Synthesis of Substituted 2-Aminoimidazoles via Pd-Catalyzed Alkyne Carboamination Reactions. Application to the Synthesis of Preclathridine Natural Products.

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Supporting Information

Experimental procedures and characterization data for new compounds

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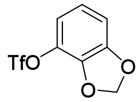
General: All reactions were carried out under a nitrogen atmosphere in flame-dried glassware unless otherwise noted. Palladium acetate and ligands used in this work were purchased from Strem Chemical Co. and used without purification. Aryl triflates were prepared according to a procedure published by Frantz and coworkers,[1] except the compounds were purified by column chromatography. All other reagents were obtained from commercial sources and were used as obtained unless otherwise noted. Bulk quantities of lithium *tert*-butoxide and sodium *tert*-butoxide were stored in nitrogen-filled glove box and small amounts were removed shortly before use. Toluene, THF, diethyl ether and dichloromethane were purified using a GlassContour solvent purification system. Benzotrifluoride was purified by distillation under N_2 prior to use. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^1H

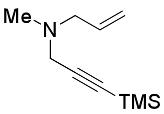
NMR analysis unless otherwise noted. The yields reported in the supporting information describe the result of a single experiment, whereas yields reported in Tables 1–2, and Scheme 2 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Tables 1–2, and Scheme 2.

Preparation and Characterization of Substrates

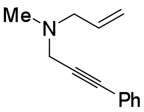


Benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (13). The title compound was prepared using a modified procedure reported by Frantz and coworkers.[1] A flame-dried flask equipped with a stirbar was cooled under a stream of N_2, and charged with benzo[*d*][1,3]dioxol-4-ol (406 mg, 2.94 mmol), toluene (6 mL, 0.5 M), and a 30% aqueous solution of tripotassium phosphate (6 mL, 0.5 M). The reaction mixture was cooled to 0 °C, and triflic anhydride (590 μL, 3.53 mmol) was added dropwise such that the temperature of the reaction mixture did not exceed 10 °C. The reaction mixture was warmed to rt, and was stirred at rt for 30 min. The reaction mixture was diluted with ethyl acetate (30 mL) and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with water (10 mL) and then was concentrated *in vacuo* to afford the crude product as a red oil. The crude product was purified by flash chromatography on silica gel to afford 606 mg (76%) of the title compound as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88–6.83 (m, 2 H), 6.79 (dd, *J* = 1.5, 8 Hz, 1 H), 6.08 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 139.5, 132.2, 122.4, 118.9 (q, *J* = 325 Hz), 115.7, 108.9, 102.8; IR (film) 2906, 1631 cm^{-1}. MS (EI) 269.9813 (269.9810 calcd for $C_8H_5F_3O_5S$, M + H$^+$).

General Procedure A for the Preparation of Tertiary Amines. These compounds were prepared using the procedure reported by Looper.[2] A flame-dried flask equipped with a stirbar was cooled under a stream of N_2, and charged with acetonitrile (0.15 M), *N*-methylallylamine (1.3 equiv), formaldehyde (5.9 equiv, 3.9 M, 37% solution in water), the appropriate alkyne (1.0 equiv), and copper (I) bromide (0.1 equiv). The resulting reaction mixture was stirred overnight (16 h) at rt. The mixture was then concentrated *in vacuo* to afford the crude product, which was then dissolved in diethyl ether (1.3 mL/mmol substrate). The mixture was filtered through a plug of celite, and the celite was washed with dichloromethane (17 mL/mmol substrate). The filtrate was transferred to a separatory funnel, and 1 M NaOH (5 mL/mmol substrate) was added to the separatory funnel. The layers were separated, and the organic layer was washed with twice with 1 M NaOH (5 mL/mmol substrate), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel.



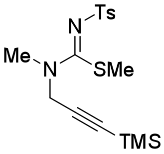
***N*-Methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (S1).** The title compound was prepared according to General Procedure A using ethynyltrimethylsilane (1.67 mL, 11.7 mmol), *N*-methylallylamine (1.5 mL, 15.6 mmol), formaldehyde (3 mL, 69 mmol, 37% solution in water), copper (I) bromide (168 mg, 1.17 mmol, and acetonitrile (78 mL). This procedure afforded 1.91 g (90%) of the title compound as a colorless oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.87–5.79 (m, 1 H), 5.21 (d, *J* = 17 Hz, 1 H), 5.15 (d, *J* = 10 Hz, 1 H), 3.31 (s, 2 H), 3.04 (d, *J* = 7 Hz, 2 H), 2.29 (s, 3 H), 0.17 (s, 9 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.6, 118.3, 101.2, 90.1, 59.3, 46.4, 41.8, 0.3; IR (film) 2218 cm^{-1}. MS (ESI) 182.1365 (182.1360 calcd for $C_{10}H_{19}NSi$, M + H$^+$).



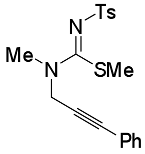
***N*-Methyl-*N*-(3-phenylpop-2-yn-1-yl)prop-2-en-1-amine (S2).**[3] The title compound was prepared according to General Procedure A using ethynylbenzene (3.5 mL, 31.4 mmol), *N*-methylallylamine (4.0 mL, 41.7 mmol), formaldehyde (8 mL, 185.3 mmol, 37% solution in water), copper (I) bromide (450 mg, 3.14 mmol), and acetonitrile (210 mL). This procedure afforded 5.67 g (98%) of the title compound as a light yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45–7.43 (m, 2 H), 7.31–7.29 (m, 3 H), 5.93–5.83 (m, 1 H), 5.28–5.16 (m, 2 H), 3.54 (s, 2 H), 3.13 (d, *J* = 6.4 Hz, 2 H), 2.38 (s, 3 H).

General Procedure B for the Preparation of Pseudothioureas. Deallylation of *N*-allyl-*N*-methylpropargylamine derivatives was accomplished using a procedure reported by Looper.[2] A flame-dried flask equipped with a stirbar was cooled under a stream of N$_2$, and charged with tetrakis(triphenylphosphine)palladium (0.02 equiv), 1,3-dimethylbarbituric acid (1.5 equiv), the appropriate tertiary amine (1.0 equiv), and dichloromethane (0.2 M). The resulting solution was stirred for 6.5 h at rt. The solution was transferred to a separatory funnel, and diethyl ether (5.4 mL/mmol substrate) and saturated aqueous sodium bicarbonate (2 mL/mmol substrate) were added. The layers were separated, and the organic layer was washed with a solution of saturated aqueous sodium bicarbonate (2 mL/mmol substrate). The organic layer was then washed with 1 M HCl (3 x 2 mL/mmol substrate). The combined acidic aqueous layers were basified with potassium carbonate, then transferred to a separatory funnel and dichloromethane (2 mL/mmol substrate) was added. The layers were separated, the aqueous layer was washed with dichloromethane (2 x 2 mL/mmol substrate). The organic layers were combined, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The resulting *N*-methylpropargylamine derivatives were directly carried on to the next step of the reaction without further purification.

A flame-dried thick-walled glass pressure tube equipped with a stirbar was cooled under a stream of N_2, and charged with dimethyl tosylcarbonimidodithioate (1 equiv), the appropriate secondary amine (1.75 equiv), and toluene (0.89 M). The resulting solution was heated to 100 °C with stirring for 3 h, then was cooled to rt and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.

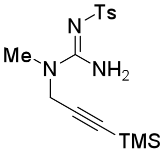


(*Z*)-Methyl *N*-methyl-*N*'-tosyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)carbamimidothioate (S3). The title compound was prepared according to General Procedure B using tetrakis(triphenylphosphine)palladium (576 mg, 0.50 mmol), 1,3-dimethylbarbituric acid (5.83 g, 37.4 mmol), **S1** (4.52 g, 24.9 mmol), dichloromethane (125 mL), dimethyl tosylcarbonimidodithioate (3.90 g, 14.2 mmol), and toluene (16 mL). This procedure afforded 5.11 g (96% over both steps) of the title compound as a white solid, m.p. 79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8 Hz, 2 H), 7.25 (d, J = 8 Hz, 2 H), 4.36 (s, 2 H), 3.25 (s, 3 H), 2.58 (s, 3 H), 2.40 (s, 3 H), 0.17 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 142.0, 141.7, 129.3, 126.3, 98.1, 91.4, 43.5, 38.6, 21.6, 18.1, –0.1; IR (film) 2178, 1527 cm^{-1}. MS (ESI) 369.1123 (369.1121 calcd for $C_{16}H_{24}N_2O_2S_2Si$, M + H$^+$).

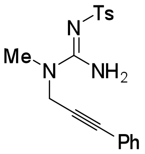


(*Z*)-Methyl *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*'-tosylcarbamimidothioate (S4). The title compound was prepared according to General Procedure B using tetrakis(triphenylphosphine)palladium (706 mg, 0.61 mmol), 1,3-dimethylbarbituric acid (5.83 g, 37.4 mmol), **S2** (5.67 g, 30.3 mmol), dichloromethane (153 mL), dimethyl tosylcarbonimidodithioate (4.76 g, 17.3 mmol), and toluene (19 mL). This procedure afforded 6.38 g (97% over both steps) of a yellow oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8 Hz, 2 H), 7.40 (dd, *J* = 8, 2 Hz, 2 H), 7.34–7.29 (m, 3 H), 7.24 (t, *J* = 8 Hz, 2 H), 4.57 (s, 2 H), 3.32 (s, 3 H), 2.59 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.5, 142.1, 141.8, 132.0, 129.3, 129.0, 128.6, 126.3, 122.2, 85.8, 82.1, 43.5, 38.9, 21.6, 18.1; IR (film) 2249, 1519 cm^{-1}. MS (ESI) 373.1051 (373.1039 calcd for $C_{19}H_{20}N_2O_2S_2$, M + H$^+$).

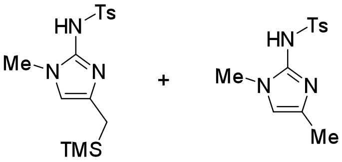
General Procedure C for the Preparation of Guanidine Substrates. A flame-dried flask equipped with a stirbar was cooled under a stream of N$_2$ and charged with the appropriate pseudothiourea (1.0 equiv), mercury (II) oxide (1.5 equiv), triethylamine (4.5 equiv), and a 2 M solution of ammonia in ethanol (0.1 M). The resulting mixture was stirred at rt for 15 h. The reaction mixture was then filtered through a plug of celite, and the celite was washed with dichloromethane (50 mL/mmol substrate). The filtrate was concentrated *in vacuo* and the crude product was purified by flash chromatography on silica gel.



(*E*)-*N*-(Amino{methyl[3-(trimethylsilyl)prop-2-yn-1-yl]amino}methylene)-4-methylbenzenesulfonamide (8a). The title compound was prepared from **S3** (1.38 g, 3.7 mmol), mercury (II) oxide (1.22 g, 5.6 mmol), ammonia (37 mL, 2 M solution in ethanol), and triethylamine (2.35 mL, 16.8 mmol) according to General Procedure C. This procedure afforded 907 mg (72%) of the title compound as an off white solid, m.p. 136–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8 Hz, 2 H), 7.23 (d, *J* = 8 Hz, 2 H), 6.35 (s, br, 2 H), 4.22 (s, 2 H), 3.00 (s, 3 H), 2.39 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 142.1, 141.2, 129.3, 126.2, 99.1, 90.8, 40.0, 34.7, 21.6, –0.1; IR (film) 3415, 3330, 2178, 1629, 1544, 1495 cm^{-1}. MS (ESI) 338.1354 (338.1353 calcd for $C_{15}H_{23}N_3O_2SSi$, M + H$^+$).



(*E*)-*N*-{Amino[methyl(3-phenylprop-2-yn-1-yl)amino]methylene}-4-methylbenzenesulfonamide (8b). The title compound was prepared from **S4** (6.32 g, 17.0 mmol), mercury (II) oxide (5.51 g, 25.4 mmol), ammonia (170 mL, 2 M solution in ethanol), and triethylamine (10.6 mL, 76.3 mmol) according to General Procedure C. This procedure afforded 1.75 g (30%) of an off-white solid: mp = 144–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2 H), 7.35 (t, *J* = 6.5 Hz, 2 H), 7.31–7.29 (m, 3 H), 7.18 (d, *J* = 8 Hz, 2 H), 6.40 (s, br, 2 H), 4.43 (s, 2 H), 3.06 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 142.1, 141.2, 132.0, 129.3, 128.9, 128.5, 126.2, 122.3, 85.2, 83.1, 40.0, 34.9, 21.6; IR (film) 3417, 3330, 2249, 1627, 1543, 1490 cm^{-1}. MS (ESI) 342.1271 (342.1271 calcd for $C_{18}H_{19}N_3O_2S$, M + H$^+$).



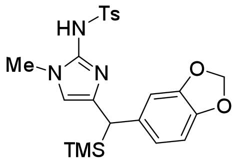
4-Methyl-*N*-{1-methyl-4-[(trimethylsilyl)methyl]-1*H*-imidazol-2-yl}benzenesulfonamide (11a) and *N*-(1,4-dimethyl-1*H*-imidazol-2-yl)-4-methylbenzenesulfonamide (11b). A flame-dried Schlenk tube equipped with a stir bar was cooled under vacuum and charged with **8a** (51 mg, 0.15 mmol), $Pd_2(dba)_3$ (2.7 mg, 0.02 mmol), Nixantphos (6.6 mg, 0.08 mmol), and sodium *tert*-butoxide (2.4 equiv). 5-bromobenzo[*d*][1,3]dioxole (27 μL, 0.225 mmol) was added. The flask was evacuated and purged with N_2. Toluene (1.5 mL) was added via syringe and the tube was heated to 107 °C and stirred for sixteen hours. The mixture was cooled to rt and H_2O (10 mL/mmol substrate) and dichloromethane (25 mL/mmol substrate) were added. The layers were separated and the aqueous layer was extracted with dichloromethane (25 mL/mmol substrate). The organic layers were combined and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 22 mg (44%) of **11a** as an off white solid, m.p. 171 °C and 18 mg (46%) of **11b** as an off white solid, m.p. 205 °C.

Data for 11a: ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.69 (s, 1 H), 7.81 (d, J = 8 Hz, 2 H), 7.20 (d, J = 8 Hz, 2 H), 5.91 (s, 1 H), 3.28 (s, 3 H), 2.37 (s, 3 H), 1.80 (s, 2 H), 0.04 (s, 9 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 146.7, 142.0, 141.7, 129.3, 126.1, 123.5, 109.5, 31.6, 21.6, 15.0, –1.63; IR (film) 3275, 1628, 1575 cm^{-1}. MS (ESI) 338.1354 (338.1353 calcd for $C_{15}H_{23}N_3O_2SSi$, M + H$^+$)

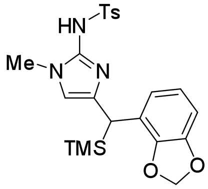
Data for 11b: ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.05 (s, 1 H), 7.83 (d, J = 8.5 Hz, 2 H), 7.21 (d, J = 8 Hz, 2 H), 6.05 (s, 1 H), 3.29 (s, 3 H), 2.37 (s, 3 H), 2.07 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.0, 141.9, 141.7, 129.3, 126.0, 121.2, 111.4, 31.6, 21.6, 10.6; IR (film) 3286, 1642, 1582 cm^{-1}. MS (ESI) 266.0961 (266.0958 calcd for $C_{12}H_{15}N_3O_2S$, M + H$^+$).

Preparation and Characterization of 2-Aminoimidazole Products

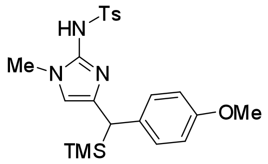
General Procedure D for the Pd-Catalyzed Synthesis of 2-Aminoimidazoles. A flame-dried Schlenk tube equipped with a stir bar was cooled under vacuum and charged with the appropriate guanidine substrate (1.0 equiv), RuPhos (0.08 equiv), and lithium *tert*-butoxide (2.4 equiv). The appropriate aryl triflate (2.0 equiv) was added. The flask was evacuated and purged with N$_2$. A pre-stirred solution of palladium (II) acetate (0.04 equiv) in trifluorotoluene (0.9 mg palladium (II) acetate/mL PhCF$_3$) was added via syringe and the tube was heated to 100 °C and stirred for 3 h. The mixture was cooled to rt and H$_2$O (100 mL/mmol substrate) and dichloromethane (250 mL/mmol substrate) were added. The layers were separated and the aqueous layer was extracted with dichloromethane (250 mL/mmol substrate). The organic layers were combined, dried, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.



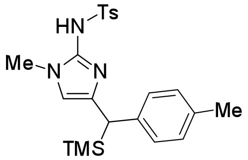
N-{4-[Benzo[*d*][1,3]dioxol-5-yl(trimethylsilyl)methyl]-1-methyl-1*H*-imidazol-2-yl}-4-methylbenzenesulfonamide (10a). The title compound was prepared from **8a** (51 mg, 0.15 mmol) and benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (31 μL, 0.18 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D (except with modified stoichiometries of reactants as noted above). This procedure afforded 55 mg (80%) of the title compound as a light orange solid, m.p. 90–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, br, 1 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.19 (d, *J* = 8 Hz, 2 H), 6.73–6.71 (m, 1 H), 6.50–6.48 (m, 2 H), 6.13 (s, 1 H), 5.94 (s, 2 H), 3.32 (s, 3 H), 3.22 (s, 1 H), 2.37 (s, 3 H), 0.05 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 146.8, 145.9, 141.7, 132.9, 129.3, 126.3, 126.0, 121.0, 111.3, 108.6, 108.4, 101.2, 34.6, 31.7, 21.6, –2.0 (one carbon signal is missing due to incidental equivalence); IR (film) 3293, 1619, 1585 cm^{-1}. MS (ESI) 458.1569 (458.1564 calcd for $C_{22}H_{27}N_3O_4SSi$, M + H$^+$).



N-{4-[Benzo[*d*][1,3]dioxol-4-yl(trimethylsilyl)methyl]-1-methyl-1*H*-imidazol-2-yl}-4-methylbenzenesulfonamide (10b). The title compound was prepared from **8a** (51 mg, 0.15 mmol) and benzo[*d*][1,3]dioxol-4-yl trifluoromethanesulfonate (52 μL, 0.30 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 65 mg (94%) of the title compound as an off-white solid, m.p. 65–66 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, br, 1 H), 7.75 (d, *J* = 8 Hz, 2 H), 7.17 (d, *J* = 8 Hz, 2 H), 6.77–6.74 (m, 1 H), 6.71–6.69 (m, 1 H), 6.50–6.48 (m, 1 H), 6.11 (s, 1 H), 6.04 (d, *J* = 1 Hz, 1 H), 6.00 (d, *J* = 1 Hz, 1 H), 3.28 (s, 3 H), 3.25 (s, 1 H), 2.35 (s, 3 H), 0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 146.9, 144.1, 141.7, 141.4, 129.1, 125.8, 125.0, 122.4, 122.3, 121.0, 110.4, 107.0, 100.6, 31.5, 31.4, 21.4, –2.1; IR (film) 3310, 1579 cm^{-1}. MS (ESI) 458.1574 (458.1564 calcd for $C_{22}H_{27}N_3O_4SSi$, M + H$^+$).

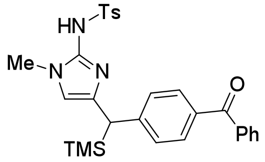


N-{4-[(4-Methoxyphenyl)(trimethylsilyl)methyl]-1-methyl-1H-imidazol-2-yl}-4-methylbenzenesulfonamide (10c). The title compound was prepared from **8a** (51 mg, 0.15 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (55 µL, 0.30 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 57 mg (85%) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, br, 1 H), 7.75 (d, J = 8.5 Hz, 2 H), 7.17 (d, J = 8 Hz, 2 H), 6.95 (d, J = 8.5 Hz, 2 H), 6.80 (d, J = 8.5 Hz, 2 H), 6.13 (s, 1 H), 3.78 (s, 3 H), 3.31 (s, 3 H), 3.28 (s, 1 H), 2.36 (s, 3 H), 0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 146.7, 141.8, 141.6, 131.1, 129.2, 129.0, 126.7, 126.0, 114.2, 111.1, 55.4, 33.9, 31.7, 21.5, 2.1; IR (film) 3289, 1616, 1581, 1508 cm^{-1}. MS (ESI) 444.1784 (444.1772 calcd for $C_{22}H_{29}N_3O_3SSi$, M + H$^+$).

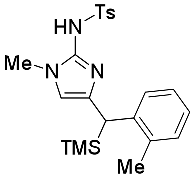


4-Methyl-N-{1-methyl-4-[p-tolyl(trimethylsilyl)methyl]-1H-imidazol-2-yl}benzenesulfonamide (10d). The title compound was prepared from **8a** (51 mg, 0.15 mmol) and p-tolyl trifluoromethanesulfonate (54 µL, 0.30 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 53 mg (82%) of the title compound as an off-white solid, m.p. 172–173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, br, 1 H), 7.74 (d, J = 8 Hz, 2 H), 7.16 (d, J = 8 Hz, 2 H), 7.06 (d, J = 7.5 Hz, 2 H), 6.91 (d, J = 8 Hz, 2 H), 6.13 (s, 1 H), 3.30 (s, 3 H), 3.27 (s, 1 H), 2.36 (s, 3 H), 2.30 (s, 3 H), 0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 141.9, 141.8, 136.1, 135.7, 129.6, 129.4, 128.0, 126.6, 126.1, 111.3, 34.7, 31.8, 21.7, 21.2, –2.0;

IR (film) 3288, 1618, 1581 cm^{-1}. MS (ESI) 428.1825 (428.1823 calcd for $C_{22}H_{29}N_3O_2SSi$, M + H$^+$).

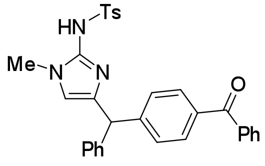


***N*-{4-[(4-Benzoylphenyl)(trimethylsilyl)methyl]-1-methyl-1*H*-imidazol-2-yl}-4-methylbenzenesulfonamide (10e).** The title compound was prepared from **8a** (51 mg, 0.15 mmol) and 4-benzoylphenyl trifluoromethanesulfonate (99.1 mg, 0.30 mmol), using a catalyst composed of Pd(OAc)$_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 74 mg (95%) of the title compound as an off-white solid, m.p. 206–208 °C. ^{1}H NMR (700 MHz, CDCl$_3$) δ 9.98 (s, br, 1 H), 7.77 (t, *J* = 8.4 Hz, 4 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.58 (t, *J* = 7.7 Hz, 1 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.16 (d, *J* = 7.7 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H) 6.24 (s, 1 H), 3.58 (s, 1 H), 3.35 (s, 3 H) 2.34 (s, 3 H), 0.04 (s, 9 H); ^{13}C NMR (175 MHz, CDCl$_3$) δ 196.4, 146.7, 144.8, 141.9, 141.7, 137.9, 135.2, 132.5, 130.7, 130.1, 129.3, 128.5, 127.8, 126.0, 125.5, 111.8, 35.3, 31.8, 21.6, –2.2; IR (film) 3290, 1619, 1581 cm^{-1}. MS (ESI) 518.1938 (518.1928 calcd for $C_{28}H_{31}N_3O_3SSi$, M + H$^+$).

