Supporting Information for

Copper-Catalyzed Borylative Cyclization of in situ-Generated *o*-Allenylaryl Nitriles with Bis(pinacolato)diboron

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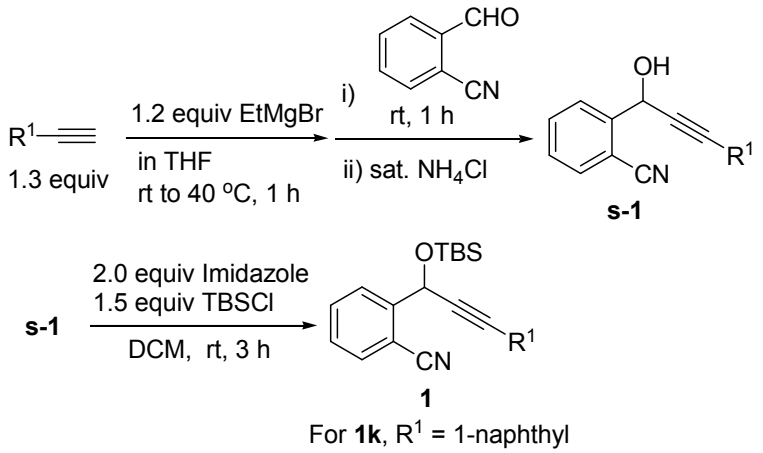
General Methods.

Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). 1,4-Dioxane was distilled from sodium. EtMgBr (3.0 M solution in Et_2O) was purchased from J&K Chemical Company, CuCl and DBU were purchased from Acros Company, dppf was purchased from J&K Chemical Company, ^{t}BuOK and bis(pinacolato)diboron were purchased from TCI Chemical Inc. 2-Cyanobenzaldehyde was purchased from Shanghai Darui Finechemical Co., Ltd. 4-Fluoro-2-formylbenzonitrile was purchased from Bide Pharmatech Ltd. Thiophene-3-carbonitrile was purchased from Energy Chemical Company. Unless noted, all commercial reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% or 1% TMS), C_6D_6 (containing 0.03% TMS) solutions or at 80 ^{o}C in DMSO-d_6 (containing 0.03% TMS) solution on Varian or Agilent XL-400 MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethylsilane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm; C_6D_6: 7.16 ppm; DMSO-d_6: 2.50 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm), C_6D_6 (128.06 ppm) or DMSO-d_6 (39.52 ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT, Agilent Technologies 6224 TOF LC/MS. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. IR spectra were obtained by using a Nicolet iS10 spectrometer. Single crystal X-ray diffraction data was collected on a Bruker SMART diffractometer at 293(2) K (for **2t'**and **5**) or Bruker APEX-II CCD diffractometer at 130 K (for **2k**).

Typical procedure for the synthesis of

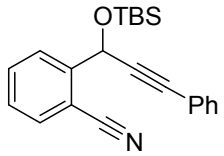
2-(1-((*tert*-butyldimethylsilyl)oxy)-3-(naphthalen-1-yl)prop-2-yn-1-yl)benzonitrile (1k).[1]



To a solution of 1-ethynylnaphthalene (989 mg, 6.5 mmol) in THF (20 mL) was added dropwise EtMgBr (2.0 mL, 3.0 M solution in Et_2O, 6.0 mmol) at room temperature under argon. Then the solution was warmed up to 40 °C and stirred for 1 h. After cooling to room temperature, 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added and the reaction mixture was stirred until the reaction was complete as monitored by TLC (1 h). The resulting reaction mixture was quenched with saturated NH_4Cl solution, and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the alcohol **s-1** as a light yellow oil, which was used directly without further purification for the next step.

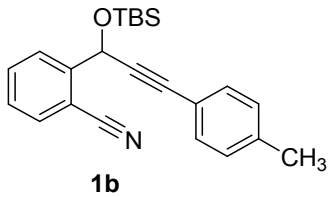
To a solution of the above crude alcohol **s-1** in DCM (15 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol) under air. The reaction mixture was then stirred at room temperature for 3 h. Then the resulting mixture was quenched with saturated ammonium chloride solution and extracted with dichloromethane, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to afford **1k** in 65% overall yield (1.283 g) as a yellow sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 3H), 0.31 (s, 3H), 0.98 (s, 9H), 6.13 (s, 1H), 7.38-7.43 (m, 2H), 7.48-7.57 (m, 2H), 7.64-7.70 (m, 3H), 7.80-7.83 (m, 2H), 7.96 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.92, -4.37, 18.28, 25.76, 63.65, 84.87, 93.07, 110.41,

117.28, 119.95, 125.09, 126.05, 126.41, 126.85, 127.23, 128.20, 128.27, 129.05, 130.65, 132.99, 133.04, 133.18, 133.21, 145.48. IR (neat): 3056, 2956, 2928, 2856, 2226, 1471, 1394, 1253, 1109, 1069, 839 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{31}N_2OSi$ $[M+NH_4]^+$: 415.2200, found 415.2202.



1a

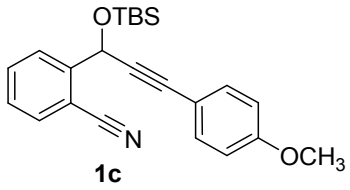
2-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylprop-2-ynyl)benzonitrile (1a). First step: ethynylbenzene (4.3 mL, 39.0 mmol) and EtMgBr (12 mL, 3.0 M solution in Et_2O, 36.0 mmol) in THF (70 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (3.93 g, 30.0 mmol) was added, the reaction mixture was stirred at room temperature for 1.5 h. Second step: To a solution of the above crude alcohol in DCM (60 mL) were added imidazole (4.08 g, 60.0 mmol) and TBSCl (6.78 g, 45 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60/1) afforded the desired product in 68% overall yield (7.14 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 3H), 0.35 (s, 3H), 1.03 (s, 9H), 6.07 (s, 1H), 7.31-7.33 (m, 3H), 7.37-7.41 (m, 1H), 7.48-7.50 (m, 2H), 7.62-7.67 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ -5.09, -4.54, 18.06, 25.60, 63.34, 86.62, 88.04, 110.35, 116.97, 122.17, 127.03, 128.09, 128.10, 128.44, 131.38, 132.76, 132.86, 145.04. HRMS (ESI) calcd for $C_{22}H_{29}N_2OSi$ $[M+NH_4]^+$: 365.2044, found 365.2044. The spectroscopic data is in agreement with that previously reported.[1]



1b

2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(*p*-tolyl)prop-2-yn-1-yl)benzonitrile (1b). First step: 1-ethynyl-4-methylbenzene (755 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution

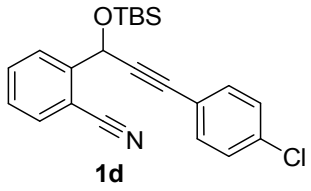
in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (10 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 70/1 to 50/1) afforded the desired product in 89% overall yield (1.61 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 3H), 0.32 (s, 3H), 0.99 (s, 9H), 2.35 (s, 3H), 6.02 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.35-7.42 (m, 3H), 7.62-7.67 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.00, -4.44, 18.19, 21.38, 25.71, 63.44, 86.88, 87.44, 110.42, 117.15, 119.19, 127.17, 128.11, 128.94, 131.42, 132.86 132.97, 138.65, 145.33. HRMS (ESI) calcd for $C_{23}H_{31}N_2OSi$ $[M+NH_4]^+$: 379.2200, found 379.2201. The spectroscopic data is in agreement with that previously reported.[2]



1c

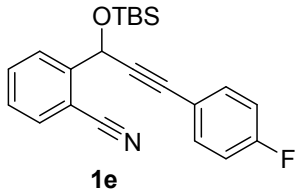
2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)prop-2-yn-1-yl)benzonitrile (1c). First step: 1-ethynyl-4-methoxybenzene (1.72 g, 13.0 mmol) and EtMgBr (4 mL, 3.0 M solution in Et_2O, 12.0 mmol) in THF (25 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (1.31 g, 10.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 54% overall yield (2.04 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.29 (s, 3H), 0.96 (s, 9H), 3.69 (s, 3H), 6.00 (s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 7.31-7.38 (m, 3H), 7.55-7.59 (m, 2H), 7.87 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.19, -4.63, 17.96, 25.51, 54.80, 63.33, 86.56, 86.63, 110.24, 113.65, 114.01, 116.91, 126.93, 127.95, 132.64, 132.74, 145.07, 159.59. One carbon is overlapped with other signals. HRMS (ESI) calcd for

$C_{23}H_{31}N_2O_2Si$ $[M+NH_4]^+$: 395.2149, found 395.2151.



1d

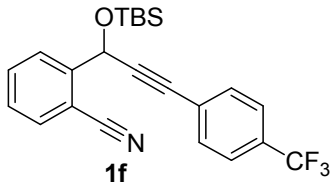
2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(4-chlorophenyl)prop-2-yn-1-yl)benzonitrile (1d). First step: 1-chloro-4-ethynylbenzene (888 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (10 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 70/1 to 50/1) afforded the desired product in 84% overall yield (1.61 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.28 (s, 3H), 0.96 (s, 9H), 5.97 (s, 1H), 7.25-7.27 (m, 2H), 7.35-7.41 (m, 3H), 7.63-7.66 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.02, -4.50, 18.19, 25.68, 63.33, 85.45, 89.13, 110.34, 117.07, 120.73, 127.06, 128.24, 128.55, 132.77, 132.94, 133.05, 134.60, 145.04. HRMS (ESI) calcd for $C_{22}H_{28}ClN_2OSi$ $[M+NH_4]^+$: 399.1654, found 399.1655. The spectroscopic data is in agreement with that previously reported.[3]



1e

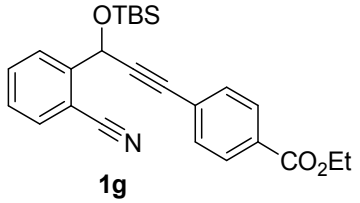
2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(4-fluorophenyl)prop-2-yn-1-yl)benzonitrile (1e). First step: 1-ethynyl-4-fluorobenzene (1.56 g, 13.0 mmol) and EtMgBr (4 mL, 3.0 M solution in Et_2O, 12.0 mmol) in THF (25 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (1.31 g, 10.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM

(20 mL) were added imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) afforded the desired product in 44% overall yield (1.61 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.29 (s, 3H), 0.97 (s, 9H), 5.99 (s, 1H), 6.97 (t, *J* = 8.4 Hz, 2H), 7.37-7.43 (m, 3H), 7.62-7.65 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.12, -4.59, 18.09, 25.59, 63.29, 85.49, 87.81 (d, *J* = 1.5 Hz), 110.32, 115.42 (d, *J* = 20.0 Hz), 116.99, 118.25 (d, *J* = 3.4 Hz), 126.97, 128.14, 132.83, 132.93, 133.39 (d, *J* = 8.3 Hz), 145.03, 162.48 (d, *J* = 248.6 Hz). HRMS (ESI) calcd for $C_{22}H_{28}FN_2OSi$ $[M+NH_4]^+$: 383.1949, found 383.195.



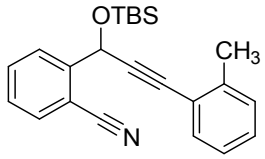
1f

2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzonitrile (1f). First step: 1-ethynyl-4-(trifluoromethyl)benzene (1.11 g, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^{o}C for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (10 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 78% overall yield (1.63 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.31 (s, 3H), 0.99 (s, 9H), 6.04 (s, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.56 (s, 4H), 7.63-7.69 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.11, -4.62, 18.13, 25.59, 63.33, 85.08, 90.62, 110.40, 116.99, 123.73 (q, *J* = 271 Hz), 125.1 (q, *J* = 3.4 Hz), 126.06 (q, *J* = 1.1 Hz), 127.04, 128.32, 130.22 (q, *J* = 32.7 Hz), 131.79, 132.95, 133.04, 144.78. The spectroscopic data is in agreement with that previously reported.[3]



1g

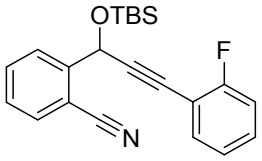
Ethyl 4-(3-(*tert*-butyldimethylsilyloxy)-3-(2-cyanophenyl)prop-1-ynyl)benzoate (1g). First step: To a solution of ethyl 4-ethynylbenzoate (1.13 g, 6.5 mmol) in THF (15 mL) was added dropwise EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) at -78 ^oC, and the reaction mixture was warmed up to room temperature. After stirring at room temperature for 1 h, 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added at -78 ^oC and stirred at the same temperature for 0.5 h, then the reaction mixture was warmed up to room temperature and stirred for 0.5 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the desired product in 41% overall yield (0.86 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.28 (s, 3H), 0.96 (s, 9H), 1.39 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 5.99 (s, 1H), 7.42 (td, J = 7.6, 0.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.63-7.69 (m, 2H), 7.86 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.98, -4.47, 14.26, 18.25, 25.72, 61.14, 63.37, 85.82, 90.01, 110.39, 117.11, 126.82, 127.15, 128.35, 129.37, 130.21, 131.49, 133.01, 133.16, 144.98, 165.94. IR (film): 3359, 2926, 2854, 2224, 1717, 1602, 1469, 1271, 1105, 1072, 841 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{33}N_2O_3Si$ $[M+NH_4]^+$: 437.2255, found 437.2258.



1h

2-(1-(*tert*-Butyldimethylsilyloxy)-3-*o*-tolylprop-2-ynyl)benzonitrile (1h). First step: 1-ethynyl-2-methylbenzene (755 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at

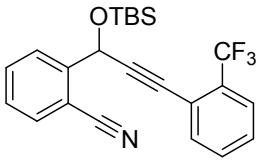
room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60/1) afforded the desired product in 72% overall yield (1.30 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.18 (s, 3H), 0.86 (s, 9H), 2.30 (s, 3H), 5.93 (s, 1H), 6.99-7.02 (m, 1H), 7.05-7.13 (m, 2H), 7.26-7.31 (m, 2H), 7.50-7.56 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.01, -4.46, 18.19, 20.60, 25.69, 63.47, 85.59, 92.06, 110.29, 117.13, 122.04, 125.41, 127.06, 128.13, 128.53, 129.35, 131.94, 132.85, 133.02, 140.31, 145.54. IR (neat): 2954, 2929, 2854, 2226, 1471, 1252, 1069, 835 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{31}N_2OSi$ $[M+NH_4]^+$: 379.22, found 379.2202.



1i

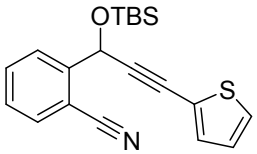
2-(1-(*tert*-Butyldimethylsilyloxy)-3-(2-fluorophenyl)prop-2-ynyl)benzonitrile (1i). First step: 1-ethynyl-2-fluorobenzene (781 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^{o}C for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford the desired product in 83% overall yield (1.52 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.28 (s, 3H), 0.95 (s, 9H), 6.01 (s, 1H), 7.02-7.09 (m, 2H), 7.25-7.32 (m, 1H), 7.39-7.45 (m, 2H), 7.62-7.67 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.02, -4.51, 18.22, 25.70, 63.47, 80.29, 93.20 (d, J = 3.0 Hz), 110.55, 110.88 (d, J = 15.6 Hz), 115.51 (d, J = 20.8 Hz), 117.13, 123.85 (d, J = 3.7 Hz), 127.38, 128.31, 130.34 (d, J = 7.4 Hz), 132.94, 133.09, 133.50, 144.92, 162.80 (d, J = 250.6 Hz). IR (neat): 2956, 2929, 2856, 2224, 1492, 1449, 1252, 1069, 834, 754 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{24}FNNaOSi$ $[M+Na]^+$: 388.1503,

found 388.1503.



1j

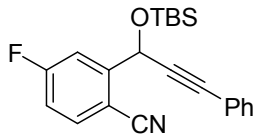
2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(2-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzonitrile (1j). First step: 1-ethynyl-2-(trifluoromethyl)benzene (1.11 g, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) afforded the desired product in 75% overall yield (1.56 g) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.27 (s, 3H), 0.95 (s, 9H), 6.02 (s, 1H), 7.37-7.42 (m, 2H), 7.45-7.48 (m, 1H), 7.58-7.67 (m, 4H), 7.89 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.17, -4.74, 18.16, 25.60, 63.39, 82.41, 93.64, 110.38, 117.09, 120.44 (q, *J* = 1.6 Hz), 123.28 (q, *J* = 271.8 Hz), 125.70 (q, *J* = 5.3 Hz), 127.39, 128.35, 128.37, 131.35, 131.48 (q, *J* = 30.4 Hz), 132.82, 133.10, 134.10, 144.73. IR (neat): 2931, 2854, 2221, 1657, 1449, 1317, 1134, 1060, 837 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{24}F_3NNaOSi$ $[M+Na]^+$: 438.1471, found 438.1470.



1l

2-(1-(*tert*-Butyldimethylsilyloxy)-3-(thiophen-2-yl)prop-2-ynyl)benzonitrile (1l). First step: 2-ethynylthiophene (0.65 mL, 6.5 mmol, d = 1.08 g/mL) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (15 mL) was stirred at 40 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM

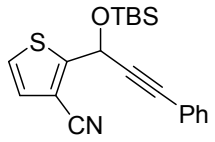
(15 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1 to 60/1) afforded the desired product in 52% overall yield (0.92 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.27 (s, 3H), 0.95 (s, 9H), 5.99 (s, 1H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.20 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.61-7.65 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.00, -4.49, 18.20, 25.70, 63.51, 80.15, 91.84, 110.39, 117.06, 122.07, 126.90, 127.27, 127.50, 128.28, 132.38, 132.88, 133.08, 144.88. HRMS (ESI) calcd for $C_{20}H_{27}N_2OSSi$ $[M+NH_4]^+$: 371.1608, found 371.1609. The spectroscopic data is in agreement with that previously reported.[3]



1m

2-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylprop-2-ynyl)-4-fluorobenzonitrile (1m). First step: ethynylbenzene (429 μL, 3.9 mmol) and EtMgBr (1.2 mL, 3.0 M solution in Et_2O, 3.6 mmol) in THF (10 mL) was stirred at 50 ^{o}C for 1 h, and after 4-fluoro-2-formylbenzonitrile (447.4 mg, 3.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (15 mL) were added imidazole (408.5 mg, 6.0 mmol) and TBSCl (678.2 mg, 4.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 75% overall yield (822 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.31 (s, 3H), 0.98 (s, 9H), 5.97 (s, 1H), 7.08-7.13 (m, 1H), 7.29-7.33 (m, 3H), 7.44-7.46 (m, 2H), 7.60 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.68 (dd, *J* = 8.4, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.02, -4.43, 18.22, 25.70, 62.96 (d, *J* = 1.5 Hz), 86.97, 87.41, 106.32, 114.83 (d, *J* = 24.3 Hz), 115.79 (d, *J* = 23.6 Hz), 116.44, 122.01, 128.27, 128.73, 131.59, 135.28 (d, *J* = 9.1 Hz), 149.00 (d, *J* = 8.4 Hz), 165.24 (d, *J* = 255.8 Hz). IR (neat): 2954, 2929, 2856, 2226, 1608, 1490, 1254, 1109, 1067, 837, 780, 756, 689 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{28}FN_2OSi$ $[M+NH_4]^+$: 383.1949, found

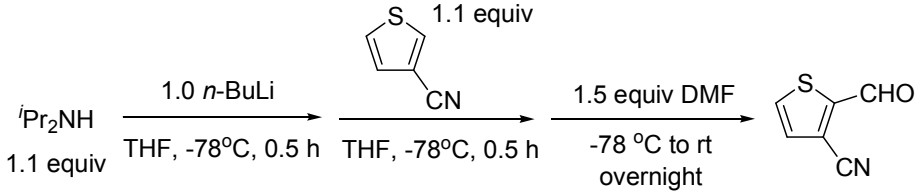
383.1943.



1n

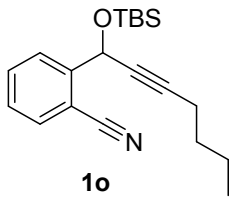
2-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylprop-2-ynyl)thiophene-3-carbonitrile (1n). First step: ethynylbenzene (357 μL, 3.25 mmol) and EtMgBr (1.0 mL, 3.0 M solution in Et_2O, 3.0 mmol) in THF (15 mL) was stirred at 40 ^oC for 1 h, and after 2-formylthiophene-3-carbonitrile[4] (342.9 mg, 2.5 mmol, for the synthesis of this compound, see belowing) was added at 0 ^oC, the reaction mixture was stirred at 0 ^oC for 1 h. Second step: To a solution of the above crude alcohol in DCM (15 mL) were added imidazole (340.4 mg, 5.0 mmol) and TBSCl (565.2 mg, 3.75 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the desired product in 84% overall yield (741 mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.29 (s, 3H), 0.97 (s, 9H), 6.09 (s, 1H), 7.17 (d, J = 5.2 Hz, 1H), 7.27-7.32 (m, 4H), 7.46-7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.07, -4.48, 18.19, 25.62, 60.57, 86.72, 86.91, 106.54, 114.16, 121.86, 125.48, 128.26, 128.79, 128.98, 131.61, 157.34. IR (neat): 2956, 2929, 2854, 2230, 1491, 1469, 1253, 1070, 836, 780, 755, 689, 675 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{27}N_2OSSi$ $[M+NH_4]^+$: 371.1608, found 371.1602.

Synthesis of 2-formylthiophene-3-carbonitrile.



This compound was synthesized according to the modified procedure of the published method.[4] Under an argon atmosphere, to a solution of diisoproylamine (1.55 mL, 11.0 mmol) in dry THF (20 mL) was added n-BuLi (4 mL, 10.0 mmol, 2.5 M in hexane)

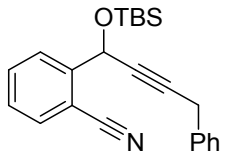
dropwise at -78 °C. After stirring for 30 min at the same temperature, the thus formed lithium diisopropylamine was added to a solution of thiophene-3-carbonitrile (1.2 g, 11 mmol) in anhydrous THF (5 mL) at -78 °C, and stired for 30 min before dimethylformamide (1.16 mL, 15 mmol) was added. Then the reaction mixture was warmed up to room temperature and stirred overnight. After the reaction was complete, the organic layer was poured into an aqueous solution of HCl (100 mL, 2 M), and stirred for 1 h. Then the organic layer was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 15/1) to afford the title product in 38% yield (525 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 5.2 Hz, 1H), 7.88 (dd, *J* = 5.2, 0.8 Hz, 1H), 10.16 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.69, 116.25, 130.86, 134.90, 149.01, 180.37. The spectroscopic data is in agreement with that previously reported.[4]



1o

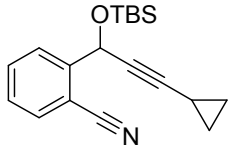
2-(1-(*tert*-Butyldimethylsilyloxy)hept-2-ynyl)benzonitrile (1o). First step: hex-1-yne (1.5 mL, 13.0 mmol, d = 0.715) and EtMgBr (4 mL, 3.0 M solution in Et_2O, 12.0 mmol) in THF (30 mL) was stirred at 50 °C for 1 h, and after 2-cyanobenzaldehyde (1.31 g, 10.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (30 mL) were added imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60/1) afforded the desired product in 75% overall yield (2.45 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 3H), 0.21 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H), 1.34-1.52 (m, 4H), 2.20 (td, *J* = 6.8, 2.0 Hz, 2H), 5.75 (t, *J* = 2.0 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.57-7.62 (m, 2H), 7.78-7.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.09, -4.56, 13.43, 18.14, 18.36, 21.81, 25.67, 30.31, 63.06, 79.32, 87.67, 110.25, 117.12, 126.94,

127.86, 132.71, 132.86, 146.02. IR (neat): 2954, 2929, 2856, 2221, 1471, 1252, 1062, 836, 777 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{33}N_2OSi$ $[M+NH_4]^+$: 345.2357, found 345.2359.



1p

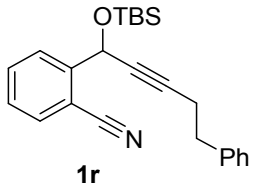
2-(1-(*tert*-Butyldimethylsilyloxy)-4-phenylbut-2-ynyl)benzonitrile (1p). First step: prop-2-ynylbenzene (755 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (15 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 72% overall yield (1.30 g) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 3H), 0.19 (s, 3H), 0.92 (s, 9H), 3.64 (s, 2H), 5.82 (s, 1H), 7.21-7.39 (m, 6H), 7.58-7.64 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.05, -4.54, 18.20, 25.09, 25.70, 63.12, 81.65, 84.91, 110.26, 117.19, 126.57, 127.08, 127.87, 128.05, 128.42, 132.82 133.01, 136.07, 145.82. IR (neat): 2954, 2929, 2854, 2224, 1599, 1449, 1252, 1062, 837, 761 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{31}N_2OSi$ $[M+NH_4]^+$: 379.2200, found 379.2201.



1q

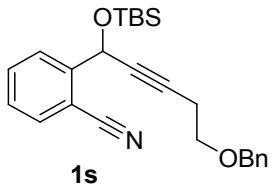
2-(1-(*tert*-Butyldimethylsilyloxy)-3-cyclopropylprop-2-ynyl)benzonitrile (1q). First step: ethynylcyclopropane (859.3 mg, 13.0 mmol) and EtMgBr (4 mL, 3.0 M solution in Et_2O, 12.0 mmol) in THF (20 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (1.31 g, 10.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added

imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1 to 80/1) afforded the desired product in 65% overall yield (2.03 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.20 (s, 3H), 0.66-0.77 (m, 4H), 0.91 (s, 9H), 1.20-1.27 (m, 1H), 5.70 (s, 1H), 7.33-7.37 (m, 1H), 7.56-7.61 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.10, -4.53, -0.56, 7.97, 7.98, 18.10, 25.65, 63.03, 74.39, 90.60, 110.20, 117.10, 126.93, 127.87, 132.73, 132.85, 145.81. The spectroscopic data is in agreement with that previously reported.[3]



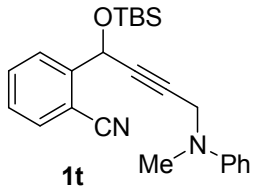
1r

2-(1-(*tert*-Butyldimethylsilyloxy)-5-phenylpent-2-ynyl)benzonitrile (1r). First step: but-3-ynylbenzene (846 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^{o}C for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 84% overall yield (1.58 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 2.51 (td, *J* = 7.6, 2.0 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 5.73 (s, 1H), 7.16-7.20 (m, 3H), 7.23-7.26 (m, 2H), 7.34-7.38 (m, 1H), 7.56-7.62 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.08, -4.55, 18.19, 20.89, 25.72, 34.60, 63.03, 80.15, 86.80, 110.24, 117.19, 126.18, 127.05, 127.94, 128.30, 128.39, 132.74, 132.94, 140.38, 145.91. IR (neat): 2951, 2829, 2856, 2224, 1469, 1252, 1059, 836, 759 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{33}N_2OSi$ $[M+NH_4]^+$: 393.2357, found 393.2356.



1s

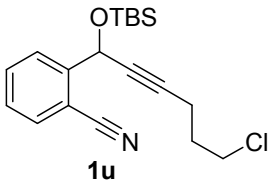
2-(5-(Benzyloxy)-1-(*tert*-butyldimethylsilyloxy)pent-2-ynyl)benzonitrile (1s). First step: ((but-3-ynyloxy)methyl)benzene (1.04 g, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (10 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 78% overall yield (1.59 g) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 3H), 0.21 (s, 3H), 0.92 (s, 9H), 2.53 (td, *J* = 6.8, 2.0 Hz, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 4.51 (s, 2H), 5.75 (s, 1H), 7.22-7.35 (m, 6H), 7.54-7.60 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.11, -4.57, 18.09, 20.12, 25.64, 62.98, 68.04, 72.81, 80.31, 84.27, 110.21, 117.08, 127.02, 127.50, 127.94, 128.23, 132.70, 132.87, 137.89, 145.60. One carbon overlapped with other signals. IR (neat): 2954, 2931, 2859, 2224, 1469, 1249, 1101, 1061, 836, 778 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{35}N_2O_2Si$ $[M+NH_4]^+$: 423.2462, found 423.2465.



1t

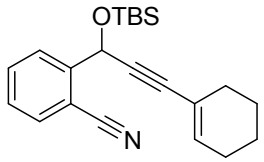
2-(1-(*tert*-Butyldimethylsilyloxy)-4-(methyl(phenyl)amino)but-2-ynyl)benzonitrile (1t). First step: *N*-methyl-*N*-(prop-2-ynyl)benzenamine (944 mg, 6.5 mmol) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^oC for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and

stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the desired product in 57% overall yield (1.11 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.87 (s, 9H), 2.92 (s, 3H), 4.06 (s, 2H), 5.71 (s, 1H), 6.76-6.82 (m, 3H), 7.19-7.23 (m, 2H), 7.29-7.33 (m, 1H), 7.49-7.53 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.21, -4.71, 18.05, 25.57, 38.58, 42.71, 62.83, 82.68, 83.03, 110.24, 114.34, 117.02, 118.12, 127.02, 128.01, 128.88, 132.72, 132.85, 145.17, 148.95. One carbon overlapped with other signals. IR (neat): 2956, 2926, 2856, 2221, 1600, 1505, 1251, 1119, 1060, 836, 753 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{31}N_2OSi$ $[M+H]^+$: 391.2200, found 391.2201.



1u

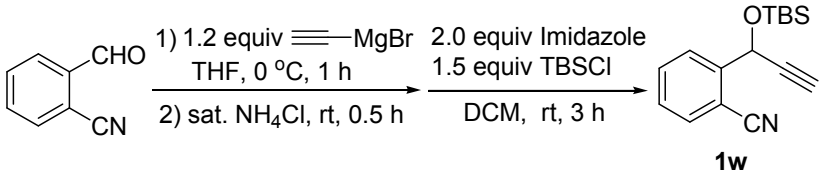
2-(1-(*tert*-Butyldimethylsilyloxy)-6-chlorohex-2-ynyl)benzonitrile (1u). First step: 5-chloropent-1-yne (0.68 mL, 6.5 mmol, d = 0.978 g/mL) and EtMgBr (2 mL, 3.0 M solution in Et_2O, 6.0 mmol) in THF (20 mL) was stirred at 50 ^{o}C for 1 h, and after 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (10 mL) were added imidazole (681 mg, 10.0 mmol) and TBSCl (1.13 g, 7.5 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60/1) afforded the desired product in 86% overall yield (1.49 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.13 (s, 3H), 0.84 (s, 9H), 1.83-1.90 (m, 2H), 2.32 (td, *J* = 6.8, 2.0 Hz, 2H), 3.53 (t, *J* = 6.4 Hz, 2H), 5.65 (t, *J* = 2.0 Hz, 1H), 7.26-7.31 (m, 1H), 7.50-7.55 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ -5.16, -4.65, 16.05, 18.07, 25.59, 30.90, 43.39, 62.90, 80.37, 85.38, 110.08, 117.00, 126.74, 127.94, 132.75, 132.89, 145.66. IR (neat): 2956, 2926, 2856, 2226, 1710, 1469, 1252, 1217, 1062, 835, 778, 759 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{30}ClN_2OSi$ $[M+NH_4]^+$: 365.1810, found 365.1810.



1v

2-(1-((*tert*-Butyldimethylsilyl)oxy)-3-(cyclohex-1-en-1-yl)prop-2-yn-1-yl)benzonitrile (1v). First step: 1-ethynylcyclohex-1-ene (1.53 mL, 13.0 mmol, d = 0.903) and EtMgBr (4 mL, 3.0 M solution in Et_2O, 12.0 mmol) in THF (30 mL) was stirred at 50 ^oC for 2 h, and after 2-cyanobenzaldehyde (1.31 g, 10.0 mmol) was added, the reaction mixture was stirred at room temperature for 2 h. Second step: To a solution of the above crude alcohol in DCM (20 mL) were added imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol), and stirred at room temperature. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 150/1 to 120/1) afforded the desired product in 63% overall yield (2.2 g) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 3H), 0.23 (s, 3H), 0.92 (s, 9H), 1.51-1.63 (m, 4H), 2.02-2.11 (m, 4H), 5.86 (s, 1H), 6.08-6.10 (m, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.57-7.62 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.07, -4.47, 18.11, 21.27, 22.02, 25.43, 25.65, 28.65, 63.34, 85.37, 88.54, 110.32, 117.08, 119.88, 127.05, 127.94, 132.76, 132.86, 135.37, 145.58. The spectroscopic data is in agreement with that previously reported.[3]

Synthesis of 2-(1-((*tert*-butyldimethylsilyl)oxy)prop-2-yn-1-yl)benzonitrile (1w).



1w

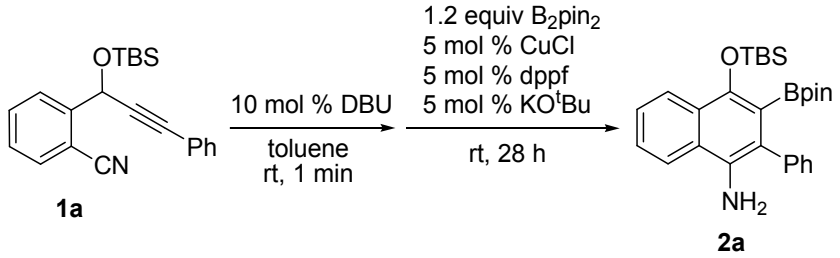
To a solution of ethynylmagnesium bromide (48.0 mL, 0.5 M solution in THF, 24.0 mmol) in THF (20.0 mL) was added 2-cyanobenzaldehyde (2.62 g, 20.0 mmol) at 0 ^oC under argon and the mixture was stirred at the same temperature for 1 h. Then the reaction mixture was quenched with saturated NH_4Cl solution, and extracted with ethyl acetate. The combined organic extracts were washed with brine, and dried over Na_2SO_4. Then the solvent was evaporated under the reduced pressure to afford the alcohol as an orange oil,

which was used directly without further purification for the next step.

To a solution of the above alcohol in DCM (50 mL) were added imidazole (2.72 g, 40.0 mmol) and TBSCl (4.52 g, 30.0 mmol) under air. The reaction mixture was then stirred at room temperature for 3 h before adding a saturated NH_4Cl solution. The reaction mixture was extracted with dichloromethane, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **1w** in 80% overall yield (4.35 g) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 3H), 0.22 (s, 3H), 0.92 (s, 9H), 2.61 (d, *J* = 2.0 Hz, 1H), 5.75 (d, *J* = 2.4 Hz, 1H), 7.38-7.41 (m, 1H), 7.60-7.64 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.17, -4.70, 18.10, 25.59, 62.62, 74.85, 82.67, 110.23, 116.93, 127.05, 128.32, 132.77, 133.08, 144.74. The spectroscopic data is in agreement with that previously reported.[1]

Synthesis of 1-naphthylamines 2a-2n.

Typical procedure for the synthesis of 4-(*tert*-butyldimethylsilyloxy)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2a).

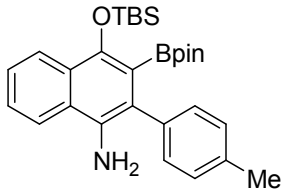


In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added (*o*-cyano)phenylpropargyl ether **1a** (104.3 mg, 0.3 mmol), toluene (1.5 mL) and DBU (4.5 μL, 0.03 mmol), and stirred for 1 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 28 h. The reaction mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate

= 20/1, containing 1% v/v Et_3N) to give **2a** in 93% yield (132.0 mg) as a brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 6H), 1.04 (s, 12H), 1.16 (s, 9H), 3.57 (bs, 2H), 7.36-7.47 (m, 7H), 7.79 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.17, 18.55, 25.13, 26.20, 83.29, 120.93, 124.04, 124.22, 125.59, 125.68, 125.99, 127.19, 127.48, 128.36, 130.77, 132.72, 139.94, 146.80. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3453, 3364, 2928, 2857, 1615, 1367, 1251, 1139, 1078, 968, 924, 829 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{39}{}^{10}BNO_3Si$ $[M+H]^+$: 475.2823, found 475.2825.

When the above reaction was carried out by adding the substrates sequentially (without stirring with DBU for 1 min), **2a** was formed in 91% yield after stirring at room temperature for 28 h.

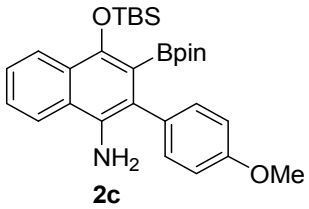
When the above reaction was performed at 50 °C, 87% of **2a** was isolated after 4 h.



2b

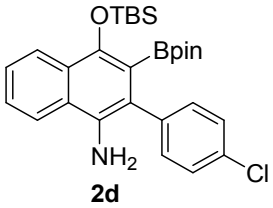
4-(*tert*-Butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-*p*-tolyl naphthalen-1-amine (2b). (*o*-Cyano)phenylpropargyl ether **1b** (108.5 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1, containing 1% v/v Et_3N) afforded the title product in 97% yield (142.6 mg) as a brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 6H), 1.02 (s, 12H), 1.13 (s, 9H), 2.38 (s, 3H), 3.54 (bs, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.38-7.42 (m, 2H), 7.74-7.77 (m, 1H), 8.10 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.18, 18.55, 21.12, 25.11, 26.21, 83.29, 120.94, 123.93, 124.19, 125.58, 126.00, 127.42, 128.96, 130.60, 132.84, 136.73, 136.85, 146.68. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3449, 3364, 2928, 2857, 1614, 1513, 1391, 1367, 1250, 1139, 1078, 918, 888 cm^{-1}. HRMS (ESI)

calcd for $C_{29}H_{41}{}^{10}BNO_3Si$ $[M+H]^+$: 489.2980, found 489.2982.



2c

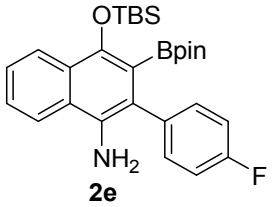
4-(*tert*-Butyldimethylsilyloxy)-2-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2c). (*o*-Cyano)phenylpropargyl ether **1c** (113.3 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1, containing 1% v/v Et_3N) afforded the title product in 85% yield (128.3 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 6H), 1.04 (s, 12H), 1.13 (s, 9H), 3.59 (bs, 2H), 3.81 (s, 3H), 6.95 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.37-7.44 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.19, 18.55, 25.16, 26.20, 55.29, 83.28, 113.77, 120.94, 123.95, 124.17, 125.52, 125.58, 127.42, 131.85, 132.16, 133.19, 146.59, 158.92. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. One carbon overlapped with other signals. IR (film): 3428, 3351, 2927, 2856, 1732, 1622, 1512, 1459, 1363, 1244, 1075, 1027, 916, 835, 806 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{41}{}^{10}BNO_4Si$ $[M+H]^+$: 505.2929, found 505.2928.



2d

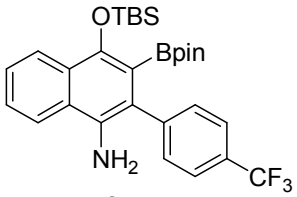
4-(*tert*-Butyldimethylsilyloxy)-2-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2d). (*o*-Cyano)phenylpropargyl ether **1d** (114.6 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were

stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1, containing 1% v/v Et_3N) afforded the title product in 96% yield (146.9 mg) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 6H), 1.07 (s, 12H), 1.16 (s, 9H), 3.55 (bs, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.40-7.45 (m, 4H), 7.76 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.21, 18.52, 25.10, 26.17, 83.36, 120.90, 124.26, 124.28, 124.36, 125.52, 125.87, 127.62, 128.44, 132.27, 132.84, 133.15, 138.50, 147.07. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3441, 3381, 2927, 2858, 1161, 1490, 1390, 1369, 1324, 1308, 1258, 1139, 1080, 918, 888, 839 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{38}{}^{10}BClNO_3Si$ $[M+H]^+$: 509.2433, found 509.2434.



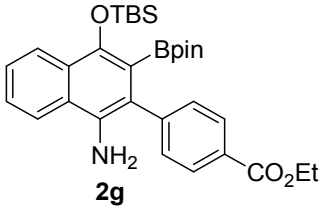
2e

4-(*tert*-Butyldimethylsilyloxy)-2-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2e). (*o*-Cyano)phenylpropargyl ether **1e** (109.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) afforded the title product in 90% yield (133.1 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 6H), 1.06 (s, 12H), 1.15 (s, 9H), 3.62 (bs, 2H), 7.11-7.15 (m, 2H), 7.34-7.46 (m, 4H), 7.77 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.18, 18.57, 25.14, 26.20, 83.37, 115.20 (d, *J* = 20.9 Hz), 120.91, 124.24, 124.30, 124.66, 125.55, 125.84, 127.62, 132.52 (d, *J* = 7.9 Hz), 133.06, 135.89 (d, *J* = 3.0 Hz), 146.97, 162.26 (d, *J* = 244.4 Hz). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3414, 3342, 2930, 2858, 1618, 1507, 1380, 1367, 1154, 1082, 941, 842, 811 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{38}{}^{10}BFNO_3Si$ $[M+H]^+$: 493.2729, found 493.2728.



2f

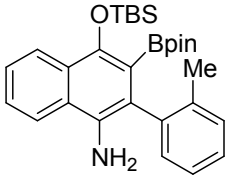
4-(*tert*-Butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)naphthalen-1-amine (2f). (*o*-Cyano)phenylpropargyl ether **1f** (124.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) afforded the title product in 98% yield (159.1 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 6H), 1.03 (s, 12H), 1.16 (s, 9H), 3.66 (bs, 2H), 7.45-7.53 (m, 4H), 7.70 (d, J = 8.0 Hz, 2H), 7.76-7.79 (m, 1H), 8.14-8.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.22, 18.54, 25.03, 26.16, 83.38, 120.91, 124.25 (q, J = 271.0 Hz), 124.28, 124.41, 124.51, 125.24 (q, J = 3.8 Hz), 125.61, 126.08, 127.81, 129.48 (q, J = 33.7 Hz), 131.31, 132.70, 144.22, 147.47. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3448, 3373, 2928, 1614, 1392, 1369, 1323, 1261, 1155, 1117, 1070, 888, 843 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{38}{}^{10}BF_3NO_3Si$ $[M+H]^+$: 543.2697, found 543.2698.



2g

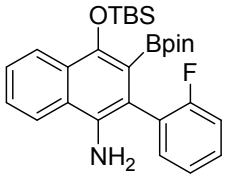
Ethyl-4-(1-amino-4-(*tert*-butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-yl)benzoate (2g). (*o*-Cyano)phenylpropargyl ether **1g** (125.9 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent:

petroleum ether/ethyl acetate = 15/1, containing 1% v/v Et_3N) afforded the title product in 96% yield (158 mg) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 6H), 1.01 (s, 12H), 1.13 (s, 9H), 1.41 (t, *J* = 7.2 Hz, 3H), 3.65 (bs, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.39-7.48 (m, 4H), 7.74-7.77 (m, 1H), 8.11 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.25, 14.21, 18.48, 25.05, 26.13, 60.83, 83.30, 120.89, 124.24, 124.32, 124.64, 125.54, 125.89, 127.65, 129.15, 129.51, 130.87, 132.60, 145.16, 147.22, 166.43. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3442, 3367, 2956, 2930, 2893, 2854, 1706, 1618, 1461, 1395, 1367, 1271, 1140, 1110, 968, 918, 828 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{43}{}^{10}BNO_5Si$ $[M+H]^+$: 547.3034, found 547.3033.



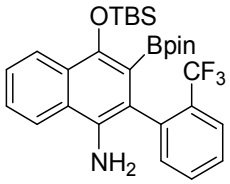
2h

4-(*tert*-Butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-*o*-tolyl naphthalen-1-amine (2h). (*o*-Cyano)phenylpropargyl ether **1h** (108.5 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1, containing 1% v/v Et_3N) afforded the title product in 98% yield (143.9 mg) as a brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.16 (s, 3H), 0.97 (s, 6H), 0.98 (s, 6H), 1.13 (s, 9H), 2.11 (s, 3H), 3.56 (bs, 2H), 7.23-7.24 (m, 4H), 7.37-7.44 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.33, -3.16, 18.54, 19.75, 24.95, 25.13, 26.22, 77.20, 83.16, 120.88, 123.95, 124.25, 125.15, 125.50, 125.79, 127.46, 127.61, 129.79, 131.14, 132.48, 138.34, 138.86, 146.73. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. One carbon is overlapped with other signals. IR (film): 3403, 3309, 3228, 3070, 2928, 2856, 1623, 1445, 1367, 1323, 1252, 1139, 1111, 1078, 968, 919, 854, 781 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{41}{}^{10}BNO_3Si$ $[M+H]^+$: 489.298, found 489.2976.



2i

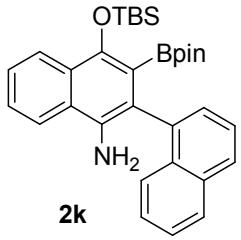
4-(*tert*-Butyldimethylsilyloxy)-2-(2-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2i). (*o*-Cyano)phenylpropargyl ether **1i** (109.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1, containing 1% v/v Et_3N) afforded the title product in 98% yield (144.9 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.14 (s, 3H), 1.01 (s, 6H), 1.05 (s, 6H), 1.13 (s, 9H), 3.66 (bs, 2H), 7.12-7.24 (m, 2H), 7.30-7.47 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.34, -3.25, 18.52, 25.07, 25.12, 26.19, 83.17, 115.65 (d, *J* = 22.3 Hz), 119.28, 120.97, 124.02 (d, *J* = 3.7 Hz), 124.42, 125.76, 125.89, 127.38 (d, *J* = 17.9 Hz), 127.97, 129.37 (d, *J* = 7.4 Hz), 133.12, 133.14, 133.55, 147.63, 160.74 (d, *J* = 246.7 Hz). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3412, 3320, 3228, 2929, 2856, 1618, 1490, 1443, 1370, 1323, 1252, 1139, 1082, 969, 889, 835 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{38}{}^{10}BFNO_3Si$ $[M+H]^+$: 493.2729, found 493.2729.



2j

4-(*tert*-Butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(2-(trifluoromethyl)phenyl)naphthalen-1-amine (2j). (*o*-Cyano)phenylpropargyl ether **1j** (124.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015

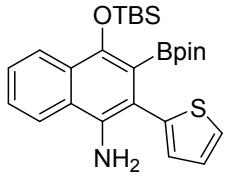
mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1, containing 1% v/v Et_3N) afforded the title product in 94% yield (154 mg) as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.13 (s, 3H), 0.95 (s, 6H), 1.01 (s, 6H), 1.13 (s, 9H), 3.49 (bs, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.41-7.48 (m, 3H), 7.53-7.56 (m, 1H), 7.74-7.79 (m, 2H), 8.16 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.71, -3.34, 18.47, 24.84, 25.15, 26.19, 82.79, 120.94, 123.40, 123.99 (q, *J* = 273.3 Hz), 124.44, 124.60, 125.980 (q, *J* = 4.5 Hz), 125.984, 126.13, 127.52, 128.01, 130.38 (q, *J* = 30.3 Hz), 131.46, 132.95, 133.29, 138.96 (q, *J* = 1.5 Hz), 148.37. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3462, 3378, 2931, 2858, 1617, 1473, 1368, 1313, 1253, 1164, 1078, 1034, 918, 856 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{38}{}^{10}BF_3NO_3Si$ $[M+H]^+$: 543.2697, found 543.2695.



2k

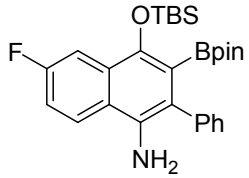
5'-(*tert*-butyldimethylsilyloxy)-6'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,7'-bi naphthyl-8'-amine (2k). (*o*-Cyano)phenylpropargyl ether **1k** (119.3 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^tBu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) afforded the title product in 87% yield (137.4 mg) as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.25 (s, 3H), 0. 70 (s, 6H), 0.77 (s, 6H), 1.18 (s, 9H), 3.59 (bs, 2H), 7.31-7.35 (m, 1H), 7.44-7.50 (m, 3H), 7.55-7.57 (m, 3H), 7.81-7.83 (m, 1H), 7.88-7.91 (m, 2H), 8.21-8.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.26, 18.52, 24.82, 24.90, 26.19, 82.91, 120.97, 123.57, 124.24, 124.37, 125.51, 125.65, 125.76, 125.78, 126.02, 126.51, 127.64, 127.70, 127.81, 128.93, 132.68, 133.56, 133.71, 137.25, 147.17. The carbon directly attached to the boron

atom was not detected, likely due to quadrupolar broadening. IR (film): 3445, 3367, 2957, 2929, 2858, 1613, 1564, 1471, 1366, 1247, 1151, 1138, 1079, 918, 834 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{41}{}^{10}BNO_3Si$ $[M+H]^+$: 525.2980, found 525.2978. Anal. Calcd. for $C_{32}H_{40}BNO_3Si$: C, 73.13, H, 7.67, N, 2.67; Found: C, 72.97, H, 7.65, N, 2.58. The structure of **2k** was determined by X-ray crystal analysis.



2l

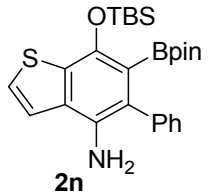
4-(*tert*-Butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)naphthalen-1-amine (2l). (*o*-Cyano)phenylpropargyl ether **1l** (106.1 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1, containing 1% v/v Et_3N) afforded the title product in 82% yield (117.9 mg) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 6H), 1.13 (s, 12H), 1.15 (s, 9H), 3.93 (bs, 2H), 7.06-7.07 (m, 1H), 7.10-7.12 (m, 1H), 7.39-7.47 (m, 3H), 7.77-7.79 (m, 1H), 8.11-8.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.18, 18.56, 25.24, 26.21, 83.41, 116.82, 121.09, 124.22, 124.64, 125.26, 125.78, 126.15, 127.04, 128.20, 128.72, 135.44, 140.47, 146.52. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3462, 3368, 2923, 2854, 1611, 1367, 1306, 1255, 1137, 1078, 904, 886, 835 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{37}{}^{10}BNO_3SSi$ $[M+H]^+$: 481.2387, found 481.2388.



2m

4-(*tert*-Butyldimethylsilyloxy)-6-fluoro-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxabor

olan-2-yl)naphthalen-1-amine (2m). (*o*-Cyano)arylpropargyl ether **1m** (109.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1, containing 1% v/v Et_3N) afforded the title product in 99% yield (147.1 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 6H), 1.02 (s, 12H), 1.14 (s, 9H), 3.58 (bs, 2H), 7.18-7.23 (m, 1H), 7.34-7.44 (m, 5H), 7.71 (dd, *J* = 11.2, 2.0 Hz, 1H), 7.78 (dd, *J* = 8.8, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.12, 18.65, 25.21, 26.25, 83.55, 107.94 (d, *J* = 22.0 Hz), 115.61 (d, *J* = 25.3 Hz), 122.76, 123.71 (d, *J* = 9.3 Hz), 125.59, 127.45, 128.54, 128.71 (d, *J* = 8.0 Hz), 130.91, 133.12, 139.67, 146.21 (d, *J* = 3.4 Hz), 160.06 (d, *J* = 242.4 Hz). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3409, 2954, 2929, 2854, 1710, 1621, 1574, 1394, 1356, 1251, 1178, 1139, 1063, 905, 835, 813, 783, 699 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{38}{}^{10}BFNO_3Si$ $[M+H]^+$: 493.2729, found 493.2724.



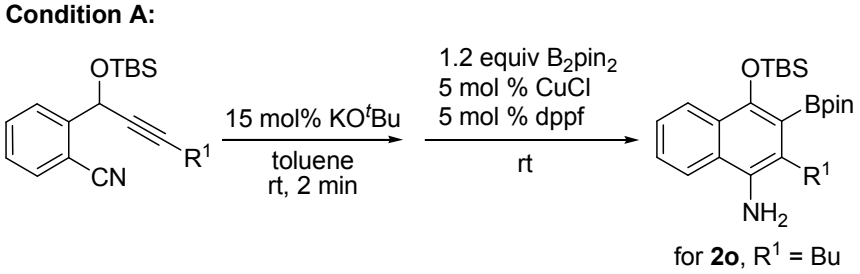
2n

7-((*tert*-Butyldimethylsilyl)oxy)-5-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-4-amine (2n). (*o*-Cyano)thienylpropargyl ether **1n** (106.1 mg, 0.3 mmol), toluene (1.5 mL), DBU (4.5 μL, 0.03 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1, containing 1% v/v Et_3N) afforded the title product in 90% yield (130.4 mg) as a light yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ 0.42 (s, 6H), 0.98 (s, 12H), 1.24 (s, 9H), 3.24 (bs, 2H), 6.83 (d, *J* = 5.6 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 7.18-7.20 (m, 1H), 7.23-7.27 (m, 2H), 7.46-7.48 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6) δ -2.43, 19.02, 25.36, 26.58, 83.33, 120.85, 125.03, 127.13, 127.28, 128.51, 131.58, 131.73,

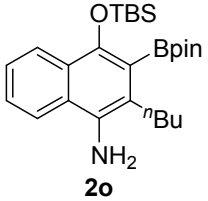
132.89, 134.06, 140.62, 145.52. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3453, 3370, 2976, 2926, 2854, 1607, 1403, 1355, 1312, 1142, 966, 909, 841, 824, 783, 700 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{37}{}^{10}BNO_3SSi$ $[M+H]^+$: 481.2387, found 481.2380.

Synthesis of 1-naphthylamines 2o-2t.

Typical procedure for the synthesis of 1-naphthylamine 2o (Condition A).



The reaction was carried out in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, to a screw-cap vial were added (*o*-cyano)phenylpropargyl ether **1o** (98.3 mg, 0.3 mmol), toluene (1.5 mL) and KO^tBu (5.0 mg, 0.045 mmol), and stirred for 2 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol) and dppf (8.3 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 40 h. The mixture was diluted with ethyl acetate, washed with saturated NH_4Cl solution, water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) to afford **2o** in 70% yield (95.6 mg) as a reddish brown solid.

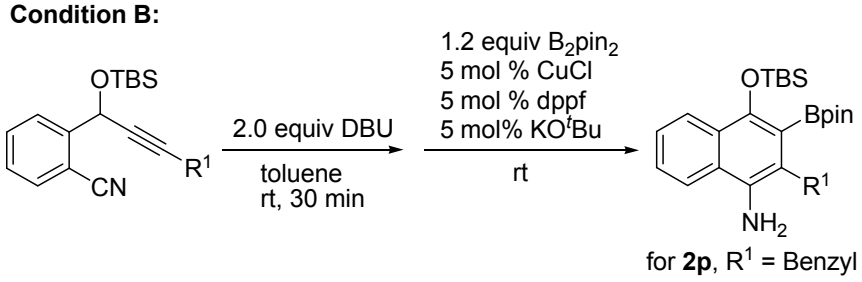


2o

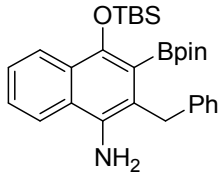
2-Butyl-4-((*tert*-butyldimethylsilyl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl

)naphthalen-1-amine (2o). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.99 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 9H), 1.43-1.51 (m, 14H), 1.59-1.63 (m, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 3.85 (bs, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.16, 14.11, 18.62, 23.26, 25.56, 26.29, 31.48, 32.11, 83.55, 120.25, 123.21, 124.29, 124.84, 125.54, 126.05, 126.70, 132.63, 147.96. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3417, 3356, 2959, 2932, 2860, 1626, 1583, 1473, 1392, 1379, 1365, 1304, 1257, 1138, 1072, 977, 857, 840 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{43}{}^{10}BNO_3Si$ $[M+H]^+$: 455.3136, found 455.3134.

Typical procedure for the synthesis of 1-naphthylamine 2p (Condition B).

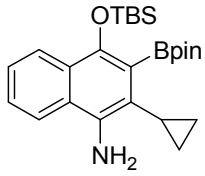


The reaction was carried out in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, to a screw-cap vial were added (*o*-cyano)phenylpropargyl ether **1p** (108.5 mg, 0.3 mmol), toluene (1.5 mL), DBU (89.6 μL, 0.6 mmol), and stirred for 30 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 40 h. The mixture was diluted with ethyl acetate, washed with saturated NH_4Cl solution, water and brine, dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) to give **2p** in 57% yield (83 mg) as a reddish brown solid.



2p

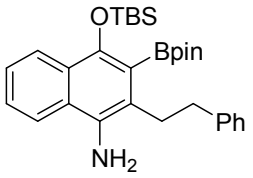
2-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2p). ^{1}H NMR (400 MHz, C_6D_6) δ 0.21 (s, 6H), 1.09 (s, 12H), 1.22 (s, 9H), 3.37 (bs, 2H), 4.42 (s, 2H), 7.00-7.03 (m, 1H), 7.09-7.13 (m, 2H), 7.21-7.25 (m, 3H), 7.29-7.33 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ -2.88, 18.94, 25.48, 26.63, 37.20, 83.49, 121.17, 122.21, 124.12, 124.67, 125.85, 126.19, 126.64, 127.93, 128.74, 128.84, 135.36, 140.89, 148.66. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3459, 3373, 3067, 2927, 2856, 1621, 1496, 1368, 1301, 1251, 1138, 1078, 982, 860 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{41}{}^{10}BNO_3Si$ $[M+H]^+$: 489.2980, found 489.2975.



2q

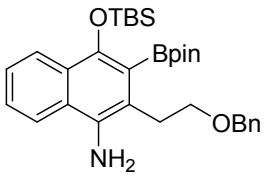
4-((*tert*-Butyldimethylsilyl)oxy)-2-cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2q). Condition A was used. (*o*-Cyano)phenylpropargyl ether **1q** (93.4 mg, 0.3 mmol), toluene (1.5 mL), KO^{t}Bu (5.0 mg, 0.045 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol) and dppf (8.3 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1 to 10/1, containing 1% v/v Et_3N) afforded the title product in 74% yield (97.2 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.66-0.68 (m, 2H), 0.98-1.00 (m, 2H), 1.11 (s, 9H), 1.43 (s, 12H), 1.97-2.03 (m, 1H), 4.26 (bs, 2H), 7.24-7.42 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -2.96, 8.23, 12.71, 18.65, 25.78, 26.33, 83.41, 120.34, 123.63, 123.70, 124.33, 125.54, 125.68, 127.09, 135.74, 147.47. The carbon directly

attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3437, 3351, 2956, 2930, 2858, 1619, 1443, 1399, 1308, 1248, 1140, 1078, 976, 840, 808 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{39}{}^{10}BNO_3Si$ $[M+H]^+$: 439.2823, found 439.2821.



2r

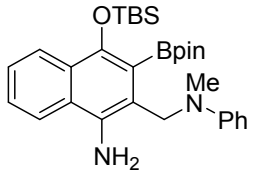
4-((*tert*-Butyldimethylsilyl)oxy)-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2r). Condition B was used. (*o*-Cyano)phenylpropargyl ether **1r** (112.7 mg, 0.3 mmol), toluene (1.5 mL), DBU (89.6 μL, 0.6 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 36 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1 to 15/1, containing 1% v/v Et_3N) afforded the title product in 73% yield (110 mg) as a reddish brown solid. ^{1}H NMR (400 MHz, C_6D_6) δ 0.19 (s, 6H), 1.211 (s, 12H), 1.214 (s, 9H), 3.06-3.30 (m, 6H), 7.09-7.13 (m, 1H), 7.18-7.22 (m, 2H), 7.26-7.32 (m, 4H), 7.54-7.56 (m, 1H), 8.33-8.35 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ -2.76, 18.99, 25.62, 26.68, 33.67, 36.27, 83.50, 121.21, 123.86, 124.33, 124.69, 125.94, 126.22, 126.82, 127.67, 128.70, 128.72, 134.16, 142.97, 149.08. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3345, 2930, 2857, 1625, 1582, 1472, 1392, 1306, 1254, 1138, 1078, 970, 839 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{43}{}^{10}BNO_3Si$ $[M+H]^+$: 503.3136, found 503.3132.



2s

2-(2-(Benzyloxy)ethyl)-4-((*tert*-butyldimethylsilyl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2s). Condition A was used.

(*o*-Cyano)phenylpropargyl ether **1s** (121.7 mg, 0.3 mmol), toluene (1.5 mL), KO^{t}Bu (5.0 mg, 0.045 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol) and dppf (8.3 mg, 0.015 mmol) were stirred at room temperature for 28 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1, containing 1% v/v Et_3N) afforded the title product in 79% yield (125.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 6H), 1.12 (s, 9H), 1.37 (s, 12H), 3.13 (t, *J* = 6.4 Hz, 2H), 3.79 (t, *J* = 6.4 Hz, 2H), 4.20 (bs, 2H), 4.50 (s, 2H), 7.21-7.40 (m, 7H), 7.72 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.24, 18.56, 25.49, 26.23, 32.17, 71.48, 73.24, 83.57, 120.32, 121.48, 123.49, 124.26, 125.58, 125.97, 127.01, 127.43, 127.53, 128.26, 134.59, 138.32, 147.88. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3453, 3364, 2959, 2929, 2856, 1621, 1368, 1252, 1140, 1079, 969, 885, 837 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{45}{}^{10}BNO_4Si$ $[M+H]^+$: 533.3242, found 533.3240.

