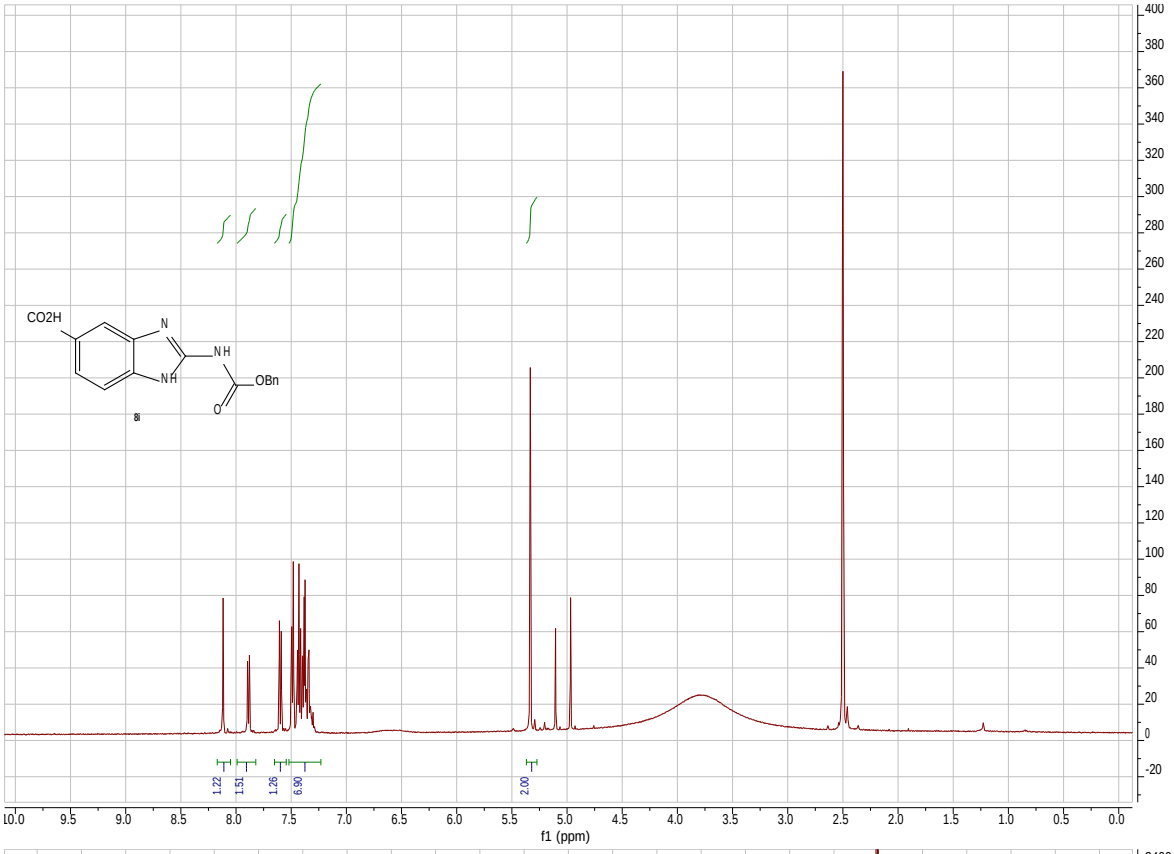
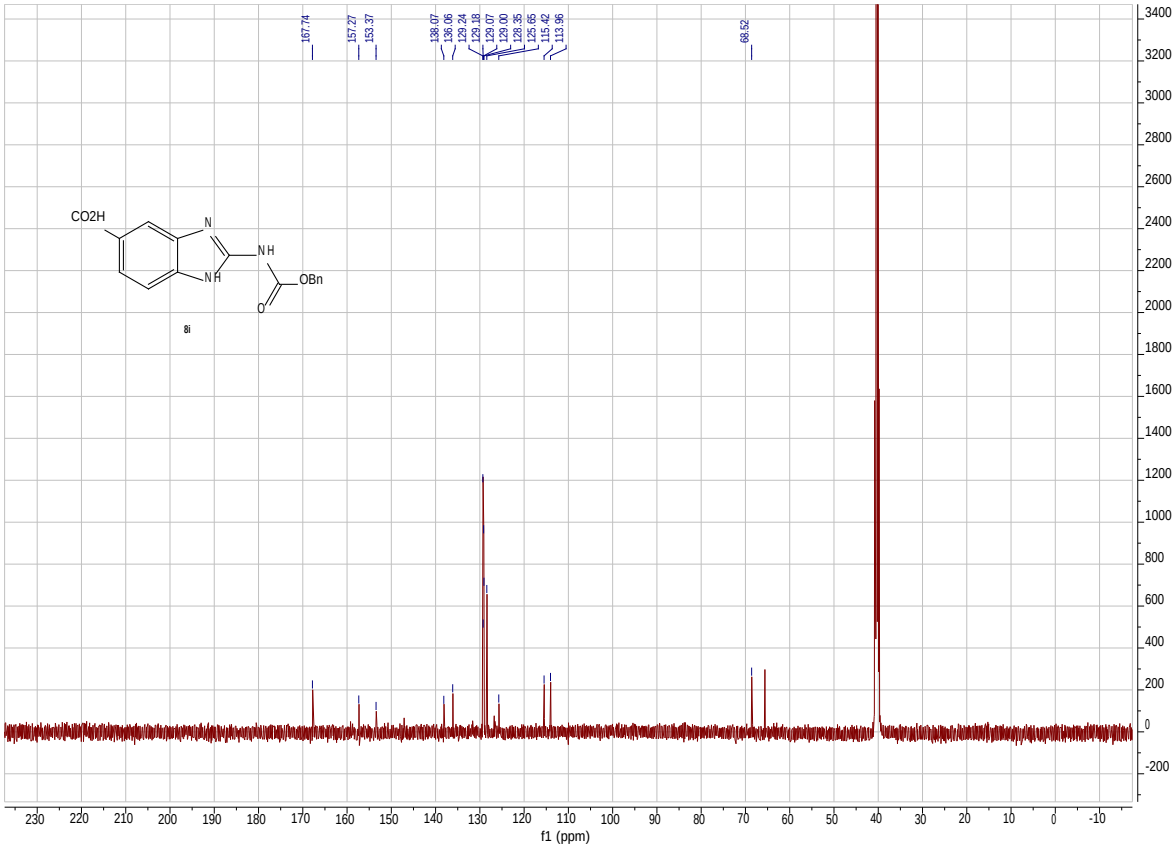
118.05
110.28
67.80
NO2
N
NH
NH
OBn
O
8h
f1 (ppm)


CO2H
N
NH
NH
OBn
O
8i
1.22
1.51
1.26
6.90
2.00
f1 (ppm)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138.07
136.06
129.24
129.18
129.07
129.00
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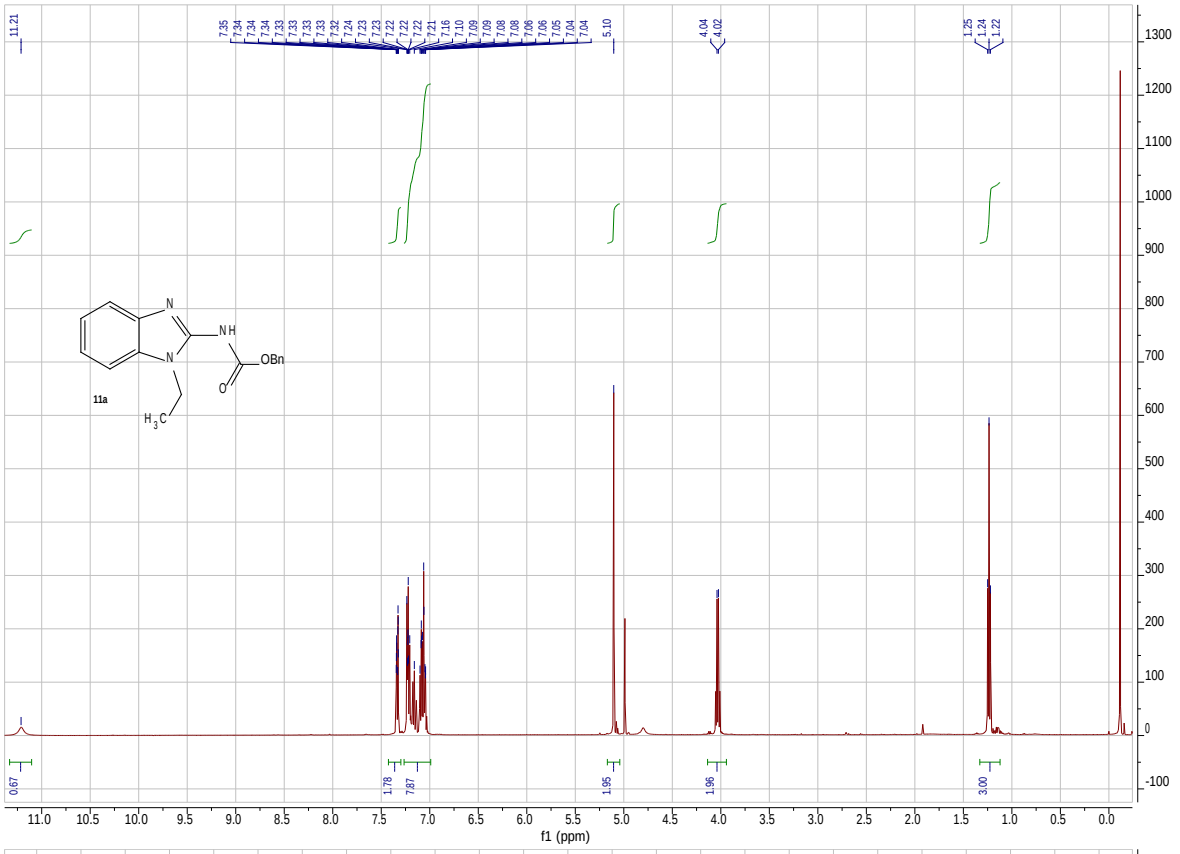
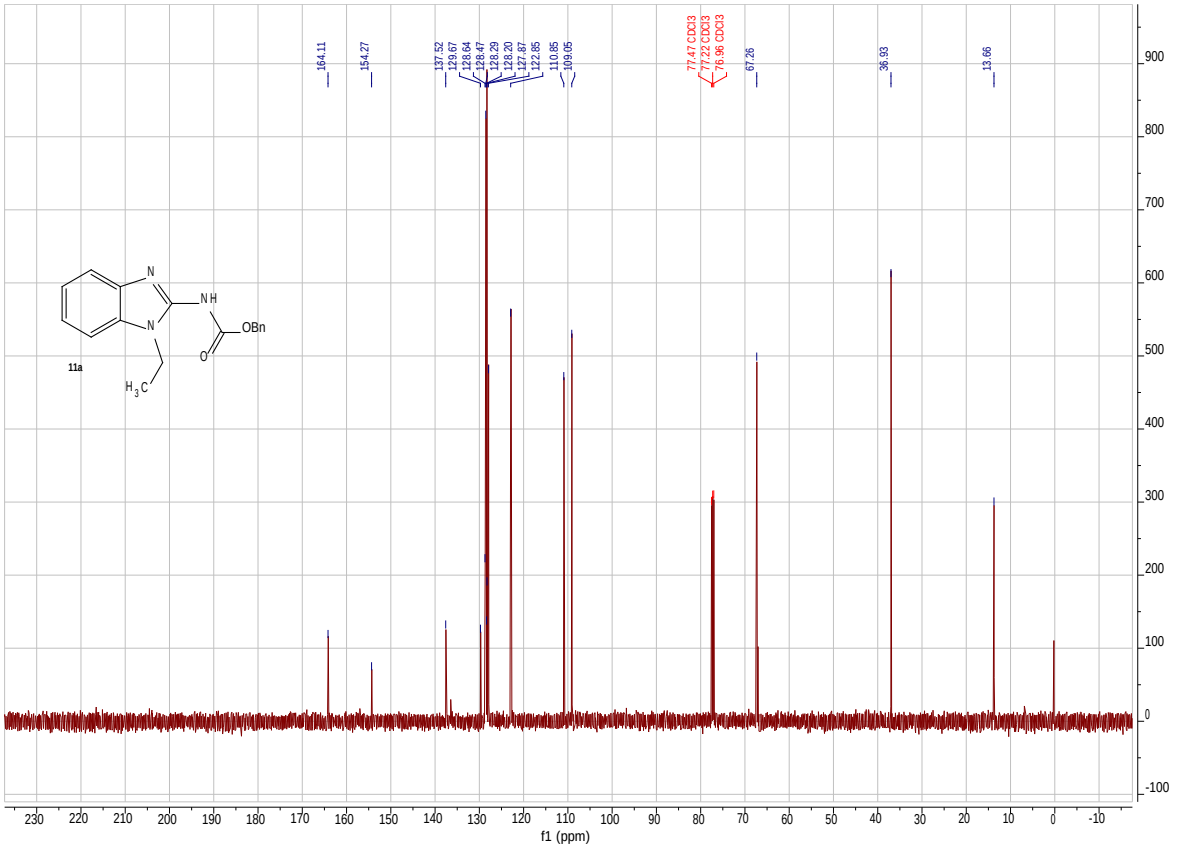
115.42
113.96
68.52
CO2H
N
NH
NH
OBn
O
8i
f1 (ppm)