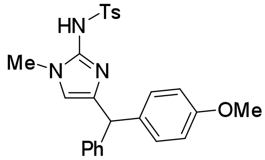


4-Methyl-*N*-{1-methyl-4-[*o*-tolyl(trimethylsilyl)methyl]-1*H*-imidazol-2-yl}benzenesulfonamide (10f): The title compound was prepared from **8a** (51 mg, 0.15 mmol) and *o*-tolyl trifluoromethanesulfonate (53 μL, 0.30 mmol), using a catalyst composed of Pd(OAc)$_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 50 mg (78%) of the title compound as an off-white solid, m.p. 188–190 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.65 (s, br, 1 H), 9.74 (d, *J* = 8.5, 2 H), 7.19–

7.09 (m, 5 H), 7.01 (d, *J* = 8 Hz, 1 H), 6.08 (s, 1 H), 3.54 (s, 1 H), 3.29 (s, 3 H), 2.36 (s, 3 H), 2.27 (s, 3 H), 0.06 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 141.9, 141.5, 137.5, 135.7, 131.3, 129.4, 127.9, 126.6, 126.5, 126.3, 126.1, 111.1, 31.8, 30.1, 21.8, 20.9, –1.7; IR (film) 3292, 1616, 1580, 1483 cm^{-1}. MS (ESI) 428.1824 (428.1823 calcd for $C_{22}H_{29}N_3O_2SSi$, M + H$^+$).

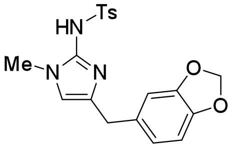


***N*-{4-[(4-Benzoylphenyl)(phenyl)methyl]-1-methyl-1*H*-imidazol-2-yl}-4-methylbenzenesulfonamide (10g).** The title compound was prepared from **8b** (51 mg, 0.15 mmol) and 4-benzoylphenyl trifluoromethanesulfonate (99.1 mg, 0.30 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D. This procedure afforded 44 mg (56%) of the title compound as an off-white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, br, 1 H), 7.79 (d, *J* = 8 Hz, 2 H), 7.73 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.50–7.47 (m, 2 H), 7.34–7.28 (m, 3 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8 Hz, 2 H), 7.13 (d, *J* = 7 Hz, 2 H), 5.77 (s, 1 H), 5.35 (s, 1 H), 3.28 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 147.7, 144.7, 142.0, 141.4, 139.3, 137.6, 137.0, 132.8, 130.8, 130.2, 129.3, 129.2, 128.8, 128.7, 128.5, 128.0, 126.9, 126.0, 114.6, 48.2, 31.8, 21.6; IR (film) 3291, 1656, 1628, 1584 cm^{-1}. MS (ESI) 522.1859 (522.1846 calcd for $C_{31}H_{27}N_3O_3S$, M + H$^+$)

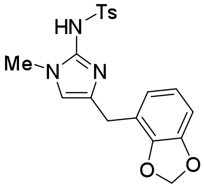


***N*-{4-[(4-Methoxyphenyl)(phenyl)methyl]-1-methyl-1*H*-imidazol-2-yl}-4-methylbenzenesulfonamide (10h).** The title compound was prepared from **8b** (51 mg, 0.15 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (136 μL, 0.75 mmol), using a catalyst composed of $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure D (except with modified stoichiometries of reactants as noted above). This procedure afforded 42 mg (63%) of the title compound as an off-white solid, m.p. 69–71 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, br, 1 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.32–7.26 (m, 3 H), 7.19 (d, *J* = 8 Hz, 2 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 6.83 (d, *J* = 8.5 Hz, 2 H), 5.73 (s, 1 H), 5.17 (s, 1 H), 3.79 (s, 3 H), 3.26 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 147.6, 141.8, 141.6, 140.3, 132.0, 129.7, 129.3, 129.0, 128.6, 127.9, 127.6, 126.0, 114.4, 114.2, 55.5 47.5, 31.7, 21.6; IR (film) 3290, 1619, 1581 cm^{-1}. MS (ESI) 448.1700 (448.1689 calcd for $C_{25}H_{25}N_3O_3S$, M + H^+).

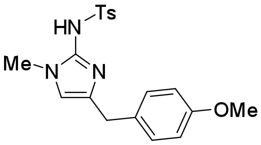
General Procedure E for the Preparation of Des-TMS Cyclic Guanidines. A flame-dried Schlenk tube equipped with a stir bar was cooled under vacuum, backfilled with nitrogen, and charged with the appropriate guanidine substrate (1.0 equiv), RuPhos (0.08 equiv), and lithium *tert*-butoxide (2.4 equiv). The flask was evacuated and backfilled with nitrogen then a pre-stirred solution of palladium (II) acetate (0.04 equiv) in trifluorotoluene (0.9 mg palladium (II) acetate/mL $PhCF_3$) was added via syringe along with the appropriate aryl triflate (2.0 equiv), and the tube was heated to 100 °C with stirring for three hours. The mixture was cooled to rt and 4 M HCl in dioxane (20 mL/mmol substrate) was added. The mixture was heated back up to 100 °C and stirred for 1.5 h. The reaction mixture was diluted with dichloromethane (120 mL/mmol substrate) and a solution of saturated sodium bicarbonate (20 mL/mmol substrate) and added to a separatory funnel. The layers were separated and the aqueous layer was extracted with dichloromethane (2 x 120 mL/mmol substrate). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.



N-[4-(Benzo[d][1,3]dioxol-5-ylmethyl)-1-methyl-1H-imidazol-2-yl]-4-methylbenzenesulfonamide (S5).[4] The title compound was prepared from **8a** (51 mg, 0.15 mmol) and benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (52 µL, 0.30 mmol), using a catalyst composed of Pd(OAc)$_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure E. This procedure afforded 55 mg (95%) of the title compound as an off-white solid, m.p. 193–194 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.95 (s, br, 1 H), 7.78 (d, *J* = 8.5 Hz, 2 H), 7.19 (d, *J* = 8 Hz, 2 H), 6.72 (d, *J* = 8.5 Hz, 1 H), 6.61 (d, *J* = 6.5 Hz, 2 H), 5.97 (s, 1 H), 5.94 (s, 2 H), 3.66 (s, 2 H), 3.27 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.2, 147.3, 146.9, 141.8, 141.7, 130.0, 129.3, 126.0, 125.0, 121.9, 112.1, 109.2, 108.6, 101.3, 31.7, 31.2, 21.6; IR (film) 3287, 1581, 1488 cm^{-1}. MS (ESI) 386.1172 (386.1169 calcd for $C_{19}H_{19}N_3O_4S$, M + H$^+$).



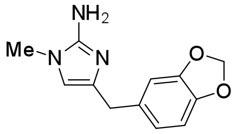
N-[4-(Benzo[d][1,3]dioxol-4-ylmethyl]-1-methyl-1H-imidazol-2-yl)-4-methylbenzenesulfonamide (S6). The title compound was prepared from **8a** (51 mg, 0.15 mmol) and benzo[*d*][1,3]dioxol-4-yl trifluoromethanesulfonate (52 µL, 0.30 mmol), using a catalyst composed of Pd(OAc)$_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure E. This procedure afforded 45 mg (78%) of the title compound as an off-white solid, m.p. 184–185 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.33 (s, br, 1 H), 7.76 (d, *J* = 8.5 Hz, 2 H), 7.17 (d, *J* = 8.5 Hz, 2 H), 6.76–6.75 (m, 2 H), 6.61 (dd, *J* = 6.5, 2.5 Hz, 1 H), 6.11 (s, 1 H), 6.03 (s, 2 H), 3.69 (s, 2 H), 3.25 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.6, 147.3, 145.4, 141.8, 141.7, 129.2, 125.9, 123.4, 122.4, 122.3, 118.5, 111.5, 108.1, 101.2, 31.6, 26.0, 21.5; IR (film) 3296, 1580 cm^{-1}. MS (ESI) 386.1179 (386.1169 calcd for $C_{19}H_{19}N_3O_4S$, M + H$^+$).



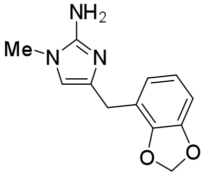
***N*-[4-(4-Methoxybenzyl)-1-methyl-1*H*-imidazol-2-yl]-4-methylbenzenesulfonamide (S7).** The title compound was prepared from **8a** (51 mg, 0.15 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (55 µL, 0.30 mmol), using a catalyst composed of Pd(OAc)$_2$ (1.3 mg, 0.006 mmol) and RuPhos (5.6 mg, 0.012 mmol) according to General Procedure E. This procedure afforded 55 mg (99%) of the title compound as an off-white solid, m.p. 184–185 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.01 (s, br, 1 H), 7.77 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8 Hz, 2 H), 7.06 (d, *J* = 9 Hz, 2 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 5.91 (s, 1 H), 3.78 (s, 3 H), 3.69 (s, 2 H), 3.26 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.8, 147.2, 141.7, 129.9, 129.3, 128.3, 126.0, 125.5, 114.3, 112.0, 55.4, 31.6 30.7, 21.6 (one carbon signal is missing due to incidental equivalence); IR (film) 3294, 1582 cm^{-1}. MS (ESI) 372.1378 (372.1376 calcd for $C_{19}H_{21}N_3O_3S$, M + H$^+$).

Synthesis of 2-Aminoimidazole Natural Products via *N*-Tosyl Deprotection

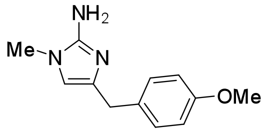
General Procedure F for the Deprotection of Tosyl Protected Cyclic Guanidines. A Schlenk tube equipped with a stir bar was flame-dried under vacuum then was cooled to rt and backfilled with nitrogen. The tube was charged with an excess of lithium wire (ca. 85 equiv), naphthalene (6 equiv), trimethylsilylchloride (6 equiv), and THF (0.16 M). The reaction mixture was allowed to stir at rt for 30 min then was cooled to –78 °C. In a scintillation vial, the appropriate guanidine substrate was dissolved in THF (0.04 M) and was stirred at 60 °C for 30 min. The solution of the appropriate guanidine substrate was quickly transferred to the cooled tube containing the mixture of lithium, naphthalene, and THF. The reaction mixture was stirred at –78 °C for 3 h then was allowed to warm to rt. The reaction was then slowly quenched with a solution of saturated sodium bicarbonate (65 mL/mmol substrate). The mixture was added to a separatory funnel, along with dichloromethane (200 mL/mmol substrate) and additional saturated sodium bicarbonate (100 mL/mmol substrate). The layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 200 mL/mmol substrate). The organic layers were combined, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo.* The crude material was purified by flash chromatography on silica gel.



Preclathridine A (1).[5] The title compound was prepared from **S5** (33 mg, 0.072 mmol), lithium wire (100 mg), naphthalene (55.5 mg, 0.43 mmol), and trimethylsilylchloride (55 µL, 0.43 mmol) according to General Procedure F. This procedure afforded 14 mg (85%) of the title compound as a light brown foam. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27 (s, br, 2 H), 6.73 (d, *J* = 8.5 Hz, 1 H), 6.68 (d, *J* = 6 Hz, 2 H), 6.00 (s, 1 H), 5.92 (s, 2 H), 3.68 (s, 2 H), 3.53 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.9, 147.2, 146.7, 129.6, 127.0, 121.9, 112.7, 109.1, 108.5, 101.0, 32.8, 30.9; IR (film) 3104, 1669, 1489 cm^{-1}. MS (ESI) 232.1089 (232.1081 calcd for $C_{12}H_{13}N_3O_2$, M + H$^+$).



Preclathridine B (2).[6] The title compound was prepared from **S6** (60 mg, 0.16 mmol), lithium wire (100 mg), naphthalene (120 mg, 0.93 mmol), and trimethylsilylchloride (118 µL, 0.93 mmol) according to General Procedure F. This procedure afforded 34 mg (91%) of the title compound as a brown foam. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.76–6.67 (m, 3 H), 6.10 (s, 1 H), 5.93 (s, 2 H), 3.70 (s, 2 H), 3.34 (s, 3 H) (two NH protons are missing due to broadening); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.8, 147.3, 145.6, 132.8, 123.0, 121.7, 120.8, 113.0, 107.0, 100.9, 31.9, 27.5; IR (film) 3318, 3138, 1671, 1638 cm^{-1}. MS (ESI) 232.1090 (232.1081 calcd for $C_{12}H_{13}N_3O_2$, M + H$^+$).



Dorimidazole B (3).[6] The title compound was prepared from **S7** (63 mg, 0.17 mmol), lithium wire (100 mg), naphthalene (131 mg, 1.0 mmol), and trimethylsilylchloride (130 μL, 1.0 mmol) according to General Procedure F. This procedure afforded 25 mg (68%) of the title compound as a light brown foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2 H), 6.79 (d, J = 8.5 Hz, 2 H), 5.97 (s, 1 H), 5.71 (s, br, 2 H), 3.75 (s, 3 H), 3.64 (s, 2 H), 3.33 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 147.8, 133.6, 131.0, 129.9, 114.0, 112.8, 55.4, 32.7, 31.9; IR (film) 3329, 1671 cm^{-1}. MS (ESI) 218.1289 (218.1288 calcd for $C_{12}H_{15}N_3O$, M + H$^+$).

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(3) Whitby, R. J.; Stec, J.; Blind, R. D.; Dixon, S.; Leesnitzer, L. M.; Orband-Miller, L. A; Williams, S. P.; Willson, T. M.; Xu, R.; Zuercher, W. J.; Cai, F.; Ingraham, H. A. *J. Med. Chem.* **2011**, *54*, 2266–2281.

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(5) Koswatta, P. B.; Lovely, C. J. *Tetrahedron Lett.* **2009**, *50*, 4998–5000.

(6) Hassan, W. H. B.; Al-Taweel, A. M.; Proksch, P. *Saudi Pharm. J.* **2009**, *17*, 295–298.

Proton Spectrum

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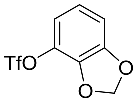

13

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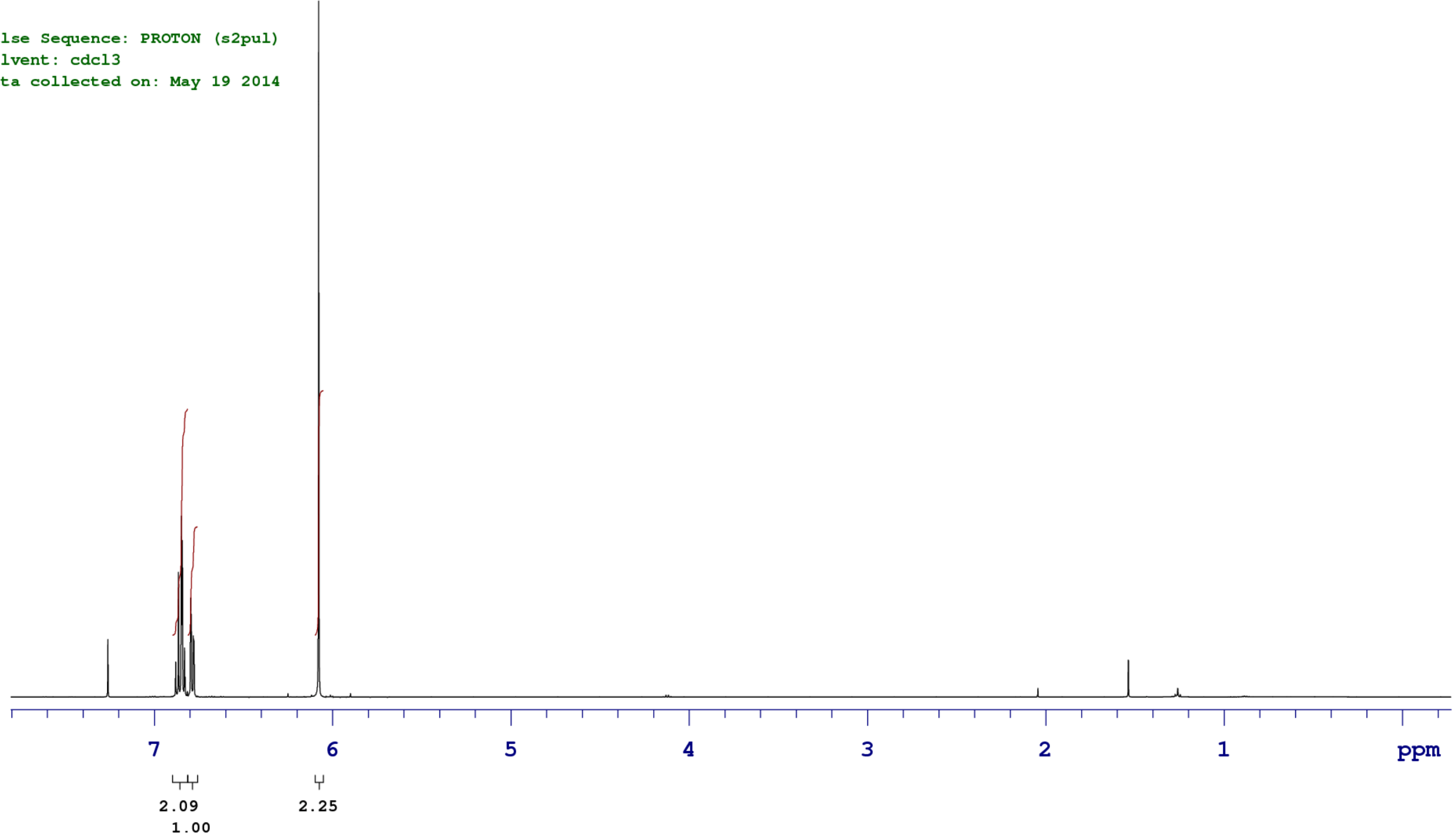

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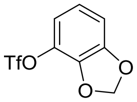

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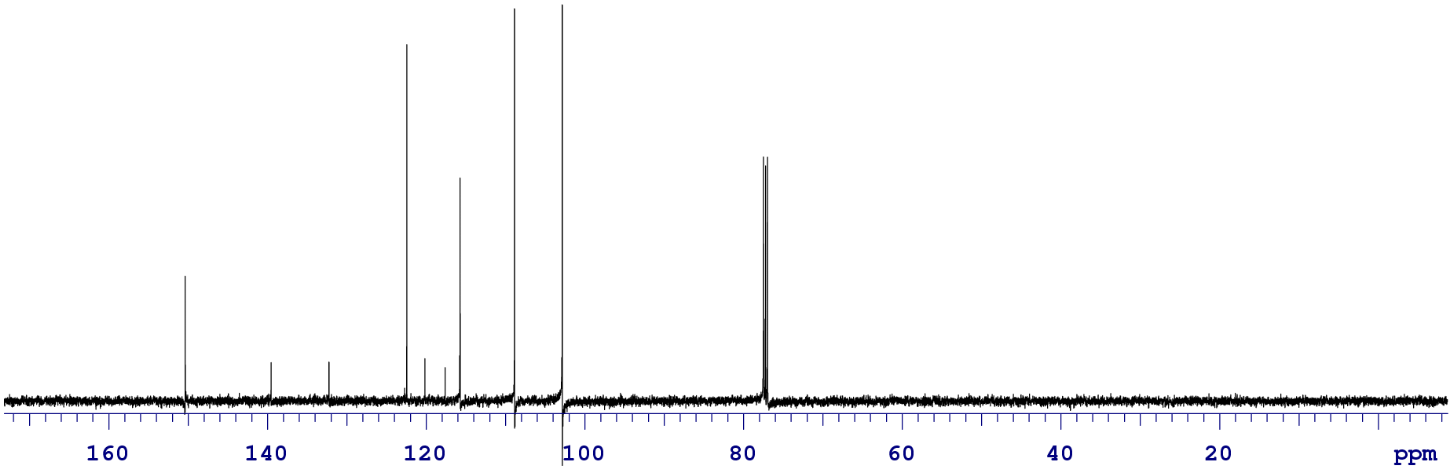
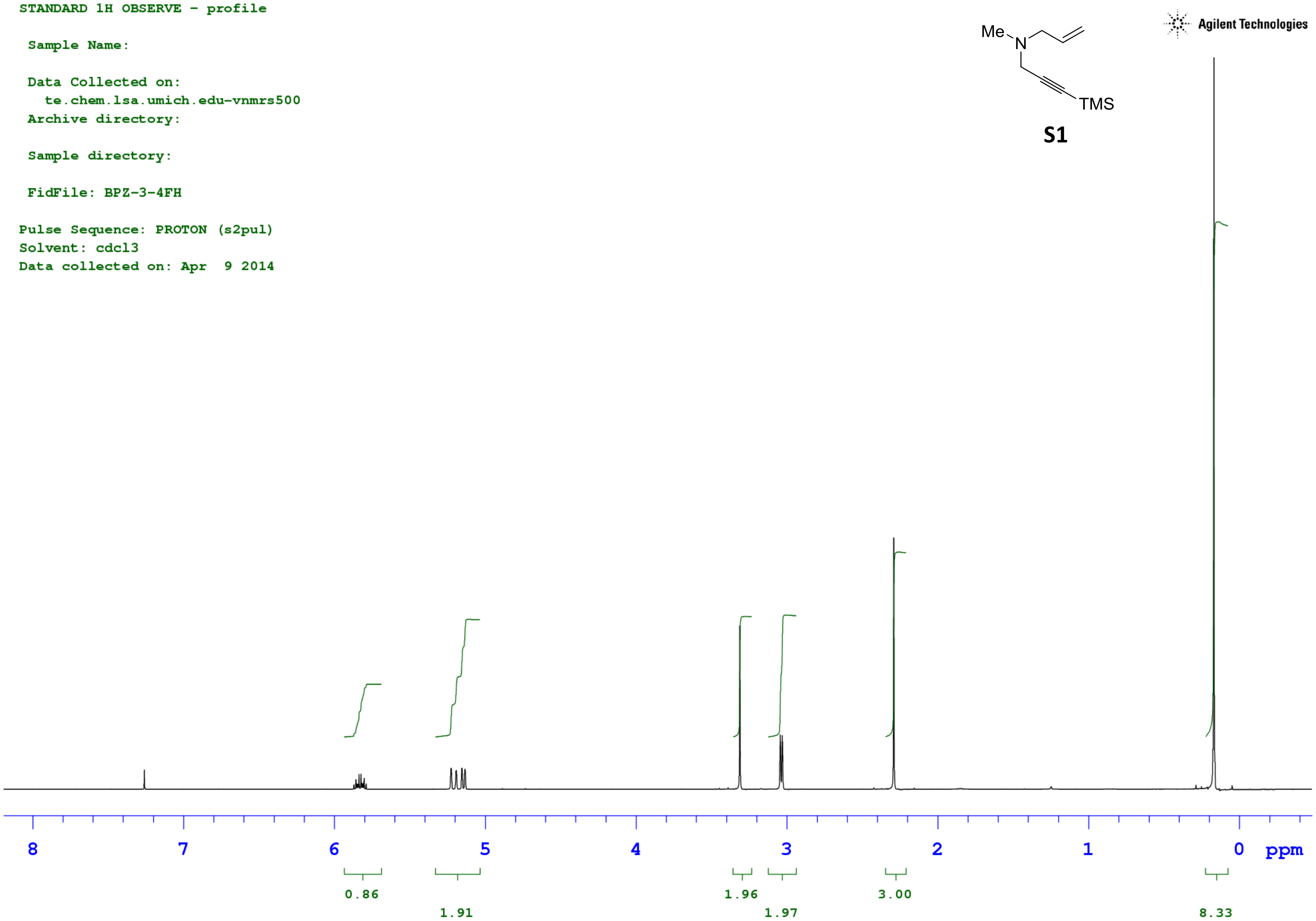
Agilent Technologies