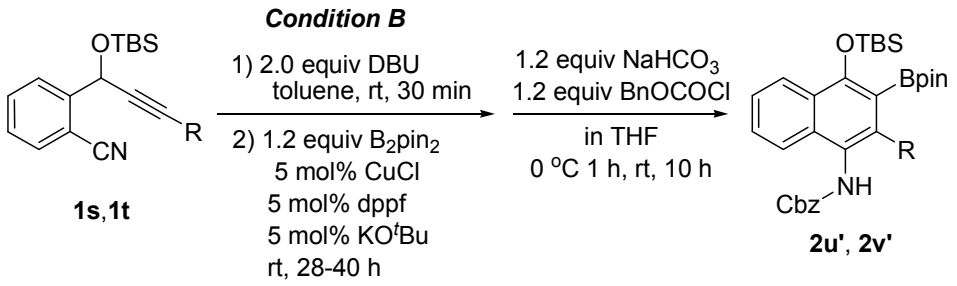


2t

4-((*tert*-Butyldimethylsilyl)oxy)-2-((methyl(phenyl)amino)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-amine (2t). Condition B was used. (*o*-Cyano)phenylpropargyl ether **1t** (117.2 mg, 0.3 mmol), toluene (1.5 mL), DBU (89.6 μL, 0.6 mmol), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1, containing 1% v/v Et_3N) afforded the title product in 85% yield (132 mg) as a yellow sticky oil. ^{1}H NMR (400 MHz, C_6D_6) δ 0.21 (s, 6H), 1.13 (s, 12H), 1.20 (s, 9H), 2.70 (s, 3H), 4.13 (bs, 2H), 4.56 (s, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.20-7.32 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ -2.71, 18.99, 25.64, 26.68, 36.12, 54.06, 83.71, 115.13, 118.75, 118.88, 121.07, 124.48, 124.64, 125.78, 125.98, 129.57, 137.28, 147.52, 151.72. The carbon directly

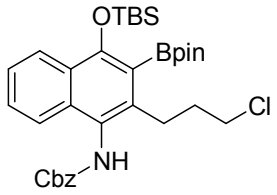
attached to the boron atom was not detected, likely due to quadrupolar broadening. One carbon is overlapped with other signals. IR (film): 3431, 3351, 2929, 2851, 1630, 1596, 1503, 1142, 1370, 1255, 1140, 1072, 928, 866 cm^{-1}. HRMS(EI) calcd for $C_{30}H_{43}{}^{10}BN_2O_3Si$ $[M]^+$: 517.3167, found 517.3164.

Synthesis of 1-naphthylamines 2u'-2v'.



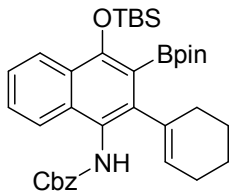
The reaction was carried out in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, to a screw-cap vial were added (*o*-cyano)phenylpropargyl ether **1u** or **1v** (0.3 mmol), toluene (1.5 mL), DBU (89.6 μL, 0.6 mmol), and stirred for 30 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were added successively. The vial cap was then securely fitted and taken outside the glove box. The reaction mixture was stirred at room temperature until the reaction was complete as monitored by TLC (for **1u**, 28 h. for **1v**, 40 h). The resulting mixture was diluted with ethyl acetate, washed with saturated NH_4Cl solution, water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the free 1-naphthylamine crude product, which was used directly without further purification for the next step.

To a solution of the above crude 1-naphthylamine in THF (5 mL) was added $NaHCO_3$ (30.2 mg, 0.36 mmol) under air, then the recation mixture was cooled down to 0 ^oC, and $ClCO_2Bn$ (61.4 mg, 0.36 mmol) was added. The resulting mixture was stirred at 0 ^oC for 1 h and at room temperature for 10 h. Then the mixture was quenched with water, extracted with ethyl acetate, washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel followed by recycling preparative HPLC to afford the title products.



2u'

Benzyl 4-(*tert*-butyldimethylsilyloxy)-2-(3-chloropropyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-ylcarbamate (2u'). (*o*-cyano)phenylpropargyl ether **1u** (104.4 mg, 0.3 mmol) was used in the reaction. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate / dichloromethane = 15/1/1 to 10/1/1) followed by recycling preparative HPLC to afford the **2u'** in 70% overall yield (128.2 mg) as a colorless oil. ^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C) δ 0.15 (s, 6H), 1.11 (s, 9H), 1.40 (s, 12H), 2.03-2.05 (m, 2H), 2.90-2.92 (m, 2H), 3.60 (t, J = 6.6 Hz, 2H), 5.17 (s, 2H), 7.34-7.40 (broad, 4H), 7.45-7.54 (m, 2H), 7.82 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.83 (bs, 1H). One of the proton was not found. ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C) δ -3.43, 17.95, 24.83, 25.75, 29.11, 33.38, 44.67, 65.35, 83.27, 117.52, 122.59, 122.78, 123.71, 124.96, 126.07, 126.66, 127.09, 127.28, 127.83, 132.87, 136.84, 140.08, 153.98, 155.11. IR (film): 2979, 2954, 2926, 2854, 1777, 1705, 1616, 1365, 1308, 1139, 837, 780, 696 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{49}{}^{10}BClN_2O_5Si$ $[M+NH_4]^+$: 626.3223, found 626.3223.

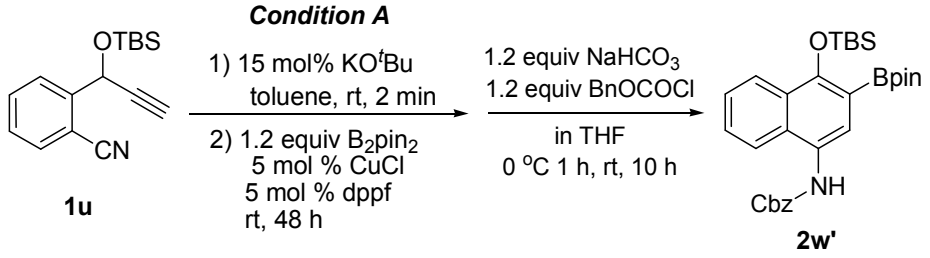


2v'

Benzyl 4-(*tert*-butyldimethylsilyloxy)-2-cyclohex-1-en-1-yl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-ylcarbamate (2v'). (*o*-cyano)phenylpropargyl ether **1v** (105.5 mg, 0.3 mmol) was used in the reaction. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1, containing 1% v/v Et_3N) followed by recycling preparative HPLC afforded the title product **2v'** in 81% overall yield (148.8 mg) as a colorless oil. ^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C) δ 0.19 (s, 6H), 1.11 (s, 9H), 1.34

(s, 12H), 1.63-1.72 (m, 4H), 2.075-2.084 (m, 2H), 2.25 (bs, 2H), 5.12 (s, 2H), 5.40 (bs, 1H), 7.32-7.36 (broad, 4H), 7.45-7.48 (m, 1H), 7.51-7.53 (m, 1H), 7.86 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 8.46 (bs, 1H). One of the proton was not found. ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C) δ -3.39, 17.95, 21.07, 21.90, 24.47, 24.85, 25.74, 28.96, 65.10, 82.88, 117.92, 122.66, 122.83, 123.68, 123.74, 124.82, 126.10, 126.33, 127.07, 127.18, 127.74, 132.64, 136.95, 137.68, 144.18, 152.90, 155.07. IR (film): 3239, 3070, 2928, 2856, 1702, 1447, 1367, 1143, 1080, 1040, 973, 839 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{52}{}^{10}BN_2O_5Si$ $[M+NH_4]^+$: 630.3769, found 630.3769. The structure of **2v'** was determined by X-ray crystal analysis.

Synthesis of 1-naphthylamine 2w'.



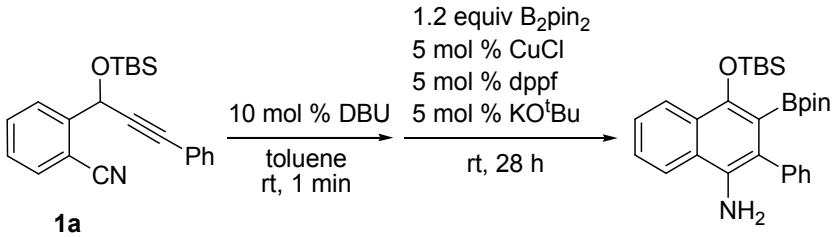
The reaction was carried out in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, to a screw-cap vial were added (*o*-cyano)phenylpropargyl ether **1w** (81.4 mg, 0.3 mmol), toluene (1.5 mL) and KO^{t}Bu (5.0 mg, 0.045 mmol), and stirred for 2 min, then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol) and dppf (8.3 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 48 h. The resulting reaction mixture was diluted with ethyl acetate, washed with saturated NH_4Cl solution, water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the free 1-naphthylamine crude product, which was used directly without further purification for the next step.

To a solution of the above crude 1-naphthylamine in THF (5 mL) was added $NaHCO_3$ (30.2 mg, 0.36 mmol) under air, then the recation mixture was cooled down to 0 ^{o}C, and $ClCO_2Bn$ (50.7 μL, 0.36 mmol) was added. The resulting mixture was stirred at 0 ^{o}C for 1 h and at room temperature for 10 h. Then the mixture was quenched with water, extracted

with ethyl acetate, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 10/1/1) to afford the title product **2w'** in 45% overall yield (72.4 mg) as a light yellow solid.

Benzyl 4-(*tert*-butyldimethylsilyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) naphthalen-1-ylcarbamate (2w'). ^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C) δ 0.17 (s, 6H), 1.12 (s, 9H), 1.35 (s, 12H), 5.20 (s, 2H), 7.32-7.35 (m, 1H), 7.38-7.44 (m, 4H), 7.52-7.59 (m, 2H), 7.71 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 9.11 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C) δ -3.91, 17.88, 24.39, 25.63, 65.43, 82.99, 113.72, 122.49, 123.38, 124.43, 126.66, 126.79, 127.22, 127.33, 127.56, 127.88, 127.97, 131.78, 136.67, 154.76, 154.82. IR (film): 3306, 2929, 2856, 1707, 1494, 1403, 1380, 1254, 1210, 1142, 1080, 880, 842, 780 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{44}{}^{10}BN_2O_5Si$ $[M+NH_4]^+$: 550.3143, found 550.3142.

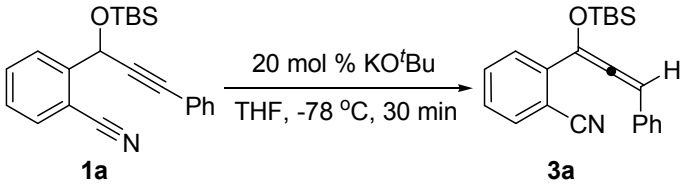
Gram scale study.



In a nitrogen-filled glove box, to a solution of (*o*-cyano)phenylpropargyl ether **1a** (1.738 g, 5 mmol) in toluene (25 mL) was added DBU (74.7 μL, 0.5 mmol), the resulting solution was stirred at room temperature for 1 min. Then B_2pin_2 (1.524 g, 6.0 mmol), CuCl (24.8 mg, 0.25 mmol), dppf (138.6 mg, 0.25 mmol) and KO^{t}Bu (28.0 mg, 0.25 mmol) were added successively. The flask was equipped with a septum, taken outside the glove box, and stirred at room temperature for 28 h. The resulting mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue

was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1, containing 1% v/v Et_3N) to afford **2a** in 94% yield (2.24 g) as a yellow solid.

Synthesis of cyano-allene 3a via KO^{t}Bu-catalyzed isomerization of 1a

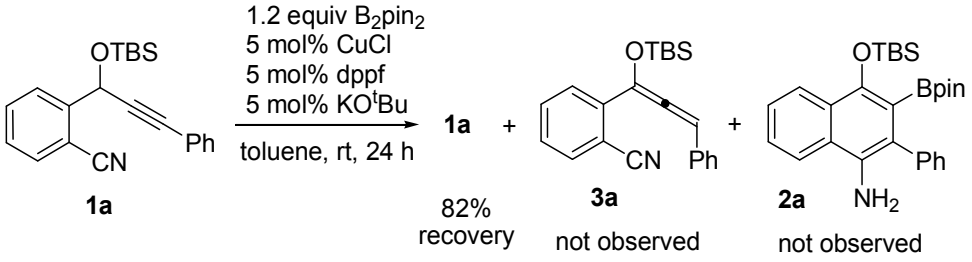


1a **3a**

The reaction was carried out in a Schlenk tube. To a stirred solution of **1a** (173.8 mg, 0.5 mmol) in THF (5.0 mL) was added KO^{t}Bu (11.2 mg, 0.1 mmol) at -78 °C, the color turned to purple immediately. After stirring at -78 °C for 30 min, water was added and the reaction mixture was warmed up to room temperature. Then the resulting reaction mixture was extracted with diethyl ether, and the combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure at ca. 30 °C to afford the pure product **3a** in 98% yield (170.3 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 3H), 0.22 (s, 3H), 0.99 (s, 9H), 6.99 (s, 1H), 7.25-7.41 (m, 6H), 7.55 (t, J = 8.0 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.81, -4.61, 18.23, 25.82, 108.97, 109.59, 118.03, 127.31, 127.34, 127.86, 128.12, 128.23, 128.62, 132.25, 133.66, 134.35, 139.06, 198.95. The spectroscopic data is in agreement with that previously reported.[1]

Mechanistic studies:

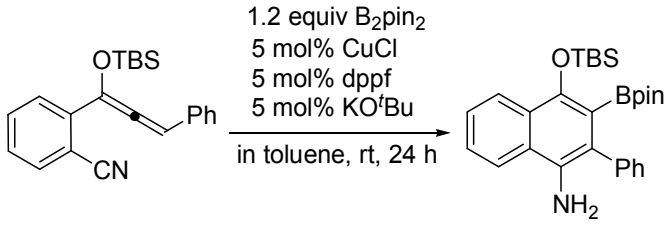
1) Copper-catalyzed reaction of 1a with B_2pin_2 in the absence of DBU.



In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added (*o*-cyano)phenylpropargyl ether **1a** (69.5 mg, 0.2 mmol), toluene (1.0 mL), B_2pin_2 (60.9 mg, 0.24 mmol), CuCl (1.0 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol) and

KO^{t}Bu (1.1 mg, 0.01 mmol) successively. The vial was tightly capped, taken outside the glove box and stirred at room temperature for 24 h. Allene **3a** and 1-naphthylamine product **2a** were not observed according to TLC analysis. The reaction mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60/1) to afford **1a** in 82% yield (57.1 mg) as a light yellow oil.

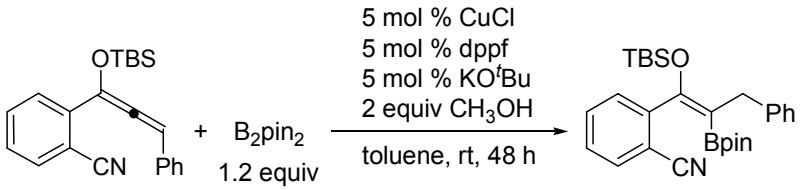
2) Copper-catalyzed reaction of allene 3a with B_2pin_2.



3a **2a**, 94%

In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added allene-nitrile **3a** (69.5 mg, 0.2 mmol), toluene (1.0 mL), B_2pin_2 (60.9 mg, 0.24 mmol), CuCl (1.0 mg, 0.01 mmol) and dppf (5.5 mg, 0.01 mmol) and KO^{t}Bu (1.1 mg, 0.01 mmol) successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 24 h. The resulting mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1, containing 1% v/v Et_3N) to afford **2a** in 94% yield (89.6 mg) as a brown solid.

3) Hydroborylation of allene 3a.

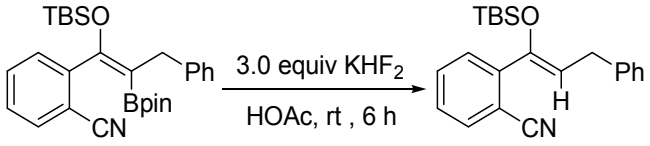


3a **4a**, 73%

In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added allene-nitrile **3a** (104.3 mg, 0.3 mmol), toluene (1.5 mL), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7

mg, 0.015 mmol) successively. The vial was tightly capped and taken outside the glove box. CH_3OH (19.2 mg, 0.6 mmol) was then added, and the resulting mixture was stirred at room temperature for 48 h. The mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **4a** in 73% yield (103.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.19 (s, 3H), -0.13 (s, 3H), 0.87-0.92 (m, 21H), 3.72 (ABq, J = 14.0 Hz, 2H), 7.12-7.14 (m, 1H), 7.22-7.26 (m, 2H), 7.34-7.43 (m, 4H), 7.49-7.53 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.32, -4.20, 18.18, 24.23, 24.34, 25.56, 33.63, 82.69, 113.28, 118.32, 125.30, 127.86, 128.16, 128.87, 130.45, 131.55, 132.07, 141.95, 143.94, 155.28. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 2923, 2856, 2224, 1616, 1591, 1371, 1255, 1143, 1177, 832, 780 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{42}{}^{10}BN_2O_3Si$ $[M+NH_4]^+$: 492.3089, found 492.3089.

4) Conversion of 4a to 5.[5]

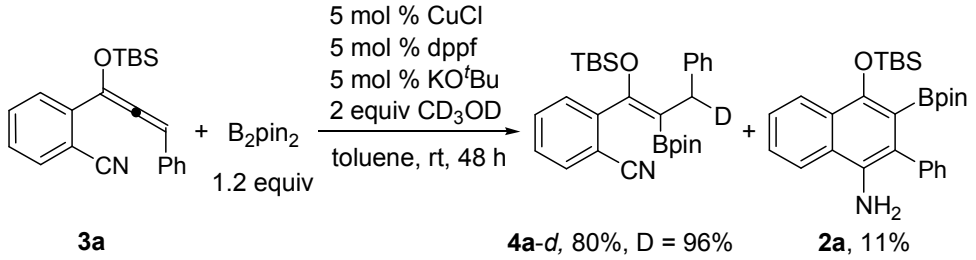


4a **5**, 92%

To a solution of **4a** (95.1 mg, 0.2 mmol) in HOAc (3 mL) was added KHF_2 (46.9 mg, 0.6 mmol) under air, the reaction mixture was stirred at room temperature until the reaction was complete as monitored by TLC (6 h). Then water was added, and the resulting mixture was extracted with diethyl ether. The organic layer was added solid K_2CO_3. The aqueous layer was neutralized by adding solid K_2CO_3 and then extracted with diethyl ether. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) to afford the **5** in 92% yield (64.5 mg) as a colorless oil, which can be solidified upon standing in the refrigerator. ^{1}H NMR (400 MHz, C_6D_6) δ -0.07 (s, 6H), 0.97 (s, 9H), 3.64 (d, J = 7.2 Hz, 2H), 5.36 (t, J = 7.6 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 6.87 (t, J = 7.6 Hz,

1H), 7.07-7.11 (m, 2H), 7.16-7.22 (m, 3H), 7.32 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6) δ -4.19, 18.41, 25.90, 32.59, 111.35, 115.85, 118.45, 126.38, 127.98, 128.83, 128.87, 128.88, 131.89, 133.40, 140.94, 143.68, 146.99. IR (film): 2955, 2929, 2857, 2224, 1653, 1472, 1254, 1200, 1026, 838, 781 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{31}N_2OSi$ $[M+NH_4]^+$: 367.2200, found 367.2205. The structure of **5** was determined by X-ray crystal analysis.

5) Deuterium-labeling experiment.

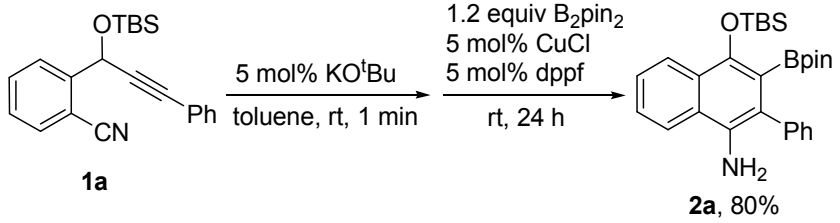


3a **4a**-*d,* 80%, D = 96% **2a**, 11%

In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added allene-nitrile **3a** (104.3 mg, 0.3 mmol), toluene (1.5 mL), B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) successively. The vial was tightly capped and taken outside the glove box. CD_3OD (21.6 mg, 0.6 mmol) was then added, and the mixture was stirred at room temperature for 48 h. The reaction mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1 to 15/1) to afford **4a**-*d* in 80% yield (114.9 mg, D = 96%) as a colorless sticky oil and **2a** in 11% yield (15.4 mg) as a brown solid.

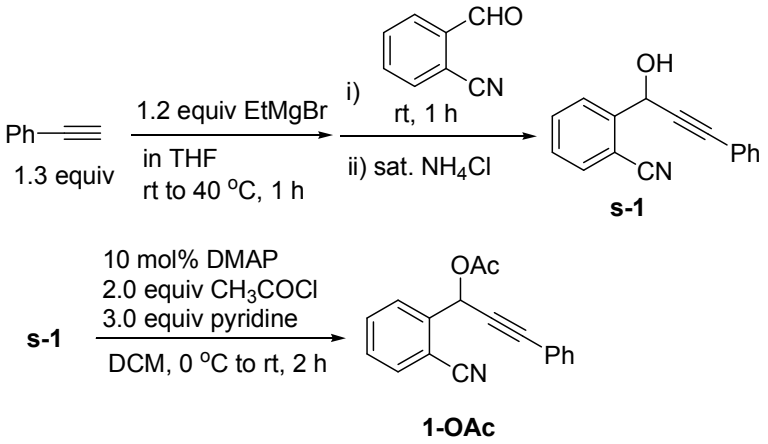
4a-*d*, ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.19 (s, 3H), -0.13 (s, 3H), 0.88-0.92 (m, 21H), 3.67, 3.73 (s, s, 1.04H), 7.10-7.14 (m, 1H), 7.22-7.26 (m, 2H), 7.35-7.43 (m, 4H), 7.49-7.53 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.33, -4.21, 18.16, 24.22, 24.32, 25.55, 33.31 (t, J = 18.7 Hz), 82.67, 113.26, 118.30, 125.29, 127.84, 128.15, 128.85, 130.44, 131.54, 132.04, 141.89, 143.92, 155.29. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 2926, 2856, 2224, 1619, 1588, 1371, 1253, 1142, 1071, 832, 781 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{41}D^{10}BN_2O_3Si$ $[M+NH_4]^+$: 493.3151, found 493.3118.

Synthesis of 1-naphthylamine 2a using KO^{t}Bu as the only base.



In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added (*o*-cyano)phenylpropargyl ether **1a** (69.5 mg, 0.2 mmol), toluene (1.0 mL) and KO^{t}Bu (1.1 mg, 0.01 mmol), the resulting dark brown solution was stirred for 1 min at room temperature. Then B_2pin_2 (60.9 mg, 0.24 mmol), CuCl (1.0 mg, 0.01 mmol) and dppf (5.5 mg, 0.01 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 24 h. The reaction mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1, containing 1% v/v Et_3N) to afford **2a** in 80% yield (76.3 mg) as a brown solid.

Synthesis of Ac-protected substrate 1-(2-cyanophenyl)-3-phenylprop-2-ynyl acetate (1-OAc).

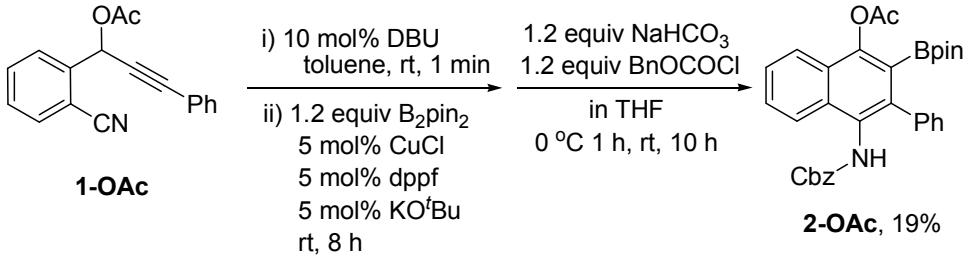


To a solution of ethynylbenzene (663.8 mg, 6.5 mmol) in THF (15 mL) was added dropwise EtMgBr (2.0 mL, 3.0 M solution in Et_2O, 6.0 mmol) at room temperature under argon. Then the reaction mixture was warmed up to 40 °C and stirred for 1 h. After cooling to room temperature, 2-cyanobenzaldehyde (656 mg, 5.0 mmol) was added and the

reaction mixture was stirred 1 h. The resulting reaction mixture was quenched with saturated NH_4Cl solution, and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the alcohol **s-1** as a light yellow oil, which was used directly without further purification for the next step.

To a solution of the above crude alcohol **s-1**, DMAP (61.1 mg, 0.5 mmol) and pyridine (1.2 mL, 15.0 mmol) in DCM (15 mL) was added acetyl chloride (0.7 mL, 10 mmol) at 0 ^{o}C under air. Then ice bath was removed, and the reaction mixture was stirred at room temperature for 2 h. Then the resulting mixture was quenched with saturated ammonium chloride solution and extracted with dichloromethane, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **1-OAC** in 86% overall yield (1.19 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 6.86 (s, 1H), 7.31-7.32 (m, 3H), 7.45-7.48 (m, 3H), 7.64-7.72 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.57, 64.03, 83.60, 88.34, 111.68, 116.62, 121.44, 128.21, 128.62, 129.02, 129.23, 131.85, 132.99, 133.43, 140.17, 169.18. IR (neat): 3065, 2926, 2224, 1746, 1488, 1363, 1207, 1016, 956, 755, 690 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2$ $[M+NH_4]^+$: 293.1285, found 293.1283.

Copper-catalyzed reaction of Ac-protected substrate (1-OAc) with Bis(pinacolato)diboron.

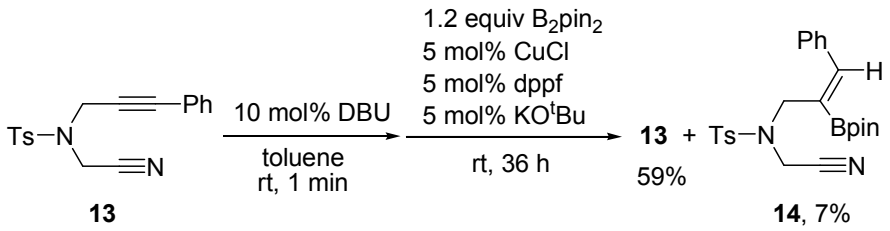


In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added 1-(2-cyanophenyl)-3-phenylprop-2-yn-1-yl acetate **1-OAc** (82.6 mg, 0.3 mmol), toluene (1.5 mL) and DBU (4.5 μL, 0.03 mmol), and stirred for 1 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and

KO^{t}Bu (1.7 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and the reaction mixture was stirred until the reaction was complete as monitored by TLC (8 h). The resulting reaction mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the free 1-naphthylamine crude product, which was used directly without further purification for the next step.

To a solution of the above crude 1-naphthylamine in THF (5 mL) was added $NaHCO_3$ (30.2 mg, 0.36 mmol) under air, then the reaction mixture was cooled down to 0 ^oC, and $ClCO_2Bn$ (50.7 μL, 0.36 mmol) was added. The resulting mixture was stirred at 0 ^oC for 1 h and at room temperature for 10 h. Then the mixture was quenched with water, extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1 to 6/1) followed by recycling preparative HPLC to afford the product **2-OAc** in 19% overall yield (31.1 mg) as a light yellow oil. ^1H NMR (600 MHz, DMSO-d_6, 80 ^oC) δ 1.05 (s, 12H), 2.42 (s, 3H), 4.99 (s, 2H), 7.18 (bs, 2H), 7.25-7.36 (m, 8H), 7.59-7.66 (m, 2H), 7.86 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 8.75 (bs, 1H). ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^oC) δ 20.13, 24.07, 65.13, 83.26, 121.50, 123.46, 125.76, 126.30, 126.65, 126.96, 127.01, 127.23, 127.33, 127.83, 128.12, 129.11, 132.49, 136.73, 139.02, 140.94, 148.63, 154.78, 168.68. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 3298, 2979, 2923, 1766, 1709, 1360, 1328, 1221, 1200, 1143, 761, 700 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{36}{}^{10}BN_2O_6$ $[M+NH_4]^+$: 554.2697, found 554.2693.

Copper-catalyzed reaction of *N*-(cyanomethyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)-benzenesulfonamide (13) with bis(pinacolato)diboron.

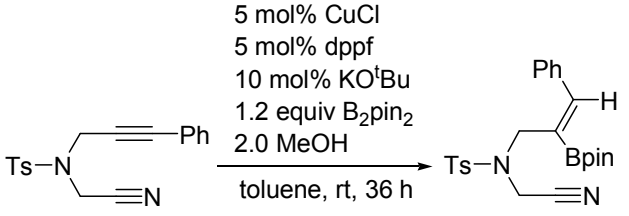


13 **14**, 7%

In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added *N*-linkered alkyne-nitrile **13**[3] (97.3 mg, 0.3 mmol), toluene (1.5 mL) and DBU (4.5 μL, 0.03 mmol), and stirred for 1 min. Then B_2pin_2 (91.4 mg, 0.36 mmol), CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol) and KO^{t}Bu (1.7 mg, 0.015 mmol) were added successively. The vial was tightly capped, taken outside the glove box, and stirred at room temperature for 36 h. Then the resulting mixture was diluted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). The products contain starting material **13** (59% NMR yield) and **14** (7% NMR yield), which could not be separated from each other by column chromatography. Further separation by Recycling Preparative HPLC was then performed, and **14** was isolated in 4% yield which contained a small amount of impurity.

Copper-catalyzed hydroborylation of *N*-(cyanomethyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)-benzenesulfonamide (13).

To further confirm the structure of compound **14**, hydroborylation of **13** was also carried out. The NMR spectra of the resulting product **14** was identical to that obtained by above reaction.



13 **14**, 62%

In a nitrogen-filled glove box, to a screw-cap vial (4 mL) equipped with a magnetic stir bar were added CuCl (1.5 mg, 0.015 mmol), dppf (8.3 mg, 0.015 mmol), KO^{t}Bu (3.4

mg, 0.03 mmol) and toluene (1.5 mL), and stirred for 2 min. Then B_2pin_2 (91.4 mg, 0.36 mmol) was added, the resulting mixture was stirred for 2 min before *N*-linkered alkyne-nitrile **13** (97.3 mg, 0.3 mmol) was added. The vial was tightly capped and taken outside the glove box. CH_3OH (19.2 mg, 0.6 mmol) was then added, and the resulting mixture was stirred at room temperature for 36 h. The mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1 to 8/1) to afford the title product 1**4** in 62% yield (84.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 12H), 2.39 (s, 3H), 4.09 (s, 2H), 4.24 (s, 2H), 7.21-7.38 (m, 7H), 7.51-7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.50, 24.67, 35.99, 45.97, 84.03, 114.14, 127.76, 128.08, 128.28, 129.11, 129.67, 134.01, 135.97, 144.14, 147.30. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (film): 2976, 2923, 1613, 1594, 1354, 1323, 1162, 1143, 1091, 861, 814, 750, 658 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{33}{}^{10}BN_3O_4S$ $[M+NH_4]^+$: 469.2316, found 469.2312.

References:

1) You, X.; Xie, X.; Chen, H.; Li, Y.; Liu, Y. *Chem. Eur. J.* **2015**, *21*, 18699.
2) Zhang, X.; Xie, X.; Liu, Y. *Chem. Sci.* **2016**, *7*, 5815.
3) You, X.; Xie, X.; Wang, G.; Xiong, M.; Sun, R.; Chen, H.; Liu, Y. *Chem. Eur. J.* **2016**, *22*, 16765.
4) Grolleau, J.; Gohier, F.; Allain, M.; Legoupy, S.; Cabanetos, C.; Frère, P. *Organic Electronics*, **2017**, *42*, 322.
5) Cade, I. A.; Ingleson, M. J. *Chem. Eur. J.* **2014**, *20*, 12874.

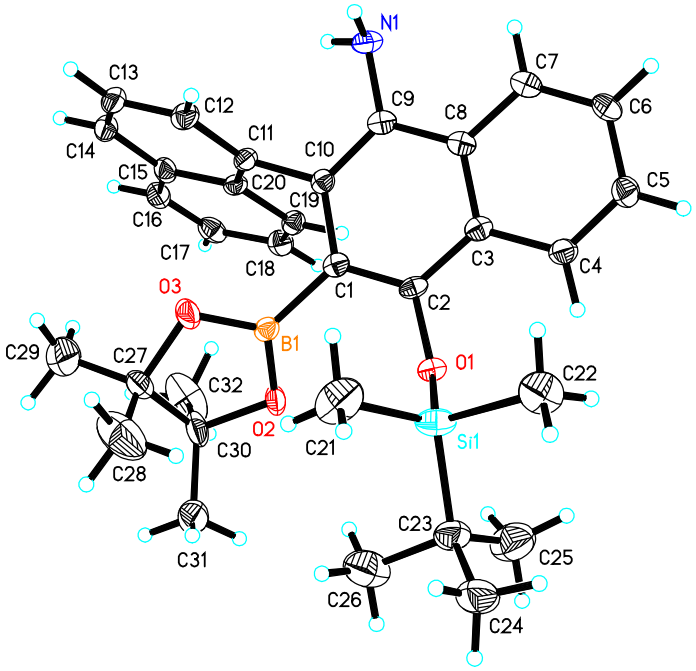


Figure S1. X-ray crystal structure of compound **2k**

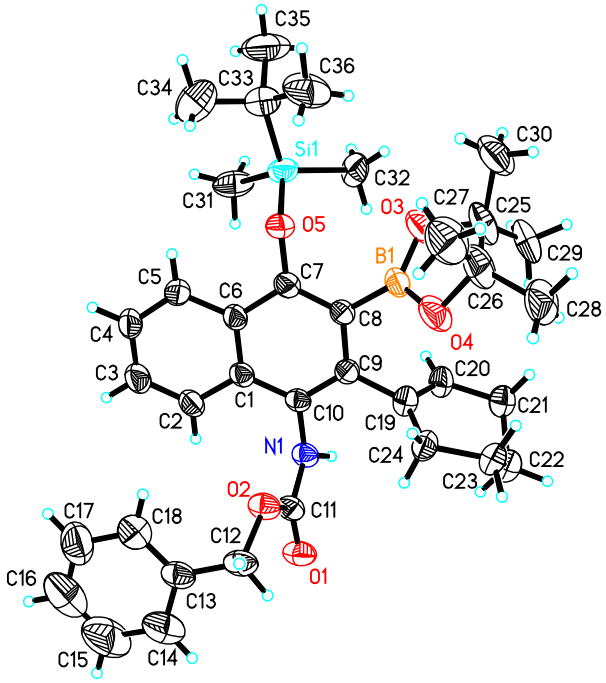


Figure S2. X-ray crystal structure of compound **2v'**

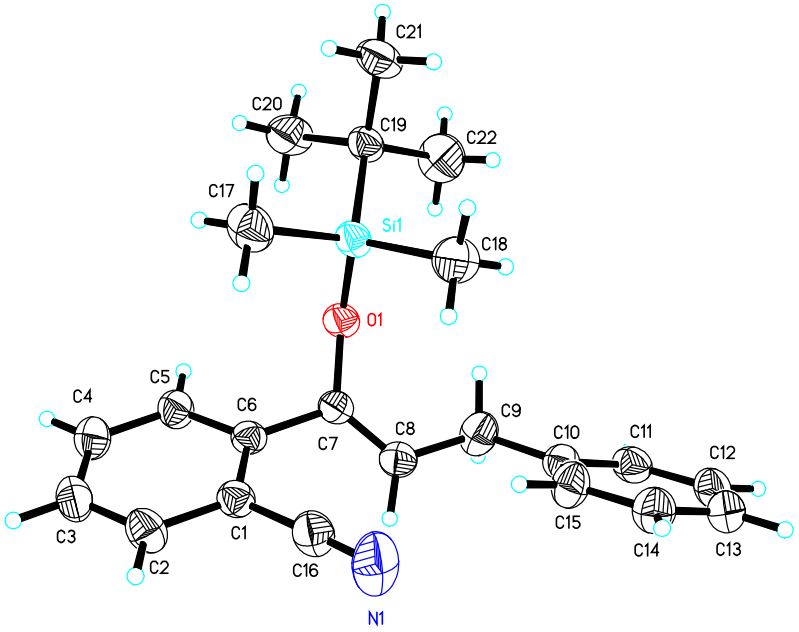
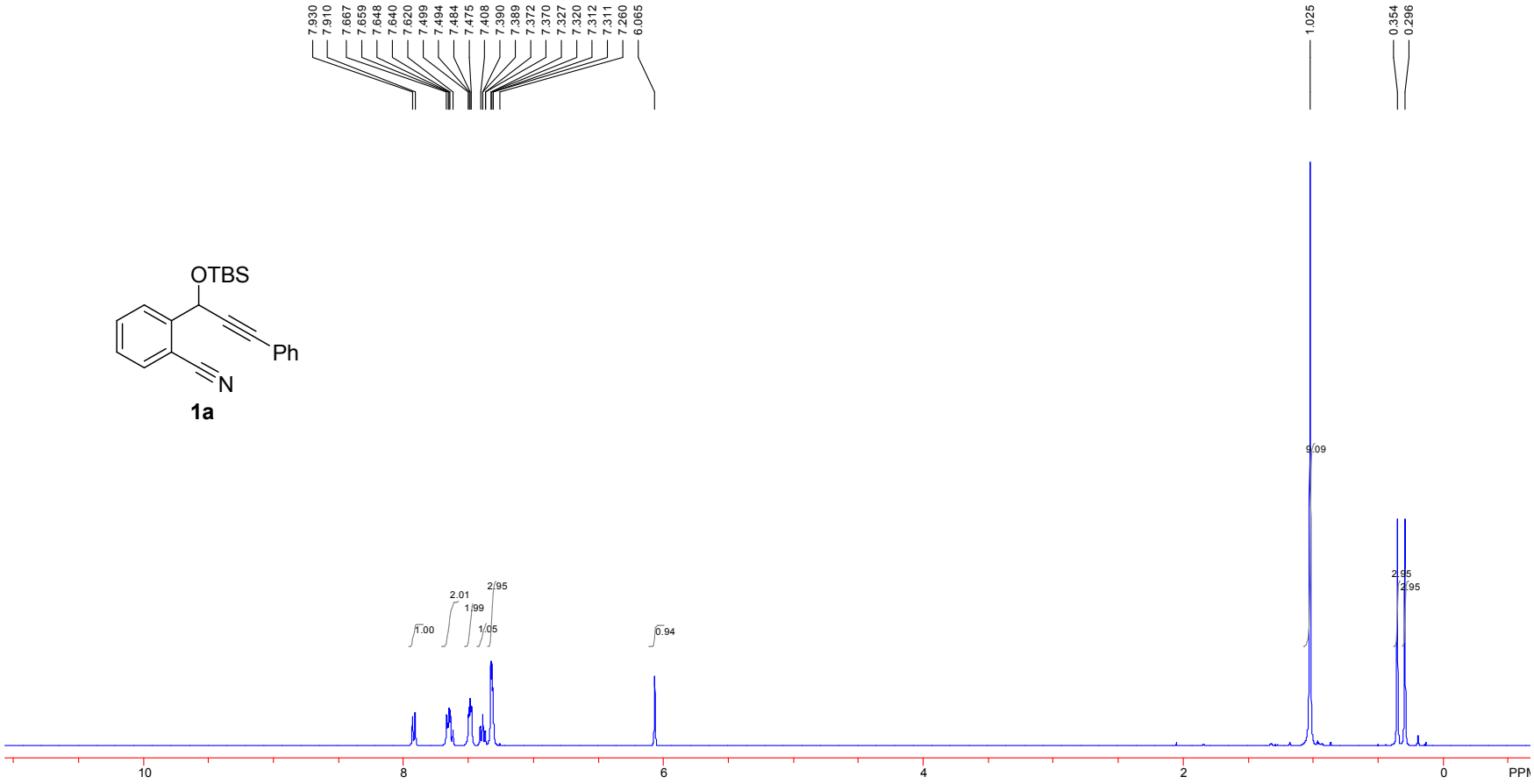
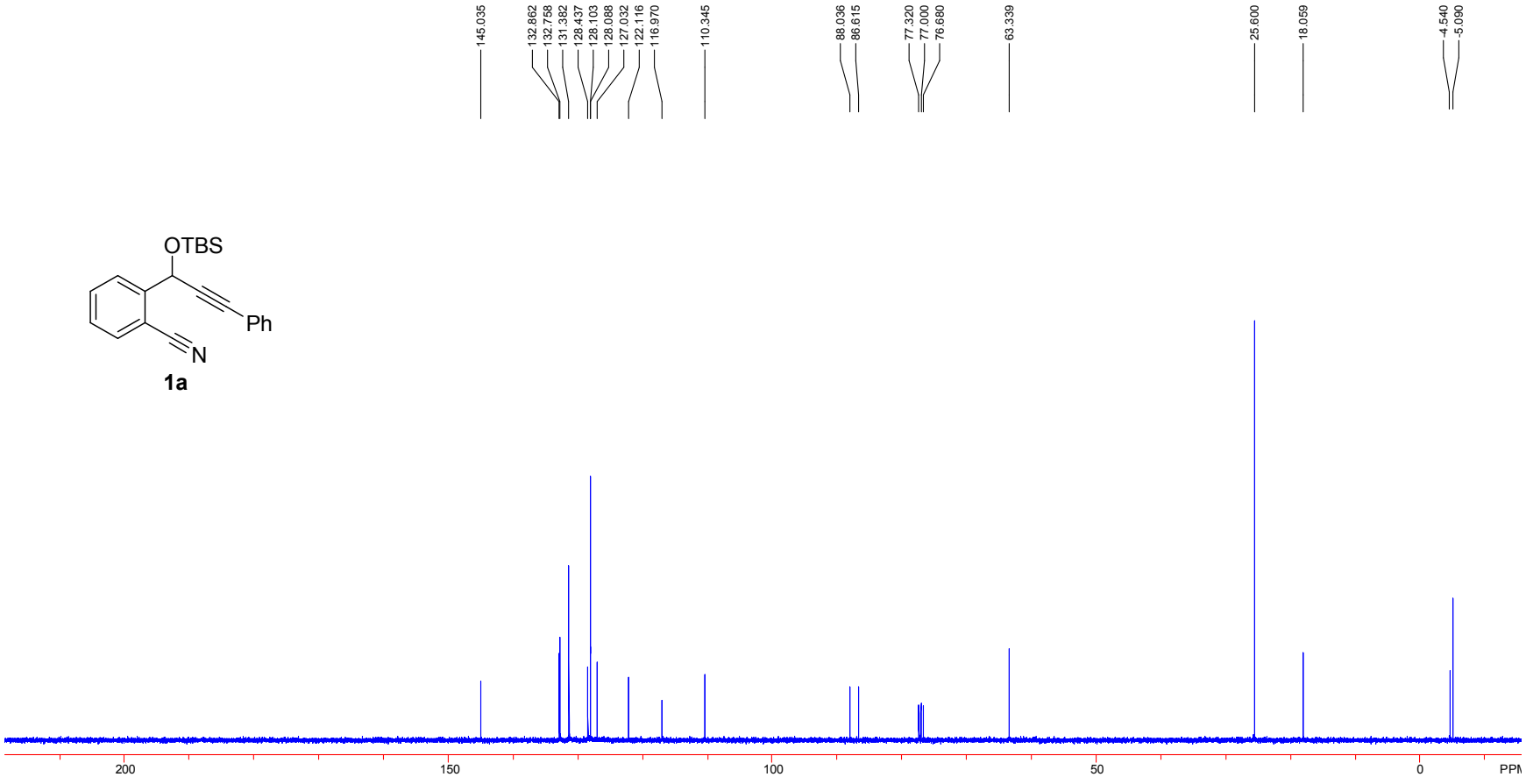


Figure S3. X-ray crystal structure of compound **5**

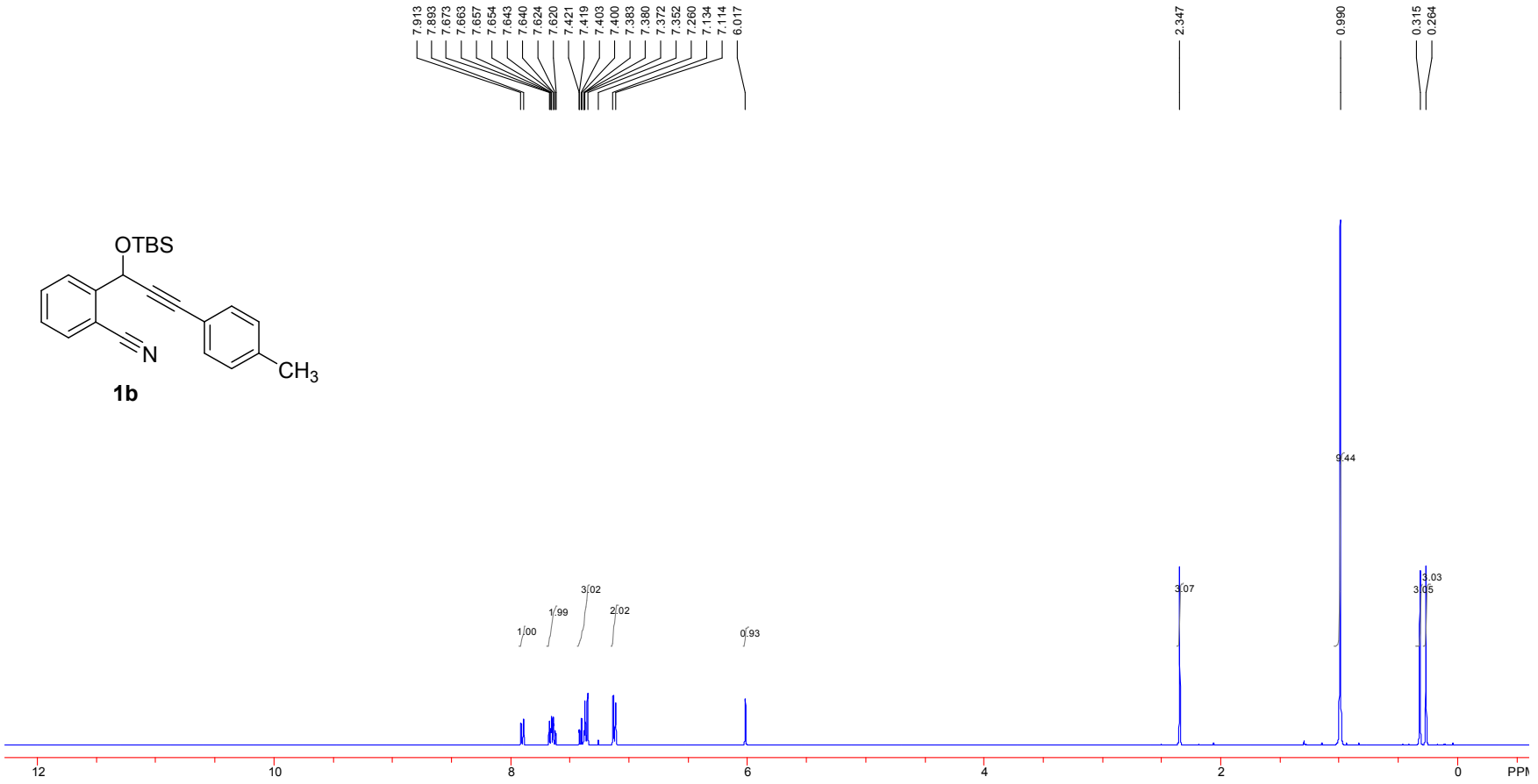
^{1}H NMR (400 MHz, $CDCl_3$)



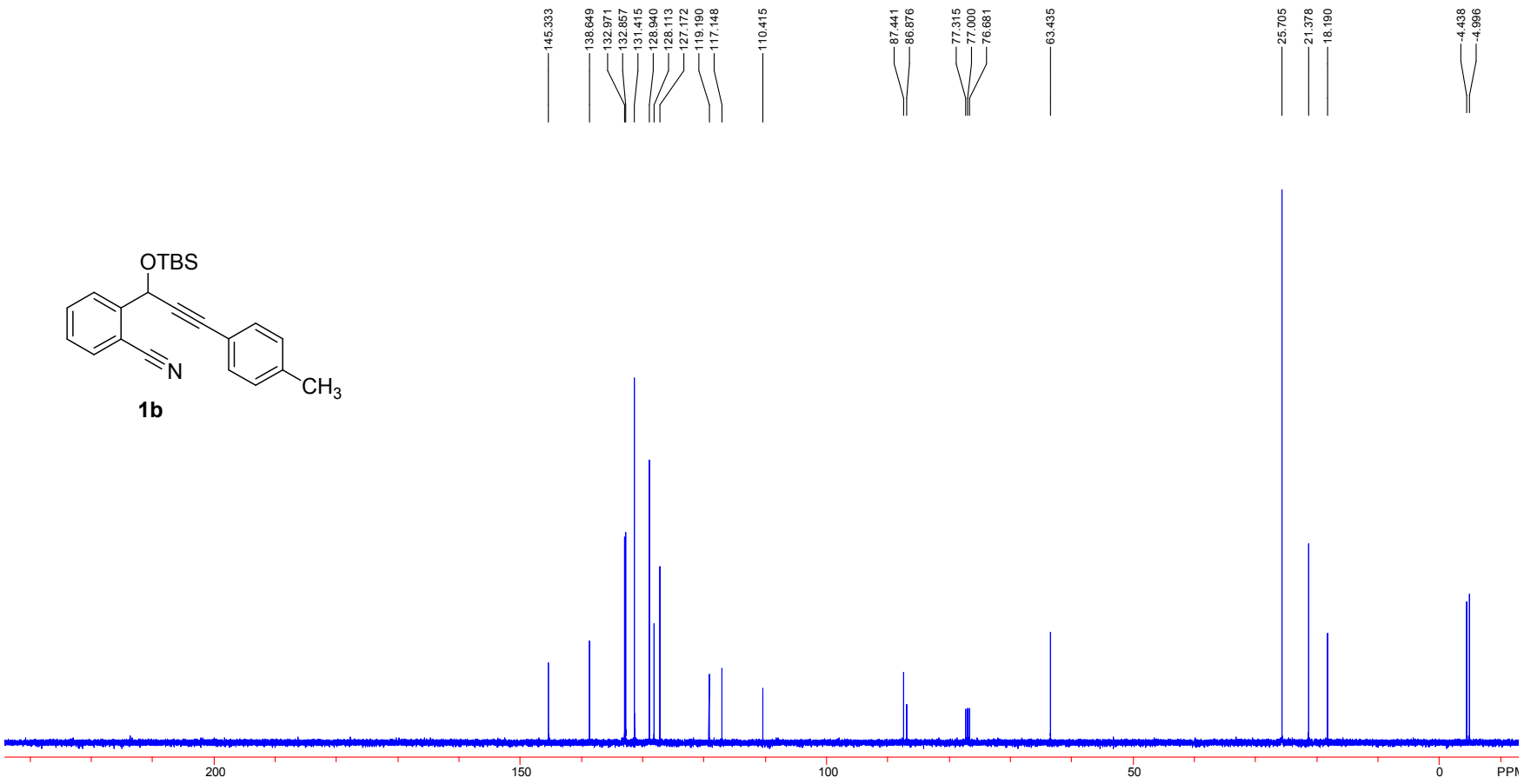
^{13}C NMR (100 MHz, $CDCl_3$)



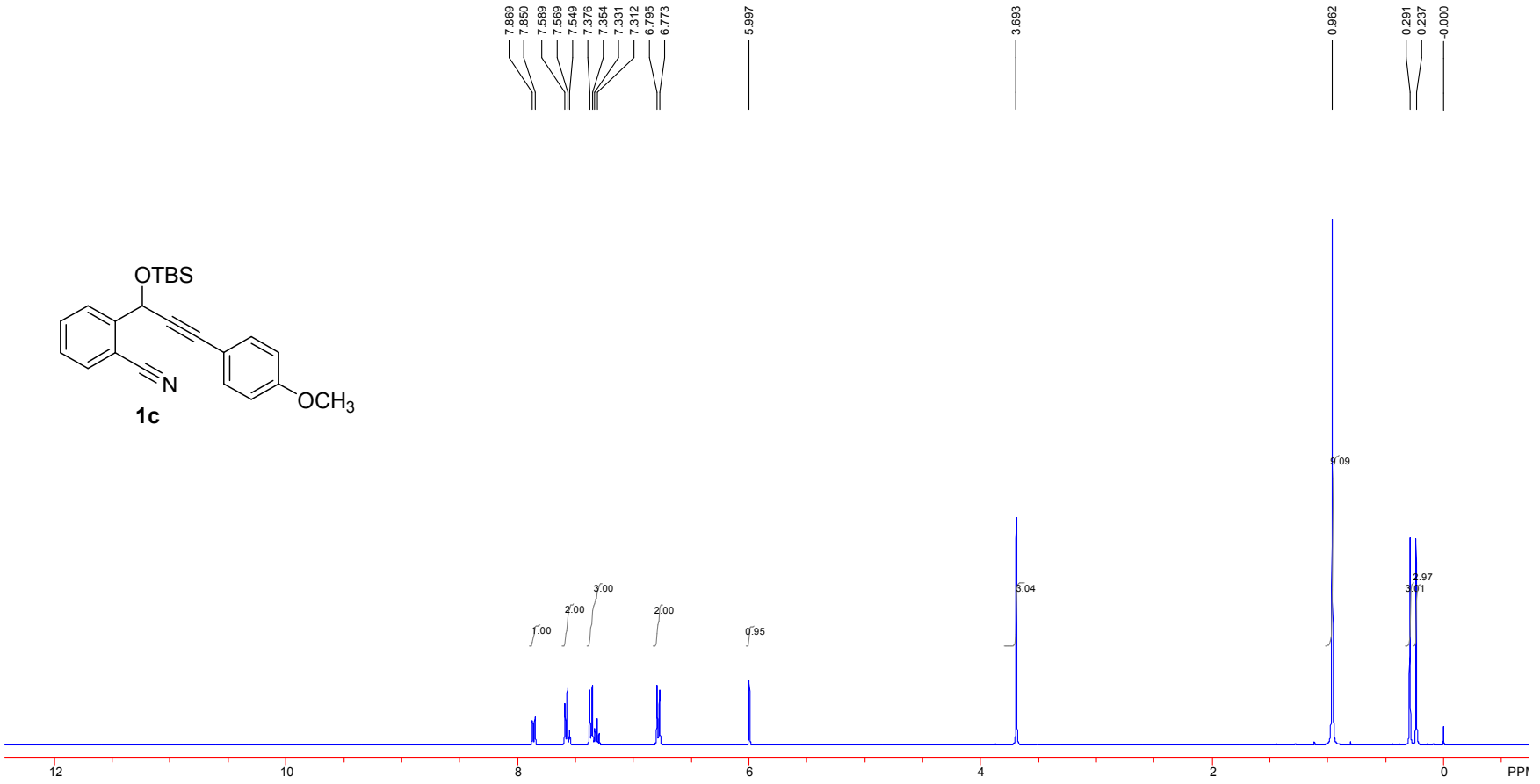
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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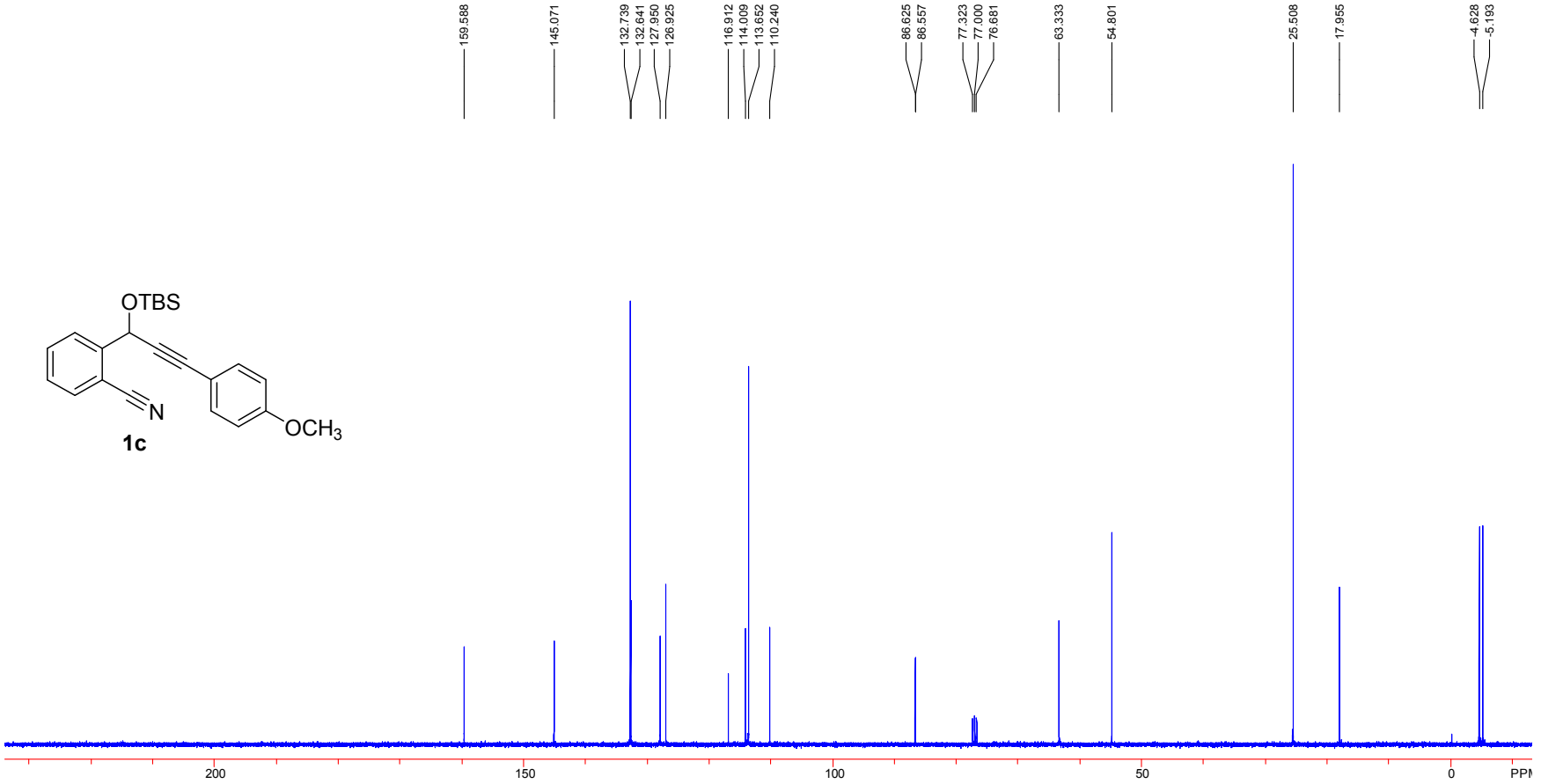
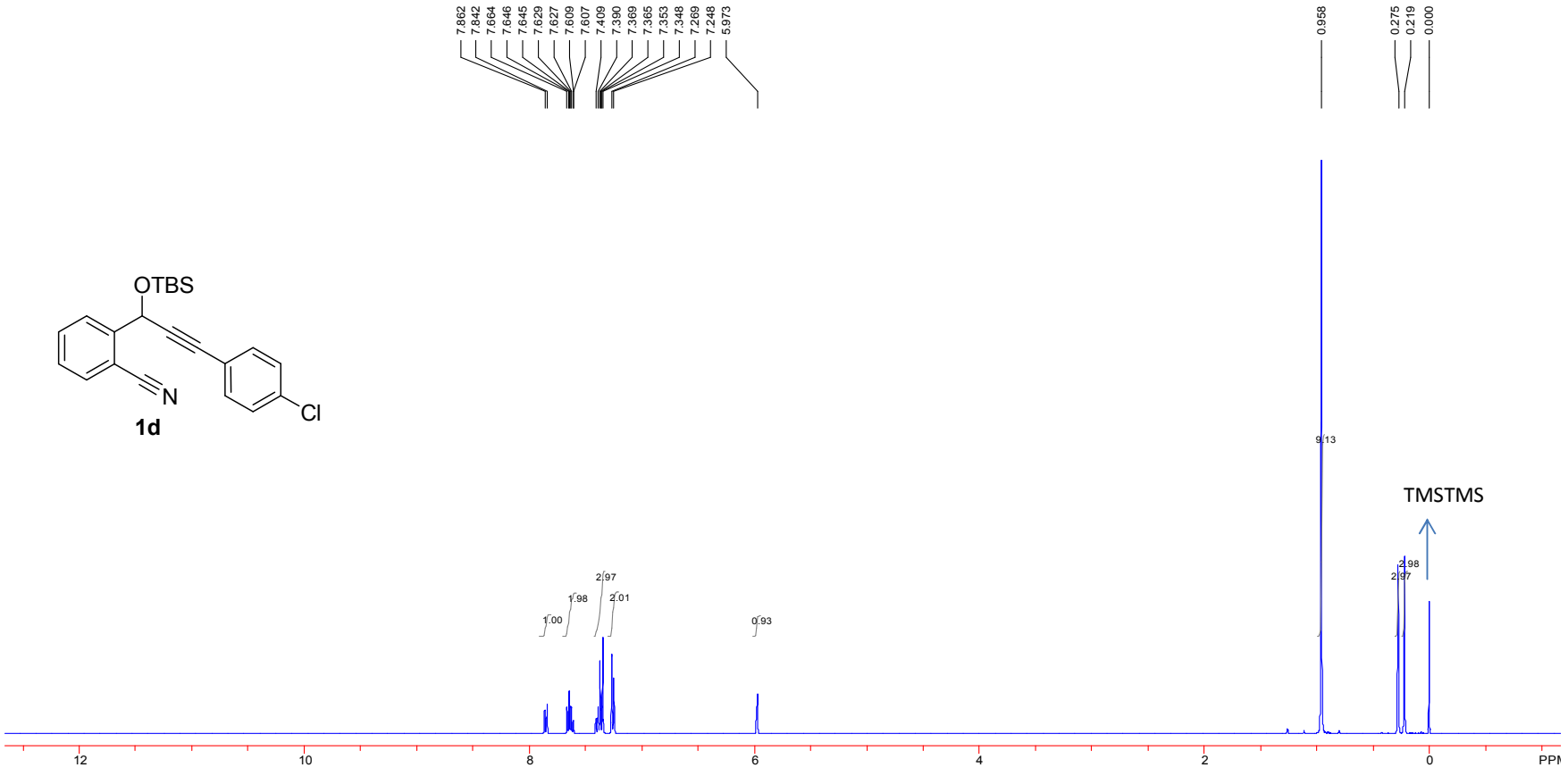


^{1}H NMR (400 MHz, $CDCl_3$)



