Supporting Information for

Multicomponent Azide-Alkyne Cycloaddition Catalyzed by Impregnated Bimetallic Nickel and Copper on Magnetite

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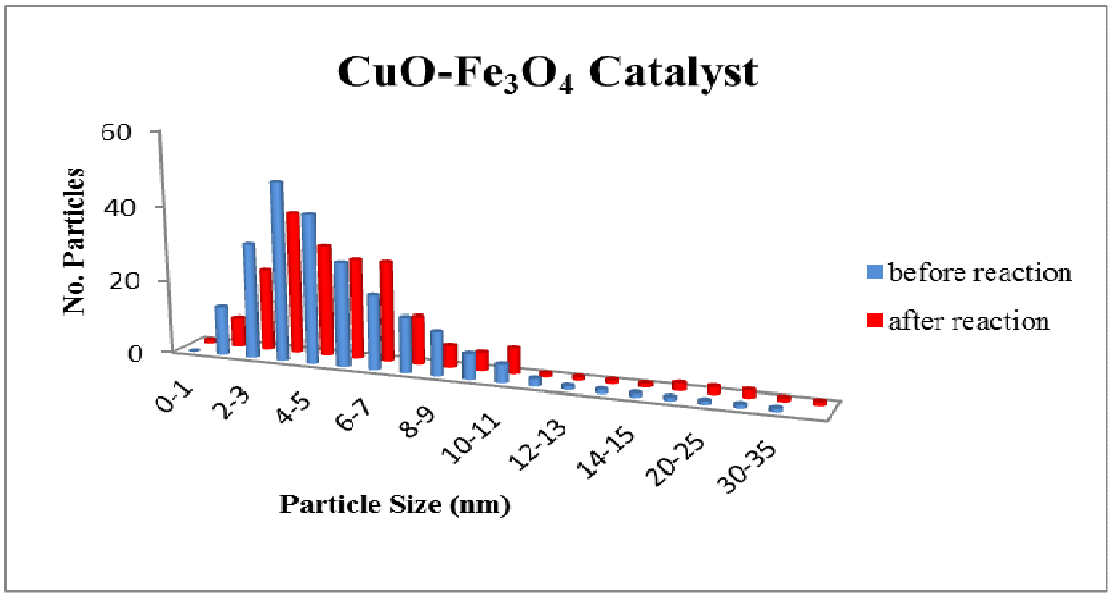
General Information

XPS analyses were carried out on a VG-Microtech Mutilab. XRD analyses were obtained on a BRUKER D-8 ADVANCE diffractometer with Göebel mirror, with a high temperature chamber (up to 900ºC), with a X-ray generator KRISTALLOFLEX K 760-80F (3KW, 20-60KV and 5-80mA). TEM images were obtained on a JEOL, model JEM-2010 equipped with an X-ray detector OXFORD INCA Energy TEM 100 for microanalysis (EDS). XRF analyses were obtained on a PHILIPS MAGIX PRO (PW2400) X-ray spectrometer equipped with a rhodium X-ray tube and a beryllium window. BET isotherms were carried out on a AUTOSORB-6 (Quantachrome), using N_2. Melting points were obtained with a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as a solvent and TMS as internal standard for ^{1}H and ^{13}C; chemical shifts are given in δ (parts per million) and coupling constants (*J*) in Hertz. FT-IR spectra were obtained on a JASCO 4100LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP-5000 spectrometer, giving fragment ions in *m/z* with relative intensities (%) in parentheses. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g $Ce(SO_4)_2$ 4 H_2O, 60 mL of concentrated H_2SO_4 and 940 mL H_2O]. Column chromatography was performed using silica gel 60 of 40-63 mesh. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received. The ICP-MS analyses were carried out on a Thermo Elemental VGPQ-ExCell spectrometer. The Elemental Analysis was performed on a Elemental Microanalyzer Thermo Finningan Flash 1112 Series.

Particle Size Distribution for the Two-Component Reaction

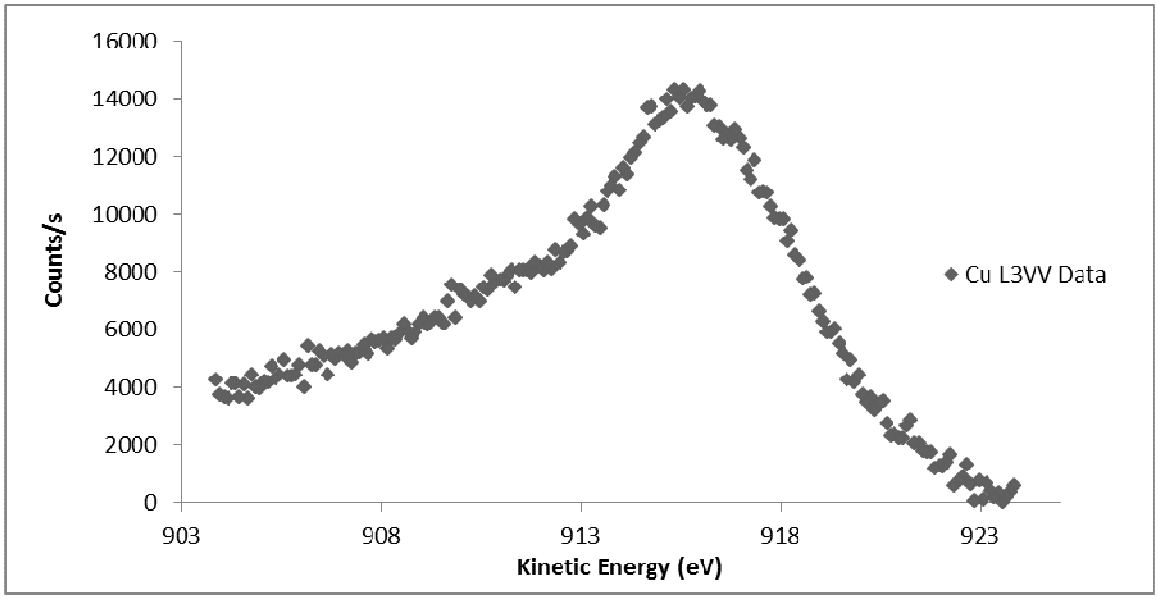


General procedure for the preparation of NiO/Cu-Fe_3O_4 catalyst

To a stirred solution of $CuCl_2$ (1 mmol, 130 mg) and $NiCl_2 \cdot H_2O$ (1 mmol, 130 mg) in deionized water (120 mL) was added commercially available Fe_3O_4 (4 g, 17 mmol, powder < 5 µm, BET area: 9.86 m^2/g). After 10 minutes at room temperature, the mixture was slowly basified with NaOH (1M) until pH around 13. The mixture was stirred during one day at room temperature in air. After that, the catalyst was filtered and washed several times with deionized water (3 × 10 mL). The solid was dried at 100ºC during 24h in a standard glassware oven, obtaining thereafter the expected catalyst.

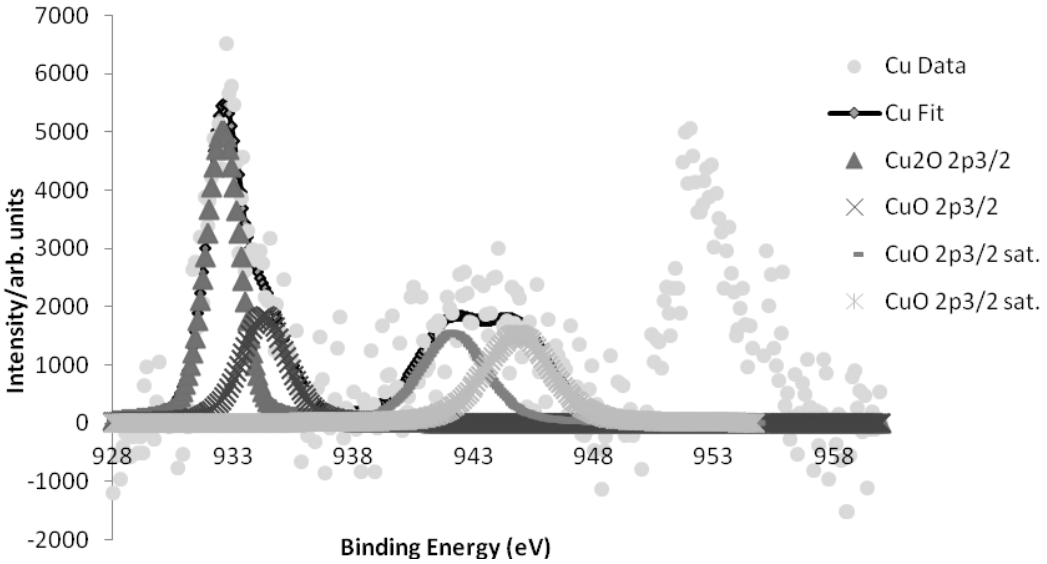
Auger Spectroscopy

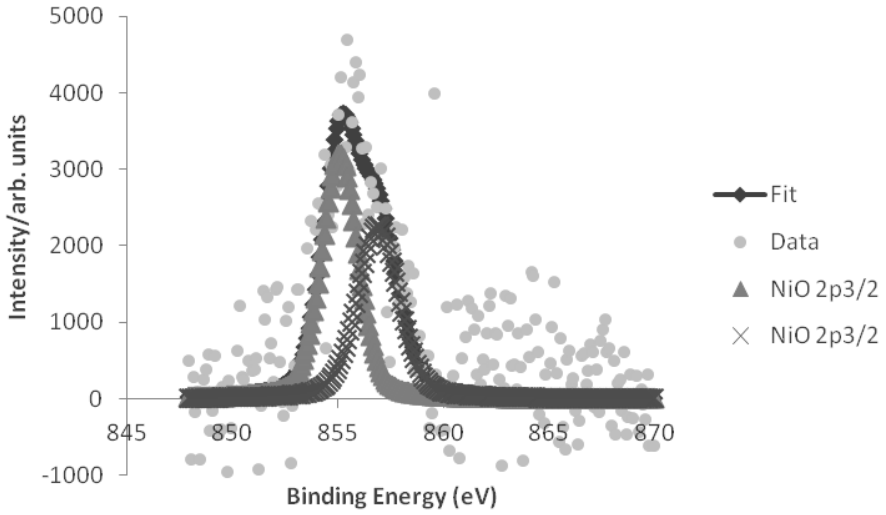
Before reaction



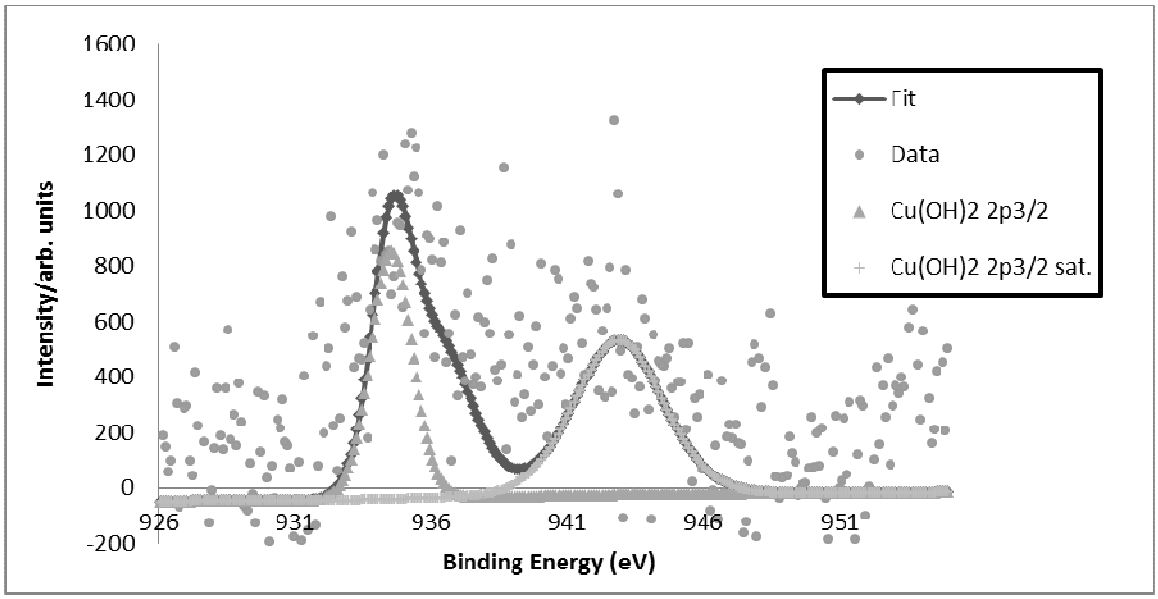
XPS Data

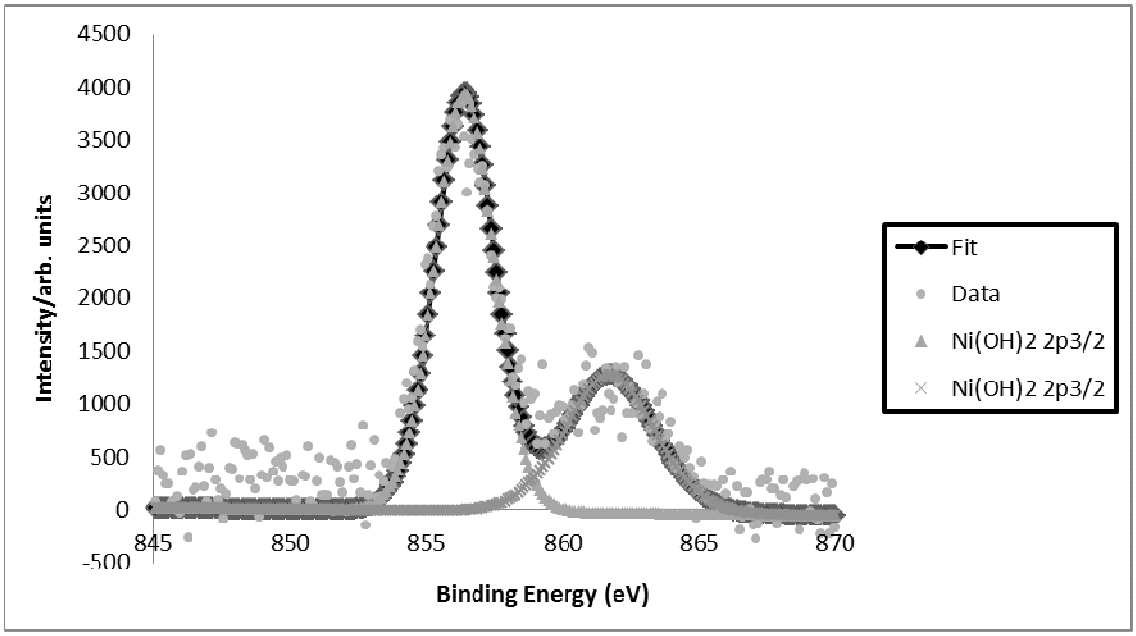
Before reaction





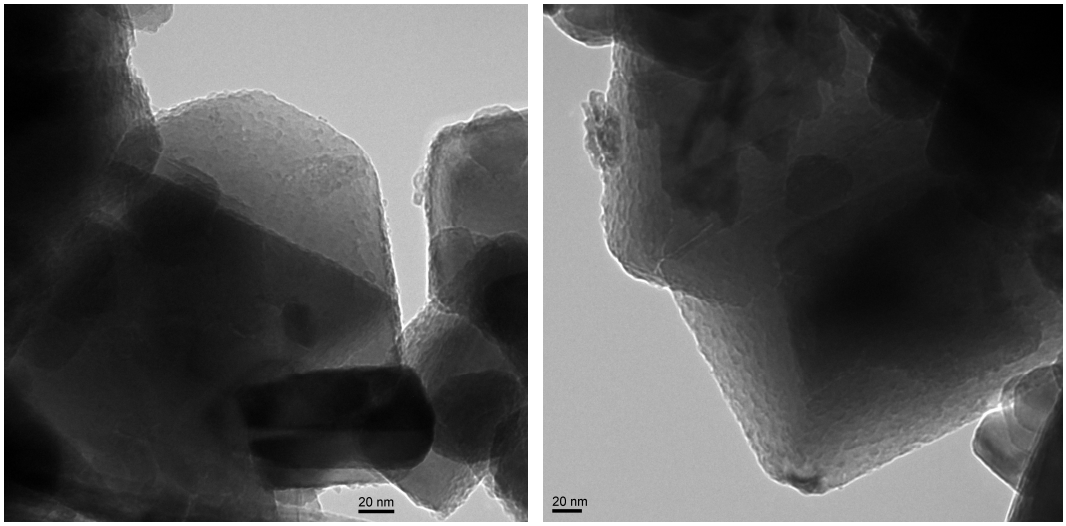
After reaction



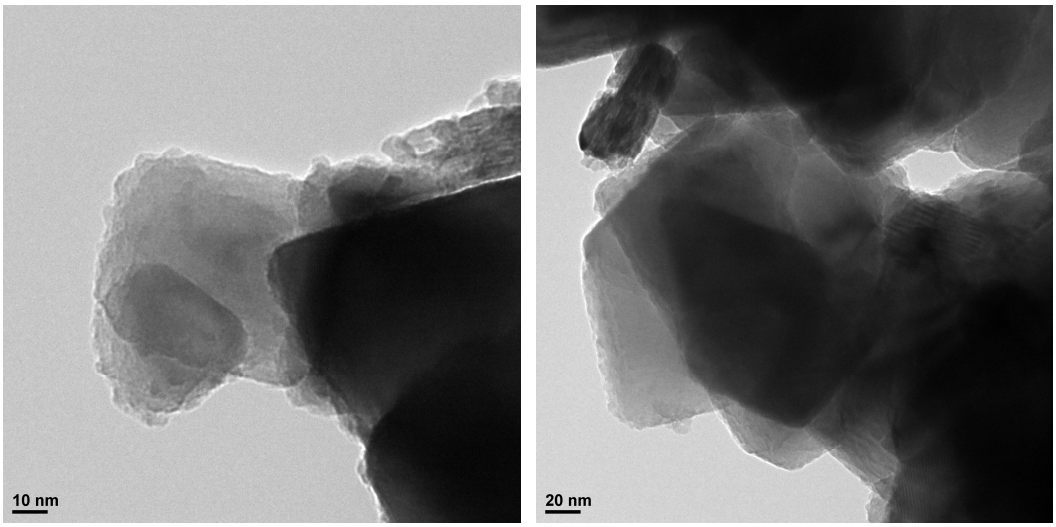


TEM Images

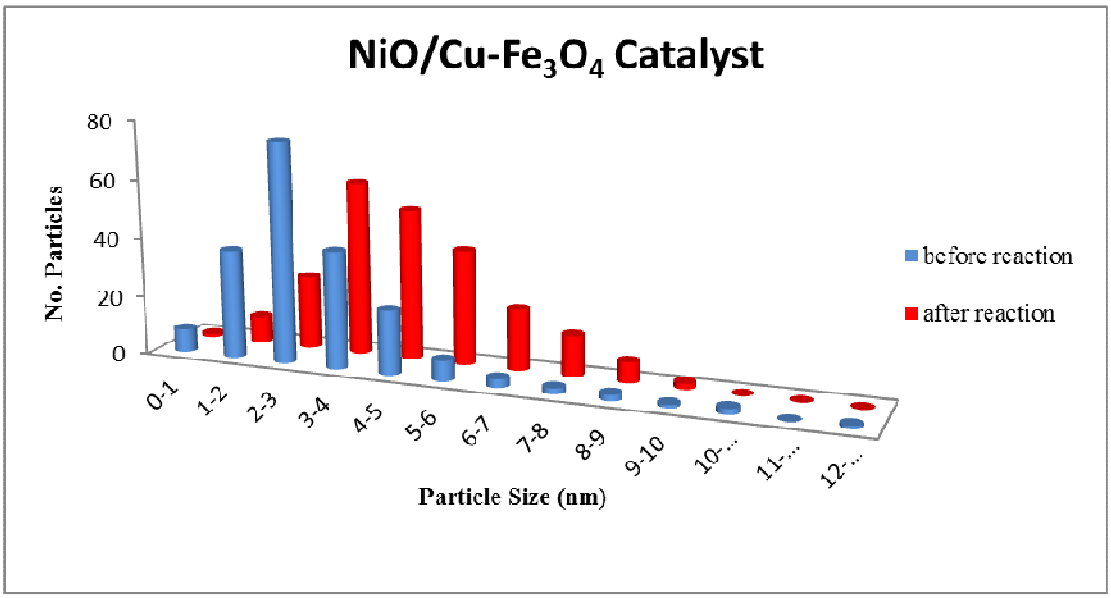
Before reaction



After reaction



Particle Size Distribution



General procedures for the preparation of the products

To a stirred solution of sodium azide (**6**, 2 mmol) and benzyl halide (**5**, 2 mmol) were added NiO/Cu-Fe_3O_4 (50 mg, 0.9 mol% of Ni, 0.9 mol% of Cu) and the corresponding alkyne (**1** or **7**, 1 mmol). The resulting mixture was stirred at 50ºC until the end of reaction. The catalyst was removed by a magnet and the resulting mixture was quenched with deionised water and extracted with AcOEt (3 × 5 mL). The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was usually purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **3** or **8**. Physical and spectroscopic data, as well as references for known compounds, follow:

1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**):[1] White solid; m.p. 104-108°C (hexane/AcOEt); IR (cm^{-1}):3021, 2920, 1450, 1223;^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 2H), 7.3-7.45 (m, 8H), 7.66 (s, 1H), 7.75-7.8 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.2, 119.4, 125.7 (2C), 128.0 (2C), 128.1, 128.8 (3C), 129.1 (2C), 130.5, 134.7, 148.2; EI-MS *m*/*z*: 235 (M^+, 22%), 207 (14), 206 (71), 180 (13), 179 (11), 116 (100), 104 (21), 91 (84), 89 (29), 65 (20), 63 (11).

1-(4-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3b**):[2] White solid; m.p. 150-152°C (hexane/AcOEt); IR (cm^{-1}):3082, 1489, 1221, 1073; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.5 (s, 2H), 7.17 (d, ^3J(H,H)=8.4 Hz, 2H), 7.3-7.35 (m, 1H), 7.4-7.45 (m, 2H), 7.52 (d, ^3J(H,H)=8.4 Hz, 2H), 7.7 (s, 1H), 7.8-7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.5, 119.4, 122.9, 125.7 (2C), 128.3, 128.8 (2C), 129.6 (2C), 130.3, 132.3 (2C), 133.6, 148.4; EI-MS *m*/*z*: 315 (M^++2, 9%), 313 (M^+, 10%), 286 (16), 284 (17), 206 (20), 171 (24), 169 (25), 116 (100), 90 (19), 89 (28).

1-(3-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3c**):[3] White solid; m.p. 85-87°C (hexane/AcOEt); IR (cm^{-1}):3084, 1460, 1432, 1222, 1046; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.54 (s, 2H), 7.2-7.25 (m, 2H), 7.3-7.35 (m, 1H), 7.4-7.45 (m, 2H), 7.45-7.5 (m, 2H), 7.71 (s, 1H), 7.8-7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.4, 119.5, 123.1, 125.7 (2C), 126.5, 128.3, 128.8 (2C), 130.2, 130.7, 130.9, 131.9, 136.8, 148.3; EI-MS *m*/*z*: 315 (M^++2, 8%), 313 (M^+, 8%), 286 (14), 284 (14), 206 (21), 171 (22), 169 (23), 116 (100), 90 (20), 89 (29).