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S1

STANDARD 1H OBSERVE - profile

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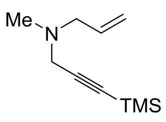
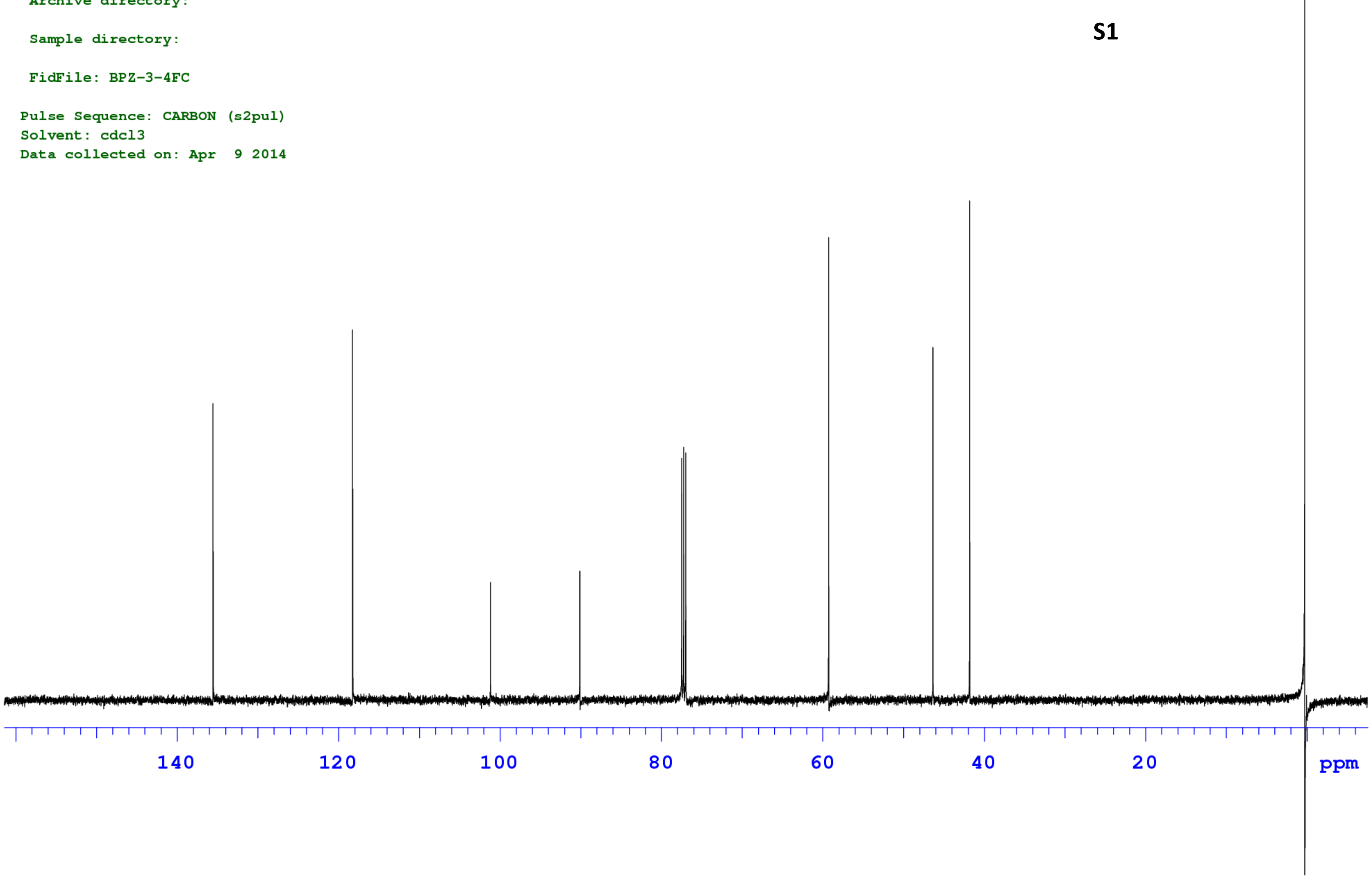


S1

Agilent Technologies



Proton Spectrum

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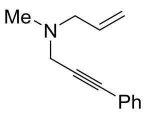
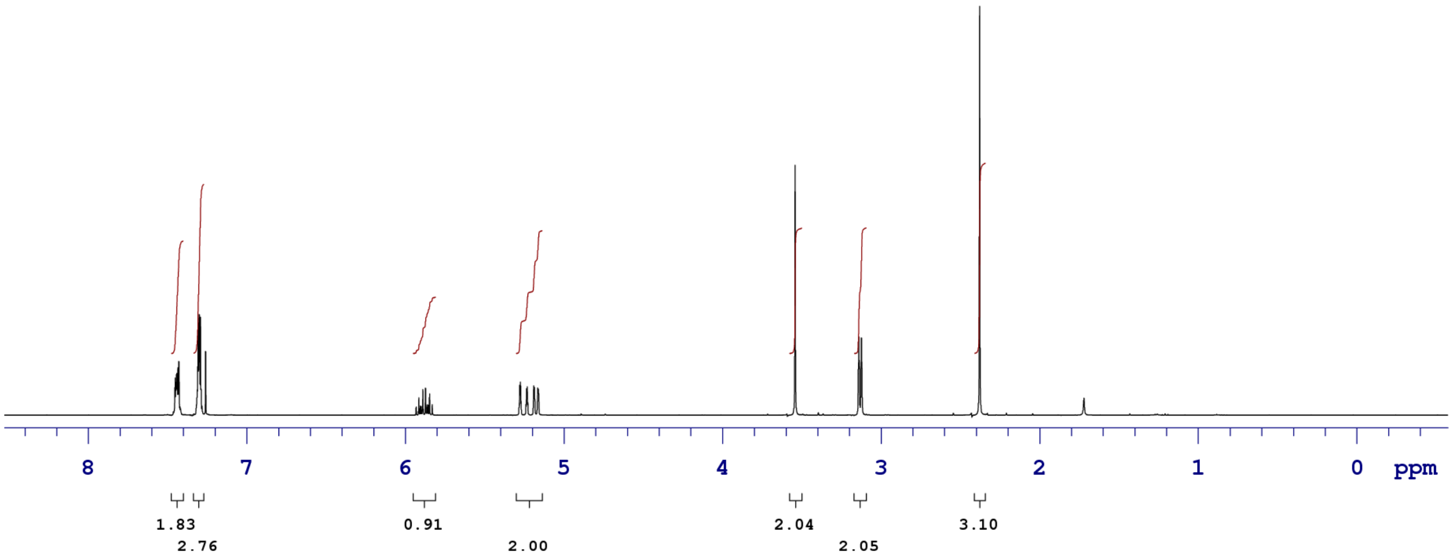
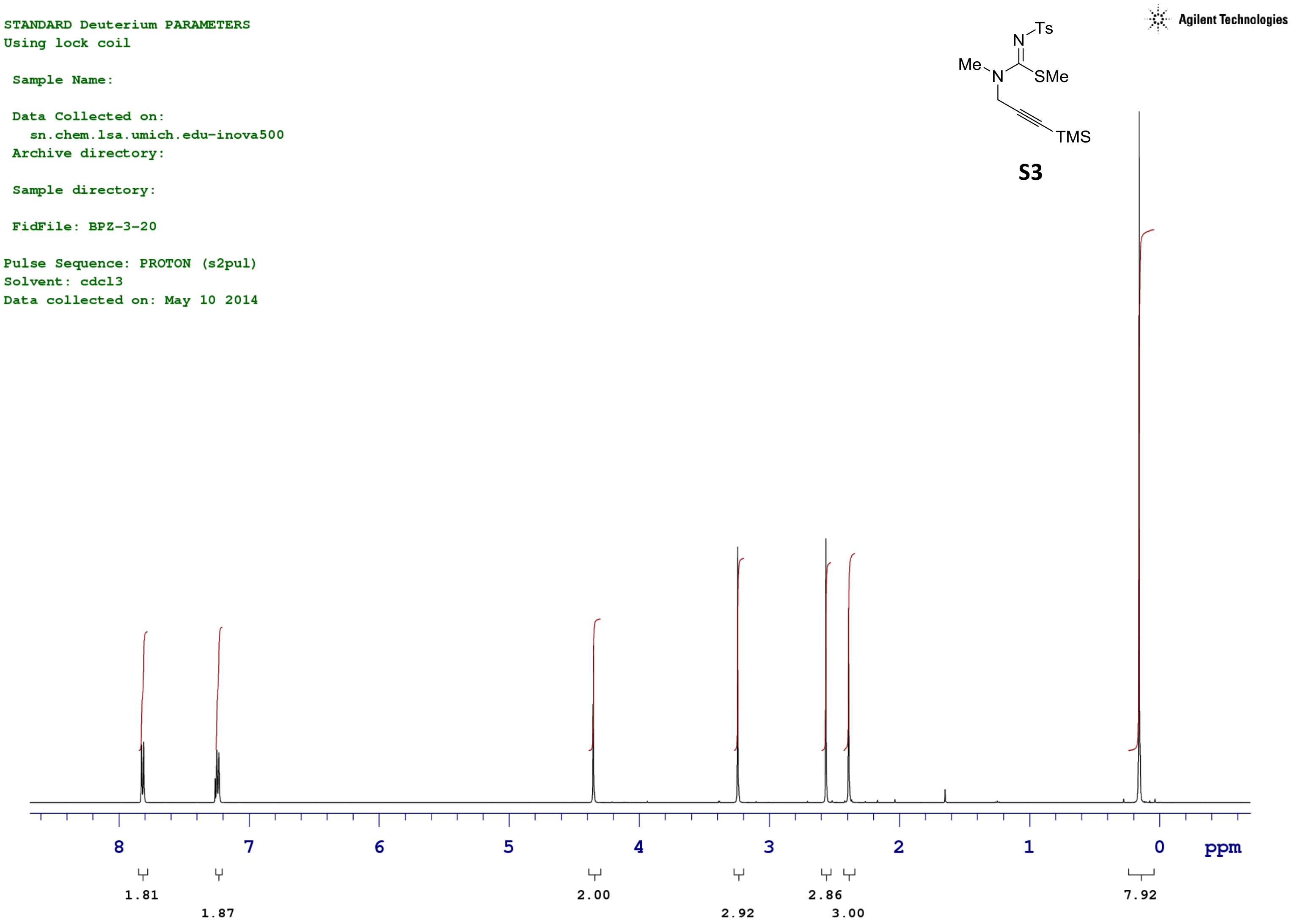


S2

Agilent Technologies




STANDARD Deuterium PARAMETERS
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S3

Carbon-13

Sample Name:

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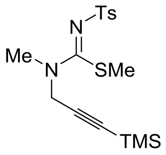
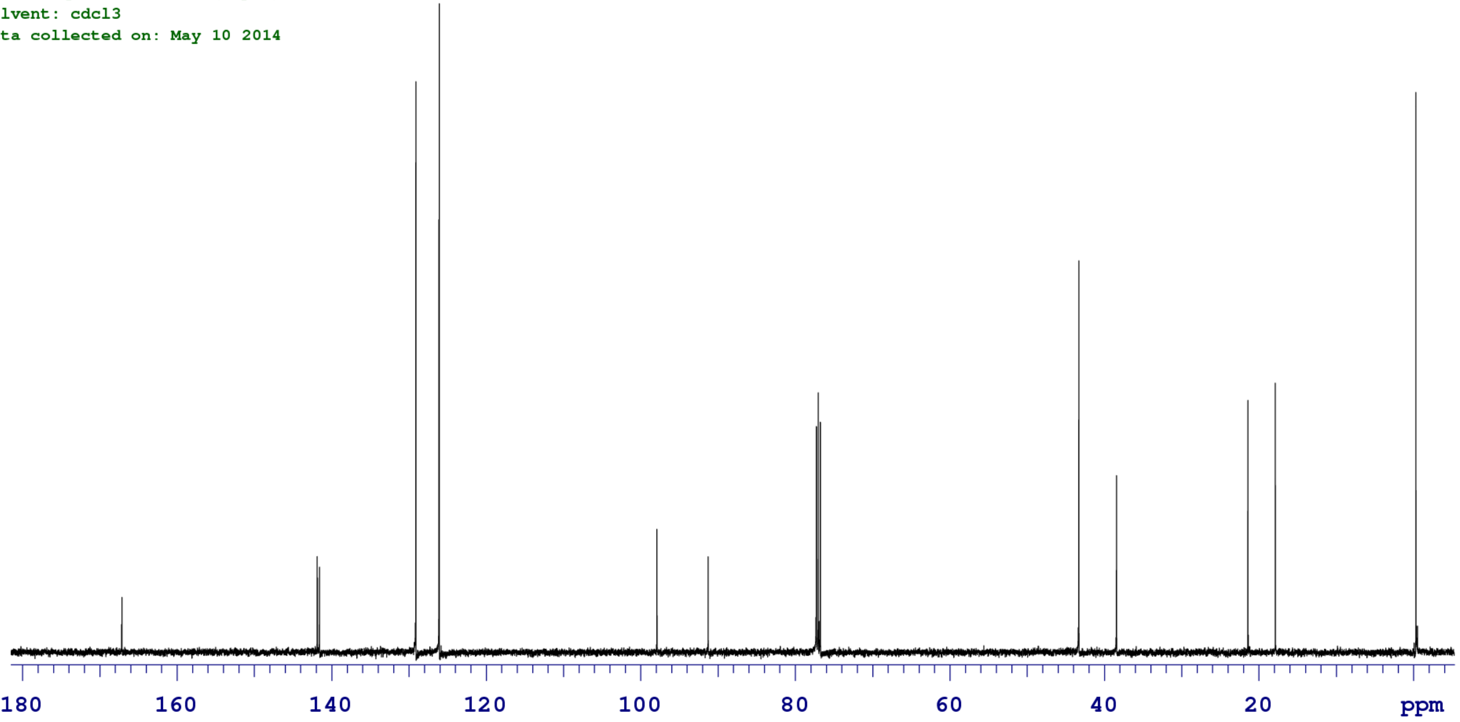
Solvent: cdcl3
Data collected on: May 10 2014

Agilent Technologies



S3



Proton Spectrum

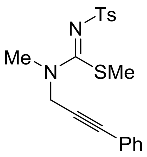
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

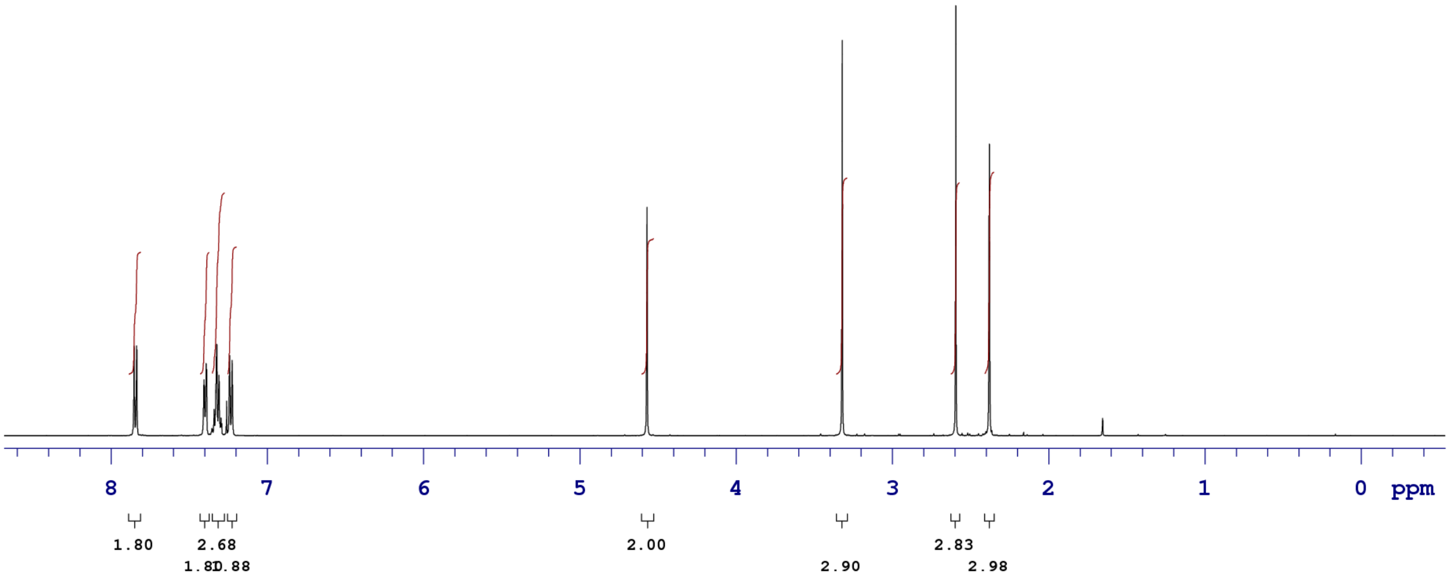
FidFile: BPZ-3-19FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 10 2014



S4

Agilent Technologies



Carbon-13

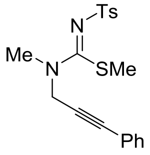
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

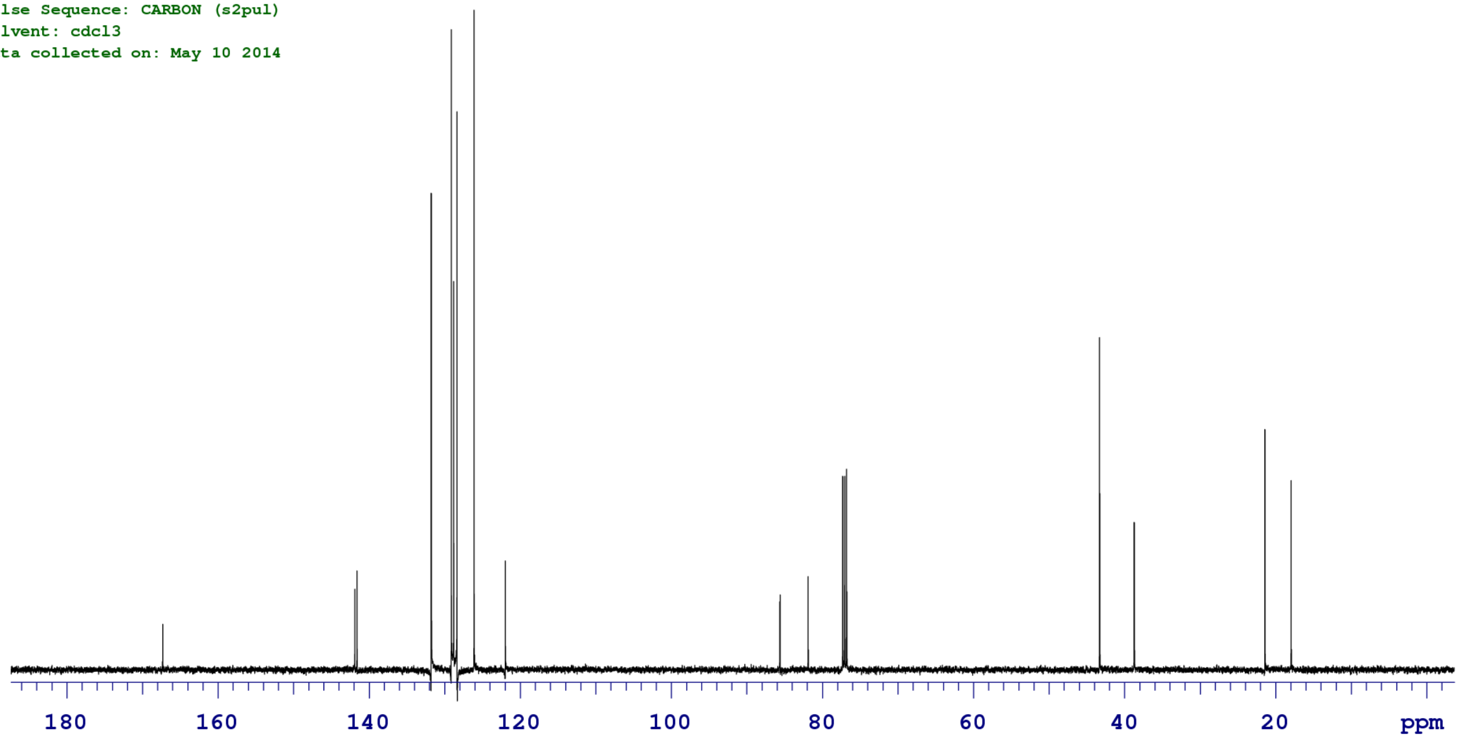
FidFile: BPZ-3-19FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 10 2014



S4

Agilent Technologies



STANDARD PROTON PARAMETERS

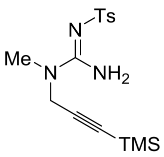
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

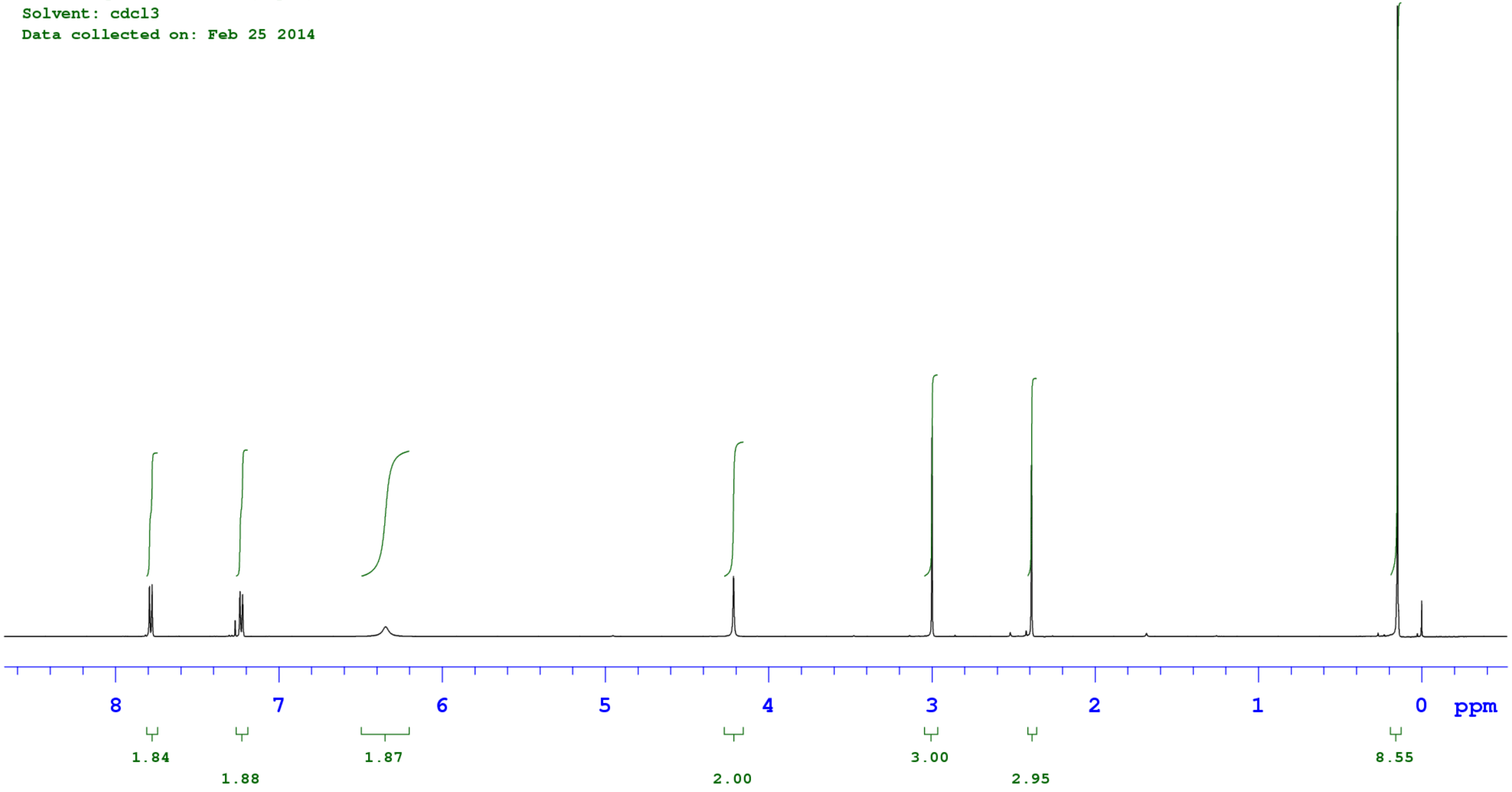
FidFile: BPZ-2-189FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 25 2014