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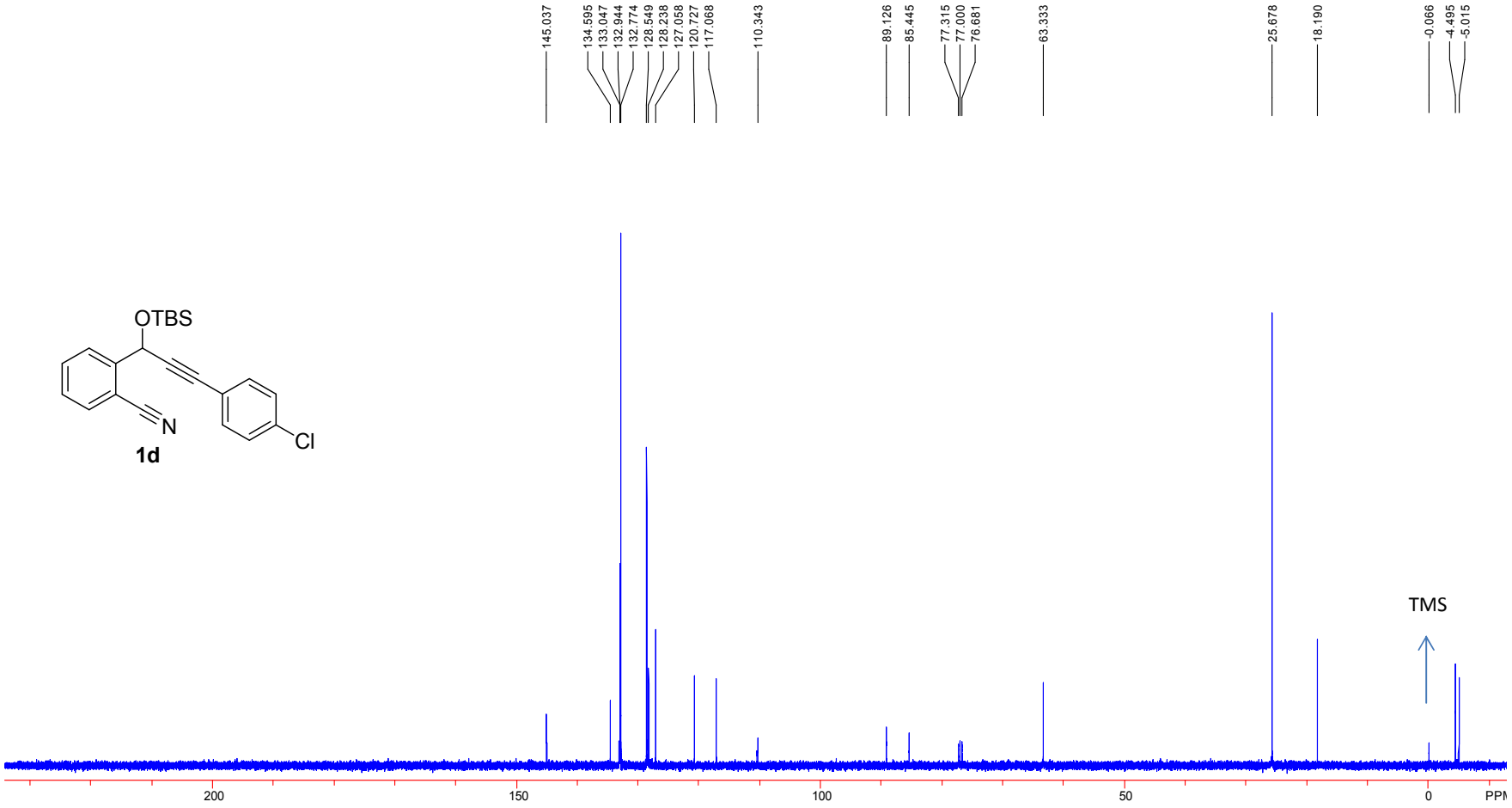

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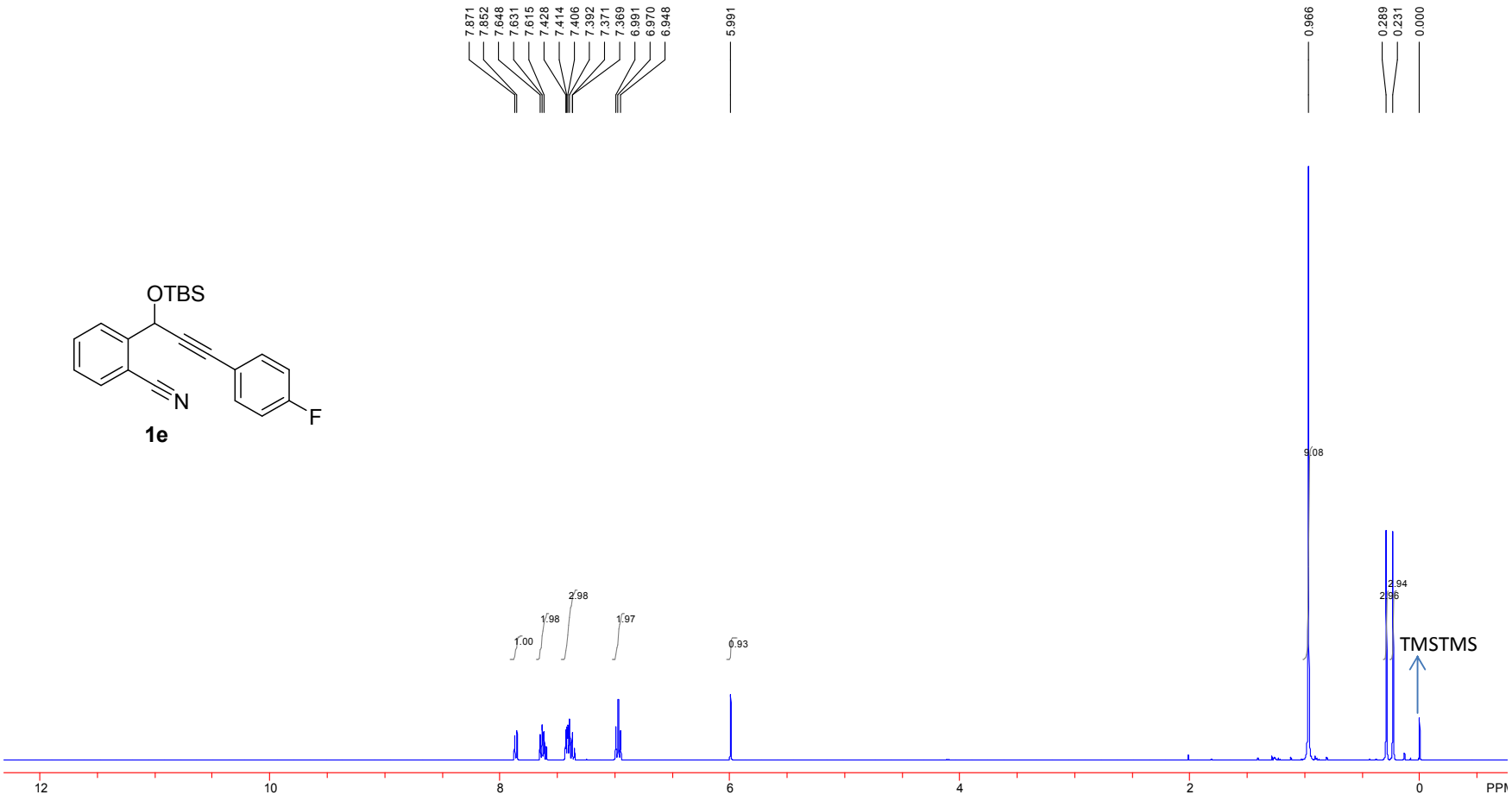

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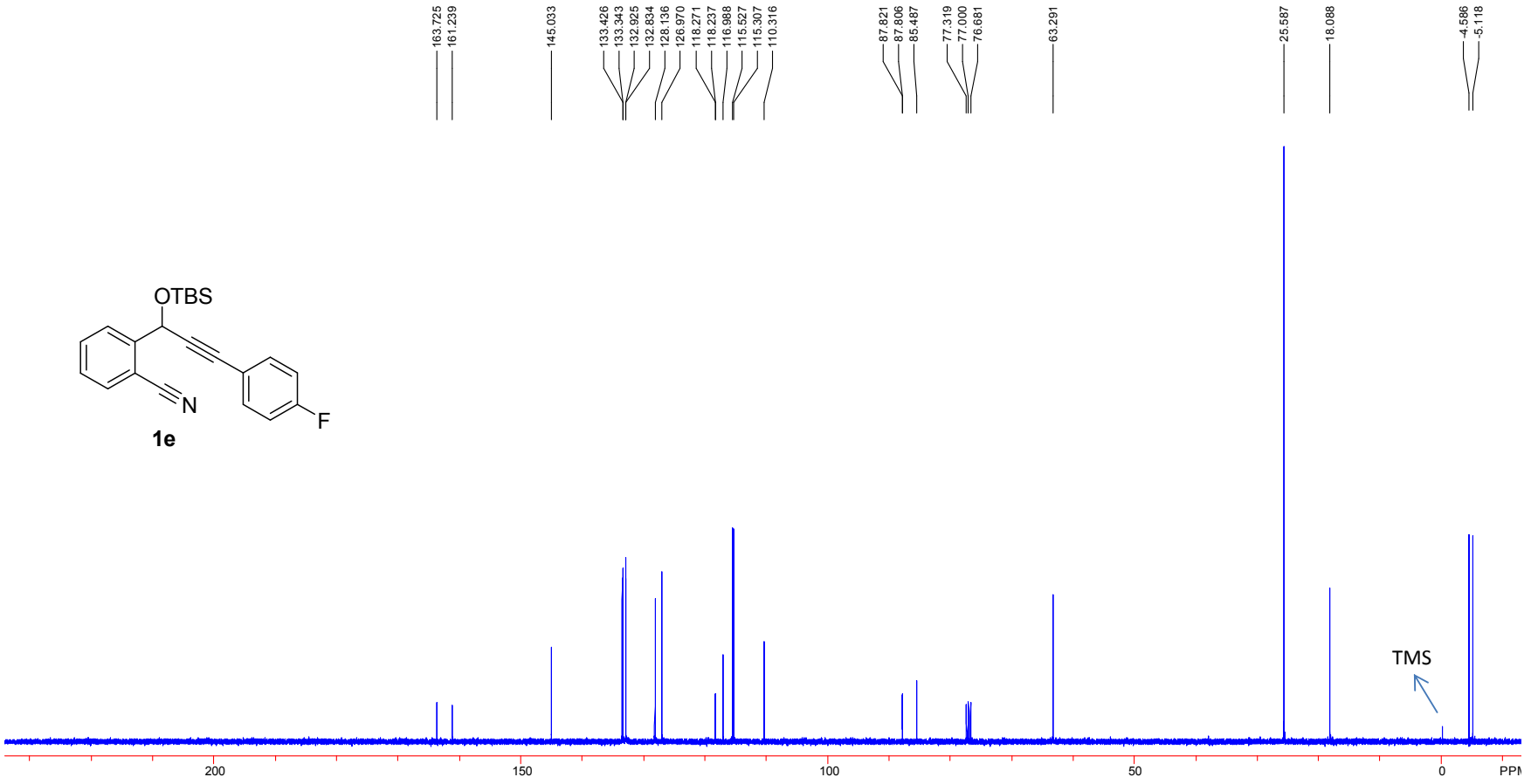
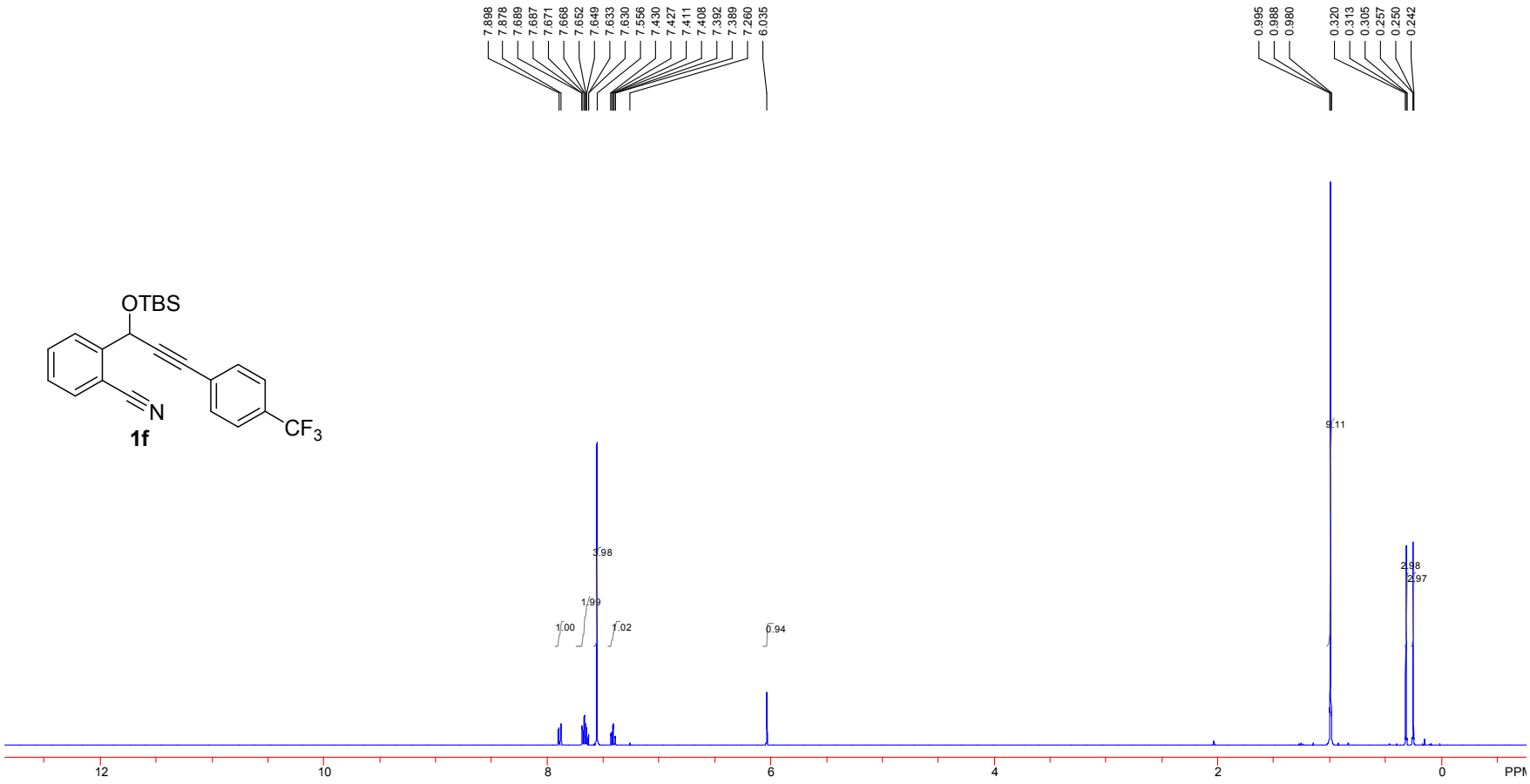
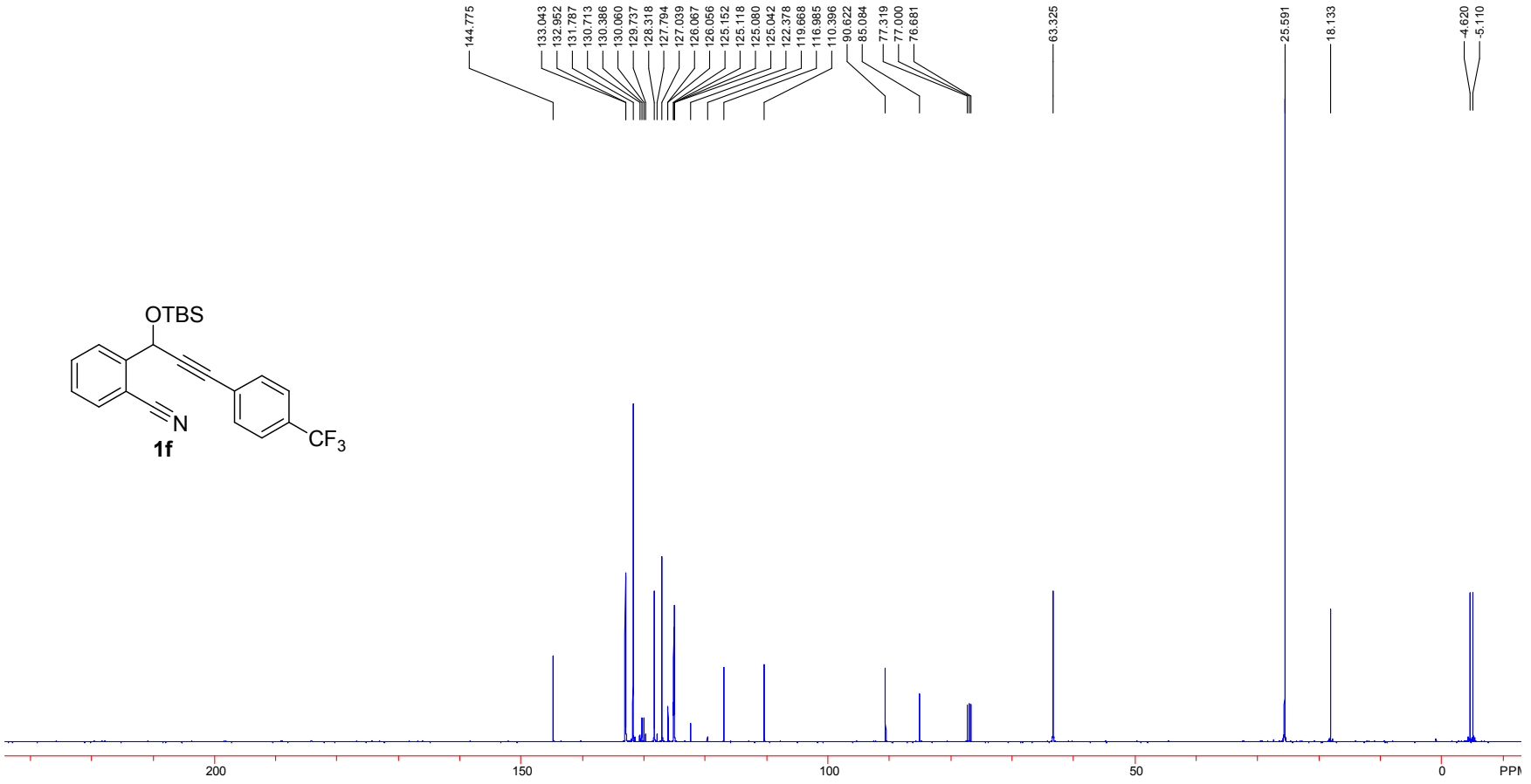


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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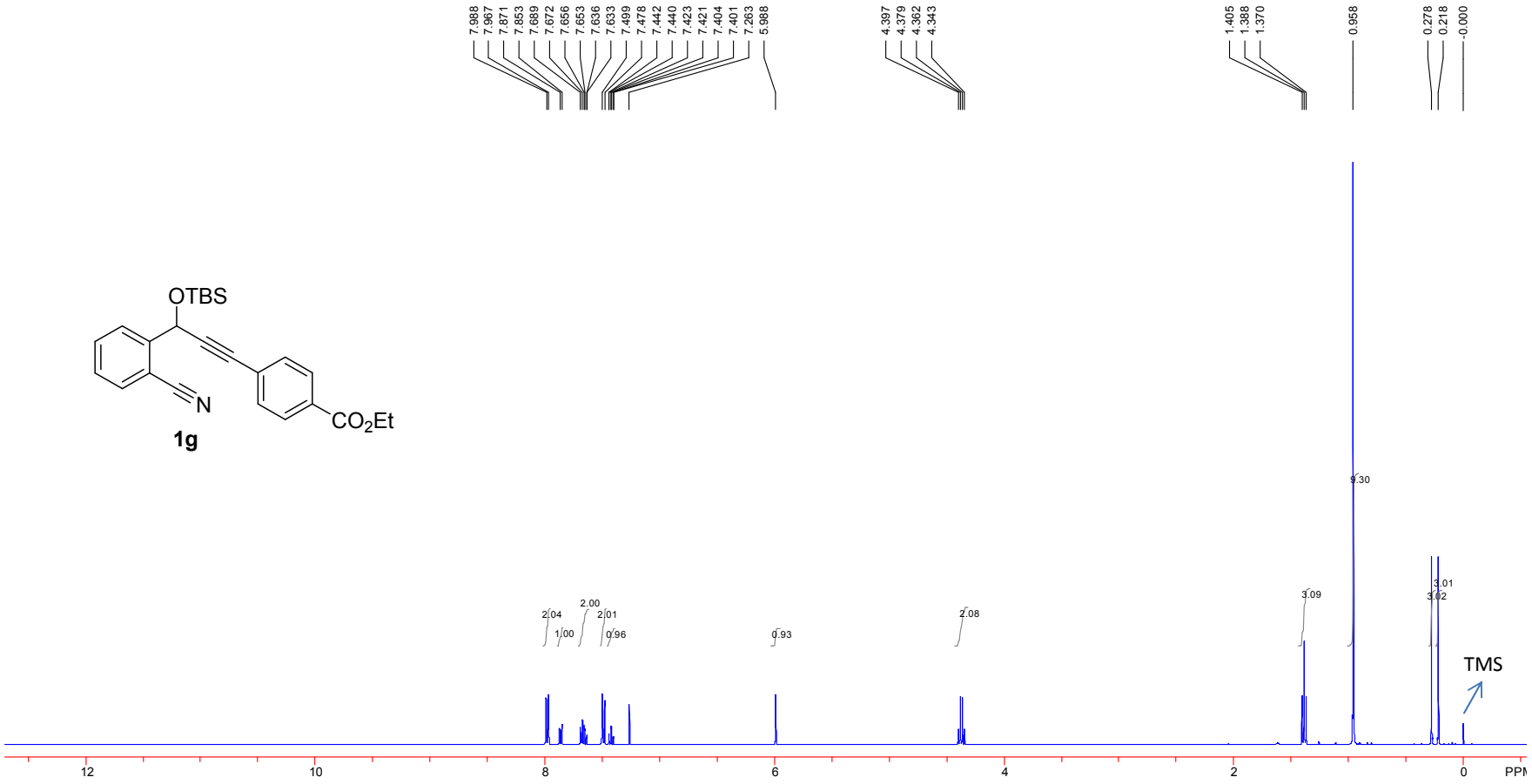
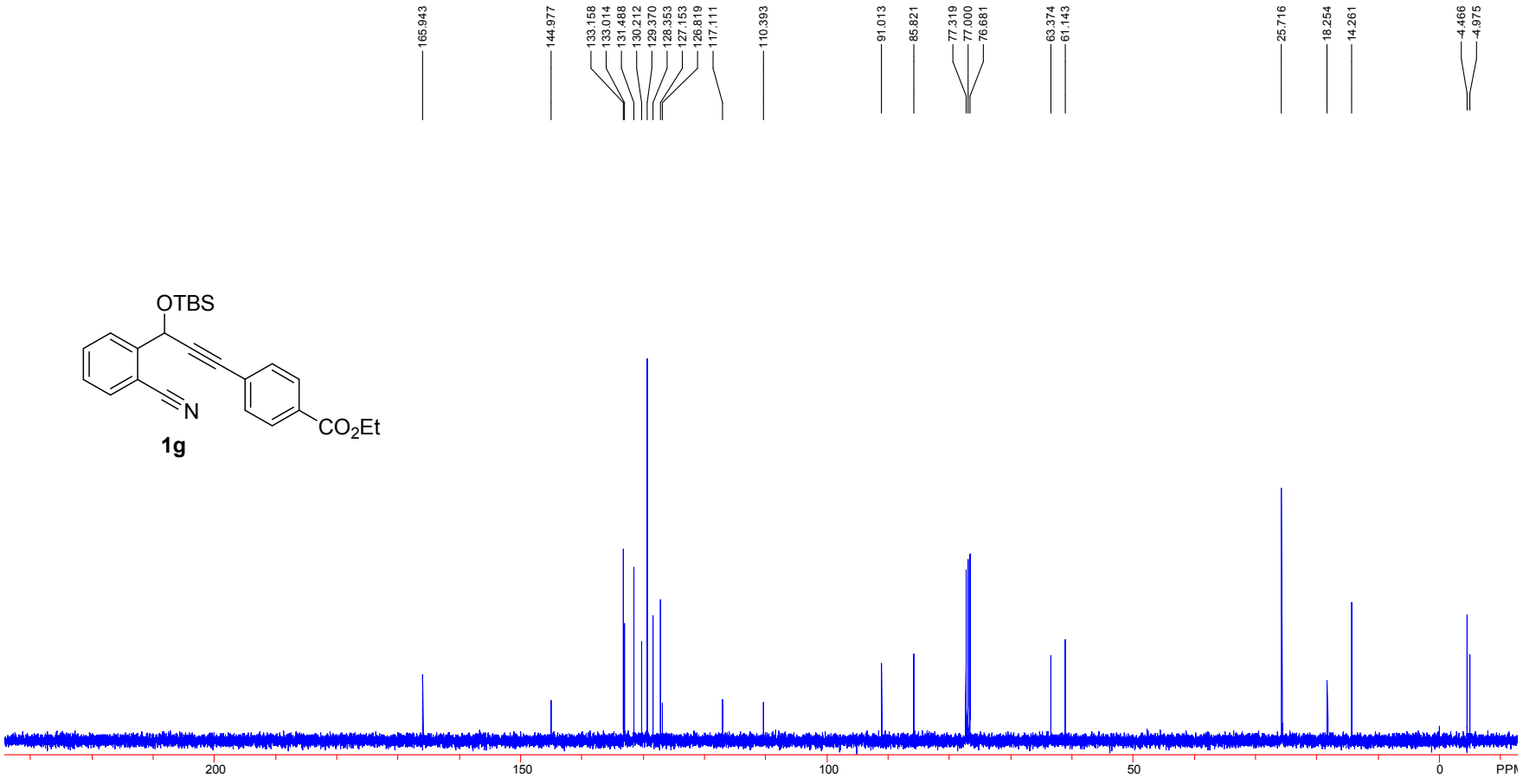


^{13}C NMR (100 MHz, $CDCl_3$)



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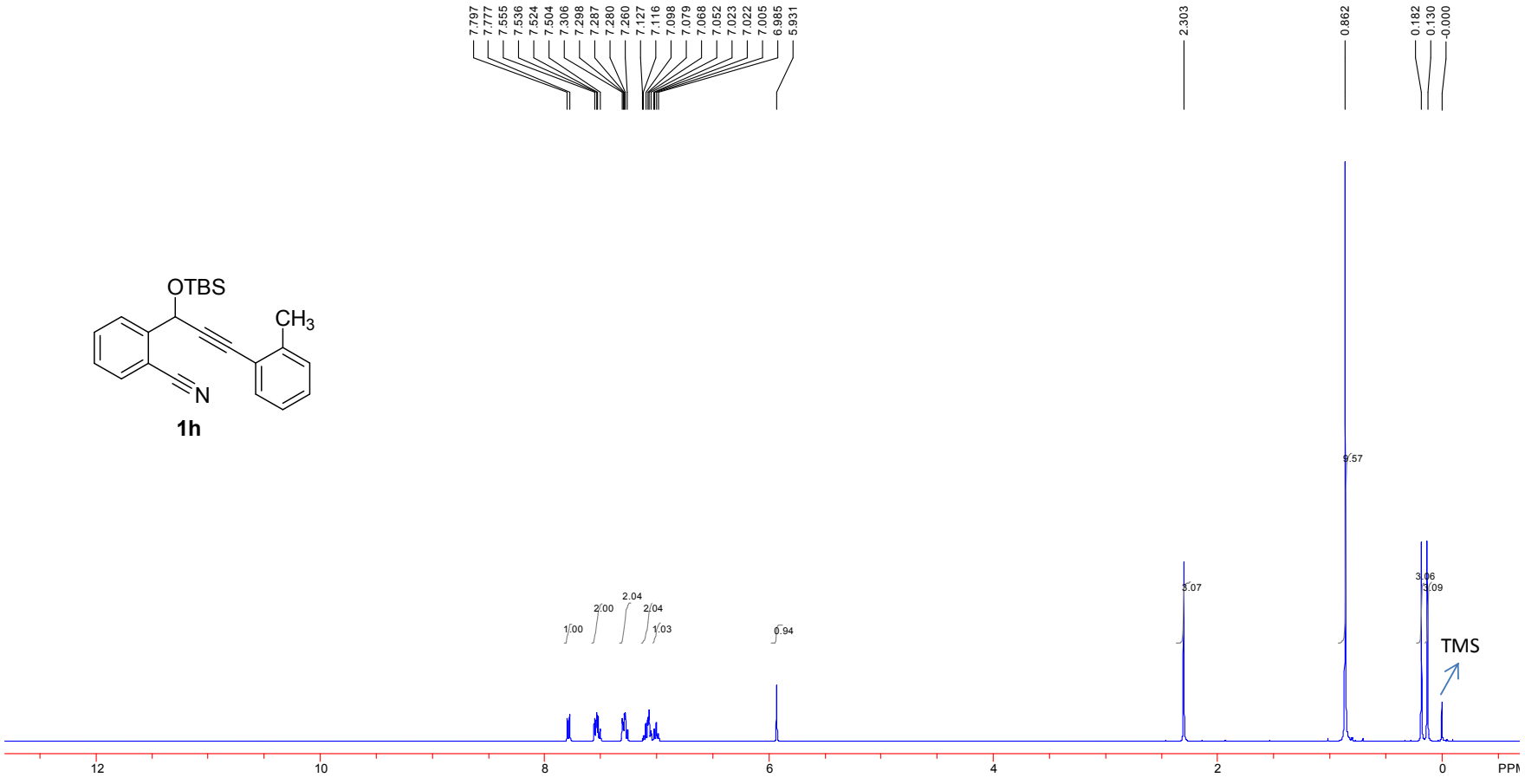

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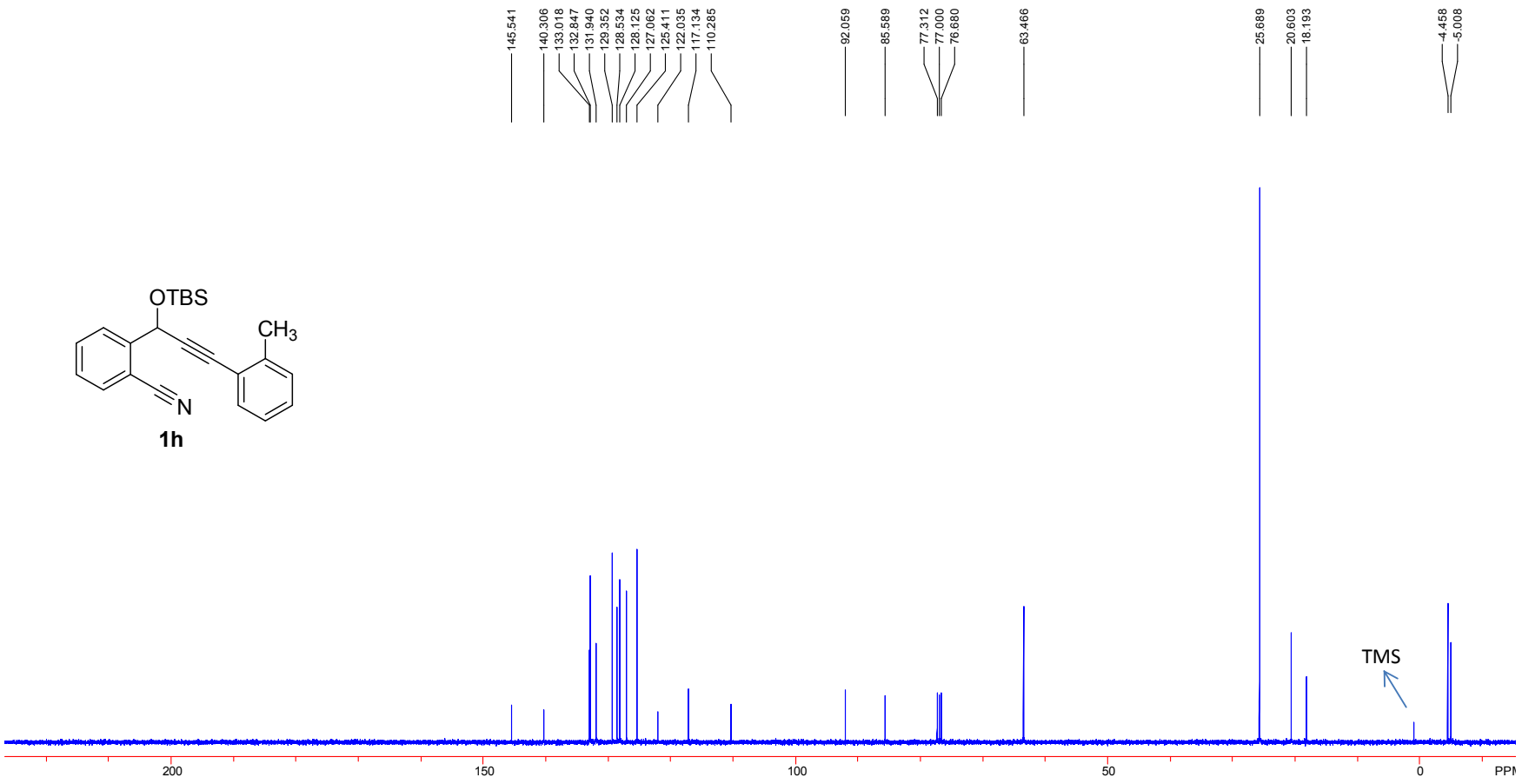

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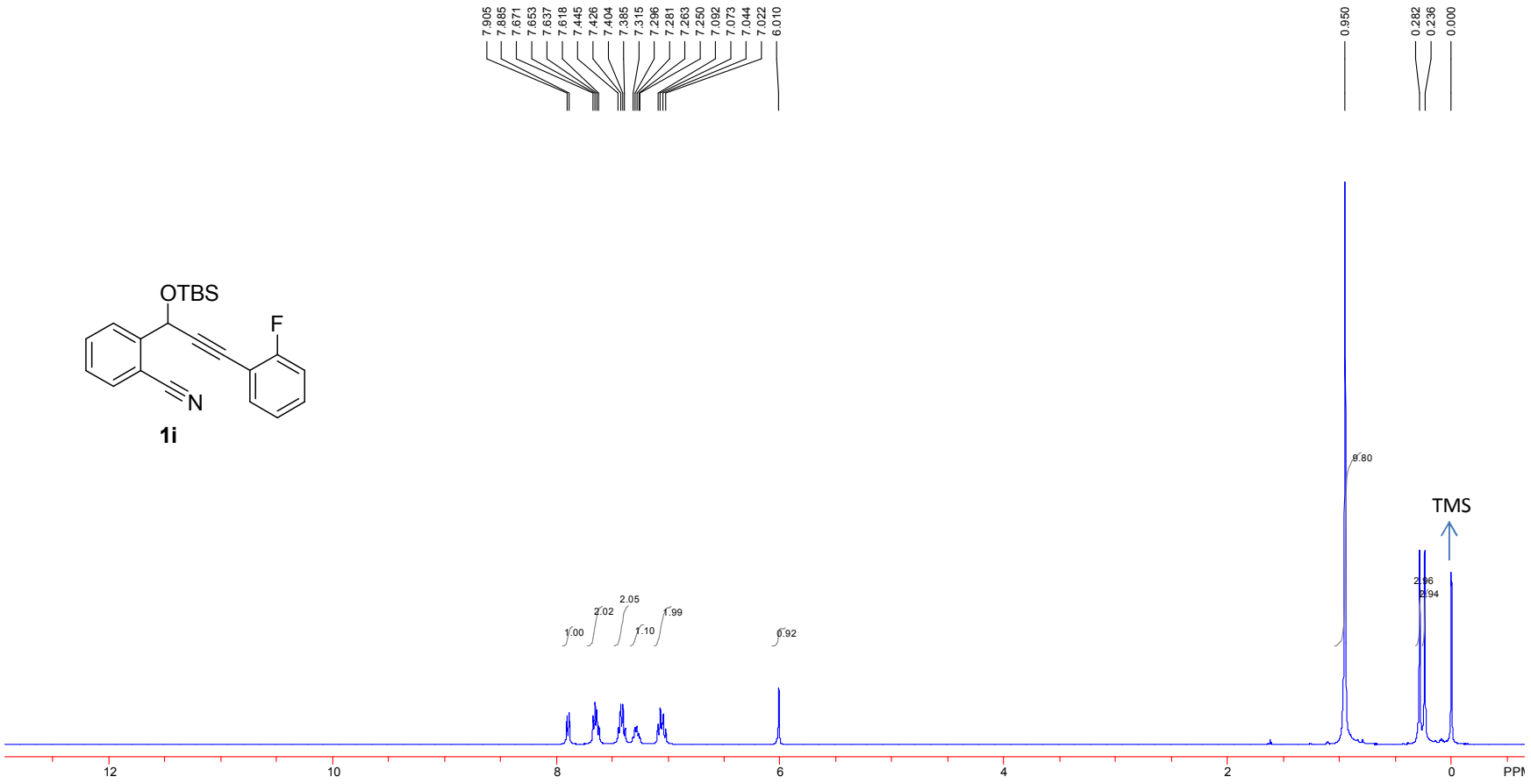

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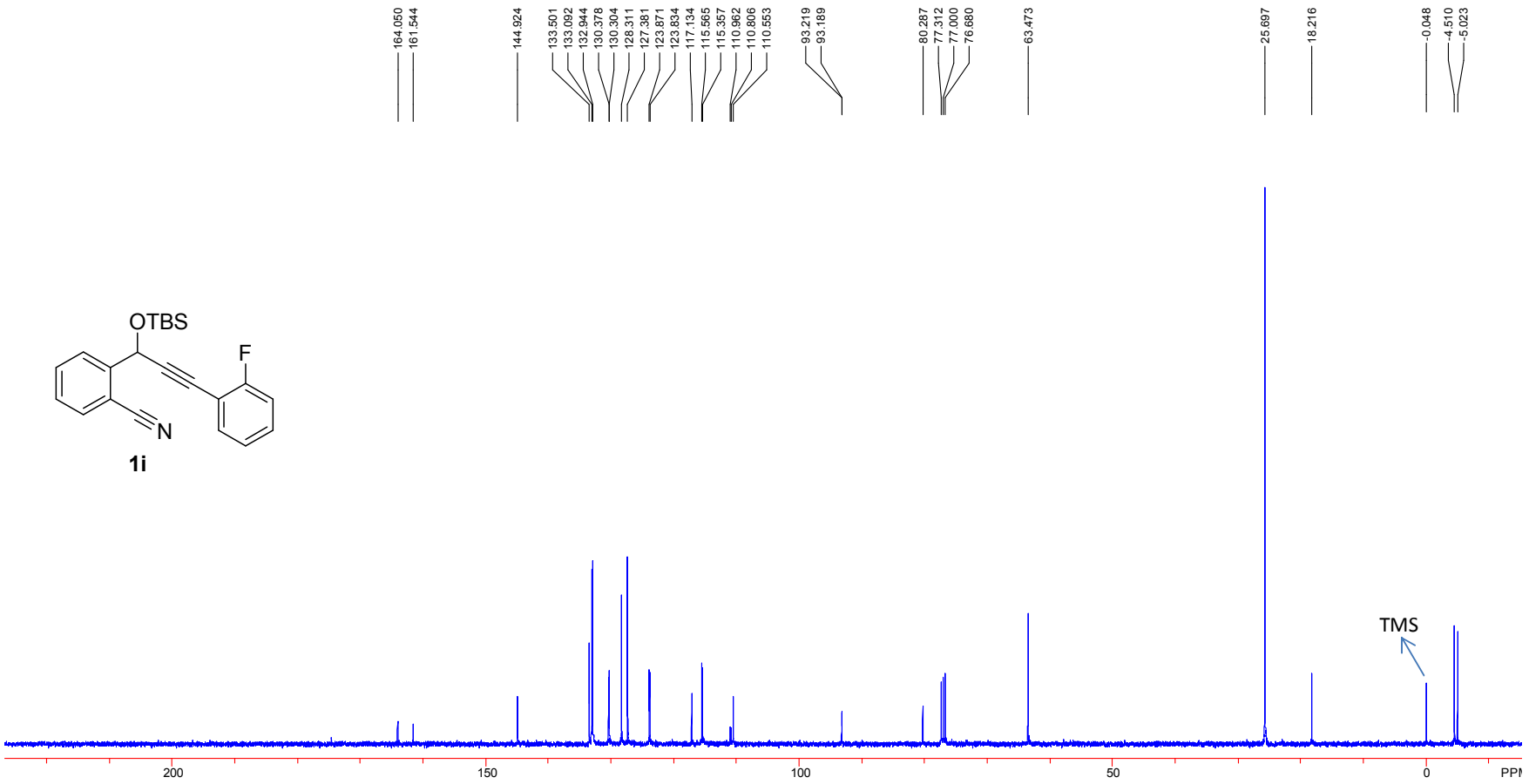
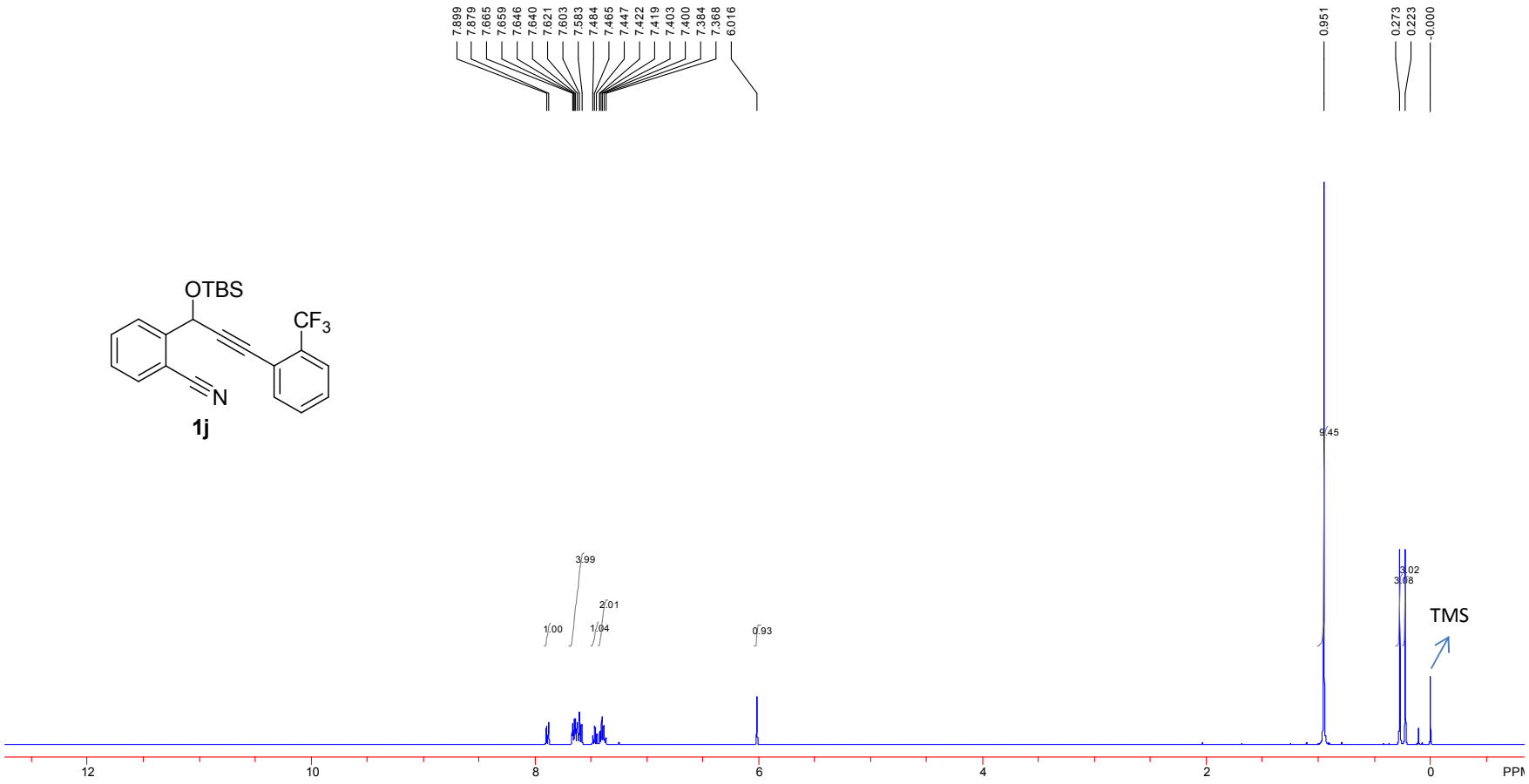


^{1}H NMR (400 MHz, $CDCl_3$)



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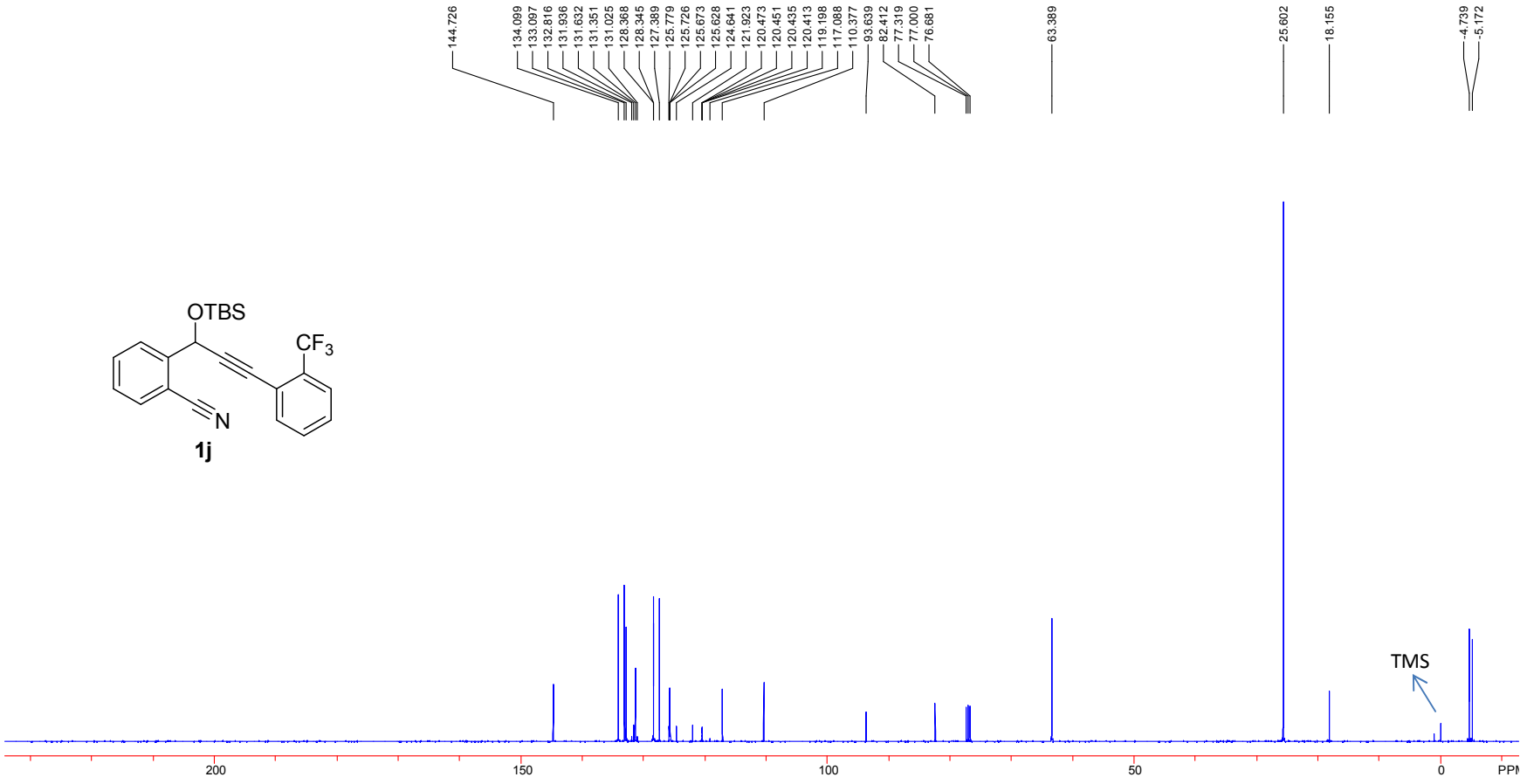
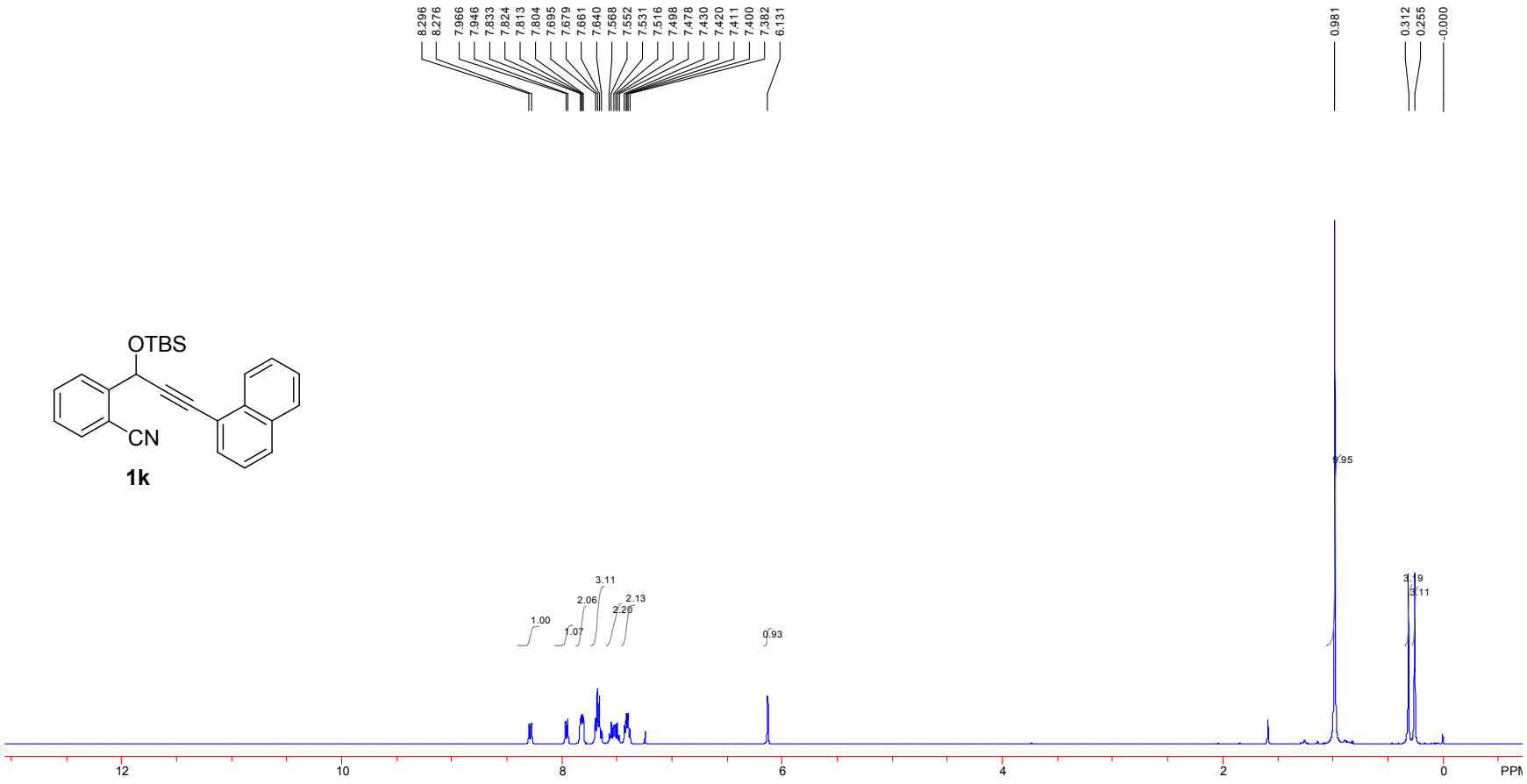


^{1}H NMR (400 MHz, $CDCl_3$)



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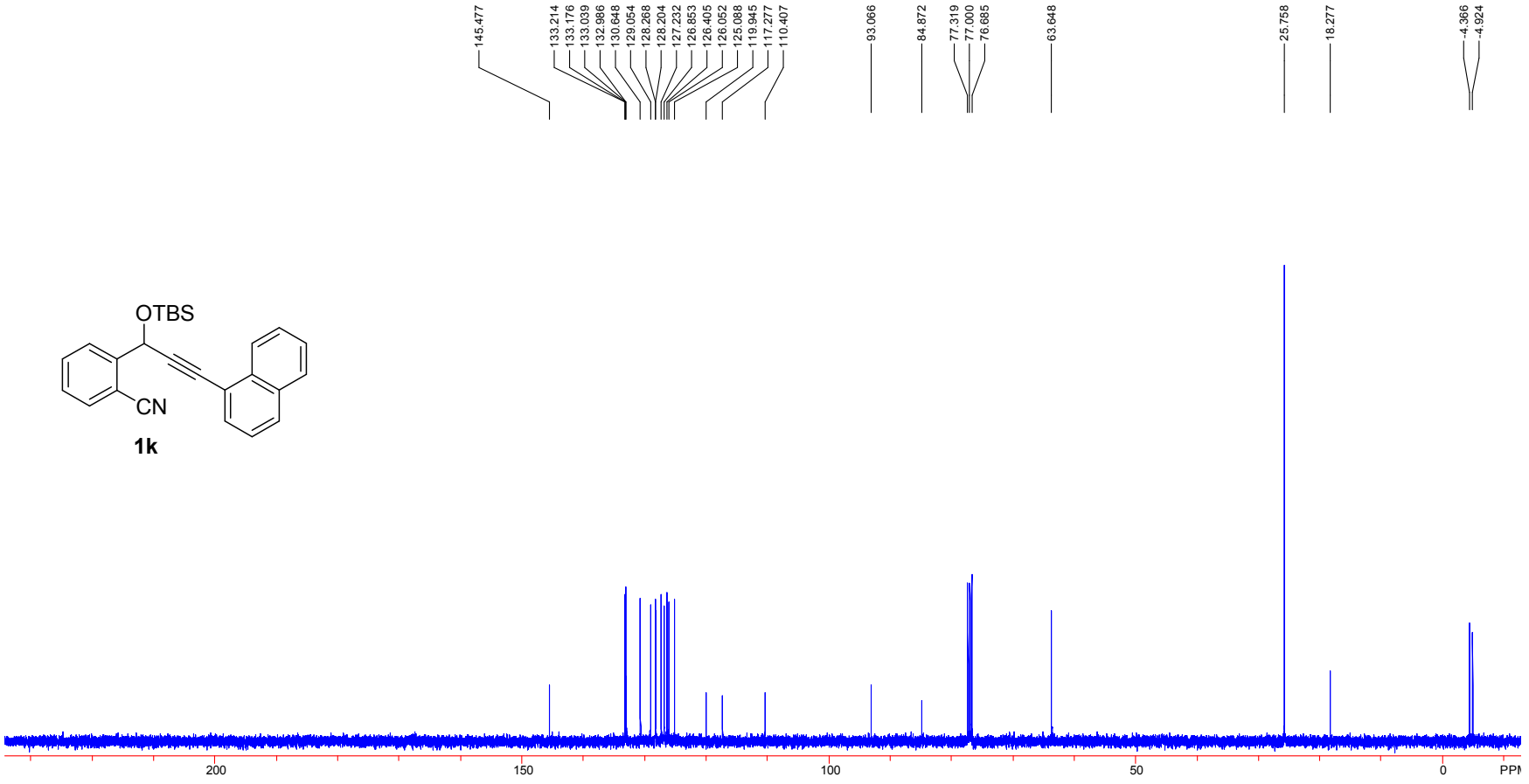
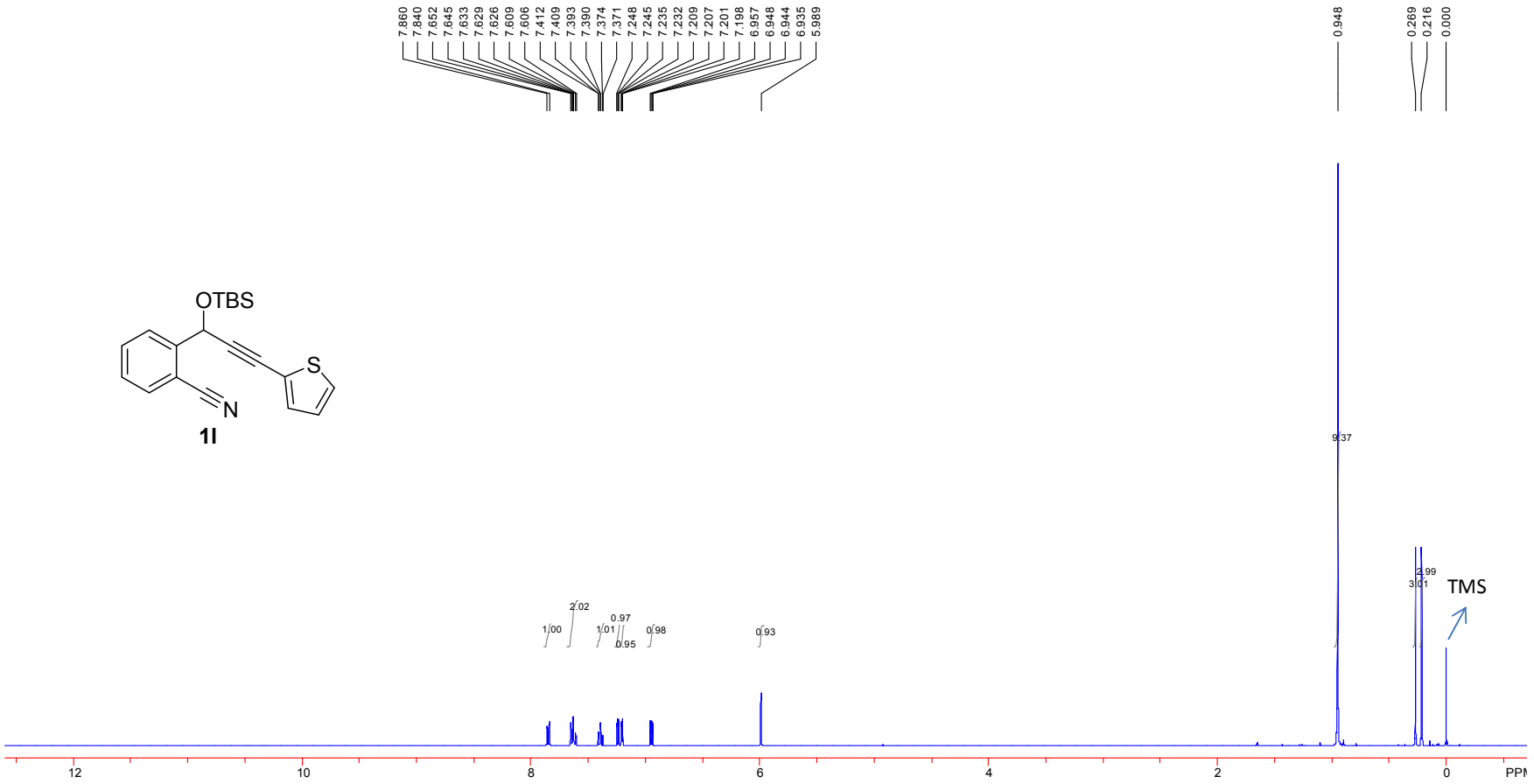
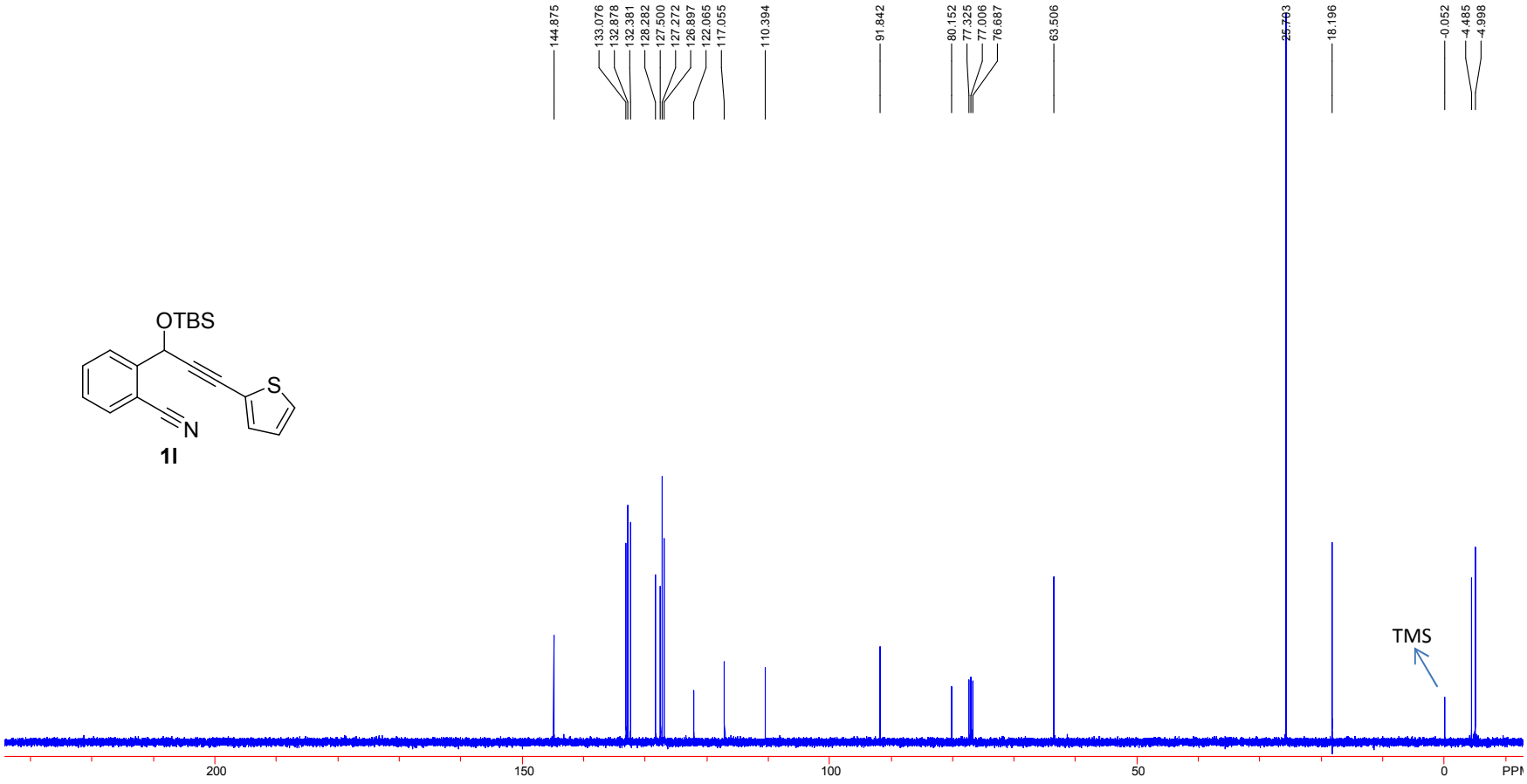