1-(2-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3d**):[3] White solid; m.p. 101-103°C (hexane/AcOEt); IR (cm^{-1}):3051, 1459, 1430, 1220, 1043; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.7 (s, 2H), 7.15-7.25 (m, 2H), 7.3-7.35 (m, 2H), 7.4-7.45 (m, 2H), 7.62 (dd, ^3J(H,H)=7.9 Hz, ^4J (H,H)=1.0 z, 1H), 7.78 (s, 1H), 7.82 (d, ^3J(H,H)=7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.8, 119.8, 123.4, 125.7 (2C), 128.2 (2C), 128.8 (2C), 130.1, 130.2, 130.4, 133.2, 134.2, 148.1; EI-MS *m*/*z*: 315 (M^++2, 12%), 313 (M^+, 11%), 208 (12), 207 (59), 206 (93), 184 (11), 171 (31), 169 (32), 117 (11), 116 (100), 103 (13), 91 (21), 90 (24), 89 (34), 63 (10).

1-(2-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3e**):[4] White solid; m.p. 98-99°C (hexane/AcOEt); IR (cm^{-1}):3096, 1462, 1216; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 5.6 (s, 2H), 7.2-7.25 (m, 3H), 7.3-7.35 (m, 2H), 7.35-7.45 (m, 2H), 7.54 (s, 1H), 7.75-7.8 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 52.5, 119.2, 125.6 (2C), 126.7, 128.1, 128.8 (2C), 129.2, 129.4, 130.5, 131.1, 132.5, 137.0, 148.0; EI-MS *m*/*z*: 249 (M^+, 22%), 220 (35), 207 (17), 206 (11), 118(31), 117 (39), 116 (100), 105 (63), 104 (10), 103 (15), 89 (23), 79 (14), 77 (21).

1-(3-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3f**):[2] White solid; m.p. 95-96°C (hexane/AcOEt); IR (cm^{-1}):3089, 1464, 1222; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 5.52 (s, 2H), 7.1-7.2 (m, 3H), 7.25-7.45 (m, 4H), 7.66 (s, 1H), 7.8-7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 54.2, 119.5, 125.1, 125.6 (2C), 128.1, 128.7, 128.8 (2C), 129.0, 129.5, 130.5, 134.5, 139.0, 148.1; EI-MS *m*/*z*: 249 (M^+, 29%), 221 (13), 220 (61), 206 (36), 179 (20), 118 (14), 117 (17), 116 (100), 105 (66), 103 (14), 89 (24), 79 (13), 77 (20).

1-(3,5-dimethoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3g**):[4] White solid; m.p. 90-92°C (hexane/AcOEt); IR (cm^{-1}):3086, 1610, 1197; ^1H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 6H), 5.49 (s, 2H), 6.44 (s, 3H), 7.3-7.35 (m, 1H), 7.35-7.4 (m, 2H), 7.68 (s, 1H), 7.75-7.8 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.2, 55.4 (2C), 100.4, 106.0 (2C), 119.5, 125.6 (2C), 128.1, 128.8 (2C), 130.5, 136.7, 148.2, 161.2 (2C); EI-MS *m*/*z*: 296 (M^++1, 13%), 295 (M^+, 74%), 281 (14), 266 (41), 252 (10), 239 (32), 236 (19), 209 (21), 208 (15), 207 (61), 164 (36), 152 (13), 151 (100), 117 (12), 116 (100), 91 (19), 89 (21), 78 (11), 77 (18), 65 (11).

1-benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole (**3h**):[5] White solid; m.p. 125-127°C (hexane/AcOEt); IR (cm^{-1}):3060, 1481, 1222, 1069; ^1H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 2H), 7.3-7.4 (m, 7H), 7.65 (s, 1H), 7.72 (d, ^3J(H,H)=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.3, 60.4, 119.5, 126.9 (2C), 128.1 (2C), 128.8, 129.0 (2C), 129.2 (2C), 133.9, 134.5, 147.1; EI-MS *m*/*z*: 271 (M^++2, 9%), 269 (M^+, 26%), 242 (23), 241 (15), 240 (70), 207 (14), 206 (27), 179 (29), 152 (36), 151 (10), 150 (100), 125 (10), 123 (25), 104 (20), 102 (11), 91 (93), 65 (22).

1-(4-bromobenzyl)-4-(4-chlorophenyl)-1*H*-1,2,3-triazole (**3i**): White solid; m.p. 146-150°C (hexane/AcOEt); IR (cm^{-1}):1487, 1456, 1227, 1092, 1072; ^1H NMR (300 MHz, $CDCl_3$): δ 5.53 (s, 2H), 7.18 (d, ^3J(H,H)=8.4 Hz, 2H), 7.36 (d, ^3J(H,H)=8.5 Hz, 2H), 7.51 (d, ^3J(H,H)=8.4 Hz, 2H), 7.66 (s, 1H), 7.72 (d, ^3J(H,H)=8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.5, 119.5, 123.0, 126.9 (2C), 128.8, 129.0 (2C), 129.6 (2C), 132.3 (2C), 133.5, 1339., 147.3; EI-MS *m*/*z*: 349 (M^++2, 17%), 347 (M^+, 13%), 320 (19), 318 (14), 240 (26), 207 (10), 171 (27), 169 (29), 152 (33), 151 (10), 150 (100), 123 (16), 90 (19), 89 (16); HRMS (ESI): *m*/*z* calcd for $C_{15}H_{11}BrClN_3$: 346.9825; found: 346.9828.

1-benzyl-4-(2-chloropehnyl)-1*H*-1,2,3-triazole (**3j**):[6] White solid; m.p. 77-78°C (hexane/AcOEt); IR (cm^{-1}):3083, 1461, 1227, 1056; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.61 (s, 2H), 7.2-7.45 (m, 8H), 8.12 (s, 1H), 8.22 (dd, ^3J(H,H)=7.8 Hz, ^4J(H,H)=1.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.2, 123.1, 127.1, 127.9 (2C), 128.7, 129.0, 129.1 (2C), 129.2, 129.8, 130.1, 131.1, 134.6, 144.4; EI-MS *m*/*z*: 271 (M^++2, 6%), 269 (M^+, 17%), 242 (12), 240 (36), 206 (40), 179 (30), 152 (28), 150 (87), 123 (14), 104 (26), 102 (10), 91 (100), 65 (19).

1-benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole (**3k**):[7] White solid; m.p. 143-145°C (hexane/AcOEt); IR (cm^{-1}):3070, 1477, 1449, 1222, 1050; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.56 (s, 2H), 7.3-7.4 (m, 5H), 7.5-7.55 (m, 2H), 7.65-7.7 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.3, 119.5, 122.0, 127.2 (2C), 128.1 (2C), 128.8, 129.1 (2C), 129.4, 131.9 (2C), 134.4, 147.1; EI-MS *m*/*z*: 315 (M^++2, 23%), 313 (M^+, 24%), 287 (10), 286 (54), 285 (11), 284 (53), 207 (12), 206 (40), 204 (11), 196 (73), 194 (75), 179 (32), 178 (12), 169 (13), 167 (13), 115 (11), 104 (18), 102 (12), 91 (100), 88 (14), 65 (19).

4-(4-bromophenyl)-1-(3-methylbenzyl)-1*H*-1,2,3-triazole (**3l**): White solid; m.p. 127-128°C (hexane/AcOEt); IR (cm^{-1}):3016, 1450, 1225, 1069; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 5.53 (s, 2H), 7.11 (d, ^3J(H,H)=7.3 Hz, 2H), 7.18 (d, ^3J(H,H)=7.3 Hz, 1H), 7.28 (d, ^3J(H,H)=7.3 Hz, 1H), 7.52 (d, ^3J(H,H)=8.6 Hz, 2H), 7.65 (s, 1H), 7.67 (d, ^3J(H,H)=8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 54.3, 119.5, 122.0, 125.2, 127.2 (2C), 128.8, 129.0, 129.5, 129.6, 131.9 (2C), 134.3, 139.1, 147.1; EI-MS *m*/*z*: 329 (M^++2, 24%), 327 (M^+, 22%), 300 (34), 298 (36), 286 (27), 284 (26), 220 (21), 207 (22), 196 (70), 194 (76), 193 (27), 178 (12), 169 (12), 167 (12), 118 (18), 117 (11), 115 (15), 105 (100), 103 (20), 102 (14), 88 (15), 79; Elemental analysis calcd. for $C_{16}H_{14}BrN_3$: C = 58.55; H = 4.30; N = 12.80; found: C = 58.50; H = 4.29; N = 12.69.

1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**3m**):[5] White solid; m.p. 135-136°C (hexane/AcOEt); IR (cm^{-1}):1455, 1250; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 5.55 (s, 2H), 6.93 (d, ^3J(H,H)=8.9 Hz, 2H), 7.25-7.4 (m, 5H), 7.58 (s, 1H), 7.72 (d, ^3J(H,H)=8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.1, 55.3, 114.2 (2C), 118.6, 123.2, 127.0 (2C), 128.0 (2C), 128.7, 129.1 (2C), 134.7, 148.0, 159.5; EI-MS *m*/*z*: 266 (M^++1, 6%), 265 (M^+, 35%), 237 (21), 236 (100), 222 (17), 210 (10), 209

(20), 206 (19), 194 (10), 193 (10), 179 (16), 160 (11), 146 (82), 119 (29), 91 (63), 89 (15), 76 (13), 65 (24).

1-benzyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole (**3n**):[6] White solid; m.p. 145-146°C (hexane/AcOEt); IR (cm^{-1}):3031, 1454, 1220; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 5.58 (s, 2H), 7.12 (d, ^{3}J(H,H)=7.6 Hz, 1H), 7.25-7.45 (m, 6H), 7.58(d, ^{3}J(H,H)=7.6 Hz, 1H), 7.65-7.7 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 54.2, 119.4, 122.8, 126.3, 128.0 (2C), 128.7, 128.8, 128.9, 129.1 (2C), 130.3, 134.7, 138.5, 148.3; EI-MS *m*/*z*: 249 (M^+, 25%), 221 (13), 220 (58), 206 (10), 179 (12), 131 (11), 130 (100), 104 (13), 103 (14), 91 (70), 77 (14), 65 (14).

1-(3-bromobenzyl)-4-(*m*-tolyl)-1*H*-1,2,3-triazole (**3o**):[7] White solid; m.p. 90-93°C (hexane/AcOEt); IR (cm^{-1}):3036, 1429, 1223, 1084; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 5.48 (s, 2H), 7.1-7.3 (m, 4H), 7.4-7.45 (m, 2H), 7.57 (d, ^{3}J(H,H)=7.8 Hz, 1H), 7.65 (s, 1H), 7.7 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 53.2, 119.5, 122.6, 122.9, 126.2, 126.4, 128.6, 128.9, 130.1, 130.5, 130.7, 131.7, 136.8, 138.4, 148.3; EI-MS *m*/*z*: 329 (M^++2, 11%), 327 (M^+, 12%), 300 (18), 298 (17), 220 (18), 207 (39), 171 (24), 169 (22), 131 (11), 130 (100), 103 814), 90 (14), 89 (13).

1-(3-methylbenzyl)-4-(*m*-tolyl)-1*H*-1,2,3-triazole (**3p**): White solid; m.p. 127-128°C (hexane/AcOEt); IR (cm^{-1}): 3017, 1446, 1220; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.37 (s, 3H), 5.52 (s, 2H), 7.1-7.2 (m, 4H), 7.25-7.3 (m, 2H), 7.57 (d, ^{3}J(H,H)=7.8 Hz, 1H), 7.64 (s, 1H), 7.66 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 21.4, 54.2, 119.4, 122.7, 125.1, 126.3, 128.6, 128.7, 128.8, 129.0, 129.5, 130.4, 134.6, 138.4, 139.0, 148.2; EI-MS *m*/*z*: 264 (M^++1, 7%), 263 (M^+, 35%), 235 (14), 234 (62), 220 (41), 207 (18), 193 (18), 131 (10), 130 (100), 118 (15), 105 (62), 103 (22), 79 (10), 77 (25); HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}N_3$ 263.1422; found: 263.1414.

1-benzyl-4,5-diphenyl-1*H*-1,2,3-triazole (**8a**):[8] White solid; m.p. 109-110°C (hexane/AcOEt); IR (cm^{-1}):3058, 1449, 1246; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.41 (s, 2H), 7.0-7.05 (m, 2H), 7.1-7.15 (m, 2H), 7.2-7.3 (m, 6H), 7.4-7.5 (m, 3H), 7.55-7.6 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.0, 126.7 (2C), 127.5 (2C), 127.7, 127.8, 128.1, 128.4 (2C), 128.7 (2C), 129.1 (2C), 129.6, 130.1 (2C), 130.9, 133.9, 135.3, 144.5; EI-MS *m*/*z*: 311 (M^+, 17%), 193 (16), 192 (100), 165 (23), 91 (75), 89 (16).

1-benzyl-4,5-bis(4-butylphenyl)-1*H*-1,2,3-triazole (**8b**): Pale yellow oil; IR (cm^{-1}): 3030, 1455, 1245; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, ^3J(H,H)=7.3 Hz, 3H), 0.97 (t, ^3J(H,H)=7.3 Hz, 3H), 1.25-1.45 (m, 4H), 1.50-1.7 (m, 4H), 2.55 (t, ^3J(H,H)=7.6 Hz, 2H), 2.67 (t, ^3J(H,H)=7.6 Hz, 2H), 5.39 (s, 2H), 7.0-7.1 (m, 6H), 7.2-7.25 (m, 5H), 7.45-7.5 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 22.3 (2C), 33.3, 35.3, 35.5, 51.9, 125.1, 126.5 (2C), 127.0, 127.5 (2C), 128.0, 128.4 (2C), 128.6 (2C), 129.1 (2C), 129.9 (2C), 133.6, 135.5, 142.4, 144.4, 144.5; EI-MS *m*/*z*: 423 (M^+, 0%), 361 (16), 360 (69), 359 (24), 328 (13), 283 (18), 282 (20), 281 (72), 209 (13), 208 (18), 207 (100); Elemental analysis calcd. for $C_{29}H_{33}N_3$: C = 82.23; H = 7.85; N = 9.92; found: C = 82.26; H = 7.75; N = 9.89.

1-(3-bromobenzyl)-4,5-diphenyl-1*H*-1,2,3-triazole (**8c**): White solid; m.p. 70-73°C (hexane/AcOEt); IR (cm^{-1}):3054, 1572, 1241; ^1H NMR (300 MHz, $CDCl_3$): δ 5.37 (s, 2H), 6.97 (d, ^3J(H,H)=7.7 Hz, 1H), 7.1-7.15 (m, 4H), 7.2-7.3 (m, 3H), 7.35-7.6 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.4, 122.7, 126.2, 126.6 (2C), 127.6 (2C), 127.8, 128.4 (2C), 129.3 (2C), 129.9, 130.0 (2C), 130.3, 130.7, 131.4, 133.8, 137.3, 144.6; EI-MS *m*/*z*: 391 (M^++2, 6%), 389 (M^+, 6%), 193 (15), 192 (100), 165 (28), 89 (15); Elemental analysis calcd. for $C_{21}H_{16}BrN_3$: C = 64.63; H = 4.13; N = 10.77; found: C = 64.65; H = 4.17; N = 10.69.

2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)isoindoline-1,3-dione (**x**): White solid; m.p. 186-188°C (hexane/AcOEt); IR (cm^{-1}):1715; ^1H NMR (300 MHz, $CDCl_3$): δ 6.26 (s, 2H), 7.25-7.4 (m, 3H), 7.75-7.85 (m, 4H), 7.9-7.95 (m, 2H), 8.11 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.7, 120.5, 124.1 (2C), 125.8 (2C), 128.3, 128.8 (2C), 130.1, 131.4 (2C), 134.9 (2C), 148.4, 166.5 (2C); EI-MS *m*/*z*: 304 (M^+, 31%), 281 (11), 248 (10), 208 (10), 207 (40), 161 (11), 160 (100), 133 (15), 116 (31), 104 (16), 77 (15), 76 (14); Elemental analysis calcd. for $C_{17}H_{12}N_4O_2$: C = 67.10; H = 3.97; N = 18.41; found: C = 67.11; H = 3.96; N = 18.42.

1-((2'-(azidomethyl)-[1,1'-biphenyl]-2-yl)-4-phenyl-1*H*-1,2,3-triazole (**x**): Colorless oil; IR (cm^{-1}):2092, 1242; ^1H NMR (300 MHz, $CDCl_3$): δ 3.95-4.05 (m, 2H), 5.25-5.35 (m, 2H), 7.15-7.2 (m, 1H), 7.2-7.3 (m, 3H), 7.35-7.5 (m, 8H), 7.7-7.8 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.7, 52.3, 119.7, 125.5 (2C), 128.0, 128.4 (2C), 128.5, 128.6, 128.7 (2C), 128.9, 129.6, 129.9, 130.1, 132.9, 133.5, 139.1 (2C), 147.5; EI-MS *m*/*z*: 194 (M^+-172, 16%), 193 (100), 192 (28), 166 (14), 165 (56), 164 (10),

163 (10); Elemental analysis calcd. for $C_{22}H_{18}N_6$: C = 72.11; H = 4.95; N = 22.94; found: C = 72.12; H = 4.98; N = 22.98.

4-(4-methoxyphenyl)-1-((2'-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-[1,1'-biphenyl]-2-yl)methyl)-1*H*-1,2,3-triazole (**x**): Pale yellow oil; IR (cm^{-1}):1245; ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 5.1-5.25 (m, 2H), 5.3-5.35 (m, 2H), 6.9-6.95 (m, 2H), 7.25-7.3 (m, 3H), 7.3-7.45 (m, 9H), 7.47 (s, 1H), 7.6-7.65 (m, 2H), 7.7-7.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.8, 55.3, 60.3, 114.2 (2C), 114.5, 119.5, 120.4, 123.0, 125.6 (2C), 126.9 (2C), 128.1, 128.6 (2C), 128.7 (2C), 128.8, 129.1, 129.9, 130.0, 130.1, 130.3, 133.3 (2C), 138.6 (2C), 147.4 (2C), 159.6; EI-MS *m*/*z*: 499 (M^++1, 5%), 498 (M^+, 14%), 339 (11), 325 (15), 324 (13), 309 (11), 295 (16), 294 (15), 292 (10), 283 (14), 282 (62), 180 (27), 179 (100), 178 (61), 166 (10), 165 (36), 146 (16), 133 (12), 132 (11), 116 (19), 89 (10); Elemental analysis calcd. for $C_{31}H_{26}N_6O$: C = 74.68; H = 5.26; N = 16.86; found: C = 74.69; H = 5.28; N = 16.87.

References

(1) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Org. Biomol. Chem.* **2011**, *9*, 6385-6395.

(2) J. Albadi, M. Keshavarz, M. Abedini, M. Vafaie-nezhad, *Chinese Chem. Lett.* **2012**, *23*, 797-800.

(3) B. S. P. A. Kumar, K. H. V. Reddy, B. Madhav, K. Ramesh, Y. V. D. Nageswar, *Tetrahedron Lett.* **2012**, *53*, 4595-4599.

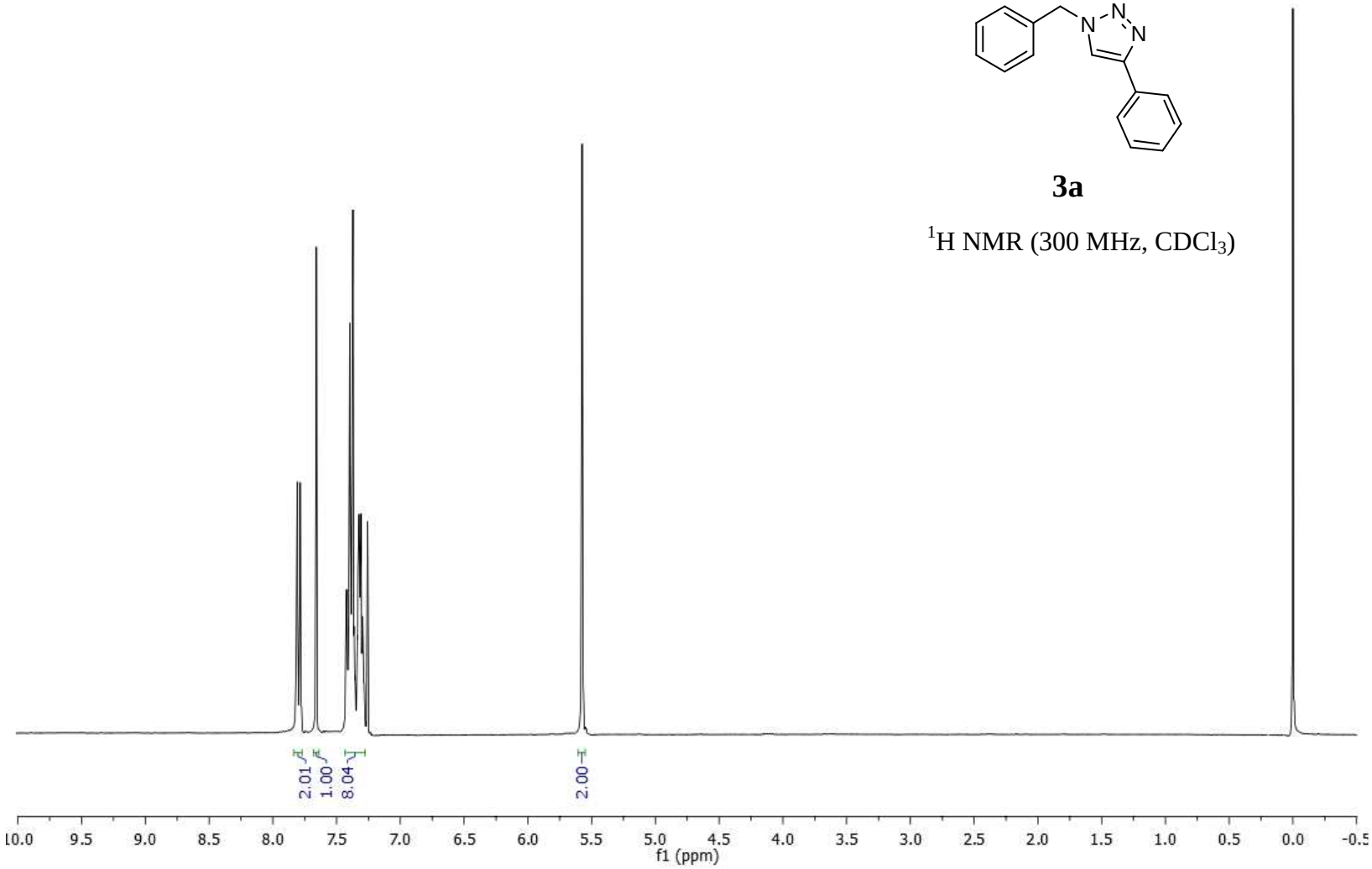
(4) L. Wan, C. Cai, *Catal. Lett.* **2012**, *142*, 1134-1140.

(5) R. B. N. Baig, R. S. Varna, *Green Chem.* **2012**, *14*, 625.632.

(6) X. Meng, X. Xu, T. Gao, B. Chen., *Eur. J. Org. Chem.* **2010**, 5409-5414.

(7) J. McNulty, K. Keshar, *Eur. J. Org. Chem.* **2012**, 5462-5470.