8a

Agilent Technologies



STANDARD 1H OBSERVE - profile

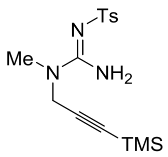
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

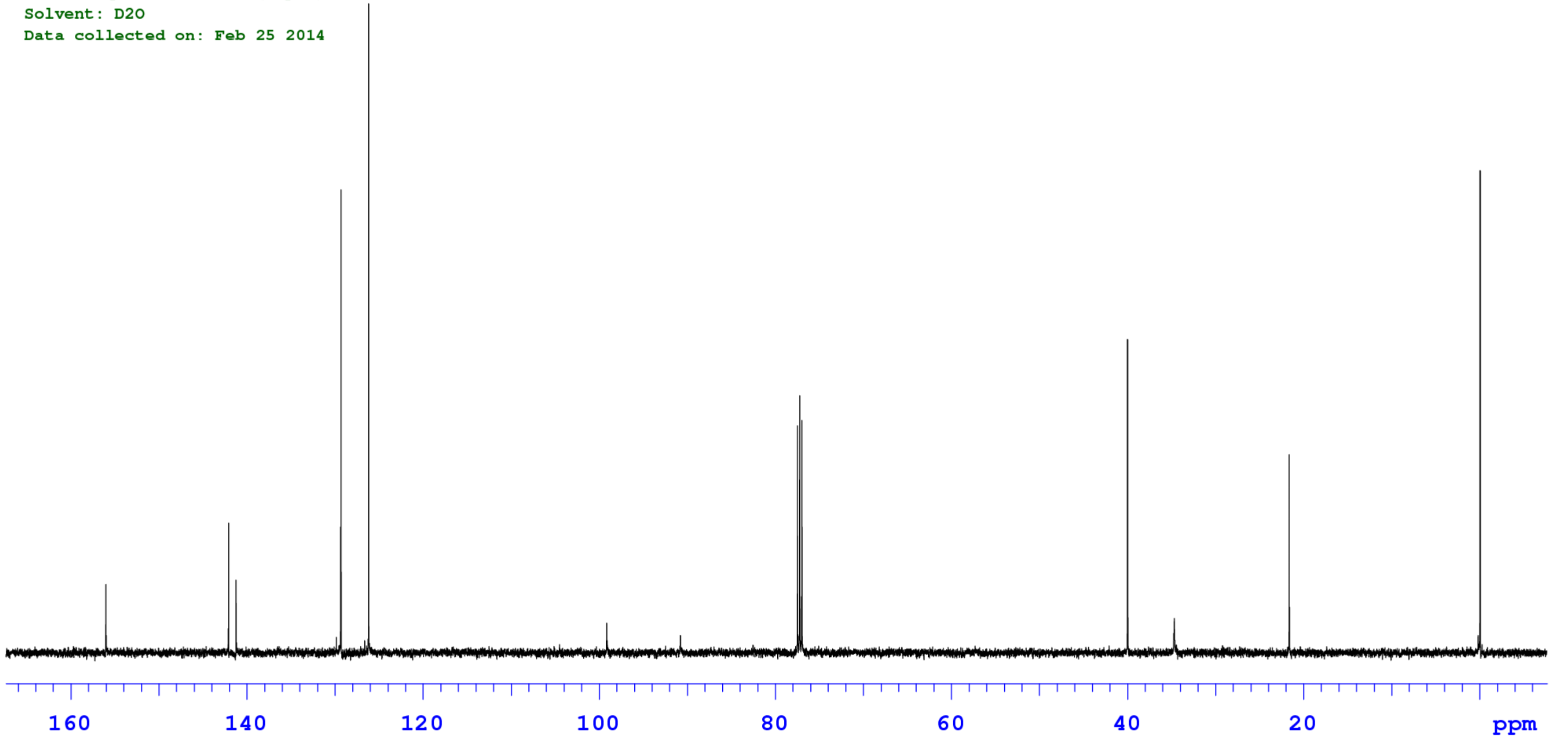
FidFile: BPZ-2-189FC

Pulse Sequence: CARBON (s2pul)
Solvent: D2O
Data collected on: Feb 25 2014



8a

Agilent Technologies



Proton Spectrum

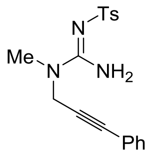
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

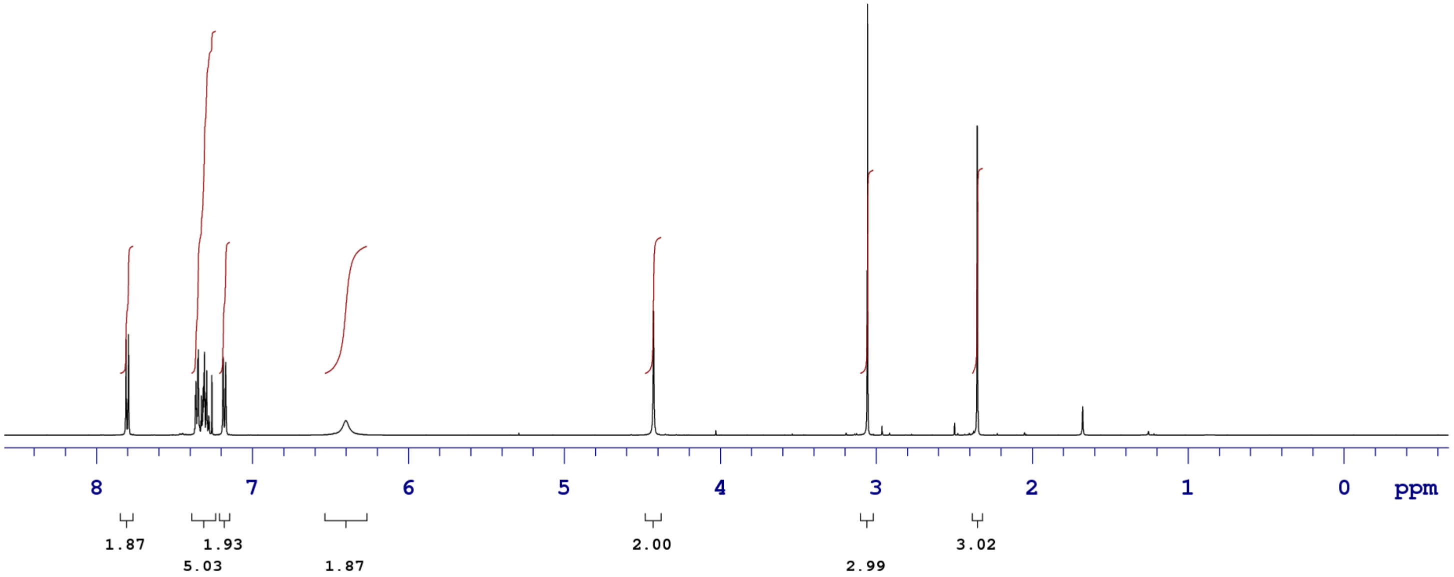
FidFile: BPZ-3-22FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2014



8b

Agilent Technologies



Carbon-13

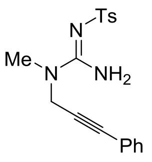
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

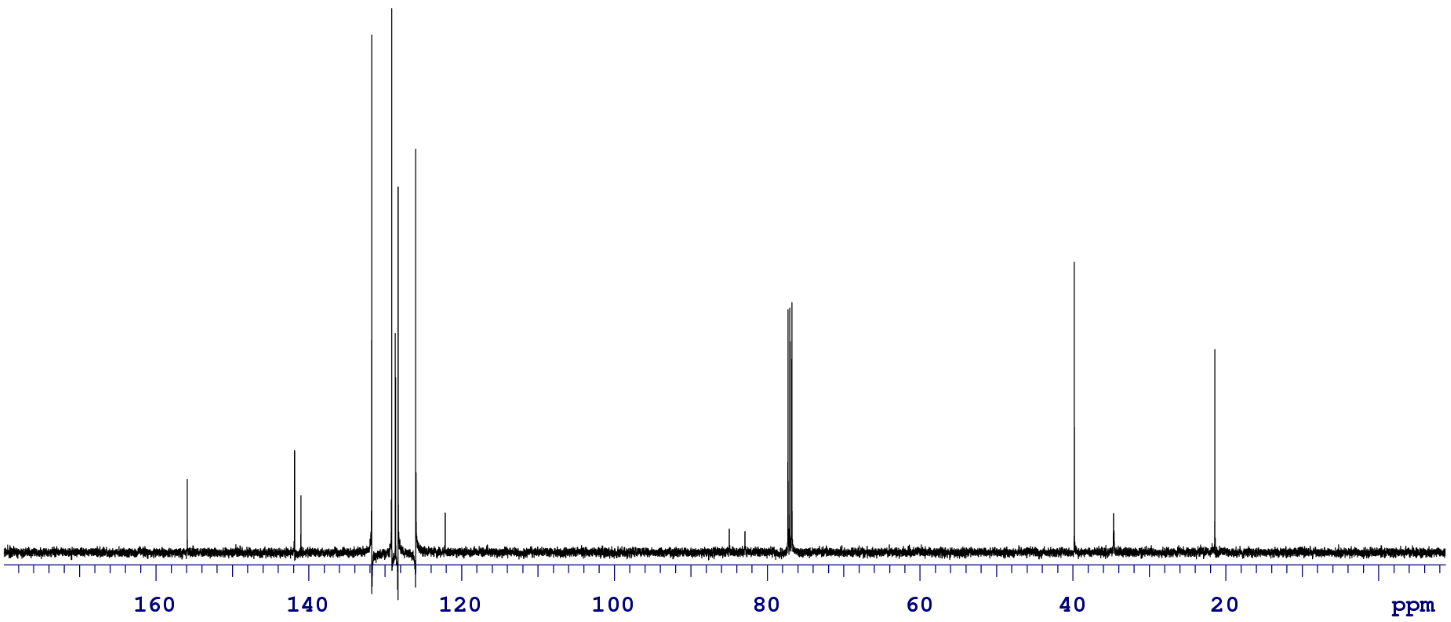
Sample directory:

FidFile: BPZ-3-22FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2014



8b



Proton Spectrum

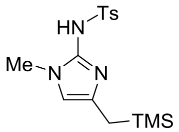
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

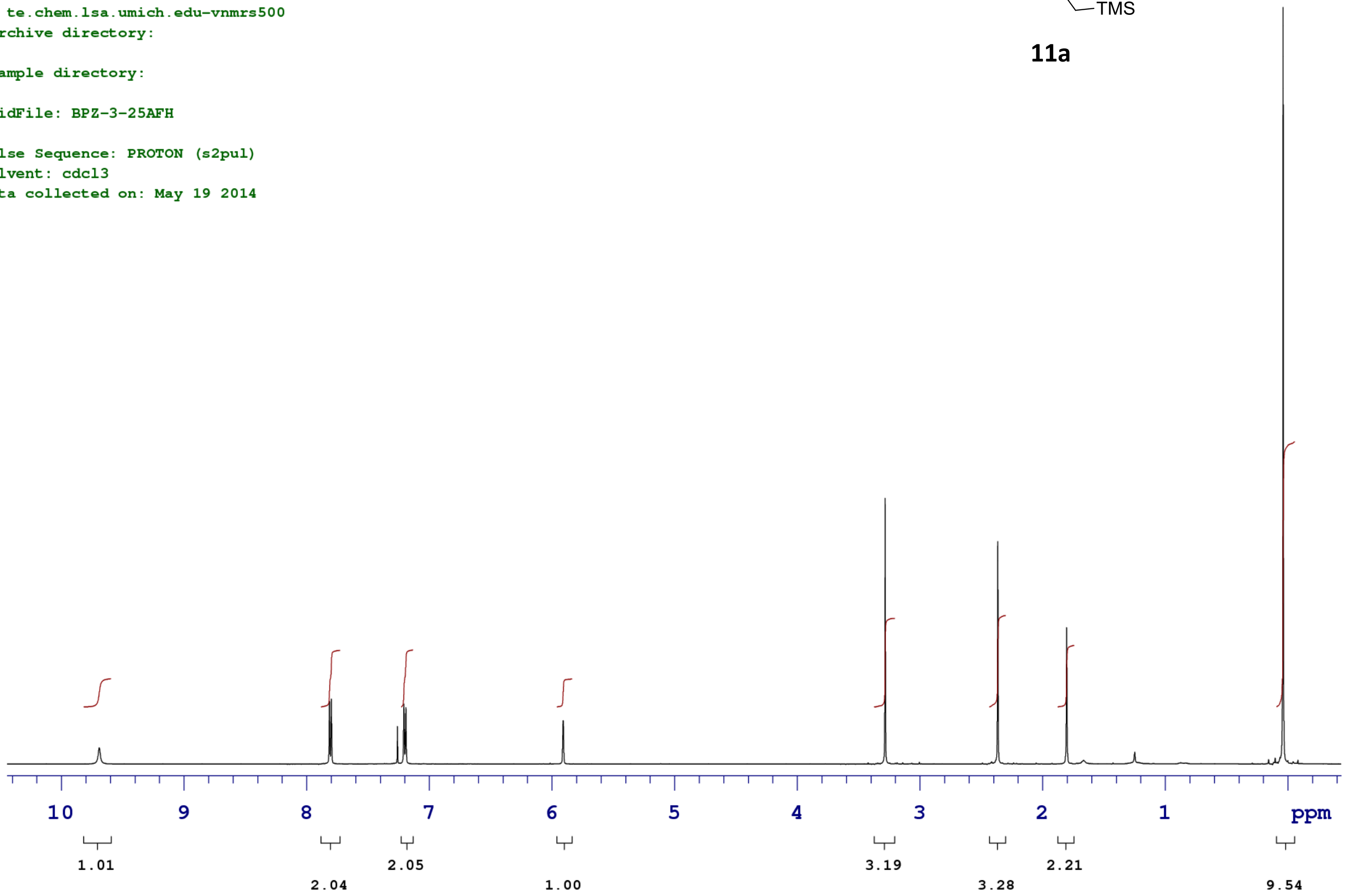
FidFile: BPZ-3-25AFH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 19 2014



11a

Agilent Technologies



Carbon-13

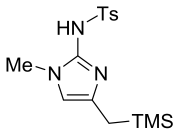
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

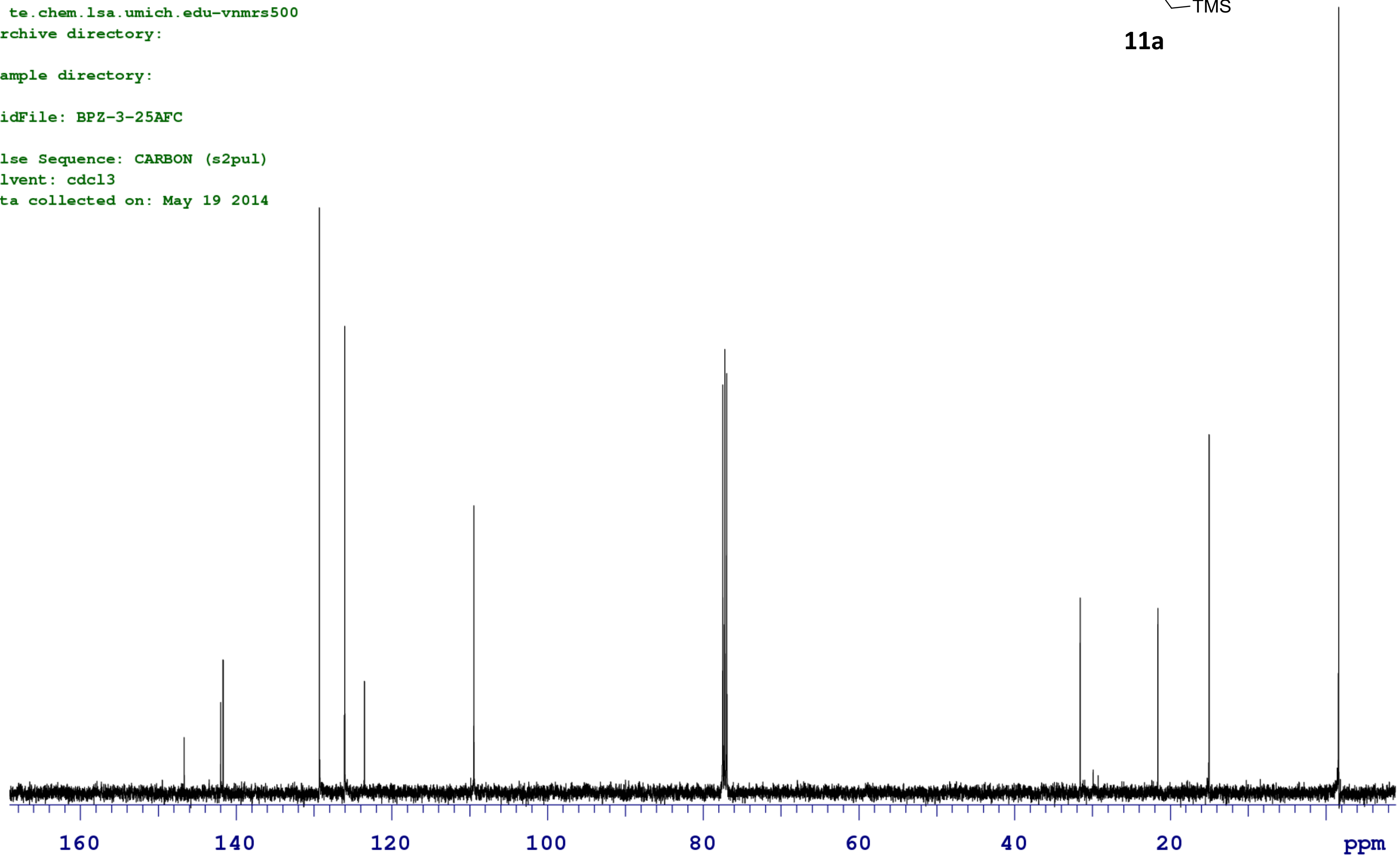
FidFile: BPZ-3-25AFC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 19 2014



11a

Agilent Technologies



Proton Spectrum

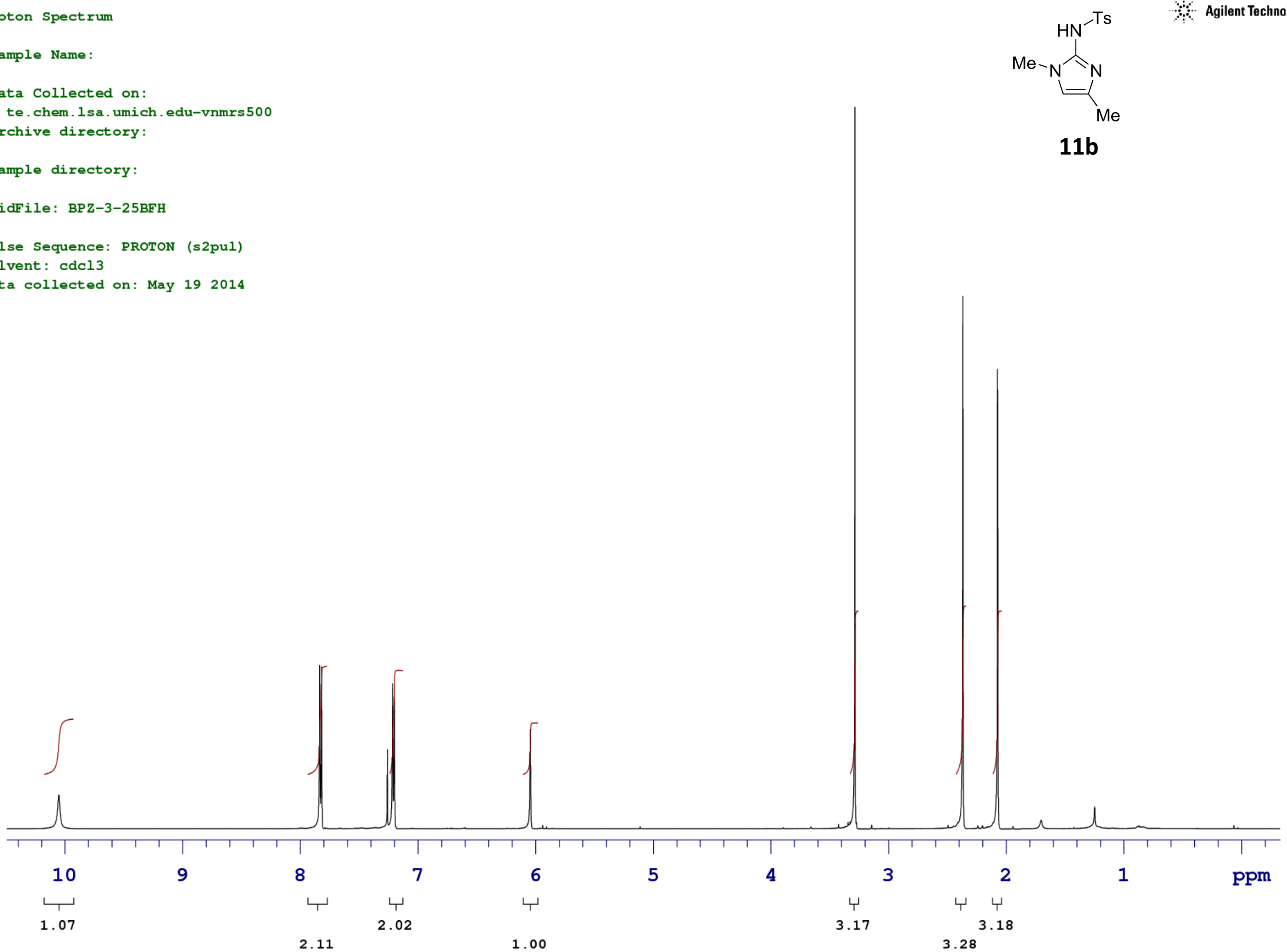
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

FidFile: BPZ-3-25BFH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 19 2014



Carbon-13

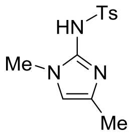
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