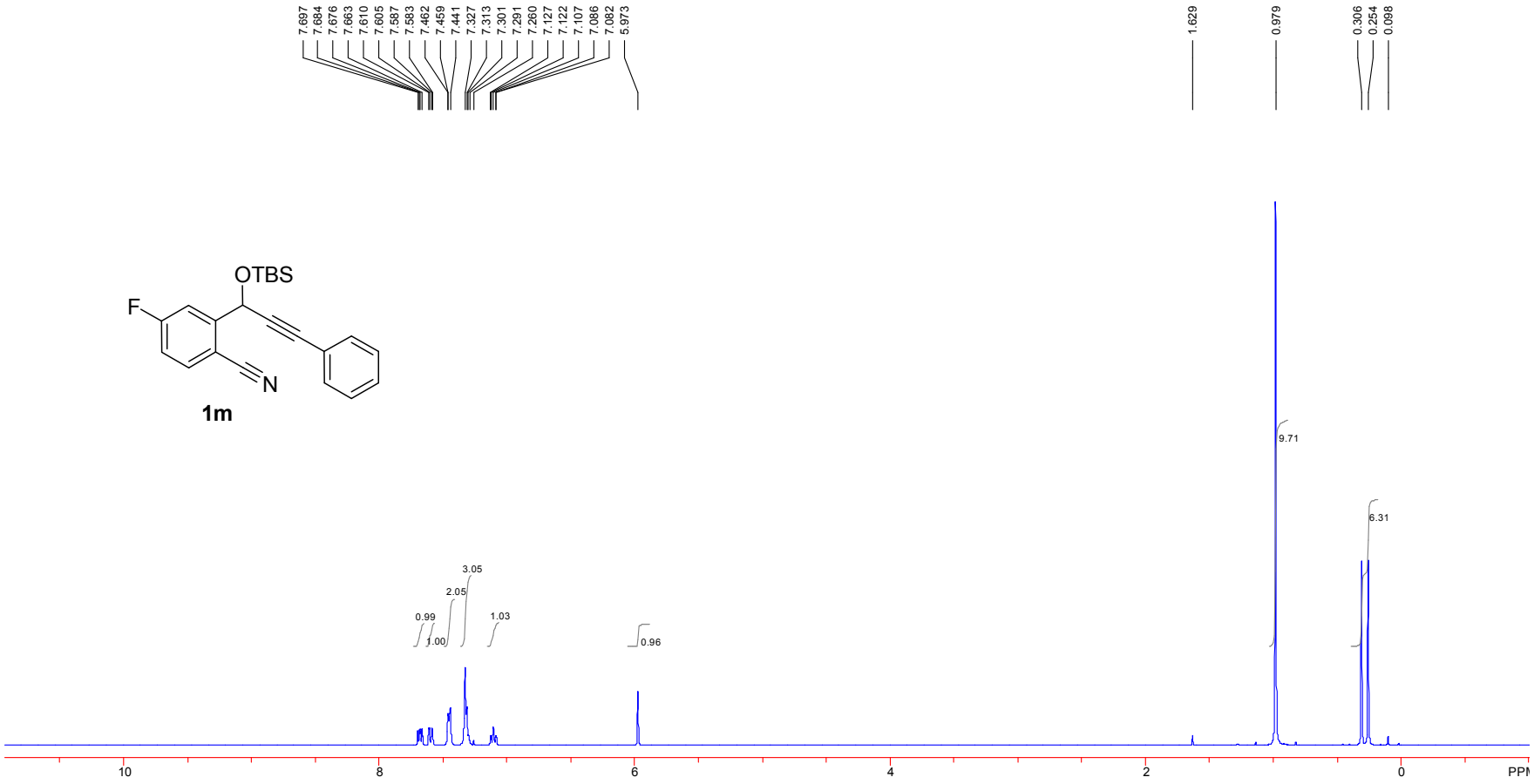
^{1}H NMR (400 MHz, $CDCl_3$)



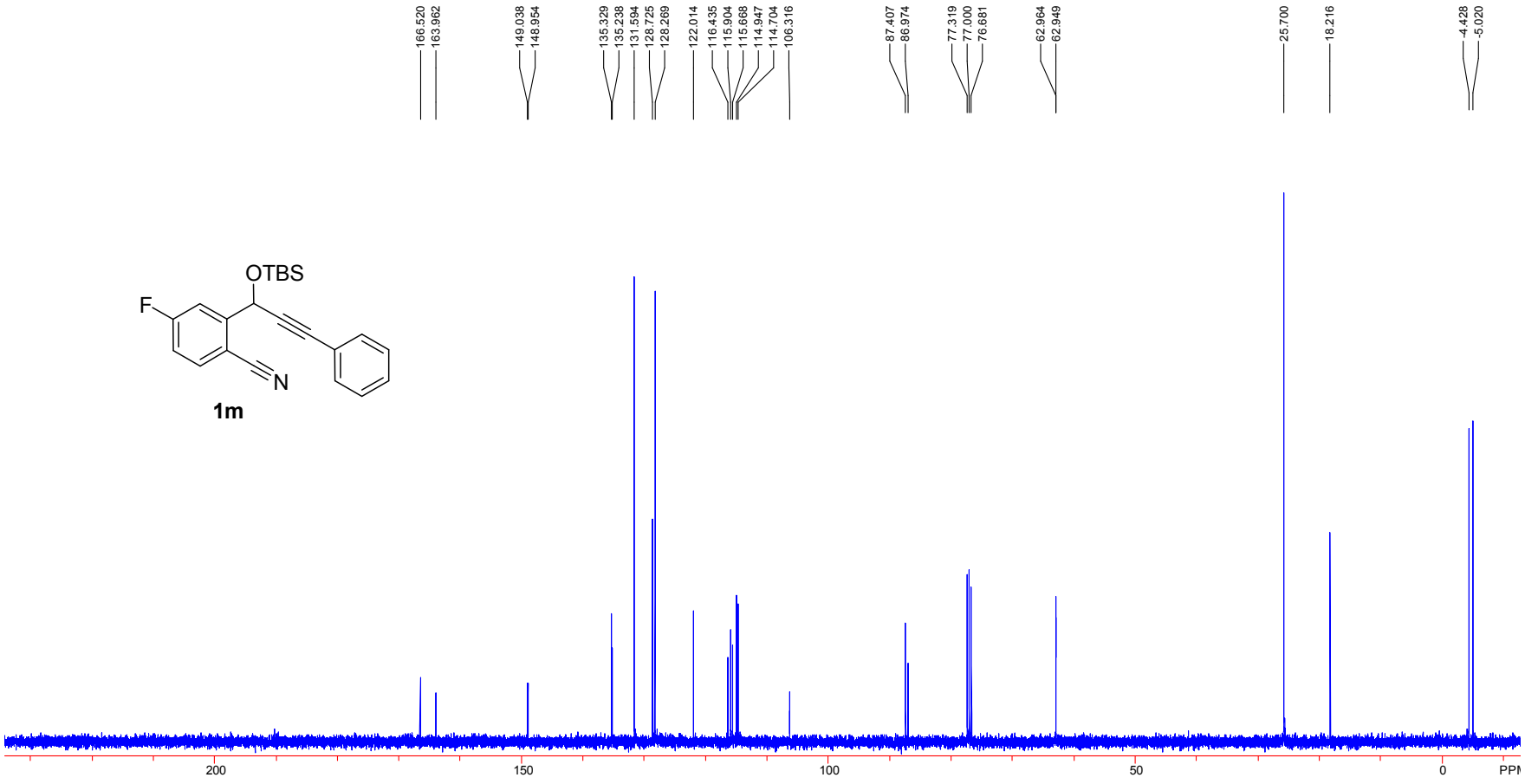
^{13}C NMR (100 MHz, $CDCl_3$)



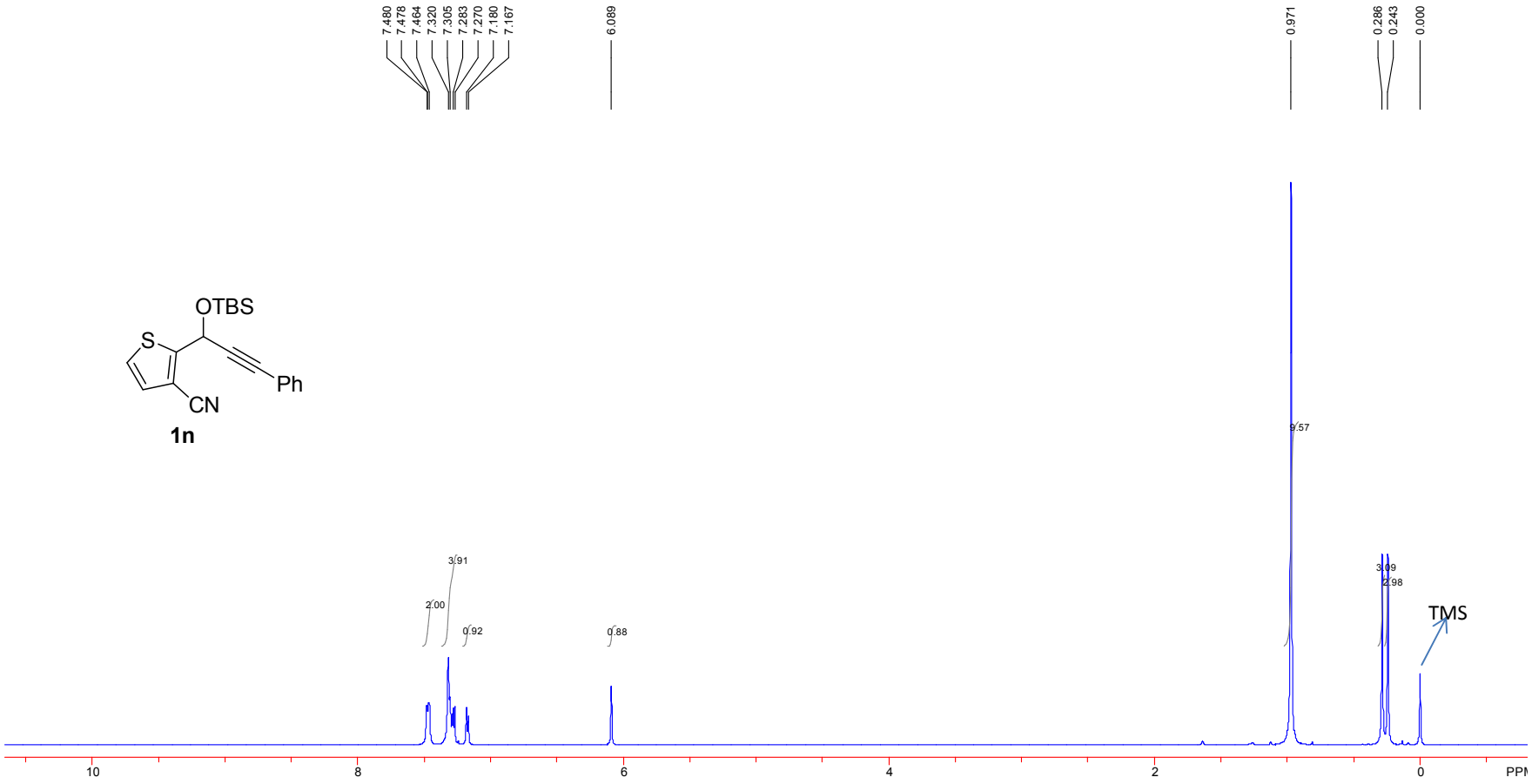
^{1}H NMR (400 MHz, $CDCl_3$)



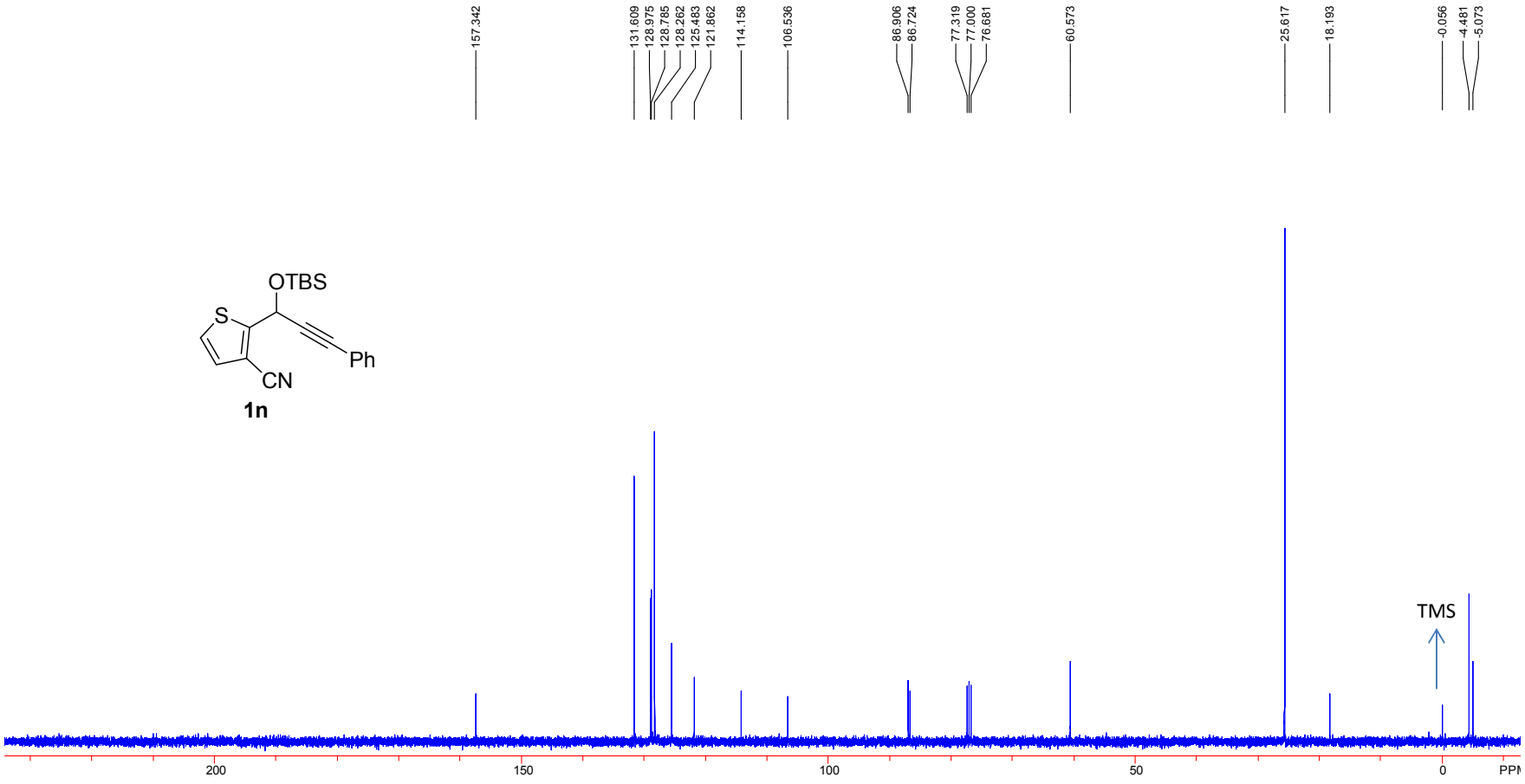
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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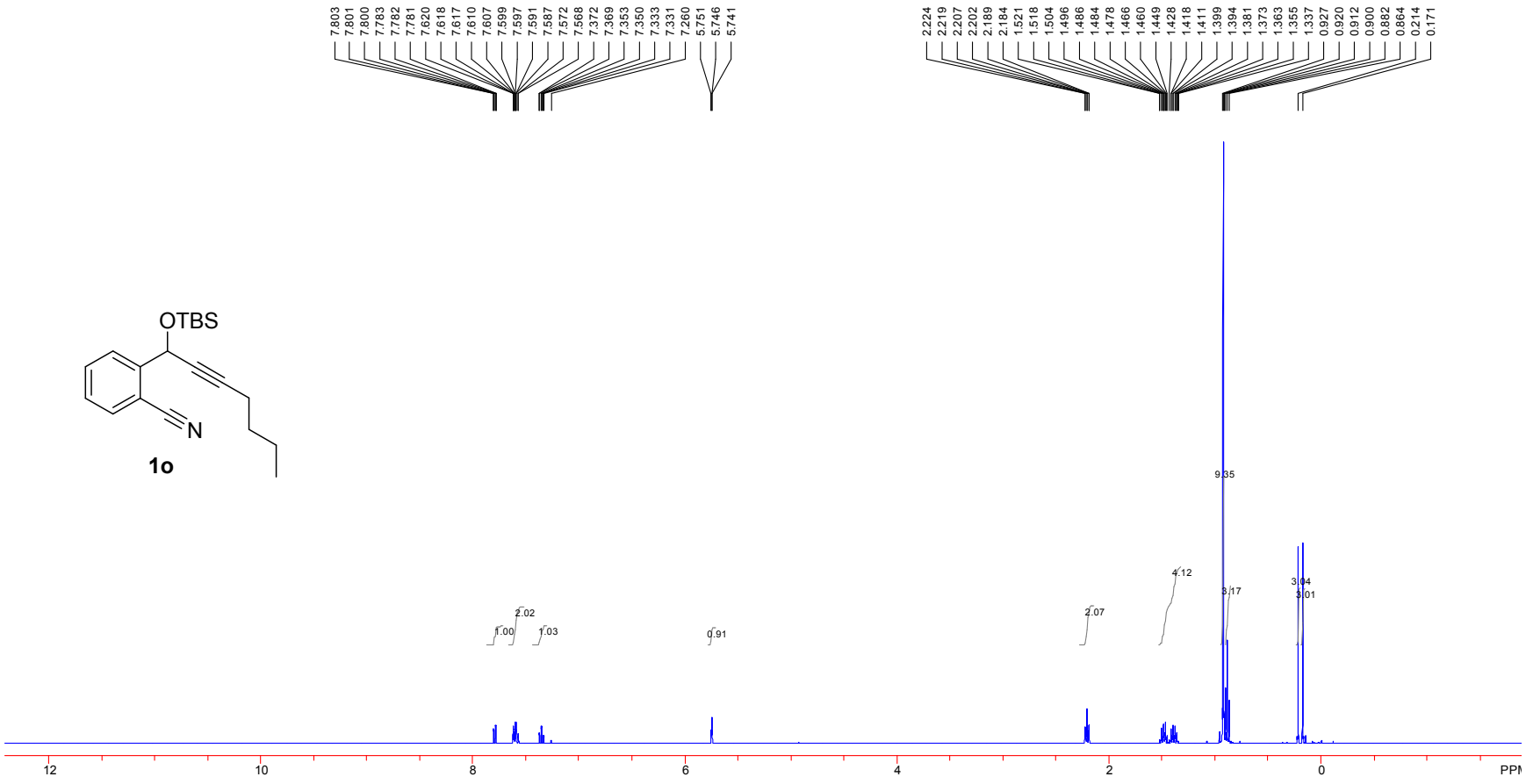
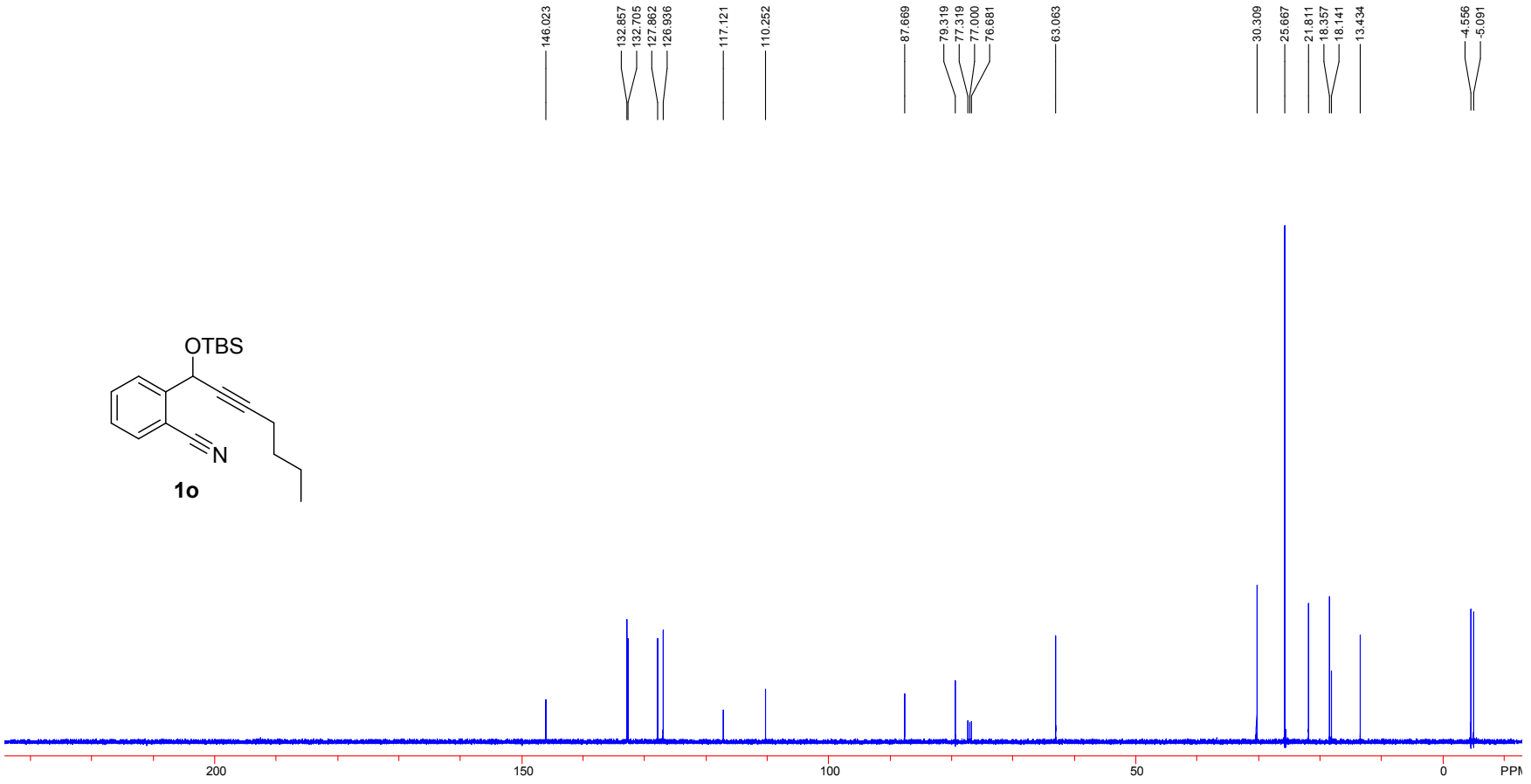


^{13}C NMR (100 MHz, $CDCl_3$)



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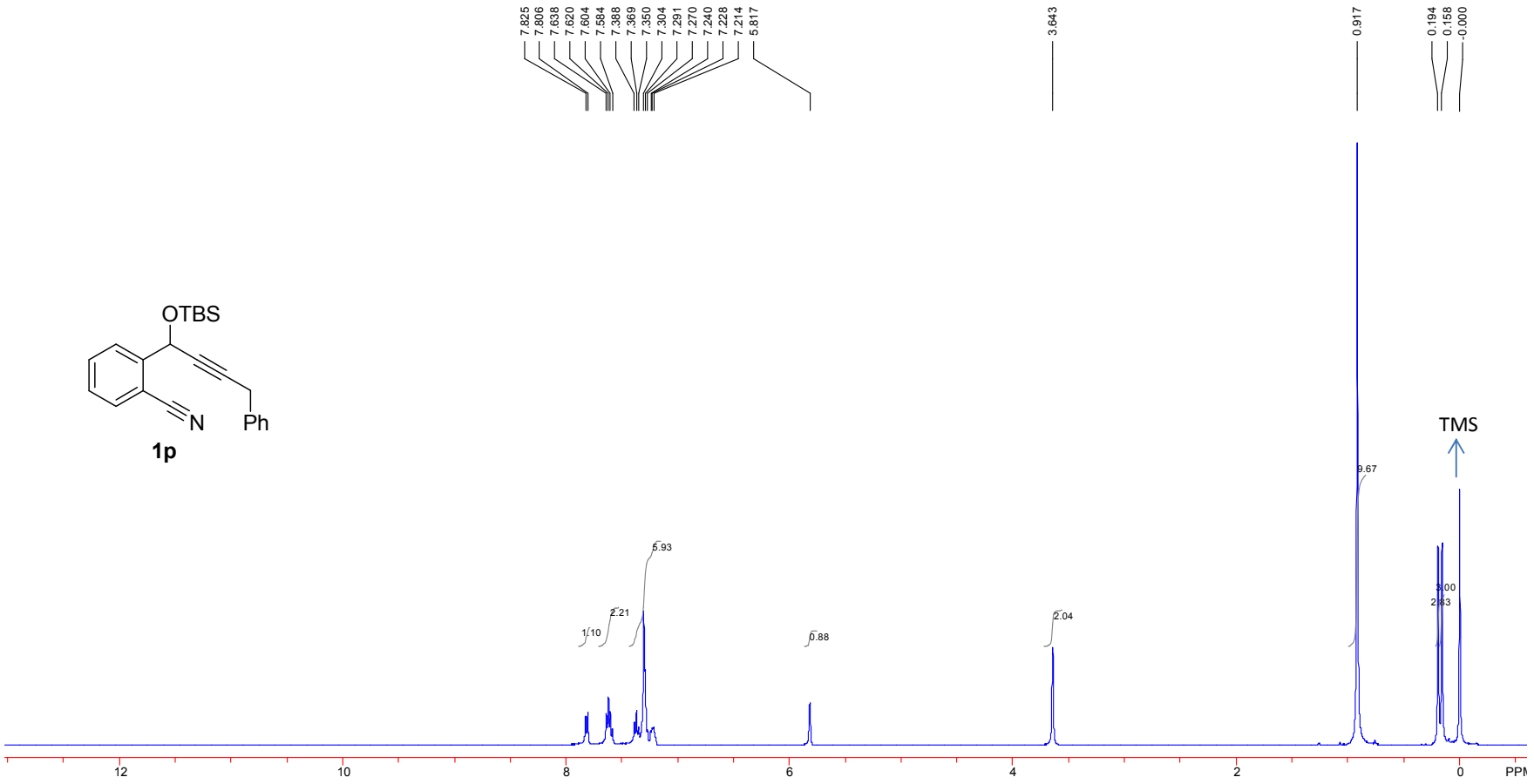

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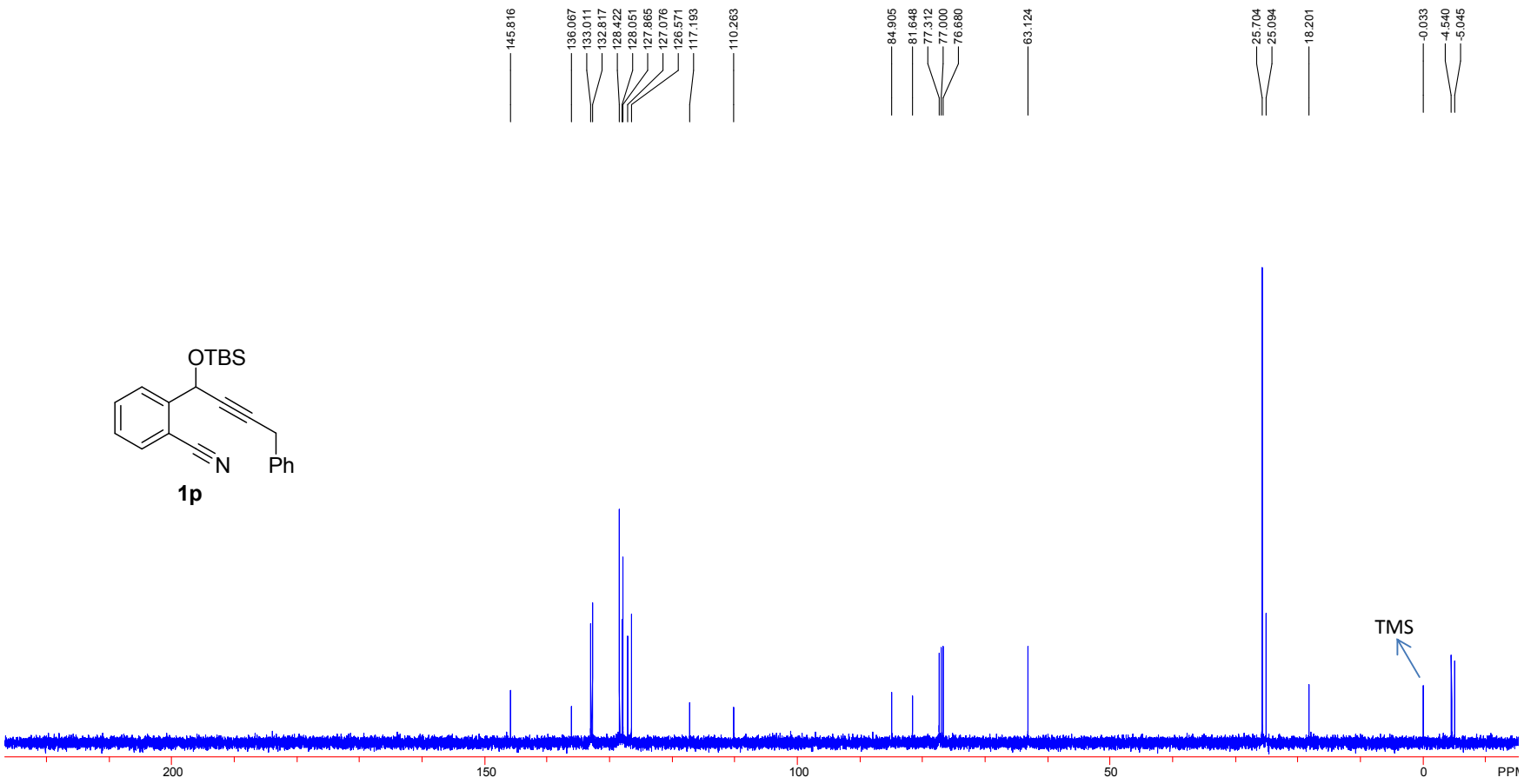

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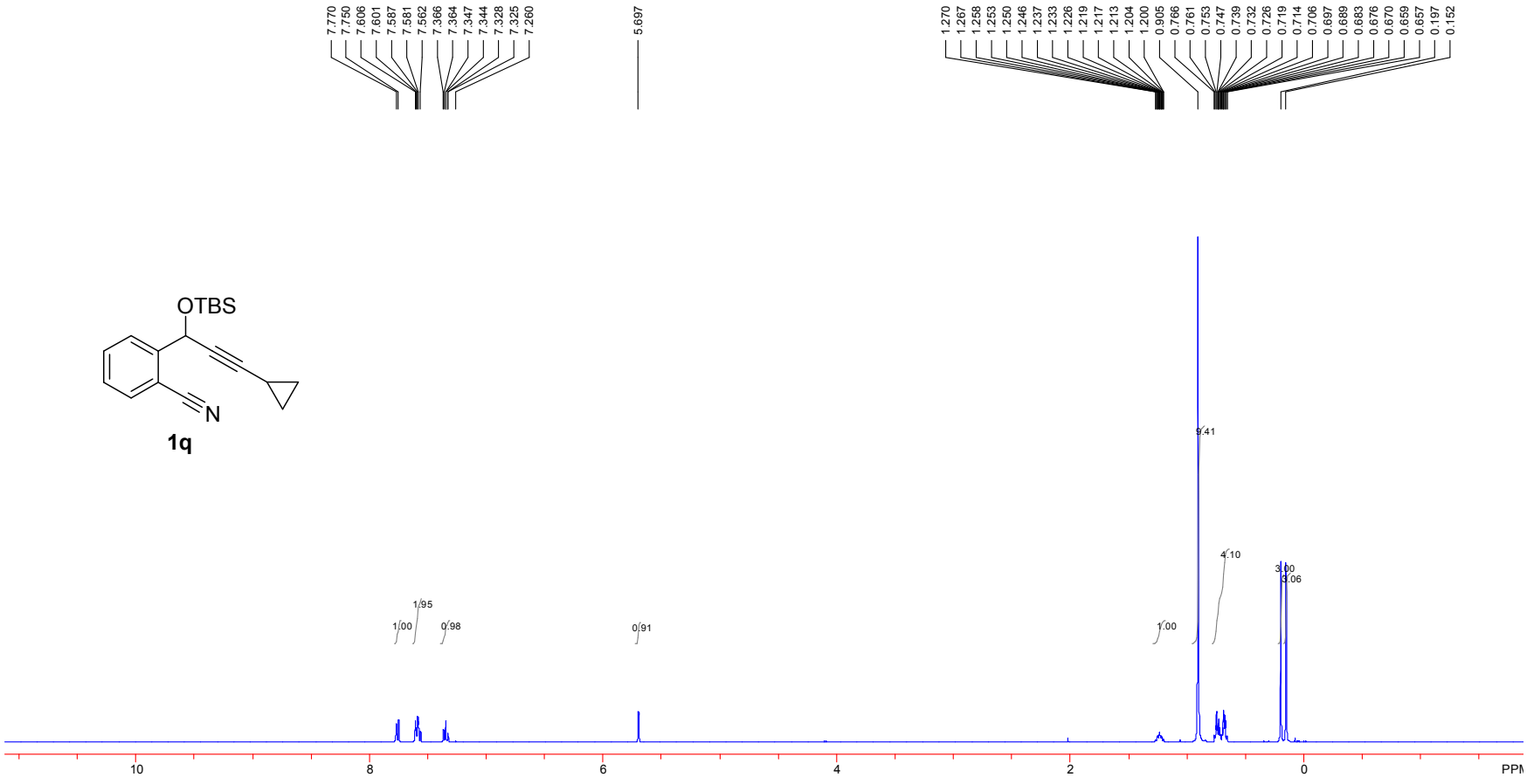

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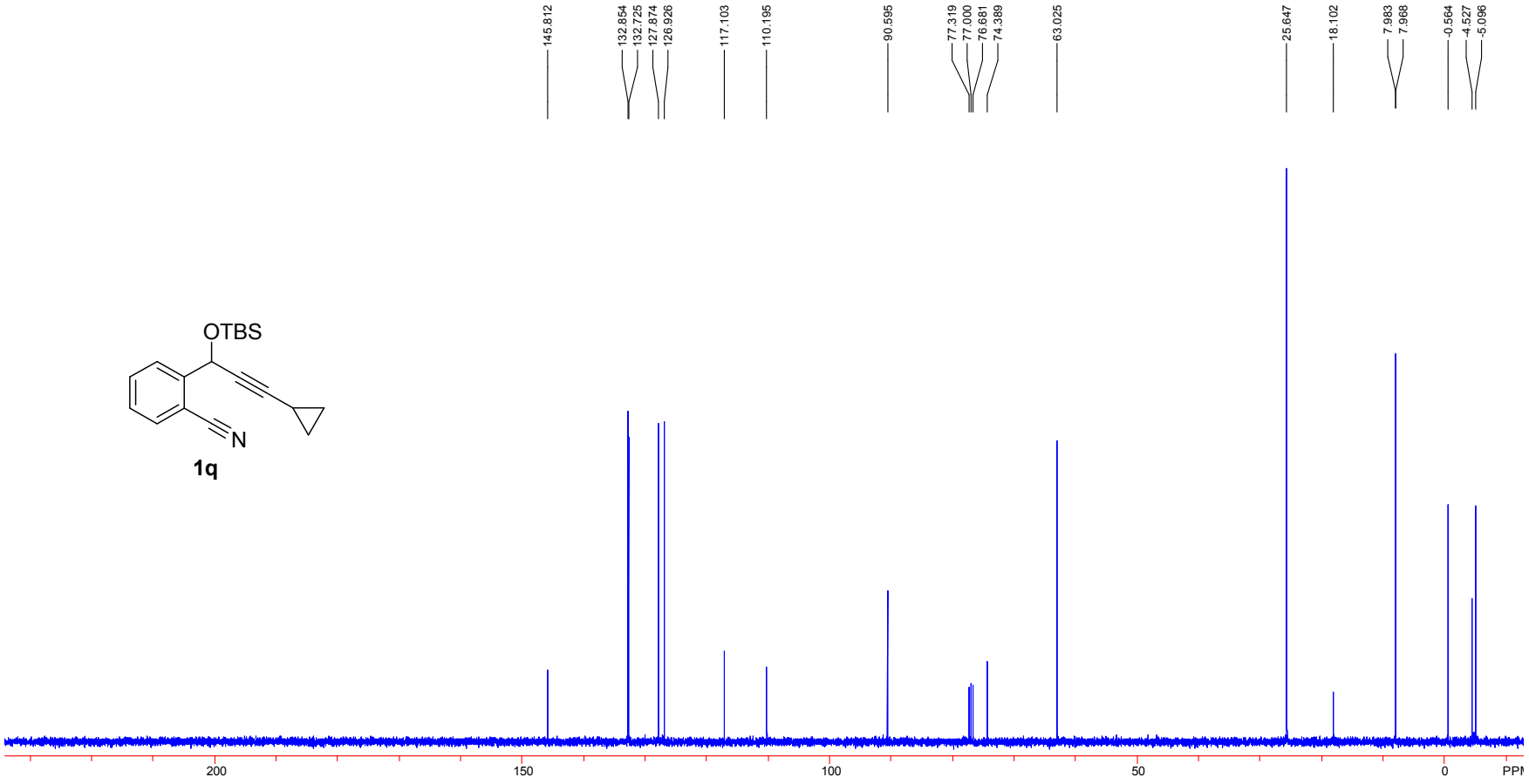

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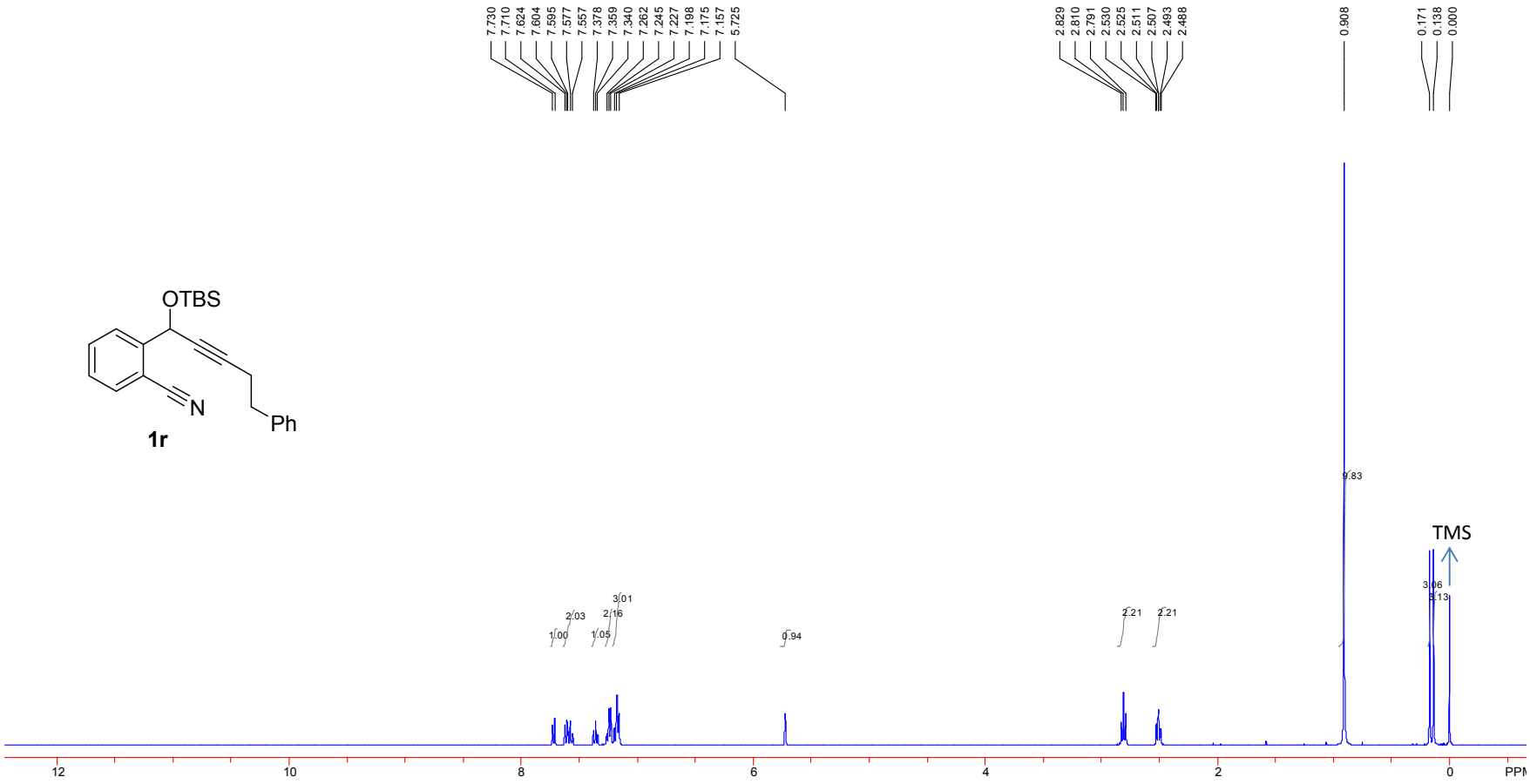

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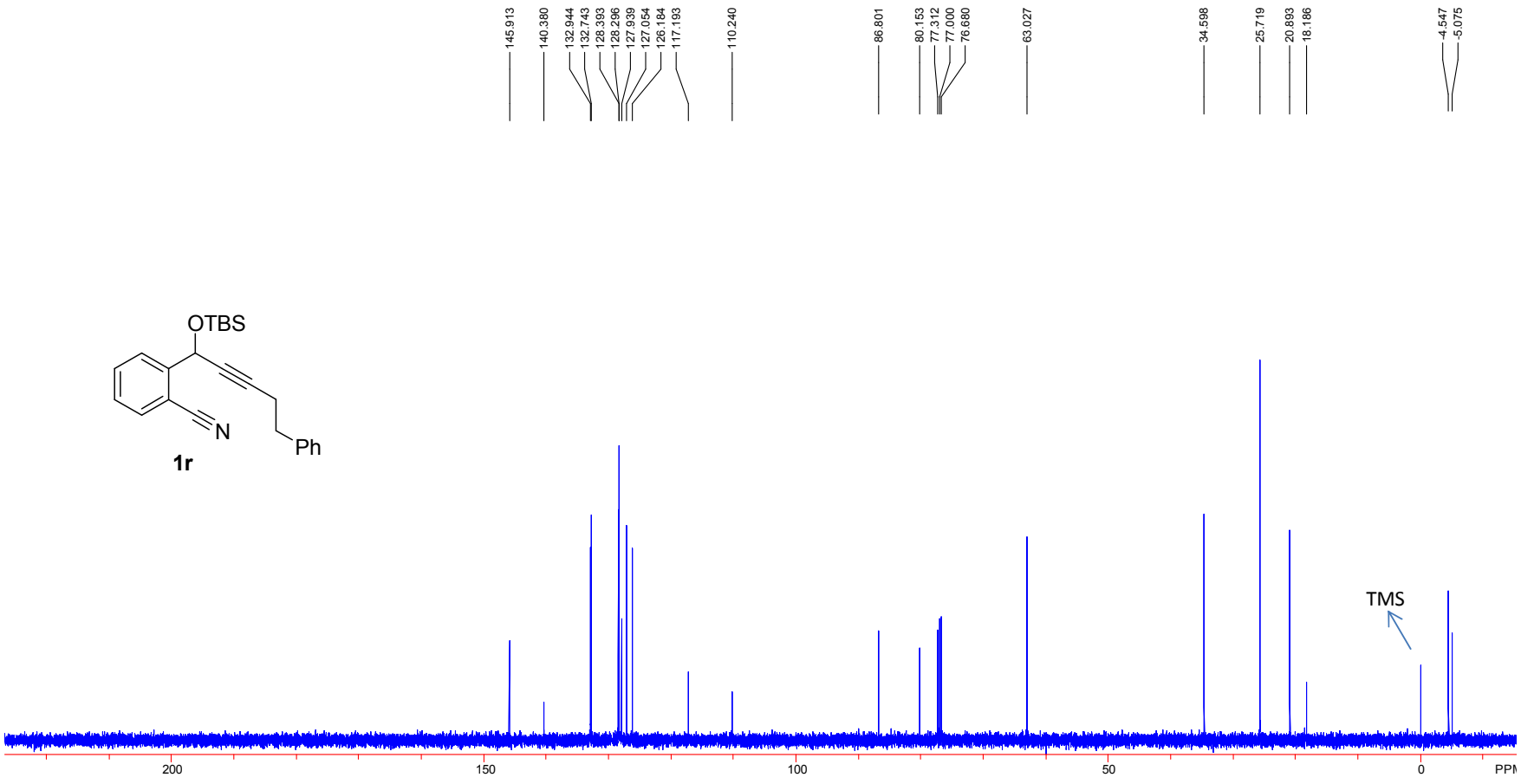
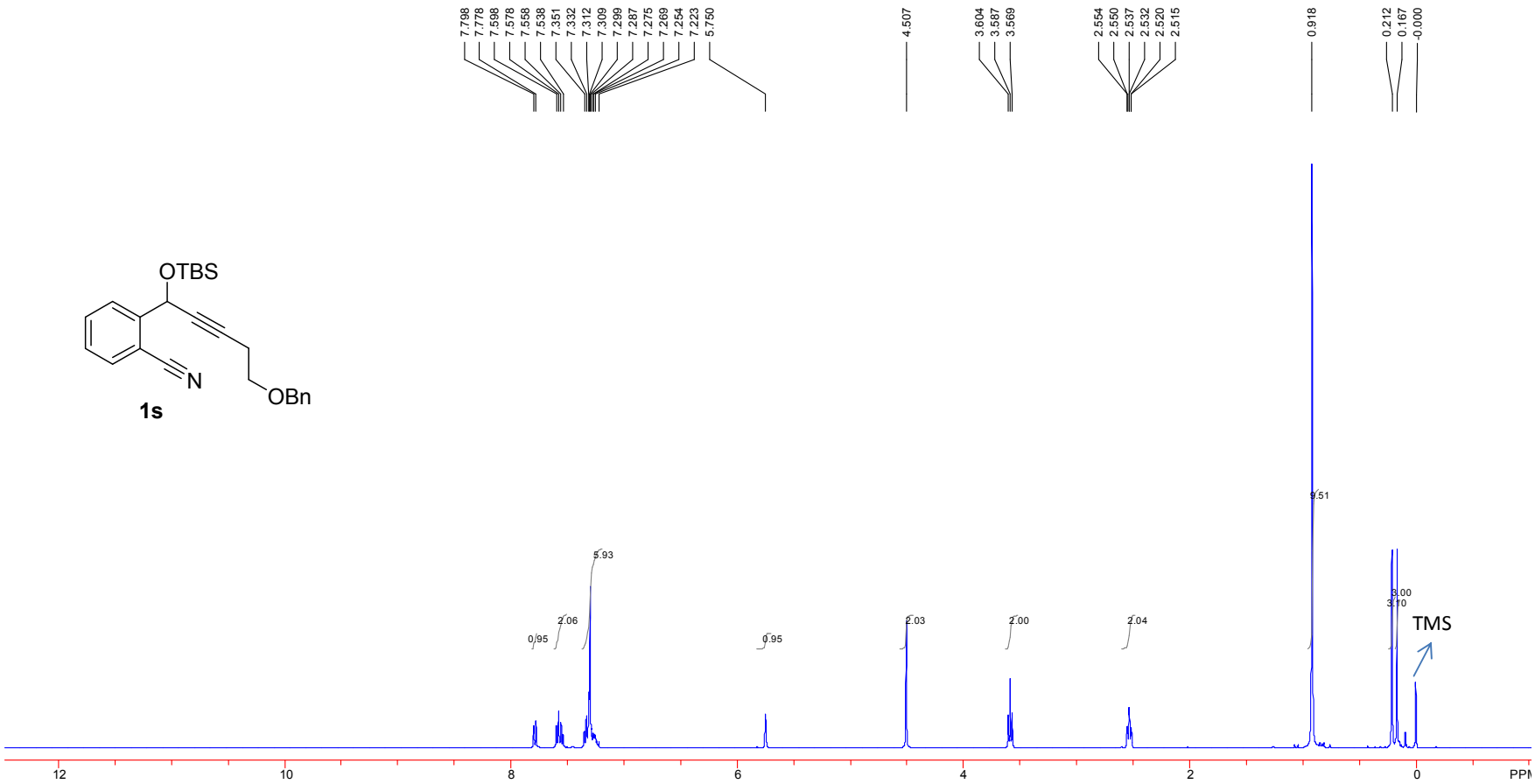


^{1}H NMR (400 MHz, $CDCl_3$)



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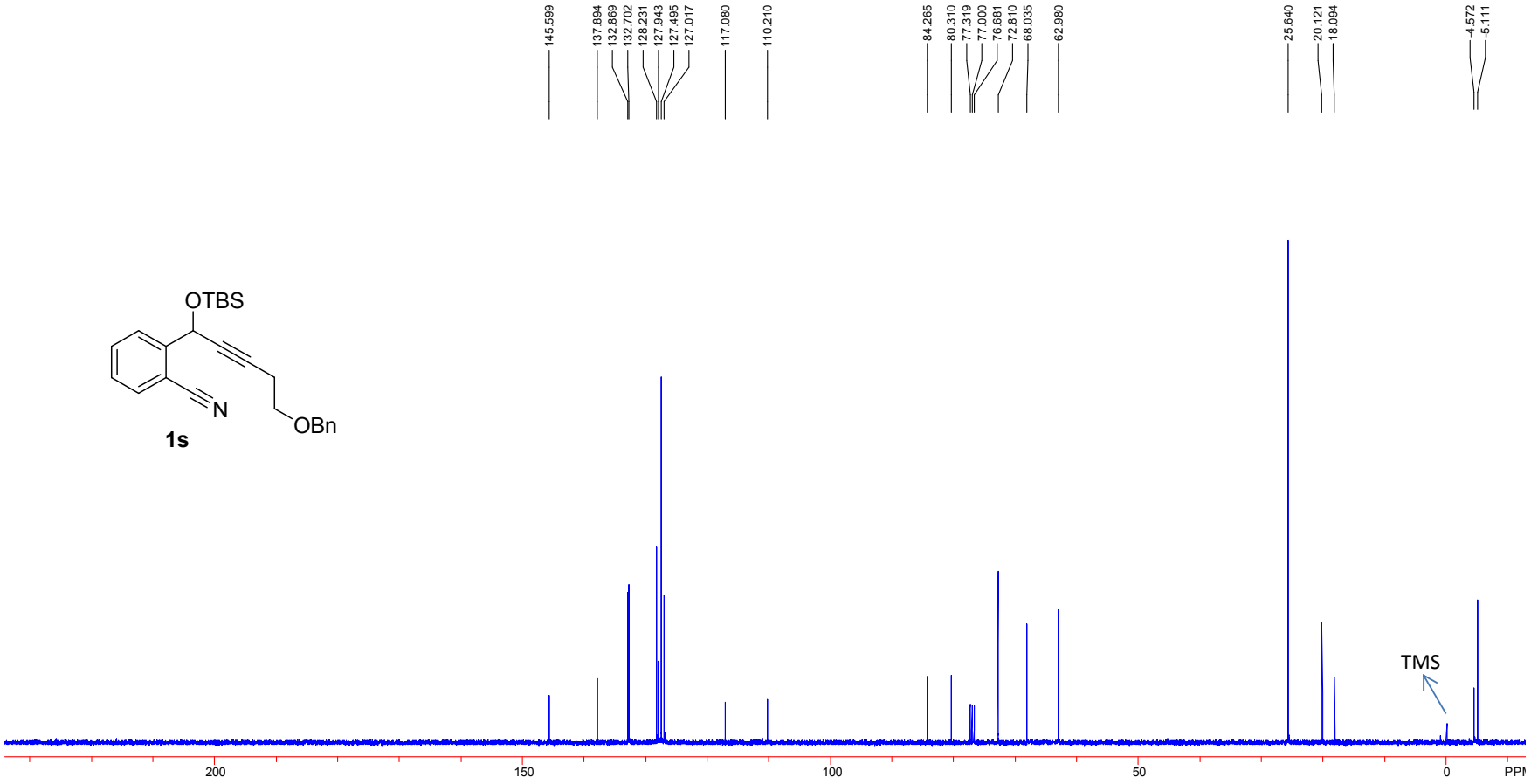

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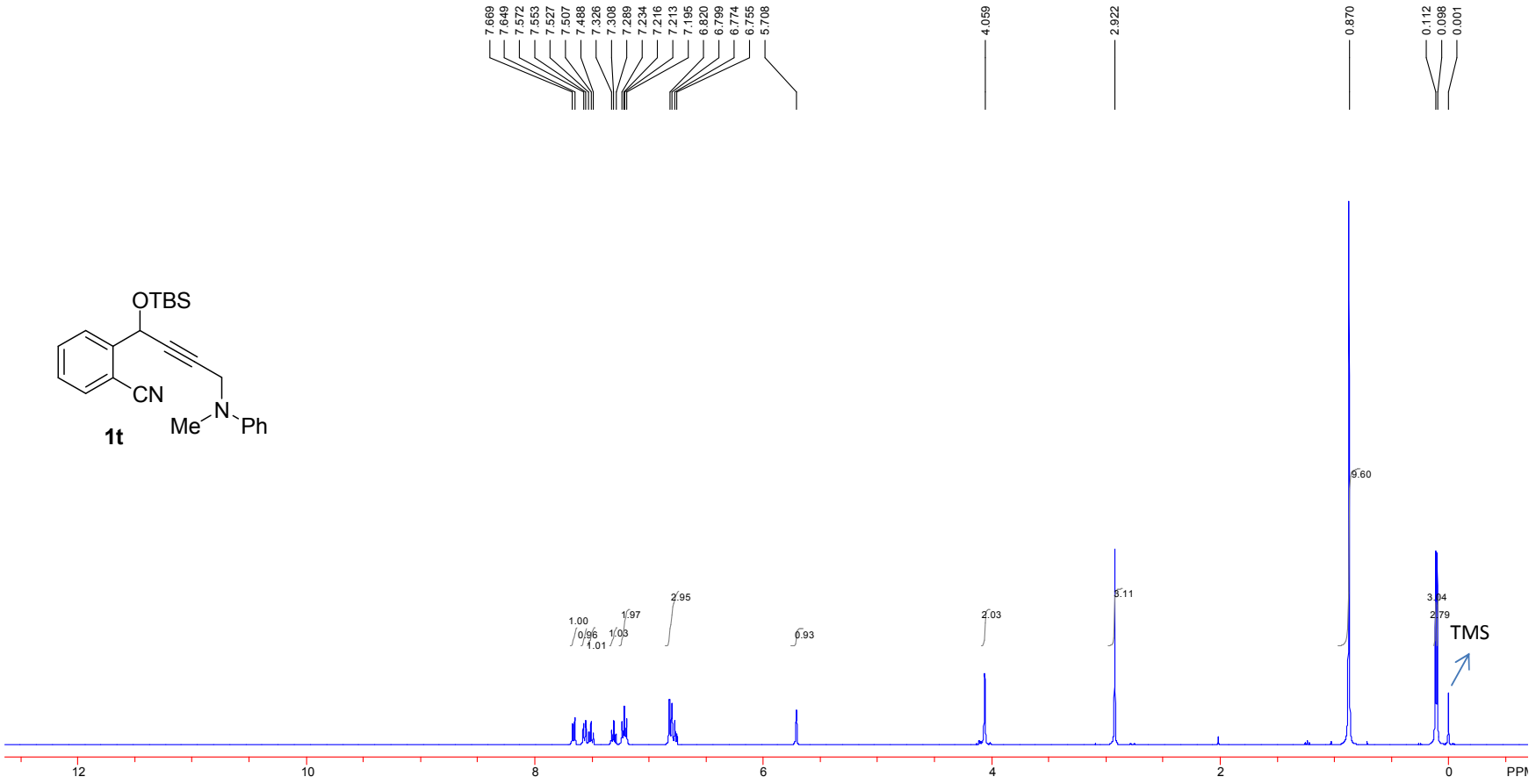
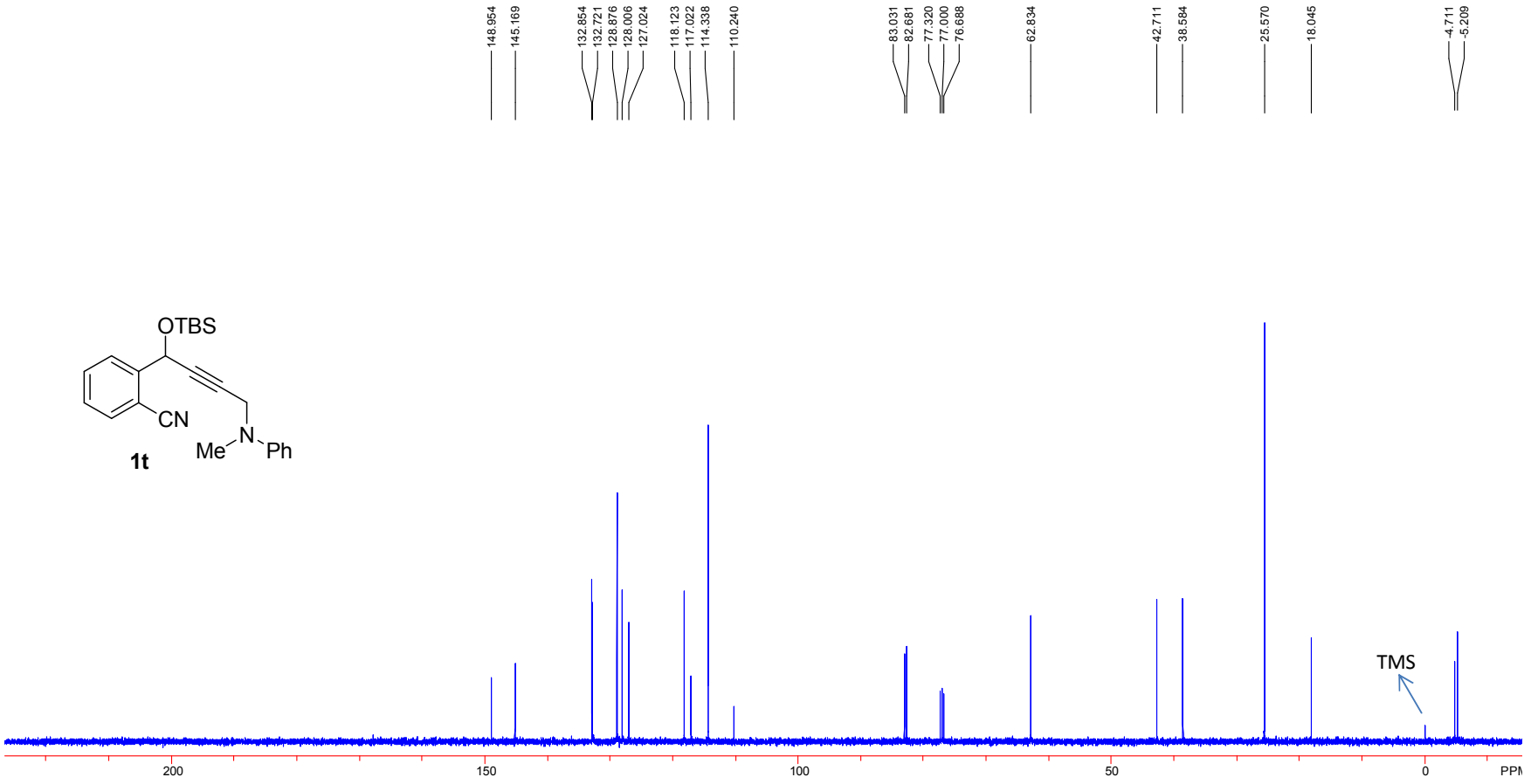


^{13}C NMR (100 MHz, $CDCl_3$)