(8) D.-R. Hou, T.-C. Kuan, Y.-K. Li, R. Lee, K.-W. Huang, *Tetrahedron*, **2010**, *66*, 9415-9420.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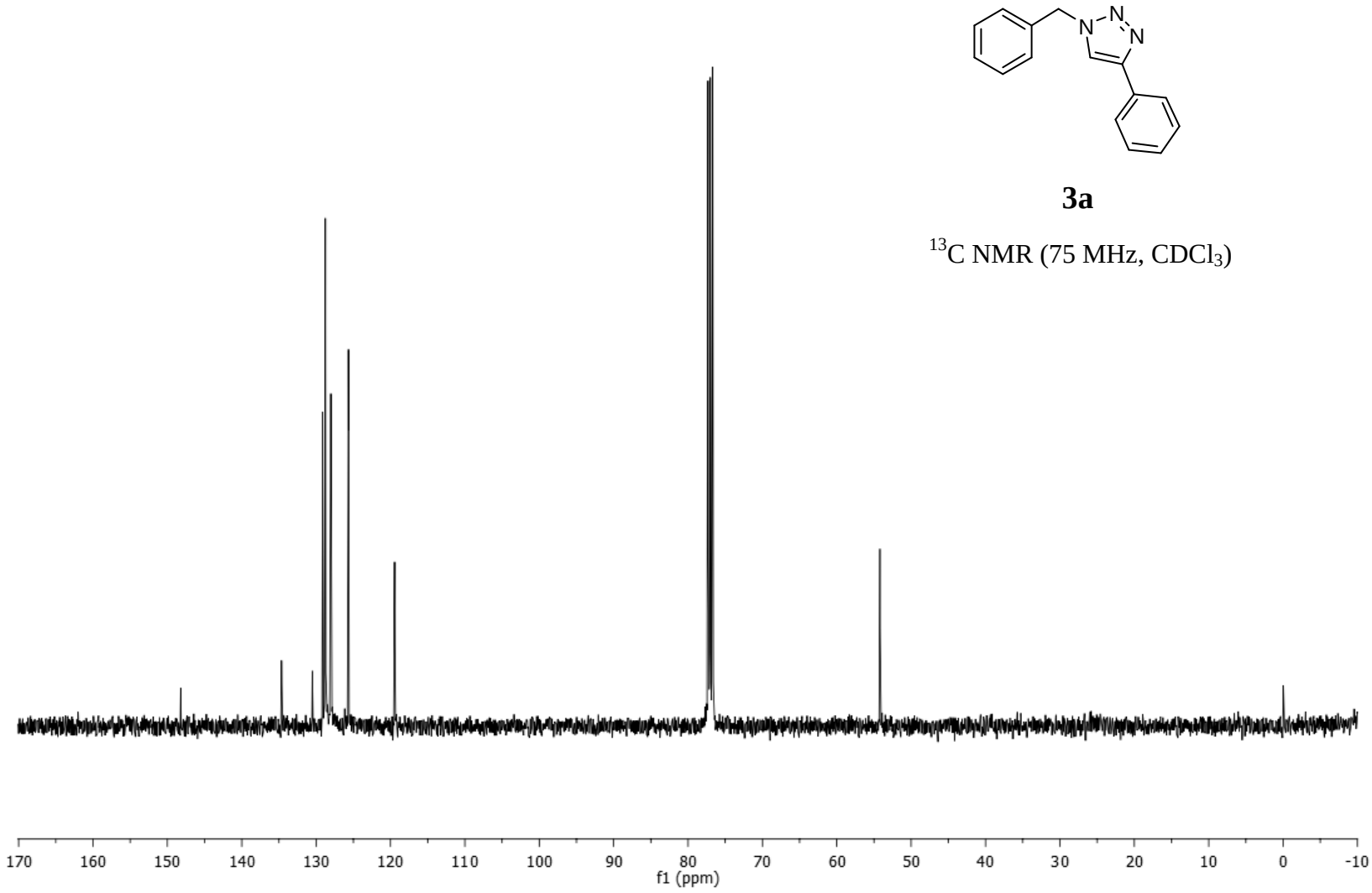
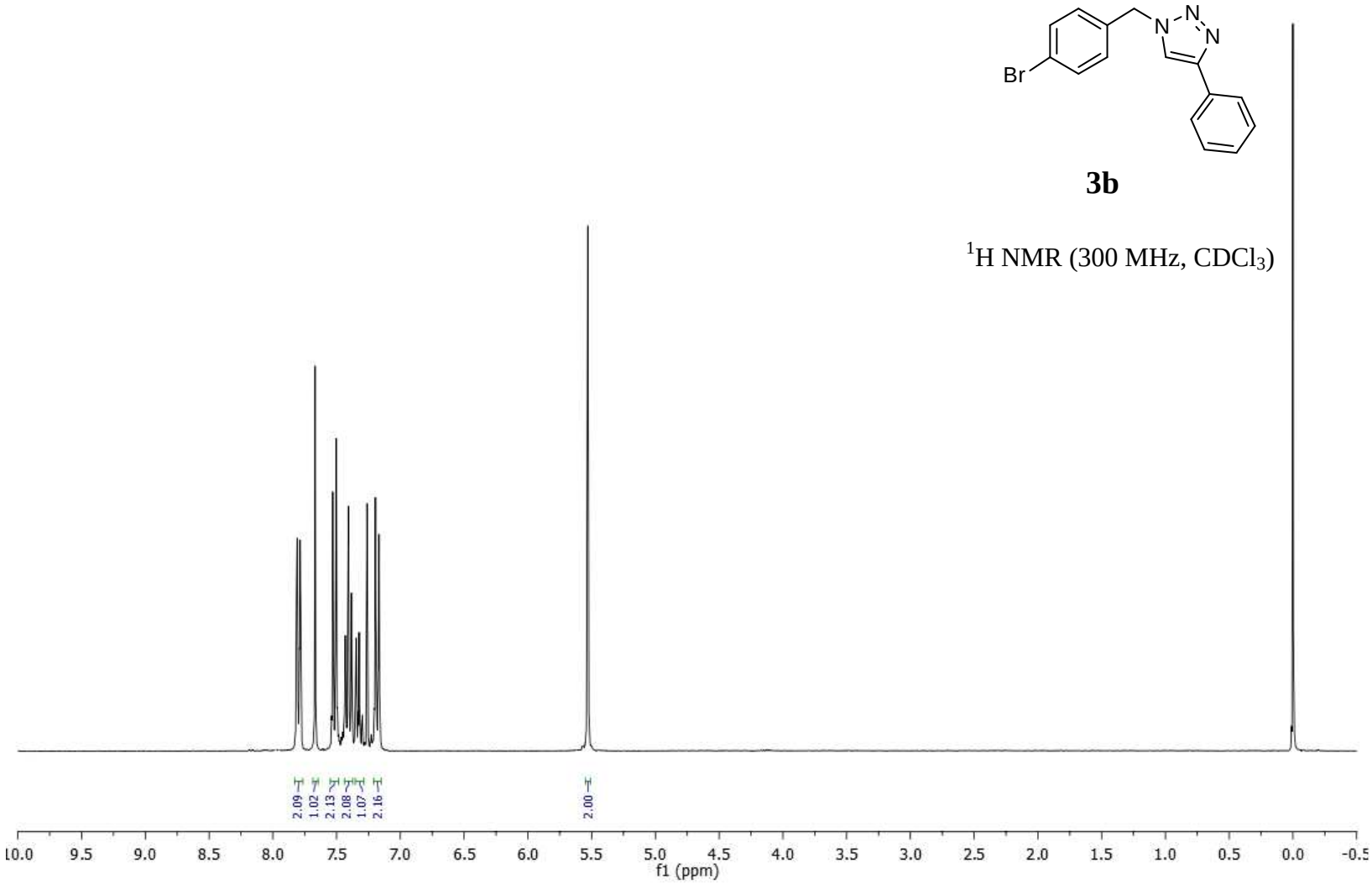
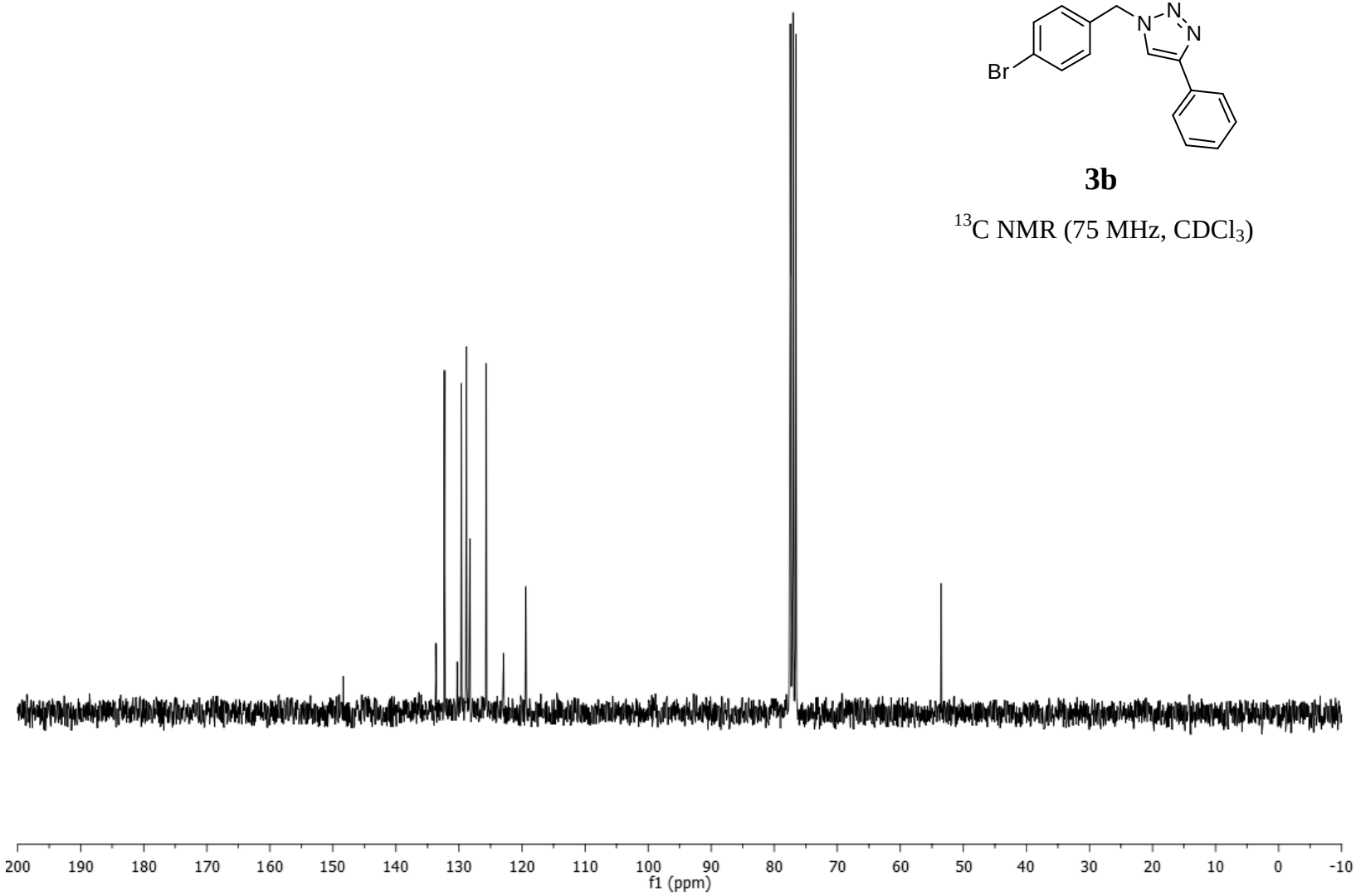
N
N
3a
1H NMR (300 MHz, CDCl3)
2.01
1.00
8.04
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3a

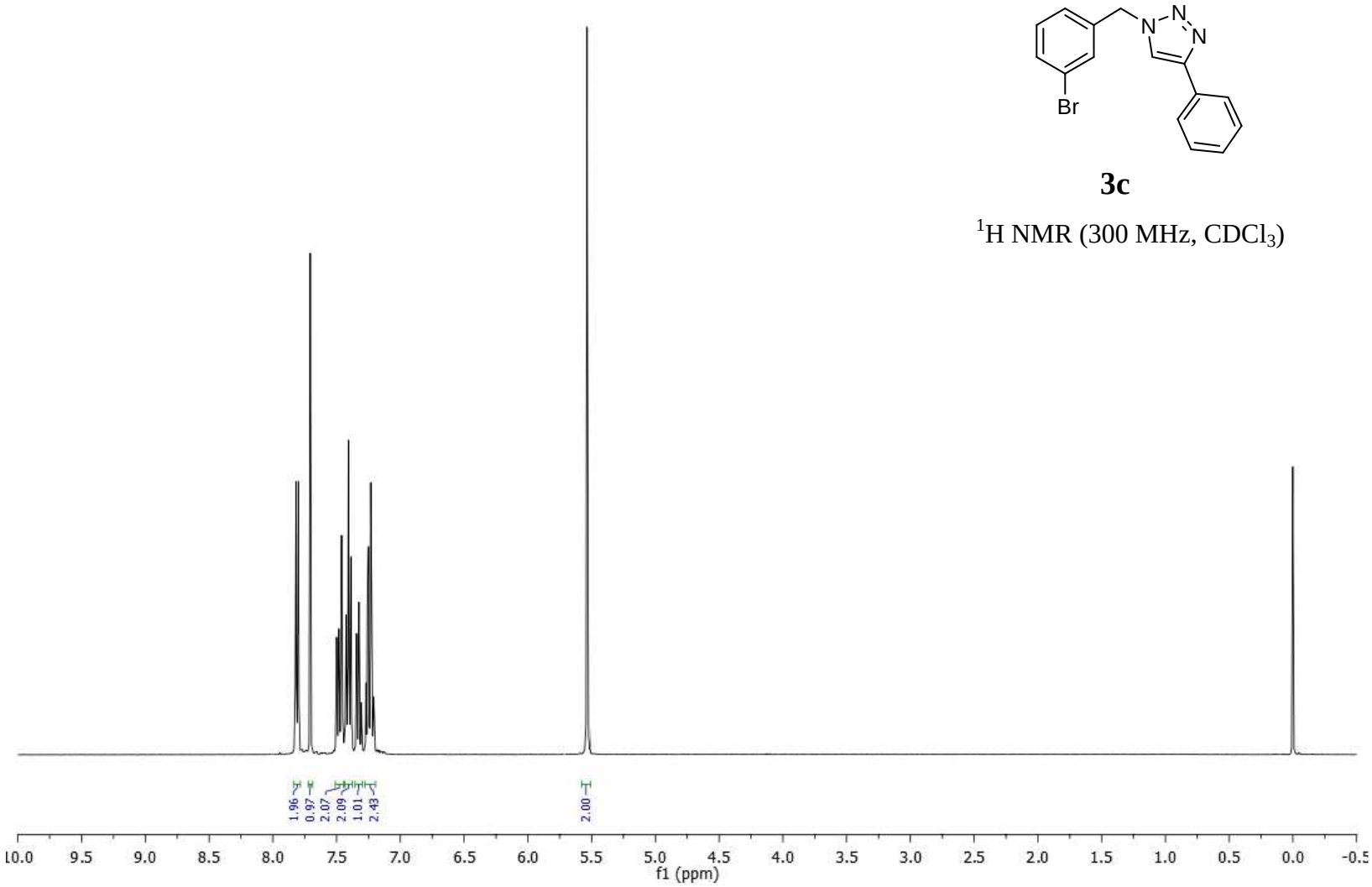
^{13}C NMR (75 MHz, $CDCl_3$)


Br
N
N
N
3b
1H NMR (300 MHz, CDCl3)
2.09
1.02
2.13
2.08
1.07
2.16
2.00
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
-0.5
f1 (ppm)



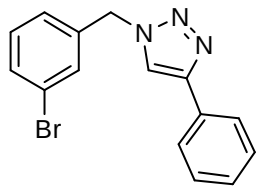
3b

^{13}C NMR (75 MHz, $CDCl_3$)



3c

^{1}H NMR (300 MHz, $CDCl_3$)



3c

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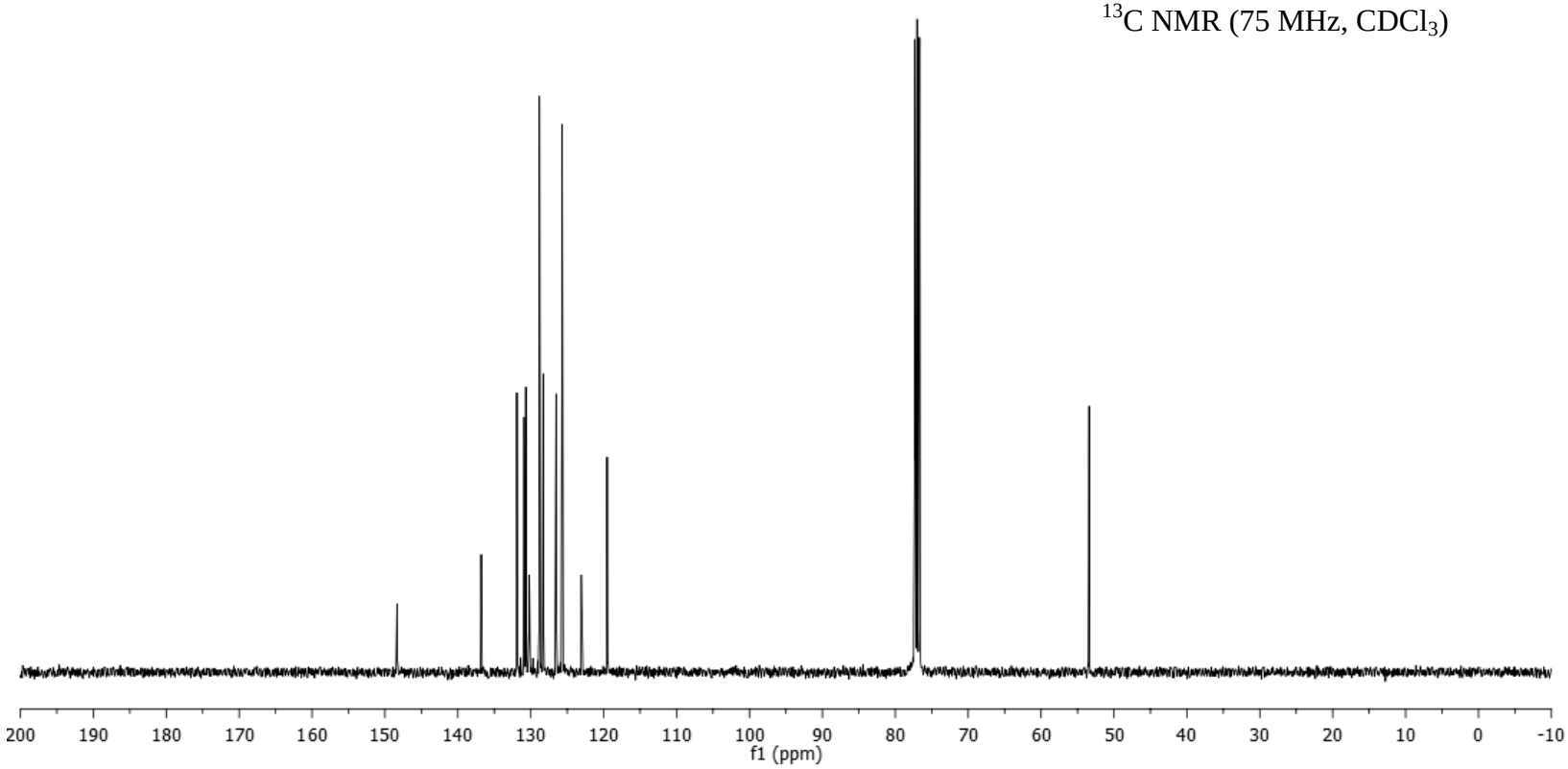
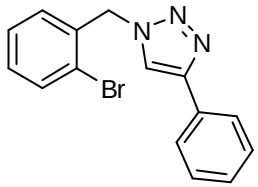
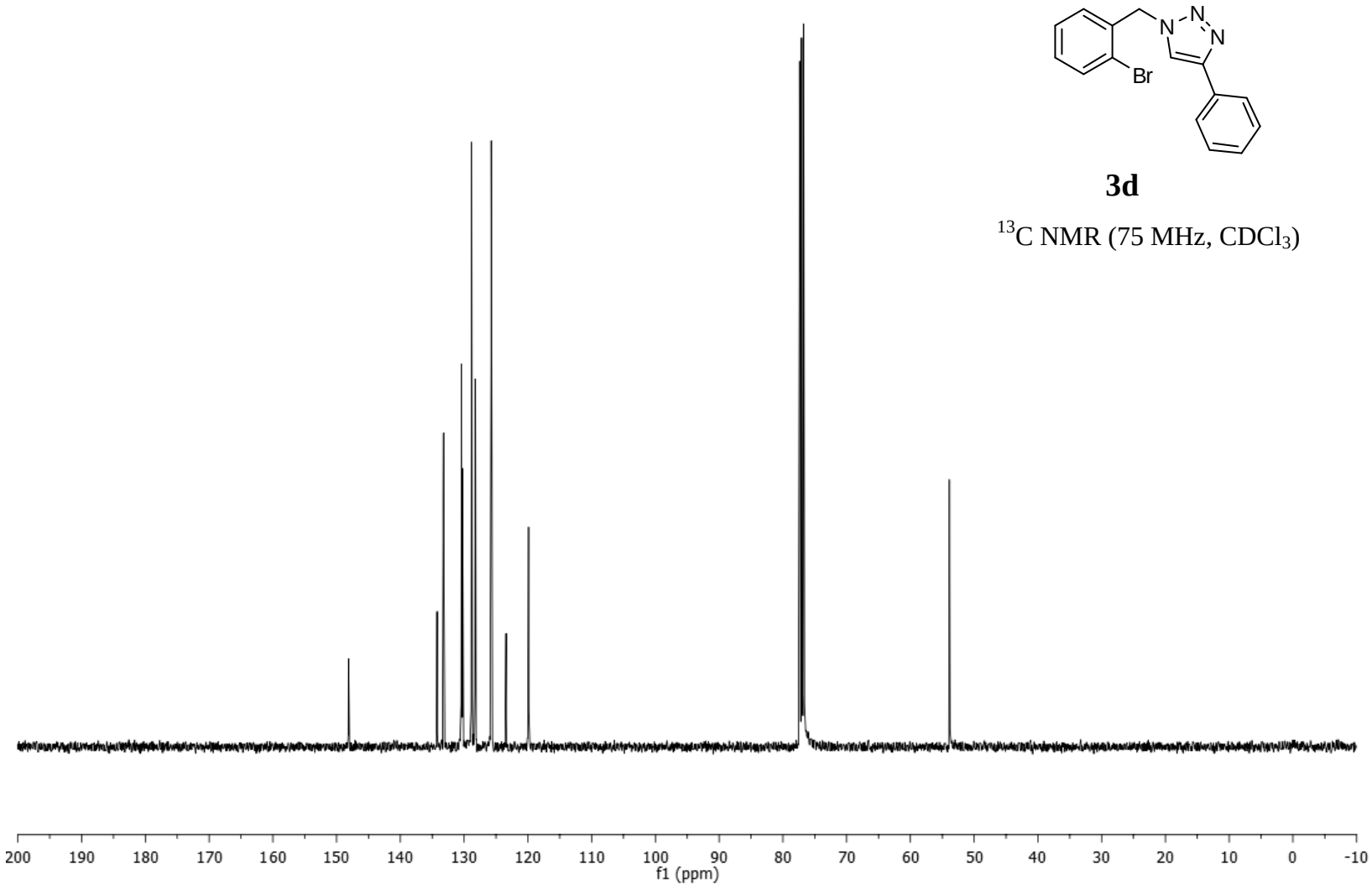




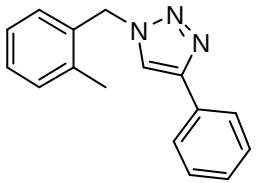
3d

^{1}H NMR (300 MHz, $CDCl_3$)



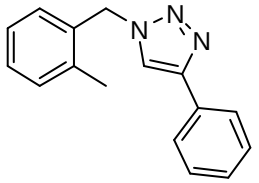
3d

^{13}C NMR (75 MHz, $CDCl_3$)



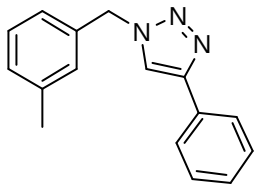
3e

^{1}H NMR (300 MHz, $CDCl_3$)



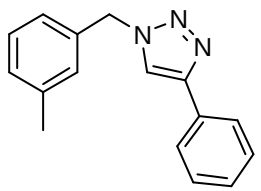
3e

^{13}C NMR (75 MHz, $CDCl_3$)