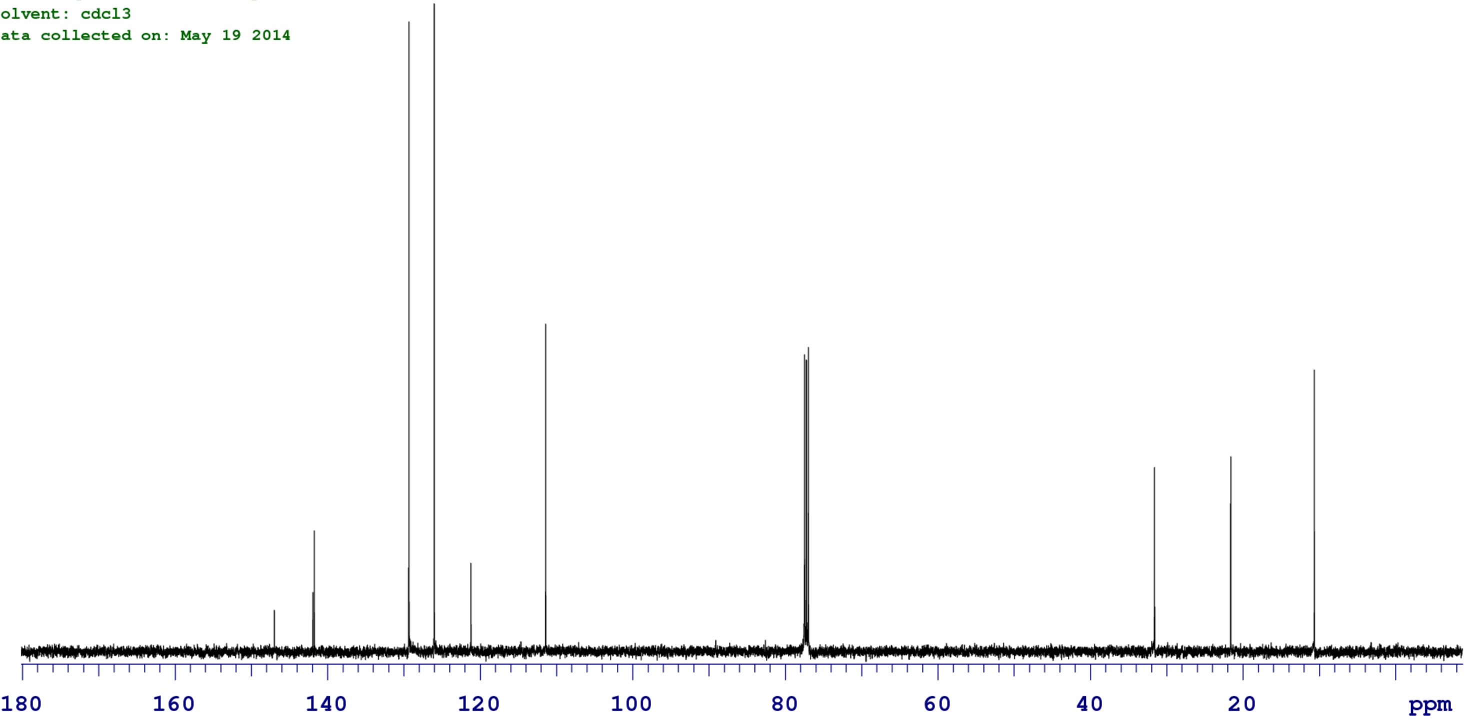
FidFile: BPZ-3-25BFC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 19 2014



11b

Agilent Technologies



STANDARD PROTON PARAMETERS

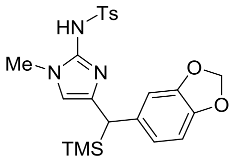
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

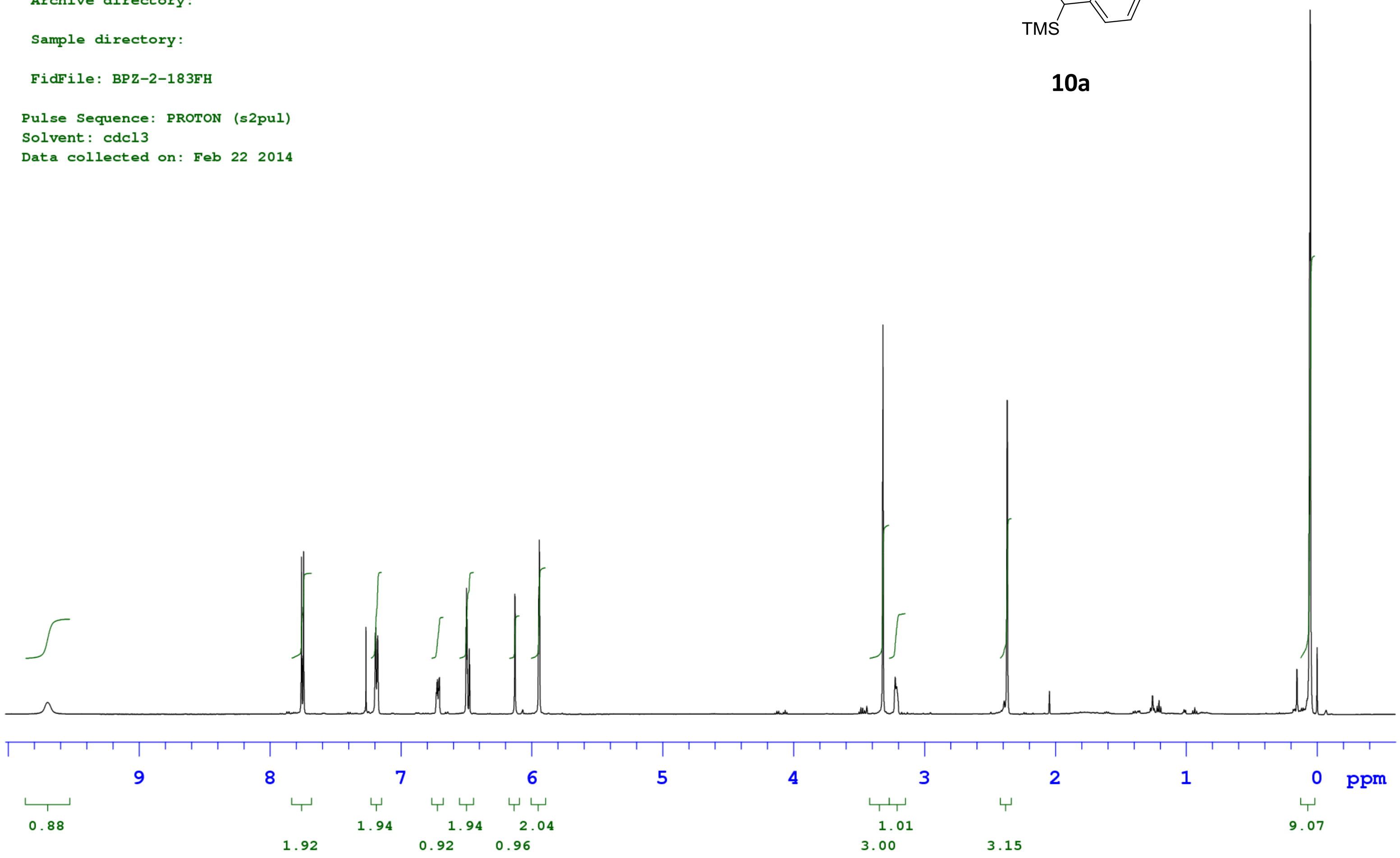
Sample directory:

FidFile: BPZ-2-183FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 22 2014



10a



STANDARD PROTON PARAMETERS

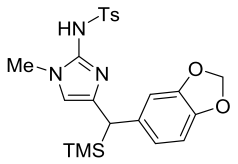
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

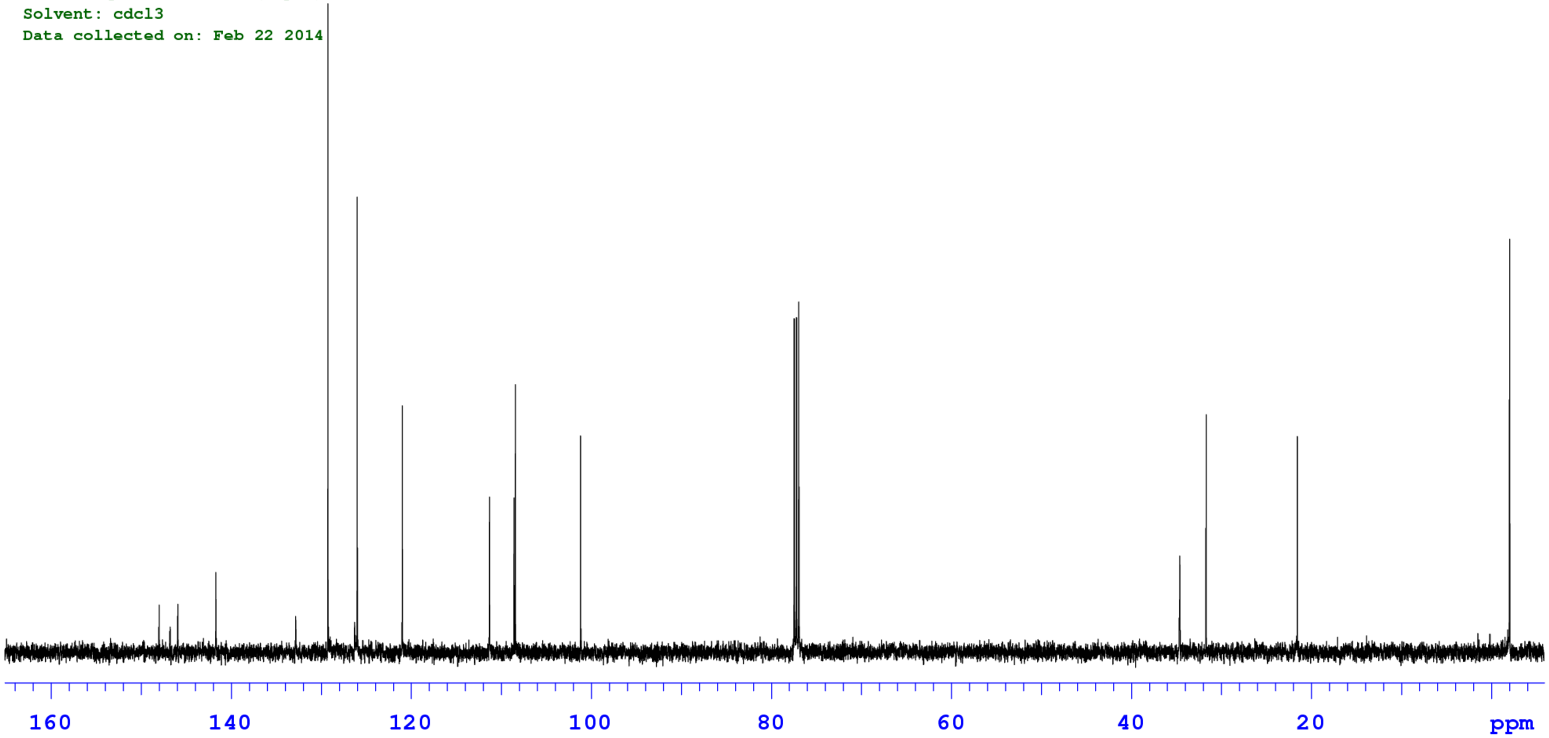
FidFile: BPZ-2-183FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 22 2014



10a

Agilent Technologies



Proton Spectrum

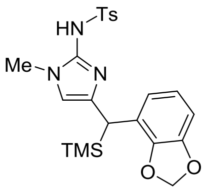
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

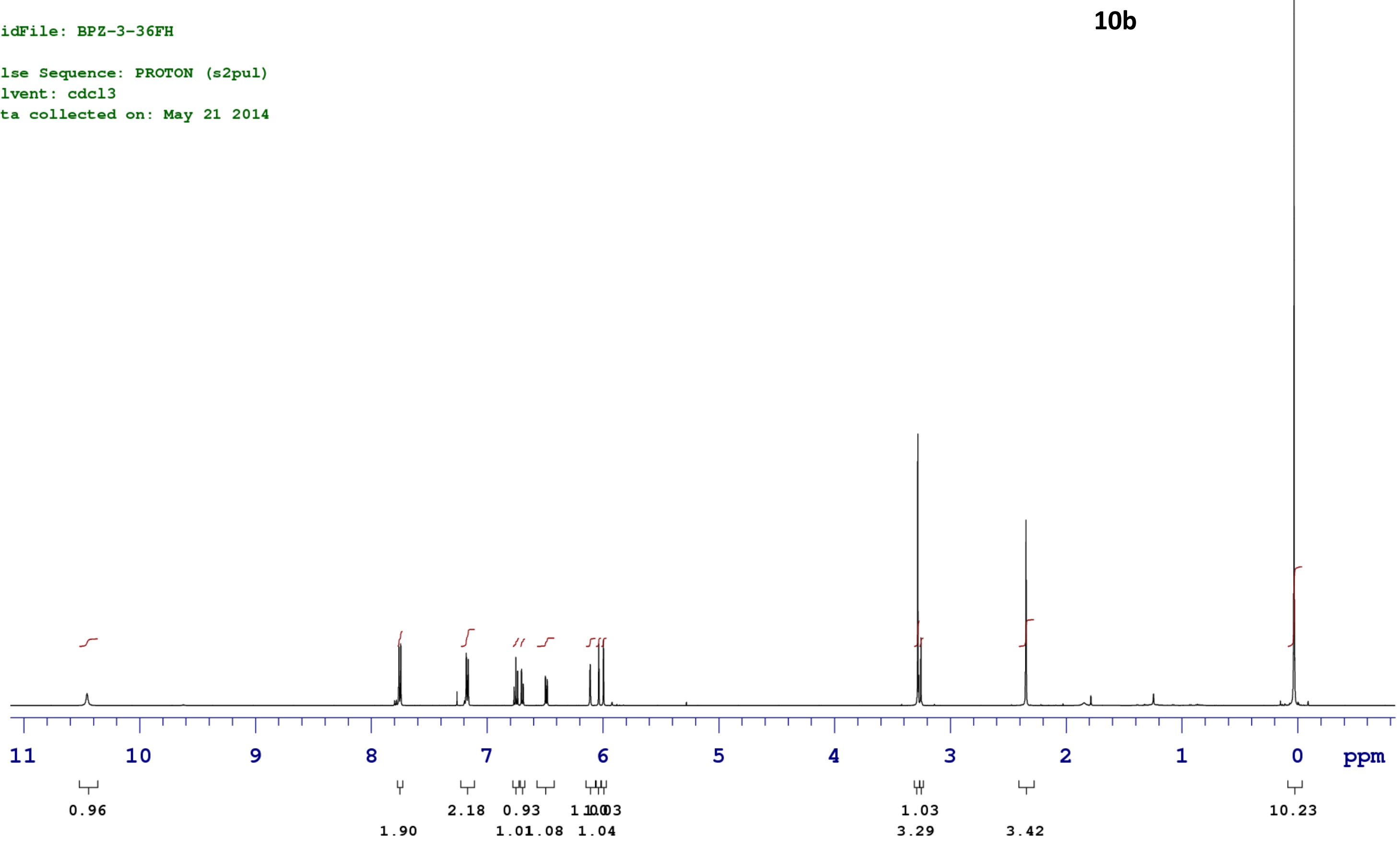
FidFile: BPZ-3-36FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2014



10b

Agilent Technologies



Carbon-13

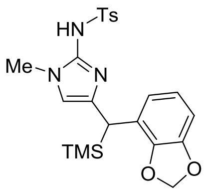
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

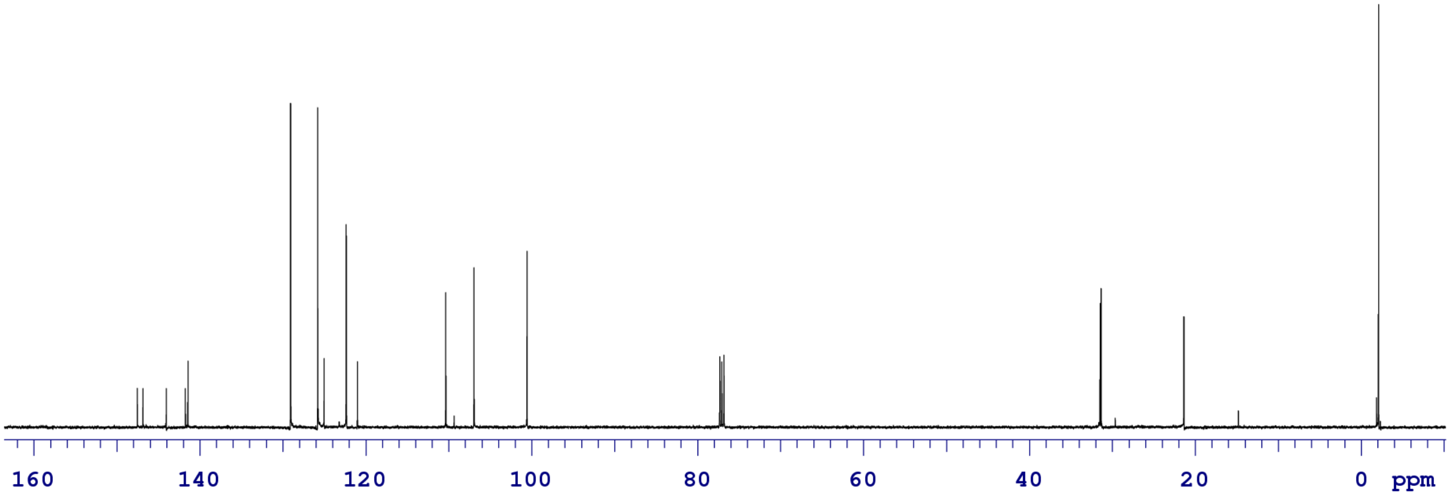
FidFile: BPZ-3-36FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2014



10b

Agilent Technologies



STANDARD 1H OBSERVE - profile

Sample Name:

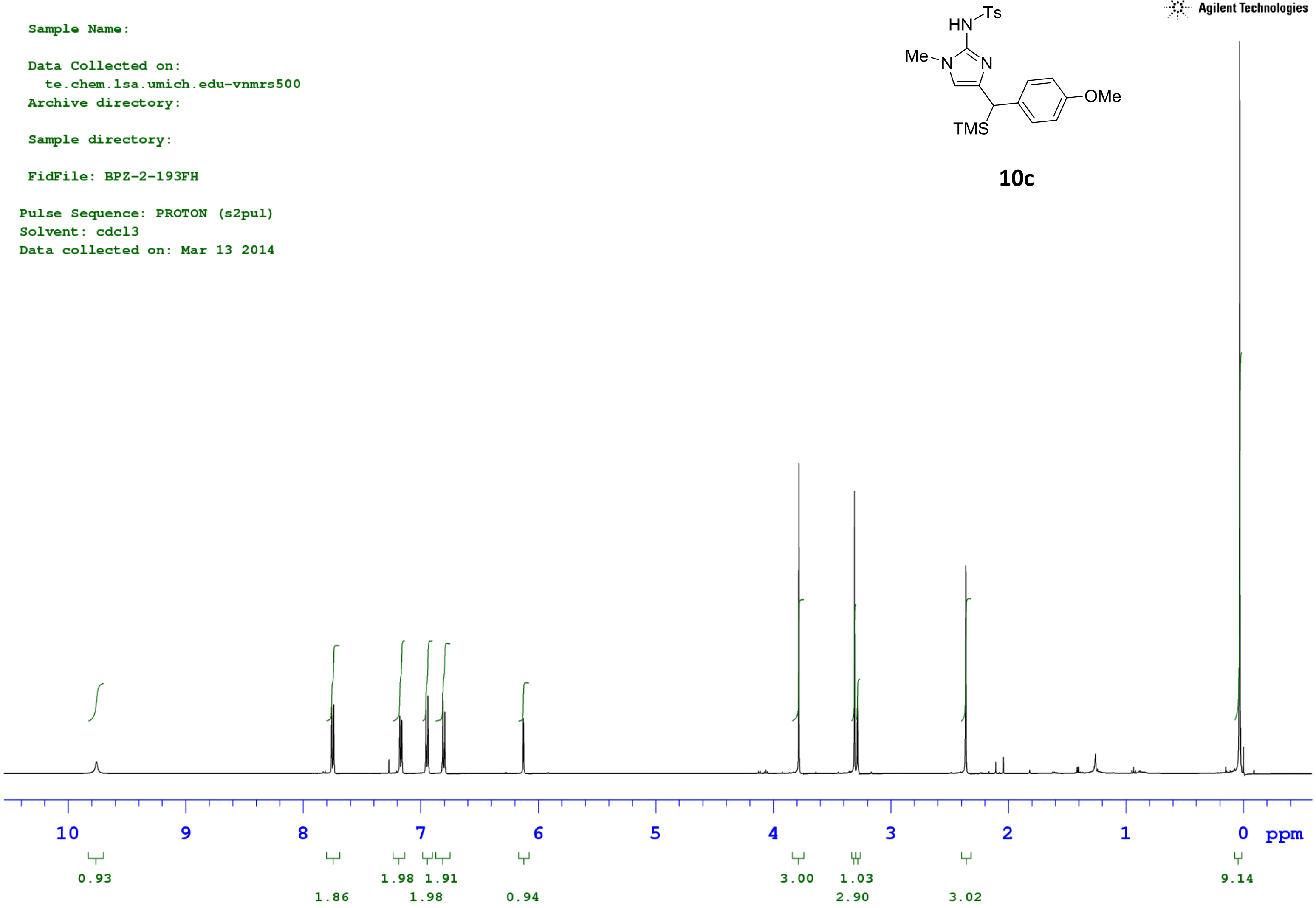
Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

FidFile: BPZ-2-193FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 13 2014

10c



STANDARD 1H OBSERVE - profile

Sample Name:

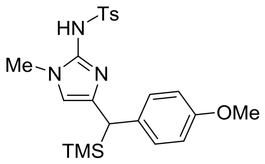
Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

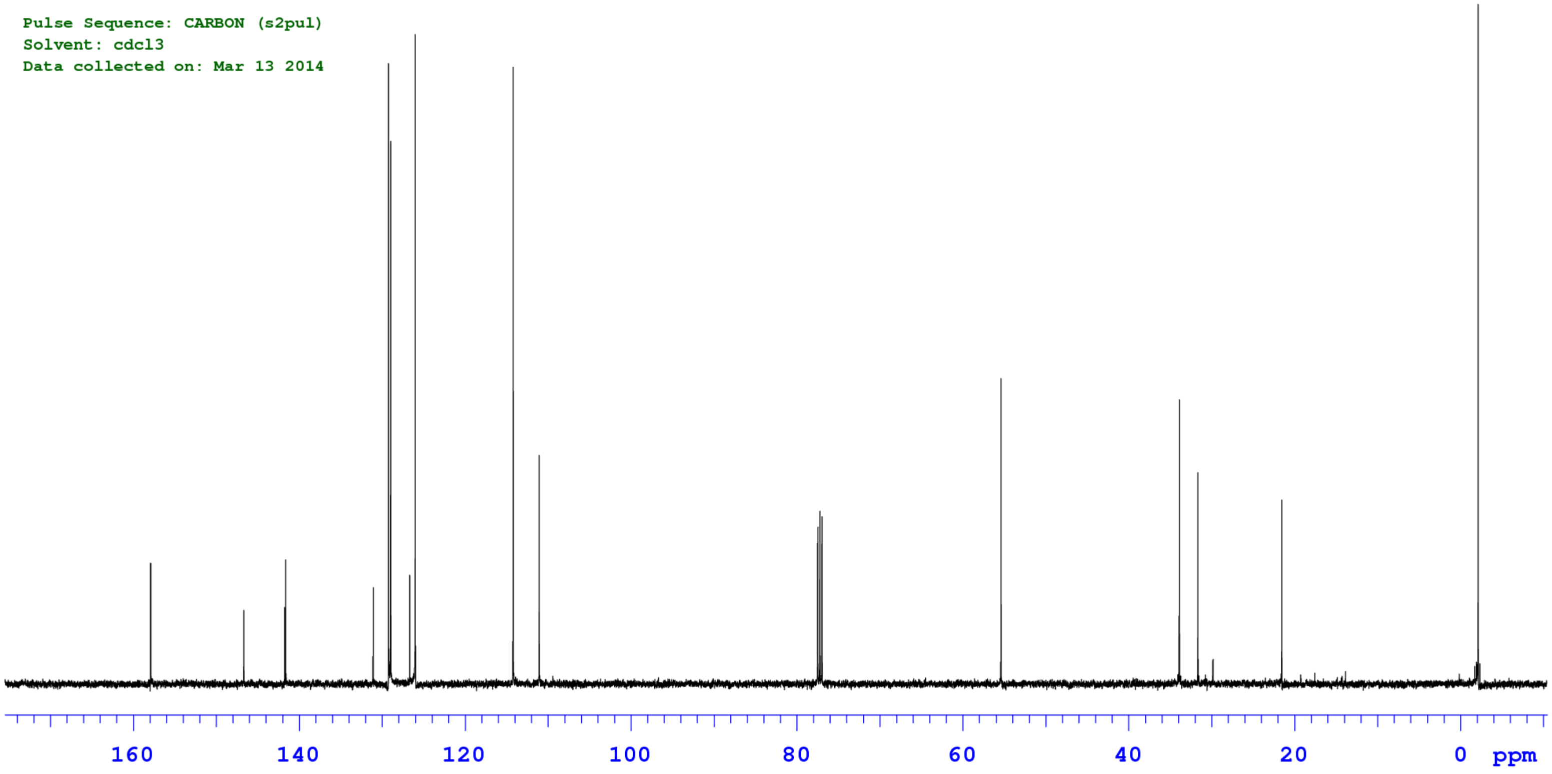
FidFile: BPZ-2-193FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 13 2014