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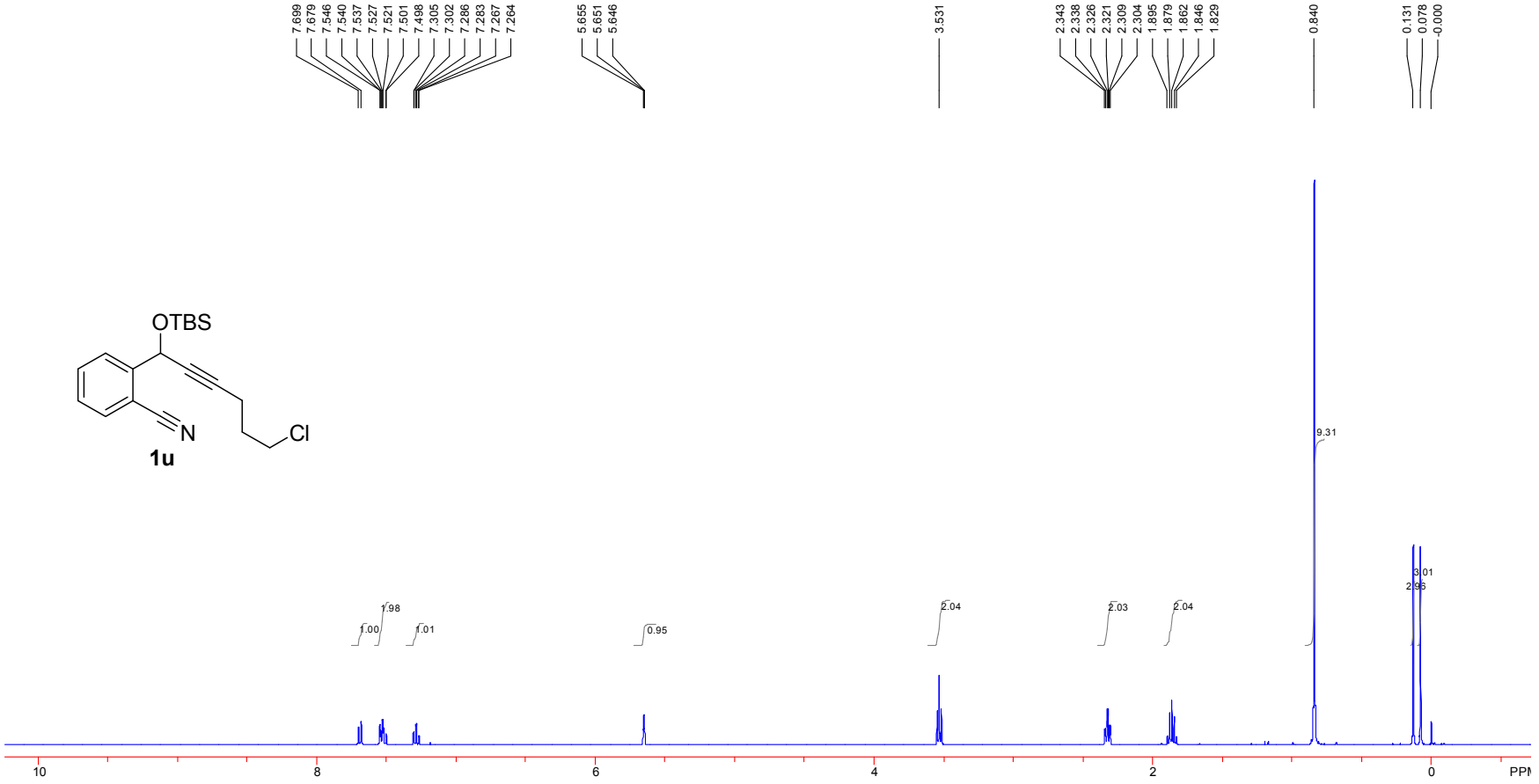
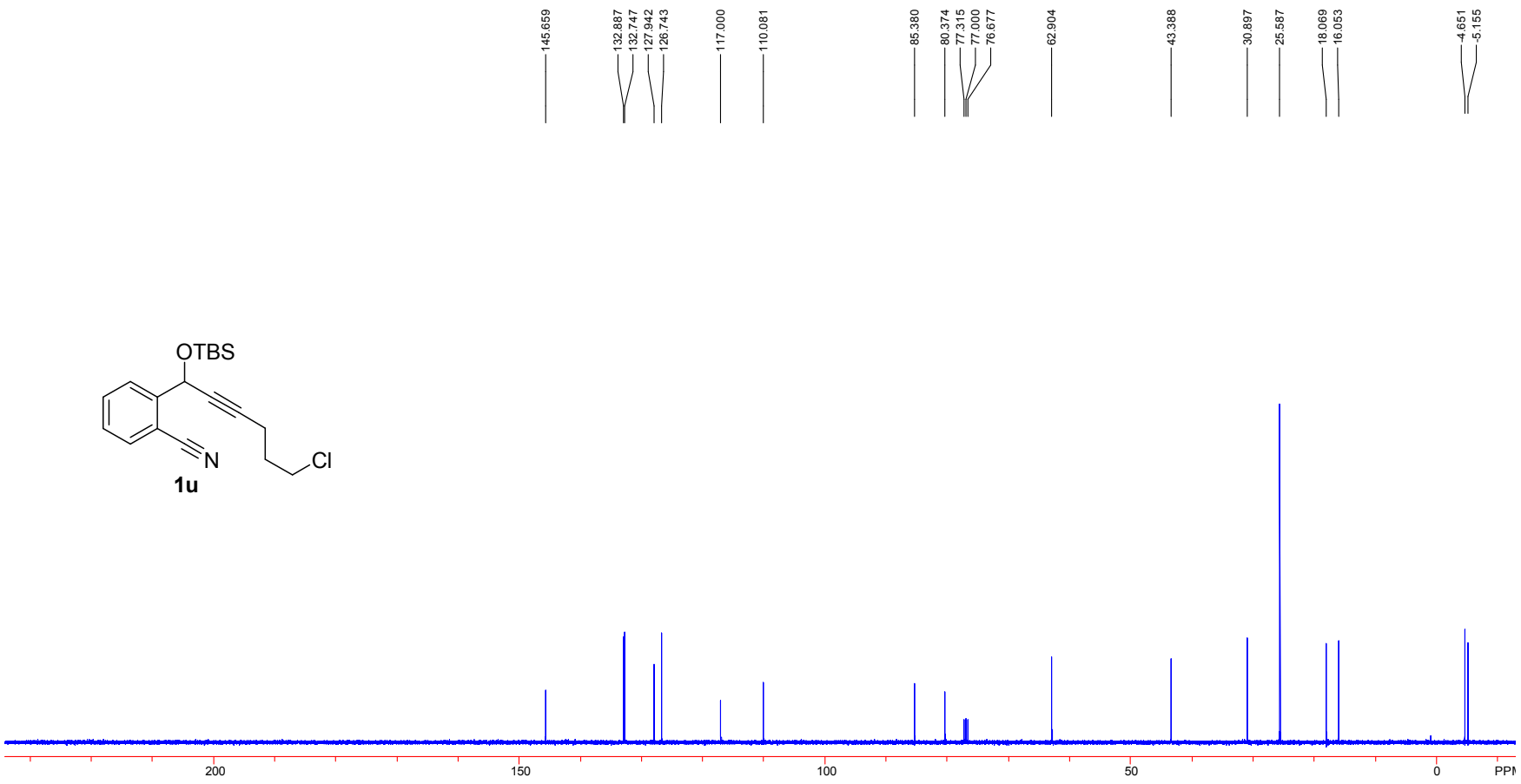


^{13}C NMR (100 MHz, $CDCl_3$)



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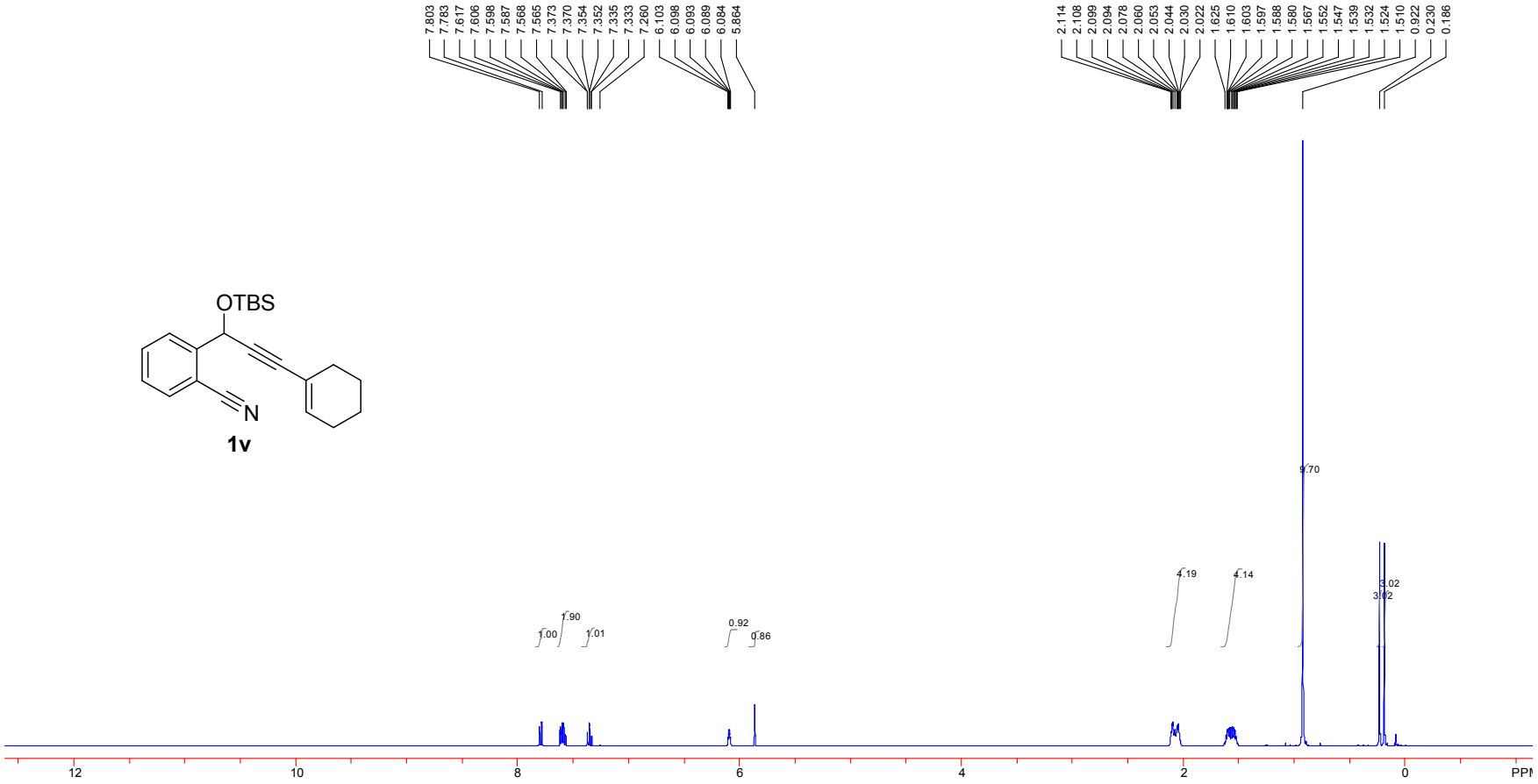

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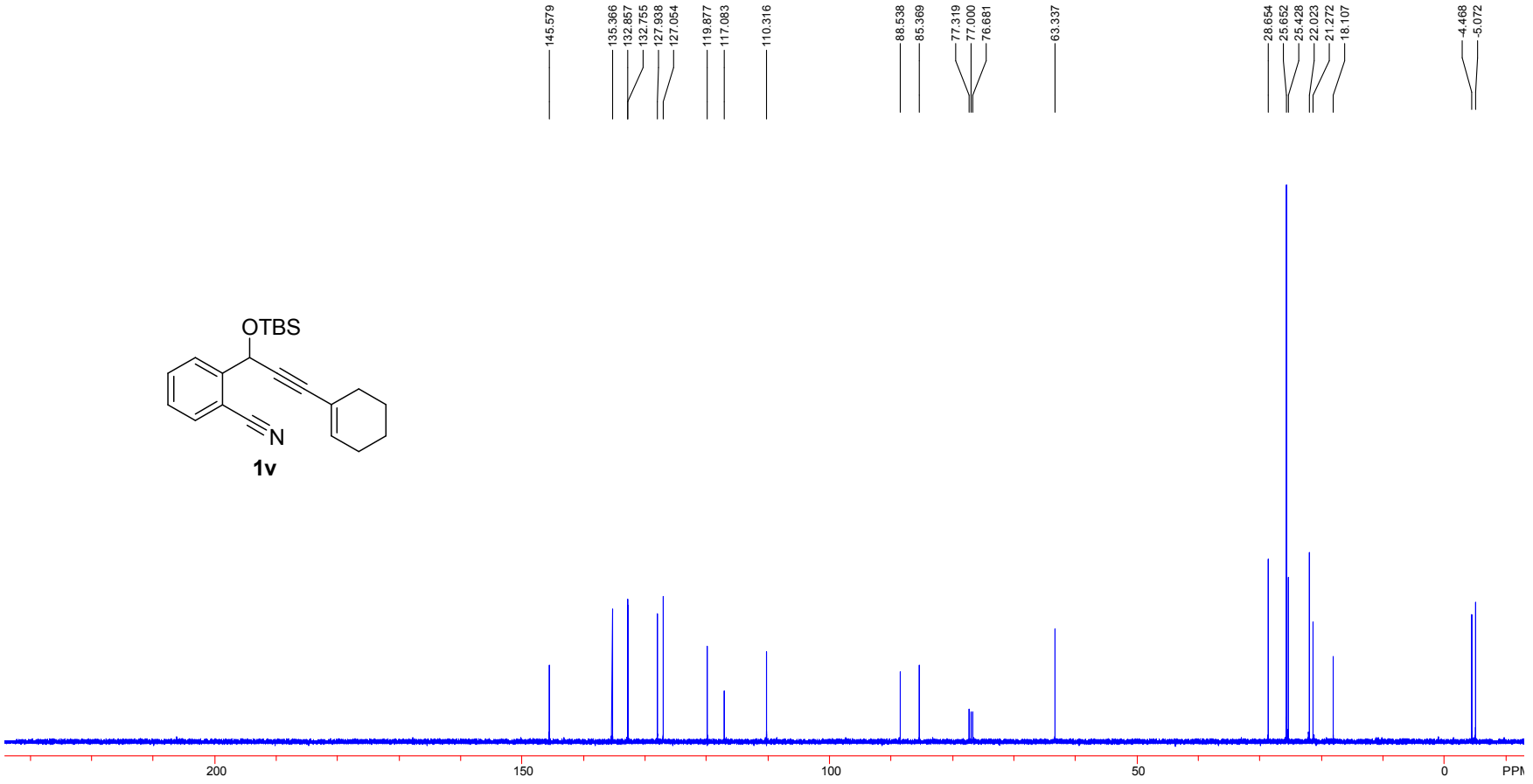

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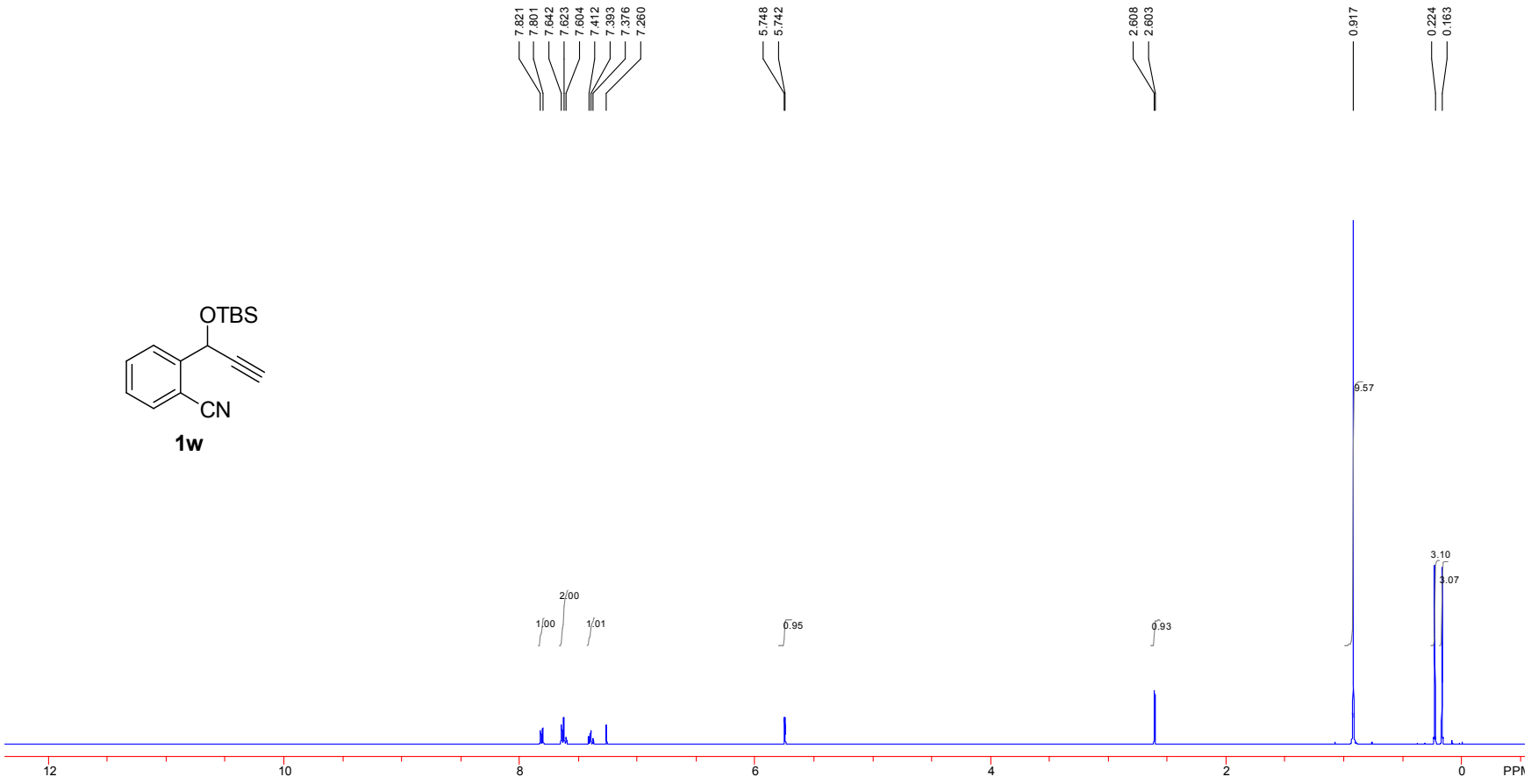
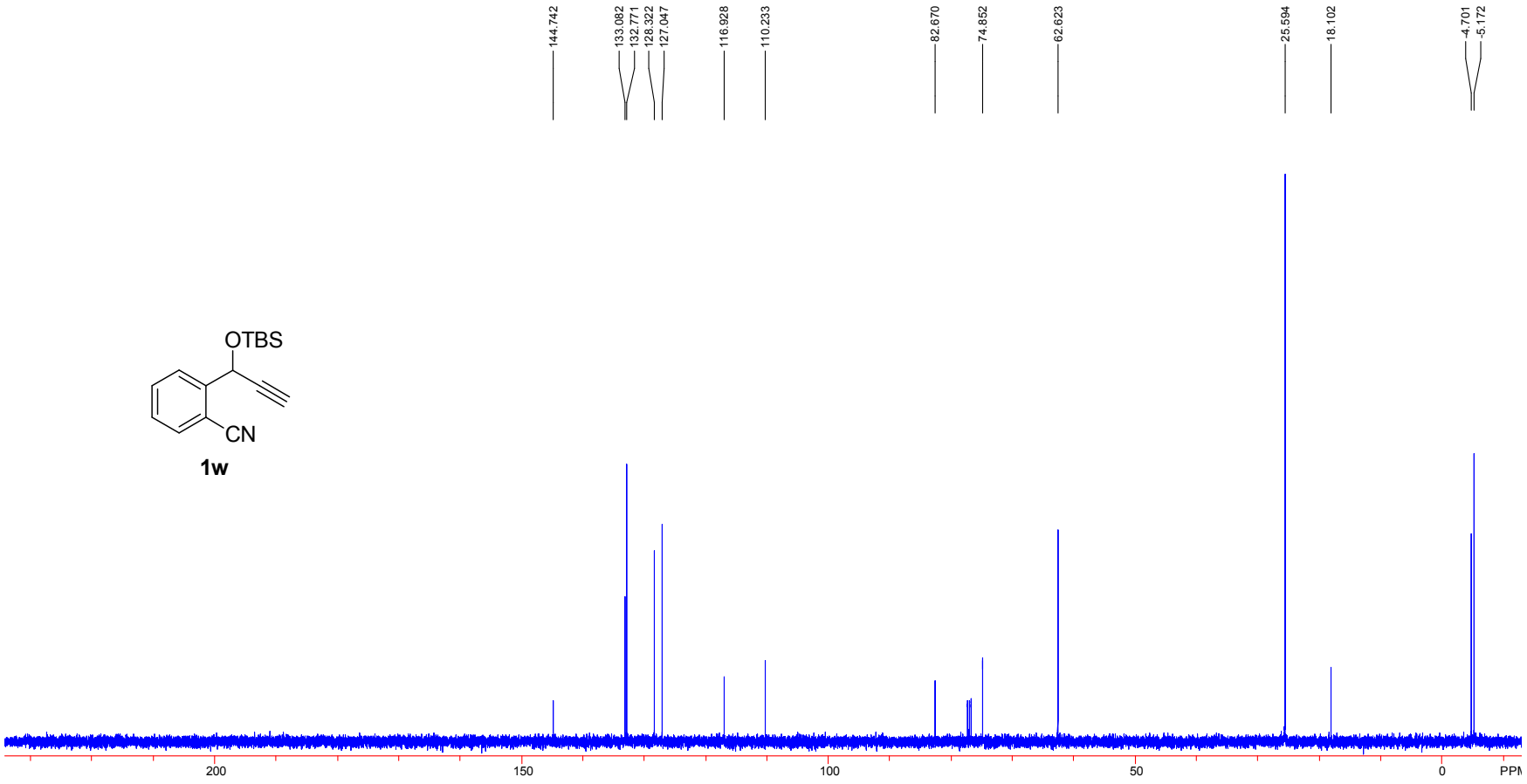


^{13}C NMR (100 MHz, $CDCl_3$)



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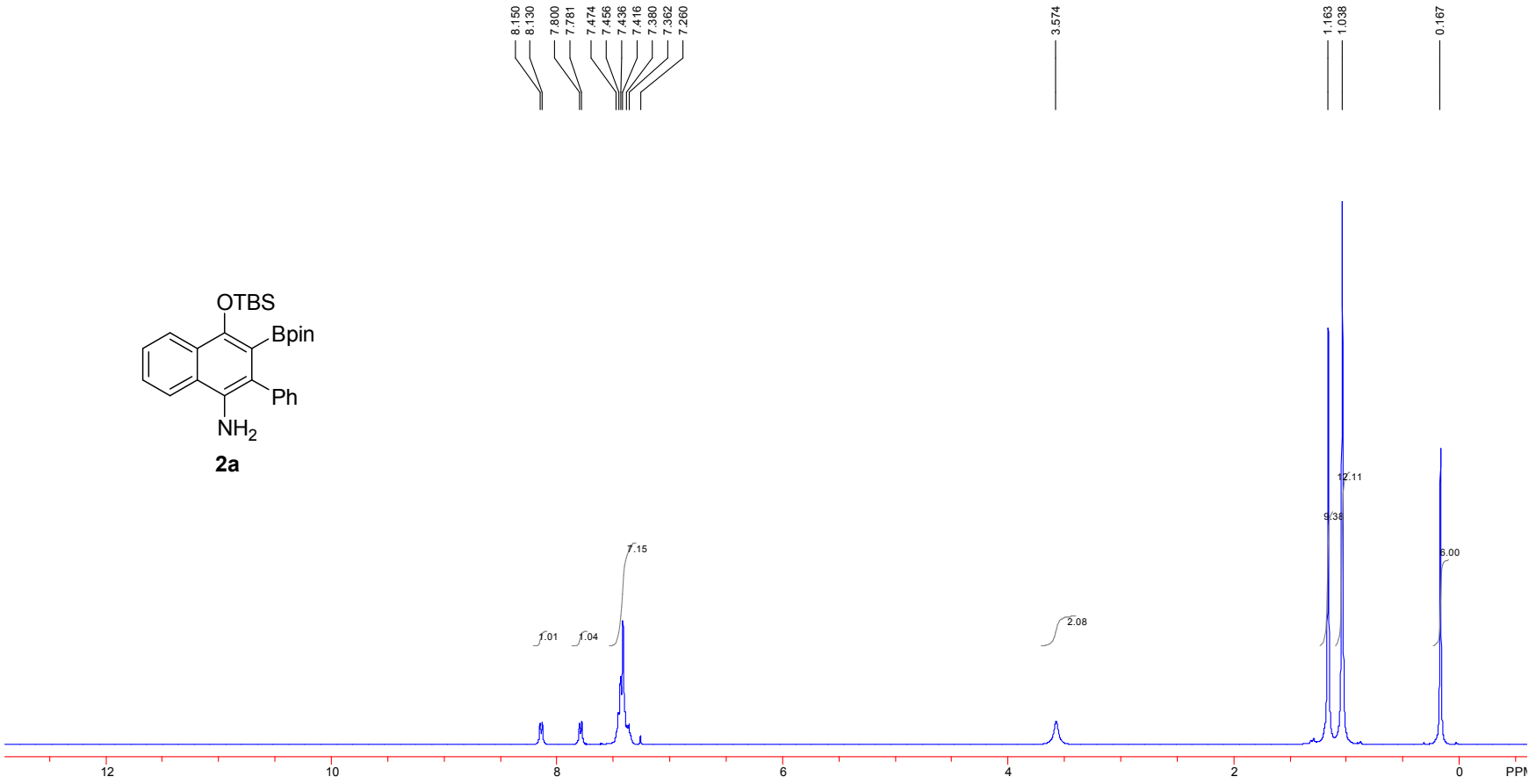

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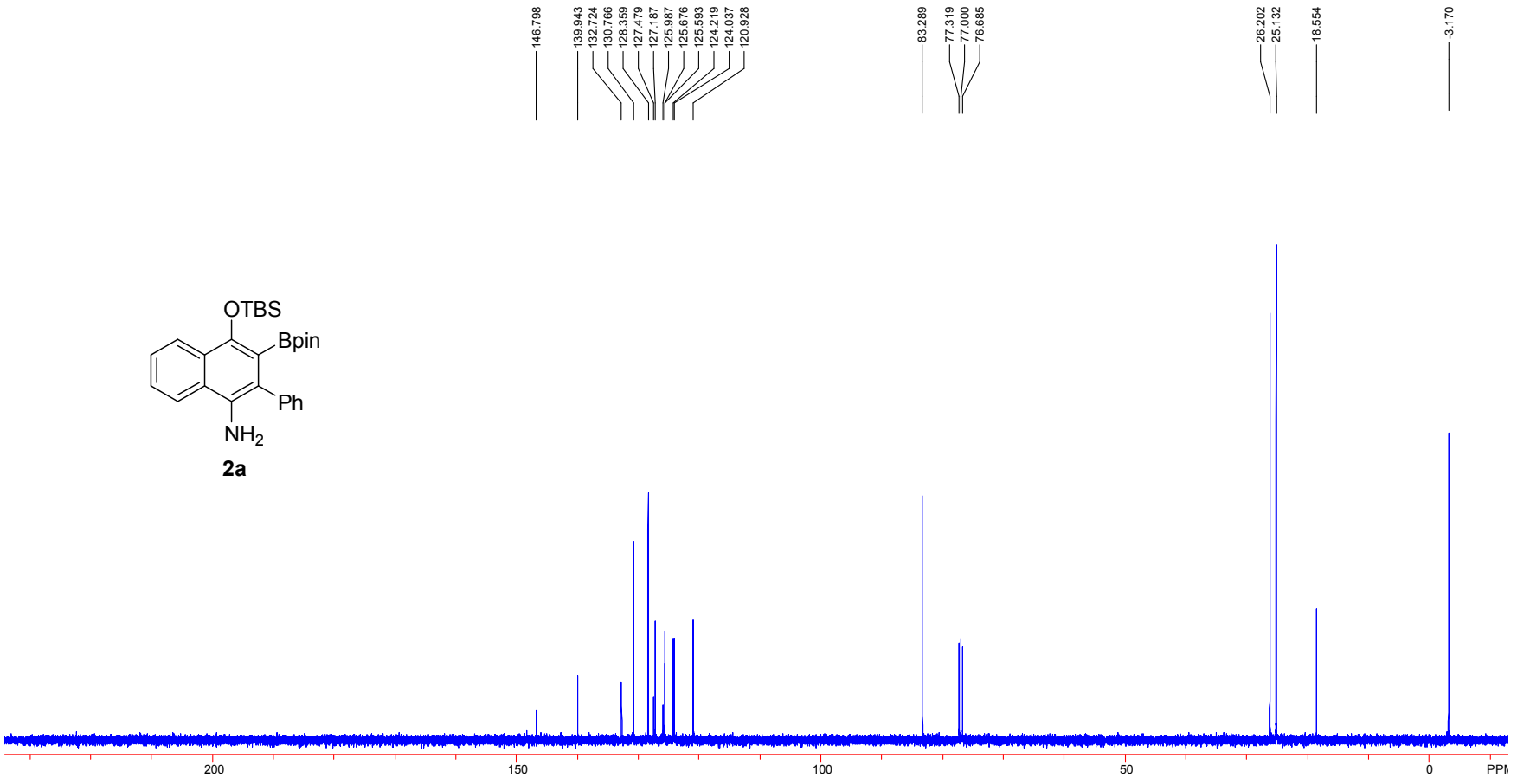

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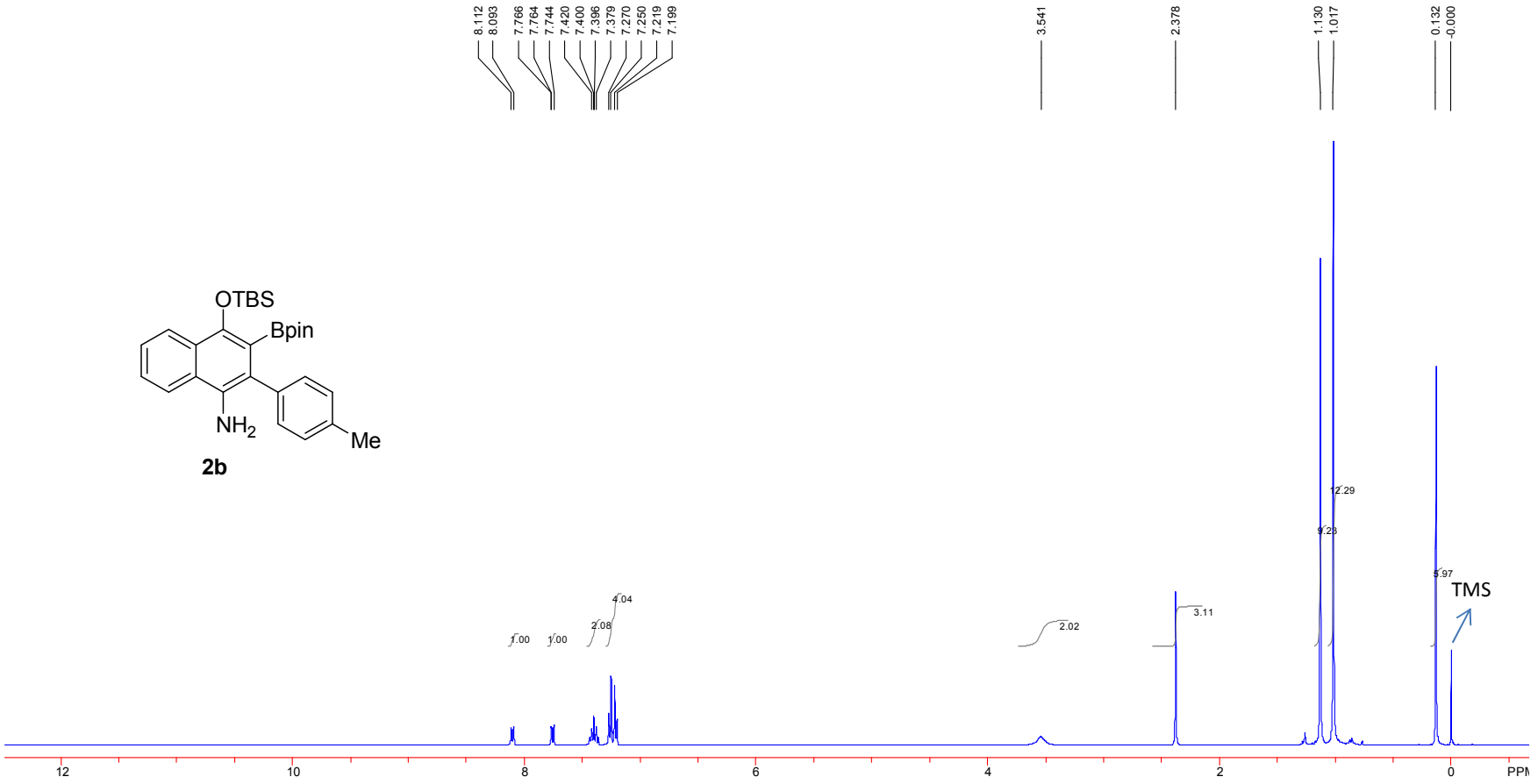
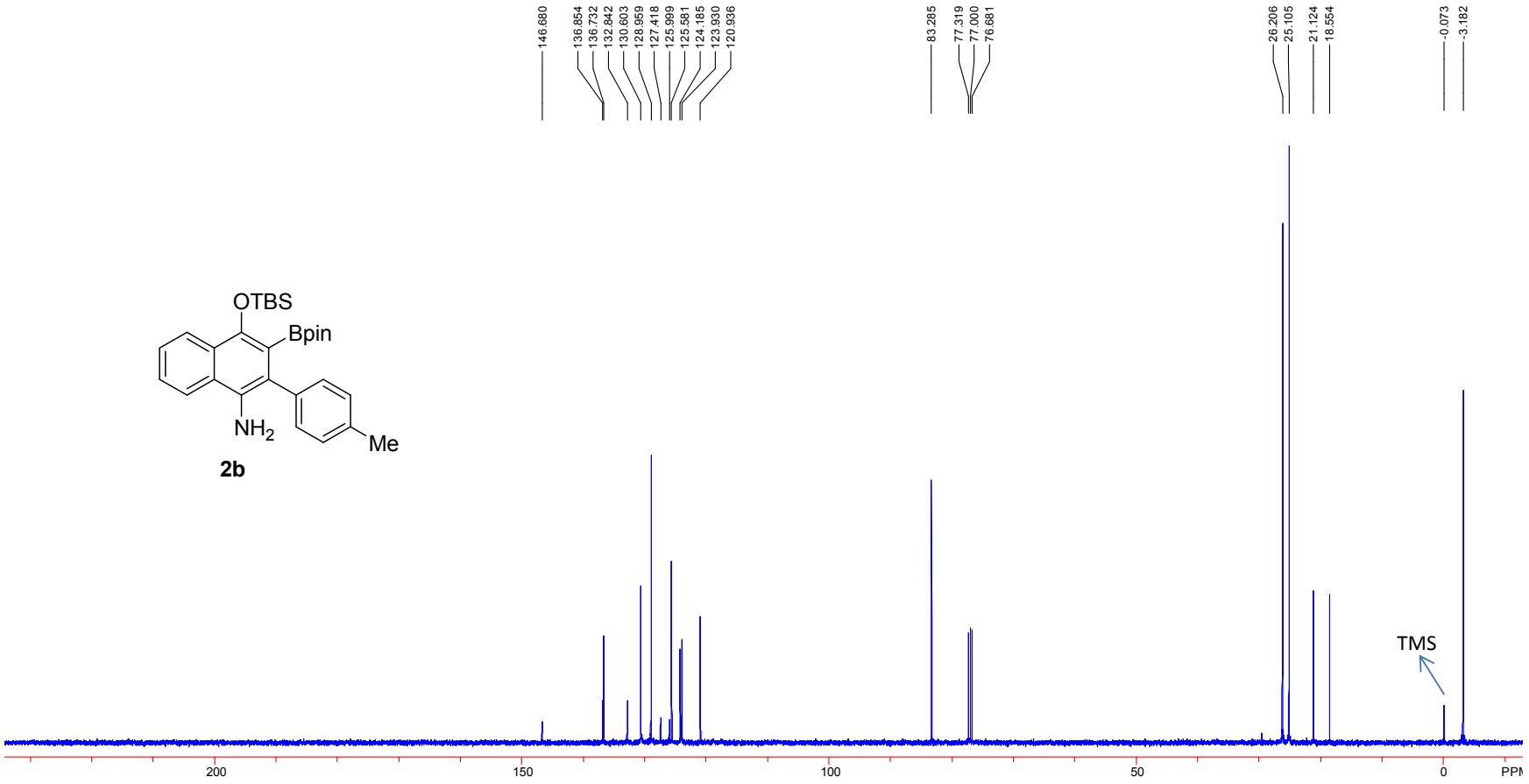


^{13}C NMR (100 MHz, $CDCl_3$)



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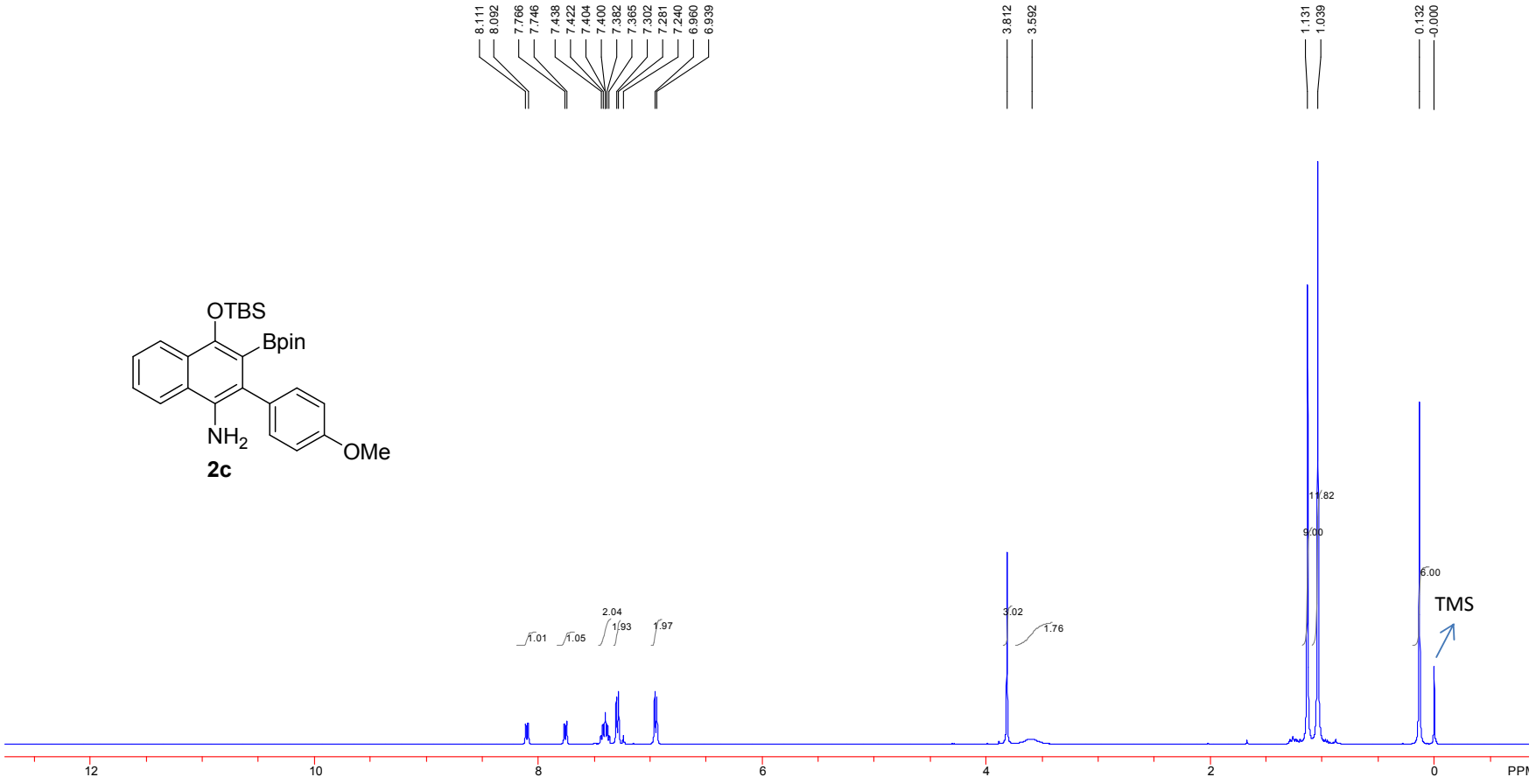

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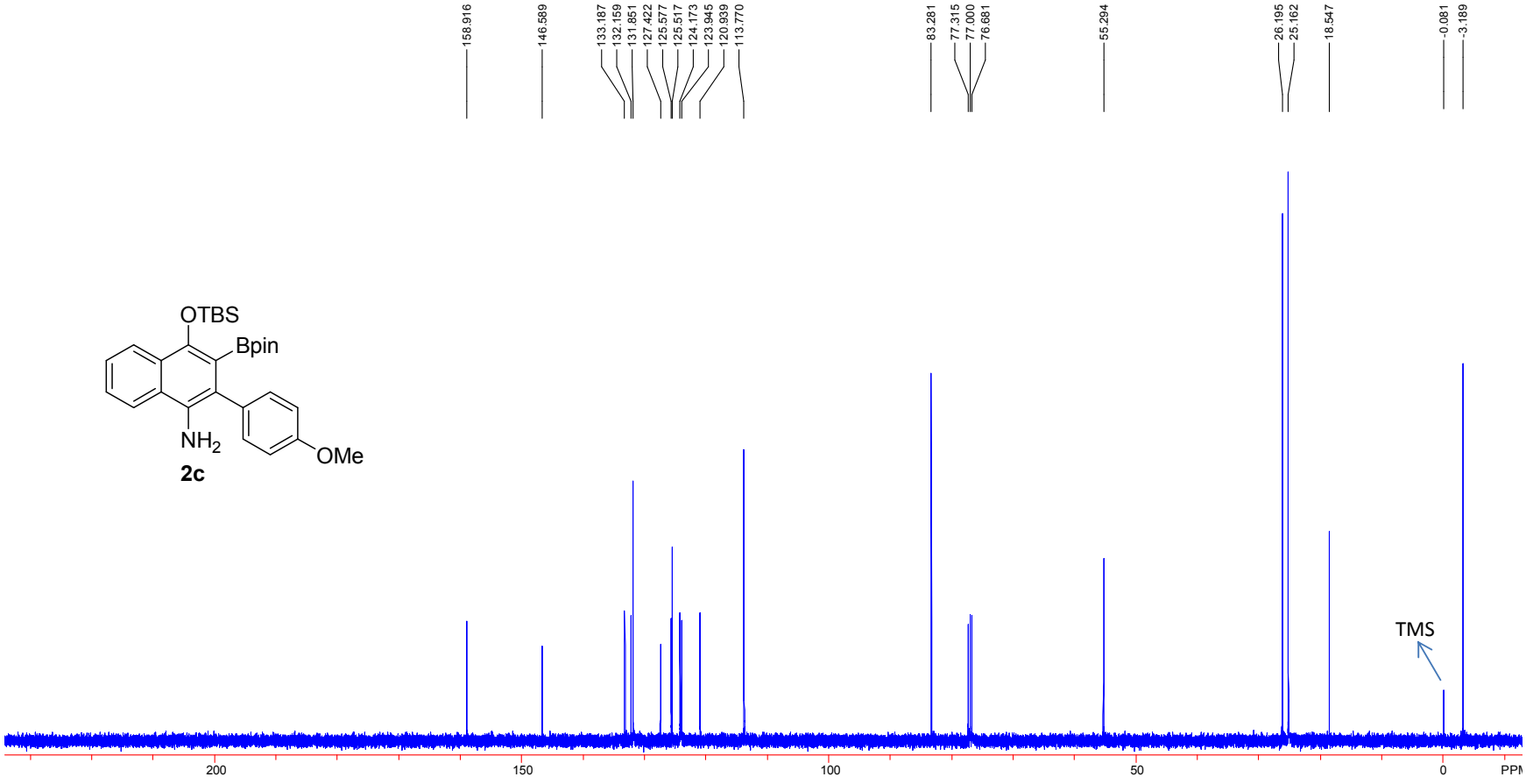
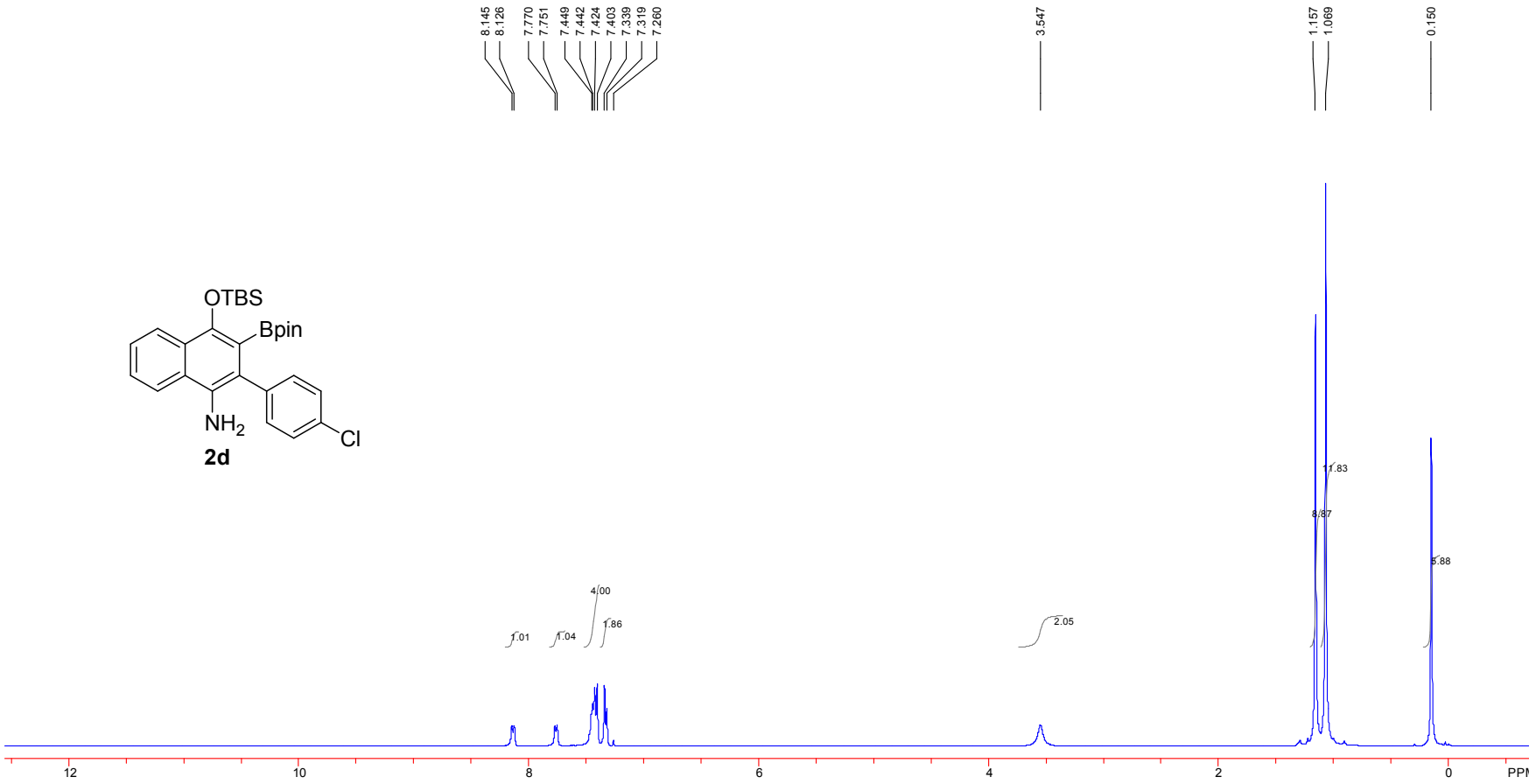


^{1}H NMR (400 MHz, $CDCl_3$)



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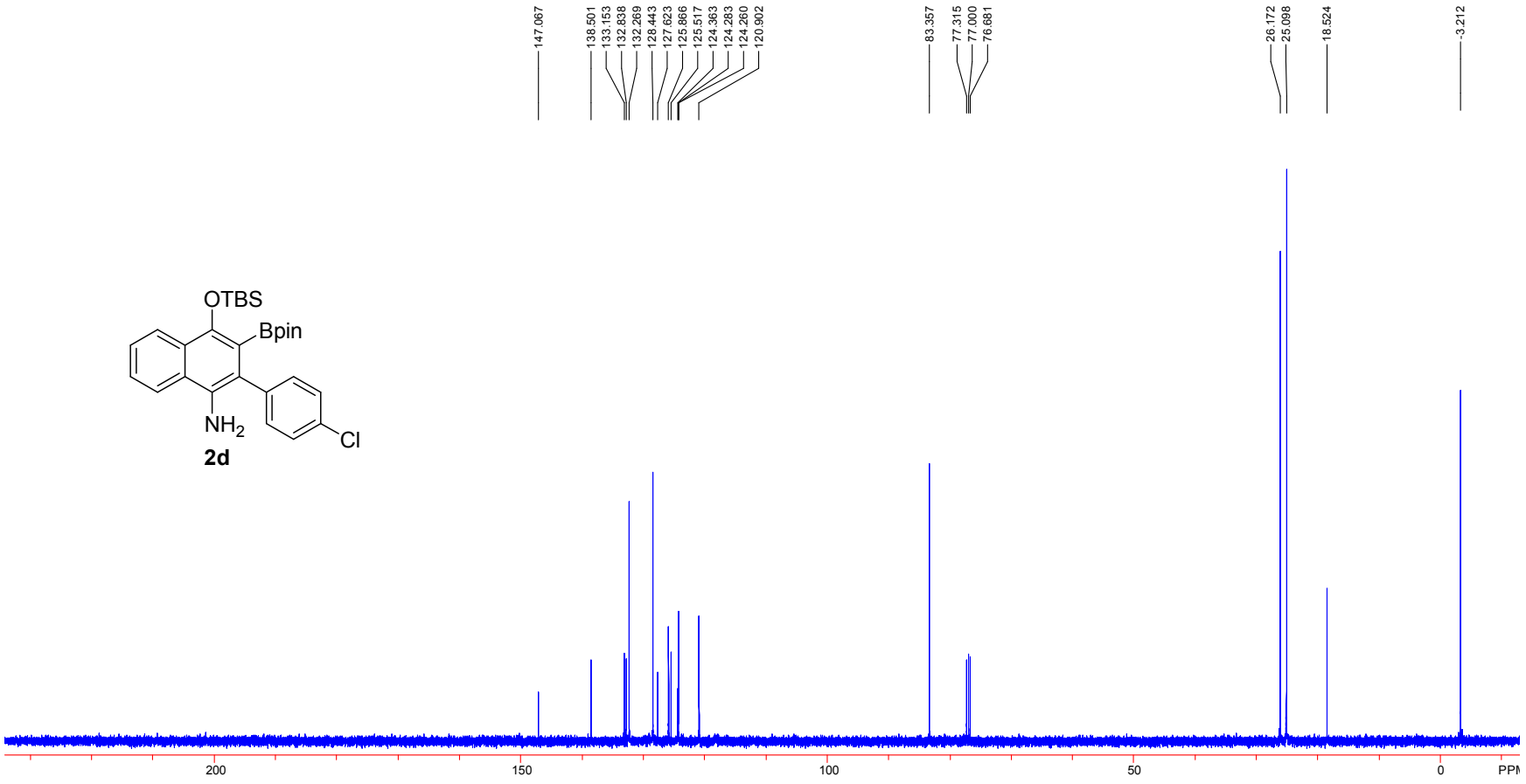

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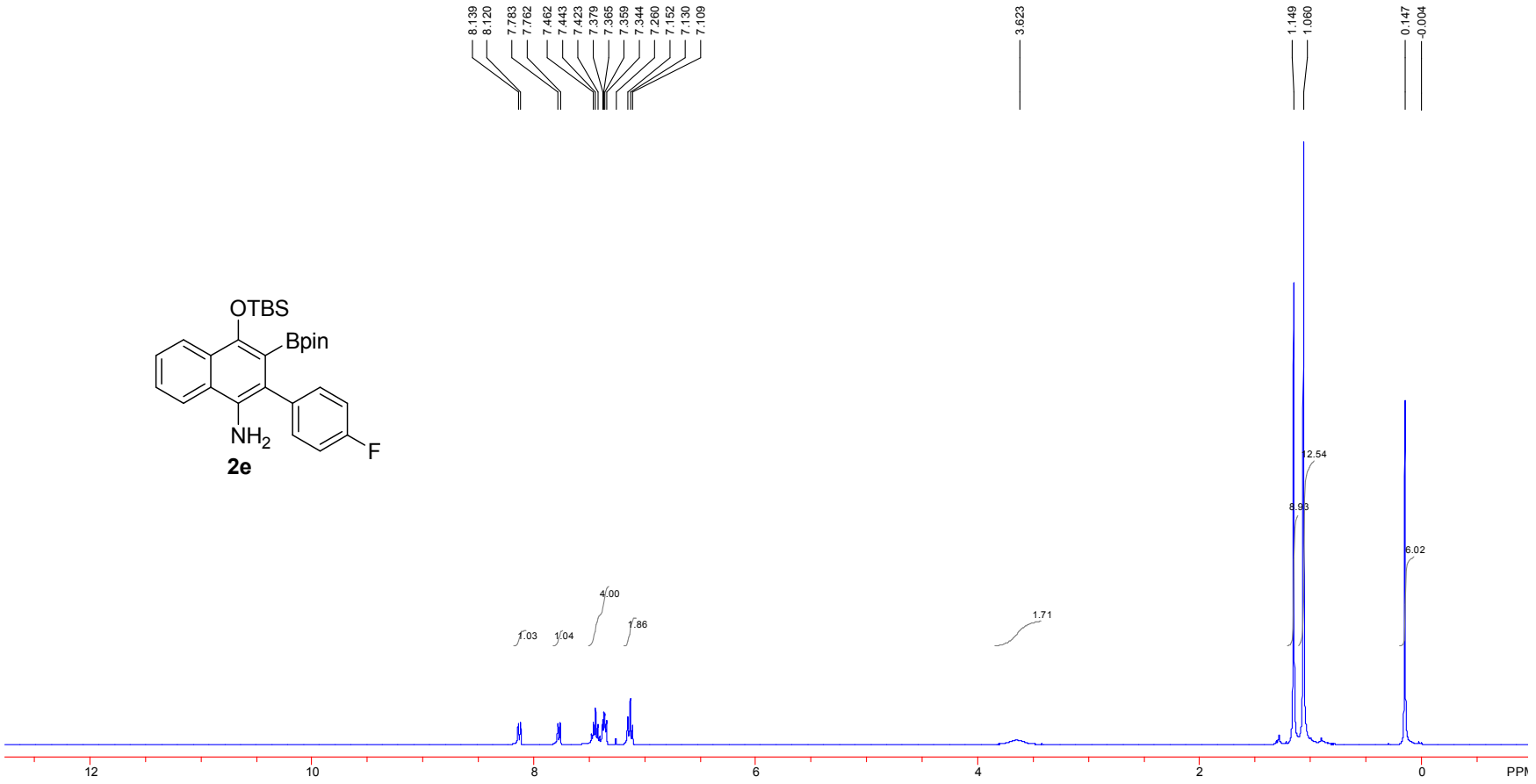

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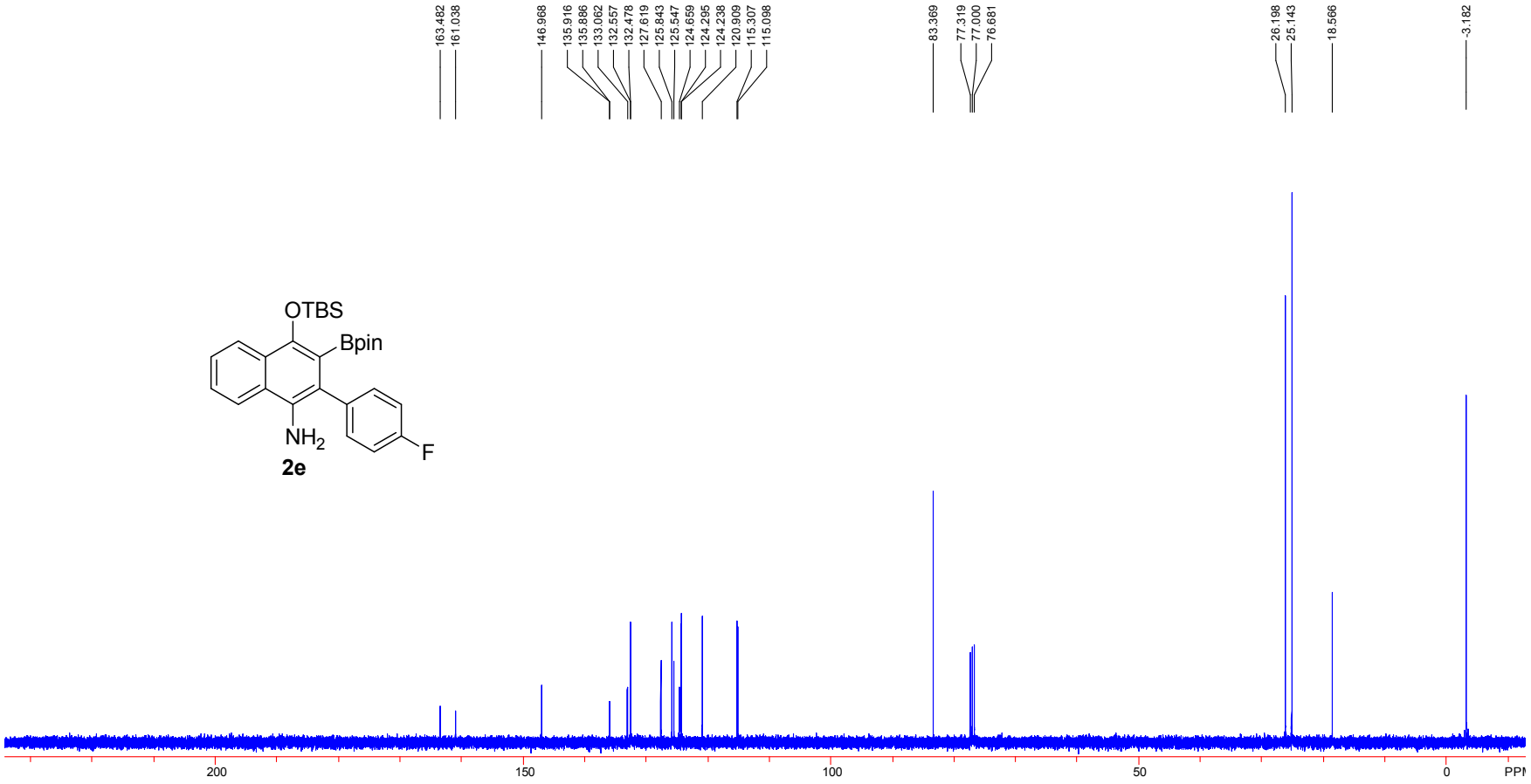
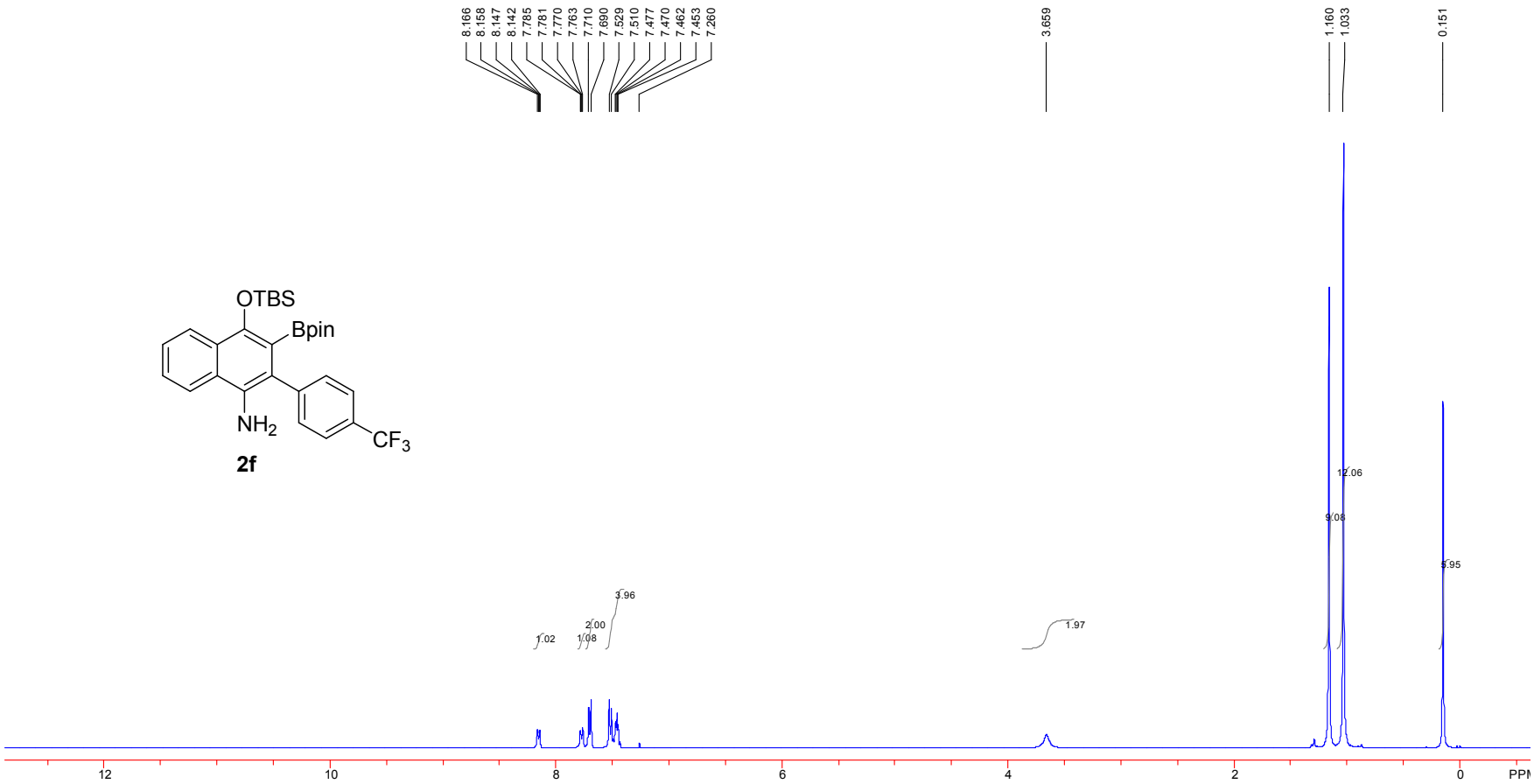