11.21
7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.16 7.10 7.09 7.09 7.08 7.08 7.06 7.06 7.05 7.04 7.04
5.10
4.04 4.02
1.25 1.24 1.22
N
NH
N
OBn
O
11a
H3C
0.67
1.78
7.87
1.95
1.96
3.00
f1 (ppm)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154.27
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128.20
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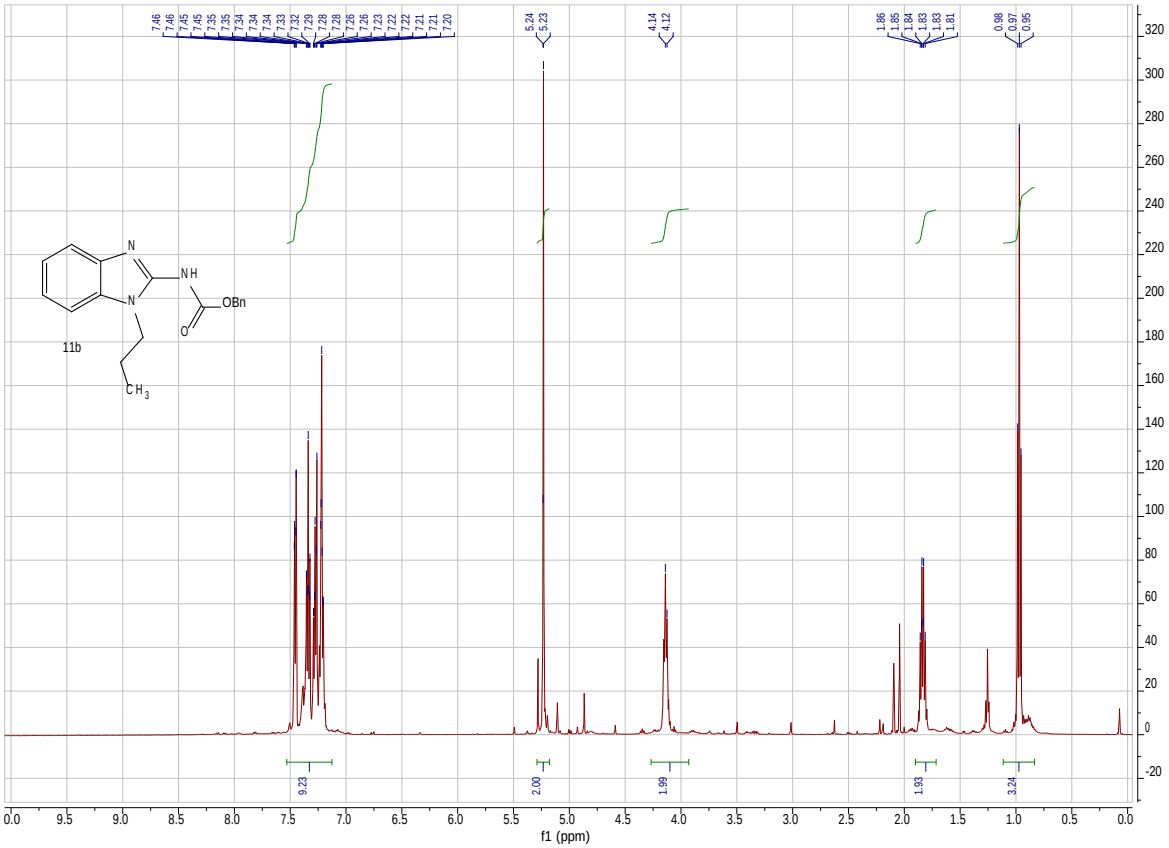
122.85
110.85
109.05
77.47 CDCl3
77.22 CDCl3
76.96 CDCl3
67.26
36.93
13.66
N
NH
N
OBn
O
11a
H3C
f1 (ppm)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7.35
7.34
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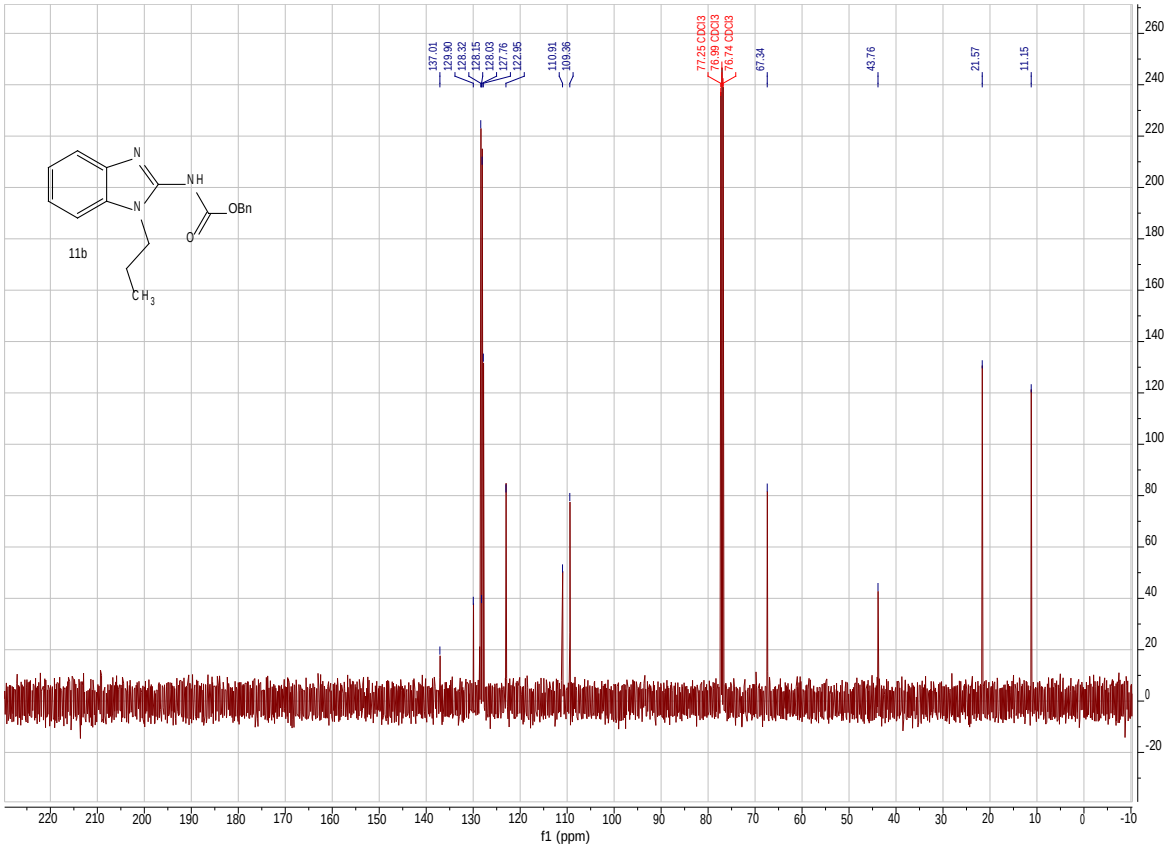
7.33
7.32
7.29
7.28
7.28
7.26
7.26
7.23
7.22
7.22
7.21
7.21
7.20
5.24
5.23
4.14
4.12
1.86
1.85
1.84
1.83
1.83
1.81
0.98
0.97
0.95
N
NH
OBn
O
11b
CH3
9.23
2.00
1.99
1.93
3.24
f1 (ppm)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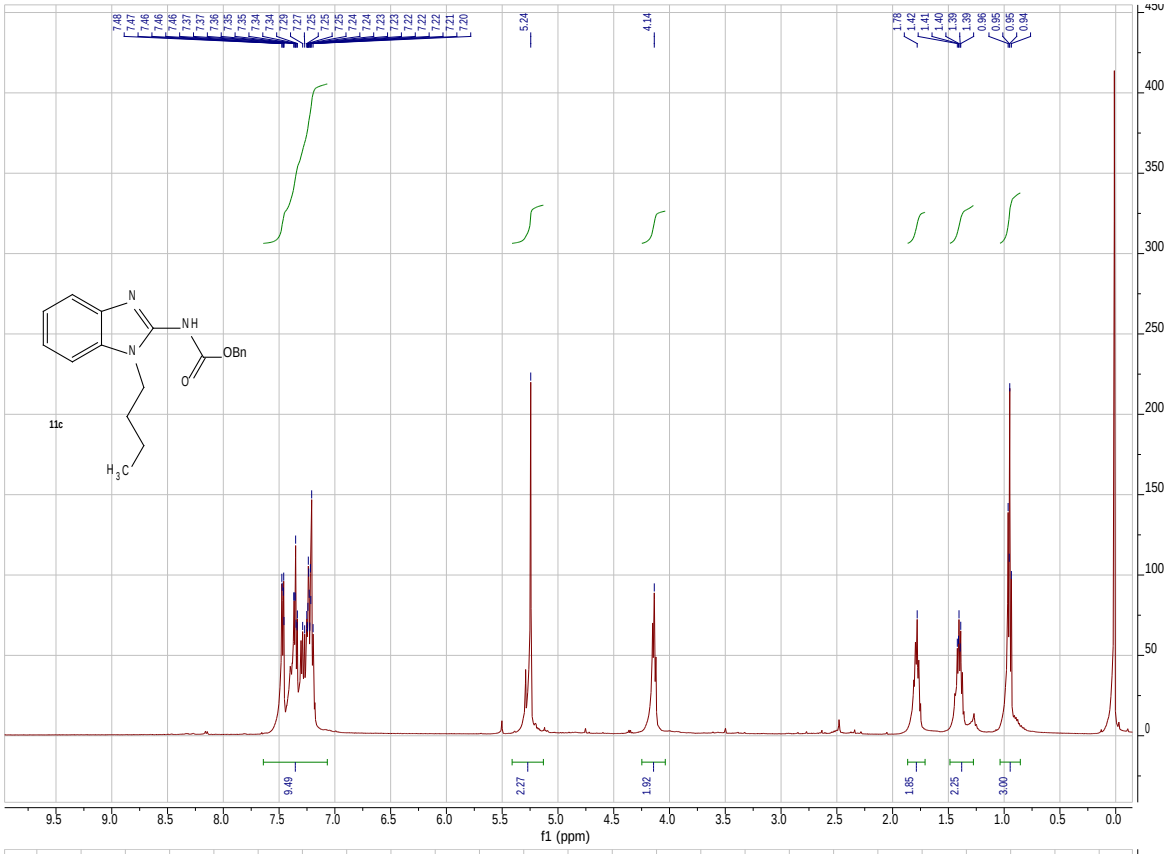
128.03
127.76
122.95
110.91
109.36
77.25 CDCl3
76.99 CDCl3
76.74 CDCl3
67.34
43.76
21.57
11.15
N
NH
OBn
O
11b
CH3
f1 (ppm)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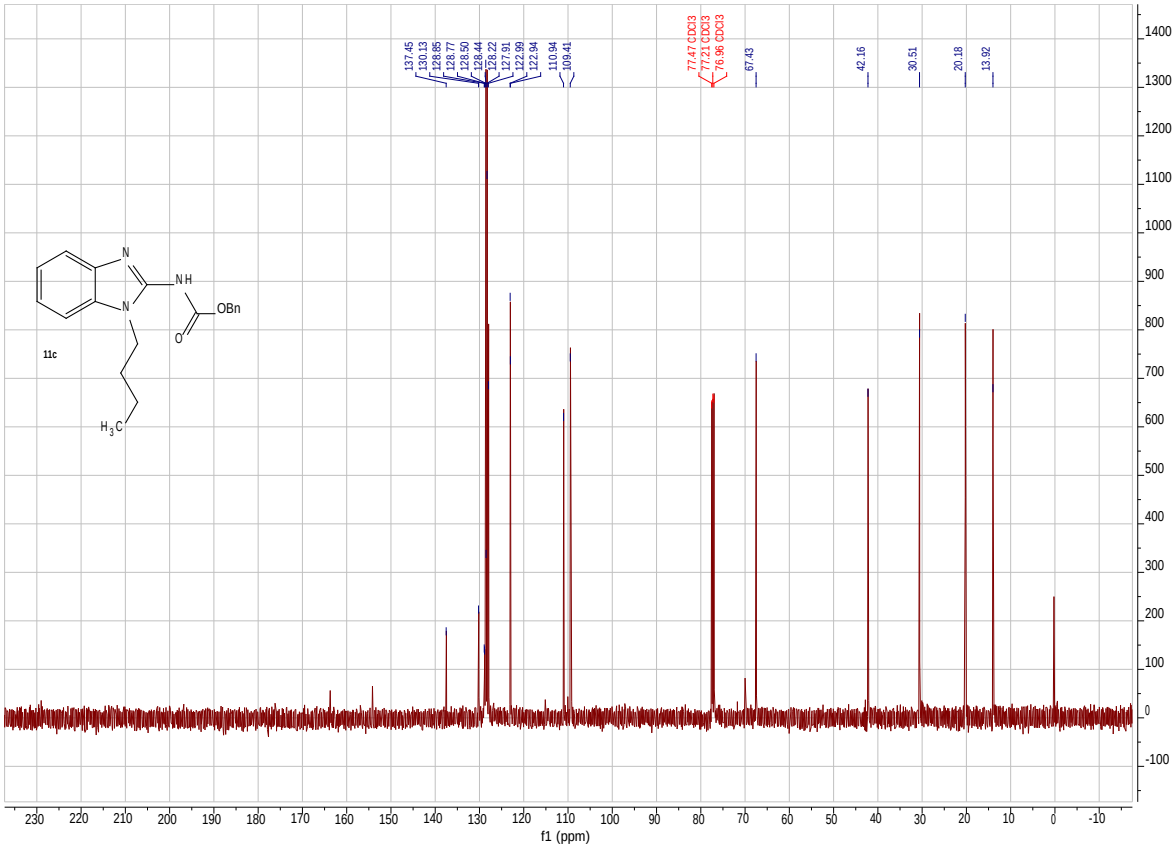
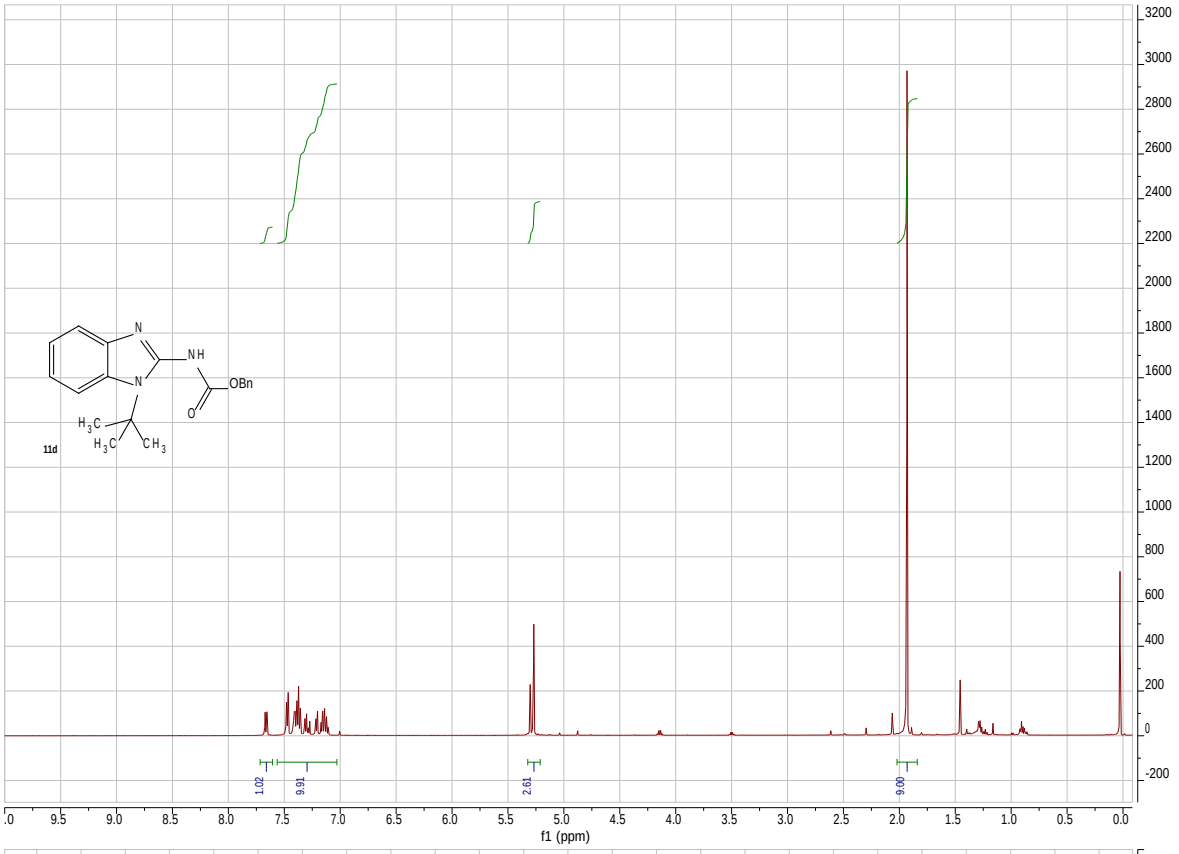
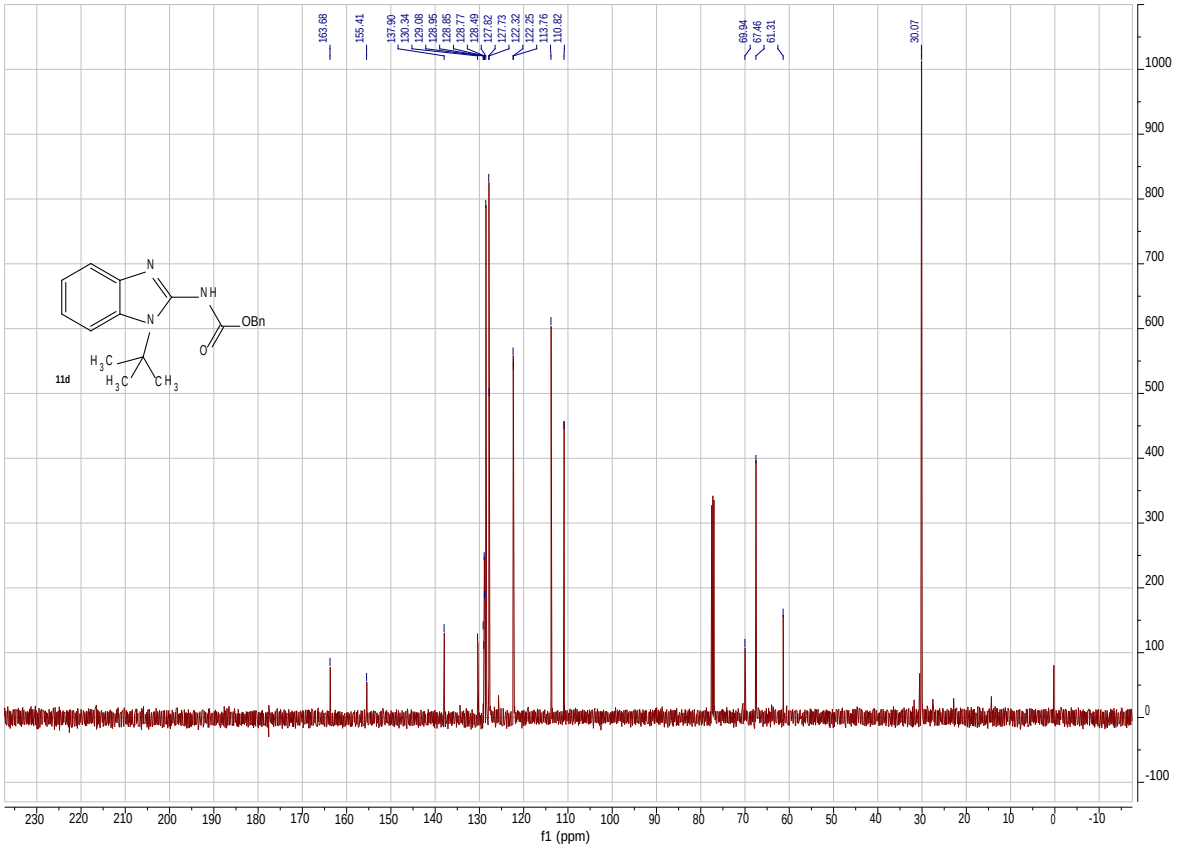
7.47
7.46
7.46
7.46
7.46
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.29
7.27
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
5.24
4.14
1.78
1.42
1.41
1.40
1.39
1.39
0.96
0.95
0.95
0.94
N
NH
N
OBn
O
11c
H3C
9.49
2.27
1.92
1.85
2.25
3.00
f1 (ppm)


137.45
130.13
129.85
128.77
128.50
128.44
128.22
127.91
122.90
122.94
110.94
109.41
77.47 CDCl3
77.21 CDCl3
76.96 CDCl3
67.43
42.16
30.51
20.18
13.92
N
NH
N
OBn
O
11c
H3C
f1 (ppm)