Agilent Technologies



10c



STANDARD 1H OBSERVE - profile

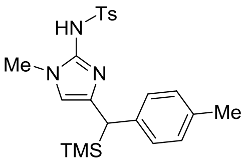
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

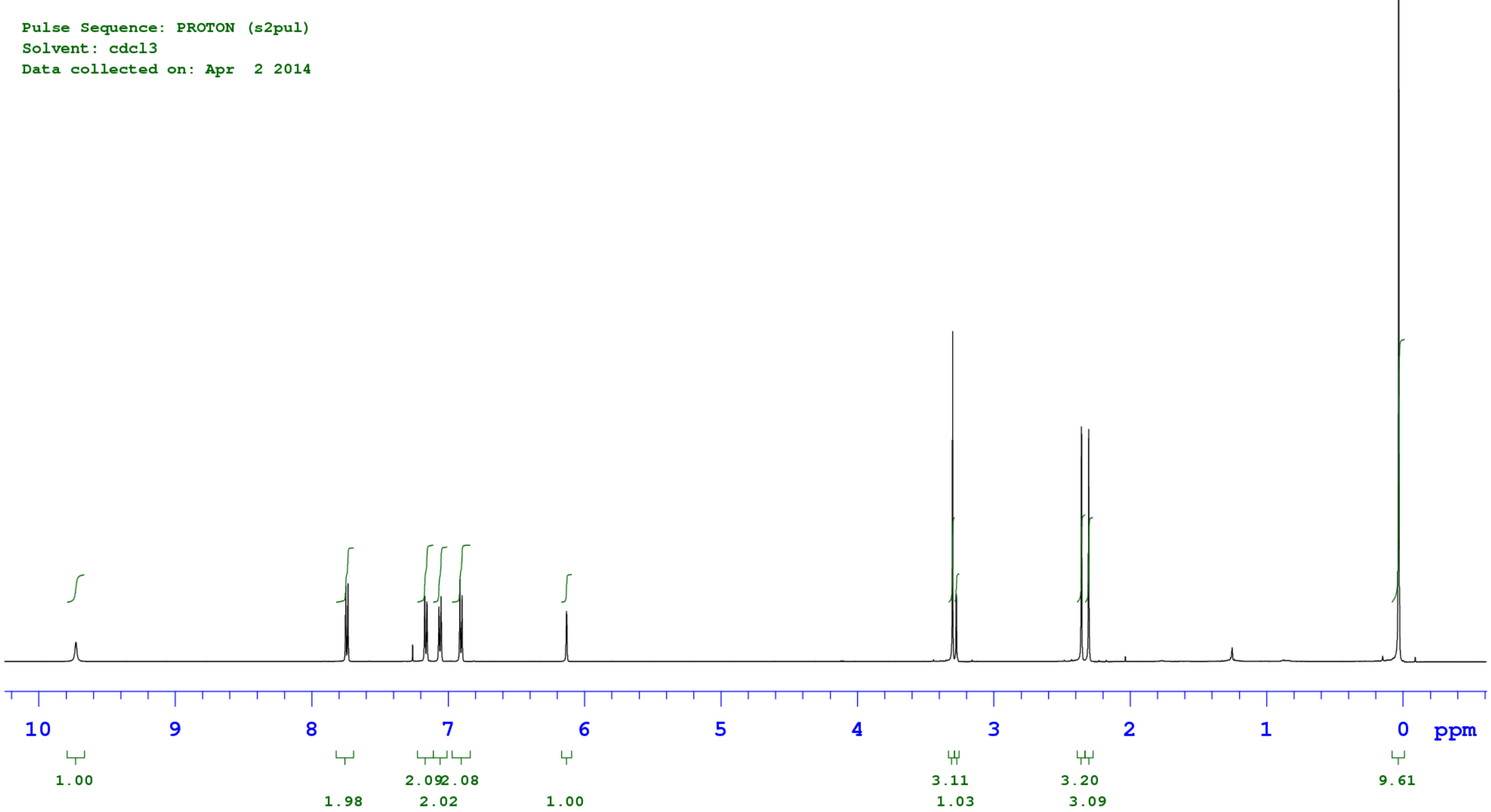
FidFile: BPZ-2-208FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 2 2014



10d

Agilent Technologies



STANDARD 1H OBSERVE - profile

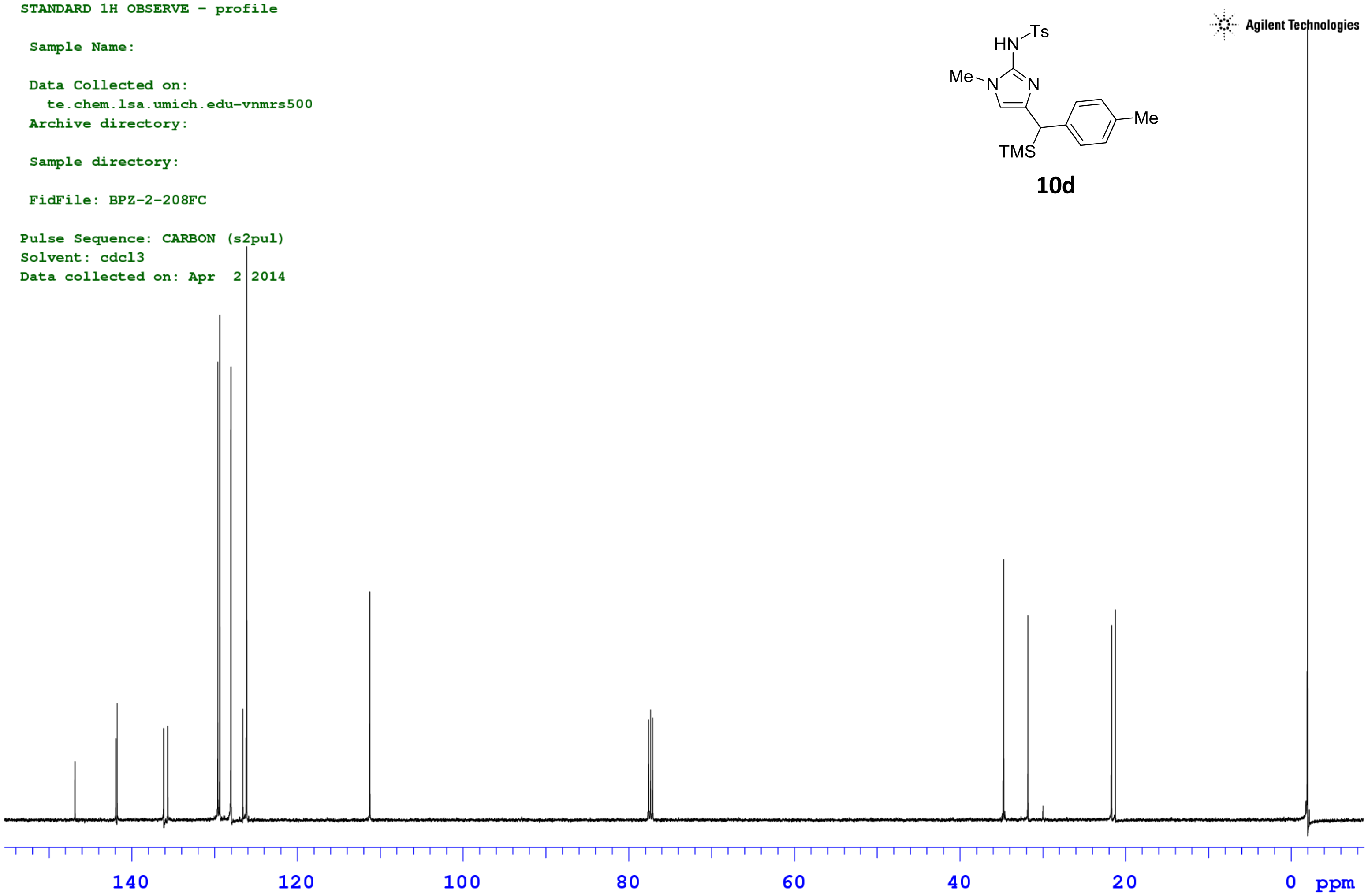
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

FidFile: BPZ-2-208FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 2 2014



10d

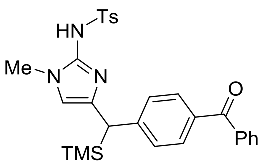
Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

Sample directory:

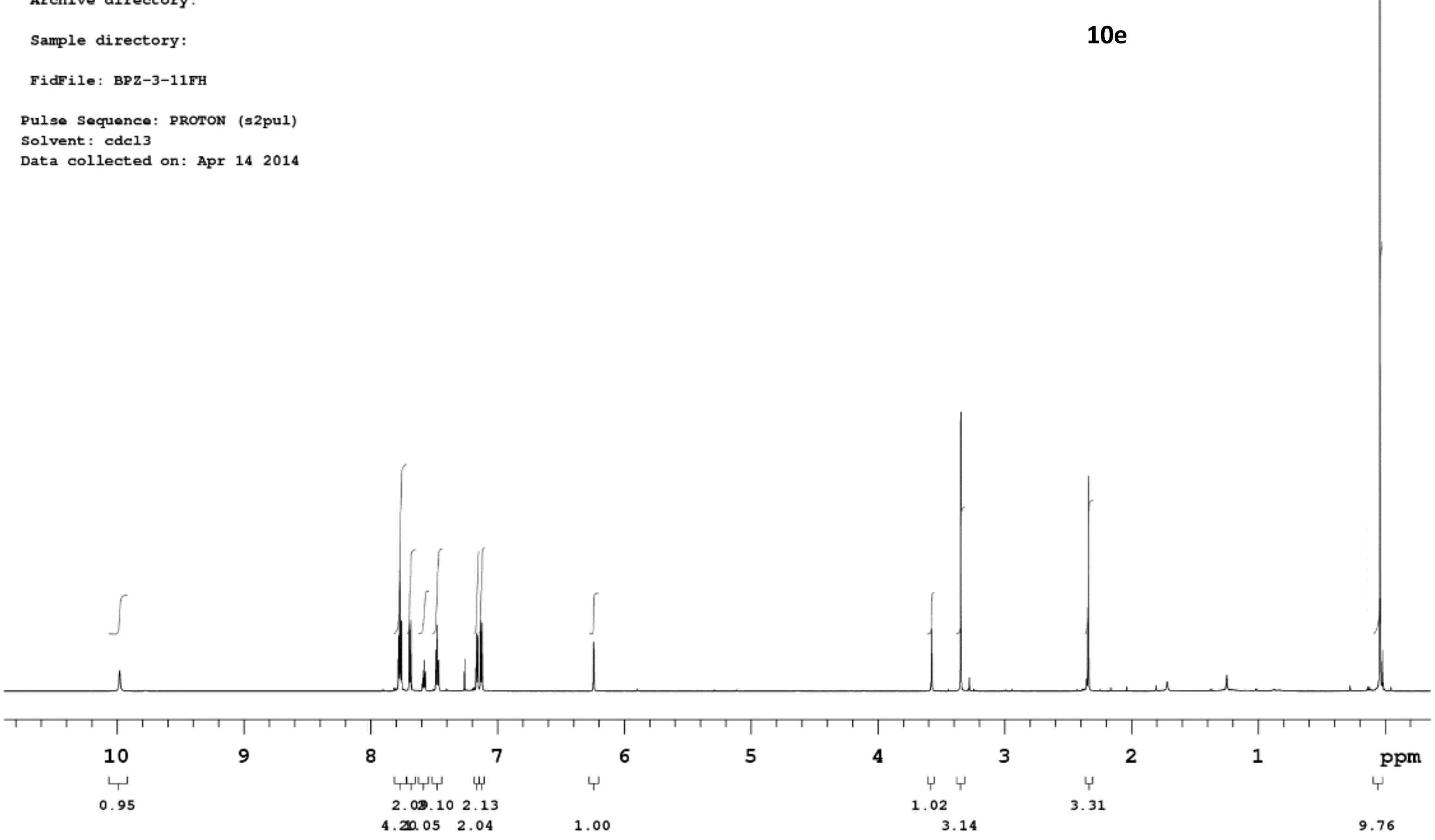
FidFile: BPZ-3-11FH

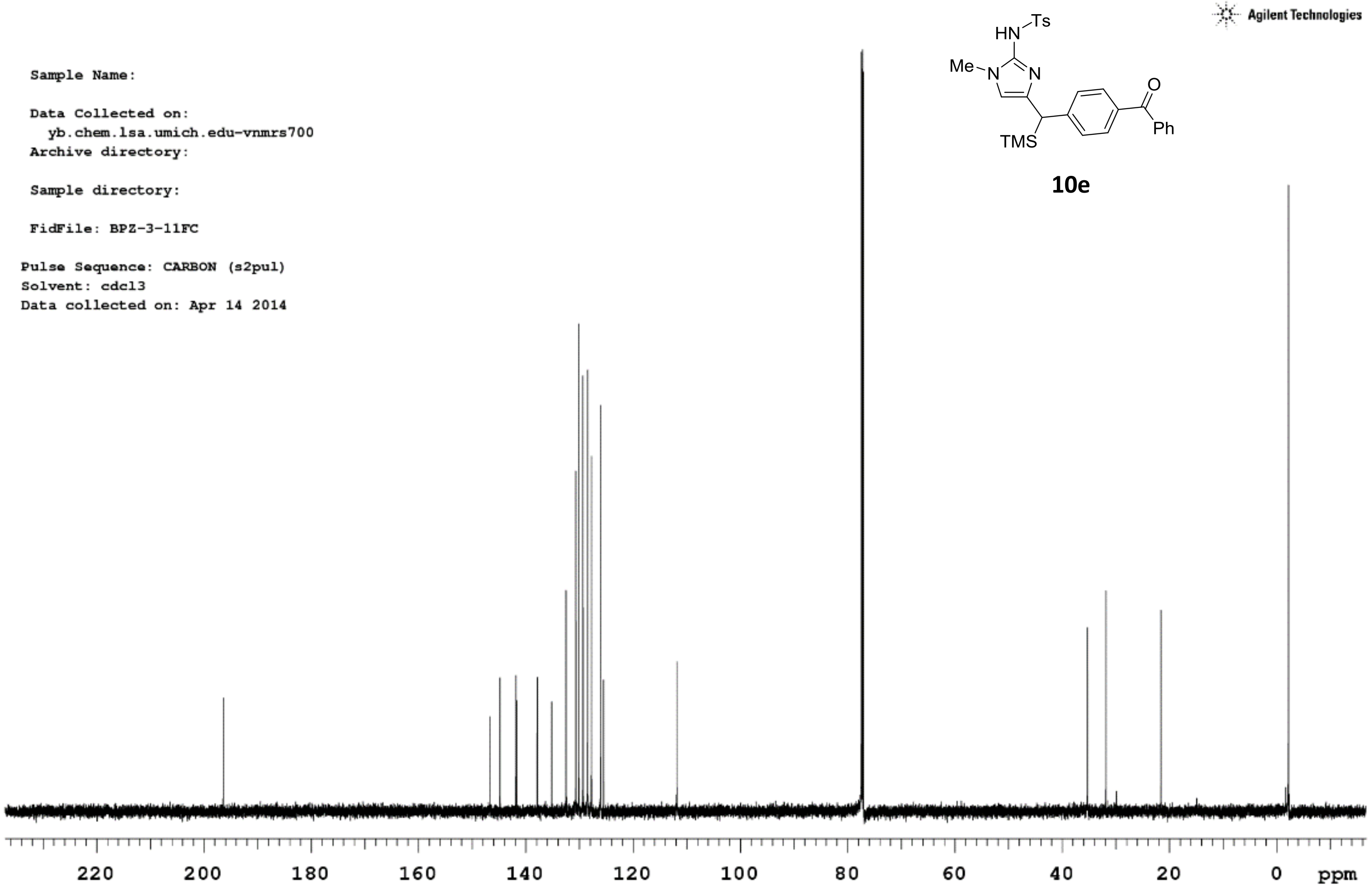
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 14 2014



10e

Agilent Technologies





10e

```
Sample Name:

Data Collected on:
  yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

Sample directory:

FidFile: BPZ-3-11FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 14 2014
```

STANDARD 1H OBSERVE - profile

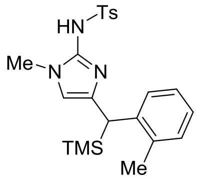
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

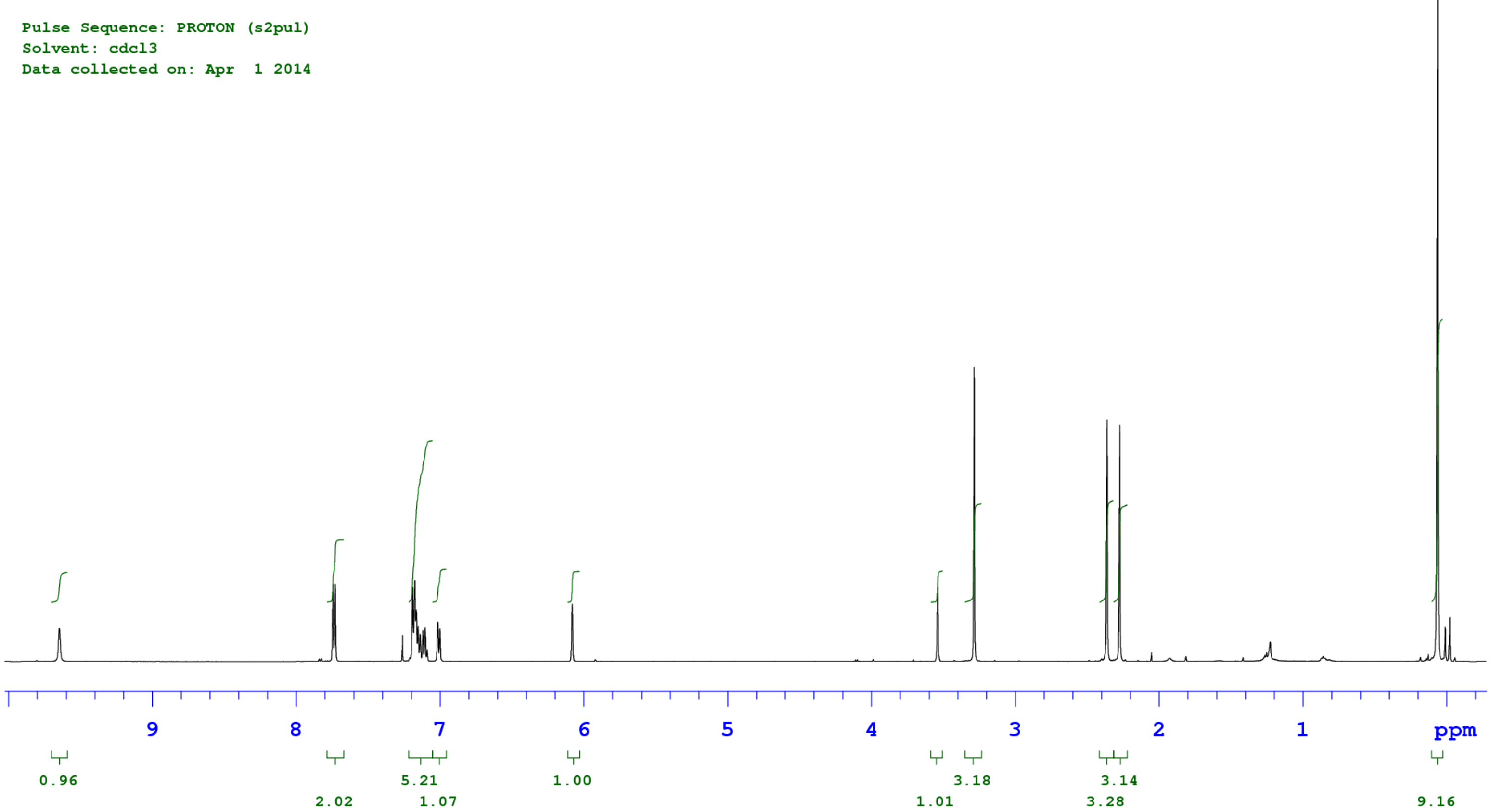
FidFile: BPZ-2-201FH

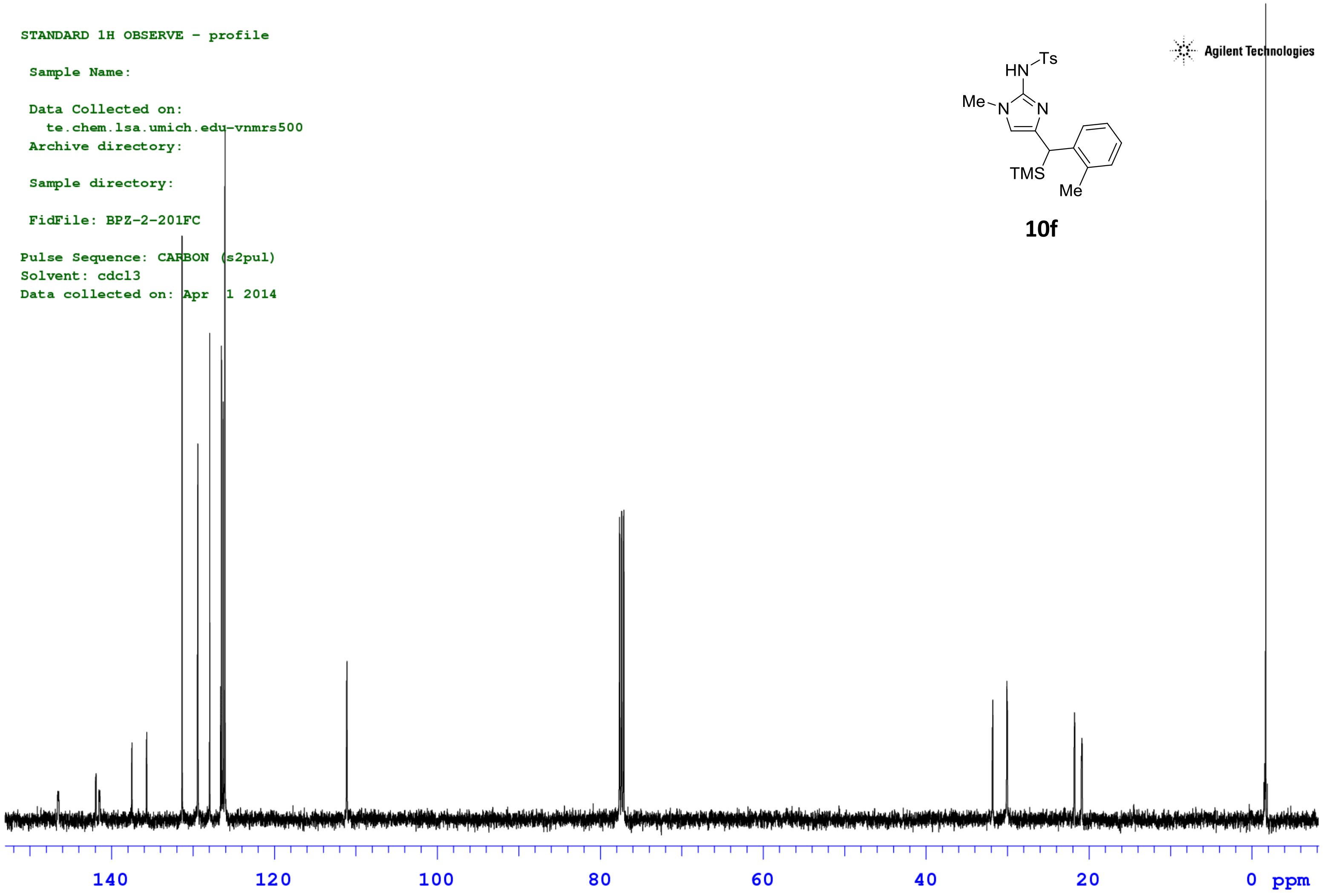
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 1 2014