^{1}H NMR (400 MHz, $CDCl_3$)



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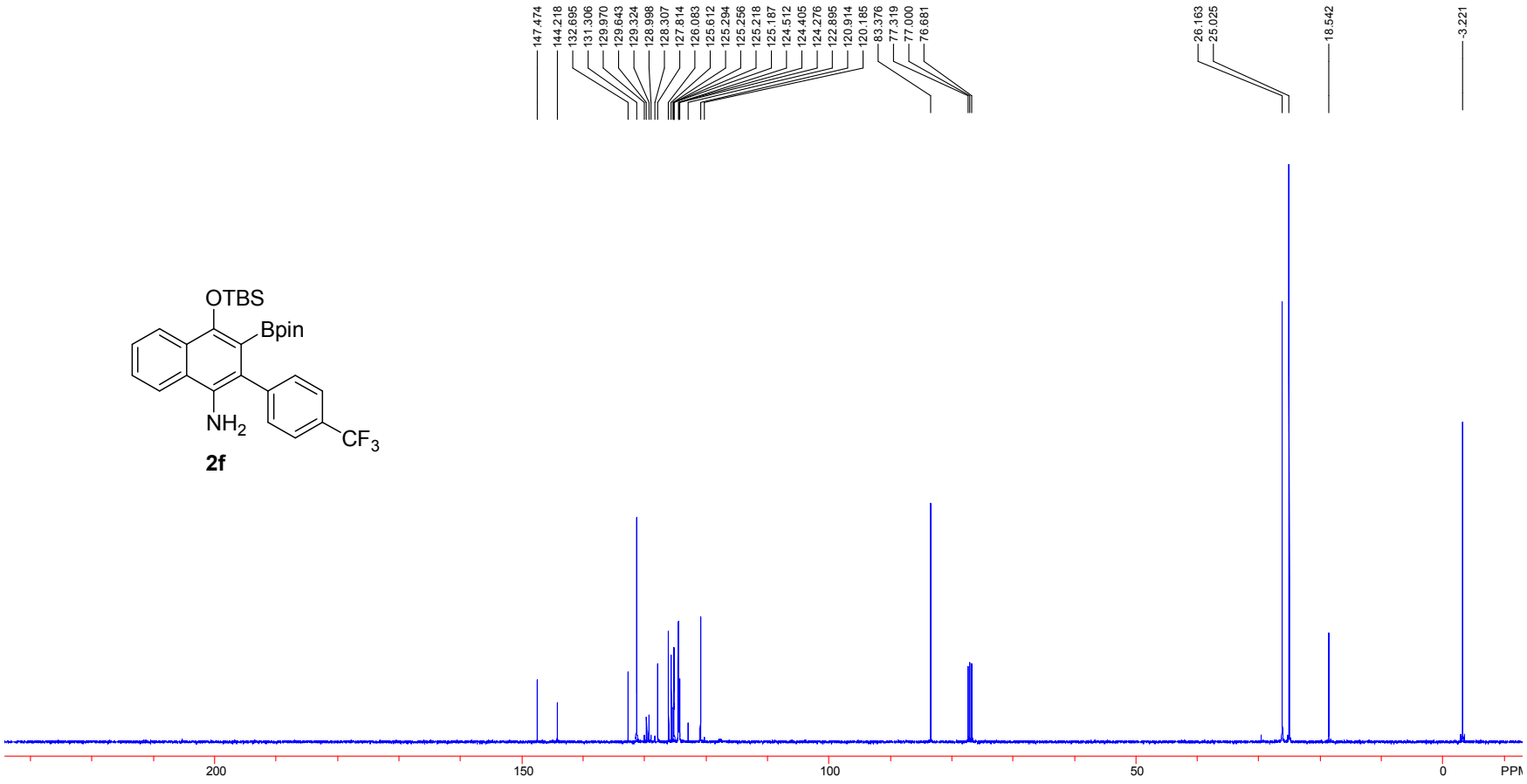
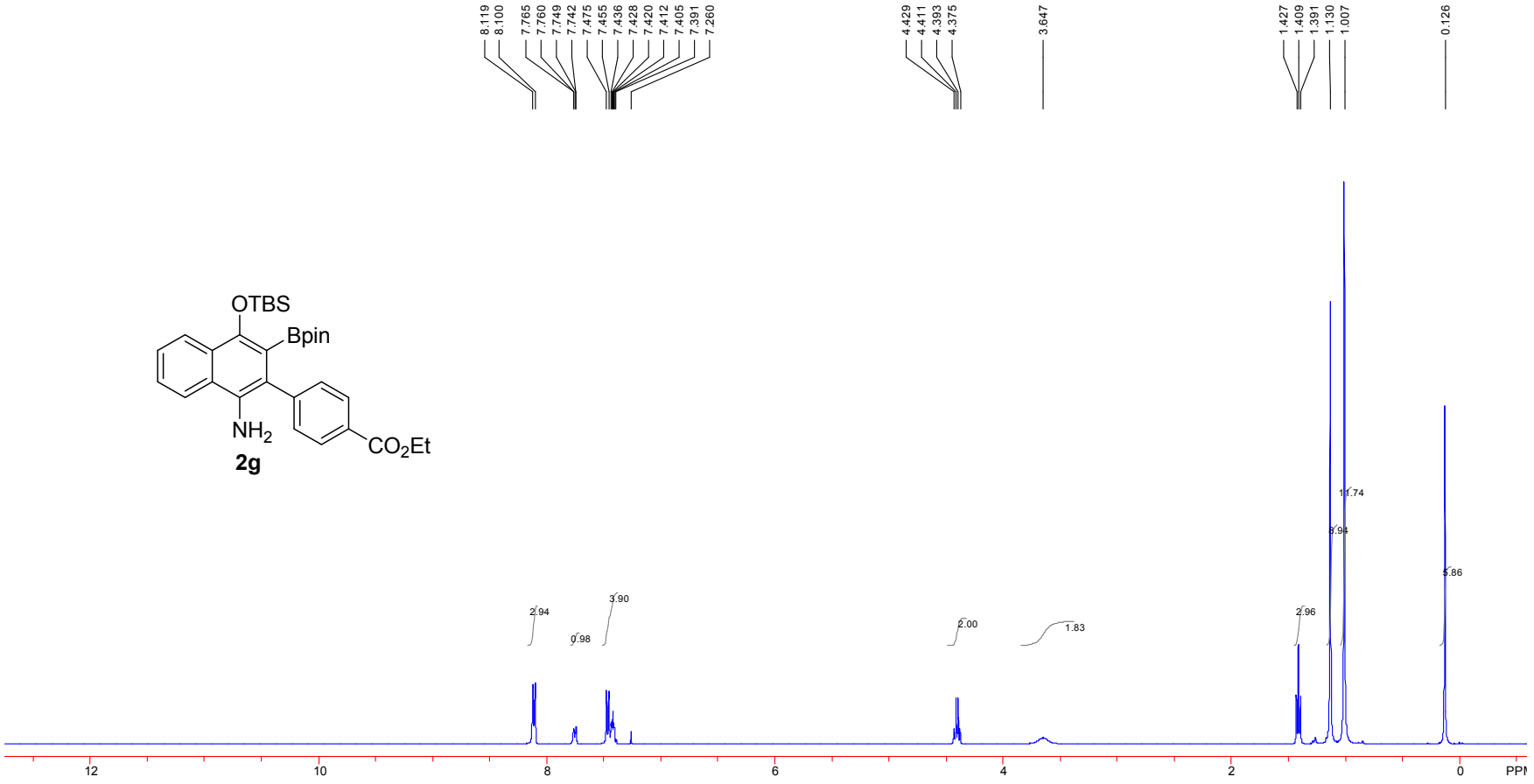


^{1}H NMR (400 MHz, $CDCl_3$)



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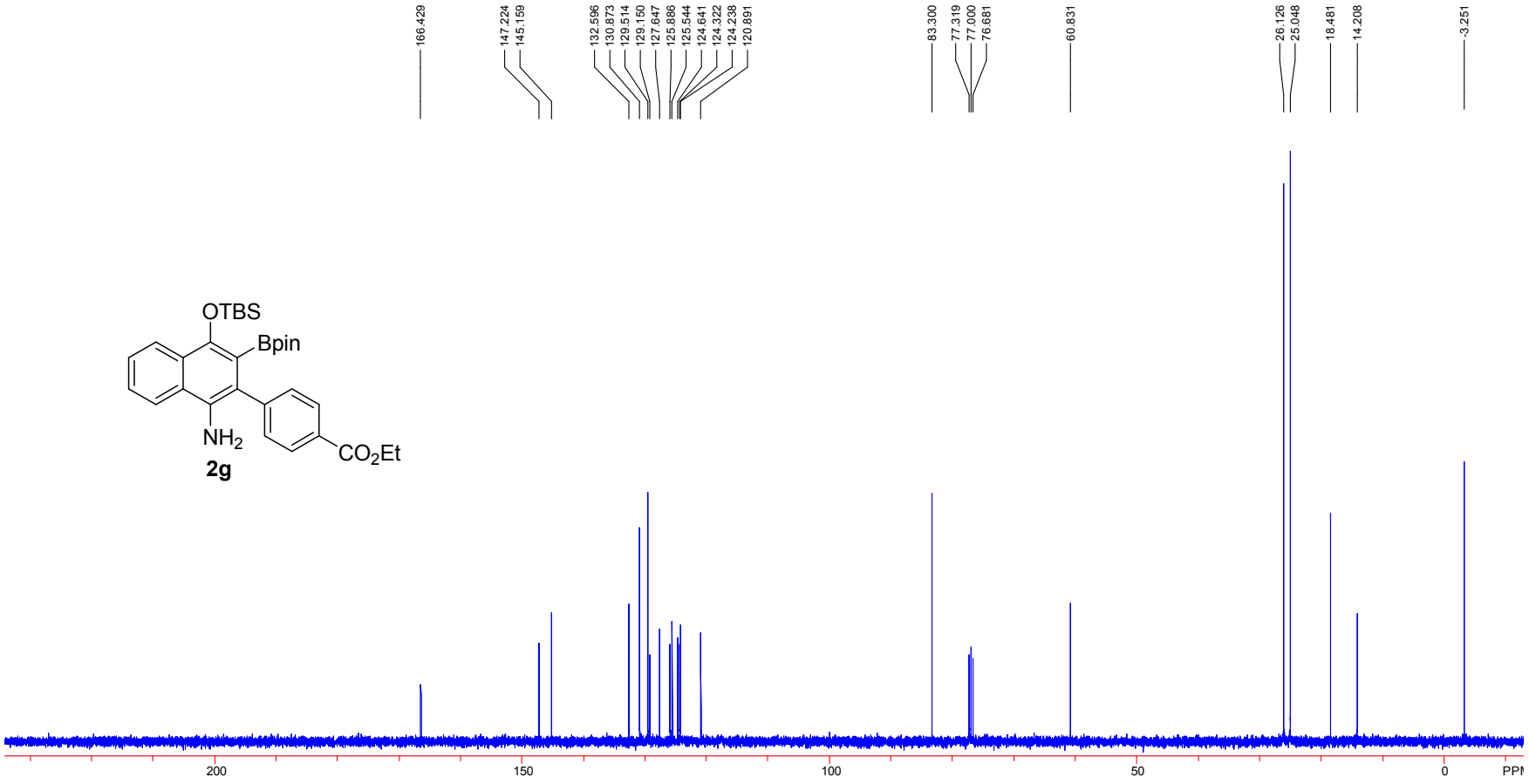
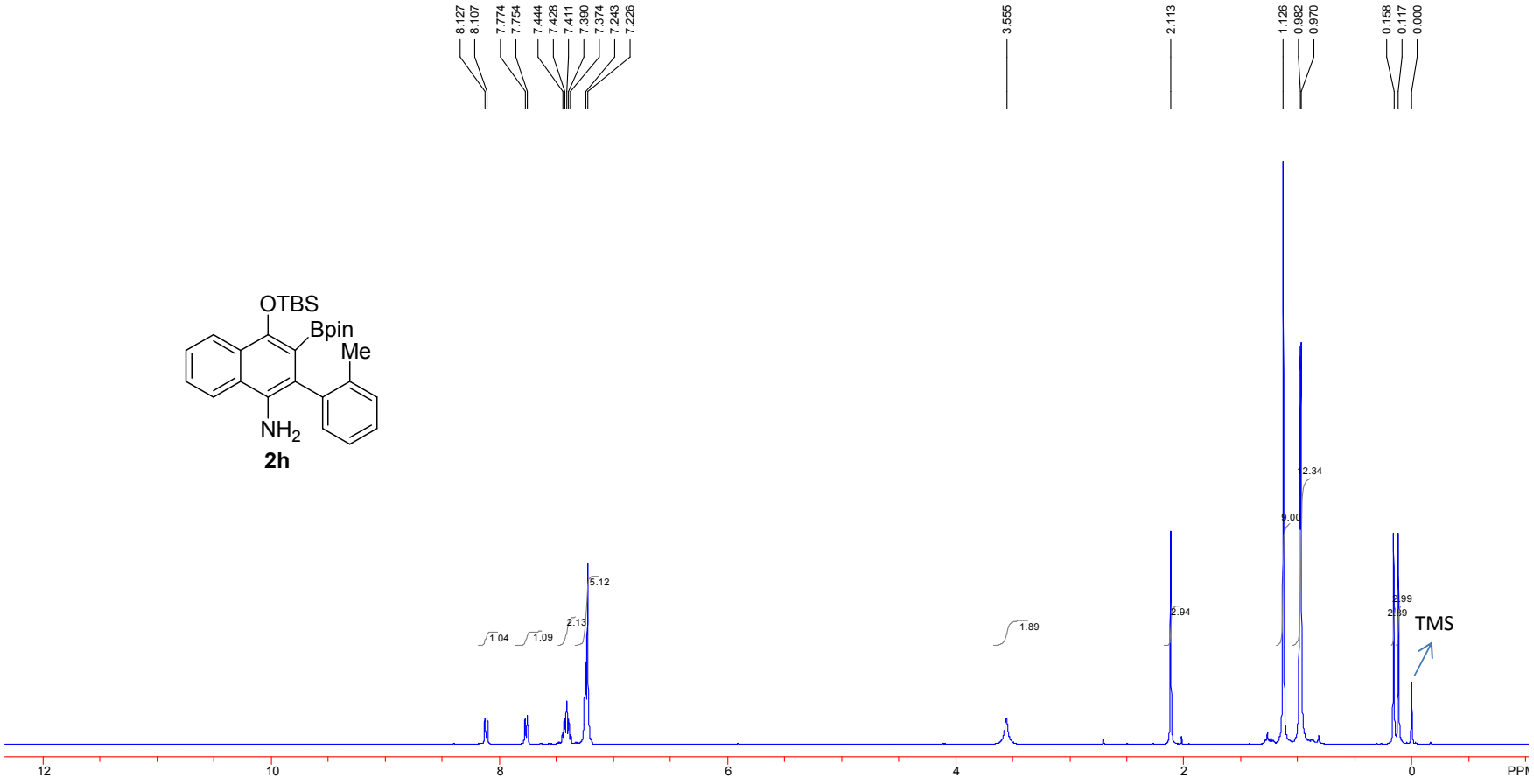
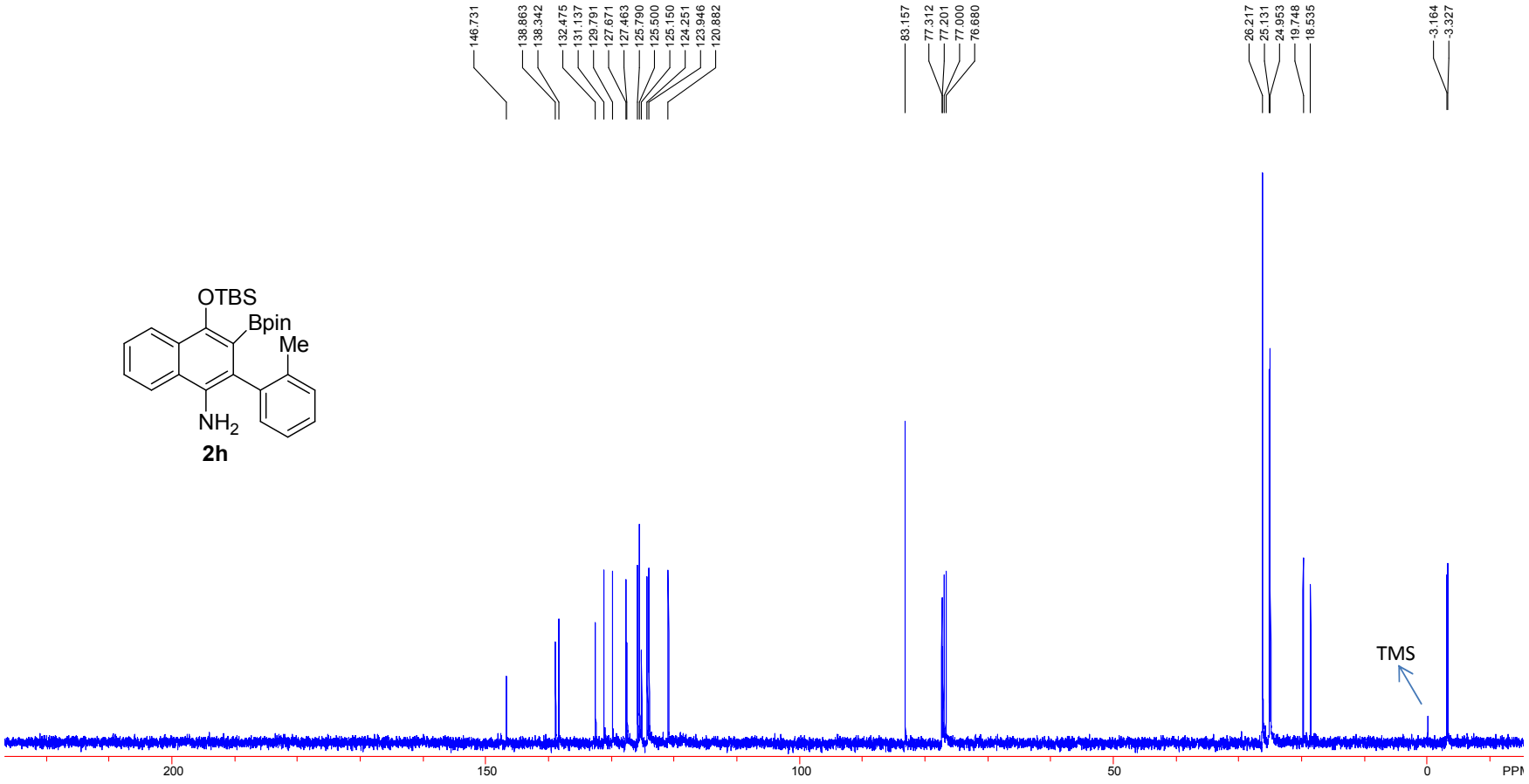


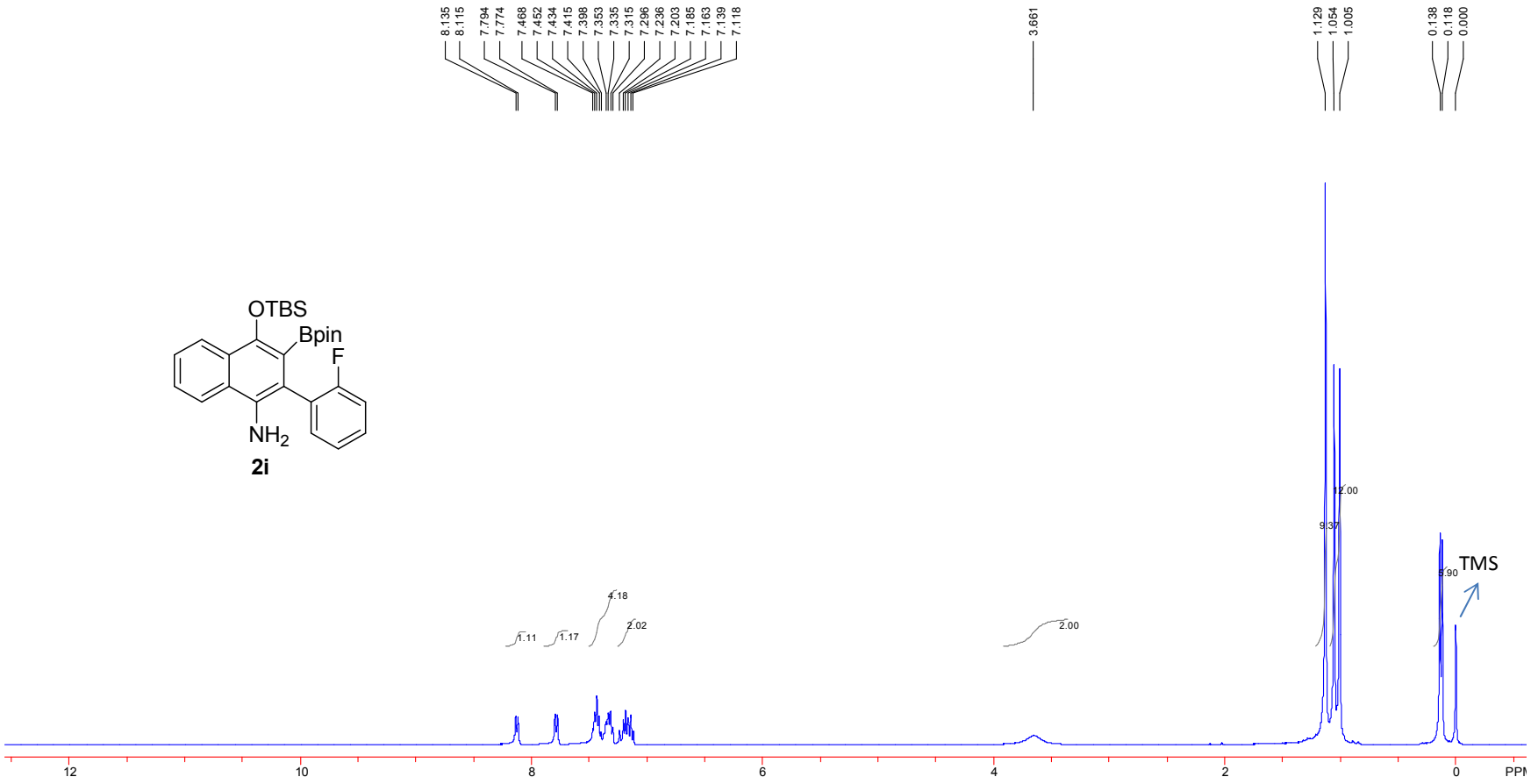
^{1}H NMR (400 MHz, $CDCl_3$)



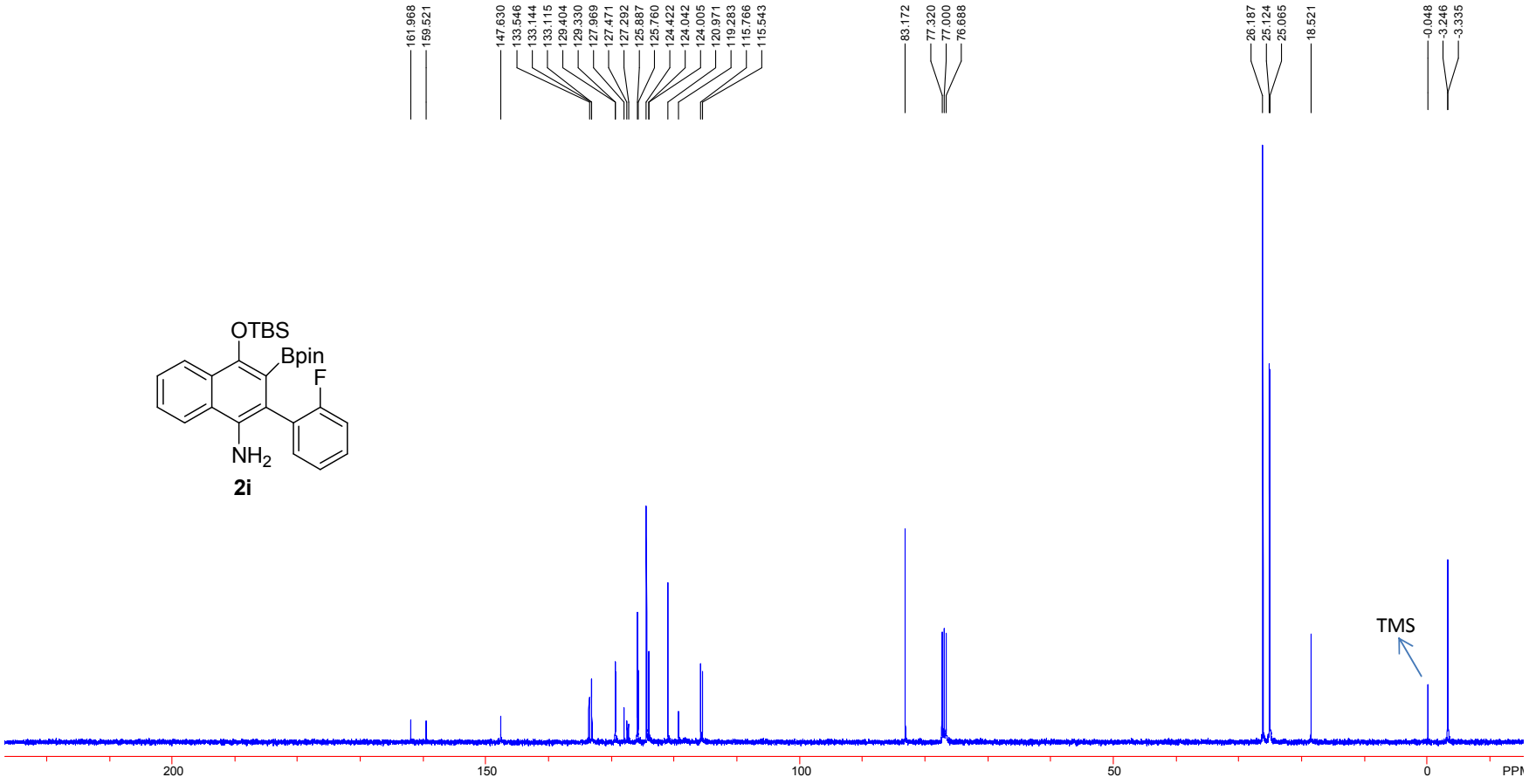
^{13}C NMR (100 MHz, $CDCl_3$)



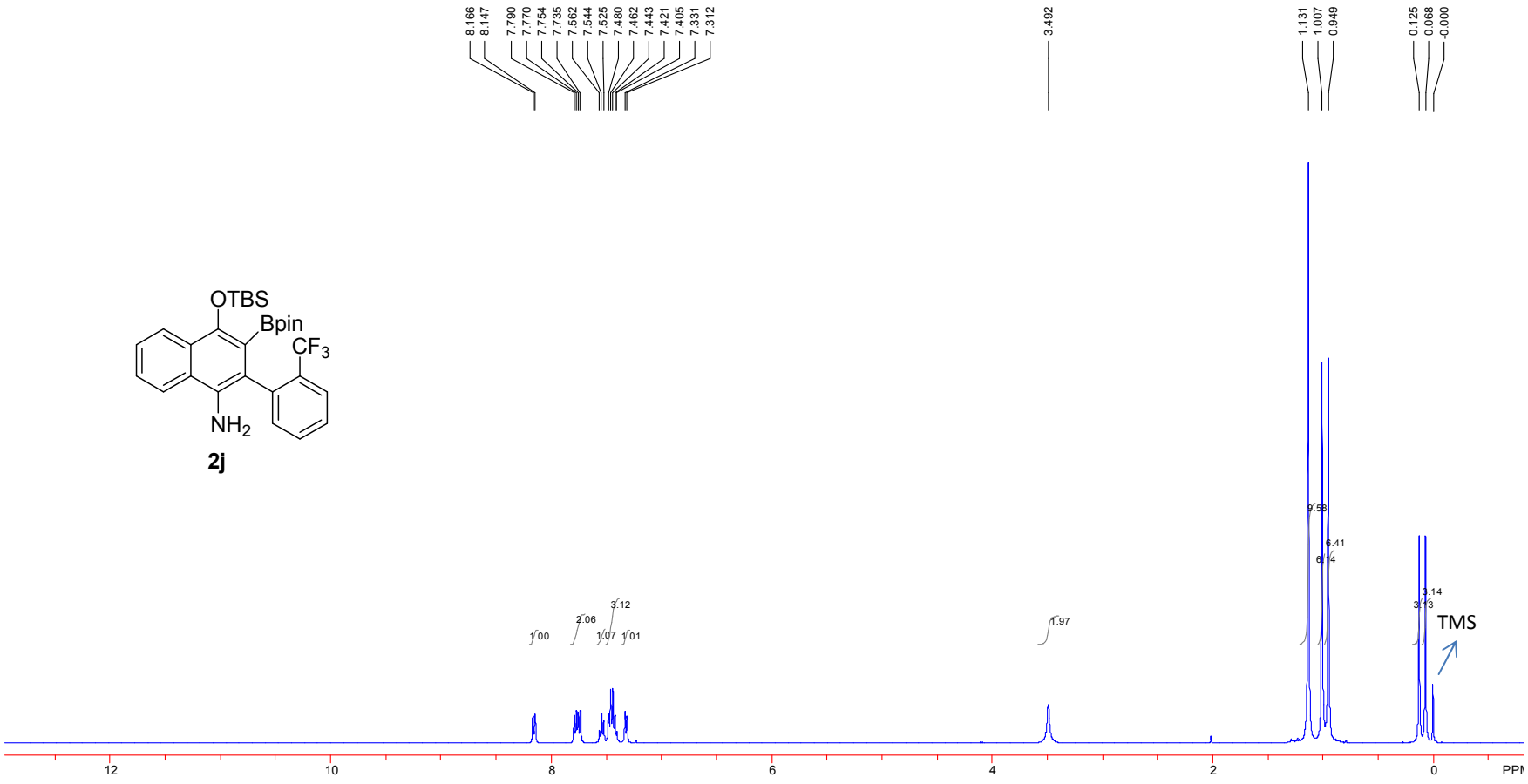
^{1}H NMR (400 MHz, $CDCl_3$)



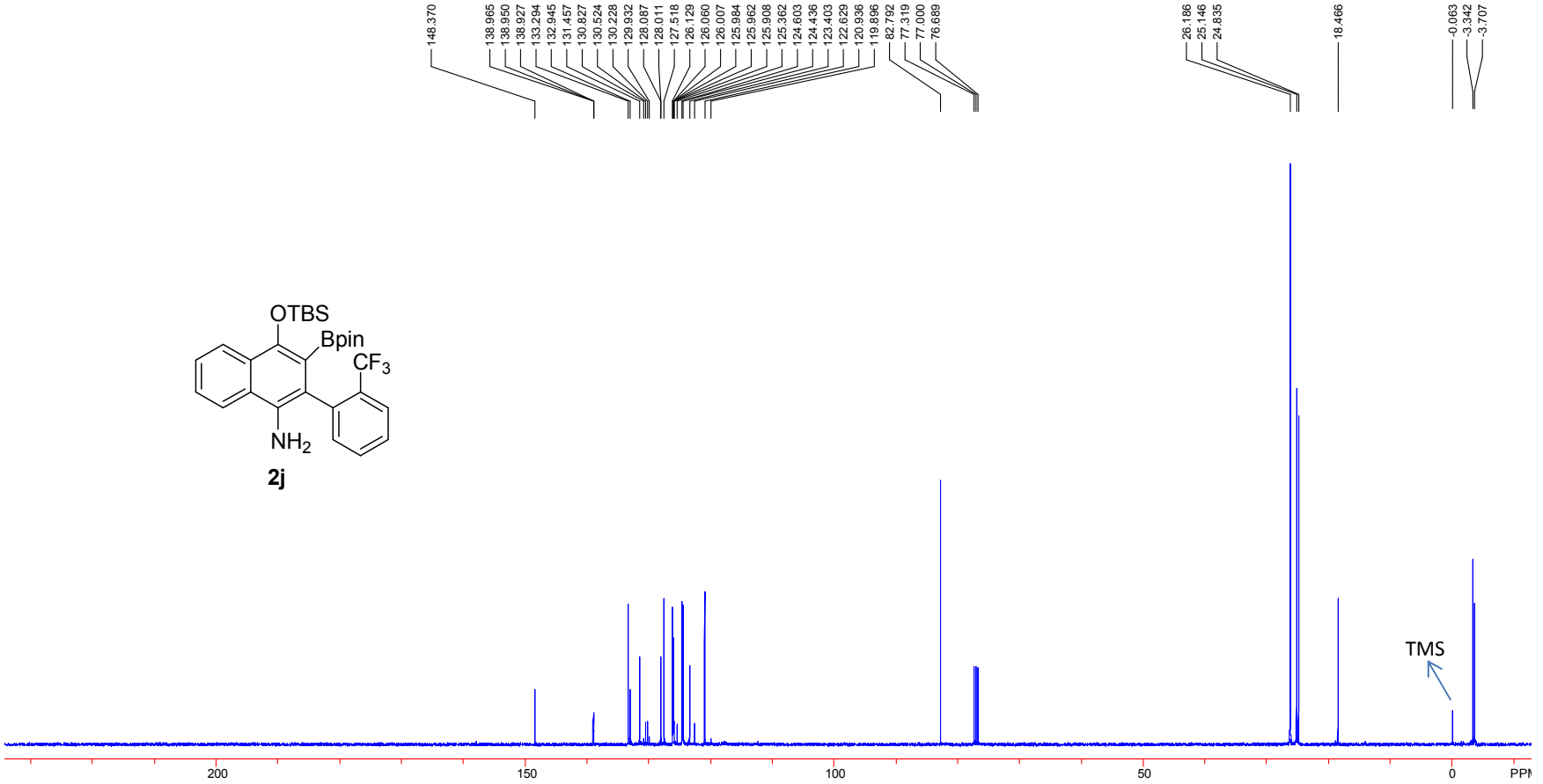
^{13}C NMR (100 MHz, $CDCl_3$)



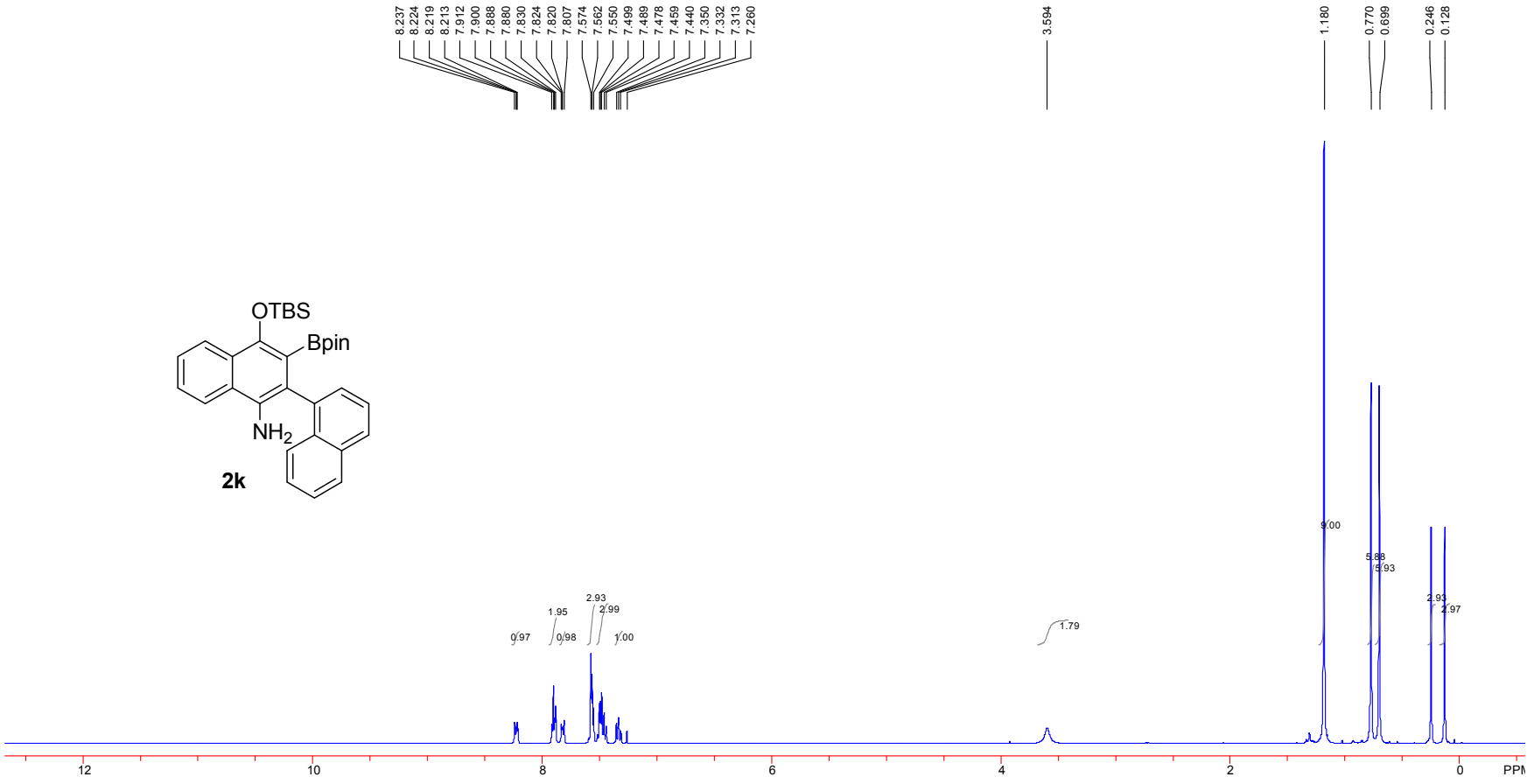
^{1}H NMR (400 MHz, $CDCl_3$)



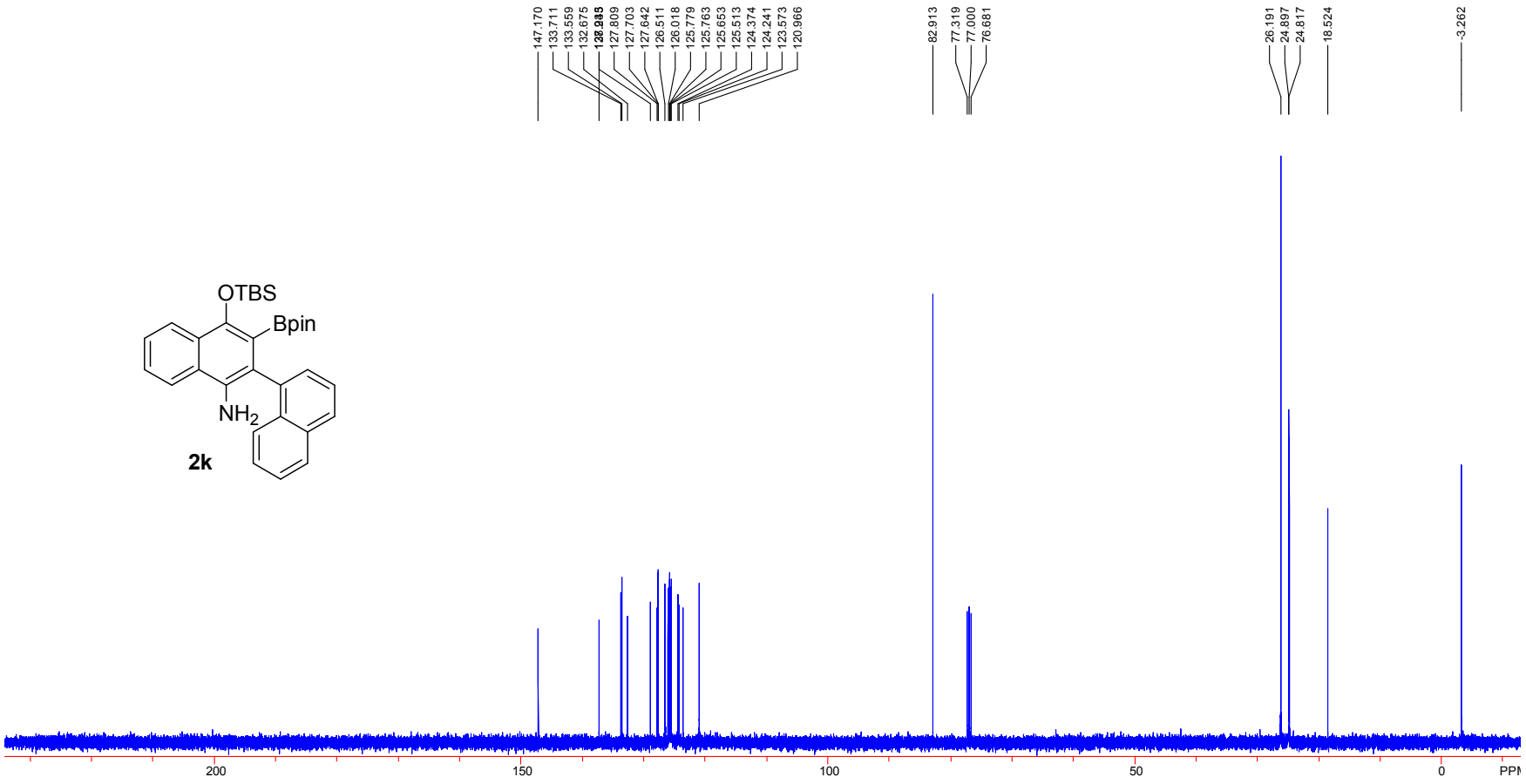
^{13}C NMR (100 MHz, $CDCl_3$)



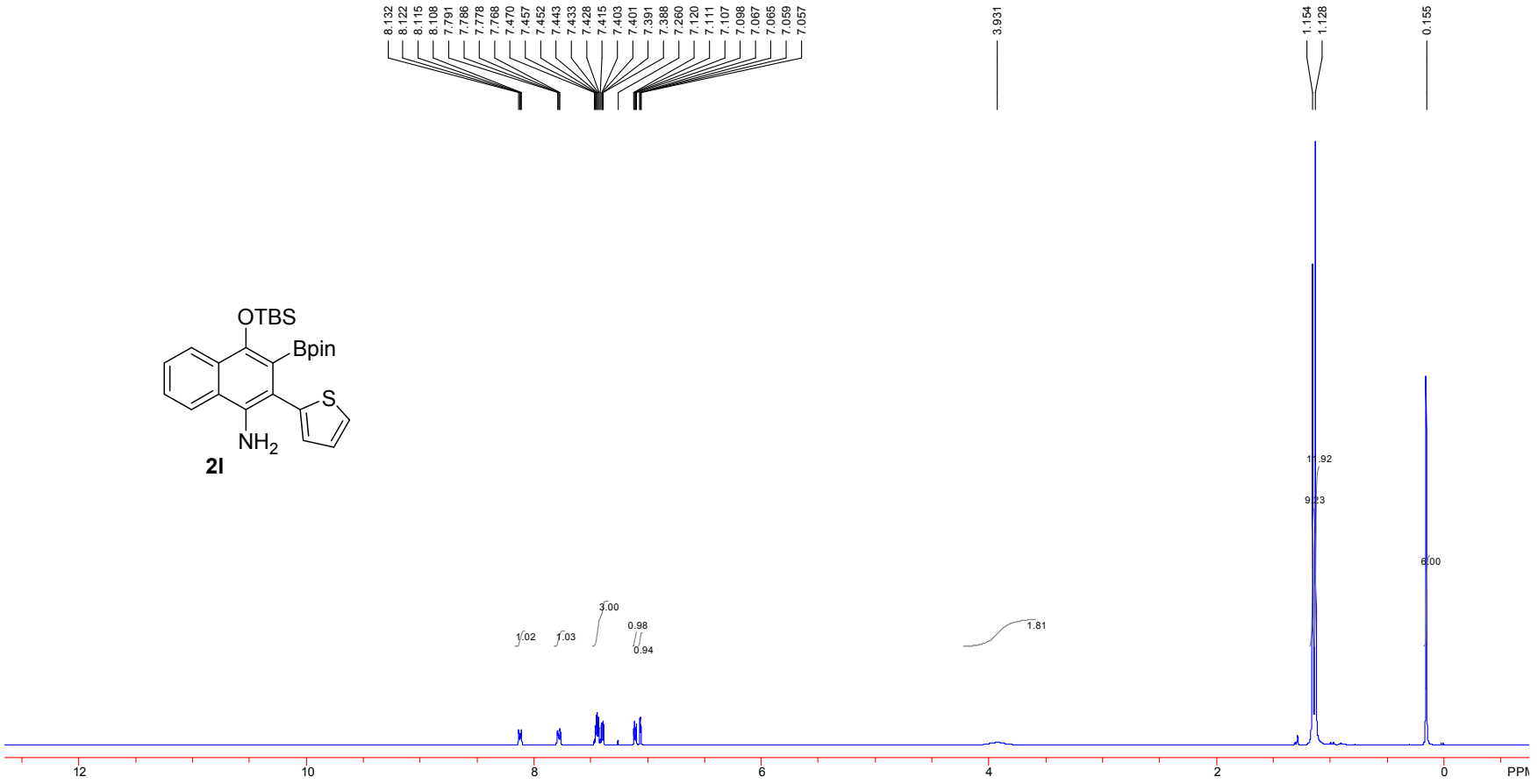
^{1}H NMR (400 MHz, $CDCl_3$)



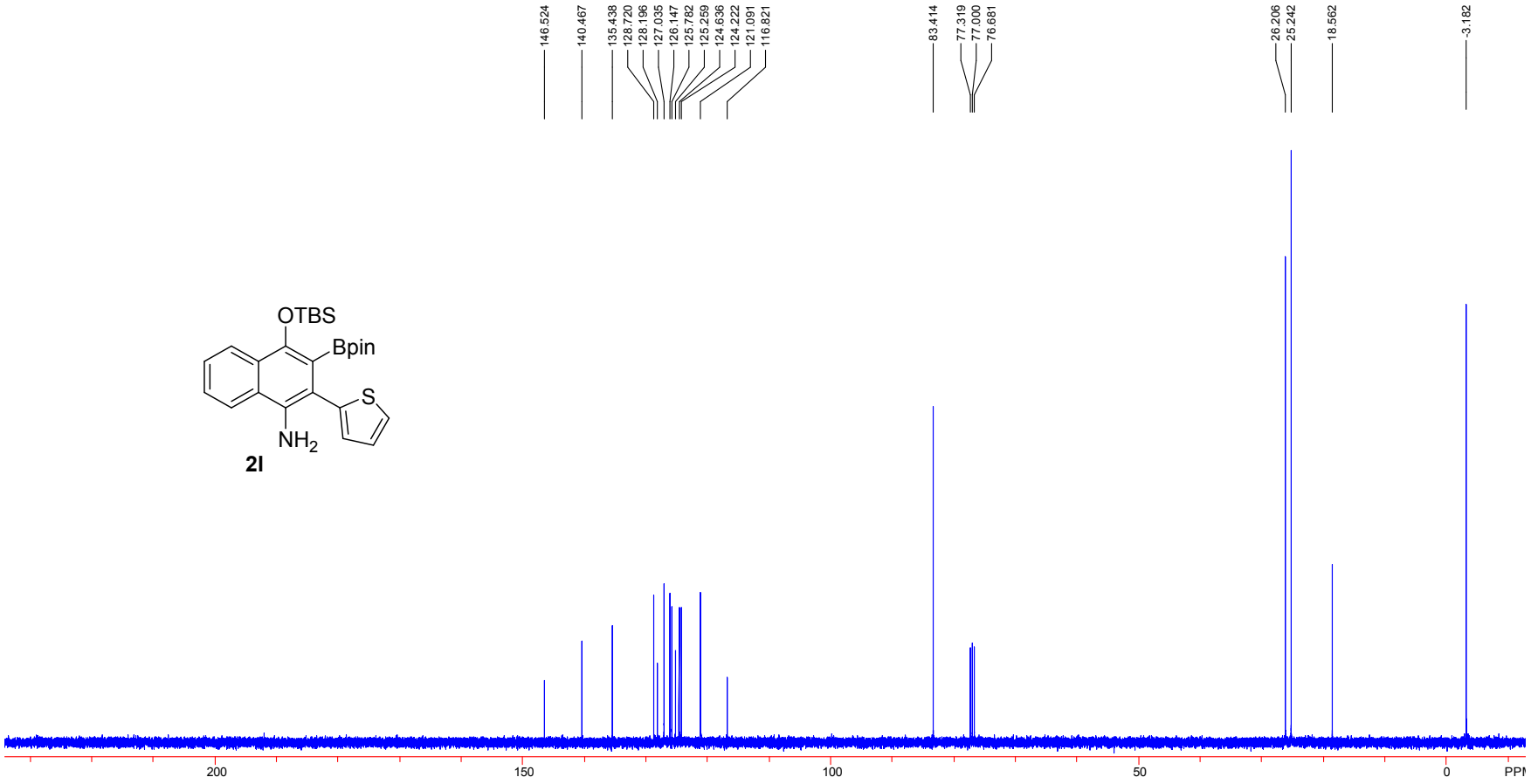
^{13}C NMR (100 MHz, $CDCl_3$)



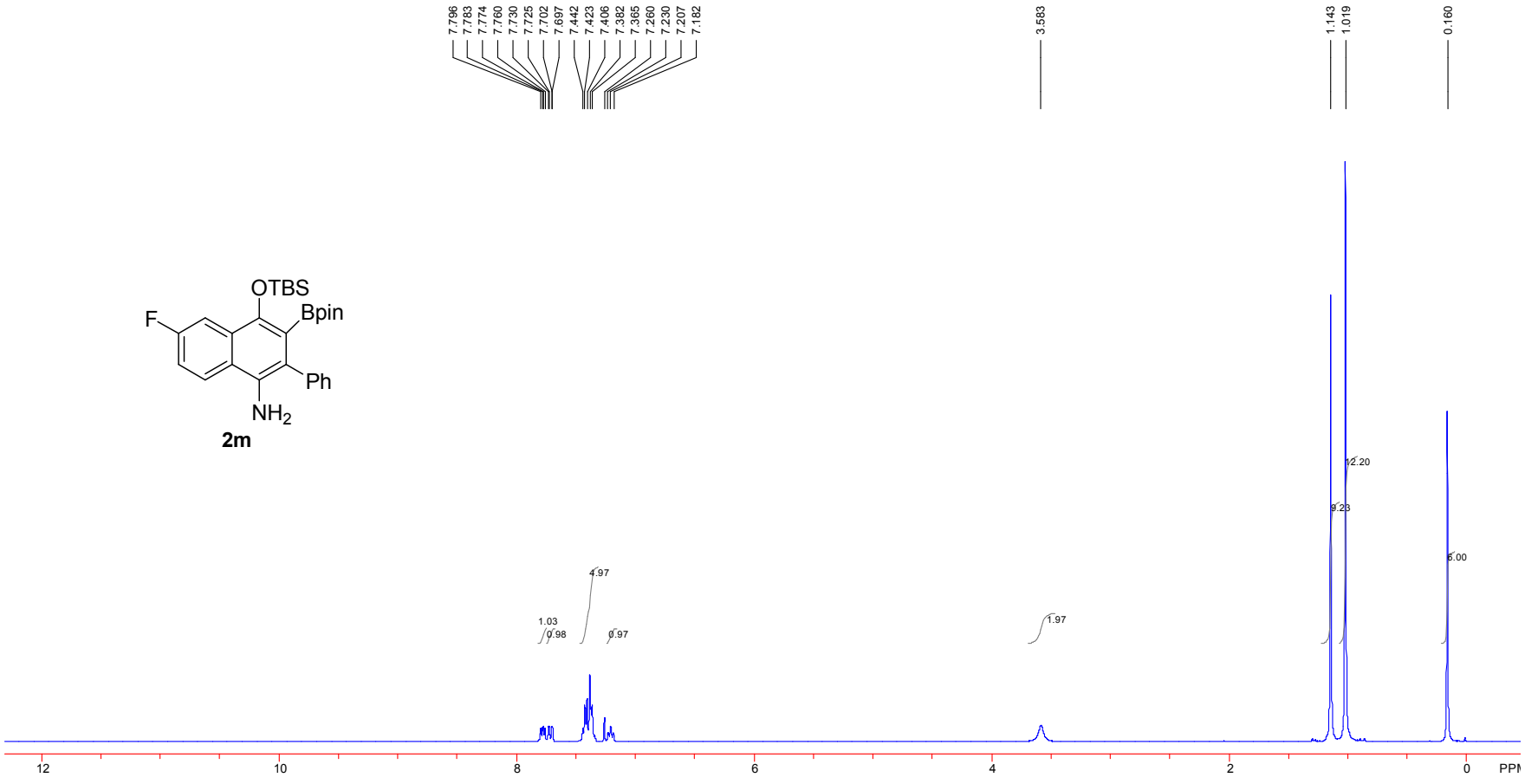
^{1}H NMR (400 MHz, $CDCl_3$)



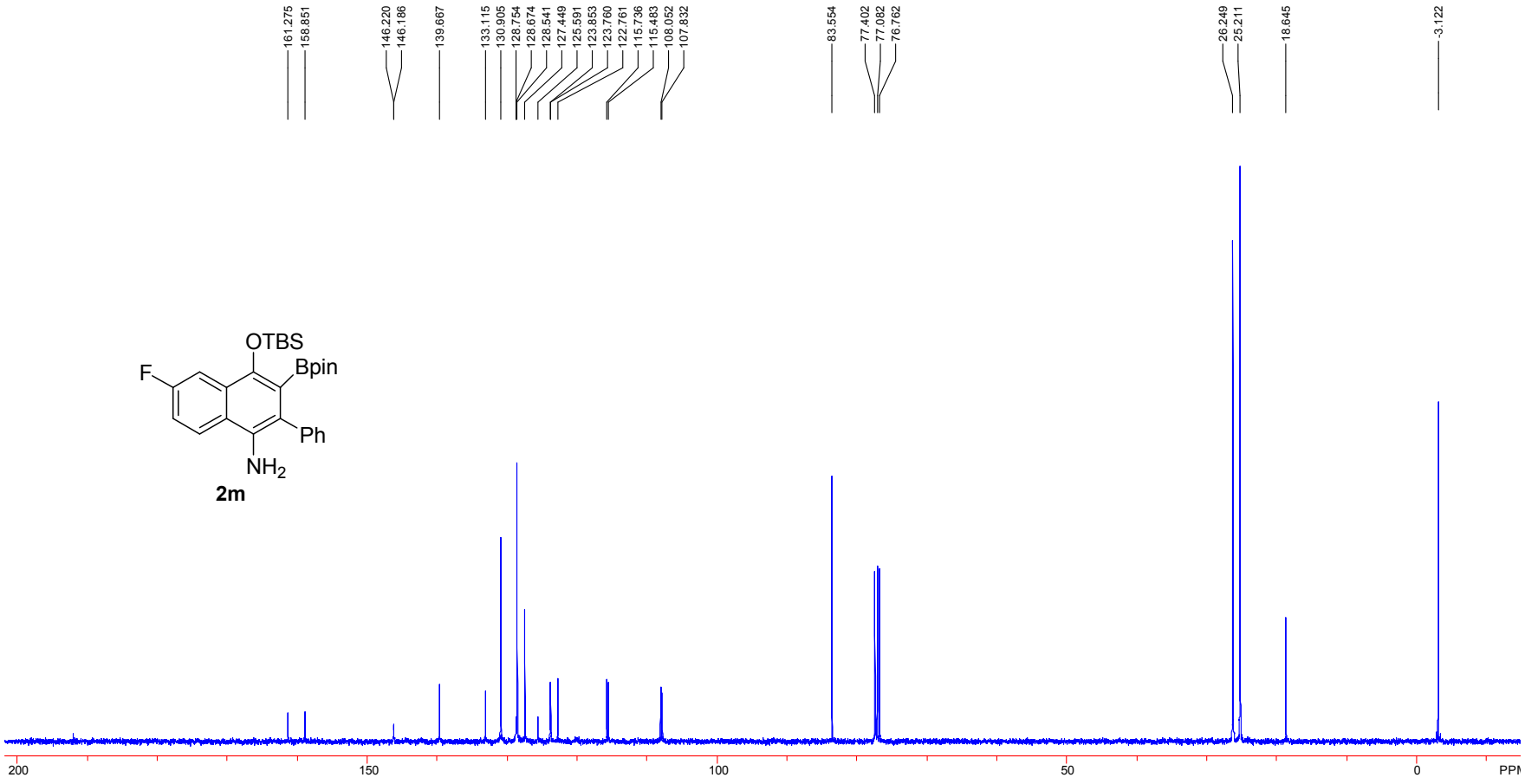
^{13}C NMR (100 MHz, $CDCl_3$)



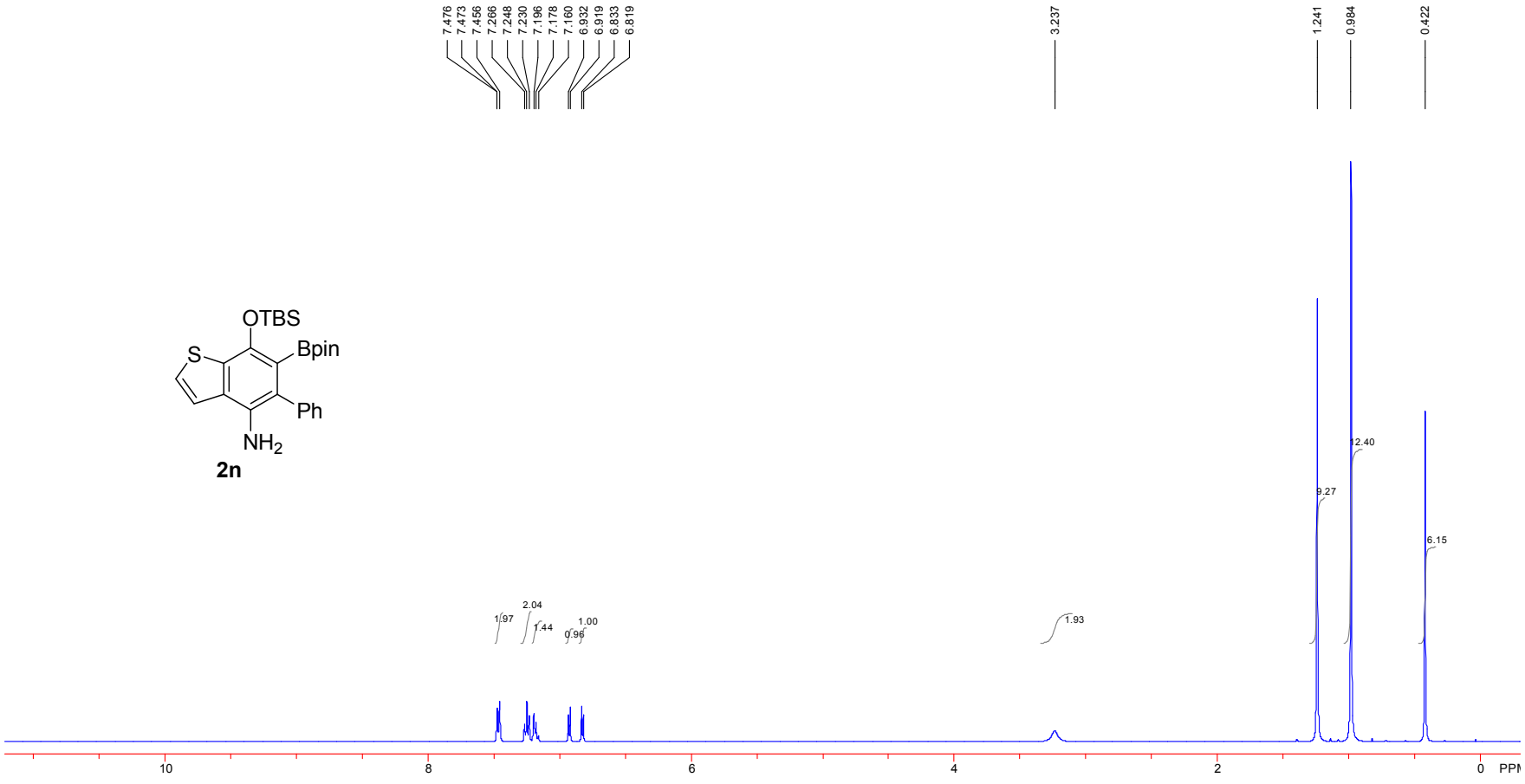
^{1}H NMR (400 MHz, $CDCl_3$)