3f

^{1}H NMR (300 MHz, $CDCl_3$)



3f

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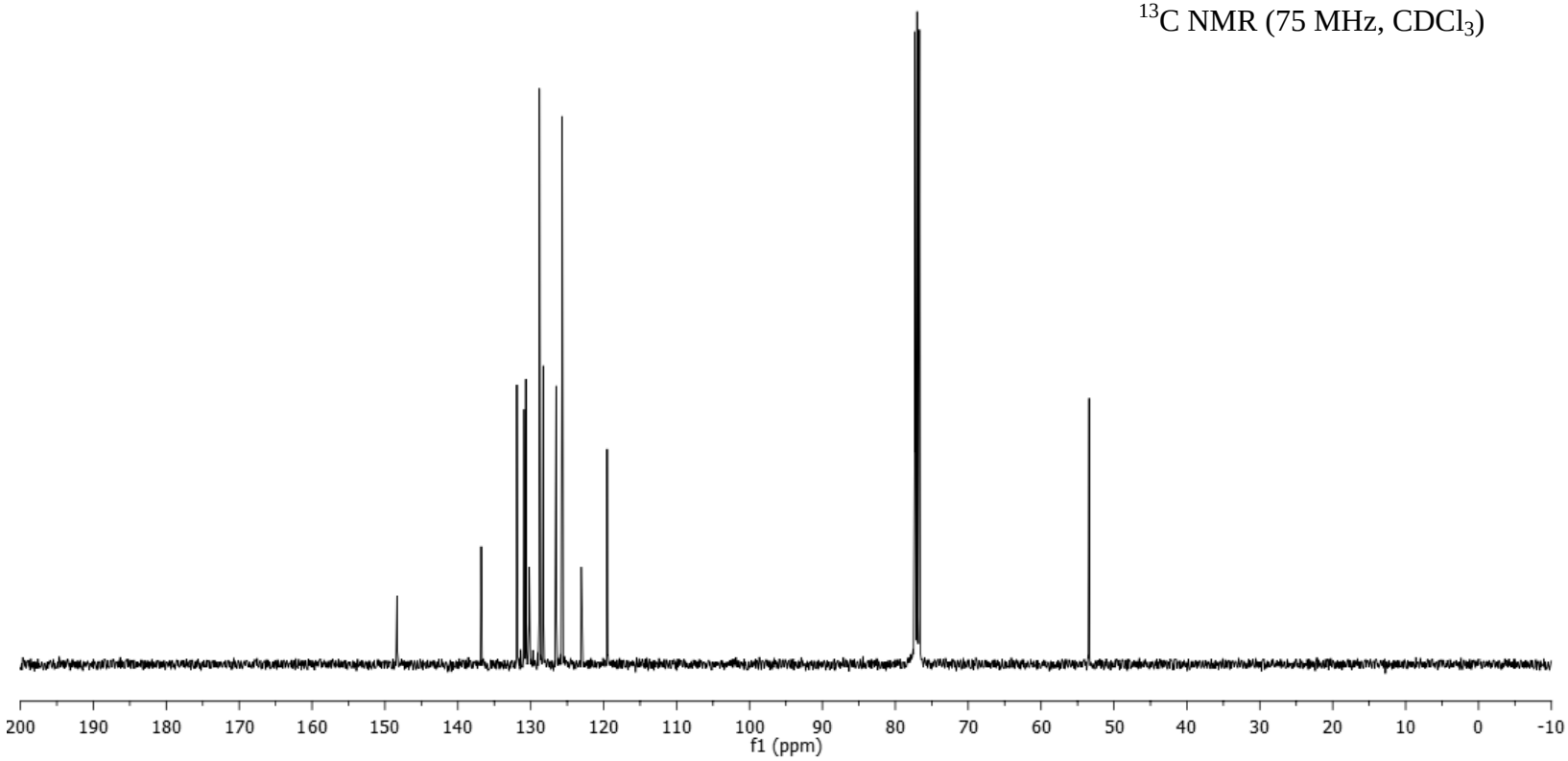

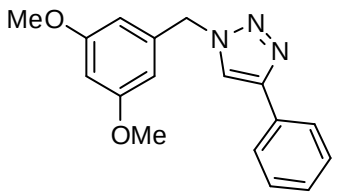

3g

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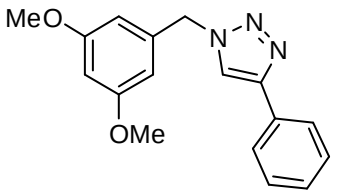

3g

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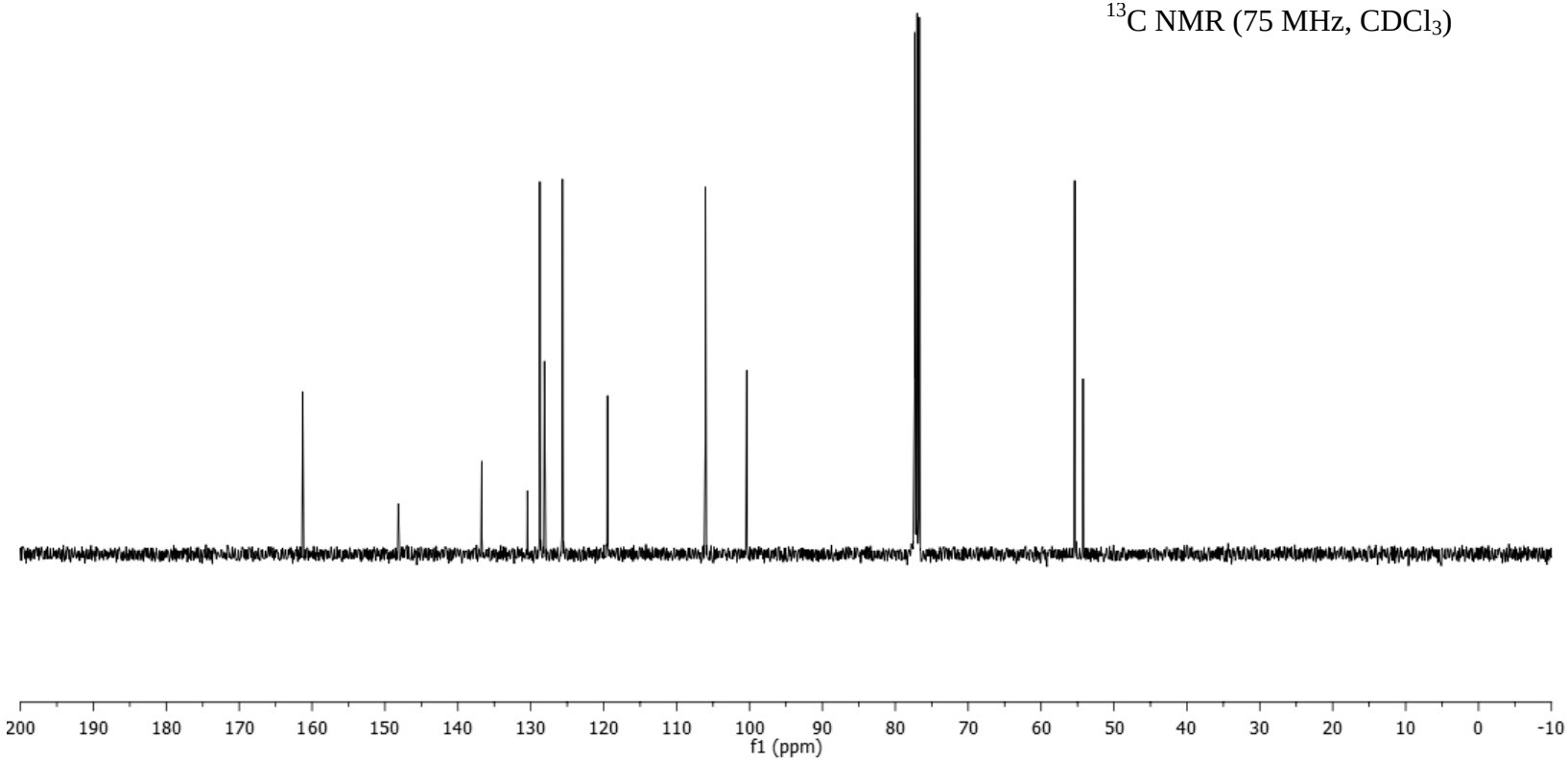

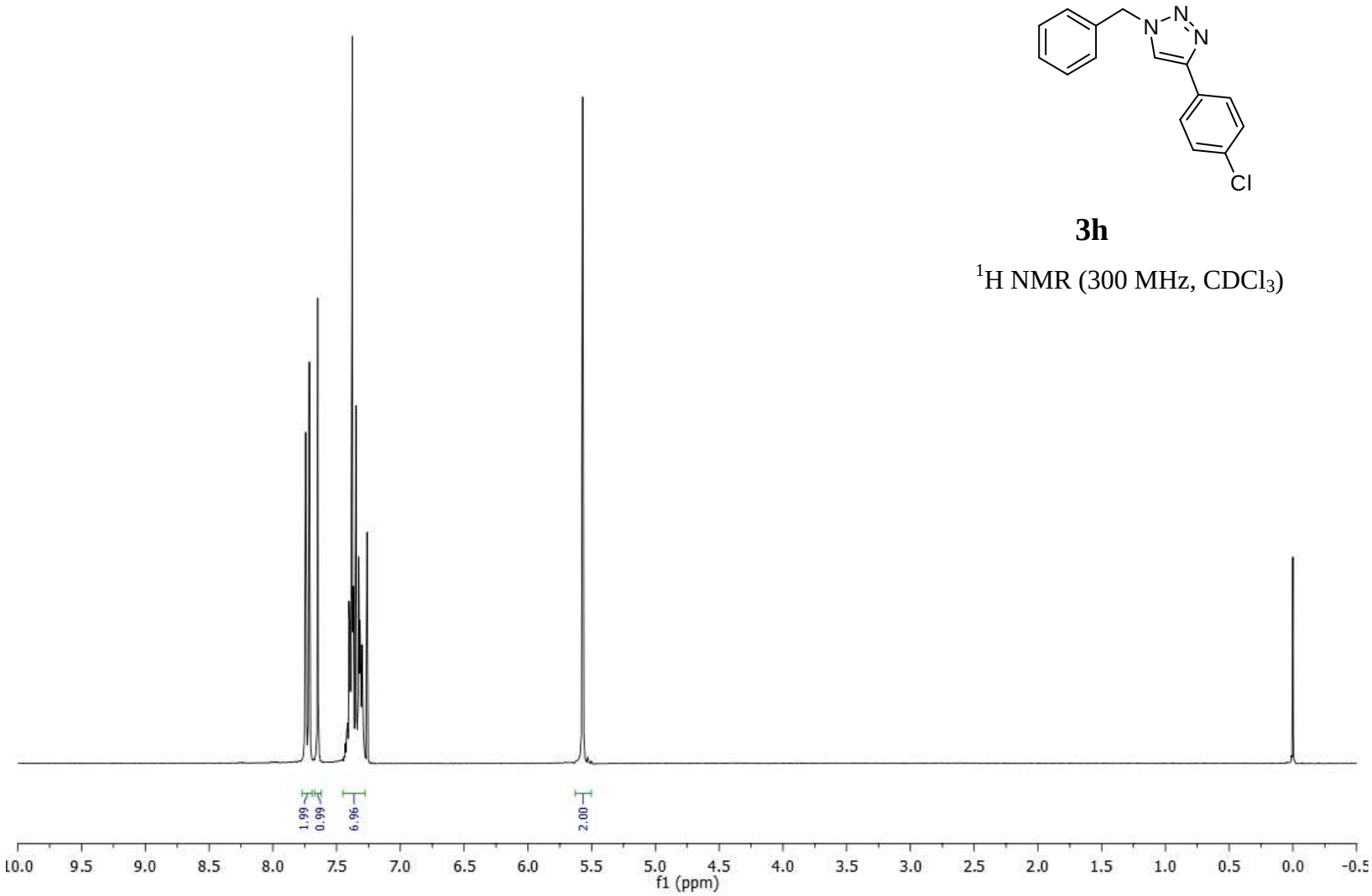

3h

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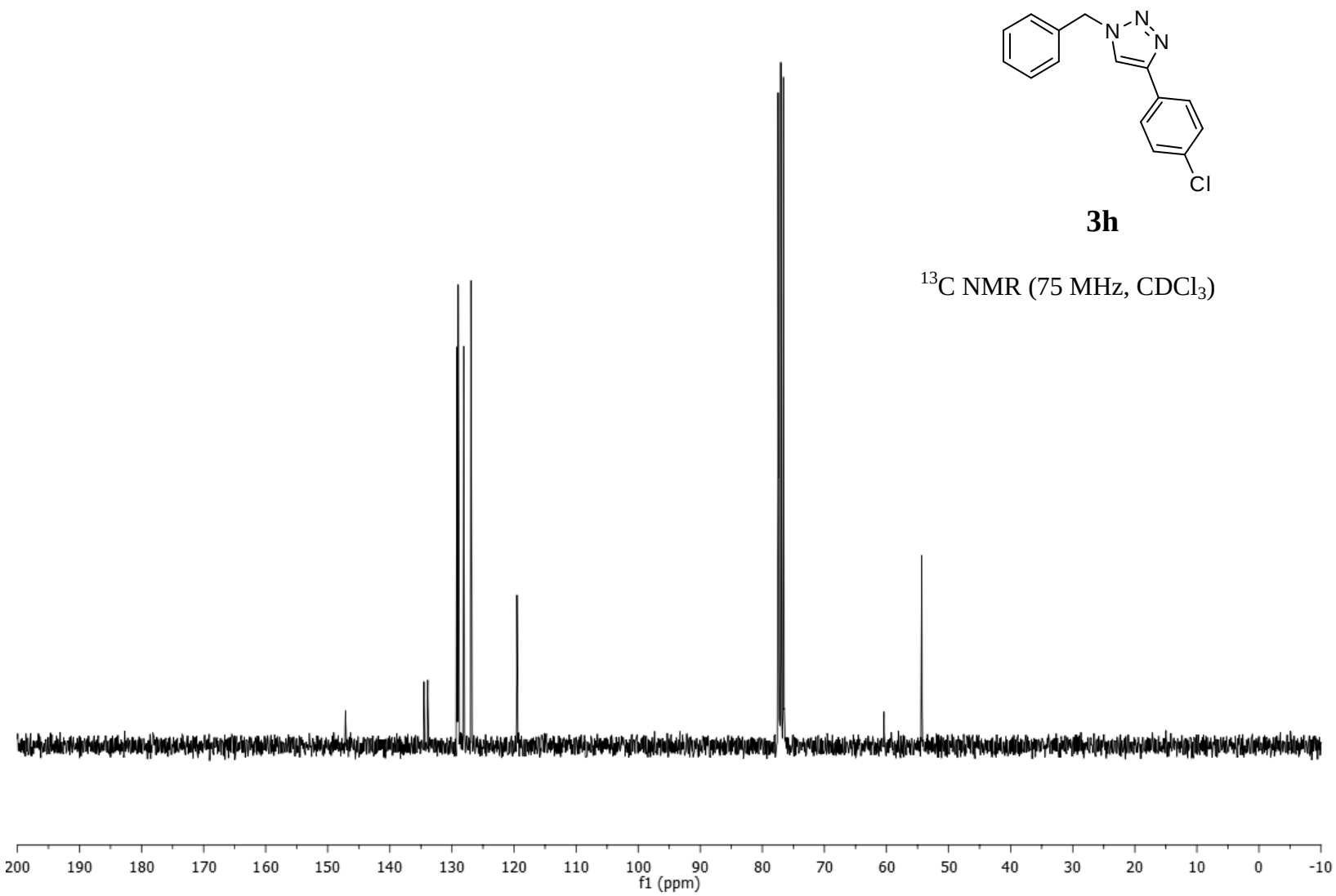

3h

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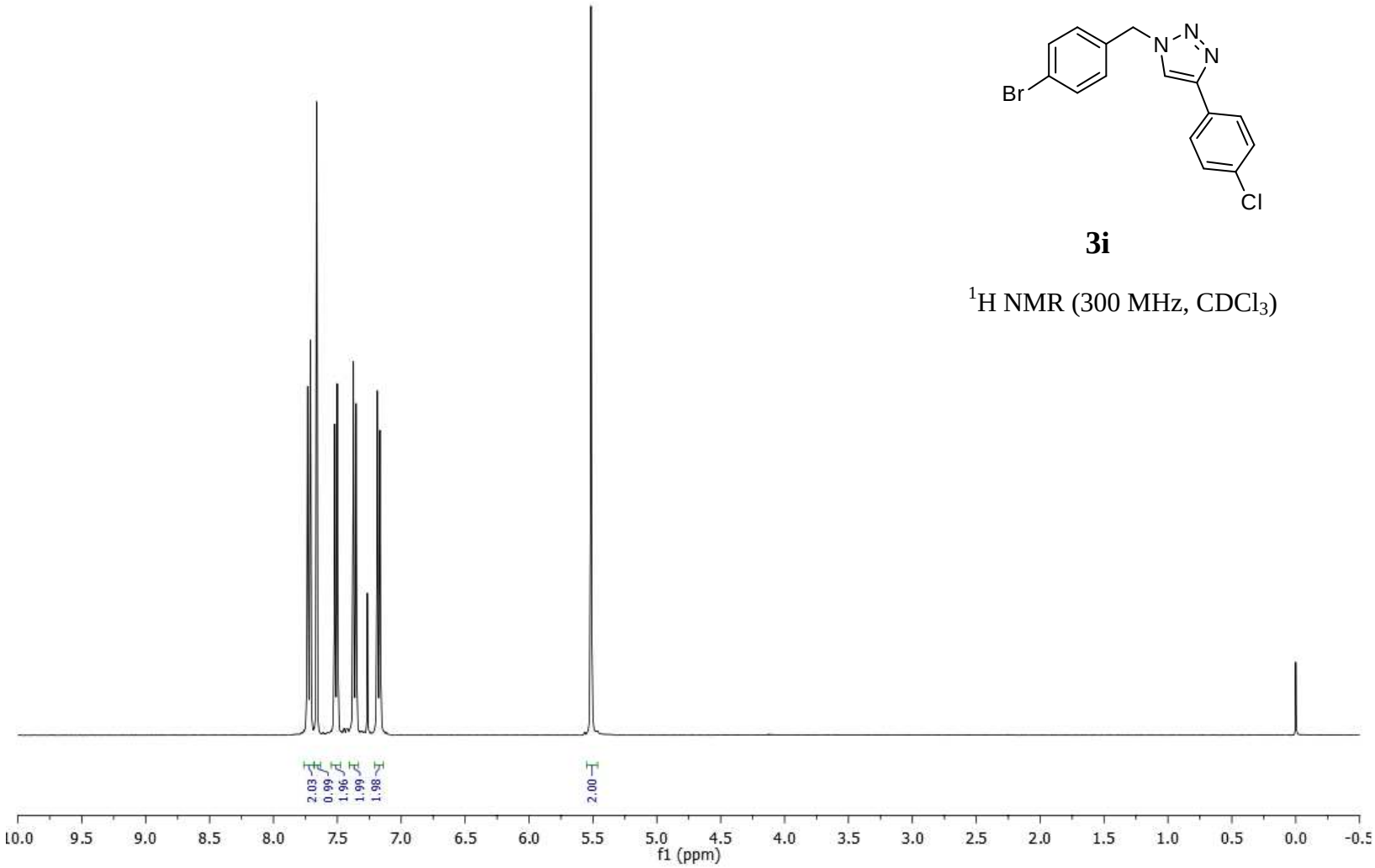

3i

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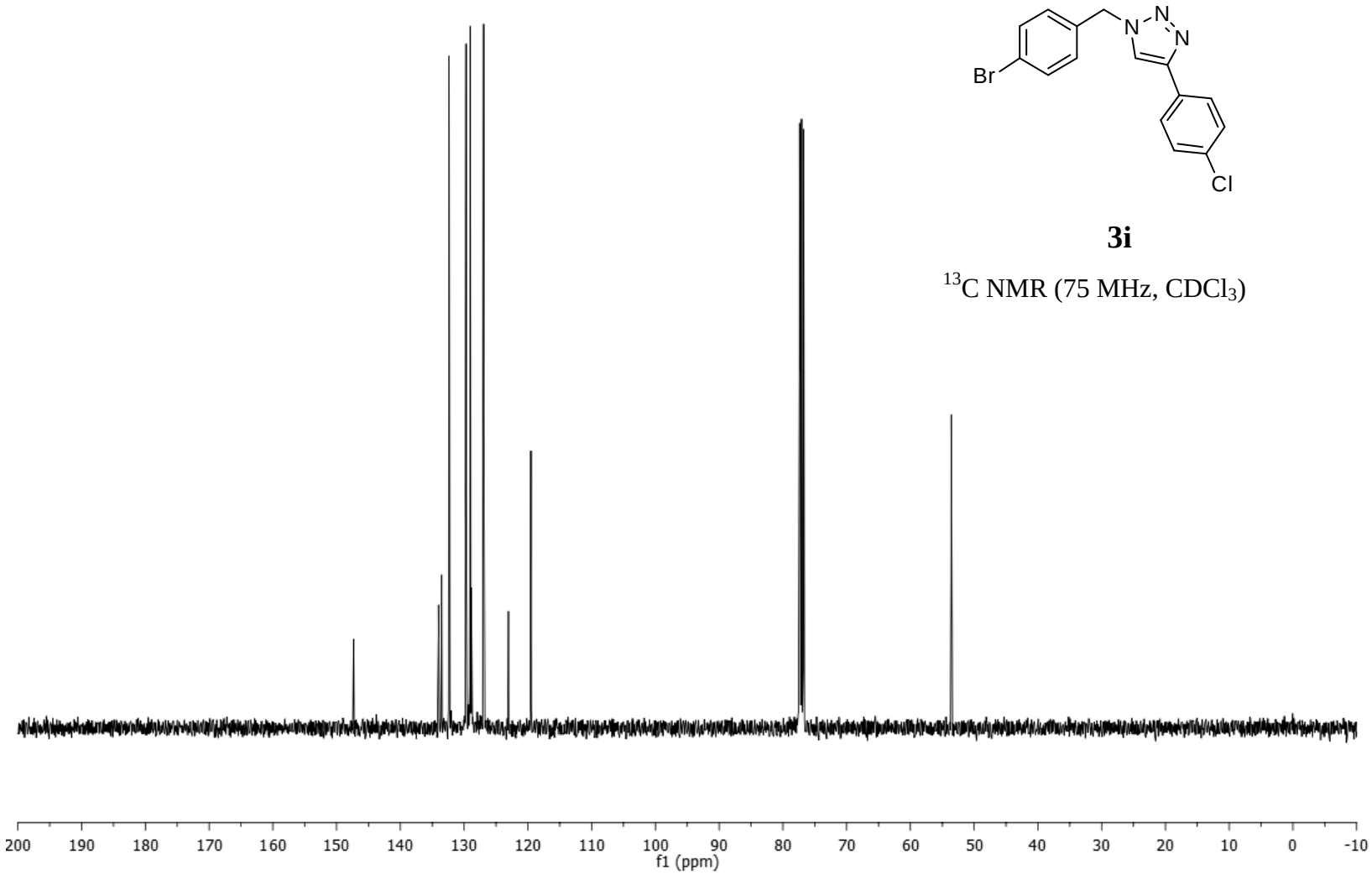