N
NH
N
OBn
O
H3C
H3C
CH3
11d
1.02
9.91
2.61
9.00
f1 (ppm)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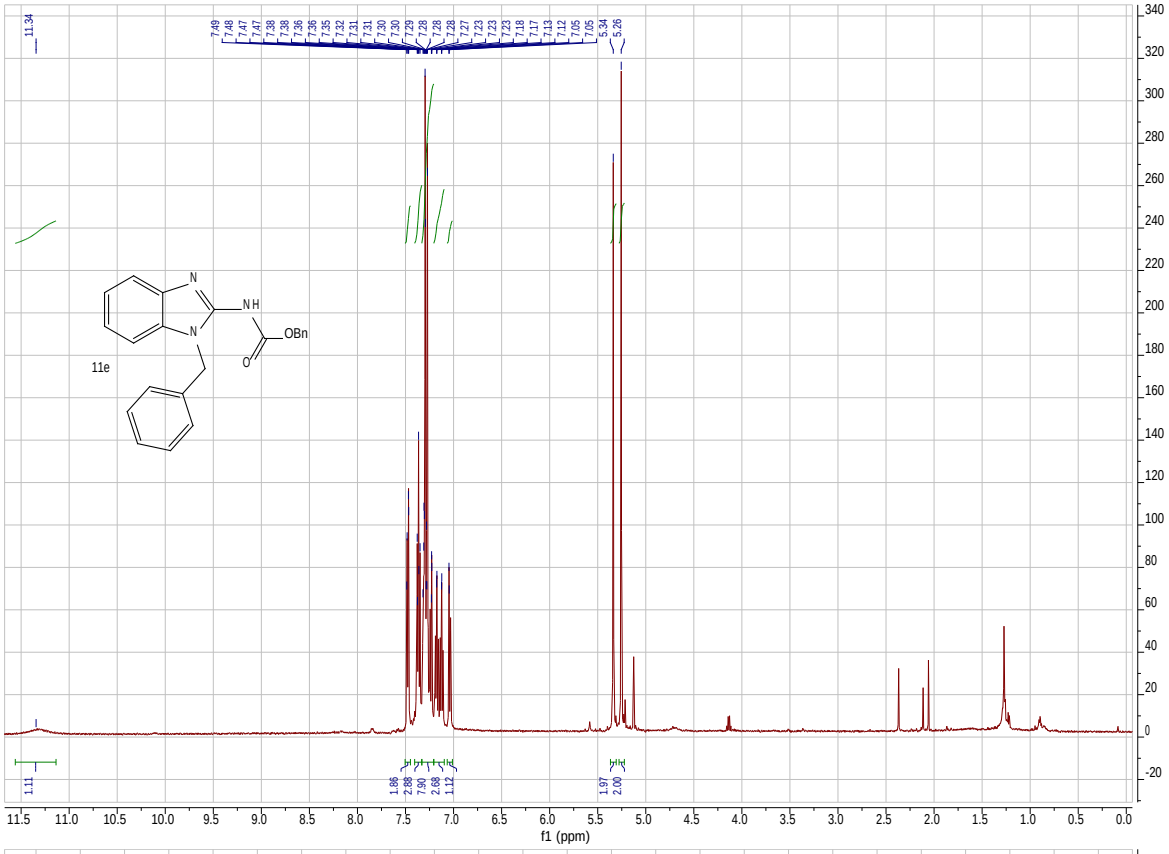
155.41
137.90
130.34
129.08
128.95
128.85
128.77
128.49
127.82
127.73
122.32
122.25
113.76
110.82
69.94
67.46
61.31
30.07
N
NH
N
OBn
O
H3C
H3C
CH3
11d
f1 (ppm)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7.49
7.48
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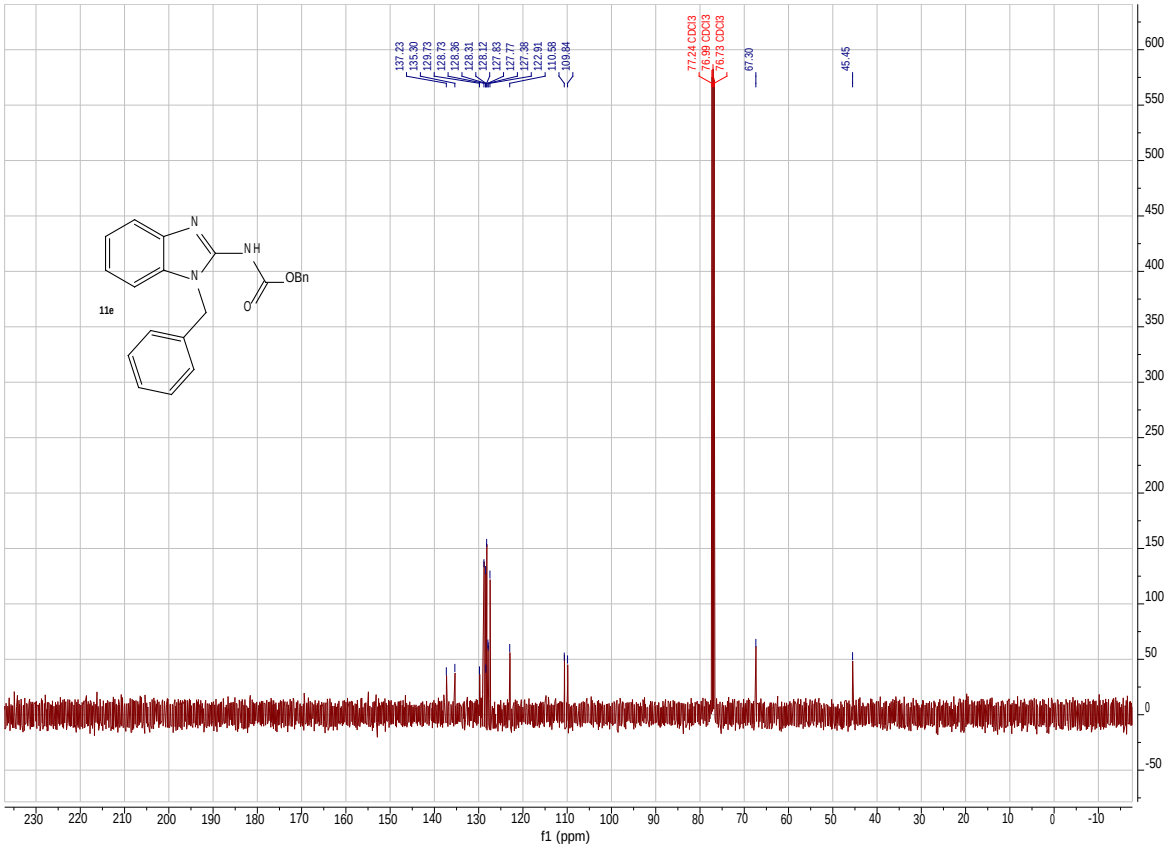
7.47
7.38
7.38
7.36
7.36
7.35
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.27
7.23
7.23
7.23
7.18
7.17
7.13
7.12
7.05
7.05
5.34
5.26
N
NH
N
OBn
O
11e
1.11
1.86
2.88
7.90
2.68
1.12
1.97
2.00
f1 (ppm)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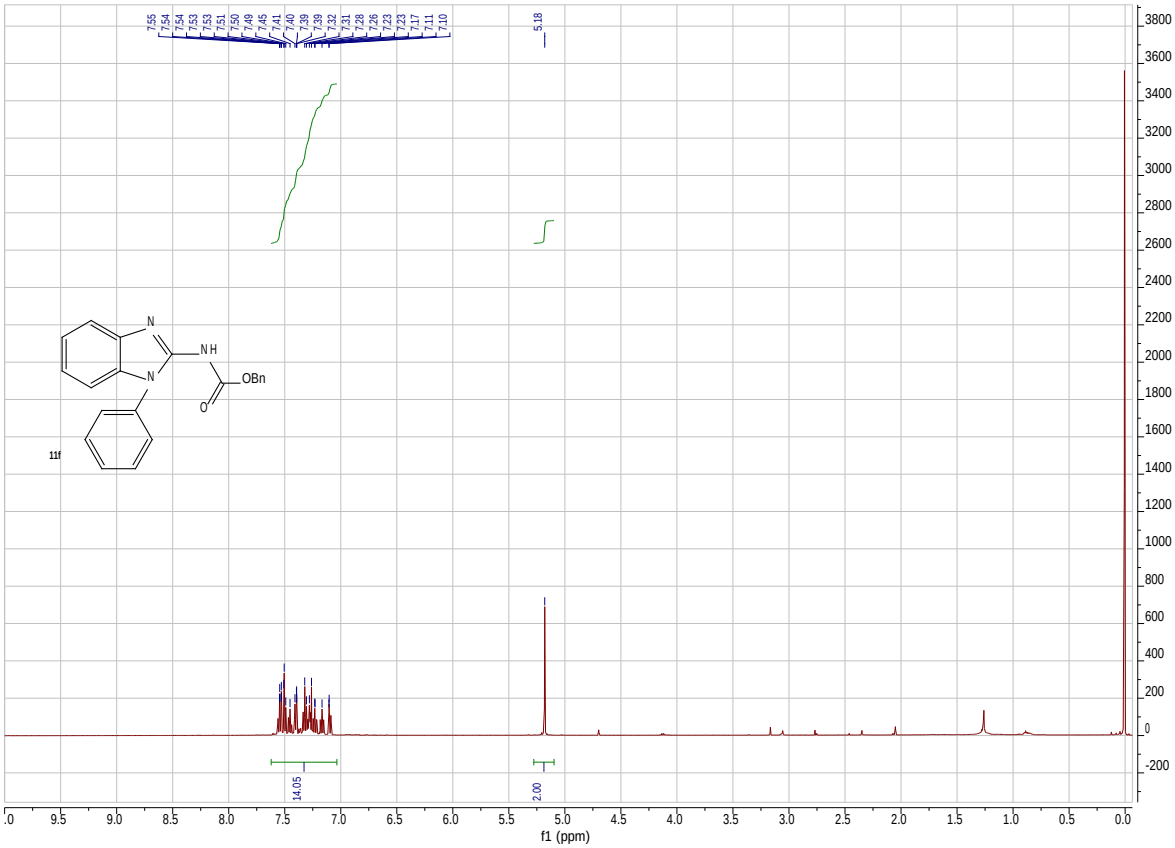
135.30
129.73
128.73
128.36
128.31
128.12
127.83
127.77
127.38
122.91
110.58
109.84
77.24 CDCl3
76.99 CDCl3
76.73 CDCl3
67.30
45.45
N
NH
N
OBn
O
11e
f1 (ppm)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7.54
7.54
7.53
7.53
7.51
7.50
7.49
7.45
7.41
7.40
7.39
7.39
7.32
7.31
7.28
7.26
7.23
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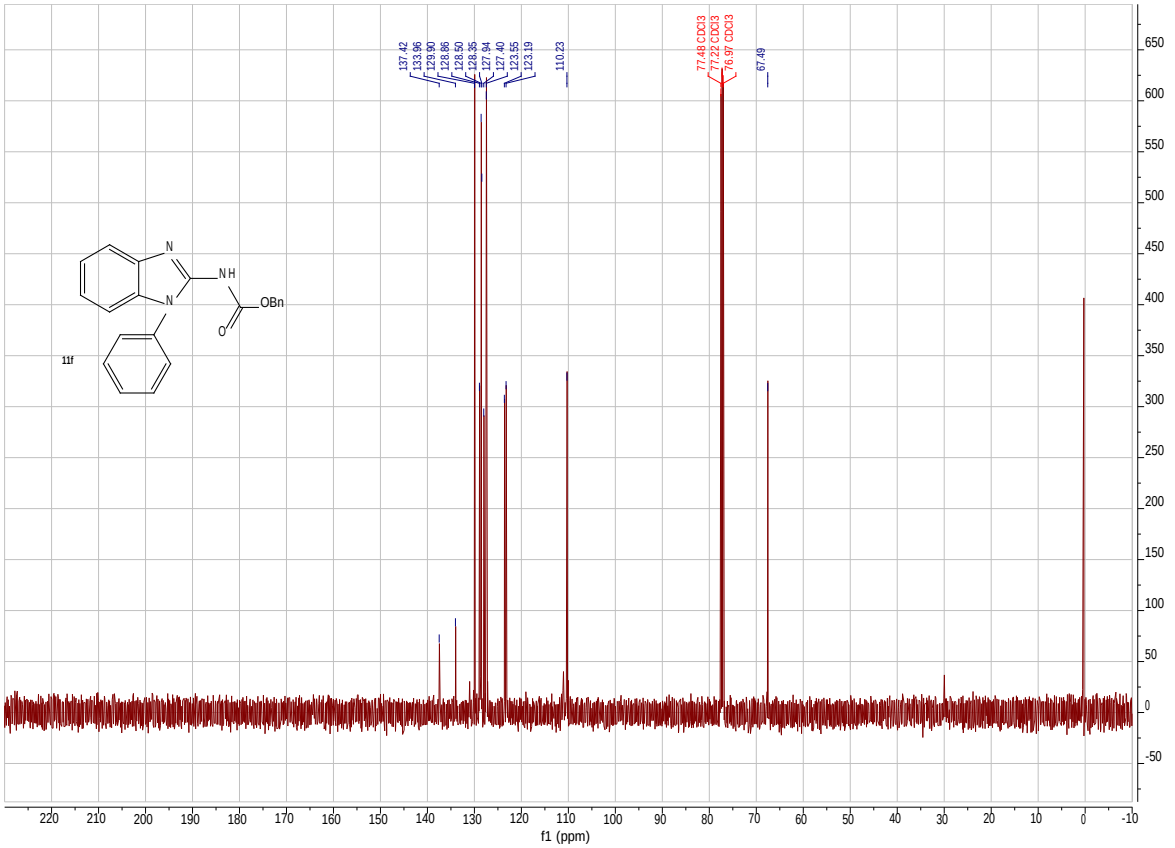
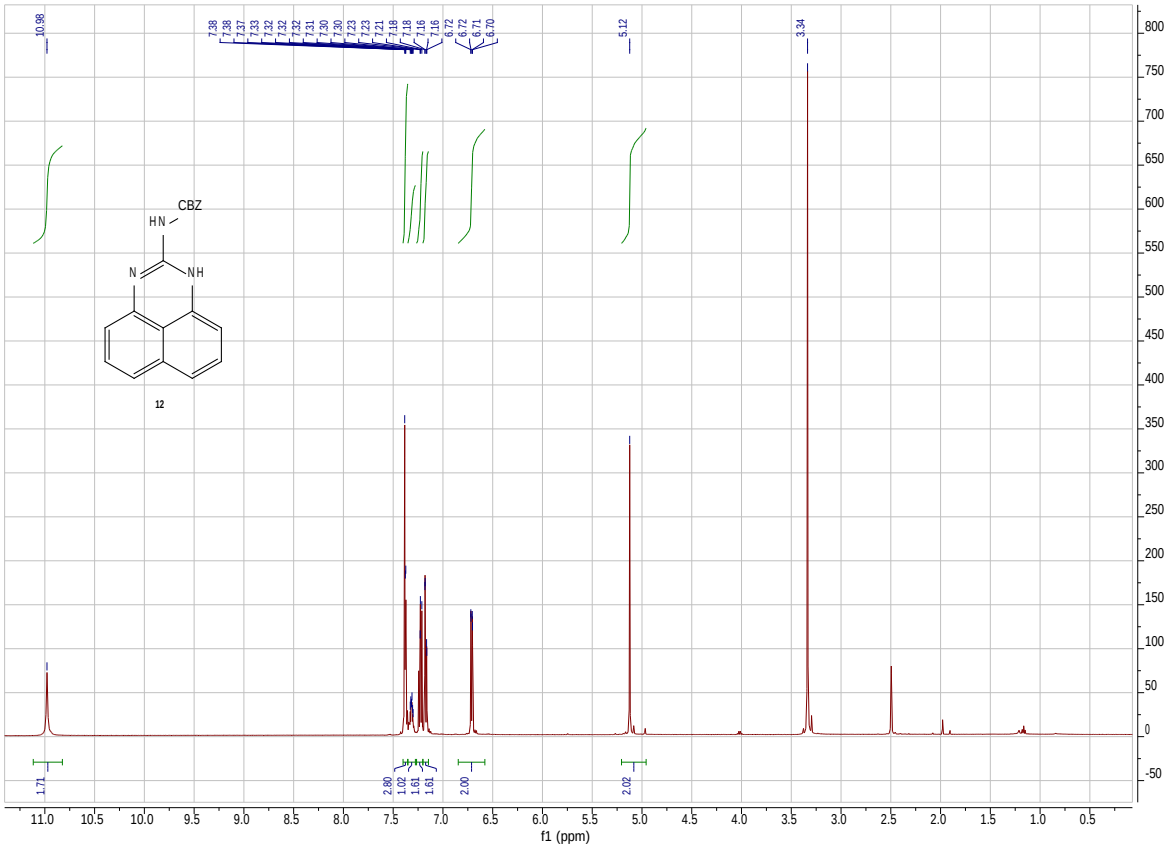
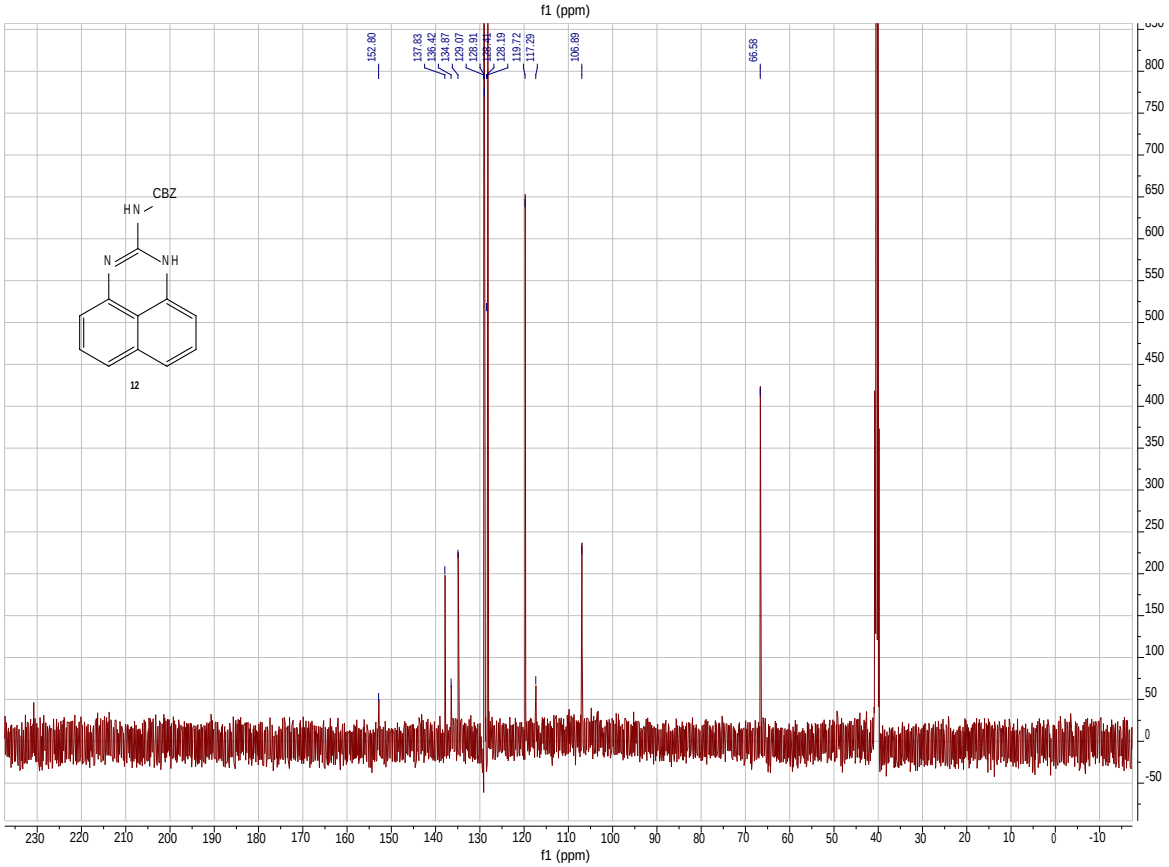
OBn
O
11f
14.05
2.00
f1 (ppm)


137.42
133.96
129.90
128.86
128.50
128.35
127.94
127.40
123.55
123.19
110.23
77.48 CDCl3
77.22 CDCl3
76.97 CDCl3
67.49
N
NH
N
OBn
O
11f
f1 (ppm)