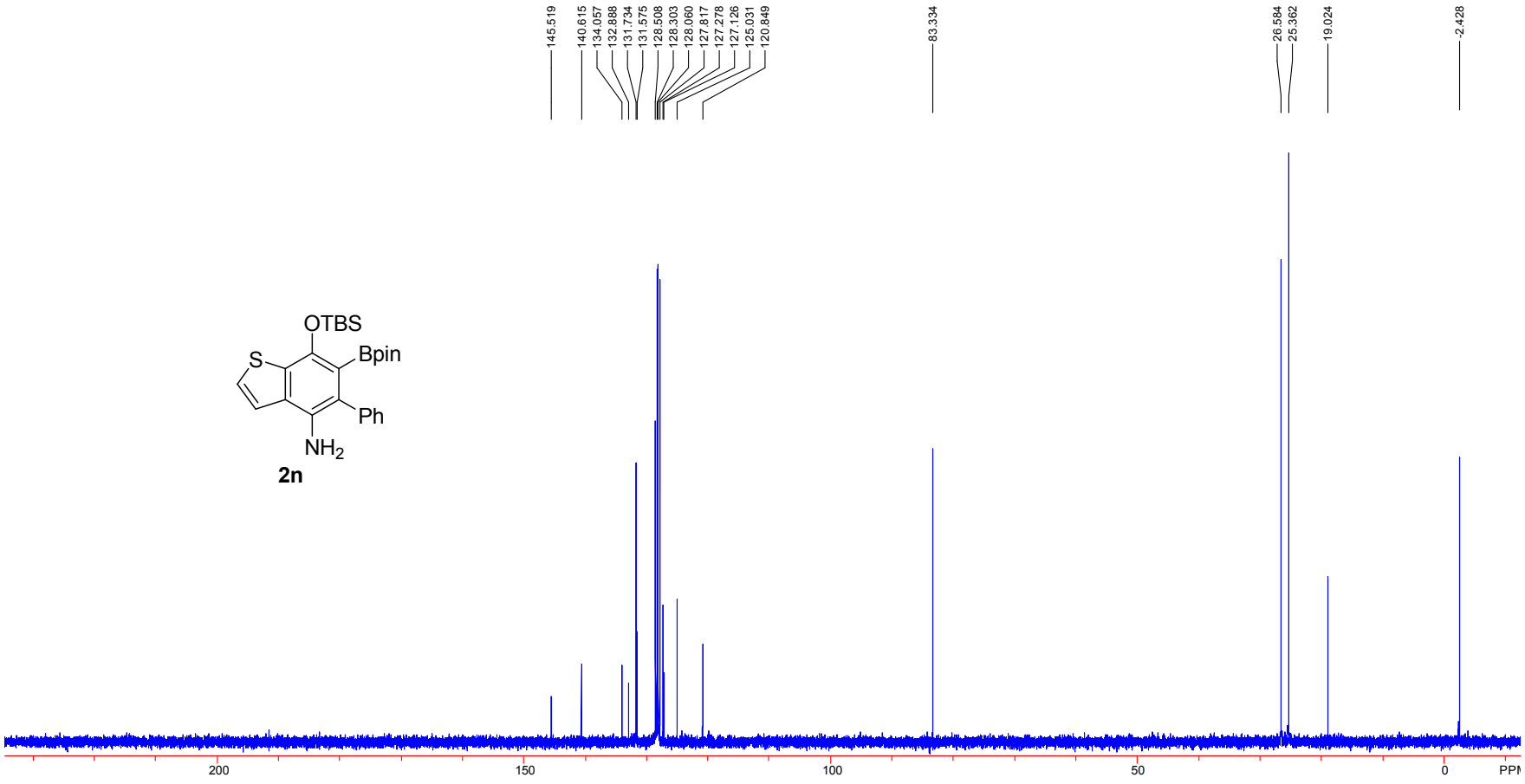
^{13}C NMR (100 MHz, $CDCl_3$)



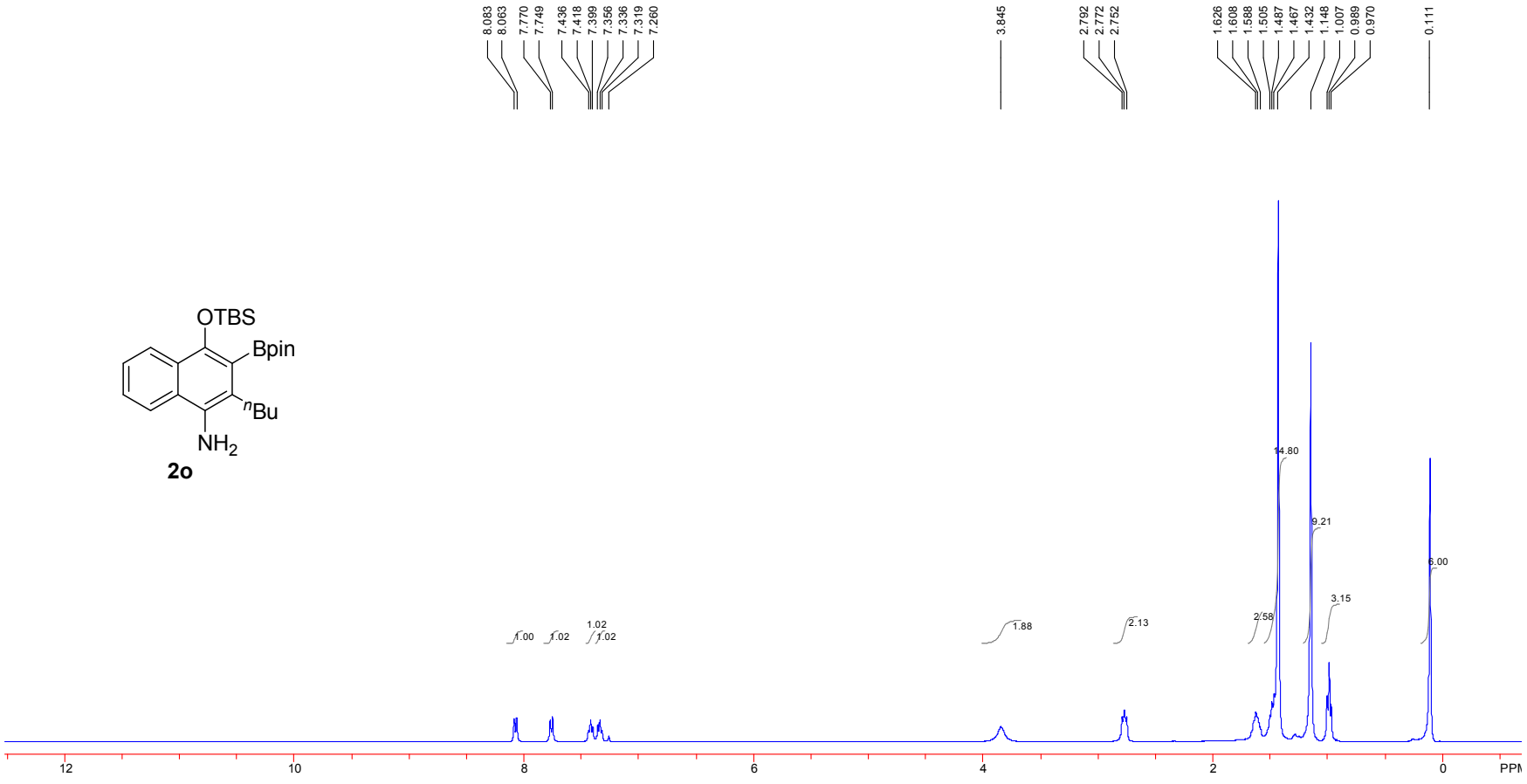
^{1}H NMR (400 MHz, C_6D_6)



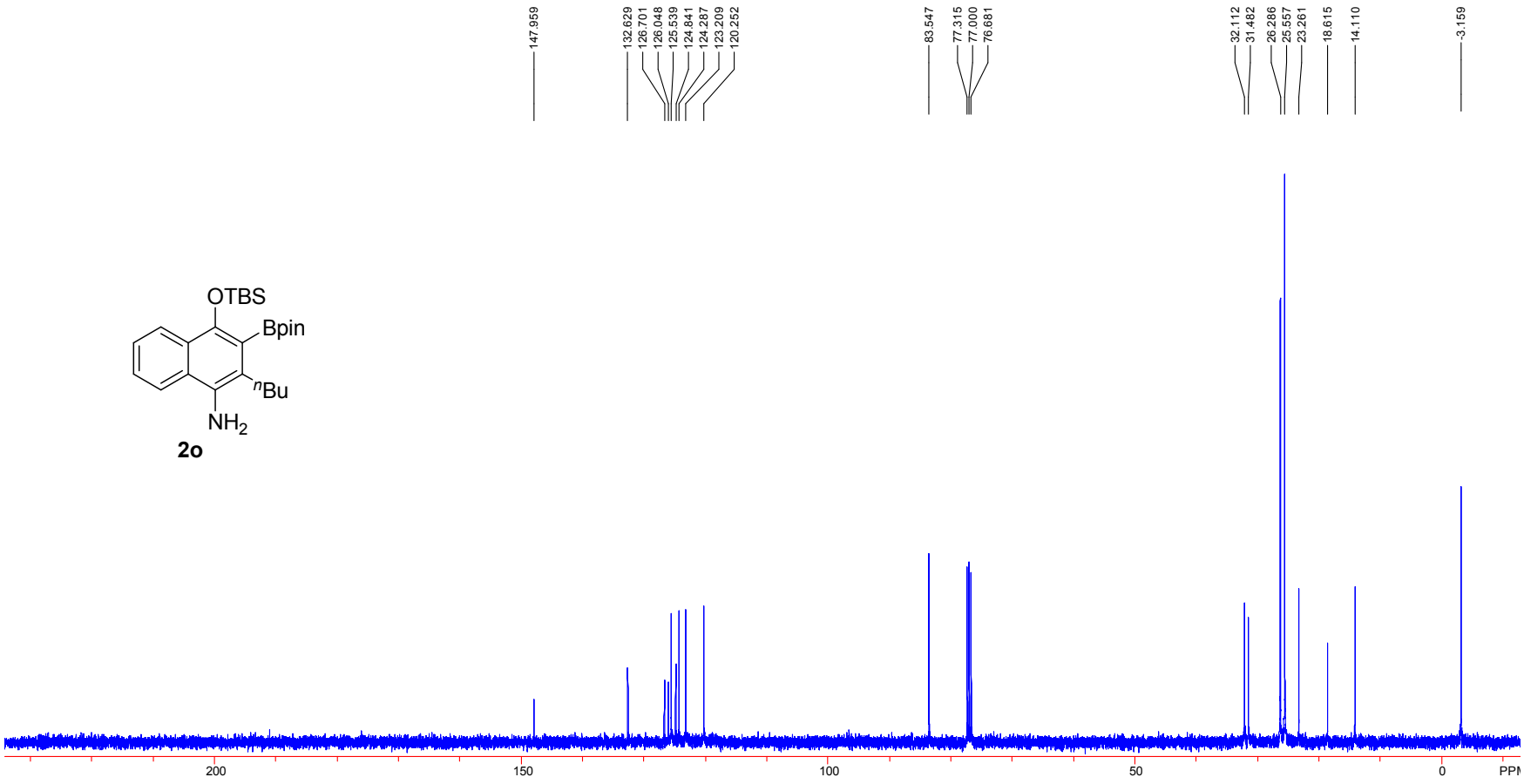
^{13}C NMR (100 MHz, C_6D_6)



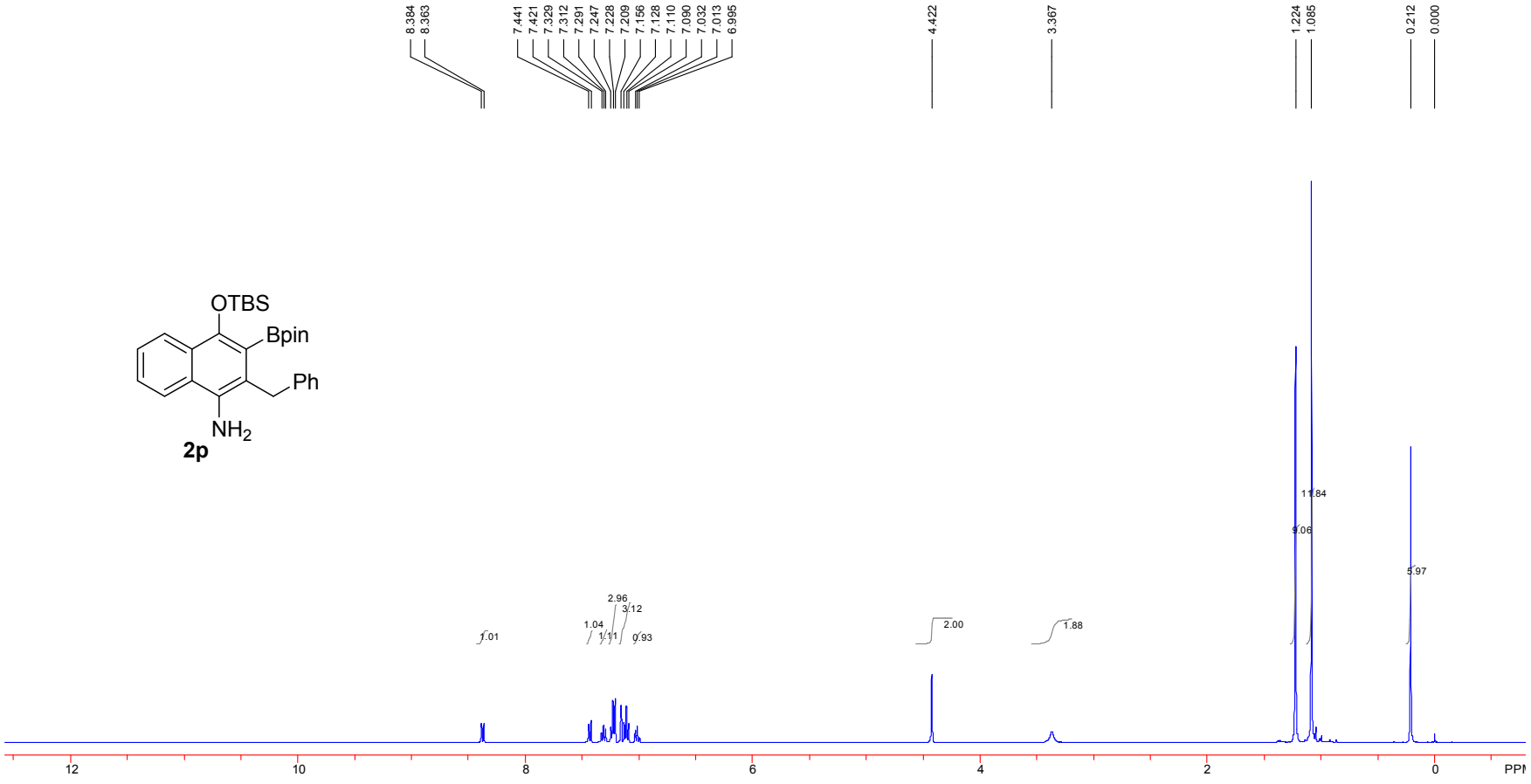
^{1}H NMR (400 MHz, $CDCl_3$)



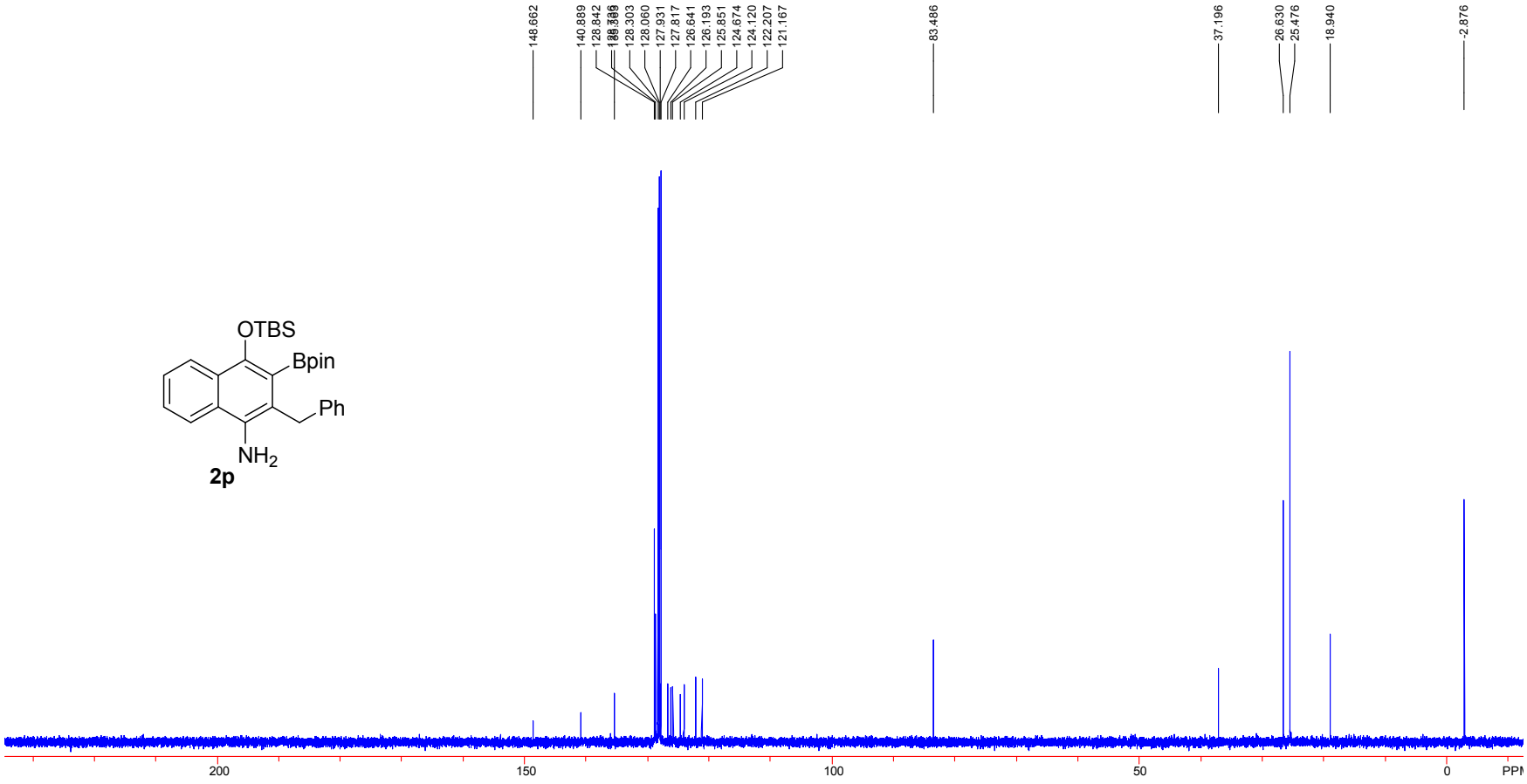
^{13}C NMR (100 MHz, $CDCl_3$)



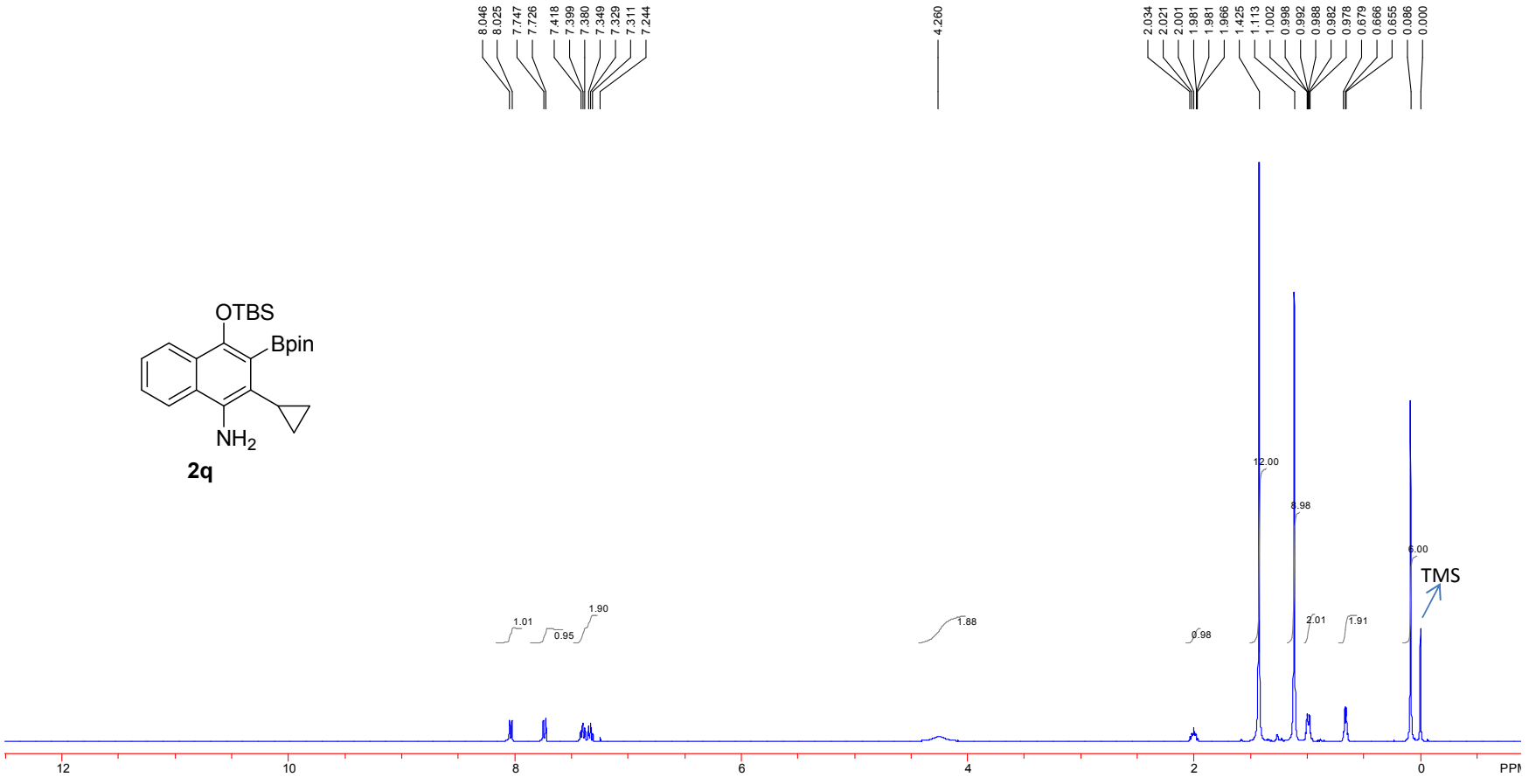
^{1}H NMR (400 MHz, C_6D_6)



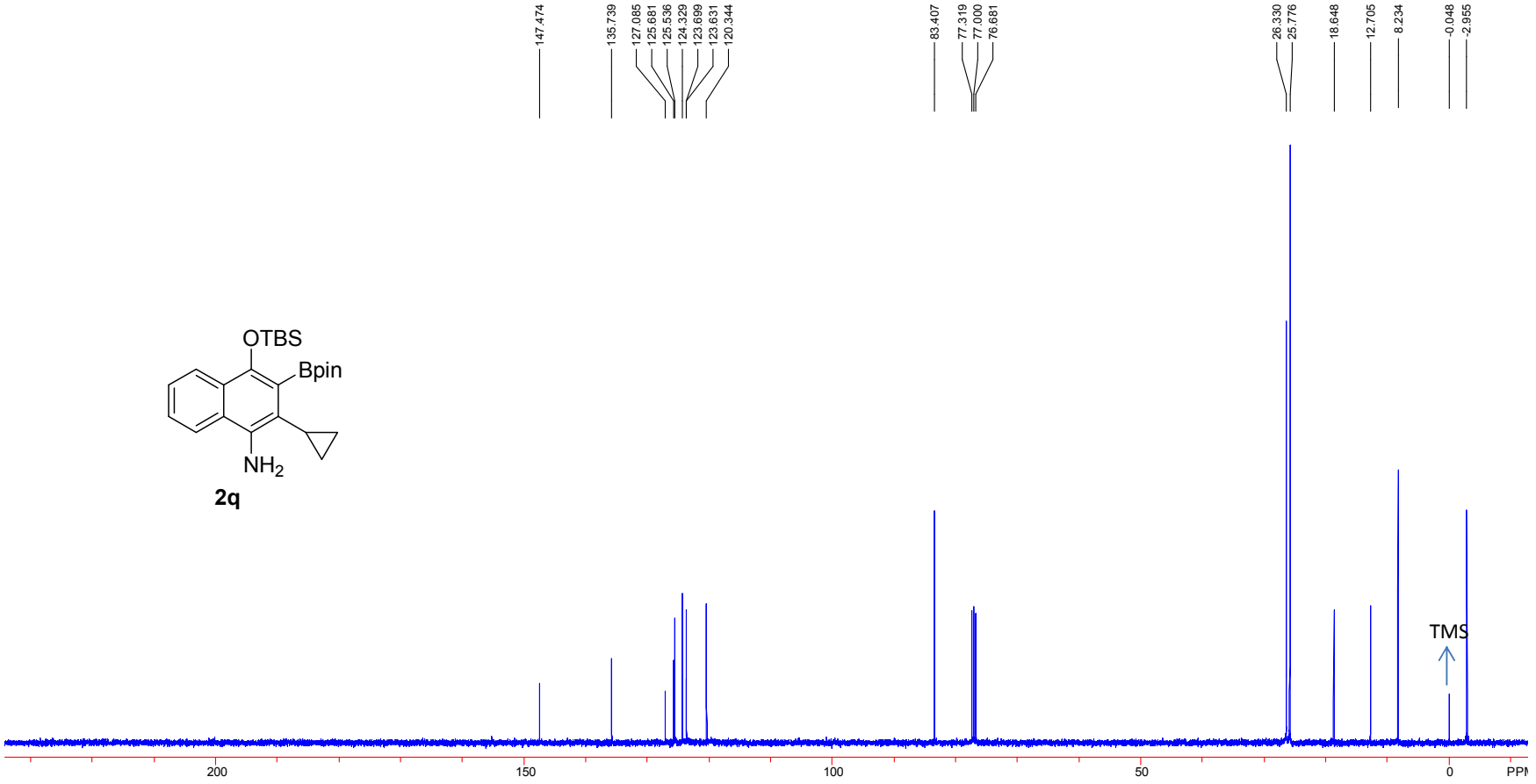
^{13}C NMR (100 MHz, C_6D_6)



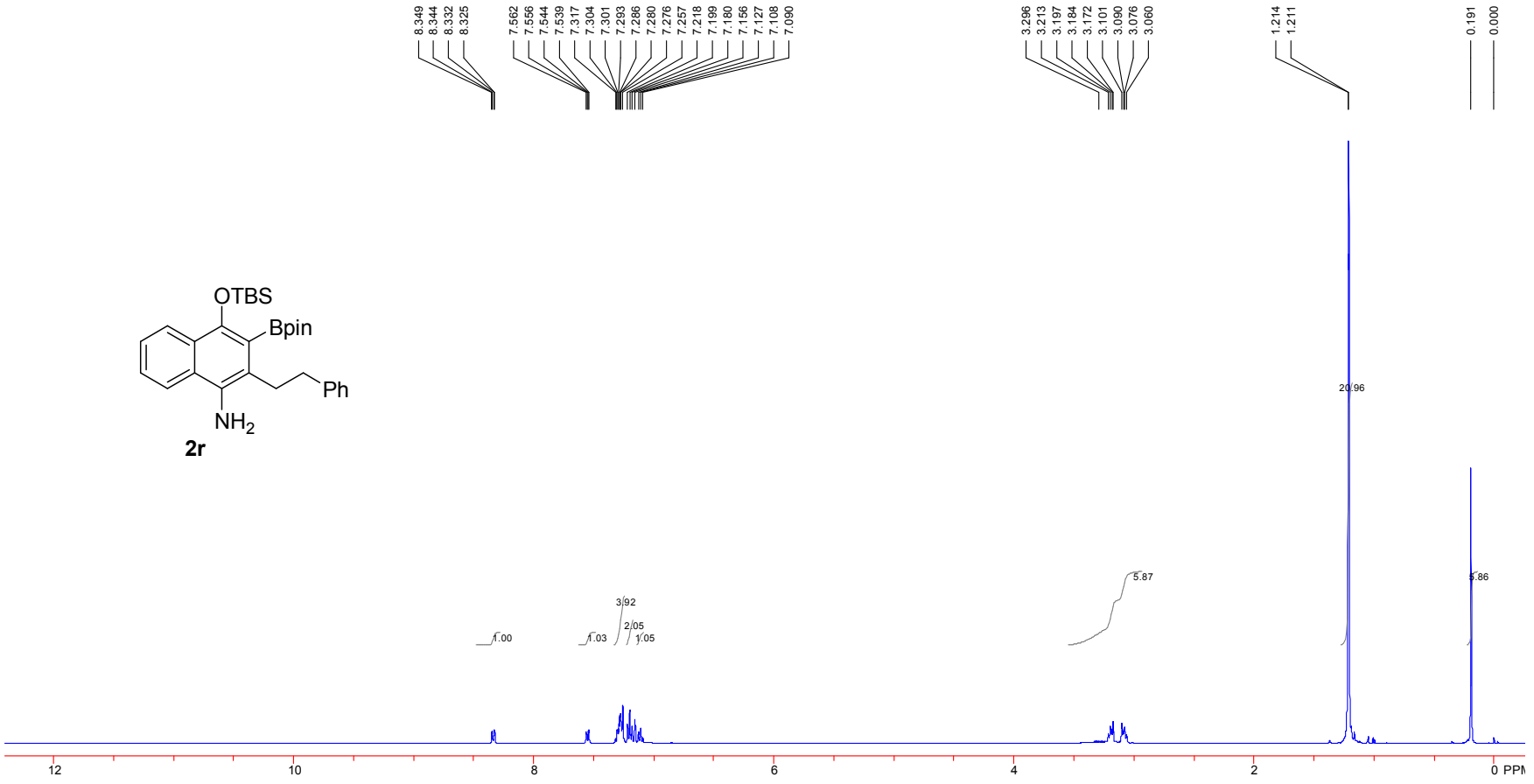
^{1}H NMR (400 MHz, $CDCl_3$)



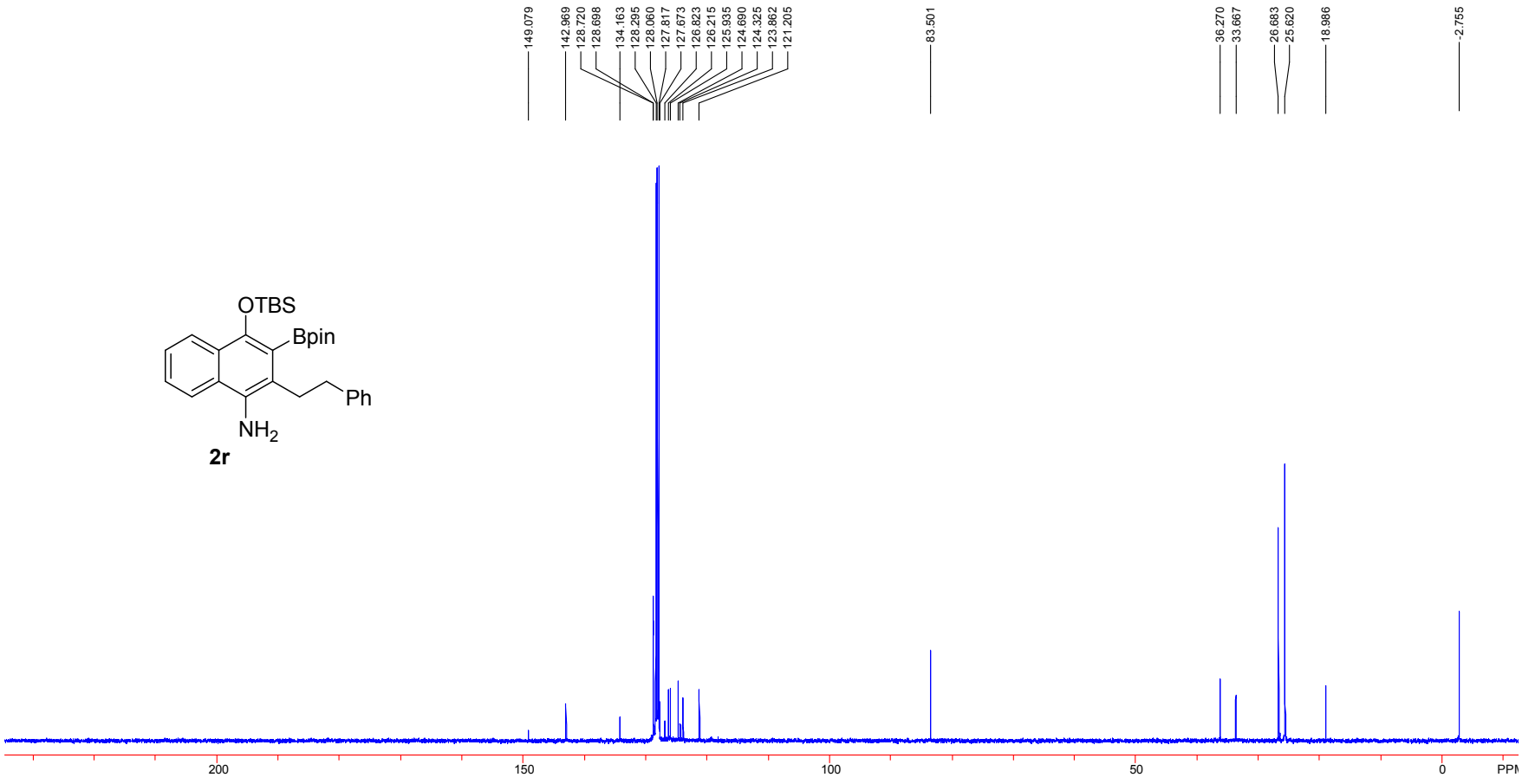
^{13}C NMR (100 MHz, $CDCl_3$)



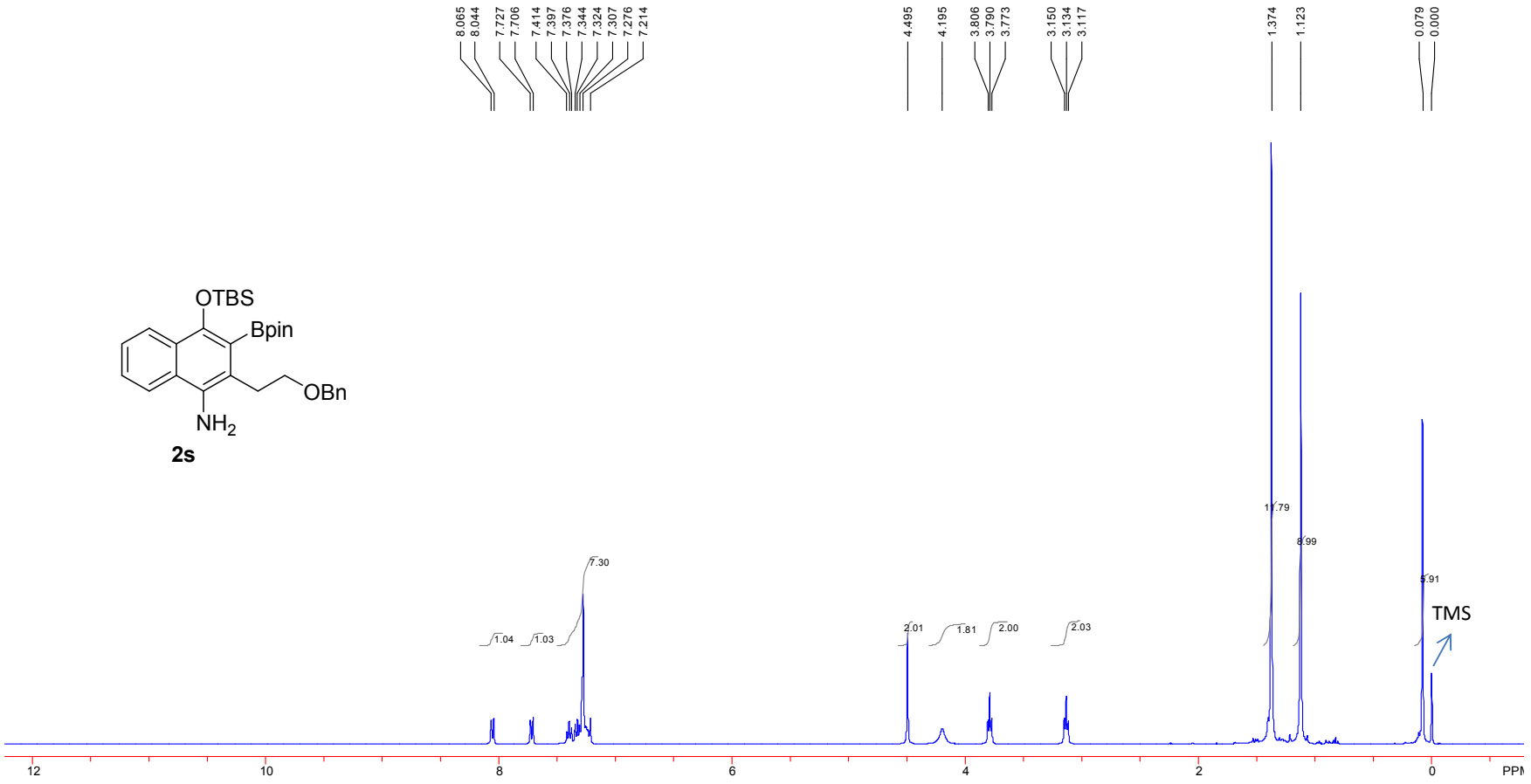
^{1}H NMR (400 MHz, C_6D_6)



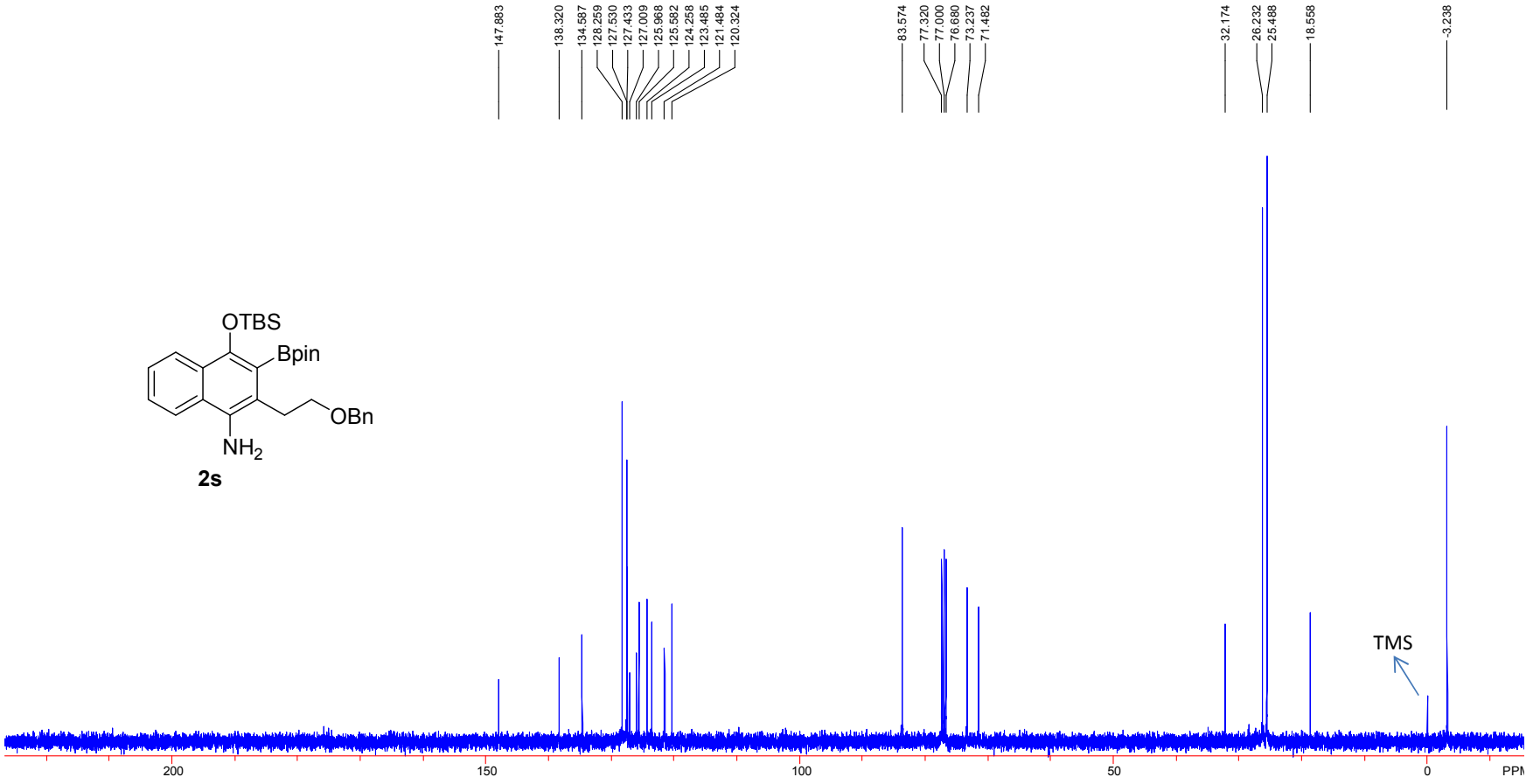
^{13}C NMR (100 MHz, C_6D_6)



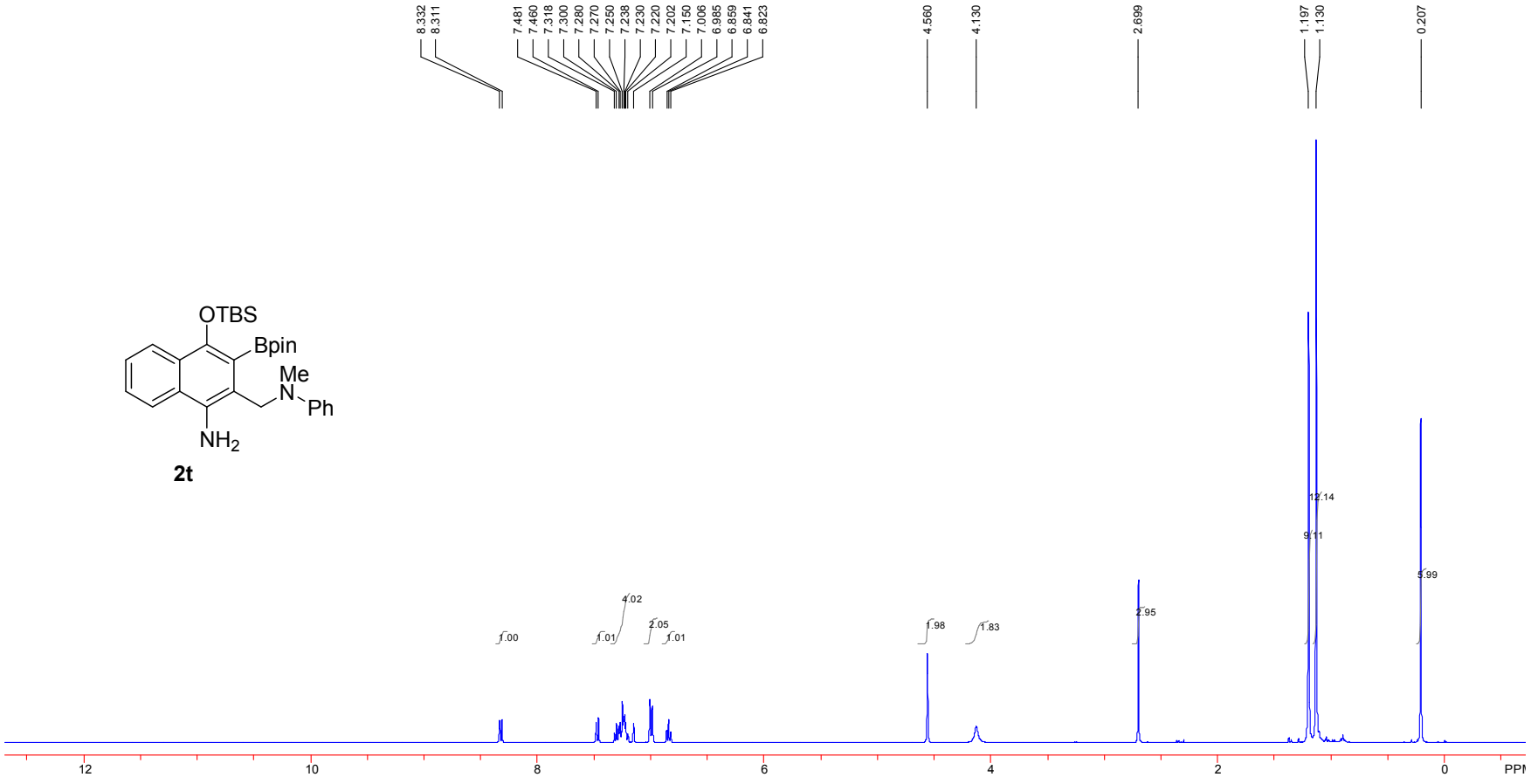
^{1}H NMR (400 MHz, $CDCl_3$)



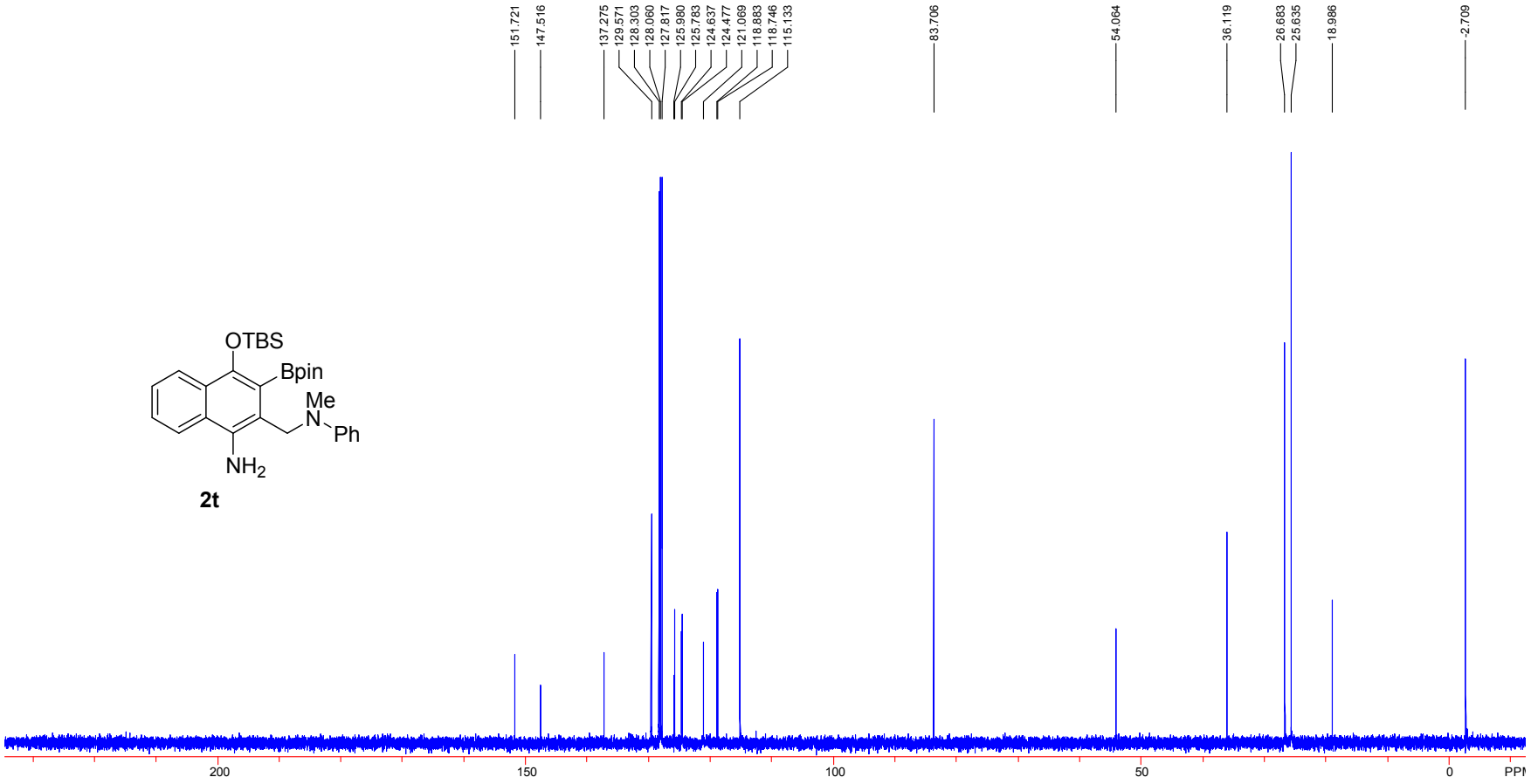
^{13}C NMR (100 MHz, $CDCl_3$)



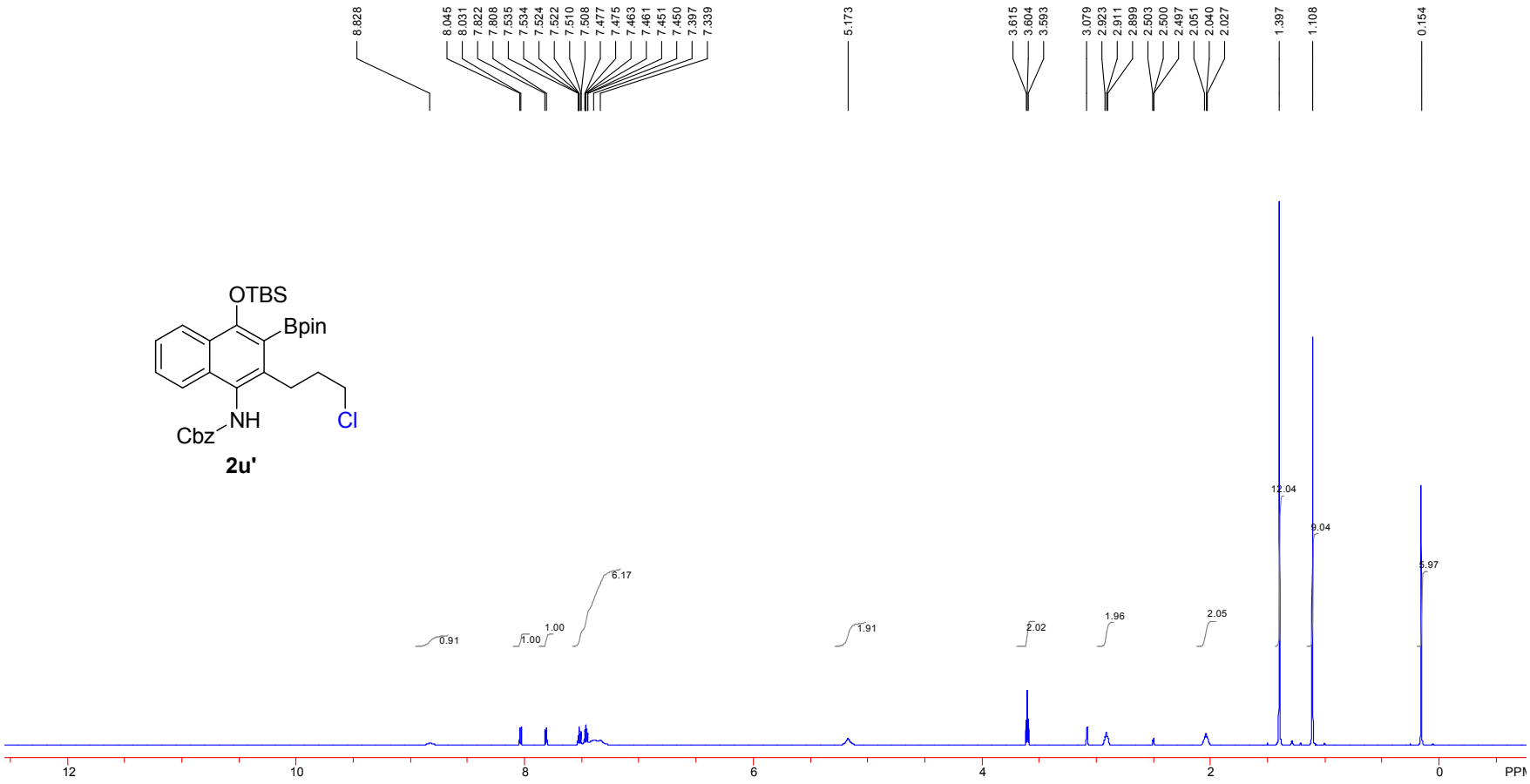
^{1}H NMR (400 MHz, C_6D_6)



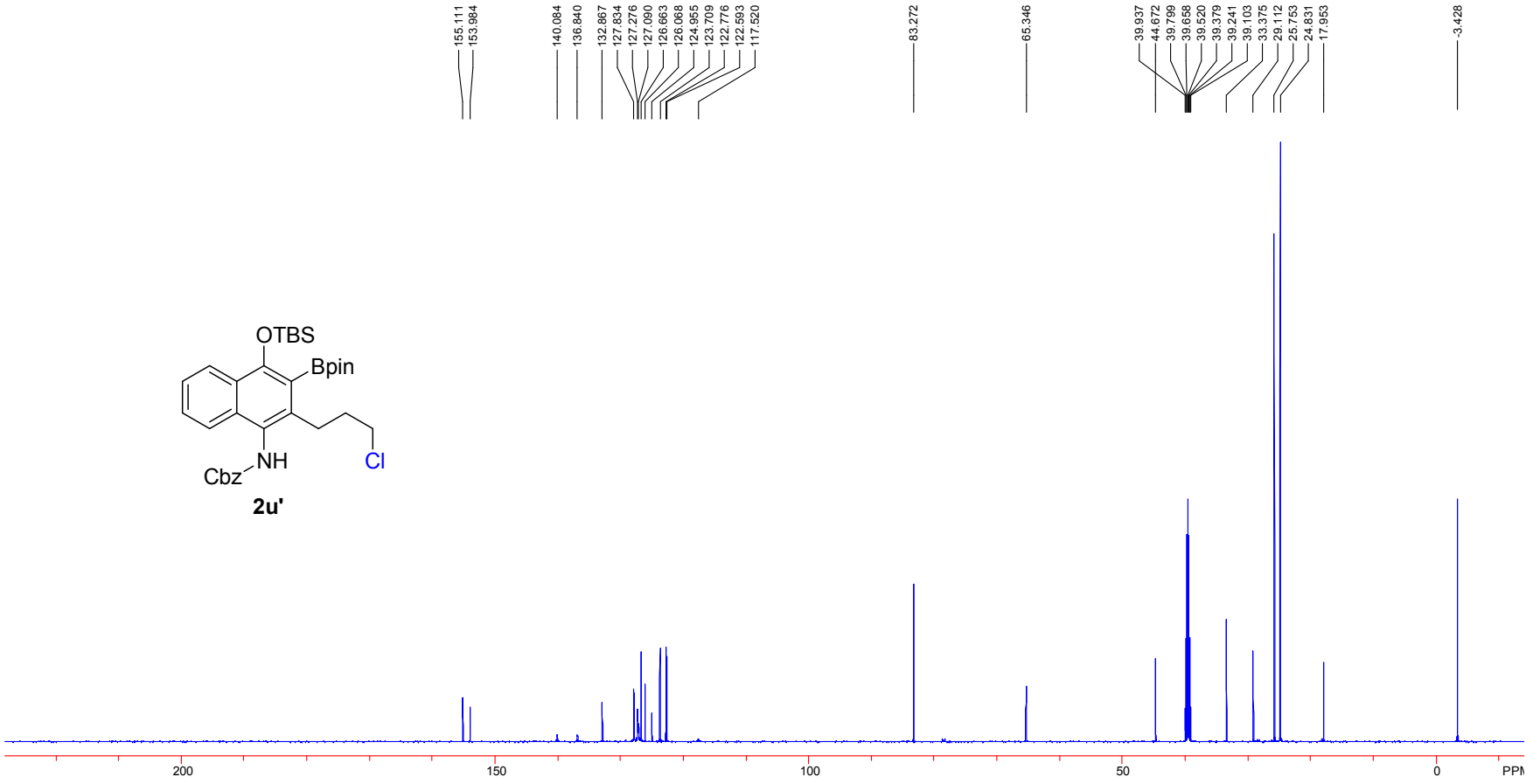
^{13}C NMR (100 MHz, C_6D_6)



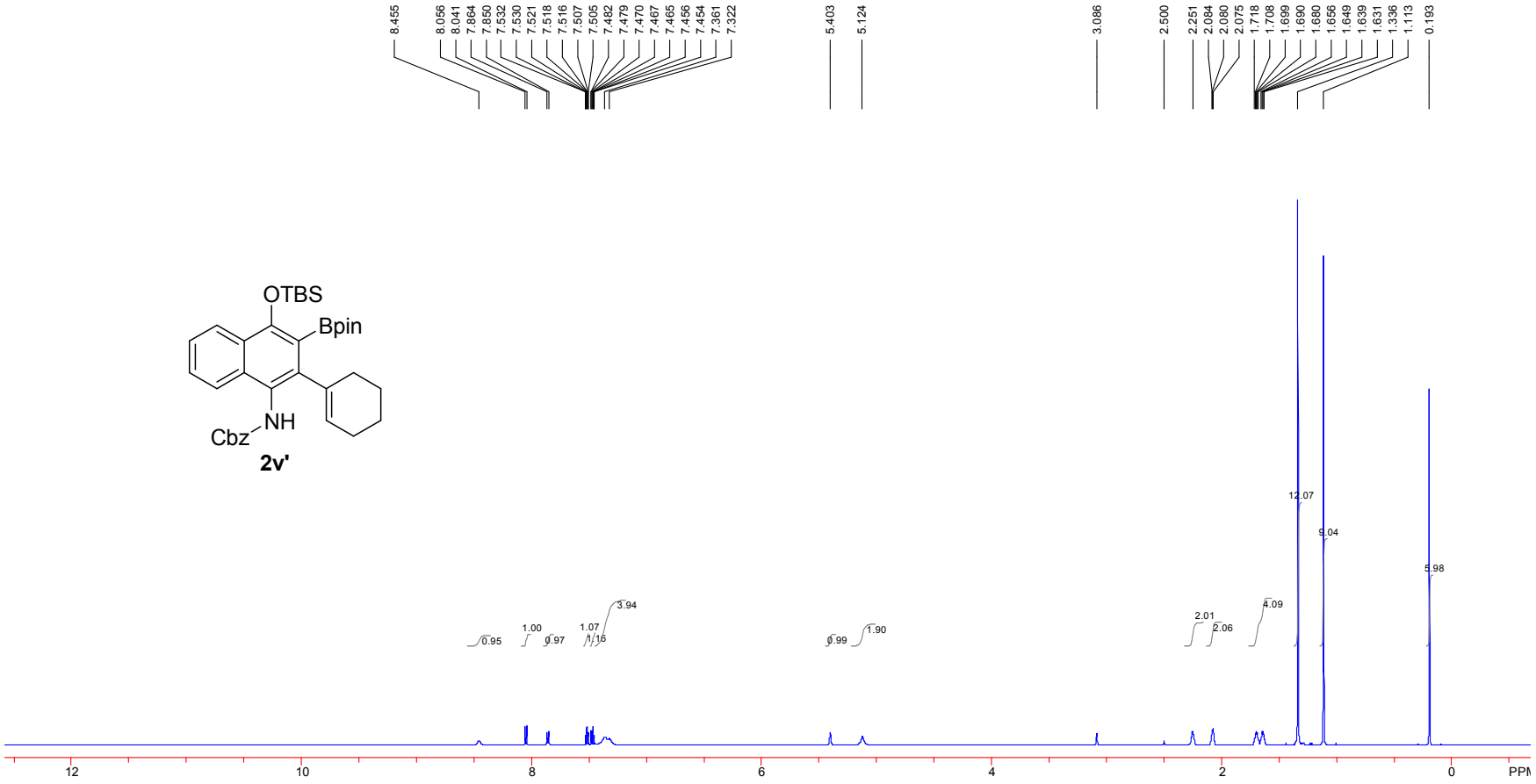
^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C)



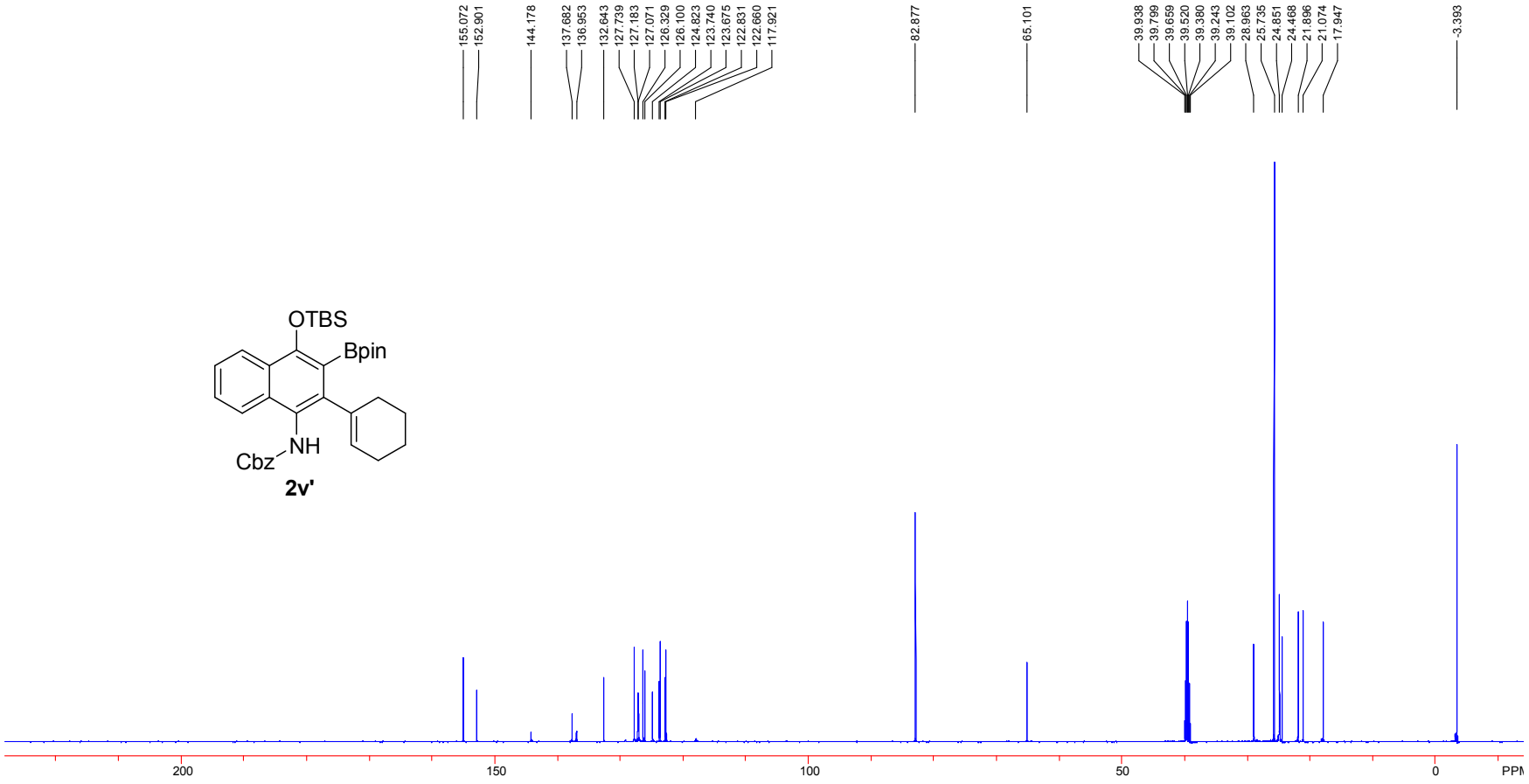
^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C)