10f

Agilent Technologies





10f

STANDARD 1H OBSERVE - profile

Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

FidFile: BPZ-2-201FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 1 2014

Proton Spectrum

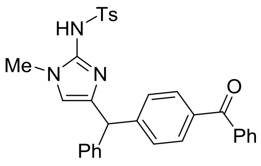
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

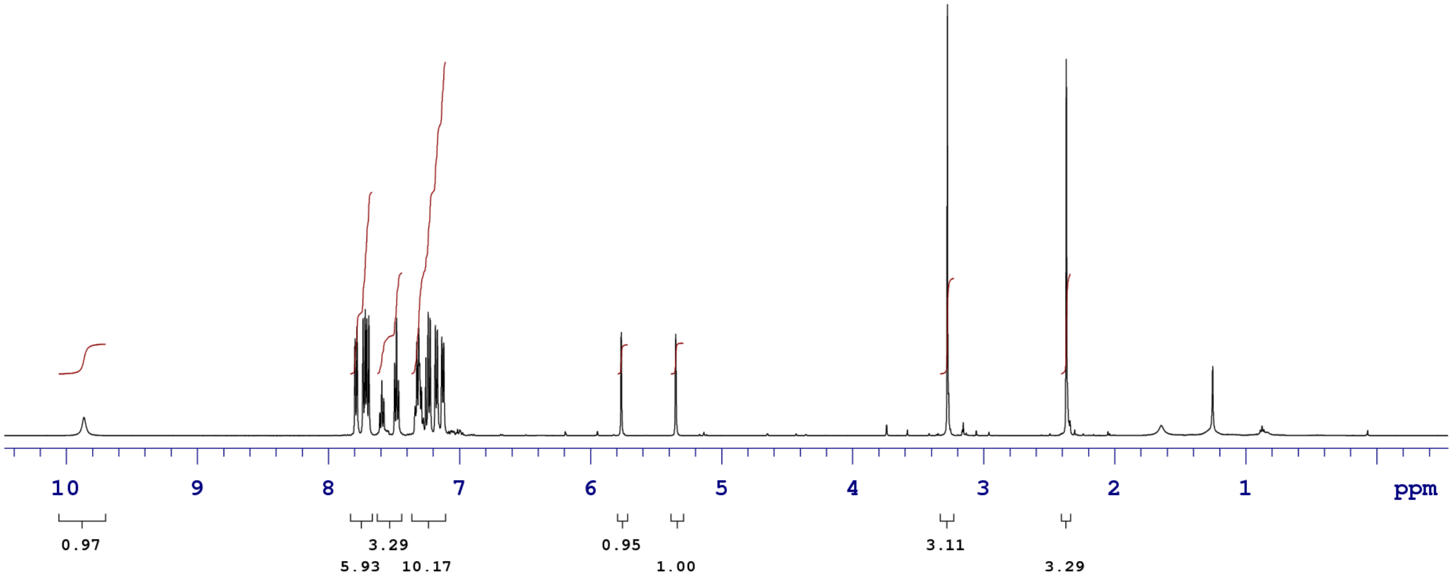
FidFile: BPZ-3-64FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 6 2014



10g

Agilent Technologies



Carbon-13

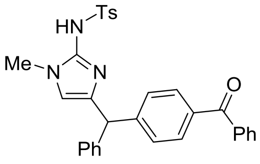
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

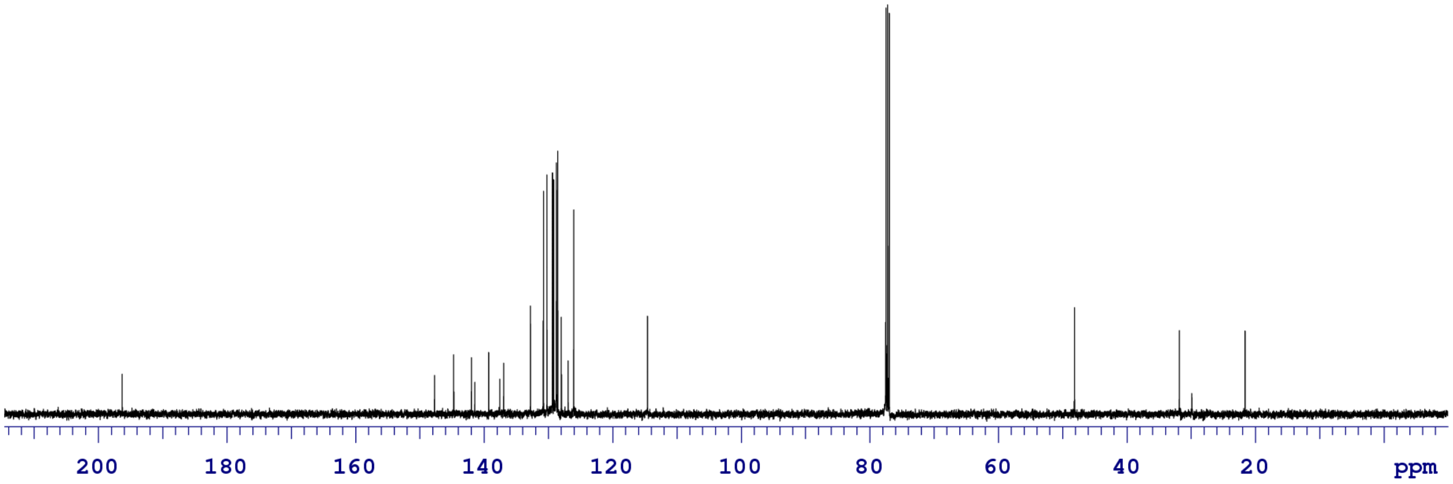
FidFile: BPZ-3-64FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 6 2014



10g

Agilent Technologies



Proton Spectrum

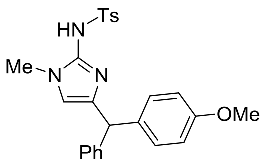
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

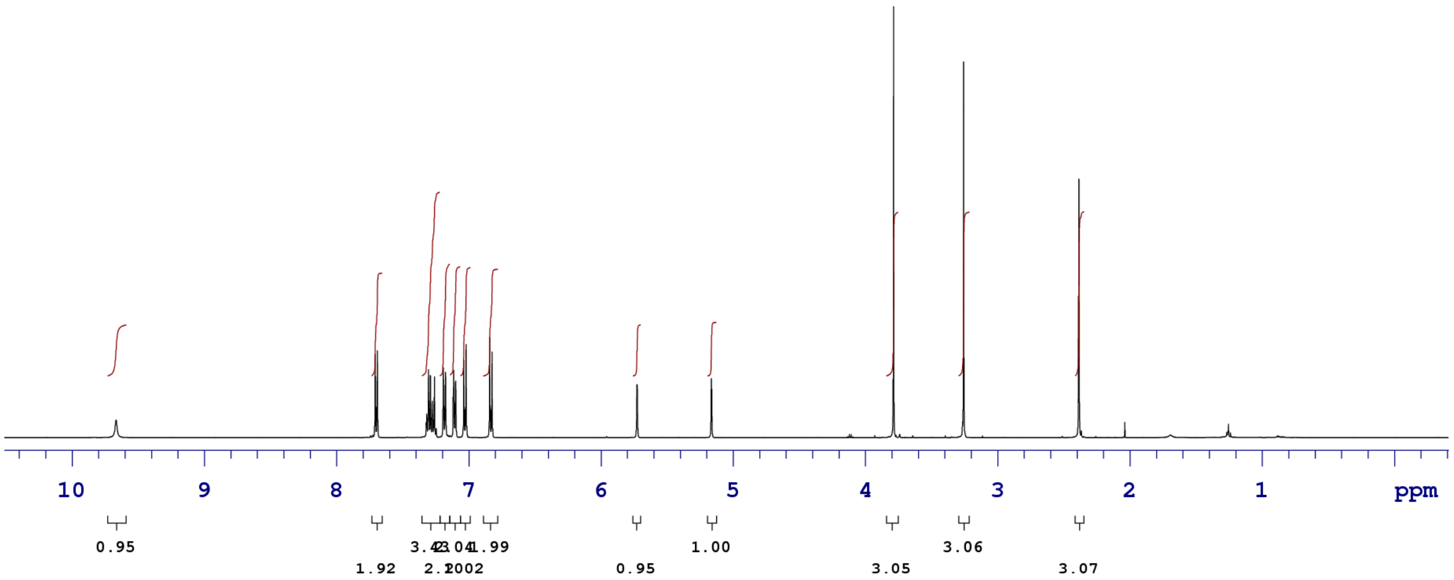
FidFile: BPZ-3-27FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 16 2014



10h

Agilent Technologies



Carbon-13

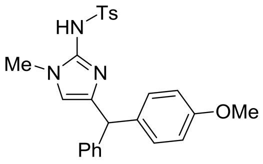
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

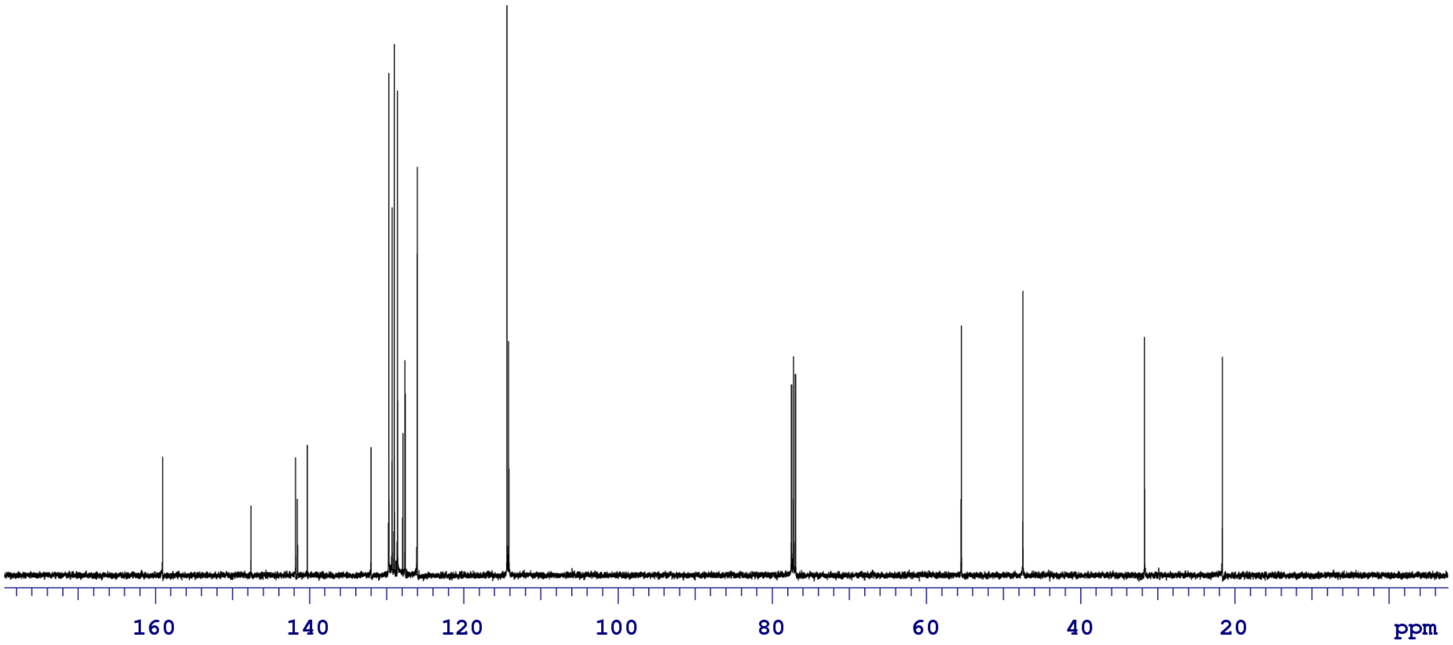
FidFile: BPZ-3-27FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 16 2014



10h

Agilent Technologies



STANDARD 1H OBSERVE - profile

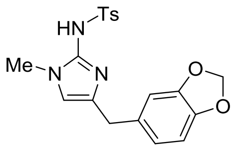
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

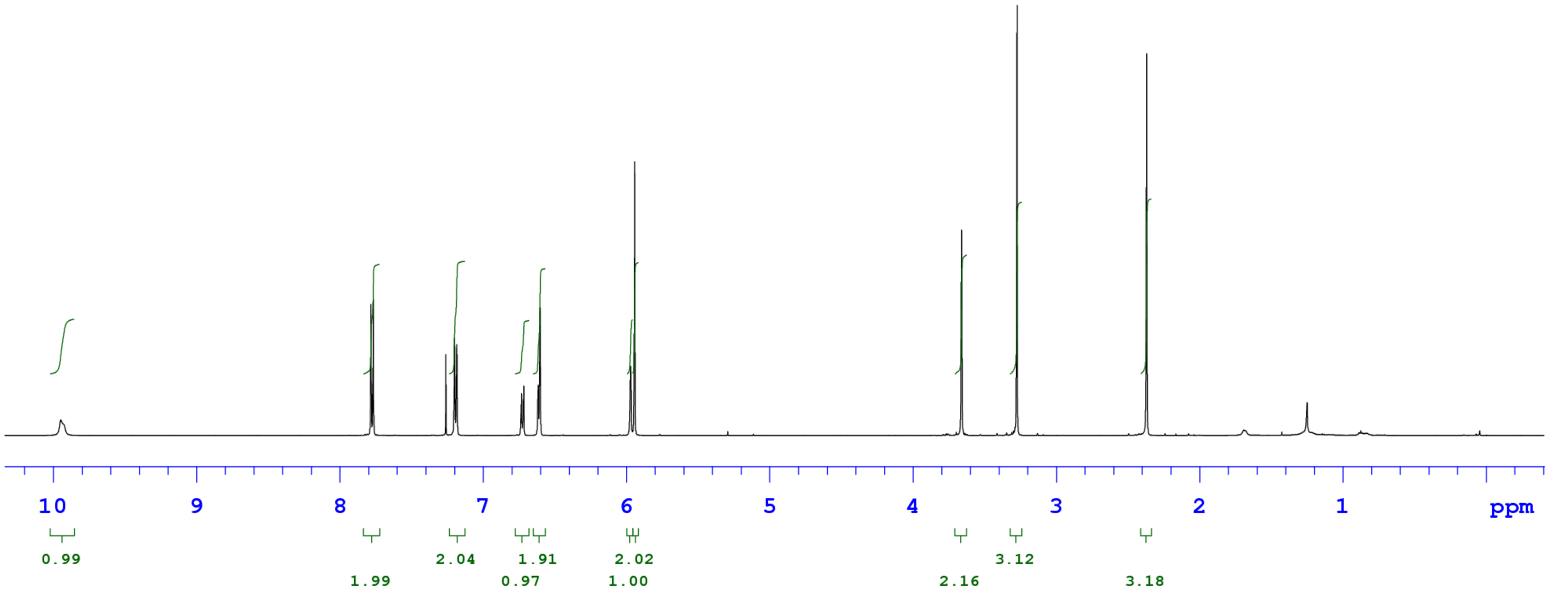
FidFile: BPZ-3-1FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 9 2014



S5

Agilent Technologies



STANDARD 1H OBSERVE - profile

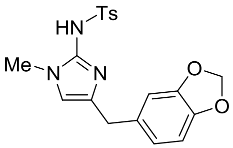
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

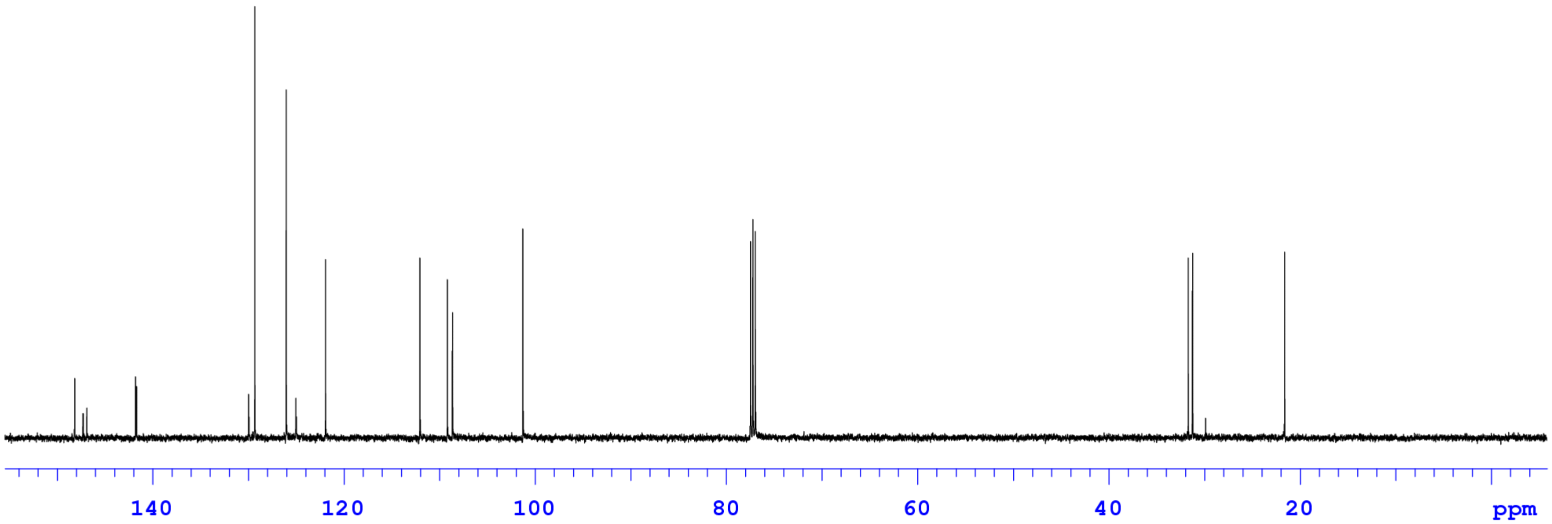
FidFile: BPZ-3-1FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 9 2014



S5

Agilent Technologies



STANDARD Deuterium PARAMETERS
Using lock coil

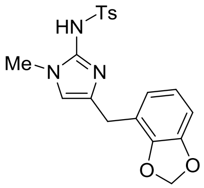
Sample Name:

Data Collected on:
sn.chem.lsa.umich.edu-inova500
Archive directory:

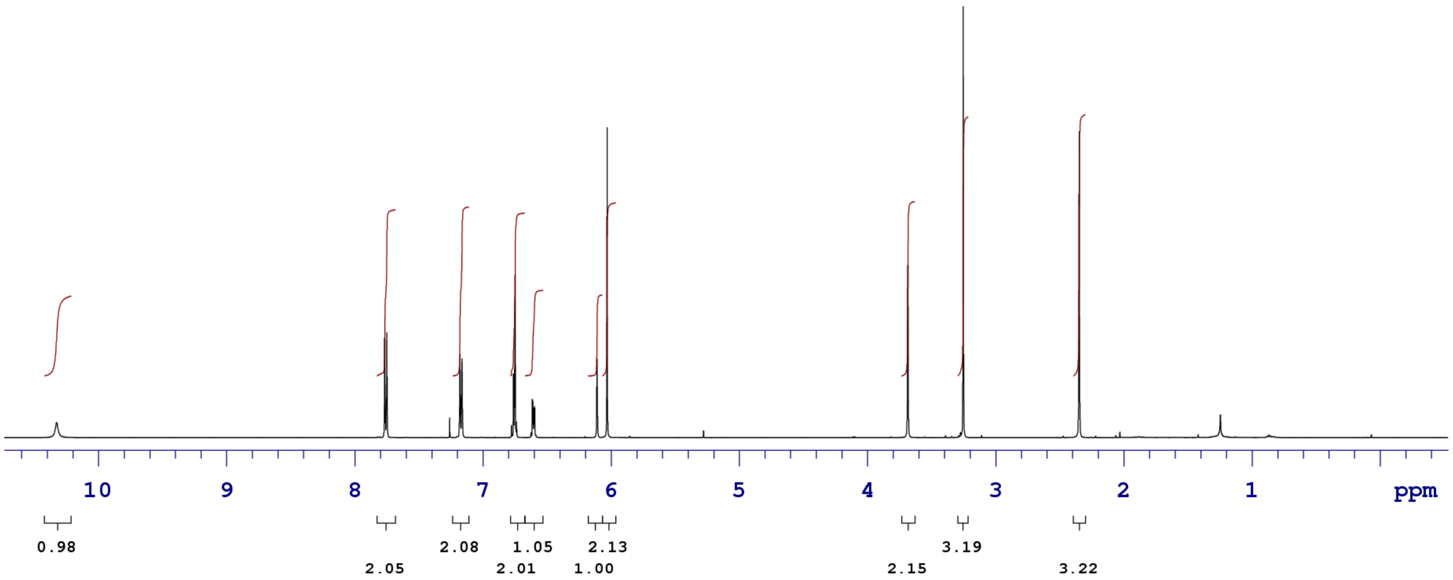
Sample directory:

FidFile: BPZ-3-37FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2014



S6



Carbon-13

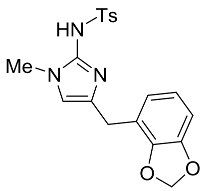
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