10.98
7.38
7.38
7.37
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.23
7.23
7.21
7.18
7.18
7.16
7.16
6.72
6.72
6.71
6.70
5.12
3.34
CBZ
HN
N
NH
12
1.71
2.80
1.02
1.61
1.61
2.00
2.02
f1 (ppm)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137.83
136.42
134.87
129.07
128.91
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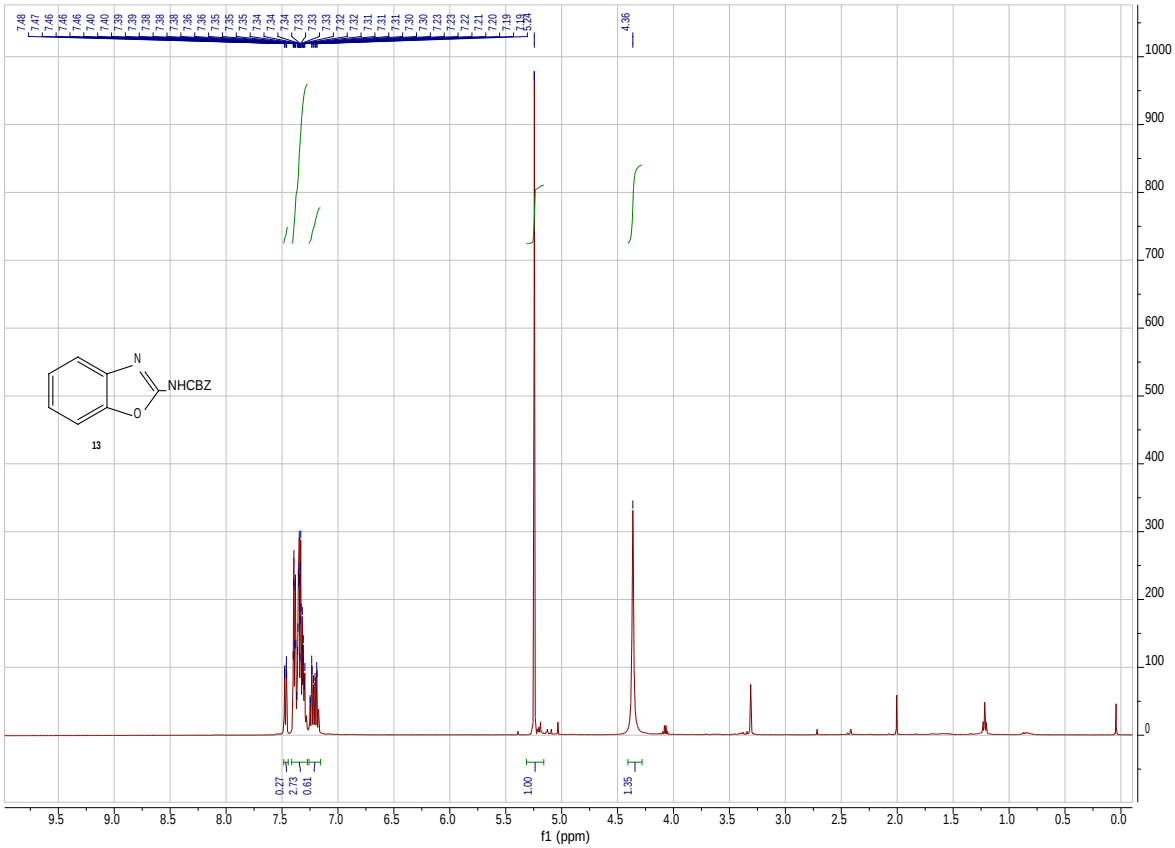
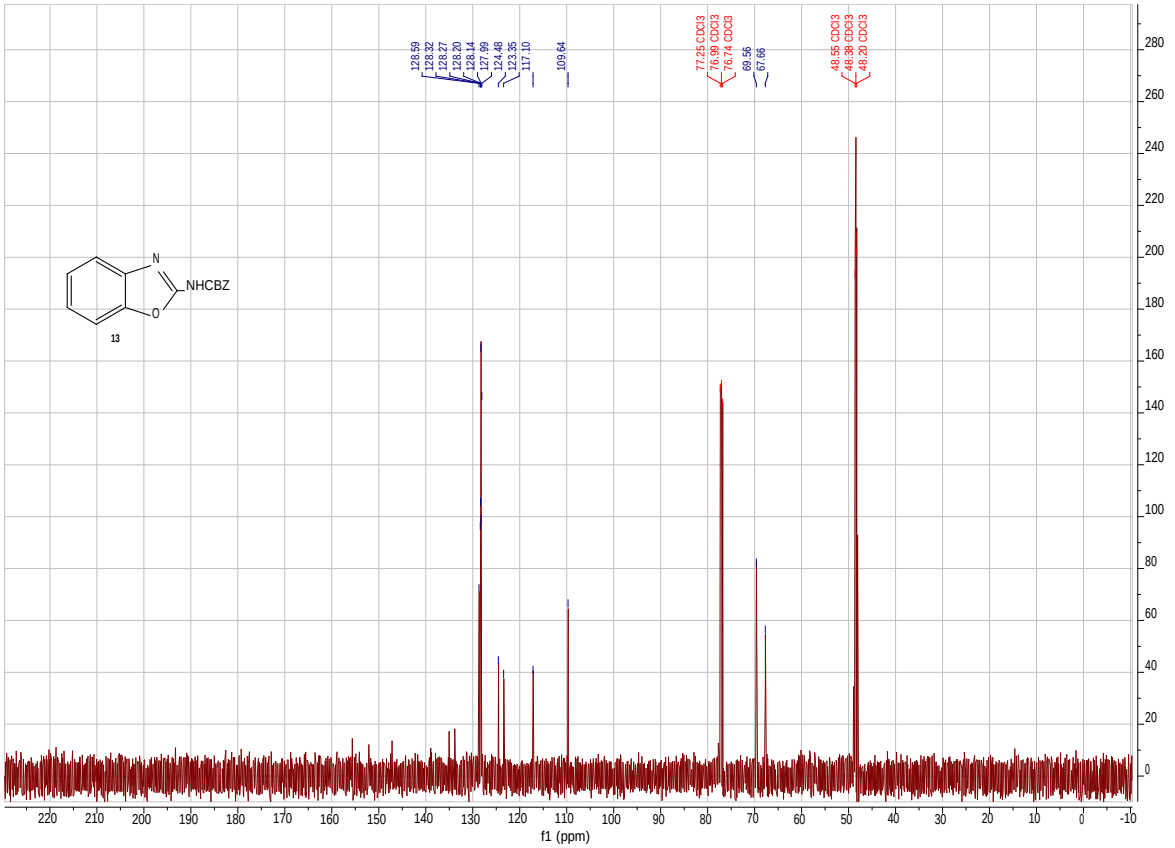
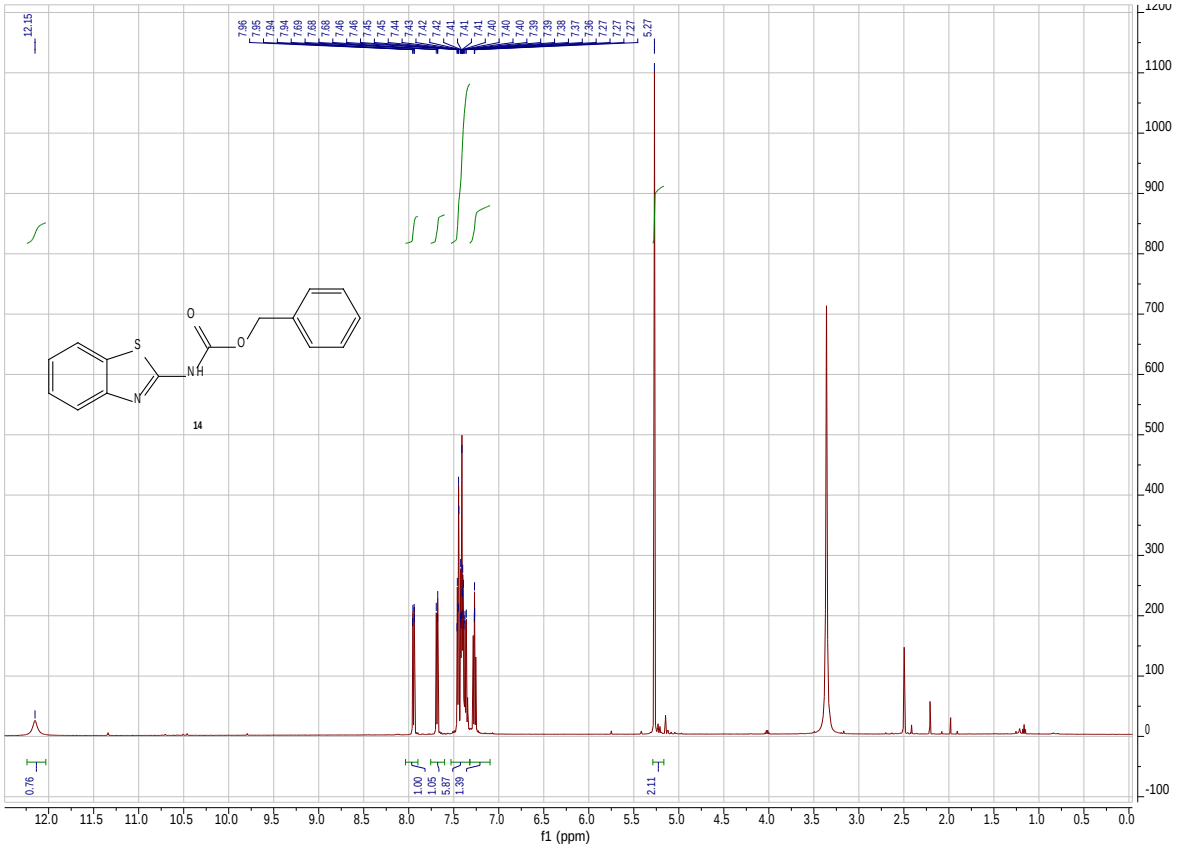
128.19
119.72
117.29
106.89
66.58
CBZ
HN
N
NH
12
f1 (ppm)


NHCBZ
13
f1 (ppm)


NHCBZ
13
f1 (ppm)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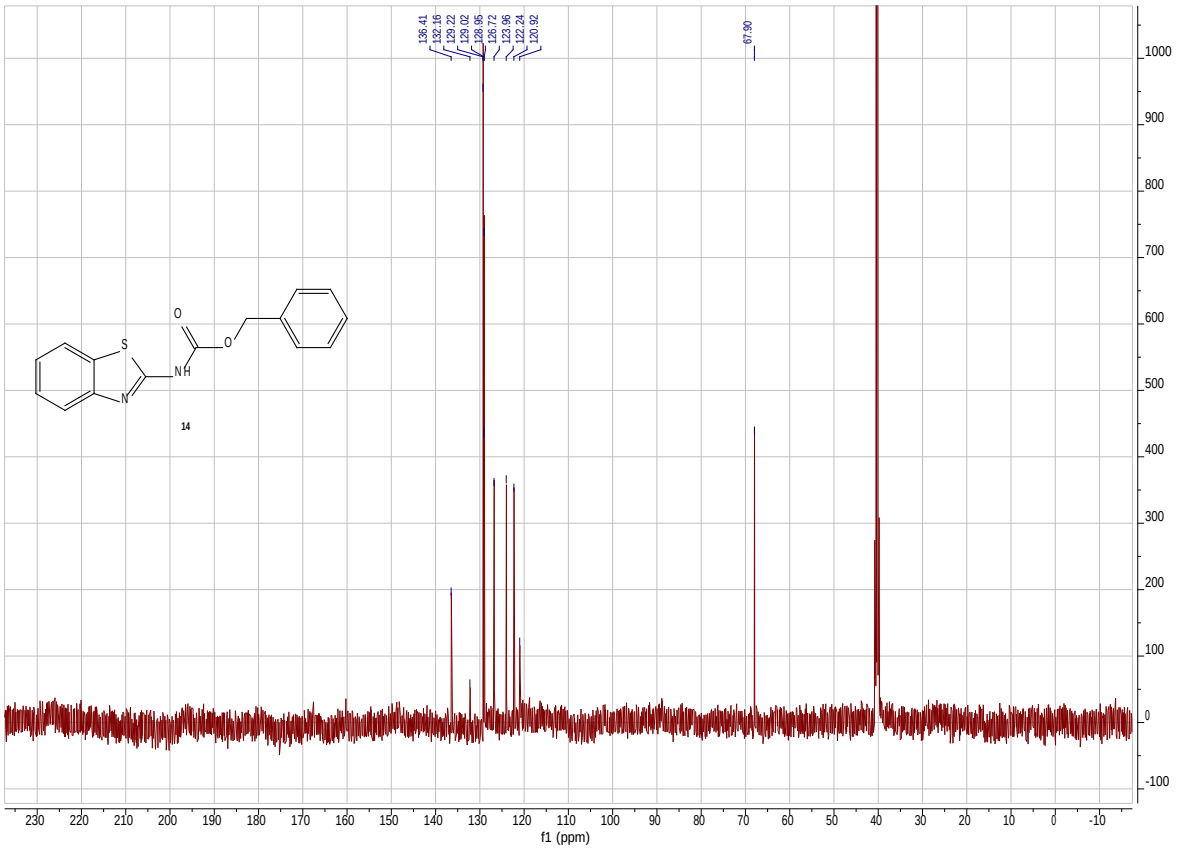
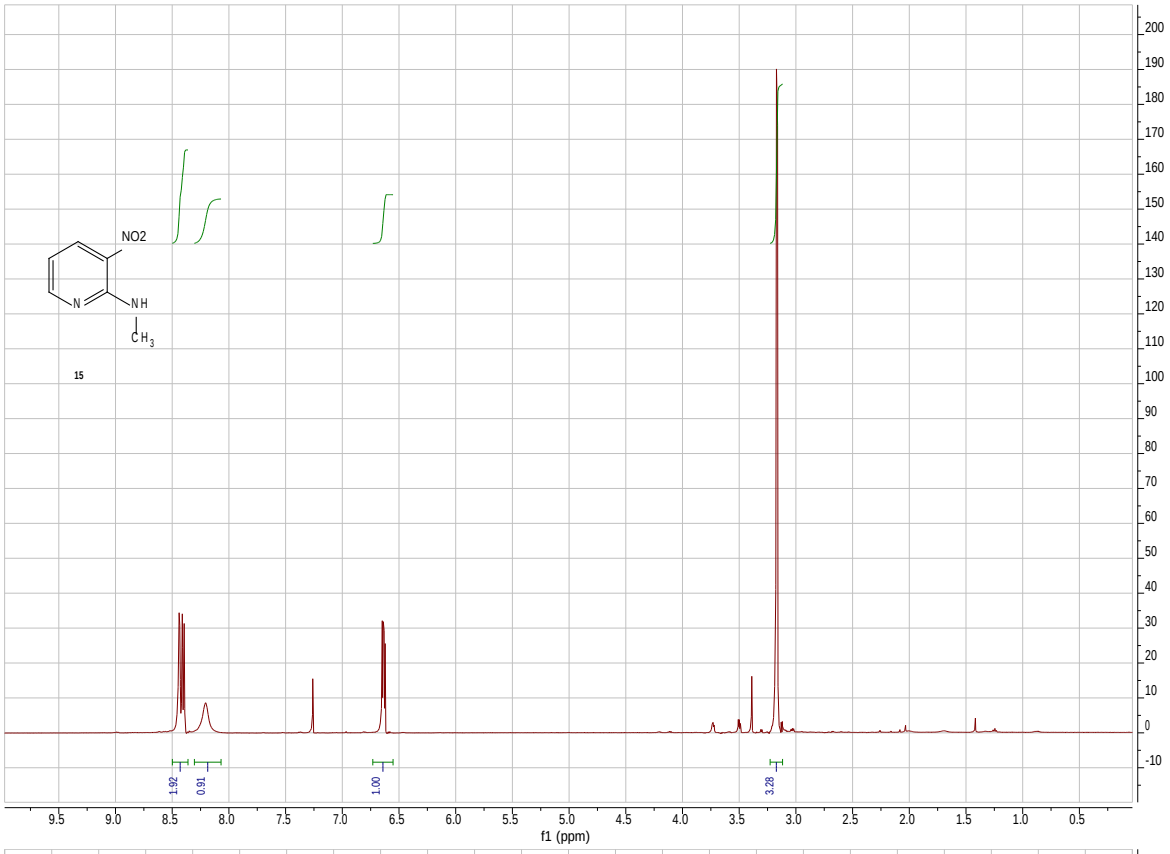
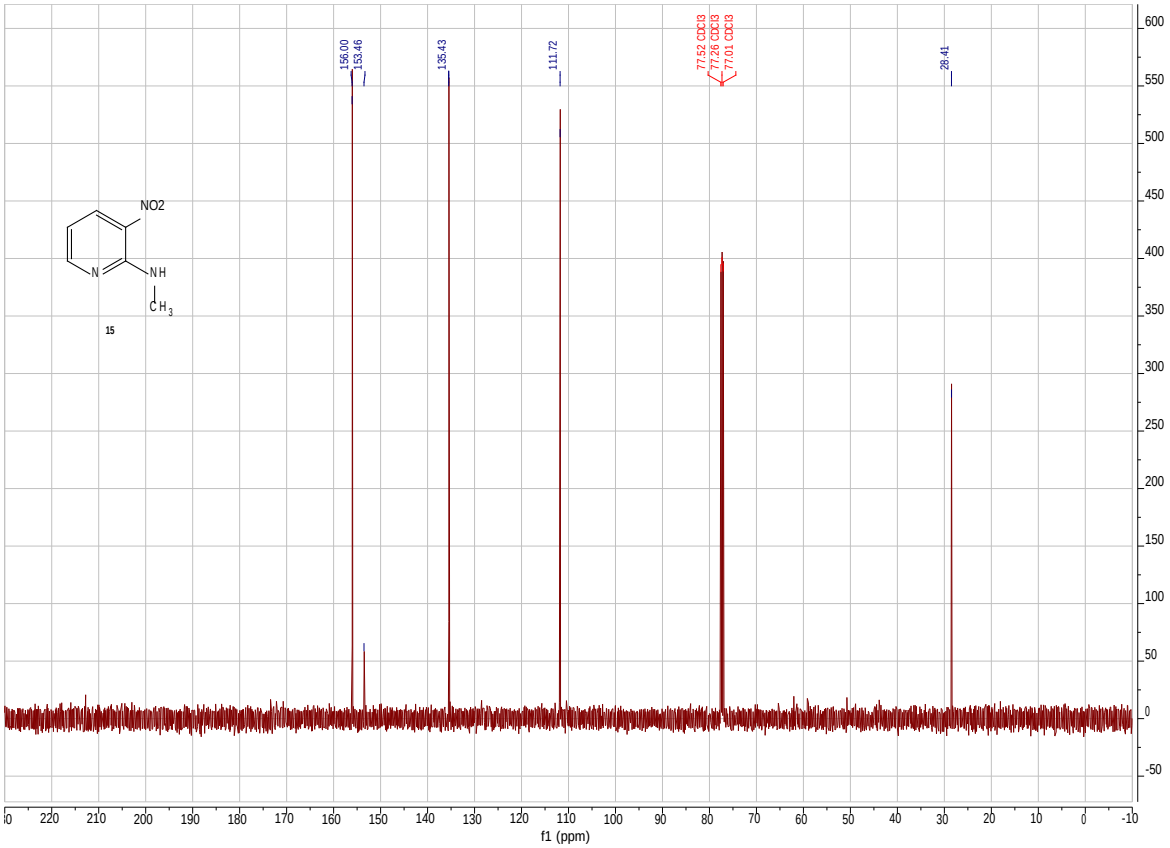
7.96
7.95
7.94
7.94
7.69
7.68
7.68
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.27
7.27
7.27
5.27
0.76
1.00
1.05
5.87
1.39
2.11
14
f1 (ppm)


136.41
132.45
132.22
129.22
128.95
126.72
123.96
122.24
120.92
67.90
14
f1 (ppm)


NO2
N
NH
CH3
15
1.92
0.91
1.00
3.28
f1 (ppm)