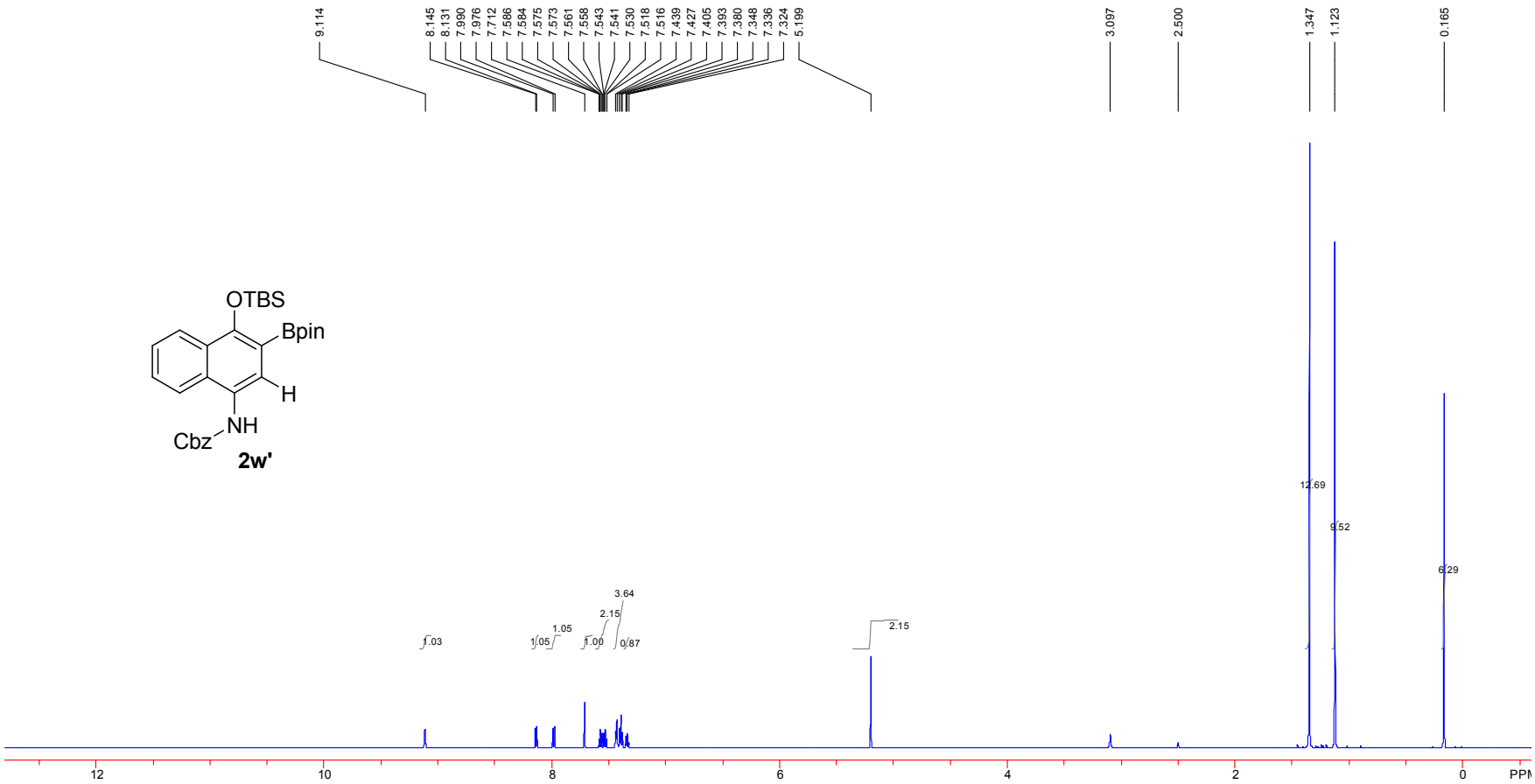
^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C)



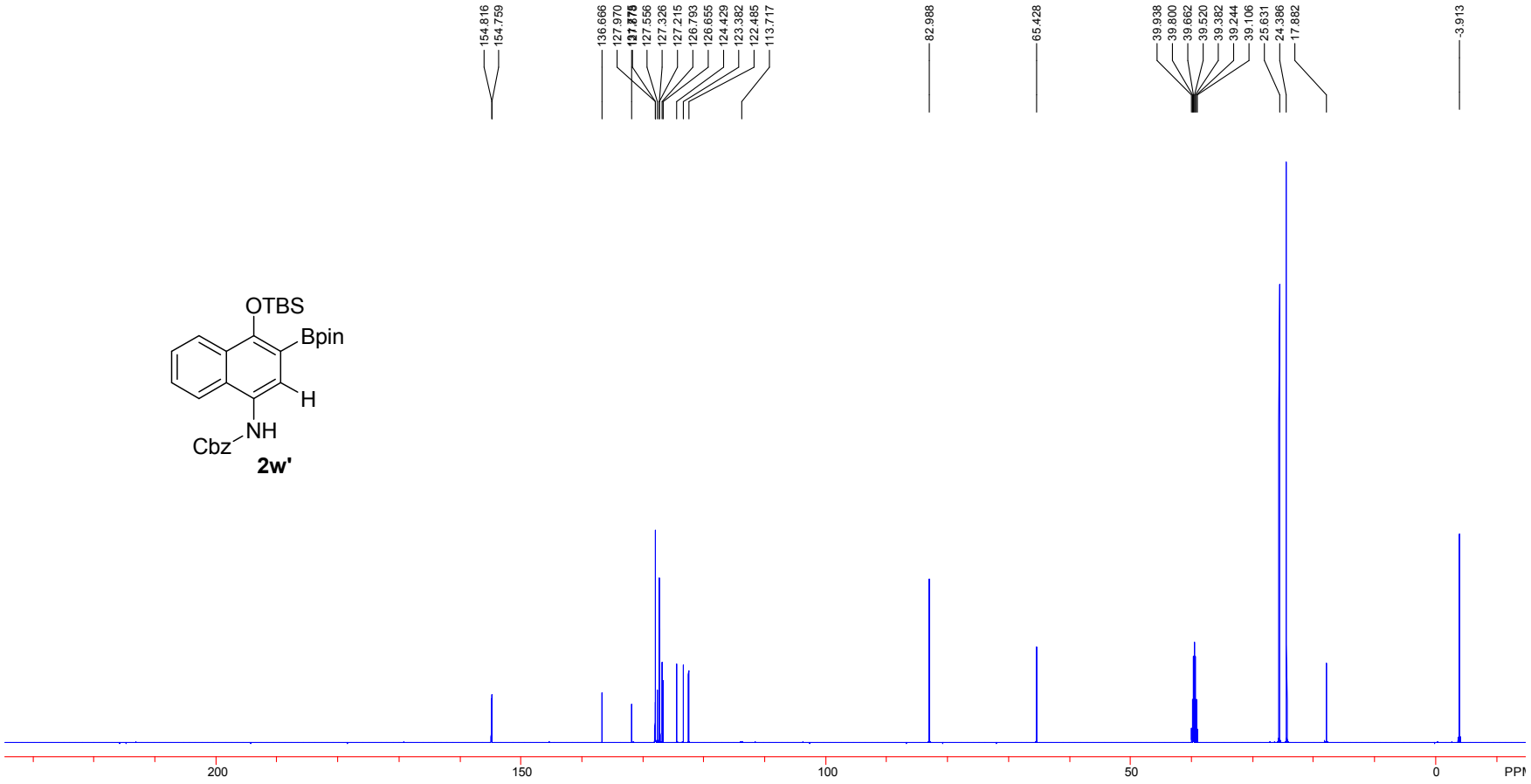
^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C)



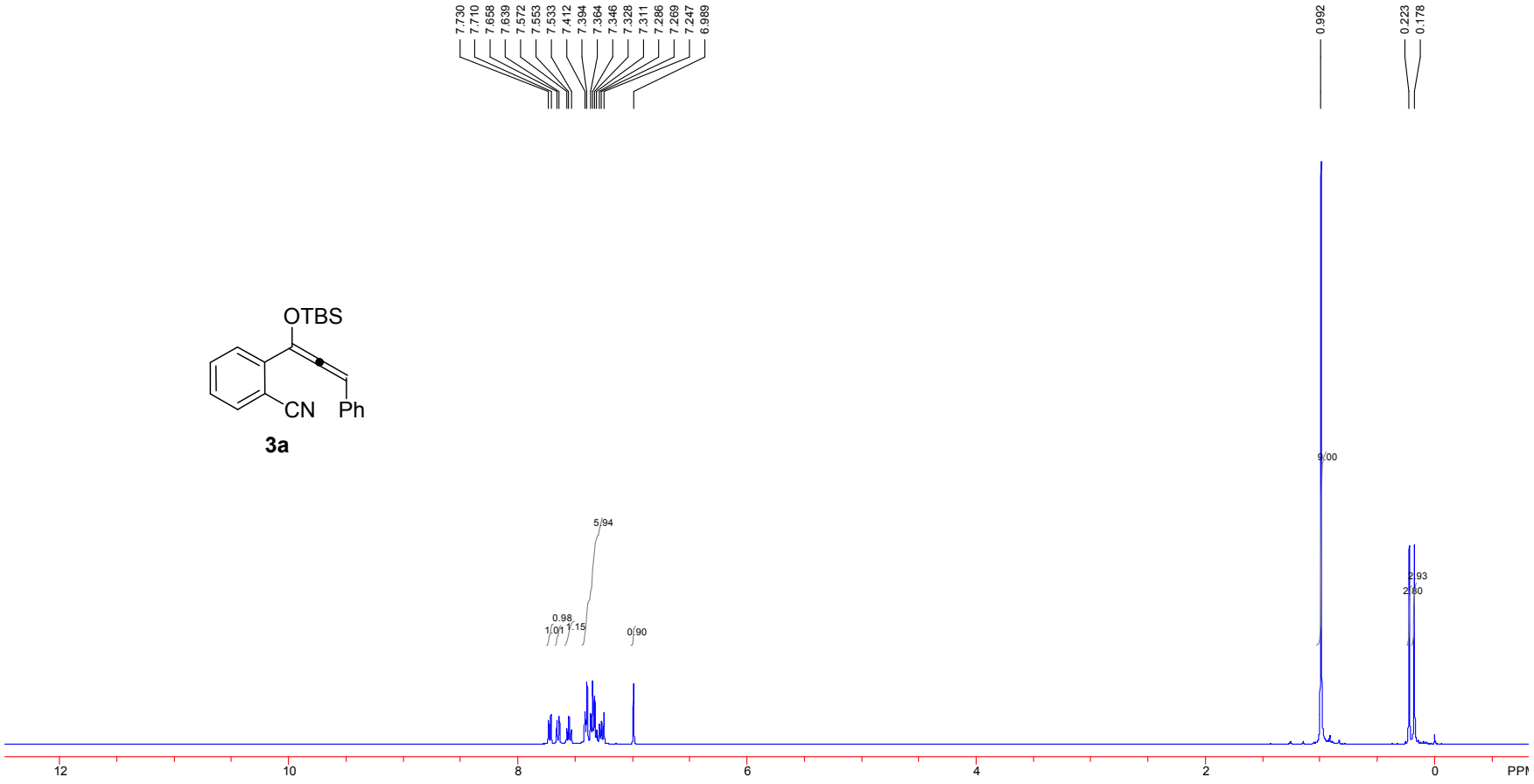
^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C)



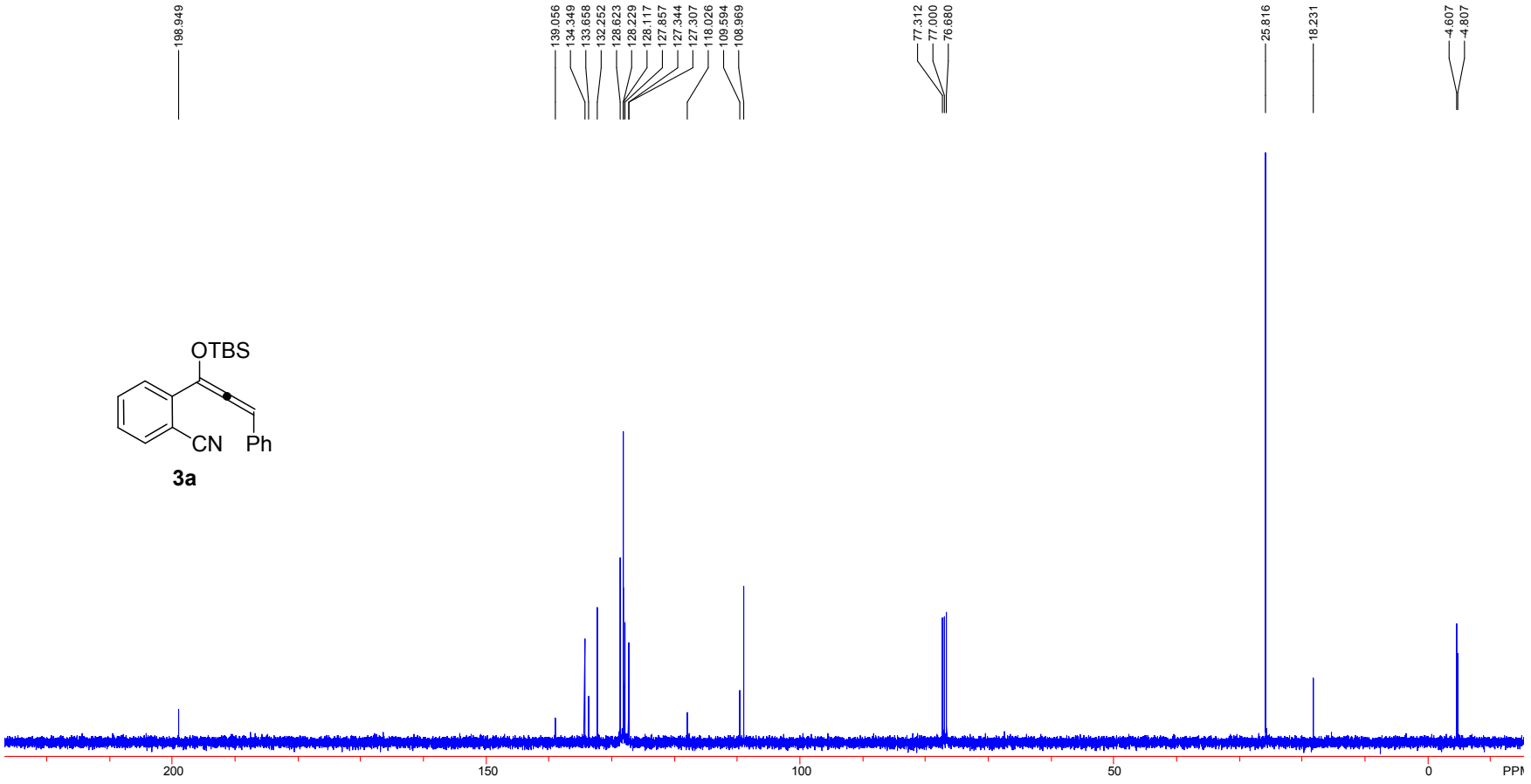
^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C)



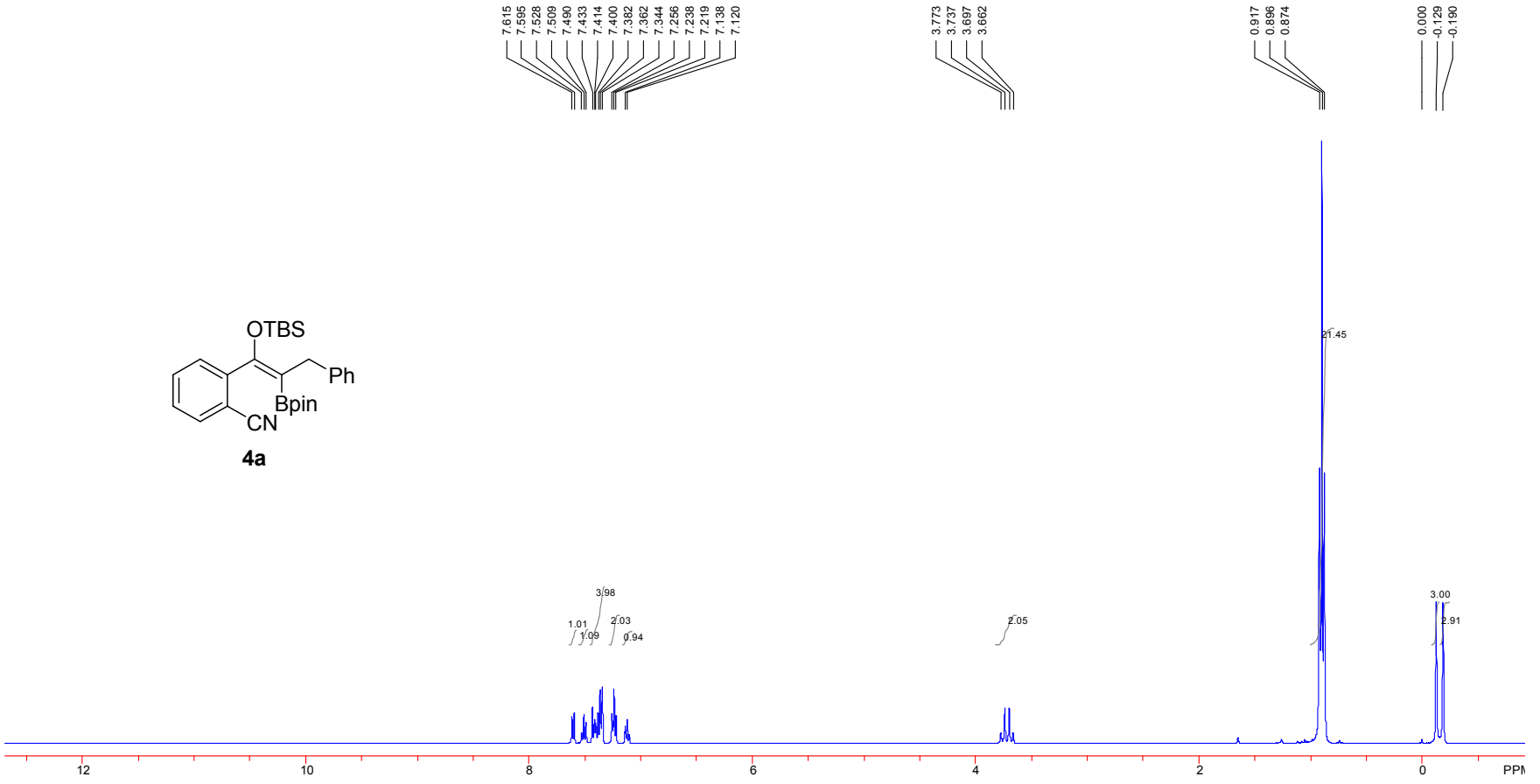
^{1}H NMR (400 MHz, $CDCl_3$)



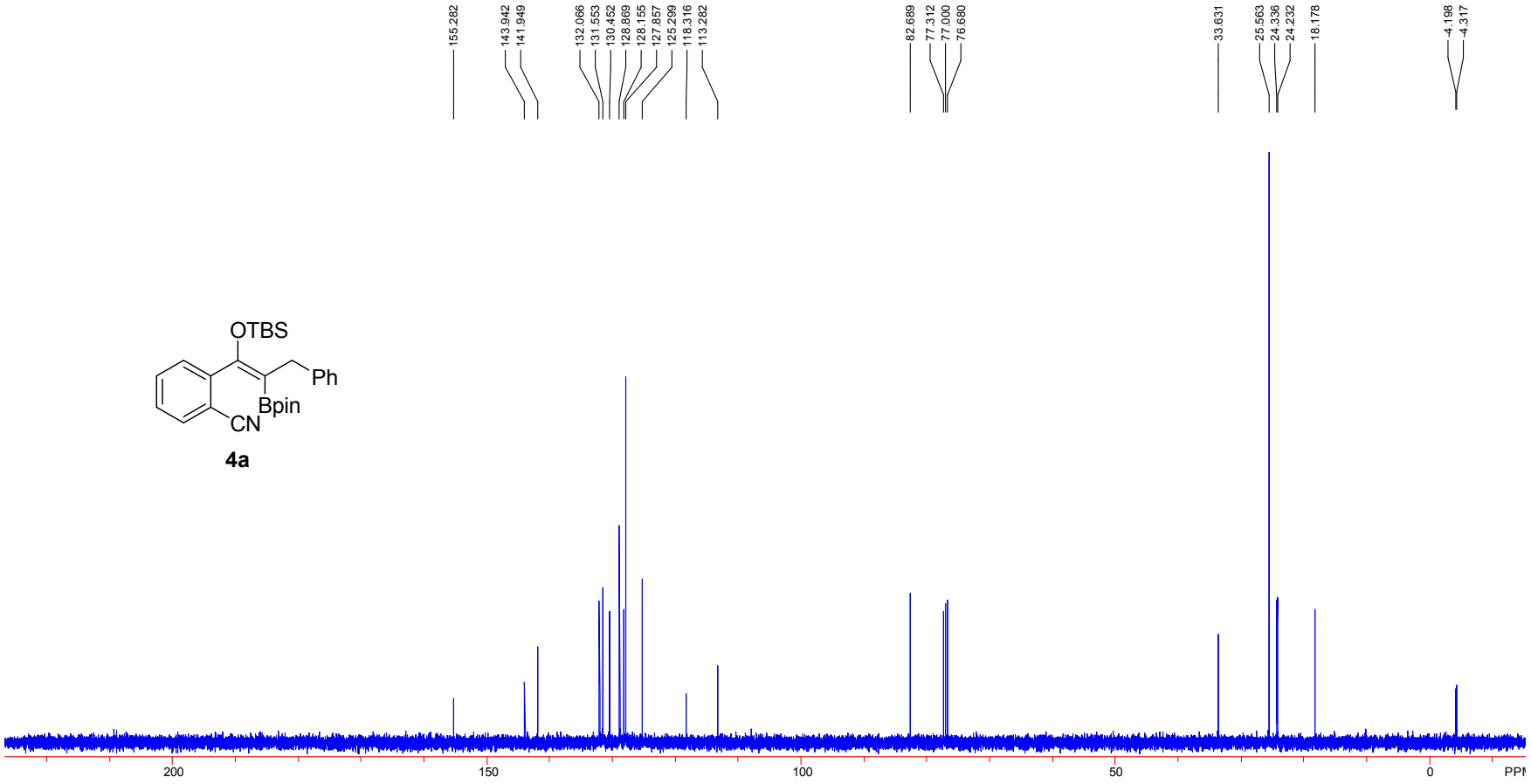
^{13}C NMR (100 MHz, $CDCl_3$)



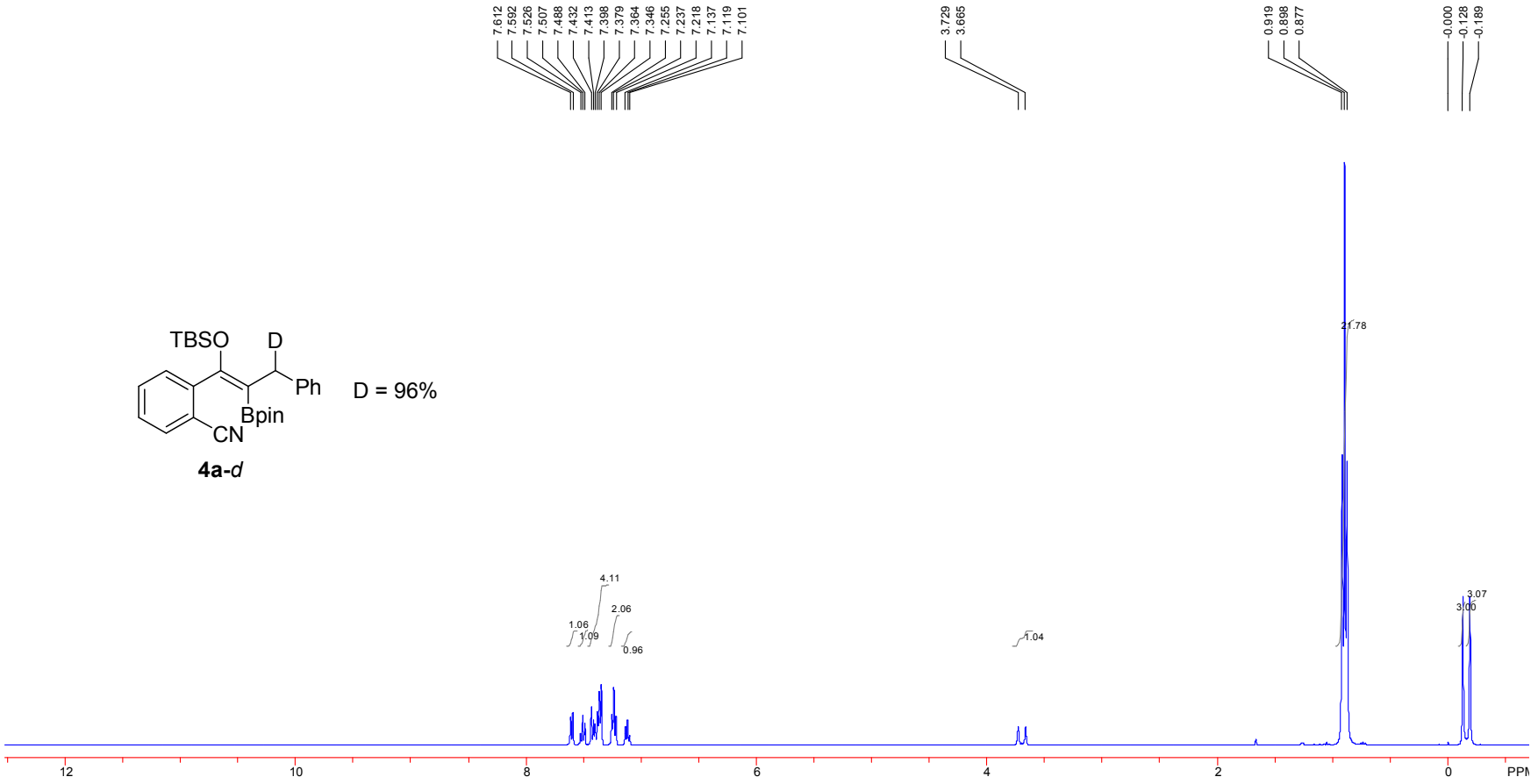
^{1}H NMR (400 MHz, $CDCl_3$)



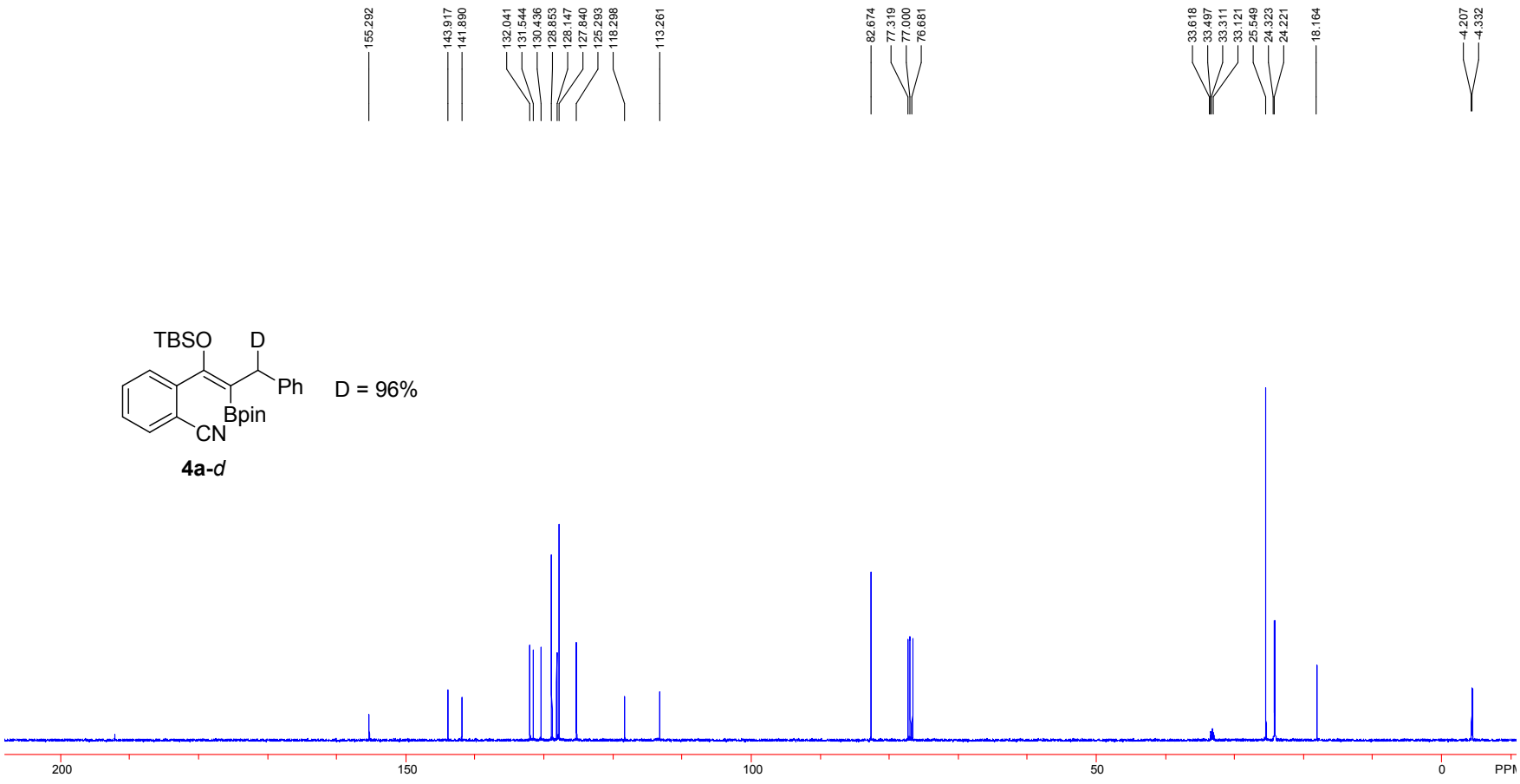
^{13}C NMR (100 MHz, $CDCl_3$)



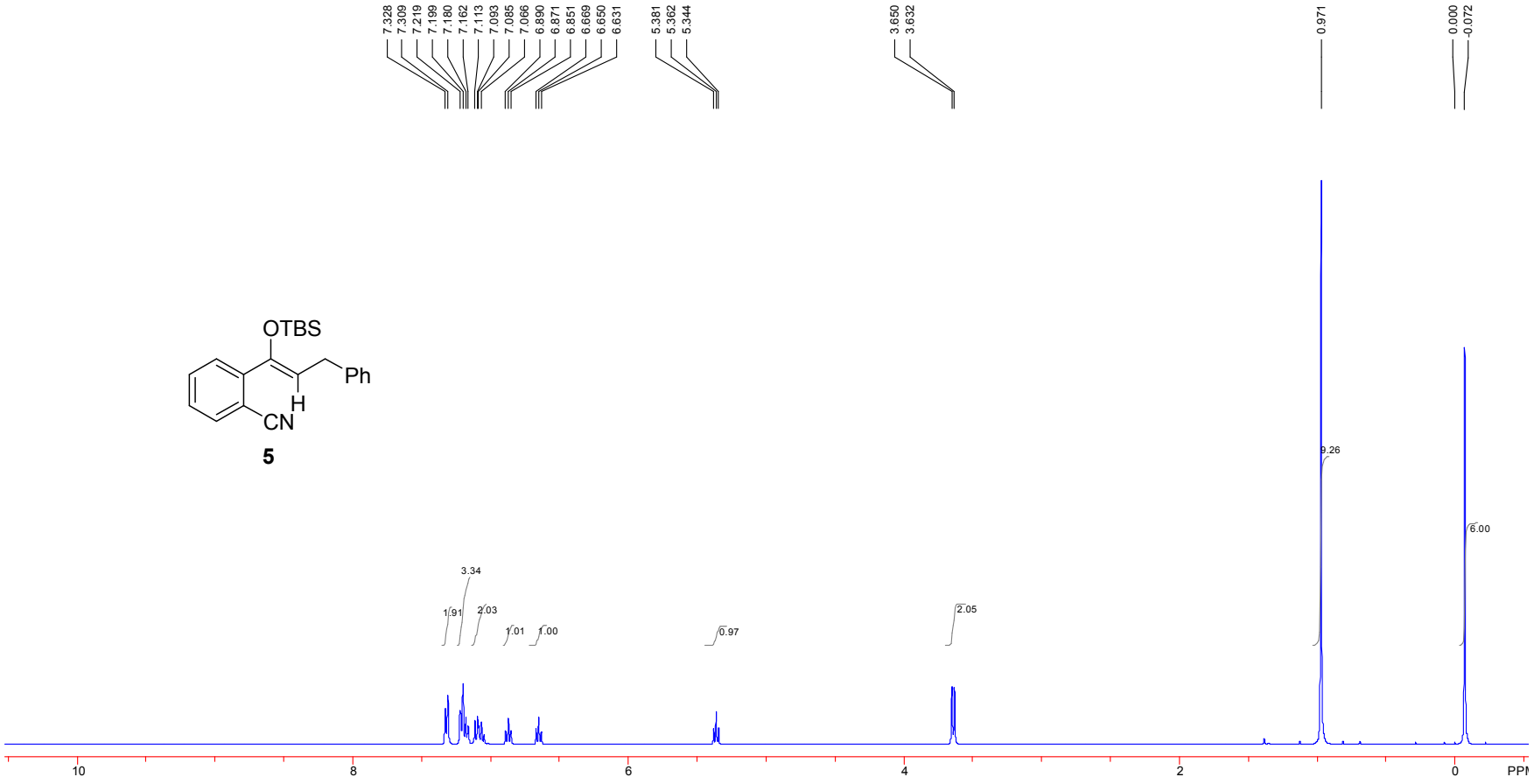
^{1}H NMR (400 MHz, $CDCl_3$)



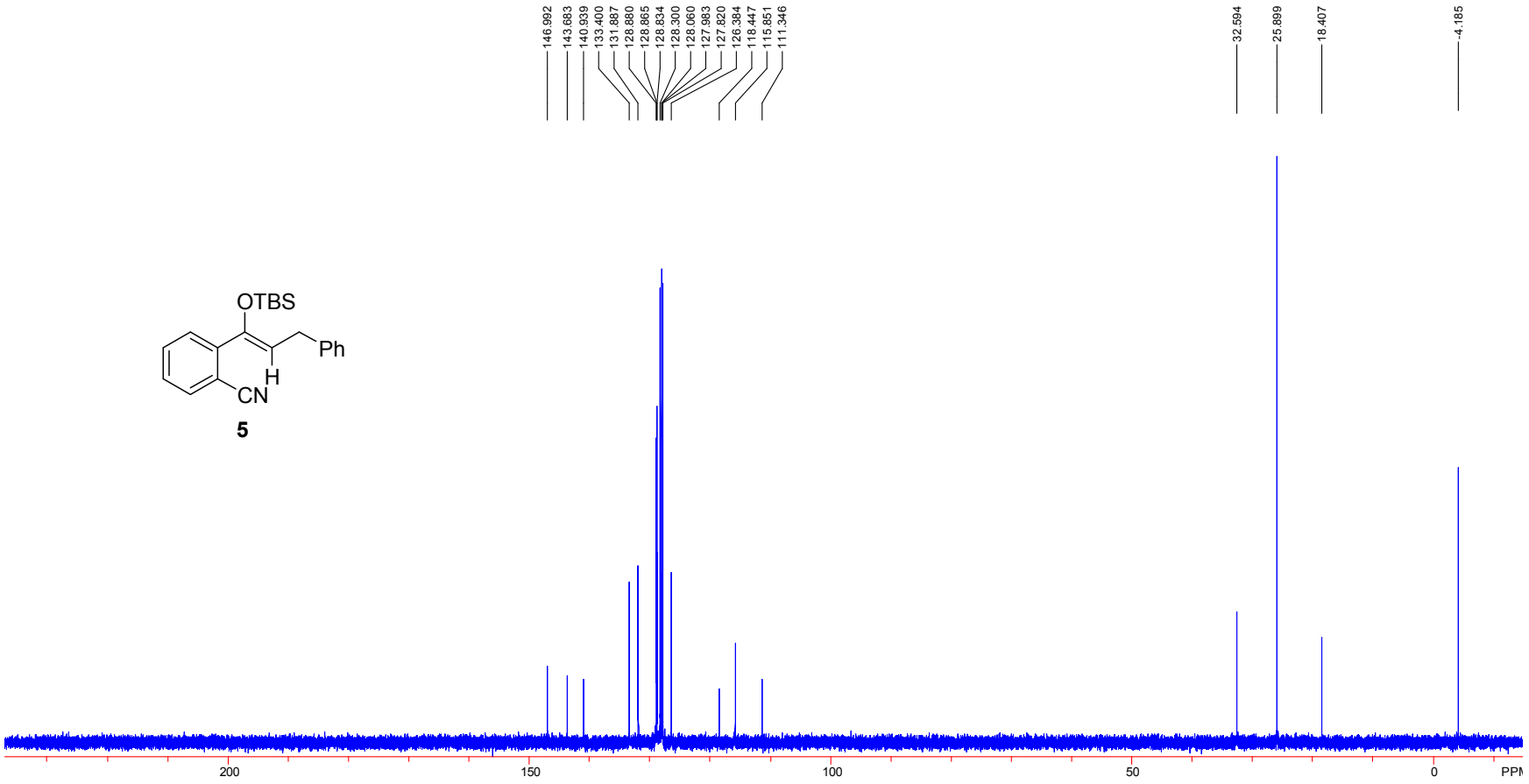
^{13}C NMR (100 MHz, $CDCl_3$)



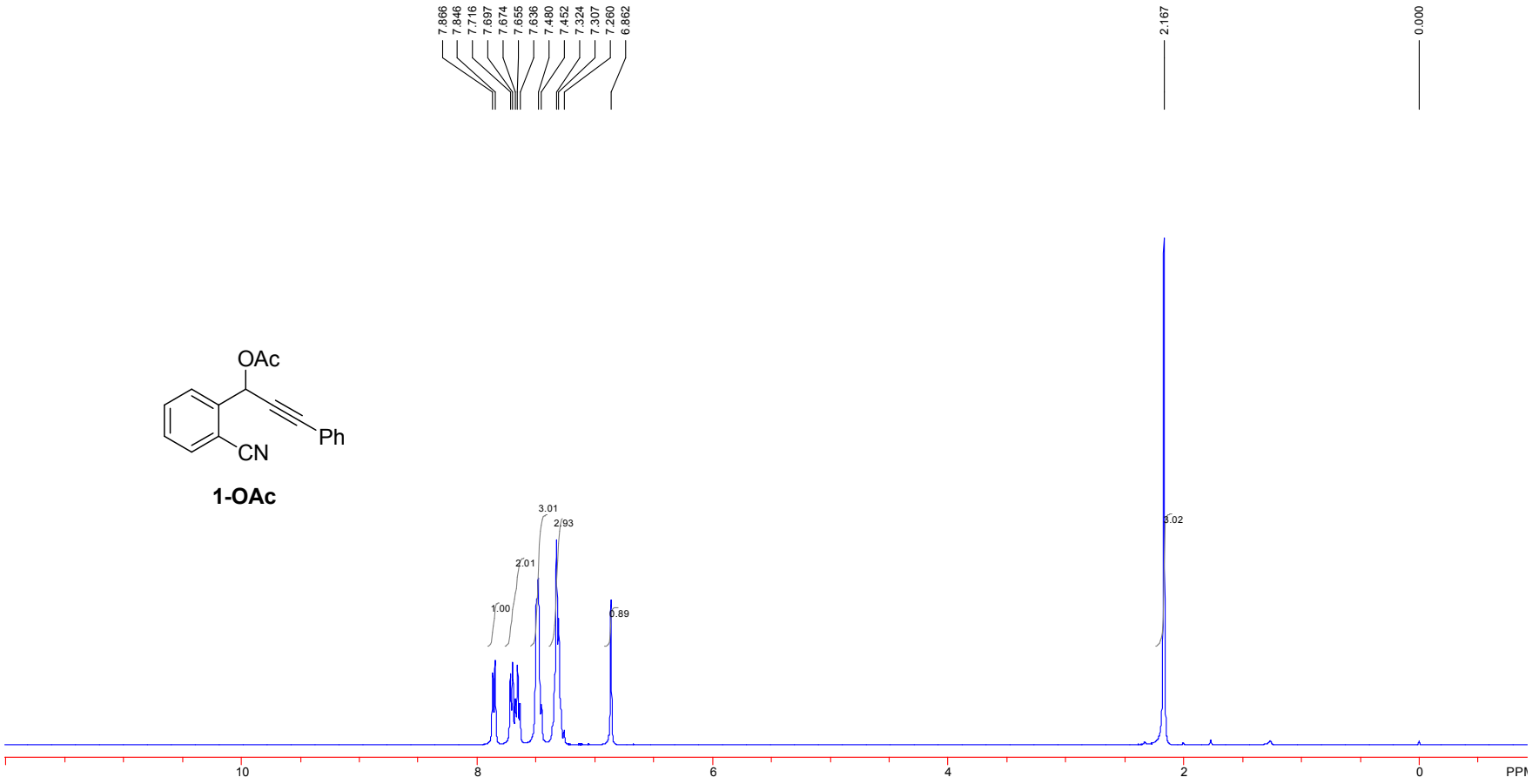
^{1}H NMR (400 MHz, C_6D_6)



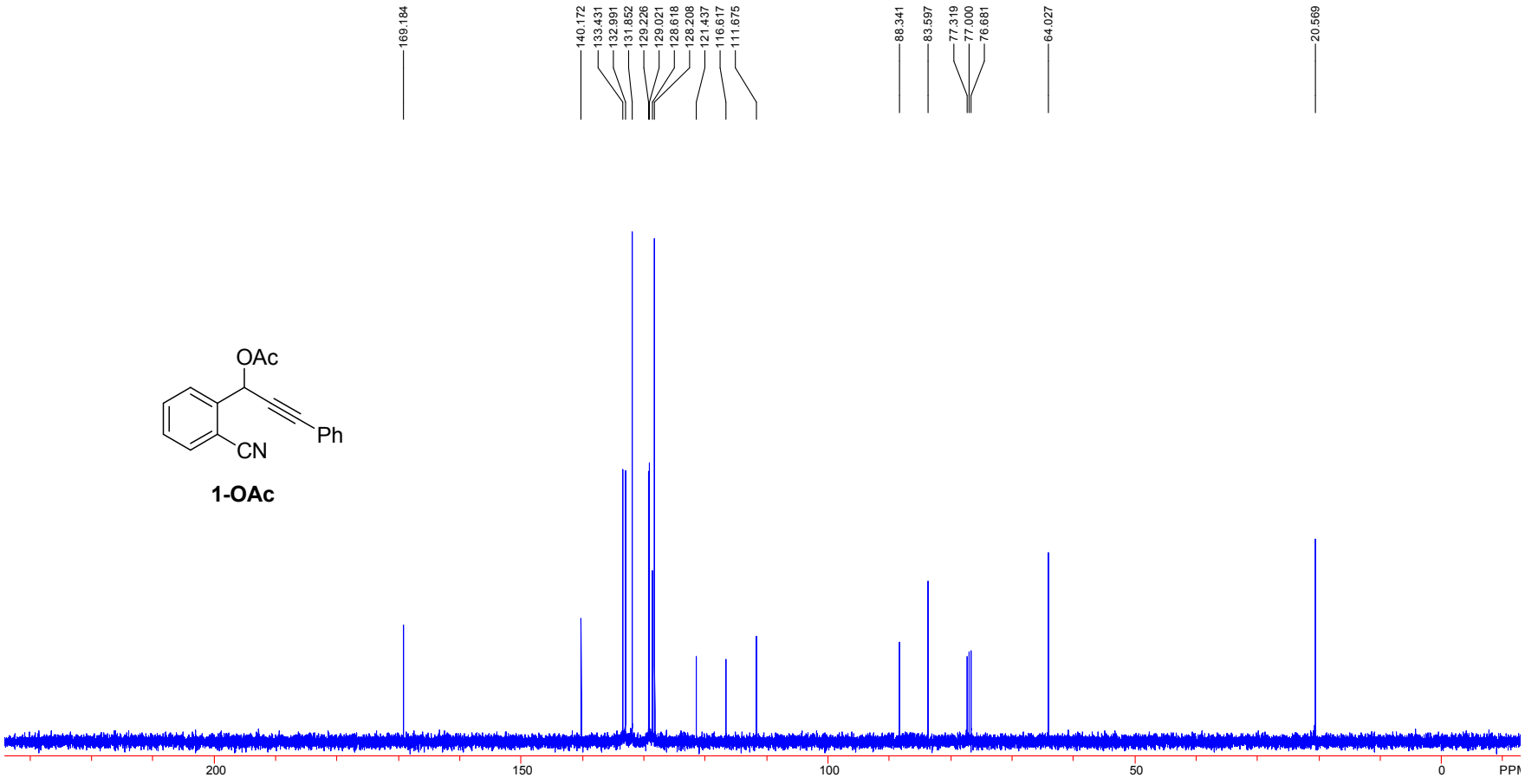
^{13}C NMR (100 MHz, C_6D_6)



^{1}H NMR (400 MHz, $CDCl_3$)

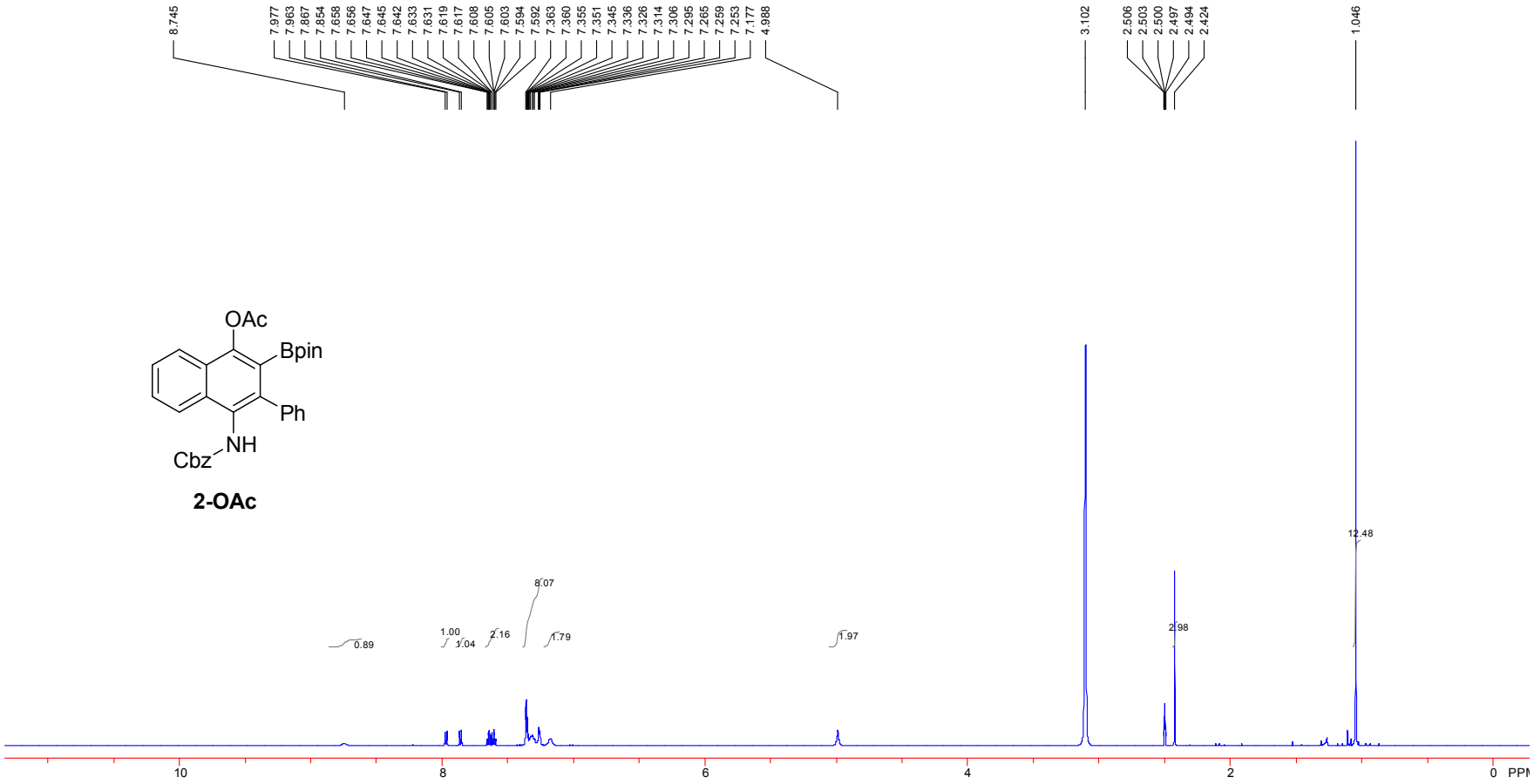


^{13}C NMR (100 MHz, $CDCl_3$)

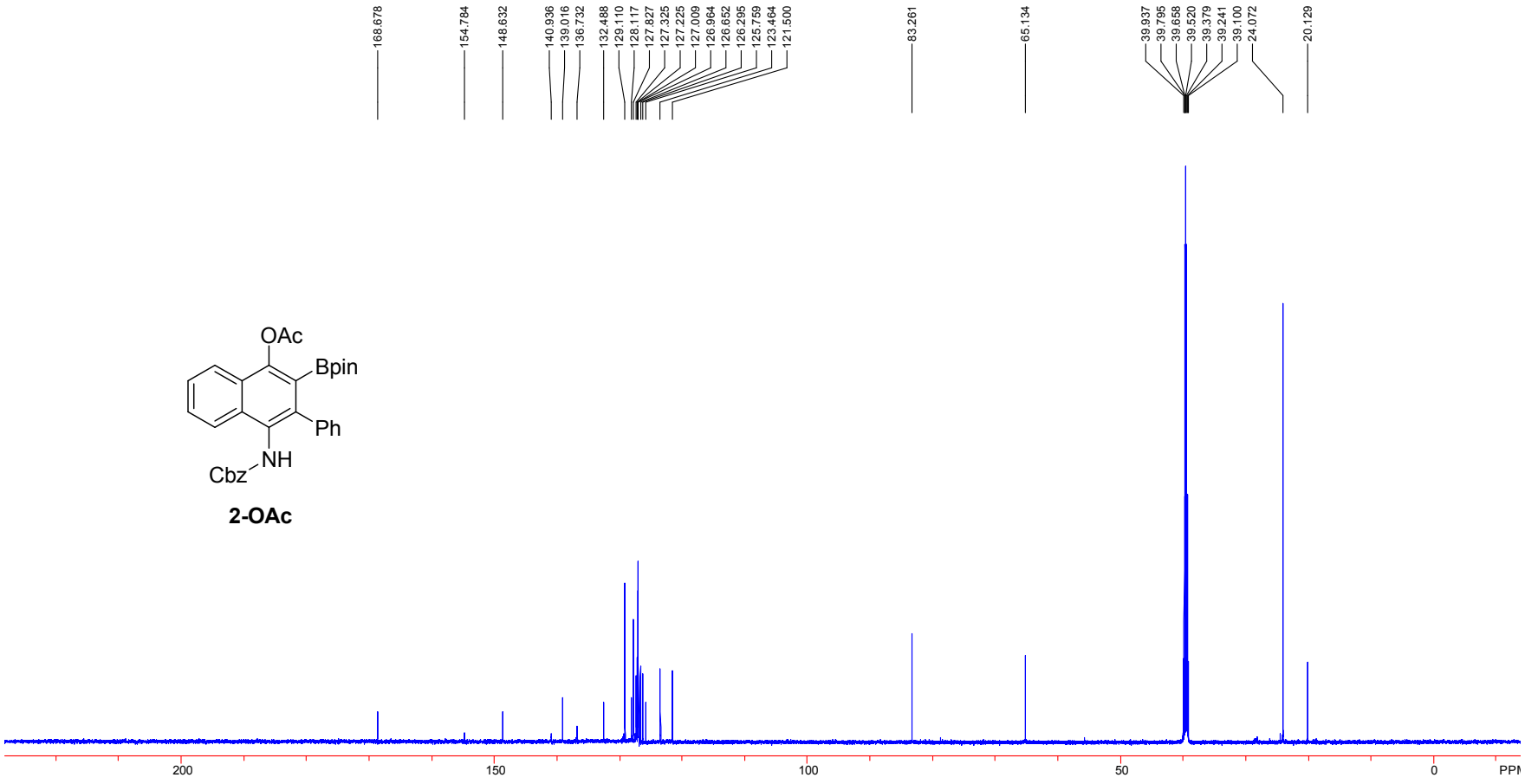


1-OAc

^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C)

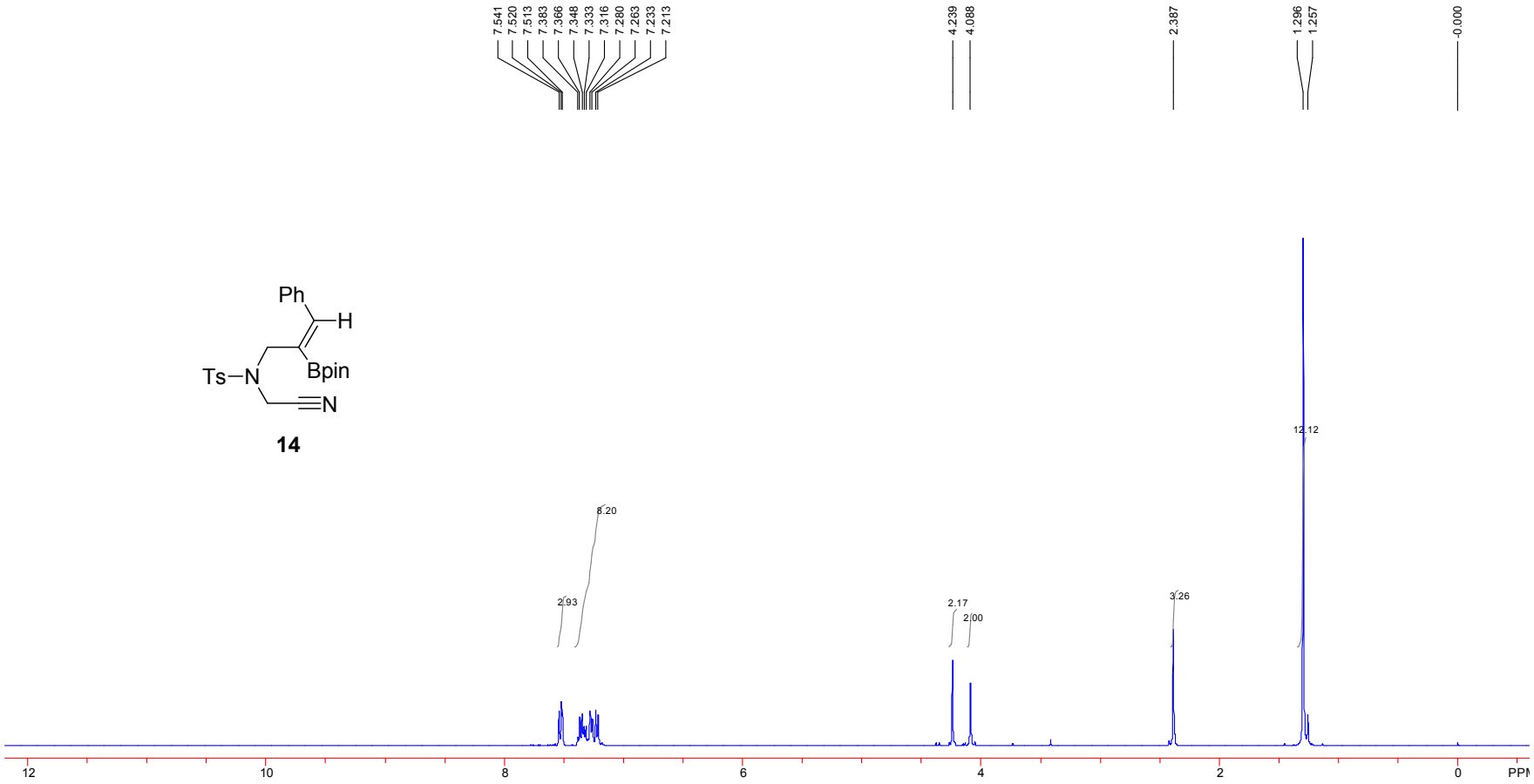


^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C)

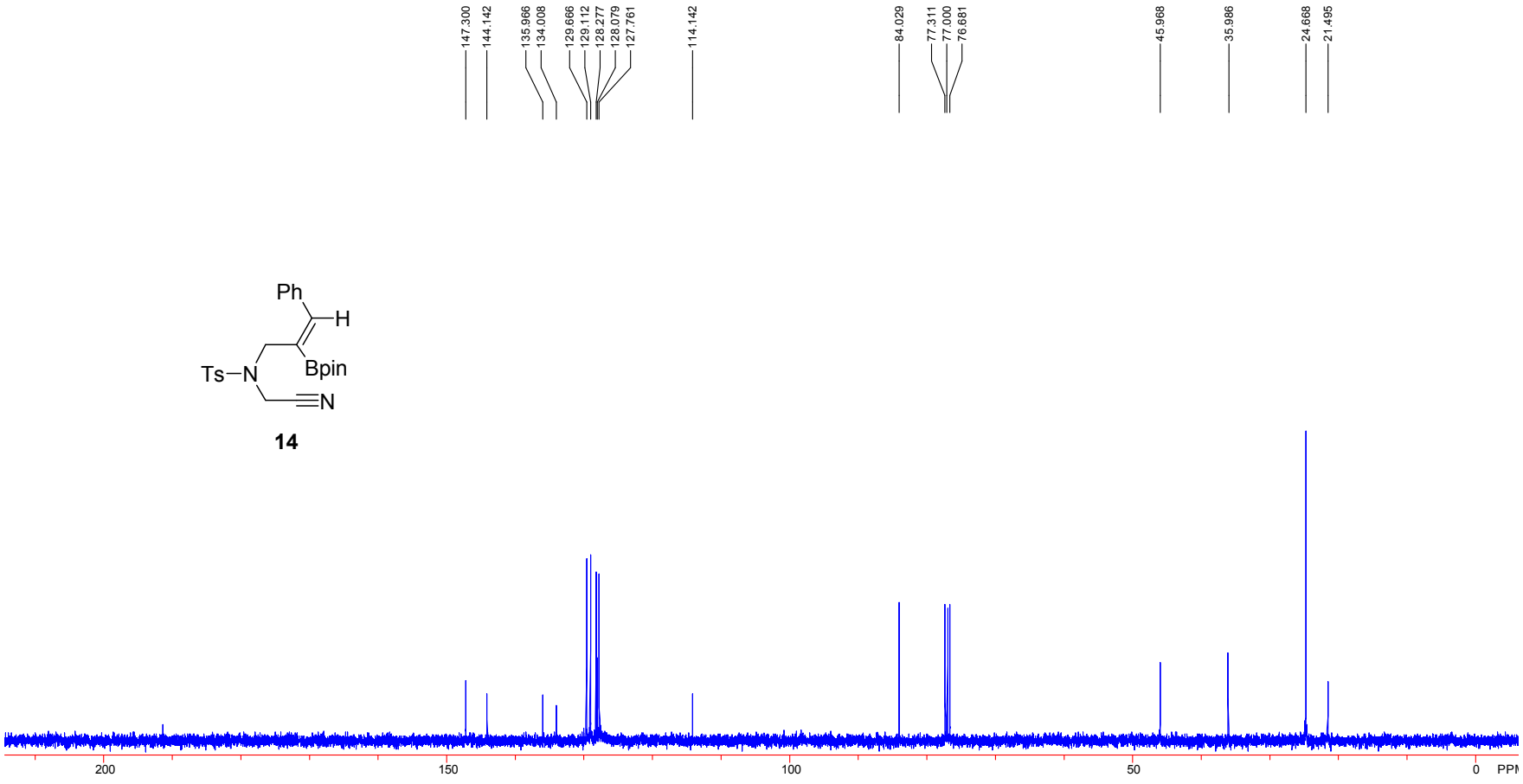


2-OAc

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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