3i

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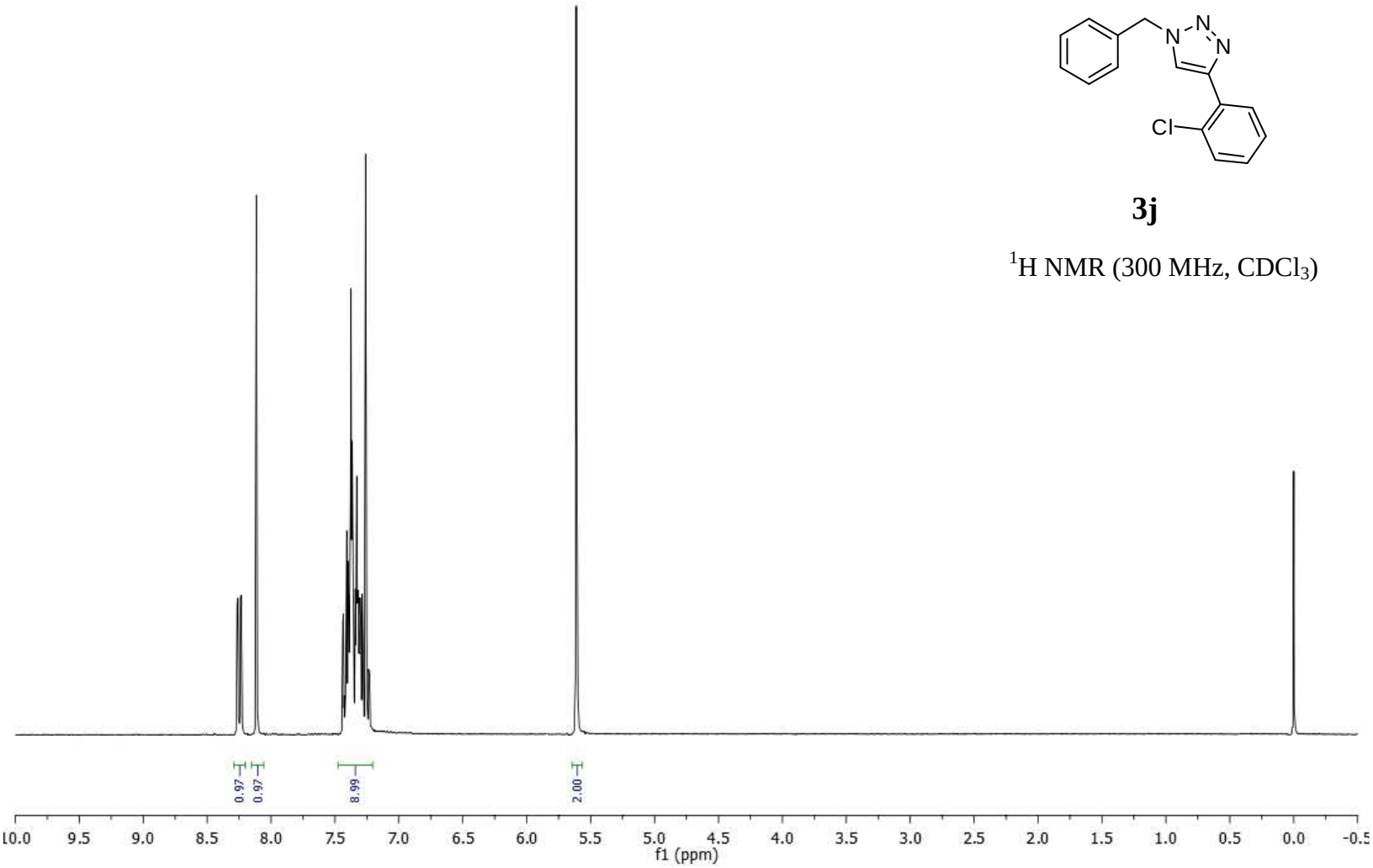

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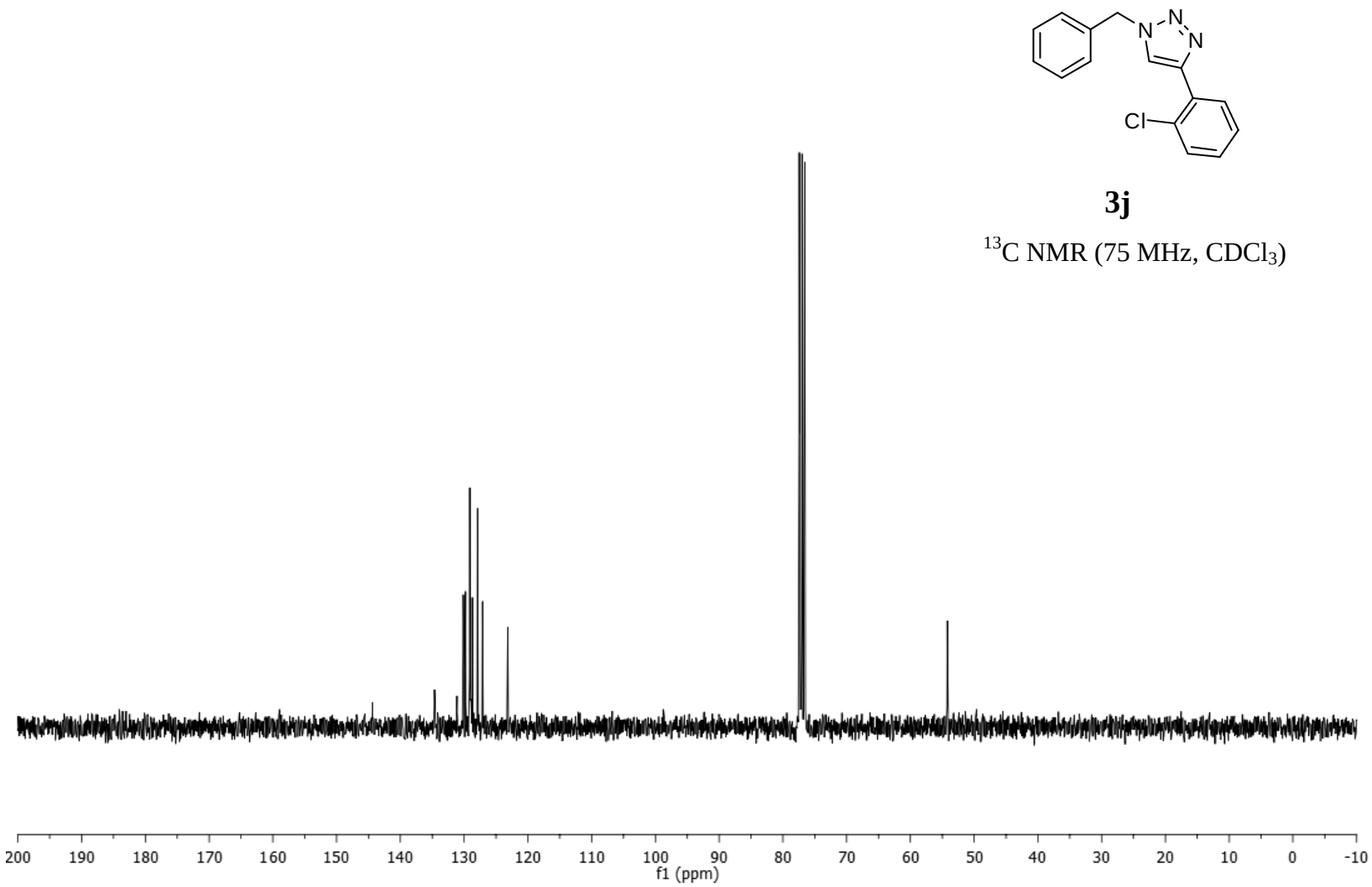

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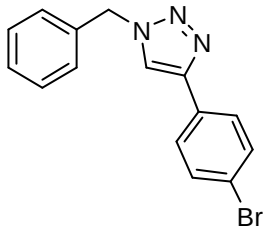
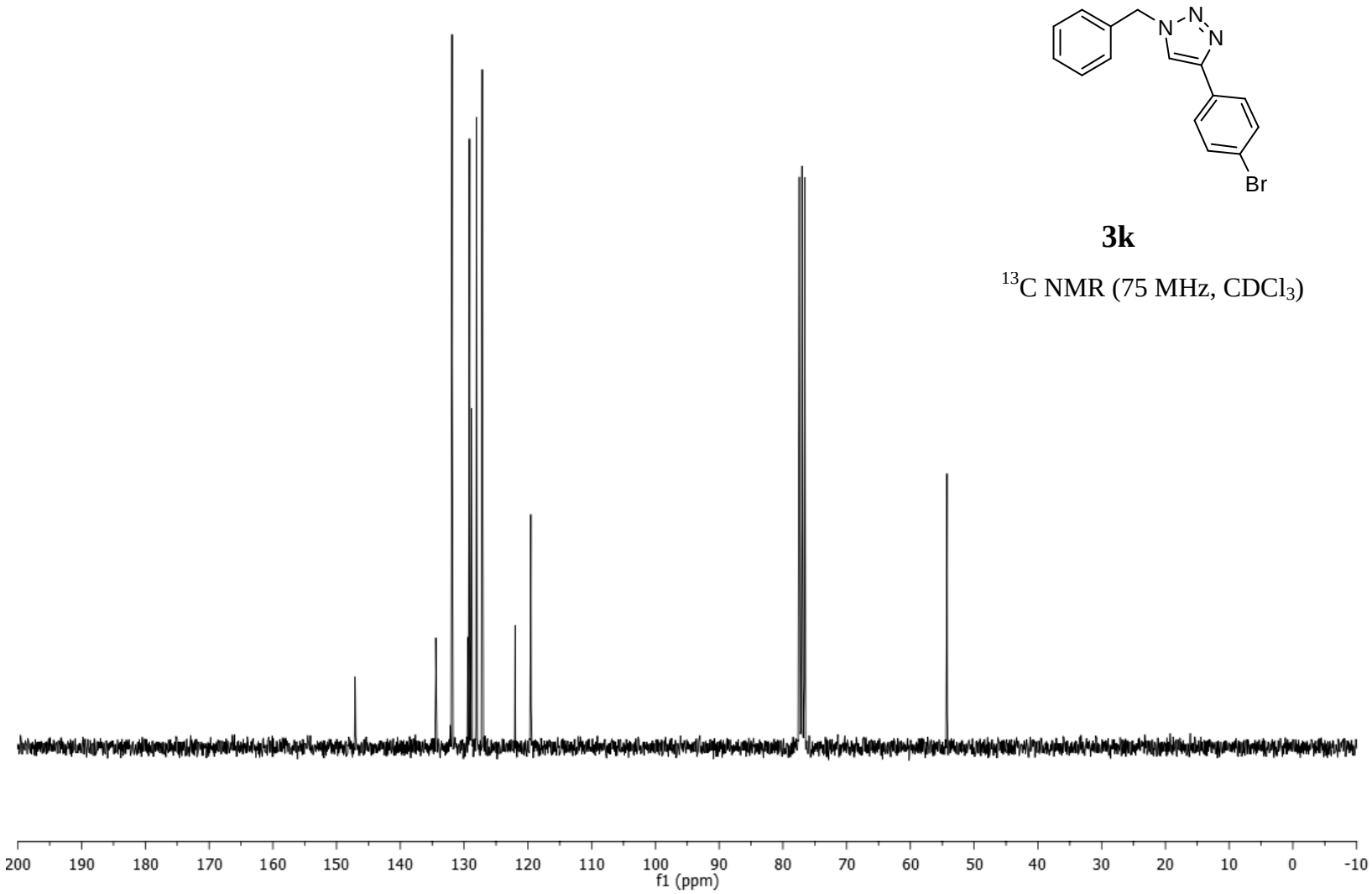


3k

^{1}H NMR (300 MHz, $CDCl_3$)



3k

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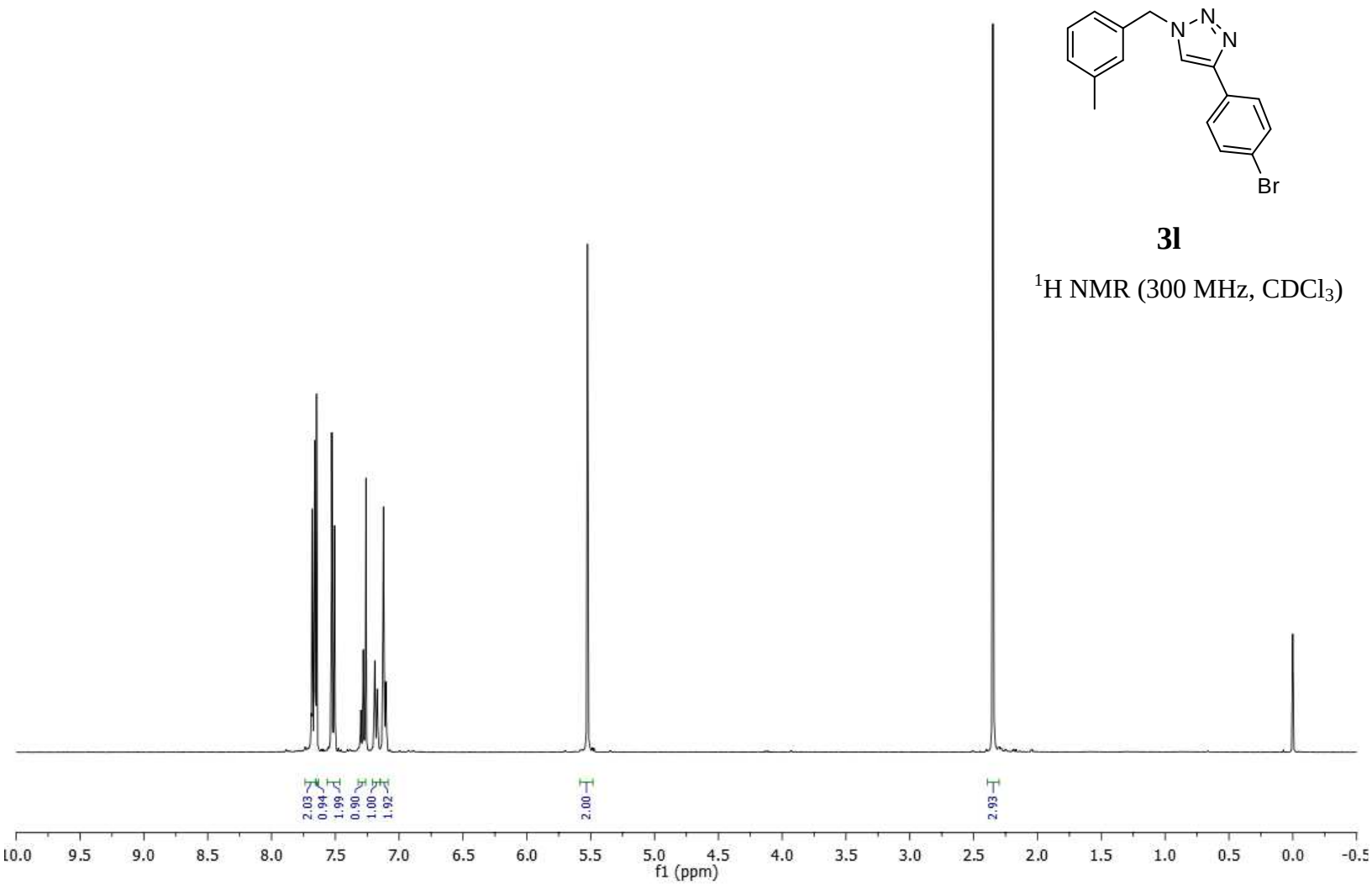

3l

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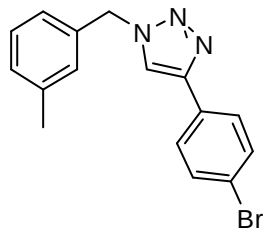

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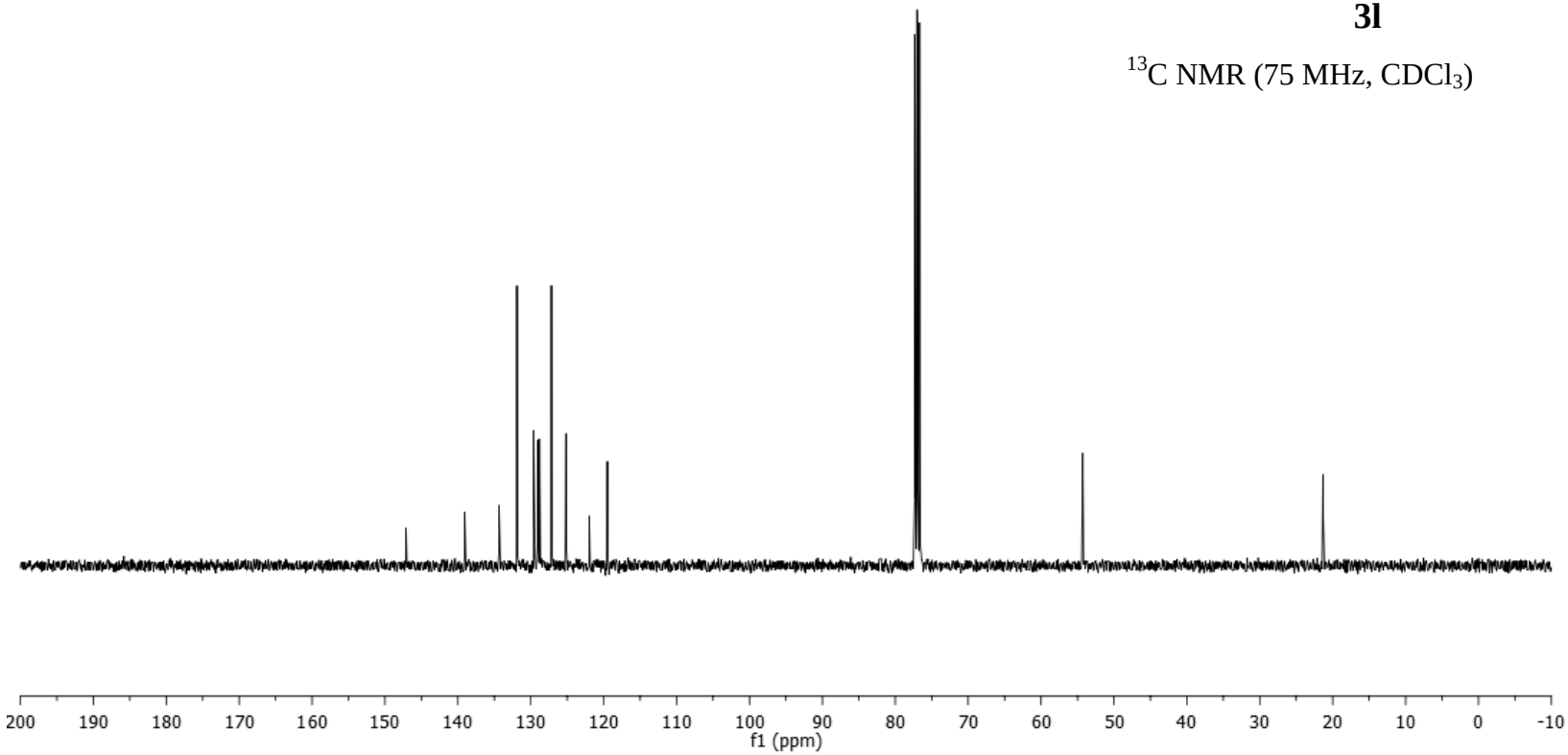

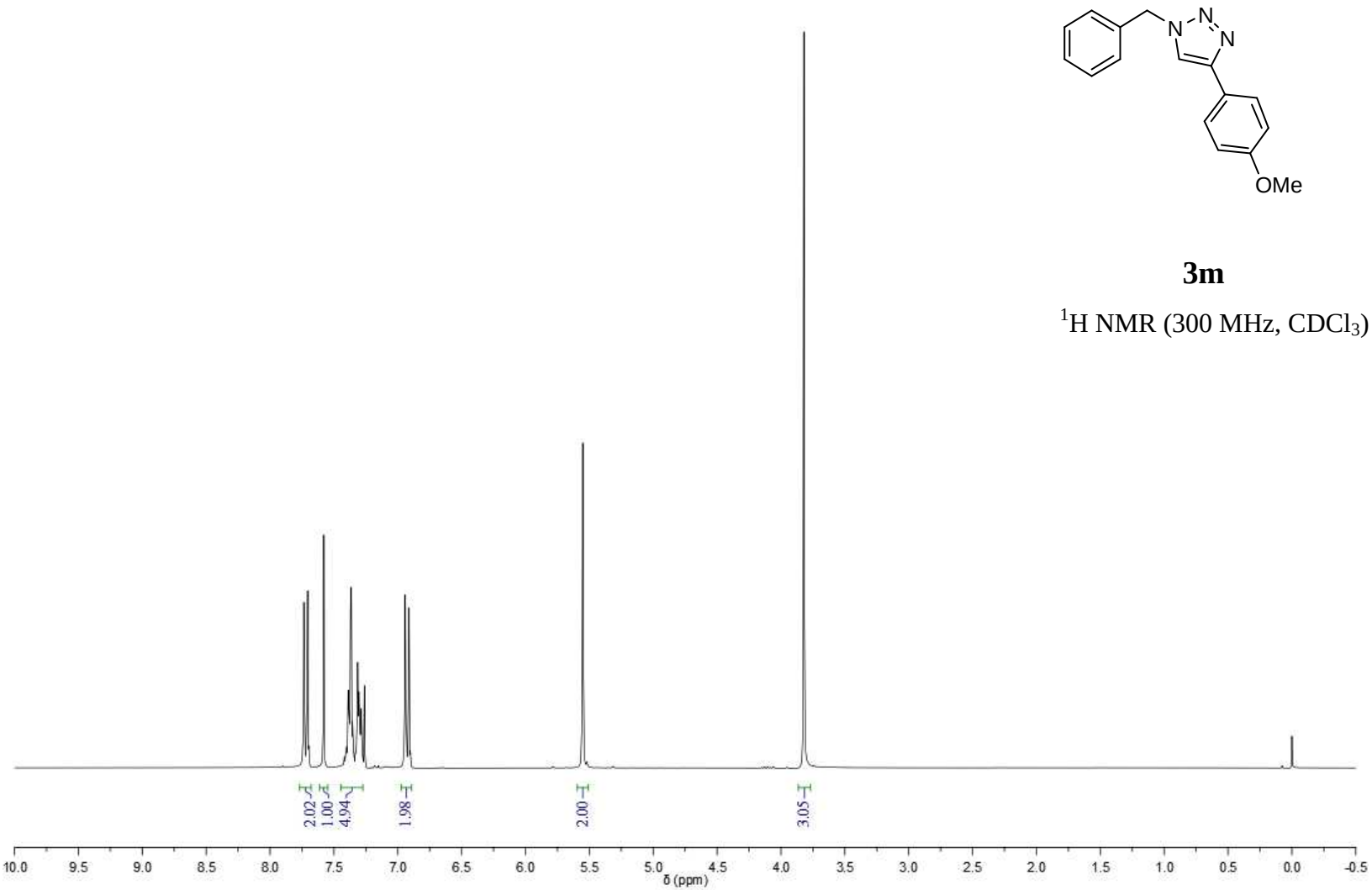

3m

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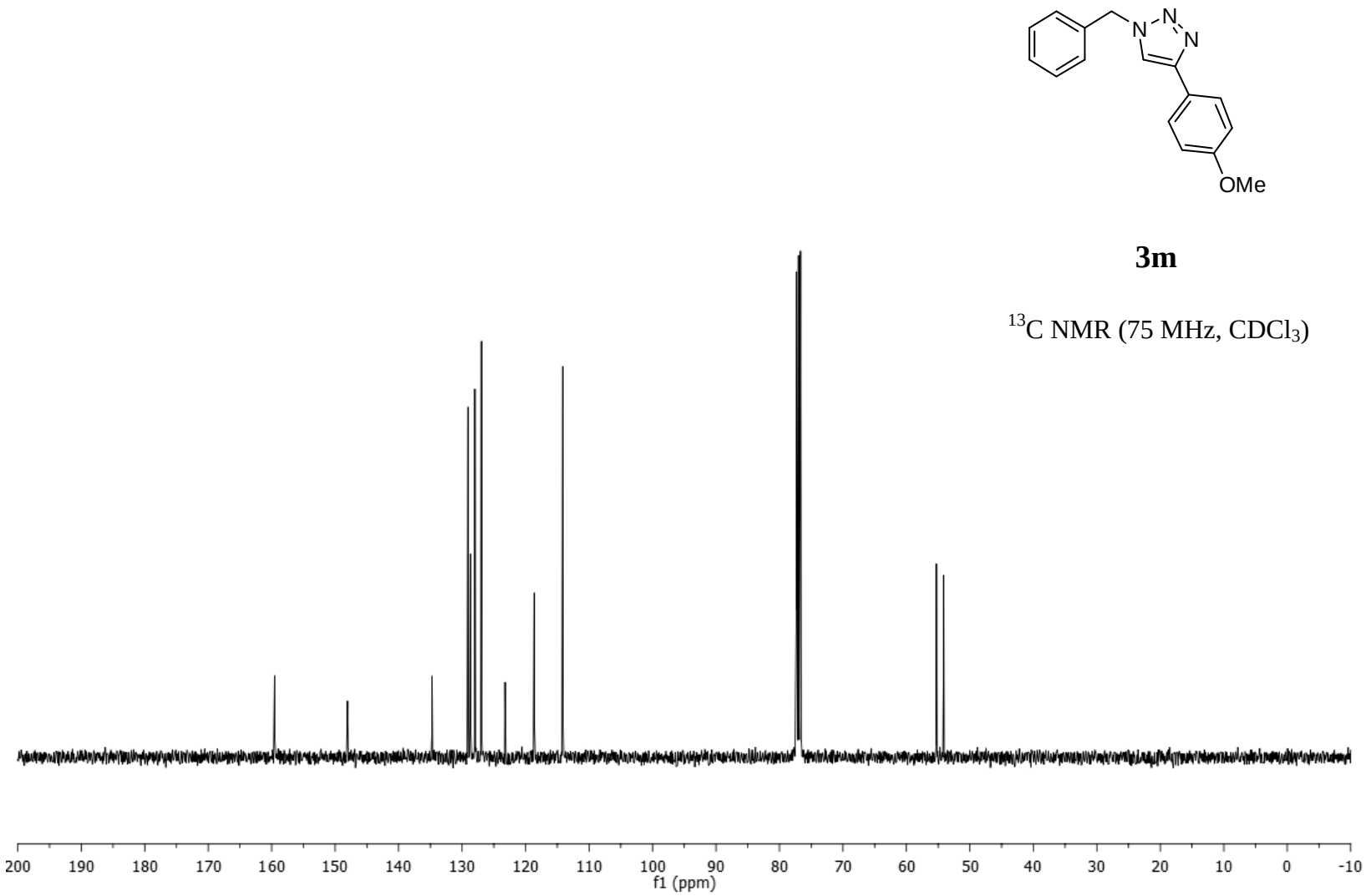