NO2
N
NH
CH3
15
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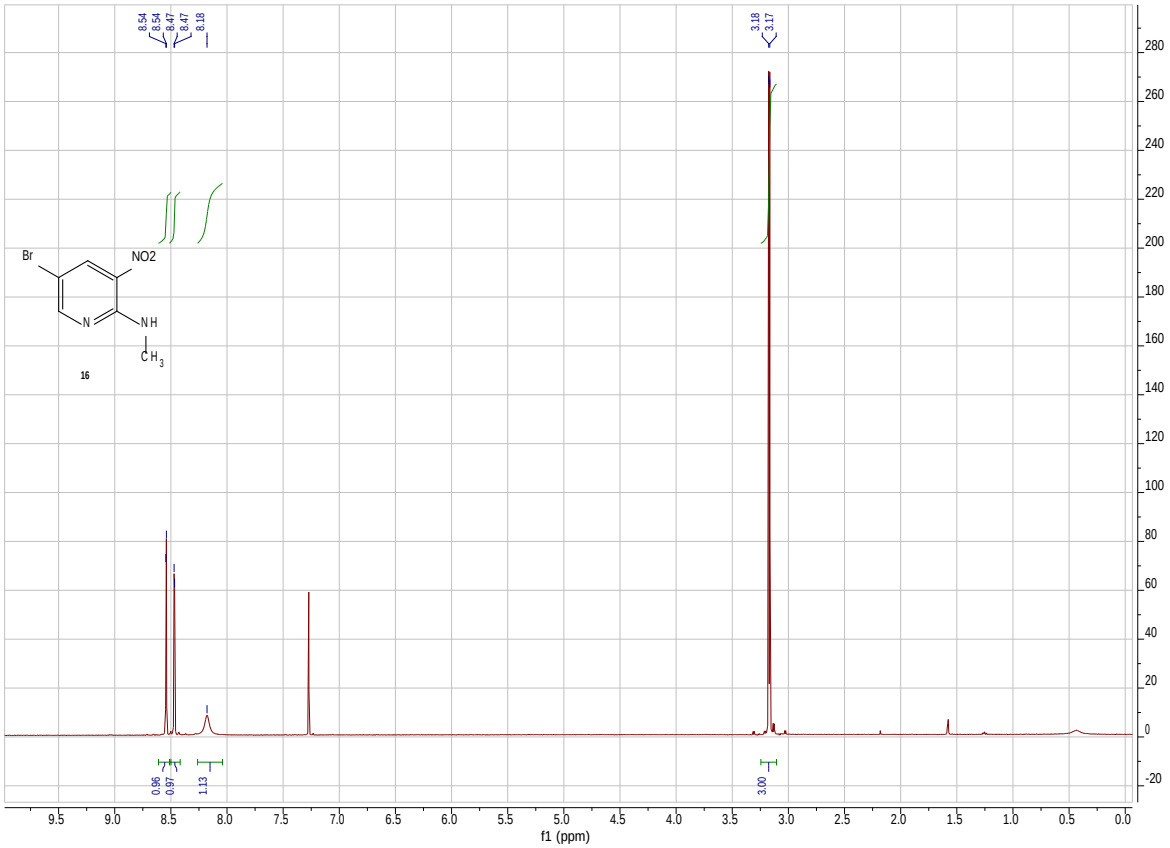
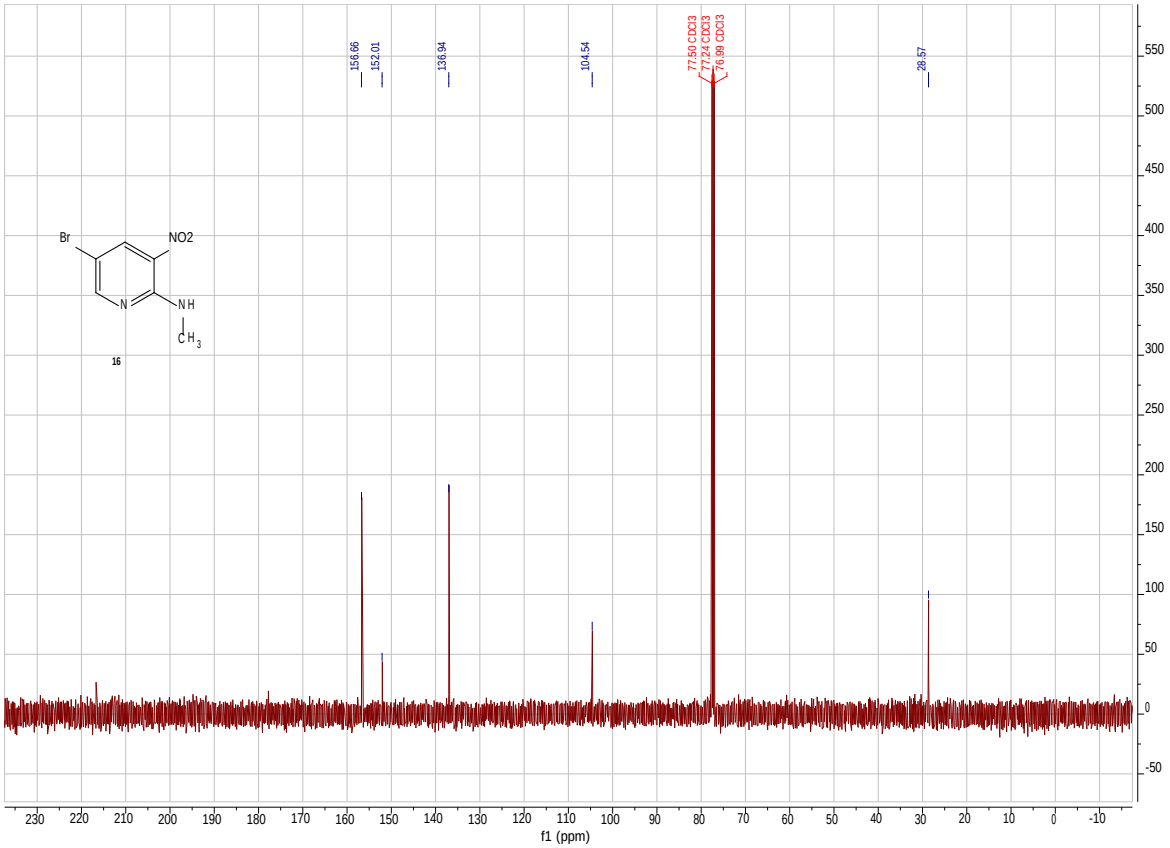
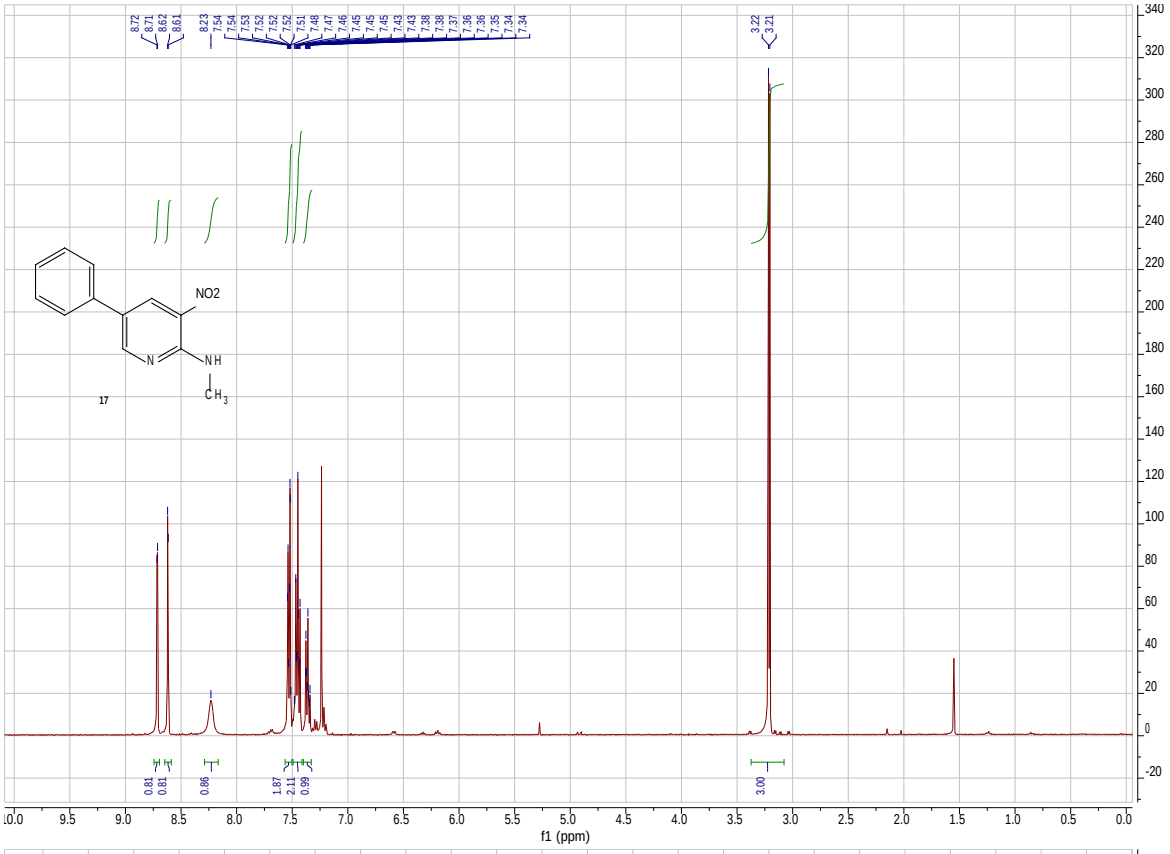
153.46
135.43
111.72
77.52 CDCl3
77.26 CDCl3
77.01 CDCl3
28.41
f1 (ppm)


8.54
8.54
8.47
8.47
8.18
3.18
3.17
Br
NO2
N
NH
CH3
16
0.96
0.97
1.13
3.00
f1 (ppm)


156.66
152.01
136.94
104.54
77.50 CDCl3
77.24 CDCl3
76.99 CDCl3
28.57
Br
NO2
N
NH
CH3
16
f1 (ppm)


8.72
8.71
8.62
8.61
8.23
7.54
7.54
7.53
7.52
7.52
7.52
7.52
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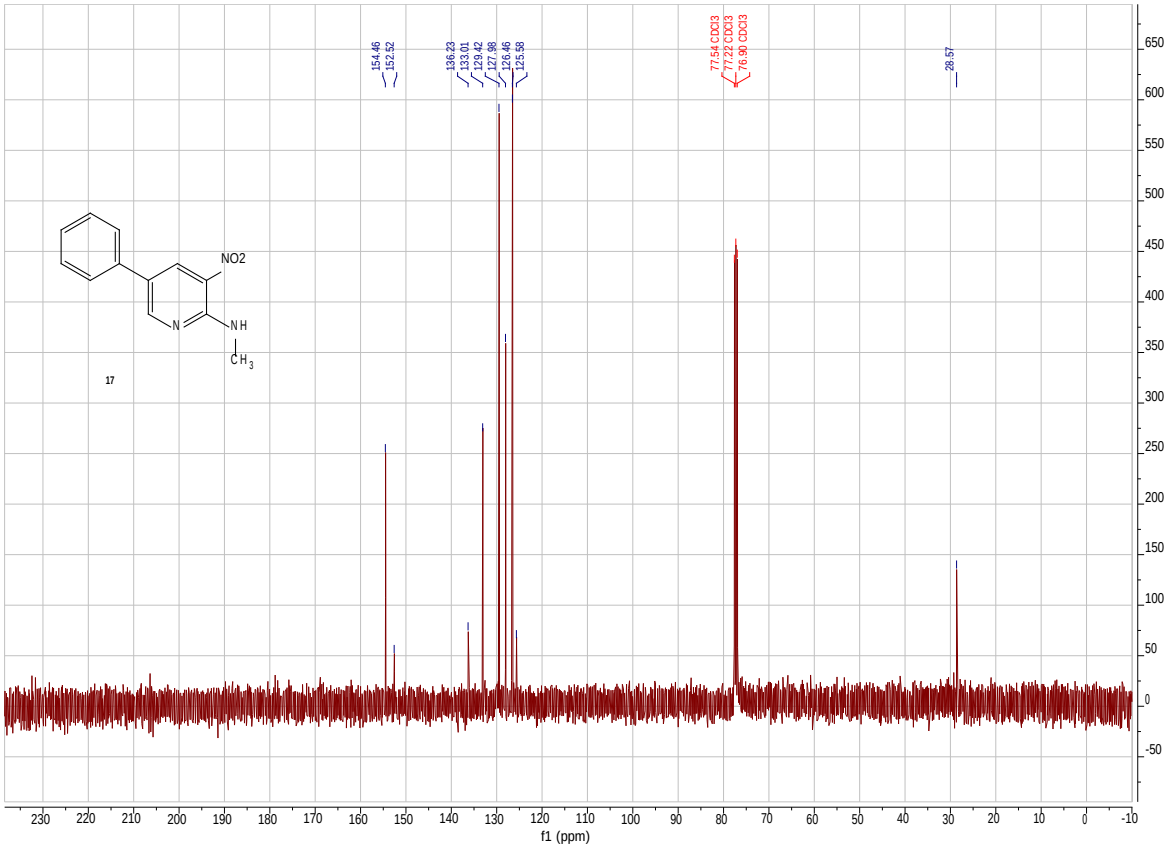
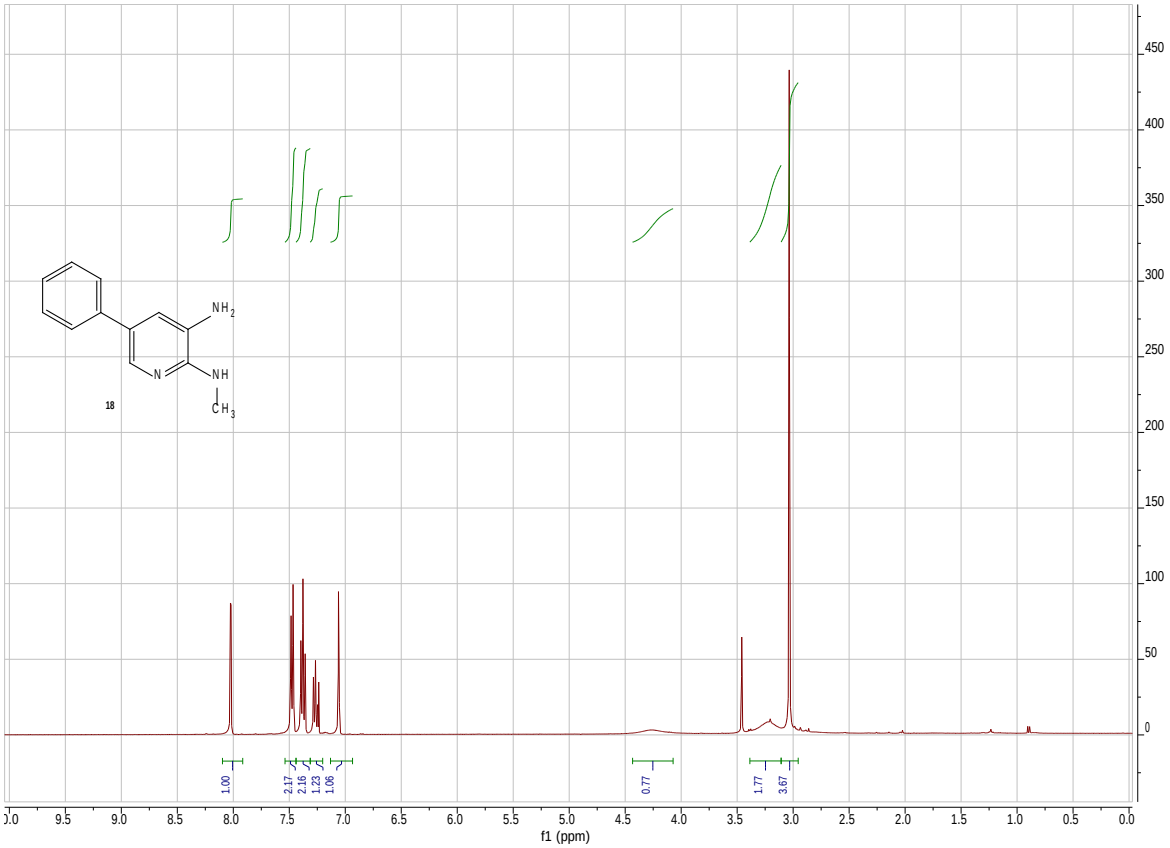
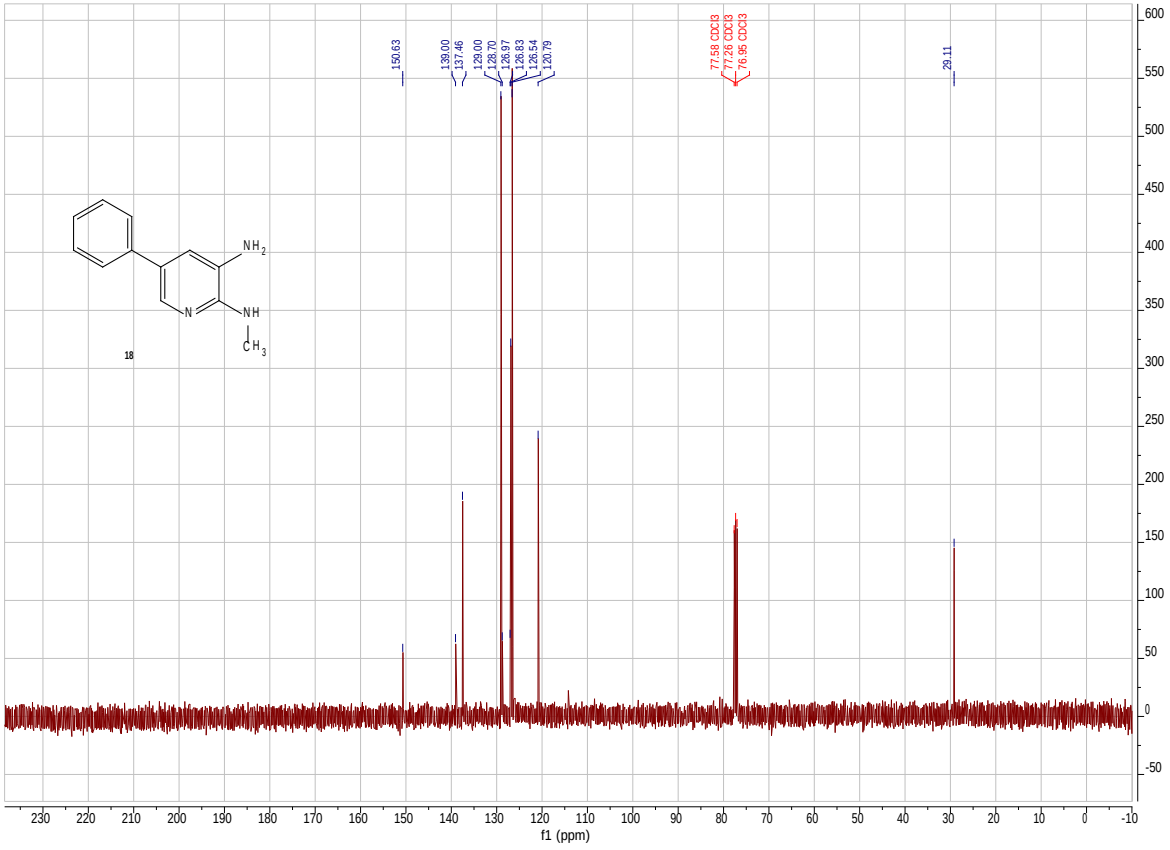
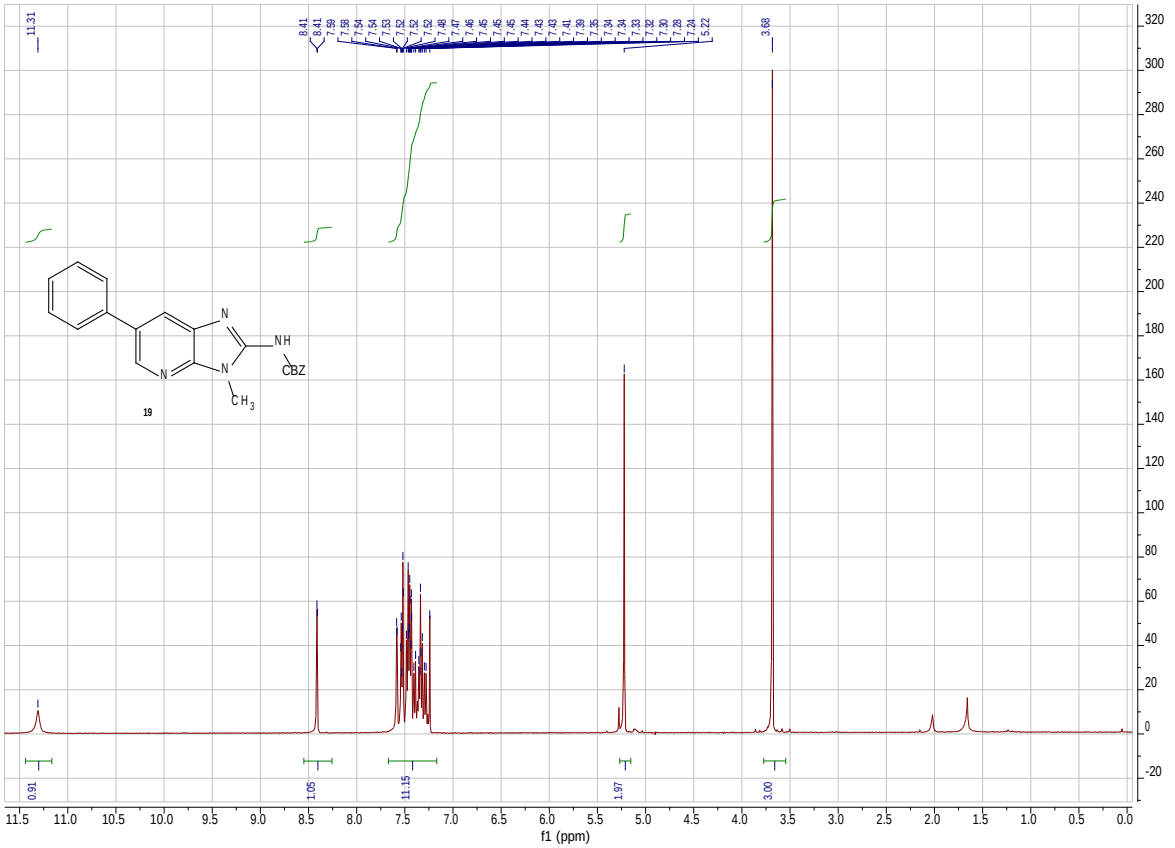
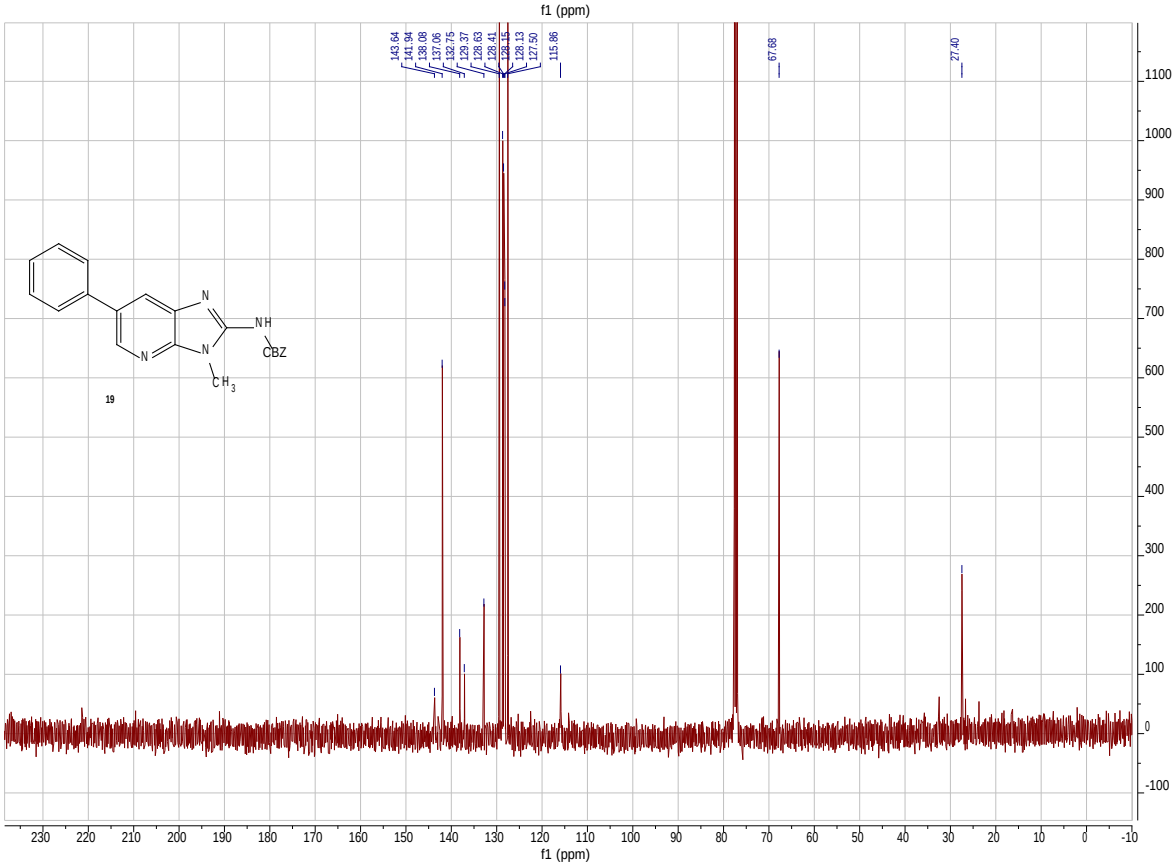
7.47
7.46
7.45
7.45
7.45
7.43
7.43
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
3.22
3.21
NO2
N
NH
CH3
17
0.81
0.81
0.86
1.87
2.11
0.99
3.00
f1 (ppm)