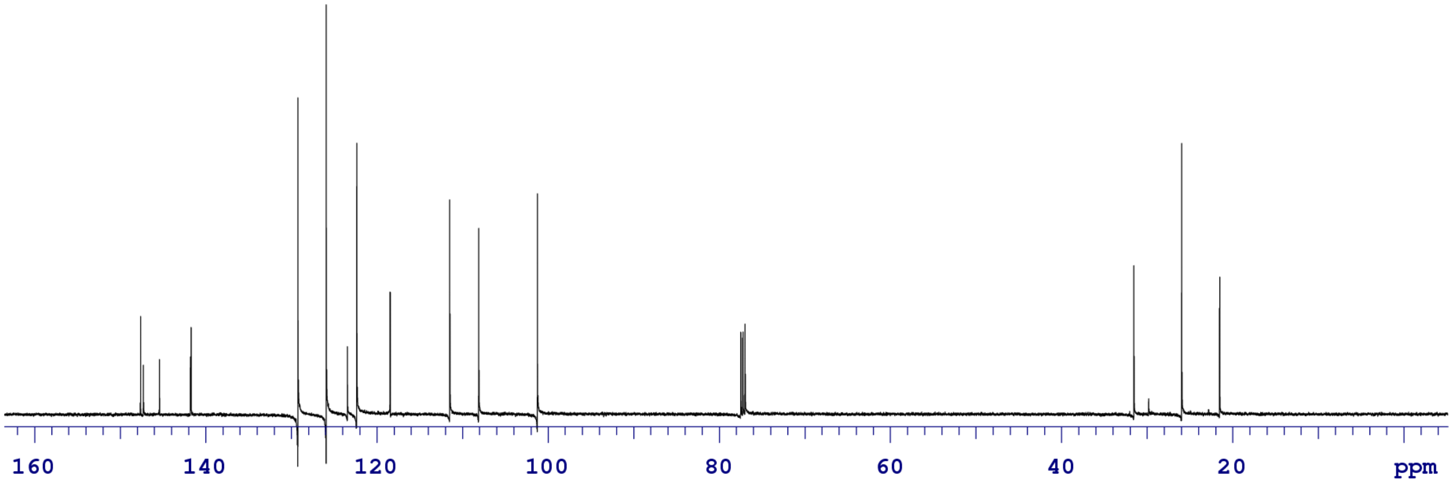
FidFile: BPZ-3-37FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2014



S6

Agilent Technologies



STANDARD 1H OBSERVE - profile

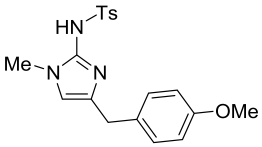
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

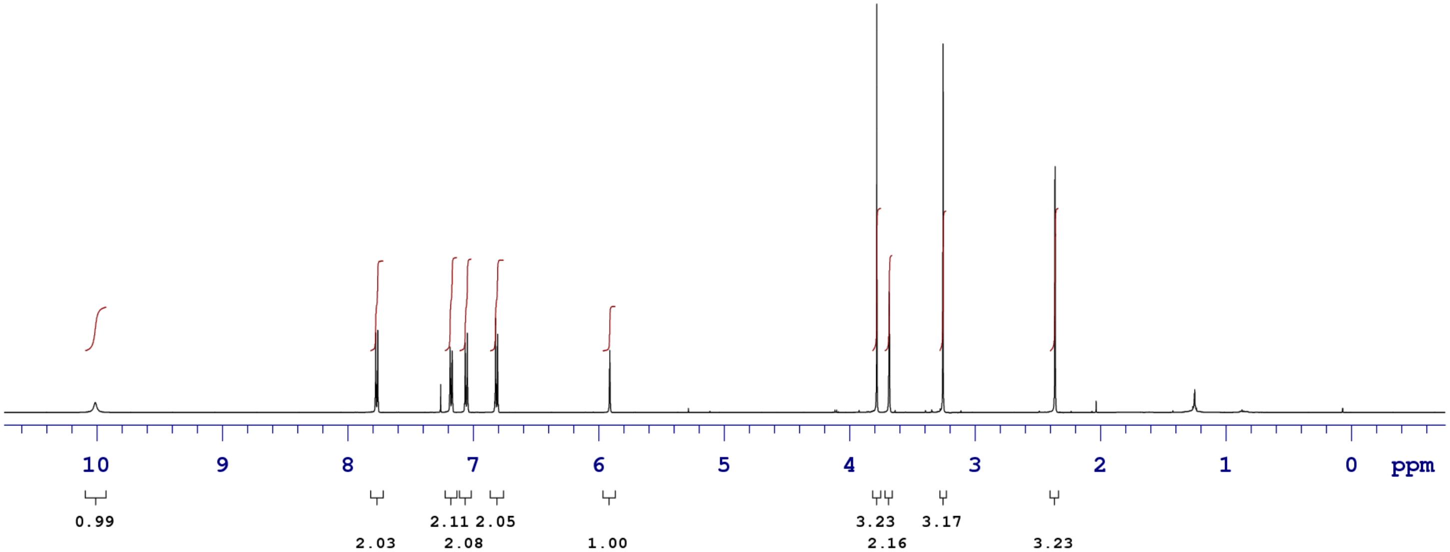
FidFile: BPZ-3-15FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 7 2014



S7

Agilent Technologies



STANDARD 1H OBSERVE - profile

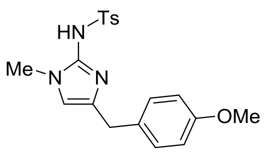
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

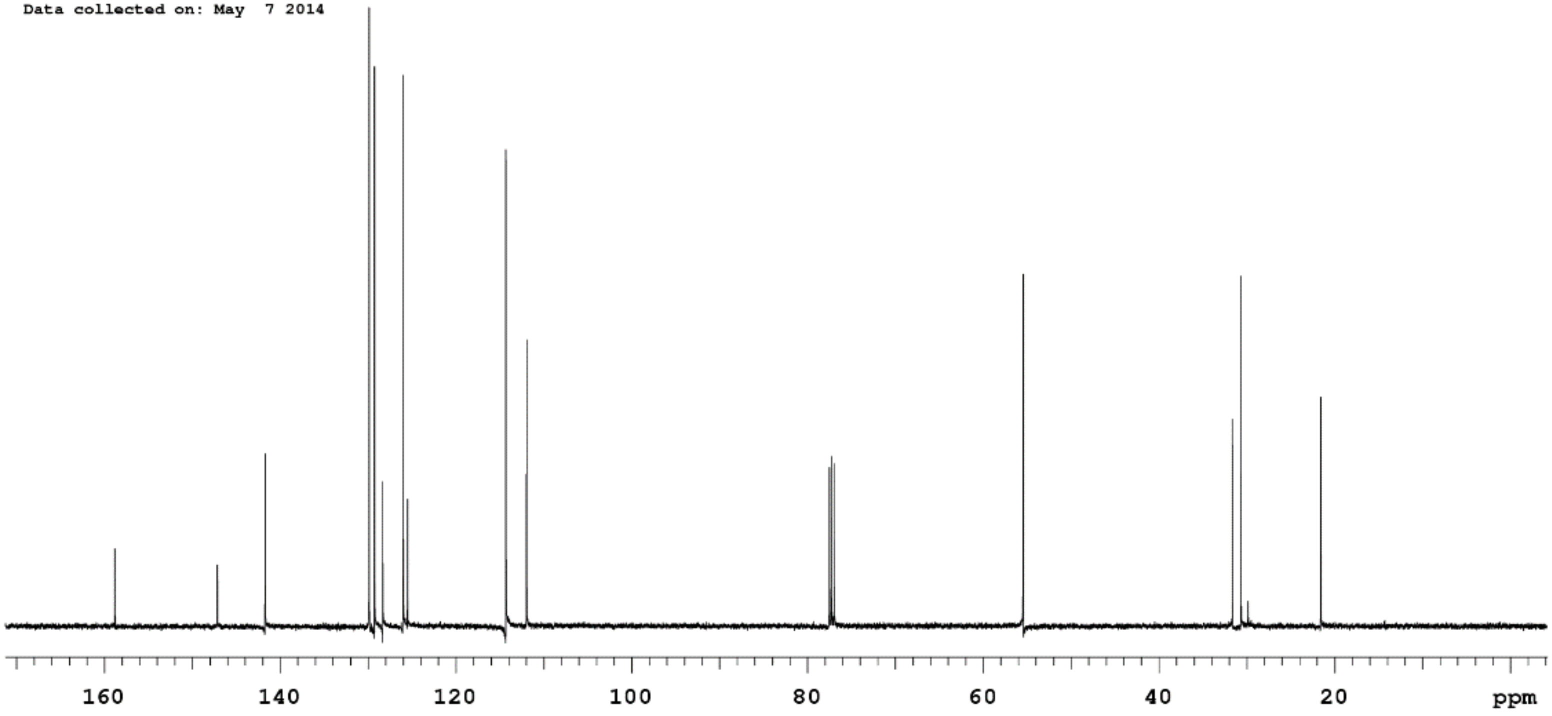
FidFile: BPZ-3-15FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 7 2014



S7

Agilent Technologies



STANDARD 1H OBSERVE - profile

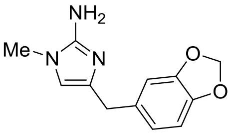
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

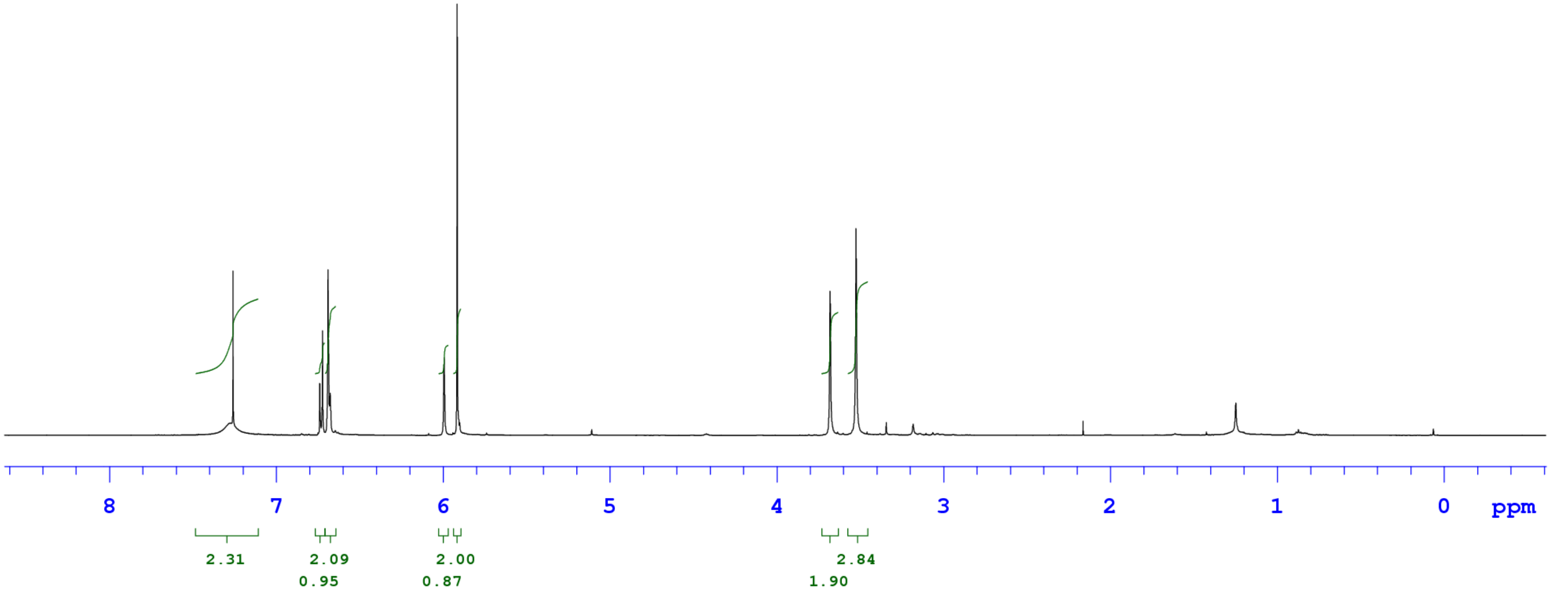
FidFile: BPZ-3-3FFH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 11 2014



1

Agilent Technologies



STANDARD 1H OBSERVE - profile

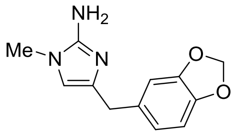
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

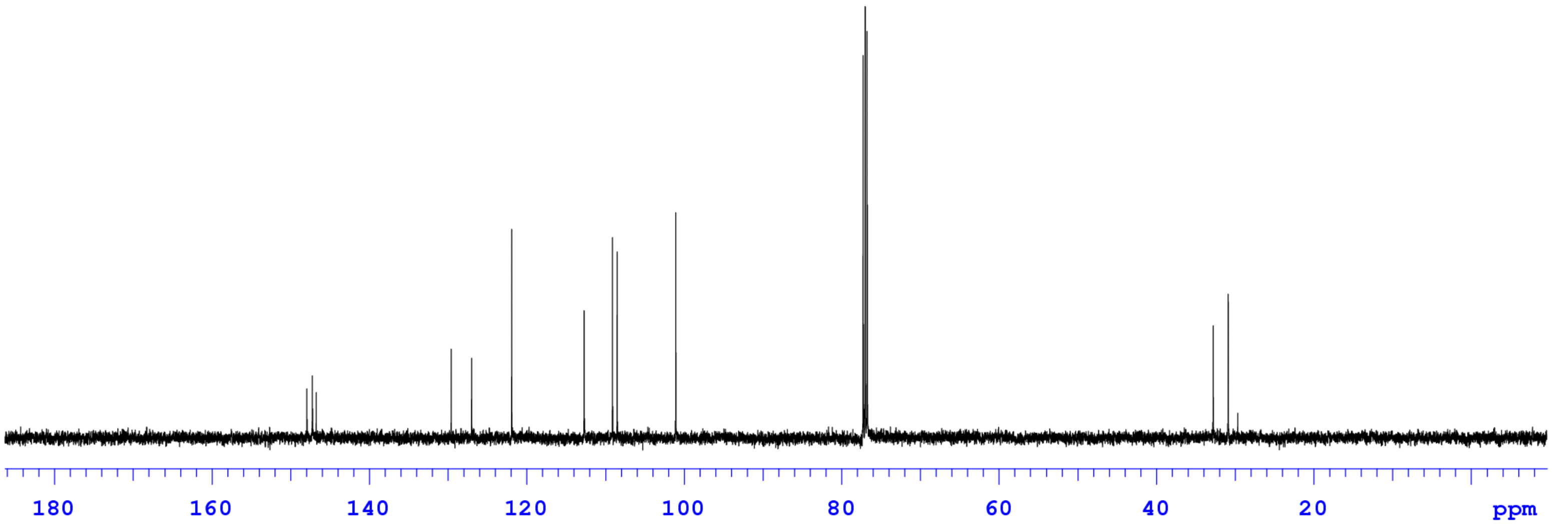
FidFile: BPZ-3-3FFC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 11 2014



1

Agilent Technologies



Proton Spectrum

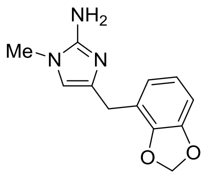
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

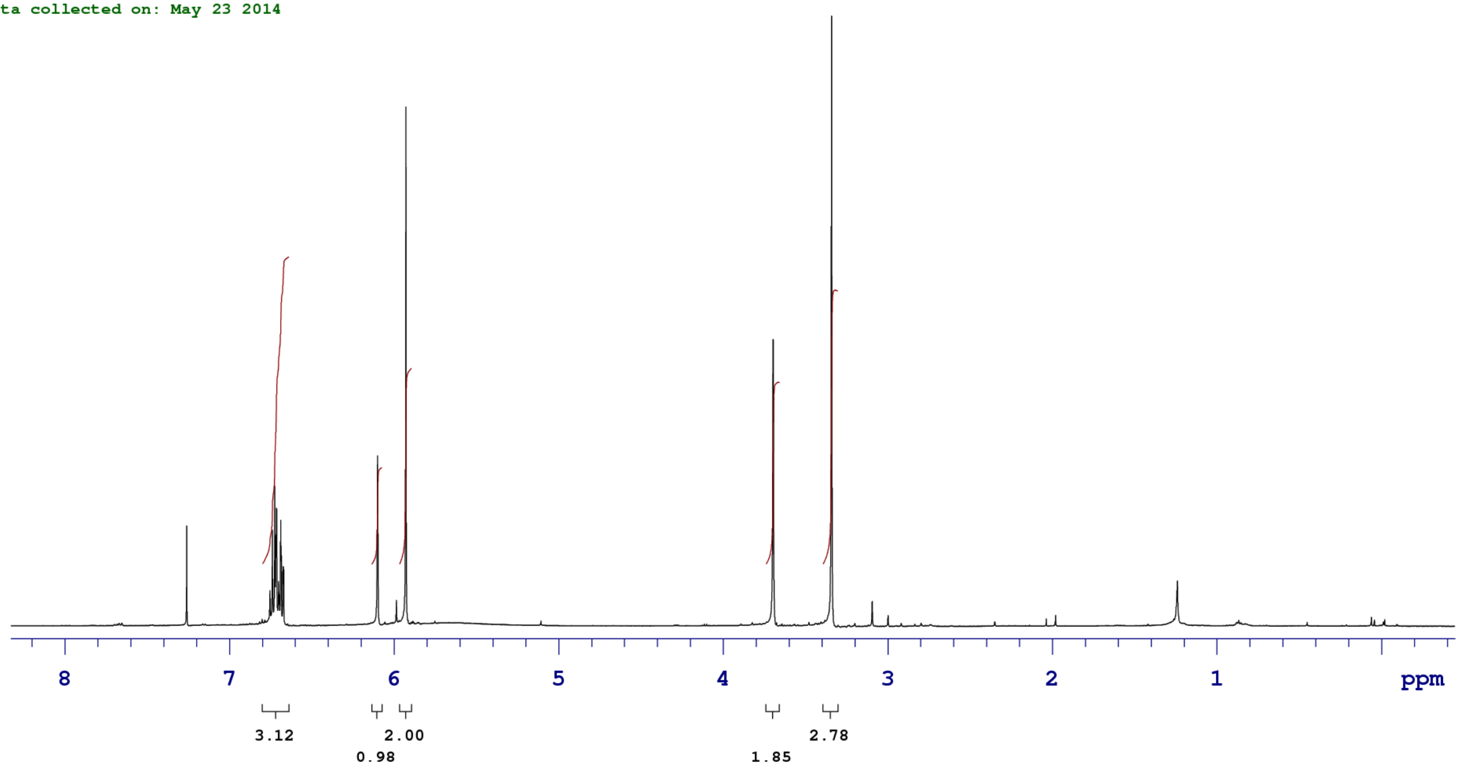
FidFile: BPZ-3-138FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 23 2014



2

Agilent Technologies



Carbon-13

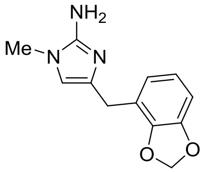
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

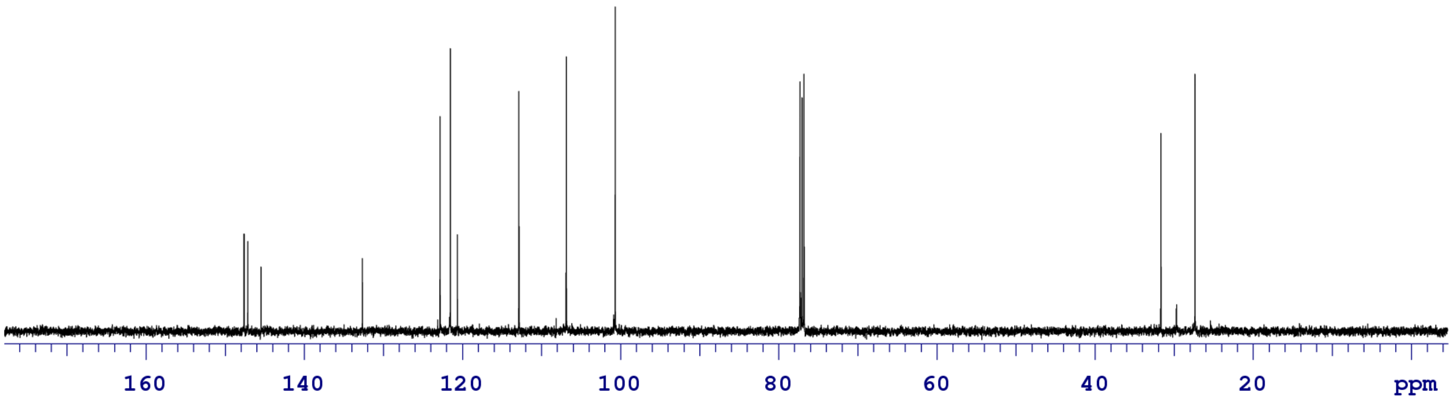
FidFile: BPZ-3-38FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 23 2014



2

Agilent Technologies



Proton Spectrum

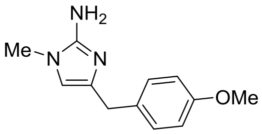
Sample Name:

Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

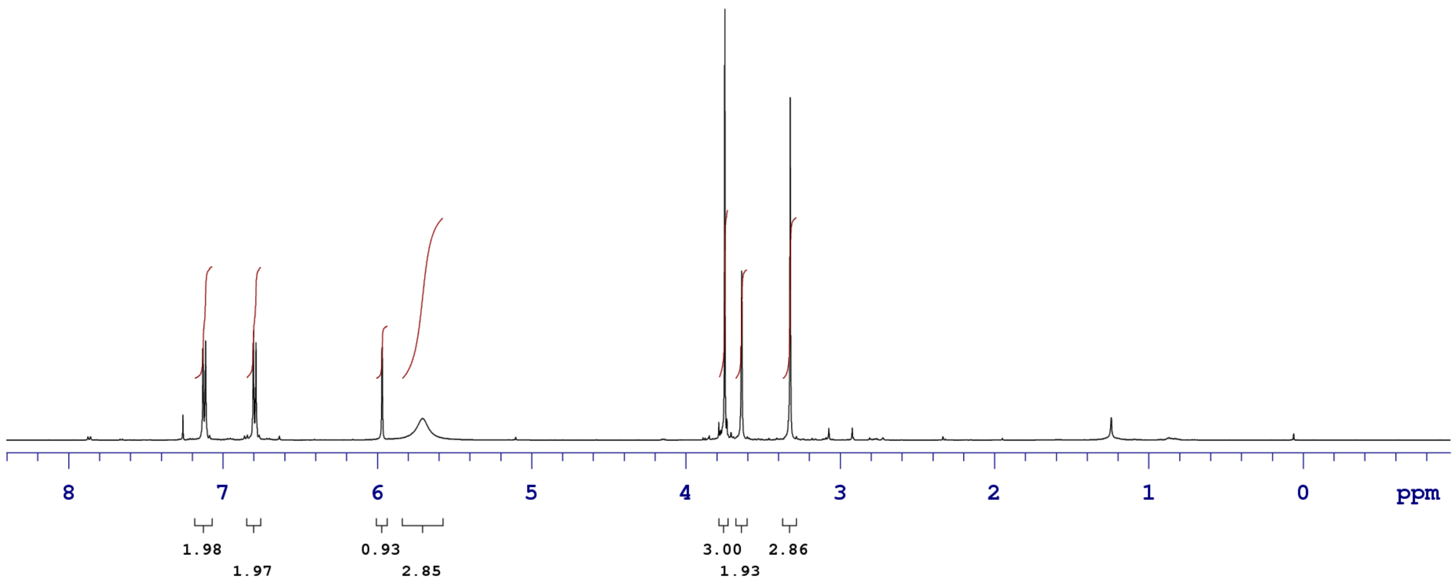
FidFile: BPZ-3-24FH

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2014



3

Agilent Technologies



Carbon-13

Sample Name:

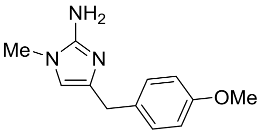
Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:

Sample directory:

FidFile: BPZ-3-24FC

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2014

Agilent Technologies



3