3m

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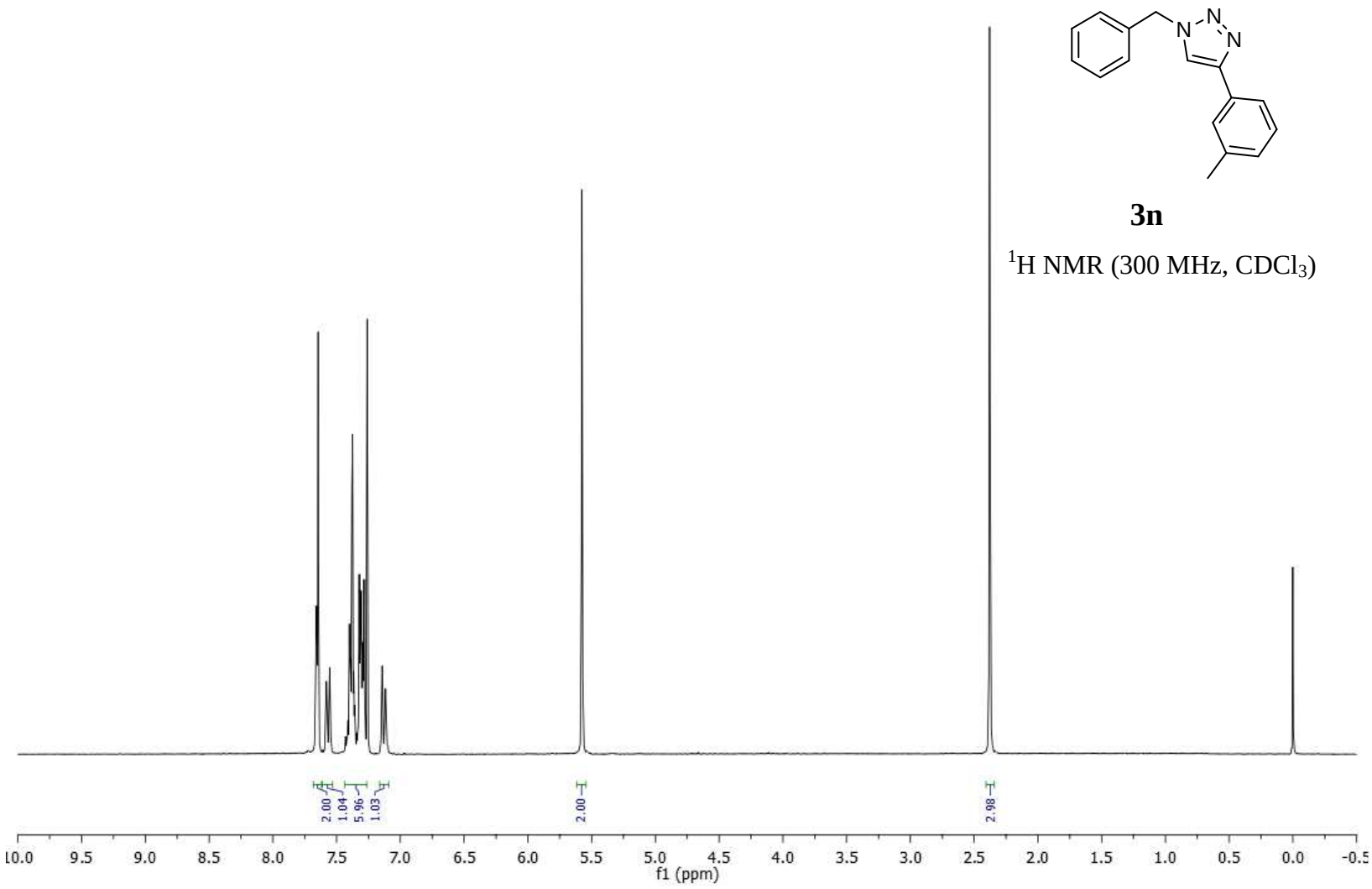

3n

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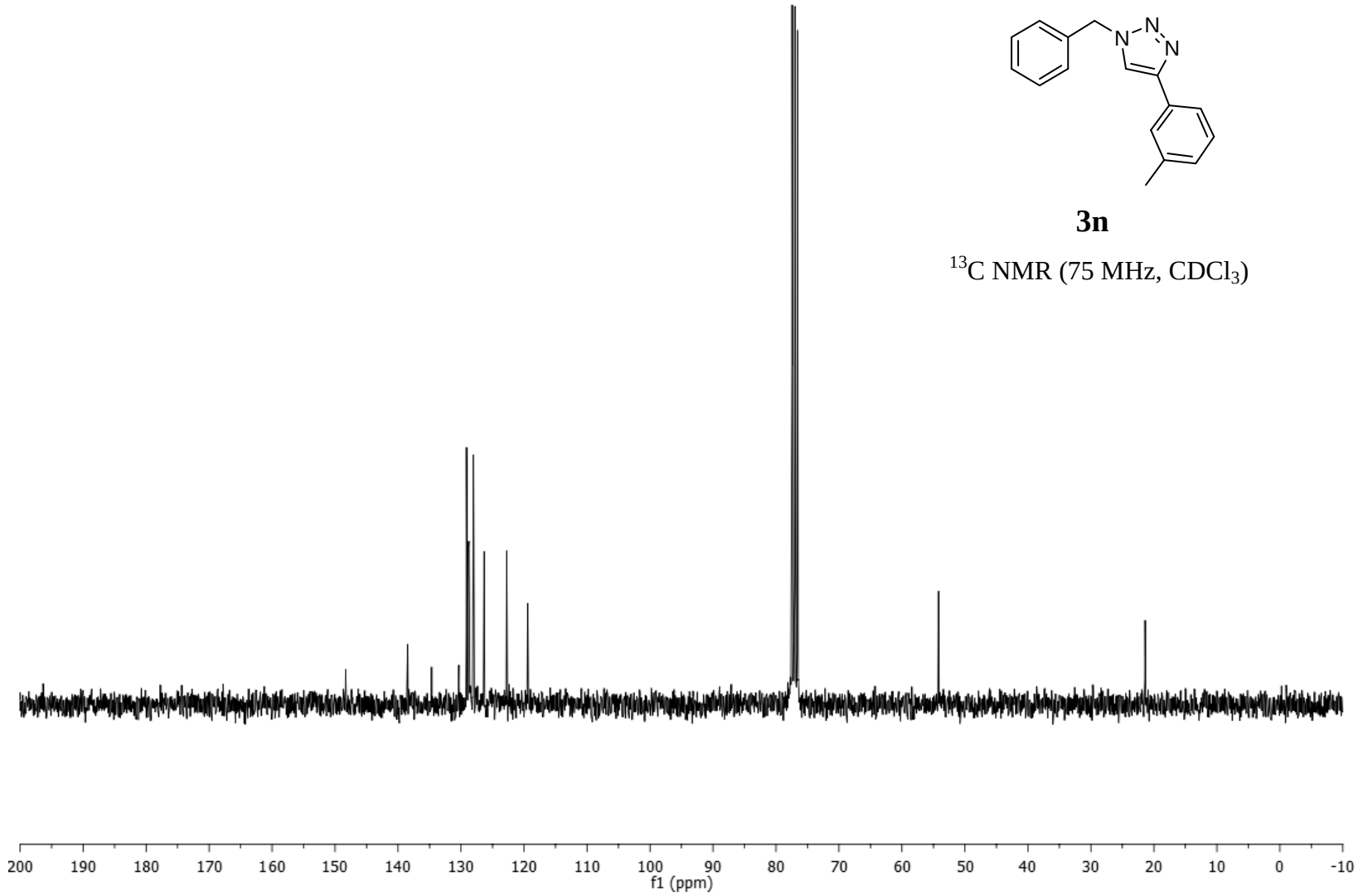
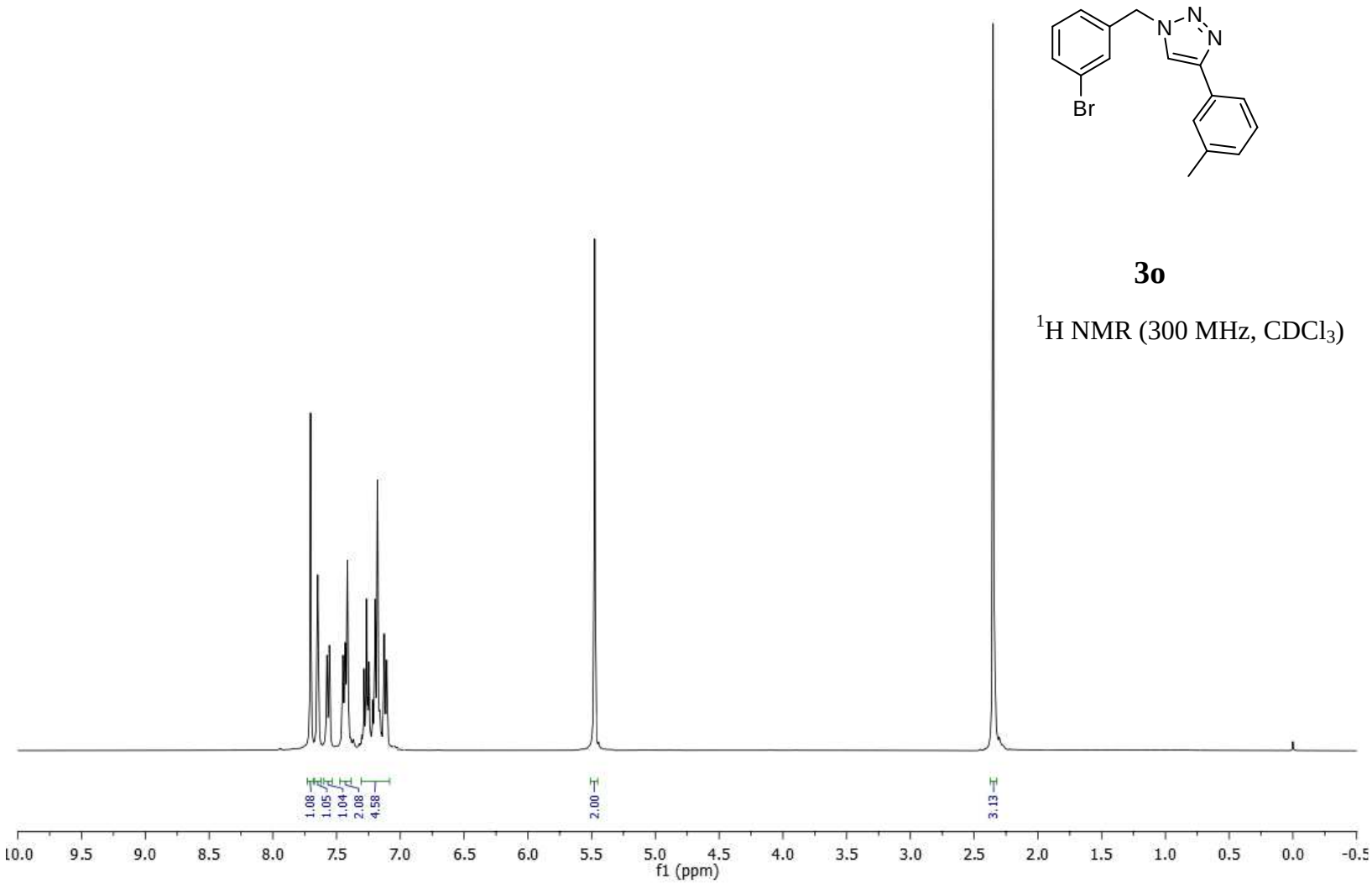


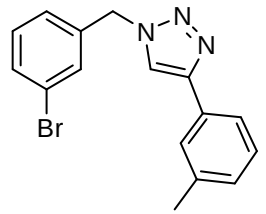
3n

^{13}C NMR (75 MHz, $CDCl_3$)



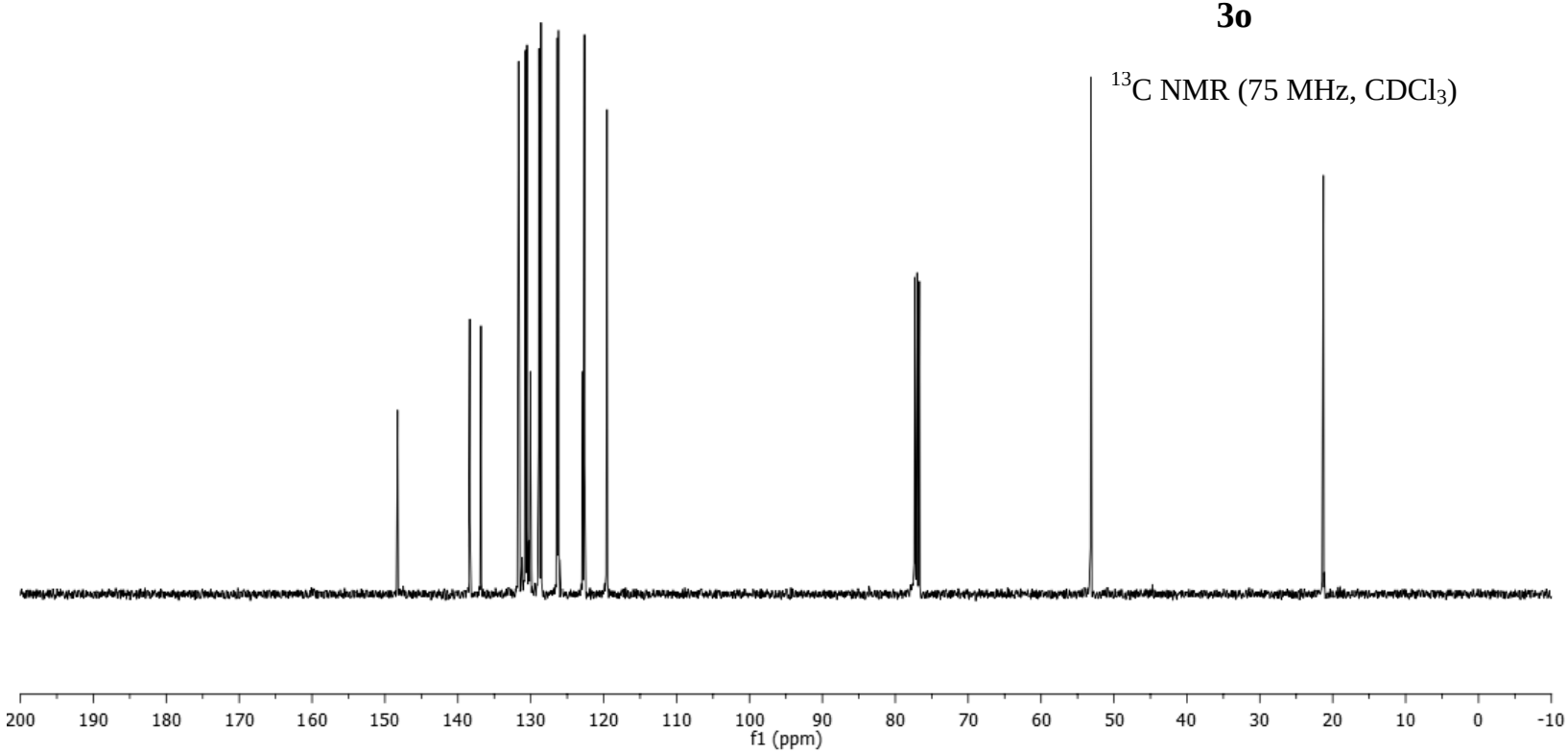
3o

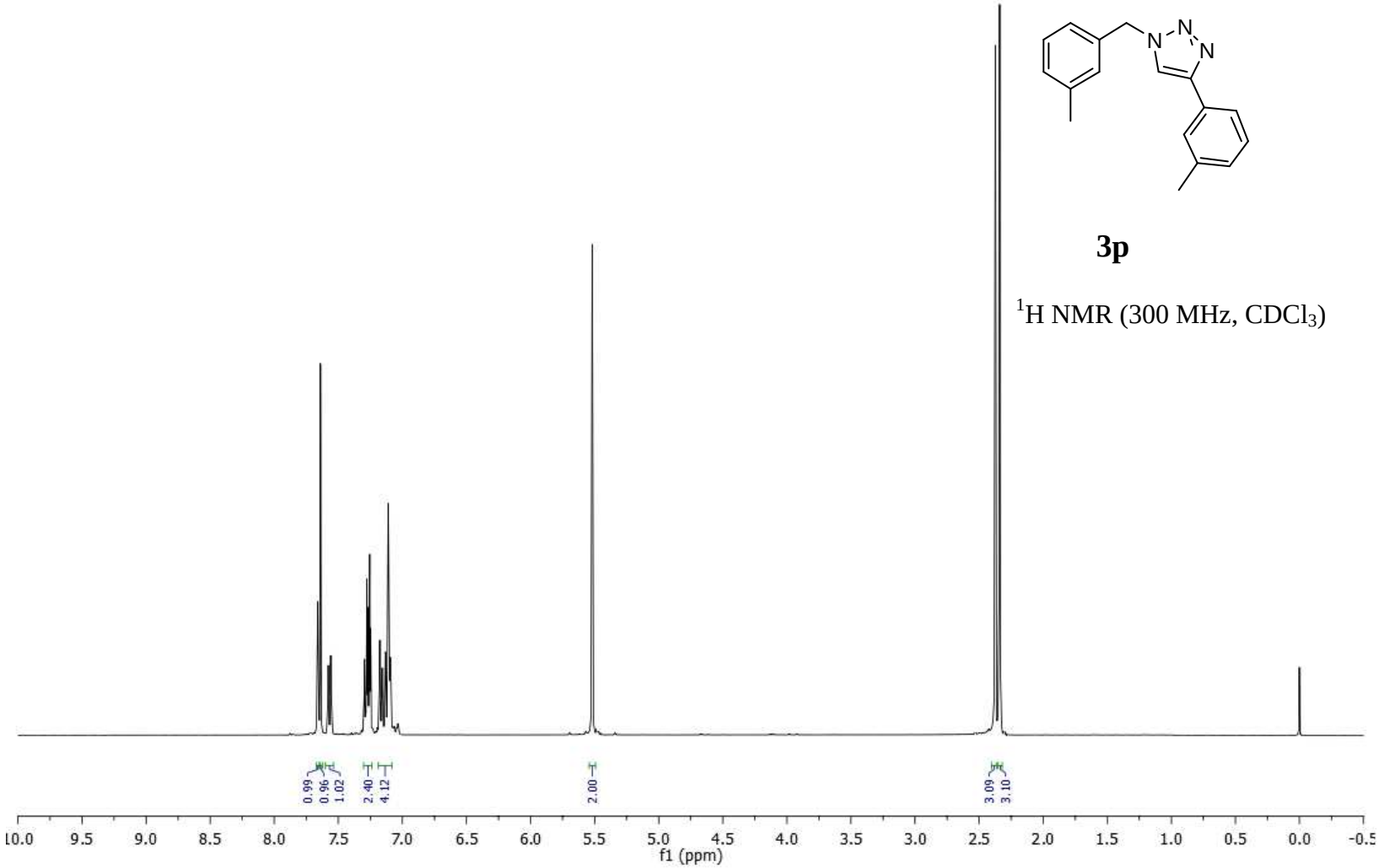
^{1}H NMR (300 MHz, $CDCl_3$)