154.46
152.52
136.23
133.01
129.42
127.98
126.46
125.98
77.54 CDCl3
77.22 CDCl3
76.90 CDCl3
28.57
NO2
N
NH
CH3
17
f1 (ppm)


NH2
N
NH
CH3
18
1.00
2.17
2.16
1.23
1.06
0.77
1.77
3.67
f1 (ppm)


150.63
139.00
137.46
129.00
128.70
126.97
126.83
126.54
120.79
77.58 CDCl3
77.26 CDCl3
76.95 CDCl3
29.11
NH2
N
NH
CH3
18
f1 (ppm)


11.31
8.41
8.41
7.59
7.58
7.54
7.54
7.53
7.52
7.52
7.52
7.48
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.41
7.39
7.35
7.34
7.34
7.33
7.32
7.30
7.28
7.24
5.22
3.68
N
NH
CBZ
N
N
CH3
19
0.91
1.05
11.15
1.97
3.00
f1 (ppm)


143.64
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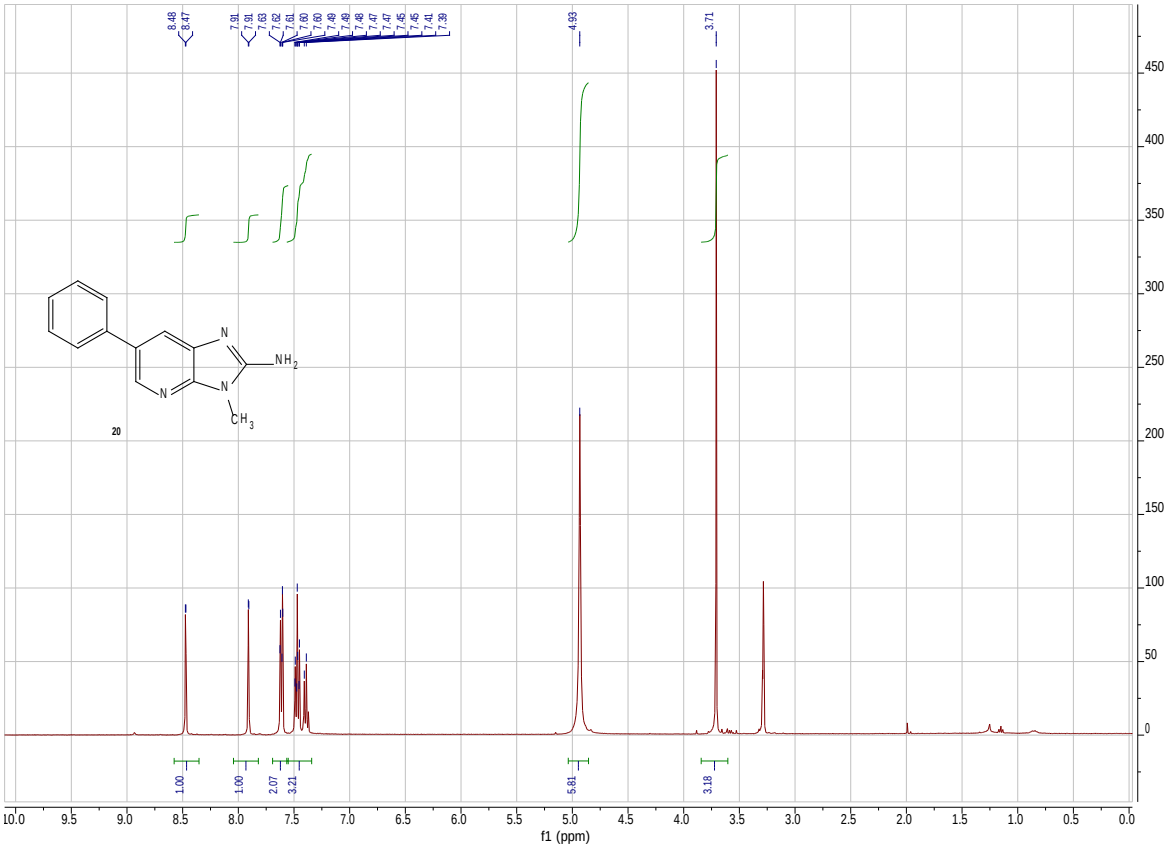
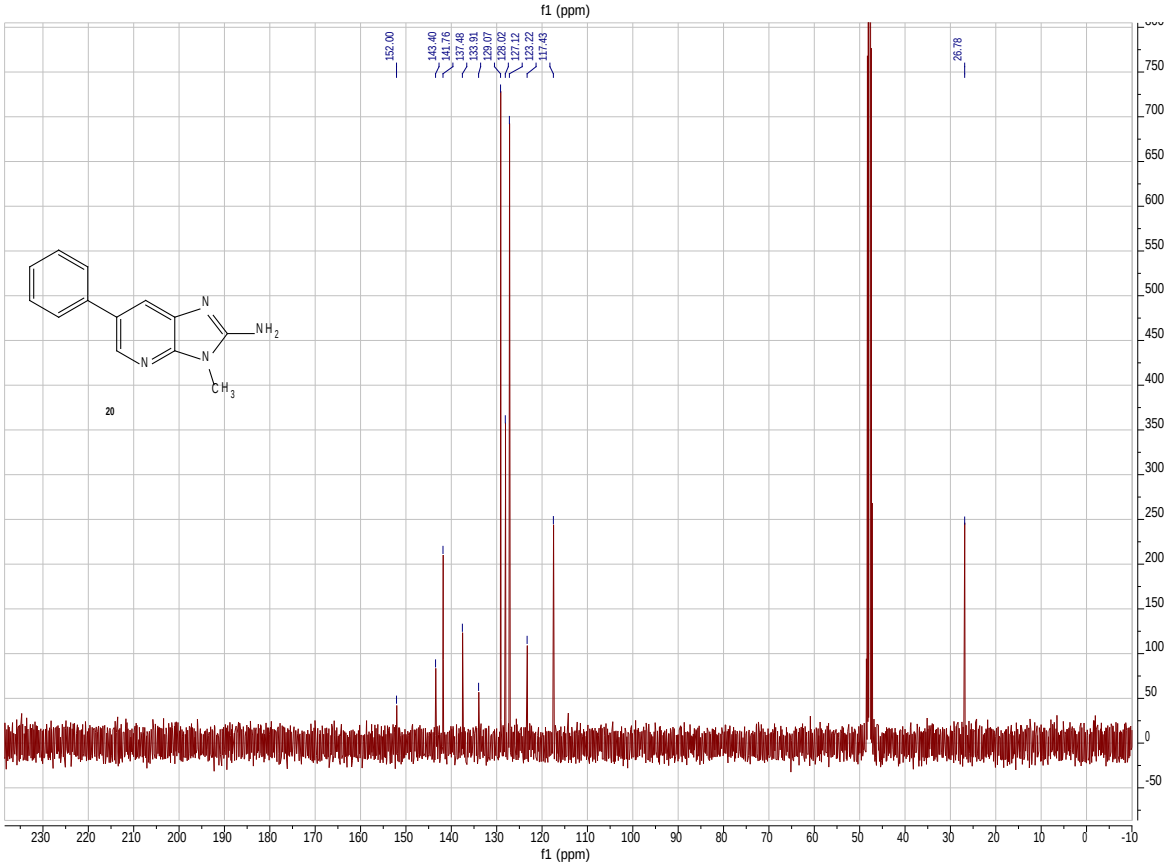
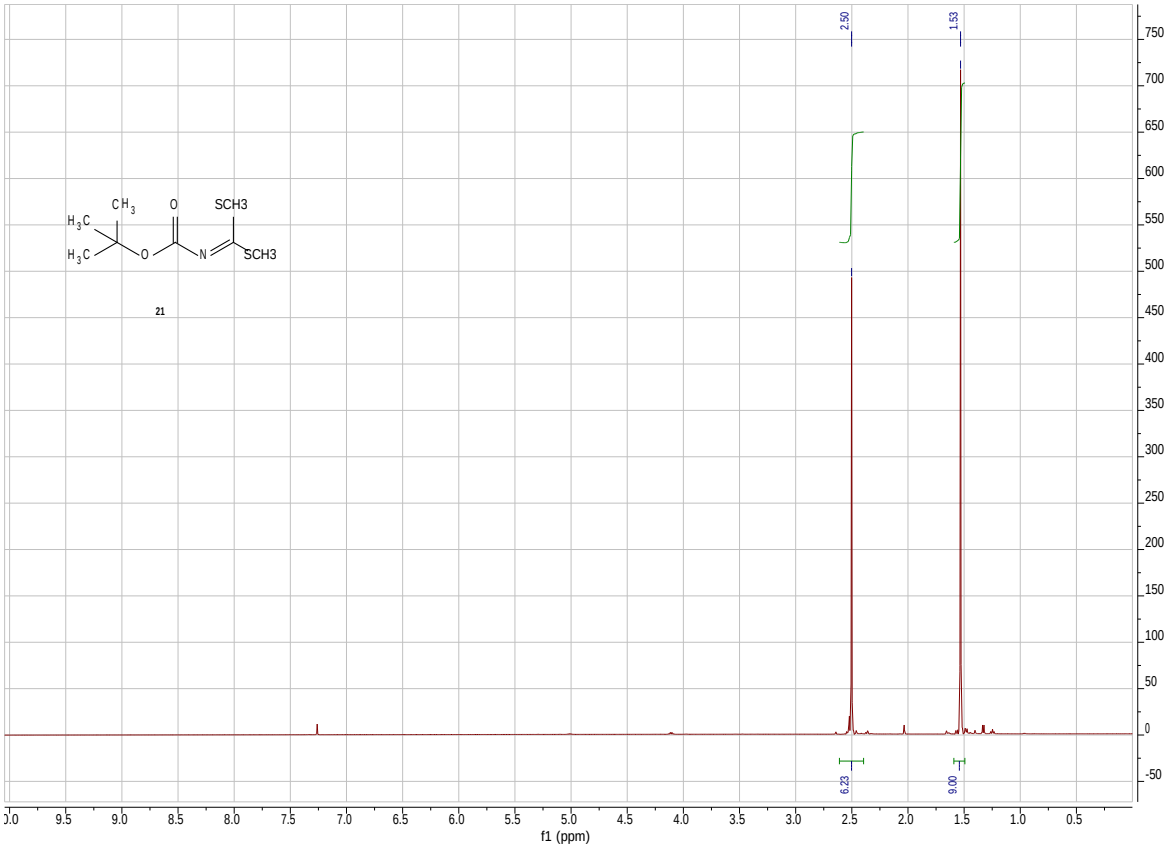
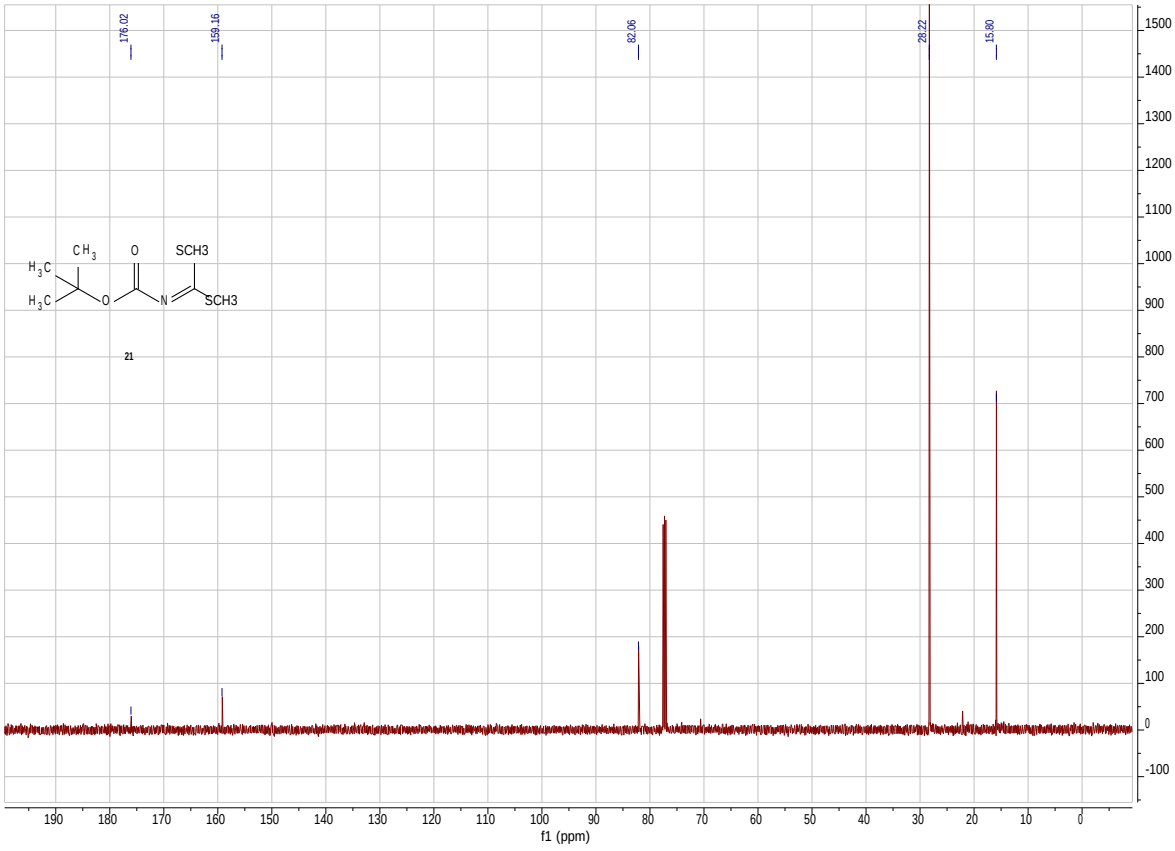
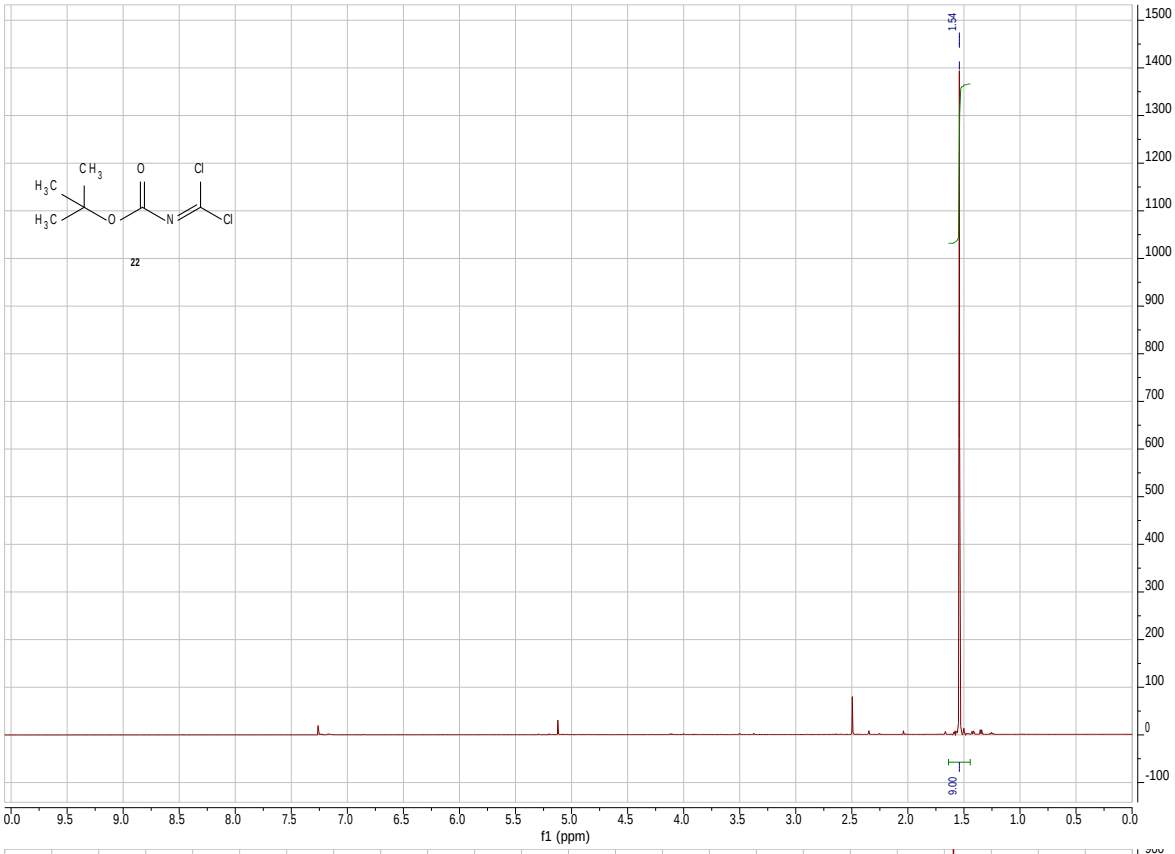
137.06
132.75
129.37
128.63
128.41
128.15
128.13
127.50
115.86
67.68
27.40
N
NH
CBZ
N
N
CH3
19
f1 (ppm)