3o

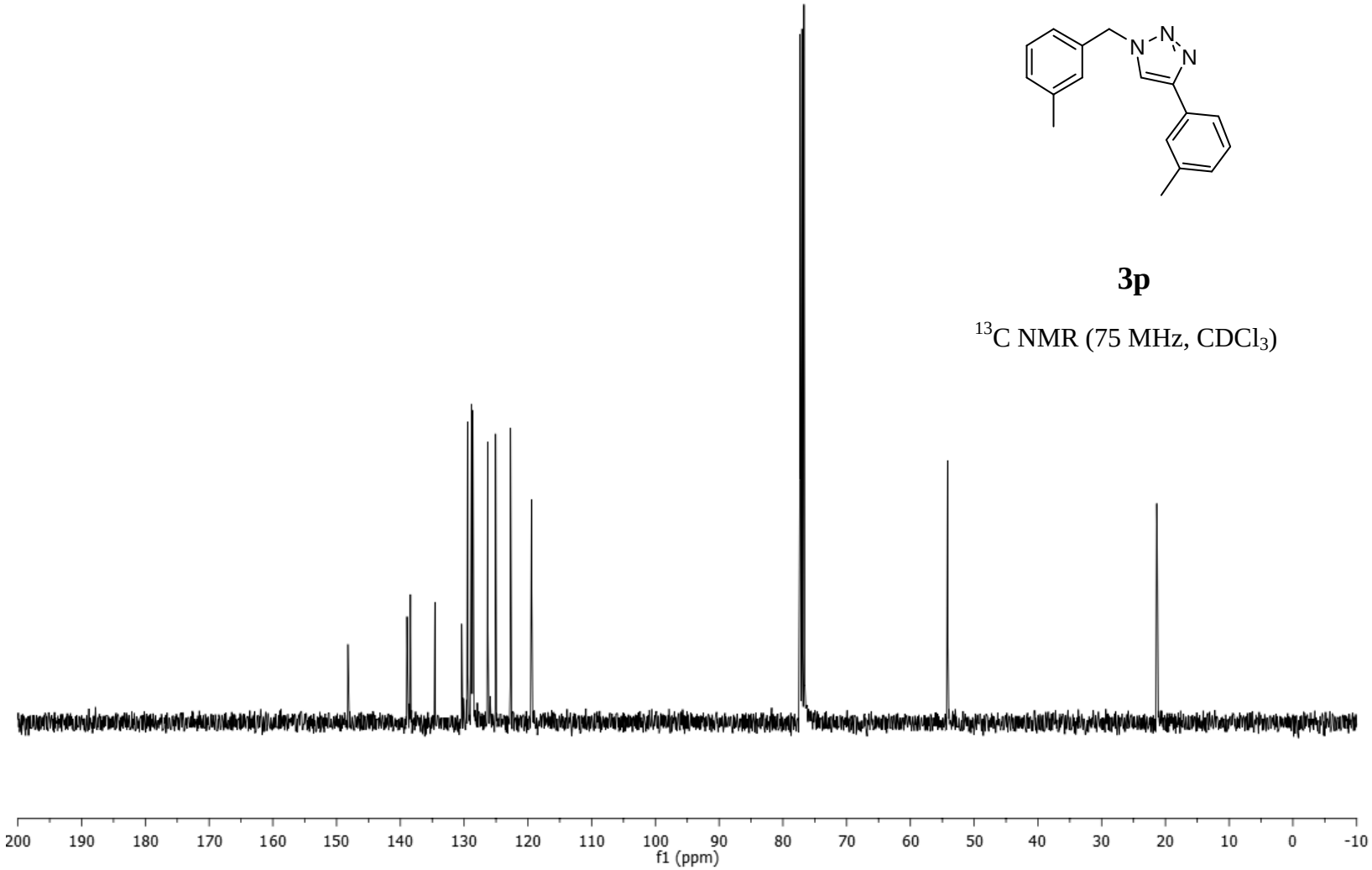
^{13}C NMR (75 MHz, $CDCl_3$)





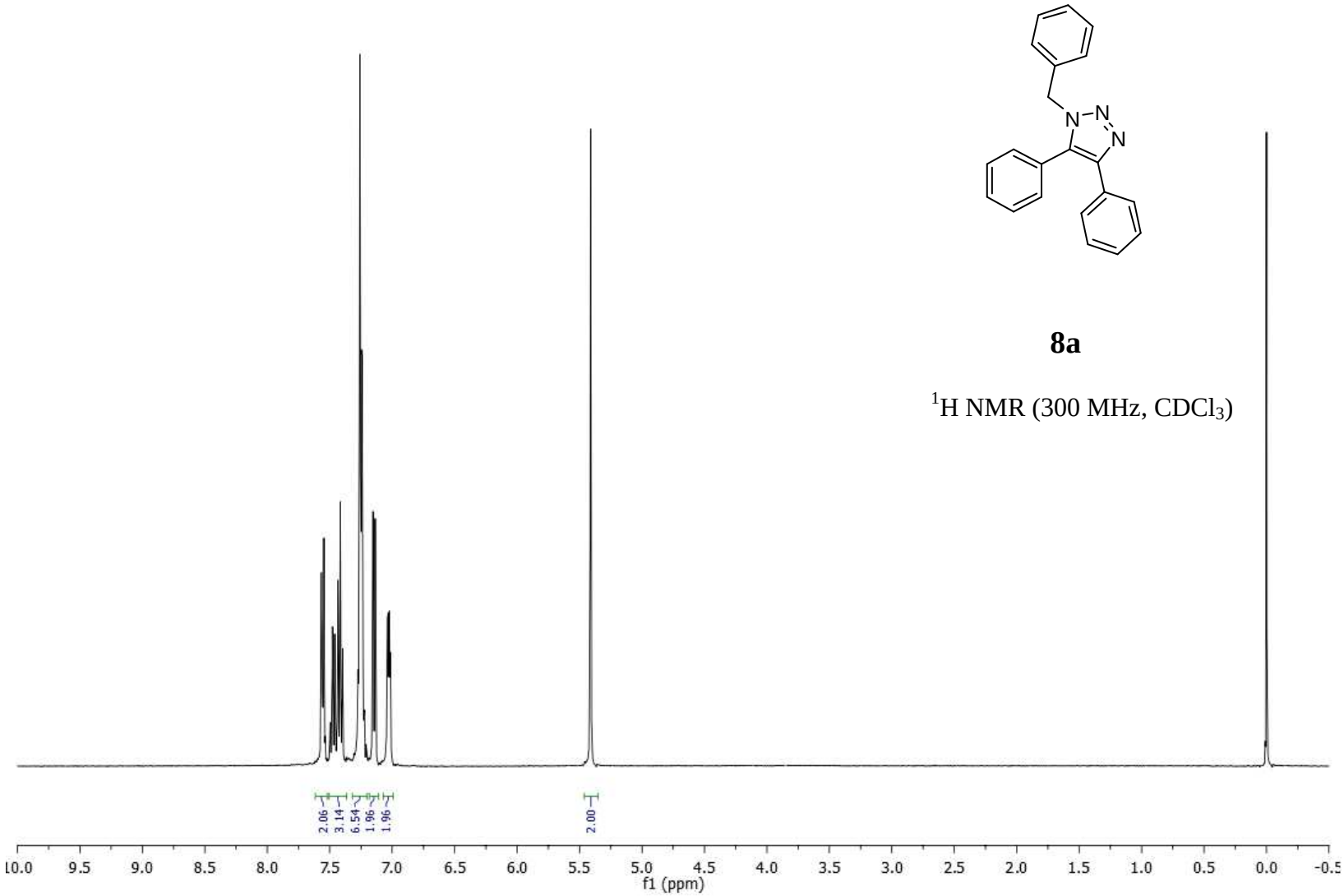
3p

^{1}H NMR (300 MHz, $CDCl_3$)



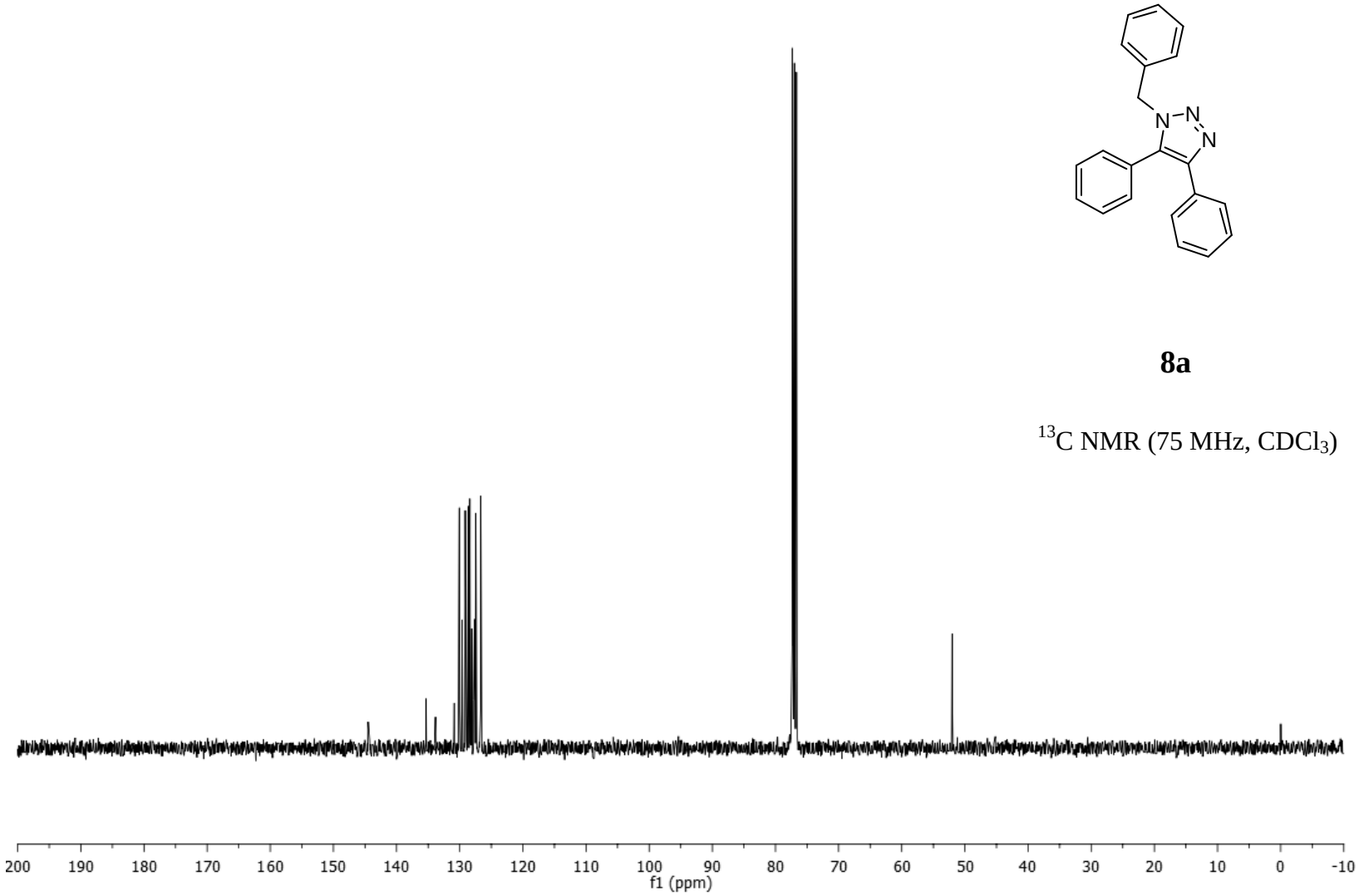
3p

^{13}C NMR (75 MHz, $CDCl_3$)



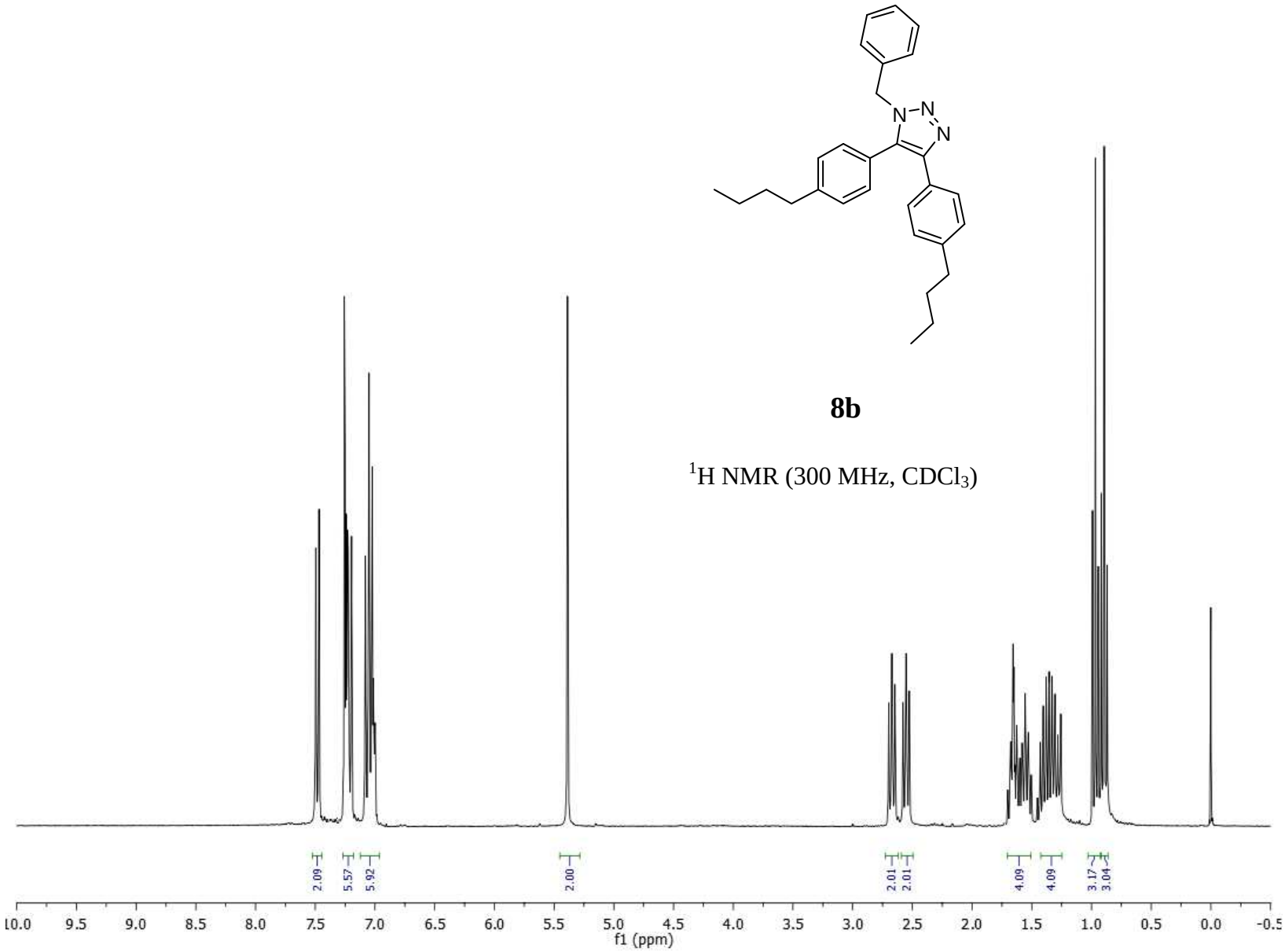
8a

^{1}H NMR (300 MHz, $CDCl_3$)



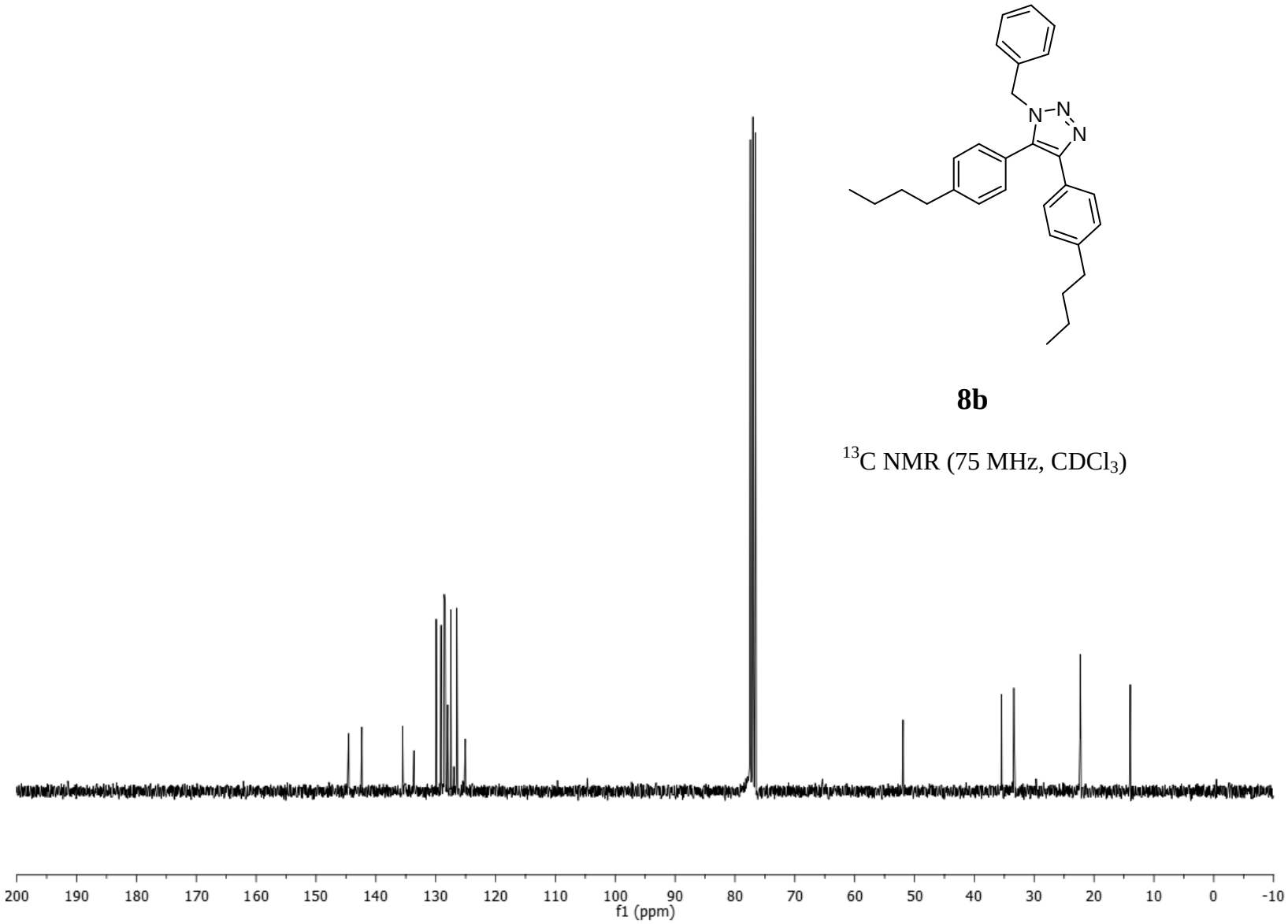
8a

^{13}C NMR (75 MHz, $CDCl_3$)



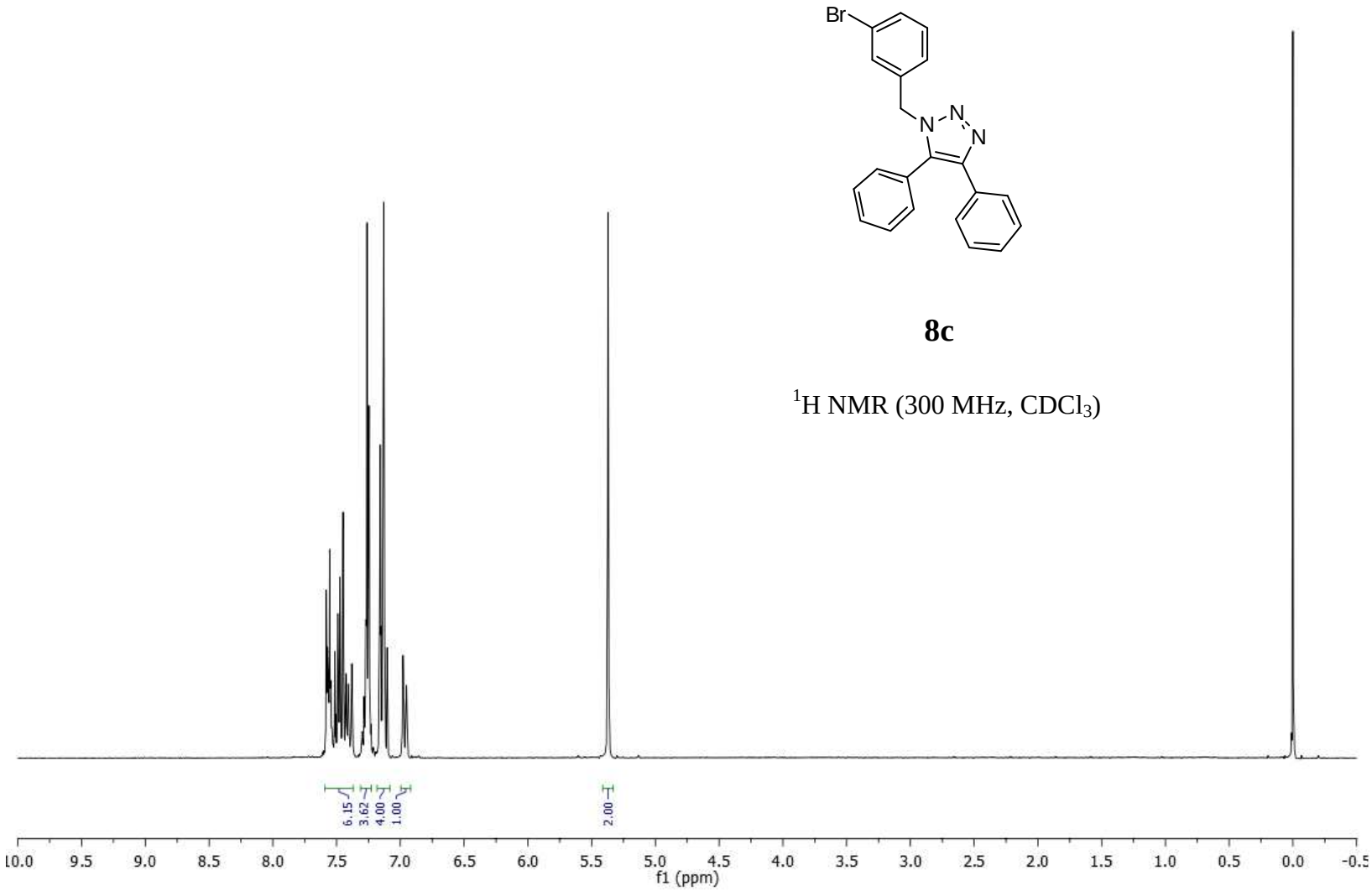
8b

^{1}H NMR (300 MHz, $CDCl_3$)



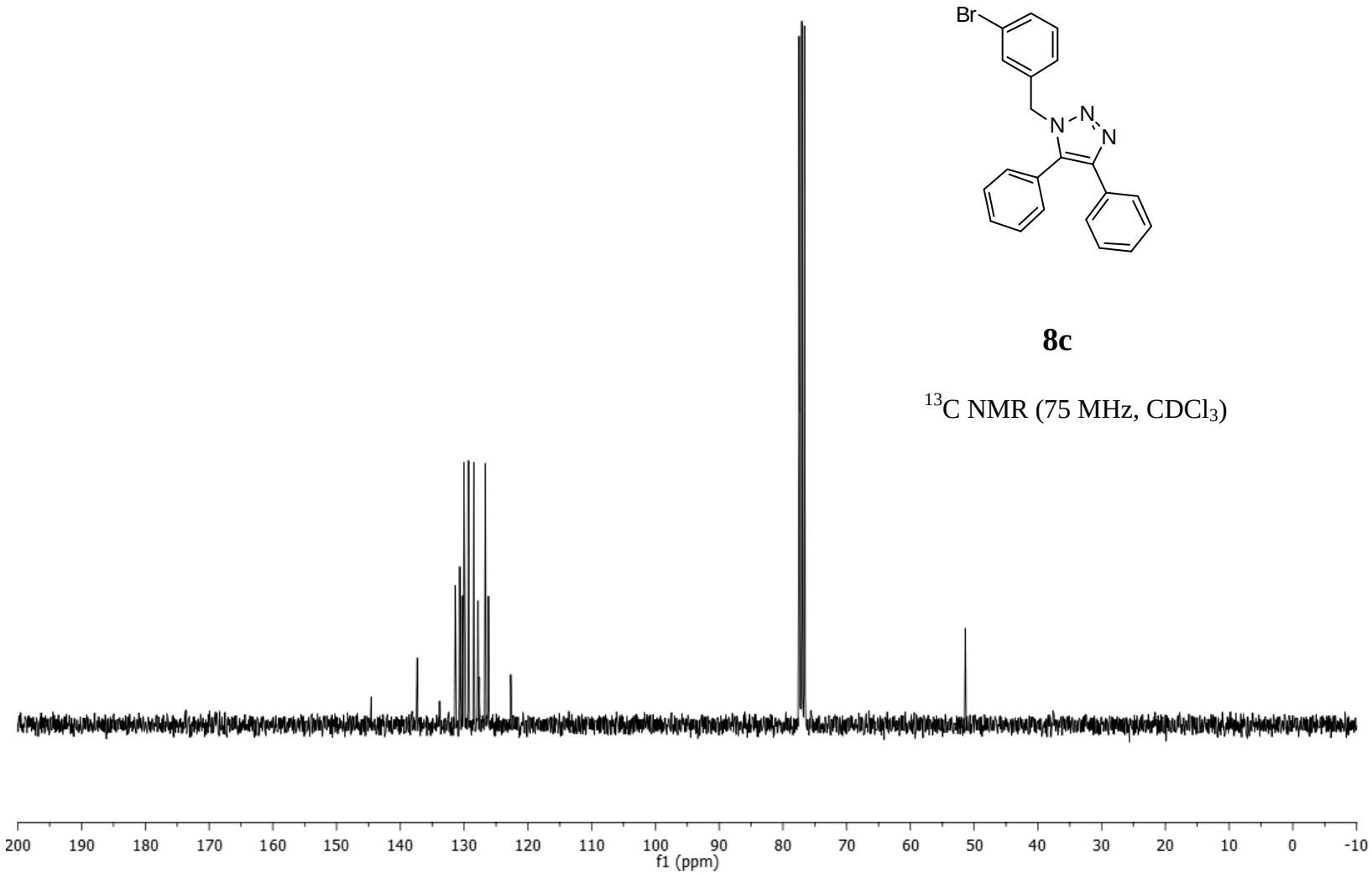
8b

^{13}C NMR (75 MHz, $CDCl_3$)