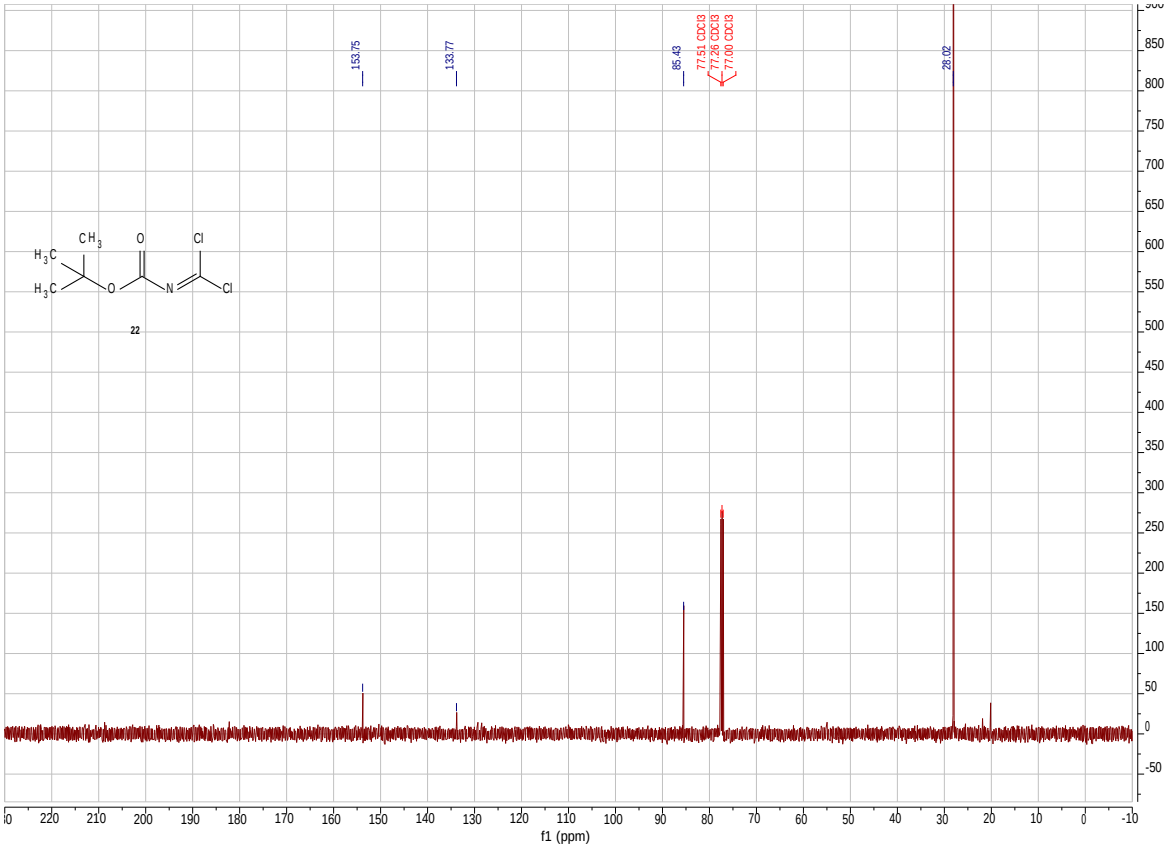

8.48
8.47
7.91
7.91
7.63
7.62
7.61
7.60
7.60
7.49
7.49
7.48
7.47
7.47
7.45
7.45
7.41
7.39
4.93
3.71
1.00
1.00
2.07
3.21
5.81
3.18
NH2
N
N
N
CH3
20
f1 (ppm)

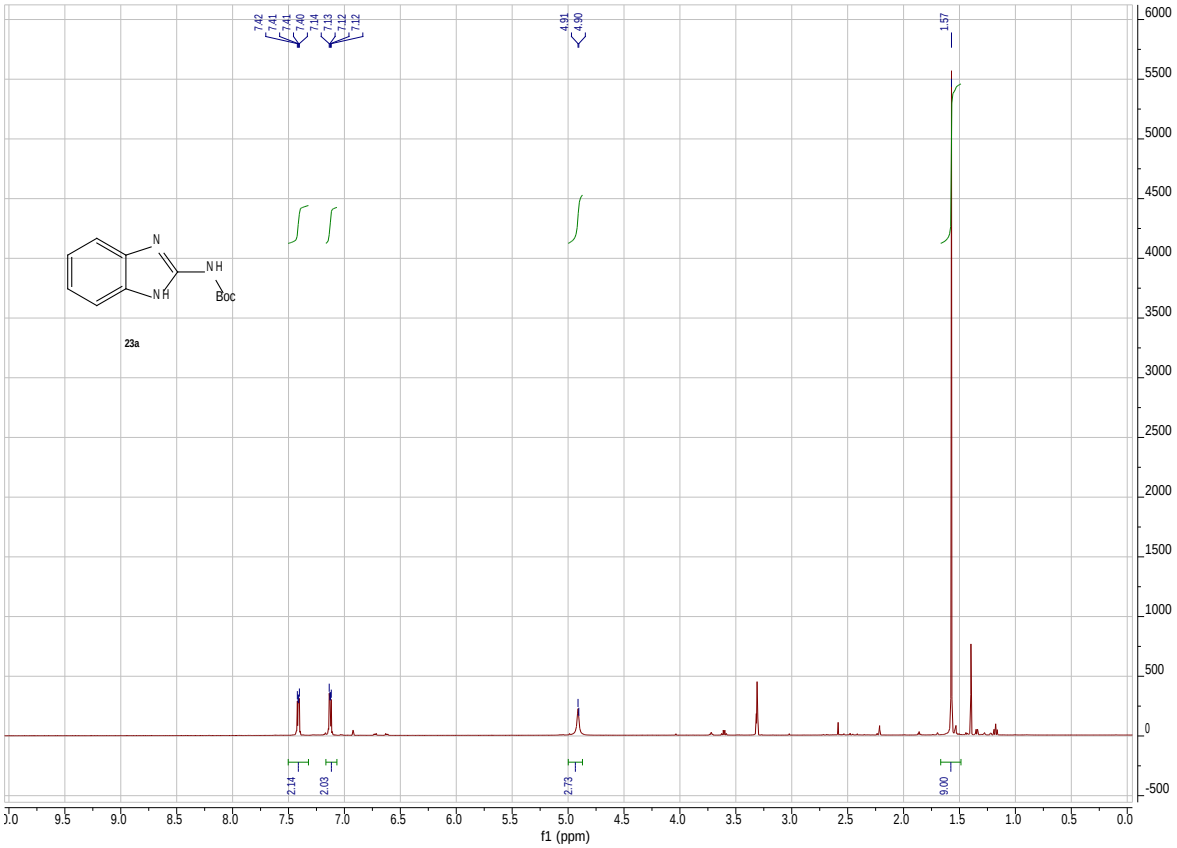

152.00
143.40
141.76
137.48
133.91
129.07
128.02
127.12
123.22
117.43
26.78
NH2
N
N
N
CH3
20
f1 (ppm)

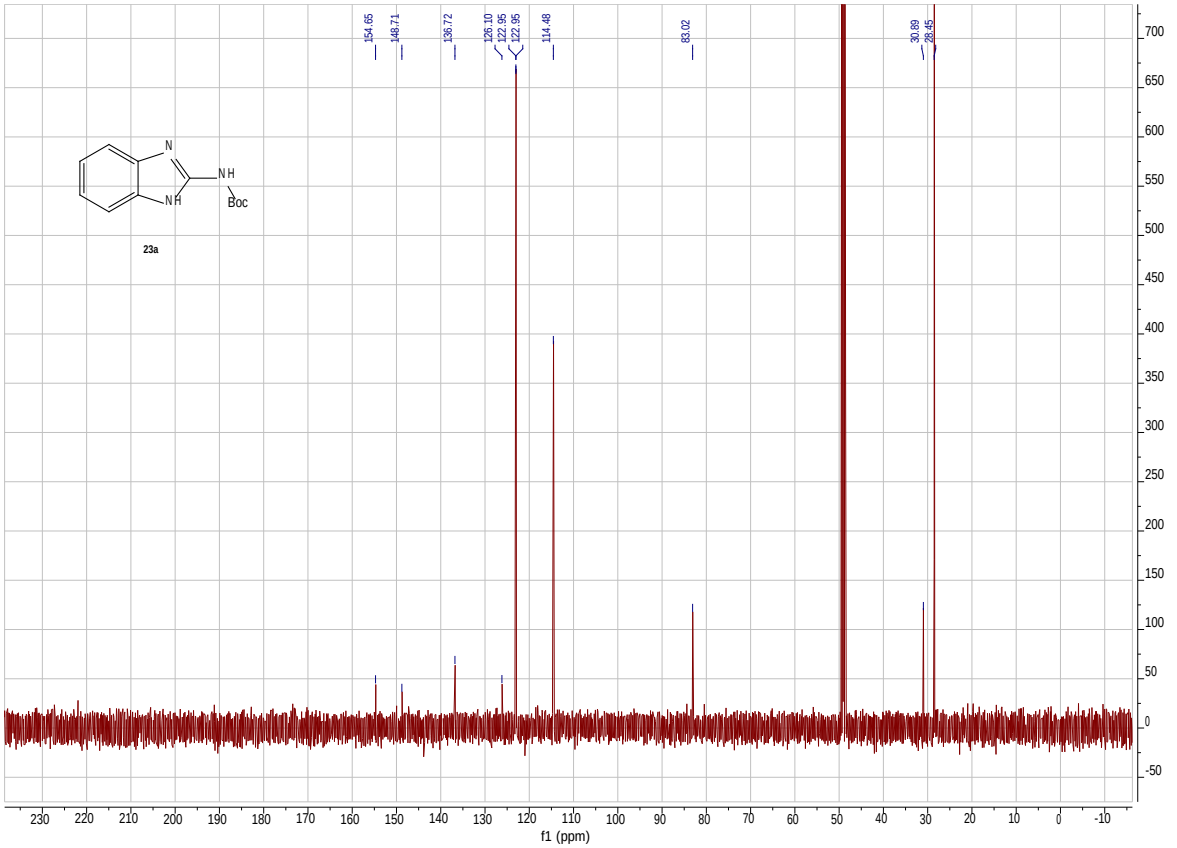

2.50
1.53
SCH3
SCH3
21
6.23
9.00
f1 (ppm)

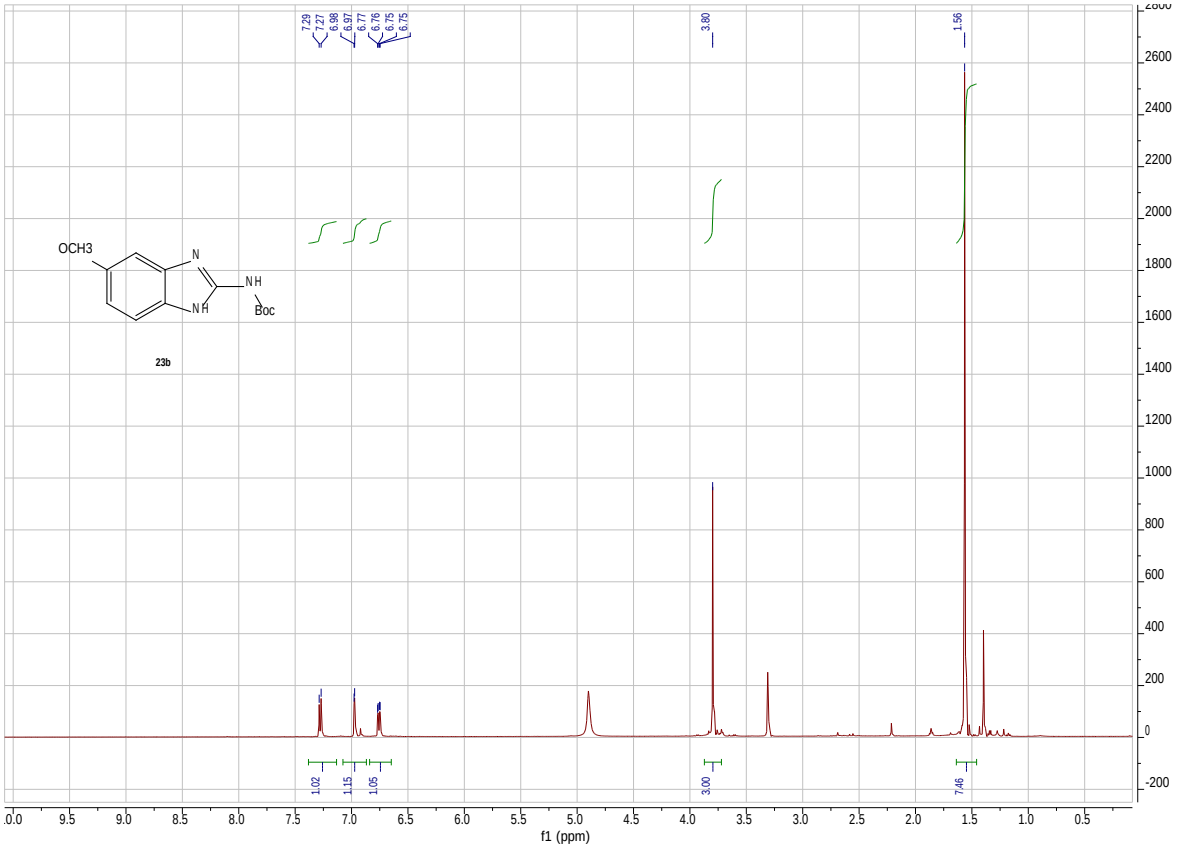

176.02
159.16
82.06
28.22
15.80
SCH3
SCH3
21
f1 (ppm)

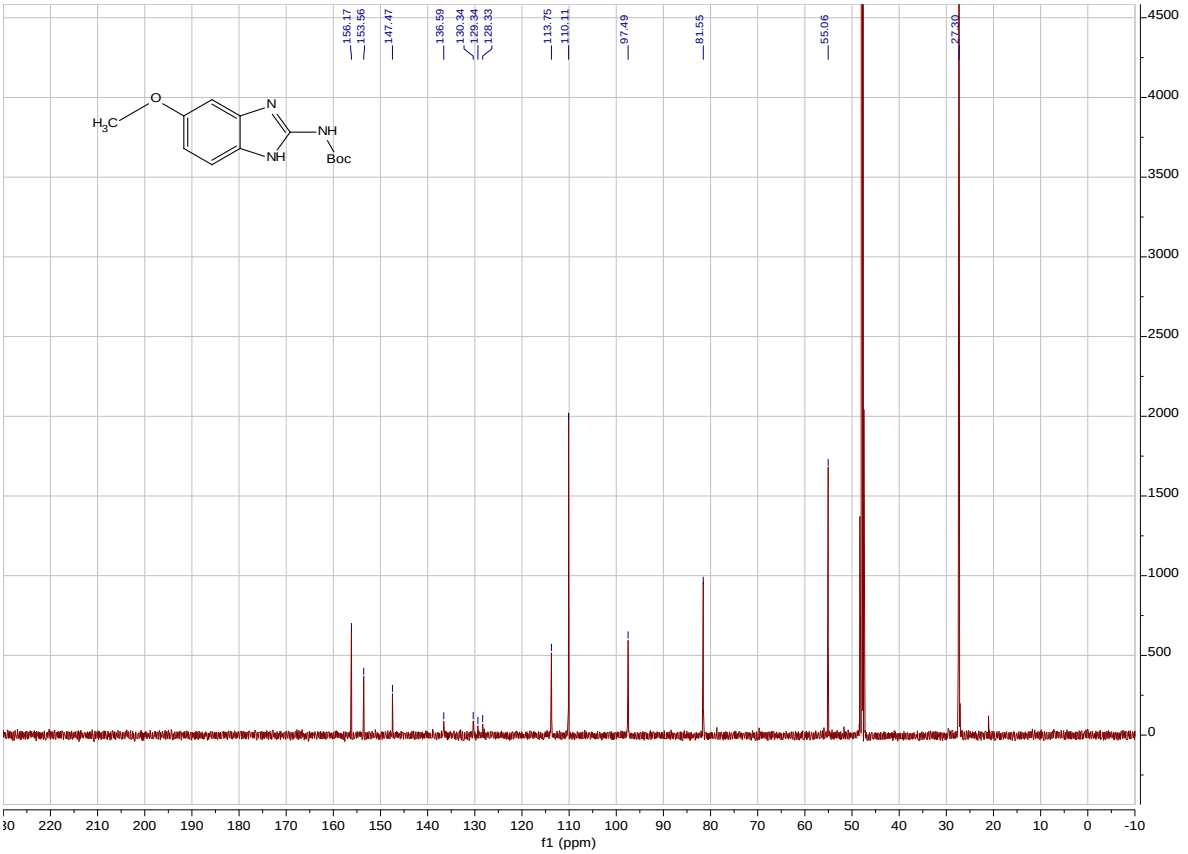

1.54
9.00
f1 (ppm)

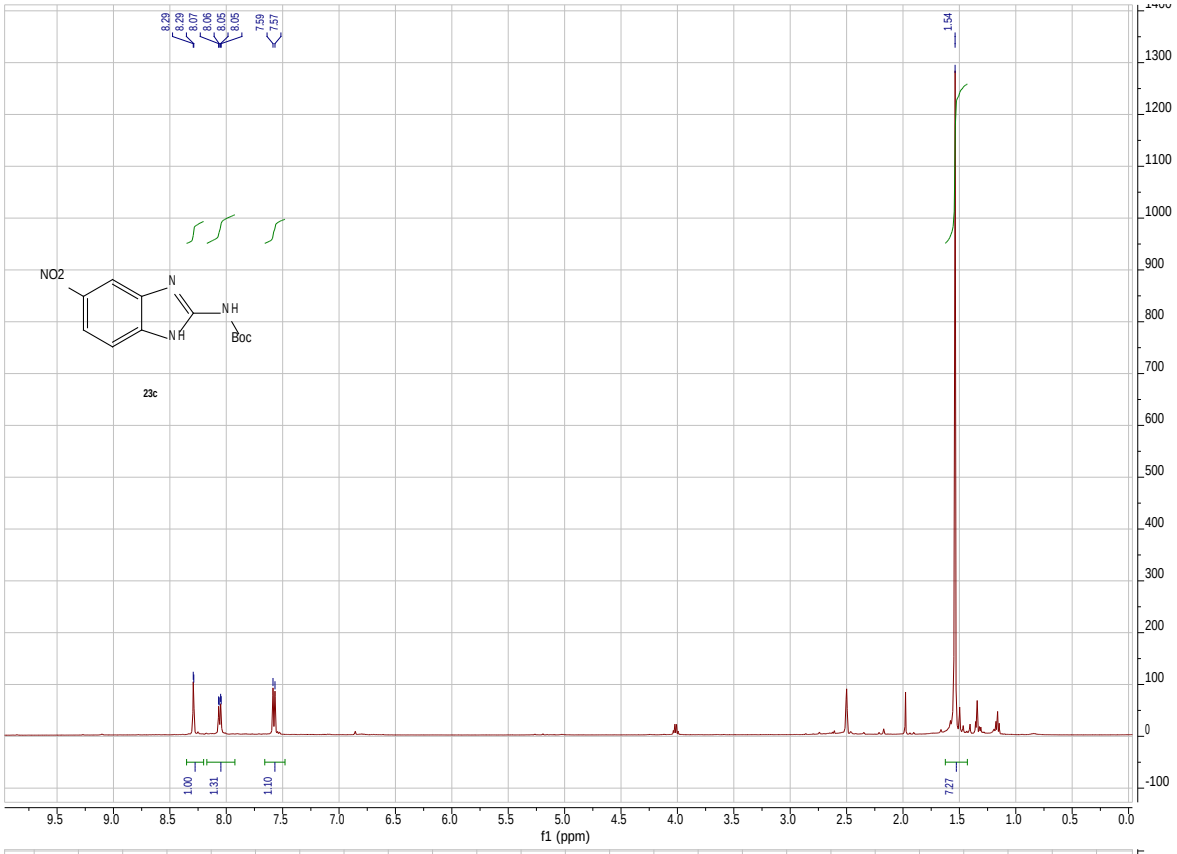

153.75
133.77
85.43
77.51 CDCl3
77.26 CDCl3
77.00 CDCl3
28.02
f1 (ppm)