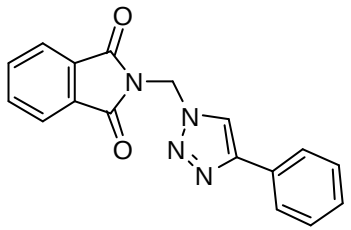
8c

^{1}H NMR (300 MHz, $CDCl_3$)

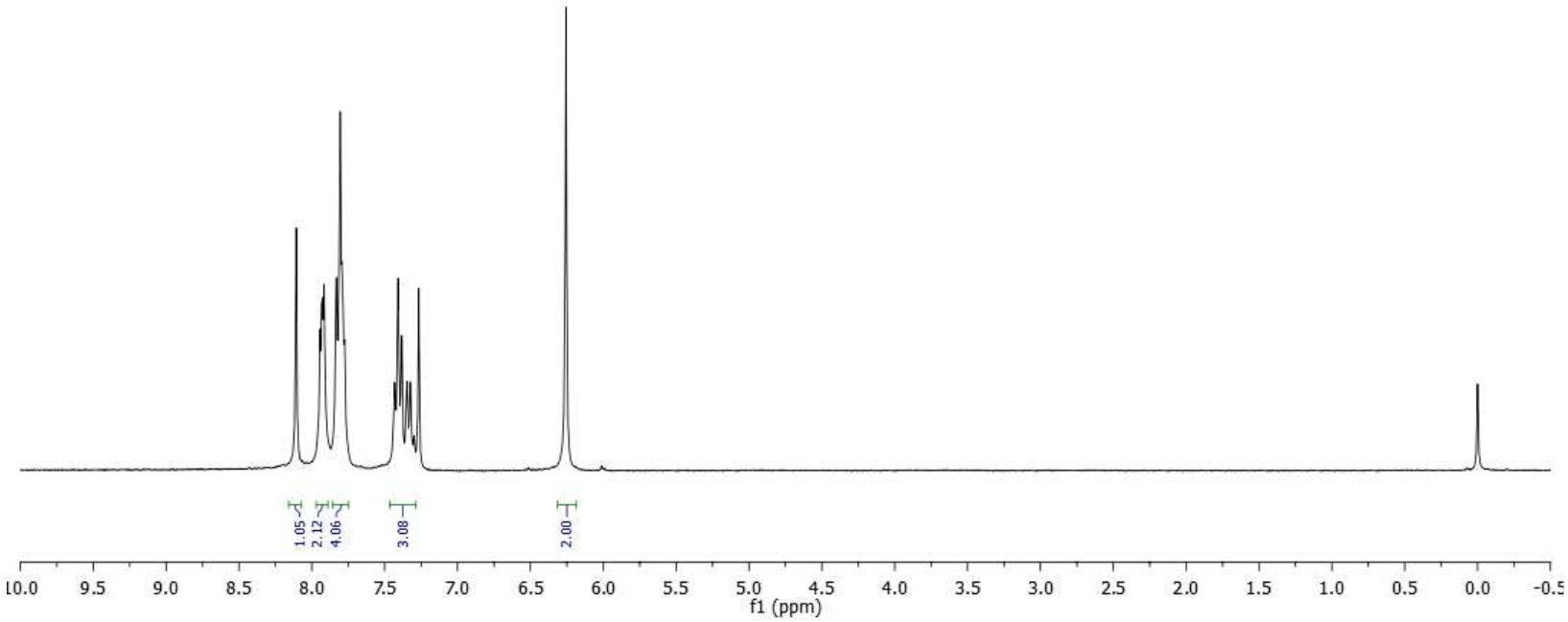


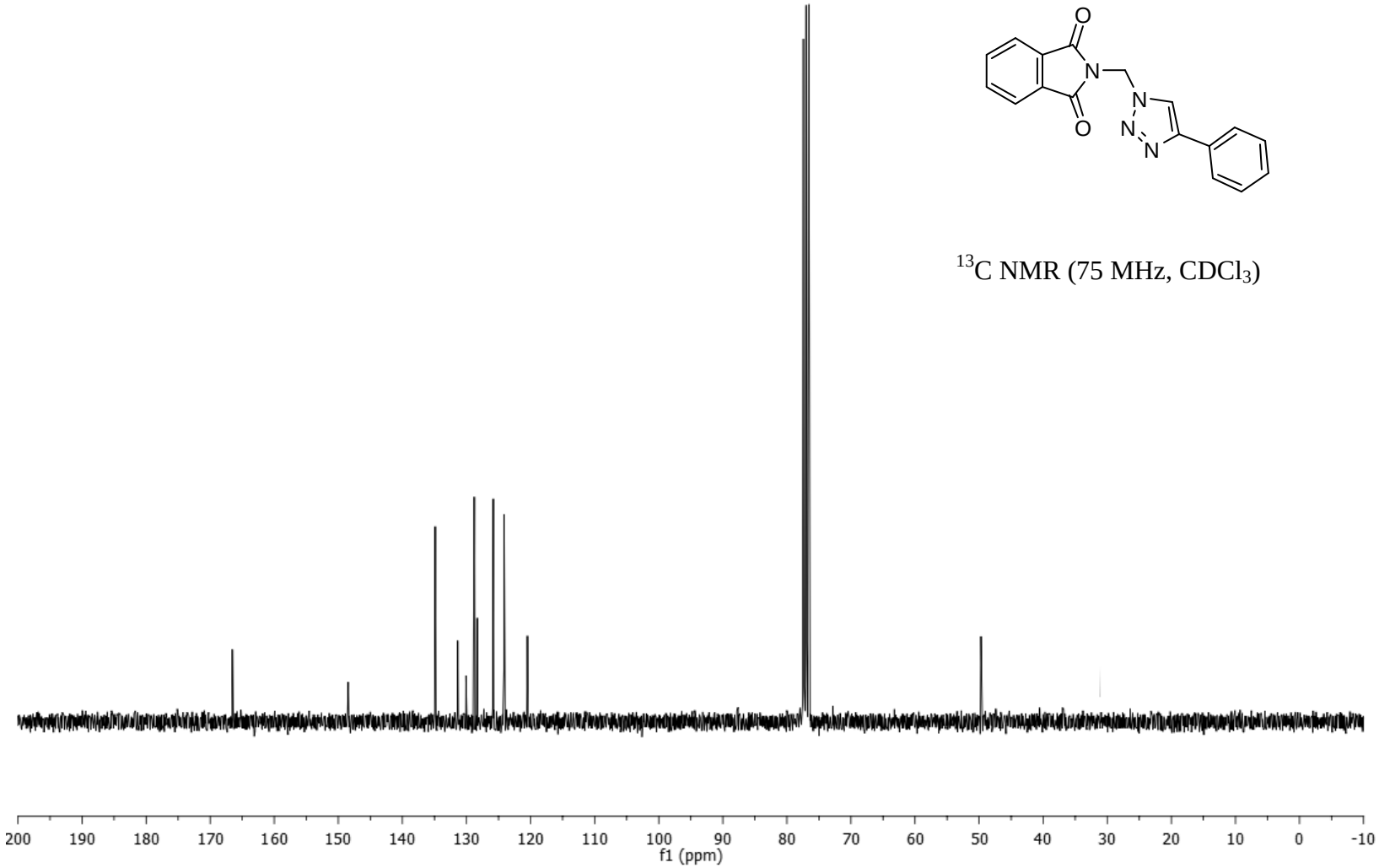
8c

^{13}C NMR (75 MHz, $CDCl_3$)

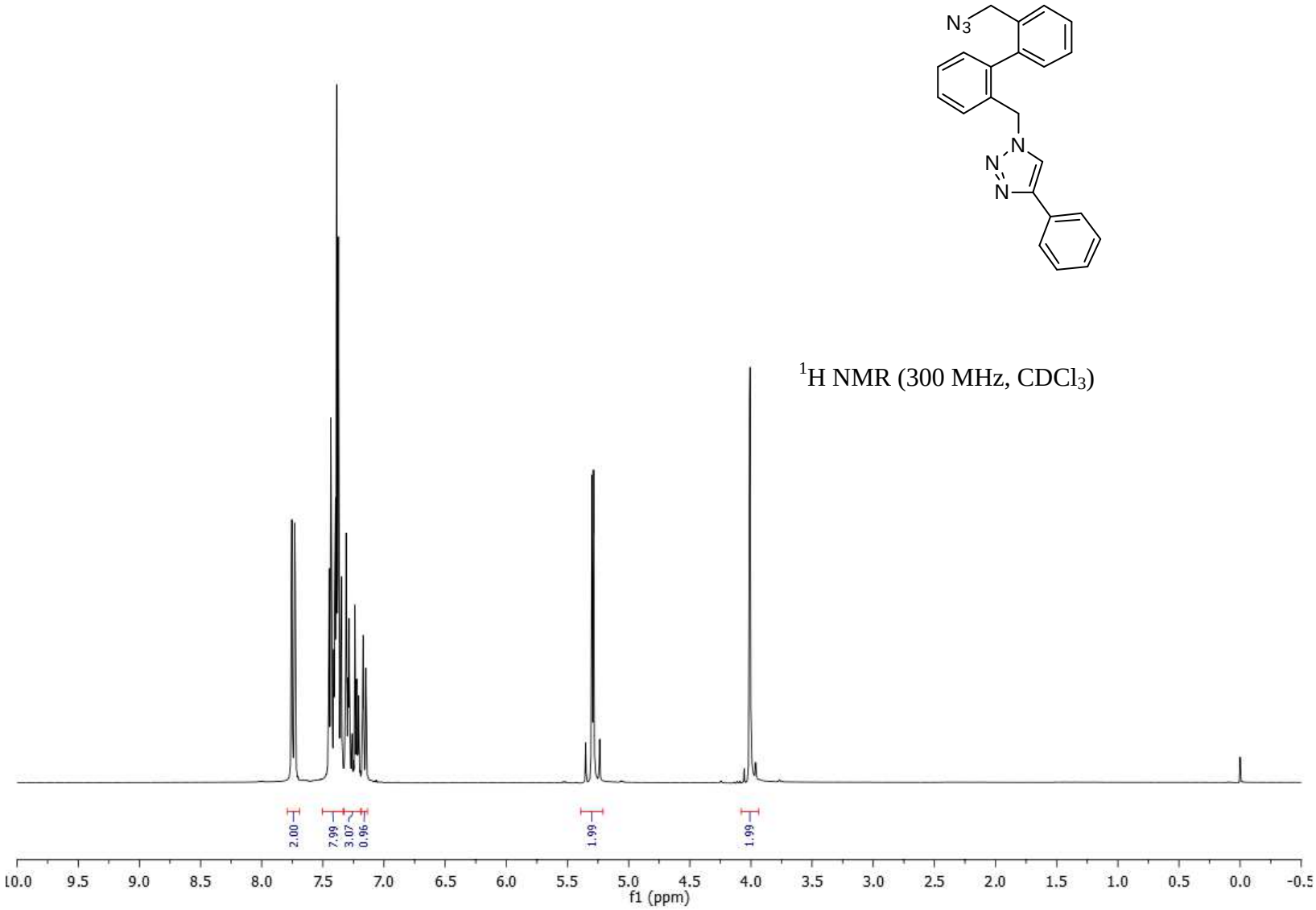


^{1}H NMR (300 MHz, $CDCl_3$)

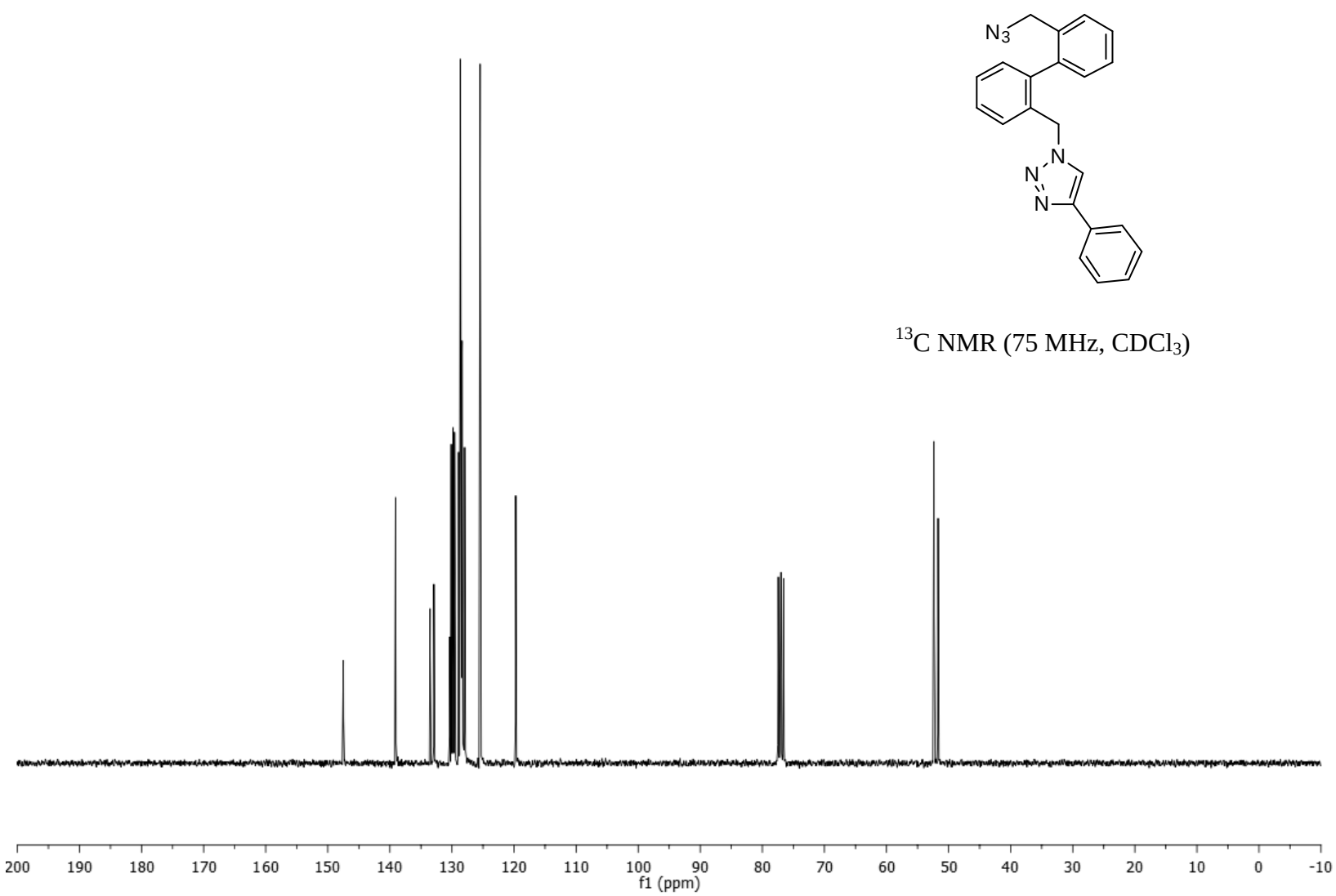




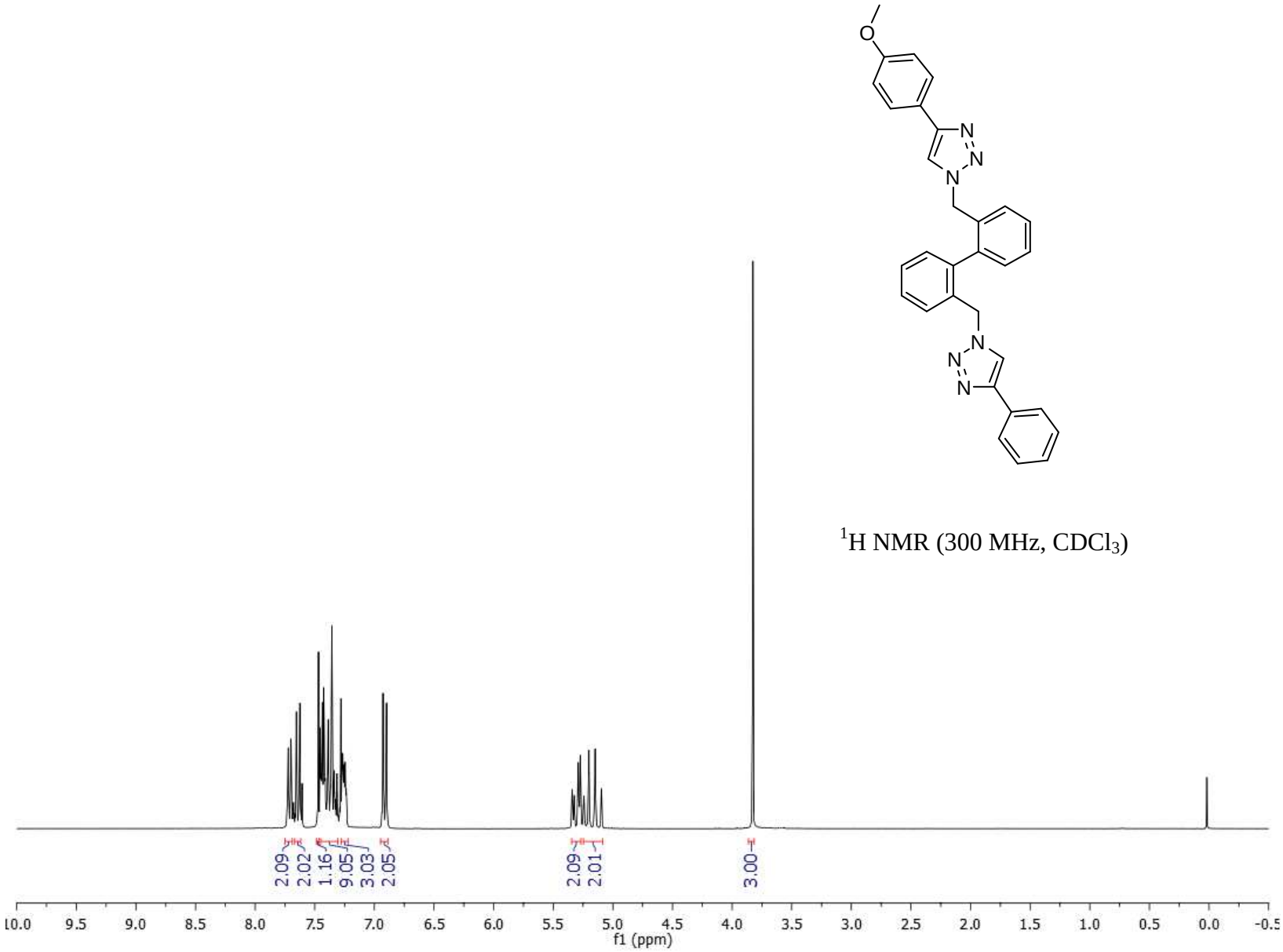
^{13}C NMR (75 MHz, $CDCl_3$)



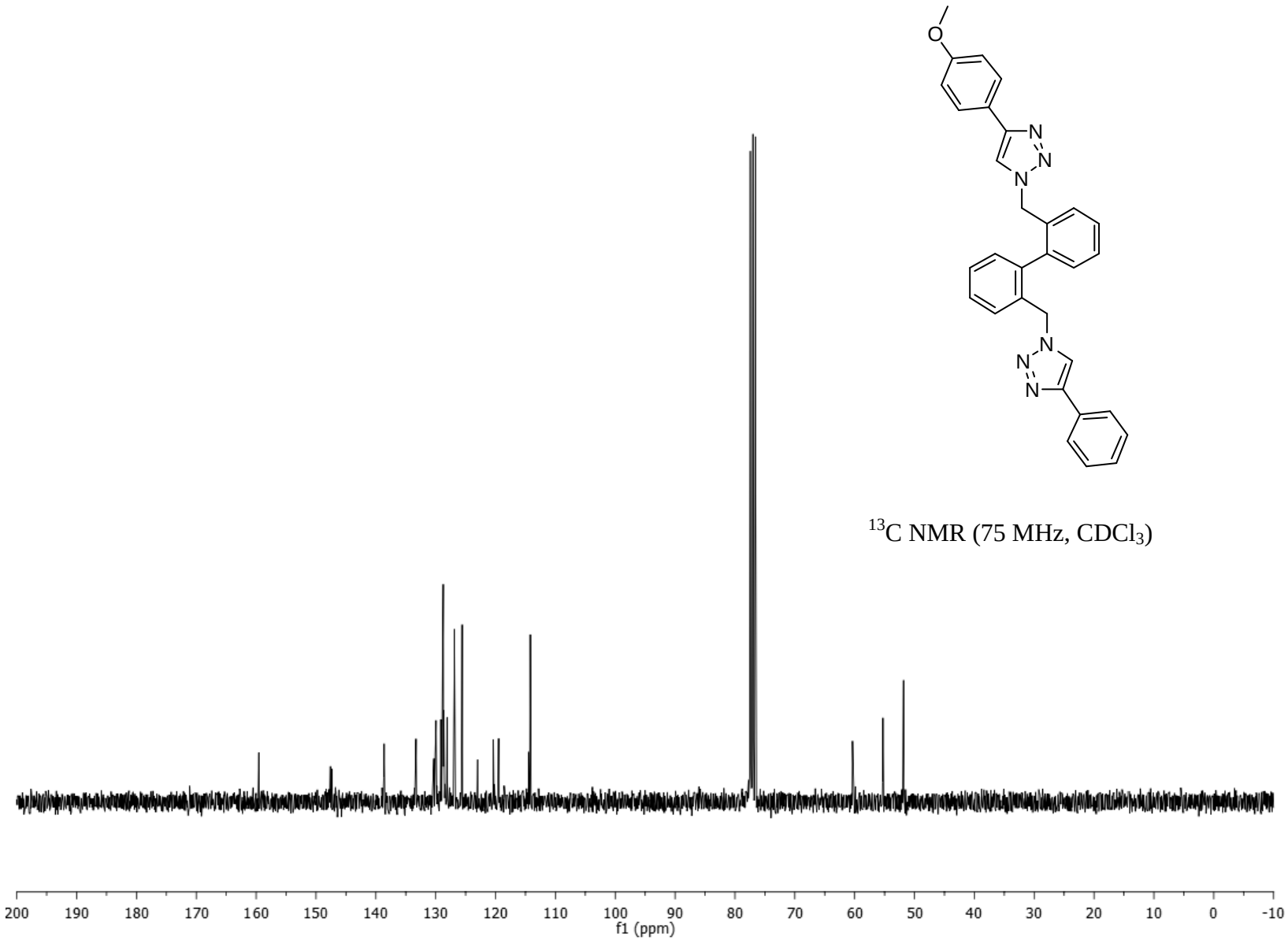
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)