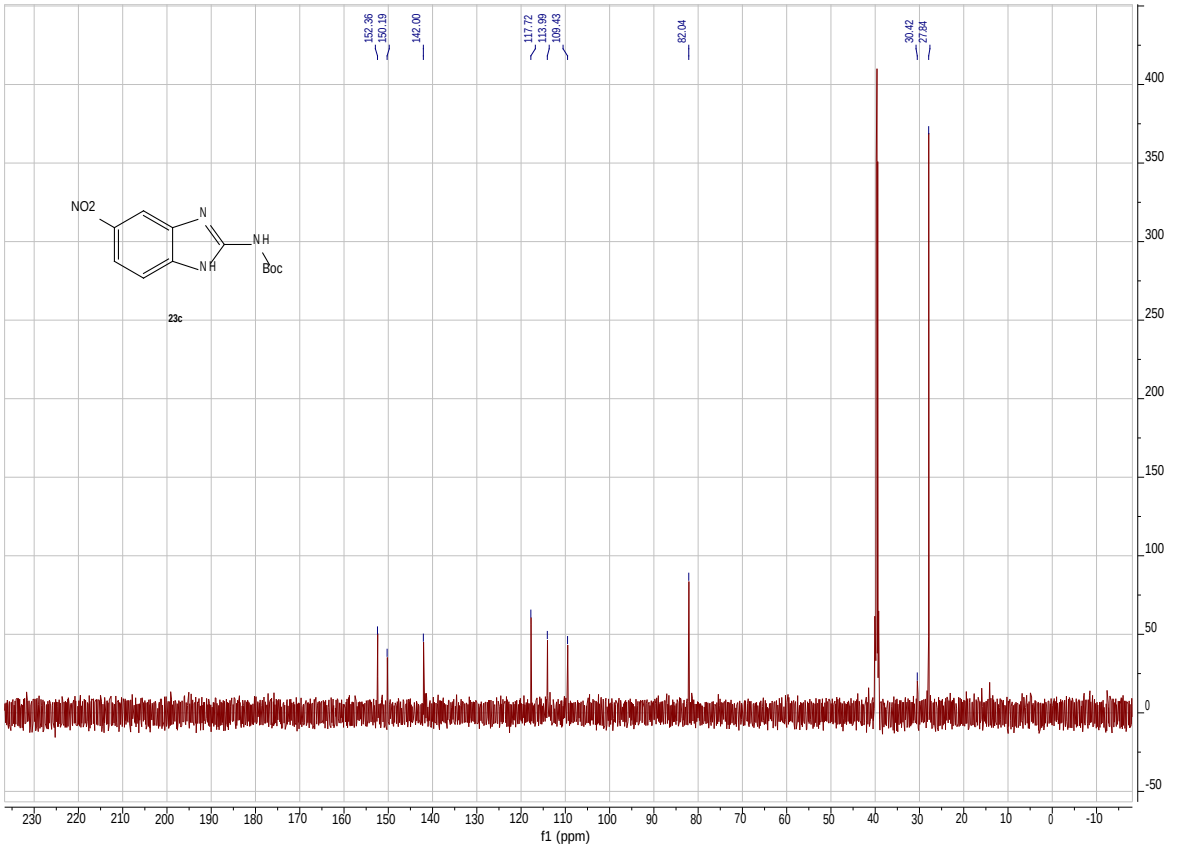

7.42
7.41
7.41
7.40
7.14
7.13
7.12
7.12
7.12
4.91
4.90
1.57
N
NH
NH
Boc
23a
2.14
2.03
2.79
9.00
f1 (ppm)

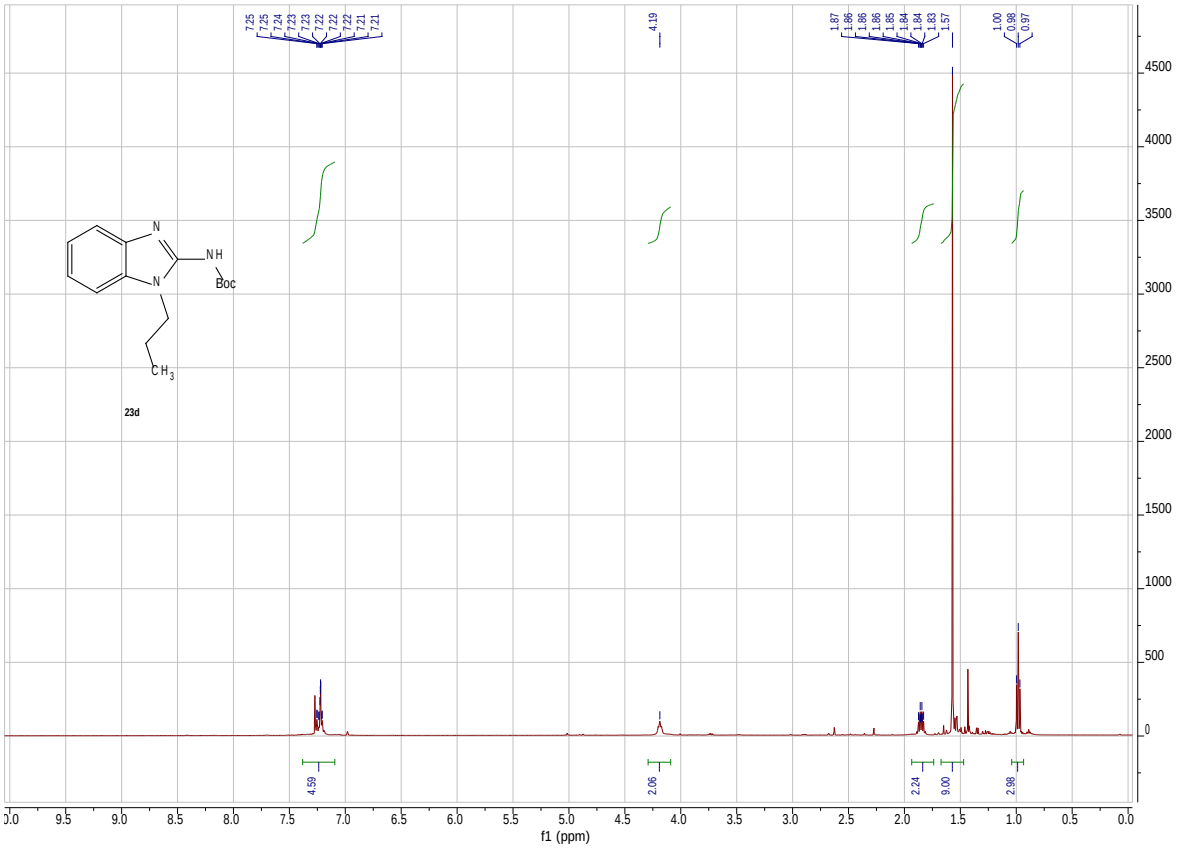

154.65
148.71
136.72
126.10
122.95
122.95
114.48
83.02
30.89
28.45
N
NH
NH
Boc
23a
f1 (ppm)

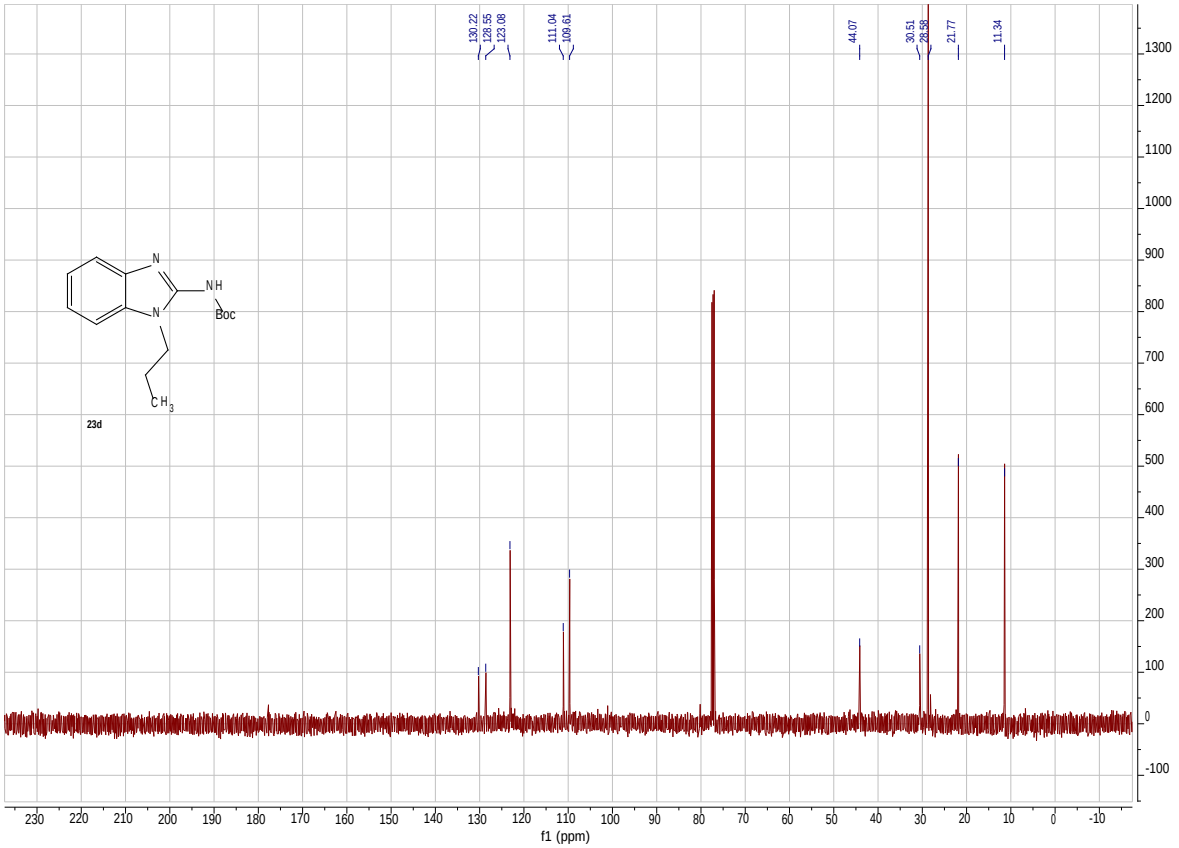

7.29
7.27
6.98
6.97
6.77
6.76
6.75
6.75
3.80
1.56
OCH3
N
NH
NH
Boc
23b
1.02
1.15
1.05
3.00
7.46
f1 (ppm)

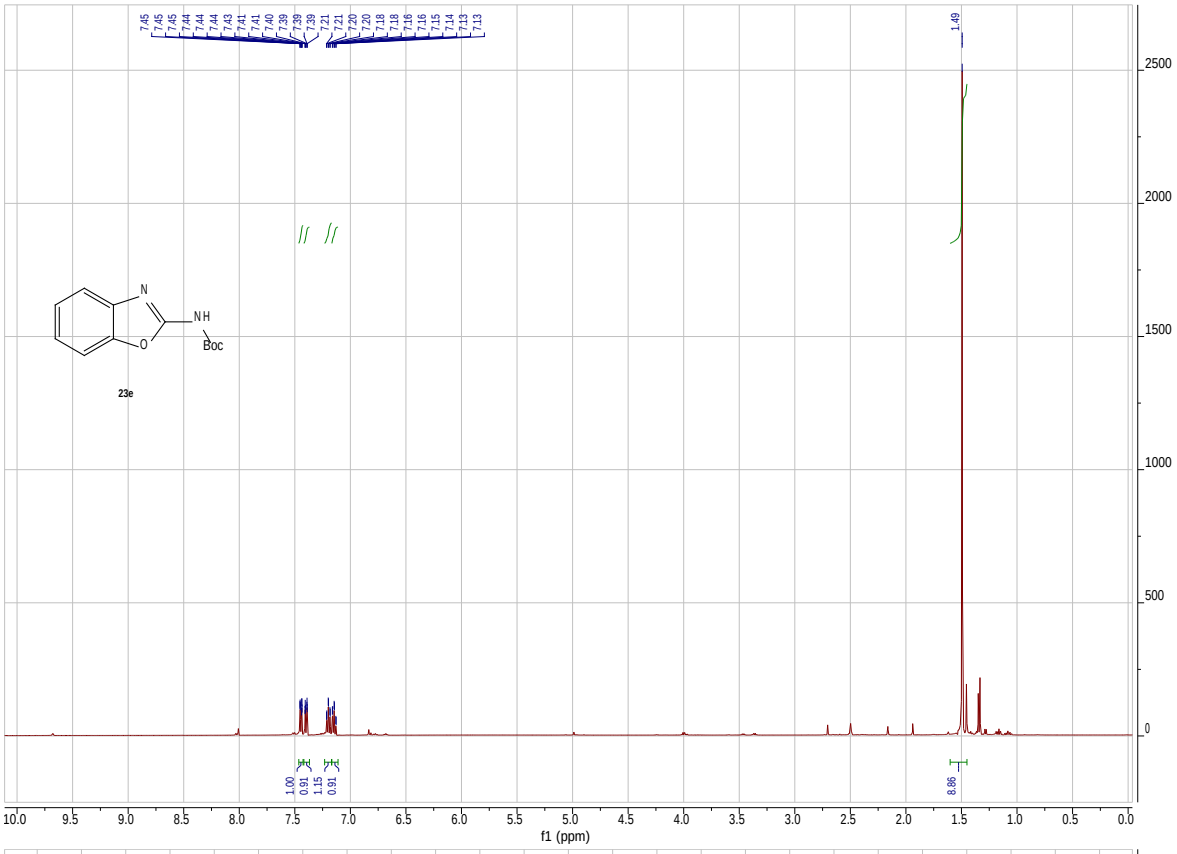

156.17
153.56
147.47
136.59
130.34
129.34
128.33
113.75
110.11
97.49
81.55
55.06
27.30
O
H3C
N
NH
NH
Boc
f1 (ppm)

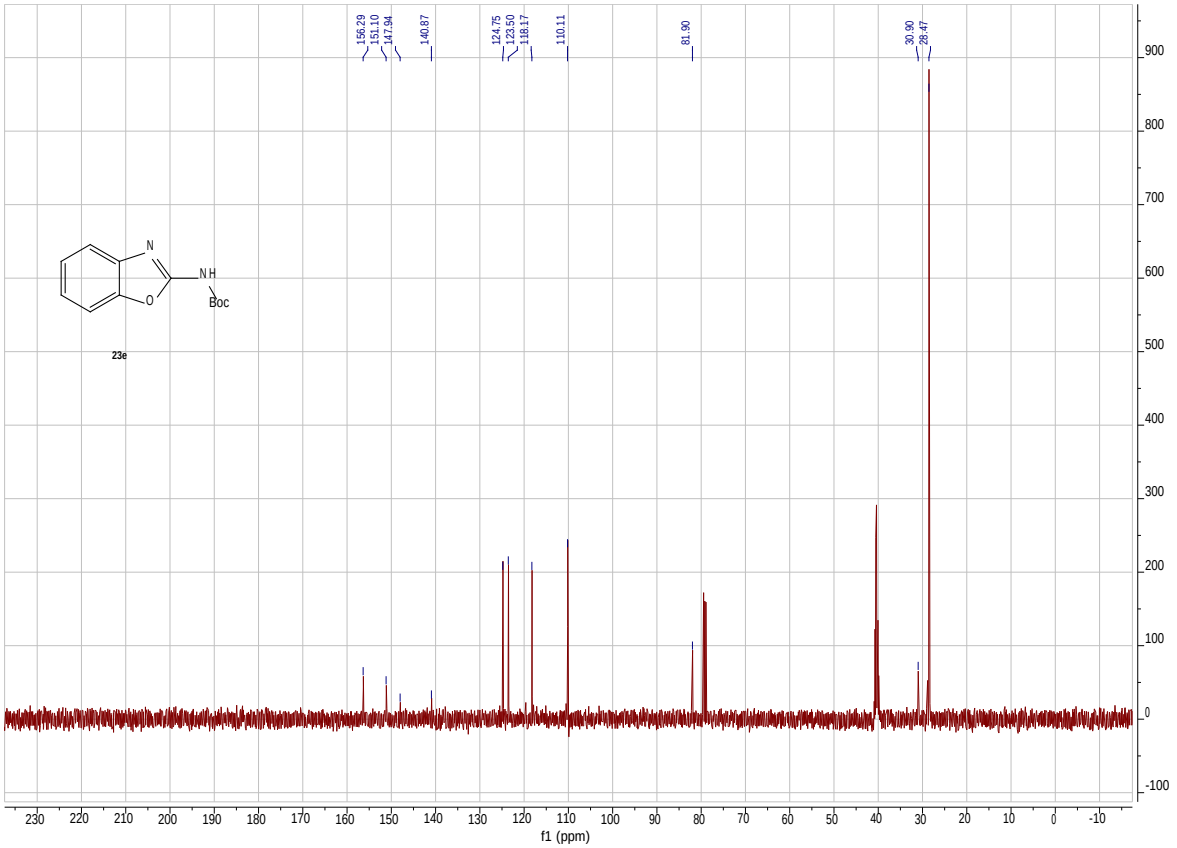

8.29
8.29
8.07
8.06
8.05
8.05
7.59
7.57
1.54
NO2
N
NH
NH
Boc
23c
1.00
1.31
1.10
7.27
f1 (ppm)


152.36
150.19
142.00
117.72
113.99
109.43
82.04
30.42
27.84
NO2
N
NH
NH
Boc
23c
f1 (ppm)


7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.22
7.22
7.21
7.21
4.19
1.87
1.86
1.86
1.86
1.85
1.84
1.84
1.83
1.57
1.00
0.98
0.97
N
NH
N
Boc
CH3
23d
4.59
2.06
2.24
9.00
2.98
f1 (ppm)


130.22
128.55
123.08
111.04
109.61
44.07
30.51
28.58
21.77
11.34
N
NH
N
Boc
CH3
23d
f1 (ppm)


7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.41
7.41
7.40
7.39
7.39
7.39
7.21
7.20
7.20
7.18
7.16
7.16
7.15
7.14
7.13
7.13
1.49
N
NH
O
Boc
23e
2500
2000
1500
1000
500
0
1.00
0.91
1.15
0.91
8.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.29
151.10
147.94
140.87
124.75
123.50
118.17
110.11
81.90
30.90
28.47
N
NH
O
Boc
23e
900
800
700
600
500
400
300
200
100
0
-100
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)